Supporting Information

Enantioselective Palladium-Catalyzed (3+2) Spiroannulation of Cyclopropenones with Cyclic 1,3-Diketones: Merging C(sp2)- C(sp2) σ Bond Activation and Desymmetrization

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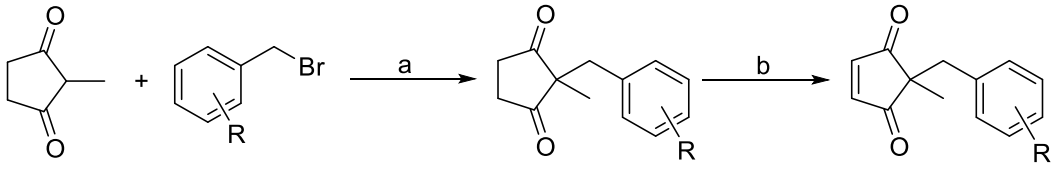
Content

1. General Information

Unless specifically stated, all reagents were commercially obtained and where appropriate, purified prior to use. Dichloromethane (DCM), toluene, were freshly distilled from CaH_2, Ether (Et_2O), tetrahydrofuran (THF) and 1, 4-dioxane were dried and distilled from metal sodium and benzophenone. Alcohol solvents were dried and distilled from metal magnesium. Other commercially available reagents and solvents were used directly without purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica (200 - 300 mesh). ^{1}H, ^{13}C NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer in $CDCl_3$. Multiplicities were given as: s (singlet); d (doublet); dd (doublets of doublet); t (triplet); q (quartet) or m (multiplets). High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics micro TOF-spectrometer. HPLC was carried out with a Agilent 1260 infinity, Waters AcQuity HPLC or Waters AcQuity UPLC using a chiralcel OD column, a chiralcel AD column, a chiralcel MD column, a chiralcel ND column.

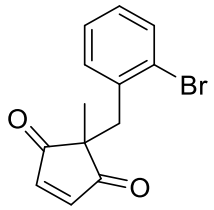
2. General procedure for the synthesis of 1,3-diones.[1,2,3]



a): To a stirred mixture of 2-Methyl-1,3-cyclopentanedione in H_2O (1 mol/L) was added portionwise powdered $NaHCO_3$ (1 equiv.) followed by addition of benzyl bromide (2 equiv.). the reaction suspension was stirred at 80 ºC overnight. After cooling down to room temperature, the reaction mixture was extracted with dichloromethane 3 times. The combined solvent was dried over Na_2SO_4. After removing the solvent under vacuum, the crude material was applied onto column chromatography to afford the intermediate product.

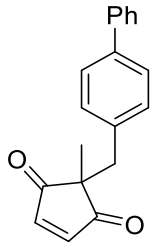
b): Dissolve the intermediate product in MeOH followed by addition of $CuBr_2$ (2.2 equiv.). The mixture was refluxed under N_2 for 1 h. It was allowed to cool down and evaporated under vacuum. The residual was subject to column chromatography to give

desired 1,3-dione.



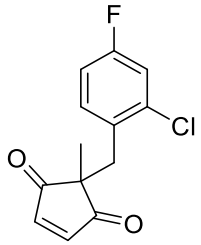
2-(2-bromobenzyl)-2-methylcyclopent-4-ene-1,3-dione (2i):

Yellow Solid, mp 74-77°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 - 7.43 (m, 1H), 7.21 - 7.12 (m, 3H), 7.05 (m, 2H), 3.19 (s, 2H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 148.5, 135.3, 133.5, 131.9, 128.9, 127.4, 125.4, 77.5, 77.16, 76.8, 51.5, 39.9, 18.5. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{13}H_{11}NaO_2$: 300.9835, found: 300.9821.



2-([1,1'-biphenyl]-4-ylmethyl)-2-methylcyclopent-4-ene-1,3-dione (2m):

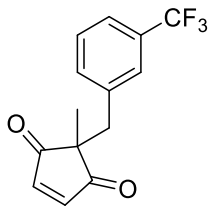
Yellow Solid, mp 112-115°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 - 7.48 (m, 2H), 7.43 - 7.36 (m, 4H), 7.34 - 7.27 (m, 1H), 7.00 (d, J = 8.8 Hz, 4H), 3.03 (s, 2H), 1.27 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 148.9, 140.5, 139.8, 134.7, 130.2, 128.9, 127.4, 127.1, 127.0, 77.5, 77.2, 76.8, 52.6, 40.5, 19.5. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{19}H_{16}NaO_2$: 299.1043, found: 299.1030.



2-(3-chloro-5-fluorobenzyl)-2-methylcyclopent-4-ene-1,3-dione (2n):

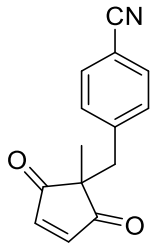
Yellow Solid, mp 64-67°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 2H), 7.09 - 6.99 (m, 2H), 6.86 (td, J = 8.2, 2.8 Hz, 1H), 3.12 (s, 2H), 1.25 (s, 3H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 206.4, 161.6 (d, J = 248.5 Hz), 148.5, 135.3 (d, J = 10.1 Hz), 133.0 (d, J = 8.6 Hz), 130.0 (d, J = 3.6 Hz), 117.3 (d, J = 24.5 Hz), 114.1 (d, J = 21.0 Hz). 51.4, 36.7, 18.6. ^{19}F NMR (500 MHz, $CDCl_3$) δ -112.7, -112.8, -112.8, -112.8.



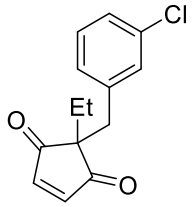
2-methyl-2-(3-(trifluoromethyl)benzyl)cyclopent-4-ene-1,3-dione (2t):

Yellow Solid, mp 34-37ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.6 Hz, 1H), 7.35 - 7.27 (m, 1H), 7.21 (d, J = 2.0 Hz, 1H), 7.15 (d, J = 7.6 Hz, 1H), 7.04 (s, 2H), 3.05 (s, 2H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.8, 148.9, 135.0 (d, J = 329.9 Hz), 130.8 (q, J = 32.0 Hz), 128.9, 126.5 (q, J = 3.7 Hz), 124.1 (q, J = 3.8 Hz), 124.0 (q, J = 270.6 Hz), 124.0 (q, J = 811.9 Hz), 52.3, 40.1, 19.7. ^{19}F NMR (500 MHz, $CDCl_3$) δ -62.8.



4-((1-methyl-2,5-dioxocyclopent-3-en-1-yl)methyl)benzonitrile (2v):

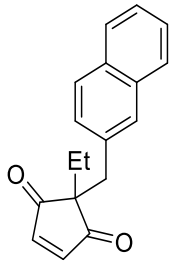
Yellow Solid, mp 116-119ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.5 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 12.0 Hz, 4H), 3.05 (s, 2H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 148.8, 141.1, 132.2, 130.7, 118.6, 111.2, 77.5, 77.2, 76.8, 52.2, 40.1, 19.8.



2-(3-chlorobenzyl)-2-ethylcyclopent-4-ene-1,3-dione (2x):

Yellow Solid, mp 102-105ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 - 6.94 (m, 4H), 6.84 (s, 1H), 6.78 - 6.67 (m, 1H), 2.86 (s, 2H), 1.75 (q, J = 7.6 Hz, 2H), 0.66 (t, J = 7.6 Hz,

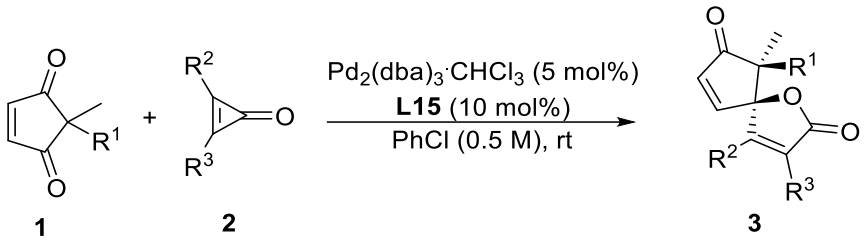
3H). ^{13}C NMR (100 MHz, CDCl3) δ 207.3, 150.3, 137.5, 134.2, 129.9, 129.7, 128.2, 127.4, 57.4, 39.6, 27.9, 9.1.



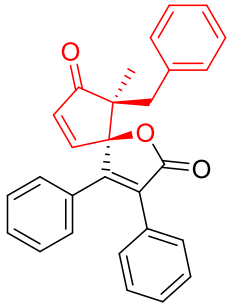
2-ethyl-2-(naphthalen-2-ylmethyl)cyclopent-4-ene-1,3-dione (2y):

Yellow Solid, mp 85-88°C.^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.68 - 7.56 (m, 2H), 7.51 (d, J = 8.4 Hz, 1H), 7.35 -7.22 (m, 3H), 6.92 (dd, J = 8.4, 1.8 Hz, 1H), 6.82 (s, 2H), 3.02 (s, 2H), 1.79 (q, J = 7.5 Hz, 2H), 0.65 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 207.7, 150.4, 133.2, 133.1, 132.4, 128.7, 128.1, 127.9, 127.6, 126.2, 125.9, 57.8, 40.5, 27.8, 9.1.

3. General procedure for the synthesis of products 3.

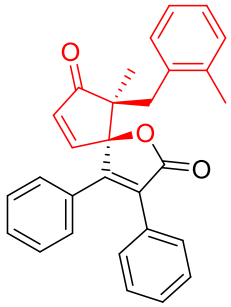


A vial was charged with 1,3-diones **1** (0.2 mmol), cyclopropenone **2** (0.4 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol%), (*R*,*R*)-**L15** (10 mol%) and evacuated under high vacuum and backfilled with N_2. MCB (0.4 mL) was next added. The mixture was stirred at 25 °C for 18 hours. Upon reaction completion, the crude was purified by column chromatography to give the corresponding product and was analyzed with ^{1}H NMR to determine the diastereomeric ratio and recovered.



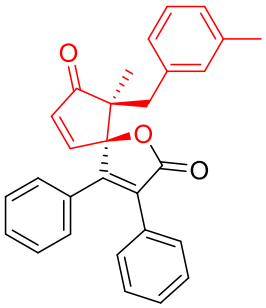
(5*R*,6*S*)-6-benzyl-6-methyl-3,4-diphenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3a):

Yellow solid (70.8 mg, 87% yield), mp 159-162°C, purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -119.2 (c = 1.23, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 6.0 Hz, 1H), 7.28 - 7.23 (m, 6H), 7.23 - 7.18 (m, 5H), 7.16 -7.10 (m, 2H), 6.99 - 6.90 (m, 2H), 6.49 (d, *J* = 6.0 Hz, 1H), 3.07 (s, 2H), 0.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.0, 170.6, 159.8, 155.9, 136.2, 131.8, 131.1, 130.1, 129.8, 129.6, 129.2, 129.0, 128.9, 128.4, 128.0, 126.9, 95.2, 58.1, 43.9, 17.9. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{28}H_{22}NaO_3$: 429.1461, found: 429.1455. The enantiomeric excess was determined by UPLC with Chiralpark ND column (hexanes:2-propanol = 75:25, 1 mL/min, 211 nm, 92% *ee*, *d.r.* > 19:1); major enantiomer tr = 4.311 min, minor enantiomer tr = 7.746 min.



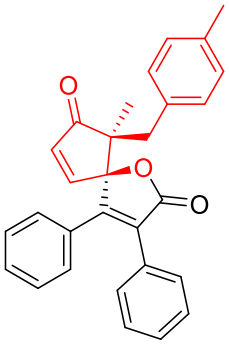
(5*R*,6*S*)-6-methyl-6-(2-methylbenzyl)-3,4-diphenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3b):

Yellow solid (68.2 mg, 81% yield), mp 140-143°C, purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -150.8 (c = 1.47, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 6.0 Hz, 1H), 7.18 (d, *J* = 14.4 Hz, 6H), 7.13 (d, *J* = 15.2 Hz, 2H), 7.06 - 6.90 (m, 6H), 6.56 (d, *J* = 5.6 Hz, 1H), 3.13 - 2.93 (m, 2H), 2.12 (s, 3H), 0.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 170.6, 159.9, 155.3, 137.5, 136.7, 134.5, 131.9, 131.6, 130.7, 130.1, 129.9, 129.6, 129.4, 129.2, 129.1, 128.9, 128.5, 127.1, 125.3, 95.6, 58.5, 41.0, 20.4, 16.0. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{29}H_{22}NaO_3$: 443.1618, found: 443.1632. The enantiomeric excess was determined by UPLC with Chiralpark ND column (hexanes:2-propanol = 90:10, 1 mL/min, 230 nm, 91% *ee*, *d.r.* = 10:1); major enantiomer tr = 6.690 min, minor enantiomer tr = 9.385 min.



(5*R*,6*S*)-6-methyl-6-(3-methylbenzyl)-3,4-diphenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3c):

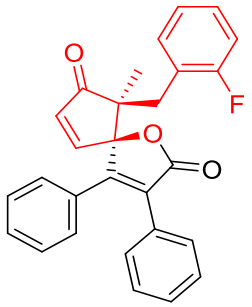
Yellow oil (74.9 mg, 89% yield), purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -87.0 (c = 2.19, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 6.0 Hz, 1H), 7.23 - 7.09 (m, 8H), 7.06 (m, 1H), 6.94 (d, J = 7.6 Hz, 1H), 6.91 - 6.81 (m, 4H), 6.43 (d, J = 6.0 Hz, 1H), 2.97 (m, 2H), 2.23 (s, 3H), 0.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 170.6, 159.8, 155.8, 137.5, 136.1, 131.9, 131.9, 130.1, 129.8, 129.6, 129.2, 129.1, 129.0, 128.9, 128.4, 128.1, 127.9, 127.6, 95.2, 58.0, 43.7, 21.5, 18.0. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{29}H_{22}NaO_3$: 443.1618, found: 443.1636. The enantiomeric excess was determined by UPLC with Chiralpark ND column (hexanes:2-propanol = 90:10, 1 mL/min, 230 nm, 93% *ee* *d.r.* > 19:1); major enantiomer tr = 10.037 min, minor enantiomer tr = 5.301 min.



(5*R*,6*S*)-6-methyl-6-(4-methylbenzyl)-3,4-diphenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3d):

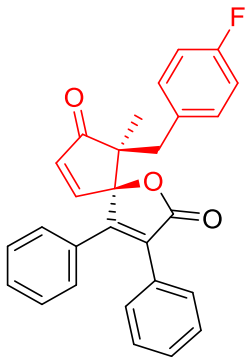
Yellow solid (72.2 mg, 86% yield), mp 128-131^{o}C, purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -337.4 (c = 0.78, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 6.0 Hz, 1H), 7.31 - 7.17 (m, 8H), 7.06 (d, J = 7.6 Hz, 1H), 7.04 - 6.93 (m, 5H), 6.50 (d, J = 6.0 Hz, 1H), 3.03 (s, 2H), 2.30 (s, 3H), 0.93 (s, 3H). ^{13}C NMR (100

MHz, $CDCl_3$) δ 206.0, 170.6, 159.8, 155.8, 136.4, 136.3, 133.1, 131.8, 131.0, 130.1, 129.8, 129.6, 129.2, 129.0, 128.9, 128.8, 128.4, 95.3, 58.2, 43.8, 21.2, 17.7. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{29}H_{22}NaO_3$: 443.1618, found: 443.1635. The enantiomeric excess was determined by UPLC with Chiralpark ND column (hexanes:2-propanol = 90:10, 1 mL/min, 230 nm, 93% *ee*, *d.r.* > 19:1); major enantiomer tr = 11.308 min, minor enantiomer tr = 5.500 min.



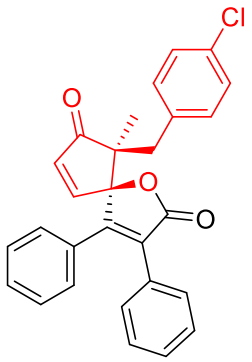
(5*R*,6*S*)-6-(2-fluorobenzyl)-6-methyl-3,4-diphenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3e):

Yellow solid (84.5 mg, 99% yield), mp 174-177°C, purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -150.2 (c = 1.65, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 5.6 Hz, 1H), 7.23 - 7.15 (m, 6H), 7.15 - 7.09 (m, 3H), 7.04 -6.92 (m, 4H), 6.92 - 6.85 (m, 1H), 6.58 (d, *J* = 6.0 Hz, 1H), 3.06 (d, *J* = 14.0 Hz, 1H), 2.97 (d, *J* = 13.6 Hz, 1H), 0.83 (s, 3H). ^{13}C NMR (100 MHz, $CHCl_3$) δ 204.3, 170.6, 161.5 (d, *J* = 244.0 Hz), 159.7, 154.9, 136.7, 133.1 (d, *J* = 4.0 Hz), 131.5, 130.0, 129.8, 129.6, 129.5, 129.3, 129.2, 129.1, 129.1, 129.1, 129.0, 128.9, 128.5, 128.4, 123.6 (d, *J* = 3.0 Hz), 123.2 (d, *J* = 16.0 Hz), 115.3 (d, *J* = 22.0 Hz), 95.4, 57.9, 37.9, 15.5. ^{19}F NMR (500 MHz, $CDCl_3$) δ -112.8 - -114.0 (m). HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{28}H_{21}FNaO_3$: 447.1367, found: 447.1378. The enantiomeric excess was determined by UPLC with Chiralpark MD column (hexanes:2-propanol = 85:15, 1 mL/min, 211 nm, 92% *ee*, *d.r.* = 9:1); major enantiomer tr = 6.542 min, major enantiomer tr = 4.901 min, minor enantiomer tr = 8.976 min.



(5*R*,6*S*)-6-(4-fluorobenzyl)-6-methyl-3,4-diphenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3f):

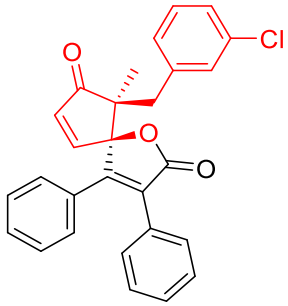
Yellow oil (80.5 mg, 95% yield), purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -407.8 (c = 0.79, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 5.6 Hz, 1H), 7.21 - 7.16 (m, 4H), 7.16 - 7.11 (m, 4H), 7.05 -6.99 (m, 2H), 6.93 - 6.82 (m, 4H), 6.40 (d, J = 5.6 Hz, 1H), 2.96 (s, 2H), 0.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.9, 170.5, 161.9 (d, J = 243.7 Hz), 159.7, 156.1, 136.3, 132.6 (d, J = 7.9 Hz), 131.9 (d, J = 3.1 Hz), 131.7, 130.0, 129.9, 129.6, 129.2, 129.1, 129.1, 129.0, 128.4, 114.9 (d, J = 20.7 Hz), 95.2, 58.0, 43.3, 17.7. ^{19}F NMR (500 MHz, $CDCl_3$) δ -115.9 - -116.1 (m). HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{28}H_{21}FNaO_3$: 447.1367, found: 447.1376. The enantiomeric excess was determined by UPLC with Chiralpark ND column (hexanes:2-propanol = 90:10, 1 mL/min, 230 nm, 92% *ee*, *d.r.* > 19:1); major enantiomer tr = 5.479 min, minor enantiomer tr = 11.969 min.



(5*R*,6*S*)-6-(4-chlorobenzyl)-6-methyl-3,4-diphenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3g):

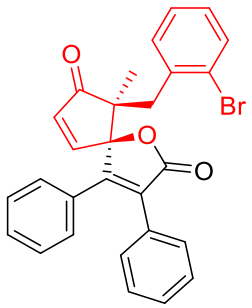
Yellow solid (87.3 mg, 99% yield), mp 141-144°C, purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -177.9 (c = 2.26, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.0 Hz, 1H), 7.21 - 7.10 (m, 10H), 7.00 (m, 2H), 6.94 - 6.87 (m, 2H), 6.40

(d, *J* = 5.6 Hz, 1H), 2.94 (m, 2H), 0.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.4, 170.5, 159.7, 154.1, 137.3, 135.8, 133.0, 133.0, 131.6, 130.1, 129.8, 129.6, 129.3, 129.2, 129.1, 128.9, 128.7, 128.4, 126.8, 126.6, 95.4, 77.5, 77.3, 77.1, 76.8, 57.9, 43.3, 15.7. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{28}H_{21}ClNaO_3$: 463.1071, found: 463.1083. The enantiomeric excess was determined by UPLC with Chiralpark ND column (hexanes:2-propanol = 90:10, 1 mL/min, 230 nm, 92% *ee*, *d.r.* > 19:1); major enantiomer tr = 5.376 min, minor enantiomer tr = 12.495 min.



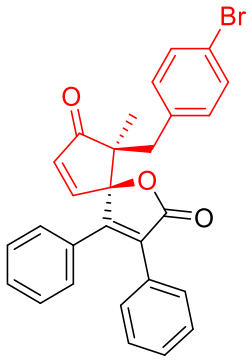
(5*R*,6*S*)-6-(3-chlorobenzyl)-6-methyl-3,4-diphenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3h):

Yellow oil (80 mg, 91% yield), purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -92.8 (c = 2.63, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 6.0 Hz, 1H), 7.21 - 7.10 (m, 10H), 7.06 (d, *J* = 2.0 Hz, 1H), 6.98 - 6.85 (m, 3H), 6.43 (d, *J* = 6.0 Hz, 1H), 2.95 (s, 2H), 0.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.7, 170.4, 159.6, 156.1, 138.3, 136.1, 133.8, 131.8, 131.0, 130.1, 129.9, 129.6, 129.3, 129.3, 129.1, 129.1, 129.1, 129.0, 128.4, 127.2, 95.0, 77.5, 77.2, 76.8, 57.7, 43.3, 18.0. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{28}H_{21}ClNaO_3$: 463.1071, found: 463.1063. The enantiomeric excess was determined by UPLC with Chiralpark ND column (hexanes:2-propanol = 90:10, 1 mL/min, 230 nm, 91% *ee*, *d.r.* > 19:1); major enantiomer tr = 6.065 min, minor enantiomer tr = 10.430 min.



(5*R*,6*S*)-6-(2-bromobenzyl)-6-methyl-3,4-diphenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3i):

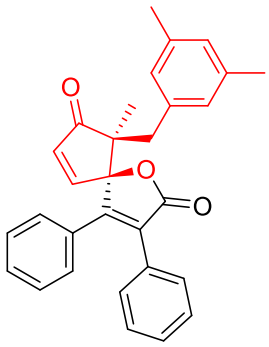
Yellow oil (81.5 mg, 84% yield), purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -52.8 (c = 1.68, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 - 7.40 (m, 3H) (major), 7.37 (dd, J = 7.7, 1.7 Hz, 0.4H) (minor), 7.25 - 7.10 (m, 12.5H), 7.07 (dd, J = 7.8, 1.9 Hz, 1.3H), 7.04 - 6.92 (m, 4.2H), 6.65 (d, J = 5.8 Hz, 1H) (major), 6.57 (d, J = 5.8 Hz, 0.2H) (minor), 3.30 - 3.10 (m, 2H) (major), 2.94 - 2.64 (m, 0.5H) (minor), 1.35 (s, 1H) (minor), 0.86 (s, 3H) (major).^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 204.5, 170.6, 159.8, 159.1, 156.0, 154.2, 137.4, 136.9, 135.9, 135., 133.1, 133.0, 132.0, 131.7, 131.5, 130.9, 130.2, 130.1, 130.0, 129.7, 129.5, 129.4, 129.3, 129.3, 129.2, 129.1, 129.0, 128.8, 128.6, 128.5, 128.4, 127.3, 126.9, 126.7, 126.7, 96.2, 95.5, 77.5, 77.4, 77.2, 76.8, 58.0, 56.8, 43.4, 37.2, 27.0, 22.9, 15.8, 14.2. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{28}H_{21}BrNaO_3$: 507.0566, found: 507.0583. The enantiomeric excess was determined by UPLC with Chiralpark ND column (hexanes:2-propanol = 85:15, 0.6 mL/min, 211 nm, 90% *ee* (major), >99% (minor), *d.r.* = 4:1); major enantiomer tr = 15.182 min, major enantiomer tr = 2.655 min, major enantiomer tr = 8.402 min.



(5*R*,6*S*)-6-(4-bromobenzyl)-6-methyl-3,4-diphenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3j):

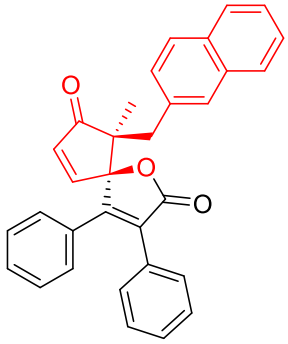
Yellow solid (93.1mg, 96% yield), mp 135-138 °C, purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -78.1 (c = 2.56, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 5.6 Hz, 1H), 7.40 - 7.34 (m, 2H), 7.31- 7.26 (m, 3H), 7.24 -7.18 (m, 5H), 7.06 - 6.93 (m, 4H), 6.48 (d, *J* = 5.6 Hz, 1H), 3.01 (m, 2H), 0.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.8, 170.5, 159.6, 156.2, 136.3, 135.3, 132.8, 131.7, 131.1, 130.1, 129.9, 129.5, 129.2, 129.1, 129.1, 129.0, 128. 5, 121.0, 95.1, 77.5, 77.4, 77.2, 76.8, 57.9, 43.5,

17.8. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{28}H_{21}BrNaO_3$: 507.0566, found: 507.0574. The enantiomeric excess was determined by HPLC with Chiralpark OD column (hexanes:2-propanol = 80:20, 0.5 mL/min, 210 nm, 90% *ee*, *d.r.* = 17:1); major enantiomer tr = 46.783 min, minor enantiomer tr = 52.708 min.



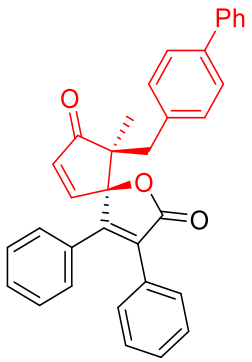
(5*R*,6*S*)-6-(3,5-dimethylbenzyl)-6-methyl-3,4-diphenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3k):

Yellow oil (80.8 mg, 93% yield), purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -117.0 (c = 2.25, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 6.0 Hz, 1H), 7.21 - 7.15 (m, 4H), 7.14 - 7.09 (m, 4H), 6.92 -6.84 (m, 2H), 6.76 (s, 1H), 6.66 (d, J = 1.6 Hz, 2H), 6.44 (d, J = 5.6 Hz, 1H), 3.00 - 2.82 (m, 2H), 2.19 (s, 6H), 0.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 170.6, 159.8, 155.7, 137.3, 136.1, 136.0, 131.9, 130.0, 129.8, 129.6, 129.2, 129.1, 129.0, 128.9, 128.5, 128.4, 95.3, 77.5, 77.2, 76.8, 57.9, 43.4, 21.3, 17.9. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{30}H_{26}NaO_3$: 457.1774, found: 457.1794. The enantiomeric excess was determined by UPLC with Chiralpark ND column (hexanes:2-propanol = 90:10, 1 mL/min, 230 nm, 92% *ee*, *d.r.* > 19:1); major enantiomer tr = 4.278 min, minor enantiomer tr = 8.875 min.



(5*R*,6*S*)-6-methyl-6-(naphthalen-2-ylmethyl)-3,4-diphenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3l):

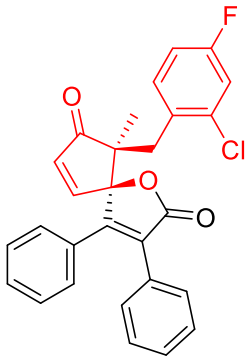
Yellow solid (89.4 mg, 98% yield), mp 146-149°C, purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -162.9 (c = 2.98, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 - 7.67 (m, 2H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 2.0 Hz, 1H), 7.39 - 7.33 (m, 2H), 7.30 (d, *J* = 6.0 Hz, 1H), 7.19 - 7.14 (m, 3H), 7.13 - 7.06 (m, 4H), 7.04 - 6.98 (m, 2H), 6.87 - 6.80 (m, 1H), 6.38 (d, *J* = 6.0 Hz, 1H), 3.15 (s, 2H), 0.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 170.6, 159.7, 156.0, 136.2, 133.9, 133.2, 132.4, 131.8, 130.1, 123.0, 129.8, 129.5, 129.2, 129.1, 129.1, 129.0, 128.9, 128.4, 127.9, 127.6, 127.4, 126.0, 125.8, 95.2, 77.5, 77.4, 77.2, 76.8, 58.0, 44.0, 18.4. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{32}H_{24}NaO_3$: 479.1618, found: 479.1633. The enantiomeric excess was determined by UPLC with Chiralpark ND column (hexanes:2-propanol = 90:10, 1 mL/min, 230 nm, 91% *ee*, *d.r.* > 19:1); major enantiomer tr = 7.973 min, minor enantiomer tr = 15.258 min.



(5*R*,6*S*)-6-([1,1'-biphenyl]-4-ylmethyl)-6-methyl-3,4-diphenyl-1-oxaspiro[4.4] nona-3,8-diene-2,7-dione (3m):

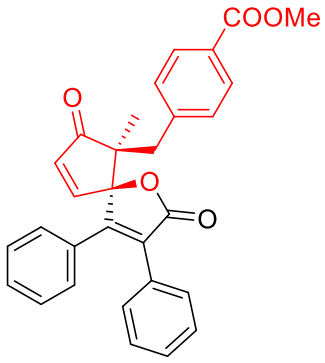
Yellow solid (76.9 mg, 80% yield), mp 173-176°C, purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -309.8 (c = 1.22, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 - 7.47 (m, 2H), 7.44 - 7.39 (m, 2H), 7.38 - 7.31 (m, 3H), 7.25 (m, 1H), 7.20 - 7.08 (m, 10H), 6.93 - 6.85 (m, 2H), 6.43 (d, *J* = 5.6 Hz, 1H), 3.03 (s, 2H), 0.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 170.6, 159.8, 156.0, 140.8, 139.6, 136.2, 135.4, 131.8, 131.5, 130.1, 129.9, 129.6, 129.2, 129.0, 129.0, 128.8, 128.4, 127.3, 127.1, 126.7, 95.2, 77.5, 77.2, 76.8, 58.1, 43.6, 18.1. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{34}H_{26}NaO_3$: 505.1774, found: 505.1794. The enantiomeric excess was determined by HPLC with Chiralpark AD column (hexanes:2-propanol = 80:20, 0.7 mL/min, 210 nm,

93% *ee*, *d.r.* > 19:1); major enantiomer tr = 17.021 min, major enantiomer tr = 14.79 min, minor enantiomer tr = 36.692 min.



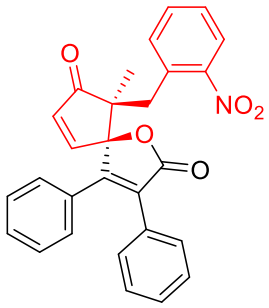
(5*R*,6*S*)-6-(2-chloro-4-fluorobenzyl)-6-methyl-3,4-diphenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3n):

Yellow oil (81.1 mg, 88% yield), purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -86.6 (c = 2.21, $CHCl_3$). ^1H NMR (400 MHz, $CHCl_3$) δ 7.46 - 7.40 (m, 1H), 7.31 - 7.08 (m, 11H), 7.05 - 6.93 (m, 5H), 6.86 - 6.77 (m, 1H), 6.61 (d, *J* = 6.0 Hz, 1H) (major), 6.54 (d, *J* = 6.0 Hz, 0.3H) (minor), 3.30 - 2.96 (m, 2H) (major), 2.78 - 2.55 (m, 0.6H) (minor), 1.12 (s, 0.8H) (minor), 0.83 (s, 3H) (major). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.6, 204.2, 170.5, 170.4, 162.6 (d, *J* = 28.0 Hz), 160.3, 160.0, 159.6, 158.9, 155.9, 154.6, 137.1, 136.1 (d, *J* = 10.0 Hz), 135.8 (d, *J* = 10.0 Hz), 133.9 (d, *J* = 8.0 Hz), 133.0 (d, *J* = 8.0 Hz), 131.5, 131.4, 130.9 (d, *J* = 3.0 Hz), 130.0 (d, *J* = 16.0 Hz), 130.0 (d, *J* = 4.0 Hz), 130.0, 129.4, 129.4, 129.2 (d, *J* = 1.9 Hz), 129.1 (d, *J* = 2.6 Hz), 129.0, 129.0, 128.5, 116.9 (d, *J* = 24.7 Hz), 116.7 (d, *J* = 24.8 Hz), 113.6 (d, *J* = 20.9 Hz), 95.9, 95.4, 57.8, 56.6, 40.6, 33.7, 22.5, 15.4. ^{19}F NMR (500 MHz, $CHCl_3$) δ -113.1 - -113.3 (m) (major), -113.4 - -113.73 (m) (minor). HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{28}H_{20}ClFNaO_3$: 481.0977, found: 481.0993. The enantiomeric excess was determined by HPLC with Chiralpark AD column (hexanes:2-propanol = 80:20, 0.7 mL/min, 210 nm, 88% *ee* (major), >99% *ee* (minor), *d.r.* = 4:1); major enantiomer tr = 13.850 min, major enantiomer tr = 10.013 min, minor enantiomer tr = 24.598 min.



Methyl 4-(((5*R*,6*S*)-6-methyl-2,7-dioxo-3,4-diphenyl-1-oxaspiro [4.4] nona-3,8-dien-6-yl) methyl) benzoate (3o):

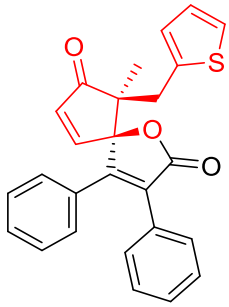
Yellow solid (92.2 mg, 99% yield), mp 138-141°C, purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -66.7 (c = 2.74, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 6.0 Hz, 1H), 7.23 - 7.08 (m, 10H), 6.95 - 6.82 (m, 2H), 6.41 (d, *J* = 5.6 Hz, 1H), 3.80 (s, 3H), 3.02 (s, 2H), 0.86 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 205.6, 170.4, 167.0, 159.5, 156.1, 141.7, 136.2, 131.6, 131.1, 130.0, 129.9, 129.5, 129.2, 129.2, 129.1, 129.1, 129.0, 128.9, 128.7, 128.4, 95.0, 77.5, 77.2, 76.8, 57.9, 52.1, 43.9, 17.8. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{30}H_{24}NaO_5$: 487.1516, found: 487.1532. The enantiomeric excess was determined by HPLC with Chiralpark OD column (hexanes:2-propanol = 80:20, 0.5 mL/min, 254 nm, 92% *ee*, *d.r.* > 19:1); major enantiomer tr = 76.447 min, major enantiomer tr = 89.884 min, minor enantiomer tr = 53.108 min.



(5*R*,6*S*)-6-methyl-6-(2-nitrobenzyl)-3,4-diphenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3p):

Yellow solid (50.8 mg, 56% yield), mp 140-143°C, purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = 75.2 (c = 1.55, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 - 7.86 (m, 1H) (major), 7.85 - 7.79 (m, 0.3H) (mionr), 7.51 - 7.38 (m, 3H), 7.31 (m,

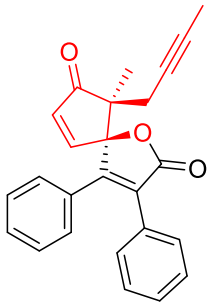
1.5H), 7.25 - 7.17 (m, 8H), 7.16 - 7.10 (m, 2H), 7.09 - 7.03 (m, 1H), 7.01 - 6.92 (m, 2H), 6.58 (d, *J* = 5.6 Hz, 1H) (major), 6.55 (d, *J* = 5.6 Hz, 0.2H) (minor), 4.17 - 3.96 (m, 1H), 3.79 (d, *J* = 14.0 Hz, 1H), 3.31 (s, 0.3H) (minor), 3.22 (d, *J* = 14.0 Hz, 1H), 3.00 (d, *J* = 14.0 Hz, 0.2H) (minor), 2.87 (d, *J* = 14.4 Hz, 0.2H) (minor), 1.96 (s, 1H), 1.20 - 1.13 (m, 1H), 1.09 (d, *J* = 14.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 205.1, 171.3, 170.4, 159.4, 156.2, 154.8, 149.8, 147.9, 136.9, 135.7, 135.0, 134.2, 133.5, 132.9, 132.5, 132.5, 132.2, 131.7, 131.6, 131.4, 131.0, 130.3, 130.1, 129.9, 129.8, 129.6, 129.3, 129.3, 129.2, 129.1, 129.0, 128.8, 128.5, 128.5, 128.5, 128.4, 125.5, 125.4, 125.0, 95.8, 95.3, 77.5, 77.2, 76.8, 60.5, 56.9, 40.4, 36.4, 16.2, 14.3. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{28}H_{21}NNaO_5$: 474.1312, found: 474.1331. The enantiomeric excess was determined by HPLC with Chiralpark OD column (hexanes:2-propanol = 75:25, 1 mL/min, 210 nm, 92% *ee*, *d.r.* = 6:1); major enantiomer tr = 21.442 min, major enantiomer tr = 10.279 min, minor enantiomer tr = 19.485 min.



(5*R*,6*S*)-6-methyl-3,4-diphenyl-6-(thiophen-2-ylmethyl)-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3q):

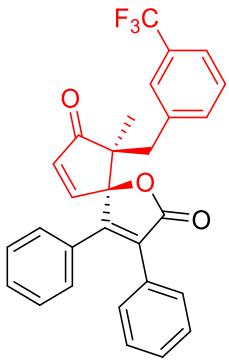
Yellow oil (43.6 mg, 53% yield), purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -10.1 (c = 0.85, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 6.0 Hz, 1H), 7.25 - 7.11 (m, 6H), 7.10 (m, 1.6 Hz, 3H), 6.96 - 6.89 (m, 2H), 6.87 (m, 3.5 Hz, 1H), 6.82 (m, 1.2 Hz, 1H), 6.45 (d, *J* = 6.0 Hz, 1H), 3.30 (d, *J* = 14.8 Hz, 1H), 3.14 (d, *J* = 14.8 Hz, 1H), 0.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 170.4, 159.4, 156.5, 138.0, 135.7, 132.1, 130.4, 129.9, 129.7, 129.2, 129.0, 129.0, 129.0, 128.9, 128.4, 126.8, 125.1, 94.9, 77.5, 77.2, 76.8, 56.9, 37.5, 19.1, 1.1. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{26}H_{20}NaO_3S$: 435.1025, found: 435.1039. The enantiomeric excess was determined by HPLC with Chiralpark AD column (hexanes:2-propanol = 80:20, 0.7

mL/min, 210 nm, 92% *ee*, *d.r.* > 19:1); major enantiomer tr = 13.817 min, major enantiomer tr = 13.048 min, minor enantiomer tr = 33.073 min.



(5*R*,6*S*)-6-(but-2-yn-1-yl)-6-methyl-3,4-diphenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3r):

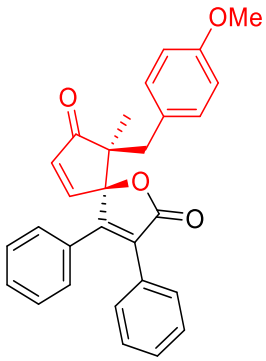
Yellow oil (32.5 mg, 44% yield), purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = 233.3 (c = 0.75, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 6.0 Hz, 1H), 7.28 - 7.18 (m, 8H), 7.08 - 7.04 (m, 2H), 6.50 (d, J = 5.6 Hz, 1H), 2.64 - 2.51 (m, 1H), 2.38 - 2.27 (m, 1H), 1.77 - 1.71 (m, 3H), 0.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 170.5, 159.0, 156.4, 135.4, 132.6, 130.3, 130.0, 129.6, 129.4, 129.1, 129.1, 128.8, 128.5, 94.2, 79.2, 77.5, 77.2, 76.8, 74.4, 54.2, 26.8, 19.9, 3.9. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{25}H_{20}NaO_3$: 391.1305, found: 391.1315. The enantiomeric excess was determined by HPLC with Chiralpark AD column (hexanes:2-propanol = 80:20, 1 mL/min, 210 nm, 94% *ee*, *d.r.* > 19:1); major enantiomer tr = 8.653 min, major enantiomer tr = 6.435 min, minor enantiomer tr = 26.965 min.



(5*R*,6*S*)-6-methyl-3,4-diphenyl-6-(3-(trifluoromethyl)benzyl)-1-oxaspiro[4.4] nona-3,8-diene-2,7-dione (3s):

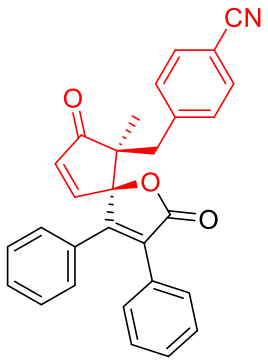
Yellow Oil (91.8 mg, 97% yield), purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -108.8 (c = 3.06, $CHCl_3$).^1H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.36 (m, 2H),

7.33 - 7.24 (m, 3H), 7.23 - 7.09 (m, 8H), 6.93 - 6.86 (m, 2H), 6.45 (d, J = 4.6 Hz, 1H), 3.12 - 2.96 (m, 2H), 0.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.6, 170.7, 159.5, 156.3, 137.2, 136.2, 134.6, 131.7, 130.3 (q, J = 31.7 Hz), 130.1, 129.9, 129.6, 129.2, 129.1, 129.0, 128.5, 128.4, 127.6 (q, J = 4.1 Hz), 124.2 (q, J = 270.8 Hz), 123.8 (q, J = 4.1 Hz), 95.0, 57.7, 43.6, 17.6. ^{19}F NMR (500 MHz, $CDCl_3$) δ -62.5. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{29}H_{21}F_3NaO_3$: 497.1335, found: 497.1356. The enantiomeric excess was determined by UPLC with Chiralpark MD column (hexanes:2-propanol = 85:15, 1 mL/min, 211 nm, 92% *ee*, *d.r.* > 19:1); major enantiomer tr = 5.355 min, minor enantiomer tr = 6.841 min.



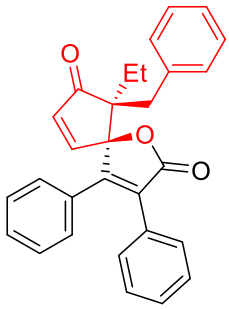
(5*R*,6*S*)-6-(4-methoxybenzyl)-6-methyl-3,4-diphenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3t) :

Yellow solid (72.9 mg, 84% yield), mp 159-162^{o}C, purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -178.0 (c = 2.43, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 6.0 Hz, 1H), 7.22 - 7.09 (m, 8H), 7.00 - 6.95 (m, 2H), 6.93 -6.86 (m, 2H), 6.75 - 6.68 (m, 2H), 6.40 (d, J = 6.0 Hz, 1H), 3.68 (s, 3H), 2.94 (s, 2H), 0.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 170.6, 159.8, 158.4, 155.9, 136.3, 132.0, 131.8, 129.9, 129.8, 129.6, 129.2, 129.2, 129.0, 128.9, 128.4, 128.2, 113.4, 95.3, 77.5, 77.2, 76.8, 58.1, 55.2, 43.3, 17.7. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{29}H_{24}NaO_4$: 459.1567, found: 459.1579. The enantiomeric excess was determined by UPLC with Chiralpark MD column (hexanes:2-propanol = 85:15, 1 mL/min, 211 nm, 93% *ee*, *d.r.* > 19:1); major enantiomer tr = 7.303 min, major enantiomer tr = 5.483 min, minor enantiomer tr = 9.260 min.



4-(((5R,6S)-6-methyl-2,7-dioxo-3,4-diphenyl-1-oxaspiro[4.4]nona-3,8-dien-6-yl)methyl) benzonitrile (3u) :

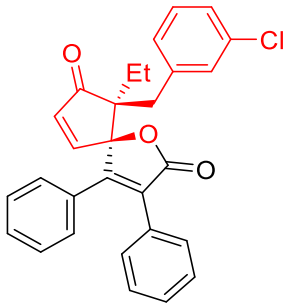
Yellow oil (85.4 mg, 99% yield), purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -41.2 (c = 0.38, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 - 7.43 (m, 2H), 7.39 (d, *J* = 6.0 Hz, 1H), 7.22 - 7.10 (m, 10H), 6.94 -6.86 (m, 2H), 6.42 (d, *J* = 6.0 Hz, 1H), 3.08 - 2.93 (m, 2H), 0.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.4, 170.3, 159.4, 156.4, 141.9, 136.2, 131.8, 131.7, 131.5, 130.0, 123.0, 129.5, 129.2, 129.1, 129.0, 128.9, 128.4, 118.9, 110.8, 94.9, 77.5, 77.2, 76.8, 57.8, 44.1, 17.7. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{29}H_{22}NO_3$: 432.1594, found: 432.1603. The enantiomeric excess was determined by UPLC with Chiralpark ND column (hexanes:2-propanol = 75:25, 1 mL/min, 211 nm, 91% *ee*, *d.r.* = 17:1); major enantiomer tr = 6.348 min, major enantiomer tr = 13.996 min, minor enantiomer tr = 5.272 min.



(5*R*,6*S*)-6-benzyl-6-ethyl-3,4-diphenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3v):

Yellow solid (26.5 mg, 32% yield), mp 111-114°C, purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -19.5 (c = 0.80, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 6.0 Hz, 1H), 7.26 - 7.11 (m, 16H), 7.10 - 7.06 (m, 1H), 7.06 - 7.01 (m, 2H), 6.99 - 6.92 (m, 2H), 6.58 (d, *J* = 6.0 Hz, 0.4H) (minor), 6.36 (d, *J* = 5.6 Hz, 1H) (major),

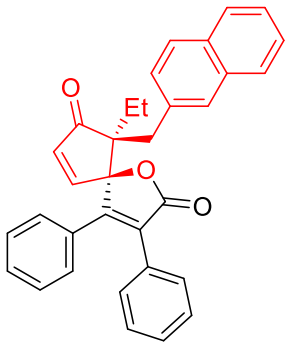
3.21 - 3.05 (m, 2H), 2.87 (d, *J* = 15.6 Hz, 0.4H) (minor), 2.50 (d, *J* = 15.6 Hz, 0.4H) (minor), 1.91 - 1.81 (m, 0.4H) (minor), 1.76 - 1.63 (m, 0.4H) (minor), 1.51 - 1.38 (m, 1H), 1.17 - 1.08 (m, 1H), 1.06 - 0.92 (m, 3H), 0.79 - 0.68 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.5, 170.4, 159.5, 157.1, 156.1, 136.5, 136.4, 136.2, 131.9, 130.9, 130.7, 130.1, 123.0, 129.9, 129.5, 129.5, 129.3, 129.3, 129.1, 129.1, 129.1, 128.8, 128.6, 128.5, 128.4, 128.2, 126.9, 126.7, 96.0, 95.4, 65.9, 61.0, 40.6, 34.7, 29.5, 22.3, 10.4, 7.7. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{29}H_{24}NaO_3$: 443.1618, found: 443.1599. The enantiomeric excess was determined by UPLC with Chiralpark ND column (hexanes:2-propanol = 75:25, 0.6 mL/min, 211 nm, 72% *ee* (major), 85% *ee* (minor),, *d.r.* = 2:1); major enantiomer tr = 6.994 min, major enantiomer tr = 14.380 min, minor enantiomer tr = 7.526 min, minor enantiomer tr = 16.758 min.



(5*R*,6*S*)-6-(3-chlorobenzyl)-6-ethyl-3,4-diphenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3w):

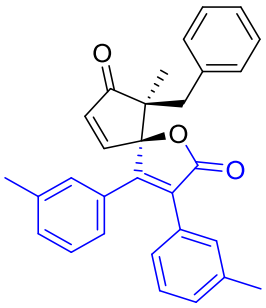
Yellow solid (31.2 mg, 34% yield), mp 100-103^{o}C, purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -5.8 (c = 1.13, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 5.6 Hz, 0.4H) (minor), 7.28 (d, *J* = 6.0 Hz, 1H) (major), 7.25 - 7.13 (m, 12H), 7.11 (d, *J* = 5.2 Hz, 2H), 7.09 - 6.99 (m, 2H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.94 - 6.91 (m, 1H), 6.61 (d, *J* = 5.6 Hz, 0.4H) (minor), 6.38 (d, *J* = 6.0 Hz, 1H) (major), 3.08 (q, *J* = 14.0 Hz, 2H), 2.83 (d, *J* = 15.6 Hz, 0.4H) (minor), 2.44 (d, *J* = 16.0 Hz, 0.4H) (minor), 1.85 - 1.75 (m, 0.4H) (minor), 1.74 - 1.64 (m, 0.4H) (minor), 1.50 - 1.38 (m, 1H), 1.17 - 1.09 (m, 1H), 1.01 - 0.92 (m, 3H), 0.77 - 0.68 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.2, 159.3, 156.3, 151.1, 138.5, 136.4, 134.0, 131.8, 130.8, 130.0, 129.5, 129.4, 129.2, 129.1, 128.8, 128.6, 128.6, 127.2, 95.3, 77.5, 77.2, 76.8, 61.6, 40.2, 22.4, 7.6. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{29}H_{23}ClNaO_3$: 477.1228, found: 477.1243.

The enantiomeric excess was determined by UPLC with Chiralpark INB column (hexanes:2-propanol = 75:25, 1 mL/min, 211 nm, 67% *ee* (major), 76% *ee* (minor), *d.r.* = 3:1); major enantiomer tr = 6.039 min, major enantiomer tr = 7.812 min, minor enantiomer tr = 4.176 min, minor enantiomer tr = 4.873 min.



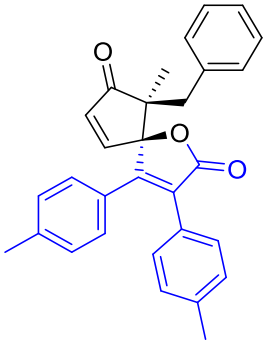
(5*R*,6*S*)-6-ethyl-6-(naphthalen-2-ylmethyl)-3,4-diphenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3x):

Yellow solid (54.5 mg, 58% yield), mp 168-171°C, purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -54.4 (c = 1.57, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 - 7.68 (m, 3H), 7.68 - 7.60 (m, 1.4H), 7.60 - 7.51 (m, 1.4H), 7.46 - 7.32 (m, 3H), 7.26 - 7.05 (m, 14H), 7.01 - 6.89 (m, 3H), 6.60 (d, *J* = 5.6 Hz, 0.4H) (minor), 6.30 (d, *J* = 5.6 Hz, 1H) (major), 3.35 (d, *J* = 13.6 Hz, 1H) (major), 3.21 (d, *J* = 13.6 Hz, 1H) (major), 3.06 (d, *J* = 16.4 Hz, 0.4H) (minor), 2.61 (d, *J* = 16.4 Hz, 0.4H) (minor), 1.84 - 1.70 (m, 0.5H) (minor), 1.60 - 1.45 (m, 1H), 1.32 - 1.21 (m, 1H), 1.08 - 0.93 (m, 3H) (major), 0.80 - 0.70 (m, 1.3H) (minor). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.8, 205.6, 170.6, 170.4, 159.4, 159.3, 157.3, 156.1, 136.5, 136.2, 134.2, 134.1, 133.3, 132.4, 132.2, 131.9, 131.8, 131.2, 130.7, 130.1, 129.9, 129.8, 129.5, 129.5, 129.2, 129.2, 129.2, 129.1, 129.1, 129.1, 129.0, 128.8, 128.5, 128.4, 128.0, 127.9, 127.8, 127.6, 127.6, 126.3, 126.0, 125.8, 125.8, 95.9, 95.4, 61.9, 60.9, 40.8, 34.9, 29.6, 22.9, 10.3, 7.7. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{33}H_{26}NaO_3$: 493.1774, found: 493.1787. The enantiomeric excess was determined by UPLC with Chiralpark MD column (hexanes:2-propanol = 75:25, 1 mL/min, 211 nm, 84% *ee* (major),71% *ee* (minor), *d.r.* = 2:1); major enantiomer tr = 4.214 min, major enantiomer tr = 6.356 min, minor enantiomer tr = 3.457 min, minor enantiomer tr = 3.828 min.



(5*R*,6*S*)-6-benzyl-6-methyl-3,4-di-m-tolyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3y):

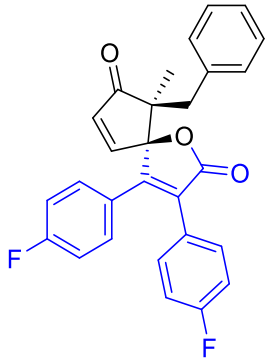
Yellow solid (86.0 mg, 99% yield), mp 140-143°C, purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -63.9 (c = 2.57, $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 5.6 Hz, 1H), 7.23 (m, 3H), 7.17 - 7.02 (m, 7H), 6.96 - 6.88 (m, 1H), 6.80 - 6.70 (m, 2H), 6.47 (d, *J* = 6.0 Hz, 1H), 3.06 (s, 2H), 2.25 (s, 3H), 2.16 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 170.7, 159.8, 156.0, 138.5, 137.9, 136.2, 136.0, 131.8, 131.1, 130.4, 130.1, 129.9, 129.7, 129.5, 129.1, 128.7, 128.1, 128.0, 126.8, 126.6, 126.4, 95.1, 77.5, 77.2, 76.8, 58.0, 43.9, 21.4, 21.4, 17.8. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{30}H_{27}O_3$: 435.1955, found: 435.1970. The enantiomeric excess was determined by HPLC with Chiralpark OD column (hexanes:2-propanol = 75:25, 1 mL/min, 245 nm, 95% *ee*, *d.r.* = 17:1); major enantiomer tr = 12.601 min, major enantiomer tr = 15.112 min, minor enantiomer tr = 10.183 min.



(5*R*,6*S*)-6-benzyl-6-methyl-3,4-di-p-tolyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3z):

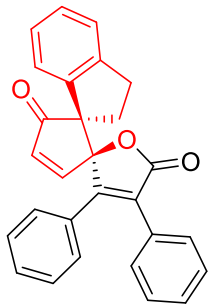
Yellow oil (36.1 mg, 42% yield), purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -53.4 (c = 0.88, $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 5.6 Hz, 1H), 7.26 - 7.18 (m, 3H), 7.16 - 7.11 (m, 4H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0

Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.48 (d, *J* = 5.6 Hz, 1H), 3.06 (s, 2H), 2.29 (d, *J* = 13.2 Hz, 6H), 0.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 171.0, 159.2, 156.1, 140.0, 139.0, 136.3, 136.2, 131.1, 129.7, 129.4, 129.4, 129.2, 129.1, 129.0, 128.0, 126.9, 126.5, 95.2, 77.5, 77.4, 77.2, 76.8, 58.2, 44.2, 21.5, 21.4, 17.7. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{30}H_{27}O_3$: 435.1955, found: 435.1960. The enantiomeric excess was determined by HPLC with Chiralpark OD column (hexanes:2-propanol = 75:25, 1 mL/min, 210 nm, 85% *ee*, *d.r.* > 19:1); major enantiomer tr = 7.219 min, minor enantiomer tr = 8.456 min.



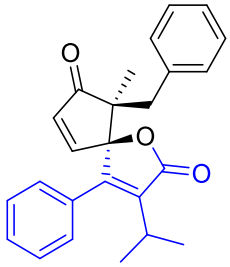
(5*R*,6*S*)-6-benzyl-3,4-bis(4-fluorophenyl)-6-methyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3aa):

Yellow oil (56.1 mg, 63% yield), purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -80.9 (c = 0.64, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 6.0 Hz, 1H), 7.25 - 7.16 (m, 4H), 7.14 - 7.10 (m, 2H), 7.00 -6.93 (m, 6H), 6.52 (d, *J* = 5.6 Hz, 1H), 3.07 (s, 2H), 0.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.7, 170.3, 164.4 (d, *J* = 28.2 Hz), 161.9 (d, *J* = 26.0 Hz), 158.5, 155.5, 136.5, 136.1, 131.6 (d, *J* = 8.4 Hz), 131.2 (d, *J* = 8.4 Hz), 131.1, 129.4, 128.1, 127.7 (d, *J* = 3.6 Hz), 127.0, 125.0 (d, *J* = 3.2 Hz), 116.5 (d, *J* = 21.7 Hz), 115.8 (d, *J* = 21.4 Hz), 95.2, 58.2, 44.0, 17.8. ^{19}F NMR (500 MHz, $CDCl_3$) δ -108.5 - -109.6 (m), -110.6 - -110.9 (m). HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{28}H_{20}F_2NaO_3$: 465.1273, found: 465.1278. The enantiomeric excess was determined by HPLC with Chiralpark OD column (hexanes:2-propanol = 75:25, 1 mL/min, 210 nm, 84% *ee*, *d.r.* > 19:1); major enantiomer tr = 9.642 min, major enantiomer tr = 8.742 min, minor enantiomer tr = 6.601 min.



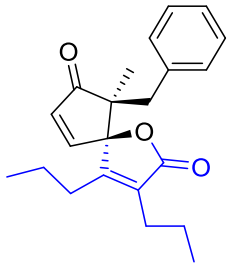
(1'*S*,2*R*)-3,4-diphenyl-2'',3''-dihydro-5H-dispiro[furan-2,2'-cyclopentane1', 1''inden] -3'-ene-5,5'-dione (3ab):

Yellow oil (75.8 mg, 94% yield), purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -302.0 (c = 2.53, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 5.8 Hz, 0.4H) (minor), 7.66 (d, J = 5.8 Hz, 1H) (major), 7.26 - 6.91 (m, 17H), 6.86 - 6.79 (m, 0.4H) (minor), 6.77 (d, J = 5.9 Hz, 0.4H) (minor), 6.66 (d, J = 5.9 Hz, 1H) (major), 6.59 - 6.50 (m, 1H), 6.36 - 6.29 (m, 0.4H) (minor), 5.74 (d, J = 7.7 Hz, 0.4H) (minor), 4.07 - 3.97 (m, 0.3H) (minor), 3.11 - 2.92 (m, 1.4H), 2.89 - 2.73 (m, 1.4H), 2.70 - 2.61 (m, 0.4H) (minor), 2.46 - 2.35 (m, 0.4H) (minor), 1.95 (s, 2.4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.9, 202.3, 170.6, 170.4, 159.9, 159.0, 157.1, 156.8, 145.4, 143.7, 140.2, 139.6, 138., 138.0, 131.9, 130.9, 130.0, 129.5, 129.1, 129.4, 129.1, 129.1, 129.0, 129.0, 129.0, 128.5, 128.5, 128.3, 128.3, 128.0, 126.2, 126.0, 125.5, 125.4, 125.3, 124.4, 95.0, 94.7, 77.5, 77.4, 77.2, 76.8, 69.8, 68.6, 36.0, 31.6, 31.3, 30.1. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{28}H_{20}NaO_3$: 427.1305, found: 427.1320. The enantiomeric excess was determined by HPLC with Chiralpark AD column (hexanes:2-propanol = 80:20, 1 mL/min, 210 nm, 83% *ee* (major), 97% *ee* (minor), *d.r.* = 3:1); major enantiomer tr = 8.228 min, major enantiomer tr = 7.479 min, minor enantiomer tr = 19.097 min, minor enantiomer tr = 15.857 min.



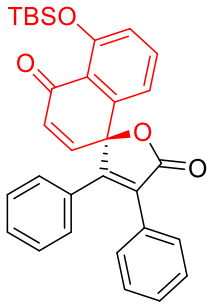
(5*R*,6*S*)-6-benzyl-3-isopropyl-6-methyl-4-phenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3ac):

Yellow oil (42.5 mg, 57% yield), purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = 50.4 (c = 1.52, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 2.1 Hz, 4H), 7.26 - 7.18 (m, 3H), 7.11 - 7.06 (m, 2H), 7.00 -6.96 (m, 2H), 6.41 (d, *J* = 5.6 Hz, 1H), 3.00 (s, 2H), 2.73 - 2.65 (m, 1H), 1.25 (d, *J* = 6.8 Hz, 3H), 1.16 (d, *J* = 7.2 Hz, 3H), 0.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 170.7, 158.7, 156.3, 136.8, 136.4, 135.7, 131.8, 131.0, 129.5, 128.9, 128.7, 128.0, 126.8, 94.9, 77.5, 77.4, 77.2, 76.8, 57.8, 43.7, 25.7, 20.6, 20.2, 17.9. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{20}NaO_3$: 395.1618, found: 395.1602. The enantiomeric excess was determined by HPLC with Chiralpark OX column (hexanes:2-propanol = 75:25, 1 mL/min, 210 nm, 86% *ee*, *d.r.* > 19:1); major enantiomer tr = 21.392 min, major enantiomer tr = 19.476 min, minor enantiomer tr = 20.405 min.



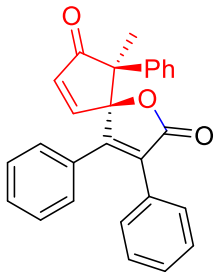
(5*R*,6*S*)-6-benzyl-6-methyl-3,4-dipropyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (3ad):

Yellow oil (37.1 mg, 55% yield), purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -97.4 (c = 0.89, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 - 7.19 (m, 3H), 7.10 - 7.01 (m, 3H), 6.34 (d, *J* = 5.9 Hz, 1H), 3.02 -2.88 (m, 2H), 2.40 - 2.17 (m, 3H), 1.65 - 1.57 (m, 2H), 1.56 - 1.47 (m, 1H), 1.43 - 1.32 (m, 1H), 1.30 - 1.18 (m, 1H), 0.99 - 0.94 (m, 3H), 0.93 (s, 3H), 0.91 - 0.84 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.8, 173.0, 162.7, 156.5, 136.3, 135.0, 130.9, 129.5, 128.1, 127.0, 95.0, 77.5, 77.2, 76.8, 58.5, 45.5, 29.2, 26.5, 22.7, 21.3, 15.8, 14.5, 14.1. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{20}NaO_3$: 361.1774, found: 361.1756. The enantiomeric excess was determined by HPLC with Chiralpark OX column (hexanes:2-propanol = 85:15, 0.6 mL/min, 210 nm, 65% *ee*, *d.r.* > 19:1); major enantiomer tr = 11.968 min, minor enantiomer tr = 12.653 min.



(*S*)-5'-((tert-butyldimethylsilyl)oxy)-3,4-diphenyl-4'H,5H-spiro[furan-2,1'-naphthalene]-4',5-dione (5):

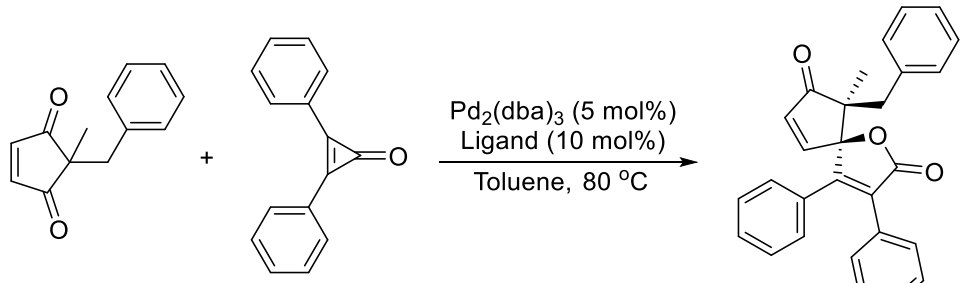
Yellow oil (85.0 mg, 86% yield), purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = 121.7 (c = 2.80, $CHCl_3$). ^{1}H NMR (400 MHz,x` $CDCl_3$) δ 7.79 - 7.73 (m, 0.2H) (minor), 7.52 (d, *J* = 6.5 Hz, 1H), 7.48 - 7.40 (m, 1.3H), 7.34 -7.20 (m, 4H), 7.20 - 7.05 (m, 3H), 7.01 - 6.95 (m, 0.8H), 6.78 - 6.70 (m, 2H), 6.65 (d, *J* = 10.0 Hz, 1H) (major), 6.56 (d, *J* = 10.0 Hz, 0.2H) (minor), 6.42 (d, *J* = 10.0 Hz, 0.2H) (minor), 6.37 (d, *J* = 10.0 Hz, 1H) (major), 1.02 (s, 7H) (major), 0.95 (s, 2H) (minor), 0.29 (s, 0.6H) (minor), 0.21 (s, 2H) (major), 0.17 (s, 2H) (major), 0.13 (s, 0.6H) (minor). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 205.1, 171.3, 170.4, 159.4, 156.2, 154.8, 149.8, 147.9, 136.9, 135.7, 135.0, 134.2, 133.5, 132.9, 132.5, 132.5, 132.2, 131.7, 131.6, 131.4, 131.0, 130.3, 130.1, 129.9, 129.8, 129.6, 129.3, 129.3, 129.2, 129.1, 129.0, 128.8, 128.5, 128.5, 128.5, 128.4, 125.5, 125.4, 125.0, 95.8, 95.3, 77.5, 77.2, 76.8, 60.5, 56.9, 40.4, 36.4, 16.2, 14.3. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{20}NaO_3$: 517.1806, found: 517.1807. The enantiomeric excess was determined by HPLC with Chiralpark OD column (hexanes:2-propanol = 85:15, 0.6 mL/min, 210 nm, 92% *ee*(major), 87% *ee* (minor), *r.r.* = 4:1); major enantiomer tr = 12.096 min, major enantiomer tr = 13.901 min, minor enantiomer tr = 10.693 min, minor enantiomer tr = 9.097 min.



(5*R*,6*S*)-6-methyl-3,4,6-triphenyl-1-oxaspiro[4.4]nona-3,8-diene-2,7-dione (10):

Yellow oil (17.7 mg, 23% yield), purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$ = -338.6 (c = 0.59, $CHCl_3$). Major: ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 5.8 Hz, 1H), 7.19 (s, 1H), 7.16 - 7.07 (m, 5H), 7.06 - 6.92 (m, 5H), 6.91 - 6.80 (m, 4H), 6.63 (d, J = 5.8 Hz, 1H), 1.70 (s, 3H). Minor: ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 5.8 Hz, 1H), 7.29 (dd, J = 7.9, 5.7 Hz, 3H), 7.23 - 7.18 (m, 6H), 7.16 - 7.03 (m, 4H), 6.71 (d, J = 5.8 Hz, 1H), 1.12 (s, 3H). Major: ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.3, 160.6, 156.0, 138.7, 136.3, 130.8, 129.5, 129.3, 129.2, 129.0, 128.7, 128.4, 128.1, 127.3, 127.1, 96.7, 77.5, 77.2, 76.8, 58.9, 29.0. Minor: ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 169.3, 158.0, 156.1, 139.1, 136.8, 132.9, 131.4, 130.2, 129.6, 129.3, 129.2, 128.8, 128.6, 128.5, 127.8, 127.7, 94.4, 77.5, 77.2, 76.8, 60.4, 22.7. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{27}H_{20}NaO_3$: 392.4512, found: 392.4516. The enantiomeric excess was determined by UPLC with Chiralpark ND column (hexanes:2-propanol = 85:15, 0.6 mL/min, 211 nm, 70% *ee* (major), 76% *ee* (minor), *d.r.* = 4:1); major: major enantiomer tr = 6.345 min, minor enantiomer tr = 13.960 min; minor: major enantiomer tr = 11.851 min, minor enantiomer tr = 26.886 min

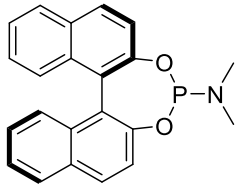
Table S1. The effect of P-ligands L1-L10 in the reaction.[a]



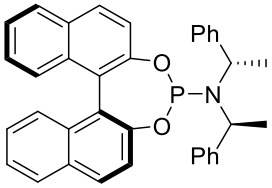
1a **2a** **3a**

Entry	Ligand	Yield of **3a** (%)[a]	*ee* of **3a** (%)[b]	*dr* of **3a** (%)[c]
1[d]	PPh_3	29	race	> 19:1
2	**L1**	nr	/	/
3	**L2**	30	22	> 19:1
4	**L3**	nr	/	/
5	**L4**	16	57	12:1
6	**L5**	24	62	4:1
7	**L6**	30	68	7:1
8	**L7**	34	70	19:1
9	**L8**	7	30	2:1
10	**L9**	trace	/	/
11	**L10**	15	57	7:1

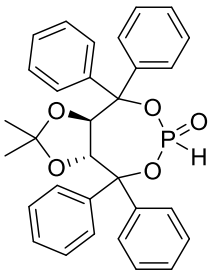
All the reactions were run on a 0.1 mmol scale in 1.0 mL solvents for 18 h. [a]Determined by ^1H NMR using dibromomethane as an internal standard. [b]Determined by HPLC. [c]Determind by ^1H NMR. [d]Yield of the isolated product.



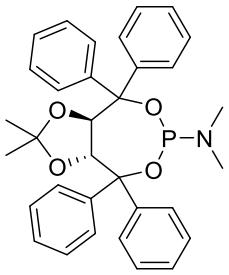
L1



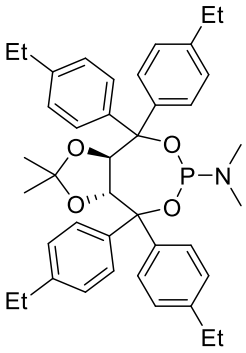
L2



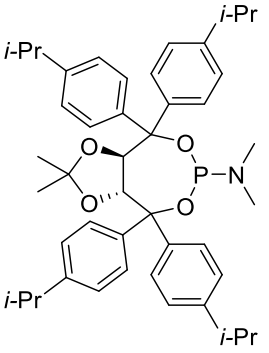
L3



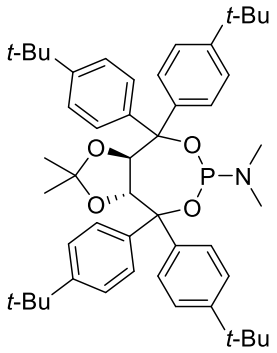
L4



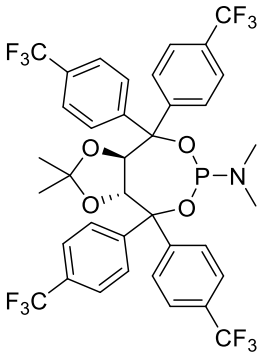
L5



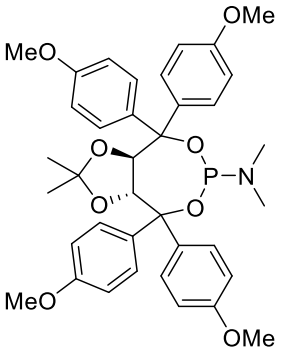
L6



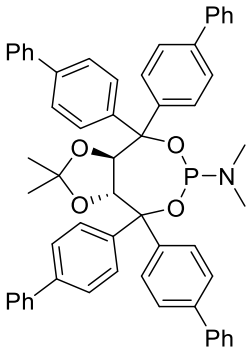
L7



L8

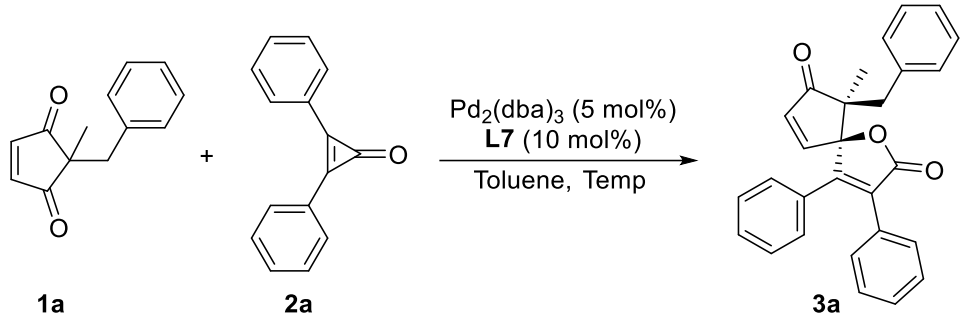


L9



L10

Table S2. The screen of temp in the reaction.[a]

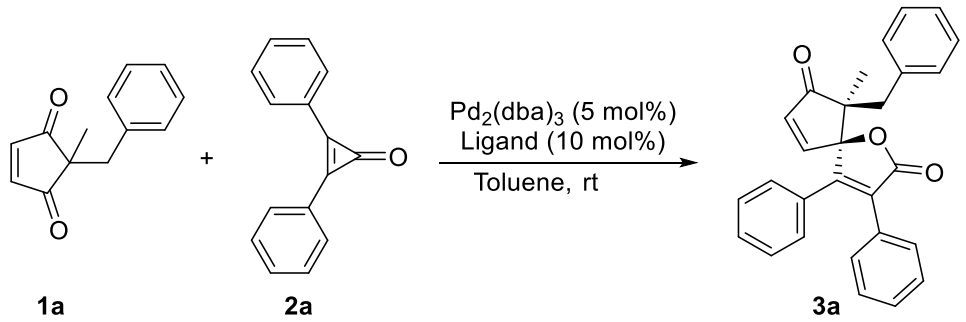


1a **2a** **3a**

Entry	Temp (°C)	Yield of **3a** (%)[a]	*ee* of **3a** (%)[b]	*dr* of **3a** (%)[c]
1	80	34	70	16:1
2	60	23	75	13:1
3	50	21	76	16:1
4	40	21	78	16:1
5	rt	15	73	> 19:1
6[d]	0	44	93	> 19:1
7[d]	rt	61	90	> 19:1

All the reactions were run on a 0.1 mmol scale in 1.0 mL solvents for 18 h. [a]Determined by ^{1}H NMR using dibromomethane as an internal standard. [b]Determined by HPLC. [c]Determind by ^{1}H NMR. [d]The reactions were performed with ligand **L15**.

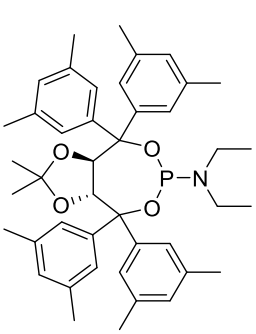
Table S3. The effect of P-ligands L11-L16 in the reaction.[a]

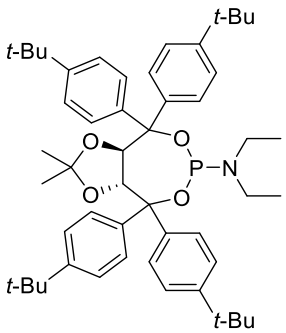


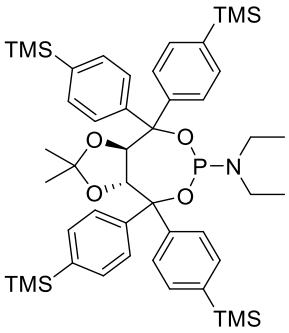
1a **2a** **3a**

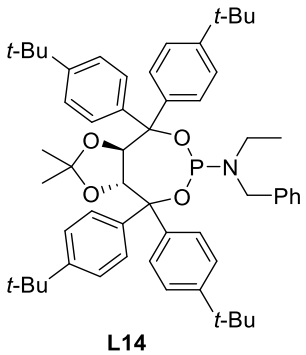
Entry	Ligand	Yield of **3a** (%)[a]	*ee* of **3a** (%)[b]	*dr* of **3a** (%)[c]
1	**L11**	trace	/	/
2	**L12**	23	89	13:1
3	**L13**	29	85	12:1
4	**L14**	24	83	16:1
5	**L15**	61	90	> 19:1
6	**L16**	57	90	19:1

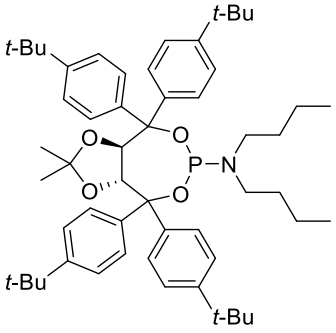
All the reactions were run on a 0.1 mmol scale in 1.0 mL solvents for 18 h. [a]Determined by ^{1}H NMR using dibromomethane as an internal standard. [b]Determined by HPLC. [c]Determind by ^{1}H NMR.











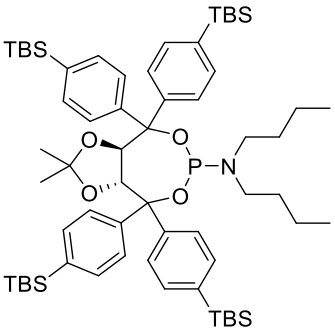
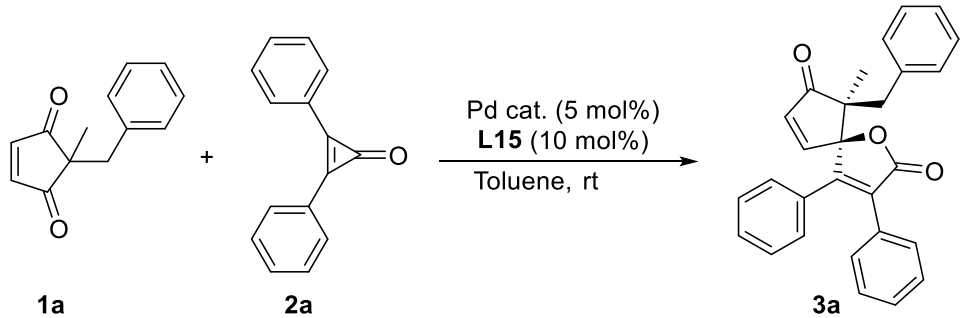


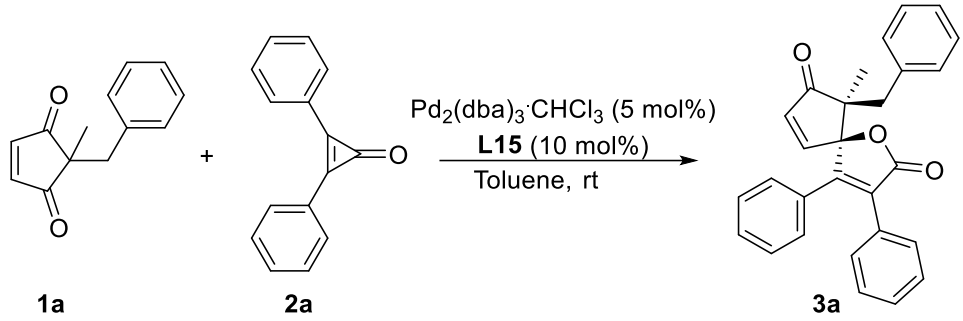
Table S4. The screen of palladium metal salts in the reaction.[a]



Entry	Pd cat.	Yield of **3a** (%)[a]	*ee* of **3a** (%)[b]	*dr* of **3a** (%)[c]
1	$Pd_2(dba)_3$	61	90	> 19:1
2	$Pd(dba)_2$	59	89	> 19:1
3	$Pd_2(dba)_3{\cdot}CHCl_3$	74	90	> 19:1
4	$Pd(MeCN)_2Cl_2$	nr	/	/
5	$PdBr_2$	nr	/	/

All the reactions were run on a 0.1 mmol scale in 1.0 mL solvents for 18 h. [a]Determined by ^{1}H NMR using dibromomethane as an internal standard. [b]Determined by HPLC. [c]Determind by ^{1}H NMR.

Table S5. The screen of the reaction concentration.[a]

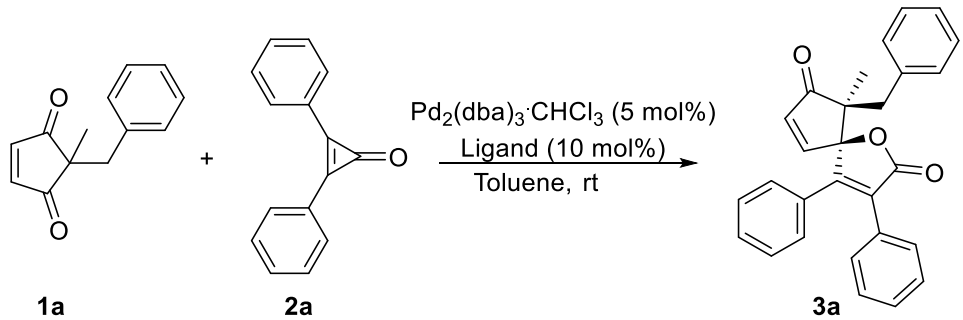


1a **2a** **3a**

Entry	Concentration	Yield of **3a** (%)[a]	*ee* of **3a** (%)[b]	*dr* of **3a** (%)[c]
1	0.025	61	90	> 19:1
2	0.05	70	90	> 19:1
3	0.1	74	90	> 19:1
4	0.2	81	90	> 19:1
5	0.5	87	90	> 19:1
6	1	78	90	> 19:1

All the reactions were run on a 0.1 mmol scale in X mL solvents for 18 h. [a]Determined by ^{1}H NMR using dibromomethane as an internal standard. [b]Determined by HPLC. [c]Determind by ^{1}H NMR.

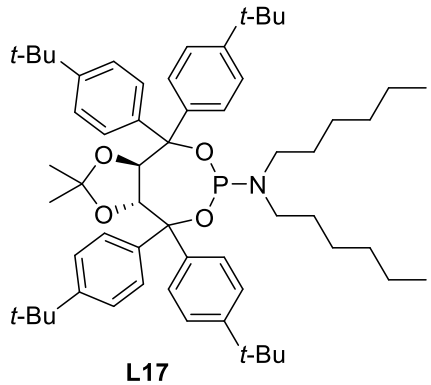
Table S6. The effect of P-ligands L17-L20 in the reaction.[a]



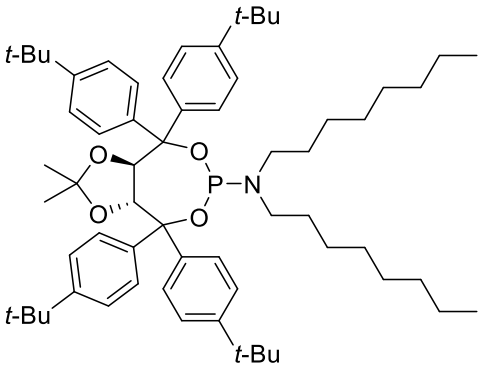
1a **2a** **3a**

Entry	Ligand	Yield of **3a** (%)[a]	*ee* of **3a** (%)[b]	*dr* of **3a** (%)[c]
1	**L15**	87	90	> 19:1
2	**L17**	85	90	> 19:1
3	**L18**	82	90	> 19:1
4	**L19**	18	61	19:1
5	**L20**	32	81	6:1

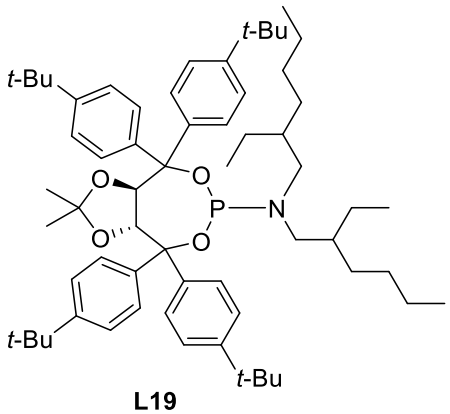
All the reactions were run on a 0.1 mmol scale in 0.2 mL solvents for 18 h. [a]Determined by ^{1}H NMR using dibromomethane as an internal standard. [b]Determined by HPLC. [c]Determind by ^{1}H NMR.



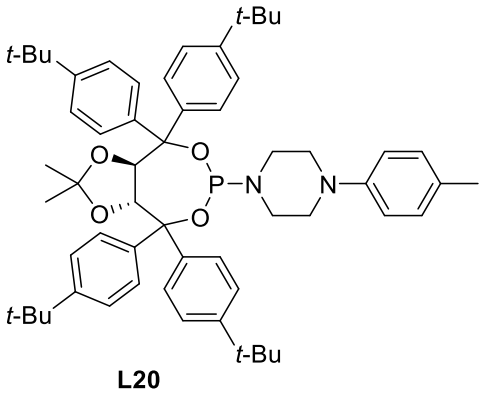
L17



L18

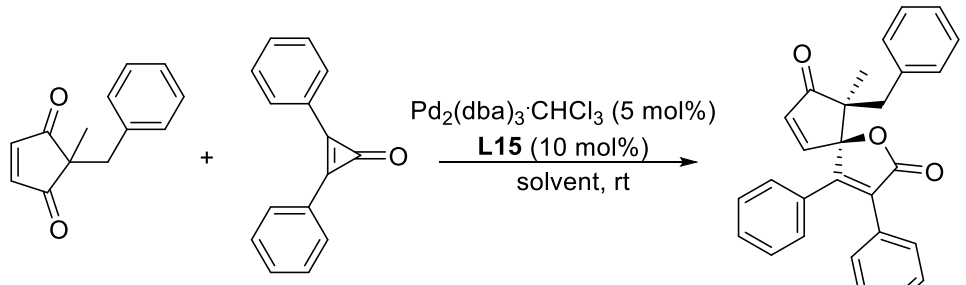


L19



L20

Table S7. The screen of solvents in the reaction.[a]



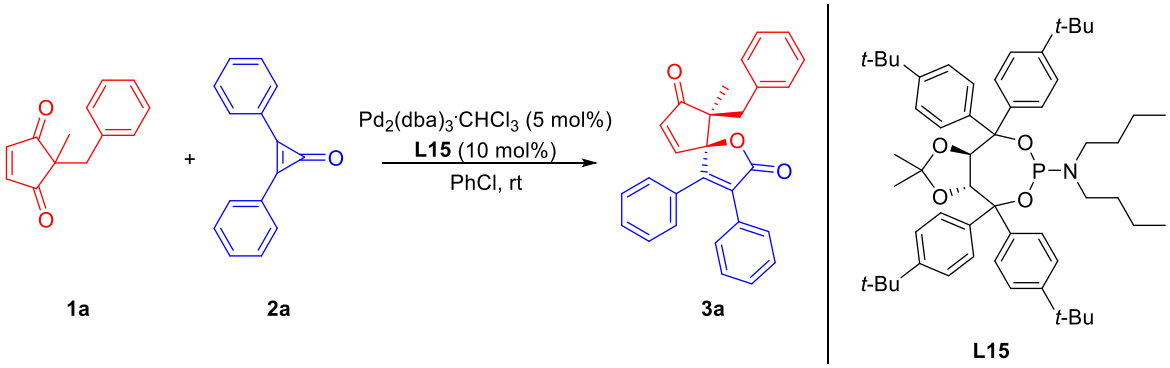
1a 2a 3a

Entry	Solvent	Yield of **3a** (%)[a]	*ee* of **3a** (%)[b]	*dr* of **3a** (%)[c]
1	Toluene	87	90	> 19:1
2	*o*-Xylene	78	90	> 19:1
3	*P*-Xylene	85	89	> 19:1
4	Mesitylene	74	88	> 19:1
5	$PhCF_3$	72	92	> 19:1
6	THF	32	92	13:1
7	2-MeTHF	24	90	13:1
8[d]	DMF	69	94	> 19:1
9[d]	DMAc	74	92	> 19:1
10[d]	NMP	67	67	> 19:1
11[d]	PhCl	87	92	> 19:1

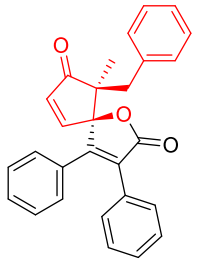
All the reactions were run on a 0.1 mmol scale in 0.2 mL solvents for 18 h. [a]Determined by ^{1}H NMR

using dibromomethane as an internal standard. [b]Determined by HPLC. [c]Determind by ^{1}H NMR. [d]Yield of the isolated product.

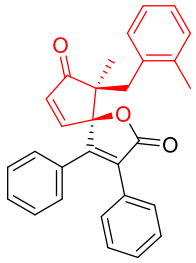
Scheme S1. Substrate scope



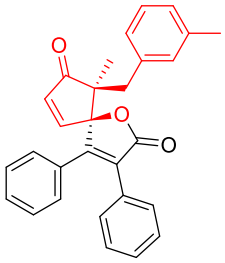
1a **2a** **3a** **L15**



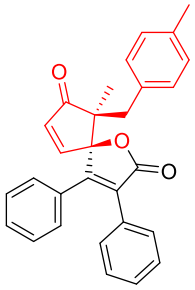
3a
87% yield,
92% *ee*, >19: 1 *dr*



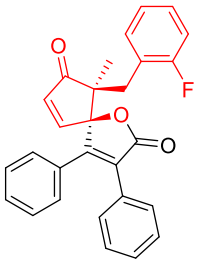
3b
81% yield,
91% *ee*, 10: 1 *dr*



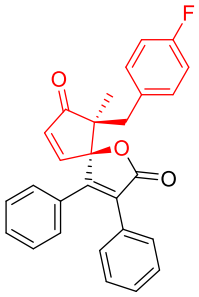
3c
89% yield,
93% *ee*, >19: 1 *dr*



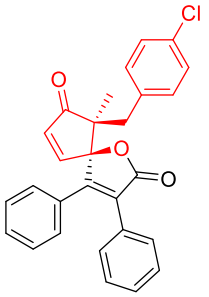
3d
86% yield,
93% *ee*, >19: 1 *dr*



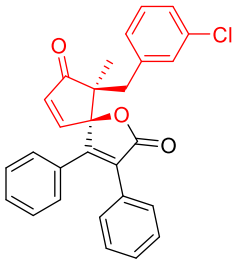
3e
99% yield,
92% *ee*, 9: 1 *dr*



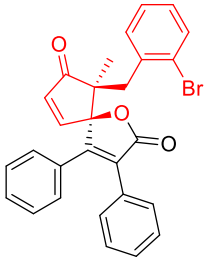
3f
95% yield,
92% *ee*, >19: 1 *dr*



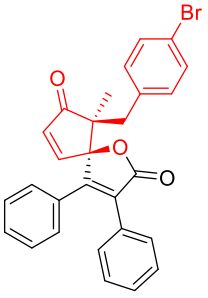
3g
99% yield,
92% *ee*, >19: 1 *dr*



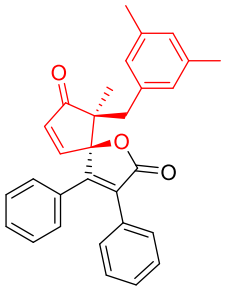
3h
91% yield,
91% *ee*, >19: 1 *dr*



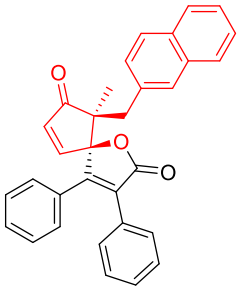
3i
86% yield,
91% *ee*, >19: 1 *dr*



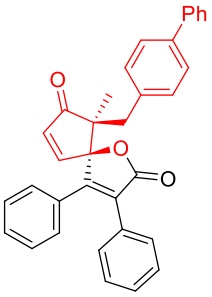
3j
96% yield,
90% *ee*, 17: 1 *dr*



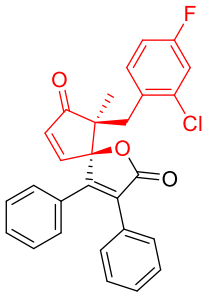
3k
93% yield,
92% *ee*, >19: 1 *dr*



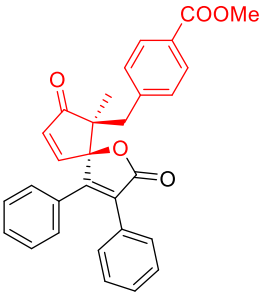
3l
98% yield,
91% *ee*, >19: 1 *dr*



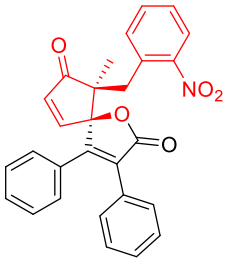
3m
80% yield,
93% *ee*, >19: 1 *dr*



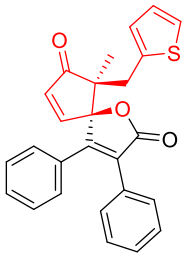
3n
88% yield,
88% *ee*, 4: 1 *dr*



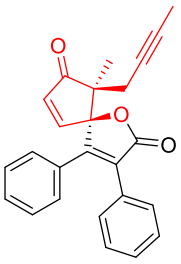
3o
99% yield,
92% *ee*, >19: 1 *dr*



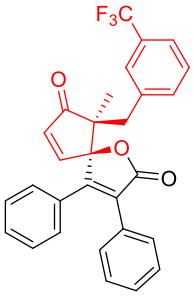
3p
56% yield,
92% *ee*, 6: 1 *dr*



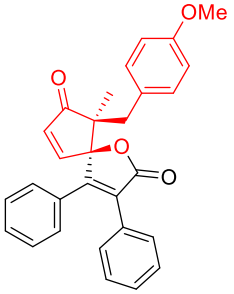
3q
53% yield,
92% *ee*, >19: 1 *dr*



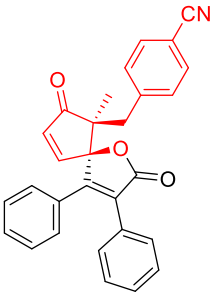
3r
44% yield,
94% *ee*, >19: 1 *dr*



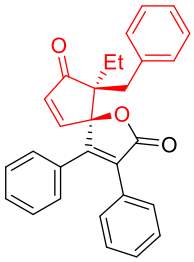
3s
97% yield,
92% *ee*, >19: 1 *dr*



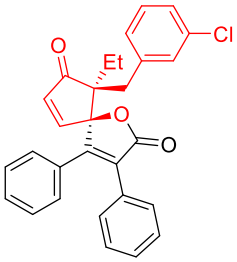
3t
84% yield,
93% *ee*, >19: 1 *dr*



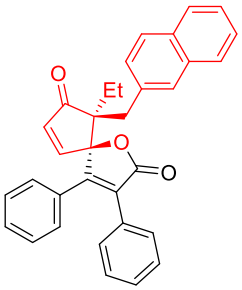
3u
99% yield,
91% *ee*, 17: 1 *dr*



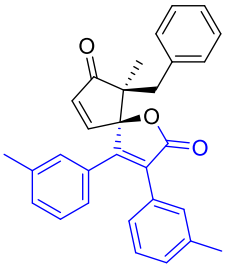
3v[a]
32% yield,
72% *ee*, 2: 1 *dr*



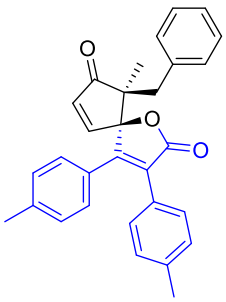
3w[a]
34% yield,
67% *ee*, 3: 1 *dr*



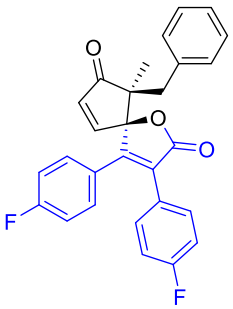
3x[a]
58% yield,
84% *ee*, 2: 1 *dr*



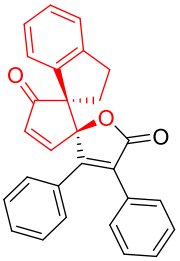
3y
99% yield,
95% *ee*, 17: 1 *dr*



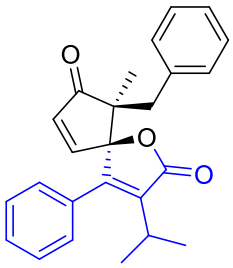
3z
42% yield,
85% *ee*, >19: 1 *dr*



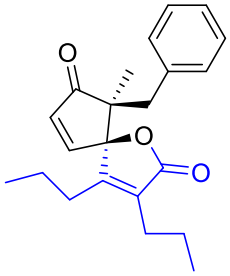
3aa
63% yield,
84% *ee*, >19: 1 *dr*



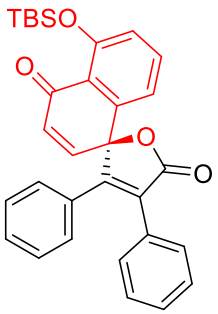
3ab
94% yield,
83% *ee*, 3: 1 *dr*



3ac
57% yield,
86% *ee*, >19: 1 *dr*



3ad
55% yield,
65% *ee*, >19: 1 *dr*

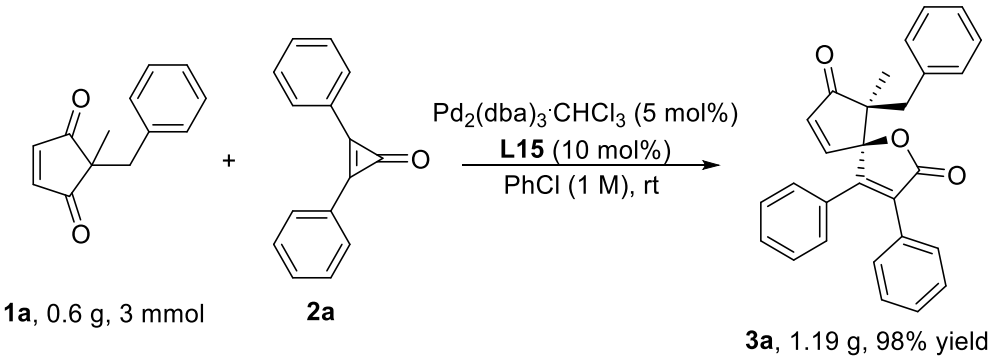


5
86% yield,
92% *ee*, 4: 1 *rr*

[a]The reaction temperature is 50 °C.

4. Transformation of Products.

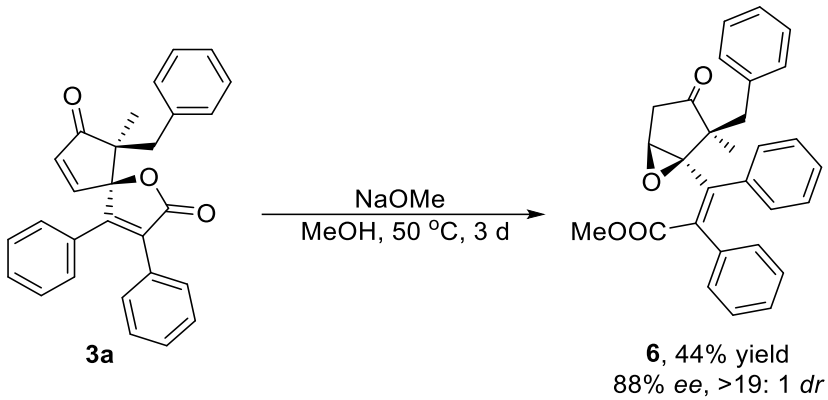
Gram reaction



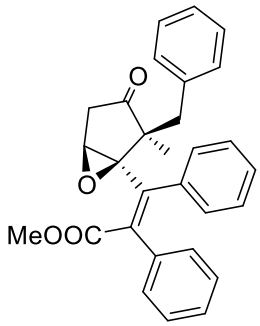
1a, 0.6 g, 3 mmol **2a** **3a**, 1.19 g, 98% yield

A vial was charged with 1,3-diones **1a** (0.6g, 3 mmol), cyclopropenone **2a** (1.24g, 0.4 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (155mg, 5 mol%), (*R*,*R*)-**L15** (255mg, 10 mol%) and evacuated under high vacuum and backfilled with N_2. PhCl (3 mL) was next added. The mixture was stirred at 25 °C for 18 hours. Upon reaction completion, the crude was purified by column chromatography to give the corresponding product and was analyzed with ^1H NMR to determine the corresponding product ratio and recovered.

Procedure for the synthesis of 6.



Prepared according to a previous reported method using **3a** (0.1mmol, 1.0 equiv), NaOMe (0.1mmol, 1.0 equiv) and 0.5mL of Methanol. The mixture was stirred at 50 °C for 3 days. After the reaction completed, the reaction solution was evaporated under reduced pressure and was the purified by silica gel column chromatography to afford **6**.



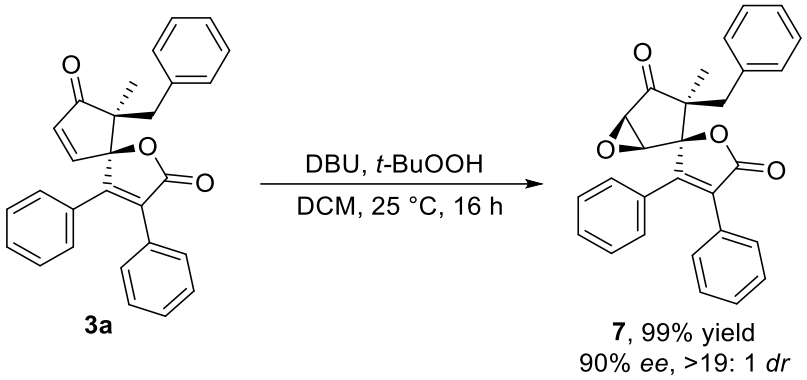
6

Methyl (Z)-3-((1R,2S,5S)-2-benzyl-2-methyl-3-oxo-6-oxabicyclo [3.1.0] hexan-1-yl)-2,3-diphenylacrylate (6):

Yellow oil (19.2 mg, 44% yield), purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$=63.9 (c = 0.77, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 - 7.11 (m, 9H), 7.11 - 7.02 (m, 4H), 6.18 (d, *J* = 7.6 Hz, 2H), 4.67 (m, 1H), 3.45 (s, 3H), 3.11 (d, *J* = 14.0 Hz, 1H), 2.97 - 2.83 (m, 2H), 2.71 (m, 1H), 0.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.7, 170.9, 157.7, 136.2, 133.2, 131.9, 131.8, 129.3, 129.3, 128.9, 128.8, 128.6, 128.2, 128.1, 127.8, 126.9, 95.4, 77.5, 77.4, 77.2, 76.8, 75.6, 58.5, 58.1, 39.5, 36.5, 29.8, 19.3. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{29}H_{26}NaO_4$: 461.1723, found: 461.1748. The enantiomeric excess was determined by UPLC with Chiralpark

INA column (hexanes:2-propanol = 75:25, 1 mL/min, 211 nm, 88% *ee*, *d.r.* > 19:1); major enantiomer tr = 3.688 min, minor enantiomer tr = 4.003 min.

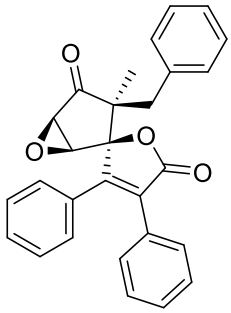
Procedure for the synthesis of 7.



3a

7, 99% yield
90% *ee*, >19: 1 *dr*

Prepared according to a previous reported method[5], *t*-BuOOH (600 μL) was diluted with H_2O (3 mL) and extracted with DCM (5 mL), combined the organic layers. **3a** (0.1 mmol, 1 equiv) was dissolved in 0.5 mL of the obtained solution, followed by the addition of DBU (0.02 mmol, 0.2 equiv). The mixture was stirred at 25 ºC for 16 hours. After the reaction completed, the reaction solution was evaporated under reduced pressure and was the purified by silica gel column chromatography to afford **7**.



7

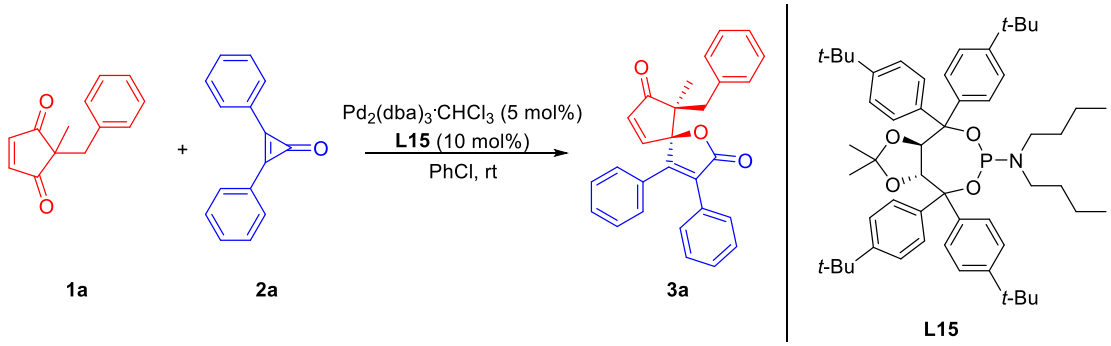
(1S,2R,3S,5R)-3-benzyl-3-methyl-3',4'-diphenyl-5'H-6-oxaspiro[bicyclo[3.1.0] hexane-2,2'-furan]-4,5'-dione (7):

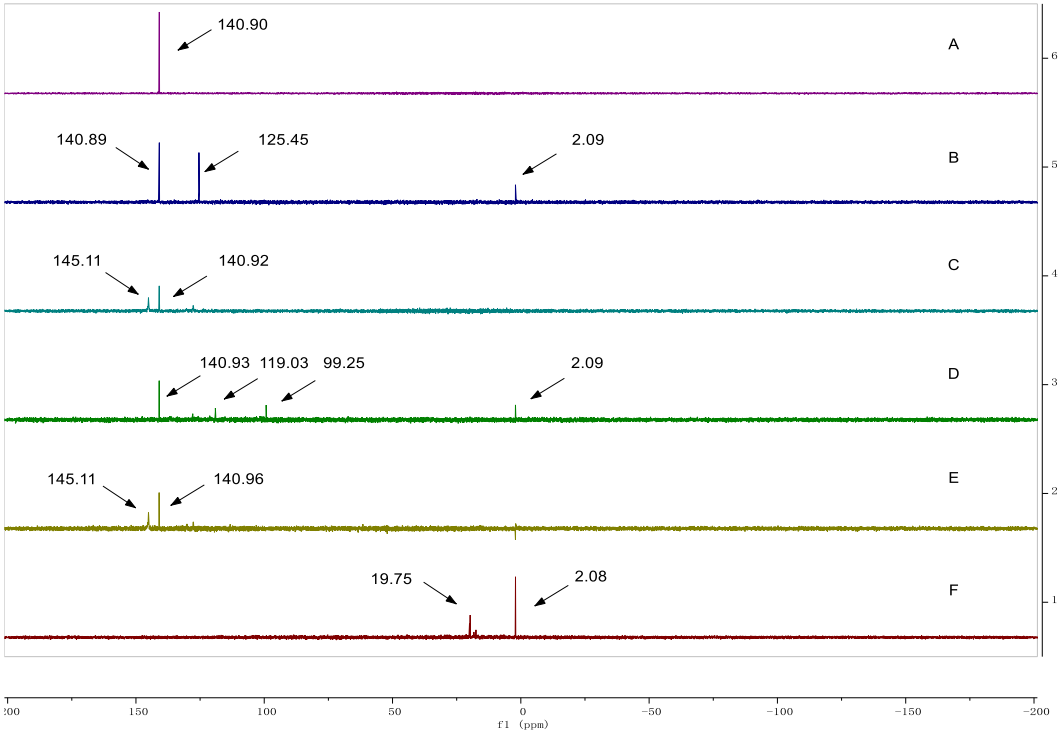
Yellow oil (41.8 mg, 99% yield), purified by column chromatography (SiO_2, PE/EA= 4:1). $[\alpha]_D^{25}$=13.3 (c = 0.80, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 - 7.21 (m, 5H), 7.21 - 7.11 (m, 6H), 7.08 - 7.01 (m, 2H), 7.01 - 6.94 (m, 2H), 4.24 (d, *J* = 2.4 Hz, 1H), 3.78 (d, *J* = 2.4 Hz, 1H), 3.71 (d, *J* = 13.2 Hz, 1H), 2.69 (d, *J* = 13.6 Hz, 1H), 0.77 (s,

3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.0, 170.5, 159.0, 136.3, 131.4, 130.9, 130.8, 130.3, 129.8, 129.4, 129.4, 129.0, 128.8, 128.6, 128.1, 126.9, 91.2, 77.5, 77.4, 77.2, 76.8, 59.6, 57.4, 52.1, 44.0, 17.0. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{29}H_{26}NaO_4$: 445.1410, found: 445.1430. The enantiomeric excess was determined by HPLC with Chiralpark OD column (hexanes:2-propanol = 75:25, 1 mL/min, 211 nm, 90% *ee*, *d.r.* > 19:1); major enantiomer tr = 21.498 min, major enantiomer tr = 18.207 min, minor enantiomer tr = 16.351 min.

5. Supplementary Figures

Figure S1. Comparison of ^{31}P NMR of ligand and Pd/L7 complex in the reaction with 1a and 2a.





A): L15 (0.02 mmol, 17.0 mg). **B): L15** (0.02 mmol, 17.0 mg) and $Pd_2(dba)_3 \cdot CHCl_3$ (0.01 mmol, 10.4 mg) were stirred for 30 mins. **C): L15** (0.02 mmol, 17.0 mg), $Pd_2(dba)_3 \cdot CHCl_3$ (0.01 mmol, 10.4 mg) and **1a** (0.2 mmol, 40.0 mg) were stirred for 30 mins. **D) L15** (0.02 mmol, 17.0 mg), $Pd_2(dba)_3 \cdot CHCl_3$ (0.01 mmol, 10.4 mg) and **2a** (0.4 mmol, 82.5 mg) were stirred for 30 mins. **E): L15** (0.02 mmol, 17.0 mg), $Pd_2(dba)_3 \cdot CHCl_3$ (0.01 mmol, 10.4 mg), **1a** (0.2 mmol, 40.0 mg) and **2a** (0.4 mmol, 82.5 mg) were stirred for 30 mins. **F): L15** (0.02 mmol, 17.0 mg), $Pd_2(dba)_3 \cdot CHCl_3$ (0.01 mmol, 10.4 mg), **1a** (0.2 mmol, 40.0 mg) and **2a** (0.4 mmol, 82.5 mg) were stirred for 24 hours.

Figure S2. Proposed catalytic cycles for the model reaction system.

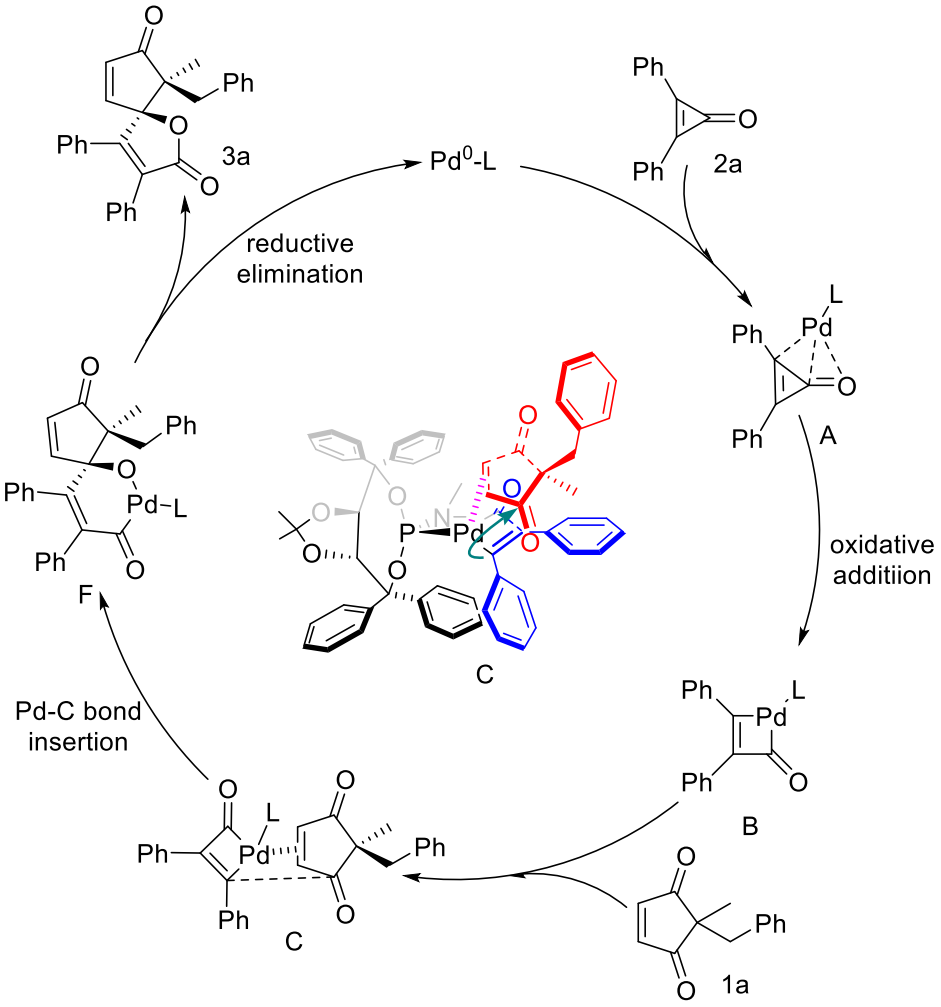
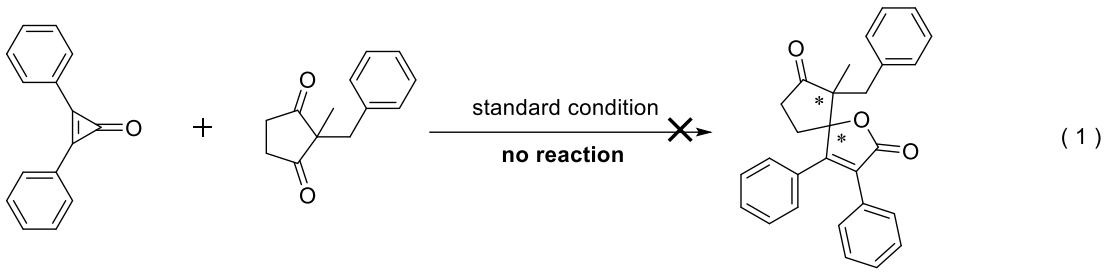
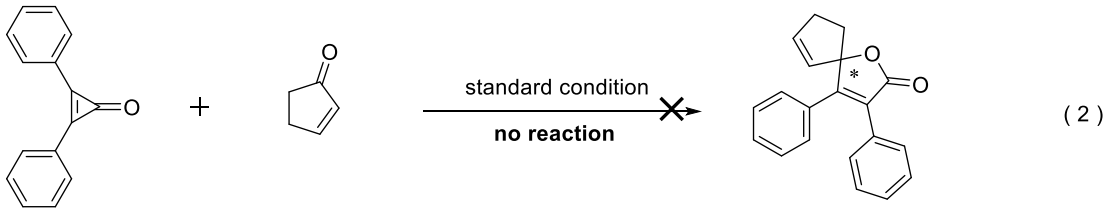


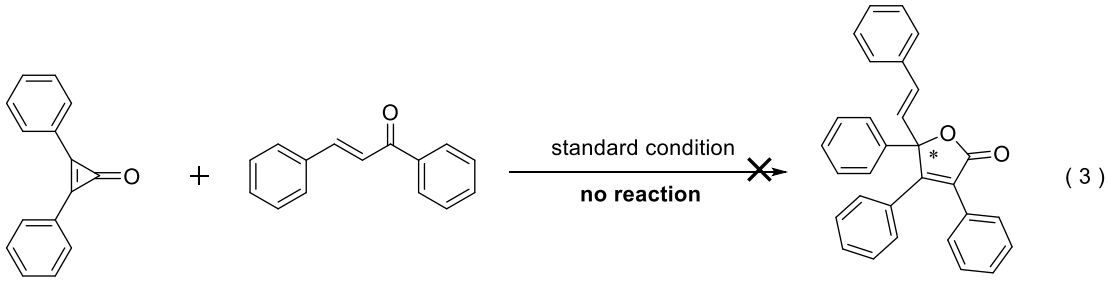
Figure S3. Control Experiments



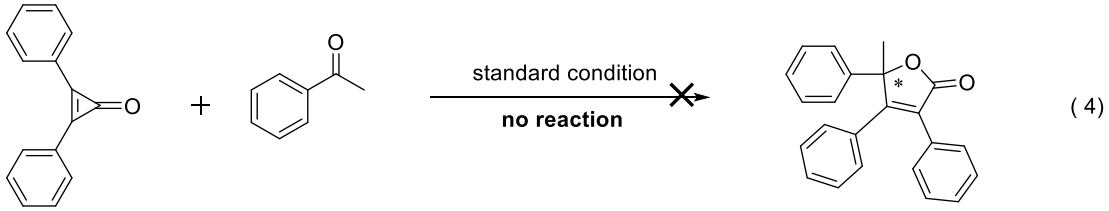
(1)



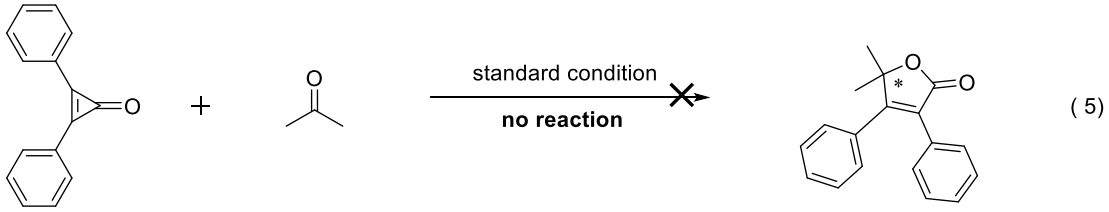
(2)



(3)



(4)



(5)

Figure S4. NOESY spectrum of 4. The determination of the structure of product 4.

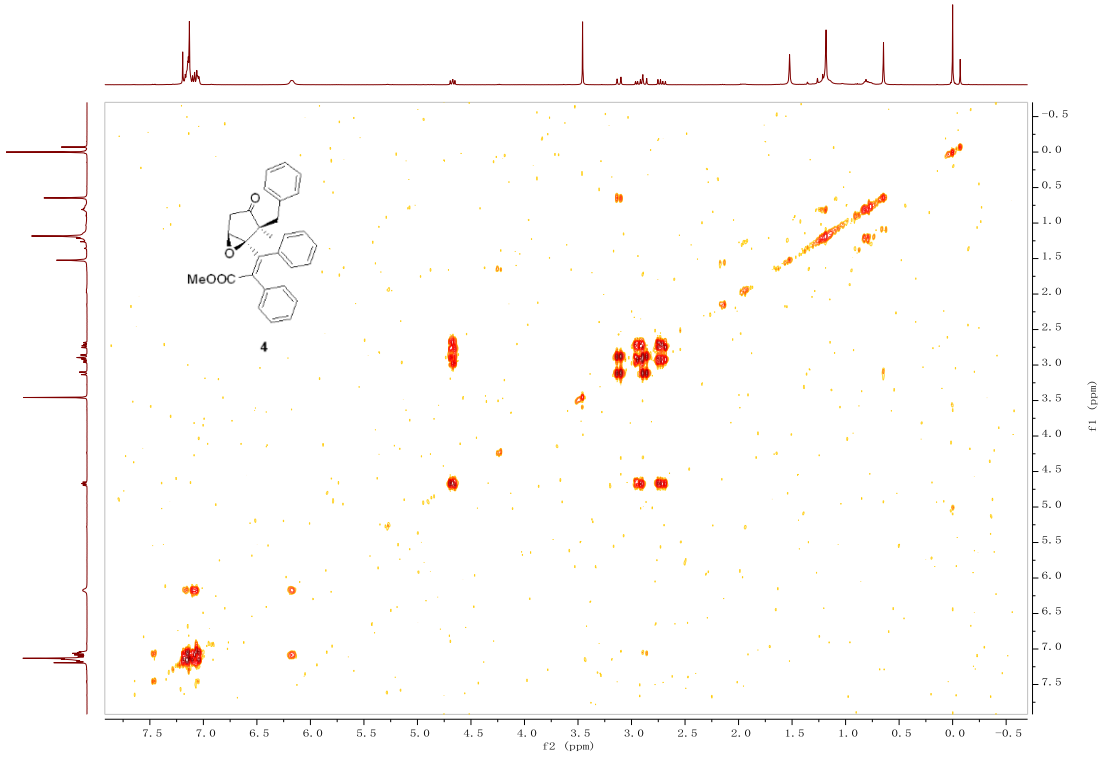
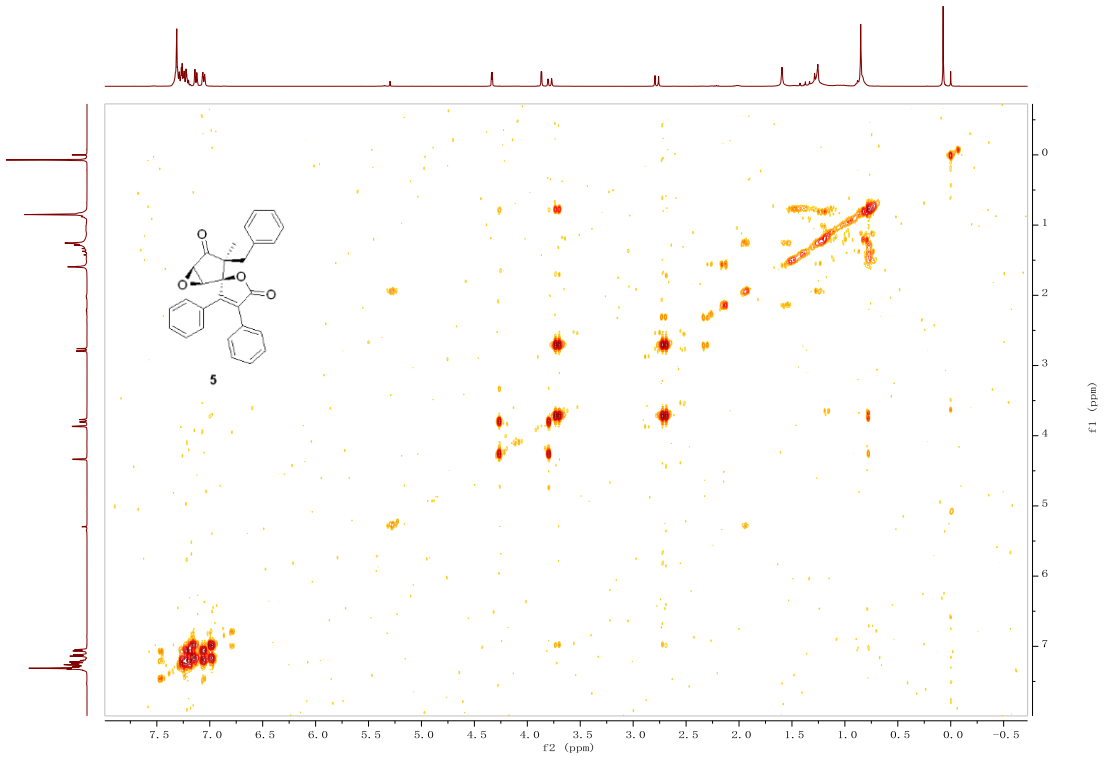
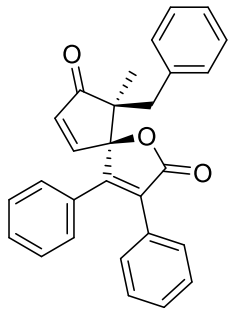


Figure S5. NOESY spectrum of 5. The determination of the structure of product 5.

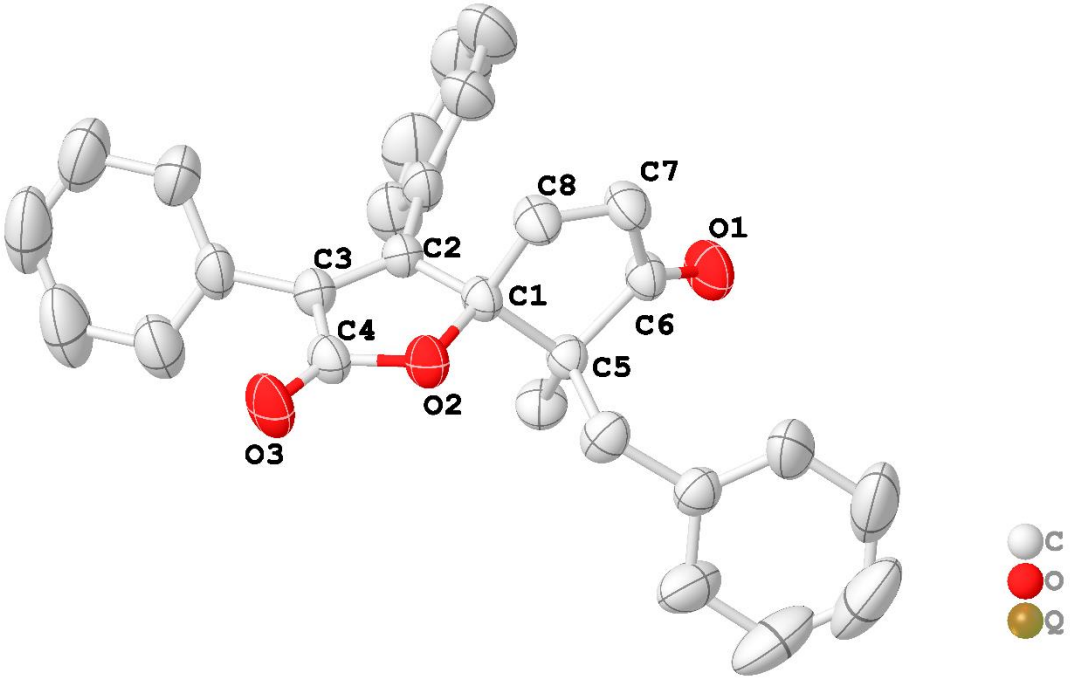


6. The confirmation of the absolute configuration of chiral product.

X-ray structures of **3a** (CCDC 2024499)



(5*R*,6*S*)-**3a**



7. References

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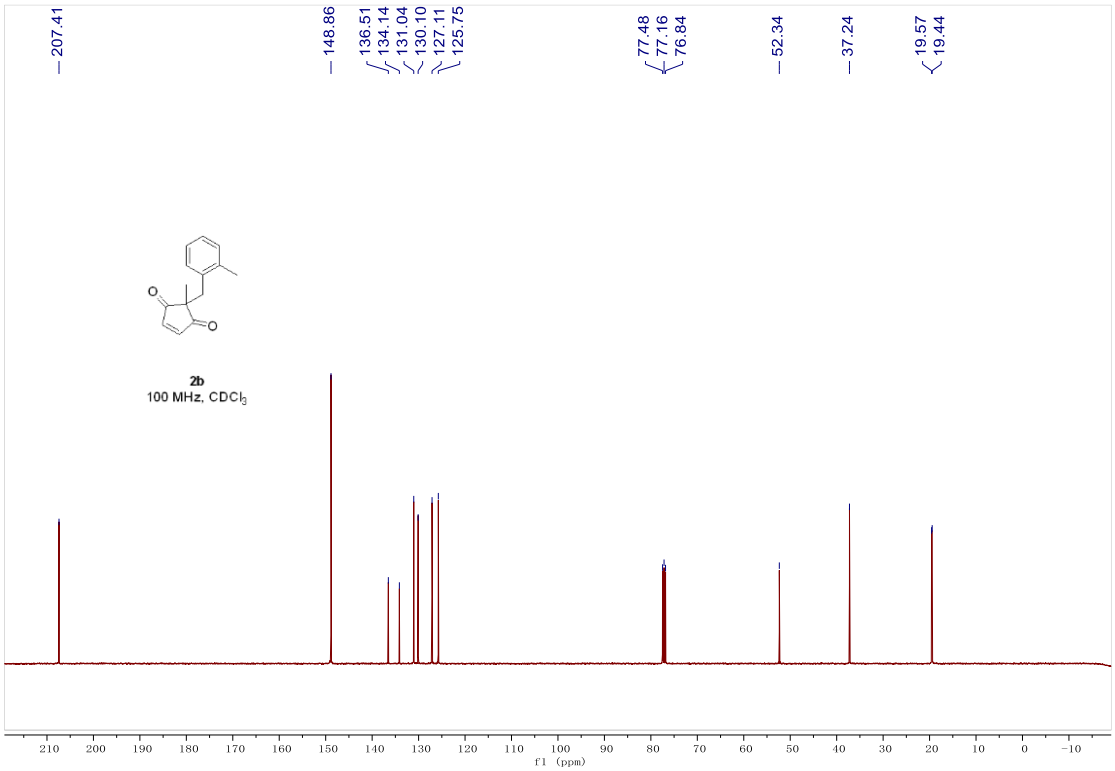
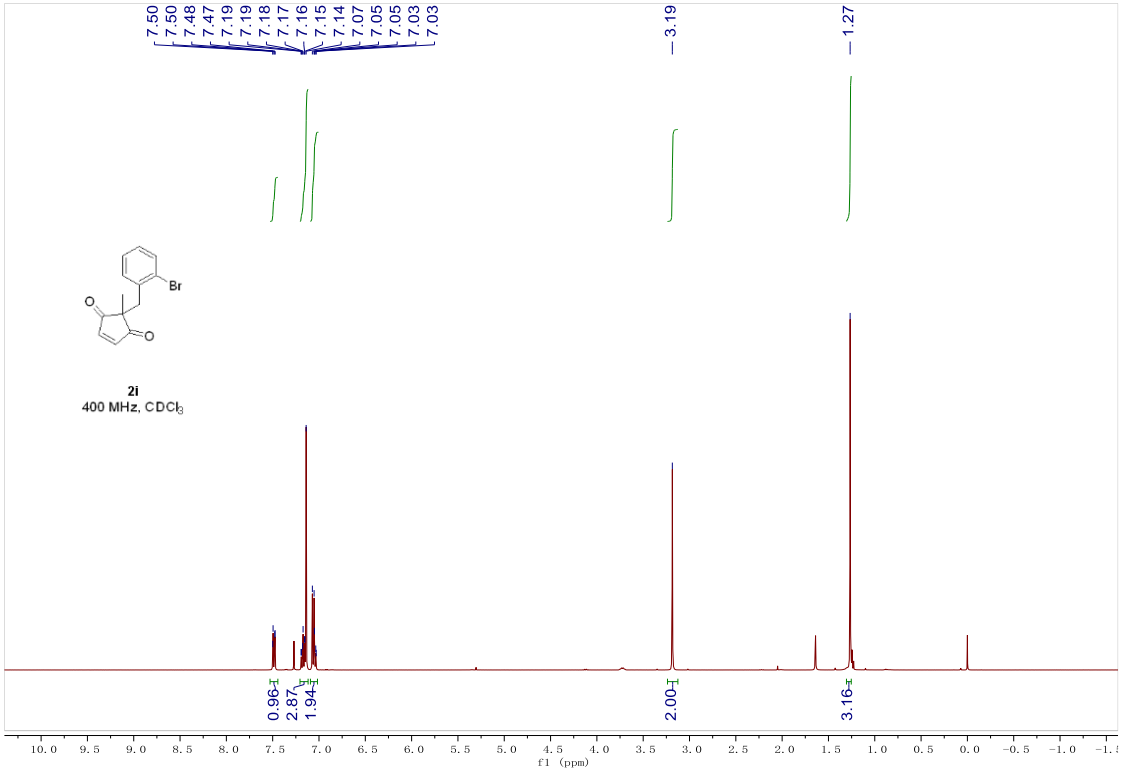
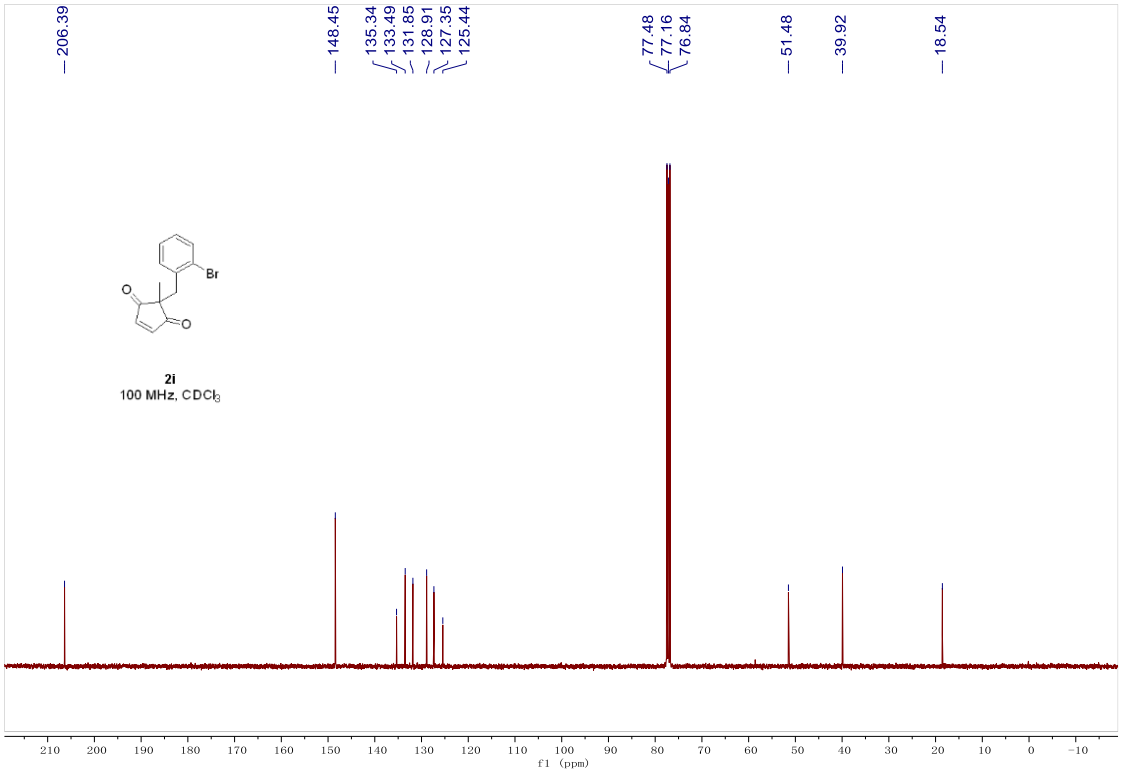
5 Al' mukhametov, A.Z.; Gimazetdinov, A.M.; Miftakhov, M.S. *Mendeleev. Commun.* **2018**, 28, 362-363.

8. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra



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135.34
133.49
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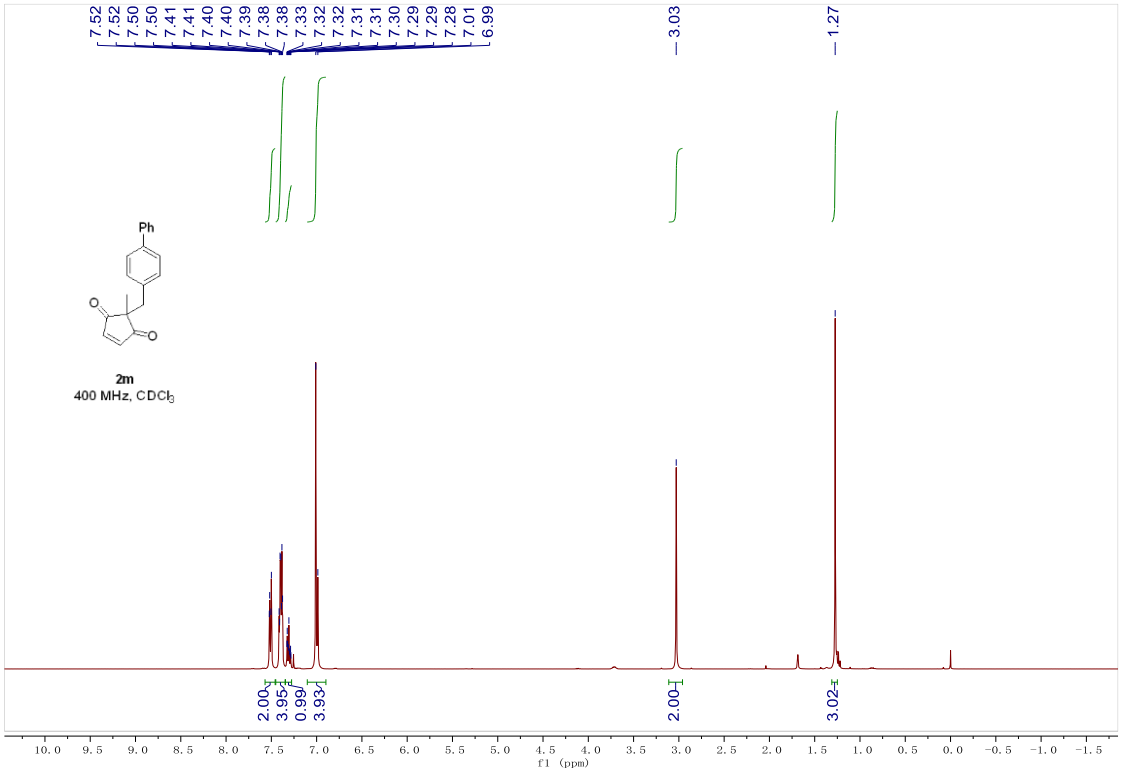
128.91
127.35
125.44
77.48
77.16
76.84
51.48
39.92
18.54
Br
O
O
2i
100 MHz, CDCl3
f1 (ppm)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7.52
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7.50
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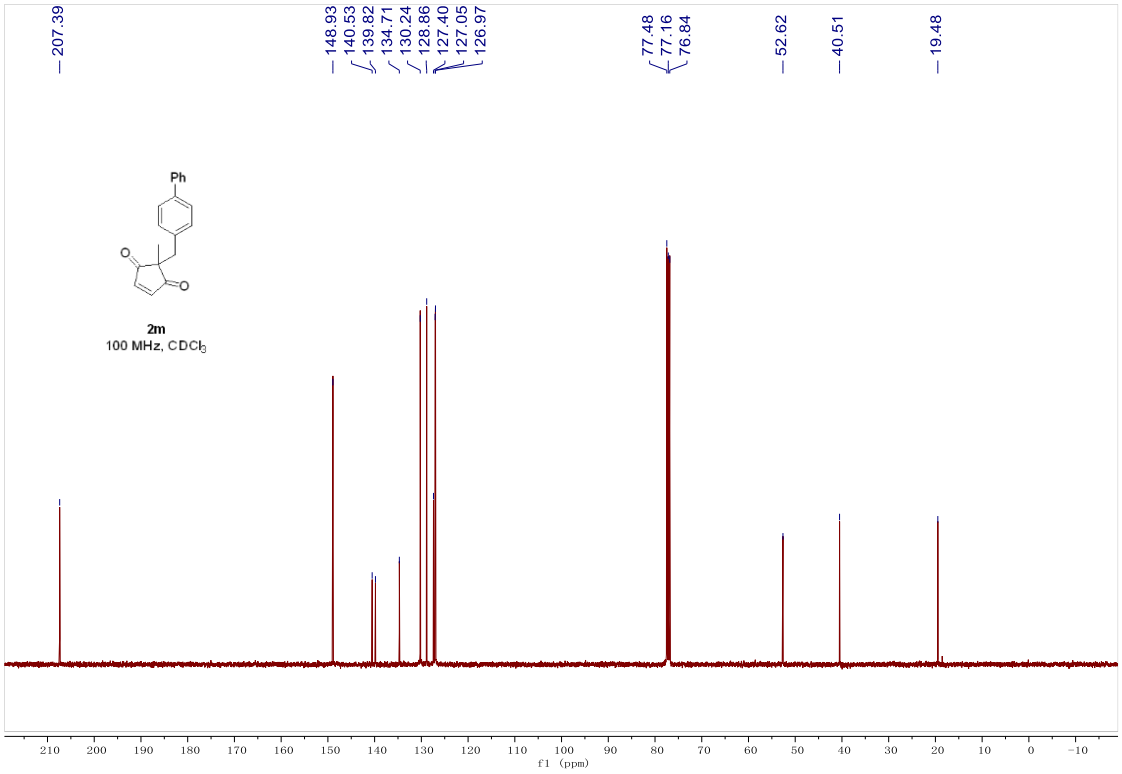
7.41
7.40
7.40
7.39
7.38
7.38
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.01
6.99
3.03
1.27
Ph
O
O
2m
400 MHz, CDCl3
2.00
3.95
0.99
3.93
2.00
3.02
f1 (ppm)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134.71
130.24
128.86
127.40
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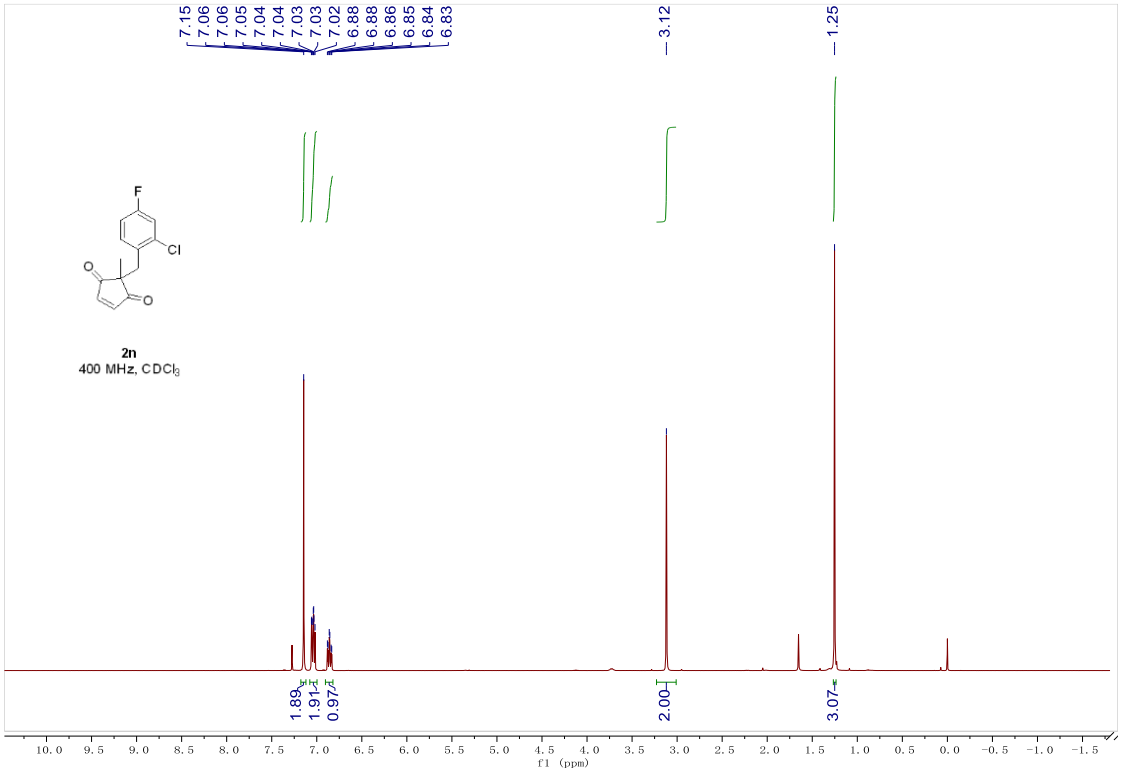
126.97
77.48
77.16
76.84
52.62
40.51
19.48
Ph
O
O
2m
100 MHz, CDCl3
f1 (ppm)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7.06
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7.04
7.04
7.03
7.03
7.02
6.88
6.88
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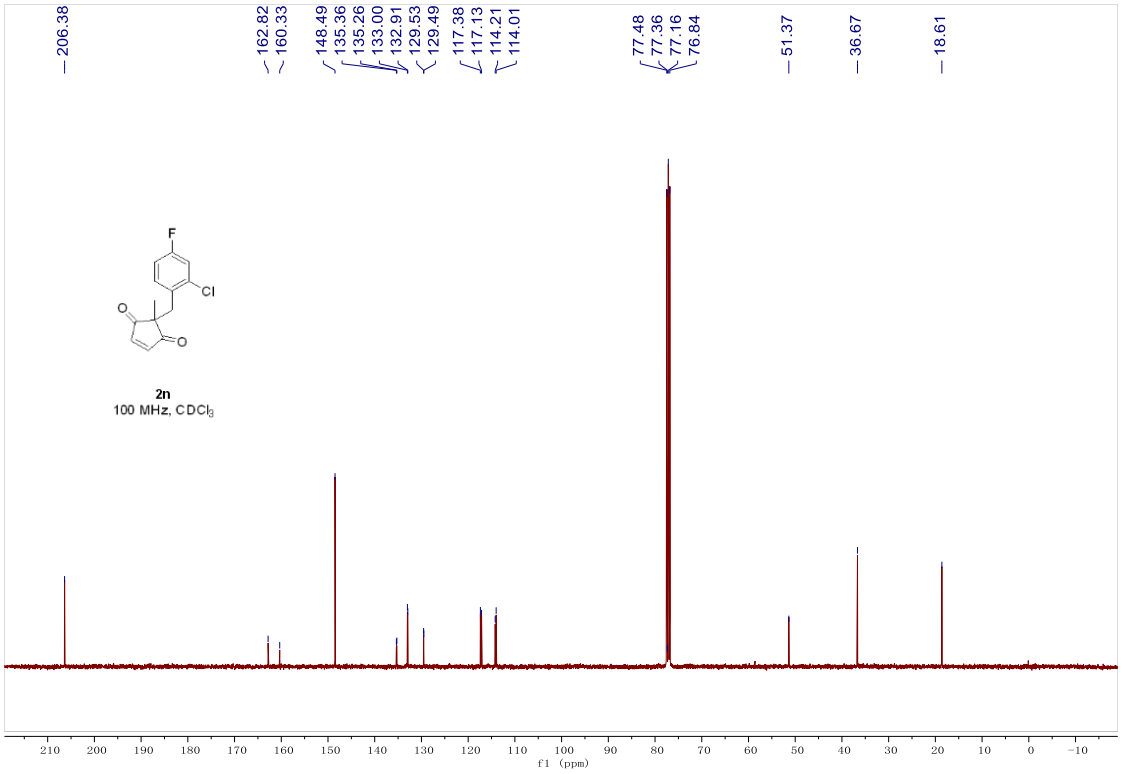
6.85
6.84
6.83
3.12
1.25
F
Cl
O
O
2n
400 MHz, CDCl3
1.89
1.91
0.97
2.00
3.07
f1 (ppm)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135.26
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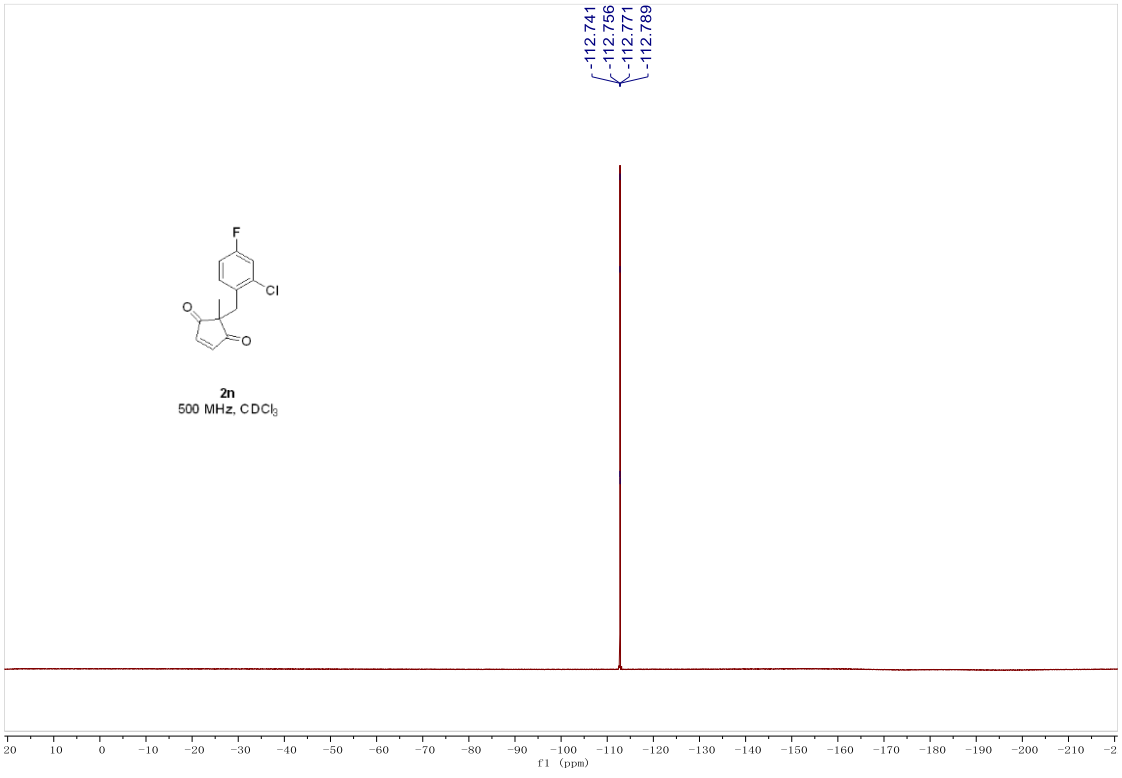
129.49
117.38
117.13
114.21
114.01
77.48
77.36
77.16
76.84
51.37
36.67
18.61
F
Cl
O
O
2n
100 MHz, CDCl3
f1 (ppm)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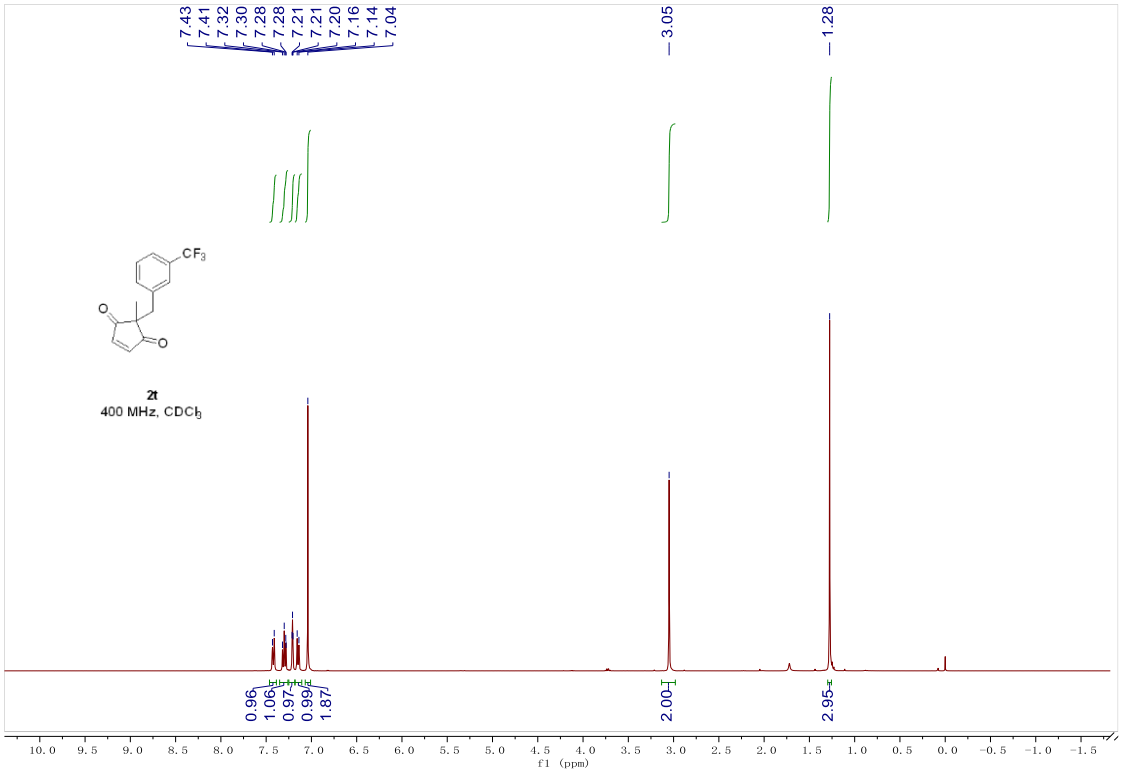
-112.771
-112.789
F
Cl
O
O
2n
500 MHz, CDCl3
f1 (ppm)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7.21
7.21
7.20
7.16
7.14
7.04
3.05
1.28
CF3
O
O
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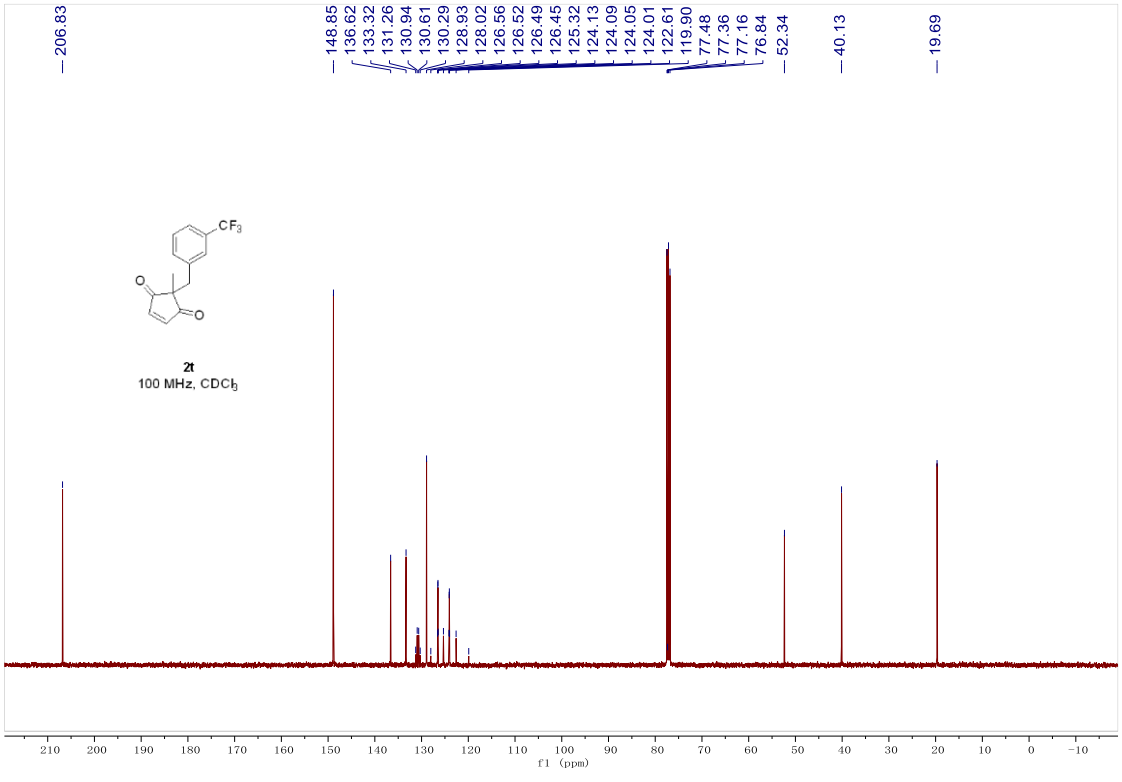
400 MHz, CDCl3
0.96
1.06
0.97
0.99
1.87
2.00
2.95
f1 (ppm)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126.52
126.49
126.45
125.32
124.13
124.09
124.05
124.01
122.61
119.90
77.48
77.36
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76.84
52.34
40.13
19.69
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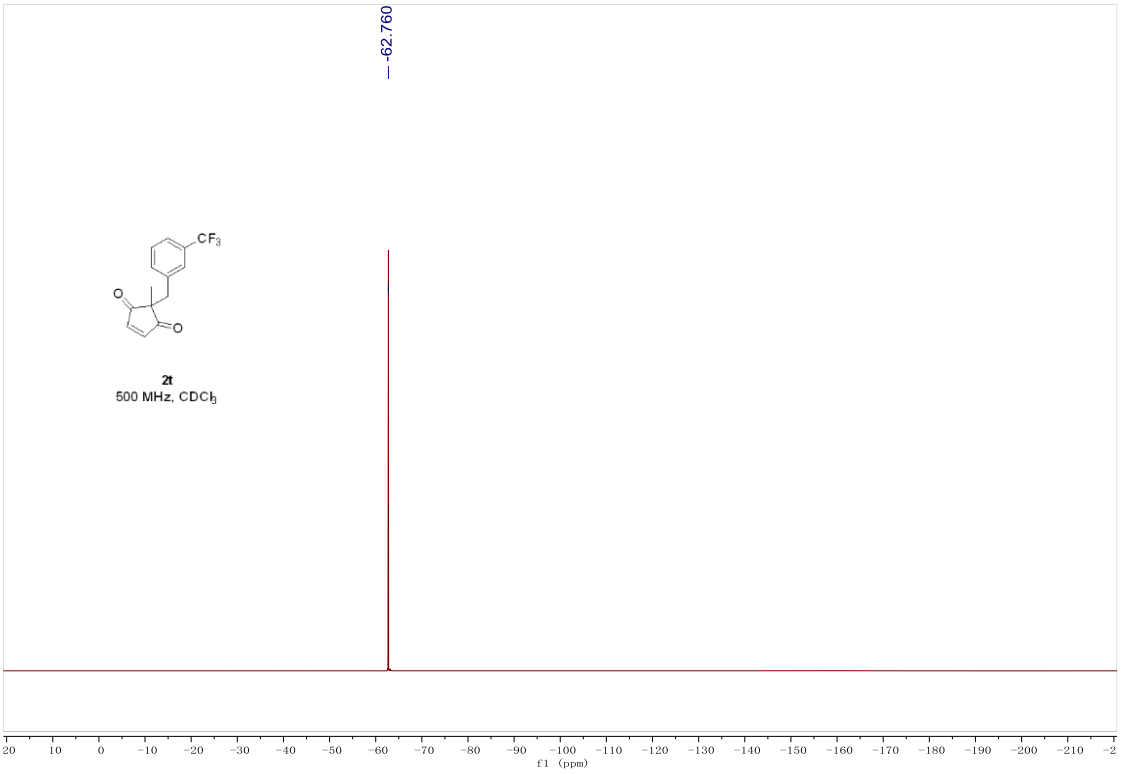
O
O
2t
100 MHz, CDCl3
f1 (ppm)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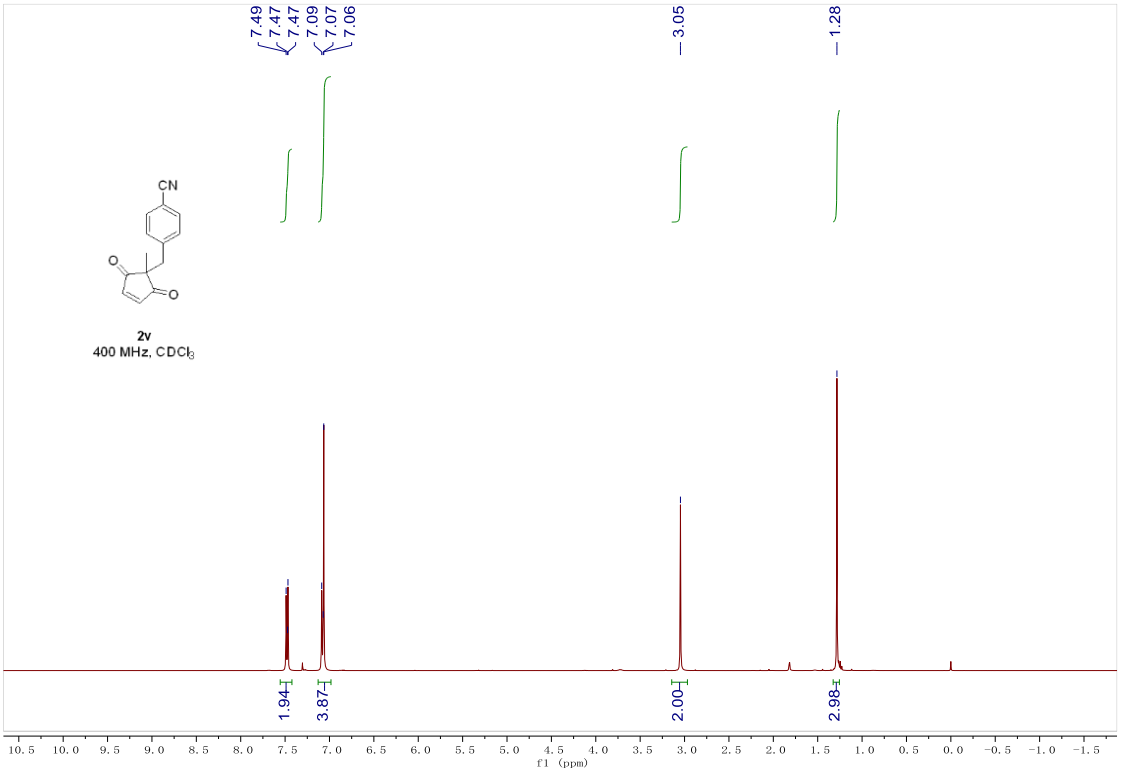
f1 (ppm)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7.07
7.06
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CN
O
O
2v
400 MHz, CDCl3
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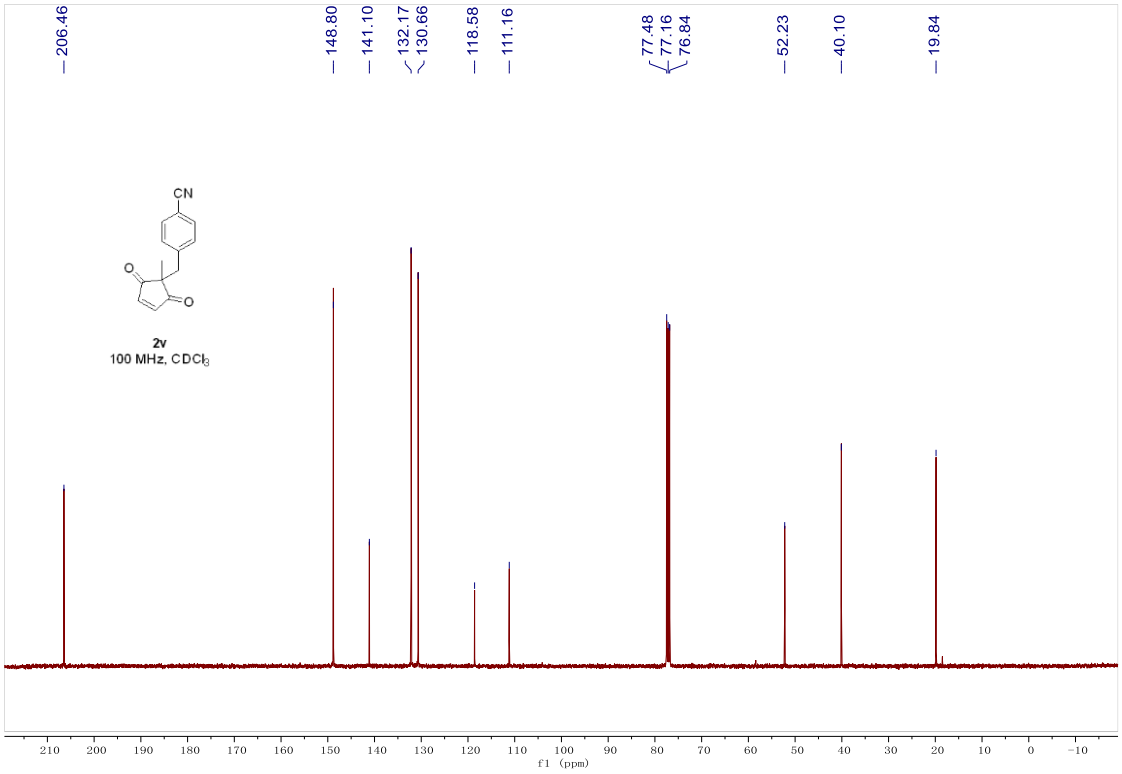
3.87
2.00
2.98
f1 (ppm)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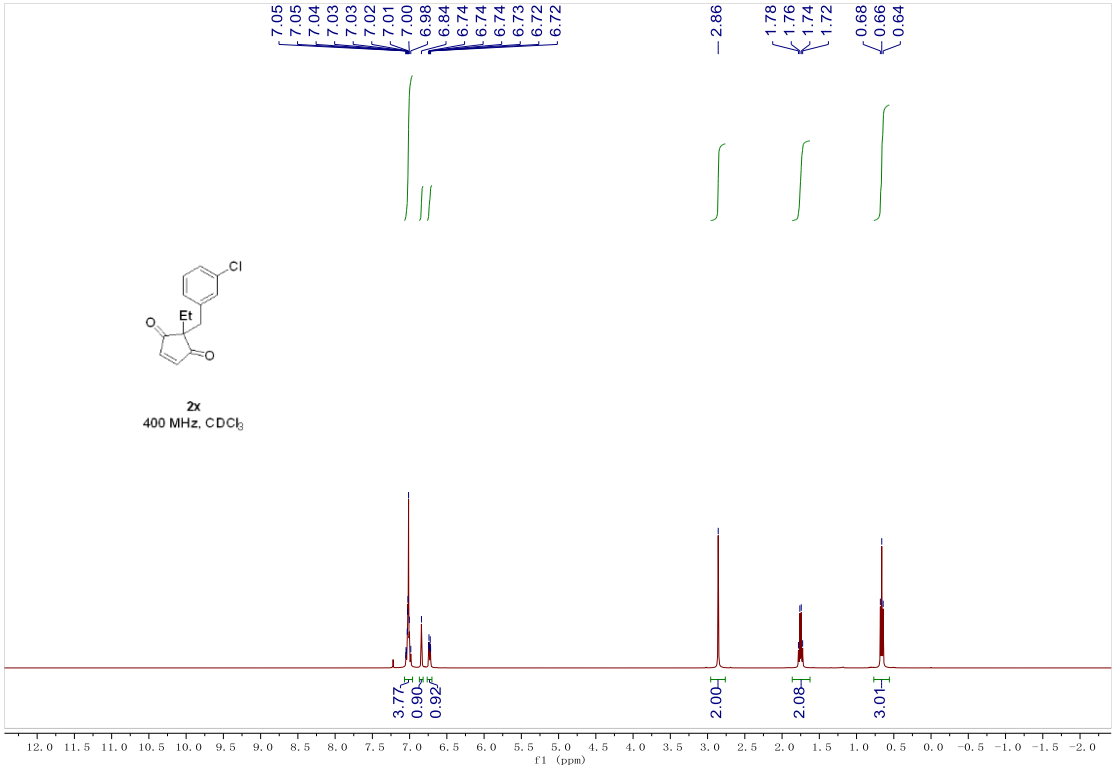
CN
O
O
2v
100 MHz, CDCl3
f1 (ppm)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7.00
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6.74
6.73
6.72
6.72
2.86
1.78
1.76
1.74
1.72
0.68
0.66
0.64
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400 MHz, CDCl3
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2.00
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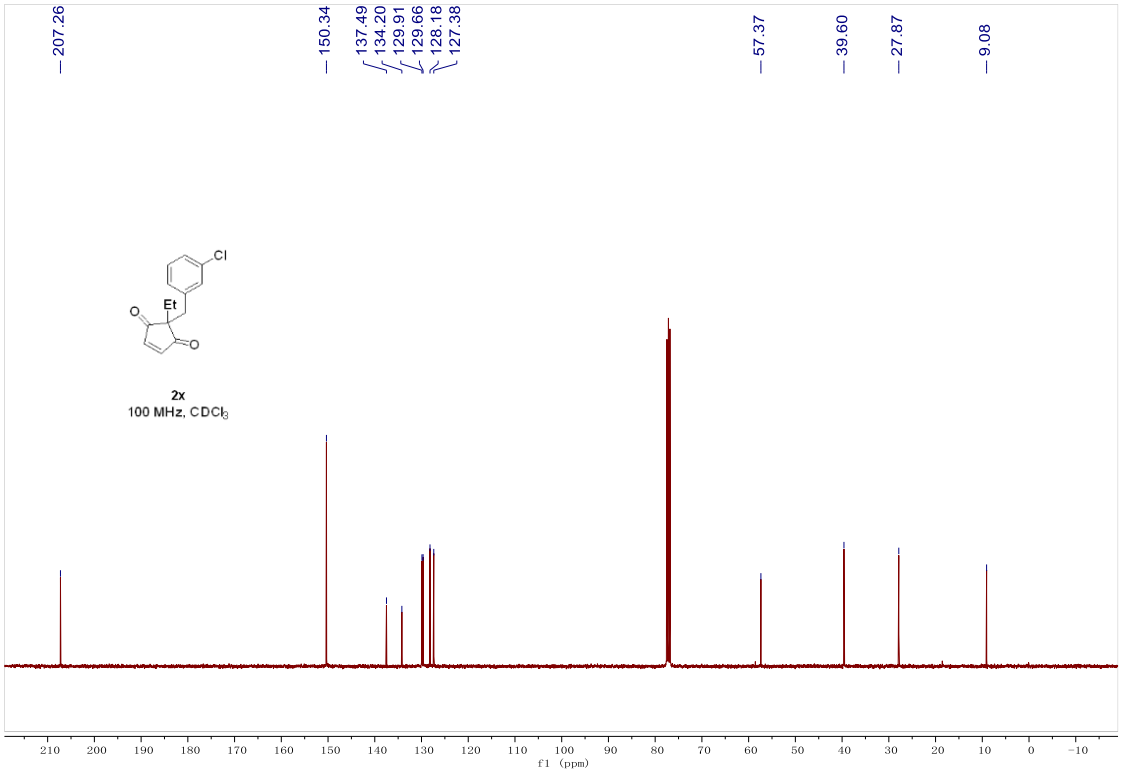
3.01
f1 (ppm)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O
O
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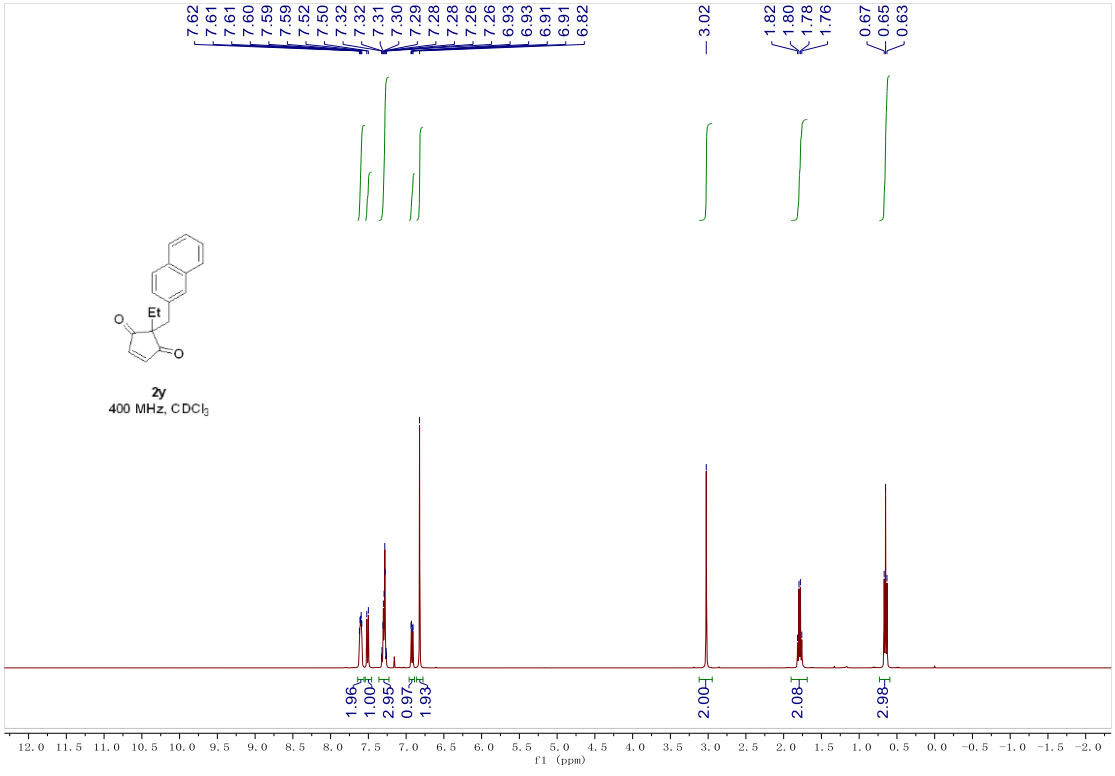
100 MHz, CDCl3
f1 (ppm)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7.28
7.26
7.26
6.93
6.91
6.91
6.82
3.02
1.82
1.80
1.78
1.76
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0.65
0.63
Et
O
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2.95
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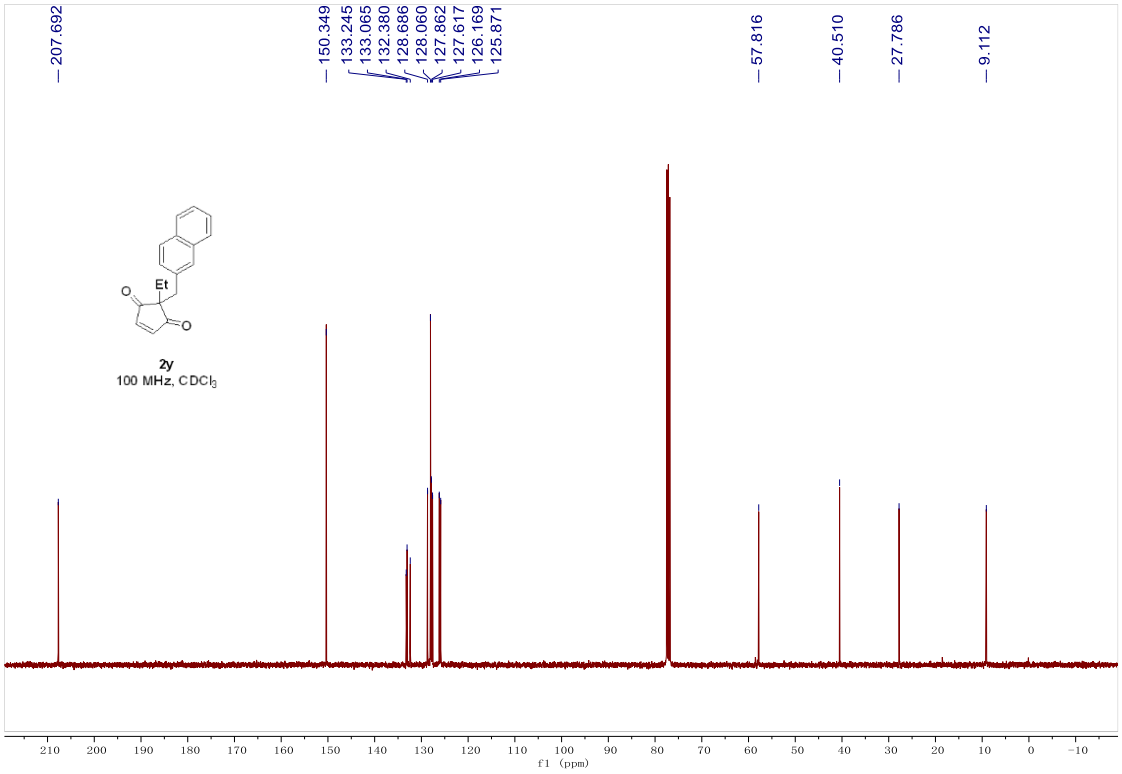
1.93
2.00
2.08
2.98
f1 (ppm)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O
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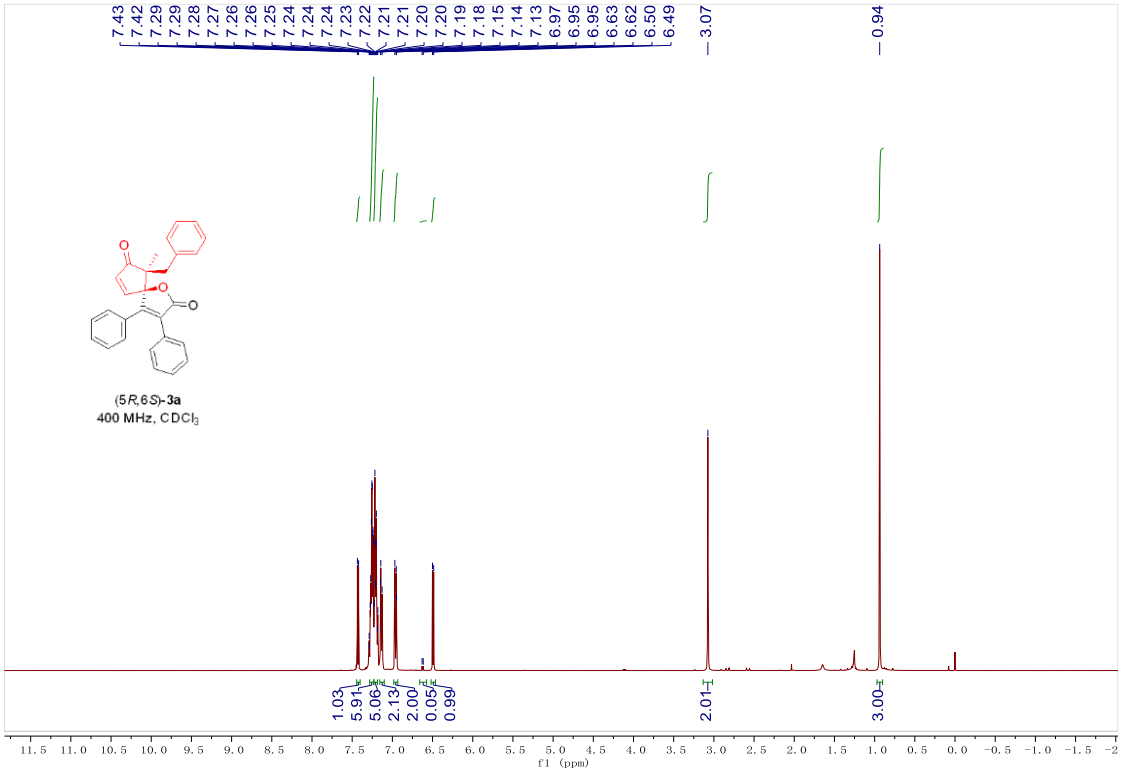
100 MHz, CDCl3
f1 (ppm)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7.23
7.22
7.21
7.21
7.20
7.20
7.19
7.18
7.15
7.14
7.13
6.97
6.95
6.95
6.63
6.62
6.50
6.49
3.07
0.94
O
O
O
(5R,6S)-3a
400 MHz, CDCl3
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5.91
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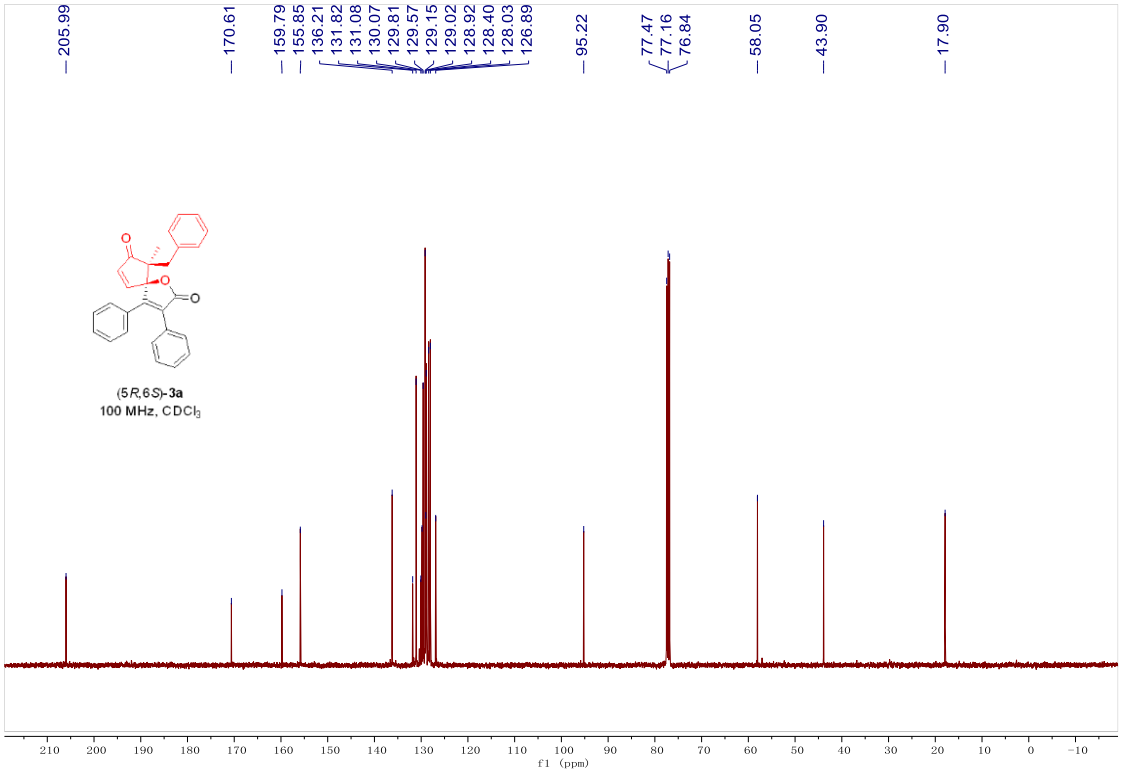
0.99
2.01
3.00
f1 (ppm)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128.92
128.40
128.03
126.89
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76.84
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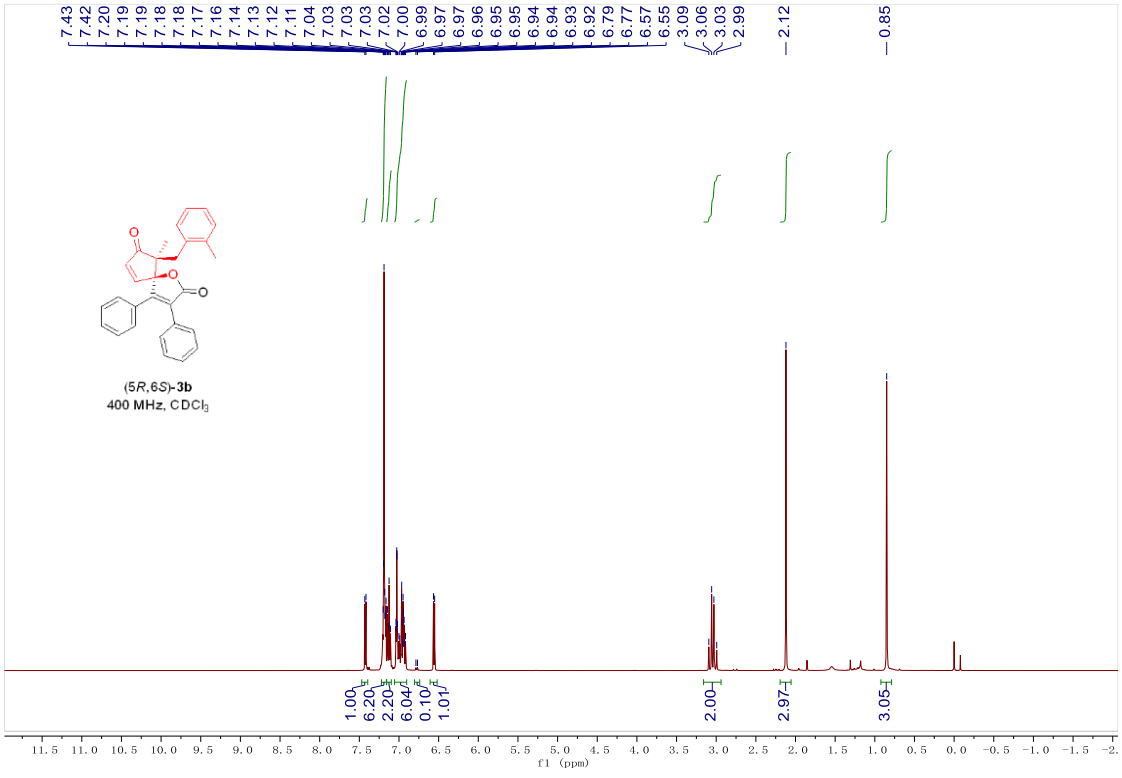
(5R,6S)-3a
100 MHz, CDCl3
f1 (ppm)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7.13
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7.03
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6.94
6.94
6.93
6.92
6.79
6.77
6.57
6.55
3.09
3.06
3.03
2.99
2.12
0.85
1.00
6.20
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0.10
1.01
2.00
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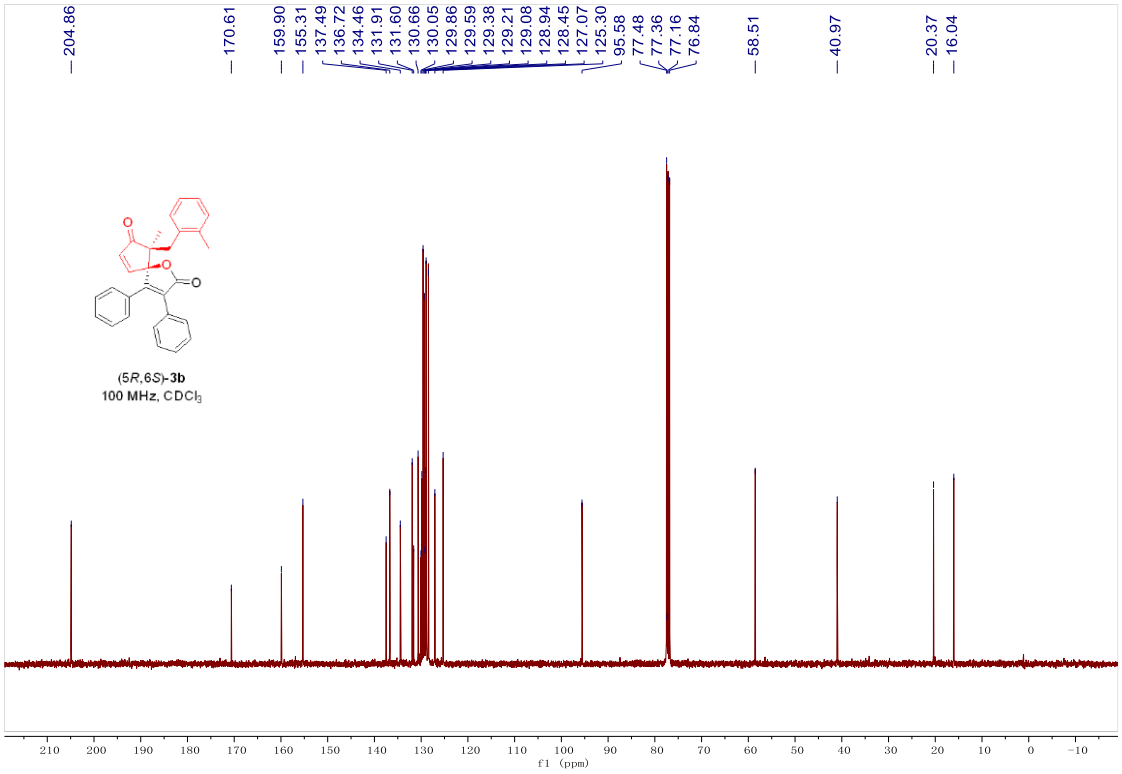
(5R,6S)-3b
400 MHz, CDCl3
f1 (ppm)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129.38
129.21
129.08
128.94
128.45
127.07
125.30
95.58
77.48
77.36
77.16
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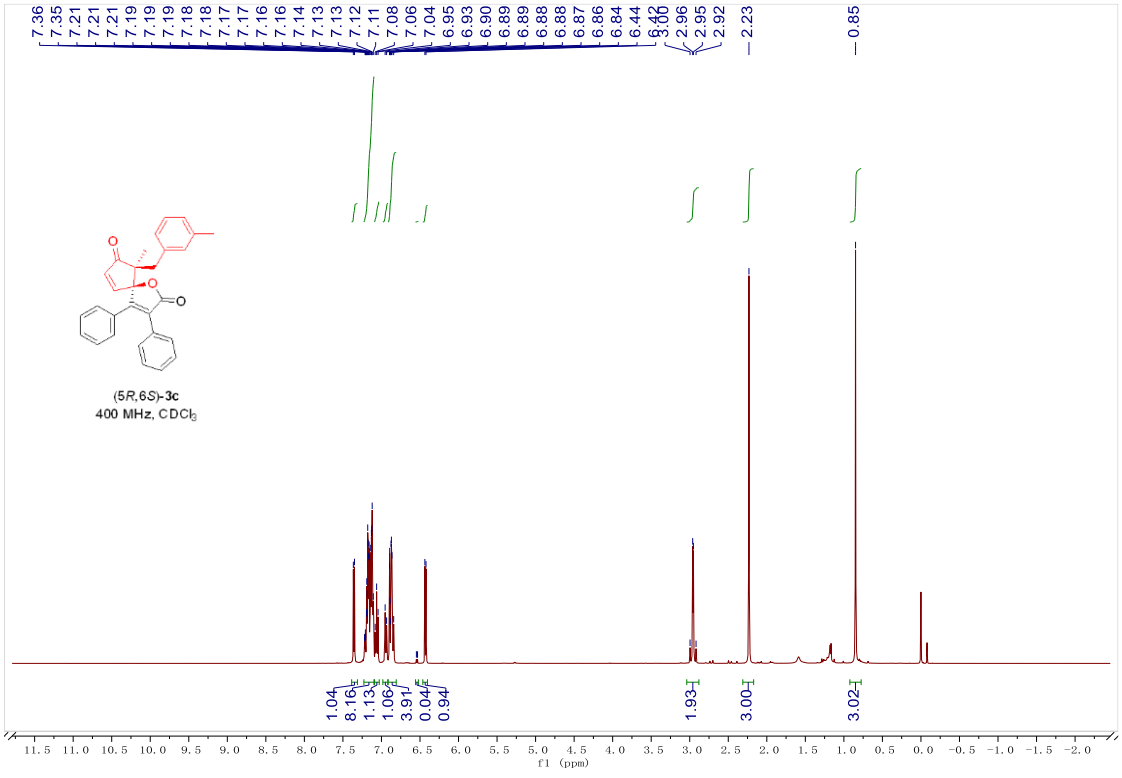
40.97
20.37
16.04
(5R,6S)-3b
100 MHz, CDCl3
f1 (ppm)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8.16
1.13
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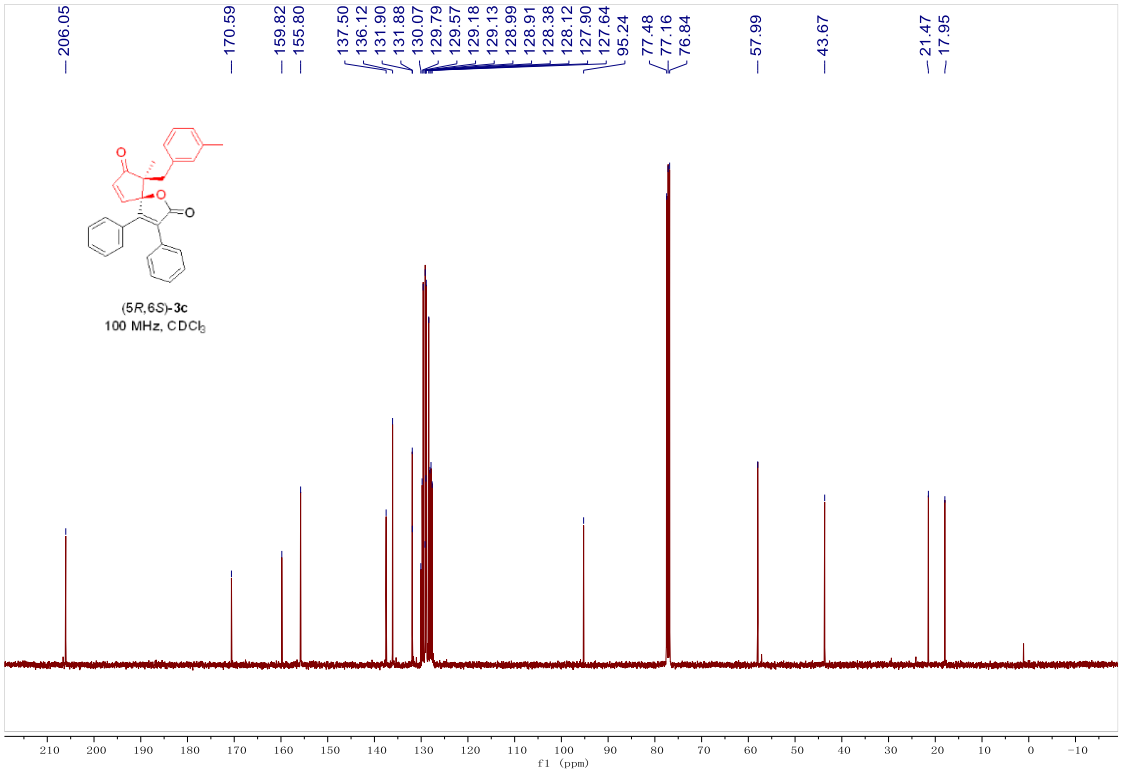
(5R,6S)-3c
400 MHz, CDCl3
f1 (ppm)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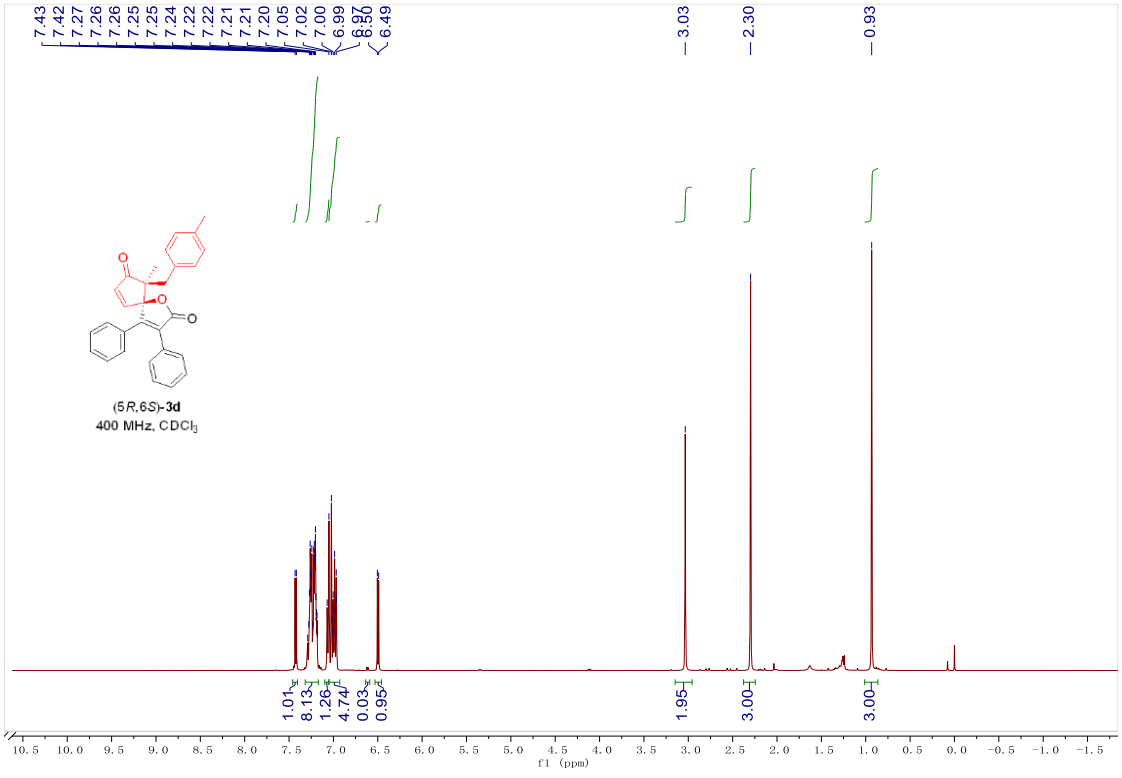
128.99
128.91
128.38
128.12
127.90
127.64
95.24
77.48
77.16
76.84
57.99
43.67
21.47
17.95
(5R,6S)-3c
100 MHz, CDCl3
f1 (ppm)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7.05
7.02
7.00
6.99
6.97
6.50
6.49
3.03
2.30
0.93
1.01
8.13
1.26
4.74
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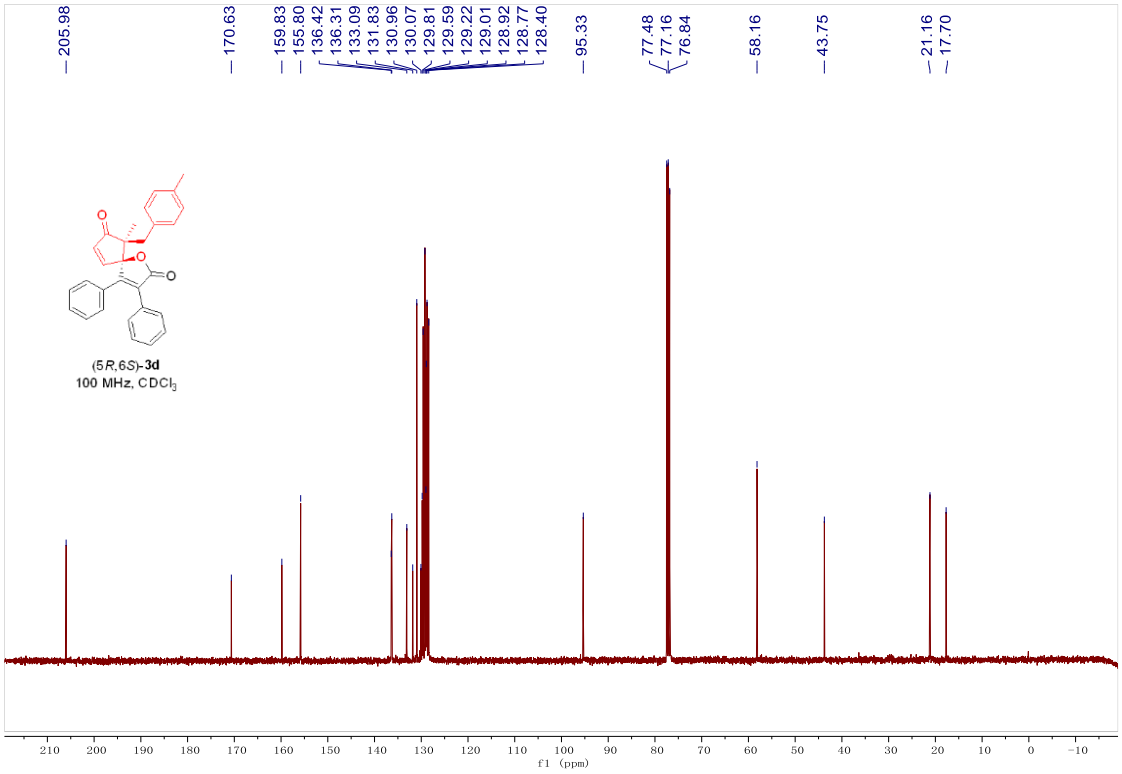
0.95
1.95
3.00
3.00
(5R,6S)-3d
400 MHz, CDCl3
f1 (ppm)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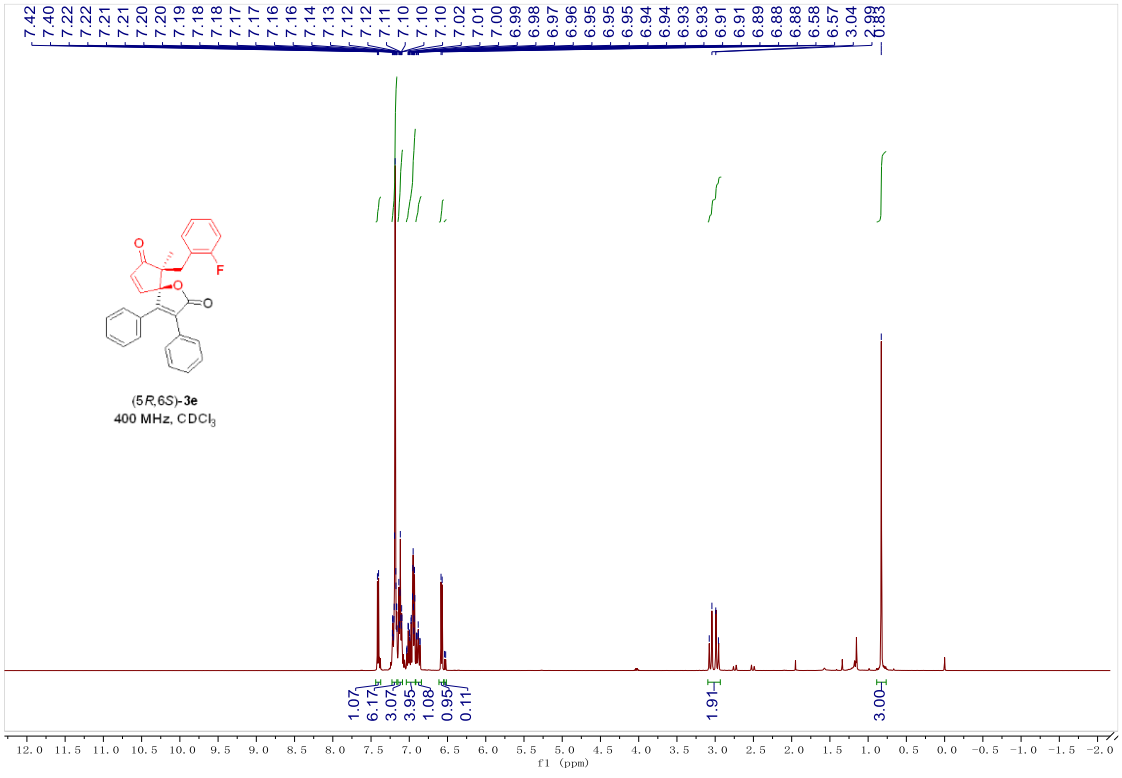
130.96
130.07
129.81
129.59
129.22
129.01
128.92
128.77
128.40
95.33
77.48
77.16
76.84
58.16
43.75
21.16
17.70
(5R,6S)-3d
100 MHz, CDCl3
f1 (ppm)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7.20
7.20
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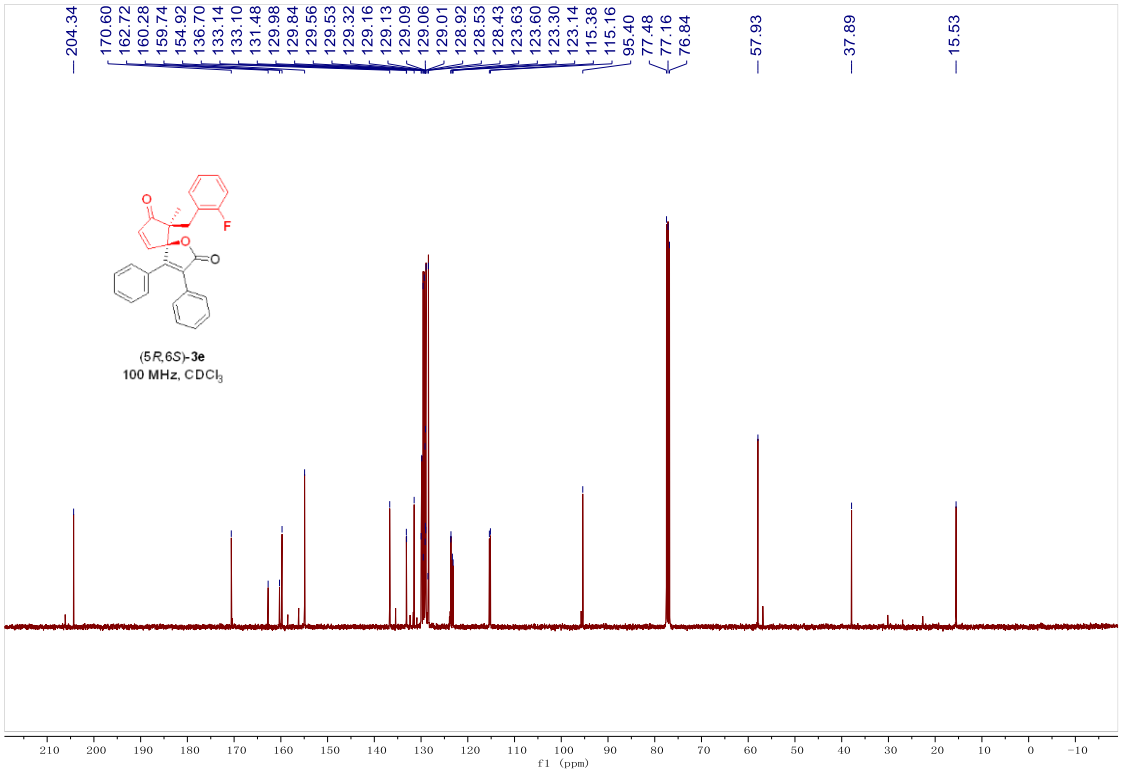
7.17
7.16
7.16
7.14
7.13
7.12
7.12
7.11
7.10
7.10
7.10
7.02
7.01
7.00
6.99
6.98
6.97
6.96
6.95
6.95
6.95
6.94
6.94
6.93
6.93
6.91
6.91
6.89
6.88
6.88
6.58
6.57
3.04
2.99
2.83
1.07
6.17
3.07
3.95
1.08
0.95
0.11
1.91
3.00
(5R,6S)-3e
400 MHz, CDCl3
f1 (ppm)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160.28
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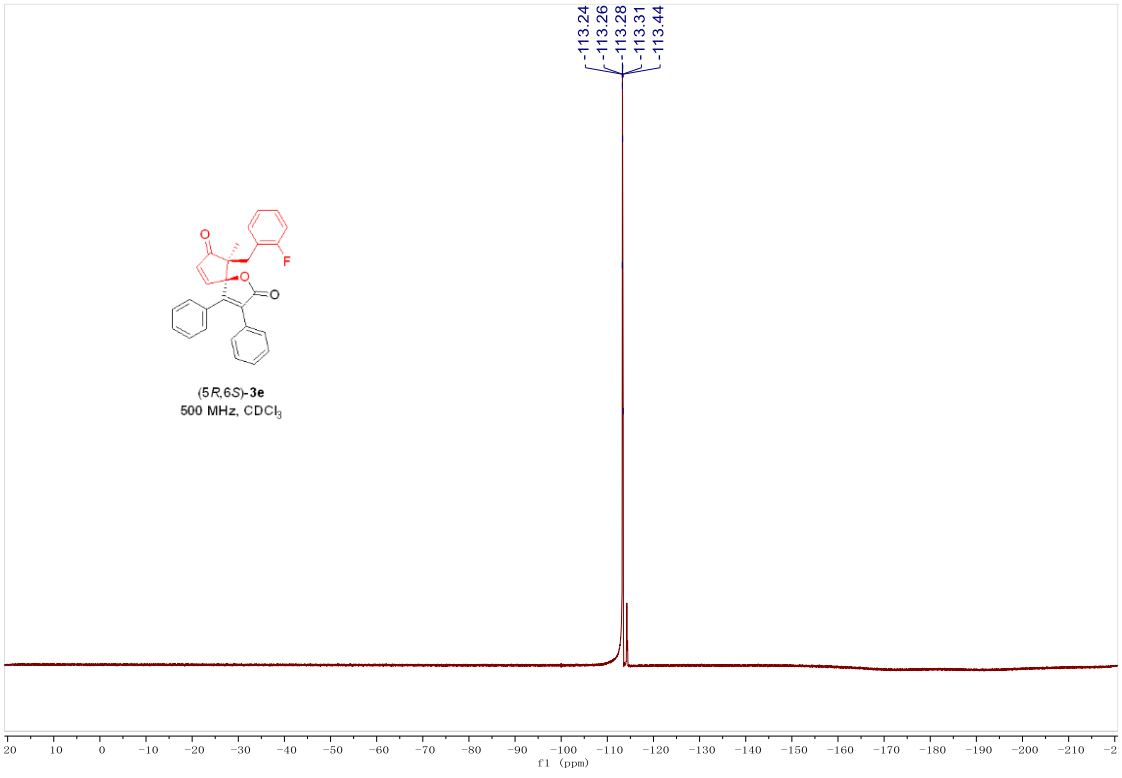
154.92
136.70
133.14
133.10
131.48
129.98
129.84
129.56
129.53
129.32
129.16
129.13
129.09
129.06
129.01
128.92
128.53
128.43
123.63
123.60
123.30
123.14
115.38
115.16
95.40
77.48
77.16
76.84
57.93
37.89
15.53
(5R,6S)-3e
100 MHz, CDCl3
f1 (ppm)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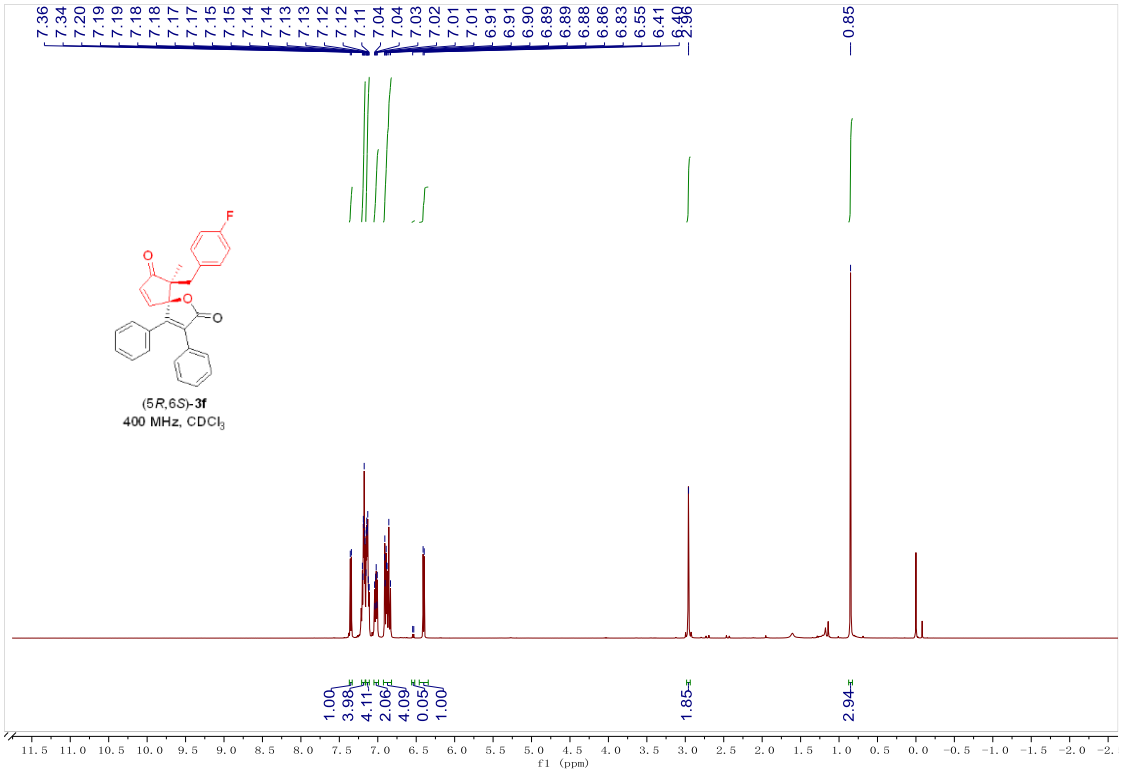
-113.28
-113.31
-113.44
(5R,6S)-3e
500 MHz, CDCl3
f1 (ppm)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7.34
7.20
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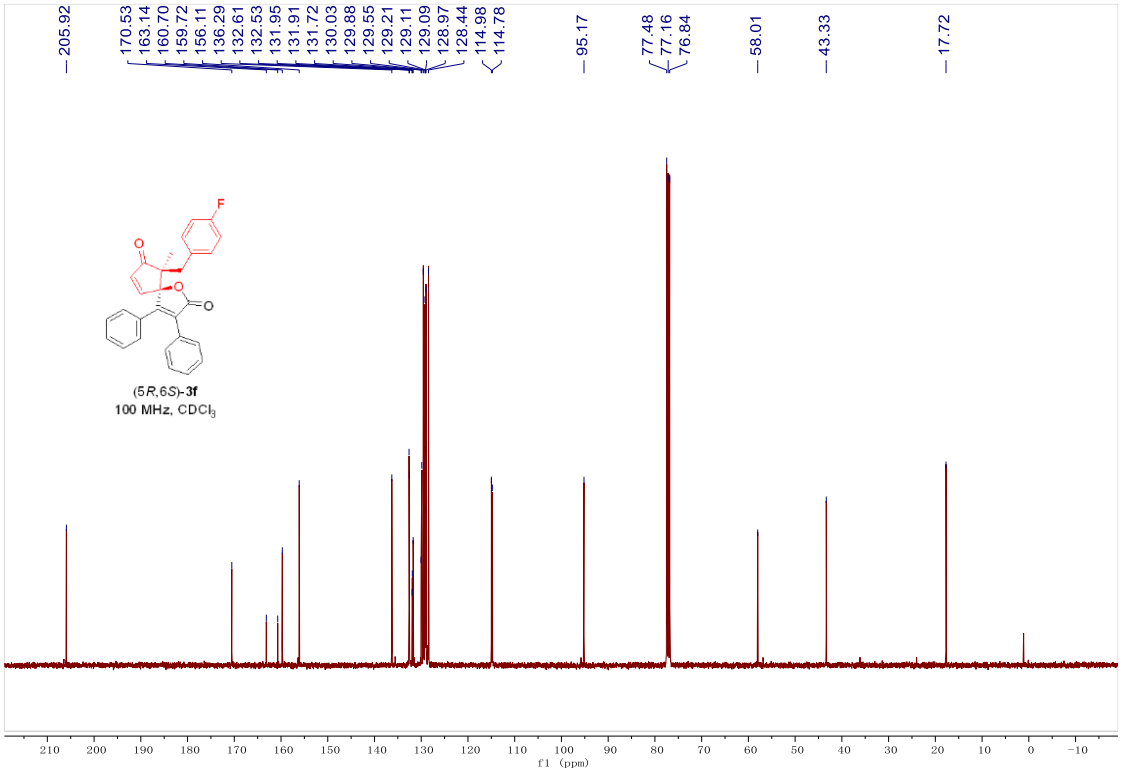
7.19
7.18
7.18
7.17
7.17
7.15
7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.11
7.04
7.04
7.03
7.02
7.01
7.01
6.91
6.91
6.90
6.89
6.89
6.88
6.86
6.83
6.55
6.41
2.96
0.85
F
O
O
O
(5R,6S)-3f
400 MHz, CDCl3
1.00
3.98
4.11
2.06
4.09
0.05
1.00
1.85
2.94
f1 (ppm)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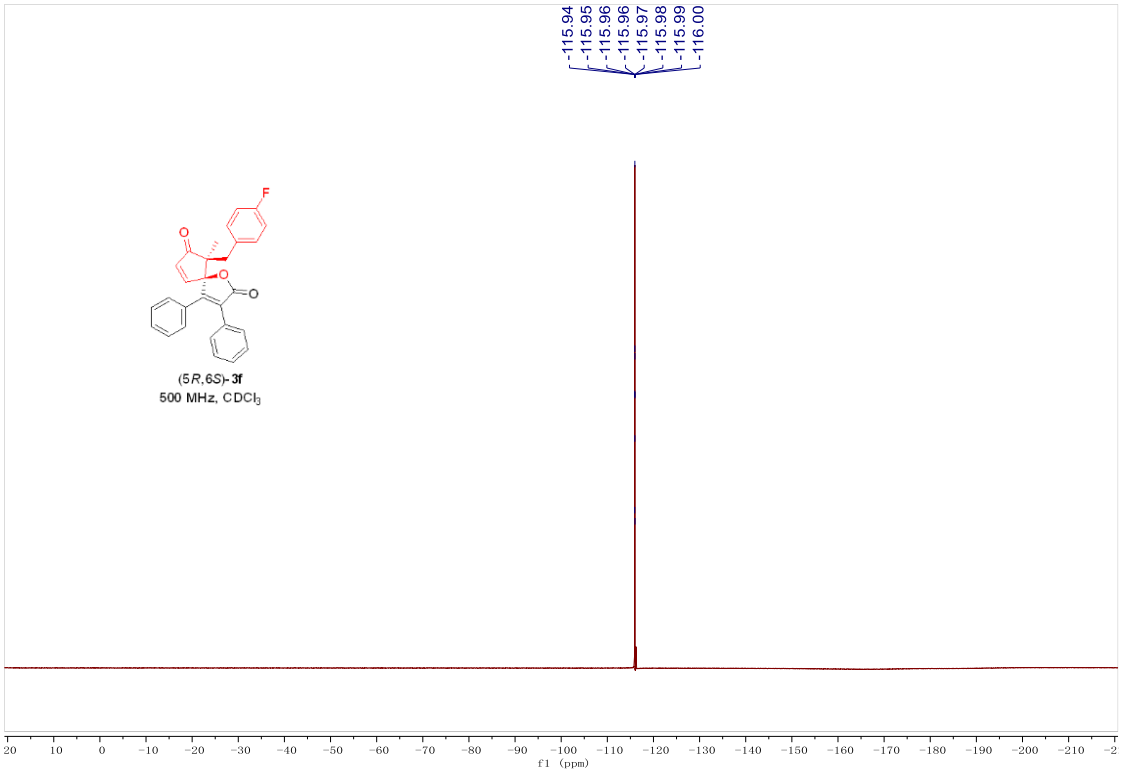
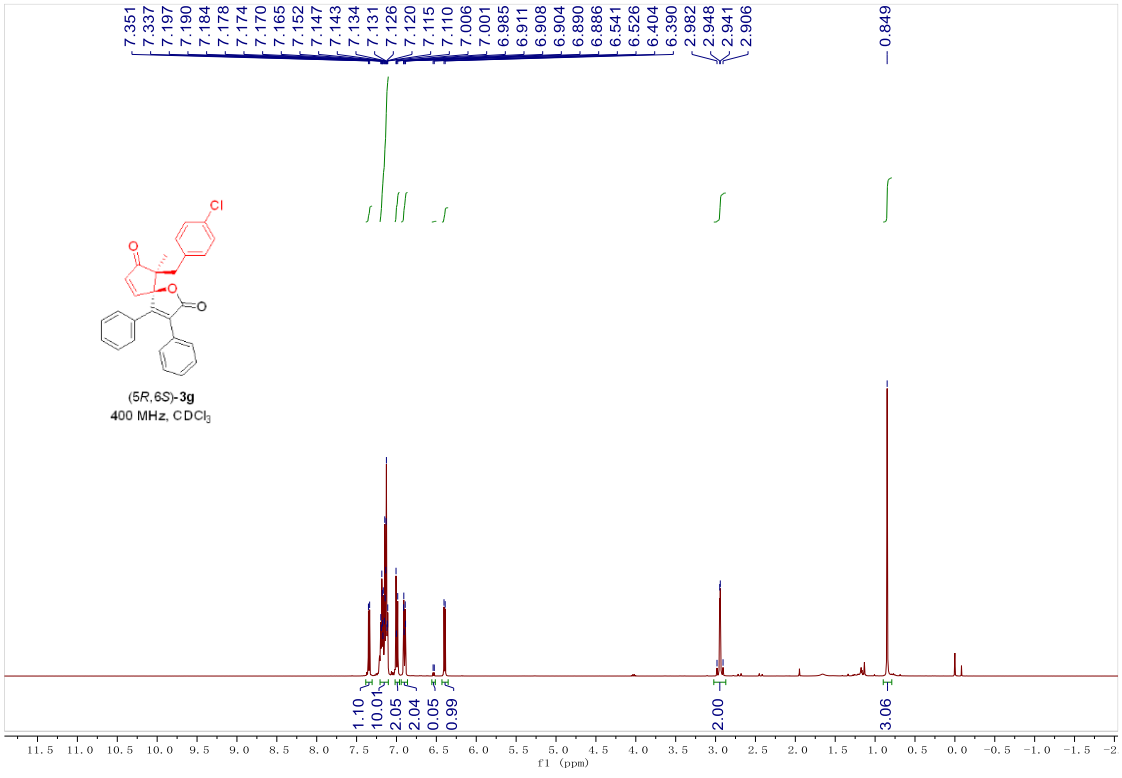
170.53
163.14
160.70
159.72
156.11
136.29
132.61
132.53
131.95
131.91
131.72
130.03
129.88
129.55
129.21
129.11
129.09
128.97
128.44
114.98
114.78
95.17
77.48
77.16
76.84
58.01
43.33
17.72
F
O
O
O
(5R,6S)-3f
100 MHz, CDCl3
f1 (ppm)


-115.94
-115.95
-115.96
-115.96
-115.97
-115.98
-115.99
-116.00
F
O
O
O
(5R,6S)-3f
500 MHz, CDCl3
f1 (ppm)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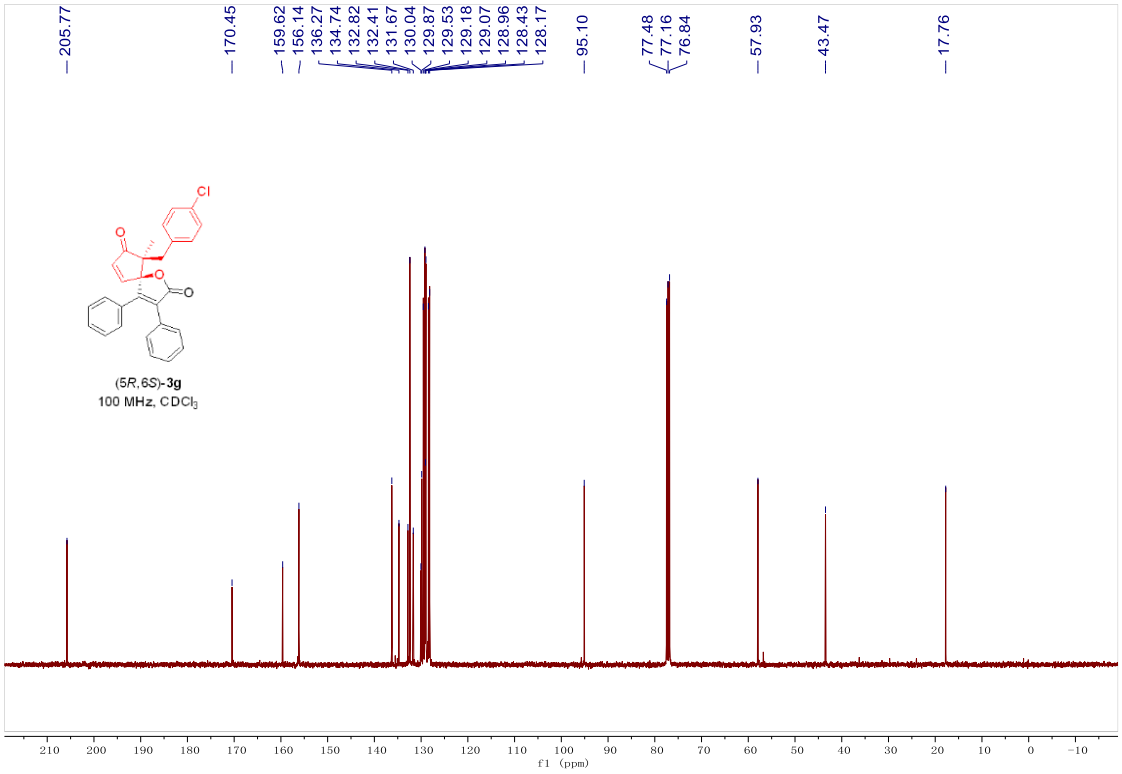
7.190
7.184
7.178
7.174
7.170
7.165
7.152
7.147
7.143
7.134
7.131
7.126
7.120
7.115
7.110
7.006
7.001
6.985
6.911
6.908
6.904
6.890
6.886
6.541
6.526
6.404
6.390
2.982
2.948
2.941
2.906
0.849
Cl
O
O
O
(5R,6S)-3g
400 MHz, CDCl3
1.10
10.01
2.05
2.04
0.05
0.99
2.00
3.06
f1 (ppm)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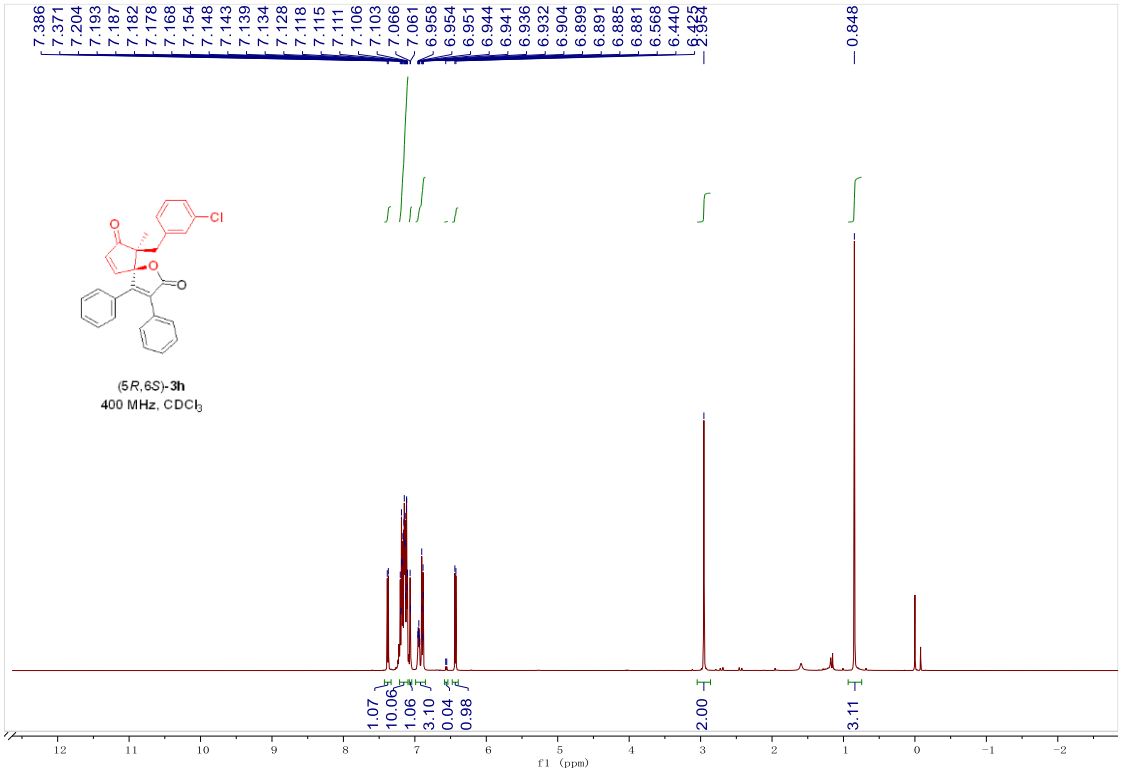
159.62
156.14
136.27
134.74
132.82
132.41
131.67
130.04
129.87
129.53
129.18
129.07
128.96
128.43
128.17
95.10
77.48
77.16
76.84
57.93
43.47
17.76
Cl
O
O
O
(5R,6S)-3g
100 MHz, CDCl3
f1 (ppm)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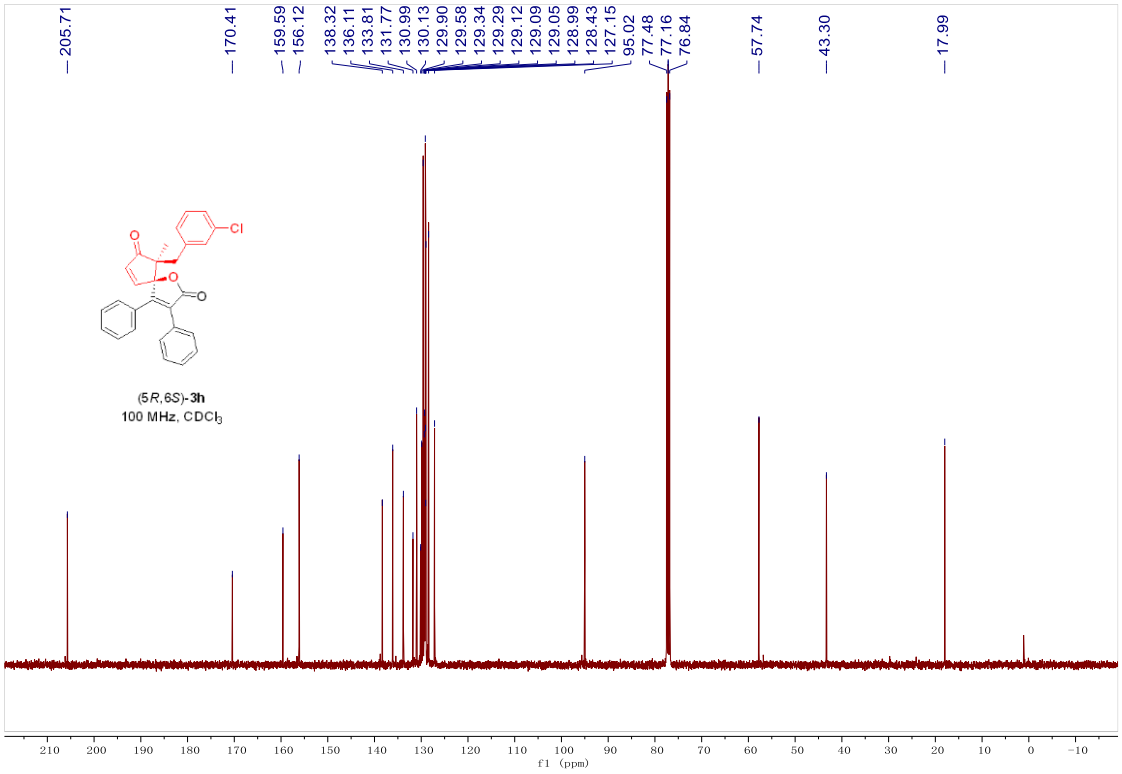
7.187
7.182
7.178
7.168
7.154
7.148
7.143
7.139
7.134
7.128
7.118
7.115
7.111
7.106
7.103
7.066
7.061
6.958
6.954
6.951
6.944
6.941
6.936
6.932
6.904
6.899
6.891
6.885
6.881
6.568
6.440
2.954
0.848
Cl
O
O
O
(5R,6S)-3h
400 MHz, CDCl3
1.07
10.06
1.06
3.10
0.04
0.98
2.00
3.11
f1 (ppm)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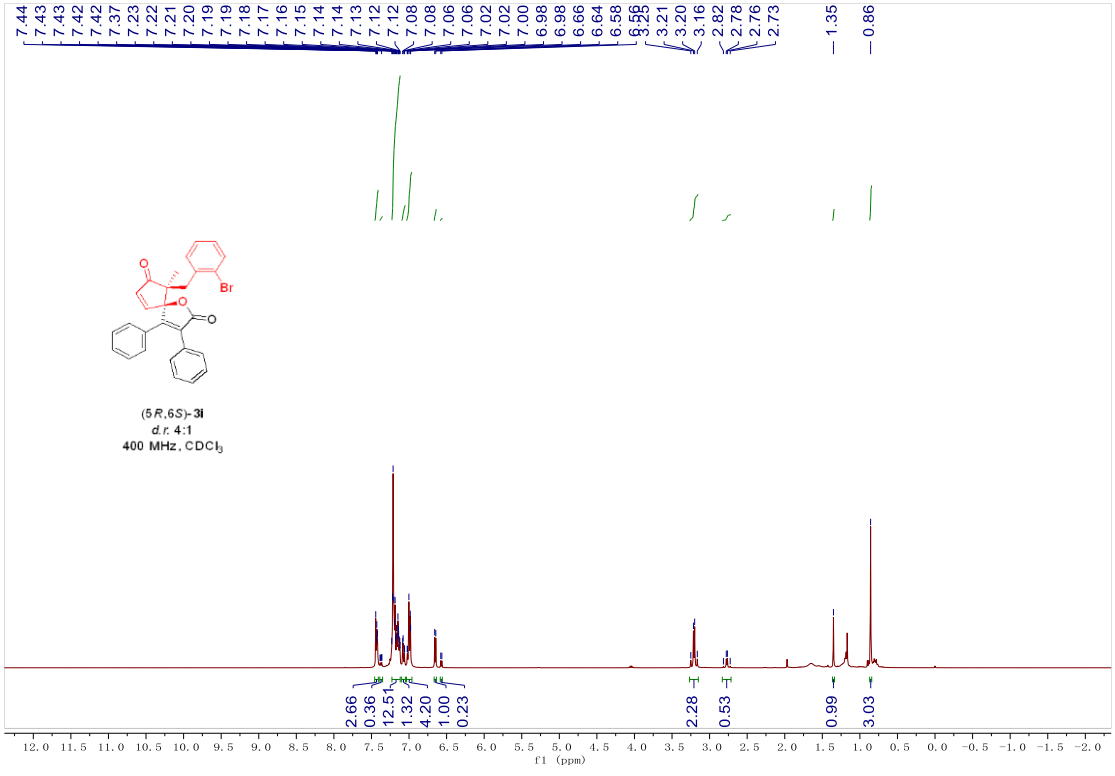
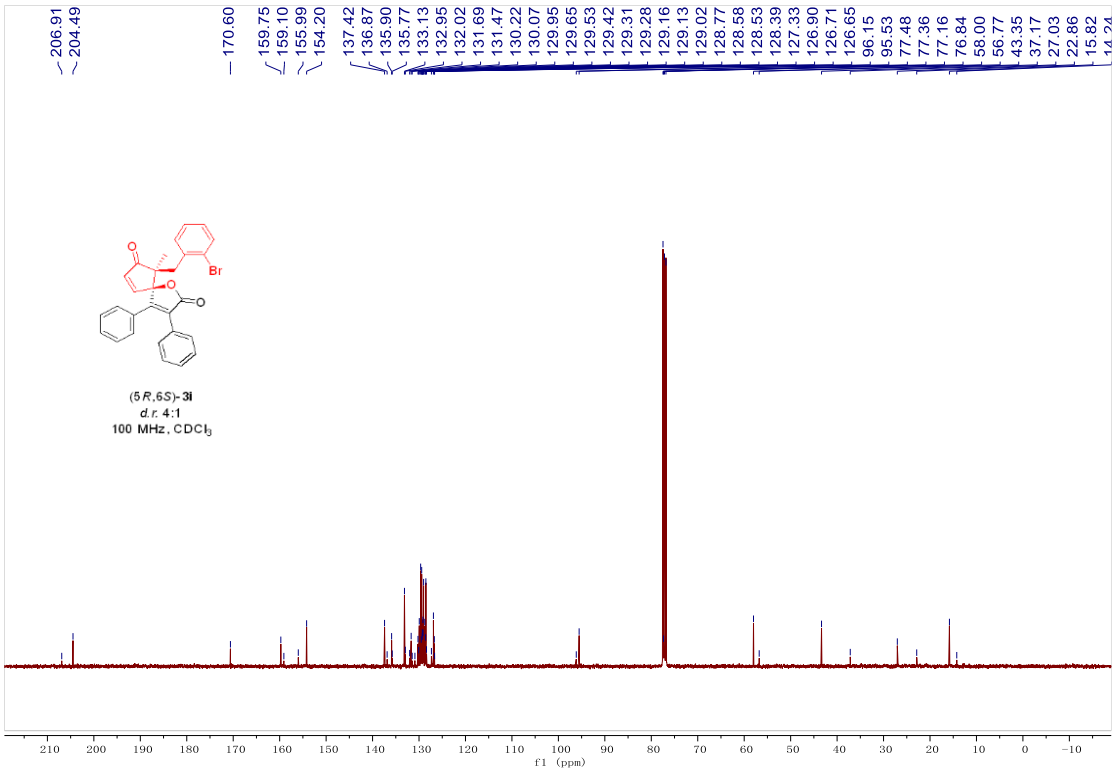
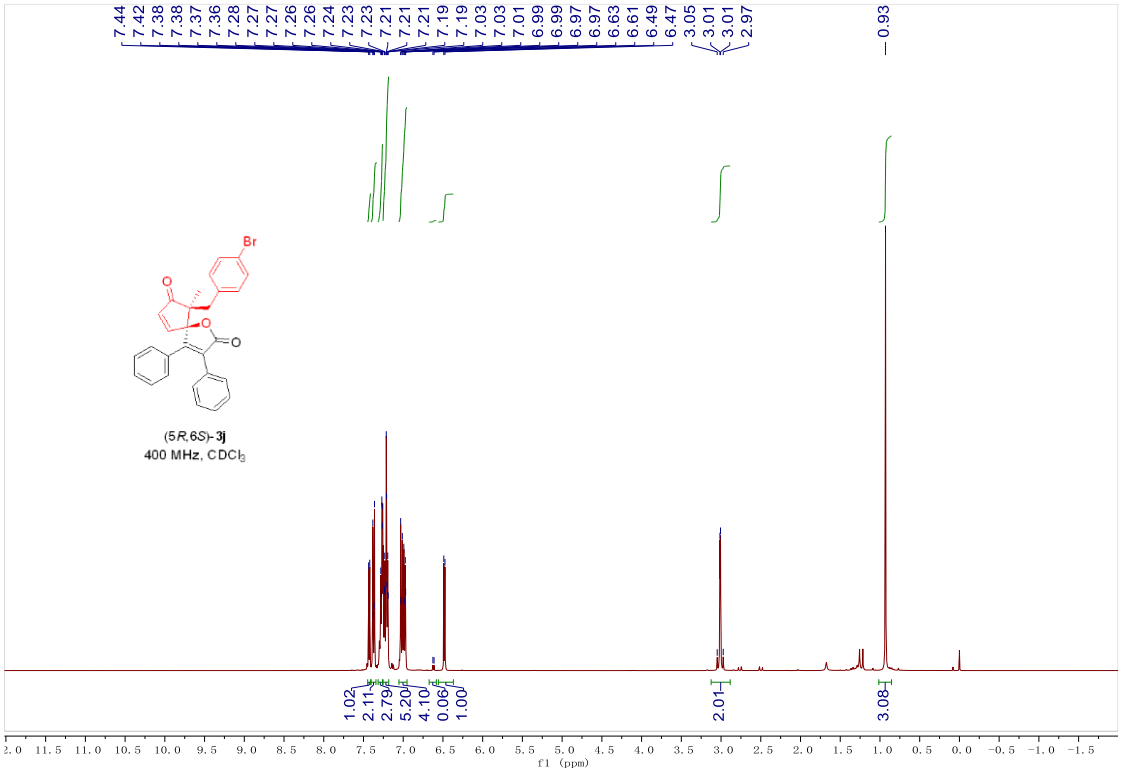
159.59
156.12
138.32
136.11
133.81
131.77
130.99
130.13
129.90
129.58
129.34
129.29
129.12
129.09
129.05
128.99
128.43
127.15
95.02
77.48
77.16
76.84
57.74
43.30
17.99
Cl
O
O
O
(5R,6S)-3h
100 MHz, CDCl3
f1 (ppm)


7.44
7.43
7.43
7.42
7.42
7.37
7.23
7.22
7.21
7.20
7.19
7.19
7.18
7.17
7.16
7.15
7.14
7.14
7.13
7.12
7.12
7.08
7.08
7.06
7.06
7.02
7.02
7.00
6.98
6.98
6.66
6.64
6.58
3.21
3.20
3.16
2.82
2.78
2.76
2.73
1.35
0.86
Br
O
O
O
(5R,6S)-3l
d.r. 4:1
400 MHz, CDCl3
2.66
0.36
12.51
1.32
4.20
1.00
0.23
2.28
0.53
0.99
3.03
f1 (ppm)


206.91
204.49
170.60
159.75
159.10
155.99
154.20
137.42
136.87
135.90
135.77
133.13
132.95
132.02
131.69
131.47
130.22
130.07
129.95
129.65
129.53
129.42
129.31
129.28
129.16
129.13
129.02
128.77
128.58
128.53
128.39
127.33
126.90
126.71
126.65
96.15
95.53
77.48
77.36
77.16
76.84
58.00
56.77
43.35
37.17
27.03
22.86
15.82
Br
O
O
O
(5R,6S)-3i
d.r. 4:1
100 MHz, CDCl3
f1 (ppm)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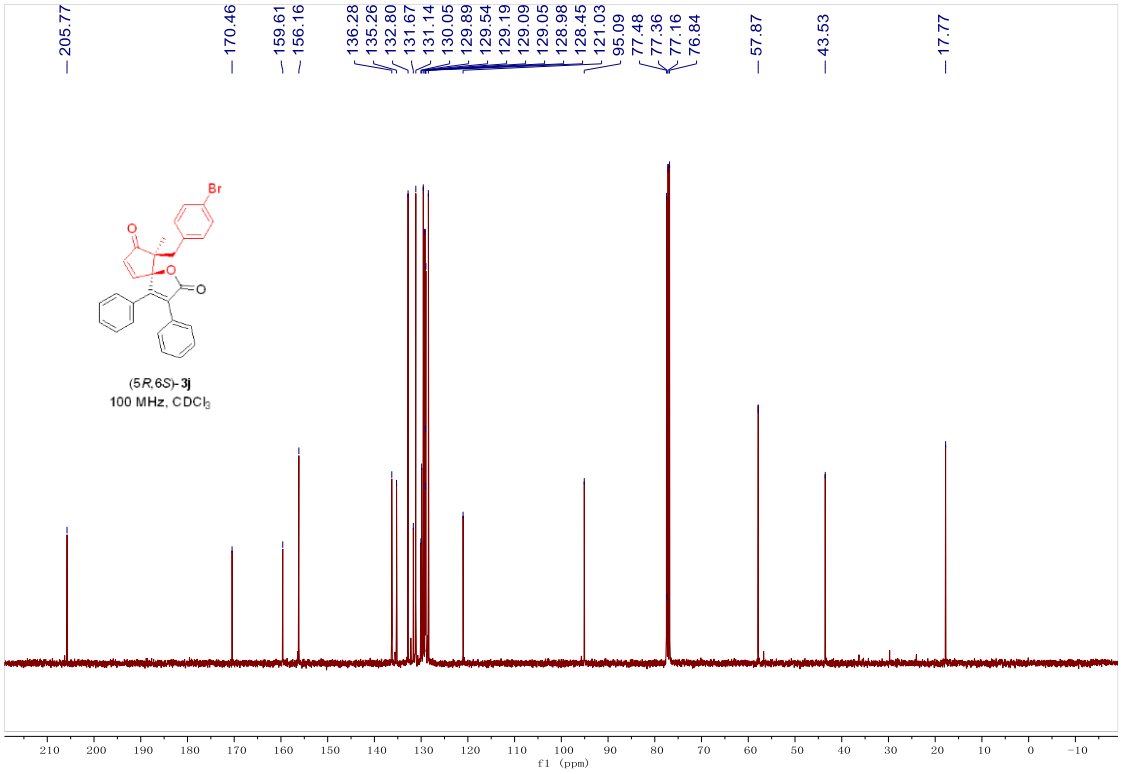
7.42
7.38
7.38
7.37
7.36
7.28
7.27
7.27
7.26
7.26
7.24
7.23
7.23
7.21
7.21
7.21
7.19
7.19
7.03
7.03
7.01
6.99
6.99
6.97
6.97
6.63
6.61
6.49
6.47
3.05
3.01
3.01
2.97
0.93
Br
O
O
O
(5R,6S)-3j
400 MHz, CDCl3
1.02
2.11
2.79
5.20
4.10
0.06
1.00
2.01
3.08
f1 (ppm)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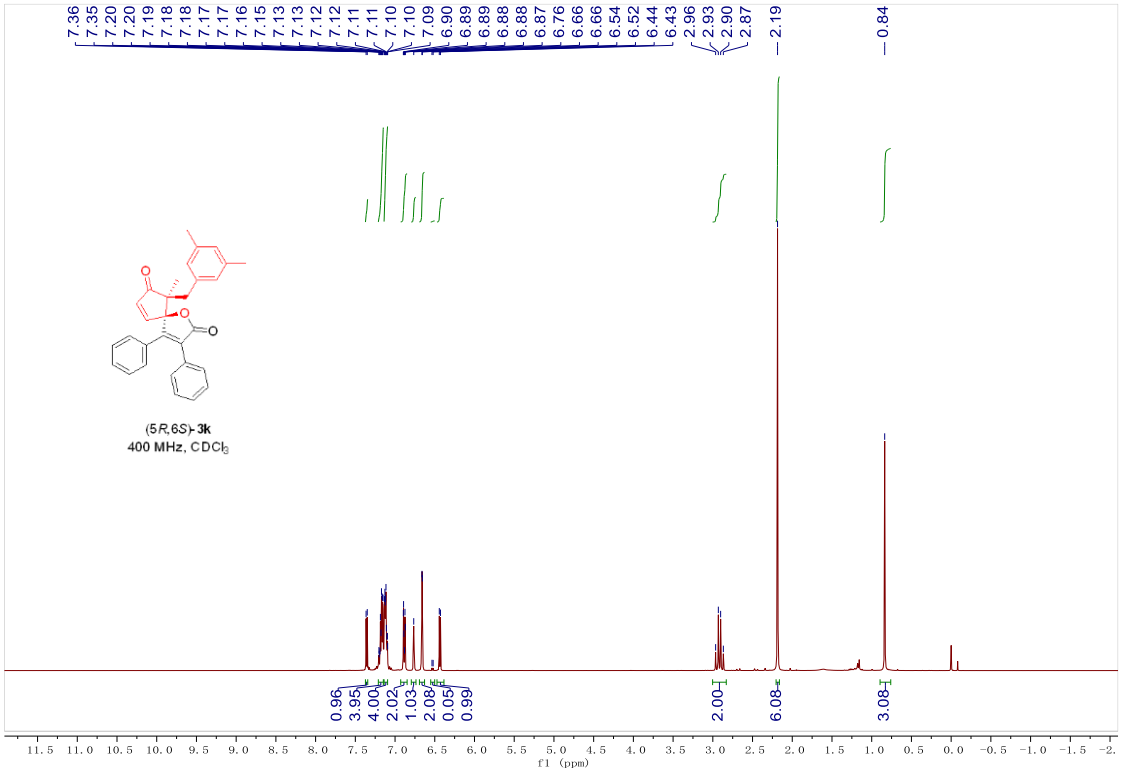
159.61
156.16
136.28
135.26
132.80
131.67
131.14
130.05
129.89
129.54
129.19
129.09
129.05
128.98
128.45
121.03
95.09
77.48
77.36
77.16
76.84
57.87
43.53
17.77
Br
O
O
O
(5R,6S)-3j
100 MHz, CDCl3
f1 (ppm)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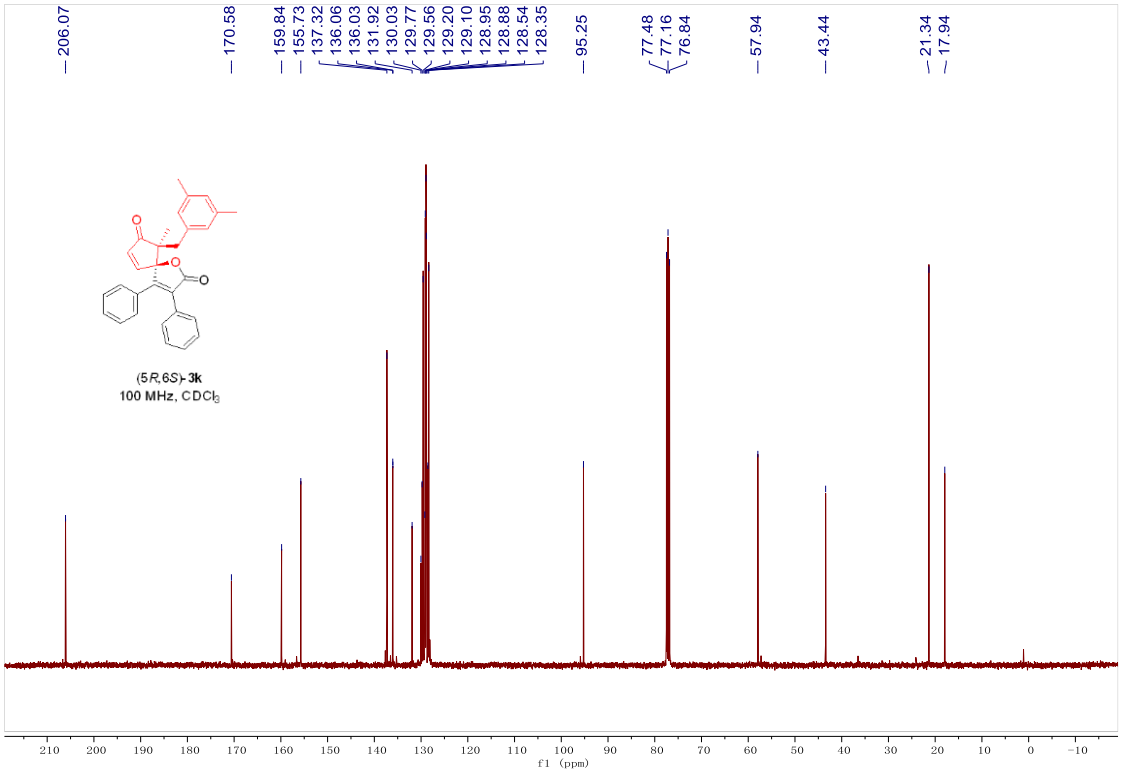
7.17
7.17
7.16
7.15
7.13
7.13
7.12
7.12
7.11
7.11
7.10
7.10
7.09
6.90
6.89
6.89
6.88
6.88
6.87
6.76
6.66
6.66
6.54
6.52
6.44
6.43
2.96
2.93
2.90
2.87
2.19
0.84
0.96
3.95
4.00
2.02
1.03
2.08
0.05
0.99
2.00
6.08
3.08
O
O
O
(5R,6S)-3k
400 MHz, CDCl3
f1 (ppm)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170.58
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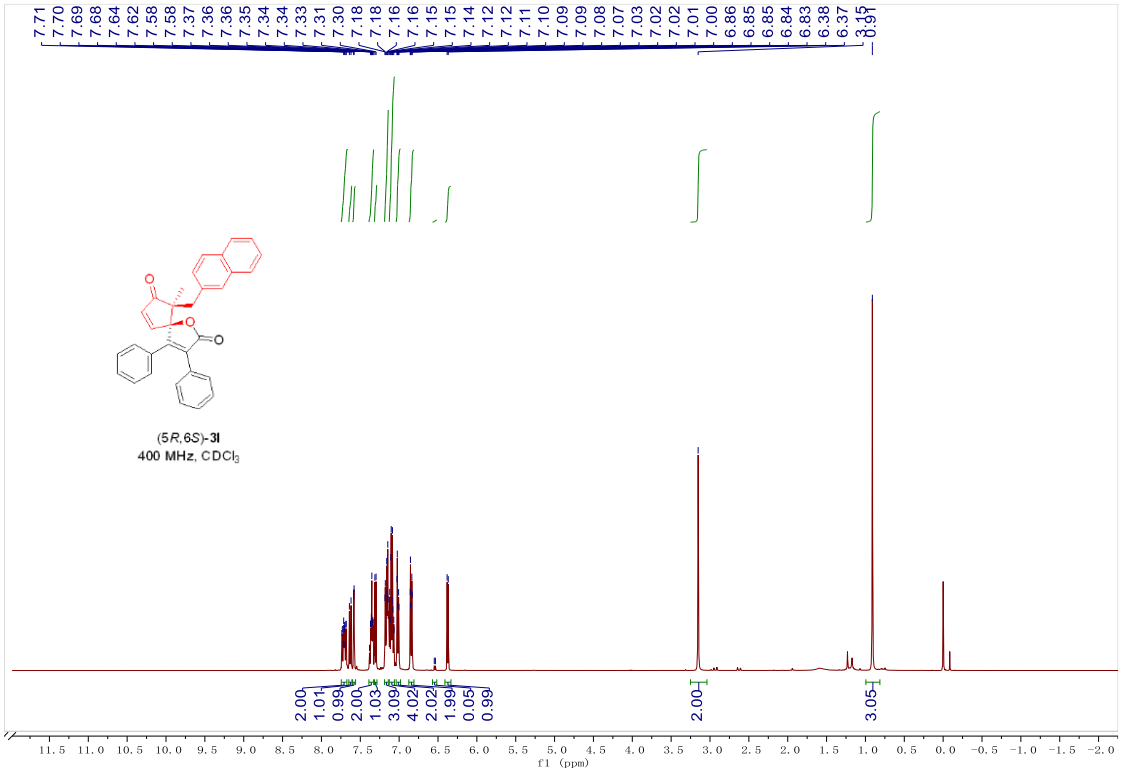
155.73
137.32
136.06
136.03
131.92
130.03
129.77
129.56
129.20
129.10
128.95
128.88
128.54
128.35
95.25
77.48
77.16
76.84
57.94
43.44
21.34
17.94
(5R,6S)-3k
100 MHz, CDCl3
f1 (ppm)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7.58
7.58
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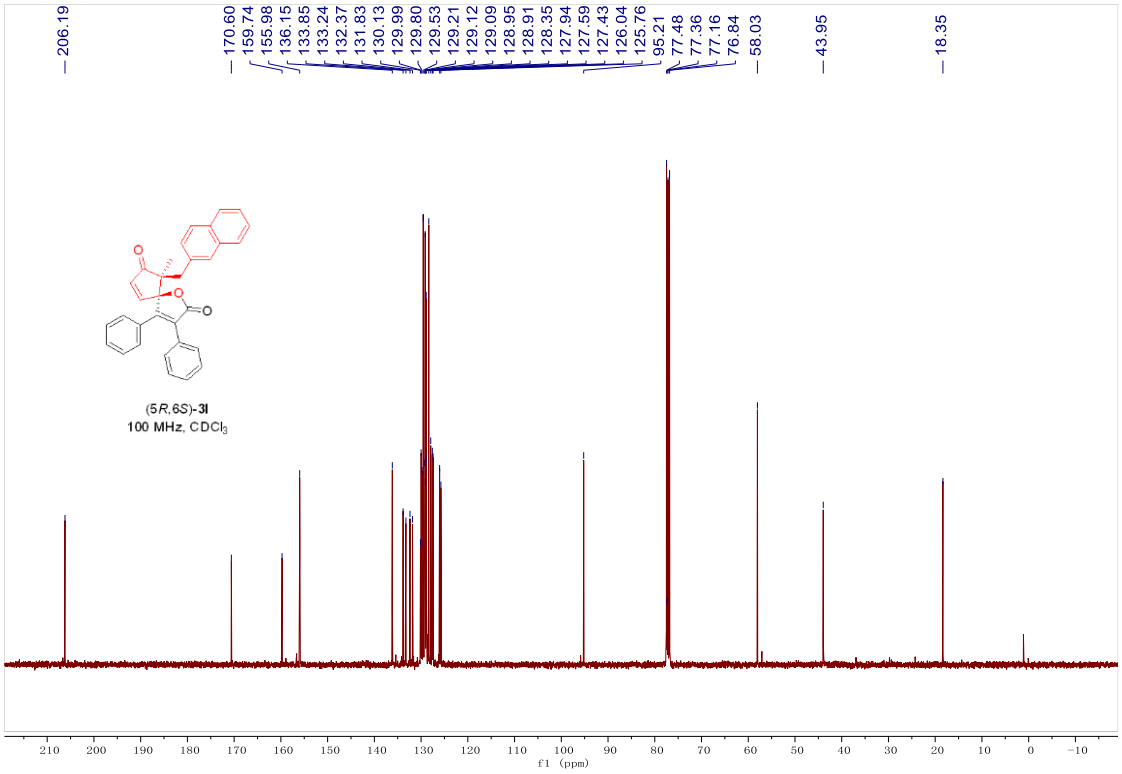
7.34
7.33
7.31
7.30
7.18
7.18
7.16
7.16
7.15
7.15
7.14
7.12
7.12
7.11
7.10
7.09
7.09
7.08
7.07
7.03
7.02
7.02
7.01
7.00
6.86
6.85
6.85
6.84
6.83
6.38
6.37
3.15
0.91
2.00
1.01
0.99
2.00
1.03
3.09
4.02
2.02
1.99
0.05
0.99
2.00
3.05
(5R,6S)-3l
400 MHz, CDCl3
f1 (ppm)


206.19
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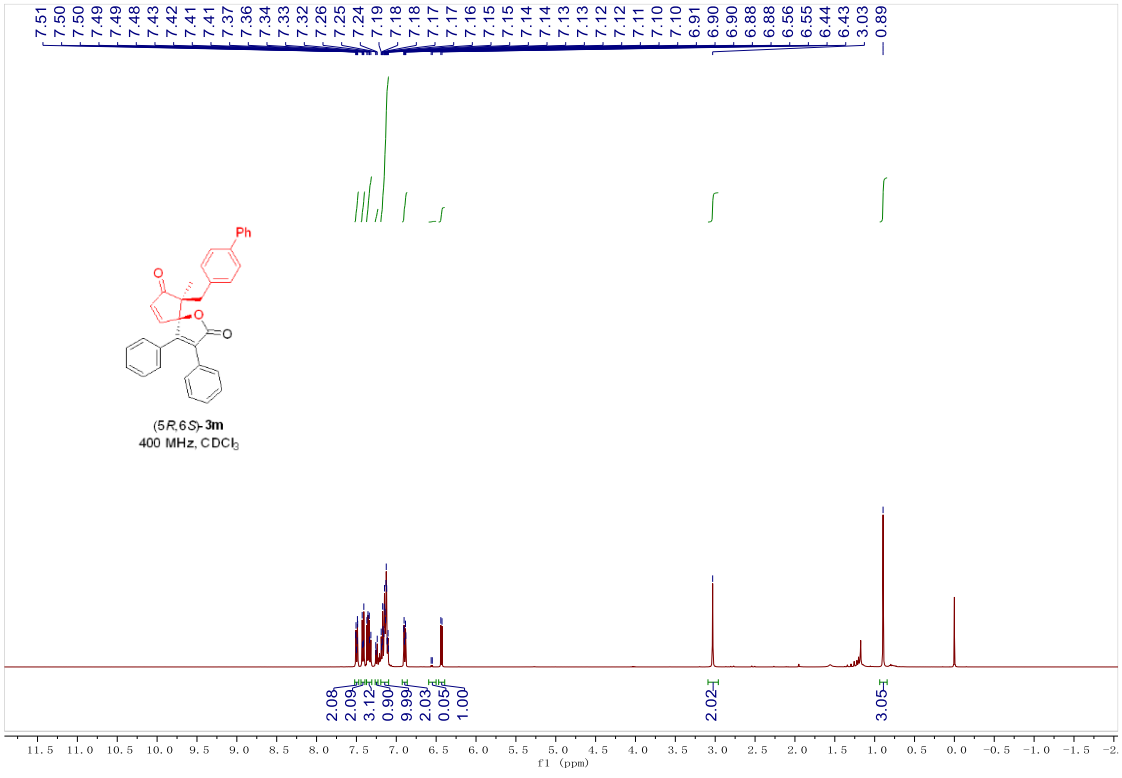
132.37
131.83
130.13
129.99
129.80
129.53
129.21
129.12
129.09
128.95
128.91
128.35
127.94
127.59
127.43
126.04
125.76
95.21
77.48
77.36
77.16
76.84
58.03
43.95
18.35
(5R,6S)-3l
100 MHz, CDCl3
f1 (ppm)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7.42
7.41
7.41
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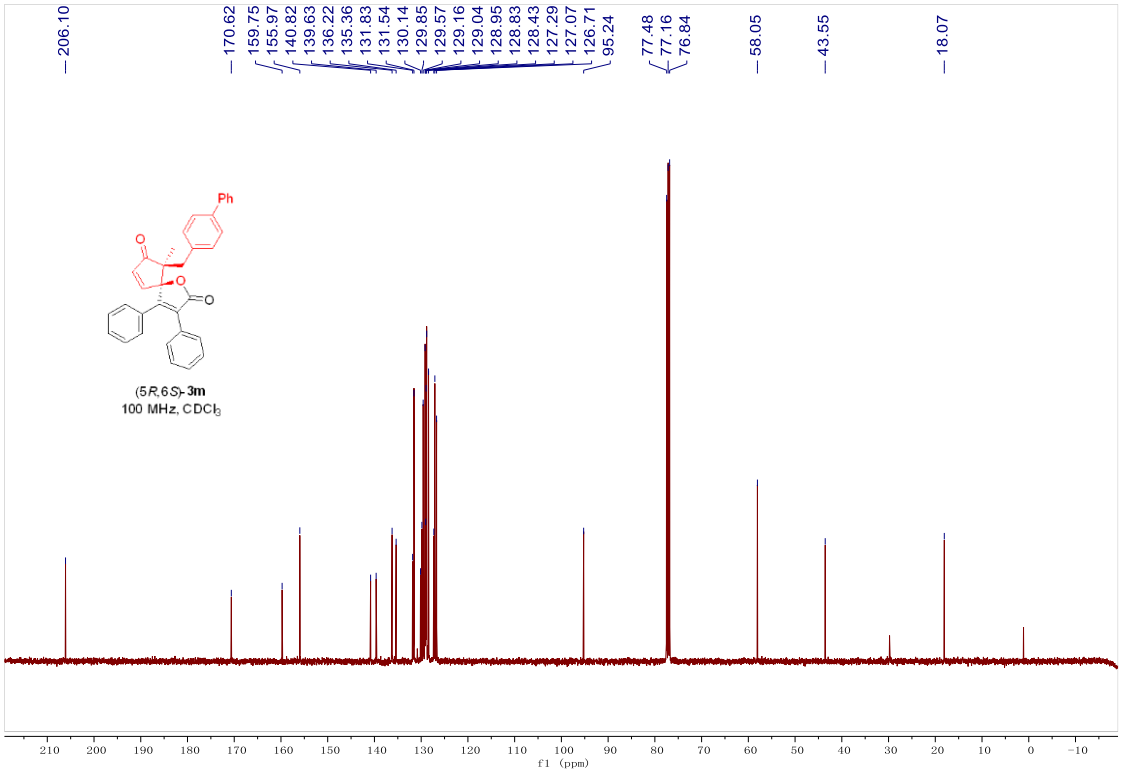
7.34
7.33
7.32
7.26
7.25
7.24
7.19
7.18
7.18
7.17
7.17
7.16
7.15
7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.11
7.10
7.10
6.91
6.90
6.90
6.88
6.88
6.56
6.55
6.44
6.43
3.03
0.89
Ph
(5R,6S)-3m
400 MHz, CDCl3
2.08
2.09
3.12
0.90
9.99
2.03
0.05
1.00
2.02
3.05
f1 (ppm)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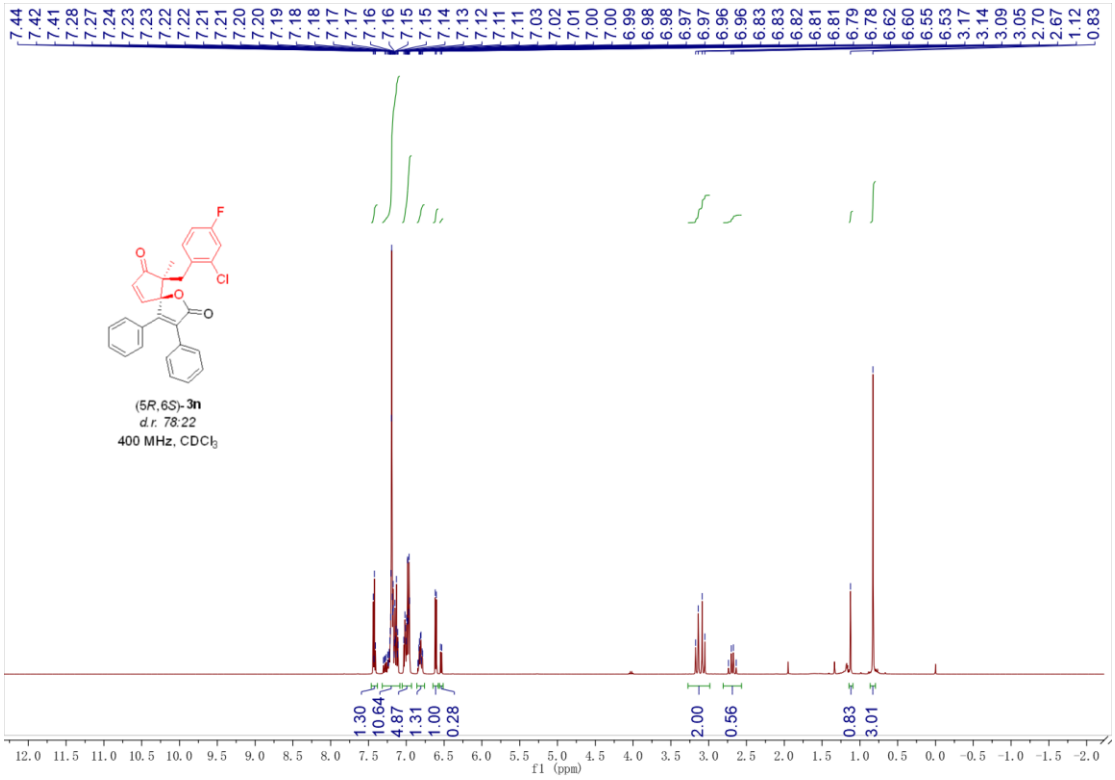
140.82
139.63
136.22
135.36
131.83
131.54
130.14
129.85
129.57
129.16
129.04
128.95
128.83
128.43
127.29
127.07
126.71
95.24
77.48
77.16
76.84
58.05
43.55
18.07
Ph
O
O
O
(5R,6S)-3m
100 MHz, CDCl3
f1 (ppm)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7.23
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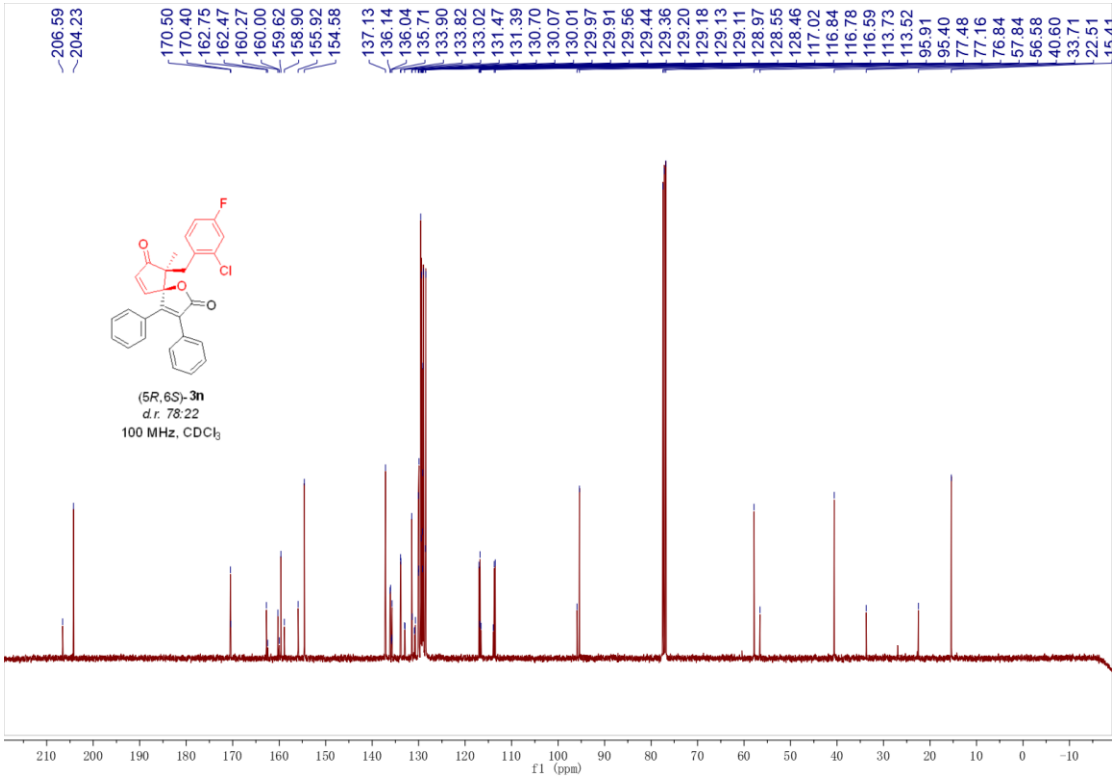
7.21
7.20
7.20
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.15
7.15
7.14
7.13
7.12
7.11
7.11
7.03
7.02
7.01
7.00
7.00
6.99
6.98
6.98
6.97
6.97
6.96
6.96
6.83
6.83
6.82
6.81
6.81
6.79
6.78
6.62
6.60
6.55
6.53
3.17
3.14
3.09
3.05
2.70
2.67
1.12
0.83
F
Cl
O
O
O
(5R,6S)-3n
d.r. 78:22
400 MHz, CDCl3
1.30
10.64
4.87
1.31
1.00
0.28
2.00
0.56
0.83
3.01
f1 (ppm)


206.59
204.23
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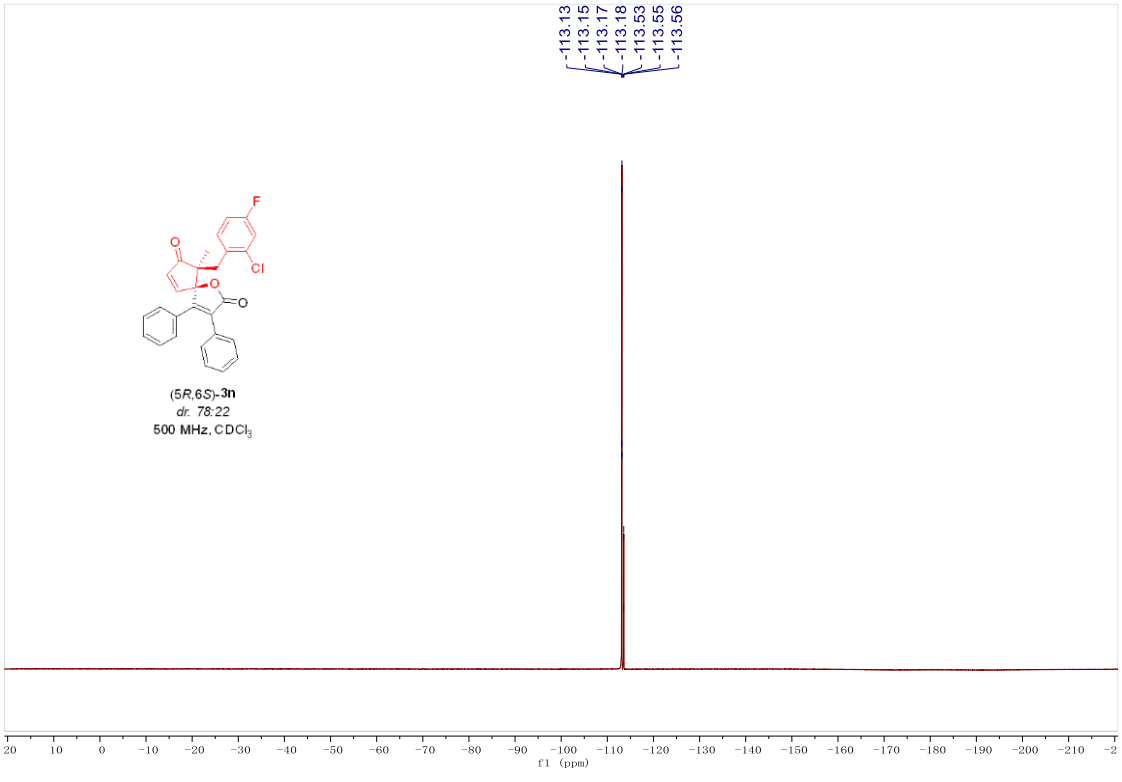
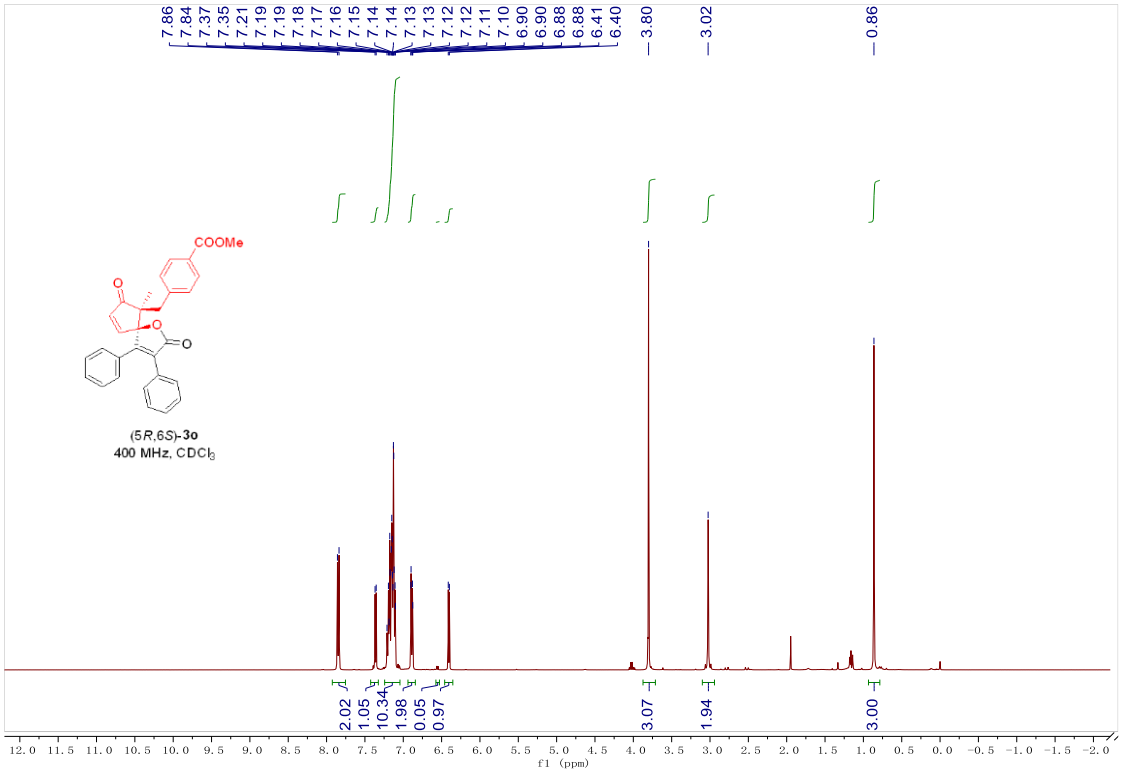
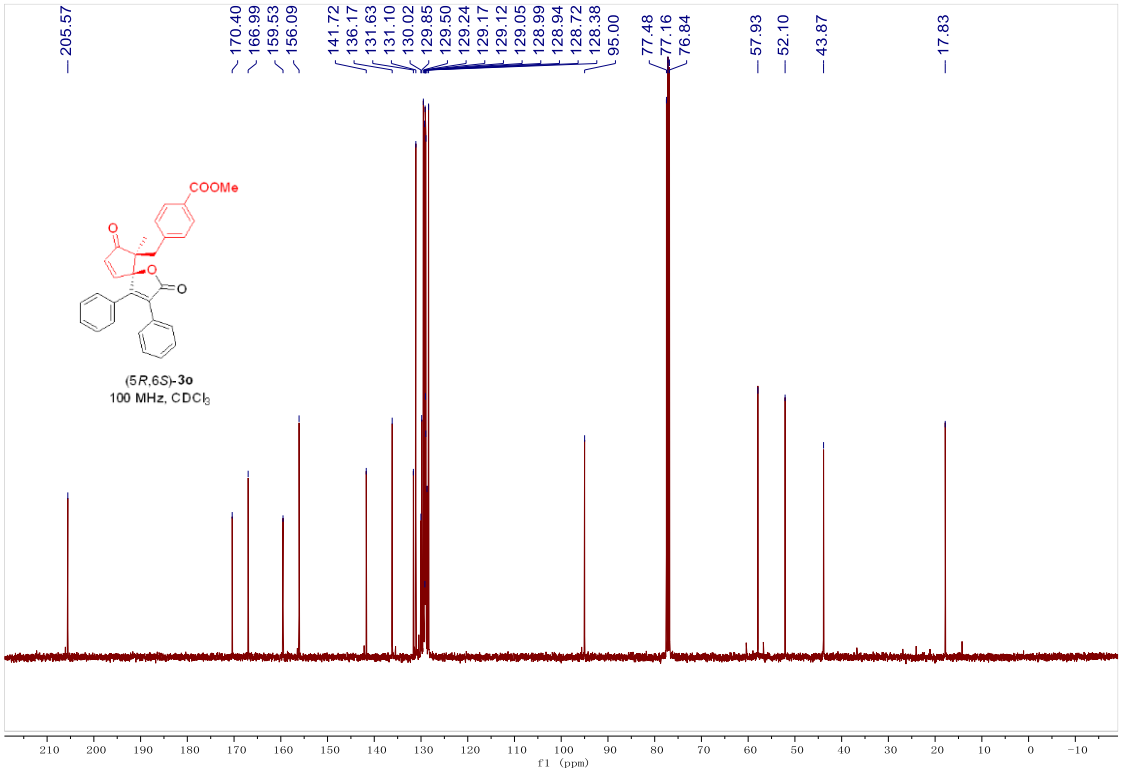
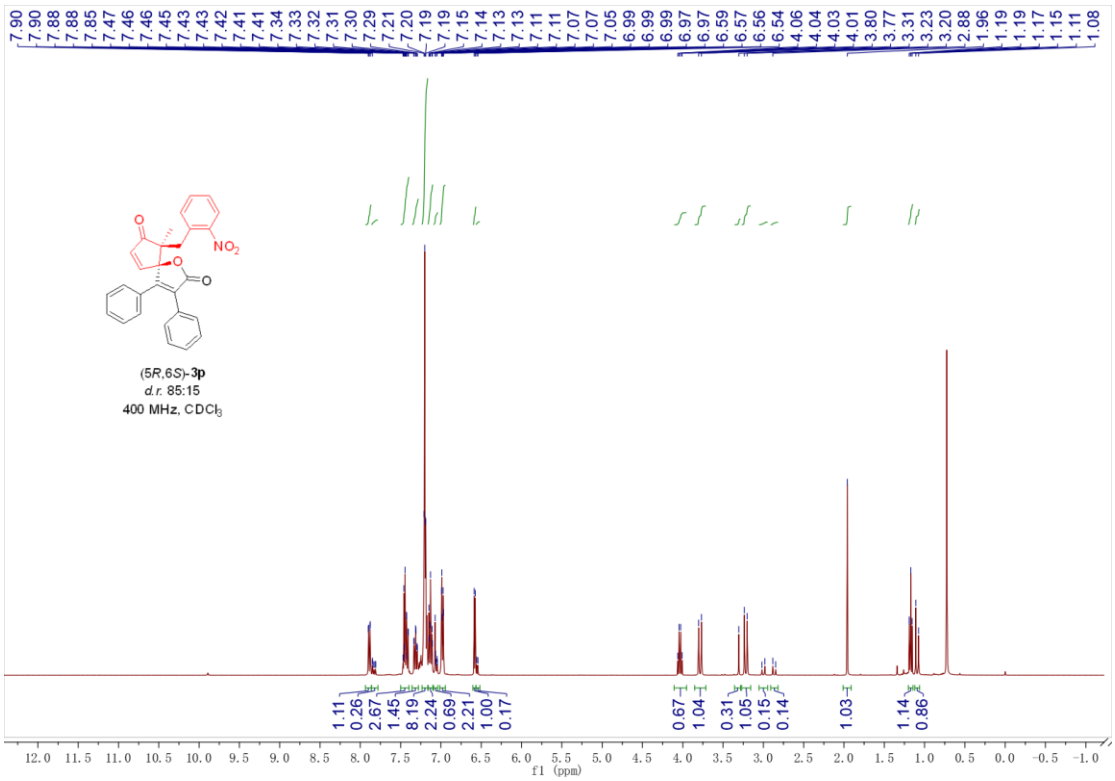
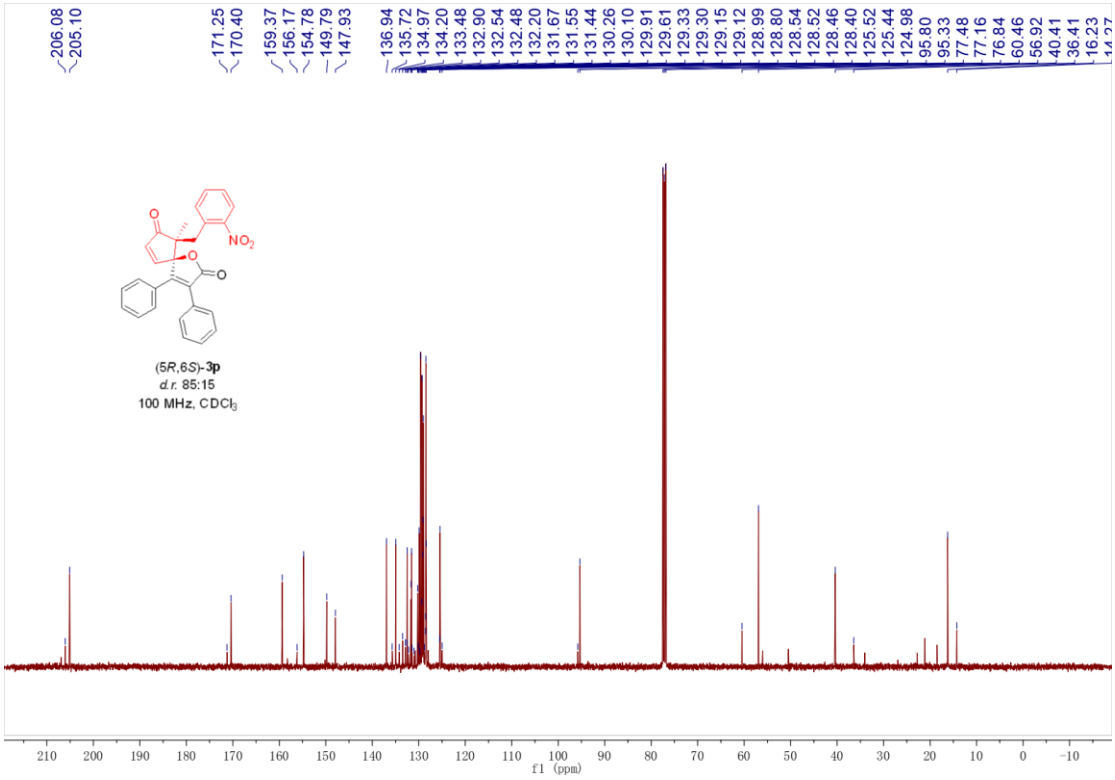
170.40
162.75
162.47
160.27
160.00
159.62
158.90
155.92
154.58
137.13
136.14
136.04
135.71
133.90
133.82
133.02
131.47
131.39
130.70
130.07
130.01
129.97
129.91
129.56
129.44
129.36
129.20
129.18
129.13
129.11
128.97
128.55
128.46
117.02
116.84
116.78
116.59
113.73
113.52
95.91
95.40
77.48
77.16
76.84
57.84
56.58
40.60
33.71
22.51
F
Cl
O
O
O
(5R,6S)-3n
d.r. 78:22
100 MHz, CDCl3
f1 (ppm)

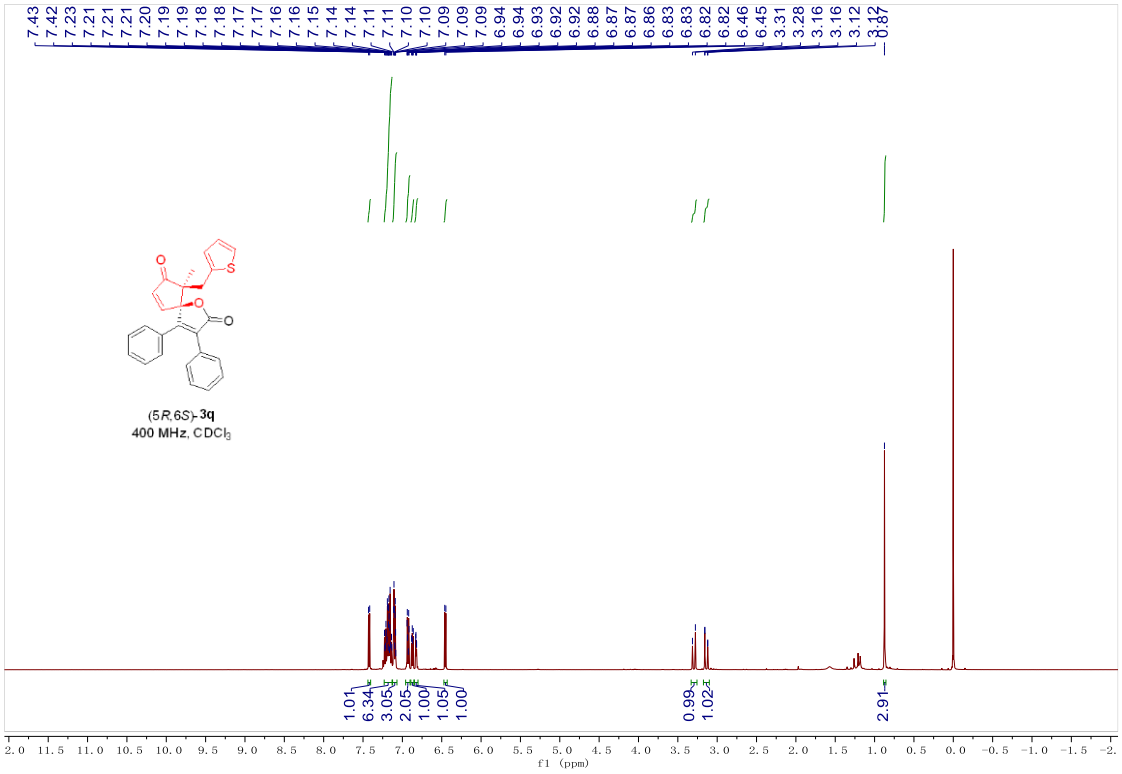

-113.13
-113.15
-113.17
-113.18
-113.53
-113.55
-113.56
F
Cl
O
O
O
(5R,6S)-3n
dr. 78:22
500 MHz, CDCl3
f1 (ppm)

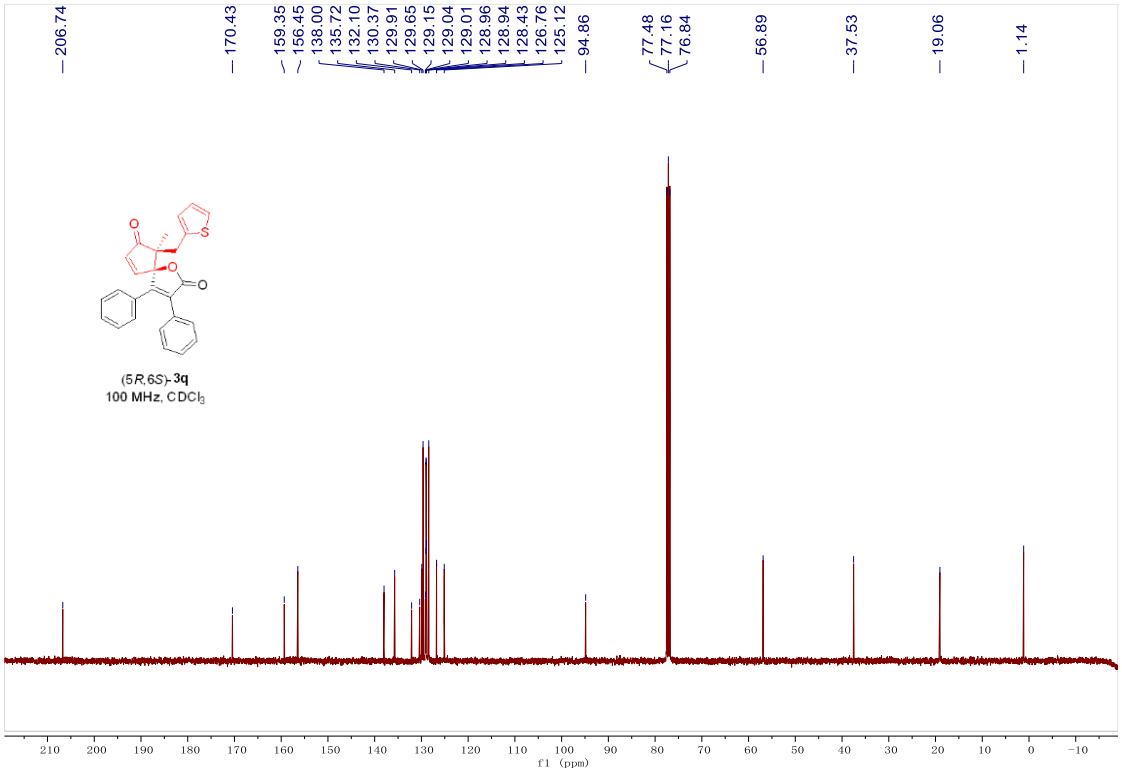

7.86
7.84
7.37
7.35
7.21
7.19
7.19
7.18
7.17
7.16
7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.11
7.10
6.90
6.90
6.88
6.88
6.41
6.40
3.80
3.02
0.86
COOMe
O
O
O
(5R,6S)-3o
400 MHz, CDCl3
2.02
1.05
10.34
1.98
0.05
0.97
3.07
1.94
3.00
f1 (ppm)

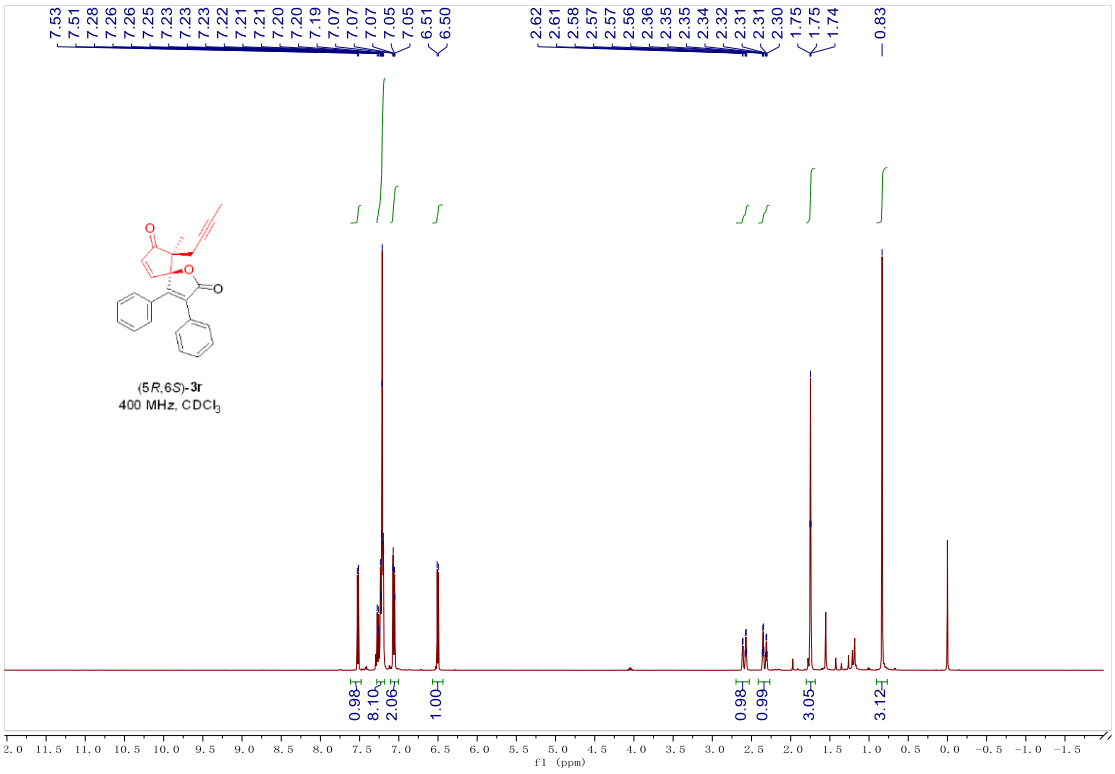

205.57
170.40
166.99
159.53
156.09
141.72
136.17
131.63
131.10
130.02
129.85
129.50
129.24
129.17
129.12
129.05
128.99
128.94
128.72
128.38
95.00
77.48
77.16
76.84
57.93
52.10
43.87
17.83
COOMe
O
O
O
(5R,6S)-3o
100 MHz, CDCl3
f1 (ppm)

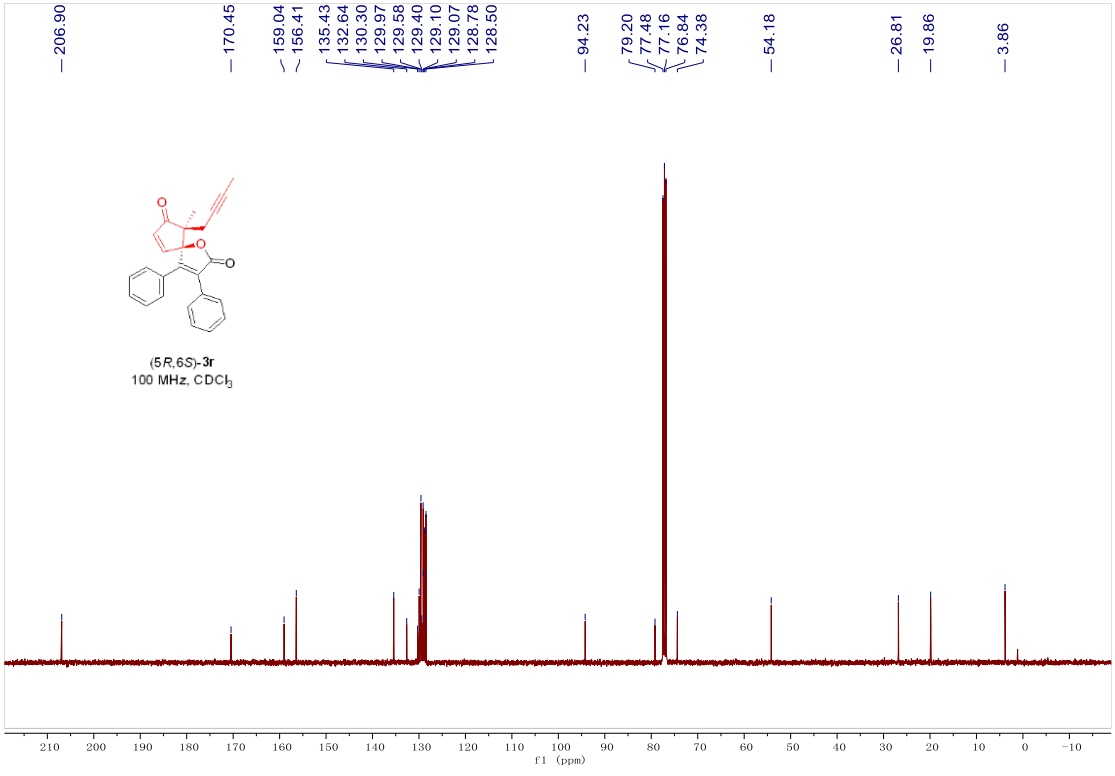

(5R,6S)-3p
d.r. 85:15
400 MHz, CDCl3
f1 (ppm)

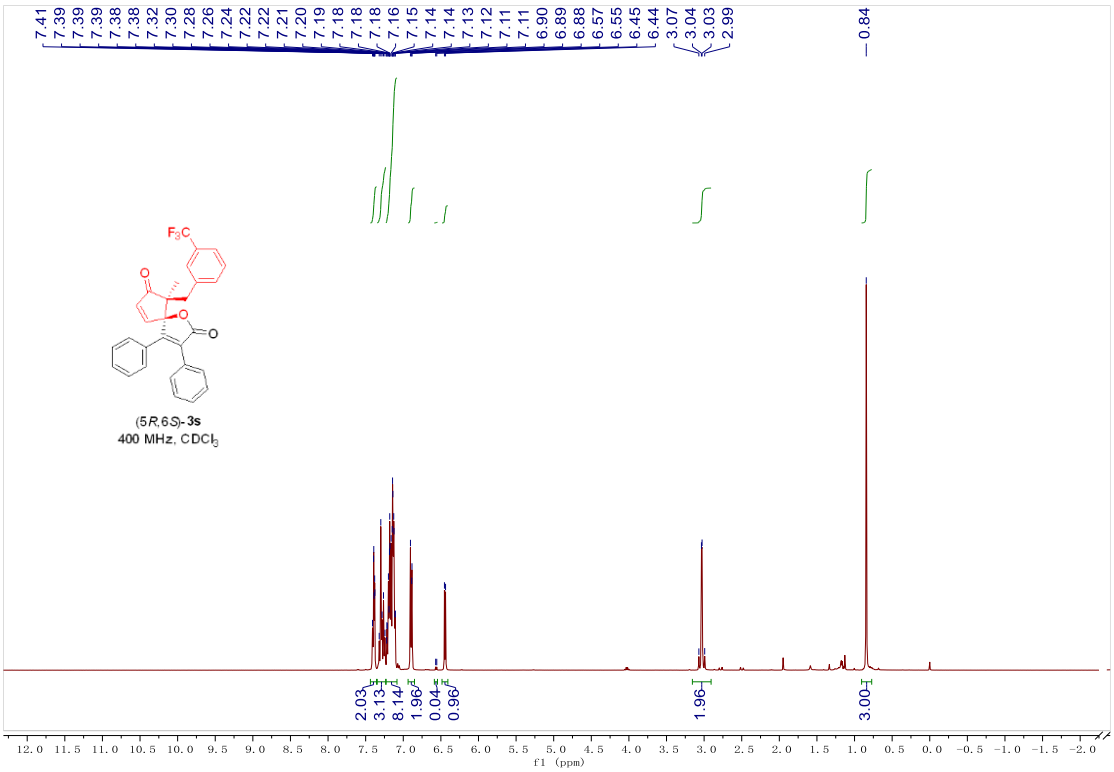

(5R,6S)-3p
d.r. 85:15
100 MHz, CDCl3
f1 (ppm)

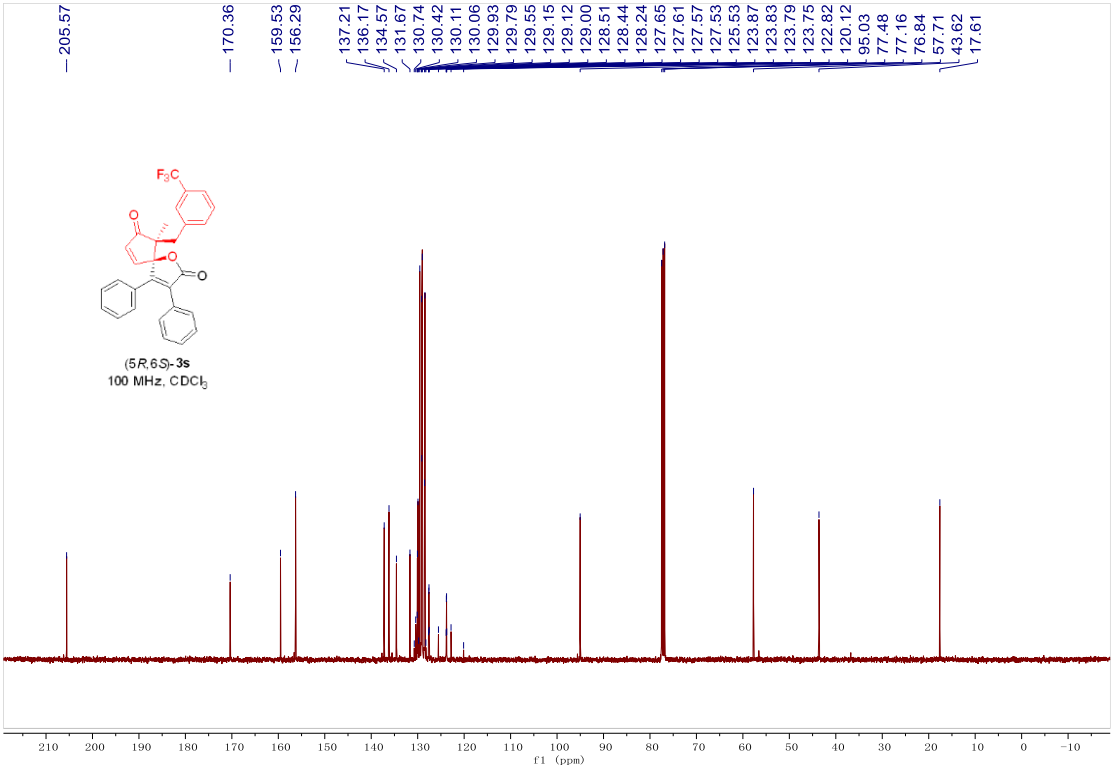

(5R,6S)-3q
400 MHz, CDCl3
f1 (ppm)

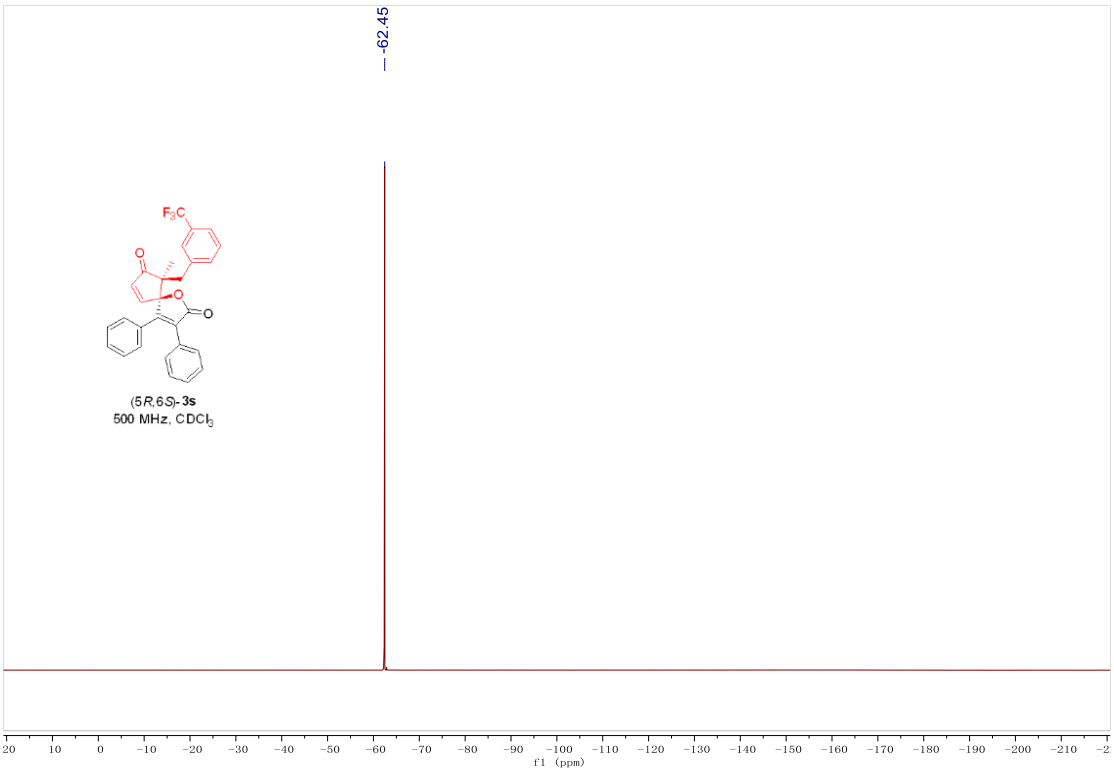

(5R,6S)-3q
100 MHz, CDCl3
f1 (ppm)

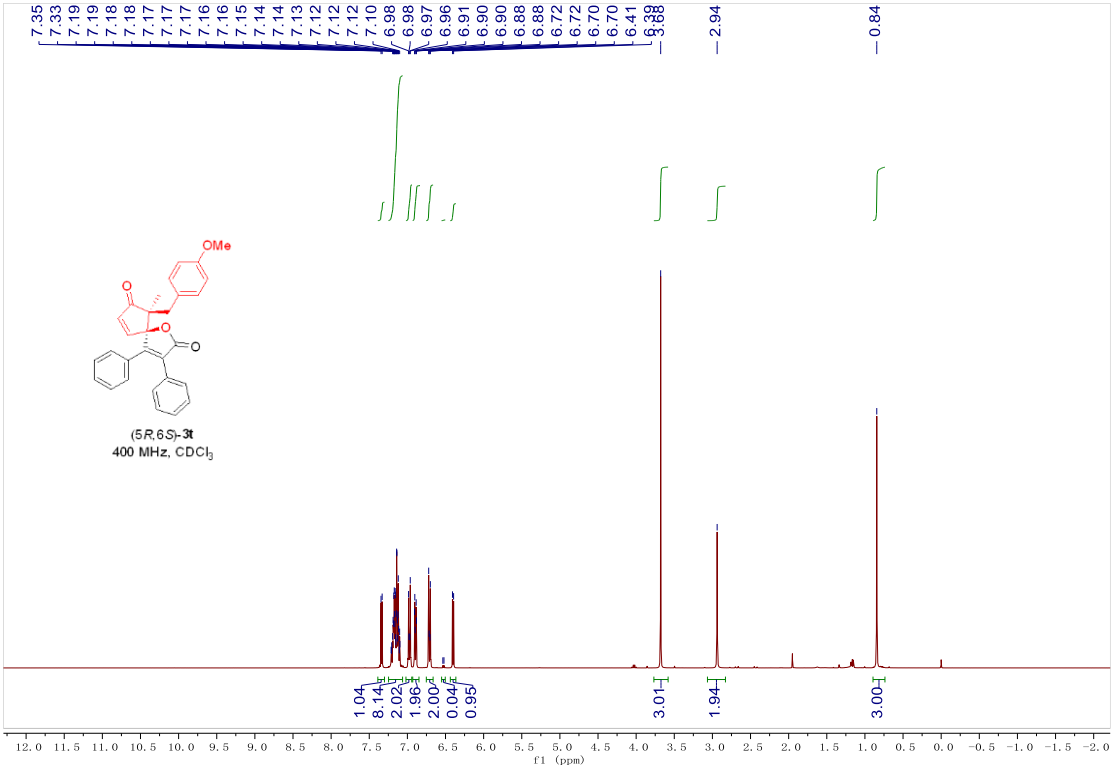

7.53
7.51
7.28
7.26
7.26
7.25
7.23
7.23
7.23
7.22
7.21
7.21
7.20
7.20
7.19
7.07
7.07
7.07
7.05
7.05
6.51
6.50
2.62
2.61
2.58
2.57
2.57
2.56
2.36
2.35
2.35
2.34
2.32
2.31
2.31
2.30
1.75
1.75
1.74
0.83
(5R,6S)-3r
400 MHz, CDCl3
0.98
8.10
2.06
1.00
0.98
0.99
3.05
3.12
f1 (ppm)

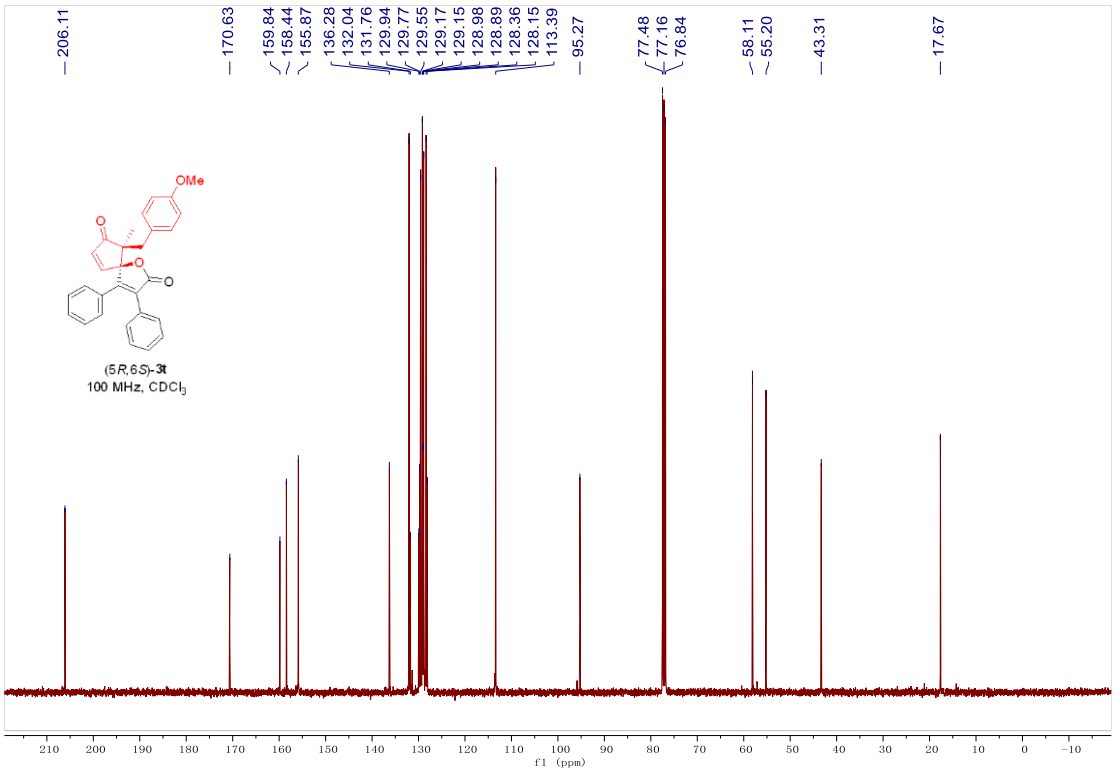

206.90
170.45
159.04
156.41
135.43
132.64
130.30
129.97
129.58
129.40
129.10
129.07
128.78
128.50
94.23
79.20
77.48
77.16
76.84
74.38
54.18
26.81
19.86
3.86
(5R,6S)-3r
100 MHz, CDCl3
f1 (ppm)

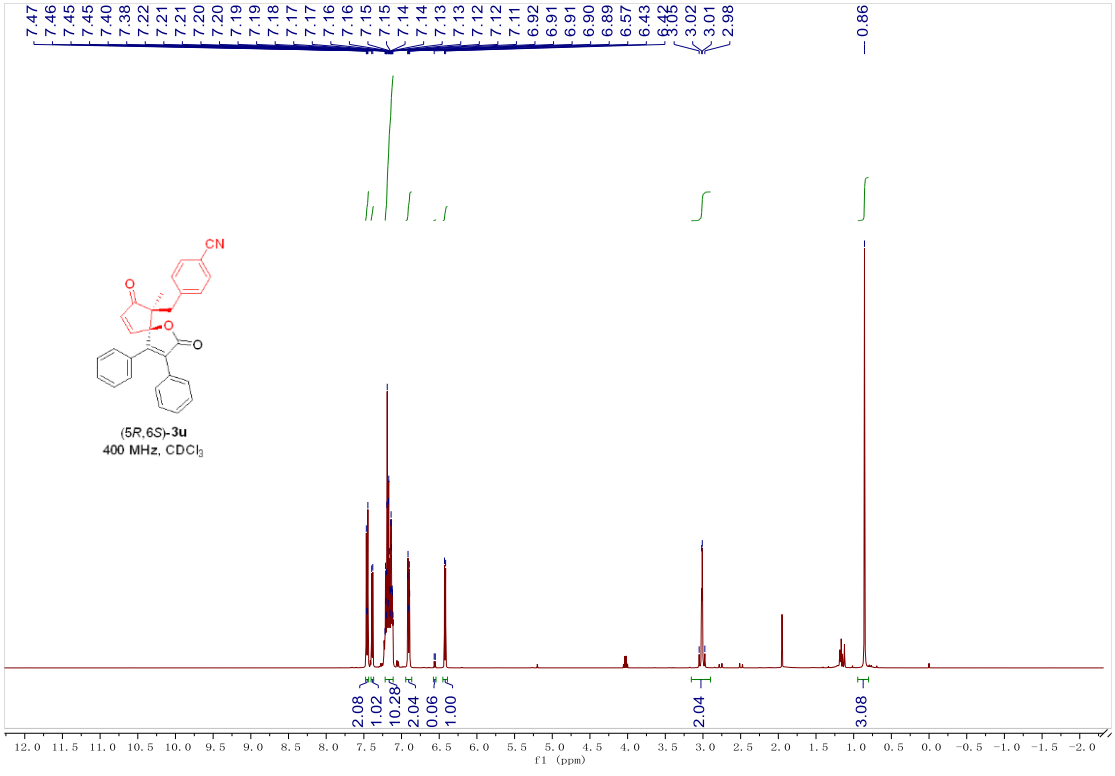

7.41
7.39
7.39
7.39
7.38
7.38
7.32
7.30
7.28
7.26
7.24
7.22
7.22
7.21
7.20
7.19
7.18
7.18
7.18
7.16
7.15
7.14
7.14
7.13
7.12
7.11
7.11
6.90
6.89
6.88
6.57
6.55
6.45
6.44
3.07
3.04
3.03
2.99
0.84
F3C
O
O
O
(5R,6S)-3s
400 MHz, CDCl3
2.03
3.13
8.14
1.96
0.04
0.96
1.96
3.00
f1 (ppm)

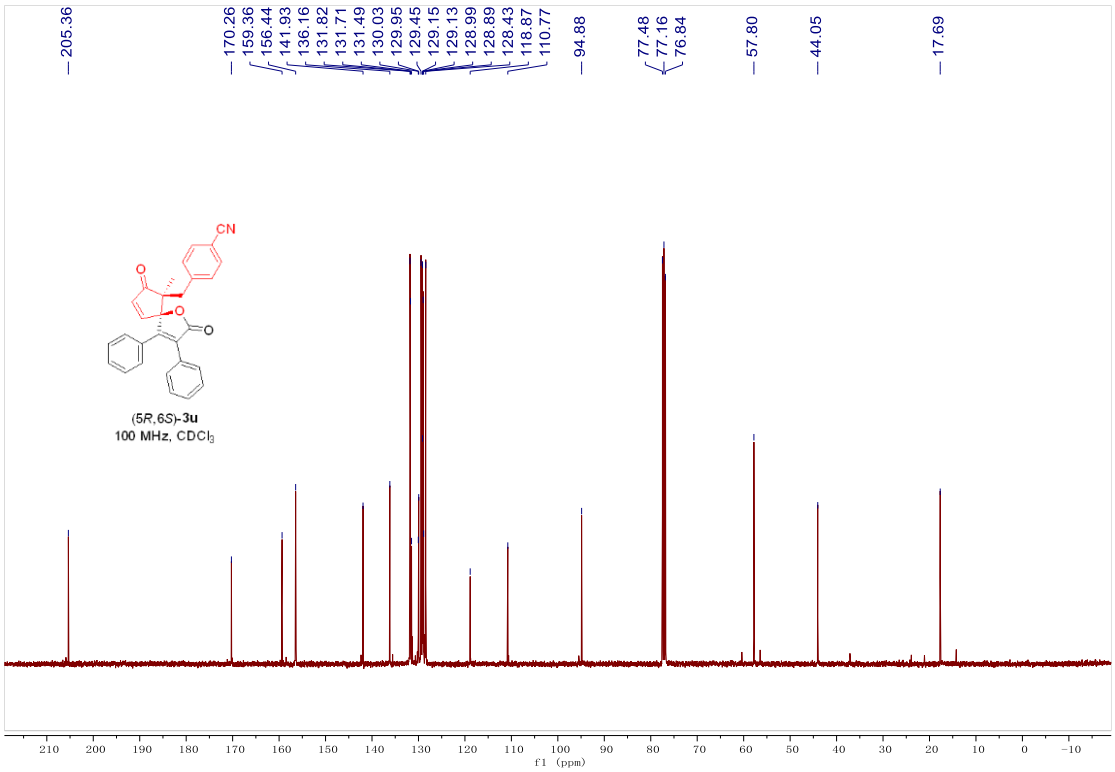

205.57
170.36
159.53
156.29
137.21
136.17
134.57
131.67
130.74
130.42
130.11
130.06
129.93
129.79
129.55
129.15
129.12
129.00
128.51
128.44
128.24
127.65
127.61
127.57
127.53
125.53
123.87
123.83
123.79
123.75
122.82
120.12
95.03
77.48
77.16
76.84
57.71
43.62
17.61
F3C
O
O
O
(5R,6S)-3s
100 MHz, CDCl3
f1 (ppm)

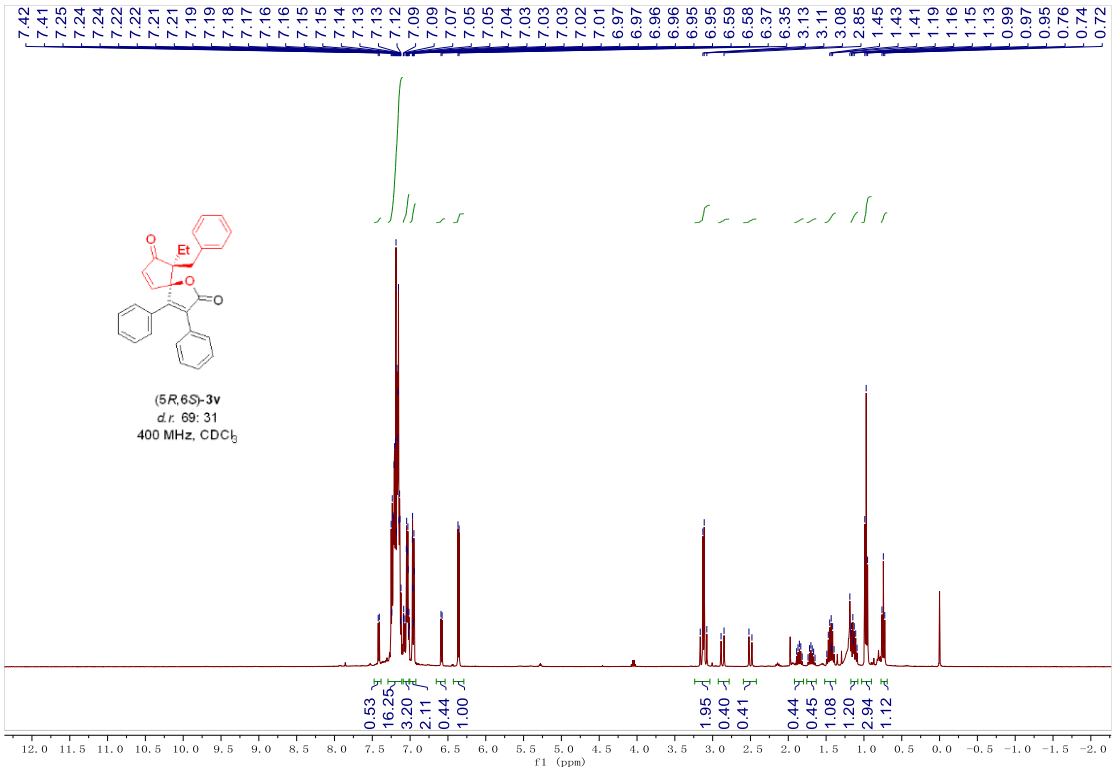

-62.45
F3C
O
O
O
(5R,6S)-3s
500 MHz, CDCl3
f1 (ppm)

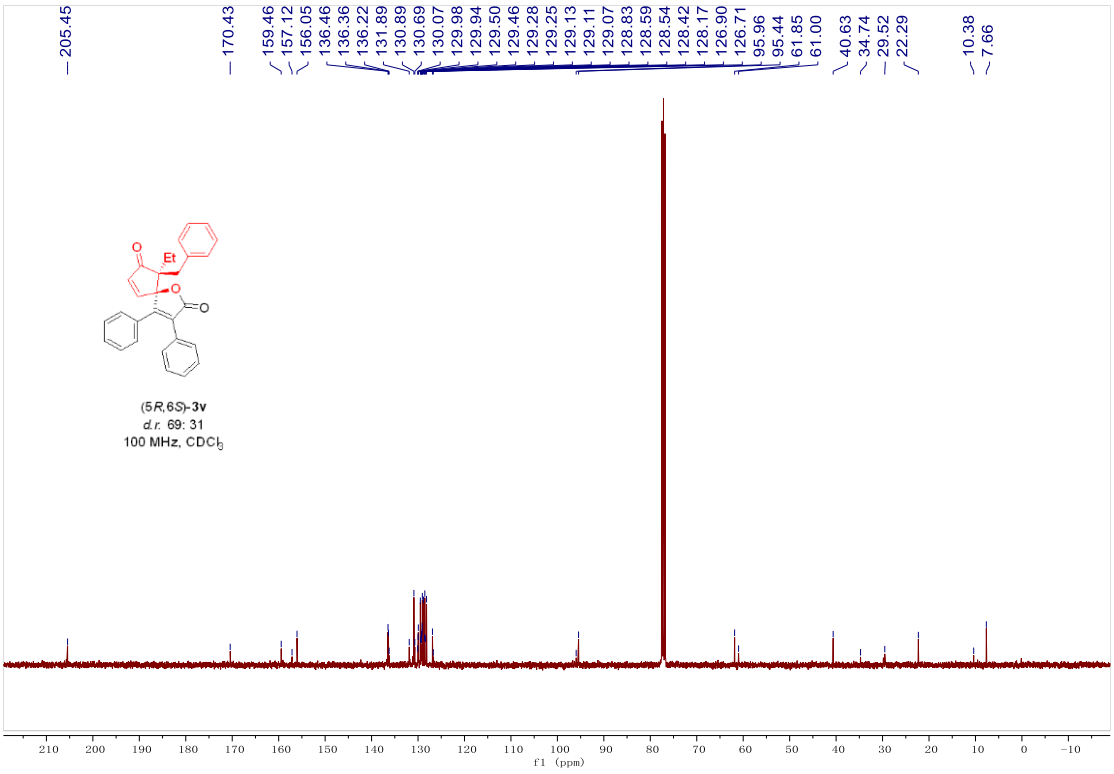

7.35
7.33
7.19
7.19
7.18
7.18
7.17
7.17
7.17
7.16
7.16
7.15
7.14
7.14
7.13
7.12
7.12
7.12
7.10
6.98
6.97
6.96
6.91
6.90
6.90
6.88
6.88
6.72
6.72
6.70
6.70
6.41
3.68
2.94
0.84
OMe
O
O
O
(5R,6S)-3t
400 MHz, CDCl3
1.04
8.14
2.02
1.96
2.00
0.04
0.95
3.01
1.94
3.00
f1 (ppm)

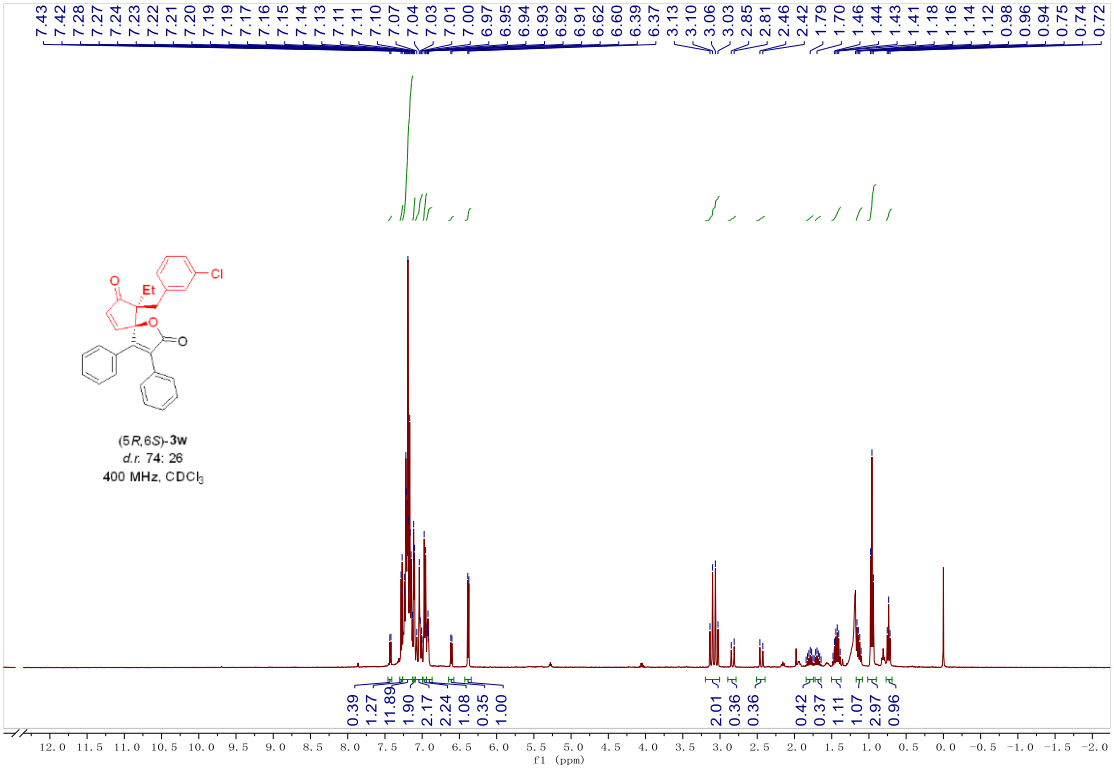

206.11
170.63
159.84
158.44
155.87
136.28
132.04
131.76
129.94
129.77
129.55
129.17
129.15
128.98
128.89
128.36
128.15
113.39
95.27
77.48
77.16
76.84
58.11
55.20
43.31
17.67
OMe
O
O
O
(5R,6S)-3t
100 MHz, CDCl3
f1 (ppm)

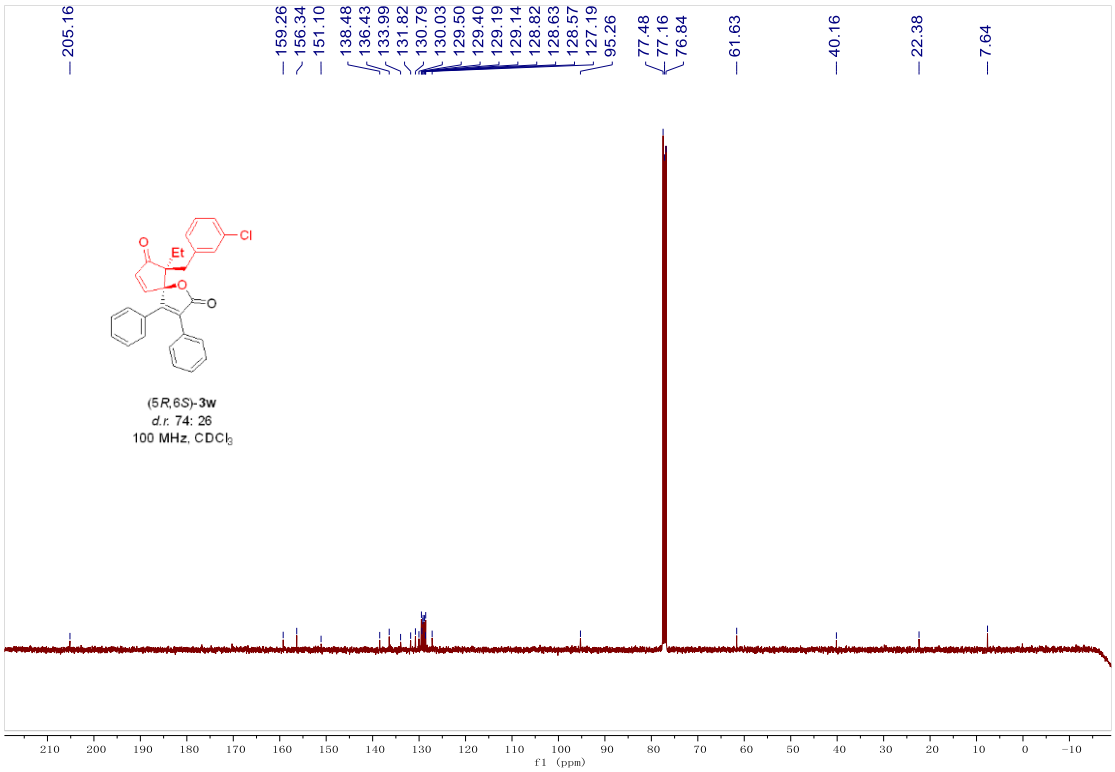

7.47
7.46
7.45
7.45
7.40
7.38
7.22
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.17
7.17
7.16
7.16
7.15
7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.11
6.92
6.91
6.91
6.90
6.89
6.57
6.43
3.05
3.02
3.01
2.98
0.86
CN
O
O
O
(5R,6S)-3u
400 MHz, CDCl3
2.08
1.02
10.28
2.04
0.06
1.00
2.04
3.08
f1 (ppm)

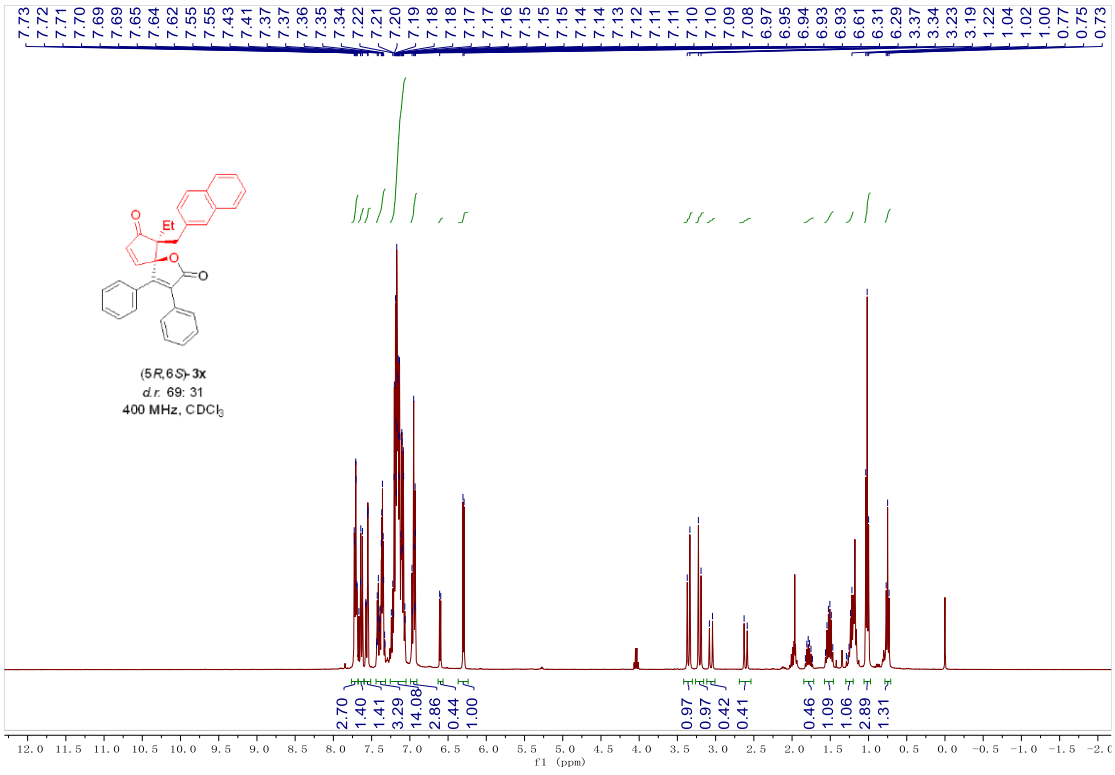

205.36
170.26
159.36
156.44
141.93
136.16
131.82
131.71
131.49
130.03
129.95
129.45
129.15
129.13
128.99
128.89
128.43
118.87
110.77
94.88
77.48
77.16
76.84
57.80
44.05
17.69
CN
O
O
O
(5R,6S)-3u
100 MHz, CDCl3
f1 (ppm)

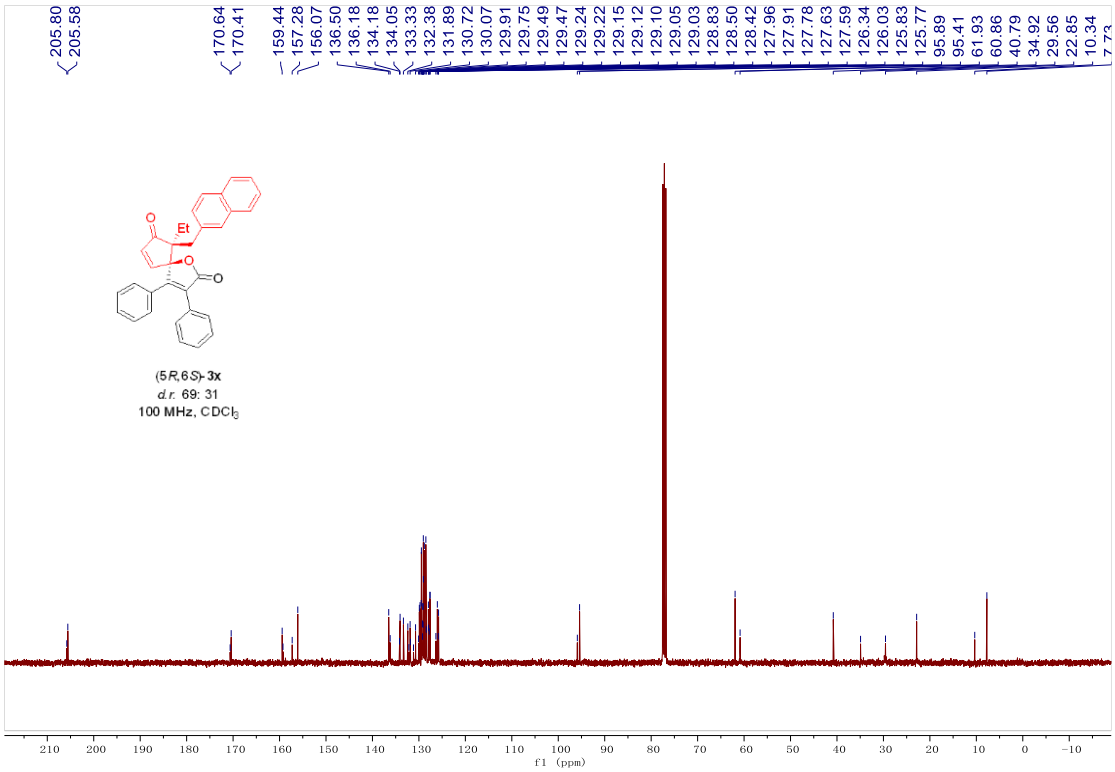

7.42
7.41
7.25
7.24
7.24
7.22
7.22
7.21
7.21
7.19
7.19
7.18
7.17
7.16
7.16
7.15
7.15
7.14
7.13
7.13
7.12
7.09
7.09
7.07
7.05
7.05
7.04
7.03
7.03
7.03
7.02
7.01
6.97
6.97
6.96
6.96
6.95
6.95
6.59
6.58
6.37
6.35
3.13
3.11
3.08
2.85
1.45
1.43
1.41
1.19
1.16
1.15
1.13
0.99
0.97
0.95
0.76
0.74
0.72
O
Et
O
O
(5R,6S)-3v
d.r. 69: 31
400 MHz, CDCl3
0.53
16.25
3.20
2.11
0.44
1.00
1.95
0.40
0.41
0.44
0.45
1.08
1.20
2.94
1.12
f1 (ppm)

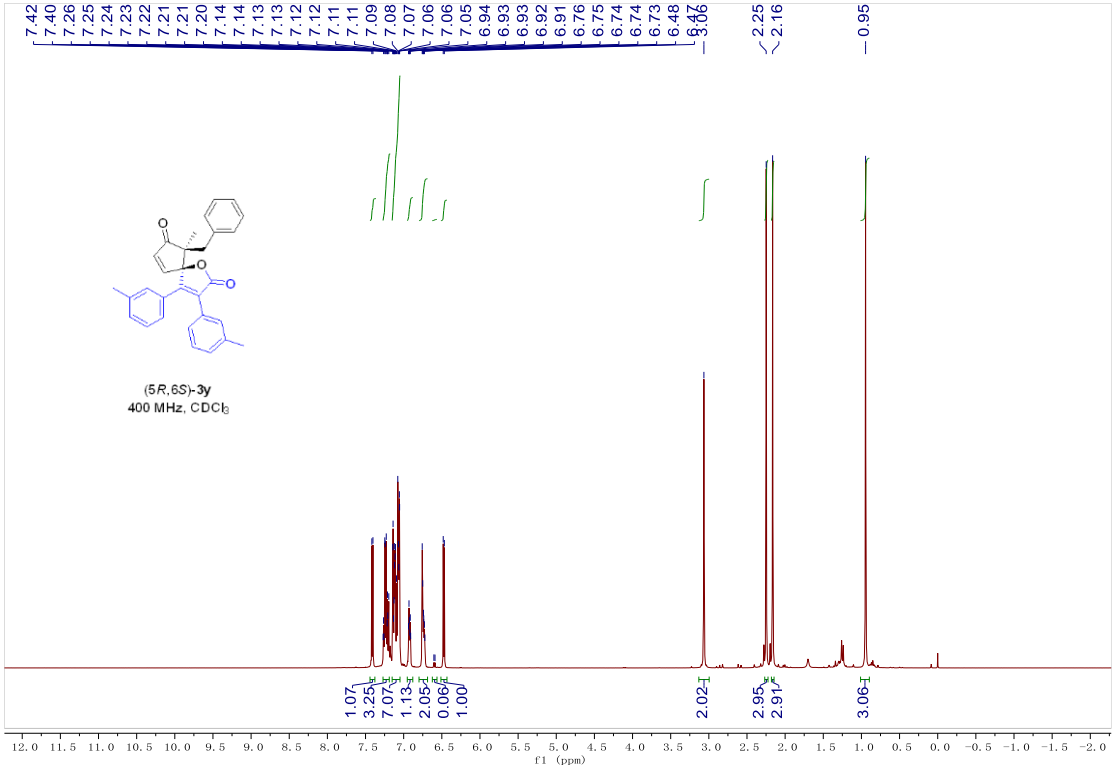

205.45
170.43
159.46
157.12
156.05
136.46
136.36
136.22
131.89
130.89
130.69
130.07
129.98
129.94
129.50
129.46
129.28
129.25
129.13
129.11
129.07
128.83
128.59
128.54
128.42
128.17
126.90
126.71
95.96
95.44
61.85
61.00
40.63
34.74
29.52
22.29
10.38
7.66
Et
O
O
O
(5R,6S)-3v
d.r. 69: 31
100 MHz, CDCl3
f1 (ppm)

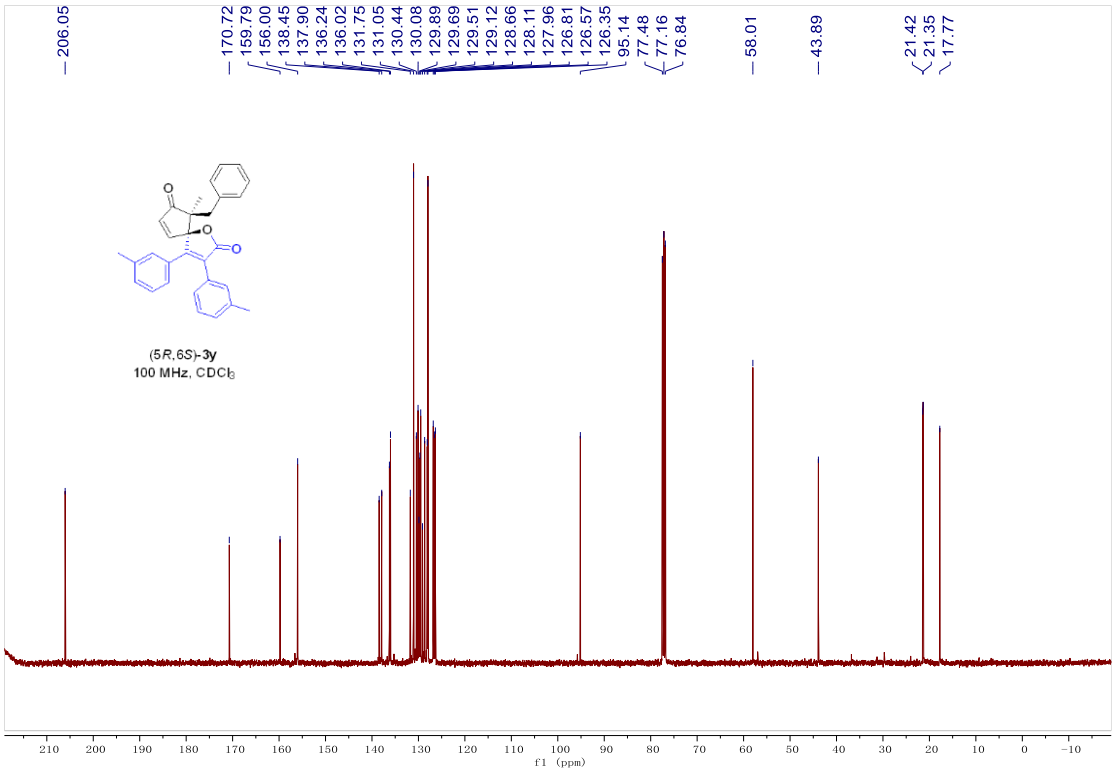

7.43
7.42
7.28
7.27
7.24
7.23
7.22
7.21
7.20
7.19
7.19
7.17
7.16
7.15
7.14
7.13
7.11
7.11
7.10
7.07
7.04
7.03
7.01
7.00
6.97
6.95
6.94
6.93
6.92
6.91
6.62
6.60
6.39
6.37
3.13
3.10
3.06
3.03
2.85
2.81
2.46
2.42
1.79
1.70
1.46
1.44
1.43
1.41
1.18
1.16
1.14
1.12
0.98
0.96
0.94
0.75
0.74
0.72
Et
Cl
O
O
O
(5R,6S)-3w
d.r. 74: 26
400 MHz, CDCl3
0.39
1.27
11.89
1.90
2.17
2.24
1.08
0.35
1.00
2.01
0.36
0.36
0.42
0.37
1.11
1.07
2.97
0.96
f1 (ppm)

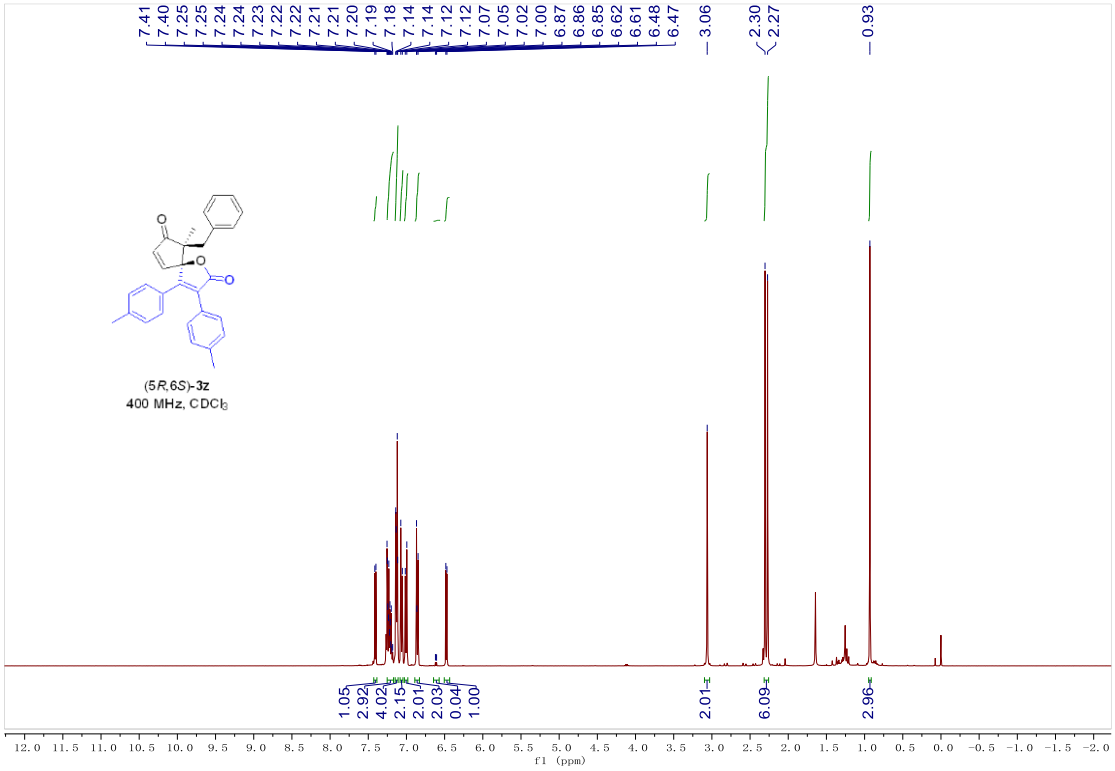

205.16
159.26
156.34
151.10
138.48
136.43
133.99
131.82
130.79
130.03
129.50
129.40
129.19
129.14
128.82
128.63
128.57
127.19
95.26
77.48
77.16
76.84
61.63
40.16
22.38
7.64
Et
Cl
O
O
O
(5R,6S)-3w
d.r. 74: 26
100 MHz, CDCl3
f1 (ppm)

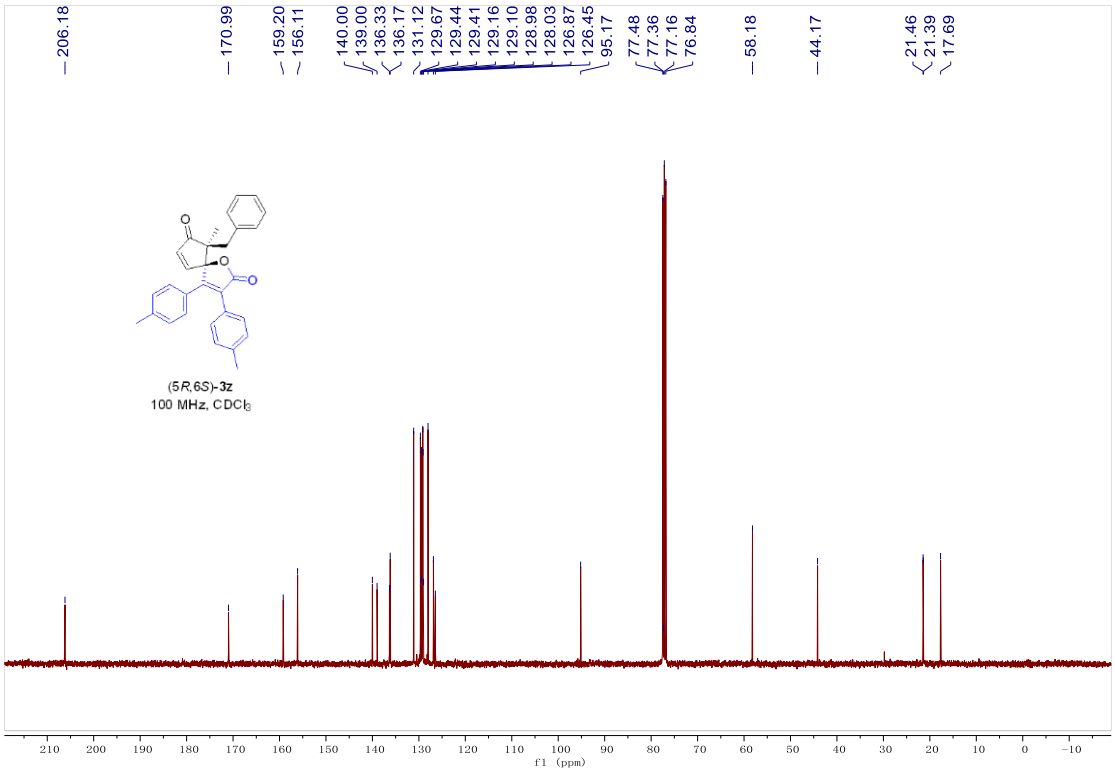

7.73
7.72
7.71
7.70
7.69
7.69
7.65
7.64
7.62
7.55
7.55
7.43
7.41
7.37
7.37
7.36
7.35
7.34
7.22
7.21
7.20
7.19
7.18
7.18
7.17
7.17
7.16
7.15
7.15
7.15
7.14
7.14
7.13
7.12
7.11
7.11
7.10
7.10
7.09
7.08
6.97
6.95
6.94
6.93
6.93
6.61
6.31
6.29
3.37
3.34
3.23
3.19
1.22
1.04
1.02
1.00
0.77
0.75
0.73
Et
O
O
O
(5R,6S)-3x
d.r. 69: 31
400 MHz, CDCl3
2.70
1.40
1.41
3.29
14.08
2.86
0.44
1.00
0.97
0.97
0.42
0.41
0.46
1.09
1.06
2.89
1.31
f1 (ppm)

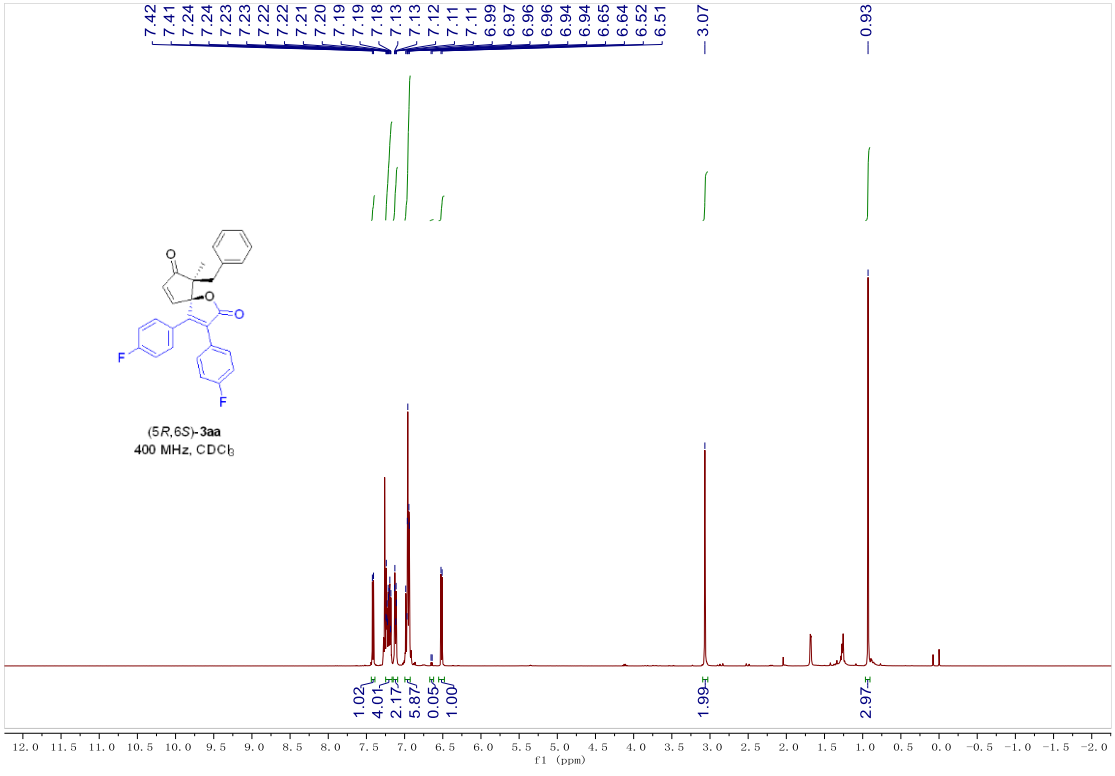

205.80
205.58
170.64
170.41
159.44
157.28
156.07
136.50
136.18
134.18
134.05
133.33
132.38
131.89
130.72
130.07
129.91
129.75
129.49
129.47
129.24
129.22
129.15
129.12
129.10
129.05
129.03
128.83
128.50
128.42
127.96
127.91
127.78
127.63
127.59
126.34
126.03
125.83
125.77
95.89
95.41
61.93
60.86
40.79
34.92
29.56
22.85
10.34
7.72
Et
O
O
O
(5R,6S)-3x
d.r. 69: 31
100 MHz, CDCl3
f1 (ppm)

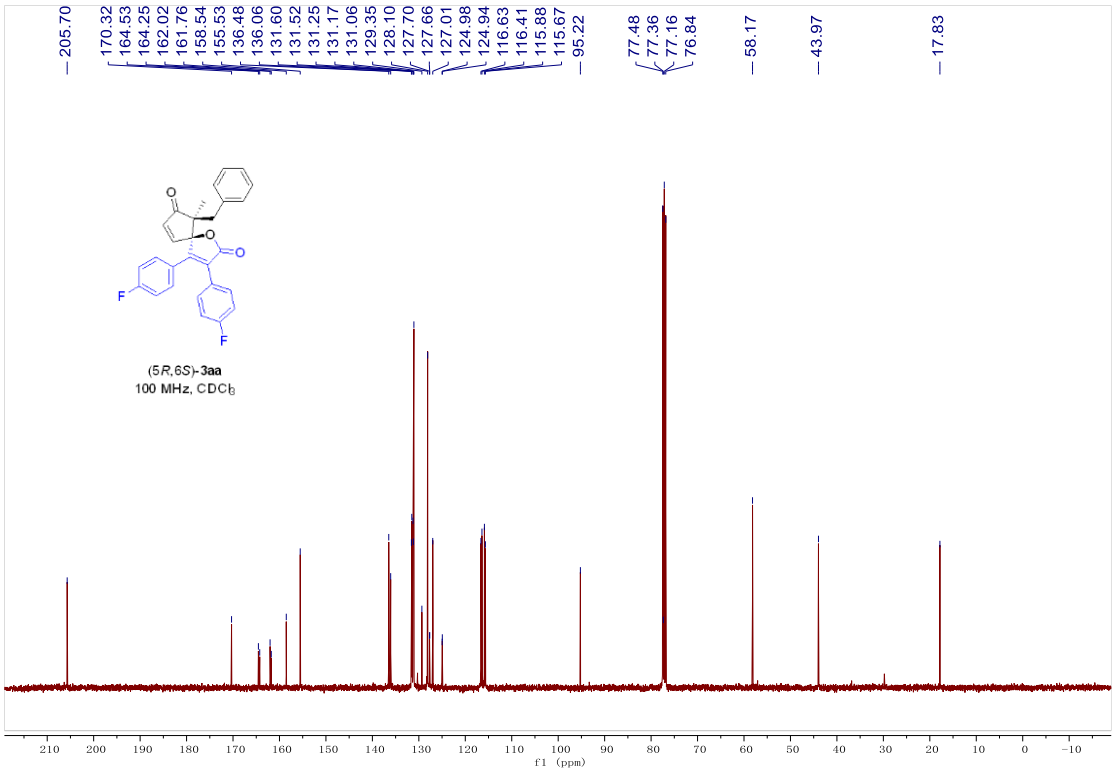

7.42
7.40
7.26
7.25
7.24
7.23
7.22
7.21
7.21
7.20
7.14
7.13
7.13
7.12
7.12
7.11
7.11
7.09
7.08
7.07
7.06
7.06
7.05
6.94
6.93
6.92
6.91
6.76
6.75
6.74
6.74
6.73
6.48
6.47
3.06
2.25
2.16
0.95
O
O
O
(5R,6S)-3y
400 MHz, CDCl3
1.07
3.25
7.07
1.13
2.05
0.06
1.00
2.02
2.95
2.91
3.06
f1 (ppm)

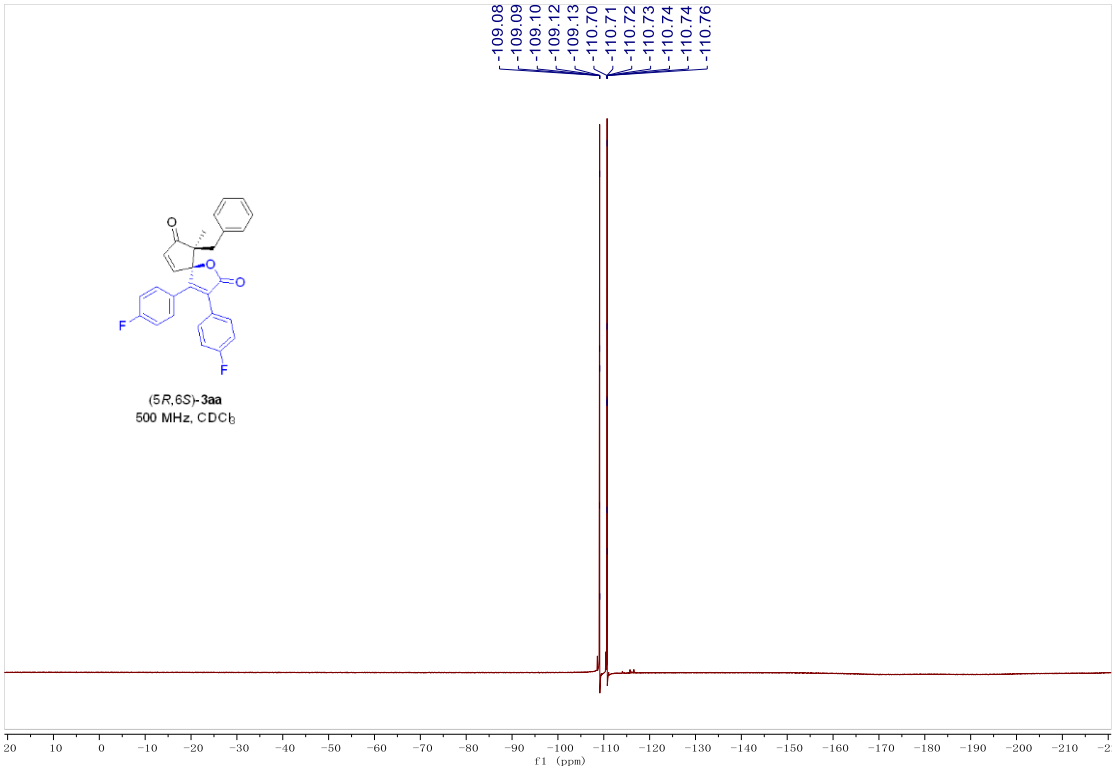

206.05
170.72
159.79
156.00
138.45
137.90
136.24
136.02
131.75
131.05
130.44
130.08
129.89
129.69
129.51
129.12
128.66
128.11
127.96
126.81
126.57
126.35
95.14
77.48
77.16
76.84
58.01
43.89
21.42
21.35
17.77
(5R,6S)-3y
100 MHz, CDCl3
f1 (ppm)

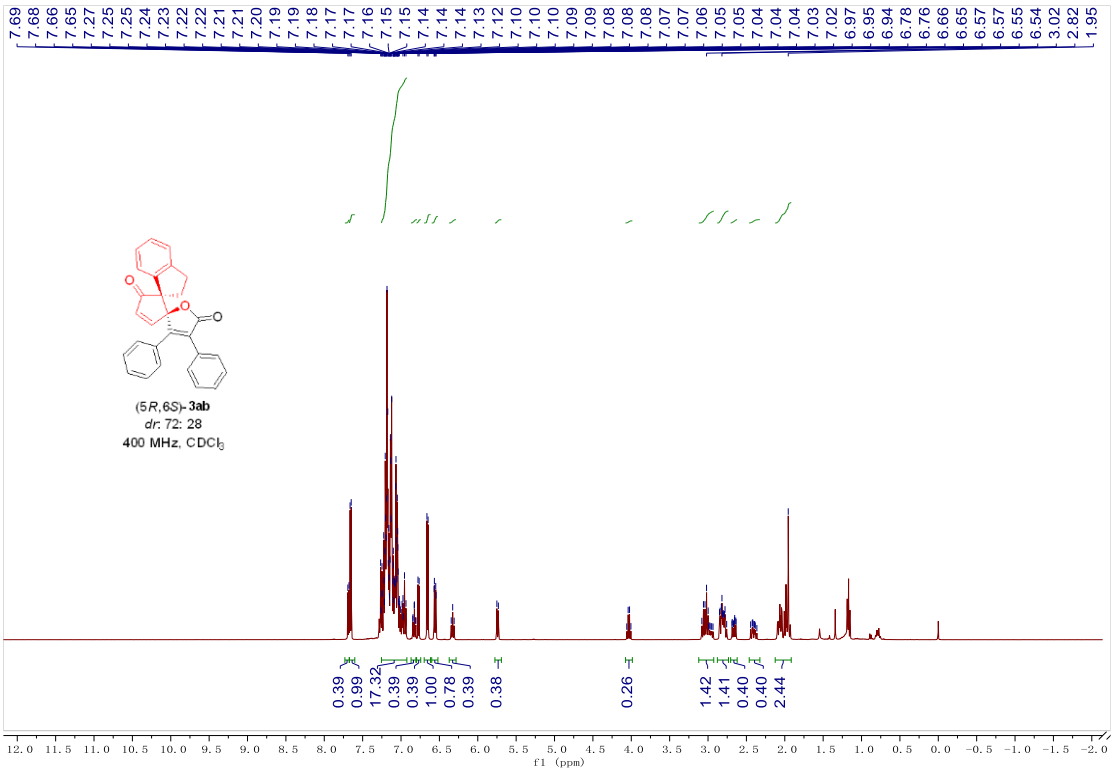

7.41
7.40
7.25
7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.21
7.20
7.19
7.18
7.14
7.14
7.12
7.12
7.07
7.05
7.02
7.00
6.87
6.86
6.85
6.62
6.61
6.48
6.47
3.06
2.30
2.27
0.93
1.05
2.92
4.02
2.15
2.01
2.03
0.04
1.00
2.01
6.09
2.96
(5R,6S)-3z
400 MHz, CDCl3
f1 (ppm)

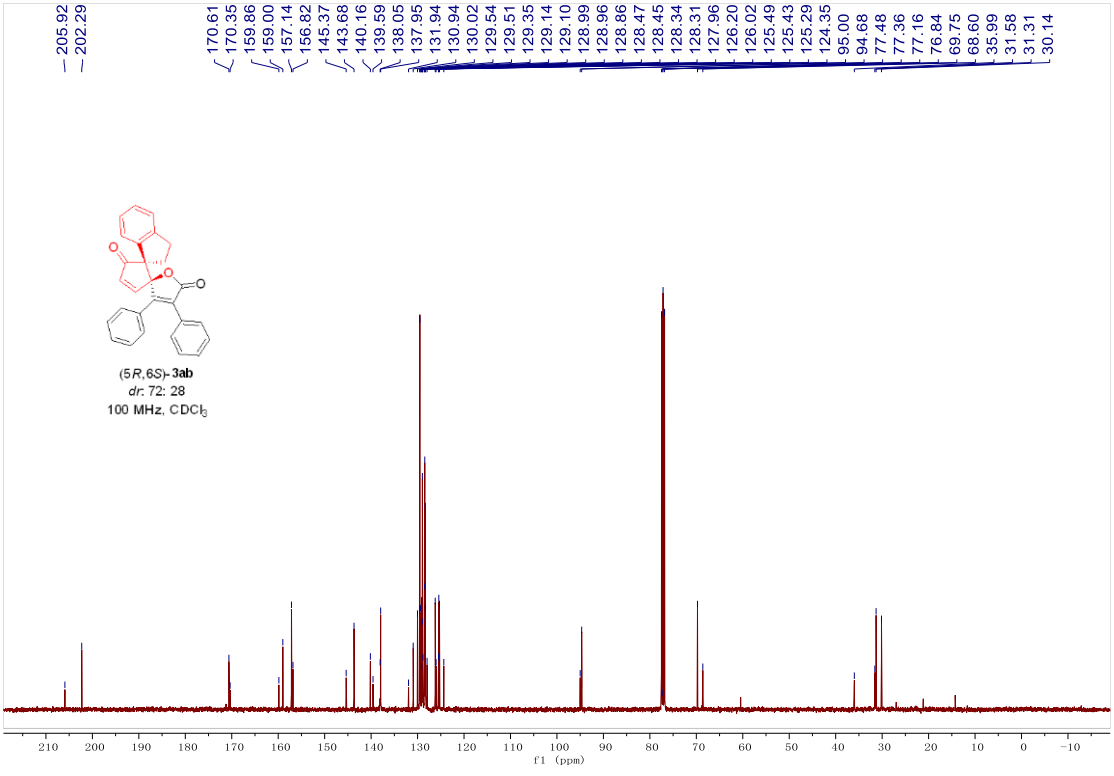

206.18
170.99
159.20
156.11
140.00
139.00
136.33
136.17
131.12
129.67
129.44
129.41
129.16
129.10
128.98
128.03
126.87
126.45
95.17
77.48
77.36
77.16
76.84
58.18
44.17
21.46
21.39
17.69
(5R,6S)-3z
100 MHz, CDCl3
f1 (ppm)

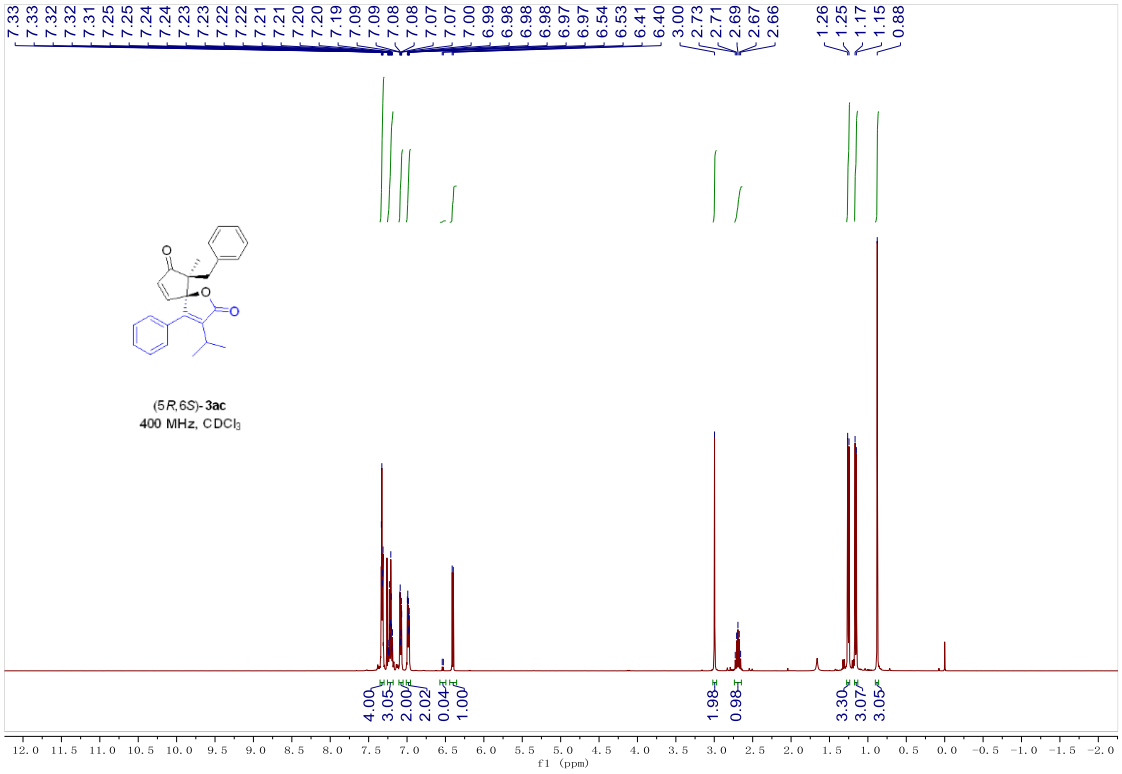

7.42
7.41
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.20
7.19
7.19
7.18
7.13
7.12
7.11
7.11
6.99
6.97
6.96
6.96
6.94
6.94
6.65
6.64
6.52
6.51
3.07
0.93
1.02
4.01
2.17
5.87
0.05
1.00
1.99
2.97
(5R,6S)-3aa
400 MHz, CDCl3
f1 (ppm)

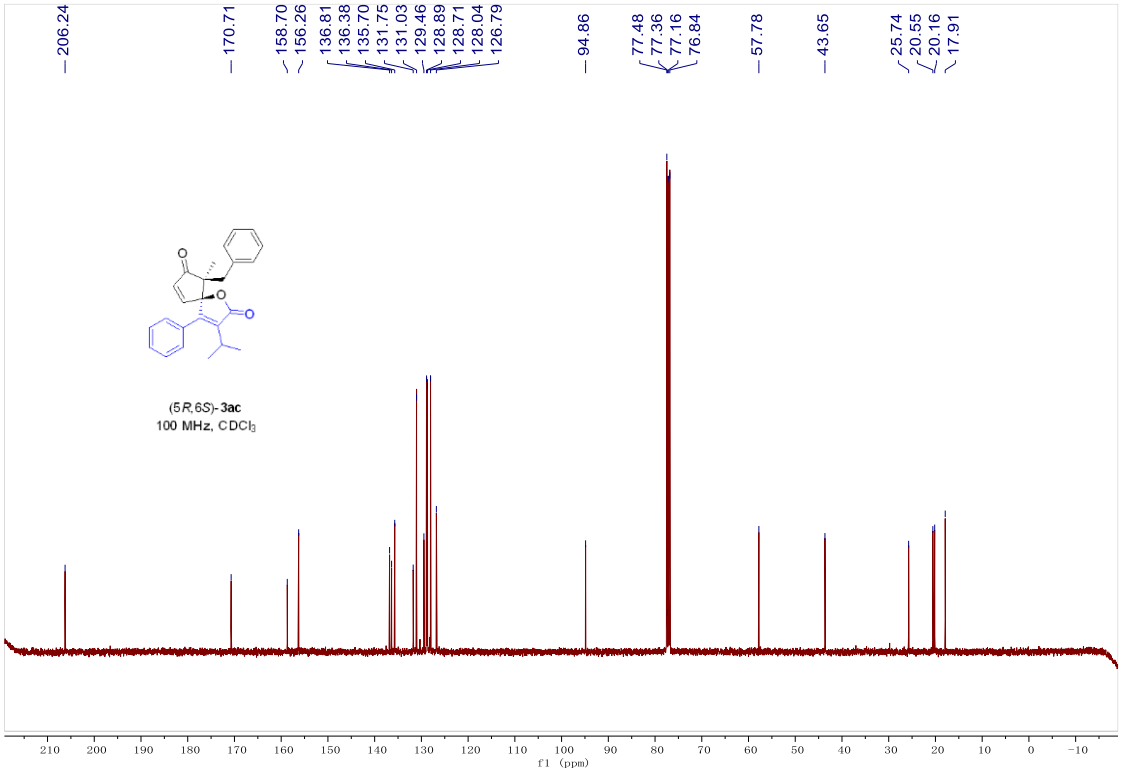

205.70
170.32
164.53
164.25
162.02
161.76
158.54
155.53
136.48
136.06
131.60
131.52
131.25
131.17
131.06
129.35
128.10
127.70
127.66
127.01
124.98
124.94
116.63
116.41
115.88
115.67
95.22
77.48
77.36
77.16
76.84
58.17
43.97
17.83
(5R,6S)-3aa
100 MHz, CDCl3
f1 (ppm)

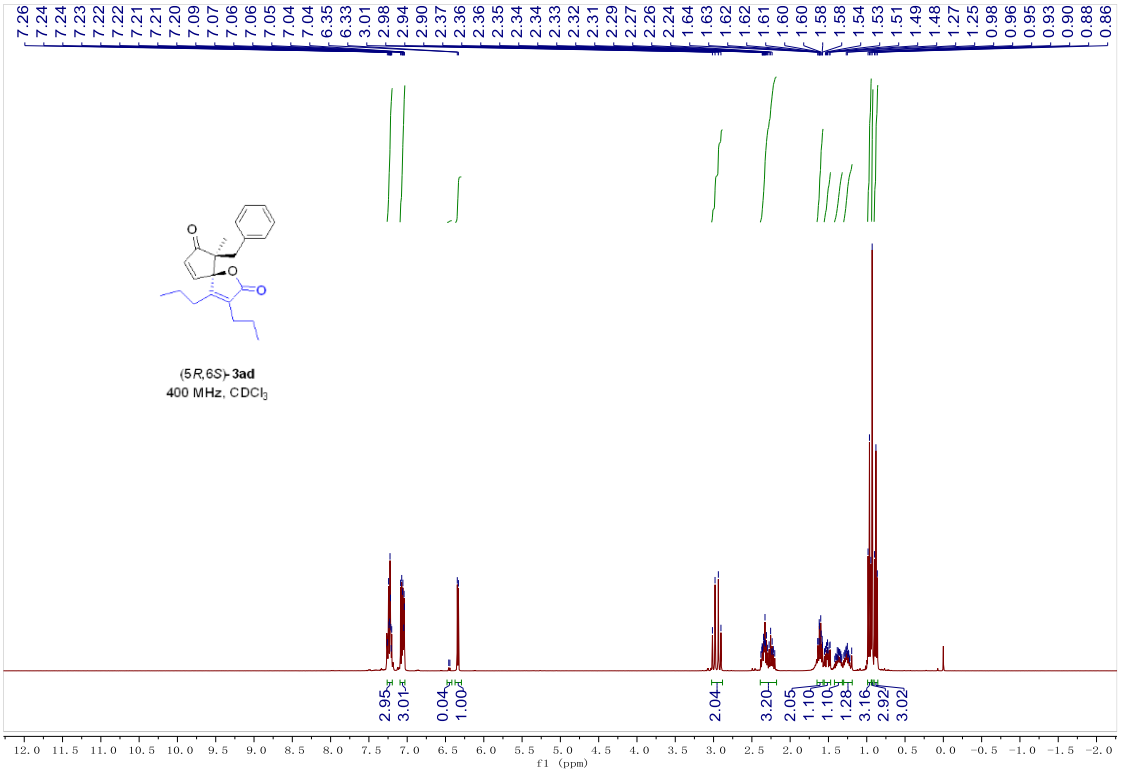

-109.08
-109.09
-109.10
-109.12
-109.13
-110.70
-110.71
-110.72
-110.73
-110.74
-110.74
-110.76
(5R,6S)-3aa
500 MHz, CDCl3
f1 (ppm)

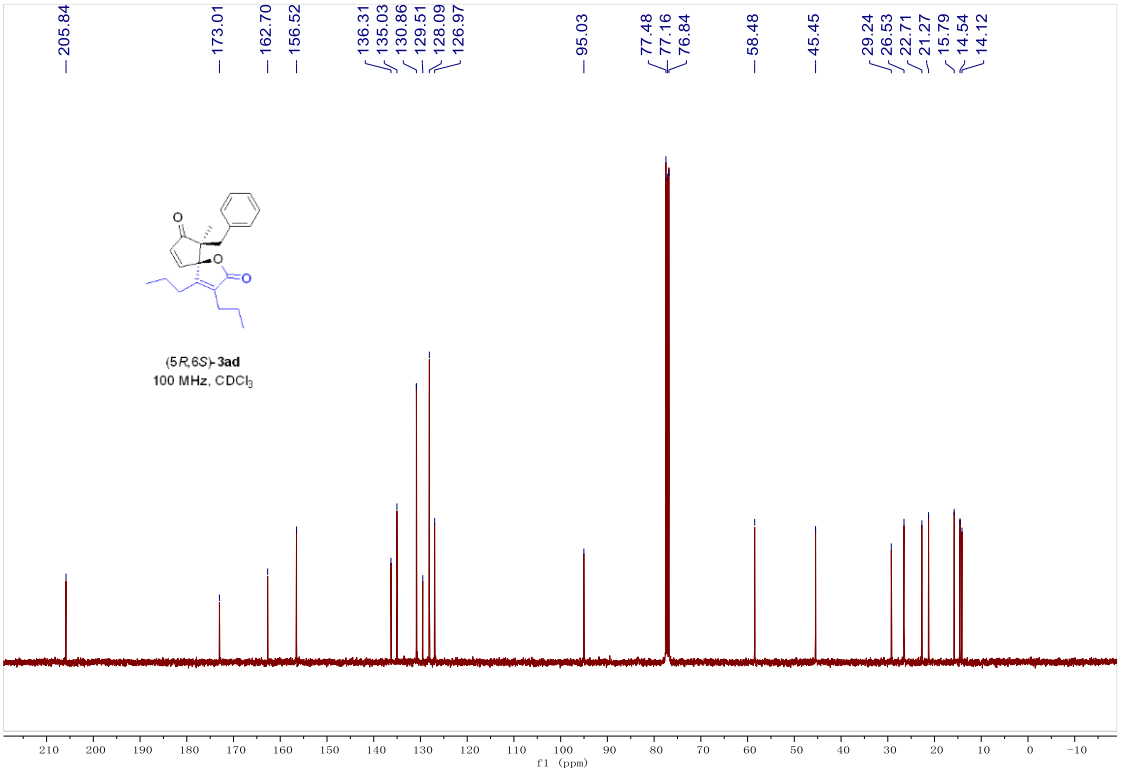

(5R,6S)-3ab
dr: 72: 28
400 MHz, CDCl3
f1 (ppm)

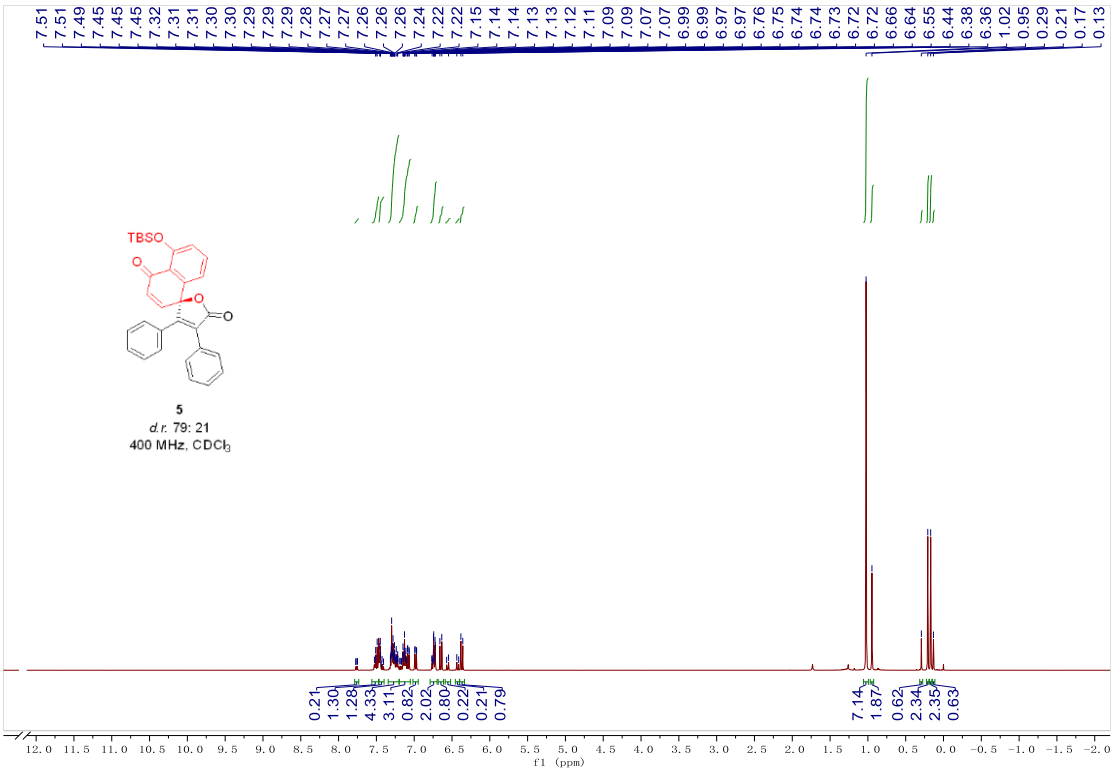

(5R,6S)-3ab
dr: 72: 28
100 MHz, CDCl3
f1 (ppm)

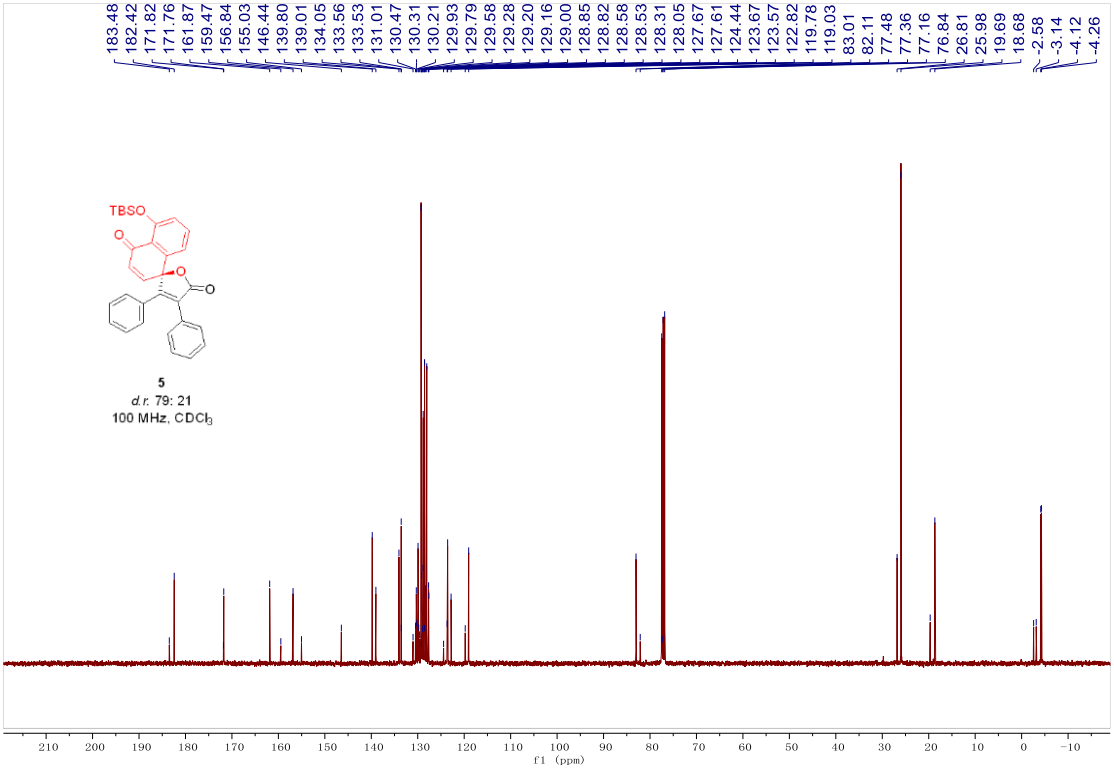

(5R,6S)-3ac
400 MHz, CDCl3

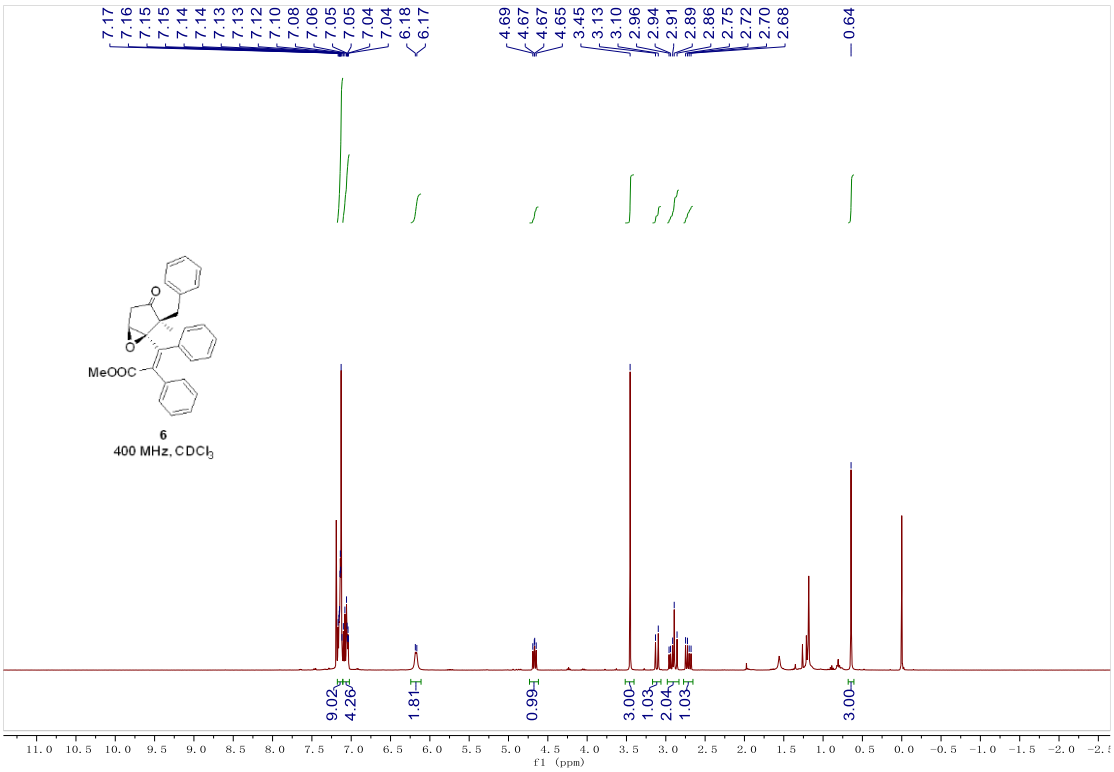

(5R,6S)-3ac
100 MHz, CDCl3

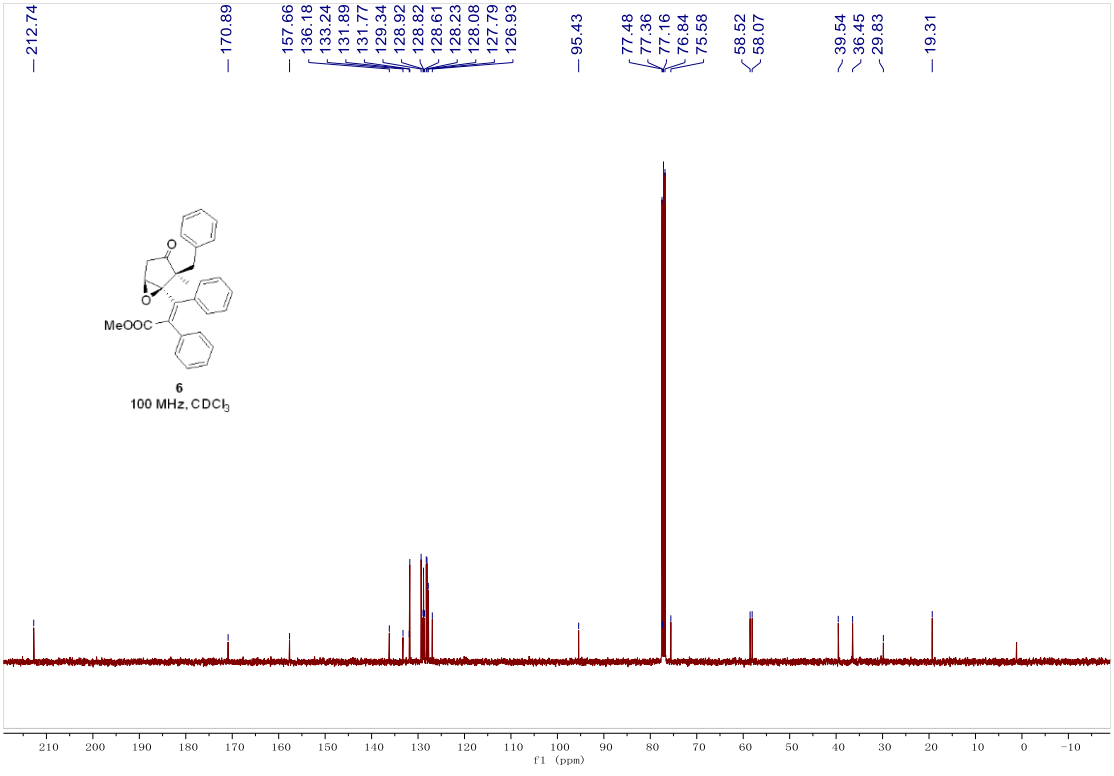

(5R,6S)-3ad
400 MHz, CDCl3

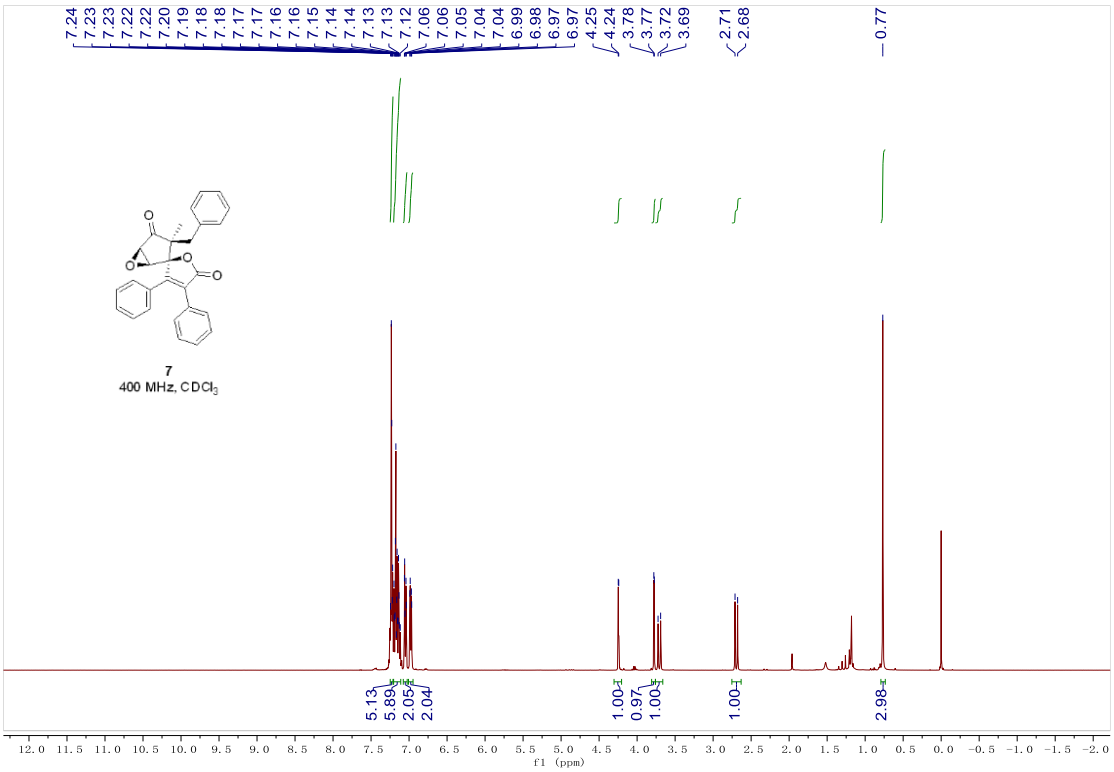

(5R,6S)-3ad
100 MHz, CDCl3

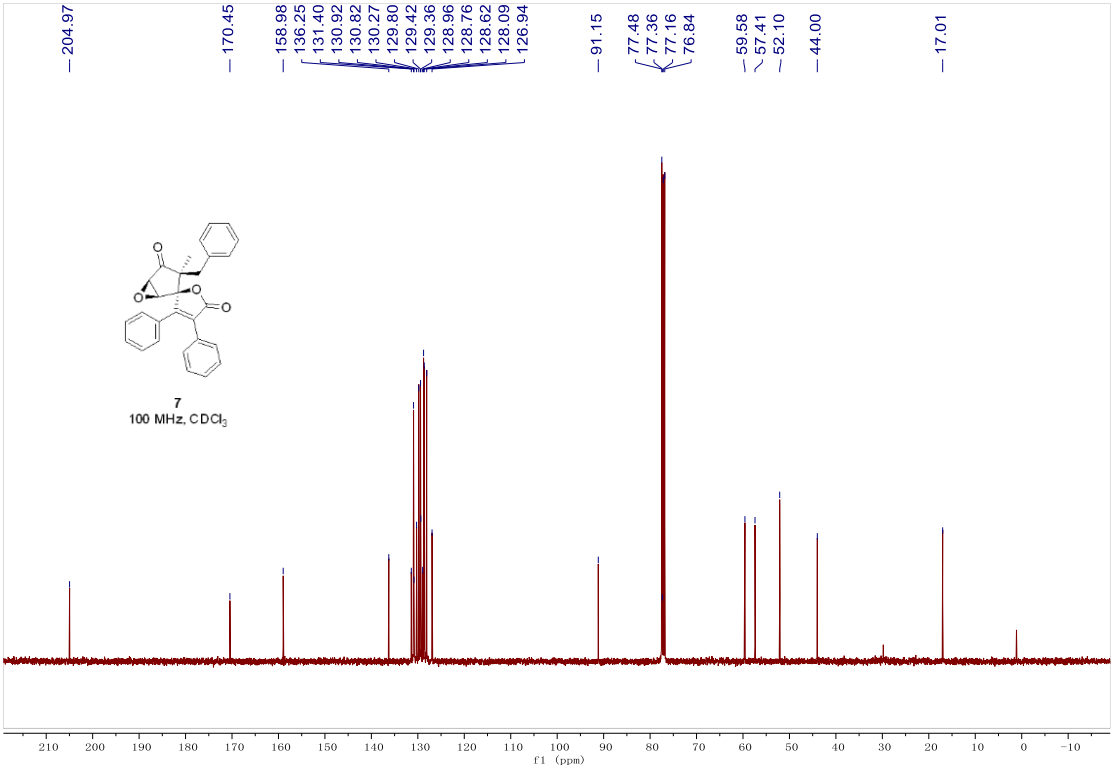

TBSO
O
O
O
5
d.r. 79: 21
400 MHz, CDCl3
f1 (ppm)

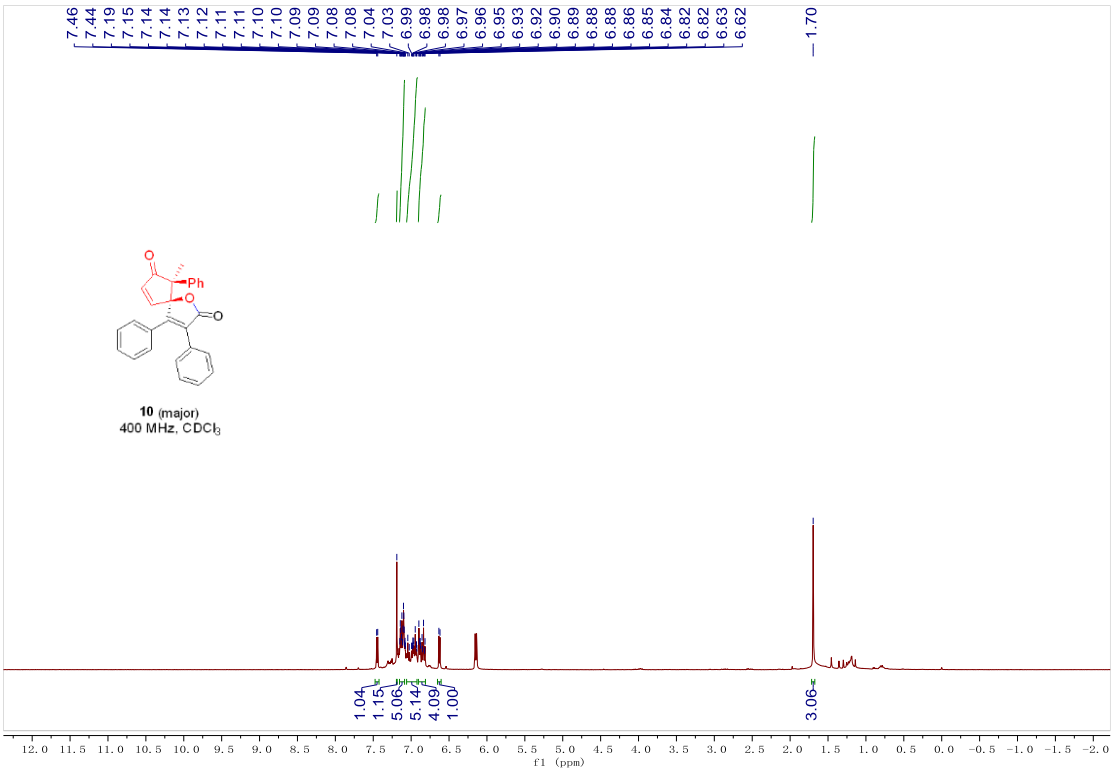

TBSO
O
O
O
5
d.r. 79: 21
100 MHz, CDCl3
f1 (ppm)

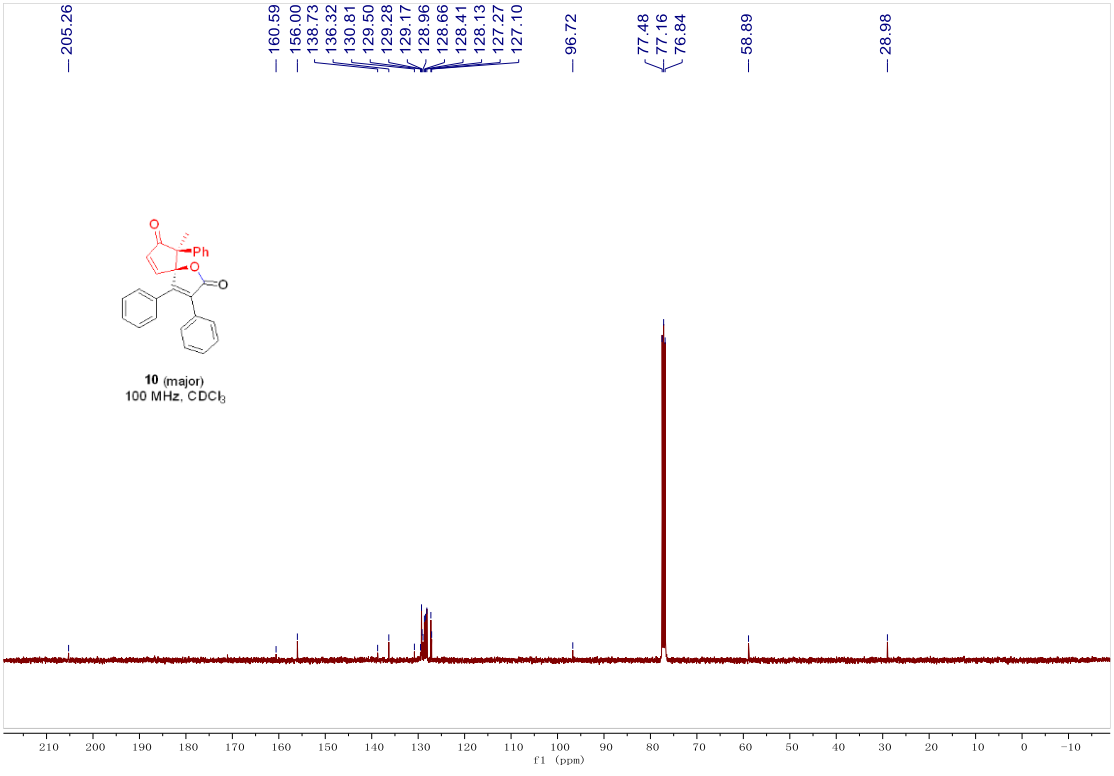

7.17
7.16
7.15
7.15
7.14
7.14
7.13
7.13
7.12
7.10
7.08
7.06
7.05
7.05
7.04
7.04
6.18
6.17
4.69
4.67
4.67
4.65
3.45
3.13
3.10
2.96
2.94
2.91
2.89
2.86
2.75
2.72
2.70
2.68
0.64
MeOOC
6
400 MHz, CDCl3
9.02
4.26
1.81
0.99
3.00
1.03
2.04
1.03
3.00
f1 (ppm)

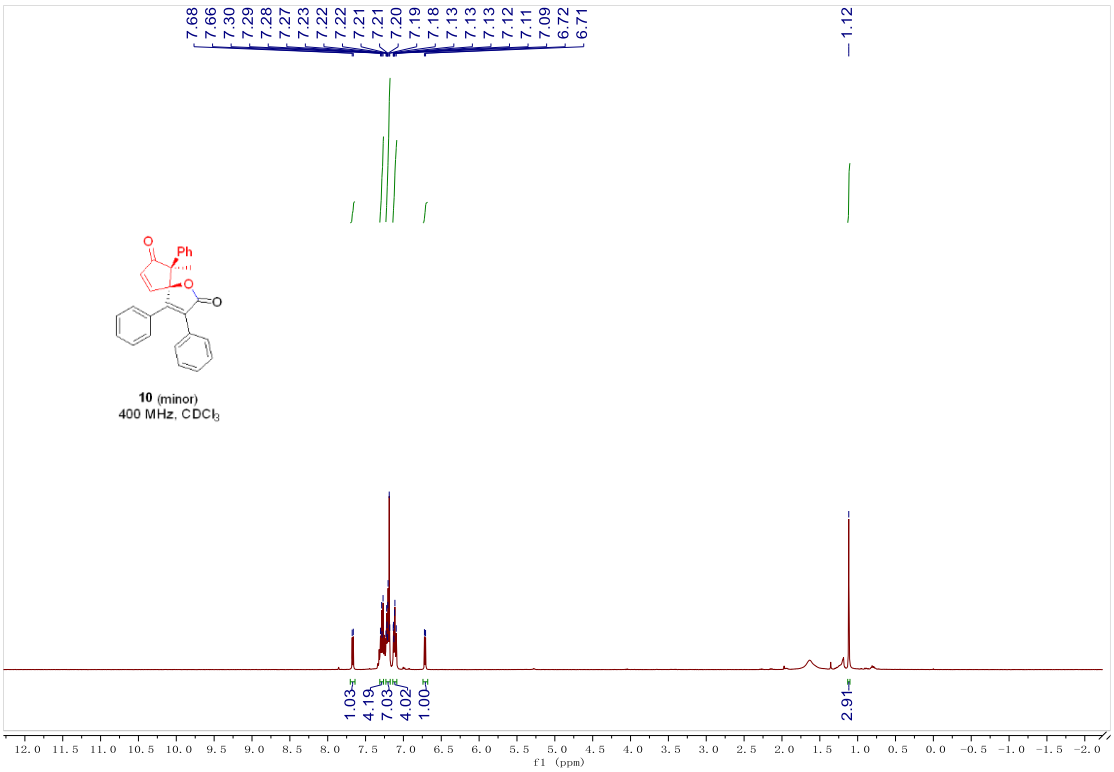

212.74
170.89
157.66
136.18
133.24
131.89
131.77
129.34
128.92
128.82
128.61
128.23
128.08
127.79
126.93
95.43
77.48
77.36
77.16
76.84
75.58
58.52
58.07
39.54
36.45
29.83
19.31
MeOOC
6
100 MHz, CDCl3
f1 (ppm)

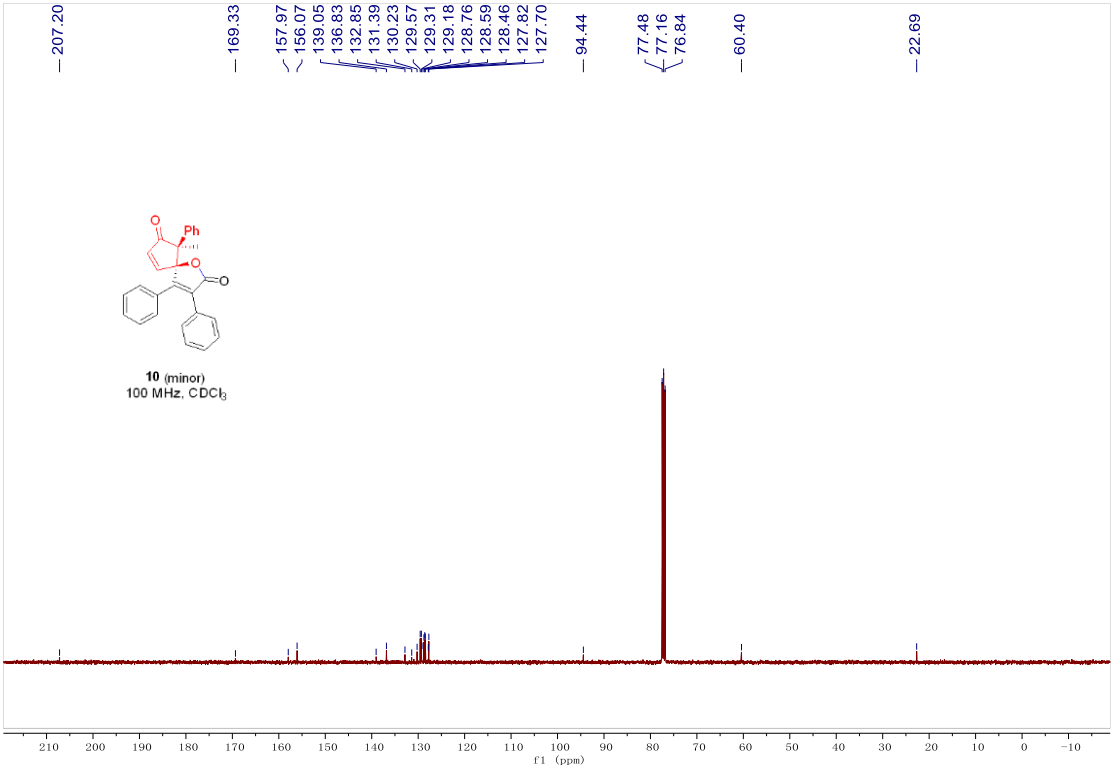

7.24
7.23
7.23
7.22
7.22
7.20
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.15
7.14
7.14
7.13
7.13
7.12
7.06
7.06
7.05
7.04
7.04
6.99
6.98
6.97
6.97
4.25
4.24
3.78
3.77
3.72
3.69
2.71
2.68
0.77
7
400 MHz, CDCl3
5.13
5.89
2.05
2.04
1.00
0.97
1.00
1.00
2.98
f1 (ppm)


204.97
170.45
158.98
136.25
131.40
130.92
130.82
130.27
129.80
129.42
129.36
128.96
128.76
128.62
128.09
126.94
91.15
77.48
77.36
77.16
76.84
59.58
57.41
52.10
44.00
17.01
7
100 MHz, CDCl3
f1 (ppm)

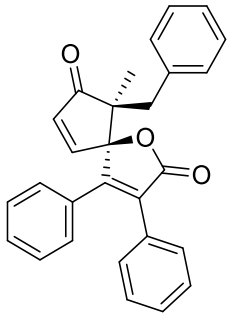

7.46
7.44
7.19
7.15
7.14
7.14
7.13
7.12
7.11
7.11
7.10
7.10
7.09
7.09
7.08
7.08
7.04
7.03
6.99
6.98
6.98
6.97
6.96
6.95
6.93
6.92
6.90
6.89
6.88
6.88
6.86
6.85
6.84
6.82
6.82
6.63
6.62
1.70
Ph
O
O
O
10 (major)
400 MHz, CDCl3
1.04
1.15
5.06
5.14
4.09
1.00
3.06
f1 (ppm)


205.26
160.59
156.00
138.73
136.32
130.81
129.50
129.28
129.17
128.96
128.66
128.41
128.13
127.27
127.10
96.72
77.48
77.16
76.84
58.89
28.98
Ph
O
O
O
10 (major)
100 MHz, CDCl3
f1 (ppm)

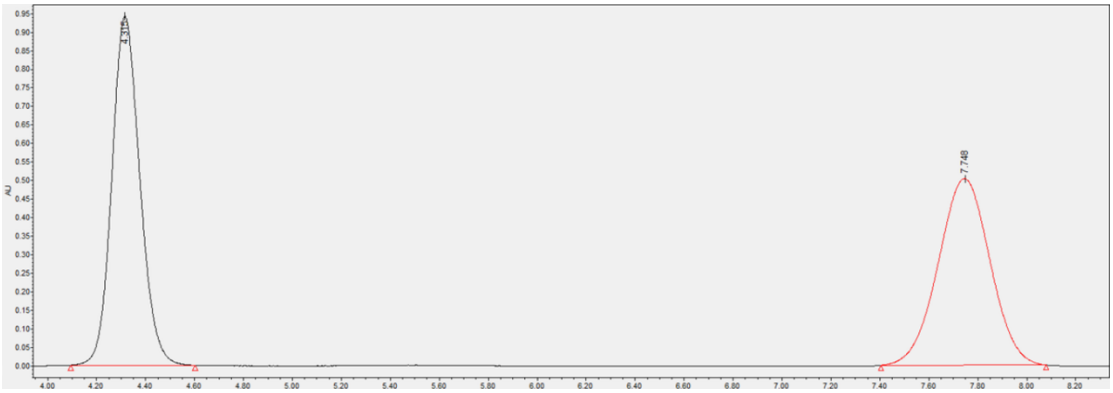

7.68
7.66
7.30
7.29
7.28
7.27
7.23
7.22
7.22
7.21
7.21
7.20
7.19
7.18
7.13
7.13
7.13
7.12
7.11
7.09
6.72
6.71
1.12
Ph
O
O
O
10 (minor)
400 MHz, CDCl3
1.03
4.19
7.03
4.02
1.00
2.91
f1 (ppm)


207.20
169.33
157.97
156.07
139.05
136.83
132.85
131.39
130.23
129.57
129.31
129.18
128.76
128.59
128.46
127.82
127.70
94.44
77.48
77.16
76.84
60.40
22.69
Ph
O
O
O
10 (minor)
100 MHz, CDCl3
f1 (ppm)

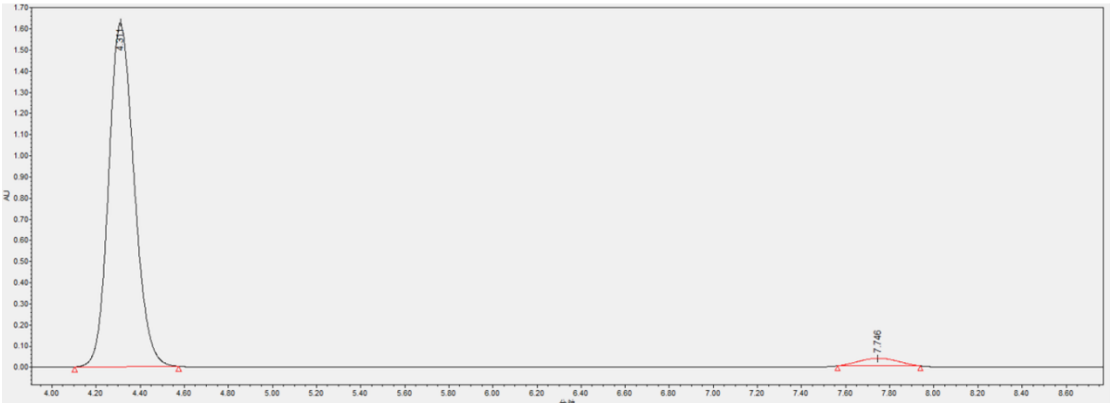
9. HPLC and UPLC Spectra



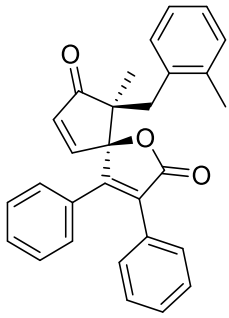
(5*R*,6*S*)-**3a**



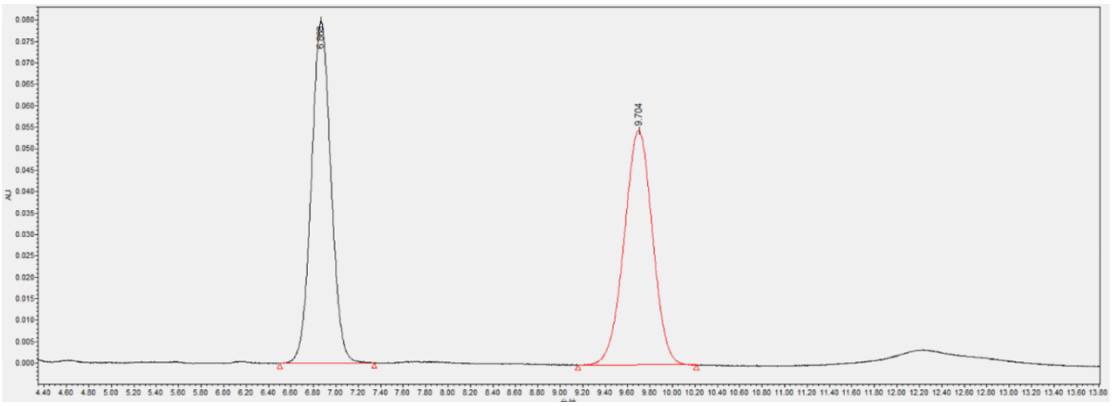
	Time/min	Area	Height	Area%
1	4.315	7477624	940299	50.34
2	7.748	7375894	502389	49.66



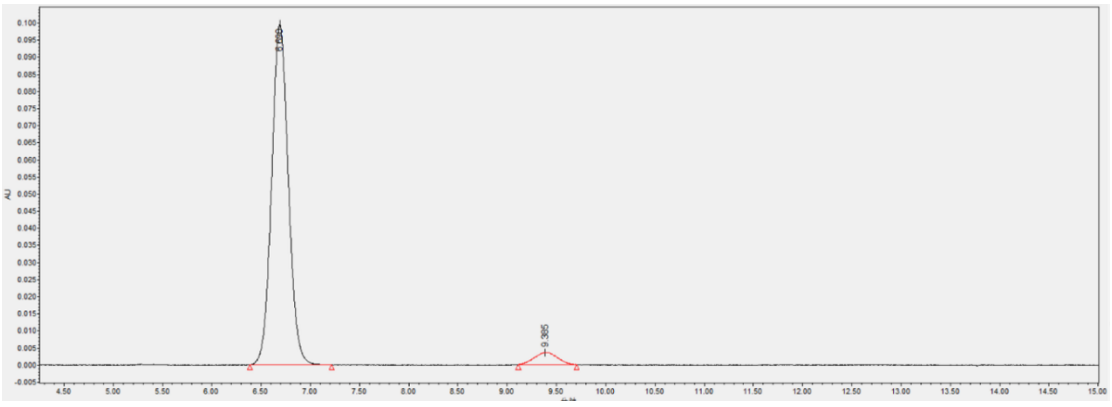
	Time/min	Area	Height	Area%
1	4.311	13077387	1626997	96.76
2	7.746	437501	35985	3.24



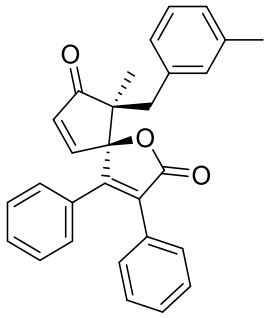
(5*R*,6*S*)-**3b**



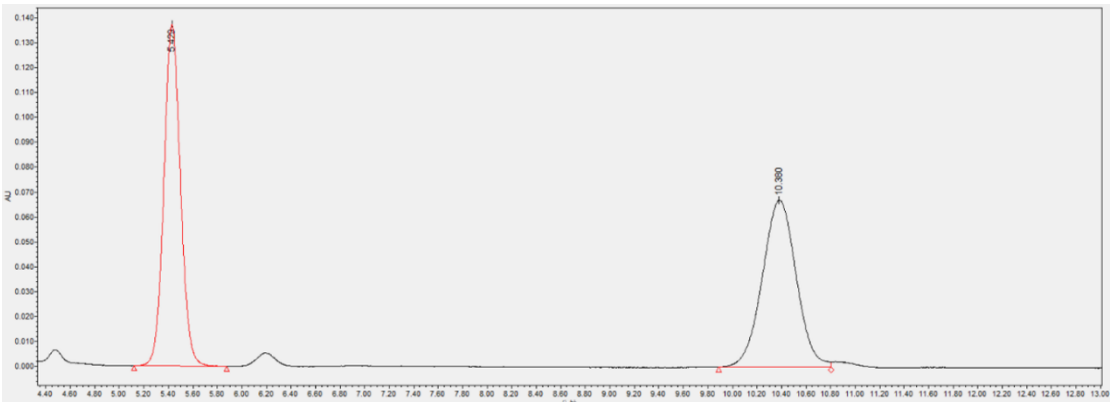
	Time/min	Area	Height	Area%
1	6.868	967677	79832	50.16
2	9.704	961531	54671	49.84



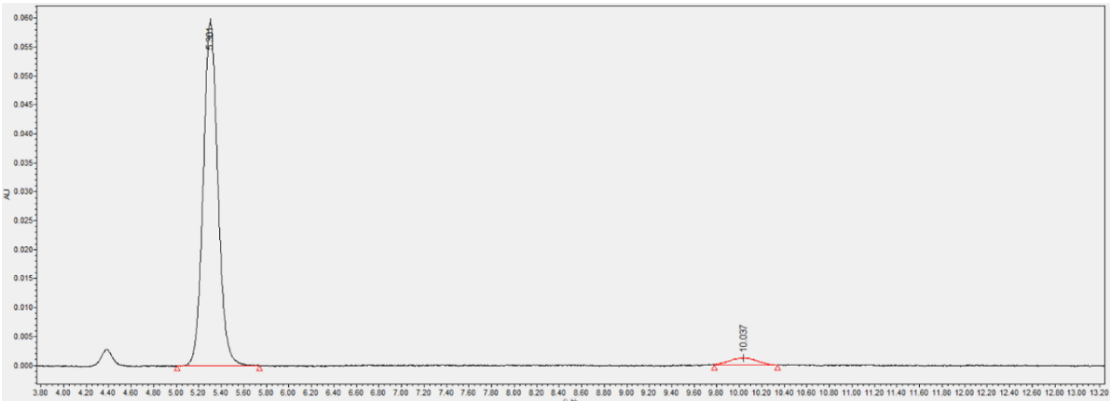
	Time/min	Area	Height	Area%
1	6.690	1173477	99556	95.42
2	9.385	56286	3539	4.58



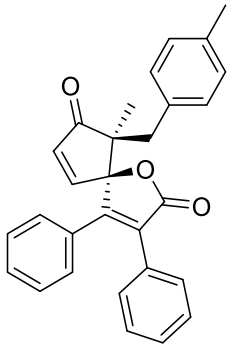
(5*R*,6*S*)-**3c**



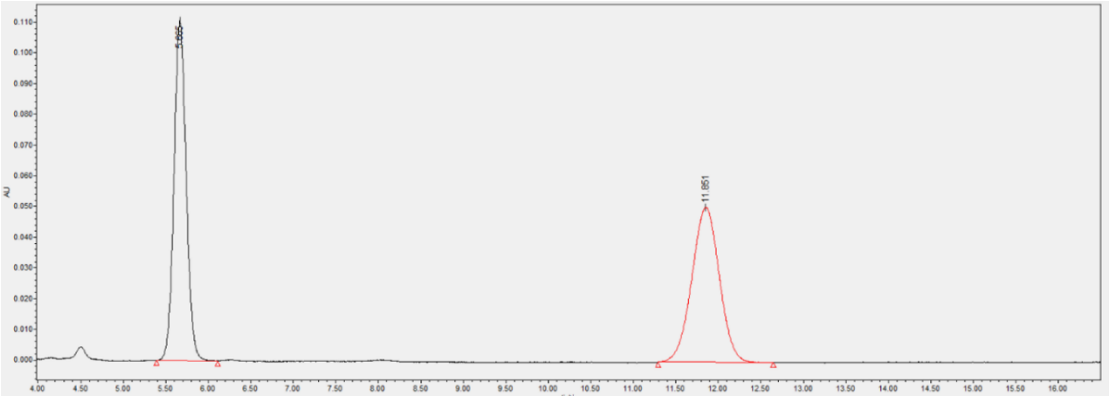
	Time/min	Area	Height	Area%
1	5.429	1288569	137190	50.00
2	10.380	1288477	67064	50.00



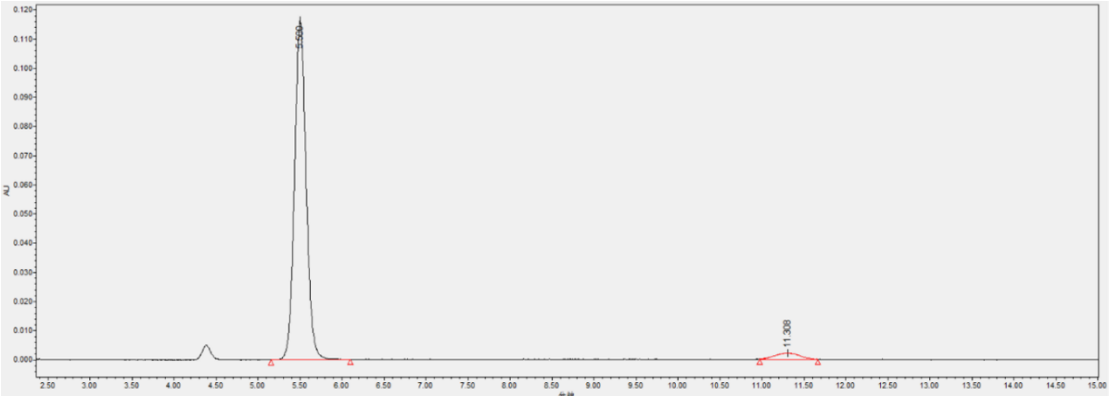
	Time/min	Area	Height	Area%
1	5.301	539364	59331	96.34
2	10.037	20475	1265	3.66



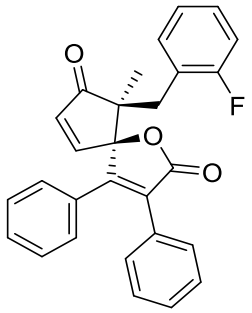
(5*R*,6*S*)-**3d**



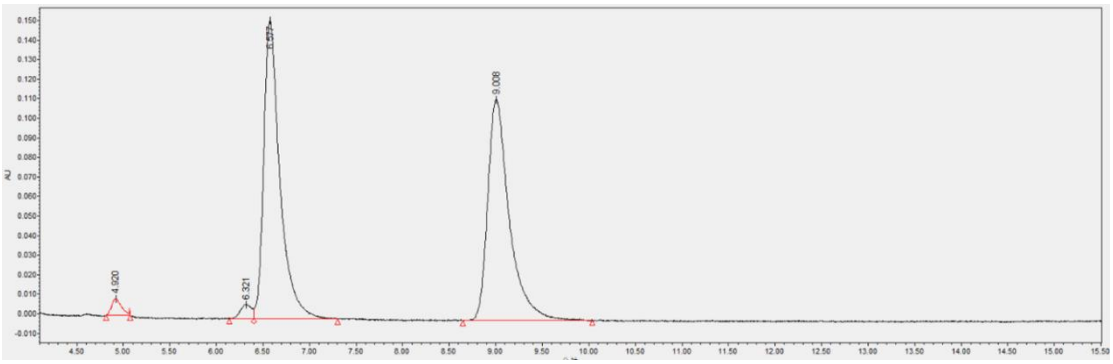
	Time/min	Area	Height	Area%
1	5.665	1102053	110646	49.21
2	11.851	1137628	50418	50.79



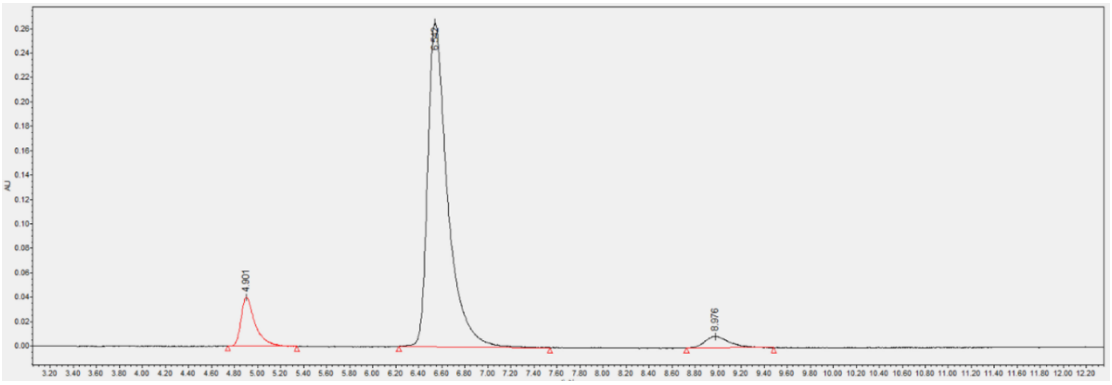
	Time/min	Area	Height	Area%
1	5.500	1115086	116239	96.43
2	11.308	41241	2164	3.57



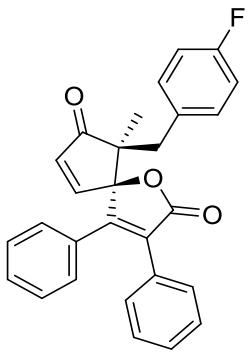
(5*R*,6*S*)-**3e**



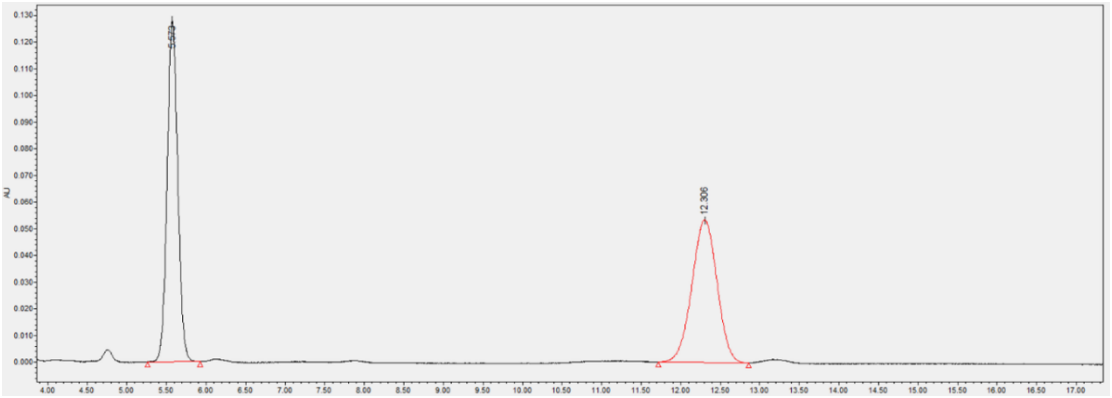
	Time/min	Area	Height	Area%
1	4.920	63728	8578	1.68
2	6.321	62660	7397	1.65
3	6.577	1846742	152547	48.69
4	9.008	1819604	113194	47.98



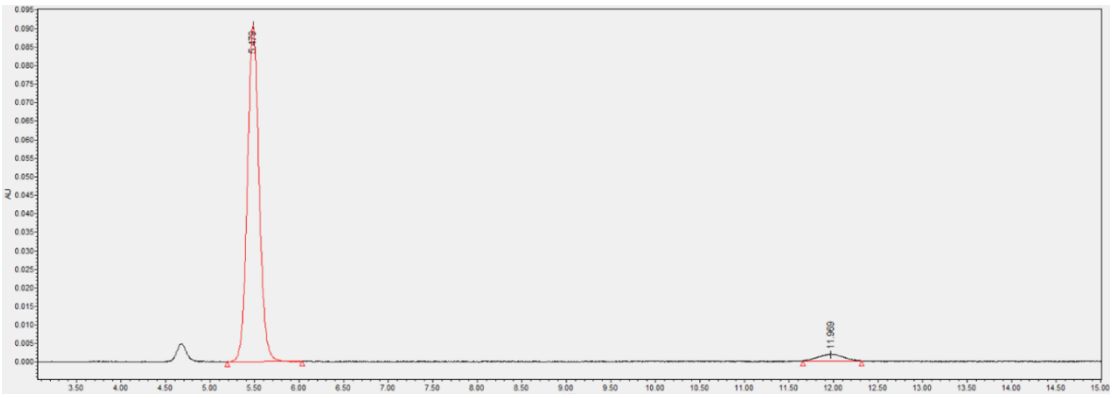
	Time/min	Area	Height	Area%
1	4.901	336030	40138	9.19
2	6.542	3181259	265428	86.98
3	8.976	139966	9546	3.83



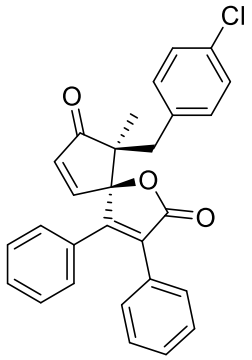
(5*R*,6*S*)-**3f**



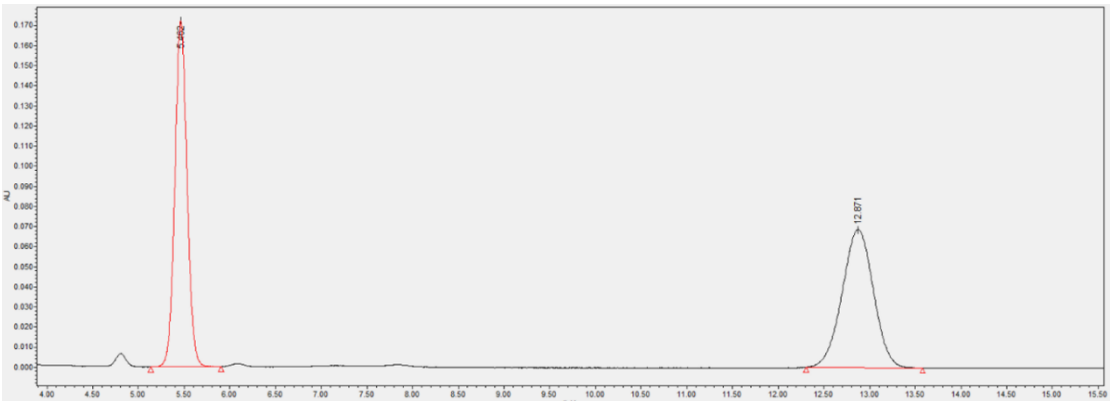
	Time/min	Area	Height	Area%
1	5.573	1192700	127985	50.32
2	12.306	1177380	53418	49.68



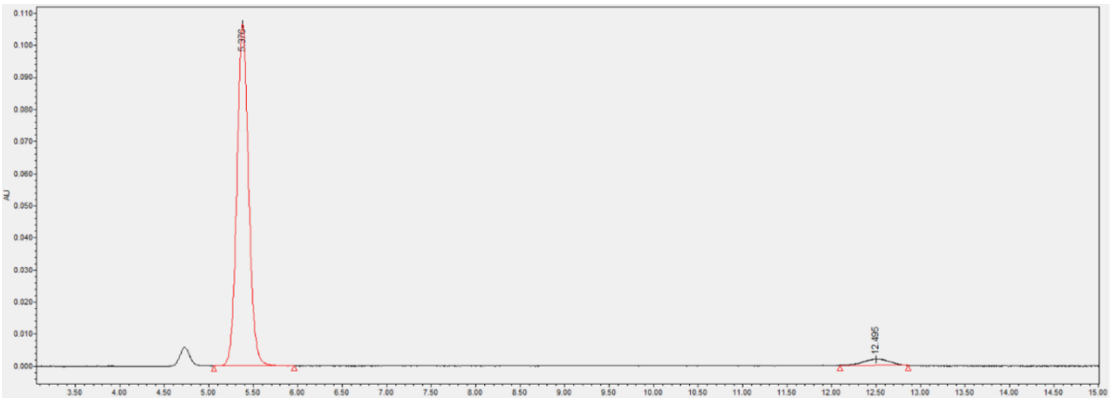
	Time/min	Area	Height	Area%
1	5.479	831456	90556	95.99
2	11.969	34713	1823	4.01



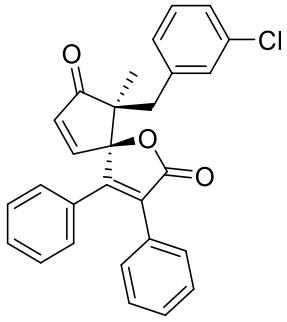
(5*R*,6*S*)-**3g**



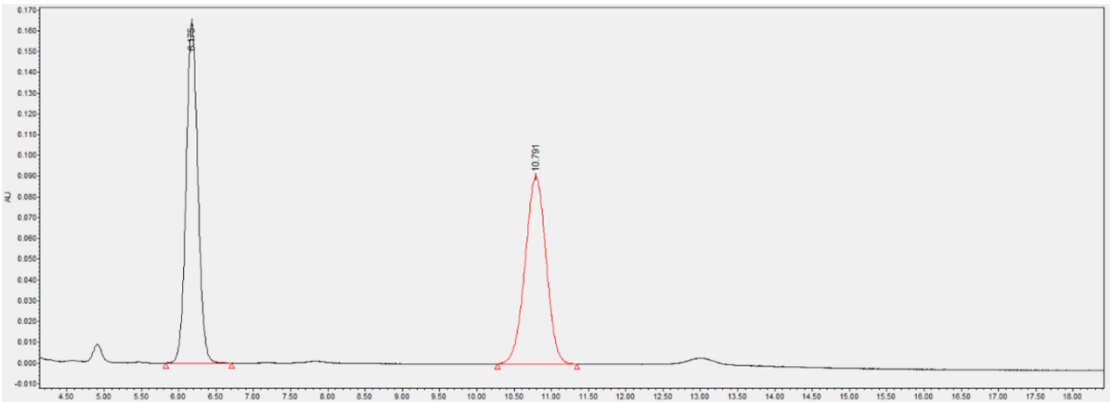
	Time/min	Area	Height	Area%
1	5.462	1594435	172094	49.33
2	12.871	1637541	68738	50.67



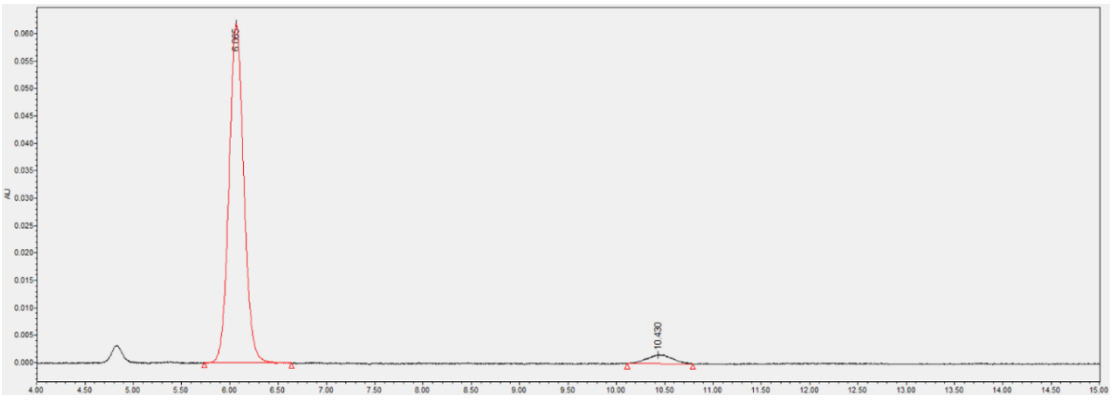
	Time/min	Area	Height	Area%
1	5.376	973930	106471	96.07
2	12.495	39849	1929	3.93



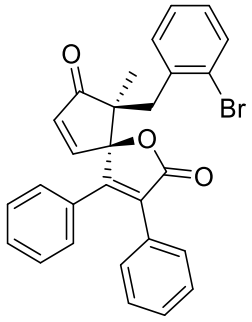
(5*R*,6*S*)-**3h**



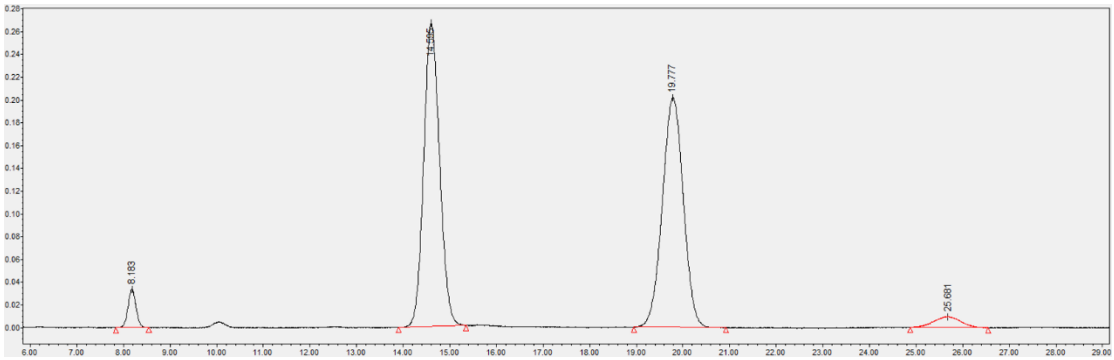
	Time/min	Area	Height	Area%
1	6.175	1794787	163876	50.39
2	10.791	1767333	90228	49.61



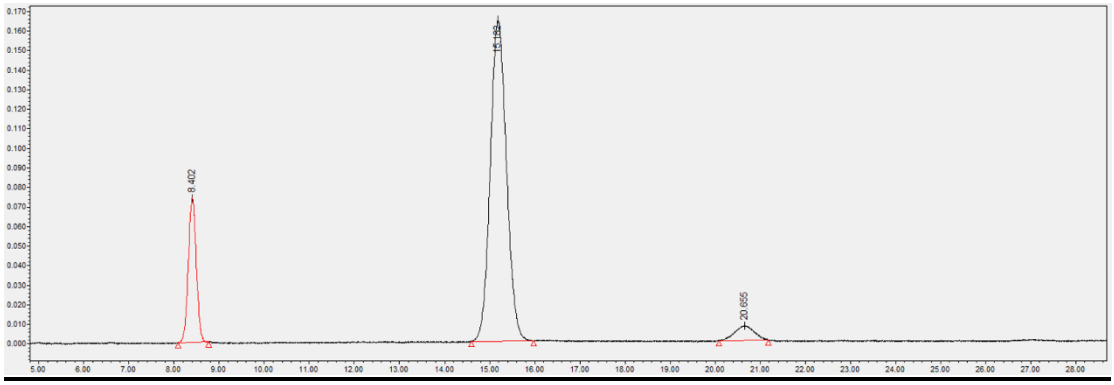
	Time/min	Area	Height	Area%
1	6.065	657249	61817	95.58
2	10.430	30388	1668	4.42



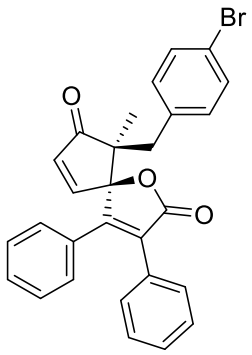
(5*R*,6*S*)-**3i**



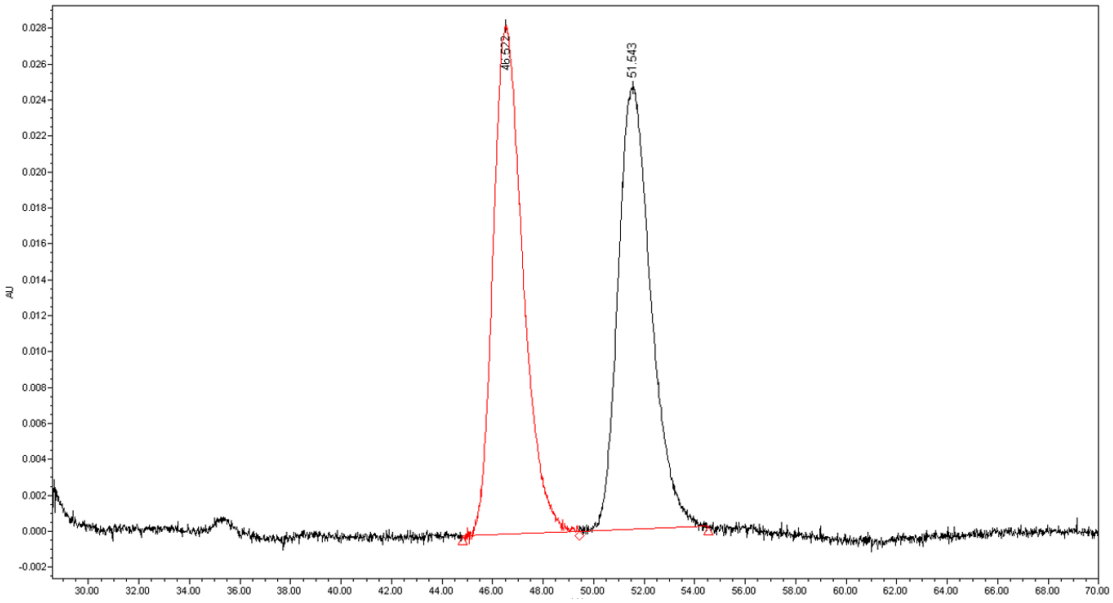
	Time/min	Area	Height	Area%
1	8.183	399387	33650	2.98
2	14.595	6321350	266256	47.15
3	19.777	6305360	201750	47.03
4	25.681	381159	9682	2.84



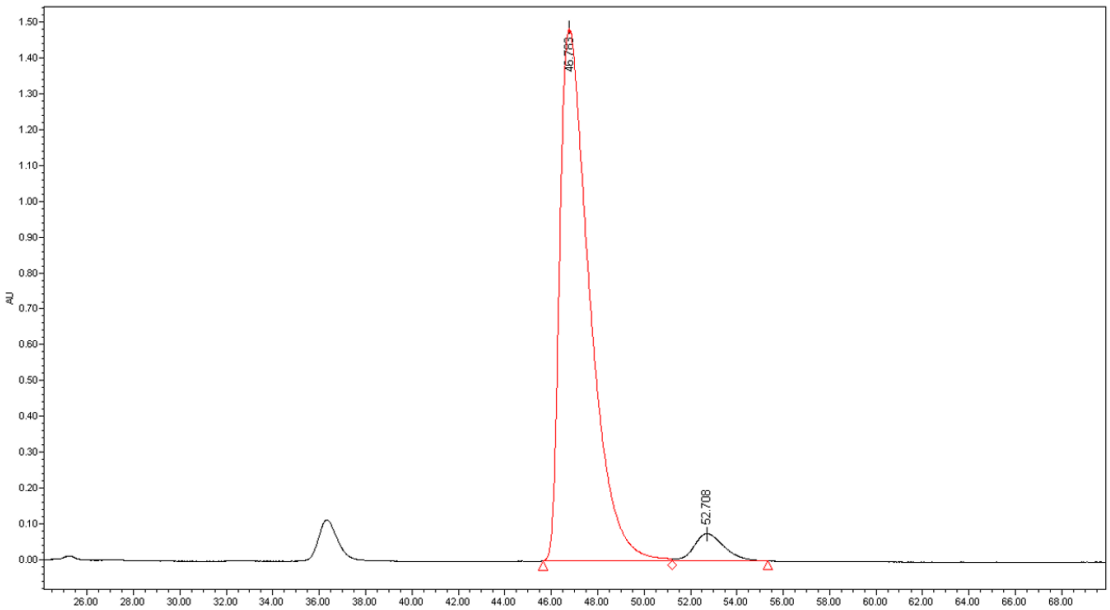
	Time/min	Area	Height	Area%
1	8.402	903437	74001	17.28
2	15.182	4102429	164157	78.46
3	20.655	222782	7661	4.26



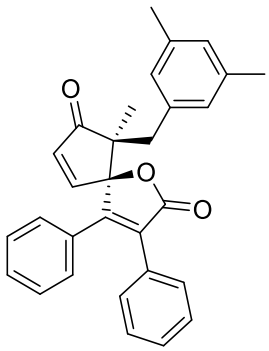
(5*R*,6*S*)-**3j**



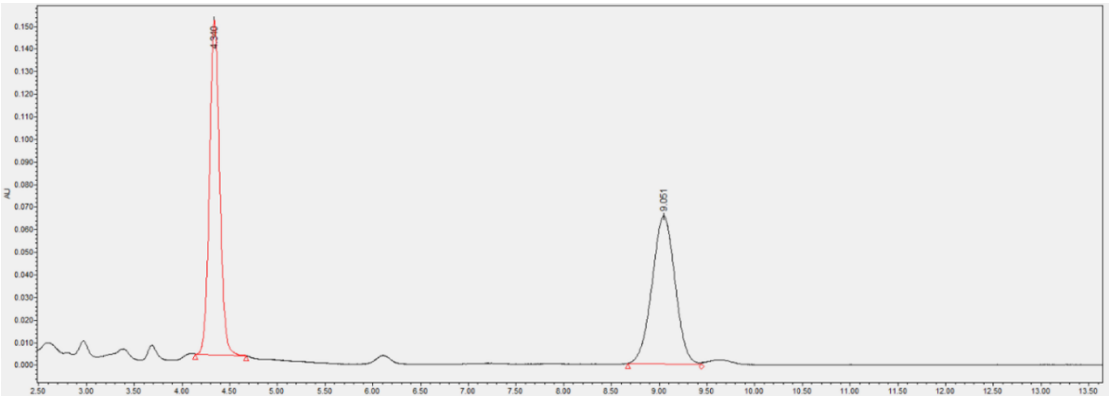
	Time/min	Area	Height	Area%
1	46.522	2316779	28290	50.89
2	51.543	2235929	24552	49.11



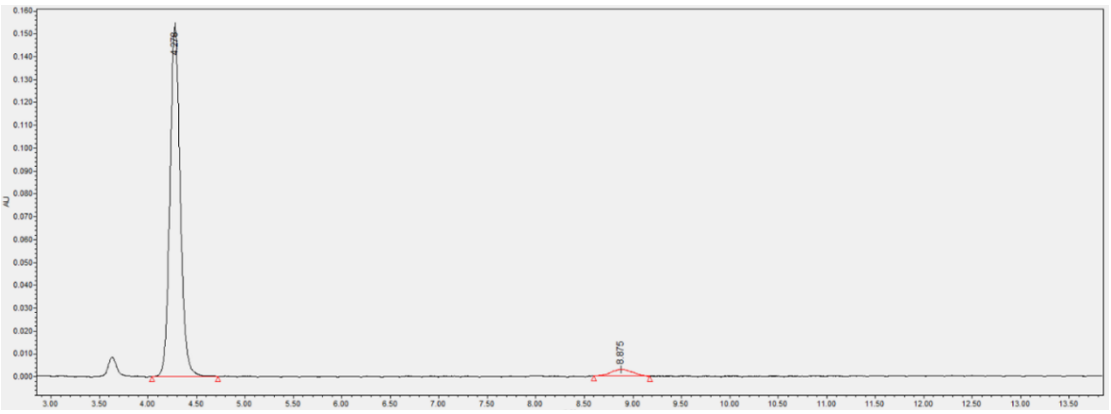
	Time/min	Area	Height	Area%
1	46.783	132055837	1483753	95.03
2	52.708	6906235	75825	4.97



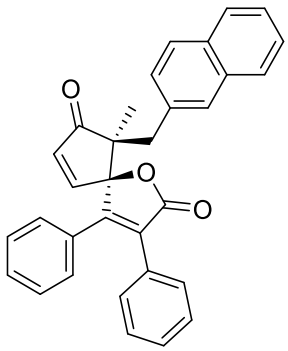
(5*R*,6*S*)-**3k**



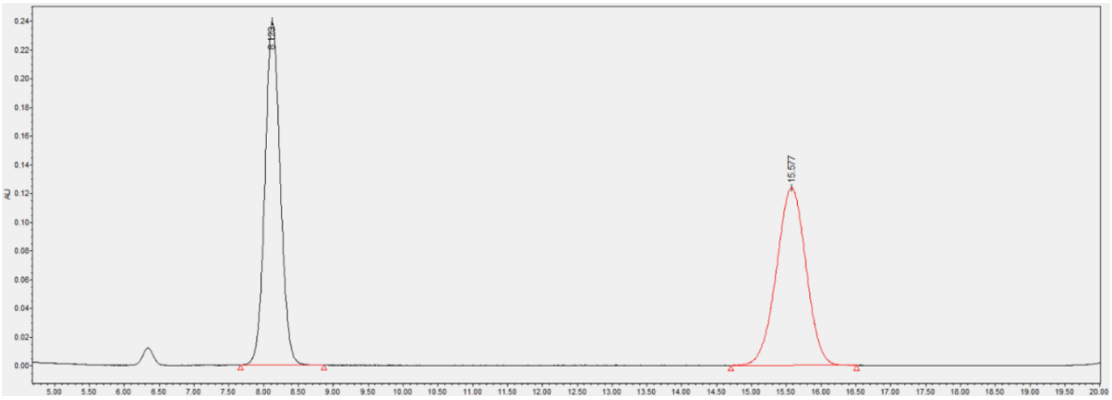
	Time/min	Area	Height	Area%
1	4.340	1094700	147891	50.08
2	9.051	1091386	65348	49.92



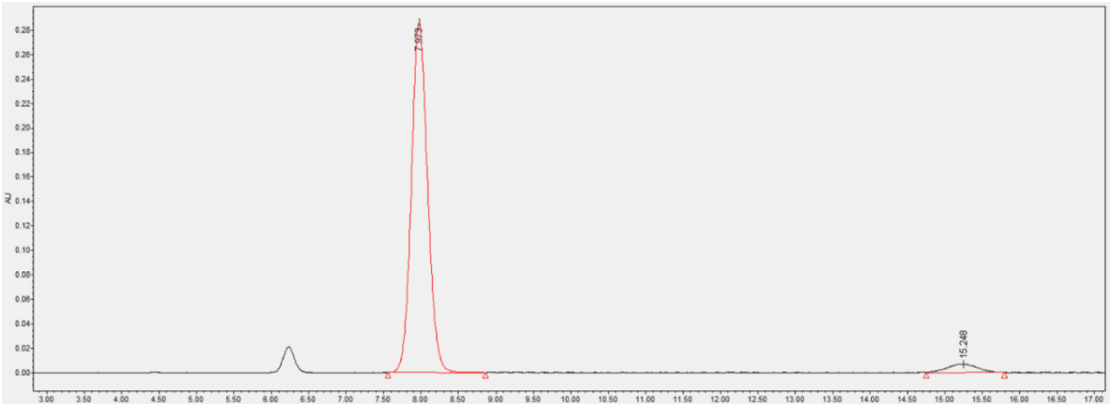
	Time/min	Area	Height	Area%
1	4.278	1134378	153021	96.19
2	8.875	44988	2973	3.81



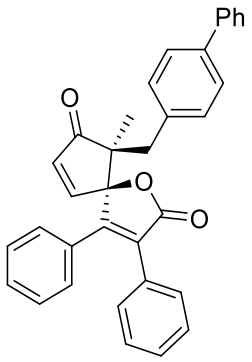
(5*R*,6*S*)-**3l**



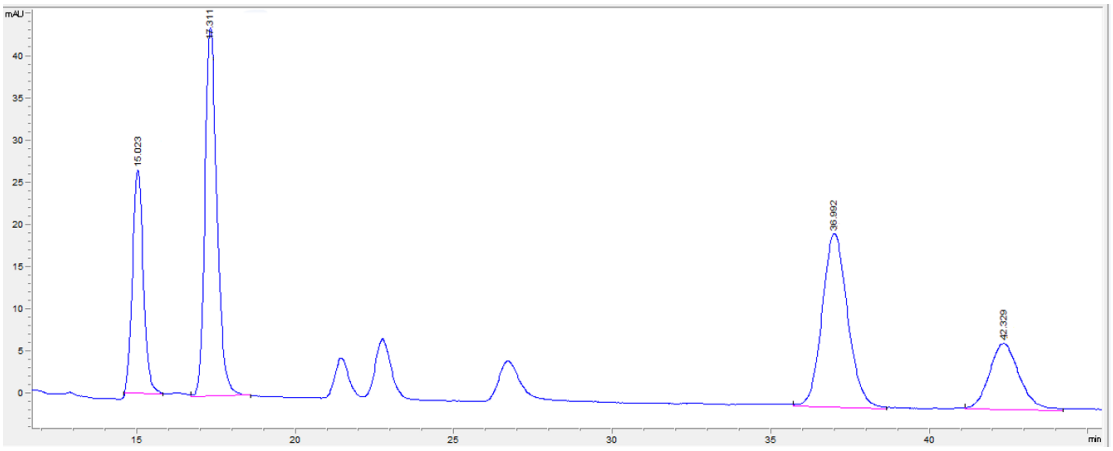
	Time/min	Area	Height	Area%
1	8.123	3666392	239161	50.05
2	15.577	3658953	123755	49.95



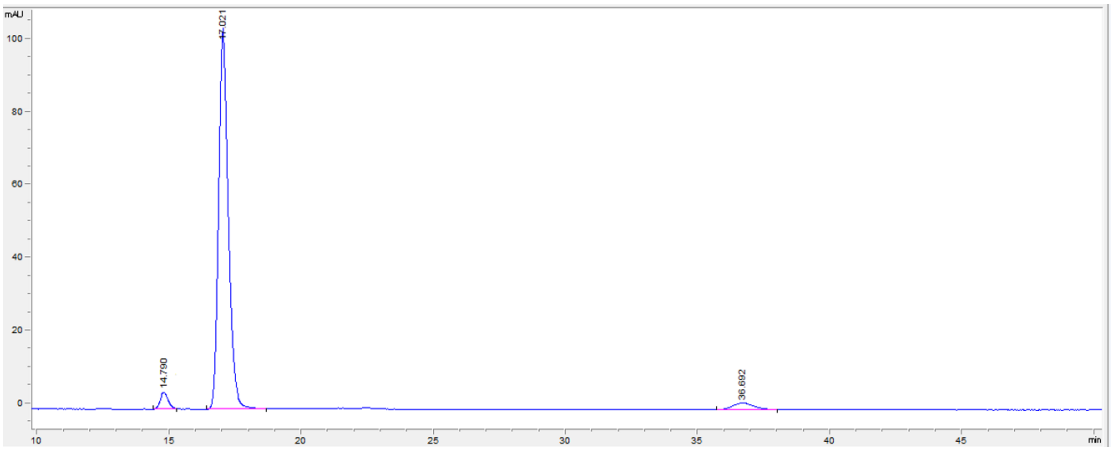
	Time/min	Area	Height	Area%
1	7.973	4310878	285820	95.67
2	15.248	194985	7026	4.33



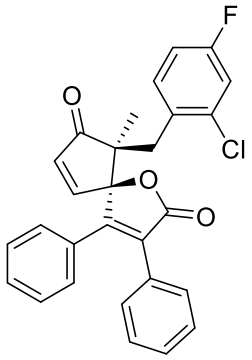
(5*R*,6*S*)-**3m**



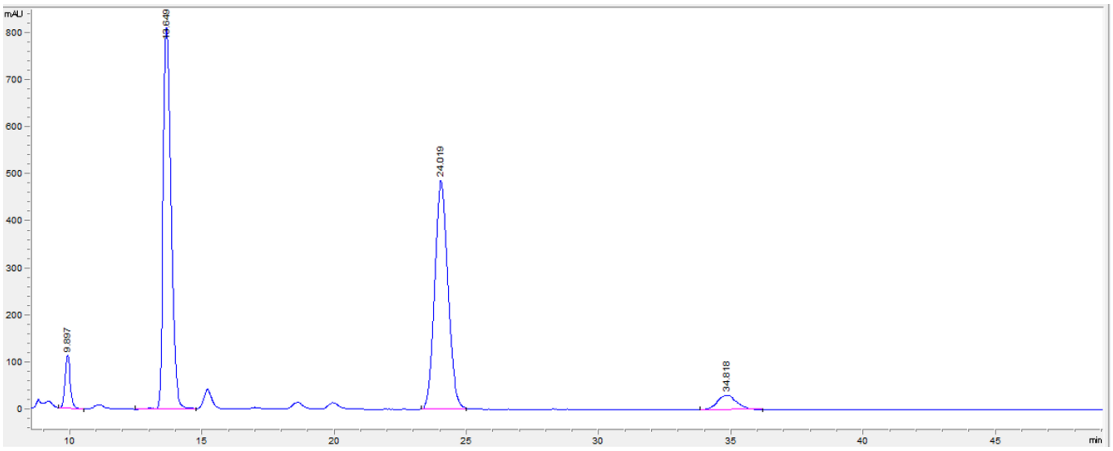
	Time/min	Area	Height	Area%
1	15.023	629.8	26.4	18.108
2	17.311	1158.8	43.7	33.318
3	36.992	1167.5	20.6	33.567
4	42.329	522	7.9	15.008



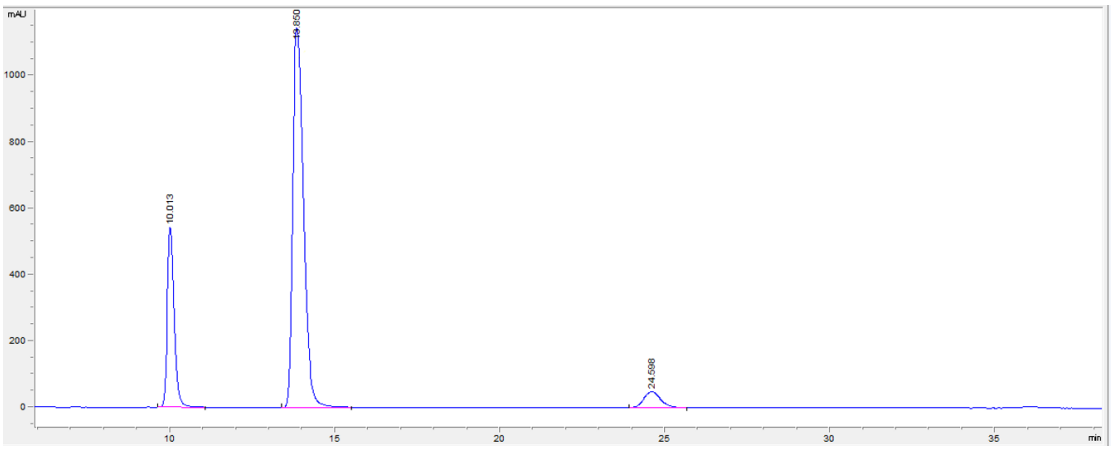
	Time/min	Area	Height	Area%
1	14.79	91	4.5	3.135
2	17.021	2714.8	104.4	93.503
3	36.692	97.6	1.8	3.362



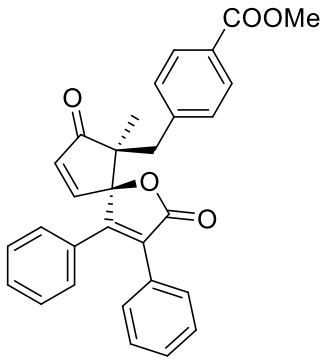
(5*R*,6*S*)-**3n**



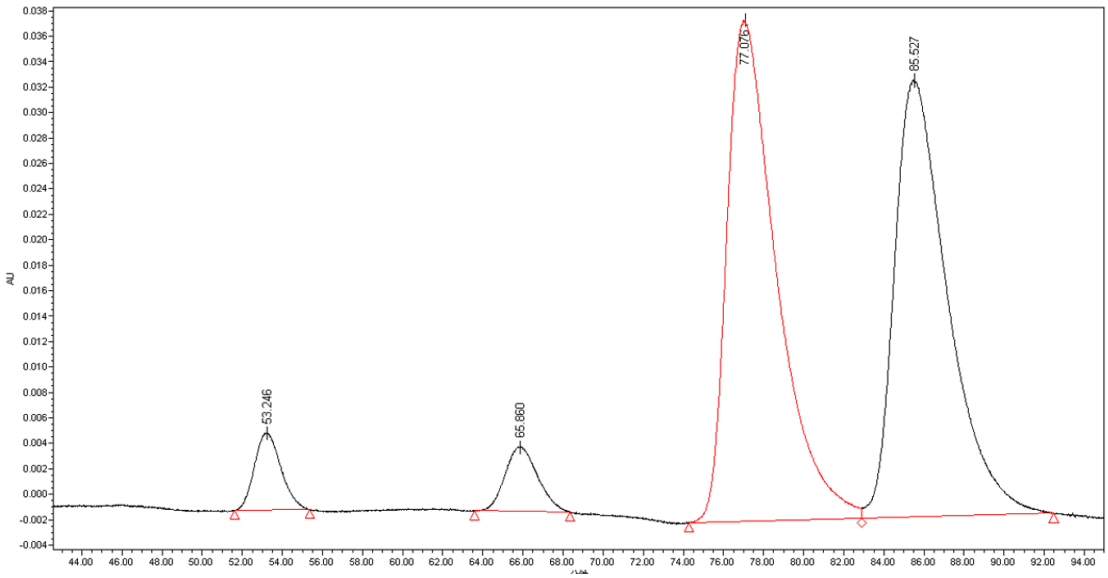
	Time/min	Area	Height	Area%
1	9.897	1614.6	112.9	4.374
2	13.649	16765.4	810.4	45.416
3	24.019	16968.8	486.3	45.967
4	34.818	1566.4	30.5	4.243



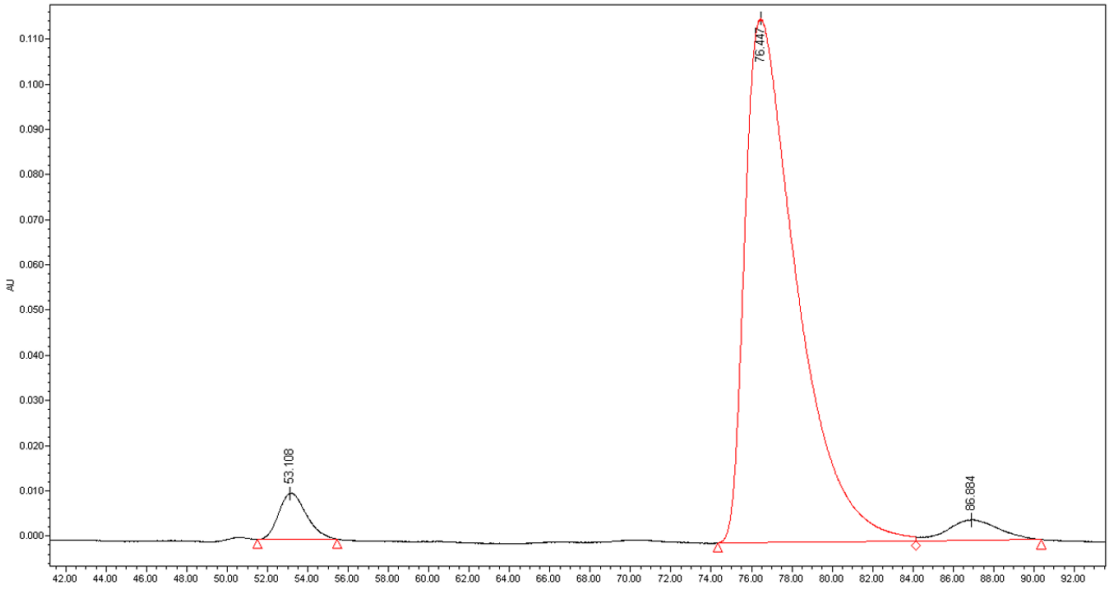
	Time/min	Area	Height	Area%
1	10.013	7945.4	542.2	21.974
2	13.85	26465.4	1144.6	73.194
3	24.598	1747.2	48	4.832



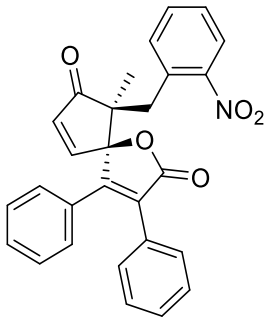
(5*R*,6*S*)-**3o**



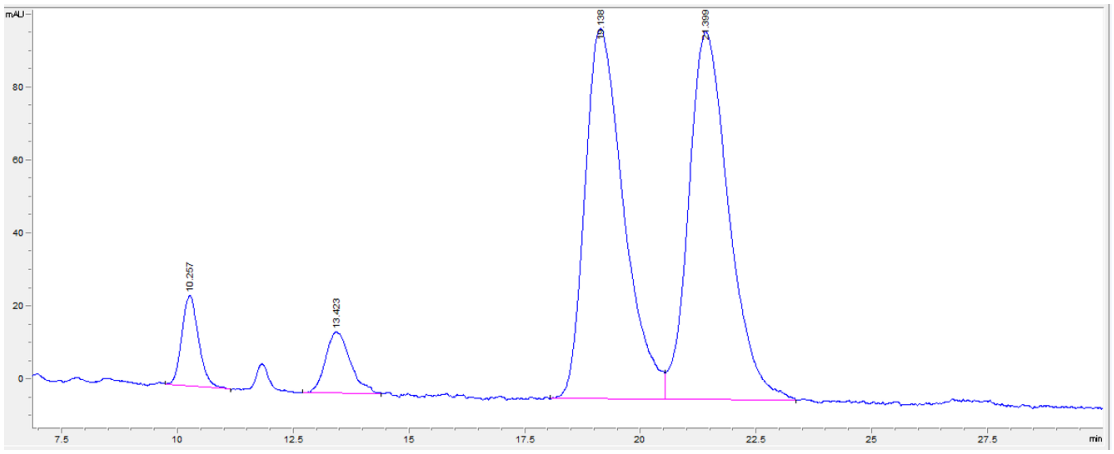
	Time/min	Area	Height	Area%
1	53.246	557176	6050	3.92
2	65.860	566503	5056	3.98
3	77.076	6773191	39390	47.61
4	85.527	6330437	34358	44.49



	Time/min	Area	Height	Area%
1	53.108	967280	10217	4.30
2	76.447	20725762	115986	92.09
3	89.884	812283	4571	3.61

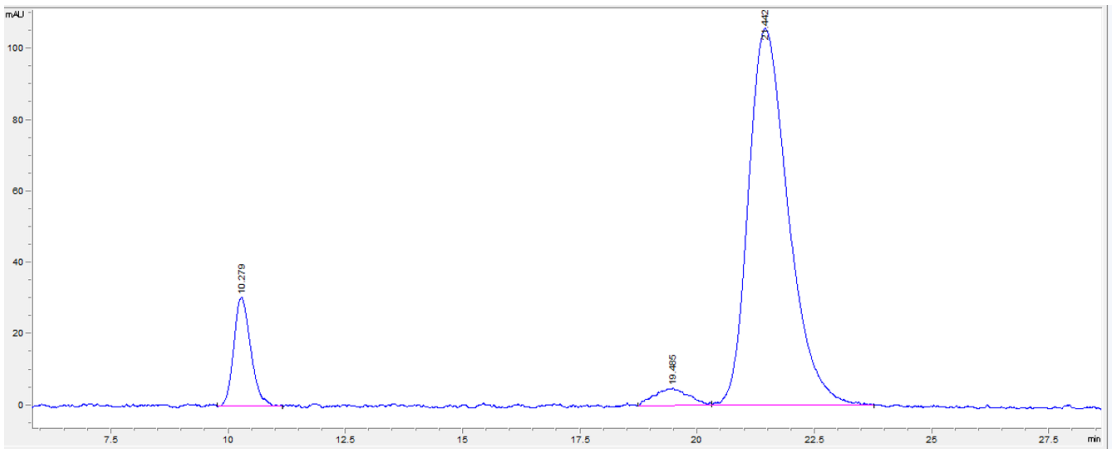


(5*R*,6*S*)-**3p**

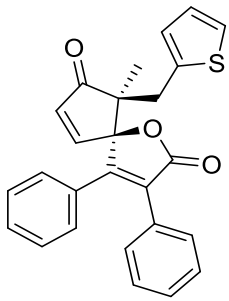


	Time/min	Area	Height	Area%
1	10.257	633.5	24.8	4.770
2	13.423	631.1	16.8	4.753
3	19.138	5929.6	101.7	44.652

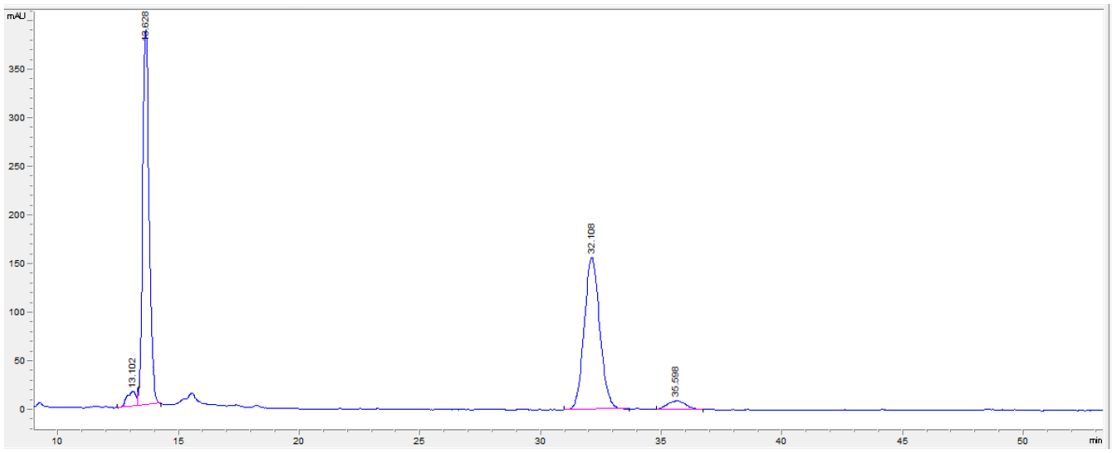
4	21.399	6085.4	101.1	45.825



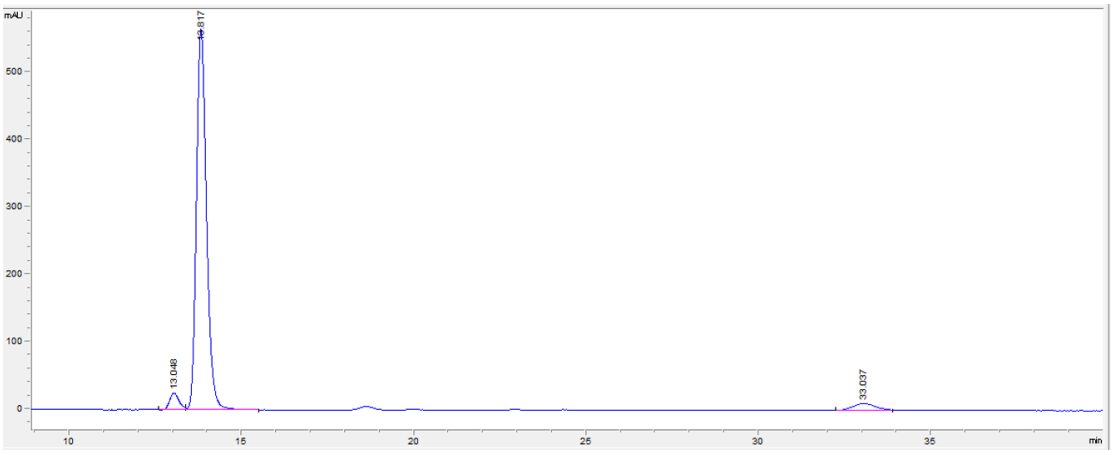
	Time/min	Area	Height	Area%
1	10.279	777.2	30.5	10.650
2	19.485	256.7	4.9	3.517
3	21.442	6264	105.7	85.833



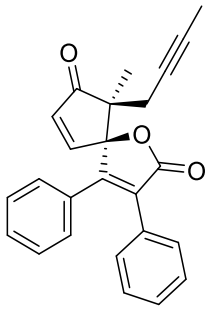
(5*R*,6*S*)-**3q**



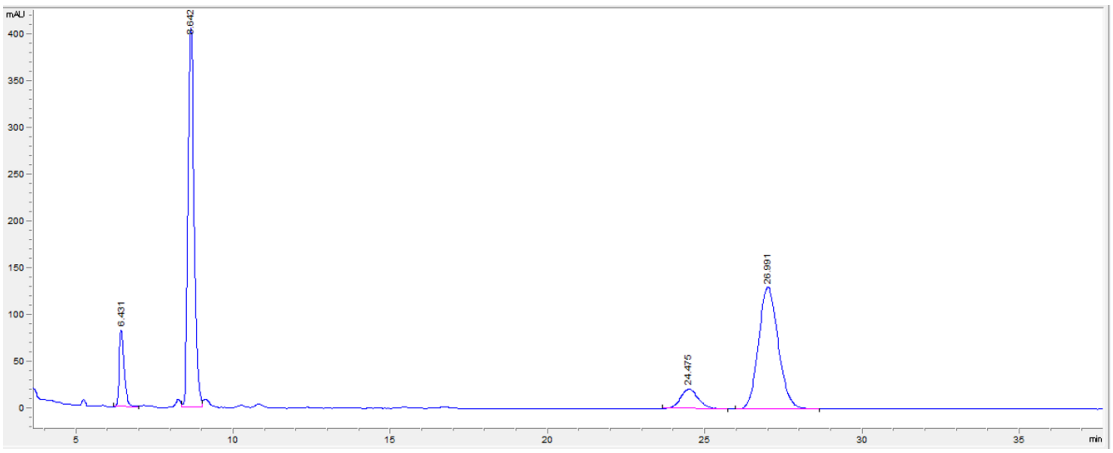
	Time/min	Area	Height	Area%
1	13.102	433.6	15.3	2.860
2	13.628	7221	385.7	47.624
3	32.108	7033.8	156.3	46.389
4	35.598	474.2	9.1	3.128



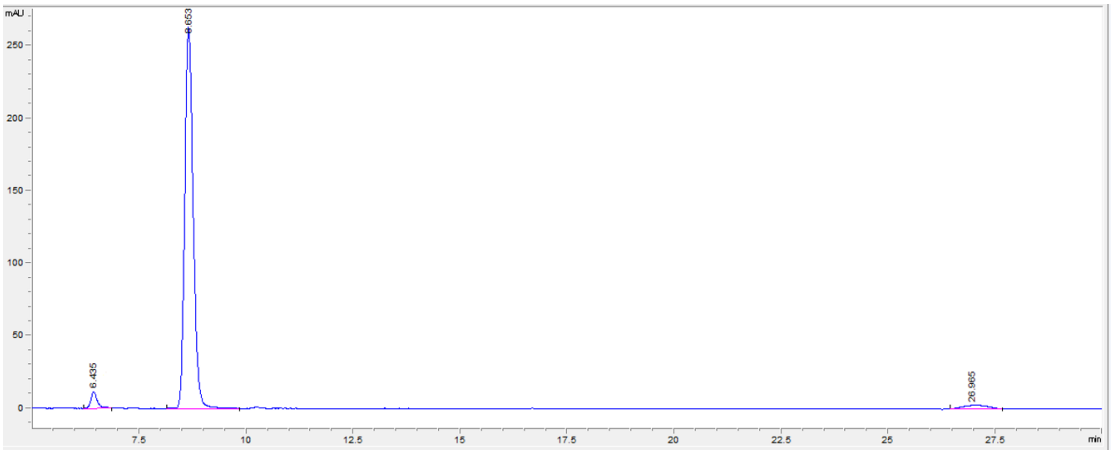
	Time/min	Area	Height	Area%
1	13.048	465.9	24.7	3.813
2	13.817	11278.1	564.7	92.297
3	33.037	475.4	10.4	3.891



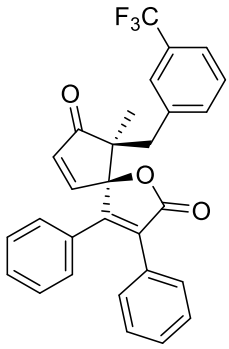
(5*R*,6*S*)-**3r**



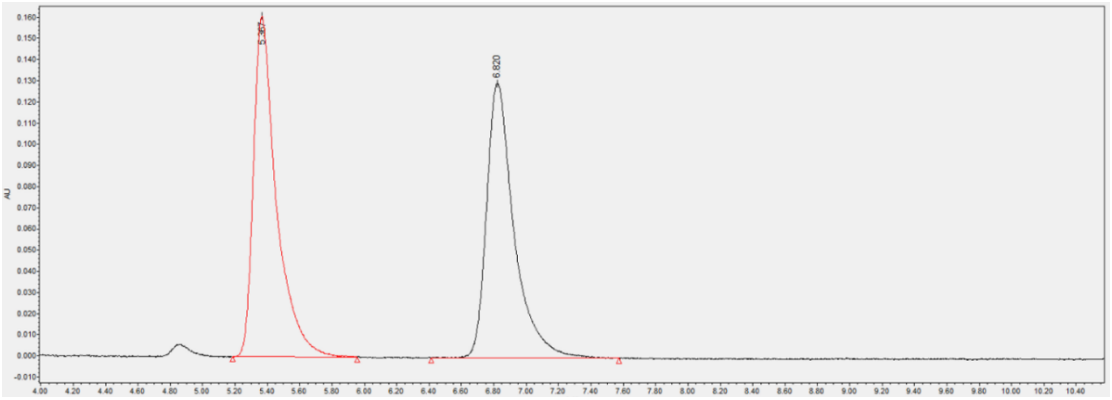
	Time/min	Area	Height	Area%
1	6.431	918.2	82.3	7.109
2	8.642	5539.7	404.5	42.894
3	24.475	810.6	20.9	6.277
4	26.991	5646.3	129.7	43.719



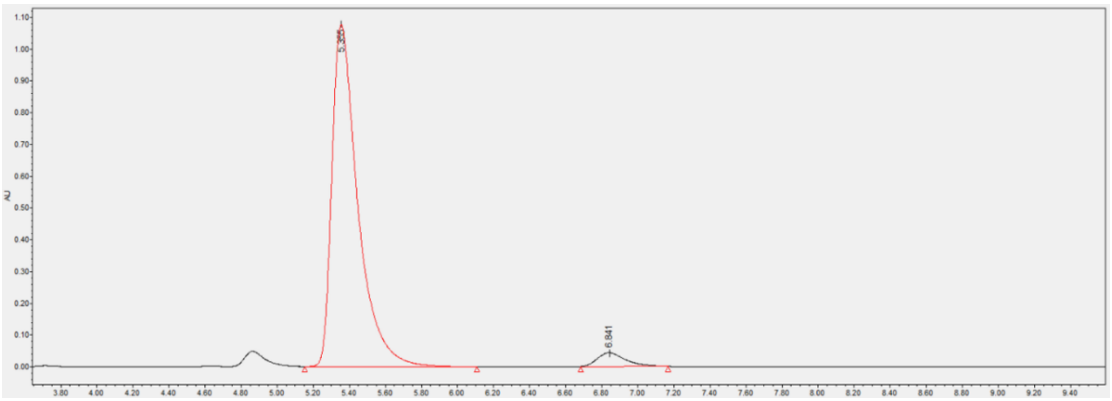
	Time/min	Area	Height	Area%
1	6.435	131.1	11.7	3.388
2	8.653	3635.4	263.6	93.907
3	26.965	104.7	2.6	2.706



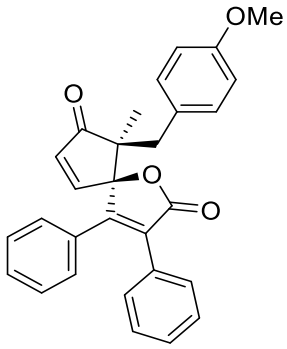
(5*R*,6*S*)-**3s**



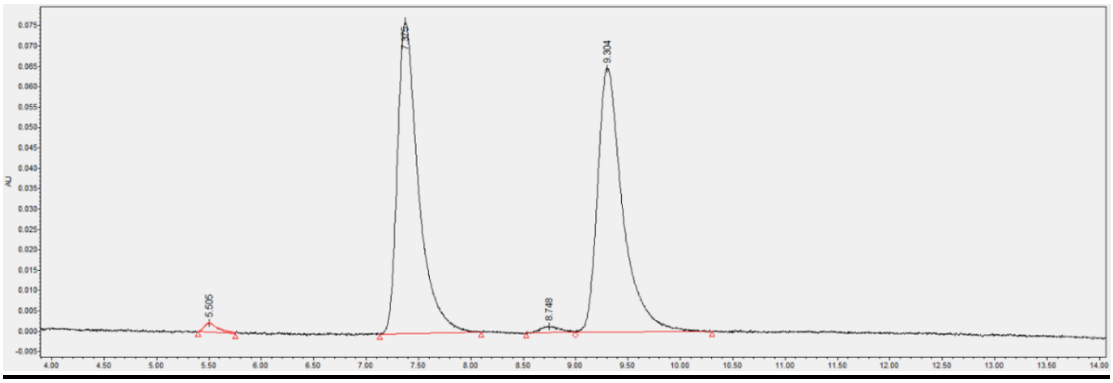
	Time/min	Area	Height	Area%
1	5.367	1581573	160745	50.72
2	6.820	1536391	129878	49.28



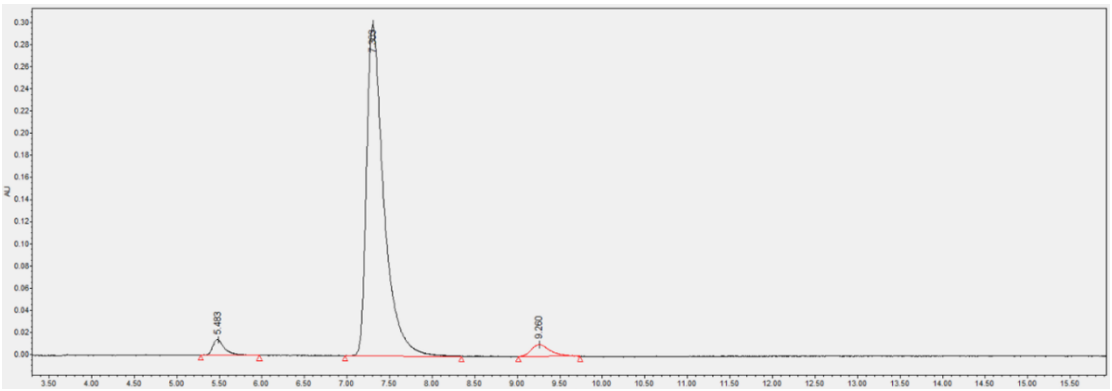
	Time/min	Area	Height	Area%
1	5.355	10767244	1076558	95.86
2	6.841	464829	43005	4.14



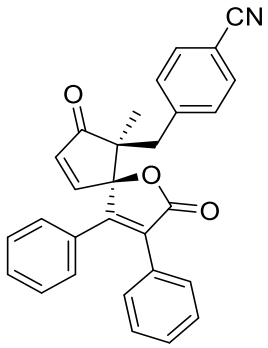
(5*R*,6*S*)-**3t**



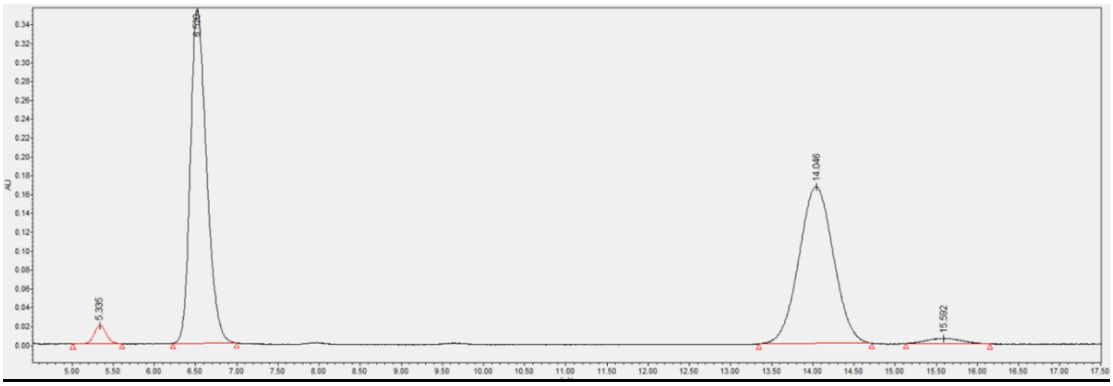
	Time/min	Area	Height	Area%
1	5.505	20599	2334	0.94
2	7.375	1069666	76653	48.76
3	8.748	20974	1594	0.96
4	9.304	1082451	64795	49.34



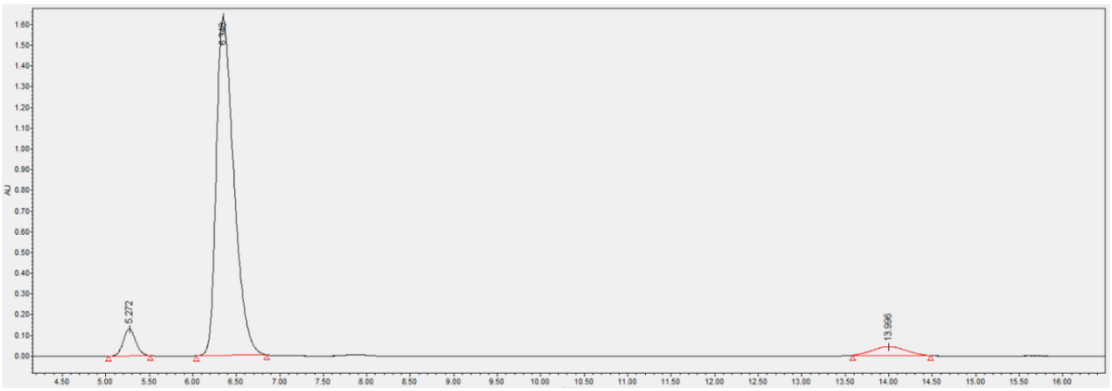
	Time/min	Area	Height	Area%
1	5.483	137833	14201	3.03
2	7.303	4242777	299926	93.39
3	9.260	162320	10820	3.57



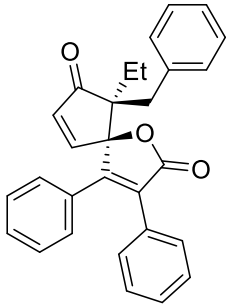
(5*R*,6*S*)-**3u**



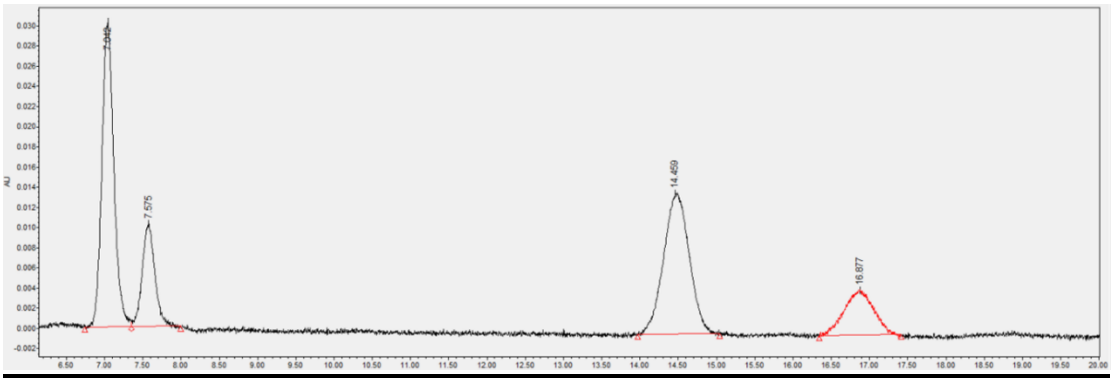
	Time/min	Area	Height	Area%
1	5.335	196109	19483	1.94
2	6.520	4864607	354429	48.23
3	14.046	4858476	166473	48.17
4	15.592	166343	5779	1.65



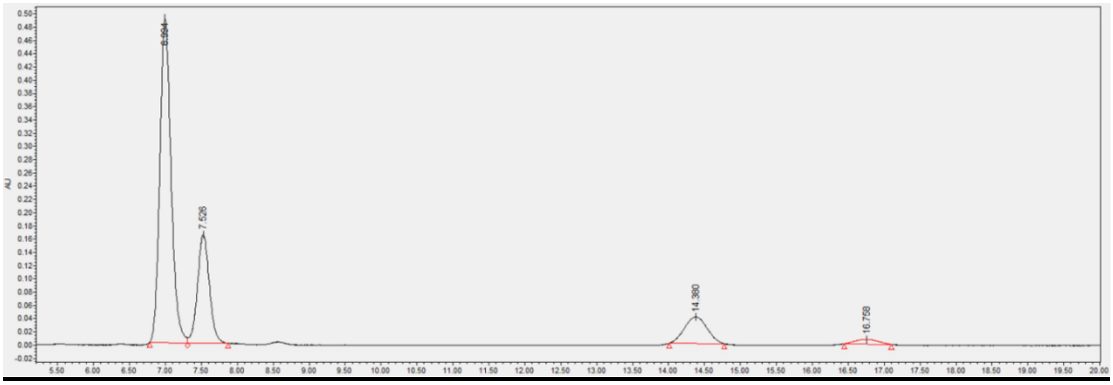
	Time/min	Area	Height	Area%
1	5.272	1287679	130941	5.08
2	6.348	22957370	1631965	90.59
3	13.996	1096891	41574	4.33



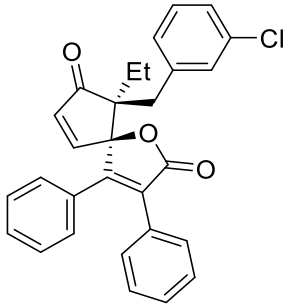
(5*R*,6*S*)-**3v**



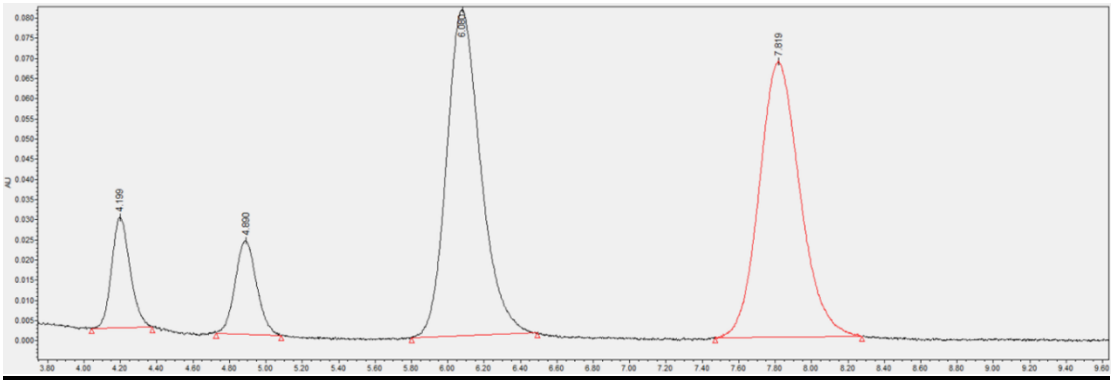
	Time/min	Area	Height	Area%
1	7.042	327985	30197	36.92
2	7.575	117330	10236	13.21
3	14.459	325100	13950	36.60
4	16.877	117977	4469	13.28



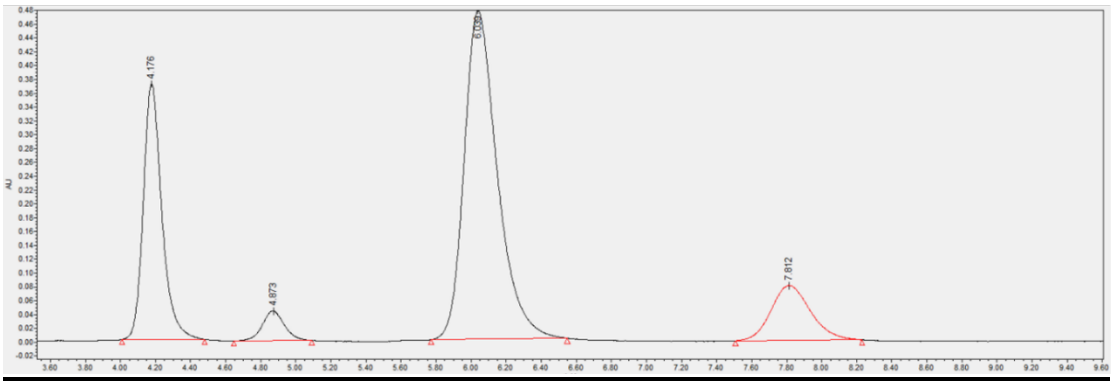
	Time/min	Area	Height	Area%
1	6.994	5279978	489797	64.53
2	7.526	1876926	164227	22.94
3	14.380	874448	40324	10.69
4	16.758	150936	7069	1.84



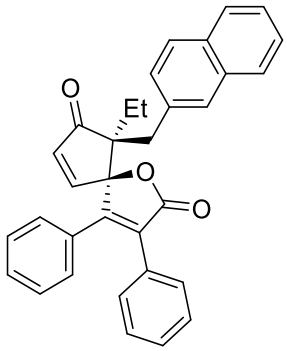
(5*R*,6*S*)-**3w**



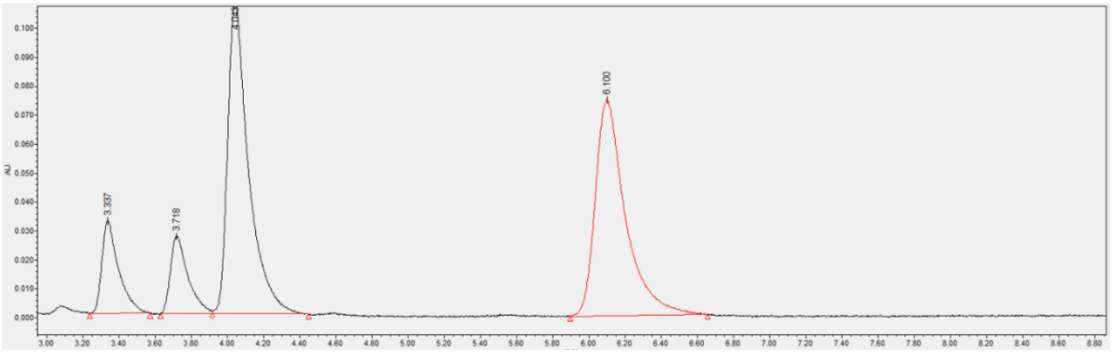
	Time/min	Area	Height	Area%
1	4.199	193715	27485	7.76
2	4.890	190576	23327	7.63
3	6.080	1051605	80950	42.10
4	7.819	1061751	68455	42.51



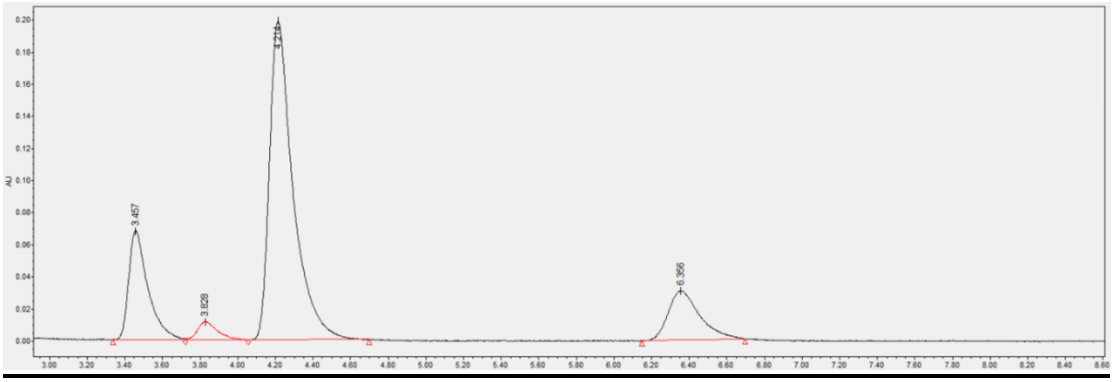
	Time/min	Area	Height	Area%
1	4.176	2719707	369963	25.74
2	4.873	369548	42696	3.50
3	6.039	6242964	475244	59.09
4	7.812	1233377	79416	11.67



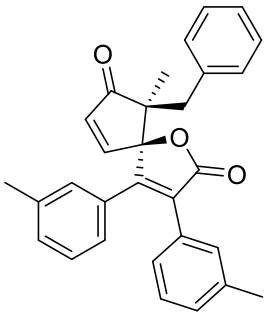
(5*R*,6*S*)-**3x**



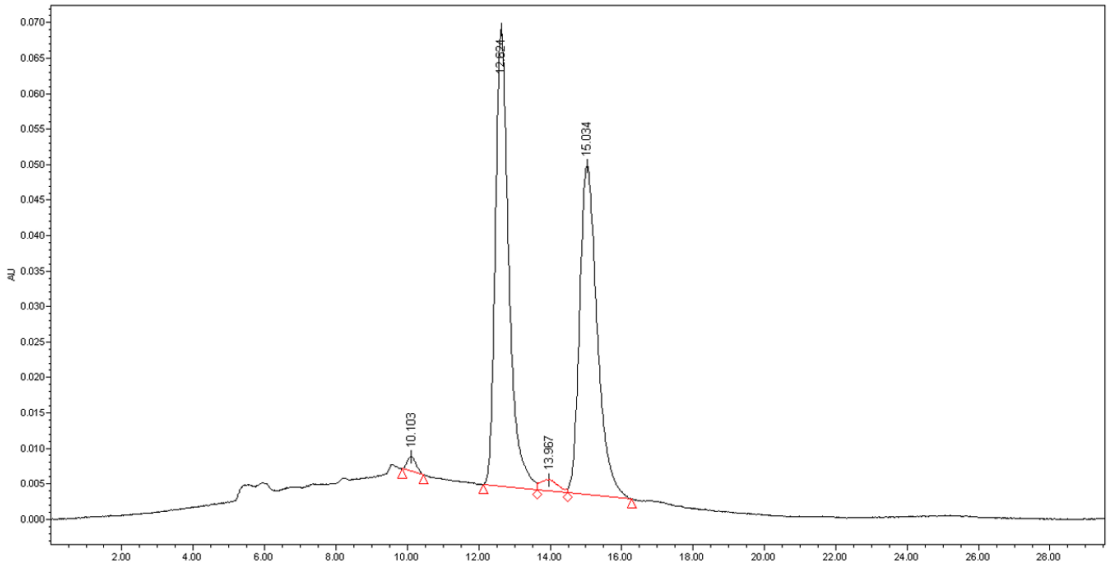
	Time/min	Area	Height	Area%
1	3.337	206403	32091	9.78
2	3.718	179670	26761	8.51
3	4.043	863427	107927	40.90
4	6.100	861582	74523	40.81



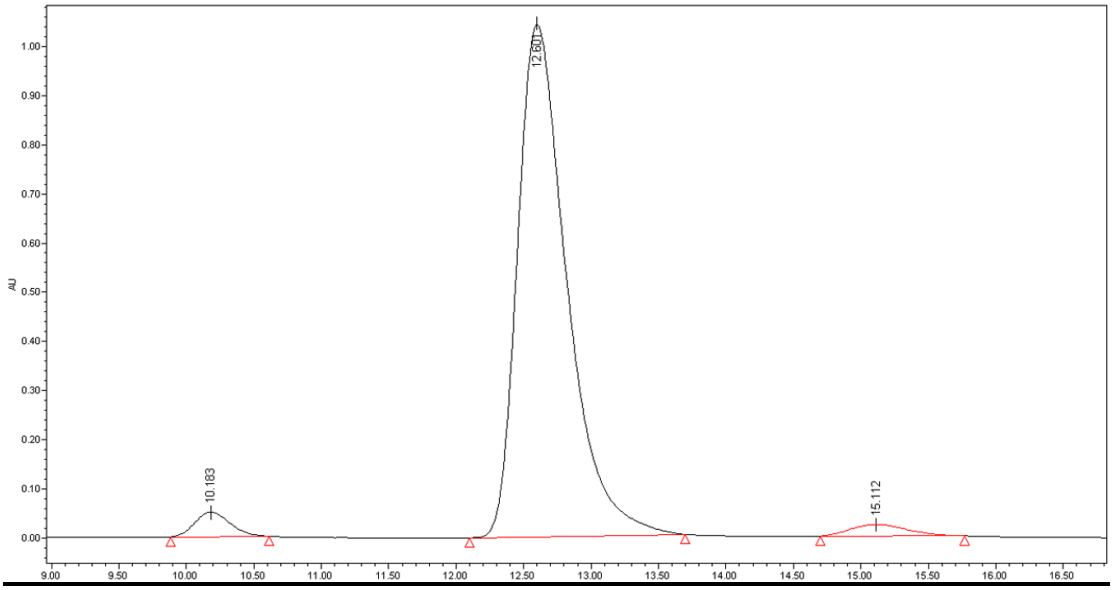
	Time/min	Area	Height	Area%
1	3.457	480457	67746	18.22
2	3.828	80223	11234	3.04
3	4.214	1720880	198362	65.25
4	6.356	355801	30743	13.49



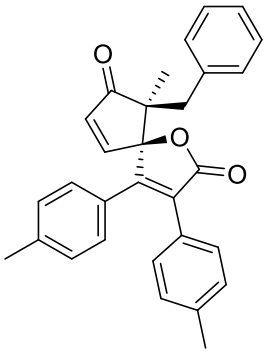
(5*R*,6*S*)-**3y**



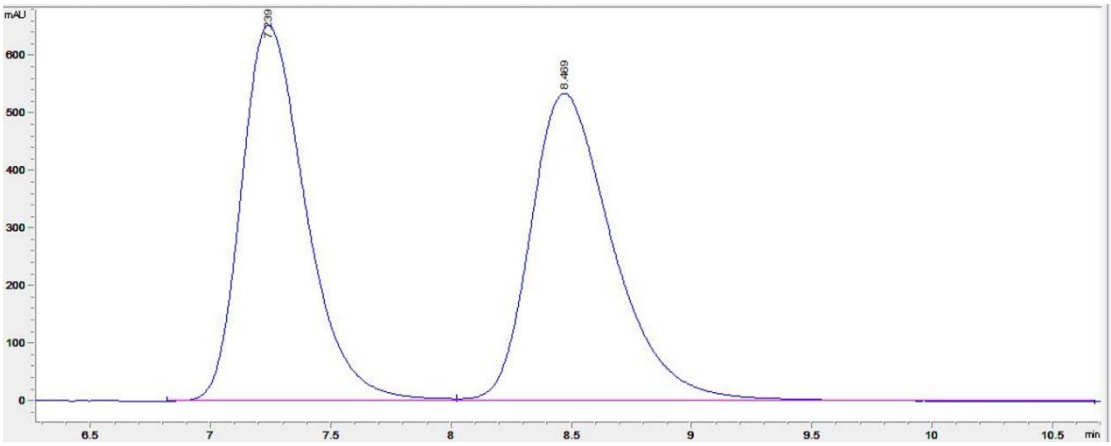
	Time/min	Area	Height	Area%
1	10.103	35398	2061	1.05
2	12.624	1696742	64370	50.34
3	13.967	53833	1580	1.60
4	15.034	1584482	46368	47.01



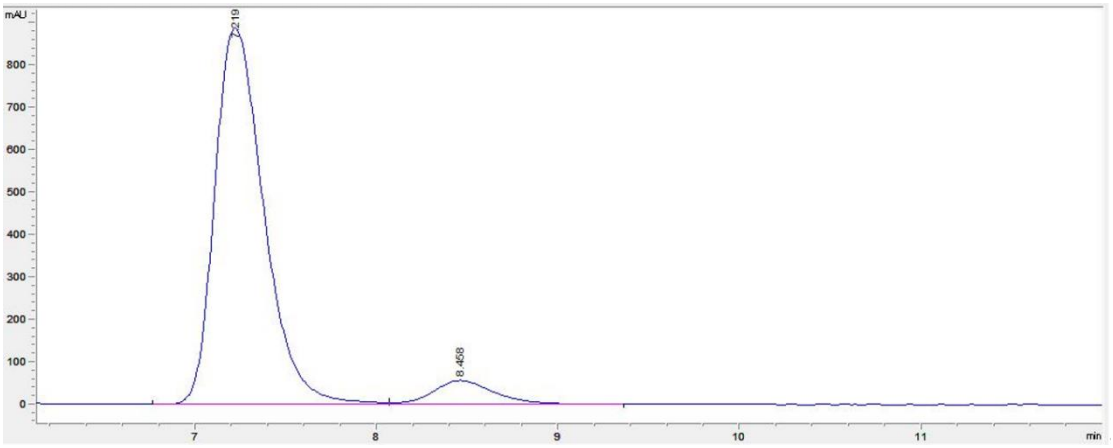
	Time/min	Area	Height	Area%
1	10.183	903540	49746	3.22
2	12.601	26424459	1044115	94.30
3	15.112	692250	23529	2.47



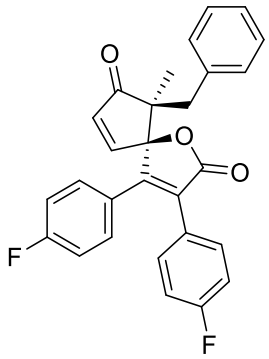
(5*R*,6*S*)-**3z**



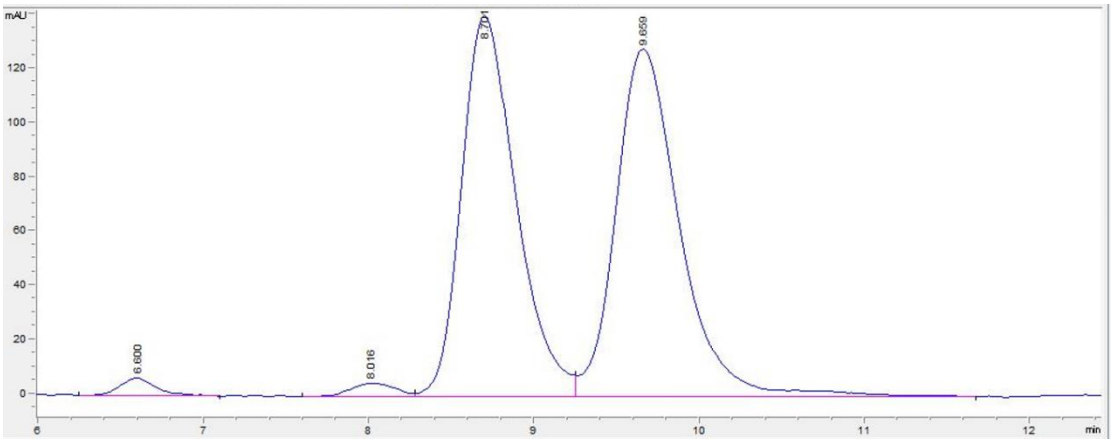
	Time/min	Area	Height	Area%
1	7.239	12203	653.5	48.814
2	8.469	12795.8	534.9	51.186



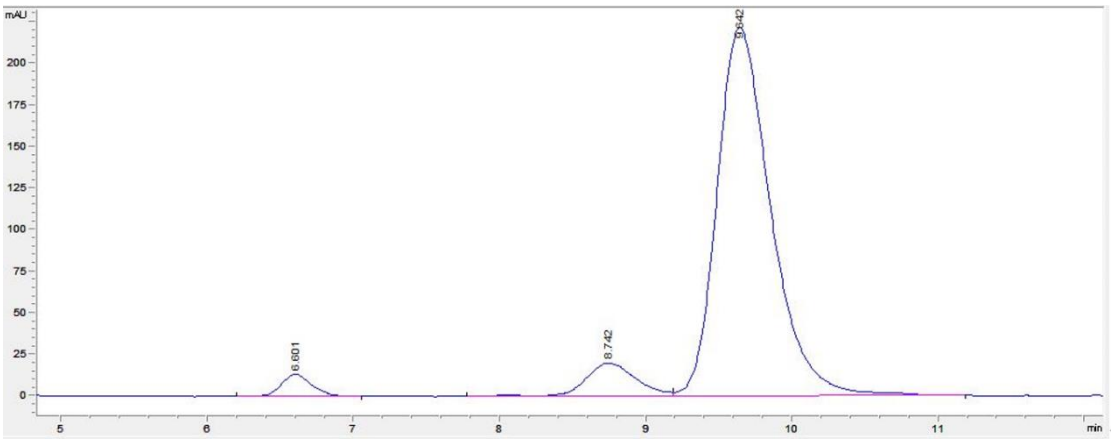
	Time/min	Area	Height	Area%
1	7.219	16666.7	887.6	92.587
2	8.456	1334.4	56.2	7.413



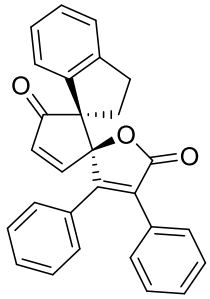
(5*R*,6*S*)-**3aa**



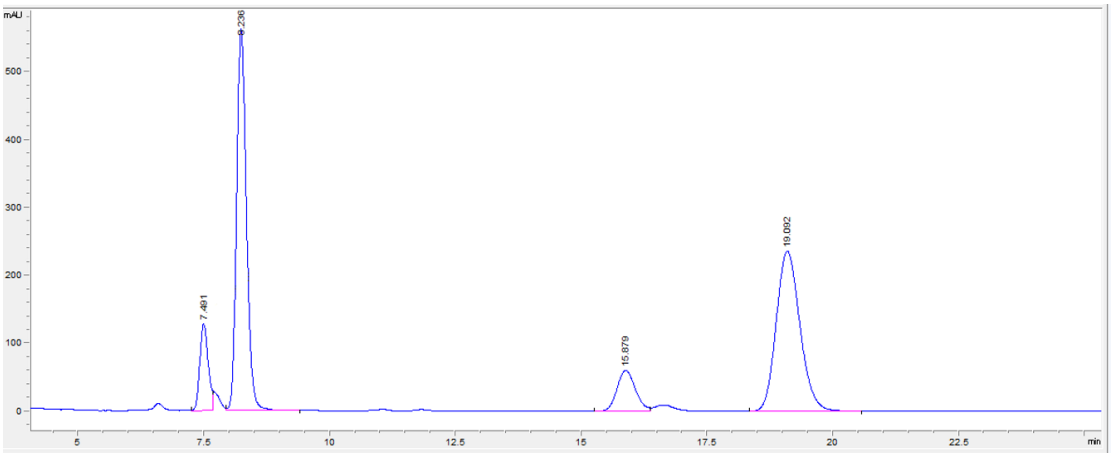
	Time/min	Area	Height	Area%
1	6.600	106	6.7	1.540
2	8.016	94.9	5.1	1.378
3	8.701	3230.8	140.7	46.936
4	9.659	3451.7	128.1	50.145



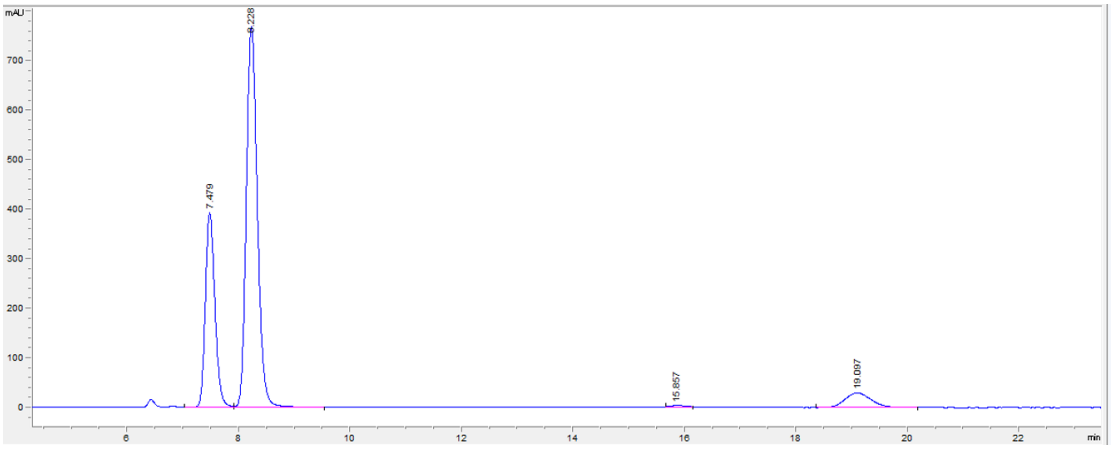
	Time/min	Area	Height	Area%
1	6.601	195.9	13.3	3.098
2	8.742	480.8	19.8	7.602
3	9.642	5648	221.5	89.300



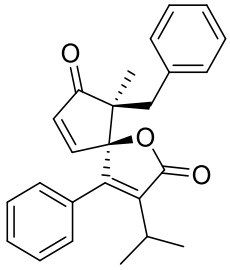
(5*R*,6*S*)-**3ab**



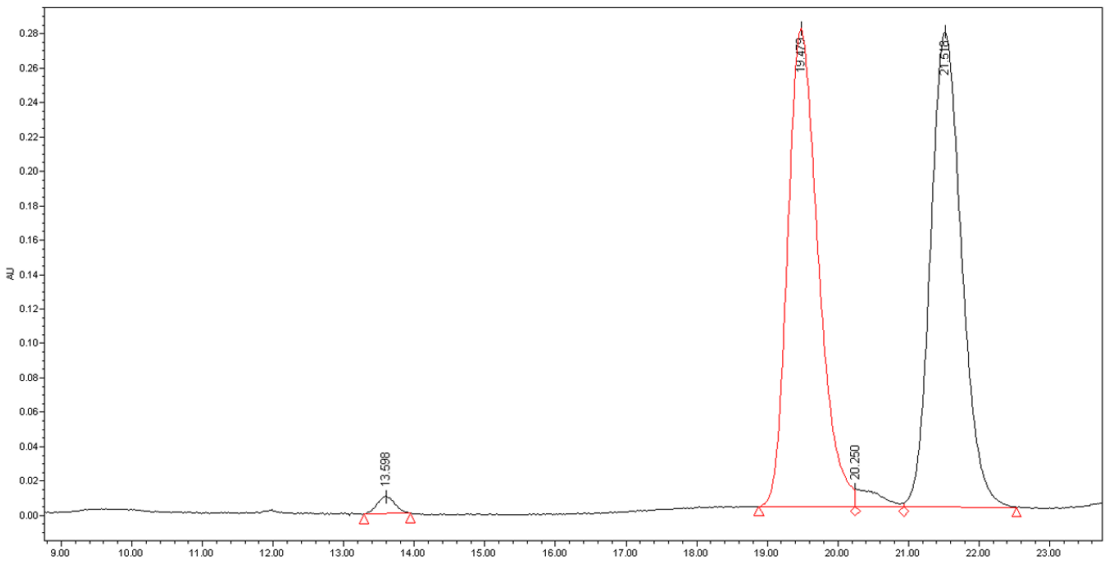
	Time/min	Area	Height	Area%
1	7.491	1518	128.2	8.266
2	8.236	7606.3	561.3	41.417
3	15.879	1523.1	60.1	8.294
4	19.092	7717.6	235.7	42.023



	Time/min	Area	Height	Area%
1	7.479	4666.7	393.6	28.764
2	8.228	10517.6	768.1	64.828
3	15.857	65.2	3.5	0.402
4	19.097	974.3	29.6	6.006

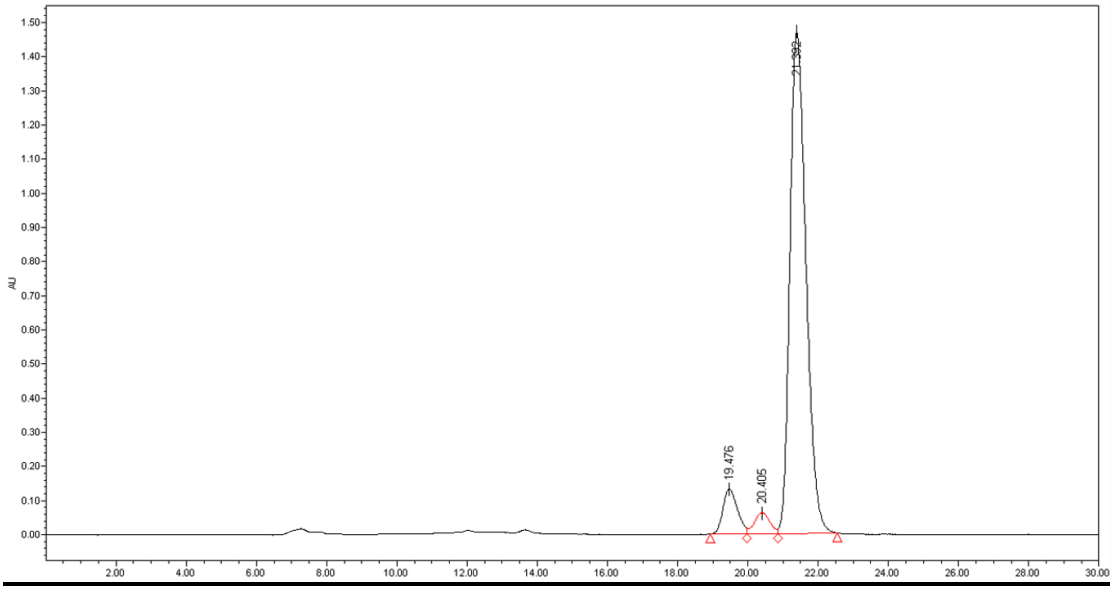


(5*R*,6*S*)-**3ac**

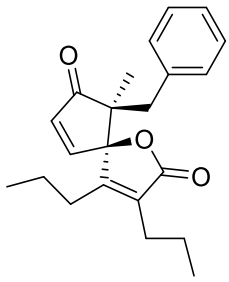


	Time/min	Area	Height	Area%
1	13.598	177486	10098	1.03
2	19.479	8353169	277679	48.60
3	20.250	255167	10399	1.48

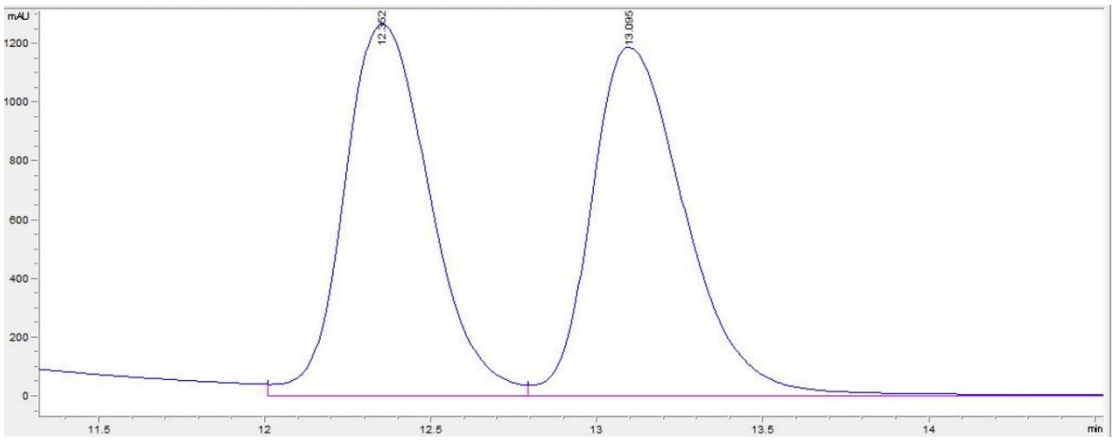
4	21.518	8402640	276270	48.89



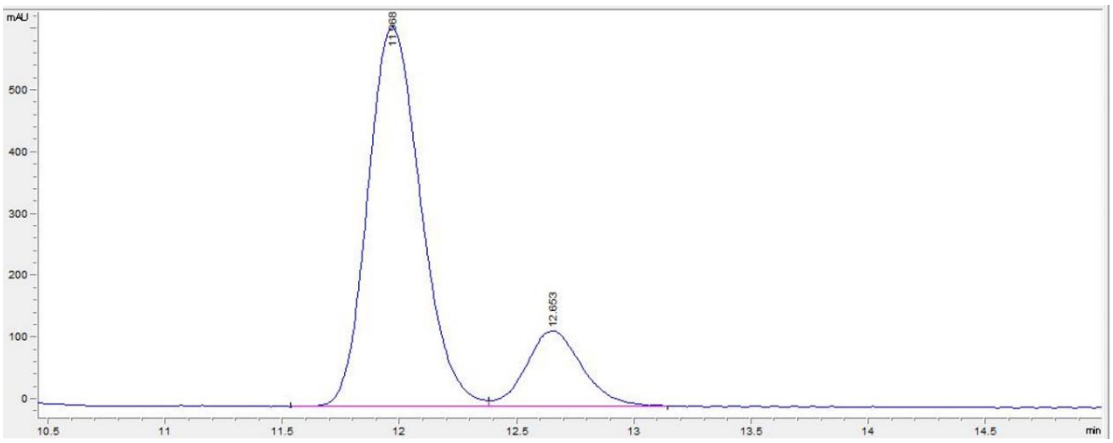
	Time/min	Area	Height	Area%
1	19.476	3730669	131307	7.09
2	20.405	1873751	61257	3.56
3	21.392	47042194	1469297	89.35



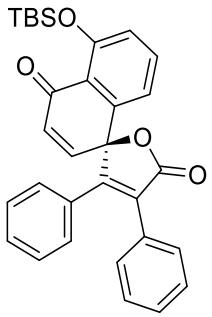
(5*R*,6*S*)-**3ad**



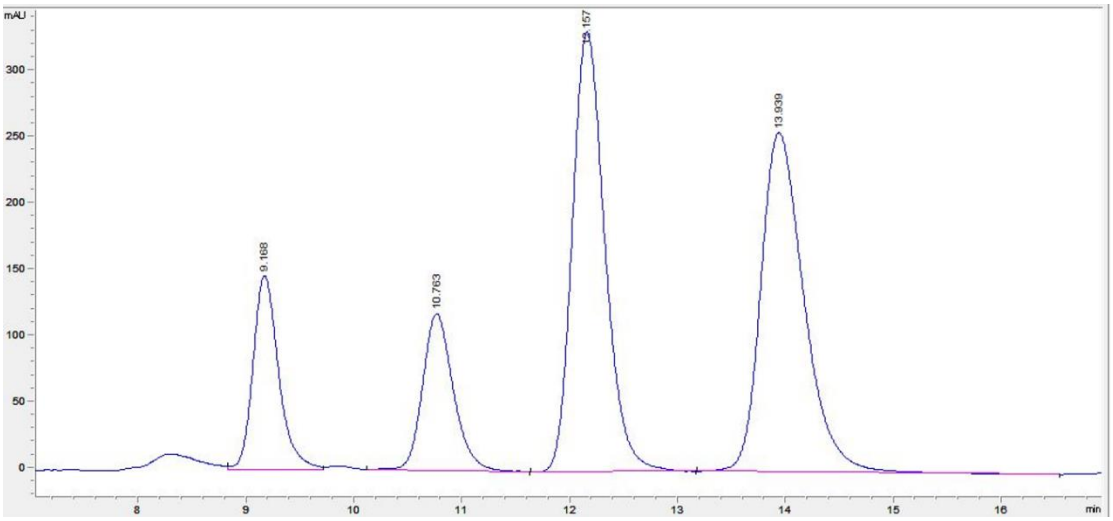
	Time/min	Area	Height	Area%
1	12.352	22774.7	1268.7	48.815
2	13.095	23880.4	1186.5	51.185



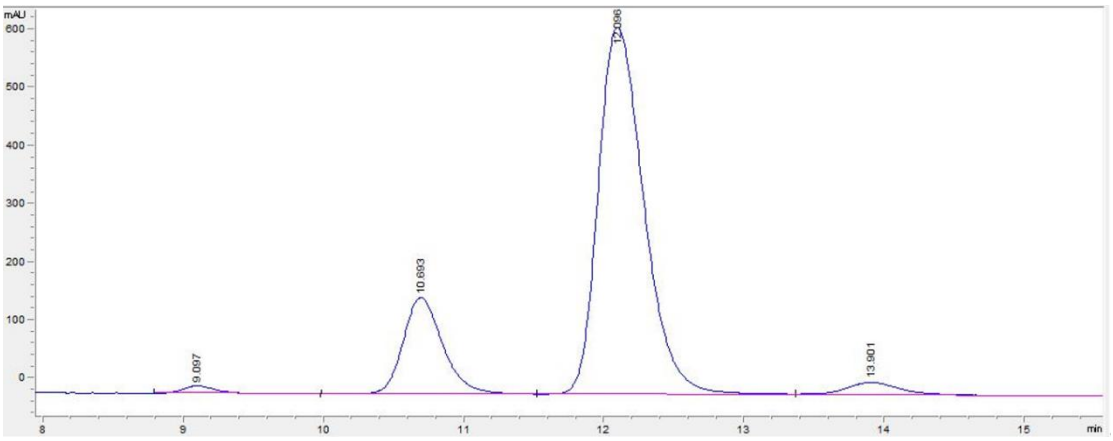
	Time/min	Area	Height	Area%
1	11.968	9682.8	614.4	82.413
2	12.653	2066.3	122.4	17.587



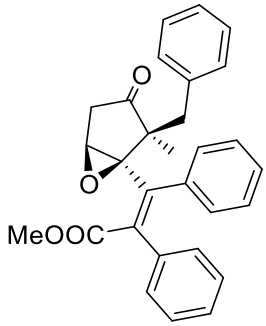
5



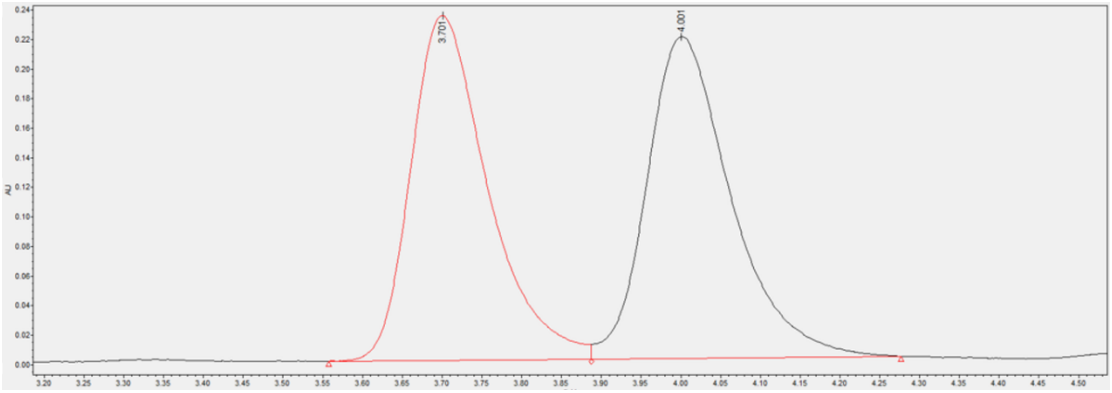
	Time/min	Area	Height	Area%
1	9.168	2429.3	146.7	12.832
2	10.763	2366.6	118.4	12.501
3	12.157	6979.7	332	36.868
4	13.999	7155.8	256.2	37.799



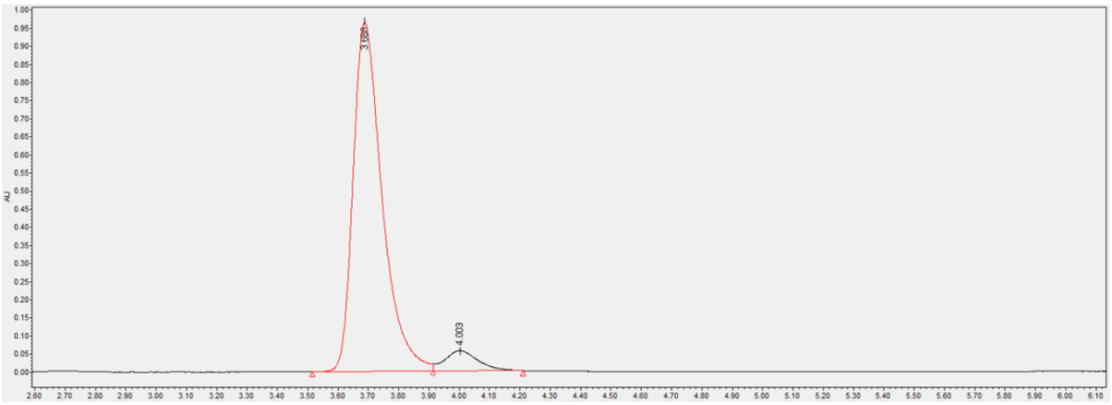
	Time/min	Area	Height	Area%
1	9.097	223.8	12.7	1.216
2	10.693	3261.8	165.6	17.729
3	12.096	14263.5	630.9	77.527
4	13.901	649.1	22	3.528



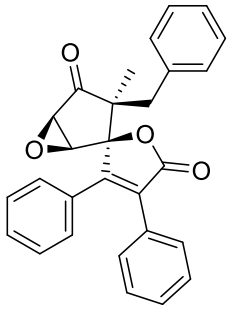
6



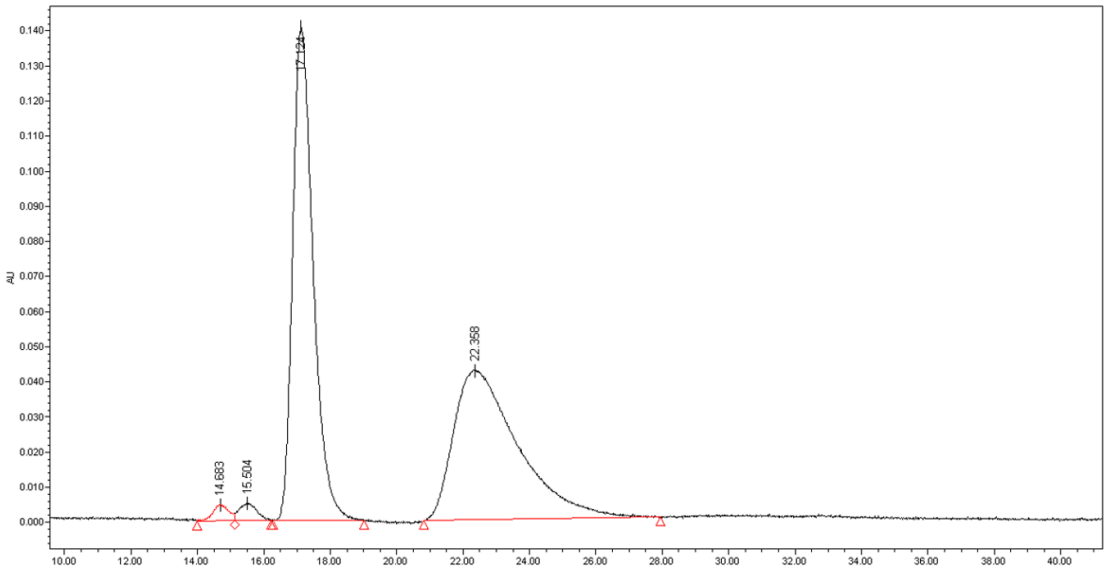
	Time/min	Area	Height	Area%
1	3.701	1567932	233152	49.48
2	4.001	1601204	217684	50.52



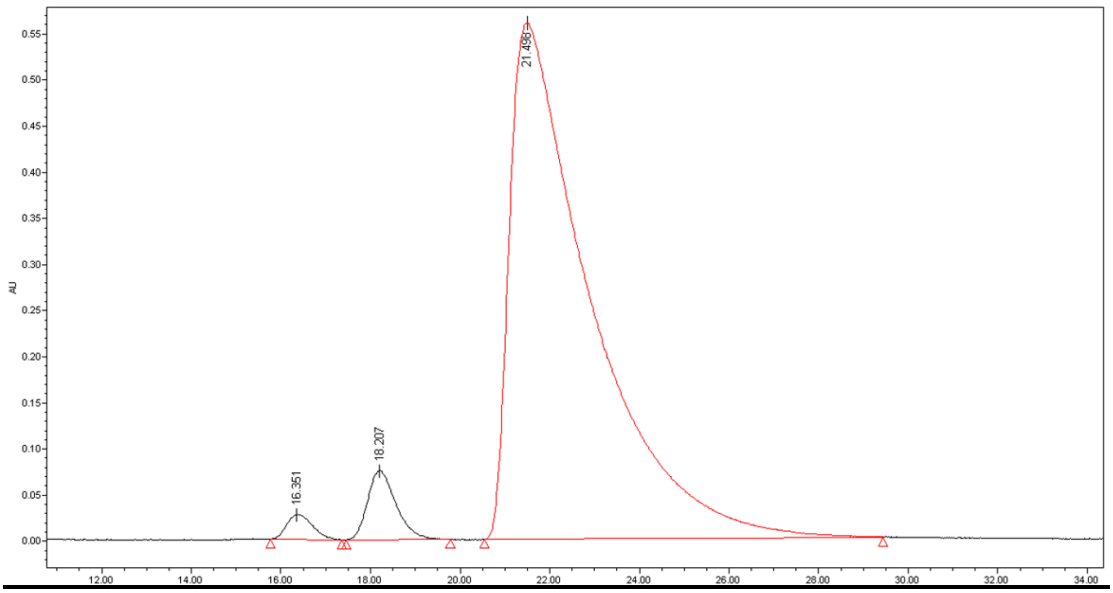
	Time/min	Area	Height	Area%
1	3.688	6413214	965843	93.74
2	4.003	428267	56032	6.26



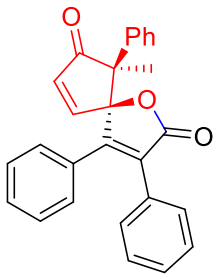
7



	Time/min	Area	Height	Area%
1	14.683	146722	4478	1.22
2	15.504	174848	4786	1.45
3	17.124	5992317	140433	49.80
4	22.358	5717953	42617	47.52

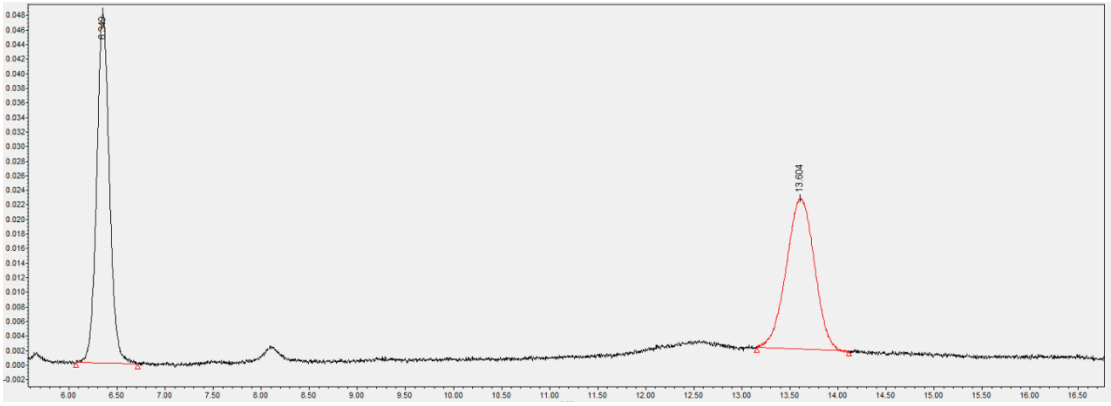


	Time/min	Area	Height	Area%
1	16.351	1063888	26697	1.43
2	18.207	3313899	75081	4.46
3	21.498	69967803	558905	94.11

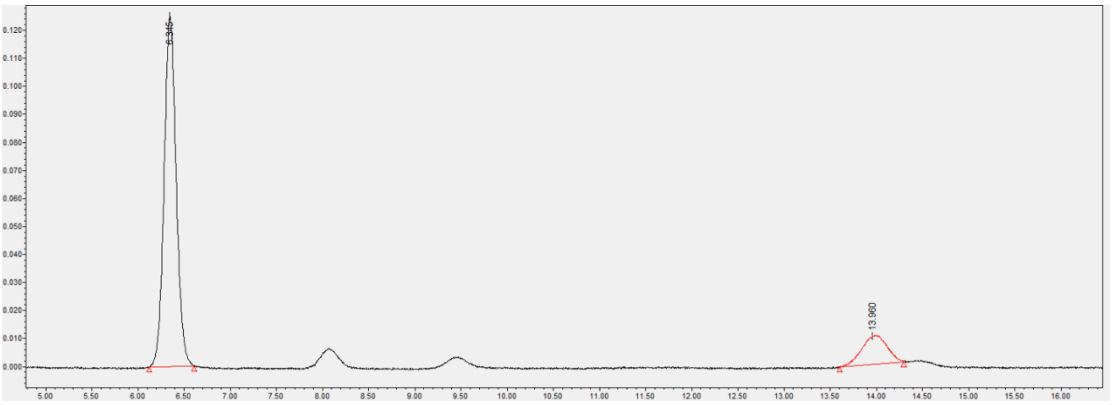


10

Major:

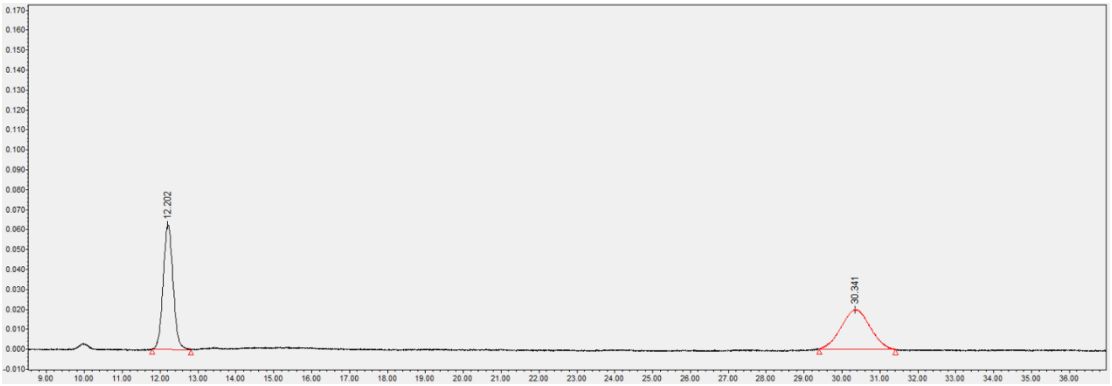


	Time/min	Area	Height	Area%
1	6.349	443040	48233	51.21
2	13.604	422110	20777	48.79

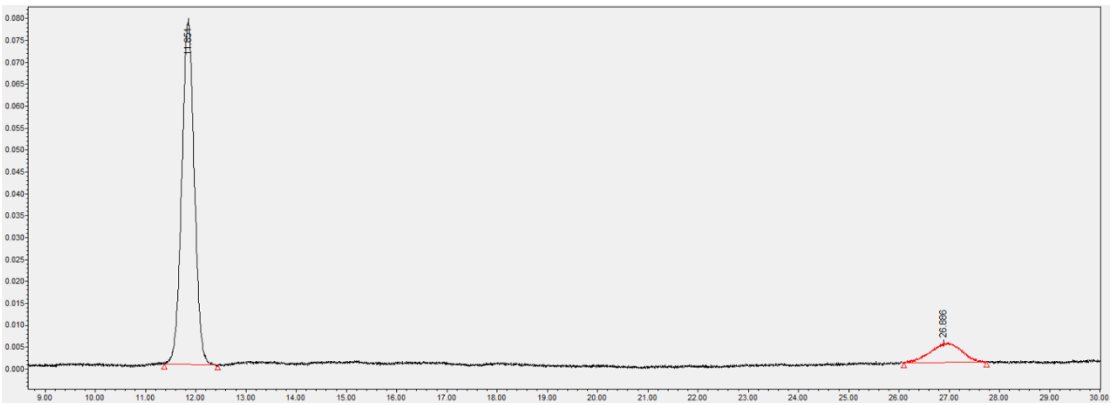


	Time/min	Area	Height	Area%
1	6.345	1139653	124925	85.19
2	13.960	198201	10278	14.81

Minor:



	Time/min	Area	Height	Area%
1	12.202	1134977	62520	51.96
2	30.341	1049354	20085	48.04



	Time/min	Area	Height	Area%
1	11.851	1362064	78159	87.99
2	26.886	185829	4475	12.01