

Supporting Information

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General Methods.

¹H-NMR spectra were recorded on Varian 400 (400 MHz) spectrometers. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuteriochloroform: 7.24 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, sept = septet, p = pseudo, b = broad, m = multiplet), coupling constants (Hz). ¹³C-NMR spectra were recorded on a Varian 400 (100 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuteriochloroform: 77.0 ppm). GC-MS spectra were taken by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection. They are reported as: *m/z* (rel. intense). LC-electrospray ionization mass spectra were obtained with Agilent Technologies MSD1100 single-quadrupole mass spectrometer. Chromatographic purification was done with 240-400 mesh silica gel. Other anhydrous solvents were supplied by Sigma Aldrich in Sureseal® bottles and used without any further purification. Commercially available chemicals were purchased from Sigma Aldrich, Stream and TCI and used without any further purification. Analytical high performance liquid chromatography (HPLC) was performed on a liquid chromatograph equipped with a variable wave-length UV detector (deuterium lamp 190-600 nm), using a Daicel Chiracel™OD-H, (0.46 cm I.D. x 25 cm Daicel Inc). HPLC grade isopropanol and *n*-hexane were used as the eluting solvents. Melting points were determined with Bibby Stuart Scientific Melting Point Apparatus SMP 3 and are not corrected. Agilent Technologies LC/MSD Trap 1100 series (nebulizer: 15.0 PSI, dry Gas: 5.0 L/min, dry Temperature: 325 °C, capillary voltage positive scan: 4000 mA, capillary voltage negative scan: 3500 mA).

Crystallographic data collection and structure determination for [NiCl{(5,5')-Me₂-bpy}(H₂O)₃]Cl·4H₂O and 1-(2-([1,1'-biphenyl]-4-yl)-4-(naphthalen-2-yl)butyl)piperidyn-2-one (+/-)-6r**.** The X-ray intensity data were measured on a Bruker Apex III CCD diffractometer. Cell dimensions and the orientation matrix were initially determined from a least-squares refinement on reflections measured in three sets of 20 exposures, collected in three different ω regions, and eventually refined against all data. A full sphere of reciprocal space was scanned by 0.3° ω steps. The software SMART¹ was used for collecting frames of data, indexing reflections and determination of lattice parameters. The collected frames were then processed for integration by the SAINT program.¹ and an empirical absorption correction was applied using SADABS.² The structures were solved by direct methods (SIR 97)³ and subsequent Fourier syntheses and refined by full-matrix least-squares on F² (SHELXTL)⁴ using anisotropic thermal parameters for all non-hydrogen atoms. In the asymmetric unit four water molecules are present. The aromatic, methylene, methino and methyl hydrogen atoms were placed in calculated positions and refined

¹ SMART & SAINT Software Reference Manuals, version 5.051 (Windows NT Version), Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1998.

² Sheldrick, G.M. SADABS, program for empirical absorption correction, University of Göttingen, Germany, 1996.

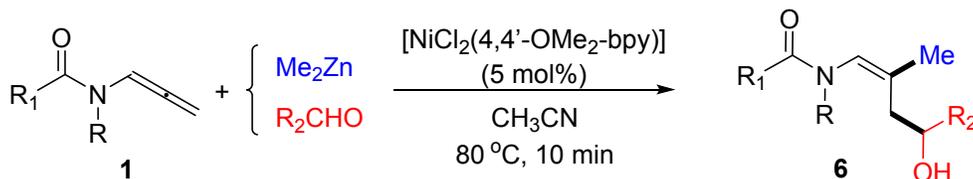
³ Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.*, 1999, 32, 115-119.

⁴ Sheldrick, G.M. SHELXTLplus (Windows NT Version) Structure Determination Package, Version 5.1. Bruker Analytical X-ray Instruments Inc.: Madison, WI, USA, 1998.

with isotropic thermal parameters $U(H) = 1.2 U_{eq}(C)$ or $U(H) = 1.5 U_{eq}(C)$ (methyl H), respectively and allowed to ride on their carrier carbons whereas the H atoms of the water molecules in $[NiCl\{(5, 5')\text{-Me}_2\text{-bpy}\}(H_2O)_3]Cl \cdot 4H_2O$ were located in the Fourier map and refined isotropically [$U(H) = 1.2 U_{eq}(O)$]. Crystal data and details of data collections for $[NiCl\{(5,5')\text{-Me}_2\text{-bpy}\}(H_2O)_3]Cl \cdot 4H_2O$ and 1-(2-([1,1'-biphenyl]-4-yl)-4-(naphthalen-2-yl)butyl)piperidin-2-one are reported in Table S1.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication numbers CCDC 1817608 and CCDC 1826529. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/getstructures.

General procedure of tri-component reaction with organozinc reagent



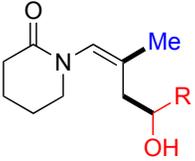
Under nitrogen atmosphere, a dry Schlenk tube was charged with stir bar and acetonitrile (1 mL). Then catalyst (3.4 mg, 0.01 mmol, 5 mol%), organozinc (0.4 mmol, 2.0 eq.), allenamide (0.2 mmol) and aldehyde (0.4 mmol, 2.0 eq.) were added sequentially at room temperature. Then the reaction was heated to $80\text{ }^\circ\text{C}$ and kept stirring. TLC showed the reaction complete in 10 mins. The reaction was quenched with H_2O (3 mL) and extracted with EtOAc (3×5 mL). Then the organic phase was combined and washed with brine (5 mL). Then the residue was purified with silica gel chromatography to give corresponding product.

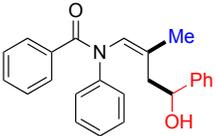
	<p>(+/-)-6a (R = Ph). Yellow oil, cHex:EtOAc = 1:1. Yield = 66% (34.2 mg). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.40 – 7.28 (m, 4H), 7.22 (t, J = 6.6 Hz, 1H), 5.66 (s, 1H), 4.99 (s, 1H), 4.89 (dd, J = 10.7, 3.7 Hz, 1H), 3.35 – 3.24 (m, 1H), 3.16 (d, J = 12.0 Hz, 1H), 2.46 (s, 2H), 2.41 (d, J = 10.9 Hz, 1H), 2.20 (dd, J = 13.8, 3.2 Hz, 1H), 1.90 (s, 3H), 1.80 (d, J = 2.9 Hz, 4H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 170.70, 146.31, 135.46, 128.34, 126.93, 125.67, 125.50, 70.48, 50.22, 42.10, 32.42, 22.95, 21.14, 19.49. LC-MS: 242.0 [M-OH], 260.2 [M+H⁺], 541.2 [2M+Na⁺]. MW: 259.16. Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_2$: C, 74.10; H, 8.16. Found: C, 74.25; H, 8.21.</p>
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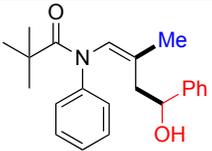
	<p>(+/-)-6b (R = $\text{pCF}_3\text{-C}_6\text{H}_4$). Yellow oil, cHex:EtOAc = 1:1. Yield = 43% (28.2 mg). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.57 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 5.63 (s, 1H), 5.47 (s, 1H), 4.94 (dd, J = 11.0, 4.0 Hz, 1H), 3.35 – 3.28 (m, 1H), 3.18 (dd, J = 7.0, 5.0 Hz, 1H), 2.45 (dd, J = 6.6, 4.1 Hz, 2H), 2.37 (dd, J = 13.8, 11.0 Hz, 1H), 2.20 (dd, J = 13.8, 3.6 Hz, 1H), 1.91 (d, J = 0.8 Hz, 3H), 1.86 – 1.75 (m, 4H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 170.72, 150.65, 135.04, 125.84, 125.80, 125.36, 125.32, 125.28, 125.24, 69.92, 50.26, 41.88, 32.44, 22.90, 21.09, 19.39. LC-MS: 310.2 [M-OH], 328.2 [M+H⁺], 677.2 [2M+Na⁺]. MW: 327.14. Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{F}_3\text{NO}_2$: C, 62.38; H, 6.16. Found: C, 62.22; H, 6.01.</p>
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	<p>(+/-)-6c (R = CH=CHPh). Yellow oil, cHex:EtOAc = 1:1. Yield = 41% (23.4 mg). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.38 (d, J = 7.5 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.21 (d, J = 7.4 Hz, 1H), 6.65 (d, J = 15.9 Hz, 1H), 6.24 (dd, J = 15.8, 5.6 Hz, 1H), 5.67 (s, 1H), 4.53 – 4.46 (m, 1H), 3.36 – 3.21 (m, 2H), 2.45 (d, J = 5.4 Hz, 2H), 2.35 (dd, J = 13.6, 10.4 Hz, 1H), 2.13 (dd, J = 13.7, 3.8 Hz, 1H), 1.86 (s, 3H), 1.81 (t, J = 8.8 Hz, 4H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 170.88, 137.22, 135.13,</p>
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133.62, 128.91, 128.58, 127.36, 126.52, 125.80, 68.91, 50.28, 39.56, 32.39, 31.03, 22.99, 21.14, 19.69. LC-MS: 268.2 [M-OH], 286.2 [M+H⁺], 571.2 [2M+H⁺]. MW: 285.17. Anal. Calcd for C₁₈H₂₃NO₂: C, 75.76; H, 8.12. Found: C, 75.61; H, 8.32.

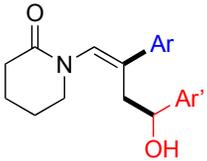
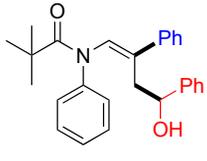
	<p>(+/-)-6d (R = iBu). Colorless oil, cHex:EtOAc = 1:1. Yield = 64% (30.6 mg). ¹H-NMR (400 MHz, CDCl₃) δ 5.68 (s, 1H), 3.90 – 3.76 (m, 1H), 3.33 – 3.20 (m, 2H), 2.45 (d, J = 3.2 Hz, 2H), 2.15 (dd, J = 13.5, 10.2 Hz, 1H), 1.96 – 1.88 (m, 1H), 1.81 (d, J = 3.5 Hz, 4H), 1.78 (s, 3H),</p>
<p>1.42 (ddd, J = 13.7, 8.3, 5.6 Hz, 1H), 1.23 (s, 1H), 1.15 (ddd, J = 13.1, 8.3, 4.6 Hz, 1H), 0.89 (d, J = 6.6 Hz, 6H). ¹³C-NMR (100 MHz, CDCl₃) δ 171.33, 136.04, 125.35, 66.32, 50.31, 48.06, 39.67, 32.31, 24.71, 23.39, 22.98, 22.36, 21.10, 19.91. LC-MS: 222.2 [M-OH], 240.2 [M+H⁺], 501.2 [2M+Na⁺]. MW: 239.19. Anal. Calcd for C₁₄H₂₅NO₂: C, 70.25; H, 10.53. Found: C, 70.02; H, 10.31.</p>	

	<p>(+/-)-6e. Colorless oil, cHex:EtOAc = 1:1. Yield = 54% (40.0 mg). ¹H NMR (401 MHz, CDCl₃) δ 7.48 – 7.47 (m, 2H), 7.42 – 7.23 (m, 11H), 7.18 – 7.07 (m, 2H), 5.82 – 5.75 (m, 1H), 5.06 – 4.92 (m, 1H), 4.52 (s, 1H), 4.34 (d, J = 14.0 Hz, 1H), 2.25 – 2.14 (m, 1H), 1.91 – 1.68 (m, 2H), 1.56 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 170.64, 144.23, 141.29, 137.31, 136.35, 134.48, 132.27, 132.17, 130.05, 129.02, 128.88, 128.74, 128.62, 128.39, 127.77, 127.08, 125.70, 125.67, 117.37, 71.29, 70.23, 51.67, 40.62, 28.11, 19.36. LC-MS: 372.2 [M+H⁺]. MW: 371.19. Anal. Calcd for C₂₅H₂₅NO₂: C, 70.25; H, 10.53. Found: C, 70.02; H, 10.31.</p>
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	<p>(+/-)-6f. Colorless oil, cHex:EtOAc = 1:1. Yield = 47% (16.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, J = 7.7 Hz, 1H), 7.47 (t, J = 7.8 Hz, 1H), 7.39 – 7.30 (m, 5H), 7.26 (dd, J = 7.8, 5.3 Hz, 1H), 7.20 (d, J = 7.2 Hz, 2H), 6.00 (s, 1H), 4.84 (dd, J = 10.8, 3.9 Hz, 2H), 2.70 (dd, J =</p>
<p>13.9, 10.8 Hz, 1H), 2.24 (dd, J = 13.9, 3.6 Hz, 2H) 1.86 (s, 3H), 1.12 (s, 9H). ¹³C-NMR (100 MHz, CDCl₃) δ 179.51, 145.97, 143.52, 133.81, 129.35, 129.06, 128.69, 128.44, 127.77, 127.18, 125.55, 71.00, 42.07, 41.40, 29.33, 27.05, 19.62. LC-MS: 310.2 [M-OH], 338.2 [M+H⁺]. MW: 337.20. Anal. Calcd for C₂₂H₂₇NO₂: C, 78.30; H, 8.06. Found: C, 78.21; H, 8.00.</p>	

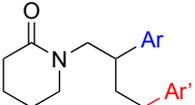
General procedure of tri-component reaction with boronic acids

To a dry Schlenk tube anhydrous 1,4-dioxane (1 mL) was added under nitrogen atmosphere, followed by [NiCl₂(4,4'-(OMe)₂-bpy)] 3.7 mg (0.01 mmol, 5 mol%), potassium carbonate 82.8 mg (0.6 mmol, 3.0 eq.), phenylboronic acid 36.9 mg (0.3 mmol, 1.5 eq.), aldehyde (0.4 mmol, 2.0 eq.) and allenamide (0.2 mmol, 1.0 eq.). Then the resulting mixture was poured into a pre-heated oil bath at 90 °C and stirred for 1 hour when TLC showed complete consumption of the allenamide. Then solvent was removed under vacuum and the residue was purified with silica gel column flash-chromatography to give corresponding product.

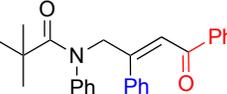
	<p>(+/-)-5r (Ar = <i>p</i>Ph-C₆H₄, Ar' = 2-naphth). White solid (M.P.: 80.6 – 81.8°C), cHex:EtOAc = 1:1. Yield = 81% (28.2 mg). ¹H-NMR (400 MHz, CDCl₃) δ 7.86 – 7.76 (m, 4H), 7.70 – 7.57 (m, 6H), 7.52 – 7.40 (m, 5H), 7.37 (t, J = 7.4 Hz, 1H), 6.06 (s, 1H), 4.87 (dd, J = 10.4, 3.3 Hz, 1H), 3.42 (d, J = 11.9 Hz, 1H), 3.30 (d, J = 11.7 Hz, 1H), 2.99 (d, J = 11.6 Hz, 1H), 2.87 – 2.78 (m, 1H), 2.57 (s, 2H), 1.88 (m, J = 15.3 Hz, 4H). ¹³C-NMR (100 MHz, CDCl₃) δ 170.65, 143.56, 141.10,</p>
<p>140.78, 138.94, 137.71, 133.52, 132.83, 128.94, 128.90, 128.07, 128.03, 127.74, 127.70, 127.54, 127.48, 127.21, 127.10, 126.64, 126.06, 125.59, 124.11, 124.01, 70.99, 50.46, 40.43, 32.60, 22.96, 21.11. LC-MS: 430.2 [M-OH], 448.2 [M+H⁺]. MW: 447.22. Anal. Calcd for C₃₁H₂₉NO₂: C, 83.19; H, 6.53. Found: C, 83.01; H, 6.41.</p>	
	<p>(+/-)-5s. Colorless oil. cHex:EtOAc = 3:1. Yield = 89% (71 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.42 (m, 2H), 7.40 – 7.34 (m, 4H), 7.34 – 7.23 (m, 9H), 6.37 (d, J = 1.0 Hz, 1H), 3.55 (s, 1H), 2.96 (dd, J = 14.5, 10.3 Hz, 1H), 2.83 (ddd, J = 14.5, 3.9, 1.5 Hz, 1H), 1.18 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 179.67, 145.52, 143.33, 139.08, 137.28, 131.51, 129.42, 128.70, 128.40, 128.05, 127.84, 127.22,</p>
<p>127.18 (2C), 125.59, 71.38, 41.52, 40.45, 29.25. LC-MS: 382.2 [M-OH], 400.2 [M+H⁺]. MW: 399.22. Anal. Calcd for C₂₇H₂₉NO₂: C, 81.17; H, 7.32. Found: C, 81.05; H, 7.24.</p>	

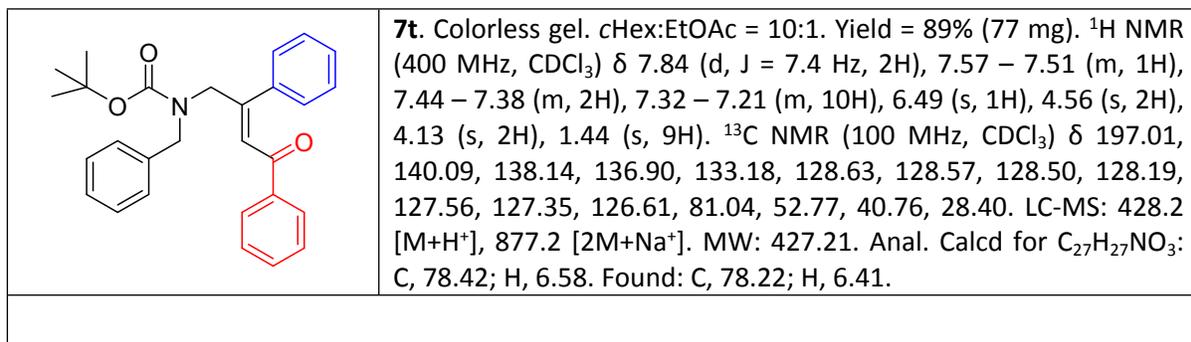
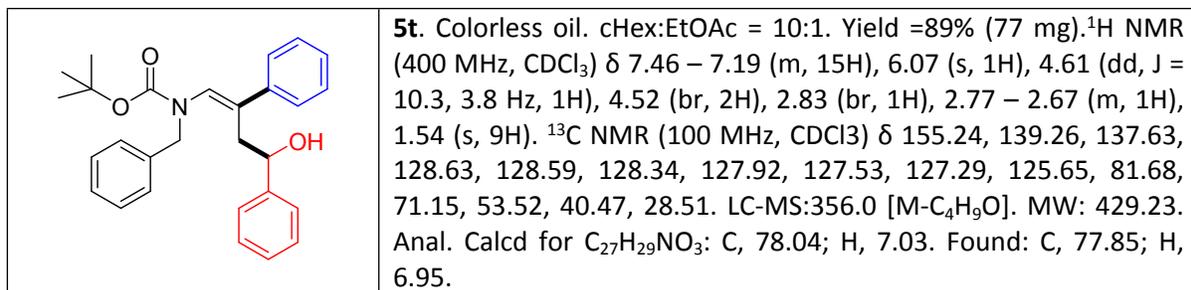
Chemical transformations of the tri-component compounds

Hydrogenation of (+/-)-5r: The substrate 90 mg (0.20 mmol) was dissolved in EtOH (5 mL) and DCM (2 mL). Then Pd/C (10.6 mg, 0.01 mol, 10%) was added, the air in vessel was evacuated and recharged with H₂ (1 atm). TLC showed the reaction complete in 12 hours. The reaction solution was filtrated with silica gel pad and washed with EtOAc (20 mL). The solvent was removed under vacuum. Then the residue was purified with silica gel chromatography to give product 76.8 mg (85%) as solid.

	<p>(+/-)-6r (Ar = pPh-C₆H₄, Ar' = 2-naphth). White solid. M.P.: 110.4 – 110.8 °C. cHex:EtOAc = 1:1. Yield = 85% (76.8 mg). ¹H-NMR (400 MHz, CDCl₃) δ 7.82 – 7.78 (m, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.66 – 7.58 (m, 4H), 7.55 (s, 1H), 7.49 – 7.39 (m, 4H), 7.38 – 7.31 (m, 3H), 7.29 (dd, J = 8.4, 1.7 Hz, 1H), 4.09 – 3.99 (m, 1H), 3.16 (ddd, J =</p>
<p>14.0, 7.0 Hz, 2H), 3.00 (ddd, J = 12.0, 7.1, 4.8 Hz, 1H), 2.77 – 2.60 (m, 3H), 2.34 (qt, J = 17.7, 6.5 Hz, 2H), 2.17 – 2.01 (m, 3H), 1.68 – 1.59 (m, 2H), 1.58 – 1.41 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ 170.11, 141.61, 140.73, 139.64, 139.51, 133.57, 131.95, 128.75, 128.51, 127.83, 127.56, 127.37, 127.25, 127.18, 127.13, 126.92, 126.35, 125.83, 125.06, 53.78, 49.05, 43.03, 34.79, 33.60, 32.20, 23.04, 21.05. LC-MS: 434.2 [M+H⁺], 867.4 [2M+H⁺]. MW: 433.24. Anal. Calcd for C₃₁H₃₁NO: C, 85.87; H, 7.21. Found: C, 85.61; H, 7.38.</p>	

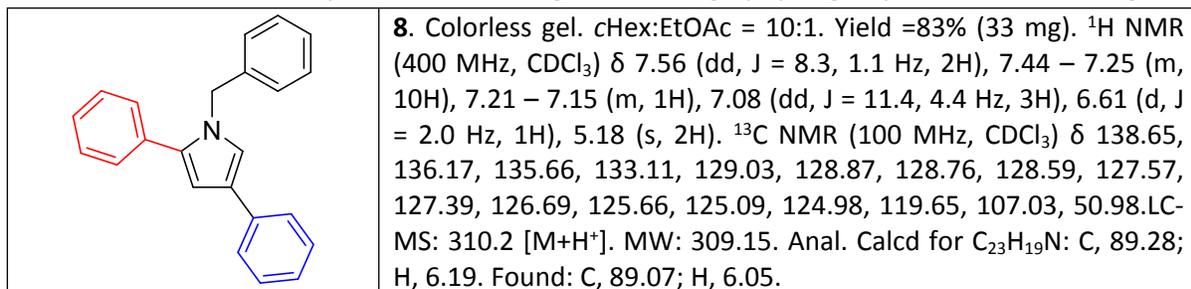
Oxidation of (+/-)-5s: To a Schlenk tube was charged with a stirring bar and DCM (3 ml), then substrate (60 mg, 0.15 mmol) and IBX (126 mg, 0.45 mmol, 3.0 eq.) were added into the tube. Then the reaction was heated to reflux overnight. TLC showed the reaction completed. The mixture diluted with DCM (20 ml) and filtrated. The organic layer was concentrated under vacuum and purified with silica gel column to give a colorless oil in 95% yield.

	<p>7s. White solid. cHex:EtOAc = 3:1. Yield = 95% (57 mg). M.P. = 113.0-114 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.73 – 77.71 (m, 2H), 7.55 – 7.49 (m, 1H), 7.42 – 7.24 (m, 7H), 7.20 (t, J = 4.5 Hz, 4H), 7.14 – 7.09 (m, 1H), 7.03 (s, 1H), 4.00 (s, 2H), 1.26 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 195.55, 178.79, 143.23, 140.60, 136.68,</p>
<p>133.11, 131.45, 130.03, 129.12, 128.63, 128.53, 128.27, 128.04, 127.63, 126.89, 126.52, 41.21, 40.49, 28.78. LC-MS: 398.2 [M+H⁺], 817.2 [2M+Na⁺]. MW: 397.2. Anal. Calcd for C₂₇H₂₇NO₂: C, 81.51; H, 6.85. Found: C, 81.33; H, 6.71.</p>	

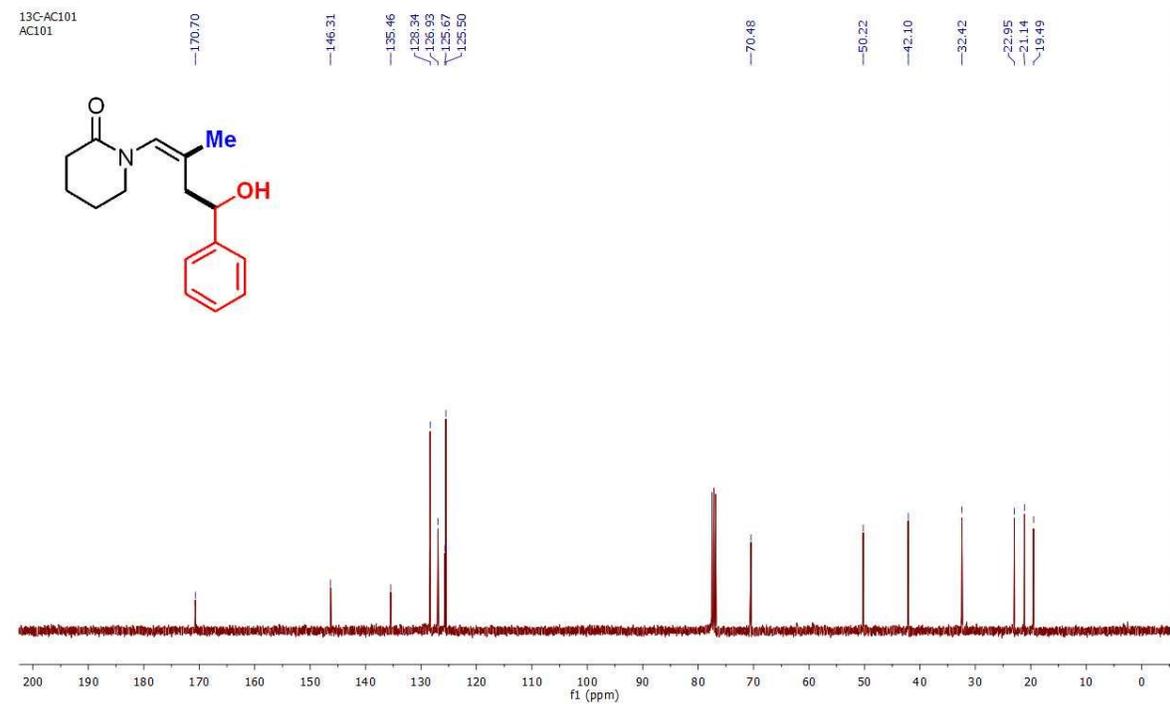
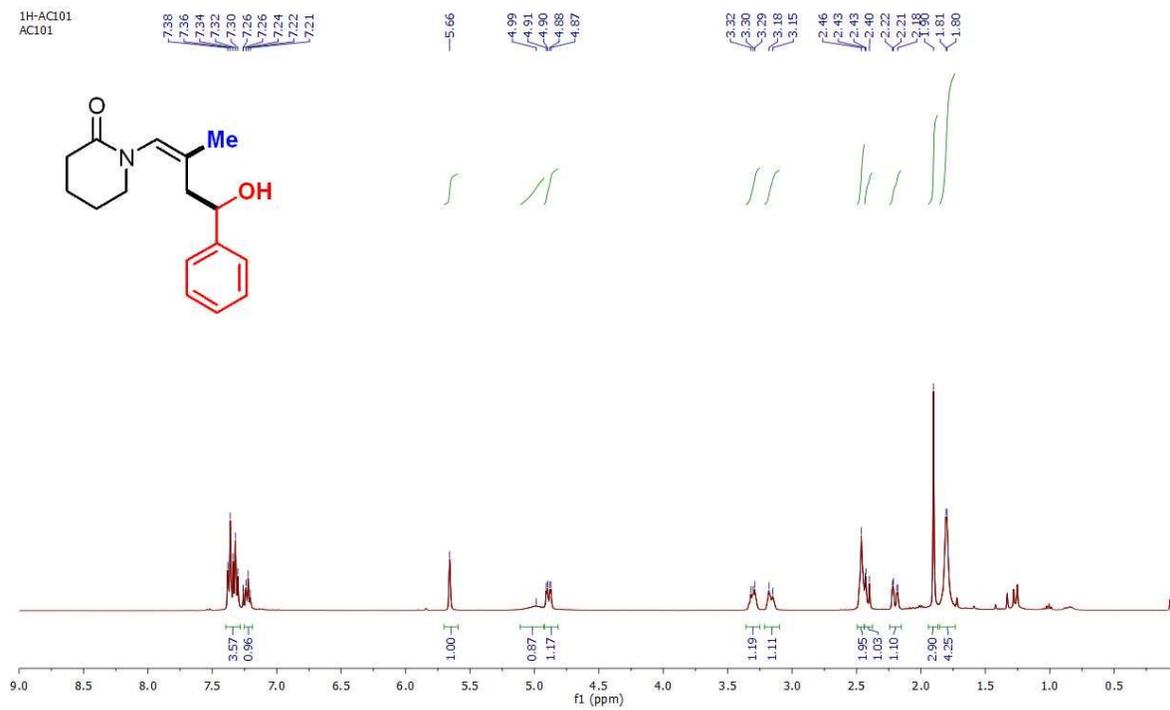


Decarboxylation/cyclization: synthesis of **8**.

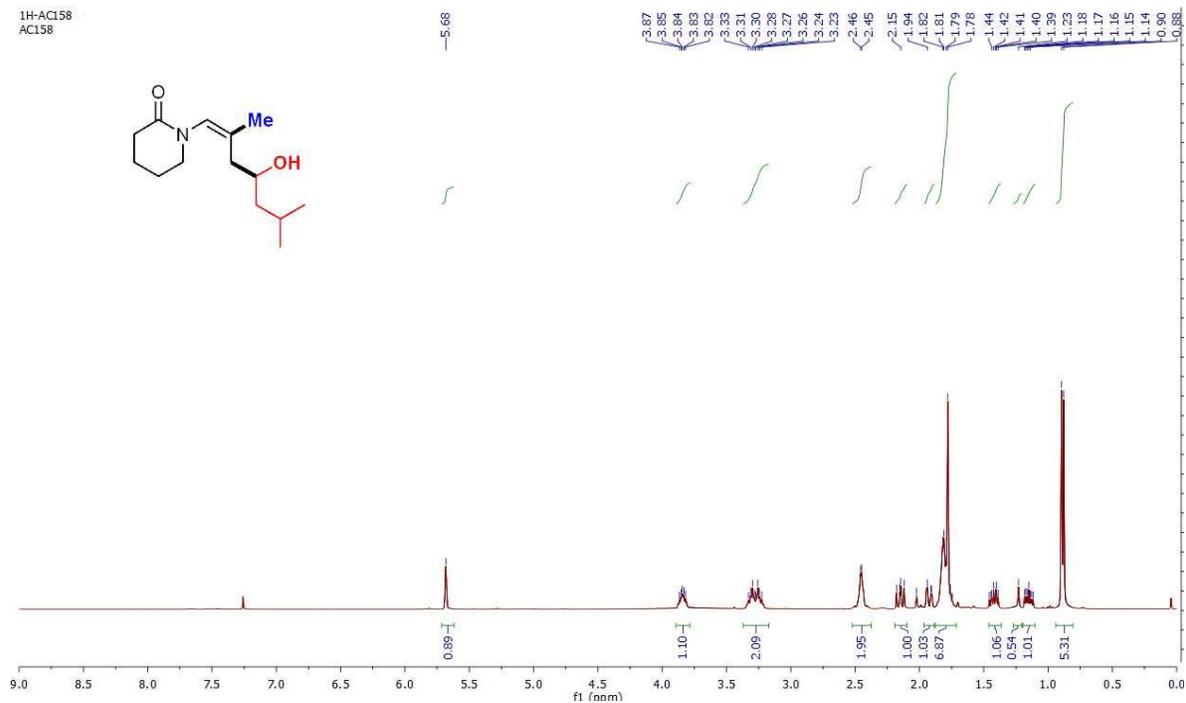
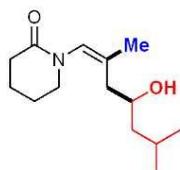
To a mixture of DCM and TFA (3 ml, 2:1) in flask was add **7t** (55 mg). The mixture was stirred at room temperature for 4 hrs. TLC showed the reaction completed. Then 20 ml saturated aqueous NaHCO₃ was added into the flask. The mixture was extracted with DCM (3x 5 ml), the organic phase washed with brine and dried over NaSO₄. Then organic phase was concentrated under vacuum. The residue was purified with silica gel chromatography to give product as colorless gel.



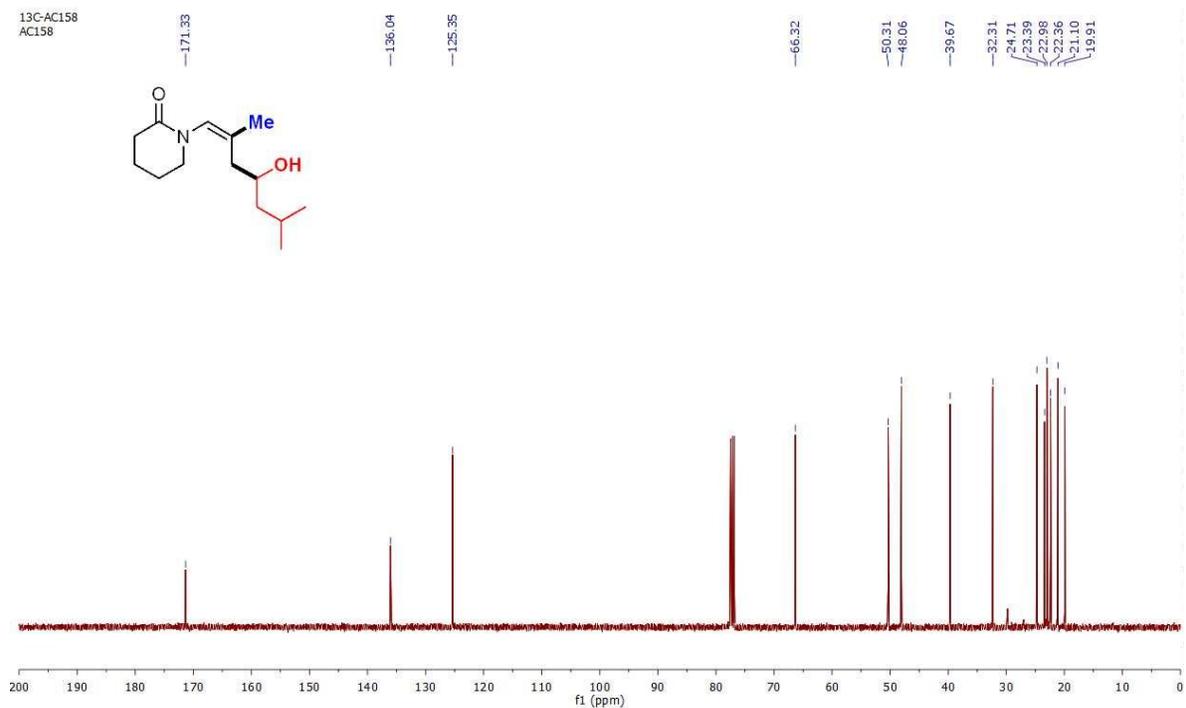
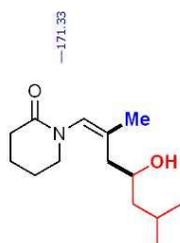
NMR spectra



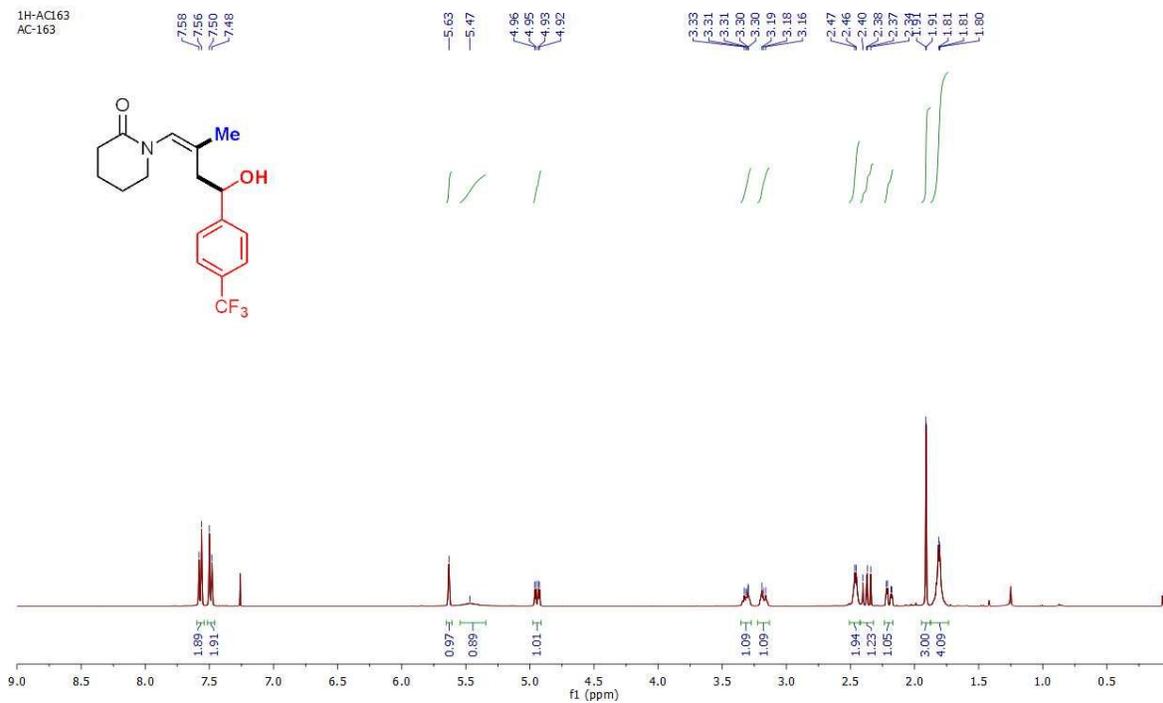
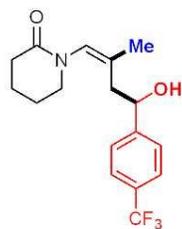
1H-AC158
AC158



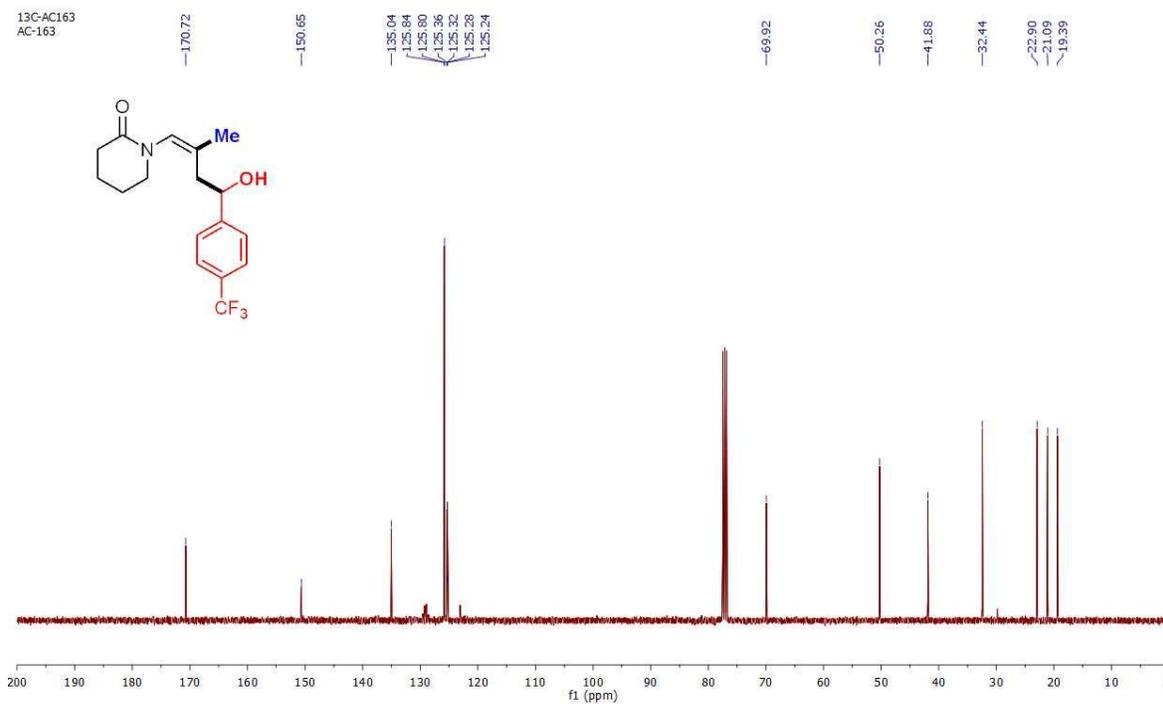
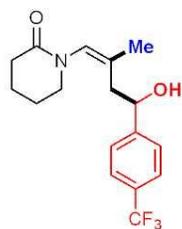
13C-AC158
AC158



1H-AC163
AC-163



13C-AC163
AC-163



1H-LY-benzoyl+me
YL-BENZOYL+ME

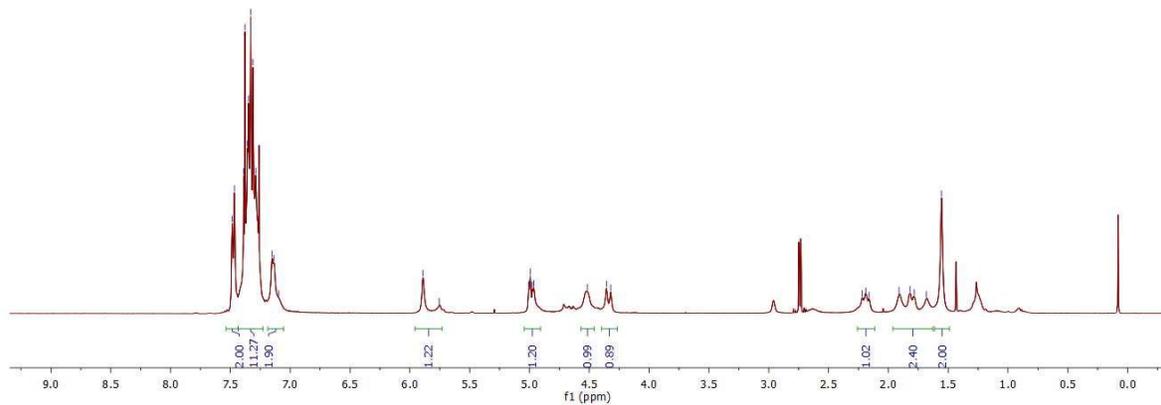
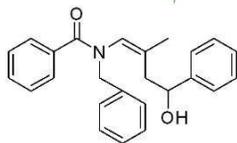
7.48
7.47
7.39
7.38
7.36
7.35
7.33
7.31
7.29
7.15
7.14
7.10

5.89
5.75

4.01
3.99
3.88
3.96

4.52
4.36
4.32

2.22
2.19
2.16
1.81
1.78
1.68
1.56



13C-AC186
AC186

170.64
144.23
141.29
137.31
136.35
134.48
132.27
132.17
130.05
129.02
128.88
128.74
128.62
128.39
127.77
125.70
125.67
117.37

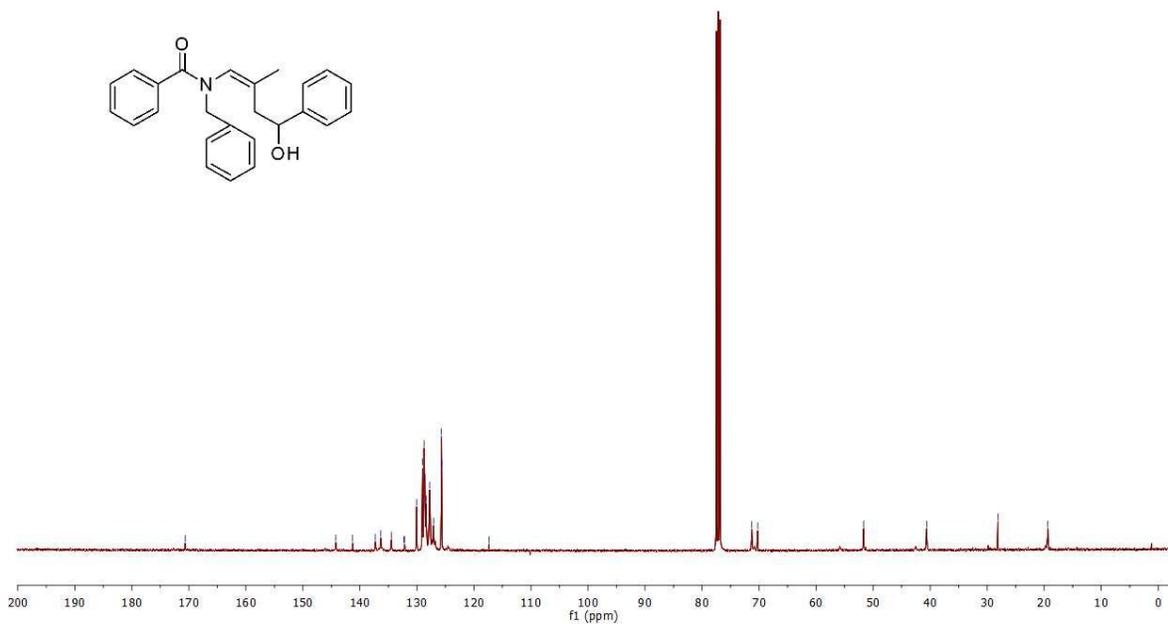
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70.23

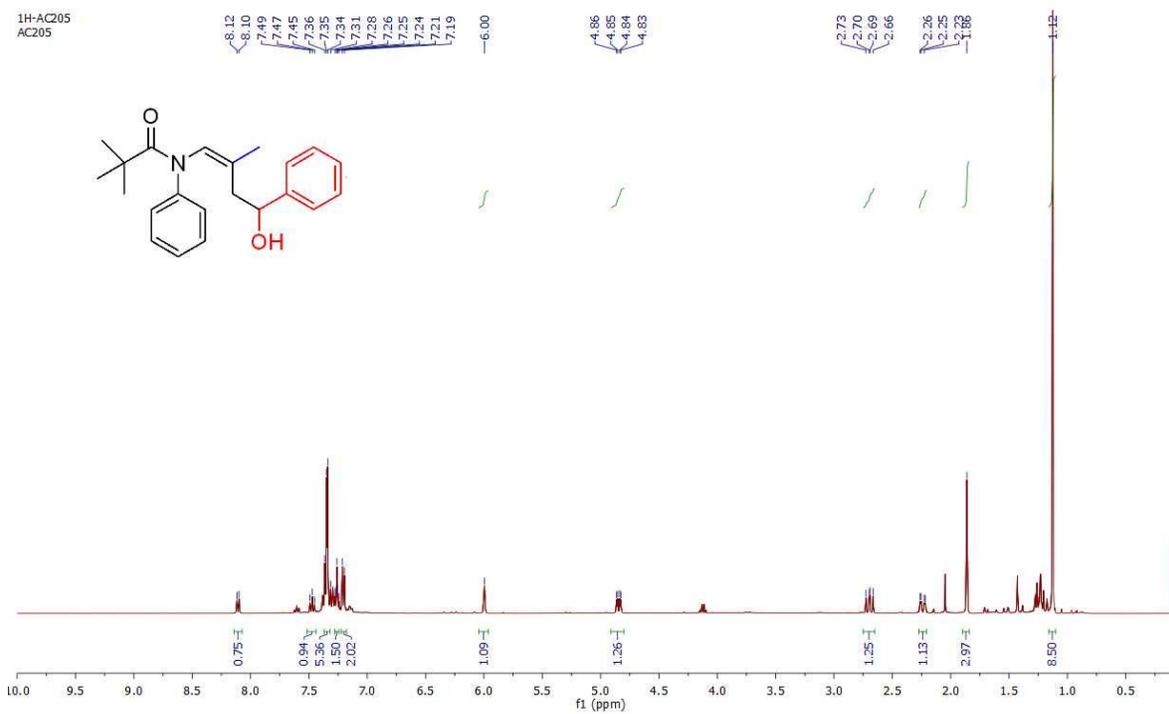
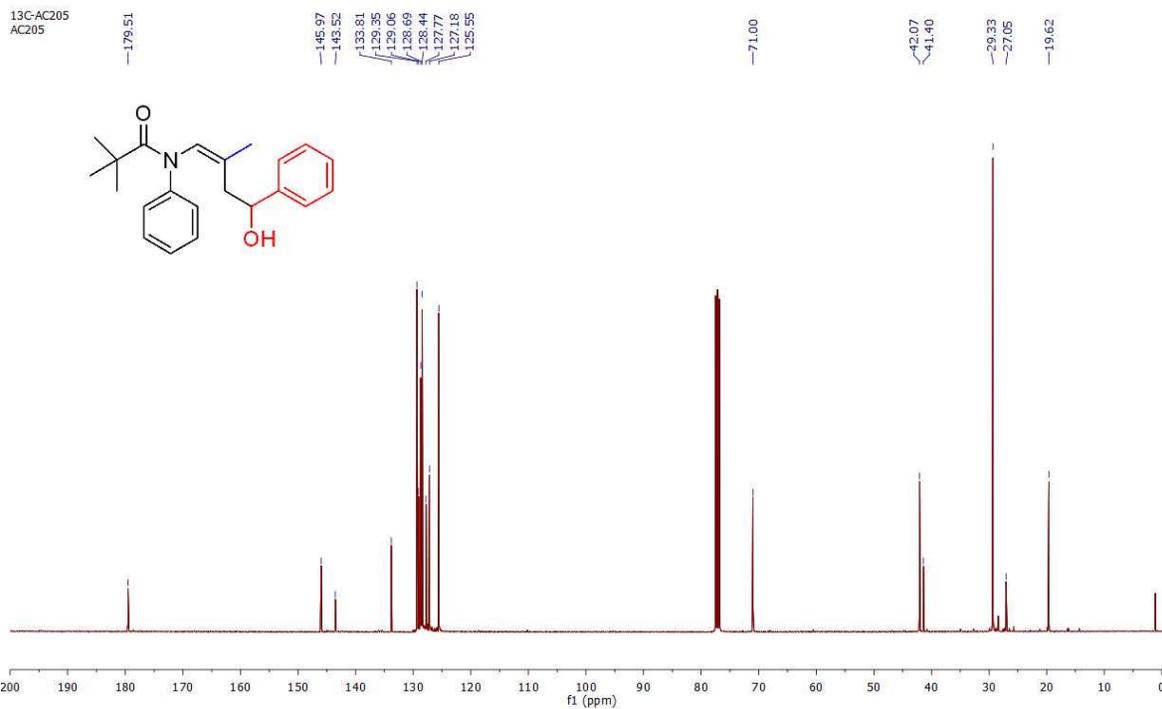
51.67

40.62

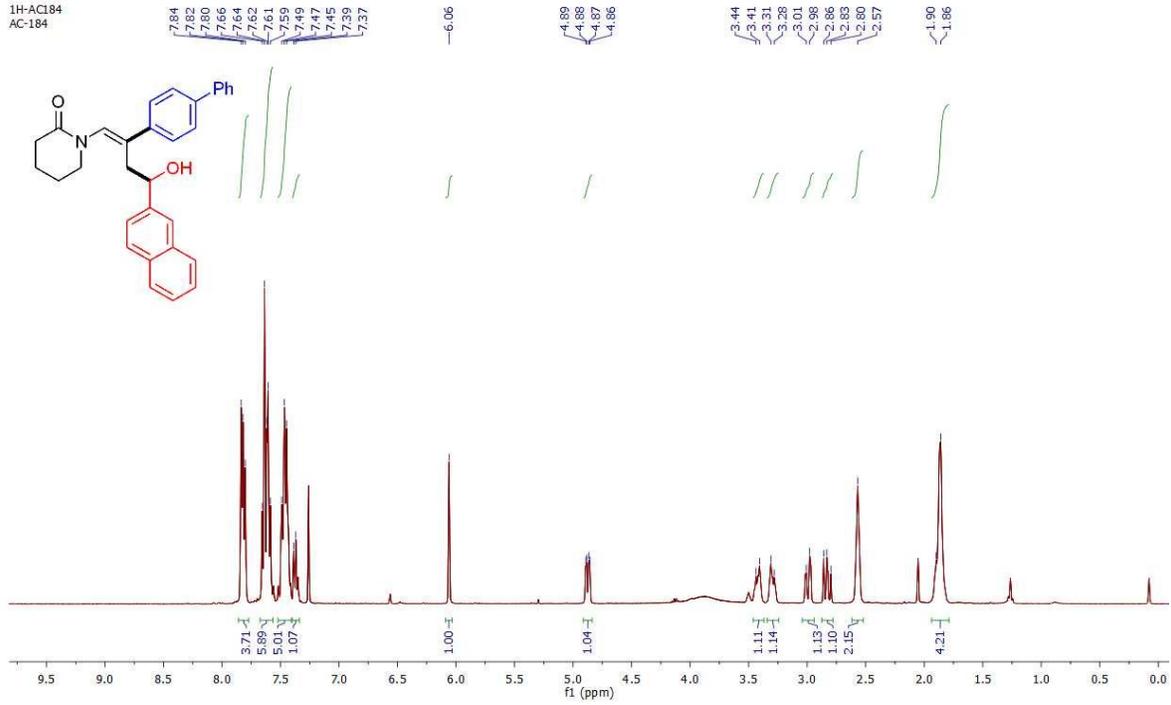
28.11

19.36

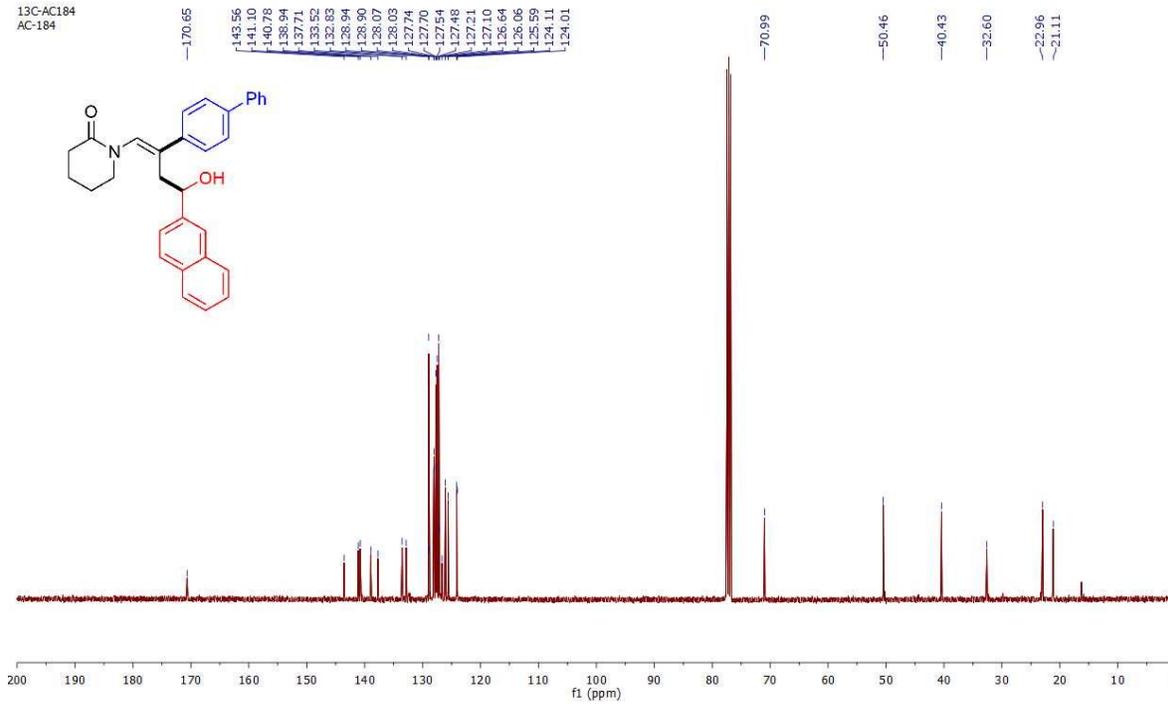


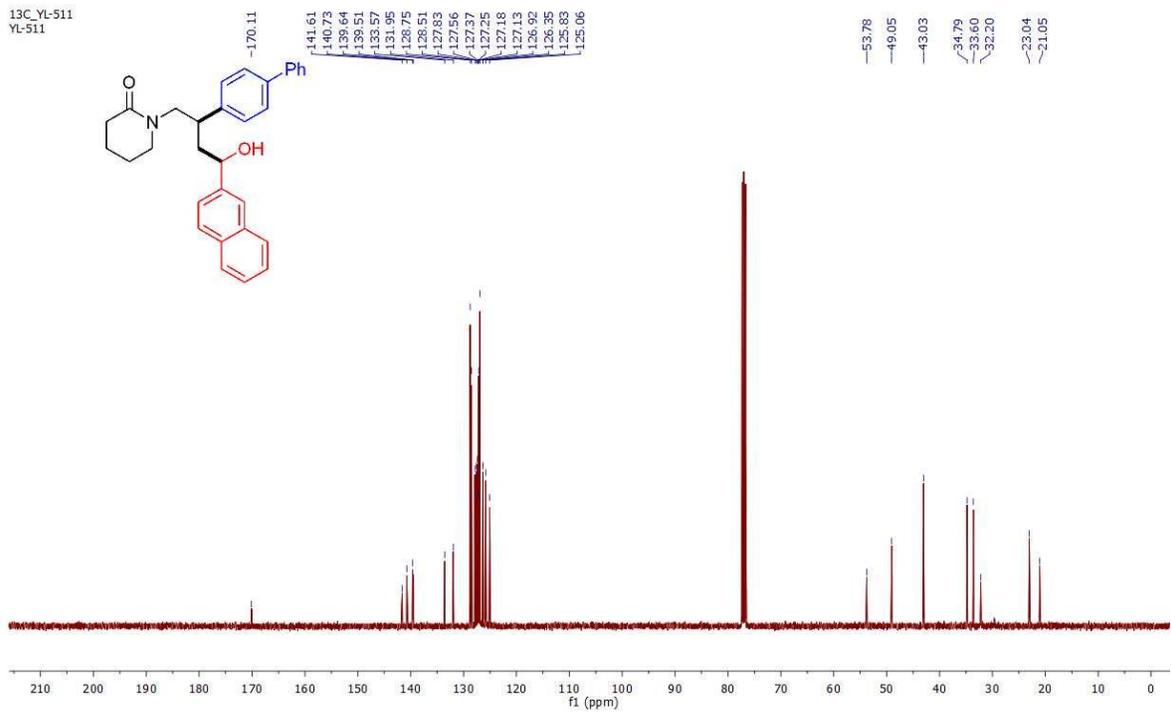
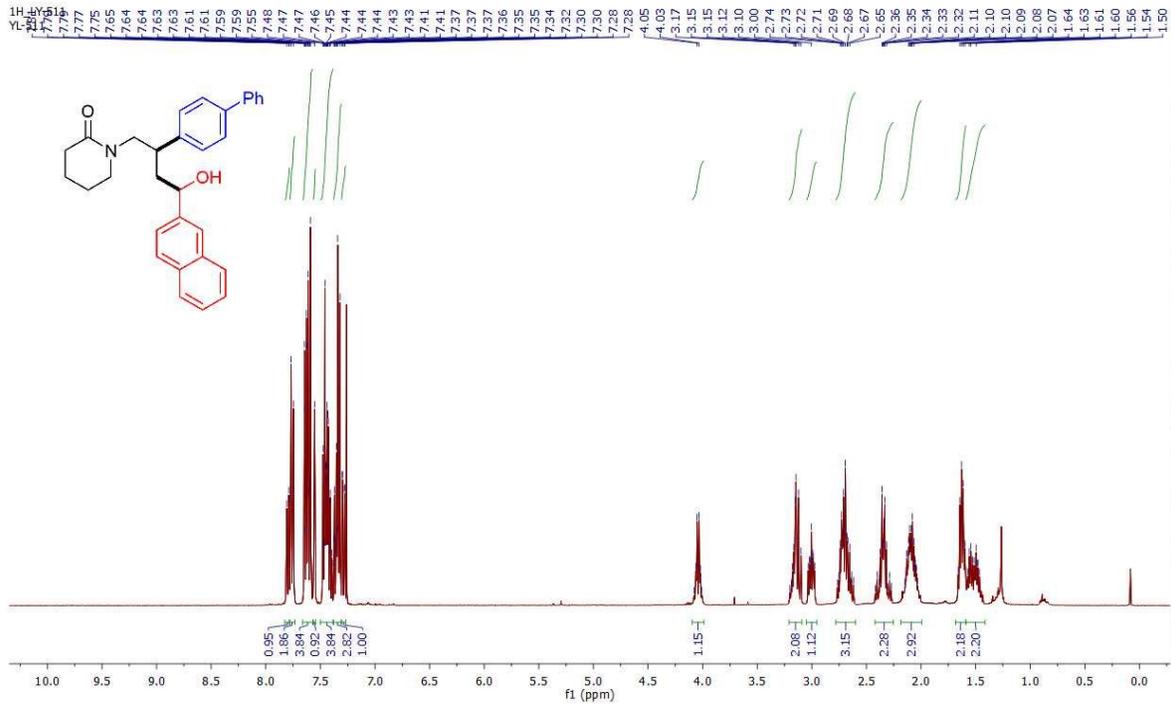


1H-AC184
AC-184

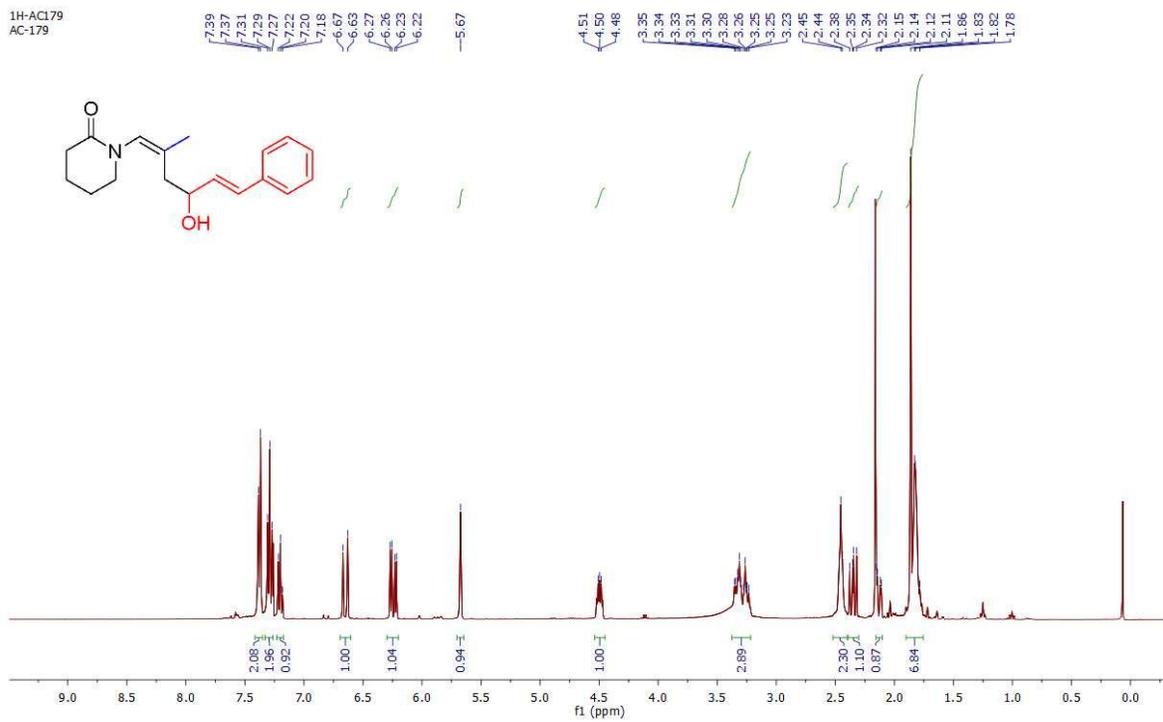


13C-AC184
AC-184

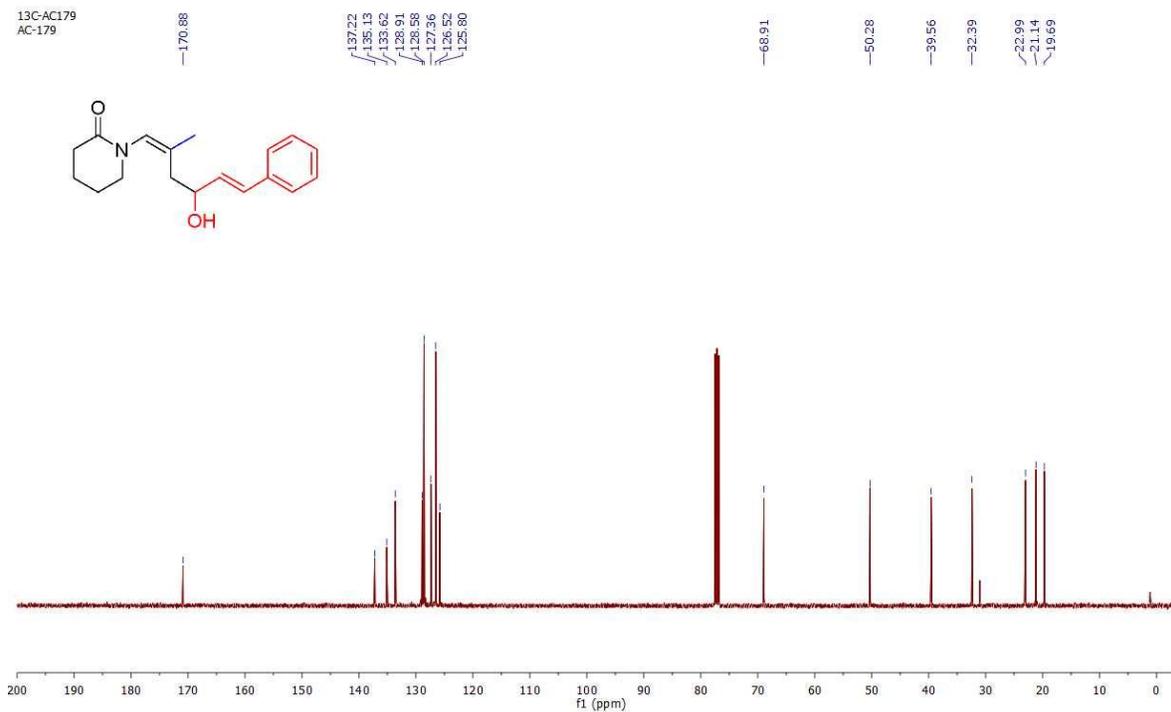


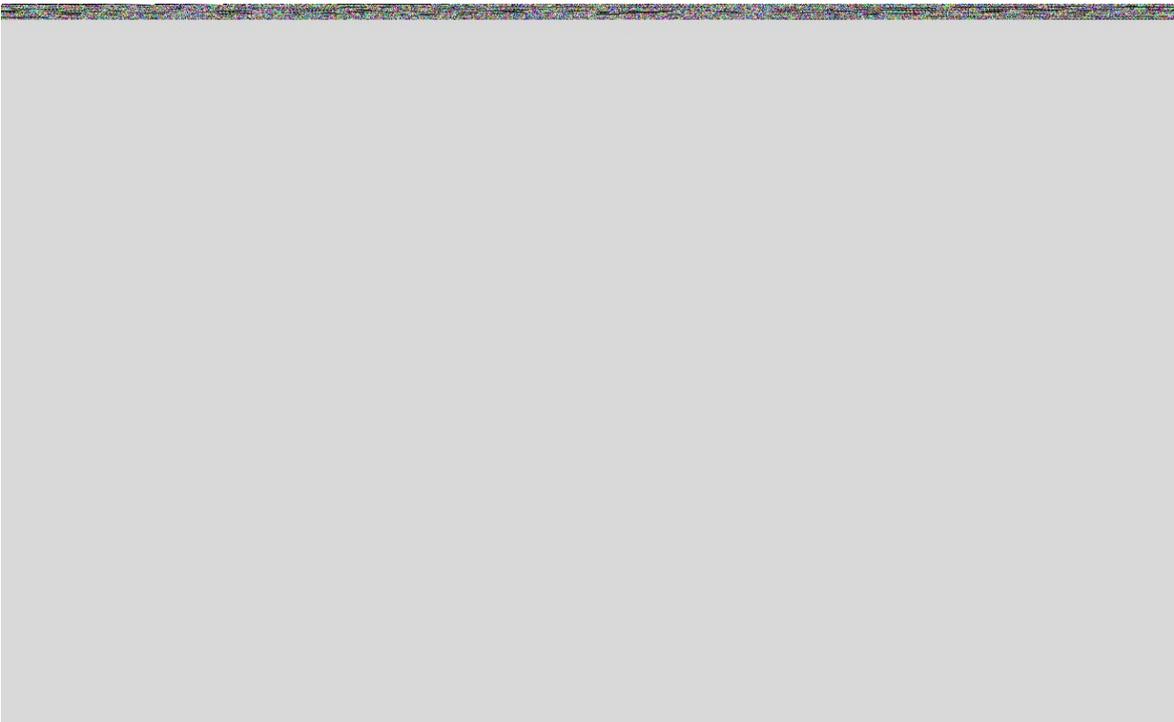
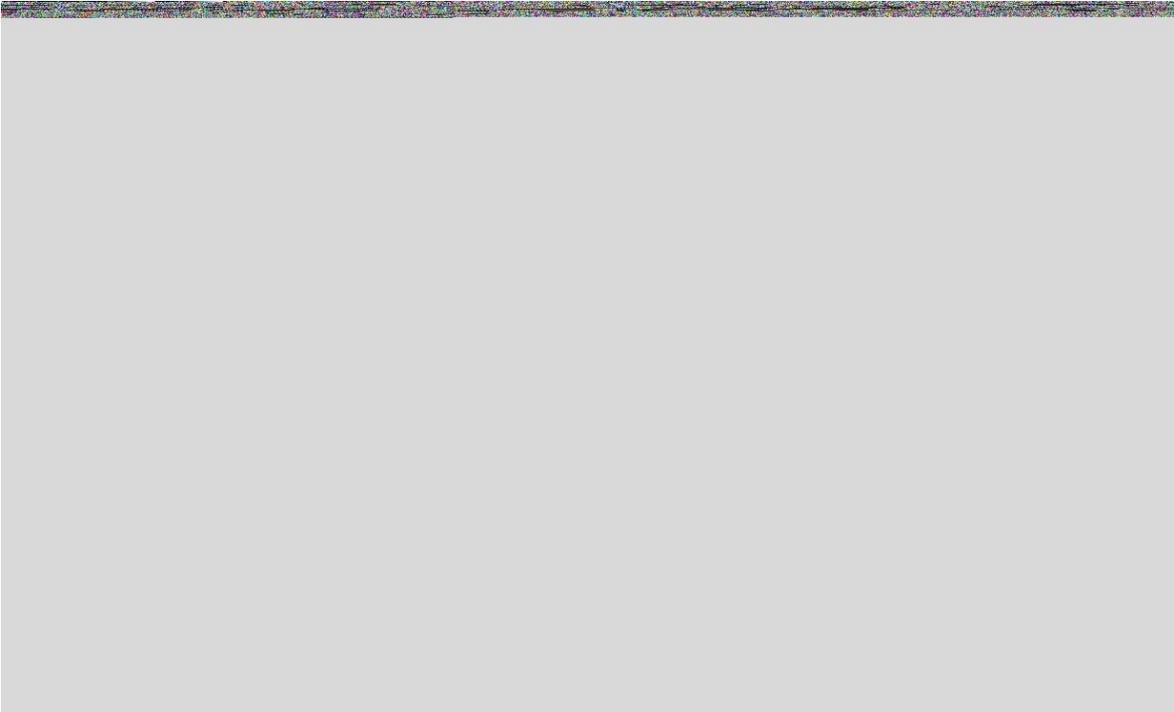


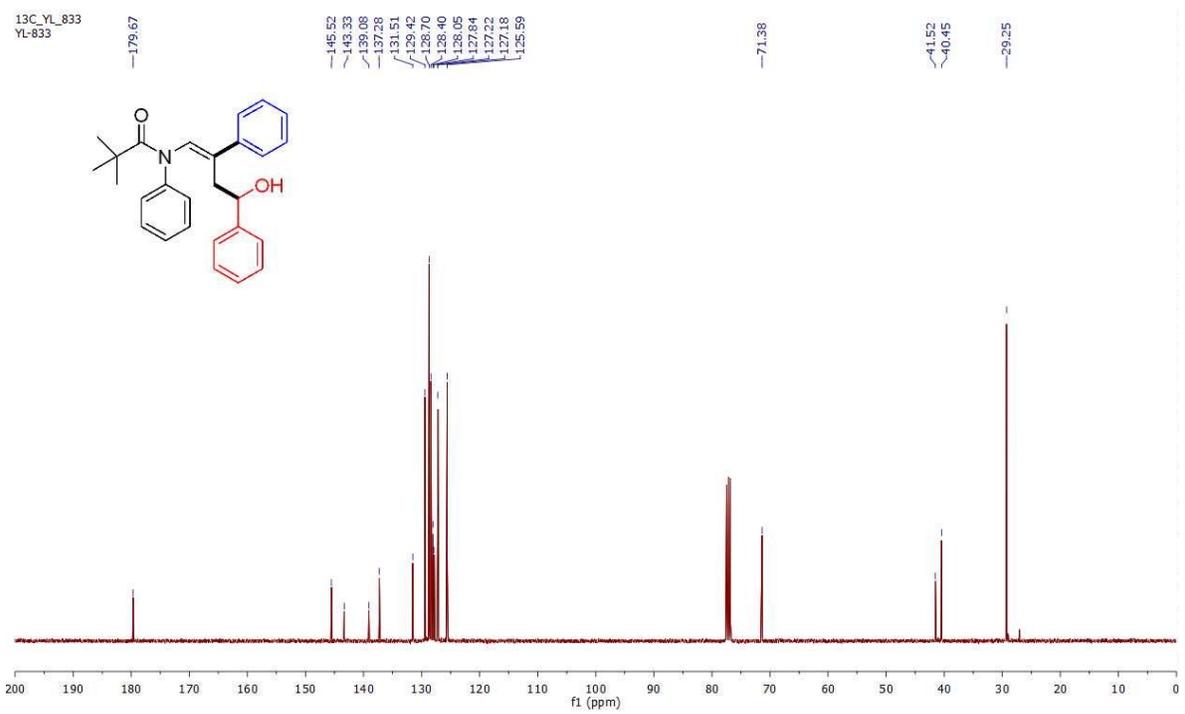
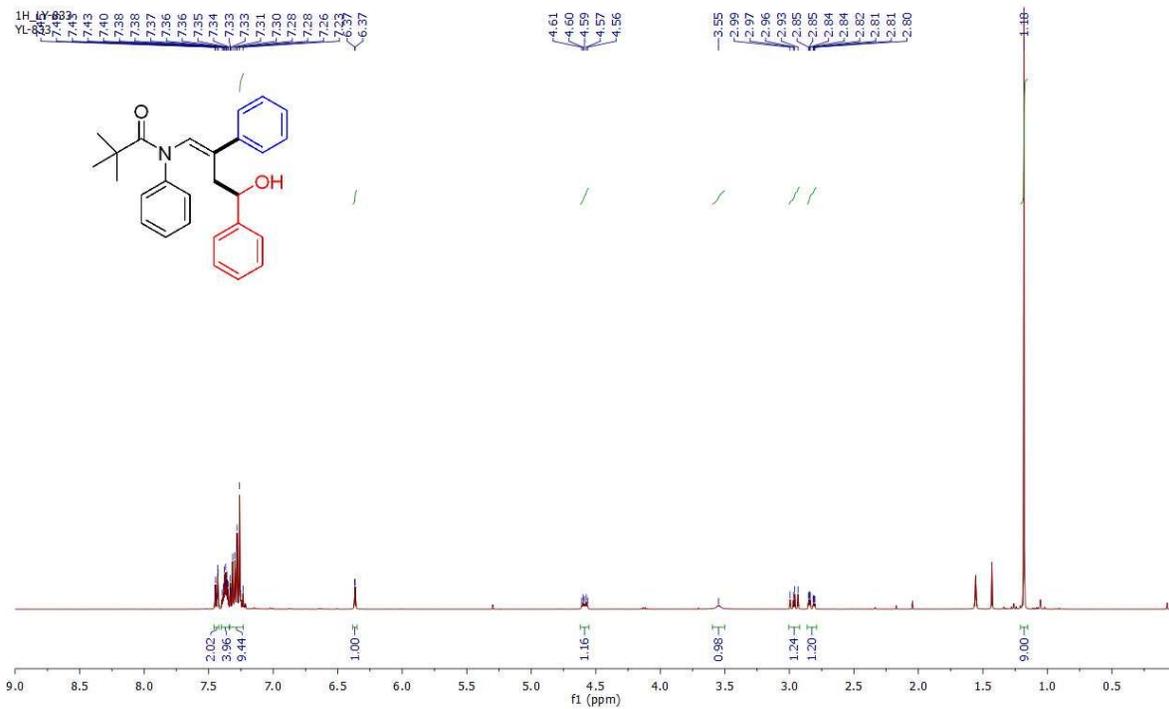
1H-AC179
AC-179

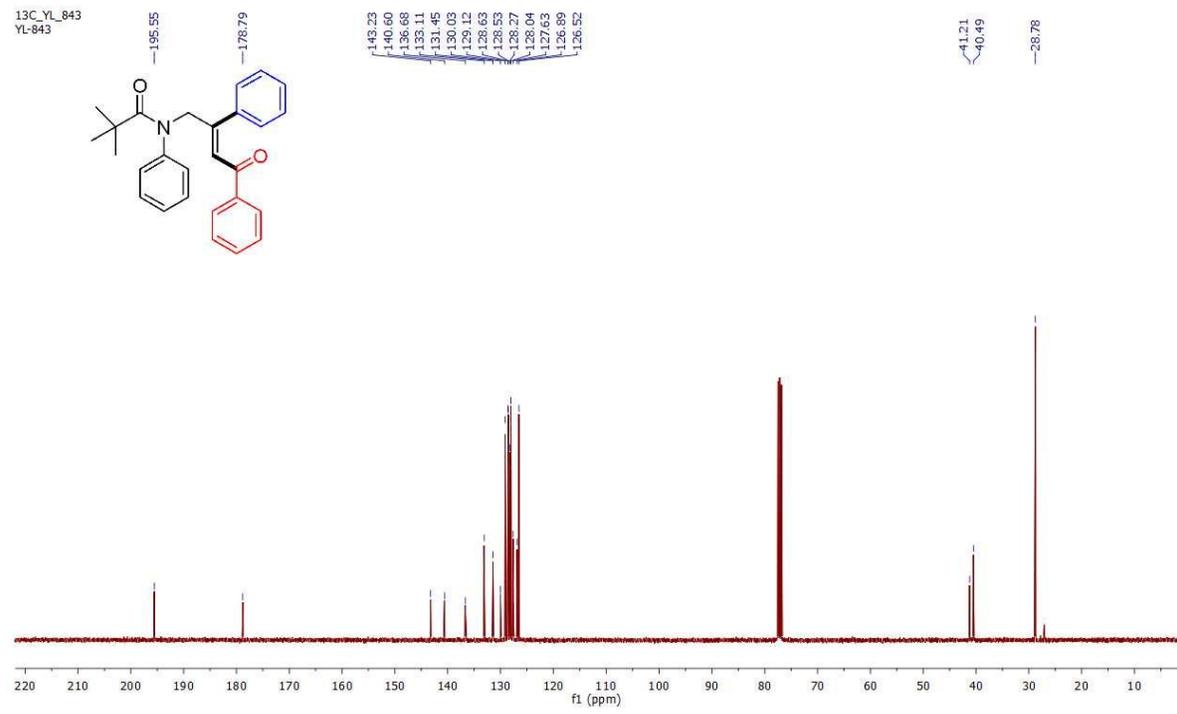
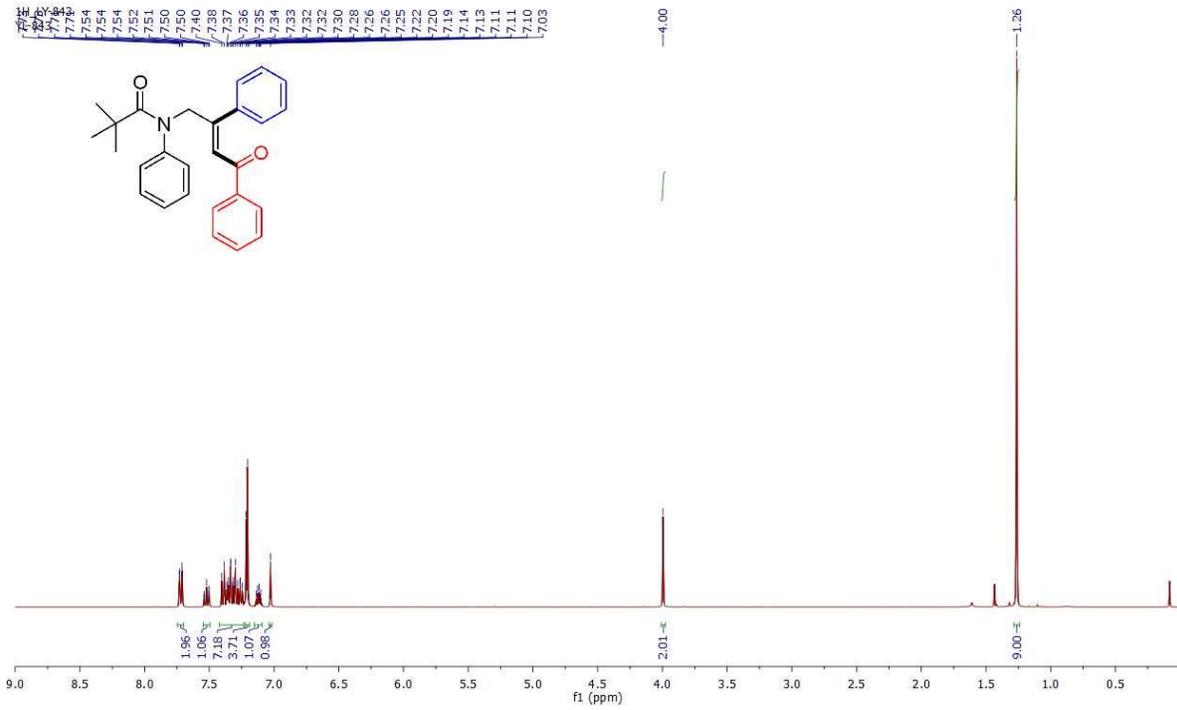


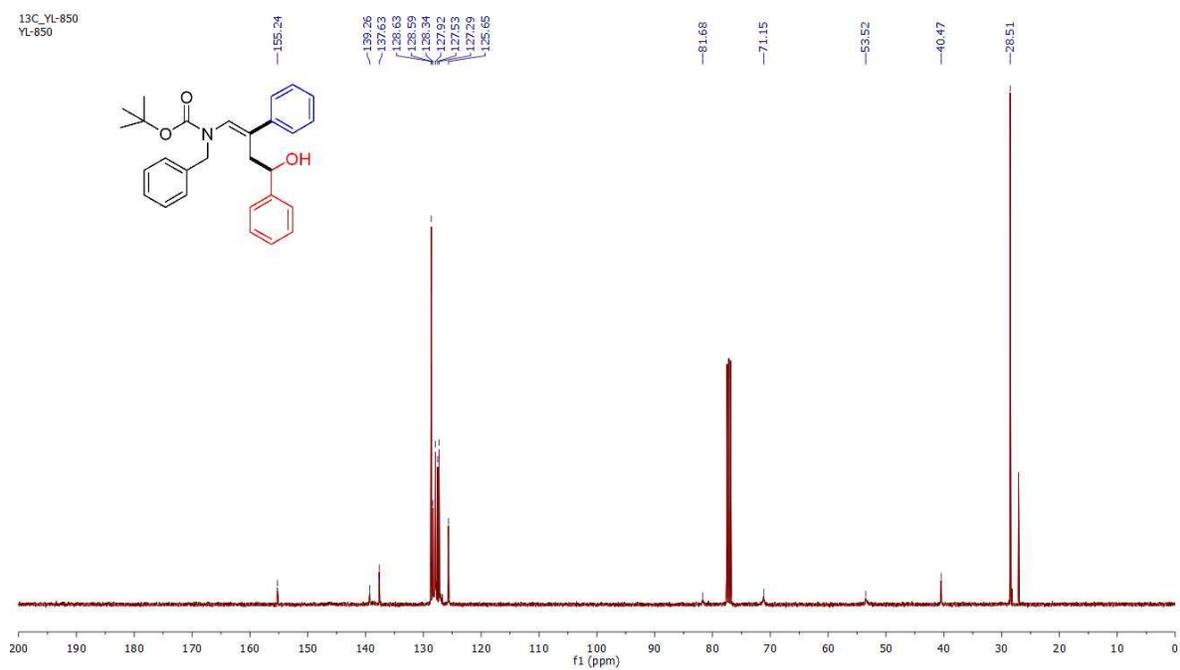
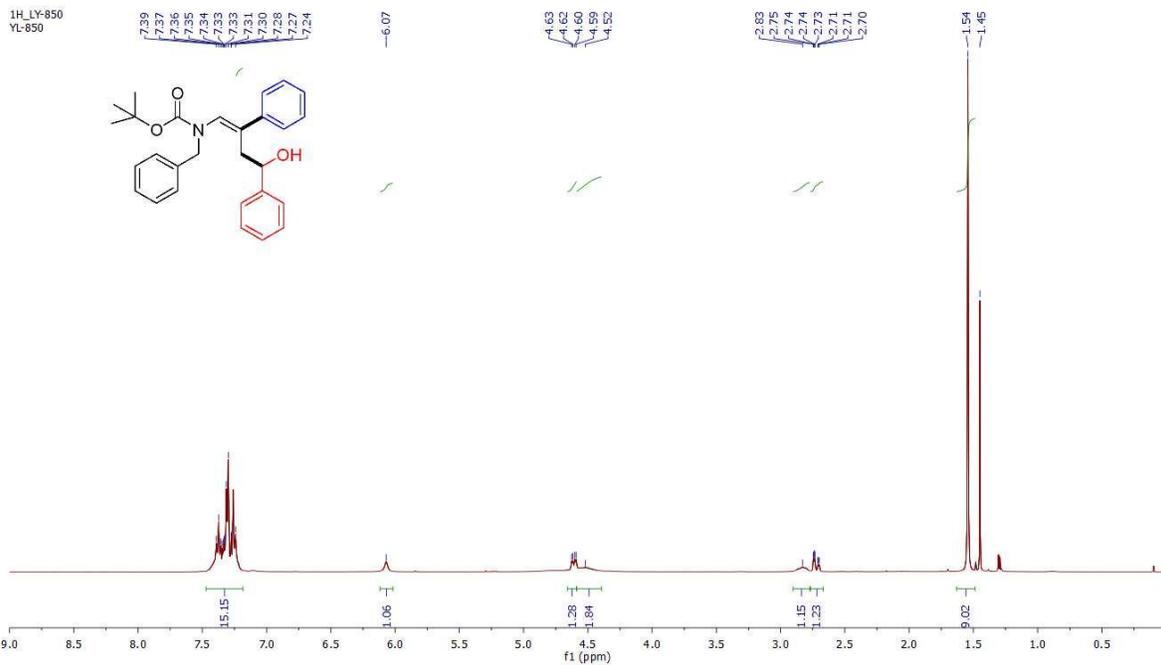
13C-AC179
AC-179



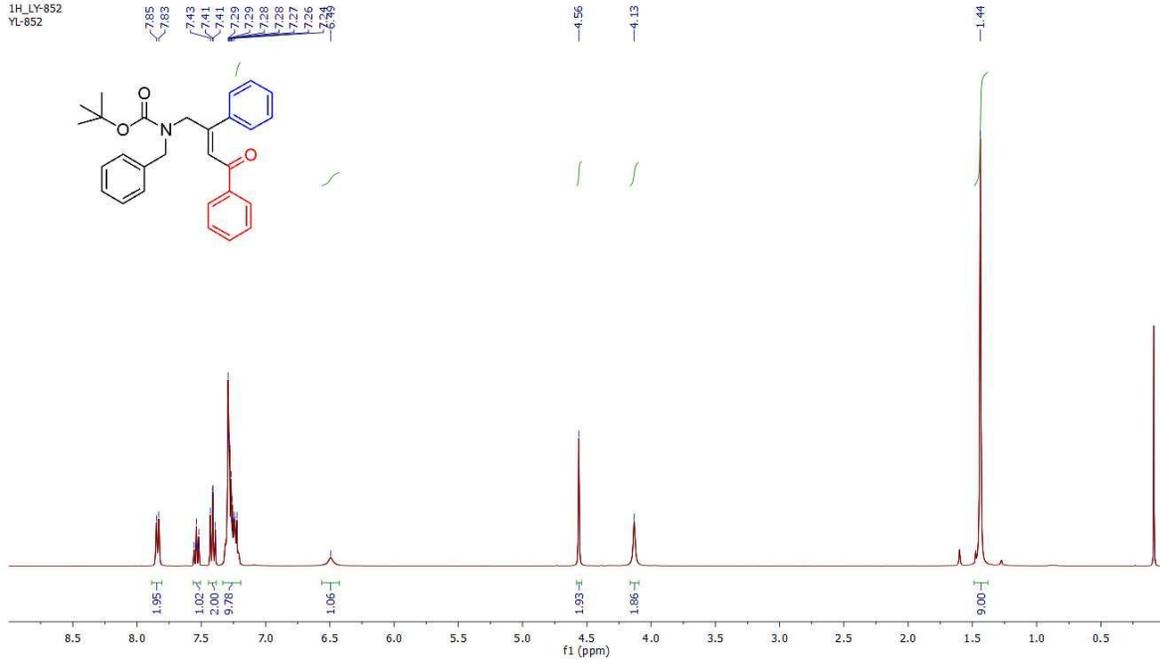




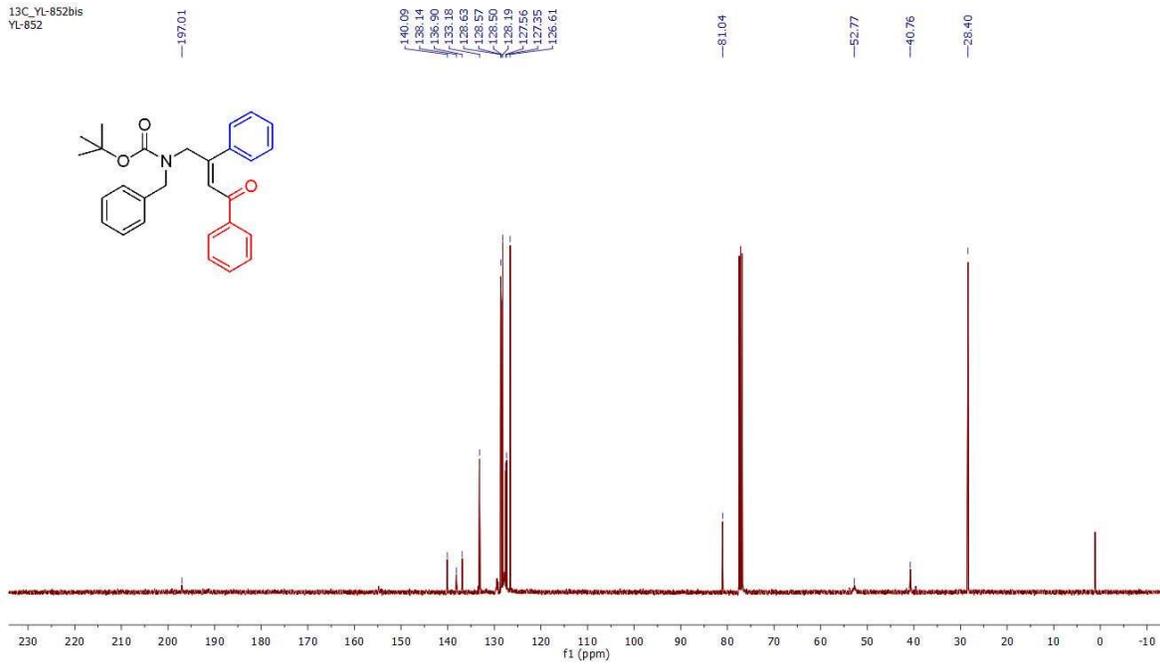


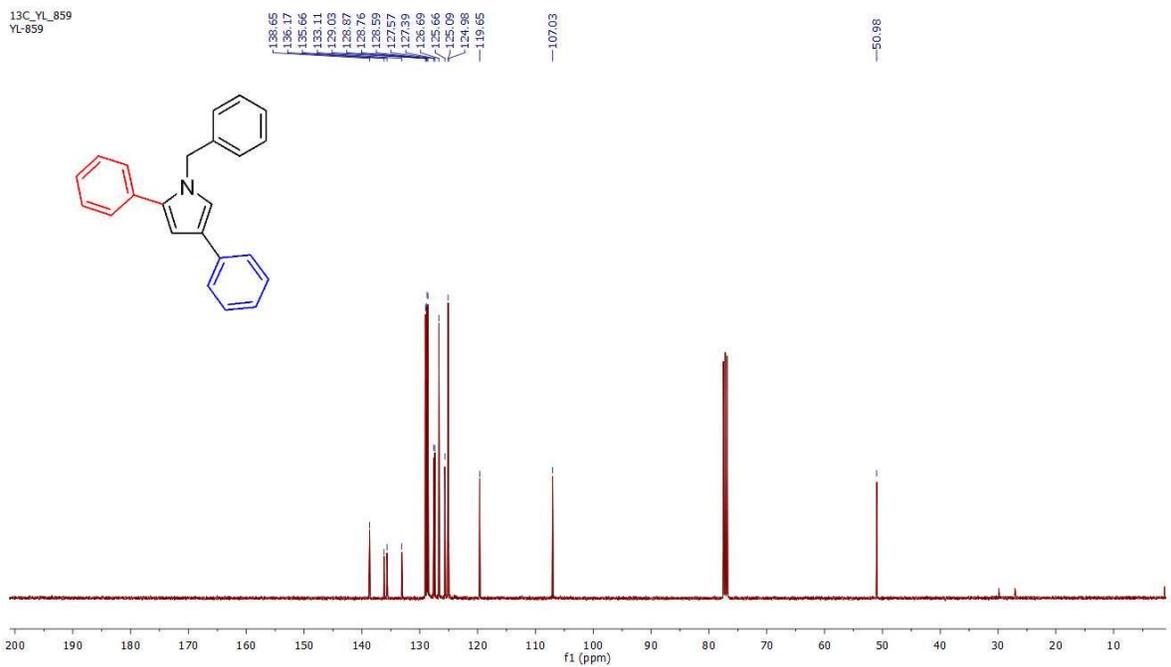
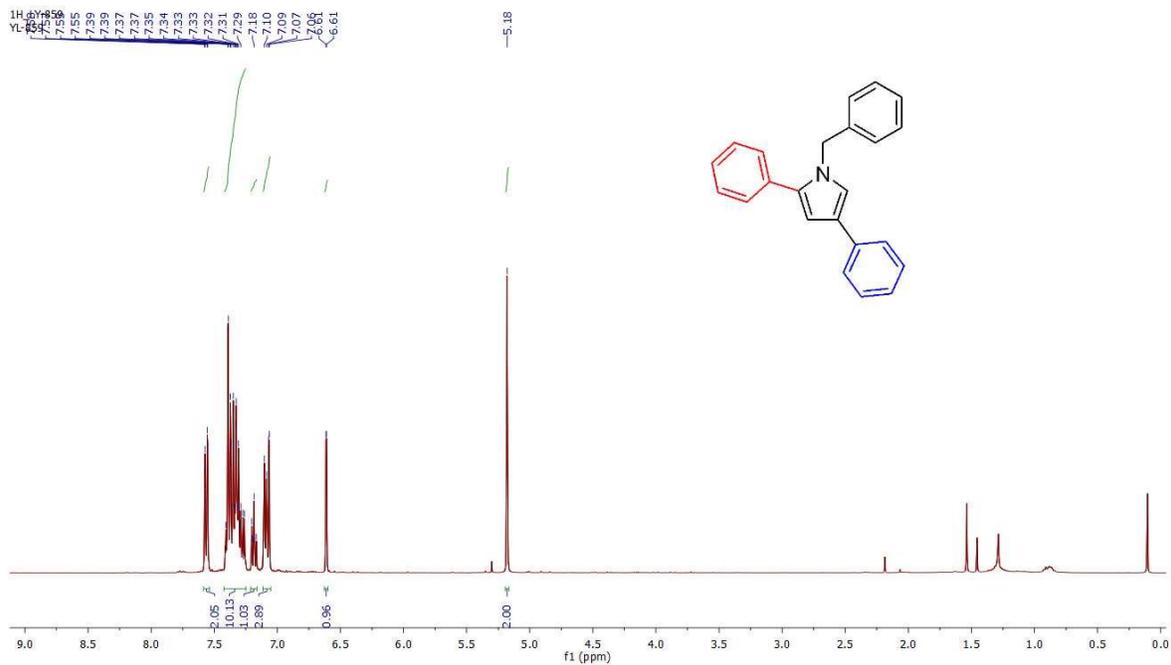


1H_LY-852
YL-852



13C_LY-852bis
YL-852





X-ray data

Table S1. Crystal data and structure refinement for the complex [NiCl{(5,5')-Me₂-bpy}(H₂O)₃]Cl·4H₂O and 1-(2-([1,1'-biphenyl]-4-yl)-4-(naphthalen-2-yl)butyl)piperidyn-2-one.

Compound	[NiCl{(5, 5')-Me ₂ -bpy}(H ₂ O) ₃]Cl·4H ₂ O	1-(2-([1,1'-biphenyl]-4-yl)-4-(naphthalen-2-yl)butyl)piperidyn-2-one
Formula	C ₁₂ H ₂₆ Cl ₂ N ₂ NiO ₇	C ₃₁ H ₃₁ NO
Fw	439.96	433.57
T, K	296	296
λ, Å	0.71073	0.71073
Crystal symmetry	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	6.9966(10)	18.713(7)
<i>b</i> , Å	12.0579(17)	5.871(2)
<i>c</i> , Å	12.9998(18)	22.603(8)
α	63.724(3)	90
β	88.610(3)	105.503(7)
γ	86.344(3)	90
Cell volume, Å ³	981.4(2)	2393.1(15)
<i>Z</i>	2	4
D _c , Mg m ⁻³	1.489	1.203
μ(Mo-Kα), mm ⁻¹	1.293	0.072
F(000)	460	928
Crystal size/ mm	0.20 x 0.10 x 0.05	0.30 x 0.15 x 0.07
θ limits, °	1.747 to 31.971	1.870 to 24.632
Reflections collected	18734	20879
Unique obs. Reflections	6699 [R _{int} = 0.0559]	3998 [R _{int} = 0.1148]
Goodness-of-fit-on F ²	1.029	1.030
R ₁ (F) ^a , wR ₂ (F ²) [I > 2σ(I)]	0.0594, 0.1625	0.0866, 0.2020
Largest diff. peak and hole, e.	1.554 and -1.185	0.215 and -0.182

- a) $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$, b) $wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}}{[\sigma^2(F_o^2) + (aP)^2 + bP]}$ where $P = (F_o^2 + F_c^2)/3$.

Table S2. Hydrogen bonds for [NiCl{(5,5')-Me₂-bpy}(H₂O)₃]Cl·4H₂O [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(1)-H(1)...O(1)	0.93	2.59	3.130(3)	117.2
C(4)-H(4)...Cl(1)#1	0.93	2.89	3.776(3)	159.8
O(3)-H(3W)...Cl(2)	0.866(18)	2.32(2)	3.181(2)	172(4)
O(3)-H(33W)...Cl(1)#2	0.868(19)	2.332(19)	3.195(2)	173(4)
O(1)-H(1W)...O(4W)	0.849(19)	1.99(3)	2.776(3)	153(4)
O(2)-H(22W)...O(3W)#3	0.874(19)	1.97(2)	2.805(4)	159(4)
O(5W)-H(5W)...O(6W)	0.860(19)	2.03(2)	2.841(4)	157(4)
O(5W)-H(55W)...Cl(1)	0.882(19)	2.34(2)	3.175(3)	157(4)
O(2)-H(2W)...O(3W)	0.872(19)	1.93(2)	2.752(4)	157(4)
O(1)-H(11W)...O(6W)#4	0.85(4)	1.93(4)	2.779(3)	178(4)
O(4W)-H(4W)...Cl(1)#4	0.89(5)	2.35(5)	2.35(5)	166(4)
O(4W)-H(44W)...O(5W)	0.68(4)	2.09(5)	2.764(4)	169(5)
O(3W)-H(31W)...Cl(2)#5	0.906(19)	2.24(2)	3.088(4)	155(4)
O(6W)-H(61W)...O(4W)#5	0.73(4)	2.08(5)	2.796(4)	166(5)
O(6W)-H(62W)...Cl(2)#6	0.87(5)	2.34(5)	3.197(3)	168(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+2 #2 x+1,y,z #3 -x+1,-y+2,-z+1

#4 -x+1,-y+1,-z+1 #5 x-1,y,z #6 x-1,y-1,z

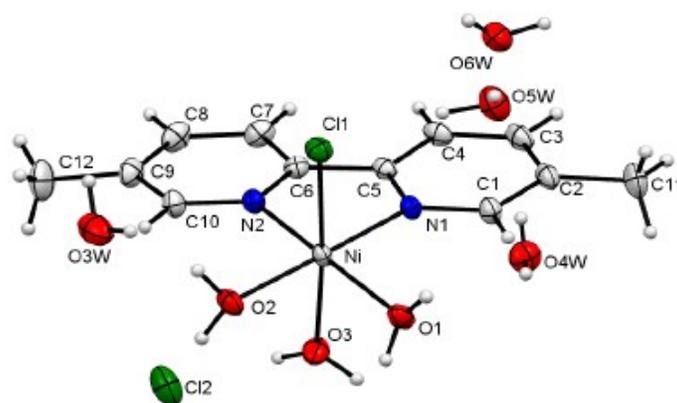


Figure S1. ORTEP drawing of $[\text{NiCl}\{(5,5')\text{-Me}_2\text{-bpy}\}(\text{H}_2\text{O})_3]\text{Cl}\cdot 4\text{H}_2\text{O}$ showing the four crystallization water molecules. Thermal ellipsoids are drawn at 30% probability level.

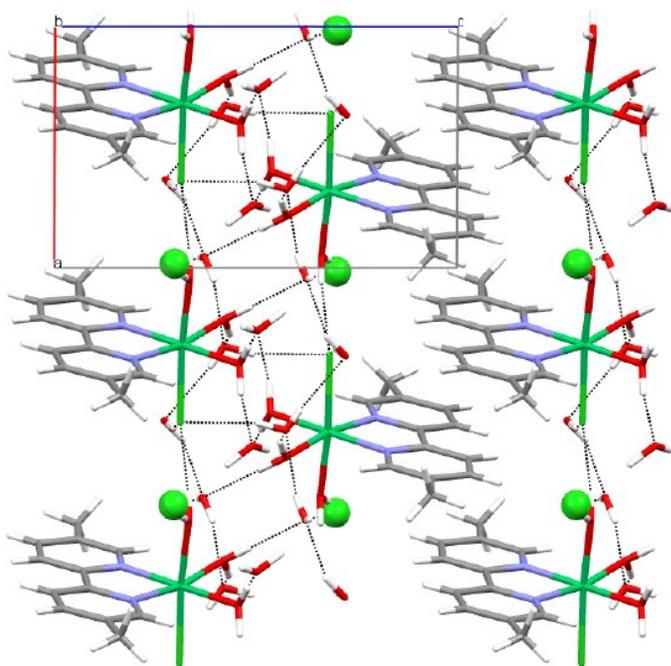


Figure S2. Crystal packing of $[\text{NiCl}\{(5,5')\text{-Me}_2\text{-bpy}\}(\text{H}_2\text{O})_3]\text{Cl}\cdot 4\text{H}_2\text{O}$ showing the H bonding network. View down the a axis.

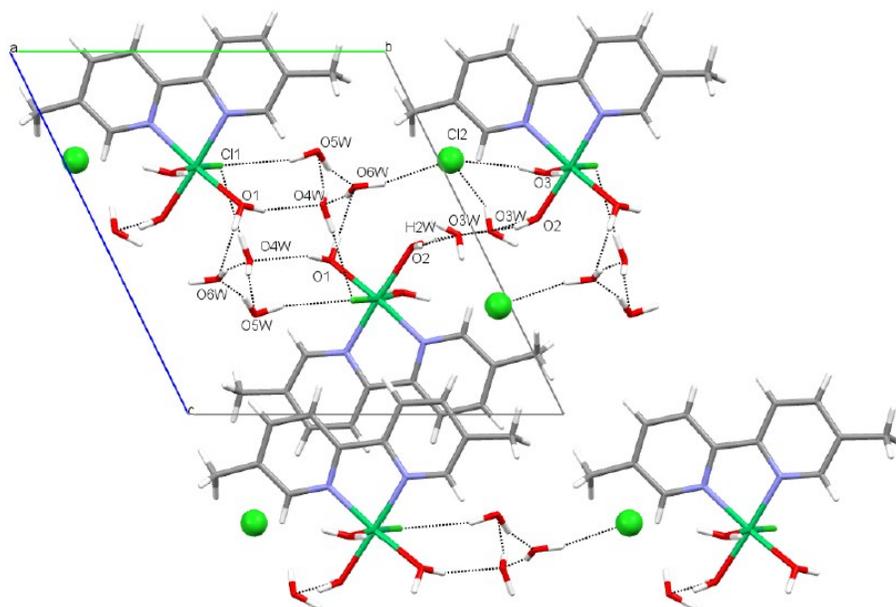


Figure S3. Crystal packing of [NiCl{(5,5')-Me₂-bpy}(H₂O)₃]Cl·4H₂O showing the H bonding network. View down the *b* axis.

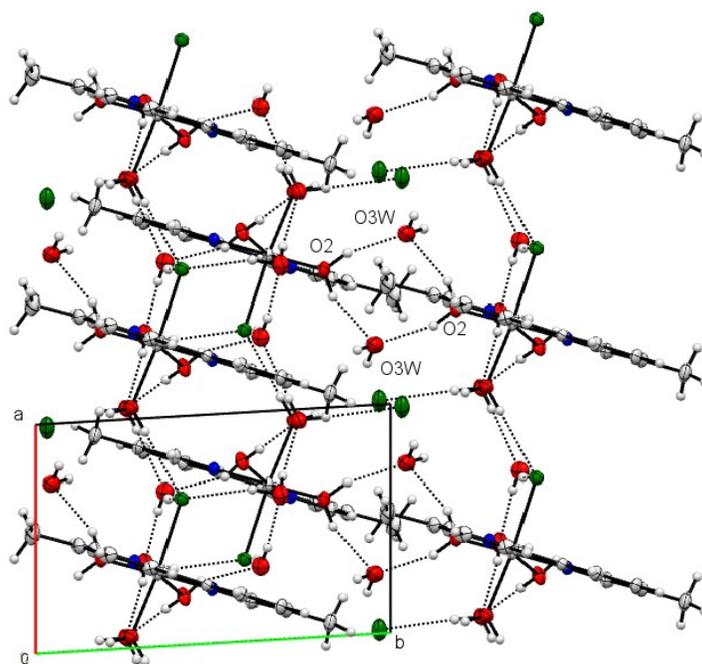


Figure S4. Crystal packing of [NiCl{(5,5')-Me₂-bpy}(H₂O)₃]Cl·4H₂O showing the H bonding network. View down the *c* axis.

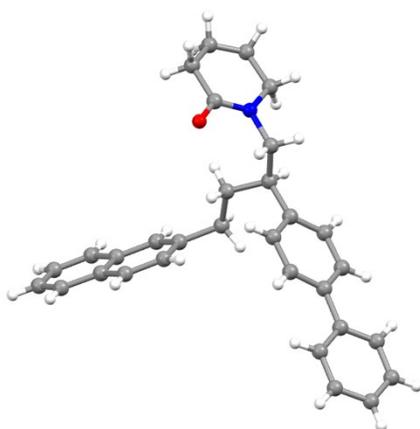


Figure S5. Molecular structure of 1-(2-([1,1'-biphenyl]-4-yl)-4-(naphthalen-2-yl)butyl)piperidin-2-one.