Supporting Information for *Chemical Communications*

An efficient route to highly enantioenriched tetrahydroazulenes and β-tetralones by desymmetrization reactions of δ,δ-diaryldiazoacetoacetates

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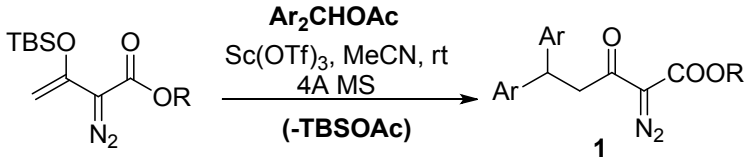
General Information

All reactions, unless noted, were carried out under an inert atmosphere of dried nitrogen in flame-dried or oven-dried glassware with magnetic stirring. Analytical thin layer chromatography (TLC) was performed on Dynamic Adsorbents precoated (0.25 mm thickness) silica gel plates with F254 indicator. Visualization was accomplished by UV light (254 nm) or phosphomolybdic acid (PMA) solution in ethanol. Flash chromatography was performed with silica gel (32-63 μm) supplied by Dynamic Adsorbents. ^{1}H NMR spectra were recorded on a Bruker DRX-400 (400 MHz) spectrometer, and chemical shifts were reported in ppm. The peak information was described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite; coupling constant(s) in Hz. ^{13}C NMR spectra were recorded on a Bruker DRX-400 (100 MHz) spectrometer with complete proton decoupling. Enantioselectivity was determined on an Agilent 1200 Series HPLC using Daicel Chiralcel OD-H column, AD-H column. Optical rotation was recorded on JASCO DIP-1000 digital polarimeter. High-resolution mass spectra (HRMS) were performed on JEOL AccuTOF-CS mass spectrometer using CsI as the standard.

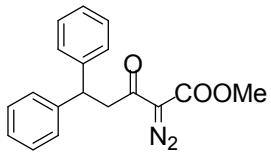
Materials

$Rh_2(PTA)_4$, Rh_2(*S*-PTTL)$_4$ and all other dirhodium carboxylates catalysts were prepared according to the literature procedures.[1] Rh_2(S-TFPTTL)$_4$ [2] was prepared by following the same synthetic procedure. Rh_2(S-PTAD)$_4$ and Rh_2(S-DOSP)$_4$ were purchased from Strem Chemicals. δ,δ-Diaryldiazoaceto- acetates **1a-i** were prepared according to the literature procedures.[3] Alkyl 3-(*tert*-butyl- dimethylsilyloxy)-2-diazobut-3-enoates (enoldiazoacetates) were prepared from their corresponding 3-oxo-2-diazo- butanoates.[4] Solvents were dried over 4 Å MS before use. All the other chemicals and Lewis acid were obtained from commercial sources and used without further purification.

General Procedure for the Preparation of δ,δ-Diaryldiazoacetoacetates

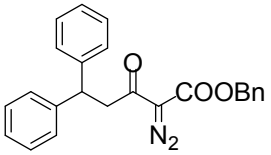


Molecular sieves (100 mg) were added to the Schlenk tube and flame dried under vacuum, then anhydrous $Sc(OTf)_3$ (3.0 mol %) was added and heated (110 ℃) under vacuum for 1 h to dehydrate the catalyst. After cooling to room temperature the benzhydryl acetate (1.0 mmol) in 3 mL of dry acetonitrile was added, and this mixture was stirred at room temperature for 5 min. Enoldiazoacetate (1.3 mmol, 1.3 equiv.) was added via syringe all at once. The bright yellow solution was stirred vigorously at room temperature. After 16 h the reaction mixture was concentrated under reduced pressure, and the resulting mixture was purified by silica gel chromatography, eluting with 1:30 EtOAc/hexane to give the corresponding product **1a-i**.

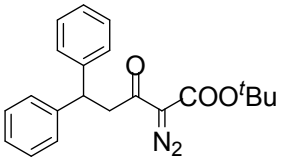


Methyl 2-Diazo-3-oxo-5,5-diphenylpentanoate (1a). Yield: 79%; Yellow oil; ^{1}H NMR (400 MHz,

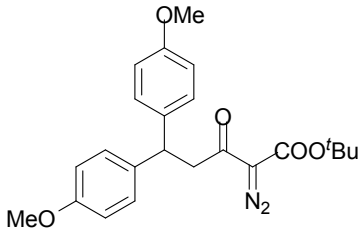
$CDCl_3$) δ 7.31 – 7.29 (comp, 8H), 7.24 – 7.17 (comp, 2H), 4.74 (t, *J* = 7.6 Hz, 1H), 3.87 (s, 3H), 3.70 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 162.1, 144.1, 128.8, 128.2, 126.7, 52.5, 46.4, 45.8 (diazo carbon not detected); HRMS (ESI) calcd for $C_{18}H_{19}N_2O_3$ $[M+H]^+$ calcd 309.1239; found 309.1228.



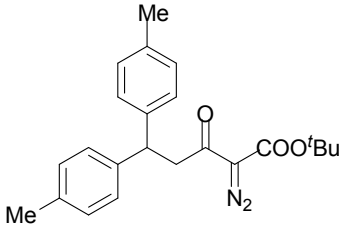
Benzyl 2-Diazo-3-oxo-5,5-diphenylpentanoate (1b). Yield: 76%; White solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.41 (comp, 5H), 7.31 – 7.28 (comp, 5H), 7.25 – 7.17 (comp, 2H), 5.32 (s, 2H), 4.75 (t, *J* = 7.6 Hz, 1H), 3.73 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 161.6, 144.2, 135.5, 129.2, 129.1, 128.9, 128.8, 128.3, 126.8, 67.4, 46.5, 45.0 (diazo carbon not detected); HRMS (ESI) calcd for $C_{24}H_{21}N_2O_3$ $[M+H]^+$ calcd 385.1552; found 385.1543.



***tert*-Butyl 2-Diazo-3-oxo-5,5-diphenylpentanoate (1c).** Yield: 72%; Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ7.20 – 7.16 (comp, 4H), 7.15 – 7.12 (comp, 4H), 7.10 – 7.08 (m, 1H), 4.59 (t, *J* = 7.6 Hz, 1H), 3.59 (dd, *J* = 17.0, 7.6 Hz, 1H), 3.50 (dd, *J* = 17.0, 7.6 Hz, 1H), 1.43 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 160.9, 144.4, 128.9, 128.3, 126.8, 83.8, 45.8, 45.7, 28.7 (diazo carbon not detected); HRMS (ESI) calcd for $C_{21}H_{23}N_2O_3$ $[M+H]^+$ calcd 351.1709; found 351.1721.

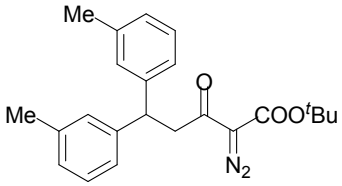


***tert*-Butyl 2-Diazo-3-oxo-5,5-di–*p*-anisyl pentanoate (1d).** Yield: 76%; Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ7.21 (d, *J* = 8.6 Hz, 4H), 6.83 (d, *J* = 8.6 Hz, 4H), 4.63 (t, *J* = 7.6 Hz, 1H), 3.79 (s, 6H), 3.62 (d, *J* = 7.6 Hz, 2H), 1.56 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 160.9, 158.4, 136.9, 129.1, 114.2, 83.6, 55.6, 46.0, 45.1, 28.7 (diazo carbon not detected); HRMS (ESI) calcd for $C_{23}H_{27}N_2O_5$ $[M+H]^+$ calcd 411.1920; found 411.1912.

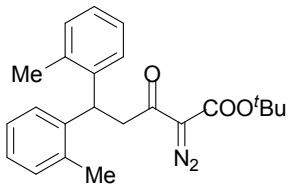


***tert*-Butyl 2-Diazo-3-oxo-5,5-di-*p*-tolylpentanoate (1e).** Yield: 70%; Pale yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.1 Hz, 4H), 6.98 (d, *J* = 8.1 Hz, 4H), 4.54 (t, *J* = 7.6 Hz, 1H), 3.53 (d, *J* = 7.6 Hz, 2H), 2.20 (s, 6H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 160.6, 141.6, 136.1,

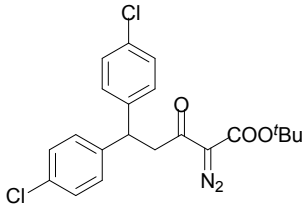
129.6, 128.1, 83.5, 45.9, 45.8, 28.4, 21.6 (diazo carbon not detected); HRMS (ESI) calcd for $C_{23}H_{27}N_2O_3$ $[M+H]^+$ calcd 379.2022; found 379.2015.



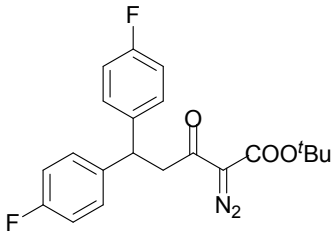
***tert*-Butyl 2-Diazo-3-oxo-5,5-di-*m*-tolylpentanoate (1f).** Yield: 58%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.20 – 7.13 (comp, 2H), 7.11 – 7.09 (comp, 4H), 7.01 – 6.98 (comp, 2H), 4.63 (t, *J* = 7.6 Hz, 1H), 3.64 (d, *J* = 7.6 Hz, 2H), 2.31 (s, 6H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 160.9, 144.4, 136.4, 129.0, 128.7, 127.5, 125.1, 83.5, 46.5, 45.5, 28.7, 21.9 (diazo carbon not detected); HRMS (ESI) calcd for $C_{23}H_{27}N_2O_3$ $[M+H]^+$ calcd 379.2022; found 379.2026.



***tert*-Butyl 2-Diazo-3-oxo-5,5-di-*o*-tolylpentanoate (1g).** Yield: 42%; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.04 (comp, 8H), 5.08 (t, *J* = 7.6 Hz, 1H), 3.55 (d, *J* = 7.6 Hz, 2H), 2.35 (s, 6H), 1.57 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 160.9, 141.8, 136.5, 131.0, 127.4, 126.6, 126.4, 83.7, 44.6, 39.0, 28.7, 19.9 (diazo carbon not detected); HRMS (ESI) calcd for $C_{23}H_{27}N_2O_3$ $[M+H]^+$ calcd 379.2022; found 379.2018.

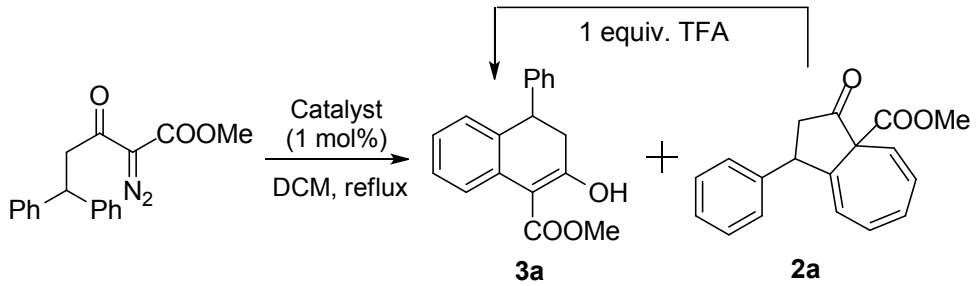


***tert*-Butyl 2-Diazo-3-oxo-5,5-di-*p*-chlorophenylpentanoate (1h).** Yield: 56%; Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.22 (comp, 4H), 7.22 – 7.16 (comp, 4H), 4.66 (t, *J* = 7.6 Hz, 1H), 3.61 (d, *J* = 7.6 Hz, 2H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 160.7, 142.1, 132.7, 129.6, 129.1, 83.8, 83.5, 45.3, 28.7 (diazo carbon not detected); HRMS (ESI) calcd for $C_{21}H_{21}Cl_2N_2O_3$ $[M+H]^+$ calcd 419.0929; found 419.0925.



***tert*-Butyl 2-Diazo-3-oxo-5,5-di-*p*-fluorophenylpentanoate (1i).** Yield: 51%; Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.03 (comp, 4H), 6.99 – 6.67 (comp, 4H), 4.58 (t, *J* = 7.6 Hz, 1H), 3.51 (d, *J* = 7.6 Hz, 2H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 163.1, 160.8, 160.6, 139.9, 139.8, 129.7, 129.6, 115.8, 115.6, 83.7, 45.8, 45.1, 28.7 (diazo carbon not detected); HRMS (ESI) calcd for $C_{21}H_{21}F_2N_2O_3$ $[M+H]^+$ calcd 387.1520; found 387.1528.

Catalyst Screening [a]

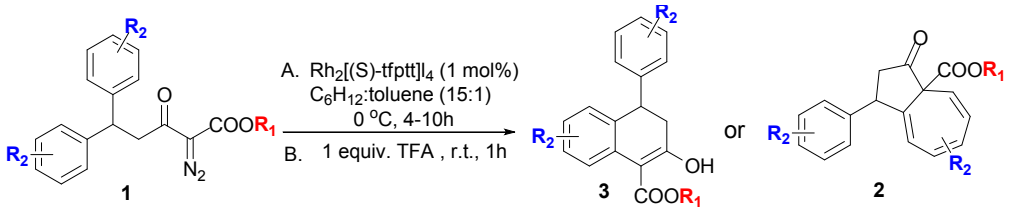


3a **2a**

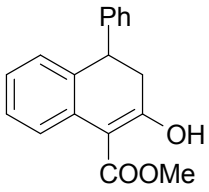
Entry	Catalyst	Yield [b] (%)	ee [c] of 3a (%)	Product ratio (3a:2a)
1	$[Rh_2\{(S)\text{-pttl}\}_4]$	90	52	1:0.8
2	$[Rh_2\{(S)\text{-ptpa}\}_4]$	89	34	1:0.6
3	$[Rh_2\{(S)\text{-pta}\}_4]$	90	38	1:1.5
4	$[Rh_2\{(S)\text{-ptad}\}_4]$	90	55	1:1.4
5	$[Rh_2\{(S)\text{-tcpttl}\}_4$	92	64	1:2.4
6	$[Rh_2\{(S)\text{-tfpttl}\}_4]$	91	**70**	**1:2.7**
7	$[Rh_2\{(S)\text{-nttl}\}_4]$	90	60	1:2.2

[a] A solution of methyl 2-diazo-3-oxo-5,5-diphenylpentanoate (**1a**) (0.1 mmol) in 0.5 mL of anhydrous DCM was added via syringe pump to a solution of the Hashimoto catalyst (0.0010 mmol) in 0.5 mL of anhydrous refluxing DCM for 1h. The reaction mixture then passed through a short flash column of silica gel (dimensions: 0.5 cm x 10 cm) and, after removal of the solvent under reduced pressure, then subjected to ^{1}H NMR spectroscopic analysis to determine the ratio of two products. After ^{1}H NMR spectroscopic analysis, the reaction mixture followed by in situ treatment with TFA (0.1 mmol, 1.0 equiv.) for 1 hour. Then the crude reaction mixture was purified by column chromatography on silica gel (eluent hexanes/EtOAc =50:1-30:1) to give the corresponding product **3a**. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

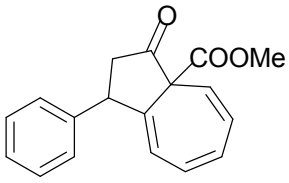
General Procedure for the Catalytic Enantioselective Synthesis of β-Tetralones and Tetrahydroazulenes



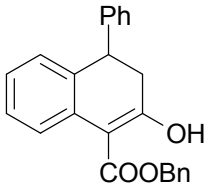
δ,δ-Diaryldiazoacetoacetates **1a-i** (0.15 mmol) in 1.2 mL solvent (cyclohexane: toluene = 15:1) was added over a 1h period by a syringe pump at 0 °C to a solution of Rh_2[(*S*)-tfpttl]$_4$ catalyst (0.0015 mmol) in 0.4 mL of solvent. The reaction mixture was stirred for 4-10 hours at 0 °C, and/or followed by in situ treatment with TFA (0.15 mmol, 1.0 equiv.) for 1 hour. The reaction mixture then passed through a short flash column of silica gel (dimensions: 0.5 cm x 10 cm) and , after removal of the solvent under reduced pressure, then subjected to ^{1}H NMR spectroscopic analysis to determine product diastereoselectivity. The crude reaction mixture was purified by column chromatography on silica gel (eluent hexanes/EtOAc =50:1-30:1) to give the corresponding product **3a-f / 2g-i**.



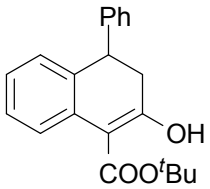
Methyl (*R*)-2-Hydroxy-4-phenyl-3,4-dihydronaphthalene-1-carboxylate (3a). Catalyzed by Rh_2[(S)-tfpttl]$_4$ at 0 °C to give **3a** in 90% isolated yield with 90% *ee*; Pale yellow oil; $[\alpha]_D^{21\ °C}$ = + 79.0 (*c* = 0.14, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.18 (s, 1H), 7.70 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.29 – 7.18 (comp, 3H), 7.17 – 7.07 (comp, 3H), 6.99 – 6.98 (m, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 4.09 (t, *J* = 5.9 Hz, 1H), 3.86 (s, 3H), 2.85 (dd, *J* = 14.3, 5.9 Hz, 1H), 2.80 (dd, *J* = 14.3, 5.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 171.5, 141.0, 134.9, 130.6, 127.9, 127.4, 126.9, 126.1, 126.0, 125.4, 124.6, 99.3, 51.1, 42.5, 35.9; HRMS (ESI) for $C_{18}H_{17}O_3$ $[M+H]^+$ calcd 281.1178; found 281.1177. HPLC conditions for determination of enantiomeric excess: AD-H column, 254 nm, 0.5 mL/min, Hexane:IPA = 95:5, minor enantiomer t_r = 10.3 min, major enantiomer t_r = 11.1 min.



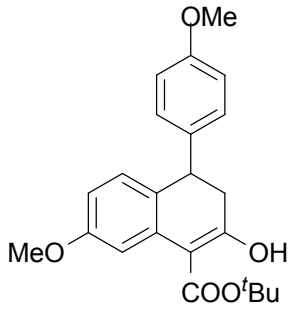
Methyl (1*R*,3a*S*)-3-Oxo-1-phenyl-1,2,3,3a-tetrahydroazulene-3a-carboxylate (2a). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (comp, 2H), 7.28 – 7.23 (m, 1H), 7.20 – 7.14 (comp, 2H), 6.66 – 6.36 (comp, 3H), 6.19 – 5.98 (m, 1H), 5.59 – 5.33 (m, 1H), 4.58 (td, *J* = 9.3, 2.3 Hz, 1H), 3.63 (s, 3H), 3.21 (dd, *J* = 18.3, 9.3 Hz, 1H), 2.65 (dd, *J* = 18.3, 9.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.2, 168.2, 143.1, 142.3, 130.0, 129.6, 129.5, 129.3, 128.5, 127.5,124.5, 120.2, 64.7, 53.3, 47.4, 46.9; HRMS (ESI) for $C_{18}H_{19}O_3$ $[M+H]^+$ calcd 281.1178; found 281.1173.



Benzyl (*R*)-2-Hydroxy-4-phenyl-3,4-dihydronaphthalene-1-carboxylate (3b). Catalyzed by Rh_2[(S)-tfpttl]$_4$ at 0 ^{O}C to give **3b** in 88% isolated yield with 82% *ee*. Colorless oil; $[\alpha]_D^{21\ °C}$ = + 38.3 (*c* = 0.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.29 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.28 (comp, 8H), 7.22 – 7.20 (comp, 3H), 7.06 – 6.89 (m, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 5.69 – 5.27 (comp, 2H), 4.39 – 3.97 (t, *J* = 7.4, 1H), 2.95 (dd, *J* = 15.5, 7.4 Hz, 1H), 2.89 (dd, *J* = 15.5, 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 172.0, 142.1, 136.2, 136.0, 131.8, 129.1, 129.0, 128.8,128.6, 128.5, 127.9, 127.3, 127.1, 126.6, 125.7, 100.5, 67.1, 43.7, 37.2; HRMS (ESI) for $C_{24}H_{21}O_3$ $[M+H]^+$ calcd 357.1491; found 357.1495. HPLC conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.5 mL/min, Hexane:IPA = 99:1,major enantiomer t_r = 22.1 min, minor enantiomer t_r = 23.7 min.

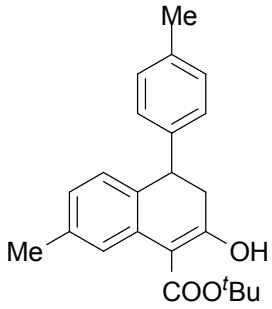


***tert*-Butyl (*R*)-2-Hydroxy-4-phenyl-3,4-dihydronaphthalene-1-carboxylate (3c).** Catalyzed by Rh_2[(S)-tfpttl]$_4$ at 0 ^{O}C to give **3c** in 87% isolated yield with 91% *ee*. Colorless oil; $[\alpha]_D^{21\ °C}$ = + 42.2 (c = 0.30, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.67 (s, 1H), 7.88 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.42 – 7.36 (comp, 2H), 7.36 – 7.30 (m, 1H), 7.30 – 7.22 (comp, 3H), 7.08 (td, *J* = 8.0, 1.1 Hz, 1H), 6.89 – 6.83 (m, 1H), 4.21 (t, *J* = 6.1 Hz, 1H), 2.95 (dd, *J* = 16.4, 6.1 Hz, 1H), 2.86 (dd, *J* = 16.4, 6.1 Hz, 1H), 1.69 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 171.0, 141.3, 135.4, 131.5, 128.1, 127.7, 126.9, 126.3, 125.8, 125.5, 124.3, 100.4, 82.2, 42.9, 36.2, 27.9; HRMS (ESI) for $C_{21}H_{23}O_3$ $[M+H]^+$ calcd 323.1647; found 323.1632. HPLC conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.5 mL/min, Hexane:IPA = 99.5:0.5, major enantiomer t_r = 11.3 min, minor enantiomer t_r = 12.5 min.

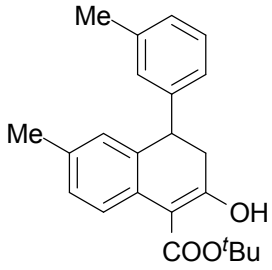


***tert*-Butyl (*R*)-2-Hydroxy-7-methoxy-4-(*p*-anisyl)-3,4-dihydronaphthalene-1-carboxylate (3d)**. Catalyzed by Rh_2[(S)-tfpttl]$_4$ at 0 ^{O}C to give **3d** in 68% isolated yield with 80% *ee*. Colorless oil; $[\alpha]_D^{21\ °C}$ = + 77.5 (c = 0.04, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.42 (s, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.20 – 7.07 (comp, 2H), 6.97 – 6.86 (comp, 2H), 6.77 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.40 (dd, *J* = 2.8, 0.6 Hz, 1H), 4.08 (dd, *J* = 9.8, 6.0 Hz, 1H), 3.83 (s, 3H), 3.73 (s, 3H), 2.84 (dd, *J* = 16.3, 9.8 Hz, 1H), 2.77 (dd, *J* = 16.3, 6.0 Hz, 1H), 1.65 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 172.0, 158.9, 157.4,

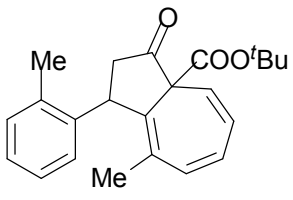
138.6, 134.1, 129.6, 127.5, 125.1, 114.5, 114.0, 111.4, 101.0, 83.0, 55.7, 55.6, 43.5, 37.3, 28.9; HRMS (ESI) for $C_{23}H_{27}O_5$ $[M+H]^+$ calcd 383.1859; found 383.1863. HPLC conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.4 mL/min, Hexane:IPA = 99.5:0.5, major enantiomer t_r = 25.8 min, minor enantiomer t_r = 35.3 min.



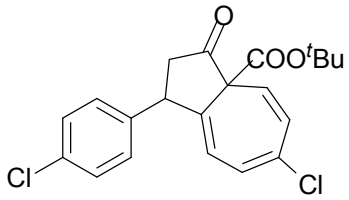
***tert*-Butyl (*R*)-2-Hydroxy-7-methyl-4-(*p*-tolyl)-3,4-dihydronaphthalene-1-carboxylate (3e).** Catalyzed by Rh_2[(S)-tfpttl]$_4$ at 0 ^{O}C to give **3e** in 70% isolated yield with 87% *ee*. Colorless oil; $[\alpha]_D^{21}$ $^{\circ C}$ = + 58.3 (c = 0.13, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.41 (s, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 1H), 6.56 (s, 1H), 3.99 (dd, *J* = 8.8, 6.5 Hz, 1H), 2.75 (dd, *J* = 16.4, 8.8 Hz, 1H), 2.68 (dd, *J* = 16.4, 6.5 Hz, 1H), 2.26 (s, 3H), 2.14 (s, 3H), 1.53 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 171.1, 138.4, 135.8, 135.5, 133.9, 128.8, 127.6, 126.5, 125.5, 100.3, 82.1, 42.6, 36.5, 28.0, 20.5; HRMS (ESI) for $C_{23}H_{27}O_3$ $[M+H]^+$ calcd 351.1960; found 351.1962. HPLC conditions for determination of enantiomeric excess: AD-H column, 254 nm, 0.5 mL/min, Hexane:IPA = 99:1, minor enantiomer t_r = 9.1 min, major enantiomer t_r = 9.9 min.



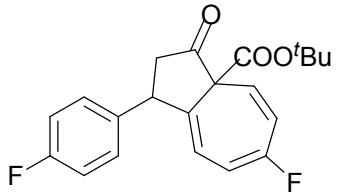
***tert*-Butyl (*R*)-2-Hydroxy-6-methyl-4-(*m*-tolyl)-3,4-dihydronaphthalene-1-carboxylate (3f)**. Catalyzed by Rh_2[(S)-tfpttl]$_4$ at 0 ^{O}C to give **3f** in 78% isolated yield with 80% *ee*. Colorless oil; $[\alpha]_D^{21}$ $^{\circ C}$ = + 45.1 (c = 0.49, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.41 (s, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.16 – 7.12 (m, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.96 – 6.86 (comp, 3H), 6.55 (s, 1H), 3.99 (dd, *J* = 9.2, 6.3 Hz, 1H), 2.76 (dd, *J* = 16.3, 9.2 Hz, 1H), 2.69 (dd, *J* = 16.3, 6.3 Hz, 1H), 2.26 (s, 3H), 2.14 (s, 3H), 1.54 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 170.7, 143.6, 141.1, 137.2, 135.1, 133.6, 128.3, 128.1, 127.6, 127.1, 126.7, 126.1, 125.1, 124.5, 99.9, 81.7, 42.6, 36.1, 27.6, 20.6, 20.1; HRMS (ESI) for $C_{23}H_{27}O_3$ $[M+H]^+$ calcd 351.1960; found 351.1957. HPLC conditions for determination of enantiomeric excess: AD-H column, 254 nm, 0.5 mL/min, Hexane:IPA = 98:2, minor enantiomer t_r = 8.2 min, major enantiomer t_r = 9.2 min.



***tert*-Butyl (1*R*,3a*S*)-8-Methyl-3-oxo-1-(*o*-tolyl)-1,2,3,3a-tetrahydroazulene-3a-carboxylate (2g).** Catalyzed by Rh_2[(S)-tfpttl]$_4$ at 0 ^{O}C to give **2g** in 80% isolated yield with 72% *ee*. Colorless oil; $[\alpha]_D^{21}$ $^{\circ C}$ = + 50.1 (c = 0.09, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 7.1 Hz, 1H), 7.12 – 6.97 (comp, 2H), 6.77 (dd, *J* = 7.1, 1.2 Hz, 1H), 6.55 – 6.32 (comp, 3H), 5.47 – 5.38 (m, 1H), 4.67 (dd, *J* = 10.9, 3.8 Hz, 1H), 3.43 (dd, *J* = 18.2, 10.9 Hz, 1H), 2.40 (s, 3H), 2.32 (dd, *J* = 18.2, 3.8 Hz, 1H), 1.68 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.9, 165.4, 140.8, 134.3, 132.5, 130.0, 129.6, 128.1, 126.1, 125.8, 125.7, 125.6, 81.4, 62.3, 44.7, 40.3, 26.7, 19.1, 18.4; HRMS (ESI) for $C_{23}H_{27}O_3$ $[M+H]^+$ calcd 351.1960; found 351.1964. HPLC conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.3 mL/min, Hexane:IPA = 98:2, minor enantiomer t_r = 20.7 min, major enantiomer t_r = 22.3 min.

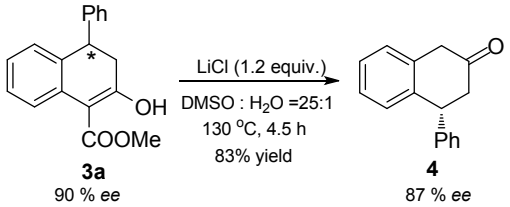


***tert*-Butyl (1*R*,3a*S*)-6-Chloro-1-(4-chlorophenyl)-3-oxo-1,2,3,3a-tetrahydroazulene-3a-carboxylate (2h).** Catalyzed by Rh_2[(S)-tfpttl]$_4$ at 0 ^{O}C to give **2h** in 70% isolated yield with 97% *ee*. Colorless solid; $[\alpha]_D^{21}$ $^{\circ C}$ = - 77.1 (c = 0.14, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.20 (m, 1H), 7.19 – 7.18 (m, 1H), 6.99 – 6.93 (comp, 2H), 6.52 (d, *J* = 7.1 Hz, 1H), 6.37 (dd, *J* = 10.2, 1.4 Hz, 1H), 5.92 (dd, *J* = 7.1, 1.4 Hz, 1H), 5.42 (d, *J* = 10.2 Hz, 1H), 4.41 (t, *J* = 8.1 Hz, 1H), 3.16 (dd, *J* = 18.3, 8.1 Hz, 1H), 2.45 (dd, *J* = 18.3, 8.1 Hz, 1H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.4, 166.2, 143.6, 141.7, 135.1, 133.3, 130.8, 129.6, 129.5, 128.1, 123.1, 122.7, 83.6, 65.5, 47.1, 46.0, 28.0; HRMS (ESI) for $C_{21}H_{21}Cl_2O_3$ $[M+H]^+$ calcd 391.0868; found 391.0873. HPLC conditions for determination of enantiomeric excess: OD-H column, 230 nm, 0.5 mL/min, Hexane:IPA = 98:2, major enantiomer t_r = 17.4 min, minor enantiomer t_r = 19.3 min.



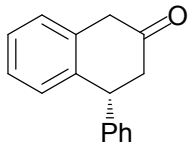
***tert*-Butyl (1*R*,3a*S*)-6-Fluoro-1-(4-fluorophenyl)-3-oxo-1,2,3,3a-tetrahydroazulene-3a-carboxylate (2i).** Catalyzed by Rh_2[(S)-tfpttl]$_4$ at 0 ^{O}C to give **2i** in 74% isolated yield with 97% *ee*. White solid; $[\alpha]_D^{21}$ $^{\circ C}$ = - 141.3 (c = 0.16, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 7.09 (comp, 2H), 7.05 – 6.98 (comp, 2H), 6.48 (ddd, *J* = 15.1, 10.8, 3.3 Hz, 1H), 6.17 (dd, *J* = 15.1, 7.6 Hz, 1H), 6.01 (ddd, *J* = 7.6, 5.3, 3.3 Hz, 1H), 5.64 (dd, *J* = 10.8, 5.3 Hz, 1H), 4.53 (t, *J* = 8.9 Hz, 1H), 3.26 (dd, *J* = 18.4, 8.9 Hz, 1H), 2.53 (dd, *J* = 18.4, 8.9 Hz, 1H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.4, 164.9, 162.0, 161.3, 159.5, 158.8, 139.3, 137.7, 128.5, 128.4, 123.2, 123.0, 122.8, 122.4 , 119.6, 119.4, 114.9, 114.7, 109.1, 108.8, 82.2, 64.4, 45.9, 44.6, 26.7; HRMS (ESI) for $C_{21}H_{21}F_2O_3$ $[M+H]^+$ calcd 359.1459; found 359.1454. HPLC conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.5 mL/min, Hexane:IPA = 98:2, major enantiomer t_r = 16.0 min, minor enantiomer t_r = 18.4 min.

General Procedure for the Synthesis of (*R*)-4-Phenyl-3,4-dihydronaphthalen-2(1*H*)-one



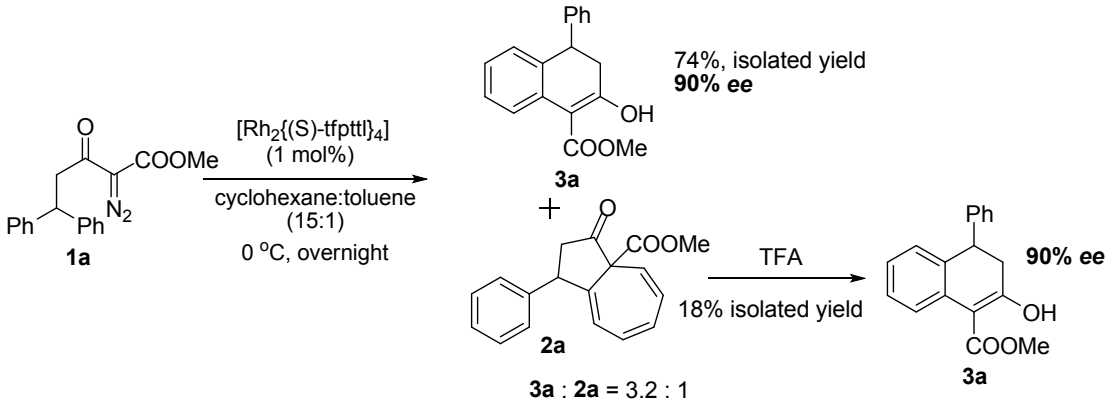
3a 90 % *ee* **4** 87 % *ee*

Compound **3a** (1.5 mmol) was dissolved in 5.2 mL of solvent (DMSO:H_2O = 25:1), followed by addition of lithium chloride (1.8 mmol, 1.2 equiv.). The reaction was allowed to reflux for 4.5 h during which the color of the reaction solution turned from colorless to yellow. The crude material was filtered through a silica gel plug (eluent cyclohexane-ethyl acetate, 7:3), and the resulting yellow oil was purified by Kugelrohr distillation obtaining a light yellow oil.



(*R*)-4-Phenyl-3,4-dihydronaphthalen-2(1*H*)-one (4). Catalyzed by Rh_2[(S)-tfpttl]$_4$ at 0 ^{O}C to give **4** in 83% isolated yield with 87% *ee*. Light yellow oil; $[\alpha]_D^{21\ °C}$ = + 16.2 (c = 0.70, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 1H), 7.19 – 7.04 (comp, 7H), 6.93 – 6.91 (m, 1H), 4.37 (t, *J* = 6.6 Hz, 1H), 3.56 (dd, *J* = 20.0, 6.6 Hz, 2H), 2.89 – 2.78 (comp, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.6, 142.5, 136.4, 132.4, 128.0, 127.7, 127.2, 127.0, 126.4, 126.2, 126.1, 44.9, 44.0, 43.7; HRMS (ESI) for $C_{16}H_{15}O$ $[M+H]^+$ calcd 223.1123; found 223.1119. HPLC conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.5 mL/min, Hexane:IPA = 90:10, minor enantiomer t_r = 19.2 min, major enantiomer t_r = 26.5 min.

Determination of Enantioselectivity for 2a and 3a



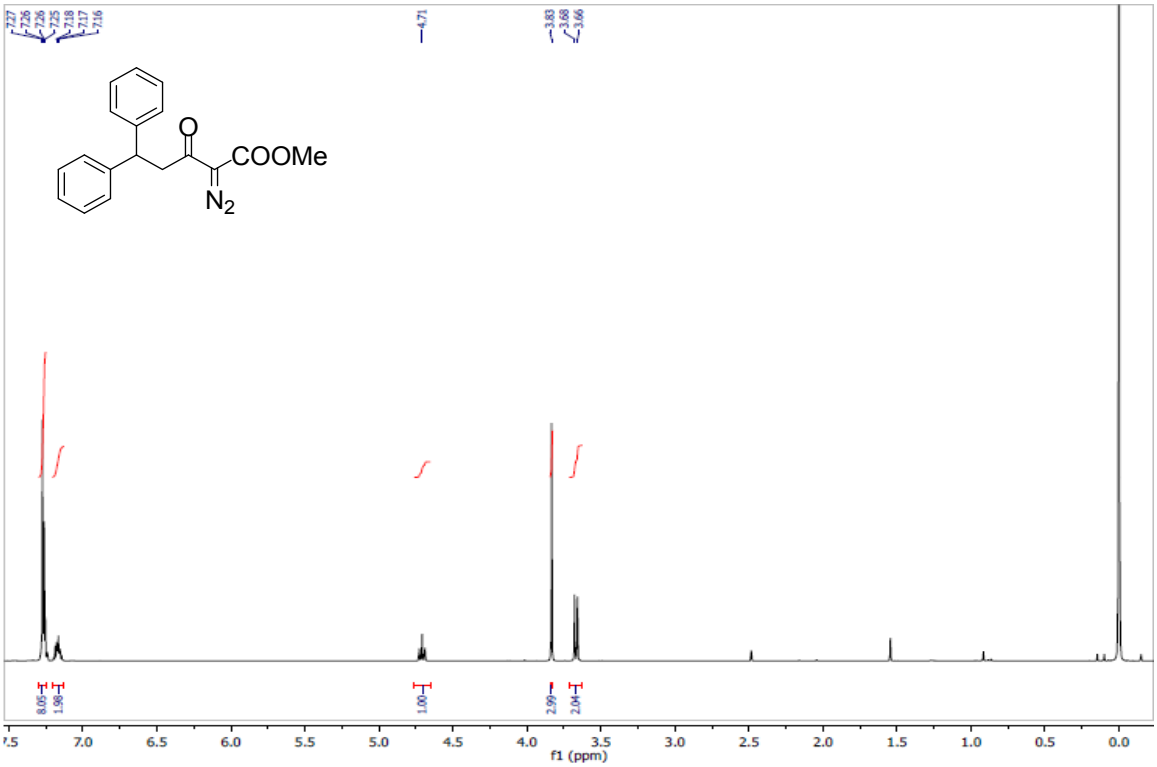
δ,δ-Diaryldiazoacetoacetates **1a** (0.15 mmol) in 1.2 mL solvent (cyclohexane: toluene = 15:1) was added over 1h by a syringe pump at 0 °C to 0.4 mL solvent of Rh_2[(*S*)-tfpttl]$_4$ (0.0015 mmol). After 6 h of reaction time at 0 °C**,** the reaction mixture was purified by column chromatography on silica gel (eluent: hexanes/EtOAc/TEA = 100:5:0.5) to give the corresponding product **2a** (18% yield) and **3a** (74% yield) separately. Enantiomeric excess of isolated compound **3a** was determined by HPLC using Daicel Chiralcel AD-H column (**3a**, 90% *ee*). Isolated compound **2a** was treated with TFA (1.5 equiv.) to generate **3a** for enantioselectivity determination (**2a**, 90% *ee*).

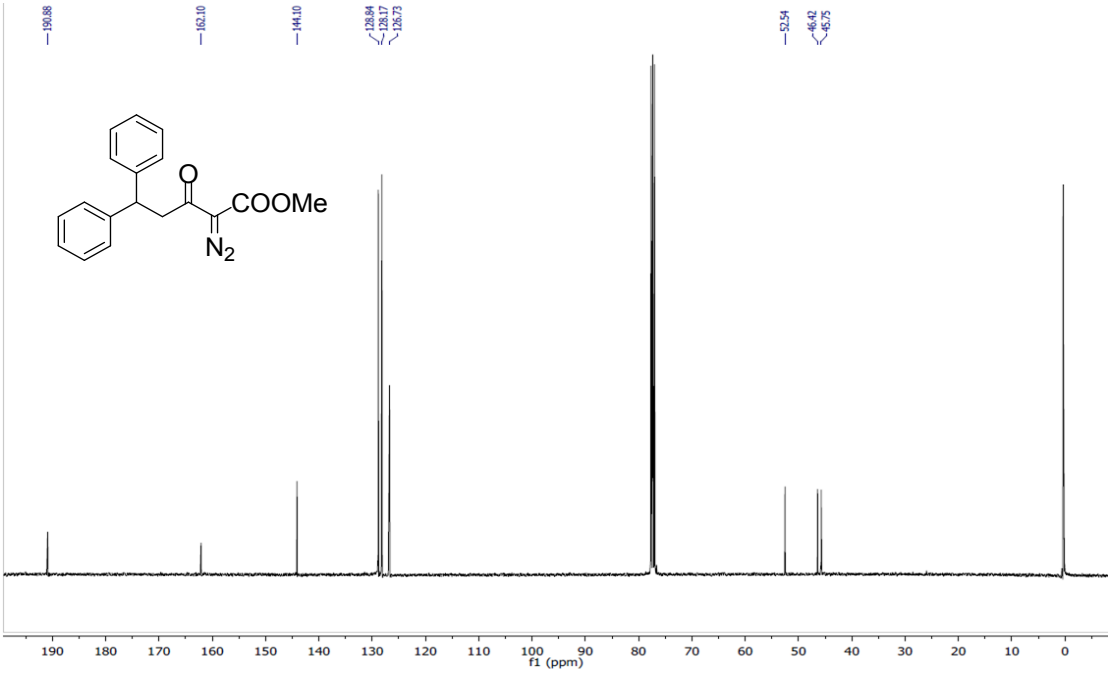
References

[1] (a) S. Hashimoto, N. Watanabe, T. Sato, M. Shiro, S. Ikegami, *Tetrahedron Lett.* 1993, **34**, 5109.
(b) H. Tsutsui, T. Abe, S. Nakamura, M. Anada, S. Hashimoto, *Chem. Pharm. Bull.* 2005, **53**, 1366;
(c) S. Kitagaki, M. Anada, O. Kataoka, K. Matsuno, C. Umeda, N. Watanabe, S. Hashimoto, *J. Am. Chem. Soc.* 1999, **121**, 1417.
[2] H. Tsutsui, Y. Yamaguchi, S. Kitagaki, S. Nakamura, S. Hashimoto. *Tetrahedron: Asymmetry*, 2003, **14**, 817.
[3] X. Liu, X. Liu, C. S. Shanahan, X. Xu, M. P. Doyle. *Org. & Biomol. Chem.* 2014, **12**, 5227.
[4] H. M. L. Davies, G. Ahmed, M. R. Churchill, *J. Am. Chem. Soc.* 1996, **118**, 10774.

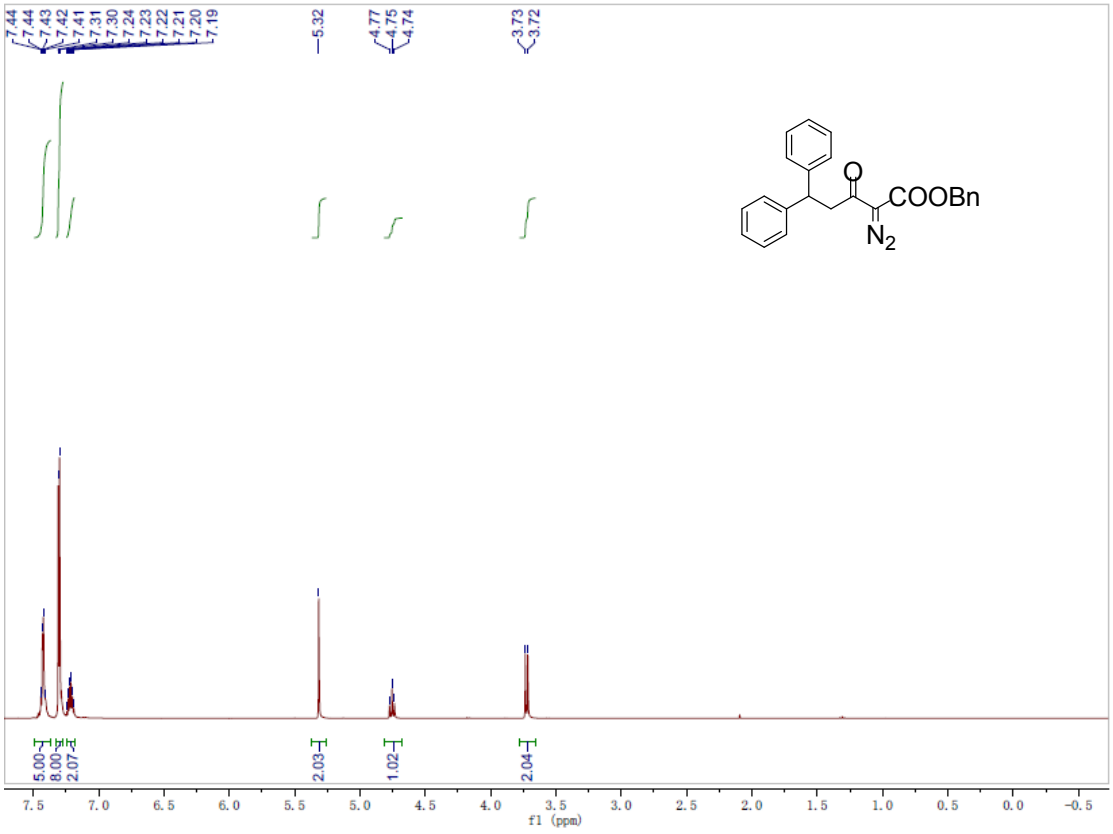
NMR Spectra

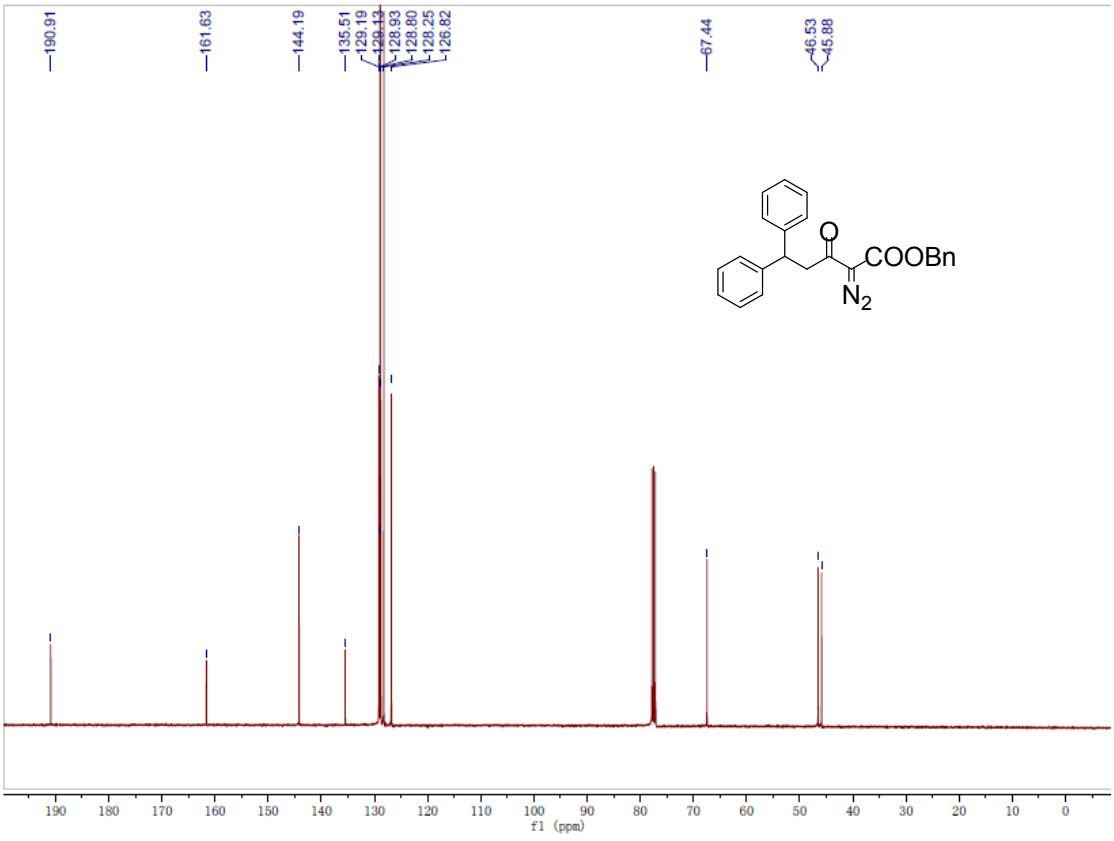
Methyl 2-Diazo-3-oxo-5,5-diphenylpentanoate (1a)



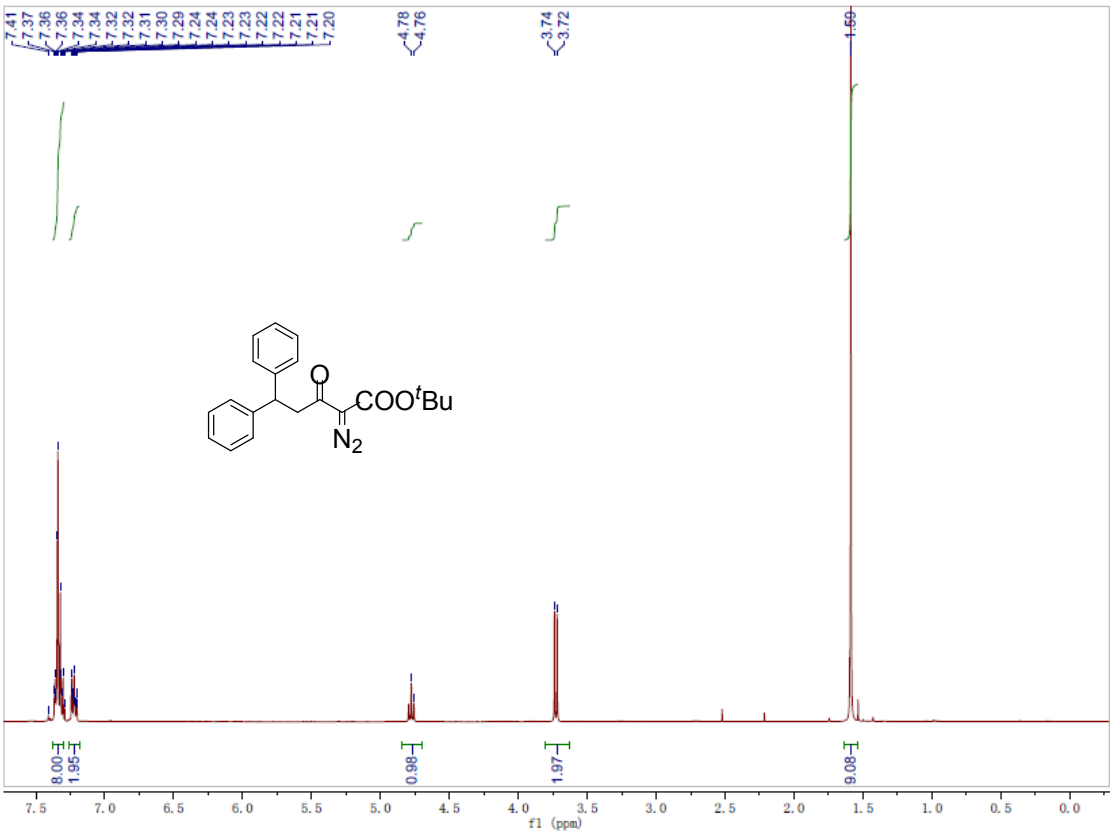


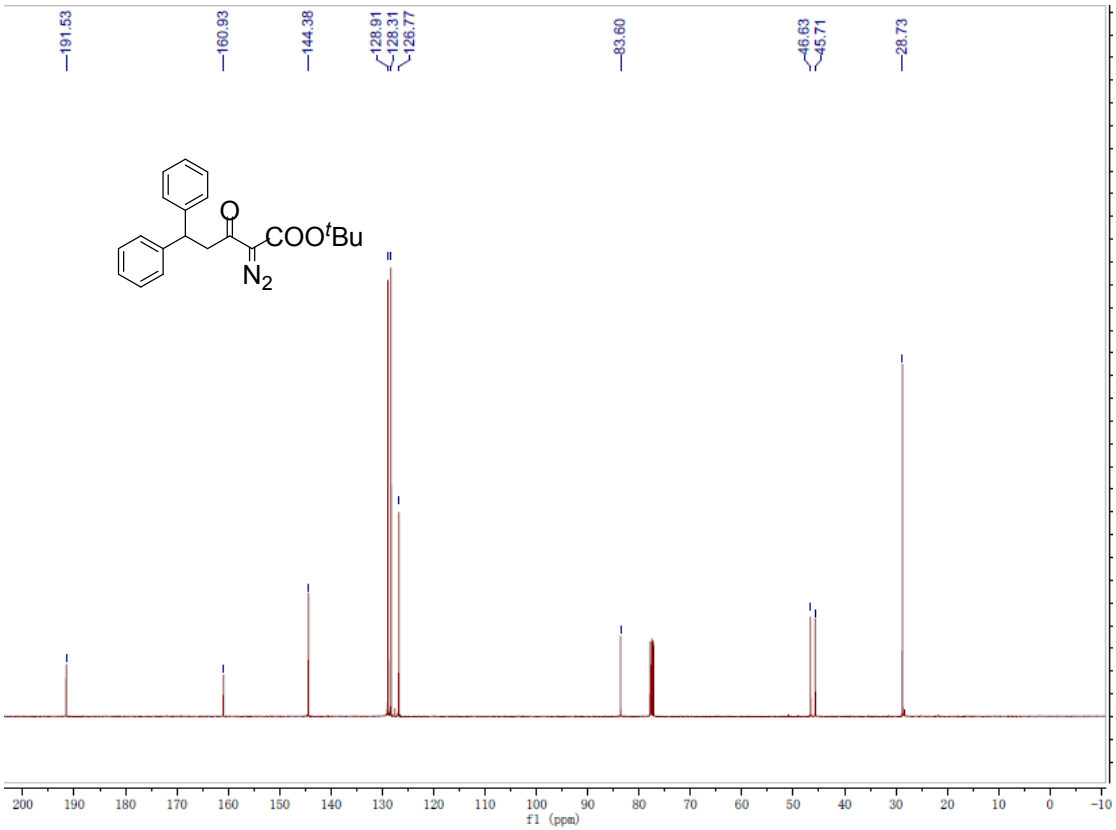
Benzyl 2-Diazo-3-oxo-5,5-diphenylpentanoate (1b)



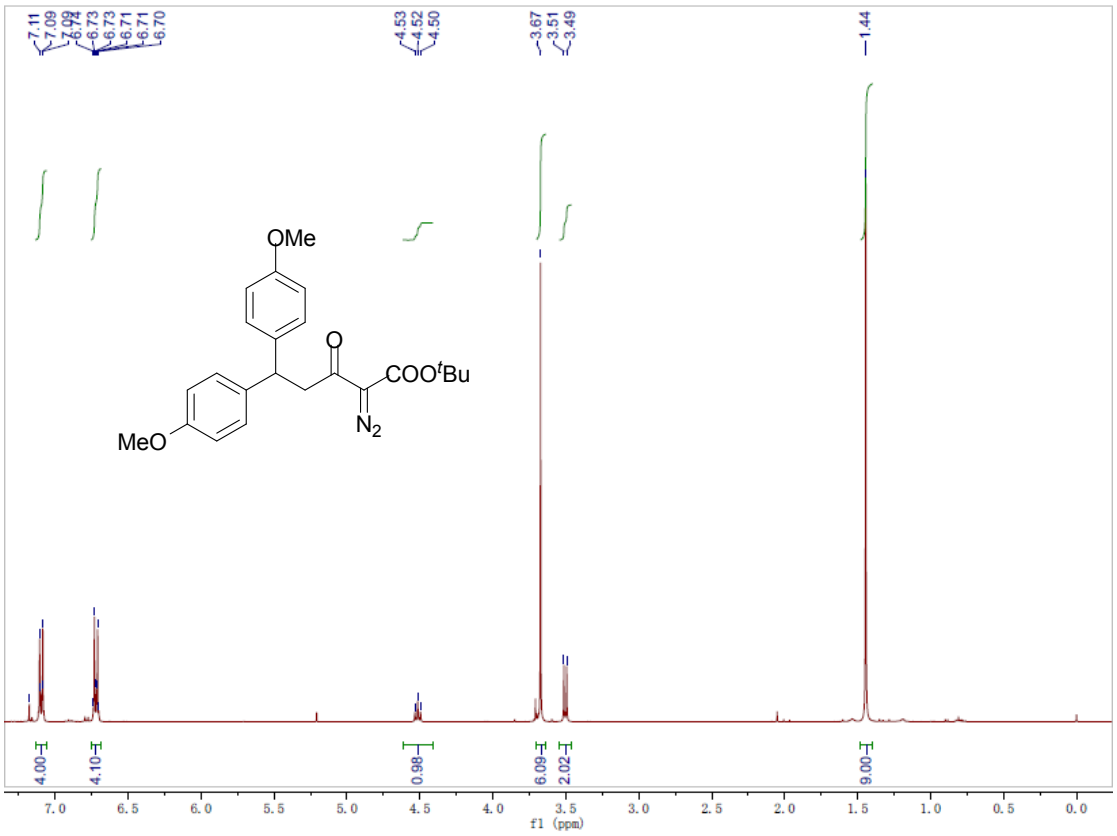


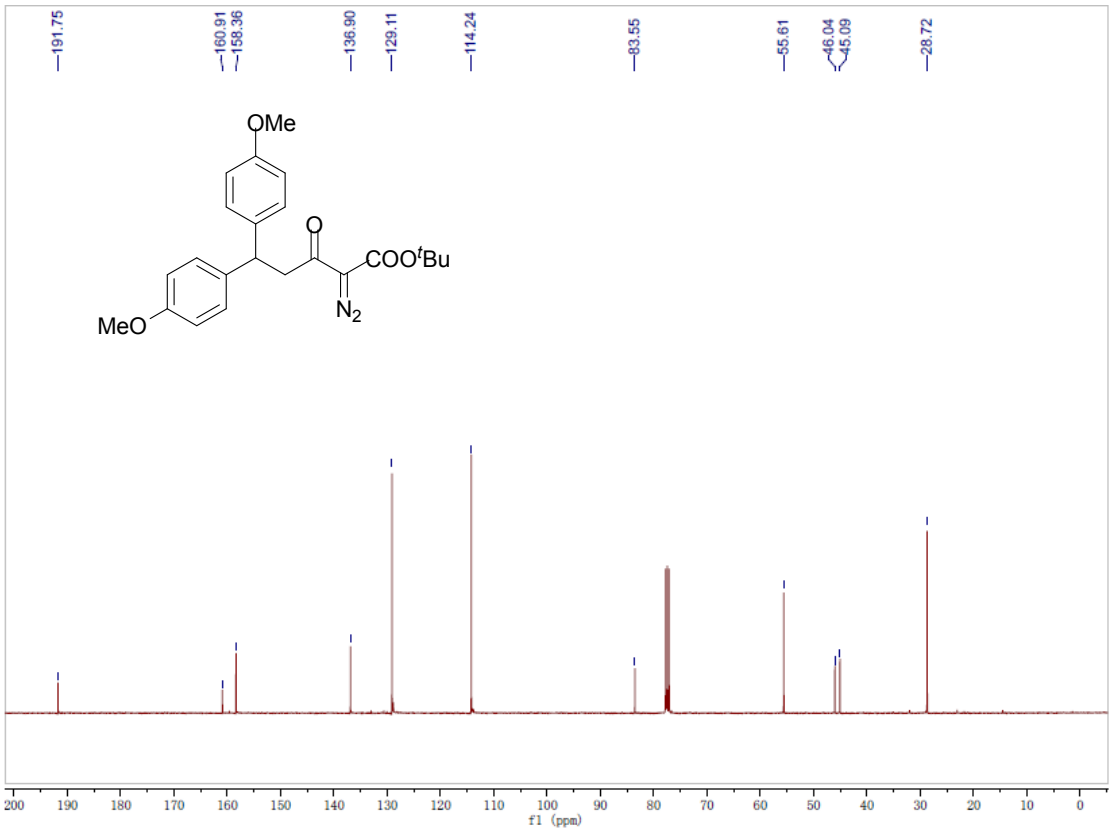
***tert*-Butyl 2-Diazo-3-oxo-5,5-diphenylpentanoate (1c)**



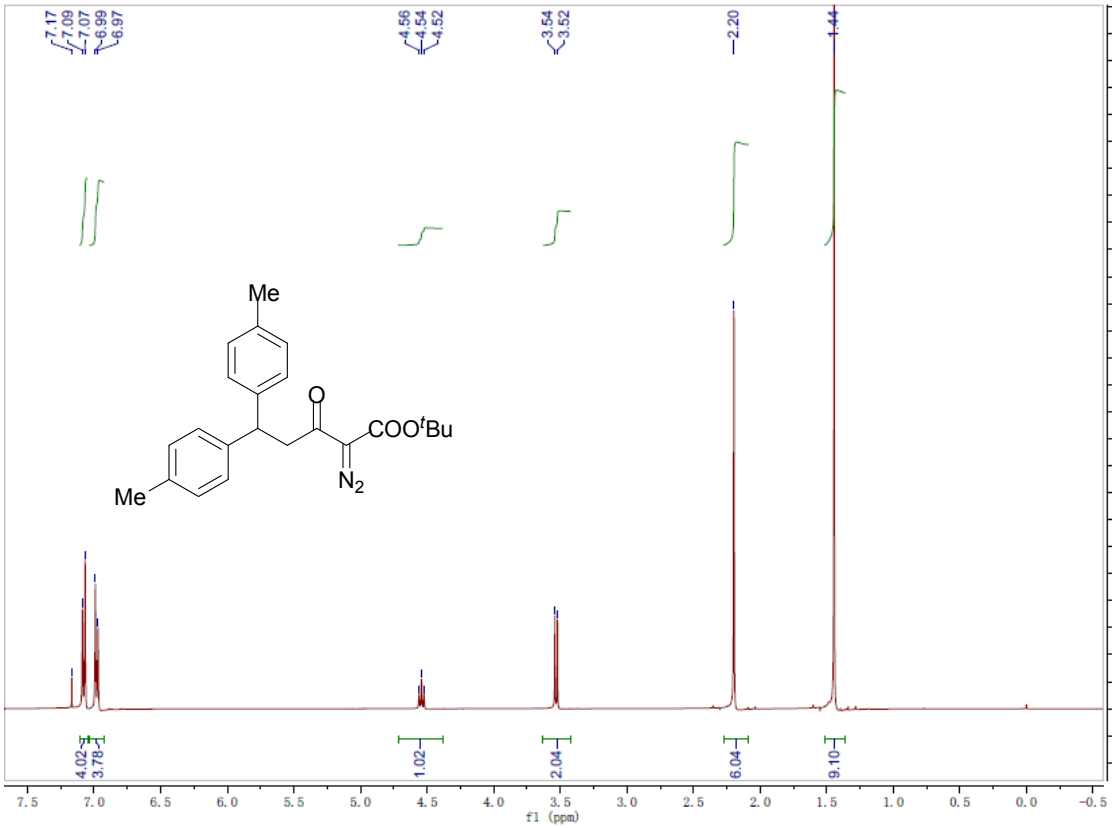


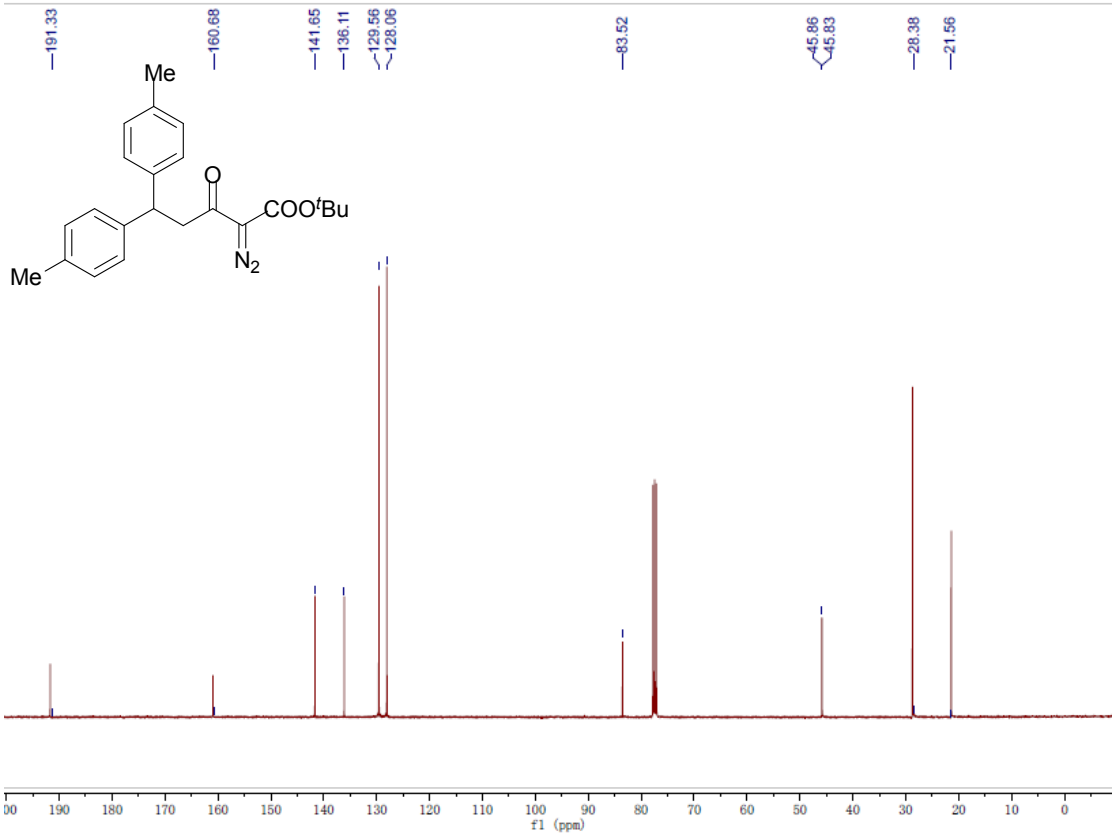
***tert*-Butyl 2-Diazo-3-oxo-5,5-di–*p*-anisyl pentanoate (1d)**



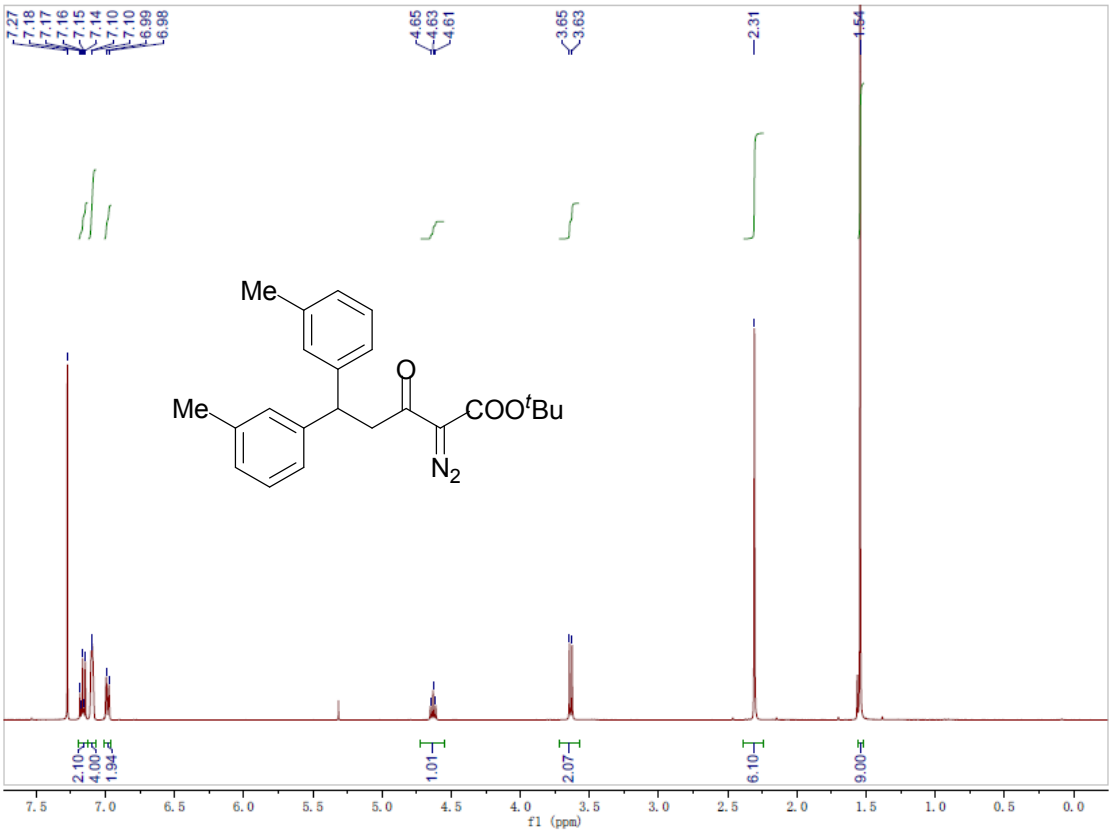


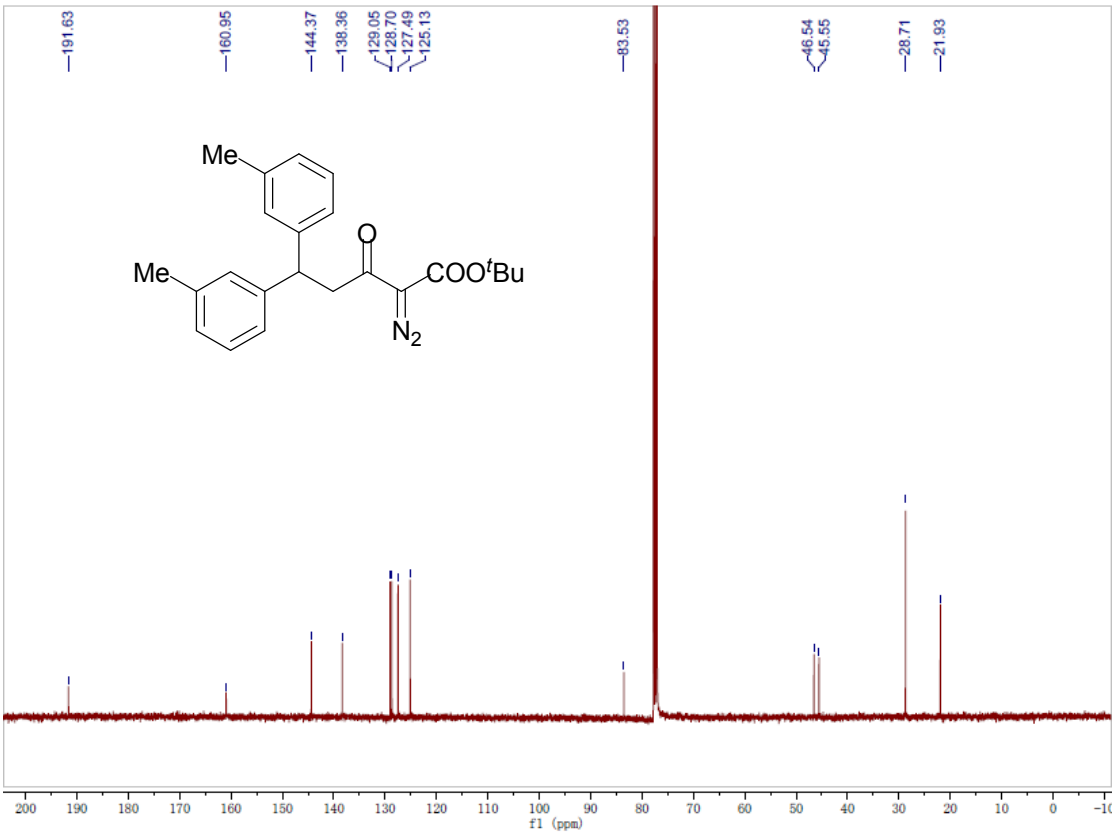
***tert*-Butyl 2-Diazo-3-oxo-5,5-di-*p*-tolylpentanoate (1e)**



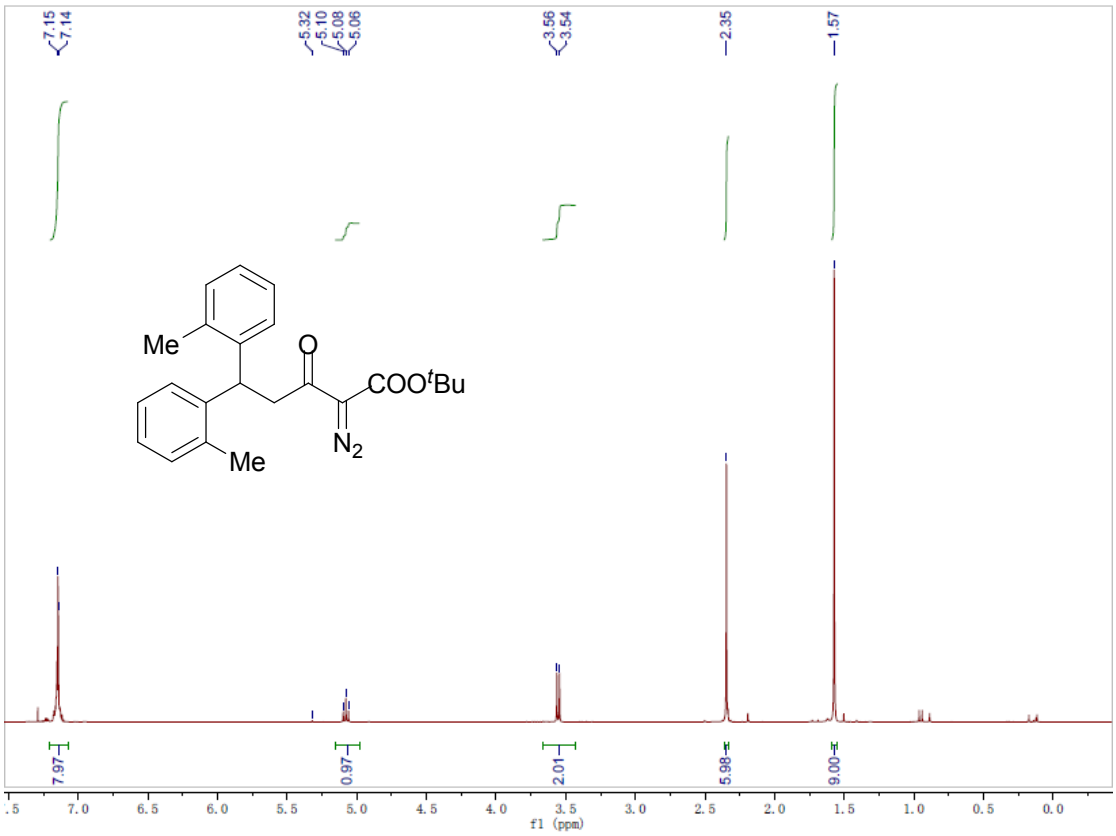


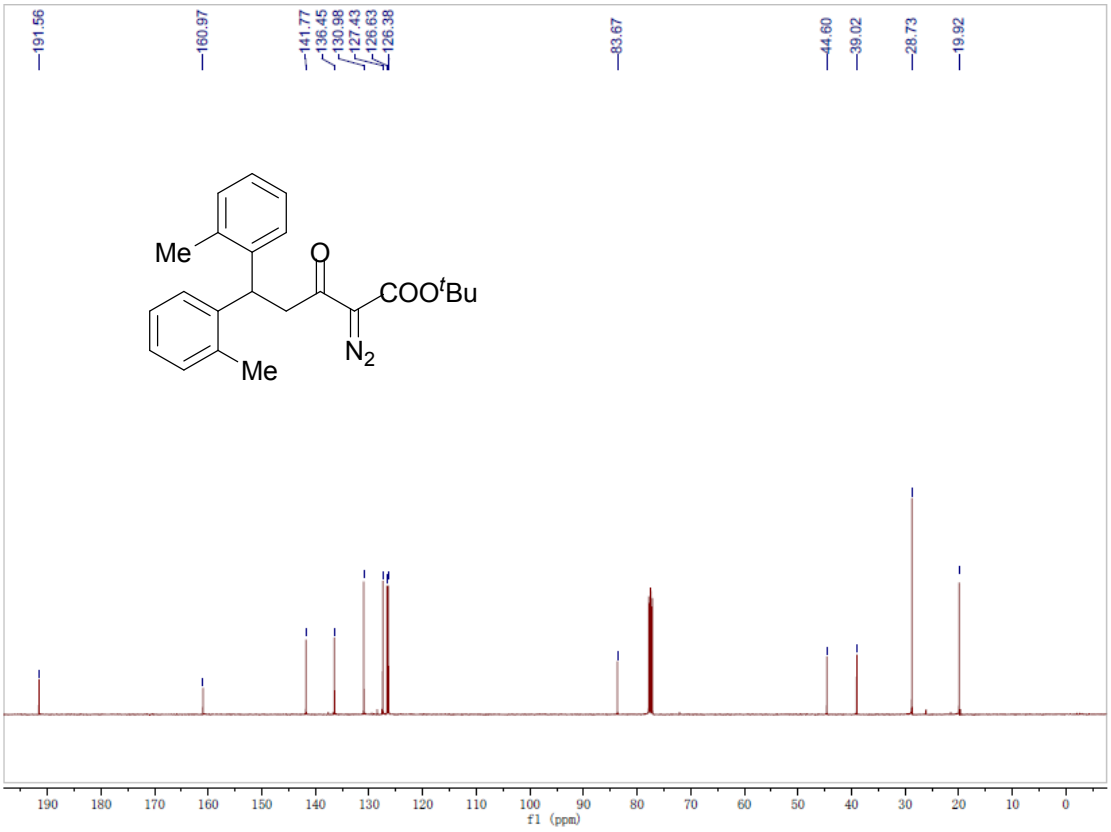
***tert*-Butyl 2-Diazo-3-oxo-5,5-di-*m*-tolylpentanoate (1f)**



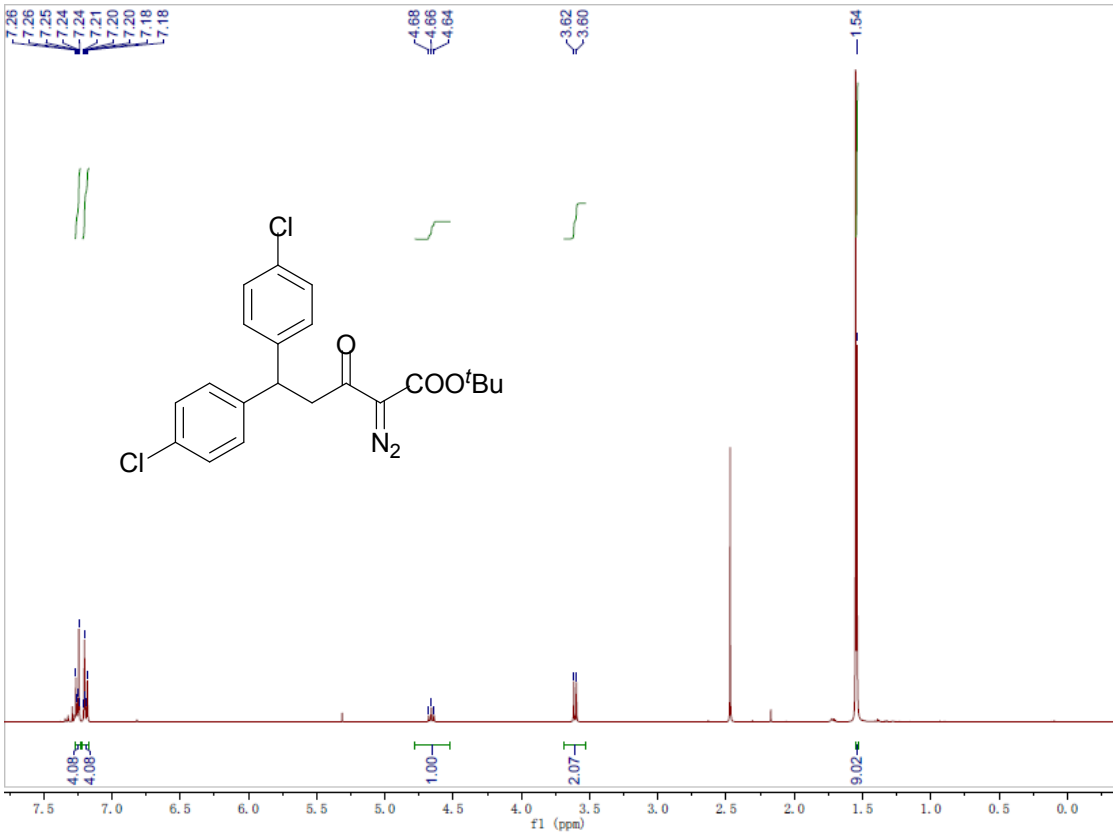


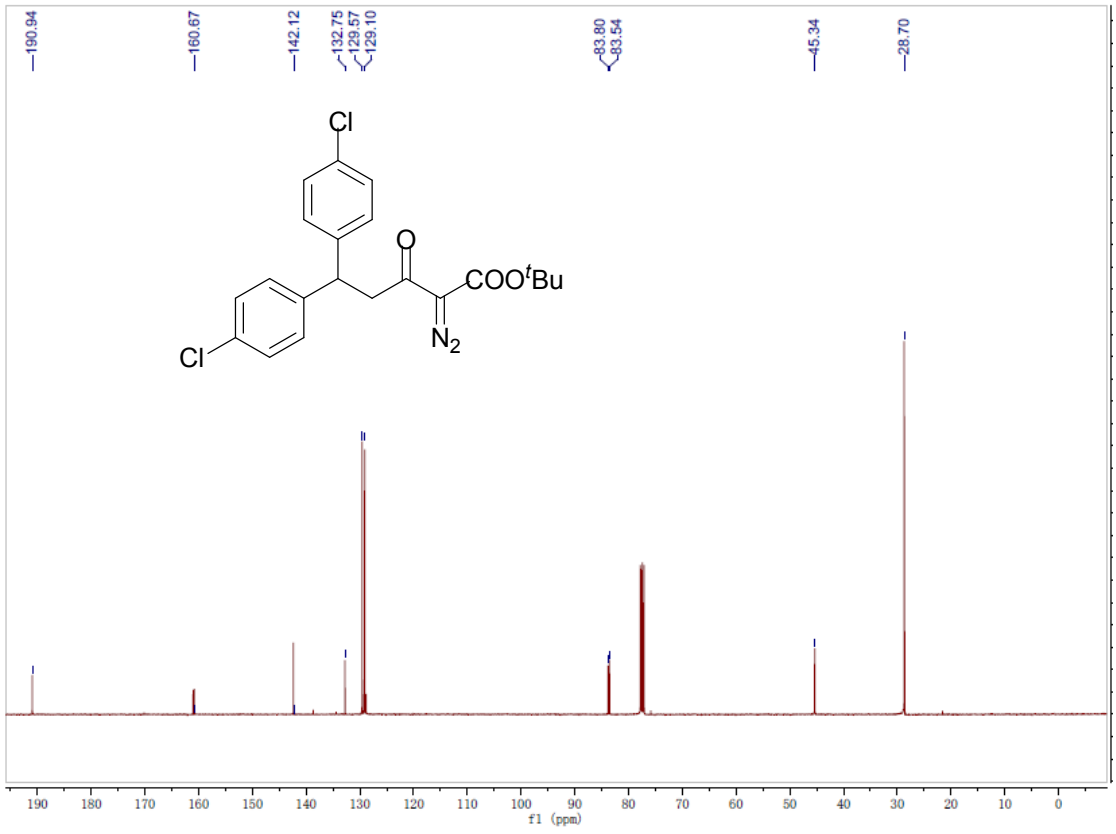
***tert*-Butyl 2-Diazo-3-oxo-5,5-di-*o*-tolylpentanoate (1g)**



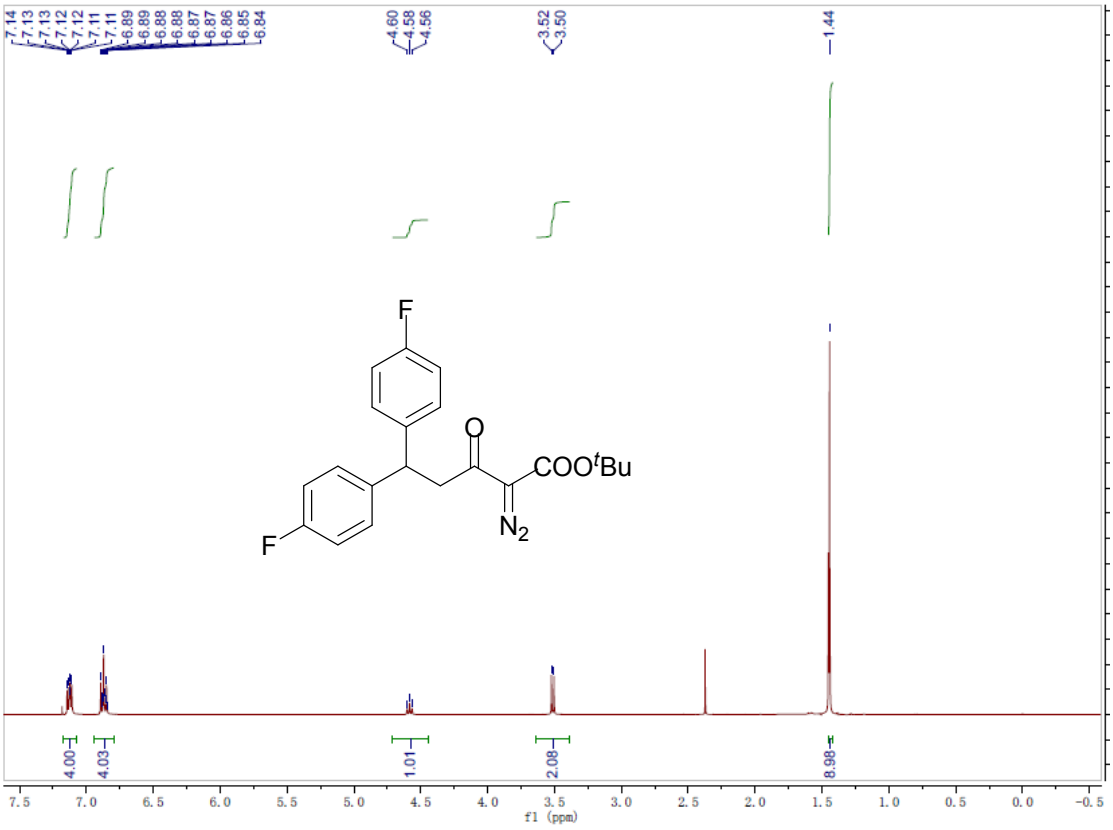


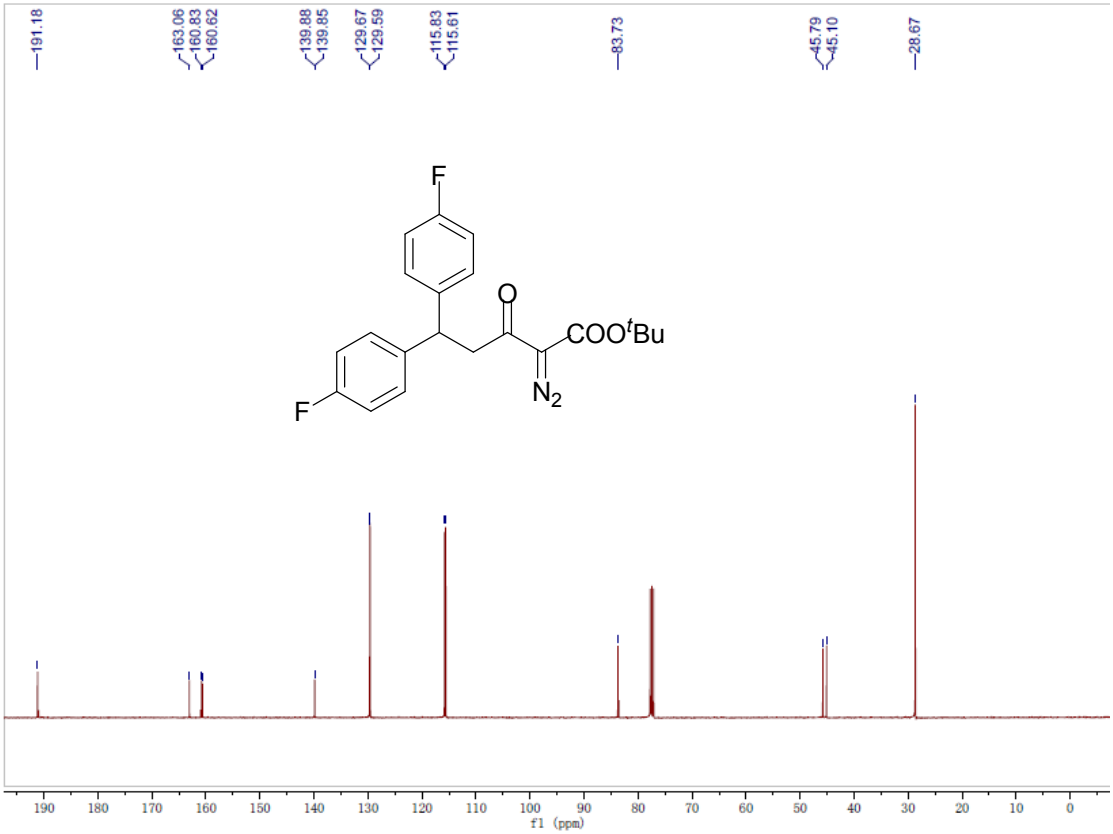
***tert*-Butyl 2-Diazo-3-oxo-5,5-di-*p*-chlorophenylpentanoate (1h)**



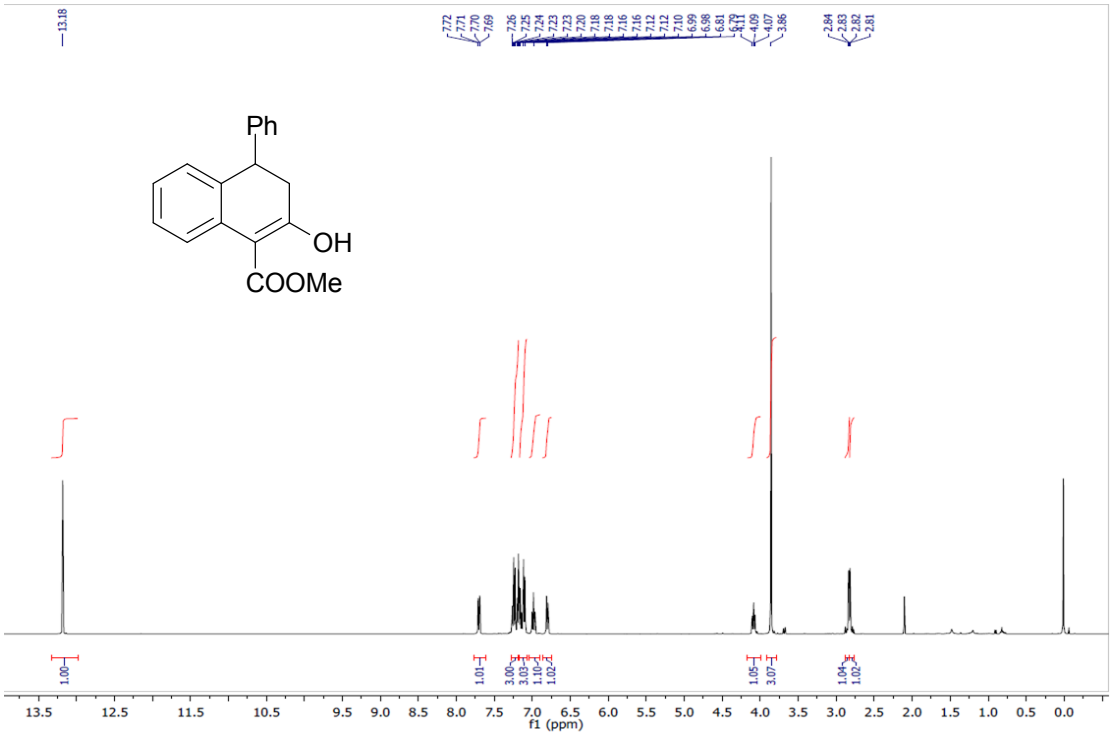


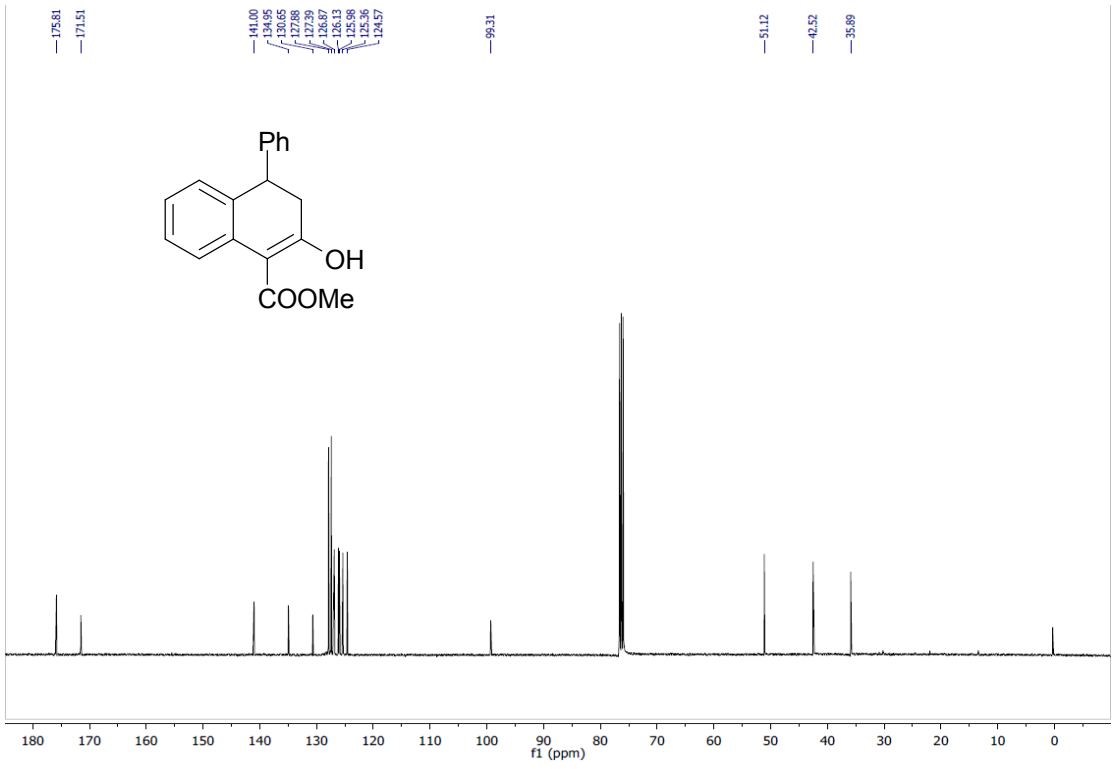
***tert*-Butyl 2-Diazo-3-oxo-5,5-di-*p*-fluorophenylpentanoate (1i)**



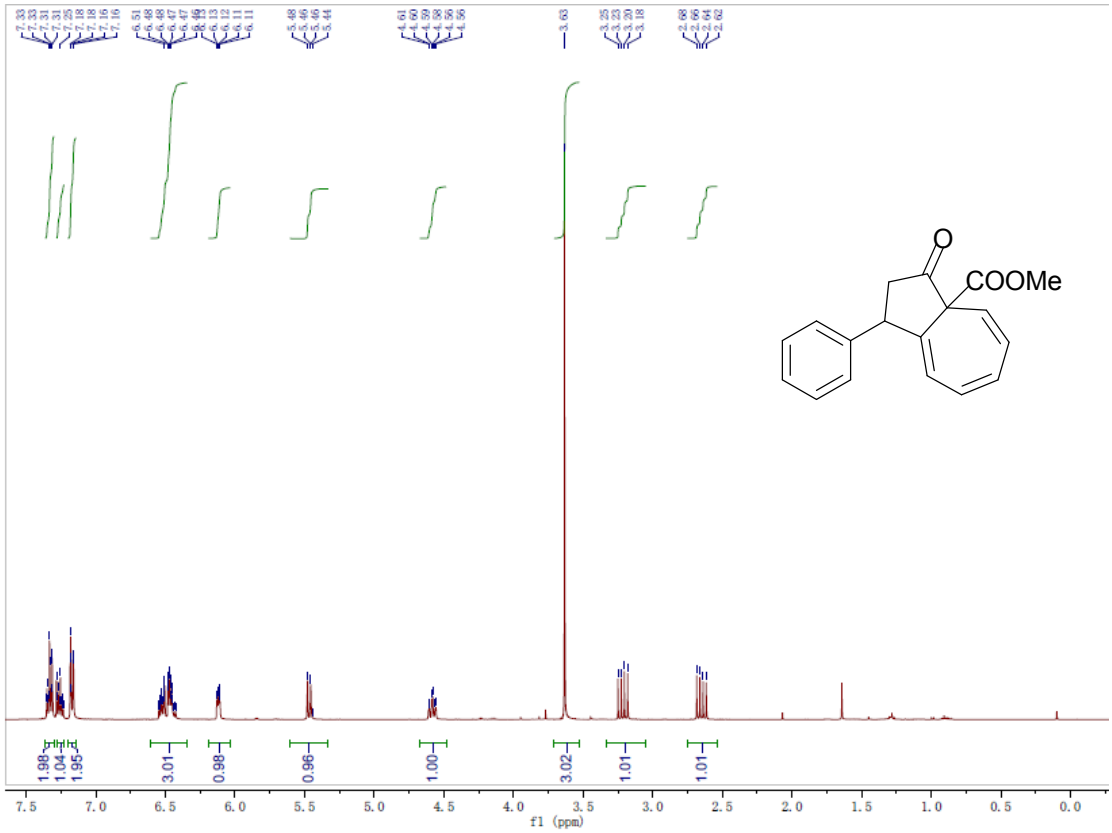


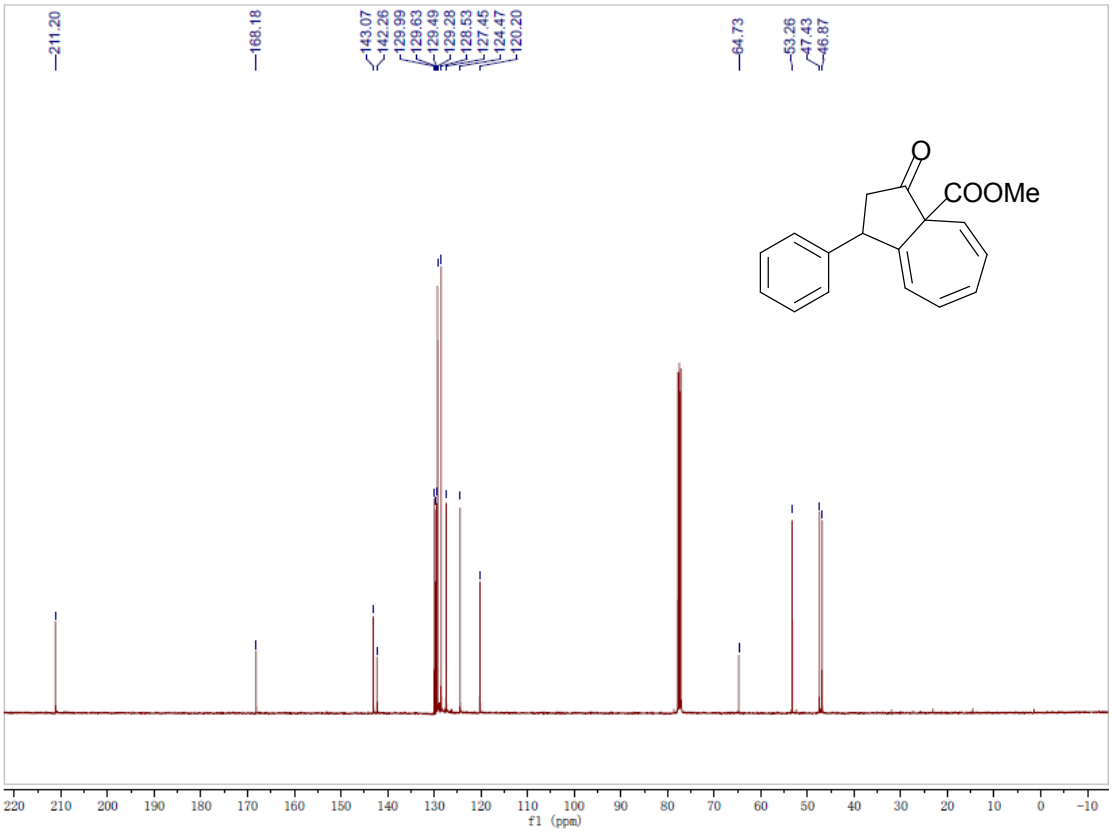
Methyl (*R*)-2-Hydroxy-4-phenyl-3,4-dihydronaphthalene-1-carboxylate (3a)



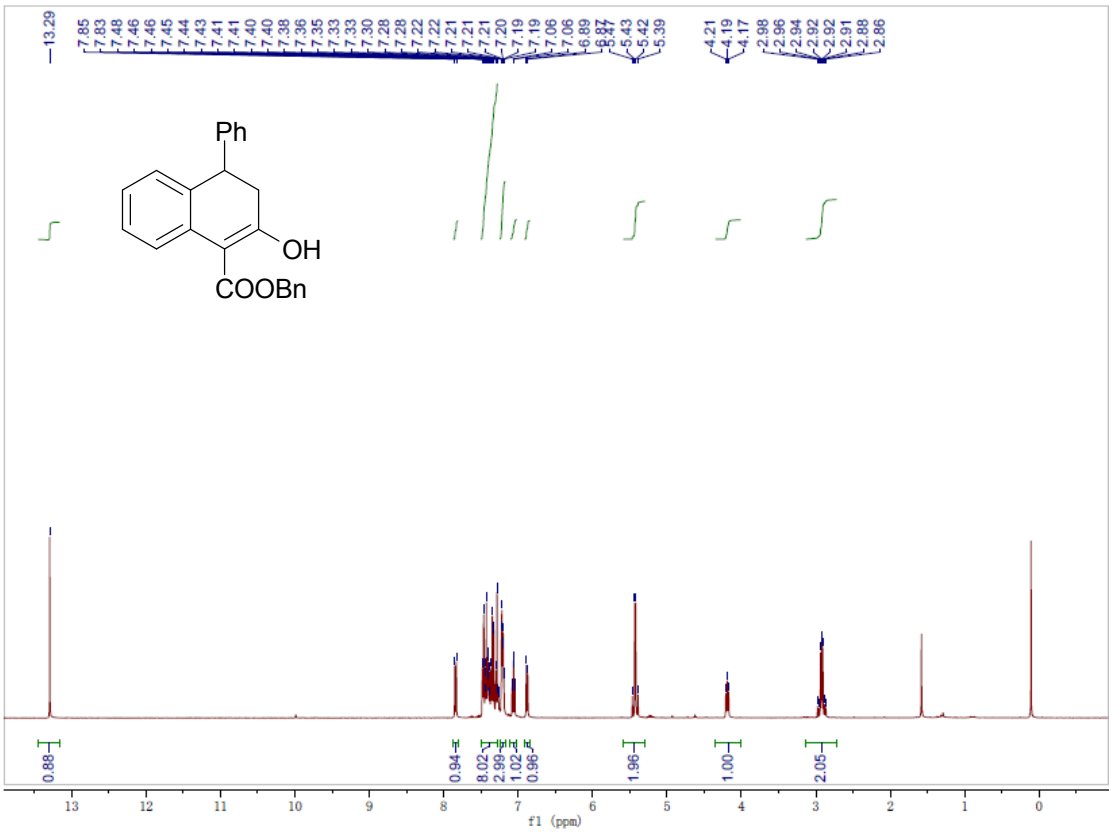


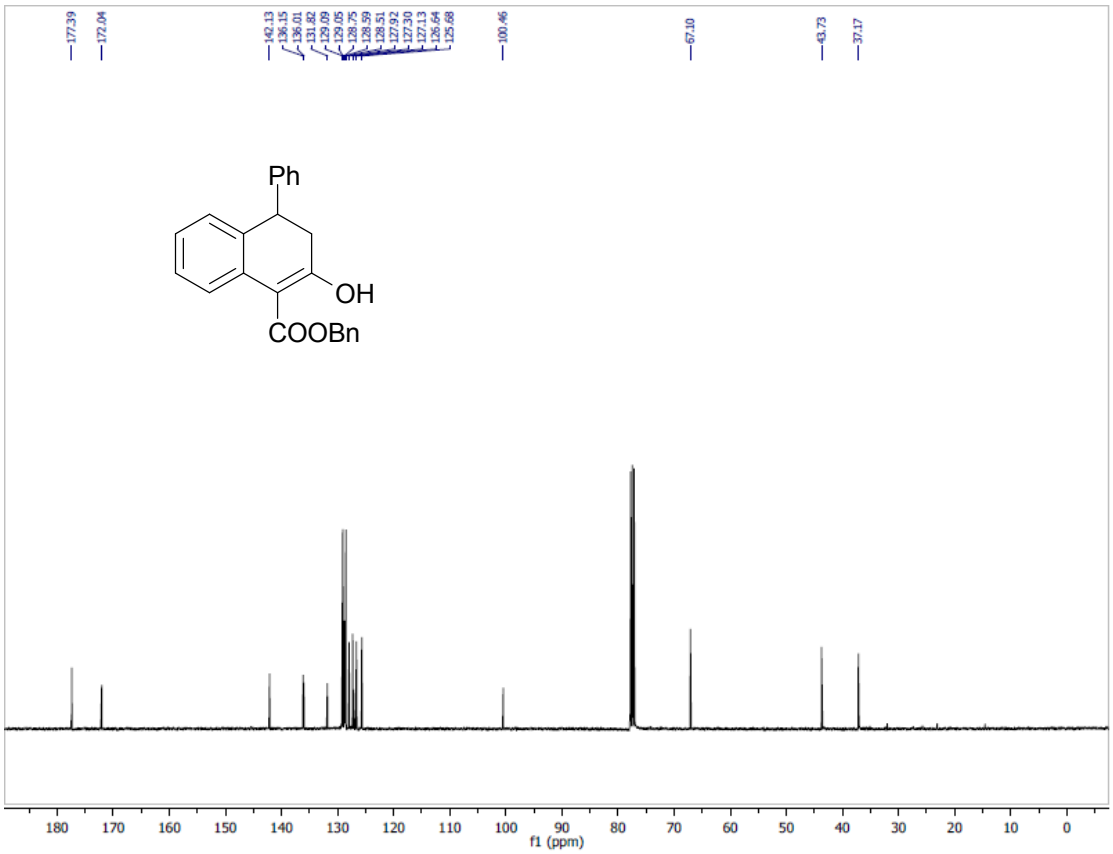
Methyl (1*R*,3a*S*)-3-Oxo-1-phenyl-1,2,3,3a-tetrahydroazulene-3a-carboxylate (2a)



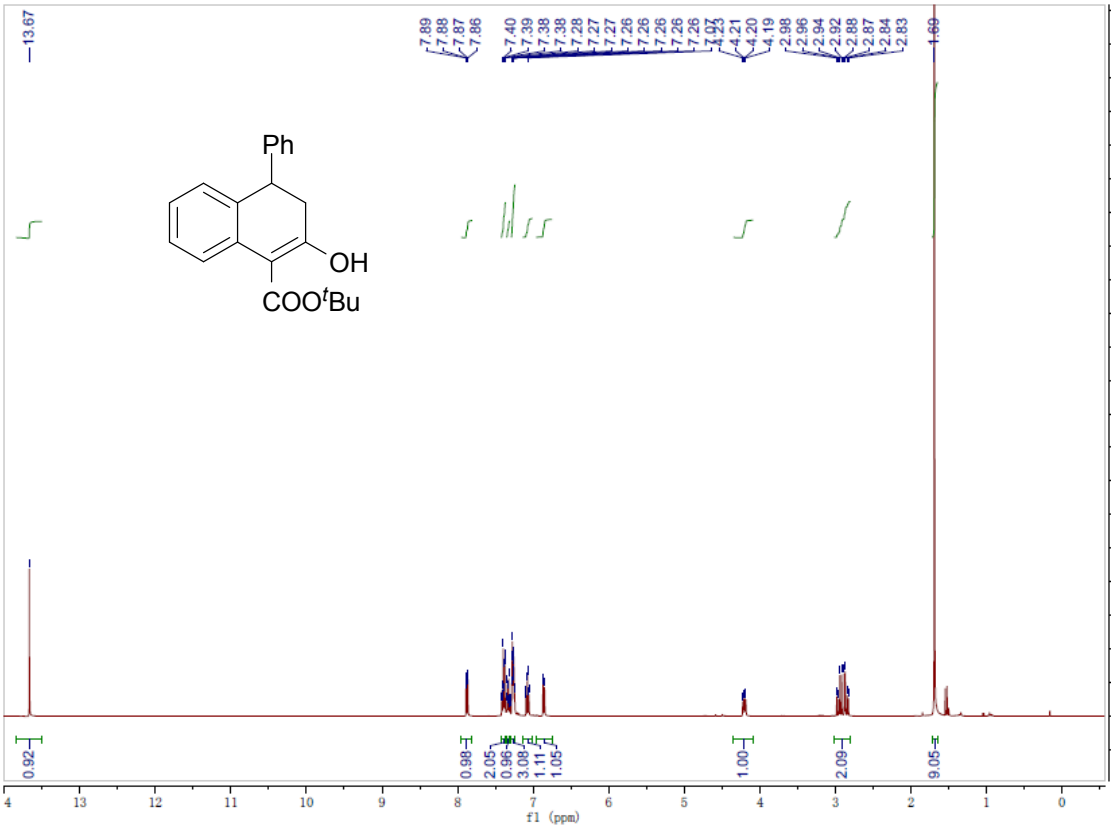


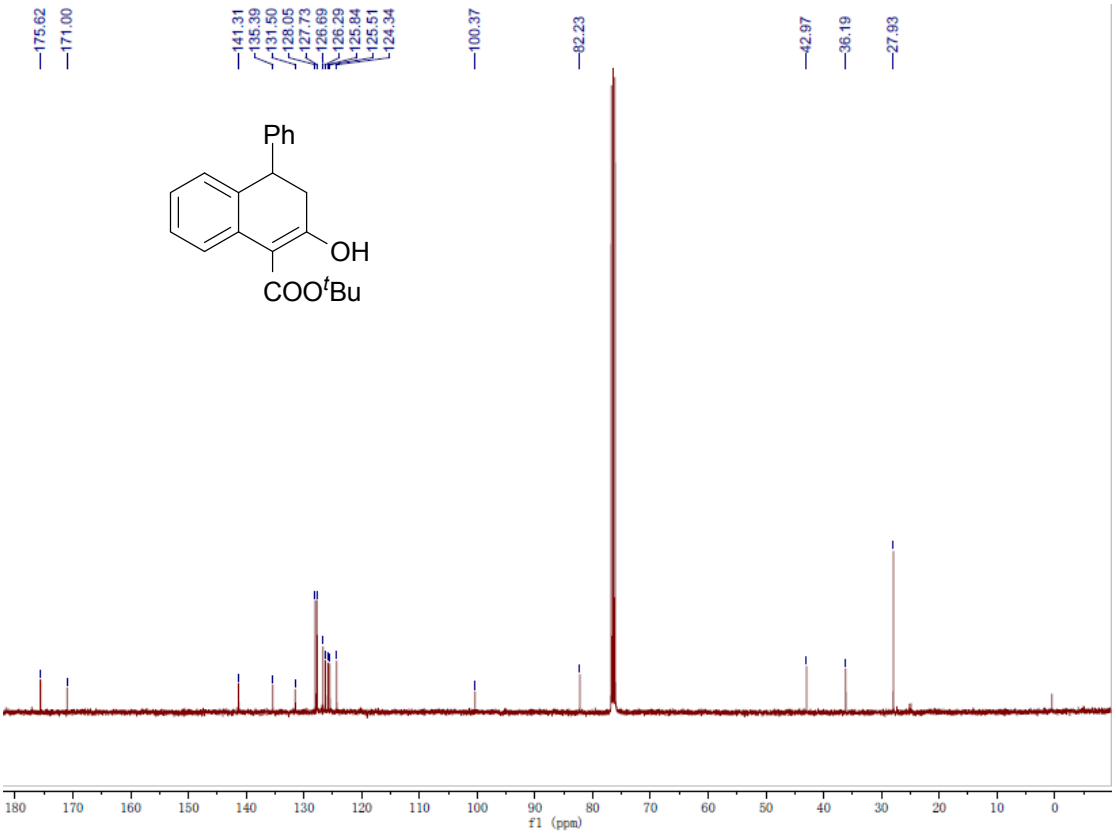
Benzyl (*R*)-2-Hydroxy-4-phenyl-3,4-dihydronaphthalene-1-carboxylate (3b)



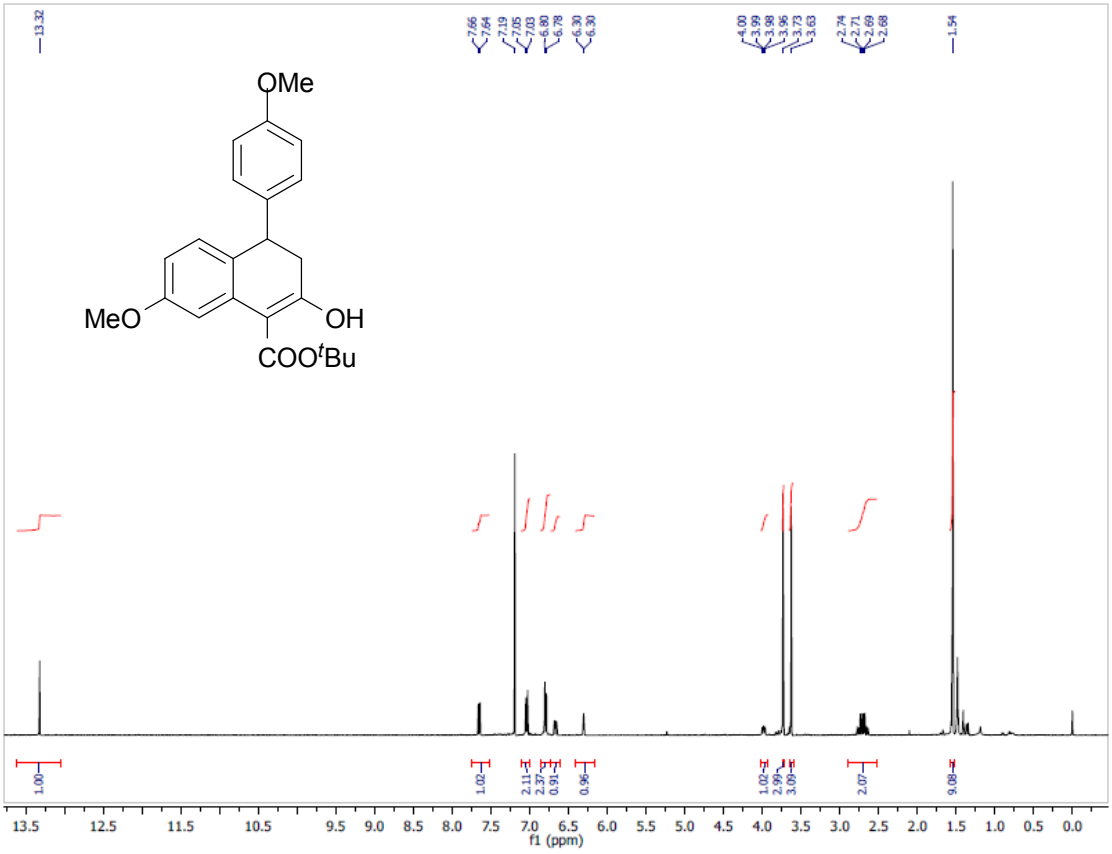


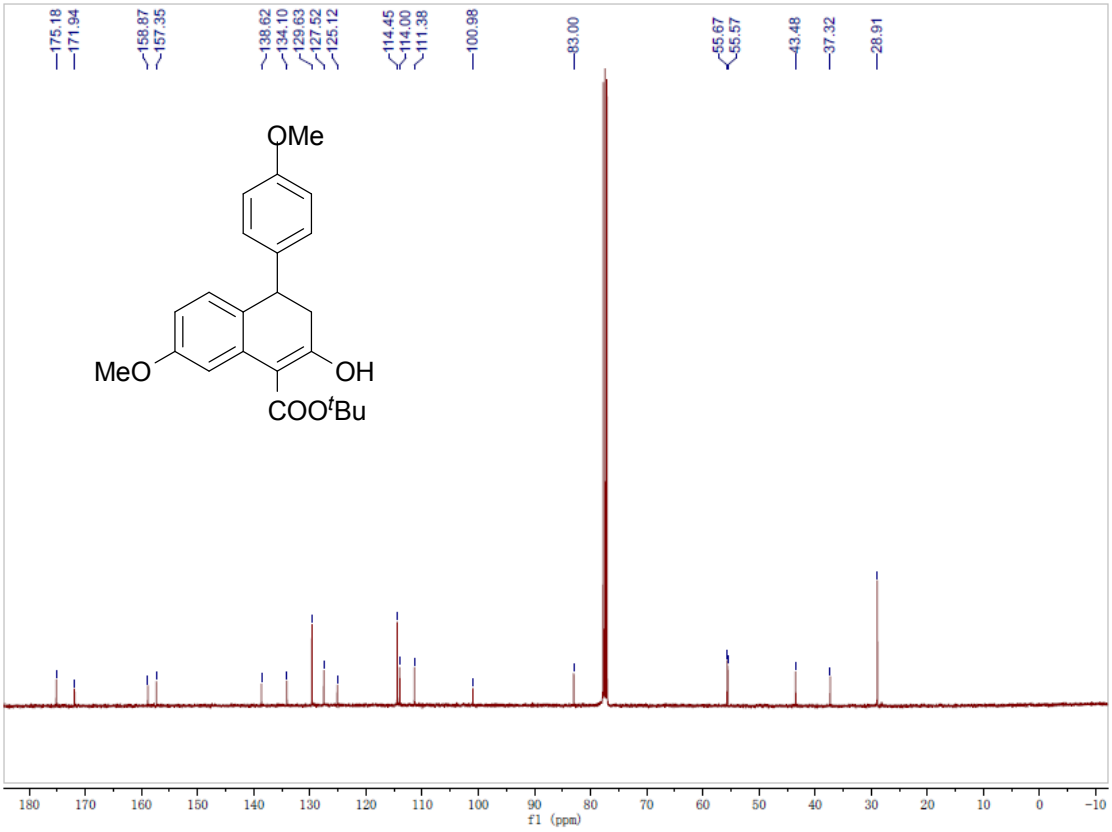
***tert*-Butyl (*R*)-2-Hydroxy-4-phenyl-3,4-dihydronaphthalene-1-carboxylate (3c)**



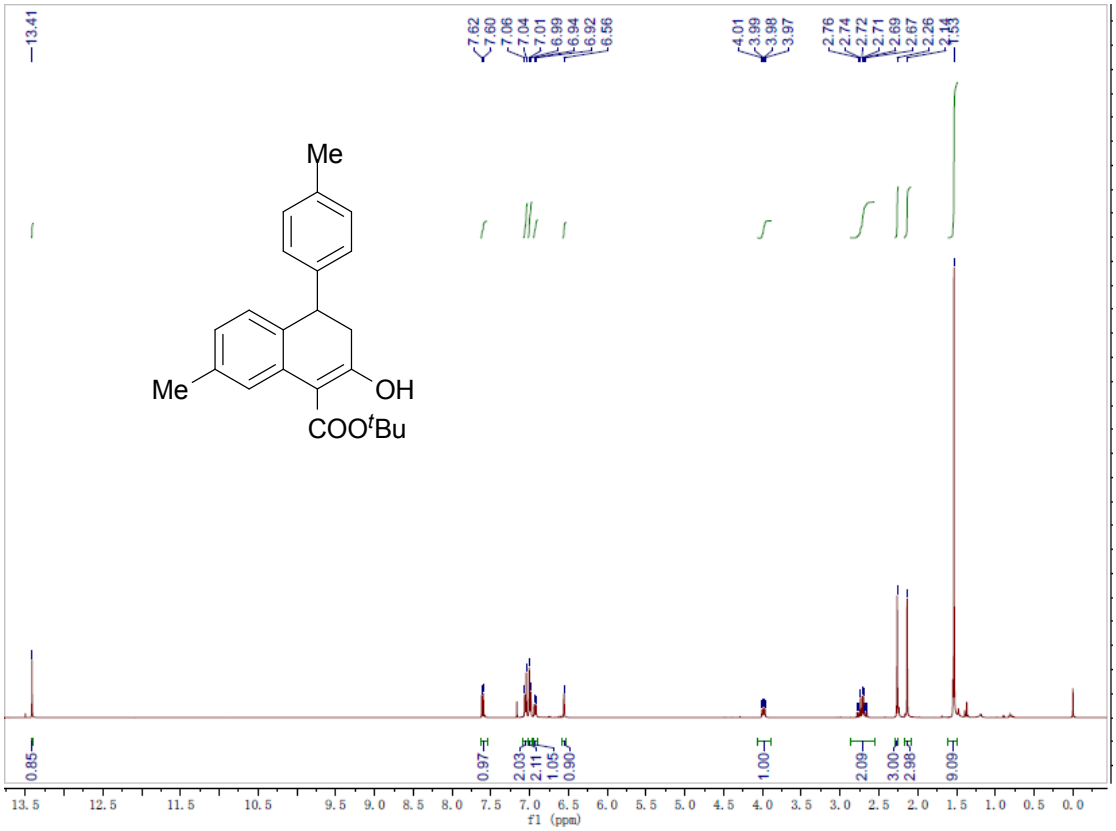


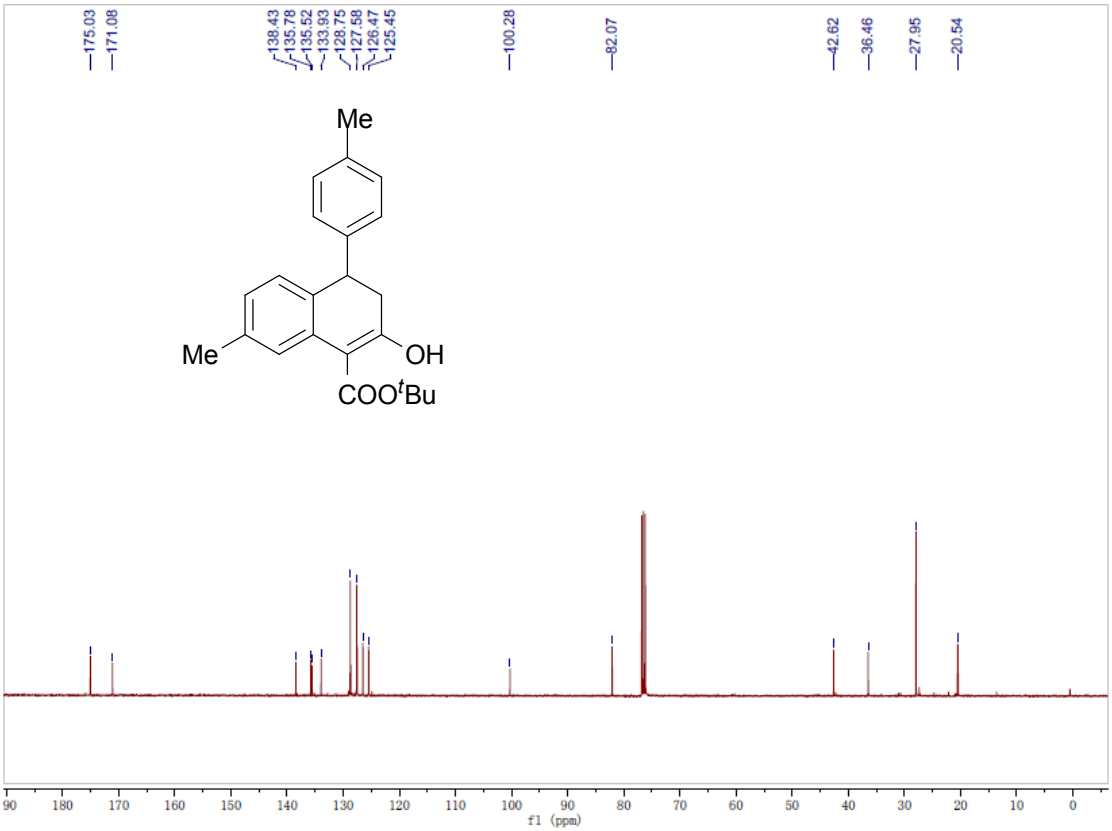
***tert*-Butyl (*R*)-2-Hydroxy-7-methoxy-4-(*p*-anisyl)-3,4-dihydronaphthalene-1-carboxylate (3d)**



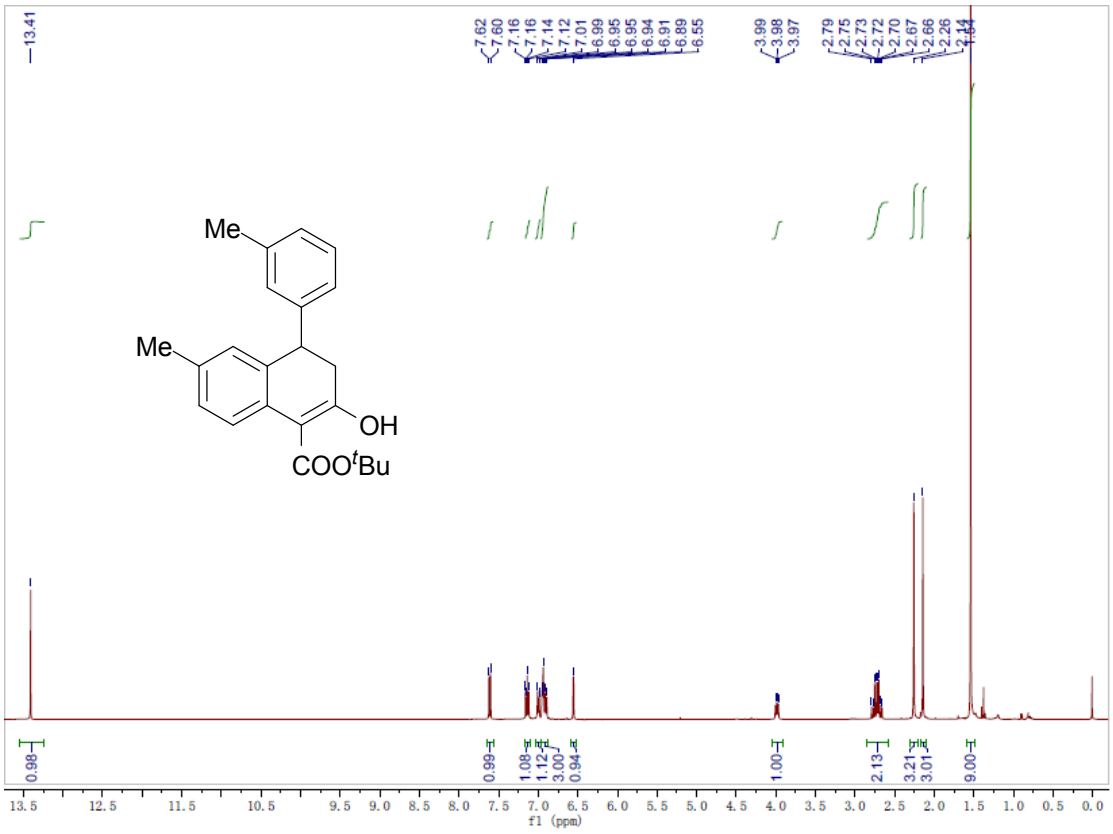


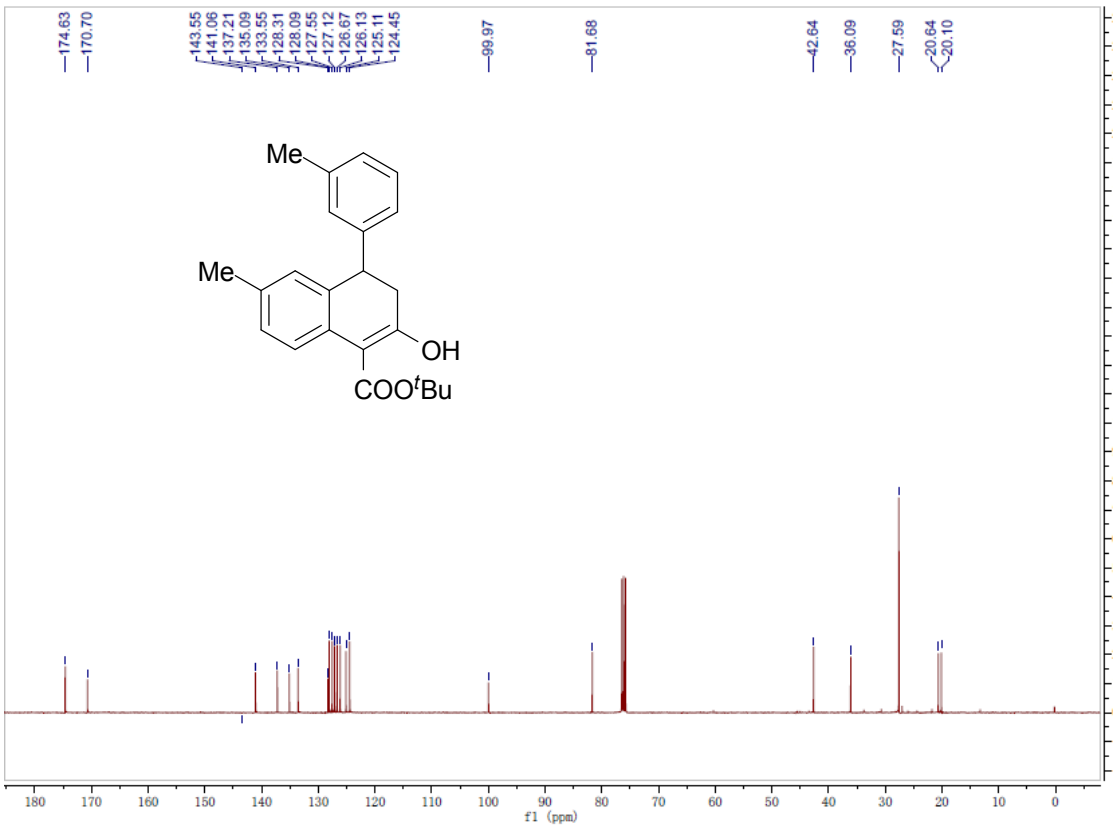
***tert*-Butyl (*R*)-2-Hydroxy-7-methyl-4-(*p*-tolyl)-3,4-dihydronaphthalene-1-carboxylate (3e)**



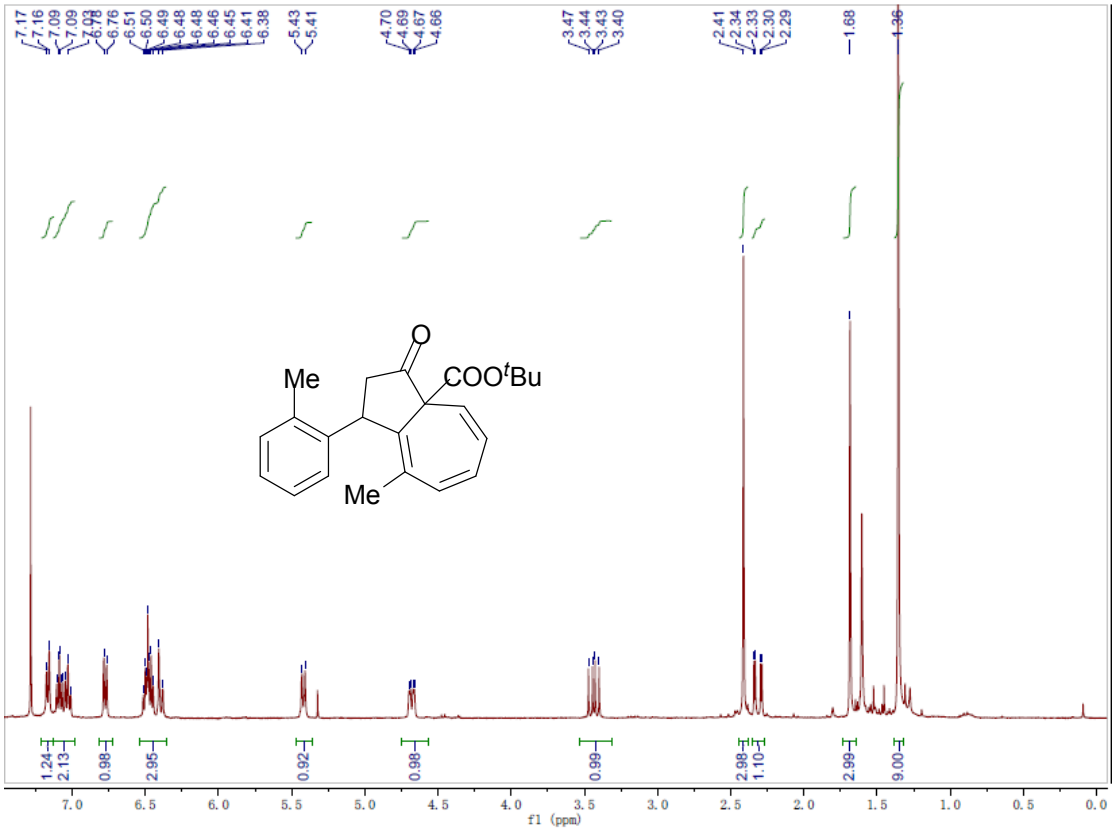


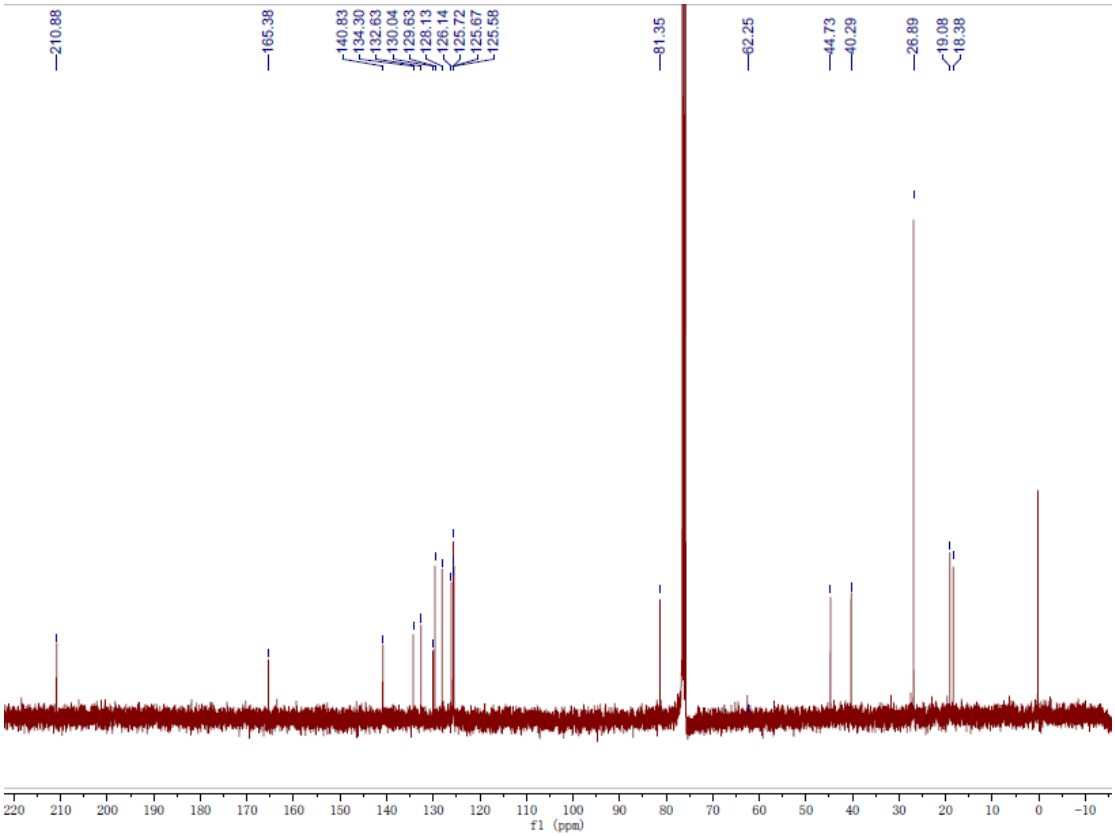
***tert*-Butyl (*R*)-2-Hydroxy-6-methyl-4-(*m*-tolyl)-3,4-dihydronaphthalene-1-carboxylate (3f)**



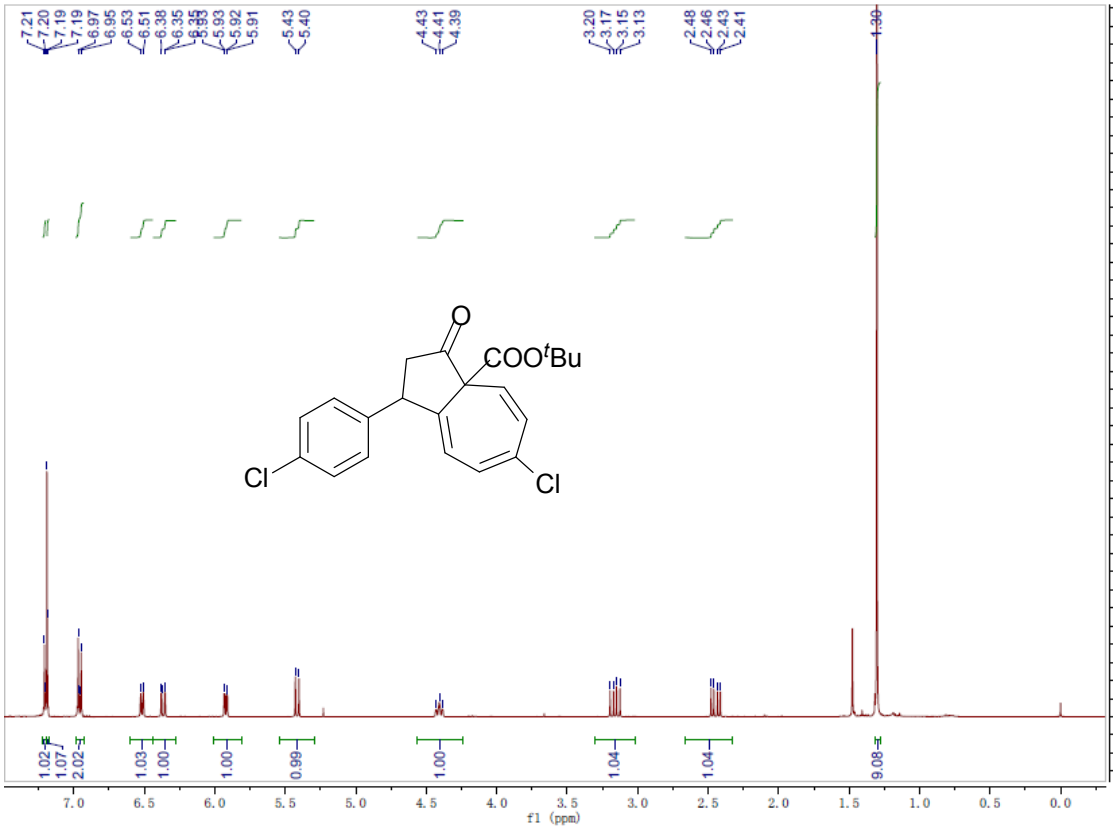


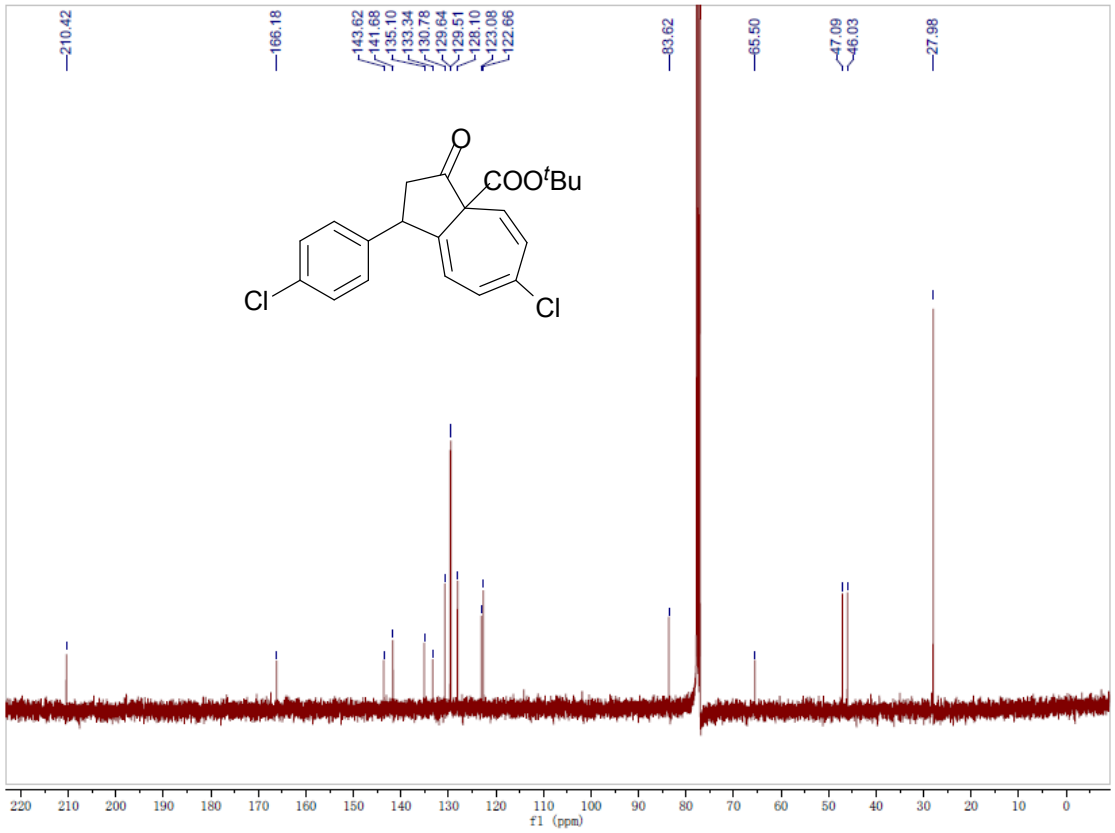
***tert*-Butyl (1*R*,3a*S*)-8-Methyl-3-oxo-1-(*o*-tolyl)-1,2,3,3a-tetrahydroazulene-3a-carboxylate (2g)**



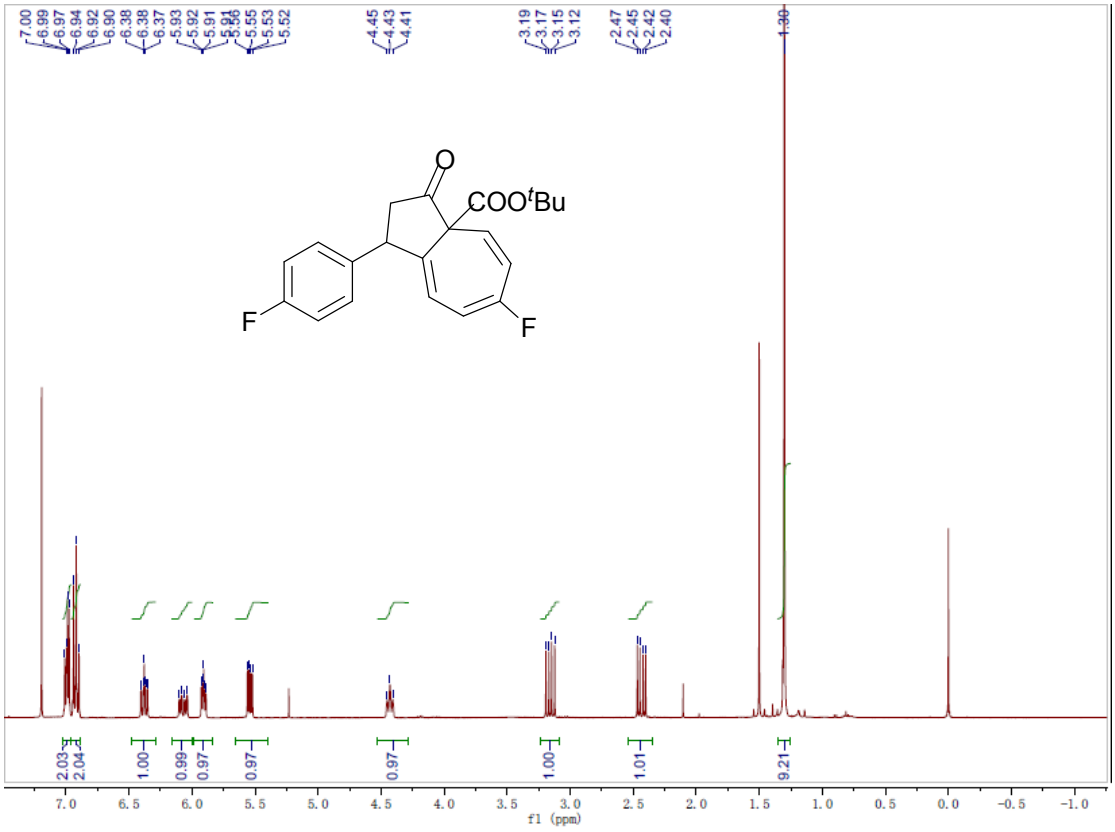


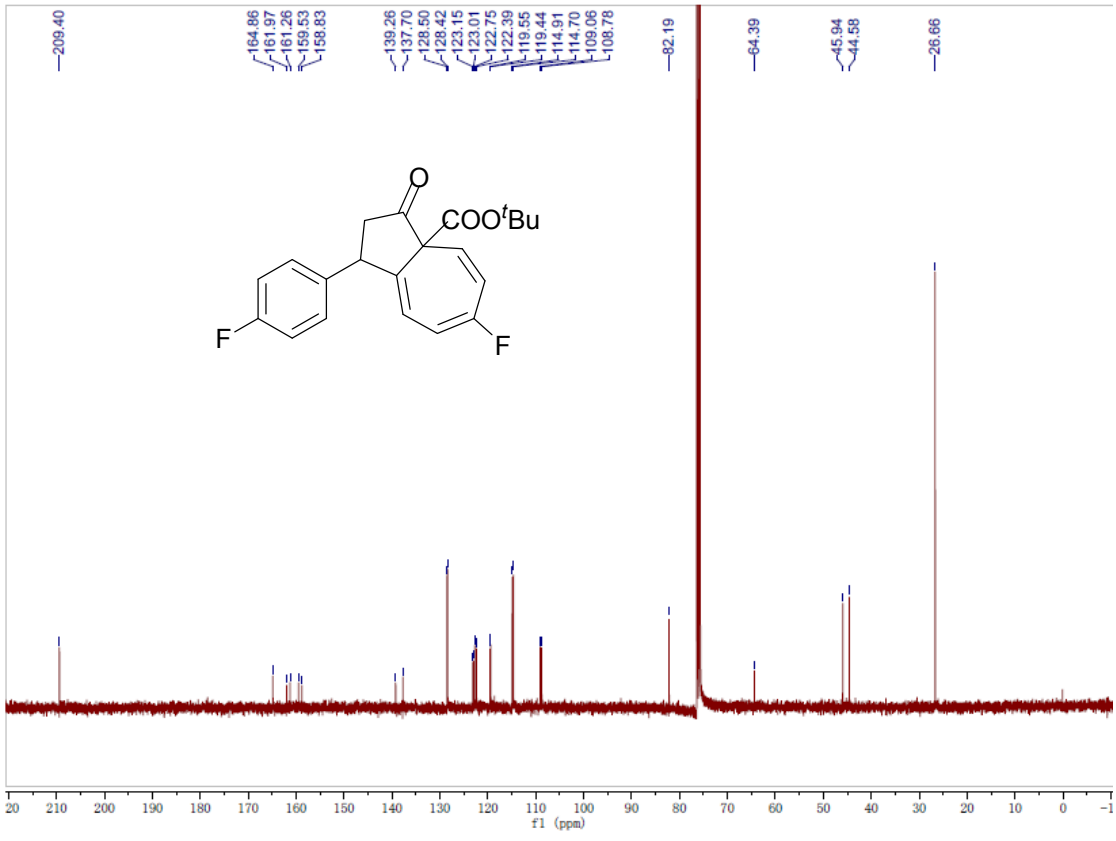
***tert*-Butyl (1*R*,3a*S*)-6-Chloro-1-(4-chlorophenyl)-3-oxo-1,2,3,3a-tetrahydroazulene-3a-carboxylate (2h)**



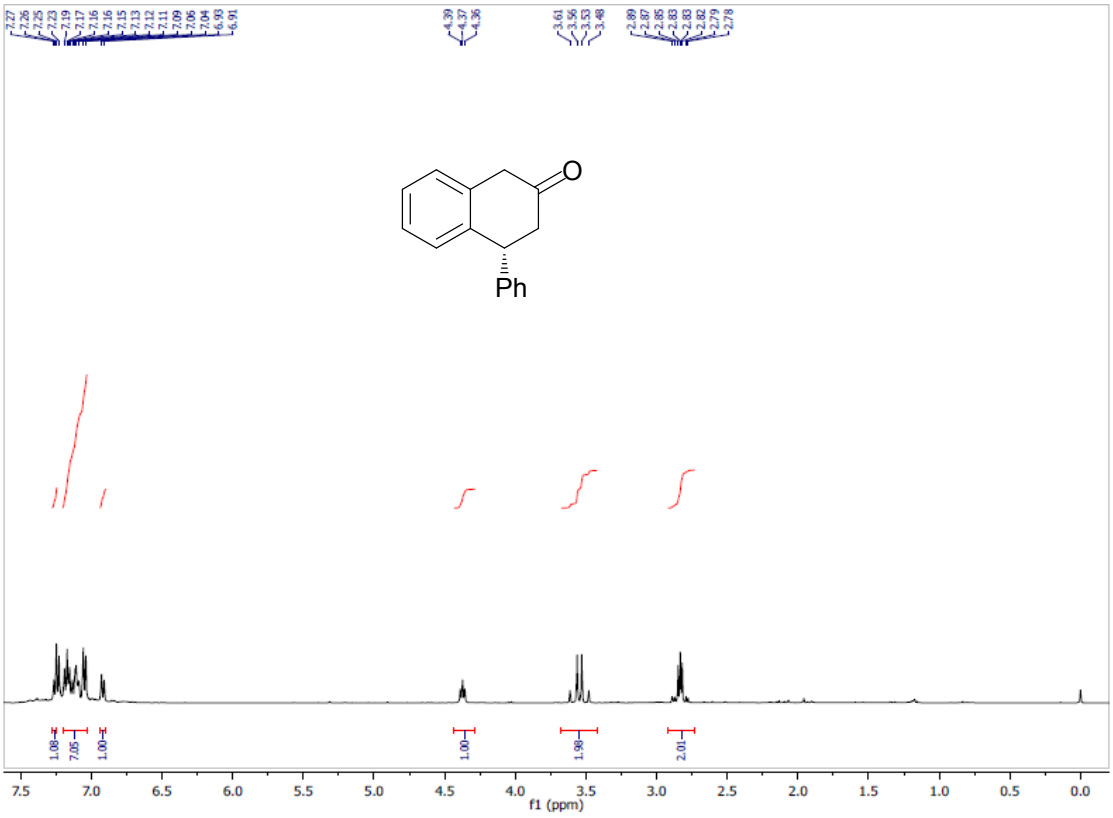


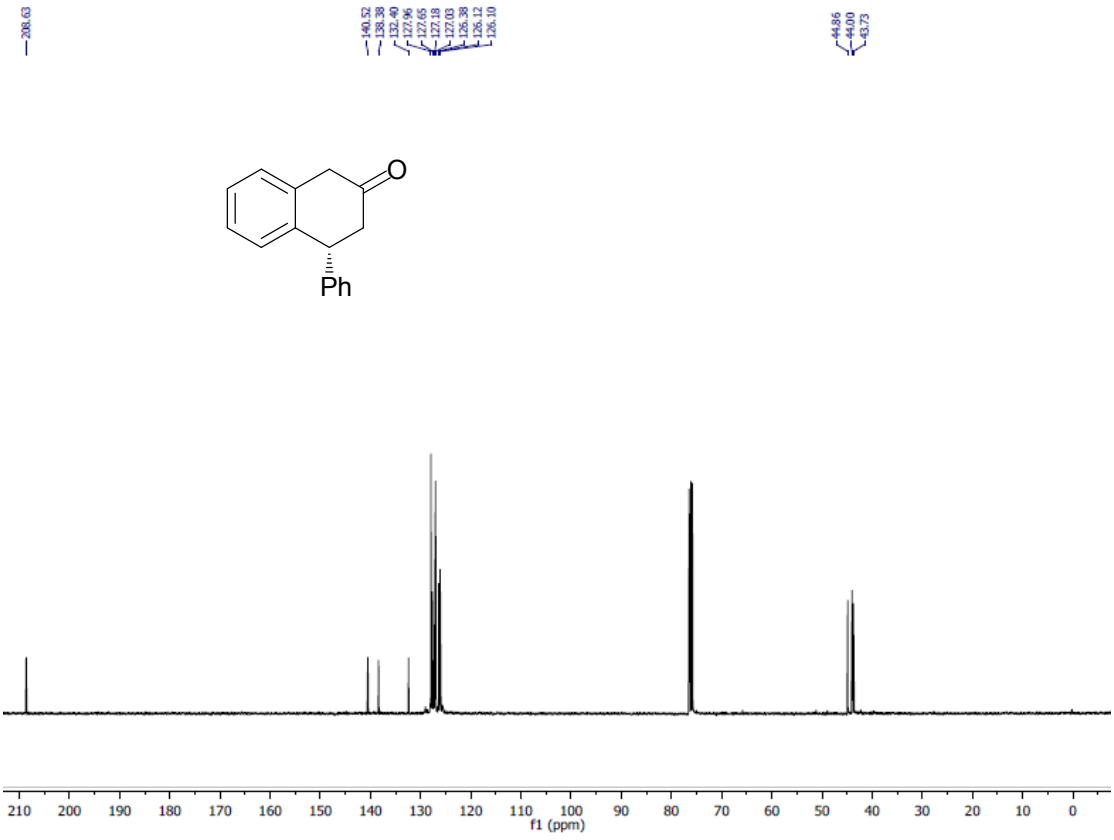
***tert*-Butyl (1*R*,3a*S*)-6-Fluoro-1-(4-fluorophenyl)-3-oxo-1,2,3,3a-tetrahydroazulene-3a-carboxylate (2i)**



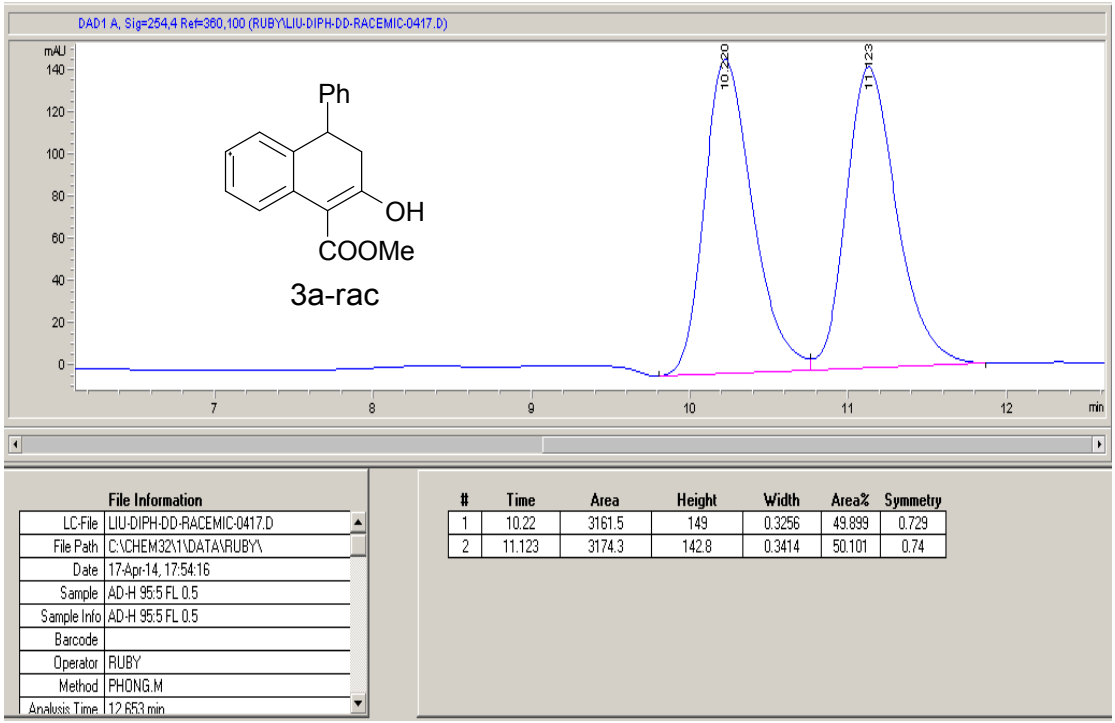


(*R*)-4-Phenyl-3,4-dihydronaphthalen-2(1*H*)-one (4)



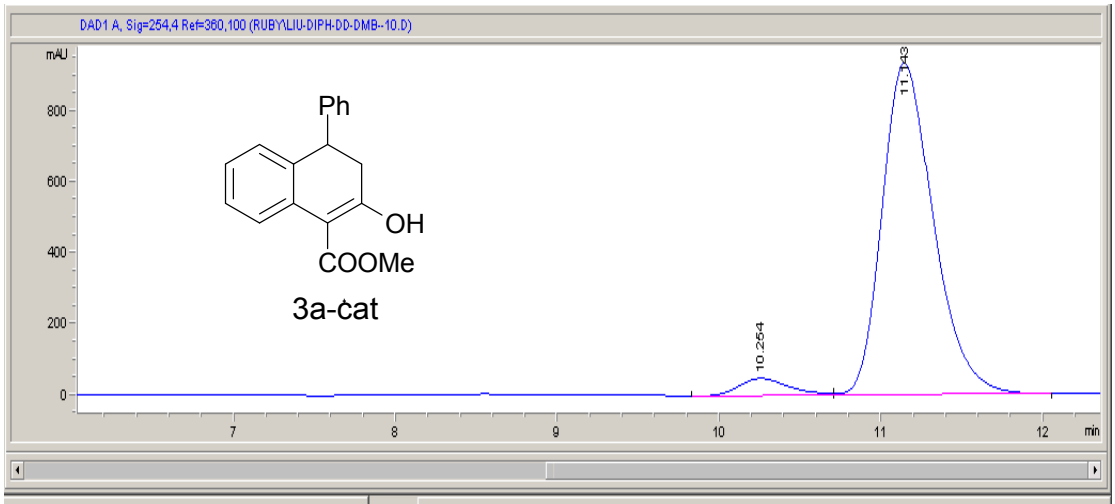


HPLC Analyses Figures



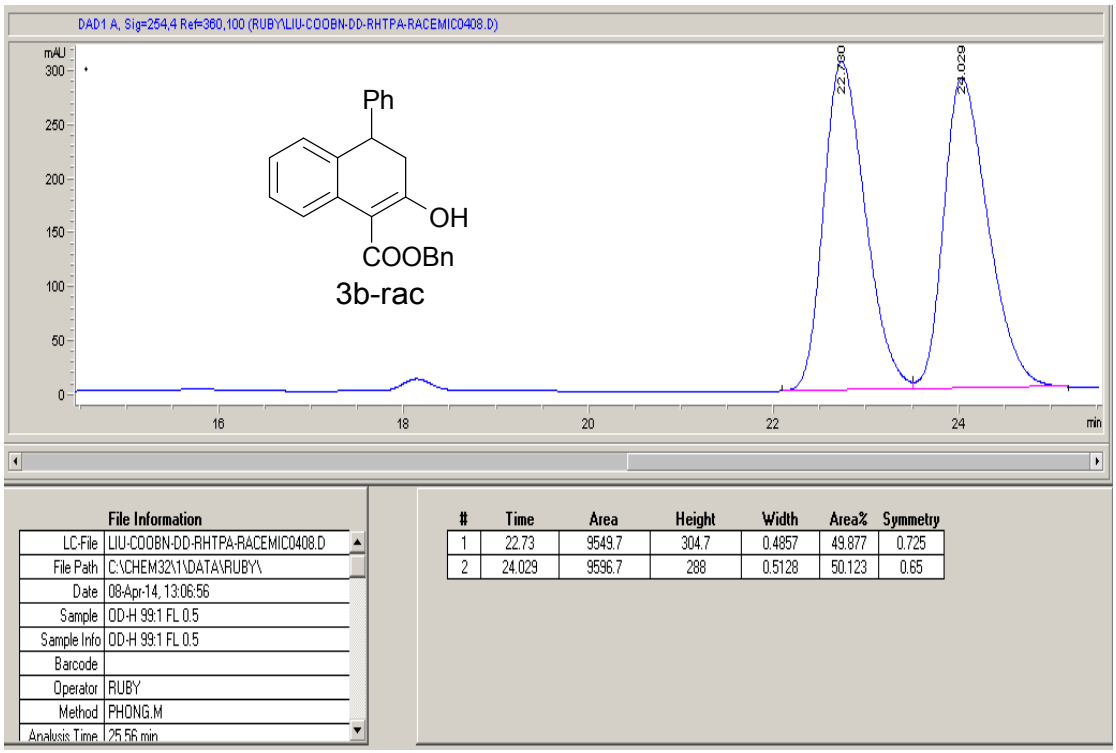
File Information	
LC-File	LIU-DIPH-DD-RACEMIC-0417.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	17-Apr-14, 17:54:16
Sample	AD-H 95:5 FL 0.5
Sample Info	AD-H 95:5 FL 0.5
Barcode	
Operator	RUBY
Method	PHONG.M
Analysis Time	12.653 min

#	Time	Area	Height	Width	Area%	Symmetry
1	10.22	3161.5	149	0.3256	49.899	0.729
2	11.123	3174.3	142.8	0.3414	50.101	0.74



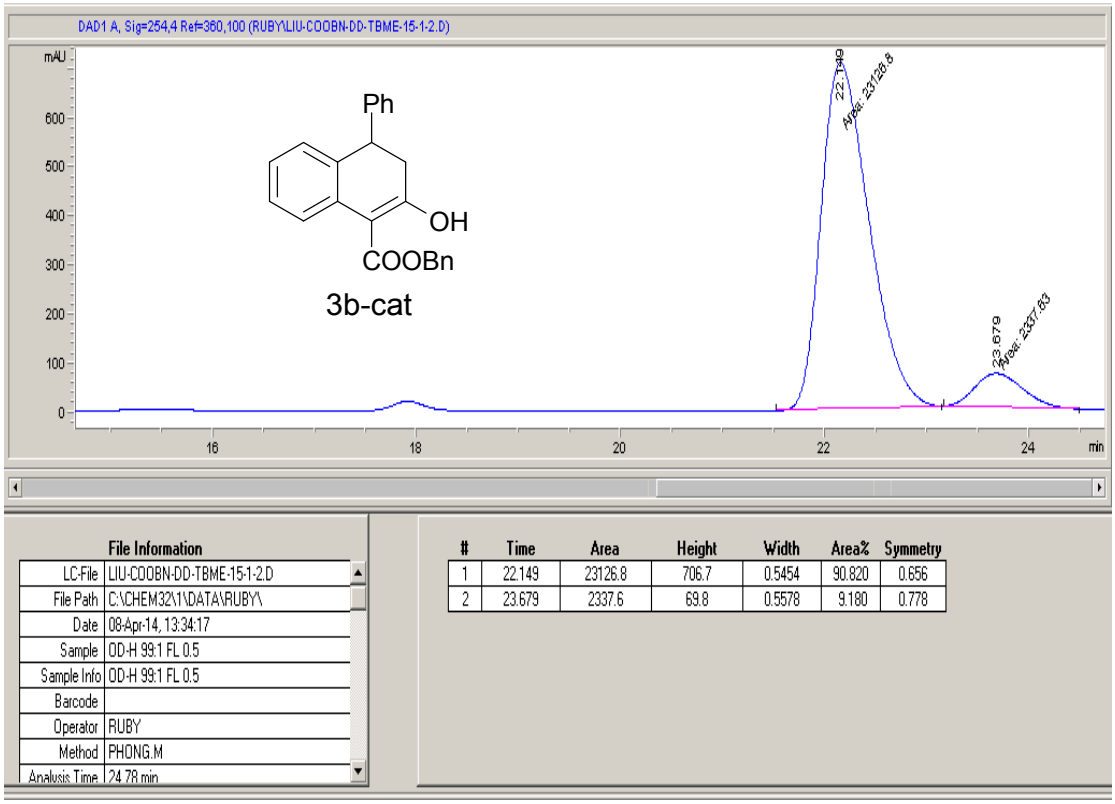
File Information	
LC-File	LIU-DIPH-DD-DMB--10.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	17-Apr-14, 18:12:36
Sample	AD-H 95:5 FL 0.5
Sample Info	AD-H 95:5 FL 0.5
Barcode	
Operator	RUBY
Method	PHONG.M
Analysis Time	12.393 min

#	Time	Area	Height	Width	Area%	Symmetry
1	10.254	1098.3	49.4	0.3396	5.062	0.746
2	11.143	20597.4	934.8	0.3391	94.938	0.736



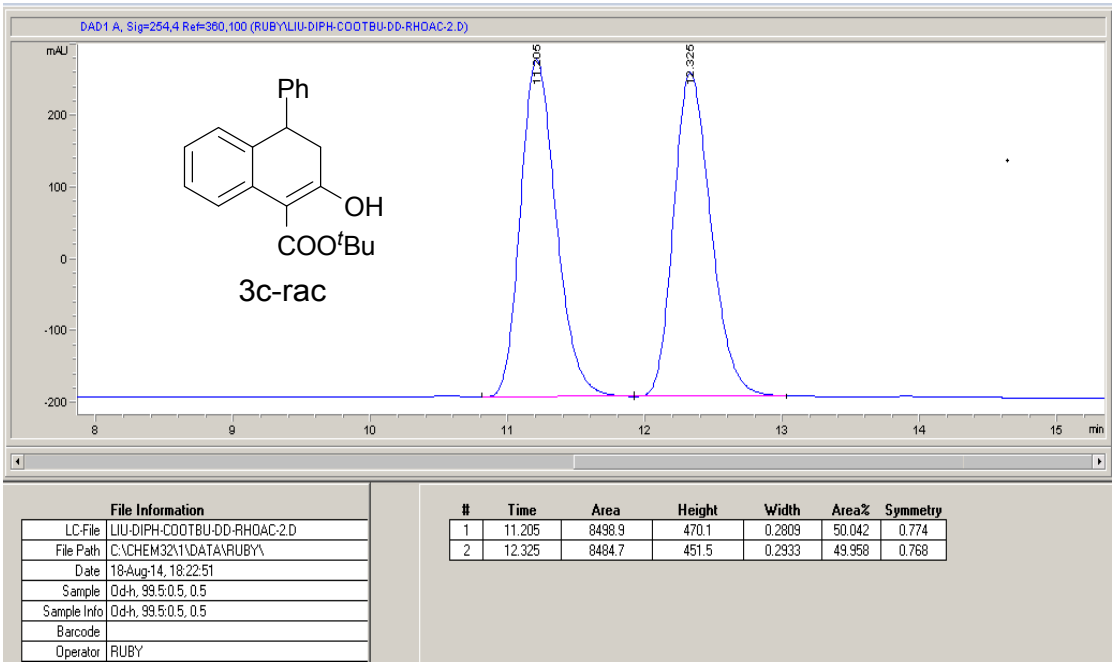
File Information	
LC-File	LIU-COOBN-DD-RHTPA-RACEMIC0408.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	08-Apr-14, 13:06:56
Sample	OD-H 99:1 FL 0.5
Sample Info	OD-H 99:1 FL 0.5
Barcode	
Operator	RUBY
Method	PHONG.M
Analysis Time	25.56 min

#	Time	Area	Height	Width	Area%	Symmetry
1	22.73	9549.7	304.7	0.4857	49.877	0.725
2	24.029	9596.7	288	0.5128	50.123	0.65



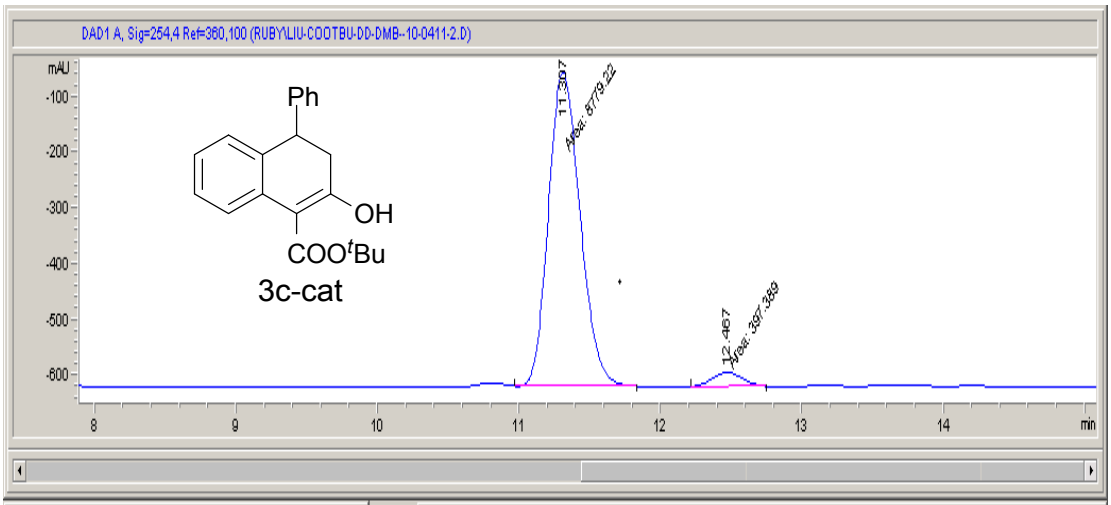
File Information	
LC-File	LIU-COOBN-DD-TBME-15-1-2.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	08-Apr-14, 13:34:17
Sample	OD-H 99:1 FL 0.5
Sample Info	OD-H 99:1 FL 0.5
Barcode	
Operator	RUBY
Method	PHONG.M
Analysis Time	24.78 min

#	Time	Area	Height	Width	Area%	Symmetry
1	22.149	23126.8	706.7	0.5454	90.820	0.656
2	23.679	2337.6	69.8	0.5578	9.180	0.778



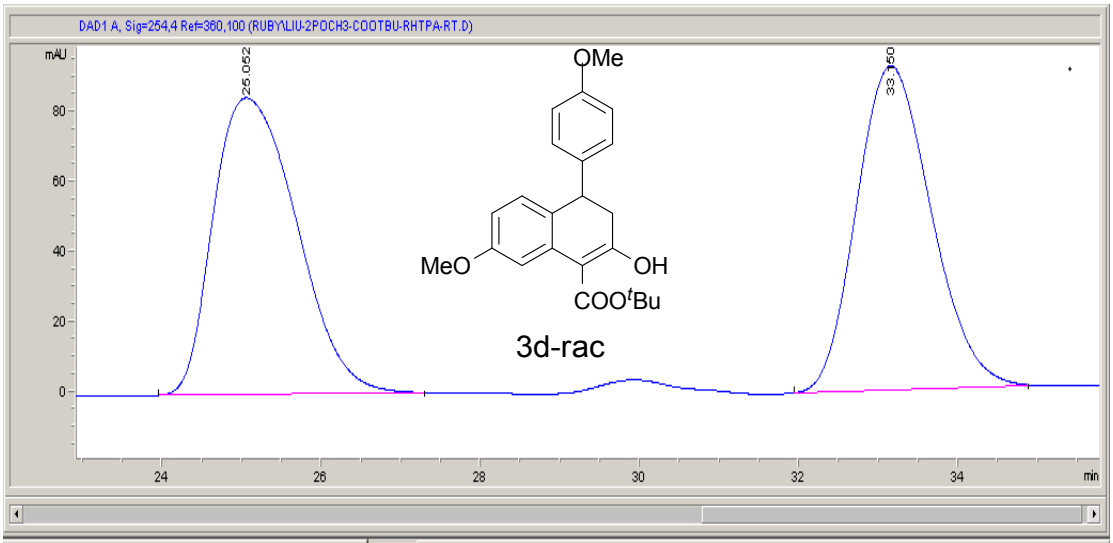
File Information	
LC-File	LIU-DIPH-COOTBU-DD-RHOAC-2.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	18-Aug-14, 18:22:51
Sample	Od-h, 99.5:0.5, 0.5
Sample Info	Od-h, 99.5:0.5, 0.5
Barcode	
Operator	RUBY

#	Time	Area	Height	Width	Area%	Symmetry
1	11.205	8498.9	470.1	0.2809	50.042	0.774
2	12.325	8484.7	451.5	0.2933	49.958	0.768



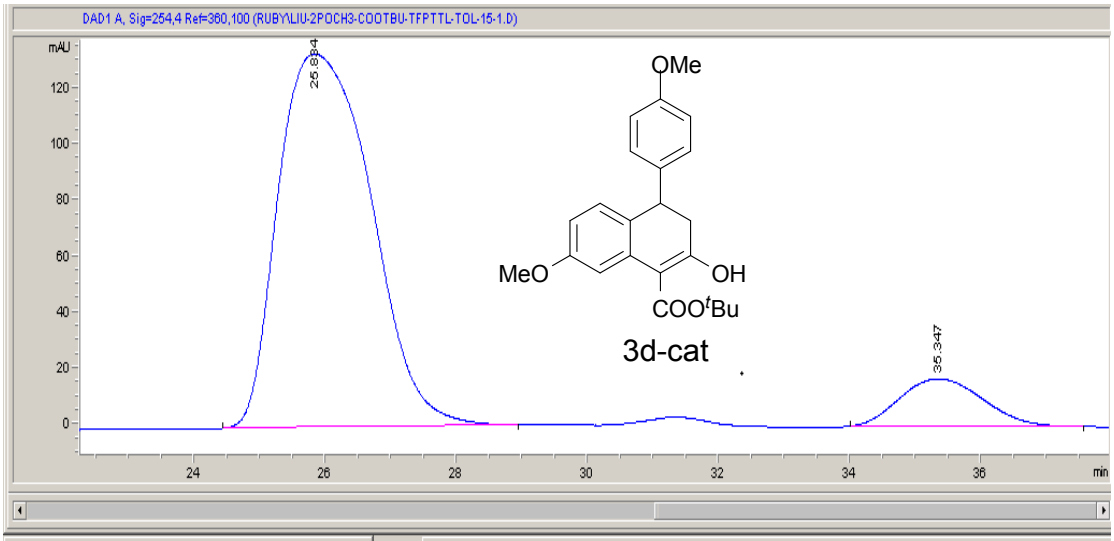
File Information	
LC-File	LIU-COOTBU-DD-DMB--10-0411-2.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	11-Apr-14, 19:07:02
Sample	OD-H 99.5:0.5 FL 0.5
Sample Info	OD-H 99.5:0.5 FL 0.5
Barcode	
Operator	RUBY

#	Time	Area	Height	Width	Area%	Symmetry
1	11.307	8779.2	563.9	0.2595	95.670	0.814
2	12.467	397.4	25.8	0.2569	4.330	0.98



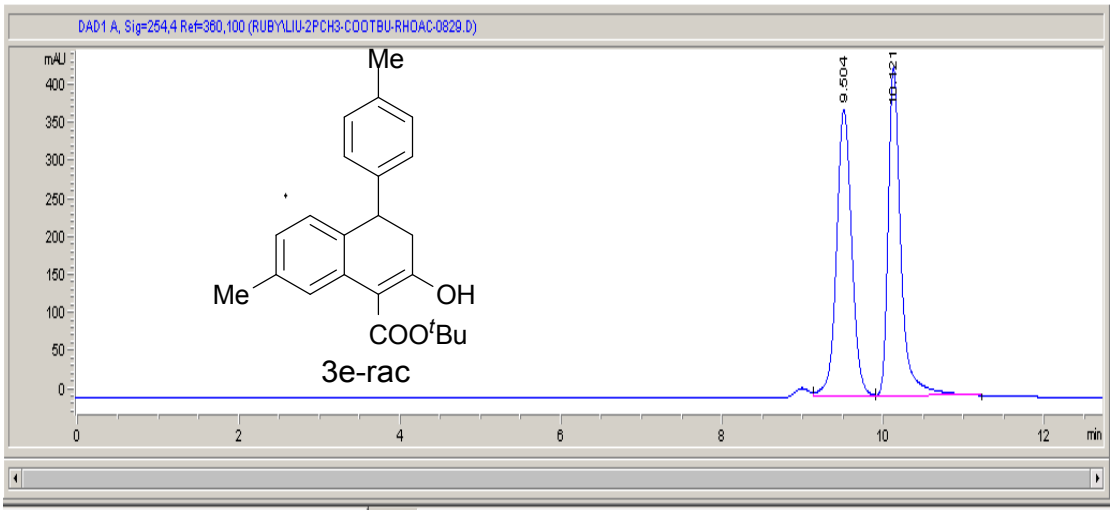
File Information	
LC-File	LIU-2POCH3-COOTBU-RHTPA-RT.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	10-May-14, 17:23:50
Sample	OD-H,99.5: 0.5 ,0.4
Sample Info	OD-H,99.5: 0.5 ,0.4
Barcode	
Operator	RUBY
Method	PHONG.M
Analysis Time	36.007 min

#	Time	Area	Height	Width	Area%	Symmetry
1	25.052	6174.1	84.8	1.1857	50.503	0.627
2	33.15	6051.2	92.7	1.0216	49.497	0.81



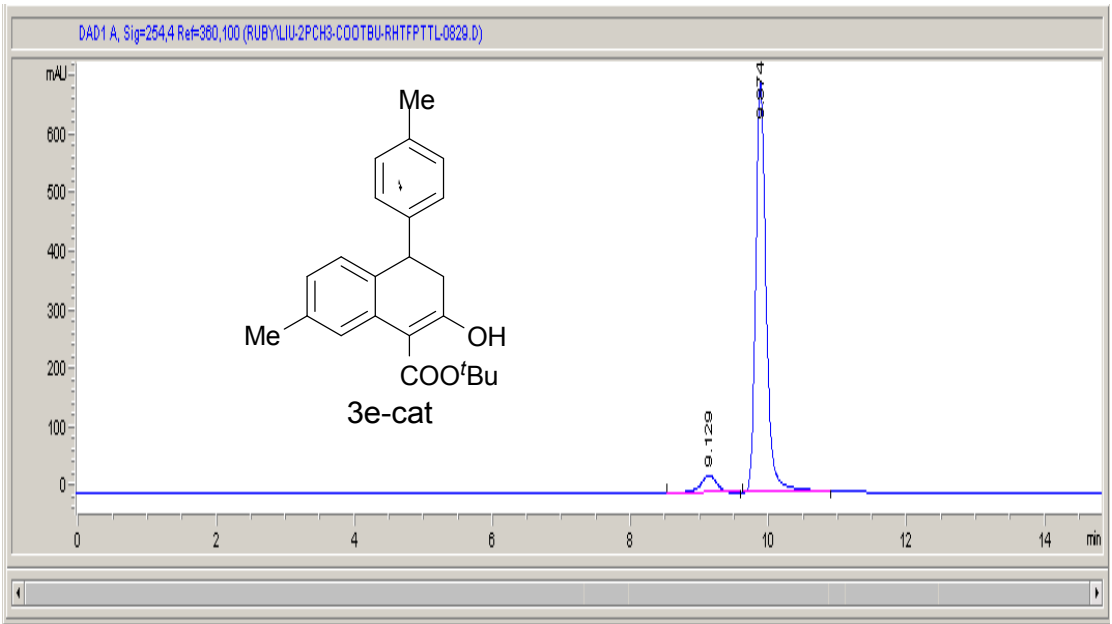
File Information	
LC-File	LIU-2POCH3-COOTBU-TFPTTL-TOL-15-1.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	10-May-14, 16:41:38
Sample	OD-H,99.5: 0.5 ,0.4
Sample Info	OD-H,99.5: 0.5 ,0.4
Barcode	
Operator	RUBY
Method	PHONG.M
Analysis Time	38 min

#	Time	Area	Height	Width	Area%	Symmetry
1	25.834	13151.6	133.3	1.6173	89.742	0.629
2	35.347	1503.3	17	1.2163	10.258	0.827



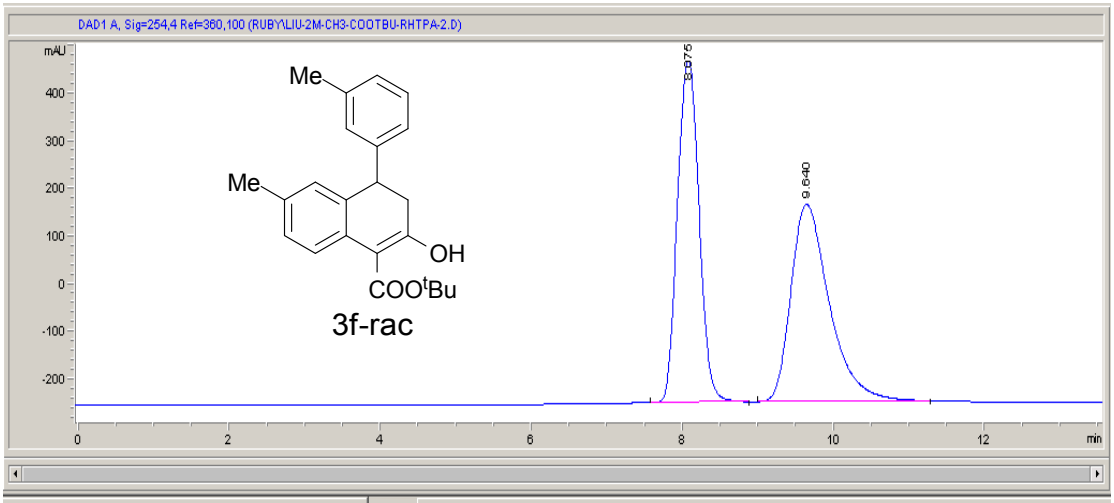
File Information	
LC-File	LIU-2PCH3-COOTBU-RHOAC-0829.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	29-Aug-14, 13:21:39
Sample	aD-H 99:1,0.5
Sample Info	aD-H 99:1,0.5
Barcode	
Operator	RUBY

#	Time	Area	Height	Width	Area%	Symmetry
1	9.504	5023.6	378.7	0.2028	50.938	0.932
2	10.121	4838.7	434.6	0.1679	49.062	0.639



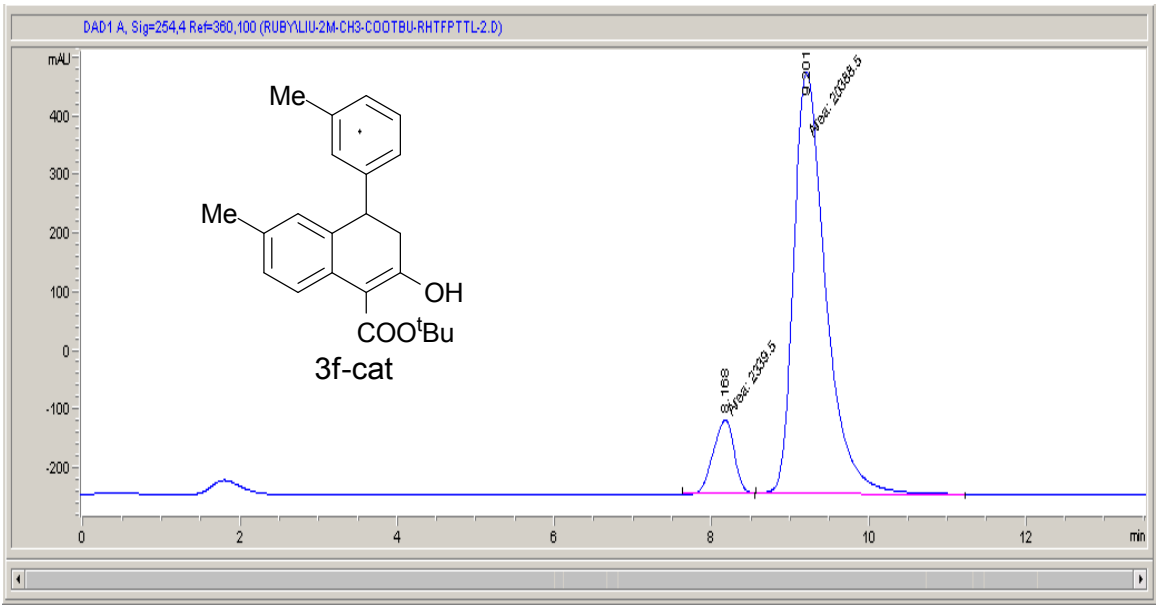
File Information	
LC-File	LIU-2PCH3-COOTBU-RHTFPTTL-0829.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	29-Aug-14, 15:27:33
Sample	aD-H 99:1,0.5
Sample Info	aD-H 99:1,0.5
Barcode	
Operator	RUBY

#	Time	Area	Height	Width	Area%	Symmetry
1	9.129	517.4	30.1	0.2562	6.554	1.124
2	9.874	7377.1	700	0.159	93.446	0.755



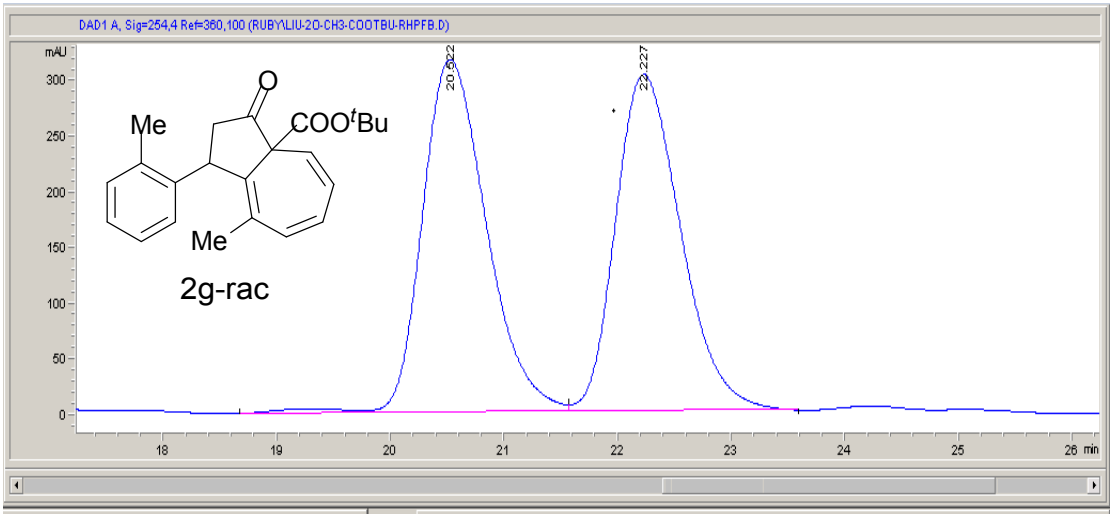
File Information	
LC-File	LIU-2M-CH3-COOTBU-RHTPA-2.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	28-Jul-14, 16:17:19
Sample	ad-h, 98:2, 0.5
Sample Info	ad-h, 98:2, 0.5
Barcode	
Operator	RUBY
Method	PHONG.M
Analysis Time	13.607 min

#	Time	Area	Height	Width	Area%	Symmetry
1	8.075	14301.9	717.4	0.3186	49.301	0.953
2	9.64	14707.5	415	0.5374	50.699	0.64



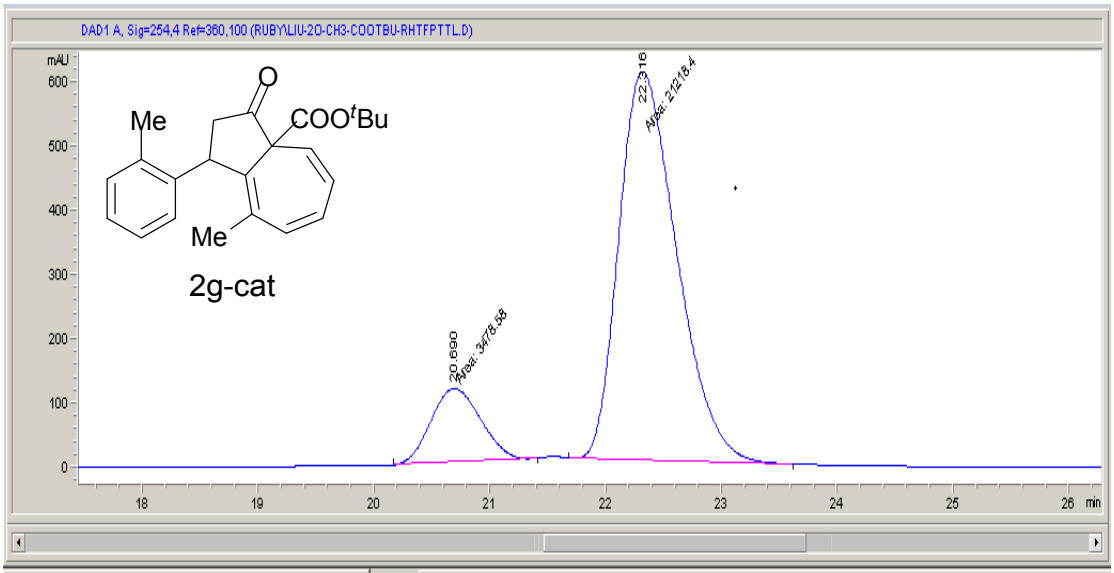
File Information	
LC-File	LIU-2M-CH3-COOTBU-RHTFPTTL-2.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	28-Jul-14, 16:48:30
Sample	ad-h, 98:2, 0.5
Sample Info	ad-h, 98:2, 0.5
Barcode	
Operator	RUBY
Method	PHONG.M
Analysis Time	13.567 min

#	Time	Area	Height	Width	Area%	Symmetry
1	8.168	2339.5	126.6	0.3081	10.293	1.324
2	9.201	20388.5	720.3	0.4717	89.707	0.644



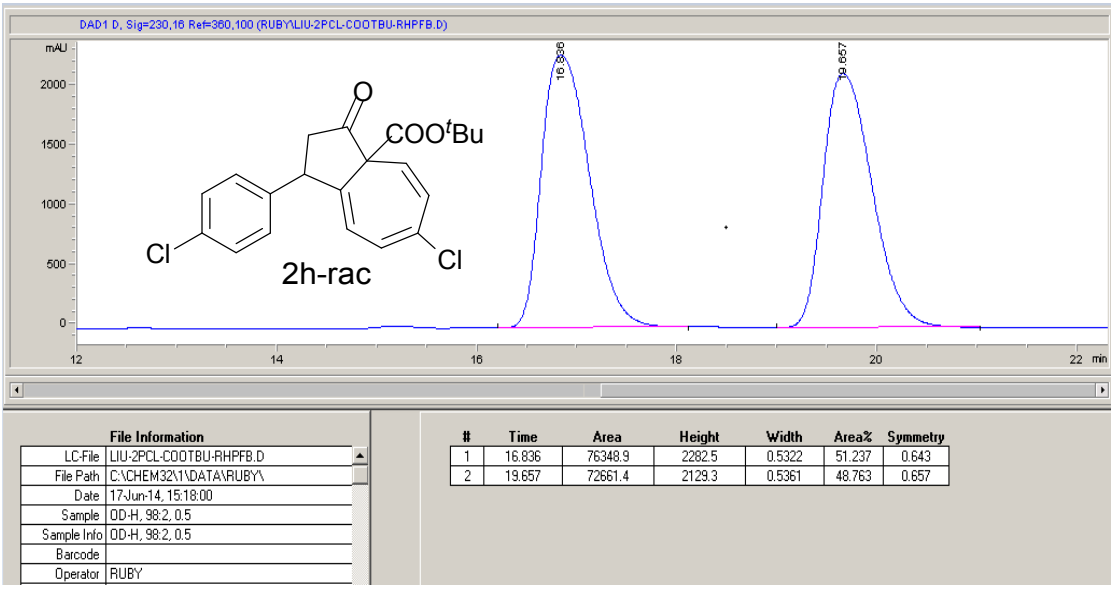
File Information	
LC-File	LIU-2O-CH3-COOTBU-RHPFB.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	22-Jul-14, 14:01:57
Sample	OD-H 98:2 0.3ml/min
Sample Info	OD-H 98:2 0.3ml/min
Barcode	
Operator	RUBY
Method	PHONG.M
Analysis Time	28.773 min

#	Time	Area	Height	Width	Area%	Symmetry
1	20.522	12527.6	317.2	0.6107	50.917	0.747
2	22.227	12076.3	302.8	0.6233	49.083	0.725



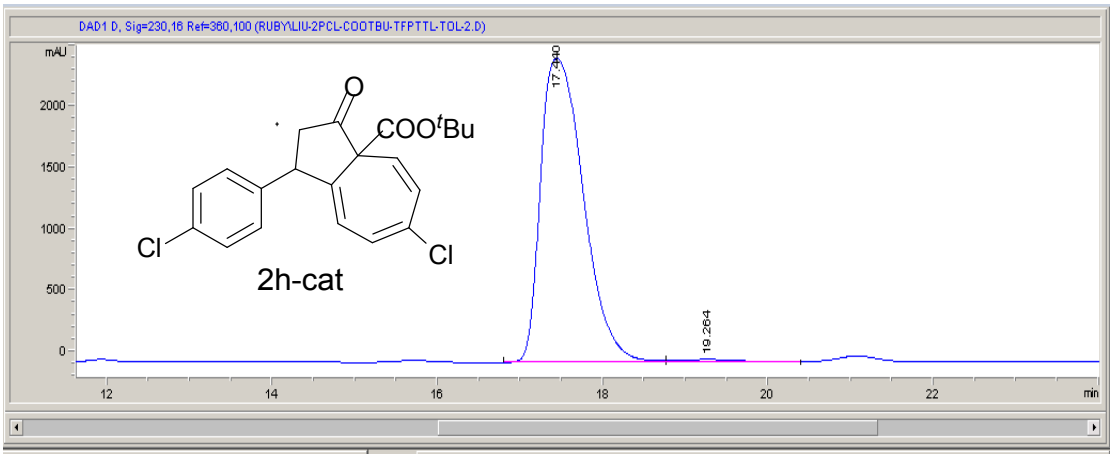
File Information	
LC-File	LIU-2O-CH3-COOTBU-RHTFPTTL.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	22-Jul-14, 14:40:28
Sample	OD-H 98:2 0.3ml/min
Sample Info	OD-H 98:2 0.3ml/min
Barcode	
Operator	RUBY
Method	PHONG.M
Analysis Time	35.867 min

#	Time	Area	Height	Width	Area%	Symmetry
1	20.69	3478.6	115.6	0.5014	14.085	0.864
2	22.316	21218.4	606.5	0.5831	85.915	0.674



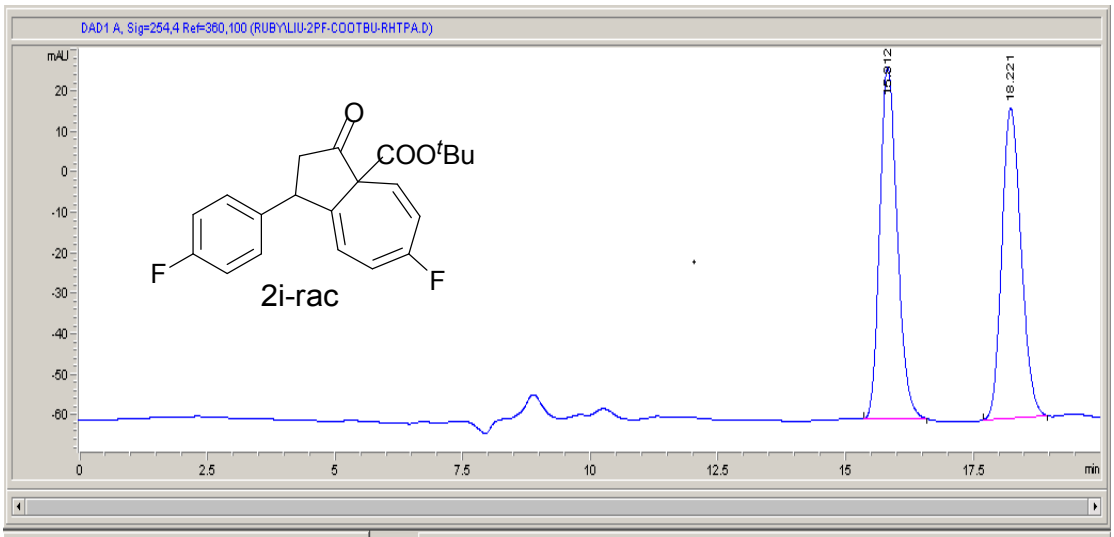
File Information	
LC-File	LIU-2PCL-COOTBU-RHPFB.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	17-Jun-14, 15:18:00
Sample	OD-H, 98:2, 0.5
Sample Info	OD-H, 98:2, 0.5
Barcode	
Operator	RUBY

#	Time	Area	Height	Width	Area%	Symmetry
1	16.836	76348.9	2282.5	0.5322	51.237	0.643
2	19.657	72661.4	2129.3	0.5361	48.763	0.657



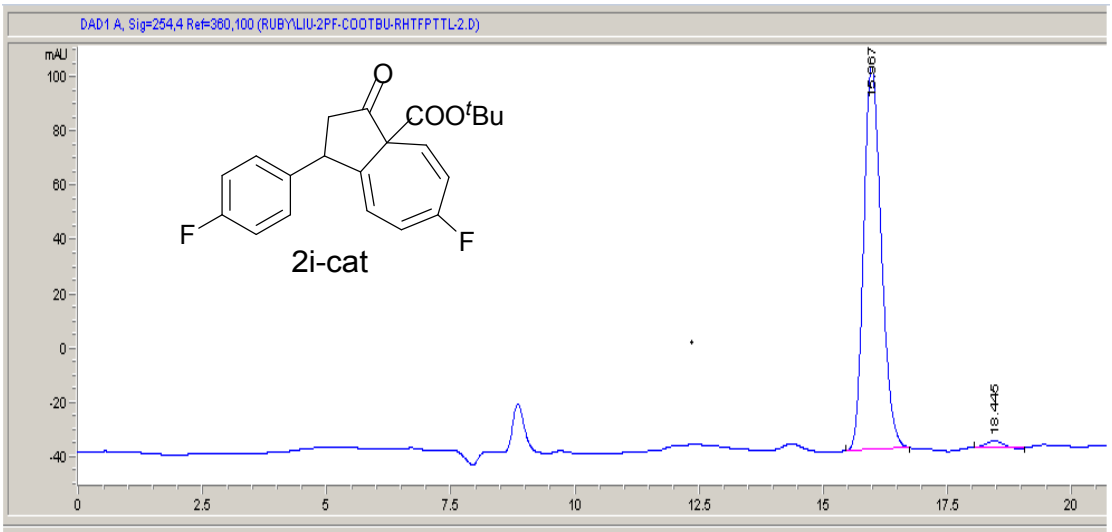
File Information	
LC-File	LIU-2PCL-COOTBU-TFPTTL-TOL-2.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	17-Jun-14, 13:23:10
Sample	OD-H, 98:2, 0.5
Sample Info	OD-H, 98:2, 0.5
Barcode	
Operator	RUBY

#	Time	Area	Height	Width	Area%	Symmetry
1	17.44	89614	2480.6	0.5715	98.571	0.566
2	19.264	1298.9	22.6	0.8182	1.429	0.656



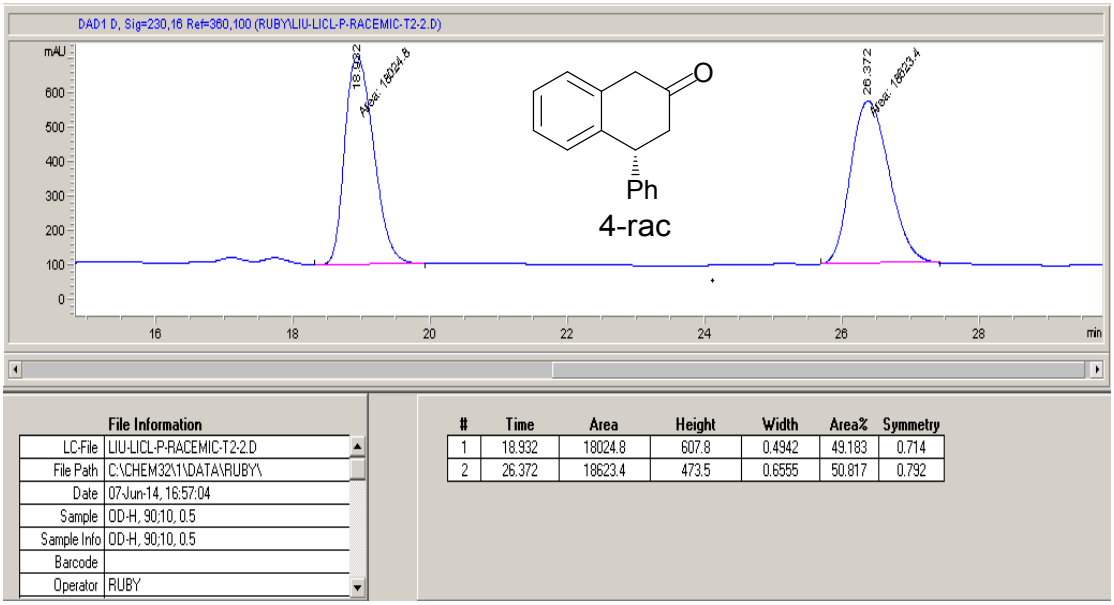
File Information	
LC-File	LIU-2PF-COOTBU-RHTPA.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	10-Jul-14, 18:52:10
Sample	OD-H 98:2, 0.5
Sample Info	OD-H 98:2, 0.5
Barcode	
Operator	RUBY
Method	PHONG.M
Analysis Time	20.027 min

#	Time	Area	Height	Width	Area%	Symmetry
1	15.812	2083.2	87	0.3712	50.648	0.775
2	18.221	2029.9	76.9	0.41	49.352	0.804



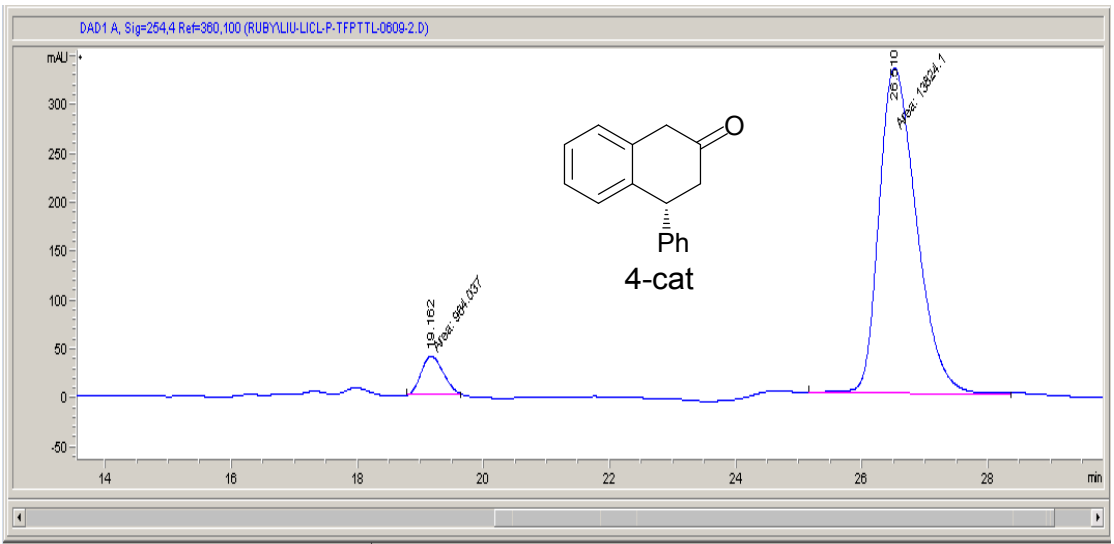
File Information	
LC-File	LIU-2PF-COOTBU-RHTFPTTL-2.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	10-Jul-14, 19:55:27
Sample	OD-H 98:2, 0.5
Sample Info	OD-H 98:2, 0.5
Barcode	
Operator	RUBY
Method	PHONG.M
Analysis Time	21.567 min

#	Time	Area	Height	Width	Area%	Symmetry
1	15.967	3512.1	141.5	0.3856	98.460	0.767
2	18.445	54.9	2.5	0.3426	1.540	1.085



File Information	
LC-File	LIU-LICL-P-RACEMIC-T2-2.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	07-Jun-14, 16:57:04
Sample	OD-H, 90:10, 0.5
Sample Info	OD-H, 90:10, 0.5
Barcode	
Operator	RUBY

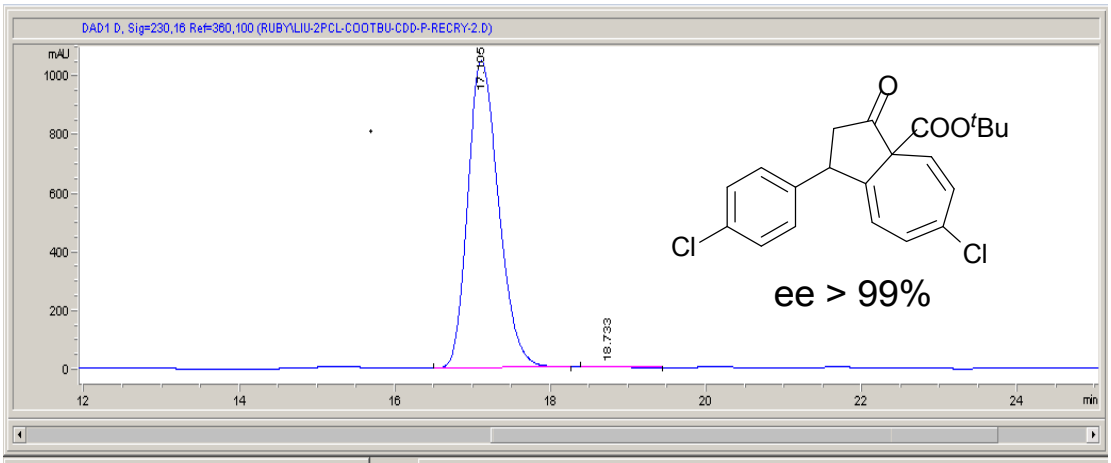
#	Time	Area	Height	Width	Area%	Symmetry
1	18.932	18024.8	607.8	0.4942	49.183	0.714
2	26.372	18623.4	473.5	0.6555	50.817	0.792



File Information	
LC-File	LIU-LICL-P-TFPTTL-0609-2.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	10-Jun-14, 17:15:16
Sample	OD-H, 90:10, 0.5
Sample Info	OD-H, 90:10, 0.5
Barcode	
Operator	RUBY

#	Time	Area	Height	Width	Area%	Symmetry
1	19.162	964	39.5	0.4069	6.519	0.821
2	26.51	13824.1	332.9	0.692	93.481	0.689

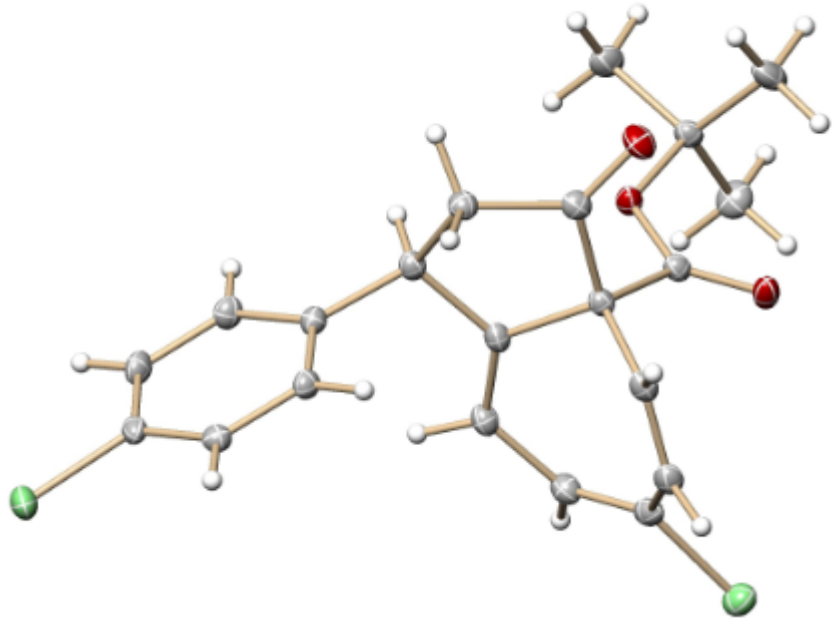
The pure product **2h** was recrystallized in EtOAc and hexanes, and the generated single-crystal was suitable for the X-ray analysis, see S-43.



File Information	
LC-File	LIU-2PCL-COOTBU-CDD-P-RECRY-2.D
File Path	C:\CHEM32\1\DATA\RUBY\
Date	30-Jun-14, 15:30:15
Sample	od-H, 98:2 0.5
Sample Info	od-H, 98:2 0.5
Barcode	
Operator	RUBY

#	Time	Area	Height	Width	Area%	Symmetry
1	17.105	28915.3	1046.6	0.4283	99.844	0.747
2	18.733	45.3	1.8	0.3922	0.156	0.889

Data Collection and Structure Refinement for *tert*-Butyl (1*R*,3a*S*)-6-Chloro-1-(4-chloro-phenyl)-3-oxo-1,2,3,3a-tetrahydroazulene-3a-carboxylate (2h) (UM-2601, CCDC 1029454)



A colorless prism-like specimen of $C_{21}H_{20}Cl_2O_3$, approximate dimensions 0.40 mm × 0.47 mm × 0.50 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker APEX-II CCD system equipped with a graphite monochromator and a MoKα sealed tube (λ = 0.71073 Å). Data collection temperature was 150 K.

The total exposure time was 12.63 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 32314 reflections to a maximum θ angle of 29.99° (0.71 Å resolution), of which 5686 were independent (average redundancy 5.683, completeness = 100.0%, R_{int} = 1.46%) and 5582 (98.17%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.9383(8) Å, b = 11.4949(8) Å, c = 15.5104(11) Å, V = 1950.2(2) Å^3, are based upon the refinement of the XYZ-centroids of 9955 reflections above 20 σ(I) with 4.556° < 2θ < 61.17°. Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8120 and 0.8690.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_12_12_1$, with Z = 4 for the formula unit, $C_{21}H_{20}Cl_2O_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 238 variables converged at R_1 = 2.49%, for the observed data and wR_2 = 5.25% for all data. The goodness-of-fit was 1.000. The largest peak in the final difference electron density synthesis was 0.356 e$^-$/Å^3 and the largest hole was -0.261 e$^-$/Å^3 with an RMS deviation of 0.089 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.333 g/cm^3 and F(000), 816 e$^-$.