Supporting Information

Nickel-Catalyzed Asymmetric Reductive Aryl-Allylation of Unactivated Alkenes

Zhiyang Lin,^a Youxiang Jin,^a Weitao Hu,^a and Chuan Wang^{*,a}

^aHefei National Laboratory for Physical Science at the Microscale, Department of Chemistry, Center for Excellence in Molecular Synthesis, University of Science and Technology of China, Hefei, Anhui, 230026 (P. R. China).

E-mail: chuanw@ustc.edu.cn

Table of Contents

I. General Information	S2
II. Preparation of Substrates	S3
III. Procedures for the Nickel-Catalyzed Asymmetric Reductive Aryl-Allylation	S8
IV. Derivatizations of the Aryl-Allylation Products	S34
V. Determination of the Absolute Configuration of the Aryl-Allylation Products	S37
VI. Determination of the <i>E</i> / <i>Z</i> -Configuration of the Aryl-Allylation Products	S38
VII. References	
VIII. NMR Spectra	S40
XI. HPLC Chromatograms	S169

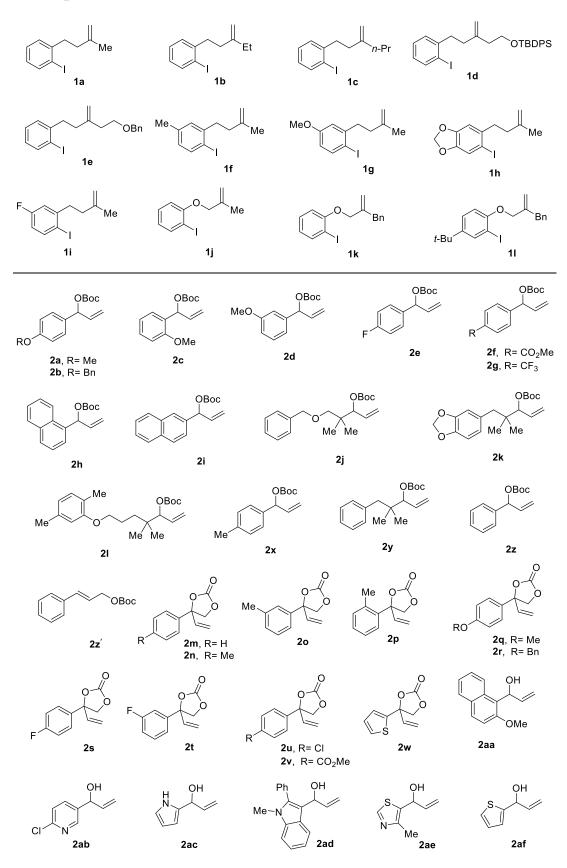
I. General Information

¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded on a Bruker Advance 400M NMR spectrometers at ambient temperature in CDCl₃ at 400, 101 and 376 MHz, respectively. ¹⁹F NMR were reported as ¹⁹F exp. comp. pulse decoupling (F¹⁹CPD) unless otherwise noted. The chemical shifts are given in ppm relative to tetramethylsilane [¹H: δ =(SiMe₄) = 0.00 ppm] as an internal standard or relative to the resonance of the solvent [¹H: δ (CDCl₃) = 7.26, ¹³C: δ (CDCl₃) = 77.16 ppm]. Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets), etc. Coupling constants are reported as *J* values in Hz. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. Flash chromatography was performed using 300-400 mesh silica gel with the indicated solvent system.

All Ni-salts were purchased from Adamas-beta, Sigma-Aldrich, Alfa Aesar, TCI, and were used as received. All solvents were purchased from Adamas-beta China and used as received. Other commercial reagents were purchased from Sigma-Aldrich, Alfa Aesar, TCI, Strem, Acros and Energy Chemical, and were used as received.

Reactions were monitored through thin layer chromatography [Merck 60 F254 precoated silica gel plate (0.2 mm thickness)]. Subsequent to elution, spots were visualized using UV radiation (254 nm) on Spectroline Model ZF-7 254 nm. Other visualization methods include staining with a basic solution of potassium permanganate or acidic solution of ceric ammonium molybdate, followed by heating.

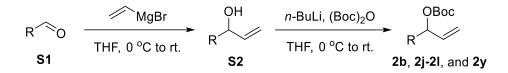
II. Preparation of Substrates



The unactivated alkenes $1a-1i^1$ and $1j-1l^2$, the allylic carbonates $2a^3$, $2c-2g^3$, $2i^3$, $2x^3$,

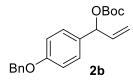
 $2h^4$, $2z^5$, and $2m-2w^6$, the allylic alcohols $2aa-2ab^7$, $2ad^7$, and $2af^7$ are known compounds in the literature.

Procedure for Preparation of the Allylic Carbonates 2b, 2j-2l, and 2y.



Step 1: Allylic carbonates was synthesized according to the reported method⁴. Vinyl magnesium bromide (6 mL, 6 mmol, 1.2 equiv, 1 M in THF) was added to a solution of the corresponding aldehydes S1 (5 mmol, 1.0 equiv) in THF at 0 °C. After 15 min, the reaction was allowed to warm to RT and stirred for additional 3 h. The reaction mixture was quenched by addition of saturated aqueous solution of NH₄Cl and extracted with Et₂O. The combined organic phases were washed with brine, dried over MgSO₄, filtered and evaporated in vacuo. The mixture was passed through a short silica gel pad to remove the polar compounds to get the crude material S2. Step 2: To a flamedried round-bottomed flask with stir bar was added allylic alcohols S2 (1 equiv) and dry THF. The solution was cooled to -78 °C and *n*-butyllithium (1 equiv, 2.5 M in hexane) was added, dropwise. The solution was stirred for 30 minutes at -78 °C, before (Boc)₂O (1.5 equiv) in 4 mL THF was added. The reaction was allowed to warm to room temperature and stirred overnight. The reaction mixture was diluted with 10 mL of diethyl ether and 7 mL of water, and stirred for 15 minutes. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 x 15 mL). The combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. The crude reaction mixture was purified by flash column chromatography to afford the allylic carbonates.

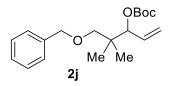
1-(4-(Benzyloxy)phenyl)allyl tert-butyl carbonate (2b)



The title compound **2b** was isolated as a colorless oil (1.15 g, 68% over two steps) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1).

¹**H NMR (500 MHz, Chloroform-***d***)** δ = 7.44-7.37 (m, 4H), 7.36-7.29 (m, 3H), 6.92 (d, *J*= 8.7 Hz, 2H), 6.68-6.50 (m, 1H), 6.16 (dt, *J*= 15.8, 6.6 Hz, 1H), 5.06 (s, 2H), 4.75-4.60 (m, 1H), 1.50 (s, 9H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 158.8, 153.4, 136.8, 134.3, 129.2, 128.6 (2C), 128.1, 127.9 (2C), 127.5, 120.7 (2C), 114.9 (2C), 82.2, 70.0, 67.8, 27.8 (3C) ppm. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₂₄O₄Na 363.1567; Found 363.1566. 5-(Benzyloxy)-4,4-dimethylpent-1-en-3-yl tert-butyl carbonate (2j)



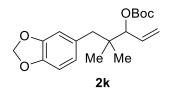
The title compound 2j was isolated as a colorless oil (0.83 g, 52% over two steps) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1).

¹**H NMR (400 MHz, Chloroform-***d*) δ = 7.35-7.24 (m, 5H), 5.90-5.73 (m, 1H), 5.33-5.18 (m, 2H), 5.14-5.08 (m, 1H), 4.55-4.40 (m, 2H), 3.27 (d, *J*= 8.9 Hz, 1H), 3.20 (d, *J*= 8.8 Hz, 1H), 1.47 (s, 9H), 0.98 (s, 3H), 0.93 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 153.2, 138.7, 133.3, 128.3 (2C), 127.4 (3C), 118.4, 81.7, 81.5, 76.5, 73.3, 38.6, 27.9 (3C), 21.1, 20.7 ppm.

HRMS (**ESI**) m/z: [M+Na]⁺ Calcd for C₁₉H₂₈O₄Na 343.1880; Found 343.1881.

5-(Benzo[d][1,3]dioxol-5-yl)-4,4-dimethylpent-1-en-3-yl tert-butyl carbonate (2k)

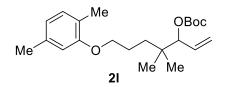


The title compound 2k was isolated as a colorless oil (0.83 g, 52% over two steps) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1).

¹**H NMR (500 MHz, Chloroform-***d*) δ = 6.71 (d, *J*= 7.9 Hz, 1H), 6.62 (s, 1H), 6.56 (d, *J*= 7.9 Hz, 1H), 5.92 (s, 2H), 5.88-5.82 (m, 1H), 5.30-5.22 (m, 2H), 4.73 (d, *J*= 7.0 Hz, 1H), 2.61 (d, *J*= 13.3 Hz, 1H), 2.46 (d, *J*= 13.3 Hz, 1H), 1.50 (s, 9H), 0.91 (s, 3H), 0.85 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 153.2, 147.1, 145.9, 133.3, 131.7, 123.6, 118.9, 111.1, 107.7, 100.8, 83.9, 81.9, 44.0, 38.1, 27.9 (3C), 23.2, 22.5 ppm. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₉H₂₆O₅Na 357.1678; Found 357.1682.

tert-Butyl (7-(2,5-dimethylphenoxy)-4,4-dimethylhept-1-en-3-yl) carbonate (21)



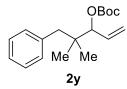
The title compound **2l** was isolated as a colorless oil (1.10 g, 61% over two steps) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1).

¹**H NMR (400 MHz, Chloroform-***d*) δ= 6.99 (d, *J*= 7.4 Hz, 1H), 6.65 (d, *J*= 7.5 Hz, 1H), 6.61 (s, 1H), 5.94-5.78 (m, 1H), 5.36-5.13 (m, 2H), 4.85 (d, *J*= 5.9 Hz, 1H), 3.96-3.84 (m, 2H), 2.30 (s, 3H), 2.17 (s, 3H), 1.85-1.71 (m, 2H), 1.52-1.44 (m, 2H), 1.47 (s, 9H), 0.96 (s, 3H), 0.94 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 157.0, 153.4, 136.4, 133.3, 130.3, 123.6, 120.6, 118.6, 111.9, 84.0, 81.7, 68.4, 36.7, 35.0, 27.9 (3C), 23.9, 23.0, 22.9, 21.4, 15.8 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₂H₃₄O₄Na 385.2349; Found 385.2356.

tert-Butyl (4,4-*dimethyl-5-phenylpent-1-en-3-yl*) *carbonate* (2y)



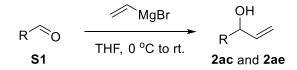
The title compound 2y was isolated as a colorless oil (0.93 g, 64% over two steps) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1).

¹**H** NMR (400 MHz, Chloroform-*d*) δ = 7.28-7.20 (m, 3H), 7.15-7.11 (m, 2H), 5.94-5.84 (m, 1H), 5.31-5.25 (m, 2H), 4.77 (d, *J*= 7.1 Hz, 1H), 2.69 (d, *J*= 13.1 Hz, 1H), 2.55 (d, *J*= 13.0 Hz, 1H), 1.50 (s, 9H), 0.92 (s, 3H), 0.85 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 153.2, 138.1, 133.3, 130.8 (2C), 127.8 (2C), 126.1, 118.9, 84.0, 81.8, 44.2, 38.1, 27.9 (3C), 23.1, 22.5 ppm.

HRMS (**ESI**) m/z: [M+Na]⁺ Calcd for C₁₈H₂₆O₃Na 313.1774; Found 313.1770.

Procedure for Preparation of the Allylic Alcohols 2ac and 2ae⁴



Vinyl magnesium bromide (6 mL, 6 mmol, 1.2 equiv, 1 M in THF) was added to a solution of the corresponding aldehydes **S1** (5 mmol, 1.0 equiv) in THF at 0 °C. After 15 min, the reaction was allowed to warm to RT and stirred for additional 3 h. The reaction mixture was quenched by addition of saturated aqueous solution of NH₄Cl and extracted with Et₂O. The combined organic phases were washed with brine, dried over MgSO₄, and removed in vacuum. The residue was purified by column chromatography (petroleum ether/ethyl acetate) to provide the allylic alcohols.

1-(1H-Pyrrol-2-yl)prop-2-en-1-ol (2ac)



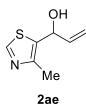
The title compound **2ac** was isolated as a colorless oil (0.22 g, 35%) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (2:1).

¹**H NMR (400 MHz, Chloroform-***d***)** δ = 8.41 (s, 1H), 6.81-6.71 (m, 1H), 6.20-6.11 (m, 1H), 6.12-6.03 (m, 2H), 5.39 (dt, *J*= 17.0, 1.4 Hz, 1H), 5.29-5.21 (m, 2H), 2.19-2.11 (brs, 1H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 138.3, 132.4, 118.2, 115.6, 108.4, 106.1, 68.9 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₇H₉NONa 146.0582; Found 146.0588.

1-(4-Methylthiazol-5-yl)prop-2-en-1-ol (2ae)



The title compound **2ae** was isolated as a colorless oil (0.61 g, 79%) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (3:1).

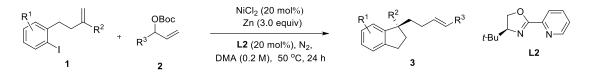
¹**H NMR (500 MHz, Chloroform-***d***)** δ = 8.59 (s, 1H), 6.13-6.01 (m, 1H), 5.49 (d, *J*= 5.7 Hz, 1H), 5.36 (d, *J*= 18.6 Hz, 1H), 5.22 (d, *J*= 10.2 Hz, 1H), 3.56-3.38 (brs, 1H), 2.40 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ= 151.1, 148.8, 138.9, 134.2, 115.8, 68.4, 15.2 ppm.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₇H₁₀NOS 156.0483; Found 156.0481.

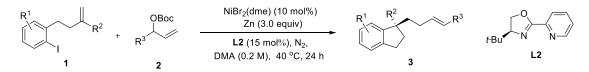
III. Procedures for the Nickel-Catalyzed Asymmetric Reductive Aryl-Allylation

Standard Procedure A for Synthesis of 3aa-3ad and 3fa.



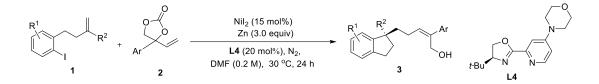
NiCl₂ (5.2 mg, 0.04 mmol, 20 mol %), Zn (39 mg, 0.6 mmol, 3 equiv) and ligand L2 (8.2 mg, 0.04 mmol, 20 mol %) were placed in a Schlenk tube equipped with a stir bar. Subsequently, the Schlenk tube was evacuated and filled with nitrogen (three cycles). To these solids, 1.0 mL dry DMA, unactivated alkenes 1 (0.2 mmol, 1.0 equiv) and allylic carbonates 2 (0.3 mmol, 1.5 equiv) were added successively under nitrogen atmosphere. The reaction mixture was stirred at 50 °C for 24 hours, before it was quenched by addition of water. The aqueous phase was extracted with ethyl acetate (3×20 mL), and the combined organic phases were washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The crude materials were then purified through column chromatography on silica gel (petroleum ether/ethyl acetate) to give the products **3**.

Standard Procedure B for Synthesis of 3ae-3al, 3bk, 3ck, 3fx, 3gy and 3ik.



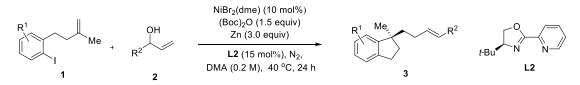
NiBr₂(dme) (6.2 mg, 0.02 mmol, 10 mol %), Zn (39 mg, 0.6 mmol, 3 equiv) and ligand L2 (6.1 mg, 0.03 mmol, 15 mol %) were placed in a Schlenk tube equipped with a stir bar. Then the Schlenk tube was evacuated and filled with nitrogen (three cycles). To these solids, 1.0 mL dry DMA, unactivated alkenes 1 (0.2 mmol, 1.0 equiv) and allylic carbonates 2 (0.3 mmol, 1.5 equiv) were added successively under nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 24 hours, before it was quenched by addition of water. The aqueous phase was extracted with ethyl acetate (3×20 mL), and the combined organic phases were washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The crude materials were purified through column chromatography on silica gel (petroleum ether/ethyl acetate) to give the products 3.

Standard Procedure C for Synthesis of 3am-3aw, 3bm-3jm, 3jn-3jo and 3km-3lm.



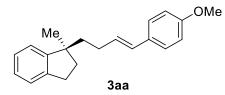
NiI₂ (9.4 mg, 0.03 mmol, 15 mol %), Zn (39 mg, 0.6 mmol, 3 equiv) and ligand (11.6 mg, 0.04 mmol, 20 mol %) were placed in a Schlenk tube equipped with a stir bar. Then the Schlenk tube was evacuated and filled with nitrogen (three cycles). To these solids, 1.0 mL dry DMF, unactivated alkenes **1** (0.3 mmol, 1.5 equiv) and vinyl ethylene carbonates **2** (0.2 mmol, 1.0 equiv) were added successively under nitrogen atmosphere. The reaction mixture was stirred at 30 °C for 24 hours,^a before it was quenched by addition of water. The aqueous phase was extracted with ethyl acetate (3×20 mL), and the combined organic phases were washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The crude materials were purified through column chromatography on silica gel (petroleum ether/ethyl acetate) to give the **3** as products. ^a 48 h for **3km**.

Standard Procedure D for Synthesis of 3aaa-3aae and 3gaf.



NiBr₂(dme) (6.2 mg, 0.02 mmol, 10 mol %), (Boc)₂O (65.4 mg, 0.3 mmol, 1.5 equiv), Zn (39 mg, 0.6 mmol, 3 equiv) and ligand **L2** (6.1 mg, 0.03 mmol, 15 mol %) were placed in a Schlenk tube equipped with a stir bar. Then the Schlenk tube was evacuated and filled with nitrogen (three cycles). To these solids, 1.0 mL dry DMA and unactivated alkenes **1** (0.2 mmol, 1.0 equiv) and the allyl alcohols **2** (0.3 mmol, 1.5 equiv) were added successively under nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 24 hours, before it was quenched by addition of water. The aqueous phase was extracted with ethyl acetate (3×20 mL), and the combined organic phases were washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The crude products were purified through column chromatography on silica gel (petroleum ether/ethyl acetate) to give the products **3**.

(*S*,*E*)-1-(4-(4-Methoxyphenyl)but-3-en-1-yl)-1-methyl-2,3-dihydro-1H-indene (**3aa**)



Following the Standard Procedure A, the title compound **3aa** was isolated as a colorless oil (43 mg, 74%, 96% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1).

Following the Standard Procedure D, the title compound **3aa** was isolated as a colorless oil (34 mg, 58%, 93% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1).

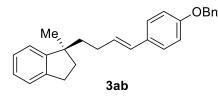
¹**H NMR (400 MHz, Chloroform-***d*) δ= 7.25-7.18 (m, 4H), 7.17-7.13 (m, 2H), 6.81 (d, *J*= 8.7 Hz, 2H), 6.29 (d, *J*= 15.8 Hz, 1H), 6.03 (dt, *J*= 15.8, 6.7 Hz, 1H), 3.78 (s, 3H), 2.94-2.86 (m, 2H), 2.22-2.03 (m, 3H), 1.87 (dt, *J*= 12.6, 7.8 Hz, 1H), 1.81-1.66 (m, 2H), 1.28 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 158.6, 151.2, 143.2, 130.7, 129.1, 128.8, 126.9 (2C), 126.3, 126.2, 124.6, 122.7, 113.9 (2C), 55.3, 47.3, 41.1, 38.6, 30.3, 28.7, 26.9 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₂₄ONa 315.1719; Found 315.1722.

HPLC-Data: (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 97/3, flow rate = 0.5 mL/min): t_R = 10.0 (major), 11.4 (minor).

(S,E)-1-(4-(4-(Benzyloxy)phenyl)but-3-en-1-yl)-1-methyl-2,3-dihydro-1H-indene (**3ab**)



The title compound **3ab** was isolated as a colorless oil (38 mg, 51%, 97% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1).

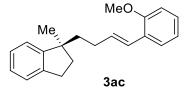
¹**H NMR (500 MHz, Chloroform**-*d*) δ = 7.45-7.32 (m, 5H), 7.25-7.12 (m, 6H), 6.89 (d, *J*= 8.7 Hz, 2H), 6.29 (d, *J*= 15.8 Hz, 1H), 6.04 (dt, *J*= 15.8, 6.8 Hz, 1H), 5.05 (s, 2H), 2.94-2.86 (m, 2H), 2.22-2.16 (m, 1H), 2.12-2.03 (m, 2H), 1.87 (dt, *J*= 12.6, 7.7 Hz, 1H), 1.81-1.71 (m, 1H), 1.71-1.64 (m, 1H), 1.28 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 157.8, 151.2, 143.2, 137.1, 131.0, 129.2, 128.8, 128.6 (2C), 127.9, 127.5 (2C), 126.9 (2C), 126.3, 126.2, 124.6, 122.7, 114.9 (2C), 70.0, 47.3, 41.1, 38.6, 30.3, 28.7, 26.9 ppm.

HRMS (**ESI**) m/z: [M+H]⁺ Calcd for C₂₇H₂₉O 369.2213; Found 369.2210.

HPLC-Data: (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 96/4, flow rate = 0.4 mL/min): t_R= 20.3 (minor), 21.0 (major).

(*S*,*E*)-1-(4-(2-Methoxyphenyl)but-3-en-1-yl)-1-methyl-2,3-dihydro-1H-indene (**3ac**)



The title compound **3ac** was isolated as a colorless oil (36 mg, 61%, 90% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1).

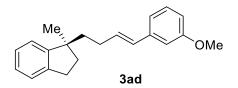
¹**H NMR (400 MHz, Chloroform-***d*) δ = 7.36 (dd, *J*= 7.6, 1.7 Hz, 1H), 7.24-7.09 (m, 5H), 6.93-6.79 (m, 2H), 6.67 (d, *J*= 15.9 Hz, 1H), 6.17 (dt, *J*= 15.9, 6.8 Hz, 1H), 3.82 (s, 3H), 2.94-2.86 (m, 2H), 2.26-2.19 (m, 1H), 2.17-2.05 (m, 2H), 1.87 (dt, *J*= 12.6, 7.7 Hz, 1H), 1.81-1.68 (m, 2H), 1.28 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 156.2, 151.3, 143.2, 131.9, 127.8, 126.9, 126.4, 126.3, 126.2, 124.5, 124.0, 122.7, 120.6, 110.8, 55.4, 47.4, 41.0, 38.7, 30.3, 29.2, 26.8 ppm.

HRMS (**ESI**) m/z: [M+H]⁺ Calcd for C₂₁H₂₅O 293.1900; Found 293.1888.

HPLC-Data: (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 98/2, flow rate = 0.4 mL/min): t_R= 12.7 (minor), 13.3 (major).

(*S*,*E*)-1-(4-(3-Methoxyphenyl)but-3-en-1-yl)-1-methyl-2,3-dihydro-1H-indene (**3ad**)



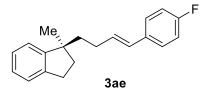
The title compound **3ad** was isolated as a colorless oil (33 mg, 56%, 93% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1).

¹**H** NMR (400 MHz, Chloroform-*d*) δ = 7.23-7.12 (m, 5H), 6.92-6.81 (m, 2H), 6.77-6.69 (m, 1H), 6.32 (d, *J*= 15.9 Hz, 1H), 6.18 (dt, *J*= 15.8, 6.6 Hz, 1H), 3.79 (s, 3H), 2.94-2.86 (m, 2H), 2.25-2.04 (m, 3H), 1.87 (dt, *J* = 12.7, 7.6 Hz, 1H), 1.77 – 1.67 (m, 2H), 1.29 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 159.8, 151.1, 143.2, 139.4, 131.6, 129.42, 129.37, 126.3, 126.2, 124.6, 122.7, 118.6, 112.4, 111.2, 55.2, 47.3, 40.9, 38.6, 30.3, 28.7, 26.9 ppm.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for C₂₁H₂₅O 293.1900; Found 293.1183. **HPLC-Data:** (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 97/3, flow rate = 0.4 mL/min): t_R= 43.5 (minor), 44.8 (major).

(*S*,*E*)-1-(4-(4-Fluorophenyl)but-3-en-1-yl)-1-methyl-2,3-dihydro-1H-indene (**3ae**)

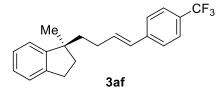


The title compound **3ae** was isolated as a colorless oil (24 mg, 42%, 95% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1). ¹H NMR (500 MHz, Chloroform-*d*) δ = 7.27-7.23 (m, 2H), 7.20-7.12 (m, 4H), 6.95 (t, *J*= 8.7 Hz, 2H), 6.30 (d, *J*= 16.0 Hz, 1H), 6.09 (dt, *J*= 15.8, 6.8 Hz, 1H), 2.94-2.86 (m, 2H), 2.25-2.18 (m, 1H), 2.14-2.08 (m, 2H), 1.87 (dt, *J*= 12.6, 7.7 Hz, 1H), 1.80-1.74 (m, 1H), 1.70-1.66 (m, 1H), 1.28 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 161.9 (d, *J*= 245.4 Hz), 151.1, 143.2, 134.0 (d, *J*= 3.6 Hz), 130.9 (d, *J*= 1.8 Hz), 128.3, 127.3 (d, *J*= 8.2 Hz, 2C), 126.3 (d, *J*= 17.5 Hz, 2C), 124.6, 122.7, 115.4, 115.2, 47.3, 40.9, 38.6, 30.3, 28.7, 26.9 ppm. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₀H₂₂F 281.1700; Found 281.1697. ¹⁹F NMR (471 MHz, Chloroform-*d*) δ = -116.74 (s, 1F) ppm.

HPLC-Data: (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 97/3, flow rate = 0.4 mL/min): t_R= 11.2 (minor), 12.3 (major).

(*S*,*E*)-1-*Methyl*-1-(4-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)-2,3-dihydro-1H-indene (**3af**)



The title compound **3af** was isolated as a colorless oil (24 mg, 37%, 95% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1).

¹**H** NMR (400 MHz, Chloroform-*d*) δ = 7.51 (d, *J*= 8.2 Hz, 2H), 7.37 (d, *J*= 8.1 Hz, 2H), 7.23-7.10 (m, 4H), 6.37 (d, *J*= 15.9 Hz, 1H), 6.28 (dt, *J*= 15.8, 6.4 Hz, 1H), 2.94-2.87 (m, 2H), 2.26-2.04 (m, 3H), 1.88 (dt, *J*= 12.6, 7.7 Hz, 1H), 1.81-1.69 (m, 2H), 1.29 (s, 3H) ppm.

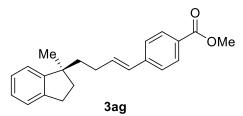
¹³C NMR (101 MHz, Chloroform-*d*) δ= 150.9, 143.2, 141.3, 134.1, 128.8 (q, *J*= 32.5 Hz), 128.3, 126.4, 126.3, 125.9 (2C), 124.3 (q, *J*= 272.7 Hz), 125.4 (q, *J*= 3.8 Hz, 2C), 124.6, 122.7, 47.3, 40.7, 38.6, 30.3, 28.8, 26.9 ppm.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ = -62.35 (s, 3F) ppm.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₁H₂₂F₃ 331.1668; Found 331.1683.

HPLC-Data: (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 97/3, flow rate = 0.4 mL/min): t_R= 9.4 (minor), 11.1 (major).

Methyl (S,E)-4-(4-(1-methyl-2,3-dihydro-1H-inden-1-yl)but-1-en-1-yl)benzoate (3ag)



The title compound **3ag** was isolated as a colorless oil (33 mg, 51%, 97% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1).

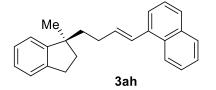
¹**H NMR** (**400 MHz**, **Chloroform**-*d*) δ = 7.94 (d, *J*= 8.3 Hz, 2H), 7.34 (d, *J*= 8.3 Hz, 2H), 7.22-7.09 (m, 4H), 6.38 (d, *J*= 15.9 Hz, 1H), 6.32 (dt, *J*= 15.9, 6.4 Hz, 1H), 3.89 (s, 3H), 2.93-2.87 (m, 2H), 2.27-2.20 (m, 1H), 2.14-2.04 (m, 2H), 1.88 (dt, *J*= 12.6, 7.7 Hz, 1H), 1.81-1.69 (m, 2H), 1.29 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 167.0, 150.9, 143.2, 142.4, 134.3, 129.9 (2C), 128.8, 128.3, 126.4, 126.3, 125.7 (2C), 124.6, 122.7, 52.0, 47.3, 40.7, 38.6, 30.3, 28.9, 26.9 ppm.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₂H₂₅O₂ 321.1849; Found 321.1853.

HPLC-Data: (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): t_R= 14.3 (major), 15.1 (minor).

(*S*,*E*)-1-(4-(1-Methyl-2,3-dihydro-1H-inden-1-yl)but-1-en-1-yl)naphthalene (**3ah**)



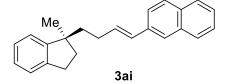
The title compound **3ah** was isolated as a colorless oil (35 mg, 56%, 96% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1).

¹**H** NMR (400 MHz, Chloroform-*d*) δ = 8.09 (d, *J*= 9.3 Hz, 1H), 7.81 (dd, *J*= 7.8, 1.9 Hz, 1H), 7.72 (d, *J*= 8.1 Hz, 1H), 7.52-7.40 (m, 4H), 7.23-7.15 (m, 4H), 7.07 (d, *J*= 15.5 Hz, 1H), 6.19 (dt, *J*= 15.5, 6.7 Hz, 1H), 2.93-2.84 (m, 2H), 2.36-2.21 (m, 2H), 2.14-2.06 (m, 1H), 1.99-1.75 (m, 3H), 1.32 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 151.2, 143.3, 135.7, 134.6, 133.6, 131.1, 128.5, 127.2, 126.6, 126.4, 126.3, 125.8, 125.7, 125.6, 124.6, 123.9, 123.5, 122.8, 47.4, 41.0, 38.7, 30.4, 29.2, 26.9 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₄H₂₄Na 335.1770; Found 335.1783. **HPLC-Data:** (Chiralcel OJ-H column, $\lambda = 254$ nm, hexane/isopropanol = 70/30, flow rate = 0.7 mL/min): t_R= 9.4 (major), 11.3 (minor).

(*S*,*E*)-2-(4-(1-Methyl-2,3-dihydro-1H-inden-1-yl)but-1-en-1-yl)naphthalene (**3ai**)



The title compound **3ai** was isolated as a colorless oil (34 mg, 54%, 95% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1).

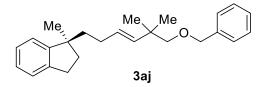
¹**H NMR (400 MHz, Chloroform-***d*) δ = 7.79-7.71 (m, 3H), 7.62 (s, 1H), 7.52 (dd, *J*= 8.5, 1.8 Hz, 1H), 7.45-7.36 (m, 2H), 7.22-7.13 (m, 4H), 6.50 (d, *J*= 15.8 Hz, 1H), 6.30 (dt, *J*= 15.8, 6.7 Hz, 1H), 2.94-2.86 (m, 2H), 2.27-2.06 (m, 3H), 1.93-1.72 (m, 3H), 1.30 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 151.1, 143.3, 135.4, 133.7, 132.7, 131.8, 129.6, 128.1, 127.8, 127.6, 126.4, 126.3, 126.1, 125.5, 125.3, 124.6, 123.6, 122.7, 47.4, 40.9, 38.7, 30.4, 28.9, 26.9 ppm.

HRMS (**ESI**) m/z: [M+Na]⁺ Calcd for C₂₄H₂₄Na 335.1770; Found 335.1783.

HPLC-Data: (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): t_R= 12.1 (major), 16.1 (minor).

(*S*,*E*)-1-(6-(*Benzyloxy*)-5,5-*dimethylhex-3-en-1-yl*)-1-*methyl*-2,3-*dihydro-1H-indene* (**3aj**)



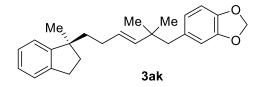
The title compound **3aj** was isolated as a colorless oil (36 mg, 51%, 95% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1).

¹**H NMR (400 MHz, Chloroform**-*d*) δ= 7.35-7.24 (m, 5H), 7.20-7.08 (m, 4H), 5.43 (d, *J*= 15.7 Hz, 1H), 5.35 (dt, *J*= 15.7, 5.9 Hz, 1H), 4.50 (s, 2H), 3.13 (s, 2H), 2.91-2.84 (m, 2H), 2.09-1.97 (m, 2H), 1.97-1.79 (m, 2H), 1.70-1.62 (m, 1H), 1.60-1.54 (m, 1H), 1.25 (s, 3H), 0.98 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 151.4, 143.2, 138.9, 137.3, 128.2 (2C), 127.5, 127.33 (2C), 127.30, 126.2, 126.1, 124.5, 122.7, 79.6, 73.2, 47.3, 41.3, 38.6, 37.2, 30.3, 28.4, 26.8, 24.8 (2C) ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₅H₃₂ONa 371.2345; Found 371.2340. **HPLC-Data:** (Chiralcel OJ-H column, $\lambda = 254$ nm, hexane/isopropanol = 70/30, flow rate = 0.7 mL/min): t_R= 5.5 (minor), 9.9 (major).

(*S*,*E*)-5-(2,2-*Dimethyl*-6-(1-*methyl*-2,3-*dihydro*-1*H*-*inden*-1-*yl*)*hex*-3-*en*-1-*yl*)*benzo*[*d*][1,3]*dioxole* (**3ak**)



Following the Standard Procedure B, The title compound **3ak** was isolated as a colorless oil (45 mg, 62%, 95% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1).

Following the Standard Procedure D, the title compound **3ak** was isolated as a colorless oil (37 mg, 51%, 94% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1).

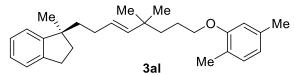
¹**H NMR (400 MHz, Chloroform-***d*) δ = 7.20-7.10 (m, 4H), 6.69 (s, 1H), 6.57 (s, 1H), 6.51 (dd, *J*= 7.9, 1.7 Hz, 1H), 5.91-5.87 (m, 2H), 5.37 (dt, *J*= 15.5, 1.4 Hz, 1H), 5.16 (dt, *J*= 15.7, 6.6 Hz, 1H), 2.91-2.85 (m, 2H), 2.43 (s, 2H), 2.06-1.98 (m, 2H), 1.92-1.81 (m, 2H), 1.66-1.60 (m, 1H), 1.58-1.52 (m, 1H), 1.24 (s, 3H), 0.92 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 151.4, 146.7, 145.6, 143.2, 139.4, 132.9, 126.7, 126.2, 126.1, 124.5, 123.4, 122.7, 111.1, 107.4, 100.6, 49.3, 47.3, 41.5, 38.5, 36.8, 30.3, 28.4, 27.1 (2C), 26.8 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₅H₃₀O₂Na 385.2143; Found 385.2147.

HPLC-Data: (Chiralcel OJ-H column, $\lambda = 254$ nm, hexane/isopropanol = 70/30, flow rate = 0.7 mL/min): t_R= 6.1 (minor), 8.8 (major).

(*S*,*E*)-1-(8-(2,5-*Dimethylphenoxy*)-5,5-*dimethyloct-3-en-1-yl*)-1-*methyl*-2,3-*dihydro-1H-indene* (**3al**)



The title compound **3al** was isolated as a colorless oil (45 mg, 58%, 96% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1).

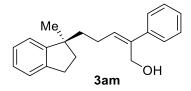
¹**H NMR (400 MHz, Chloroform-***d***)** δ = 7.22-7.07 (m, 4H), 6.99 (d, *J*= 7.5 Hz, 1H), 6.64 (d, *J*= 7.2 Hz, 1H), 6.60 (s, 1H), 5.34 (d, *J*= 15.6 Hz, 1H), 5.28 (dt, *J*= 15.6, 5.7 Hz, 1H), 3.87 (t, *J*= 6.5 Hz, 2H), 2.91-2.85 (m, 2H), 2.30 (s, 3H), 2.17 (s, 3H), 2.06-1.90 (m, 3H), 1.88-1.80 (m, 1H), 1.70-1.53 (m, 4H), 1.42-1.36 (m, 2H), 1.25 (s, 3H), 0.96 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 157.1, 151.4, 143.2, 139.5, 136.4, 130.2, 126.6, 126.2, 126.1, 124.5, 123.6, 122.7, 120.5, 111.9, 68.5, 47.3, 41.6, 39.3, 38.6, 35.4, 30.3, 28.4, 27.5, 27.4, 26.8, 24.9, 21.5, 15.8 ppm.

HRMS (**ESI**) m/z: [M+H]⁺ Calcd for C₂₈H₃₉O 391.2995; Found 391.2994.

HPLC-Data: (Chiralcel OJ-H column, $\lambda = 254$ nm, hexane/isopropanol = 96/4, flow rate = 0.4 mL/min): t_R= 9.5 (minor), 10.9 (major).

(S,Z)-5-(1-Methyl-2,3-dihydro-1H-inden-1-yl)-2-phenylpent-2-en-1-ol (3am)



The title compound **3am** was isolated as a colorless oil (47 mg, 81%, 98% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

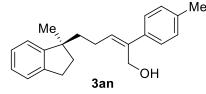
¹**H NMR (400 MHz, Chloroform-***d*) δ= 7.42-7.35 (m, 2H), 7.35-7.27 (m, 2H), 7.27-7.19 (m, 2H), 7.23-7.14 (m, 2H), 7.17-7.11 (m, 1H), 5.83 (t, *J*= 7.5 Hz, 1H), 4.49 (s, 2H), 2.94-2.87 (m, 2H), 2.32-2.16 (m, 2H), 2.11-2.05 (m, 1H), 1.93-1.86 (m, 1H), 1.79-1.64 (m, 2H), 1.45-1.37 (brs, 1H), 1.29 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ= 150.9, 143.2, 140.9, 138.5, 132.7, 128.5 (2C), 127.1, 126.5, 126.32, 126.29 (2C), 124.7, 122.6, 59.7, 47.5, 41.5, 38.5, 30.3, 27.0, 24.3 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₂₄ONa 315.1725; Found 315.1730.

HPLC-Data: (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): t_R= 17.9 (minor), 20.1 (major).

S,Z)-5-(1-Methyl-2,3-dihydro-1H-inden-1-yl)-2-(p-tolyl)pent-2-en-1-ol (3an)



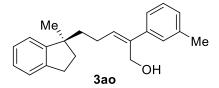
The title compound **3an** was isolated as a colorless oil (50 mg, 82%, 95% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹**H** NMR (500 MHz, Chloroform-*d*) δ = 7.28 (d, *J*= 8.2 Hz, 2H), 7.22-7.15 (m, 3H), 7.14-7.10 (m, 3H), 5.80 (t, *J*= 7.5 Hz, 1H), 4.48 (s, 2H), 2.94-2.85 (m, 2H), 2.33 (s, 3H), 2.30-2.24 (m, 1H), 2.19-2.04 (m, 2H), 1.88 (dt, *J*= 12.5, 7.6 Hz, 1H), 1.81-1.71 (m, 1H), 1.71-1.61 (m, 1H), 1.29 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 150.9, 143.2, 138.3, 137.9, 136.8, 131.8, 129.2 (2C), 126.4, 126.3, 126.1 (2C), 124.6, 122.6, 59.7, 47.4, 41.5, 38.5, 30.3, 26.9, 24.2, 21.1 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₂H₂₆ONa 329.1876; Found 329.1879. **HPLC-Data:** (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): t_R= 15.8 (minor), 17.1 (major).

(S,Z)-5-(1-Methyl-2,3-dihydro-1H-inden-1-yl)-2-(m-tolyl)pent-2-en-1-ol (3ao)



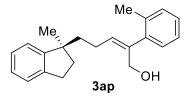
The title compound **3ao** was isolated as a colorless oil (46 mg, 76%, 94% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹**H NMR (500 MHz, Chloroform-***d*) δ = 7.22-7.10 (m, 7H), 7.08-7.04 (m, 1H), 5.81 (t, *J*= 7.5 Hz, 1H), 4.48 (s, 2H), 2.94-2.86 (m, 2H), 2.34 (s, 3H), 2.30-2.22 (m, 1H), 2.19-2.14 (m, 1H), 2.08 (dt, *J*= 12.5, 7.0 Hz, 1H), 1.88 (dt, *J*= 12.6, 7.6 Hz, 1H), 1.81-1.71 (m, 1H), 1.71-1.64 (m, 1H), 1.29 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ= 150.9, 143.2, 140.8, 138.6, 138.1, 132.5, 128.4, 127.9, 127.1, 126.5, 126.3, 124.7, 123.4, 122.6, 59.8, 47.4, 41.5, 38.5, 30.4, 26.9, 24.2, 21.6 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₂H₂₆ONa 329.1876; Found 329.1882. **HPLC-Data:** (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): t_R= 15.0 (minor), 16.0 (major).

(S,Z)-5-(1-Methyl-2,3-dihydro-1H-inden-1-yl)-2-(o-tolyl)pent-2-en-1-ol (3ap)



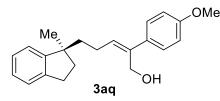
The title compound **3ap** was isolated as a colorless oil (29 mg, 47%, 97% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹**H NMR** (**400 MHz**, **Chloroform**-*d*) δ = 7.23-7.05 (m, 8H), 5.42 (t, *J*= 7.5 Hz, 1H), 4.36 (s, 2H), 2.95-2.88 (m, 2H), 2.26 (s, 3H), 2.18-2.04 (m, 3H), 1.89 (dt, *J*= 12.7, 7.7 Hz, 1H), 1.79-1.62 (m, 2H), 1.29 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 150.9, 143.2, 141.2, 139.1, 135.9, 132.9, 130.2, 129.3, 127.1, 126.4, 126.3, 125.6, 124.6, 122.6, 61.1, 47.4, 41.4, 38.5, 30.3, 26.9, 23.8, 20.0 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₂H₂₆ONa 329.1876; Found 329.1881. **HPLC-Data:** (Chiralpak AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 96/4, flow rate = 0.5 mL/min): t_R= 19.6 (major), 20.8 (minor).

(S,Z)-2-(4-Methoxyphenyl)-5-(1-methyl-2,3-dihydro-1H-inden-1-yl)pent-2-en-1-ol (**3aq**)



The title compound **3aq** was isolated as a colorless oil (46 mg, 71%, 97% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (4:1).

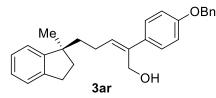
¹**H NMR** (**500 MHz**, **Chloroform**-*d*) δ = 7.33 (d, *J*= 8.8 Hz, 2H), 7.24-7.10 (m, 4H), 6.86 (d, *J*= 8.8 Hz, 2H), 5.76 (t, *J*= 7.5 Hz, 1H), 4.47 (s, 2H), 3.80 (s, 3H), 2.95-2.86 (m, 2H), 2.30-2.23 (m, 1H), 2.19-2.13 (m, 1H), 2.11-2.06 (m, 1H), 1.88 (dt, *J*= 12.6, 7.6 Hz, 1H), 1.81-1.71 (m, 1H), 1.70-1.65 (m, 1H), 1.29 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 158.8, 150.9, 143.2, 137.8, 133.2, 131.1, 127.4 (2C), 126.4, 126.3, 124.6, 122.6, 113.9 (2C), 59.7, 55.3, 47.4, 41.6, 38.5, 30.3, 26.9, 24.2 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₂H₂₆O₂Na 345.1825; Found 345.1827. **HPLC-Data:** (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate

= 0.6 mL/min): t_R= 26.2 (major), 29.4 (minor).

(*S*,*Z*)-2-(4-(*Benzyloxy*)*phenyl*)-5-(1-*methyl*-2,3-*dihydro*-1*H*-*inden*-1-*yl*)*pent*-2-*en*-1-*ol* (**3ar**)



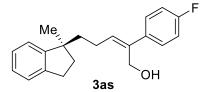
The title compound **3ar** was isolated as a colorless oil (57 mg, 72%, 96% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (4:1). ¹H NMR (400 MHz, Chloroform-*d*) δ = 7.44-7.35 (m, 4H), 7.34-7.30 (m, 3H), 7.22-7.11 (m, 4H), 6.92 (d, *J*= 8.7 Hz, 2H), 5.75 (t, *J*= 7.5 Hz, 1H), 5.05 (s, 2H), 4.46 (s, 2H), 2.94-2.88 (m, 2H), 2.29-2.03 (m, 3H), 1.88 (dt, *J*= 12.6, 7.6 Hz, 1H), 1.80-1.64 (m, 2H), 1.29 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 158.1, 150.9, 143.2, 137.8, 137.0, 133.5, 131.2, 128.6 (2C), 128.0, 127.5 (2C), 127.4 (2C), 126.5, 126.3, 124.7, 122.7, 114.9 (2C), 70.1, 59.7, 47.4, 41.6, 38.5, 30.4, 27.0, 24.2 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₈H₃₀O₂Na 421.2138; Found 421.2146.

HPLC-Data: (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): t_R= 24.6 (major), 27.6 (minor).

(S,Z)-2-(4-Fluorophenyl)-5-(1-methyl-2,3-dihydro-1H-inden-1-yl)pent-2-en-1-ol (3as)



The title compound **3as** was isolated as a colorless oil (46 mg, 74%, 98% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹**H** NMR (400 MHz, Chloroform-*d*) δ = 7.39-7.31 (m, 2H), 7.24-7.09 (m, 4H), 7.04-6.95 (m, 2H), 5.78 (t, *J*= 7.5 Hz, 1H), 4.46 (s, 2H), 2.95-2.85 (m, 2H), 2.31-2.12 (m, 2H), 2.14-2.02 (m, 1H), 1.92-1.84 (m, 1H), 1.81-1.64 (m, 2H), 1.47-1.37 (brs, 1H), 1.29 (s, 3H) ppm.

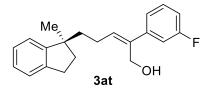
¹³C NMR (126 MHz, Chloroform-*d*) δ= 162.1 (d, *J*= 246.1 Hz), 150.8, 143.2, 137.5, 137.0, 132.7, 127.9 (d, *J*= 7.5 Hz, 2C), 126.5, 126.3, 124.7, 122.6, 115.3 (d, *J*= 21.2 Hz, 2C), 59.8, 47.4, 41.5, 38.5, 30.3, 27.0, 24.2 ppm.

¹⁹**F NMR (376 MHz, Chloroform-d)** δ= -115.81 (s, 1F) ppm.

HRMS (**ESI**) m/z: [M+Na]⁺ Calcd for C₂₁H₂₃FONa 333.1625; Found 333.1610.

HPLC-Data: (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): t_R= 15.3 (minor), 16.3 (major).

(S,Z)-2-(3-Fluorophenyl)-5-(1-methyl-2,3-dihydro-1H-inden-1-yl)pent-2-en-1-ol (3at)



The title compound **3at** was isolated as a colorless oil (43 mg, 69%, 97% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

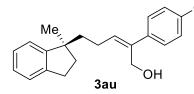
¹**H** NMR (500 MHz, Chloroform-*d*) δ = 7.30-7.26 (m, 1H), 7.22-7.09 (m, 6H), 6.97-6.90 (m, 1H), 5.87 (t, *J*= 7.5 Hz, 1H), 4.47 (s, 2H), 2.95-2.87 (m, 2H), 2.32-2.23 (m, 1H), 2.21-2.14 (m, 1H), 2.08 (dt, *J*= 12.6, 7.0 Hz, 1H), 1.89 (dt, *J*= 12.6, 7.6 Hz, 1H), 1.82-1.72 (m, 1H), 1.73-1.63 (m, 1H), 1.29 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 163.0 (d, *J*= 244.7 Hz), 150.7, 143.3 (d, *J*= 7.5 Hz), 143.2, 137.5, 133.8, 129.8 (d, *J*= 8.4 Hz), 126.5, 126.3, 124.7, 122.6, 121.8 (d,

J= 2.8 Hz), 113.8 (d, *J*= 21.2 Hz), 113.2 (d, *J*= 21.8 Hz), 59.6, 47.4, 41.4, 38.5, 30.3, 27.0, 24.3 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₁H₂₃FONa 333.1625; Found 333.1615. **HPLC-Data:** (Chiralpak AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 96/4, flow rate = 0.5 mL/min): t_R= 32.4 (major), 34.5 (minor).

(S,Z)-2-(4-Chlorophenyl)-5-(1-methyl-2,3-dihydro-1H-inden-1-yl)pent-2-en-1-ol (3au)



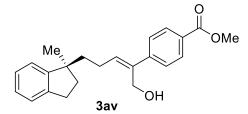
The title compound **3au** was isolated as a colorless oil (42 mg, 65%, 97% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹**H** NMR (500 MHz, Chloroform-*d*) δ = 7.32 (d, *J*= 8.6 Hz, 2H), 7.27 (d, *J*= 8.7 Hz, 2H), 7.22-7.11 (m, 4H), 5.83 (t, *J*= 7.5 Hz, 1H), 4.46 (s, 2H), 2.94-2.86 (m, 2H), 2.32-2.23 (m, 1H), 2.20-2.14 (m, 1H), 2.08 (dt, *J*= 12.6, 7.0 Hz, 1H), 1.89 (dt, *J*= 12.7, 7.6 Hz, 1H), 1.81-1.72 (m, 1H), 1.72-1.65 (m, 1H), 1.29 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ= 150.8, 143.2, 139.4, 137.4, 133.3, 132.8, 128.6 (2C), 127.6 (2C), 126.5, 126.3, 124.7, 122.6, 59.6, 47.4, 41.4, 38.5, 30.3, 27.0, 24.3 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₁H₂₃ClONa 349.1330; Found 349.1321. **HPLC-Data:** (Chiralpak AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 93/7, flow rate = 0.5 mL/min): t_R= 29.2 (major), 32.4 (minor).

Methyl (*S*,*Z*)-4-(1-Hydroxy-5-(1-methyl-2,3-dihydro-1H-inden-1-yl)pent-2-en-2-yl)benzoate (**3av**)



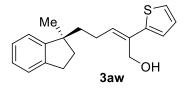
The title compound **3av** was isolated as a colorless oil (38 mg, 54%, 98% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (3:1).

¹**H** NMR (500 MHz, Chloroform-*d*) δ = 7.97 (d, *J*= 8.4 Hz, 2H), 7.46 (d, *J*= 8.5 Hz, 2H), 7.24-7.11 (m, 4H), 5.96 (t, *J*= 7.5 Hz, 1H), 4.51 (s, 2H), 3.90 (s, 3H), 2.96-2.88 (m, 2H), 2.35-2.27 (m, 1H), 2.24-2.17 (m, 1H), 2.08 (dt, *J*= 12.6, 7.0 Hz, 1H), 1.90 (dt, *J*= 12.6, 7.6 Hz, 1H), 1.83-1.73 (m, 1H), 1.75-1.66 (m, 1H), 1.30 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ= 166.9, 150.7, 145.6, 143.2, 137.8, 134.8, 129.8 (2C), 128.6, 126.5, 126.3, 126.1 (2C), 124.7, 122.6, 59.5, 52.0, 47.4, 41.3, 38.5, 30.3, 27.0, 24.4 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₃H₂₆O₃Na 373.1774; Found 373.1772. **HPLC-Data:** (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 88/12, flow rate = 0.5 mL/min): t_R= 20.3 (major), 23.9 (minor).

(S,E)-5-(1-Methyl-2,3-dihydro-1H-inden-1-yl)-2-(thiophen-2-yl)pent-2-en-1-ol (**3aw**)

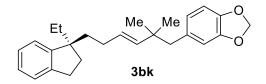


The title compound **3aw** was isolated as a colorless oil (35 mg, 58%, 96% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹**H NMR (500 MHz, Chloroform-***d*) δ = 7.29-7.23 (m, 2H), 7.24-7.10 (m, 5H), 5.96 (t, *J*= 7.6 Hz, 1H), 4.45 (s, 2H), 2.94-2.85 (m, 2H), 2.32-2.22 (m, 1H), 2.21-2.13 (m, 1H), 2.08 (dt, *J*= 12.6, 7.0 Hz, 1H), 1.88 (dt, *J*= 12.6, 7.6 Hz, 1H), 1.81-1.70 (m, 1H), 1.71-1.61 (m, 1H), 1.29 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 150.8, 143.2, 141.9, 133.4, 131.4, 126.5, 126.3, 125.7, 125.6, 124.7, 122.6, 119.8, 59.8, 47.4, 41.5, 38.5, 30.3, 26.9, 23.9 ppm. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₉H₂₂OSNa 321.1284; Found 321.1284. HPLC-Data: (Chiralpak IB column, λ = 254 nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): t_R= 26.2 (minor), 30.4 (major).

(*S*,*E*)-5-(6-(1-*E*thyl-2,3-dihydro-1*H*-inden-1-yl)-2,2-dimethylhex-3-en-1yl)benzo[d][1,3]dioxole (**3bk**)



The title compound **3bk** was isolated as a colorless oil (48 mg, 64%, 91% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1).

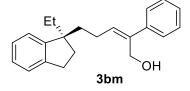
¹**H NMR (400 MHz, Chloroform-***d*) δ= 7.21-7.13 (m, 3H), 7.08-7.04 (m, 1H), 6.68 (d, *J*= 7.9 Hz, 1H), 6.57 (d, *J*= 1.7 Hz, 1H), 6.51 (dd, *J*= 7.9, 1.7 Hz, 1H), 5.91-5.87 (m, 2H), 5.35 (d, *J*= 15.6 Hz, 1H), 5.14 (dt, *J*= 15.6, 6.6 Hz, 1H), 2.90-2.84 (m, 2H), 2.43 (s, 2H), 1.99-1.90 (m, 3H), 1.88-1.76 (m, 1H), 1.71-1.63 (m, 2H), 1.59-1.52 (m, 2H), 0.92 (s, 6H), 0.79 (t, *J*= 7.4 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 149.6, 146.7, 145.6, 143.9, 139.4, 132.9, 126.8, 126.2, 125.8, 124.5, 123.5, 123.4, 111.1, 107.4, 100.7, 51.1, 49.3, 39.1, 36.8, 35.9, 31.8, 30.6, 27.9, 27.1 (2C), 8.9 ppm.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₆H₃₃O₂ 377.2475; Found 377.2474.

HPLC-Data: (Chiralcel OJ-H column, $\lambda = 254$ nm, hexane/isopropanol = 85/15, flow rate = 0.7 mL/min): t_R= 5.9 (minor), 7.3 (major).

(S,Z)-5-(1-Ethyl-2,3-dihydro-1H-inden-1-yl)-2-phenylpent-2-en-1-ol (**3bm**)



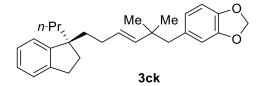
The title compound **3bm** was isolated as a colorless oil (47 mg, 76%, 97% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹**H** NMR (500 MHz, Chloroform-*d*) δ = 7.39 (d, *J*= 7.4 Hz, 2H), 7.31 (t, *J*= 7.6 Hz, 2H), 7.27-7.13 (m, 4H), 7.12-7.06 (m, 1H), 5.83 (t, *J*= 7.5 Hz, 1H), 4.47 (s, 2H), 2.95-2.88 (m, 2H), 2.27-2.17 (m, 1H), 2.16-2.06 (m, 1H), 1.99 (t, *J*= 7.5 Hz, 2H), 1.85-1.66 (m, 3H), 1.66-1.57 (m, 1H), 0.81 (t, *J*= 7.4 Hz, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ= 149.1, 143.9, 140.9, 138.4, 132.8, 128.5 (2C), 127.1, 126.5, 126.3 (2C), 126.0, 124.6, 123.5, 59.7, 51.3, 39.2, 35.7, 32.0, 30.6, 23.8, 8.9 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₂H₂₆ONa 329.1876; Found 329.1886. **HPLC-Data:** (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 98/2, flow rate = 0.5 mL/min): t_R= 12.8 (minor), 13.4 (major).

(*S*,*E*)-5-(2,2-*Dimethyl*-6-(1-*propyl*-2,3-*dihydro*-1*H*-*inden*-1-*yl*)*hex*-3-*en*-1-*yl*)*benzo*[*d*][1,3]*dioxole* (**3ck**)



The title compound **3ck** was isolated as a colorless oil (59 mg, 76%, 96% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1).

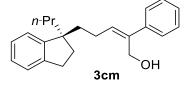
¹**H NMR (400 MHz, Chloroform-***d*) δ= 7.20-7.10 (m, 3H), 7.11-7.04 (m, 1H), 6.68 (d, *J*= 8.0 Hz, 1H), 6.57 (d, *J*= 1.6 Hz, 1H), 6.51 (dd, *J*= 7.9, 1.6 Hz, 1H), 5.92-5.83 (m, 2H), 5.35 (d, *J*= 15.6 Hz, 1H), 5.14 (dt, *J*= 15.6, 6.6 Hz, 1H), 2.90-2.85 (m, 2H), 2.43 (s, 2H), 1.93 (t, *J*= 7.4 Hz, 2H), 1.89-1.75 (m, 1H), 1.69-1.59 (m, 2H), 1.58-1.41 (m, 3H), 1.34-1.14 (m, 2H), 0.92 (s, 6H), 0.86 (t, *J*= 7.3 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 149.9, 146.7, 145.6, 143.8, 139.3, 132.9, 126.8, 126.2, 125.8, 124.4, 123.5, 123.4, 111.1, 107.4, 100.6, 50.9, 49.3, 42.1, 39.6, 36.8, 36.4, 30.6, 27.9, 27.0 (2C), 17.7, 14.9 ppm.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₇H₃₅O₂ 391.2632; Found 391.2631.

HPLC-Data: (Chiralcel OJ-H column, $\lambda = 254$ nm, hexane/isopropanol = 96/4, flow rate = 0.4 mL/min): t_R= 10.8 (minor), 13.0 (major).

(S,Z)-2-Phenyl-5-(1-propyl-2,3-dihydro-1H-inden-1-yl)pent-2-en-1-ol (3cm)



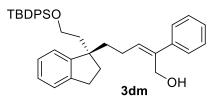
The title compound **3cm** was isolated as a colorless oil (49 mg, 76%, 96% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹**H NMR (400 MHz, Chloroform-***d***)** δ = 7.41-7.37 (m, 2H), 7.35-7.29 (m, 2H), 7.26-7.23 (m, 1H), 7.22-7.15 (m, 3H), 7.13-7.06 (m, 1H), 5.83 (t, *J*= 7.5 Hz, 1H), 4.47 (s, 2H), 2.92-2.86 (m, 2H), 2.27-2.09 (m, 2H), 2.00 (t, *J*= 7.5 Hz, 2H), 1.86-1.74 (m, 1H), 1.72-1.62 (m, 2H), 1.59-1.46 (m, 1H), 1.35-1.26 (m, 1H), 1.21-1.13 (m, 1H), 0.87 (t, *J*= 7.2 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 149.4, 143.8, 140.8, 138.4, 132.8, 128.5 (2C), 127.1, 126.4, 126.3 (2C), 126.0, 124.6, 123.4, 59.7, 51.1, 42.3, 39.6, 36.2, 30.7, 23.8, 17.8, 14.9 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₃H₂₈ONa 343.2032; Found 343.2042. **HPLC-Data:** (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 94/6, flow rate = 0.5 mL/min): t_R= 14.3 (minor), 15.1 (major).

(*S*,*Z*)-5-(1-(2-((tert-Butyldiphenylsilyl)oxy)ethyl)-2,3-dihydro-1H-inden-1-yl)-2-phenylpent-2-en-1-ol (**3dm**)



The title compound **3dm** was isolated as a colorless oil (69 mg, 62%, 94% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

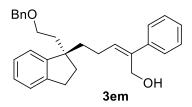
¹**H NMR (400 MHz, Chloroform-***d*) δ = 7.67-7.58 (m, 4H), 7.44-7.26 (m, 10H), 7.24-7.20 (m, 1H), 7.20-7.08 (m, 3H), 7.01-6.94 (m, 1H), 5.75 (t, *J*= 7.5 Hz, 1H), 4.41 (s, 2H), 3.73-3.60 (m, 2H), 2.90-2.80 (m, 2H), 3.03-2.77 (m, 6H), 2.18-1.86 (m, 1H), 1.79-1.58 (m, 1H), 1.02 (s, 9H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 148.7, 143.6, 140.8, 138.4, 135.6 (4C), 133.9 (2C), 132.6, 129.6 (2C), 128.5 (2C), 127.6 (4C), 127.0, 126.6, 126.2 (2C), 126.1, 124.7, 123.3, 61.2, 59.7, 49.8, 41.6, 39.9, 36.4, 30.5, 26.9 (3C), 23.7, 19.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₈H₄₄O₂SiNa 583.3003; Found 583.3013.

HPLC-Data: (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 86/14, flow rate = 0.7 mL/min): t_R= 6.9 (minor), 7.4 (major).

(*S*,*Z*)-5-(1-(2-Benzyloxy)ethyl)-2,3-dihydro-1H-inden-1-yl)-2-phenylpent-2-en-1-ol (**3em**)



The title compound **3em** was isolated as a colorless oil (42 mg, 51%, 95% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (4:1).

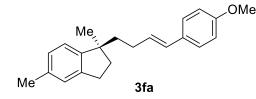
¹**H NMR (400 MHz, Chloroform-***d*) δ= 7.42-7.34 (m, 2H), 7.35-7.25 (m, 7H), 7.26-7.17 (m, 2H), 7.20-7.13 (m, 2H), 7.13-7.05 (m, 1H), 5.80 (t, *J*= 7.5 Hz, 1H), 4.44 (s, 2H), 4.43 (s, 2H), 3.53-3.41 (m, 2H), 2.93-2.86 (m, 2H), 2.29-2.15 (m, 2H), 2.11-1.97 (m, 4H), 1.90-1.77 (m, 1H), 1.74-1.65 (m, 1H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 148.7, 143.6, 140.9, 138.6, 138.4, 132.5, 128.5 (2C), 128.4 (2C), 127.7 (2C), 127.5, 127.0, 126.7, 126.23 (2C), 126.15, 124.7, 123.4, 73.1, 67.6, 59.7, 49.9, 39.9, 38.5, 36.7, 30.5, 23.8 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₉H₃₂O₂Na 435.2295; Found 435.2305.

HPLC-Data: (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 86/14, flow rate = 0.5 mL/min): t_R= 19.9 (major), 25.3 (minor).

(S,E)-1-(4-(4-Methoxyphenyl)but-3-en-1-yl)-1,5-dimethyl-2,3-dihydro-1H-indene (**3fa**)



The title compound **3fa** was isolated as a colorless oil (47 mg, 77%, 96% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1).

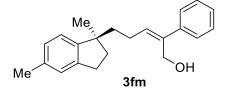
¹**H** NMR (400 MHz, Chloroform-*d*) δ = 7.22 (d, *J*= 8.7 Hz, 2H), 7.03-6.96 (m, 3H), 6.81 (d, *J*= 8.7 Hz, 2H), 6.28 (d, *J*= 15.9 Hz, 1H), 6.03 (dt, *J*= 15.8, 6.8 Hz, 1H), 3.78 (s, 3H), 2.90-2.84 (m, 2H), 2.32 (s, 3H), 2.19-2.03 (m, 3H), 1.85 (dt, *J*= 12.6, 7.7 Hz, 1H), 1.78-1.64 (m, 2H), 1.26 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ= 158.6, 148.4, 143.5, 135.9, 130.8, 129.2, 128.8, 127.0, 126.9 (2C), 125.3, 122.5, 113.9 (2C), 55.3, 46.9, 41.1, 38.9, 30.2, 28.7, 26.9, 21.3 ppm.

HRMS (**ESI**) m/z: [M+H]⁺ Calcd for C₂₂H₂₇O 307.2056; Found 307.2039.

HPLC-Data: (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 98/2, flow rate = 0.5 mL/min): t_R= 9.1 (major), 10.1 (minor).

(S,Z)-5-(1,5-Dimethyl-2,3-dihydro-1H-inden-1-yl)-2-phenylpent-2-en-1-ol (3fm)



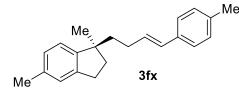
The title compound **3fm** was isolated as a colorless oil (51 mg, 83%, 97% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹**H** NMR (400 MHz, Chloroform-*d*) δ = 7.38 (d, *J*= 7.1 Hz, 2H), 7.31 (t, *J*= 7.5 Hz, 2H), 7.28-7.21 (m, 1H), 7.05-6.98 (m, 3H), 5.83 (t, *J*= 7.5 Hz, 1H), 4.50 (s, 2H), 2.90-2.85 (m, 2H), 2.32 (s, 3H), 2.27-2.04 (m, 3H), 1.87 (dt, *J*= 12.6, 7.6 Hz, 1H), 1.79-1.63 (m, 2H), 1.27 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 147.9, 143.4, 140.9, 138.4, 136.1, 132.8, 128.5 (2C), 127.11, 127.05, 126.3 (2C), 125.4, 122.4, 59.7, 47.1, 41.5, 38.7, 30.2, 27.1, 24.3, 21.3 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₂H₂₆ONa 329.1876; Found 329.1880. **HPLC-Data:** (Chiralcel OJ-H column, $\lambda = 254$ nm, hexane/isopropanol = 80/20, flow rate = 1.0 mL/min): t_R= 7.2 (major), 16.0 (minor).

(S,E)-1,5-Dimethyl-1-(4-(p-tolyl)but-3-en-1-yl)-2,3-dihydro-1H-indene (**3fx**)



The title compound **3fx** was isolated as a colorless oil (41 mg, 71%, 96% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1).

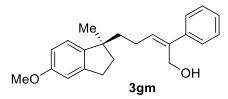
¹**H** NMR (400 MHz, Chloroform-*d*) δ = 7.19 (d, *J*= 8.1 Hz, 2H), 7.07 (d, *J*= 7.9 Hz, 2H), 7.04-6.99 (m, 3H), 6.31 (d, *J*= 15.9 Hz, 1H), 6.12 (dt, *J*= 15.8, 6.7 Hz, 1H), 2.91-2.86 (m, 2H), 2.32 (s, 3H), 2.31 (s, 3H), 2.20-2.02 (m, 3H), 1.86 (dt, *J*= 12.6, 7.7 Hz, 1H), 1.77-1.64 (m, 2H), 1.26 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ= 148.3, 143.5, 136.5, 135.9, 135.1, 130.3, 129.2 (2C), 129.2, 127.0, 125.8 (2C), 125.3, 122.5, 46.9, 41.0, 38.9, 30.2, 28.8, 26.9, 21.3, 21.2 ppm.

HRMS (**ESI**) m/z: [M+H]⁺ Calcd for C₂₂H₂₇ 291.2107; Found 291.2092.

HPLC-Data: (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 99/1, flow rate = 0.2 mL/min): t_R= 22.0 (minor), 23.3 (major).

(*S*,*Z*)-5-(5-*Methoxy*-1-*methy*l-2,3-*dihydro*-1*H*-*inden*-1-*y*l)-2-*pheny*l*pent*-2-*en*-1-*o*l (**3gm**)



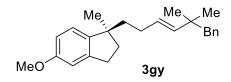
The title compound **3gm** was isolated as a colorless oil (51 mg, 79%, 96% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹**H NMR (400 MHz, Chloroform-***d***)** δ = 7.45-7.37 (m, 2H), 7.34-7.28 (m, 2H), 7.28-7.19 (m, 1H), 7.02 (d, *J*= 8.1 Hz, 1H), 6.78-6.70 (m, 2H), 5.83 (t, *J*= 7.5 Hz, 1H), 4.50 (s, 2H), 3.78 (s, 3H), 2.91-2.87 (m, 2H), 2.30-2.15 (m, 2H), 2.08 (dt, *J*= 12.6, 7.0 Hz, 1H), 1.89 (dt, *J*= 12.7, 7.6 Hz, 1H), 1.79-1.70 (m, 1H), 1.67-1.61 (m, 1H), 1.27 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 158.8, 144.7, 143.1, 140.9, 138.4, 132.8, 128.5 (2C), 127.1, 126.3 (2C), 123.1, 112.2, 109.9, 59.7, 55.4, 46.7, 41.7, 38.9, 30.5, 27.2, 24.3 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₂H₂₆O₂Na 345.1825; Found 345.1826. **HPLC-Data:** (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 86/14, flow rate = 0.5 mL/min): t_R= 12.1 (minor), 16.9 (major).

(*S*,*E*)-1-(5,5-*Dimethyl*-6-*phenylhex*-3-*en*-1-*yl*)-5-*methoxy*-1-*methyl*-2,3-*dihydro*-1*H*-*indene* (**3gy**)



The title compound **3gy** was isolated as a colorless oil (43 mg, 62%, 96% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1).

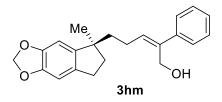
¹**H NMR (400 MHz, Chloroform**-*d*) δ= 7.24-7.17 (m, 3H), 7.09-7.05 (m, 2H), 6.99 (d, *J*= 8.1 Hz, 1H), 6.76-6.71 (m, 2H), 5.40 (d, *J*= 15.6 Hz, 1H), 5.16 (dt, *J*= 15.6, 6.6 Hz, 1H), 3.78 (s, 3H), 2.90-2.86 (m, 2H), 2.51 (s, 2H), 2.05-1.96 (m, 2H), 1.91-1.81 (m, 2H), 1.61-1.46 (m, 2H), 1.22 (s, 3H), 0.93 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 158.6, 144.7, 143.6, 139.5, 139.1, 130.7 (2C), 127.4 (2C), 126.6, 125.8, 123.2, 112.1, 109.8, 55.4, 49.6, 46.6, 41.7, 38.9, 36.7, 30.5, 28.4, 27.1 (3C) ppm.

HRMS (**ESI**) m/z: [M+H]⁺ Calcd for C₂₅H₃₃O 349.2526; Found 349.2523.

HPLC-Data: (Chiralcel OJ-H column, $\lambda = 254$ nm, hexane/isopropanol = 70/30, flow rate = 0.7 mL/min): t_R= 6.3 (minor), 8.6 (major).

(*S*,*Z*)-5-(5-*Methyl*-6,7-*dihydro*-5*H*-*indeno*[5,6-*d*][1,3]*dioxo*l-5-*y*l)-2-*phenylpent*-2-*en*-*1-ol* (**3hm**)



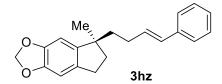
The title compound **3hm** was isolated as a colorless oil (47 mg, 70%, 94% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹**H NMR (400 MHz, Chloroform-***d*) δ= 7.44-7.38 (m, 2H), 7.36-7.29 (m, 3H), 6.66 (s, 1H), 6.59 (s, 1H), 5.90 (s, 2H), 5.83 (t, *J*= 7.5 Hz, 1H), 4.52 (s, 2H), 2.86-2.80 (m, 2H), 2.32-2.23 (m, 1H), 2.20-2.05 (m, 2H), 1.89 (dt, *J*= 12.6, 7.6 Hz, 1H), 1.73-1.59 (m, 2H), 1.24 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 146.49, 146.47, 143.8, 140.8, 138.5, 135.7, 132.7, 128.5 (2C), 127.1, 126.3 (2C), 105.1, 103.3, 100.9, 59.7, 47.2, 41.7, 38.9, 30.3, 27.3, 24.2 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₂H₂₄O₃Na 359.1618; Found 359.1622. **HPLC-Data:** (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): t_R= 18.2 (minor), 19.2 (major).

(*S*,*E*)-5-*Methyl*-5-(4-*phenylbut*-3-*en*-1-*yl*)-6,7-*dihydro*-5*H*-*indeno*[5,6-*d*][1,3]*dioxole* (**3hz**)



Starting from **2z**, the title compound **3hz** was isolated as a colorless oil (40 mg, 66%, 93% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1).

Starting from **2z'**, The title compound **3hz** was isolated as a colorless oil (36 mg, 59%, 94% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1).

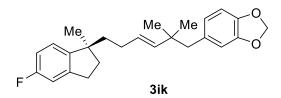
¹**H NMR (400 MHz, Chloroform-***d***)** δ = 7.34-7.24 (m, 4H), 7.19-7.15 (m, 1H), 6.66 (s, 1H), 6.60 (s, 1H), 6.34 (d, *J*= 16.0 Hz, 1H), 6.17 (dt, *J*= 15.8, 6.7 Hz, 1H), 5.90 (s, 2H), 2.85-2.76 (m, 2H), 2.23-2.16 (m, 1H), 2.12-2.05 (m, 2H), 1.88 (dt, *J*= 12.7, 7.7 Hz, 1H), 1.77-1.63 (m, 2H), 1.24 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 146.42, 146.38, 144.1, 137.9, 135.7, 131.2, 129.5, 128.5 (2C), 126.8, 125.9 (2C), 105.0, 103.4, 100.9, 47.2, 41.2, 39.0, 30.3, 28.7, 27.2 ppm.

HRMS (**ESI**) m/z: [M+H]⁺ Calcd for C₂₁H₂₃O₂ 307.1693; Found 307.1698.

HPLC-Data: (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 97/3, flow rate = 0.5 mL/min): t_R= 11.8 (minor), 12.2 (major).

(*S*,*E*)-5-(6-(5-Fluoro-1-methyl-2,3-dihydro-1H-inden-1-yl)-2,2-dimethylhex-3-en-1-yl)benzo[d][1,3]dioxole (**3ik**)



The title compound **3ik** was isolated as a colorless oil (31 mg, 41%, 95% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1).

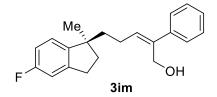
¹**H NMR (400 MHz, Chloroform-***d***)** δ = 7.01 (dd, *J*= 8.0, 5.3 Hz, 1H), 6.90-6.80 (m, 2H), 6.68 (d, *J*= 7.9 Hz, 1H), 6.56 (d, *J*= 1.7 Hz, 1H), 6.51 (dd, *J*= 7.9, 1.7 Hz, 1H), 5.89 (s, 2H), 5.37 (d, *J*= 15.6 Hz, 1H), 5.15 (dt, *J*= 15.5, 6.6 Hz, 1H), 2.90-2.80 (m, 2H), 2.43 (s, 2H), 2.10-1.92 (m, 2H), 1.92-1.79 (m, 2H), 1.64-1.46 (m, 2H), 1.22 (s, 3H), 0.92 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 161.9 (d, *J*= 242.2 Hz), 146.9 (d, *J*= 2.4 Hz), 146.7, 145.6, 145.3 (d, *J*= 7.8 Hz), 139.5, 132.9, 126.5, 123.5, 123.4, 112.9 (d, *J*= 22.2 Hz), 111.3 (d, *J*= 21.6 Hz), 111.1, 107.4, 100.7, 49.2, 46.7, 41.6, 38.8, 36.8, 30.3 (d, *J*= 2.1 Hz), 28.4, 27.03 (2C), 27.0 ppm.

¹⁹**F NMR (376 MHz, Chloroform-***d*) δ = -117.96 (s, 1F) ppm.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for C₂₅H₃₀FO₂ 381.2224; Found 381.2225. **HPLC-Data:** (Chiralcel OJ-H column, $\lambda = 254$ nm, hexane/isopropanol = 96/4, flow rate = 0.4 mL/min): t_R= 13.6 (minor), 17.6 (major).

(S,Z)-5-(5-Fluoro-1-methyl-2,3-dihydro-1H-inden-1-yl)-2-phenylpent-2-en-1-ol (3im)



The title compound **3im** was isolated as a colorless oil (39 mg, 63%, 92% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

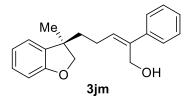
¹**H NMR (400 MHz, Chloroform-***d*) δ= 7.42-7.37 (m, 2H), 7.34-7.29 (m, 2H), 7.27-7.22 (m, 1H), 7.04 (dd, *J*= 8.1, 5.2 Hz, 1H), 6.92-6.81 (m, 2H), 5.83 (t, *J*= 7.5 Hz, 1H), 4.51 (s, 2H), 2.92-2.86 (m, 2H), 2.30-2.23 (m, 1H), 2.20-2.07 (m, 2H), 1.91 (dt, *J*= 12.7, 7.6 Hz, 1H), 1.81-1.68 (m, 1H), 1.71-1.58 (m, 1H), 1.27 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 162.1 (d, *J*= 242.5 Hz), 146.3 (d, *J*= 2.5 Hz), 145.3 (d, *J*= 7.9 Hz), 140.8, 138.6, 132.5, 128.5 (2C), 127.1, 126.3 (2C), 123.4 (d, *J*= 8.9 Hz), 113.1 (d, *J*= 22.4 Hz), 111.5 (d, *J*= 21.6 Hz), 59.7, 46.8, 41.6, 38.8, 30.3 (d, *J*= 2.2 Hz), 27.1, 24.2 ppm.

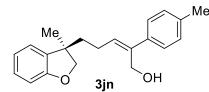
¹⁹**F** NMR (**376** MHz, Chloroform-d) δ = -117.57 (s, 1F) ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₁H₂₃FONa 333.1631; Found 333.1615. **HPLC-Data:** (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): t_R= 18.7 (minor), 22.8 (major).

(*R*,*Z*)-5-(3-Methyl-2,3-dihydrobenzofuran-3-yl)-2-phenylpent-2-en-1-ol (**3jm**)



The title compound **3jm** was isolated as a colorless oil (36 mg, 61%, 96% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1). ¹H NMR (400 MHz, Chloroform-*d*) δ = 7.40-7.36 (m, 2H), 7.34-7.29 (m, 2H), 7.27-7.23 (m, 1H), 7.18-7.07 (m, 2H), 6.90 (td, *J*= 7.4, 1.1 Hz, 1H), 6.80 (d, *J*= 8.0 Hz, 1H), 5.78 (t, *J*= 7.5 Hz, 1H), 4.47 (s, 2H), 4.44 (d, *J*= 8.8 Hz, 1H), 4.19 (d, *J*= 8.8 Hz, 1H), 2.35-2.27 (m, 1H), 2.15-2.05 (m, 1H), 1.84-1.73 (m, 2H), 1.39 (s, 3H) ppm. ¹³C NMR (126 MHz, Chloroform-*d*) δ = 159.6, 140.8, 138.9, 134.5, 131.8, 128.5 (2C), 128.3, 127.2, 126.3 (2C), 122.8, 120.7, 109.7, 82.2, 59.7, 45.3, 41.0, 25.8, 23.9 ppm. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₀H₂₂O₂Na 317.1512; Found 317.1511. HPLC-Data: (Chiralpak IB column, λ = 254 nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): t_R= 16.6 (minor), 20.3 (major). (*R*,*Z*)-5-(*3*-Methyl-2,3-dihydrobenzofuran-3-yl)-2-(*p*-tolyl)pent-2-en-1-ol (**3jn**)



The title compound **3jn** was isolated as a colorless oil (37 mg, 60%, 98% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (4:1).

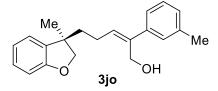
¹**H** NMR (500 MHz, Chloroform-*d*) δ = 7.27 (t, *J*= 6.9 Hz, 2H), 7.17-7.08 (m, 4H), 6.90 (t, *J*= 7.4 Hz, 1H), 6.80 (d, *J*= 8.0 Hz, 1H), 5.75 (t, *J*= 7.5 Hz, 1H), 4.45 (s, 2H), 4.43 (d, *J*= 8.7 Hz, 1H), 4.19 (d, *J*= 8.7 Hz, 1H), 2.33 (s, 3H), 2.33-2.24 (m, 1H), 2.13-2.02 (m, 1H), 1.81-1.73 (m, 2H), 1.39 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ= 159.6, 138.8, 137.8, 136.9, 134.5, 130.9, 129.2 (2C), 128.3, 126.2 (2C), 122.8, 120.7, 109.7, 82.2, 59.7, 45.3, 41.1, 25.8, 23.9, 21.1 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₂₄O₂Na 331.1669; Found 331.1673.

HPLC-Data: (Chiralpak AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 20/80, flow rate = 0.2 mL/min): t_R= 34.2 (minor), 35.5 (major).

(R,Z)-5-(3-Methyl-2,3-dihydrobenzofuran-3-yl)-2-(m-tolyl)pent-2-en-1-ol (**3jo**)



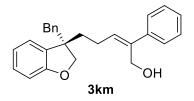
The title compound **3jo** was isolated as a colorless oil (41 mg, 67%, 98% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (4:1).

¹**H** NMR (400 MHz, Chloroform-*d*) δ = 7.23-7.10 (m, 5H), 7.08-7.04 (m, 1H), 6.90 (td, *J*= 7.4, 1.0 Hz, 1H), 6.80 (d, *J*= 7.9 Hz, 1H), 5.76 (t, *J*= 7.5 Hz, 1H), 4.46 (s, 2H), 4.44 (d, *J*= 8.7 Hz, 1H), 4.19 (d, *J*= 8.8 Hz, 1H), 2.34 (s, 3H), 2.34-2.24 (m, 1H), 2.14-2.06 (m, 1H), 1.82-1.73 (m, 2H), 1.39 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 159.6, 140.7, 139.1, 138.1, 134.5, 131.5, 128.4, 128.3, 127.9, 127.1, 123.4, 122.8, 120.7, 109.7, 82.2, 59.7, 45.3, 41.0, 25.8, 23.9, 21.5 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₁H₂₄O₂Na 331.1669; Found 331.1671. **HPLC-Data:** (Chiralcel OJ-H column, $\lambda = 254$ nm, hexane/isopropanol = 60/40, flow rate = 0.7 mL/min): t_R= 10.5 (major), 17.6 (minor).

(S,Z)-5-(3-Benzyl-2,3-dihydrobenzofuran-3-yl)-2-phenylpent-2-en-1-ol (3km)



The title compound **3km** was isolated as a colorless oil (35 mg, 46%, 87% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (4:1).

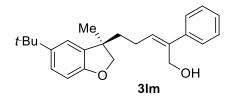
¹**H NMR (400 MHz, Chloroform-***d***)** δ = 7.40-7.36 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.21 (m, 4H), 7.15 (td, *J*= 7.7, 1.4 Hz, 1H), 7.03-6.96 (m, 3H), 6.90 (t, *J*= 7.4 Hz, 1H), 6.76 (d, *J*= 8.1 Hz, 1H), 5.77 (t, *J*= 7.5 Hz, 1H), 4.50 (d, *J*= 9.0 Hz, 1H), 4.43 (s, 2H), 4.31 (d, *J*= 9.0 Hz, 1H), 3.04 (d, *J*= 13.5 Hz, 1H), 2.98 (d, *J*= 13.5 Hz, 1H), 2.35-2.26 (m, 1H), 2.15-2.05 (m, 1H), 1.90-1.80 (m, 2H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 160.1, 140.7, 138.9, 137.1, 132.3, 131.6, 130.3 (2C), 128.53, 128.5 (2C), 128.1 (2C), 127.2, 126.6, 126.3 (2C), 123.8, 120.4, 109.7, 79.5, 59.7, 49.9, 45.5, 38.1, 23.8 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₆H₂₆O₂Na 393.1825; Found 393.1827.

HPLC-Data: (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 86/14, flow rate = 0.7 mL/min): t_R= 12.7 (minor), 15.0 (major).

(R,Z)-5-(5-(tert-Butyl)-3-methyl-2,3-dihydrobenzofuran-3-yl)-2-phenylpent-2-en-1-ol (**3lm**)



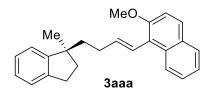
The title compound **3lm** was isolated as a colorless oil (46 mg, 65%, 98% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹**H NMR (400 MHz, Chloroform-***d***)** δ = 7.41-7.34 (m, 2H), 7.35-7.27 (m, 2H), 7.27-7.19 (m, 1H), 7.17-7.10 (m, 2H), 6.72 (d, *J*= 8.3 Hz, 1H), 5.78 (t, *J*= 7.5 Hz, 1H), 4.47 (s, 2H), 4.43 (d, *J*= 8.7 Hz, 1H), 4.18 (d, *J*= 8.7 Hz, 1H), 2.35-2.27 (m, 1H), 2.17-2.10 (m, 1H), 1.82-1.73 (m, 2H), 1.40 (s, 3H), 1.30 (s, 9H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 157.3, 143.8, 140.8, 138.9, 134.1, 131.8, 128.5 (2C), 127.1, 126.3 (2C), 125.0, 119.5, 108.8, 82.4, 59.6, 45.5, 41.1, 34.4, 31.8 (3C), 25.7, 24.0 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₄H₃₀O₂Na 373.2138; Found 373.2141. **HPLC-Data:** (Chiralcel OJ-H column, $\lambda = 254$ nm, hexane/isopropanol = 86/14, flow rate = 0.7 mL/min): t_R= 10.3 (minor), 12.6 (major).

(*S*,*E*)-2-*Methoxy*-1-(4-(1-*methyl*-2,3-*dihydro*-1*H*-*inden*-1-*yl*)*but*-1-*en*-1-*yl*)*naphthalene* (**3aaa**)

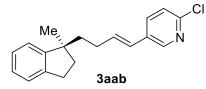


The title compound **3aaa** was isolated as a colorless oil (38 mg, 55%, 92% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1).

¹**H** NMR (400 MHz, Chloroform-*d*) δ = 8.13 (d, *J*= 8.7 Hz, 1H), 7.77-7.69 (m, 2H), 7.46-7.37 (m, 1H), 7.33-7.29 (m, 1H), 7.24-7.17 (m, 5H), 6.70 (d, *J*= 16.2 Hz, 1H), 6.15 (dt, *J*= 16.0, 6.7 Hz, 1H), 3.91 (s, 3H), 2.99-2.89 (m, 2H), 2.40-2.24 (m, 2H), 2.16-2.10 (m, 1H), 1.95-1.78 (m, 3H), 1.34 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 154.0, 151.3, 143.3, 137.7, 132.6, 129.3, 128.2, 128.1, 126.4, 126.23, 126.17, 124.6, 124.5, 123.4, 122.8, 122.3, 121.3, 113.3, 56.5, 47.4, 41.1, 38.8, 30.4, 29.8, 26.9 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₅H₂₆ONa 365.1881; Found 365.1866. **HPLC-Data:** (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 97/3, flow rate = 0.5 mL/min): t_R= 10.1 (minor), 10.5 (major). (*S*,*E*)-2-*Chloro-5-*(4-(1-*methyl*-2,3-*dihydro-1H-inden-1-yl*)*but-1-en-1-yl*)*pyridine* (**3aab**)



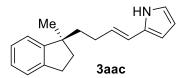
The title compound **3aab** was isolated as a colorless oil (29 mg, 49%, 70% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

¹**H NMR** (**400 MHz**, **Chloroform**-*d*) δ = 8.26 (d, *J*= 2.5 Hz, 1H), 7.57 (dd, *J*= 8.3, 2.5 Hz, 1H), 7.23-7.10 (m, 5H), 6.29 (d, *J*= 16.1 Hz, 1H), 6.27-6.18 (m, 1H), 2.95-2.86 (m, 2H), 2.28-2.18 (m, 1H), 2.17-2.11 (m, 1H), 2.09-2.03 (m, 1H), 1.88 (dt, *J*= 12.7, 7.7 Hz, 1H), 1.80-1.68 (m, 2H), 1.29 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 150.8, 149.2, 147.5, 143.2, 135.1, 134.6, 132.4, 126.5, 126.3, 124.7, 124.6, 123.9, 122.7, 47.3, 40.6, 38.6, 30.3, 28.9, 26.9 ppm. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₉H₂₁ClN 293.1363; Found 293.1360.

HPLC-Data: (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): t_R= 23.5 (major), 26.7 (minor).

(*S*,*E*)-2-(4-(1-Methyl-2,3-dihydro-1H-inden-1-yl)but-1-en-1-yl)-1H-pyrrole (**3aac**)



The title compound **3aac** was isolated as a colorless oil (26 mg, 52%, 96% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (3:1).

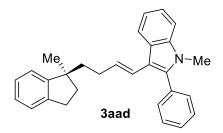
¹**H NMR (400 MHz, Chloroform**-*d*) δ= 8.08 (s, 1H), 7.22-7.03 (m, 4H), 6.72-6.66 (m, 1H), 6.21 (d, *J*= 16.0 Hz, 1H), 6.17-6.12 (m, 1H), 6.08 (s, 1H), 5.72 (dt, *J*= 16.1, 6.8 Hz, 1H), 2.95-2.85 (m, 2H), 2.18-2.03 (m, 3H), 1.86 (dt, *J*= 12.6, 7.6 Hz, 1H), 1.75-1.64 (m, 2H), 1.27 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 151.2, 143.2, 130.9, 126.3, 126.2, 126.1, 124.6, 122.7, 120.2, 117.7, 109.3, 106.7, 47.3, 41.2, 38.6, 30.3, 28.5, 26.9 ppm.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₈H₂₂N 252.1752; Found 252.1751.

HPLC-Data: (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): t_R= 18.9 (minor), 19.6 (major).

(S,E)-1-Methyl-3-(4-(1-methyl-2,3-dihydro-1H-inden-1-yl)but-1-en-1-yl)-2-phenyl-1H-indole (**3aad**)



The title compound **3aad** was isolated as a colorless oil (50 mg, 64%, 97% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1).

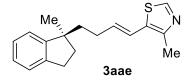
¹**H NMR** (**400 MHz**, **Chloroform**-*d*) δ = 7.92 (d, *J*= 7.9 Hz, 1H), 7.52-7.43 (m, 3H), 7.41-7.37 (m, 2H), 7.34 (d, *J*= 8.1 Hz, 1H), 7.28 (dd, *J*= 7.0, 1.2 Hz, 1H), 7.21-7.12 (m, 5H), 6.33 (d, *J*= 16.0 Hz, 1H), 6.16 (dt, *J*= 16.0, 6.8 Hz, 1H), 3.58 (s, 3H), 2.90-2.84 (m, 2H), 2.15-2.03 (m, 3H), 1.89-1.82 (m, 1H), 1.79-1.73 (m, 1H), 1.70-1.64 (m, 1H), 1.26 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 151.4, 143.2, 138.8, 137.7, 131.7, 131.1 (2C), 128.8, 128.4 (2C), 128.2, 126.23, 126.16, 125.8, 124.5, 122.8, 122.6, 122.1, 120.5, 120.1, 111.9, 109.5, 47.4, 41.7, 38.7, 30.9, 30.3, 29.8, 26.9 ppm.

HRMS (**ESI**) m/z: [M+H]⁺ Calcd for C₂₉H₃₀N 392.2378; Found 392.2380.

HPLC-Data: (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 97/3, flow rate = 0.5 mL/min): t_R= 9.6 (minor), 10.1 (major).

(*S*,*E*)-4-*Methyl*-5-(4-(1-*methyl*-2,3-*dihydro*-1*H*-*inden*-1-*yl*)*but*-1-*en*-1-*yl*)*thiazole* (**3aae**)



The title compound **3aae** was isolated as a colorless oil (35 mg, 61%, 93% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1).

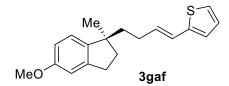
¹**H NMR (400 MHz, Chloroform-***d*) δ = 8.45 (s, 1H), 7.24-7.09 (m, 4H), 6.42 (d, *J*= 15.5 Hz, 1H), 5.93 (dt, *J*= 15.5, 6.9 Hz, 1H), 2.95-2.86 (m, 2H), 2.41 (s, 3H), 2.23-2.17 (m, 1H), 2.12-2.03 (m, 1H), 1.88 (dt, *J*= 12.6, 7.7 Hz, 1H), 1.77-1.67 (m, 3H), 1.29 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 150.9, 148.7, 148.5, 143.2, 134.5, 130.7, 126.4, 126.3, 124.6, 122.7, 119.4, 47.3, 40.8, 38.6, 30.3, 28.9, 26.9, 15.2 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₈H₂₁NSNa 306.1292; Found 306.1299.

HPLC-Data: (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): t_R= 10.6 (minor), 11.6 (major).

(*S*,*E*)-2-(4-(5-*Methoxy*-1-*methy*l-2,3-*dihydro*-1*H*-*inden*-1-*y*l)*but*-1-*en*-1-*y*l)*thiophene* (**3gaf**)



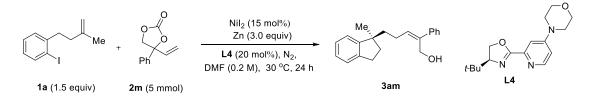
The title compound **3gaf** was isolated as a colorless oil (32 mg, 54%, 96% *ee*) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1).

¹**H NMR** (**400 MHz**, **Chloroform**-*d*) δ = 7.09-7.05 (m, 1H), 7.01 (d, *J*= 8.1 Hz, 1H), 6.91 (dd, *J*= 5.1, 3.5 Hz, 1H), 6.82 (d, *J*= 3.5 Hz, 1H), 6.76-6.72 (m, 2H), 6.47 (d, *J*= 15.7 Hz, 1H), 6.03 (dt, *J*= 15.7, 6.8 Hz, 1H), 3.78 (s, 3H), 2.90-2.84 (m, 2H), 2.16-2.04 (m, 3H), 1.92-1.83 (m, 1H), 1.76-1.64 (m, 2H), 1.25 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 158.7, 144.7, 143.2, 143.2, 131.3, 127.2, 124.1, 123.2, 123.0, 122.7, 112.1, 109.8, 55.4, 46.6, 40.9, 39.0, 30.5, 28.7, 27.1 ppm. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₉H₂₃OS 299.1464; Found 299.1467.

HPLC-Data: (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 97/3, flow rate = 0.5 mL/min): t_R= 9.4 (minor), 10.4 (major).

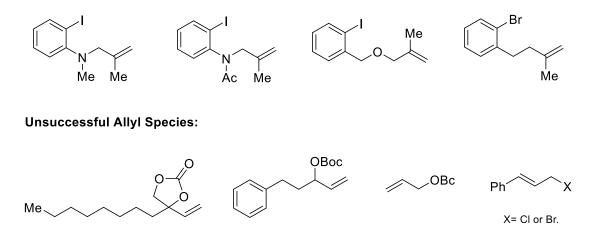
Procedure for Synthesis of 3am on a 5-mmol Scale.



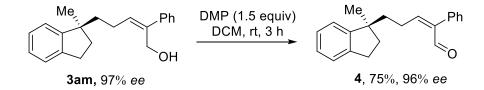
NiI₂ (234 mg, 0.75 mmol, 15 mol %), Zn (975 mg, 15 mmol, 3 equiv) and ligand L4 (289 mg, 1.0 mmol, 20 mol %) were placed in a Schlenk tube equipped with a stir bar. Then the Schlenk tube was evacuated and filled with nitrogen (three cycles). To these solids, 25 mL dry DMF, the aryl iodide-tethered alkene 1a (2.04 g, 7.5 mmol, 1.5 equiv) and the allyl ethylene carbonate 2m (0.95 g, 5 mmol, 1.0 equiv) were added successively under nitrogen atmosphere. The reaction mixture was stirred at 30 °C for 24 hours, before it was quenched by addition of water. The aqueous phase was extracted with ethyl acetate (3×30 mL), and the combined organic phases were washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The crude materials were purified through column chromatography on silica gel (petroleum ether/ethyl acetate=5:1) to give compound 3am (1.17 g, 80%, 97% *ee*) as a colorless oil.

Unsuccessful Substrates

Unsuccessful Tethered Alkenes:



IV. Derivatizations of the Aryl-Allylation Products



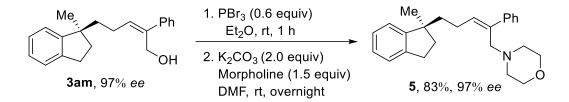
To a stirred suspension of Dess-Martin periodinane (127 mg, 0.3 mmol, 1.5 equiv) in DCM (0.2 M, 1.0 mL) was added a solution of the alcohol **3am** (58 mg, 0.2 mmol, 1.0 equiv). After stirring for 3 h at room temperature, the mixture was quenched with brine. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate=20:1) to give (*S*,*Z*)-*5*-(*1*-*methyl*-2,*3*-*dihydro*-1*H*-*inden*-1-*yl*)-2-*phenylpent*-2-*en*-1-*ol* (**4**) (44 mg, 75%, 96% *ee*) as a colorless oil.

¹**H NMR (400 MHz, Chloroform-***d***)** δ = 10.20 (s, 1H), 7.35-7.29 (m, 3H), 7.26-7.14 (m, 6H), 6.72 (t, *J*= 8.2 Hz, 1H), 2.99-2.90 (m, 2H), 2.74-2.59 (m, 2H), 2.10 (dt, *J*= 12.7, 6.9 Hz, 1H), 1.96-1.76 (m, 3H), 1.33 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 190.2, 151.8, 150.2, 143.2, 139.9, 136.6, 128.3 (2C), 128.2 (2C), 127.8, 126.7, 126.4, 124.8, 122.6, 47.5, 41.2, 38.5, 30.3, 27.0, 23.6 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₂₂ONa 313.1563; Found 313.1564.

HPLC-Data: (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 98/2, flow rate = 0.4 mL/min): t_R= 19.5 (major), 20.7 (min).

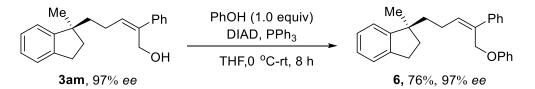


To a stirred suspension of compound **3am** (58 mg, 0.2 mmol, 1.0 equiv) in Et₂O (0.2 M, 1.0 mL) was added a solution of the PBr₃ (32 mg, 0.12 mmol, 0.6 equiv) at 0 °C. After stirring for 1 h at room temperature, the mixture was quenched with saturated aqueous solution of NaCl. The organic layer was separated and the aqueous layer was extracted with Et₂O. The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The resultant crude product was used in the next step without further purification. To a stirred suspension of K₂CO₃ (55 mg, 0.4 mmol, 2.0 equiv) and morpholine (26 mg, 0.3 mmol, 1.5 equiv) in DMF (0.2 M, 1.0 mL) was added the solution of the crude allyl bromide. After stirring overnight at room temperature, the mixture was quenched with brine. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The resultant crude product was used and the aqueous layer was quenched with brine. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give (*S*,*Z*)-*4*-(*5*-(*1*-*methyl*-*2*,*3*-*dihydro*-*1H*-*inden*-*1*-*yl*)-*2*-*phenylpent*-*2*-*en*-*1*-*yl*)*morpholine* (**5**) (60 mg, 95%, 97% *ee*) as a colorless oil.

¹**H NMR** (**500 MHz**, **Chloroform**-*d*) δ = 7.44 (d, *J*= 8.6 Hz, 2H), 7.30-7.23 (m, 2H), 7.23-7.11 (m, 5H), 5.88 (t, *J*= 7.4 Hz, 1), 3.65-3.55 (m, 4H), 3.28 (s, 2H), 2.96-2.85 (m, 2H), 2.41-2.33 (m, 4H), 2.28-2.20 (m, 1H), 2.18-2.13 (m, 1H), 2.08 (dt, *J*= 13.4, 6.9 Hz, 1H), 1.89 (dt, *J*= 12.6, 7.7 Hz, 1H), 1.73 (td, *J*= 12.7, 12.2, 5.2 Hz, 1H), 1.64 (td, *J*= 12.8, 4.9 Hz, 1H), 1.30 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ= 150.9, 143.20, 143.17, 135.0, 133.8, 128.0 (2C), 126.6, 126.43, 126.38 (2C), 126.3, 124.6, 122.7, 67.1 (2C), 57.1, 53.4 (2C), 47.4, 41.2, 38.6, 30.4, 26.9, 24.5 ppm.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₂₅H₃₁NONa 384.2303; Found 384.2306. **HPLC-Data:** (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 98/2, flow rate = 0.4 mL/min): t_R= 15.3 (minor), 15.8 (major).



To a stirred solution of PPh₃ (53 mg, 0.2 mmol, 1.0 equiv), phenol (21 mg, 0.22 mmol, 1.1 equiv) and compound **3am** (58 mg, 0.2 mmol, 1.0 equiv) in THF (0.2 M, 1.0 mL) was added a solution of the DIAD (diisopropyl azodicarboxylate) (41 mg, 0.2 mmol, 1.0 equiv) at 0 °C. After stirring for 8 h at room temperature, the mixture was quenched with brine. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by column

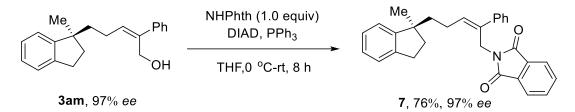
chromatography on silica gel (petroleum ether/ethyl acetate=20:1) to give (S,Z)-*1-methyl*-1-(5-phenoxy-4-phenylpent-3-en-1-yl)-2,3-dihydro-1H-indene (**6**) (56 mg, 76%, 97% *ee*) as a colorless oil.

¹**H NMR** (**400 MHz**, **Chloroform**-*d*) δ = 7.32 (d, *J*= 8.1 Hz, 2H), 7.27-7.17 (m, 4H), 7.19-7.07 (m, 2H), 7.08-6.98 (m, 3H), 6.90 (t, *J*= 7.4 Hz, 1H), 6.85 (d, *J*= 8.8 Hz, 2H), 6.00 (t, *J*= 7.5 Hz, 1H), 4.70 (s, 2H), 2.85-2.75 (m, 2H), 2.26-2.19 (m, 1H), 2.15-2.07 (m, 1H), 1.97 (dt, *J*= 12.7, 7.0 Hz, 1H), 1.83-1.75 (m, 1H), 1.74-1.59 (m, 2H), 1.18 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ= 157.8, 149.8, 142.1, 140.2, 134.1, 133.6, 128.4 (2C), 127.2 (2C), 125.9, 125.3, 125.2, 124.9 (2C), 123.5, 121.6, 119.9, 113.9 (2C), 64.2, 46.3, 40.1, 37.4, 29.2, 25.9, 23.5 ppm.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₇H₂₉O 369.2213; Found 369.2205.

HPLC-Data: (Chiralcel OJ-H column, $\lambda = 254$ nm, hexane/isopropanol = 85/15, flow rate = 0.7 mL/min): t_R= 11.0 (major), 15.2 (minor).



To a stirred solution of PPh₃ (53 mg, 0.2 mmol, 1.0 equiv), phthalimide (21 mg, 0.22 mmol, 1.1 equiv) and compound **3am** (58 mg, 0.2 mmol, 1.0 equiv) in THF (0.2 M, 1.0 mL) was added a solution of DIAD (Diisopropyl Azodicarboxylate) (41 mg, 0.2 mmol, 1.0 equiv) at 0 °C. After stirring for 8 h at room temperature, the mixture was quenched with brine. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate=3:1) to give (*S*,*Z*)-2-(5-(1-methyl-2,3-dihydro-1H-inden-1-yl)-2-phenylpent-2-en-1-yl)isoindoline-1,3-dione (7) (44 mg, 80%, 97% *ee*) as a colorless oil.

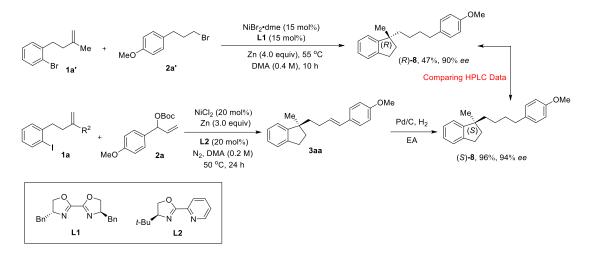
¹**H NMR (500 MHz, Chloroform-***d*) δ= 7.71 (dd, *J*= 5.5, 3.1 Hz, 2H), 7.61 (dd, *J*= 5.5, 3.0 Hz, 2H), 7.35-7.31 (m, 2H), 7.24-7.12 (m, 7H), 5.80 (t, *J*= 7.3 Hz, 1H), 4.70 (s, 2H), 2.99-2.90 (m, 2H), 2.52-2.43 (m, 1H), 2.39-2.32 (m, 1H), 2.19-2.10 (m, 1H), 1.96-1.90 (m, 1H), 1.88-1.82 (m, 1H), 1.82-1.72 (m, 1H), 1.33 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ= 168.0 (2C), 151.2, 143.3, 140.3, 134.21, 134.15, 133.8 (2C), 131.9, 128.1 (2C), 127.1, 126.9 (2C), 126.4, 126.3, 124.6 (2C), 123.1 (2C), 122.7, 47.4, 40.9, 38.5, 36.7, 30.4, 26.9, 24.5 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₉H₂₇NO₂Na 444.1934; Found 444.1937.

HPLC-Data: (Chiralpak IB column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): t_R= 12.2 (minor), 12.7 (major).

V. Determination of the Absolute Configuration of the Aryl-Allylation Products



The aryl-allylation product **3aa** was hydrogenated to compound **8**. It is known in the literature that the compound **8** with *R*-configuration can be synthesized through Nicatalyzed asymmetric aryl-alkylation.⁸ The absolute configuration of compound **3aa** prepared using our method was determined to be *S* through comparison of the HPLC data (Page 222-223) with these reported in the literature. The absolute stereochemistry of the other aryl-allylation products was assigned assuming a common reaction pathway.

Procedure for Hydrogenation of Compound 3aa

A flask is charged with compound **3aa** (58 mg, 0.2 mmol, 1.0 equiv), ethyl acetate (3.0 mL) and Pd/C (5.0 mg, 5%) with a H₂ ballon. The reaction mixture was stirred for 6 h at room temperature. Then the reaction mixture was diluted with ethyl acetate, filtered, dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified through column chromatography on silica gel (petroleum ether/ethyl acetate=20:1) to afford (*S*)-1-(4-(4-methoxyphenyl)butyl)-1-methyl-2,3-dihydro-1H-indene ((*S*)-**8**) (56 mg, 96%, 94% *ee*) as a colorless oil.

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.13-6.95 (m, 6H), 6.72 (d, *J*= 8.6 Hz, 2H), 3.69 (s, 3H), 2.85-2.75 (m, 2H), 2.49-2.33 (m, 2H), 1.92 (dt, *J*= 12.5, 7.0 Hz, 1H), 1.73 (dt, *J*= 12.5, 7.6 Hz, 1H), 1.56-1.42 (m, 4H), 1.33-1.23 (m, 2H), 1.15 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 156.5, 150.6, 142.1, 133.9, 128.1 (2C), 125.12, 125.06, 123.4, 121.6, 112.6 (2C), 54.2, 46.3, 40.2, 37.5, 33.9, 31.5, 29.2, 25.7, 23.6 ppm.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₂₆ONa 295.2062; Found 295.2052.

HPLC-Data: (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): t_R= 9.0 (major), 9.9 (minor).

Procedure for Preparation of Compound 8 through Ni-Catalyzed Aryl-Alkylation

A sealed test tube charged with NiBr₂(dme) (9.3 mg, 0.03 mmol, 15mol%), ligand L1 (9.6 mg, 0.03 mmol, 15 mol%), Zn-powder (52 mg, 0.8 mmol, 4.0 equiv) and a stir bar was evacuated and filled with nitrogen (three cycles) before adding DMA (0.5 mL) under nitrogen atmosphere. Then the reaction mixture was stirred at 40 °C for 15 minutes. Next, the aryl bromide-tethered alkene **1a**' (44.8 mg, 0.2mmol, 1.0 equiv) and 1-(3-bromopropyl)-4-methoxybenzene (**2a'**) (91.2 mg, 0.4 mmol, 2.0 equiv) were added, and the resulting mixture was stirred at 40 °C for 10 hours. The mixture was then filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether/ethyl acetate=20:1) to afford (*R*)-1-(4-(4-methoxyphenyl)butyl)-1-methyl-2,3-dihydro-1H-indene ((*R*)-8) (31 mg, 47%, 90% ee) as a colorless oil.

HPLC-Data: (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): t_R= 9.0 (minor), 9.9 (major)

VI. Determination of the E/Z-Configuration of the Aryl-

Allylation Products

The ${}^{3}J$ coupling constants between the two alkene hydrogens of the aryl-allylation products **3aa-al**, **3bk**, **3ck**, **3fa**, **3fx**, **3gy**, **3hz** and **3ik** range from 15.5 to 16.0 Hz, which are typical for *E*-alkenes.

Furthermore, the NOESY spectrum of **3ma** (Page 82-83) indicates that the trisubstituted alkene is Z-configured. Therefore, the geometry of all the other aryl-allylation products **3am-av**, **3bm-lm**, **3jn** and **3jo** and derived from vinyl ethylene carbonates is assigned to be *Z* assuming a common reaction pathway (Exception: **3aw** is *E*-configured).

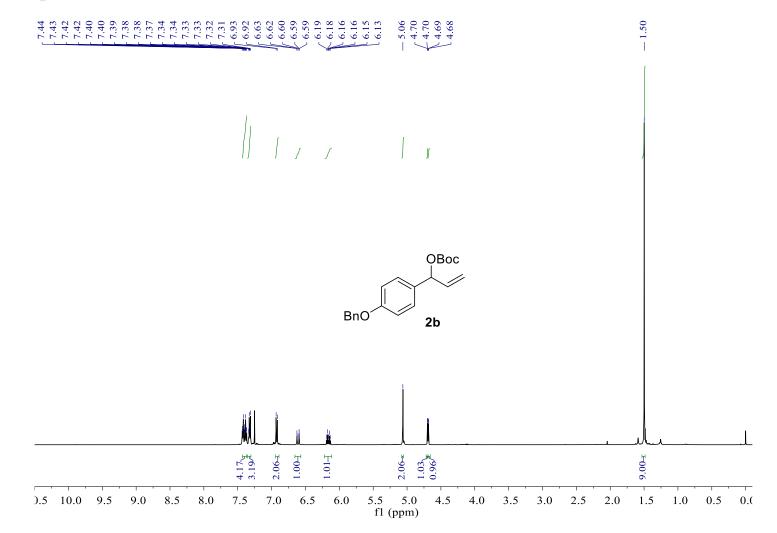
VII. References

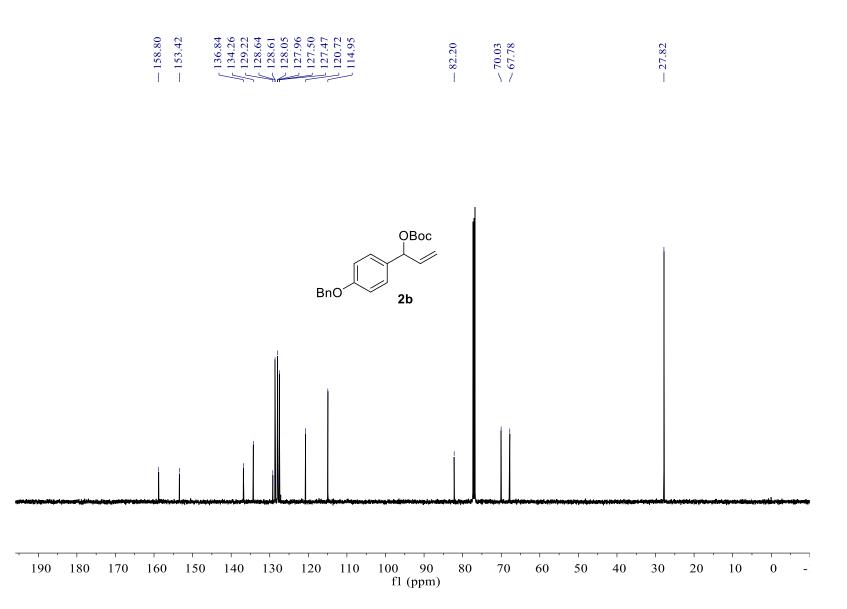
- 1. Jin, Y.; Yang, H.; Wang, C. Nickel-Catalyzed Asymmetric Reductive Arylbenzylation of Unactivated Alkenes. *Org. Lett.* **2020**, *22*, 2724–2729.
- Tian, Z.; Qiao, J.; Xu, G.; Pang, X.; Qi, L.; Ma, W.; Zhao, Z.; Duan, J.; Du, Y.; Su, P.; Liu, X.; Shu, X. Highly Enantioselective Cross-Electrophile Aryl-Alkenylation of Unactivated Alkenes. *J. Am. Chem. Soc.* **2019**, *141*, 7637–7643.
- Lee, Y.; Park, J.; Cho, S. H. Generation and Application of (Diborylmethyl)zinc(II) Species: Access to Enantioenriched gem-Diborylalkanes by an Asymmetric Allylic Substitution. *Angew.Chem. Int.Ed.* 2018, 57, 12930–12934.
- 4. Han, M.; Yang, M.; Wu, R.; Li, Y.; Jia, T.; Gao, Y.; Ni, H.; Hu, P.; Wang, B.; Cao, P. Highly Enantioselective Iridium-Catalyzed Coupling Reaction of Vinyl Azides and Racemic Allylic Carbonates. J. Am. Chem. Soc. 2020, 142, 13398–13405.
- 5. Song, T.; Arseniyadis, S.; Cossy, J. Asymmetric Synthesis of α-Quaternary

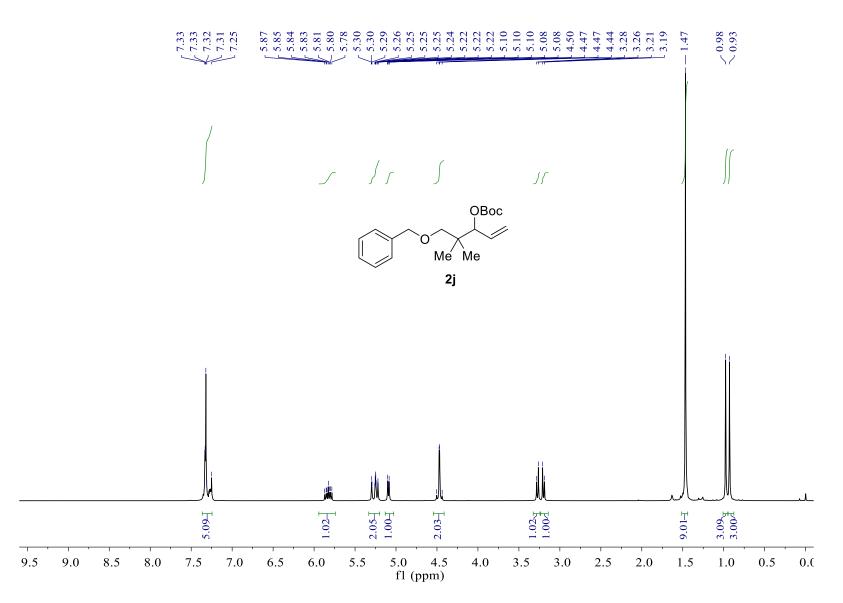
γ-Lactams through Palladium-Catalyzed Asymmetric Allylic Alkylation. *Org. Lett.* **2019**, *21*, 603–607.

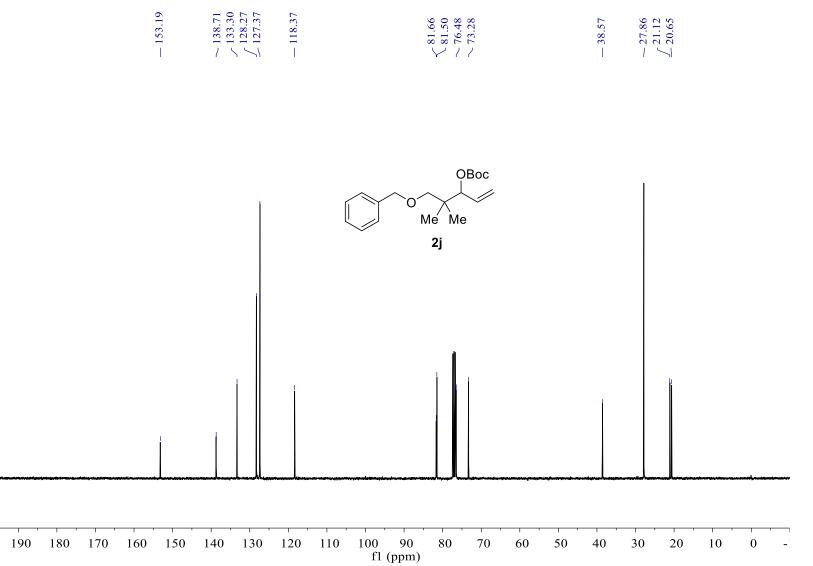
- Deng, L.; Kleij, A. K.; Yang, W. B. Diversity-OrientatedStereoselective Synthesis through Pd-Catalyzed Switchable Decarboxylative C-N/C-S Bond Formation in Allylic Surrogates. *Chem. Eur. J.* 2018, 24,19156–19161.
- 7. Garza, V. J.; Krische, M. J. Hydroxymethylation beyond Carbonylation: Enantioselective Iridium-Catalyzed Reductive Coupling of Formaldehyde with Allylic Acetates via Enantiotopic π -Facial Discrimination. *J. Am. Chem. Soc.* **2016**, *138*, 3655–3658.
- 8. Jin, Y.; Wang, C. Nickel-Catalyzed Asymmetric Reductive Arylalkylation of Unactivated Alkenes. *Angew.Chem. Int.Ed.* **2019**, *58*, 6722–6726.



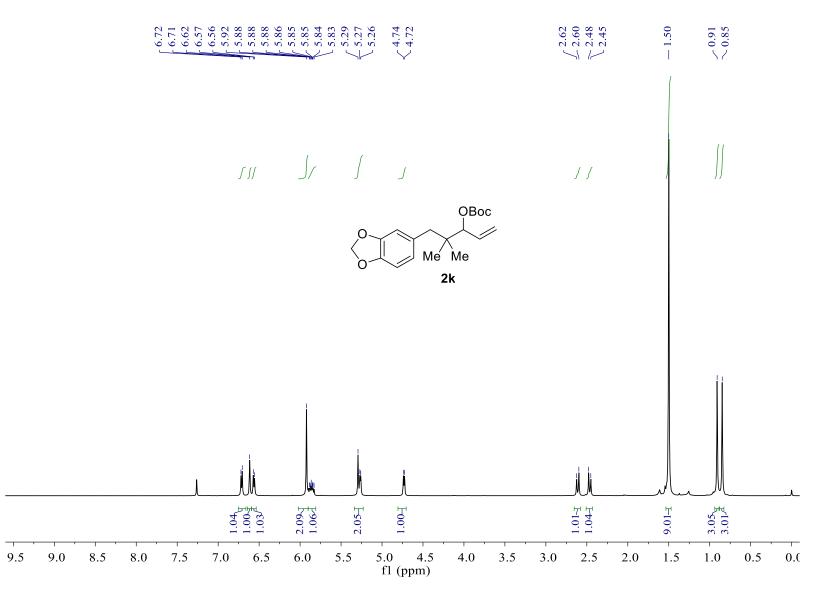




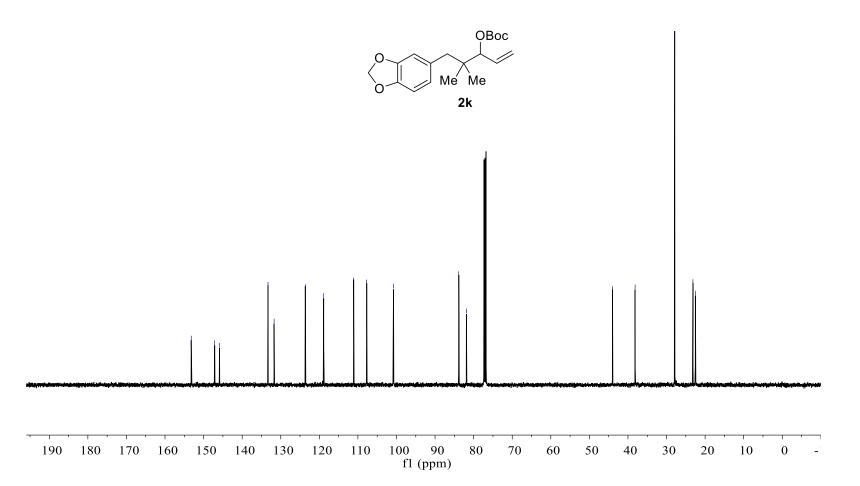


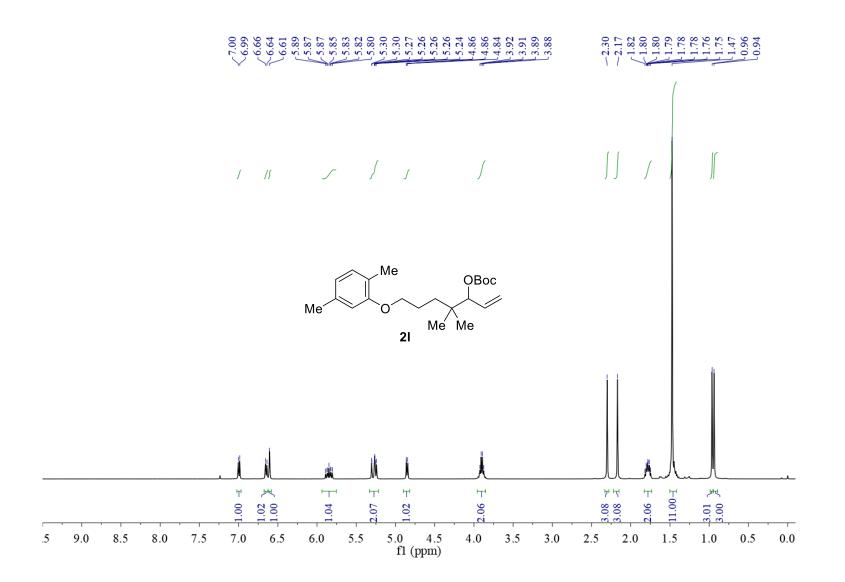


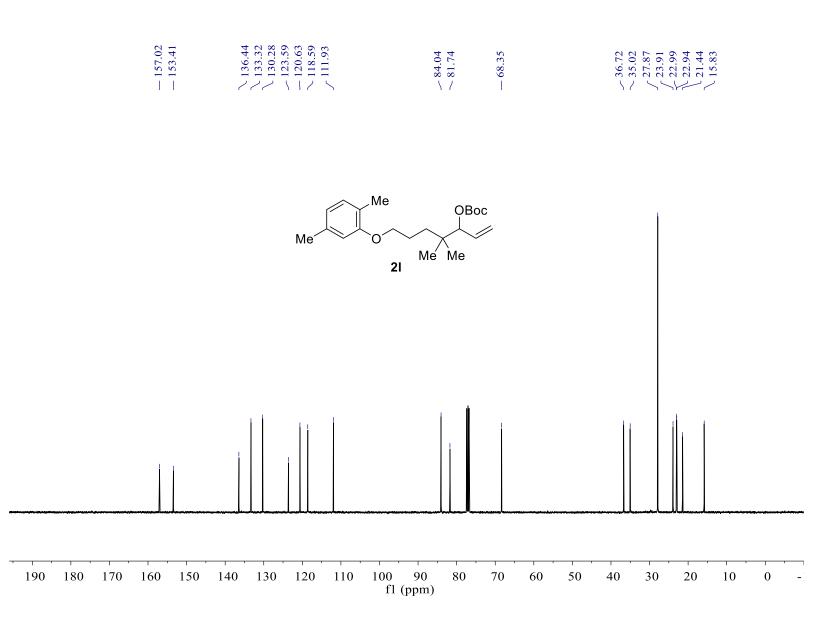


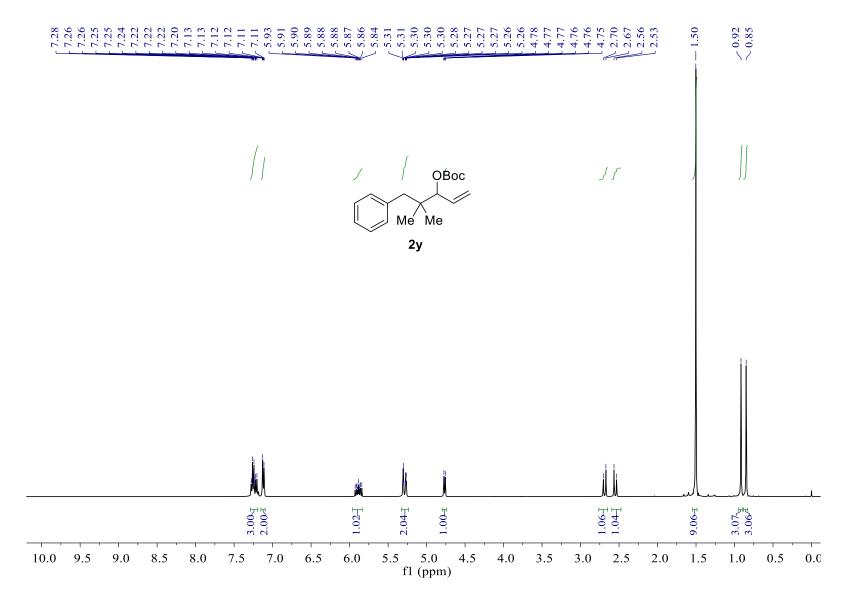


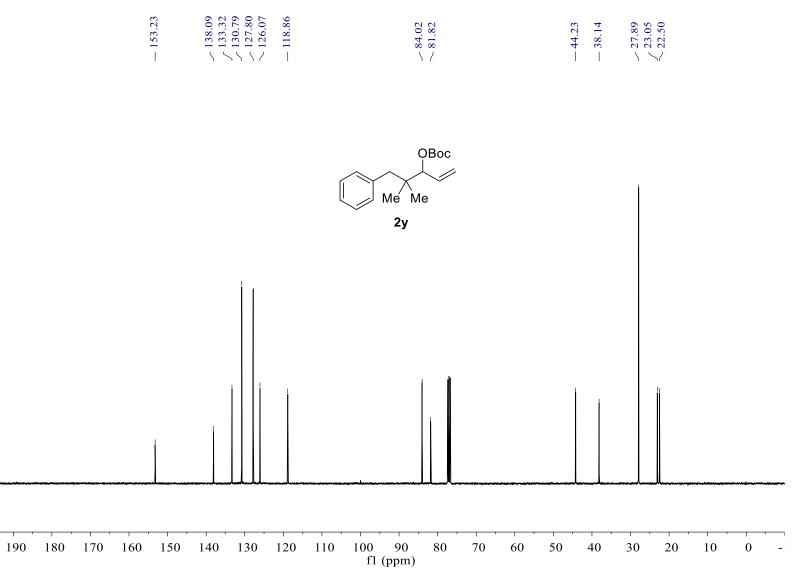




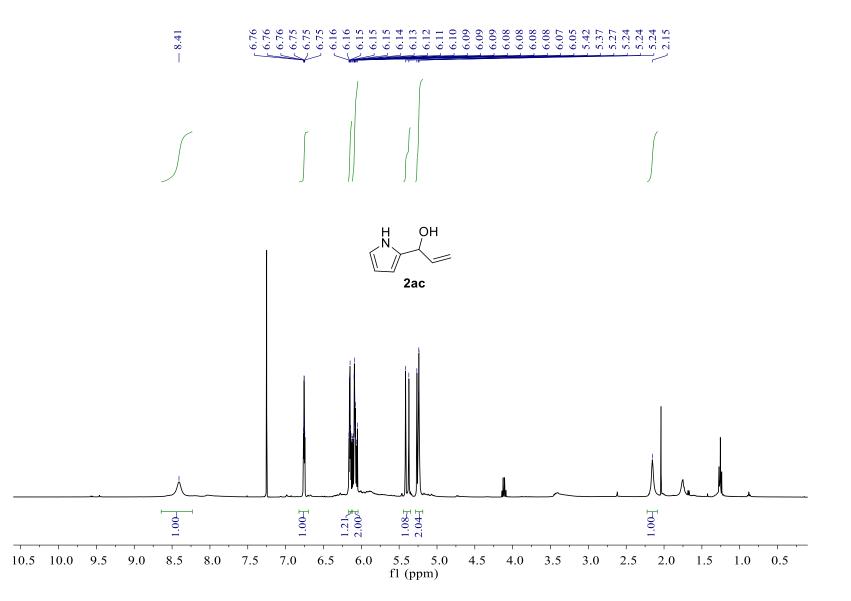


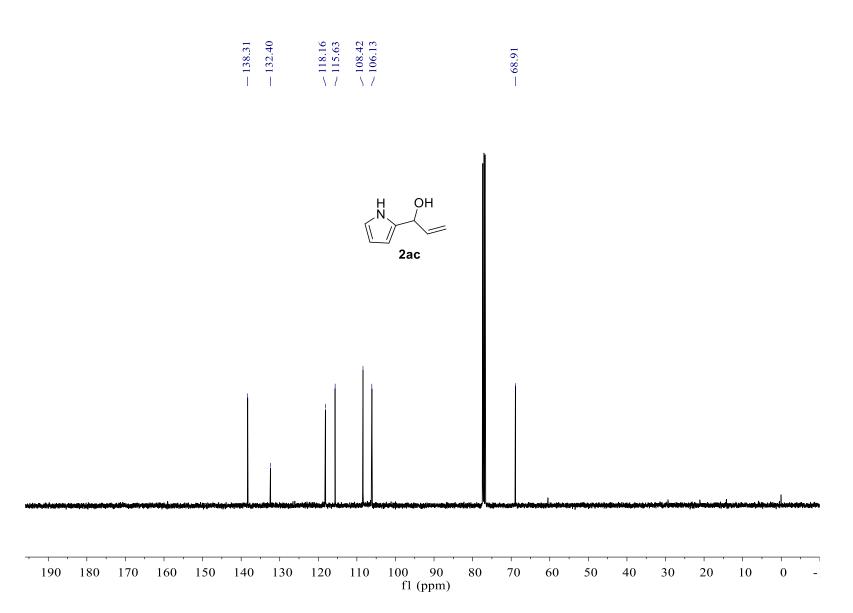


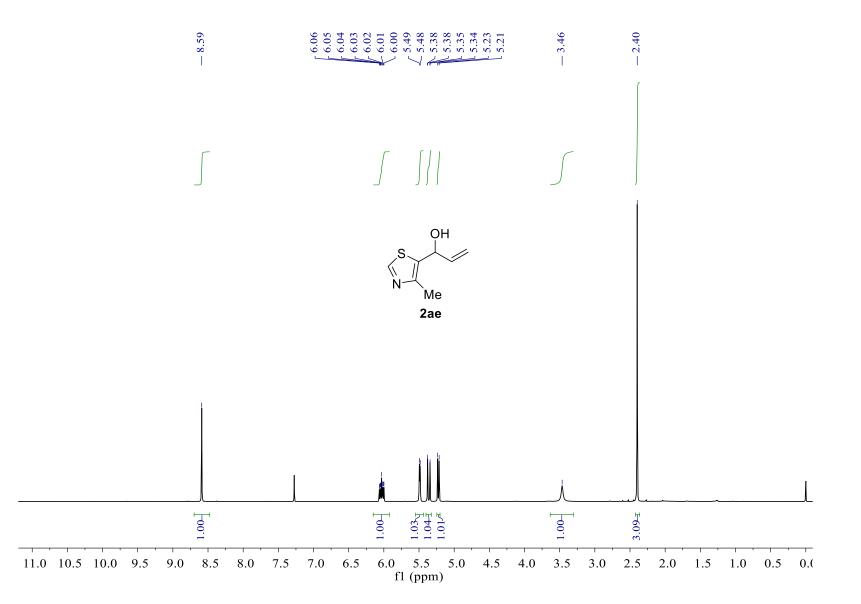


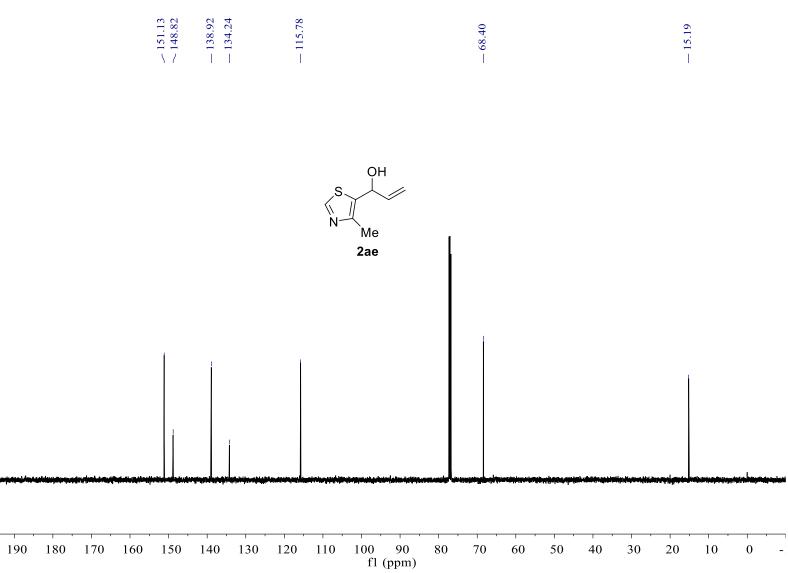




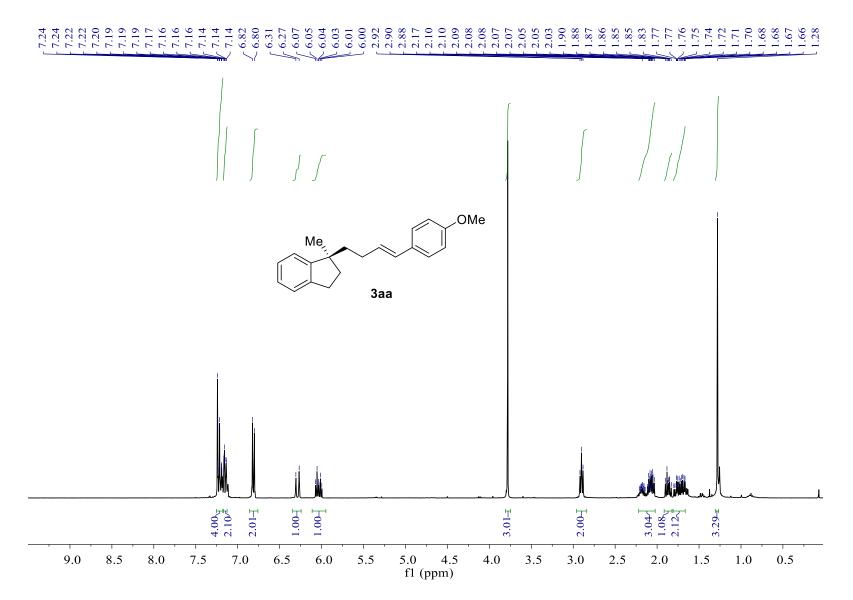


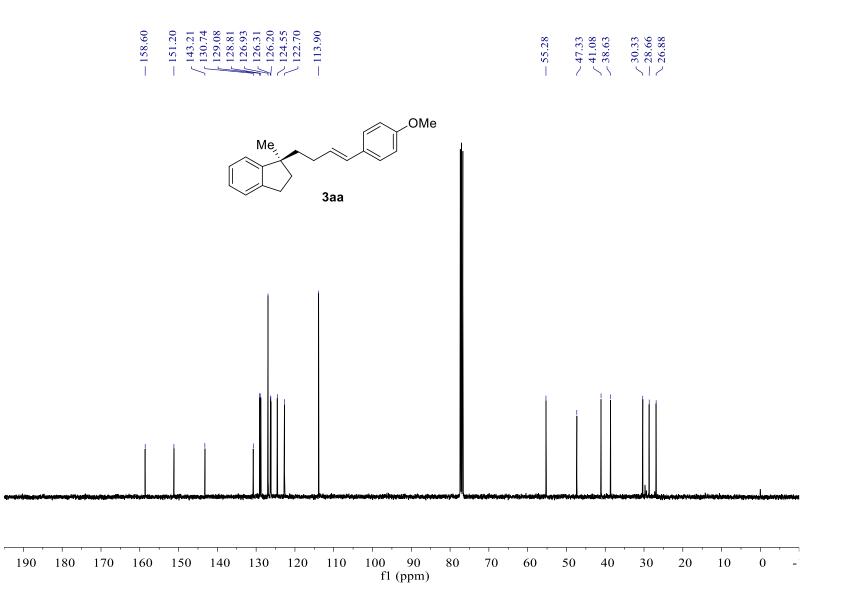


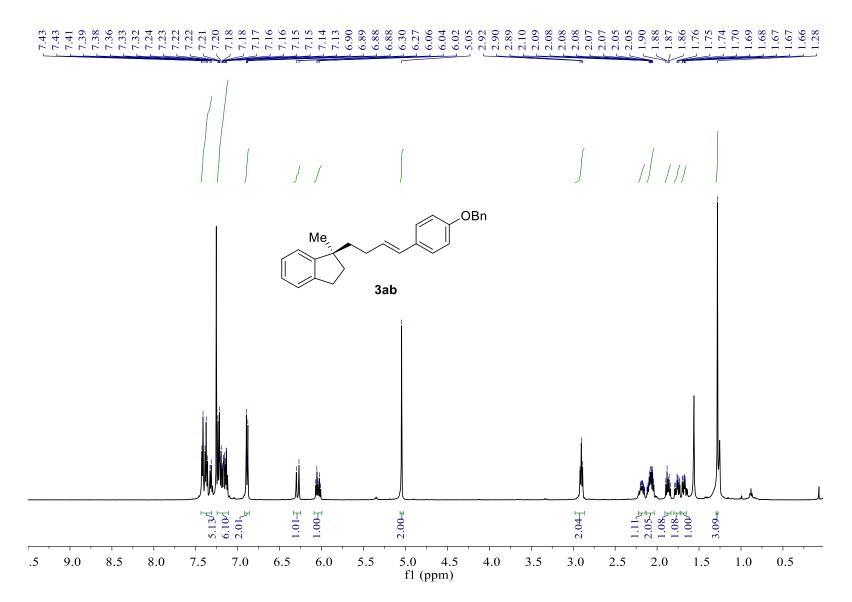


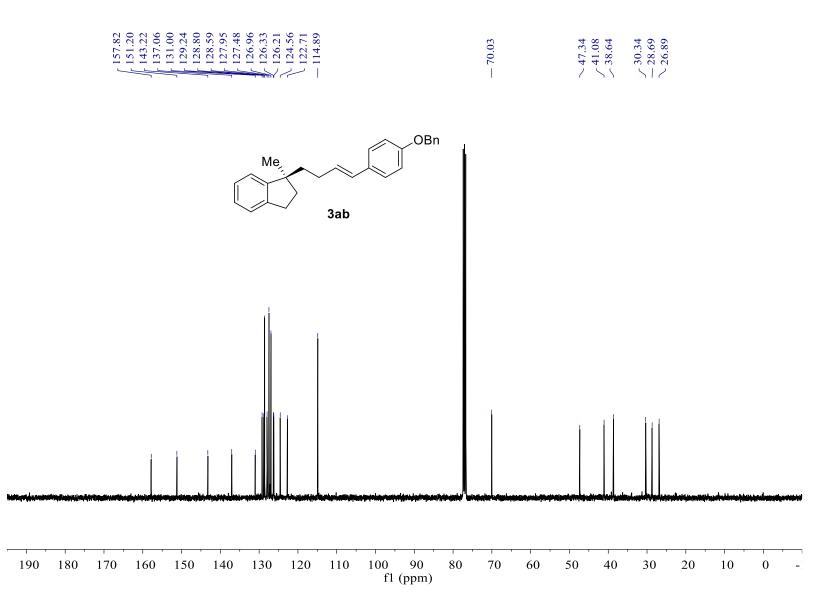


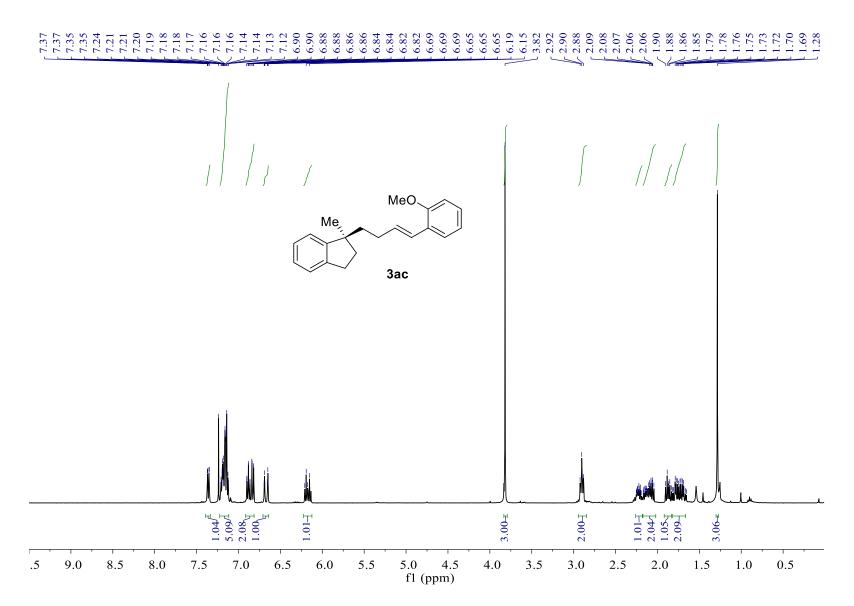


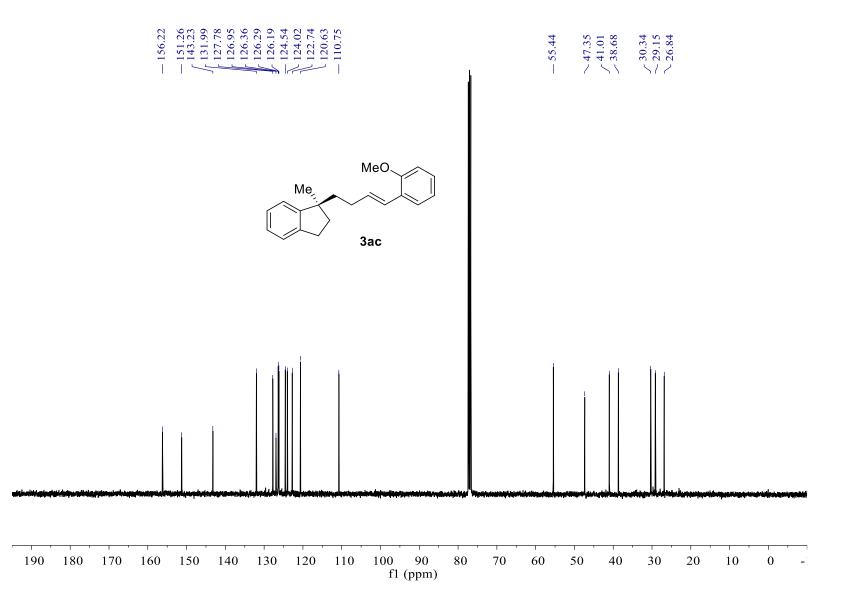


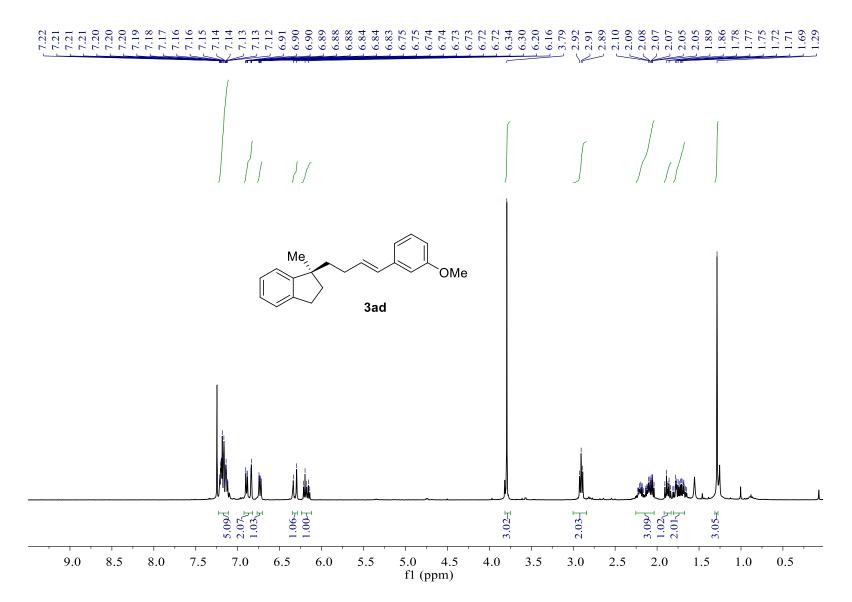


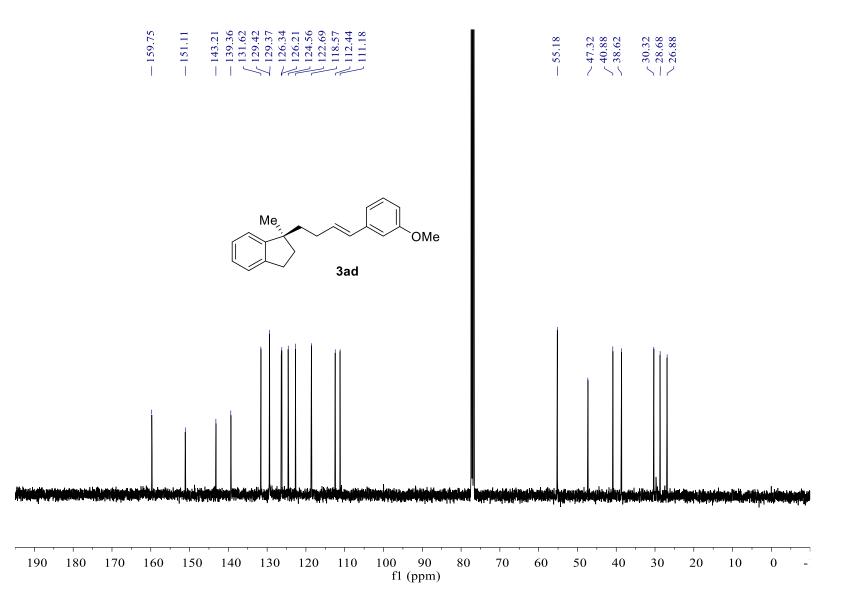


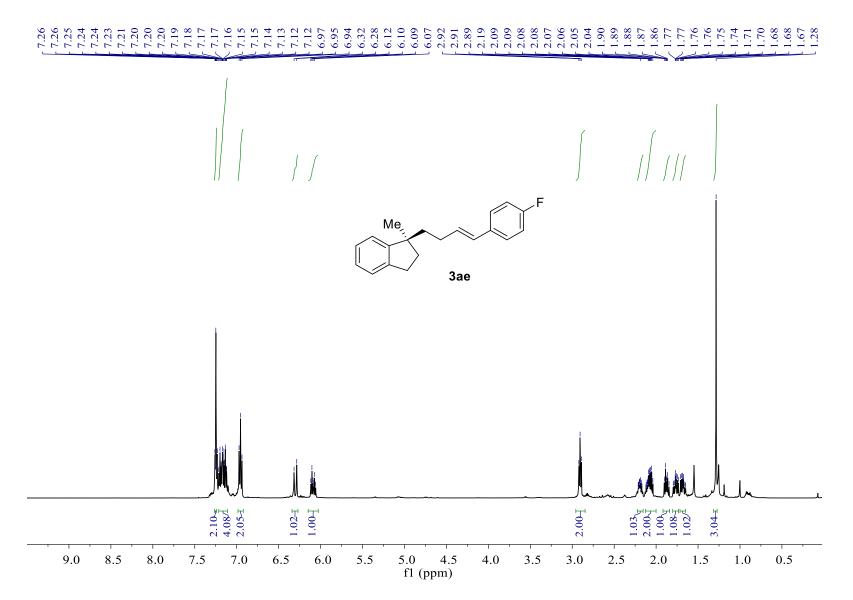


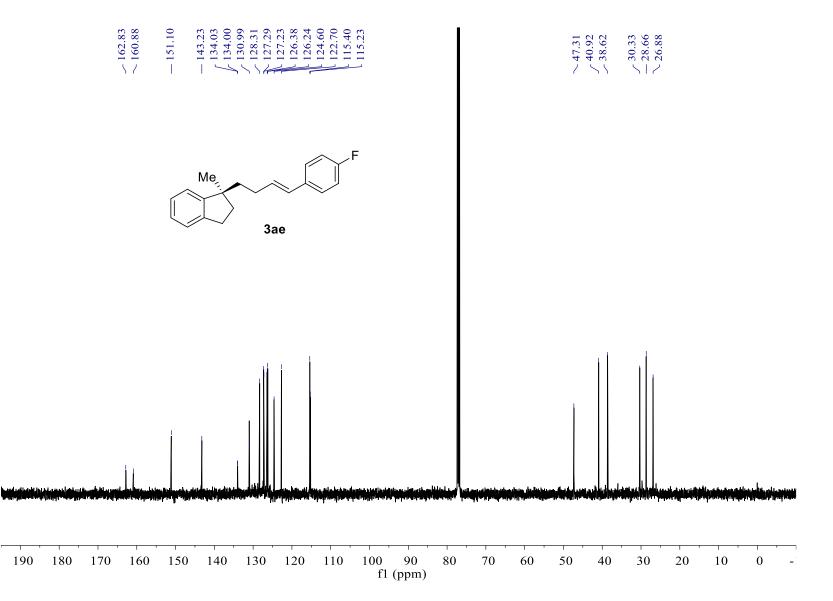


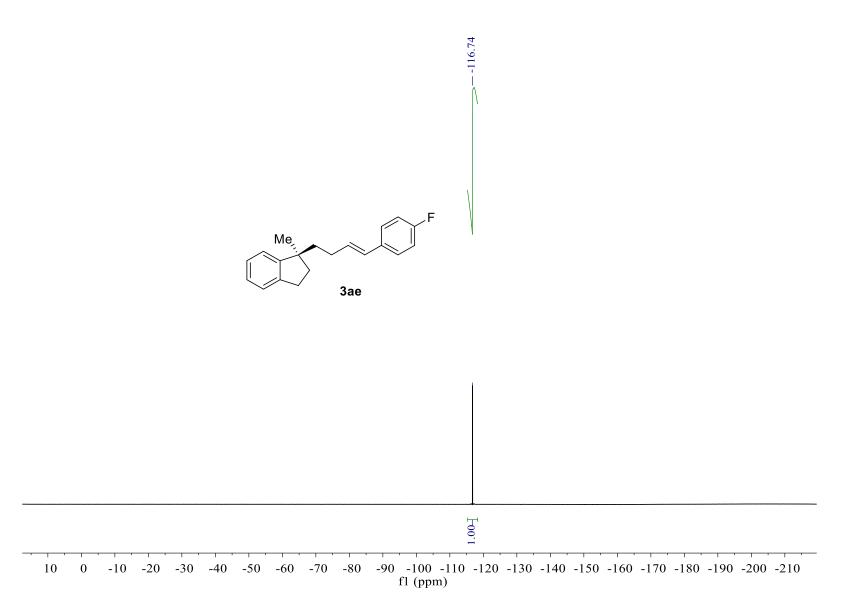


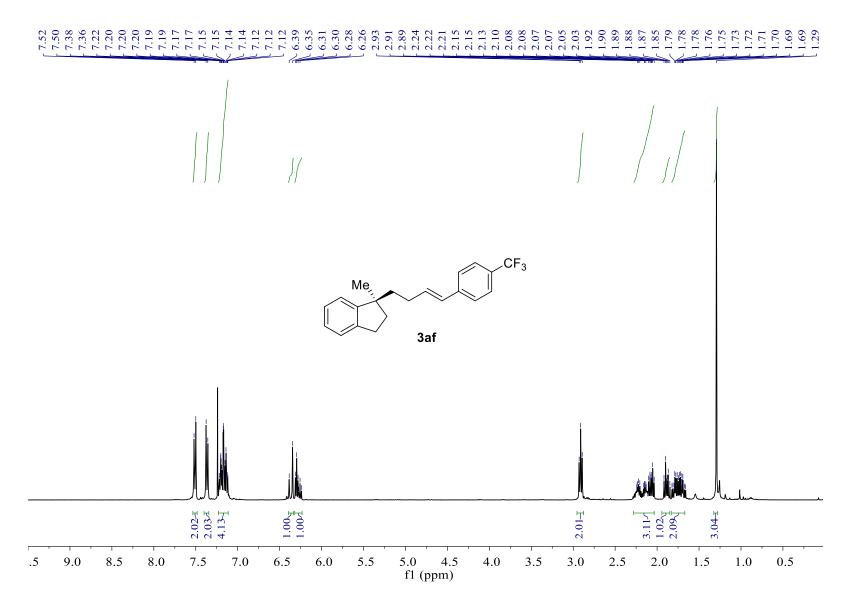


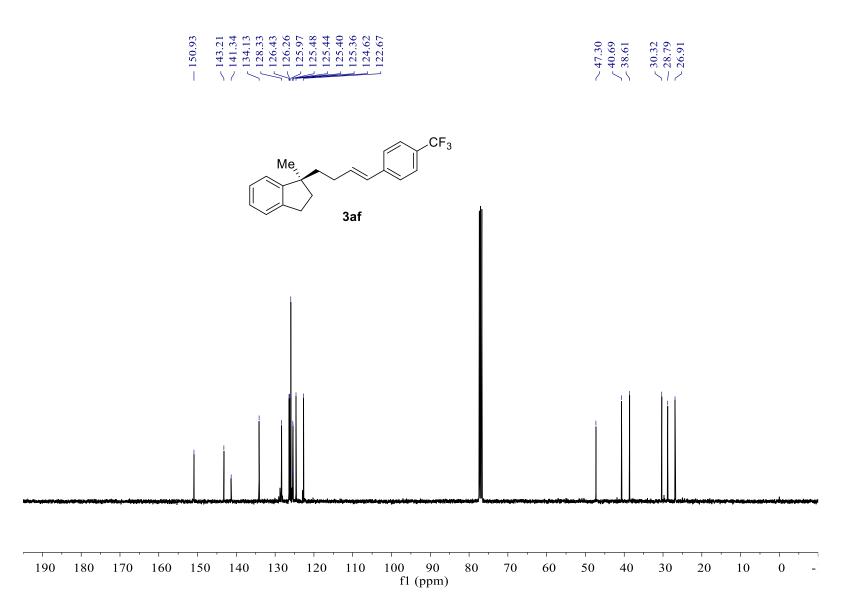


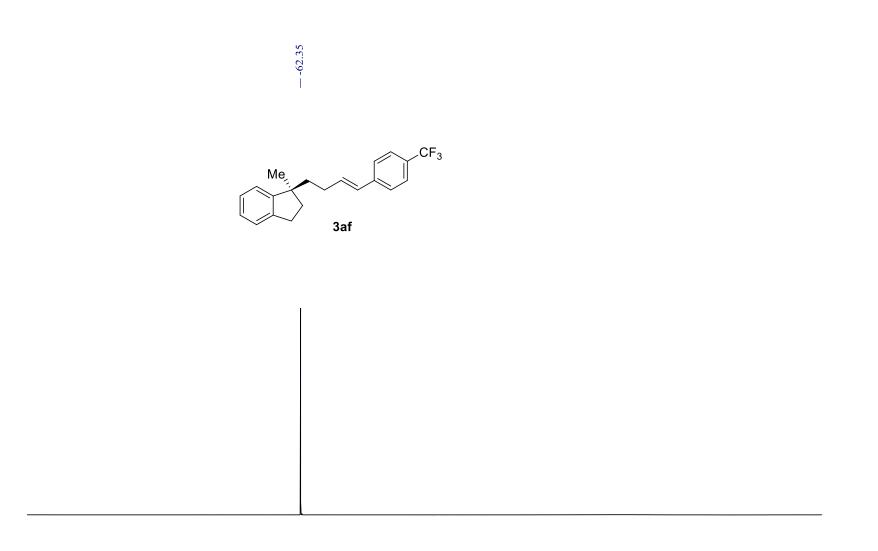








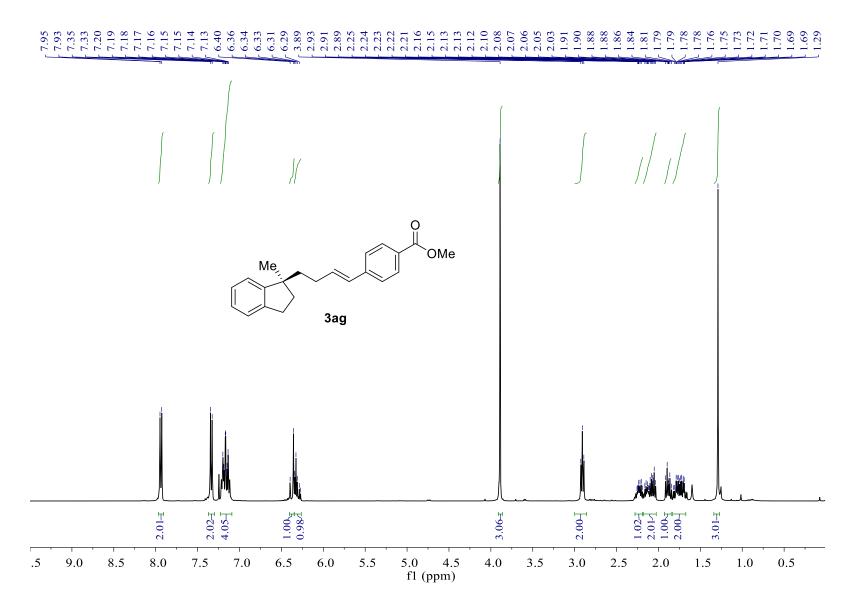


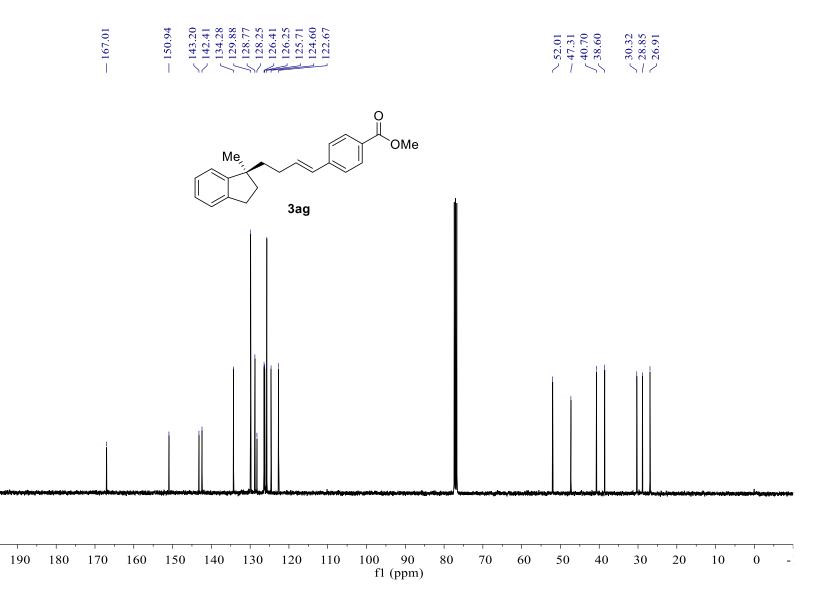


20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2. f1 (ppm)

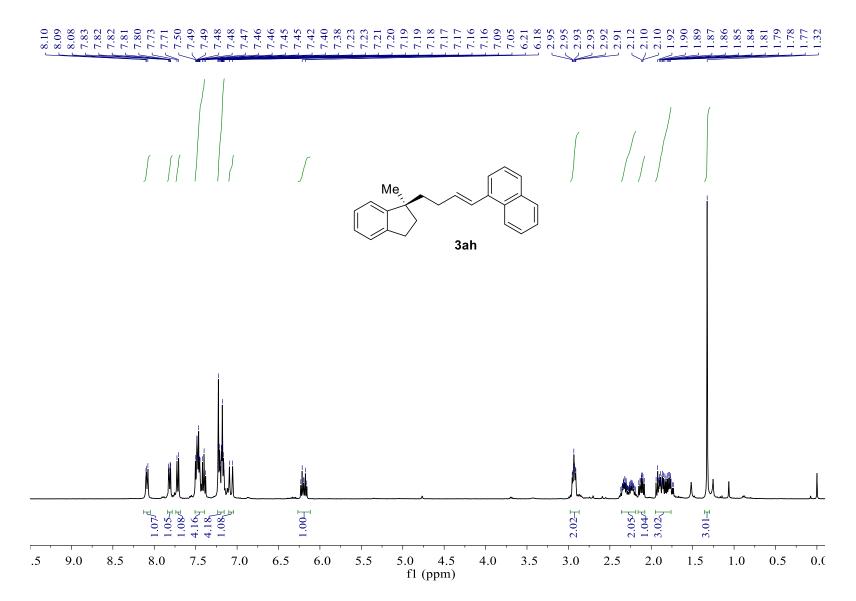
Т

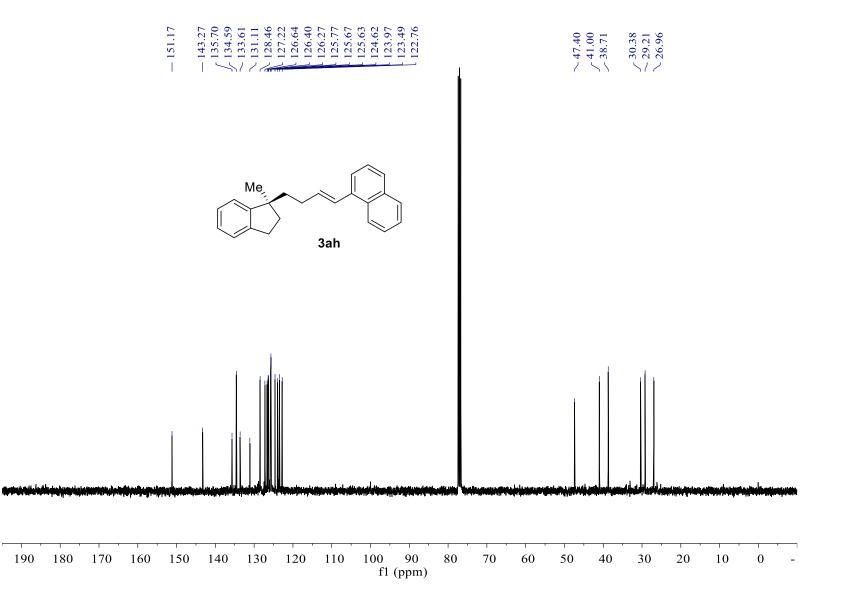
- T

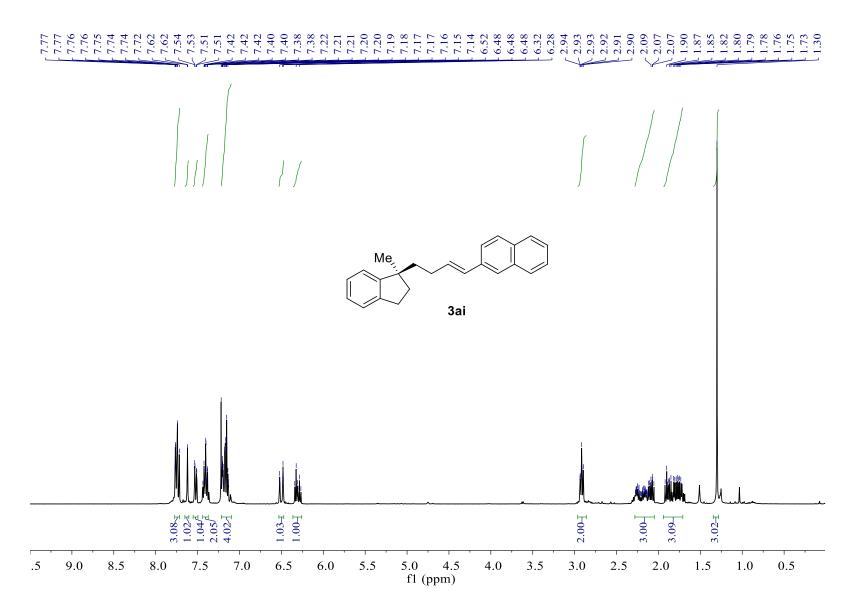


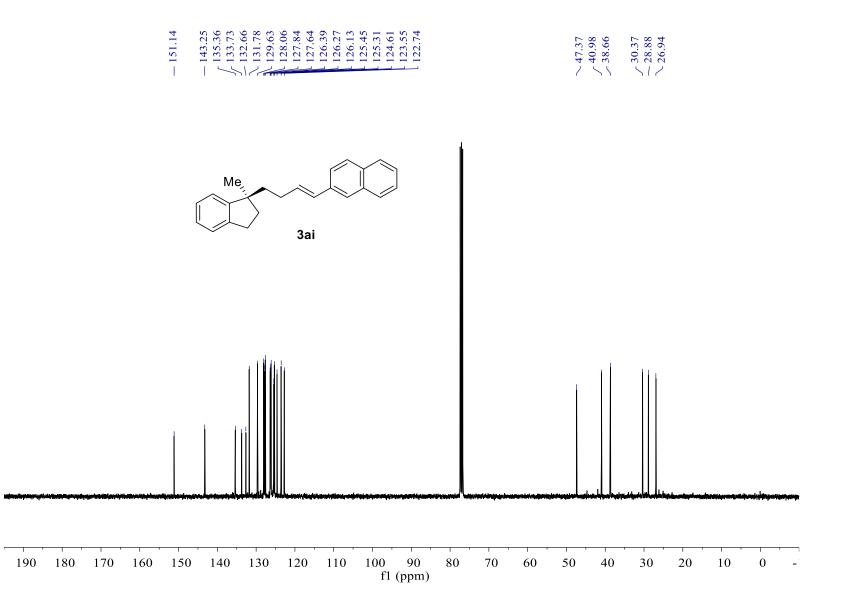


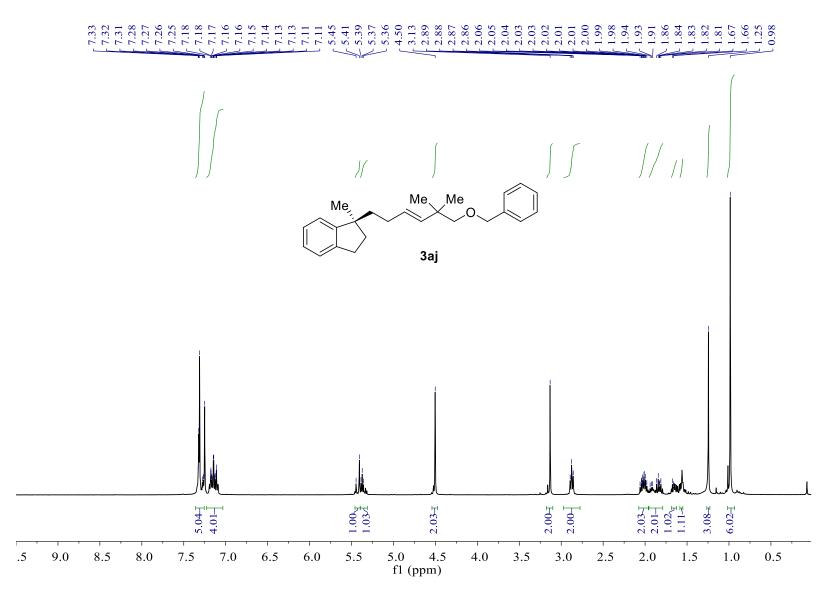
S69

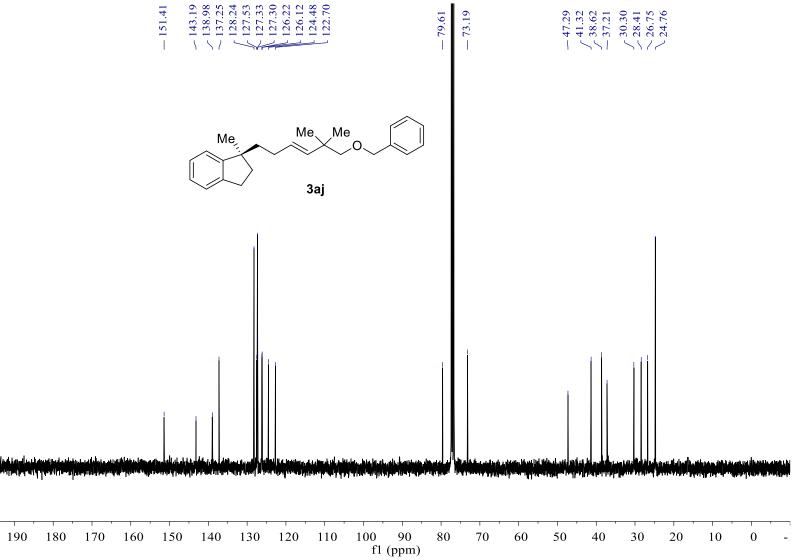




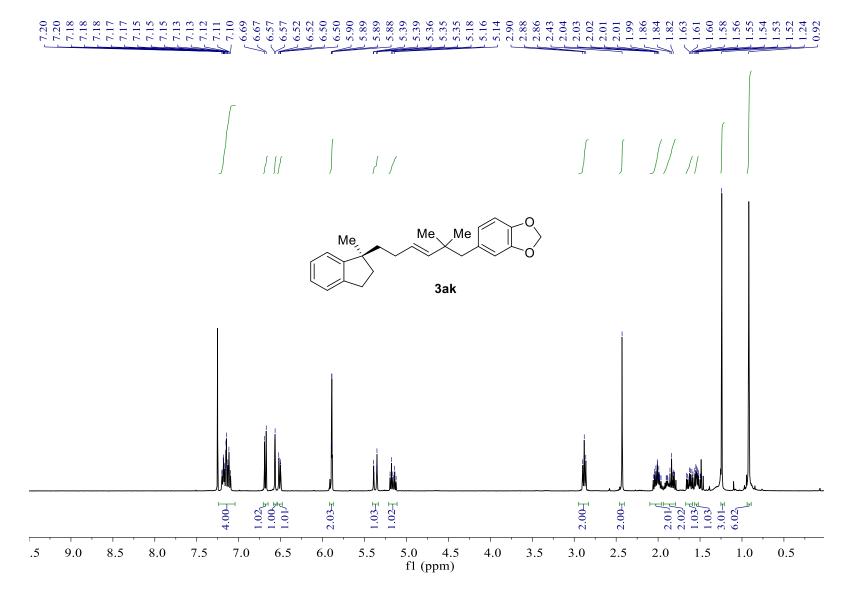


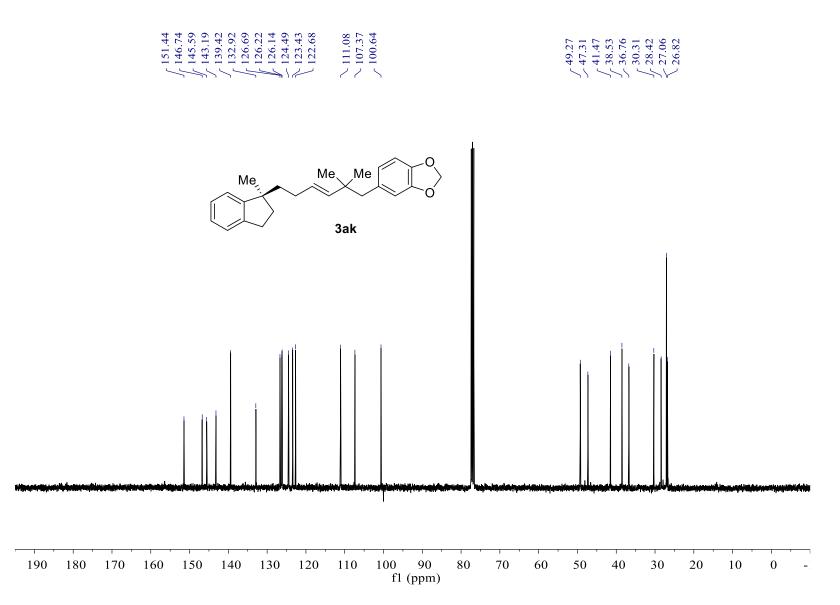


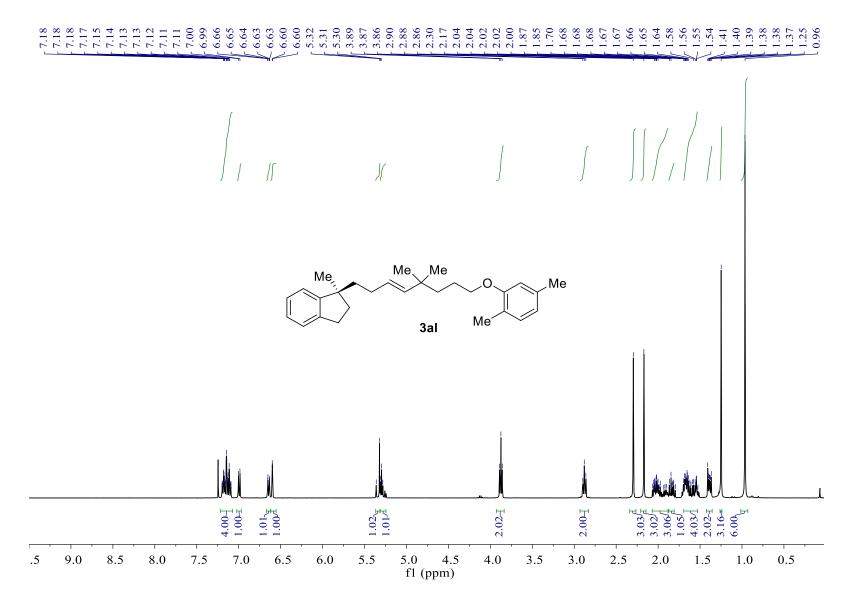


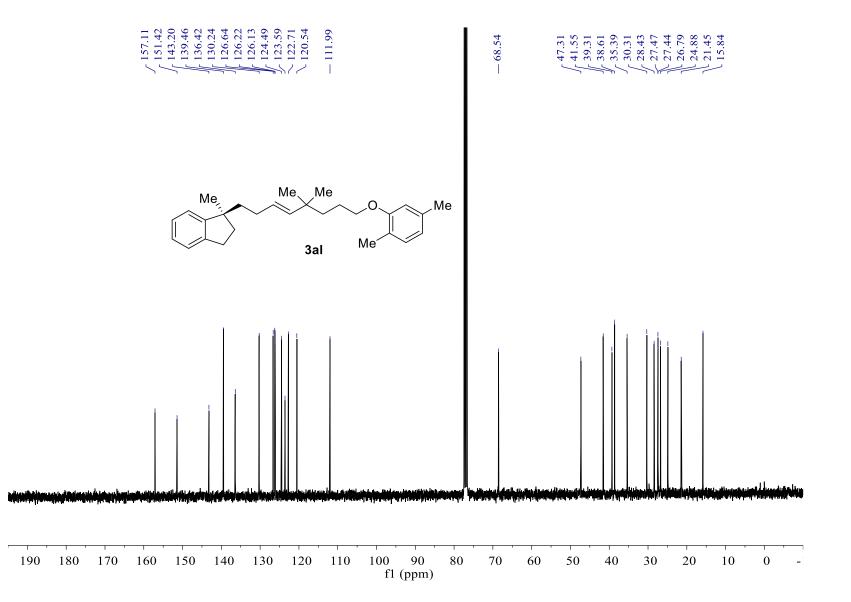


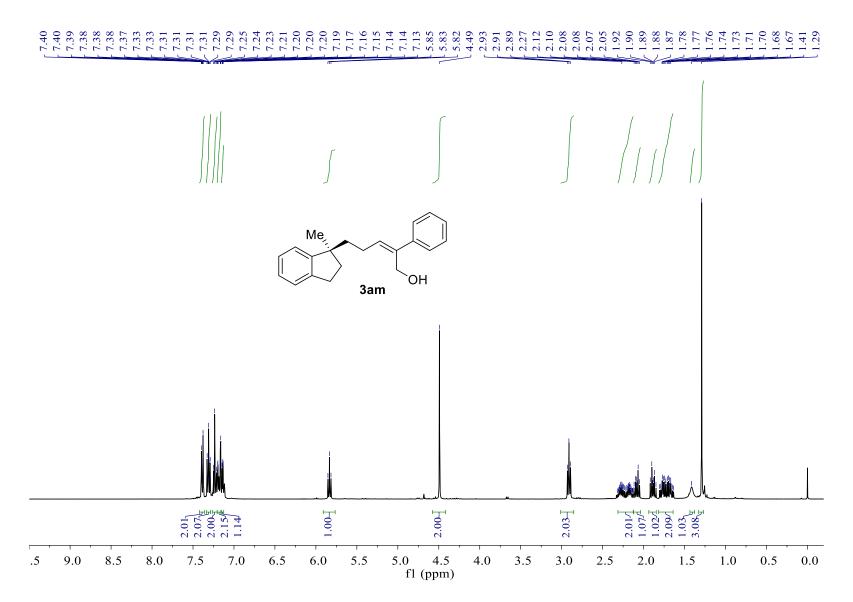


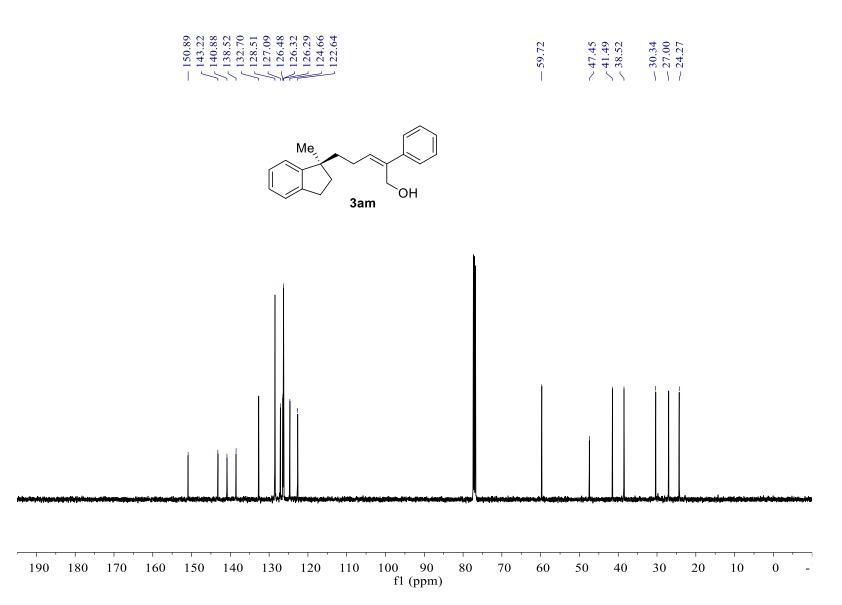




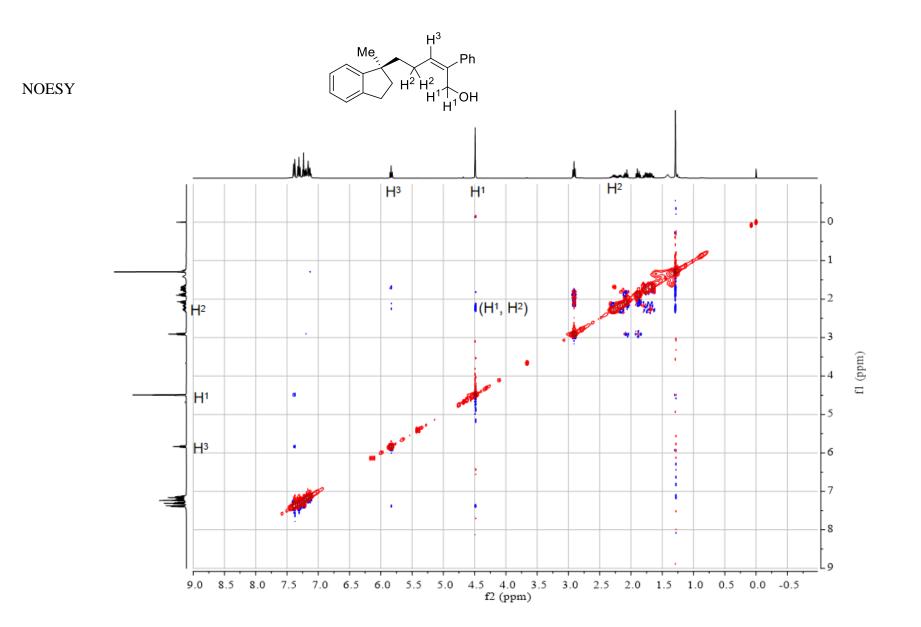


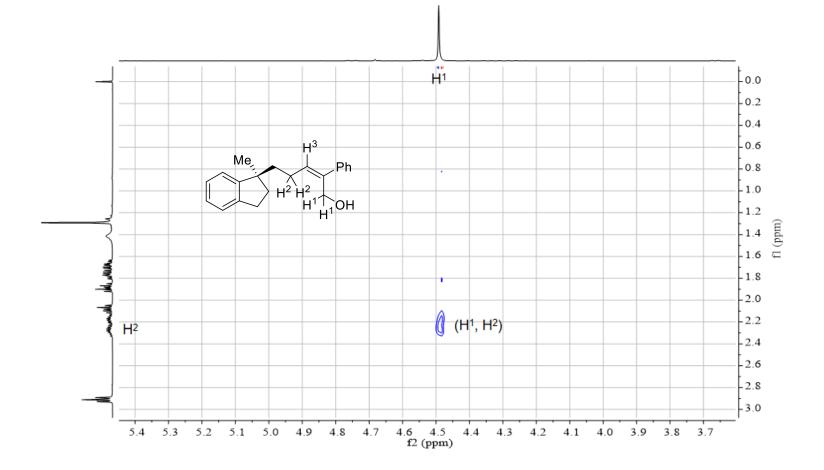


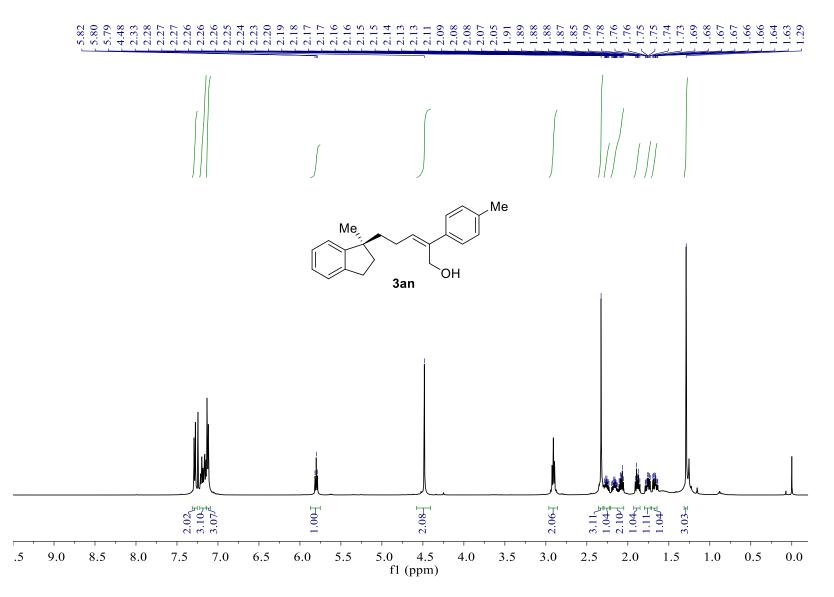


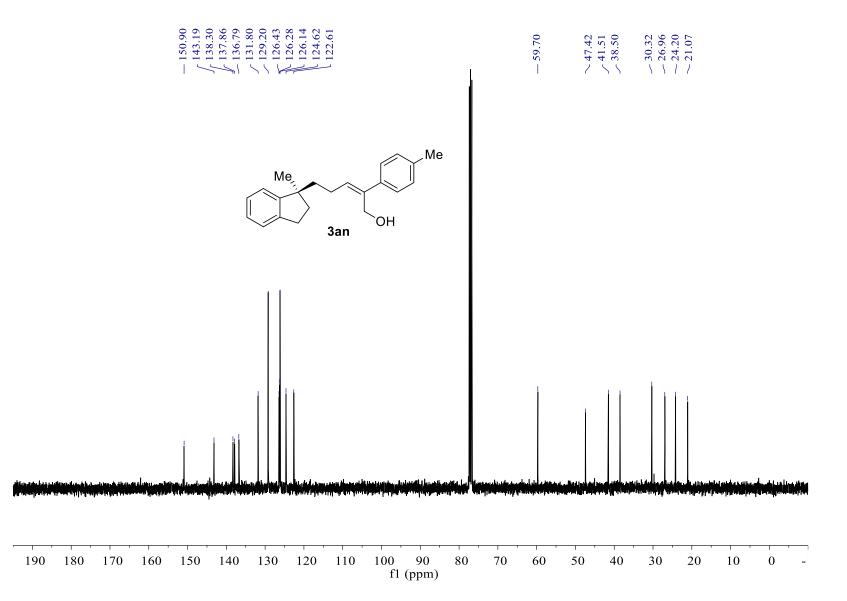


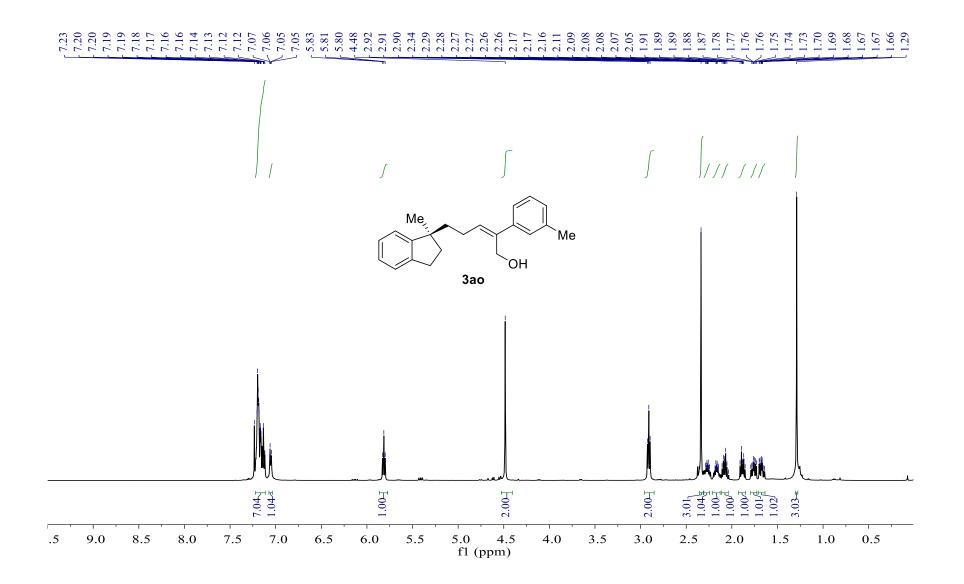


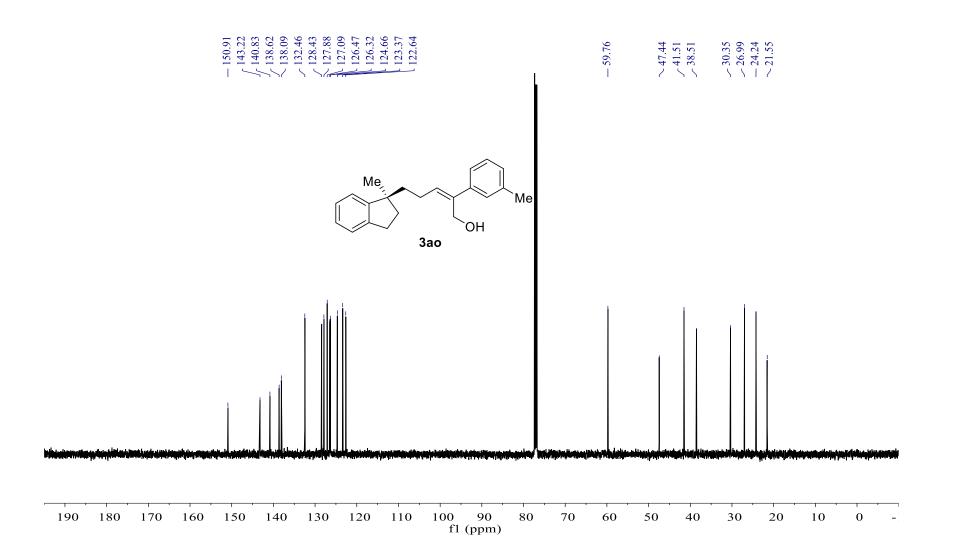


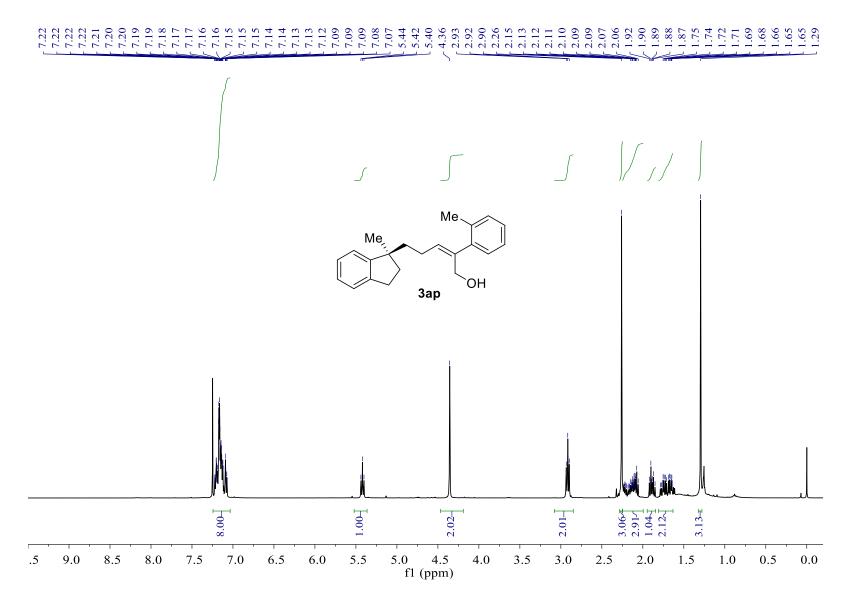


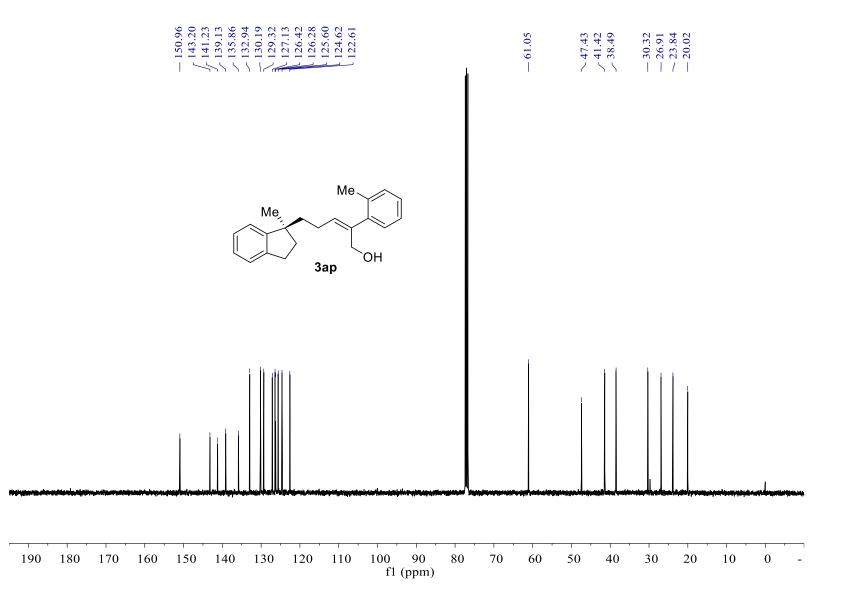


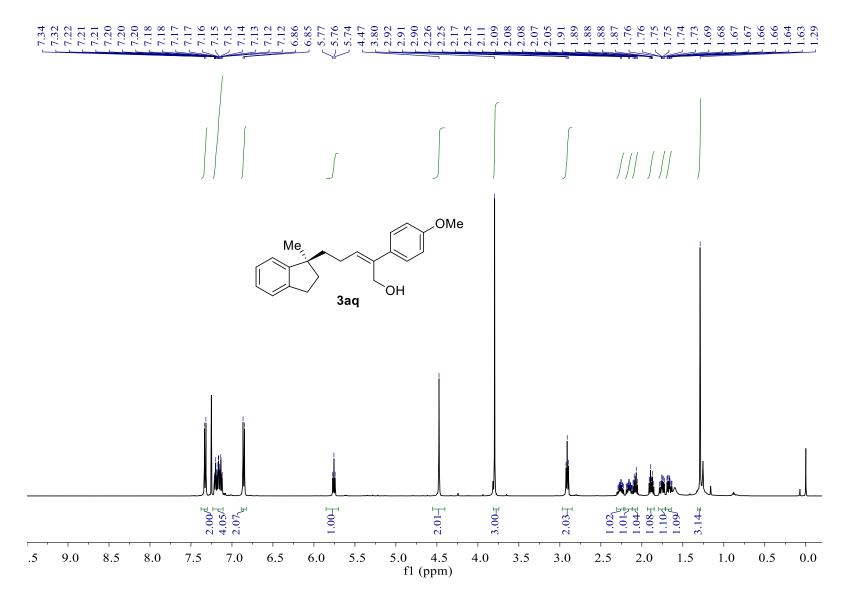


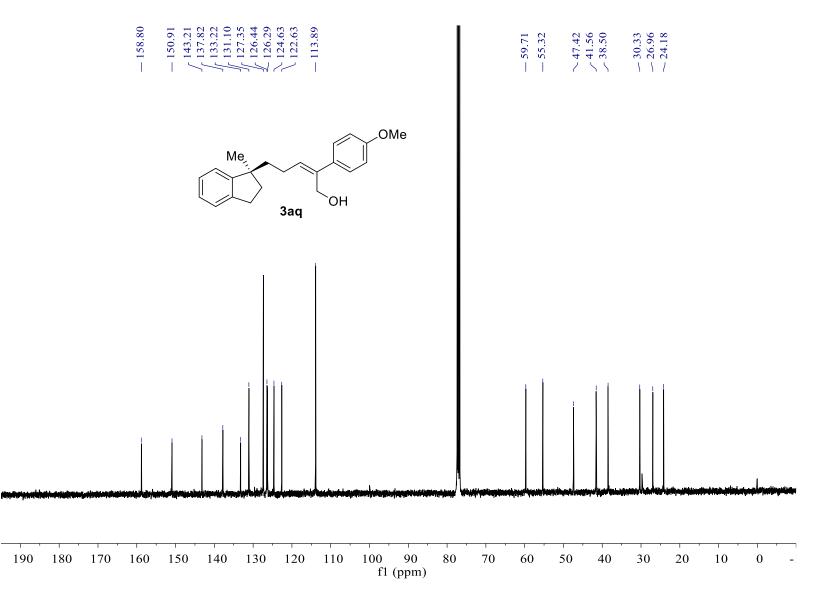


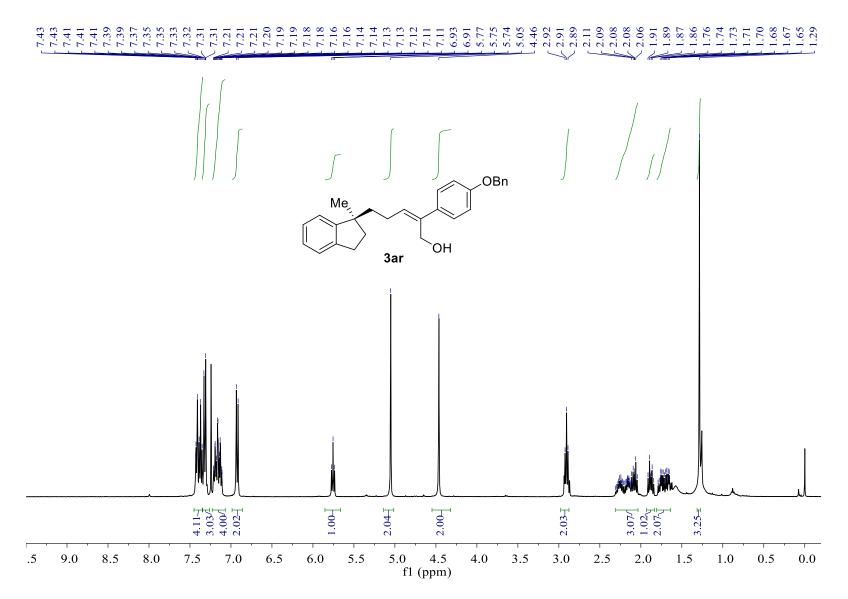


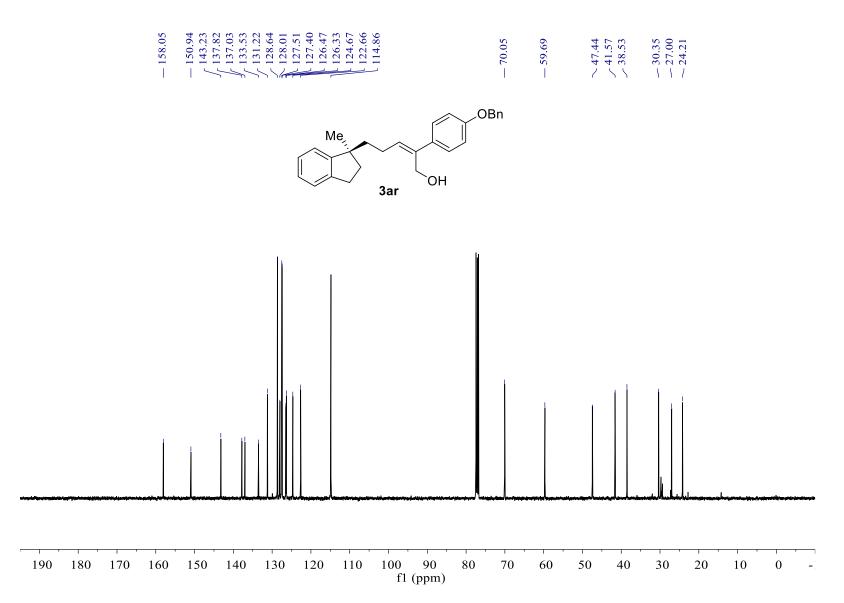




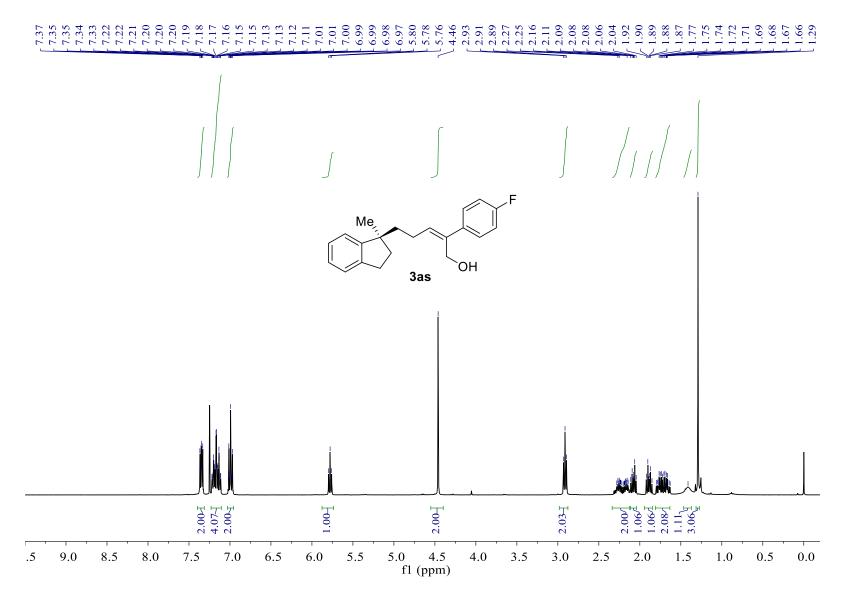


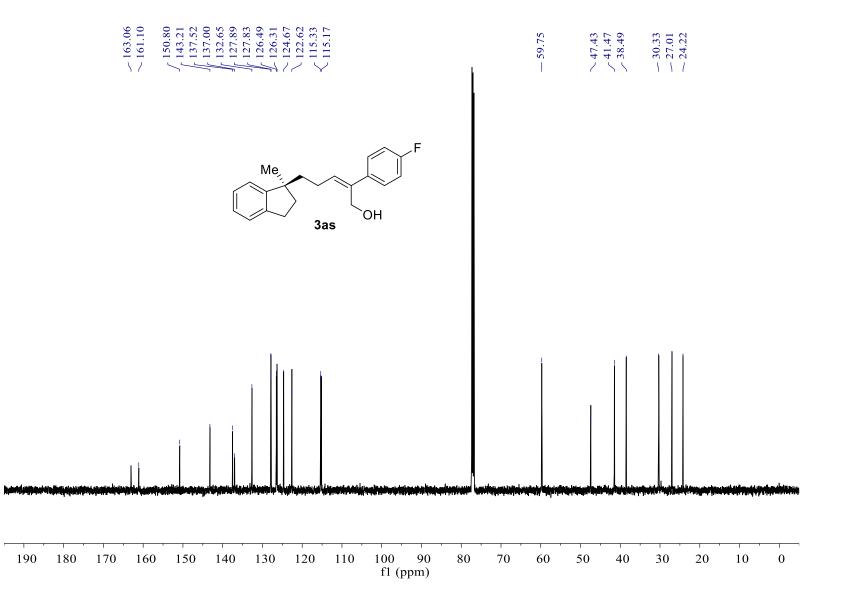


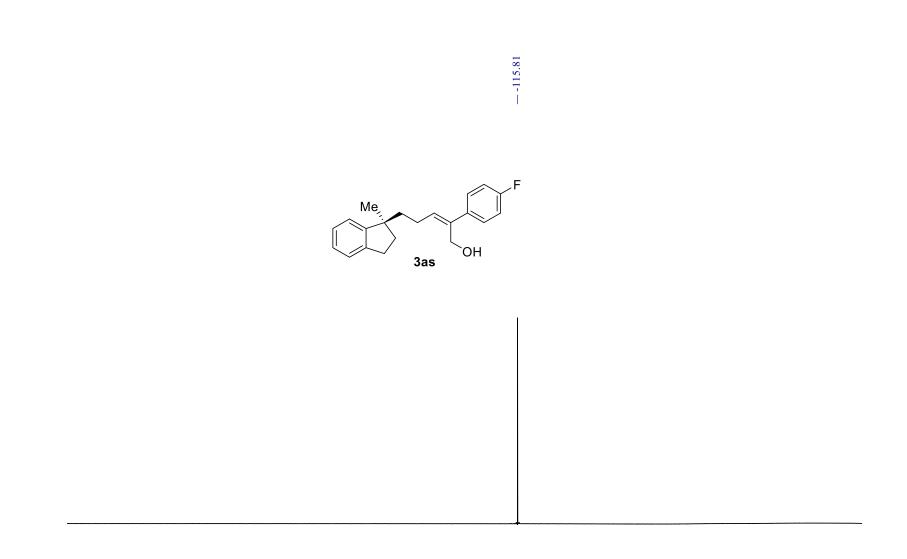




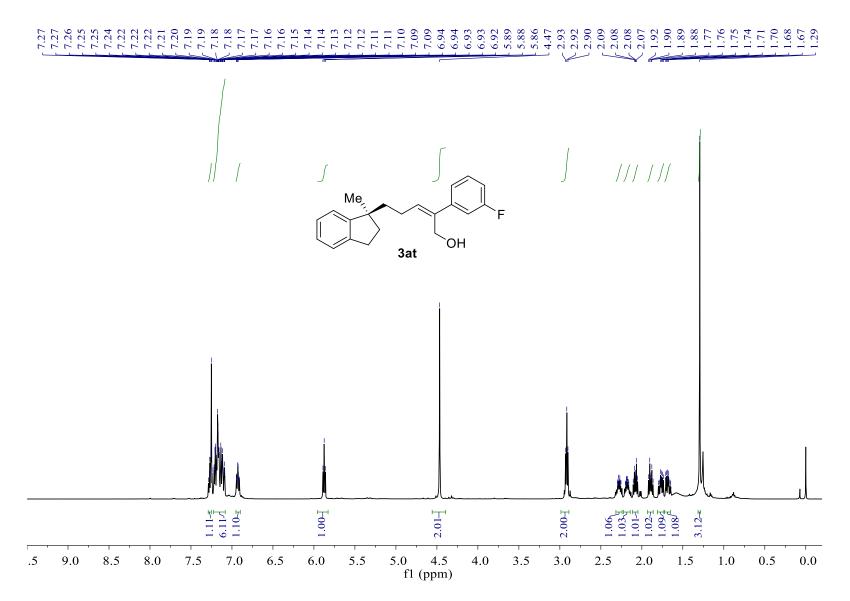


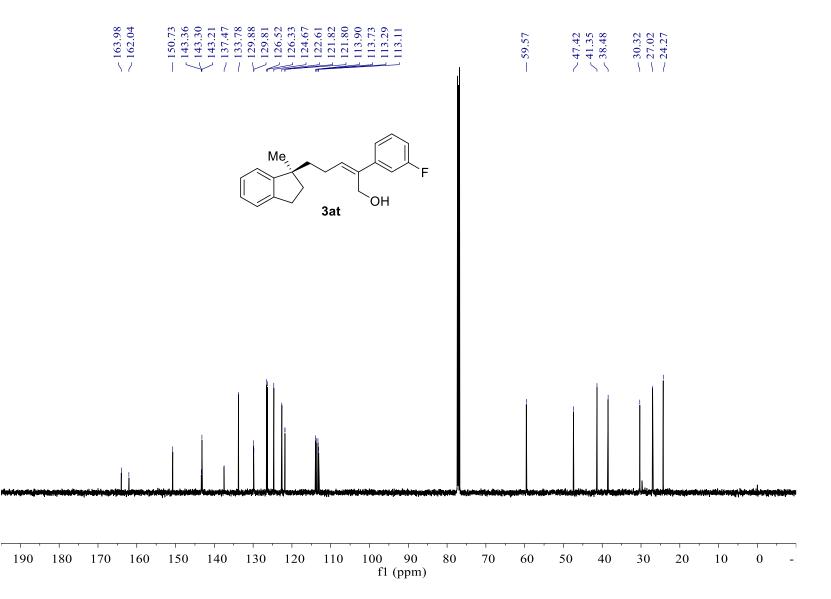


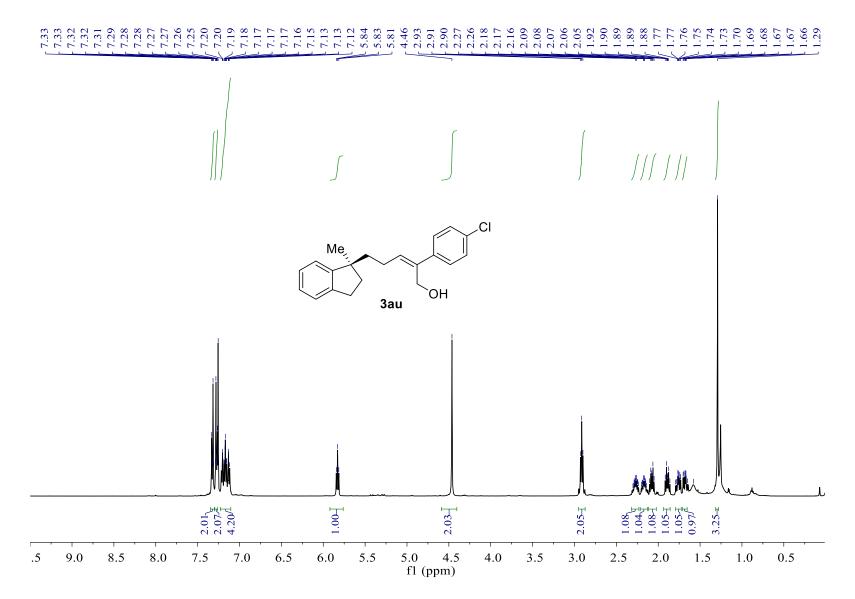


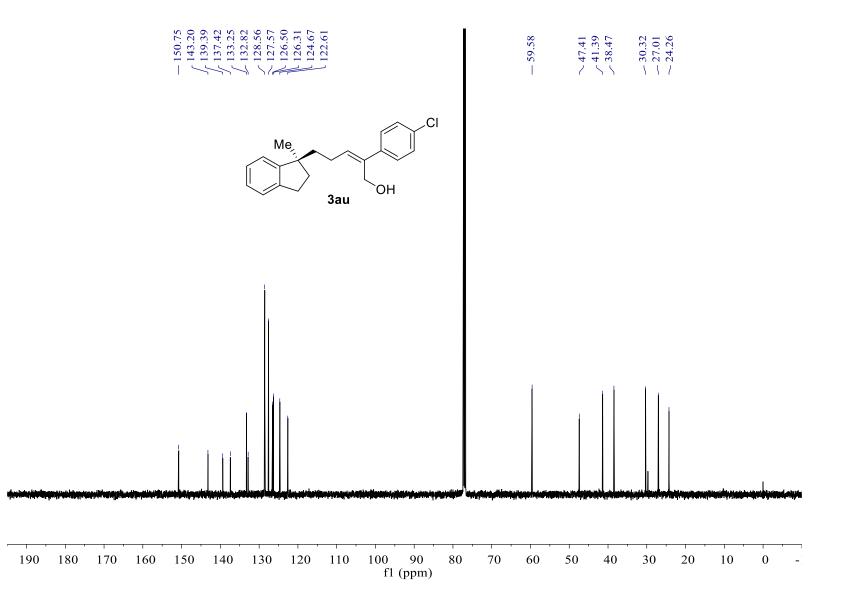


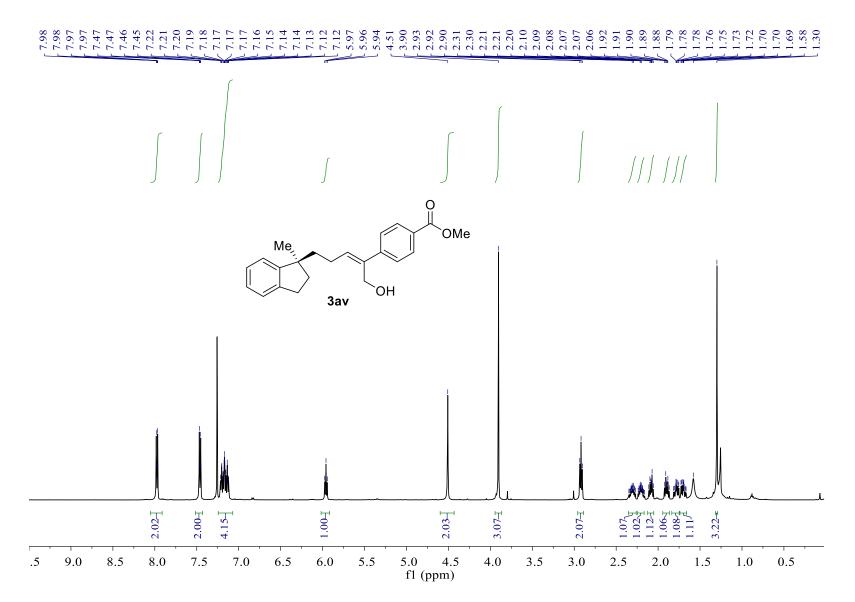
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 fl (ppm)

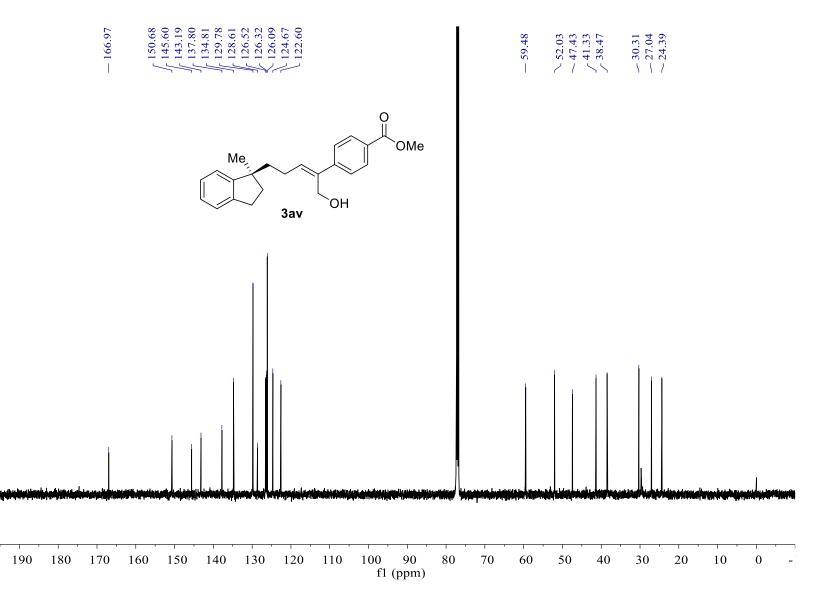


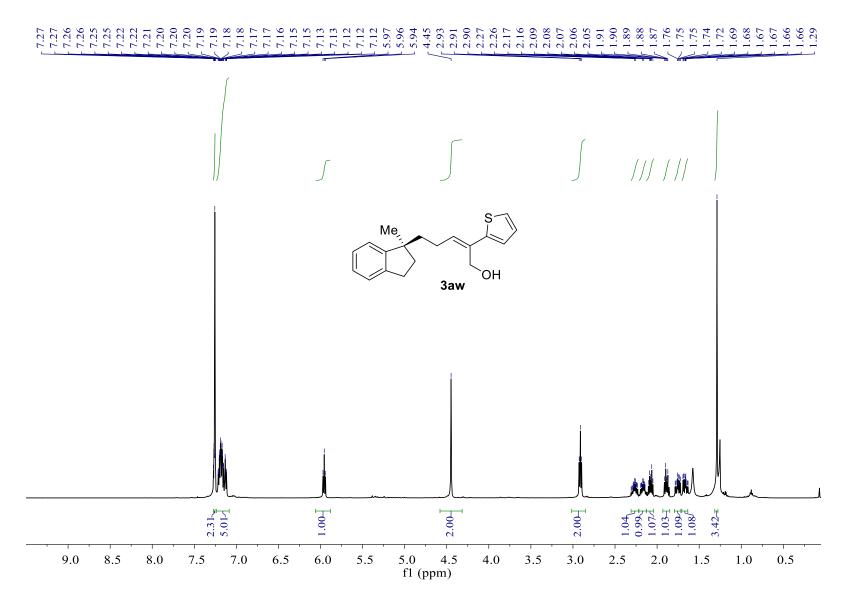


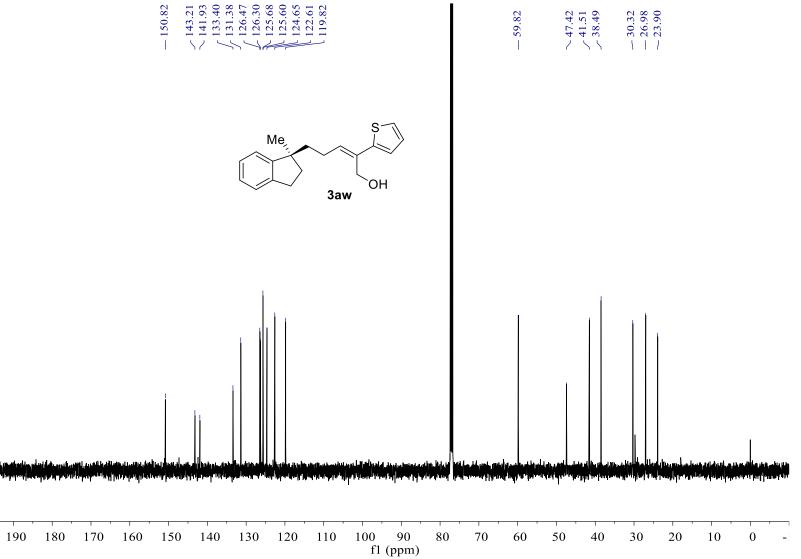




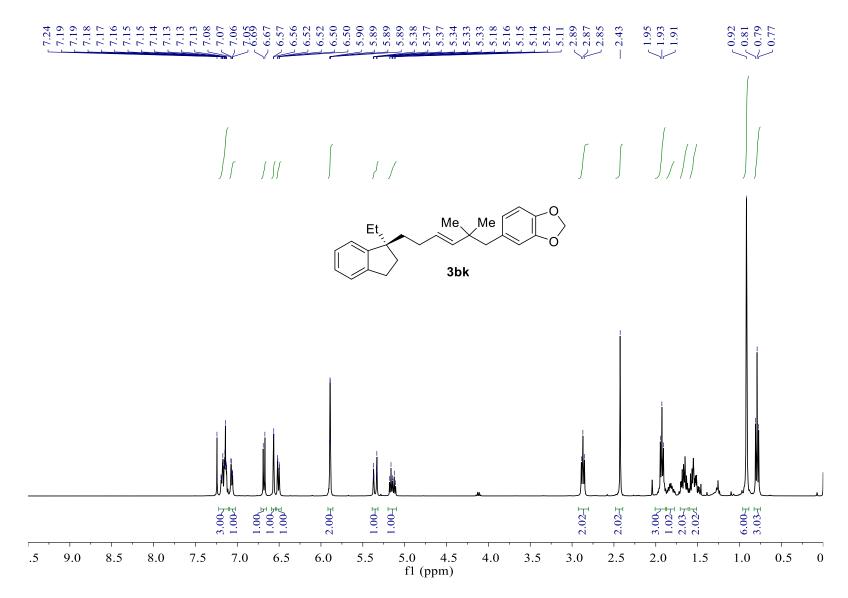


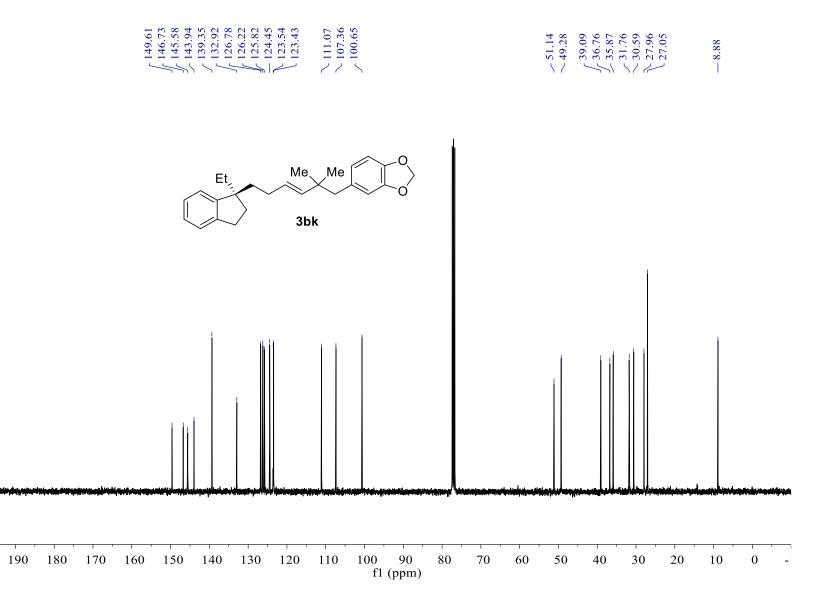


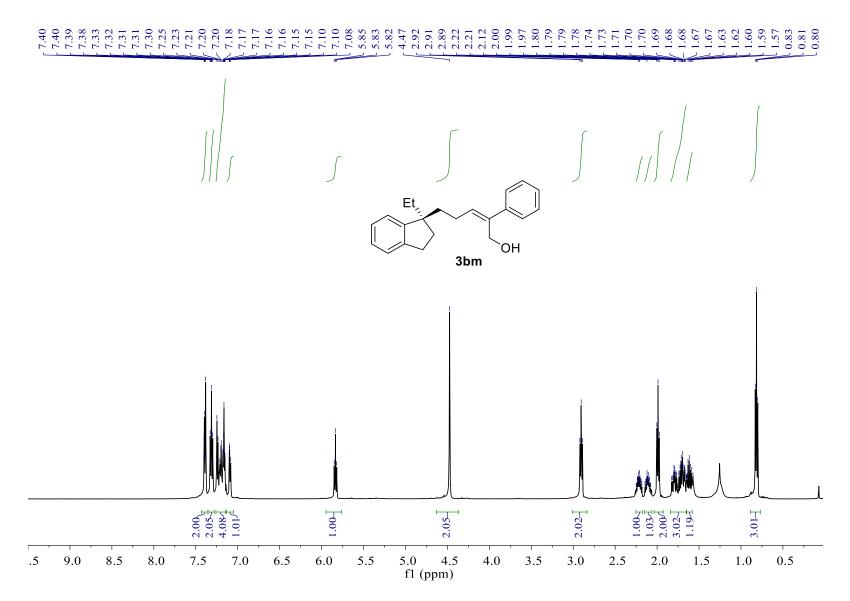


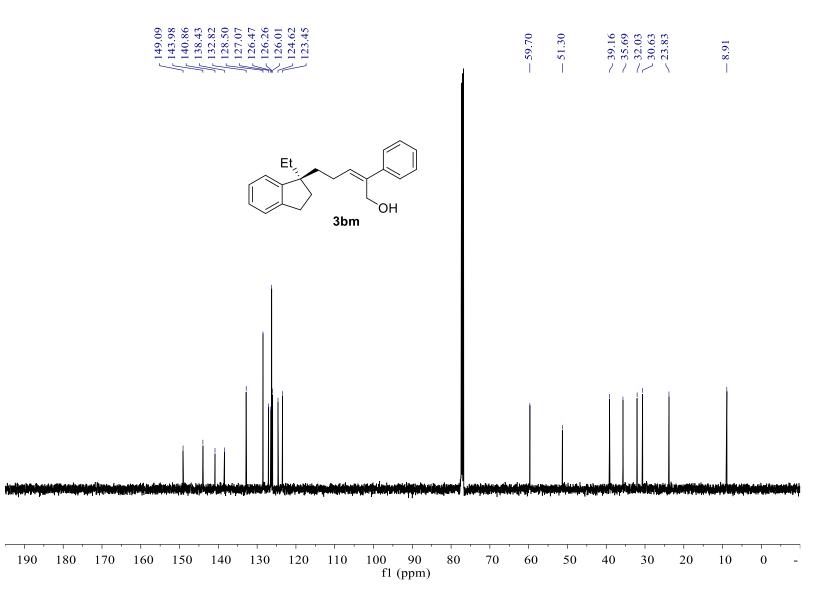


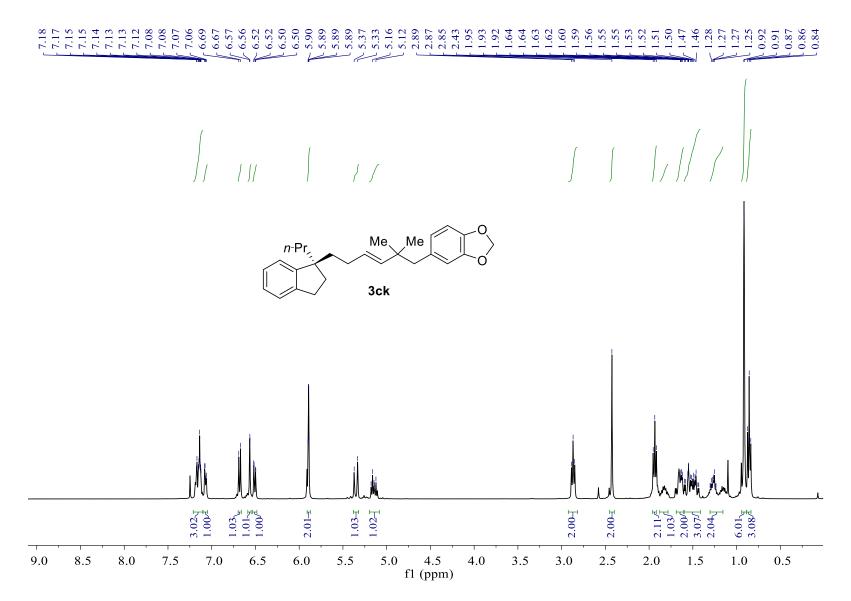


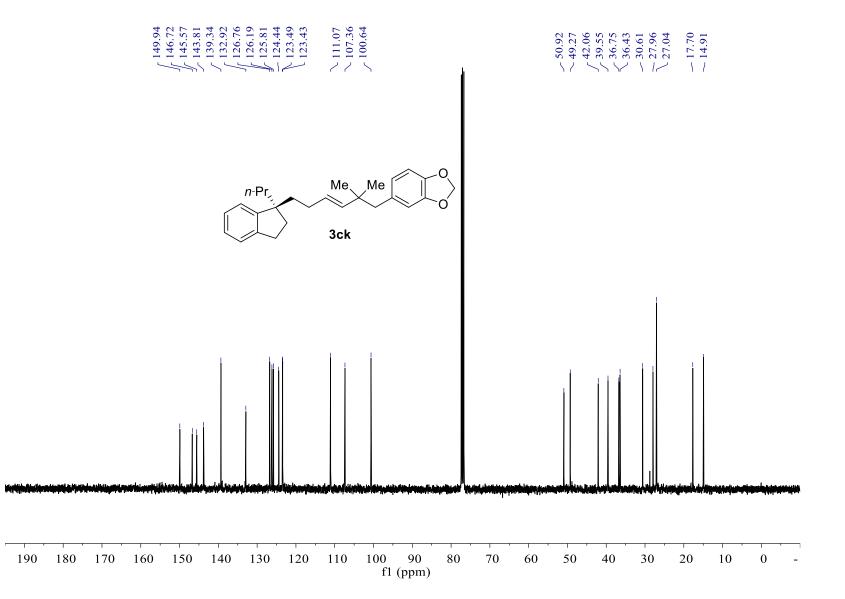


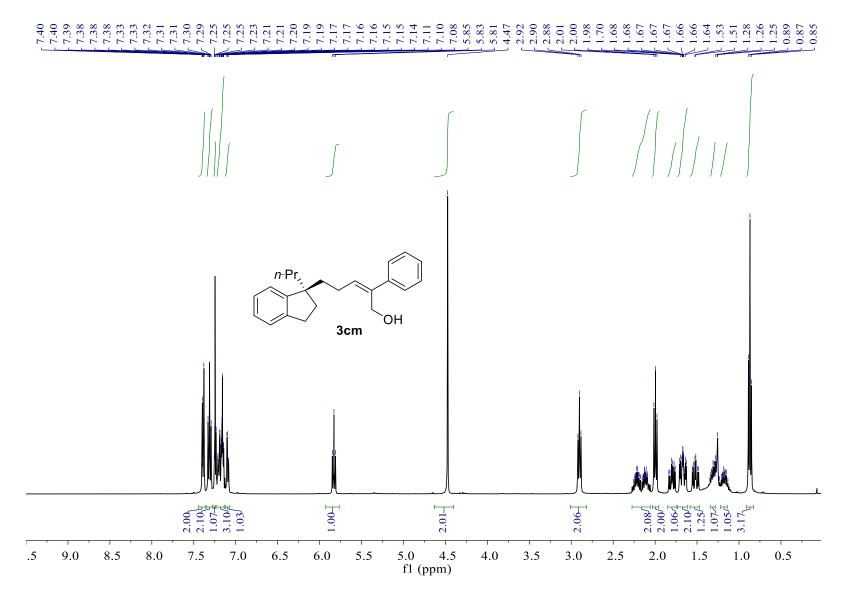


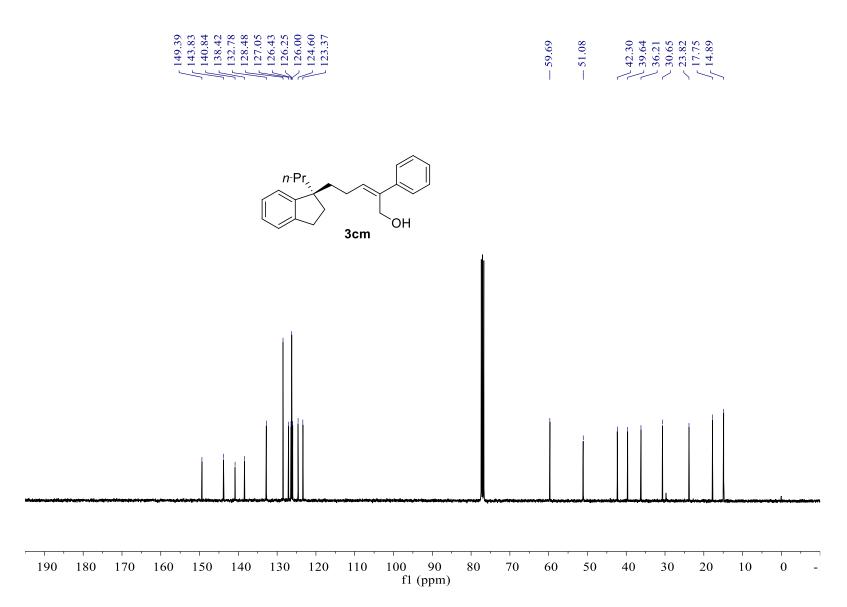


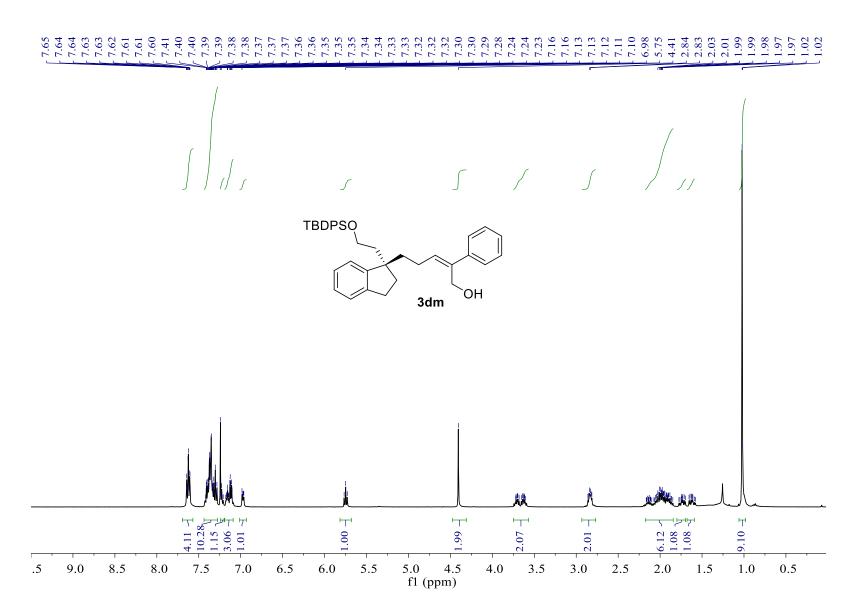


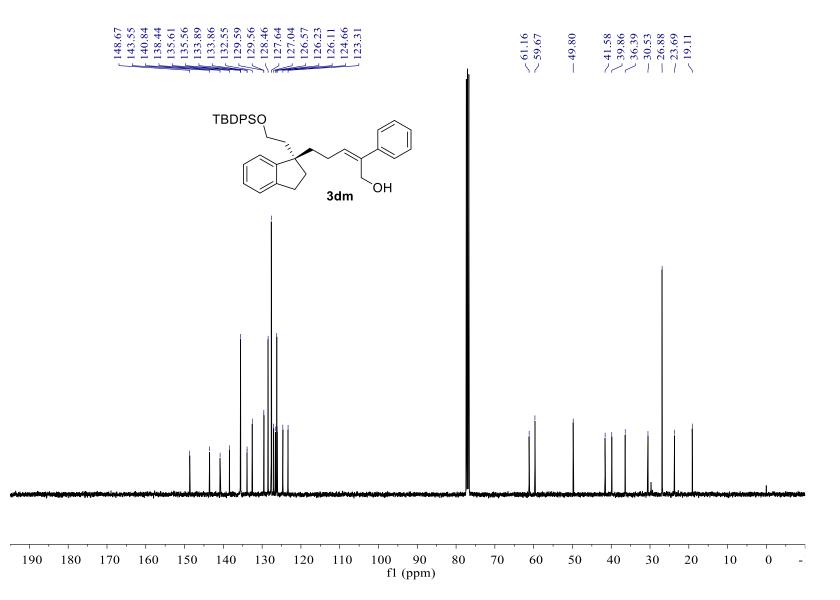


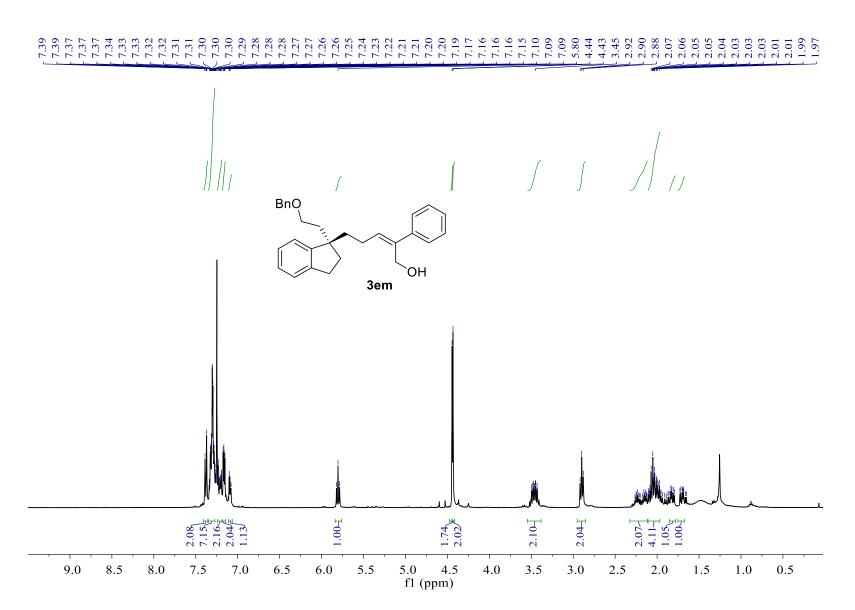


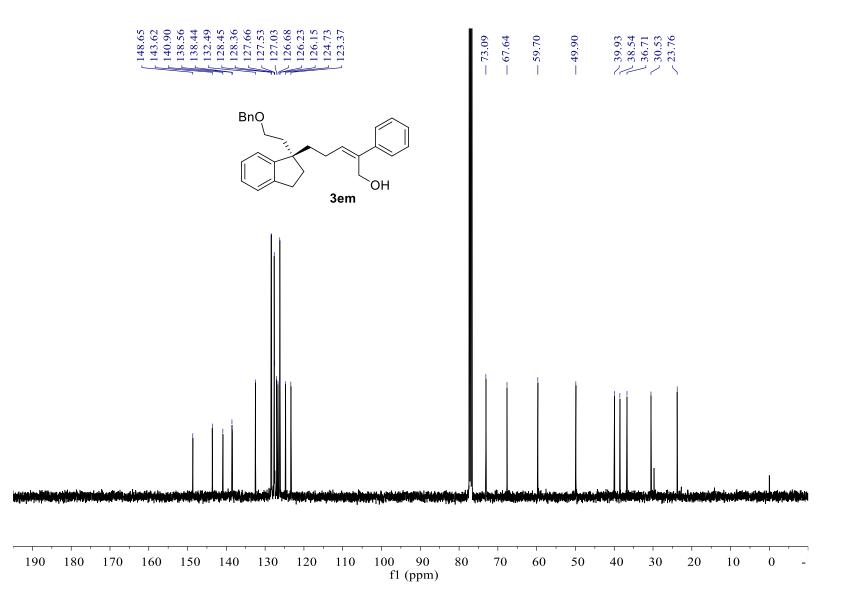


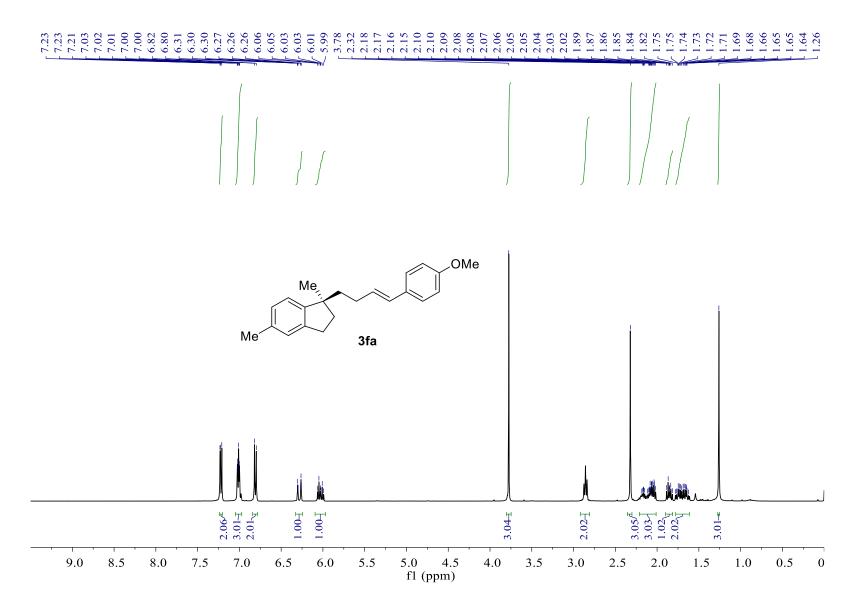


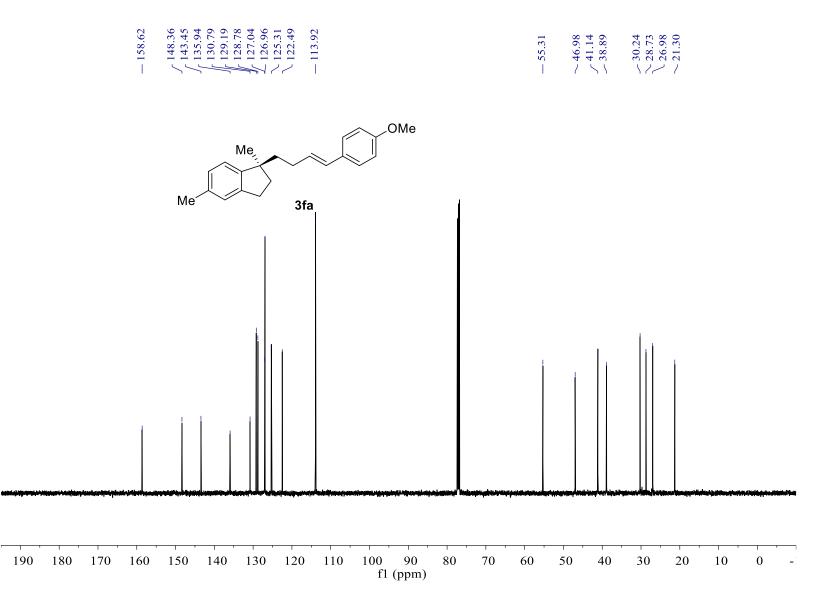


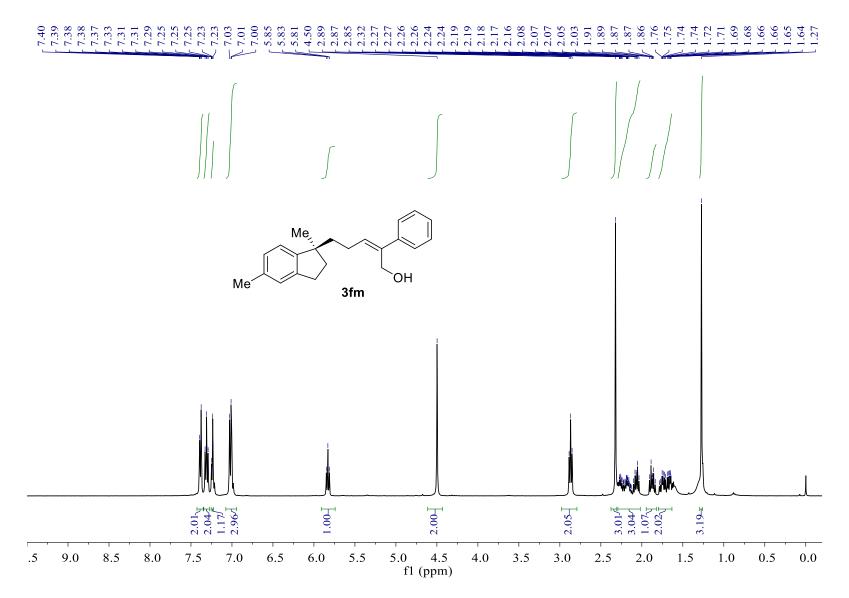


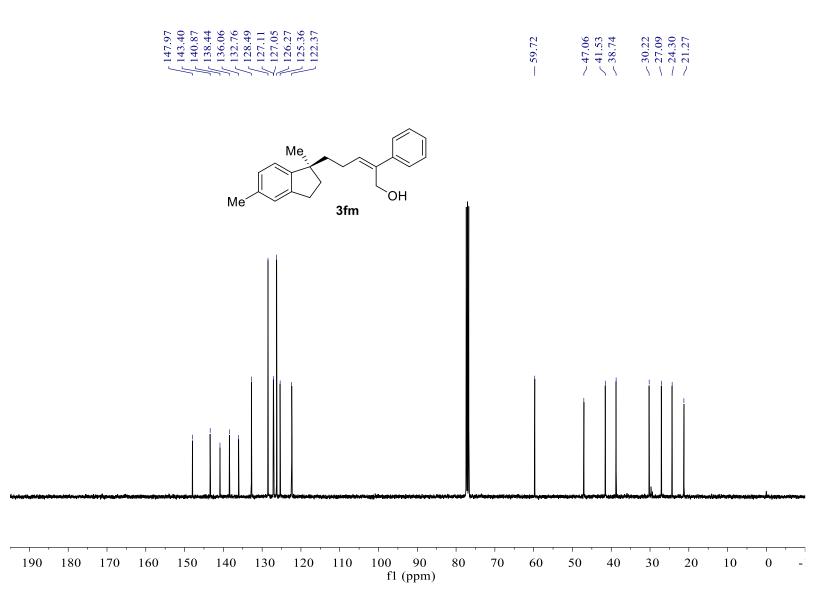


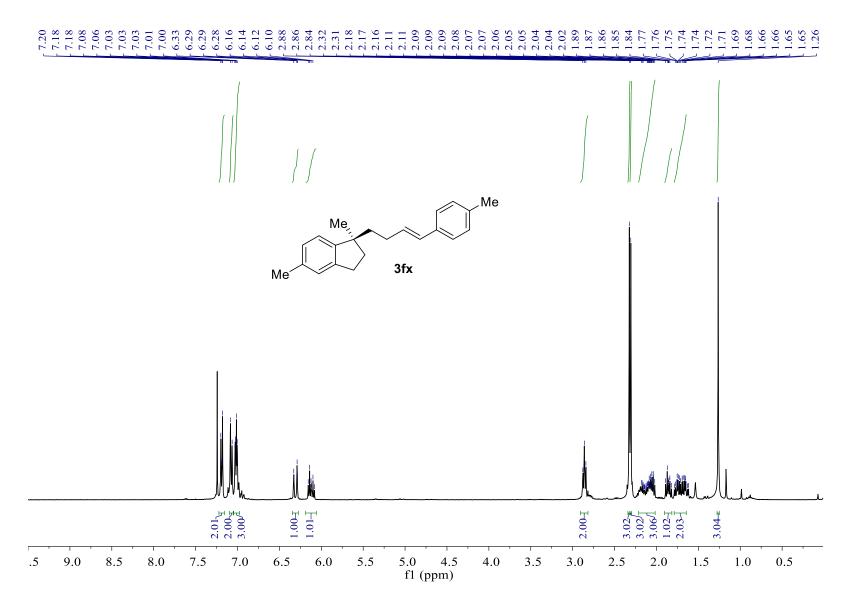


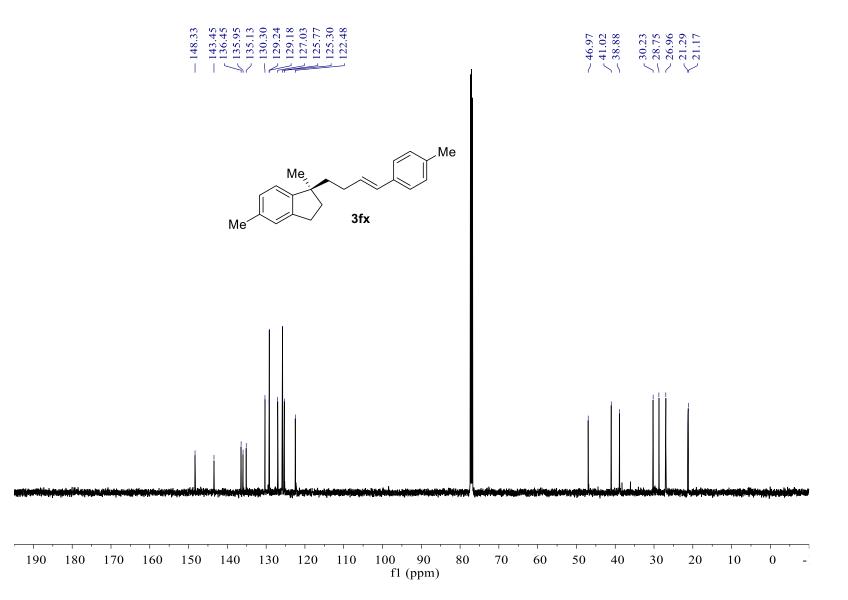


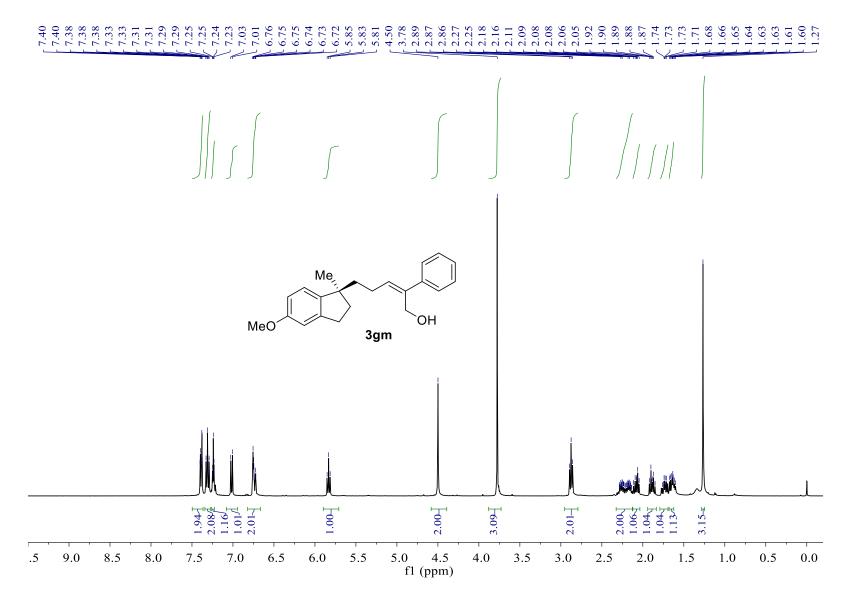


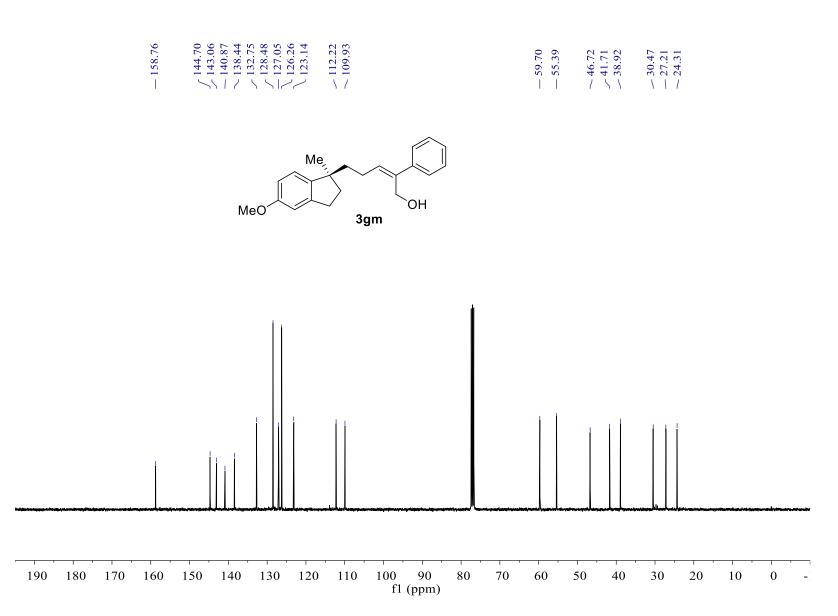


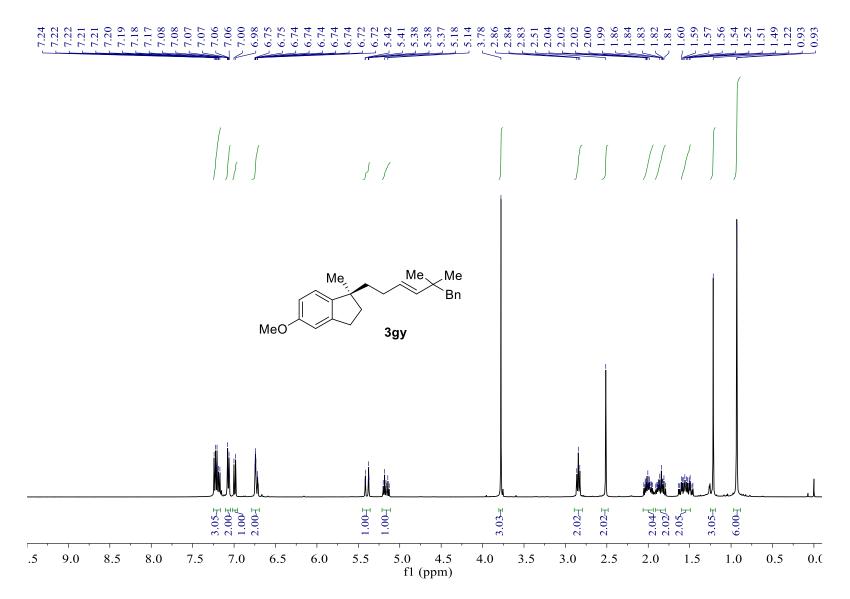


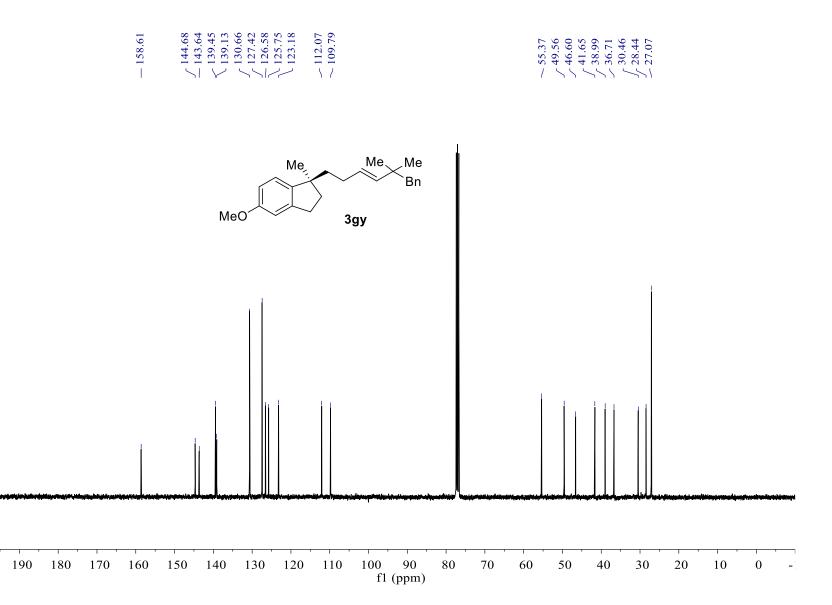


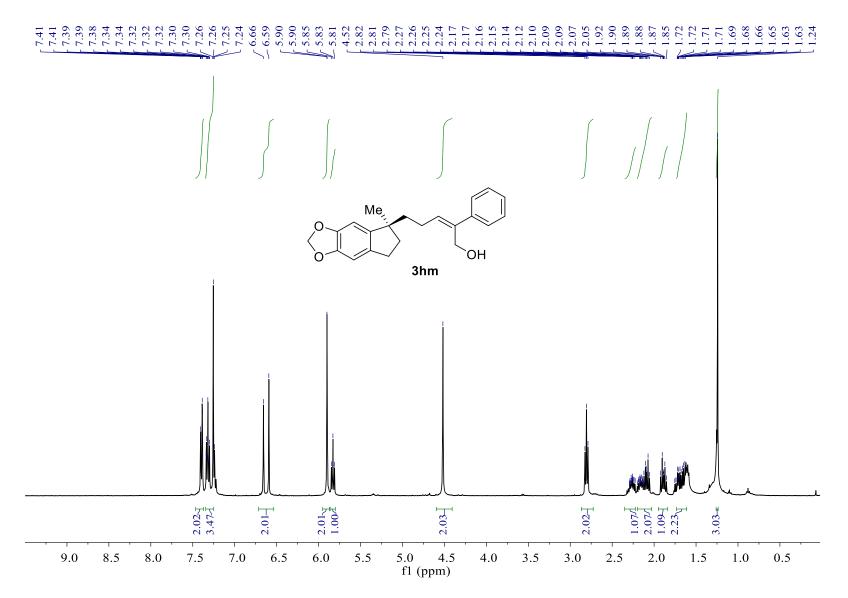


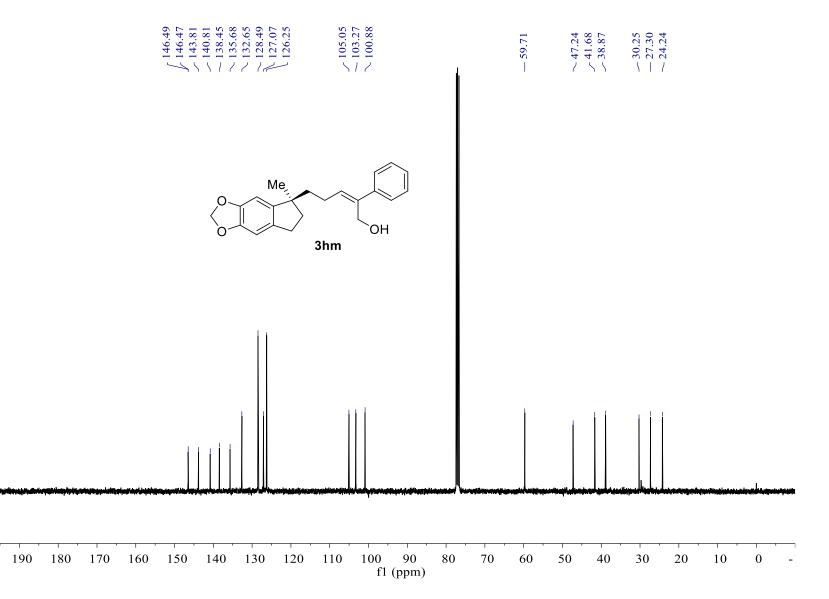


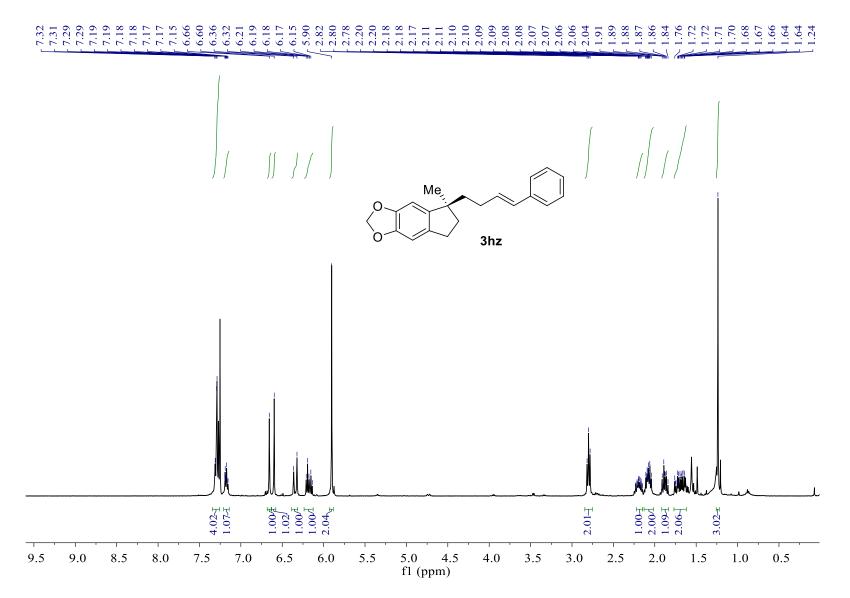


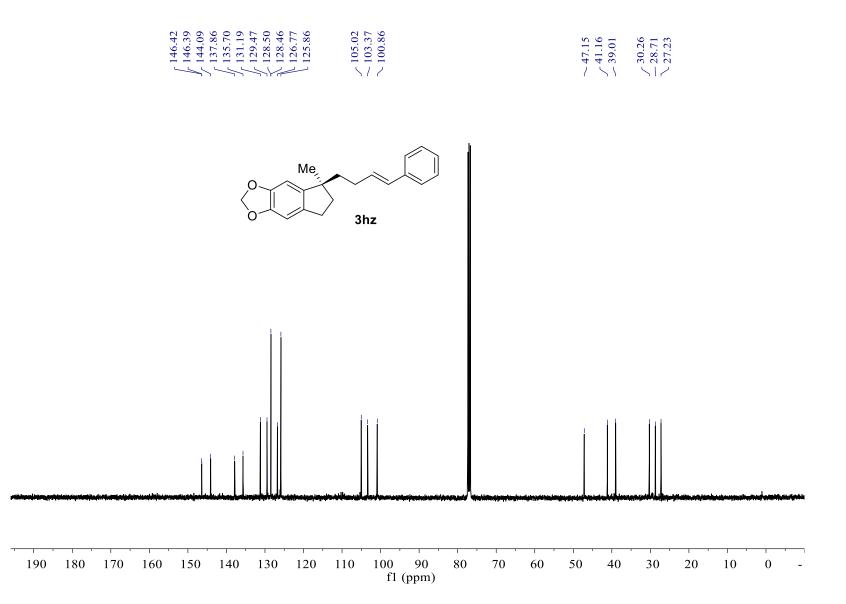


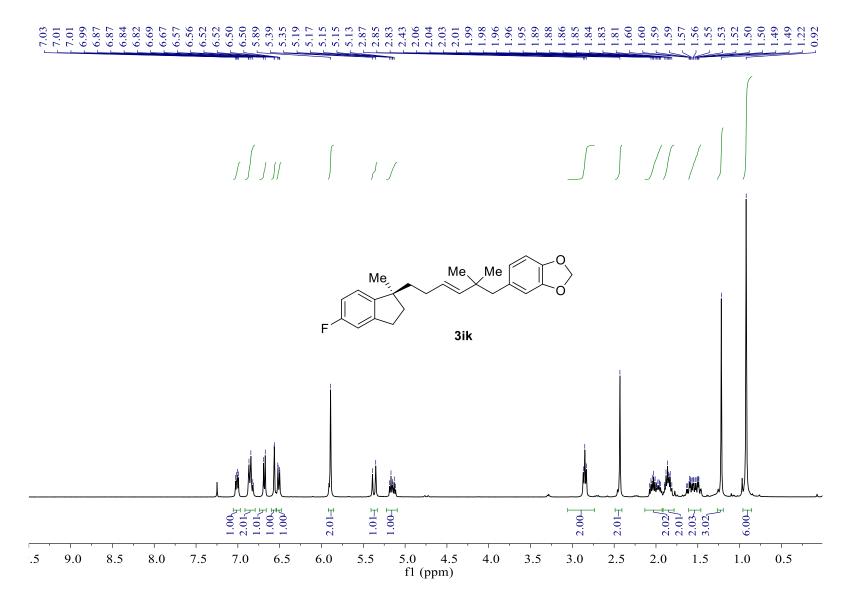


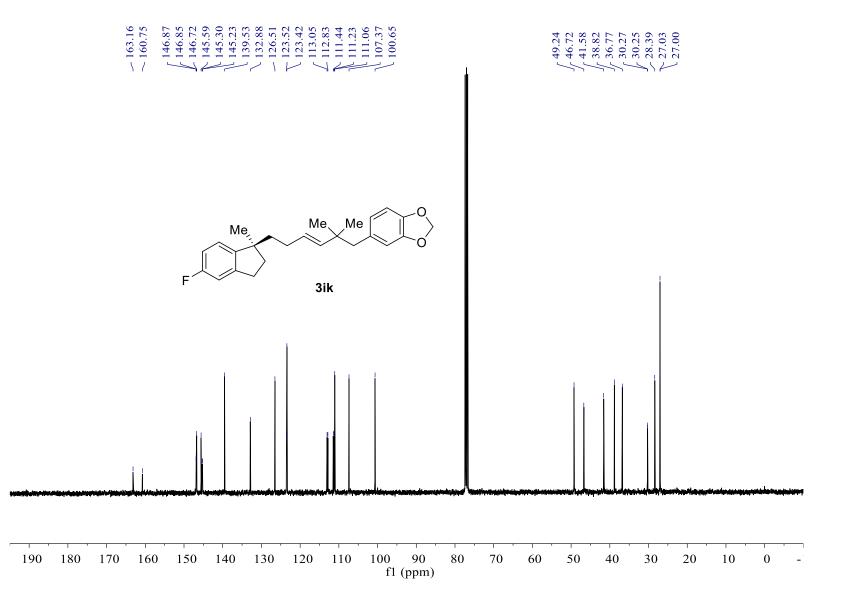


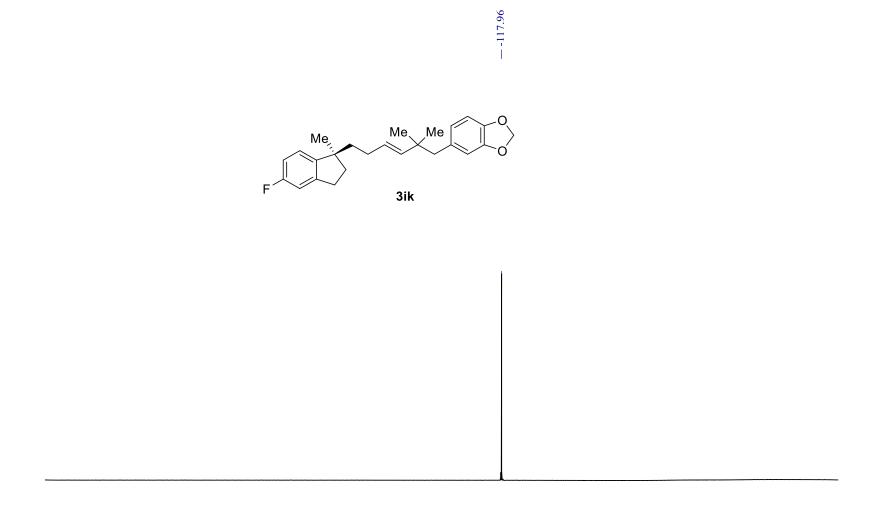




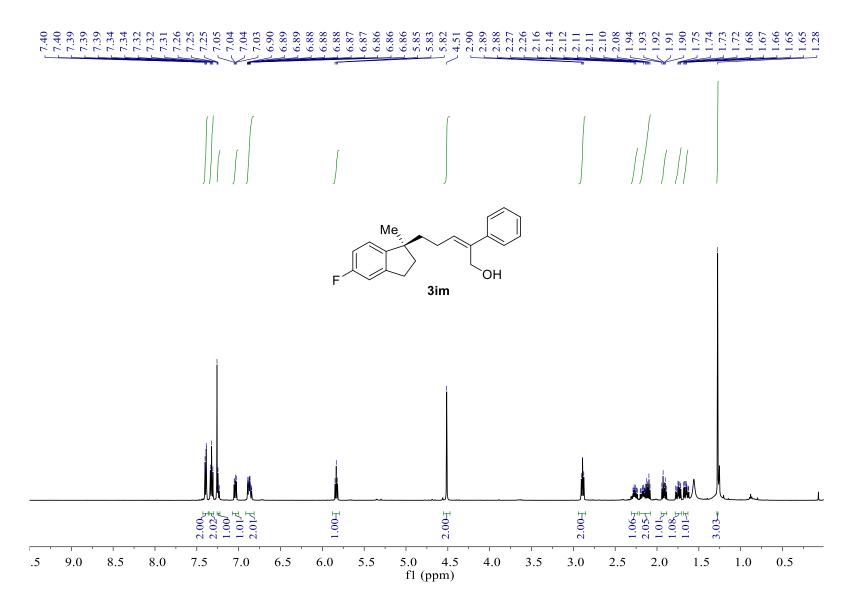




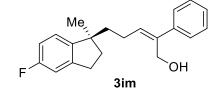


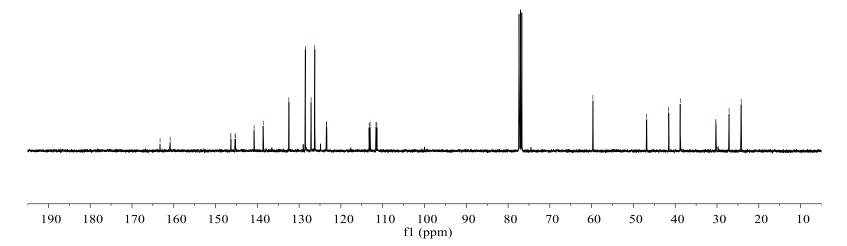


10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 fl (ppm)

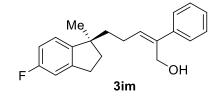


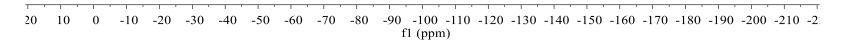


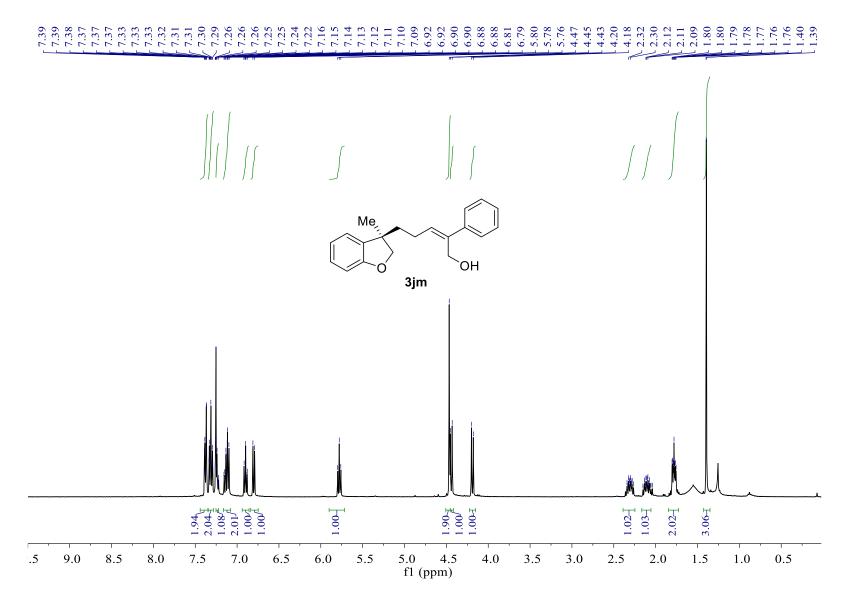


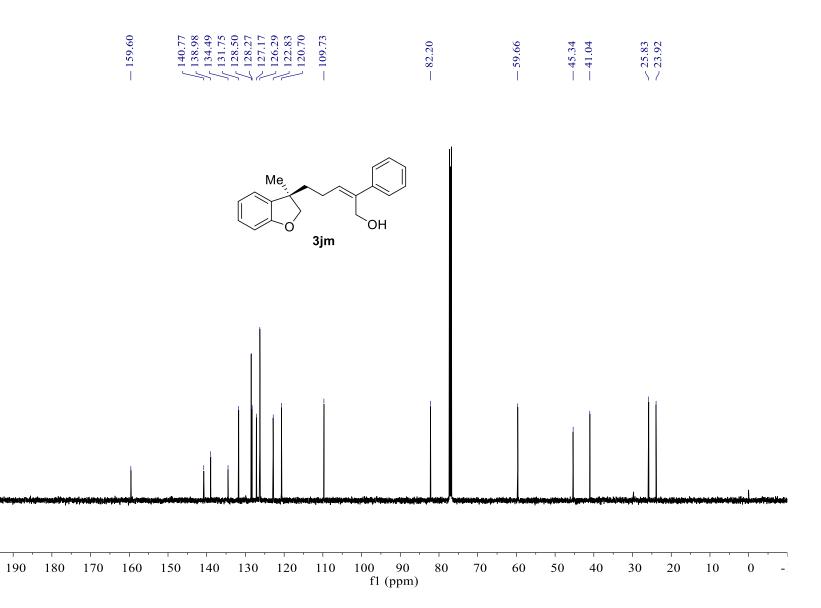




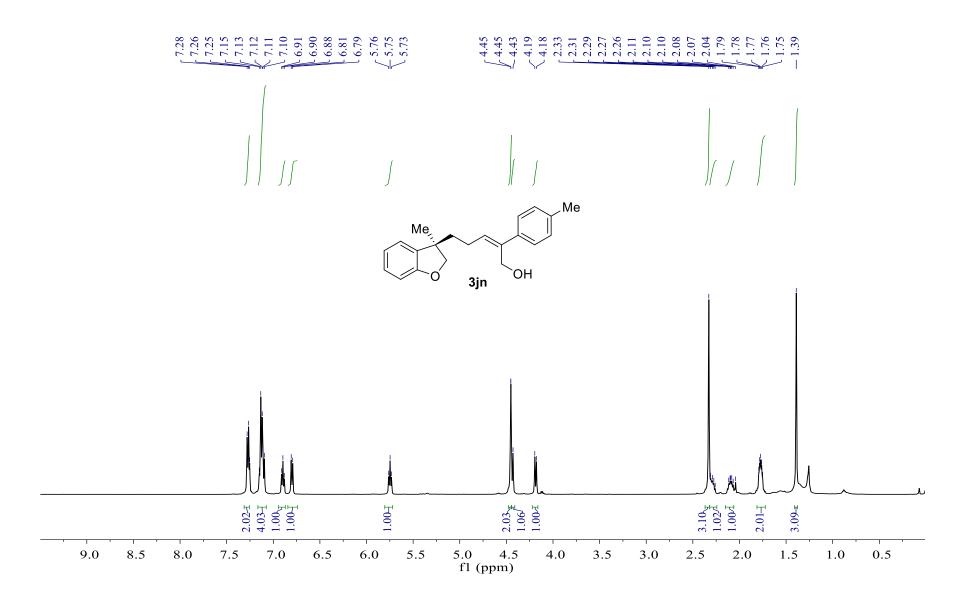


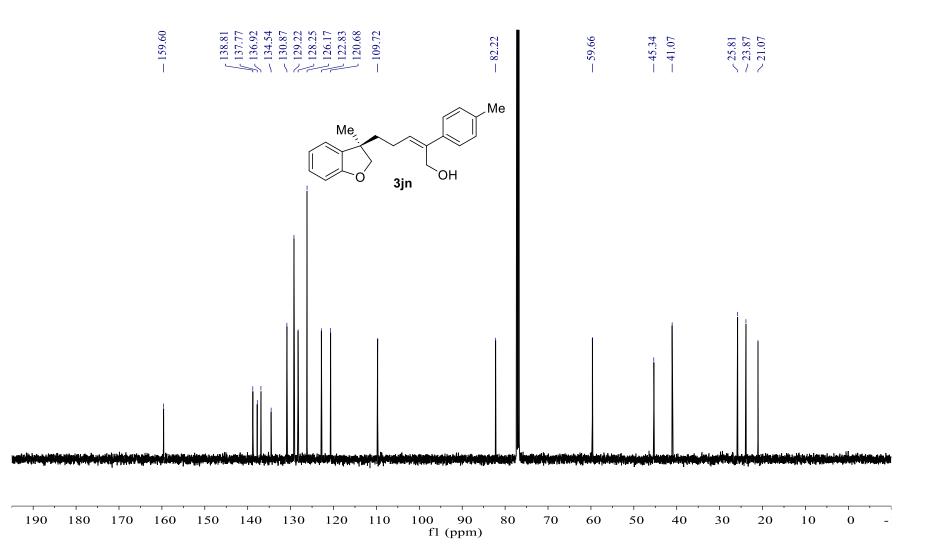


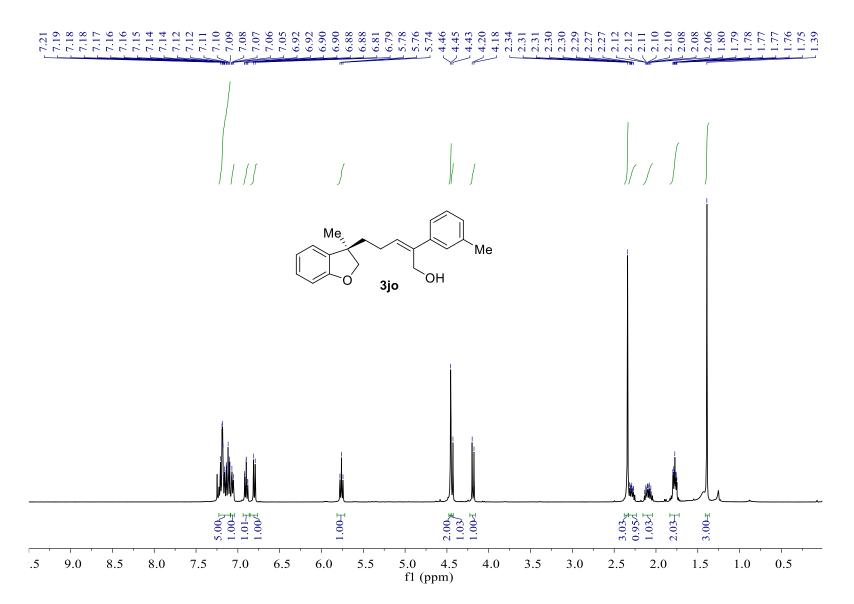


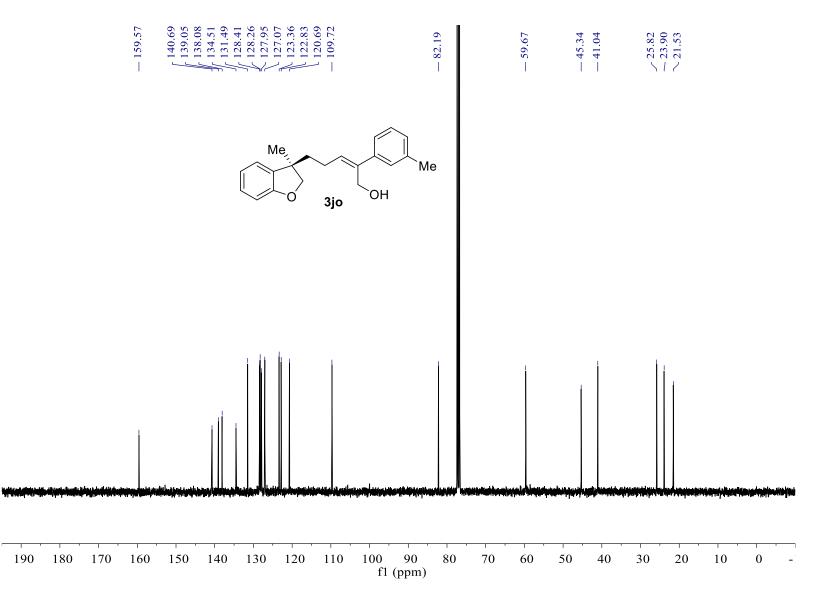


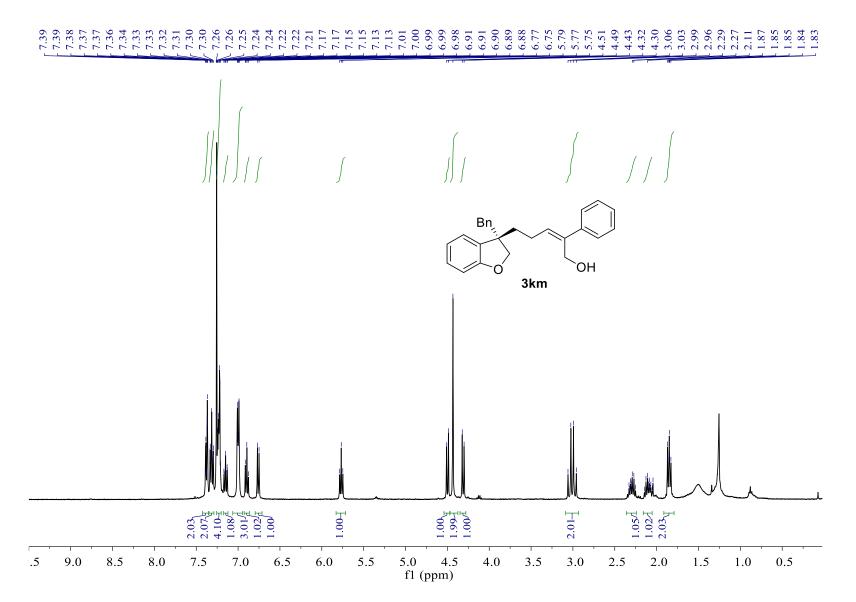


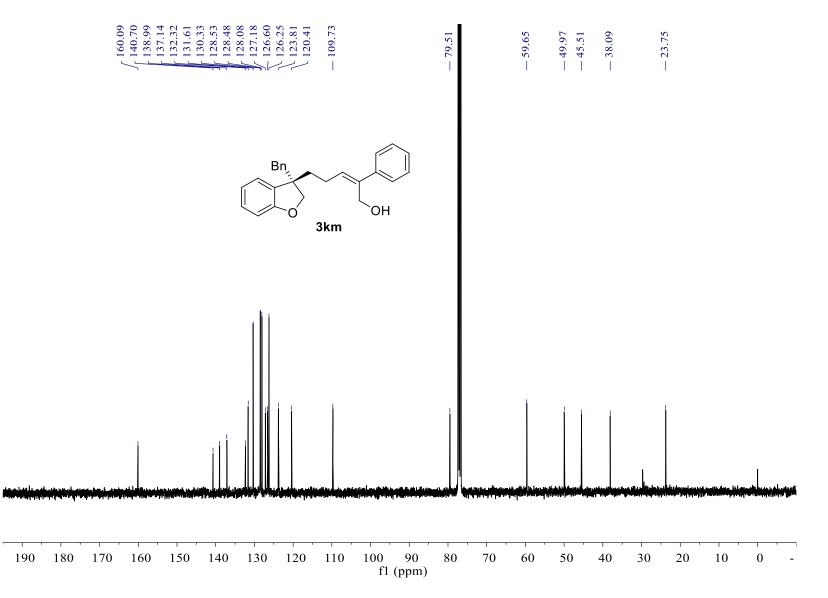


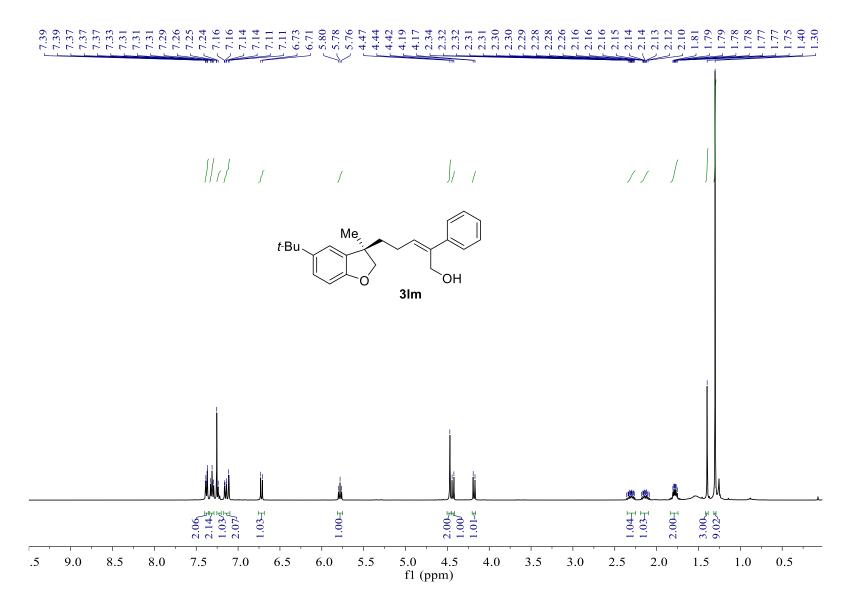


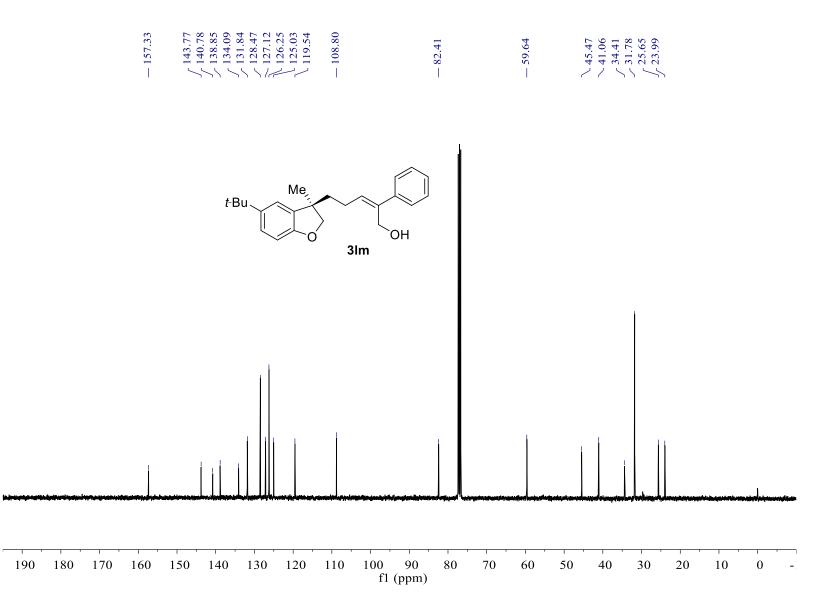


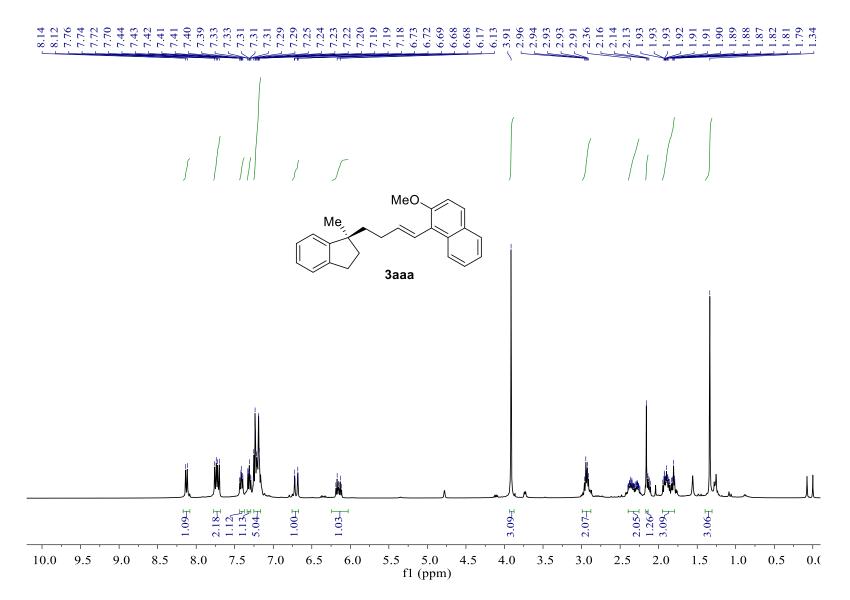


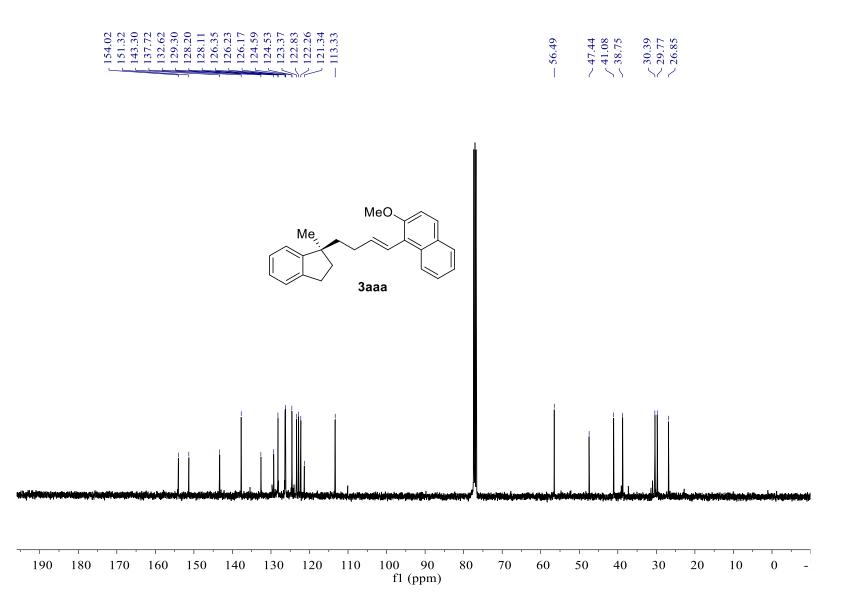


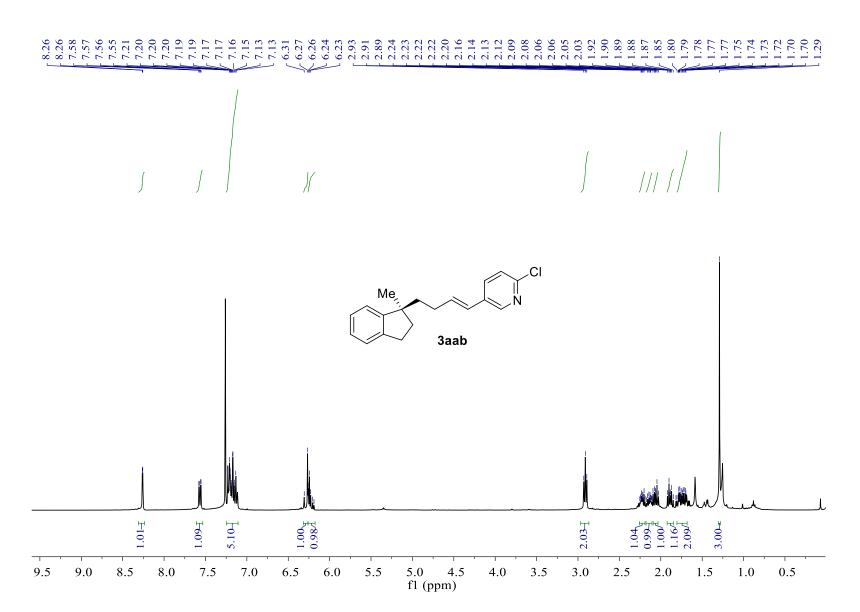


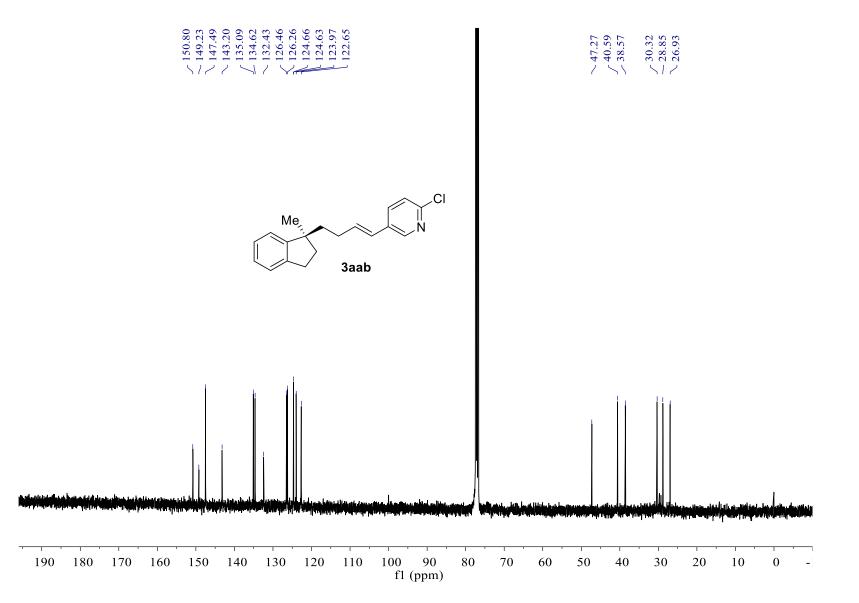


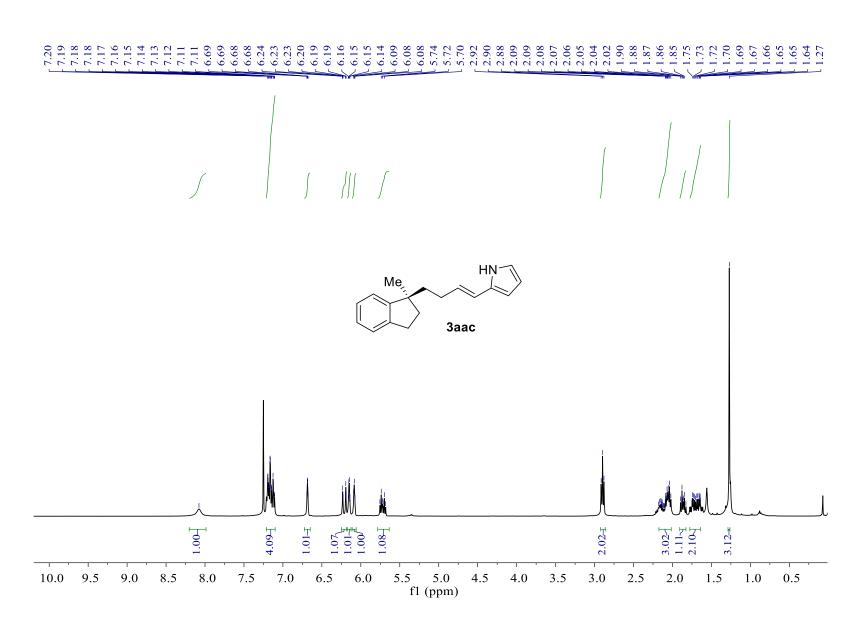


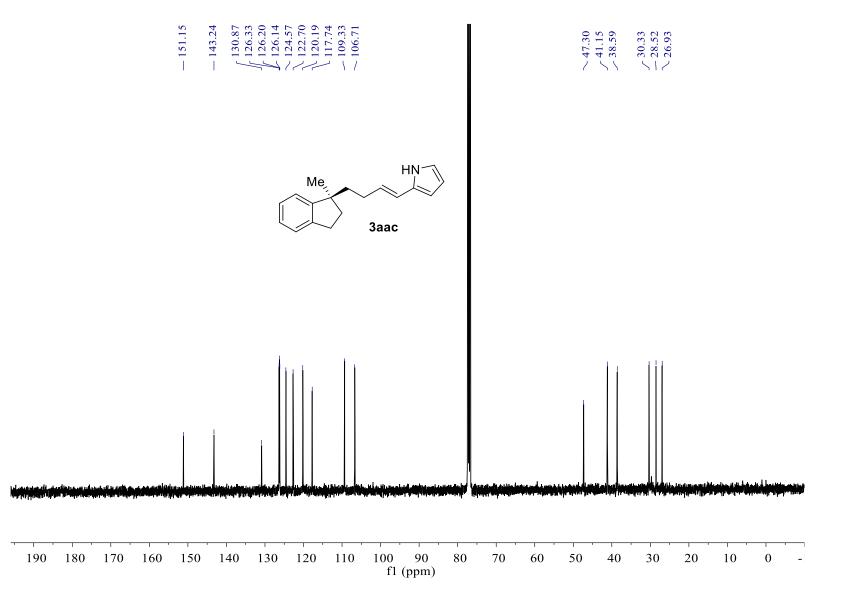


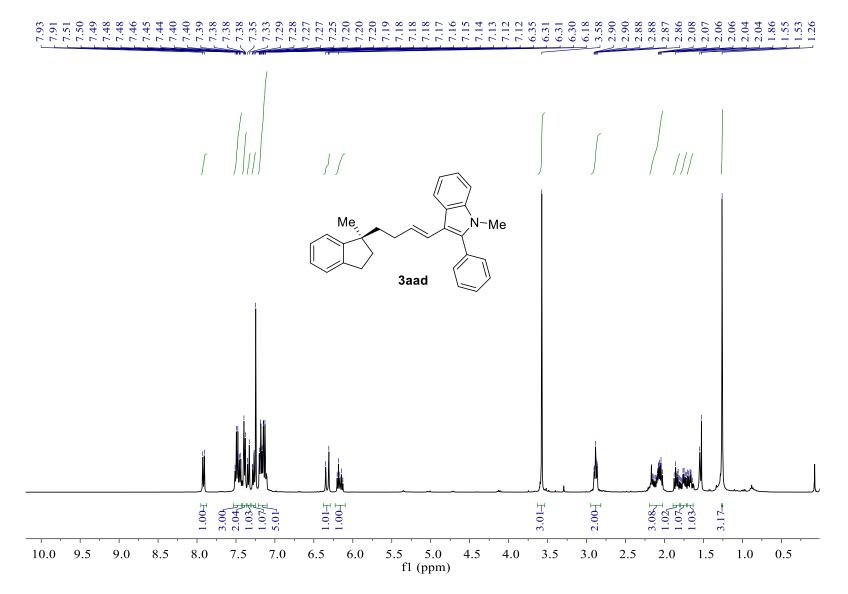


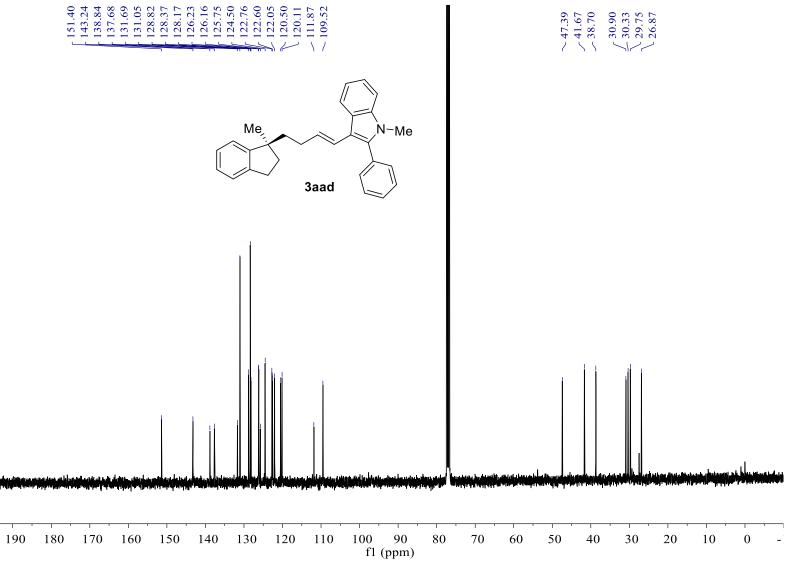




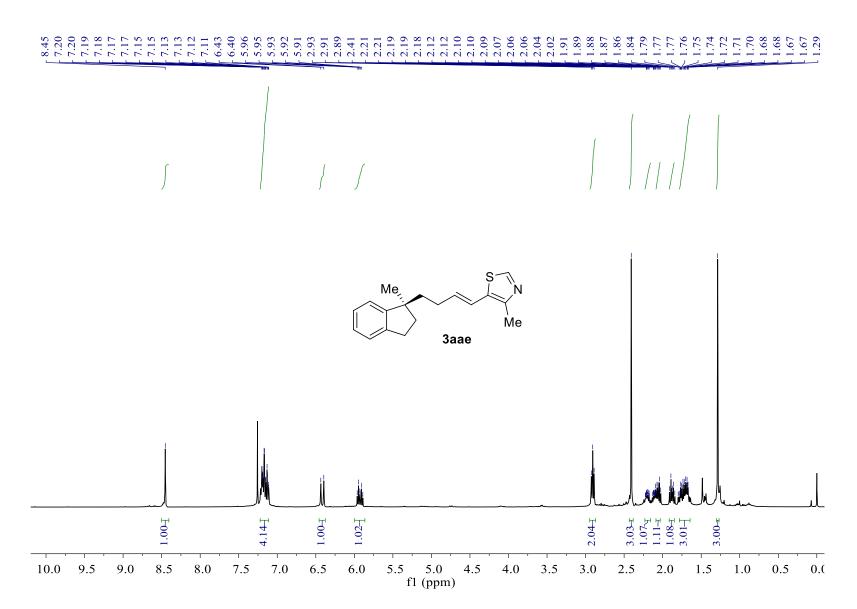


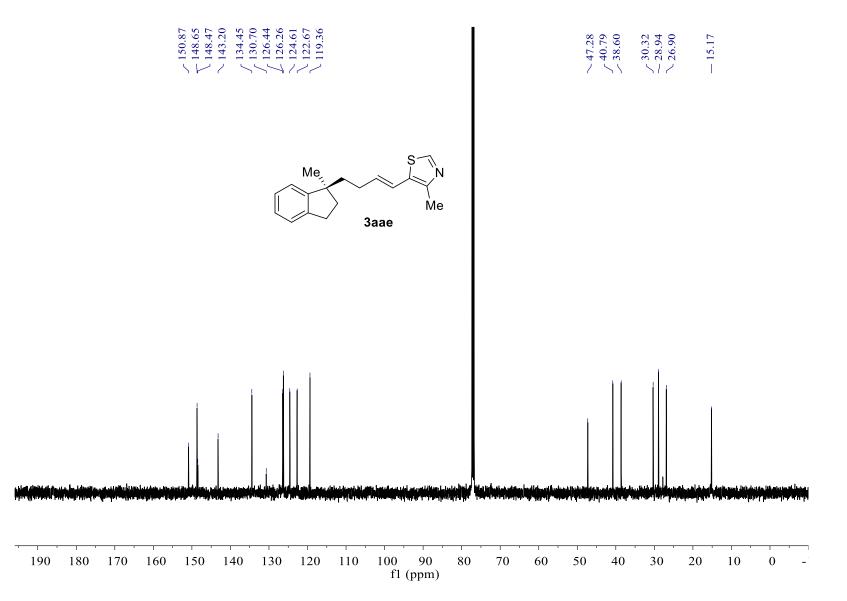


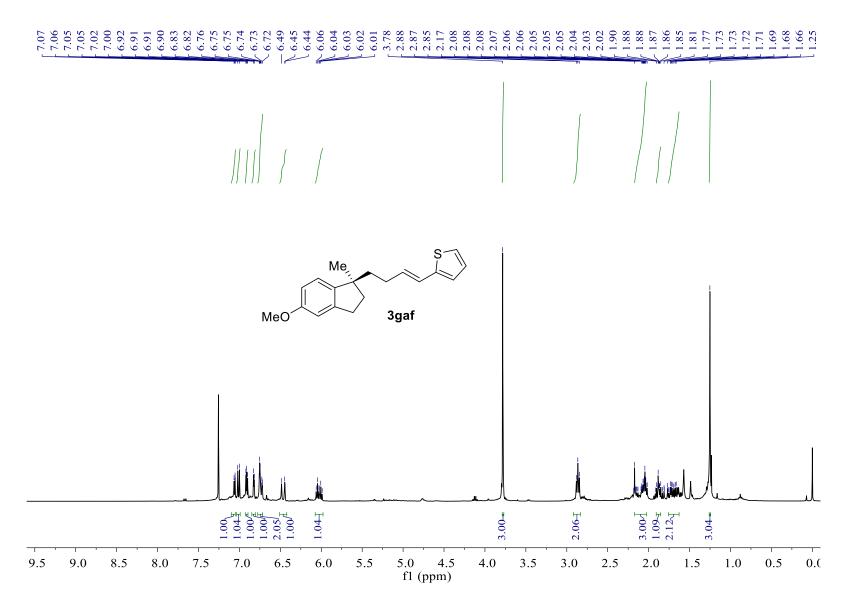


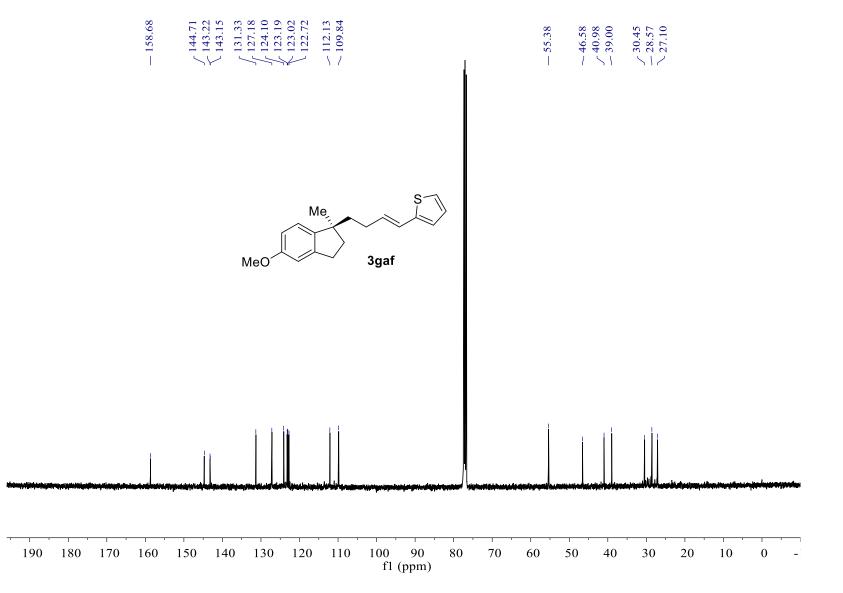


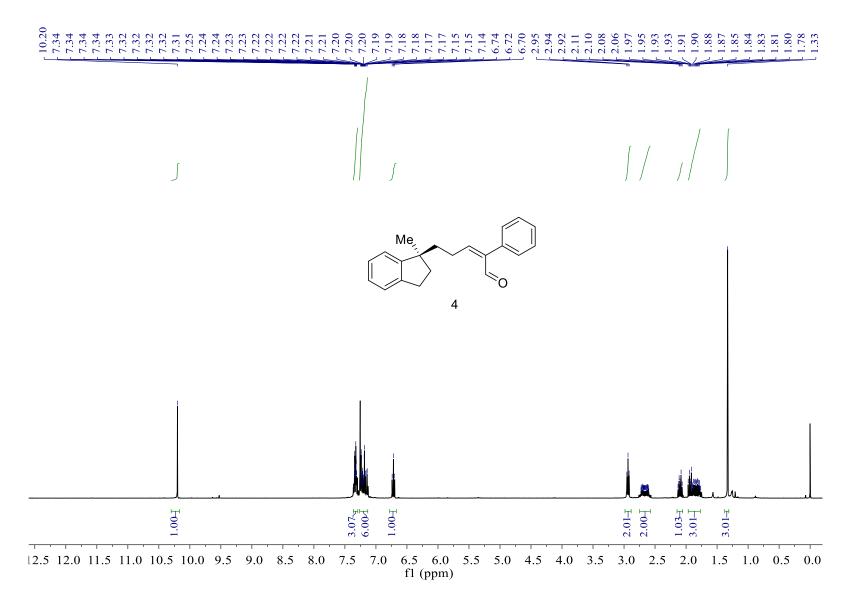


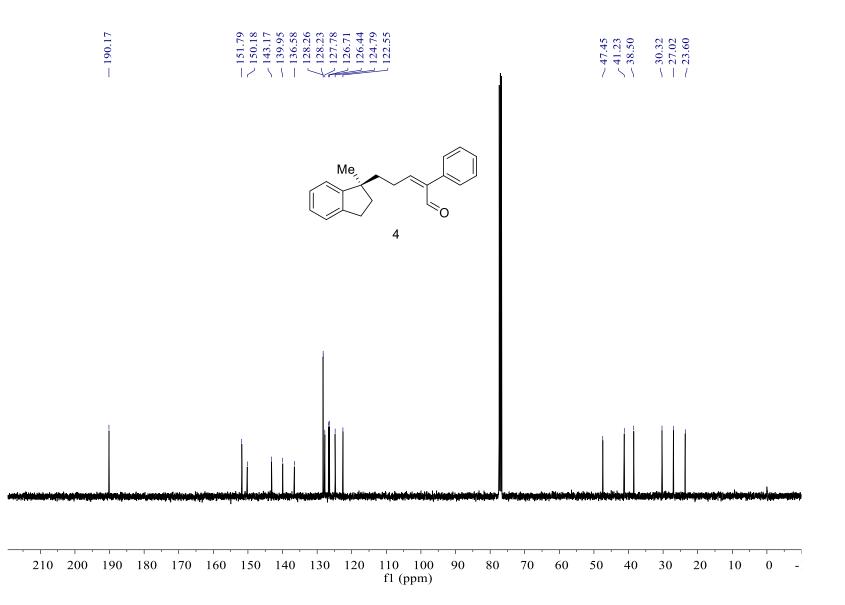


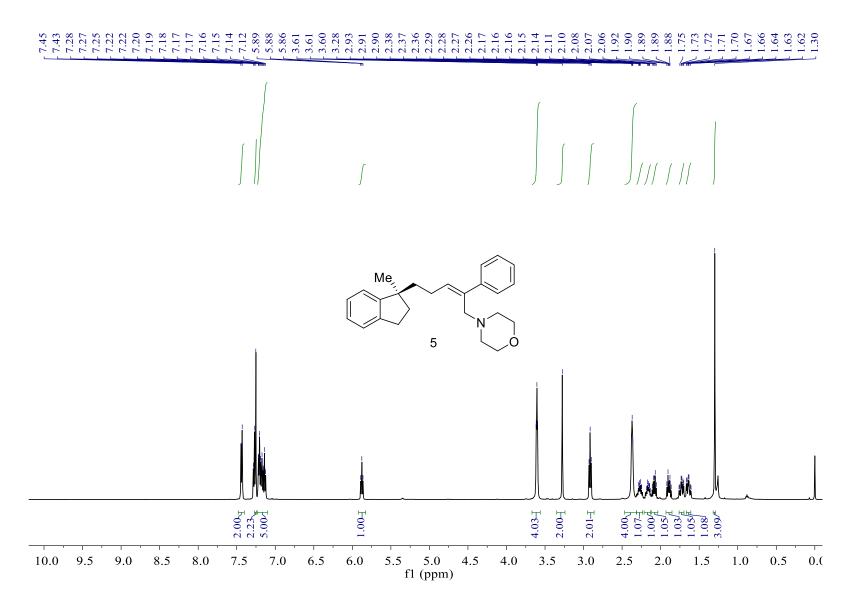


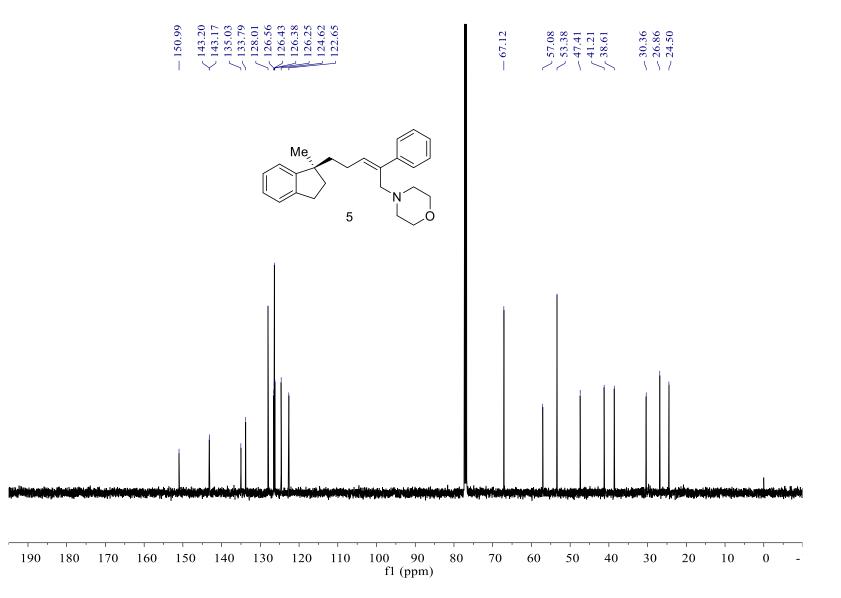


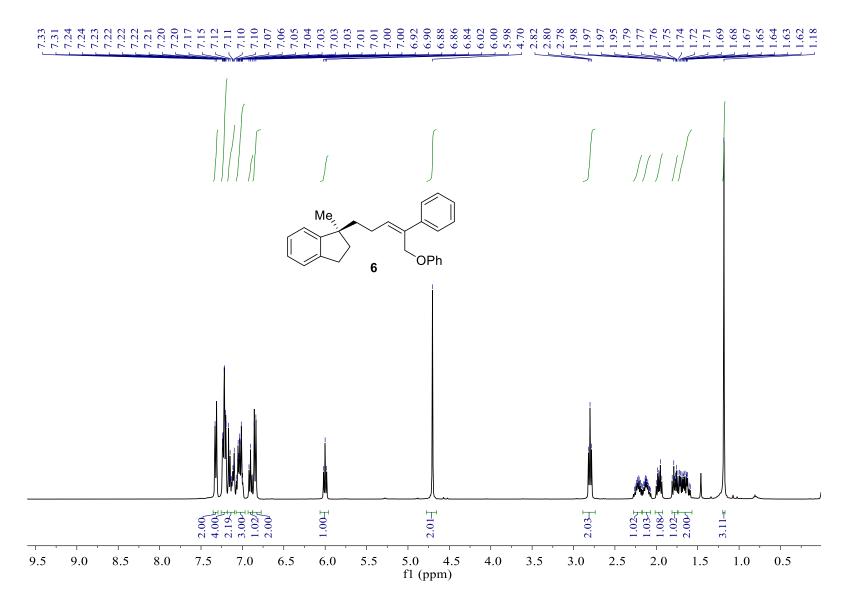


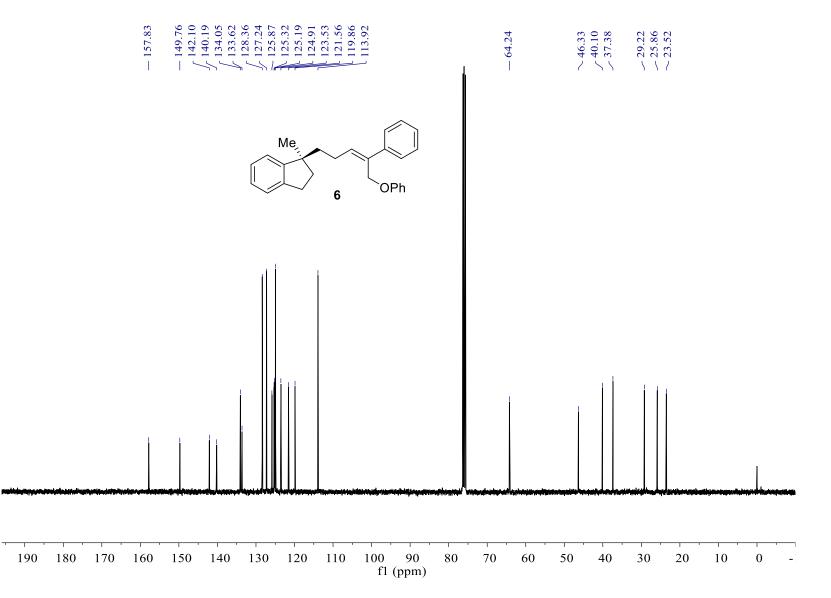


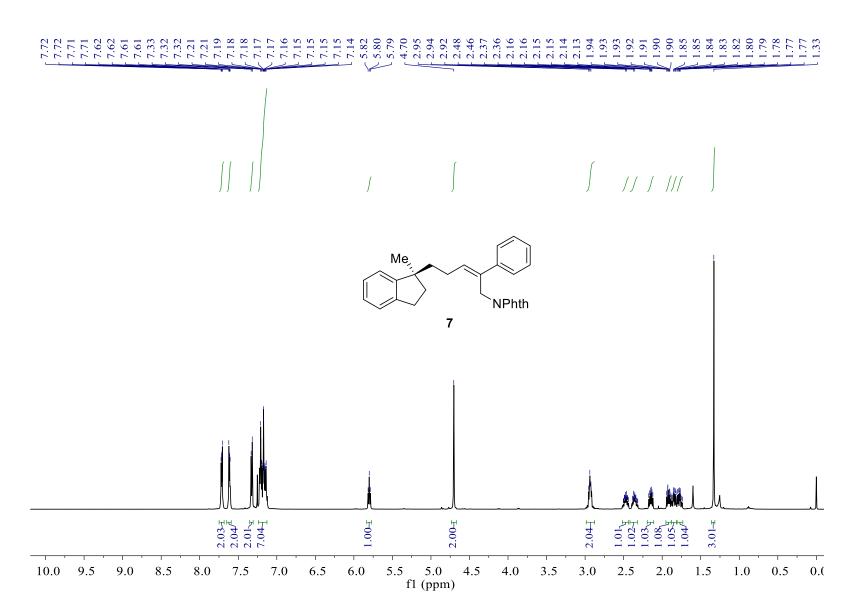


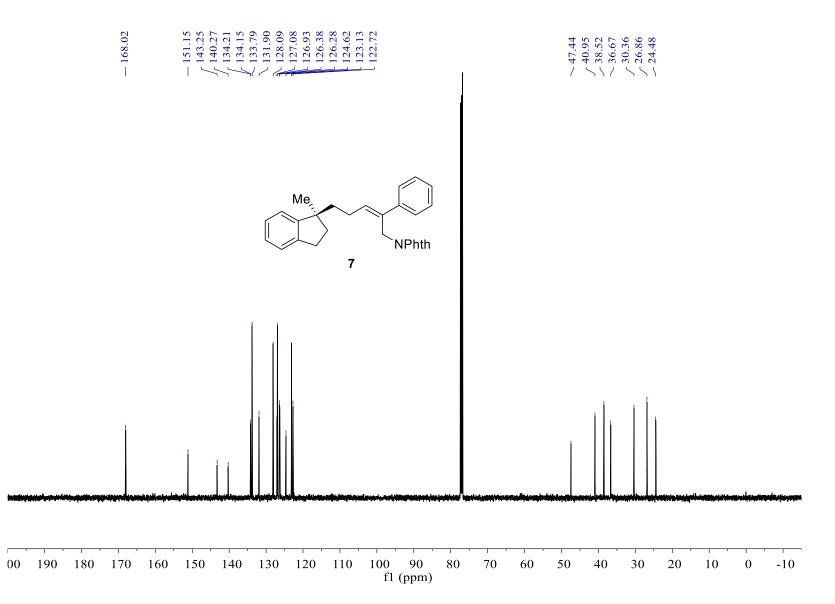


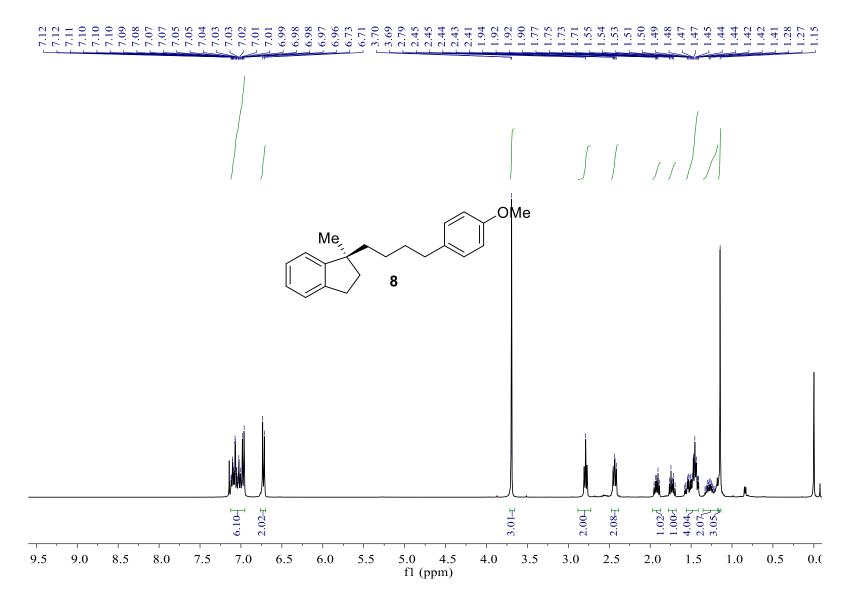


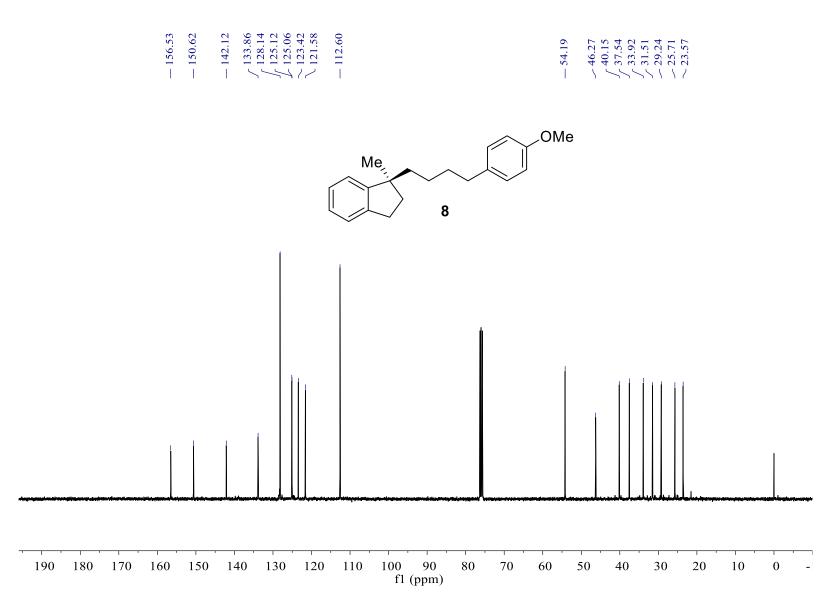




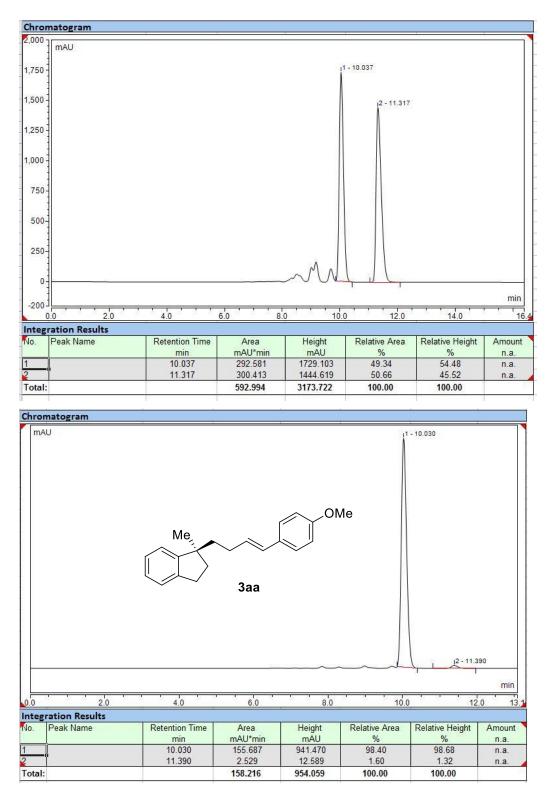






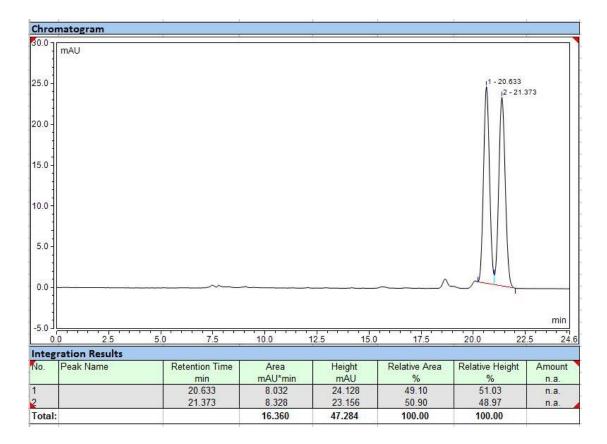


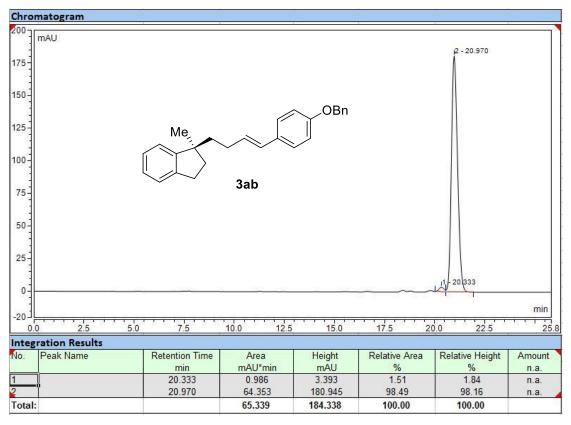
XI. HPLC Chromatograms



HPLC (Chiralpak IB): t_R= 10.0 (major), 11.4 (minor)

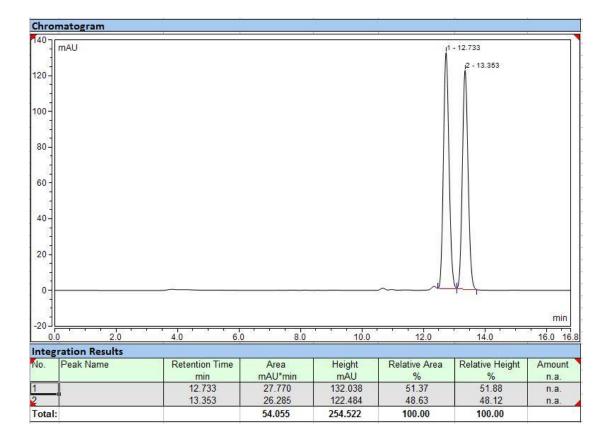
Condition: 97:3 n-Hexane:i-PrOH, flow rate 0.5 mL/min, 25°C.

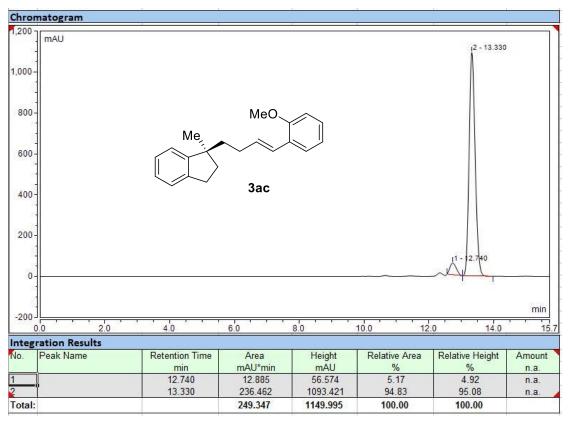




HPLC (Chiral MD): t_R= 20.3 (minor), 21.0 (major)

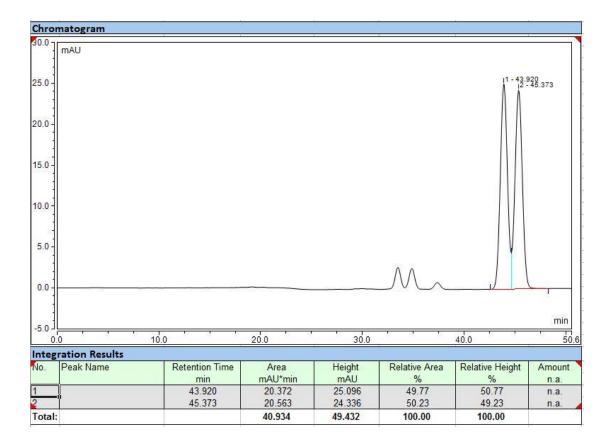
Condition: 96:4 n-Hexane:i-PrOH, flow rate 0.4 mL/min, 25°C.

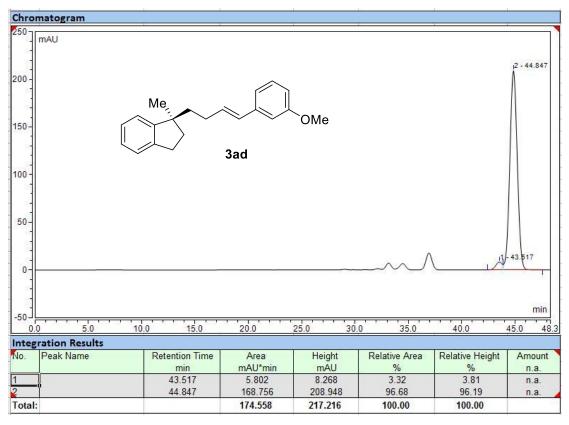




HPLC (Chiralpak IB): t_R= 12.7 (minor), 13.3 (major)

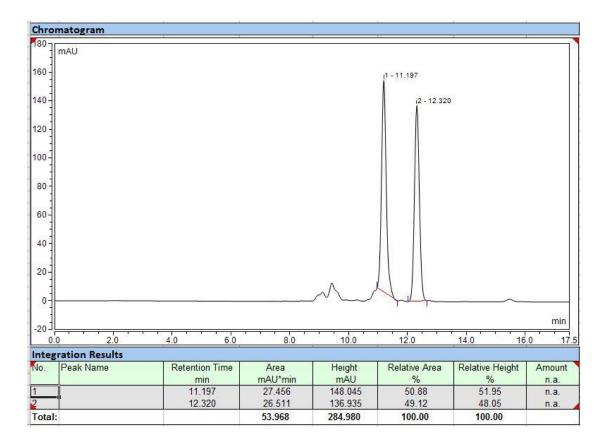
Condition: 98:2 n-Hexane:i-PrOH, flow rate 0.4 mL/min, 25°C.

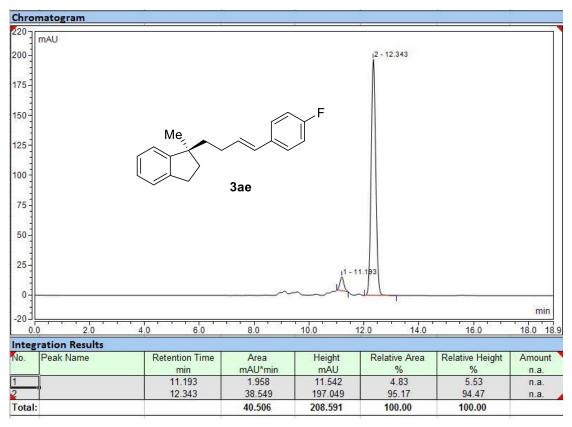




HPLC (Chiral MD): t_R = 43.5 (minor), 44.8 (major)

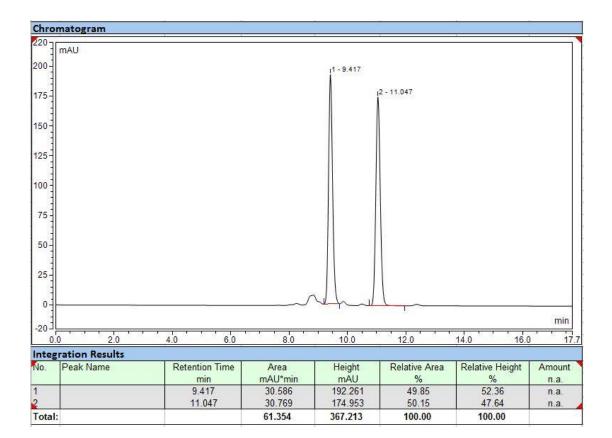
Condition: 97:3 n-Hexane:i-PrOH, flow rate 0.4 mL/min, 25°C.

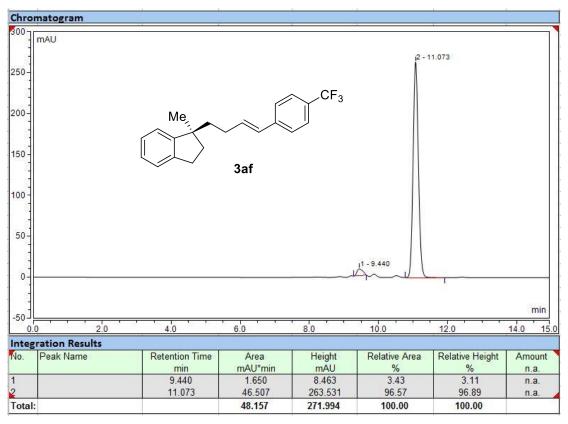




HPLC (Chiral MD): t_R= 11.2 (minor), 12.3 (major)

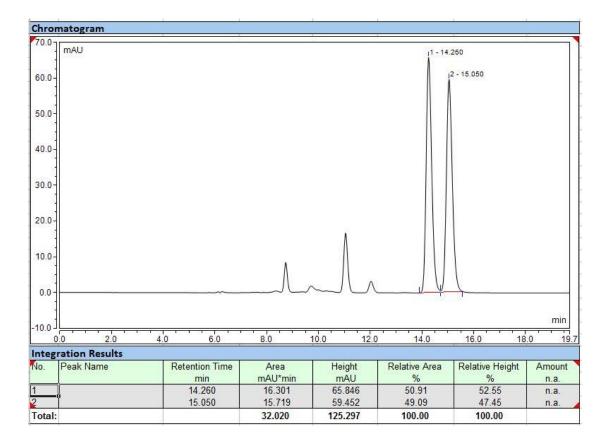
Condition: 97:3 n-Hexane:i-PrOH, flow rate 0.4 mL/min, 25°C.

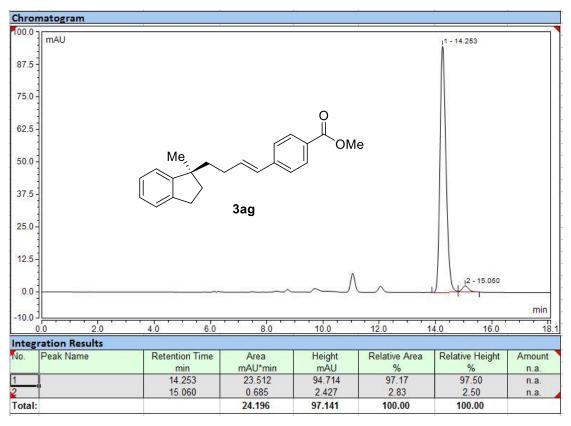




HPLC (Chiralpak IB): t_R= 9.4 (minor), 11.1 (major)

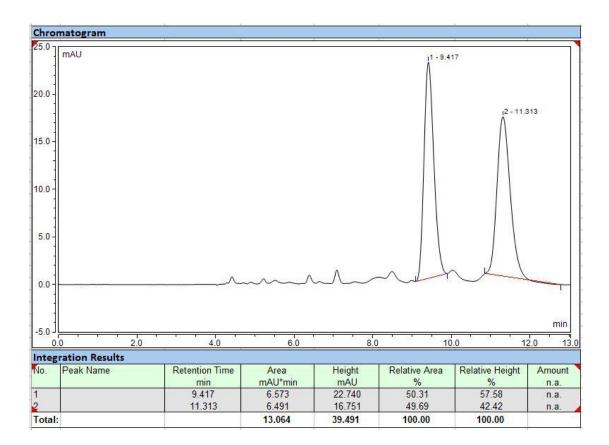
Condition: 97:3 n-Hexane:i-PrOH, flow rate 0.4 mL/min, 25°C.

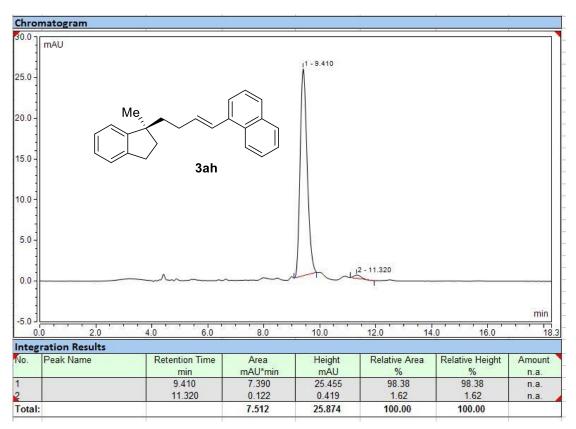




HPLC (Chiralpak IB): t_R= 14.3 (major), 15.1 (minor)

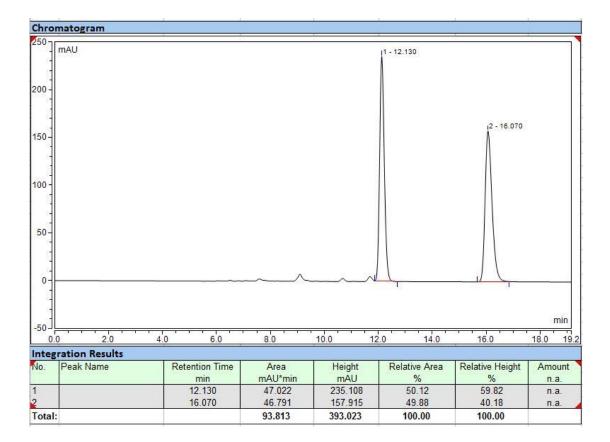
Condition: 95:5 n-Hexane:i-PrOH, flow rate 0.5 mL/min, 25°C.

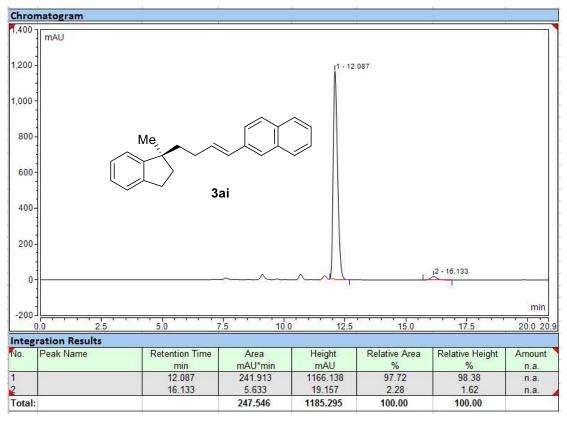




HPLC (Chiralcel OJ-H): t_R= 9.4 (major), 11.3 (minor)

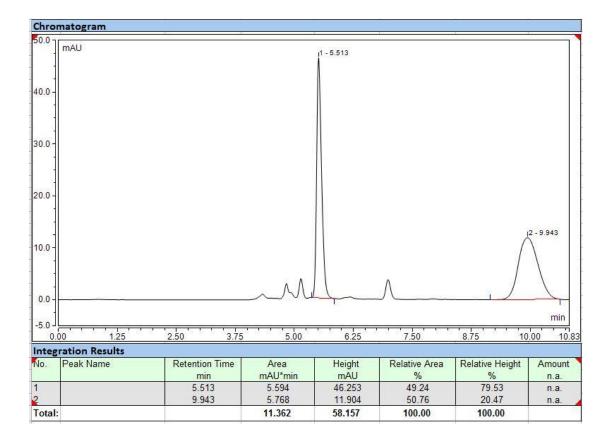
Condition: 70:30 n-Hexane:i-PrOH, flow rate 0.7 mL/min, 25°C.

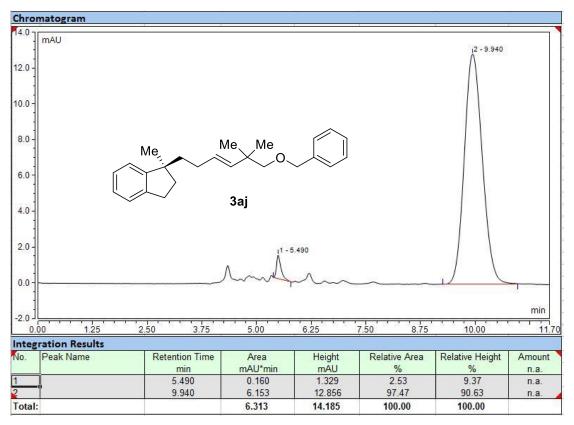




HPLC (Chiralpak IB): t_R= 12.1 (major), 16.1 (minor)

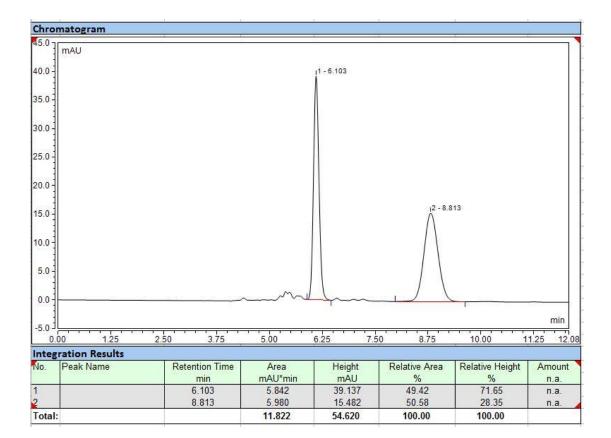
Condition: 95:5 n-Hexane:i-PrOH, flow rate 0.5 mL/min, 25°C.

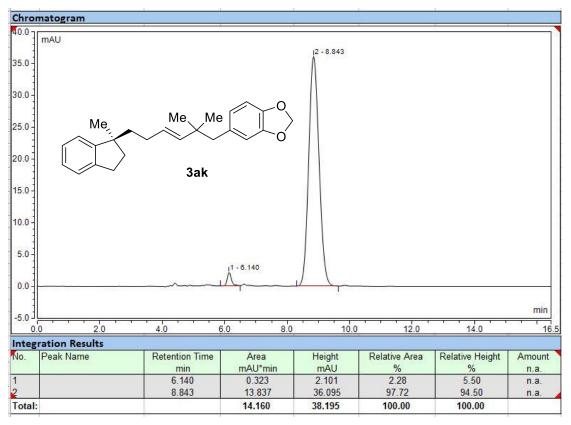




HPLC (Chiralcel OJ-H): t_R= 5.5 (minor), 9.9 (major)

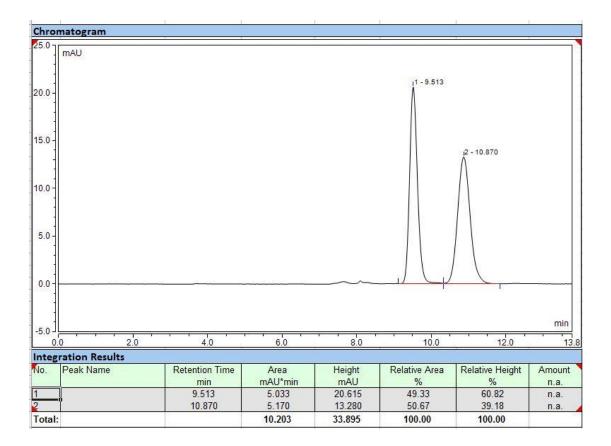
Condition: 70:30 n-Hexane:i-PrOH, flow rate 0.7 mL/min, 25°C.

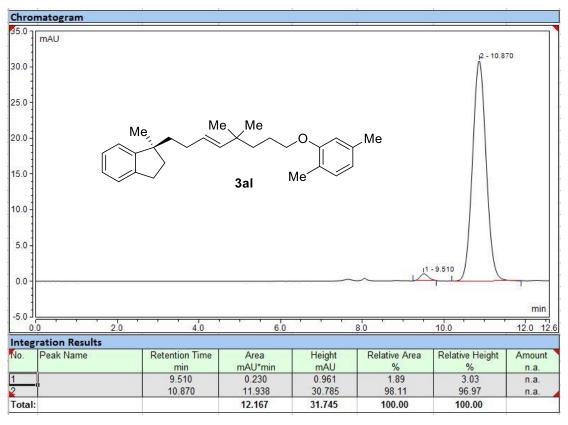




HPLC (Chiralcel OJ-H): t_R= 6.1 (minor), 8.8 (major)

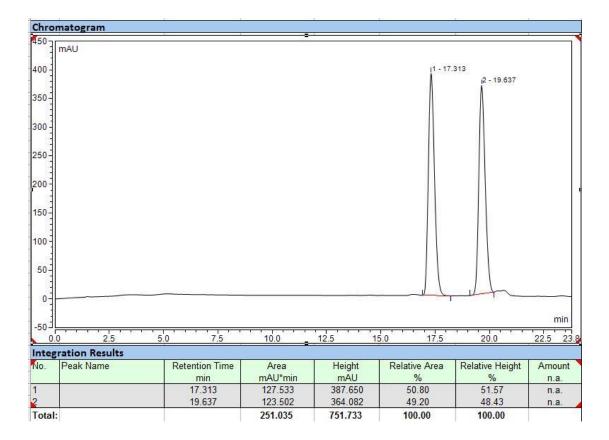
Condition: 70:30 n-Hexane:i-PrOH, flow rate 0.7 mL/min, 25°C.

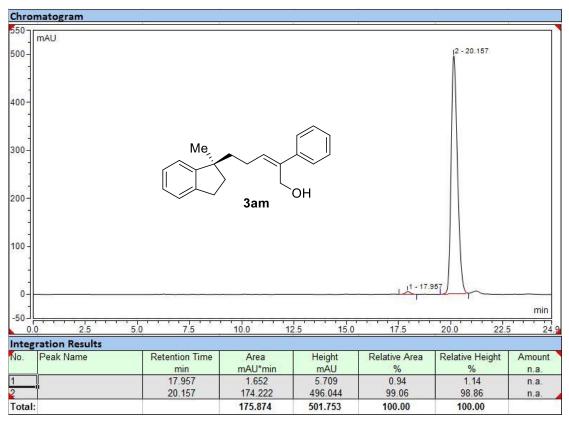




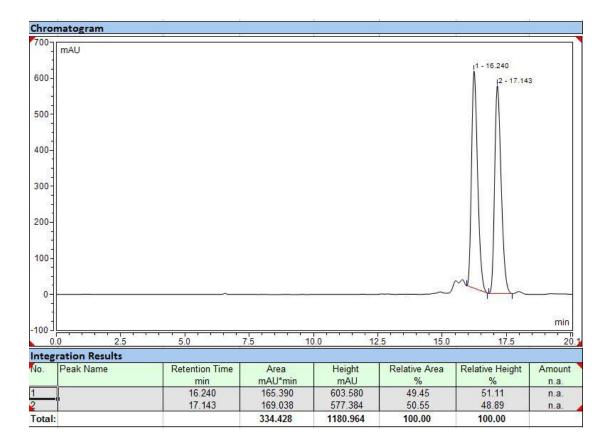
HPLC (Chiralcel OJ-H): t_R= 9.5 (minor), 10.9 (major)

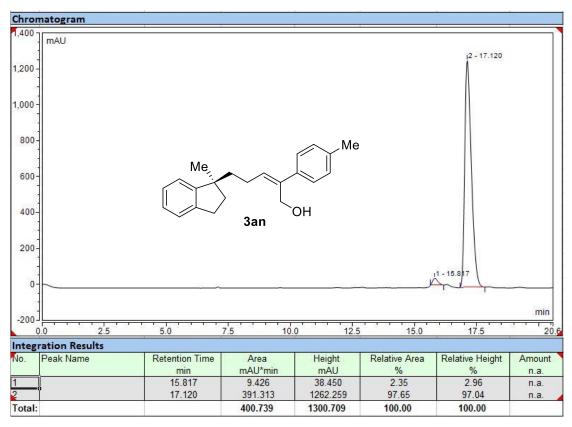
Condition: 96:4 n-Hexane:i-PrOH, flow rate 0.4 mL/min, 25°C.



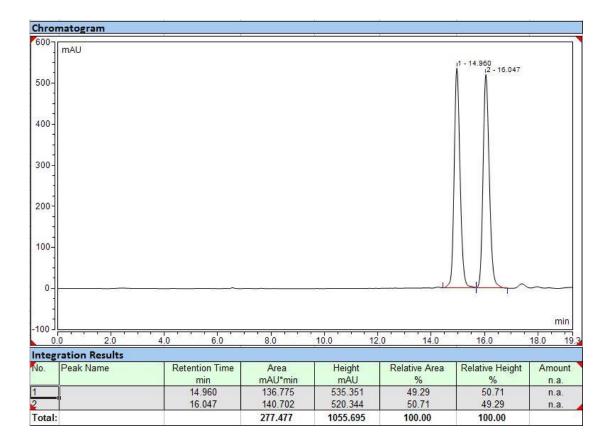


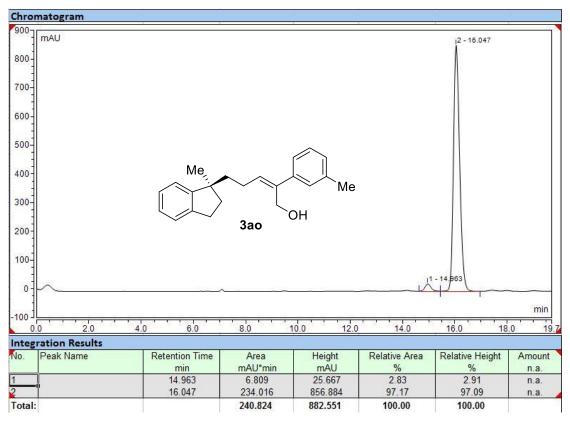
HPLC (Chiralpak IB): t_R= 17.9 (minor), 20.1 (major)



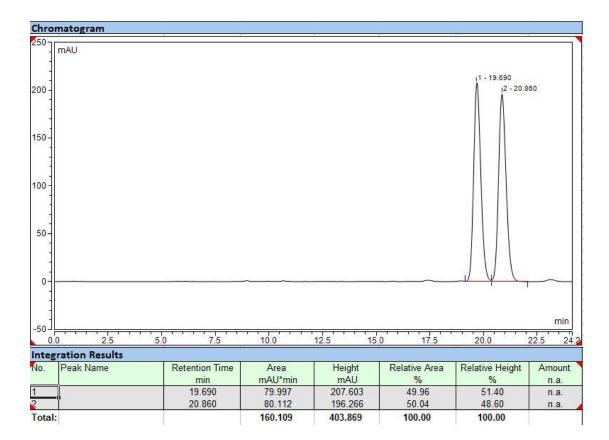


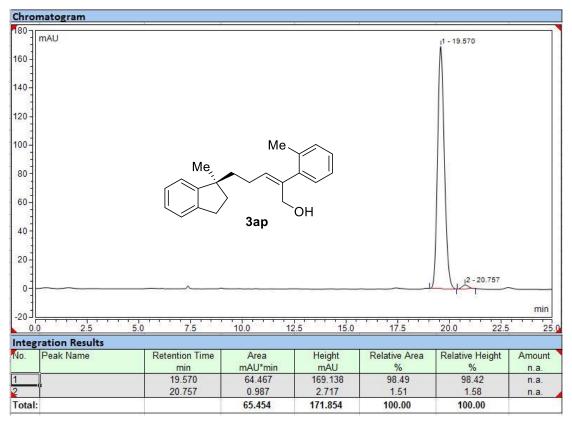
HPLC (Chiralpak IB): t_R= 15.8 (minor), 17.1 (major)



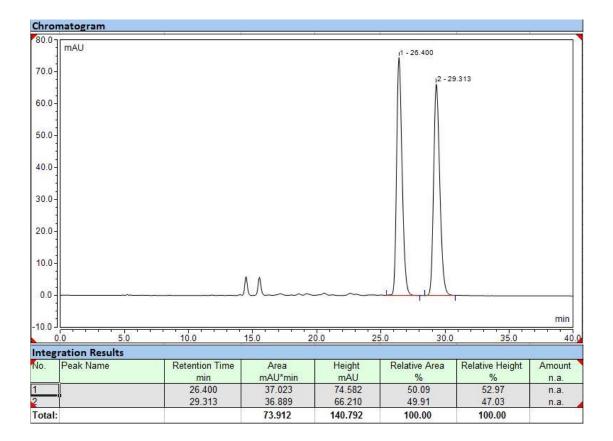


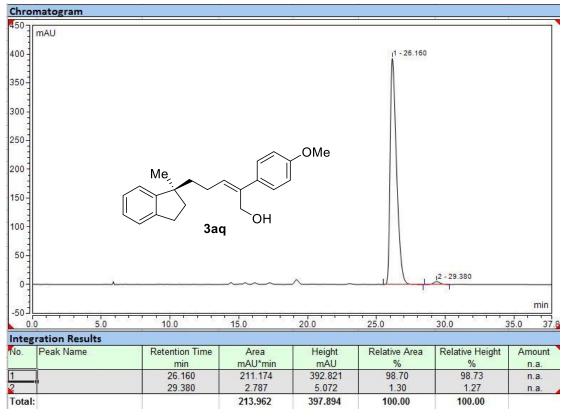
HPLC (Chiralpak IB): t_R= 15.0 (minor), 16.0 (major)



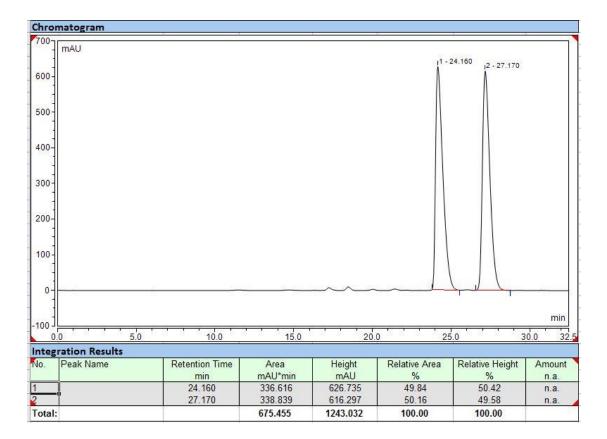


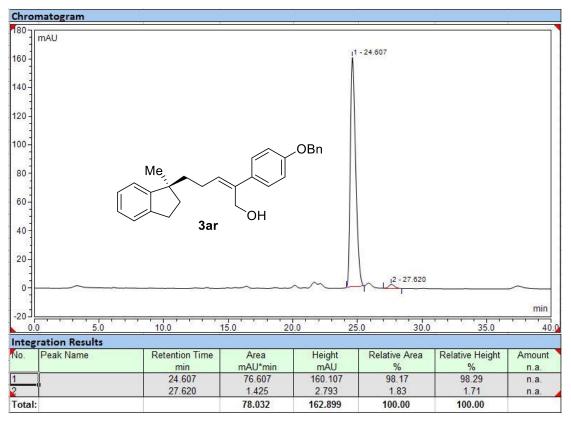
HPLC (Chiralpak AD-H): t_R= 19.6 (major), 20.8 (minor)



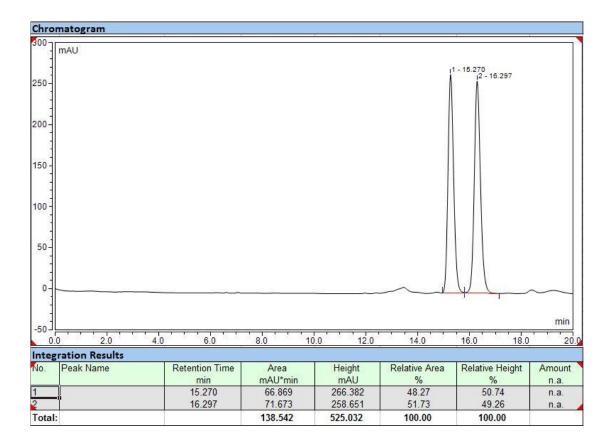


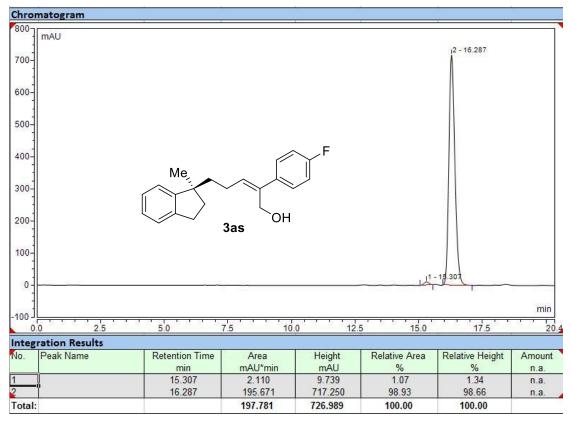
HPLC (Chiralpak IB): t_R= 26.2 (major), 29.4 (minor)



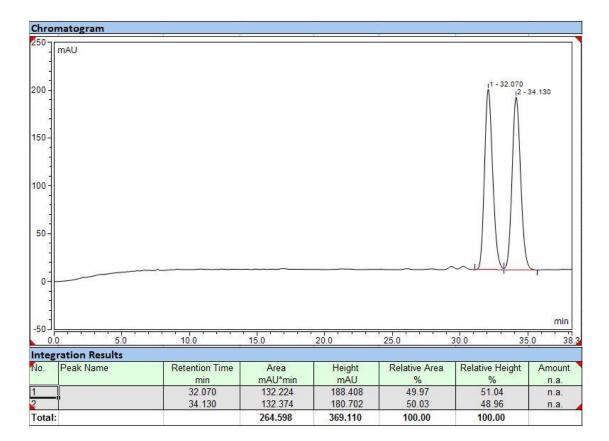


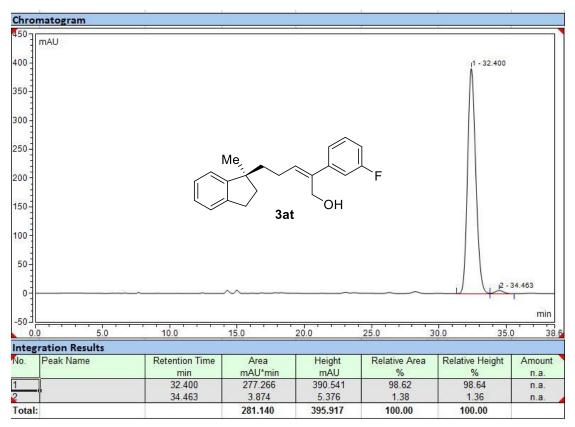
HPLC (Chiralpak IB): t_R= 24.6 (major), 27.6 (minor)



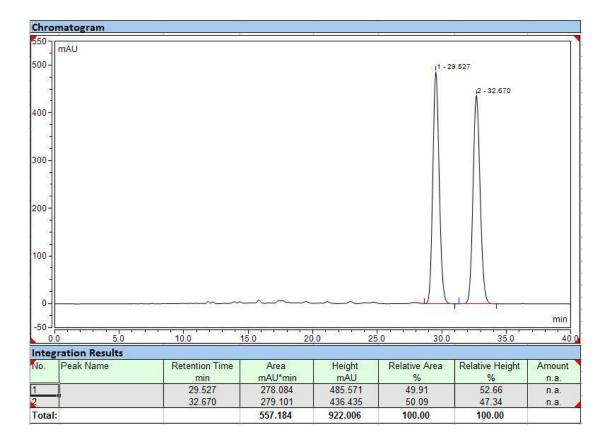


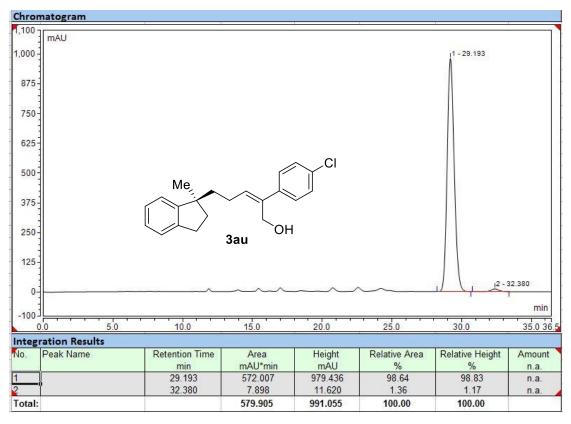
HPLC (Chiralpak IB): t_R= 15.3 (minor), 16.3 (major)



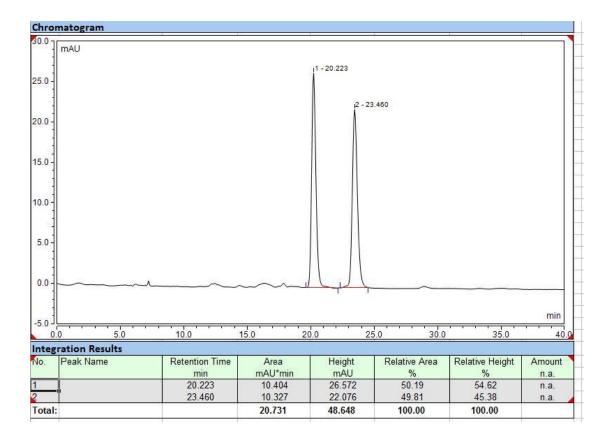


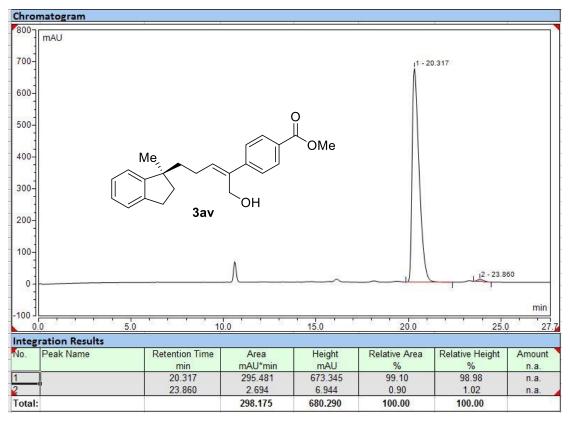
HPLC (Chiralpak AD-H): t_R= 32.4 (major), 34.5 (minor)



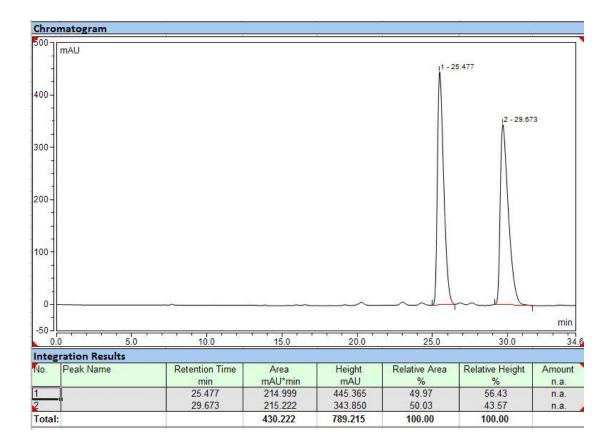


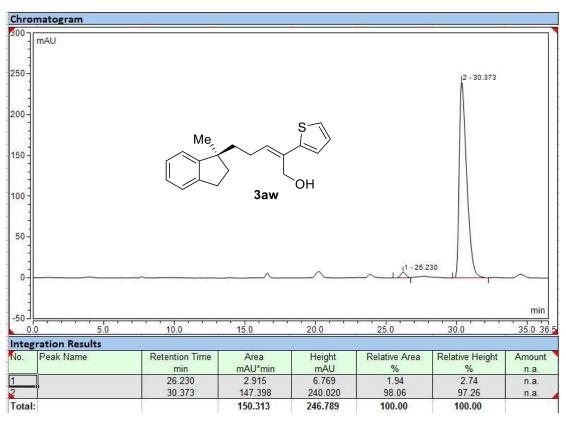
HPLC (Chiralpak AD-H): t_R= 29.2 (major), 32.4 (minor)



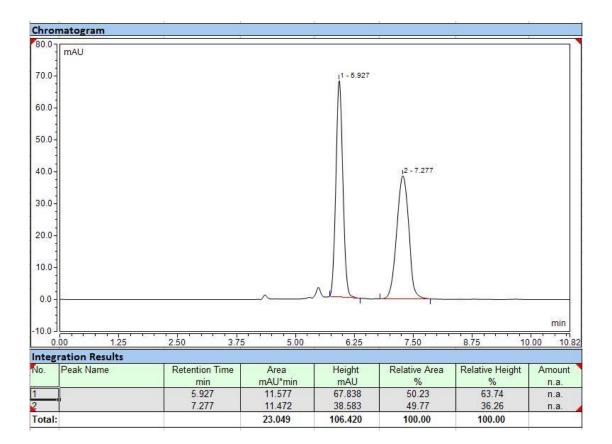


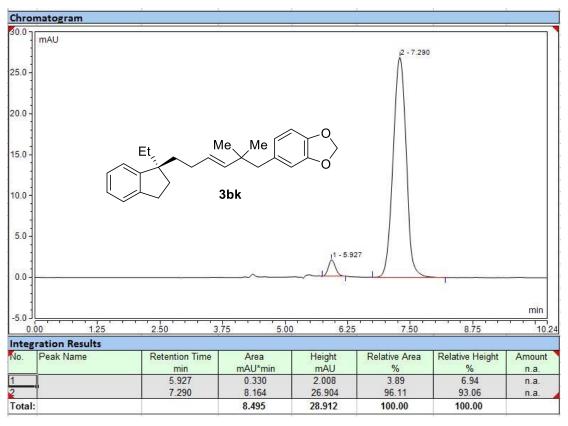
HPLC (Chiralpak IB): t_R= 20.3 (major), 23.9 (minor)



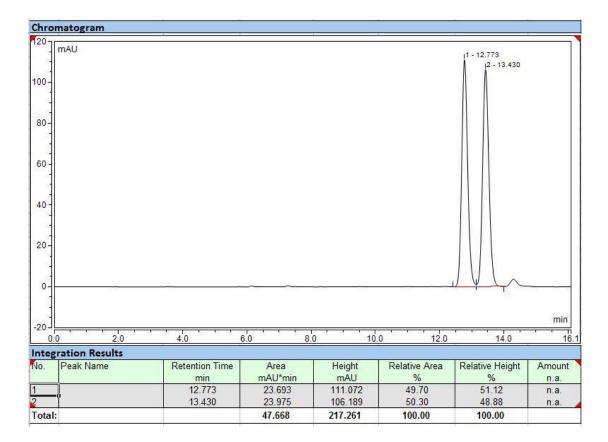


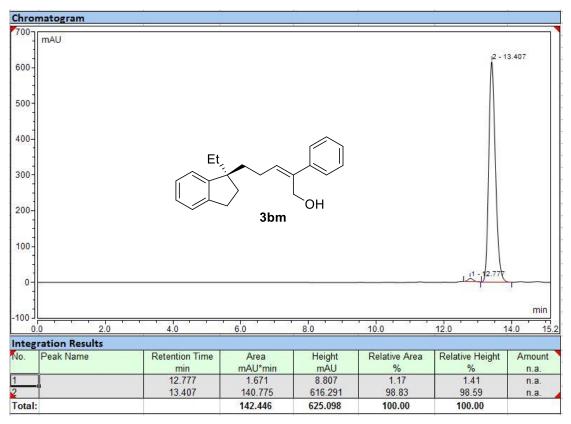
HPLC (Chiralpak IB): t_R= 26.2 (minor), 30.4 (major)



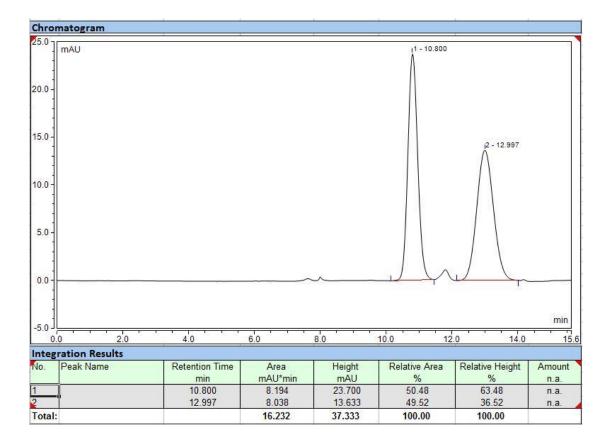


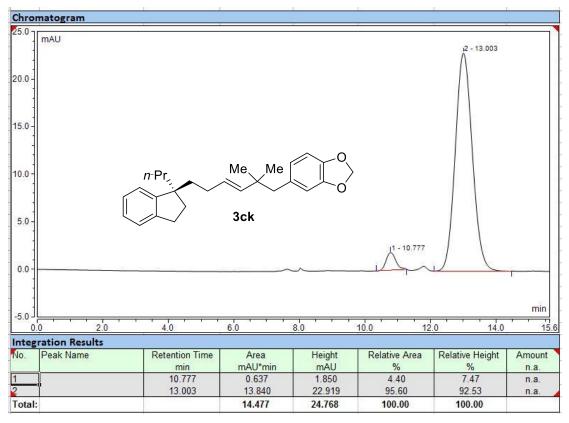
HPLC (Chiralcel OJ-H): t_R= 5.9 (minor), 7.3 (major)



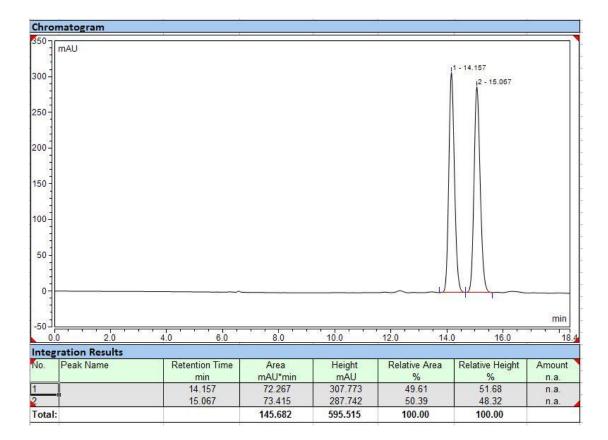


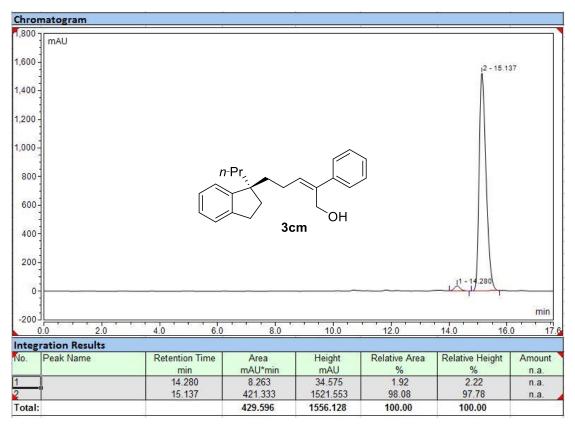
HPLC (Chiralpak IB): t_R= 12.8 (minor), 13.4 (major)



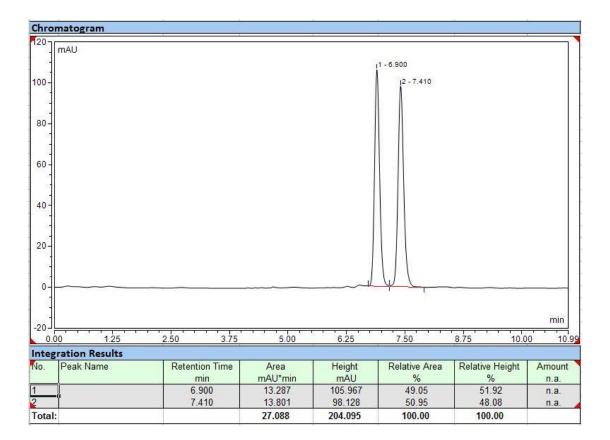


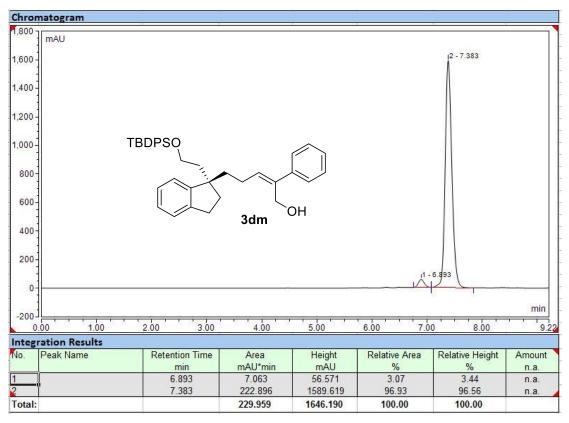
HPLC (Chiralcel OJ-H): t_R= 10.8 (minor), 13.0 (major)



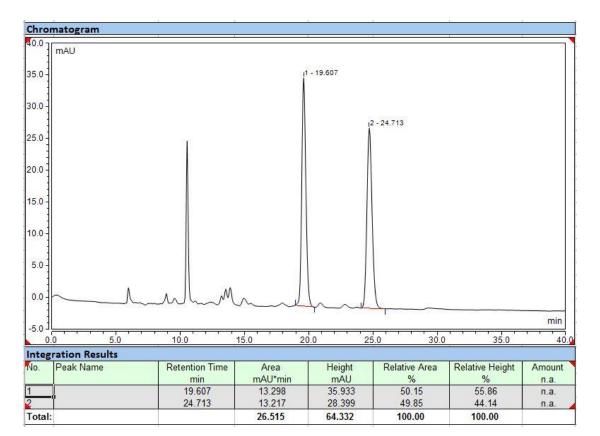


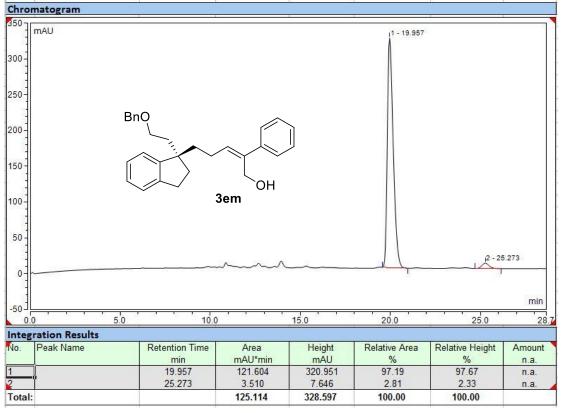
HPLC (Chiralpak IB): t_R= 14.3 (minor), 15.1 (major)



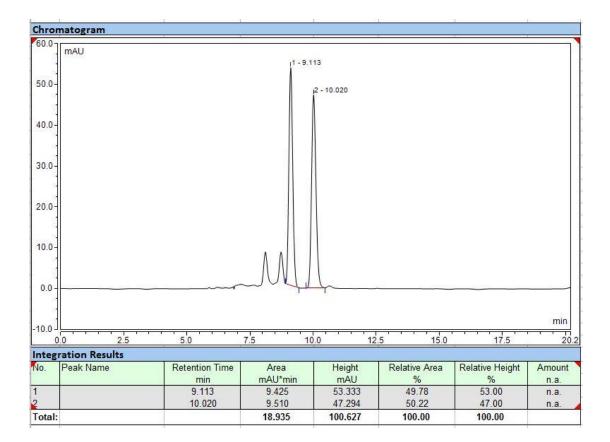


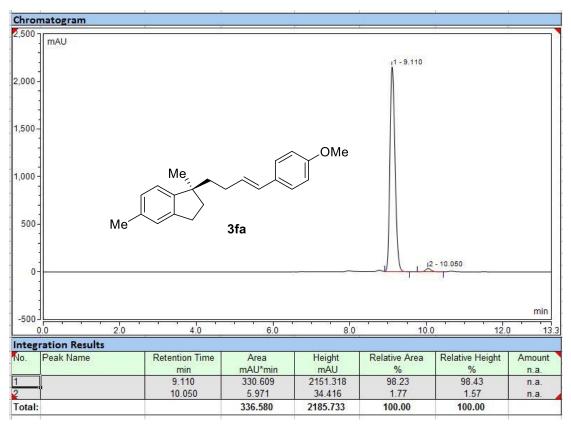
HPLC (Chiralpak IB): t_R= 6.9 (minor), 7.4 (major)



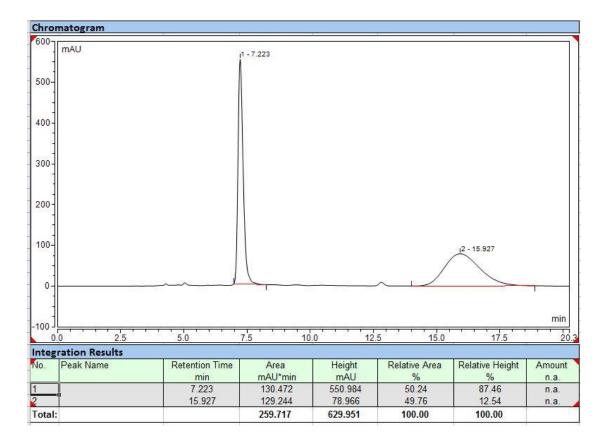


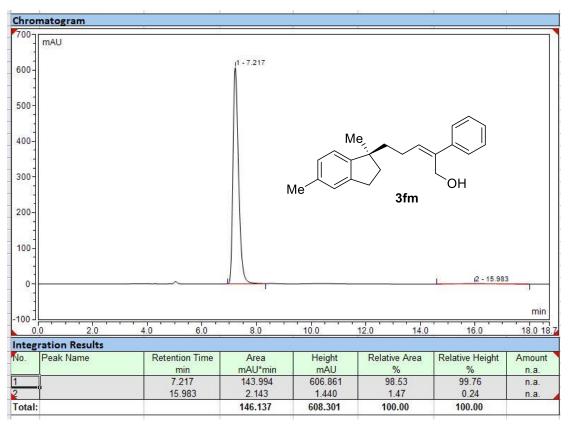
HPLC (Chiralpak IB): t_R= 19.9 (major), 25.3 (minor)



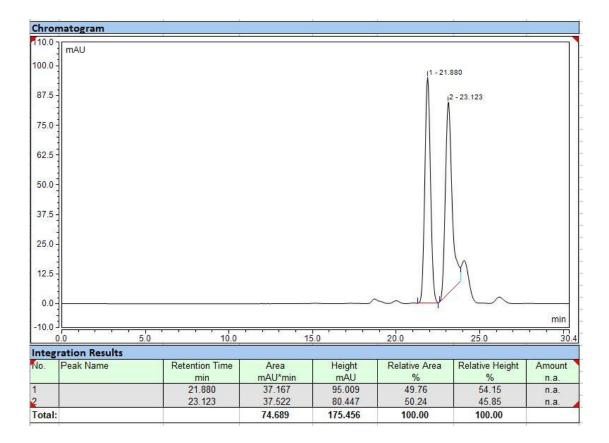


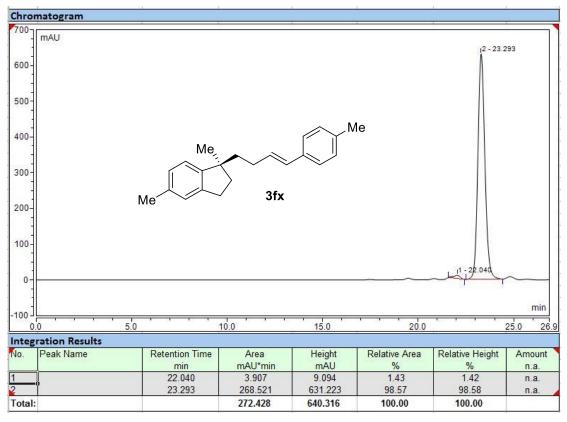
HPLC (Chiralpak IB): t_R= 9.1 (major), 10.1 (minor)



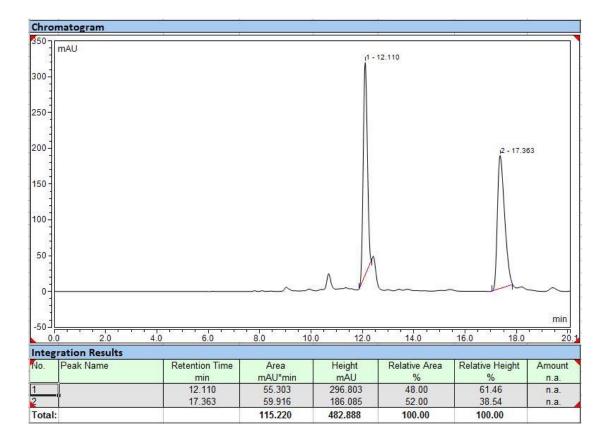


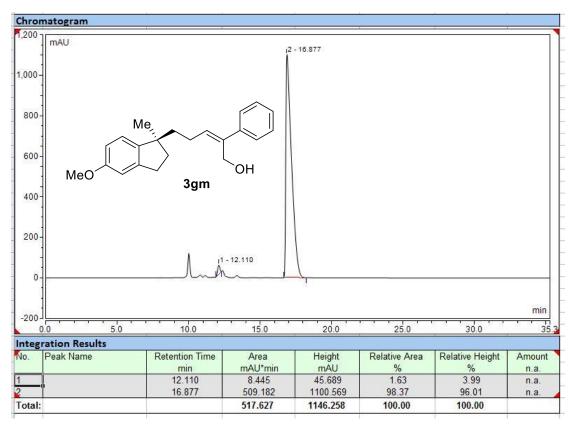
HPLC (Chiralcel OJ-H): $t_R = 7.2$ (major), 16.0 (minor)



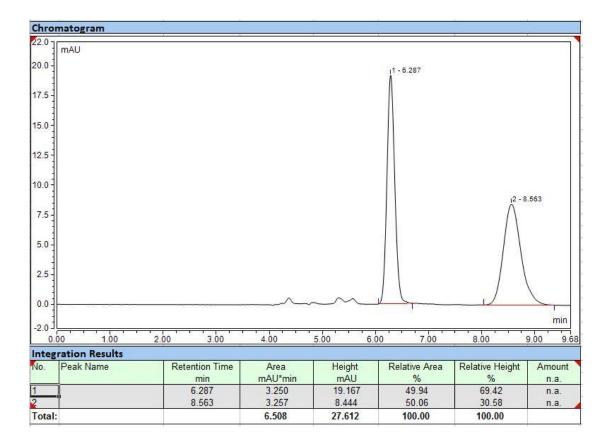


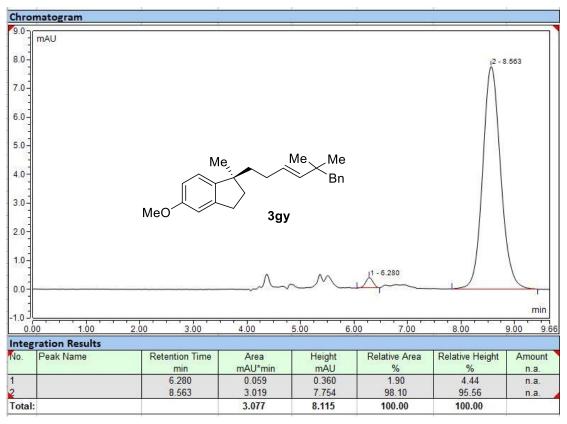
HPLC (Chiral MD): t_R = 22.0 (minor), 23.3 (major)



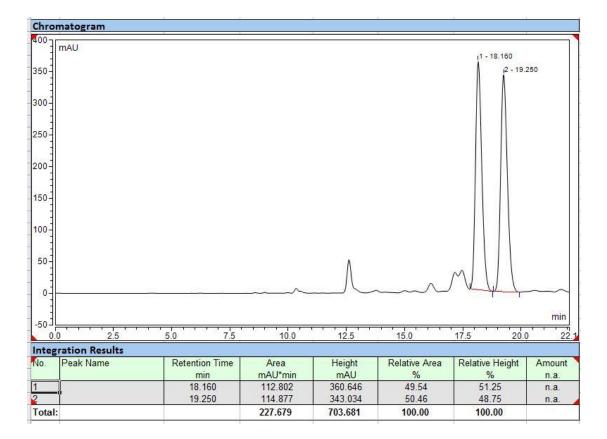


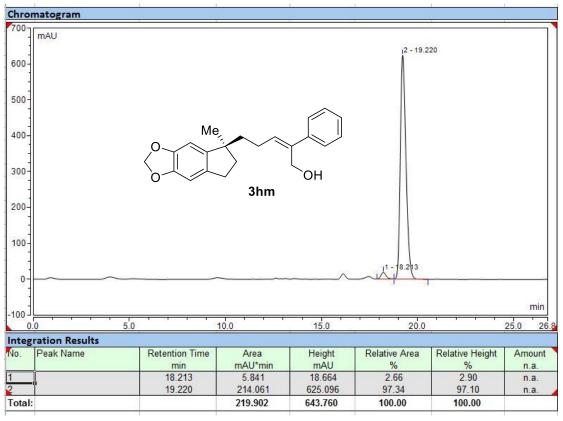
HPLC (Chiralpak IB): t_R= 12.1 (minor), 16.9 (major)



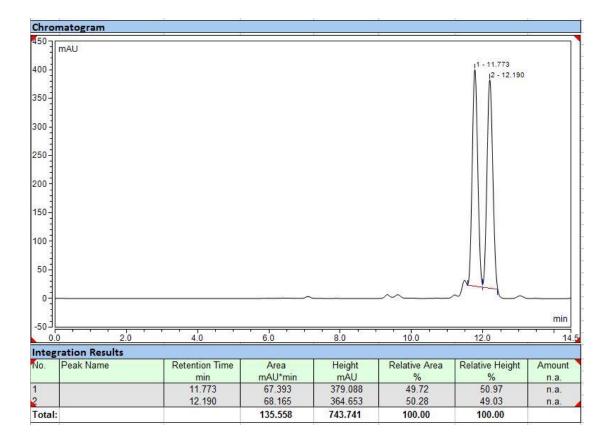


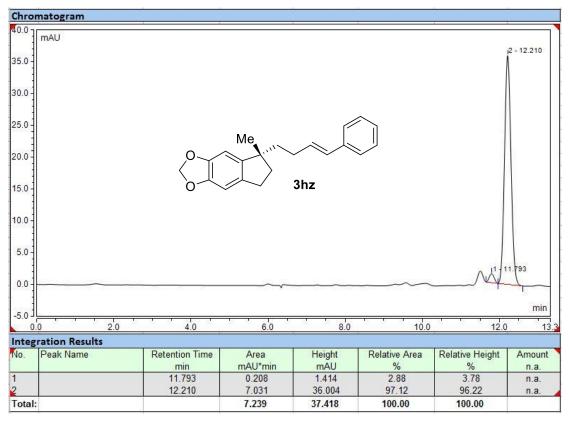
HPLC (Chiralcel OJ-H): t_R= 6.3 (minor), 8.6 (major)



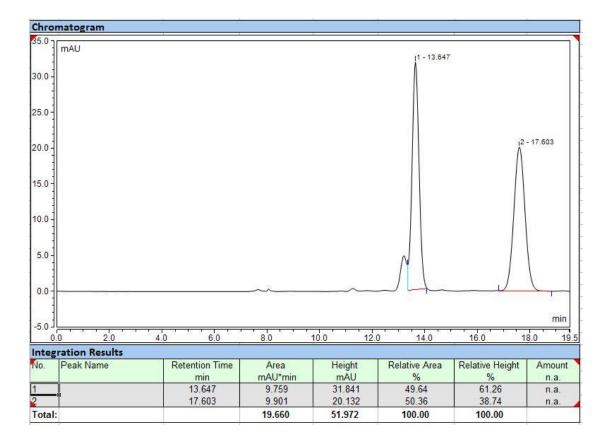


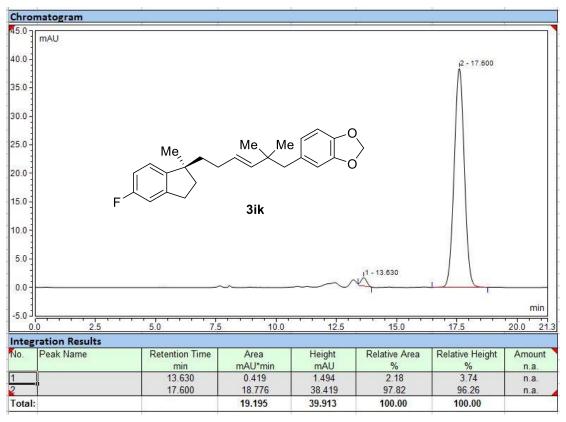
HPLC (Chiralpak IB): t_R= 18.2 (minor), 19.2 (major)



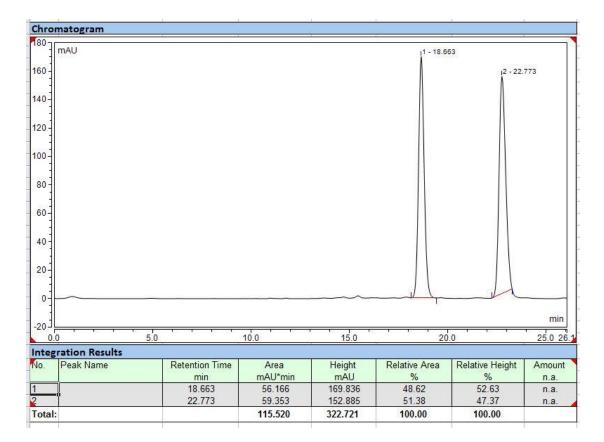


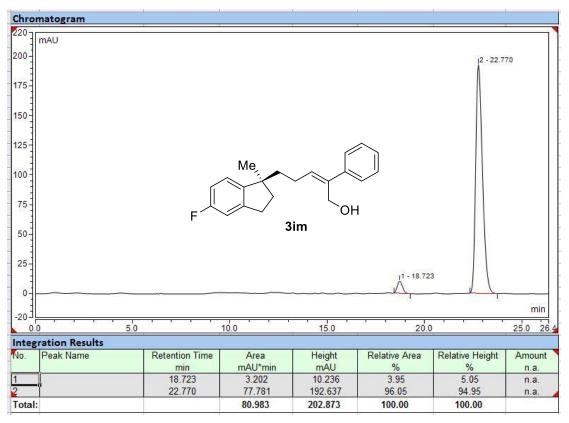
HPLC (Chiral MD): t_R= 11.8 (minor), 12.2 (major)



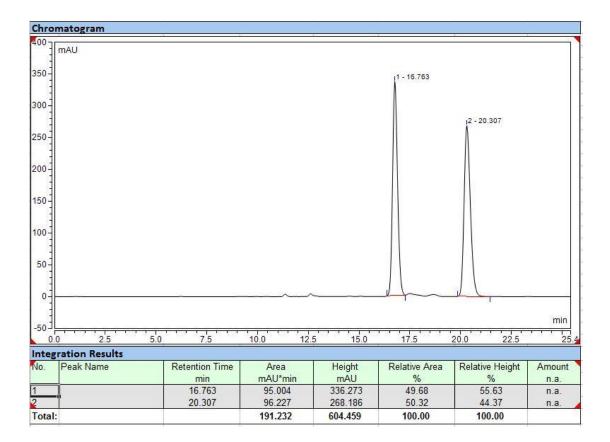


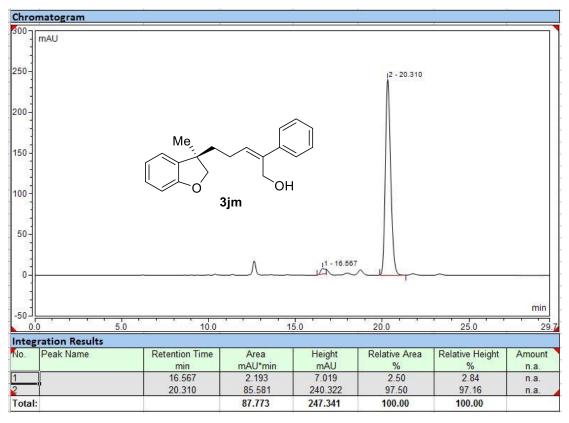
HPLC (Chiralcel OJ-H): t_R= 13.6 (minor), 17.6 (major)



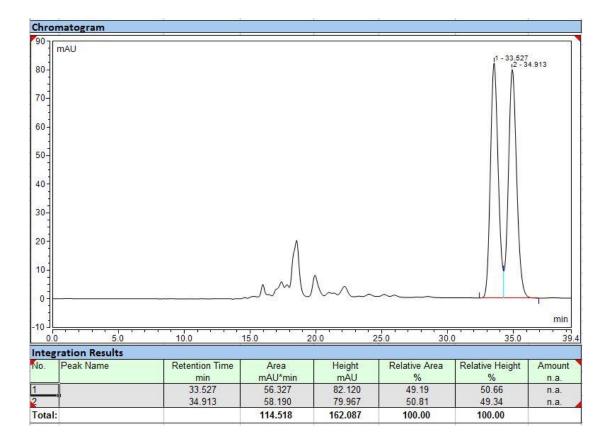


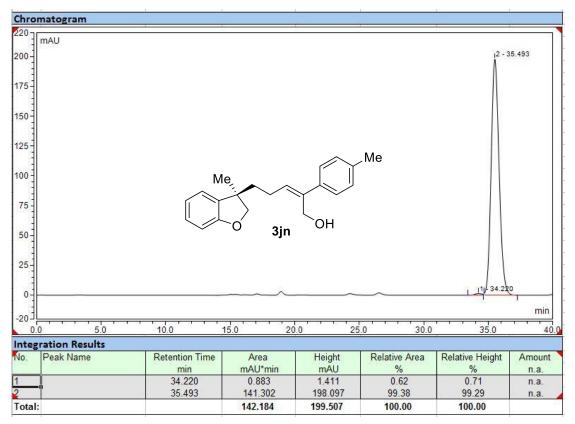
HPLC (Chiralpak IB): t_R= 18.7 (minor), 22.8 (major)



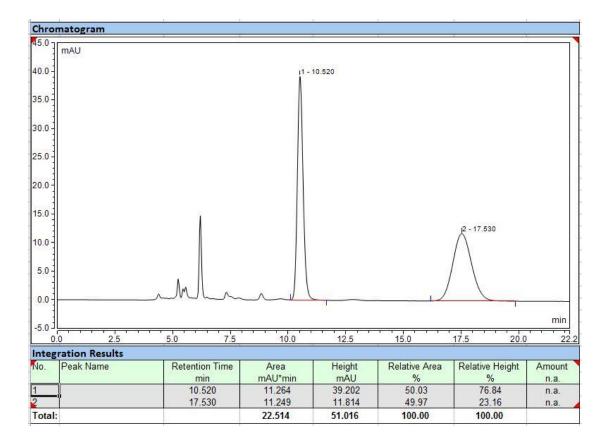


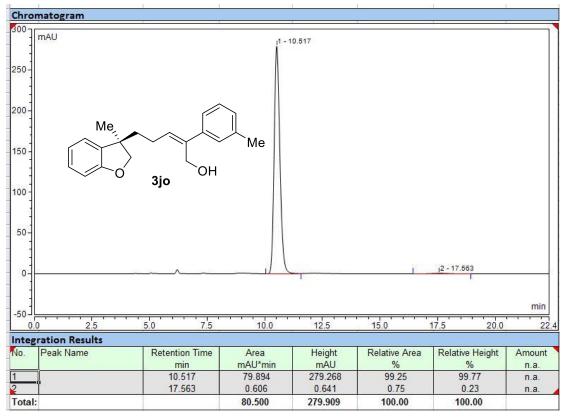
HPLC (Chiralpak IB): t_R= 16.6 (minor), 20.3 (major)



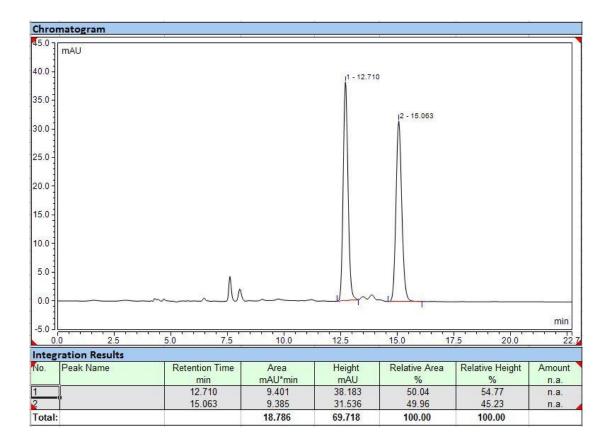


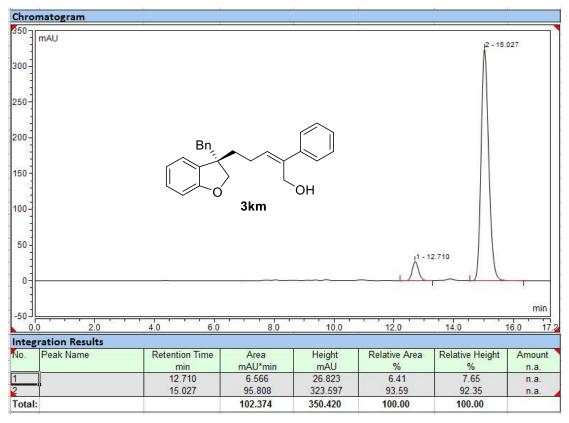
HPLC (Chiralpak AD-H): t_R= 34.2 (minor), 35.5 (major)



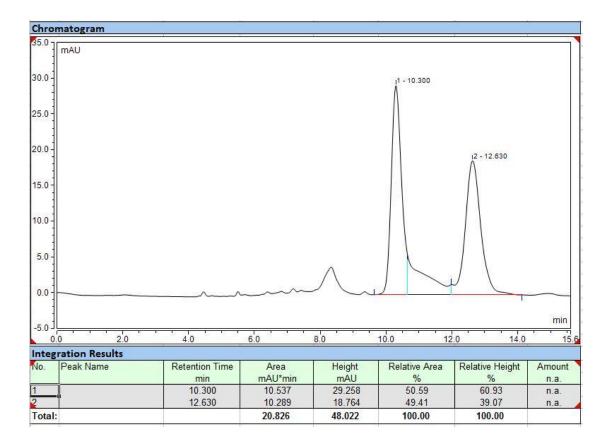


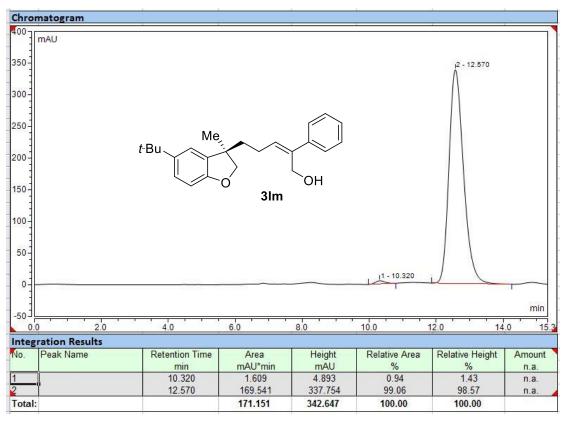
HPLC (Chiralcel OJ-H): t_R= 10.5 (major), 17.6 (minor)



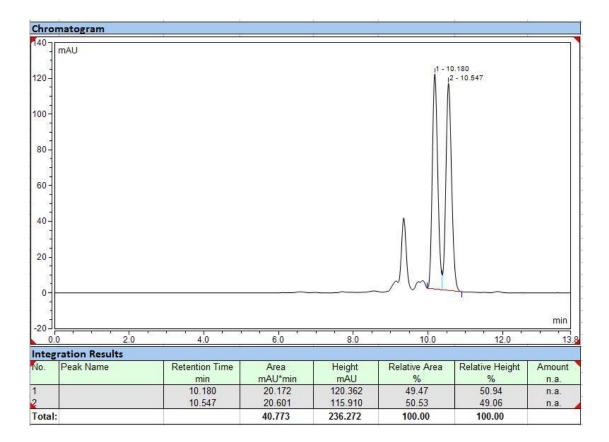


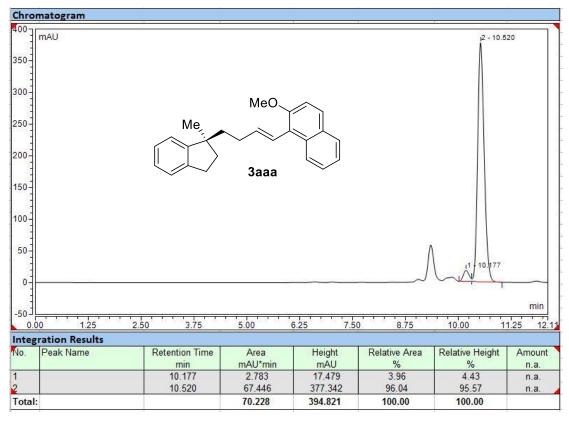
HPLC (Chiralpak IB): t_R= 12.7 (minor), 15.0 (major)



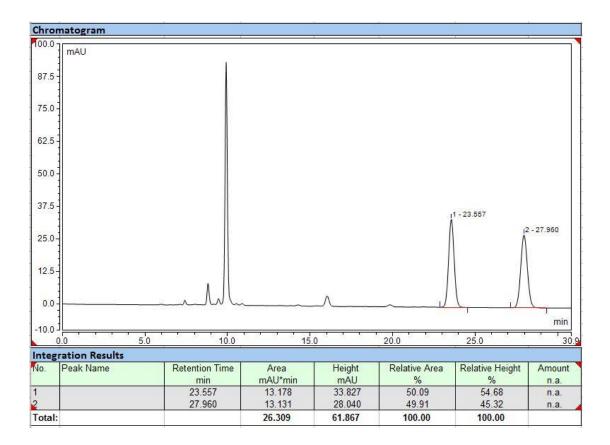


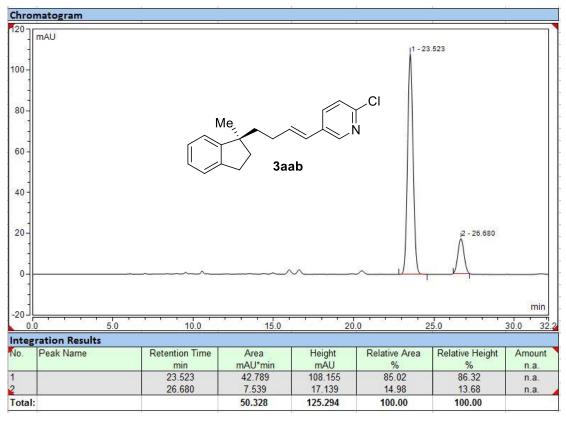
HPLC (Chiralcel OJ-H): t_R= 10.3 (minor), 12.6 (major)



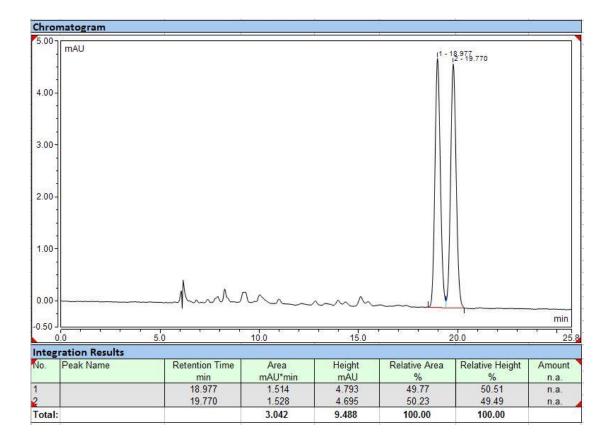


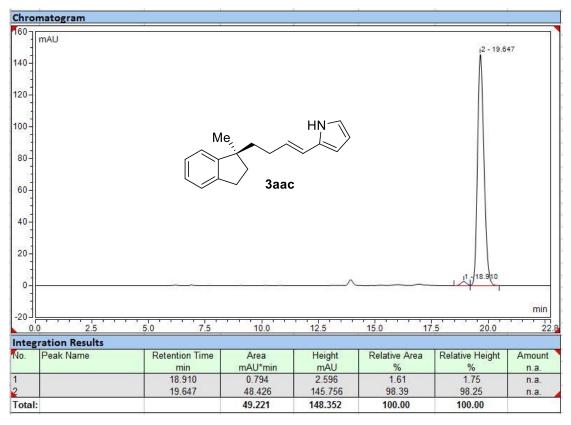
HPLC (Chiralpak IB): t_R= 10.1 (minor), 10.5 (major)



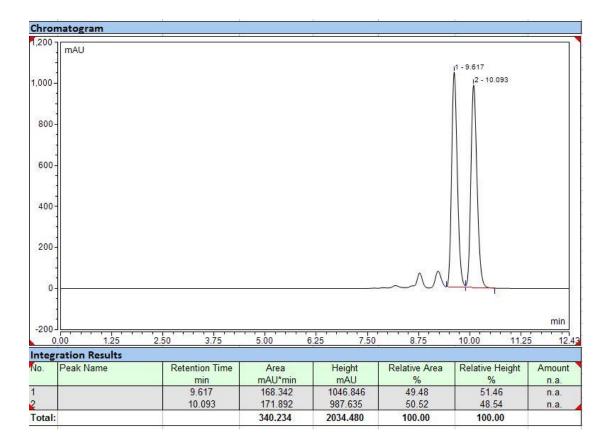


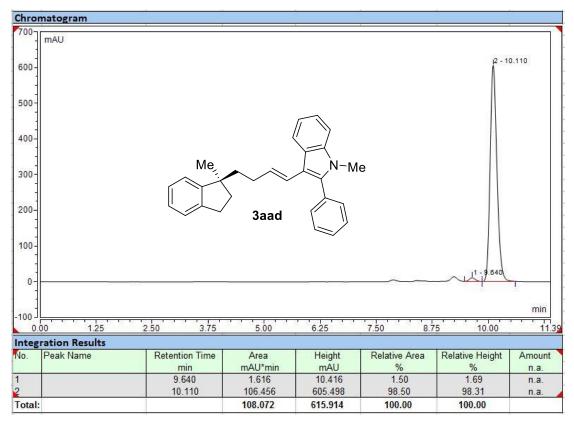
HPLC (Chiral MD): t_R = 23.5 (major), 26.7 (minor)



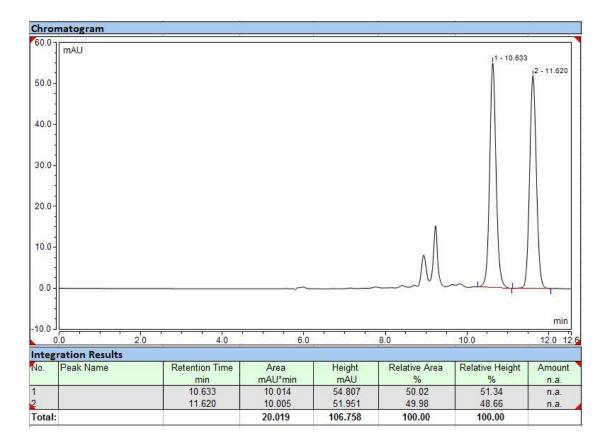


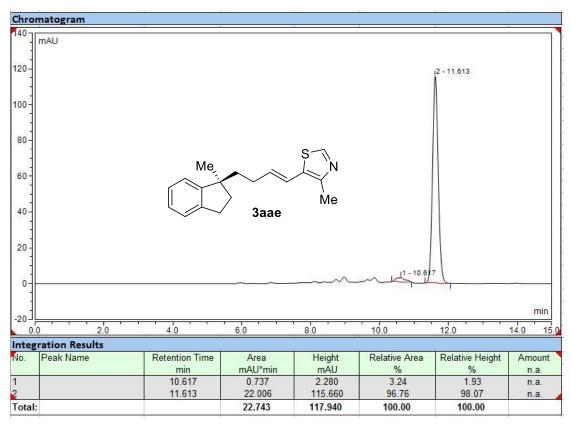
HPLC (Chiralpak IB): t_R= 18.9 (minor), 19.6 (major)



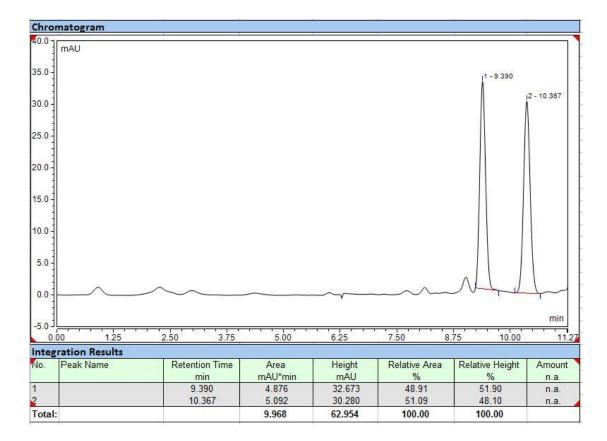


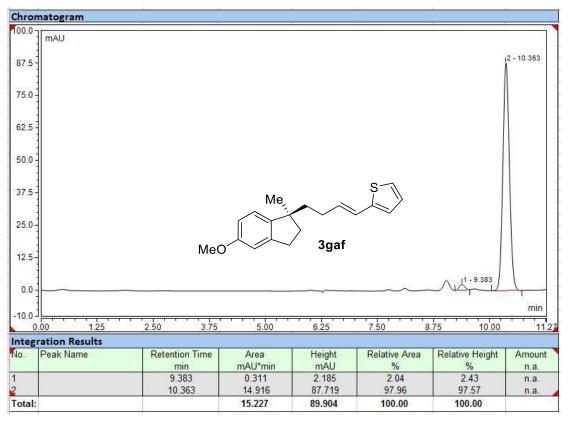
HPLC (Chiralpak IB): t_R= 9.6 (minor), 10.1 (major)



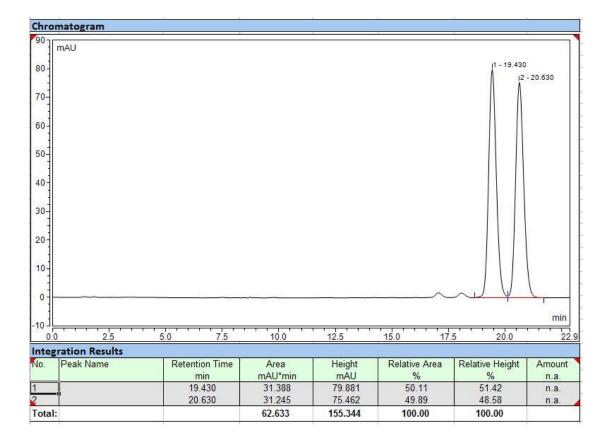


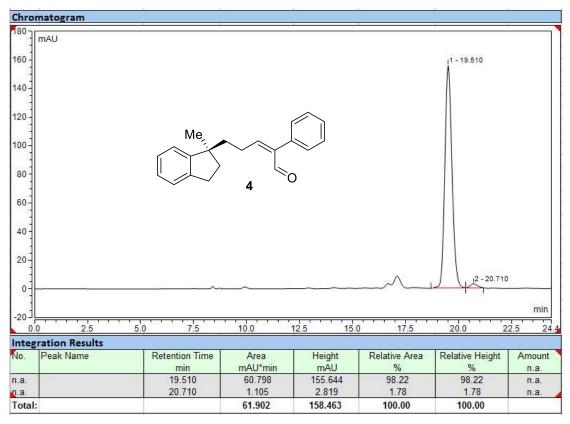
HPLC (Chiral MD): t_R= 10.6 (minor), 11.6 (major)



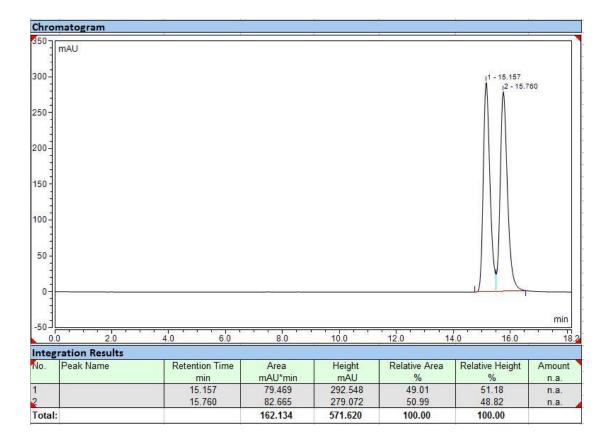


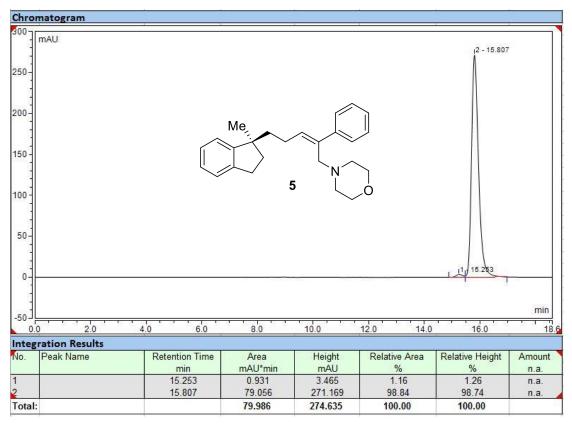
HPLC (Chiral MD): t_R= 9.4 (minor), 10.4 (major)



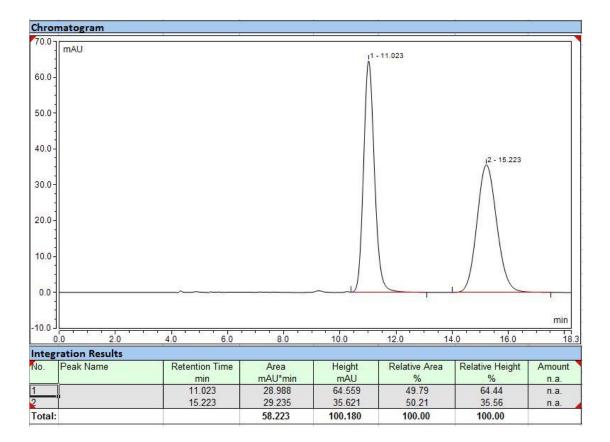


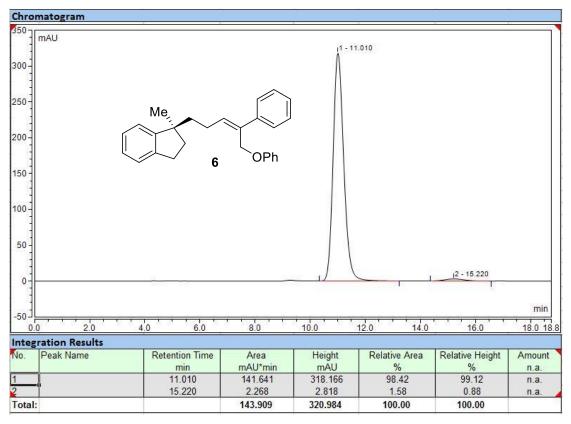
HPLC (Chiral MD): t_R= 19.5 (major), 20.7 (minor)



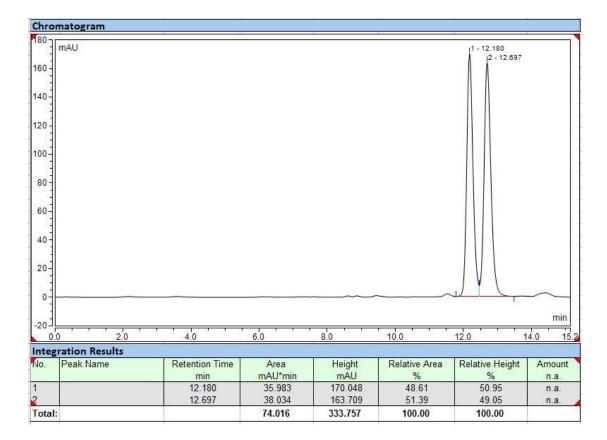


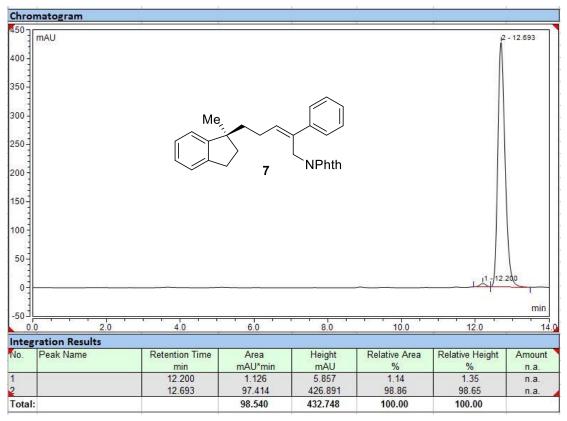
HPLC (Chiral MD): t_R= 15.3 (minor), 15.8 (major)



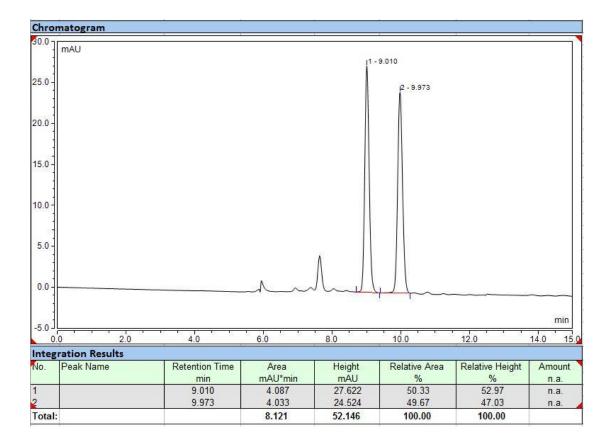


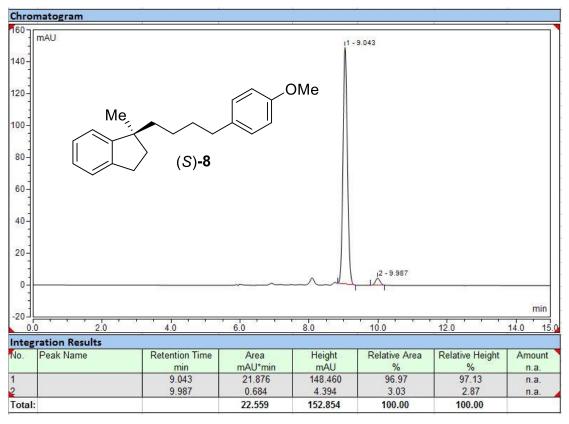
HPLC (Chiralcel OJ-H): t_R= 11.0 (major), 15.2 (minor)



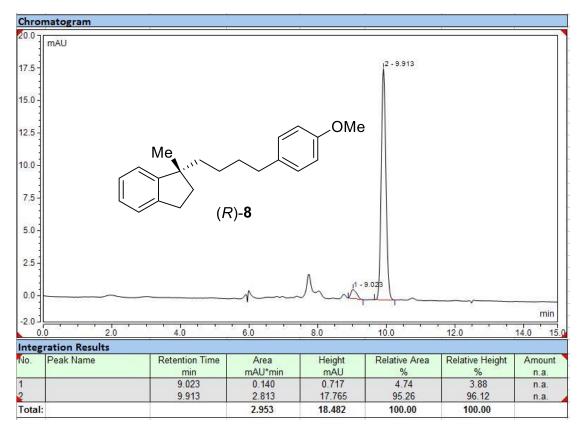


HPLC (Chiralpak IB): t_R= 12.2 (minor), 12.7 (major)





HPLC (Chiral MD): t_R= 9.0 (major), 9.9 (minor)



HPLC (Chiral MD): t_R= 9.0 (minor), 9.9 (major)