

Highly Enantioselective [3+3]- Cycloaddition with Nitrones Catalyzed by Copper(I) with Chiral Box Ligands *via* Z- γ -Substituted Metallo- enolcarbene Intermediates

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Supporting Information

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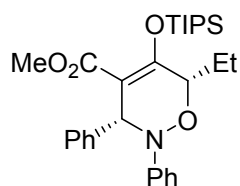
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1. General Information.

Unless otherwise noted, all reactions were performed in 10 mL oven-dried (120 °C) glassware under a dinitrogen atmosphere. Solvents were dried using a JC Meyer solvent purification system. Analytical thin-layer chromatography was performed using glass plates pre-coated with 200–300 mesh silica gel impregnated with a fluorescent indicator (254 nm). Column chromatography was performed on CombiFlash® Rf200 and Rf+ purification systems using normal phase silica gel columns (300–400 mesh). High-resolution mass spectra (HRMS) were performed on a Bruker MicroTOF-ESI mass spectrometer with an ESI resource using CsI or LTQ ESI Positive Ion Calibration Solution as the standard. Accurate masses were reported for the molecular ions $[M+H]^+$. ^1H and ^{13}C NMR spectra were recorded on Bruker 300 MHz and 500 MHz spectrometers. ^1H NMR spectra were recorded in CDCl_3 at 300 or 500 MHz with residual CHCl_3 (δ 7.26 ppm) and H_2O (δ 1.56 ppm). Chemical shifts are reported in ppm with the residual solvent signals as reference, and coupling constants (J) are given in Hertz. Peak information is described as: s = singlet, d = doublet, dd = doublet of doublets, td = triplet of doublets, t = triplet, m = multiplet, comp = composite of magnetically non-equivalent protons. ^{13}C NMR spectra were recorded in CDCl_3 at 75 or 126 MHz with the central resonance of CDCl_3 of δ 77.16 ppm. Enantiomeric excess HPLC analyses were carried out at 25 °C on Agilent 1260 Infinity HPLC System. Chiralpak AD-H (0.46 mm x 250 mm), Chiralcel OD-H (0.46 mm x 250 mm), Chiralpak IC-3 (0.46 mm x 250 mm) columns were obtained from Daicel Chiral Technologies, Japan. HPLC-grade *n*-hexane and 2-propanol were obtained from Fisher Scientific, USA. Chiral HPLC separation conditions were determined by obtaining an optimum separation for standard racemic samples prepared using $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$. Staring martials TIPS-protected enoldiazoacetates **1** and nitrones **2** were prepared according to the literature¹

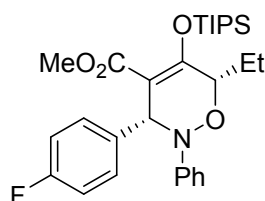
2. Procedure for Copper(I)-Catalyzed [3 + 3]-Cycloaddition Reaction with Chiral BOX Ligand

The chiral catalyst was prepared by stirring $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ (3.7 mg, 0.010 mmol, 5.0 mol %) and the chiral bisoxazoline ligand (4.3 mg, 0.012 mmol, 6.0 mol %) in dry chloroform (2.0 mL) in an oven-dried 8.0 mL Schlenk tube for 1 h under N_2 at room temperature, then chloroform was removed and dry toluene (2.0 mL) was added. A solution of nitrone **2** (0.20 mmol, 1.0 equiv.) in dry toluene (1.0 mL) was introduced to the reaction mixture. Then TIPS-protected enoldiazoacetate **1** (0.30 mmol, 1.5 equiv.) in dry toluene (1.0 mL) was added dropwise over 5 min. The reaction solution was stirred at room temperature for 12 h. Subsequently, solvent was then removed under reduced pressure, and the residue was purified by silica gel column chromatography using a 20:1 to 15:1 gradient of hexane/ethyl acetate (v/v) as the eluent to afford **3**.



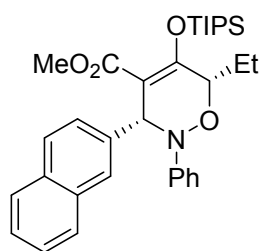
Methyl (3*S*,6*R*)-6-ethyl-2,3-diphenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3a)

colorless oil; 92 mg, 93% yield, $[\alpha]_{\text{D}}^{20} = +129^\circ$ ($c = 1.0$, CHCl_3), 93% *ee*, [HPLC: Chiralpak AD-H column, 1% IPA in hexane (v/v), 1.0 mL/min, 254 nm, $t_1 = 4.6$ min (*major*), $t_2 = 4.9$ min (*minor*)]. ^1H NMR (500 MHz, CDCl_3) δ 7.31 – 7.25 (comp, 2H), 7.23 – 7.13 (comp, 5H), 7.02 (d, $J = 7.7$ Hz, 2H), 6.89 (t, $J = 7.3$ Hz, 1H), 5.68 (d, $J = 1.7$ Hz, 1H), 4.41 (td, $J = 8.7, 1.7$ Hz, 1H), 3.62 (s, 3H), 2.19 – 2.04 (m, 1H), 1.92 – 1.74 (m, 1H), 1.20 – 1.13 (comp, 3H), 1.12 – 1.05 (comp, 21H), ^{13}C NMR (125 MHz, CDCl_3) δ 166.1, 161.7, 148.1, 138.1, 129.5, 128.7, 127.7, 127.5, 122.1, 117.0, 110.0, 78.9, 63.6, 51.4, 24.4, 18.0, 17.9, 13.8, 10.4, HRMS (ESI) m/z calc. for $\text{C}_{29}\text{H}_{42}\text{NO}_4\text{Si}$ ($\text{M}+\text{H}$) $^+$: 496.2878, found: 496.2872.



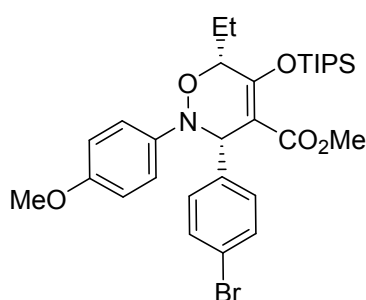
Methyl (3*R*,6*S*)-6-ethyl-3-(4-fluorophenyl)-2-phenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3b)

colorless oil; 89 mg, 87 % yield, $[\alpha]_{\text{D}}^{20} = +182^\circ$ ($c = 1.0$, CHCl_3), 91% *ee*, [HPLC: Chiralpak ADH column, 1% IPA in hexane (v/v), 1.0 mL/min, 250 nm, $t_1 = 4.8$ min (*major*), $t_2 = 5.6$ min (*minor*)], ^1H NMR (500 MHz, CDCl_3) δ 7.26 – 7.18 (comp, 4H), 7.00 (d, $J = 7.8$ Hz, 2H), 6.91 (t, $J = 7.3$ Hz, 1H), 6.88 – 6.83 (comp, 2H), 5.65 (d, $J = 1.5$ Hz, 1H), 4.44 (td, $J = 8.7, 1.5$ Hz, 1H), 3.63 (s, 3H), 2.20 – 2.09 (m, 1H), 1.90 – 1.80 (m, 1H), 1.21 – 1.10 (comp, 24H), ^{13}C NMR (125 MHz, CDCl_3) δ 166.0, 162.3 (d, $J = 245.4$ Hz), 162.1, 148.0, 133.8 (d, $J = 2.9$ Hz), 131.1 (d, $J = 8.0$ Hz), 128.7, 122.3, 117.0, 114.5 (d, $J = 21.2$ Hz), 111.0, 79.2, 63.3, 51.3, 24.4, 18.0, 17.9, 13.8, 10.4, ^{19}F NMR (500 MHz, CDCl_3) δ -115.3. HRMS (ESI) m/z calc. for $\text{C}_{29}\text{H}_{41}\text{FNO}_4\text{Si}$ ($\text{M}+\text{H}$) $^+$: 514.2783, found: 514.2779.



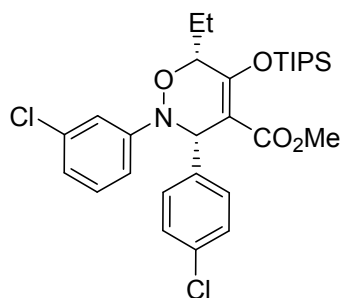
Methyl (3*R*,6*S*)-6-ethyl-3-(naphthalen-2-yl)-2-phenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3c)

colorless oil; 98 mg, 89 % yield, $[\alpha]_{\text{D}}^{20} = +181^\circ$ ($c = 1.0$, CHCl_3), 91% *ee*, [HPLC: Chiralpak ADH column, 1% IPA in hexane (v/v), 1.0 mL/min, 250 nm, $t_1 = 5.7$ min (*major*), $t_2 = 7.0$ min (*minor*)], ^1H NMR (500 MHz, CDCl_3) δ 7.79 – 7.70 (comp, 3H), 7.65 (d, $J = 8.5$ Hz, 1H), 7.46 – 7.36 (comp, 3H), 7.23 – 7.16 (comp, 2H), 7.06 (d, $J = 7.8$ Hz, 2H), 6.88 (t, $J = 7.3$ Hz, 1H), 5.86 (d, $J = 1.6$ Hz, 1H), 4.46 (td, $J = 8.5, 1.6$ Hz, 1H), 3.60 (s, 3H), 2.22 – 2.10 (m, 1H), 1.98 – 1.85 (m, 1H), 1.23 – 1.10 (comp, 24H), ^{13}C NMR (125 MHz, CDCl_3) δ 166.1, 161.8, 148.0, 135.8, 133.0, 133.0, 128.8, 128.7, 128.3, 127.7, 127.6, 127.2, 125.7, 125.6, 122.1, 117.0, 111.0, 78.8, 63.5, 51.4, 24.5, 18.0, 17.95, 13.8, 10.4, HRMS (ESI) m/z calc. for $\text{C}_{33}\text{H}_{44}\text{NO}_4\text{Si}$ ($\text{M}+\text{H}$) $^+$: 546.3034, found: 546.3031.



Methyl (3*R*,6*S*)-3-(4-bromophenyl)-6-ethyl-2-(4-methoxyphenyl)-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3d)

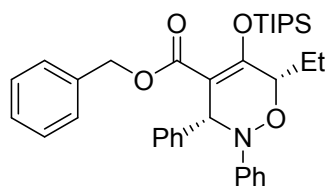
colorless oil; 104 mg, 86 % yield, $[\alpha]_{\text{D}}^{20} = +139^\circ$ ($c = 1.0$, CHCl_3), 96% *ee*, [HPLC: Chiralpak ADH column, 3% IPA in hexane (v/v), 1.0 mL/min, 250 nm, $t_1 = 5.6$ min (*major*), $t_2 = 7.8$ min (*minor*)], ^1H NMR (500 MHz, CDCl_3) δ 7.27 (t, $J = 5.6$ Hz, 2H), 7.05 (d, $J = 8.4$ Hz, 2H), 6.91 – 6.86 (comp, 2H), 6.77 – 6.72 (comp, 2H), 5.42 (s, 1H), 4.36 (d, $J = 8.7$ Hz, 1H), 3.74 (s, 3H), 3.59 (s, 3H), 2.14 – 2.04 (m, 1H), 1.91 – 1.80 (m, 1H), 1.21 – 1.15 (comp, 3H), 1.13 – 1.08 (comp, 21H), ^{13}C NMR (125 MHz, CDCl_3) δ 166.0, 162.4, 155.7, 141.5, 137.0, 131.3, 130.8, 121.6, 119.6, 114.0, 109.7, 79.4, 64.8, 55.6, 51.3, 24.4, 18.1, 18.0, 13.8, 10.4, HRMS (ESI) m/z calc. for $\text{C}_{30}\text{H}_{43}\text{BrNO}_5\text{Si}$ ($\text{M}+\text{H}$) $^+$: 604.2088, found: 604.2085.



Methyl (3*R*,6*S*)-2-(3-chlorophenyl)-3-(4-chlorophenyl)-6-ethyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3e)

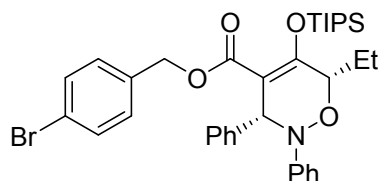
colorless oil; 98 mg, 87 % yield, $[\alpha]_{\text{D}}^{20} = +184^\circ$ ($c = 1.0$, CHCl_3), 82% *ee*, [HPLC:

Chiralpak ADH column, 1% IPA in hexane (v/v), 1.0 mL/min, 250 nm, t_1 = 5.6 min (*major*), t_2 = 4.9 min (*minor*), ^1H NMR (500 MHz, CDCl_3) δ 7.20 (d, J = 8.5 Hz, 2H), 7.15 (d, J = 8.5 Hz, 2H), 7.12 (t, J = 8.1 Hz, 1H), 6.99 (t, J = 2.0 Hz, 1H), 6.88 – 6.84 (comp, 2H), 5.60 (d, J = 1.7 Hz, 1H), 4.43 (td, J = 8.5, 1.7 Hz, 1H), 3.62 (s, 3H), 2.18 – 2.09 (m, 1H), 1.90 – 1.78 (m, 1H), 1.20 – 1.09 (comp, 24H), ^{13}C NMR (125 MHz, CDCl_3) δ 165.8, 162.1, 149.1, 136.1, 134.7, 133.6, 130.8, 129.8, 128.0, 122.0, 116.8, 114.8, 109.6, 79.8, 63.2, 51.4, 24.3, 18.0, 17.9, 13.8, 10.3, HRMS (ESI) m/z calc. for $\text{C}_{29}\text{H}_{40}\text{Cl}_2\text{NO}_4\text{Si}$ ($\text{M}+\text{H}$) $^+$: 564.2098, found: 564.2097.



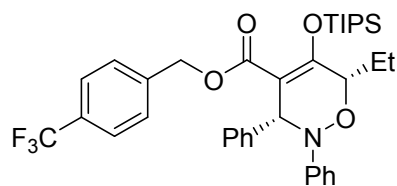
Benzyl (3*R*,6*S*)-6-ethyl-2,3-diphenyl-5-((triisopropylsilyl)oxy)-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3f)

colorless oil; 104 mg, 91 % yield, $[\alpha]_{\text{D}}^{20}$ = + 155° (c = 1.0, CHCl_3), 98% *ee*, [HPLC: Chiralpak AD-H column, 1% IPA in hexane (v/v), 1.0 mL/min, 254 nm, t_1 = 4.5 min (*major*), t_2 = 5.7 min (*minor*)]. ^1H NMR (500 MHz, CDCl_3) δ 7.28 – 7.23 (comp, 5H), 7.22 – 7.15 (comp, 5H), – 7.01 (comp, 4H), 6.91 (t, J = 7.3 Hz, 1H), 5.70 (d, J = 1.5 Hz, 1H), 5.12 (d, J = 12.5 Hz, 1H), 5.03 (d, J = 12.5 Hz, 1H), 4.46 (td, J = 8.7, 1.5 Hz, 1H), 2.22 – 2.11 (m, 1H), 1.95 – 1.87 (m, 1H), 1.22 – 1.15 (comp, 6H), 1.13 – 1.09 (comp, 18H), ^{13}C NMR (125 MHz, CDCl_3) δ 164.8, 162.5, 148.1, 138.0, 136.2, 129.7, 128.7, 128.4, 128.1, 127.9, 127.7, 127.5, 122.1, 117.2, 109.6, 79.2, 65.8, 63.9, 24.4, 18.1, 18.0, 13.9, 10.4, HRMS (ESI) m/z calc. for $\text{C}_{35}\text{H}_{46}\text{NO}_4\text{Si}$ ($\text{M}+\text{H}$) $^+$: 572.3191, found: 572.3179.



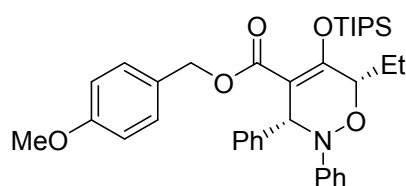
4-Bromobenzyl (3*R*,6*S*)-6-ethyl-2,3-diphenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3g)

colorless oil; 113 mg, 87 % yield, $[\alpha]_{\text{D}}^{20}$ = + 108° (c = 1.0, CHCl_3), 99% *ee*, [HPLC: Chiralpak ADH column, 1% IPA in hexane (v/v), 1.0 mL/min, 250 nm, t_1 = 5.2 min (*major*)], ^1H NMR (500 MHz, CDCl_3) δ 7.30 (d, J = 8.4 Hz, 2H), 7.22 – 7.12 (comp, 7H), 6.99 (d, J = 7.7 Hz, 2H), 6.90 (t, J = 7.3 Hz, 1H), 6.83 (d, J = 8.4 Hz, 2H), 5.62 (d, J = 1.5 Hz, 1H), 4.98 (s, 2H), 4.43 (td, J = 8.6, 1.5 Hz, 1H), 2.19 – 2.08 (m, 1H), 1.94 – 1.82 (m, 1H), 1.21 – 1.11 (comp, 6H), 1.10 – 1.07 (m, 18H), ^{13}C NMR (125 MHz, CDCl_3) δ 164.6, 163.0, 148.1, 137.9, 135.3, 131.5, 129.7, 129.6, 128.7, 127.7, 127.5, 122.3, 121.9, 117.3, 109.4, 79.5, 64.9, 64.1, 24.4, 18.1, 18.0, 13.9, 10.4, HRMS (ESI) m/z calc. for $\text{C}_{35}\text{H}_{45}\text{BrNO}_4\text{Si}$ ($\text{M}+\text{H}$) $^+$: 650.2296, found: 650.2287.



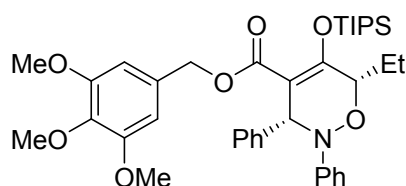
4-(Trifluoromethyl)benzyl (3*R*,6*S*)-6-ethyl-2,3-diphenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3h)

colorless oil; 113 mg, 88 % yield, $[\alpha]_D^{20} = +154^\circ$ ($c = 1.0$, CHCl_3), 97% *ee*, [HPLC: Chiralpak ADH column, 1% IPA in hexane (v/v), 1.0 mL/min, 250 nm, $t_1 = 3.8$ min (*major*), $t_2 = 8.0$ min (*minor*)], ^1H NMR (500 MHz, CDCl_3) δ 7.44 (d, $J = 8.1$ Hz, 2H), 7.25 – 7.14 (comp, 7H), 7.07 – 6.99 (comp, 4H), 6.92 (t, $J = 7.3$ Hz, 1H), 5.66 (s, 1H), 5.13 (d, $J = 13.0$ Hz, 1H), 5.08 (d, $J = 13.0$ Hz, 1H), 4.47 (d, $J = 8.7$ Hz, 1H), 2.23 – 2.10 (m, 1H), 1.97 – 1.84 (m, 1H), 1.25 – 1.15 (comp, 6H), 1.14 – 1.10 (m, 18H), ^{13}C NMR (125 MHz, CDCl_3) δ 164.5, 163.4, 148.1, 140.3, 137.8, 130.0 (q, $J = 32.2$ Hz), 129.7, 128.7, 127.9, 127.7, 127.6, 125.3 (q, $J = 3.8$ Hz), 122.3, 119.4 (q, $J = 246.8$ Hz), 117.3, 109.3, 79.6, 64.7, 64.3, 24.4, 18.1, 18.0, 13.9, 10.4, ^{19}F NMR (500 MHz, CDCl_3) δ -62.60, HRMS (ESI) m/z calc. for $\text{C}_{36}\text{H}_{45}\text{F}_3\text{NO}_4\text{Si}$ ($\text{M}+\text{H}$) $^+$: 640.3064, found: 640.3053.



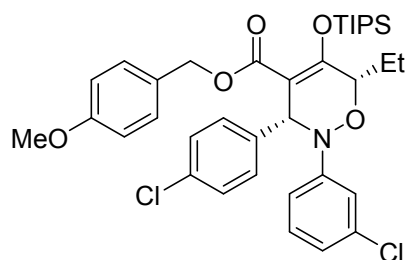
4-Methoxybenzyl(3*R*,6*S*)-6-ethyl-2,3-diphenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3i)

colorless oil; 108 mg, 90 % yield, $[\alpha]_D^{20} = +155^\circ$ ($c = 1.0$, CHCl_3), 98% *ee*, [HPLC: Chiralpak ADH column, 1% IPA in hexane (v/v), 1.0 mL/min, 254 nm, $t_1 = 4.5$ min (*major*), $t_2 = 7.4$ min (*minor*)], ^1H NMR (500 MHz, CDCl_3) δ 7.26 – 7.14 (comp, 7H), 7.02 (d, $J = 8.6$ Hz, 4H), 6.91 (t, $J = 7.3$ Hz, 1H), 6.82 – 6.76 (comp, 2H), 5.66 (d, $J = 1.1$ Hz, 1H), 5.04 (d, $J = 12.1$ Hz, 1H), 4.95 (d, $J = 12.1$ Hz, 1H), 4.43 (td, $J = 8.7, 1.1$ Hz, 1H), 3.82 (s, 3H), 2.20 – 2.09 (m, 1H), 1.95 – 1.83 (m, 1H), 1.19 – 1.12 (comp, 6H), 1.11 – 1.08 (m, 18H), ^{13}C NMR (125 MHz, CDCl_3) δ 165.0, 159.5, 148.1, 138.1, 130.0, 129.7, 128.7, 128.4, 127.6, 127.4, 122.1, 117.2, 113.7, 109.7, 79.2, 65.7, 63.8, 55.4, 24.4, 18.1, 18.0, 13.9, 10.4, HRMS (ESI) m/z calc. for $\text{C}_{36}\text{H}_{48}\text{NO}_5\text{Si}$ ($\text{M}+\text{H}$) $^+$: 602.3296, found: 602.3289.



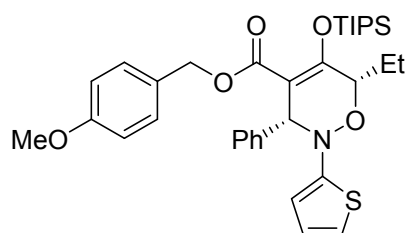
3,4,5-Trimethoxybenzyl (3*R*,6*S*)-6-ethyl-2,3-diphenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3j)

colorless oil; 122 mg, 92 % yield, $[\alpha]_{\text{D}}^{20} = +156^{\circ}$ ($c = 1.0$, CHCl_3), 99% *ee*, [HPLC: Chiralpak ADH column, 1% IPA in hexane (v/v), 1.0 mL/min, 250 nm, $t_1 = 8.0$ min (*major*), $t_2 = 12.4$ min (*minor*)], ^1H NMR (500 MHz, CDCl_3) δ 7.23 – 7.16 (comp, 4H), 7.15 – 7.10 (comp, 3H), 7.02 – 6.98 (comp, 2H), 6.89 (s, 1H), 6.39 (s, 2H), 5.67 (d, $J = 1.5$ Hz, 1H), 5.03 (d, $J = 12.2$ Hz, 1H), 4.93 (d, $J = 12.2$ Hz, 1H), 4.41 (td, $J = 8.7, 1.5$ Hz, 1H), 3.83 (s, 3H), 3.75 (s, 6H), 2.16 – 2.05 (m, 1H), 1.93 – 1.81 (m, 1H), 1.17 – 1.10 (comp, 6H), 1.09 – 1.05 (comp, 18H), ^{13}C NMR (125 MHz, CDCl_3) δ 164.9, 162.4, 153.2, 148.0, 138.1, 137.8, 131.8, 129.4, 128.7, 127.6, 127.4, 122.2, 117.1, 109.5, 105.7, 78.9, 66.2, 63.5, 60.9, 56.1, 24.3, 18.1, 17.9, 13.9, 10.3, HRMS (ESI) m/z calc. for $\text{C}_{38}\text{H}_{52}\text{NO}_7\text{Si}$ ($\text{M}+\text{H}$) $^+$: 662.3508, found: 662.3492.



4-Methoxybenzyl (3*R*,6*S*)-2-(3-chlorophenyl)-3-(4-chlorophenyl)-6-ethyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3k)

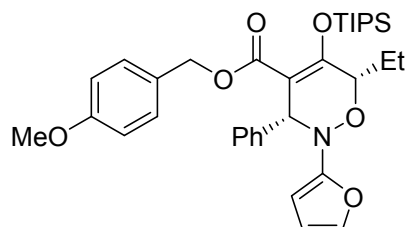
colorless oil; 114 mg, 85 % yield, $[\alpha]_{\text{D}}^{20} = +149^{\circ}$ ($c = 1.0$, CHCl_3), 90% *ee*, [HPLC: Chiralpak ADH column, 1% IPA in hexane (v/v), 1.0 mL/min, 250 nm, $t_1 = 4.5$ min (*major*), $t_2 = 6.0$ min (*minor*)], ^1H NMR (500 MHz, CDCl_3) δ 7.18 – 7.09 (comp, 5H), 7.05 – 7.00 (comp, 3H), 6.91 – 6.87 (comp, 2H), 6.81 (d, $J = 8.6$ Hz, 2H), 5.60 (d, $J = 1.4$ Hz, 1H), 5.02 (s, 2H), 4.47 (td, $J = 8.6, 1.4$ Hz, 1H), 3.83 (s, 3H), 2.24 – 2.14 (m, 1H), 1.94 – 1.83 (m, 1H), 1.23 – 1.18 (comp, 3H), 1.16 – 1.10 (comp, 21H), ^{13}C NMR (125 MHz, CDCl_3) δ 164.5, 162.5, 159.6, 149.1, 136.1, 134.6, 133.5, 130.9, 130.1, 129.7, 128.1, 127.9, 122.1, 116.9, 115.0, 113.7, 109.3, 80.0, 65.7, 63.4, 55.3, 24.2, 18.1, 18.0, 13.9, 10.3, HRMS (ESI) m/z calc. for $\text{C}_{36}\text{H}_{46}\text{Cl}_2\text{NO}_5\text{Si}$ ($\text{M}+\text{H}$) $^+$: 670.2517, found: 670.2517.



4-Methoxybenzyl (3*R*,6*S*)-6-ethyl-3-phenyl-2-(thiophen-2-yl)-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3l)

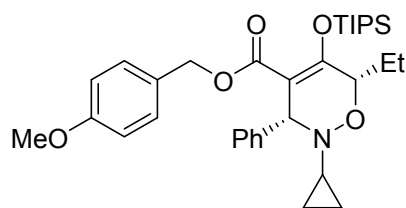
colorless oil; 106 mg, 87 % yield, $[\alpha]_{\text{D}}^{20} = +152^{\circ}$ ($c = 1.0$, CHCl_3), 92% *ee*, [HPLC: Chiralpak ADH column, 1% IPA in hexane (v/v), 1.0 mL/min, 250 nm, $t_1 = 4.6$ min (*major*), $t_2 = 8.1$ min (*minor*)], ^1H NMR (500 MHz, CDCl_3) δ 7.22 (t, $J = 7.9$ Hz, 2H), 7.11 (d, $J = 8.6$ Hz, 2H), 7.08 (d, $J = 5.0$ Hz, 1H), 7.03 (d, $J = 7.9$ Hz, 2H), 6.91 (t, $J = 7.4$ Hz, 1H), 6.81 (d, $J = 8.6$ Hz, 2H), 6.77 – 6.70 (comp, 2H), 5.89 (d, $J = 1.3$ Hz,

1H), 5.08 (d, $J = 12.1$ Hz, 1H), 5.00 (d, $J = 12.1$ Hz, 1H), 4.5 (td, $J = 8.6, 1.3$ Hz, 1H), 3.80 (s, 3H), 2.17 – 2.07 (m, 1H), 1.94 – 1.83 (m, 1H), 1.20 – 1.14 (comp, 6H), 1.09 (d, $J = 5.9$ Hz, 18H), ^{13}C NMR (125 MHz, CDCl_3) δ 164.8, 162.7, 159.5, 148.0, 140.4, 130.2, 128.7, 128.4, 127.7, 125.7, 125.4, 122.2, 116.7, 113.8, 110.9, 80.5, 65.8, 60.2, 55.4, 24.3, 18.1, 18.0, 13.9, 10.3, HRMS (ESI) m/z calc. for $\text{C}_{34}\text{H}_{46}\text{NO}_5\text{SSi}$ ($\text{M}+\text{H}$) $^+$: 608.2860, found: 608.2862.



4-Methoxybenzyl (3R,6S)-6-ethyl-2-(furan-2-yl)-3-phenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2H-1,2-oxazine-4-carboxylate (3m)

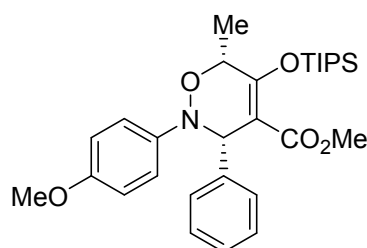
colorless oil; 104 mg, 88 % yield, $[\alpha]_{\text{D}}^{20} = +162^\circ$ ($c = 1.0$, CHCl_3), 98% *ee*, [HPLC: Chiralpak ADH column, 1% IPA in hexane (v/v), 1.0 mL/min, 250 nm, $t_1 = 4.3$ min (*major*), $t_2 = 5.1$ min (*minor*)], ^1H NMR (500 MHz, CDCl_3) δ 7.27 – 7.22 (comp, 2H), 7.20 – 7.17 (m, 1H), 7.13 (d, $J = 8.6$ Hz, 2H), 7.09 (d, $J = 7.8$ Hz, 2H), 6.94 (t, $J = 7.3$ Hz, 1H), 6.83 (d, $J = 8.6$ Hz, 2H), 6.22 – 6.17 (m, 1H), 6.12 (d, $J = 3.2$ Hz, 1H), 5.76 (d, $J = 1.6$ Hz, 1H), 5.06 (dd, $J = 17.1, 12.1$ Hz, 1H), 4.43 (td, $J = 7.9, 1.6$ Hz, 1H), 3.80 (s, 3H), 2.13 – 2.02 (m, 1H), 1.90 – 1.79 (m, 1H), 1.19 – 1.11 (comp, 6H), 1.09 – 1.05 (comp, 18H), ^{13}C NMR (125 MHz, CDCl_3) δ 164.6, 163.1, 159.5, 152.5, 148.0, 141.8, 130.0, 128.7, 128.5, 122.2, 116.7, 113.8, 110.0, 109.4, 108.2, 79.3, 65.7, 57.6, 55.4, 24.2, 18.1, 18.0, 13.9, 10.0, HRMS (ESI) m/z calc. for $\text{C}_{34}\text{H}_{46}\text{NO}_6\text{Si}$ ($\text{M}+\text{H}$) $^+$: 592.3089, found: 592.3081.



4-Methoxybenzyl (3R,6S)-2-cyclopropyl-6-ethyl-3-phenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2H-1,2-oxazine-4-carboxylate (3n)

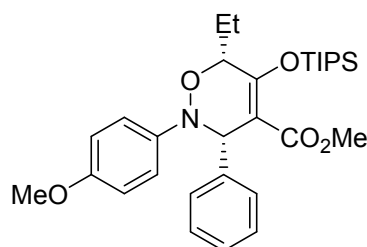
colorless oil; 93 mg, 82 % yield, $[\alpha]_{\text{D}}^{20} = +134^\circ$ ($c = 1.0$, CHCl_3), 90 % *ee*, [HPLC: Chiralpak ADH column, 1% IPA in hexane (v/v), 1.0 mL/min, 250 nm, $t_1 = 3.9$ min (*major*), $t_2 = 5.2$ min (*minor*)], ^1H NMR (500 MHz, CDCl_3) δ 7.36 (d, $J = 8.6$ Hz, 2H), 7.26 – 7.20 (comp, 2H), 7.06 (d, $J = 7.8$ Hz, 2H), 6.93 – 6.87 (comp, 3H), 5.28 (d, $J = 11.9$ Hz, 1H), 5.02 (d, $J = 11.9$ Hz, 1H), 4.24 (td, $J = 7.3, 1.1$ Hz, 1H), 4.04 (dd, $J = 8.5, 1.1$ Hz, 1H), 3.81 (s, 3H), 2.07 – 1.94 (m, 1H), 1.84 – 1.71 (m, 1H), 1.30 – 1.21 (m, 1H), 1.17 – 1.03 (comp, 6H), 0.96 (d, $J = 3.6$ Hz, 18H), 0.34 – 0.26 (comp, 3H), 0.11 – 0.03 (m, 1H), ^{13}C NMR (125 MHz, CDCl_3) δ 166.2, 159.7, 158.5, 148.3, 130.7, 128.9, 128.4, 121.7, 116.6, 113.9, 111.2, 76.5, 65.9, 62.4, 55.4, 24.4, 17.9,

17.8, 13.9, 13.7, 9.8, 3.9, 2.4, HRMS (ESI) m/z calc. for $C_{33}H_{48}NO_5Si$ (M+H)⁺: 566.3296, found: 566.3288.



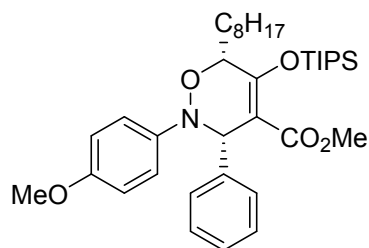
Methyl 3*S*,6*R*)-2-(4-methoxyphenyl)-6-methyl-3-phenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3o)

colorless oil; 89 mg, 87 % yield, $[\alpha]_D^{20} = +174^\circ$ ($c = 1.0$, $CHCl_3$), 83% *ee*, [HPLC: Chiralpak ADH column, 1% IPA in hexane (v/v), 1.0 mL/min, 250 nm, $t_1 = 9.3$ min (*major*), $t_2 = 11.5$ min (*minor*)], 1H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.13 (comp, 5H), 6.90 (d, $J = 9.0$ Hz, 2H), 6.73 (d, $J = 9.0$ Hz, 2H), 5.46 (d, $J = 1.4$ Hz, 1H), 4.55 (qd, $J = 6.6, 1.4$ Hz, 1H), 3.73 (s, 3H), 3.59 (s, 3H), 1.56 (d, $J = 6.6$ Hz, 3H), 1.22 – 1.16 (comp, 3H), 1.12 (t, $J = 6.2$ Hz, 18H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 162.6, 155.6, 141.7, 137.6, 129.7, 127.6, 127.5, 119.7, 113.9, 109.5, 74.4, 55.6, 51.3, 18.1, 18.0, 17.9, 17.0, 13.8, HRMS (ESI) m/z calc. for $C_{29}H_{42}NO_5Si$ (M+H)⁺: 512.2827, found: 512.2829.



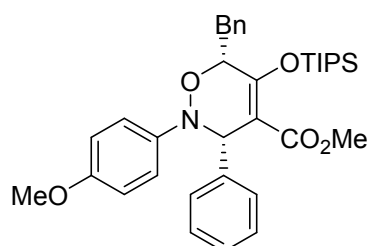
Methyl (3*R*,6*S*)-6-ethyl-2-(4-methoxyphenyl)-3-phenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3p)

colorless oil; 96 mg, 91 % yield, $[\alpha]_D^{20} = +203^\circ$ ($c = 1.0$, $CHCl_3$), 96% *ee*, [HPLC: Chiralpak ADH column, 1% IPA in hexane (v/v), 1.0 mL/min, 250 nm, $t_1 = 5.8$ min (*major*), $t_2 = 6.9$ min (*minor*)], 1H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.18 (comp, 2H), 7.18 – 7.12 (comp, 3H), 6.92 (d, $J = 9.0$ Hz, 2H), 6.74 (d, $J = 9.0$ Hz, 2H), 5.50 (s, 1H), 4.35 (d, $J = 8.8$ Hz, 1H), 3.73 (s, 3H), 3.59 (s, 3H), 2.14 – 2.03 (m, 1H), 1.96 – 1.81 (m, 1H), 1.22 – 1.14 (comp, 3H), 1.14 – 1.08 (comp, 21H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 161.7, 155.5, 141.8, 138.0, 129.7, 127.6, 127.4, 119.6, 113.9, 110.0, 79.0, 65.0, 55.6, 51.3, 24.4, 18.0, 17.95, 17.8, 13.8, 10.4, HRMS (ESI) m/z calc. for $C_{30}H_{44}NO_5Si$ (M+H)⁺: 526.2983, found: 526.2985.



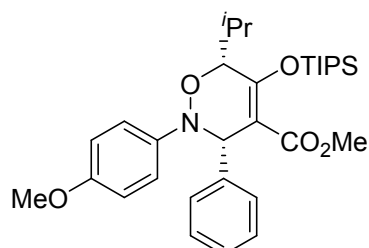
Methyl (3*S*,6*R*)-2-(4-methoxyphenyl)-6-octyl-3-phenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3q)

colorless oil; 101 mg, 83 % yield, $[\alpha]_D^{20} = +234^\circ$ ($c = 1.0$, CHCl_3), 93% *ee*, [HPLC: Chiralpak ADH column, 1% IPA in hexane (v/v), 1.0 mL/min, 250 nm, $t_1 = 4.8$ min (*major*), $t_2 = 5.3$ min (*minor*)], ^1H NMR (500 MHz, CDCl_3) δ 7.22 – 7.12 (comp, 5H), 6.91 (d, $J = 9.0$ Hz, 2H), 6.73 (d, $J = 9.0$ Hz, 2H), 5.48 (s, 1H), 4.38 (d, $J = 9.1$ Hz, 1H), 3.73 (s, 3H), 3.58 (s, 3H), 2.08 – 2.00 (m, 1H), 1.83 (m, 1H), 1.66 – 1.59 (m, 1H), 1.50 – 1.39 (m, 1H), 1.28 (comp, 12H), 1.17 – 1.05 (comp, 21H), 0.88 (t, $J = 6.9$ Hz, 3H), ^{13}C NMR (125 MHz, CDCl_3) δ 166.2, 162.0, 155.5, 141.8, 138.0, 129.7, 127.6, 127.4, 119.6, 113.9, 109.8, 78.2, 65.0, 55.6, 51.3, 32.0, 31.2, 29.8, 30.0, 29.4, 26.0, 22.8, 18.1, 18.0, 14.3, 13.8., HRMS (ESI) m/z calc. for $\text{C}_{36}\text{H}_{56}\text{NO}_5\text{Si}$ ($\text{M}+\text{H}$) $^+$: 610.3922, found: 610.3927.



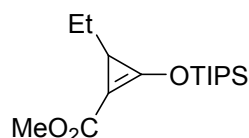
Methyl (3*S*,6*R*)-6-benzyl-2-(4-methoxyphenyl)-3-phenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3r)

colorless oil; 100 mg, 85 % yield, $[\alpha]_D^{20} = +183^\circ$ ($c = 1.0$, CHCl_3), 96% *ee*, [HPLC: Chiralpak ADH column, 1% IPA in hexane (v/v), 1.0 mL/min, 250 nm, $t_1 = 5.4$ min (*major*), $t_2 = 7.2$ min (*minor*)], ^1H NMR (500 MHz, CDCl_3) δ 7.35 – 7.27 (comp, 4H), 7.07 (t, $J = 7.3$ Hz, 1H), 6.99 (t, $J = 7.5$ Hz, 2H), 6.78 (comp, 4H), 6.67 (d, $J = 8.8$ Hz, 2H), 5.35 (s, 1H), 4.68 (t, $J = 4.3$ Hz, 1H), 3.70 (s, 3H), 3.55 (s, 3H), 3.31 (d, $J = 4.6$ Hz, 2H), 1.30 – 1.13 (comp, 21H)., ^{13}C NMR (125 MHz, CDCl_3) δ 165.9, 161.0, 155.6, 141.7, 137.4, 137.1, 130.0, 129.8, 128.5, 127.5, 127.3, 126.7, 120.0, 113.8, 111.3, 79.1, 66.3, 55.6, 51.3, 36.8, 18.2, 18.1, 17.9, 14.0, HRMS (ESI) m/z calc. for $\text{C}_{35}\text{H}_{46}\text{NO}_5\text{Si}$ ($\text{M}+\text{H}$) $^+$: 588.3140, found: 588.3143.



Methyl (3*S*,6*R*)-6-isopropyl-2-(4-methoxyphenyl)-3-phenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3*s*)

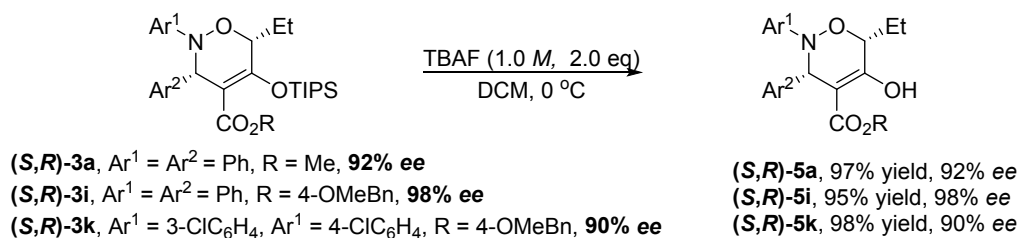
colorless oil; 83 mg, 77 % yield, $[\alpha]_{\text{D}}^{20} = +263^\circ$ ($c = 1.0$, CHCl_3), 99% *ee*, [HPLC: Chiralpak IC-3 column, 1% IPA in hexane (v/v), 1.0 mL/min, 250 nm, $t_1 = 5.8$ min (*major*), $t_2 = 7.5$ min (*minor*)], ^1H NMR (500 MHz, CDCl_3) δ 7.24 (d, $J = 1.5$ Hz, 2H), 7.18 – 7.12 (comp, 3H), 6.92 (d, $J = 9.0$ Hz, 2H), 6.75 (d, $J = 9.0$ Hz, 2H), 5.56 (d, $J = 1.4$ Hz, 1H), 4.31 (t, $J = 2.0$ Hz, 1H), 3.73 (s, 3H), 3.60 (s, 3H), 2.49 – 2.40 (m, 1H), 1.13 (d, $J = 7.2$ Hz, 6H), 1.11 – 1.04 (comp, 21H), ^{13}C NMR (125 MHz, CDCl_3) δ 166.4, 161.6, 155.2, 141.8, 138.6, 129.5, 127.6, 127.3, 118.9, 114.0, 110.3, 81.1, 64.0, 55.7, 51.3, 29.2, 19.7, 18.1, 18.0, 16.4, 13.9, HRMS (ESI) m/z calc. for $\text{C}_{31}\text{H}_{46}\text{NO}_5\text{Si}$ ($\text{M}+\text{H}$) $^+$: 540.3140, found: 540.3144.



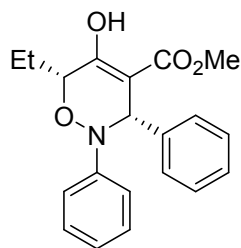
Methyl 3-ethyl-2-[(triisopropylsilyl)oxy]cycloprop-1-ene-1-carboxylate (4*a*)

colorless oil; 58 mg, 97 % yield, ^1H NMR (500 MHz, CDCl_3) δ 3.73 (s, 3H), 2.39 – 2.30 (m, 1H), 2.17 (s, 2H), 1.73 – 1.60 (m, 1H), 1.52 – 1.36 (comp, 4H), 1.10–1.18 (comp, 18H), 0.94 (t, $J = 7.5$ Hz, 3H), ^{13}C NMR (125 MHz, CDCl_3) δ 207.1, 160.5, 148.4, 76.1, 51.5, 31.4, 26.9, 17.6, 12.4, 12.1, HRMS (ESI) m/z calc. for $\text{C}_{16}\text{H}_{31}\text{O}_3\text{Si}$ ($\text{M}+\text{H}$) $^+$: 299.2037, found: 299.2035.

3. General Procedure for TIPS-Group Removal Reactions

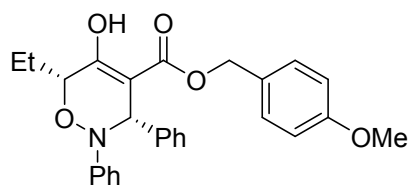


To a solution of the TIPS-protected 6-ethyl-3,6-dihydro-2*H*-1,2-oxazine derivative **3** (1.0 equiv.) in dry dichloromethane stirred at 0 °C under N_2 was added tetra-*n*-butylammonium fluoride (1.0 M in THF, 2.0 equiv.) dropwise *via* syringe over 5 min. The reaction solution was then allowed to stir at room temperature for 1 hour. The reaction solvent was then removed under reduced pressure, and the residue was purified by column chromatography on silica gel using a 10:1 mixture of hexane/ethyl acetate as the eluent to afford the corresponding TIPS-deprotected compound **5**.



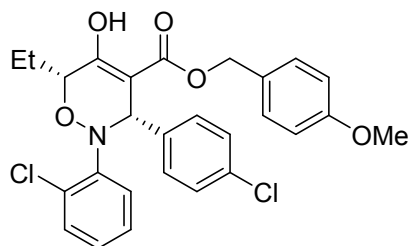
Methyl (3*S*,6*R*)-6-ethyl-5-hydroxy-2,3-diphenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (5a)

colorless oil; 33 mg, 97 % yield, $[\alpha]_{\text{D}}^{20} = +134^{\circ}$ ($c = 1.0$, CHCl_3), 92% *ee*, [HPLC: Chiralpak ADH column, 2% IPA in hexane (v/v), 1.0 mL/min, 250 nm, $t_1 = 6.2$ min (*major*), $t_2 = 5.6$ min (*minor*)], ^1H NMR (500 MHz, CDCl_3) δ 12.22 (br, 1H), 7.21 – 7.12 (comp, 7H), 6.95 (d, $J = 8.0$ Hz, 2H), 6.90 (t, $J = 7.3$ Hz, 1H), 5.38 (d, $J = 0.8$ Hz, 1H), 4.62 (dd, $J = 8.4, 2.5$ Hz, 1H), 3.66 (s, 3H), 2.21 – 2.12 (m, 1H), 1.94 – 1.84 (m, 1H), 1.16 (t, $J = 7.5$ Hz, 3H), ^{13}C NMR (125 MHz, CDCl_3) δ 172.3, 148.2, 137.7, 129.5, 128.7, 127.6, 127.5, 122.4, 117.2, 99.4, 78.3, 62.9, 51.9, 23.5, 10.2, HRMS (ESI) m/z calc. for $\text{C}_{20}\text{H}_{22}\text{NO}_4$ ($\text{M}+\text{H}$) $^+$: 340.1543, found: 340.1539.



4-Methoxybenzyl (3*S*,6*R*)-6-ethyl-5-hydroxy-2,3-diphenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (5i)

colorless oil; 42 mg, 95 % yield, $[\alpha]_{\text{D}}^{20} = +134^{\circ}$ ($c = 1.0$, CHCl_3), 98% *ee*, [HPLC: Chiralpak ADH column, 10% IPA in hexane (v/v), 1.0 mL/min, 250 nm, $t_1 = 4.6$ min (*major*), $t_2 = 7.7$ min (*minor*)], ^1H NMR (500 MHz, CDCl_3) δ 12.17 (br, 1H), 7.20 – 7.11 (comp, 7H), 6.93 (d, $J = 7.7$ Hz, 2H), 6.90 – 6.83 (comp, 3H), 6.74 (d, $J = 8.7$ Hz, 2H), 5.36 (d, $J = 1.2$ Hz, 1H), 5.05 (d, $J = 12.2$ Hz, 1H), 4.99 (d, $J = 12.2$ Hz, 1H), 4.62 (dd, $J = 8.4, 2.2$ Hz, 1H), 3.79 (s, 3H), 2.22 – 2.10 (m, 1H), 1.96 – 1.83 (m, 1H), 1.17 (t, $J = 7.4$ Hz, 3H), ^{13}C NMR (125 MHz, CDCl_3) δ 172.4, 170.6, 159.6, 148.2, 137.8, 129.8, 129.4, 128.6, 127.6, 127.5, 122.4, 117.3, 113.9, 99.6, 78.4, 66.2, 63.1, 55.4, 23.5, 10.2, HRMS (ESI) m/z calc. for $\text{C}_{27}\text{H}_{28}\text{NO}_5$ ($\text{M}+\text{H}$) $^+$: 446.1962, found: 446.1963.



4-Methoxybenzyl (3*S*,6*R*)-2-(2-chlorophenyl)-3-(4-chlorophenyl)-6-ethyl-5-

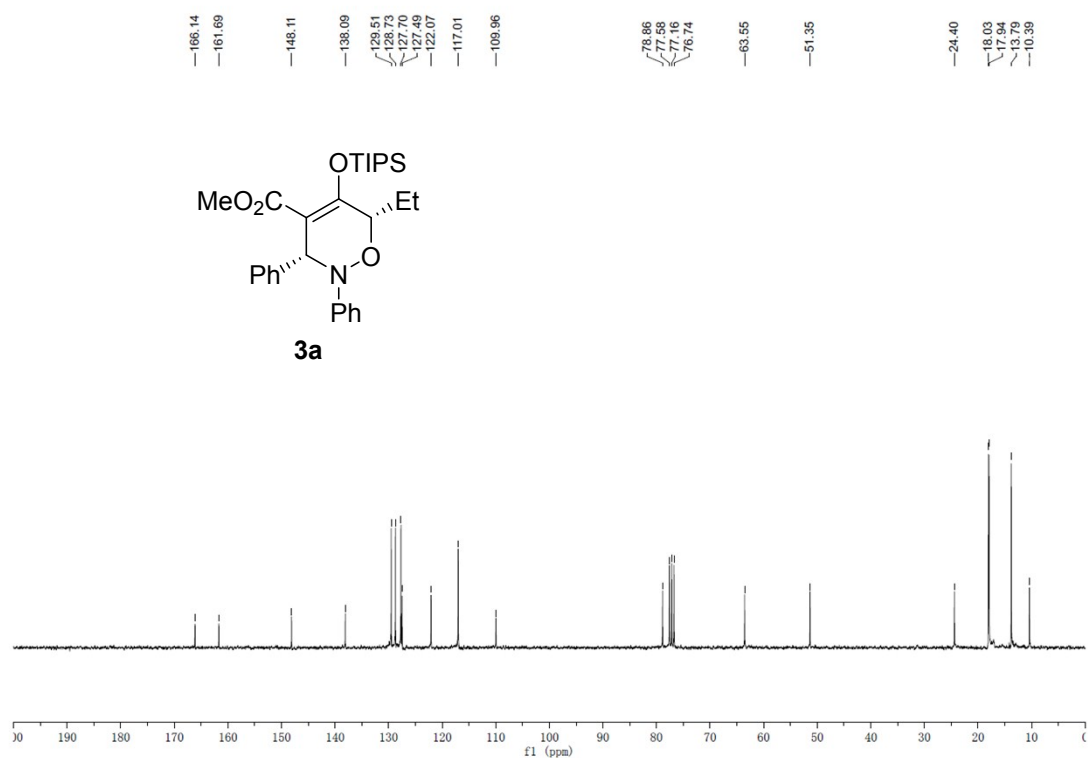
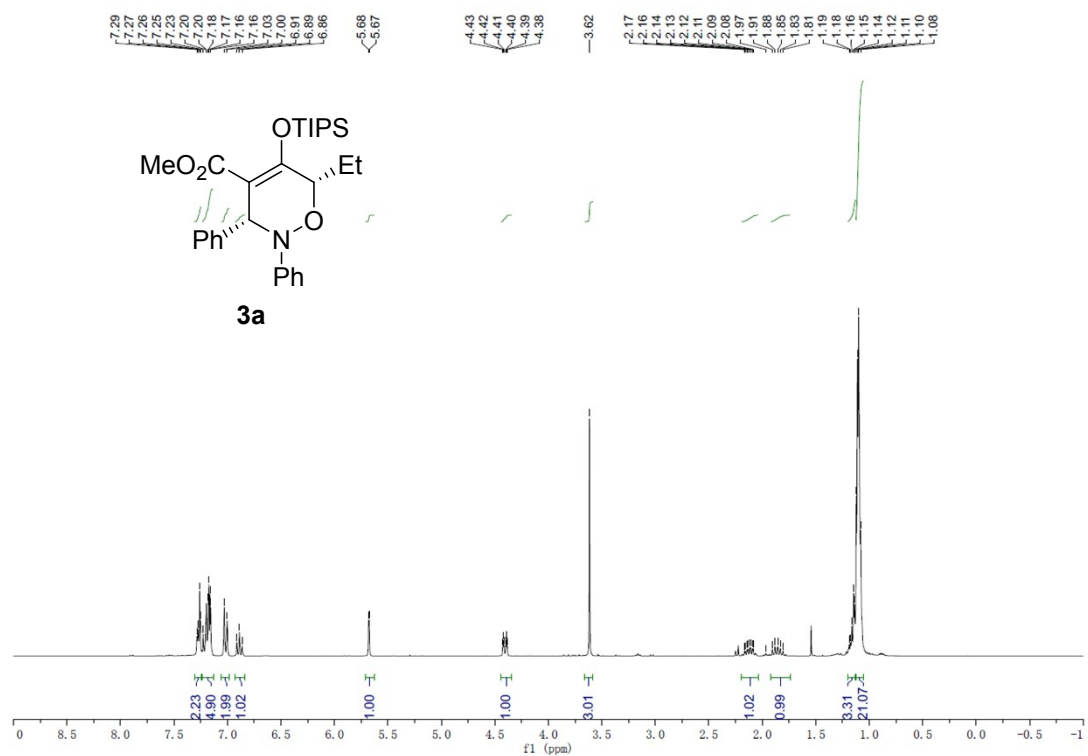
hydroxy-3,6-dihydro-2H-1,2-oxazine-4-carboxylate (5k)

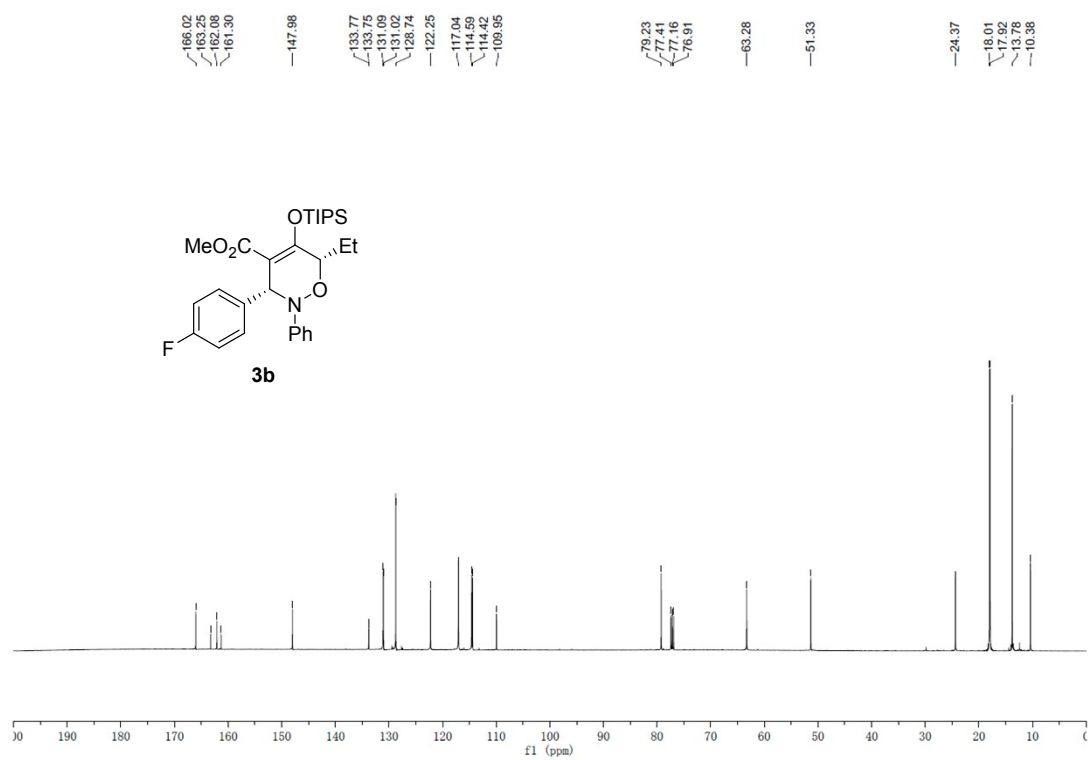
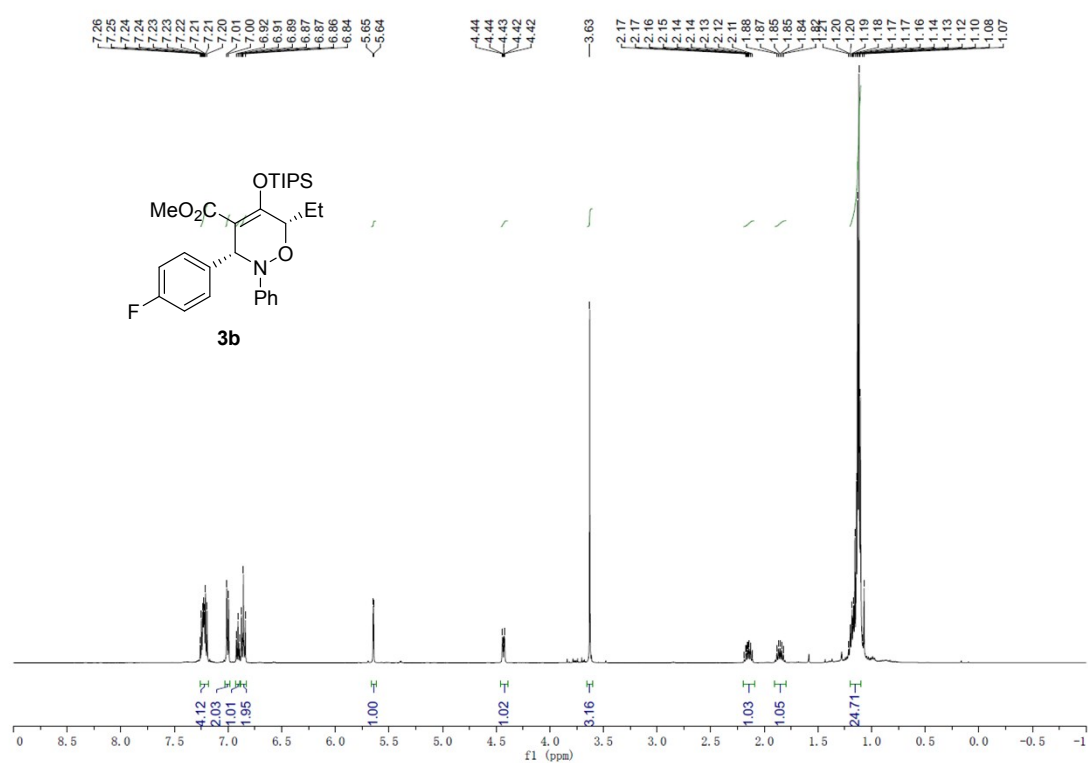
colorless oil; 50 mg, 98 % yield, $[\alpha]_{\text{D}}^{20} = +134^{\circ}$ ($c = 1.0$, CHCl_3), 90% *ee*, [HPLC: Chiralpak ADH column, 10% IPA in hexane (v/v), 1.0 mL/min, 250 nm, $t_1 = 4.9$ min (*major*), $t_2 = 6.3$ min (*minor*)], ^1H NMR (500 MHz, CDCl_3) δ 12.18 (br, 1H), 7.13 – 7.03 (comp, 5H), 6.93 (t, $J = 2.0$ Hz, 1H), 6.90 – 6.83 (comp, 3H), 6.81 – 6.75 (comp, 3H), 5.30 (d, $J = 1.1$ Hz, 1H), 5.09 (d, $J = 12.1$ Hz, 1H), 4.96 (d, $J = 12.1$ Hz, 1H), 4.65 – 4.60 (m, 1H), 3.80 (s, 3H), 2.22 – 2.11 (m, 1H), 1.94 – 1.83 (m, 1H), 1.17 (t, $J = 7.5$ Hz, 3H), ^{13}C NMR (125 MHz, CDCl_3) δ 172.4, 170.3, 159.8, 149.1, 136.0, 134.7, 133.6, 131.0, 129.7, 127.9, 127.3, 122.4, 117.0, 115.0, 113.9, 99.3, 79.0, 66.4, 62.4, 55.4, 23.3, 10.1, HRMS (ESI) m/z calc. for $\text{C}_{27}\text{H}_{26}\text{Cl}_2\text{NO}_5$ ($\text{M}+\text{H}$) $^+$: 514.1183, found: 514.1177.

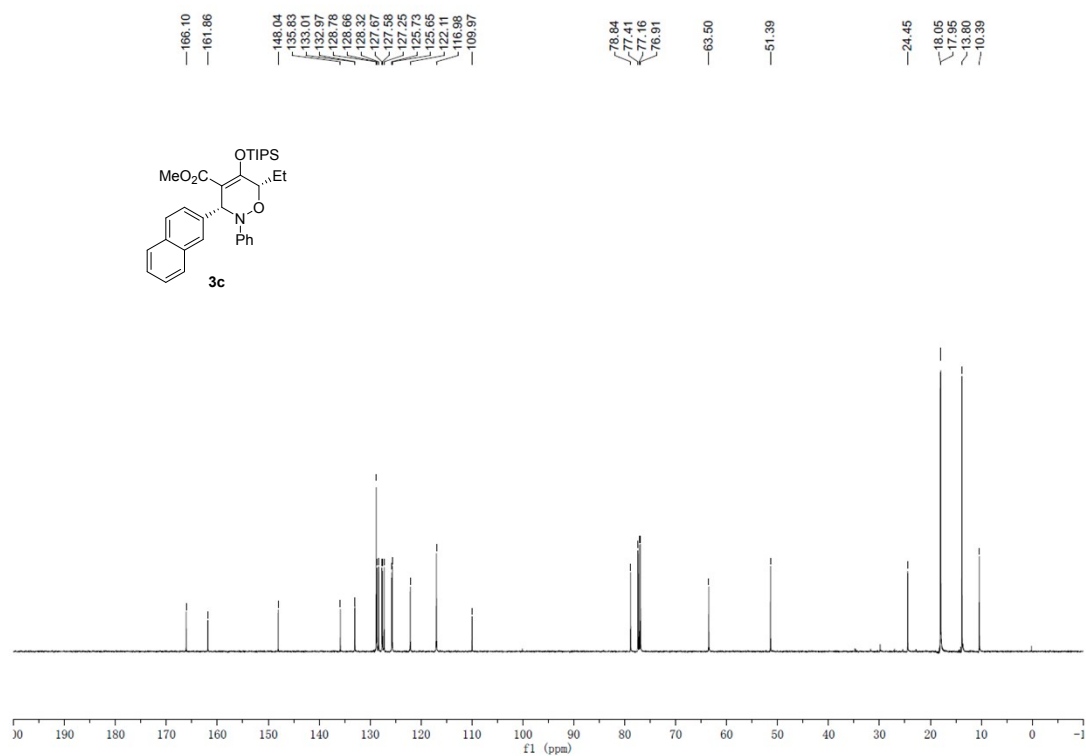
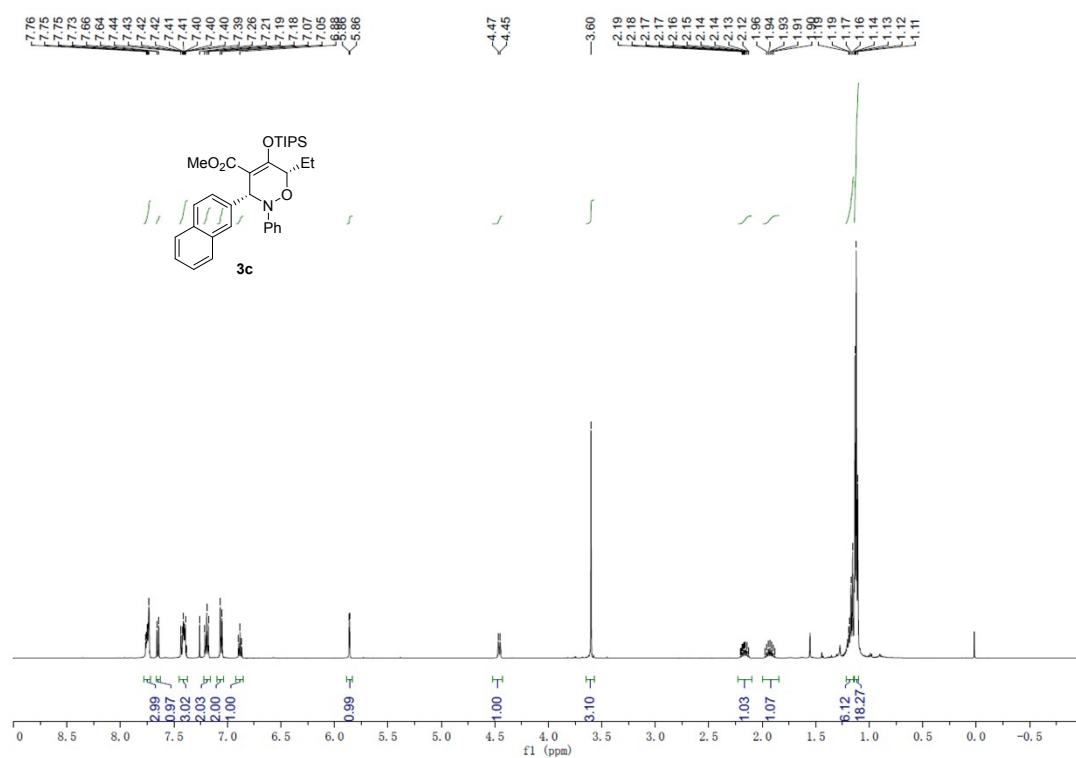
4. Reference

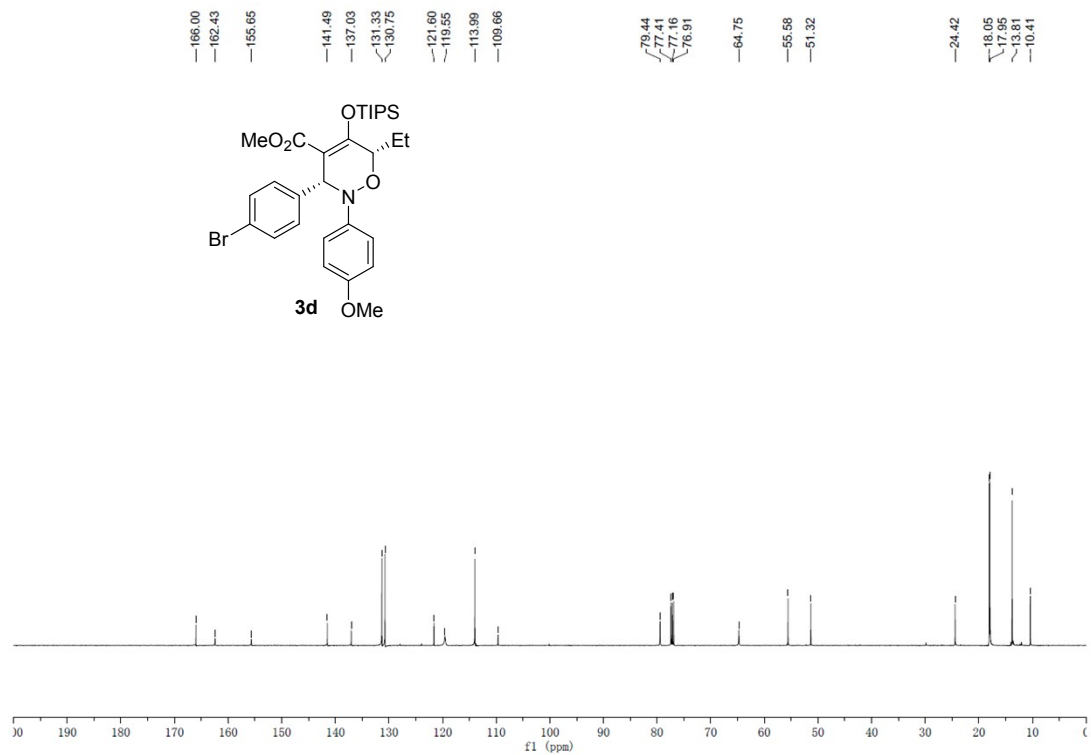
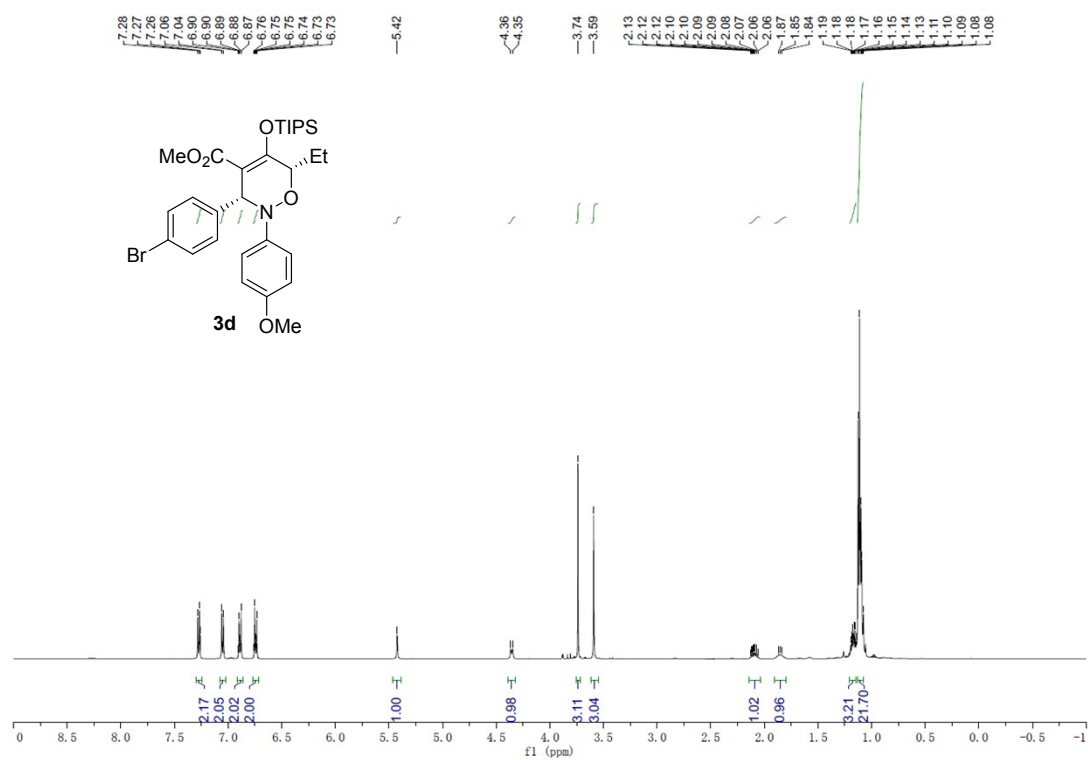
1. K. Dong, K., Marichev, X. Xu, and M. P. Doyle, High Stereocontrol in the Preparation of Silyl-Protected γ -Substituted Enoldiazoacetates, *Synlett.*, 2019, **30**, 1457-1461.
2. (a) L. Zheng, F. Gao, C. Yang, G. L. Gao, Y. Zhao, Y. Gao, W. Xia, Visible-Light Mediated Anti-Regioselective Nitron 1,3-Dipolar Cycloaddition Reaction and Synthesis of Bisindolylmethanes. *Org. Lett.*, 2017, **19**, 5086–5089. (b) M. M. Lo and G. C. Fu, Cu(I)/Bis(azaferrocene)-Catalyzed Enantioselective Synthesis of β -Lactams *via* Couplings of Alkynes with Nitrones, *J. Am. Chem. Soc.*, 2002, **124**, 4572-4573.

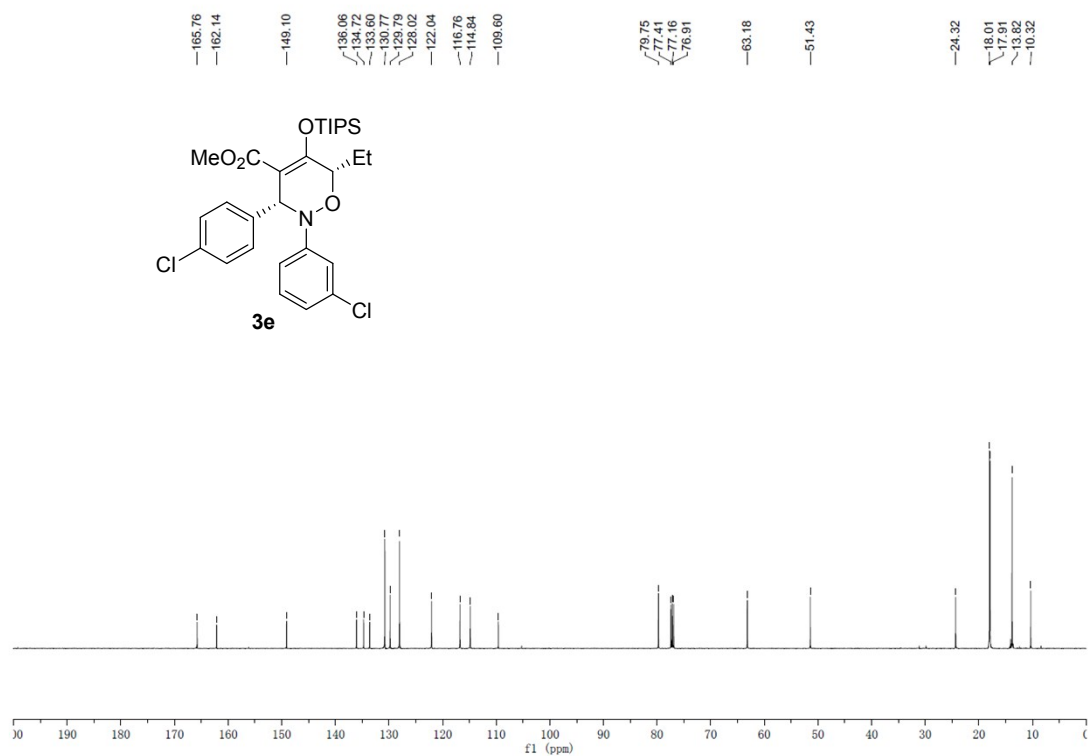
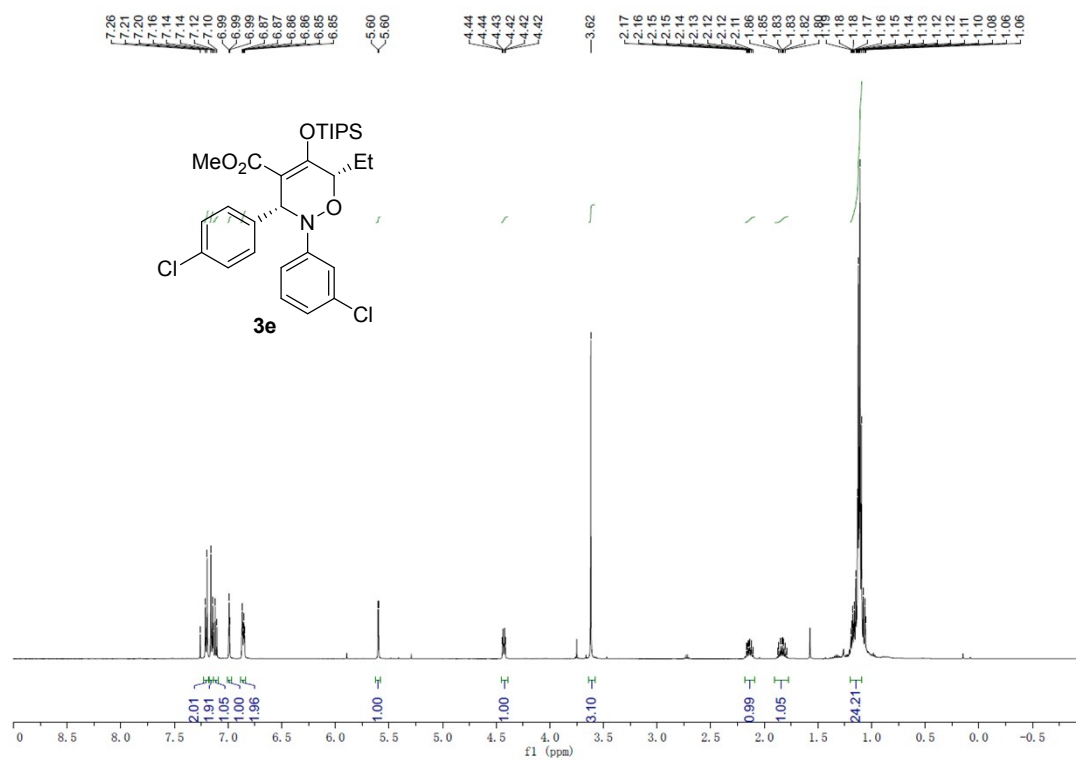
5. NMR Spectra of New Compounds

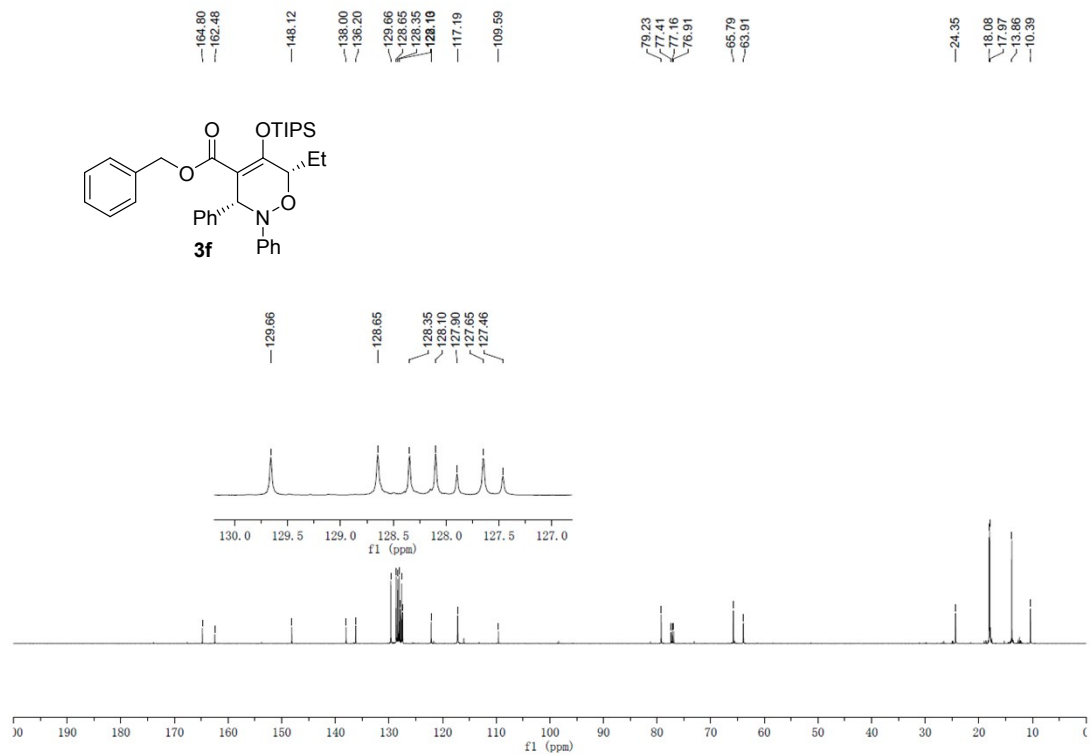
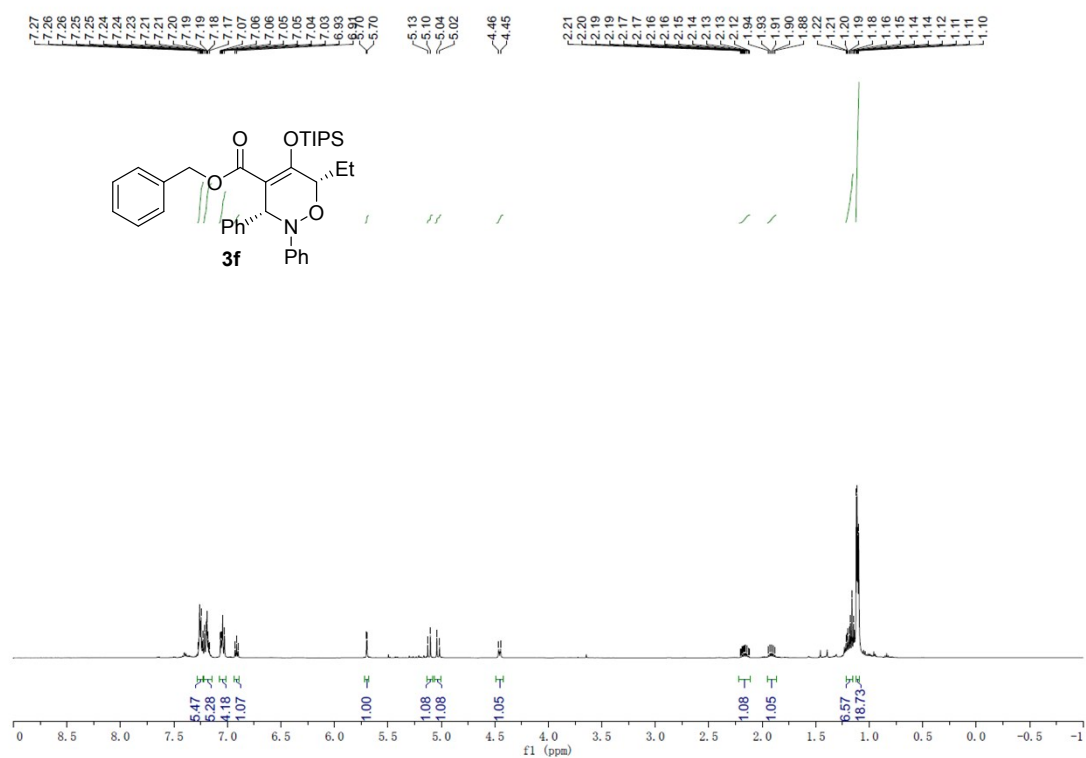


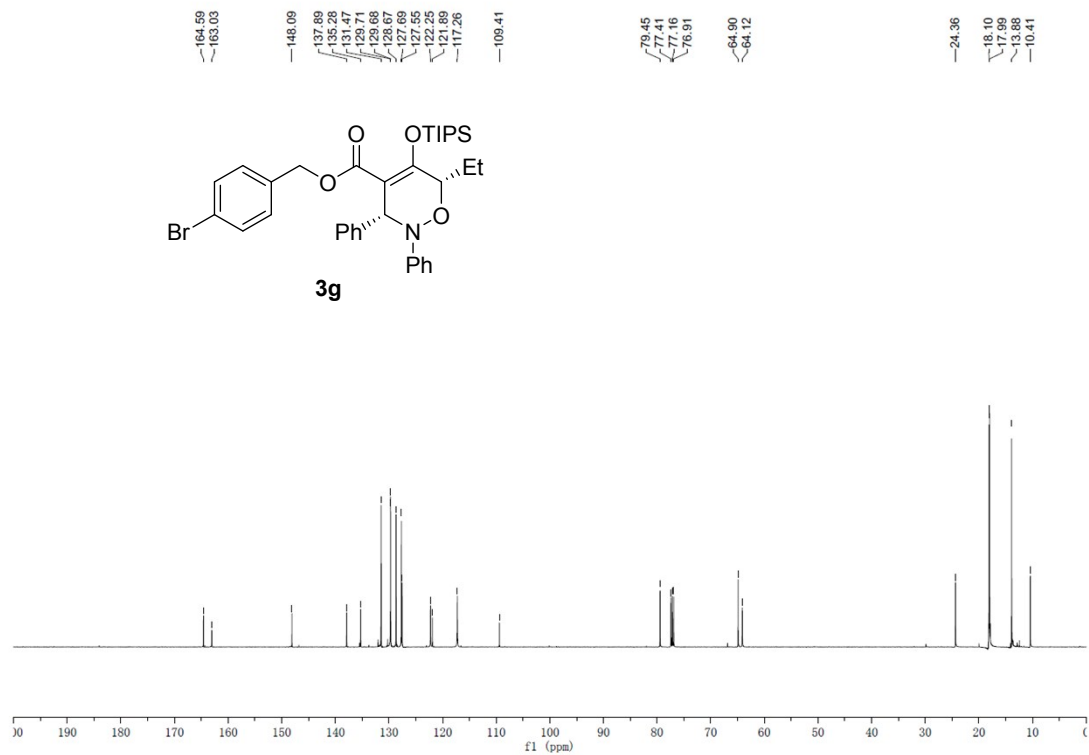
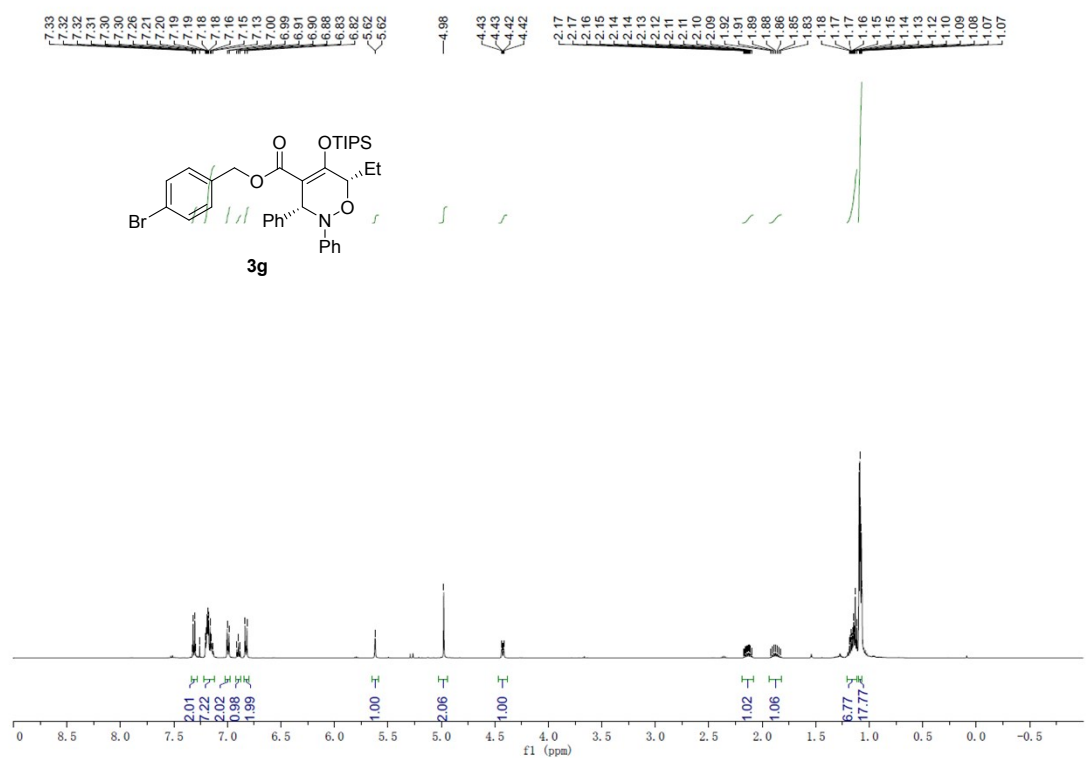


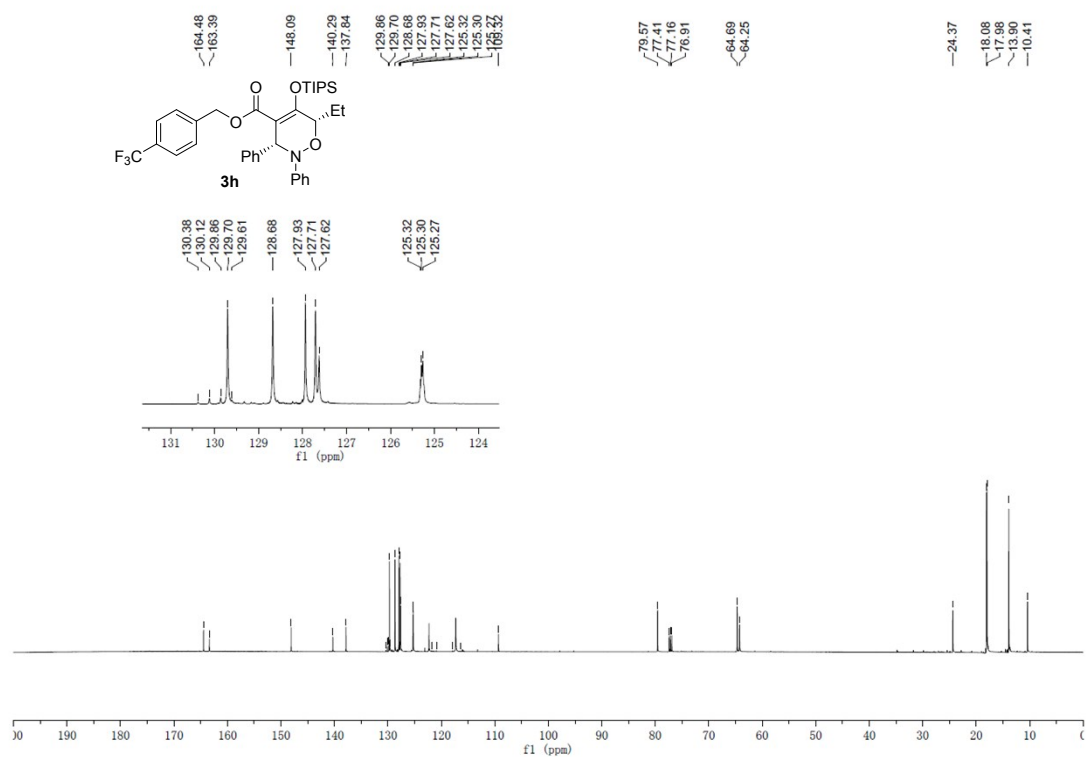
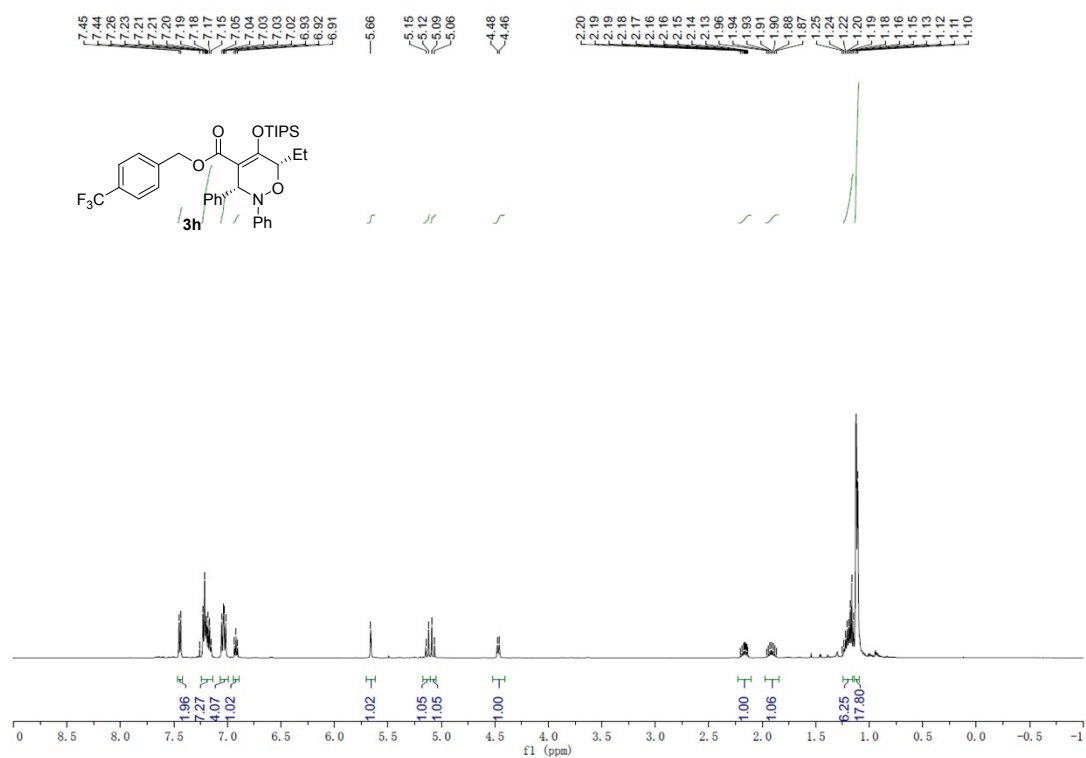


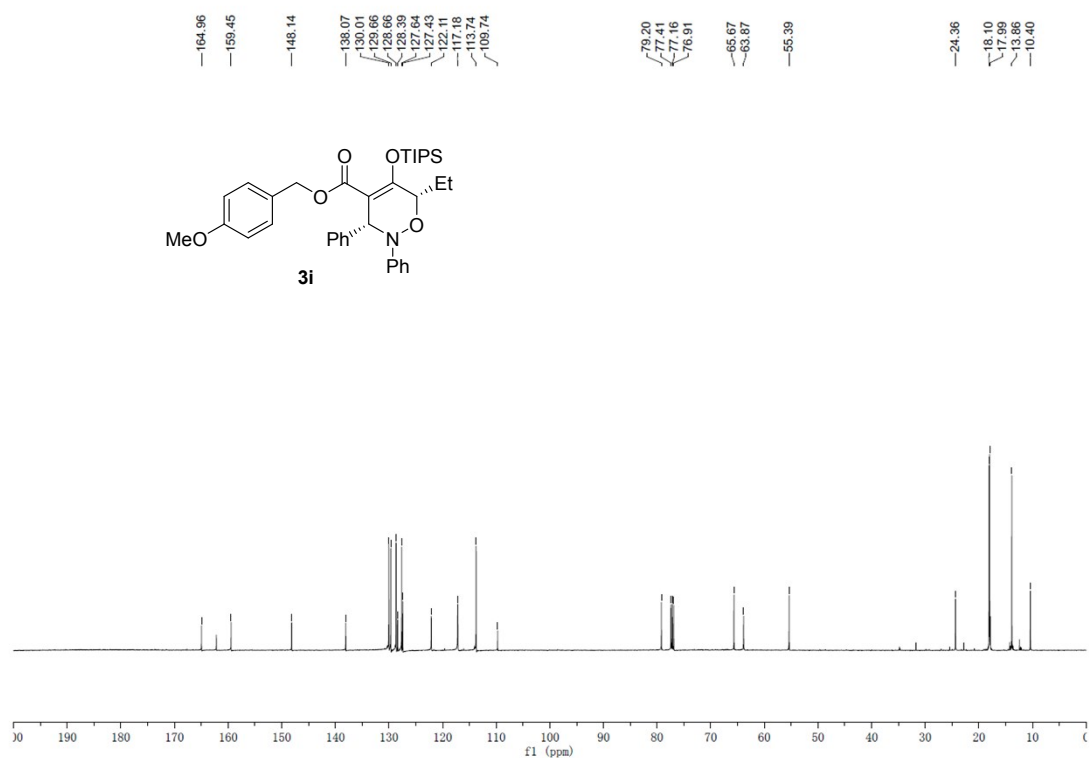
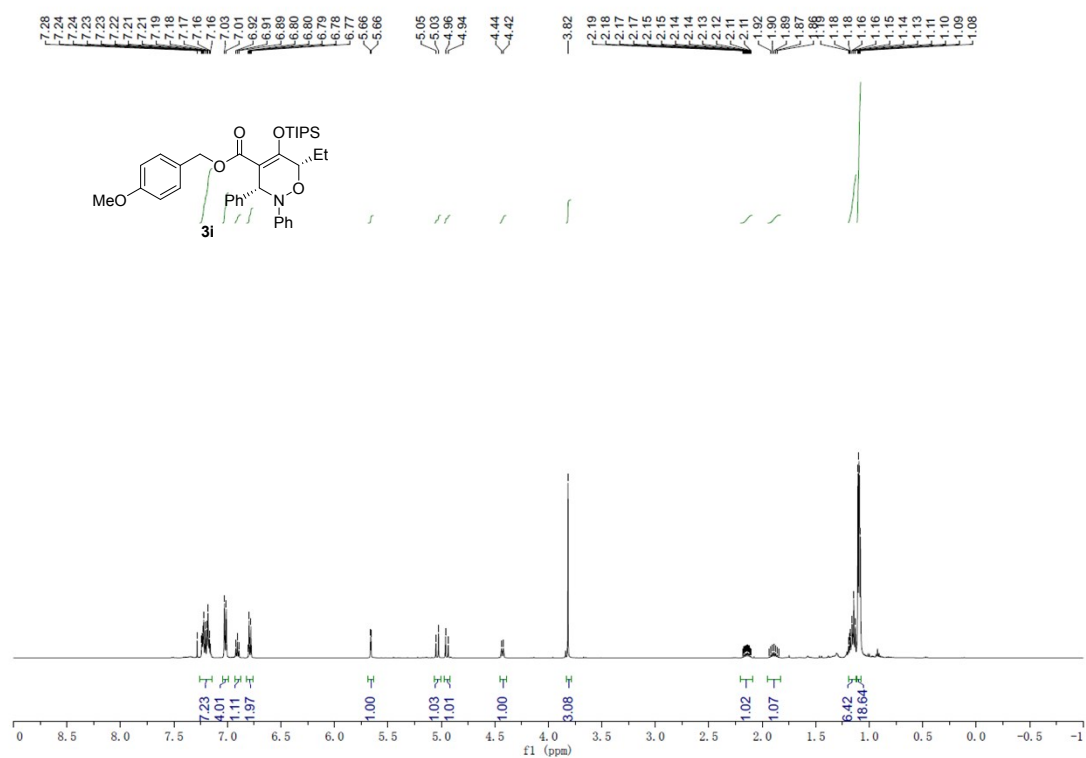


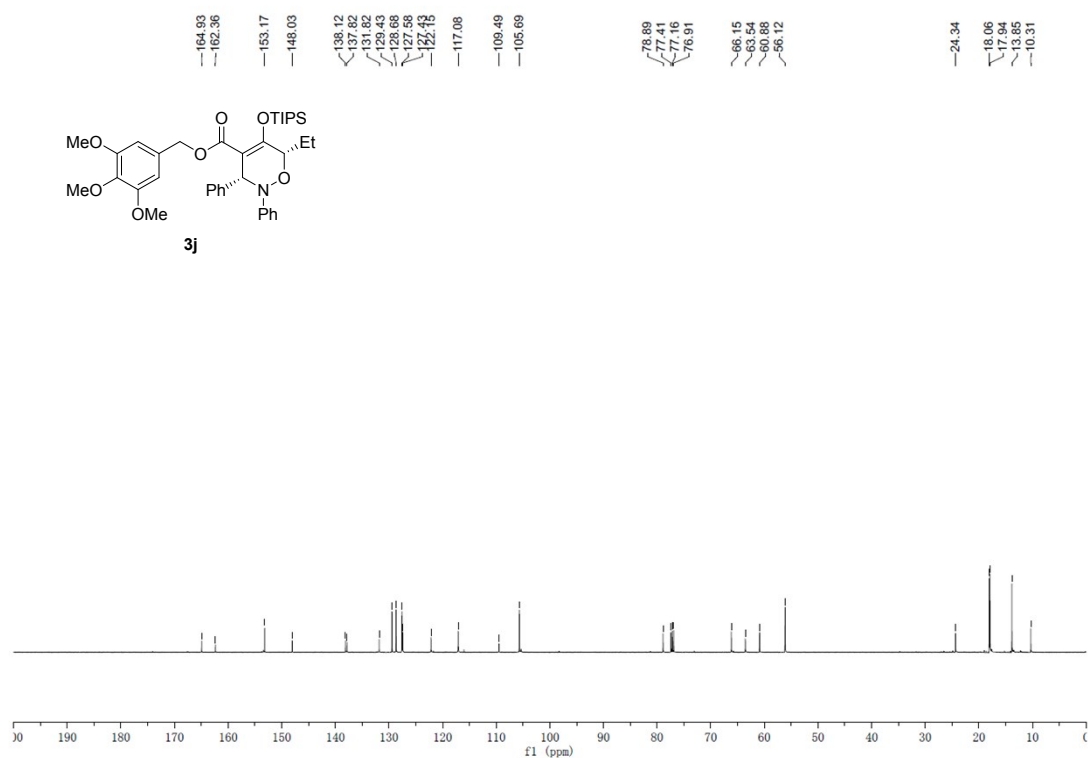
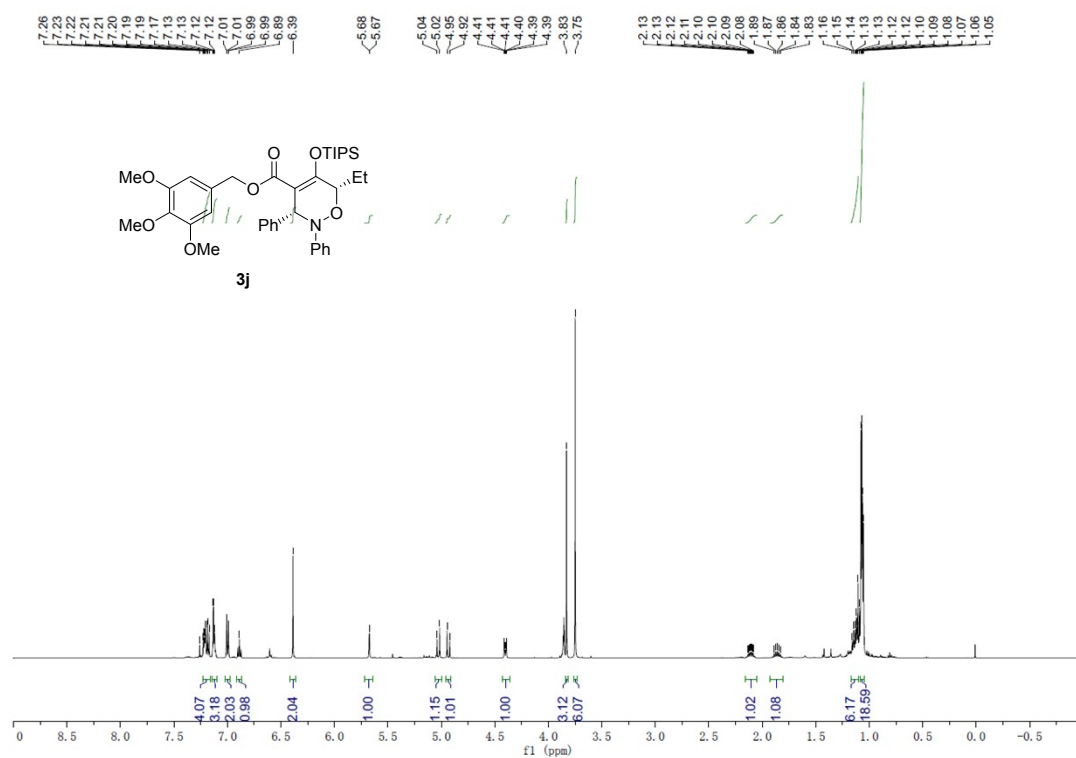


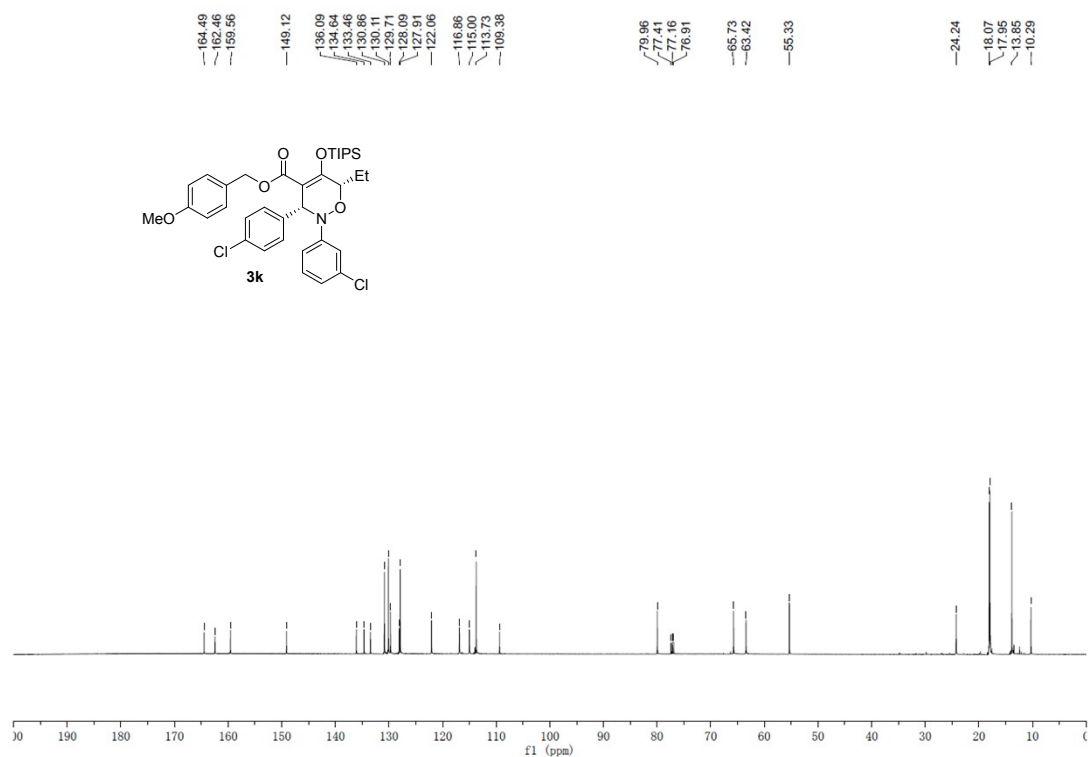
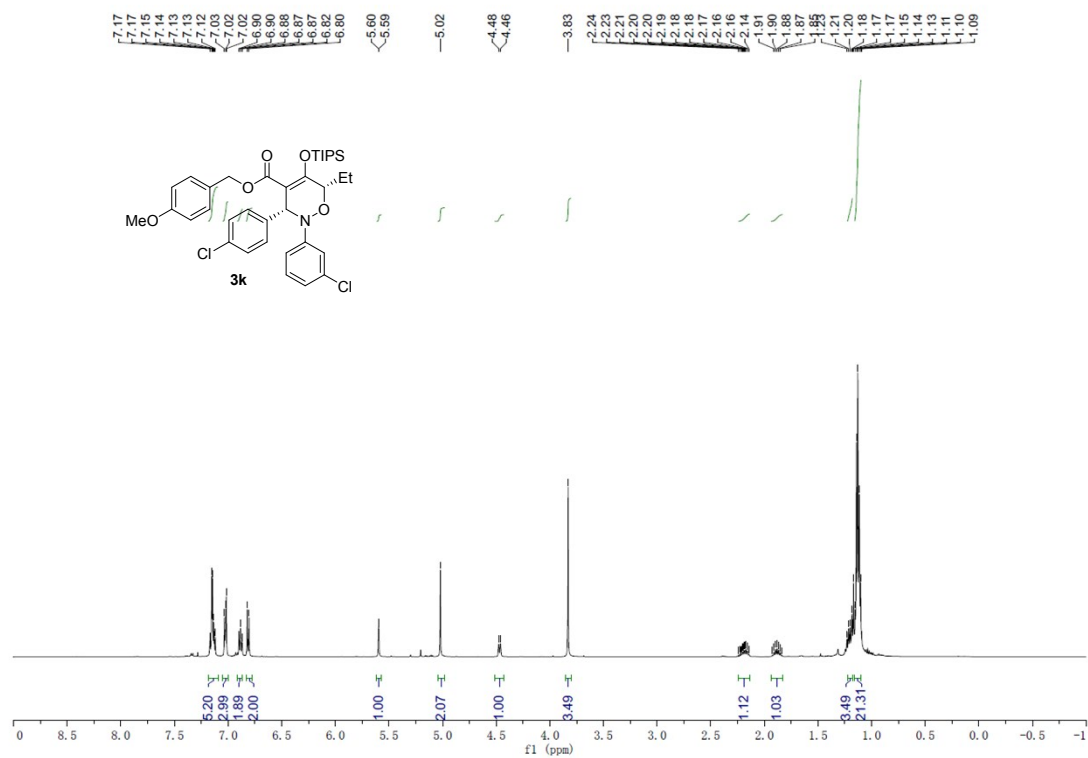


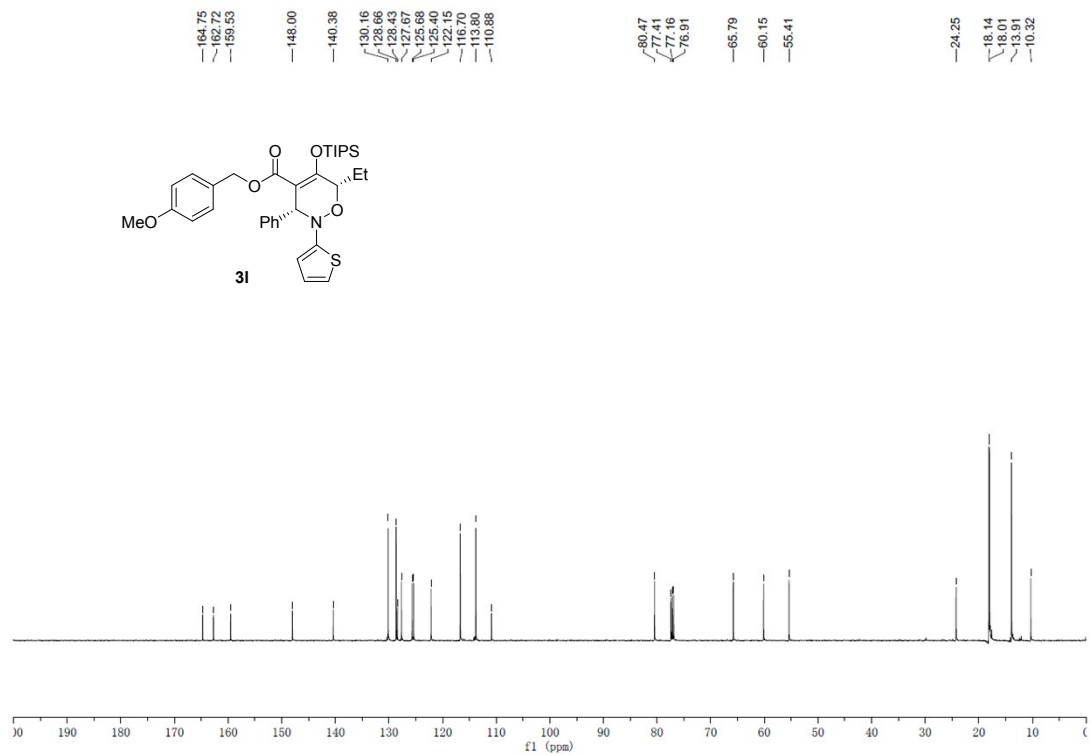
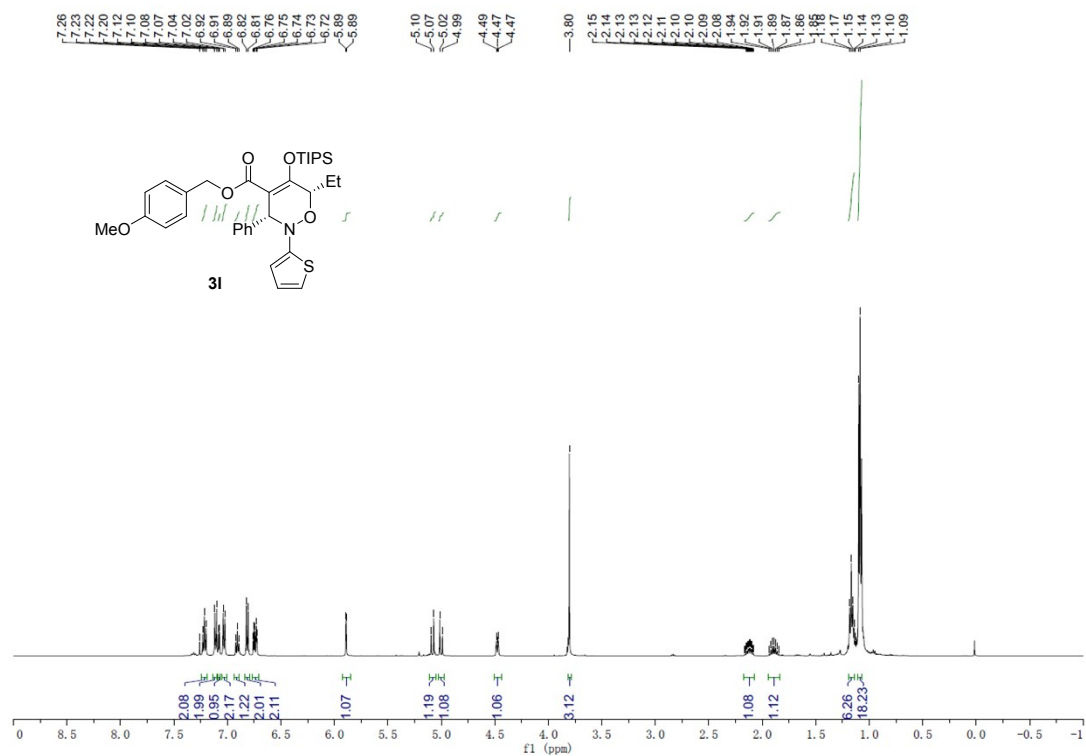


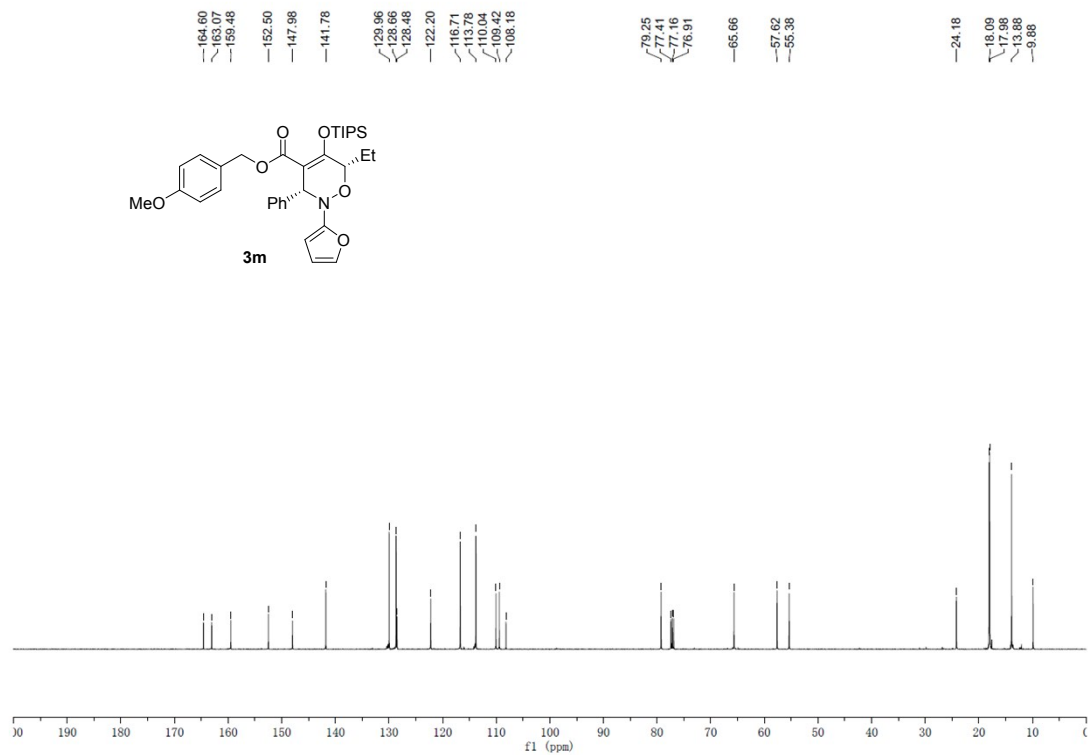
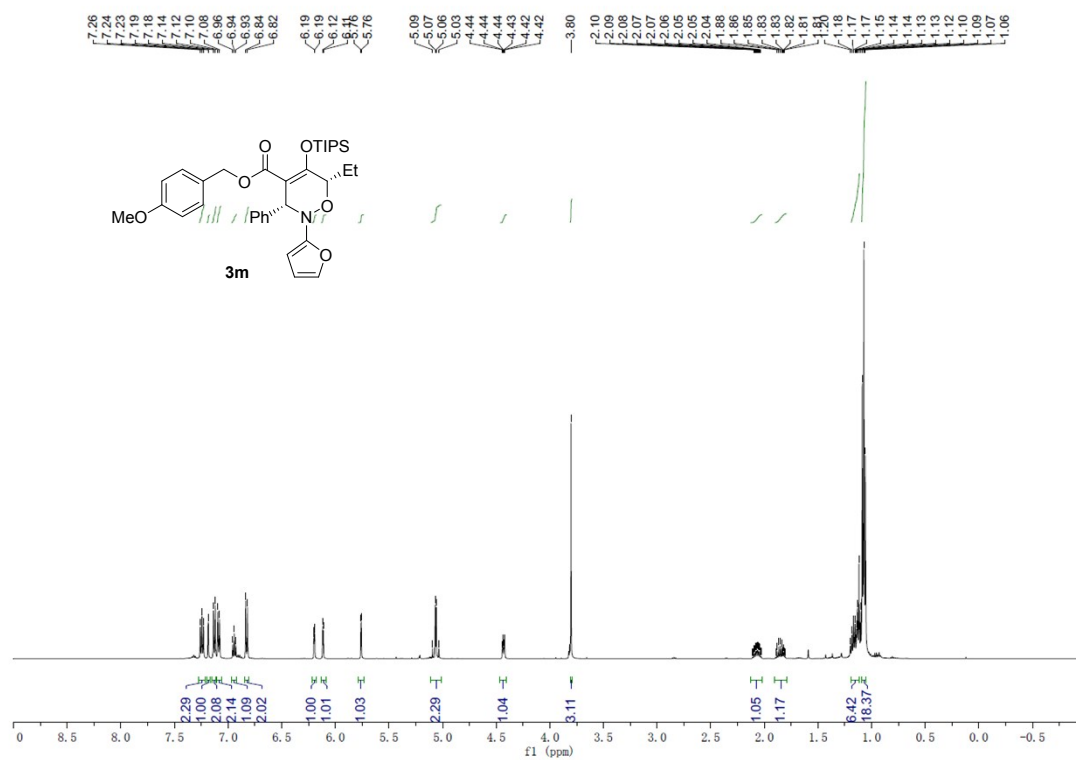


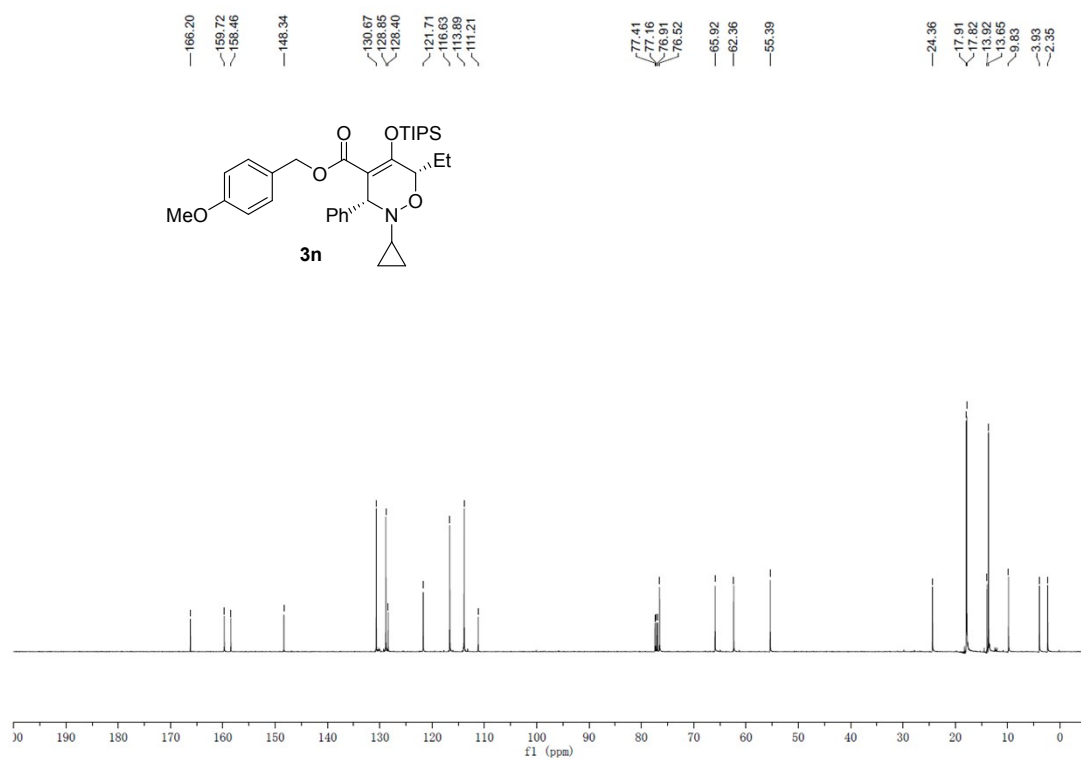
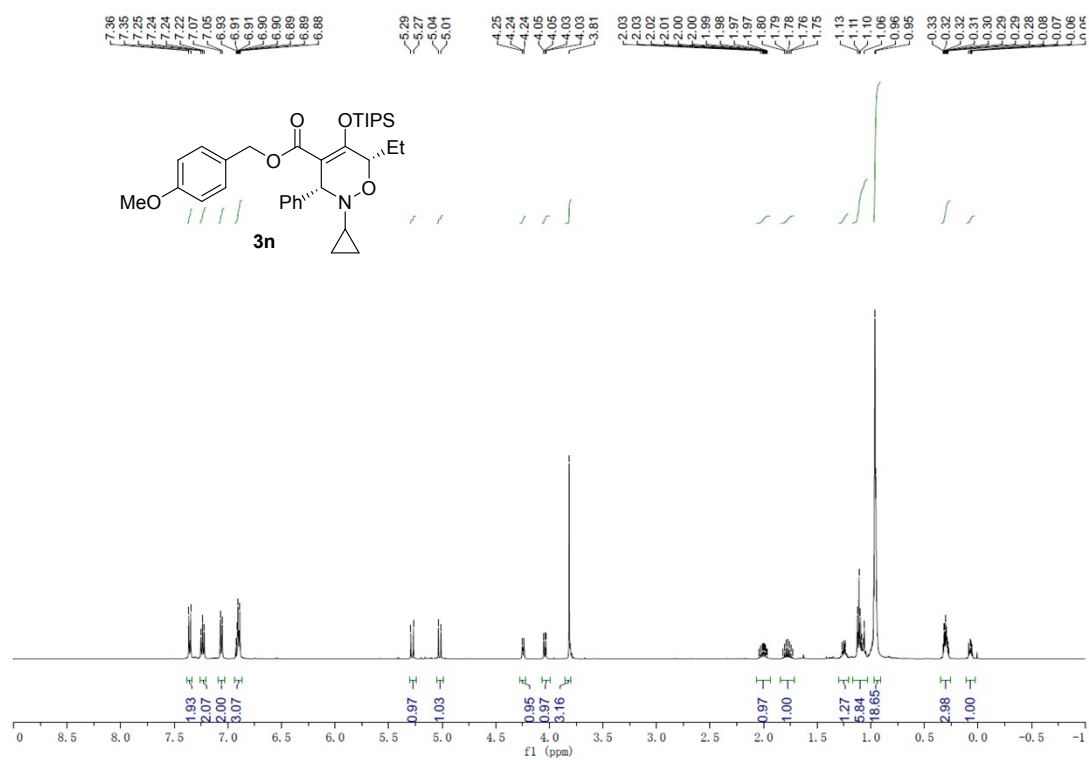




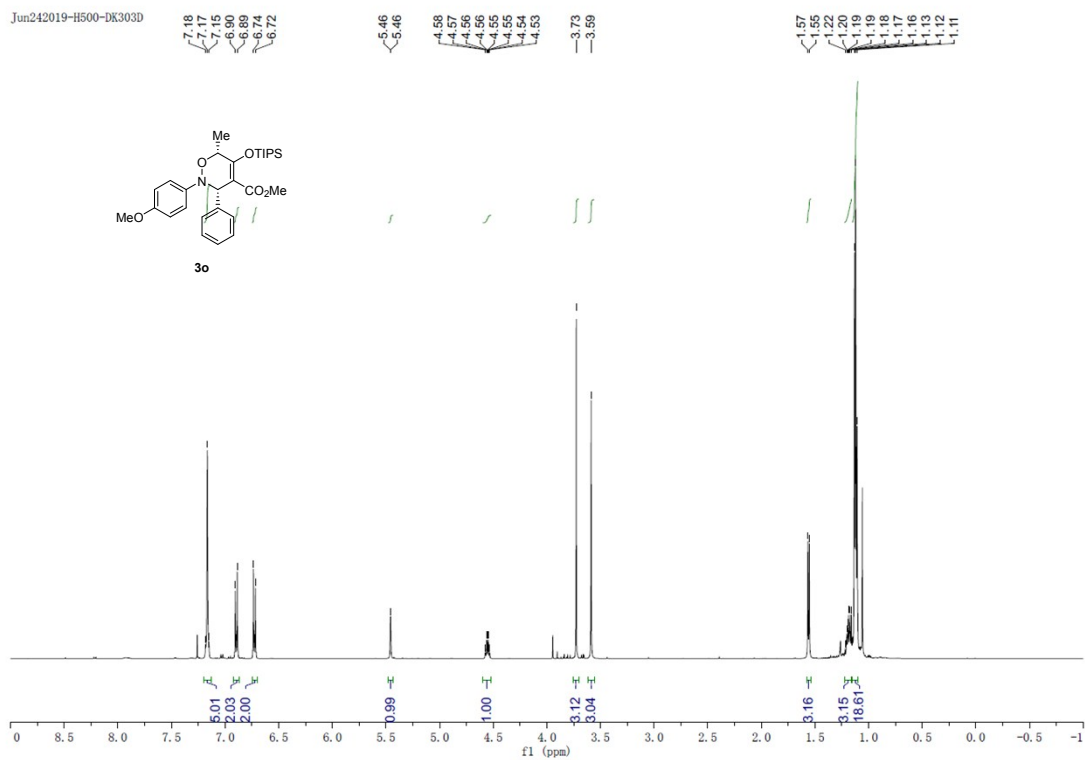




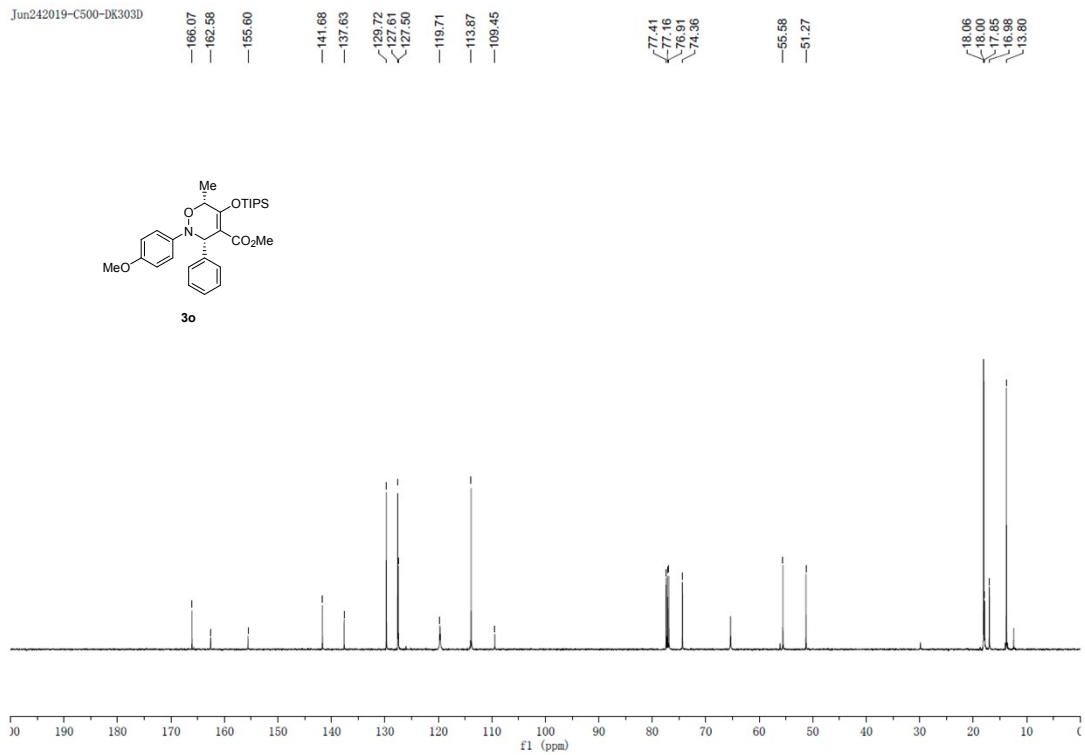


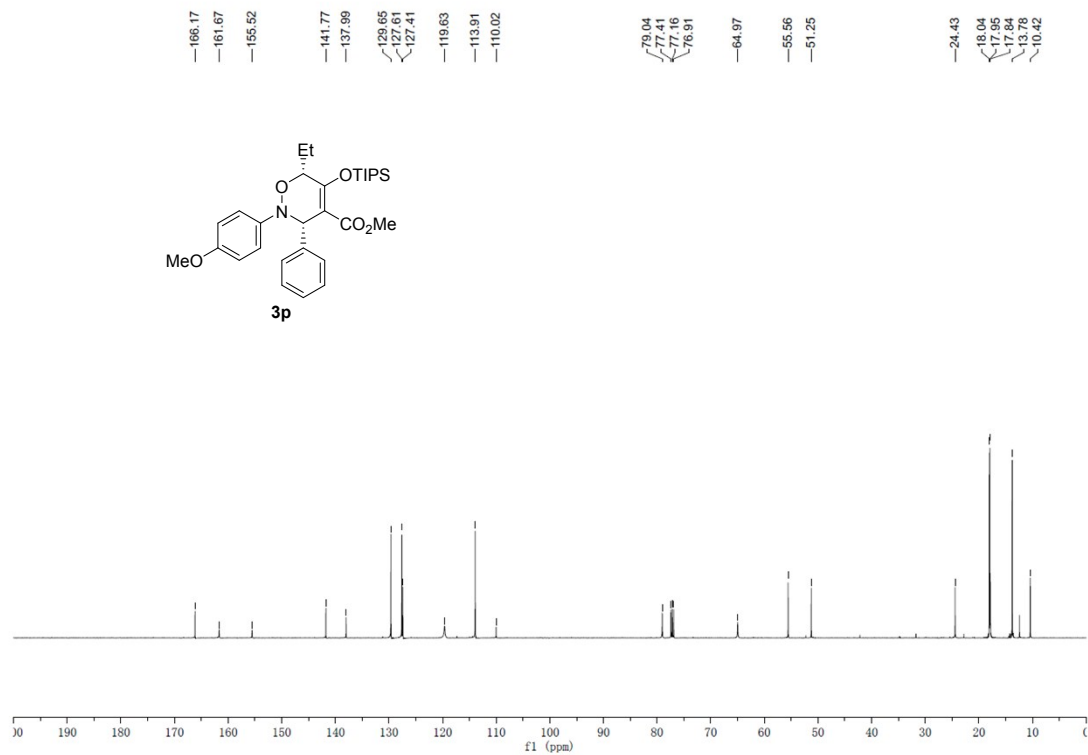
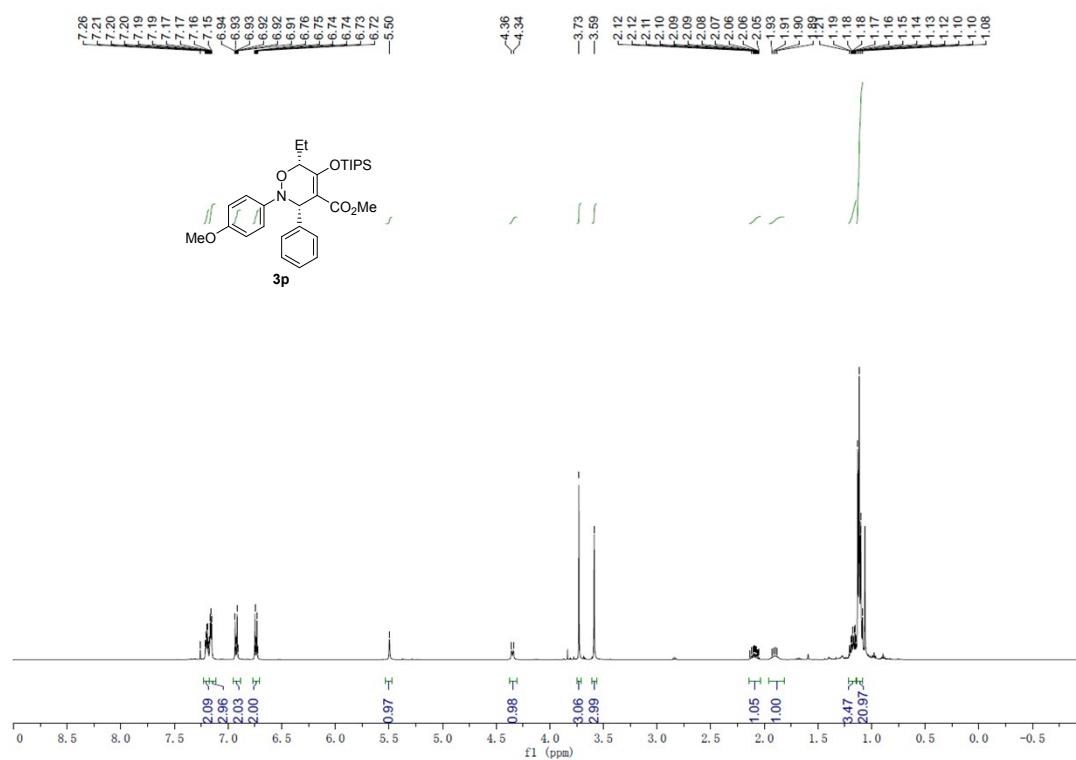


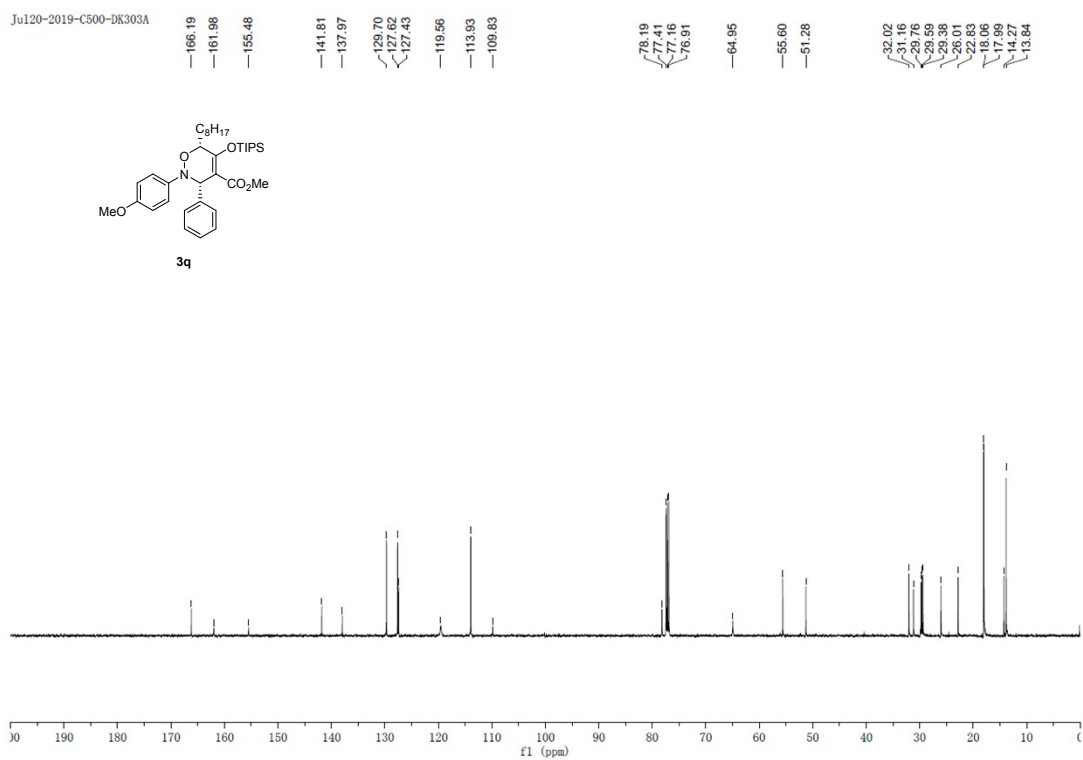
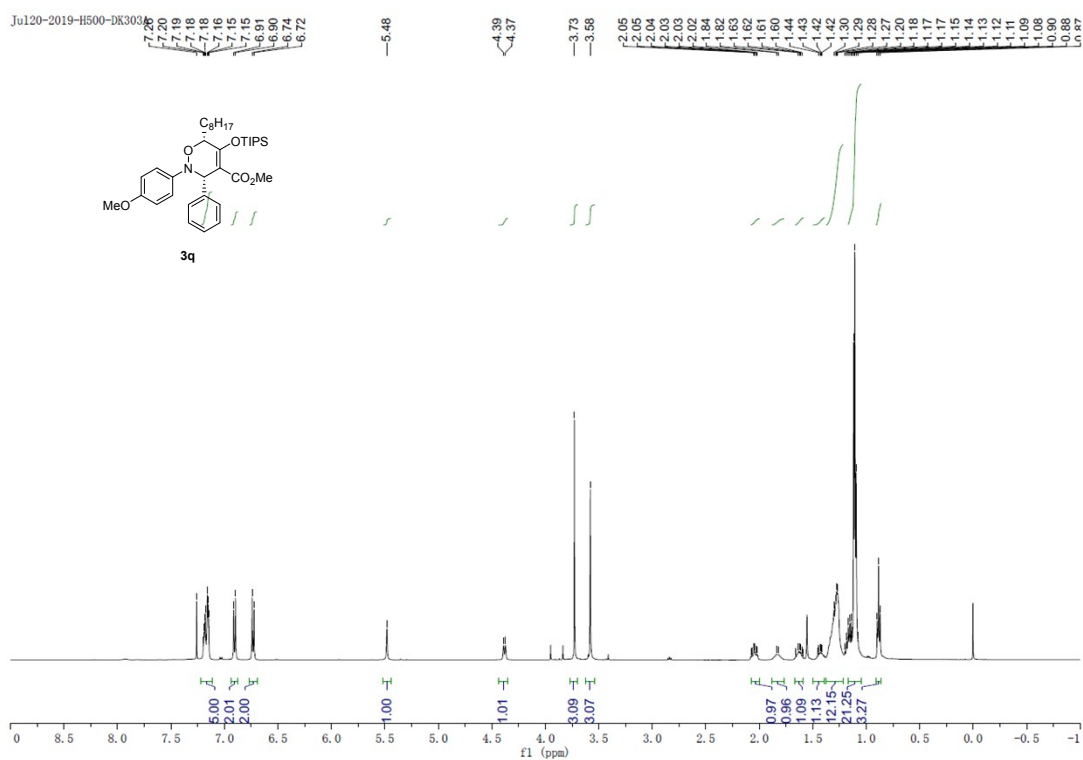
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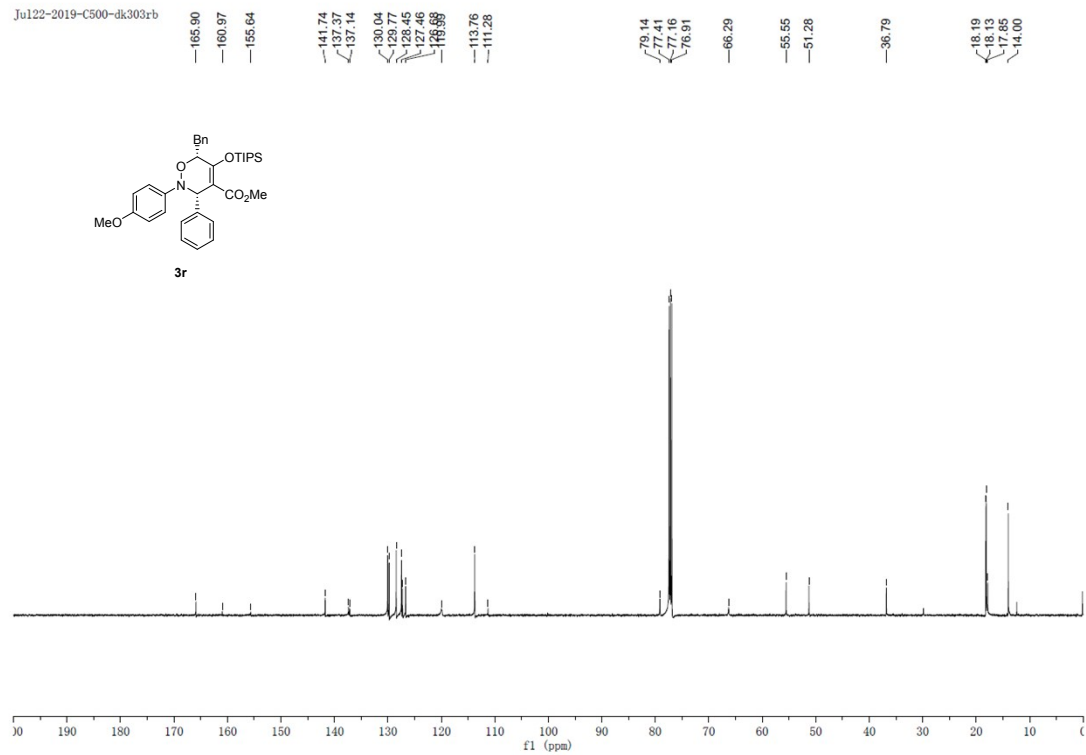
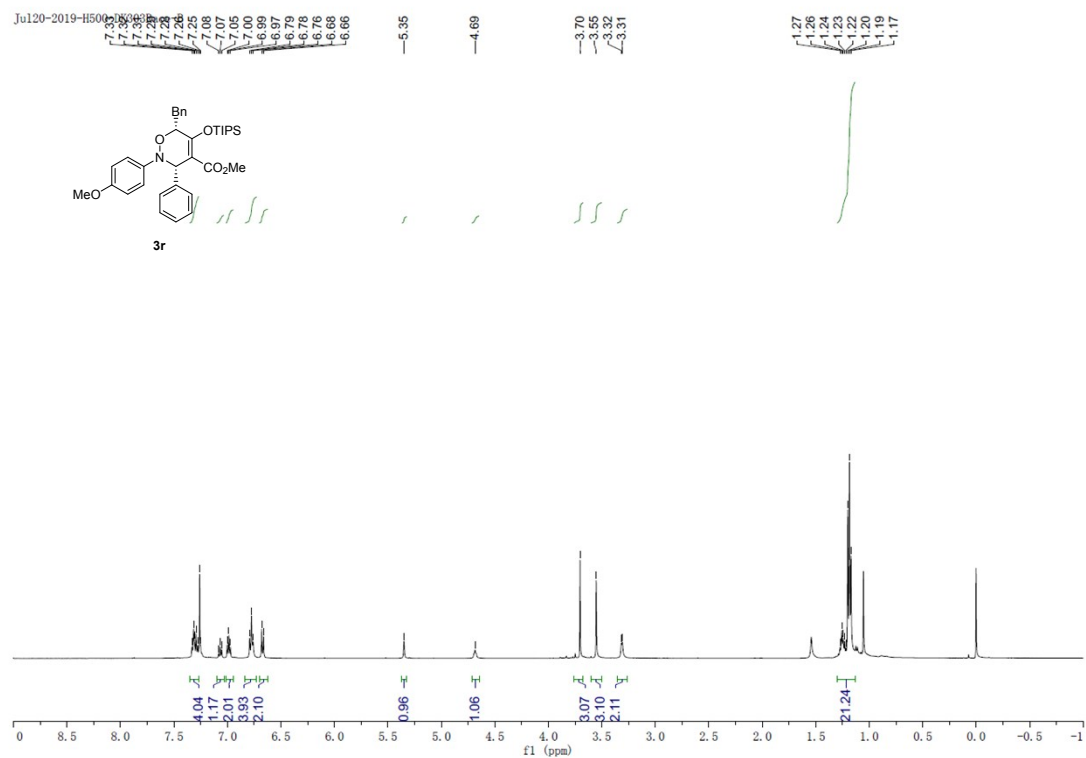


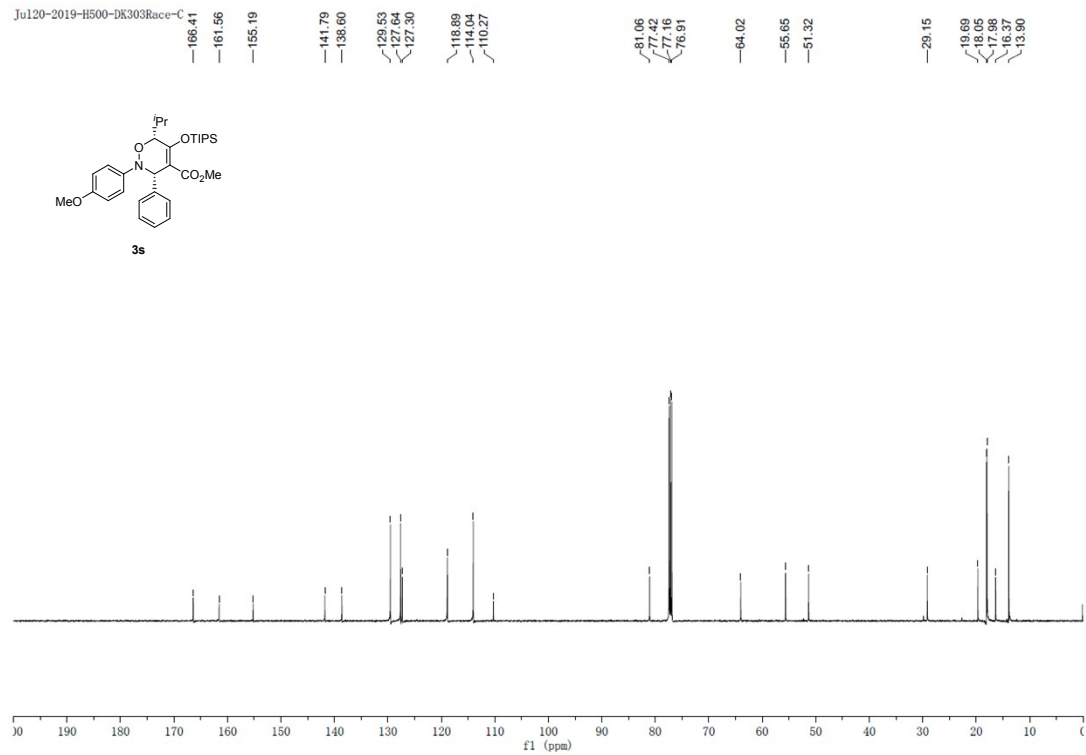
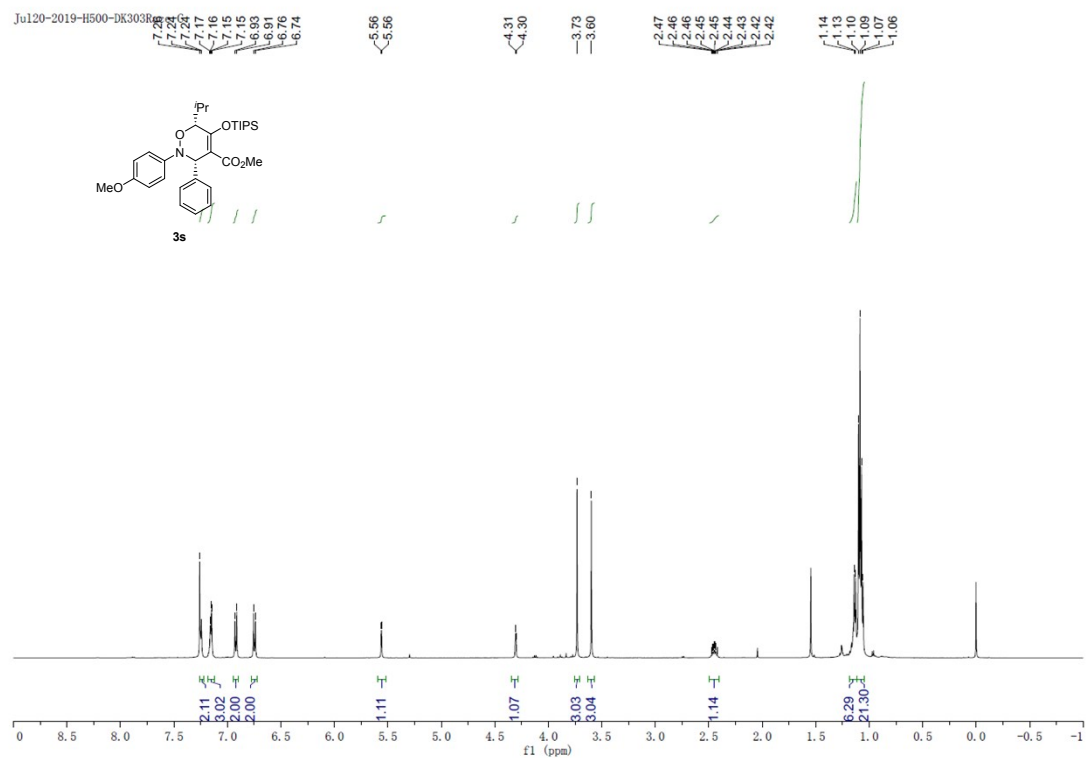
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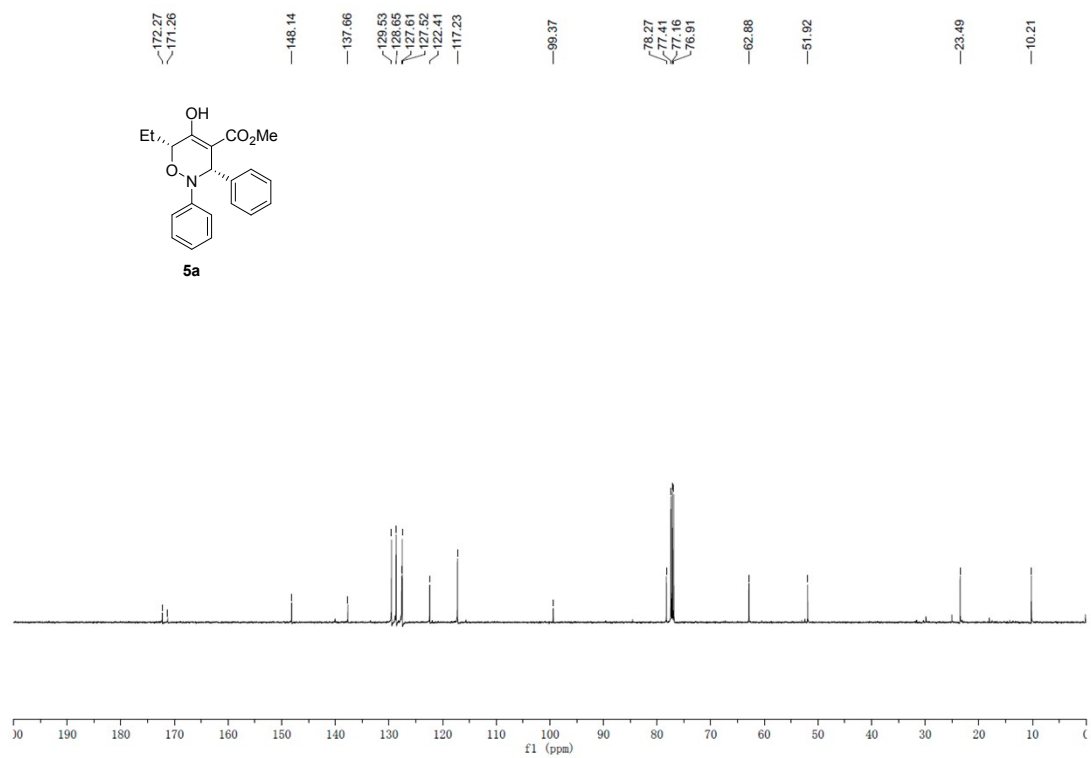
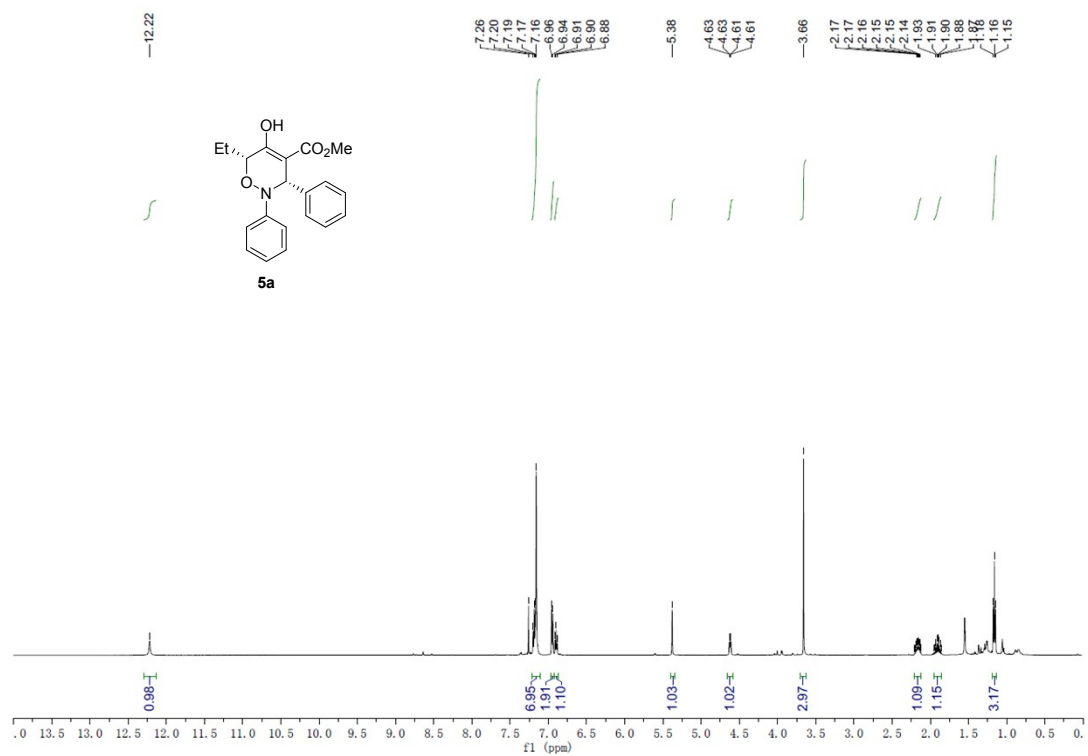


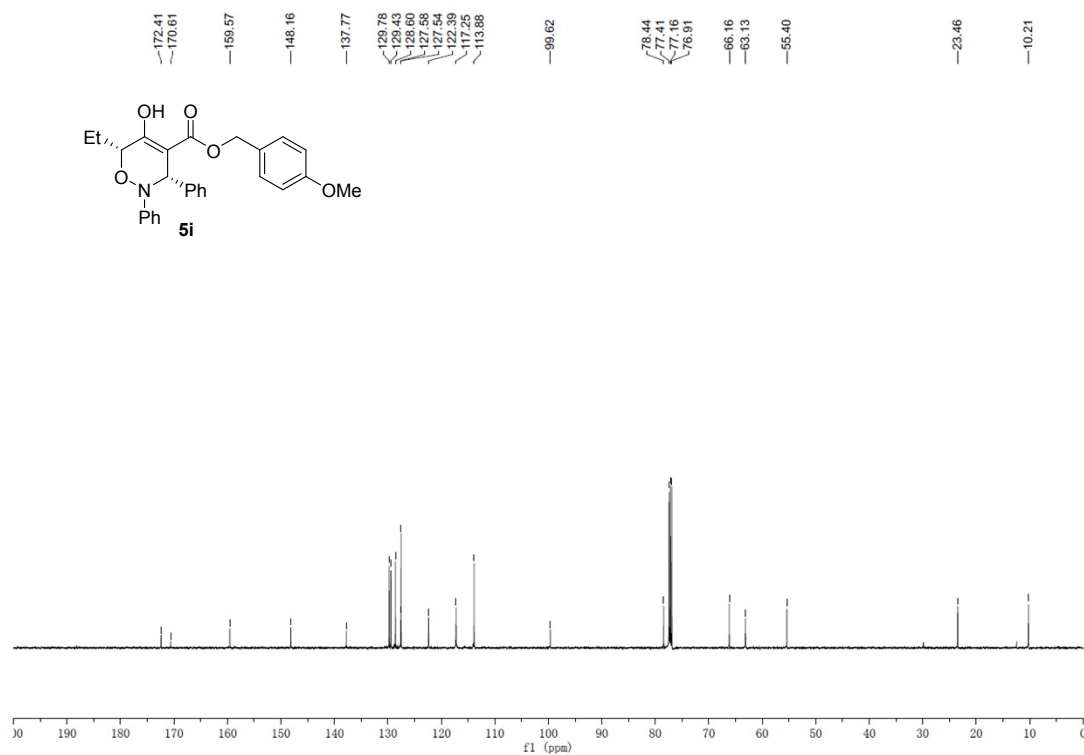
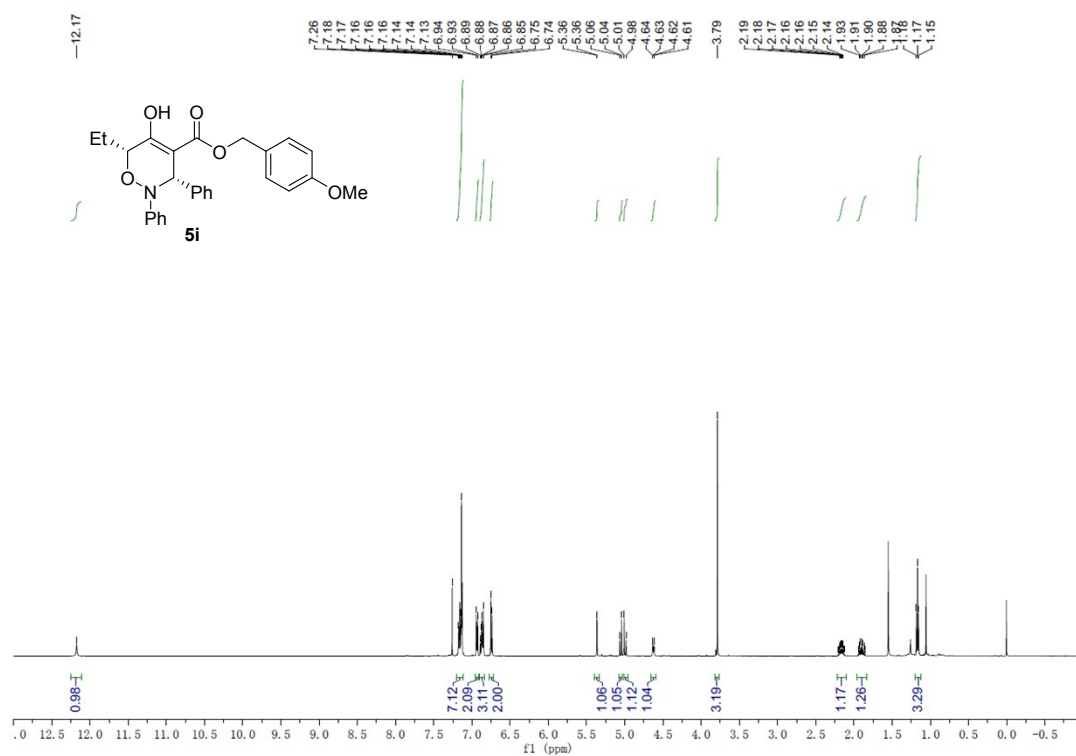


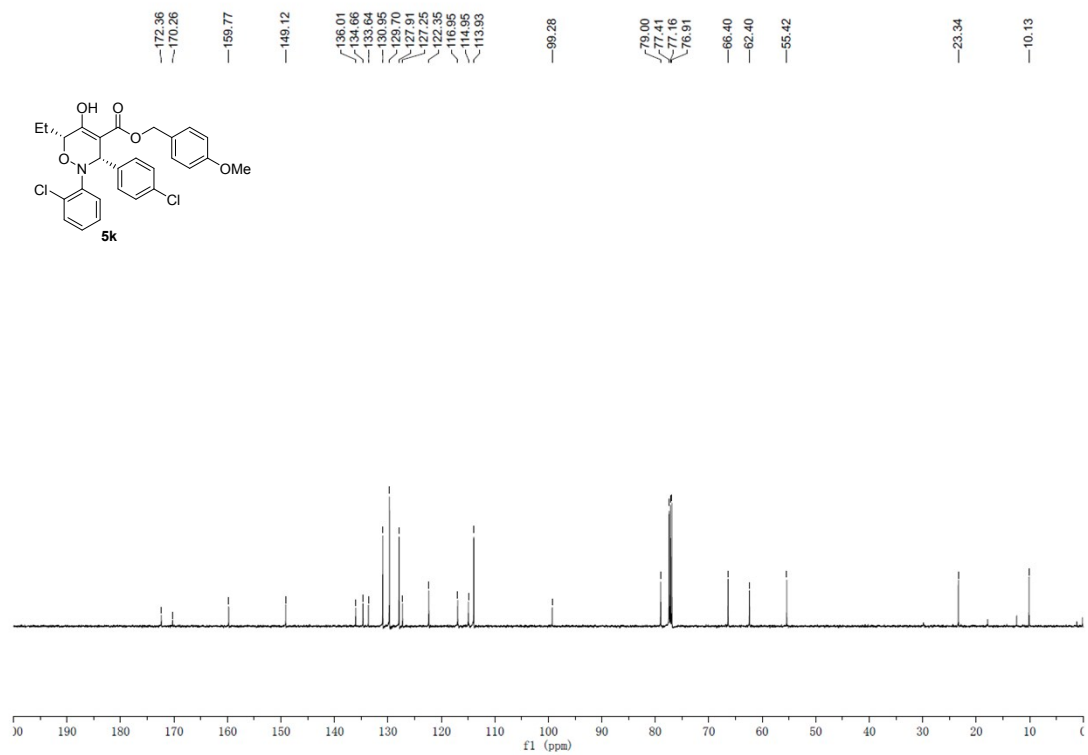
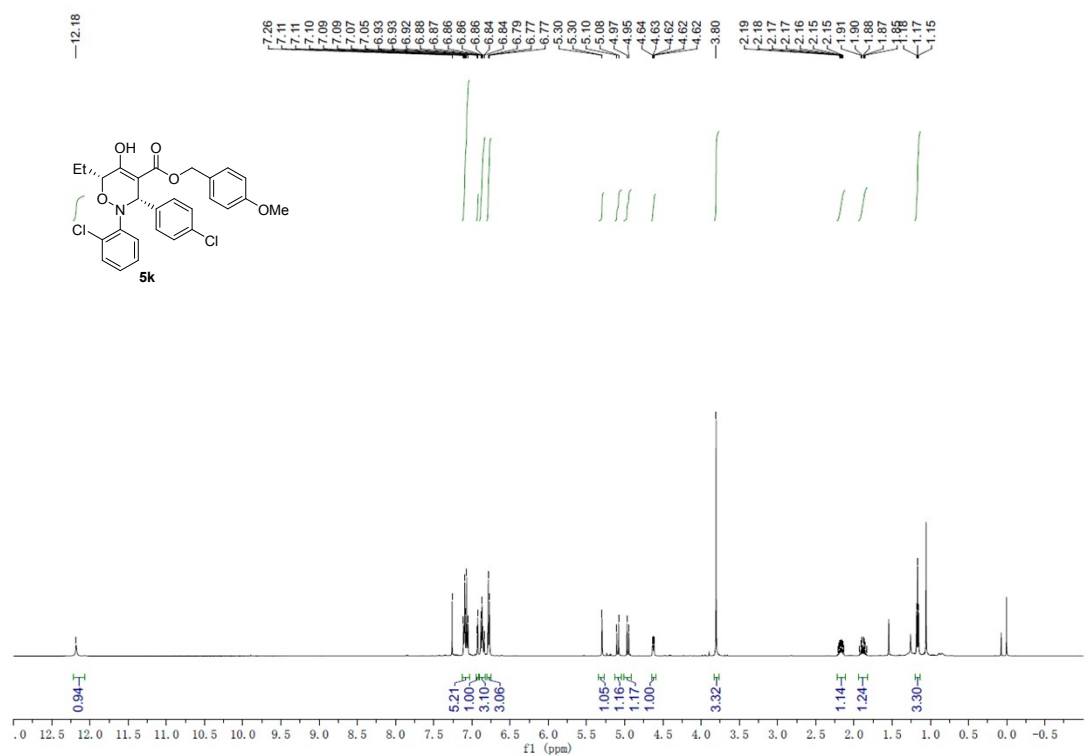


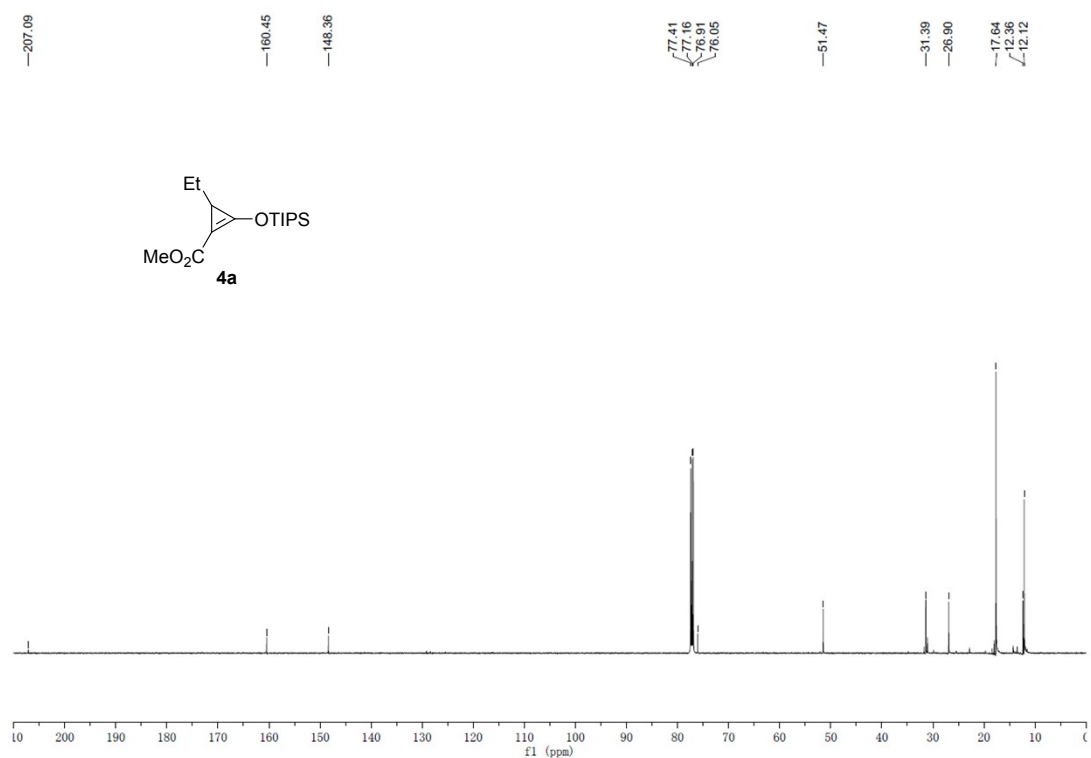
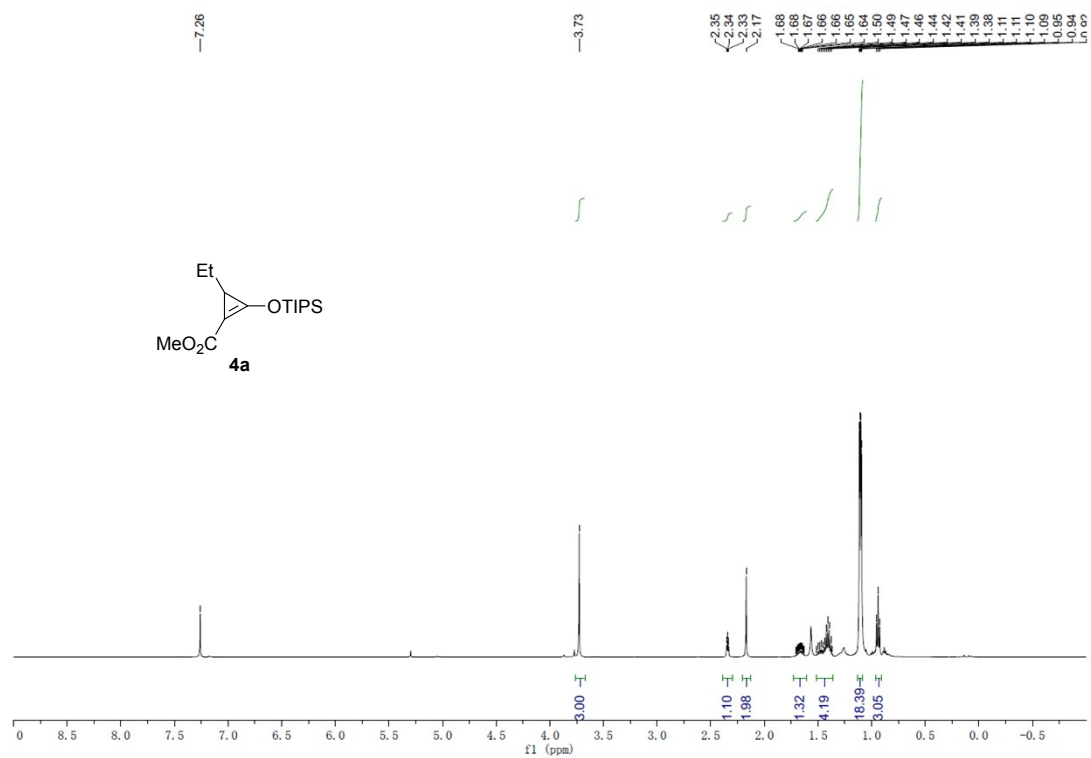






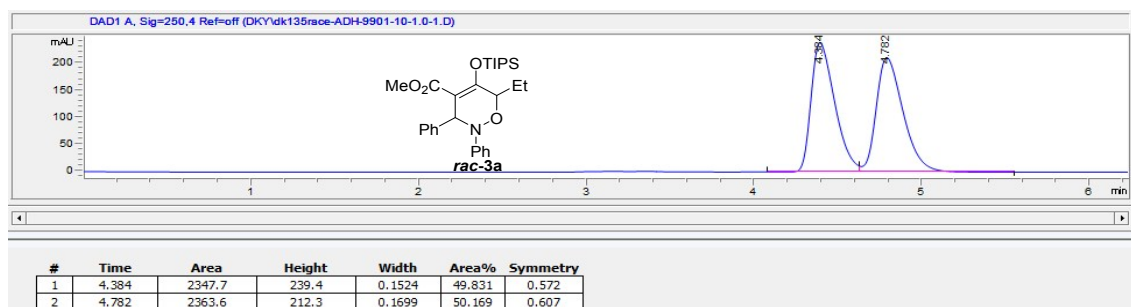




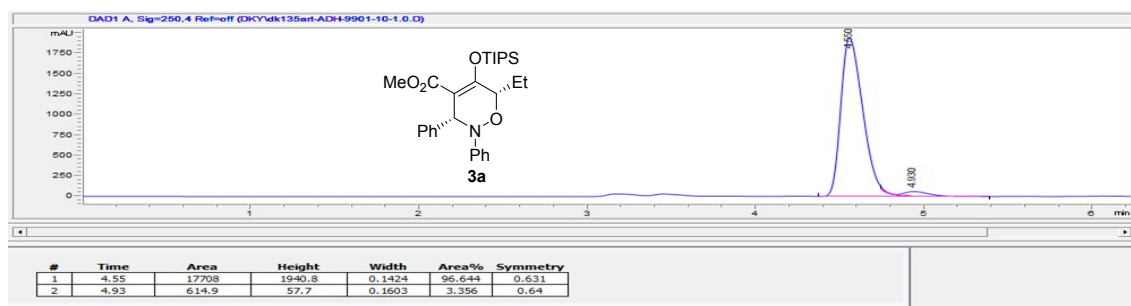


6. HPLC Traces for Racemic and Chiral Compounds

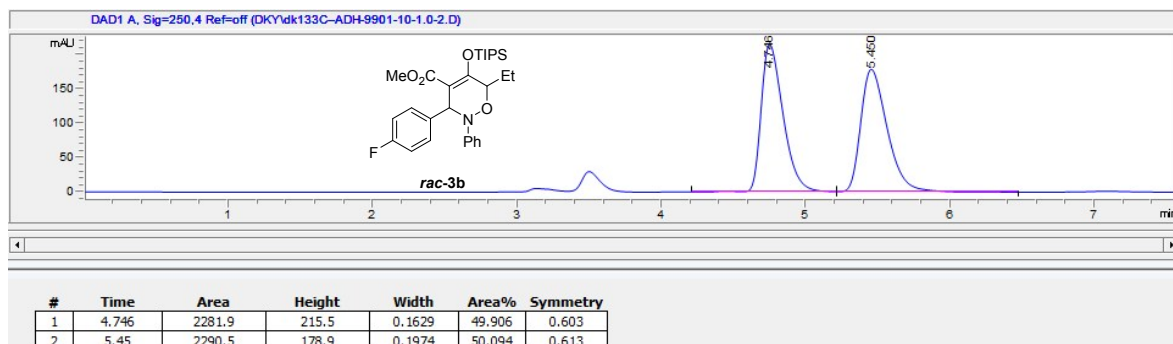
Methyl-6-ethyl-2,3-diphenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (*rac*-3a)



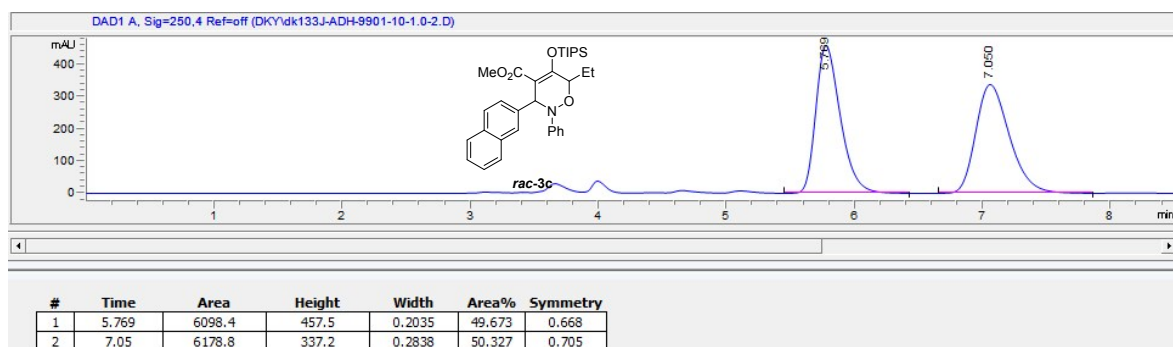
Methyl (3*S*,6*R*)-6-ethyl-2,3-diphenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3a)



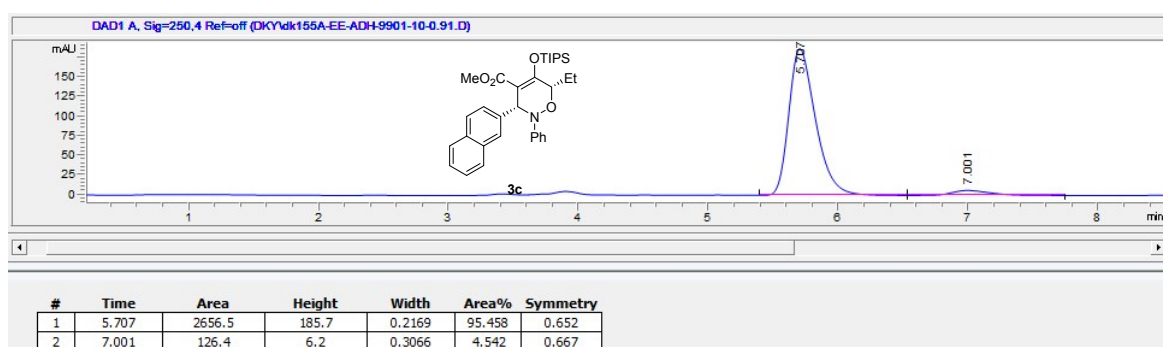
Methyl-6-ethyl-3-(4-fluorophenyl)-2-phenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (*rac*-3b)



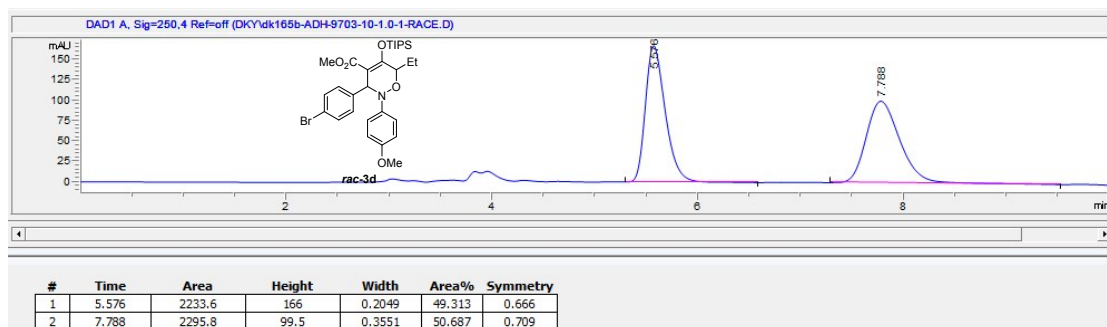
Methyl-6-ethyl-3-(naphthalen-2-yl)-2-phenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2H-1,2-oxazine-4-carboxylate (*rac*-3c)



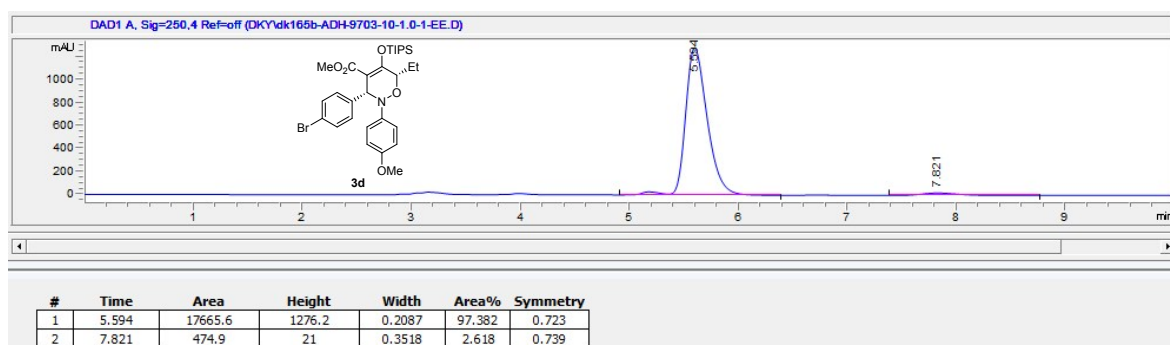
Methyl (3*R*,6*S*)-6-ethyl-3-(naphthalen-2-yl)-2-phenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2H-1,2-oxazine-4-carboxylate (3c)



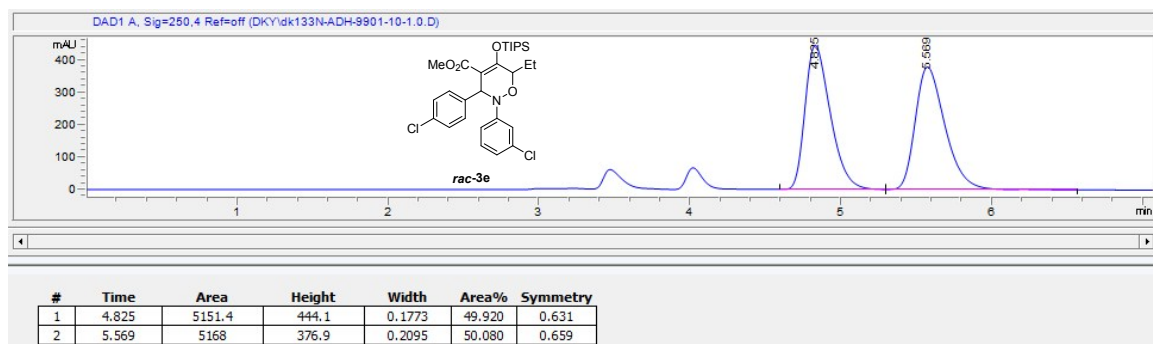
Methyl-3-(4-bromophenyl)-6-ethyl-2-(4-methoxyphenyl)-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (*rac*-3d)



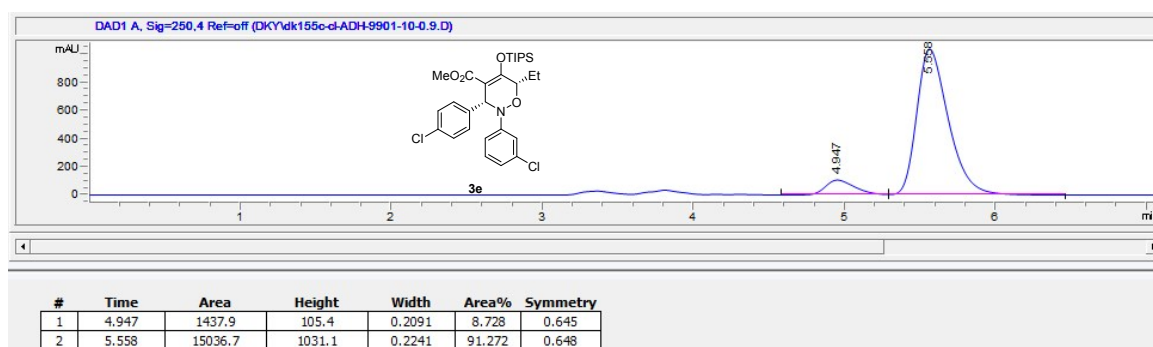
Methyl (3*R*,6*S*)-3-(4-bromophenyl)-6-ethyl-2-(4-methoxyphenyl)-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3d)



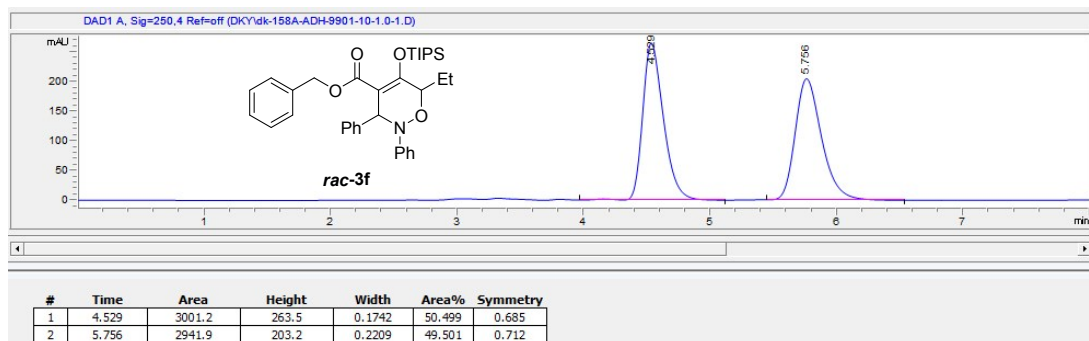
**Methyl-2-(3-chlorophenyl)-3-(4-chlorophenyl)-6-ethyl-5-
[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (*rac*-3e)**



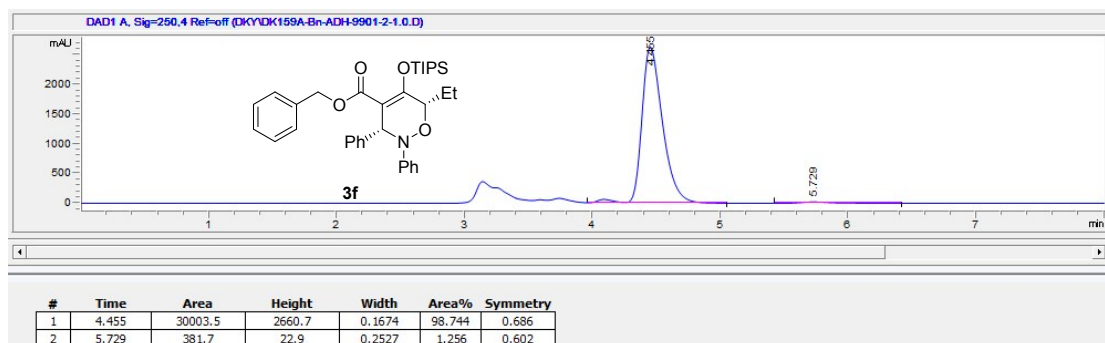
**Methyl-(3*R*,6*S*)-2-(3-chlorophenyl)-3-(4-chlorophenyl)-6-ethyl-5-
[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3e)**



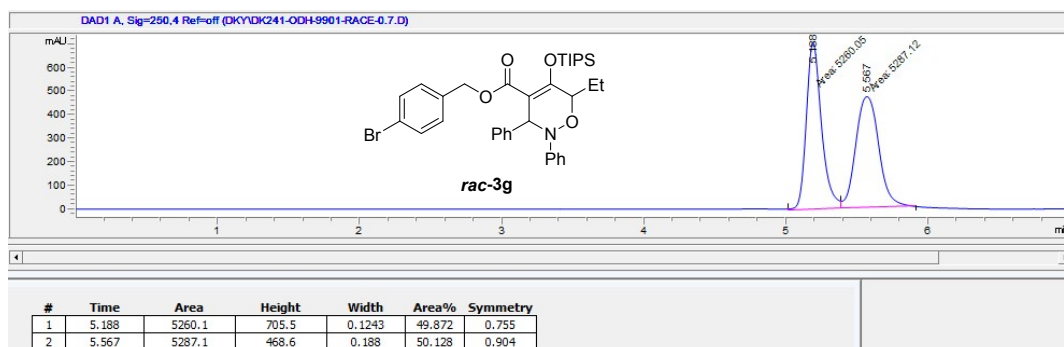
Benzyl-6-ethyl-2,3-diphenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (*rac*-3f)



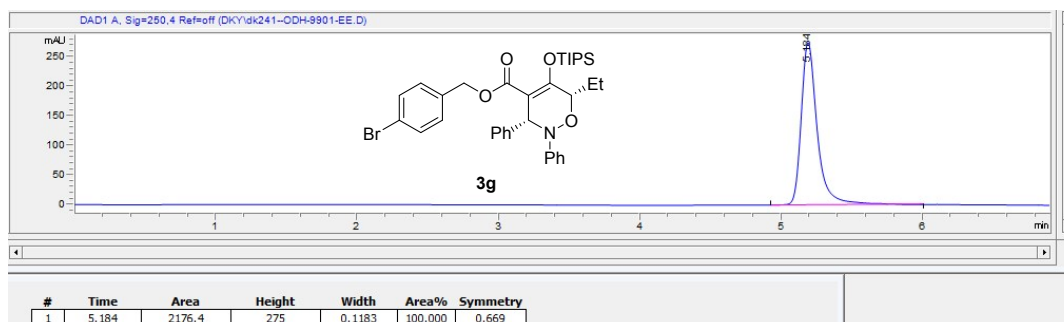
Benzyl (3*R*,6*S*)-6-ethyl-2,3-diphenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3f)



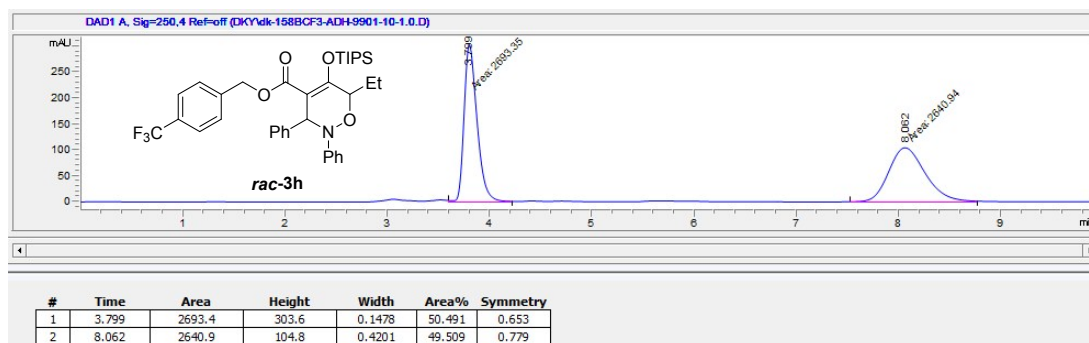
4-Bromobenzyl-6-ethyl-2,3-diphenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (*rac*-3g)



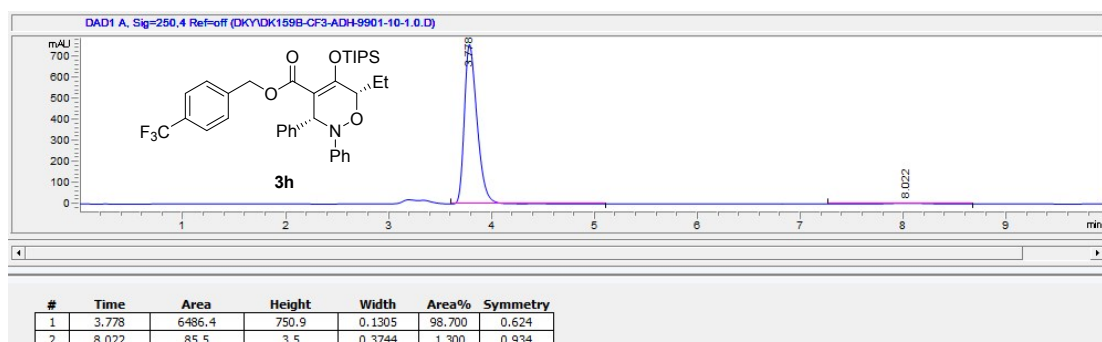
4-Bromobenzyl 3*R*,6*S*)-6-ethyl-2,3-diphenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3g)



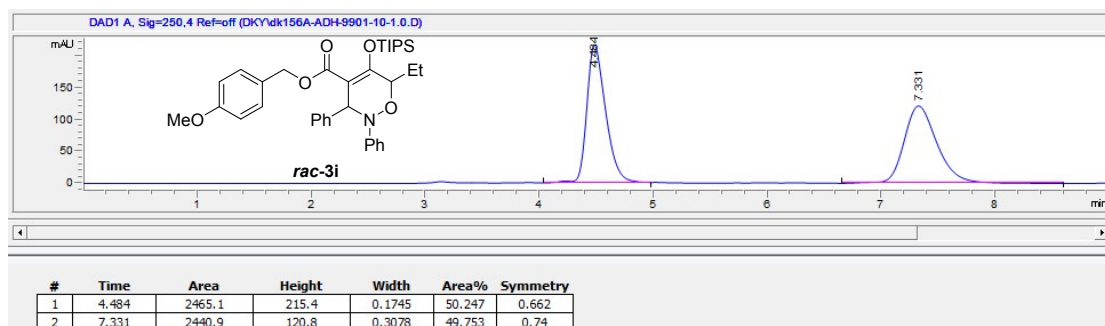
**4-(Trifluoromethyl)benzyl-6-ethyl-2,3-diphenyl-5-[(triisopropylsilyl)oxy]
-3,6-dihydro-2H-1,2-oxazine-4-carboxylate (*rac*-3h)**



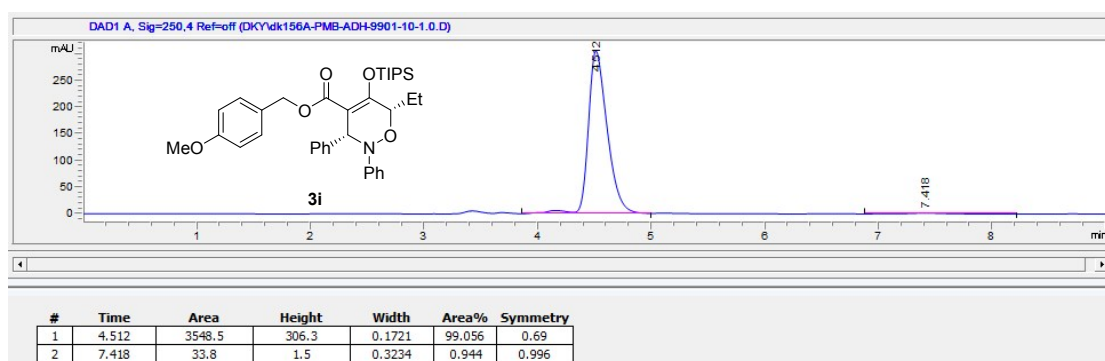
**4-(Trifluoromethyl)benzyl (3*R*,6*S*)-6-ethyl-2,3-diphenyl-5-[(triisopropylsilyl)oxy]
-3,6-dihydro-2H-1,2-oxazine-4-carboxylate (3h)**



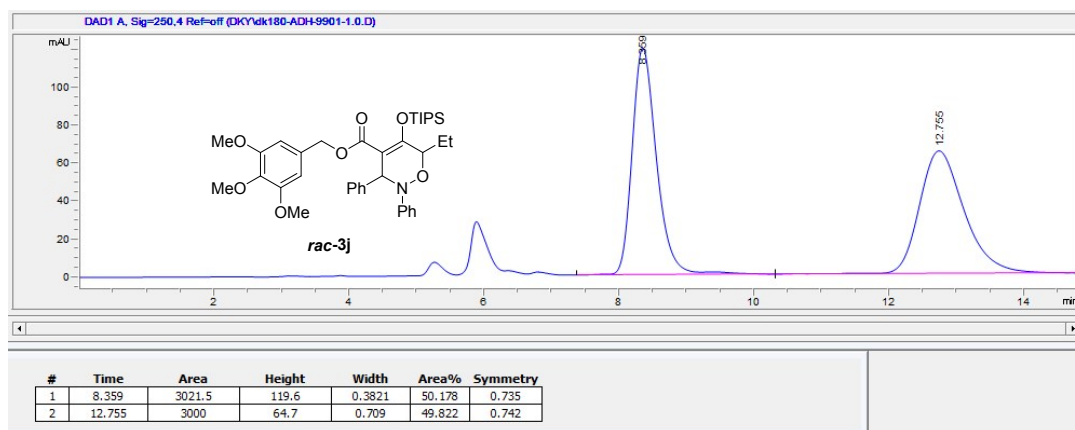
**4-Methoxybenzyl-6-ethyl-2,3-diphenyl-5-[(triisopropylsilyl)oxy]
-3,6-dihydro-2H-1,2-oxazine-4-carboxylate (*rac*-3i)**



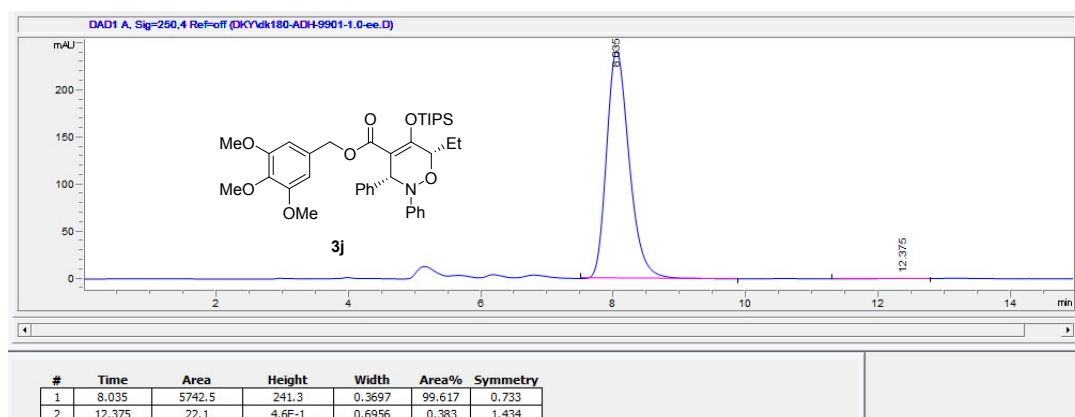
**4-Methoxybenzyl (3*R*,6*S*)-6-ethyl-2,3-diphenyl-5-[(triisopropylsilyl)oxy]
-3,6-dihydro-2H-1,2-oxazine-4-carboxylate (3i)**



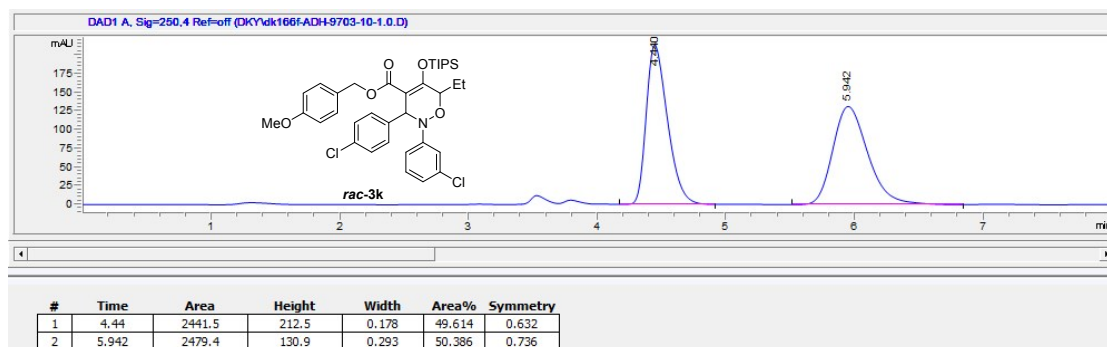
**3,4,5-Trimethoxybenzyl-6-ethyl-2,3-diphenyl-5-[(triisopropylsilyl)oxy]
-3,6-dihydro-2H-1,2-oxazine-4-carboxylate (*rac*-3j)**



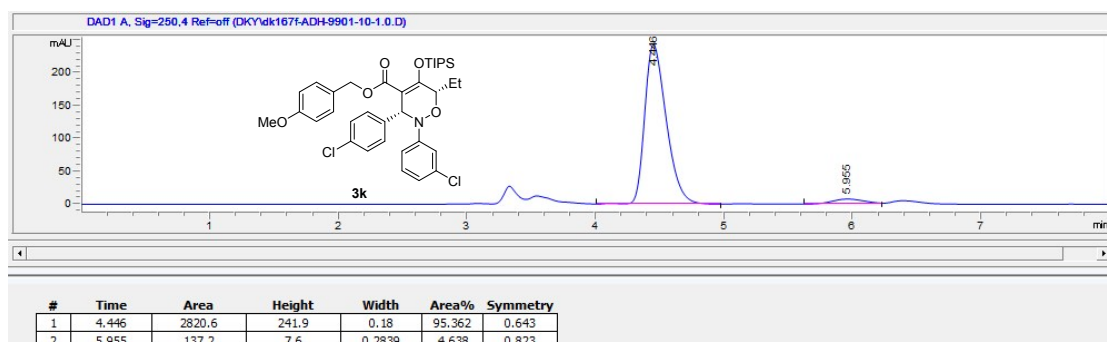
**3,4,5-Trimethoxybenzyl (3*R*,6*S*)-6-ethyl-2,3-diphenyl-5-[(triisopropylsilyl)oxy]
-3,6-dihydro-2H-1,2-oxazine-4-carboxylate (3j)**



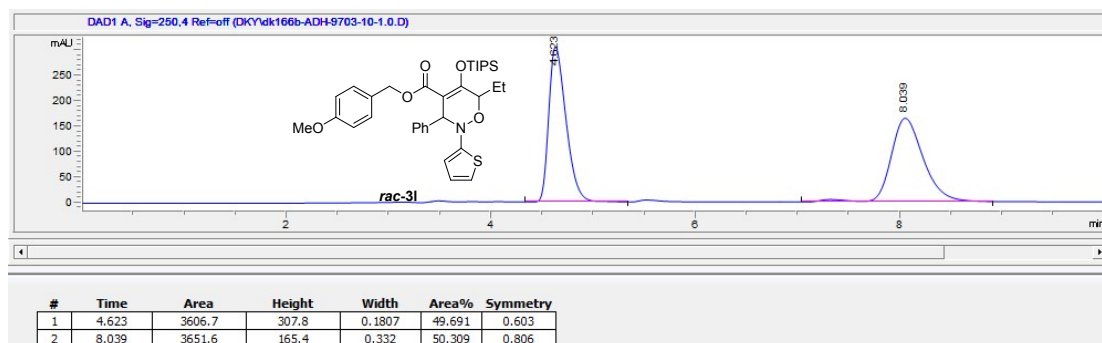
4-Methoxybenzyl-2-(3-chlorophenyl)-3-(4-chlorophenyl)-6-ethyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (*rac*-3k)



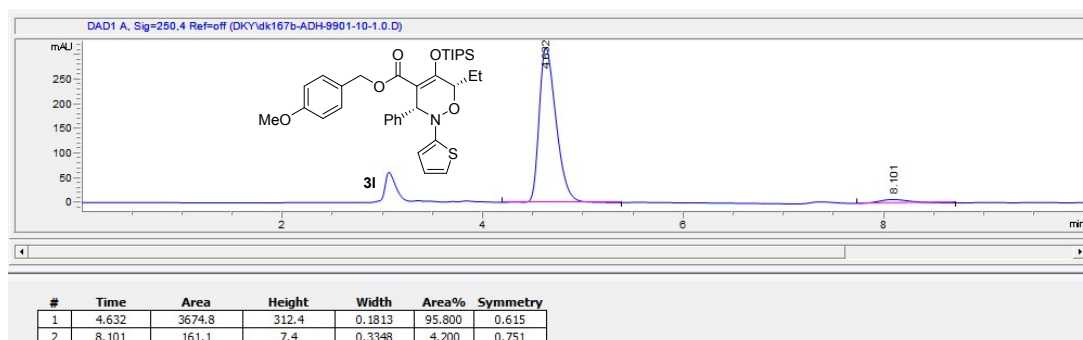
4-Methoxybenzyl (3*R*,6*S*)-2-(3-chlorophenyl)-3-(4-chlorophenyl)-6-ethyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3k)



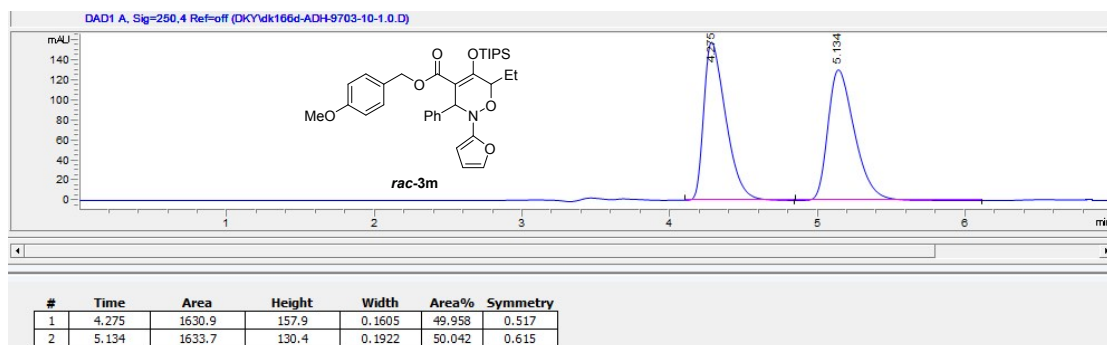
4-Methoxybenzyl-6-ethyl-3-phenyl-2-(thiophen-2-yl)-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (*rac*-3l)



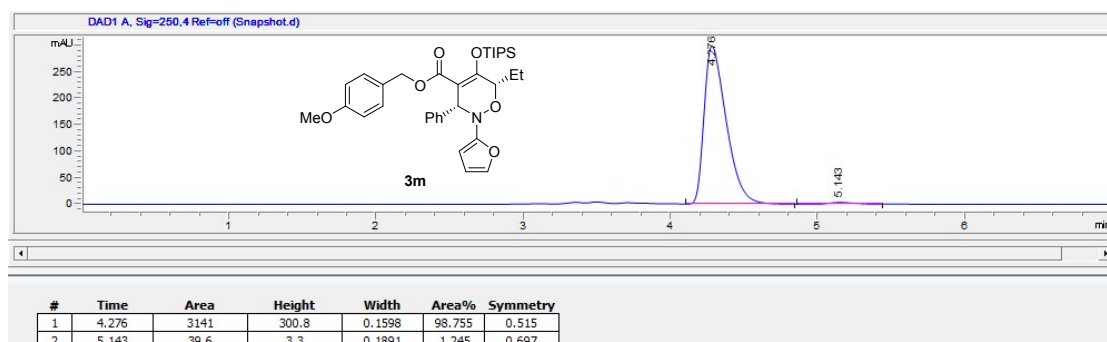
4-Methoxybenzyl (3*R*,6*S*)-6-ethyl-3-phenyl-2-(thiophen-2-yl)-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3l)



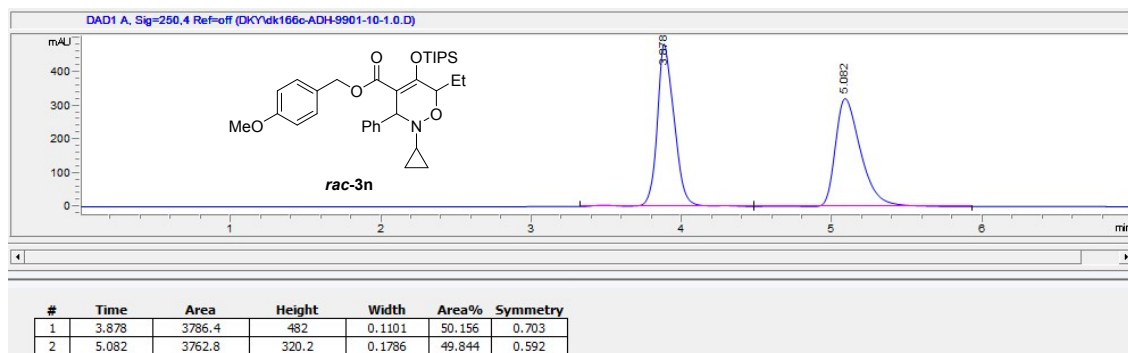
**4-Methoxybenzyl)-6-ethyl-2-(furan-2-yl)-3-phenyl-5-
[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (*rac*-3m)**



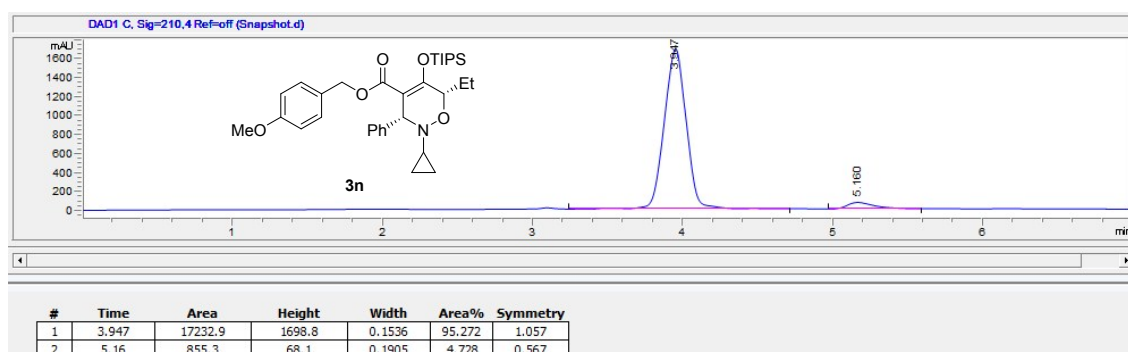
**(3*R*,6*S*)-4-Methoxybenzyl-6-ethyl-2-(furan-2-yl)-3-phenyl-5-
[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3m)**



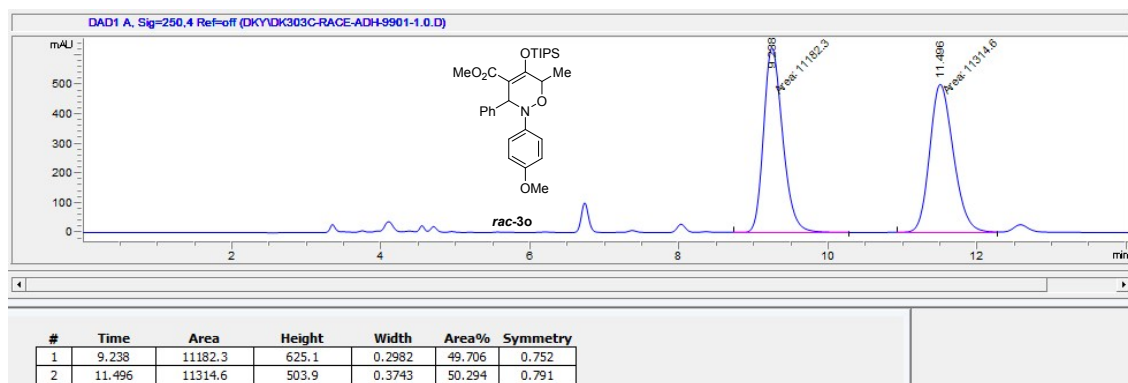
4-Methoxybenzyl-2-cyclopropyl-6-ethyl-3-phenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (*rac*-3n)



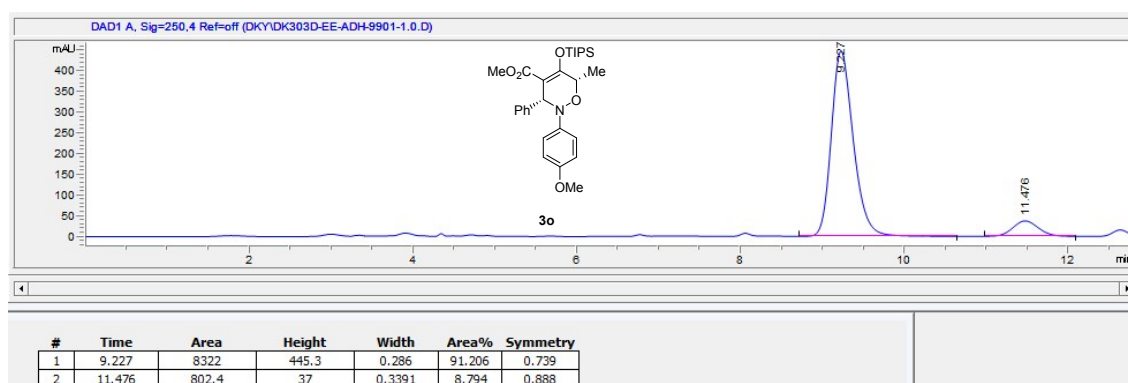
4-Methoxybenzyl (3*S*,6*R*)-2-cyclopropyl-6-ethyl-3-phenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3n)



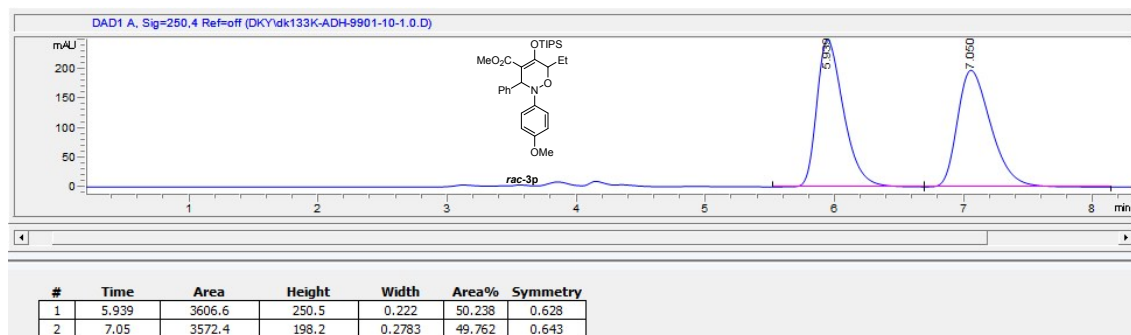
Methyl -2-(4-methoxyphenyl)-6-methyl-3-phenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (*rac*-3o)



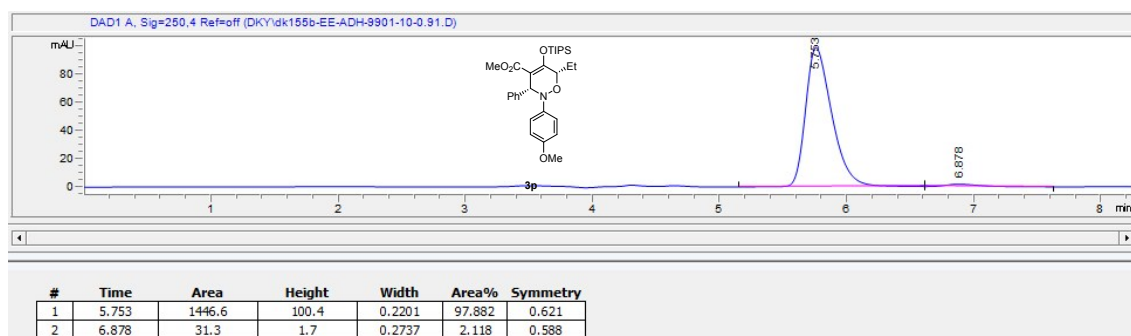
Methyl (3*R*,6*S*)-2-(4-methoxyphenyl)-6-methyl-3-phenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3o)



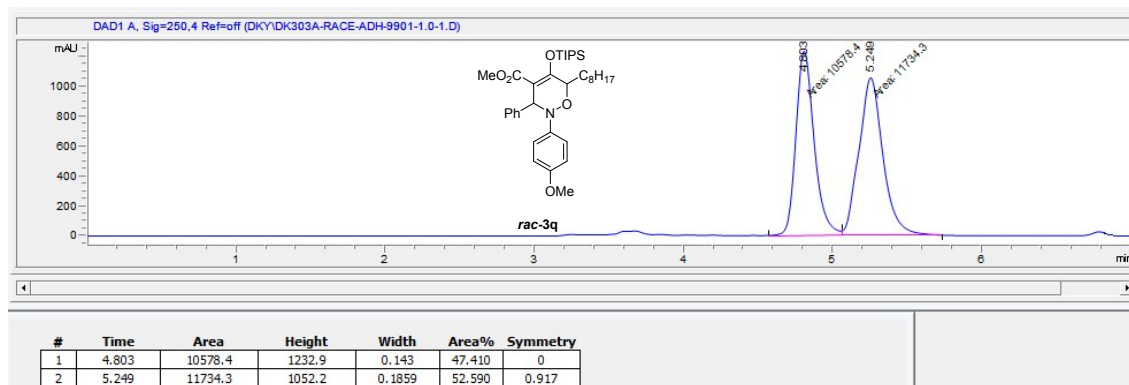
**Methyl-6-ethyl-2-(4-methoxyphenyl)-3-phenyl-5-[(triisopropylsilyl)oxy]
-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (*rac*-3p)**



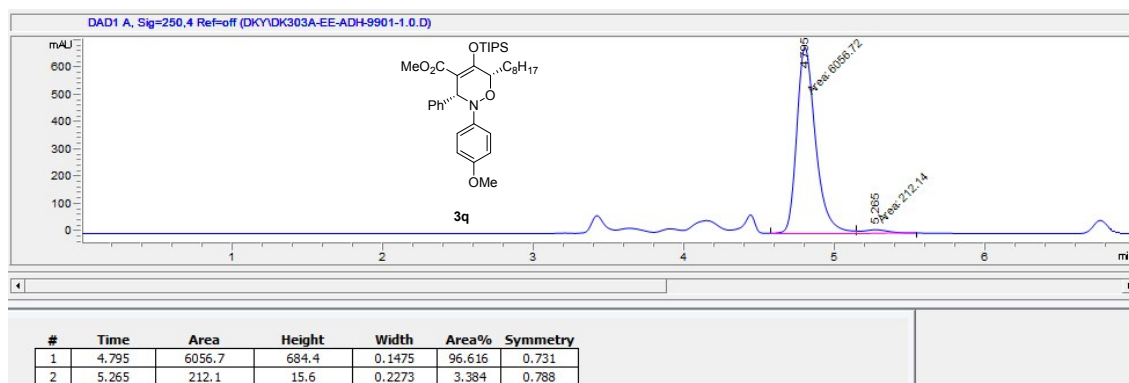
**Methyl (3*R*,6*S*)-6-ethyl-2-(4-methoxyphenyl)-3-phenyl-5-[(triisopropylsilyl)oxy]
-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3p)**



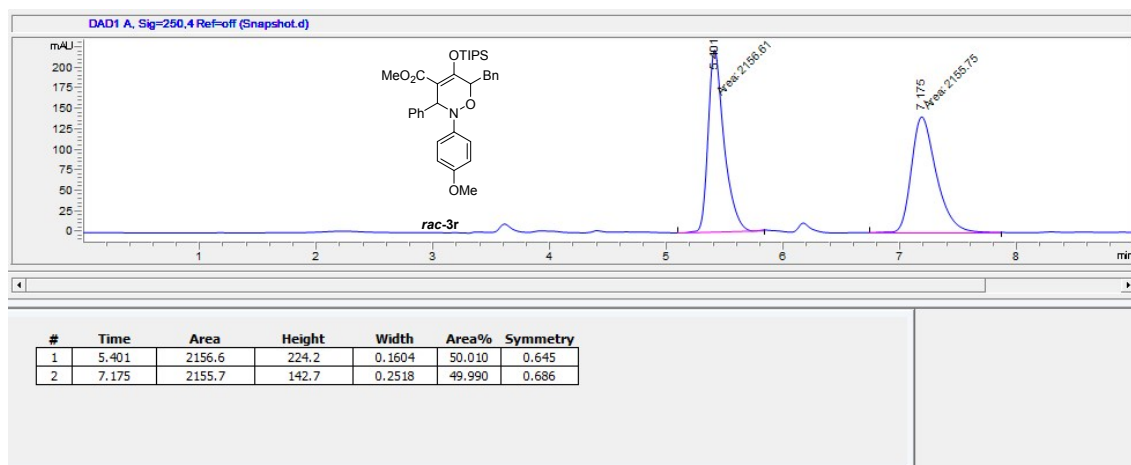
**Methyl -2-(4-methoxyphenyl)-6-octyl-3-phenyl-5-[(triisopropylsilyl)oxy]
-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (*rac*-3q)**



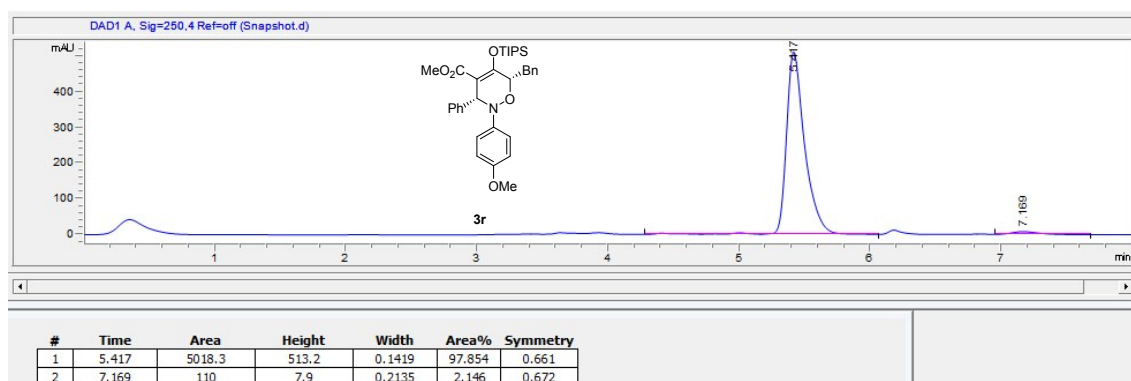
**Methyl (3*R*,6*S*)-2-(4-methoxyphenyl)-6-octyl-3-phenyl-5-[(triisopropylsilyl)oxy]
-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3q)**



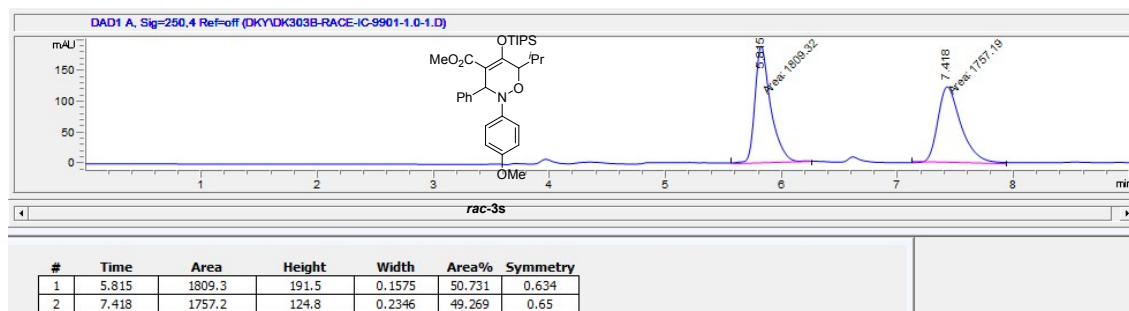
**Methyl-6-benzyl-2-(4-methoxyphenyl)-3-phenyl-5-[(triisopropylsilyl)oxy]
-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (*rac*-3r)**



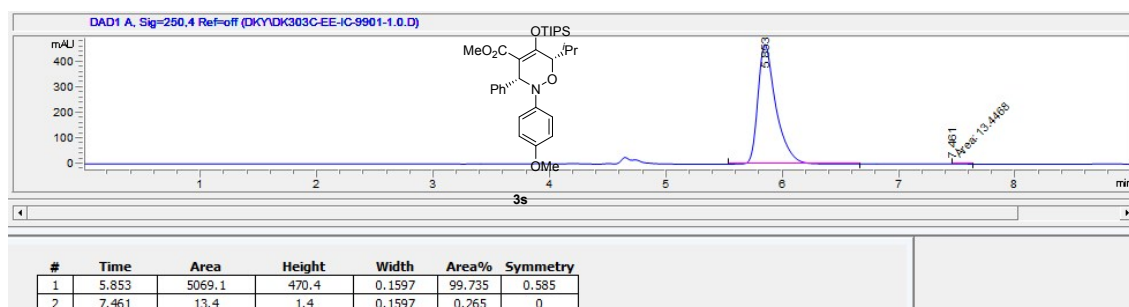
**Methyl (3*R*,6*S*)-6-benzyl-2-(4-methoxyphenyl)-3-phenyl-5-[(triisopropylsilyl)oxy]
-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3r)**



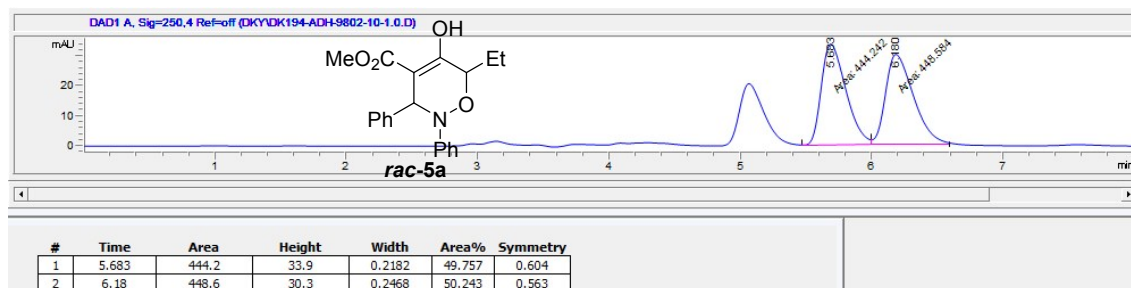
Methyl -6-isopropyl-2-(4-methoxyphenyl)-3-phenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (*rac*-3s)



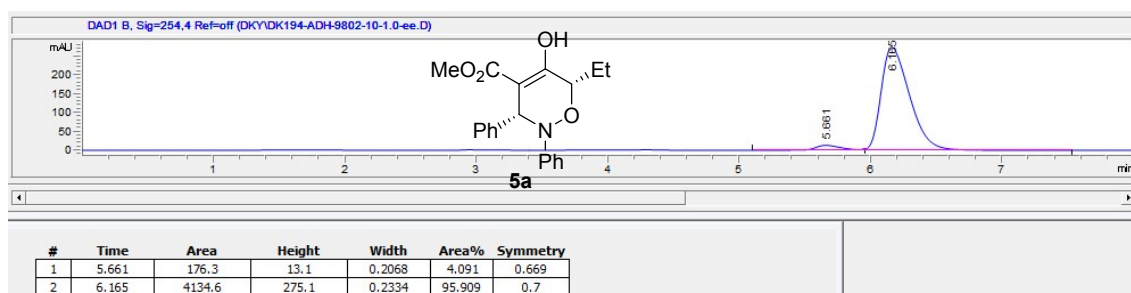
Methyl (3*R*,6*S*)-6-isopropyl-2-(4-methoxyphenyl)-3-phenyl-5-[(triisopropylsilyl)oxy]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (3s)



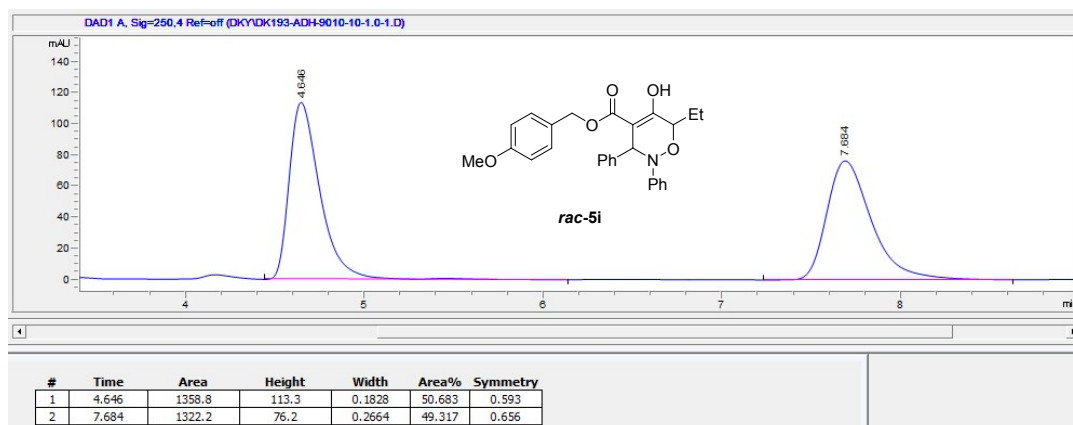
Methyl-6-ethyl-5-hydroxy-2,3-diphenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (*rac*-5a)



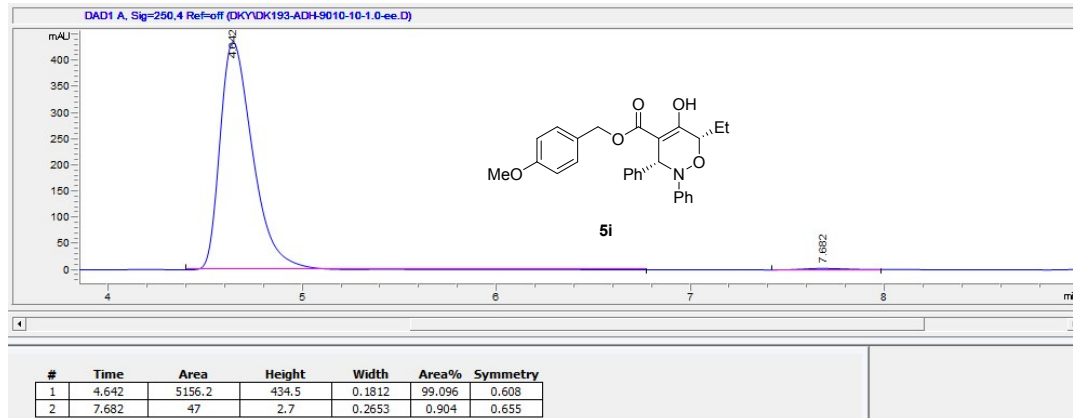
Methyl (3*R*,6*S*)-6-ethyl-5-hydroxy-2,3-diphenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (5a)



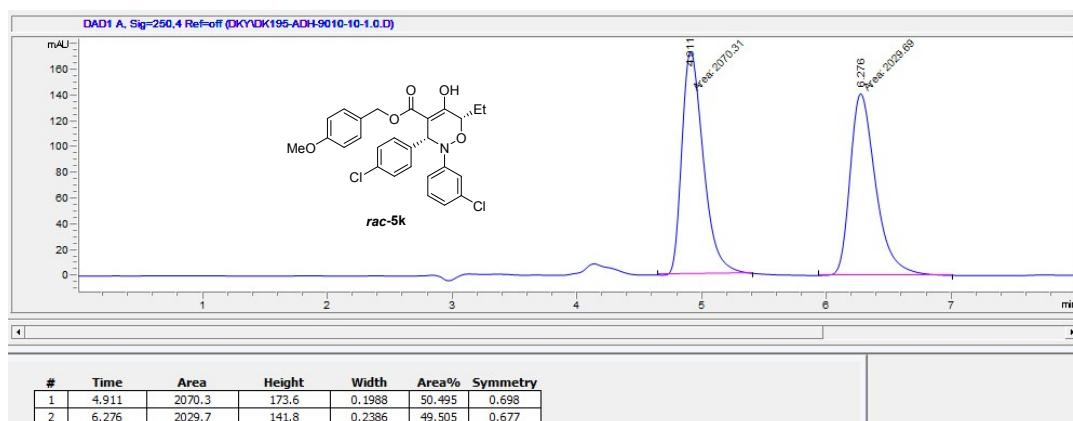
**4-Methoxybenzyl-6-ethyl-5-hydroxy-2,3-diphenyl-3,6-dihydro-2H
-1,2-oxazine-4-carboxylate (*rac*-5i)**



**4-Methoxybenzyl (3*R*,6*S*)-6-ethyl-5-hydroxy-2,3-diphenyl-3,6-dihydro-2H
-1,2-oxazine-4-carboxylate (5i)**



4-Methoxybenzyl-(3-chlorophenyl)-3-(4-chlorophenyl)-6-ethyl-5-hydroxy-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (5k)



4-Methoxybenzyl (3*R*,6*S*) (3-chlorophenyl)-3-(4-chlorophenyl)-6-ethyl-5-hydroxy-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (5k)

