Supporting Information

Cobalt-Catalyzed Regio- and Diastereoselective Formal [3+2] Cycloaddition between Cyclopropanols and Allenes

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Contents

Materials and Methods

General. All reactions dealing with air- or moisture-sensitive compound were performed by standard Schlenk techniques in oven-dried reaction vessels under nitrogen atmosphere or in the argon-filled glove box. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates. Flash chromatography was performed as described by Still et al., using 40–63 μm silica gel (Si 60, Merck). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV-400 (400 MHz) and Bruker AV-300 (300 MHz) NMR spectrometers. ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm) and $CHCl_3$ (77.1 ppm), respectively. Gas chromatographic (GC) analysis was performed on a Shimadzu GC-2010 system equipped with an FID detector and a capillary column, DB-5 (Agilent J&W, 0.25 mm i.d. x 30 m, 0.25 μm film thickness). High-resolution mass spectra (HRMS) were obtained with a Q-Tof Premier LC HR mass spectrometer. Melting points were determined using a capillary melting point apparatus and are uncorrected.

Materials. Unless otherwise noted, commercial reagents were purchased from Aldrich, Alfa Aesar, and other commercial suppliers and were used as received. MeCN was distilled over CaH_2 and stored under N_2. Anhydrous $CoCl_2$ (99.7%) was purchased from Aldrich. Anhydrous $CoBr_2$ (99%) was purchased from Alfa Aesar. Anhydrous CoI_2 (99.5%) was purchased from Strem. Anhydrous $Co(OAc)_2$ (98%) was purchased from Alfa Aesar. Anhydrous DMSO (Aldrich) and anhydrous DMF (Alfa Aesar) was used without further purification and stored under N_2. Cyclopropanols **1a**,[1] **1b**,[11] **1c**,[11] **1d**,[11] **1e**,[2] **1f**,[3] **1g**, **1h**, **1i**,[2] **1j**,[3] **1k**, **1l**,[3] **1m**,[4] **1n**,[5] **1o**,[6] **1p**,[3] and **1q**[7] were prepared according to the literature procedure starting from aryl methyl ketone (for **1a**–**1n**) or methyl alkanoate (for **1o** and **1p**). Allene **2a**,[8] **2b**,[9] **2c**,[10] **2d**,[9] **2e**,[11] **2f**, **2g**,[12] **2h**,[9] **2i**,[13] **2j**,[14] **2k**,[15] **2l**,[15] **2m**,[15] **2n**,[16] and **2o**[10] were prepared according to the literature procedure.

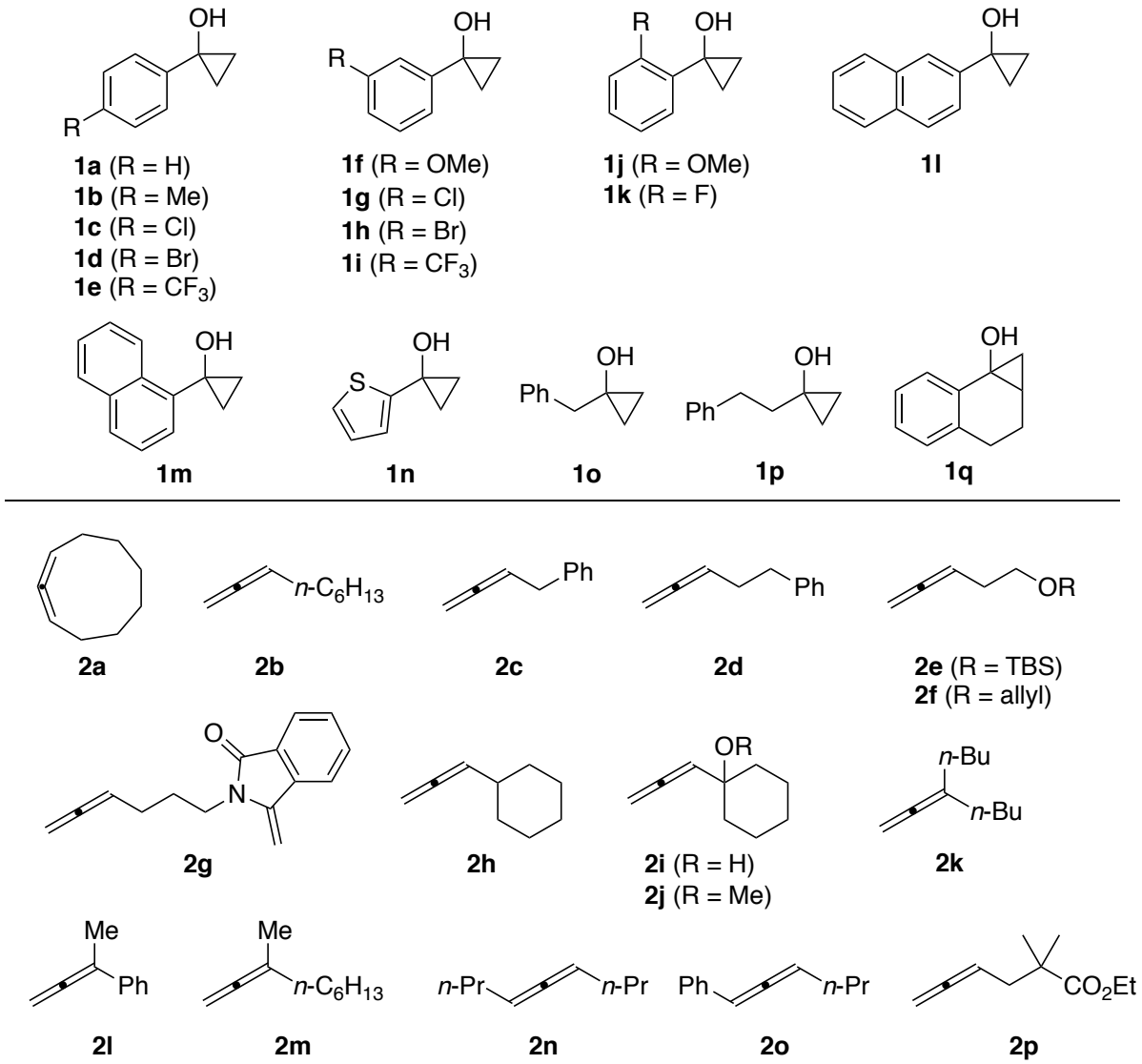


Figure S1. Cyclopropanols and allenes used in this study.

1-(3-Chlorophenyl)cyclopropan-1-ol (1g)

Yellow oil; R_f 0.3 (hexane/EtOAc = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.27 (m, 1H), 7.23-7.21 (m, 1H), 7.18-7.16 (m, 1H), 7.12-7.09 (m, 1H), 2.72 (s, 1H), 1.28-1.22 (m, 2H), 1.04-1.01 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.7, 134.4, 129.6, 126.4, 124.6, 122.3, 56.1, 18.4; **HRMS** (ESI) Calcd for $C_9H_{10}ClO$ $[M + H]^+$ 169.0420, found 169.0430.

1-(3-Bromophenyl)cyclopropan-1-ol (1h)

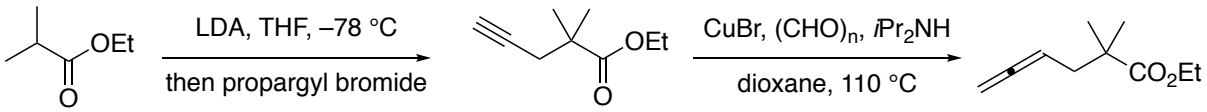
Yellow oil; R_f 0.3 (hexane/EtOAc = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.36-7.31 (m, 1H), 7.20-7.16 (m, 2H), 2.47 (s, 1H), 1.30-1.27 (m, 2H), 1.05-1.02 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.9, 129.9, 129.4, 127.6, 122.8, 122.7, 56.1, 18.4; **HRMS** (ESI) Calcd for $C_9H_{10}BrO$ $[M + H]^+$ 212.9915, found 212.9911.

1-(2-Fluorophenyl)cyclopropan-1-ol (1k)

Yellow oil; R_f 0.3 (hexane/EtOAc = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.36 (m, 1H), 7.28-7.23 (m, 1H), 7.11-7.02 (m, 2H), 2.75 (br, 1H), 1.18-1.15 (m, 2H), 1.03-1.00 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.8 (d, $J_{C\text{-}F}$ = 247.5 Hz), 129.8 (d, $J_{C\text{-}F}$ = 13.1 Hz), 129.3 (d, $J_{C\text{-}F}$ = 8.6 Hz), 129.2 (d, $J_{C\text{-}F}$ = 3.5 Hz), 124.0 (d, $J_{C\text{-}F}$ = 3.5 Hz), 115.7 (d, $J_{C\text{-}F}$ = 21.7 Hz), 53.9, 14.1 (d, $J_{C\text{-}F}$ = 1.1 Hz); **HRMS** (ESI) Calcd for $C_9H_{10}FO$ $[M + H]^+$ 153.0716, found 153.0717.

5-(Allyloxy)penta-1,2-diene (2f)

2f was synthesized according to literature procedure.[17] Colorless oil; R_f 0.5 (hexane/EtOAc = 25/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.97-5.87 (m, 1H), 5.28 (dq, J = 17.2, 1.6 Hz, 1H), 5.19-5.10 (m, 2H), 4.70-4.67 (m, 2H), 3.99 (dt, J = 5.5, 1.2 Hz, 2H), 3.15 (t, J = 6.8 Hz, 2H), 2.33-2.27 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 208.9, 134.9, 116.9, 86.7, 74.9, 71.9, 69.5, 28.8; **HRMS** (ESI) Calcd for $C_8H_{13}O$ $[M + H]^+$ 125.0966, found 125.0963.



Ethyl 2,2-dimethylhexa-4,5-dienoate (2p)

The allene **2p** was synthesized from ethyl isobutylate by adopting the literature procedure for related compounds.[18] Light Yellow oil; R_f 0.3 (Pentane/Et_2O = 15/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.05-4.98 (m, 1H), 4.65-4.62 (m, 2H), 4.12 (q, J = 7.1 Hz, 2H), 2.24 (td, J = 7.9, 2.4 Hz, 2H), 1.28-1.23 (m, 4H), 1.19 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 209.9, 177.3, 85.8, 74.0, 60.4, 42.7, 39.6, 24.7, 14.2; **HRMS** (ESI) Calcd for $C_{10}H_{17}O_2$ $[M + H]^+$ 169.1229, found 169.1232.

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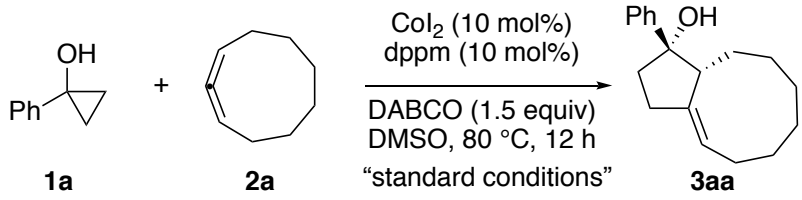
Table S1. Screening of reaction conditions.[a]



1a **2a** "standard conditions" **3aa**

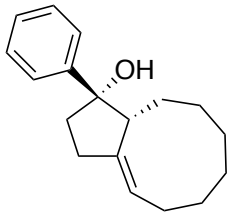
Entry	Deviation from standard conditions	Yield [%][b]
1	None	99
2	dppe instead of dppm	10
3	dppp instead of dppm	35
4	dppb instead of dppm	53
5	PPh_3 (20 mol%) instead of dppm	85
6	PCy_3 (20 mol%) instead of dppm	47
7	$CoCl_2$ instead of CoI_2	86
8	$CoBr_2$ instead of CoI_2	94
9	$Co(OAc)_2$ instead of CoI_2	50
10	DABCO (0.5 equiv)	93
11	DABCO omitted	0
12	DMF instead of DMSO	78
13	MeCN instead of DMSO	27
14	THF instead of DMSO	0
15	Zn (50 mol%) added	83

[a]The reaction was performed on using 0.15 mmol of **1a** and 0.1 mmol of **2a** (0.3 M). [b]Determined by GC using mesitylene as an internal standard.

General Procedure: In an argon-filled glove box, a 4-mL vial equipped with a magnetic stirrer bar was charged sequentially with CoI_2 (9.4 mg, 0.030 mmol), bis(diphenylphopshino)methane (11.5 mg, 0.030 mmol), DABCO (50.4 mg, 0.45 mmol), a cyclopropanol (0.45 mmol) and an allene (0.30 mmol), followed by the addition of DMSO (0.9 mL). The vial was closed and removed from the glove box, and the mixture was stirred at 80 °C for 12 h. Upon cooling to room temperature, the reaction mixture was diluted with ethyl acetate (3 mL) and filtered through a pad of silica gel with additional ethyl acetate (10 mL) as an eluent. The organic solution was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel to afford the desired product.

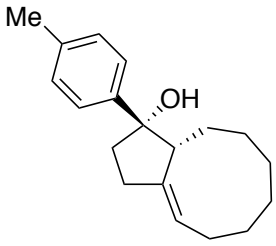
The relative configuration of the cycloaddition products except **3al** and **3ql** was assumed to

be *syn* on the basis of X-ray crystallographic analysis of the products **3oa** and **5** (derived from **3ab**). The relative configuration of the product **3ql**, derived from 1-phenyl-1-methylallene, was determined to be *anti* by X-ray crystallographic analysis, and the same *anti* configuration was assumed for the analogous product **3al**.



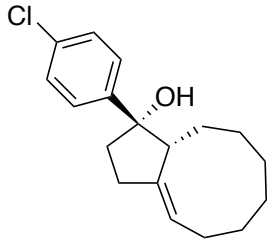
(1*S,10a*R**,*Z*)-1-Phenyl-1,2,3,5,6,7,8,9,10,10a-decahydrocyclopenta[9]annulen-1-ol**

(3aa): Colorless oil (68.0 mg, 89%); R_f 0.3 (hexane/EtOAc = 30/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49-7.48 (m, 2H), 7.35-7.31 (m, 2H), 7.25-7.21 (m, 1H), 5.37 (t, *J* = 8.4 Hz, 1H), 2.80-2.73 (m, 2H), 2.38-2.31 (m, 1H), 2.21-2.13 (m, 2H), 2.06-1.98 (m, 1H), 1.95-1.86 (m, 2H), 1.82-1.75 (m, 2H), 1.56-1.24 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.3, 145.8, 128.2, 126.8, 125.3, 121.6, 84.5, 54.0, 40.9, 32.8, 29.5, 28.6, 28.0, 27.3, 25.6, 22.3; **HRMS** (ESI) Calcd for $C_{18}H_{25}O$ $[M + H]^+$ 257.1905, found 257.1901.

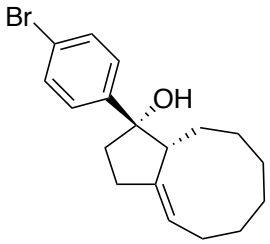


(1*S,10a*R**,*Z*)-1-(*p*-Tolyl)-1,2,3,5,6,7,8,9,10,10a-decahydrocyclopenta[9]annulen-1-ol**

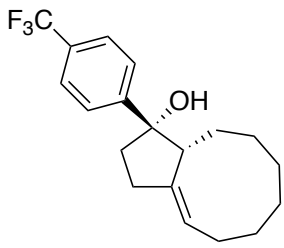
(3ba): Colorless oil (72.0 mg, 89%); R_f 0.3 (hexane/EtOAc = 30/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39-7.37 (m, 2H), 7.16-7.14 (m, 2H), 5.38-5.34 (m, 1H), 2.79-2.71 (m, 2H), 2.37-2.31 (m, 4H), 2.21-2.13 (m, 2H), 2.05-1.86 (m, 3H), 1.81-1.75 (m, 1H), 1.66 (s, 1H), 1.59-1.42 (m, 6H), 1.40-1.28 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.9, 144.3, 136.4, 128.9, 125.2, 121.5, 84.4, 53.9, 40.9, 32.8, 29.5, 28.6, 28.0, 27.3, 25.6, 22.2, 21.0; **HRMS** (ESI) Calcd for $C_{19}H_{27}O$ $[M + H]^+$ 271.2062, found 271.2069.



(1*S,10a*R**,*Z*)-1-(4-Chlorophenyl)-1,2,3,5,6,7,8,9,10,10a-decahydrocyclopenta[9]annulen-1-ol (3ca):** Colorless oil (70.0 mg, 80%); R_f 0.3 (hexane/EtOAc = 30/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.41 (m, 2H), 7.31-7.26 (m, 2H), 5.40-5.36 (m, 1H), 2.79-2.67 (m, 2H), 2.38-2.32 (m, 1H), 2.19-2.13 (m, 2H), 2.03-1.75 (m, 4H), 1.70 (s, 1H), 1.56-1.26 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.8, 145.2, 132.5, 128.2, 126.8, 122.0, 84.2, 54.1, 40.9, 32.6, 29.3, 28.6, 27.9, 27.2, 25.5, 22.3; **HRMS** (ESI) Calcd for $C_{18}H_{24}ClO$ $[M + H]^+$ 291.1516, found 291.1503.

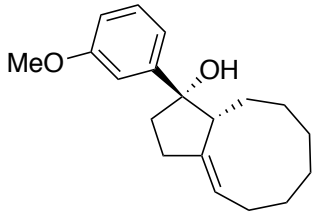


(1*S,10a*R**,*Z*)-1-(4-Bromophenyl)-1,2,3,5,6,7,8,9,10,10a-decahydrocyclopenta[9]annulen-1-ol (3da):** Colorless oil (74.0 mg, 74%); R_f 0.3 (hexane/EtOAc = 30/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46-7.44 (m, 2H), 7.38-7.36 (m, 2H), 5.38 (t, J = 8.3 Hz, 1H), 2.79-2.66 (m, 2H), 2.38-2.32 (m, 1H), 2.18-2.13 (m, 2H), 2.02-1.71 (m, 5H), 1.57-1.26 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.3, 145.2, 131.2, 127.2, 122.0, 120.7, 84.2, 54.2, 40.9, 32.6, 29.3, 28.6, 27.9, 27.2, 25.5, 22.3; **HRMS** (ESI) Calcd for $C_{18}H_{24}BrO$ $[M + H]^+$ 335.1011, found 335.1019.

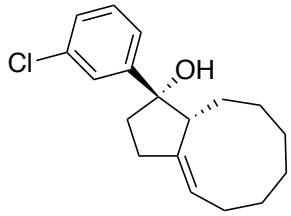


(1*S,10a*R**,*Z*)-1-(4-(Trifluoromethyl)phenyl)-1,2,3,5,6,7,8,9,10,10a-decahydrocyclopenta[9]annulen-1-ol (3ea):** Colorless oil (71.0 mg, 73%); R_f 0.3 (hexane/EtOAc = 30/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63-7.58 (m, 4H), 5.41 (t, J = 8.3

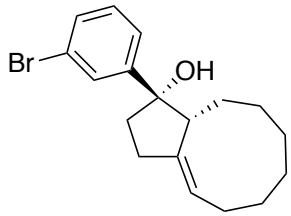
Hz, 1H), 2.82-2.71 (m, 2H), 2.42-2.36 (m, 1H), 2.19-2.13 (m, 2H), 2.07-1.75 (m, 5H), 1.56-1.26 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.3, 145.0, 129.0 (q, $^2J_{C\text{-}F}$ = 33.6 Hz), 125.7, 125.1 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 124.3 (q, $^1J_{C\text{-}F}$ = 270.0 Hz), 122.2, 84.4, 54.4, 41.1, 32.8, 29.3, 28.6, 27.8, 27.2, 25.5, 22.3; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -62.4; **HRMS** (ESI) Calcd for $C_{19}H_{24}F_3O$ $[M + H]^+$ 325.1779, found 325.1786.



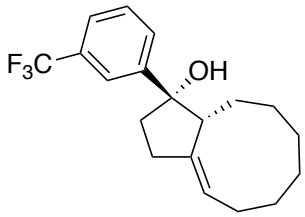
(1*S,10a*R**,*Z*)-1-(3-Methoxyphenyl)-1,2,3,5,6,7,8,9,10,10a-decahydrocyclopenta[9]annulen-1-ol (3fa):** Colorless oil (53.0 mg, 62%); R_f 0.3 (hexane/EtOAc = 15/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.24 (m, 1H), 7.09-7.05 (m, 2H), 6.80-6.77 (m, 1H), 5.39-5.35 (m, 1H), 3.82 (s, 3H), 2.80-2.72 (m, 2H), 2.39-2.33 (m, 1H), 2.21-2.13 (m, 2H), 2.06-1.85 (m, 3H), 1.82-1.70 (m, 2H), 1.57-1.29 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.5, 149.1, 145.8, 129.1, 121.6, 117.6, 111.8, 111.5, 84.5, 55.2, 54.0, 41.0, 32.8, 29.4, 28.6, 27.9, 27.3, 25.6, 22.3; **HRMS** (ESI) Calcd for $C_{19}H_{27}O_2$ $[M + H]^+$ 287.2011, found 287.2017.



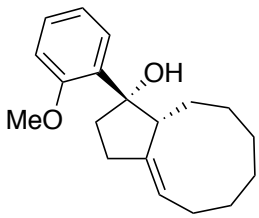
(1*S,10a*R**,*Z*)-1-(3-Chlorophenyl)-1,2,3,5,6,7,8,9,10,10a-decahydrocyclopenta[9]annulen-1-ol (3ga):** White solid (78.0 mg, 90%); R_f 0.3 (hexane/EtOAc = 30/1); m.p. 98-99 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.41-7.36 (m, 2H), 7.22-7.18 (m, 1H), 5.39 (t, *J* = 8.6 Hz, 1H), 2.81-2.68 (m, 2H), 2.40-2.34 (m, 1H), 2.19-2.09 (m, 2H), 2.04-1.74 (m, 4H), 1.70 (s, 1H), 1.55-1.26 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.8, 145.2, 129.8, 129.7, 128.6, 123.9, 122.5, 122.0, 84.3, 54.3, 41.2, 32.9, 29.4, 28.6, 27.9, 27.2, 25.4, 22.3; **HRMS** (ESI) Calcd for $C_{18}H_{24}ClO$ $[M + H]^+$ 291.1516, found 291.1515.



(1*S,10a*R**,*Z*)-1-(3-Bromophenyl)-1,2,3,5,6,7,8,9,10,10a-decahydrocyclopenta[9]annulen-1-ol (3ha):** White solid (65.0 mg, 65%); R_f 0.3 (hexane/EtOAc = 30/1); m.p. 88-89 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51-7.50 (m, 1H), 7.36-7.35 (m, 1H), 7.28-7.20 (m, 2H), 5.39 (t, J = 8.7 Hz, 1H), 2.81-2.68 (m, 2H), 2.40-2.34 (m, 1H), 2.19-2.13 (m, 2H), 2.04-1.77 (m, 4H), 1.71 (s, 1H), 1.55-1.26 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.5, 145.2, 134.2, 129.4, 126.9, 125.7, 123.4, 122.0, 84.3, 54.3, 41.1, 32.8, 29.4, 28.6, 27.9, 27.2, 25.5, 22.3; **HRMS** (ESI) Calcd for $C_{18}H_{24}BrO$ $[M + H]^+$ 335.1011, found 335.1021.

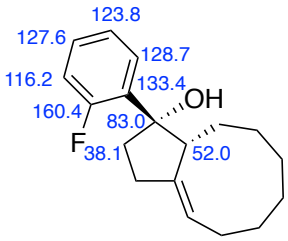


(1*S,10a*R**,*Z*)-1-(3-(Trifluoromethyl)phenyl)-1,2,3,5,6,7,8,9,10,10a-decahydrocyclopenta[9]annulen-1-ol (3ia):** Colorless oil (75.0 mg, 77%); R_f 0.3 (hexane/EtOAc = 30/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.68-7.66 (m, 1H), 7.52-7.43 (m, 2H), 5.44-5.40 (m, 1H), 2.83-2.71 (m, 2H), 2.43-2.36 (m, 1H), 2.20-2.15 (m, 2H), 2.05-1.92 (m, 2H), 1.88-1.74 (m, 3H), 1.55-1.30 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.4, 145.0, 130.5 (q, $^2J_{C\text{-}F}$ = 31.9 Hz), 128.7, 128.6, 124.3 (q, $^1J_{C\text{-}F}$ = 272.4 Hz), 123.6 (overlap), 122.2, 84.3, 54.3, 41.2, 32.7, 29.3, 28.6, 27.8, 27.1, 25.4, 22.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -62.4; **HRMS** (ESI) Calcd for $C_{19}H_{24}F_3O$ $[M + H]^+$ 325.1779, found 325.1780.



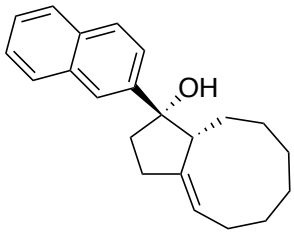
(1*S,10a*R**,*Z*)-1-(2-Methoxyphenyl)-1,2,3,5,6,7,8,9,10,10a-decahydrocyclopenta[9]annulen-1-ol (3ja):** White solid (71.0 mg, 83%); R_f 0.3 (hexane/EtOAc = 15/1); m.p. 69-70 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.20 (m, 2H),

6.93-6.90 (m, 2H), 5.23-5.18 (m, 1H), 4.05 (s, 1H), 3.91 (s, 3H), 2.92-2.90 (m, 1H), 2.67-2.60 (m, 1H), 2.29-2.00 (m, 6H), 1.86-1.80 (m, 1H), 1.61-1.34 (m, 8H), 1.30-1.22 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.9, 145.4, 134.5, 128.1, 126.3, 121.6, 120.8, 111.3, 83.1, 55.4, 51.1, 35.6, 30.1, 28.2, 27.6, 27.3, 27.0, 25.9, 22.7; **HRMS** (ESI) Calcd for $C_{19}H_{27}O_2$ $[M + H]^+$ 287.2011, found 287.2003.



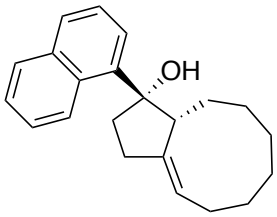
(1*S,10a*R**,*Z*)-1-(2-Fluorophenyl)-1,2,3,5,6,7,8,9,10,10a-decahydrocyclopenta[9]annulen-1-ol (3ka):**

Colorless oil (63.0 mg, 77%); R_f 0.3 (hexane/EtOAc = 30/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.5 (dt, J = 8.1, 1.7 Hz, 1H), 7.27-7.22 (m, 1H), 7.11 (dt, J = 7.6, 1.2 Hz, 1H), 7.06-7.00 (m, 1H), 5.37-5.33 (m, 1H), 2.94 (d, J = 9.1 Hz, 1H), 2.80-2.71 (m, 1H), 2.38-2.26 (m, 2H), 2.17-2.12 (m, 3H), 1.96-1.88 (m, 2H), 1.83-1.77 (m, 1H), 1.61-1.45 (m, 6H), 1.40-1.28 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.4 (d, $^1J_{C\text{-}F}$ = 245.0 Hz), 145.1, 133.4 (d, $^2J_{C\text{-}F}$ = 10.2 Hz), 128.7 (d, $^3J_{C\text{-}F}$ = 9.0 Hz), 127.6 (d, $^3J_{C\text{-}F}$ = 4.5 Hz), 123.8 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 121.9, 116.2 (d, $^2J_{C\text{-}F}$ = 23.4 Hz), 83.0 (d, $^3J_{C\text{-}F}$ = 3.5 Hz), 52.0 (d, $^4J_{C\text{-}F}$ = 2.5 Hz), 38.1 (d, $^4J_{C\text{-}F}$ = 3.4 Hz), 32.3, 29.1, 28.4, 27.8, 27.3, 25.6, 22.2 ($^nJ_{C\text{–}F}$ is the C–F coupling constant, where n refers to the number of bonds separating the C and F nuclei. See the assigned chemical shifts of the relevant C nuclei in the above structure); **^{19}F NMR** (376 MHz, $CDCl_3$): δ -111.9; **HRMS** (ESI) Calcd for $C_{18}H_{24}FO$ $[M + H]^+$ 275.1811, found 275.1815.

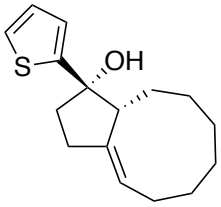


(1*S,10a*R**,*Z*)-1-(Naphthalen-2-yl)-1,2,3,5,6,7,8,9,10,10a-decahydrocyclopenta[9]annulen-1-ol (3la):** Colorless oil (77.0 mg, 84%); R_f 0.3 (hexane/EtOAc = 30/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 1.2 Hz, 1H), 7.86-7.80 (m, 3H), 7.56 (dd, J = 8.6, 1.9 Hz, 1H), 7.49-7.43 (m, 2H), 5.43-5.39 (m, 1H), 2.86-2.79 (m,

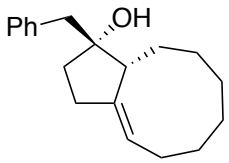
2H), 2.44-2.38 (m, 1H), 2.24-2.12 (m, 3H), 2.01-1.88 (m, 2H), 1.83-1.74 (m, 2H), 1.57-1.33 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.8, 144.4, 133.1, 132.4, 128.2, 127.9, 127.4, 126.1, 125.8, 124.0, 123.7, 121.7, 84.7, 54.1, 41.0, 33.0, 29.5, 28.6, 28.0, 27.3, 25.5, 22.2; **HRMS** (ESI) Calcd for $C_{22}H_{27}O$ $[M + H]^+$ 307.2062, found 307.2066.



(1*S,10a*R**,*Z*)-1-(Naphthalen-1-yl)-1,2,3,5,6,7,8,9,10,10a-decahydrocyclopenta[9]annulen-1-ol (3ma):** White solid (70.0 mg, 76%); R_f 0.3 (hexane/EtOAc = 30/1); m.p. 82-84 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.2 Hz, 1H), 7.87-7.84 (m, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.55-7.43 (m, 3H), 7.38 (t, *J* = 7.7 Hz, 1H), 5.32-5.27 (m, 1H), 3.28 (d, *J* = 9.7 Hz, 1H), 2.78-2.69 (m, 1H), 2.63-2.56 (m, 1H), 2.39-2.31 (m, 1H), 2.27-2.02 (m, 5H), 1.91-1.85 (m, 1H), 1.59-1.43 (m, 6H), 1.39-1.31 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.8, 141.7, 135.1, 130.8, 129.2, 128.6, 126.9, 125.3, 125.1, 124.7, 123.3, 122.4, 84.4, 52.3, 38.2, 30.4, 28.4, 28.1, 27.2, 27.0, 26.1, 22.5; **HRMS** (ESI) Calcd for $C_{22}H_{27}O$ $[M + H]^+$ 307.2062, found 307.2072



(1*S,10a*R**,*Z*)-1-(Thiophen-2-yl)-1,2,3,5,6,7,8,9,10,10a-decahydrocyclopenta[9]annulen-1-ol (3na):** Light yellow oil (50.0 mg, 64%); R_f 0.3 (hexane/EtOAc = 25/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 5.0, 1.2 Hz, 1H), 6.99 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.94 (dd, *J* = 5.0, 3.6 Hz, 1H), 5.35-5.29 (m, 1H), 2.81-2.78 (m, 1H), 2.73-2.65 (m, 1H), 2.37-2.30 (m, 1H), 2.23-2.01 (m, 5H), 1.99 (s, 1H), 1.88-1.81 (m, 1H), 1.63-1.44 (m, 6H), 1.41-1.29 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.9, 144.9, 126.7, 124.0, 122.6, 122.2, 82.8, 54.3, 40.8, 31.5, 28.9, 28.5, 27.6, 27.0, 25.8, 22.4; **HRMS** (ESI) Calcd for $C_{16}H_{23}OS$ $[M + H]^+$ 263.1470, found 263.1466.



(1*R,10a*R**,*Z*)-1-Benzyl-1,2,3,5,6,7,8,9,10,10a-decahydrocyclopenta[9]annulen-1-ol (3oa):** White solid (49.0 mg, 60%); R_f 0.3 (hexane/EtOAc = 15/1); m.p. 73-74 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.20 (m, 5H), 5.33-5.28 (m, 1H), 2.81 (d, J = 13.4 Hz, 1H), 2.73 (d, J = 13.4 Hz, 1H), 2.59-2.46 (m, 1H), 2.38-2.14 (m, 4H), 1.85-1.73 (m, 2H), 1.66-1.58 (m, 2H), 1.50-1.31 (m, 8H), 1.14-1.01 (m,1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.3, 137.7, 130.4, 128.3, 126.5, 122.2, 81.8, 50.5, 46.3, 35.6, 29.6, 28.4, 27.9, 27.2, 26.9, 25.5, 22.5; **HRMS** (ESI) Calcd for $C_{19}H_{27}O$ $[M + H]^+$ 271.2068, found 271.2062. Recrystallization from CH_2Cl_2/pentane afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structure of **3oa** and its relative configuration (Figure S2).[19]

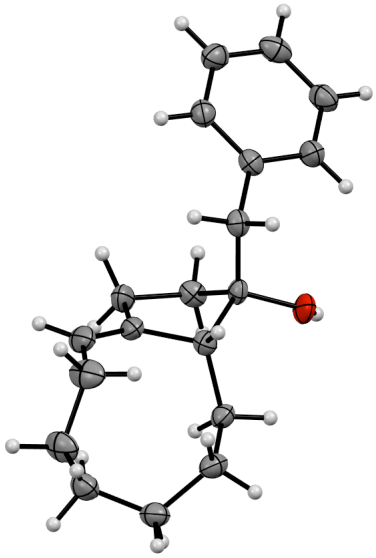
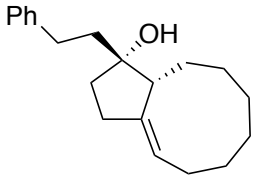
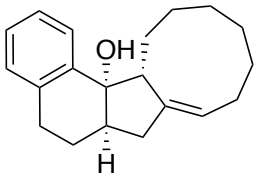


Figure S2. ORTEP drawing of **3oa** (thermal ellipsoids set at 50% probability).

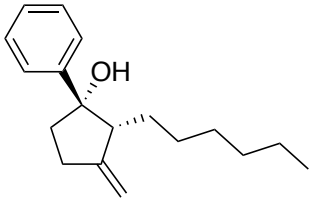


(1*R,10a*R**,*Z*)-1-Phenethyl-1,2,3,5,6,7,8,9,10,10a-decahydrocyclopenta[9]annulen-1-ol (3pa):** Colorless oil (48.0 mg, 56%); R_f 0.3 (hexane/EtOAc = 15/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 7.21-7.15 (m, 3H), 5.29-5.24 (m, 1H), 2.81-2.66 (m, 2H), 2.61-

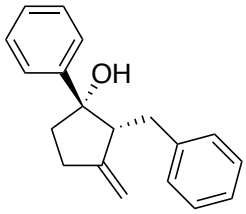
2.50 (m, 1H), 2.34-2.31 (m, 1H), 2.27-2.04 (m, 3H), 1.95-1.68 (m, 6H), 1.58-1.35 (m, 8H), 1.19-1.12 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.3, 142.7, 128.4 (overlap), 125.7, 122.1, 82.3, 51.4, 42.6, 35.8, 30.4, 30.1, 28.4, 28.3, 27.4, 26.9, 25.7, 22.5; **HRMS** (ESI) Calcd for $C_{20}H_{29}O$ $[M + H]^+$ 285.2218, found 285.2208.



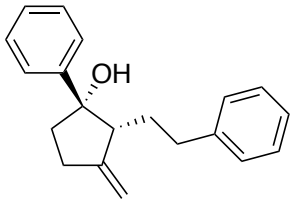
(6a*R,14a*R**,14b*S**,*Z*)-6,6a,7,9,10,11,12,13,14,14a-Decahydrocyclonona[4,5]cyclopenta[1,2-*a*]naphthalen-14b(5*H*)-ol (3qa):** Colorless oil (53.0 mg, 63%); R_f 0.3 (hexane/EtOAc = 30/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.6 (dd, J = 7.8, 1.1 Hz, 1H), 7.24-7.14 (m, 2H), 7.07-7.06 (m, 1H), 5.23-5.19 (m, 1H), 2.88-2.75 (m, 4H), 2.34-2.22 (m, 2H), 2.13-2.04 (m, 2H), 1.99-1.80 (m, 3H), 1.75-1.65 (m, 2H), 1.62-1.34 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.3, 142.2, 136.3, 128.7, 127.0, 126.7, 126.6, 122.1, 80.8, 52.6, 43.7, 36.0, 28.6, 28.4, 27.5, 27.2, 26.8, 25.6, 23.7, 22.4; **HRMS** (ESI) Calcd for $C_{20}H_{27}O$ $[M + H]^+$ 283.2062, found 283.2057.



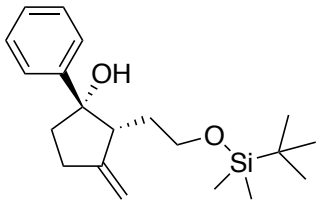
(1*S,2*R**)-2-Hexyl-3-methylene-1-phenylcyclopentan-1-ol (3ab):** Colorless oil (70.0 mg, 91%); R_f 0.3 (hexane/EtOAc = 30/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49-7.48 (m, 2H), 7.37-7.33 (m, 2H), 7.26-7.22 (m, 1H), 5.03 (d, J = 2.0 Hz, 1H), 4.98 (d, J = 2.2 Hz, 1H), 2.68-2.59 (m, 3H), 2.15-2.07 (m, 1H), 1.99-1.93 (m, 1H), 1.64 (s, 1H), 1.50-1.36 (m, 2H), 1.29-1.07 (m, 8H), 0.80 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.4, 145.6, 128.1, 126.6, 125.0, 106.6, 83.7, 54.7, 41.3, 31.5, 29.8, 29.5, 28.5, 26.7, 22.6, 14.0; **HRMS** (ESI) Calcd for $C_{18}H_{27}O$ $[M + H]^+$ 259.2062, found 259.2065.



(1*S,2*R**)-2-Benzyl-3-methylene-1-phenylcyclopentan-1-ol (3ac):** Colorless oil (60.0 mg, 76%); R_f 0.3 (hexane/EtOAc = 20/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.45 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.19 (m, 1H), 7.16-7.13 (m, 2H), 7.09-7.03 (m, 3H), 5.00 (q, *J* = 2.0 Hz, 1H), 4.88 (q, *J* = 2.2 Hz, 1H), 3.13-3.12 (m, 1H), 2.84-2.61 (m, 4H), 2.25-2.17 (m, 1H), 2.02-1.95 (m, 1H), 1.70 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.4, 144.8, 140.8, 128.6, 128.2 (overlap), 126.7, 125.7, 125.1, 108.1, 84.1, 55.8, 41.0, 32.8, 29.8; **HRMS** (ESI) Calcd for $C_{19}H_{21}O$ $[M + H]^+$ 265.1592, found 265.1590.

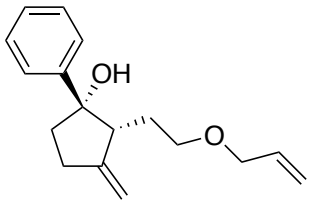


(1*S,2*R**)-3-Methylene-2-phenethyl-1-phenylcyclopentan-1-ol (3ad):** Colorless oil (54.0 mg, 65%); R_f 0.3 (hexane/EtOAc = 20/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.39 (m, 2H), 7.34-7.30 (m, 2H), 7.26-7.23 (m, 1H), 7.22-7.17 (m, 2H), 7.14-7.11 (m, 1H), 6.98-6.96 (m, 2H), 5.07-5.04 (m, 2H), 2.73-2.60 (m, 3H), 2.54-2.47 (m, 1H), 2.43-2.36 (m, 1H), 2.16-2.07 (m, 1H), 1.98-1.92 (m, 1H), 1.88-1.72 (m, 2H), 1.63 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.9, 145.3, 142.2, 128.3, 128.2 (overlap), 126.7, 125.7, 125.0, 106.8, 83.6, 53.9, 41.3, 34.4, 29.8, 28.4; **HRMS** (ESI) Calcd for $C_{20}H_{23}O$ $[M + H]^+$ 279.1749, found 279.1740.

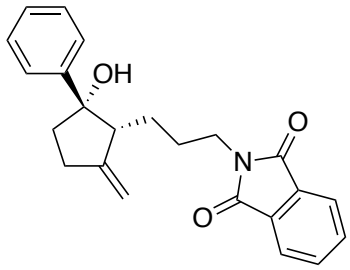


(1*S,2*R**)-2-(2-((tert-Butyldimethylsilyl)oxy)ethyl)-3-methylene-1-phenylcyclopentan-1-ol (3ae):** Colorless oil (60.0 mg, 60%); R_f 0.3 (hexane/EtOAc = 15/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.51 (m, 2H), 7.34-7.31 (m, 2H), 7.24-7.20 (m, 1H), 5.06 (q, *J* = 2.1 Hz, 1H), 4.83 (q, *J* = 2.1 Hz, 1H), 4.01 (s, 1H), 3.76-3.71 (m, 1H), 3.50-3.45 (m, 1H), 3.04 (br, 1H), 2.78-2.68 (m, 1H), 2.59-2.53 (m, 1H), 2.02-1.95 (m, 2H), 1.89-1.74 (m, 2H), 0.83 (s, 9H), -

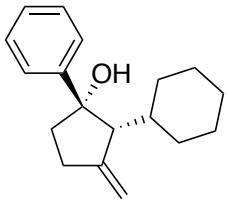
0.03 (s, 3H), -0.05 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.7, 146.4, 128.0, 126.4, 125.2, 106.1, 82.6, 60.2, 52.4, 41.6, 30.4, 29.7, 25.9, 18.3, -5.5, -5.6; **HRMS** (ESI) Calcd for $C_{20}H_{33}O_2Si$ $[M + H]^+$ 333.2252, found 333.2257.



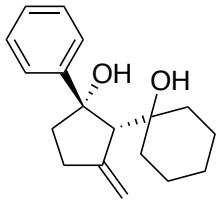
(1*S,2*R**)-2-(2-(Allyloxy)ethyl)-3-methylene-1-phenylcyclopentan-1-ol (3af):** Colorless oil (60.0 mg, 78%); R_f 0.3 (hexane/EtOAc = 15/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52-7.50 (m, 2H), 7.35-7.31 (m, 2H), 7.24-7.20 (m, 1H), 5.78-5.68 (m, 1H), 5.19-5.10 (m, 2H), 5.06 (q, *J* = 2.3 Hz, 1H), 4.85 (q, *J* = 2.4 Hz, 1H), 3.78 (s, 1H), 3.61-3.51 (m, 2H), 3.47-3.42 (m, 1H), 3.18-3.12 (m, 1H), 3.08-3.04 (m, 1H), 2.77-2.67 (m, 1H), 2.57-2.52 (m, 1H), 1.99-1.82 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.2, 146.7, 134.1, 128.0, 126.3, 125.0, 117.0, 106.2, 82.8, 71.4, 67.3, 52.5, 42.0, 30.6, 27.5; **HRMS** (ESI) Calcd for $C_{17}H_{23}O_2$ $[M + H]^+$ 259.1698, found 259.1692.



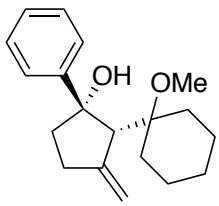
2-(3-((1*R,2*S**)-2-Hydroxy-5-methylene-2-phenylcyclopentyl)propyl)isoindoline-1,3-dione (3ag):** Colorless oil (23.0 mg, 21%); R_f 0.3 (hexane/EtOAc = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.78 (m, 2H), 7.71-7.68 (m, 2H), 7.48-7.46 (m, 2H), 7.33-7.30 (m, 2H), 7.22-7.18 (m, 1H), 5.02 (d, *J* = 1.8 Hz, 1H), 4.93 (d, *J* = 2.0 Hz, 1H), 3.55-3.44 (m, 2H), 2.71 (s, 1H), 2.63-2.58 (m, 2H), 2.19-2.10 (m, 1H), 1.97-1.91 (m, 1H), 1.70 (s, 1H), 1.66-1.45 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.4, 153.6, 145.4, 133.8, 132.1, 128.3, 126.7, 124.9, 123.2, 107.0, 83.4, 54.4, 41.3, 38.1, 29.8, 27.2, 24.0; **HRMS** (ESI) Calcd for $C_{23}H_{24}NO_3$ $[M + H]^+$ 362.1756, found 362.1766.



(1*S,2*R**)-2-Cyclohexyl-3-methylene-1-phenylcyclopentan-1-ol (3ah):** Colorless oil (58.0 mg, 76%); R_f 0.3 (hexane/EtOAc = 30/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54-7.51 (m, 2H), 7.39-7.35 (m, 2H), 7.29-7.24 (m, 1H), 5.11 (d, *J* = 2.0 Hz, 1H), 4.98 (d, *J* = 1.8 Hz, 1H), 2.71-2.61 (m, 2H), 2.57-2.50 (m, 1H), 2.12-2.04 (m, 1H), 1.96-1.90 (m, 1H), 1.75-1.63 (m, 6H), 1.32-1.05 (m, 5H), 0.91-0.86 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.3, 147.3, 128.0, 126.4, 124.9, 107.6, 84.4, 59.5, 43.0, 38.0, 32.5, 32.1, 31.3, 27.4, 27.0, 26.5; **HRMS** (ESI) Calcd for $C_{18}H_{25}O$ $[M + H]^+$ 257.1905, found 257.1913.

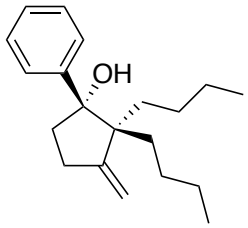


1-((1*S,2*S**)-2-Hydroxy-5-methylene-2-phenylcyclopentyl)cyclohexan-1-ol (3ai):** Colorless oil (63.0 mg, 77%); R_f 0.3 (hexane/EtOAc = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52-7.50 (m, 2H), 7.34-7.30 (m, 2H), 7.21-7.18 (m, 1H), 5.20 (s, 1H), 4.94 (s, 1H), 4.91 (s, 1H), 2.89 (s, 1H), 2.85-2.76 (m, 1H), 2.41 (dd, *J* = 14.3, 6.4 Hz, 1H), 2.30 (s, 1H), 2.02-1.85 (m, 3H), 1.67-1.36 (m, 7H), 1.20-1.09 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.9, 149.4, 128.0, 126.1, 124.8, 110.1, 85.1, 76.5, 62.1, 45.4, 37.4, 36.2, 35.5, 25.4, 21.8, 21.7; **HRMS** (ESI) Calcd for $C_{18}H_{25}O_2$ $[M + H]^+$ 273.1855, found 273.1860.

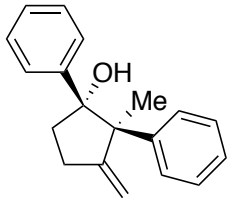


(1*S,2*R**)-2-(1-Methoxycyclohexyl)-3-methylene-1-phenylcyclopentan-1-ol (3aj):** Colorless oil (41.0 mg, 48%); R_f 0.3 (hexane/EtOAc = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95-7.93 (m, 2H), 7.56-7.52 (m, 1H), 7.46-7.42 (m, 2H), 5.51-5.45 (m, 1H), 5.20-5.17 (m, 1H), 3.12 (s, 3H), 3.01-2.97 (m, 2H), 2.43-2.37 (m, 2H), 1.85-1.71 (m, 4H), 1.62-1.24 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.2, 137.0, 133.0, 132.9, 132.7, 128.6, 128.0, 76.7,

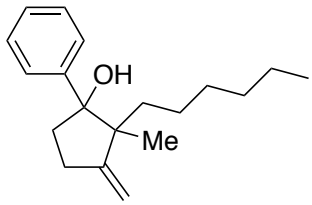
49.2, 38.3, 36.0, 27.7, 25.6, 24.3, 22.0; **HRMS** (ESI) Calcd for $C_{19}H_{27}O_2$ $[M + H]^+$ 287.2011, found 287.2005.



2,2-Dibutyl-3-methylene-1-phenylcyclopentan-1-ol (3ak): Colorless oil (72.0 mg, 84%); R_f 0.3 (hexane/EtOAc = 30/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51-7.49 (m, 2H), 7.32-7.28 (m, 2H), 7.24-7.21 (m, 1H), 5.04 (s, 1H), 4.74 (s, 1H), 2.72-2.62 (m, 1H), 2.58-2.42 (m, 2H), 1.94-1.87 (m, 1H), 1.82 (s, 1H), 1.79-1.71 (m, 1H), 1.41-1.34 (m, 1H), 1.31-1.21 (m, 3H), 1.49-1.06 (m, 4H), 1.04-1.00 (m, 2H), 0.92-0.83 (m, 4H), 0.80-0.76 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.0, 144.9, 127.4, 126.6, 126.4, 108.0, 86.3, 55.7, 38.1, 31.8, 29.3, 28.6, 26.0, 25.6, 23.8, 23.4, 14.1, 14.0; **HRMS** (ESI) Calcd for $C_{20}H_{31}O$ $[M + H]^+$ 287.2375, found 287.2371.

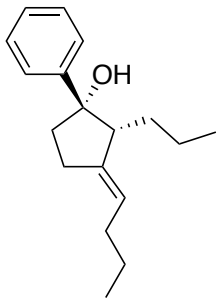


(1*R,2*R**)-2-Methyl-3-methylene-1,2-diphenylcyclopentan-1-ol (3al):** Colorless oil (66.0 mg, 83%); R_f 0.3 (hexane/EtOAc = 25/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24-7.16 (m, 3H), 7.09-7.03 (m, 3H), 7.00-6.96 (m, 2H), 6.64-6.61 (m, 2H), 5.32 (t, J = 2.0 Hz, 1H), 5.07 (t, J = 2.5 Hz, 1H), 2.94-2.79 (m, 2H), 2.51-2.43 (m, 1H), 1.73-1.68 (m, 2H), 1.53 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.5, 145.2, 142.2, 128.3, 127.3, 127.2, 126.9 (overlap), 125.9, 109.5, 86.5, 59.2, 34.5, 29.4, 20.2; **HRMS** (ESI) Calcd for $C_{19}H_{21}O$ $[M + H]^+$ 265.1592, found 265.1602.

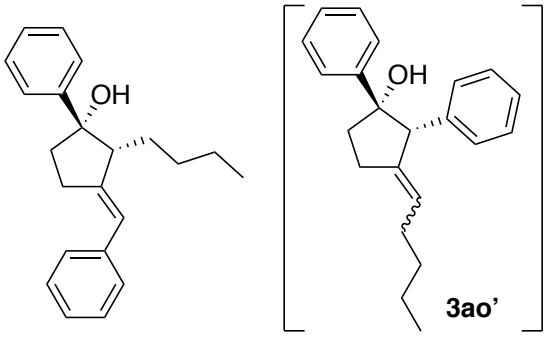


2-Hexyl-2-methyl-3-methylene-1-phenylcyclopentan-1-ol (3am): Silica gel

chromatography of the crude product afforded cleanly separable diastereomers in near 1:1 ratio. **Diastereomer 1:** Colorless oil (34.0 mg, 42%); R_f 0.3 (hexane/EtOAc = 30/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.32-7.28 (m, 2H), 7.25-7.21 (m, 1H), 4.95 (s, 1H), 4.74 (s, 1H), 2.76-2.67 (m, 1H), 2.60-2.45 (m, 2H), 2.01-1.94 (m, 1H), 1.75 (s, 1H), 1.55-1.51 (m, 2H), 1.26-1.18 (m, 8H), 0.89-0.85 (m, 3H), 0.67 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.3, 144.8, 127.5, 126.7, 126.4, 106.7, 86.1, 52.7, 37.4, 34.0, 31.9, 30.5, 29.1, 24.8, 22.7, 21.9, 14.1; **HRMS** (ESI) Calcd for $C_{19}H_{29}O$ $[M + H]^+$ 273.2218, found 273.2215. **Diastereomer 2:** Colorless oil (33.0 mg, 40%); R_f 0.2 (hexane/EtOAc = 30/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.51 (m, 2H), 7.37-7.33 (m, 2H), 7.30-7.25 (m, 1H), 5.06 (s, 1H), 4.84 (s, 1H), 2.84-2.76 (m, 1H), 2.62-2.58 (m, 2H), 1.83-1.77 (m, 1H), 1.68 (s, 1H), 1.25-1.06 (m, 8H), 1.00-0.95 (m, 4H), 0.84-0.81 (m, 3H), 0.69-0.63 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.2, 142.1, 127.7, 127.1, 127.0, 107.9, 86.0, 54.0, 36.1, 34.4, 31.9, 30.0, 27.6, 24.0, 22.6, 14.9, 14.1; **HRMS** (ESI) Calcd for $C_{19}H_{29}O$ $[M + H]^+$ 273.2218, found 273.2226.

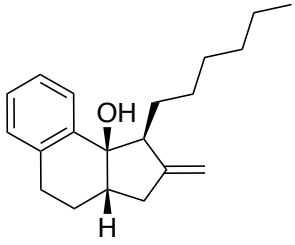


(1*S,2*R**,*E*)-3-Butylidene-1-phenyl-2-propylcyclopentan-1-ol (3an):** Colorless oil (63.0 mg, 81%, *E*/*Z* = 5:1 as determined by ^{1}H NMR); R_f 0.3 (hexane/EtOAc = 30/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.46 (m, 2H), 7.35-7.29 (m, 2H), 7.25-7.21 (m, 1H), 5.33-5.29 (m, 1H), 2.70 (brs, 1H), 2.54-2.41 (m, 2H), 2.11-1.93 (m, 4H), 1.62 (s, 1H), 1.47-1.39 (m, 4H), 1.28-1.15 (m, 1H), 1.10-1.02 (m, 1H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.74 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.8, 144.0, 128.1, 126.4, 125.1, 122.0, 83.5, 54.3, 41.3, 31.2, 29.6, 26.4, 22.8, 22.0, 14.5, 13.9; **HRMS** (ESI) Calcd for $C_{18}H_{27}O$ $[M + H]^+$ 259.2062, found 259.2060. A stereochemically purer sample of the major isomer was obtained by additional purification on silica gel. Using this sample, the *E*-stereochemistry of the olefin was confirmed by ^{1}H–^{1}H NOESY analysis (see the attached spectrum).



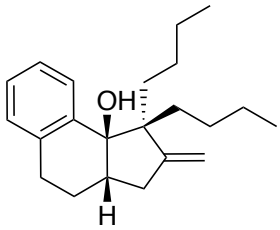
(1*S,2*R**)-3-((*E*)-Benzylidene)-2-butyl-1-phenylcyclopentan-1-ol (3ao):** Colorless oil (50.0 mg, 54%); R_f 0.3 (hexane/EtOAc = 30/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54-7.52 (m, 2H), 7.40-7.33 (m, 6H), 7.28-7.19 (m, 2H), 6.38 (q, *J* = 2.3 Hz, 1H), 2.92-2.85 (m, 3H), 2.25-2.17 (m, 1H), 2.11-2.05 (m, 1H), 1.66-1.50 (m, 3H), 1.34-1.10 (m, 4H), 0.78 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.7, 145.5, 138.3, 128.4, 128.2, 128.1, 126.6, 126.1, 125.1, 122.3, 82.9, 56.2, 41.9, 30.9, 28.9, 27.0, 23.0, 13.8; **HRMS** (ESI) Calcd for $C_{22}H_{27}O$ $[M + H]^+$ 307.2062, found 307.2066. The *E*-stereochemistry of the olefin was confirmed by ^{1}H–^{1}H NOESY analysis (see the attached spectrum).

Along with **3ao**, silica gel chromatography afforded another product, whose structure was assigned as the regioisomer **3ao'** (colorless oil, 36.0 mg, 39%, *E*/*Z* = ca. 3:1); R_f 0.4 (hexane/EtOAc = 30/1); **^{1}H NMR** (400 MHz, $CDCl_3$, major isomer) δ 7.40-7.19 (m, 8H), 7.03-7.00 (m, 2H), 5.13-5.09 (m, 1H), 4.17 (s, 1H), 2.82-2.73 (m, 2H), 2.31-2.07 (m, 3H), 1.72 (d, *J* = 2.0 Hz, 1H), 1.57-1.55 (m, 2H), 1.36-1.31 (m, 3H), 0.92-0.89 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, major isomer): δ 142.9, 138.0, 130.3, 128.4, 128.2, 128.0, 127.0, 126.6, 125.2, 125.1, 83.6, 63.0, 40.4, 31.6, 29.1, 27.8, 22.5, 14.0; **HRMS** (ESI) Calcd for $C_{22}H_{27}O$ $[M + H]^+$ 307.2062, found 307.2054.

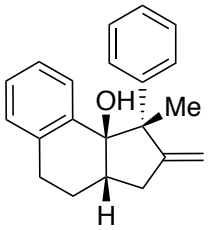


(1*S,3a*S**,9b*R**)-1-Hexyl-2-methylene-1,2,3,3a,4,5-hexahydro-9b*H*-cyclopenta[*a*]naphthalen-9b-ol (3qb):** Colorless oil (42.0 mg, 48%); R_f 0.3 (hexane/EtOAc = 30/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.23 (dt, *J* = 7.4, 1.4 Hz, 1H), 7.17 (dt, *J* = 7.4, 1.4 Hz, 1H), 7.09 (d, *J* = 7.4 Hz, 1H), 4.93 (d, *J* = 1.2 Hz, 1H), 4.89 (d, *J* = 1.2 Hz, 1H), 2.85-2.77 (m, 3H), 2.43-2.41 (m, 1H), 2.33-2.26 (m, 1H), 2.21-2.15

(m, 1H), 1.92-1.81 (m, 2H), 1.78-1.70 (m, 1H), 1.63 (s, 1H), 1.54-1.46 (m, 2H), 1.31-1.19 (m, 7H), 0.88-0.84 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.6, 141.0, 136.6, 128.4, 127.0, 126.9, 126.2, 107.0, 80.6, 54.1, 44.8, 36.1, 31.7, 29.8, 28.7, 27.5, 26.9, 26.5, 22.7, 14.1; **HRMS** (ESI) Calcd for $C_{20}H_{29}O$ $[M + H]^+$ 285.2218, found 285.2209.



(3a*S,9b*R**)-1,1-Dibutyl-2-methylene-1,2,3,3a,4,5-hexahydro-9b*H*-cyclopenta[*a*]naphthalen-9b-ol (3qk):** Colorless oil (41.0 mg, 44%); R_f 0.3 (hexane/EtOAc = 30/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, J = 6.9 Hz, 1H), 7.21-7.13 (m, 2H), 7.06 (d, J = 7.3 Hz, 1H), 4.90 (s, 1H), 4.59 (s, 1H), 2.84-2.76 (m, 2H), 2.67-2.60 (m, 1H), 2.42-2.35 (m, 1H), 2.21-2.16 (m, 1H), 1.81-1.77 (m, 2H), 1.72-1.67 (m, 1H), 1.40-1.33 (m, 4H), 1.28-1.20 (m, 4H), 1.11-0.84 (m, 7H), 0.78-0.74 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.3, 140.2, 138.5, 128.7, 128.3, 126.8, 125.5, 106.5, 84.3, 55.9, 46.1, 36.5, 33.9, 32.7, 27.2, 27.1, 26.7, 26.4, 24.0, 23.4, 14.2, 14.0; **HRMS** (ESI) Calcd for $C_{22}H_{33}O$ $[M + H]^+$ 313.2531, found 313.2533.



(1*S,3a*S**,9b*S**)-1-Methyl-2-methylene-1-phenyl-1,2,3,3a,4,5-hexahydro-9b*H*-cyclopenta[*a*]naphthalen-9b-ol (3ql):** Colorless oil (42.0 mg, 48%); R_f 0.3 (hexane/EtOAc = 25/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.8 Hz, 1H), 7.33-7.21 (m, 2H), 7.02-6.94 (m, 4H), 6.65-6.62 (m, 2H), 5.39 (s, 1H), 5.18 (s, 1H), 3.04 (dd, J = 17.1, 9.3 Hz, 1H), 2.65-2.57 (m, 1H), 2.40 (dq, J = 17.2, 2.8 Hz, 1H), 2.31-2.19 (m, 2H), 1.94 (s, 1H), 1.62 (s, 3H), 1.49-1.43 (m, 1H), 0.94-0.83 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.1, 145.3, 138.9, 138.2, 128.5, 128.0, 127.6, 127.5, 127.4, 125.9, 125.8, 110.0, 83.7, 59.6, 45.7, 36.7, 29.1, 28.7, 23.3; **HRMS** (ESI) Calcd for $C_{21}H_{23}O$ $[M + H]^+$ 291.1749, found 291.1746. Recrystallization from CH_2Cl_2/pentane afforded single crystals suitable for X-ray diffraction analysis, which

unambiguously confirmed the molecular structure of **3ql** and its relative configuration (Figure S3).[19]

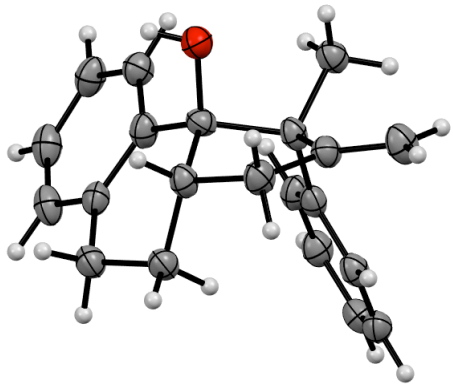
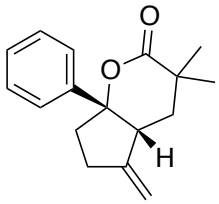
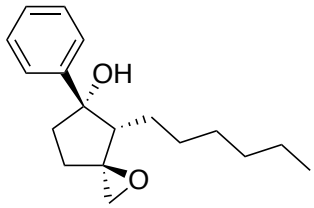


Figure S3. ORTEP drawing of **3ql** (thermal ellipsoids set at 50% probability).

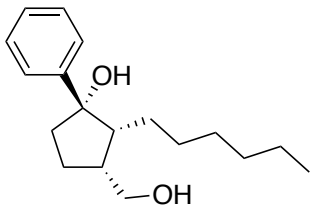


(4a*R,7a*S**)-3,3-Dimethyl-5-methylene-7a-phenylhexahydrocyclopenta[b]pyran-2(3H)-one (3ap):** Colorless oil (41.0 mg, 53%); R_f 0.3 (hexane/EtOAc = 20/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41-7.33 (m, 4H), 7.31-7.26 (m, 1H), 5.13 (q, J = 2.0 Hz, 1H), 5.05 (d, J = 2.0 Hz, 1H), 3.19-3.16 (m, 1H), 2.72-2.62 (m, 1H), 2.57-2.50 (m, 1H), 2.40-2.34 (m, 1H), 2.16-2.08 (m, 1H), 1.97 (dd, J = 14.3, 6.9 Hz, 1H), 1.82 (dd, J = 14.3, 6.0 Hz, 1H), 1.33 (s, 3H), 1.07 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.8, 151.5, 143.8, 128.6, 127.5, 124.6, 108.3, 93.6, 46.7, 41.8, 36.6, 36.5, 30.3, 29.6, 27.7; **HRMS** (ESI) Calcd for $C_{17}H_{21}O_2$ $[M + H]^+$ 257.1542, found 257.1549.

Product Transformations



(3*S,4*S**,5*S**)-4-Hexyl-5-phenyl-1-oxaspiro[2.4]heptan-5-ol (4):** To a solution of **3ab** (51.6 mg, 0.20 mmol) and $NaHCO_3$ (16.8 mg, 0.20 mmol) in CH_2Cl_2 (1 mL) was added *m*CPBA (106 mg, 0.40 mmol) at 0 °C. The mixture was stirred at room temperature for 12 h until complete consumption of the starting material (monitored by TLC). The reaction mixture was diluted with CH_2Cl_2, and the excess *m*CPBA was decomposed by the addition of aqueous $Na_2S_2O_3$. Upon extraction with CH_2Cl_2, the organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the title compound as a colorless oil (49.0 mg, 89%, dr = 7:1 as determined by ^{1}H NMR. A pure fraction of the major diastereomer could be obtained); R_f 0.3 (hexane/EtOAc = 15/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51-7.49 (m, 2H), 7.37-7.33 (m, 2H), 7.26-7.23 (m, 1H), 2.84 (d, *J* = 4.6 Hz, 1H), 2.74 (d, *J* = 4.6 Hz, 1H), 2.41-2.38 (m, 1H), 2.28-2.20 (m, 1H), 2.17-2.08 (m, 4H), 1.22-1.08 (m, 4H), 1.03-1-01 (m, 4H), 0.93-0.84 (m, 2H), 0.78 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.3, 128.1, 126.7, 125.0, 83.7, 64.9, 51.7, 48.9, 40.6, 31.4, 30.5, 29.4, 28.4, 22.5, 21.7, 14.0; **HRMS** (ESI) Calcd for $C_{18}H_{27}O_2$ $[M + H]^+$ 275.2011, found 275.2003.



(1*S,2*R**,3*R**)-2-Hexyl-3-(hydroxymethyl)-1-phenylcyclopentan-1-ol (5):** Under nitrogen atmosphere, to a solution of **3ab** (51.6 mg, 0.20 mmol) in THF (0.5 mL) was added BH_3•THF (1.0 M, 0.60 mL, 0.60 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 2 h, followed by the addition of aq. NaOH (3.0 M, 0.30 mL, 0.90 mmol) and H_2O_2 (ca. 30 %, 0.5 mL). After stirring for 3 h at room temperature, the resulting mixture was quenched with saturated aqueous $NaHCO_3$ solution. Upon extraction with ethyl acetate, the organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the title compound as a colorless oil (46.0

mg, 83%); R_f 0.3 (hexane/EtOAc = 5/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46-7.44 (m, 2H), 7.33-7.29 (m, 2H), 7.23-7.19 (m, 1H), 4.41 (brs, 2H), 3.80 (dd, *J* = 10.7, 2.1 Hz, 1H), 3.57 (dd, *J* = 10.8, 3.0 Hz, 1H), 2.55-2.45 (m, 1H), 2.24-2.19 (m, 1H), 2.11-1.94 (m, 4H), 1.43-1.35 (m, 1H), 1.24-1.03 (m, 9H), 0.81 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.7, 127.9, 126.2, 125.3, 83.2, 61.8, 53.7, 43.2, 40.4, 31.7, 29.5, 28.8, 24.7, 24.0, 22.6, 14.0; **HRMS** (ESI) Calcd for $C_{18}H_{29}O_2$ $[M + H]^+$ 277.2168, found 277.2169. Recrystallization from CH_2Cl_2/pentane afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structure of **5** and its relative configuration (Figure S4).

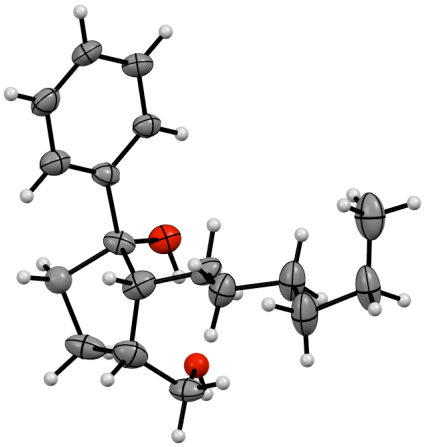
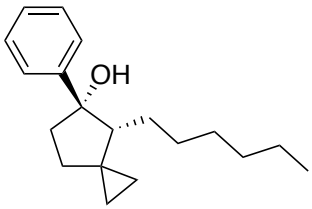
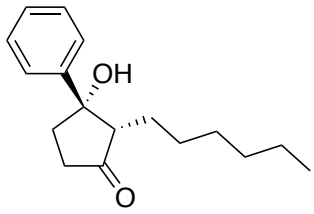


Figure S4. ORTEP drawing of **5** (thermal ellipsoids set at 50% probability).

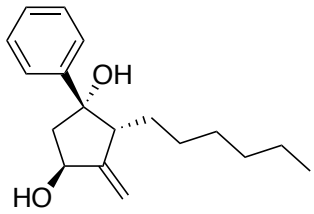


(4*R,5*S**)-4-Hexyl-5-phenylspiro[2.4]heptan-5-ol (6):** Under nitrogen atmosphere, to a solution of **3ab** (51.6 mg, 0.20 mmol) and CH_2I_2 (48 µl, 0.60 mmol) in CH_2Cl_2 (0.2 mL) was added Et_2Zn (1.0 M, 0.60 mL, 0.60 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 6 h until complete consumption of the starting material (monitored by TLC). The reaction mixture was quenched with saturated aqueous NH_4Cl and filtered through a pad of Celite. After being washed with brine and extracted with CH_2Cl_2, the organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the title compound as a colorless oil (40.0 mg, 74%); R_f 0.3 (hexane/EtOAc = 30/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51-7.49 (m, 2H), 7.35-7.31 (m, 2H),

7.23-7.19 (m, 1H), 2.30-2.19 (m, 2H), 2.01-1.85 (m, 4H), 1.26-1.08 (m, 3H), 1.10-1.01 (m, 4H), 0.88-0.76 (m, 7H), 0.56-0.52 (m, 1H), 0.45-0.40 (m, 1H), 0.33-0.29 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.3, 128.0, 126.3, 125.0, 84.9, 53.0, 42.6, 34.5, 31.5, 29.6, 27.9, 24.7, 24.4, 22.5, 14.0, 10.3, 9.5; **HRMS** (ESI) Calcd for $C_{19}H_{29}O$ $[M + H]^+$ 273.2218, found 273.2215.



(2*S,3*S**)-2-Hexyl-3-hydroxy-3-phenylcyclopentan-1-one (7):** The ozonolysis was carried out according to the reported procedure.[20] A solution of **3ab** (77.4 mg, 0.30 mmol) in CH_2Cl_2 (10 mL) was purged with O_3 at –78 °C until no more starting material was observed by TLC analysis (10 min). The light blue color would be observed once the starting material was fully consumed. The excess O_3 in the solution was removed by purging of oxygen and argon at –78 °C for 5 min, respectively. To the mixture was added PPh_3 (79 mg, 0.30 mmol) at –78 °C, and the resulting mixture was stirred and allowed to gradually warm to room temperature under nitrogen overnight. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography to afford the title compound as a colorless oil (31.0 mg, 40%); R_f 0.3 (hexane/EtOAc = 7/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.48 (m, 2H), 7.42-7.38 (m, 2H), 7.32-7.29 (m, 1H), 2.61-2.43 (m, 3H), 2.33-2.18 (m, 2H), 1.88 (s, 1H), 1.70-1.62 (m, 1H), 1.38-1.04 (m, 9H), 0.80 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 217.6, 144.7, 128.5, 127.3, 124.7, 81.8, 59.6, 37.6, 35.3, 31.4, 29.3, 28.0, 23.3, 22.5, 14.0; **HRMS** (ESI) Calcd for $C_{17}H_{25}O_2$ $[M + H]^+$ 261.1855, found 261.1850.



(1*S,3*S**,5*R**)-5-Hexyl-4-methylene-1-phenylcyclopentane-1,3-diol (8):** The allylic oxidation was carried out according to the reported procedure.[21] To a solution of **3ab** (51.6 mg, 0.20 mmol) in CH_2Cl_2 (10 mL) was added selenium dioxide (133 mg, 1.2 mmol) and *tert*-butyl hydroperoxide (70% solution, 1.2 mL). The resulting mixture was stirred at room

temperature for 24 h. The mixture was filtered through a silica gel pad, eluted with CH_2Cl_2 and then concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the product as light yellow oil (16.0 mg, 29%); R_f 0.3 (hexane/EtOAc = 2/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.39-7.32 (m, 3H), 5.52 (d, *J* = 1.2 Hz, 1H), 5.47 (d, *J* = 1.6 Hz, 1H), 4.57 (s, 1H), 3.18 (s, 1H), 2.85 (dd, *J* = 15.0, 7.4 Hz, 1H), 2.67 (s, 1H), 2.60-2.48 (m, 1H), 2.10 (d, *J* = 15.0 Hz, 1H), 1.35-1.02 (m, 10H), 0.81 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.7, 140.6, 128.3, 127.9, 126.3, 114.1, 84.7, 83.6, 69.9, 41.9, 35.8, 31.8, 29.5, 22.9, 22.5, 14.0; **HRMS** (ESI) Calcd for $C_{18}H_{27}O_2$ $[M + H]^+$ 275.2011, found 275.2016.

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NMR Spectra

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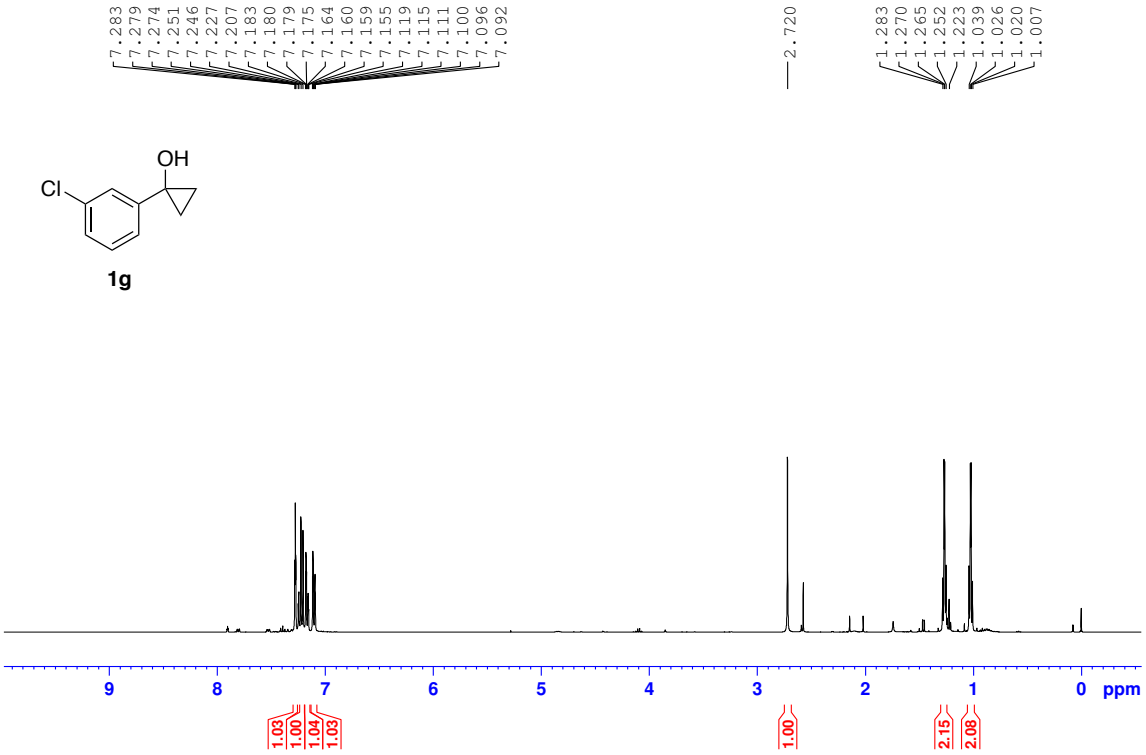

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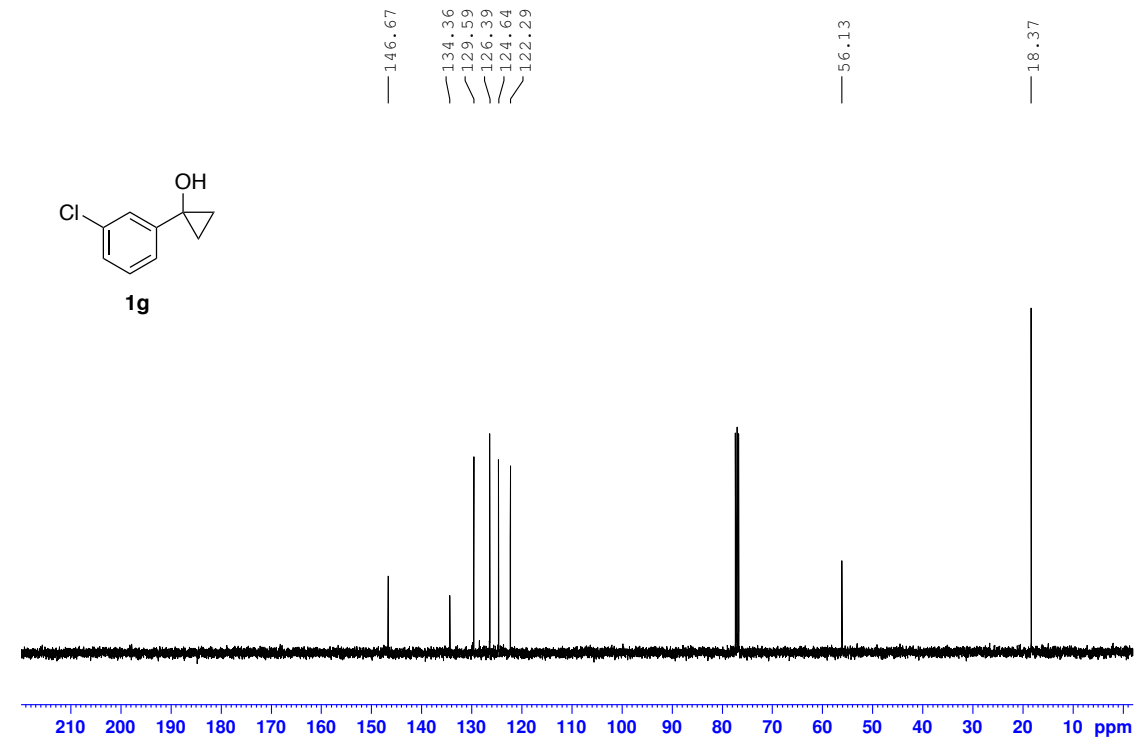

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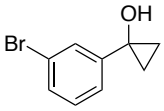

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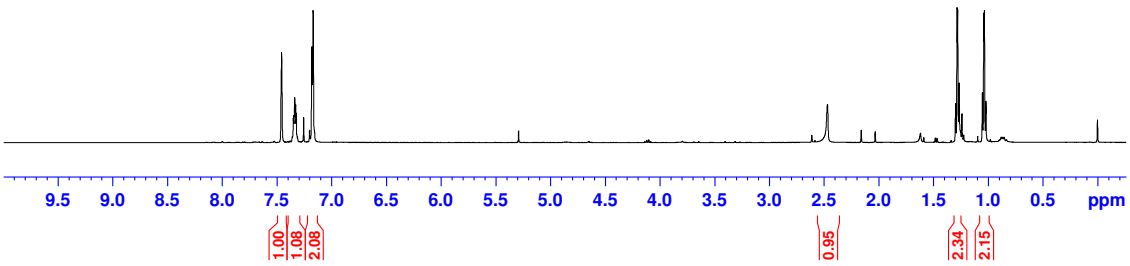

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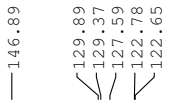

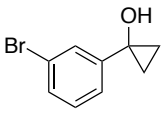

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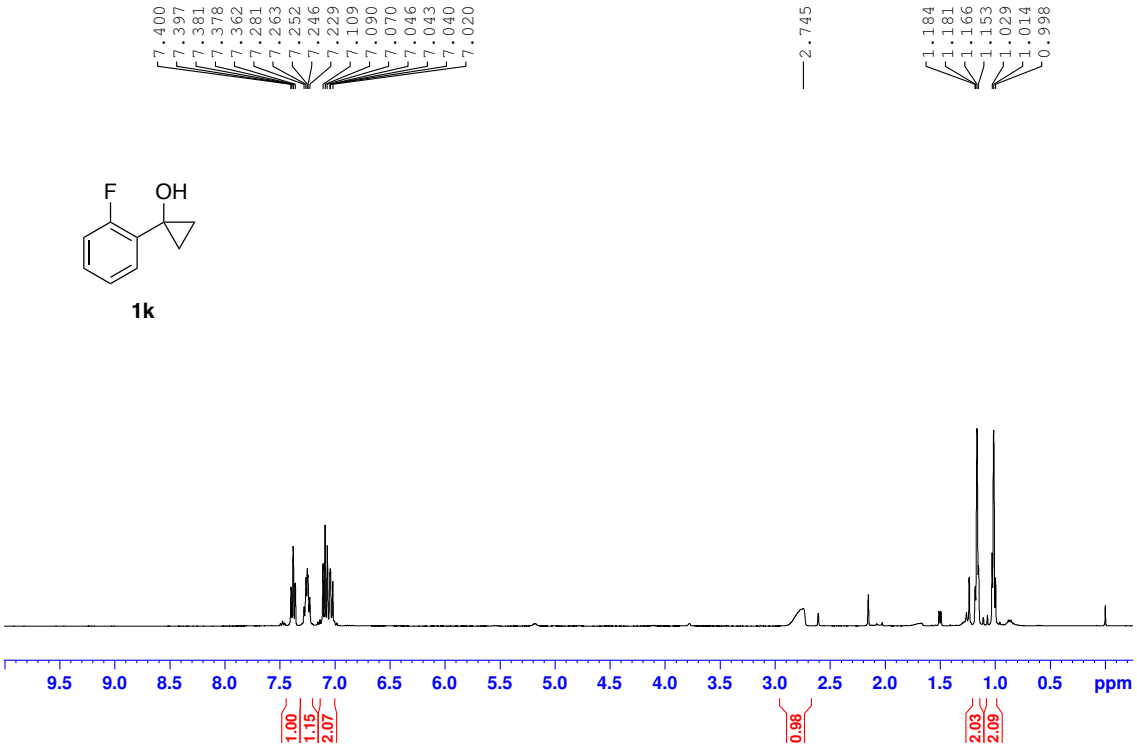

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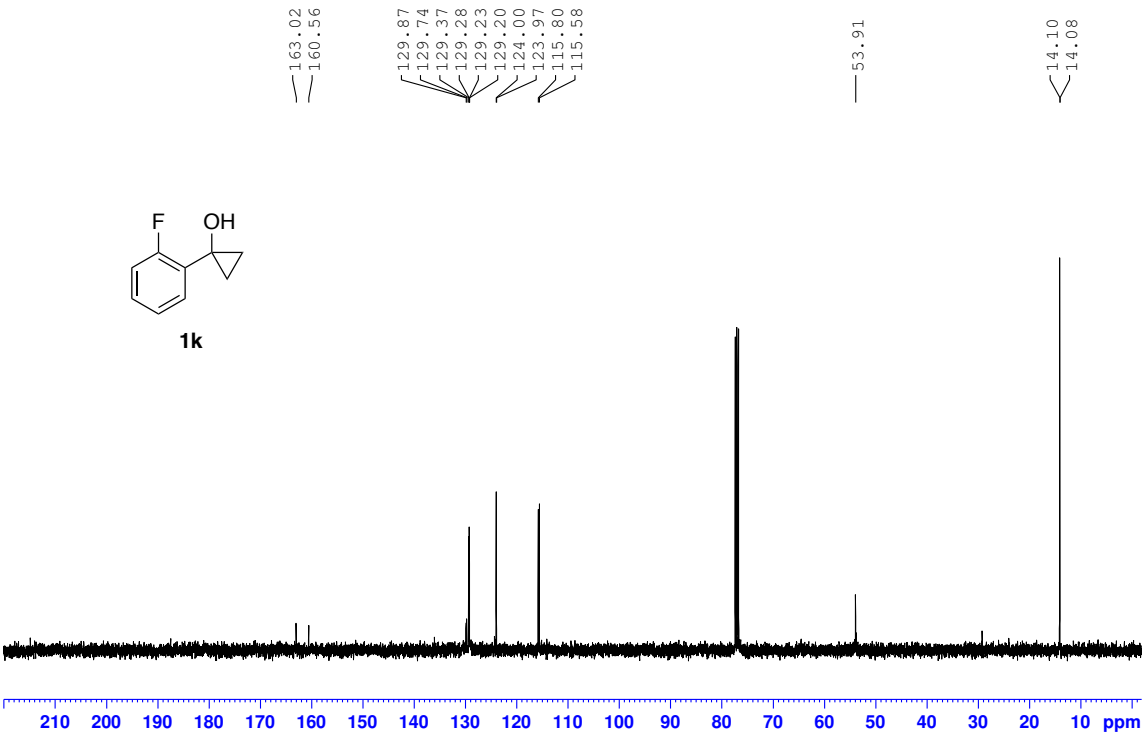

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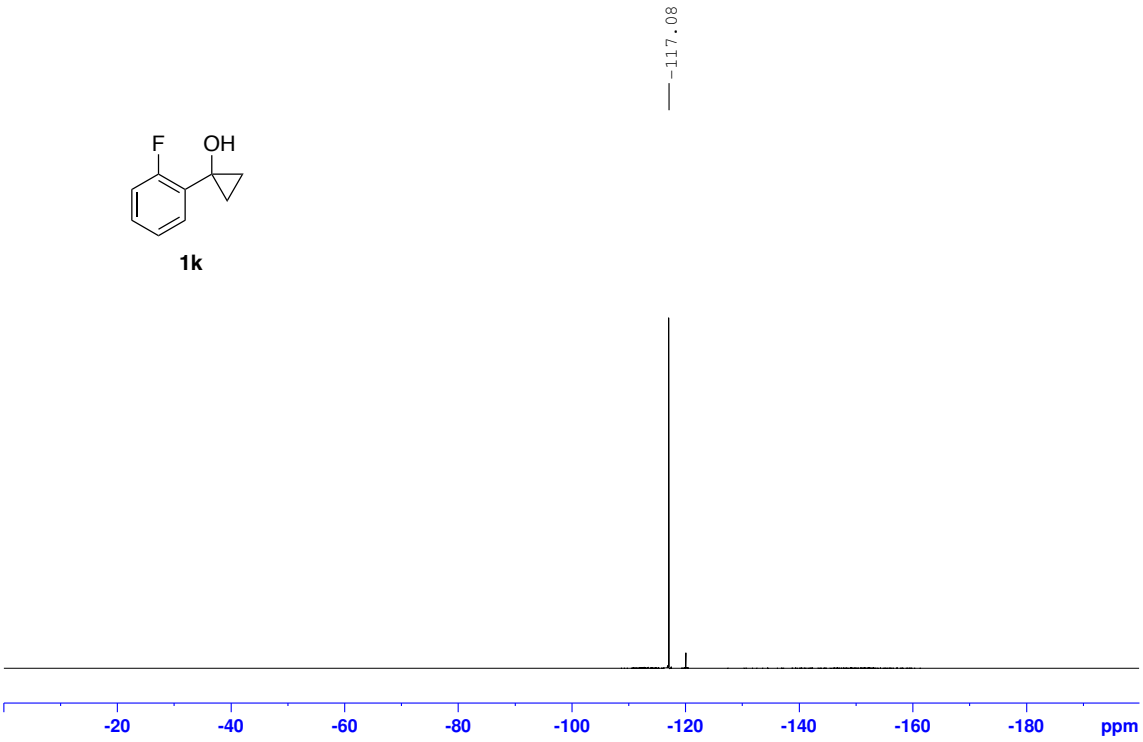

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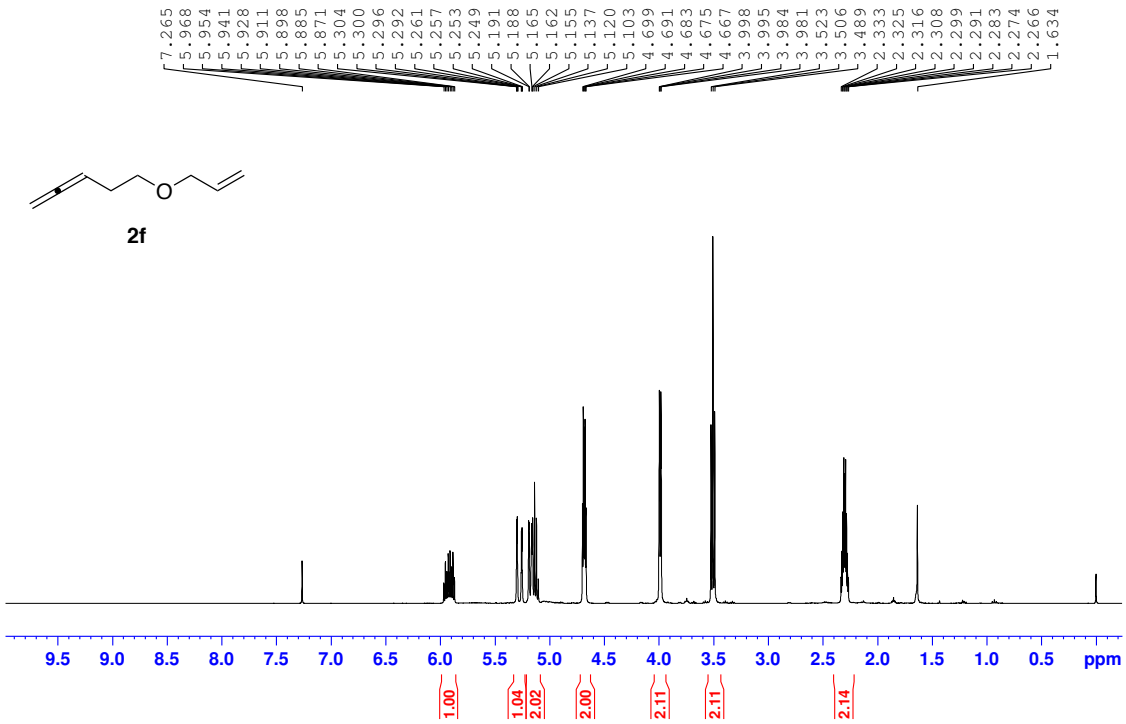

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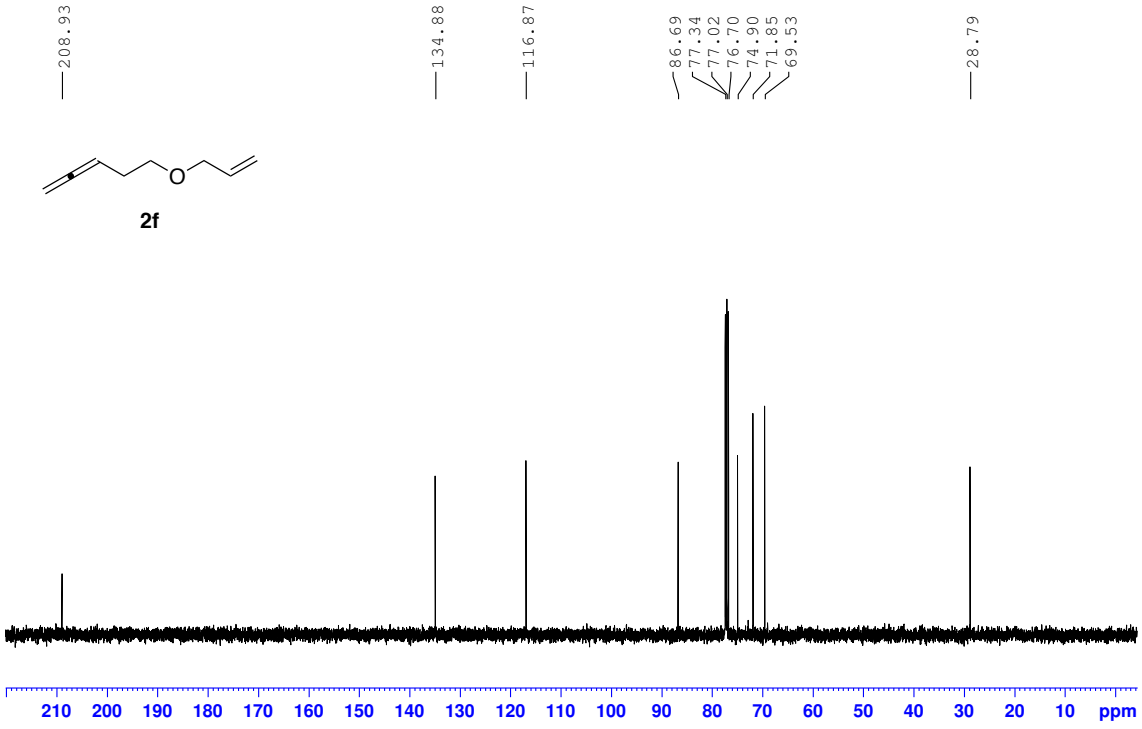

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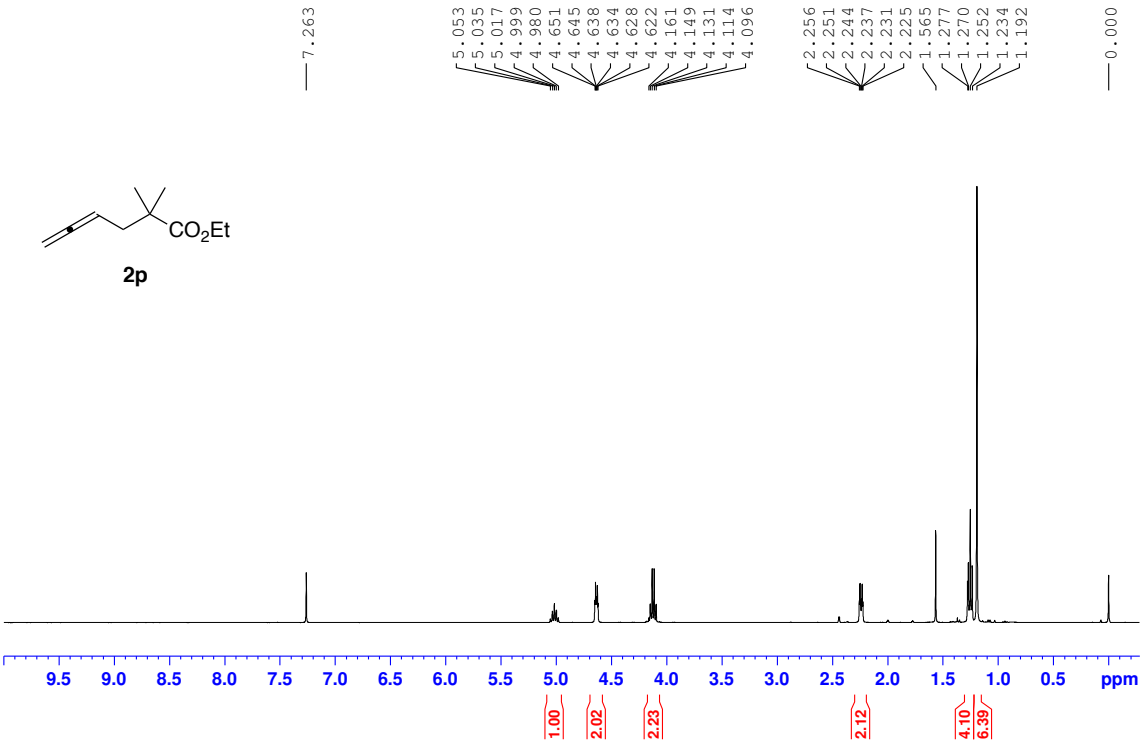

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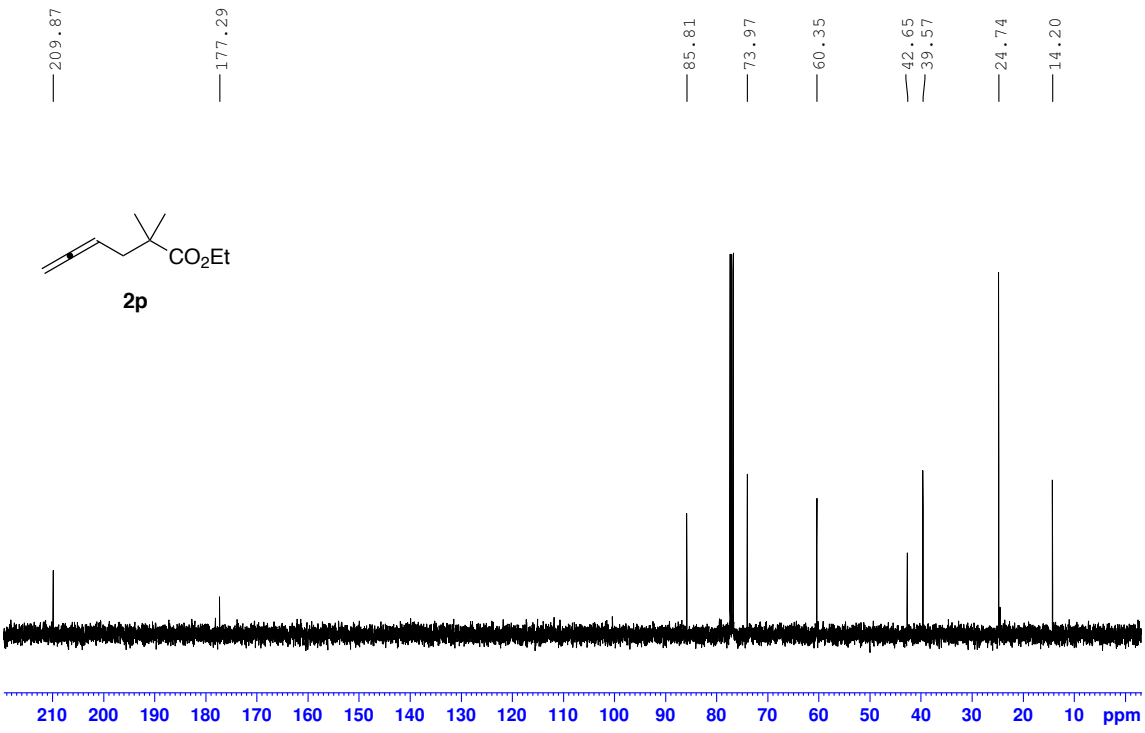

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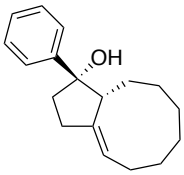

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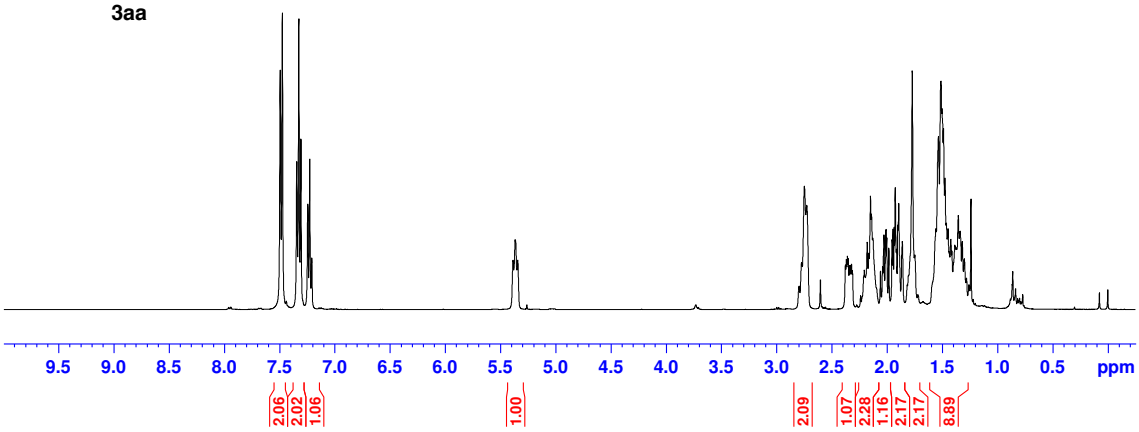

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

2.06 2.02 1.06 1.00 2.09 1.07 2.28 1.16 2.17 2.17 8.89

JF09-455C
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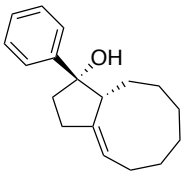

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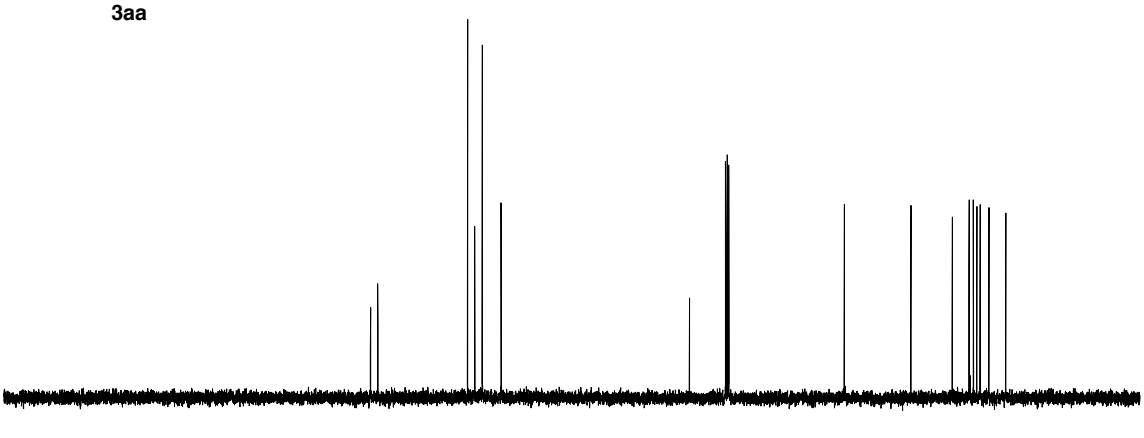

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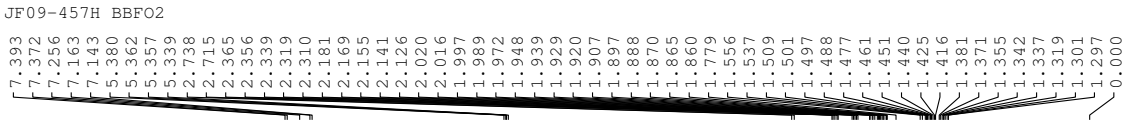

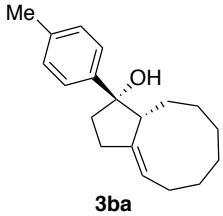

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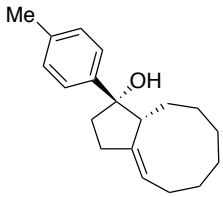

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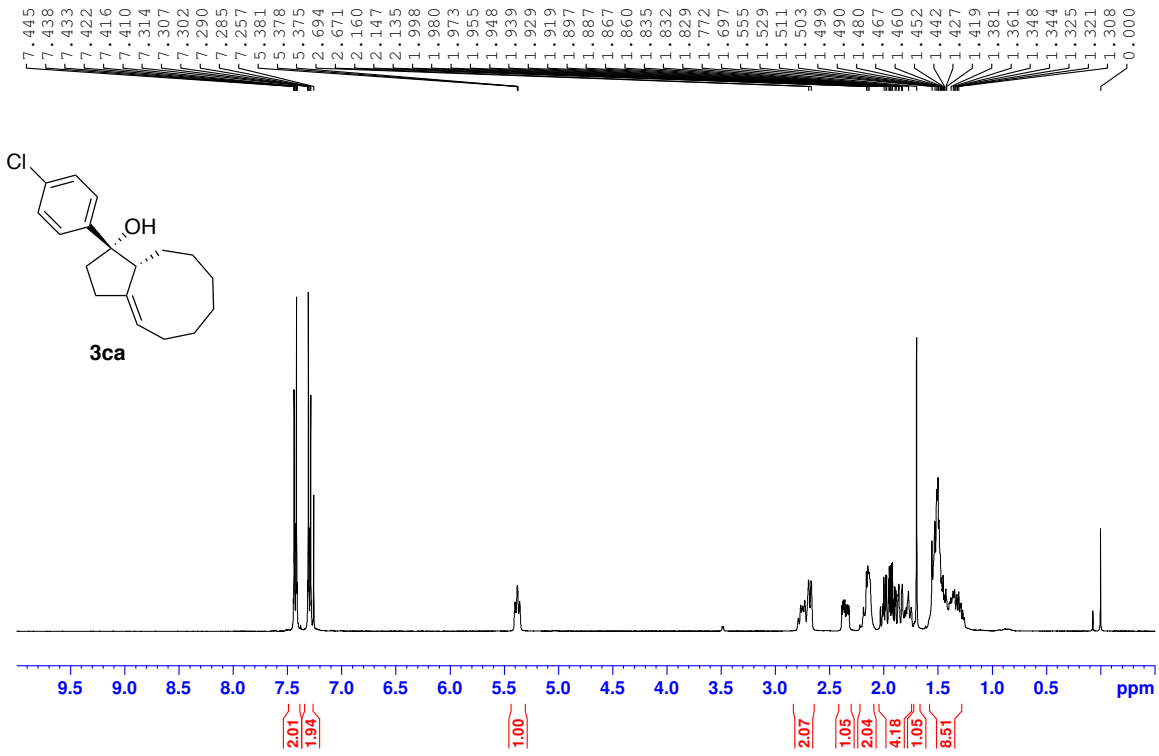

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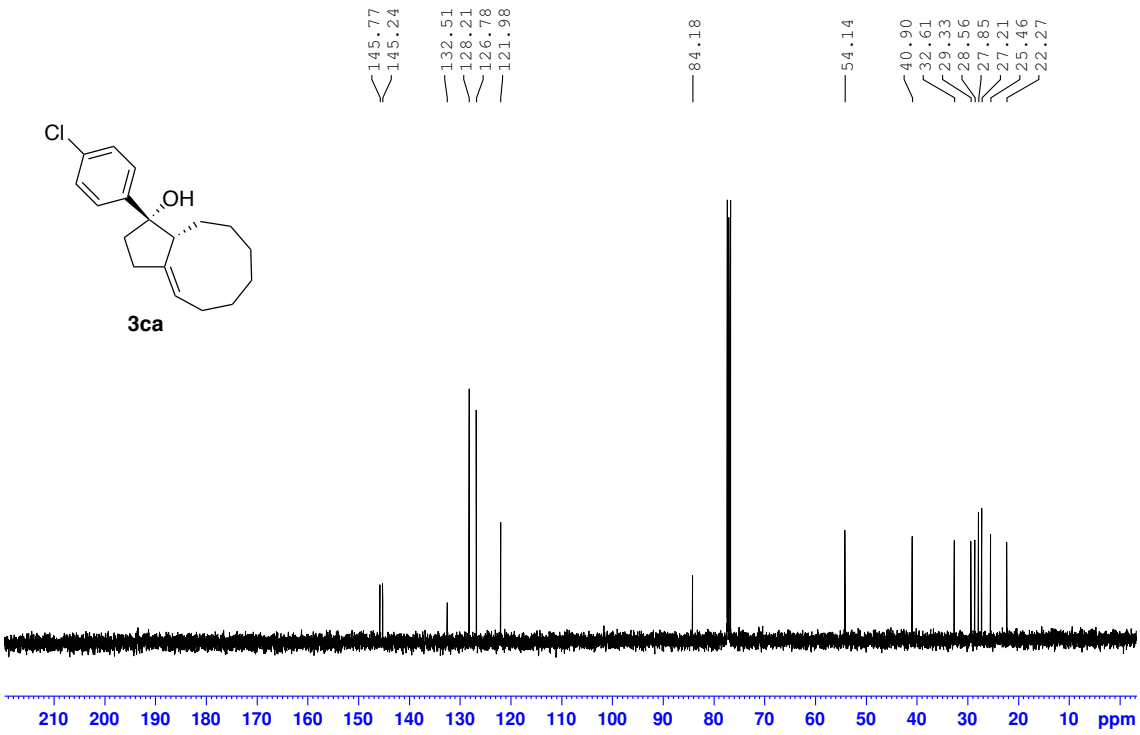

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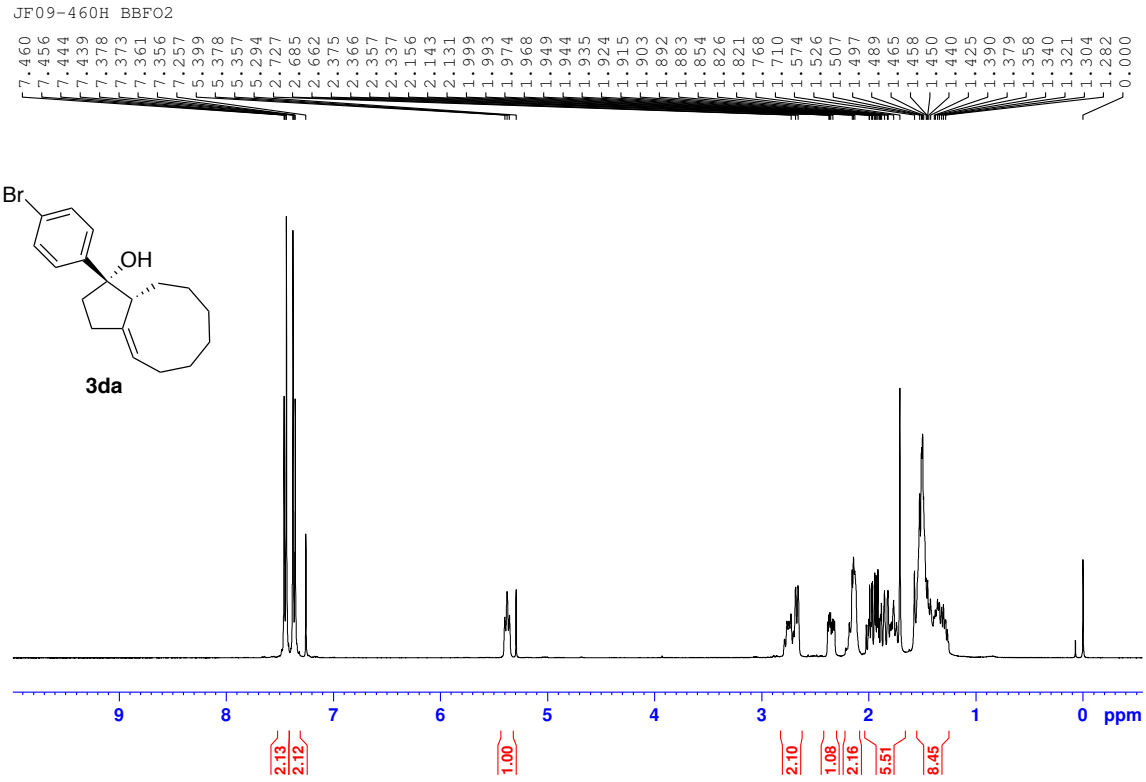

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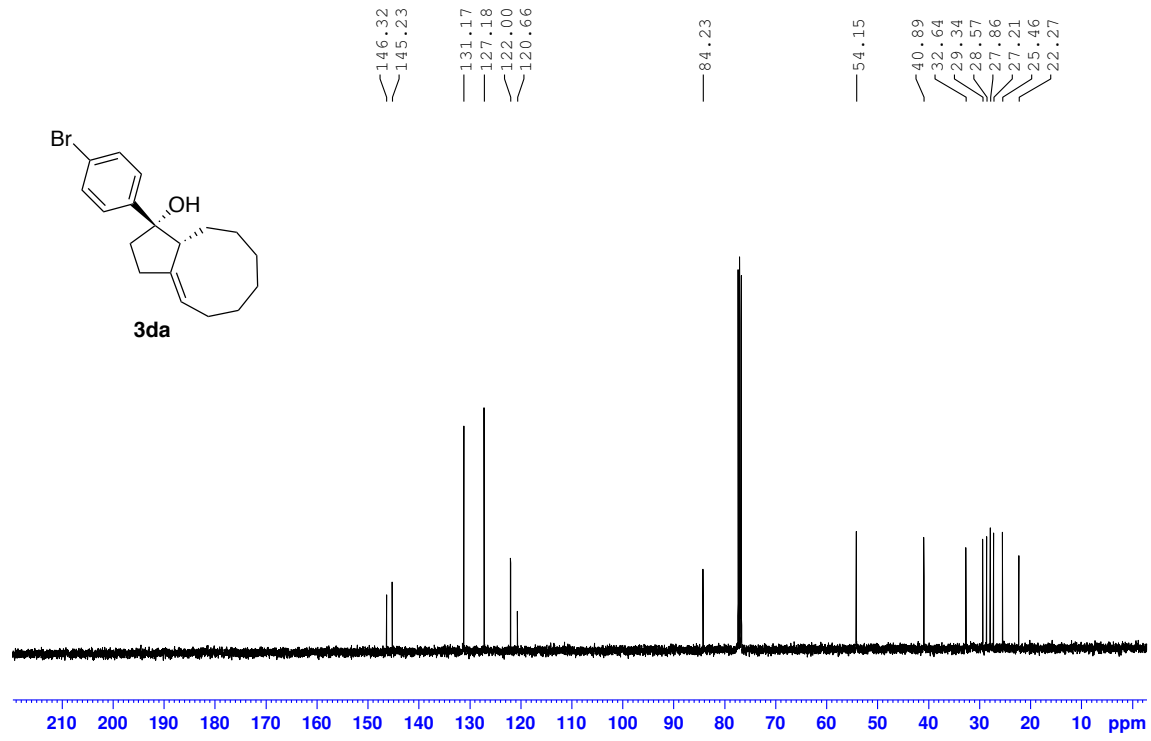

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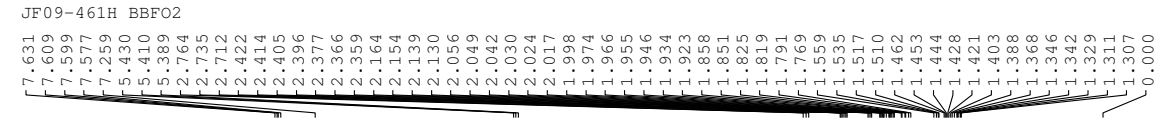

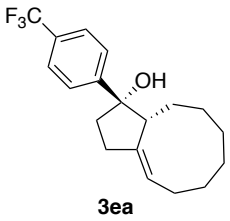

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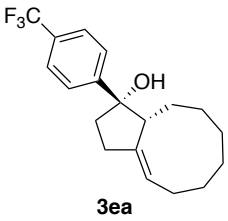

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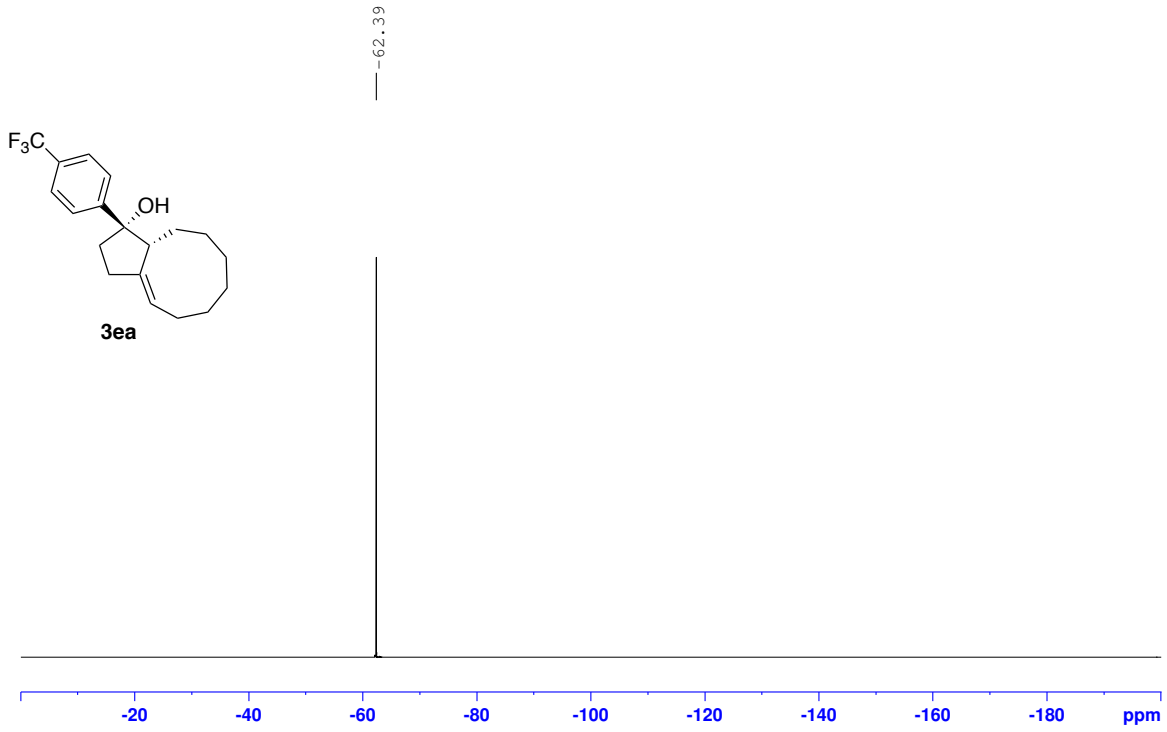

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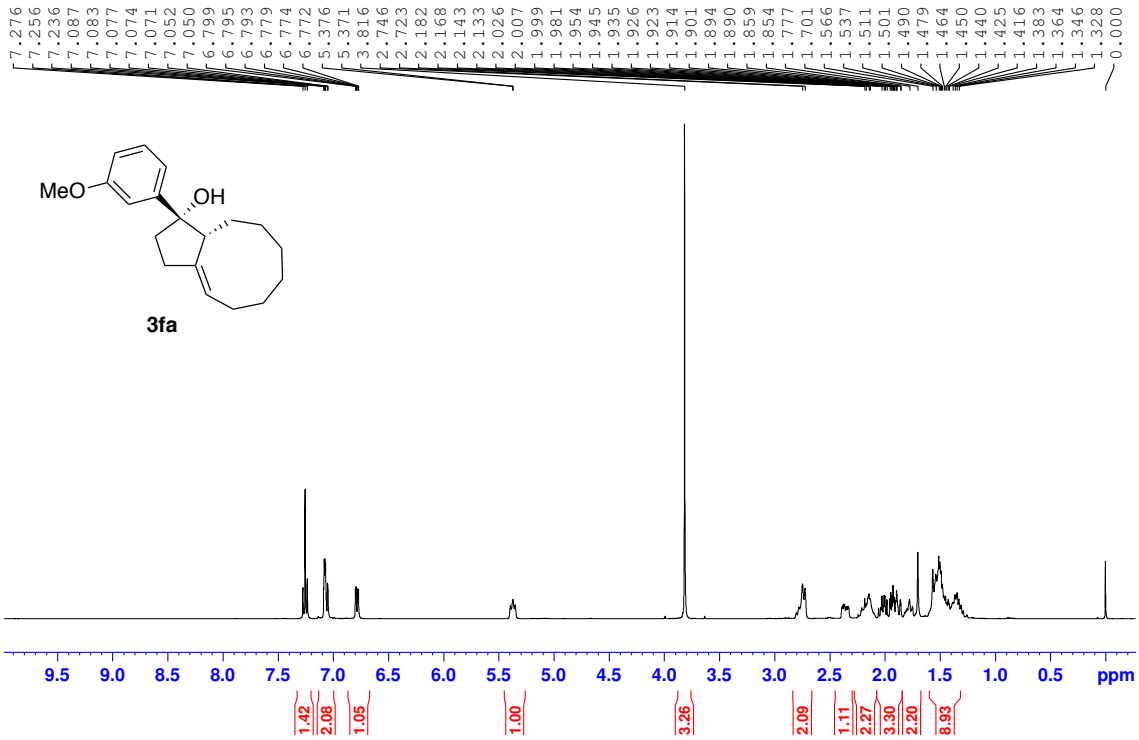

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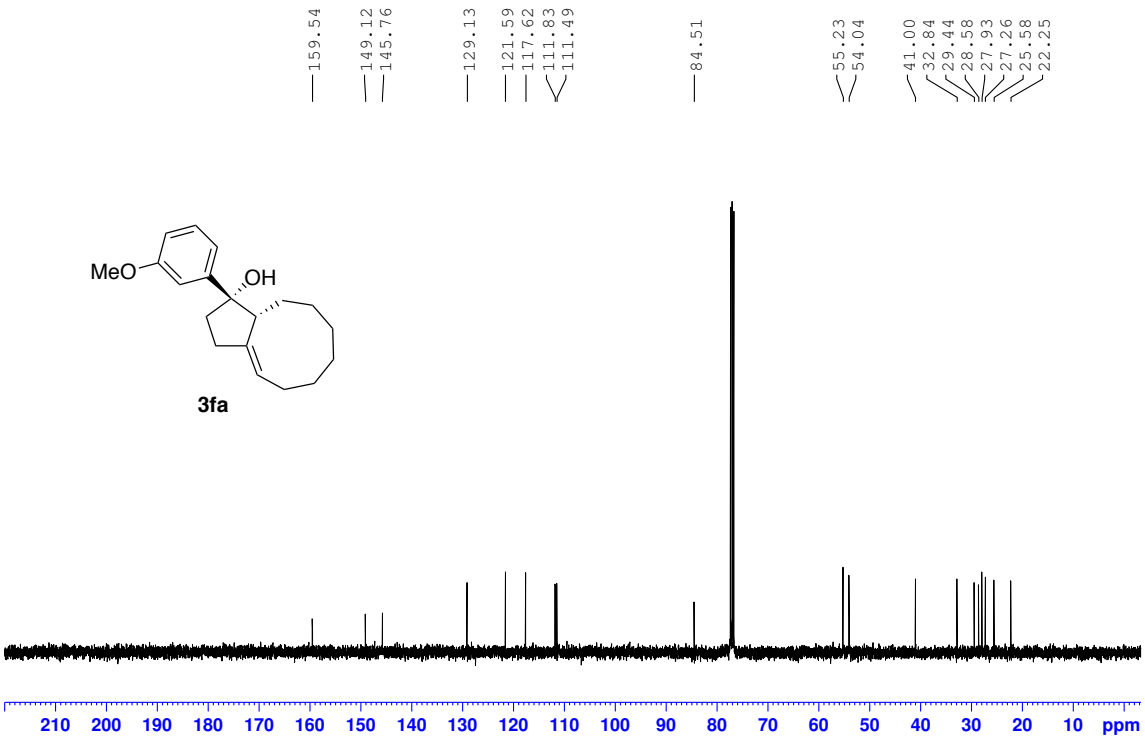

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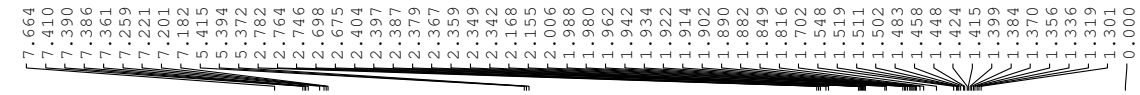

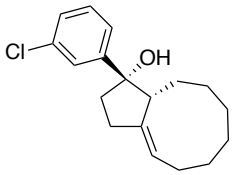

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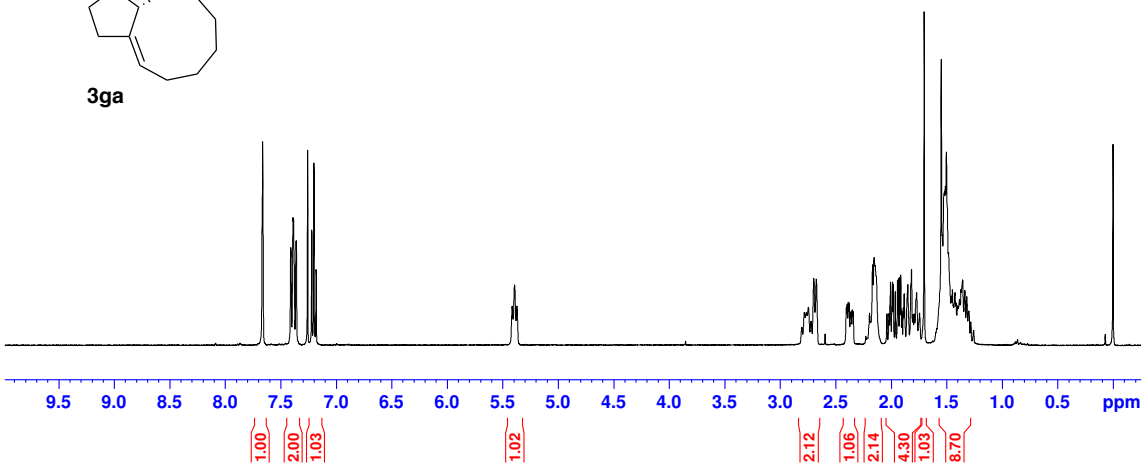

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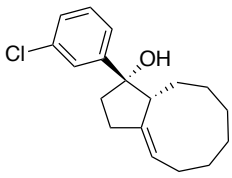

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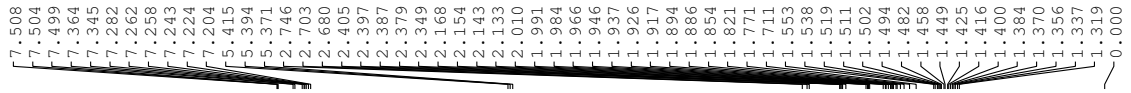

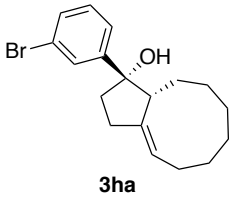

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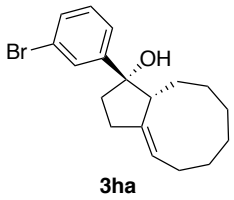

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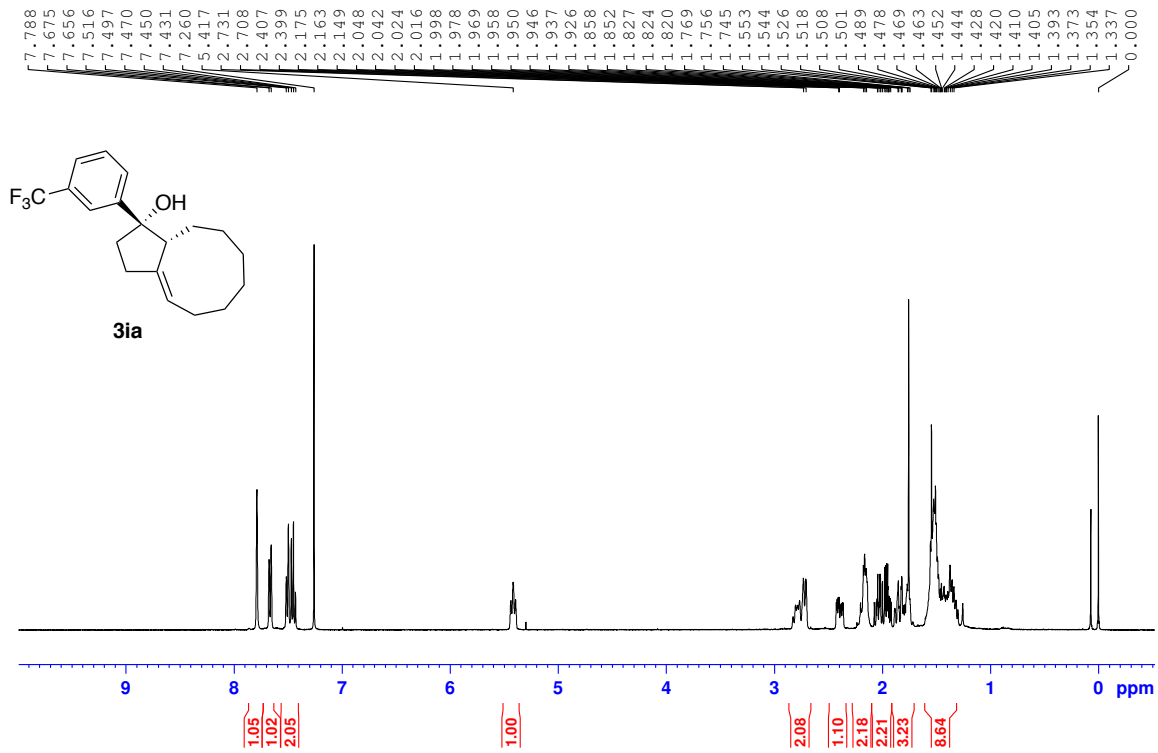

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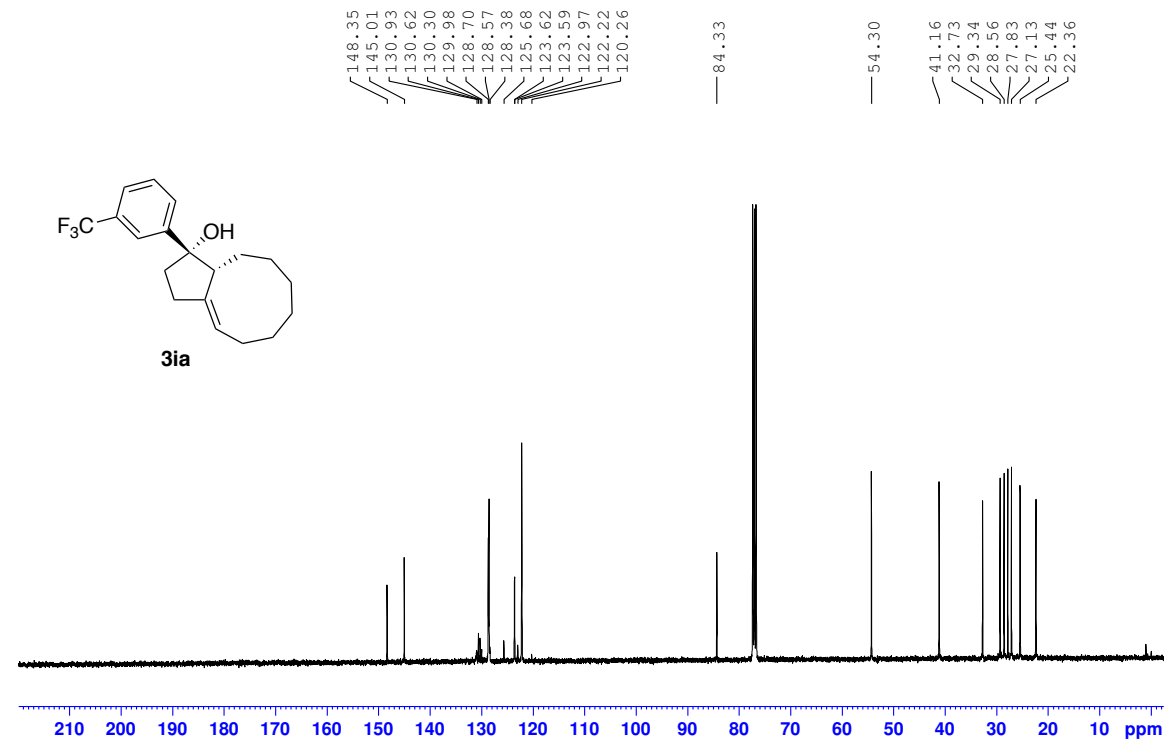

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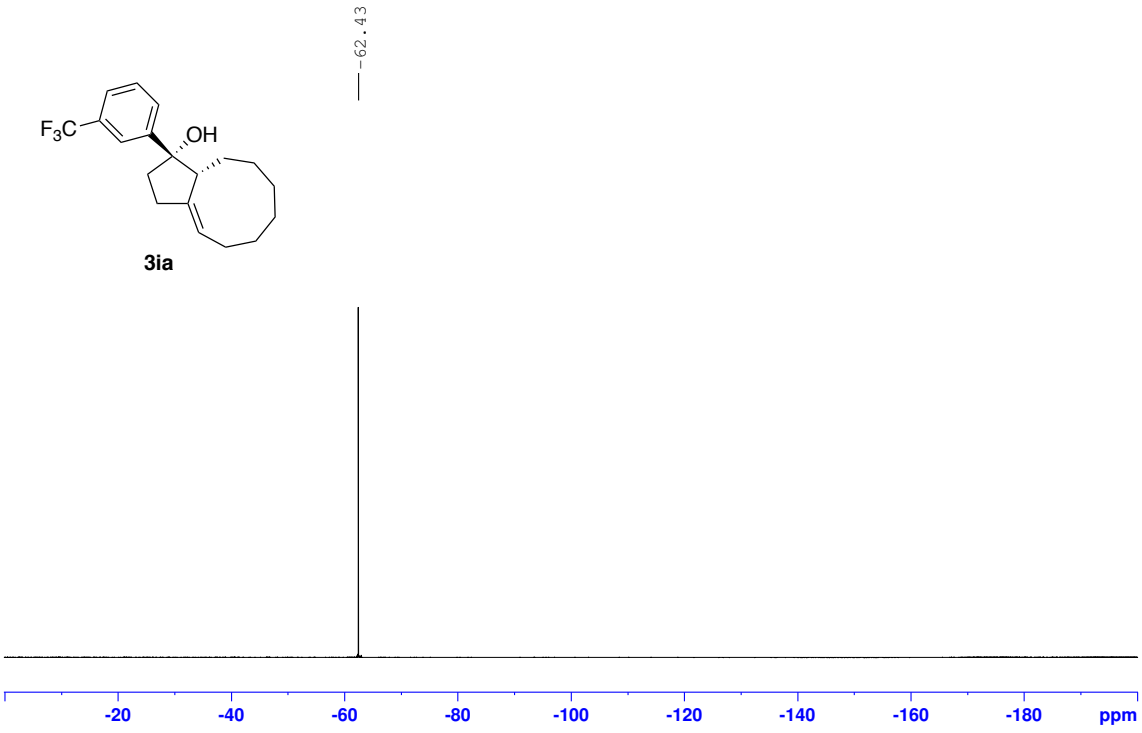

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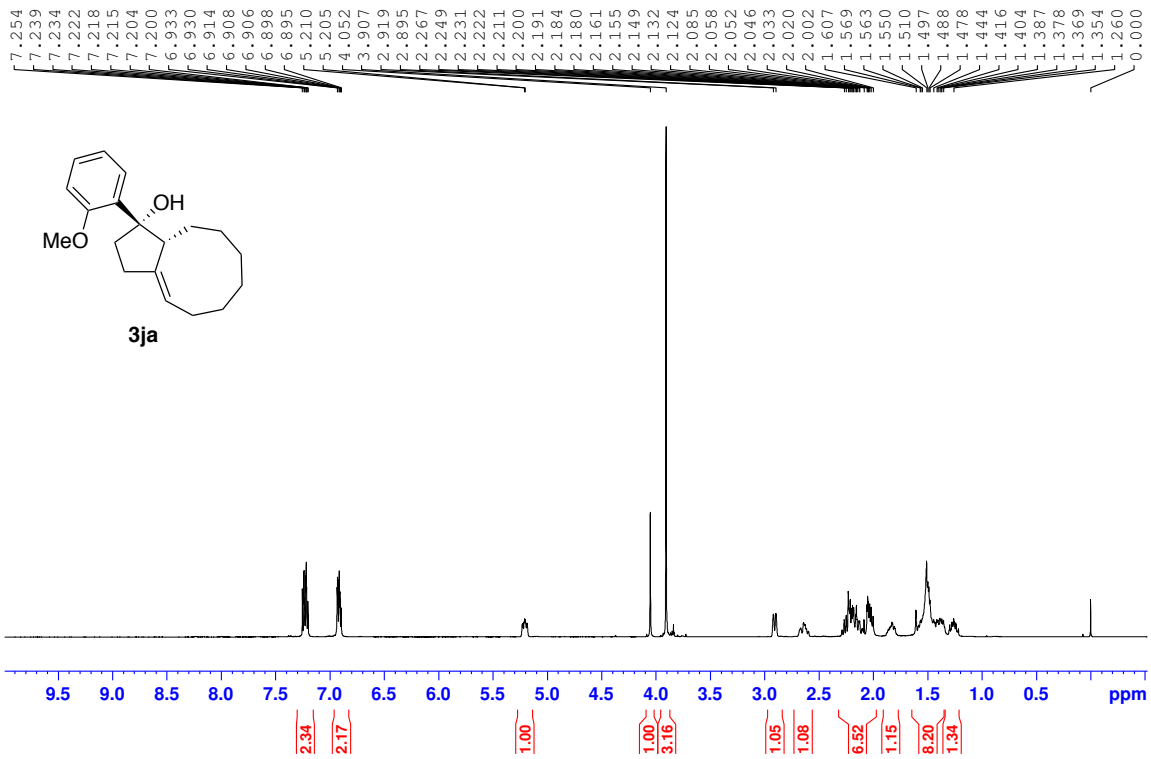

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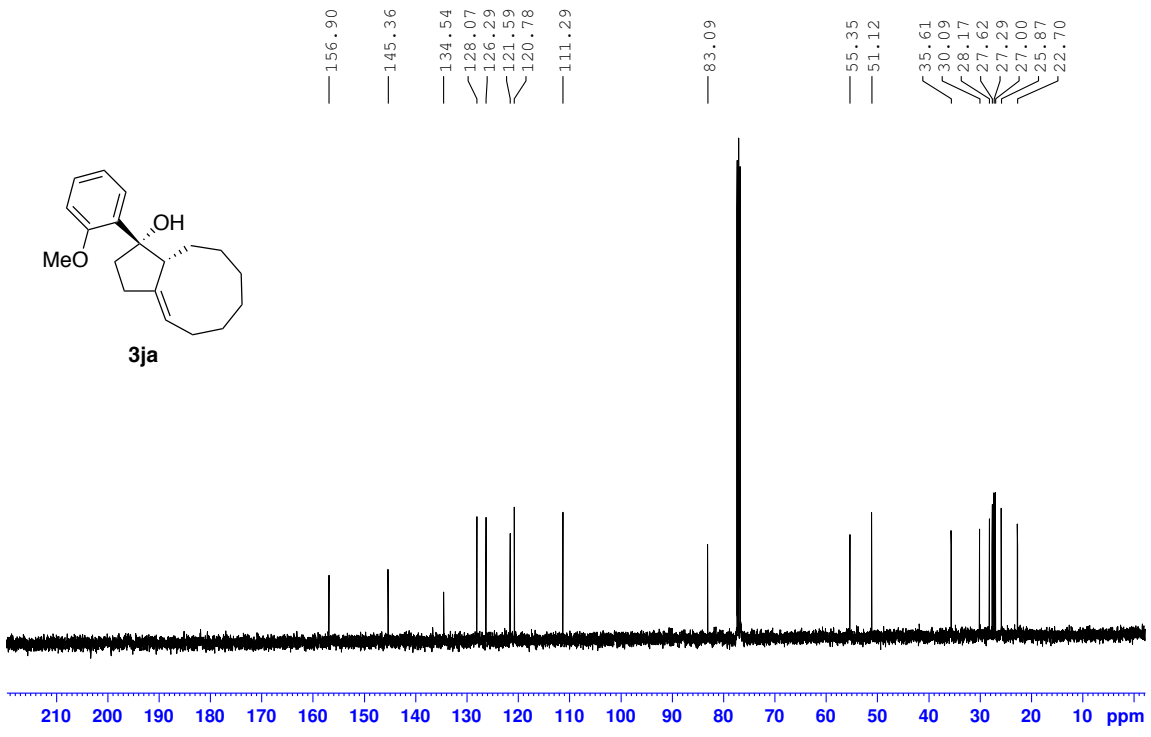

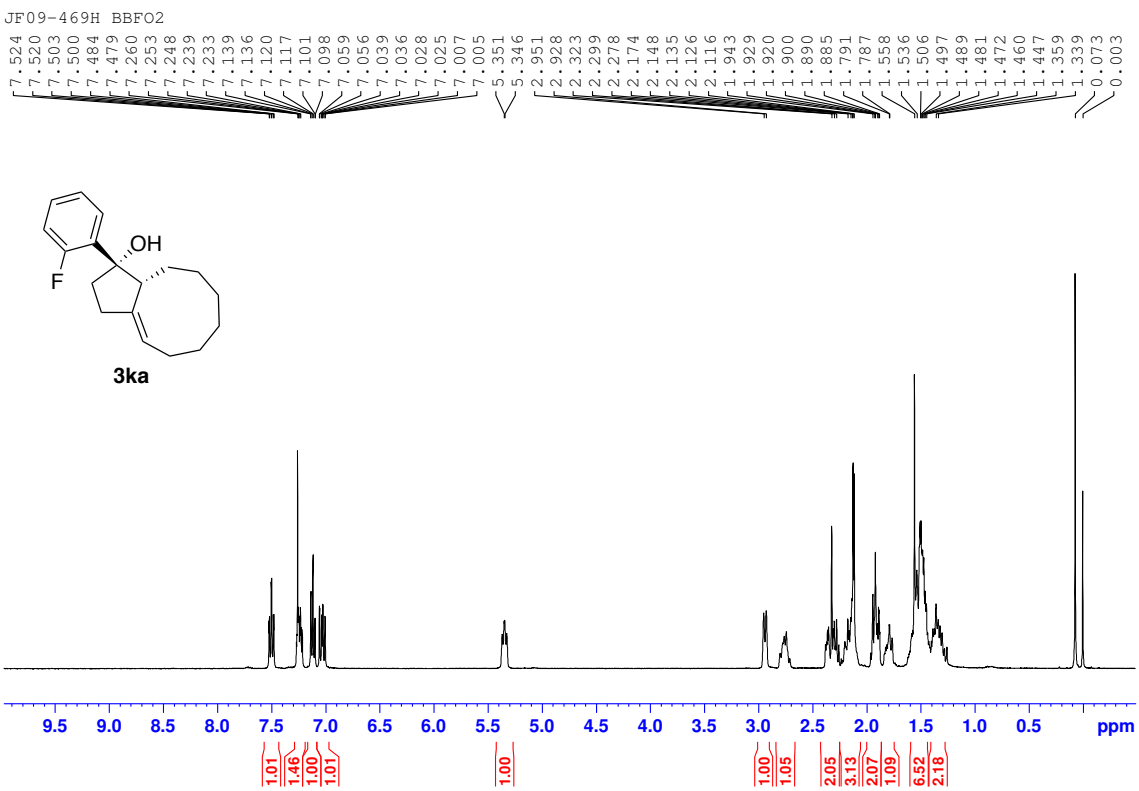
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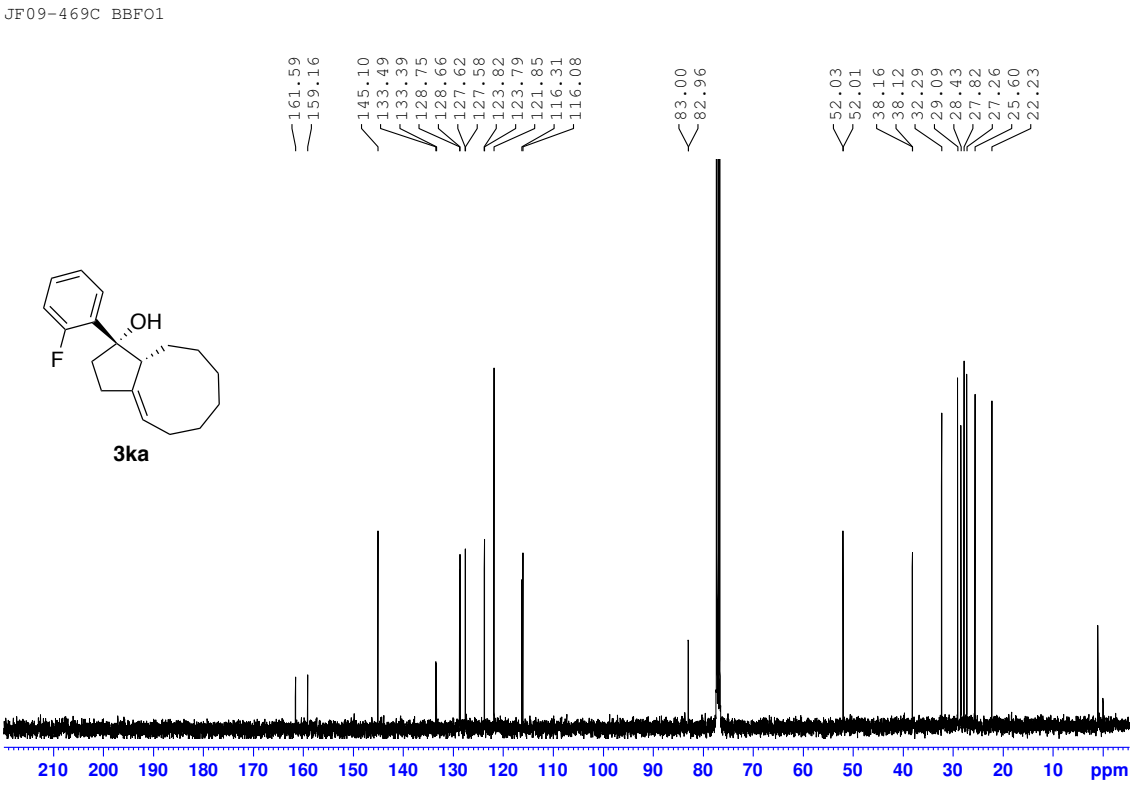
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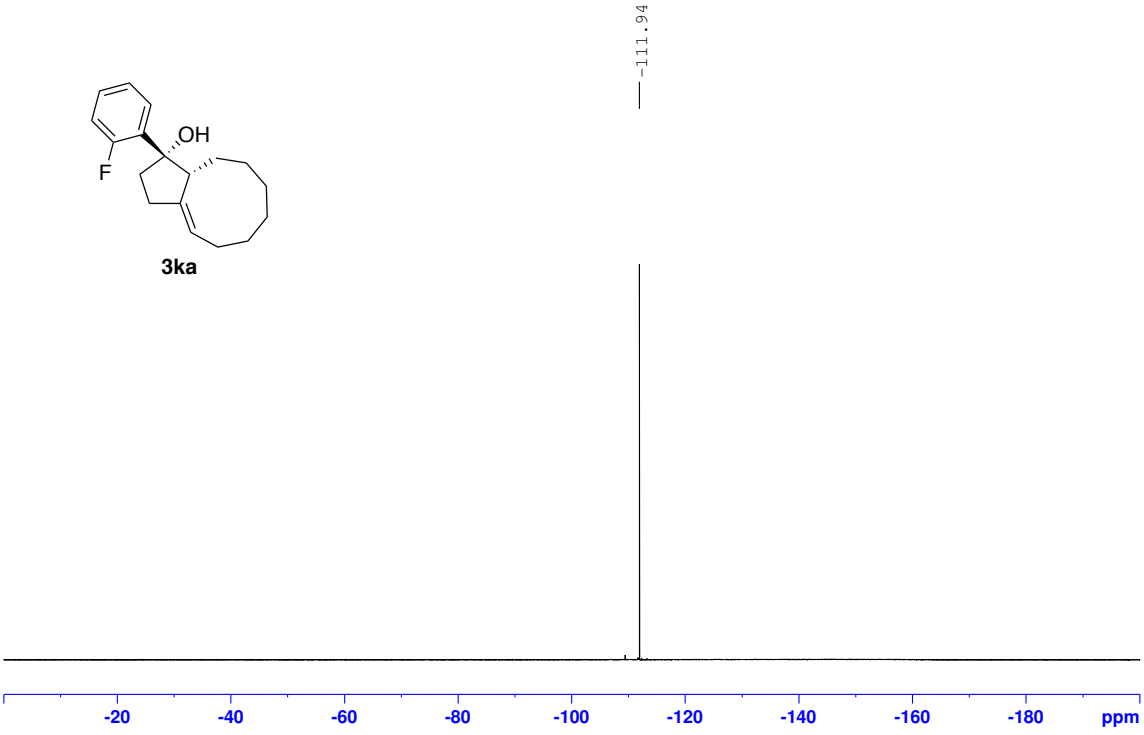
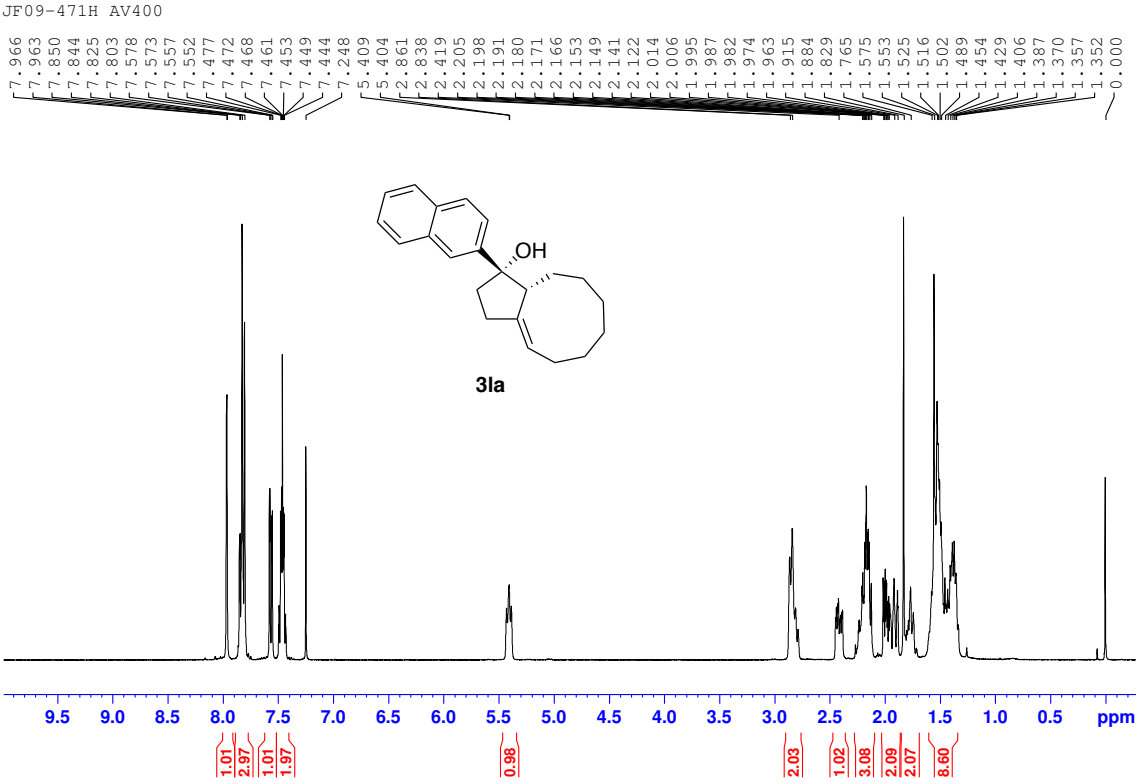
JF09-469F BBFO2



JF09-471H AV400



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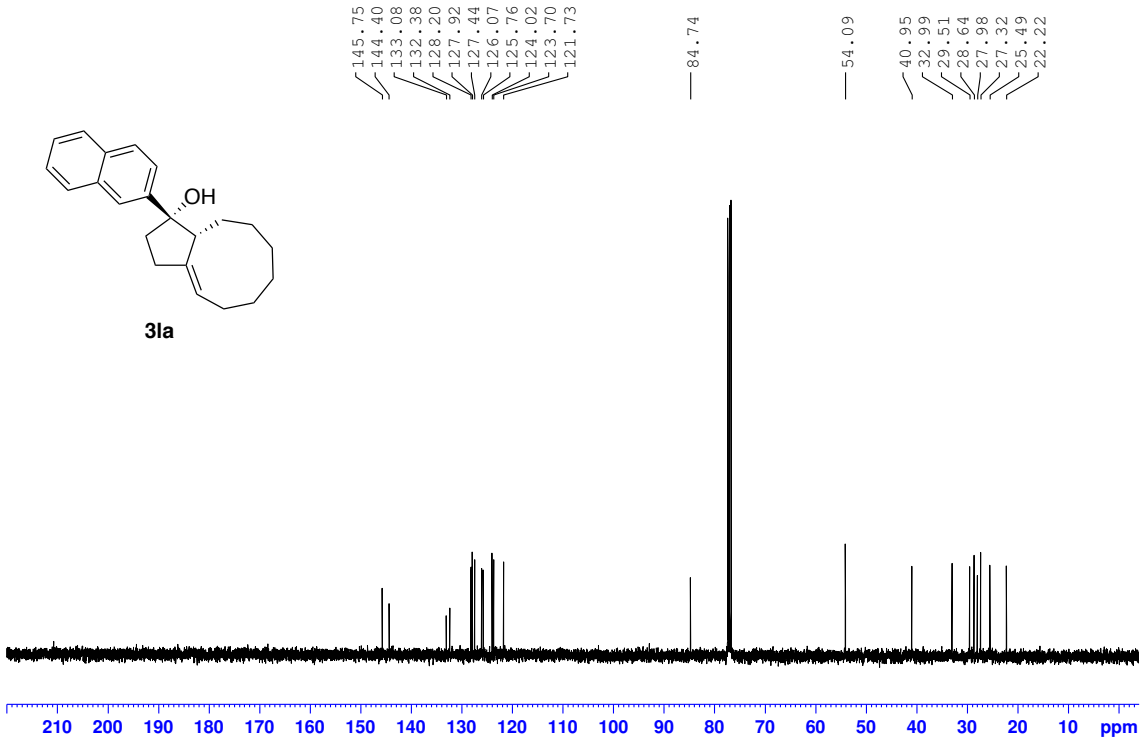

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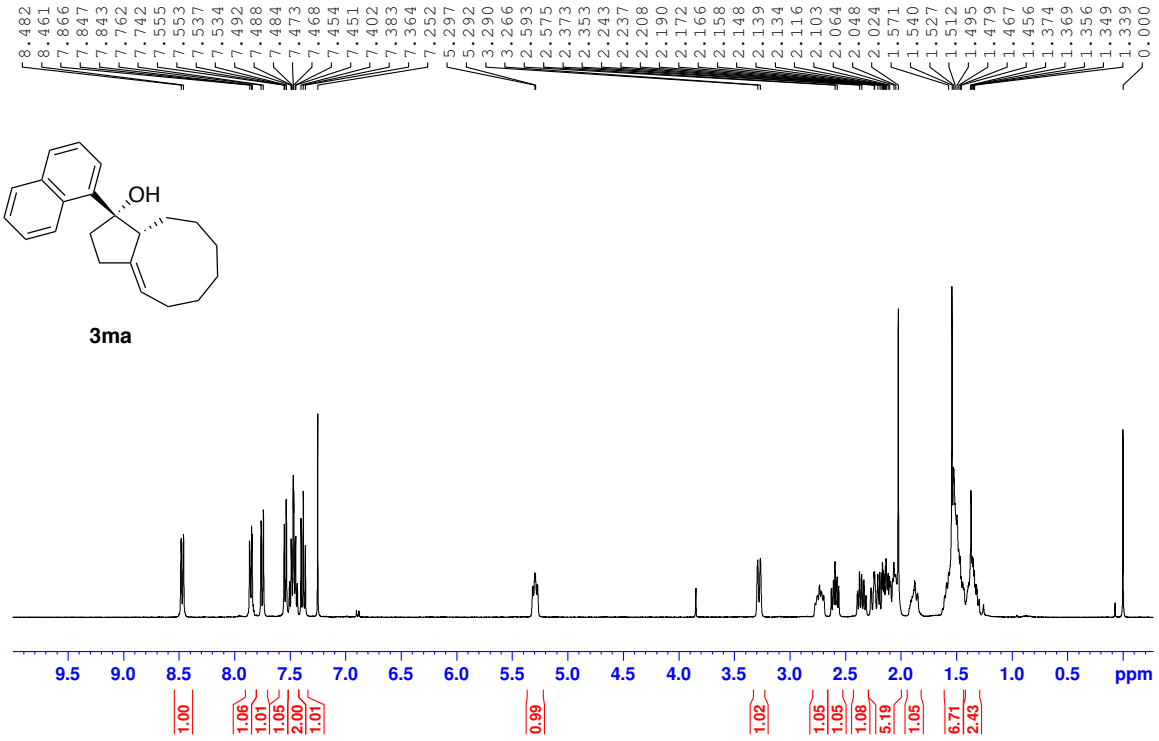
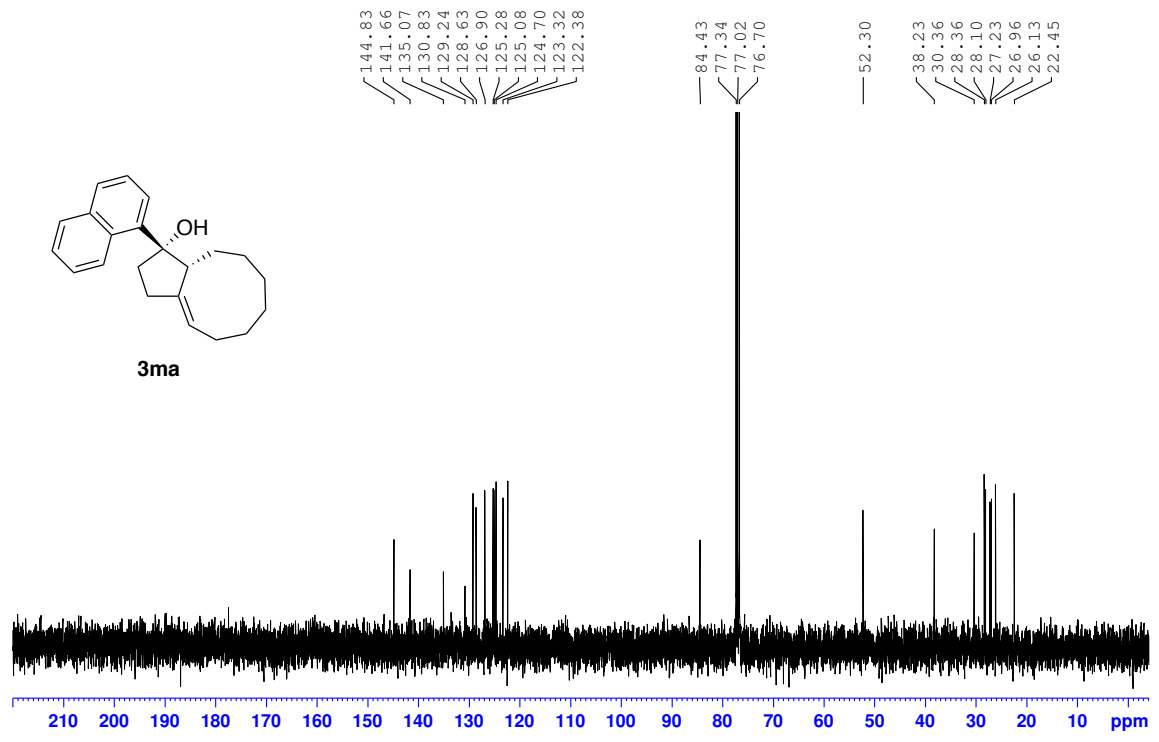


JF09-470C AV400



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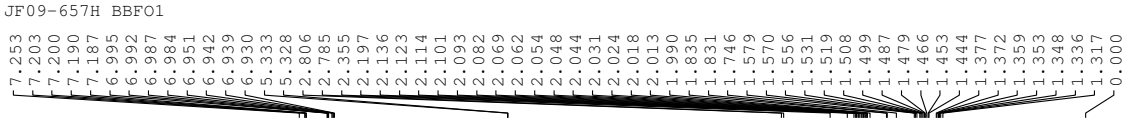

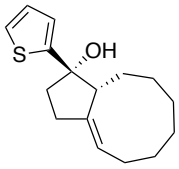

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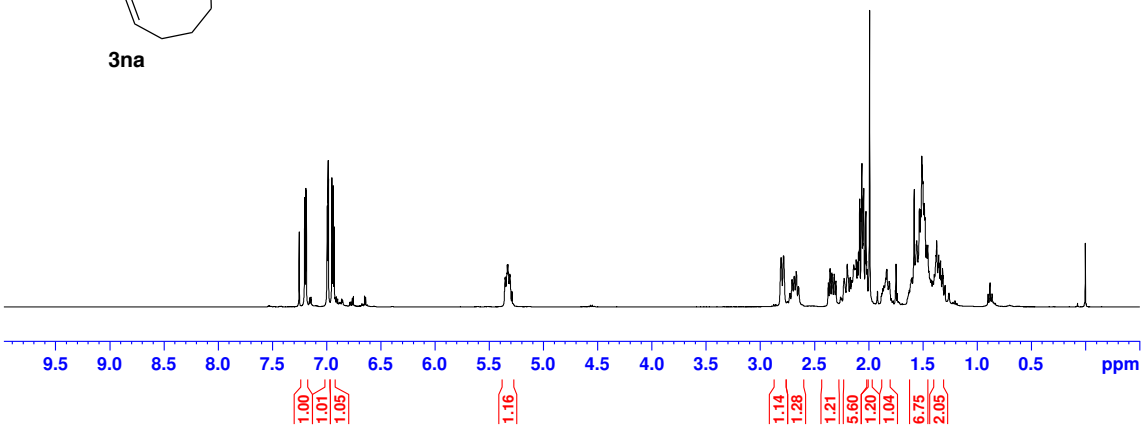

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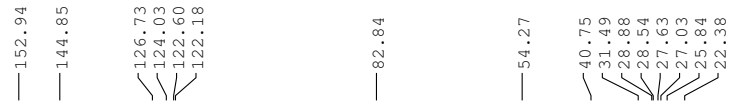

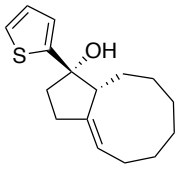

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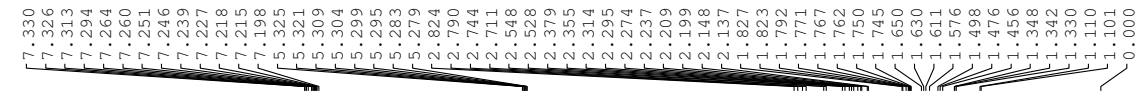

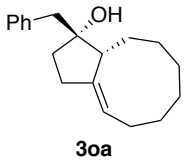

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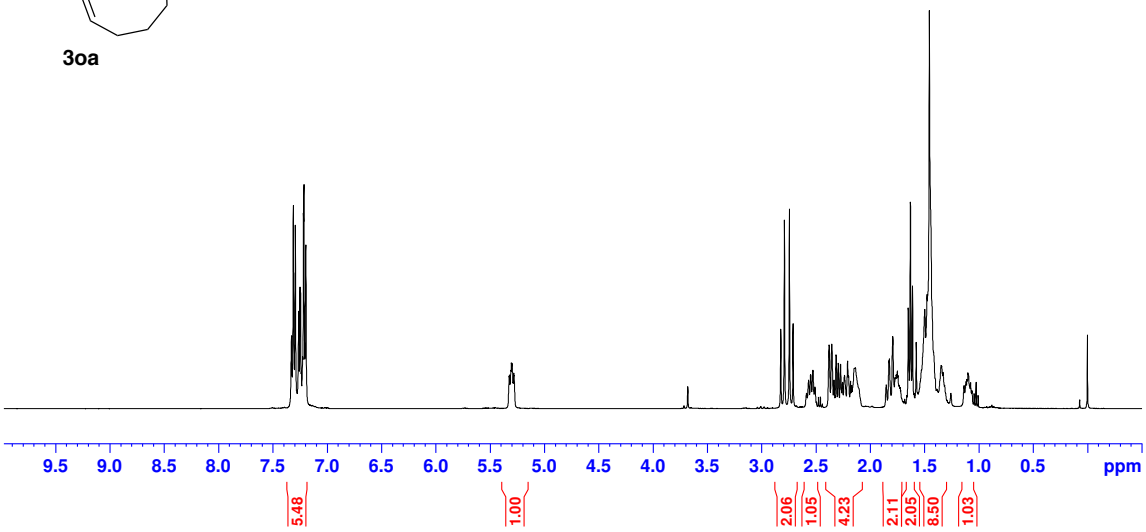

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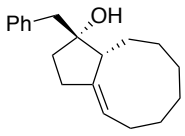

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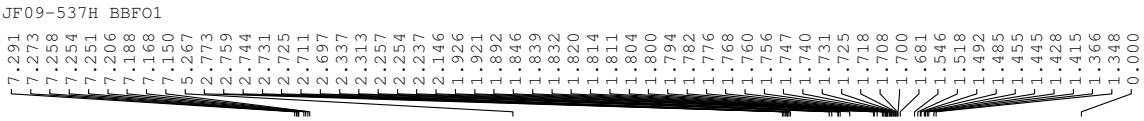

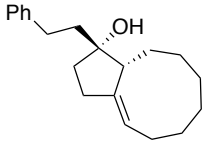

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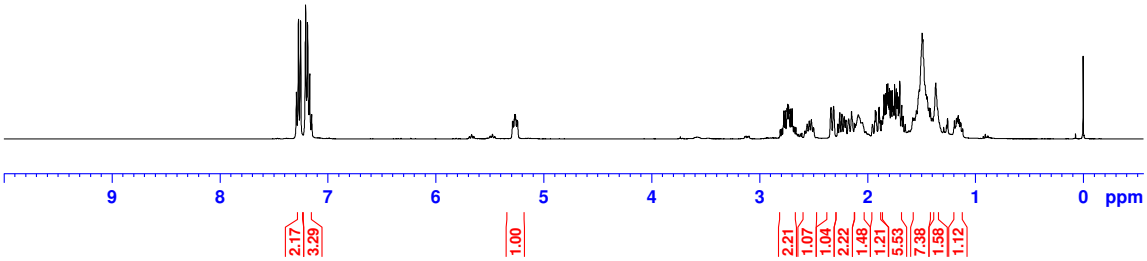

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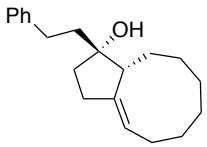

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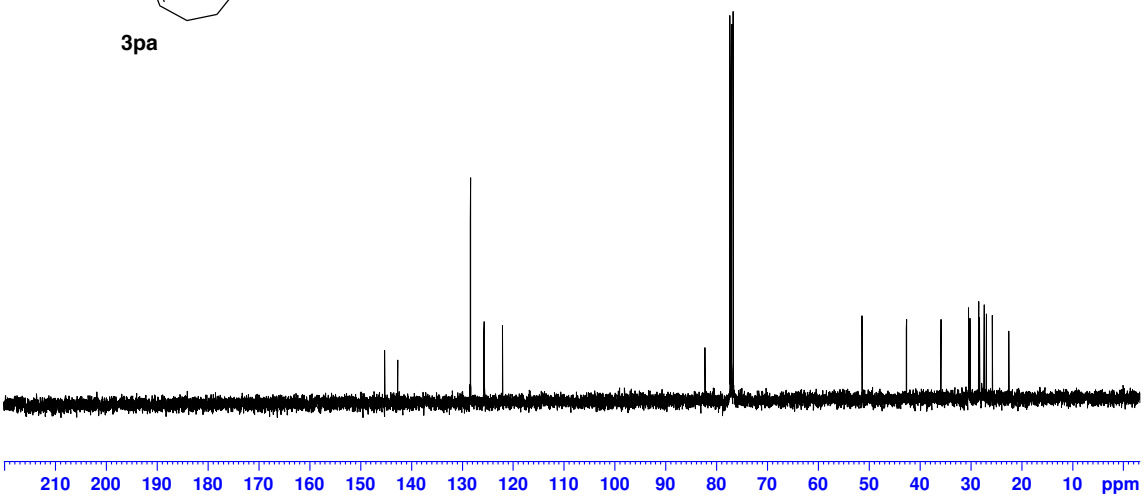

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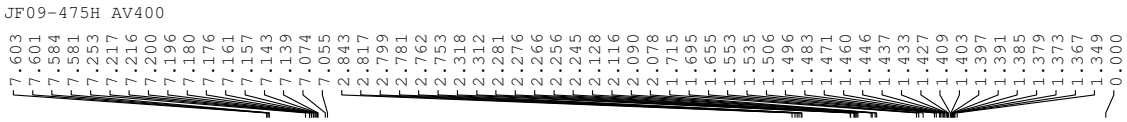

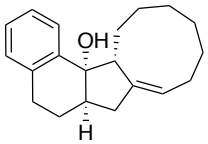

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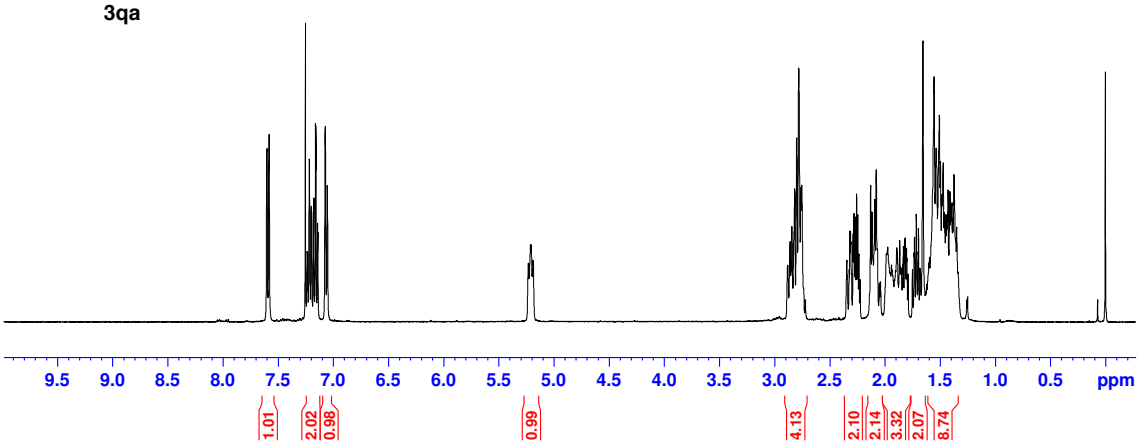

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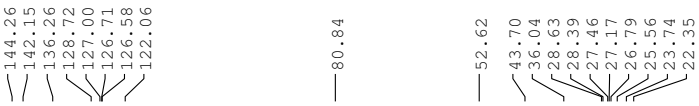

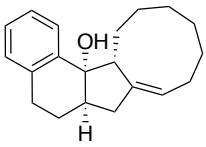

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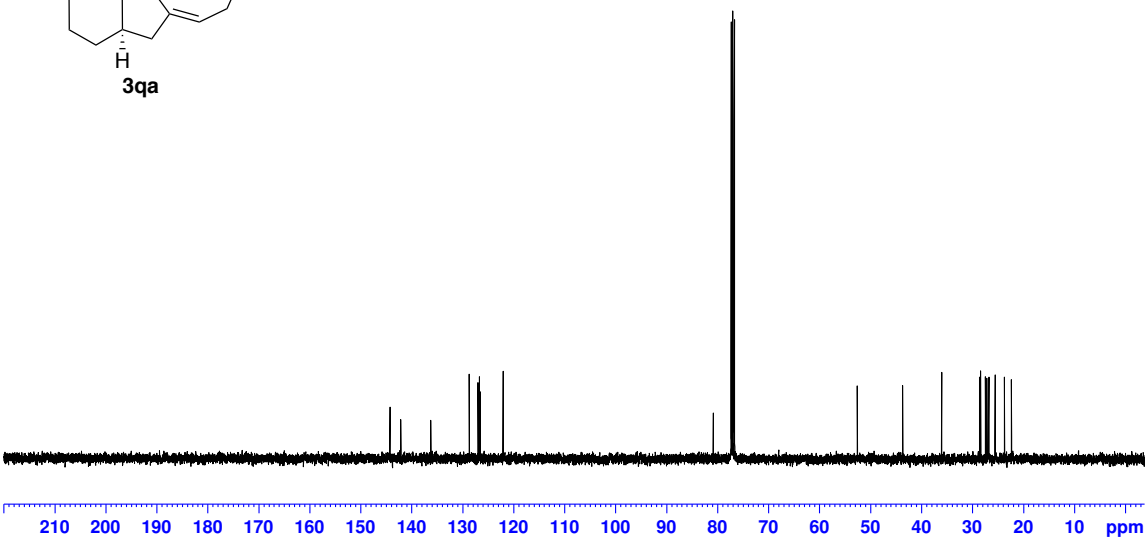
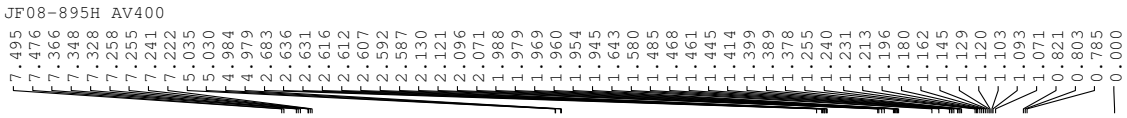
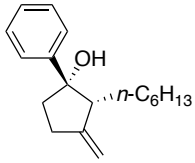


JF08-895H AV400





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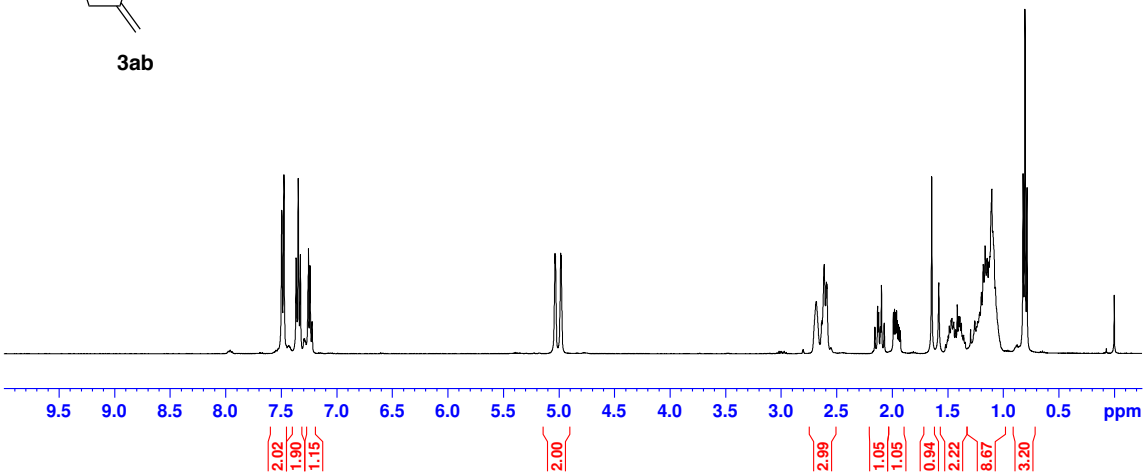
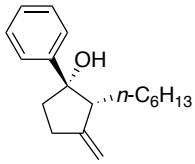
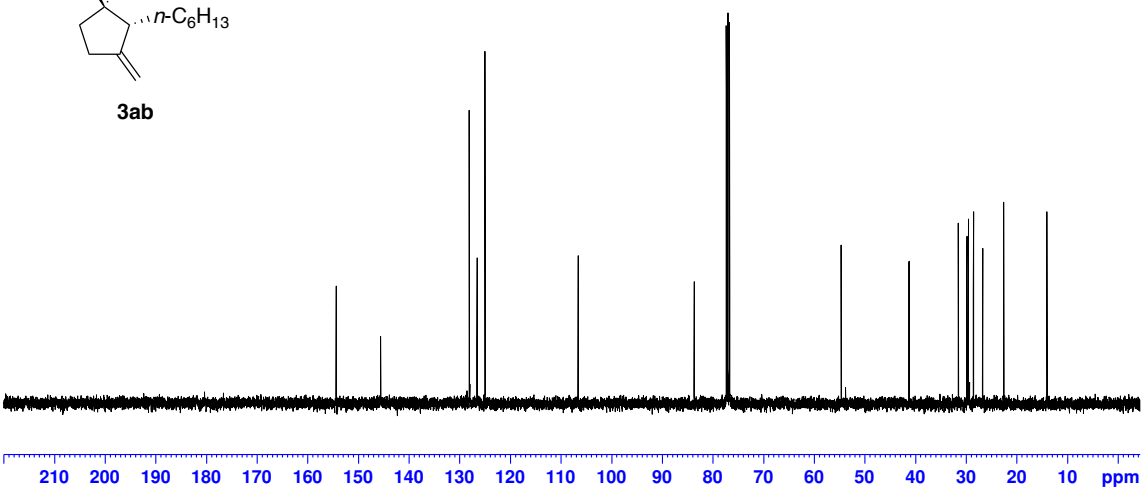


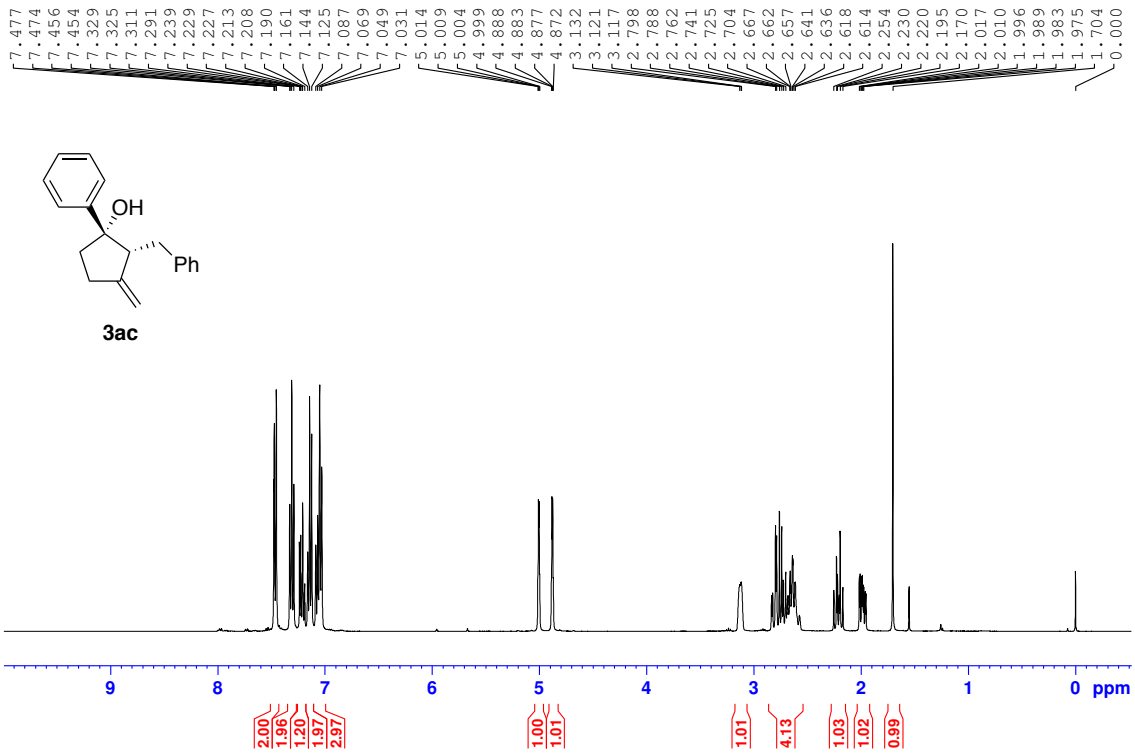
JF08-895C BBFO1



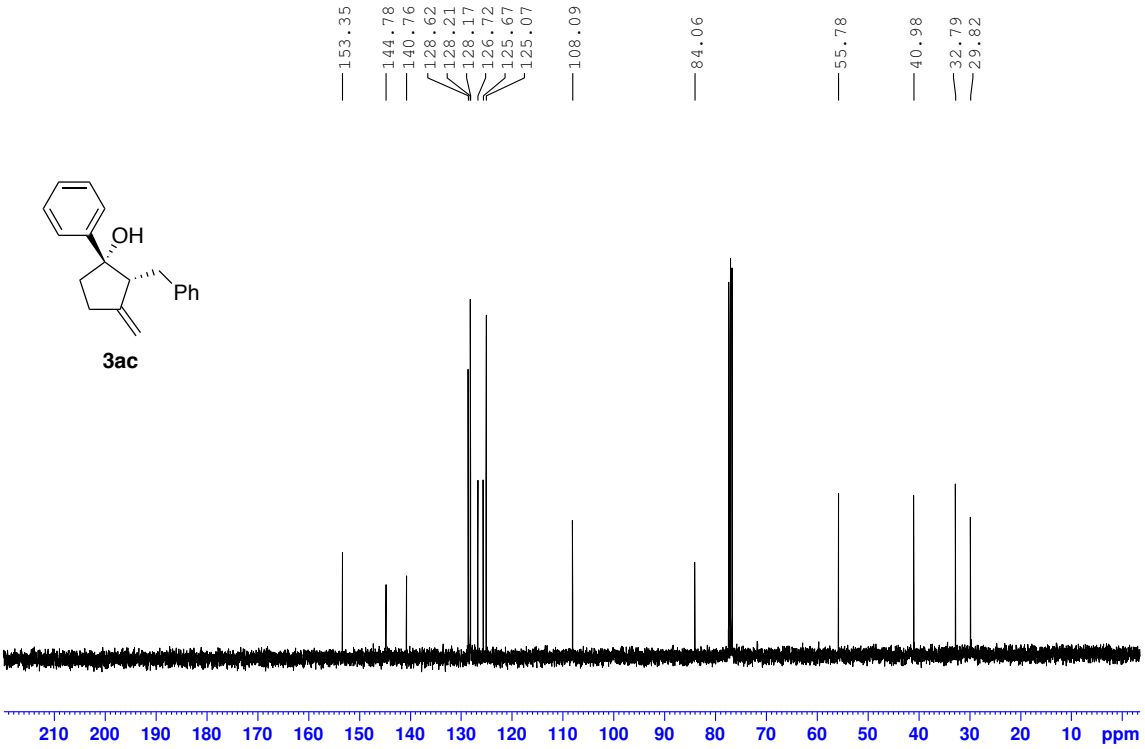
3ab



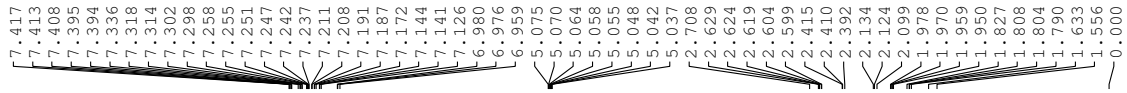
JF09-658H BBFO1

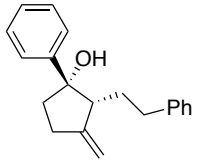


JF09-658C BBFO1

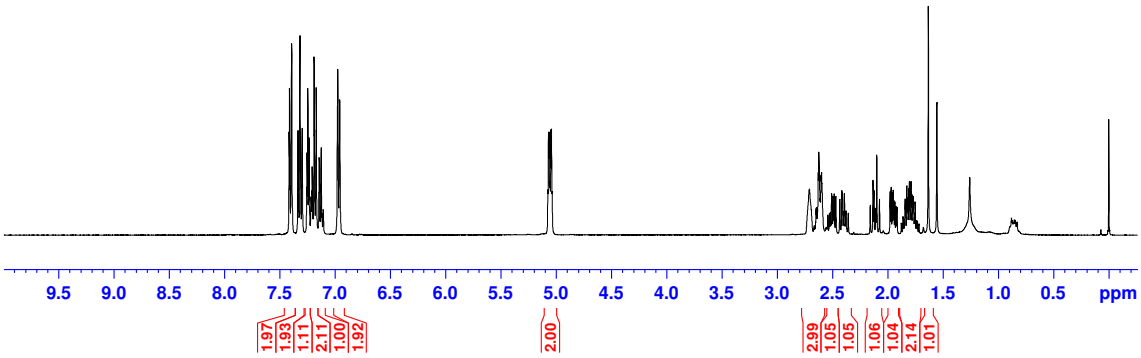


JF09-676H AV400

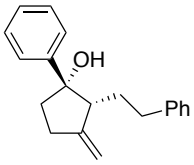




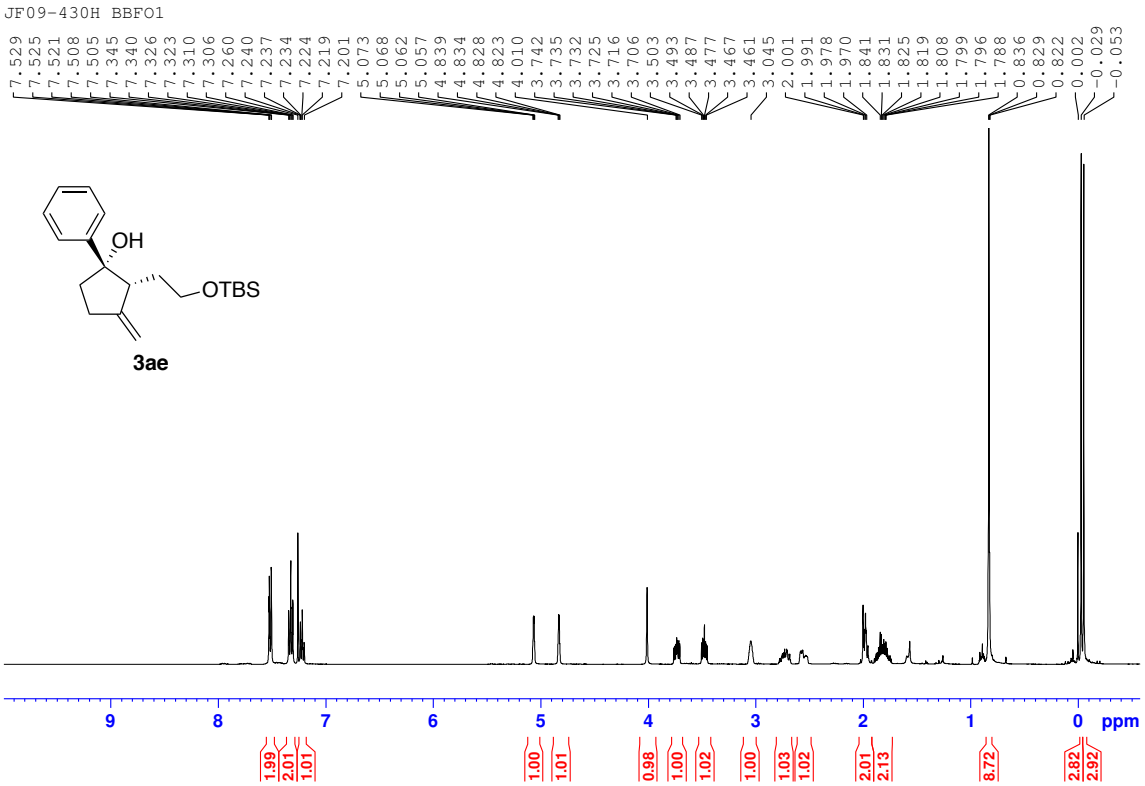
3ad

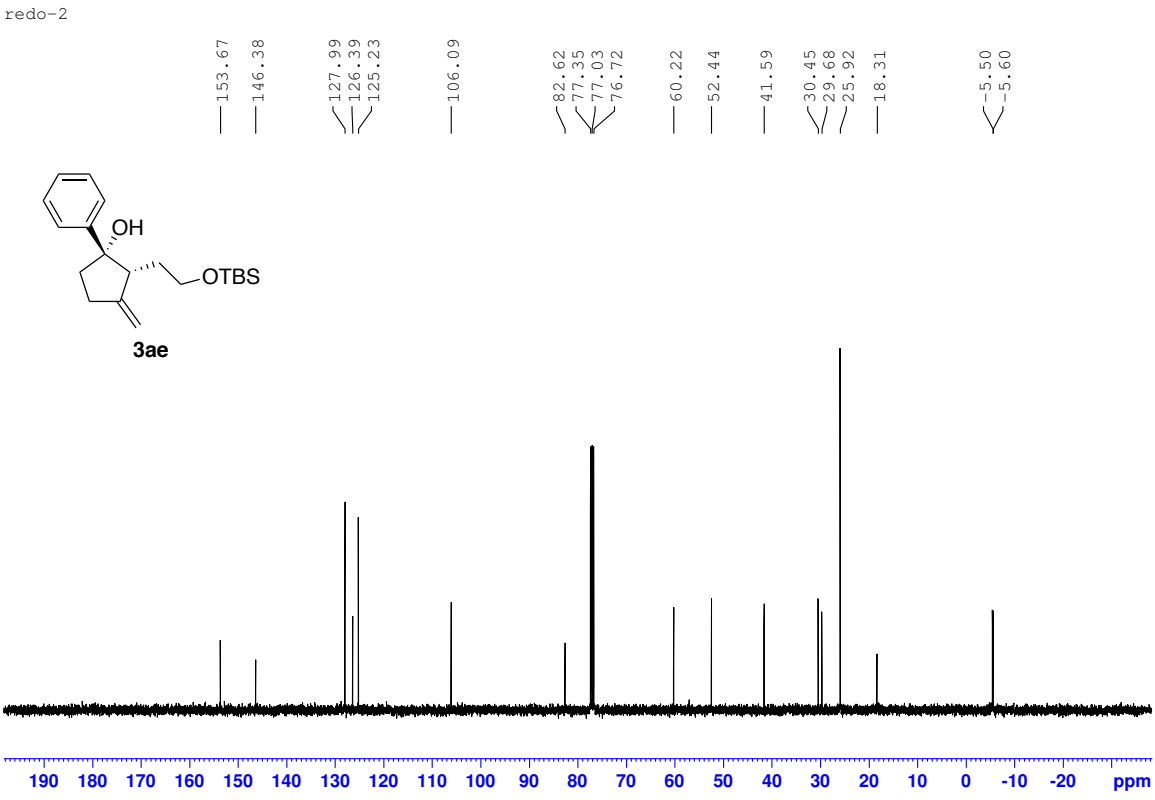


JF09-676C AV400

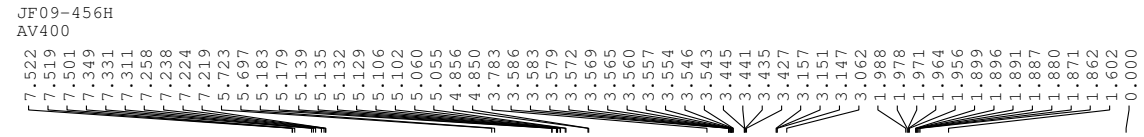


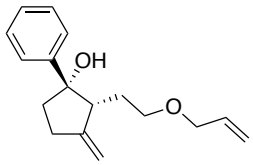
3ad


JF09-430H BBFO1
7.529
7.525
7.521
7.508
7.505
7.345
7.340
7.326
7.323
7.310
7.306
7.260
7.240
7.237
7.234
7.224
7.219
7.201
5.073
5.068
5.062
5.057
4.839
4.834
4.828
4.823
4.010
3.742
3.735
3.732
3.725
3.716
3.706
3.503
3.493
3.487
3.477
3.467
3.461
3.045
2.001
1.991
1.978
1.970
1.841
1.831
1.825
1.819
1.808
1.799
1.796
1.788
0.836
0.829
0.822
0.002
-0.029
-0.053
OH
OTBS
3ae
9
8
7
6
5
4
3
2
1
0
ppm
1.99
2.01
1.01
1.00
1.01
0.98
1.00
1.02
1.00
1.03
1.02
2.01
2.13
8.72
2.82
2.92

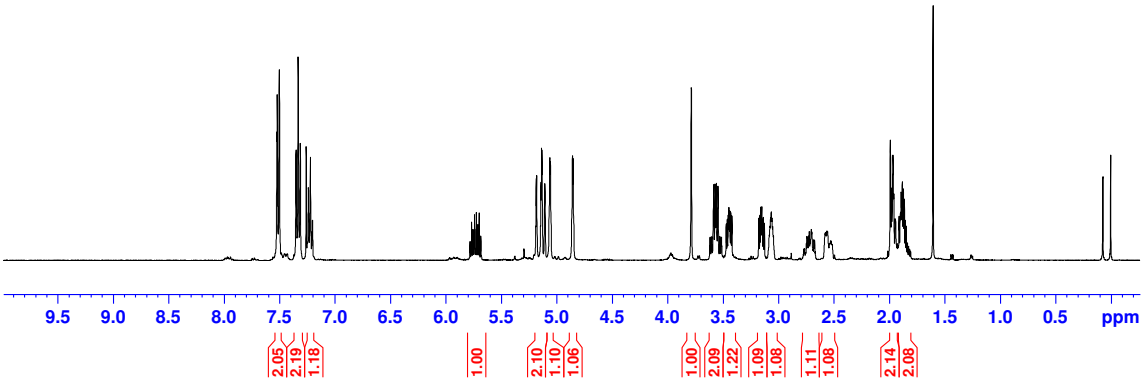

redo-2
153.67
146.38
127.99
126.39
125.23
106.09
82.62
77.35
77.03
76.72
60.22
52.44
41.59
30.45
29.68
25.92
18.31
-5.50
-5.60
OH
OTBS
3ae
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
ppm

JF09-456H
AV400

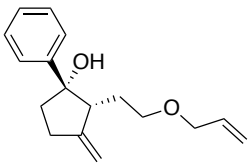




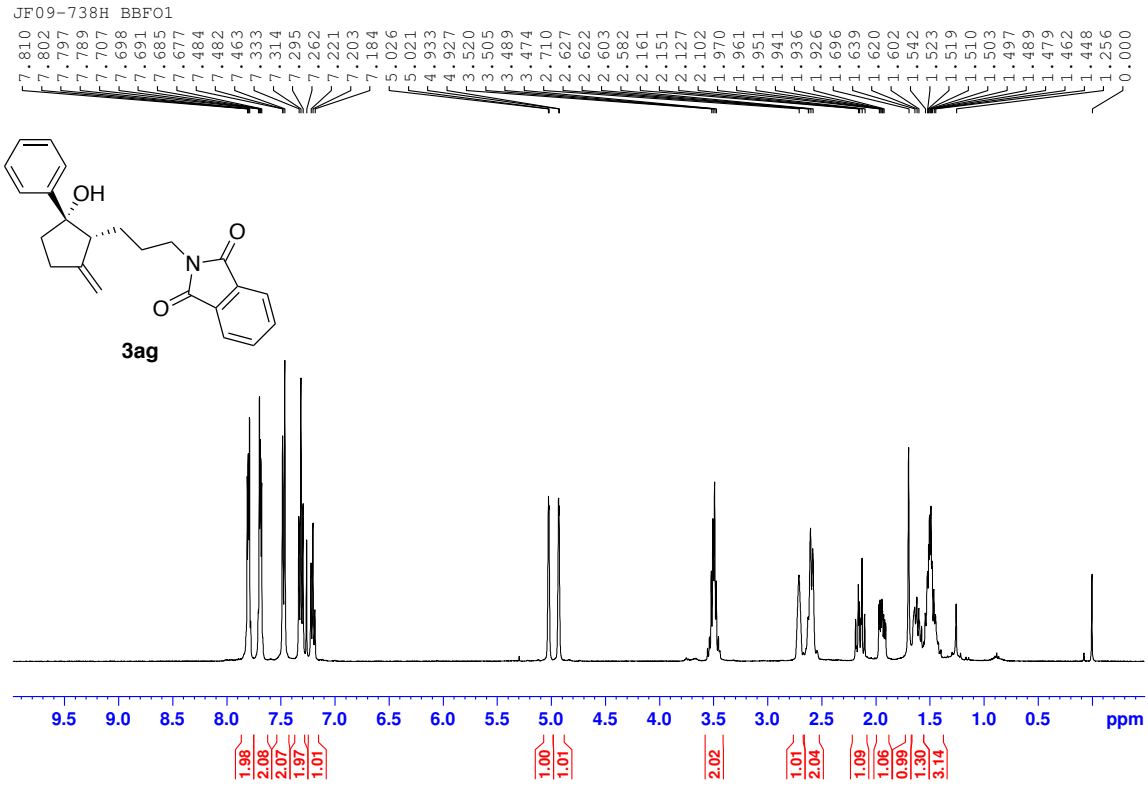
3af

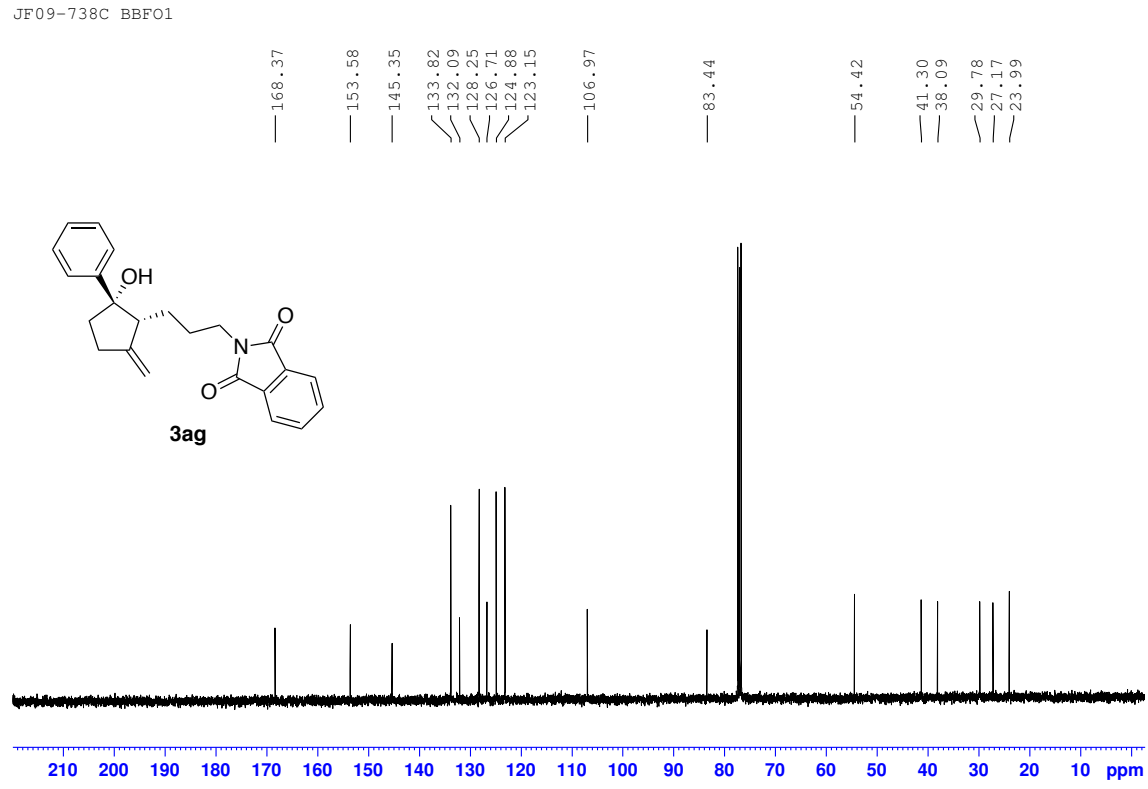


JF09-456C
AV400

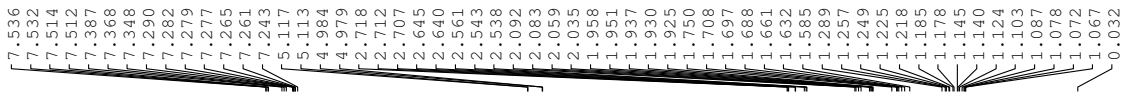


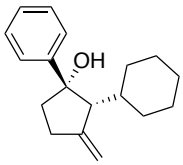
3af


JF09-738H BBFO1
7.810
7.802
7.797
7.789
7.707
7.698
7.691
7.685
7.677
7.484
7.482
7.463
7.333
7.314
7.295
7.262
7.221
7.203
7.184
5.026
5.021
4.933
4.927
3.520
3.505
3.489
3.474
2.710
2.627
2.622
2.603
2.582
2.161
2.151
2.127
2.102
1.970
1.961
1.951
1.941
1.936
1.926
1.696
1.639
1.620
1.602
1.542
1.523
1.519
1.510
1.503
1.497
1.489
1.479
1.462
1.448
1.256
0.000
OH
O
N
O
3ag
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.98
2.08
2.07
1.97
1.01
1.00
1.01
2.02
1.01
2.04
1.09
1.06
0.99
1.30
3.14

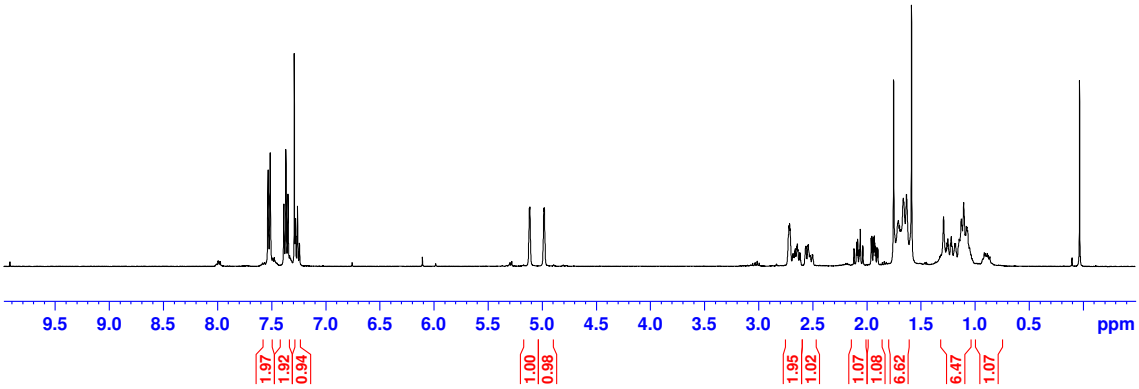

JF09-738C BBFO1
168.37
153.58
145.35
133.82
132.09
128.25
126.71
124.88
123.15
106.97
83.44
54.42
41.30
38.09
29.78
27.17
23.99
OH
O
N
O
3ag
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

JF09-243H BBFO2

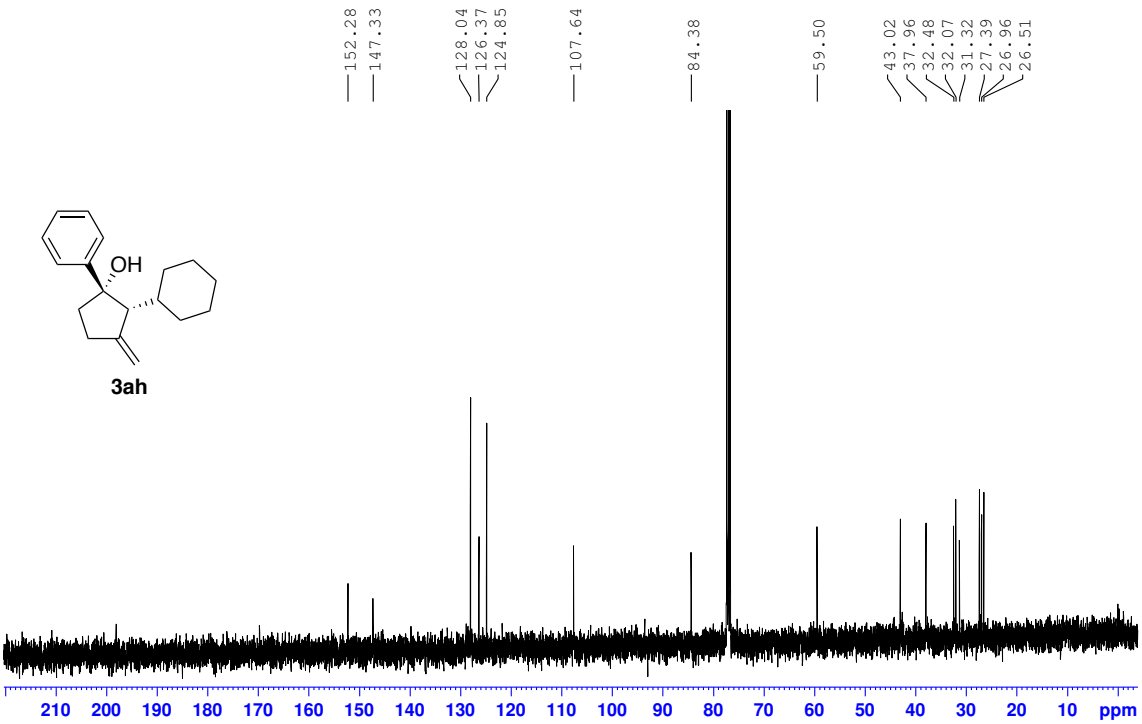




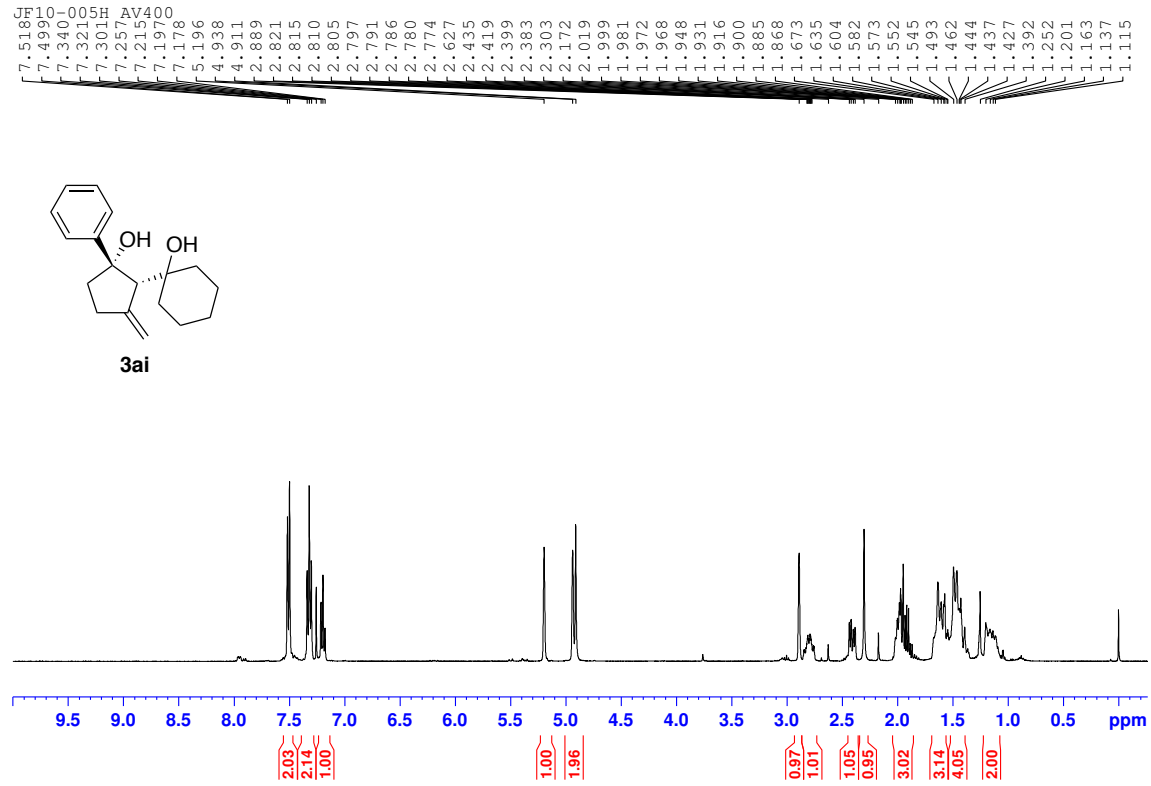
3ah

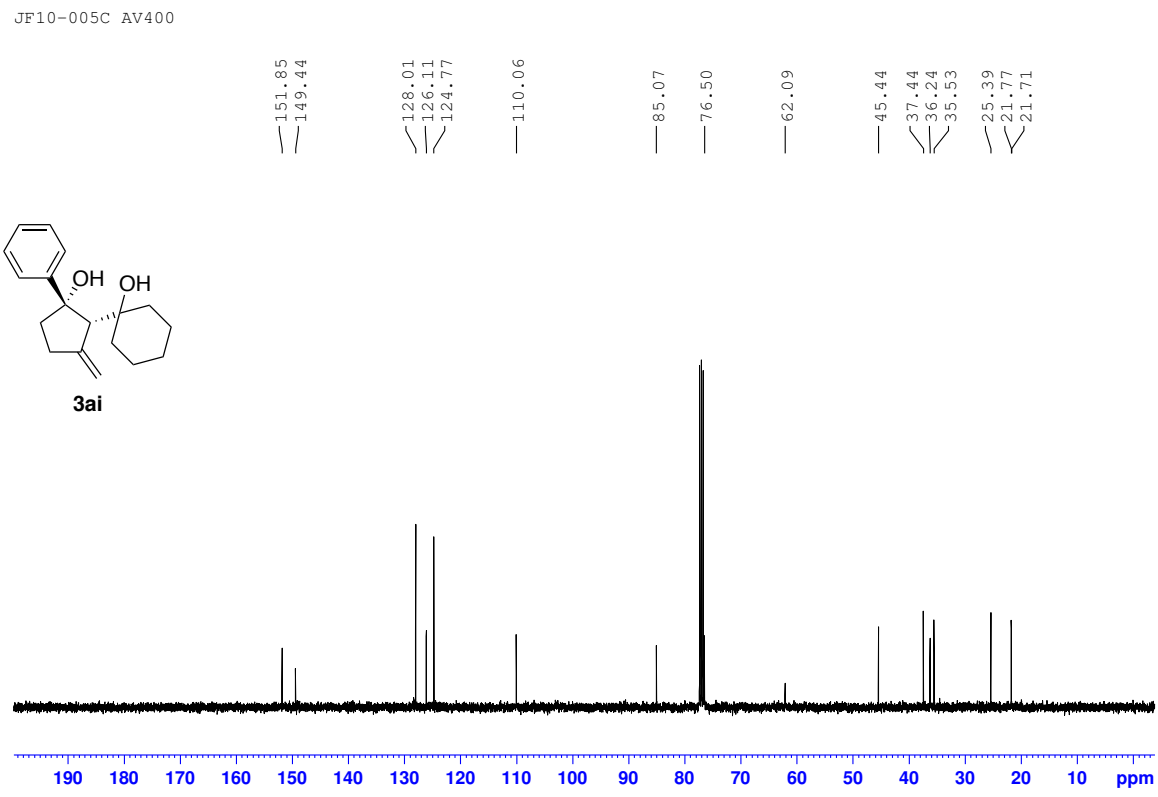


JF09-243C BBFO2

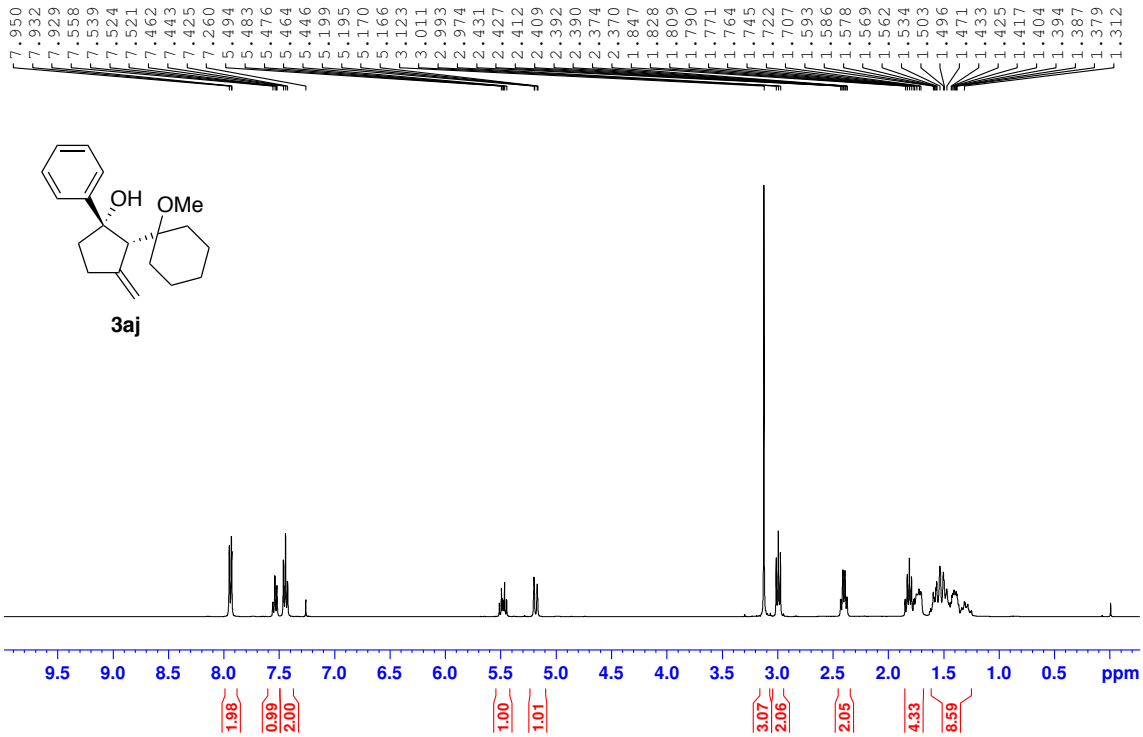


3ah

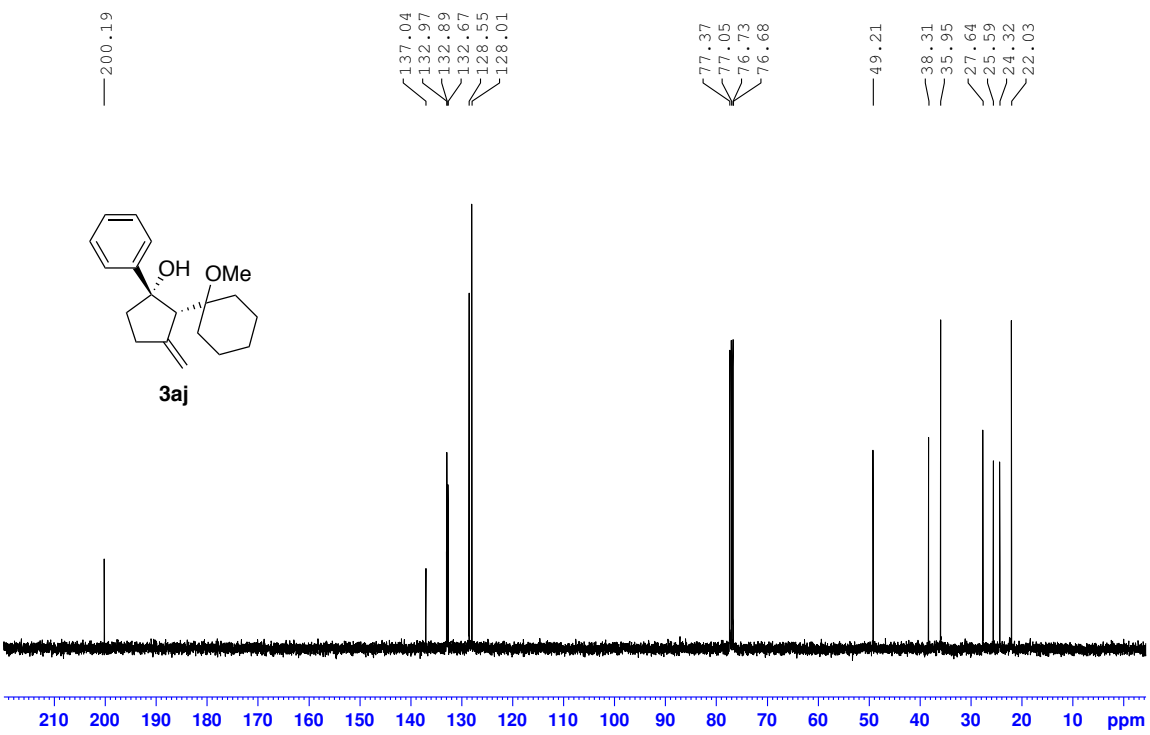

JF10-005H AV400
7.518
7.499
7.340
7.321
7.301
7.257
7.215
7.197
7.178
5.196
4.938
4.911
2.889
2.821
2.815
2.810
2.805
2.797
2.791
2.786
2.780
2.774
2.627
2.435
2.419
2.399
2.383
2.303
2.172
2.019
1.999
1.981
1.972
1.968
1.948
1.931
1.916
1.900
1.885
1.868
1.673
1.635
1.604
1.582
1.573
1.552
1.545
1.493
1.462
1.444
1.437
1.427
1.392
1.252
1.201
1.163
1.137
1.115
OH
OH
3ai
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.03
2.14
1.00
1.00
1.96
0.97
1.01
1.05
0.95
3.02
3.14
4.05
2.00


JF10-005C AV400
151.85
149.44
128.01
126.11
124.77
110.06
85.07
76.50
62.09
45.44
37.44
36.24
35.53
25.39
21.77
21.71
OH
OH
3ai
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

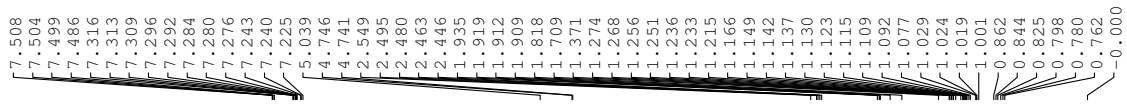
JF09-739H AV400

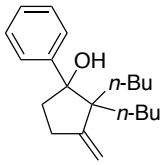


JF09-739C AV400

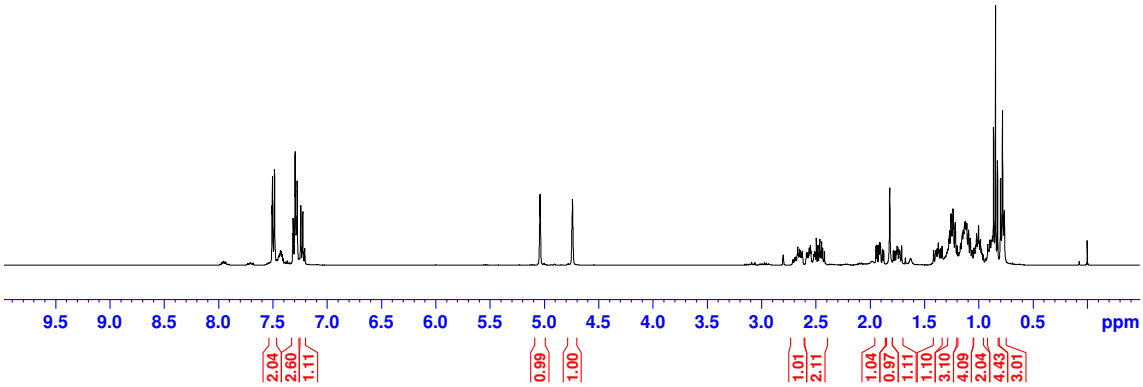


JF09-271H BBFO1

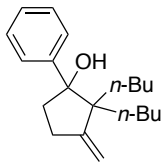




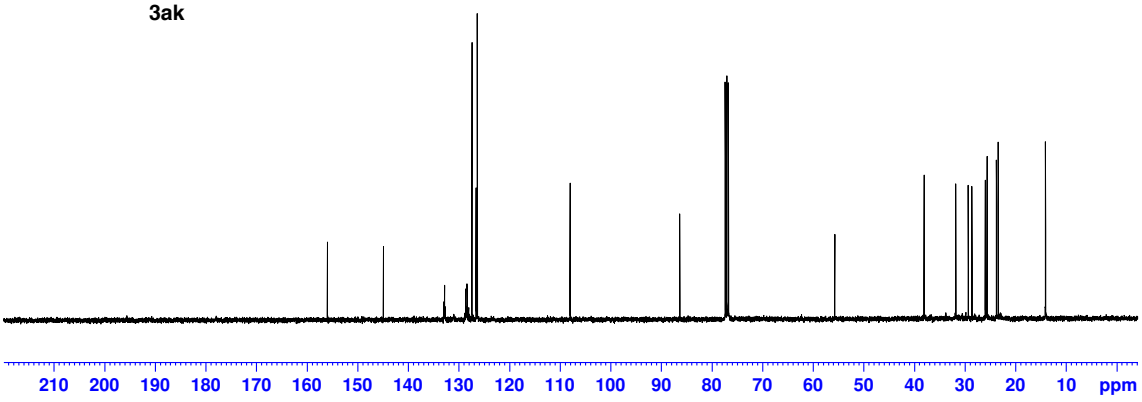
3ak



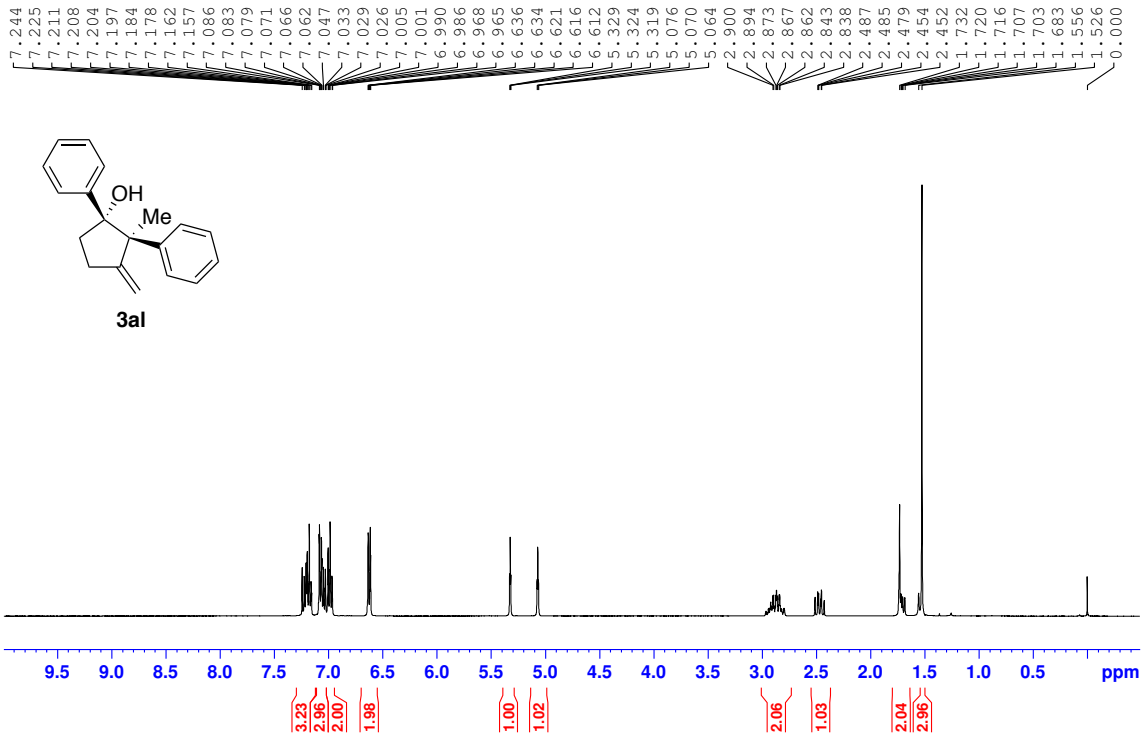
JF09-271C BBFO1



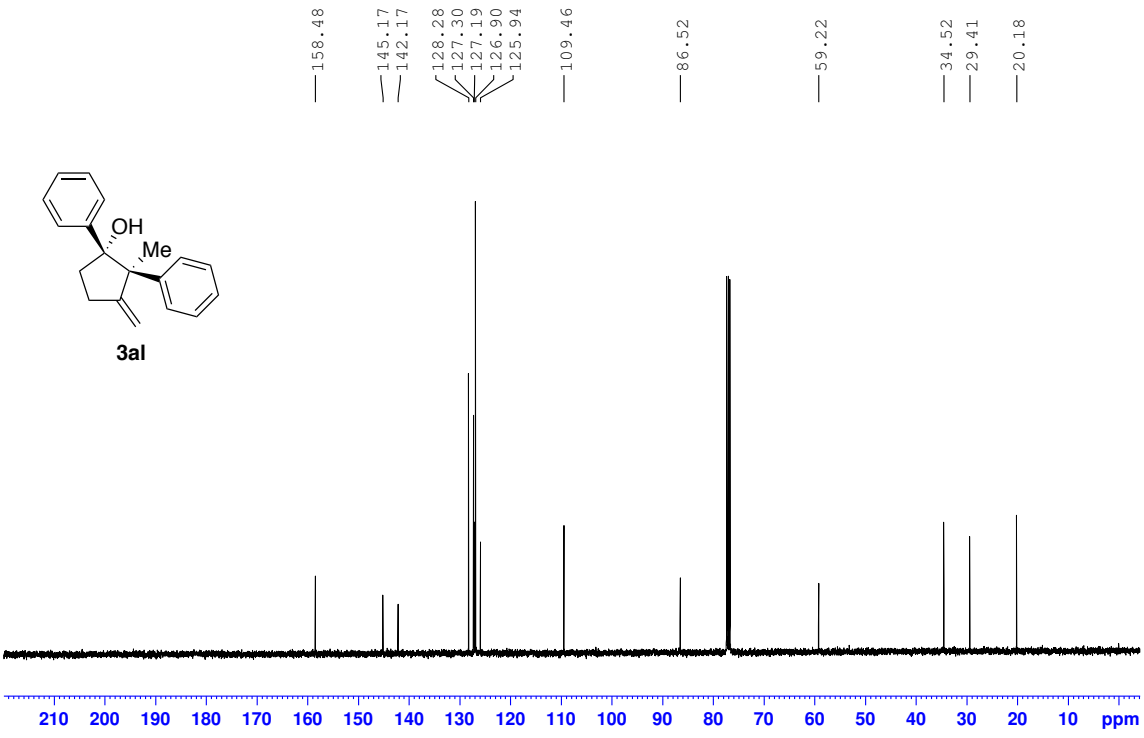
3ak



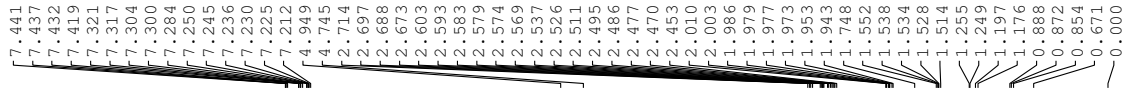
JF09-740H BBFO1

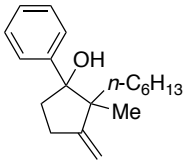


JF09-740C BBFO1



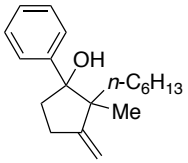
JF09-659-1H AV400



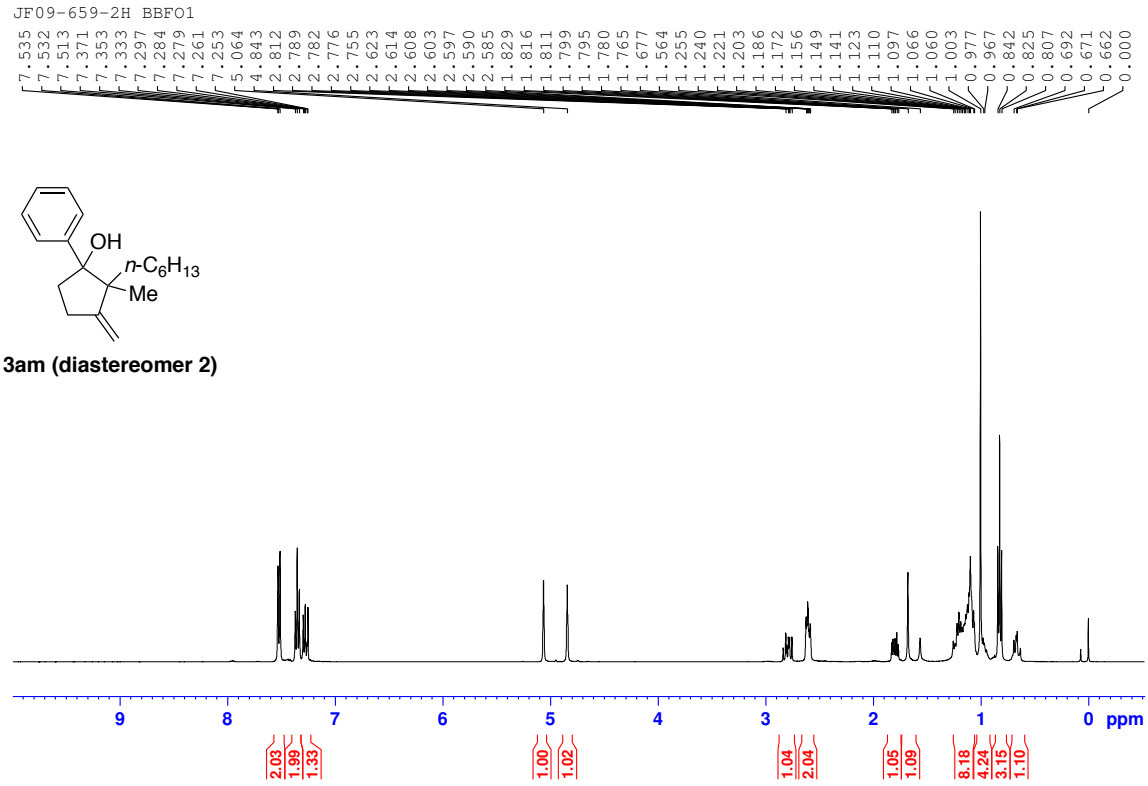


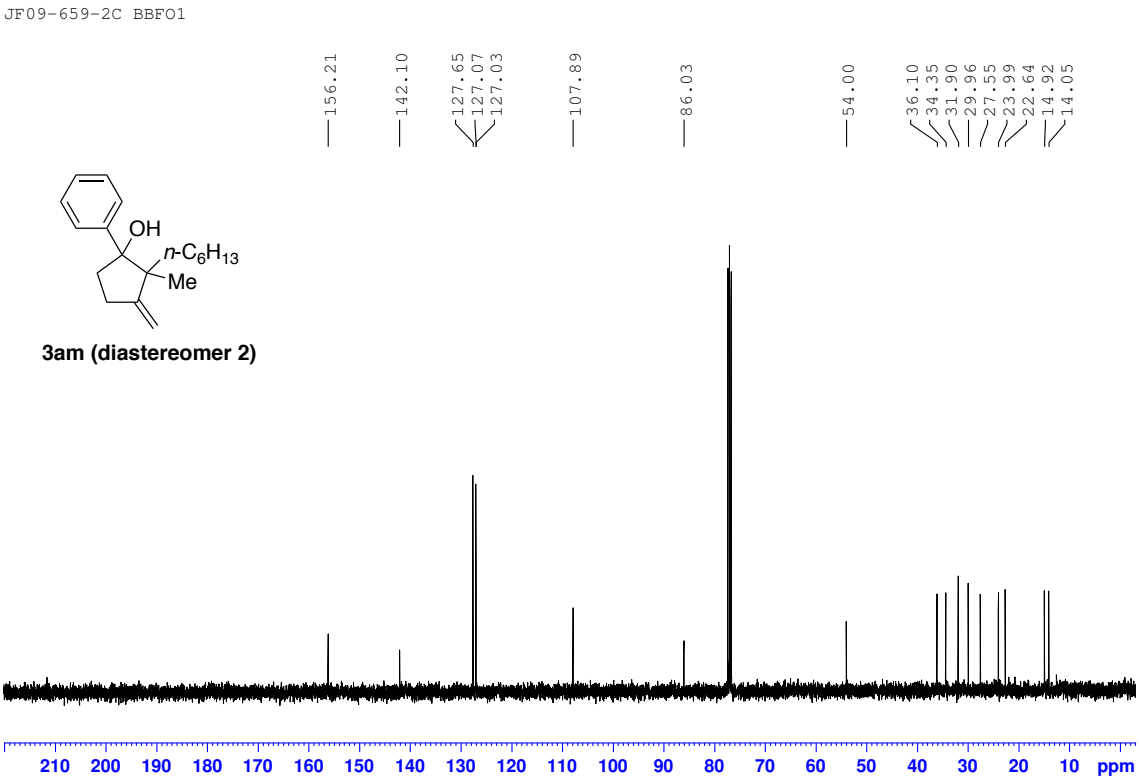
3am (diastereomer 1)

JF09-659-1C AV400

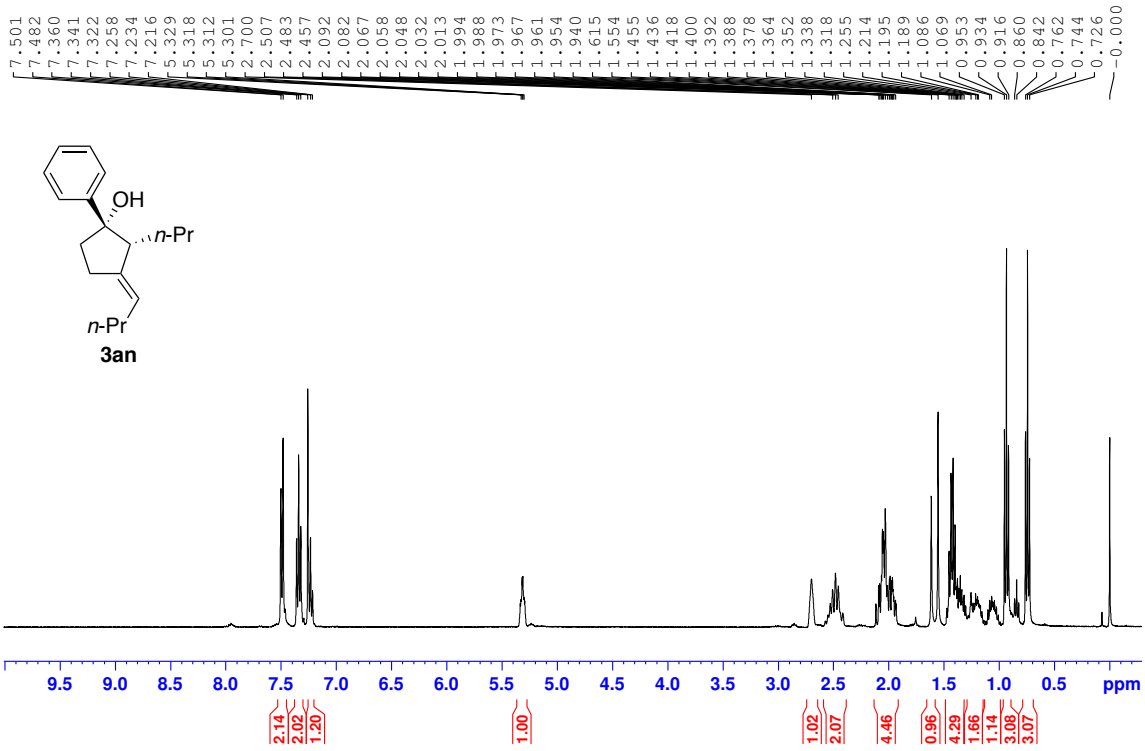


3am (diastereomer 1)

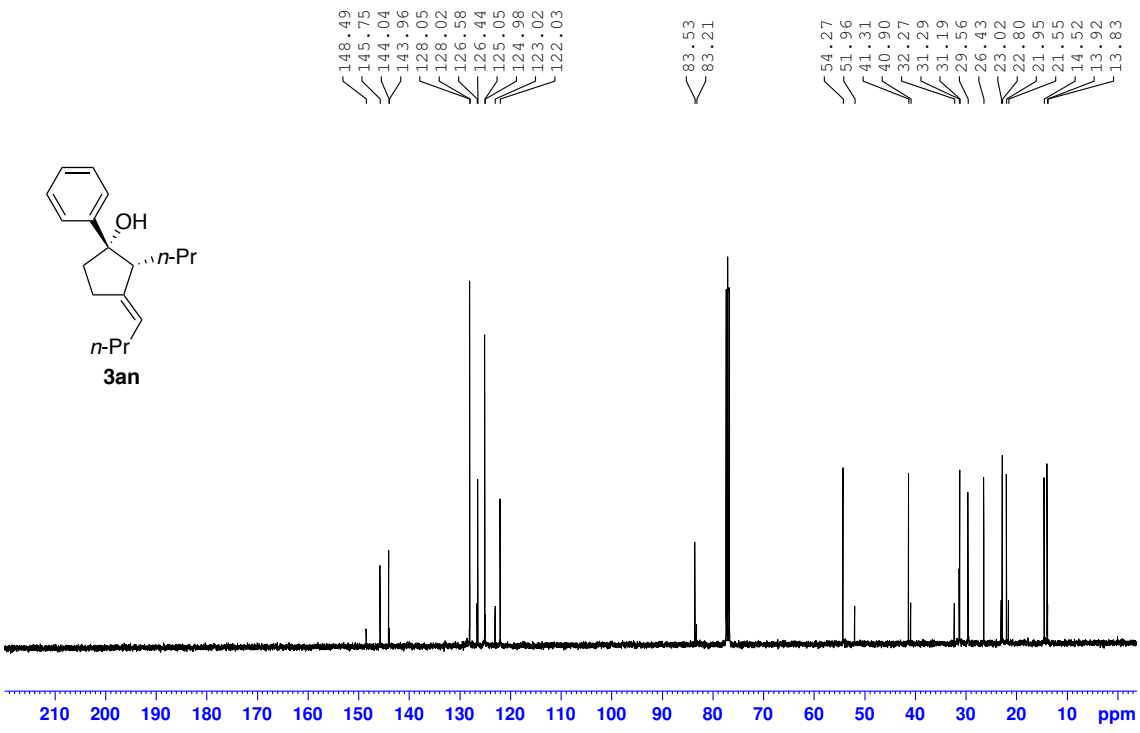

JF09-659-2H BBFO1
7.535
7.532
7.513
7.371
7.353
7.333
7.297
7.284
7.279
7.261
7.253
5.064
4.843
2.812
2.789
2.782
2.776
2.755
2.623
2.614
2.608
2.603
2.597
2.590
2.585
1.829
1.816
1.811
1.799
1.795
1.780
1.765
1.677
1.564
1.255
1.240
1.221
1.203
1.186
1.172
1.156
1.149
1.141
1.123
1.110
1.097
1.066
1.060
1.003
0.977
0.967
0.842
0.825
0.807
0.692
0.671
0.662
0.000
OH
n-C6H13
Me
3am (diastereomer 2)
9
8
7
6
5
4
3
2
1
0 ppm
2.03
1.99
1.33
1.00
1.02
1.04
2.04
1.05
1.09
8.18
4.24
3.15
1.10

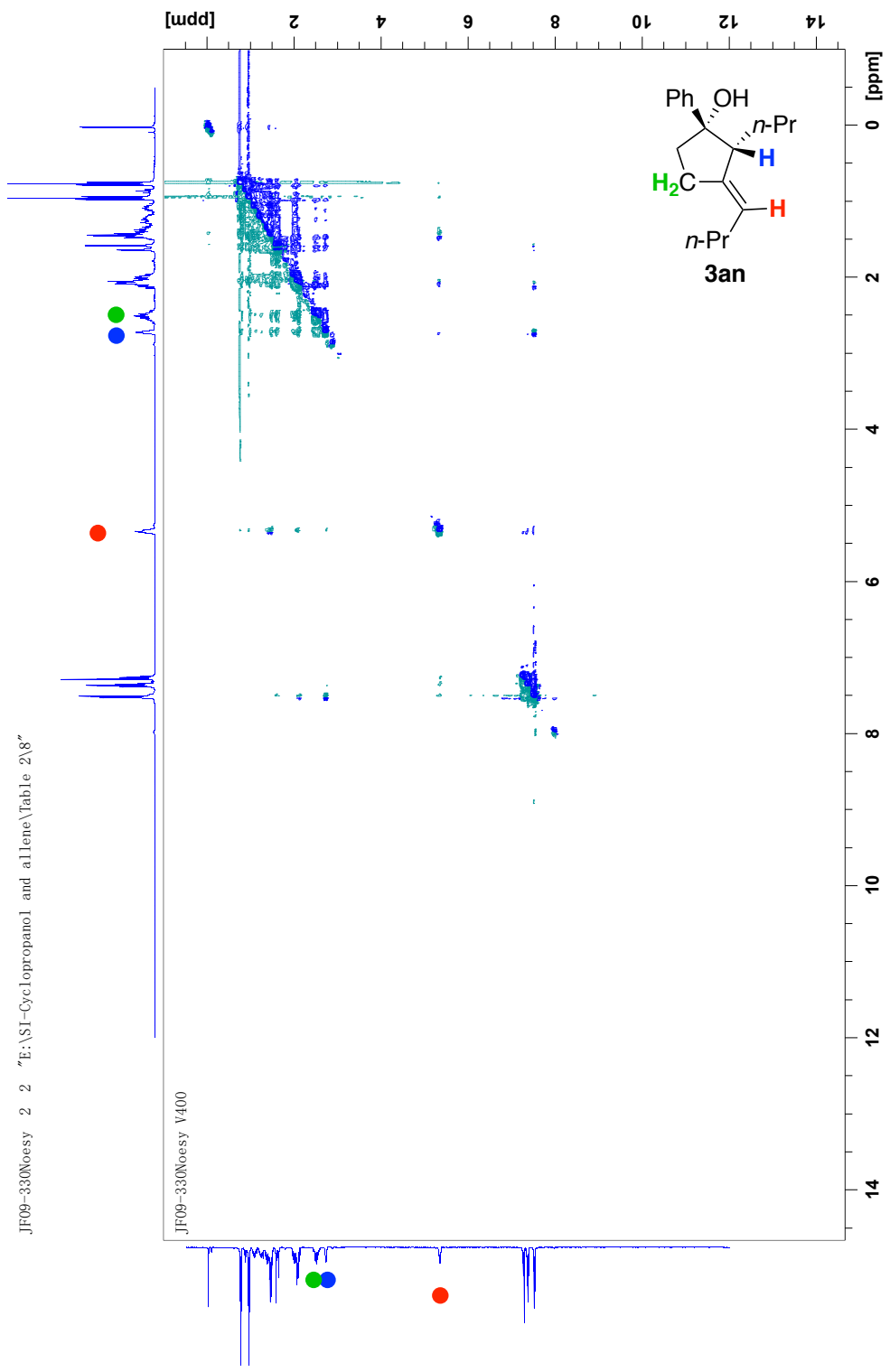

JF09-659-2C BBFO1
156.21
142.10
127.65
127.07
127.03
107.89
86.03
54.00
36.10
34.35
31.90
29.96
27.55
23.99
22.64
14.92
14.05
OH
n-C6H13
Me
3am (diastereomer 2)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

JF09-330H AV400

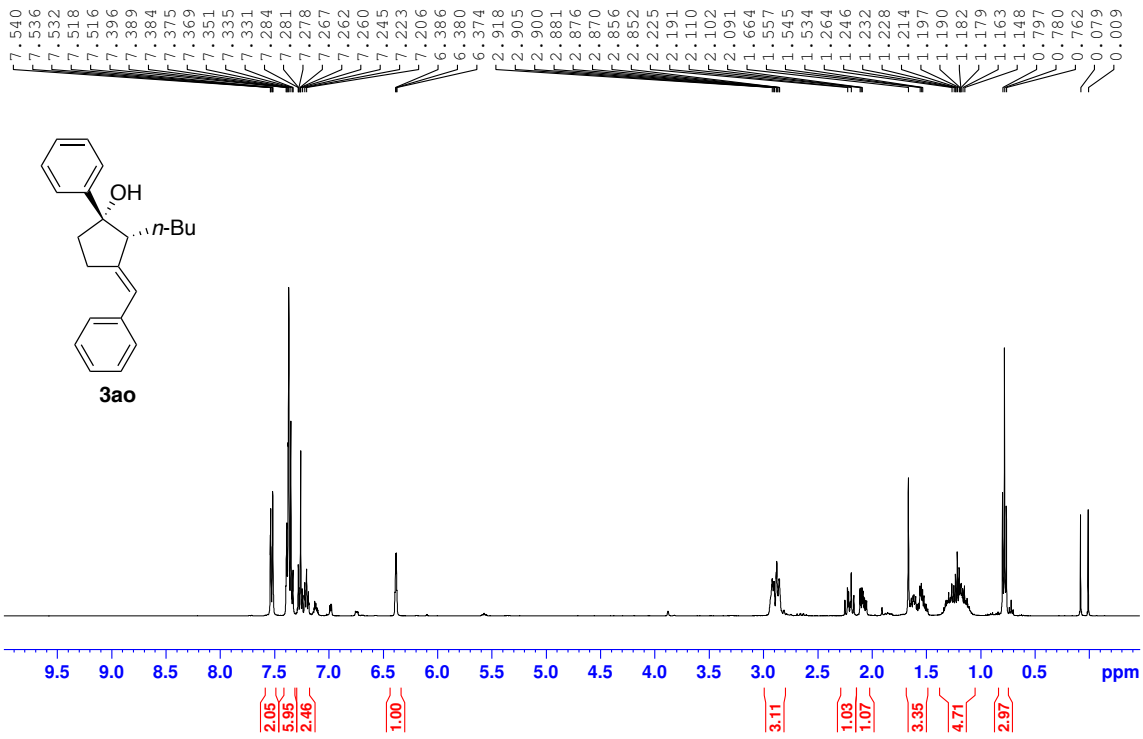


JF09-330C BBFO1

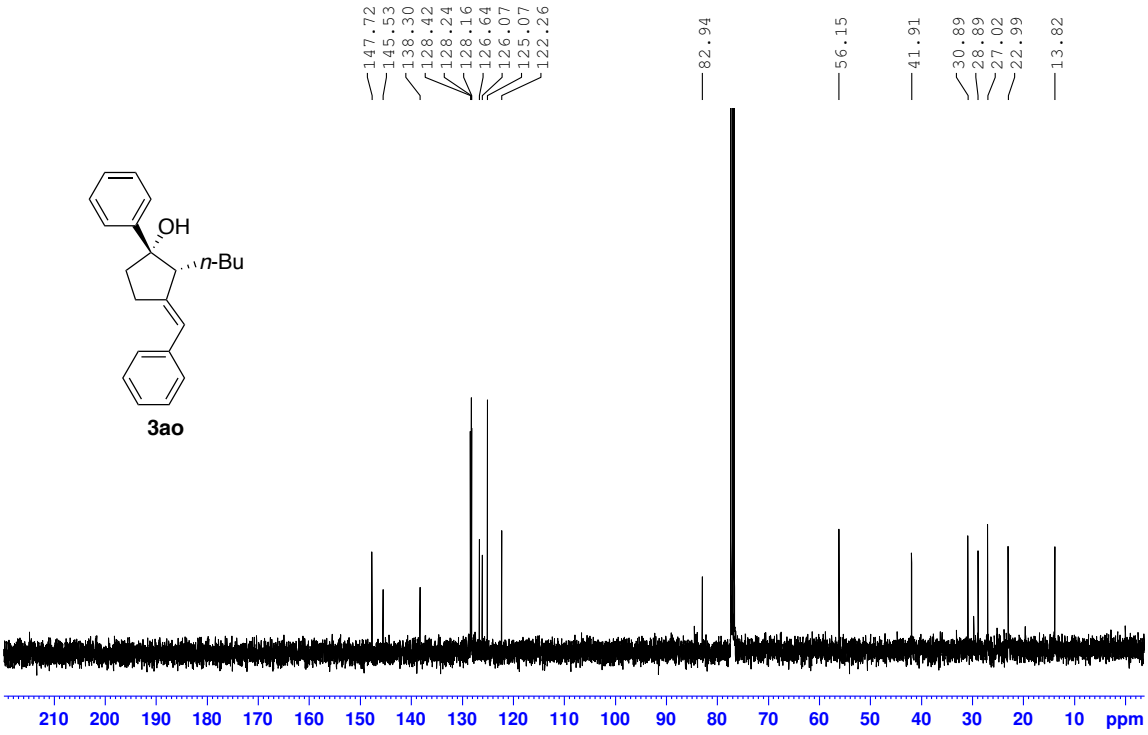


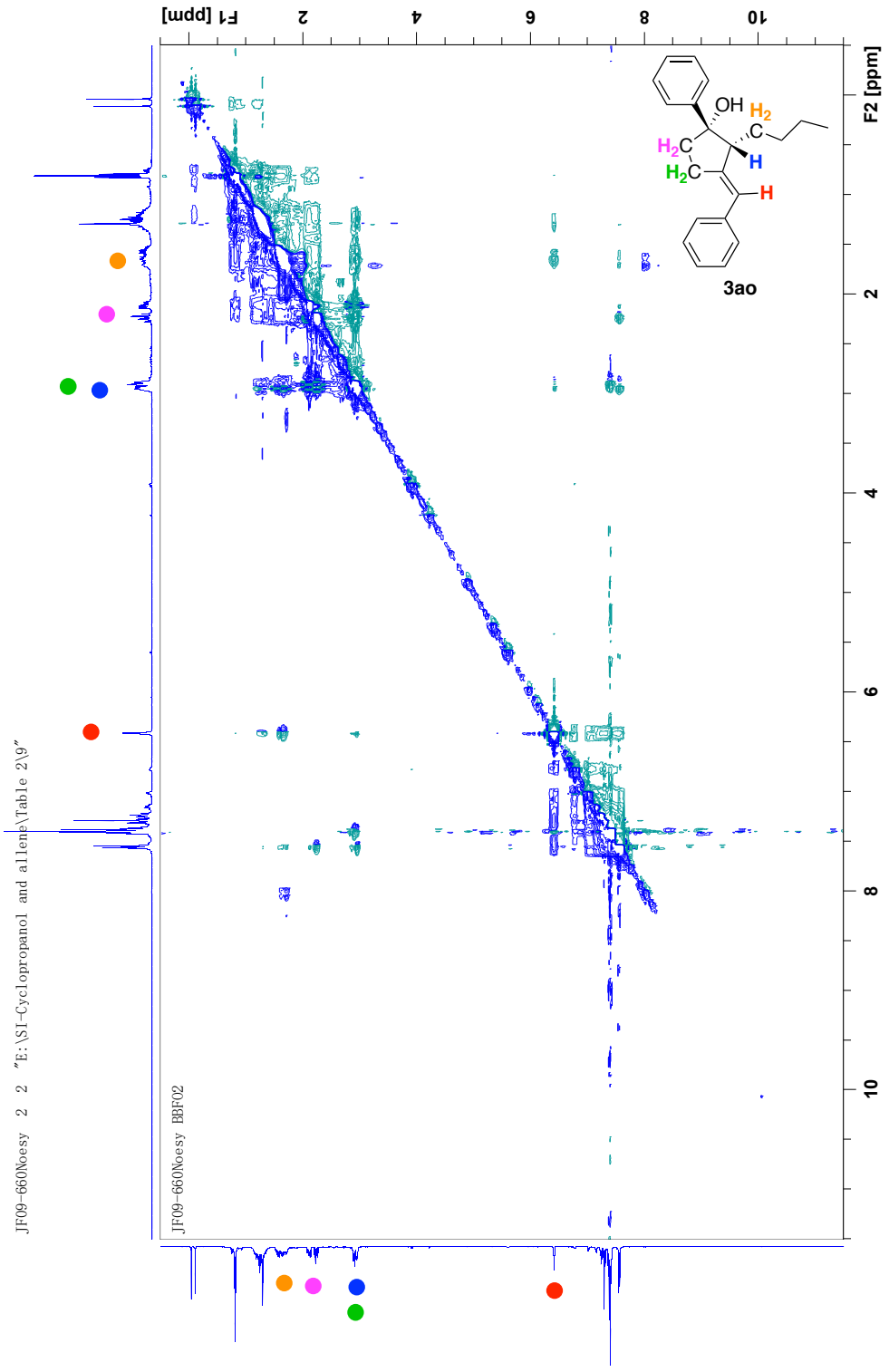

[ppm]
14
12
10
8
6
4
2
0
Ph
OH
n-Pr
H
H2C
H
n-Pr
3an
JF09-330Noesy V400
JF09-330Noesy 2 2 "E:\SI-Cyclopropanol and allene\Table 2\8"

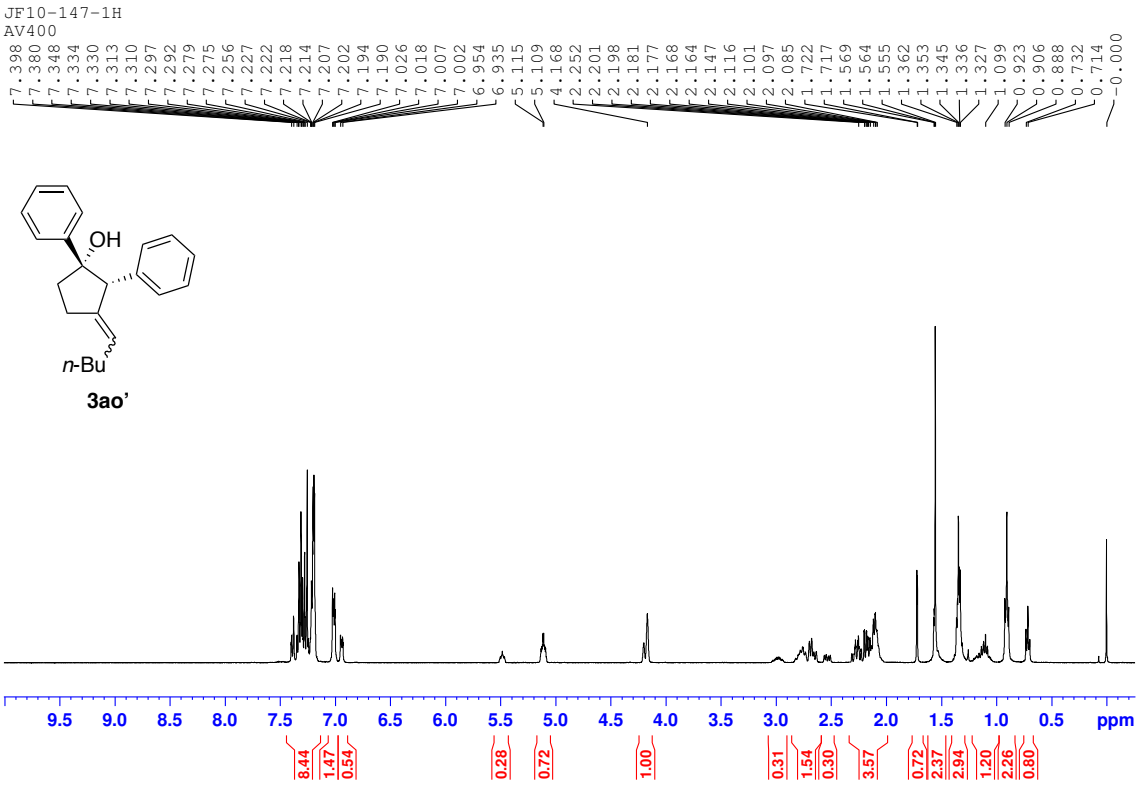
JF09-660H BBF02

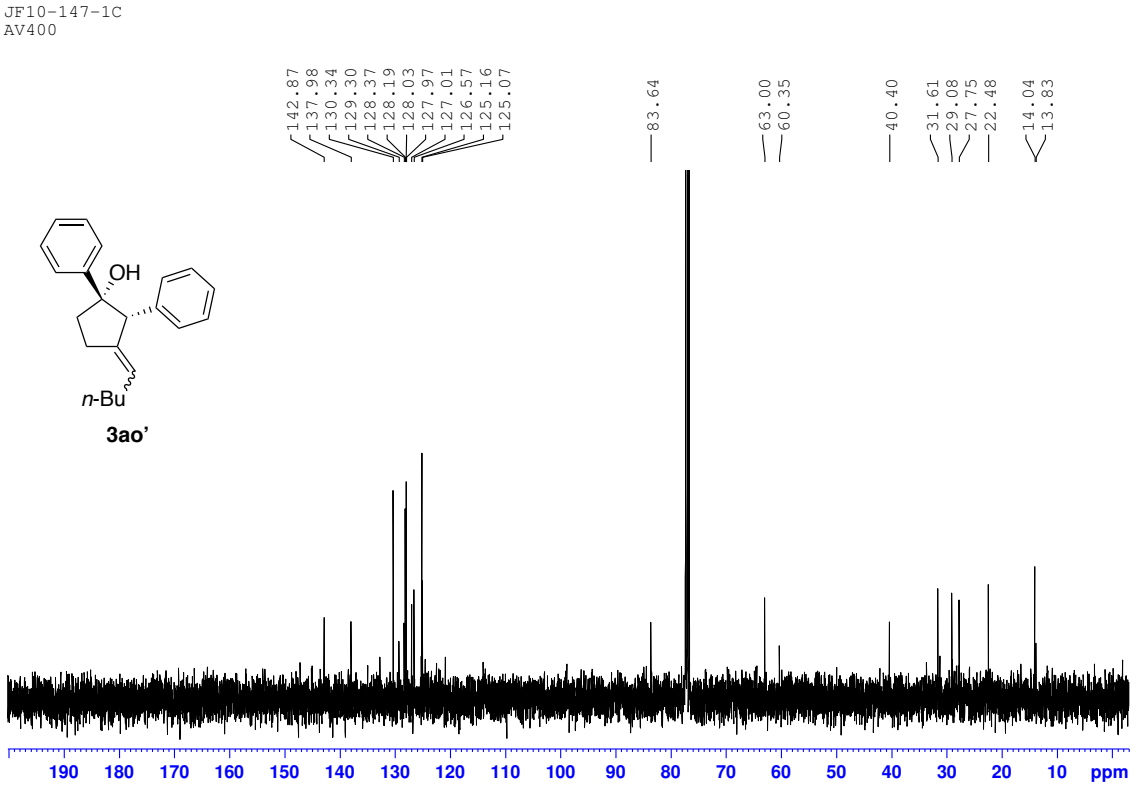


JF09-660C BBF02

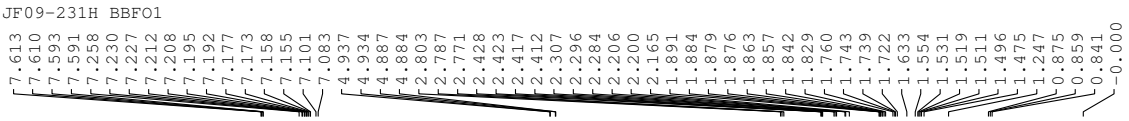


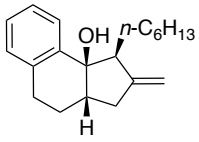

F1 [ppm]
F2 [ppm]
JF09-660Noesy BBF02
JF09-660Noesy 2 2 "E:\SI-Cyclopropanol and allene\Table 2\9"
OH
H2
C
H2C
H
H2C
H
3ao


JF10-147-1H
AV400
7.398 7.380 7.348 7.334 7.330 7.313 7.310 7.297 7.292 7.279 7.275 7.256 7.227 7.222 7.218 7.214 7.207 7.202 7.194 7.190 7.026 7.018 7.007 7.002 6.954 6.935 5.115 5.109 4.168 2.252 2.201 2.198 2.181 2.177 2.168 2.164 2.147 2.116 2.101 2.097 2.085 1.722 1.717 1.569 1.564 1.555 1.362 1.353 1.345 1.336 1.327 1.099 0.923 0.906 0.888 0.732 0.714 -0.000
OH
n-Bu
3ao'
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
8.44 1.47 0.54 0.28 0.72 1.00 0.31 1.54 0.30 3.57 0.72 2.37 2.94 1.20 2.26 0.80

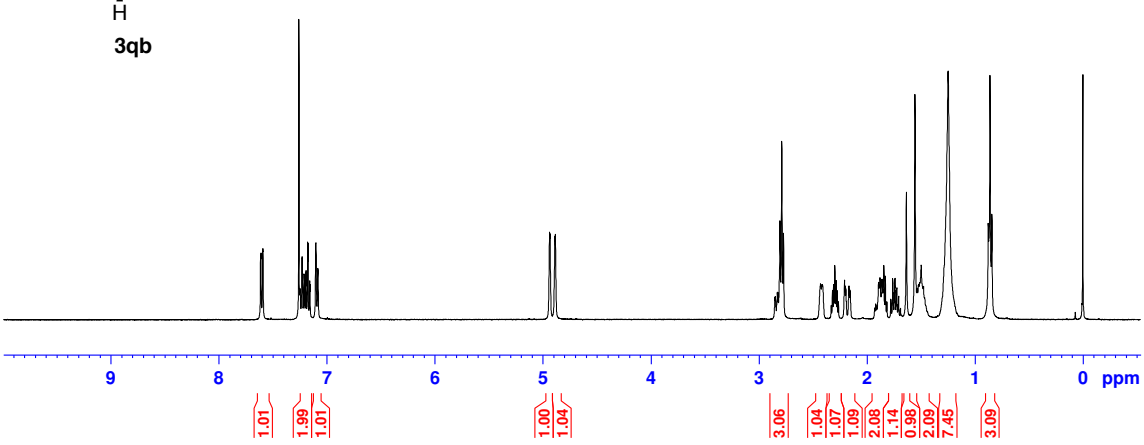

JF10-147-1C
AV400
142.87 137.98 130.34 129.30 128.37 128.19 128.03 127.97 127.01 126.57 125.16 125.07
83.64
63.00 60.35
40.40
31.61 29.08 27.75 22.48
14.04 13.83
OH
n-Bu
3ao'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

JF09-231H BBFO1

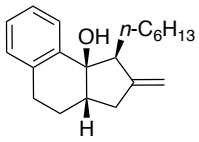




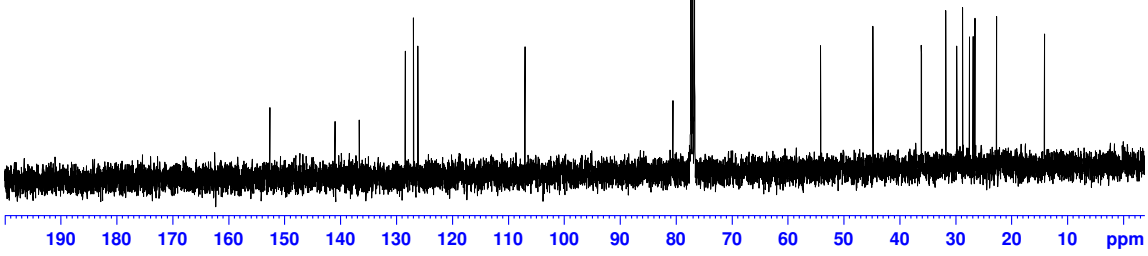
3qb



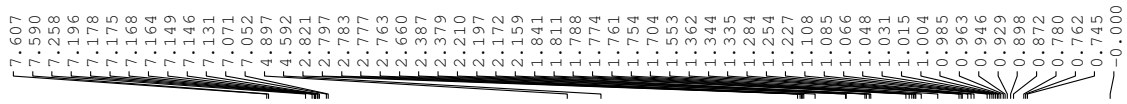
JF09-231C BBFO1

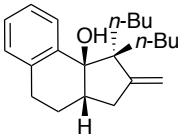


3qb

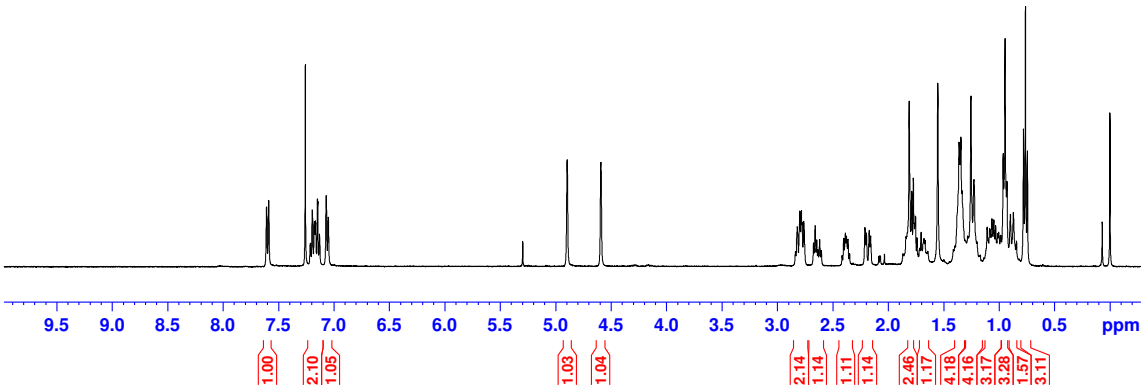


JF10-119H AV400

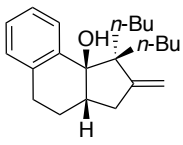




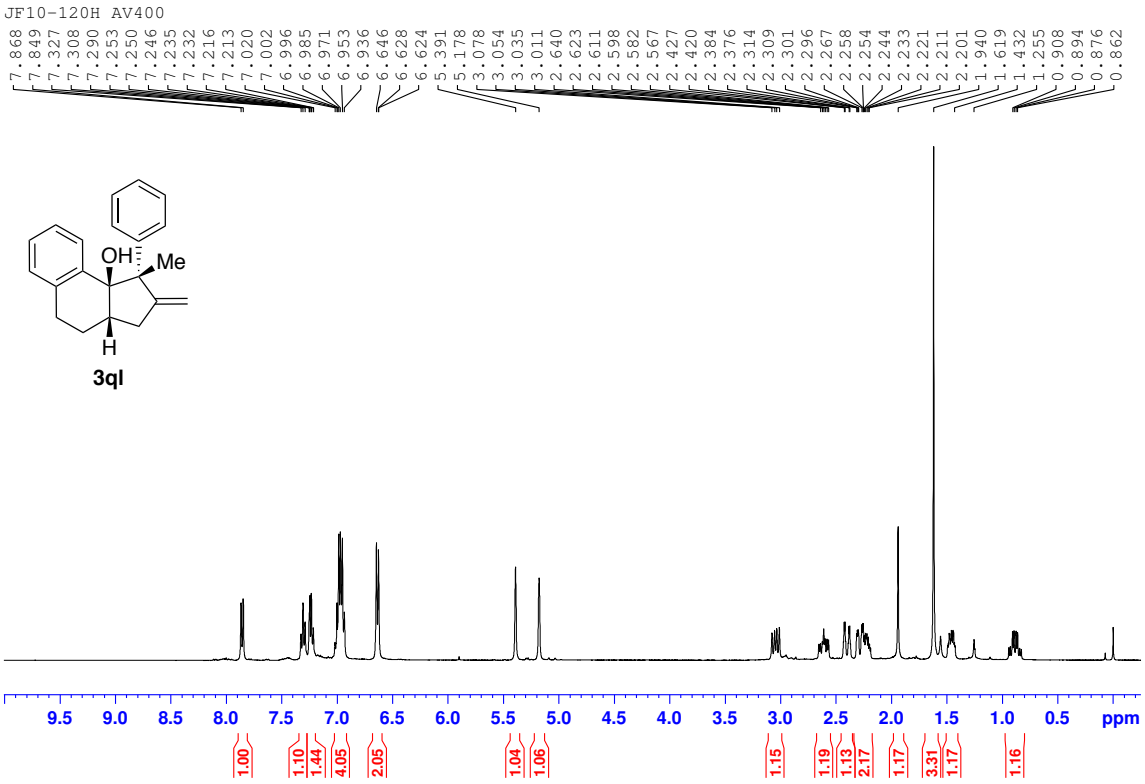
3qk

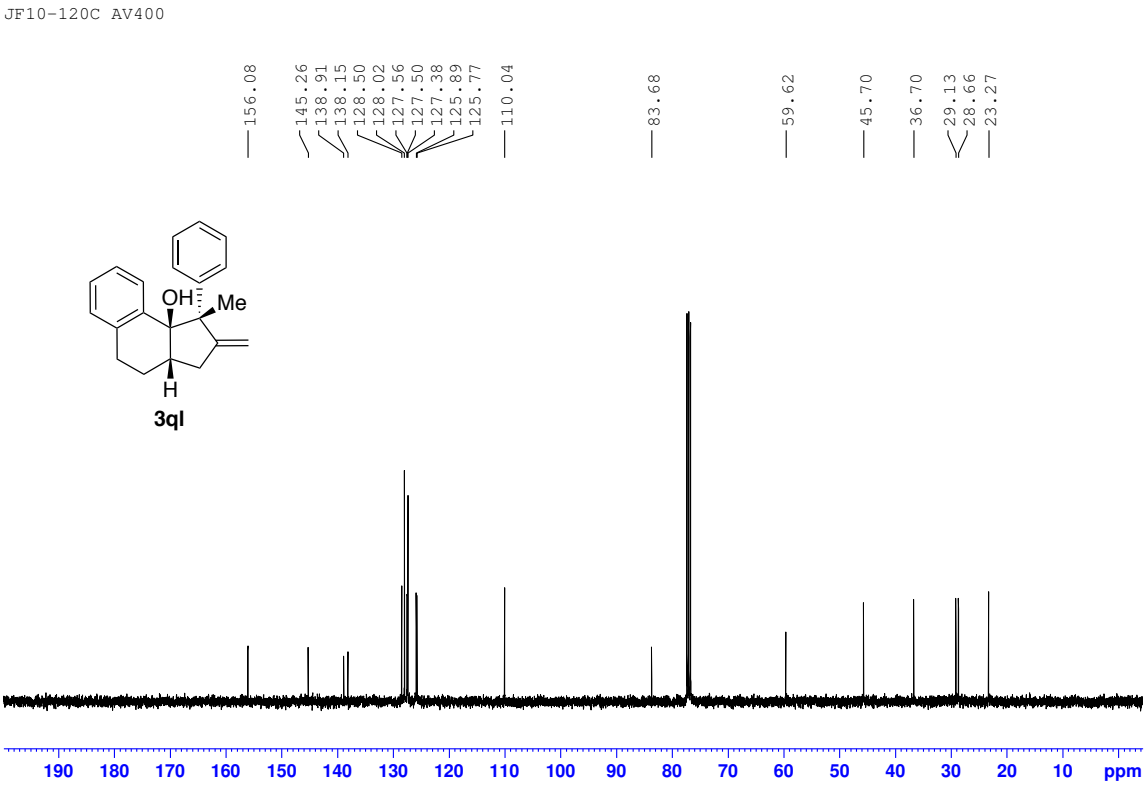


JF10-119C AV400

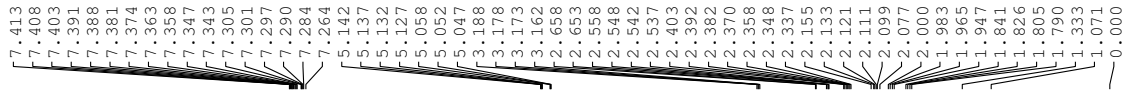


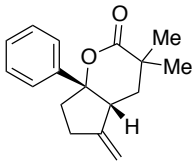
3qk


JF10-120H AV400
7.868 7.849 7.327 7.308 7.290 7.253 7.250 7.246 7.235 7.232 7.216 7.213 7.020 7.002 6.996 6.985 6.971 6.953 6.936 6.646 6.628 6.624 5.391 5.178 3.078 3.054 3.035 3.011 2.640 2.623 2.611 2.598 2.582 2.567 2.427 2.420 2.384 2.376 2.314 2.309 2.301 2.296 2.267 2.258 2.254 2.244 2.233 2.221 2.211 2.201 1.940 1.619 1.432 1.255 0.908 0.894 0.876 0.862
OH
Me
H
3ql
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 1.10 1.44 4.05 2.05 1.04 1.06 1.15 1.19 1.13 2.17 1.17 3.31 1.17 1.16

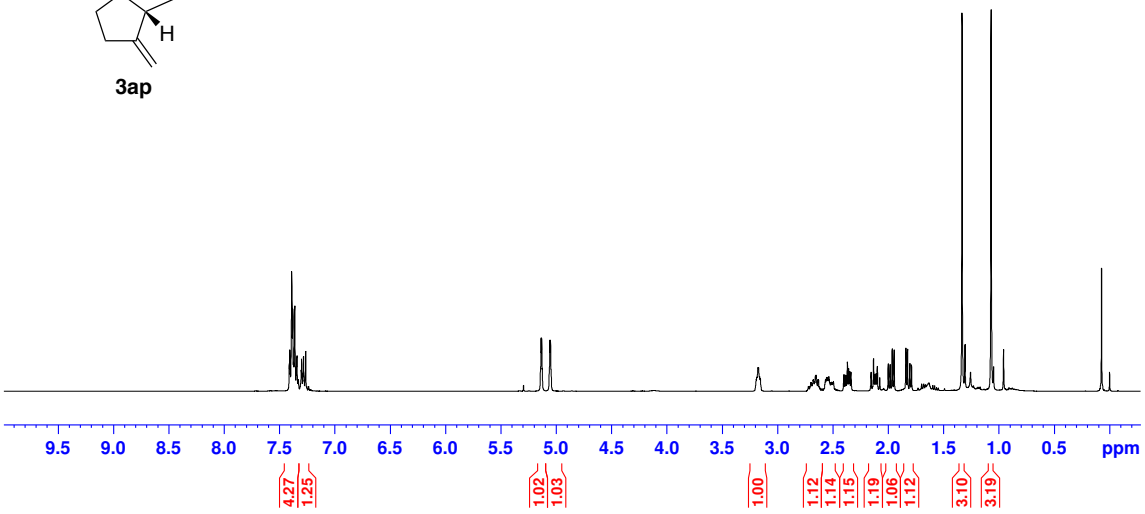

JF10-120C AV400
156.08 145.26 138.91 138.15 128.50 128.02 127.56 127.50 127.38 125.89 125.77 110.04 83.68 59.62 45.70 36.70 29.13 28.66 23.27
OH
Me
H
3ql
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

JF10-150H-1
AV400

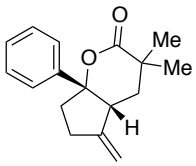




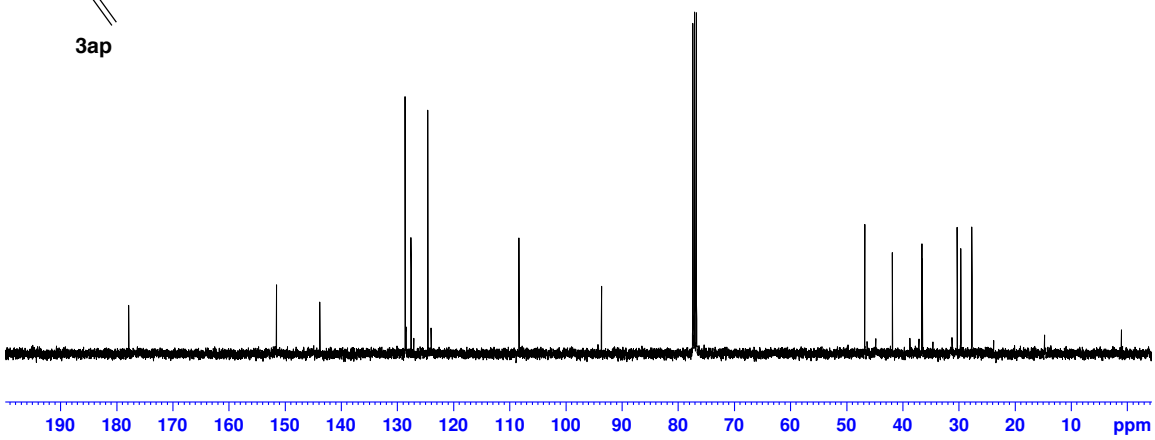
3ap



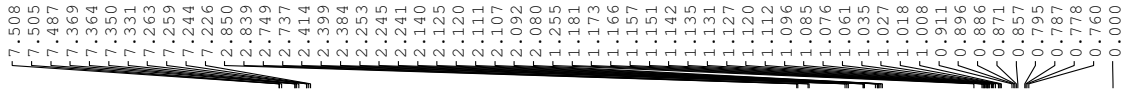
JF10-150C-1
AV400

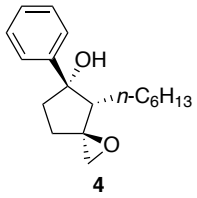


3ap



JF10-136-1H
AV400





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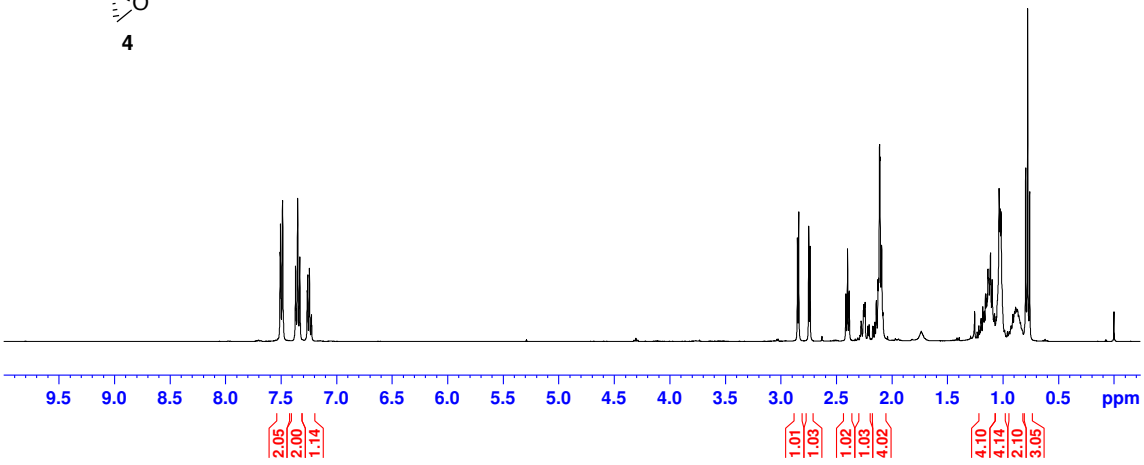
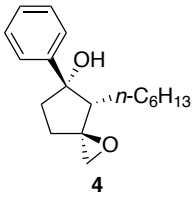
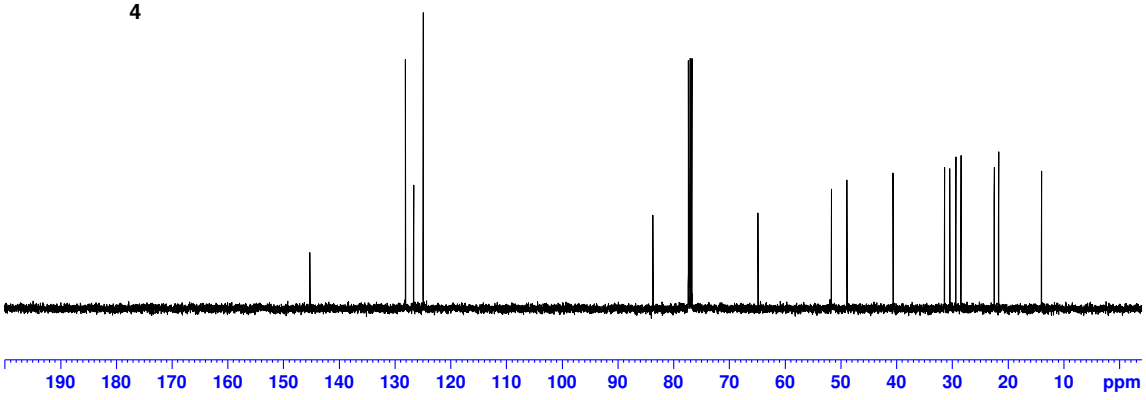


JF10-136-1C
AV400

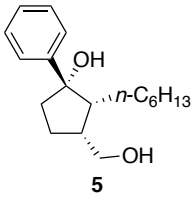


4



JF10-15H-2
AV400

7.461 7.458 7.440 7.328 7.310 7.290 7.255 7.226 7.207 7.189 3.820 3.815 3.793 3.788 3.584 3.577 3.557 3.550 2.497 2.490 2.235 2.215 2.191 2.170 2.164 2.115 2.093 2.078 2.069 2.063 2.051 2.046 2.038 2.024 2.010 2.001 1.990 1.976 1.970 1.957 1.951 1.400 1.381 1.375 1.350 1.253 1.236 1.202 1.185 1.168 1.153 1.130 1.028 0.828 0.811 0.793 0.073 -0.000



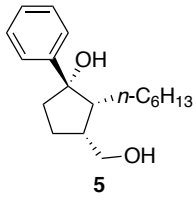
5

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

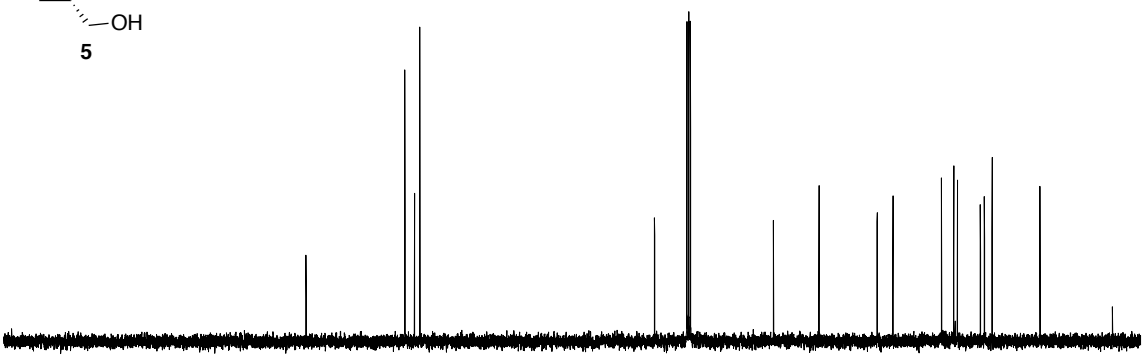
2.01 1.98 1.00 1.80 1.05 1.04 1.00 1.02 4.41 1.29 9.51 3.00

JF10-15C-2
AV400

145.67 127.94 126.21 125.27 83.15 61.83 53.66 43.23 40.40 31.68 29.50 28.83 24.72 23.99 22.61 14.05

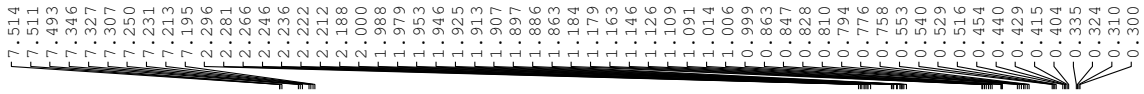


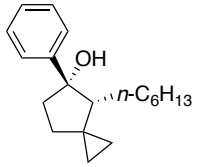
5



190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

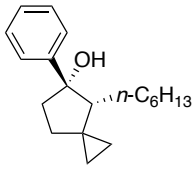
JF10-138H
AV400



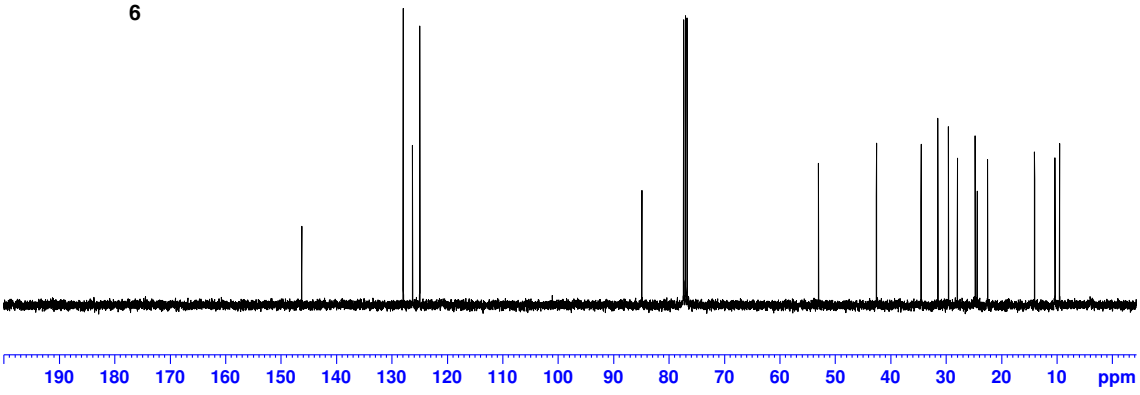


6

JF10-138C
AV400

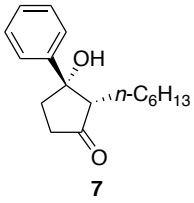


6

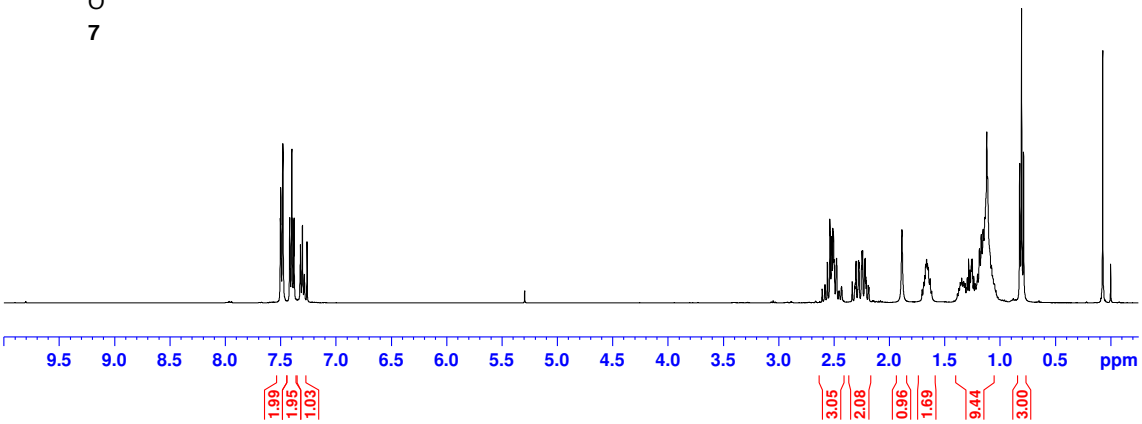


JF10-145H-1
AV400

7.502 7.499 7.481 7.417 7.413 7.399 7.379 7.322 7.303 7.285 7.262 2.560 2.538 2.533 2.521 2.510 2.505 2.498 2.477 2.301 2.278 2.274 2.251 2.247 2.241 2.224 2.219 2.212 2.207 1.886 1.680 1.672 1.663 1.655 1.647 1.630 1.346 1.295 1.284 1.271 1.263 1.257 1.251 1.238 1.202 1.185 1.169 1.153 1.137 1.119 1.112 1.076 1.068 0.822 0.805 0.787 0.072 0.000

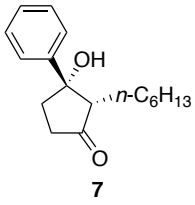


7

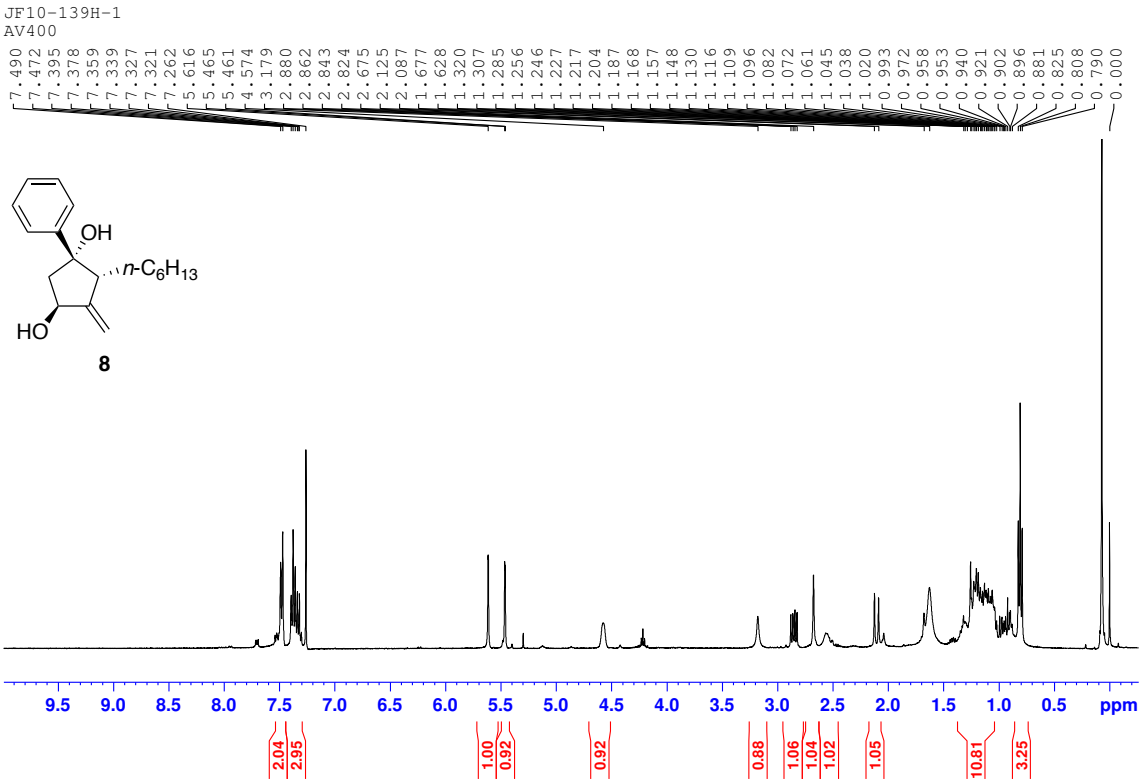


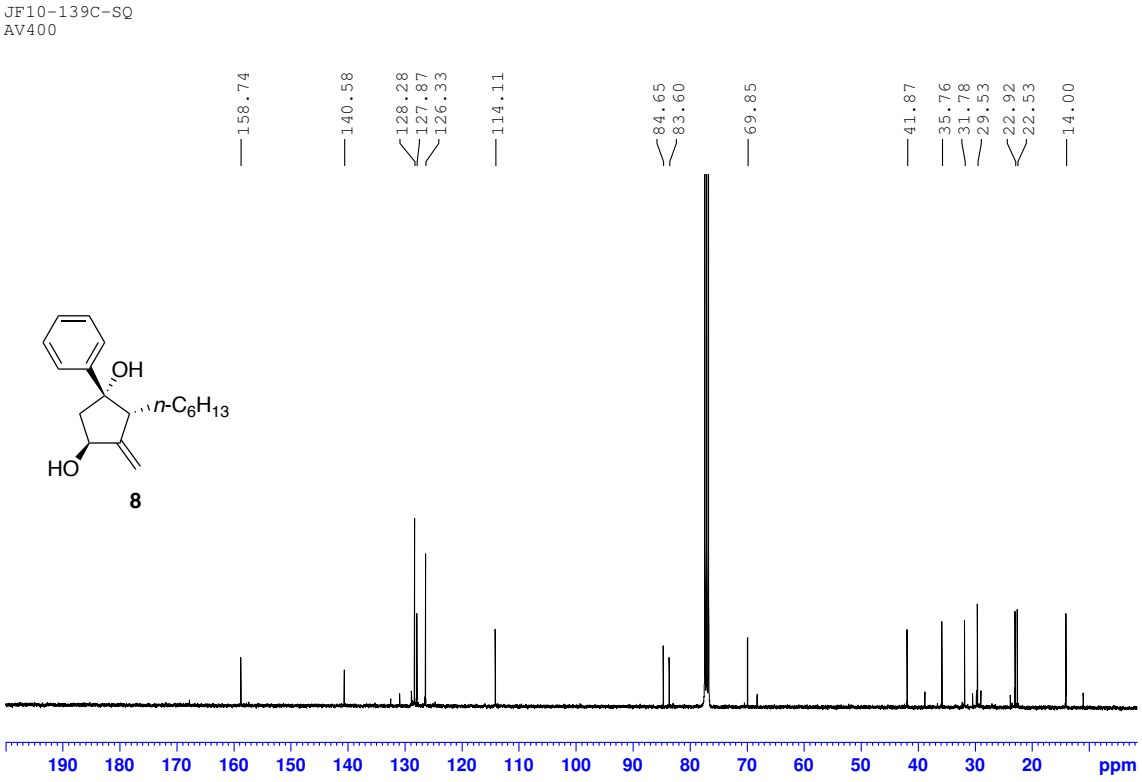
JF10-145C
AV400

217.62 144.66 128.54 127.32 124.68 81.81 59.64 37.63 35.25 31.44 29.28 27.98 23.28 22.53 14.02



7


JF10-139H-1
AV400
7.490
7.472
7.395
7.378
7.359
7.339
7.327
7.321
7.262
5.616
5.465
5.461
4.574
3.179
2.880
2.862
2.843
2.824
2.675
2.125
2.087
1.677
1.628
1.320
1.307
1.285
1.256
1.246
1.227
1.217
1.204
1.187
1.168
1.157
1.148
1.130
1.116
1.109
1.096
1.082
1.072
1.061
1.045
1.038
1.020
0.993
0.972
0.958
0.953
0.940
0.921
0.902
0.896
0.881
0.825
0.808
0.790
0.000
OH
n-C6H13
HO
8
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.04
2.95
1.00
0.92
0.92
0.88
1.06
1.04
1.02
1.05
10.81
3.25


JF10-139C-SQ
AV400
158.74
140.58
128.28
127.87
126.33
114.11
84.65
83.60
69.85
41.87
35.76
31.78
29.53
22.92
22.53
14.00
OH
n-C6H13
HO
8
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm