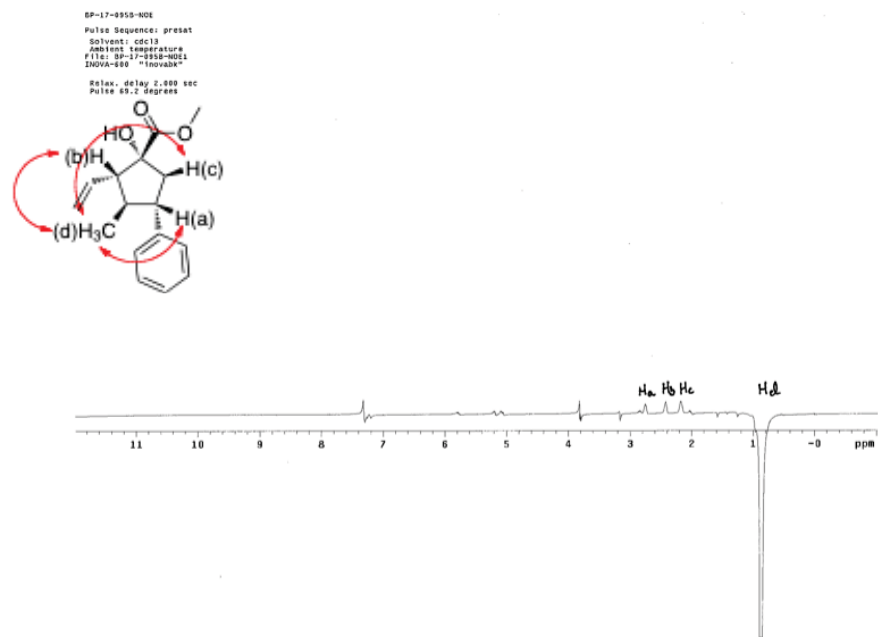
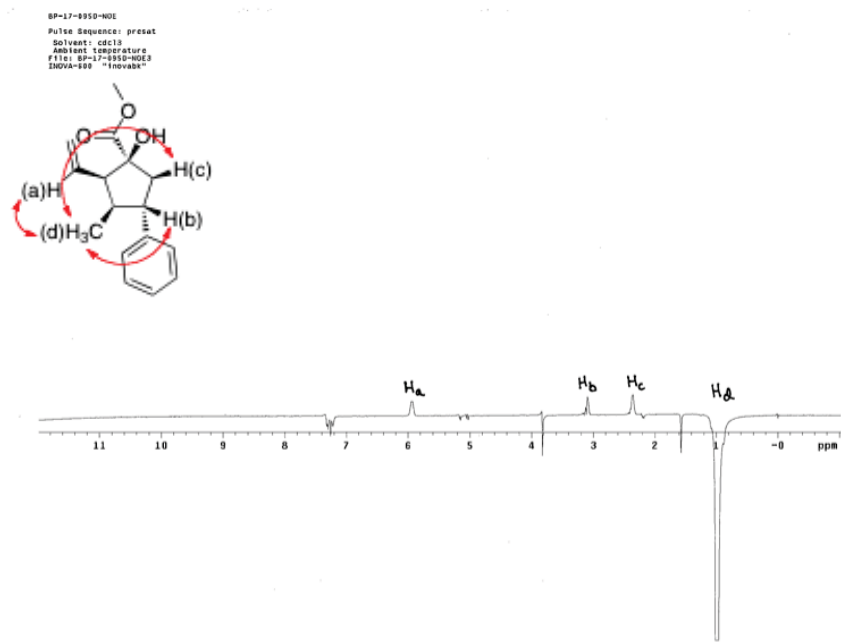


Supplementary Information

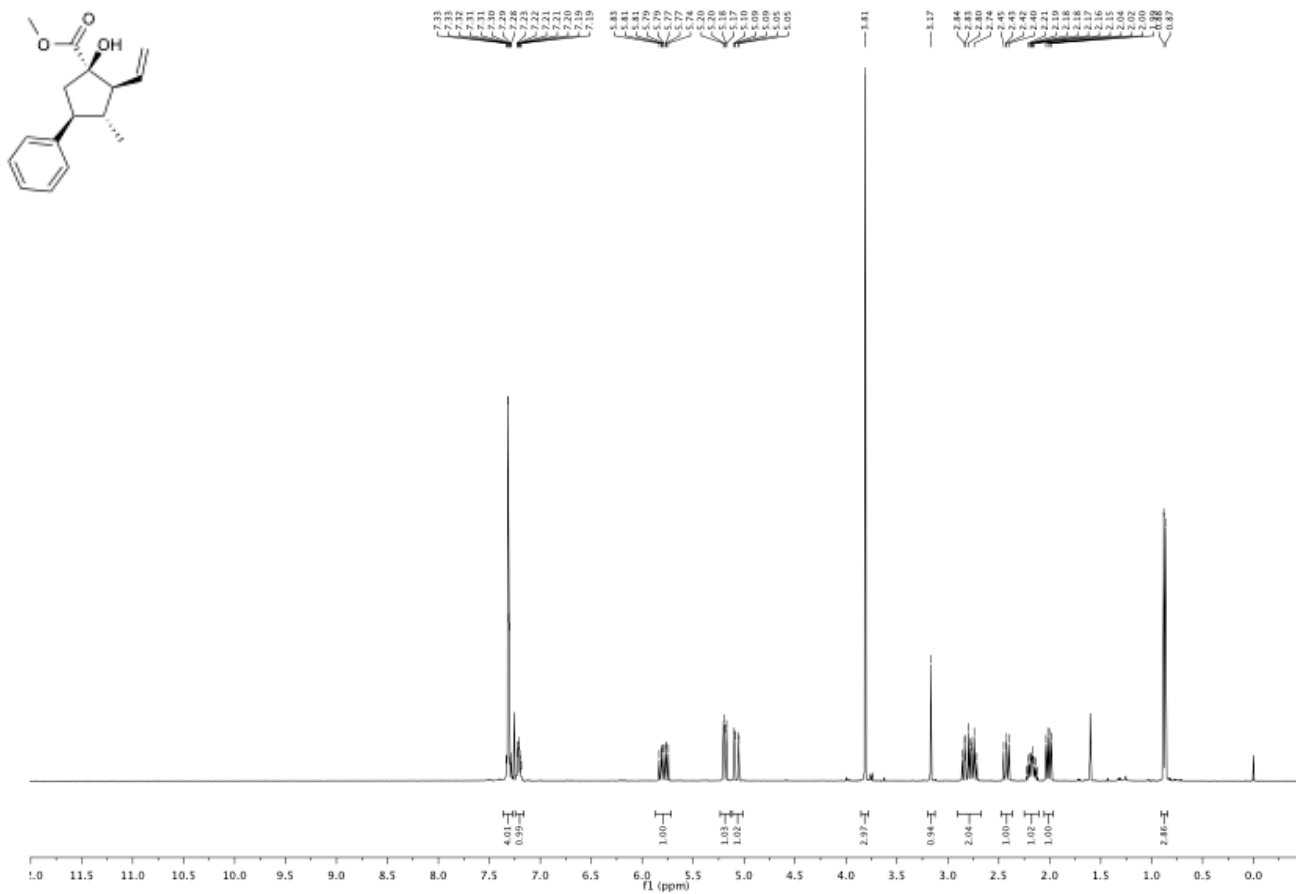
Supplementary Figures



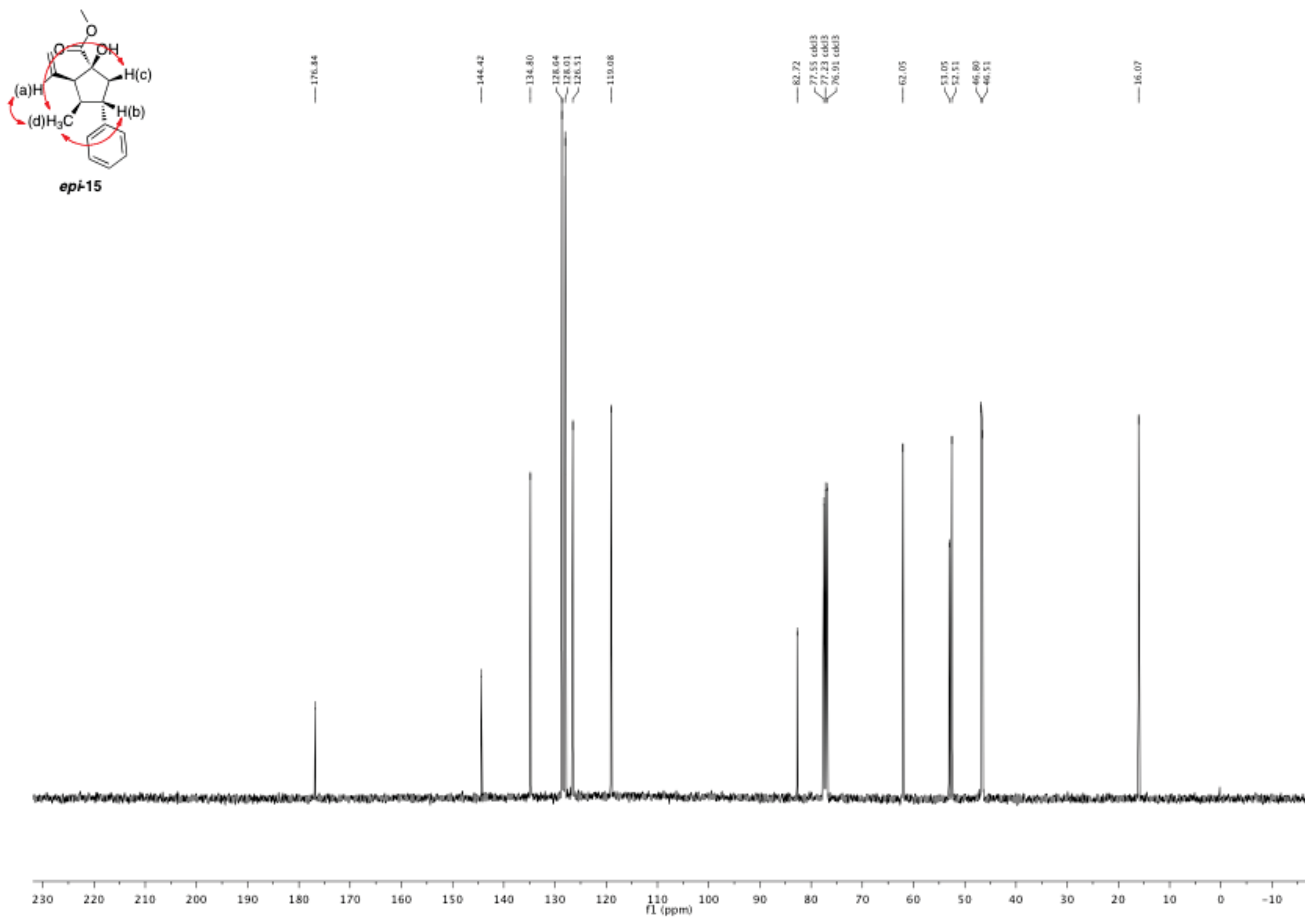
Supplementary Figure 1. 1D-nOe Spectrum of 15



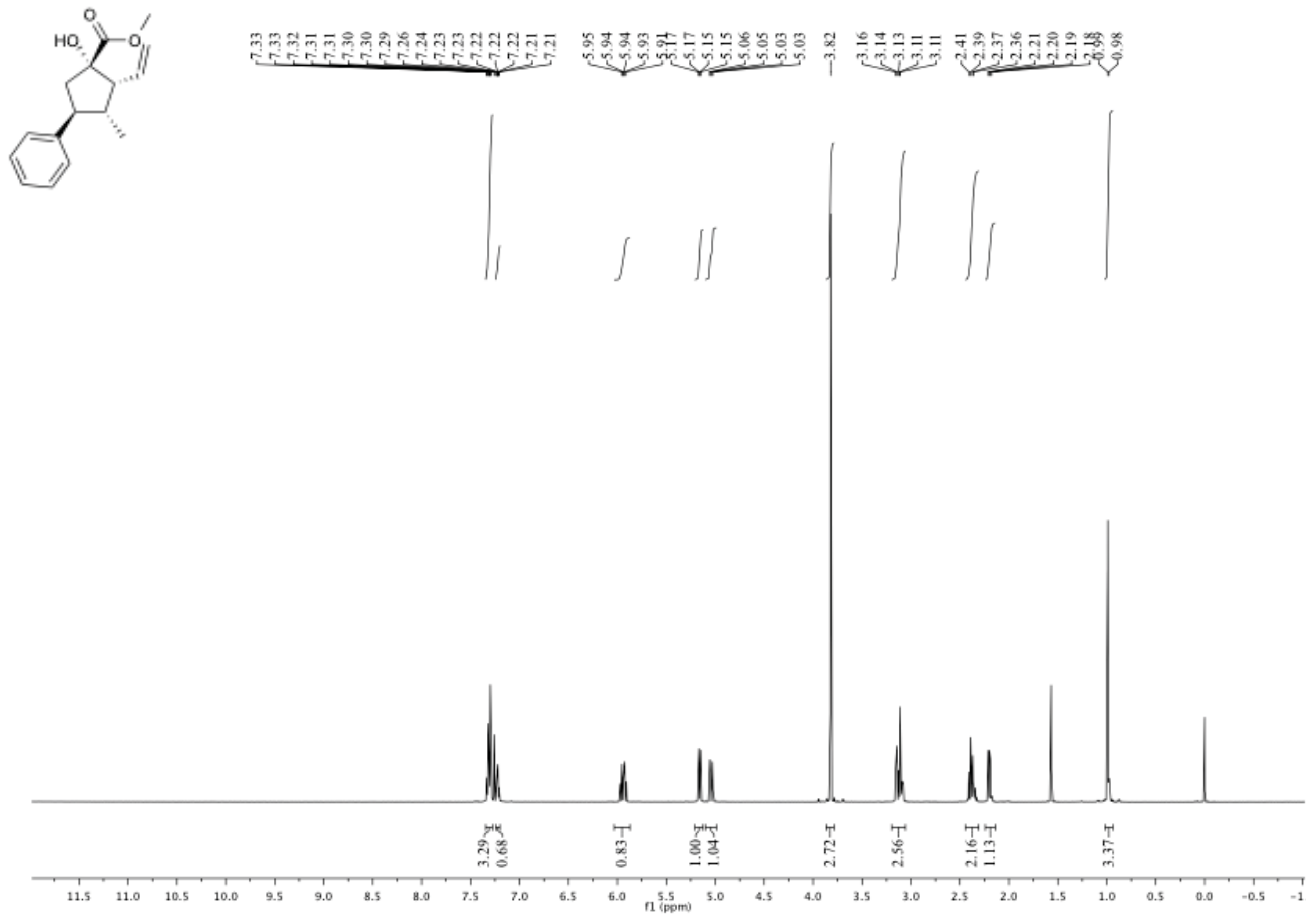
Supplementary Figure 2. 1D-nOe Spectrum of *epi-15*



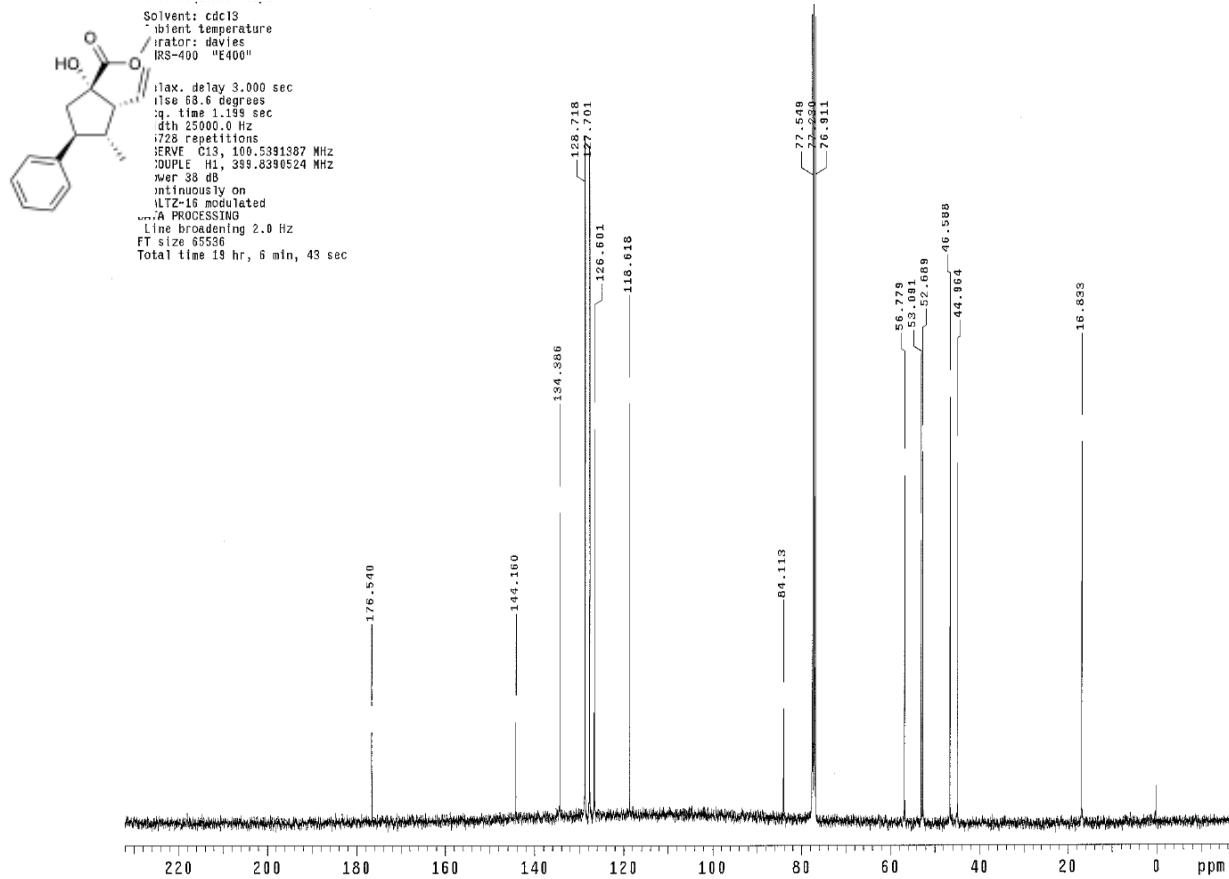
Supplementary Figure 3. ¹H NMR Spectrum of 15



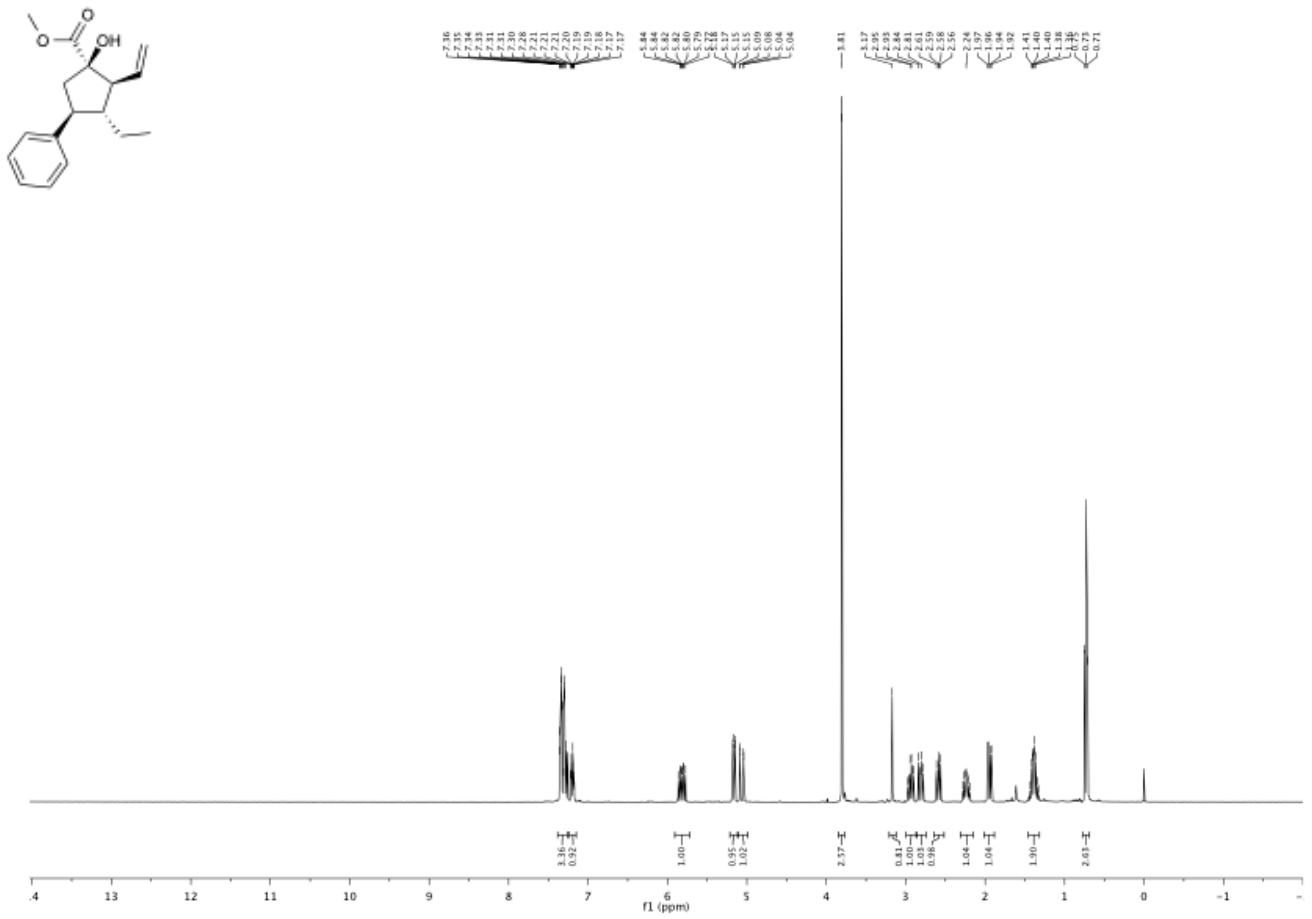
Supplementary Figure 4. ^{13}C NMR Spectrum of 15



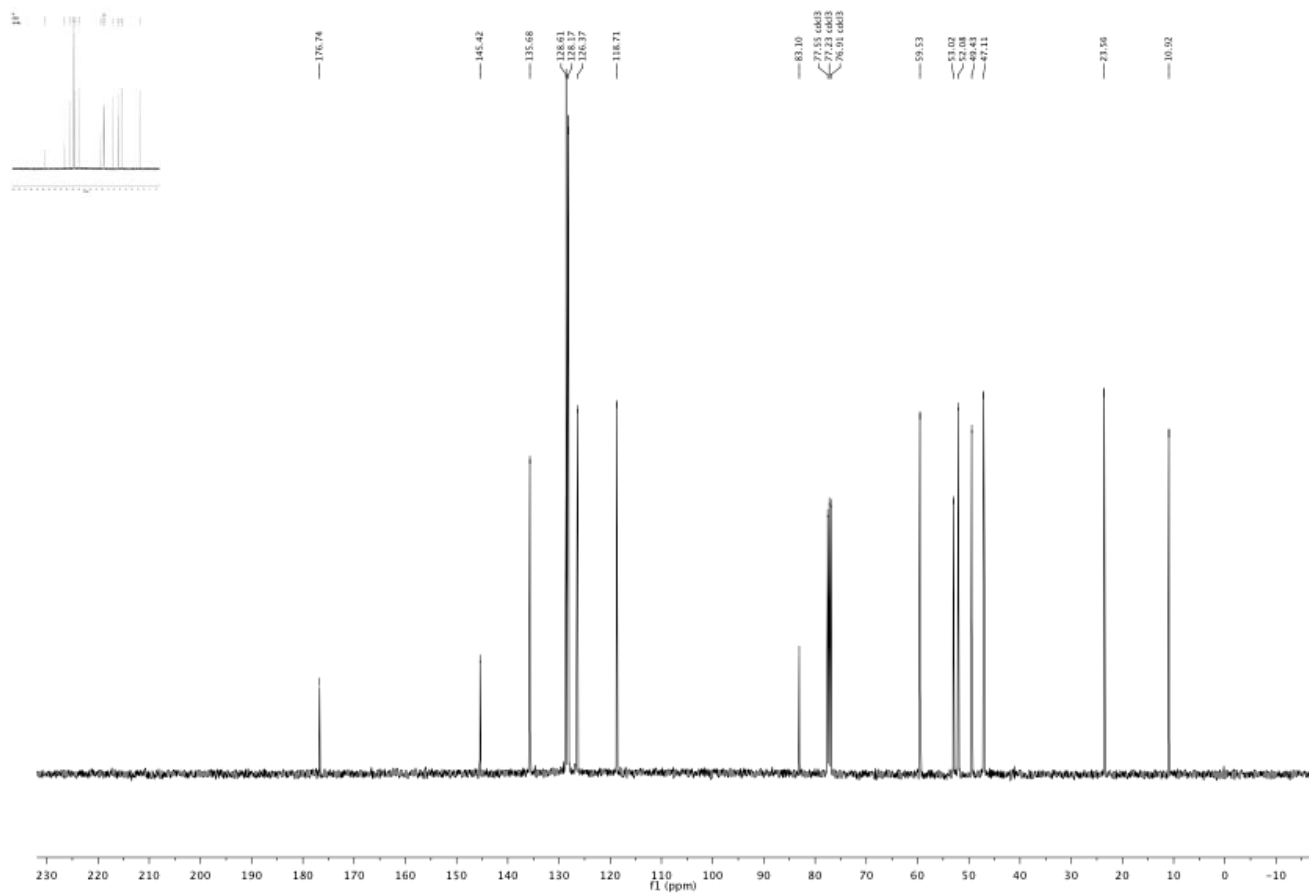
Supplementary Figure 5. ¹H NMR Spectrum of *epi-15*



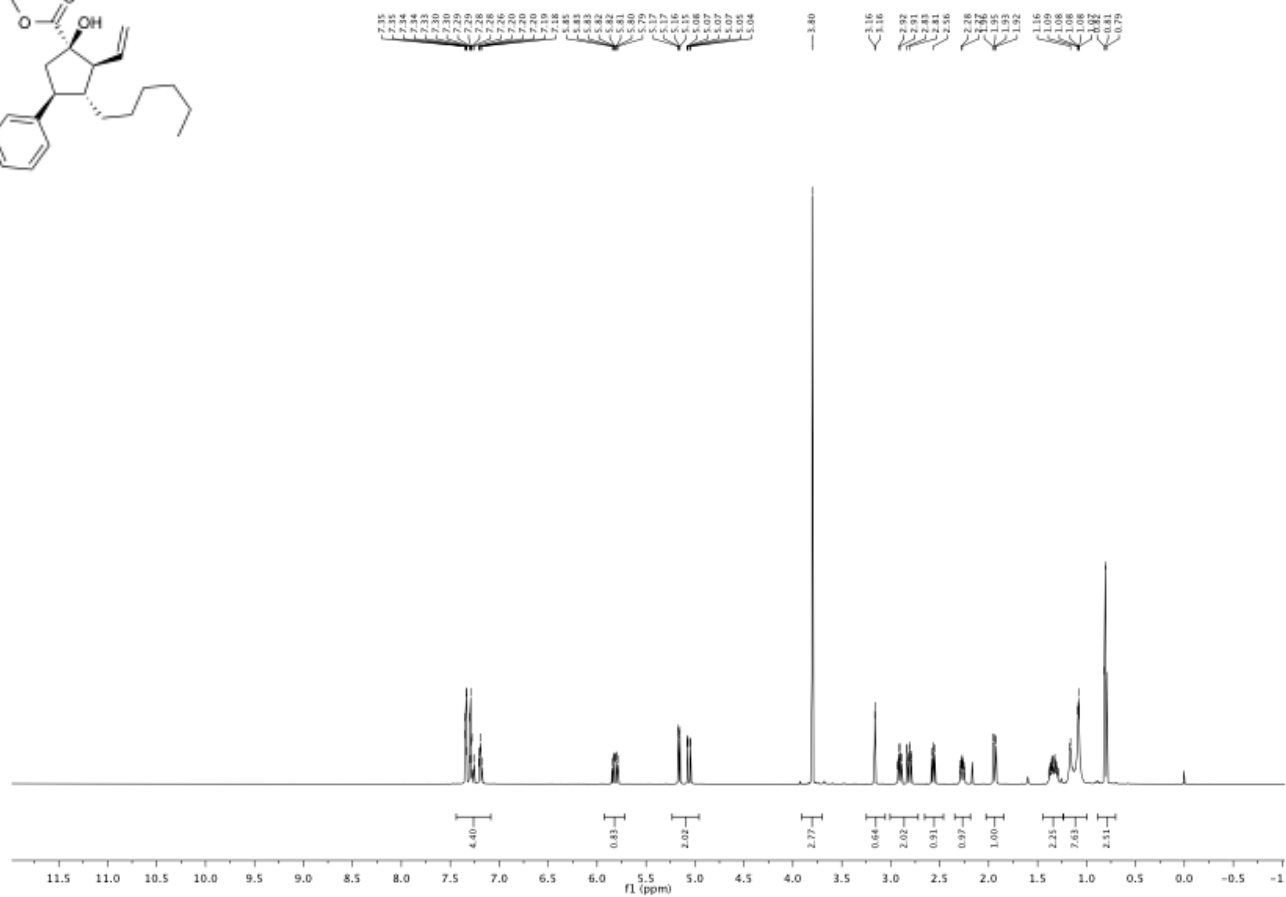
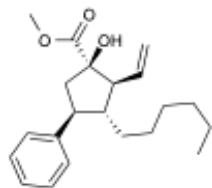
Supplementary Figure 6. ¹³C NMR Spectrum of *epi-15*



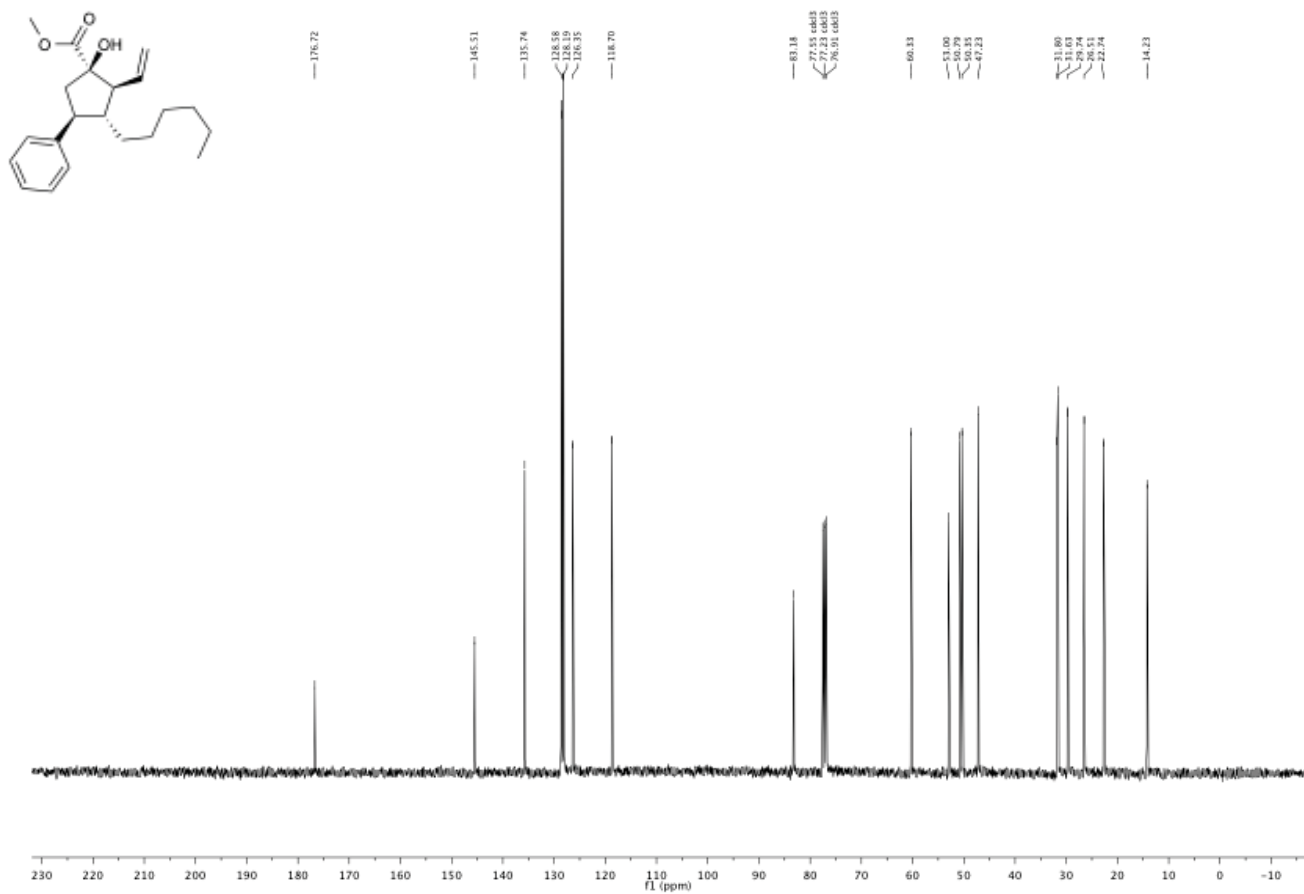
Supplementary Figure 7. ¹H NMR Spectrum of 18a



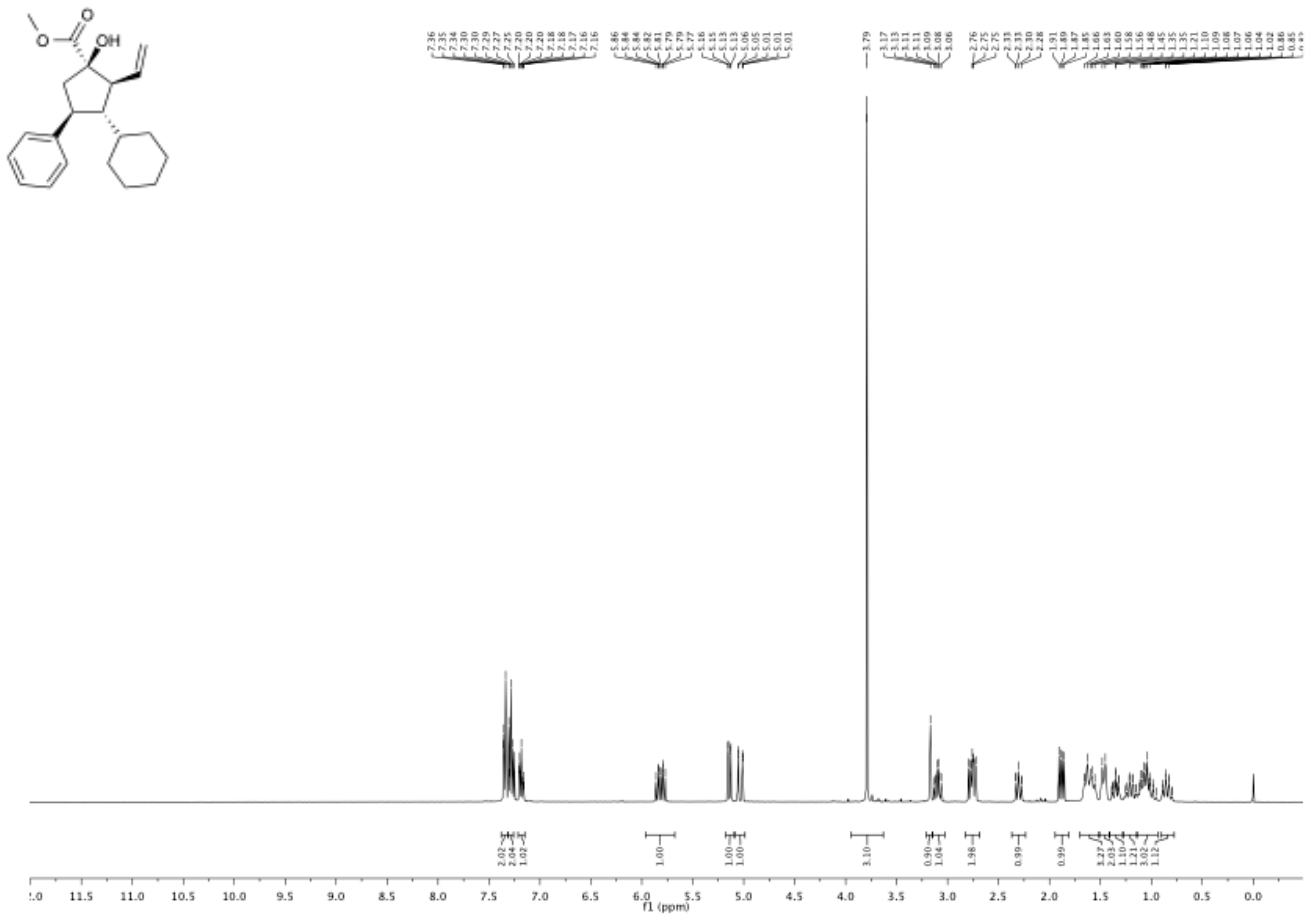
Supplementary Figure 8. ^{13}C NMR Spectrum of 18a



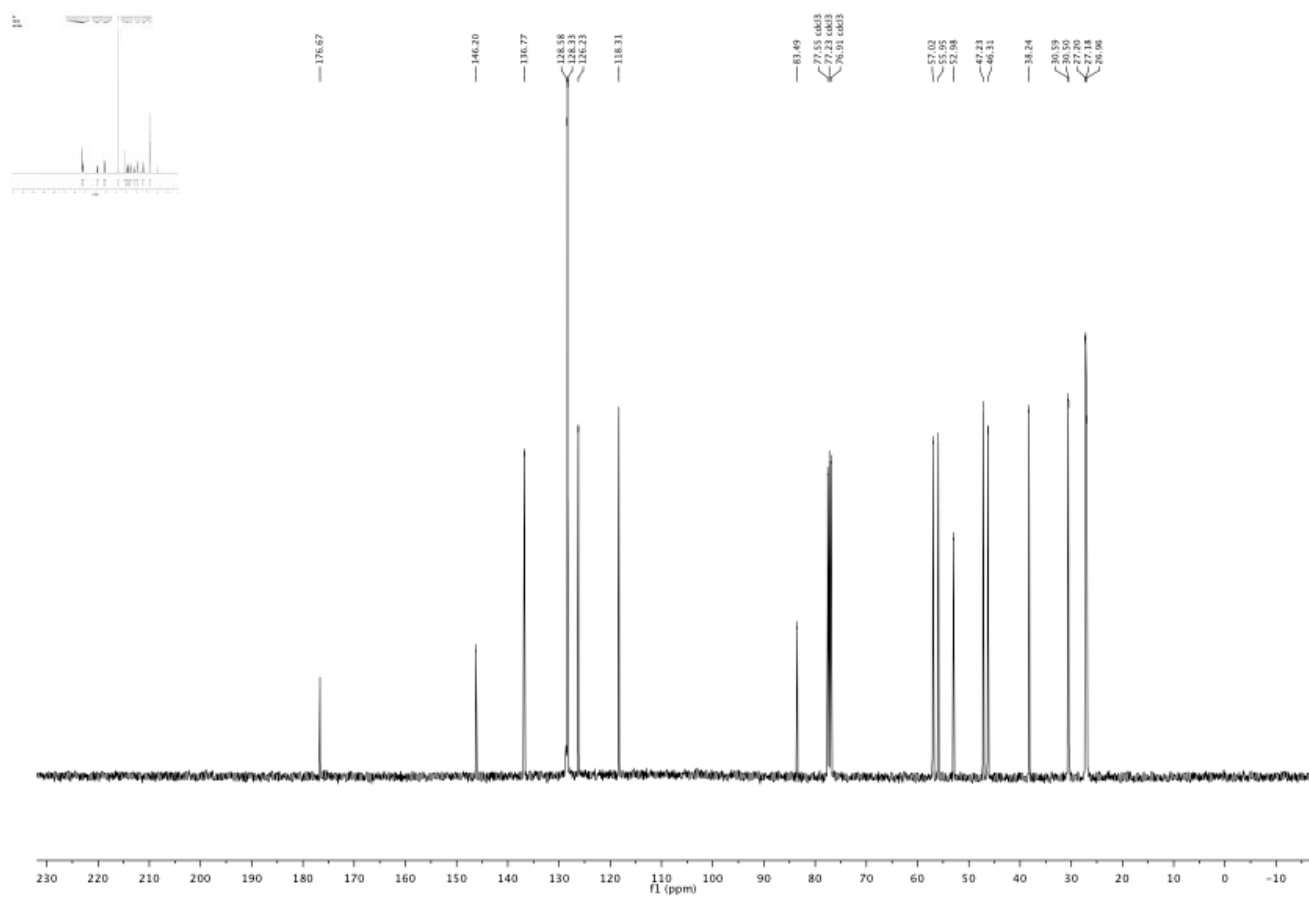
Supplementary Figure 9. ¹H NMR Spectrum of 18b



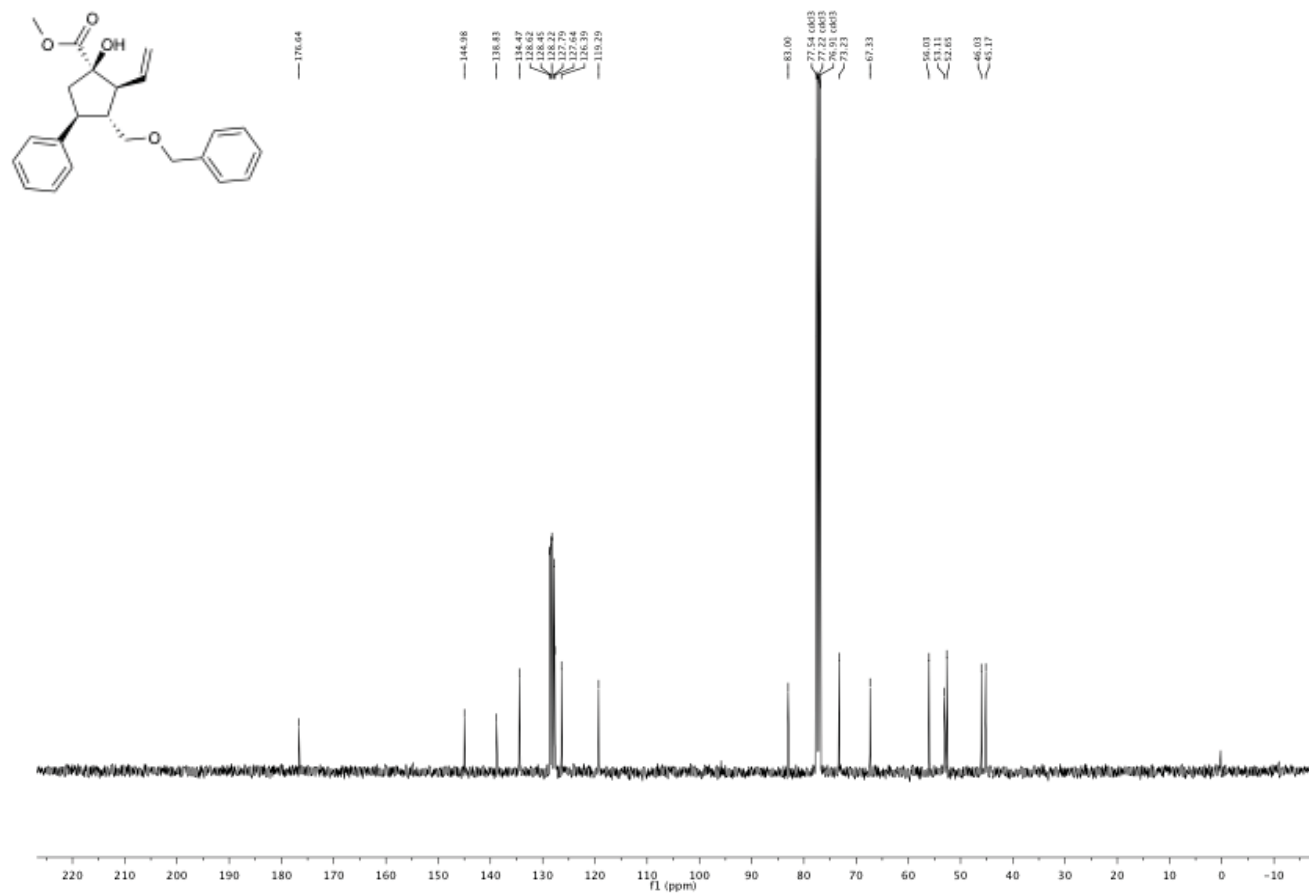
Supplementary Figure 10. ¹³C NMR Spectrum of 18b



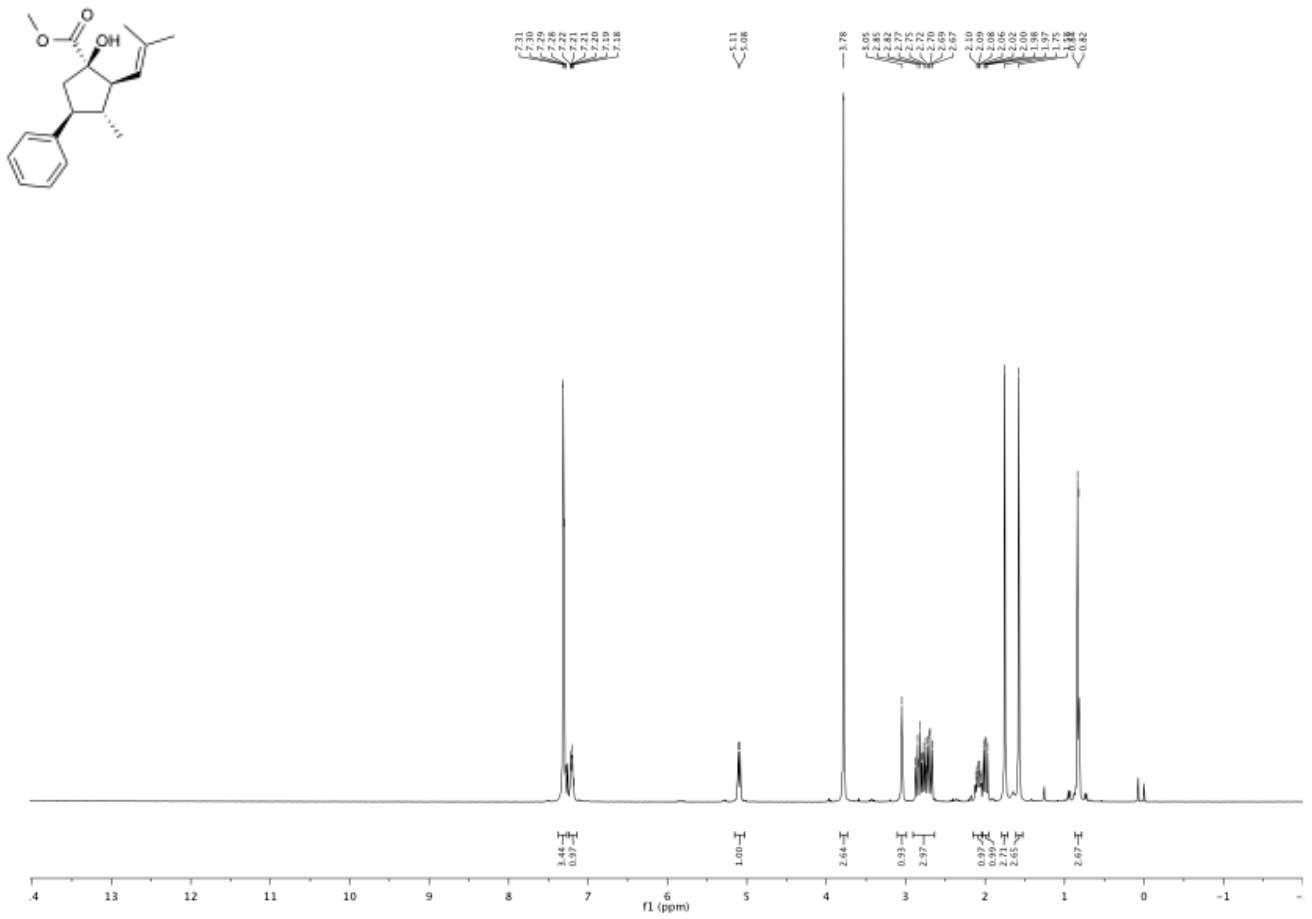
Supplementary Figure 11. ¹H NMR Spectrum of 18c



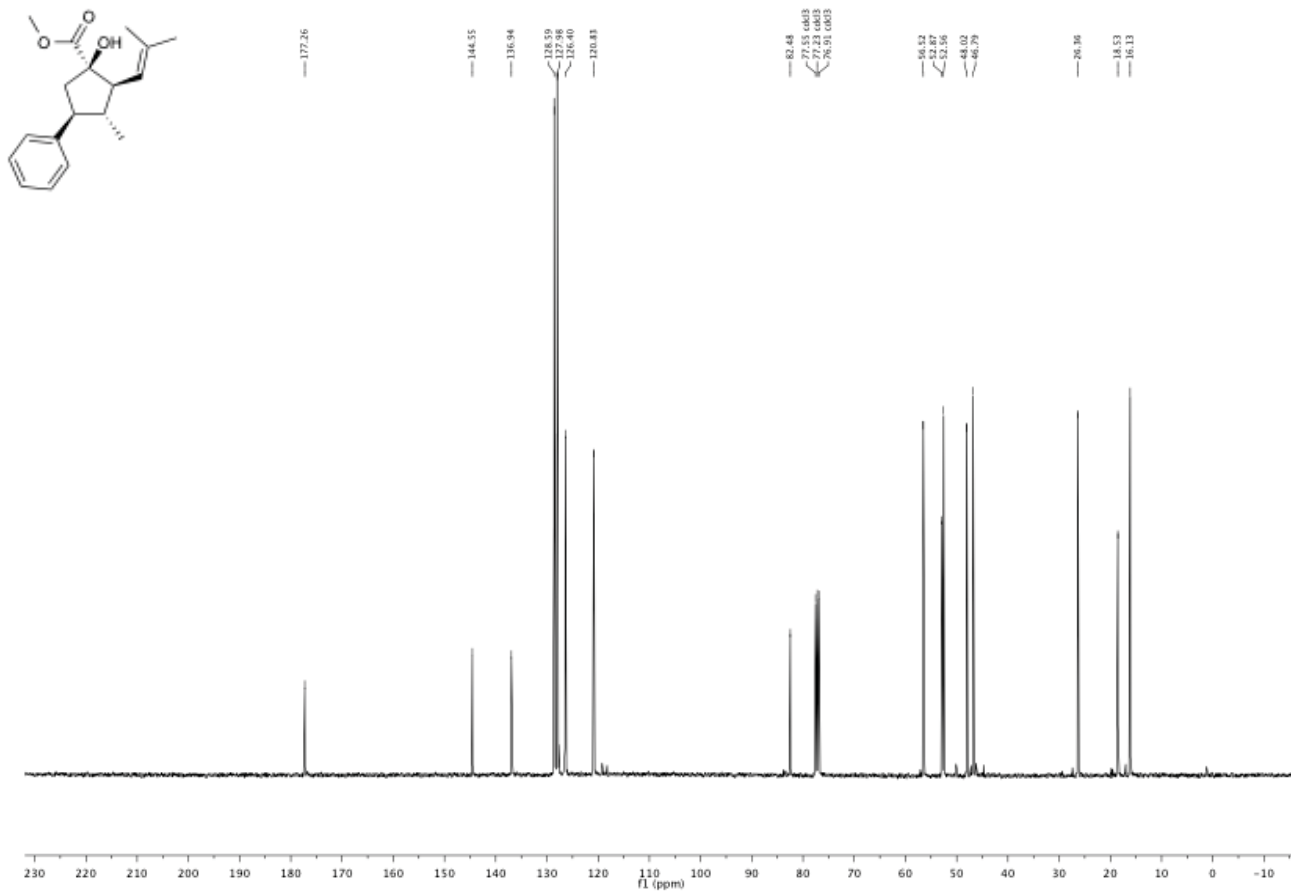
Supplementary Figure 12. ^{13}C NMR Spectrum of 18c



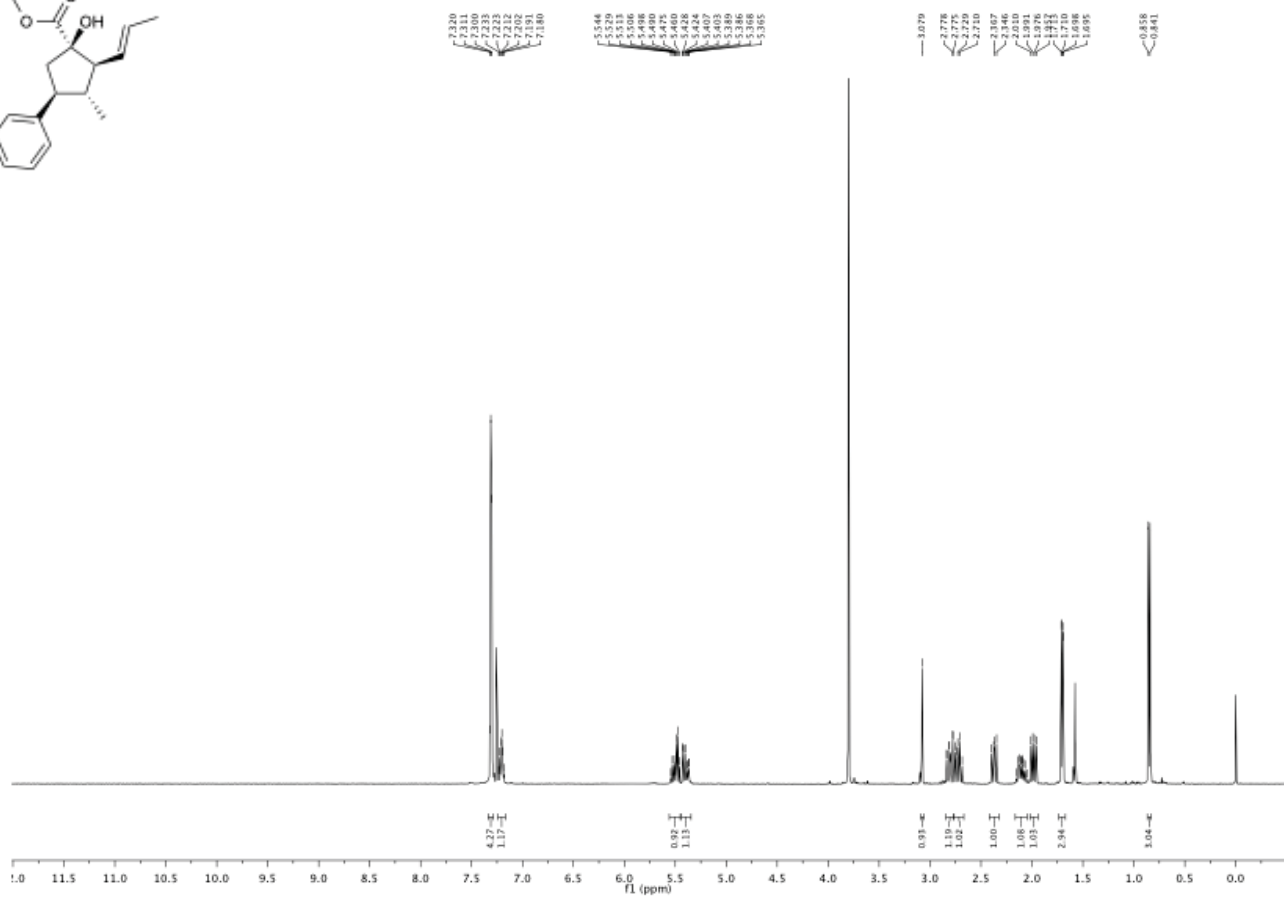
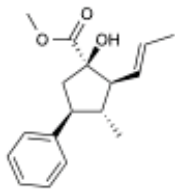
Supplementary Figure 14. ^{13}C NMR Spectrum of 18d



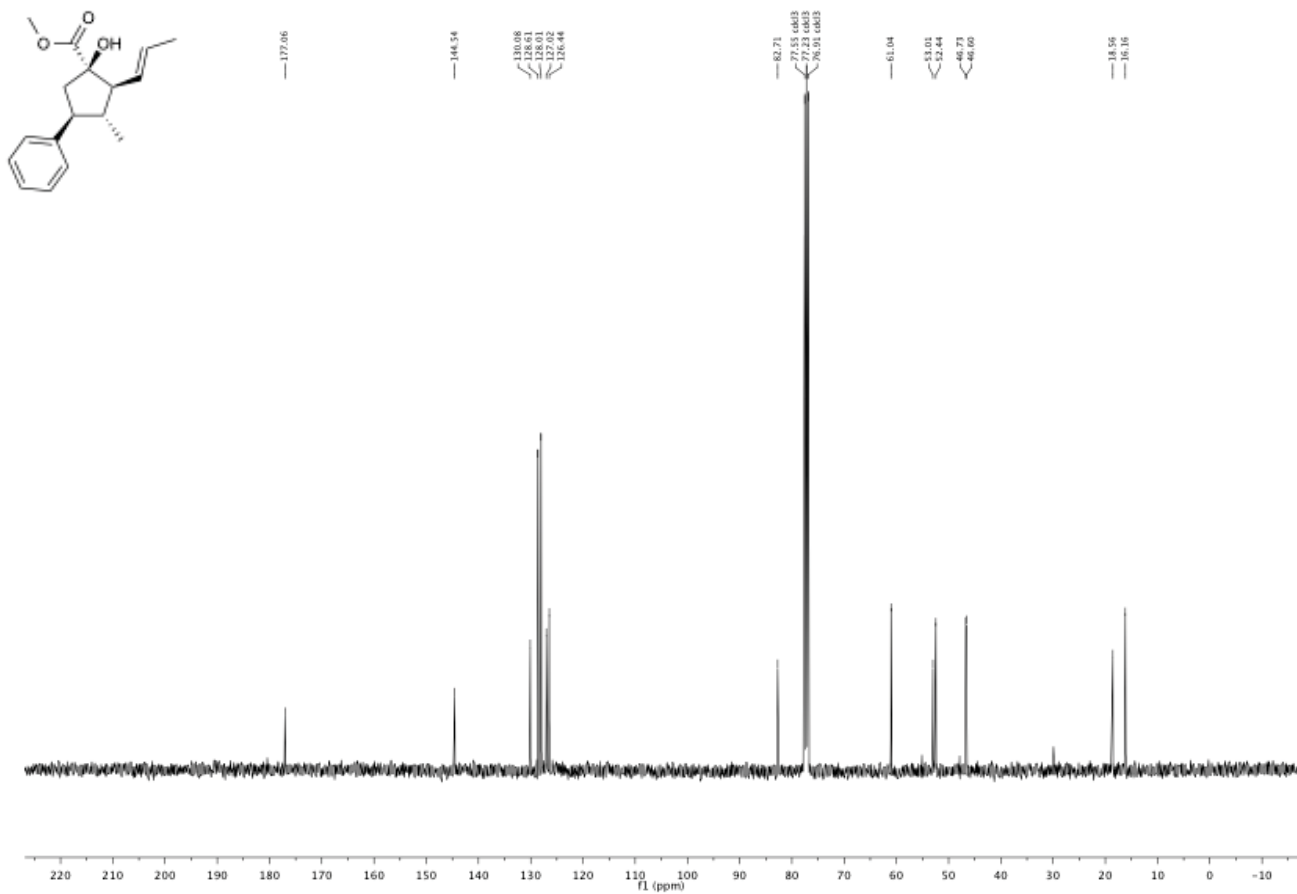
Supplementary Figure 15. ¹H NMR Spectrum of 20a



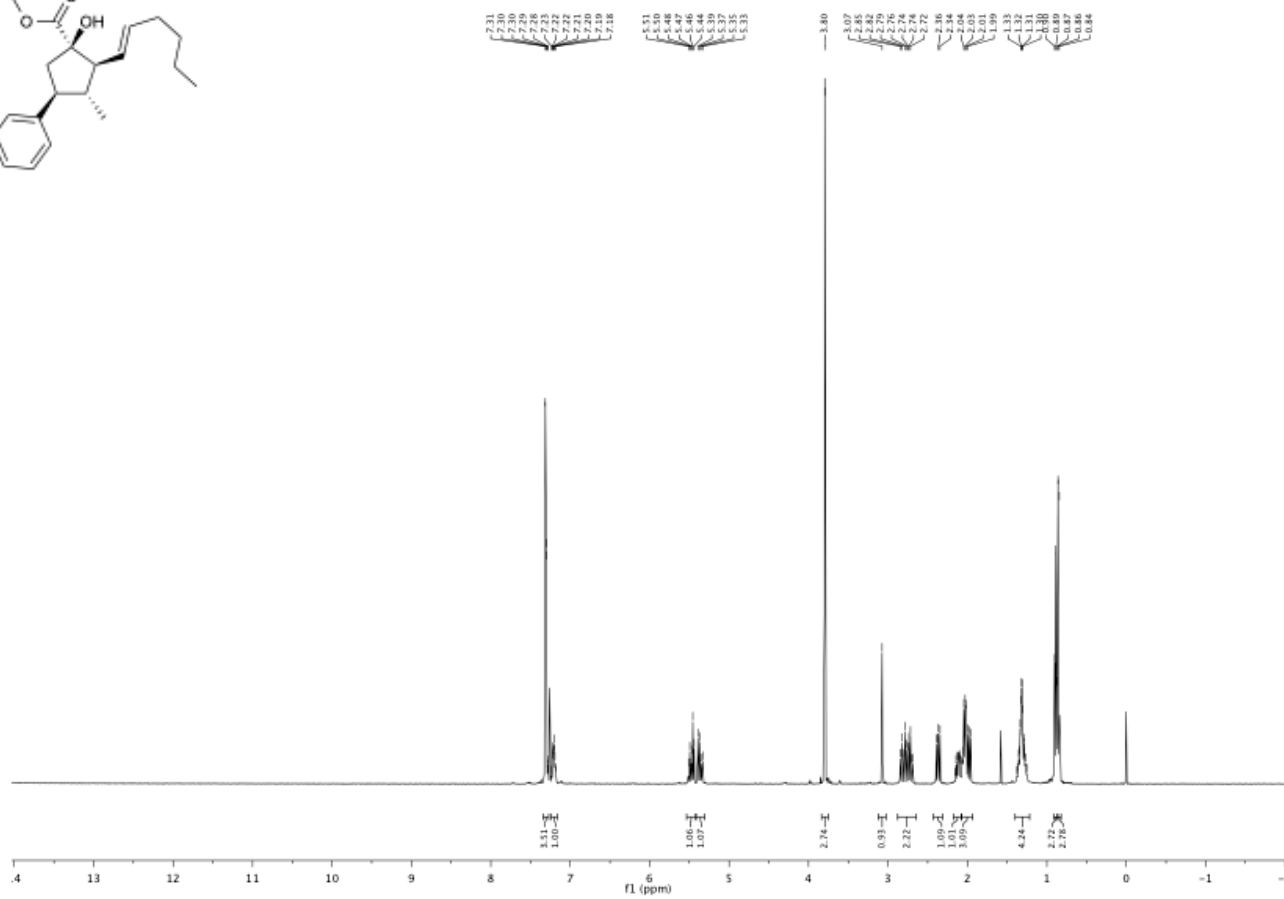
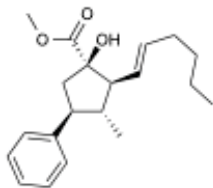
Supplementary Figure 16. ¹³C NMR Spectrum of 20a



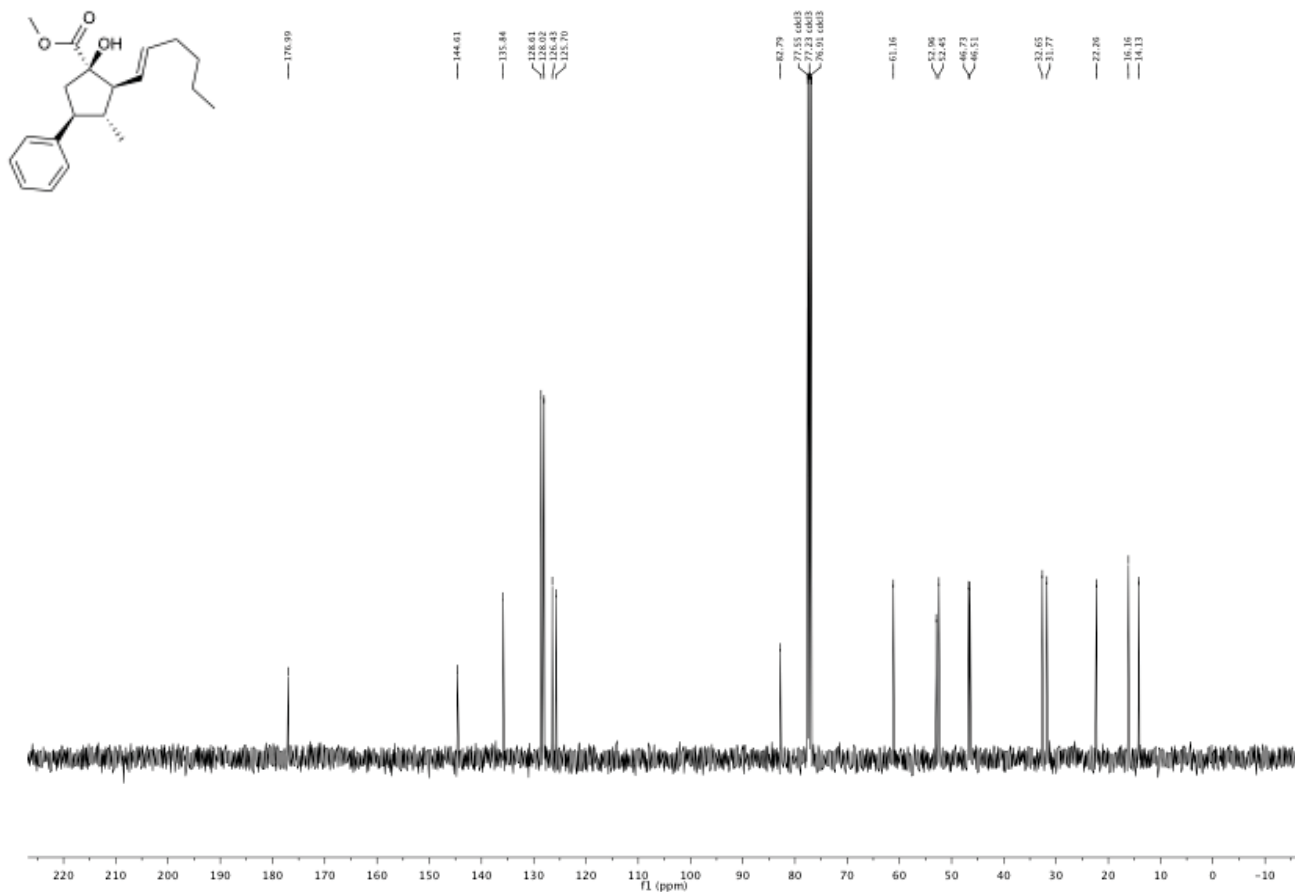
Supplementary Figure 17. ^1H NMR Spectrum of 20b



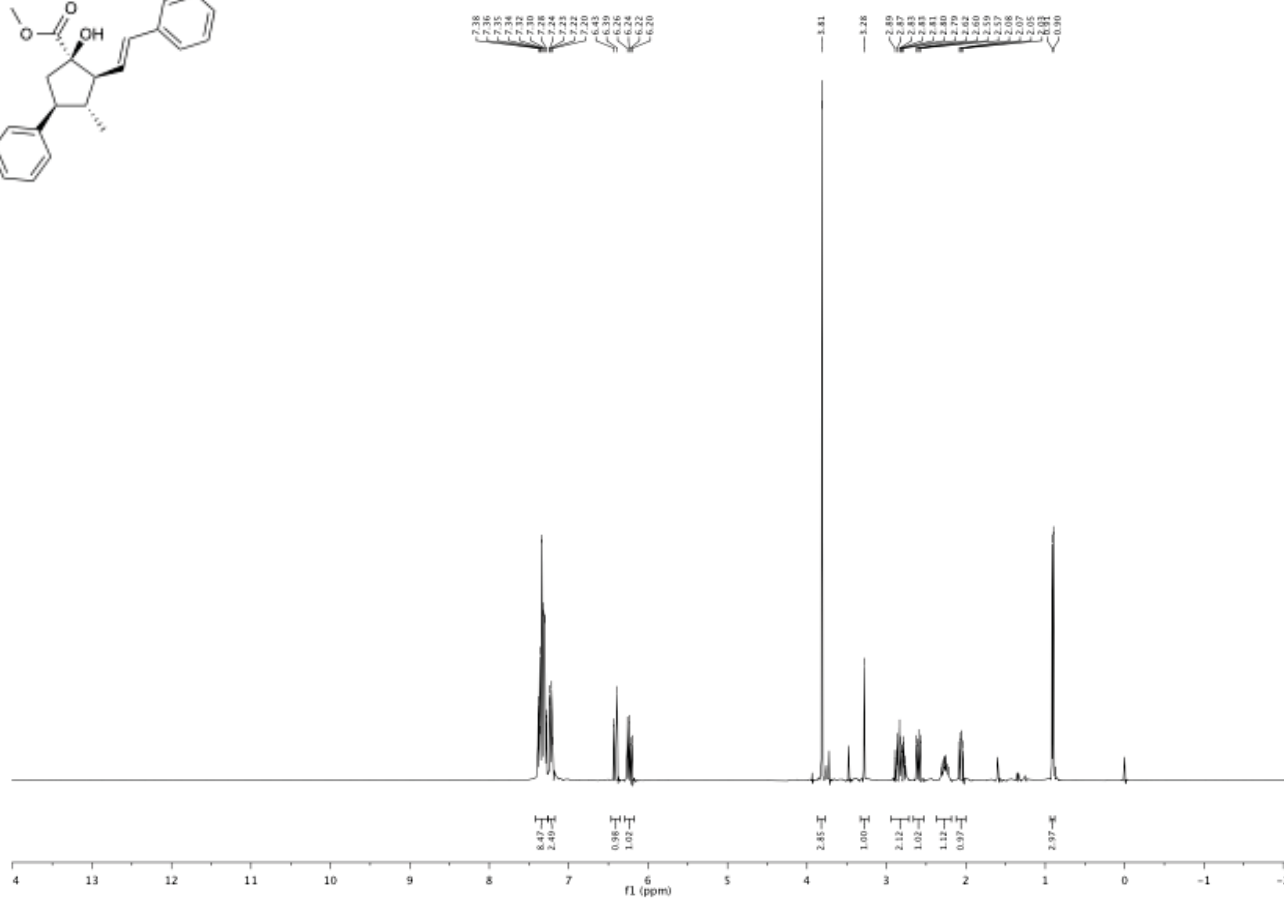
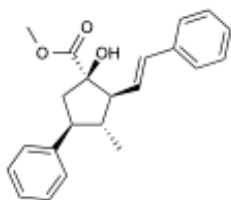
Supplementary Figure 18. ¹³C NMR Spectrum of 20b



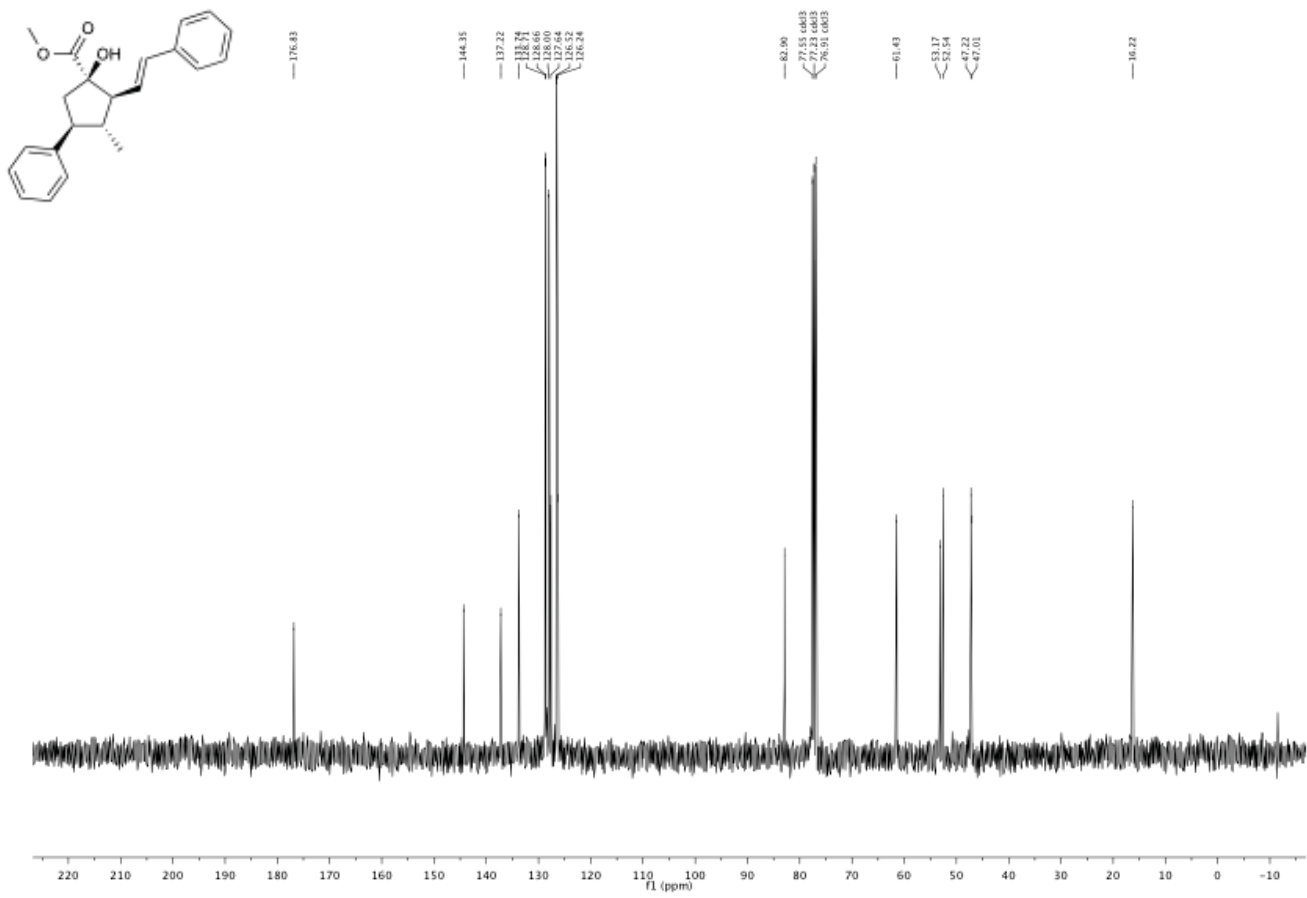
Supplementary Figure 19. ¹H NMR Spectrum of 20c



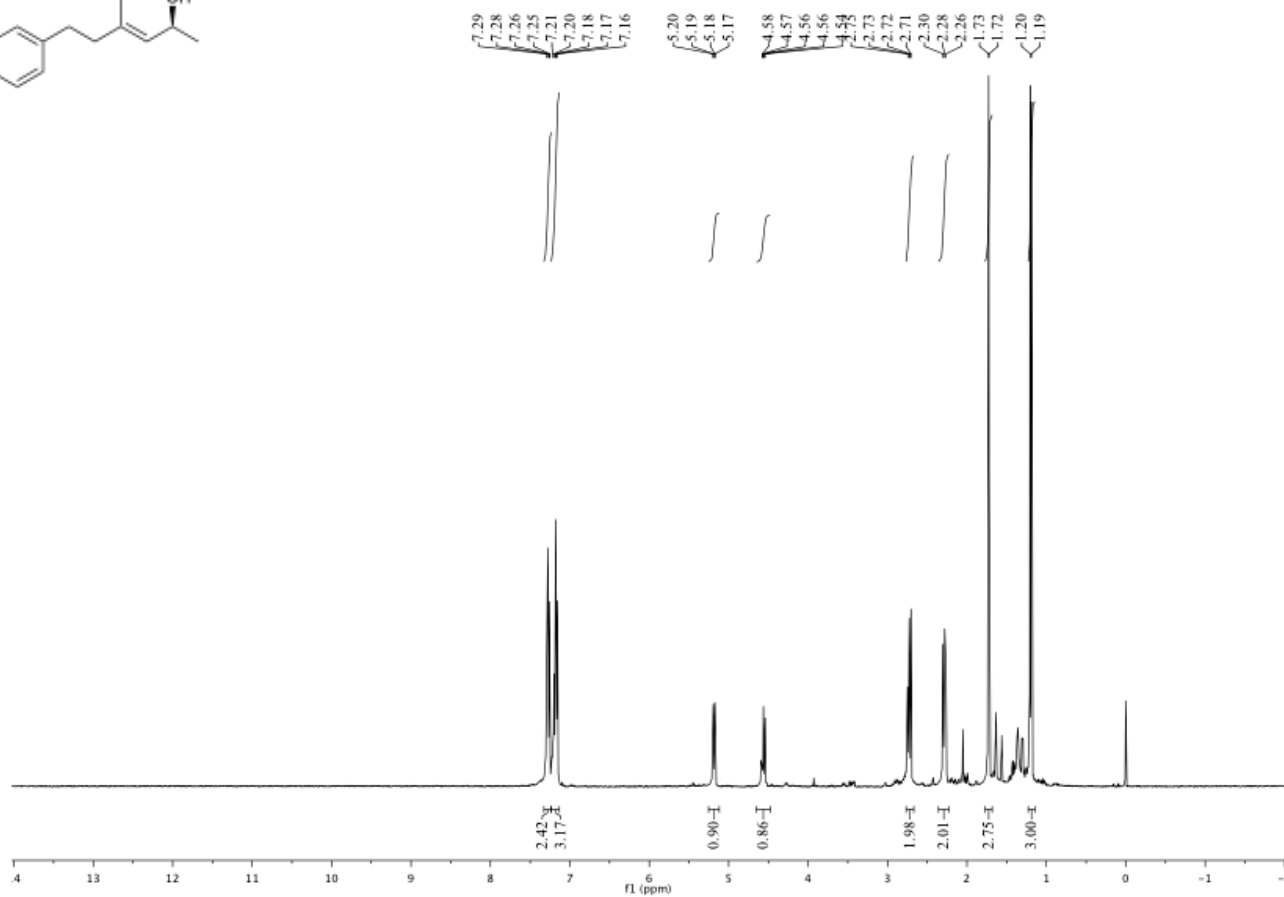
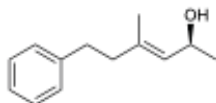
Supplementary Figure 20. ¹³C NMR Spectrum of 20c



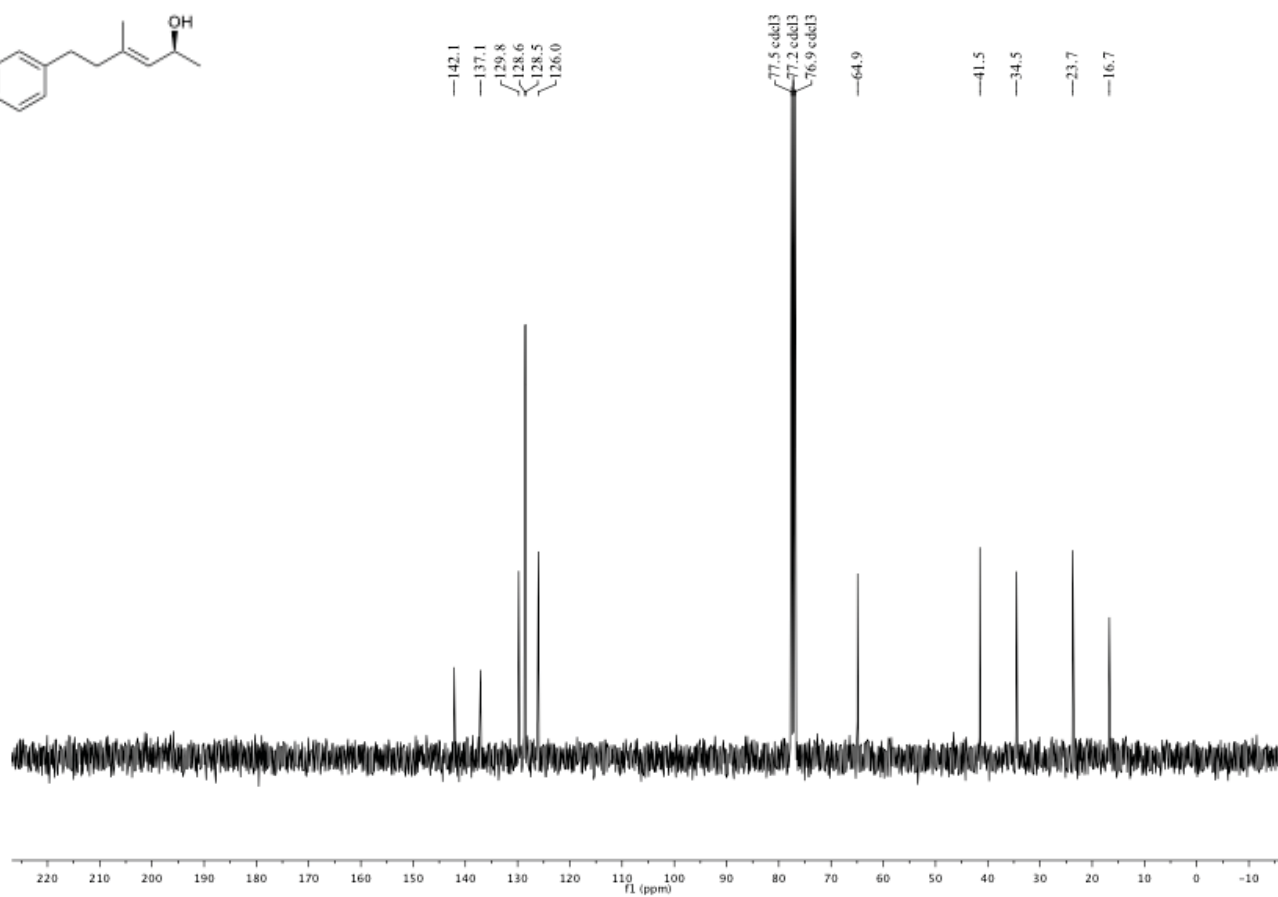
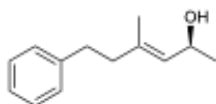
Supplementary Figure 21. ^1H NMR Spectrum of 20d



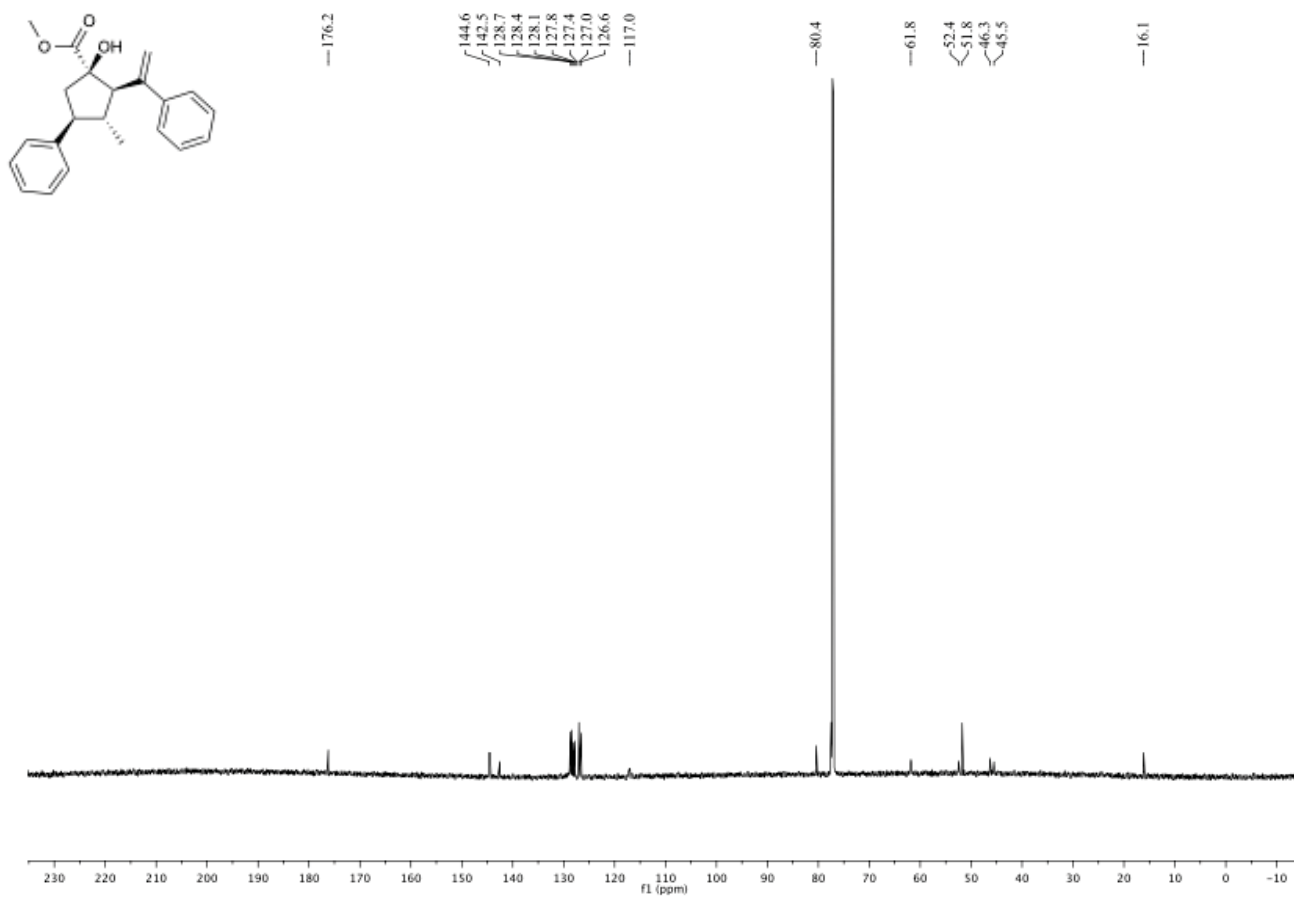
Supplementary Figure 22. ¹³C NMR Spectrum of 20d



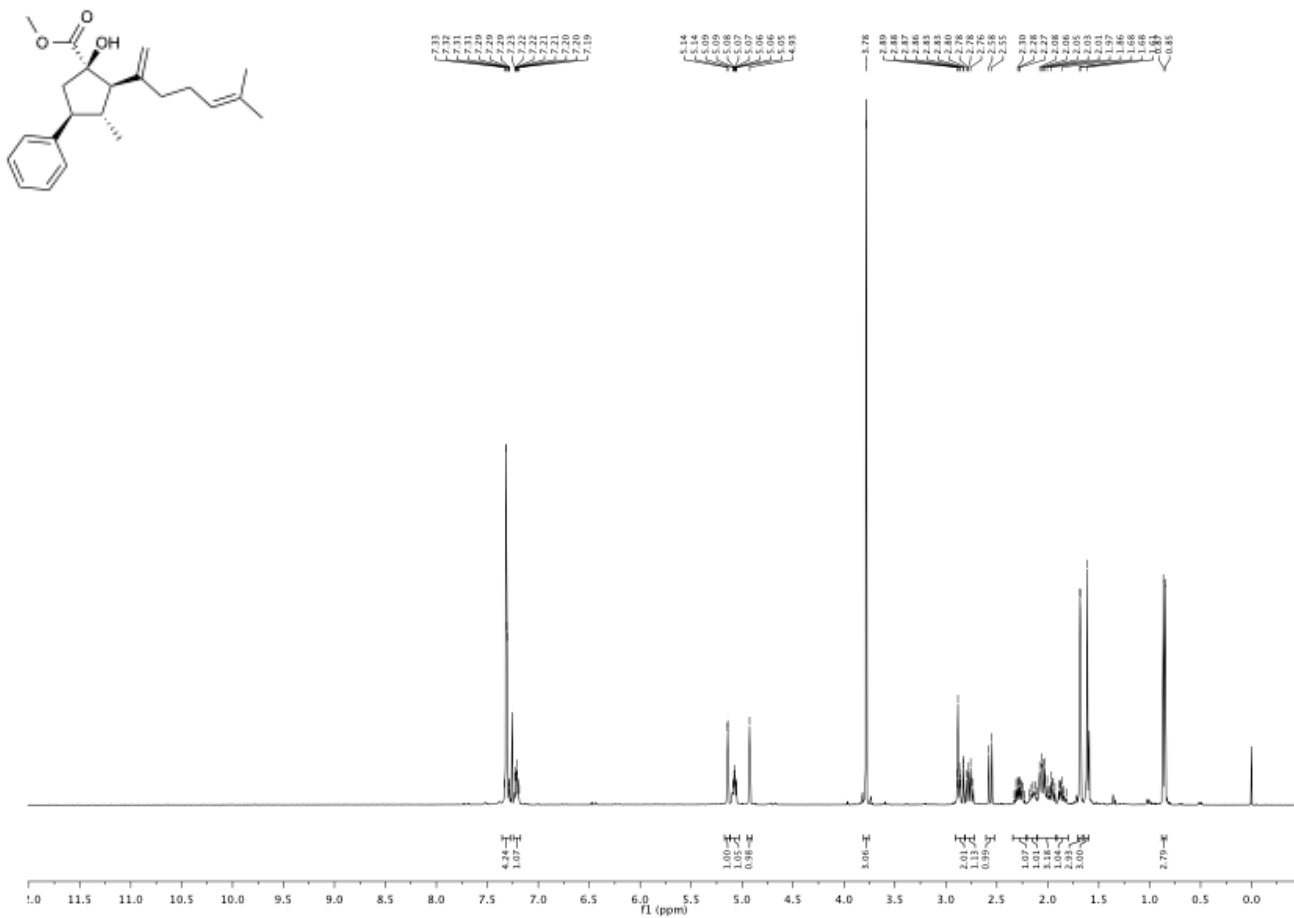
Supplementary Figure 23. ^1H NMR Spectrum of 23c



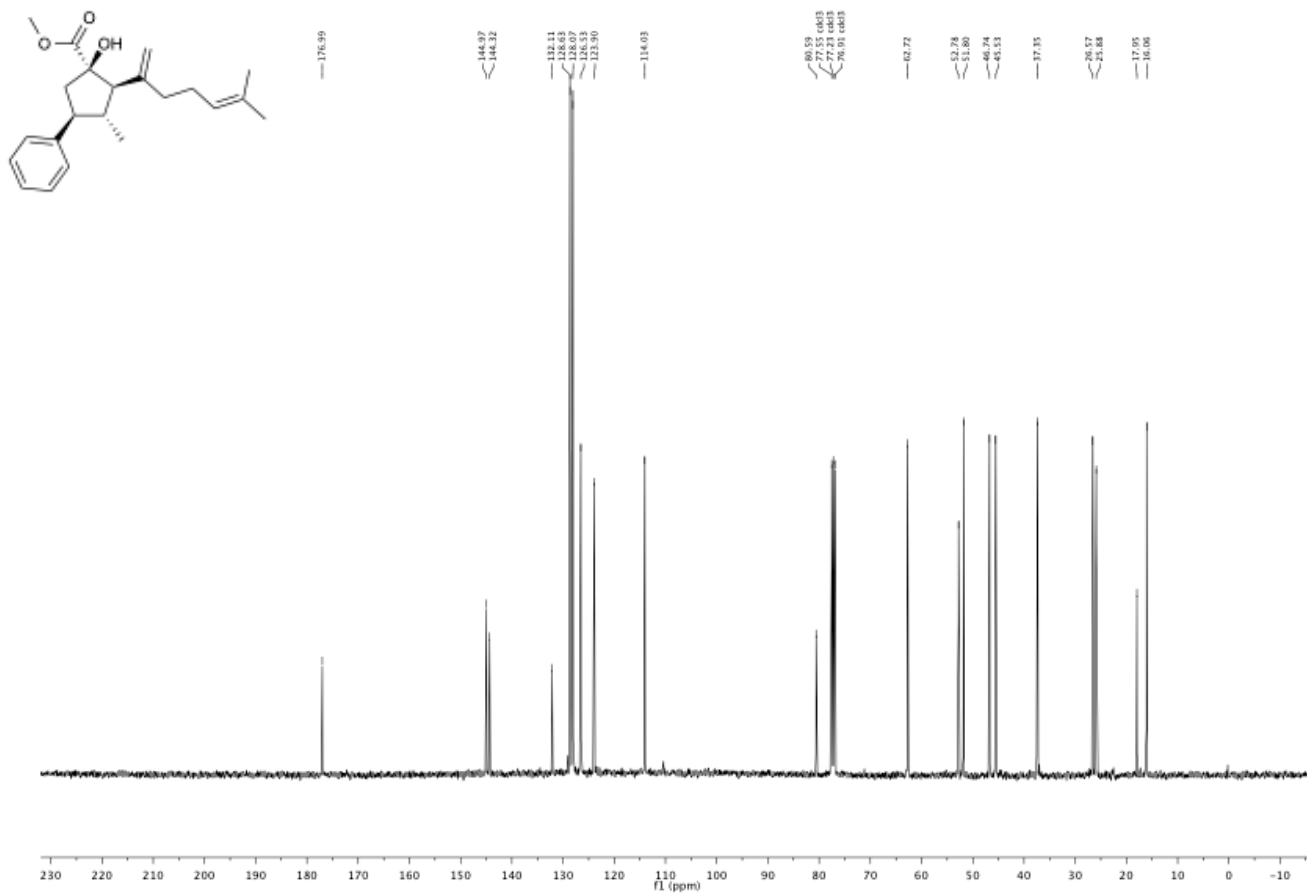
Supplementary Figure 24. ^{13}C NMR Spectrum of 23c



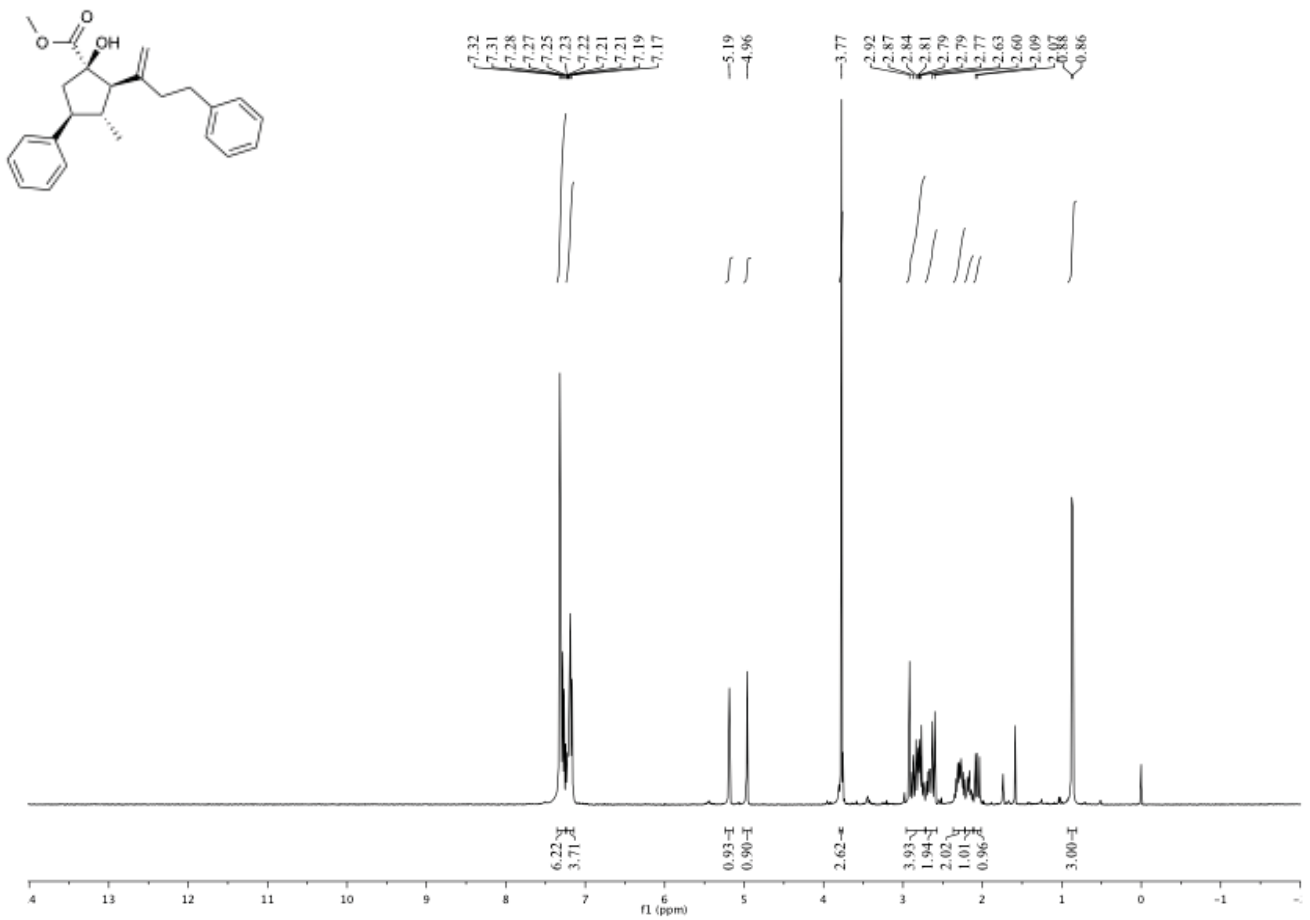
Supplementary Figure 26. ¹³C NMR Spectrum of 24a



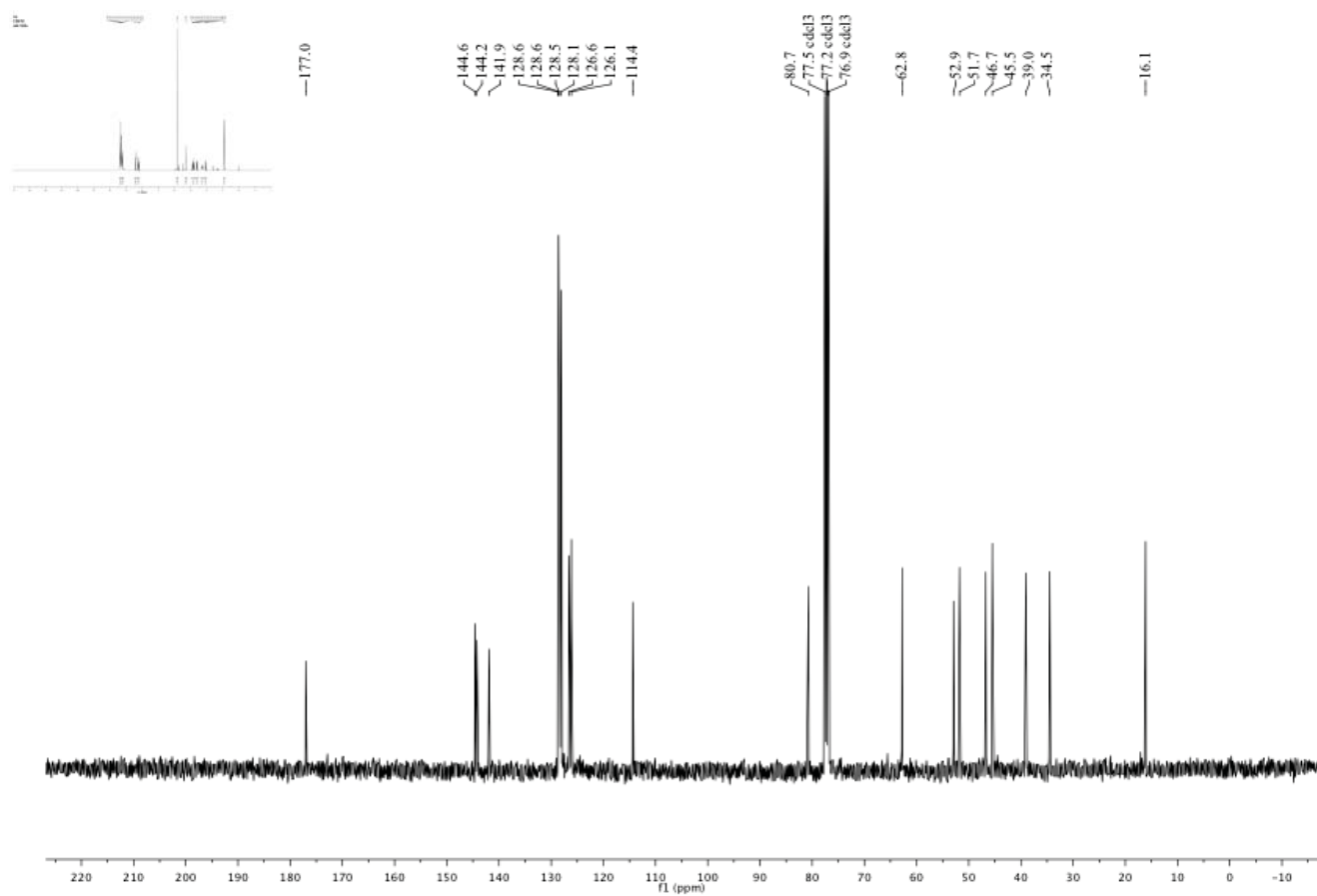
Supplementary Figure 27. ¹H NMR Spectrum of 24b



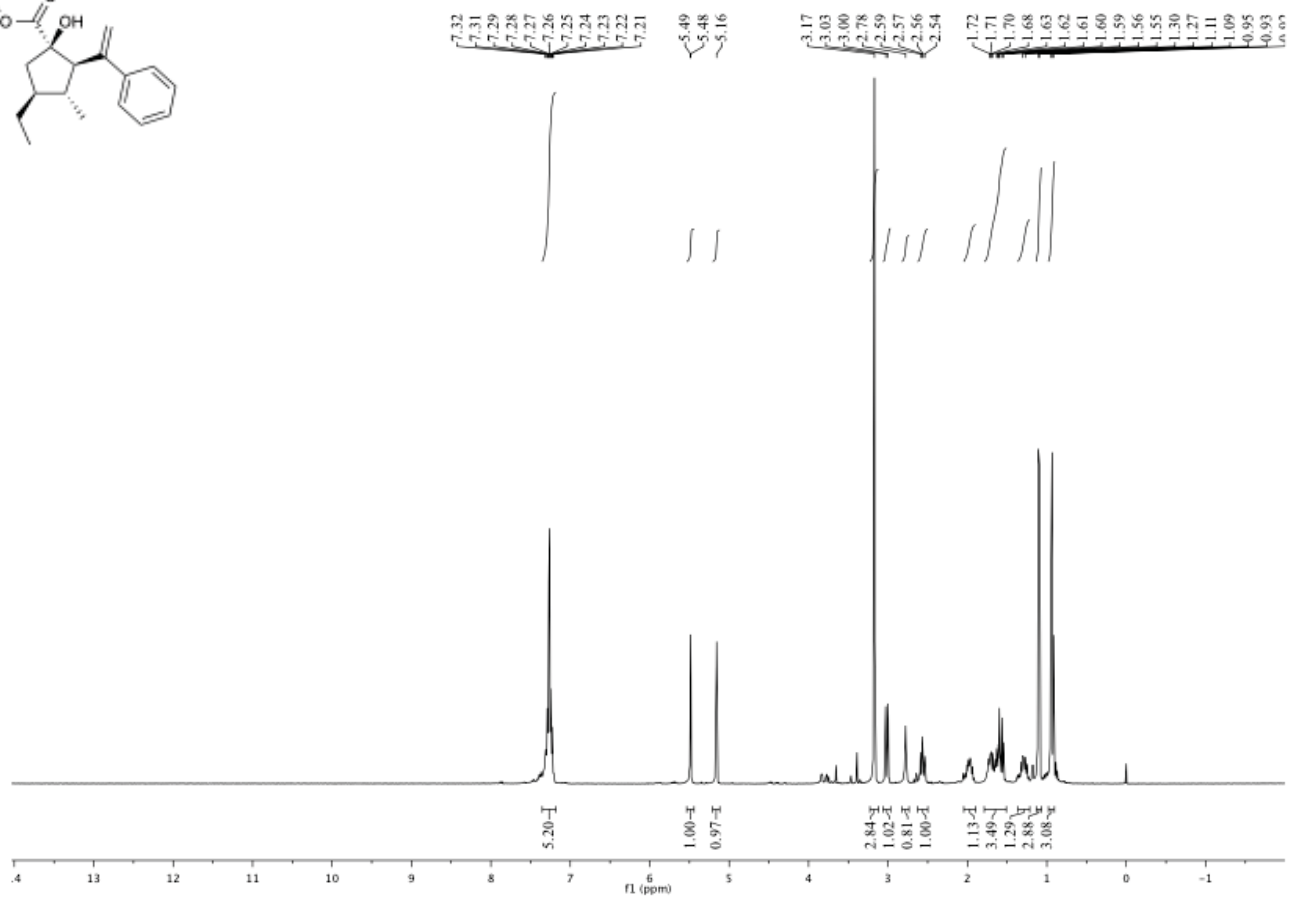
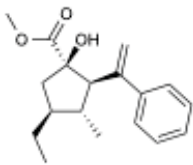
Supplementary Figure 28. ¹³C NMR Spectrum of 24b



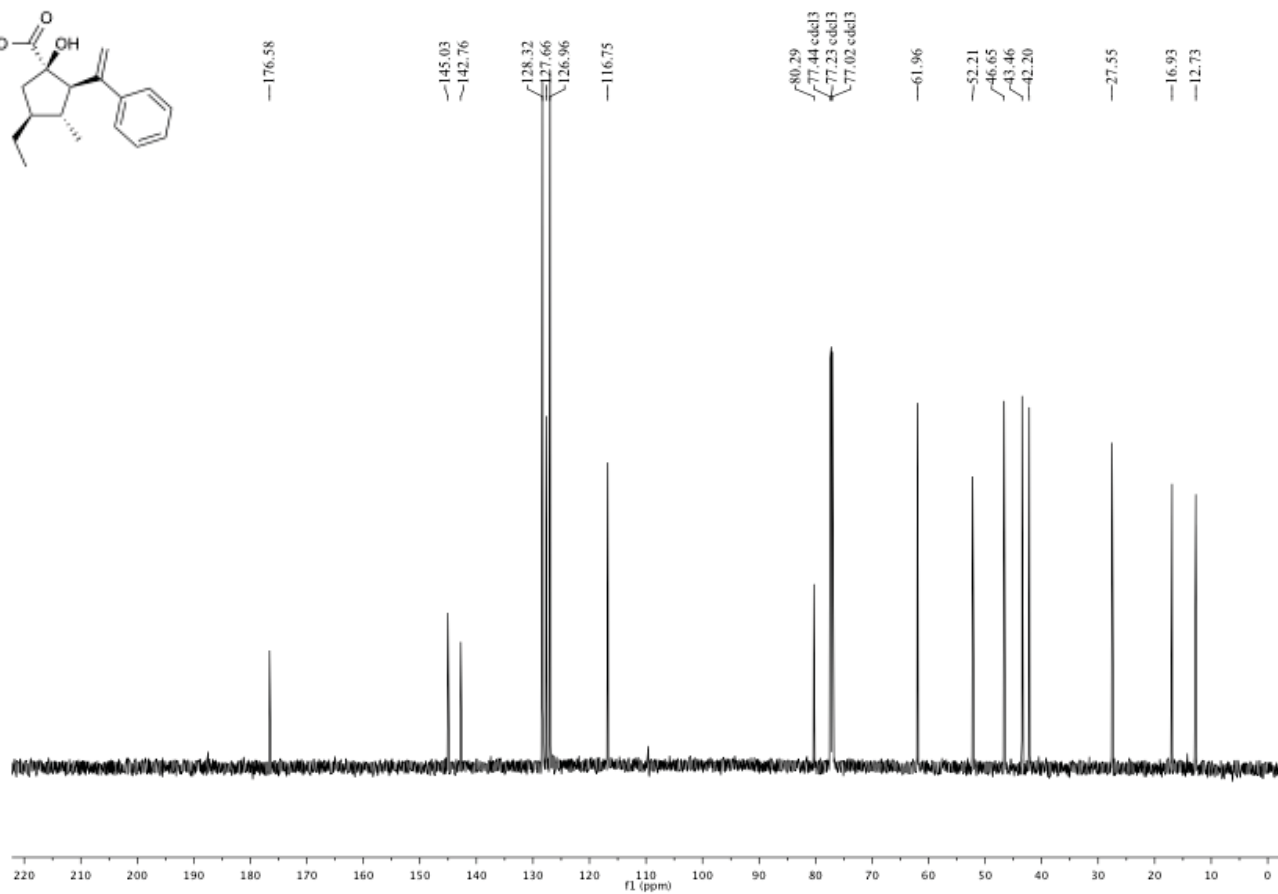
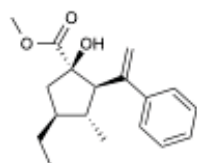
Supplementary Figure 29. ¹H NMR Spectrum of 24c



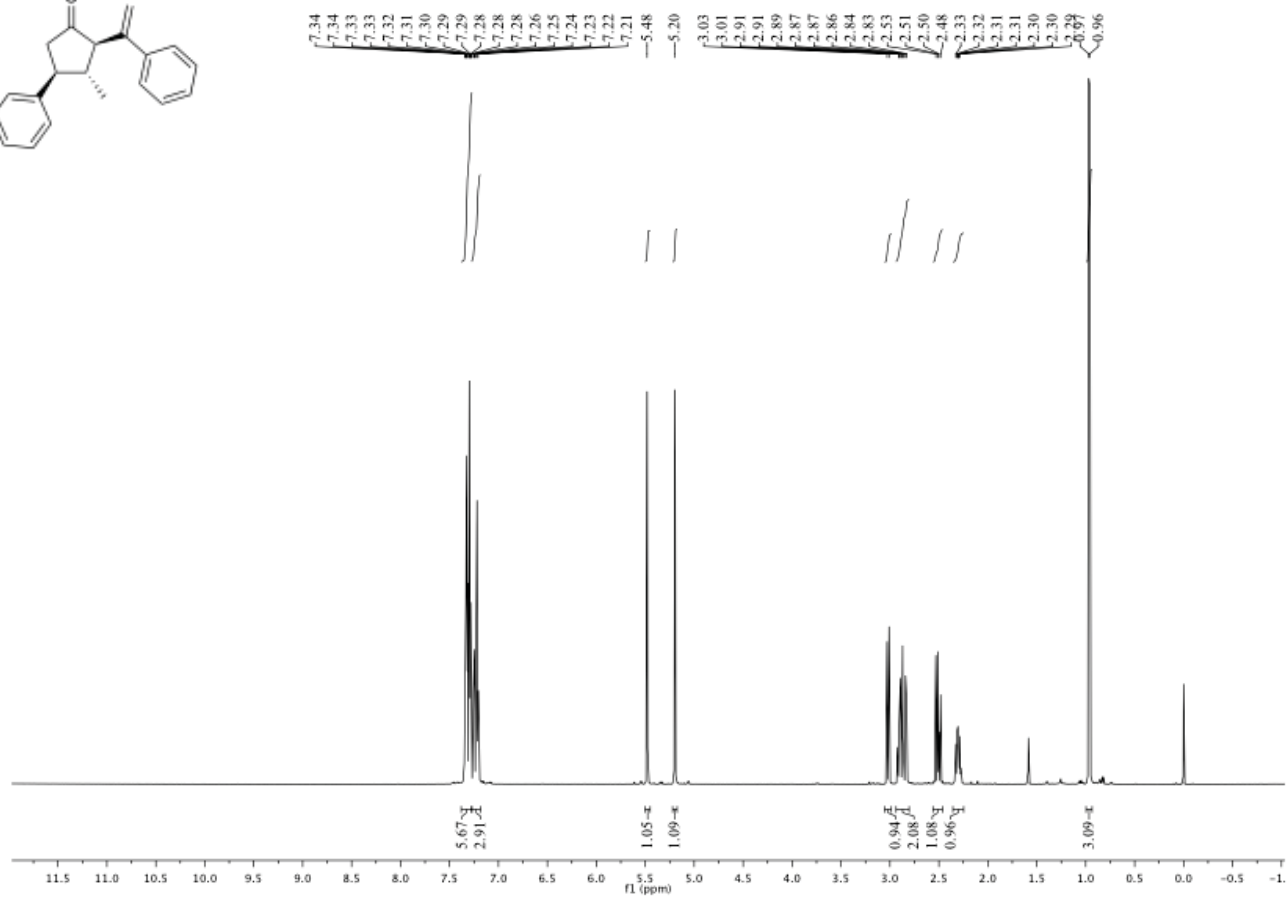
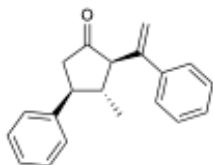
Supplementary Figure 30. ¹³C NMR Spectrum of 24c



Supplementary Figure 31. ¹H NMR Spectrum of 24d

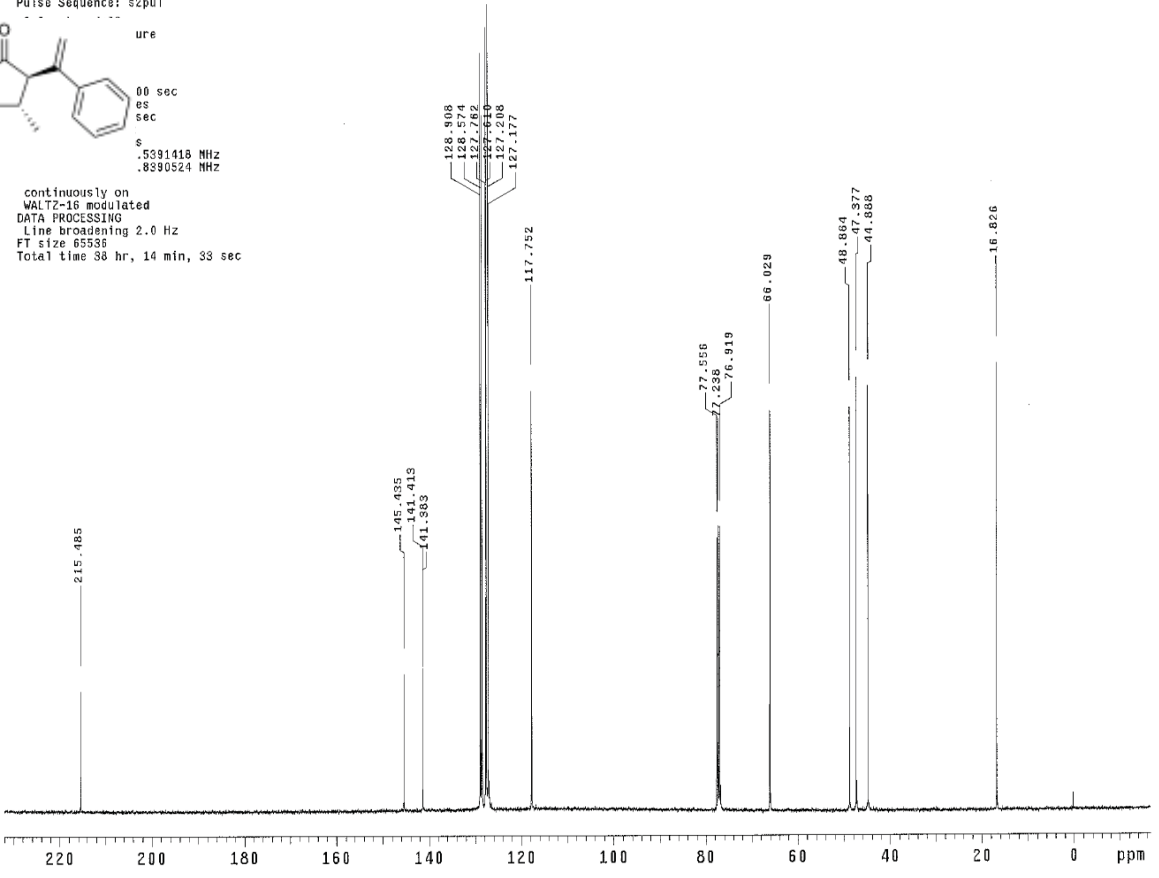
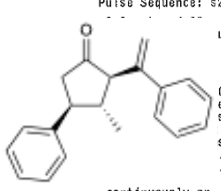


Supplementary Figure 32. ^{13}C NMR Spectrum of 24d

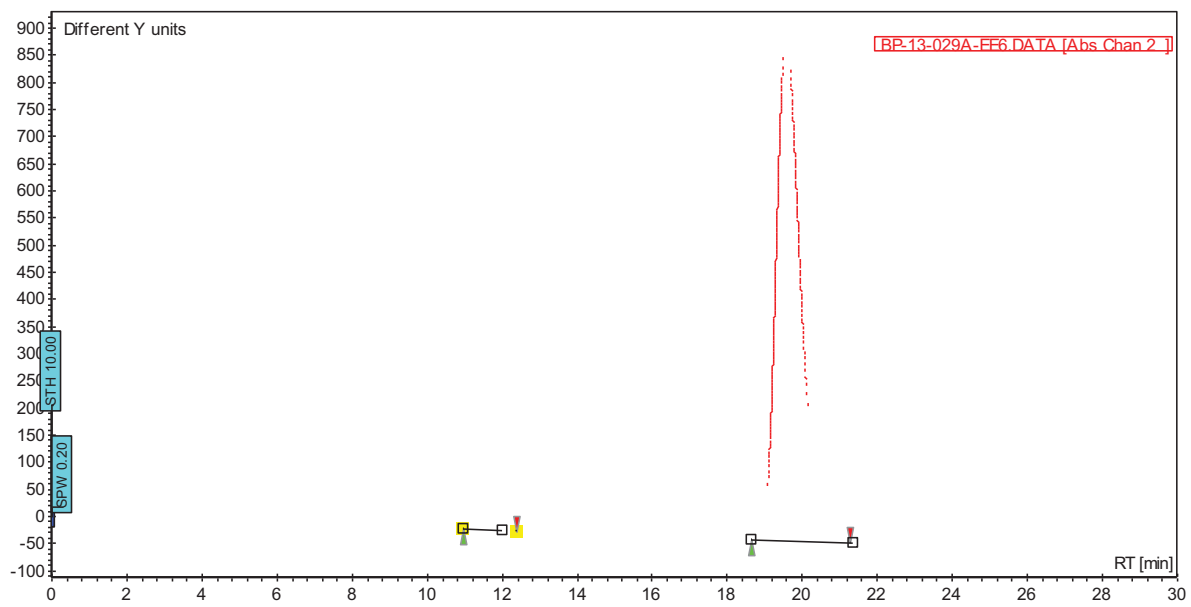


Supplementary Figure 33. ¹H NMR Spectrum of 25

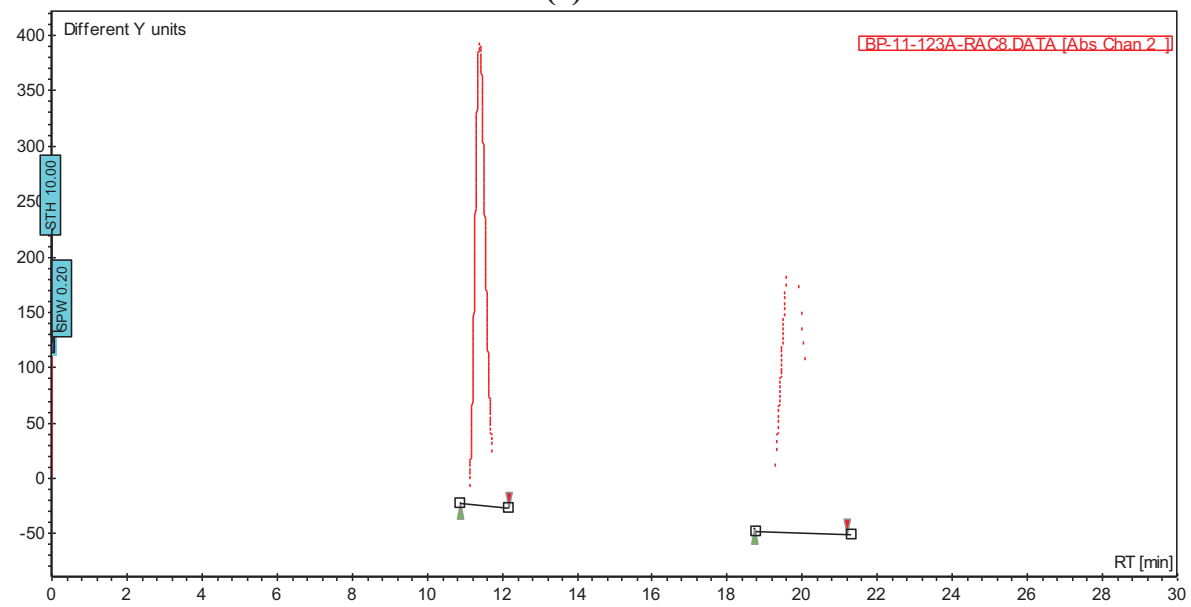
Pulse Sequence: s2pul
 ure
 00 sec
 65 sec
 6
 5391418 MHz
 8390524 MHz
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 2.0 Hz
 FT size 65536
 Total time 38 hr, 14 min, 33 sec



Supplementary Figure 34. ¹³C NMR Spectrum of 25

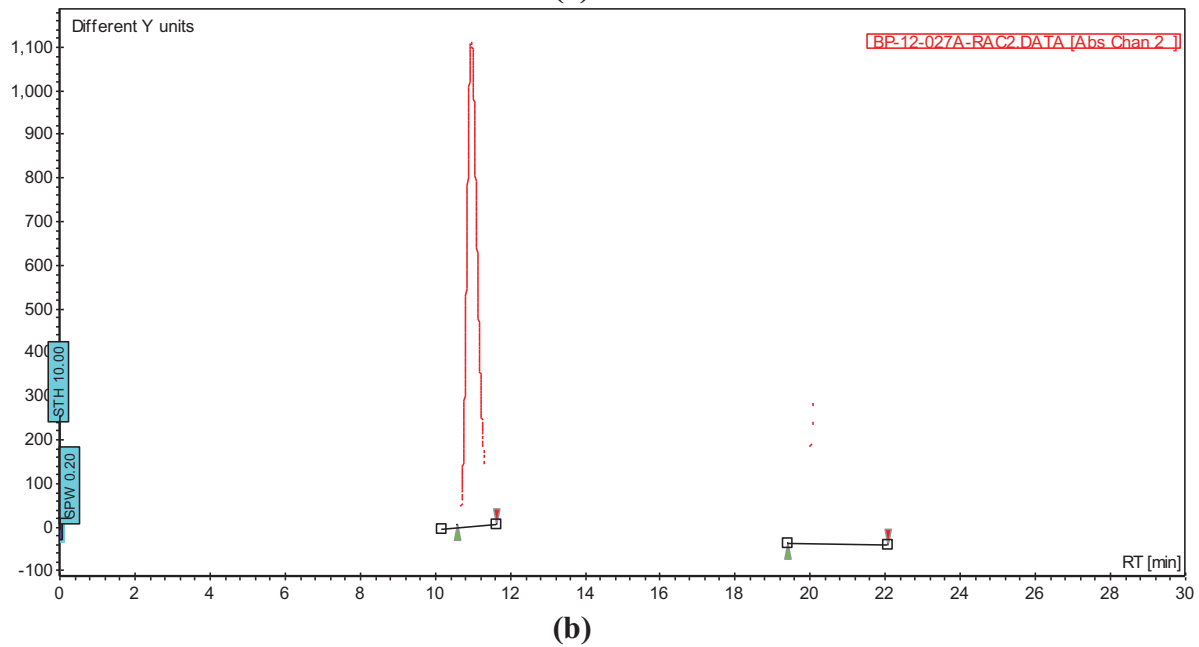
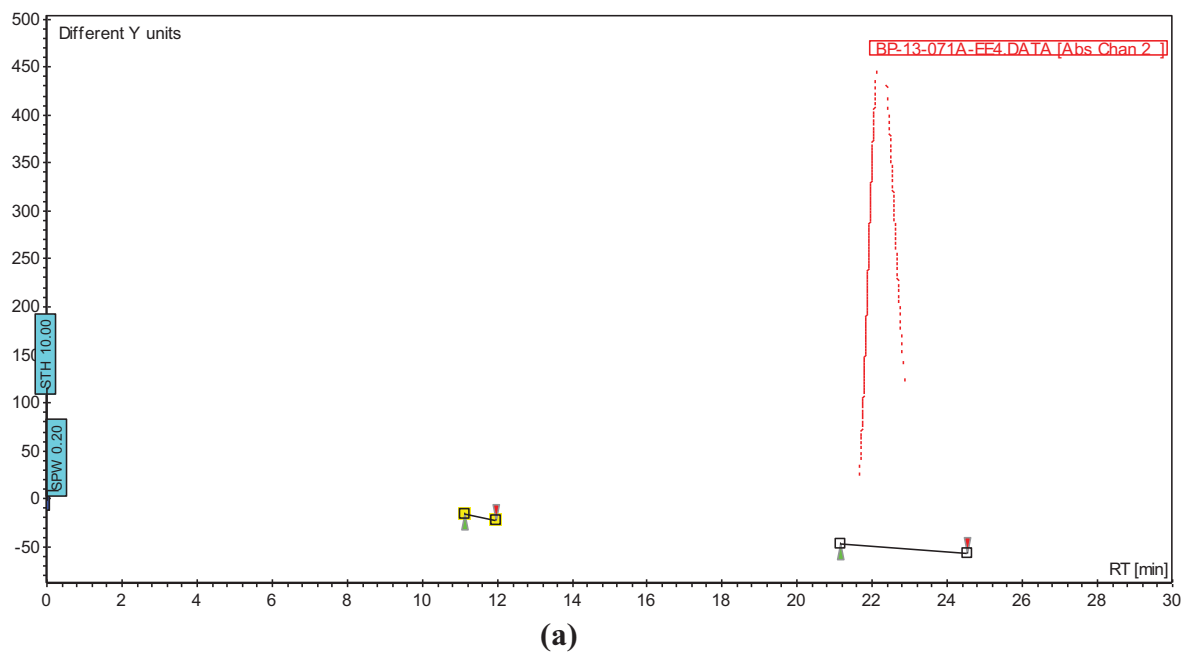


(a)

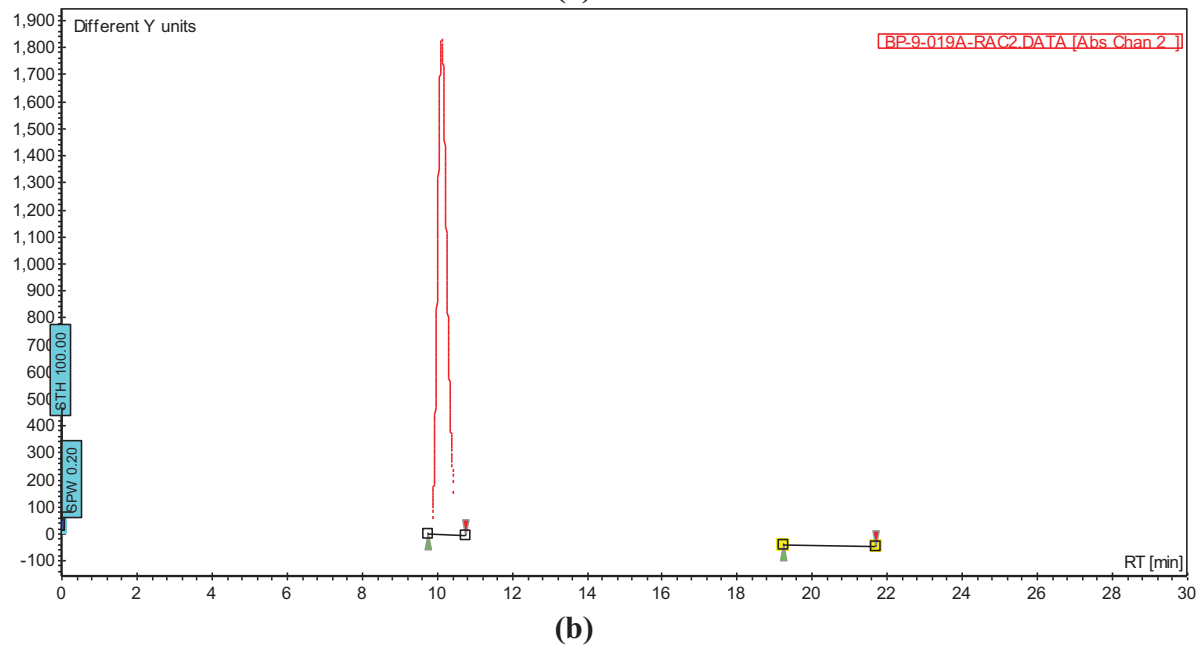
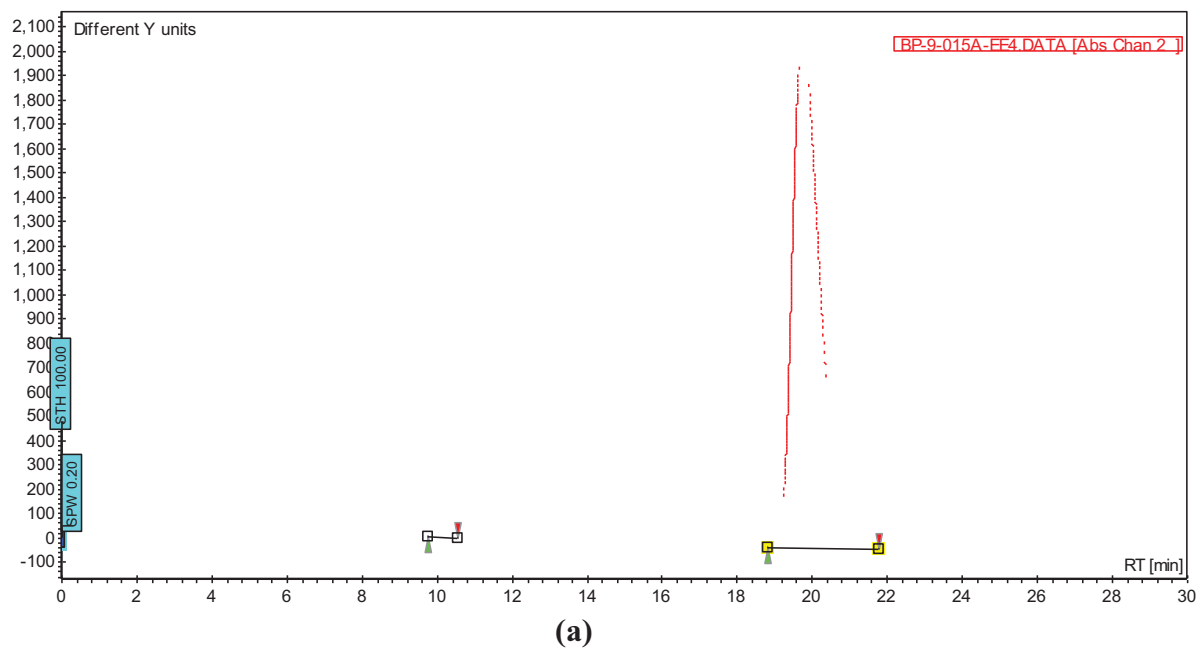


(b)

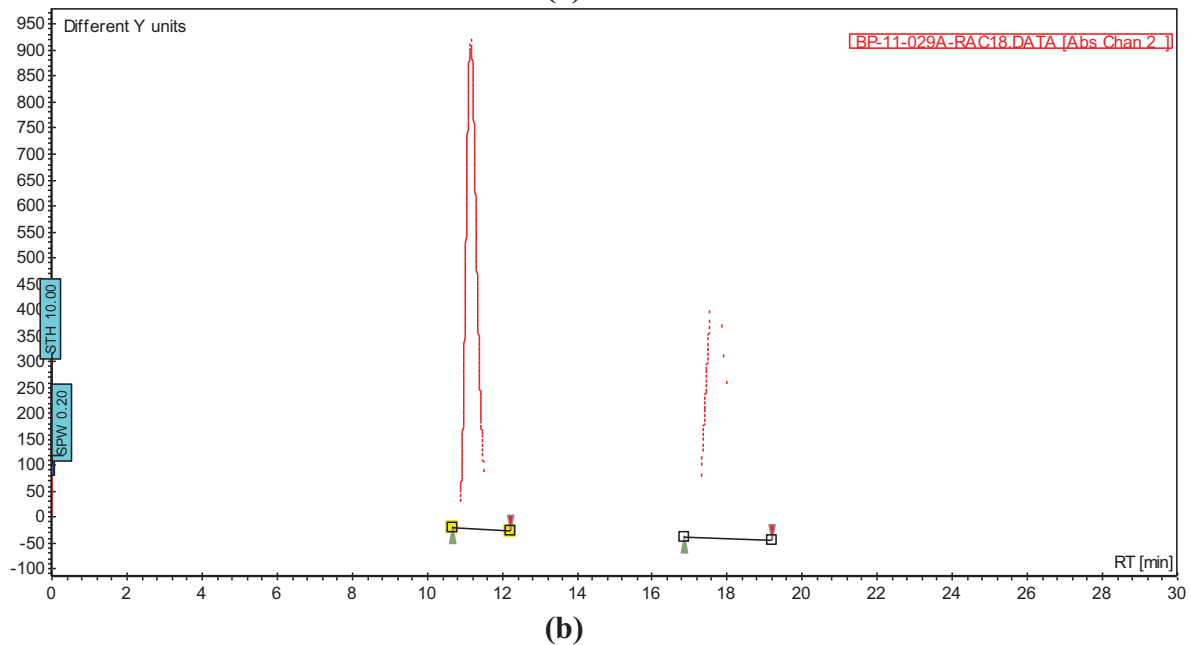
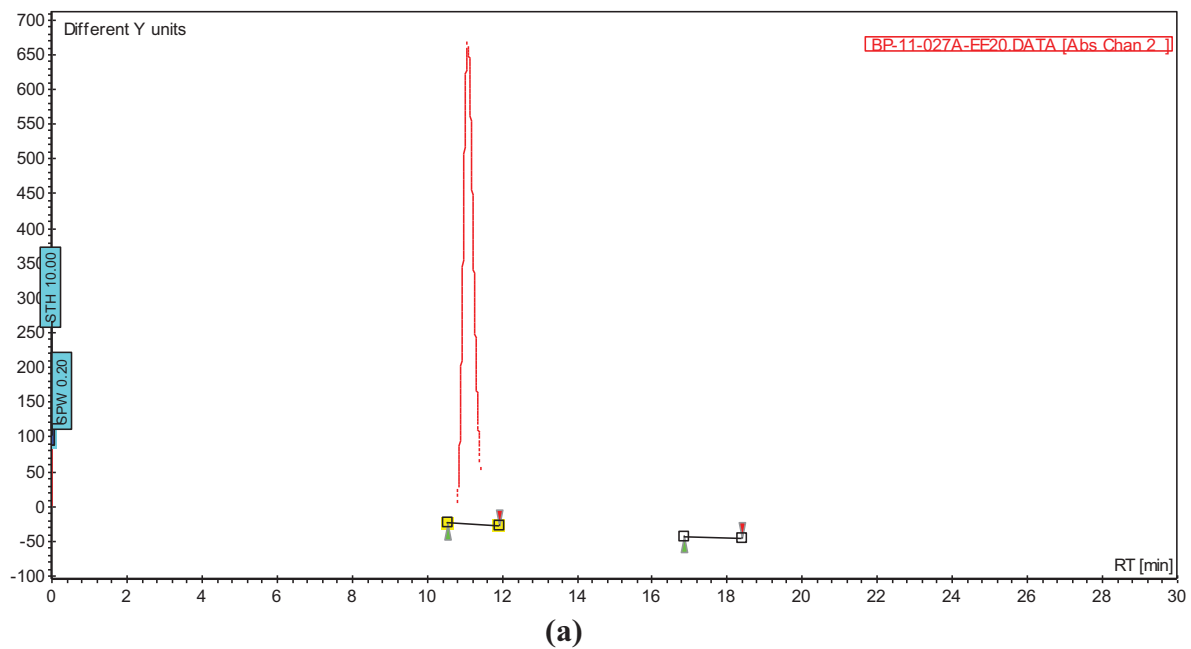
Supplementary Figure 35. (a) Enantioenriched and (b) Racemic HPLC Traces for 15



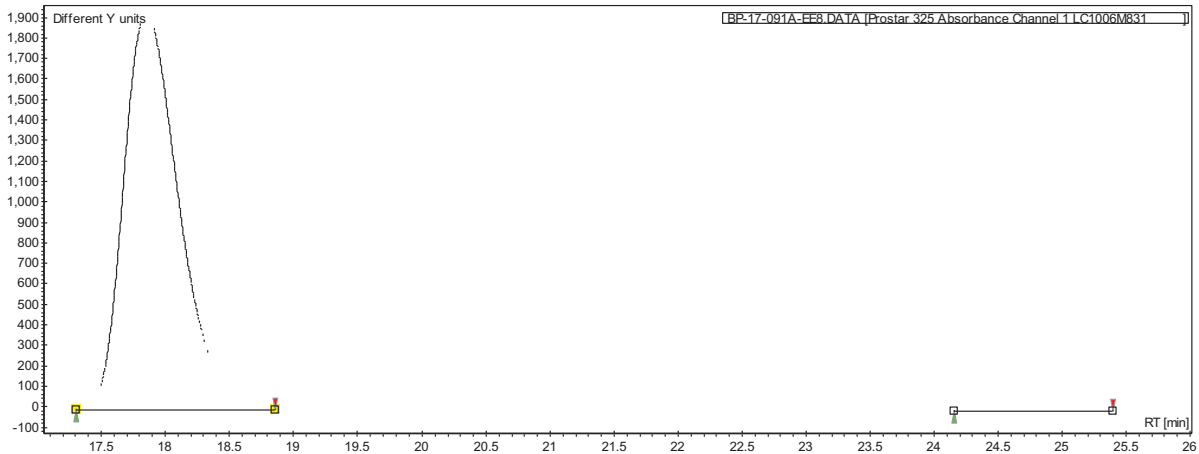
Supplementary Figure 36. (a) Enantioenriched and (b) Racemic HPLC Traces for 18a



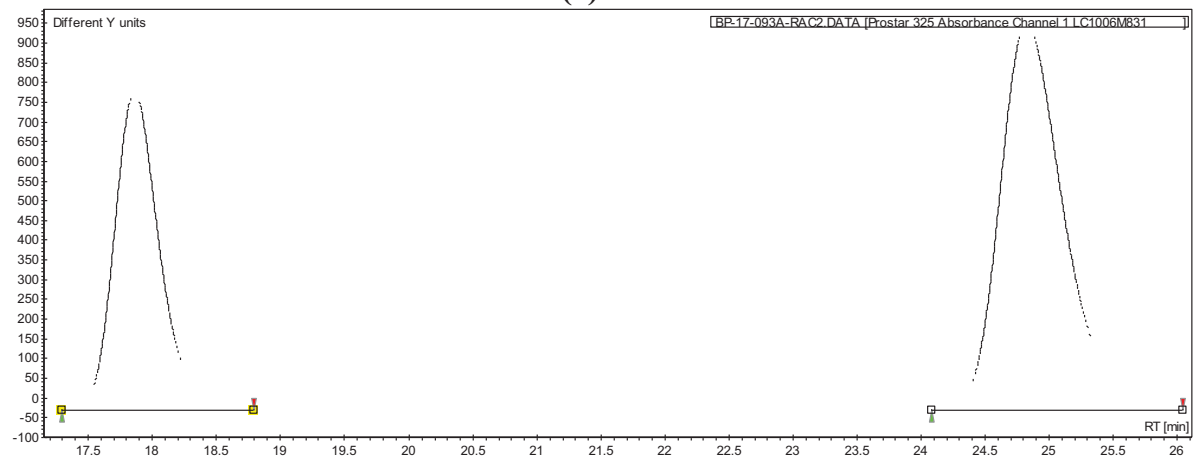
Supplementary Figure 37. (a) Enantioenriched and (b) Racemic HPLC Traces for 18b



Supplementary Figure 38. (a) Enantioenriched and (b) Racemic HPLC Traces for 18c

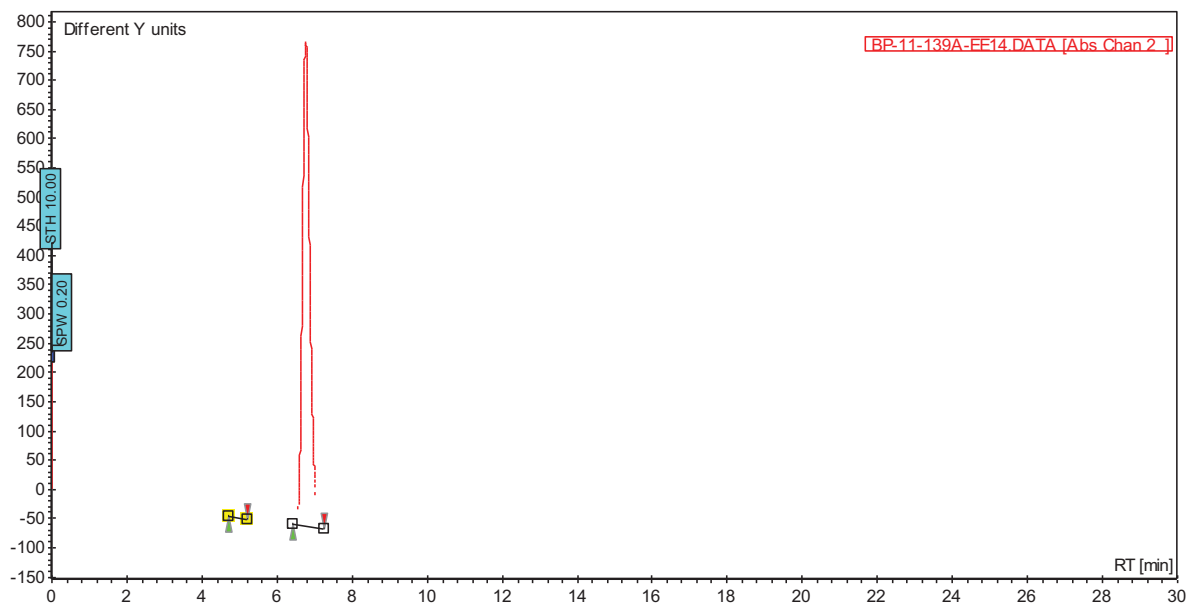


(a)

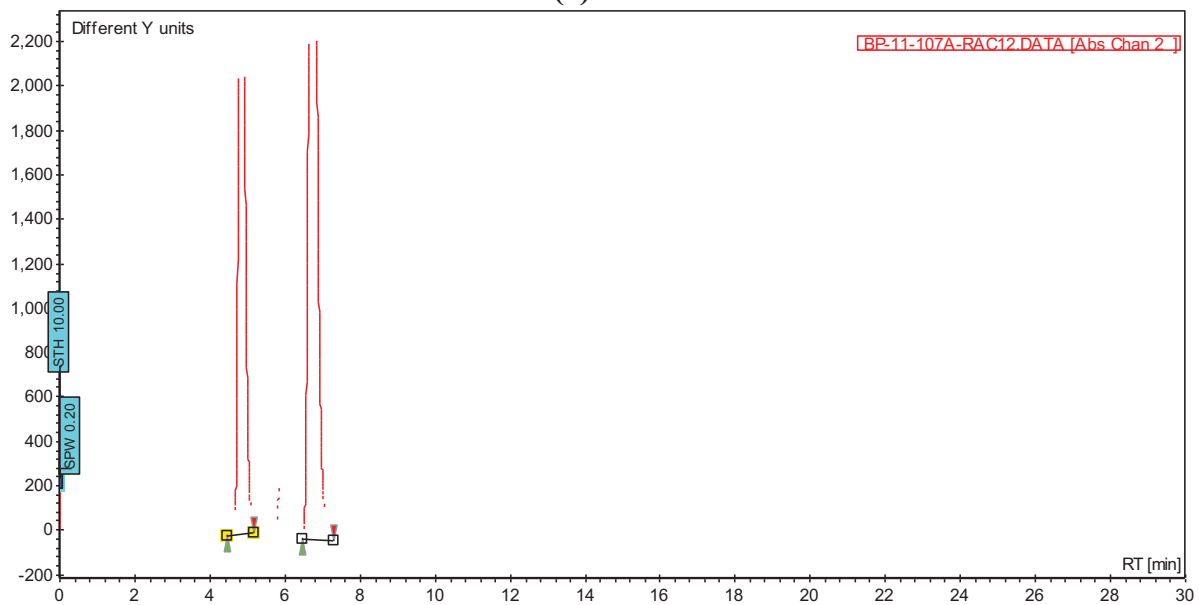


(b)

Supplementary Figure 39. (a) Enantioenriched and (b) Racemic HPLC Traces for 18d

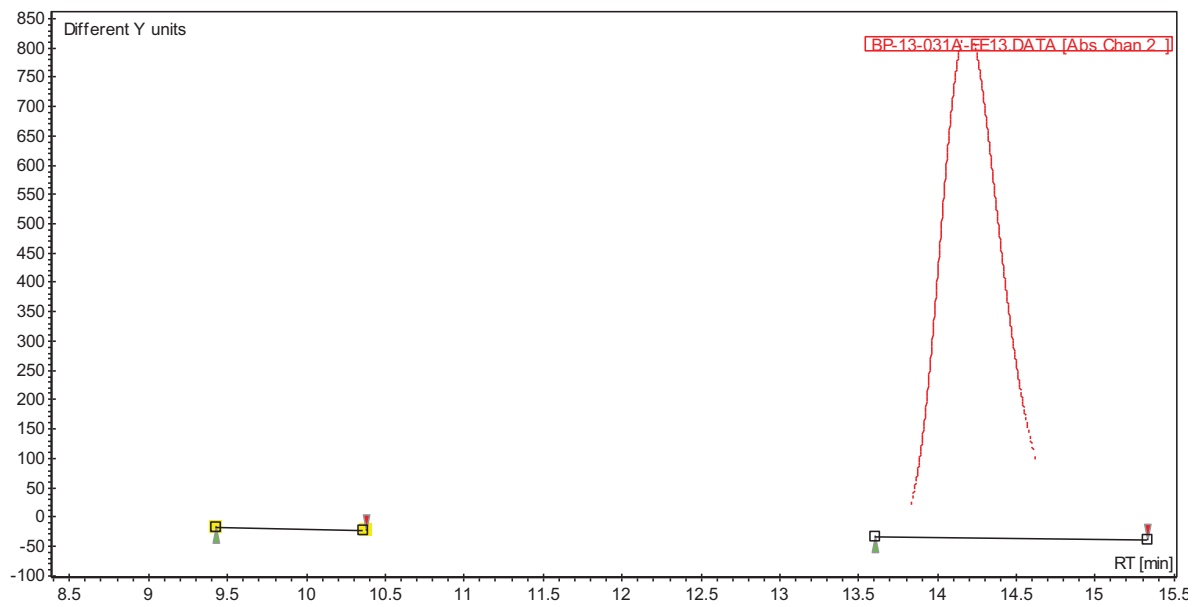


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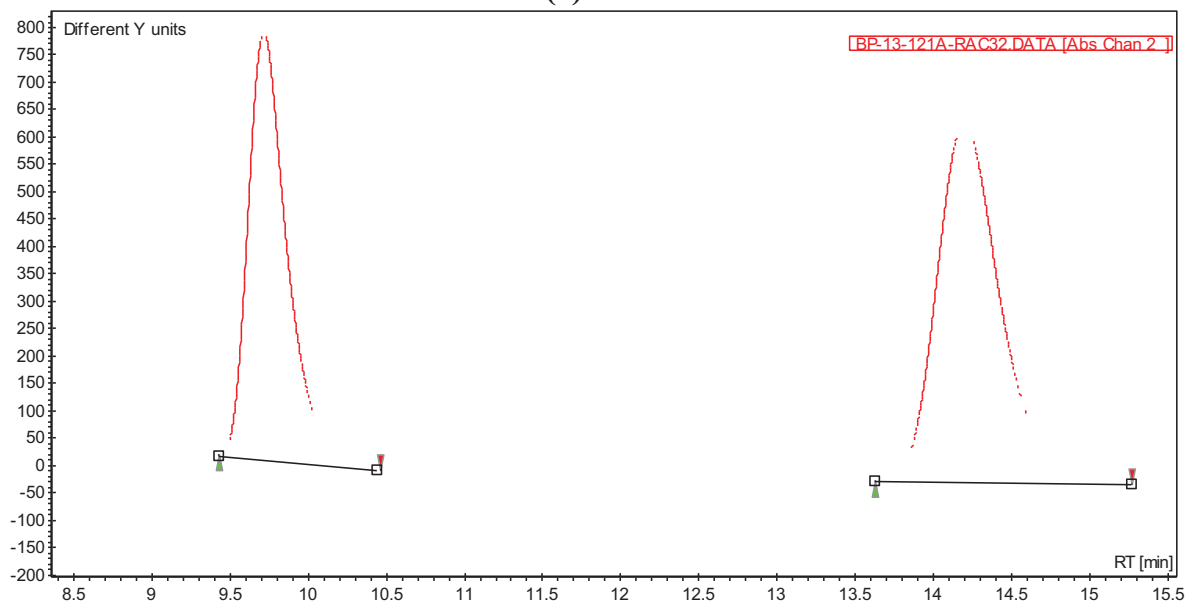


(b)

Supplementary Figure 40. (a) Enantioenriched and (b) Racemic HPLC Traces for 20a

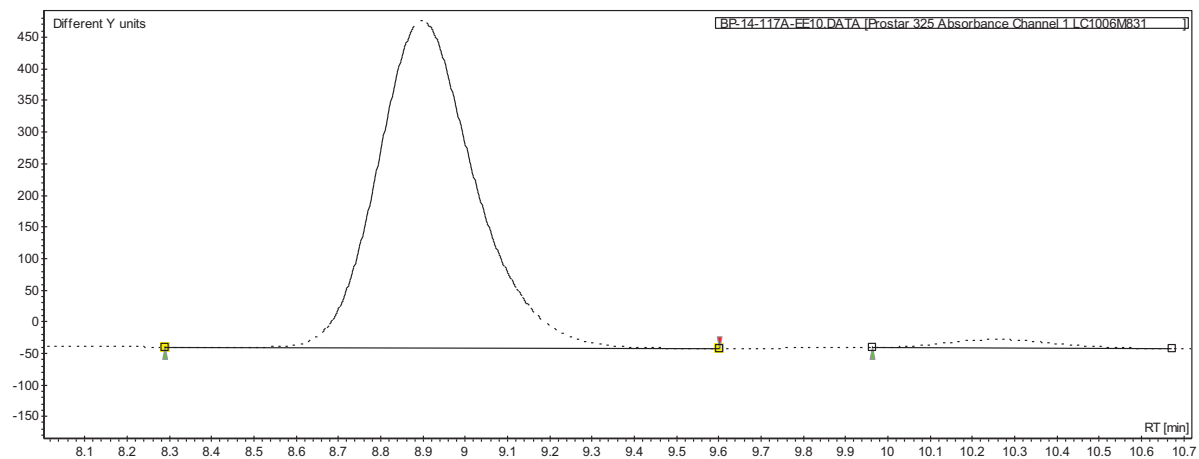


(a)

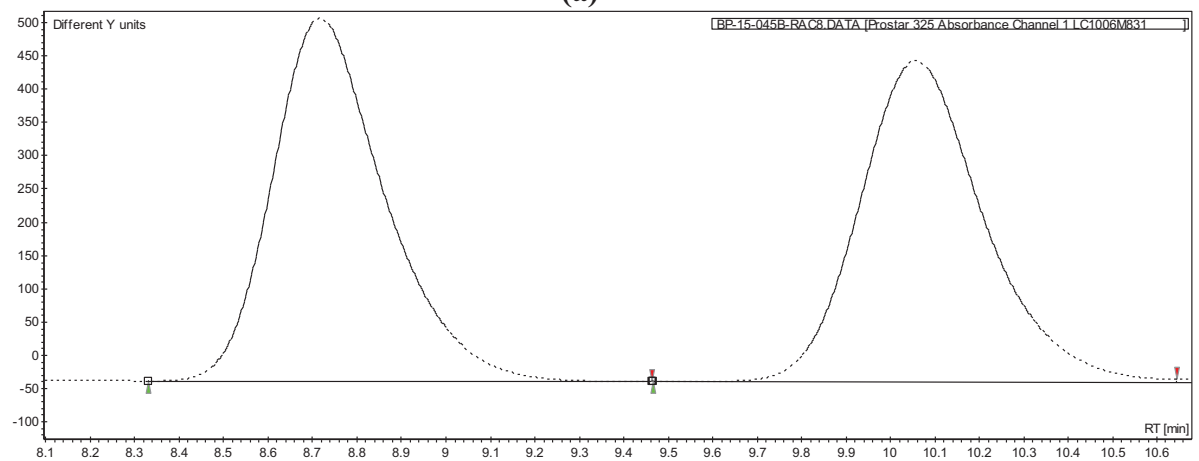


(b)

Supplementary Figure 41. (a) Enantioenriched and (b) Racemic HPLC Traces for 20b

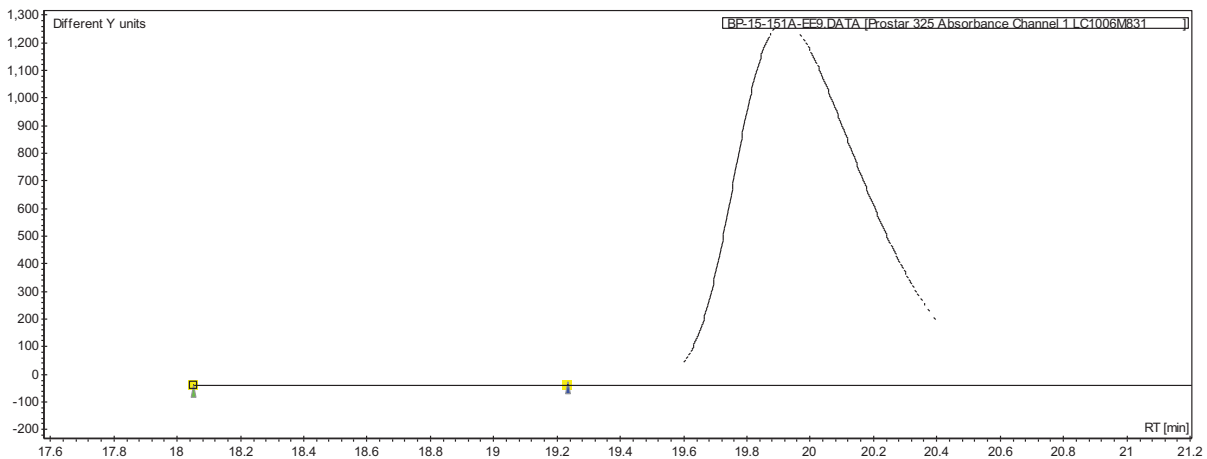


(a)

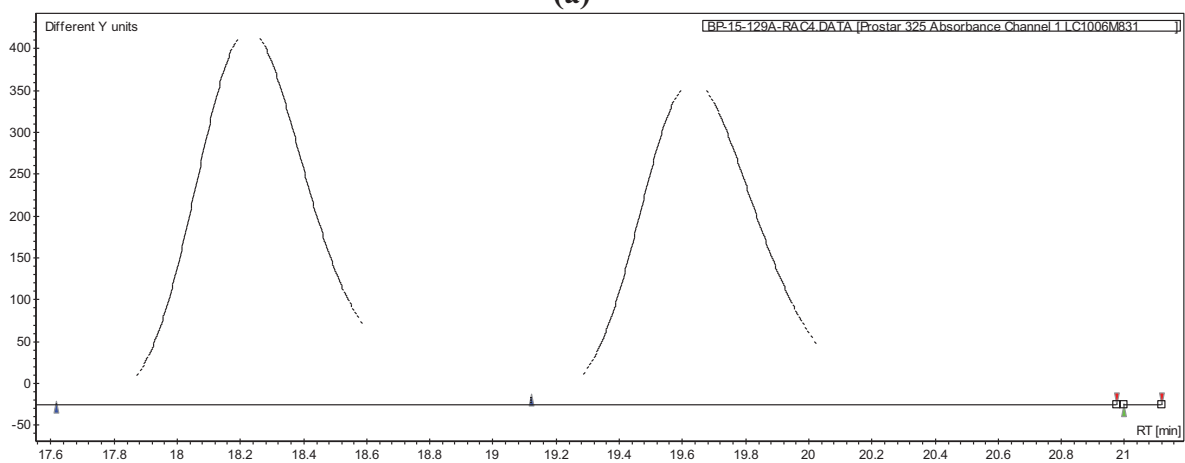


(b)

Supplementary Figure 42. (a) Enantioenriched and (b) Racemic HPLC Traces for 20c

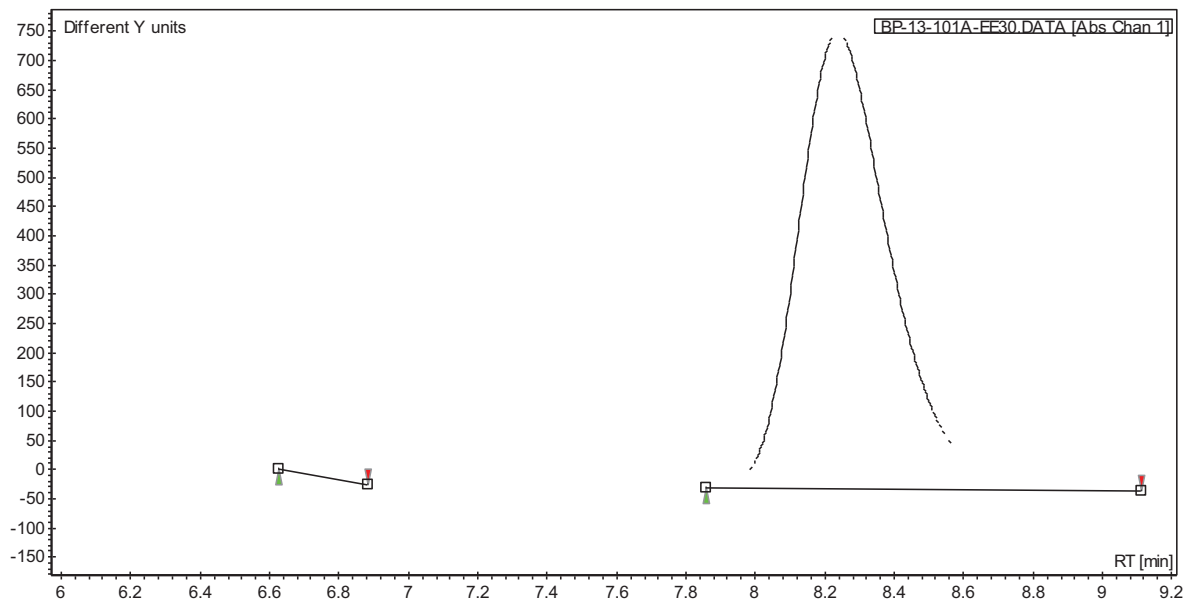


(a)

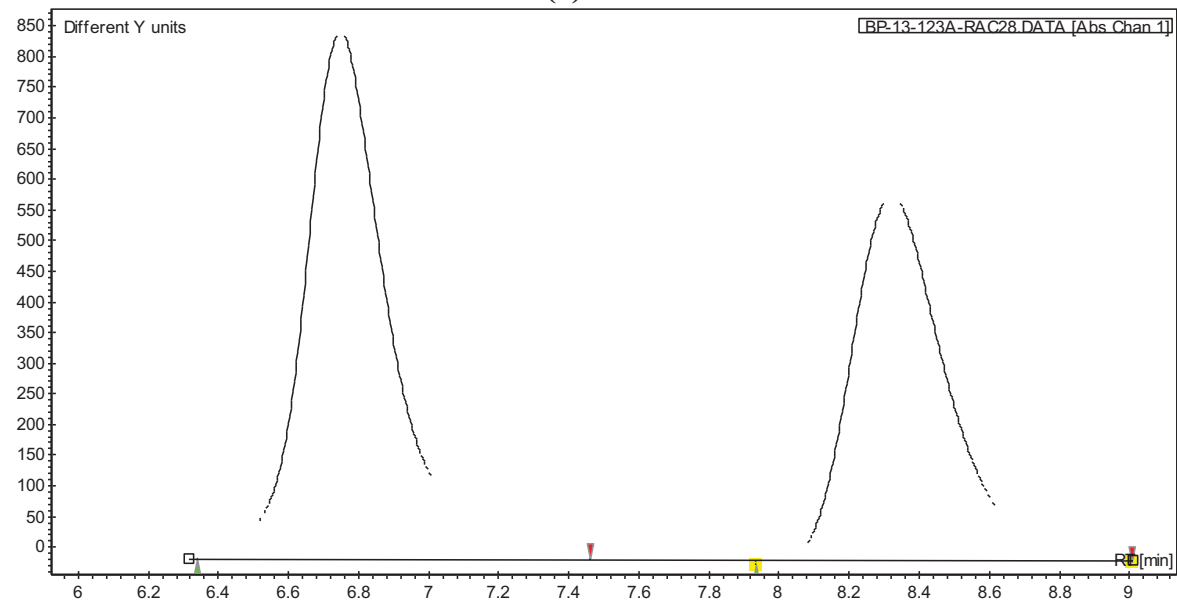


(b)

Supplementary Figure 43. (a) Enantioenriched and (b) Racemic HPLC Traces for 20d

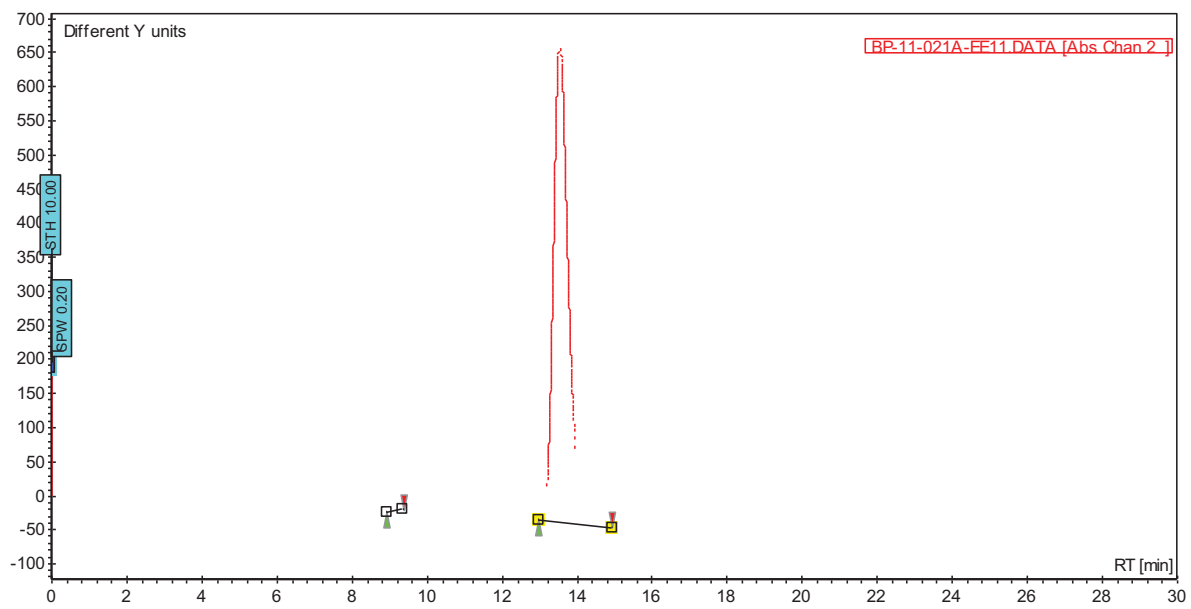


(a)

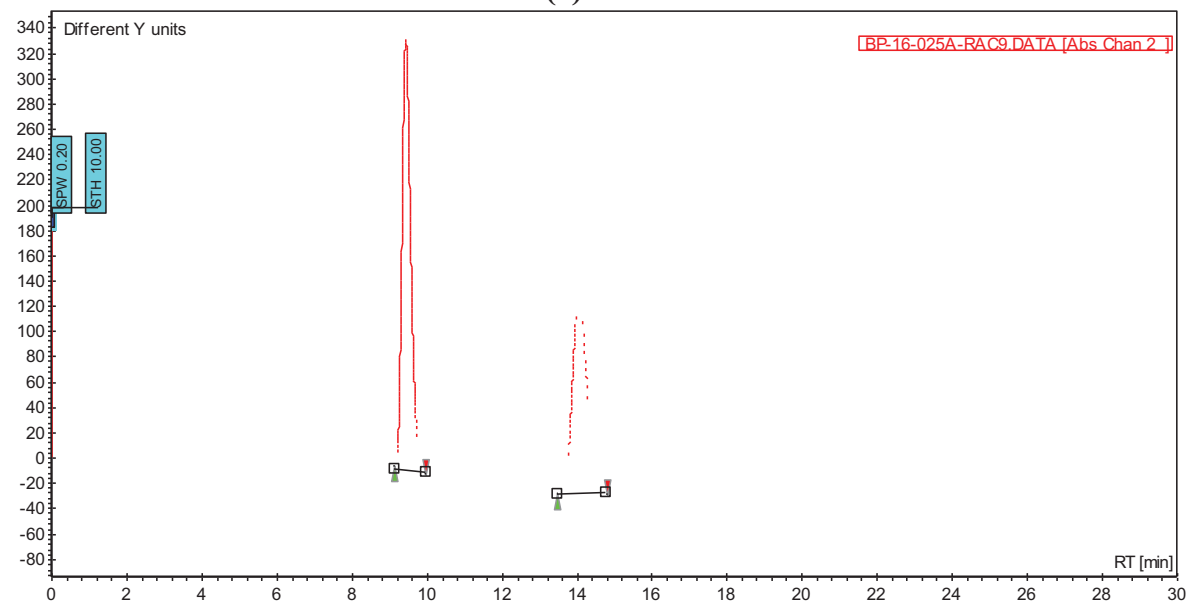


(b)

Supplementary Figure 44. (a) Enantioenriched and (b) Racemic HPLC Traces for 24a

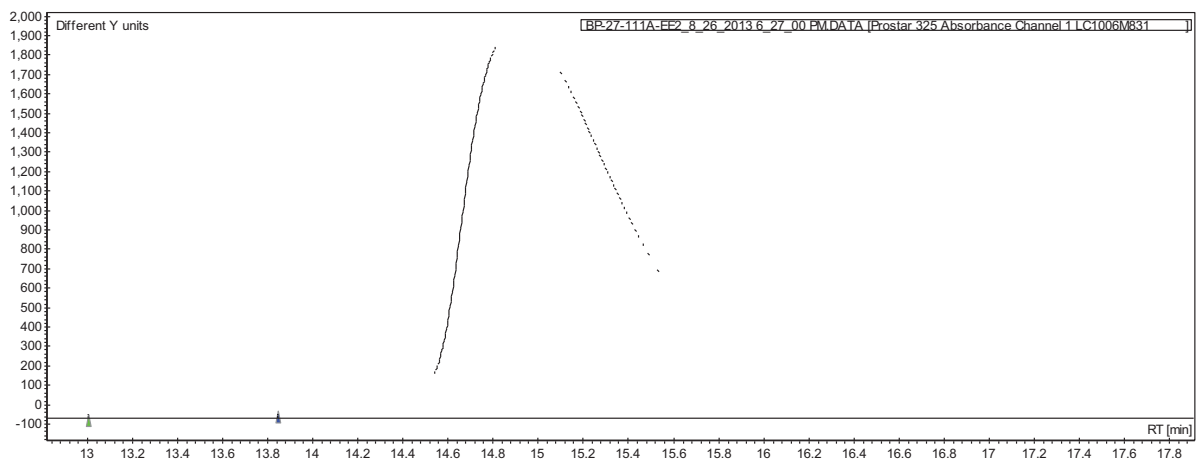


(a)

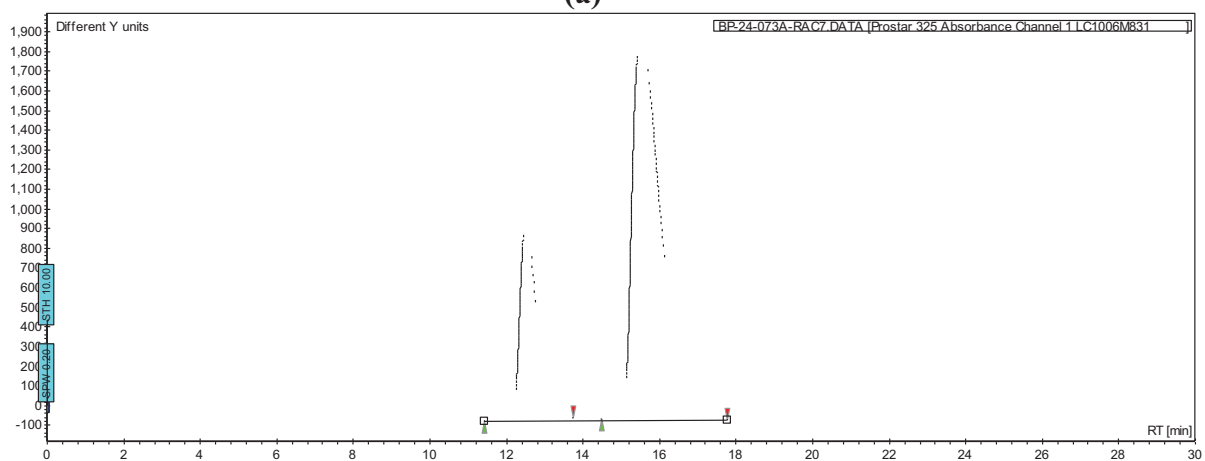


(b)

Supplementary Figure 45. (a) Enantioenriched and (b) Racemic HPLC Traces for 24b

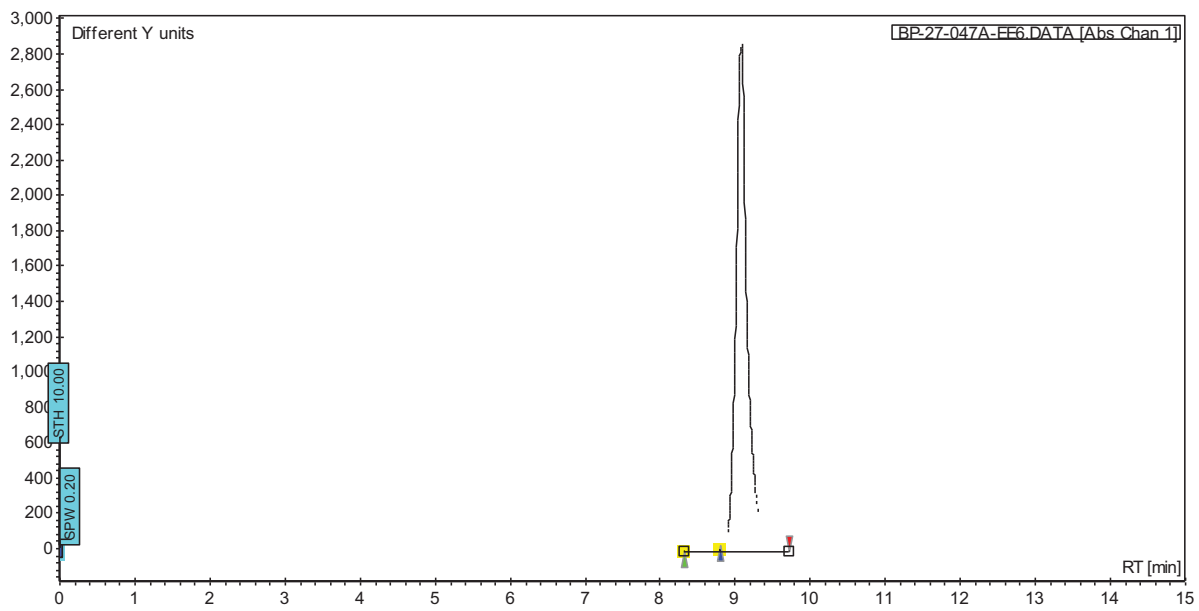


(a)

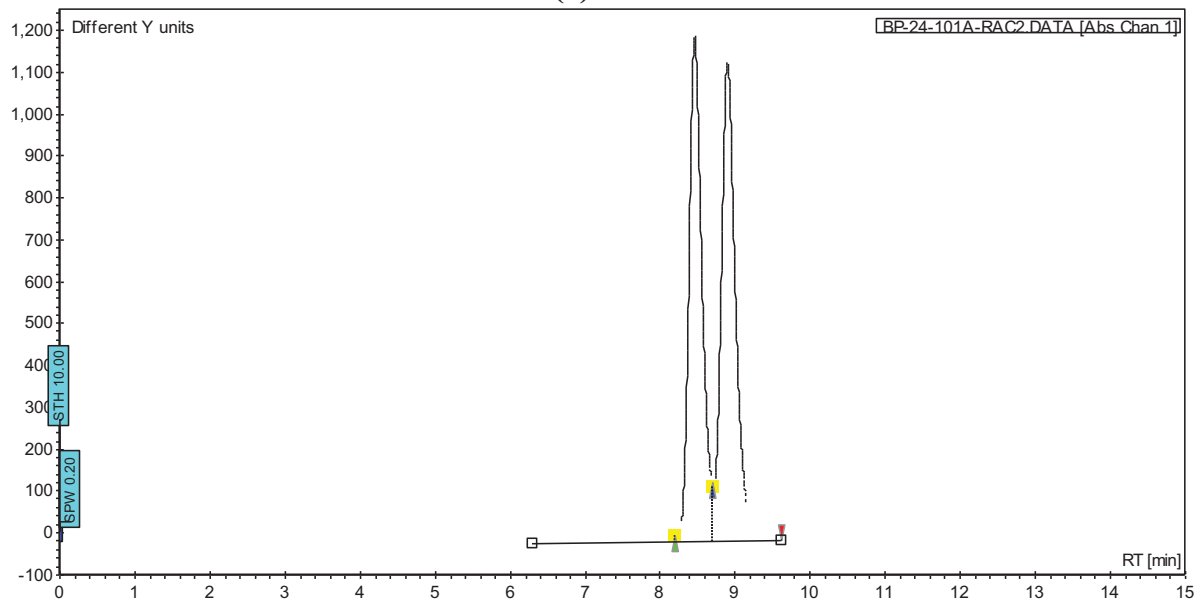


(b)

Supplementary Figure 46. (a) Enantioenriched and (b) Racemic HPLC Traces for 24c

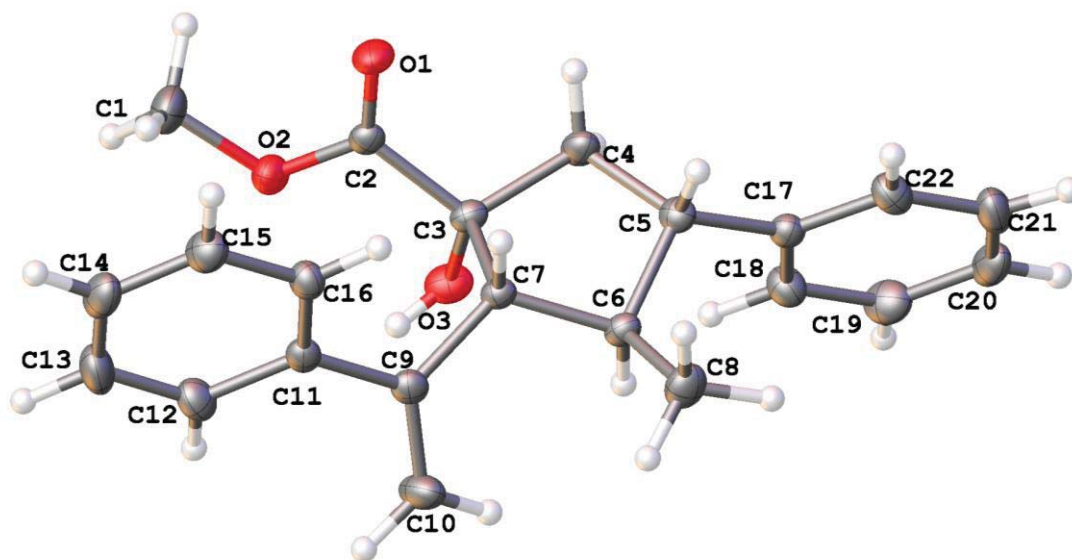


(a)



(b)

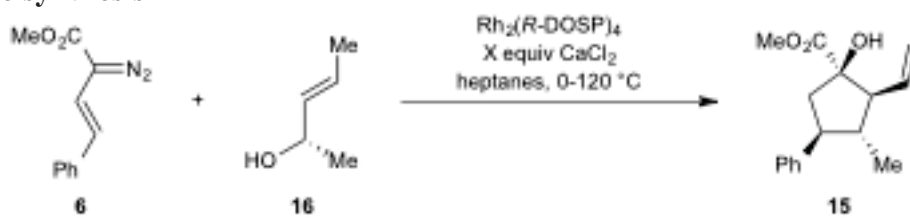
Supplementary Figure 47. (a) Enantioenriched and (b) Racemic HPLC Traces for 24d



Supplementary Figure 48. ORTEP Diagram of 24a

Supplementary Tables

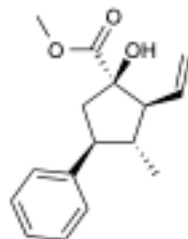
Supplementary Table 1. Effect of calcium chloride on the catalyst loading for the cyclopentane synthesis



entry	$\text{Rh}_2(\text{R-DOSP})_4$	CaCl_2 , equiv	yield, % ^a	dr ^b	ee, % ^c
1	0.1 mol %	-	45	88 : 12	86
2	0.5 mol %	2.0	68	88 : 12	91
3	0.1 mol %	2.0	66	89 : 11	92
4	0.01 mol %	2.0	51	87 : 13	90
5	0.001 mol %	2.0	8	87 : 13	90

^a Isolated yields. ^b Determined by ^1H NMR of the crude residue. ^c Determined by HPLC on a chiral stationary phase.

Supplementary Methods



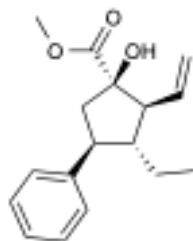
(-)-(1R,2S,3R,4S)-methyl 1-hydroxy-3-methyl-4-phenyl-2-vinylcyclopentanecarboxylate

(15)

Prepared by *General Procedure 1.2.1* with **6** (121 mg, 0.60 mmol, 1.2 equiv), **16** (43 mg, 0.50 mmol, 1.0 equiv), Rh₂(*R*-DOSP)₄ (0.9 mg, 0.0005 mmol, 0.1 mol %), and CaCl₂ (111 mg, 1.0 mmol, 2.0 equiv), heating to 125 °C for 40 h. Purification by flash chromatography (SiO₂, pentane/Et₂O, 10:1) afforded the title compound as a colorless oil (85 mg, 66% yield). A minor component eluted second off the column, which ¹H NMR analysis indicated to contain a mixture of **15** and *epi*-**15**. Preparative HPLC of the mixture (hexanes/*i*-propanol, 99:1) afforded a small quantity of pure *epi*-**15**.

[α]_D²⁰ -7.2° (*c* 1.65, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.29-7.33 (m, 4H), 7.19-7.23 (m, 1H), 5.79 (ddd, *J* = 17.2, 10.2, 8.8 Hz, 1H), 5.19 (dd, *J* = 10.2, 2.0 Hz, 1H), 5.07 (m, 1H), 3.81 (s, 1H), 3.17 (s, 1H), 2.72-2.86 (m, 2H), 2.43 (dd, *J* = 11.8, 8.8 Hz, 1H), 2.12-2.23 (m, 1H), 2.01 (dd, *J* = 13.6, 7.2 Hz, 1H), 0.87 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 176.9, 144.4, 134.8, 128.7, 128.0, 126.5, 119.1, 82.7, 62.0, 53.1, 52.5, 46.8, 46.5, 16.1; IR (neat): 3521, 3075, 3027, 2953, 2923, 2868, 1728, 1638, 1602, 1494, 1455, 1437 cm⁻¹; HRMS (*m/z*): [M+H]⁺ calc for C₁₆H₂₀NaO₃, 283.1305; found, 283.1305; HPLC: 91% ee, CHIRALCEL ODR, 0.5% isopropanol/hexanes, 0.5 mL/min, UV: 210 nm, *t*_R: 11.4 min (minor), 19.6 min (major); ¹H NMR (*epi*-**15**) (600 MHz, CDCl₃): δ 7.34-7.28 (m, 4H), 7.24-7.20 (m, 1H), 5.94 (dt, *J* = 16.8, 10.8 Hz, 1H), 5.16 (dd, *J* = 16.2, 2.1 Hz, 1H), 5.04 (dd, *J* = 17.4, 2.1 Hz, 1H), 3.82 (s, 3H), 3.16-3.07 (m,

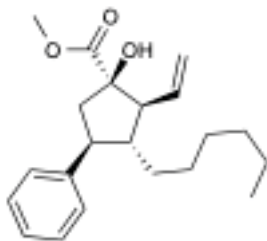
3H), 2.42-2.33 (m, 2H), 2.19 (dd, $J = 13.0, 7.0$ Hz, 1H), 0.98 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (*epi-15*) (100 MHz, CDCl_3): δ 176.5, 144.2, 134.4, 128.7, 127.7, 126.6, 118.6, 84.1, 56.8, 53.1, 52.7, 46.6, 45.0, 16.8.



(-)-(1*R*,2*S*,3*R*,4*S*)-methyl 3-ethyl-1-hydroxy-4-phenyl-2-vinylcyclopentanecarboxylate (18a**)**

Prepared by *General Procedure 1.2.1* with **6** (121 mg, 0.60 mmol, 1.2 equiv), **17a** (50 mg, 0.50 mmol, 1.0 equiv), $\text{Rh}_2(\text{R-DOSP})_4$ (0.9 mg, 0.0005 mmol, 0.1 mol %), and CaCl_2 (111 mg, 1.0 mmol, 2.0 equiv), heating to 125 °C for 40 h. Purification by flash chromatography (SiO_2 , pentane/ Et_2O , 12:1) afforded the title compound as a colorless oil (91 mg, 66% yield).

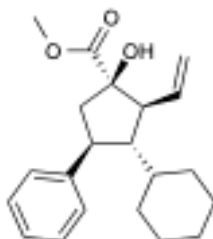
$[\alpha]_D^{20} -17.1^\circ$ (c 2.15, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.28-7.36 (m, 4H), 7.17-7.21 (m, 1H), 5.82 (ddd, $J = 18.4, 10.0, 8.8$ Hz, 1H), 5.16 (dd, $J = 10.0, 1.6$ Hz, 1H), 5.06 (dd, $J = 18.4, 1.6$ Hz, 1H), 3.81 (s, 3H), 3.17 (s, 1H), 2.94 (ddd, $J = 10.0, 7.2, 7.2$ Hz, 1H), 2.81 (dd, $J = 14.4, 10.8$ Hz, 1H), 2.59 (dd, $J = 11.8, 9.0$ Hz, 1H), 2.20-2.28 (m, 1H), 1.95 (dd, $J = 14.4, 7.4$ Hz, 1H), 1.33-1.45 (m, 2H), 0.73 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 176.7, 145.4, 135.7, 128.6, 128.2, 126.4, 118.7, 83.1, 59.5, 53.0, 52.1, 49.4, 47.1, 23.6, 10.9; IR (neat): 3520, 3027, 2956, 2918, 2877, 1728, 1638, 1602, 1494, 1456, 1437 cm^{-1} ; HRMS (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{23}\text{NaO}_3$, 2971.1461; found, 297.1462; HPLC: 93% ee, CHIRALCEL ODR, 0.5% isopropanol/hexanes, 0.5 mL/min, UV: 210 nm, t_R : 11.5 min (minor), 22.2 min (major).



**(-)-(1*R*,2*S*,3*R*,4*S*)-methyl 3-hexyl-1-hydroxy-4-phenyl-2-vinylcyclopentanecarboxylate
(18b)**

Prepared by *General Procedure 1.2.1* with **6** (121 mg, 0.60 mmol, 1.2 equiv), **17b** (78 mg, 0.50 mmol, 1.0 equiv), Rh₂(*R*-DOSP)₄ (0.9 mg, 0.0005 mmol, 0.1 mol %), and CaCl₂ (111 mg, 1.0 mmol, 2.0 equiv), heating to 125 °C for 28 h. Purification by flash chromatography (SiO₂, pentane/Et₂O, 15:1) afforded the title compound as a colorless oil (118 mg, 71% yield).

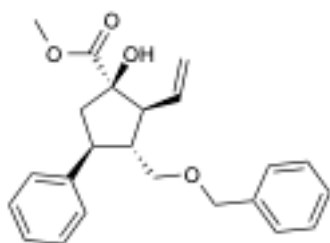
[α]_D²⁰ -1.4° (*c* 1.72, CHCl₃); ¹H NMR (600 MHz, CDCl₃): δ 7.33 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.6 Hz, 1H), 5.82 (ddd, *J* = 17.4, 10.3, 9.0 Hz, 1H), 5.16 (dd, *J* = 10.3, 1.9 Hz, 1H), 5.06 (dd, *J* = 17.4, 1.9 Hz, 1H), 3.80 (s, 3H), 3.16 (s, 1H), 2.92 (dt, *J* = 10.2, 7.2 Hz, 1H), 2.81 (dd, *J* = 14.4, 10.2 Hz, 1H), 2.56 (dd, *J* = 12.0, 9.0 Hz, 1H), 2.27 (dtd, *J* = 11.4, 11.4, 5.4 Hz, 1H), 1.94 (dd, *J* = 14.4, 7.2 Hz, 1H), 1.28-1.39 (m, 2H), 1.05-1.19 (m, 8H), 0.80 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 176.5, 145.3, 135.5, 128.4, 128.0, 126.1, 118.5, 83.0, 60.1, 52.8, 50.6, 50.1, 47.0, 31.6, 31.4, 29.5, 26.3, 22.5, 14.0; IR (neat): 3525, 3063, 3027, 2953, 2925, 2855, 1730, 1638, 1602, 1494, 1456, 1437 cm⁻¹; HRMS (*m/z*): [M-OH]⁺ calcd for C₂₁H₂₉O₂, 313.2162; found, 313.2164; HPLC: 92% ee, CHIRALCEL ODR, 0.5% isopropanol/hexanes, 0.5 mL/min, UV: 210 nm, *t*_R: 10.1 min (minor), 19.7 min (major).



(+)-(1*R*,2*S*,3*R*,4*S*)-methyl 3-cyclohexyl-1-hydroxy-4-phenyl-2-vinylcyclopentanecarboxylate (18c).

Prepared by *General Procedure 1.2.1* with **6** (121 mg, 0.60 mmol, 1.2 equiv), **17c** (77 mg, 0.50 mmol, 1.0 equiv), Rh₂(*R*-DOSP)₄ (0.9 mg, 0.0005 mmol, 0.1 mol %), and CaCl₂ (111 mg, 1.0 mmol, 2.0 equiv), heating to 125 °C for 40 h. Purification by flash chromatography (SiO₂, pentane/Et₂O, 12:1) afforded the title compound as a white solid (115 mg, 70% yield).

mp = 80–82 °C; [α]_D²⁰ +4.1° (*c* 1.89, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.34-7.36 (m, 2H), 7.27-7.31 (m, 2H), 7.16-7.20 (m, 1H), 5.82 (m, 1H), 5.14 (dd, *J* = 10.4, 1.6 Hz, 1H), 5.03 (m, 1H), 3.79 (s, 3H), 3.17 (s, 1H), 3.10 (ddd, *J* = 10.8, 6.8, 6.8 Hz, 1H), 2.72-2.79 (m, 2H), 2.27-2.33 (m, 1H), 1.88 (dd, *J* = 14.2, 6.8 Hz, 1H), 1.56-1.66 (m, 3H), 1.47 (m, 2H), 1.31-1.39 (m, 1H), 0.95-1.26 (m, 4H), 0.79-0.89 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 176.7, 146.2, 136.8, 128.6, 128.3, 126.2, 118.3, 83.5, 57.0, 56.0, 53.0, 47.2, 46.3, 38.2, 30.6, 30.5, 27.2, 27.2, 26.9; IR (neat): 3513, 3026, 2921, 2851, 1727, 1639, 1601, 1495, 1440 cm⁻¹; HRMS (*m/z*): [M+Na]⁺ calcd for C₂₁H₂₈NaO₃, 351.1931; found, 351.1934; HPLC: 90% ee, CHIRALCEL ODR, 0.5% isopropanol/hexanes, 0.5 mL/min, UV: 210 nm, *t*_R: 11.1 min (major), 17.4 min (minor).

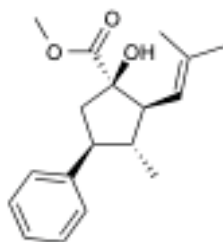


(+)-(1*R*,2*S*,3*R*,4*S*)-methyl 3-((benzyloxy)methyl)-1-hydroxy-4-phenyl-2-vinylcyclopentanecarboxylate (18d)

Prepared by *General Procedure 1.2.1* with **6** (121 mg, 0.60 mmol, 1.2 equiv), **17d** (96 mg, 0.50 mmol, 1.0 equiv), Rh₂(*R*-DOSP)₄ (0.9 mg, 0.0005 mmol, 0.1 mol %), and CaCl₂ (111 mg, 1.0

mmol, 2.0 equiv), heating to 125 °C for 36 h. Purification by flash chromatography (SiO₂, pentane/Et₂O, 6:1) afforded the title compound as a pale yellow oil (101 mg, 55% yield).

$[\alpha]_D^{20} +1.9^\circ$ (*c* 1.08, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.24 (m, 9H), 7.22-7.16 (m, 1H), 5.79 (ddd, *J* = 17.3, 10.3, 8.9 Hz, 1H), 5.17 (dd, *J* = 10.3, 2.0 Hz, 1H), 5.09 (dd, *J* = 17.3, 1.7 Hz, 1H), 4.50-4.37 (m, 2H), 3.81 (s, 3H), 3.42-3.31 (m, 3H), 3.24 (d, *J* = 0.8 Hz, 1H), 2.97 (dd, *J* = 12.0, 8.9 Hz, 1H), 2.84 (dd, *J* = 14.3, 11.2 Hz, 1H), 2.36-2.25 (m, 1H), 2.02 (dd, *J* = 14.4, 6.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 176.7, 145.0, 138.8, 134.5, 128.6, 128.5, 128.2, 127.8, 127.7, 126.4, 119.3, 83.0, 73.2, 67.3, 56.0, 53.1, 52.7, 46.0, 45.2; IR (neat): 3521, 3063, 2979, 2951, 2854, 2790, 1729, 1638, 1602, 1495, 1455, 1437 cm⁻¹; HRMS (*m/z*): [M+Na]⁺ calcd for C₂₃H₂₆NaO₄, 389.1723; found, 389.1726; HPLC: 92% ee, CHIRALPAK ADH, 1.0% isopropanol/hexanes, 1.0 mL/min, UV: 210 nm, *t*_R: 17.9 min (major), 24.7 min (minor).

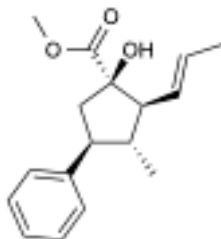


(-)-(1*R*,2*R*,3*R*,4*S*)-methyl 1-hydroxy-3-methyl-2-(2-methylprop-1-en-1-yl)-4-phenylcyclopentanecarboxylate (20a)

Prepared by *General Procedure 1.2.1* with **6** (121 mg, 0.60 mmol, 1.2 equiv), **19a** (57 mg, 0.50 mmol, 1.0 equiv), Rh₂(*R*-DOSP)₄ (0.9 mg, 0.0005 mmol, 0.1 mol %), and CaCl₂ (111 mg, 1.0 mmol, 2.0 equiv), heating to 125 °C for 48 h. Purification by flash chromatography (SiO₂, pentane/Et₂O, 12:1) afforded the title compound as a colorless oil (102 mg, 71% yield).

$[\alpha]_D^{20} -2.1^\circ$ (*c* 1.82, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.30-7.36 (m, 4H), 7.19-7.25 (m, 1H), 5.11 (d, *J* = 10.0 Hz, 1H), 3.80 (s, 3H), 3.06 (s, 1H), 2.68-2.89 (m, 3H), 2.05-2.15 (m, 1H), 2.08 (dd, *J* = 13.4, 4.8 Hz, 1H), 1.77 (s, 3H), 1.59 (s, 3H), 0.84 (d, *J* = 6.8 Hz, 3H); ¹³C NMR

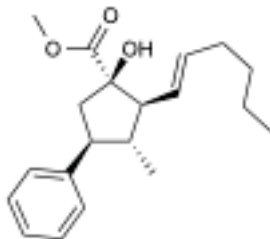
(100 MHz, CDCl₃): δ 177.3, 144.6, 136.9, 128.6, 128.0, 126.4, 120.8, 82.5, 56.5, 53.0, 52.6, 48.0, 46.8, 26.3, 18.5, 16.1; FTIR (neat): 3525, 3061, 3027, 2951, 2922, 2866, 1728, 1602, 1495, 1455, 1436 cm⁻¹; HRMS (*m/z*): [M+Na]⁺ calcd for C₁₈H₂₄NaO₃, 311.1618; found, 311.1618; HPLC: 95% ee, CHIRALCEL ODR, 1.0% isopropanol/hexanes, 1.0 mL/min, UV: 210 nm, *t*_R: 4.9 min (minor), 6.8 min (major).



(-)-(1*R*,2*S*,3*R*,4*S*)-methyl 1-hydroxy-3-methyl-4-phenyl-2-((*E*)-prop-1-en-1-yl)cyclopentanecarboxylate (20b)

Prepared by *General Procedure 1.2.1* with **6** (121 mg, 0.60 mmol, 1.2 equiv), **19b** (51 mg, 0.50 mmol, 1.0 equiv), Rh₂(*R*-DOSP)₄ (0.9 mg, 0.0005 mmol, 0.1 mol %), and CaCl₂ (111 mg, 1.0 mmol, 2.0 equiv), heating to 125 °C for 44 h. Purification by flash chromatography (SiO₂, pentane/Et₂O, 11:1) afforded the title compound as a colorless oil (89 mg, 71% yield).

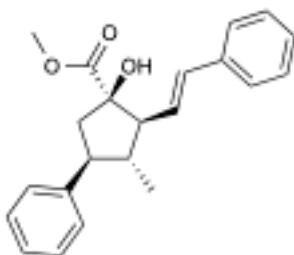
[α]_D²⁰ -3.0° (*c* 1.03, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.34-7.28 (m, 4H), 7.24-7.17 (m, 1H), 5.51-5.45 (m, 1H), 5.44-5.35 (m, 1H), 3.80 (s, 3H), 3.08 (s, 1H), 2.85-2.77 (m, 1H), 2.76-2.67 (m, 1H), 2.37 (dd, *J* = 11.7, 8.4 Hz, 1H), 2.16-2.05 (m, 1H), 1.98 (dd, *J* = 13.7, 7.5 Hz, 1H), 1.70 (dd, *J* = 6.1, 1.2 Hz, 3H), 0.85 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 177.1, 144.5, 130.1, 128.6, 128.0, 127.0, 126.4, 82.7, 61.0, 53.0, 52.4, 46.7, 46.6, 18.6, 16.2; IR (neat): 3526, 3027, 2952, 2921, 2866, 1731, 1602, 1495, 1455, 1437 cm⁻¹; HRMS (*m/z*): [M+Na]⁺ calcd for C₁₇H₂₂NaO₃, 297.1461; found, 297.1461; HPLC: 95% ee, CHIRALCEL ODR, 0.5% isopropanol/hexanes, 0.5 mL/min, UV: 210 nm, *t*_R: 9.9 min (minor), 14.6 min (major).



(+)-(1R,2S,3R,4S)-methyl 2-((E)-hex-1-en-1-yl)-1-hydroxy-3-methyl-4-phenylcyclopentanecarboxylate (20c)

Prepared by *General Procedure 1.2.1* with **6** (121 mg, 0.60 mmol, 1.2 equiv), **19c** (71 mg, 0.50 mmol, 1.0 equiv), Rh₂(R-DOSP)₄ (0.9 mg, 0.0005 mmol, 0.1 mol %), and CaCl₂ (111 mg, 1.0 mmol, 2.0 equiv), heating to 125 °C for 48 h. Purification by flash chromatography (SiO₂, pentane/Et₂O, 15:1) afforded the title compound as a colorless oil (106 mg, 67% yield).

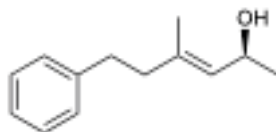
[α]_D²⁰ +1.2° (*c* 0.65, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.26-7.35 (m, 4H), 7.20 (dq, *J* = 8.6, 5.1, 4.2 Hz, 1H), 5.48 (dt, *J* = 15.4, 6.5 Hz, 1H), 5.36 (dd, *J* = 15.5, 8.5 Hz, 1H), 3.80 (s, 3H), 3.07 (s, 1H), 2.66-2.89 (m, 3H), 2.37 (dd, *J* = 11.8, 8.5 Hz, 1H), 1.94-2.18 (m, 2H), 1.25-1.38 (m, 5H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.85 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 176.7, 144.6, 135.8, 128.6, 128.0, 126.4, 125.7, 82.8, 61.2, 53.0, 52.5, 46.7, 46.5, 32.7, 31.8, 22.3, 16.2, 14.1; IR (neat): 3527, 3027, 2953, 2925, 2870, 1729, 1602, 1495, 1455, 1436 cm⁻¹; HRMS (*m/z*): [M+Na]⁺ calcd for C₂₀H₂₈NaO₃, 339.1931; found, 339.1931; HPLC: 94% ee, CHIRALPAK ADH, 0.5% isopropanol/hexanes, 1.0 mL/min, UV: 210 nm, *t*_R: 8.9 min (major), 10.3 min (minor).



(+)-(1R,2S,3R,4S)-methyl 1-hydroxy-3-methyl-4-phenyl-2-((E)-styryl)cyclopentanecarboxylate (20d)

Prepared by *General Procedure 1.2.1* with **6** (121 mg, 0.60 mmol, 1.2 equiv), **19d** (81 mg, 0.50 mmol, 1.0 equiv), Rh₂(*R*-DOSP)₄ (0.9 mg, 0.0005 mmol, 0.1 mol %), and CaCl₂ (111 mg, 1.0 mmol, 2.0 equiv), heating to 125 °C for 48 h. Purification by flash chromatography (SiO₂, pentane/Et₂O, 9:1) afforded the title compound as a pale yellow solid (134 mg, 80% yield).

mp = 79–82 °C; [α]_D²⁰ +9.2° (*c* 1.19, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.28-7.39 (m, 8H), 7.19-7.24 (m, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.23 (dd, *J* = 16.0, 8.9 Hz, 1H), 3.81 (s, 3H), 3.28 (s, 1H), 2.73-2.94 (m, 2H), 2.60 (dd, *J* = 11.7, 9.0 Hz, 1H), 2.26 (m, 1H), 2.06 (dd, *J* = 8.0, 8.0 Hz, 1H), 0.91 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 176.8, 144.4, 137.2, 133.7, 128.7, 128.7, 128.0, 127.6, 126.5, 126.5, 126.2, 82.9, 61.4, 53.2, 52.5, 47.2, 47.0, 16.2; IR (neat): 3509, 3026, 2952, 2866, 1728, 1601, 1495, 1450, 1436 cm⁻¹; HRMS (*m/z*): [M+Na]⁺ calcd for C₂₂H₂₄NaO₃, 359.1618; found, 359.1618; HPLC: 95% ee, CHIRALPAK ADH, 1.0% isopropanol/hexanes, 1.0 mL/min, UV: 230 nm, *t*_R: 18.5 min (minor), 19.9 min (major).

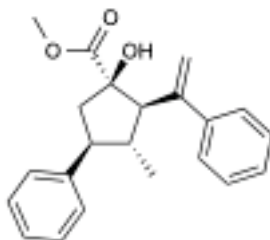


(*S,E*)-4-methyl-6-phenylhex-3-en-2-ol (23c)

The carbometallation procedure for the synthesis of *racemic* **23c** was conducted in accordance with the literature procedure⁷⁸ using Cp₂ZrCl₂ (8.8 g, 30 mmol, 3.0 equiv), AlMe₃ (2.0 M in hexanes, 20 mL, 40 mmol, 4.0 equiv), 4-phenyl-1-butyne (1.75 g, 13 mmol, 1.3 equiv), and acetaldehyde (0.44 g, 10 mmol, 1.0 equiv) and purified by column chromatography (SiO₂, hexanes/ether, 3:1) to afford *racemic* **23c** as a colorless oil (1.5 g, 78% yield). Kinetic resolution was conducted in accordance with the literature procedure⁷⁴ using **23c** (1.0 g, 5.3 mmol, 1.0

equiv), Amano AK Lipase (0.5 g, 50 wt %), vinyl acetate (2.9 mL, 32 mmol, 6.0 equiv), and activated 4 Å molecular sieves (1.0 g, 100 wt %) in hexanes (100 mL) for 24 h. Purification by column chromatography (SiO₂, hexanes/ether, 3:1) afforded the title compound as a colorless oil (0.48g, 48% yield).

$[\alpha]_D^{20} -11.0^\circ$ (*c* 2.05, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.33-7.23 (m, 2H), 7.23-7.13 (m, 3H), 5.25-5.12 (m, 1H), 5.46 (dq, *J* = 8.4, 6.2 Hz, 1H), 2.77-2.67 (m, 2H), 2.36-2.23 (m, 2H), 1.73 (d, *J* = 1.2 Hz, 3H), 1.20 (d, *J* = 6.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 142.1, 137.1, 129.8, 128.6, 128.5, 126.0, 64.9, 41.5, 34.5, 23.7, 16.7; IR (neat): 3351, 3026, 2969, 2925, 2858, 1602, 1495, 1453 cm⁻¹; HRMS (*m/z*): [M+H]⁺ calcd for C₁₃H₁₉O, 191.1430; found, 191.1432; HPLC: 99% ee, DIACEL OJ-H, 1.0% isopropanol/hexanes, 1.0 mL/min, UV: 230 nm, *t*_R: 21.6 min (minor), 26.4 min (major).

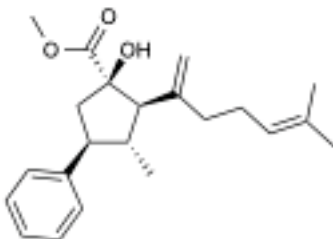


(+)-(1R,2R,3R,4S)-methyl 1-hydroxy-3-methyl-4-phenyl-2-(1-phenylvinyl)cyclopentanecarboxylate (24a)

Prepared by *General Procedure 1.2.1* with **6** (121 mg, 0.60 mmol, 1.2 equiv), **23a** (81 mg, 0.50 mmol, 1.0 equiv), Rh₂(*R*-DOSP)₄ (0.9 mg, 0.0005 mmol, 0.1 mol %), and CaCl₂ (111 mg, 1.0 mmol, 2.0 equiv), heating to 125 °C for 20 h. Purification by flash chromatography (SiO₂, pentane/Et₂O, 7:1) afforded the title compound as a white solid (146 mg, 87% yield).

mp = 110–115 °C; $[\alpha]_D^{20} +48.2^\circ$ (*c* 3.40, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.13-7.50 (m, 10H), 5.52 (s, 1H), 5.19 (s, 1H), 3.19 (s, 3H), 3.17 (d, *J* = 15.4 Hz, 1H), 2.98 (s, 1H), 2.81-2.93 (m, 1H), 2.36-2.46 (m, 1H), 2.06 (dd, *J* = 19.2, 12.8 Hz, 1H), 1.02 (d, *J* = 6.4 Hz, 3H); ¹³C NMR

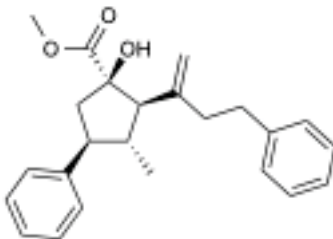
(100 MHz, CDCl₃): δ 176.2, 144.6, 144.6, 142.5, 128.7, 128.4, 128.1, 127.8, 127.4, 127.0, 126.6, 117.0, 80.4, 61.8, 52.4, 51.8, 46.2, 45.5, 16.1; IR (neat): 3468, 3028, 2952, 1728, 1600, 1494, 1447 cm⁻¹; HRMS (*m/z*): [M+Na]⁺ calcd for C₂₂H₂₄NaO₃, 359.1618; found, 359.1621; HPLC: 99% ee, CHIRALCEL ODR, 1.0% isopropanol/hexanes, 1.0 mL/min, UV: 230 nm, *t*_R: 7.1 min (minor), 8.4 min (major).



(+)-(1*R*,2*R*,3*R*,4*S*)-methyl 1-hydroxy-3-methyl-2-(6-methylhepta-1,5-dien-2-yl)-4-phenylcyclopentanecarboxylate (24b)

Prepared by *General Procedure 1.2.1* with **6** (121 mg, 0.60 mmol, 1.2 equiv), **23b** (84 mg, 0.50 mmol, 1.0 equiv), Rh₂(*R*-DOSP)₄ (0.9 mg, 0.0005 mmol, 0.1 mol %), and CaCl₂ (111 mg, 1.0 mmol, 2.0 equiv), heating to 125 °C for 20 h. Purification by flash chromatography (SiO₂, pentane/Et₂O, 15:1) afforded the title compound as a colorless oil (146 mg, 85% yield).

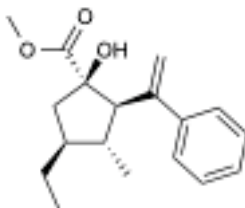
[α]_D²⁰ +2.4° (*c* 1.42, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.29-7.33 (m, 4H), 7.19-7.24 (m, 1H), 5.14 (d, *J* = 1.2 Hz, 1H), 5.06-5.10 (m, 1H), 4.93 (s, 1H), 3.78 (s, 3H), 2.89 (s, 1H), 2.83-2.89 (m, 1H), 2.77 (ddd, *J* = 10.2, 8.0, 8.0 Hz, 1H), 2.56 (d, *J* = 12.4 Hz, 1H), 2.23-2.32 (m, 1H), 2.09-2.20 (m, 1H), 1.93-2.08 (m, 3H), 1.82-1.89 (m, 1H), 1.68 (s, 3H), 1.61 (s, 3H), 0.86 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 177.0, 145.0, 144.3, 132.1, 128.6, 128.1, 126.5, 123.9, 114.0, 80.6, 62.7, 52.8, 51.8, 46.7, 45.5, 37.3, 26.6, 25.9, 17.9, 16.1; IR (neat): 3501, 3027, 2952, 2925, 2969, 1730, 1640, 1602, 1495, 1455, 1436 cm⁻¹; HRMS (*m/z*): [M+Na]⁺ calcd for C₂₂H₃₀NaO₃, 365.2093; found, 365.2091; HPLC: 99% ee, CHIRALCEL ODR, 0.3% isopropanol/hexanes, 0.5 mL/min, UV: 210 nm, *t*_R: 9.2 min (minor), 13.5 min (major).



(+)-(1*R*,2*R*,3*R*,4*S*)-methyl 1-hydroxy-3-methyl-4-phenyl-2-(4-phenylbut-1-en-2-yl)cyclopentanecarboxylate (24c)

Prepared by *General Procedure 1.2.1* with **6** (121 mg, 0.60 mmol, 1.2 equiv), **23c** (95 mg, 0.50 mmol, 1.0 equiv), Rh₂(*R*-DOSP)₄ (0.9 mg, 0.0005 mmol, 0.1 mol %), and CaCl₂ (111 mg, 1.0 mmol, 2.0 equiv), heating to 125 °C for 16 h. Purification by flash chromatography (SiO₂, pentane/Et₂O, 8:1) afforded the title compound as a white solid (157 mg, 86% yield).

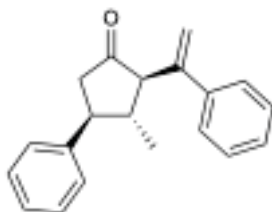
mp = 74–77 °C; [α]_D²⁰ +1.2° (*c* 1.09, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.37–7.24 (m, 6H), 7.24–7.14 (m, 4H), 5.19 (s, 1H), 4.96 (s, 1H), 3.77 (s, 3H), 2.96–2.72 (m, 4H), 2.72–2.58 (m, 2H), 2.37–2.22 (m, 2H), 2.22–2.11 (m, 1H), 2.06 (dd, *J* = 13.7, 7.6 Hz, 1H), 0.87 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 177.0, 144.6, 144.2, 141.9, 128.6, 128.5, 128.5, 128.1, 126.6, 126.1, 114.4, 80.7, 62.8, 52.9, 51.7, 46.7, 45.4, 39.0, 34.5, 16.1; IR (neat): 3534, 3084, 3061, 3026, 2950, 2925, 2867, 1729, 1602, 1495, 1454, 1435 cm⁻¹; HRMS (*m/z*): [M+H]⁺ calcd for C₂₄H₂₉O₃, 365.2111; found, 365.2117; HPLC: 99% ee, DACH DNB, 0.5% isopropanol/hexanes, 1.0 mL/min, UV: 230 nm, *t*_R: 11.2 min (minor), 14.7 min (major).



(+)-(1*R*,2*R*,3*R*,4*S*)-methyl 4-ethyl-1-hydroxy-3-methyl-2-(1-phenylvinyl)cyclopentanecarboxylate (24d)

Prepared by *General Procedure 1.2.1* with **22** (154 mg, 1.0 mmol, 2.0 equiv), **23a** (81 mg, 0.50 mmol, 1.0 equiv), $\text{Rh}_2(\text{R-DOSP})_4$ (0.9 mg, 0.0005 mmol, 0.1 mol %), and CaCl_2 (111 mg, 1.0 mmol, 2.0 equiv), heating to 125 °C for 20 h. Purification by flash chromatography (SiO_2 , pentane/ Et_2O , 7:1) afforded the title compound as a white solid (130 mg, 90% yield).

mp = 48–52 °C; $[\alpha]_D^{20} +20.6^\circ$ (c 0.90, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.35–7.18 (m, 5H), 5.49 (s, 1H), 5.16 (s, 1H), 3.17 (s, 3H), 3.01 (d, $J = 12.0$ Hz, 1H), 2.78 (s, 1H), 2.63–2.50 (dd, $J = 13.0, 9.0$ Hz, 1H), 2.04–1.91 (m, 1H), 1.79–1.51 (m, 3H), 1.33–1.22 (m, 1H), 1.10 (d, $J = 6.4$ Hz, 3H), 0.93 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 176.6, 145.0, 142.8, 128.3, 127.7, 127.0, 116.8, 80.3, 62.0, 52.2, 46.6, 43.5, 42.2, 27.5, 16.9, 12.7; IR (neat): 3527, 3055, 3025, 2957, 2929, 2873, 1730, 1626, 1493, 1437, 1377, 1237 cm^{-1} ; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{25}\text{O}_3$, 289.1798; found, 289.1800; HPLC: 99% ee, DIACEL OD-H, 0.2% isopropanol/hexanes, 0.5 mL/min, UV: 230 nm, t_R : 8.4 min (minor), 8.9 min (major).



(2R,3R,4S)-3-methyl-4-phenyl-2-(1-phenylvinyl)cyclopentanone (25)

To a THF (0.5 mL) solution of **24a** (66 mg, 0.20 mmol, 1.0 equiv), was added lithium borohydride (2.0 M in THF, 0.21 mL, 0.42 mmol, 2.1 equiv) dropwise over 15 min at 0 °C. The reaction was gradually warmed to ambient temperature over 2 h. The reaction was then carefully quenched with pH 7.0 buffer solution (1 drop) and stirred at ambient temperature for an additional 30 min. To the crude mixture was added sodium periodate (430 mg, 2.0 mmol, 10 equiv) in a single portion, and the reaction was then heated in an oil bath to 60 °C for 4h. The reaction was again returned to ambient temperature, dilute with diethyl ether (20 mL), and

washed with a saturated, aqueous solution of sodium thiosulfate (3 x 5 mL). The organic was dried over sodium sulfate and concentrated *in vacuo*. Purification by flash chromatography (SiO₂, pentane/Et₂O, 15→10:1) afforded the title compound as a pale yellow oil (37 mg, 67% yield).

¹H NMR (600 MHz, CDCl₃): δ 7.38-7.27 (m, 7H), 7.27-7.18 (m, 3H), 5.48 (s, 1H), 5.20 (s, 1H), 3.02 (d, 1H), 2.94-2.81 (m, 2H), 2.51 (dd, *J* = 18.2, 11.5 Hz, 1H), 2.35-2.26 (m, 1H), 0.96 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 215.5, 145.4, 141.4, 141.4, 128.9, 128.6, 127.8, 127.6, 127.2, 117.8, 66.0, 48.9, 47.4, 44.9, 16.8; IR (neat): *v*_{max}/cm⁻¹ 3030, 2951, 2873, 1715, 1490, 1451; HRMS (*m/z*): [M+H]⁺ calcd for C₂₀H₂₁O, 277.1587; found, 277.1585.

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