Padlocking Furannulation for the Control of Small Degree of Helicity Built on a Fused-Tetracyclic core

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Supporting information

1. General information

Reactions were run under argon atmosphere. Unless specified, commercial reagents and solvents were used as received. Commercially available catalysts were purchased from Sigma-Aldrich. $CHCl_3$ was dried over 4Å molecular sieve.

Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 aluminum plates (Macherey-Nagel) containing a 254 nm fluorescent indicator. TLC plates were visualized by exposure to short wave ultraviolet light (254 nm) and further visualization was achieved by staining p-anisaldehyde and heating by a hot air gun. Flash column chromatography was performed using silica gel (35–70 µm, 60 , Acros).

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Bruker AV 300 and AV 400 spectrometer. Proton chemical shifts are reported in parts per million (δ scale) and are referenced using residual protium in the NMR solvent (δ 7.26 ($CHCl_3$)). Data are reported as follows: chemical shift (multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quadruplet, quint = quintuplet, sept = septuplet, m = multiplet), coupling constant(s) (Hz), integration). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with Bruker AV 300 and AV 400 MHz spectrometers. Carbon chemical shifts are reported in parts per million (δ scale) and are referenced using the carbon resonances of the solvent (δ 77.16 ($CHCl_3$)). Data are reported as follows: chemical shift (δ scale).

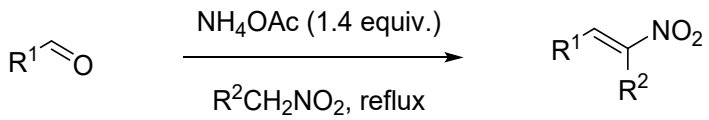
HPLC analyses for the determination of enantiomeric excesses were performed on an Agilent system equipped with Chiralpak AZ-H, Chiralpak IF, Lux-Amylose-1, Lux-Amylose-2, Lux-Cellulose-2 and Lux-Cellulose-4. Optical Rotations were recorded on an Anton Paar MCP 200 Polarimeter at 589 nm, in a thermostated cell (10 cm) and specific rotations are reported as follows: specific rotation (concentration in grams/100 mL of solution, solvent).

High resolution mass spectra (HRMS) were recorded on a Waters Synapt G2 HDMS apparatus using a positive electrospray (ESI) ionization source.

2. Preparation of starting materials

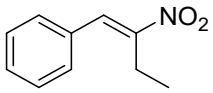
a) Preparation of alkylnitroalkenes

General procedure



The alkylnitroalkenes were prepared according to the literature known procedure.[1] In a 100 mL round-bottom flask, NH_4OAc (1.4 equiv.) was added to a solution of aldehyde (1.0 equiv.) in 1-nitropropane (0.6 M) or nitroethane (0.3 M) and the mixture was stirred at reflux (132 °C or 120 °C) for 24 h. Once concentrated, the oily residue was purified on silica column using ethyl EtOAc/ Petroleum ether mixture to yield the pure product.

(E)-(2-nitrobut-1-en-1-yl)benzene



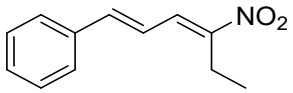
Molecular Weight: 177,2030

Prepared following the general procedure using benzaldehyde (1.80 mL, 17.7 mmol) and NH_4OAc (1.9 g, 24.6 mmol). The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 5:95) to yield a yellow oil (1.95 g, 11.0 mmol, 62%)

R_f = 0.67 (EtOAc/ Petroleum ether = 1:9), **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.03 (s, 1H), 7.53 – 7.37 (m, 5H), 2.87 (q, *J* = 7.4 Hz, 2H), 1.28 (t, *J* = 7.4 Hz, 3H).

^{1}H NMR spectroscopic data are in accordance with the literature.[2]

((1E,3E)-4-nitrohexa-1,3-dien-1-yl)benzene



Molecular Weight: 203,2410

Prepared following the general procedure using cinnamaldehyde (0.38 mL, 3.0 mmol) and NH_4OAc (324 mg, 4.2 mmol). The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 3:97) to yield a brown oil (252 mg, 1.2 mmol, 41%)

R_f = 0.44 (EtOAc/ Petroleum ether = 1:9), **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.71 (dd, *J* = 11.5, 0.8 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.44 – 7.34 (m, 3H), 7.10 (d, *J* = 15.4 Hz, 1H), 6.90 (dd, *J* = 15.4, 11.5 Hz, 1H), 2.82 (q, *J* = 7.4 Hz, 2H), 1.22 (t, *J* = 7.4 Hz, 3H).

^{1}H NMR spectroscopic data are in accordance with the literature.[3]

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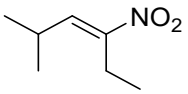
[1] Akula, P. S.; Hong, B-C.; Lee, G-H. *Org. Lett.* **2018**, *20*, 7835-7839.
[2] Duschmalé, J.; Wennemers, H. *Chem. Eur. J.* **2012**, *18*, 1111.
[3] El-Atawi, M.; Ferretti, F.; Raini, F. *Eur. J. Org. Chem.* **2018**, *34*, 4818-4825.

(E)-2-methyl-4-nitrohex-3-ene



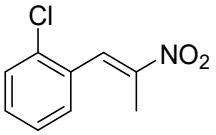
Molecular Weight: 143,1860

Prepared following the general procedure using isobutyraldehyde (5.0 mL, 54.8 mmol) and NH_4OAc (5.9 g, 76.7 mmol). The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 0:100 to 3:97) to yield a light orange oil (2.0 g, 14.0 mmol, 26%)

R_f = 0.57 (EtOAc/ Petroleum ether = 1:9), **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 6.87 (d, *J* = 10.5 Hz, 1H), 2.60 (q, *J* = 7.4 Hz, 2H), 2.68 – 2.51 (m, 1H), 1.12 (t, 3H), 1.10 (d, 6H).

^{1}H NMR spectroscopic data are in accordance with the literature.[4]

(E)-1-chloro-2-(2-nitroprop-1-en-1-yl)benzene



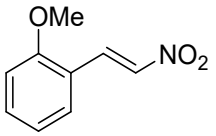
Molecular Weight: 197,6180

Prepared following the general procedure using 2-chlorobenzaldehyde (0.9 mL, 8.0 mmol) and NH_4OAc (802 mg, 10.4 mmol). The crude product was purified by column chromatography (SiO_2, liquid deposit, 100% Petroleum ether) to yield a yellow oil (1.44 g, 7.3 mmol, 91%)

R_f = 0.67 (EtOAc/ Petroleum ether = 1:9), **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.17 (q, *J* = 1.1 Hz, 1H), 7.51 – 7.44 (m, 1H), 7.42 – 7.29 (m, 3H), 2.34 (d, *J* = 1.2 Hz, 3H).

^{1}H NMR spectroscopic data are in accordance with the literature.[5]

(E)-1-methoxy-2-(2-nitrovinyl)benzene



Molecular Weight: 179,1750

Prepared following the general procedure using 2-anisaldehyde (1.23 g, 9.0 mmol) and NH_4OAc (971 mg, 12.6 mmol). The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:19 to 1:10) to yield a yellow solid (1.39 g, 7.8 mmol, 86%)

R_f = 0.4 (EtOAc/ Petroleum ether = 1:9), **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.14 (d, *J* = 13.6 Hz, 1H), 7.87 (d, *J* = 13.6 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.07 – 6.94 (m, 2H), 3.95 (s, 3H).

^{1}H NMR spectroscopic data are in accordance with the literature.[6]

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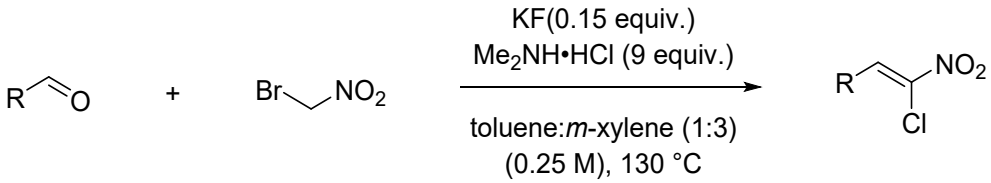
[4] Kumaran, G.; Kulkarni, G. H. *Synthesis* **1995**, *12*, 1545-1548

[5] Li, S.; Huang, K.; Zhang, X. *Chem. Commun*. **2014**, *50*, 8878-8881.

[6] Luo, M.; Yan, B.; *Tetrahedron Letters*, **2010**, *51*, 42, 5577-5580.

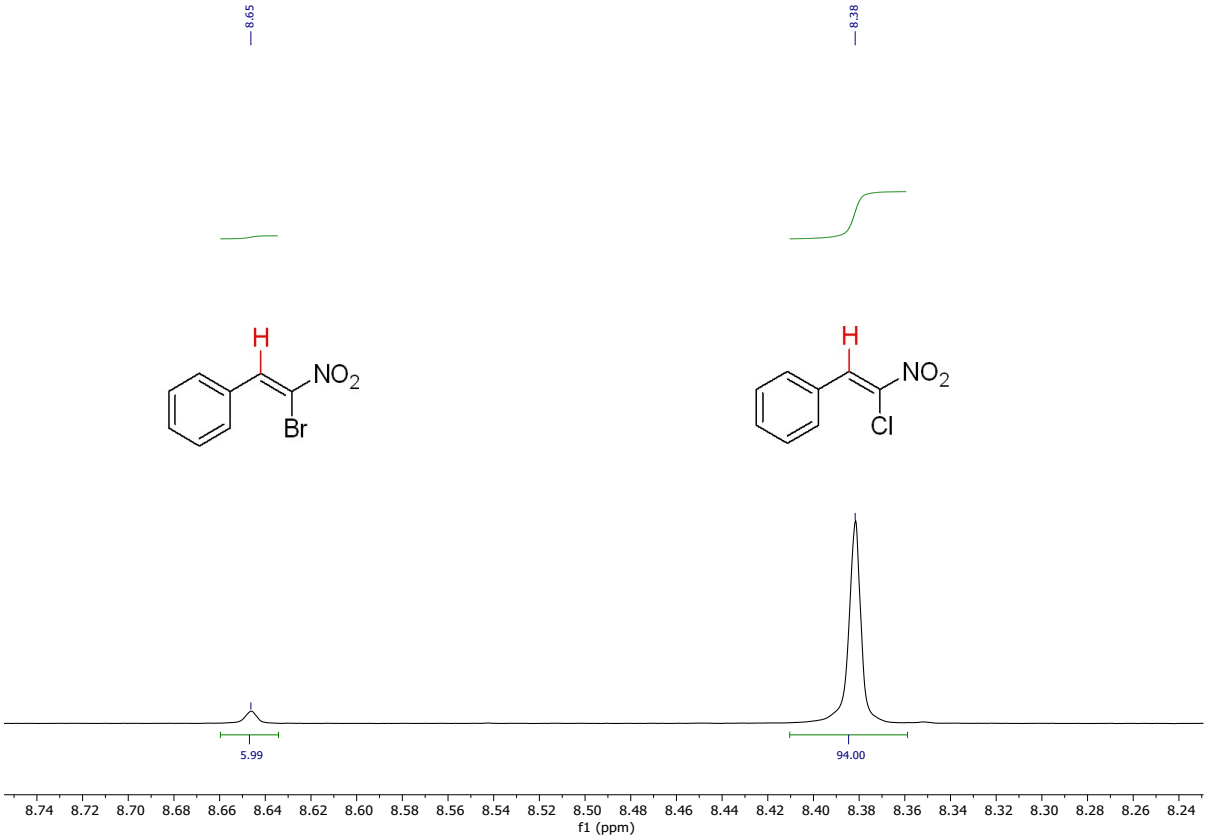
b) Preparation of chloronitroalkenes

General procedure



The chloronitroalkenes were prepared according to the literature known procedure[7] with slight modifications. In a 100 mL round-bottom flask, aldehyde (10 mmol, 1.0 equiv.), bromonitromethane (20 mmol, 2.0 equiv.), $Me_2NH{\cdot}HCl$ (90 mmol, 9.0 equiv.) and KF (1.5 mmol, 0.15 equiv.) were combined with toluene (10 mL) and *m*-xylene (30 mL) and the mixture was stirred at 130 °C, fitted with a Dean-Stark trap until completion of the reaction monitored by TLC. The mixture was treated with saturated aqueous $NaHSO_3$ (20 mL) and the aqueous phase was extracted thrice with DCM. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to dryness. Once concentrated, the crude product was either purified on silica column using ethyl EtOAc/ Petroleum ether mixture or recrystallized to yield the pure product.

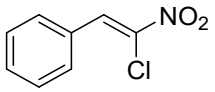
Note that the products were isolated as a mixture of **chloro**nitroalkene (major) and **bromo**nitroalkene (minor). The proportion was determined by ^{1}H NMR spectroscopy as follows.



Chemical shift of (Z)-2-bromo-2-nitrostyrene in $CDCl_3$ is in accordance with the literature[8]

[7] Dauzonne, D.; Royer, R.; *Synthesis,* **1990**, 66-70.
[8] Ganesh, M.; Namboothiri. I.N.N. *Tetrahedron*, **2007**, *63*, 11973-11983.

*(Z)-(2-chloro-2-nitrovinyl)benzene (**2a**)*



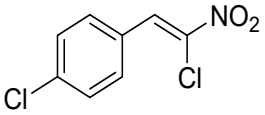
Molecular Weight: 183,5910

Prepared following general procedure using benzaldehyde (1.06 g, 1.02 mL, 10.0 mmol), bromonitromethane (2.80 g, 1.4 mL, 20.0 mmol), $Me_2NH{\cdot}HCl$ (7.30 g, 90.0 mmol) and KF (87 mg, 1.5 mmol) overnight. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 0:100 to 1:49) to yield a yellow solid (1.43 g, 7.8 mmol, 78%)

6% of Br, $\mathbf{R_f}$ = 0.43 (EtOAc/ Petroleum ether = 1:9), **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.38 (s, 1H), 7.91 – 7.83 (m, 2H), 7.54 – 7.47 (m, 3H).

^{1}H NMR spectroscopic data are in accordance with the literature[5]

*(Z)-1-chloro-4-(2-chloro-2-nitrovinyl)benzene (**2b**)*



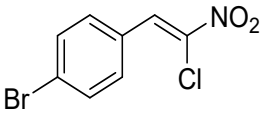
Molecular Weight: 218,0330

Prepared following general procedure using 4-chlorobenzaldehyde (1.41 g, 10.0 mmol), bromonitromethane (2.80 g, 1.4 mL, 20.0 mmol), $Me_2NH{\cdot}HCl$ (7.30 g, 90.0 mmol) and KF (87 mg, 1.5 mmol) for 40 h. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:49 to 1:24) and the yellow solid was washed with Petroleum ether to yield a light-yellow solid (0.61 g, 2.7 mmol, 27%)

12% of Br, $\mathbf{R_f}$ = 0.61 (EtOAc/ Petroleum ether = 1:9), **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.33 (s, 1H), 7.88 – 7.74 (m, 2H), 7.56 – 7.43 (m, 2H).

^{1}H NMR spectroscopic data are in accordance with the literature[5]

*(Z)-1-bromo-4-(2-chloro-2-nitrovinyl)benzene (**2f**)*



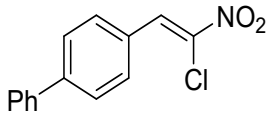
Molecular Weight: 262,4870

Prepared following general procedure using 4-bromobenzaldehyde (1.85 g, 10.0 mmol), bromonitromethane (2.80 g, 1.4 mL, 20.0 mmol), $Me_2NH{\cdot}HCl$ (7.30 g, 90.0 mmol) and KF (87 mg, 1.5 mmol) for 64 h. The crude product was recrystallized from Petroleum ether to yield a light-brown solid (0.82 g, 3.1 mmol, 31%)

4% of Br, $\mathbf{R_f}$ = 0.35 (EtOAc/ Petroleum ether = 1:9), **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.31 (s, 1H), 7.74 – 7.70 (m, 2H), 7.66 – 7.62 (m, 2H).

^{1}H NMR spectroscopic data are in accordance with the literature[9]

*(Z)-4-(2-chloro-2-nitrovinyl)-1,1'-biphenyl (**2k**)*



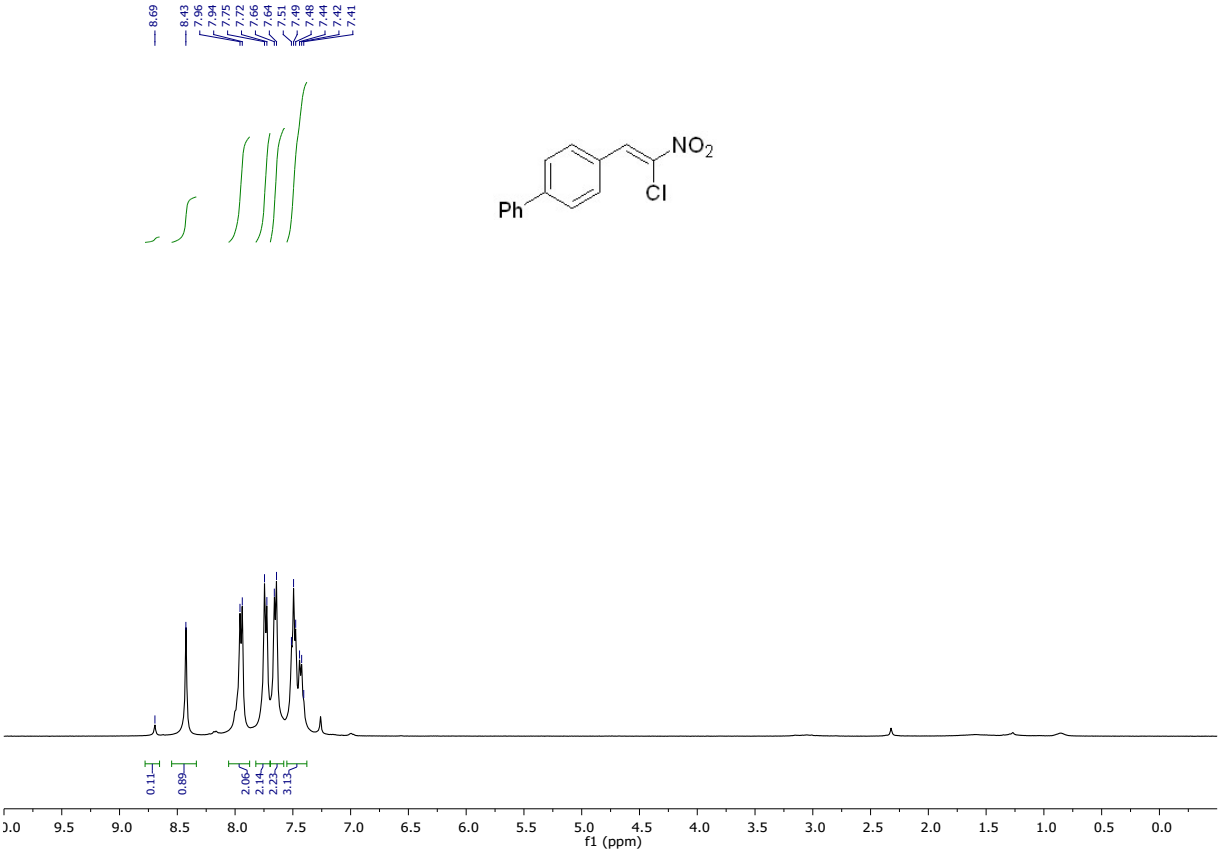
Molecular Weight: 259,6890

Prepared following general procedure using [1,1'-biphenyl]-4-carbaldehyde (1.82 g, 10.0 mmol), bromonitromethane (2.80 g, 1.4 mL, 20.0 mmol), $Me_2NH{\cdot}HCl$ (7.30 g, 90.0 mmol) and KF (87 mg, 1.5 mmol) for 43 h. The crude product was recrystallized from Petroleum ether to yield an orange powder (1.67 g, 6.3 mmol, 63%)

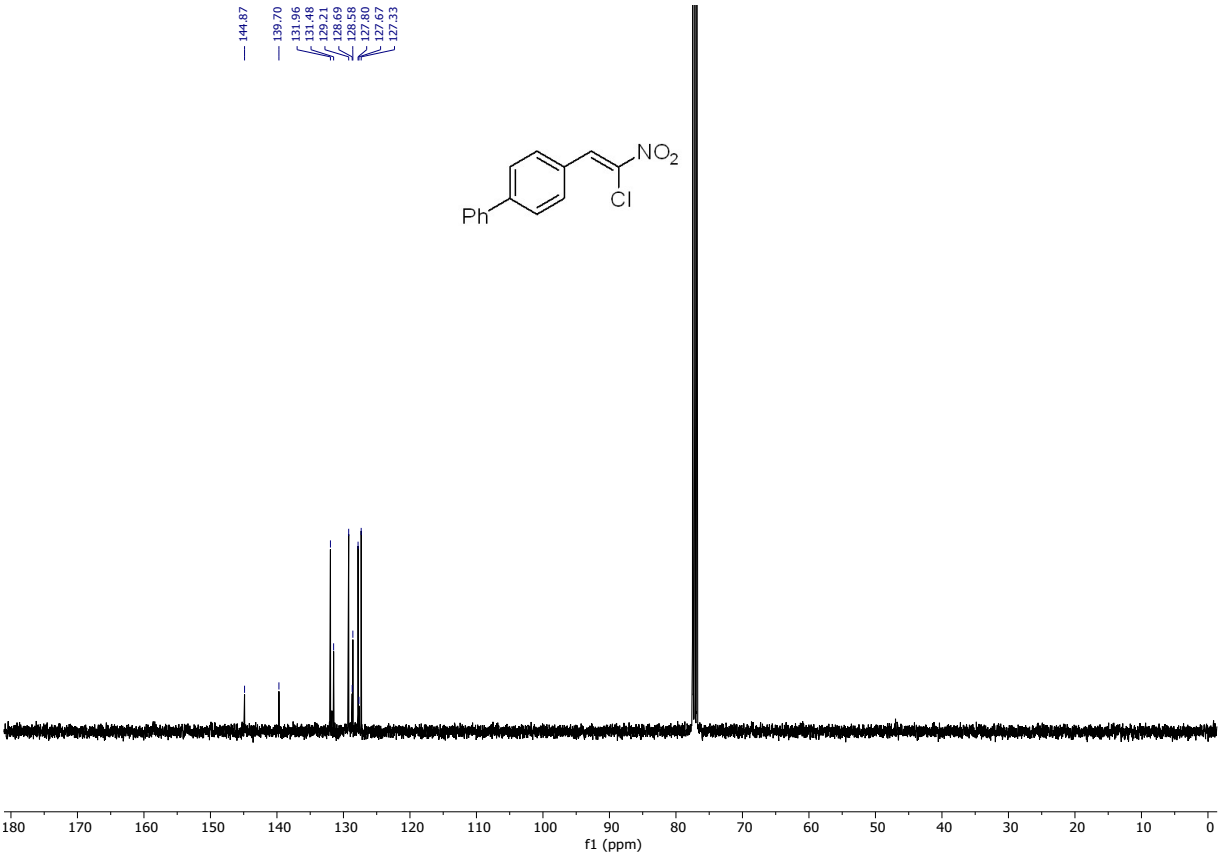
11% of Br, $\mathbf{R_f}$ = 0.53 (EtOAc/ Petroleum ether = 1:9), **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.43 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.55 – 7.38 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 144.9, 139.7, 132.0, 131.5, 129.21, 128.7, 128.6, 127.8, 127.7, 127.3. **MP** = 133 °C, **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{14}H_{10}ClNO_2Ag^+$ 367.9436, found 367.9435.

[9] Liu, L.; Zhang-Negrerie, D.; Du, Y.; Zhao, K. *Org. Lett.* **2014**. *16*, 436-439

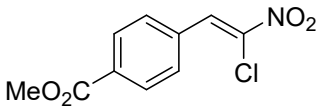
^{1}H NMR spectrum of **2k** in $CDCl_3$



^{13}C NMR spectrum of **2k** in $CDCl_3$



*methyl (Z)-4-(2-chloro-2-nitrovinyl)benzoate (**2g**)*



Molecular Weight: 241,6270

Prepared following general procedure using methyl 4-formylbenzoate (1.64 g, 10.0 mmol), bromonitromethane (2.80 g, 1.4 mL, 20.0 mmol), $Me_2NH{\cdot}HCl$ (7.30 g, 90.0 mmol) and KF (87 mg, 1.5 mmol) overnight. The crude product was recrystallized from pentane to yield an orange powder (1.49 g, 6.0 mmol, 60%)

15% of Br, $\mathbf{R_f}$ = 0.33 (EtOAc/ Petroleum ether = 1:9), **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.38 (s, 1H), 8.18 – 8.12 (m, 2H), 7.96 – 7.87 (m, 2H), 3.96 (s, 3H).

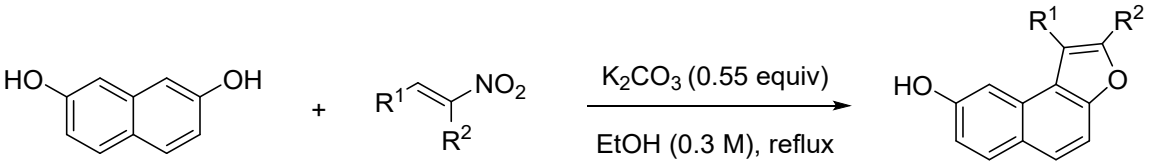
^{1}H NMR spectroscopic data are in accordance with the literature[10]

The rest of the chloronitroalkenes used were generously provided by Daniel Dauzonne (Institut Curie).

[10] Fadeeva, A.; Ioffe, S.L.; Tabolin, A.A. *Tetrahedron Letters* **2021**, *73*, 153106

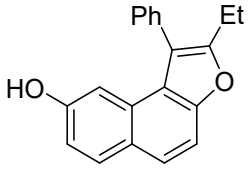
c) Preparation of naphtho[2,1-b]furan-8-ols (3)

General procedure



The naphtho[2,1-b]furan-8-ols were prepared according to the literature known procedure.[11] In a round-bottom flask, 2,7-dihydroxynaphthalene (1.0 equiv.) and K_2CO_3 (0.55 equiv.) were added to a solution of nitroalkene (1 equiv.) in absolute ethanol and the yellow mixture was stirred at reflux (80 °C) until completion of the reaction monitored by TLC. Once cooled to room temperature, the black mixture was treated with water and the aqueous phase was extracted thrice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to dryness. The crude black oil was purified on silica column using EtOAc/ Petroleum ether mixture to yield the product.

*2-ethyl-1-phenylnaphtho[2,1-b]furan-8-ol (**3a**)*



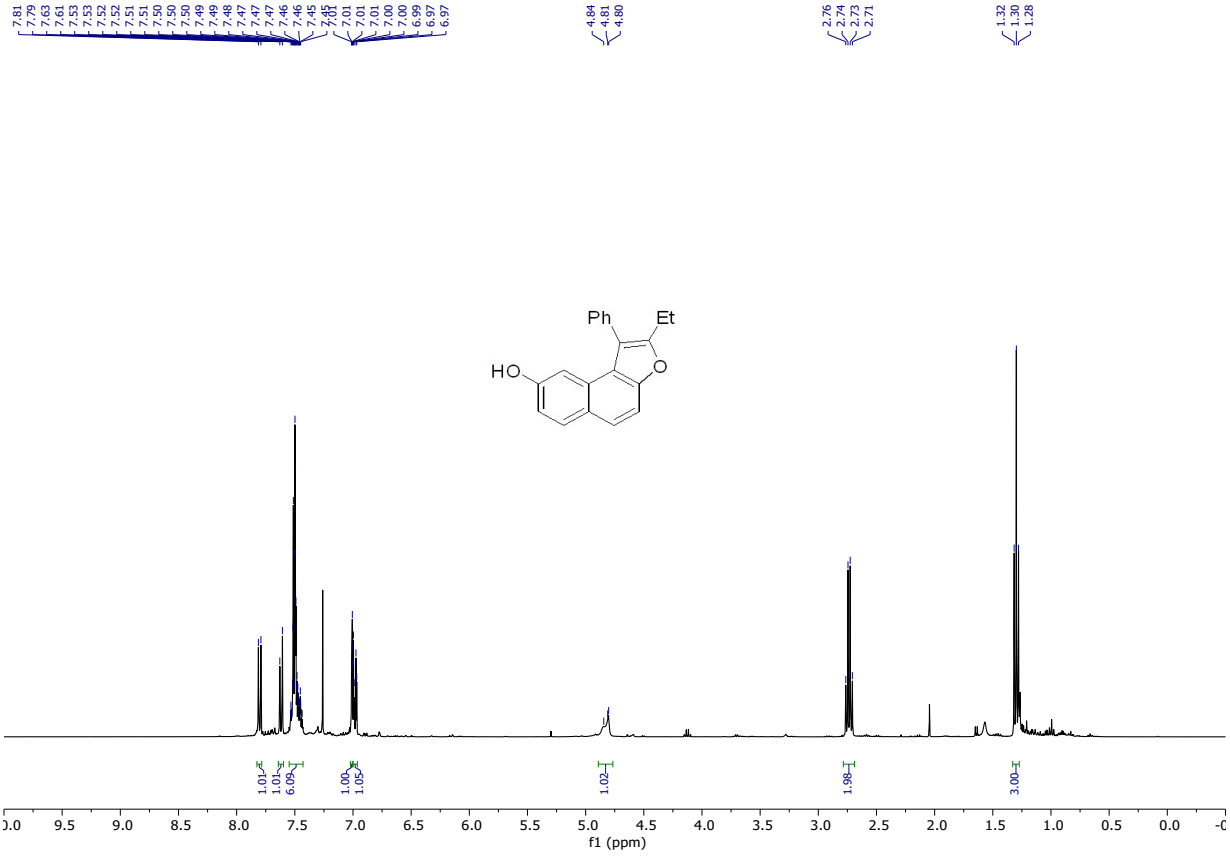
Molecular Weight: 288,3460

Prepared following general procedure using 2,7-dihydroxynaphthalene (1.76 g, 11.0 mmol), K_2CO_3 (0.83 g, 6.0 mmol), and *(E)*-(2-nitrobut-1-en-1-yl)benzene (1.95 g, 11.0 mmol) for 3 h. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 5:95 to 3:22) to yield a yellow slurry oil that darken upon storage (1.90 g, 6.59 mmol, 60%)

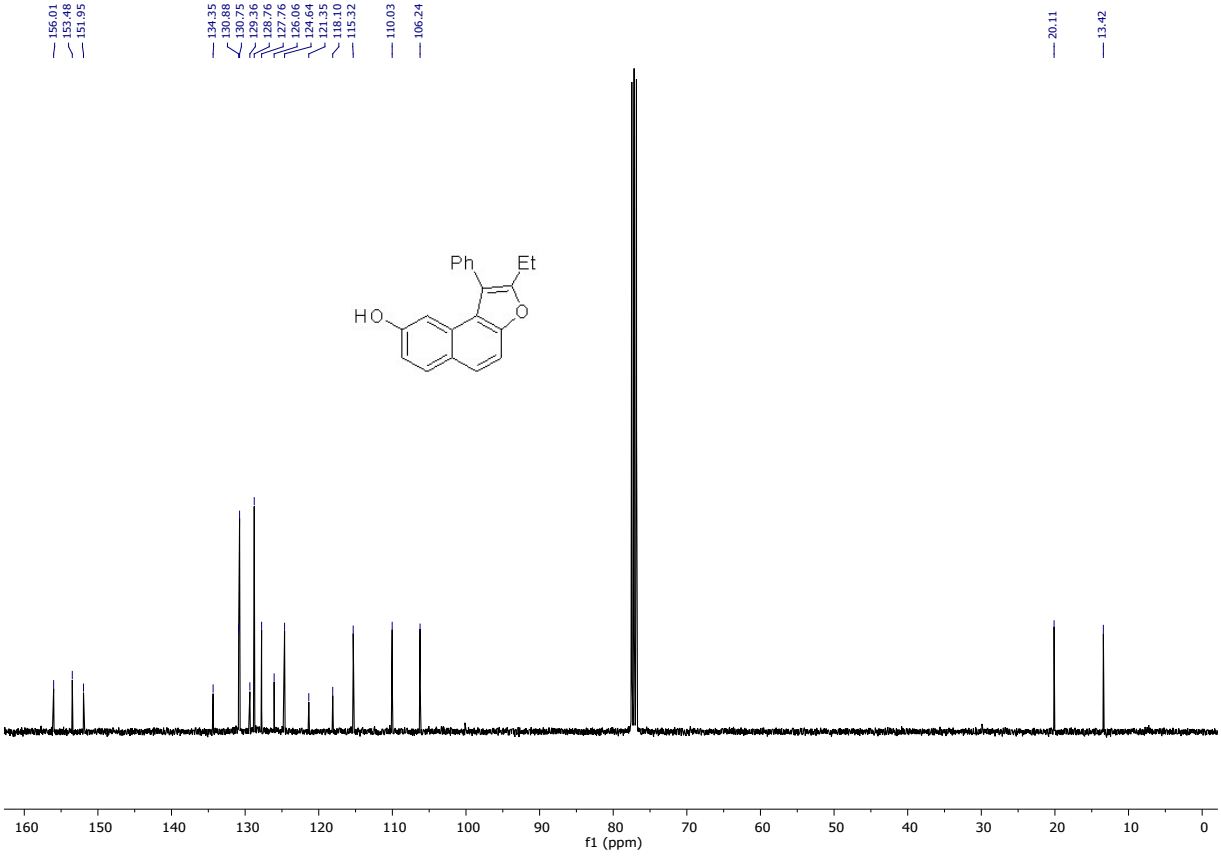
R_f = 0.23 (EtOAc/ Petroleum ether = 1:9), **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.80 (d, *J* = 8.7 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.55 – 7.43 (m, 6H), 7.01 (d, *J* = 2.6 Hz, 1H), 6.98 (dd, *J* = 8.7, 2.6 Hz, 1H), 4.88 – 4.78 (m, 1H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 156.0, 153.5, 152.0, 134.4, 130.9, 130.8, 129.4, 128.8, 127.8, 126.1, 124.6, 121.4, 118.1, 115.3, 110.0, 106.2, 20.1, 13.4. **MP** = 117 °C, **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{20}H_{16}O_2Ag^+$ 397.0194, found 397.0194.

[11] Gosh, M.; Santra, S.; Monal, P.; Kundu, D.; Hajra, A. *Chem. Asia. J*. **2015**, *10*, 2526-2536

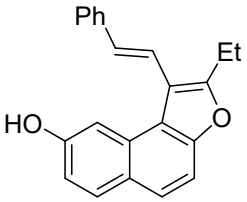
^{1}H NMR spectrum of **3a** in $CDCl_3$



^{13}C NMR spectrum of **3a** in $CDCl_3$



*(E)-2-ethyl-1-styrylnaphtho[2,1-b]furan-8-ol (**3c**)*

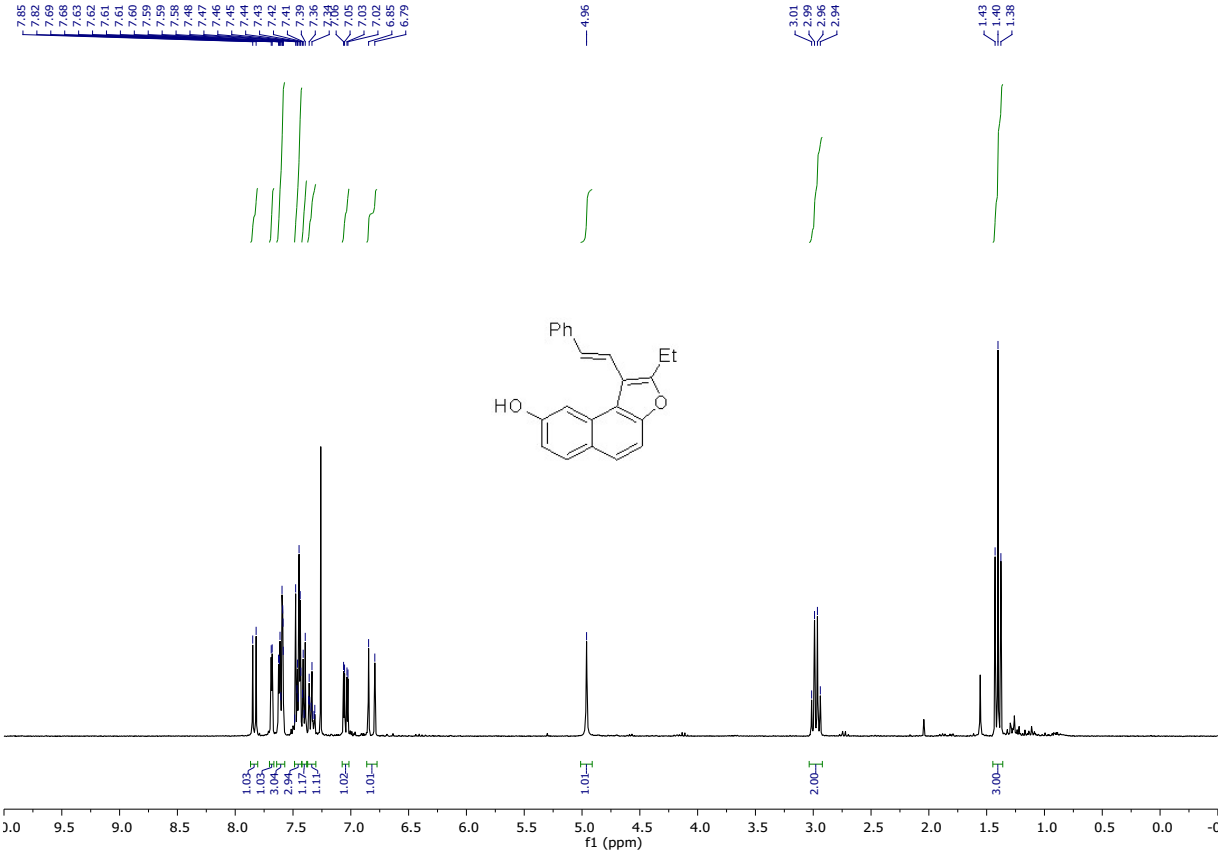


Molecular Weight: 314,3840

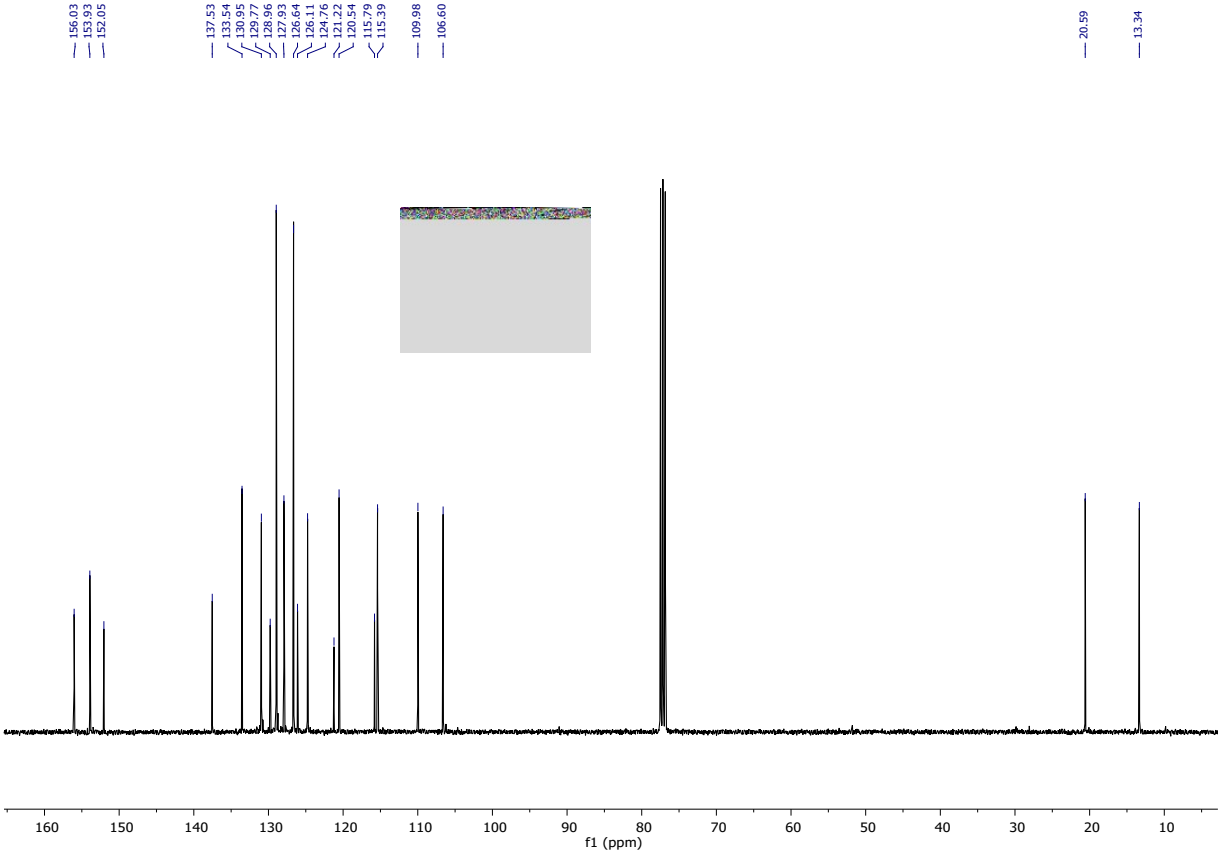
Prepared following general procedure using 2,7-dihydroxynaphthalene (409 mg, 2.55 mmol), K_2CO_3 (194 mg, 1.40 mmol), and (*(1E,3E)*-4-nitrohexa-1,3-dien-1-yl)benzene (519 mg, 2.55 mmol) for 40 min. The reaction mixture was neutralized with HCl (1M aq.). The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 5:95 to 3:17) to yield a yellow solid that darken upon storage (327 mg, 1.04 mmol, 41%)

R_f = 0.20 (EtOAc/ Petroleum ether = 1:9), **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.83 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 2.5 Hz, 1H), 7.64 – 7.57 (m, 3H), 7.48 – 7.30 (m, 5H), 7.04 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.82 (d, *J* = 16.1 Hz, 1H), 4.96 (s, 1H), 2.98 (q, *J* = 7.5 Hz, 2H), 1.40 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 156.0, 153.9, 152.1, 137.5, 133.5, 131.0, 129.8, 129.0, 127.9, 126.6, 126.1, 124.8, 121.2, 120.5, 115.8, 115.4, 110.0, 106.6, 20.6, 13.3. **MP** = 156 °C, **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{22}H_{18}O_2Ag^+$ 421.0352, found 421.0348.

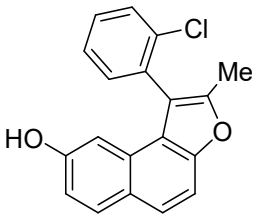
^{1}H NMR spectrum of **3c** in $CDCl_3$



^{13}C NMR spectrum of **3c** in $CDCl_3$



*1-(2-chlorophenyl)-2-methylnaphtho[2,1-b]furan-8-ol (**3m**)*

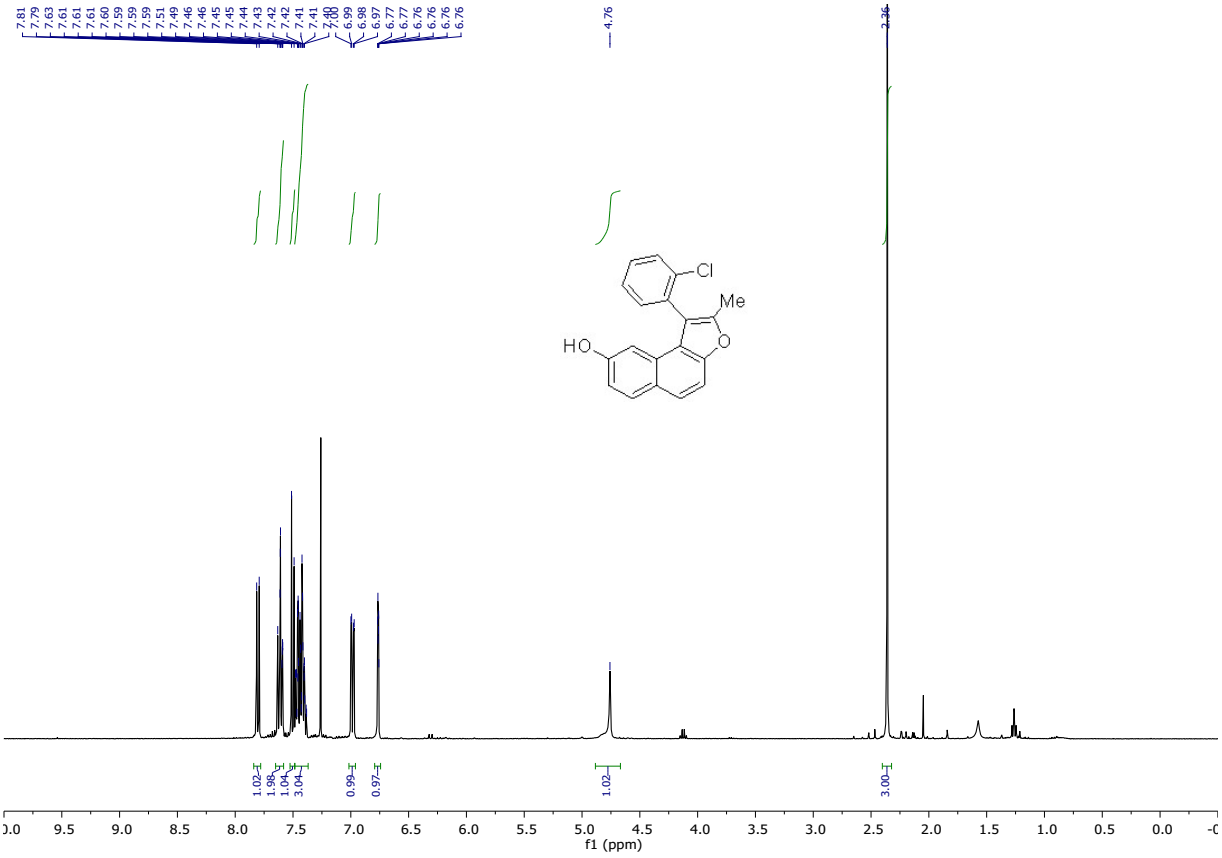


Molecular Weight: 308,7610

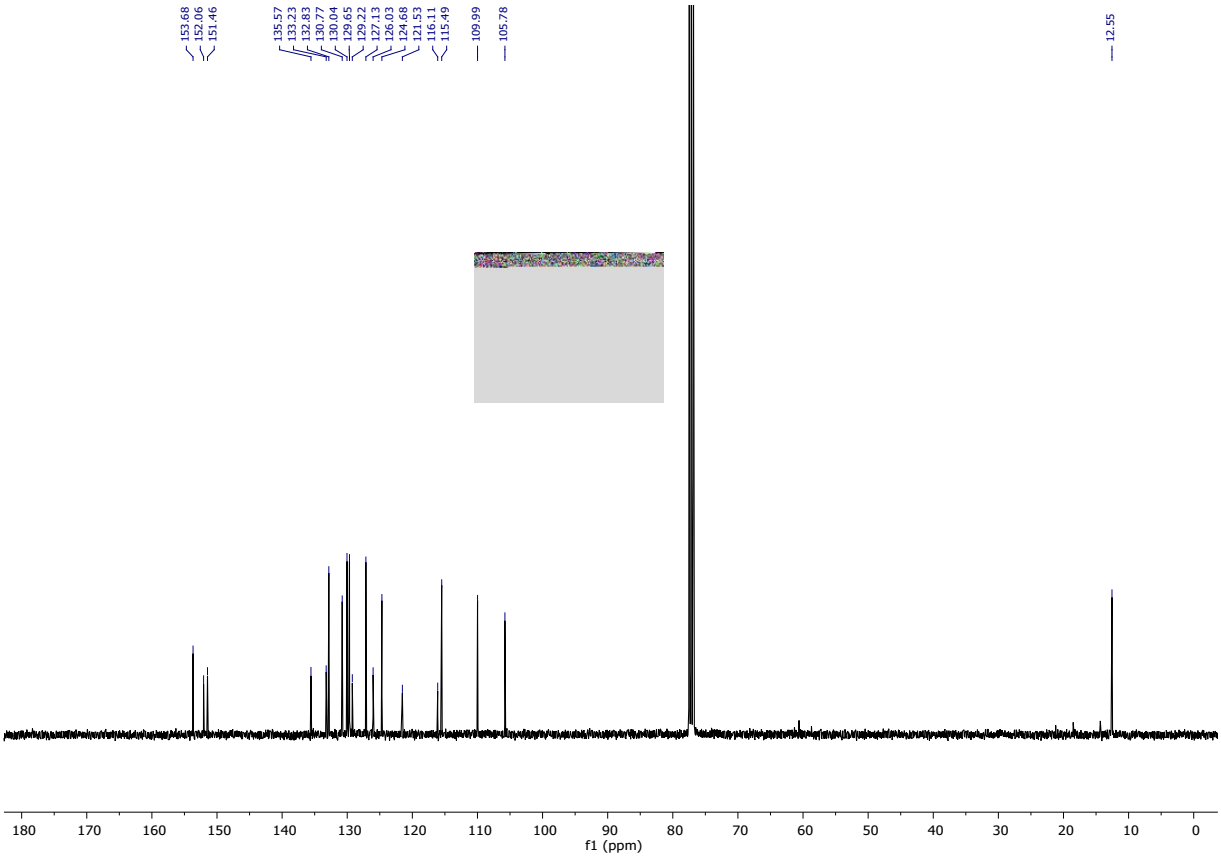
Prepared following general procedure using 2,7-dihydroxynaphthalene (526 mg, 3.28 mmol), K_2CO_3 (250 mg, 1.81 mmol), and *(E)*-1-chloro-2-(2-nitroprop-1-en-1-yl)benzene (649 mg, 3.28 mmol) for 1.5 h. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:9) to yield a white sticky solid that darken upon storage (552 mg, 1.79 mmol, 54%)

R_f = 0.12 (EtOAc/ Petroleum ether = 1:9), **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.80 (d, *J* = 8.8 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.50 (d, *J* = 8.9 Hz, 1H), 7.48 – 7.38 (m, 3H), 6.98 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.76 (dt, *J* = 2.5, 0.6 Hz, 1H), 4.76 (s, 1H), 2.36 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 153.68, 152.06, 151.46, 135.57, 133.23, 132.83, 130.77, 130.04, 129.65, 129.22, 127.13, 126.03, 124.68, 121.53, 116.11, 115.49, 109.99, 105.78, 12.55. **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{19}H_{13}ClO_2Ag^+$ 416.9641, found 416.9634.

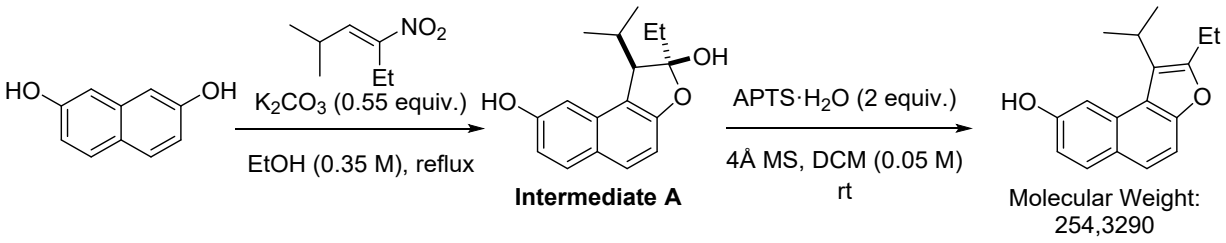
^{1}H NMR spectrum of **3m** in $CDCl_3$



^{13}C NMR spectrum of **3m** in $CDCl_3$



*2-ethyl-1-isopropylnaphtho[2,1-b]furan-8-ol (**3b**)*

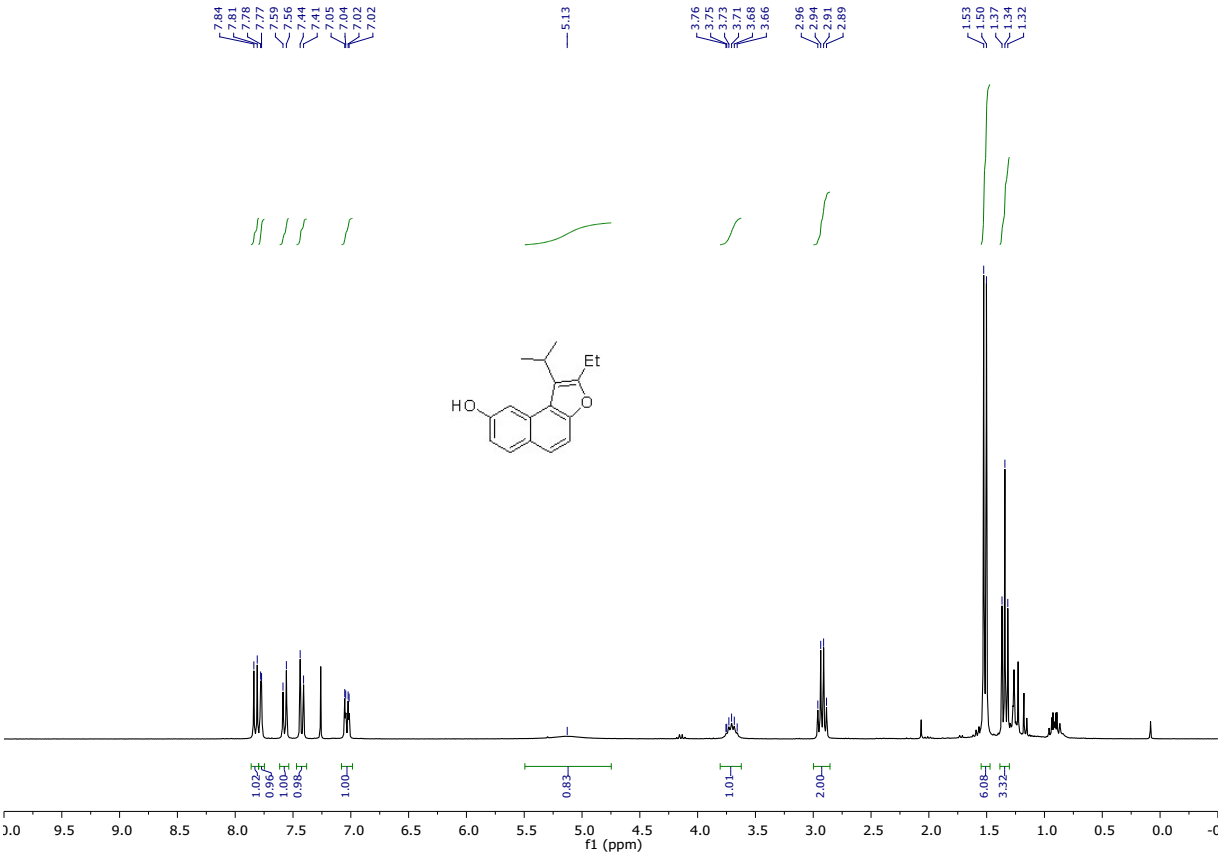


Intermediate A was prepared following general procedure using 2,7-dihydroxynaphthalene (2.24 g, 14.0 mmol), K_2CO_3 (1.06 g, 7.7 mmol), and *(E)*-2-methyl-4-nitrohex-3-ene (2.00 g, 14.0 mmol) for 24 h. The crude product was purified by column chromatography (SiO2, liquid deposit, EtOAc/ Petroleum ether = 1:4 to 2:3) to yield 619 mg (2.27 mmol, 16%)

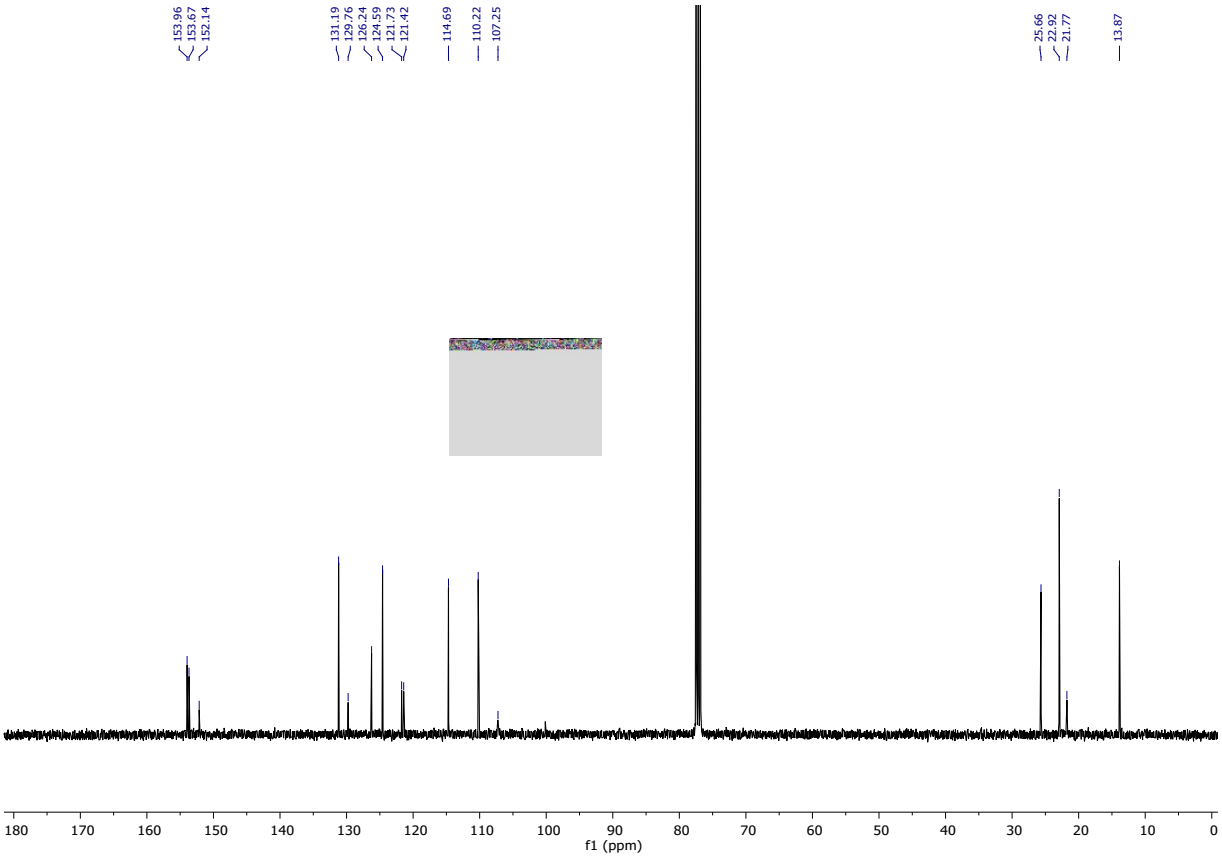
In a 100 mL round-bottom flask, APTS (796 mg, 4.2 mmol, 2.0 equiv.) was added to a brown mixture of 4Å MS (9 g) and **intermediate A** (570 mg, 2.1 mmol, 1.0 equiv.) in DCM (0.05 M) and the mixture was stirred at room temperature for 18 h. The reaction was quenched with saturated aqueous $NaHCO_3$ and the aqueous phase was extracted thrice with DCM. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to dryness. The crude oil was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:9) to yield a brown sticky solid (372 mg, 1.46 mmol, 70%)

R_f = 0.41 (EtOAc/ Petroleum ether = 1:4), **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.82 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 2.5 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.03 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.13 (s, 1H), 3.80 – 3.62 (m, 1H), 2.92 (q, *J* = 7.5 Hz, 2H), 1.51 (d, *J* = 7.1 Hz, 6H), 1.34 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 154.0, 153.7, 152.1, 131.2, 129.8, 126.2, 124.6, 121.7, 121.4, 114.7, 110.2, 107.3, 25.7, 22.9, 21.8, 13.9. **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{17}H_{18}O_2Ag^+$ 361.0352, found 361.0351.

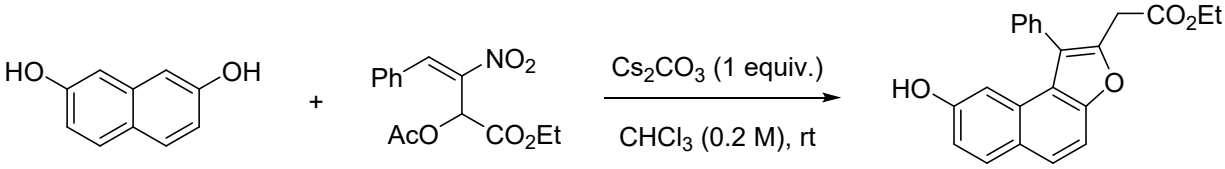
^{1}H NMR spectrum of **3b** in $CDCl_3$



^{13}C NMR spectrum of **3b** in $CDCl_3$



*ethyl 2-(8-hydroxy-1-phenylnaphtho[2,1-b]furan-2-yl)acetate (**3d**)*



Molecular Weight: 346,3820

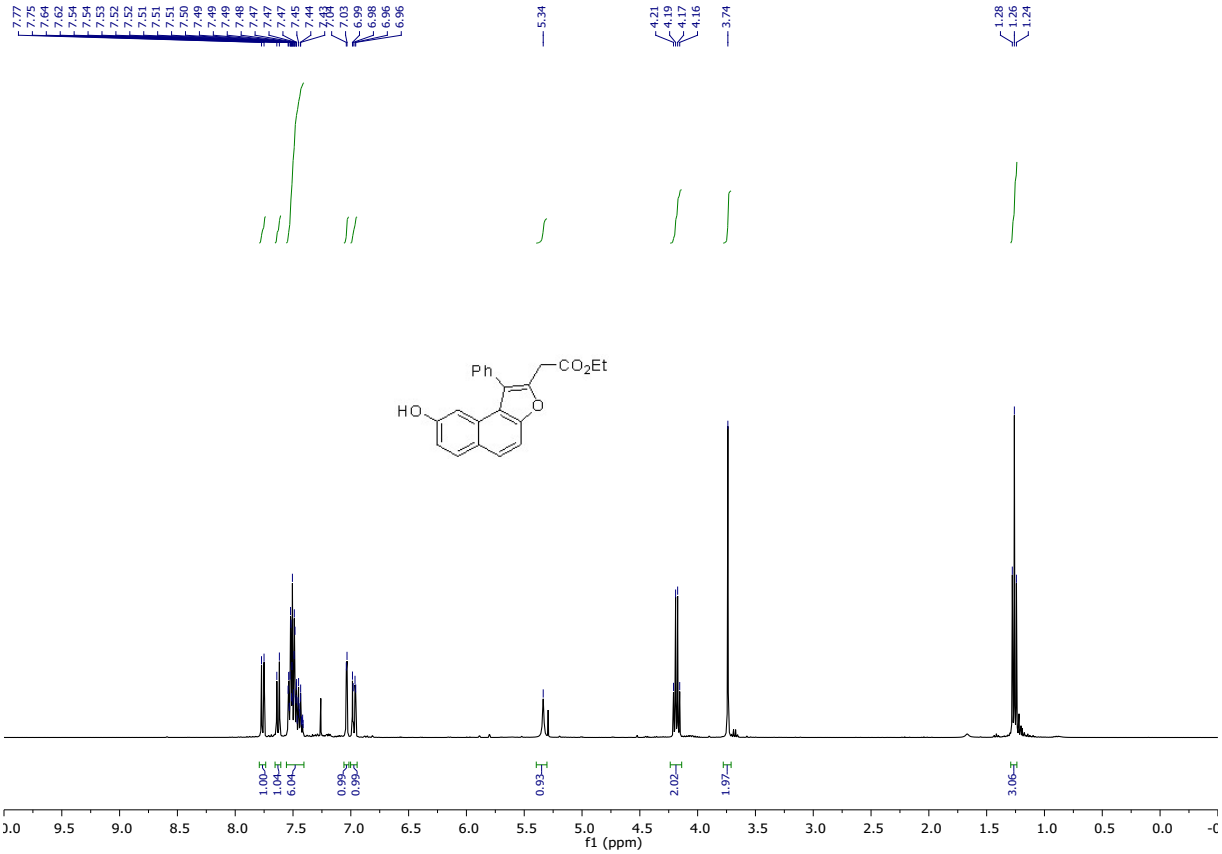
3d was prepared according to the literature known procedure.[12] In a reaction tube, 2,7-dihydroxynaphtalene (71 mg, 0.44 mmol, 1.0 equiv.), ethyl *(E)*-2-acetoxy-3-nitro-4-phenylbut-3-enoate (130 mg, 0.44 mmol, 1.0 equiv.); and C_2CO_3 (145 mg, 0.44 mmol, 1.0 equiv.) were combined with $CHCl_3$ and the yellow mixture was stirred at room temperature for 22h. Once concentrated, the crude red oil was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:9 to 1:4) to yield a yellow solid (85 mg, 0.24 mmol, 55%)

R_f = 0.25 (EtOAc/ Petroleum ether = 1:4), **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.76 (d, *J* = 8.8 Hz, 1H), 7.63 (d, *J* = 8.9 Hz, 1H), 7.56 – 7.41 (m, 6H), 7.04 (d, *J* = 2.5 Hz, 1H), 6.97 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.34 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 169.6, 153.8, 152.6, 146.4, 133.3, 130.9, 130.6, 129.4, 128.9, 128.1, 126.0, 125.6, 121.7, 120.9, 115.6,

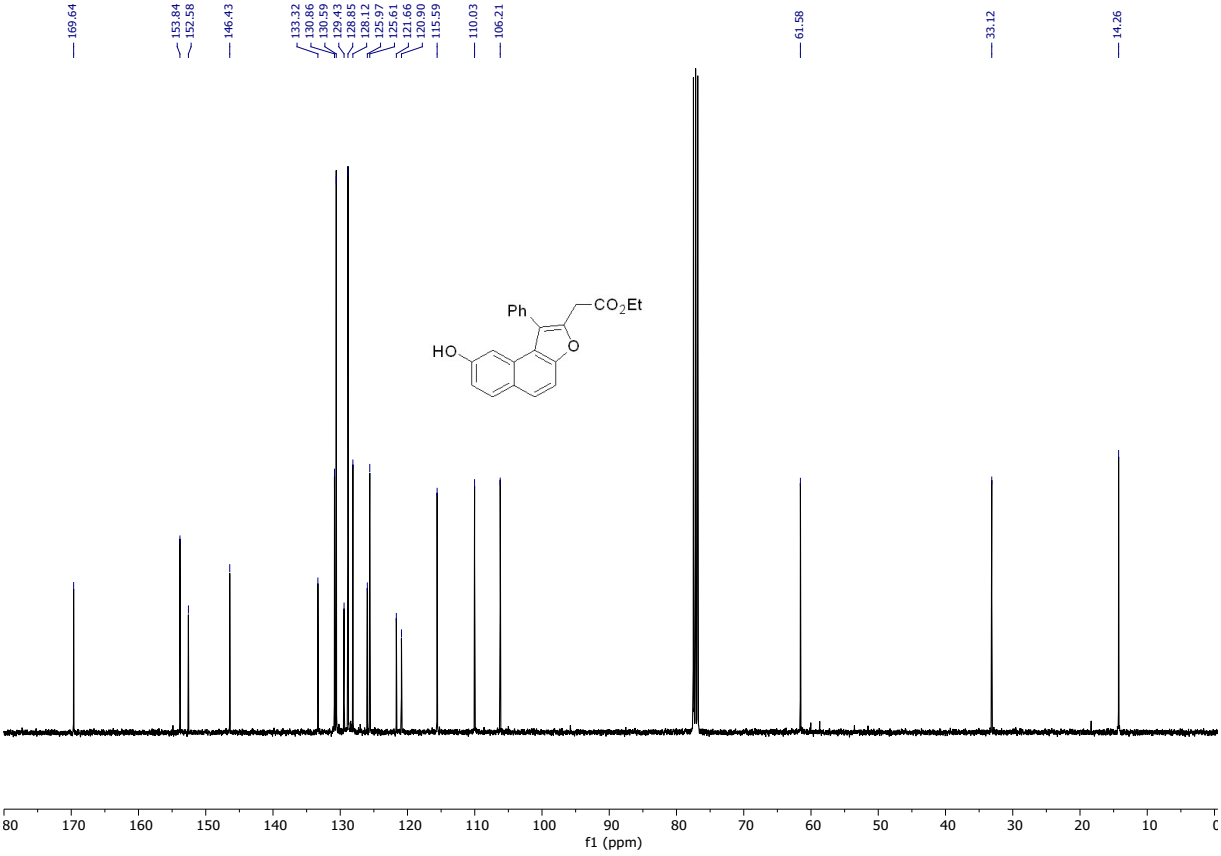
[12] Anwar, S.; Huang, W-Y.; Chen, C-H.; Cheng, Y-S.; Chen, K. *Chem. Eur. J.* **2013**, *19*, 4344-4351

110.0, 106.2, 61.6, 33.1, 14.3. **MP** = 114 °C, **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{22}H_{18}O_4Ag^+$ 453.0251, found 453.0247.

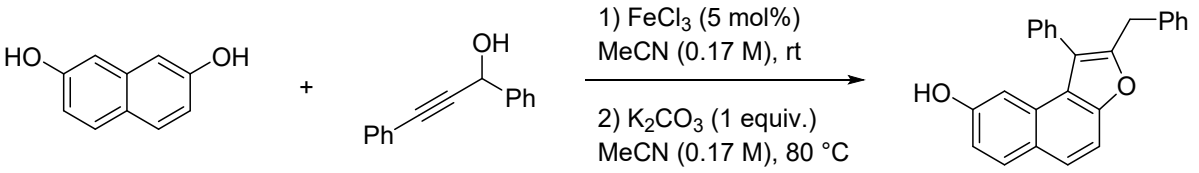
^{1}H NMR spectrum of **3d** in $CDCl_3$



^{13}C NMR spectrum of **3d** in $CDCl_3$



*2-benzyl-1-phenylnaphtho[2,1-b]furan-8-ol (**3e**)*



Molecular Weight: 350,42

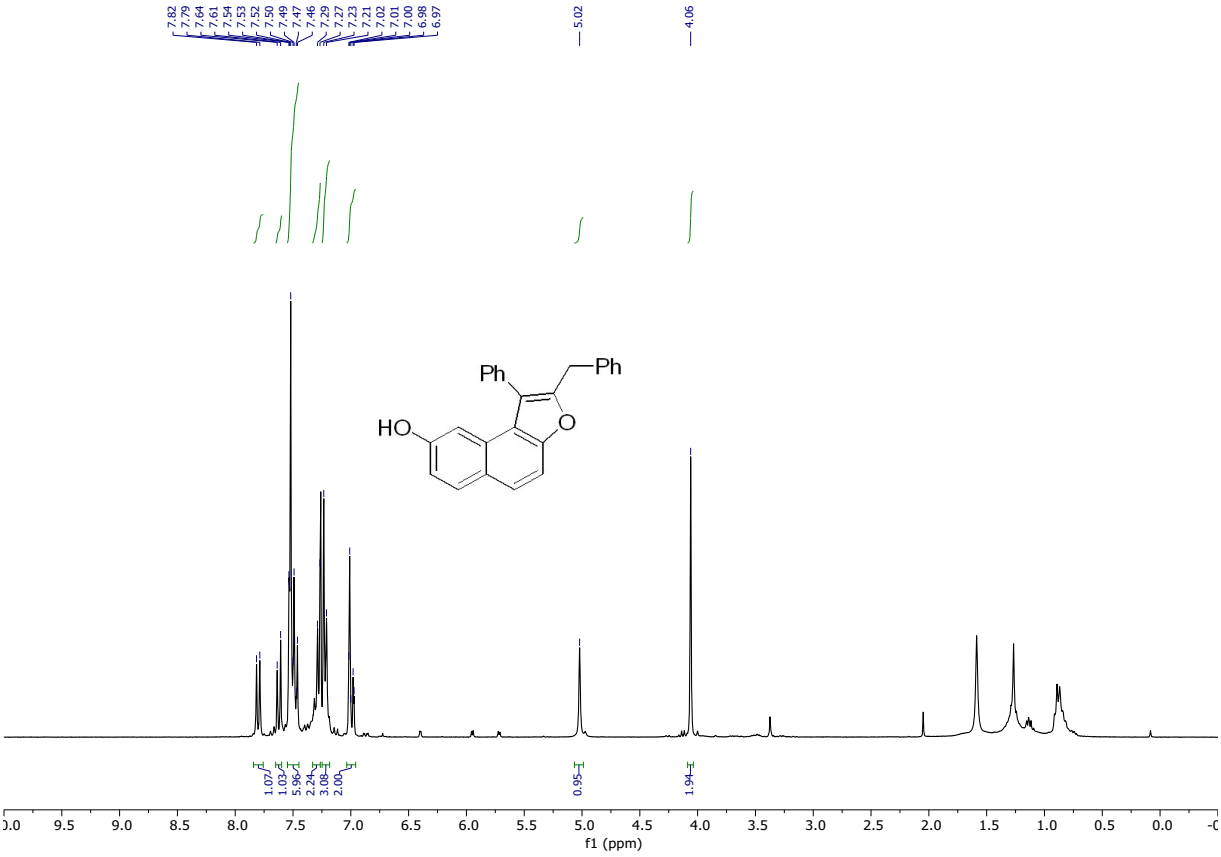
3e was prepared according to the literature known procedure.[13] In a dry Schlenk tube, 1,3-diphenylprop-2-yn-1-ol (95 µL, 0.5 mmol, 1.0 equiv.) was added to a mixture of 2,7-dihydroxynaphtalene (96 mg, 0.6 mmol, 1.2 equiv.) and $FeCl_3$ (4 mg, 0.025 mmol, 5%mol) in MeCN and the brown mixture was stirred at room temperature for 4 days. K_2CO_3 (69 mg, 0.5 mmol, 1.0 equiv.) was added to the now red mixture that was then heated to 80 °C for 24 h. Once cooled to room temperature, the black mixture was filtered on celite, washed with DCM, and the filtrate was concentrated to dryness. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 5:95 to 2:8) to yield an orange sticky solid (100 mg, 0.29 mmol, 57%)

R_f = 0.54 (EtOAc/ Petroleum ether = 3:7), **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 7.80 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.56 – 7.44 (m, 6H), 7.35 – 7.24 (m, 2H), 7.22 (d, *J* = 7.1 Hz, 3H), 7.04 – 6.96 (m, 2H), 5.02 (s, 1H), 4.06 (s, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 153.7, 152.5, 152.4, 138.3, 134.0,

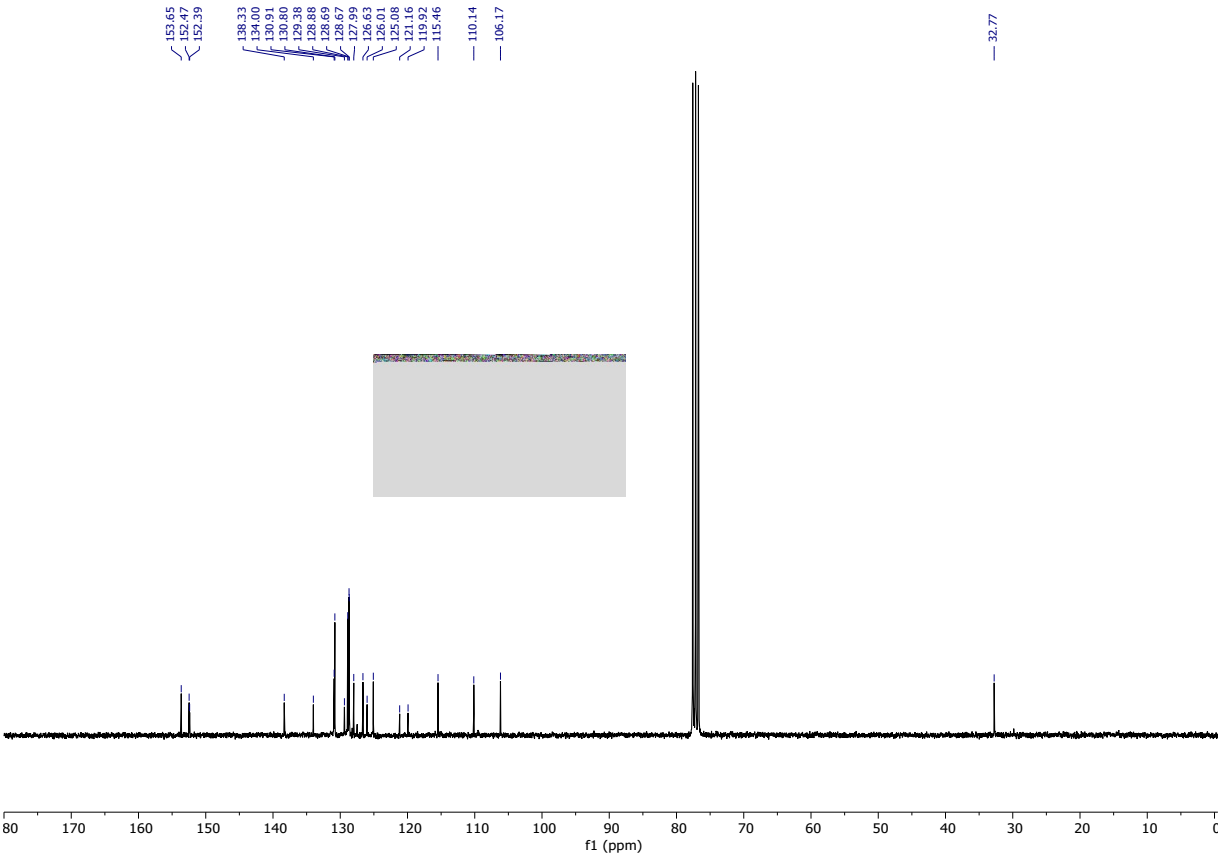
[13] Yuan, F-Q.; Han, F-S.; *Adv. Synth. Catal.* **2013**, *355*, 537-547.

130.9, 130.8, 129.4, 128.9, 128.7, 128.7, 128.0, 126.6, 126.0, 125.1, 121.2, 119.9, 115.5, 110.1, 106.2, 32.8. **HRMS-ESI$^+$ (m/z)**: [M+Ag]$^+$ calculated for $C_{25}H_{18}O_2Ag^+$ 457.0352, found 457.0349.

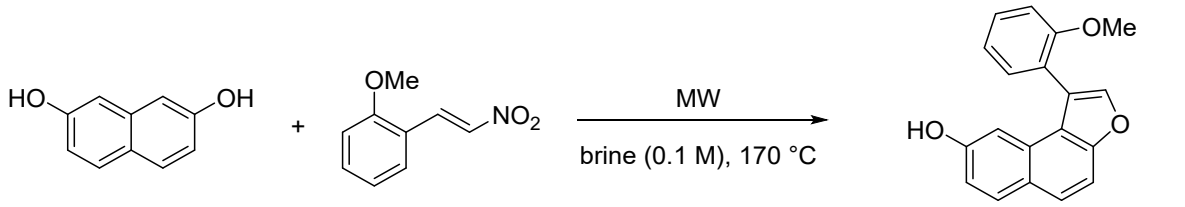
^{1}H NMR spectrum of **3e** in $CDCl_3$



^{13}C NMR spectrum of **3e** in $CDCl_3$



*1-(2-methoxyphenyl)naphtho[2,1-b]furan-8-ol (**3n**)*



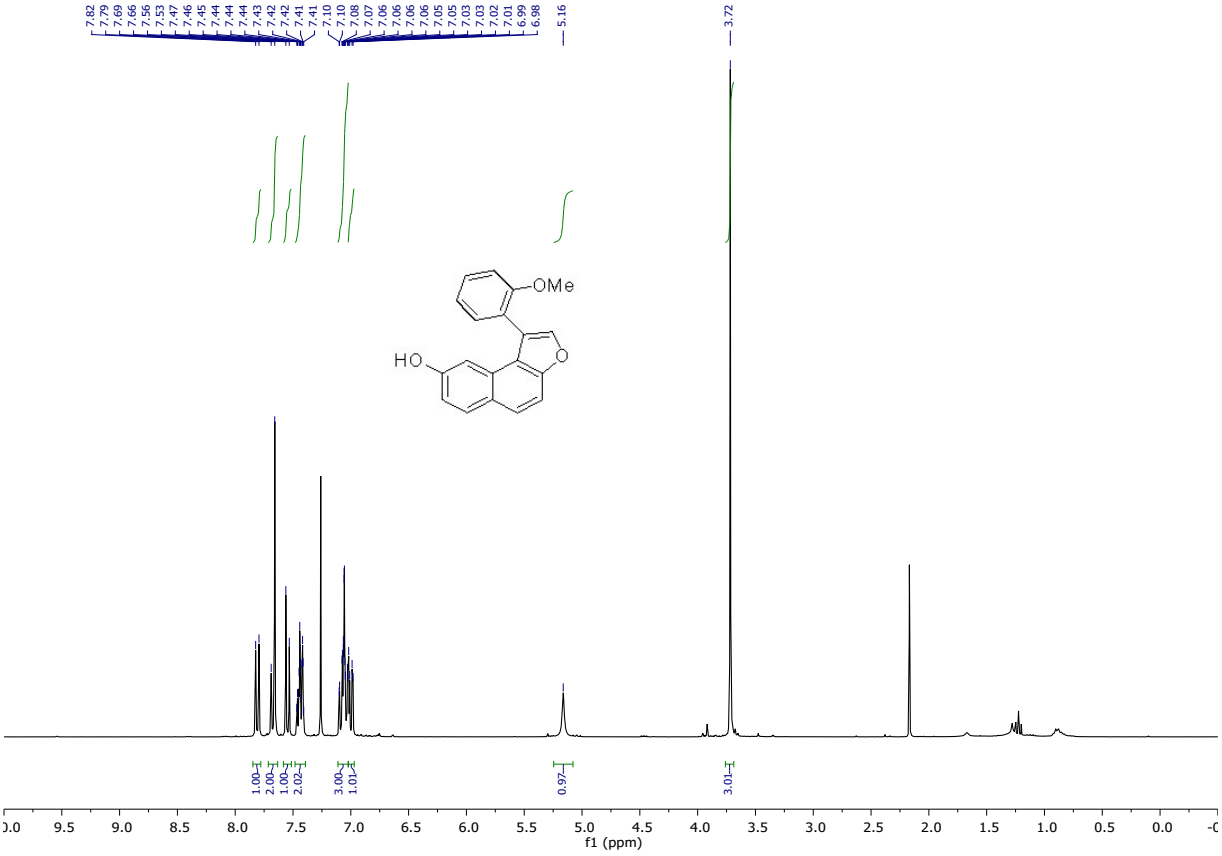
Molecular Weight: 290,3180

3n was prepared according to the literature known procedure.[14] In a G30 MW vessel, dihydroxynaphtalene (160 mg, 1.0 mmol, 2.0 equiv.) and 1-methoxy-2-[*(1E)*-2-nitroethenyl]benzene (90 mg, 0.5 mmol, 1.0 equiv.) were combined with brine and the heterogenous mixture was stirred at 170 °C under microwaves for 25 min. The now purple mixture was extracted with EtOAc thrice. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to dryness. The crude purple residue was purified by column chromatography (SiO_2, solid deposit, EtOAc/ Petroleum ether = 1:4) to yield a yellow sticky solid (40 mg, 0.14 mmol, 28%).

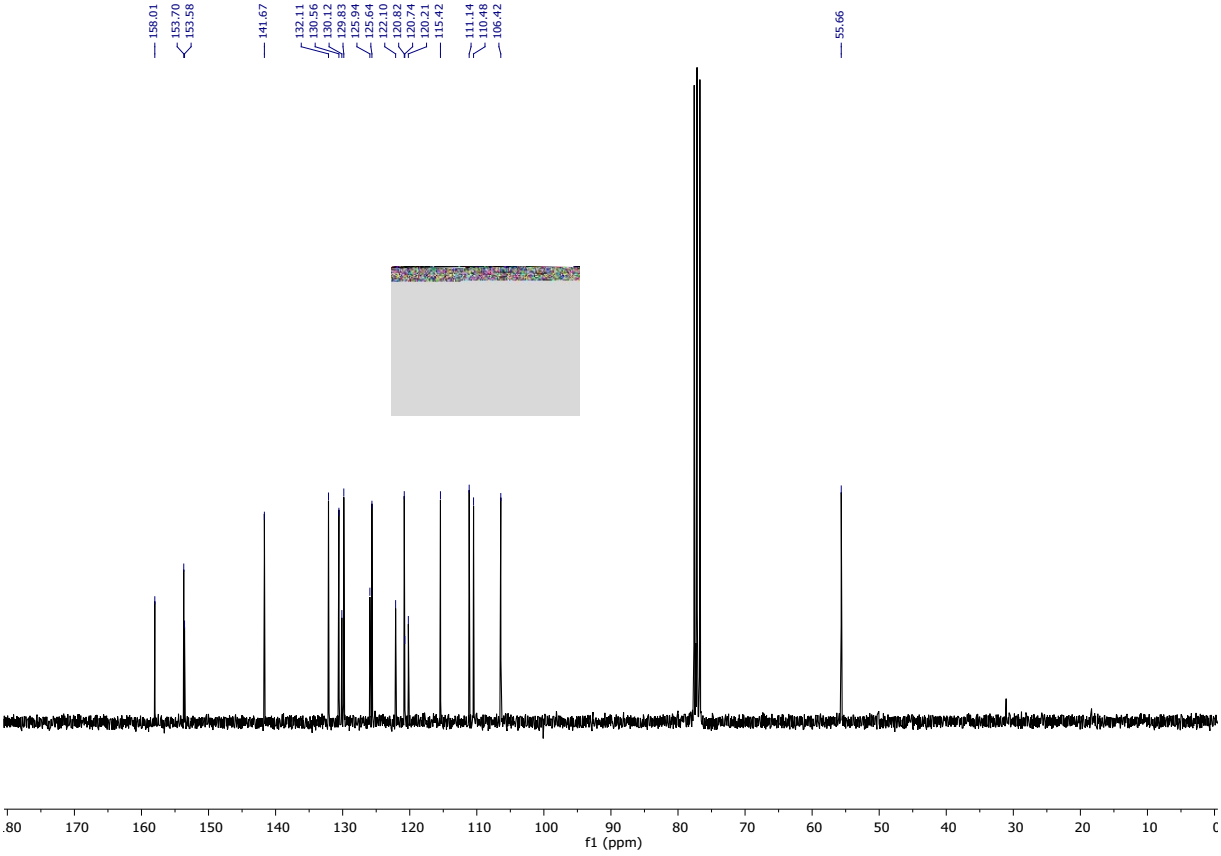
R_f = 0.34 (EtOAc/ Petroleum ether = 3:7), **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 7.81 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 9.3 Hz, 1H), 7.66 (s, 1H), 7.55 (d, *J* = 8.9 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.10 – 7.02 (m, 3H), 7.00 (dd, *J* = 8.7, 2.6 Hz, 1H), 5.16 (s, 1H), 3.72 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 158.0, 153.7, 153.6, 141.7, 132.1, 130.6, 130.1, 129.8, 125.9, 125.6, 122.1, 120.8, 120.7, 120.2, 115.4, 111.1, 110.5, 106.4, 55.7. **HRMS-ESI$^+$ (m/z)**: $[M-H]^-$ calculated for $C_{19}H_{13}O_3^-$ 289.0870, found 289.0868.

[14] Wang, B.; Zhang, J.; Liao, J.; Peng, Y.; Zheng, H.; *Heterocycles* **2016**, *92*, 8, 1468-1478.

^{1}H NMR spectrum of **3n** in $CDCl_3$

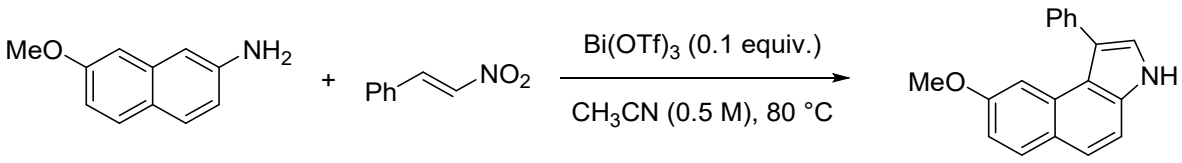


^{13}C NMR spectrum of **3n** in $CDCl_3$



d) Preparation of pyrroles

8-methoxy-1-phenyl-3H-benzo[e]indole



Molecular Weight: 273,3350

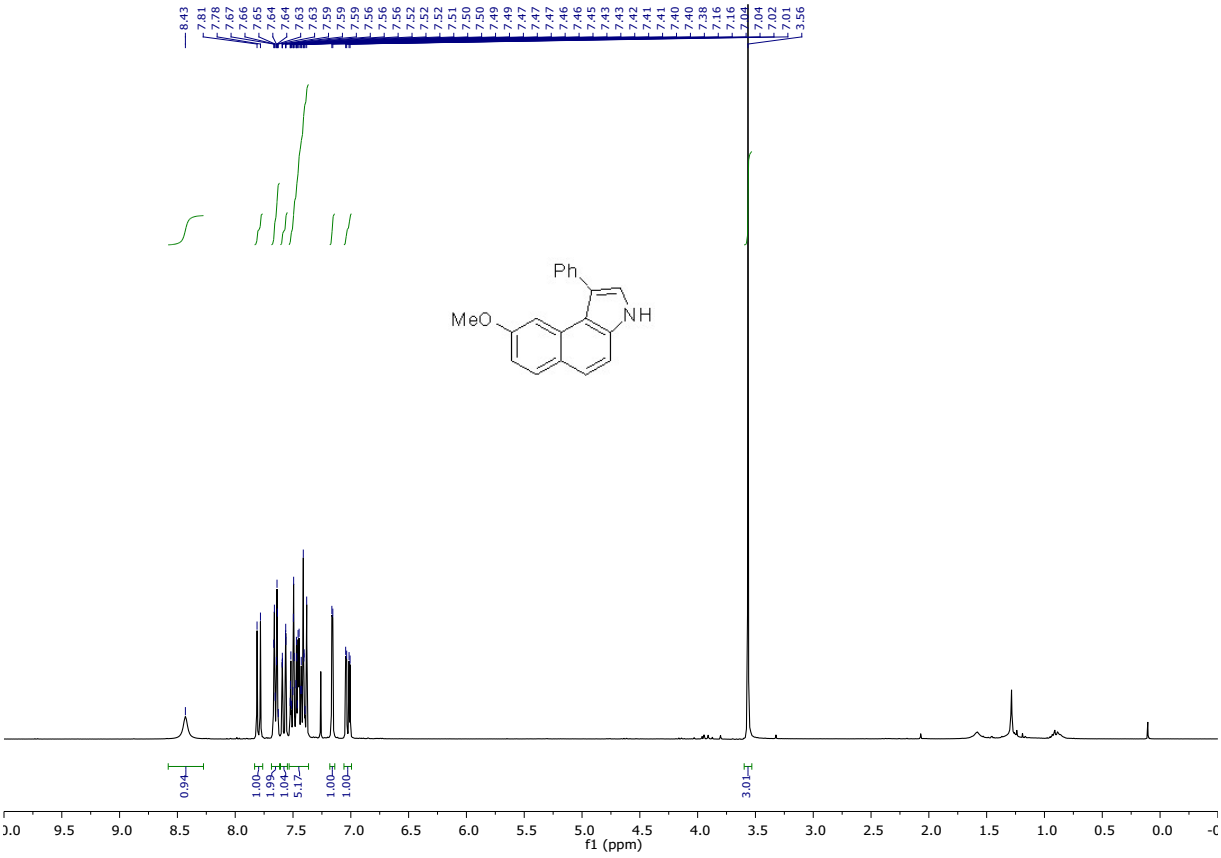
8-methoxy-1-phenyl-3H-benzo[e]indole was prepared according to the literature known procedure.[15] In a dry reaction tube, 7-methoxynaphthalen-2-amine (173 mg, 1.0 mmol, 1.0 equiv.), nitrostyrene (149 mg, 1.0 mmol, 1.0 equiv.) and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 0.1 equiv.) were combined with freshly distilled CH_3CN and the brown mixture was stirred at 80 °C overnight. At room temperature, the mixture was partitioned between water and DCM and the aqueous phase was extracted with DCM twice. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to dryness. The crude brown oil was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:9) to yield a brown oil (159 mg, 0.58 mmol, 58%).

R_f = 0.31 (EtOAc/ Petroleum ether = 1:4), **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.43 (s, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.70 – 7.62 (m, 2H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.53 – 7.37 (m, 5H), 7.16 (d, *J* = 2.5 Hz, 1H),

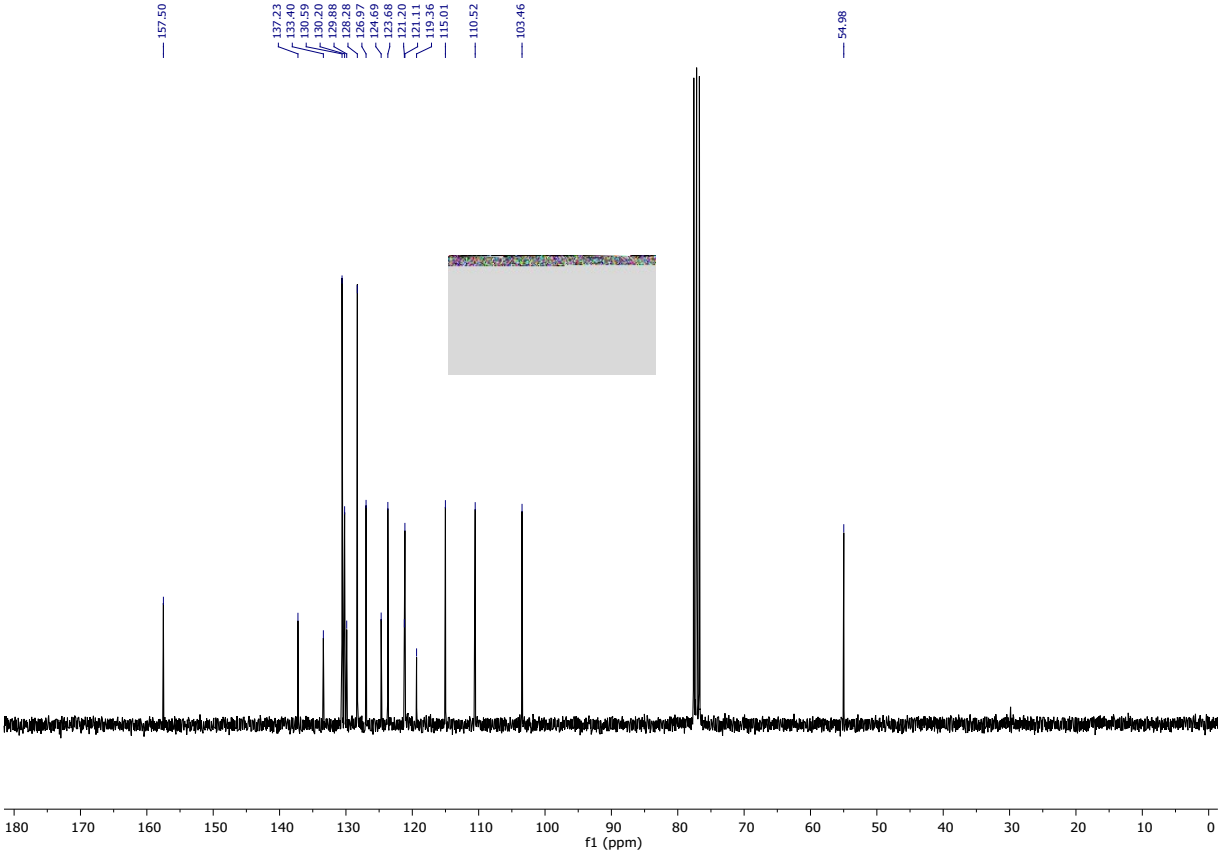
[15] Gattu, R.; Bhattacharjee, S.; Mahato, K.; Khan, A.T. *Org. Biomol. Chem.* **2018**, *16*, 3760-3770.

7.03 (dd, *J* = 8.8, 2.6 Hz, 1H), 3.56 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 157.5, 137.2, 133.4, 130.6, 130.2, 129.9, 128.3, 127.0, 124.7, 123.7, 121.2, 121.1, 119.4, 115.0, 110.5, 103.5, 55.0. **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{19}H_{15}NOAg^+$ 380.0199, found 380.0196.

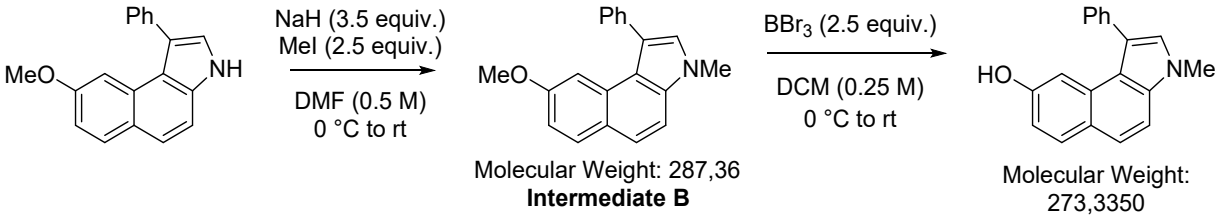
^{1}H NMR spectrum of **8-methoxy-1-phenyl-3H-benzo[e]indole** in $CDCl_3$



^{13}C NMR spectrum of **8-methoxy-1-phenyl-3H-benzo[e]indole** in $CDCl_3$



*3-methyl-1-phenyl-3H-benzo[e]indol-8-ol (**3f**)*

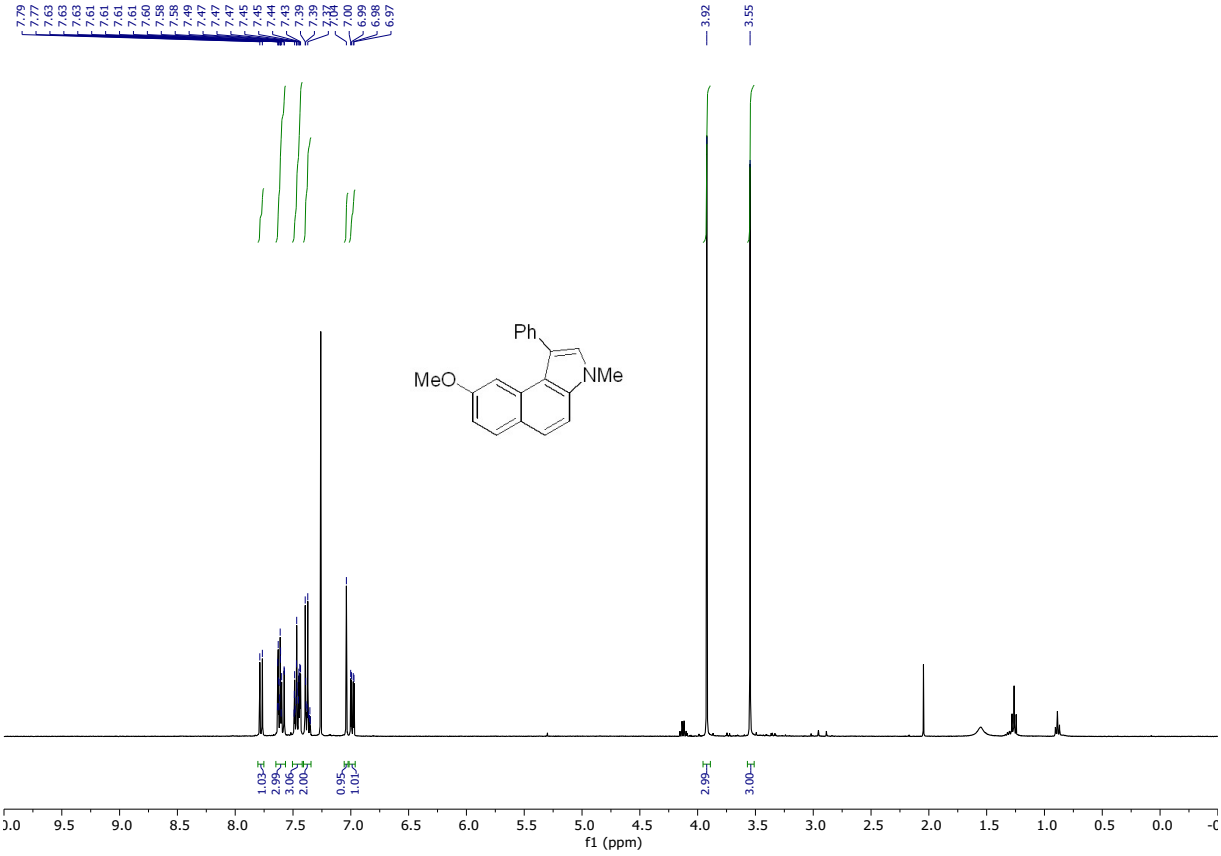


Intermediate B

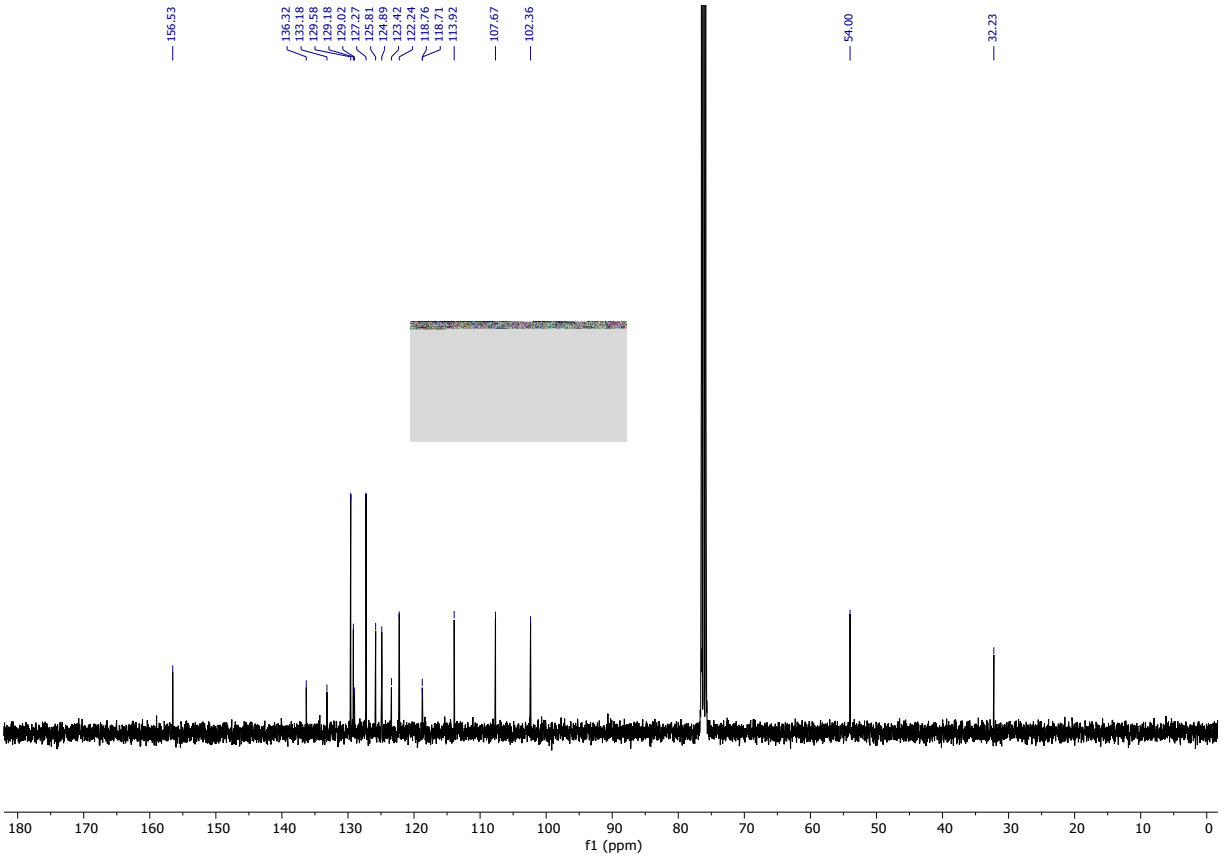
In a dry tube, NaH (47 mg, 1.97 mmol, 3.5 equiv.) was added to a solution of 8-methoxy-1-phenyl-3H-benzo[e]indole (154 mg, 0.56 mmol, 1.0 equiv.) in anhydrous DMF at 0 °C followed by the dropwise addition of MeI (88 µL, 1.41 mmol, 2.5 equiv.) at the same temperature. After 30 minutes of stirring et room temperature, the mixture was partionned between brine and EtOAc. The organic layer was washed thrice with LiCl (5% aq.), dried over Na_2SO_4, filtered, and concentrated to dryness to yield an orange oil (132 mg, 0.46 mmol, 82%)

R_f = 0.50 (EtOAc/ Petroleum ether = 1:4), **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.78 (d, *J* = 8.9 Hz, 1H), 7.64 – 7.56 (m, 3H), 7.50 – 7.43 (m, 3H), 7.41 – 7.35 (m, 2H), 7.04 (s, 1H), 6.99 (dd, *J* = 8.8, 2.6 Hz, 1H), 3.92 (s, 3H), 3.55 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 156.53, 136.32, 133.18, 129.58, 129.18, 129.02, 127.27, 125.81, 124.89, 123.42, 122.24, 118.76, 118.71, 113.92, 107.67, 102.36, 54.00, 32.23. **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{20}H_{17}NOAg^+$ 394.0356, found 394.0352.

^{1}H NMR spectrum of **intermediate B** in $CDCl_3$



^{13}C NMR spectrum of **intermediate B** in $CDCl_3$

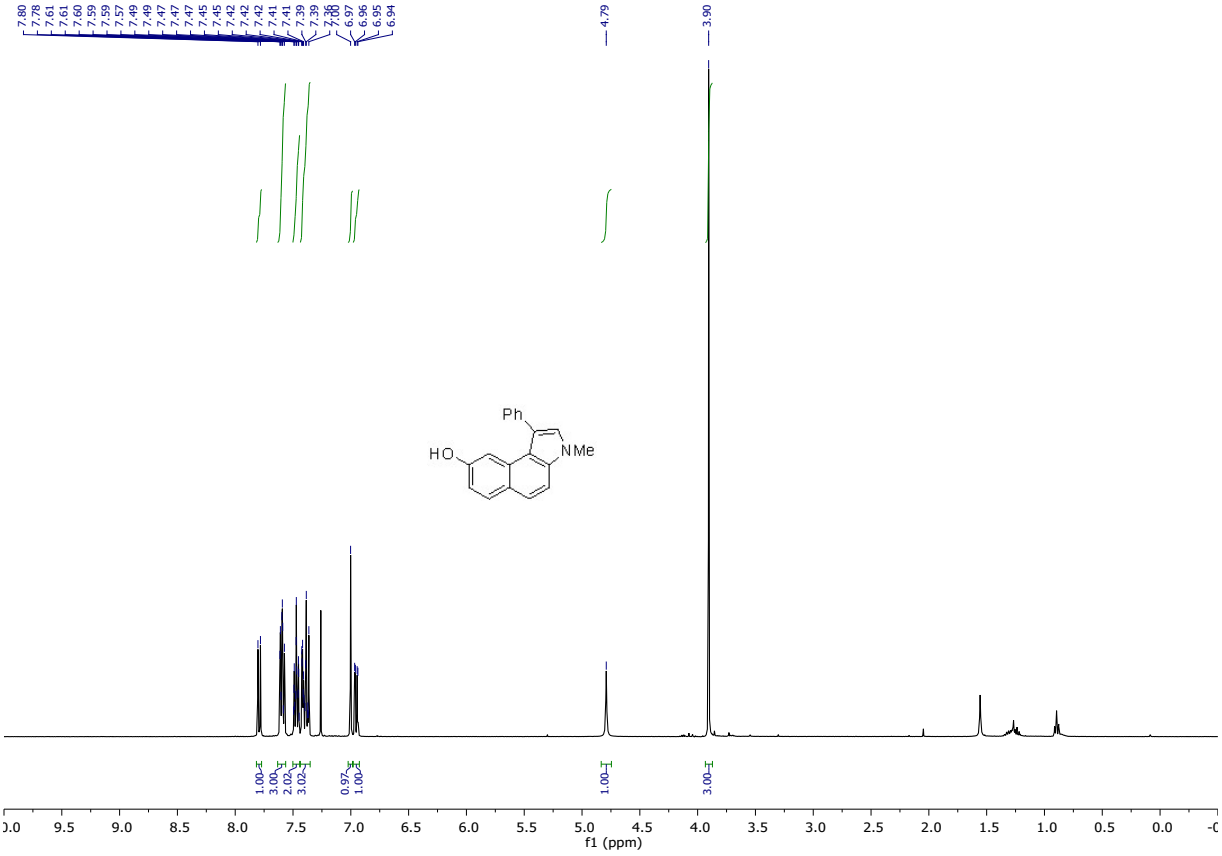


3f

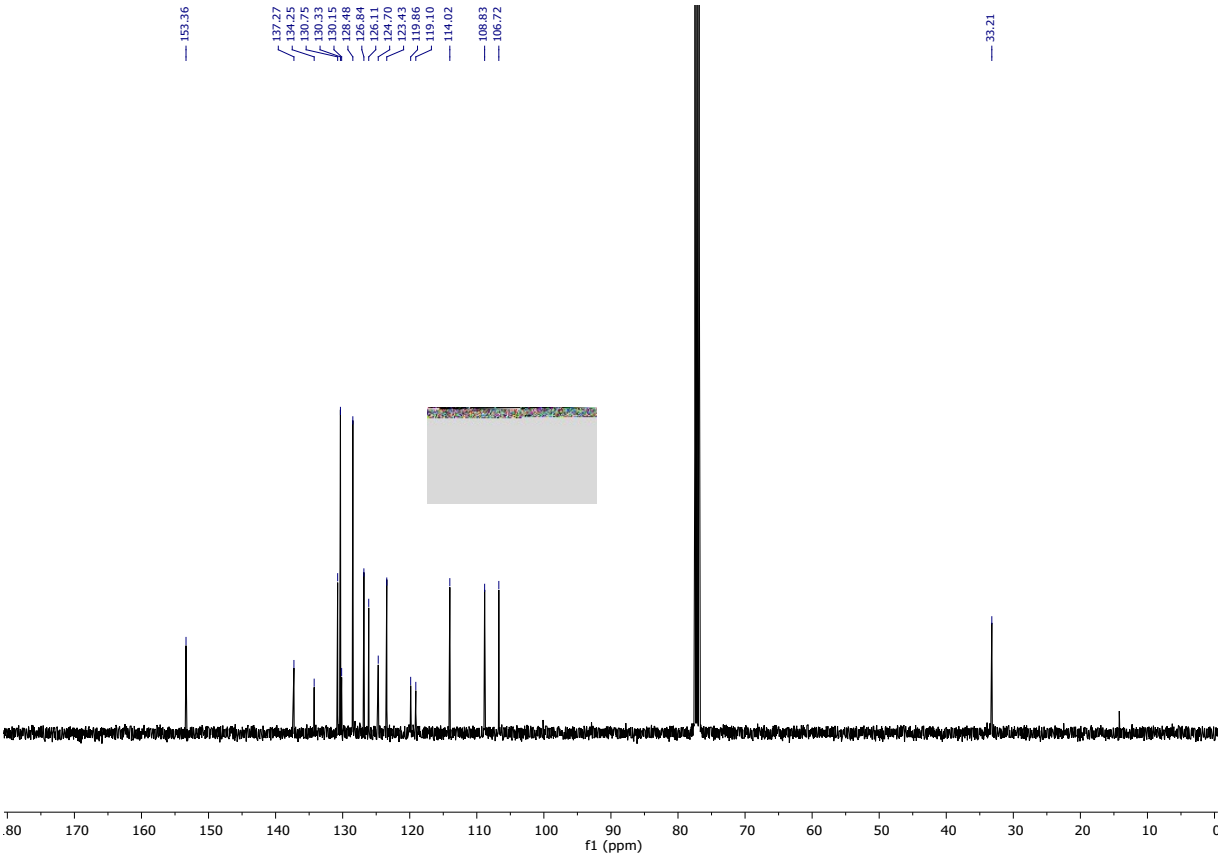
In a dry tube, BBr_3 (1M, 1.15 mL, 1.15 mmol, 2.5 equiv.) was added dropwise to a solution of **intermediate B** (132 mg, 0.46 mmol, 1.0 equiv.) in freshly distilled DCM at 0 °C and the dark mixture was stirred at room temperature for 3 h. The reaction mixture was then poured into ice-cold water and the aqueous phase was extracted thrice with DCM . The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to dryness. The crude brown residue was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:4) to yield a yellow solid (90 mg, 0.33 mmol, 72%).

R_f = 0.26 (EtOAc/ Petroleum ether = 1:4), **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.79 (d, *J* = 8.7 Hz, 1H), 7.63 – 7.56 (m, 3H), 7.51 – 7.44 (m, 2H), 7.43 – 7.35 (m, 3H), 7.00 (s, 1H), 6.95 (dd, *J* = 8.7, 2.5 Hz, 1H), 4.79 (s, 1H), 3.90 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 153.4, 137.3, 134.3, 130.8, 130.3, 130.2, 128.5, 126.8, 126.1, 124.7, 123.4, 119.9, 119.1, 114.0, 108.8, 106.7, 33.2. **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{19}H_{15}NOAg^+$, 380.0199 found 380.0196.

^{1}H NMR spectrum of **3f** in $CDCl_3$

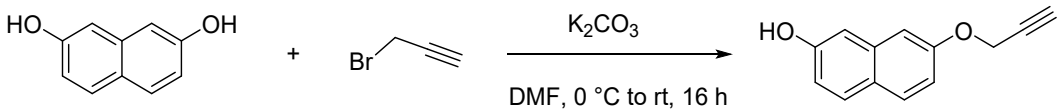


^{13}C NMR spectrum of **3f** in $CDCl_3$



e) Preparation of pyrans

7-(prop-2-yn-1-yloxy)naphthalen-2-ol)



To a cooled (0 °C) mixture of naphthalene-2,7-diol (1.00 g, 6.22 mmol, 1.0 equiv.), K_2CO_3 (1.04 g, 7.50 mmol, 1.2 equiv.) in DMF (10 mL) was added dropwise the propargyl bromide (0.71 mL, 7.50 mmol, 1.2 equiv., 80% in toluene). The stirring was maintained for 16 h with slow warming to room temperature. The mixture was partitioned between EtOAc and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness. Purification of the crude by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether 0:1 to 1:4) afforded the expected product (651 mg, 3.28 mmol, 53% yield).

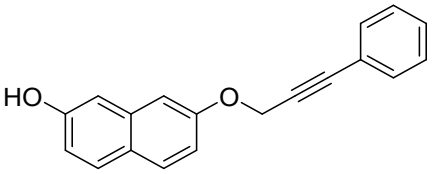
The spectroscopic data were in accordance with the reported literature.[16]

[16] *J. Org. Chem.* **2020**, *85*, 7739–7747

General procedure for the Sonogashira coupling

Under inert atmosphere, to a solution of CuI (2 mol%) and $PdCl_2(PPh_3)_2$ (1 mol%) in dry DMF (5 mL/mmol of aryl halide) were added the alkyne (1.2 equiv.), NEt_3 (20 equiv.) and the aryl halide (1 equiv.). The mixture was stirred at room temperature for 16 h and was then partitioned between EtOAc and NH_4Cl sat. The organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness. Purification of the crude by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether) afforded the expected product.

7-((3-Phenylprop-2-yn-1-yl)oxy)naphthalen-2-ol

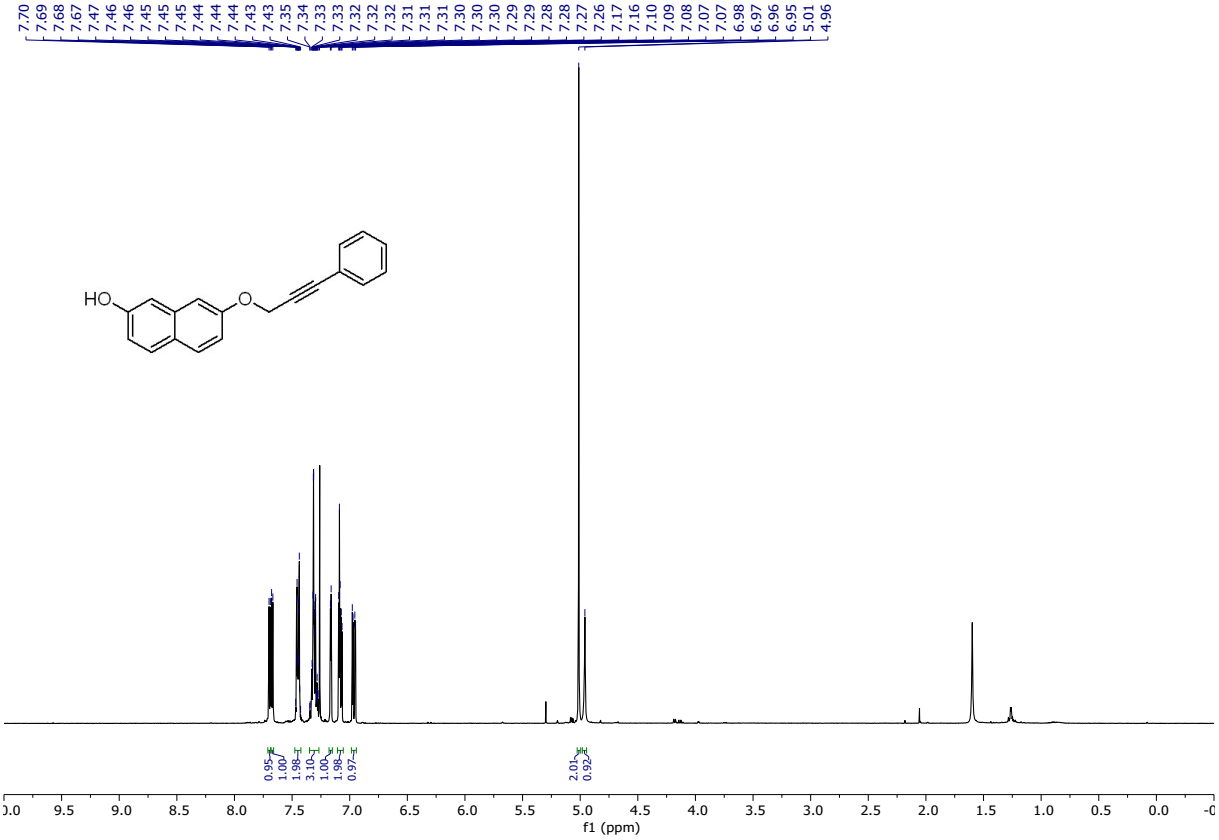


Molecular Weight: 274,3190

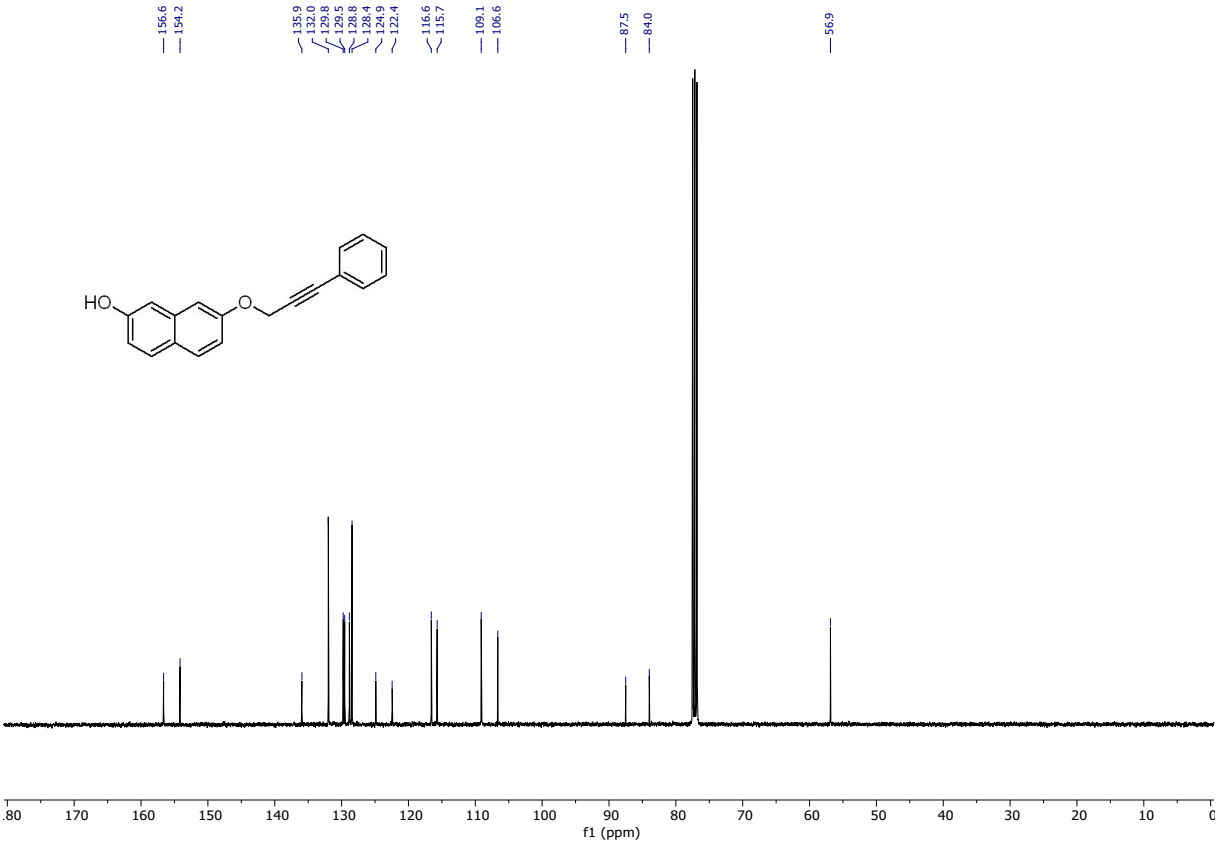
Following the general procedure, starting from iodobenzene (112 µL, 1.0 mmol), 7-(prop-2-yn-1-yloxy)naphthalen-2-ol (238 mg, 1.2 mmol), 7-((3-Phenylprop-2-yn-1-yl)oxy)naphthalen-2-ol was obtained as an off-white powder (204 mg, 0.74 mmol, 74% yield).

R_f = 0.28 (EtOAc/P.E. = 1:4), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 4.6 Hz, 1H), 7.67 (d, *J* = 4.4 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.35 – 7.27 (m, 3H), 7.16 (d, *J* = 2.5 Hz, 1H), 7.11 – 7.06 (m, 2H), 6.96 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.01 (s, 2H), 4.96 (s, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.6, 154.1, 135.9, 132.0, 129.7, 129.5, 128.8, 128.4, 124.9, 122.4, 116.6, 115.7, 109.1, 106.6, 87.5, 84.0, 56.9. **MP** = 153.7 °C**, HRMS-ESI$^+$ (m/z)**: $[M+H]^+$ calculated for $C_{19}H_{15}O_2^+$ 275.1067, found 275.1067

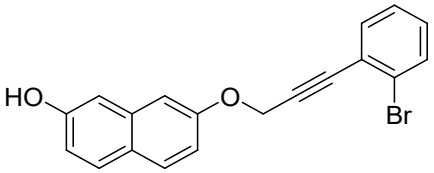
^{1}H NMR spectrum of **7-((3-Phenylprop-2-yn-1-yl)oxy)naphthalen-2-ol** in $CDCl_3$



^{13}C NMR spectrum of **7-((3-Phenylprop-2-yn-1-yl)oxy)naphthalen-2-ol** in $CDCl_3$



7-((3-(2-Bromophenyl)prop-2-yn-1-yl)oxy)naphthalen-2-ol

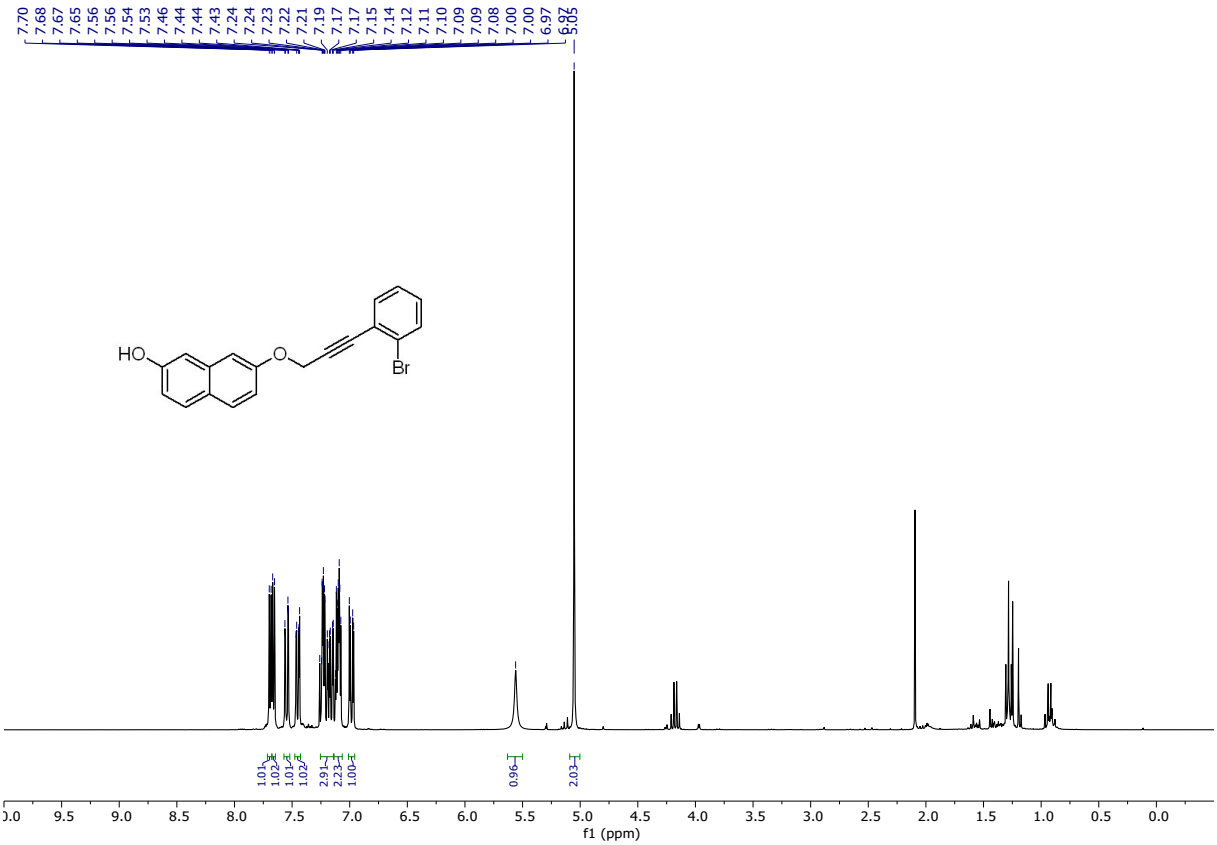


Molecular Weight: 353,2150

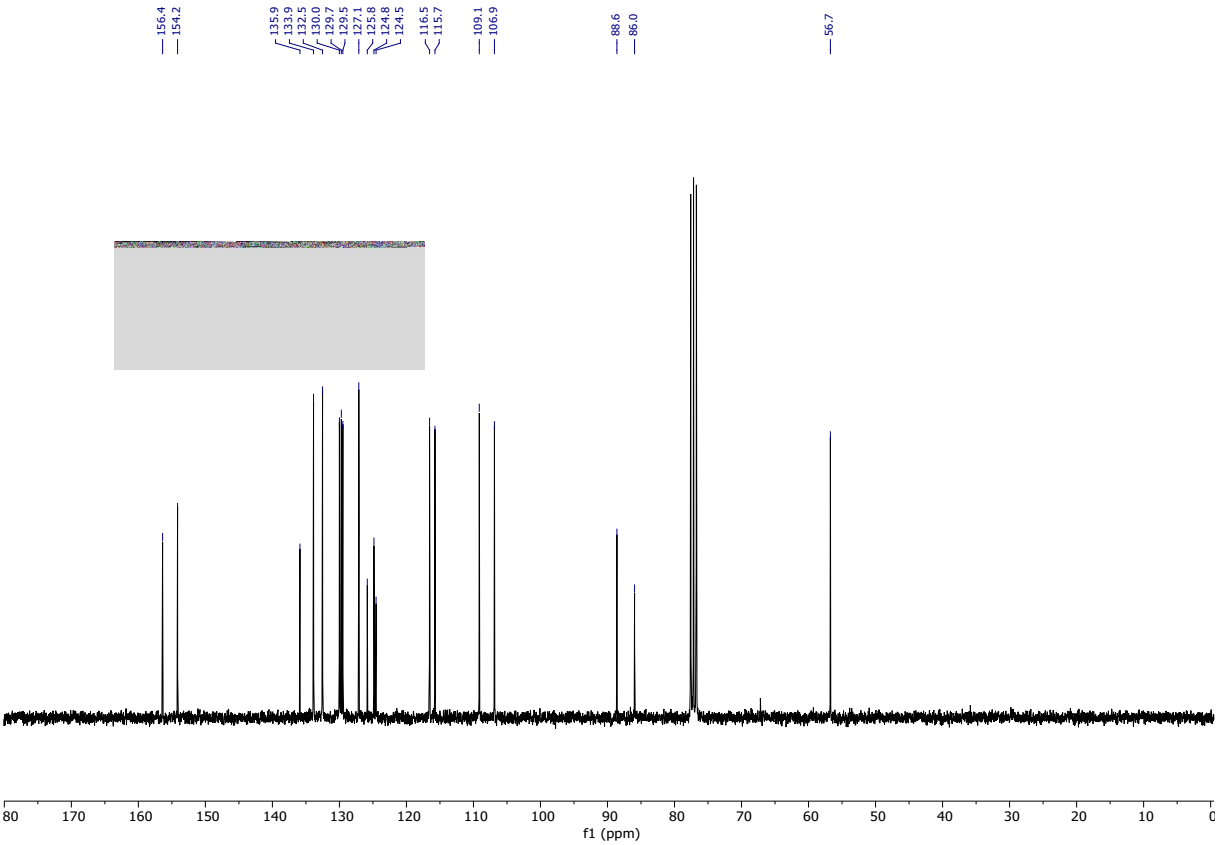
Following the general procedure, starting from 1-bromo-2-iodobenzene (75 µL, 0.6 mmol), 7-(prop-2-yn-1-yloxy)naphthalen-2-ol (125 mg, 0.63 mmol), 7-((3-Phenylprop-2-yn-1-yl)oxy)naphthalen-2-ol was obtained as an orange oil (136 mg, 0.38 mmol, 61% yield).

R_f = 0.1 (EtOAc/ Petroleum ether = 1:4) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 4.9 Hz, 1H), 7.59 (d, *J* = 4.7 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.41 – 7.36 (m, 1H), 7.19 – 7.07 (m, 3H), 7.03 (ddd, *J* = 6.7, 4.6, 2.5 Hz, 2H), 6.92 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.49 (s, 1H), 4.99 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.4, 154.2, 135.9, 133.9, 132.5, 130.0, 129.7, 129.5, 127.1, 125.8, 124.8, 124.5, 116.5, 115.7, 109.1, 106.9, 88.6, 85.9, 56.7. **HRMS-ESI$^+$ (m/z)**: $[M+Na]^+$ calculated for $C_{19}H_{13}BrO_2Na^+$ 374.9991, found 374.9993.

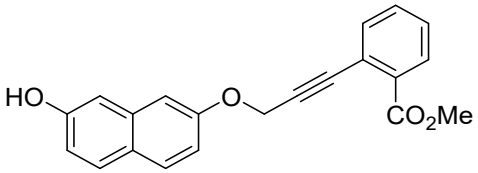
^{1}H NMR spectrum of **7-((3-(2-Bromophenyl)prop-2-yn-1-yl)oxy)naphthalen-2-ol** in $CDCl_3$



^{13}C NMR spectrum of **7-((3-(2-Bromophenyl)prop-2-yn-1-yl)oxy)naphthalen-2-ol** in $CDCl_3$



Methyl 2-(3-((7-hydroxynaphthalen-2-yl)oxy)prop-1-yn-1-yl)benzoate

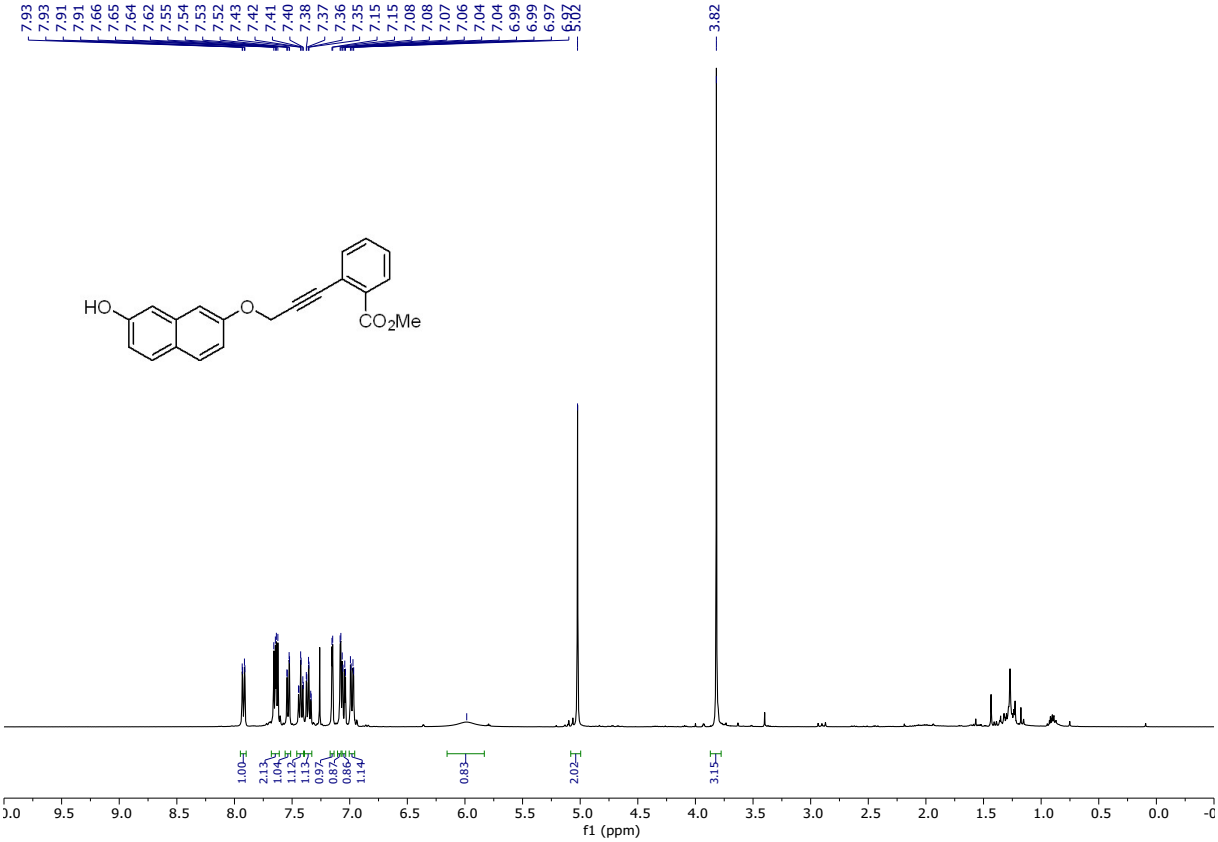


Molecular Weight: 332,3550

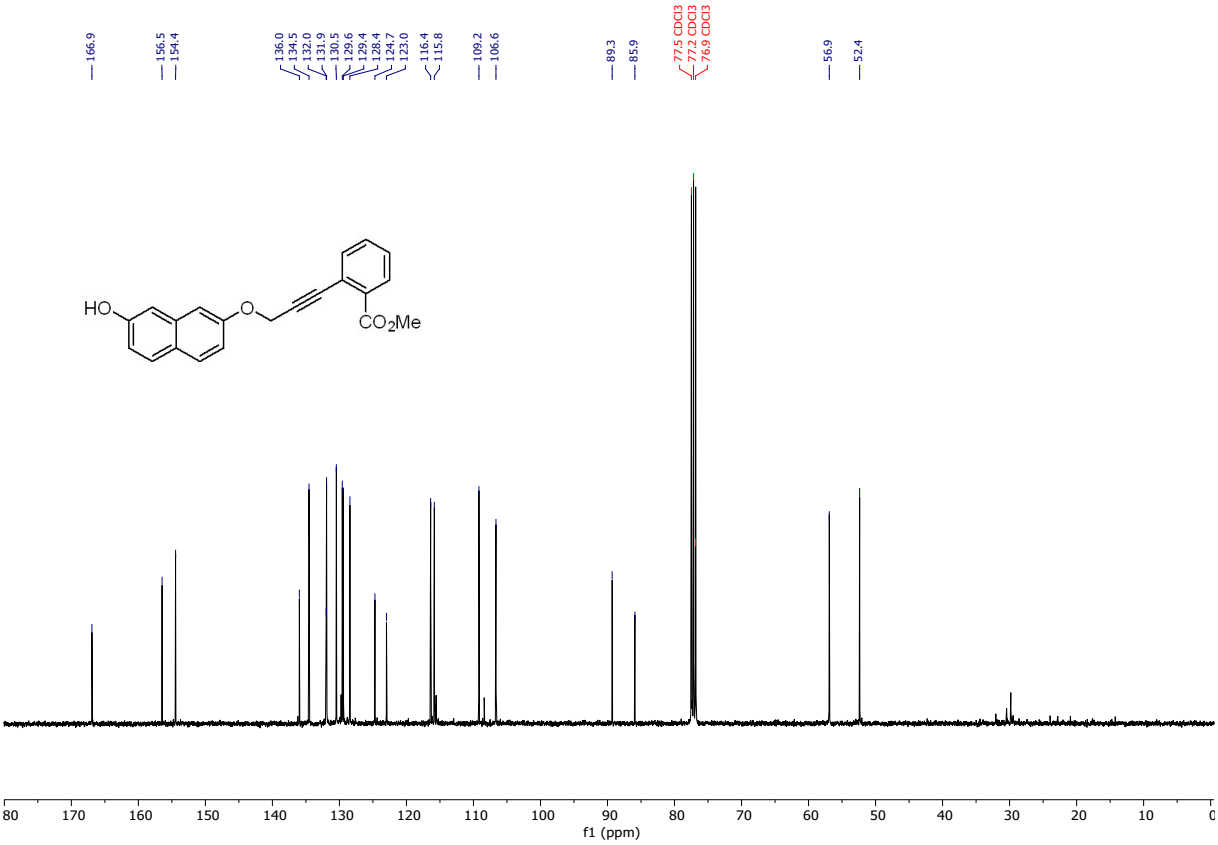
Following the general procedure, starting from methyl 2-iodobenzoate (38 µL, 0.26 mmol) and 7-(prop-2-yn-1-yloxy)naphthalen-2-ol (59.2 mg, 0.30 mmol), methyl 2-(3-((7-hydroxynaphthalen-2-yl)oxy)prop-1-yn-1-yl)benzoate was obtained as an orange solid (68 mg, 0.20 mmol, 79% yield).

R_f = 0.26 (EtOAc/P.E. = 1:4) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.64 (dd, *J* = 8.8, 5.3 Hz, 2H), 7.53 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.42 (td, *J* = 7.6, 1.5 Hz, 1H), 7.36 (td, *J* = 7.6, 1.5 Hz, 1H), 7.15 (d, *J* = 2.5 Hz, 1H), 7.10 – 7.03 (m, 2H), 6.98 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.00 (s, 1H), 5.02 (s, 2H), 3.82 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9, 156.4, 154.4, 135.9, 134.5, 131.9(7), 131.9(2), 130.4, 129.6, 129.4, 128.4, 124.7, 123.0, 116.4, 115.8, 109.2, 106.6, 89.3, 85.9, 56.9, 52.4. **MP** =170.1 °C **, HRMS-ESI$^+$ (m/z)**: $[M+Na]^+$ calculated for $C_{21}H_{16}O_4Na^+$ 355.0941, found 355.0939.

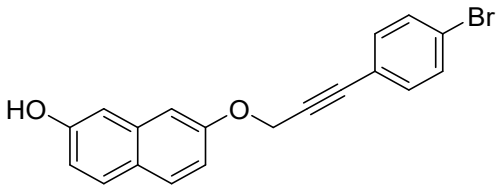
^{1}H NMR spectrum of **methyl 2-(3-((7-hydroxynaphthalen-2-yl)oxy)prop-1-yn-1-yl)benzoate** in $CDCl_3$



^{13}C NMR spectrum of **methyl 2-(3-((7-hydroxynaphthalen-2-yl)oxy)prop-1-yn-1-yl)benzoate** in $CDCl_3$



7-((3-(4-Bromophenyl)prop-2-yn-1-yl)oxy)naphthalen-2-ol

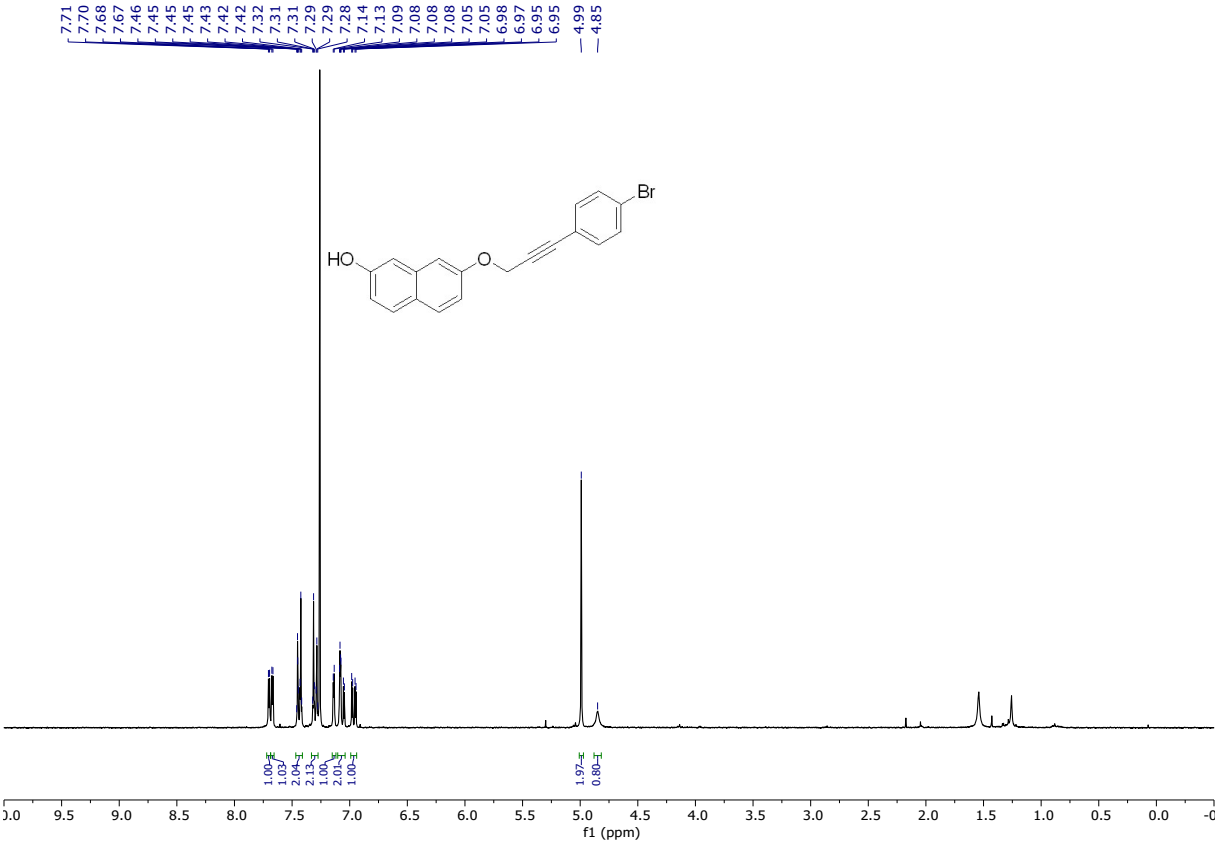


Molecular Weight: 353,2150

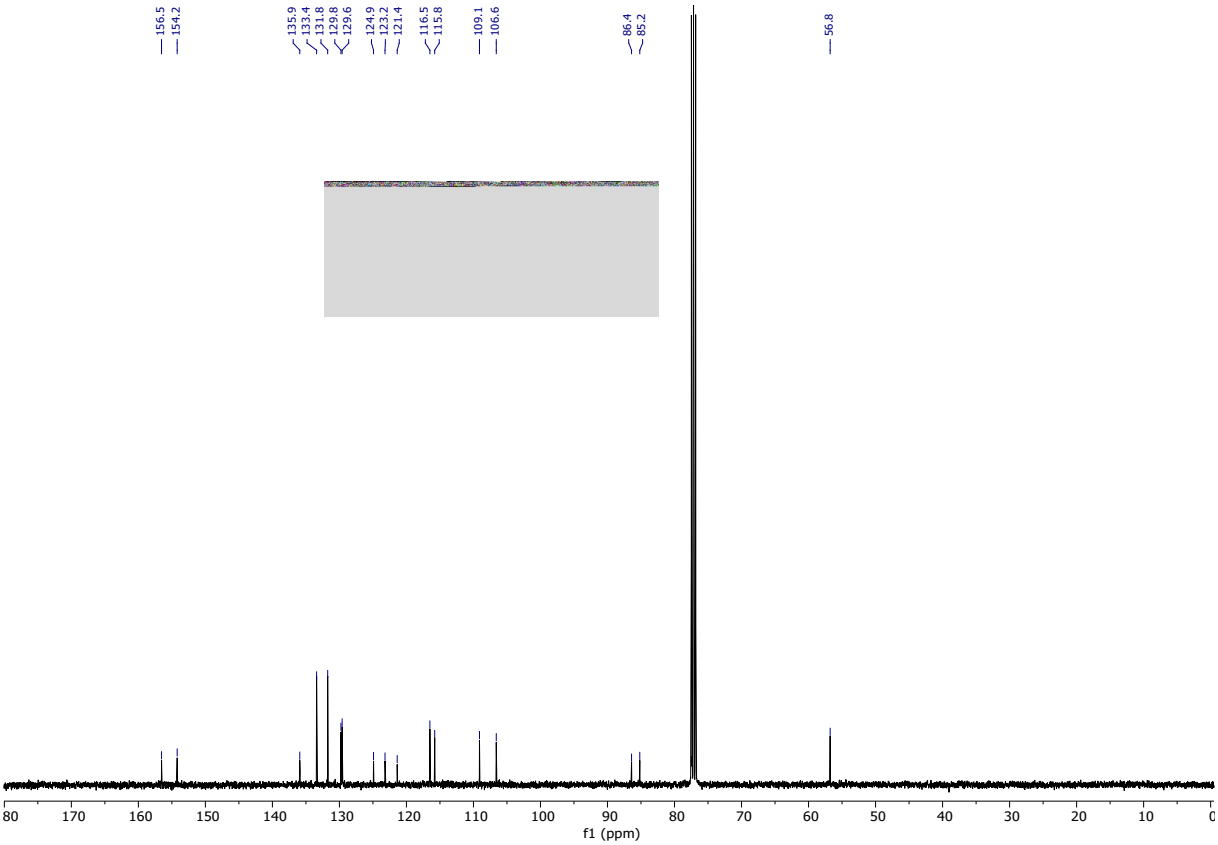
Following the general procedure, starting from 1-bromo-4-iodobenzene (100 mg, 0.36 mmol), 7-(prop-2-yn-1-yloxy)naphthalen-2-ol (62.5 mg, 0.31 mmol), the product was obtained as white oil (82.0 mg, 0.23 mmol, 75% yield).

R_f = 0.6 (EtOAc/ Petroleum ether = 1:4) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 2.9 Hz, 1H), 7.67 (d, *J* = 2.8 Hz, 1H), 7.44 (dd, *J* = 8.7, 2.2 Hz, 2H), 7.30 (dd, *J* = 8.6, 2.1 Hz, 2H), 7.14 (d, *J* = 2.5 Hz, 1H), 7.10 – 7.04 (m, 2H), 6.96 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.99 (s, 2H), 4.85 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.5, 154.2, 135.9, 133.4, 131.7, 129.8, 129.6, 124.9, 123.2, 121.4, 116.5, 115.8, 109.1, 106.6, 86.4, 85.2, 56.8 .**MP** = 177.1°C**, HRMS-ESI$^+$ (m/z)**: $[M+Na]^+$ calculated for $C_{19}H_{13}BrO_2Na^+$ 374.9991, found 374.9990.

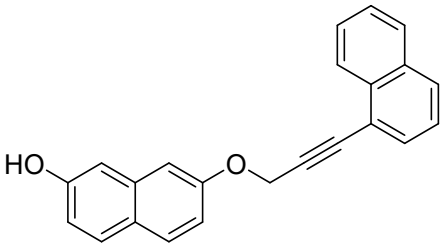
^{1}H NMR spectrum of **7-((3-(4-Bromophenyl)prop-2-yn-1-yl)oxy)naphthalen-2-ol** in $CDCl_3$



^{13}C NMR spectrum of **7-((3-(4-Bromophenyl)prop-2-yn-1-yl)oxy)naphthalen-2-ol** in $CDCl_3$



7-((3-(naphthalen-1-yl)prop-2-yn-1-yl)oxy)naphthalen-2-ol

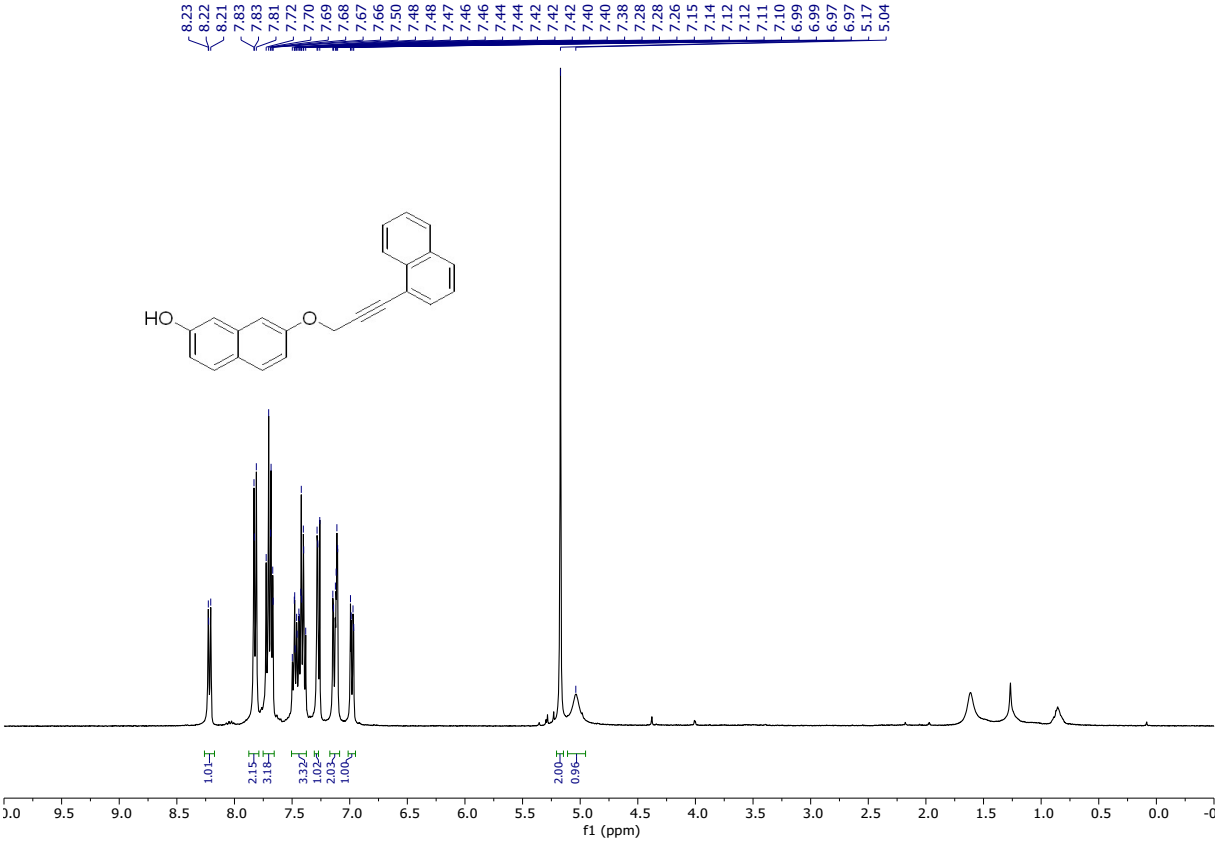


Molecular Weight: 324,3790

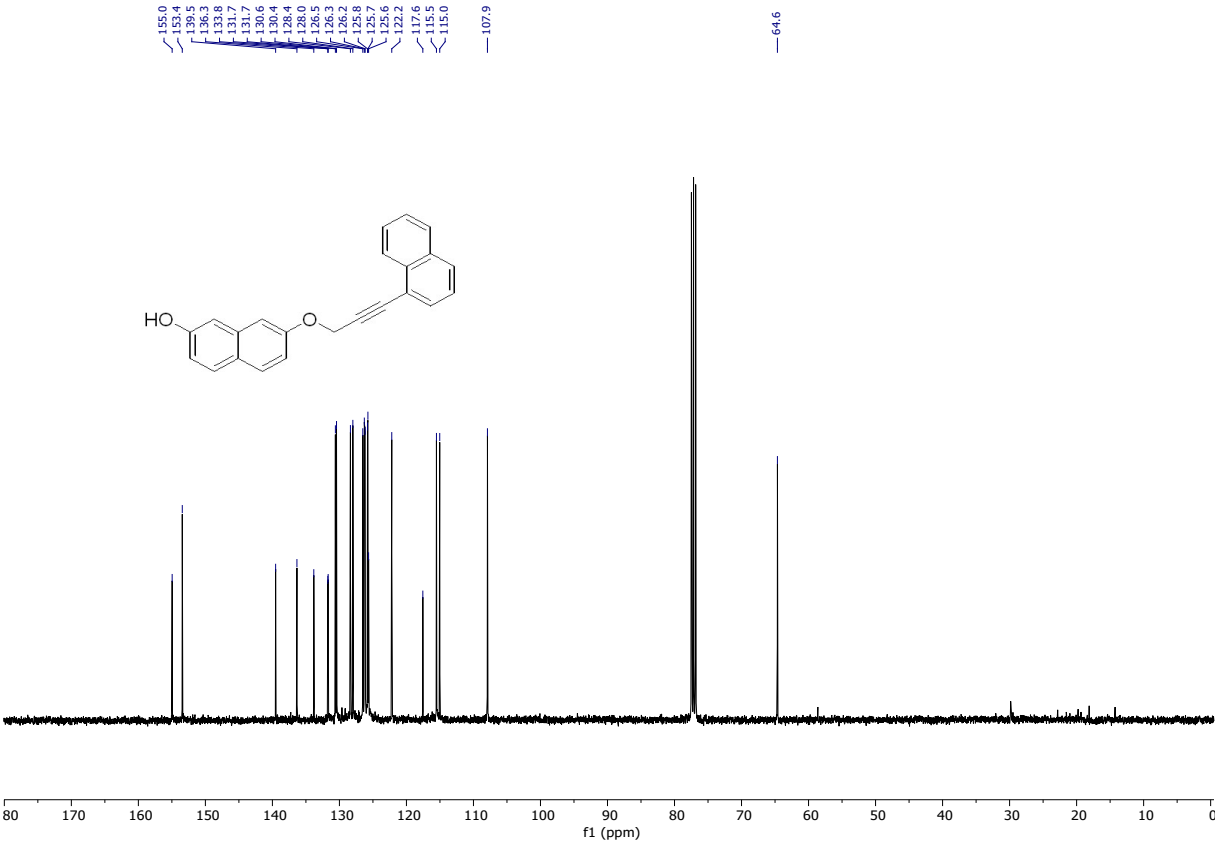
Following the general procedure, starting from 1- iodonaphthalene (175 µL, 1.2 mmol), 7-(prop-2-yn-1-yloxy)naphthalen-2-ol (187.5 mg, 0.94 mmol), 7-((3-(naphthalen-1-yl)prop-2-yn-1-yl)oxy)naphthalen-2-ol was obtained as an off-white solid (224 mg, 0.69 mmol, 73% yield).

R_f = 0.52 (EtOAc/ Petroleum ether 1:4) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.75 – 7.66 (m, 3H), 7.52 – 7.35 (m, 3H), 7.28 (d, *J* = 2.5 Hz, 1H), 7.17 – 7.07 (m, 2H), 6.98 (dd, *J* = 8.7, 2.5 Hz, 1H), 5.17 (s, 2H), 5.03 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.6, 154.2, 135.9, 133.5, 133.2, 130.9, 129.8, 129.6, 129.3, 128.4, 127.0, 126.6, 126.2, 125.2, 124.9, 120.0, 116.7, 115.7, 109.1, 107.0, 88.8, 85.8, 57.0. **MP** = 134.9°C**, HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{23}H_{16}O_2Ag^+$ 431.0196, found 431.0193.

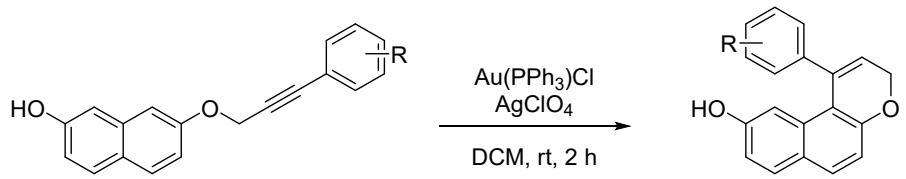
^{1}H NMR spectrum of **7-((3-(naphthalen-1-yl)prop-2-yn-1-yl)oxy)naphthalen-2-ol** in $CDCl_3$



^{13}C NMR spectrum of **7-((3-(naphthalen-1-yl)prop-2-yn-1-yl)oxy)naphthalen-2-ol** in $CDCl_3$

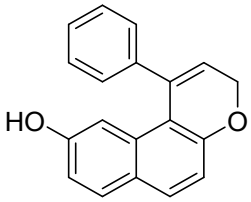


General procedure for the hydroarylation



Under inert atmosphere, a mixture of $Au(PPh_3)Cl$ (5 mol%) and $AgClO_4$ (10 mol%) in dry DCM (0.1 M) was stirred for 15 min. The naphthol (1 equiv.) was added and the mixture was stirred at room temperature for two hours. The brownish solution was concentrated *in vacuo.* The crude was purified by column chromatography (SiO_2, EtOAc/ Petroleum ether) to afford the desired compound.

*1-Phenyl-3H-benzo[f]chromen-9-ol (**3h**)*

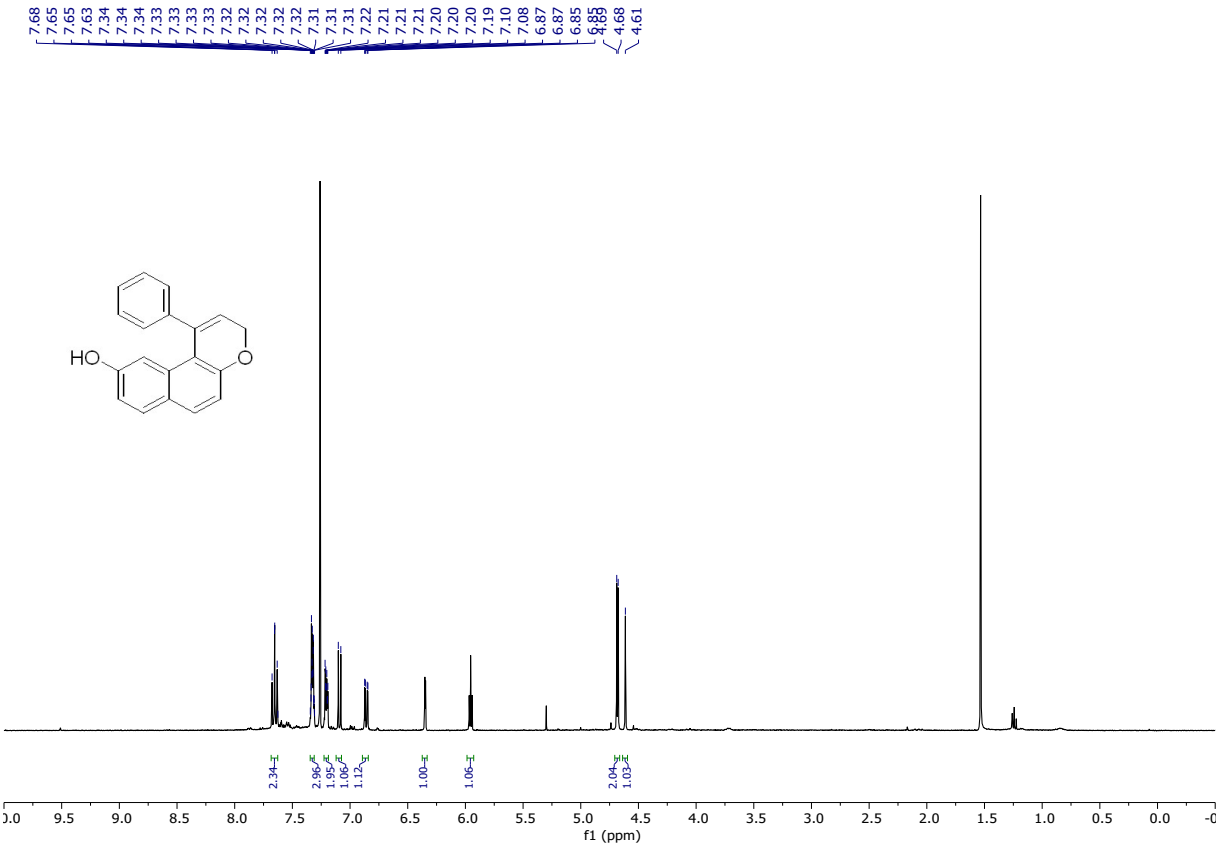


Molecular Weight: 274,3190

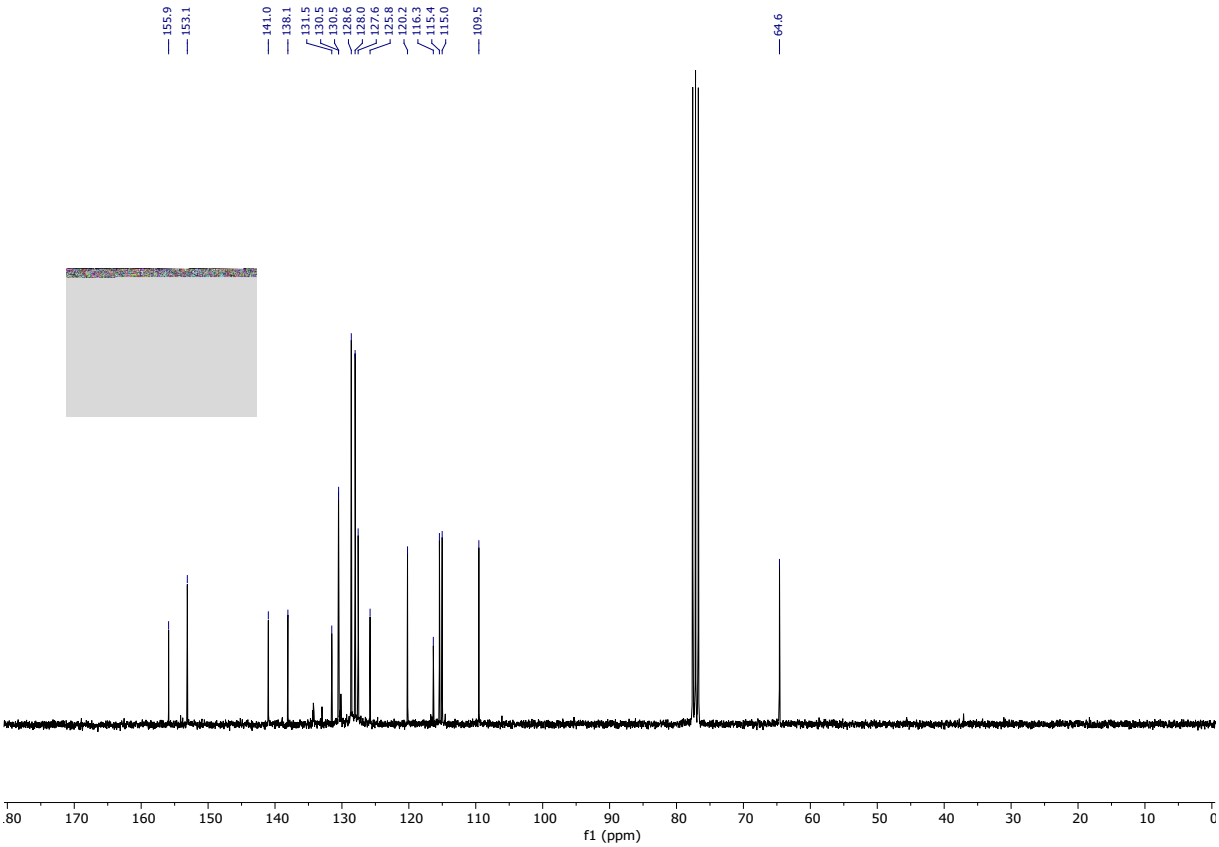
Following the general procedure, starting from 7-((3-Phenylprop-2-yn-1-yl)oxy)naphthalen-2-ol (204 mg, 0.74 mmol), the product was obtained as light pink solid (168 mg, 0.62 mmol, 82% yield).

R_f = 0.48 (EtOAc/ Petroleum ether = 1:4) **^{1}H NMR** (400 MHz, $CDCl_3$) 7.68 – 7.63 (m, 2H), 7.35 – 7.31 (m, 3H), 7.23 – 7.19 (m, 2H), 7.09 (d, *J* = 8.7 Hz, 1H), 6.86 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.35 (dt, *J* = 2.5, 0.7 Hz, 1H), 5.95 (t, *J* = 4.9 Hz, 1H), 4.68 (d, *J* = 4.9 Hz, 2H), 4.61 (s, 1H), **^{13}C NMR** (75 MHz, $CDCl_3$) δ 155.9, 153.1, 141.0, 138.1, 131.5, 130.5, 130.5, 128.6, 128.0, 127.6, 125.8, 120.2, 116.3, 115.4, 115.0, 109.5, 64.6. **MP** = 96.8 °C, **HRMS-ESI$^+$ (m/z):** $[M+H]^+$ calculated for $C_{19}H_{15}O_2^+$ 275.1067, found 275.1069

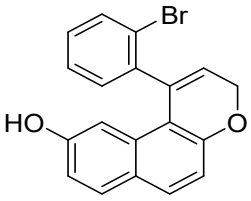
^{1}H NMR spectrum of **3h** in $CDCl_3$



^{13}C NMR spectrum of **3h** in $CDCl_3$



*1-(2-Bromophenyl)-3H-benzo[f]chromen-9-ol (**3k**)*

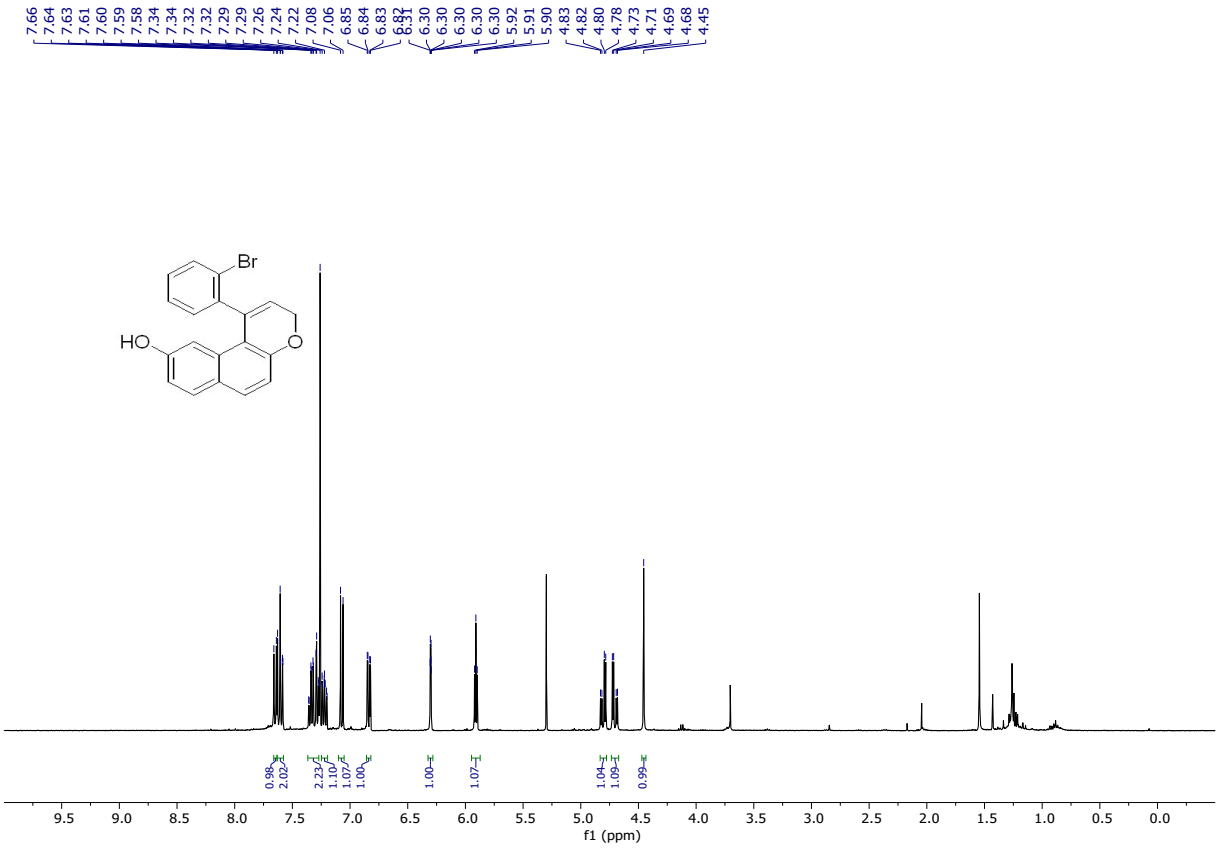


Molecular Weight: 353,2150

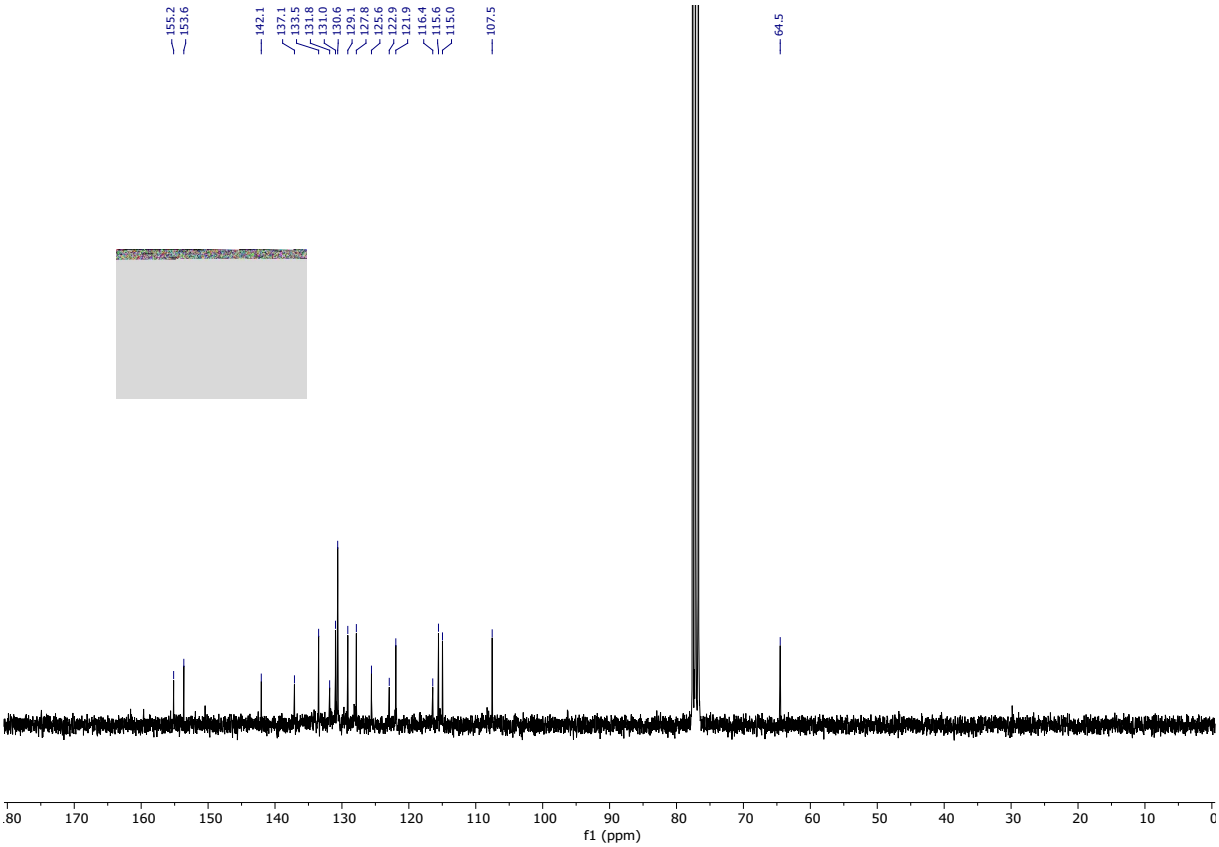
Following the general procedure, starting from 7-((3-(2-Bromophenyl)prop-2-yn-1-yl)oxy)naphthalen-2-ol (136 mg, 0.38 mmol), the product was obtained as bright red solid (101 mg, 0.28 mmol, 74% yield).

R_f = 0.57 (EtOAc/ Petroleum ether = 1:9) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.7 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.37 – 7.27 (m, 2H), 7.22 (ddd, *J* = 7.9, 7.1, 2.0 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.84 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.30 (dt, *J* = 2.4, 0.6 Hz, 1H), 5.91 (t, *J* = 4.7 Hz, 1H), 4.81 (dd, *J* = 13.3, 4.9 Hz, 1H), 4.70 (dd, *J* = 13.3, 4.5 Hz, 1H), 4.45 (s, 1H)., **^{13}C NMR** (75 MHz, $CDCl_3$) δ 155.2, 153.6, 142.1, 137.1, 133.5, 131.8, 131.0, 130.6 (2C), 129.1, 127.8, 125.6, 122.9, 121.9, 116.4, 115.6, 115.0, 107.5, 64.5. **MP** = 101.2 – 102.4 °C. **HRMS-ESI$^+$ (m/z)**: **)**: $[M+Na]^+$ calculated for $C_{19}H_{13}BrO_2Na^+$ 374.9991, found 374.9966

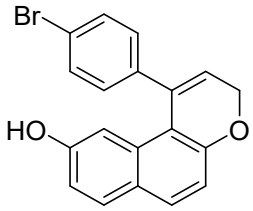
^{1}H NMR spectrum of **3k** in $CDCl_3$



^{13}C NMR spectrum of **3k** in $CDCl_3$



*1-(4-bromophenyl)-3H-benzo[f]chromen-9-ol (**3j**)*

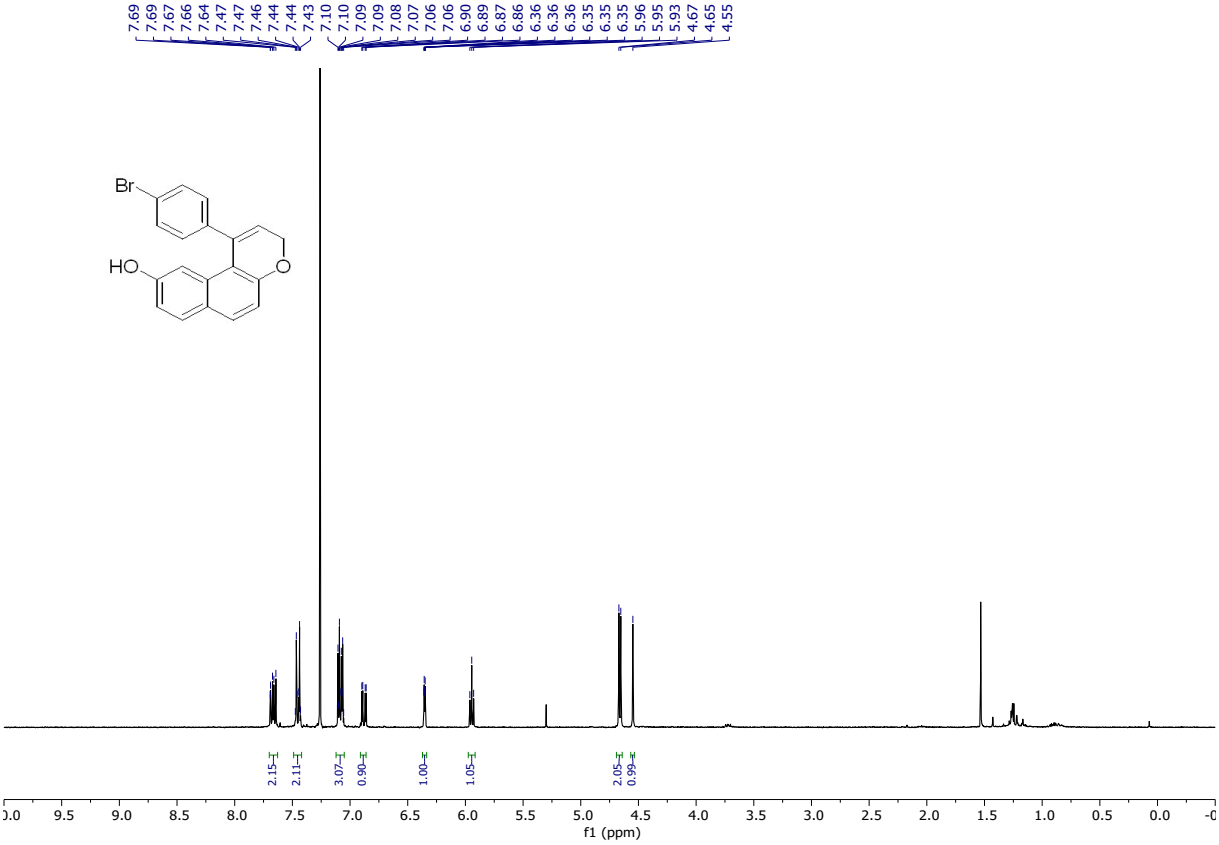


Molecular Weight: 353,2150

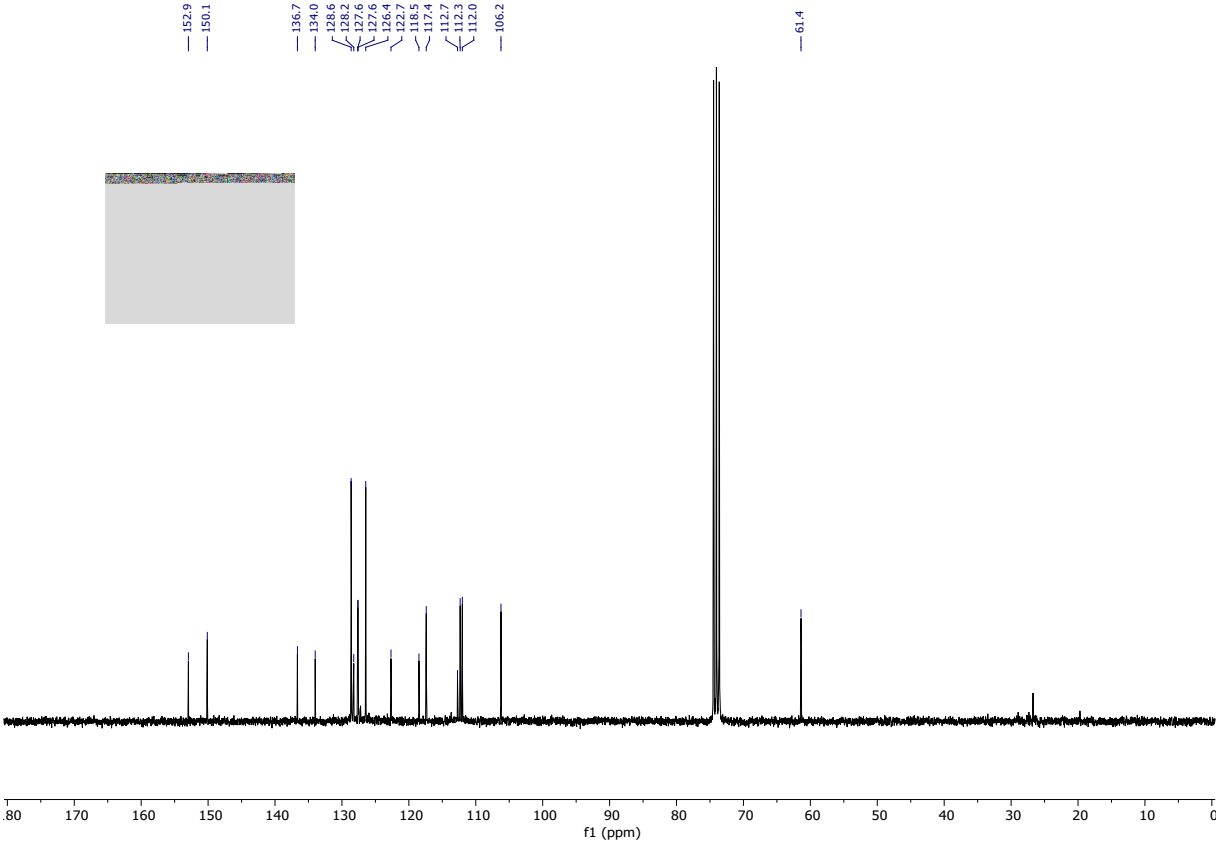
Following the general procedure, starting from 7-((3-(4-Bromophenyl)prop-2-yn-1-yl)oxy)naphthalen-2-ol (154 mg, 0.43 mmol), the product was obtained as pale pink solid (142 mg, 0.40 mmol, 92% yield).

R_f = 0.32 (EtOAc/ Petroleum ether = 1:4) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 8.7, 5.2 Hz, 2H), 7.49 – 7.42 (m, 2H), 7.12 – 7.05 (m, 3H), 6.91 – 6.86 (m, 1H), 6.35 (dt, *J* = 2.5, 0.6 Hz, 1H), 5.95 (t, *J* = 4.9 Hz, 1H), 4.66 (d, *J* = 5.0 Hz, 2H), 4.55 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.9, 150.1, 136.7, 134.0, 128.6, 128.2, 127.6, 127.6, 126.4, 122.7, 118.5, 117.4, 112.7, 112.3, 112.0, 106.2, 61.4. **MP** = 188.6 °C **HRMS-ESI$^+$ (m/z)**: $[M+Na]^+$ calculated for $C_{19}H_{13}BrO_2Na^+$ 374.9991, found 374.9988.

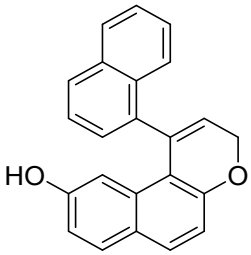
^{1}H NMR spectrum of **3j** in $CDCl_3$



^{13}C NMR spectrum of **3j** in $CDCl_3$



*1-(naphthalen-1-yl)-3H-benzo[f]chromen-9-ol (**3l**)*

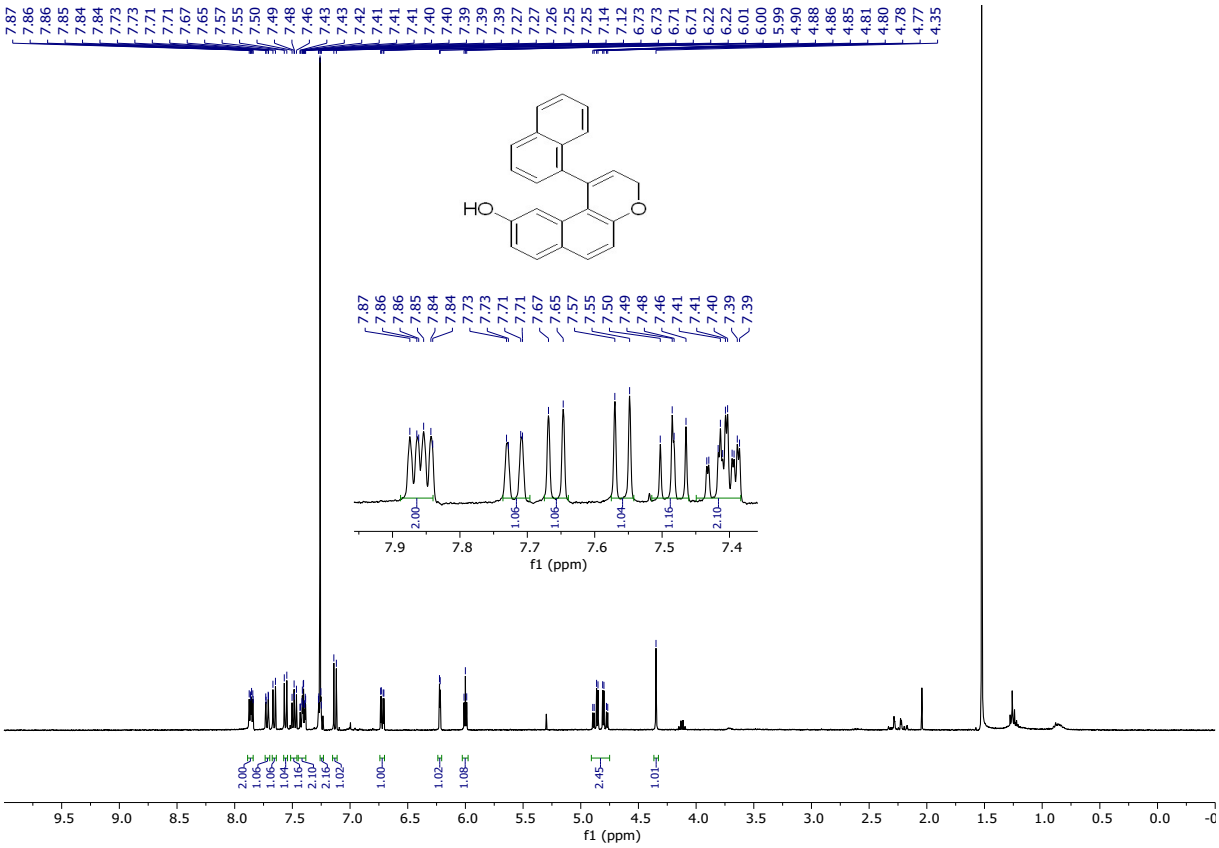


Molecular Weight: 324,3790

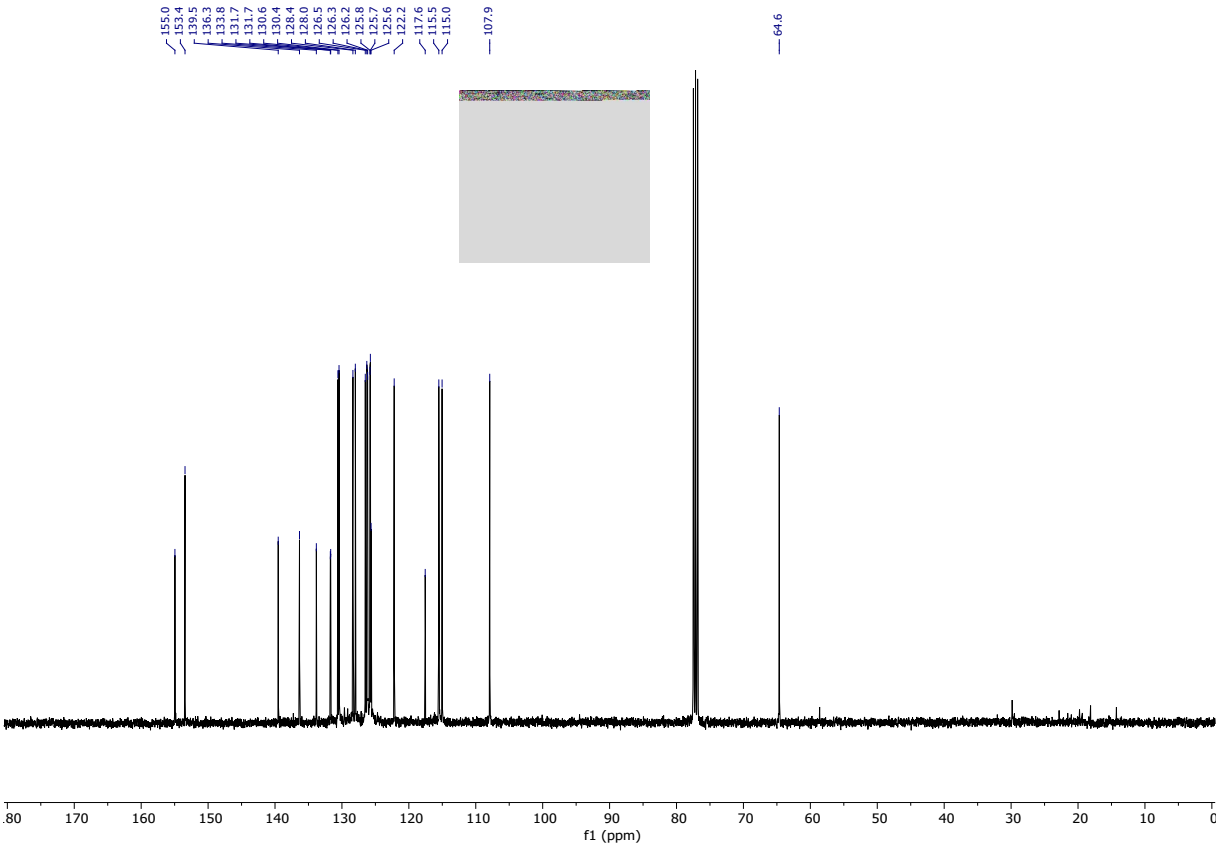
Following the general procedure, starting from 7-((3-(naphthalen-1-yl)prop-2-yn-1-yl)oxy)naphthalen-2-ol (100 mg, 0.30 mmol), the product was obtained as yellowish solid (68 mg, 0.21 mmol, 68% yield).

R_f = 0.41 (EtOAc/ Petroleum ether = 15:85) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 2H), 7.74 – 7.70 (m, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.48 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.24 (dd, *J* = 6.9, 1.4 Hz, 1H), 7.13 (d, *J* = 8.8 Hz, 1H), 6.72 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.22 (d, *J* = 2.5 Hz, 1H), 6.00 (t, *J* = 4.7 Hz, 1H), 4.87 (dd, *J* = 13.2, 4.9 Hz, 1H), 4.79 (dd, *J* = 13.2, 4.4 Hz, 1H), 4.35 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.0, 153.4, 139.5, 136.3, 133.8, 131.7, 131.7, 130.6, 130.4, 128.4, 128.0, 126.5, 126.3, 126.2, 125.8, 125.7, 125.6, 122.2, 117.5, 115.5, 115.0, 107.9, 64.6. **MP** = 147.9°C **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{23}H_{16}O_2Ag^+$ 431.0196, found 431.0198.

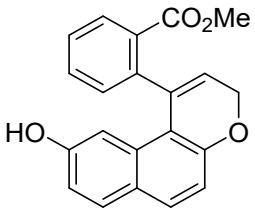
^{1}H NMR spectrum of **3l** in $CDCl_3$



^{13}C NMR spectrum of **3l** in $CDCl_3$



*methyl 2-(9-hydroxy-3H-benzo[f]chromen-1-yl)benzoate (**3i**)*

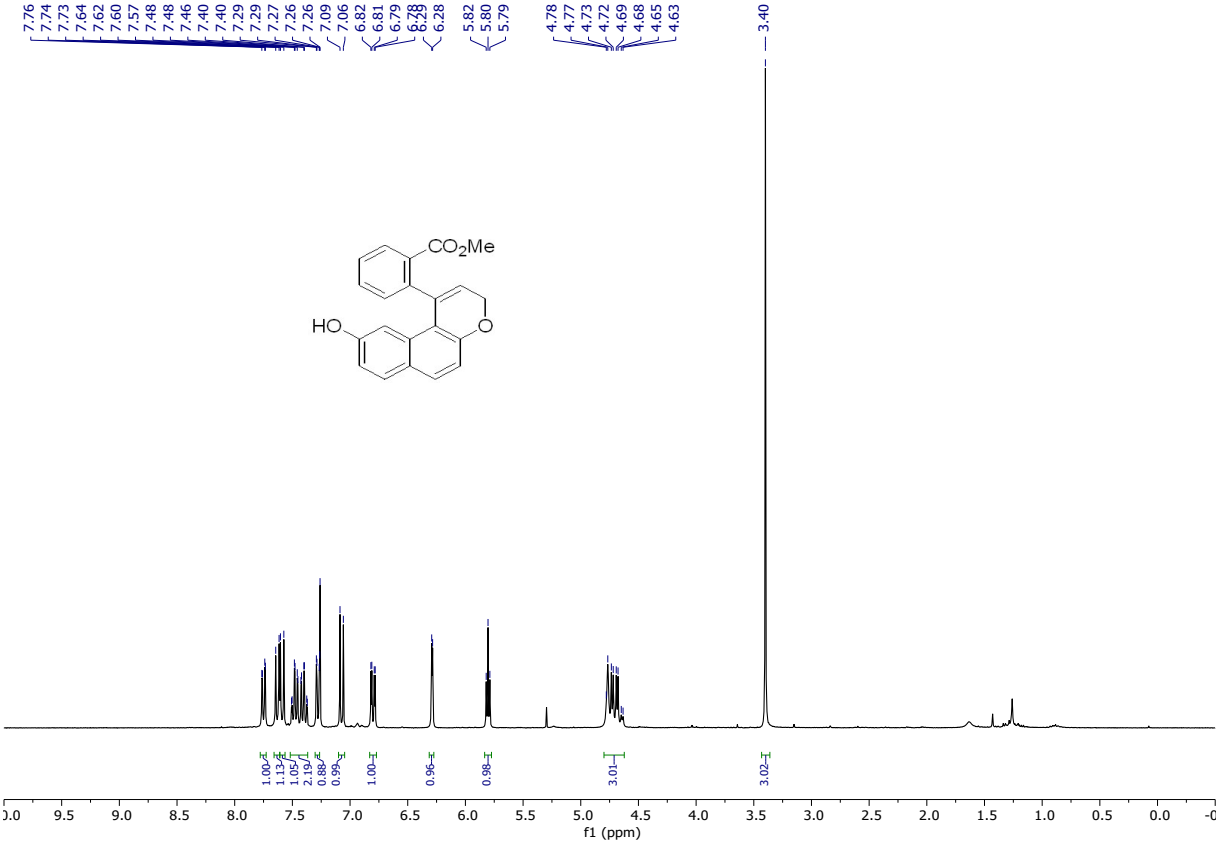


Molecular Weight: 332,3550

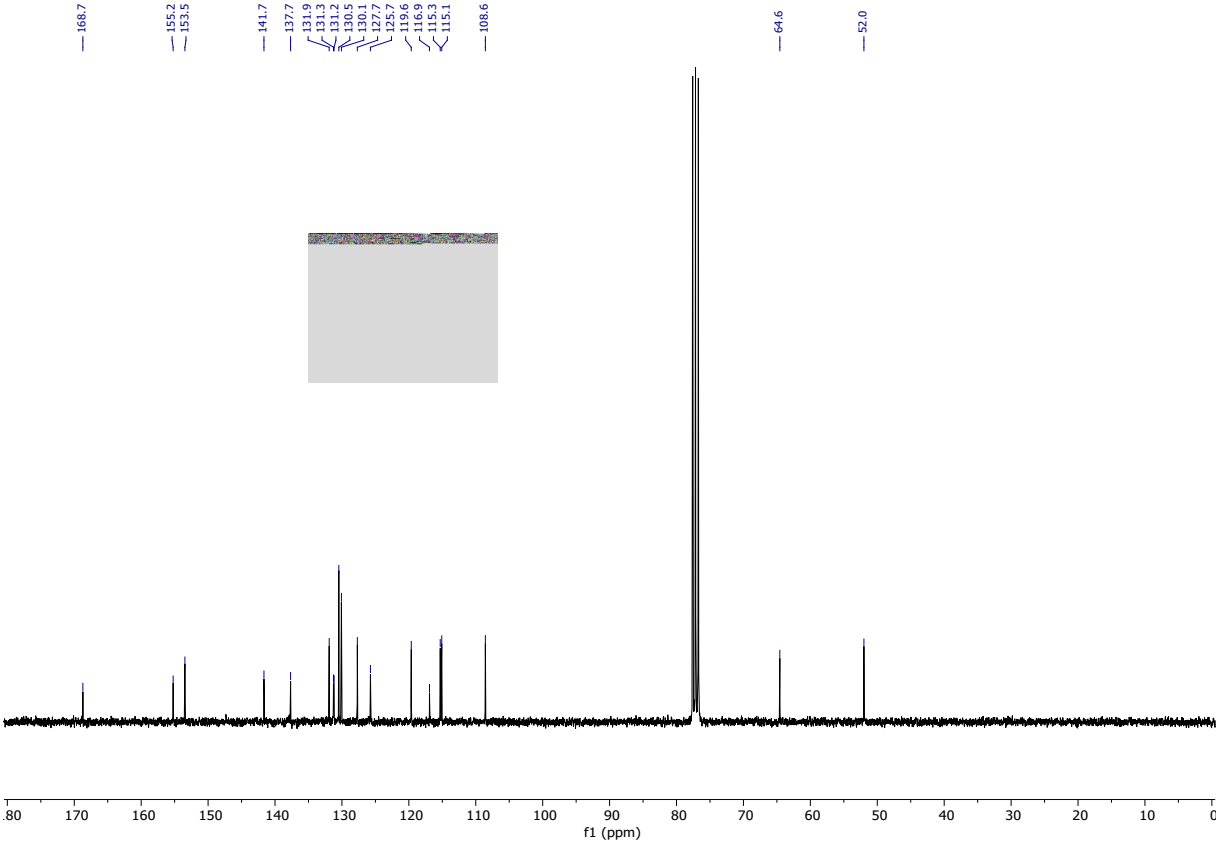
Following the general procedure, starting from methyl 2-(3-((7-hydroxynaphthalen-2-yl)oxy)prop-1-yn-1-yl)benzoate (58 mg, 0.17 mmol), the product was obtained as pale pink solid (38 mg, 0.11 mmol, 65% yield).

R_f = 0.30 (EtOAc/ Petroleum ether = 1:4) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.63 (d, *J* = 8.7 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.44 (dtd, *J* = 24.5, 7.5, 1.5 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.07 (d, *J* = 8.7 Hz, 1H), 6.80 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.29 (d, *J* = 2.4 Hz, 1H), 5.80 (t, *J* = 4.8 Hz, 1H), 4.80 – 4.62 (m, 3H), 3.40 (s, 3H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.7, 155.2, 153.5, 141.7, 137.7, 131.9, 131.3, 131.2, 130.5(2C), 130.1(2C), 127.7, 125.7, 119.6, 116.9, 115.3, 115.1, 108.6, 64.6, 52.0. **MP** = 165.5°C, **HRMS-ESI$^+$ (m/z)**: $[M+Na]^+$ calculated for $C_{21}H_{16}O_4Na^+$ 355.0941, found 355.0944.

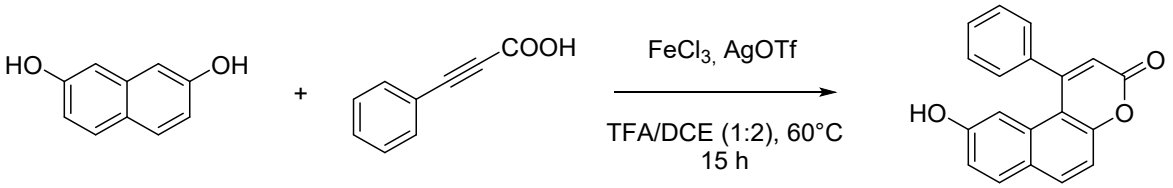
^{1}H NMR spectrum of **3i** in $CDCl_3$



^{13}C NMR spectrum of **3i** in $CDCl_3$



*9-hydroxy-1-phenyl-3H-benzo[f]chromen-3-one (**3g**)*

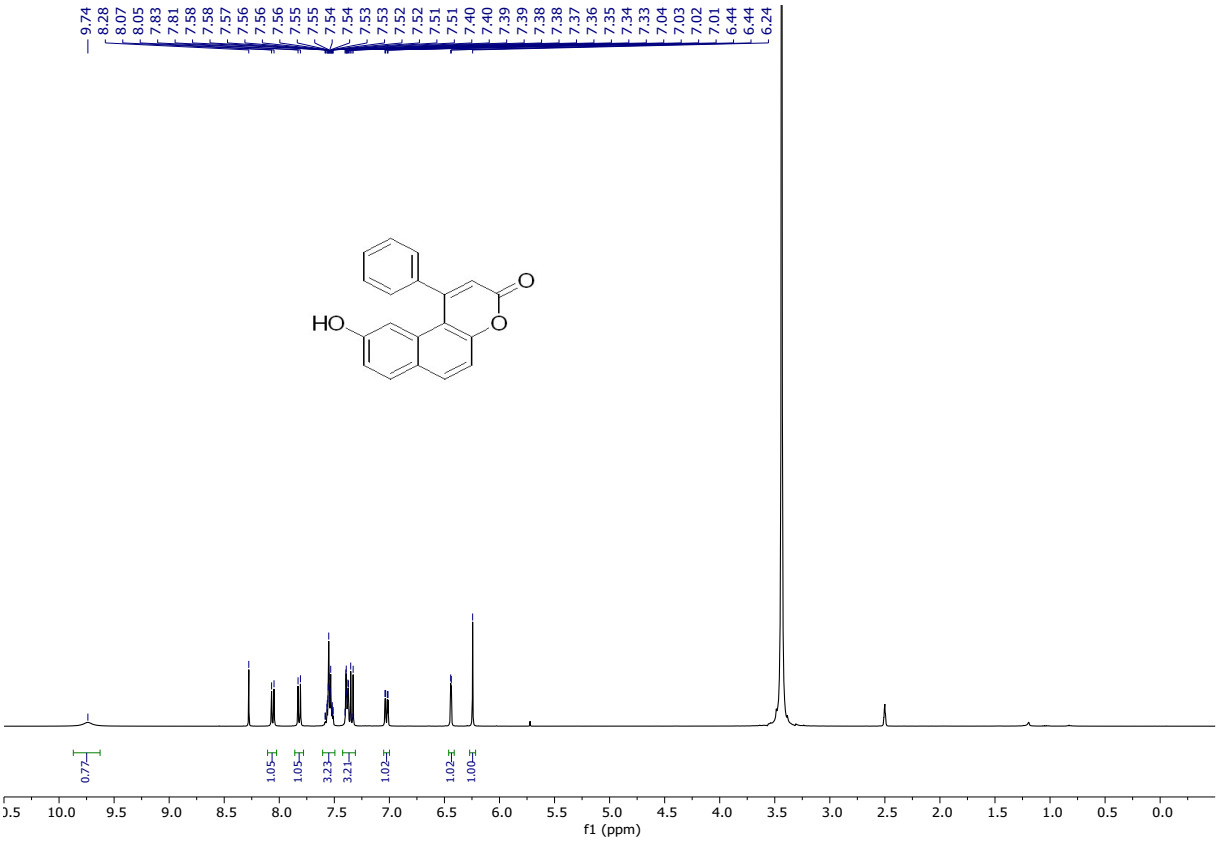


Molecular Weight: 288,3020

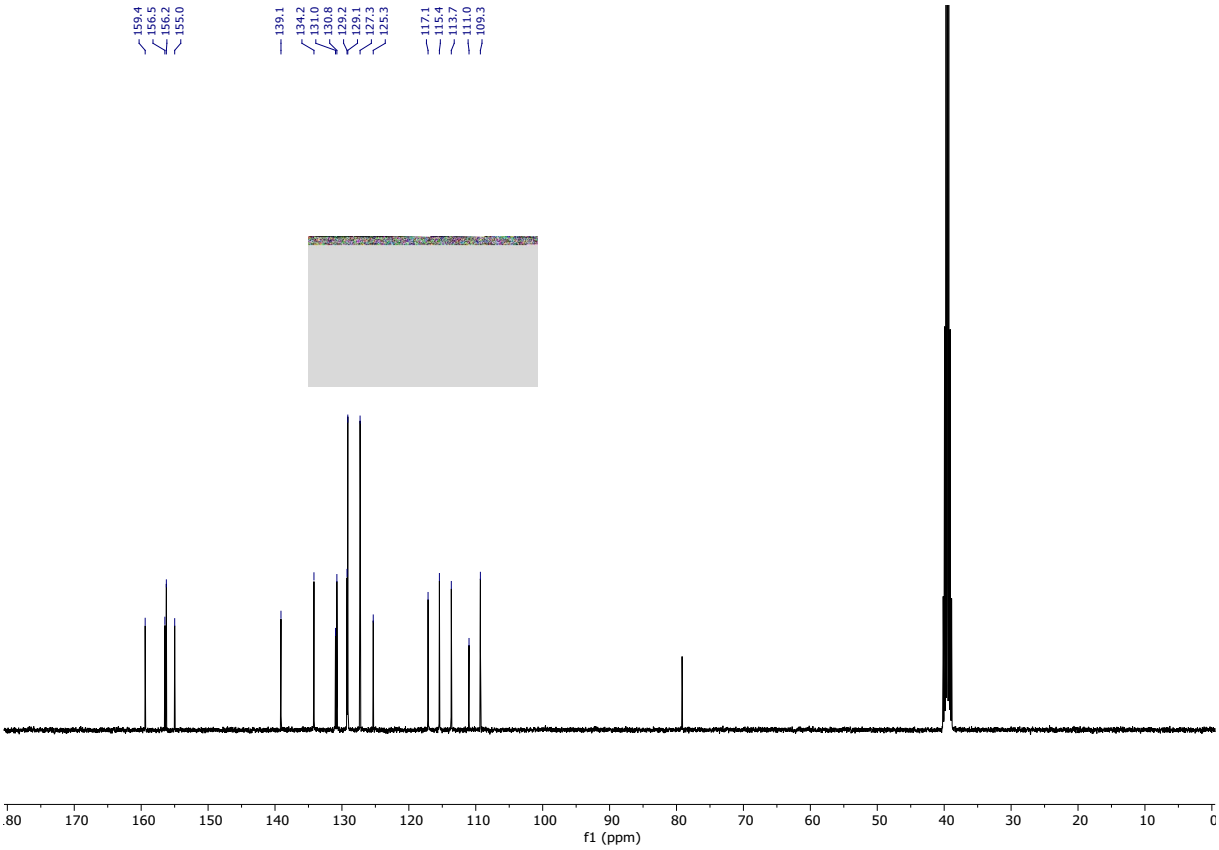
In a sealable vial, a solution of $FeCl_3$ (65 mg, 0.4 mmol) and AgOTf (308 mg, 1.2 mmol) in DCE (1 mL) and TFA (0.5 mL) was stirred at room temperature for 10 min. Dihydroxynaphthalene (320 mg, 2 mmol) and phenylpropiolic acid (585 mg, 4 mmol) was then added and the reaction mixture was stirred at 60 °C for 16 h. After cooling at room temperature, the mixture was treated with an aq. solution of $NaHCO_3$ and extracted with AcOEt (3 times) . The combined organic layers were dried over Na_2SO_4, filtered and concentrated to dryness. Purification by silica gel chromatography (eluent 100% DCM) afforded the desired product as a light pink solid (286 mg, 0.99 mmol, 49% yield)

R_f = 0.24 (P.E./EtOAc 8:2) **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.74 (s, 1H), 8.06 (d, *J* = 8.9 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.62 – 7.50 (m, 3H), 7.46 – 7.30 (m, 3H), 7.03 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.44 (d, *J* = 2.2 Hz, 1H), 6.24 (s, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 159.4, 156.4, 156.2, 155.0, 139.1, 134.2, 130.9, 130.7, 129.2, 129.1, 127.3, 125.3, 117.1, 115.4, 113.6, 111.0, 109.3. **MP** = 214 °C, **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{19}H_{12}O_3Ag^+$ 394.9832, found 394.9832.

^{1}H NMR spectrum of **3g** in DMSO-d6 (traces of $CHCl_3$ at 8.28 ppm)

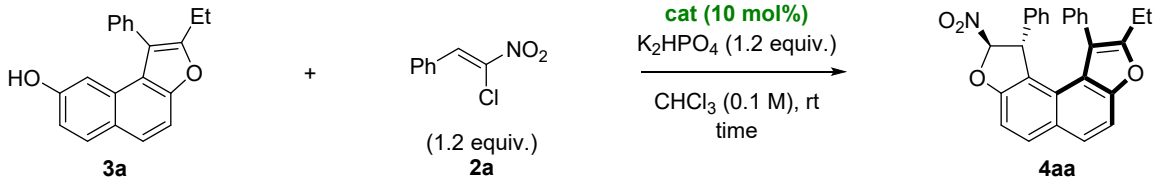


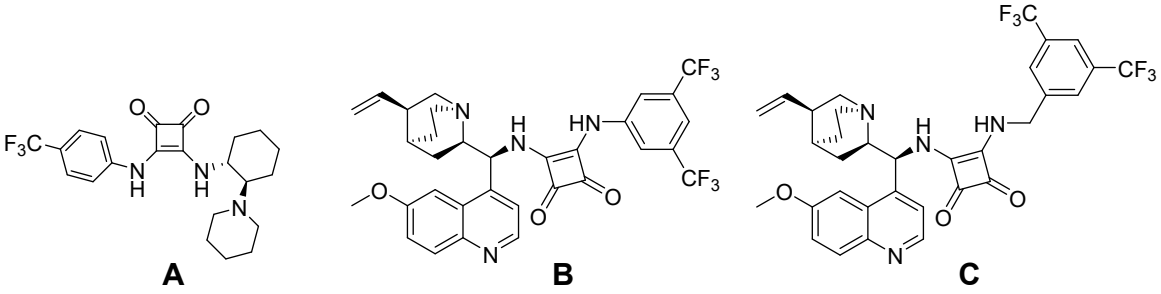
^{13}C NMR spectrum of **3g** in DMSO-d6 (traces of $CHCl_3$ at 79.2 ppm)

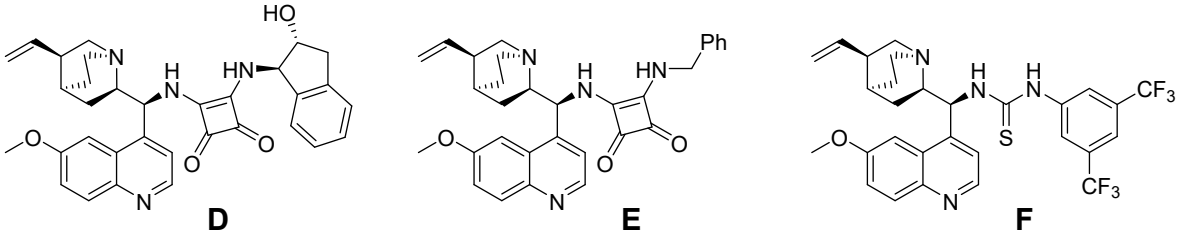


3. Optimization of the synthesis of dihydrofurans

a) Choice of the organocatalyst

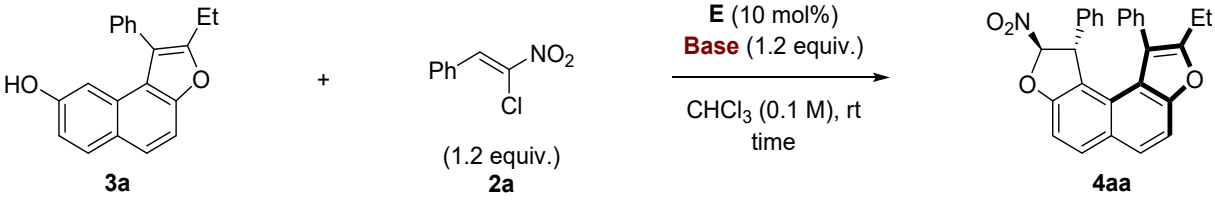






Entry	Catalyst	Time (days)	Yield (%)	ee (%)
1	**A**	12	30	86
2	**B**	7	57	82
3	**C**	7	76	94
4	**D**	7	62	90
5	**E**	4	57	97
6	**F**	13	26	90

b) Optimization of the reaction conditions

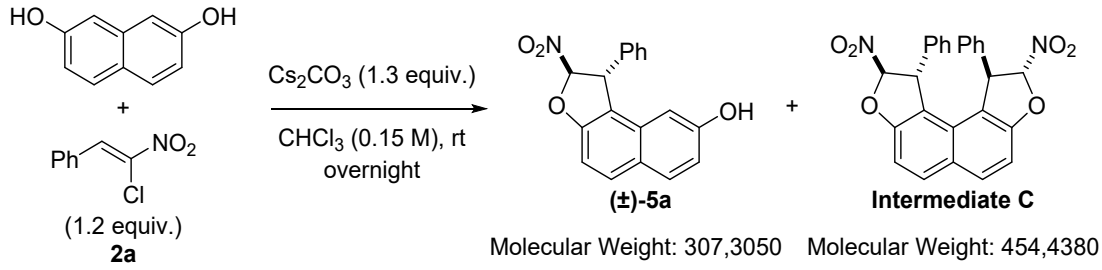


Entry	Base	Time (days)	Yield (%)	ee (%)
1	K_2HPO_4	4	57	97
2	$K_2HPO_4 \cdot 3H_2O$	6	64	95
3	K_3PO_4	3	75	10
4	Na_2CO_3	4	67	97
5	K_2CO_3	3	76	45
6	Cs_2CO_3	0.5	67	6
7[a]	TMEDA	7	18	74
8[b]	Na_2CO_3	6	39	90
9[c]	Na_2CO_3	4	61	96
10[d]	Na_2CO_3	7	50	78
11[e]	Na_2CO_3	3	55	97
12[f]	Na_2CO_3	3	71	95
13[g]	Na_2CO_3	6	69	96
14[h]	Na_2CO_3	7	80	96

[a]1 equiv. of base was used. [b]0.5 equiv. of base were used. [c]5 equiv. of base were used. [d]Toluene was used as solvent. [e]CH_2Cl_2 was used as solvent. [f]$(ClCH_2)_2$ was used as solvent. [g]1 equiv. of **2a** was used. [h]1 equiv. of **2a** and 1.2 equiv. of **3a** were used.

4. Synthesis of dioxa[4]helicene 1 and determination of its enantimerization barrier

a) Synthesis of 1



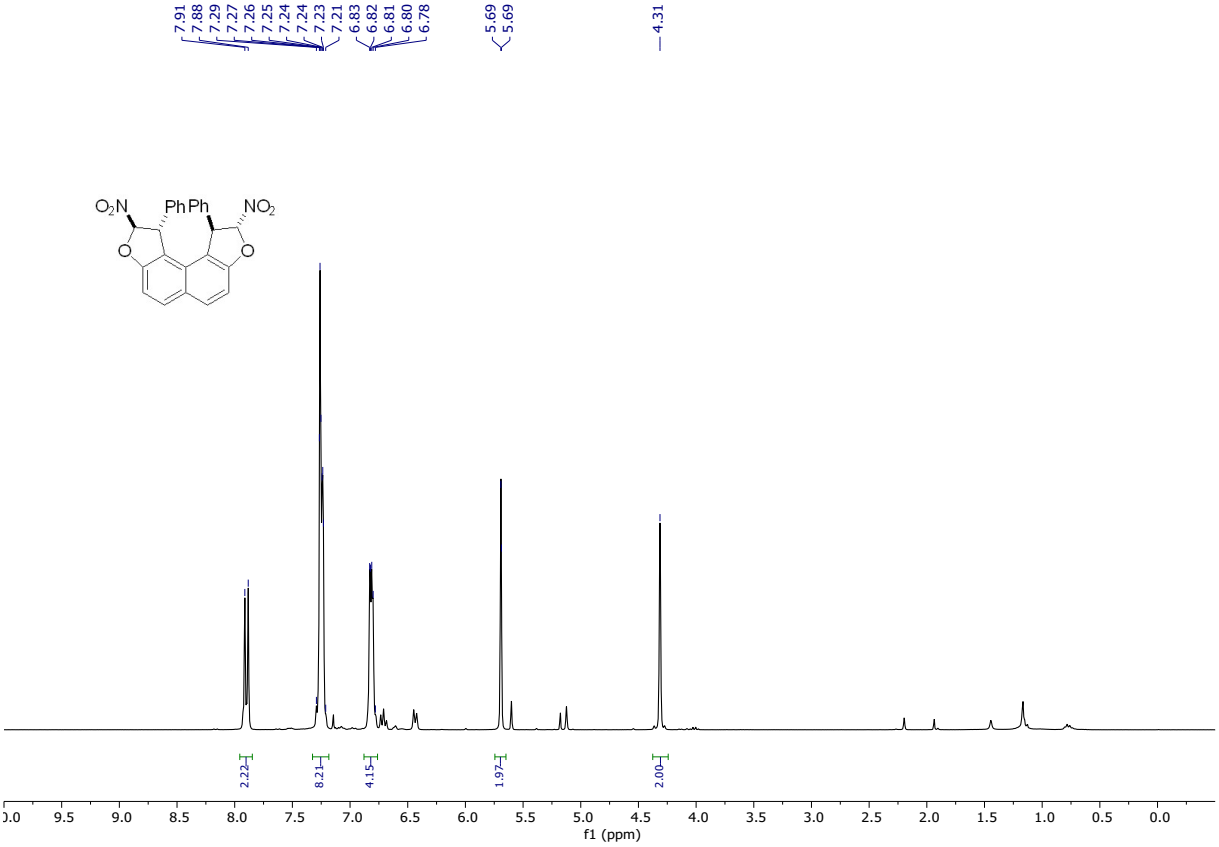
*Note that the number of equivalents of **2a** was intentionally below 2 in order to isolated both desired products.*

In a 50 mL round-bottom flask, 2,7-dihydroxynaphthalene (480 mg, 3.0 mmol, 1.0 equiv), **2a** (693 mg, 3.6 mmol, 1.0 equiv.), Cs_2CO_3 (1.3 g, 4.0 mmol, 1.33 equiv.) were combined with $CHCl_3$ (20 mL) and the mixture was stirred at room temperature overnight. The resulting mixture was treated with aqueous HCl (0.5 M) and the aqueous phase was extracted thrice with DCM. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to dryness. Once concentrated, the crude brown oil was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 5:95 to 15:85) to yield **Intermediate C** as a white powder (219 mg, 0.48 mmol, 80%) and **(±)-5a** as a yellow powder 510 mg, 1.66 mmol, 69%)

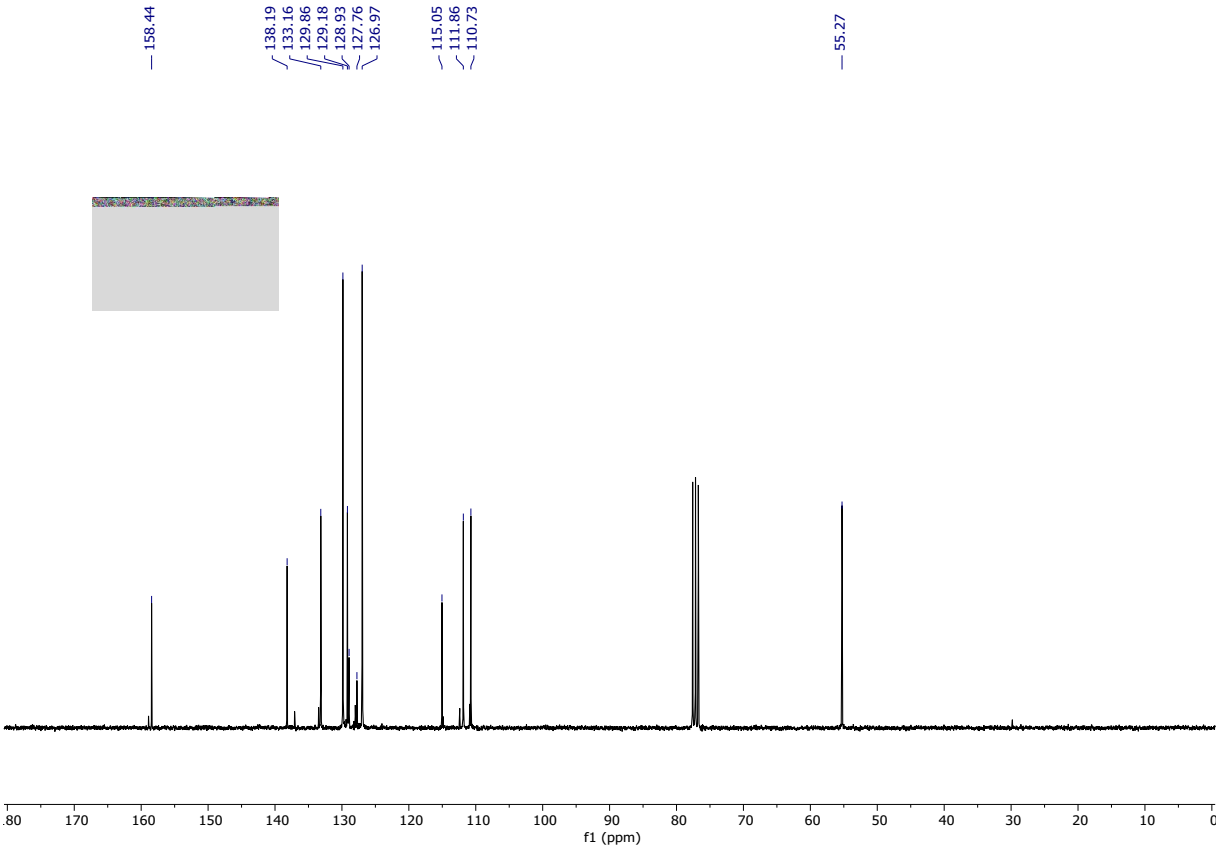
Intermediate C

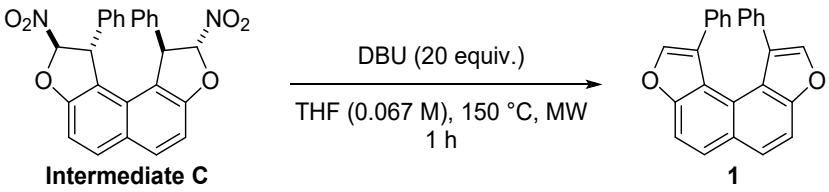
R_f = 0.43 (EtOAc/ Petroleum ether = 1:4), **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 7.90 (d, J = 8.8 Hz, 2H), 7.32 – 7.18 (m, 8H), 6.82 (m, 4H), 5.69 (d, J = 1.7 Hz, 2H), 4.31 (s, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 158.4, 138.2, 133.2, 129.9, 129.2, 128.9, 127.8, 127.0, 115.0, 111.9, 110.7, 55.3. **MP** = 210 °C, **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{26}H_{18}N_2O_6Ag^+$ 561.0210, found 561.0208.

^{1}H NMR spectrum of **Intermediate C** in $CDCl_3$



^{13}C NMR spectrum of **Intermediate C** in $CDCl_3$





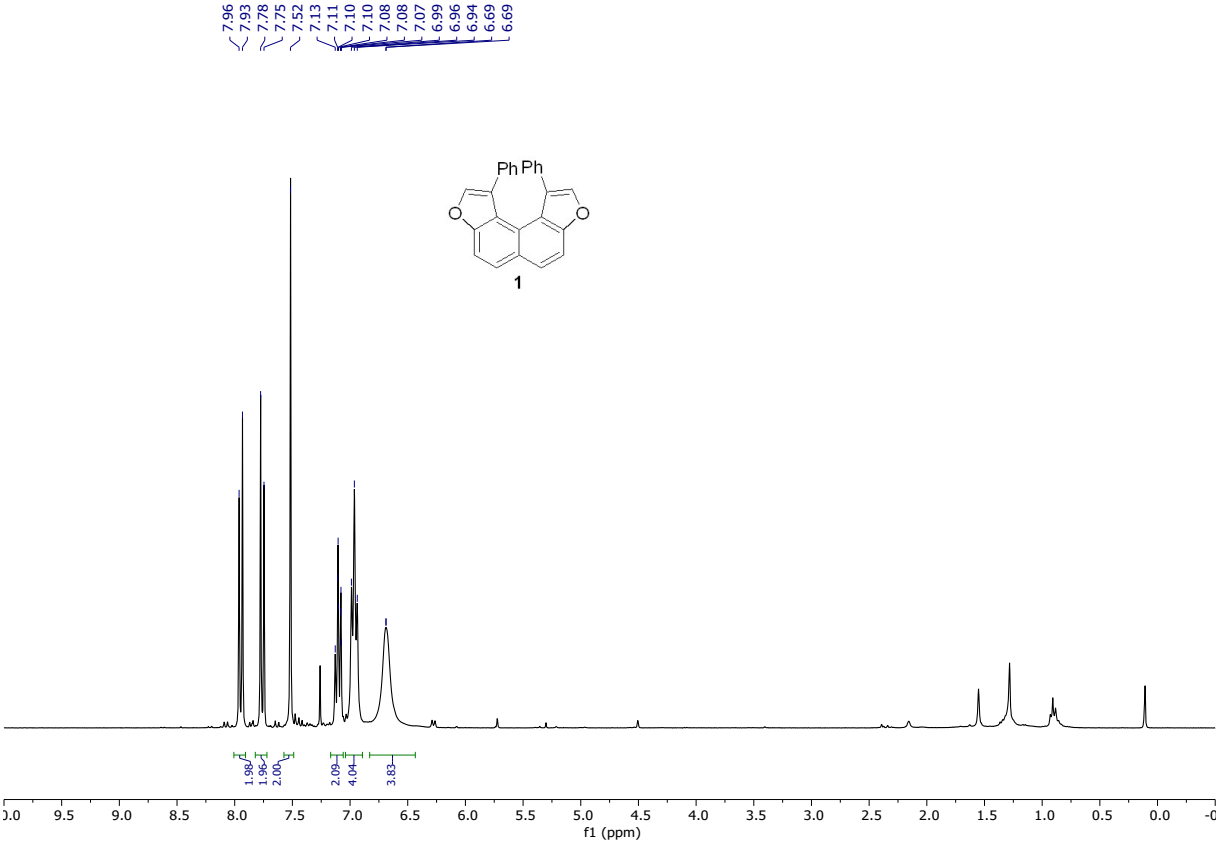
Intermediate C **1**

Molecular Weight: 360,4120

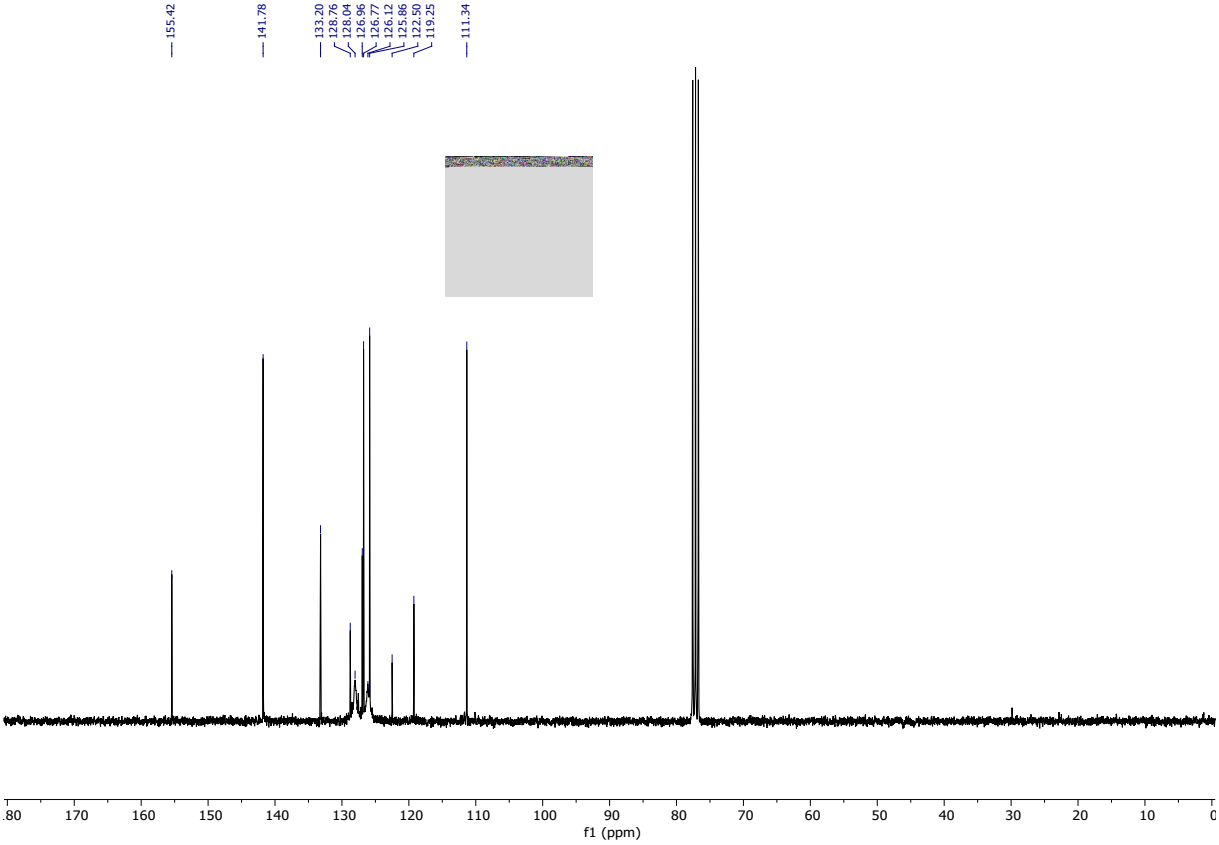
In a G-10 MW vessel, DBU (600 µL, 4.0 mmol, 4.0 equiv) was added to a solution of **Intermediate C** (91 mg, 0.2 mmol, 1.0 equiv.) in THF (3 mL) and the black mixture was stirred at 150 °C in MW for 1 h. The resulting mixture was then treated with aqueous HCl (1 M) and the aqueous phase was extracted twice with DCM. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to dryness. Once concentrated, the crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 2:98) to yield **1** as a yellow solid (33 mg, 0.09 mmol, 46%)

R_f = 0.62 (EtOAc/ Petroleum ether = 1:4), **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 7.95 (d, J = 8.8 Hz, 2H), 7.76 (d, J = 8.8 Hz, 2H), 7.52 (s, 2H), 7.18 – 7.05 (m, 2H), 7.02 – 6.90 (m, 4H), 6.69 (s, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 155.4, 141.8, 133.2, 128.8, 128.0, 127.0, 126.8, 126.1, 125.9, 122.5, 119.3, 111.3. **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{26}H_{16}O_2Ag^+$ 467.0196, found 467.0190.

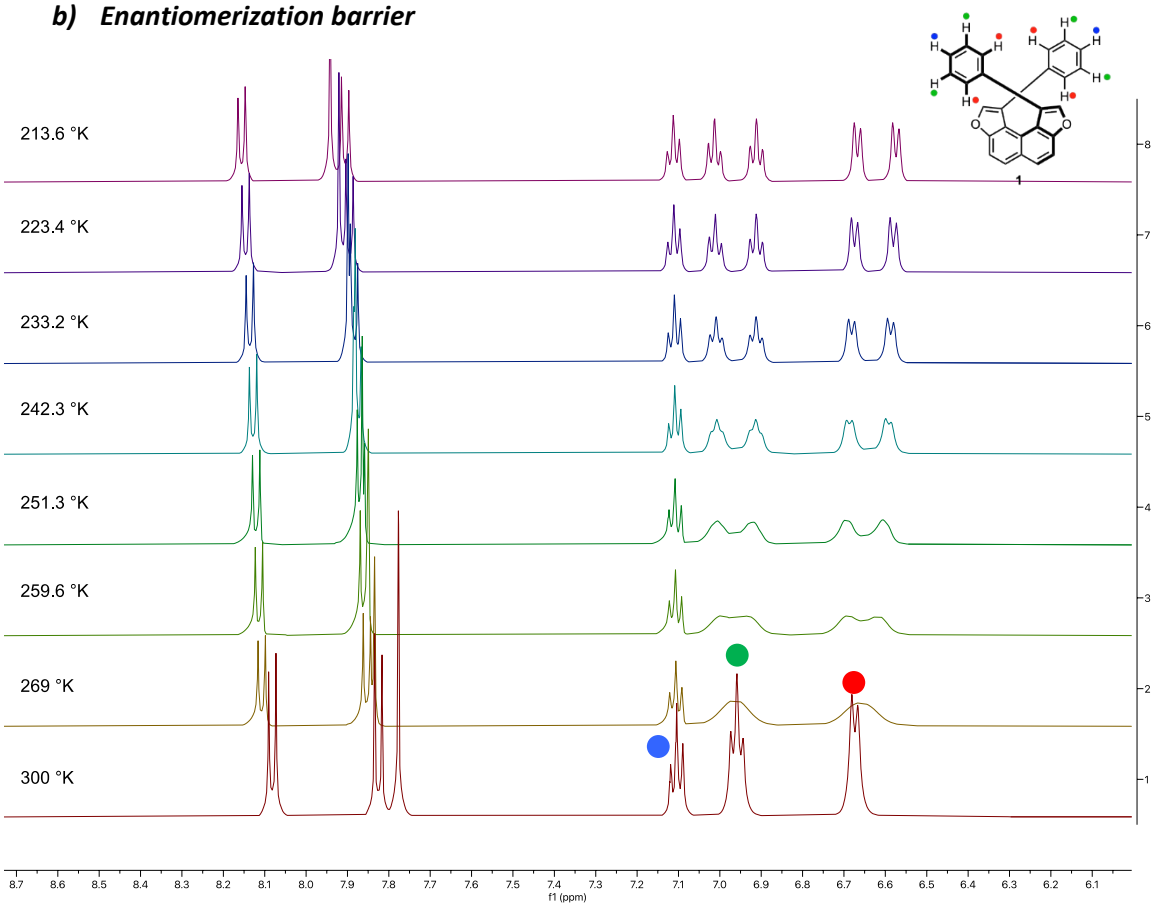
^{1}H NMR spectrum of **1** in $CDCl_3$



^{13}C NMR spectrum of **1** in $CDCl_3$



b) Enantiomerization barrier



The relatively low enantiomerization barrier of **1** allows the kinetics to be studied by dynamic ^{1}H NMR, depending among other things on the length of the alkyl bridge. The system possesses two phenyl groups that shows diastereotopic protons at low temperature due to the helical conformation of the structure. The highlighted protons can be used to determine the rate of inversion by measuring the peaks broadening and subsequently determining the coalescence temperature. The determined coalescence temperature ($T_c =$ 269 °K) as well as the difference in chemical shift of two diastereotopic protons without exchange ($\Delta\nu =$ 47 Hz)

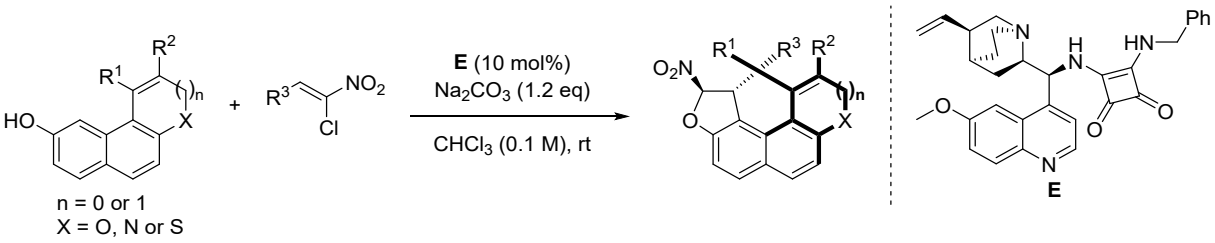
can be used to calculate the barrier by using the following equation.[17]

$$\Delta G_{eT_c}^{\neq} = RT_c\left[ln\left(\frac{k_B T_c}{h}\right) - ln\left(\pi\frac{\Delta\nu}{\sqrt{2}}\right)\right]$$

$$\Delta G_{eT_c}^{\neq} = 8.31 \cdot 10^{-3} \cdot 269\left[ln\left(\frac{1.38 \cdot 10^{-23} \cdot 269}{6.63 \cdot 10^{-34}}\right) - ln\left(\pi\frac{47}{\sqrt{2}}\right)\right] = 55\ kJ.mol^{-1}$$

5. Experimental procedures for the enantioselective synthesis and characterization of 4

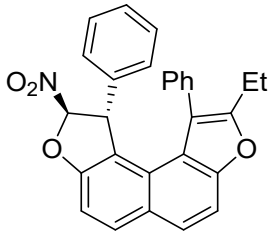
a) General procedure



In a reaction tube, naphtho[2,1-b]furan-8-ol (0.12 mmol, 1.2 equiv., *unless specified*), chloronitrovinylbenzene (0.1 mmol, 1.0 equiv.), Na_2CO_3 (13 mg, 0.12 mmol, 1.2 equiv.), and **E** (5 mg, 0.01 mmol, 0.1 equiv.) were combined with $CHCl_3$ (1 mL) and the mixture was stirred at room temperature *(unless specified)* until completion of the reaction monitored by TLC *(usually 4 days)*. Once concentrated, the crude product was purified on silica column using EtOAc/ Petroleum ether mixture to yield the pure product.

[17] Rickhaus, M.; Jundt, L.; Mayor, M. *Chimia* **2016**, *70*, 192-202.

*(1R,2R)-9-ethyl-2-nitro-1,10-diphenyl-1,2-dihydronaphtho[2,1-b:7,8-b']difuran (**4aa**)*

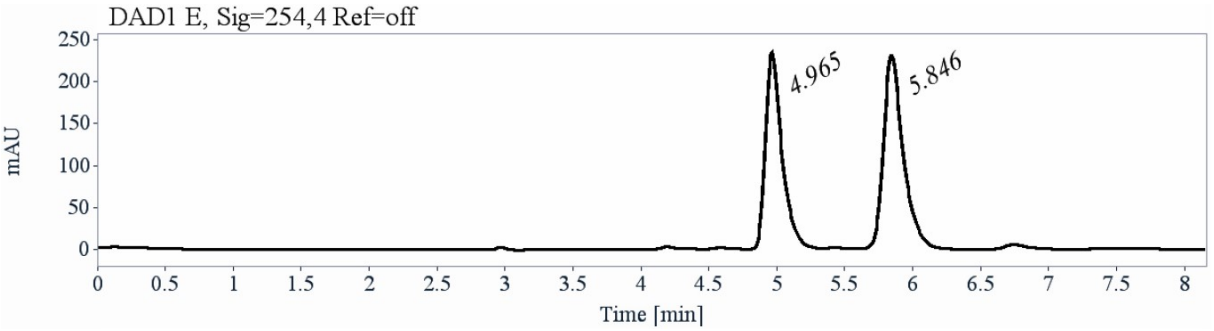


Molecular Weight: 435,4790

Prepared following general procedure using **3a** (35 mg) and **2a** (18 mg) for 4 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:49) to yield a white solid (35 mg, 0.08 mmol, 80%)

R_f = 0.53 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +252°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.04 (d, *J* = 8.7 Hz, 1H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.59 (d, *J* = 8.9 Hz, 1H), 7.51 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.44 – 7.30 (m, 3H), 7.18 – 7.09 (m, 2H), 7.09 – 7.01 (m, 2H), 6.81 – 6.73 (m, 1H), 6.36 – 6.29 (m, 2H), 5.69 (d, *J* = 1.0 Hz, 1H), 4.11 (s, 1H), 2.54 (ddt, *J* = 17.1, 15.0, 7.5 Hz, 2H), 1.14 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 157.8, 156.7, 153.4, 137.9, 134.7, 133.1, 130.8, 130.3, 129.1, 129.0, 128.7, 128.5, 128.1, 127.7, 126.4, 126.1, 121.3, 118.2, 116.0, 112.1, 111.2, 109.8, 56.2, 20.1, 13.0. **MP** = 182 °C, **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{28}H_{21}NO_4Ag^+$ 542.0516, found 542.0513. **HPLC analysis** (Lux-Cellulose-2, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **96% ee**, **t_r1**: 4.90 min, **t_r2**: 5.72 min

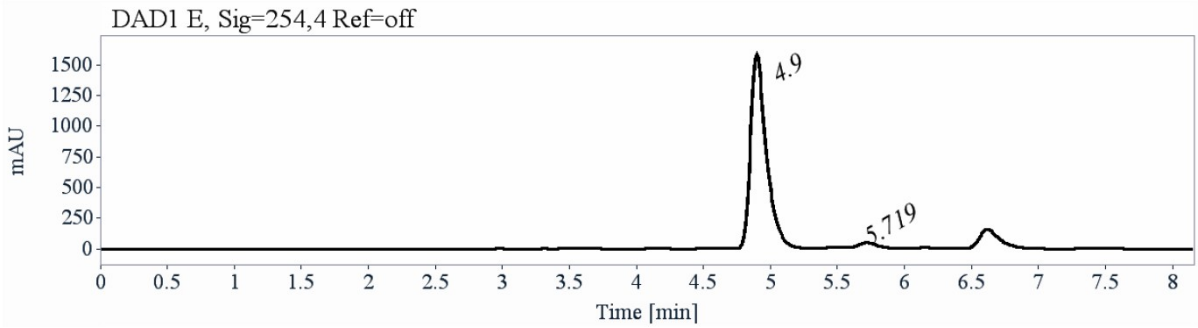
Chiral HPLC spectrum of *rac*-**4aa**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.97	1971	46.82	0.68		
5.85	2239	53.18	0.98	1.44	3.81
Sum	4209	100.00			

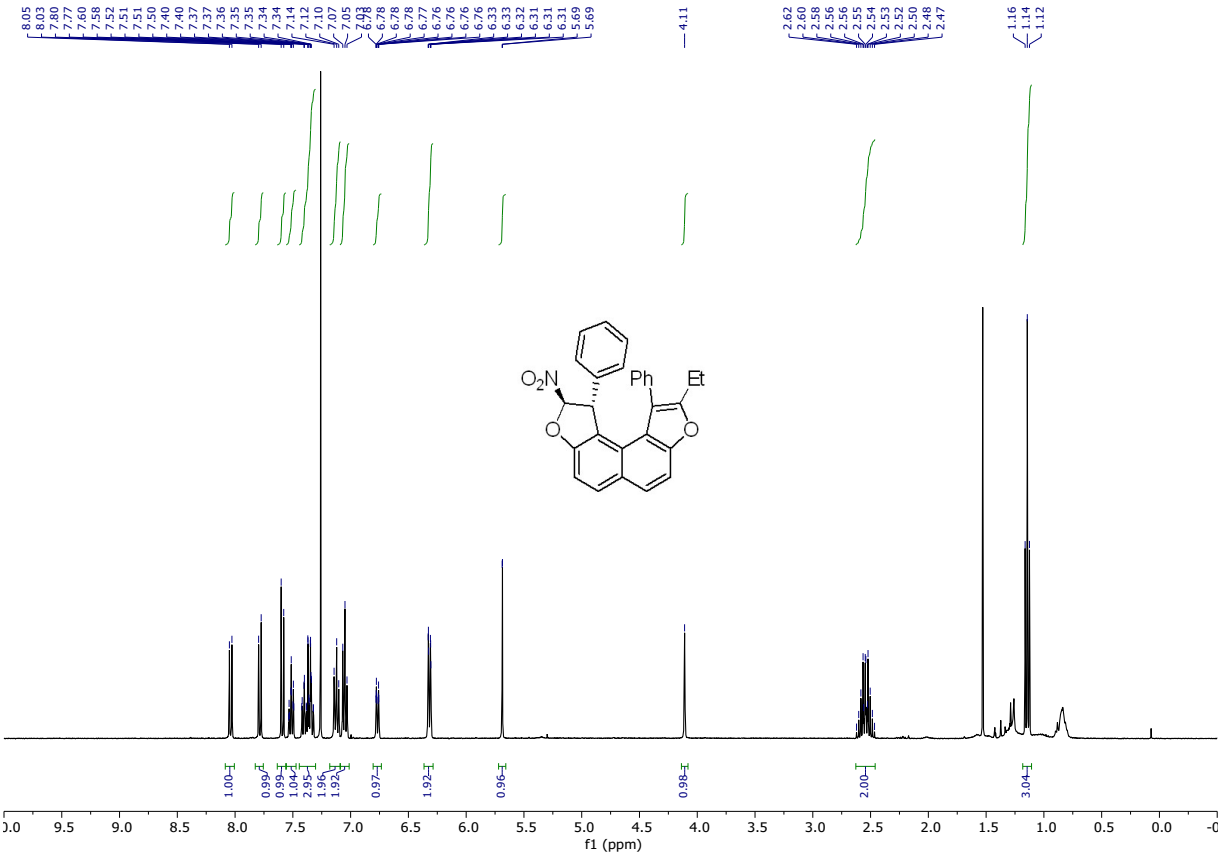
Chiral HPLC spectrum of **4aa**



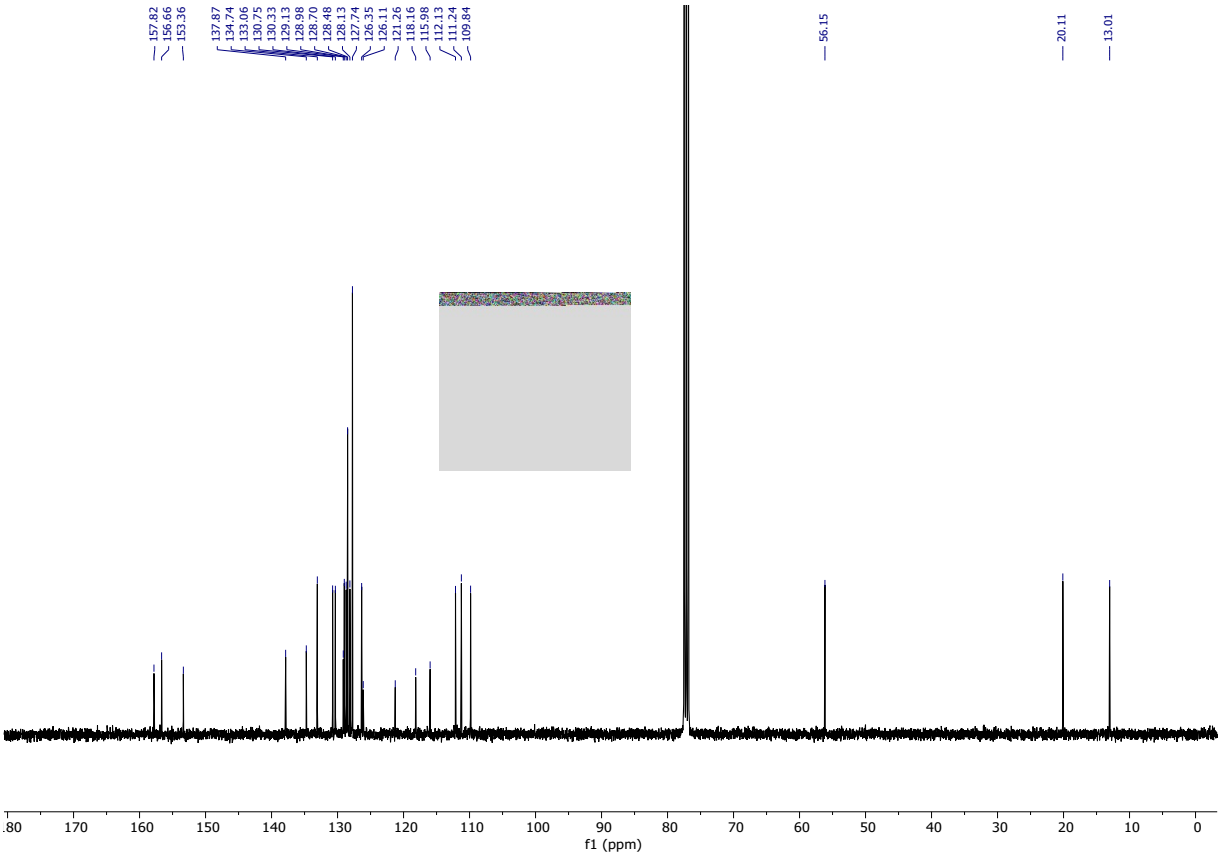
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.90	12983	97.26	0.66		
5.72	366	2.74	0.94	1.42	3.74
Sum	13349	100.00			

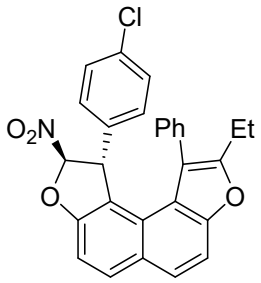
^{1}H NMR spectrum of **4aa** in $CDCl_3$



^{13}C NMR spectrum of **4aa** in $CDCl_3$



*(1R,2R)-1-(4-chlorophenyl)-9-ethyl-2-nitro-10-phenyl-1,2-dihydronaphtho[2,1-b:7,8-b']difuran (**4ab**)*



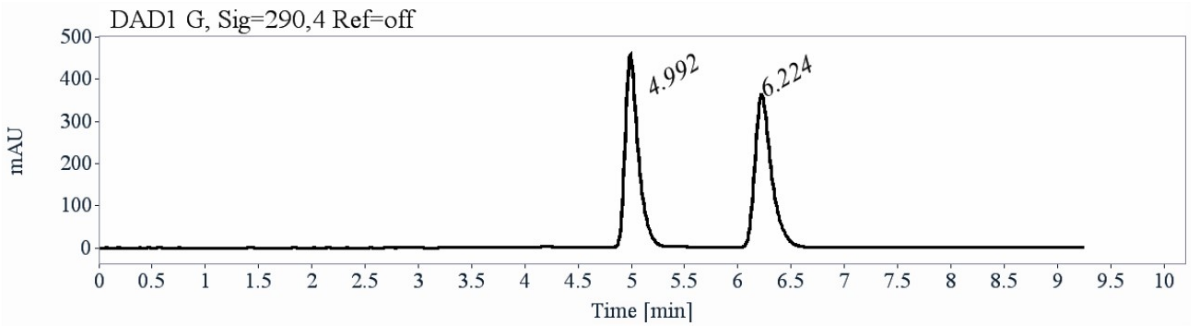
Molecular Weight: 469,9210

Prepared following general procedure using **3a** (35 mg) and **2b** (22 mg) for 3 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:49 to 3:97) to yield a yellow solid (36 mg, 0.076 mmol, 76%)

R_f = 0.53 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +191°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.05 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.53 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.46 – 7.33 (m, 3H), 7.18 – 7.10 (m, 1H), 7.07 – 6.99 (m, 2H), 6.88 – 6.80 (m, 1H), 6.31 – 6.20 (m, 2H), 5.63 (d, *J* = 1.0 Hz, 1H), 4.11 (s, 1H), 2.67 – 2.46 (m, *J* = 7.5 Hz, 2H), 1.16 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 157.8, 156.8, 153.4, 136.4, 134.7, 133.7, 133.3, 130.8, 130.3, 129.2, 129.1, 129.0, 128.8, 128.7, 128.3, 126.4, 125.9, 121.1, 118.0, 115.5, 111.7, 111.4, 109.9, 55.6, 20.1, 13.0. **MP** = 110 °C, **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{28}H_{20}ClNO_4Ag^+$ 578.0119, found 578.0106. **HPLC**

analysis (Lux-Cellulose-2, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 290 nm) indicated **96% ee**, t_r**1**: 4.98 min, t_r**2**: 6.21 min

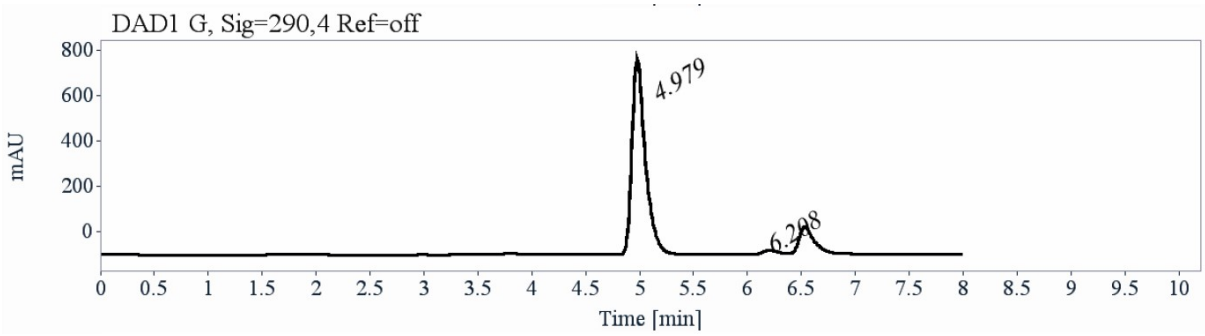
Chiral HPLC spectrum of *rac*-**4ab**



Signal: DAD1 G, Sig=290,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.99	3917	49.91	0.69		
6.22	3931	50.09	1.11	1.60	5.07
Sum	7848	100.00			

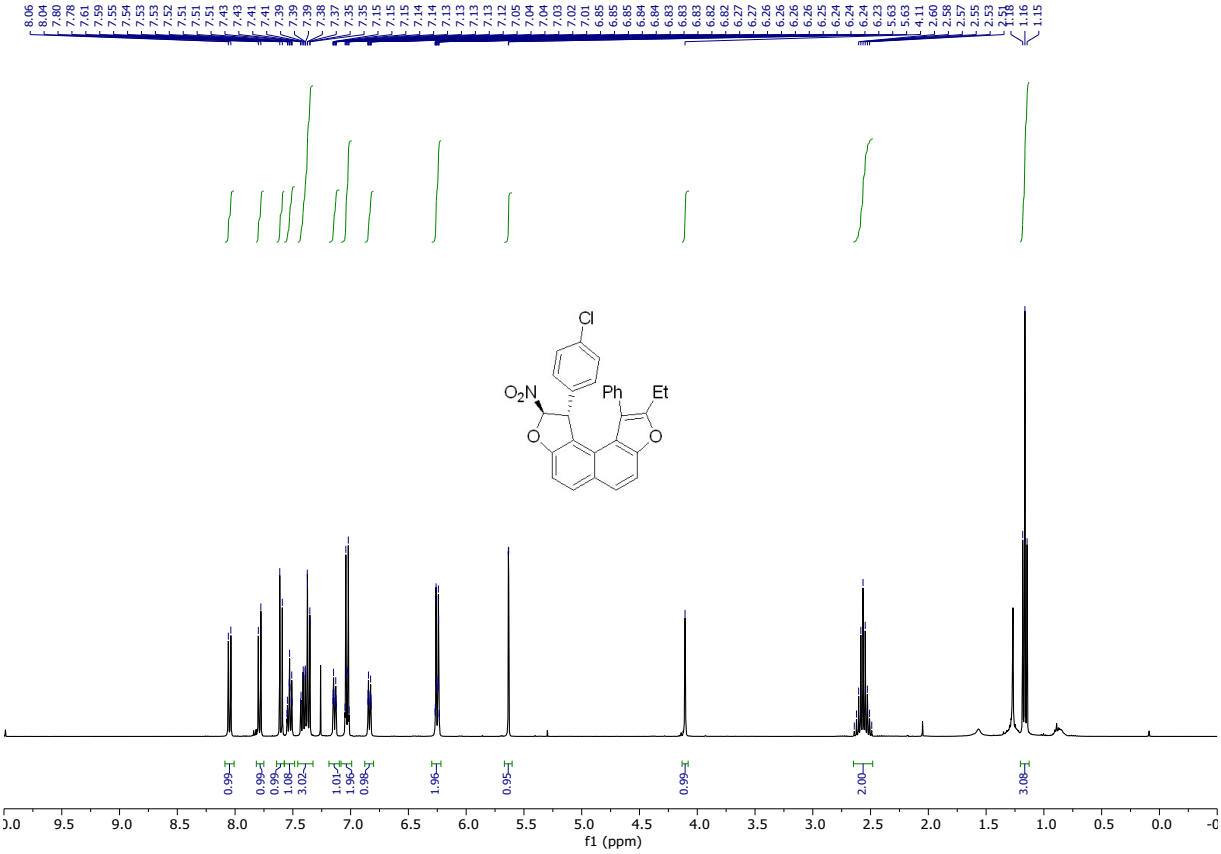
Chiral HPLC spectrum of **4ab**



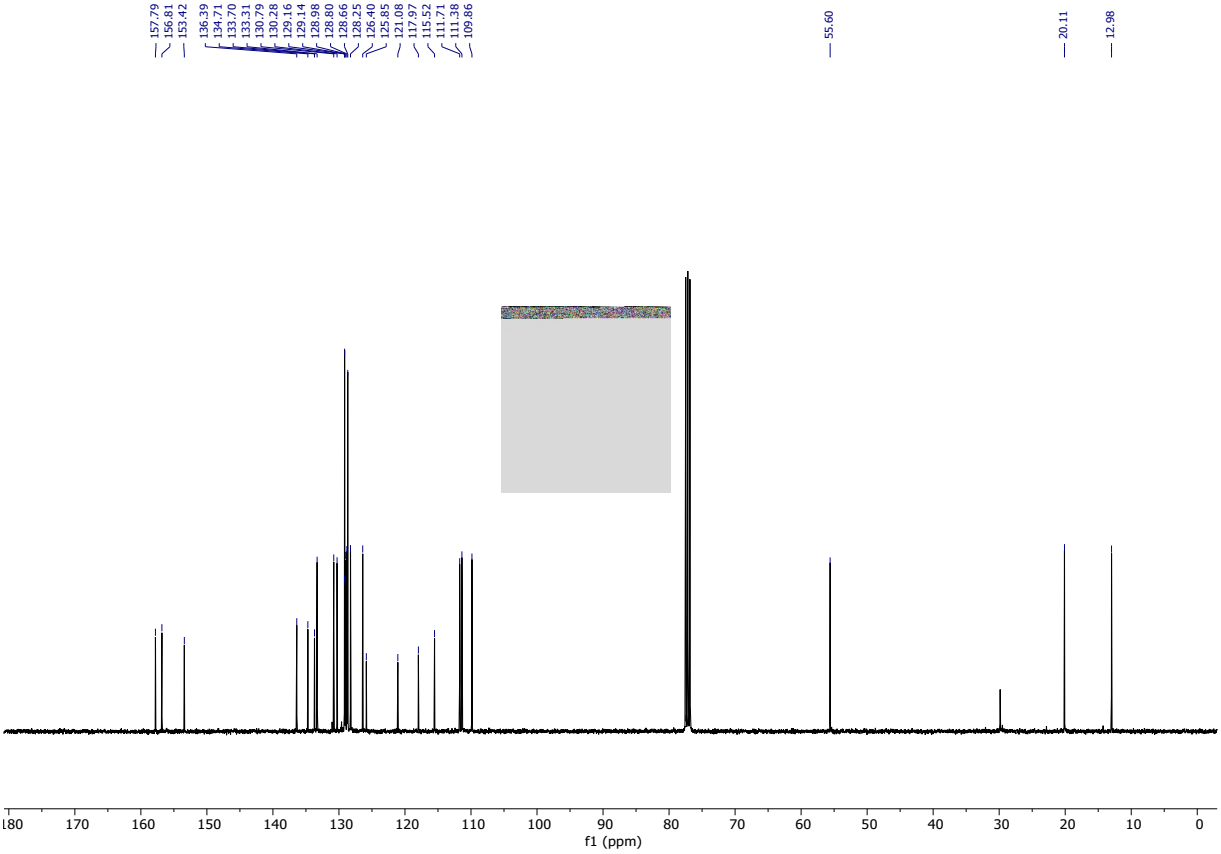
Signal: DAD1 G, Sig=290,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.98	7452	98.05	0.69		
6.21	148	1.95	1.10	1.61	5.37
Sum	7600	100.00			

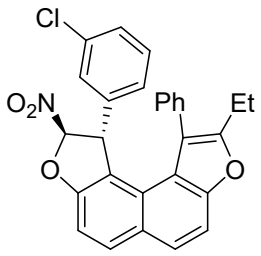
^{1}H NMR spectrum of **4ab** in $CDCl_3$



^{13}C NMR spectrum of **4ab** in $CDCl_3$



*(1R,2R)-1-(3-chlorophenyl)-9-ethyl-2-nitro-10-phenyl-1,2-dihydronaphtho[2,1-b:7,8-b']difuran (**4ac**)*



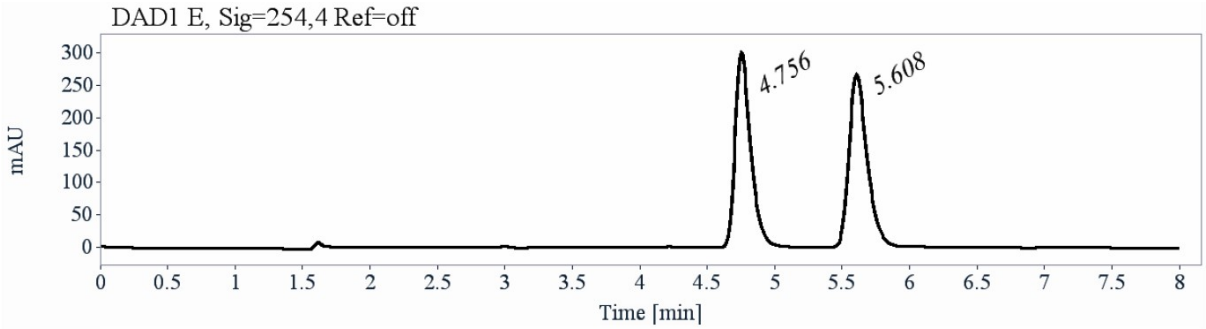
Molecular Weight: 469,9210

Prepared following general procedure using **3a** (35 mg) and **2c** (22 mg) for 4 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:49 to 1:24) to yield a yellow solid (30 mg, 0.063 mmol, 63%)

R_f = 0.44 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +168°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.05 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.55 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.46 – 7.35 (m, 3H), 7.16 (dt, *J* = 7.6, 1.7 Hz, 1H), 7.14 – 7.10 (m, 1H), 6.94 (t, *J* = 7.9 Hz, 1H), 6.82 (dt, *J* = 7.5, 1.7 Hz, 1H), 6.41 (t, *J* = 2.0 Hz, 1H), 6.10 (ddt, *J* = 7.8, 1.8, 0.9 Hz, 1H), 5.66 (d, *J* = 1.1 Hz, 1H), 4.22 (s, 1H), 2.64 – 2.48 (m, 2H), 1.16 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 157.8, 156.9, 153.4, 139.9, 134.7, 134.4, 133.4, 130.8, 130.5, 129.7, 129.2, 128.9, 128.8, 128.4, 128.3, 128.1, 126.5, 125.9, 125.6, 121.1, 117.9, 115.2, 111.6, 111.4, 109.9, 55.8, 20.1, 13.0. **MP** = 152 °C, **HRMS-ESI$^+$ (m/z)**: $[2M+Ag]^+$ calculated for $C_{56}H_{40}Cl_2N_2O_8Ag^+$ 1047.1203, found 1047.1193. **HPLC analysis** (Lux-

Cellulose-2, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **94% ee**, t_r**1**: 4.76 min, t_r**2**: 5.61 min

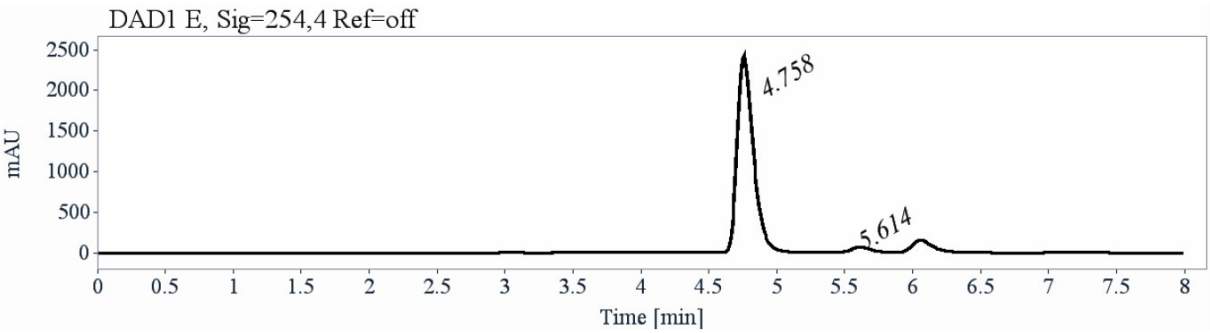
Chiral HPLC spectrum of *rac*-**4ac**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.76	2429	49.17	0.61		
5.61	2511	50.83	0.90	1.47	3.78
Sum	4941	100.00			

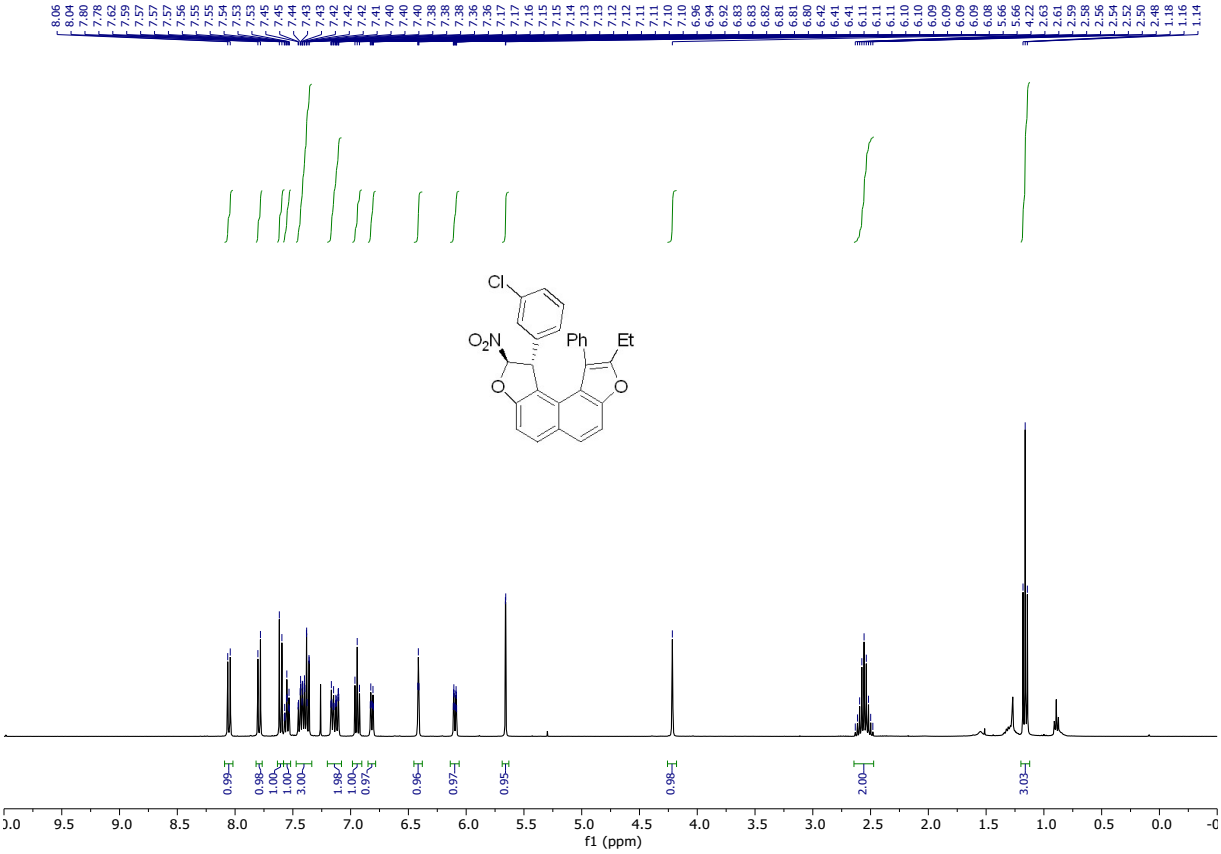
Chiral HPLC spectrum of **4ac**



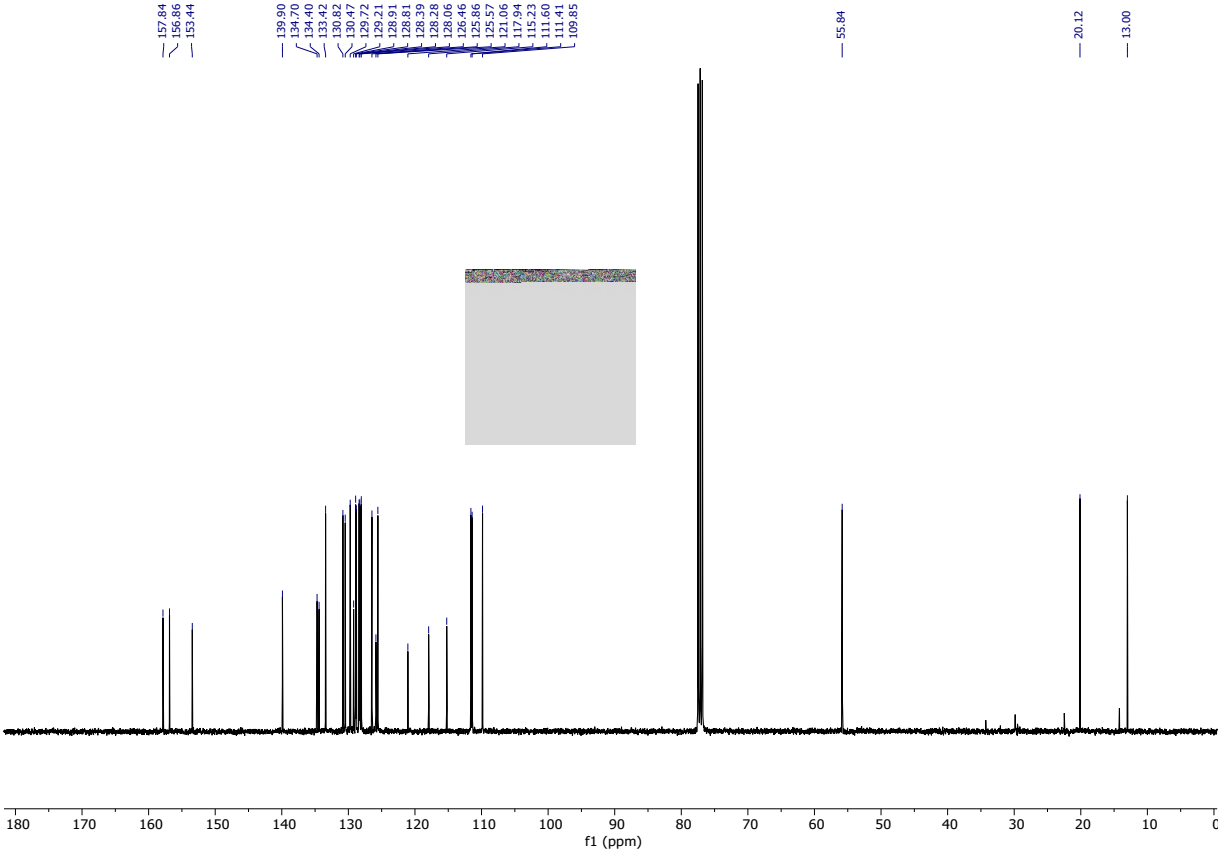
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.76	20044	97.01	0.61		
5.61	617	2.99	0.90	1.47	3.75
Sum	20661	100.00			

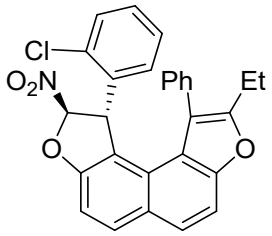
^{1}H NMR spectrum of **4ac** in $CDCl_3$



^{13}C NMR spectrum of **4ac** in $CDCl_3$



*(1S,2R)-1-(2-chlorophenyl)-9-ethyl-2-nitro-10-phenyl-1,2-dihydronaphtho[2,1-b:7,8-b']difuran (**4ad**)*



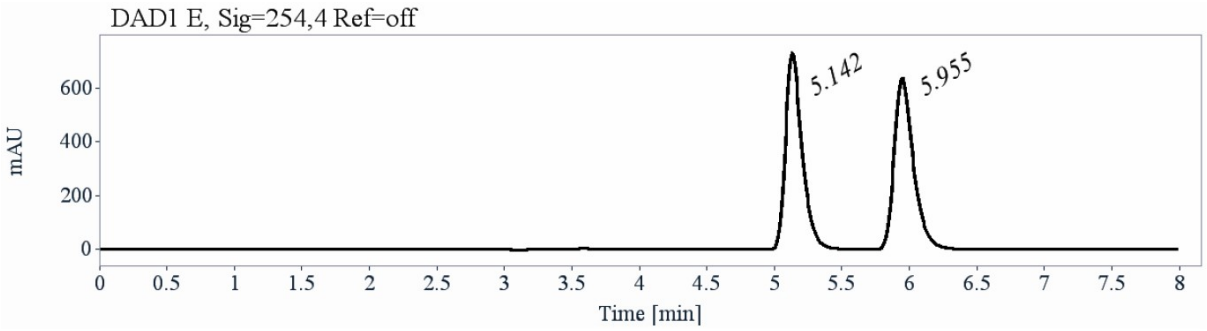
Molecular Weight: 469,9210

Prepared following general procedure using **3a** (35 mg) and **2d** (22 mg) for 6 days at 50 °C. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:49) to yield a light-yellow solid (11 mg, 0.023 mmol, 23%)

R_f = 0.29 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +35°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.06 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.51 – 7.38 (m, 2H), 7.38 – 7.26 (m, 3H), 7.25 – 7.17 (m, 1H), 7.15 – 7.05 (m, 1H), 6.75 (td, *J* = 7.7, 1.3 Hz, 1H), 6.59 (dq, *J* = 7.5, 0.9 Hz, 1H), 5.99 (d, *J* = 0.8 Hz, 1H), 5.74 (ddd, *J* = 7.9, 1.7, 0.8 Hz, 1H), 4.70 (s, 1H), 2.47 (ddt, *J* = 17.9, 15.0, 7.5 Hz, 2H), 1.12 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 158.2, 157.0, 153.5, 134.4, 134.4, 134.4, 133.5, 130.5, 130.1, 129.4, 129.2, 129.1, 129.1, 128.8, 128.8, 128.5, 126.9, 126.7, 126.5, 121.0, 118.2, 115.3, 111.3, 110.8, 110.1, 53.6, 20.1, 13.0. **MP** = 207 °C, **HRMS-ESI$^+$ (m/z)**: $[2M+Ag]^+$ calculated for $C_{56}H_{40}Cl_2N_2O_8Ag^+$ 1047.1203, found 1047.1205. **HPLC analysis** (Lux-Cellulose-2,

Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **85% ee**, t_r**1**: 5.15 min, t_r**2**: 5.96 min

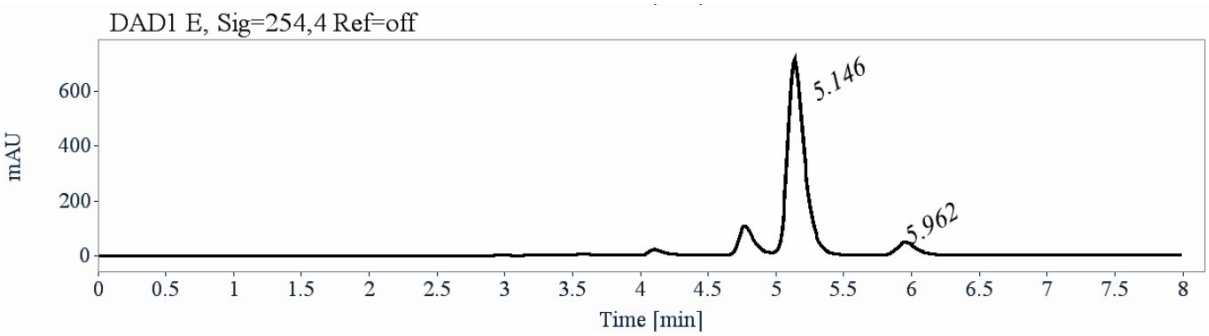
Chiral HPLC spectrum of *rac*-**4ad**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.14	6225	49.55	0.74		
5.95	6338	50.45	1.02	1.37	3.43
Sum	12563	100.00			

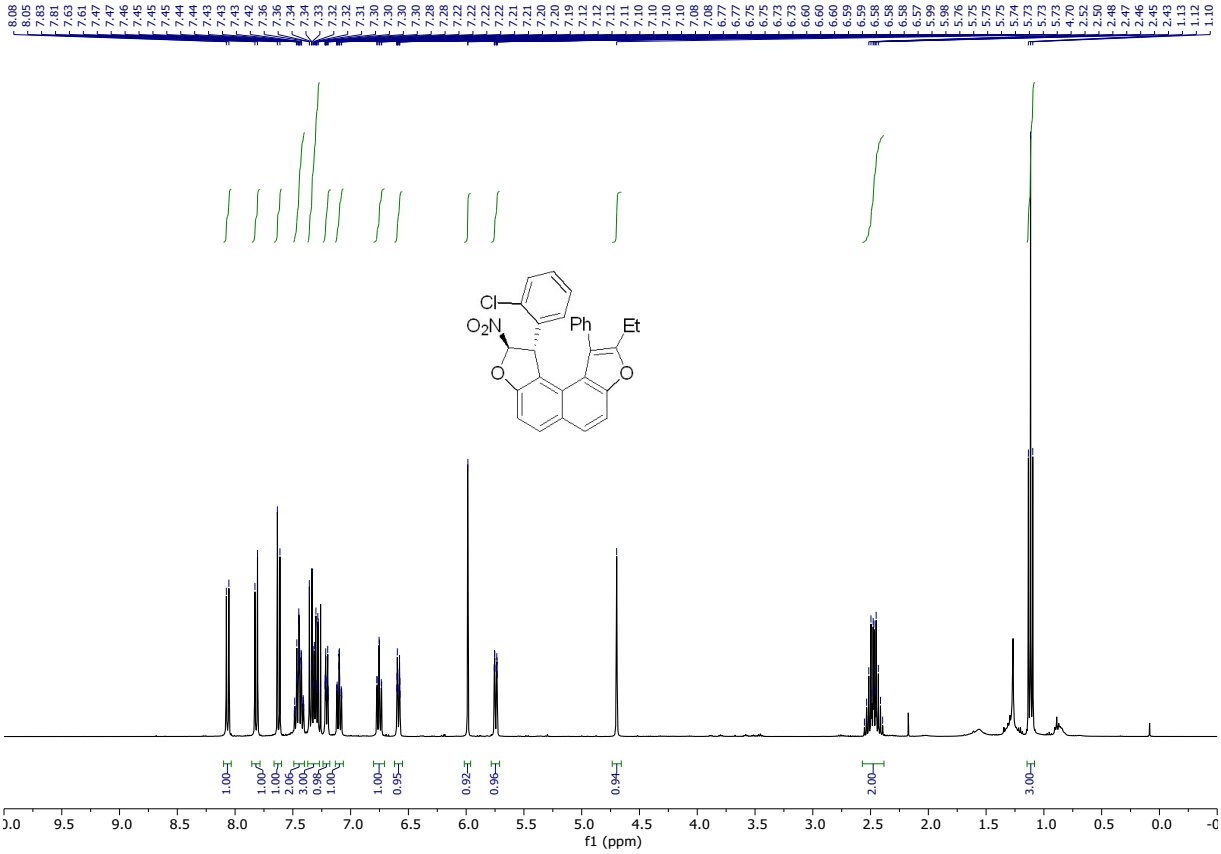
Chiral HPLC spectrum of **4ad**



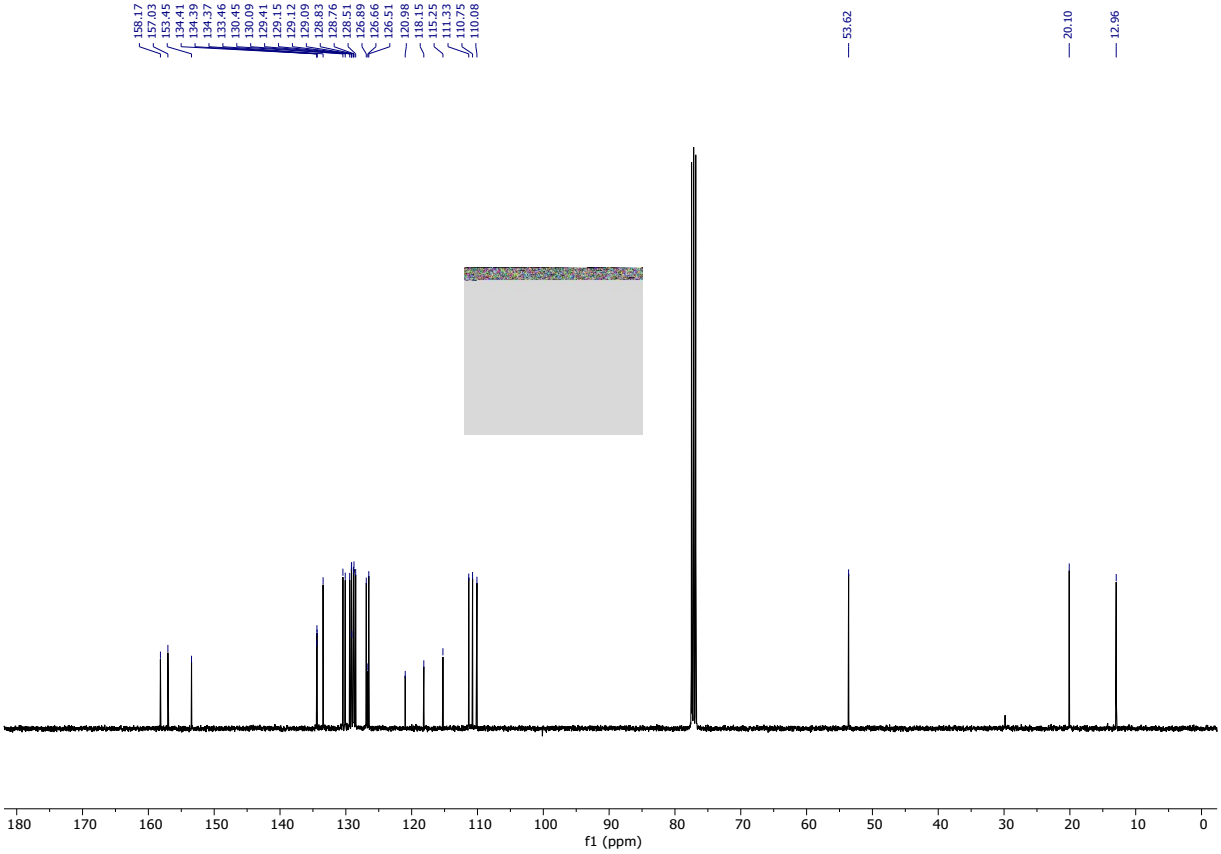
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.15	6225	92.67	0.74		
5.96	493	7.33	1.02	1.37	3.40
Sum	6718	100.00			

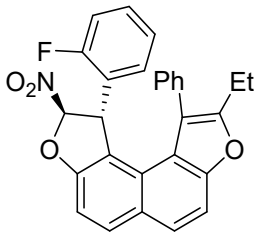
^{1}H NMR spectrum of **4ad** in $CDCl_3$



^{13}C NMR spectrum of **4ad** in $CDCl_3$



*(1S,2R)-9-ethyl-1-(2-fluorophenyl)-2-nitro-10-phenyl-1,2-dihydronaphtho[2,1-b:7,8-b']difuran (**4ae**)*



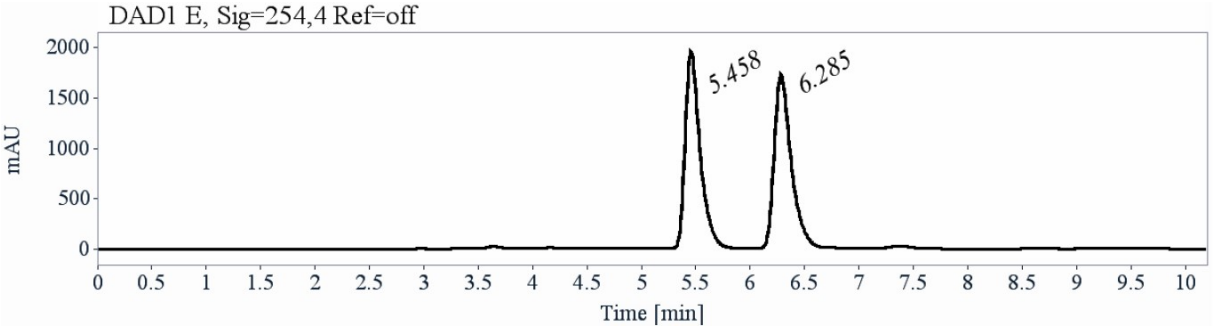
Molecular Weight: 453,4694

Prepared following general procedure using **3a** (35 mg) and **2e** (20 mg) for 8 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 3:97 to 1:24) to yield a white solid (17 mg, 0.038 mmol, 38%)

R_f = 0.53 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +113°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.05 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.9 Hz, 1H), 7.63 (d, *J* = 8.9 Hz, 1H), 7.51 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.43 (tdd, *J* = 7.5, 1.6, 0.6 Hz, 1H), 7.35 (dd, *J* = 8.8, 0.6 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.20 – 7.13 (m, 2H), 6.98 (ddd, *J* = 10.2, 8.2, 1.2 Hz, 1H), 6.66 (td, *J* = 7.6, 1.2 Hz, 1H), 6.54 – 6.48 (m, 1H), 5.86 – 5.77 (m, 2H), 4.40 (s, 1H), 2.49 (ddt, *J* = 16.2, 15.0, 7.5 Hz, 2H), 1.13 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 160.7 (d, *J* = 248.8 Hz), 157.9, 156.9, 153.3, 134.4, 133.3, 130.7, 129.7 (d, *J* = 8.1 Hz), 129.4, 129.0, 129.0 (d, *J* = 1.4 Hz), 128.7 (d, *J* = 2.9 Hz), 128.6, 128.4, 126.5, 126.5, 125.2 (d, *J* = 13.6 Hz), 124.1 (d, *J* = 3.6 Hz), 121.2, 118.1, 115.4 (d, *J* = 20.7 Hz), 114.4, 111.3, 110.7 (d, *J* = 2.6 Hz), 110.0, 50.3 (d, *J* = 2.2 Hz), 20.1, 13.0. **^{19}F NMR (282 MHz, $CDCl_3$)** δ (ppm) -110.82. **MP** = 181 °C, **HRMS-ESI$^+$**

(m/z): $[2M+Ag]^+$ calculated for $C_{56}H_{40}F_2N_2O_8Ag^+$ 1015.1808, found 1015.1794. **HPLC analysis** (Lux-Cellulose-2, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **92% ee**, $\mathbf{t_r1}$: 5.45 min, $\mathbf{t_r2}$: 6.28 min

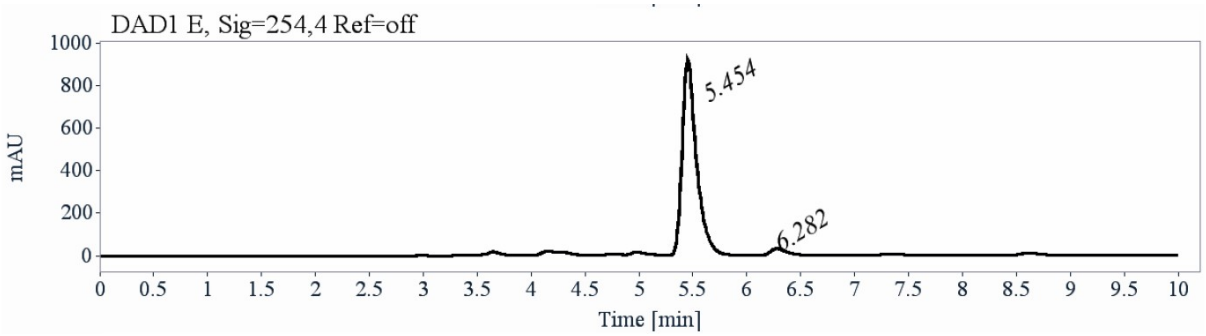
Chiral HPLC spectrum of *rac*-**4ae**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.46	18819	49.85	0.85		
6.28	18931	50.15	1.13	1.33	3.23
Sum	37751	100.00			

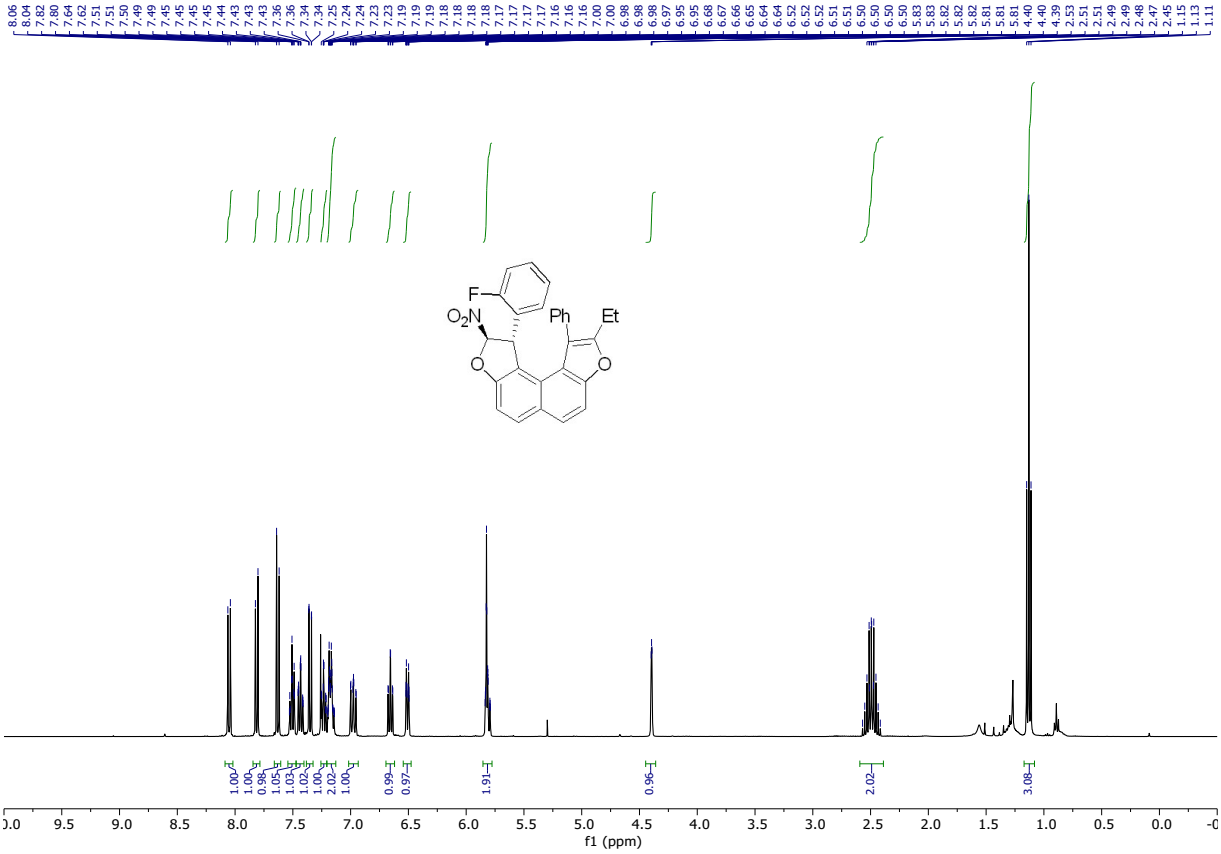
Chiral HPLC spectrum of **4ae**



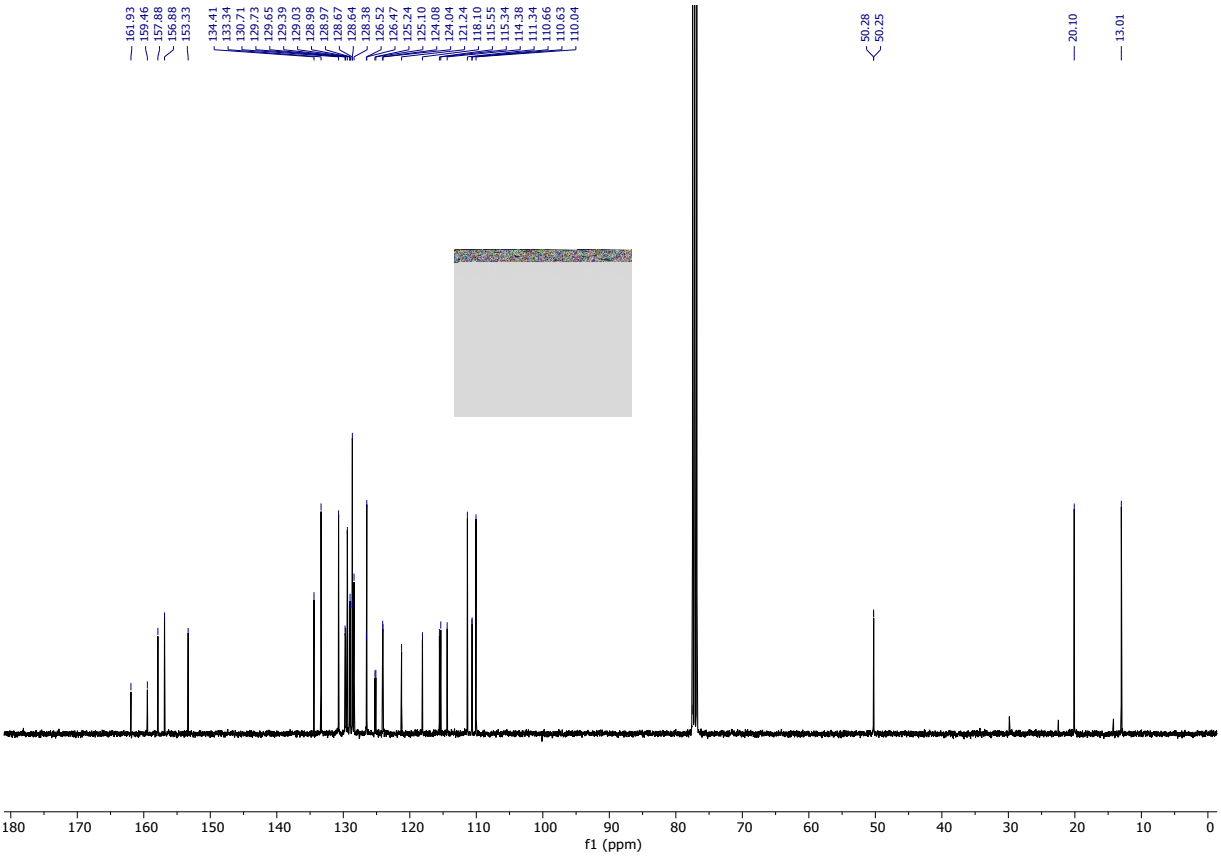
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.45	8498	96.03	0.85		
6.28	351	3.97	1.13	1.33	3.32
Sum	8849	100.00			

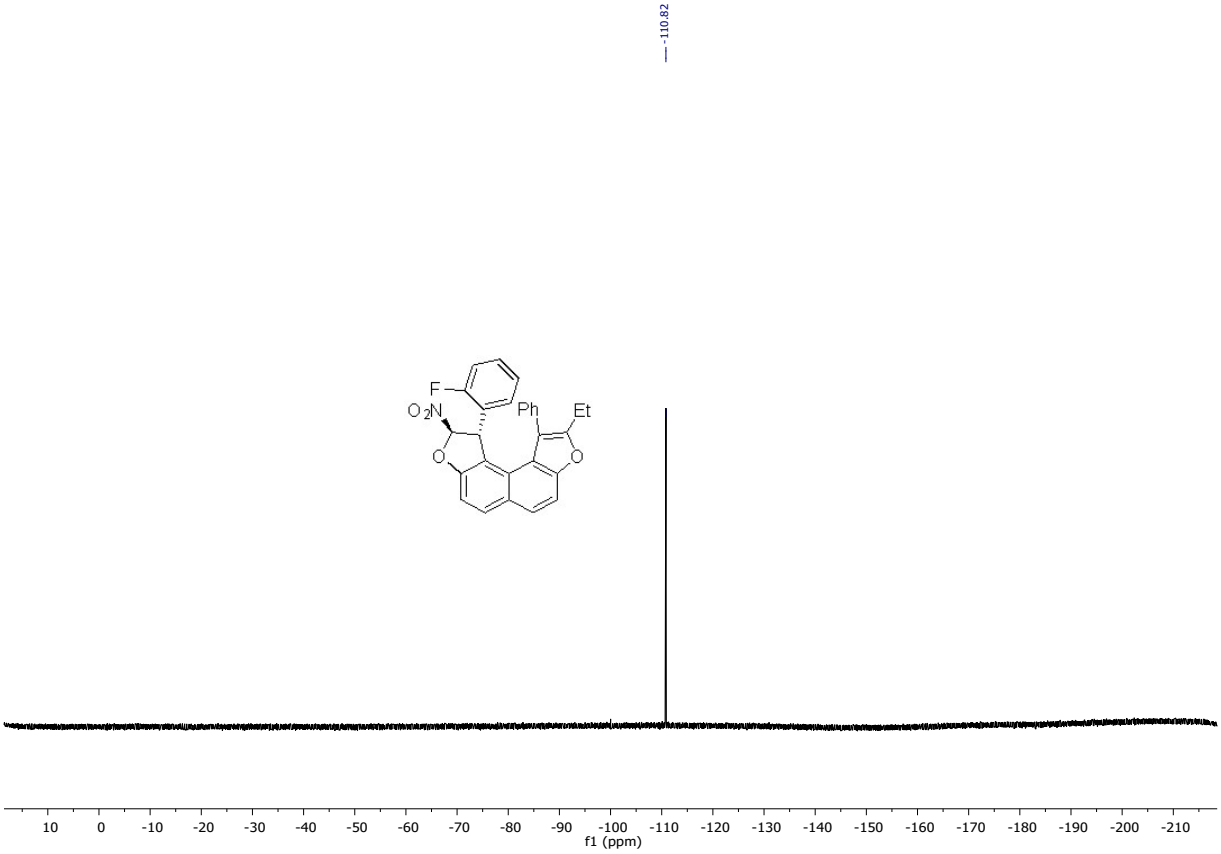
^{1}H NMR spectrum of **4ae** in $CDCl_3$



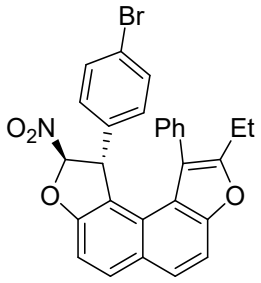
^{13}C NMR spectrum of **4ae** in $CDCl_3$



^{19}F NMR spectrum of **4ae** in $CDCl_3$



(1R,2R)-1-(4-bromophenyl)-9-ethyl-2-nitro-10-phenyl-1,2-dihydronaphtho[2,1-b:7,8-b']difuran (**4af**)



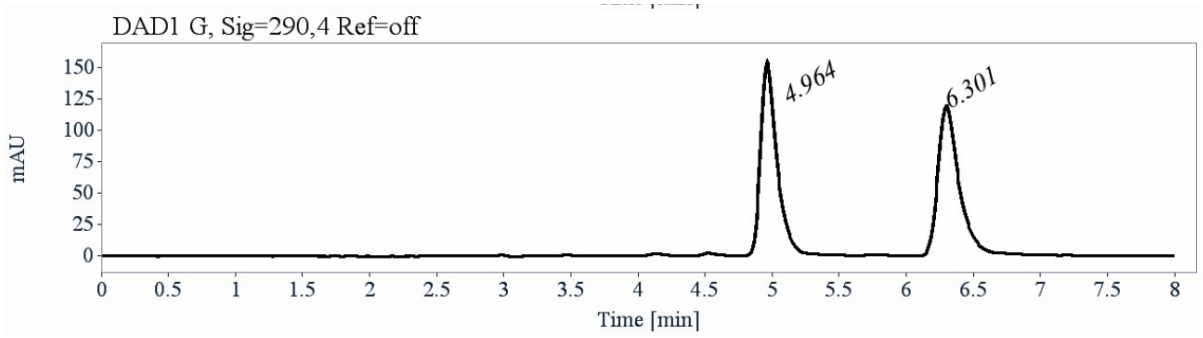
Molecular Weight: 514,3750

Prepared following general procedure using **3a** (35 mg) and **2f** (26 mg) for 4 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:49 to 3:97) to yield a white solid (32 mg, 0.063 mmol, 63%)

R_f = 0.46 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +227°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.05 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.53 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.46 – 7.32 (m, 3H), 7.22 – 7.14 (m, 2H), 7.17 – 7.10 (m, 1H), 6.88 – 6.80 (m, 1H), 6.28 – 6.13 (m, 2H), 5.63 (d, *J* = 1.0 Hz, 1H), 4.08 (s, 1H), 2.65 – 2.48 (m, *J* = 7.5 Hz, 2H), 1.17 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 157.8, 156.8, 153.4, 136.9, 134.7, 133.3, 131.6, 130.8, 130.3, 129.5, 129.2, 129.0, 128.8, 128.3, 126.4, 125.8, 121.8, 121.1, 118.0, 115.4, 111.6, 111.4, 109.9, 55.7, 20.1, 13.0. **MP** = 84 °C, **HRMS-ESI$^+$ (m/z)**: $[2M+Ag]^+$ calculated for $C_{56}H_{40}Br_2N_2O_8Ag^+$ 1137.0182, found 1137.0173.

HPLC analysis (Lux-Cellulose-2, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 290 nm) indicated **95% ee**, t_r**1**: 4.97 min, t_r**2**: 6.31 min

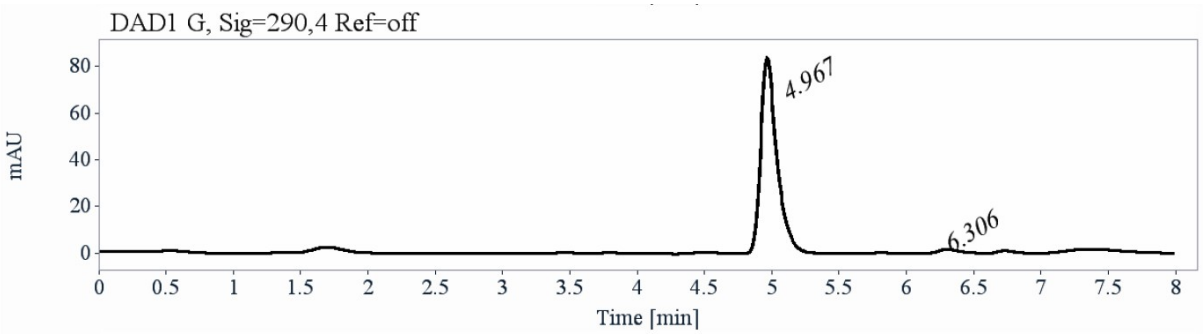
Chiral HPLC spectrum of *rac*-**4af**



Signal: DAD1 G, Sig=290,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.96	1301	50.01	0.68		
6.30	1301	49.99	1.14	1.66	5.55
Sum	2602	100.00			

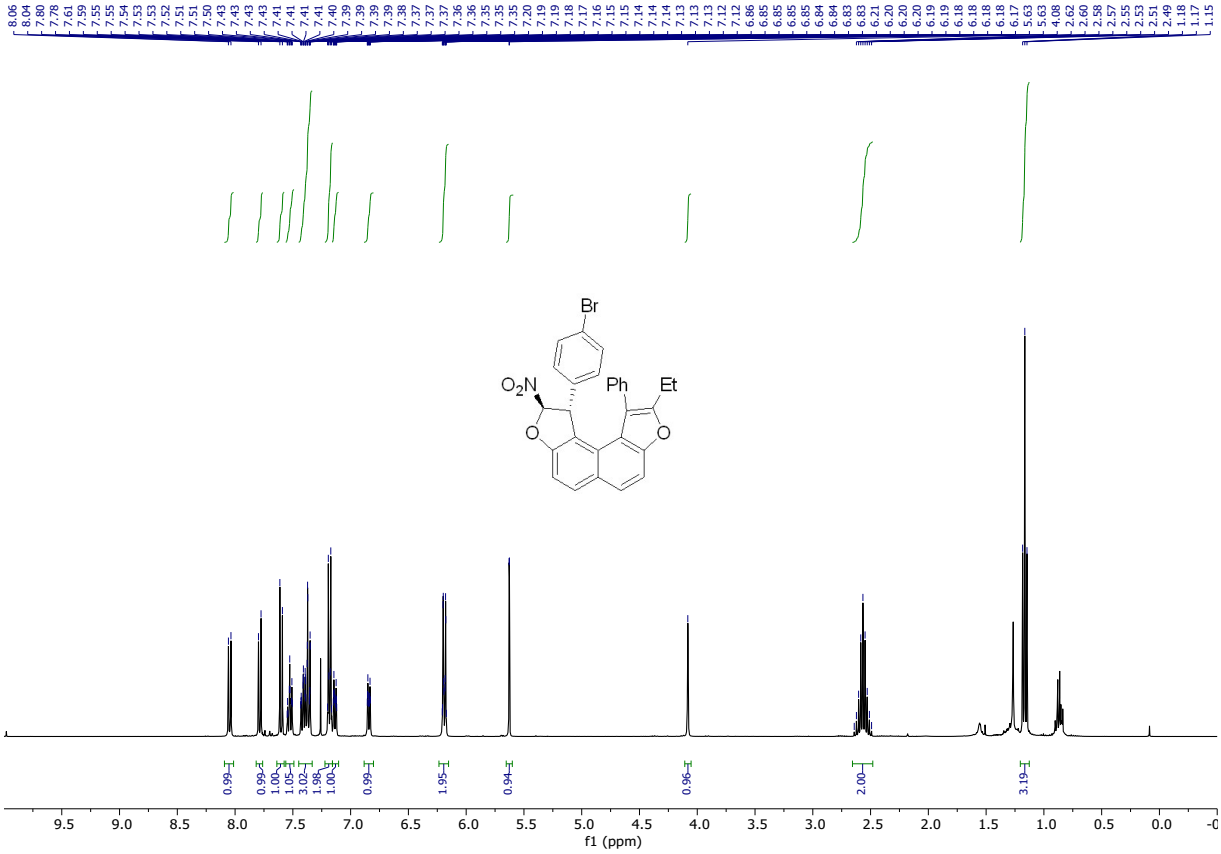
Chiral HPLC spectrum of **4af**



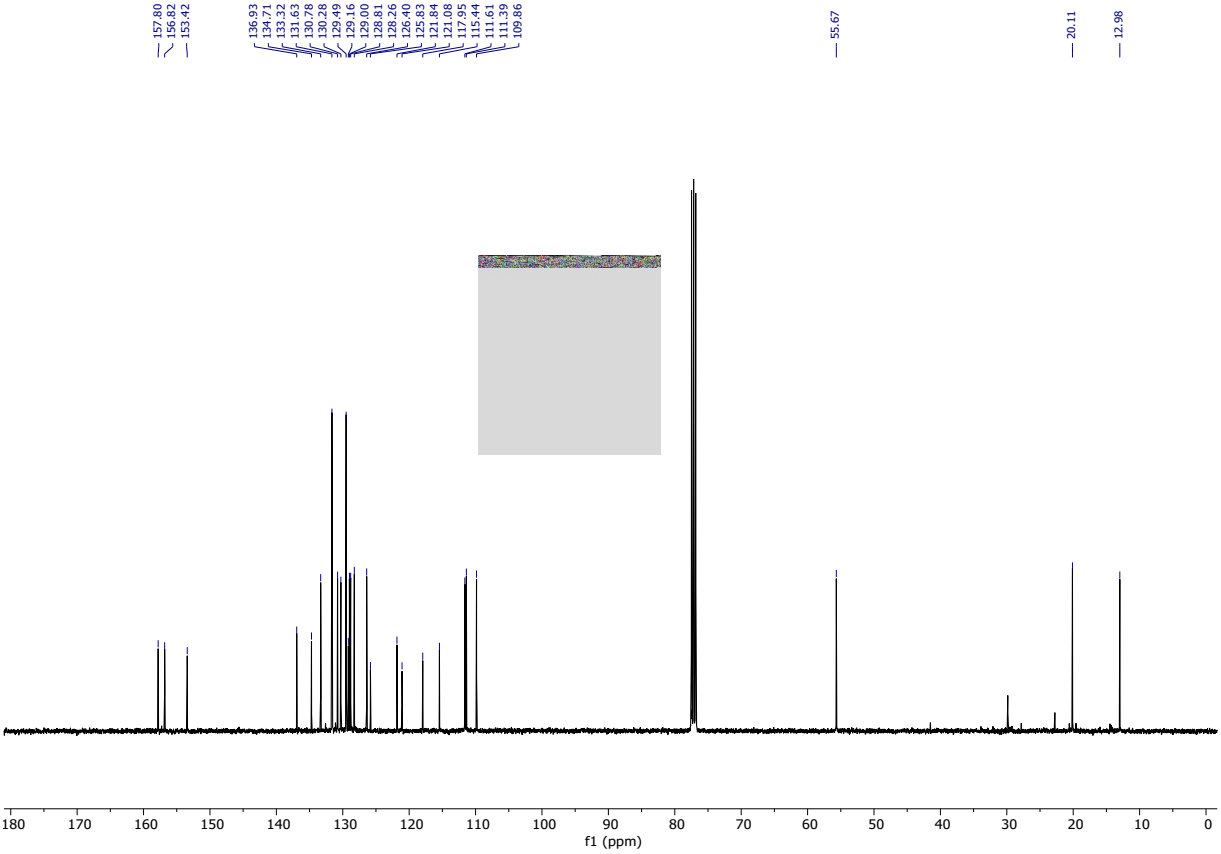
Signal: DAD1 G, Sig=290,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.97	701	97.45	0.68		
6.31	18	2.55	1.14	1.66	5.71
Sum	720	100.00			

^{1}H NMR spectrum of **4af** in $CDCl_3$

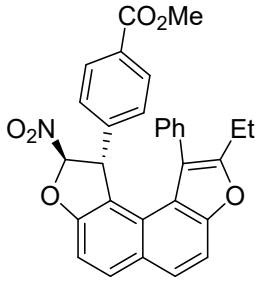


^{13}C NMR spectrum of **4af** in $CDCl_3$



methyl 4-((1R,2R)-9-ethyl-2-nitro-10-phenyl-1,2-dihydronaphtho[2,1-b:7,8-b']difuran-1-yl)benzoate

(4ag)



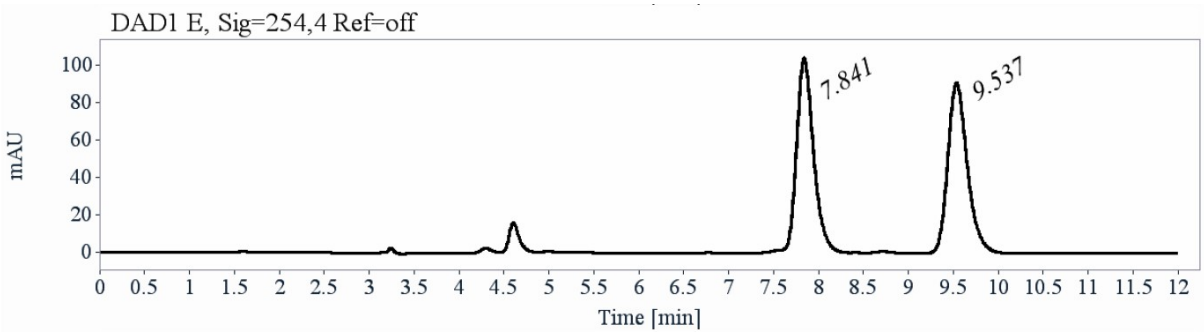
Molecular Weight: 493,5150

Prepared following general procedure using **3a** (35 mg) and **2g** (24 mg) for 5 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 5:95) to yield a white solid (49 mg, 0.10 mmol, 99%)

R_f = 0.30 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +216°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.06 (d, *J* = 8.7 Hz, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.53 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.42 (tdd, *J* = 7.6, 1.5, 0.6 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.16 – 7.12 (m, 1H), 6.77 – 6.72 (m, 1H), 6.44 – 6.40 (m, 2H), 5.68 (d, *J* = 1.1 Hz, 1H), 4.20 (s, 1H), 3.85 (s, 3H), 2.54 (ddt, *J* = 16.5, 15.0, 7.5 Hz, 2H), 1.15 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 166.7, 157.9, 156.8, 153.4, 143.0, 134.7, 133.4, 130.8, 130.3, 129.8, 129.7, 129.2, 129.1, 128.8, 128.3, 127.9, 126.4, 125.9, 121.1, 117.9, 115.3, 111.5, 111.4, 109.9, 56.1, 52.2, 20.1, 13.0. **MP** = 192 °C, **HRMS-ESI$^+$ (m/z)**: $[2M+Ag]^+$

calculated for $C_{60}H_{46}N_2O_{12}Ag^+$ 1095.2107, found 1095.2103. **HPLC analysis** (Lux-Cellulose-4, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **93% ee**, t_r**1**: 7.80 min, t_r**2**: 9.49 min

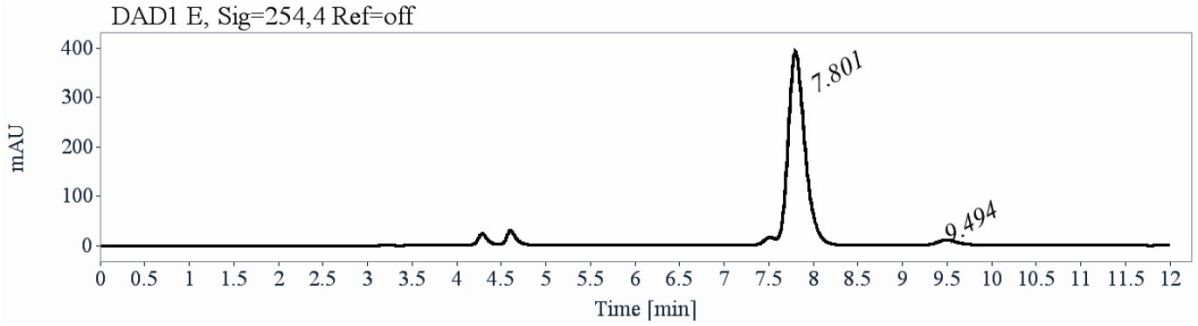
Chiral HPLC spectrum of *rac*-**4ag**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.84	1377	50.00	1.66		
9.54	1377	50.00	2.23	1.35	4.67
Sum	2754	100.00			

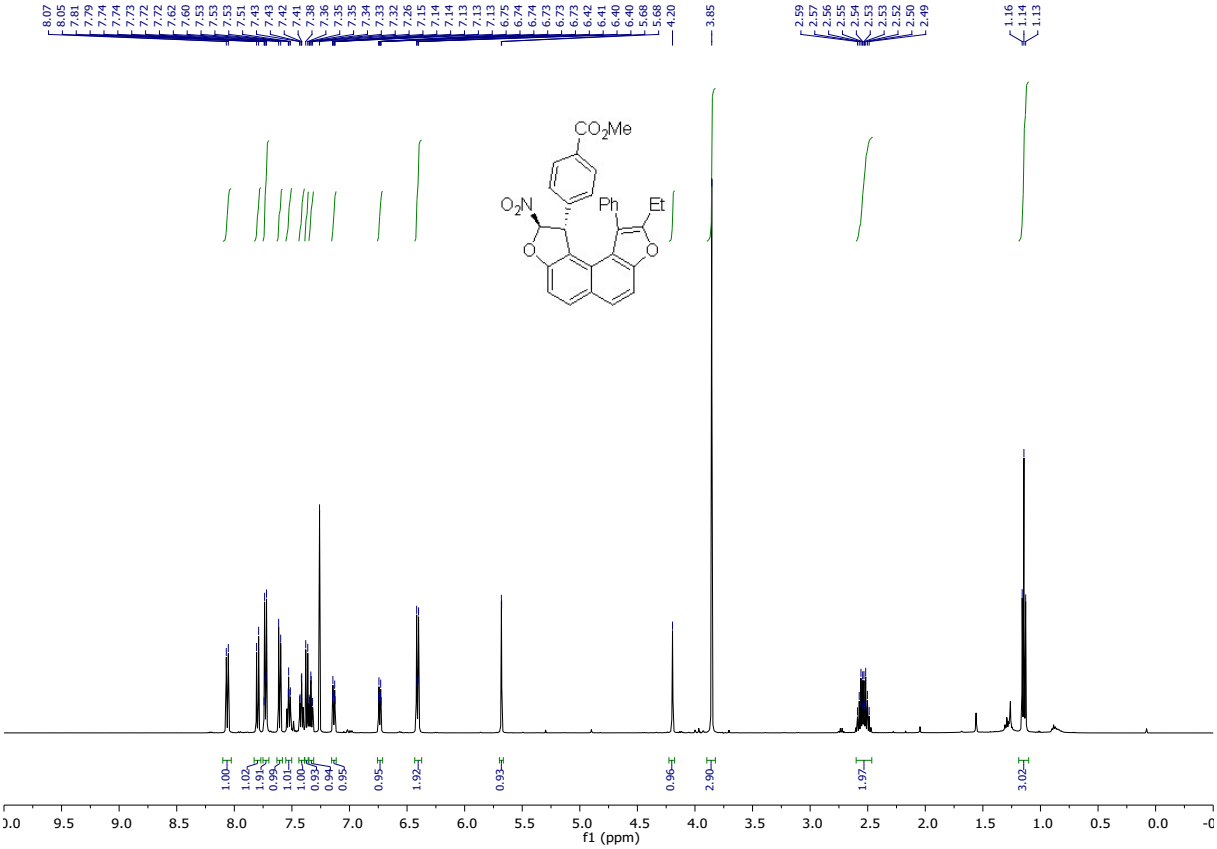
Chiral HPLC spectrum of **4ag**



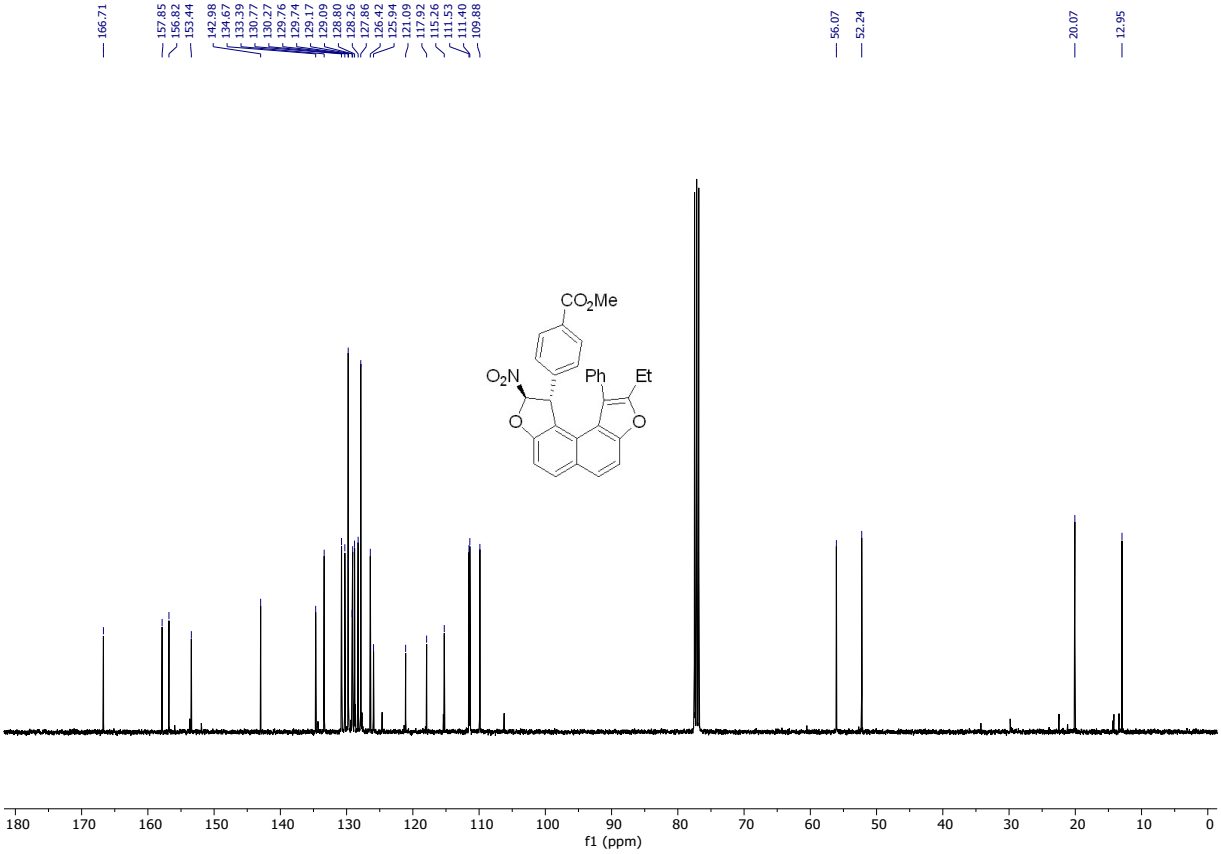
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.80	5092	96.50	1.64		
9.49	185	3.50	2.22	1.35	4.52
Sum	5277	100.00			

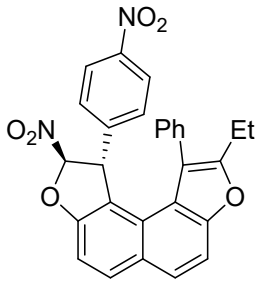
^{1}H NMR spectrum of **4ag** in $CDCl_3$



^{13}C NMR spectrum of **4ag** in $CDCl_3$



*(1R,2R)-9-ethyl-2-nitro-1-(4-nitrophenyl)-10-phenyl-1,2-dihydronaphtho[2,1-b:7,8-b']difuran (**4ah**)*



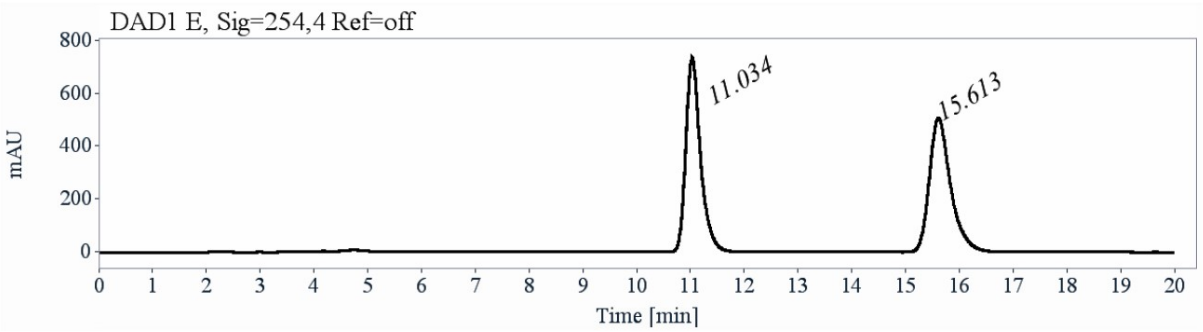
Molecular Weight: 480,4760

Prepared following general procedure using **3a** (35 mg) and **2h** (23 mg) for 4 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 3:47 to 2:23) to yield a brown solid (46 mg, 0.095 mmol, 95%)

R_f = 0.28 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +270°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.09 (d, *J* = 8.8 Hz, 1H), 7.97 – 7.88 (m, 2H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.63 (d, *J* = 8.9 Hz, 1H), 7.55 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.44 (tdd, *J* = 7.5, 1.5, 0.6 Hz, 1H), 7.42 – 7.31 (m, 2H), 7.19 – 7.11 (m, 1H), 6.80 – 6.72 (m, 1H), 6.56 – 6.47 (m, 2H), 5.66 (d, *J* = 1.1 Hz, 1H), 4.29 (s, 1H), 2.65 – 2.45 (m, 2H), 1.15 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 157.9, 157.1, 153.6, 147.6, 145.2, 134.7, 133.8, 130.9, 130.1, 129.3, 129.1, 129.0, 128.8, 128.5, 126.6, 125.7, 123.7, 120.9, 117.7, 114.6, 111.6, 111.0, 110.0, 55.9, 20.1, 13.0. **MP** = 144 °C, **HRMS-ESI$^-$ (m/z)**: $[M-H]^-$ calculated for $C_{28}H_{19}N_2O_6^-$ 479.1249, found

479.1250. **HPLC analysis** (Lux-Cellulose-2, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **93% ee**, t_r**1**: 11.04 min, t_r**2**: 15.61 min

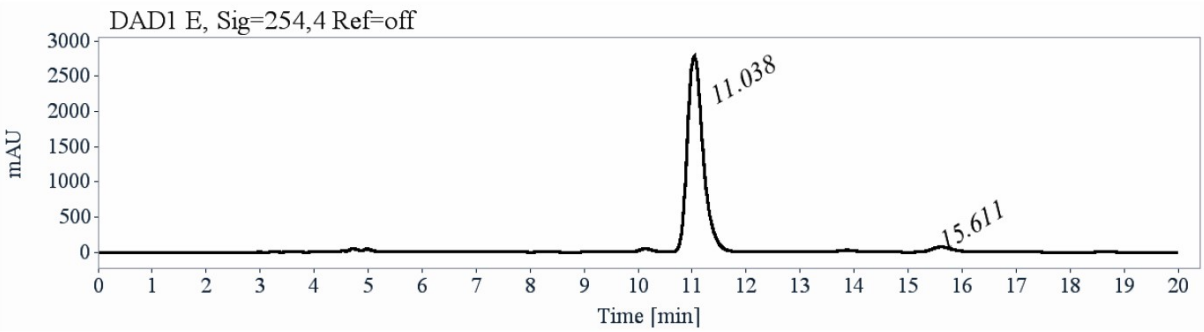
Chiral HPLC spectrum of *rac*-**4ah**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
11.03	13997	50.05	2.74		
15.61	13972	49.95	4.29	1.57	7.81
Sum	27969	100.00			

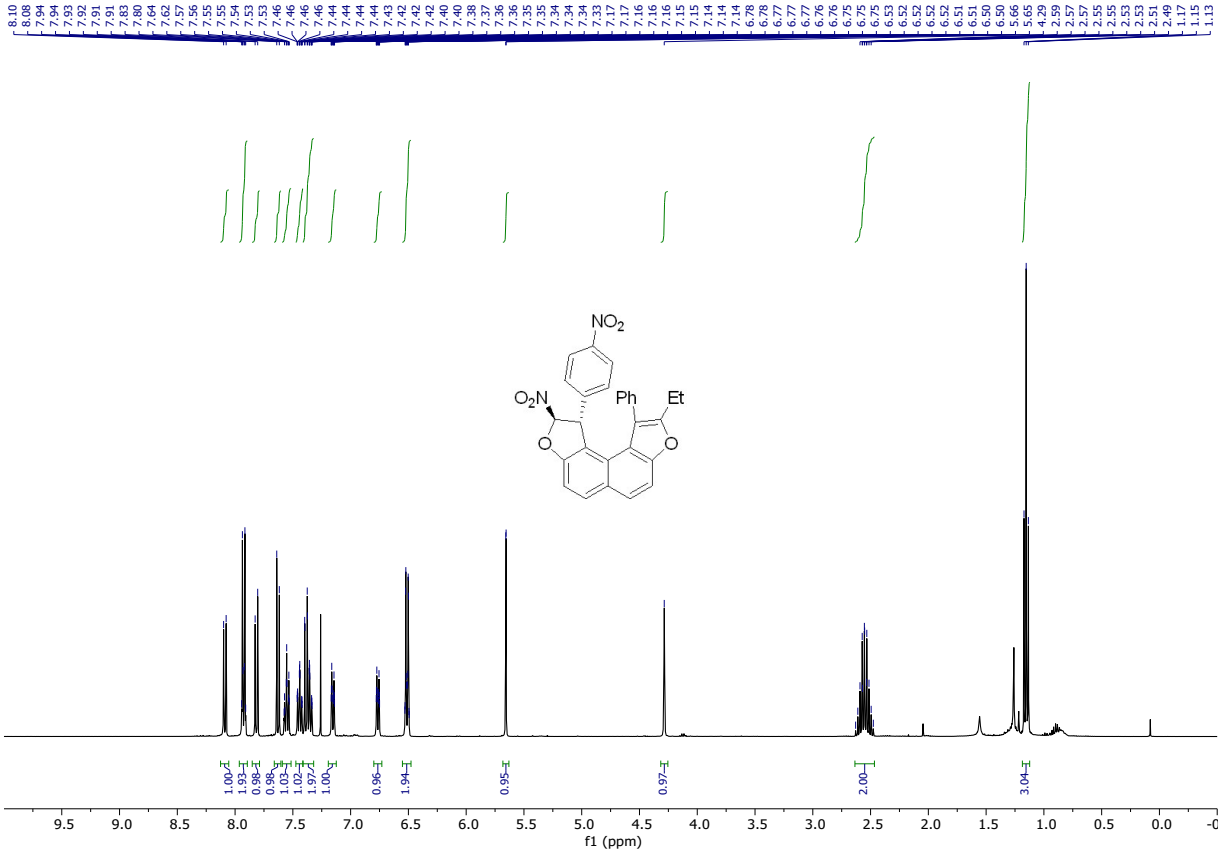
Chiral HPLC spectrum of **4ah**



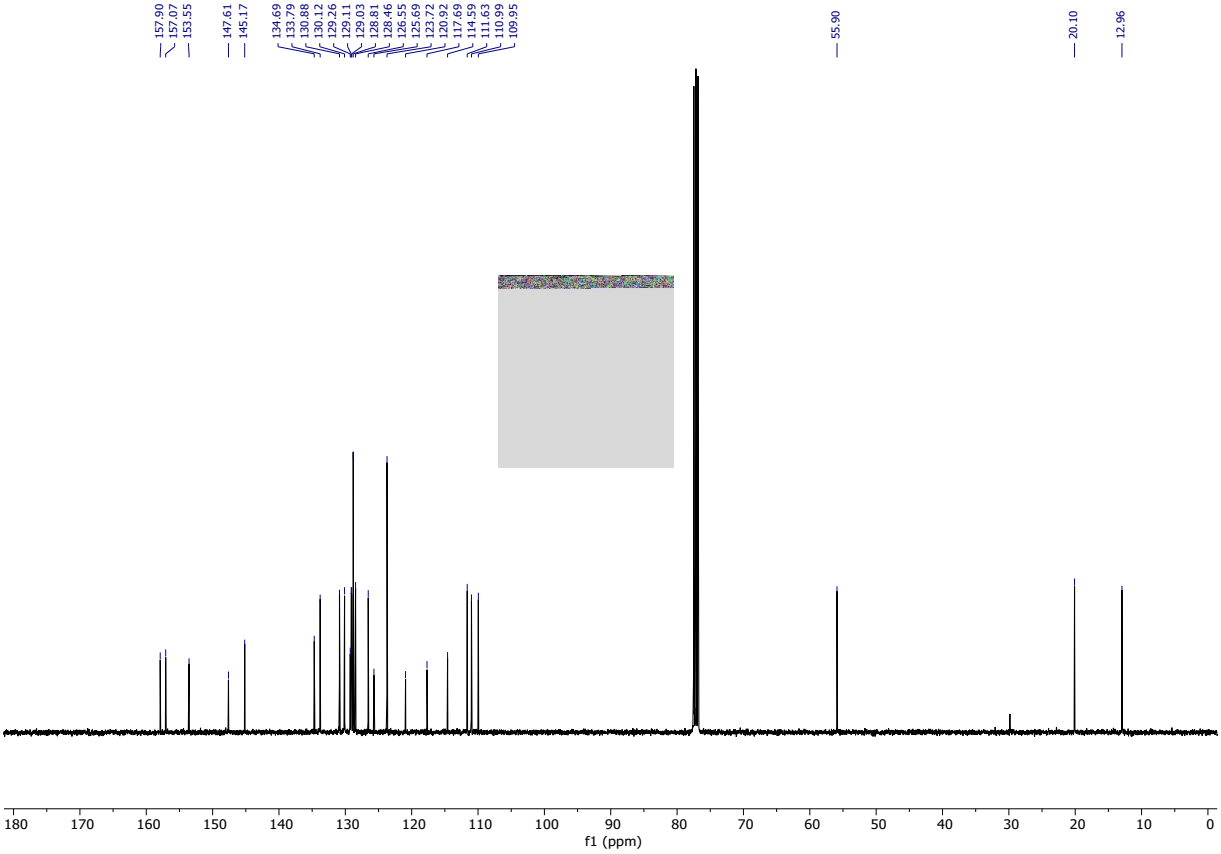
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
11.04	56528	96.58	2.74		
15.61	2002	3.42	4.29	1.57	7.70
Sum	58530	100.00			

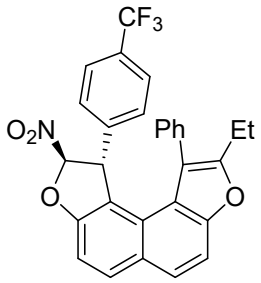
^{1}H NMR spectrum of **4ah** in $CDCl_3$



^{13}C NMR spectrum of **4ah** in $CDCl_3$



*(1R,2R)-9-ethyl-2-nitro-10-phenyl-1-(4-(trifluoromethyl)phenyl)-1,2-dihydronaphtho[2,1-b:7,8-b']difuran (**4ai**)*



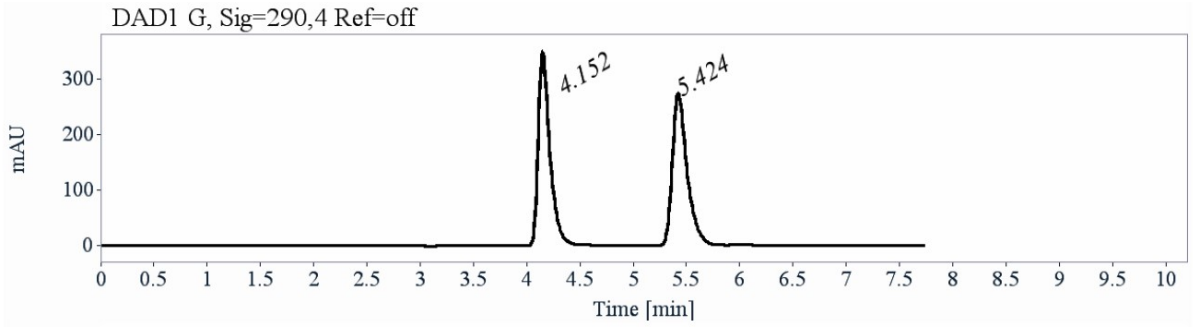
Molecular Weight: 503,4772

Prepared following general procedure using **3a** (35 mg) and **2i** (25 mg) for 4 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 3:97 to 1:24) to yield a white solid (50 mg, 0.098 mmol, 98%)

R_f = 0.49 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +213°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.07 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.54 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.43 (td, *J* = 7.6, 0.9 Hz, 1H), 7.40 – 7.31 (m, 4H), 7.15 (dt, *J* = 7.7, 1.2 Hz, 1H), 6.77 (dt, *J* = 7.5, 1.2 Hz, 1H), 6.46 (d, *J* = 8.1 Hz, 2H), 5.66 (d, *J* = 1.0 Hz, 1H), 4.23 (s, 1H), 2.65 – 2.48 (m, 2H), 1.16 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 157.9, 156.9, 153.5, 141.9, 134.7, 133.5, 130.8, 130.2, 130.2 (q, $^2J_{C\text{-}F}$ = 32.6 Hz), 129.2, 129.0, 128.9, 128.3, 128.2, 126.5, 125.9, 125.5 (q, $^4J_{C\text{-}F}$ = 3.8 Hz), 124.0 (q, $^1J_{C\text{-}F}$ = 272.2 Hz), 121.1, 117.9, 115.1, 111.5, 111.5, 109.9, 55.9, 20.1, 13.0. **^{19}F NMR (282 MHz, $CDCl_3$)**

δ (ppm) -62.67. **MP** = 185 °C, **HRMS-ESI$^+$ (m/z)**: [M-H]$^-$ calculated for $C_{29}H_{19}F_3NO_4^-$ 502.1272, found 502.1271. **HPLC analysis** (Lux-Cellulose-2, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 290 nm) indicated **95% ee**, **t_r1**: 4.15 min, **t_r2**: 5.42 min

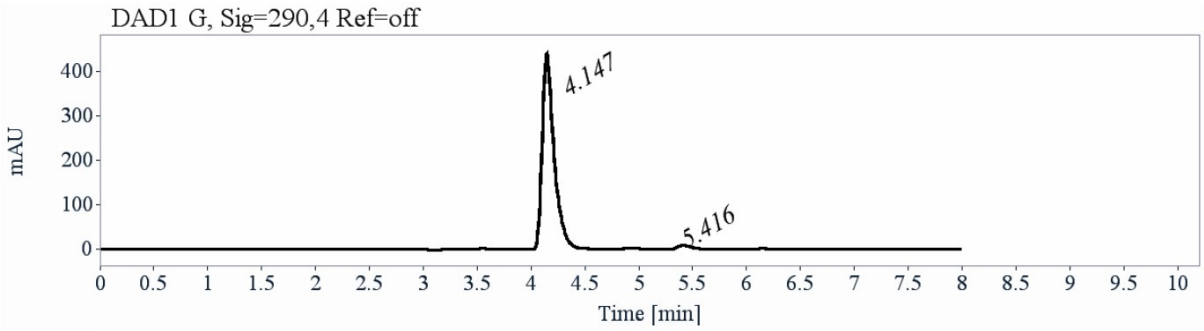
Chiral HPLC spectrum of *rac*-**4ai**



Signal: DAD1 G, Sig=290,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.15	2620	49.99	0.41		
5.42	2621	50.01	0.84	2.06	5.89
Sum	5241	100.00			

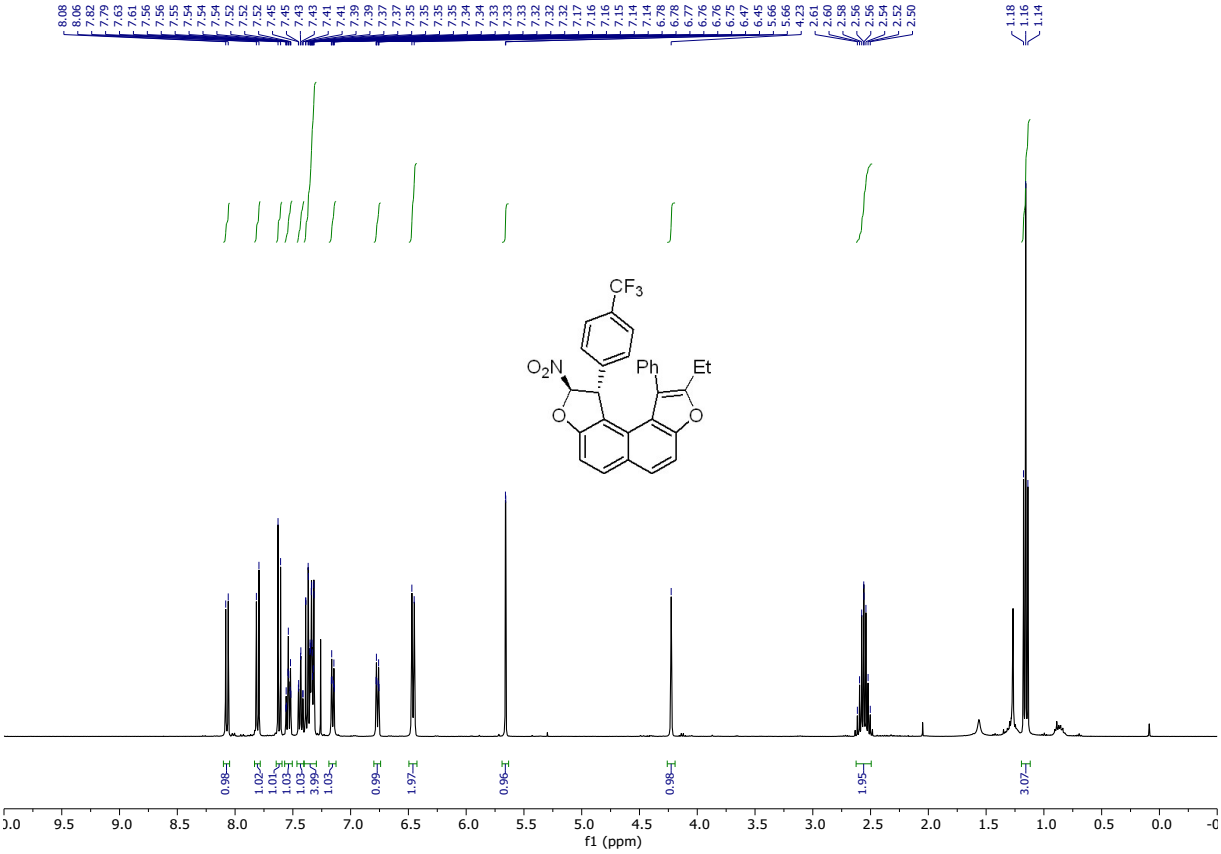
Chiral HPLC spectrum of **4ai**



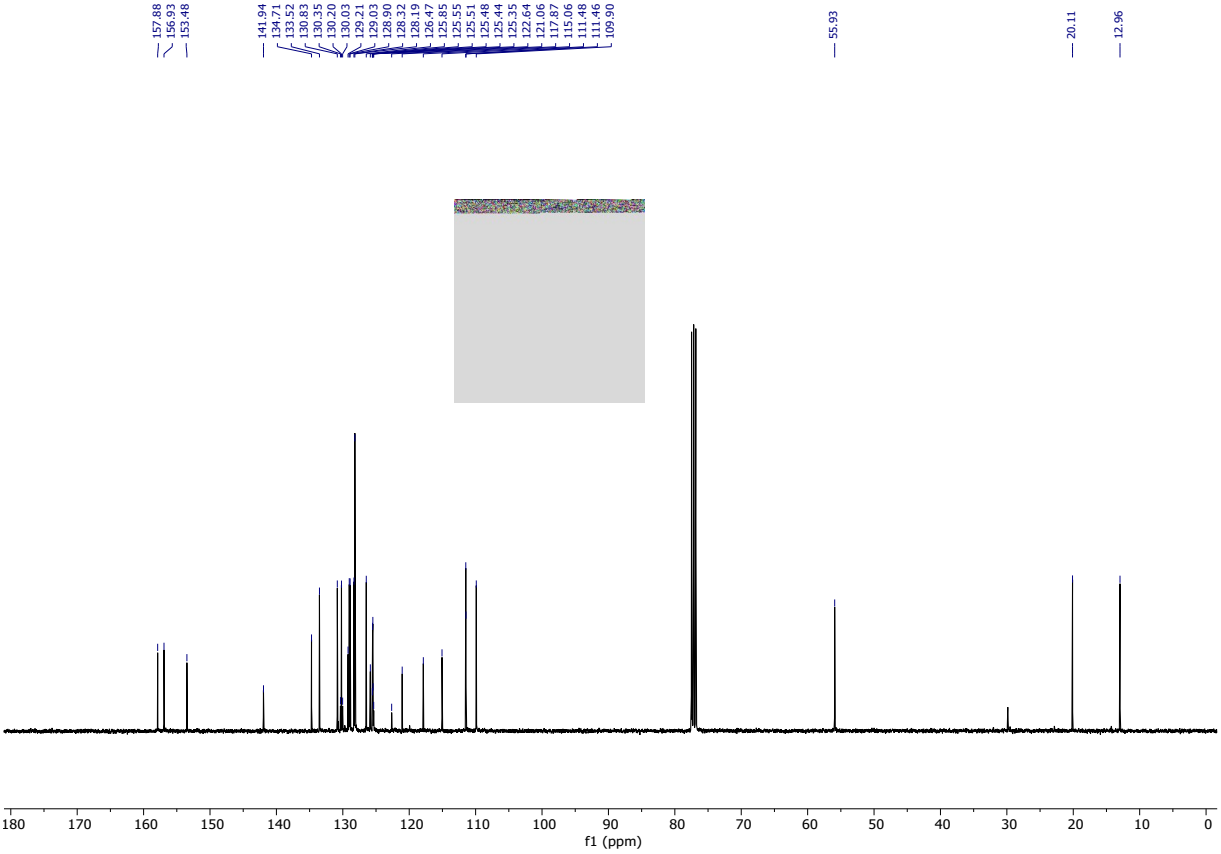
Signal: DAD1 G, Sig=290,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.15	3352	97.37	0.41		
5.42	91	2.63	0.84	2.06	5.77
Sum	3443	100.00			

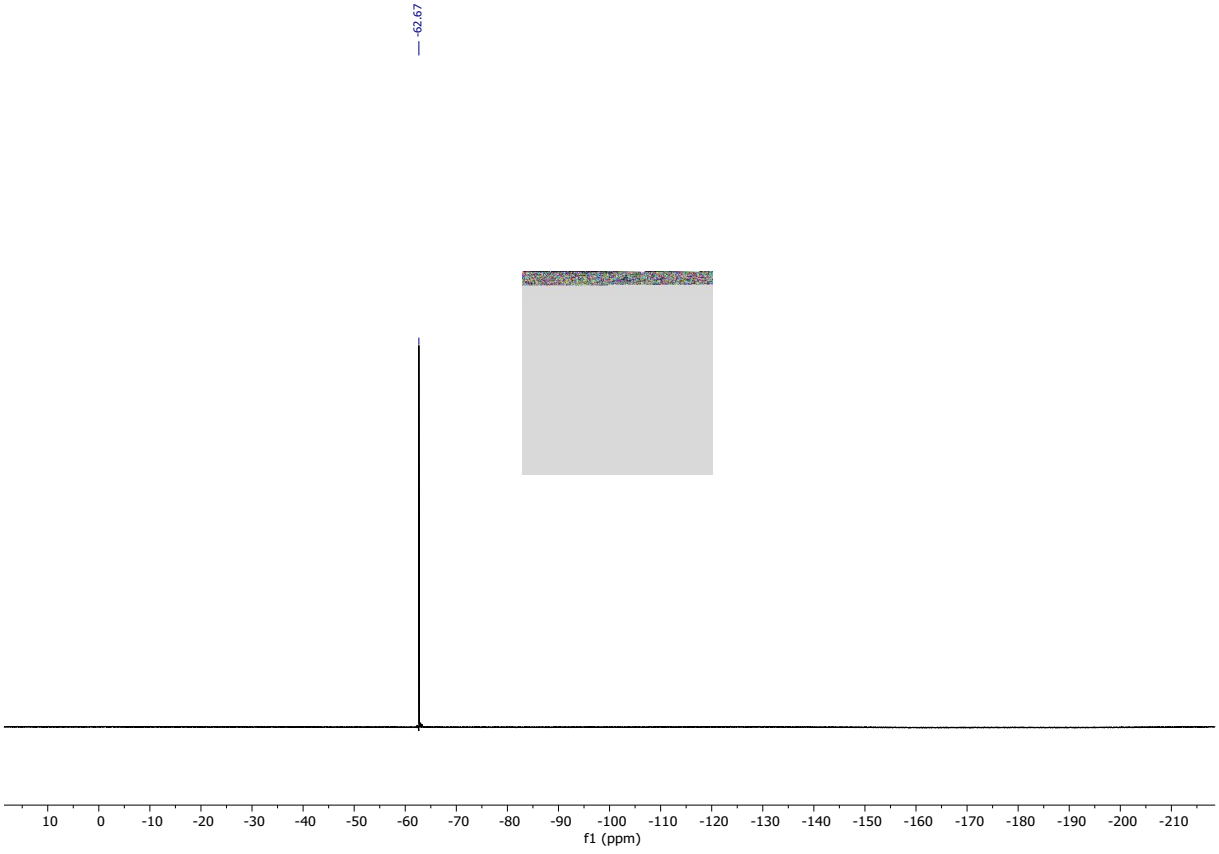
^{1}H NMR spectrum of **4ai** in $CDCl_3$



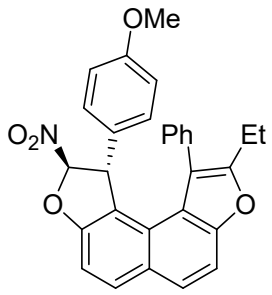
^{13}C NMR spectrum of **4ai** in $CDCl_3$



^{19}F NMR spectrum of **4ai** in $CDCl_3$



*(1R,2R)-9-ethyl-1-(4-methoxyphenyl)-2-nitro-10-phenyl-1,2-dihydronaphtho[2,1-b:7,8-b']difuran (**4aj**)*



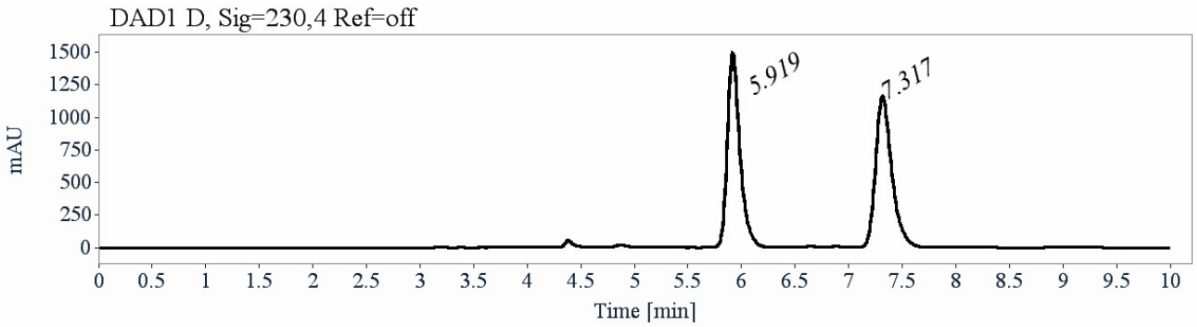
Molecular Weight: 465,5050

Prepared following general procedure using **3a** (35 mg) and **2j** (21 mg) for 7 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:24) to yield an orange solid (19 mg, 0.041 mmol, 41%)

R_f = 0.41 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +153°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.03 (d, *J* = 8.7 Hz, 1H), 7.78 (d, *J* = 8.9 Hz, 1H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.52 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.45 – 7.33 (m, 3H), 7.13 (dq, *J* = 7.7, 1.3, 0.8 Hz, 1H), 6.92 – 6.80 (m, 1H), 6.64 – 6.54 (m, 2H), 6.27 – 6.16 (m, 2H), 5.64 (d, *J* = 1.0 Hz, 1H), 4.03 (s, 1H), 3.69 (s, 3H), 2.56 (qd, *J* = 7.5, 5.8 Hz, 2H), 1.16 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 159.1, 157.7, 156.6, 153.3, 134.8, 133.0, 130.7, 130.4, 129.8, 129.1, 128.9, 128.7, 128.1, 126.3, 126.0, 121.2, 118.2, 116.4, 113.8, 112.2, 111.2, 109.8, 55.6, 55.3, 20.1, 13.0. **MP** = 69 °C, **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{29}H_{23}NO_5Ag^+$ 572.0622, found

572.0619. **HPLC analysis** (Lux-Cellulose-4, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 230 nm) indicated **95% ee**, t_r**1**: 5.91 min, t_r**2**: 7.31 min

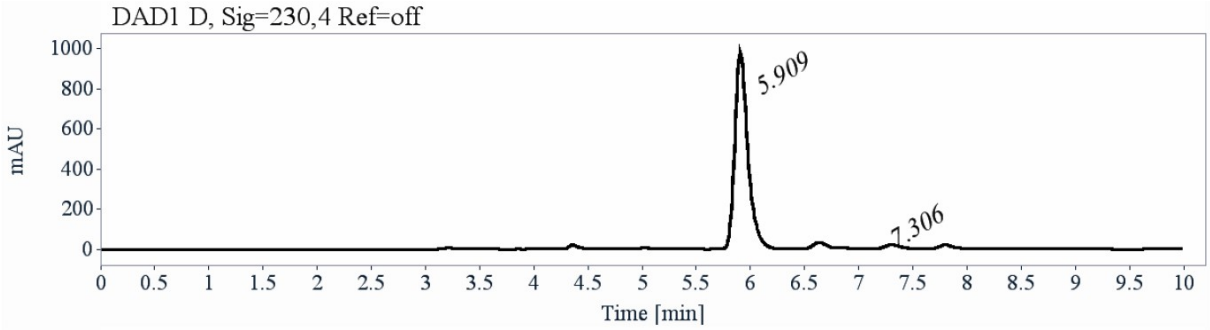
Chiral HPLC spectrum of *rac*-**4aj**



Signal: DAD1 D, Sig=230,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.92	12279	50.11	1.01		
7.32	12223	49.89	1.48	1.47	5.86
Sum	24502	100.00			

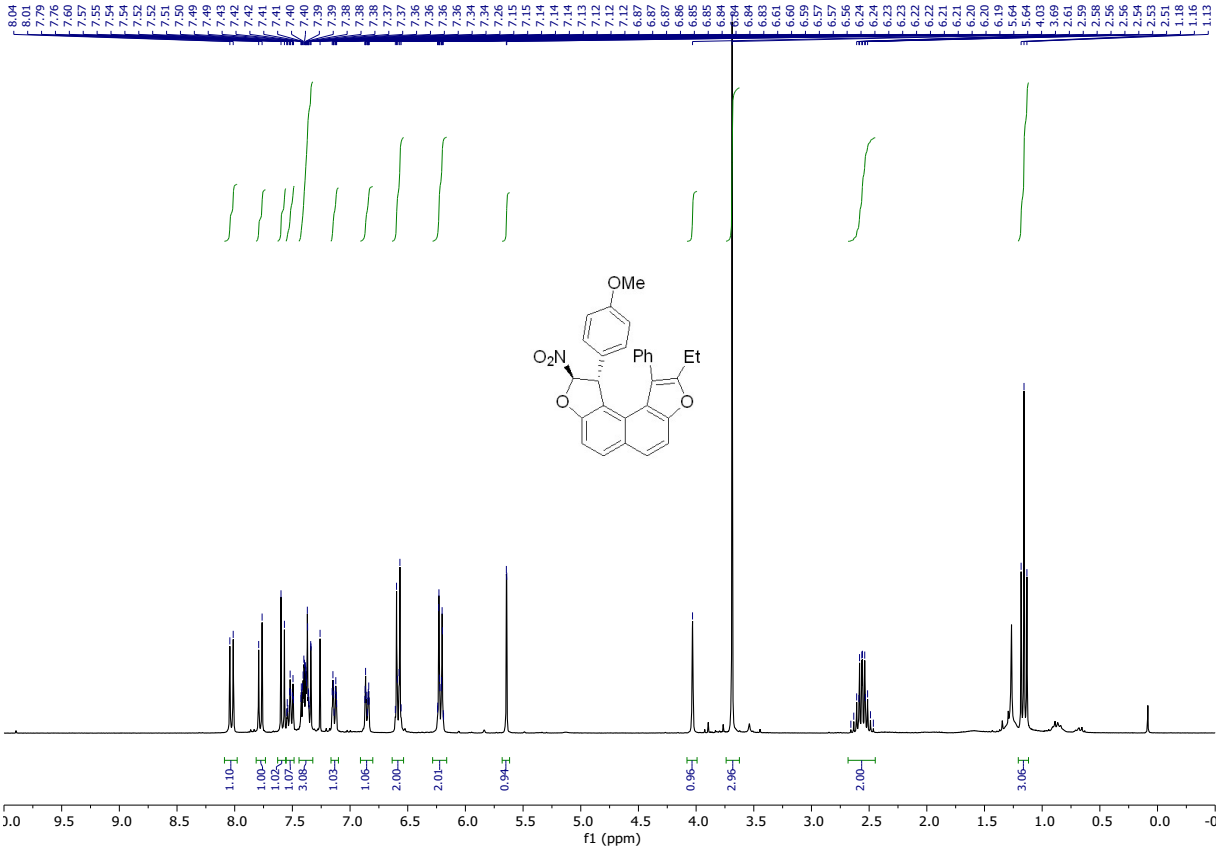
Chiral HPLC spectrum of **4aj**



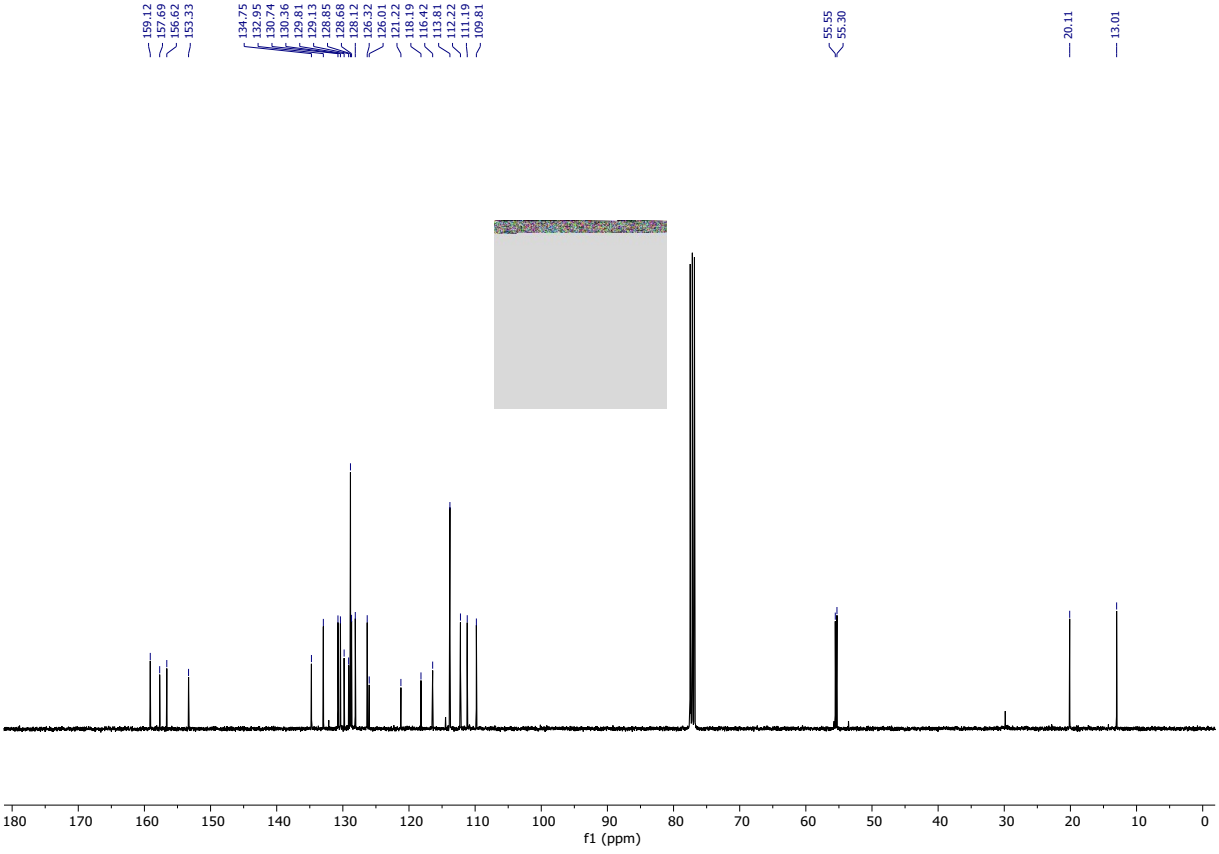
Signal: DAD1 D, Sig=230,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.91	8227	97.54	1.00		
7.31	208	2.46	1.48	1.47	5.89
Sum	8435	100.00			

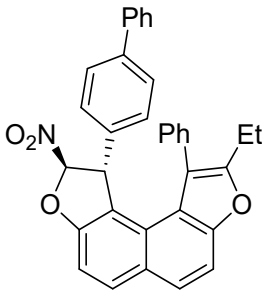
^{1}H NMR spectrum of **4aj** in $CDCl_3$



^{13}C NMR spectrum of **4aj** in $CDCl_3$



(1R,2R)-1-([1,1'-biphenyl]-4-yl)-9-ethyl-2-nitro-10-phenyl-1,2-dihydronaphtho[2,1-b:7,8-b']difuran ***(4ak)***



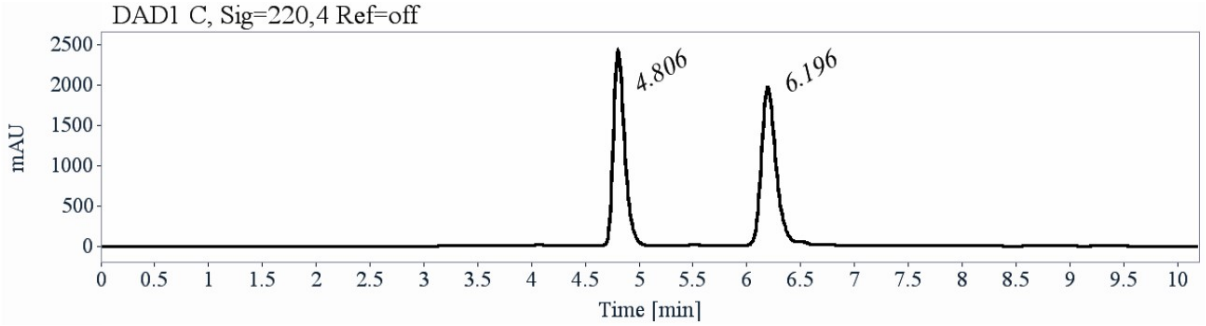
Molecular Weight: 511,5770

Prepared following general procedure using **3a** (35 mg) and **2k** (26 mg) for 8 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 3:97 to 1:24) to yield a white solid (35 mg, 0.068 mmol, 68%)

R_f = 0.40 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +263°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.06 (d, *J* = 8.7 Hz, 1H), 7.81 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.55 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.53 – 7.34 (m, 7H), 7.36 – 7.26 (m, 3H), 7.17 (dt, *J* = 7.6, 1.7 Hz, 1H), 6.86 (dt, *J* = 7.6, 1.6 Hz, 1H), 6.45 – 6.35 (m, 2H), 5.74 (d, *J* = 1.0 Hz, 1H), 4.17 (s, 1H), 2.57 (ddt, *J* = 16.5, 15.0, 7.5 Hz, 2H), 1.16 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 157.81, 156.70, 153.37, 140.59, 140.42, 136.88, 134.75, 133.11, 130.76, 130.40, 129.15, 128.99, 128.90, 128.73, 128.17, 127.56, 127.11, 127.02,

126.37, 126.07, 121.25, 118.15, 115.99, 112.03, 111.27, 109.87, 55.92, 20.11, 13.00. **MP** = 144 °C, **HRMS-ESI$^+$ (m/z)**: [2M+Ag]$^+$ calculated for $C_{68}H_{50}N_2O_8Ag^+$ 1131.2626, found 1131.2608. **HPLC analysis** (Lux-Cellulose-4, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 220 nm) indicated **95% ee**, **t_r1**: 4.81 min, **t_r2**: 6.20 min

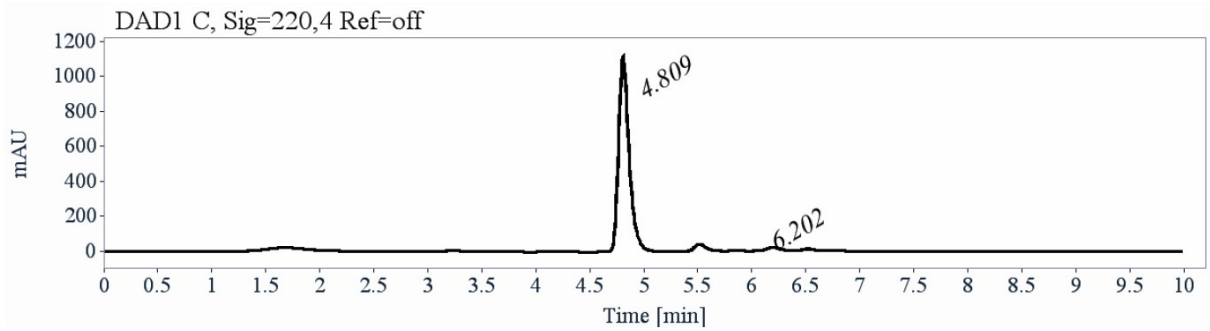
Chiral HPLC spectrum of *rac*-**4ak**



Signal: DAD1 C, Sig=220,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.81	17806	49.16	0.63		
6.20	18412	50.84	1.10	1.75	6.59
Sum	36218	100.00			

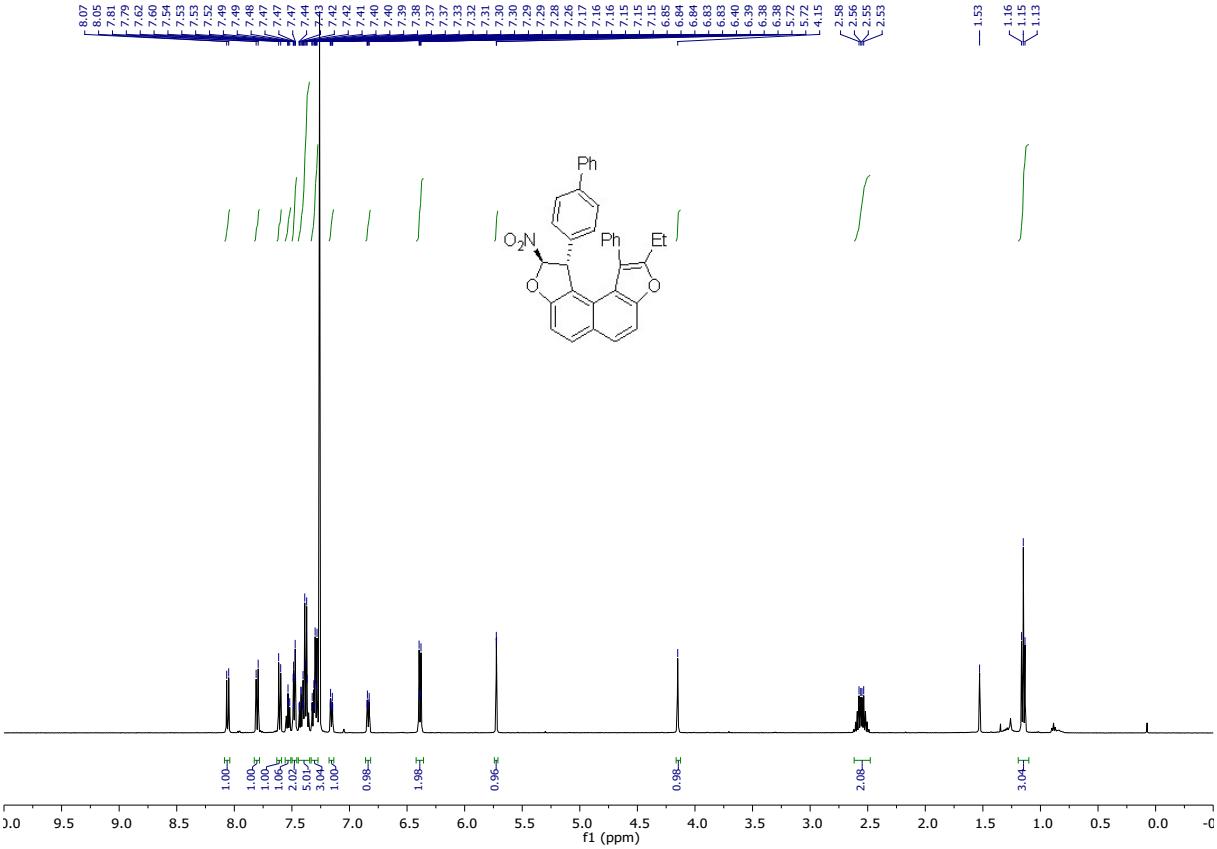
Chiral HPLC spectrum of *rac*-**4ak**



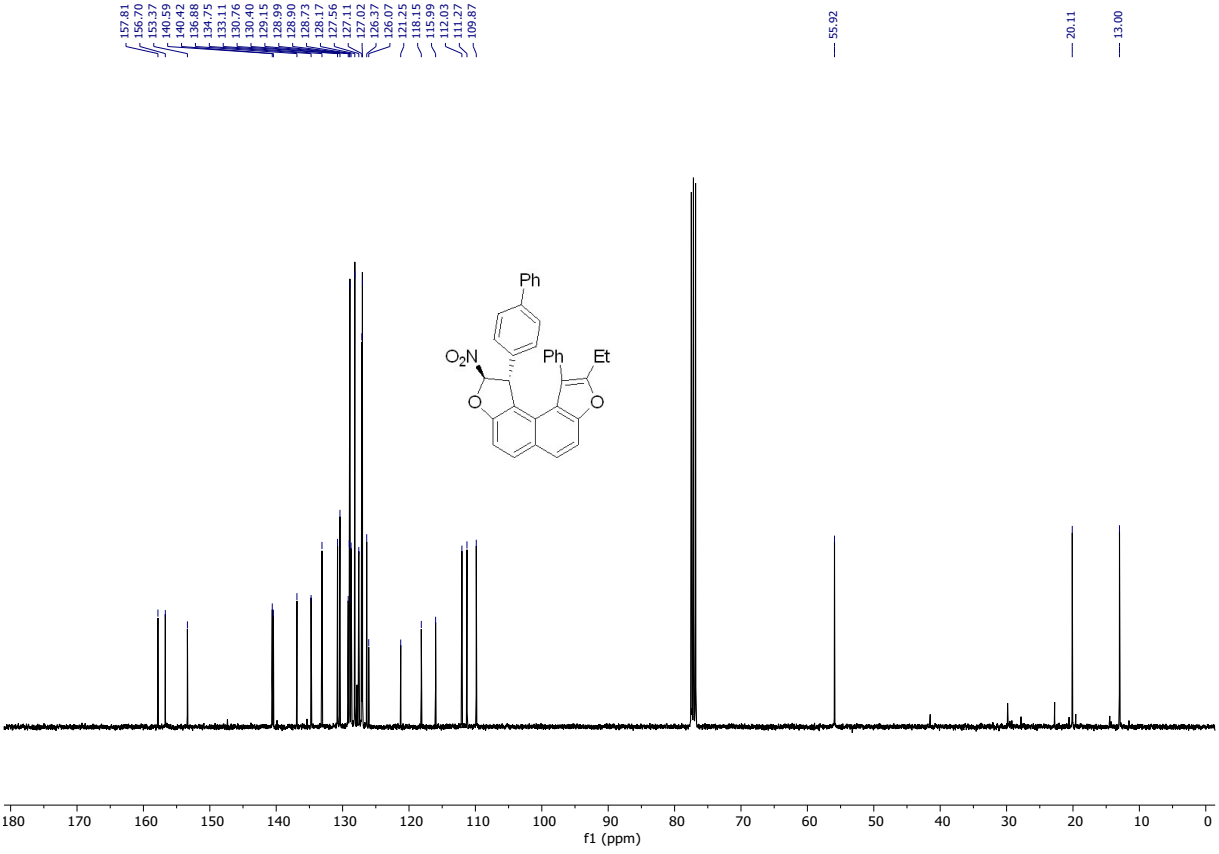
Signal: DAD1 C, Sig=220,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.81	7631	97.74	0.63		
6.20	176	2.26	1.10	1.75	6.96
Sum	7808	100.00			

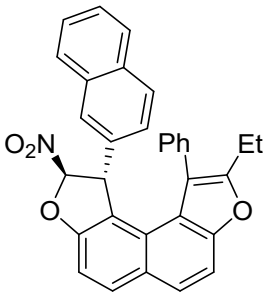
^{13}H NMR spectrum of **4ak** in $CDCl_3$



^{13}C NMR spectrum of **4ak** in $CDCl_3$



*(1R,2R)-9-ethyl-1-(naphthalen-2-yl)-2-nitro-10-phenyl-1,2-dihydronaphtho[2,1-b:7,8-b']difuran (**4al**)*



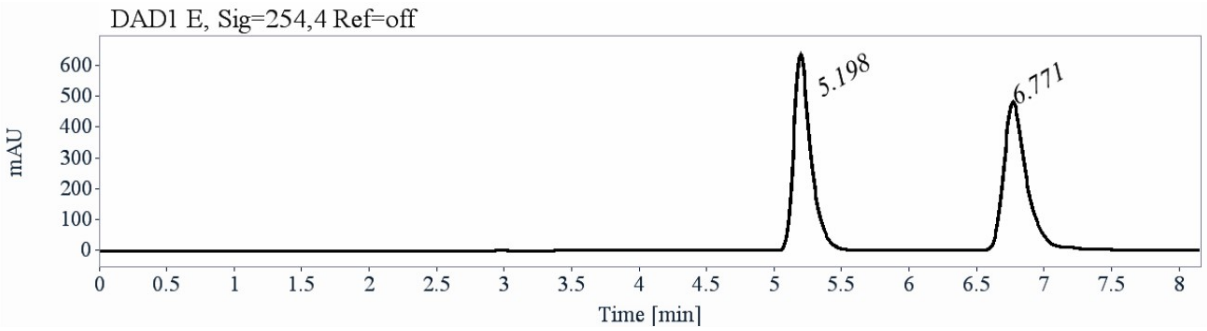
Molecular Weight: 485,5390

Prepared following general procedure using **3a** (35 mg) and **2l** (23 mg) for 8 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:49 to 3:97) to yield a white solid (32 mg, 0.066 mmol, 66%)

R_f = 0.44 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +284°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.09 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.64 – 7.51 (m, 3H), 7.48 – 7.32 (m, 6H), 7.20 – 7.16 (m, 1H), 6.72 – 6.68 (m, 1H), 6.61 – 6.55 (m, 2H), 5.74 (d, *J* = 1.0 Hz, 1H), 4.28 (s, 1H), 2.50 (ddt, *J* = 19.8, 15.1, 7.5 Hz, 2H), 1.10 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 157.9, 156.7, 153.4, 135.3, 134.8, 133.2, 133.0, 132.9, 130.8, 130.5, 129.2, 128.9, 128.8, 128.3, 128.2, 128.1, 127.6, 126.6, 126.4, 126.3, 126.3, 126.1, 126.0, 121.2, 118.1, 116.0, 111.9, 111.3, 109.9, 56.4, 20.1, 12.9. **MP** = 160 °C, **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{32}H_{23}NO_4Ag^+$ 592.0673, found

592.0670. **HPLC analysis** (Lux-Cellulose-2, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **95% ee**, t_r**1**: 5.20 min, t_r**2**: 6.77 min

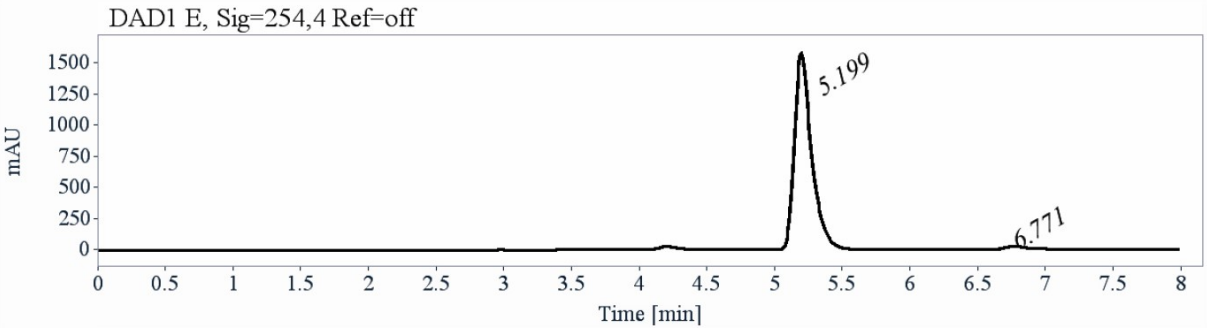
Chiral HPLC spectrum of *rac*-**4al**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.20	5590	49.81	0.76		
6.77	5633	50.19	1.30	1.70	6.11
Sum	11223	100.00			

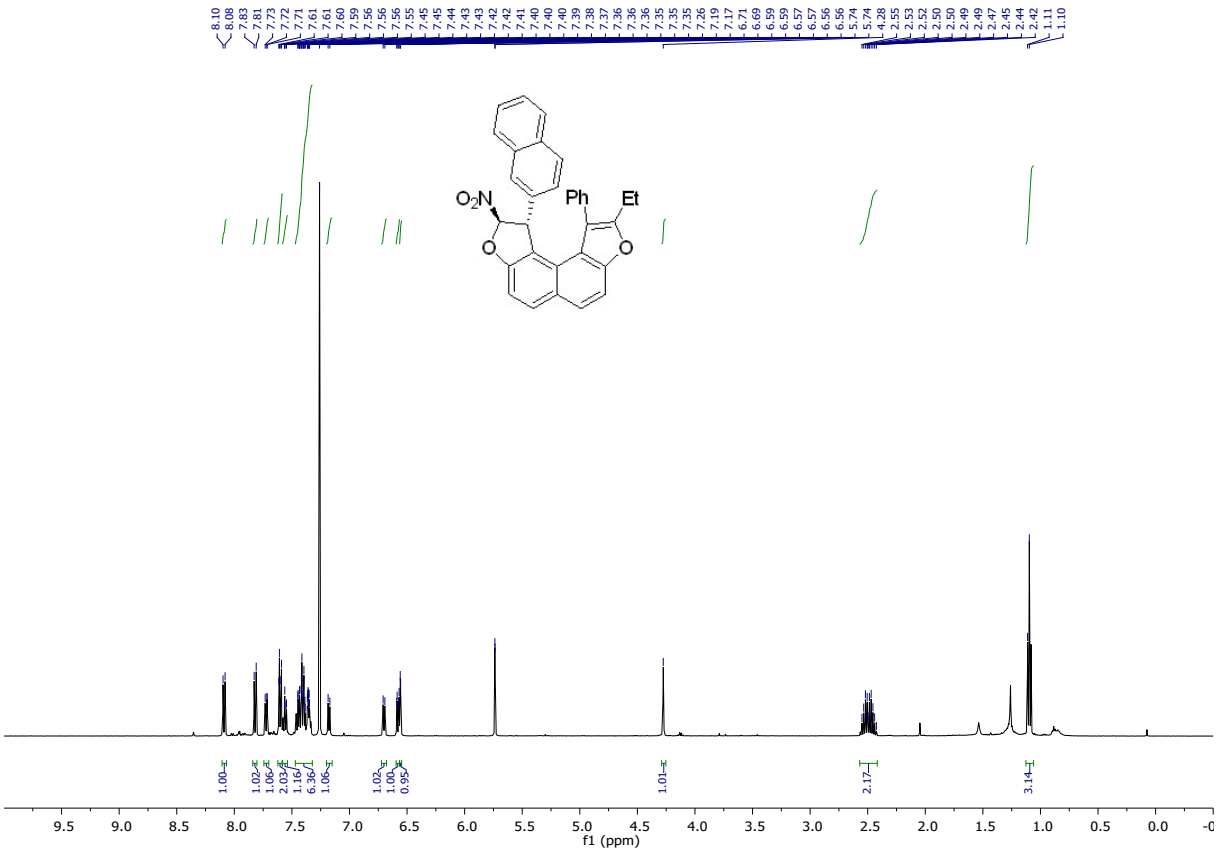
Chiral HPLC spectrum of **4al**



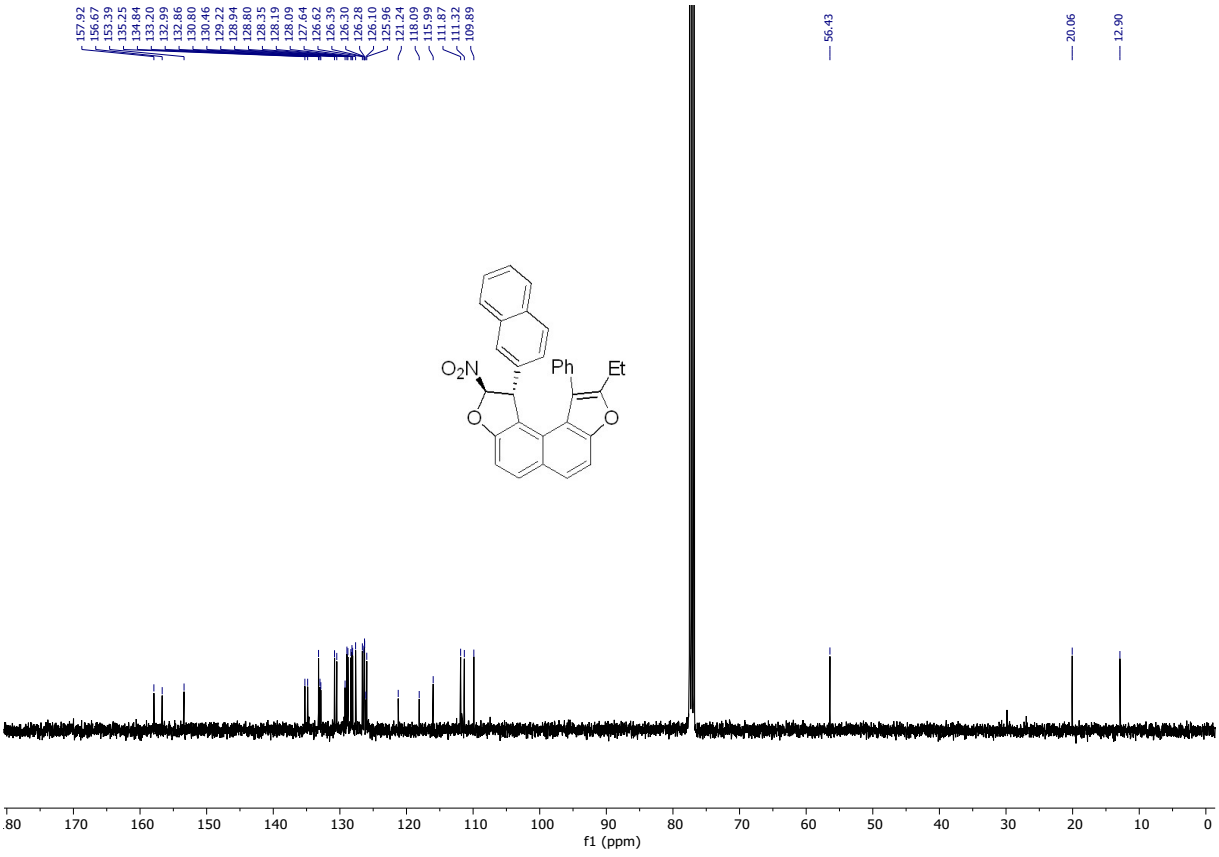
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.20	13920	97.57	0.76		
6.77	346	2.43	1.30	1.70	6.14
Sum	14266	100.00			

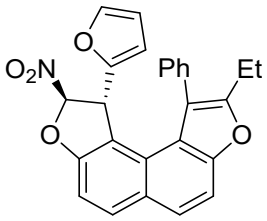
^{1}H NMR spectrum of **4al** in $CDCl_3$



^{13}C NMR spectrum of **4al** in $CDCl_3$



*(1S,2R)-9-ethyl-1-(furan-2-yl)-2-nitro-10-phenyl-1,2-dihydronaphtho[2,1-b:7,8-b']difuran (**4am**)*

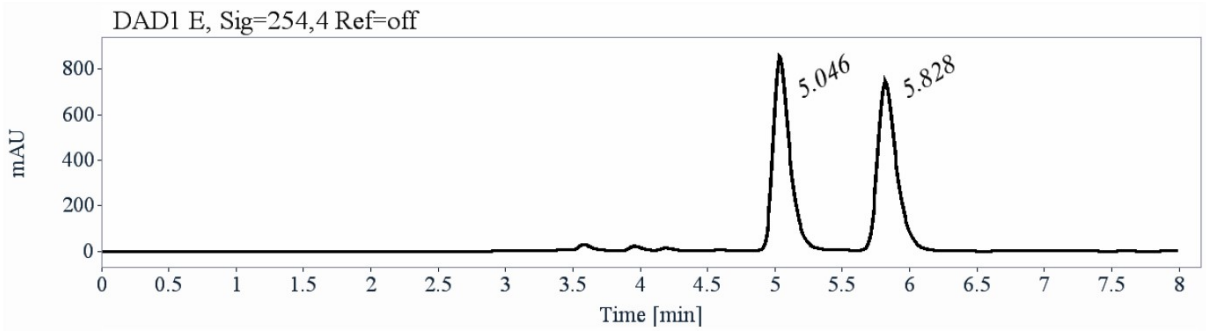


Molecular Weight: 425,4400

Prepared following general procedure using **3a** (35 mg) and **2m** (17 mg) for 10 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:49 to 1:24) to yield a yellow solid (11 mg, 0.027 mmol, 27%)

R_f = 0.30 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +233°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.00 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.49 (tt, *J* = 7.5, 1.4 Hz, 1H), 7.40 (dtd, *J* = 15.0, 7.5, 1.6 Hz, 2H), 7.33 – 7.30 (m, 2H), 7.18 (dt, *J* = 7.4, 1.7 Hz, 1H), 6.67 (dt, *J* = 7.5, 1.6 Hz, 1H), 6.05 (dd, *J* = 3.3, 1.8 Hz, 1H), 5.91 (d, *J* = 1.0 Hz, 1H), 5.14 (dt, *J* = 3.3, 1.1 Hz, 1H), 3.88 (s, 1H), 2.55 (qd, *J* = 7.5, 5.3 Hz, 2H), 1.18 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 157.5, 156.7, 153.2, 149.5, 142.3, 134.6, 133.3, 130.8, 130.1, 129.1, 128.7, 128.2, 128.1, 126.3, 125.8, 121.4, 118.2, 114.2, 111.3, 110.6, 109.9, 109.1, 108.6, 50.4, 20.2, 13.1. **MP** = 110 °C, **HRMS-ESI$^+$ (m/z)**: $[2M+Ag]^+$ calculated for $C_{52}H_{38}N_2O_{10}Ag^+$ 959.1580, found 959.1568. **HPLC analysis** (Lux-Cellulose-2, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **97% ee**, **t_r1**: 5.04 min, **t_r2**: 5.82 min

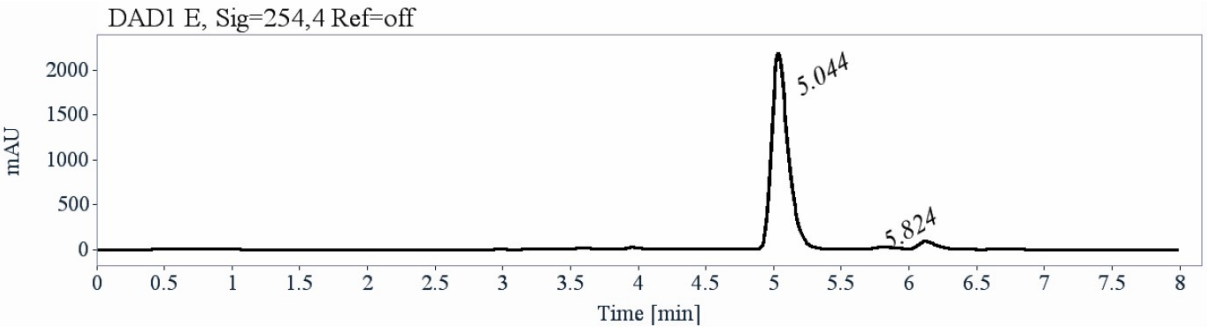
Chiral HPLC spectrum of *rac*-**4am**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.05	7407	50.18	0.71		
5.83	7354	49.82	0.98	1.37	3.33
Sum	14761	100.00			

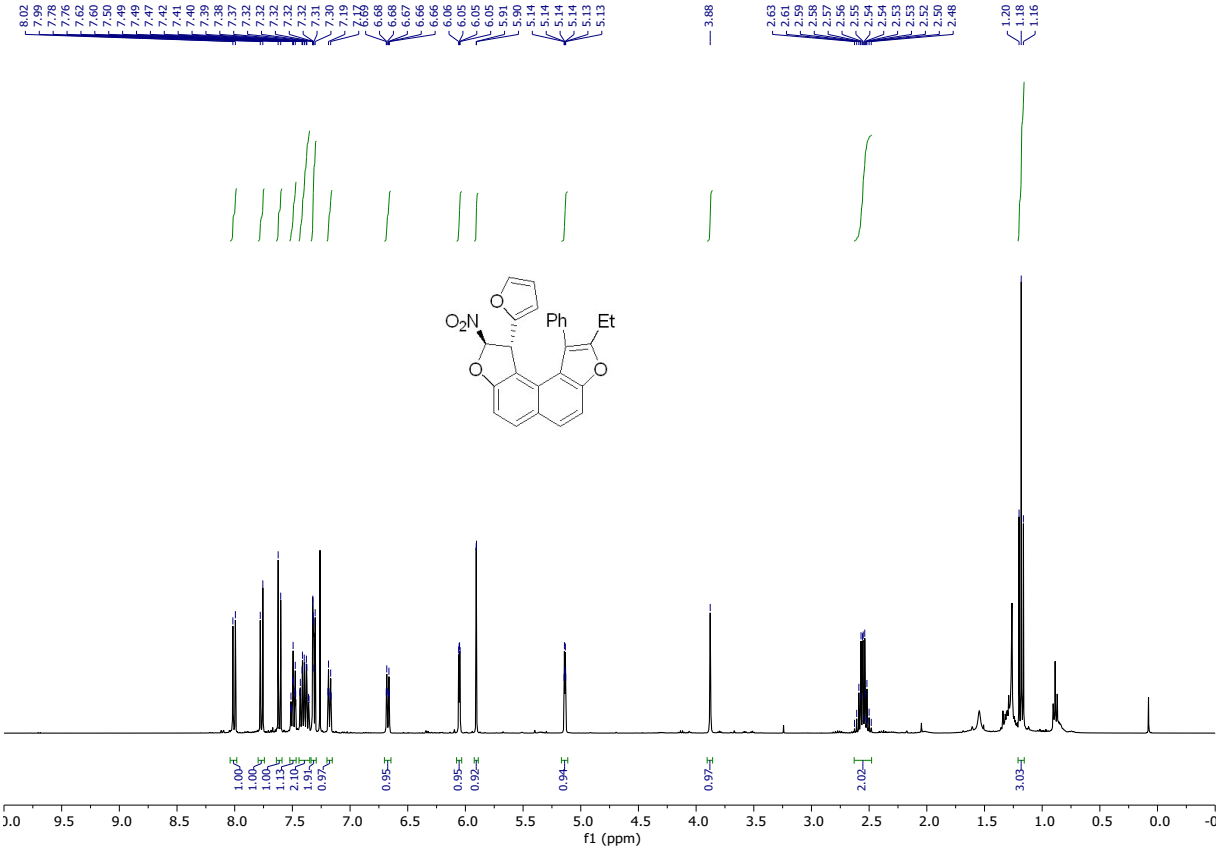
Chiral HPLC spectrum of *rac*-**4am**



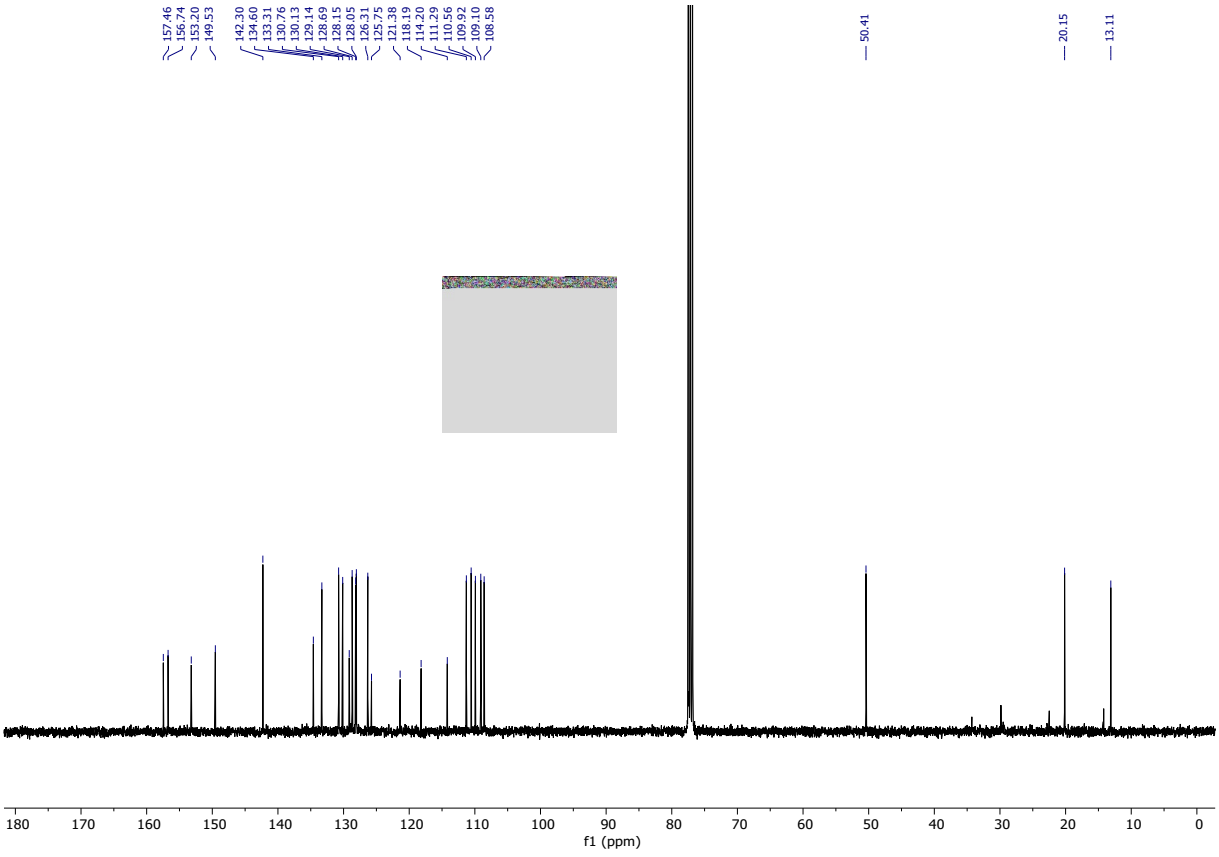
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.04	18745	98.44	0.71		
5.82	297	1.56	0.97	1.37	3.15
Sum	19041	100.00			

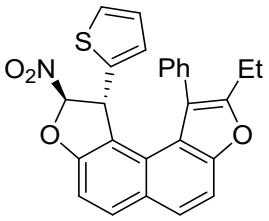
^{1}H NMR spectrum of **4am** in $CDCl_3$



^{13}C NMR spectrum of **4am** in $CDCl_3$



*(1R,2R)-9-ethyl-2-nitro-10-phenyl-1-(thiophen-2-yl)-1,2-dihydronaphtho[2,1-b:7,8-b']difuran (**4an**)*

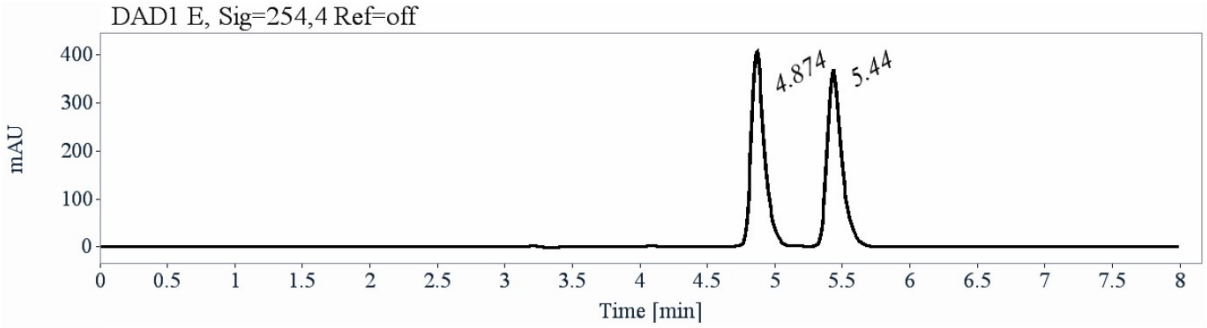


Molecular Weight: 441,5010

Prepared following general procedure using **3a** (35 mg) and **2n** (19 mg) for 10 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:49 to 1:24) to yield a light-yellow solid (16 mg, 0.035 mmol, 35%)

R_f = 0.30 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +196°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.03 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 8.9 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.53 (tt, *J* = 7.4, 1.4 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.42 – 7.36 (m, 1H), 7.34 (dd, *J* = 8.7, 0.6 Hz, 1H), 7.15 – 7.11 (m, 1H), 7.06 – 7.01 (m, 2H), 6.70 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.10 (dt, *J* = 3.6, 1.2 Hz, 1H), 5.76 (d, *J* = 0.9 Hz, 1H), 4.09 (s, 1H), 2.70 – 2.53 (m, *J* = 7.5 Hz, 2H), 1.19 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 157.3, 156.7, 153.4, 141.7, 134.6, 133.4, 130.6, 130.3, 129.2, 129.1, 128.8, 128.3, 126.9, 126.3, 126.2, 125.5, 125.4, 121.3, 118.2, 117.0, 111.5, 111.3, 109.9, 51.7, 20.1, 13.1. **MP** = 149 °C, **HRMS-ESI$^+$ (m/z)**: $[2M+Ag]^+$ calculated for $C_{52}H_{38}N_2O_8S_2Ag^+$ 991.1120, found 991.1119. **HPLC analysis** (Lux-Cellulose-4, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **96% ee**, **t_r1**: 4.87 min, **t_r2**: 5.44 min

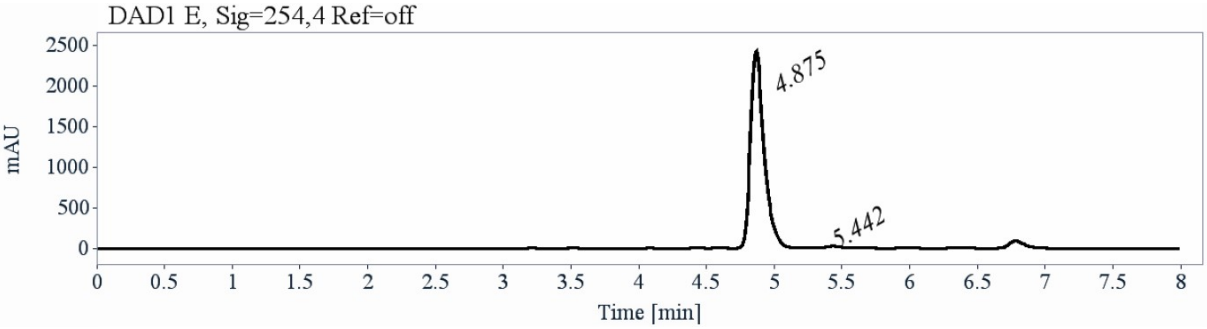
Chiral HPLC spectrum of *rac*-**4an**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.87	2798	50.05	0.65		
5.44	2792	49.95	0.84	1.29	3.13
Sum	5590	100.00			

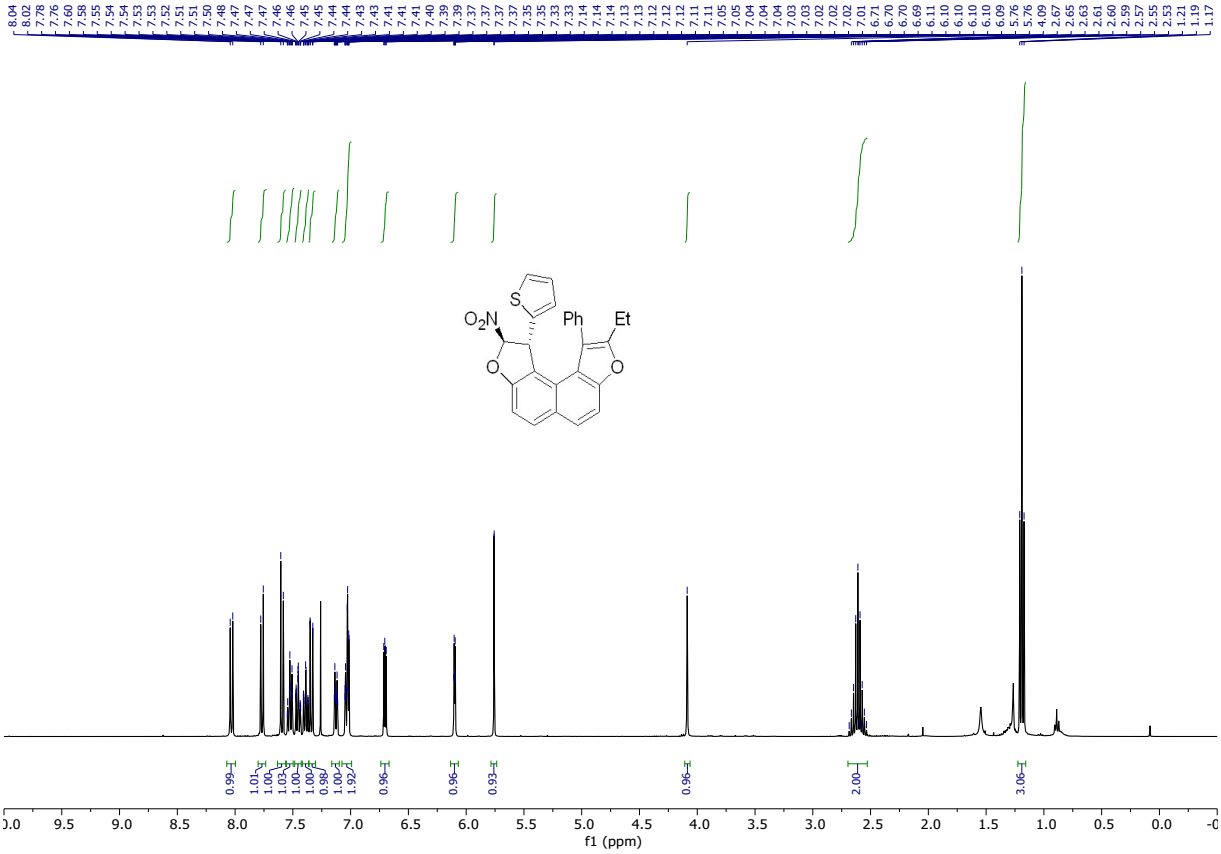
Chiral HPLC spectrum of *rac*-**4an**



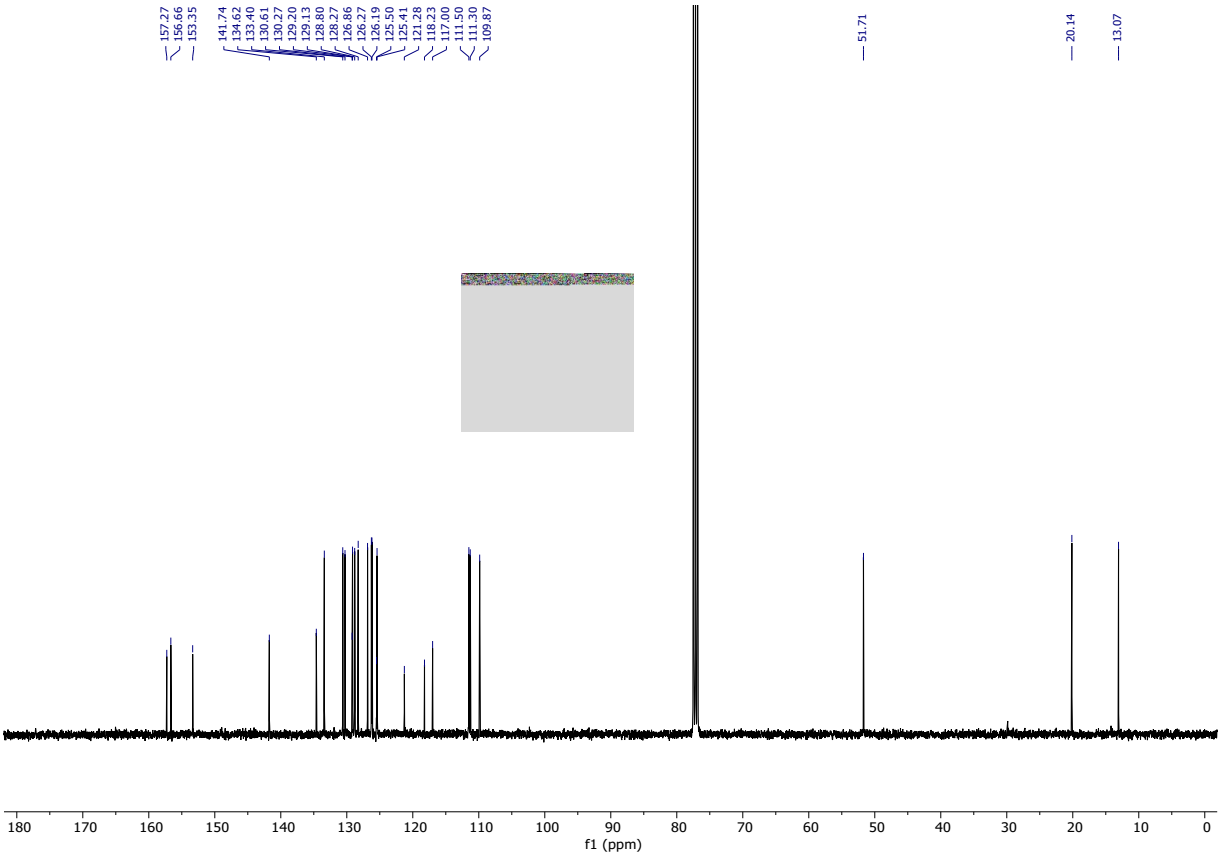
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.87	16988	98.39	0.65		
5.44	278	1.61	0.84	1.29	3.07
Sum	17266	100.00			

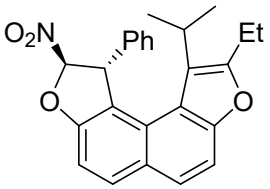
^{1}H NMR spectrum of **4an** in $CDCl_3$



^{13}C NMR spectrum of **4an** in $CDCl_3$



*(1R,2R)-9-ethyl-10-isopropyl-2-nitro-1-phenyl-1,2-dihydronaphtho[2,1-b:7,8-b']difuran (**4ba**)*

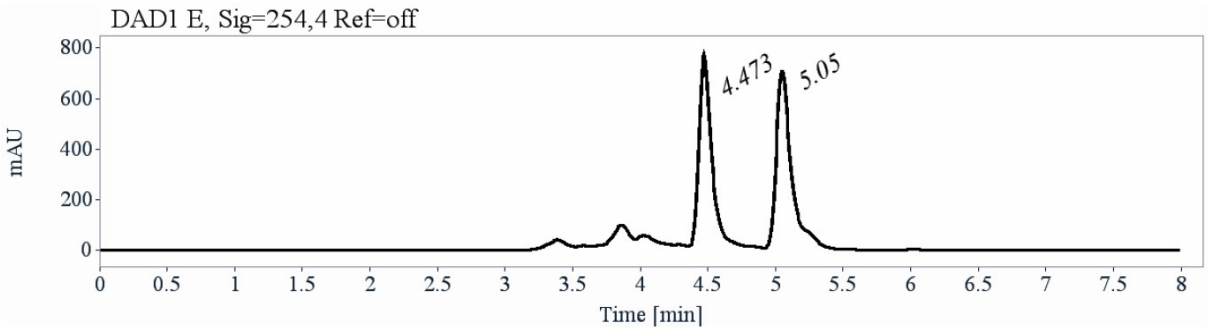


Molecular Weight: 401,4620

Prepared following general procedure using **3b** (27 mg, 1.1 mmol, 1.1 equiv.) and **2a** (18 mg) for 17 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:49 to 1:24) to yield a white solid (11 mg, 0.028 mmol, 28%)

R_f = 0.40 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +49°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.06 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.32 – 7.24 (m, 3H), 7.02 – 6.99 (m, 2H), 6.05 (d, *J* = 0.8 Hz, 1H), 5.72 (s, 1H), 3.45 (p, *J* = 7.1 Hz, 1H), 2.82 (qd, *J* = 7.5, 1.5 Hz, 2H), 1.27 (d, *J* = 7.4 Hz, 6H), 0.85 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 157.9, 154.6, 153.3, 138.9, 134.3, 129.8, 129.6, 128.3, 127.4, 127.3, 126.8, 121.4, 121.4, 114.7, 112.4, 111.5, 109.7, 58.4, 24.4, 23.6, 22.3, 21.9, 13.2. **MP** = 59 °C, **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{25}H_{23}NO_4Ag^+$ 508.0673, found 508.0672. **HPLC analysis** (Lux-Cellulose-4, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **79% ee**, **t_r1**: 4.48 min, **t_r2**: 5.06 min

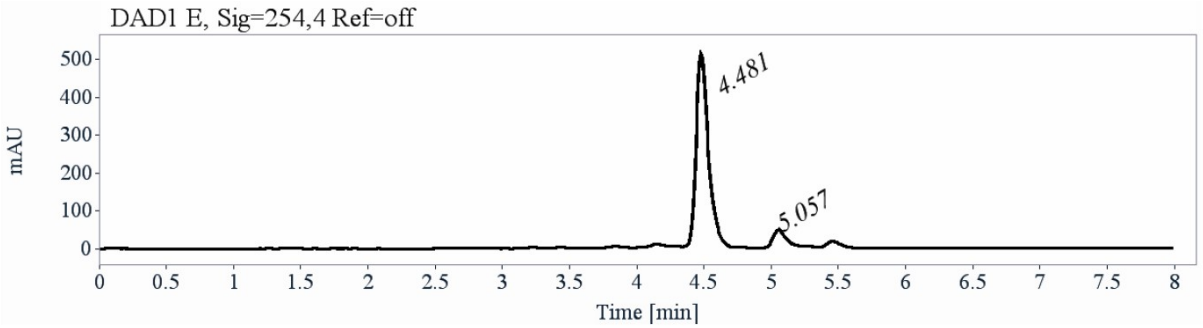
Chiral HPLC spectrum of *rac*-**4ba**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.47	4953	47.50	0.52		
5.05	5475	52.50	0.71	1.38	3.37
Sum	10428	100.00			

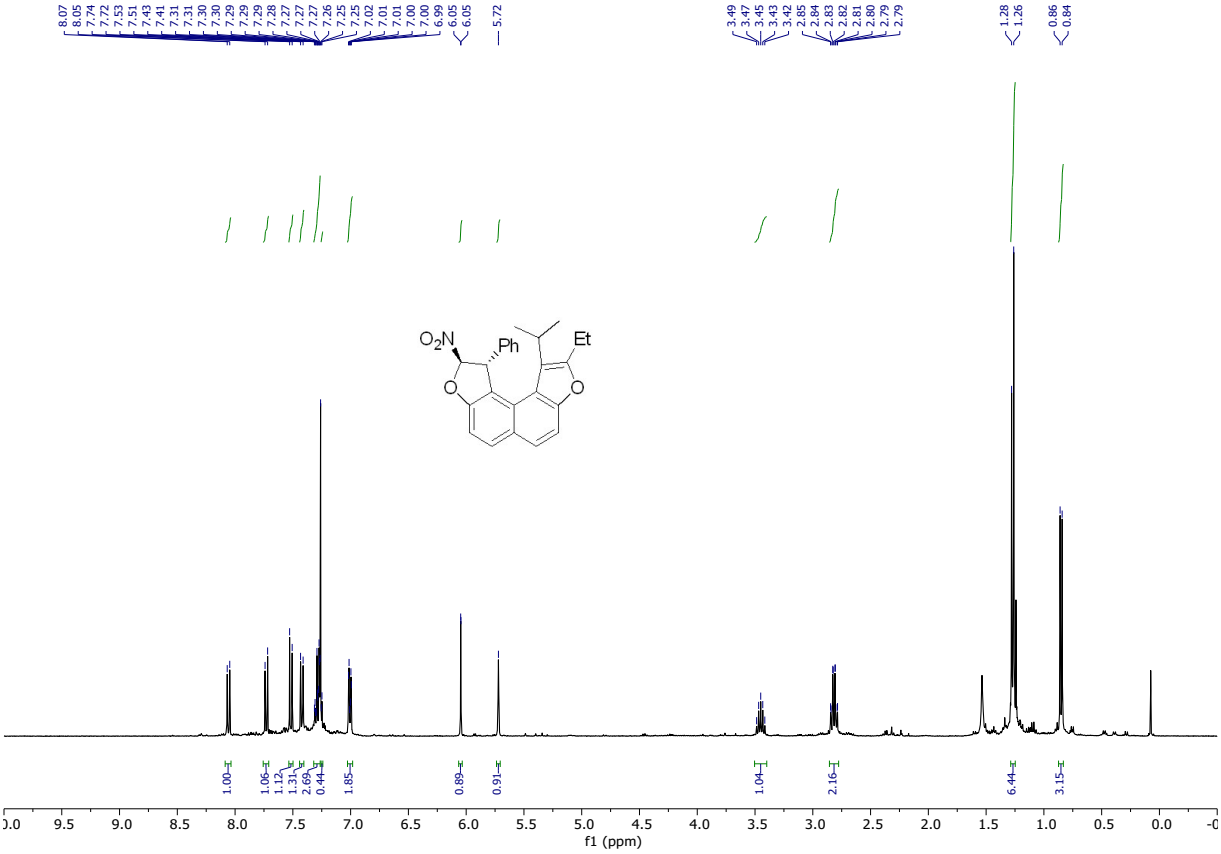
Chiral HPLC spectrum of **4ba**



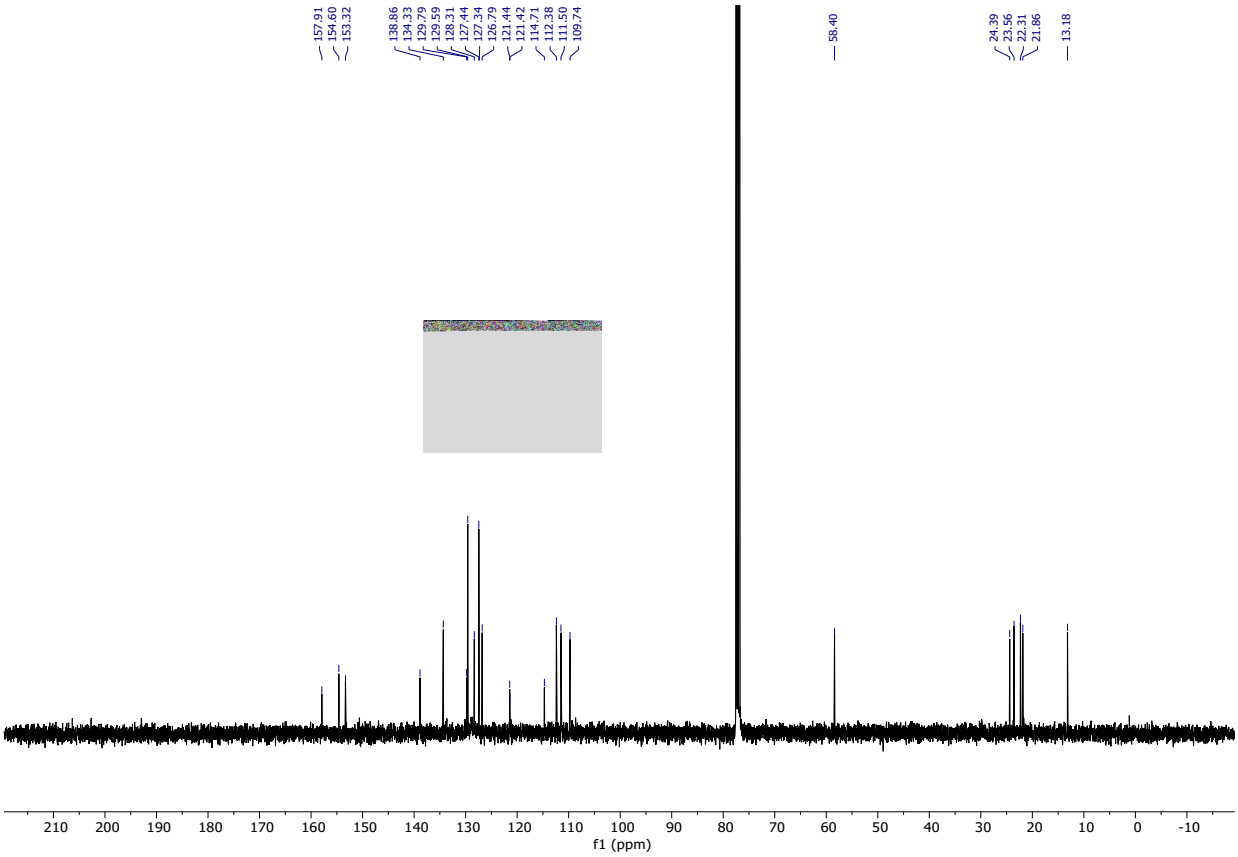
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.48	3256	89.66	0.52		
5.06	376	10.34	0.71	1.38	3.38
Sum	3632	100.00			

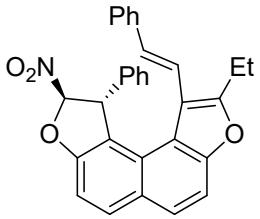
^{1}H NMR spectrum of **4ba** in $CDCl_3$



^{13}C NMR spectrum of **4ba** in $CDCl_3$



*(1R,2R)-9-ethyl-2-nitro-1-phenyl-10-((E)-styryl)-1,2-dihydronaphtho[2,1-b:7,8-b']difuran (**4ca**)*

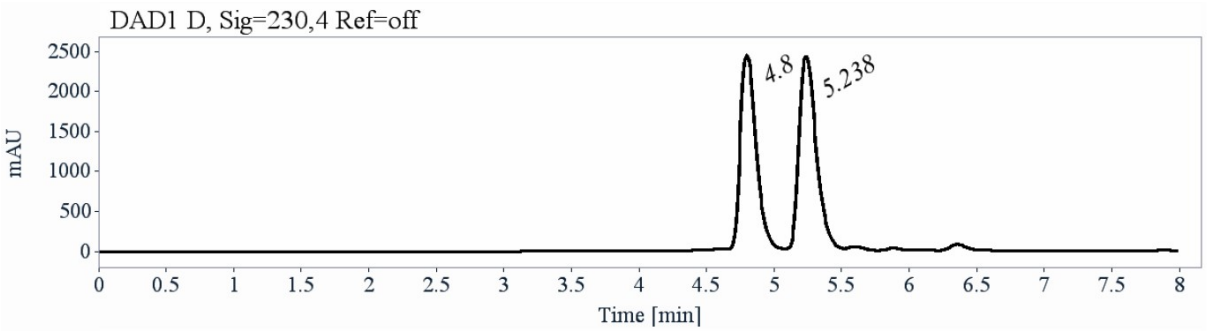


Molecular Weight: 461,5170

Prepared following general procedure using **3c** (46 mg, 0.15 mmol, 1.2 equiv.) and **2a** (18 mg, 0.12 mmol, 1.0 equiv.) for 4 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:49 to 1:24) to yield an orange solid (33 mg, 0.071 mmol, 58%)

R_f = 0.39 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +151°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.05 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.57 (d, *J* = 8.9 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.46 – 7.38 (m, 4H), 7.23 – 7.16 (m, 1H), 7.11 (m, 2H), 6.86 (d, *J* = 16.1 Hz, 1H), 6.65 – 6.59 (m, 2H), 6.34 (d, *J* = 16.1 Hz, 1H), 5.99 – 5.82 (m, 2H), 2.87 – 2.70 (m, 2H), 1.26 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 157.7, 156.6, 153.4, 138.1, 136.9, 134.6, 133.3, 129.0, 129.0, 128.9, 128.3, 127.9, 127.7, 126.8, 126.6, 126.5, 121.0, 120.9, 115.4, 115.3, 112.5, 111.3, 110.0, 57.0, 20.4, 13.2. **MP** = 78 °C, **HRMS-ESI$^+$ (m/z)**: $[2M+Ag]^+$ calculated for $C_{60}H_{46}N_2O_8Ag^+$ 1031.2310, found 1031.2315. **HPLC analysis** (Lux-Cellulose-4, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 230 nm) indicated **95% ee**, **t_r1**: 4.81 min, **t_r2**: 5.26 min

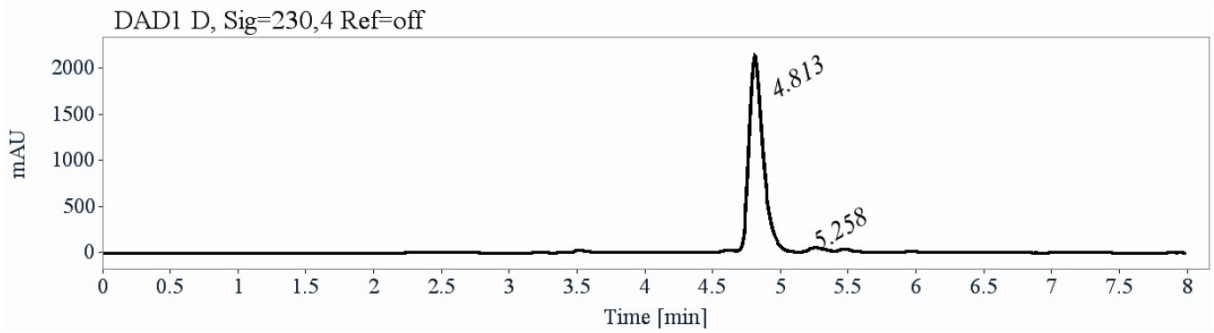
Chiral HPLC spectrum of *rac*-**4ca**



Signal: DAD1 D, Sig=230,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.80	19663	48.06	0.63		
5.24	21246	51.94	0.78	1.24	2.08
Sum	40908	100.00			

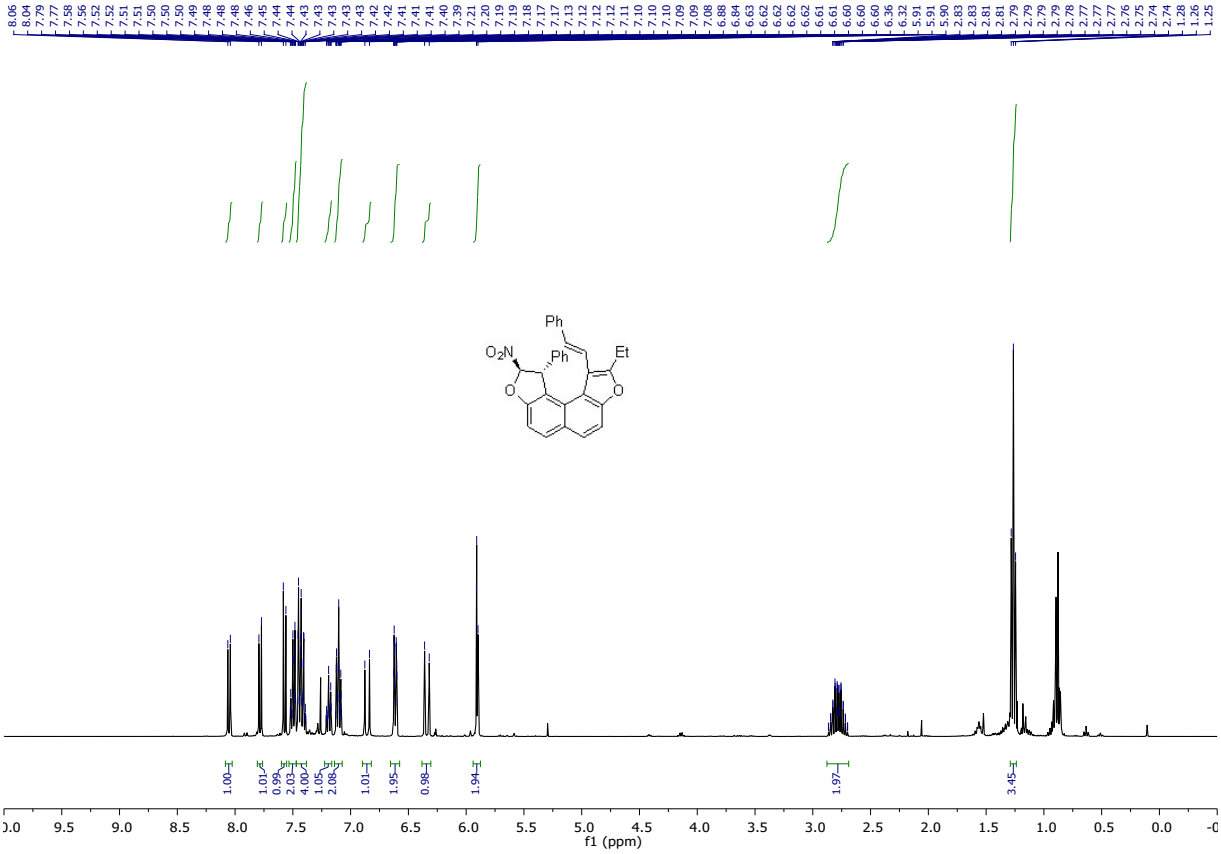
Chiral HPLC spectrum of **4ca**



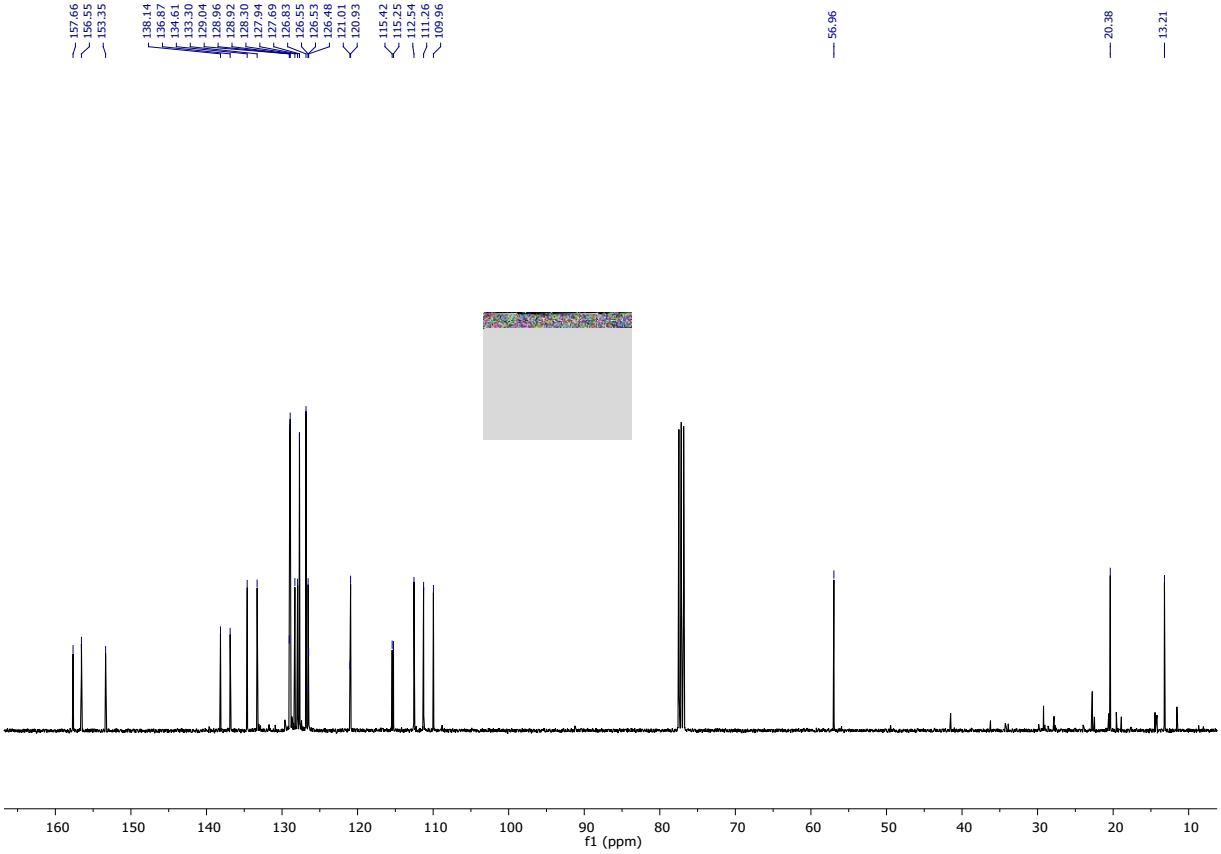
Signal: DAD1 D, Sig=230,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.81	15168	97.59	0.63		
5.26	375	2.41	0.78	1.24	2.17
Sum	15543	100.00			

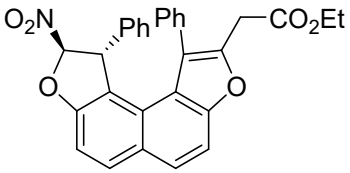
^{1}H NMR spectrum of **4ca** in $CDCl_3$



^{13}C NMR spectrum of **4ca** in $CDCl_3$



*ethyl 2-((9R,10R)-9-nitro-1,10-diphenyl-9,10-dihydronaphtho[2,1-b:7,8-b']difuran-2-yl)acetate (**4da**)*

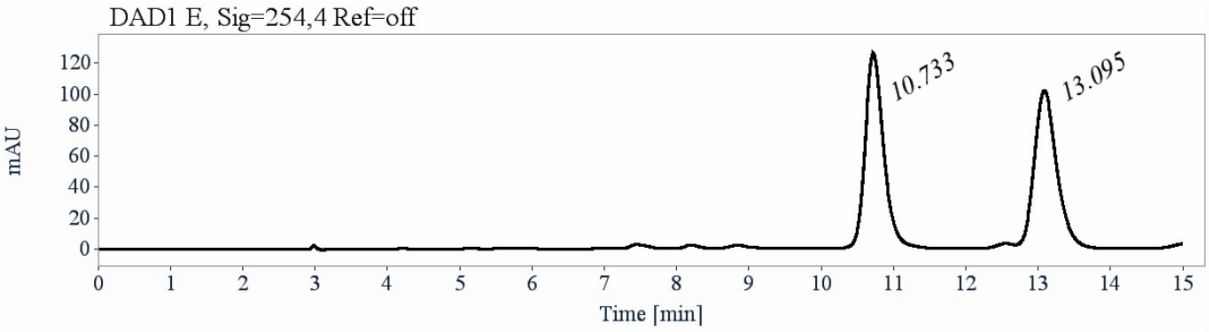


Molecular Weight: 493,5150

Prepared following general procedure using **3d** (42 mg) and **2a** (18 mg) for 4 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 5:95 to 2:23) to yield a white solid (26 mg, 0.053 mmol, 53%)

R_f = 0.18 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +138°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.05 (d, *J* = 8.7 Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.53 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.46 – 7.31 (m, 3H), 7.19 – 7.09 (m, 2H), 7.09 – 7.02 (m, 2H), 6.81 (dt, *J* = 7.5, 1.7 Hz, 1H), 6.36 – 6.30 (m, 2H), 5.71 (d, *J* = 1.0 Hz, 1H), 4.15 (s, 1H), 4.07 (qd, *J* = 7.2, 1.8 Hz, 2H), 3.63 (d, *J* = 16.5 Hz, 1H), 3.49 (d, *J* = 16.5 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 169.0, 158.0, 154.0, 147.5, 137.6, 133.8, 133.1, 130.7, 130.1, 129.1, 128.7, 128.5, 128.5, 127.8, 127.7, 127.3, 126.2, 121.6, 120.8, 116.0, 112.1, 111.4, 110.1, 61.4, 56.1, 33.2, 14.2. **MP** = 59 °C, **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{30}H_{23}NO_6Ag^+$ 600.0571, found 600.0572. **HPLC analysis** (Lux-Cellulose-2, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **96% ee**, **t_r1**: 10.75 min, **t_r2**: 13.13 min

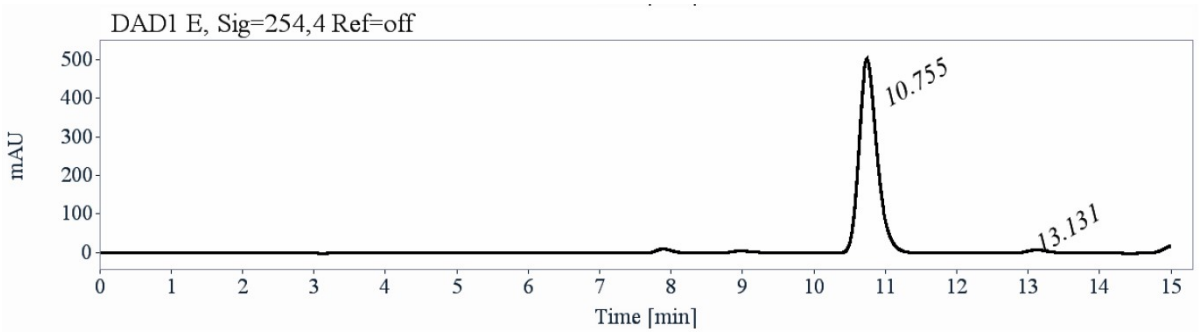
Chiral HPLC spectrum of *rac*-**4da**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
10.73	2233	51.17	2.64		
13.10	2131	48.83	3.44	1.30	4.70
Sum	4364	100.00			

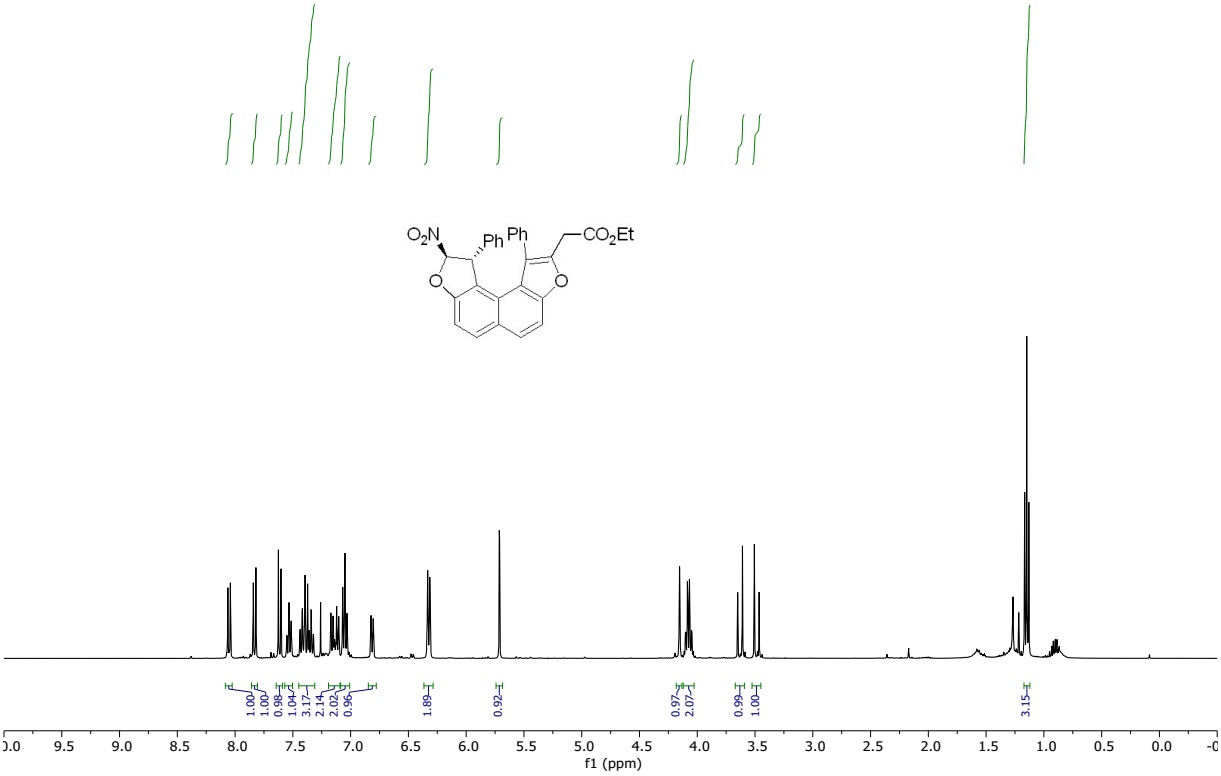
Chiral HPLC spectrum of **4da**



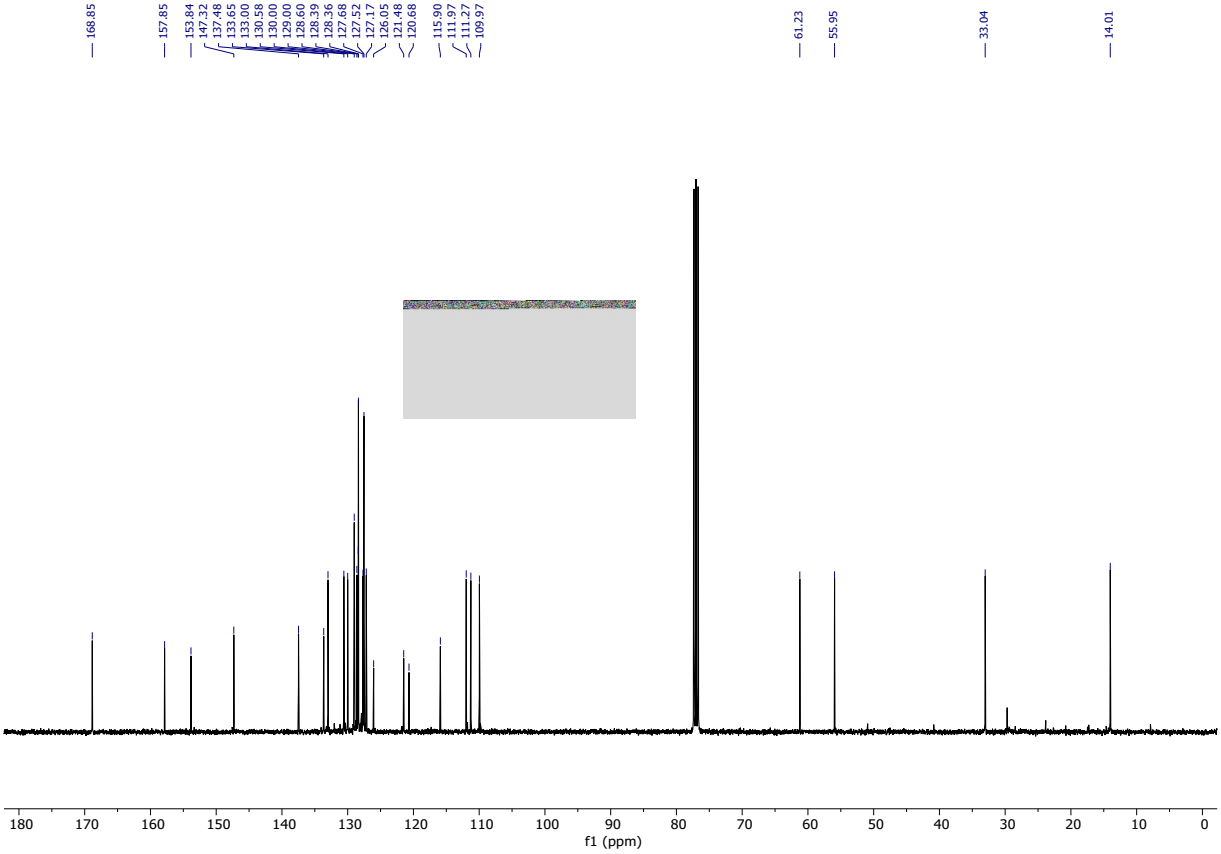
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
10.75	8801	98.06	2.65		
13.13	174	1.94	3.45	1.30	4.74
Sum	8975	100.00			

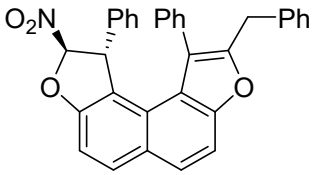
^{1}H NMR spectrum of **4da** in $CDCl_3$



^{13}C NMR spectrum of **4da** in $CDCl_3$



*(1R,2R)-9-benzyl-2-nitro-1,10-diphenyl-1,2-dihydronaphtho[2,1-b:7,8-b']difuran (**4ea**)*

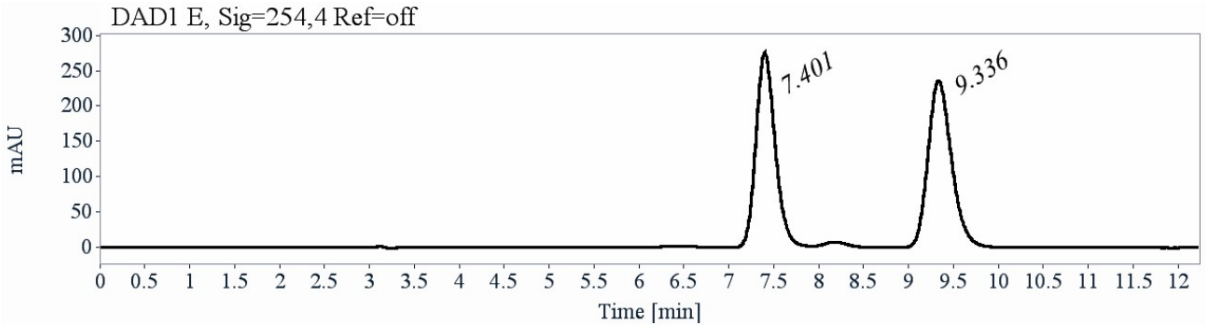


Molecular Weight: 497,55

Prepared following general procedure using **3e** (42 mg, 0.12 mmol, 1.2 equiv.) and **2a** (18 mg, 0.1 mmol, 1.0 equiv.) for 5 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:9 to 3:97) to yield a white solid (35 mg, 0.07 mmol, 69%)

R_f = 0.4 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +183°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.04 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.57 (d, *J* = 8.9 Hz, 1H), 7.54 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.43 (td, *J* = 7.6, 1.5 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 1H), 7.36 (td, *J* = 7.5, 1.4 Hz, 1H), 7.26 – 7.10 (m, 5H), 7.11 – 6.99 (m, 4H), 6.81 (dt, *J* = 7.5, 1.6 Hz, 1H), 6.38 – 6.33 (m, 2H), 5.72 (d, *J* = 1.1 Hz, 1H), 4.16 (s, 1H), 3.97 (d, *J* = 15.8 Hz, 1H), 3.80 (d, *J* = 15.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 157.91, 153.81, 153.22, 137.86, 137.76, 134.37, 133.09, 130.93, 130.24, 129.12, 128.80, 128.62, 128.55, 128.50, 128.38, 127.79, 127.74, 126.81, 126.61, 126.20, 121.04, 119.95, 116.01, 112.14, 111.38, 109.99, 56.14, 32.76. **MP** = 85 °C, **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{33}H_{23}NO_4Ag^+$, 606.0674 found 606.0670. **HPLC analysis** (Lux-Cellulose-2, Heptane/Isopropanol (95/5), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **96% ee**, **t_r1**: 7.38 min, **t_r2**: 9.31 min

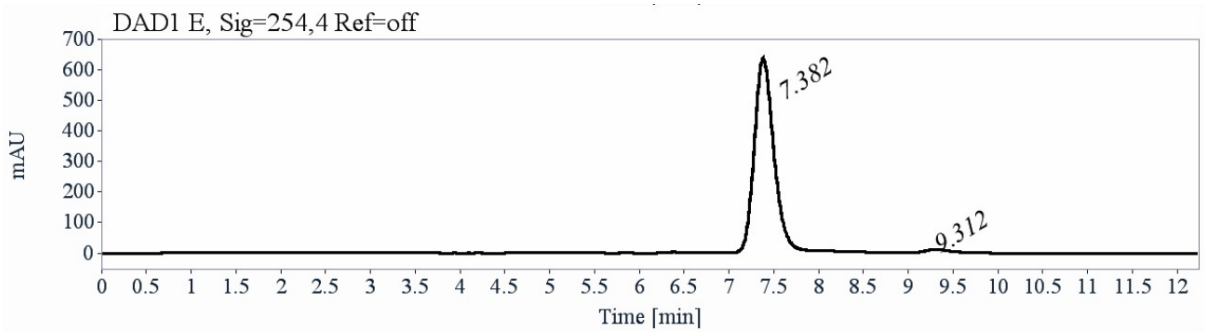
Chiral HPLC spectrum of *rac*-**4ea**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.40	4063	48.50	1.51		
9.34	4315	51.50	2.16	1.43	4.49
Sum	8377	100.00			

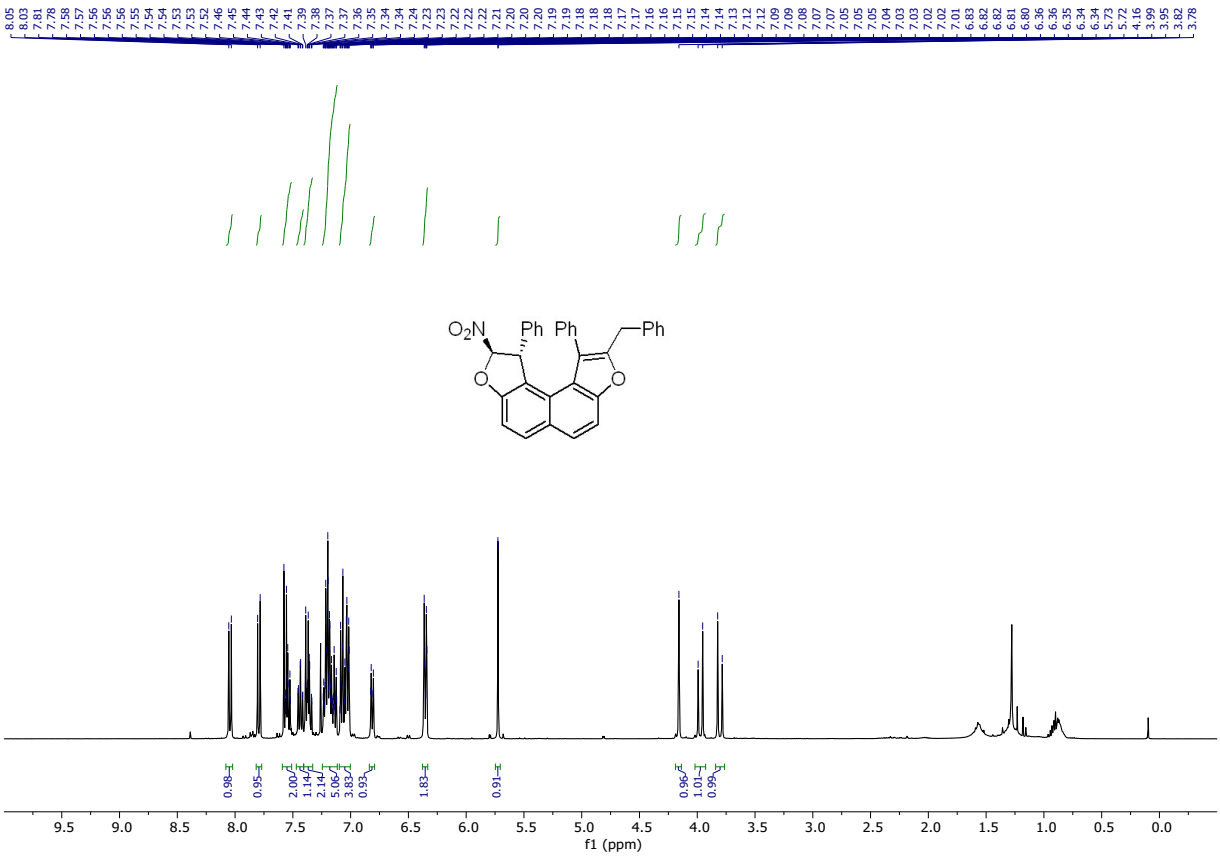
Chiral HPLC spectrum of **4ea**



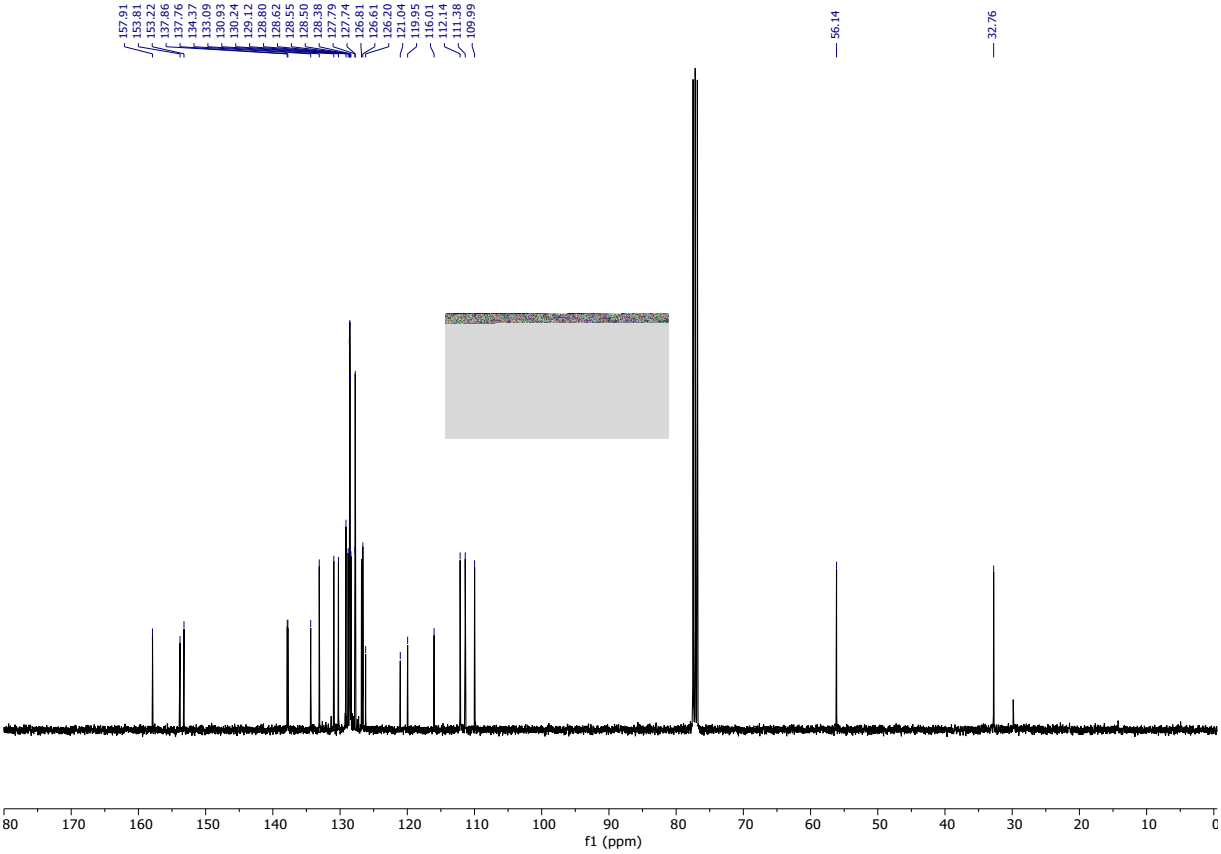
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.38	9569	97.75	1.50		
9.31	220	2.25	2.16	1.44	4.37
Sum	9789	100.00			

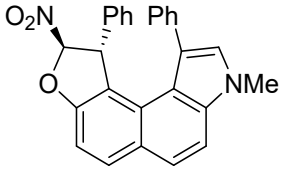
^{1}H NMR spectrum of **4ea** in $CDCl_3$



^{13}C NMR spectrum of **4ea** in $CDCl_3$



*(1R,2R)-8-methyl-2-nitro-1,10-diphenyl-1,8-dihydro-2H-benzofuro[4,5-e]indole (**4fa**)*

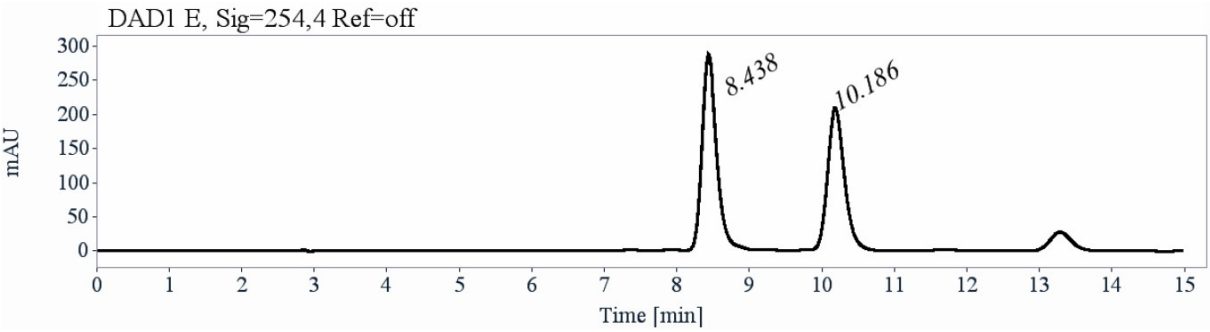


Molecular Weight: 420,4680

Prepared following general procedure using **3f** (27 mg, 0.1 mmol, 1.0 equiv.) and **2a** (18 mg, 0.1 mmol, 1.0 equiv.) for 4 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 5:95 to 3:22) to yield a white solid (29 mg, 0.069 mmol, 69%)

R_f = 0.26 (EtOAc/ Petroleum ether = 2:8), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +290°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.02 (d, *J* = 8.6 Hz, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.47 – 7.40 (m, 3H), 7.37 – 7.31 (m, 2H), 7.20 – 7.15 (m, 1H), 7.13 – 7.04 (m, 2H), 7.03 – 6.97 (m, 2H), 6.85 (s, 1H), 6.31 – 6.27 (m, 2H), 5.67 (d, *J* = 1.1 Hz, 1H), 4.41 (s, 1H), 3.83 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 157.8, 138.0, 137.8, 135.6, 132.5, 130.3, 128.9, 128.5, 128.4, 128.4, 128.0, 127.6, 127.3, 127.2, 126.7, 124.6, 120.5, 118.6, 116.49, 112.0, 109.9, 108.4, 56.5, 33.3. **MP** = 194 °C, **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{27}H_{20}N_2O_3Ag^+$ 527.0519, found 527.0523. **HPLC analysis** (Chiralpak IB N-5, Heptane/Ethanol (80/20), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **96% ee**, **t_r1**: 8.44 min, **t_r2**: 10.17 min

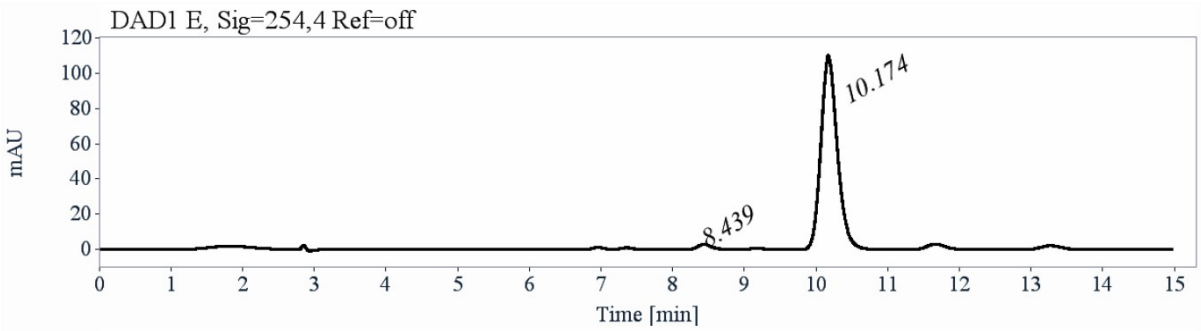
Chiral HPLC spectrum of *rac*-**4fa**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
8.44	4008	54.29	1.86		
10.19	3375	45.71	2.45	1.32	4.53
Sum	7382	100.00			

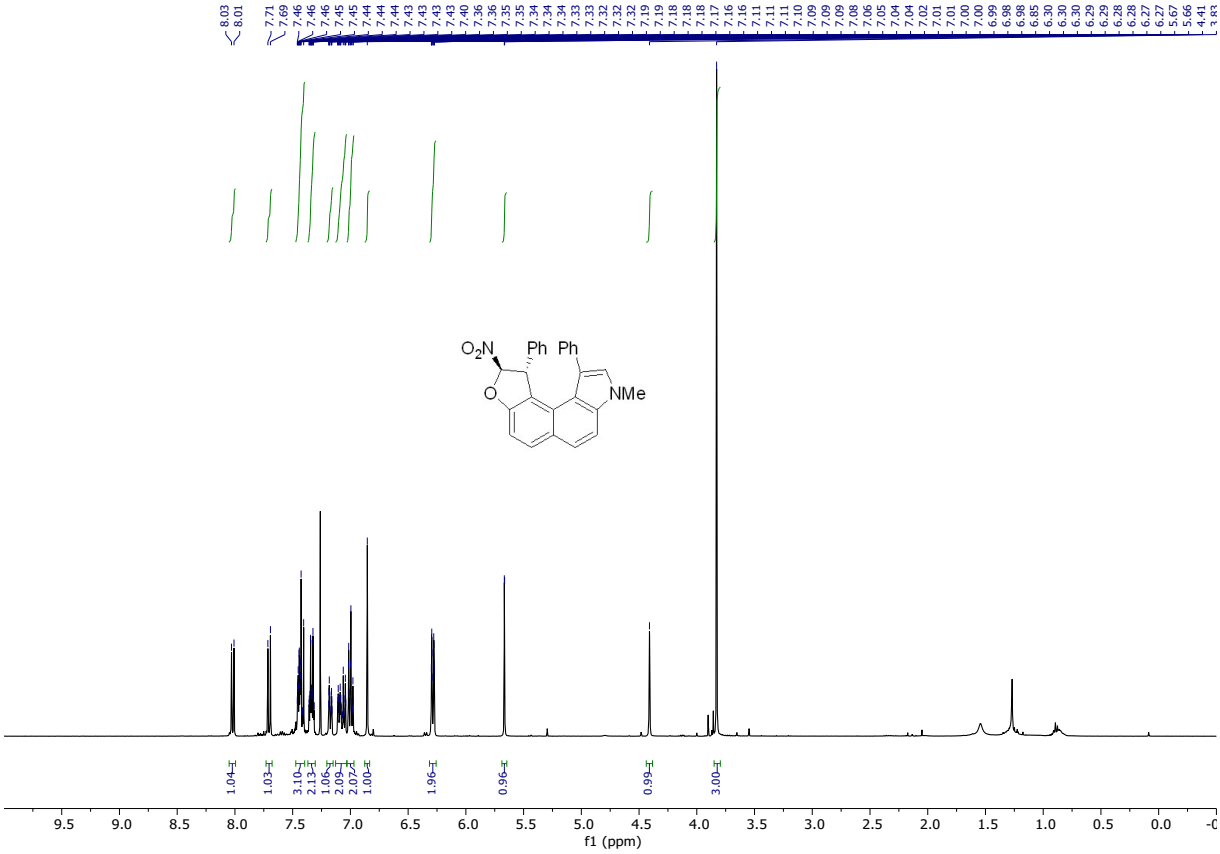
Chiral HPLC spectrum of **4fa**



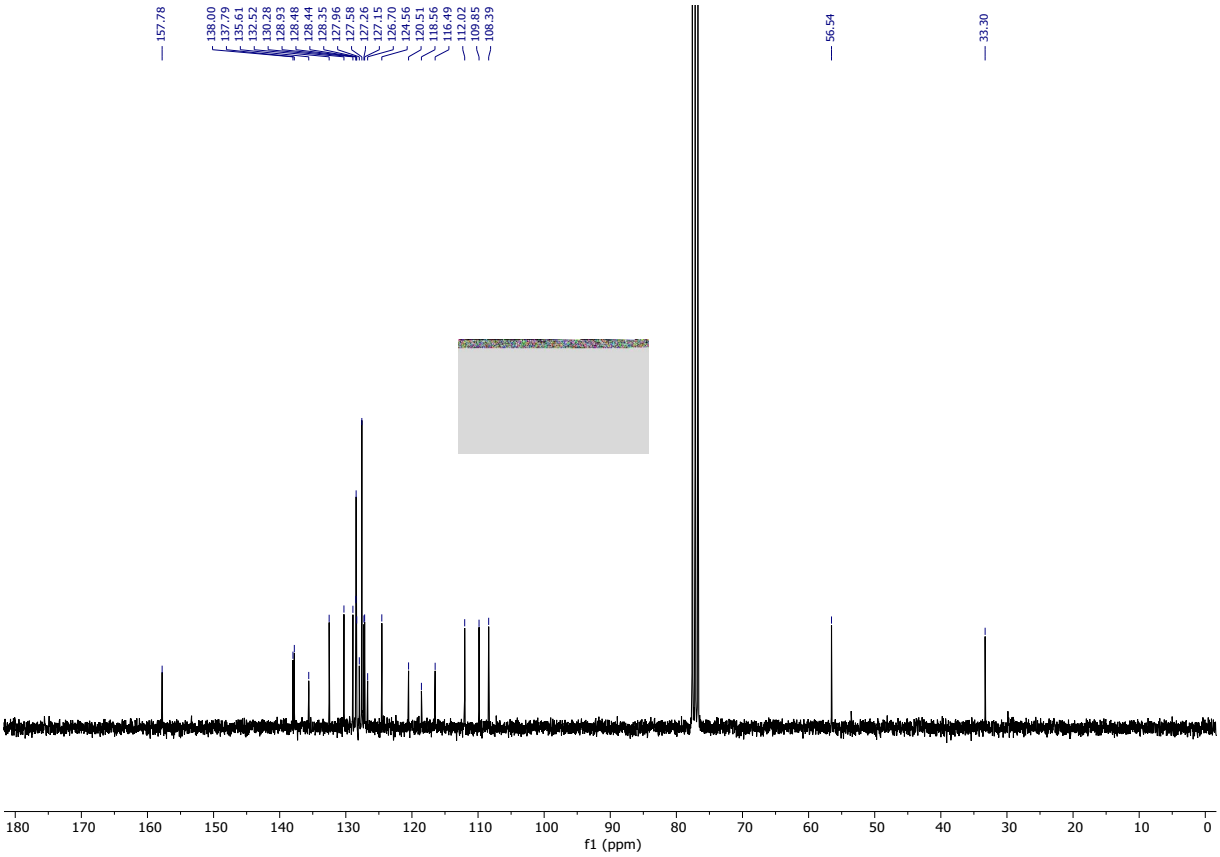
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
8.44	37	2.08	1.86		
10.17	1763	97.92	2.45	1.32	4.54
Sum	1800	100.00			

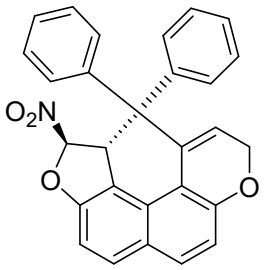
^{1}H NMR spectrum of **4fa** in $CDCl_3$



^{13}C NMR spectrum of **4fa** in $CDCl_3$



*(1R,2R)-2-nitro-1,11-diphenyl-1,2-dihydro-9H-benzofuro[4,5-f]chromene (**4ha**)*



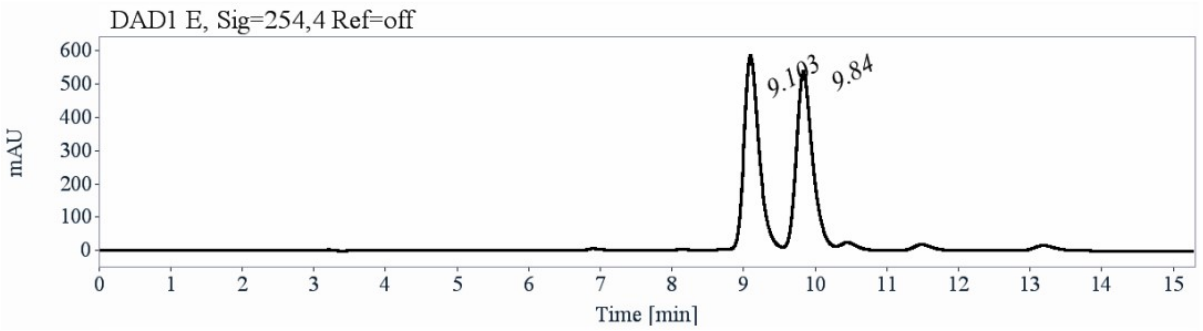
Molecular Weight: 421,4520

Prepared following general procedure using **3h** (27 mg) and **2a** (18 mg) for 3 days. The crude product was purified on silica (EtOAc/ Petroleum ether = 0:100 to 1:9) to yield an off white solid (26.1 mg, 0.06 mmol, 62%)

R_f = 0.56 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +284°, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.7 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.70 – 7.26 (m, 4H), 7.26 – 6.93 (m, 6H), 6.75 – 6.67 (m, 2H), 5.86 (dd, *J* = 6.4, 4.5 Hz, 1H), 5.64 (d, *J* = 1.5 Hz, 1H), 4.65 (dd, *J* = 12.1, 6.4 Hz, 1H), 4.00 – 3.96 (m, 1H), 3.76 (dd, *J* = 12.1, 4.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.2, 157.7, 139.7, 138.0, 137.9, 132.6, 132.2, 129.1, 129.0, 128.8, 128.7, 127.9, 127.8, 127.2, 126.1, 118.3, 117.3, 116.0, 115.6, 111.8, 109.7, 64.7, 57.2. **MP** = 159.1 – 161.1 °C **HRMS-ESI$^+$ (m/z)**: $[M+Na]^+$ calculated for $C_{27}H_{19}NO_4Na^+$ 444.1206,

found 444.1204. **HPLC analysis** (Lux-Cellulose-4, Heptane/Ethanol (95/5), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **98% ee**, t_r**1**: 9.10 min, t_r**2**: 9.84 min

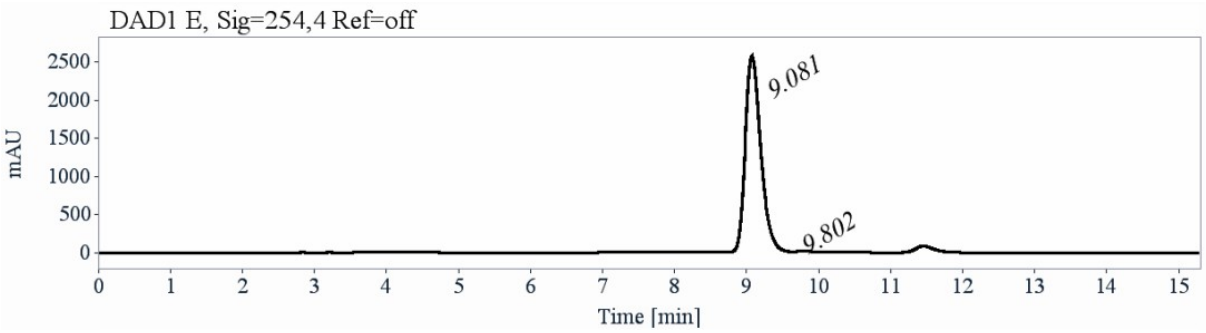
Chiral HPLC spectrum of *rac*-**4ha**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
9.10	8583	50.02	2.09		
9.84	8577	49.98	2.34	1.12	1.88
Sum	17160	100.00			

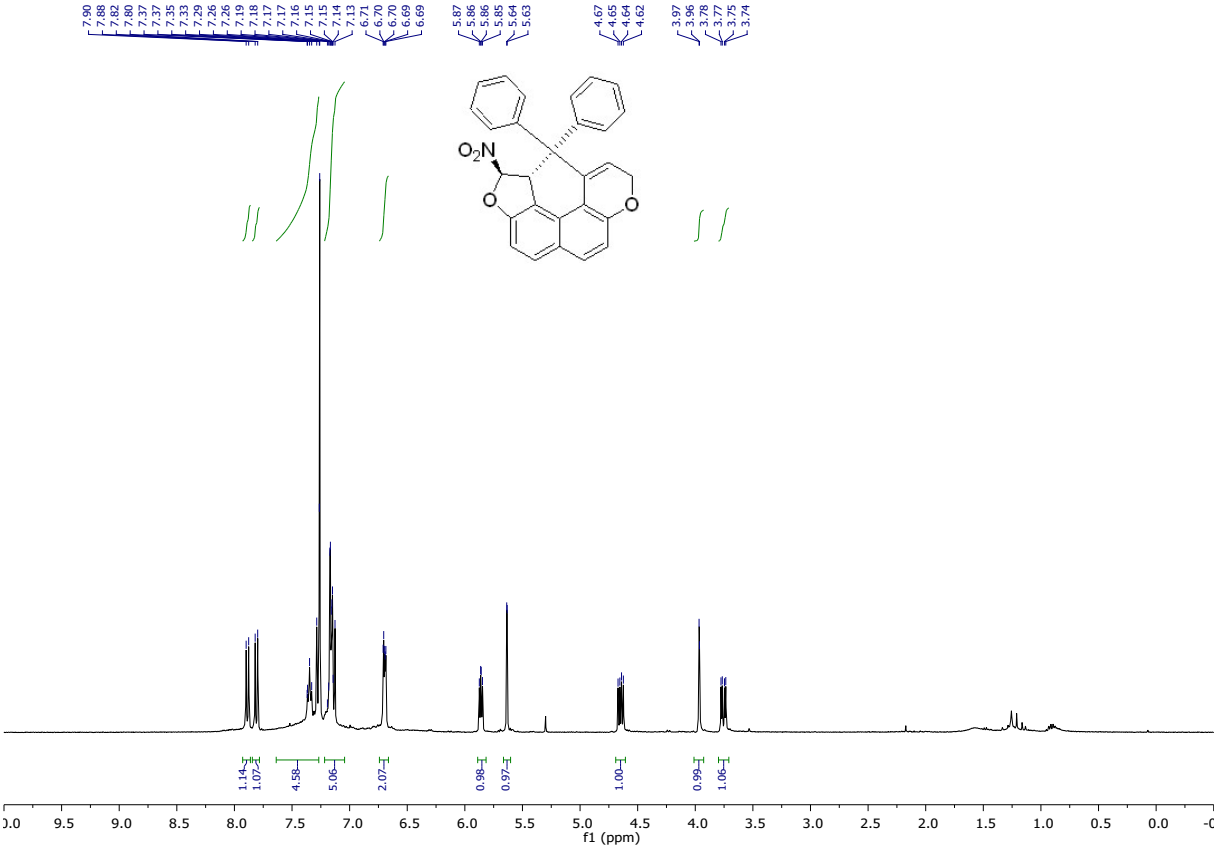
Chiral HPLC spectrum of **4ha**



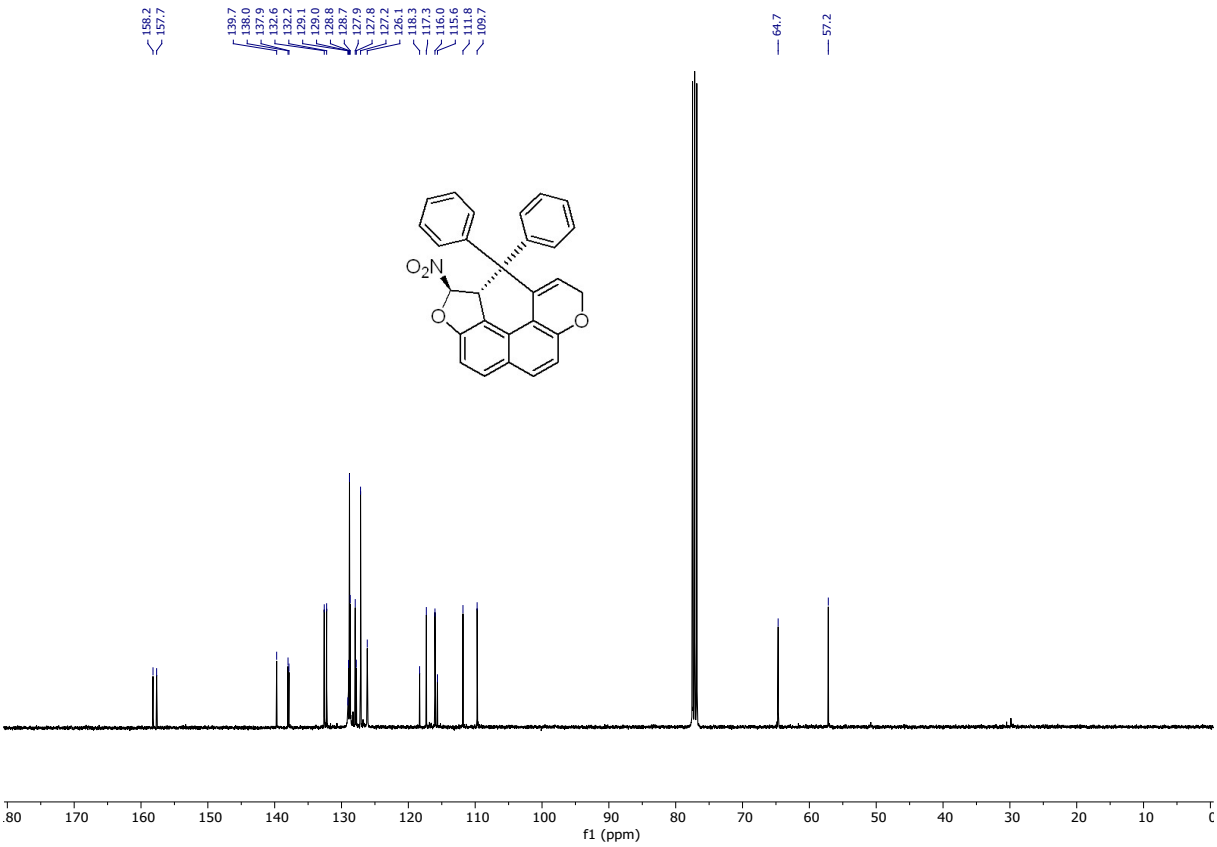
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
9.08	38894	99.12	2.08		
9.80	347	0.88	2.32	1.12	1.67
Sum	39241	100.00			

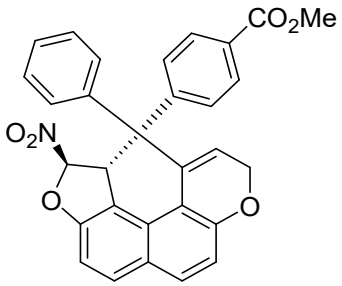
^{1}H NMR spectrum of **4ha** in $CDCl_3$



^{13}C NMR spectrum of **4ha** in $CDCl_3$



*Methyl 4-((1R,2R)-2-nitro-11-phenyl-1,2-dihydro-9H-benzofuro[4,5-f]chromen-1-yl)benzoate (**4hg**)*

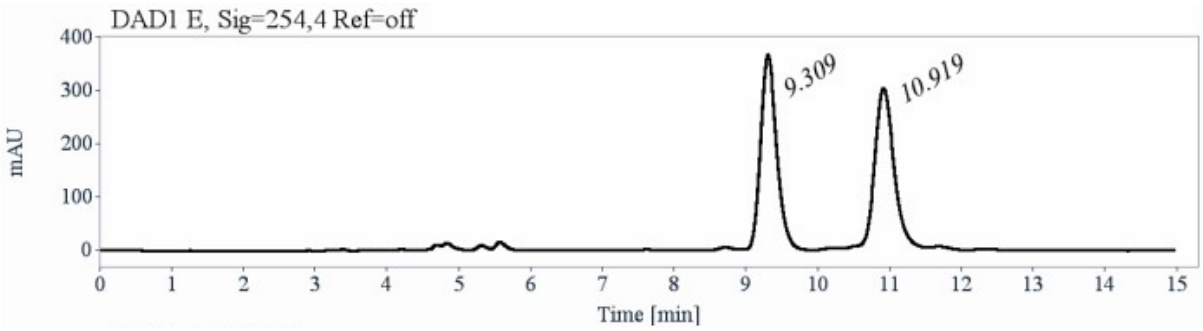


Molecular Weight: 479,4880

Prepared following general procedure using **3h** (27.4 mg) and **2g** (24.1 mg) for 40 h. The crude product was purified on silica (EtOAc/ Petroleum ether = 0:100 to 1:9) to yield a light-yellow solid (35 mg, 0.073 mmol, 73%)

R_f = 0.41 (EtOAc/ Petroleum ether = 1:9) , **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +331°, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.8 Hz, 1H), 7.87 – 7.78 (m, 3H), 7.67 – 7.27 (m, 6H), 7.15 (d, *J* = 8.8 Hz, 1H), 6.87 – 6.60 (m, 2H), 5.85 (dd, *J* = 6.4, 4.5 Hz, 1H), 5.62 (d, *J* = 1.6 Hz, 1H), 4.65 (dd, *J* = 12.2, 6.4 Hz, 1H), 4.01 (d, *J* = 1.6 Hz, 1H), 3.87 (s, 3H), 3.74 (dd, *J* = 12.2, 4.6 Hz, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 158.4, 157.7, 142.9, 139.6, 137.6, 132.9, 132.3, 130.1, 129.9, 129.1, 128.82, 127.79, 127.2, 126.0, 117.57, 117.53, 116.2, 115.4, 111.2, 109.7, 64.7, 57.0, 52.2. **MP** = 93.4 – 95.1 °C, **HRMS-ESI$^+$ (m/z)**: $[M+Na]^+$ calculated for $C_{29}H_{21}NO_6Na^+$ 502.1261, found 502.1261. **HPLC analysis** (Lux-Cellulose-4, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **99% ee**, **t_r1**: 9.30 min, **t_r2**: 10.91 min

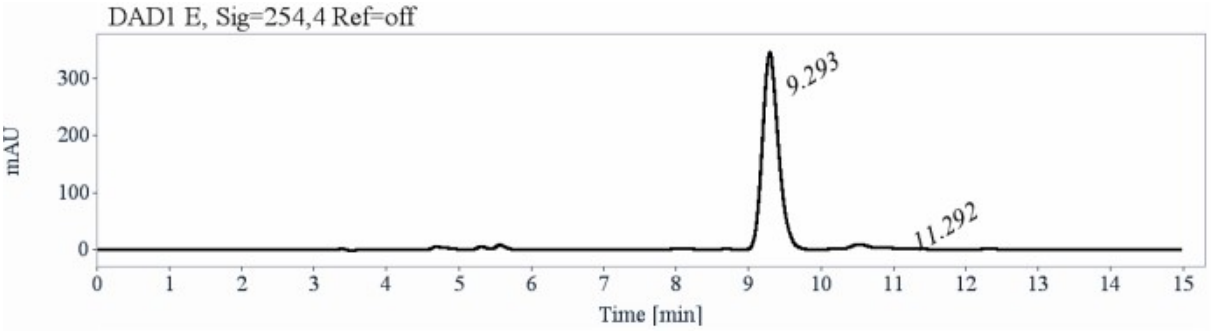
Chiral HPLC spectrum of *rac*-**4hg**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
9.31	5655	50.96	2.16		
10.92	5441	49.04	2.70	1.25	3.67
Sum	11097	100.00			

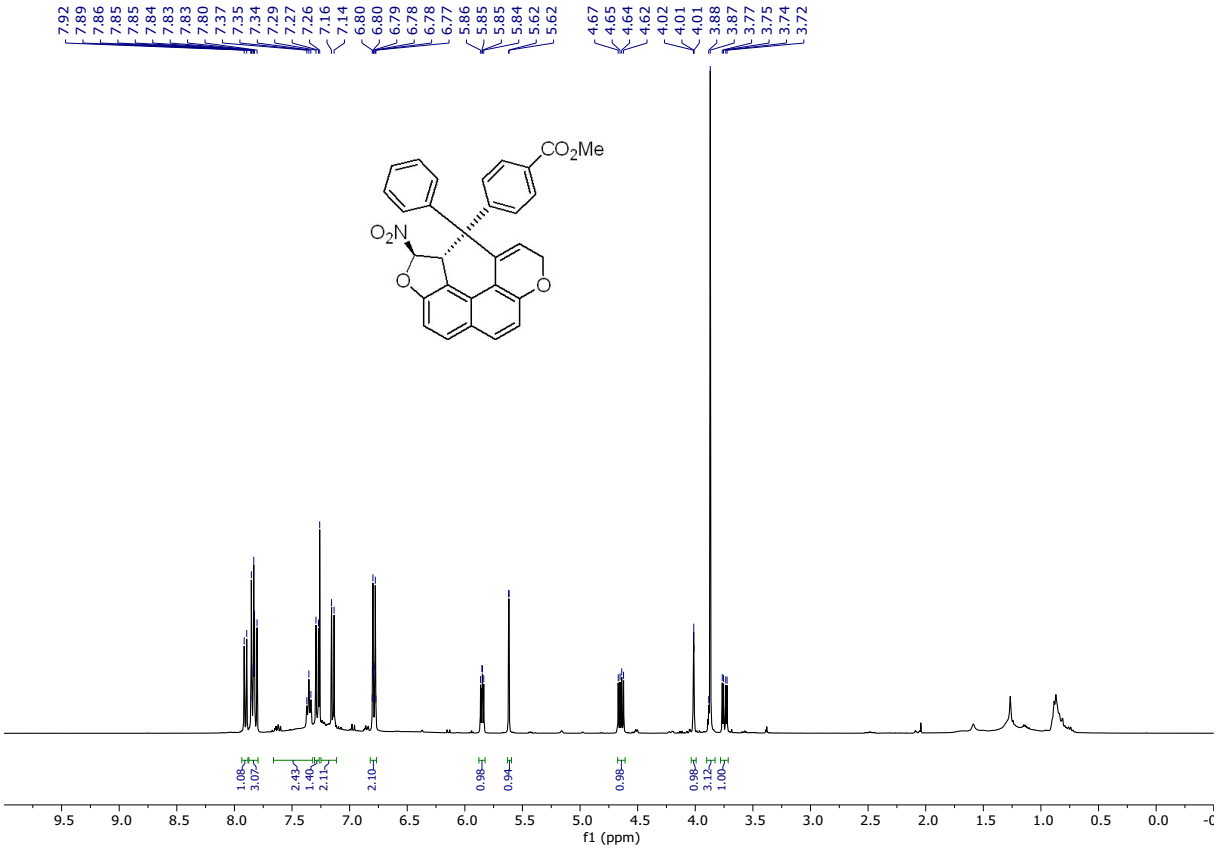
Chiral HPLC spectrum of **4hg**



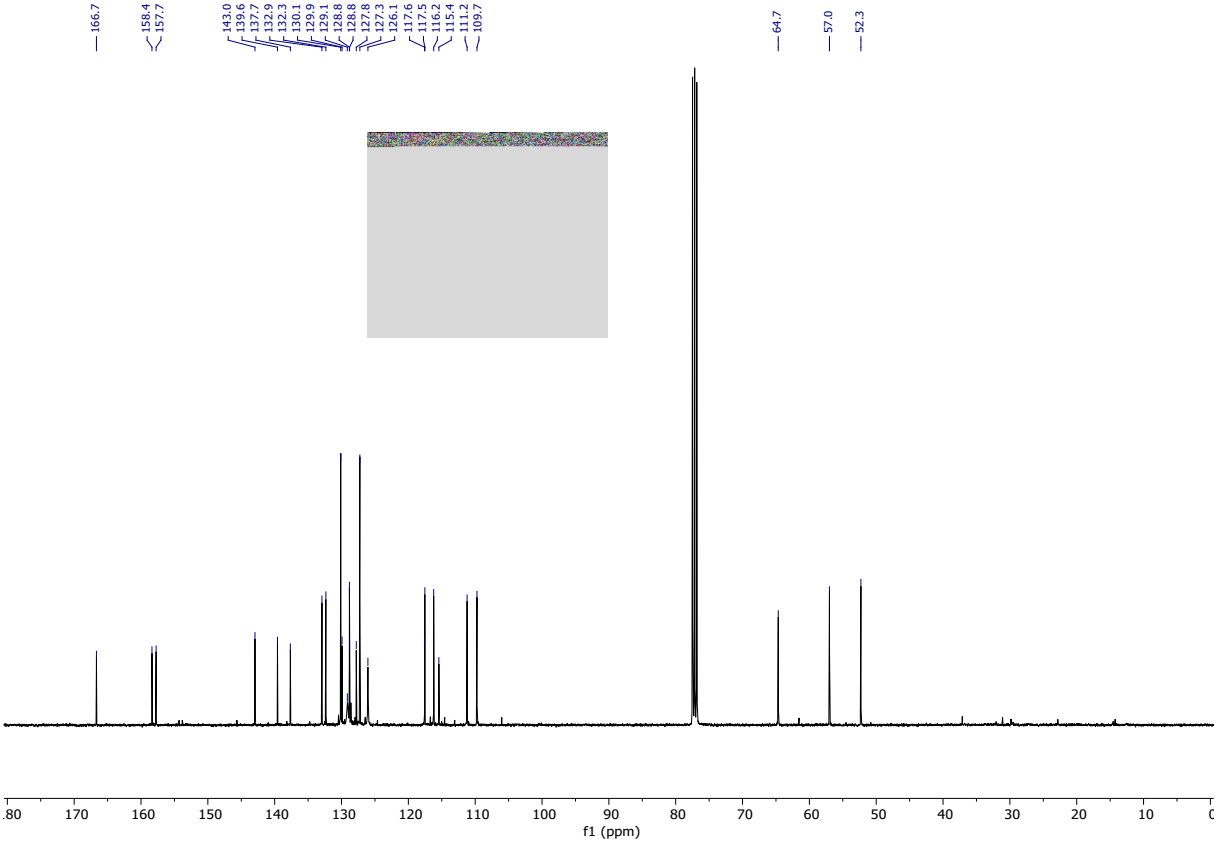
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
9.29	5314	99.57	2.15		
11.29	23	0.43	2.83	1.32	5.09
Sum	5337	100.00			

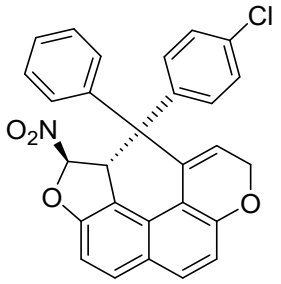
^{1}H NMR spectrum of **4hg** in $CDCl_3$



^{13}C NMR spectrum of **4hg** in $CDCl_3$



*(1R,2R)-1-(4-Chlorophenyl)-2-nitro-11-phenyl-1,2-dihydro-9H-benzofuro[4,5-f]chromene (**4hb**)*

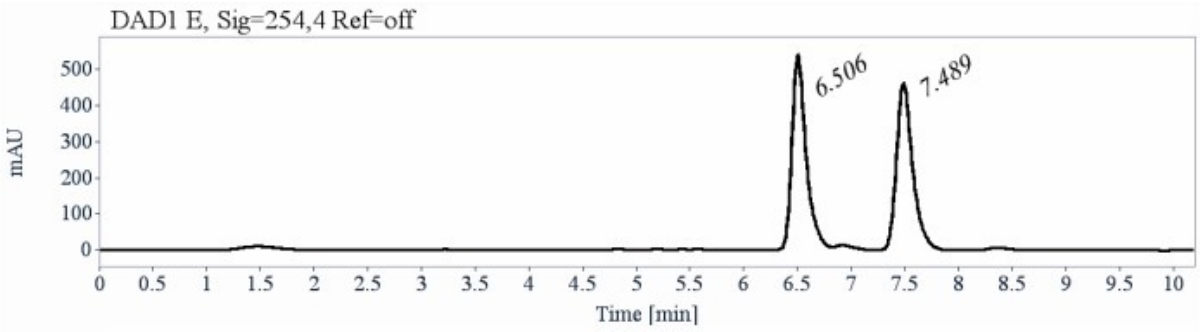


Molecular Weight: 455,8940

Prepared following general procedure using **3h** (27 mg) and **2b** (22 mg) for 1.5 days. The crude product was purified on silica (EtOAc/ Petroleum ether = 0:100 to 5:95) to yield a light-yellow solid (29 mg, 0.063 mmol, 63%)

R_f = 0.50 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +233°, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.64 – 7.27 (m, 4H), 7.19 – 6.80 (m, 5H), 6.64 (dd, *J* = 8.6, 2.5 Hz, 2H), 5.88 (dd, *J* = 6.4, 4.6 Hz, 1H), 5.58 (d, *J* = 1.5 Hz, 1H), 4.68 (dd, *J* = 12.2, 6.4 Hz, 1H), 3.93 (s, 1H), 3.80 (dd, *J* = 12.2, 4.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.4, 157.7, 139.6, 137.7, 136.5, 133.9, 132.9, 132.3, 129.0, 128.9, 128.8, 128.6, 127.8, 126.1, 117.8, 117.5, 116.2, 115.5, 111.5, 109.7, 64.7, 56.6. **MP** = 172.9 - 174.1 °C**, HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{27}H_{18}ClNO_4Ag^+$ 563.9963, found 563.9960. **HPLC analysis** (Lux-Cellulose-4, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **98% ee**, **t_r1**: 6.50 min, **t_r2**: 7.48 min

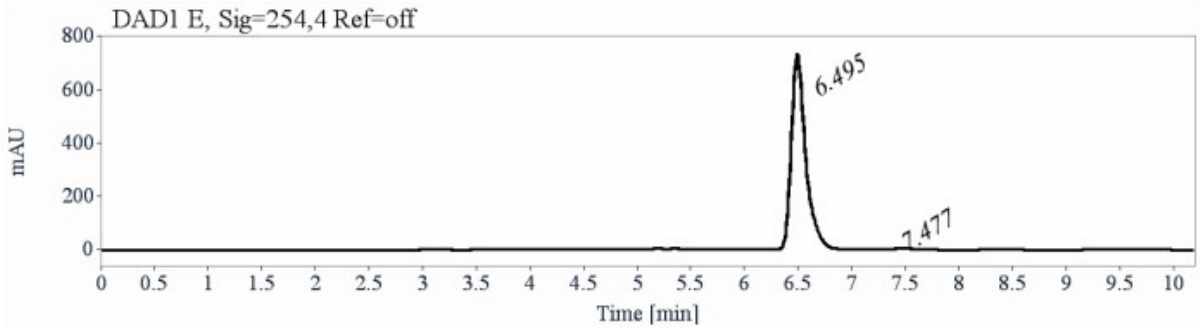
Chiral HPLC spectrum of *rac*-**4hb**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.51	4978	50.60	1.21		
7.49	4860	49.40	1.54	1.28	3.96
Sum	9838	100.00			

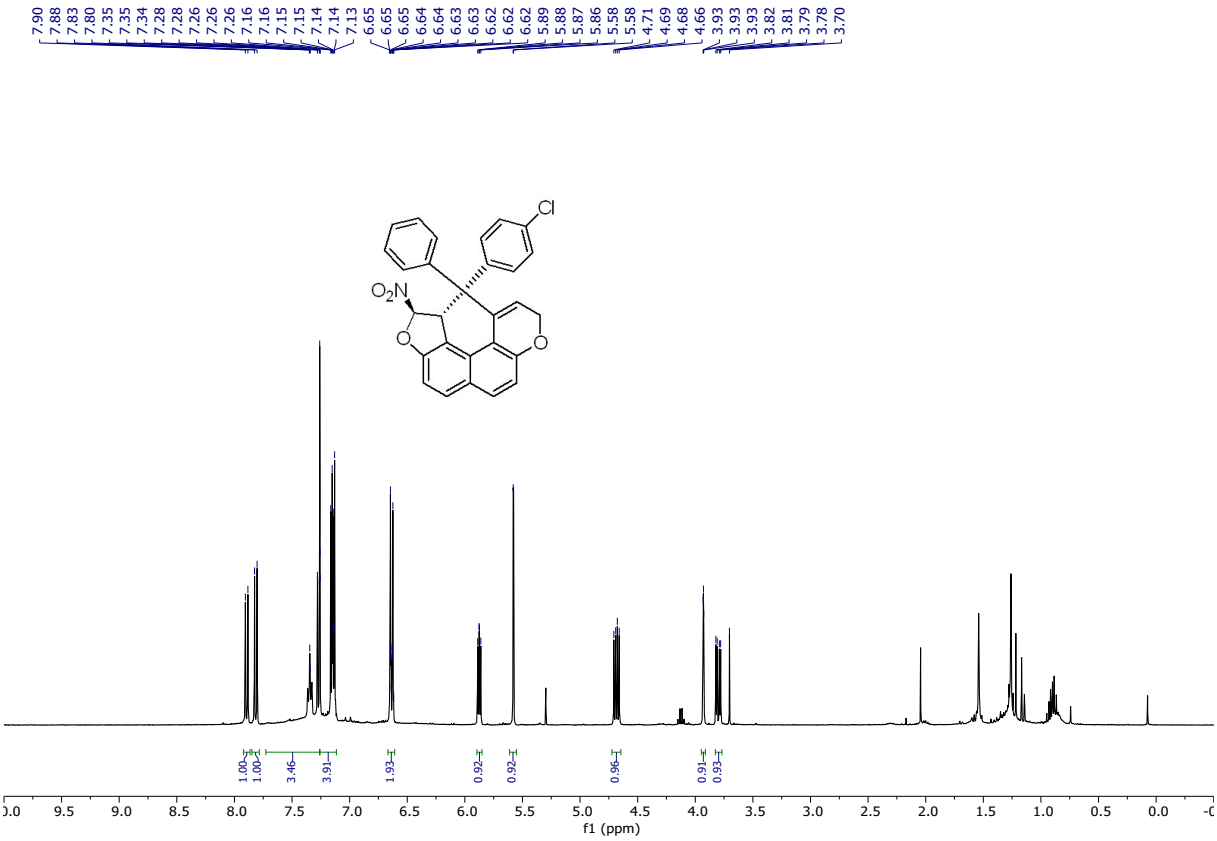
Chiral HPLC spectrum of **4hb**



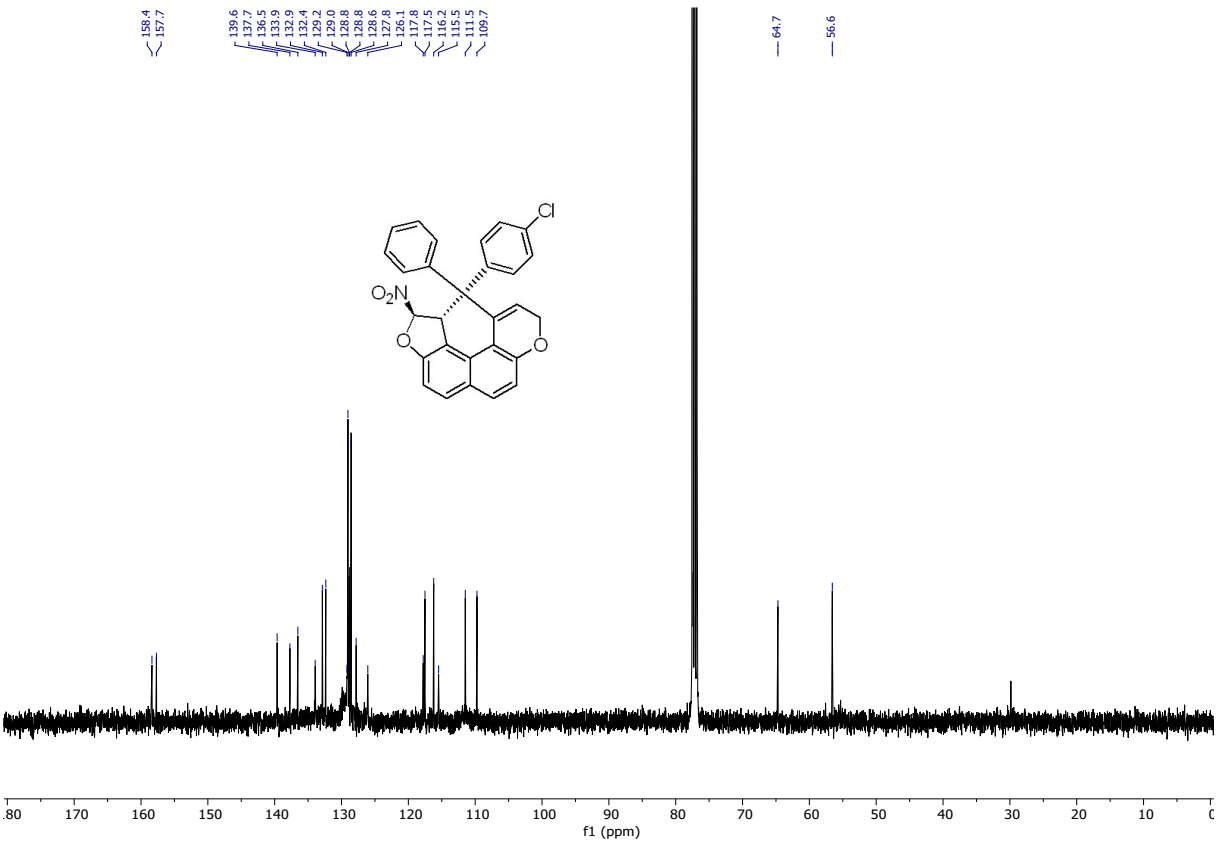
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.49	6881	98.94	1.20		
7.48	74	1.06	1.53	1.28	3.93
Sum	6954	100.00			

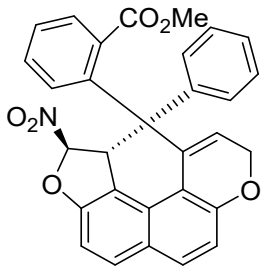
^{1}H NMR spectrum of **4hb** in $CDCl_3$



^{13}C NMR spectrum of **4hb** in $CDCl_3$



*Methyl 2-((1R,2R)-2-nitro-1-phenyl-1,2-dihydro-9H-benzofuro[4,5-f]chromen-11-yl)benzoate (**4ia**)*

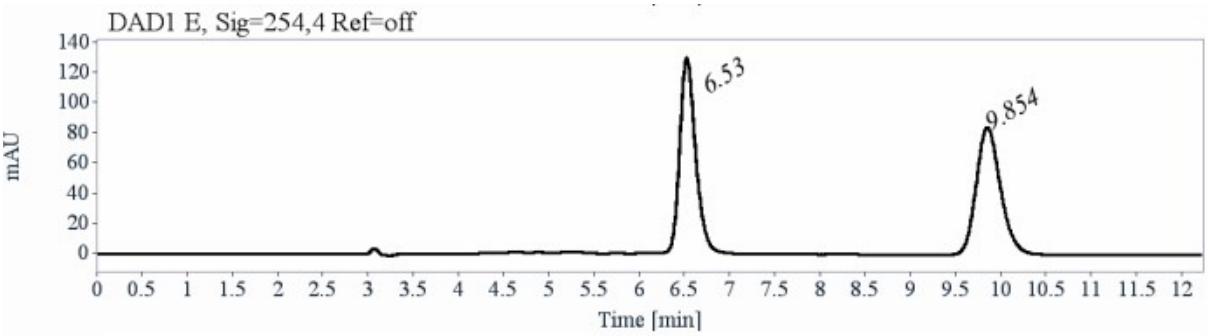


Molecular Weight: 479,4880

Prepared following general procedure using **3i** (33 mg) and **2a** (18 mg) for 4 days. The crude product was purified on silica (EtOAc/ Petroleum ether = 0:100 to 15:85) to yield a light-yellow solid (28 mg, 0.058 mmol, 58%)

R_f = 0.51 (EtOAc/ Petroleum ether 1:4) , **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +308°, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.47 (d, *J* = 41.1 Hz, 4H), 7.24 (d, *J* = 8.7 Hz, 1H), 7.21 – 7.11 (m, 4H), 6.68 (d, *J* = 5.4 Hz, 2H), 5.85 (s, 1H), 5.64 (s, 1H), 4.73 (dd, *J* = 12.2, 6.4 Hz, 1H), 3.86 (s, 2H), 2.99 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.9, 157.7, 137.8, 132.5, 132.3, 131.8, 130.5, 130.1, 129.7, 128.8, 128.7, 127.95, 127.9, 127.1 (2C), 118.2, 117.6, 116.0, 111.9, 109.9, 64.5, 56.7, 51.8 (1C missing). **MP** = 260.5 – 261.3 °C, **HRMS-ESI$^+$ (m/z)**: $[M+Na]^+$ calculated for $C_{29}H_{21}NO_6Na^+$ 502.1261, found 502.1263. **HPLC analysis** (Lux-Cellulose-4, Heptane/Ethanol (70/30), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **92% ee**, **t_r1**: 6.53 min, **t_r2**: 9.85 min

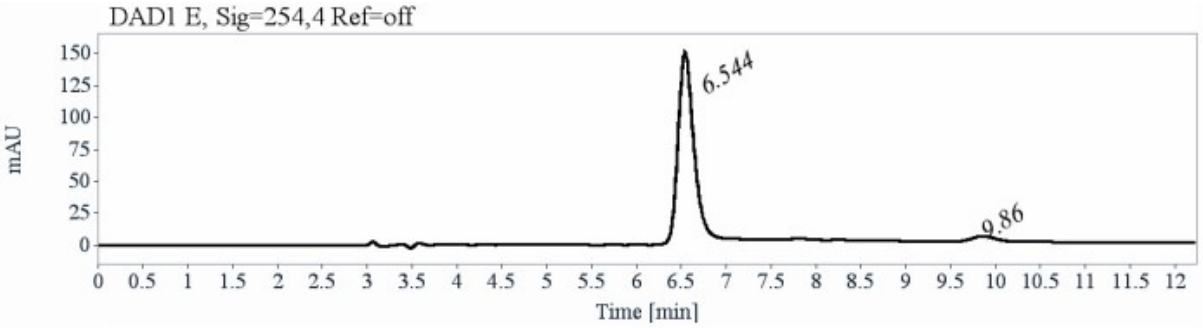
Chiral HPLC spectrum of *rac*-**4ia**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.53	1593	50.30	1.21		
9.85	1574	49.70	2.34	1.93	8.27
Sum	3166	100.00			

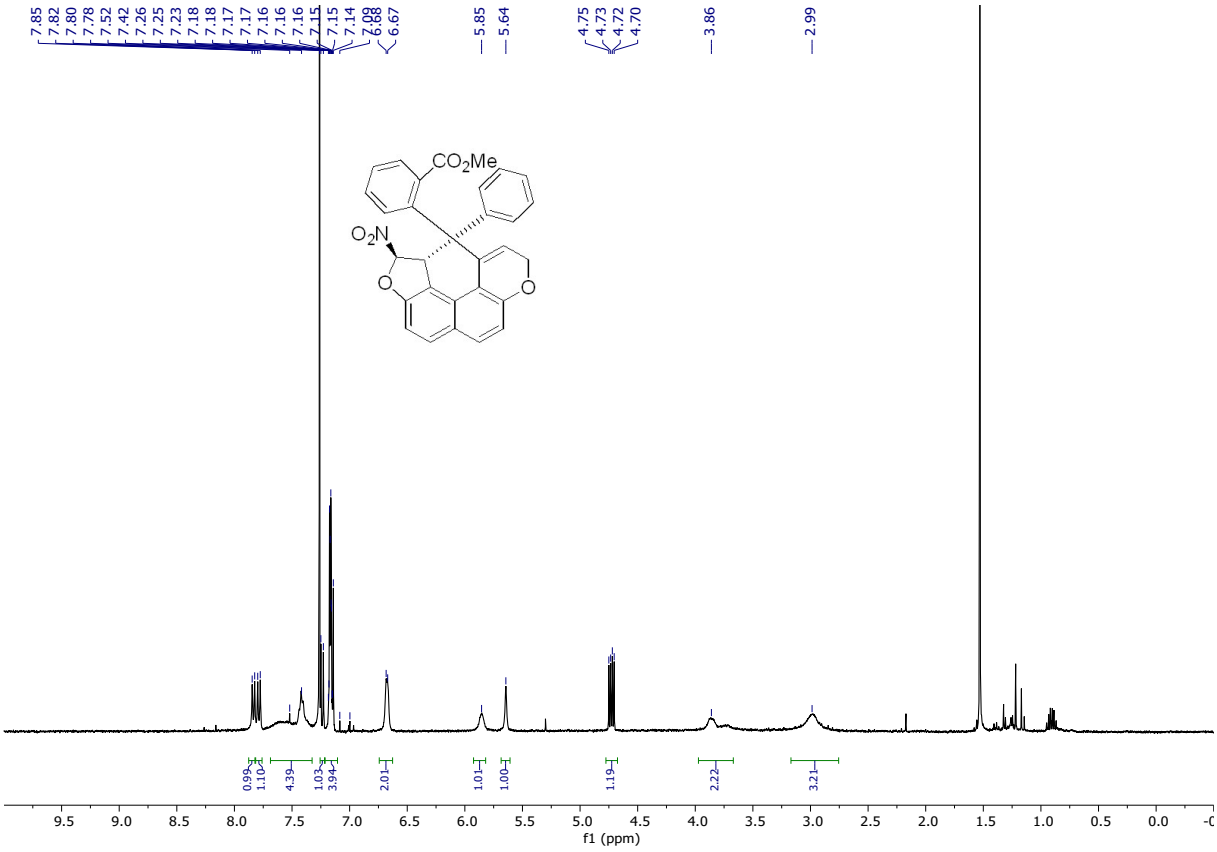
Chiral HPLC spectrum of *rac*-**4ia**



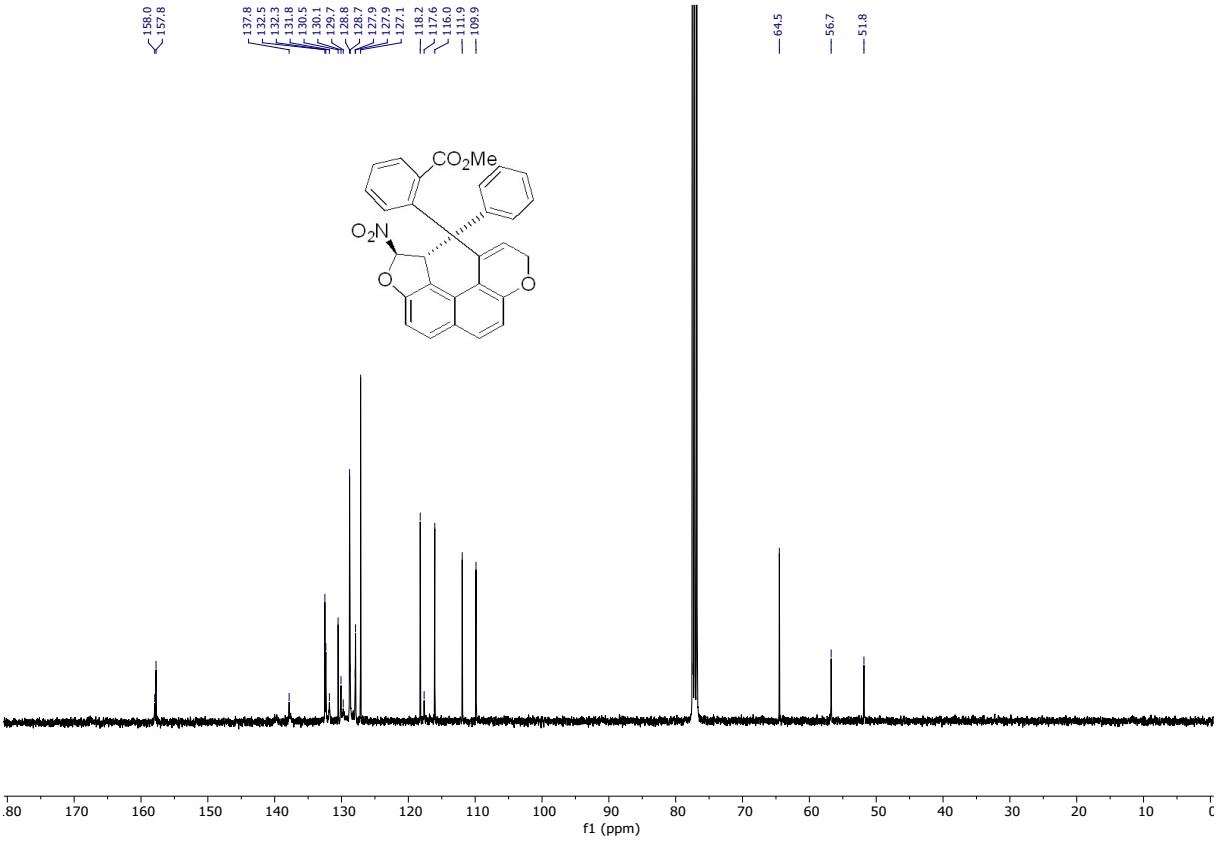
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.54	2034	96.19	1.22		
9.86	80	3.81	2.34	1.92	8.32
Sum	2115	100.00			

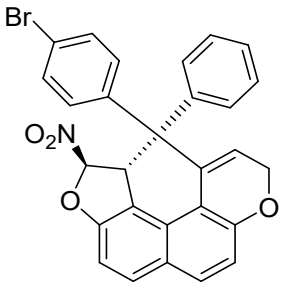
^{1}H NMR spectrum of **4ia** in $CDCl_3$



^{13}C NMR spectrum of **4ia** in $CDCl_3$



*(1R,2R)-11-(4-bromophenyl)-2-nitro-1-phenyl-1,2-dihydro-9H-benzofuro[4,5-f]chromene (**4ja**)*

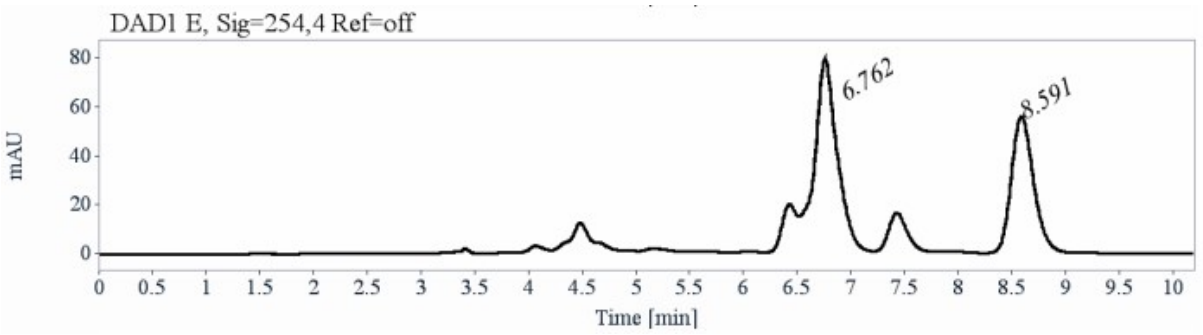


Molecular Weight: 500,3480

Prepared following general procedure using **3j** (35.3 mg) and **2a** (18 mg) for 48 h. The crude product was purified on silica (EtOAc/ Petroleum ether = 0:100 to 5:95) to yield an off-white powder (60 mg, 0.06 mmol, 60%)

R_f = 0.54 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +276°, **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.68 – 7.25 (m, 4H), 7.24 – 7.07 (m, 5H), 6.74 – 6.63 (m, 2H), 5.86 (dd, *J* = 6.4, 4.5 Hz, 1H), 5.66 (d, *J* = 1.4 Hz, 1H), 4.66 (dd, *J* = 12.3, 6.4 Hz, 1H), 4.05 (s, 1H), 3.76 (dd, *J* = 12.2, 4.6 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.3, 157.8, 138.6, 137.7, 136.9, 132.7, 132.5, 132.2, 128.9, 128.6, 128.1, 127.8, 127.6, 127.0, 122.9, 118.1, 117.7, 116.0, 115.1, 111.4, 109.9, 64.6, 57.1.**MP** = 226.1 – 227.3 °C**, HRMS-ESI$^+$ (m/z)**: $[M+Na]^+$ calculated for $C_{27}H_{18}BrNO_4Na^+$ 522.0311, found 522.0309. **HPLC analysis** (Lux-Cellulose-4, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **97% ee**, **t_r1**: 6.76 min, **t_r2**: 8.59 min

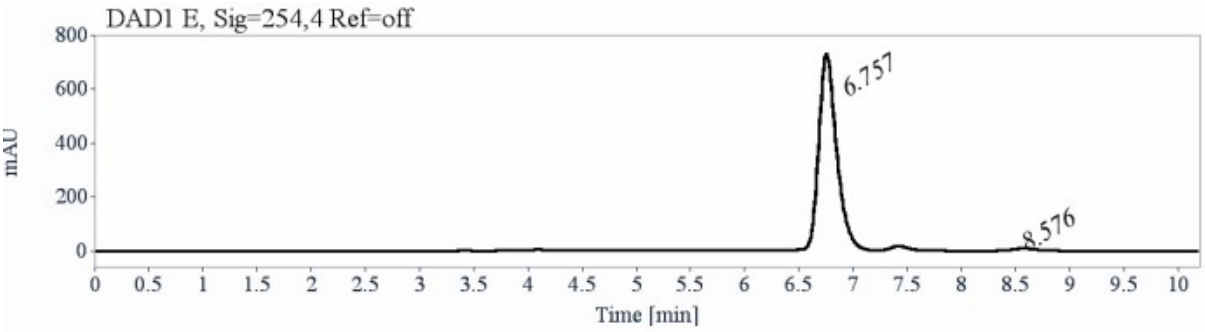
Chiral HPLC spectrum of *rac*-**4ja**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.76	1167	59.16	1.29		
8.59	806	40.84	1.91	1.48	5.04
Sum	1973	100.00			

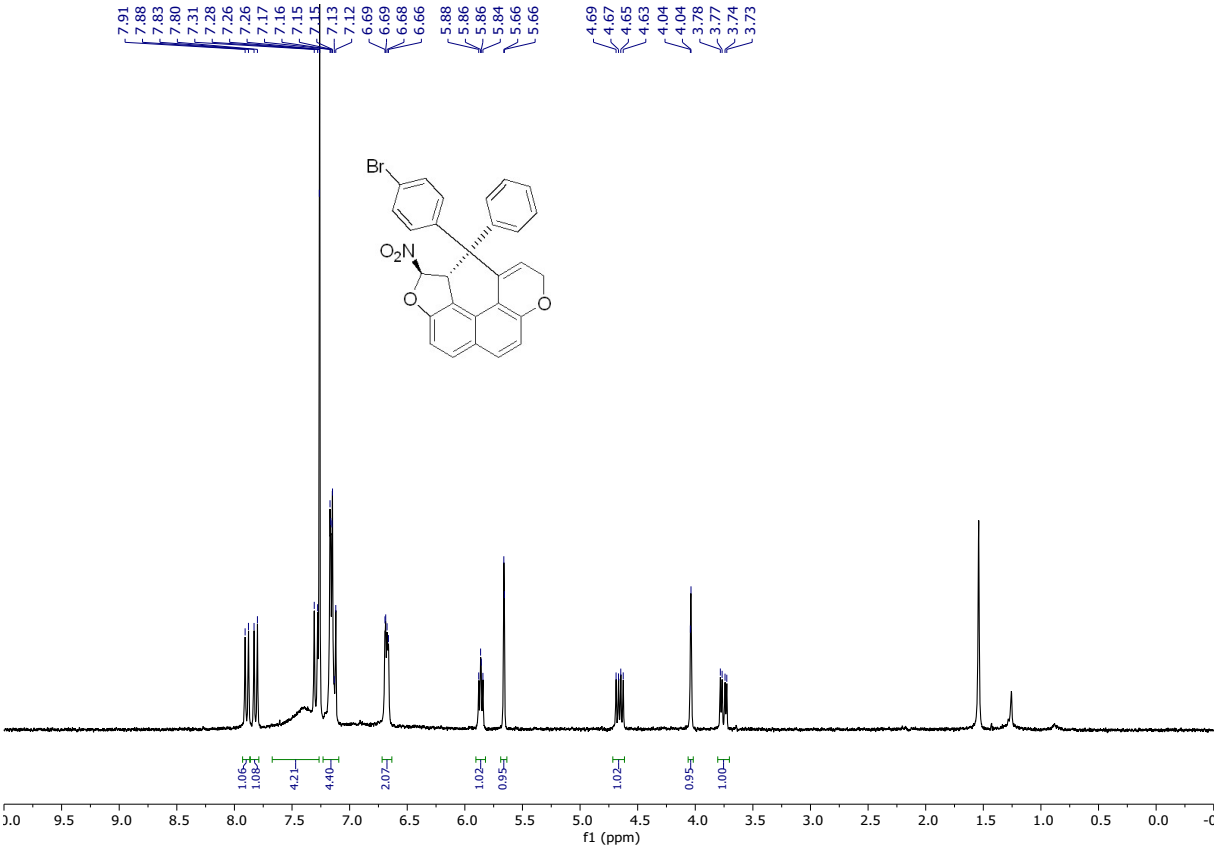
Chiral HPLC spectrum of **4ja**



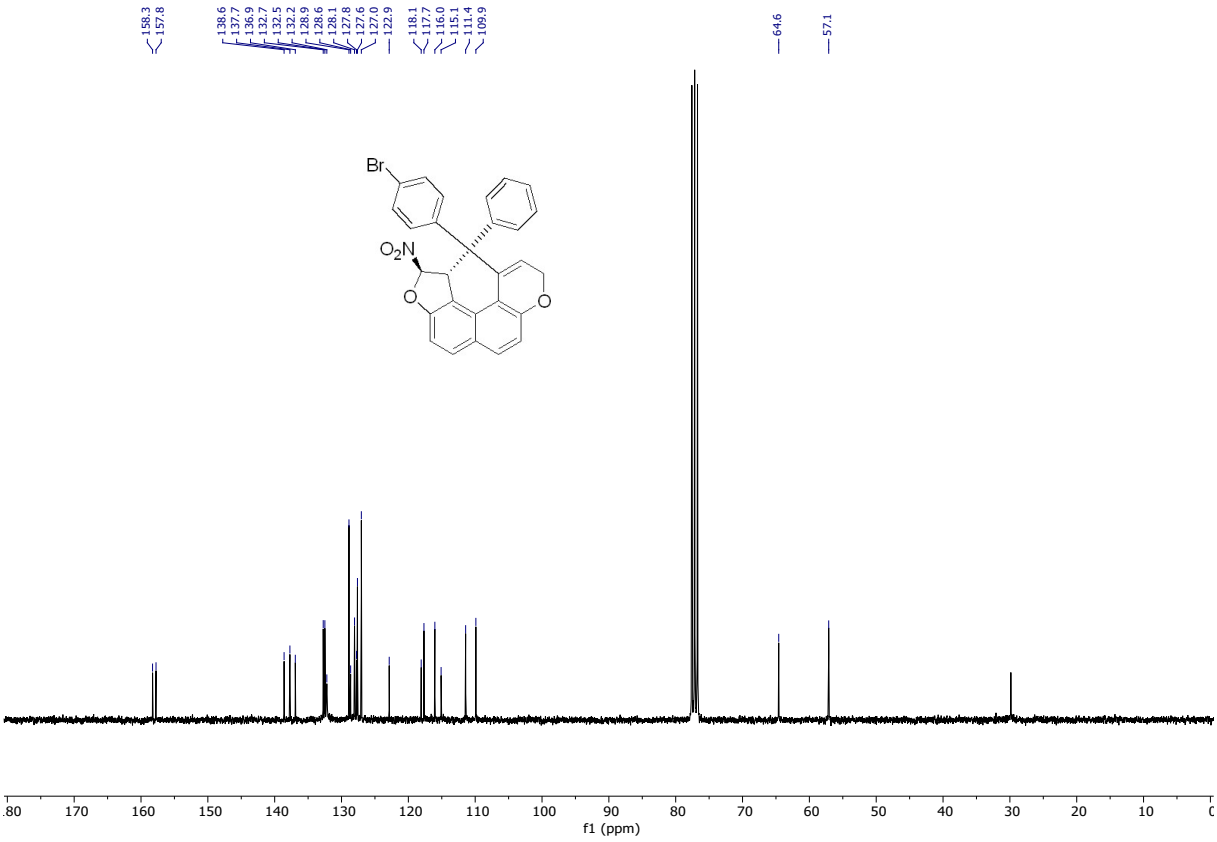
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.76	8441	98.49	1.29		
8.58	130	1.51	1.91	1.48	5.37
Sum	8571	100.00			

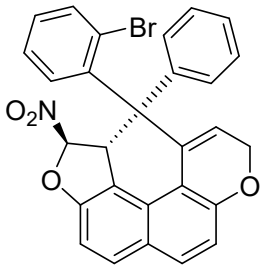
^{1}H NMR spectrum of **4ja** in $CDCl_3$



^{13}C NMR spectrum of **4ja** in $CDCl_3$



*(1R,2R)-11-(2-Bromophenyl)-2-nitro-1-phenyl-1,2-dihydro-9H-benzofuro[4,5-f]chromene (**4ka**)*

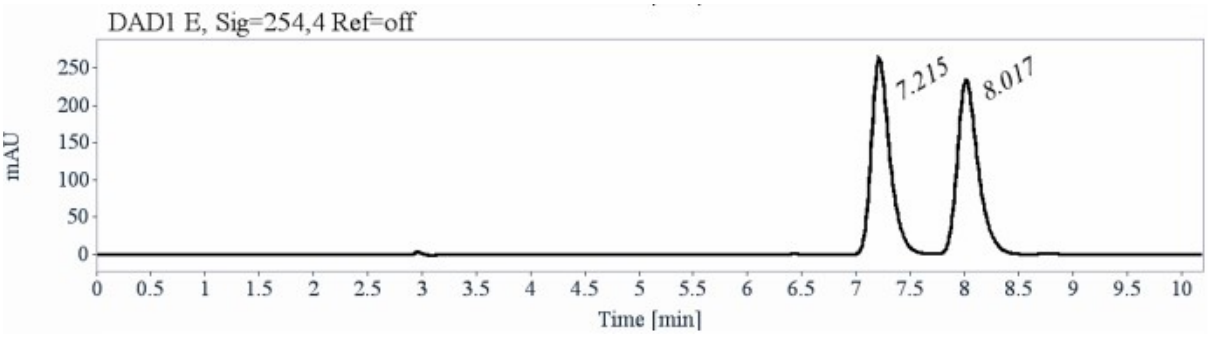


Molecular Weight: 500,3480

Prepared following general procedure using **3k** (35.3 mg) and **2a** (18.3 mg) for 72 h. The crude product was purified on silica (EtOAc/ Petroleum ether = 0:100 to 2:8) to yield a light-yellow solid (31 mg, 0.062 mmol, 62%)

R_f = 0.1 (EtOAc/ Petroleum ether 1:9) , **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +200°, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.76 – 6.96 (m, 9H), 6.80 (s, 2H), 6.18 (d, *J* = 103.8 Hz, 1H), 5.70 (s, 1H), 4.69 (dd, *J* = 12.4, 6.5 Hz, 1H), 4.63 – 3.61 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$, at 250K) mixture of diastereomers δ 158.1, 157.6, 157.2, 157.0, 140.8, 137.8, 137.7, 137.4, 137.3, 135.1, 134.4, 134.1, 132.93 132.7, 132.6, 132.4, 130.9, 129.9, 129.0, 128.8, 128.6, 128.5, 128.3, 128.0, 127.8, 127.7, 127.4, 127.4, 127.3, 127.0, 121.2, 121.1, 120.7, 119.7, 117.9, 116.2, 116.1, 116.0, 115.9, 115.8, 111.8, 111.4, 109.8, 109.5, 64.7, 64.5, 56.6, 56.5. **MP** = 178.4 – 178.9 °C**, HRMS-ESI$^+$ (m/z)**: $[M+H]^+$ calculated for $C_{27}H_{19}BrNO_4^+$ 500.0492, found 500.0489. **HPLC analysis** (Lux-Cellulose-4, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **98.5% ee**, **t_r1**: 7.21min, **t_r2**: 8.01 min.

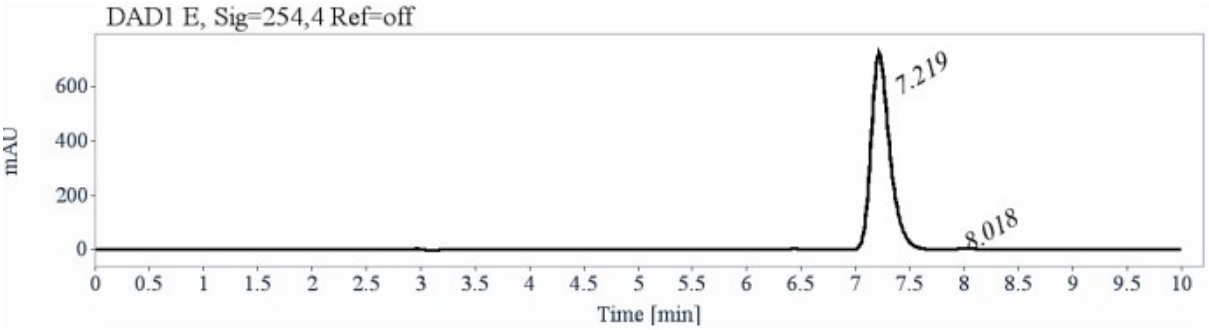
Chiral HPLC spectrum of *rac*-**4ka**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.22	3098	50.00	1.45		
8.02	3099	50.00	1.72	1.19	2.50
Sum	6197	100.00			

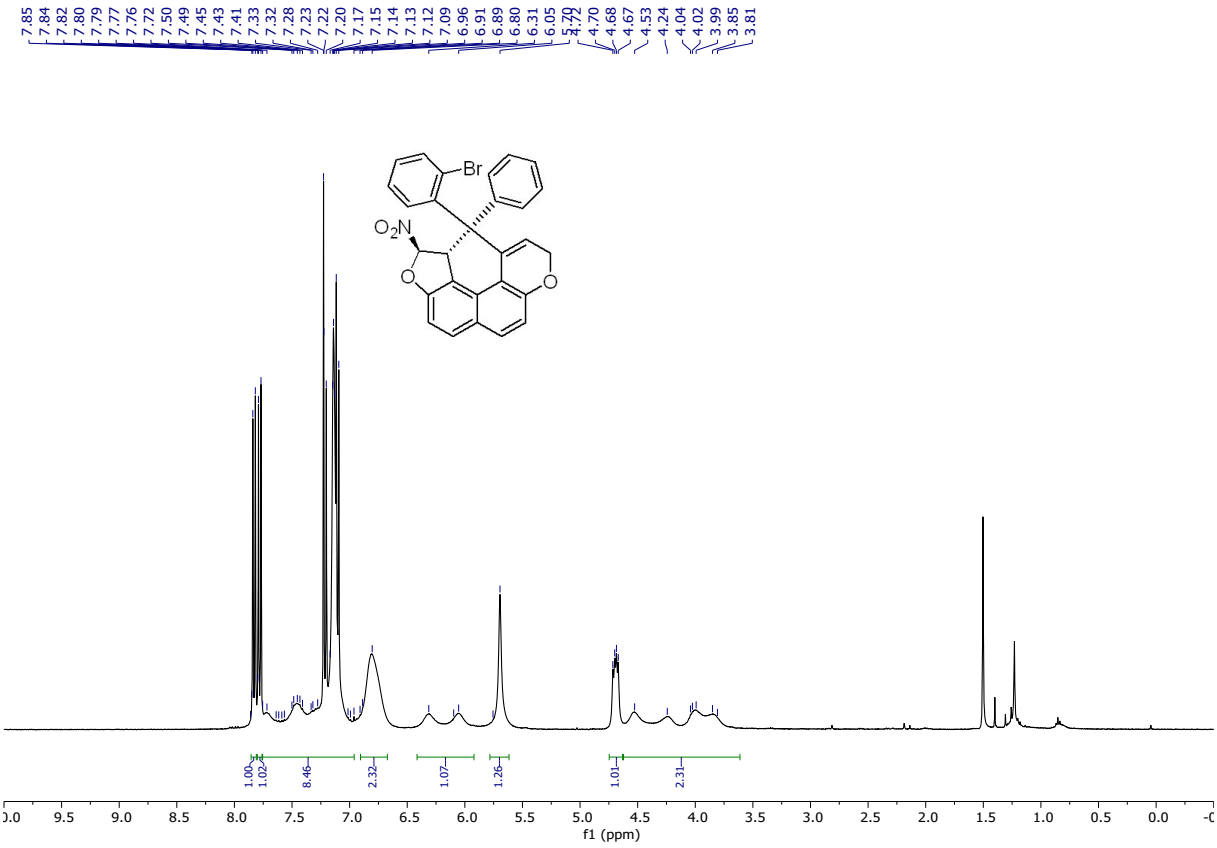
Chiral HPLC spectrum of **4ka**



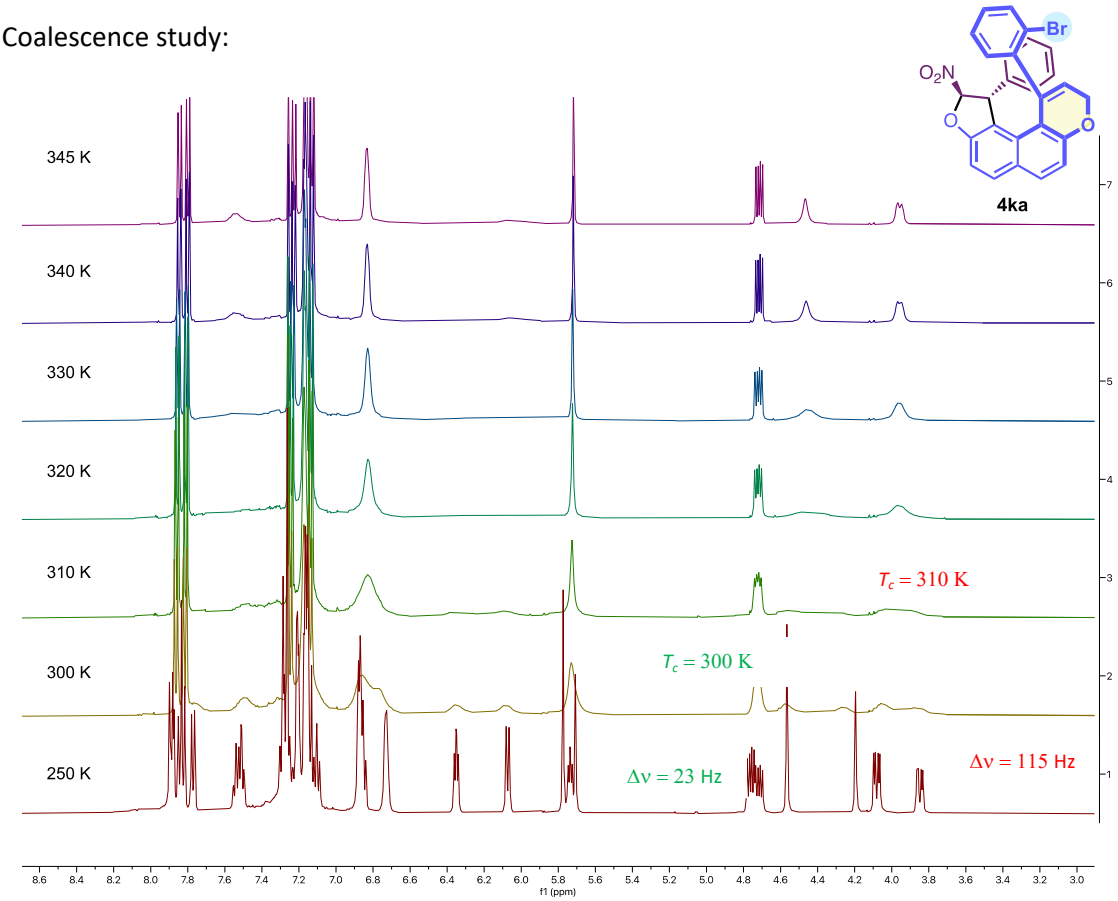
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.22	8554	99.28	1.45		
8.02	62	0.72	1.72	1.19	2.56
Sum	8616	100.00			

^{1}H NMR spectrum of **4ka** in $CDCl_3$ (at 293K)



Coalescence study:



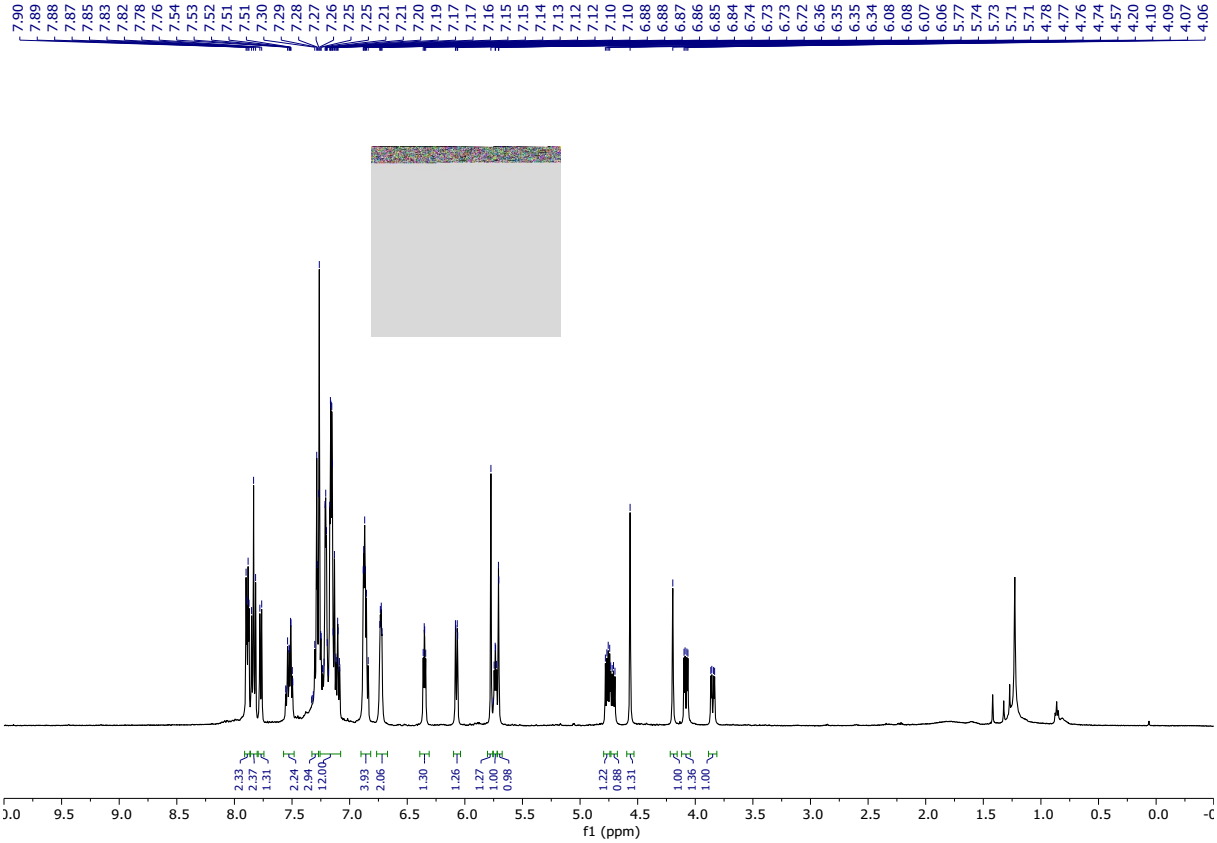
$$\Delta G^{\neq}_{eT_c} = RT_c\left[ln\left(\frac{k_B T_c}{h}\right) - ln\left(\pi\frac{\Delta\nu}{\sqrt{2}}\right)\right]$$

$$\Delta G^{\neq}_{eT_c} = 8.31\cdot 10^{-3}\cdot 310\left[ln\left(\frac{1.38\cdot 10^{-23}\cdot 310}{6.63\cdot 10^{-34}}\right) - ln\left(\pi\frac{115}{\sqrt{2}}\right)\right] = 62\ kJ.mol^{-1}$$

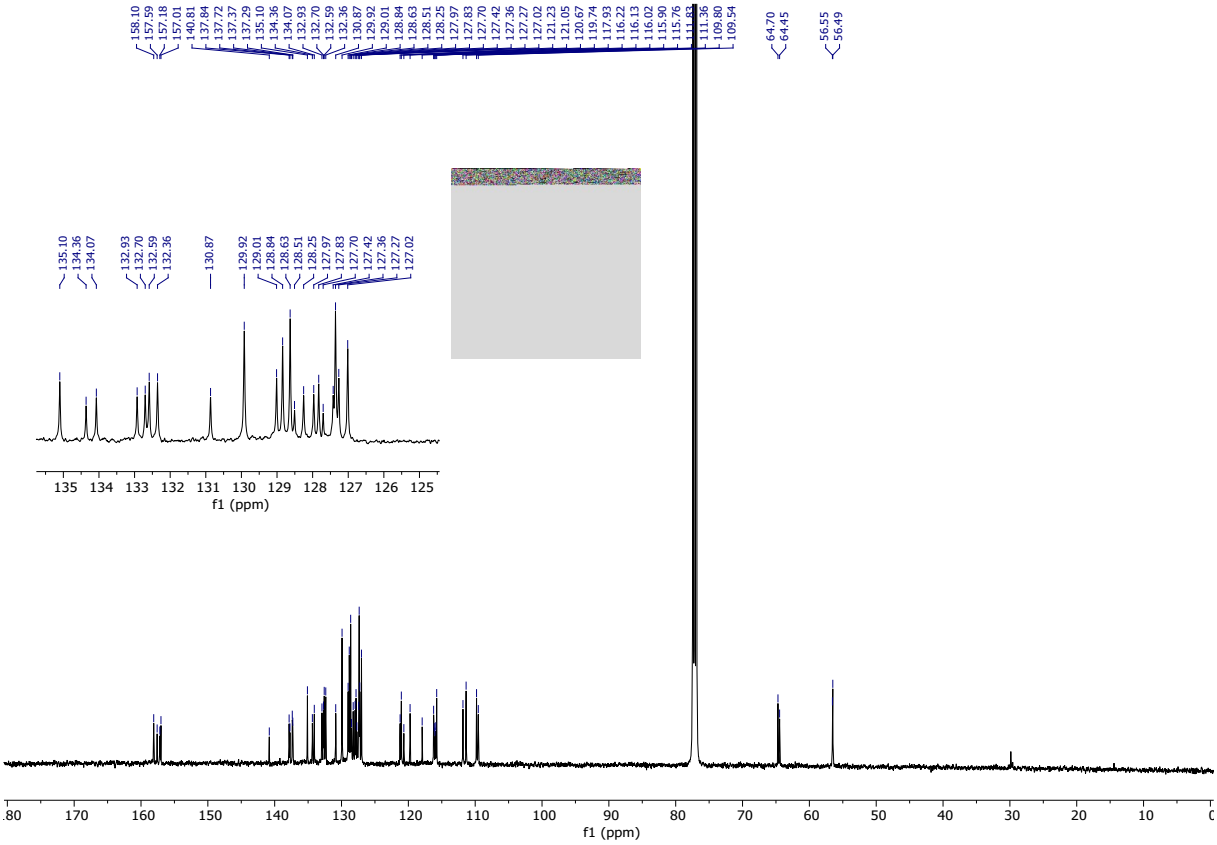
$$\Delta G^{\neq}_{eT_c} = 8.31\cdot 10^{-3}\cdot 300\left[ln\left(\frac{1.38\cdot 10^{-23}\cdot 300}{6.63\cdot 10^{-34}}\right) - ln\left(\pi\frac{23}{\sqrt{2}}\right)\right] = 64\ kJ.mol^{-1}$$

The diastereomerization barrier for 4ka is $\Delta G^{\neq}_{exp}(diast.) = 63\ kJ/mol$

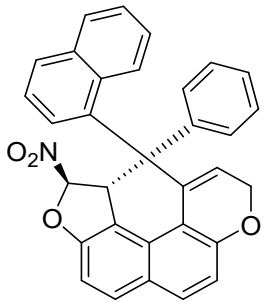
^{1}H NMR spectrum of **4ka** in $CDCl_3$ (at 250K)



^{13}C NMR spectrum of **4ka** in $CDCl_3$ (at 250K)



*(1R,2R)-11-(naphthalen-1-yl)-2-nitro-1-phenyl-1,2-dihydro-9H-benzofuro[4,5-f]chromene (**4la**)*

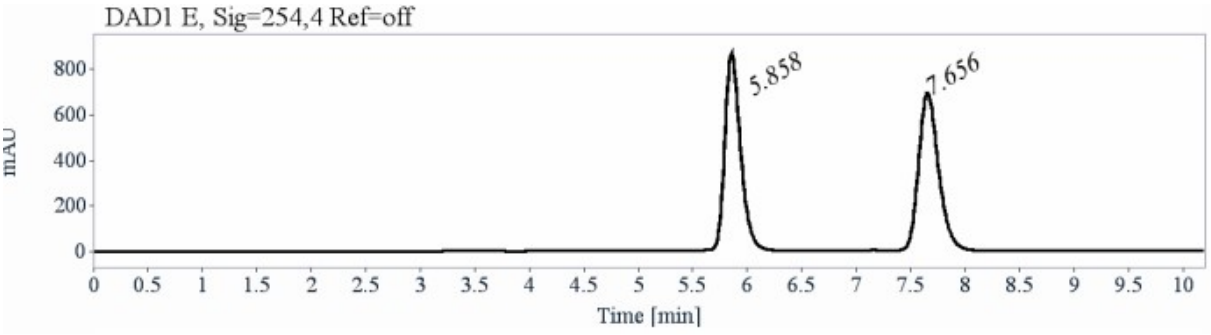


Molecular Weight: 479,4880

Prepared following general procedure using **3l** (32 mg) and **2a** (18 mg) for 96 h. The crude product was purified on silica (EtOAc/ Petroleum ether = 0:100 to 15:85) to yield a light-yellow solid (32 mg, 0.068 mmol, 68%)

R_f = 0.48 (EtOAc/ Petroleum ether 15:85) , **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +211°, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 – 8.20 (m, 1H), 8.07 – 7.96 (m, 1H), 7.95 – 7.85 (m, 2H), 7.84 – 7.72 (m, 1H), 7.69 – 7.49 (m, 2H), 7.26 – 6.63 (m, 7H), 6.51 – 6.20 (m, 2H), 6.12 – 5.85 (m, 1H), 5.55 – 5.33 (m, 1H), 4.74 (dd, *J* = 12.1, 6.4 Hz, 1H), 4.25 – 3.85 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.5, 157.7, 137.2, 136.25, 135.17, 134.8, 132.7, 132.5, 130.3, 129.34, 129.29, 128.6, 128.5, 127.9, 127.5, 126.3, 126.1, 125.8, 125.4, 125.1, 120.3, 117.4, 117.2, 116.0, 111.8, 109.7, 64.7, 56.5. **MP** = 178.8 – 179.1 °C, **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{31}H_{21}NO_4Ag^+$ 578.0516, found 578.0521 **HPLC analysis** (Lux-Cellulose-4, Heptane/Ethanol (95/5), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **97% ee**, **t_r1**: 5.85 min, **t_r2**: 7.65 min

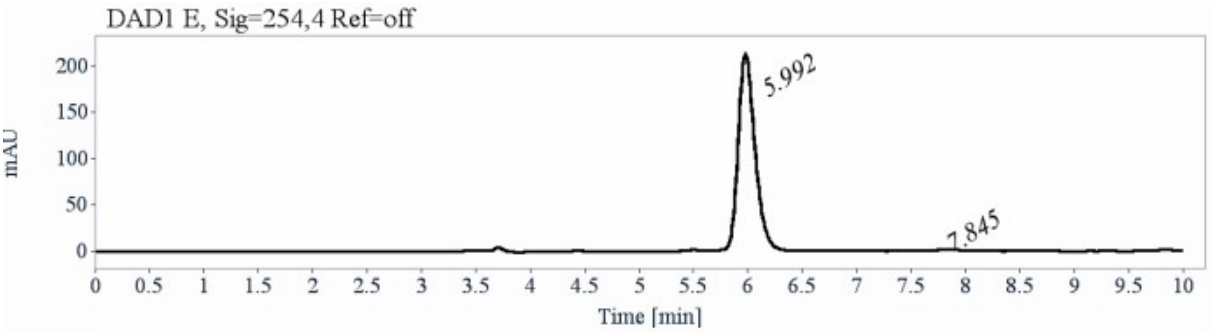
Chiral HPLC spectrum of *rac*-**4la**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.86	8863	49.80	0.99		
7.66	8934	50.20	1.60	1.62	6.08
Sum	17797	100.00			

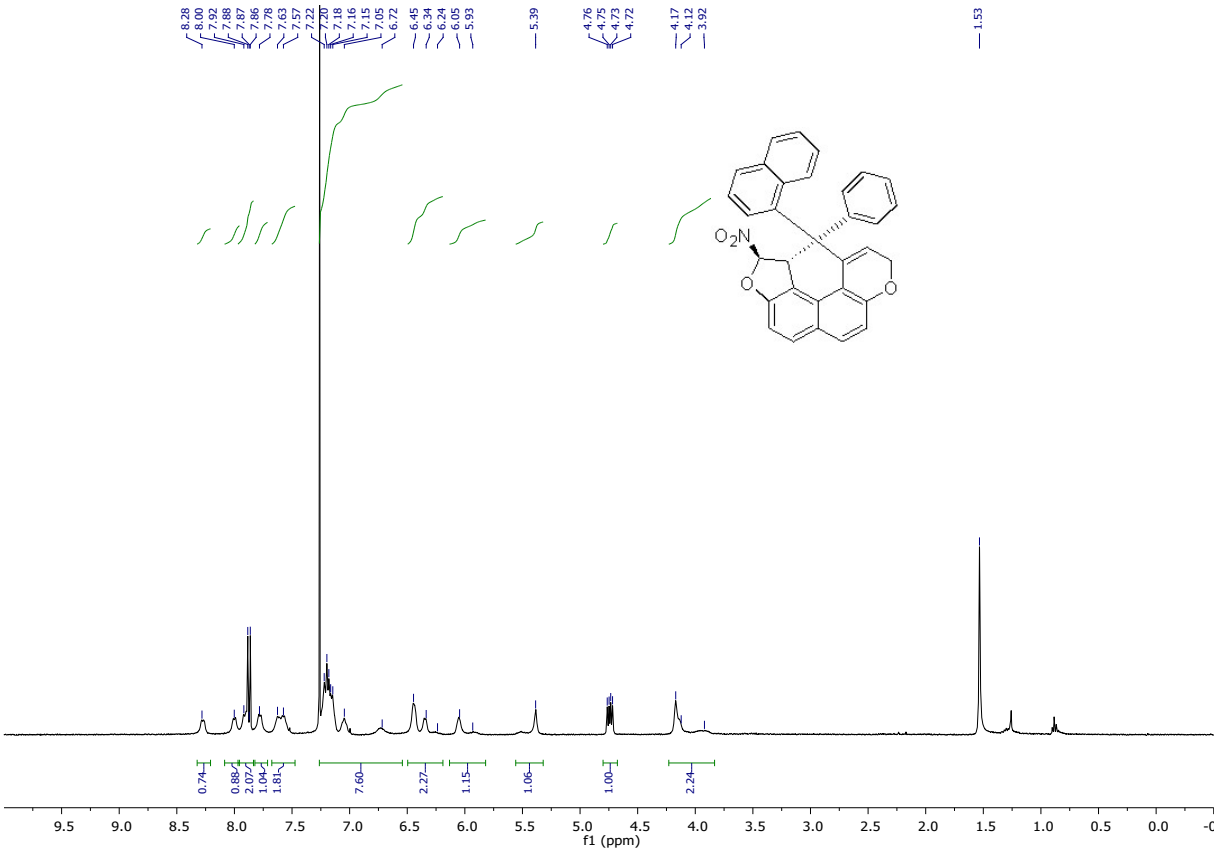
Chiral HPLC spectrum of **4la**



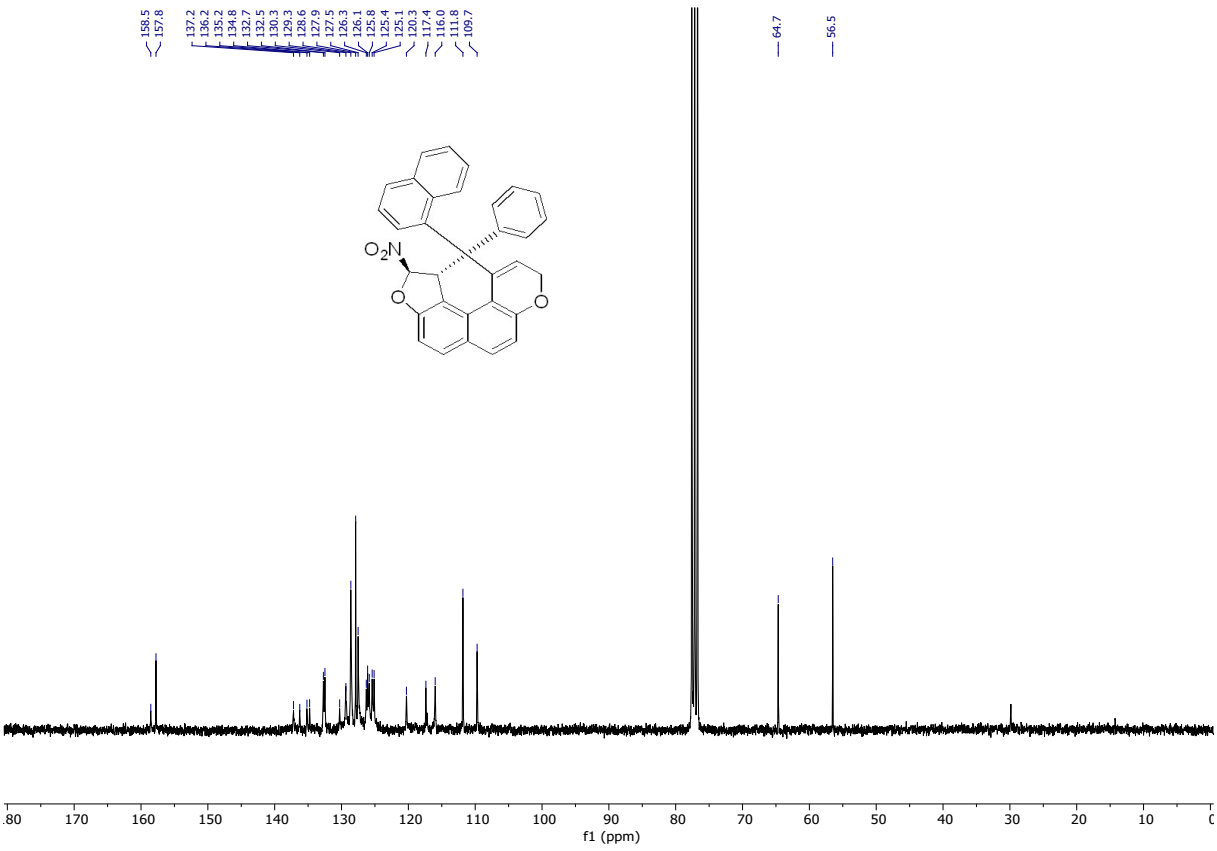
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.99	2322	98.66	1.03		
7.85	32	1.34	1.66	1.61	5.75
Sum	2353	100.00			

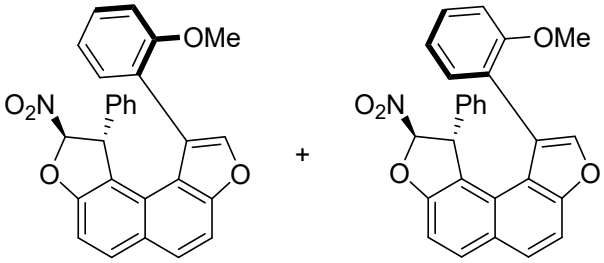
^{1}H NMR spectrum of **4la** in $CDCl_3$



^{13}C NMR spectrum of **4la** in $CDCl_3$



*(1R,2R)-9-benzyl-2-nitro-1,10-diphenyl-1,2-dihydronaphtho[2,1-b:7,8-b']difuran (**4na**)*



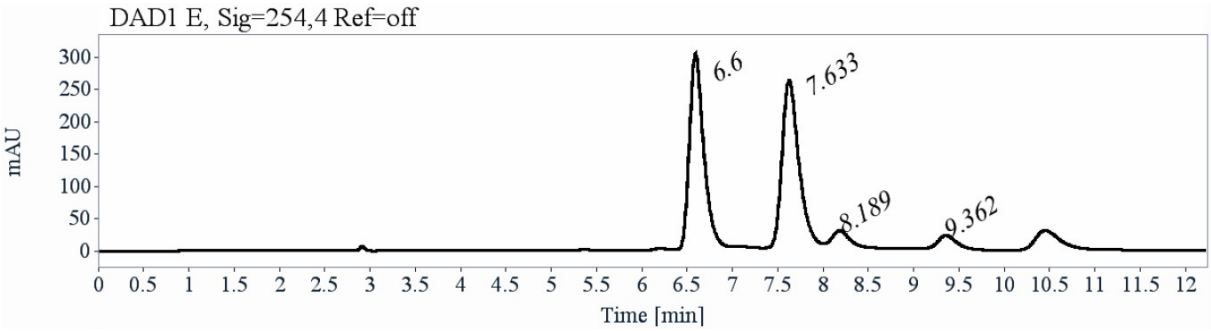
major **minor**

Molecular Weight: 437,4510

Prepared following general procedure using **3n** (29 mg, 0.1 mmol, 1.0 equiv.) and **2a** (18 mg, 0.1 mmol, 1.0 equiv.) for 10 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:99 to 1:9) to yield a white solid (35 mg, 0.08 mmol, 80%, *rd* = 5:1)

R_f = 0.29 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +285°, **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.06 (d, *J* = 8.7 Hz, 1H), 7.84 (d, *J* = 8.9 Hz, 0.85H), 7.83 (d, *J* = 8.9 Hz, 0.15H), 7.63 (d, *J* = 8.9 Hz, 1H), 7.57 (s, 0.15H), 7.52 (ddd, *J* = 8.2, 7.5, 1.8 Hz, 1H), 7.41 (s, 0.85H), 7.41 (dd, *J* = 8.7, 0.6 Hz, 0.85H), 7.39 (d, *J* = 9.0 Hz, 0.3H), 7.15 – 6.95 (m, 4H), 6.95 – 6.89 (m, 0.15H), 6.85 (td, *J* = 7.4, 1.0 Hz, 0.85H), 6.72 (dd, *J* = 7.4, 1.8 Hz, 0.85H), 6.40 – 6.30 (m, 0.3H), 6.27 – 6.17 (m, 1.7H), 5.75 (d, *J* = 1.0 Hz, 0.85H), 5.72 (d, *J* = 1.0 Hz, 0.15H), 4.74 (s, 0.85H), 4.46 (s, 0.15H), 3.48 (s, 2.55H), 3.40 (s, 0.45H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 158.2, 157.7, 154.9, 142.6, 137.6, 132.7, 131.6, 130.1, 129.0, 128.5, 127.7, 127.4, 127.4, 127.3, 127.3, 122.7, 121.3, 120.7, 116.7, 112.2, 111.8, 110.1, 109.8, 56.1, 54.9. **MP** = 82 °C, **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{27}H_{19}NO_5Ag^+$, 544.0309 found 544.0307. **HPLC analysis** (Lux-Cellulose-2, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **89% ee** and **89% ee**, **t_r1**: 6.60 min, **t_r2**: 7.63 min and, **t_r1**: 8.19 min, **t_r2**: 9.53 min

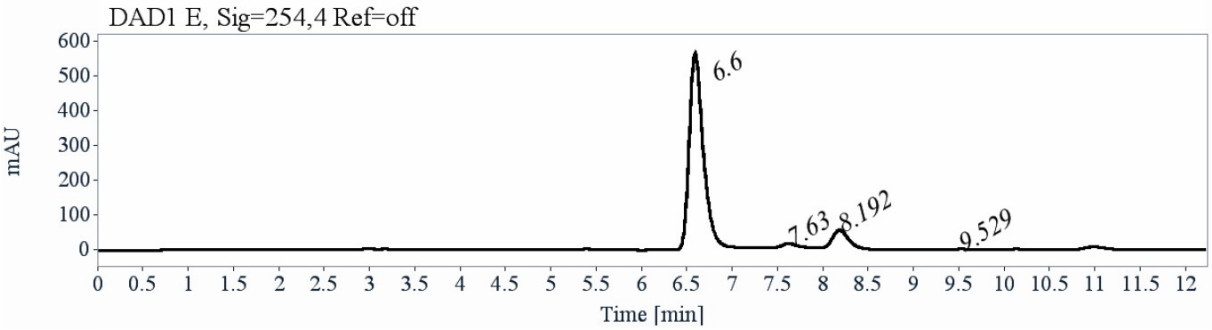
Chiral HPLC spectrum of *rac*-**4na**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.60	3478	45.29	1.24		
7.63	3461	45.06	1.59	1.28	3.33
8.19	440	5.73	1.78	1.12	1.56
9.36	301	3.92	2.17	1.22	3.12
Sum	7680	100.00			

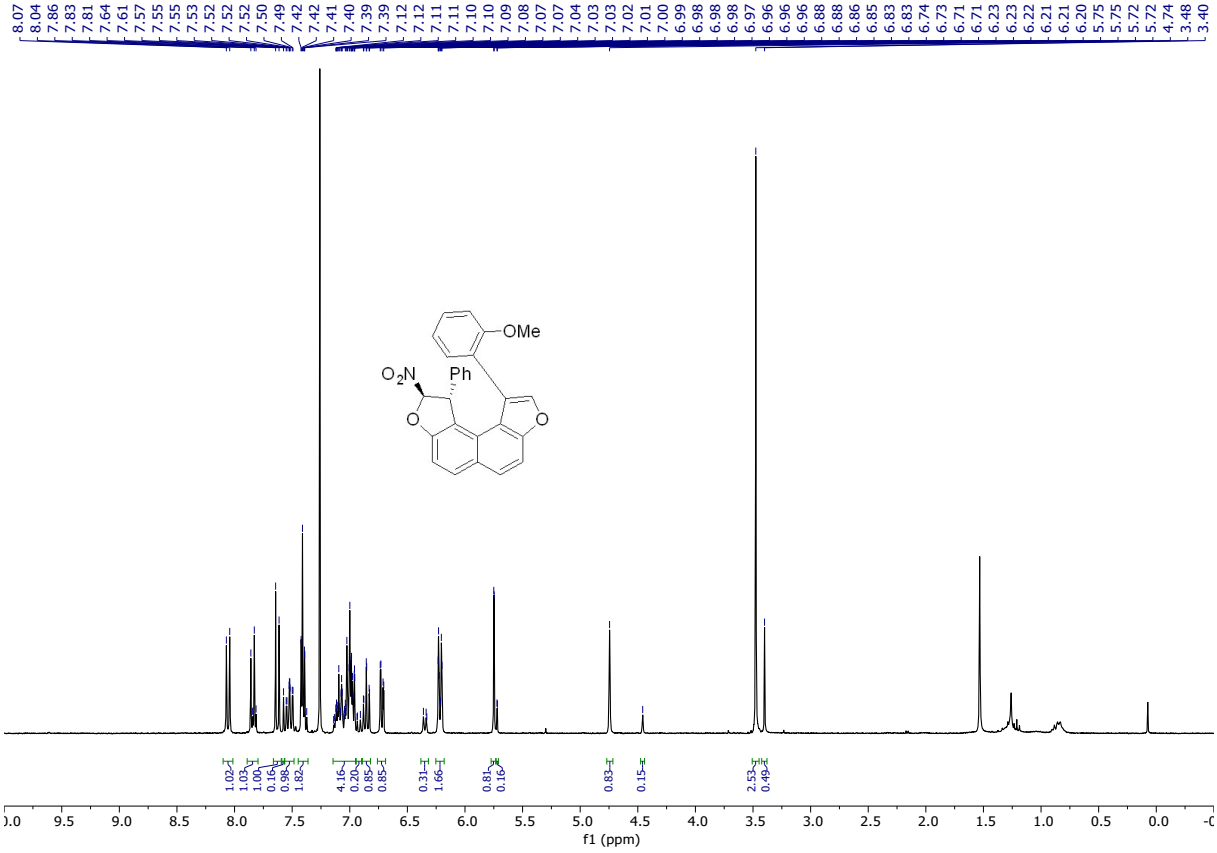
Chiral HPLC spectrum of **4na**



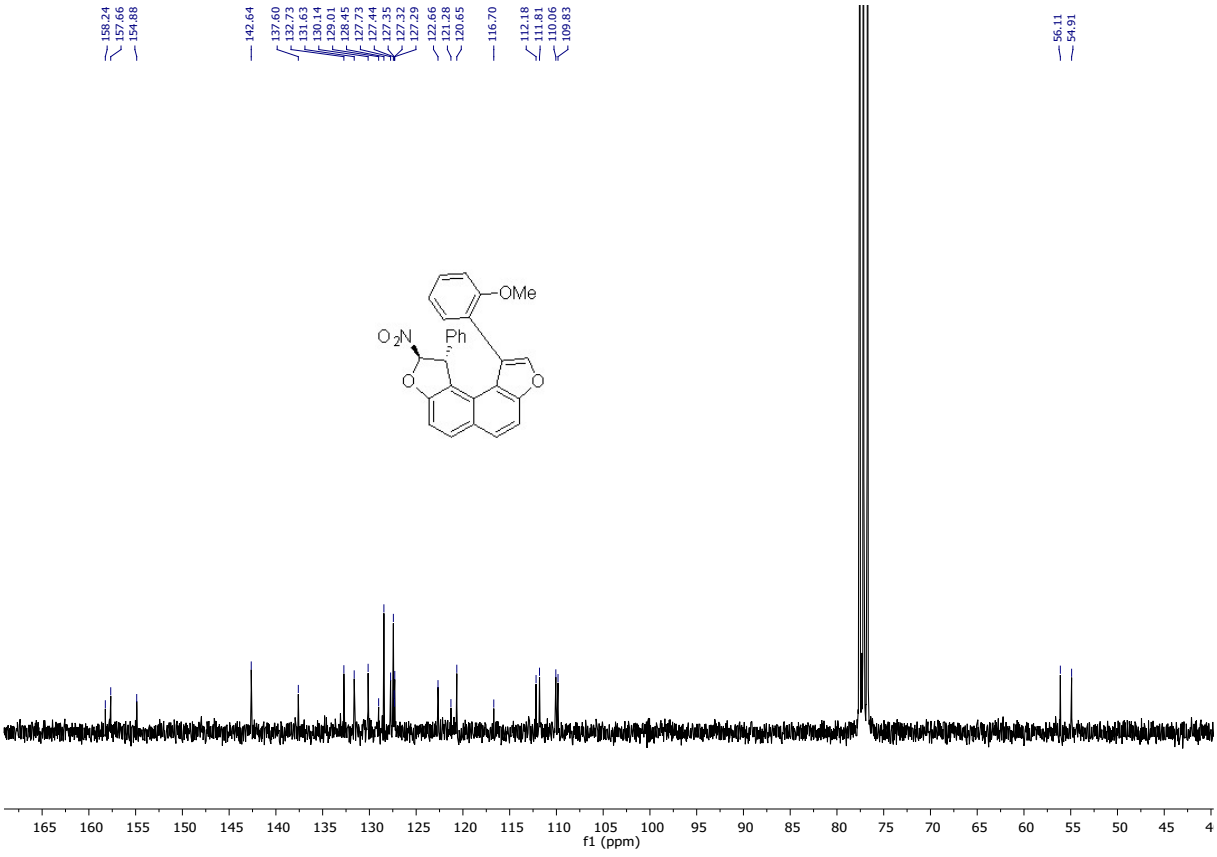
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.60	6317	83.95	1.24		
7.63	364	4.83	1.59	1.28	2.84
8.19	796	10.57	1.78	1.12	1.42
9.53	48	0.64	2.23	1.26	3.09
Sum	7525	100.00			

^{1}H NMR spectrum of **4na** in $CDCl_3$



^{13}C NMR spectrum of **4na** in $CDCl_3$



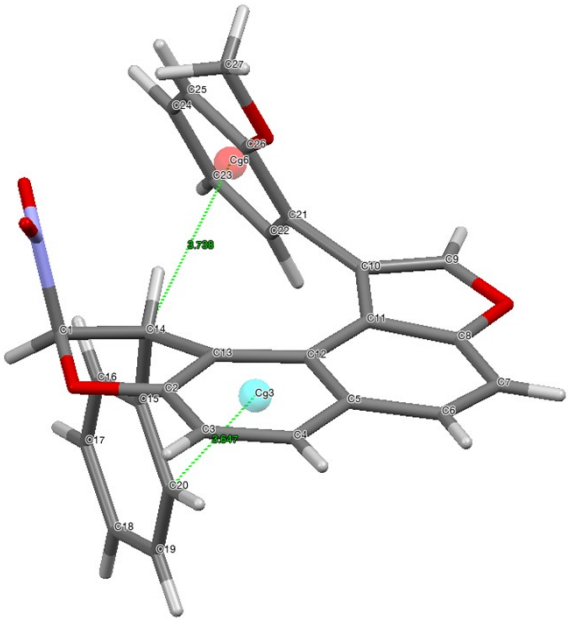
Evidence of C–H···π interactions in 4na

Interestingly, the barrier to diastereomerization of the stereogenic axis in **4na** was found to be quite high ($\Delta G^{\neq}_{calc}$ = 92.7 kJ.mol^{-1}), probably due to intramolecular C–H···p interactions, that can clearly be seen in the X-Ray structure and which may bring rigidity the structure. The molecules **4na** reveals the presence of two of these interactions: the distances C14-Cg6 and C20-Cg3 are equal to 3.738 Å and 3.647 Å respectively, Cg6 and Cg3 representing the centroids of the benzene rings of the anisole and the benzofuran respectively. The corresponding **C–H···Cg** angles are also within the typical values for such interactions, i.e. higher than 130° :

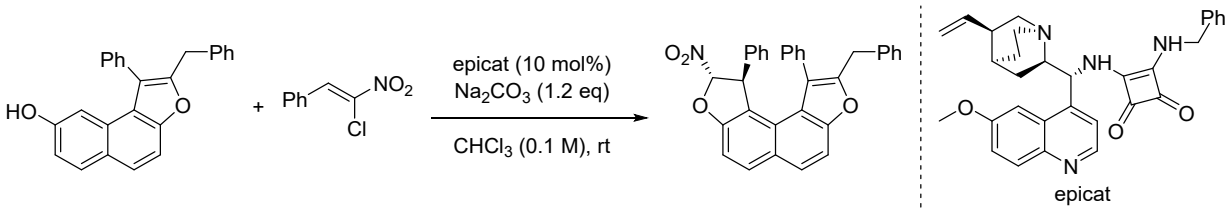
C14–H–Cg6 : 149.80°

C20–H–Cg3 : 131.31°

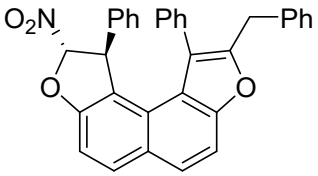
Distances C–Cg **Angles C–H–Cg**



b) Synthesis of the other enantiomer



*(1S,2S)-9-benzyl-2-nitro-1,10-diphenyl-1,2-dihydronaphtho[2,1-b:7,8-b']difuran (**enant-4ea**)*



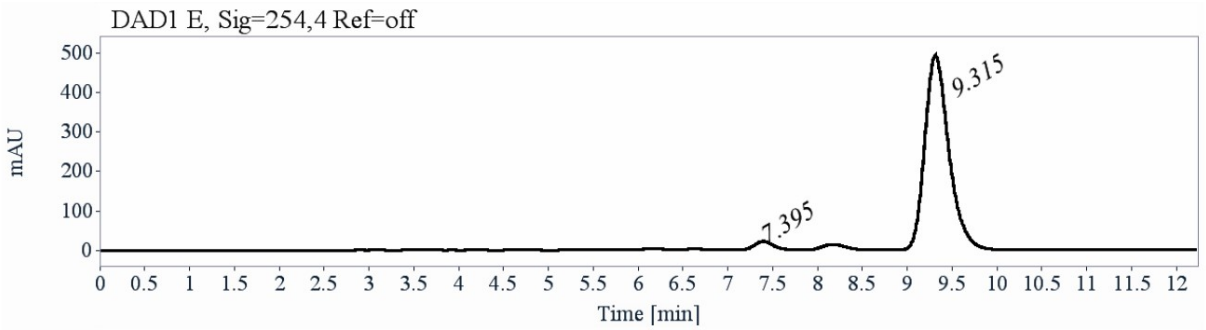
Molecular Weight: 497,55

Prepared following general procedure using **3e** (42 mg, 0.12 mmol, 1.2 equiv.), **2a** (18 mg, 0.1 mmol, 1.0 equiv.) and **epicat** for 5 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:99 to 3:97) to yield a white solid (25 mg, 0.05 mmol, 50%)

^{1}H NMR spectroscopic data are in accordance with product **4ea**.

$[\alpha]_D^{25}$ ($CHCl_3$, *c* = 1.0) = -171°, **HPLC analysis** (Lux-Cellulose-2, Heptane/Isopropanol (95/5), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **93% ee**, **t_r1**: 7.40 min, **t_r2**: 9.31 min

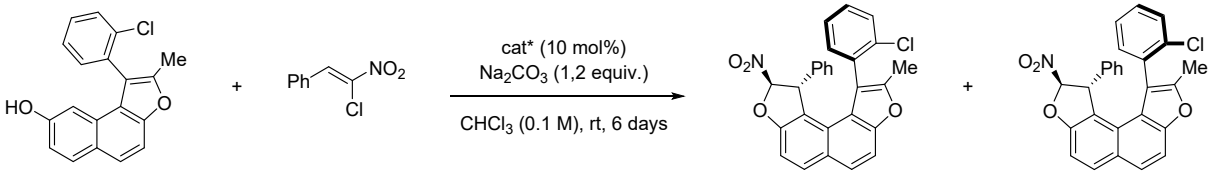
Chiral HPLC spectrum of **ag-3-054**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.40	322	3.36	1.51		
9.31	9251	96.64	2.16	1.43	4.44
Sum	9573	100.00			

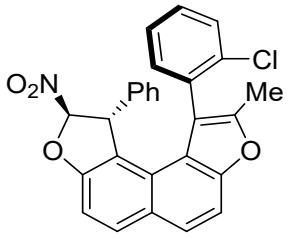
c) Deracemization of axially chiral derivative



Prepared following general procedure using **(±)-3m** (34 mg, 0.11 mmol, 1.1 equiv.) and **2a** (18 mg, 0.1 mmol, 1.0 equiv.) for 6 days. The crude product was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 1:99 to 1:24) to yield two white solids (**f1** 11 mg, 0.024 mmol, 24% and **f2** 14 mg, 0.031 mmol, 31%)

(aR)-(1R,2R)-10-(2-chlorophenyl)-9-methyl-2-nitro-1-phenyl-1,2-dihydronaphtho[2,1-b:7,8-b']difuran

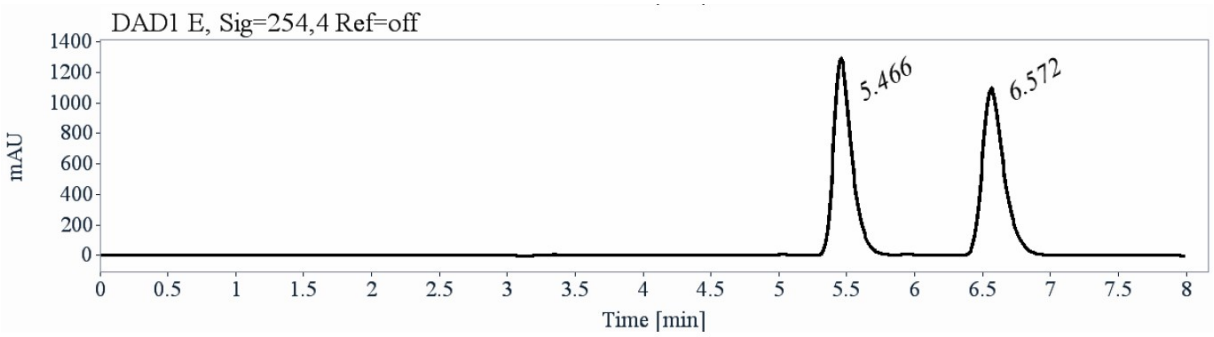
(4ma f1)



Molecular Weight: 455,89

R_f = 0.42 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +141°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.05 (d, *J* = 8.7 Hz, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.60 (d, *J* = 8.9 Hz, 1H), 7.55 – 7.47 (m, 1H), 7.43 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.39 – 7.30 (m, 2H), 7.21 – 7.04 (m, 4H), 6.39 – 6.35 (m, 2H), 5.71 (d, *J* = 1.0 Hz, 1H), 4.08 (s, 1H), 2.21 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 157.9, 153.6, 152.7, 137.4, 135.7, 133.7, 133.3, 132.9, 130.8, 130.0, 129.2, 128.9, 127.9, 127.5, 127.0, 126.6, 125.9, 121.2, 115.6, 115.4, 112.5, 111.3, 110.0, 56.2, 13.1. **MP** = 80 °C, **HRMS-ESI$^+$ (m/z)**: $[2M+Ag]^+$ calculated for $C_{54}H_{36}Cl_2N_2O_8Ag^+$ 1019.0889, found 1019.0882. **HPLC analysis** (Lux-Cellulose-2, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **93% ee**, **t_r1**: 5.47 min, **t_r2**: 6.58 min

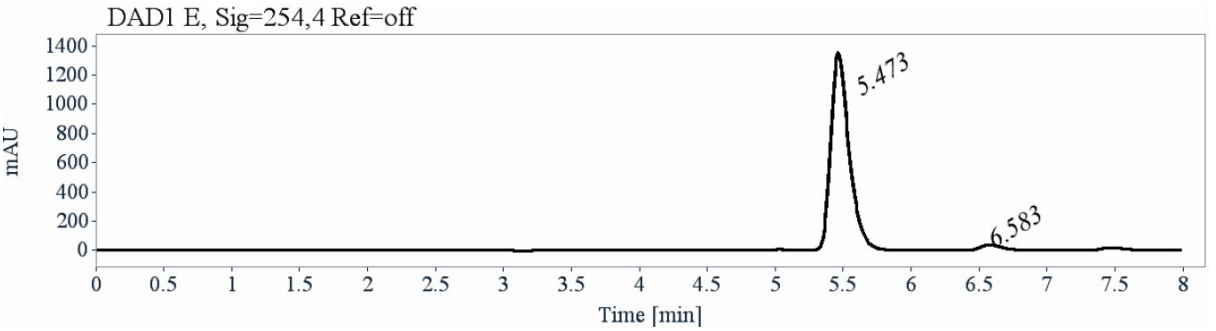
Chiral HPLC spectrum of *rac*-**4ma f1**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.47	11971	49.58	0.85		
6.57	12175	50.42	1.23	1.44	4.21
Sum	24146	100.00			

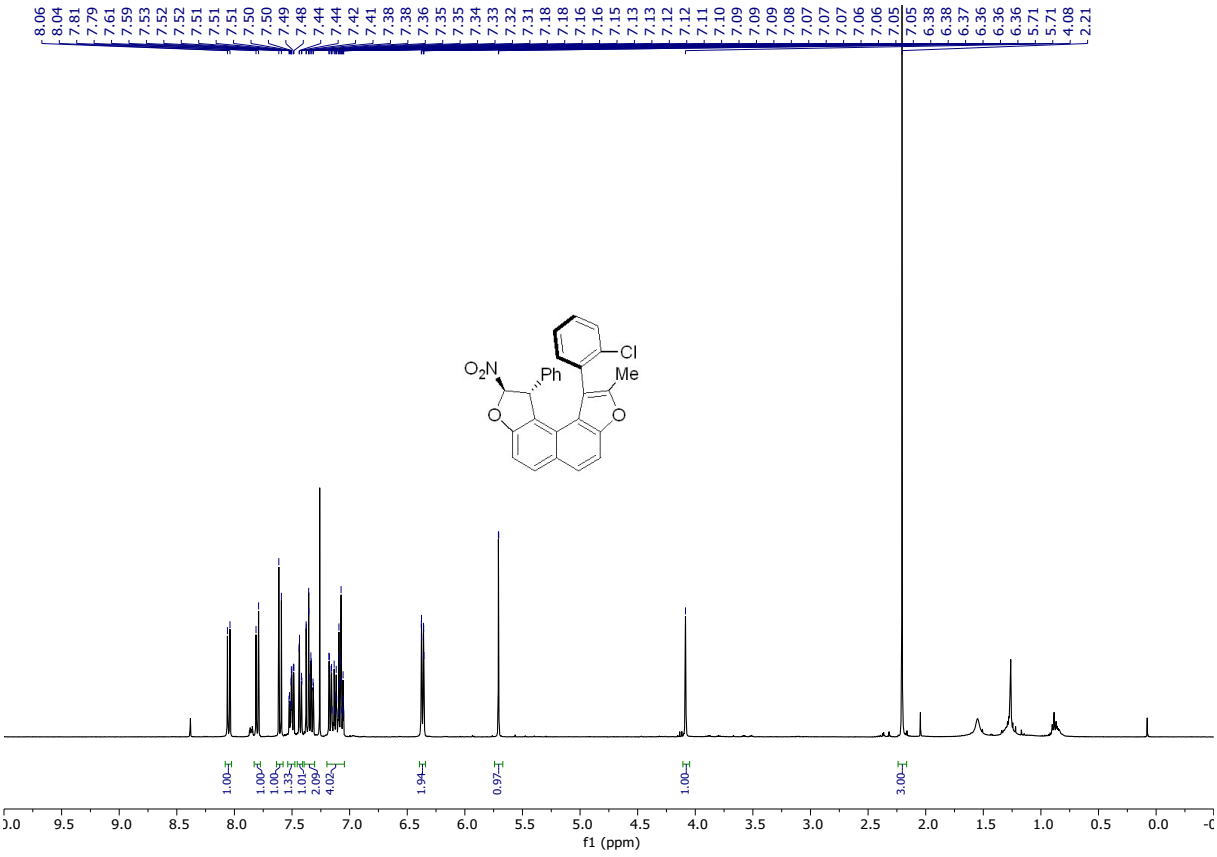
Chiral HPLC spectrum of **4ma f1**



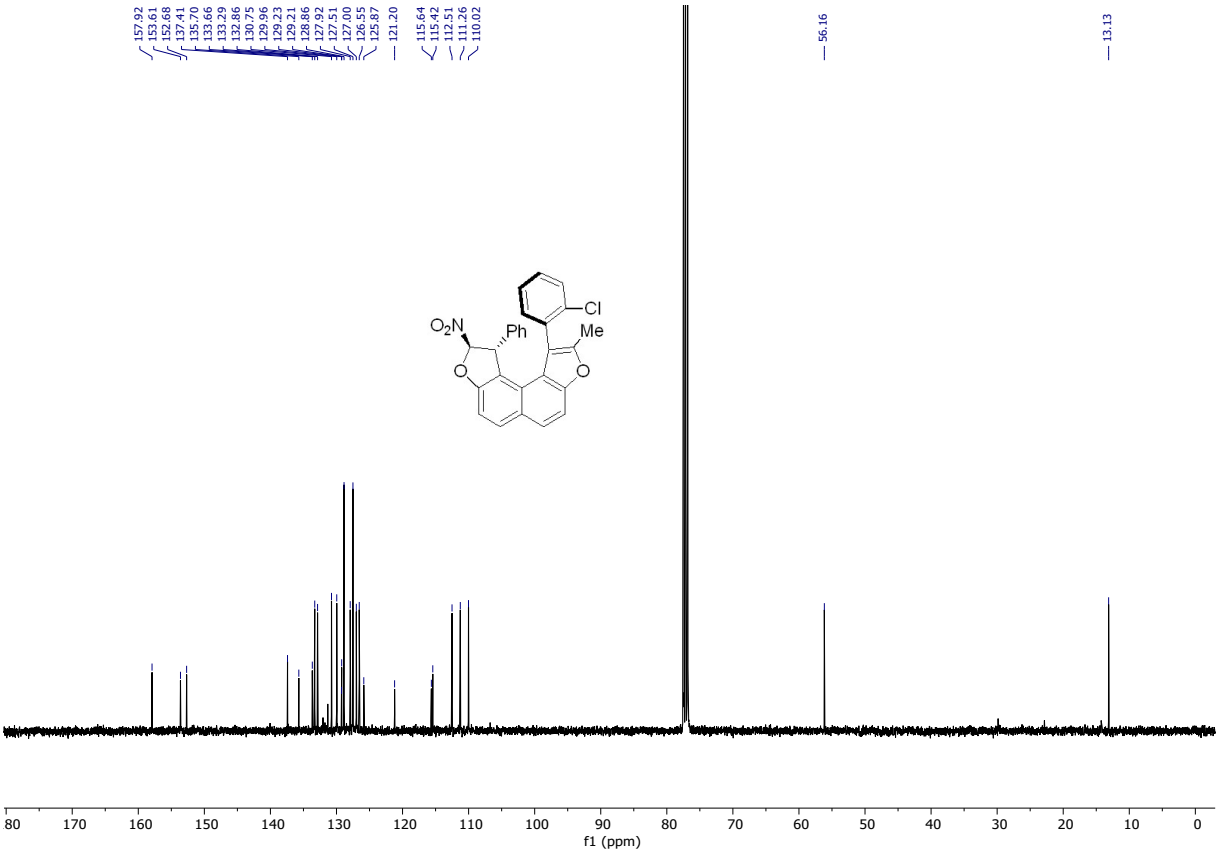
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.47	12669	96.61	0.86		
6.58	445	3.39	1.23	1.44	4.23
Sum	13114	100.00			

^{1}H NMR spectrum of **4ma f1** in $CDCl_3$

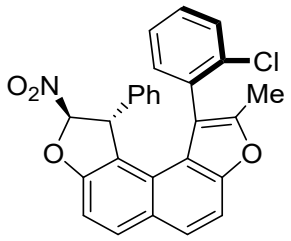


^{13}C NMR spectrum of **4ma f1** in $CDCl_3$



(aS)-(1R,2R)-10-(2-chlorophenyl)-9-methyl-2-nitro-1-phenyl-1,2-dihydronaphtho[2,1-b:7,8-b']difuran

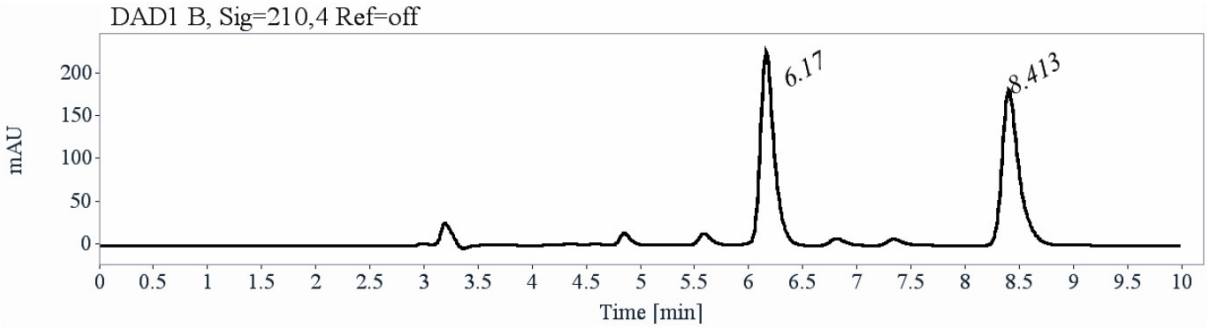
(4ma f2)



Molecular Weight: 455,89

R_f = 0.31 (EtOAc/ Petroleum ether = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +233°, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.04 (d, *J* = 8.7 Hz, 1H), 7.81 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.55 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.46 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H), 7.38 (dd, *J* = 8.8, 0.7 Hz, 1H), 7.17 – 7.08 (m, 2H), 7.08 – 7.01 (m, 2H), 6.62 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.38 – 6.25 (m, 2H), 5.76 (d, *J* = 1.0 Hz, 1H), 4.47 (s, 1H), 2.16 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 157.6, 153.2, 152.4, 137.0, 136.3, 133.3, 133.4, 132.9, 129.7, 129.7, 129.0, 128.5, 127.8, 127.7, 127.1, 126.7, 126.7, 121.4, 116.6, 115.8, 112.3, 111.2, 110.0, 55.6, 12.6. **MP** = 213 °C, **HRMS-ESI$^+$ (m/z)**: $[2M+Ag]^+$ calculated for $C_{54}H_{36}Cl_2N_2O_8Ag^+$ 1019.0889, found 1019.0880. **HPLC analysis** (Lux-Cellulose-2, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 210 nm) indicated **92% ee**, **t_r1**: 6.17 min, **t_r2**: 8.42 min

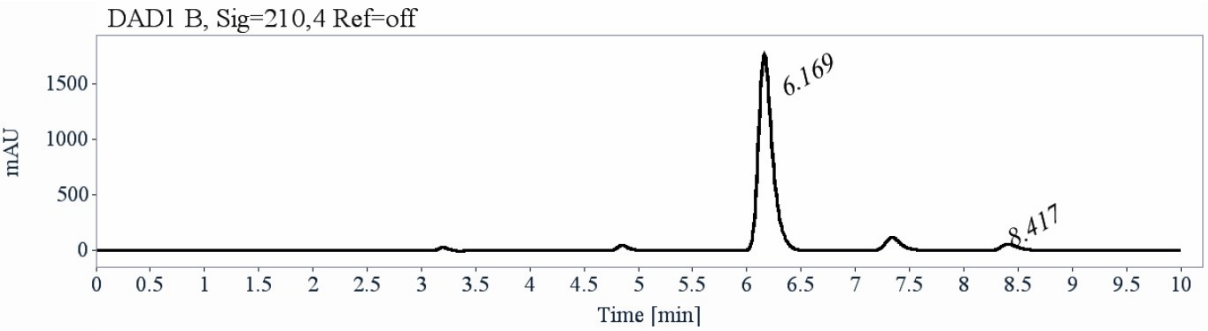
Chiral HPLC spectrum of *rac*-**4ma f2**



Signal: DAD1 B, Sig=210,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.17	1998	50.08	1.09		
8.41	1992	49.92	1.85	1.70	9.08
Sum	3990	100.00			

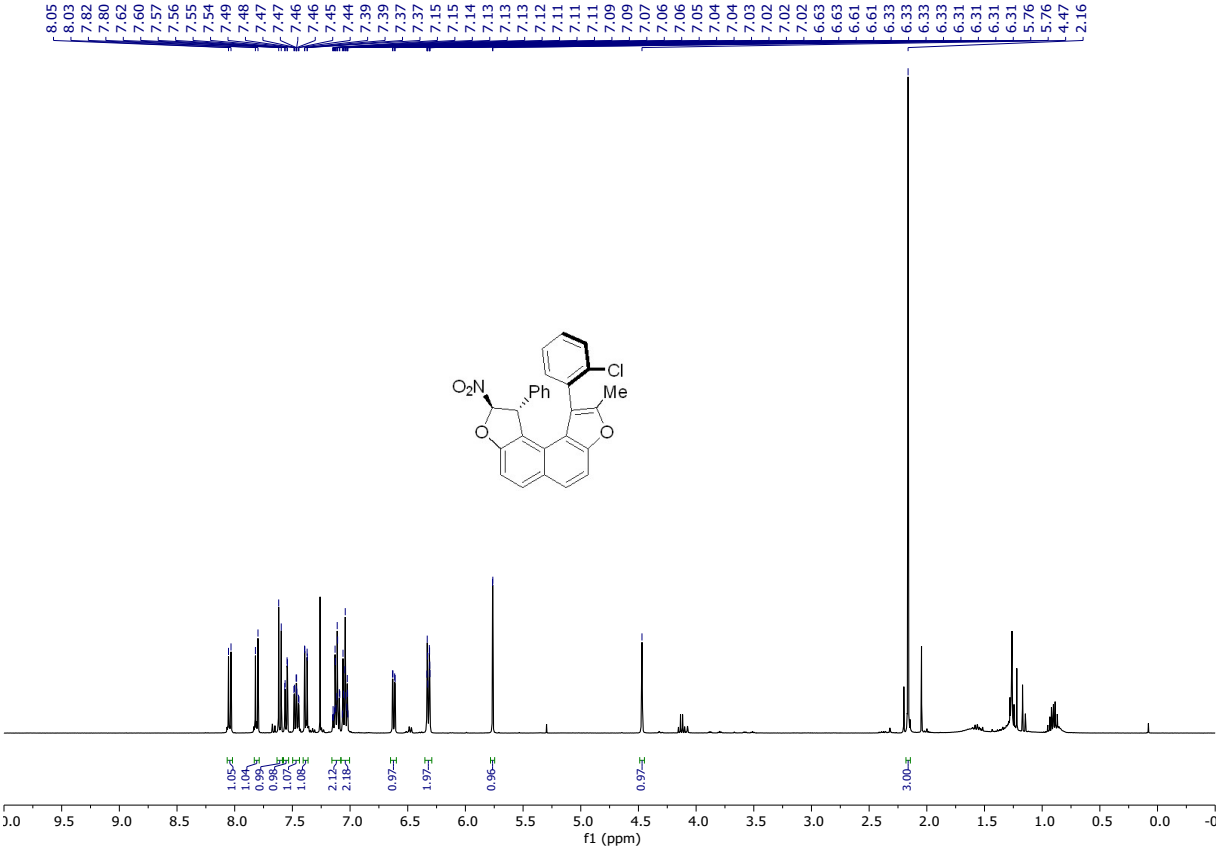
Chiral HPLC spectrum of **4ma f2**



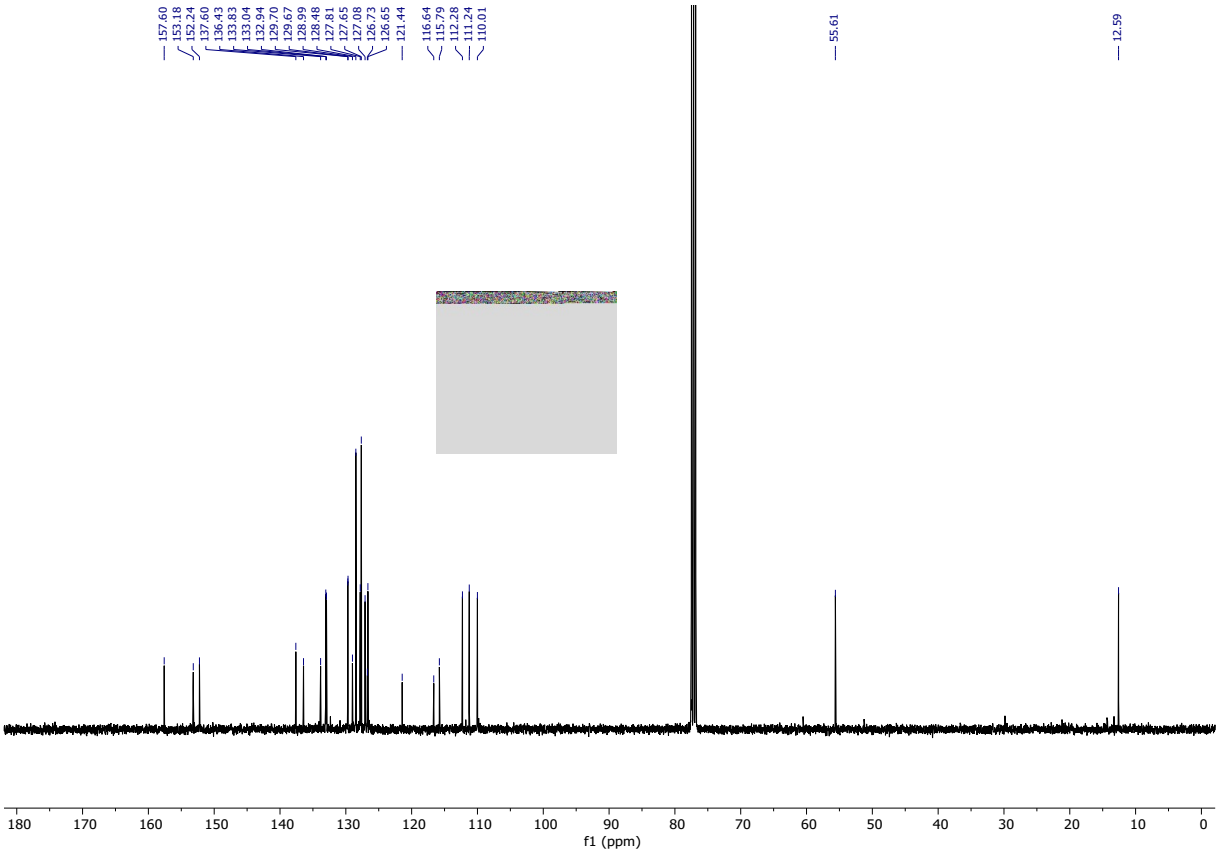
Signal: DAD1 B, Sig=210,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.17	15850	96.00	1.09		
8.42	660	4.00	1.85	1.70	8.97
Sum	16510	100.00			

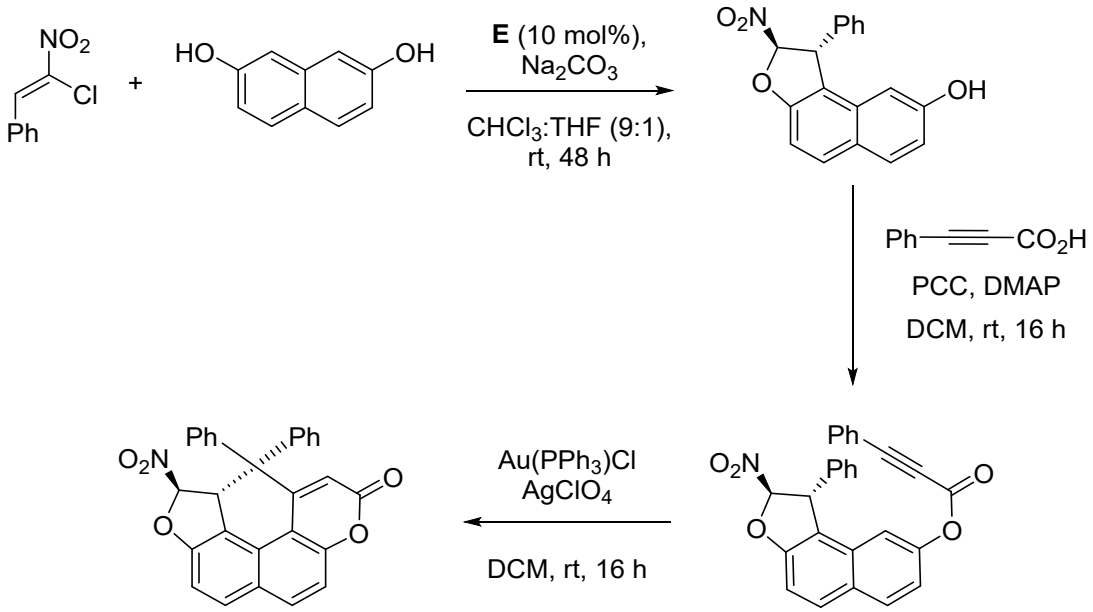
^{1}H NMR spectrum of **4ma f2** in $CDCl_3$



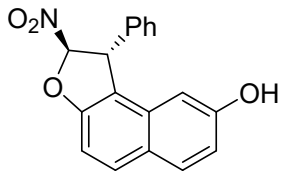
^{13}C NMR spectrum of **4ma f2** in $CDCl_3$



6. Synthesis of helically chiral molecules from dihydrofuran substrates



*(1R,2R)-2-nitro-1-phenyl-1,2-dihydronaphtho[2,1-b]furan-8-ol (**5a**)*

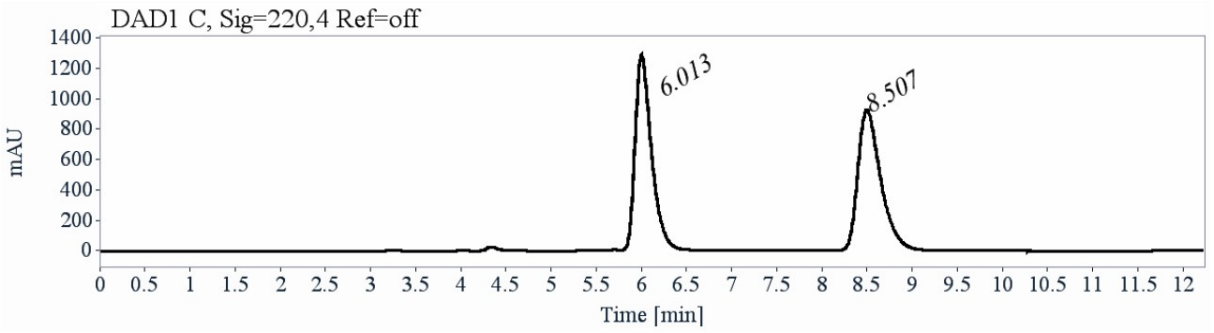


Molecular Weight: 307,3050

In a reaction tube, **2a** (93 mg, 0.5 mmol, 1.0 equiv.), 2,7-dihydroxynaphthalene (112 mg, 0.7 mmol, 1.4 equiv.), **E** (25 mg, 0.05 mmol, 10 mol%), and Na_2CO_3 (1.0 equiv.) were combined with $CHCl_3$:THF (9:1, 0.1 M) and the yellow mixture was stirred at room temperature for two days. The dark purple mixture was treated with HCl (1M aq.) and the aqueous phase was extracted thrice with DCM. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to dryness. The crude was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether 5:95 to 15:85) to afford the desired product as a yellow solid (105 mg, 0.34 mmol, 68% yield).

R_f = 0.25 (P.E./ EtOAc 9:1), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = -7°, **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.83 (dt, *J* = 8.9, 0.8 Hz, 1H), 7.78 (d, *J* = 8.9 Hz, 1H), 7.39 – 7.31 (m, 3H), 7.28 (dd, *J* = 8.8, 0.6 Hz, 1H), 7.22 – 7.16 (m, 2H), 6.96 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.62 (dt, *J* = 2.5, 0.7 Hz, 1H), 6.07 (d, *J* = 1.8 Hz, 1H), 5.21 (d, *J* = 1.8 Hz, 1H), 5.02 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 157.1, 155.0, 137.8, 131.4, 131.3, 131.2, 129.5, 128.6, 127.7, 126.4, 116.9, 116.5, 112.6, 109.4, 105.3, 55.4. **MP** = 127 °C. **HRMS-ESI$^+$ (m/z)**: $[M+Na]^+$ calculated for $C_{18}H_{13}NO_4Na^+$, 330.0737 found 330.0729. **HPLC analysis** (Chiralpak IF, Heptane/Ethanol (80/20), Flow: 1 mL/min, Temp: 25 °C, UV detection: 220 nm) indicated **94% ee**, **t_r1**: 6.01 min, **t_r2**: 8.49 min

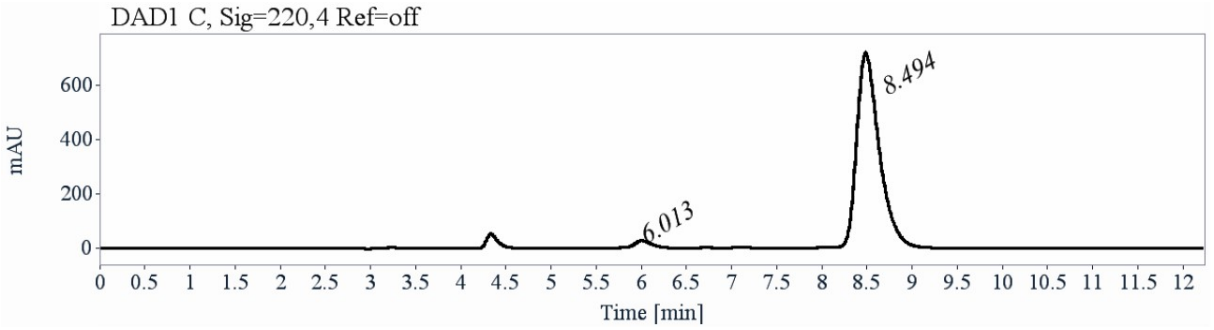
Chiral HPLC spectrum of *rac*-**5a**



Signal: DAD1 C, Sig=220,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.01	16593	50.10	1.04		
8.51	16528	49.90	1.88	1.81	6.45
Sum	33121	100.00			

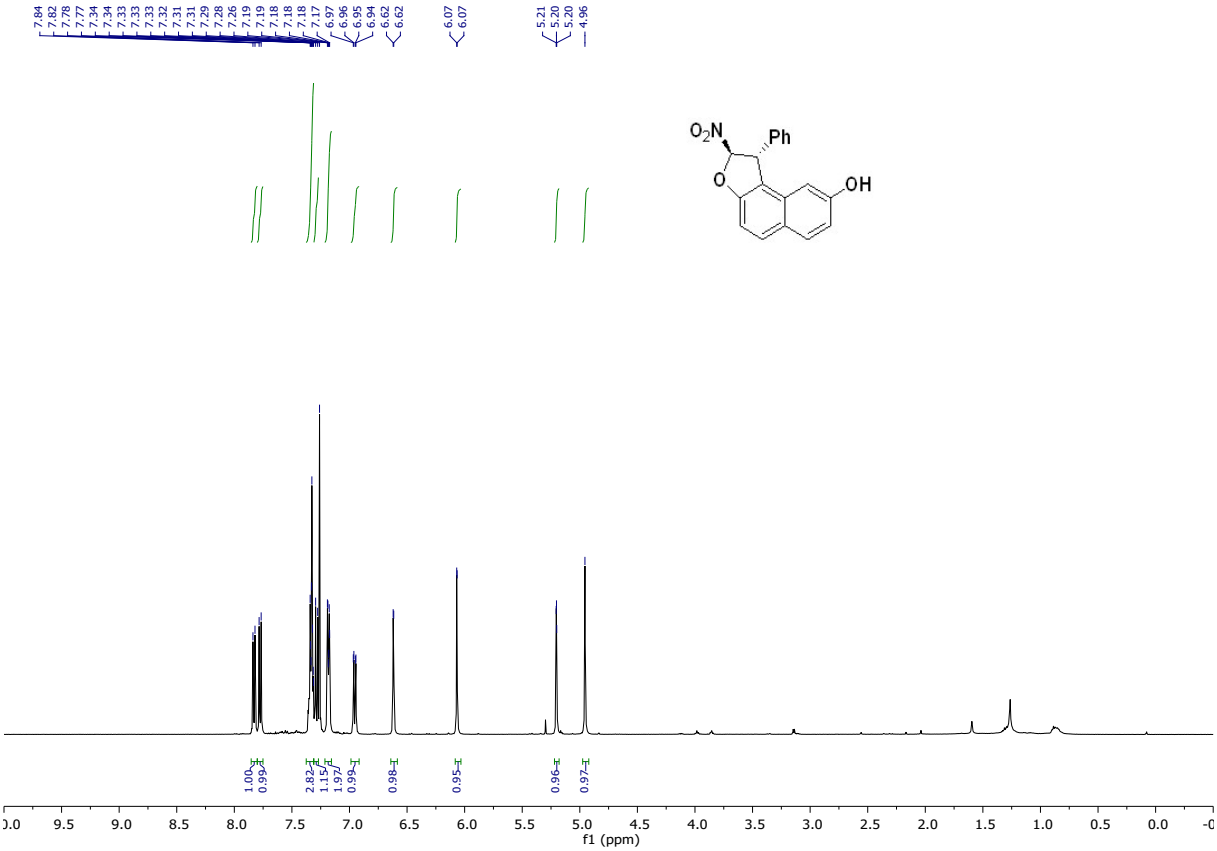
Chiral HPLC spectrum of **5a**



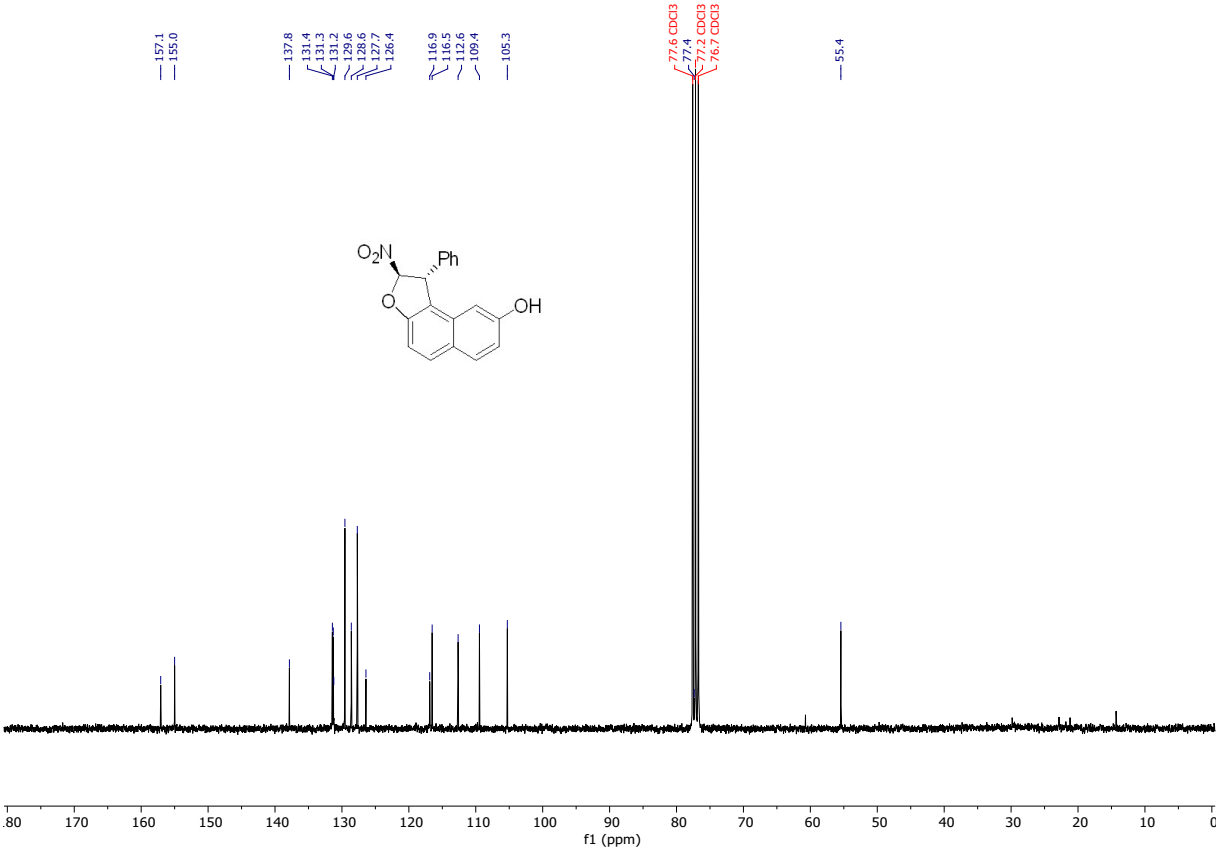
Signal: DAD1 C, Sig=220,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.01	404	3.07	1.04		
8.49	12764	96.93	1.88	1.81	6.28
Sum	13168	100.00			

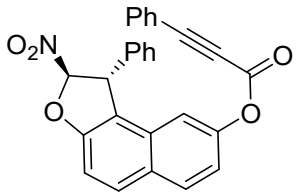
^{1}H NMR spectrum of **5a** in $CDCl_3$



^{13}C NMR spectrum of **5a** in $CDCl_3$



*(1R,2R)-2-nitro-1-phenyl-1,2-dihydronaphtho[2,1-b]furan-8-yl 3-phenylpropiolate (**6**)*



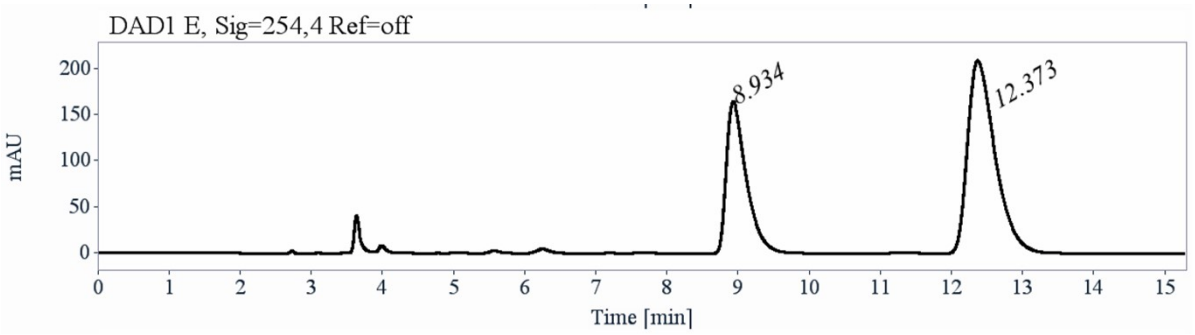
Molecular Weight: 435,4350

To a solution of 3-phenylpropiolic acid (85 mg, 0.58 mmol, 1.18 equiv.), DCC (123 mg, 0.60 mmol, 1.22 equiv.) and DMAP (6 mg, 0.05 mmol, 0.1 equiv.) in DCM (3 mL) was added dropwise a solution of compound **6** (150 mg, 0.49 mmol, 1 equiv.) in DCM (1 mL). The stirring was maintained at room temperature overnight. The reaction mixture was quenched with HCl (1M, aq.) and extracted with DCM. The organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness. The crude was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether 0:1 to 1:19) to afford the desired product as a yellow solid (160 mg, 0.36 mmol, 75% yield).

R_f = 0.26 (P.E./ EtOAc 9:1), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 3.5 Hz, 1H), 7.92 (d, *J* = 3.6 Hz, 1H), 7.60 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.53 – 7.27 (m, 7H), 7.23 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.21 – 7.16 (m, 3H), 6.11 (d, *J* = 1.8 Hz, 1H), 5.29 (d, *J* = 1.5 Hz, 1H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ 157.1, 152.1, 149.3, 137.5, 133.3, 131.6, 131.3, 131.0, 130.4, 129.6, 129.2, 128.8, 128.7, 127.6, 119.6, 119.2, 118.6, 114.2, 112.6, 112.1, 89.2, 80.2, 55.4. **MP** = 71 °C, **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{27}H_{17}NO_5Ag^+$, 542.0152 found

542.0153 **HPLC analysis** (Lux-Cellulose-4, Heptane/Ethanol (80/20), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **90% ee**, t_r**1**: 8.93 min, t_r**2**: 12.37 min

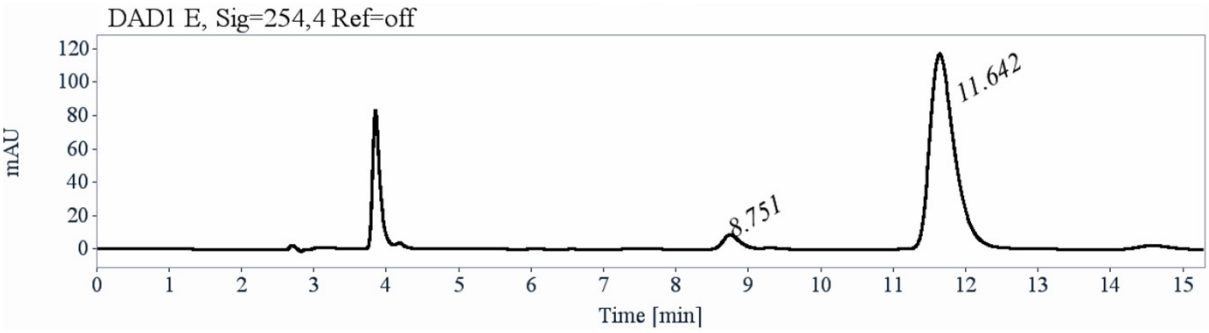
Chiral HPLC spectrum of *rac*-**6**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
8.93	3230	36.23	2.03		
12.37	5685	63.77	3.19	1.57	5.77
Sum	8915	100.00			

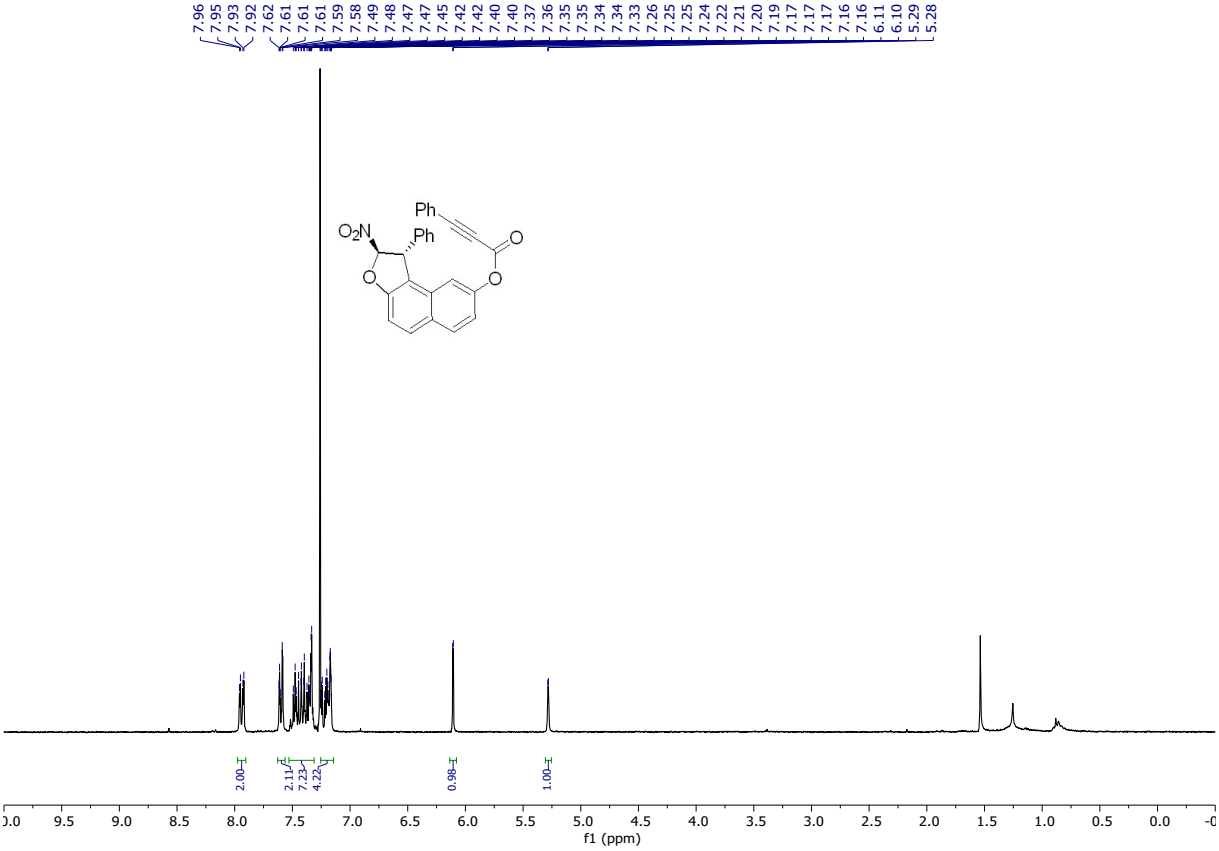
Chiral HPLC spectrum of **6**



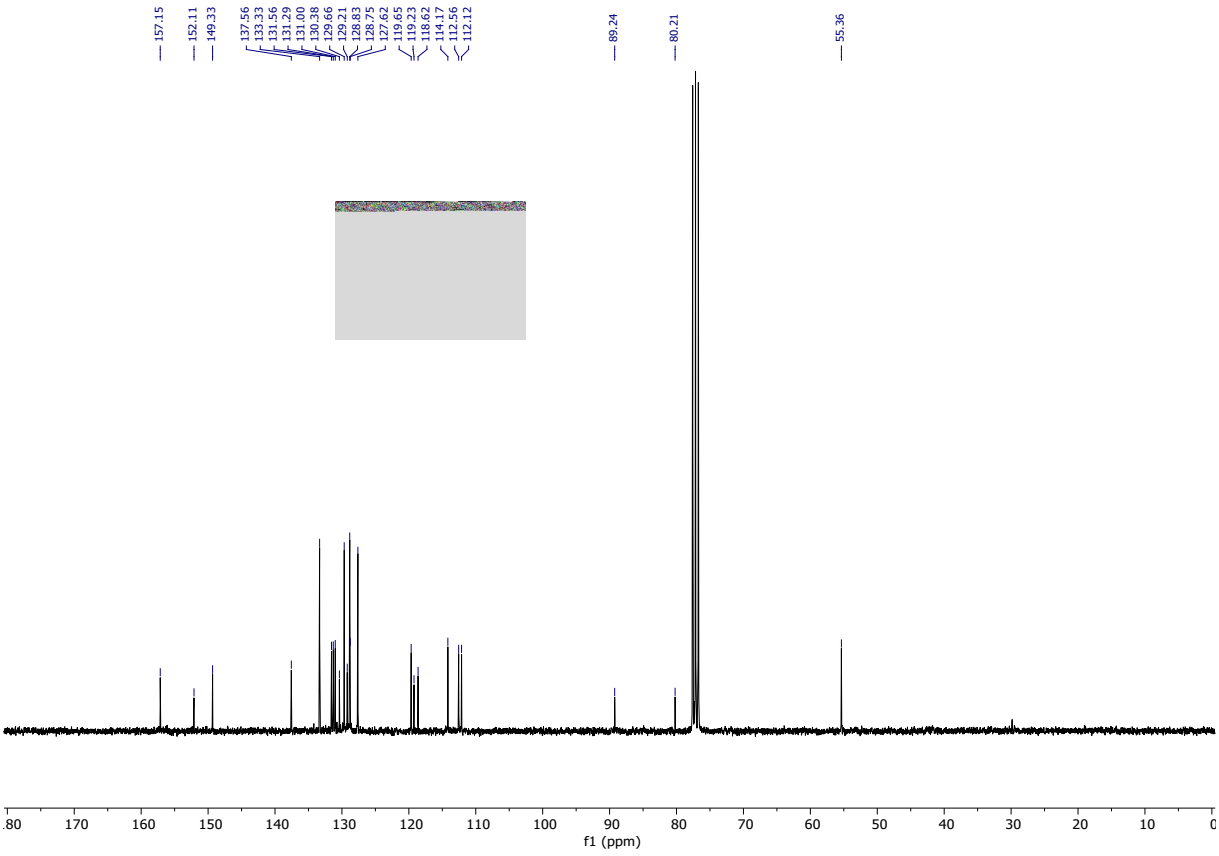
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
8.75	148	4.94	1.97		
11.64	2839	95.06	2.95	1.50	5.52
Sum	2987	100.00			

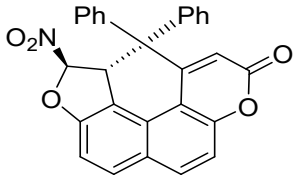
^{1}H NMR spectrum of **6** in $CDCl_3$



^{13}C NMR spectrum of **6** in $CDCl_3$



*(1R,2R)-2-nitro-1,11-diphenyl-1,2-dihydro-9H-benzofuro[4,5-f]chromen-9-one (**4ga**)*

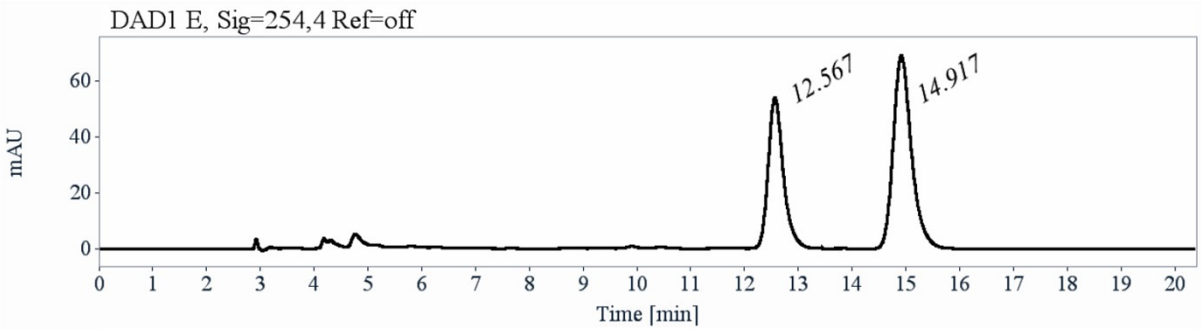


Molecular Weight: 435,4350

Under inert atmosphere, a solution of $Au(PPh_3)Cl$ (2.5 mg, 0.005 mmol, 5 mol%) and $AgClO_4$ (1 mg, 0.005 mmol, 5 mol%) in anhydrous DCM (1 mL, 0.1 M) was stirred for 5 min at room temperature. Then, compound **4ga** (43.0 mg, 0.1 mmol) was added to the mixture and the stirring was maintained for 48 h. The reaction mixture was filtered through a celite pad and rinsed with DCM. The filtrate was concentrated *in vacuo* and the crude purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether 0:1 to 1:4) to afford the desired product as an off-white solid (25 mg, 0.06 mmol, 57% yield)

R_f = 0.37 (P.E./EtOAc 8:2), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = -215°, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.9 Hz, 1H), 8.02 (d, *J* = 8.7 Hz, 1H), 7.74 – 7.65 (m, 2H), 7.57 (tt, *J* = 7.2, 1.5 Hz, 1H), 7.45 (d, *J* = 8.7 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 7.20 – 7.08 (m, 4H), 6.76 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.46 – 6.39 (m, 2H), 6.29 (s, 1H), 5.57 (d, *J* = 1.5 Hz, 1H), 3.41 (d, *J* = 1.0 Hz, 1H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.3, 158.8, 156.9, 154.6, 138.5, 136.8, 134.9, 133.2, 131.4, 130.1, 129.33, 129.03, 128.5, 128.1, 127.7, 126.8, 126.3, 119.7, 116.1, 114.7, 111.9, 111.8, 111.6, 57.5. **MP** = 216 °C, **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{54}H_{34}N_2O_{10}Ag^+$ 979.1268, found 979.1274. **HPLC analysis** (Lux-Cellulose-4, Heptane/Ethanol (70/30), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **96% ee**, **t_r1**: 12.56 min, **t_r2**: 14.91 min

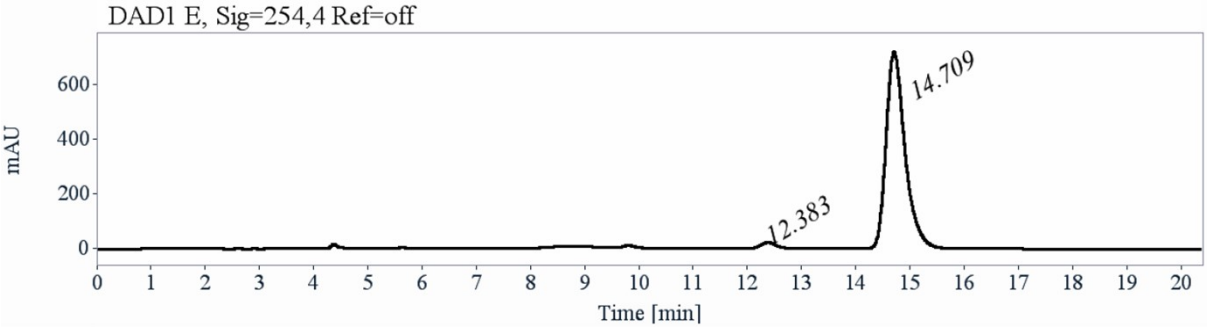
Chiral HPLC spectrum of *rac*-**4ga**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
12.57	1063	39.43	3.26		
14.92	1633	60.57	4.06	1.24	4.27
Sum	2696	100.00			

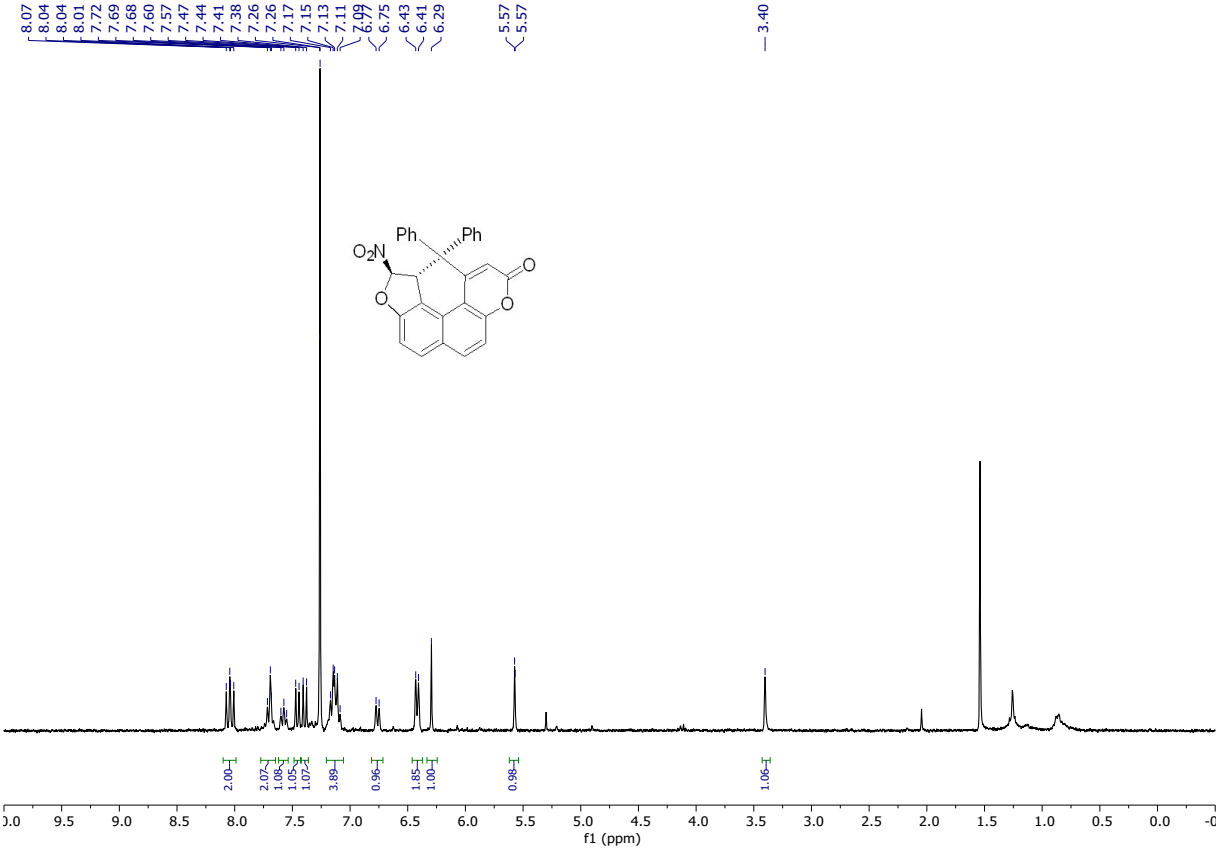
Chiral HPLC spectrum of **4ga**



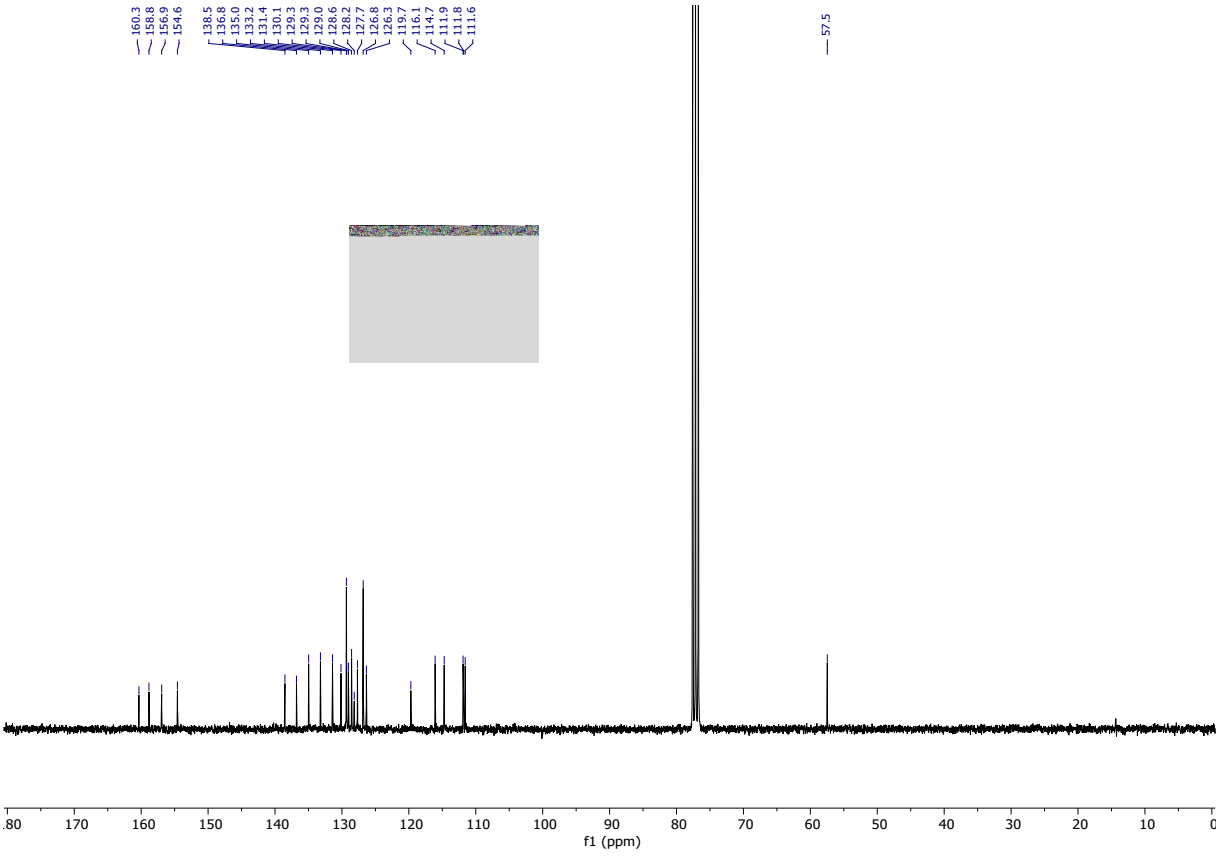
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
12.38	486	2.69	3.20		
14.71	17588	97.31	3.99	1.25	4.05
Sum	18074	100.00			

^{1}H NMR spectrum of **4ga** in $CDCl_3$

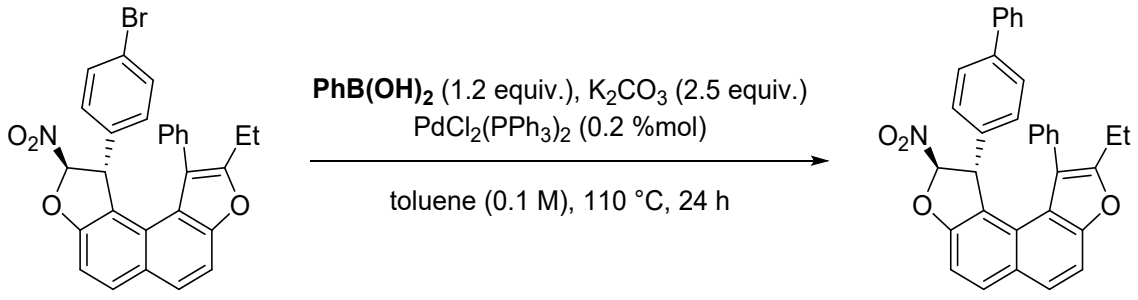


^{13}C NMR spectrum of **4ga** in $CDCl_3$



7. Experimental procedures and characterization for post-functionalization

a) Suzuki-type coupling between 4af and PhB(OH)$_2$



4af **4ak**

4ak was prepared according to the literature known procedure.[18] In a dried tube, **4af** (51 mg, 0.10 mmol, 1.0 equiv.), **PhB(OH)$_2$** (15 mg, 0.12 mmol, 1.2 equiv.), $PdCl_2(PPh_3)_2$ (0.14 mg, 0.2 µmol, 0.2%mol), and K_2CO_3 (35 mg, 0.25 mmol, 2.5 equiv.) were combined with freshly distilled toluene (1 mL). The tube was sealed and stirred at 110 °C for 24 h. Once concentrated, the black residue was purified by column chromatography (SiO_2, liquid deposit, EtOAc/ Petroleum ether = 0:1 to 1:49) to yield a white solid (24 mg, 0.048 mmol, 48%)

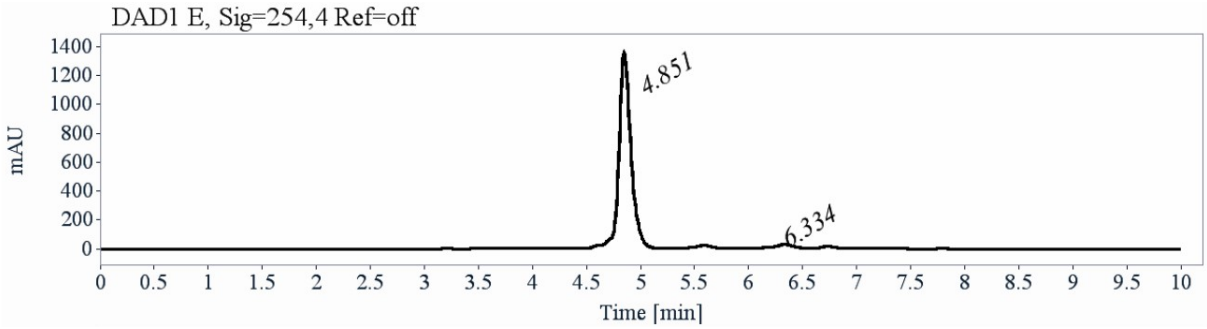
[18]Kołodziejski, M.; Brock, A.J.; Kurpik, G.; Walczak, A.; Li, F.; Clegg, J.K.; Stefankiewicz, A.R. *Inorg. Chem.* **2021**, *60, 13,* 9673-9679

R_f = 0.40 (EtOAc/ Petroleum ether = 1:9), **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.06 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.51 – 7.46 (m, 2H), 7.46 – 7.35 (m, 5H), 7.34 – 7.27 (m, 3H), 7.17 (d, *J* = 7.7 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.40 (d, *J* = 8.2 Hz, 2H), 5.73 (d, *J* = 1.0 Hz, 1H), 4.17 (s, 1H), 2.67 – 2.48 (m, 2H), 1.16 (t, *J* = 7.6 Hz, 3H).

^{1}H NMR spectroscopic data are in accordance with product **4ak**.

HPLC analysis (Lux-Cellulose-4, Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **93% ee**, **t_r1**: 4.85 min, **t_r2**: 6.33 min

Chiral HPLC spectrum of **4ak**

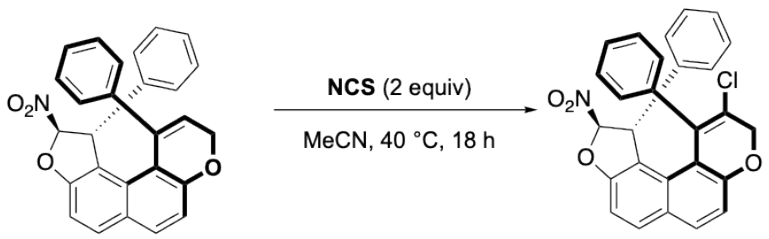


Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.85	10519	96.45	0.64		
6.33	387	3.55	1.15	1.78	6.08
Sum	10906	100.00			

b) Chlorination of compound 4ha

*(1R,2R)-10-chloro-2-nitro-1,11-diphenyl-1,2-dihydro-9H-benzofuro[4,5-f]chromene (**4ha-Cl**)*



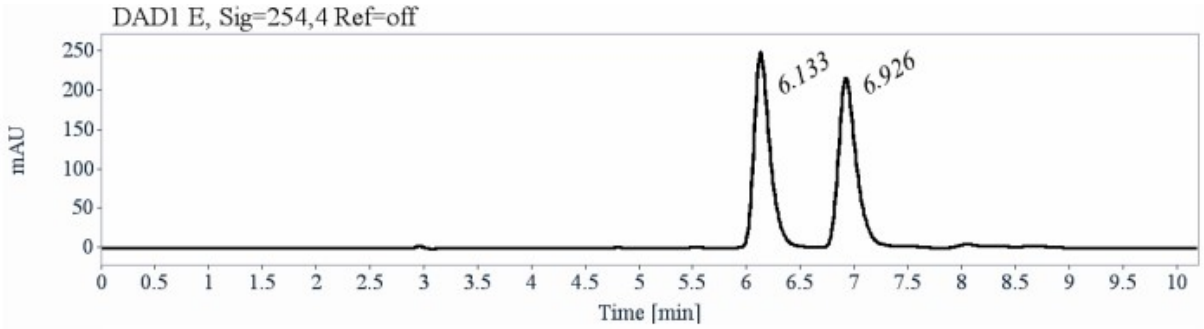
4ha **4ha-Cl**

NCS (19 mg, 0.142 mmol, 2.0 equiv.) was added to a solution of **4ha** (30 mg, 0.071 mmol, 1.0 equiv.) in MeCN (2.5 mL). The reaction mixture was stirred at 40°C for 16 h. After cooling at room temperature, the solvent was removed *in vacuo*. The crude product was purified on silica (EtOAc/P.E. = 0:100 to 2:98) to yield an off white solid (27 mg, 0.06 mmol, 84%)

R_f = 0.56 (EtOAc/P.E. = 1:9), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 1.0) = +330°, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.57 – 7.27 (m, 4H), 7.24 – 7.19 (m, 4H), 7.13 – 6.98 (m, 2H), 6.75 (dd, *J* = 6.6, 2.8 Hz, 2H), 5.67 (d, *J* = 1.6 Hz, 1H), 4.66 (d, *J* = 12.6 Hz, 1H), 4.17 – 4.10 (m, 1H), 4.04 (d, *J* = 12.6 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 157.67, 157.62, 137.9, 135.9, 132.59, 132.56, 131.5, 129.4, 129.1, 128.97, 128.93, 128.3, 128.1, 127.1, 118.4, 116.60, 116.58, 115.35, 111.8, 110.0, 71.5, 56.7. **MP** = 201 °C **HRMS-ESI$^+$ (m/z)**: $[M+Na]^+$ calculated for $C_{27}H_{19}NO_4Na^+$, found. **HPLC analysis** (Lux-Cellulose-4,

Heptane/Ethanol (90/10), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **98% ee**, t_r**1**: 6.13 min, t_r**2**: 6.92 min

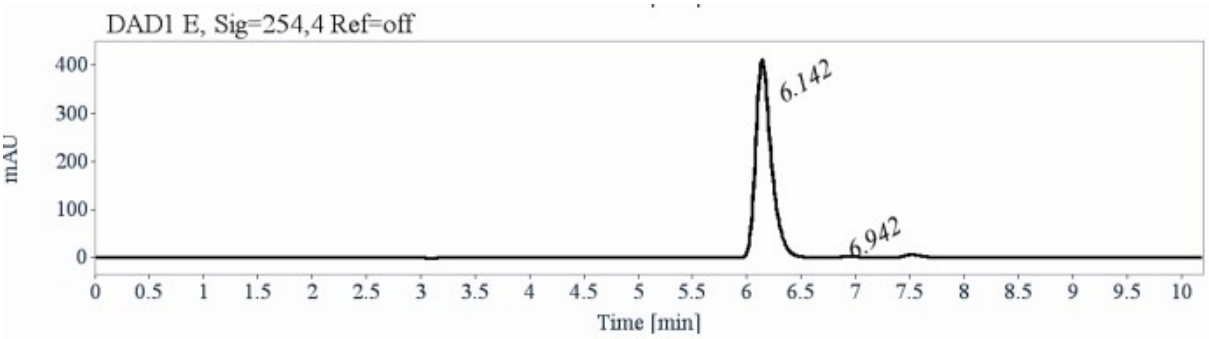
Chiral HPLC spectrum of *rac*-**4ha-Cl**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.13	2547	50.83	1.08		
6.93	2464	49.17	1.35	1.25	2.87
Sum	5011	100.00			

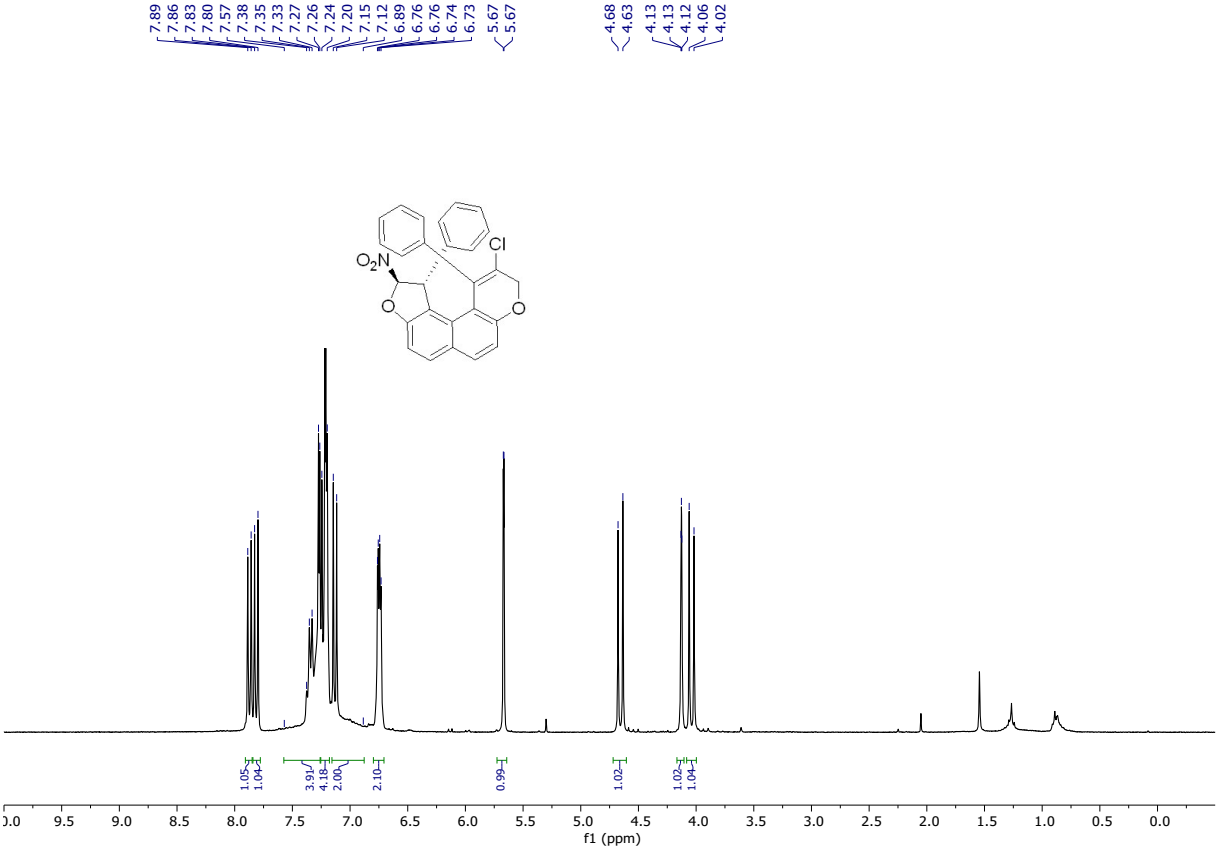
Chiral HPLC spectrum of **4ha-Cl**



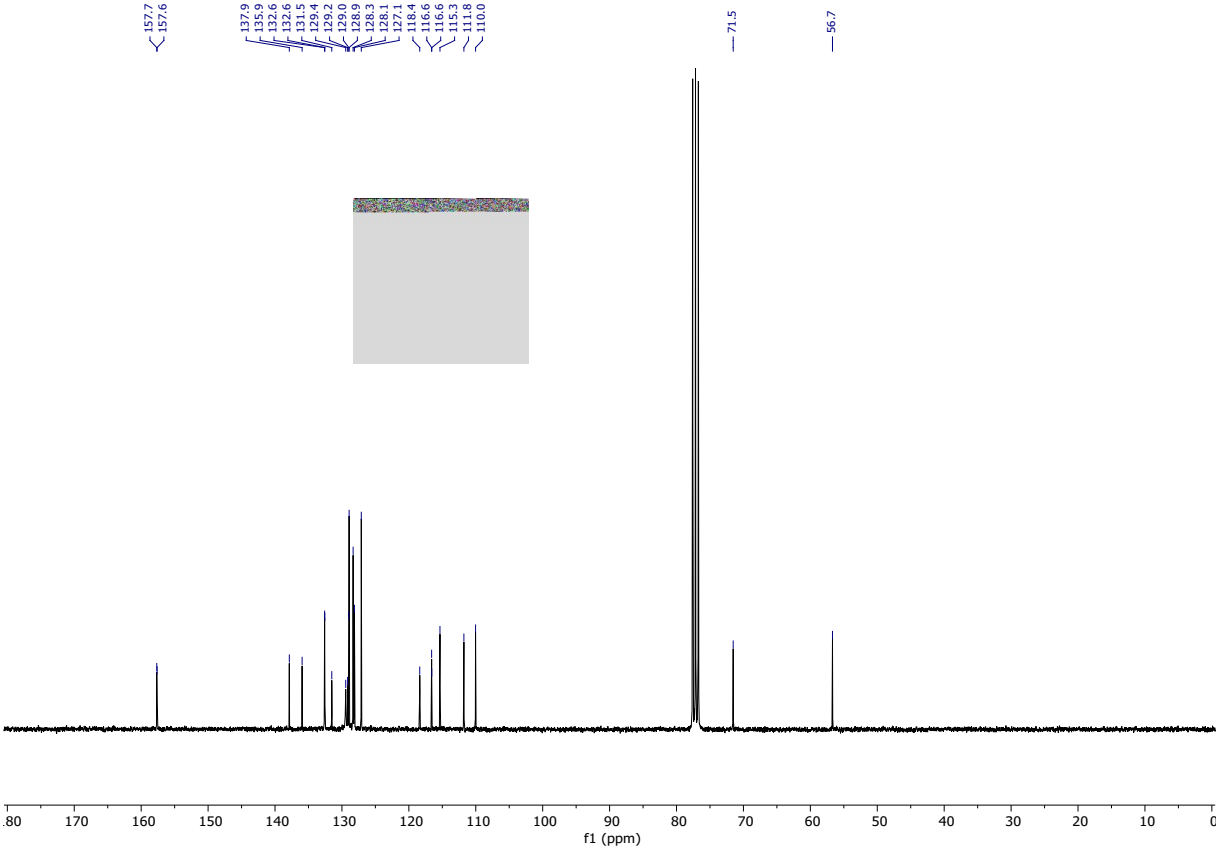
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.14	4147	99.10	1.08		
6.94	37	0.90	1.35	1.25	2.94
Sum	4185	100.00			

^{1}H NMR spectrum of **4ha-Cl** in $CDCl_3$

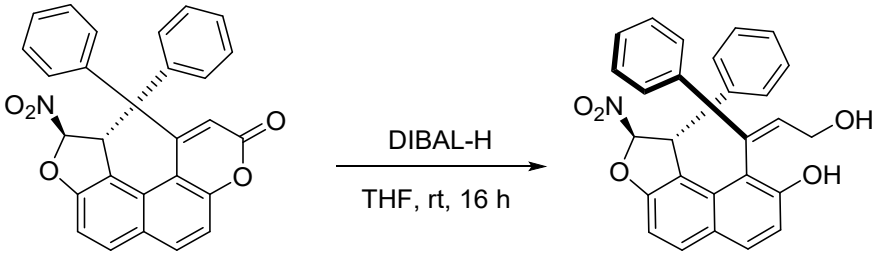


^{13}C NMR spectrum of **4ha-Cl** in $CDCl_3$



c) Reduction of chromene 4ga

*(1R,2R)-9-((Z)-3-hydroxy-1-phenylprop-1-en-1-yl)-2-nitro-1-phenyl-1,2-dihydronaphtho[2,1-b]furan-8-ol (**8**)*



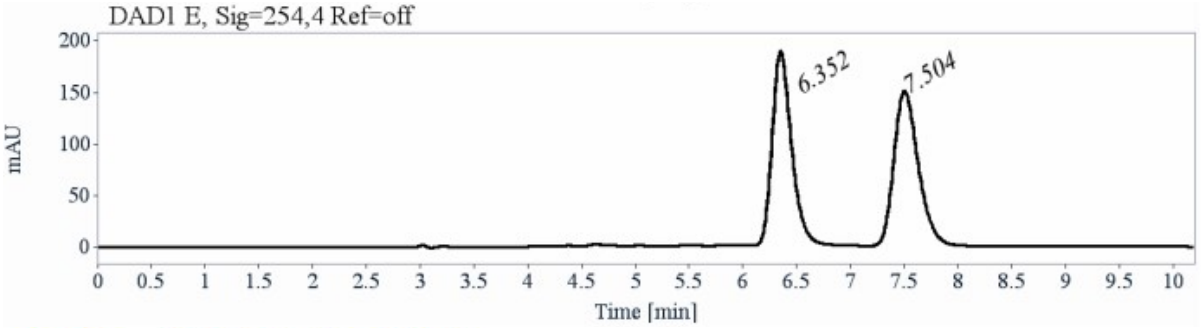
4ga **8**

Under inert atmosphere, to a mixture of **4ga** (30 mg, 0.07 mmol) in THF (1.5 mL) was added DIBAL-H (150 µL, 0.15 mmol, 1M soluton in toluene) dropwise. The mixture was stirred at room temperature for 16h. An aqueous saturated solution of NH_4Cl was added to quench the reaction and the organic layer was separated, dried over Na_2SO_4 and concentrated to dryness. Purification of the crude mixture by silica gel column chromatography (eluent: 100% DCM) afforded the desired compound as a pale yellow solid (16 mg, 0.37 mmol, 54% yield).

R_f = 0.16 (DCM), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 0.5) = -4.1°, **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 1H), 7.88 (d, *J* = 8.9 Hz, 1H), 7.38 – 7.27 (m, 7H), 7.19 (d, *J* = 8.9 Hz, 1H), 7.17 – 7.12 (m, 2H), 6.93 – 6.83 (m, 2H), 6.43 (t, *J* = 6.7 Hz, 1H), 5.87 (s, 1H), 4.87 (s, 1H), 3.50 (dd, *J* = 13.4, 6.9 Hz, 1H), 2.89 (dd, *J* = 13.5, 6.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.4, 152.9, 140.4, 138.4, 134.5, 133.0, 132.8, 131.7, 130.3,

129.5, 129.4, 129.1, 128.3, 127.5, 127.0, 125.4, 116.3, 115.8, 114.7, 111.5, 109.7, 60.5, 55.9. **MP** = 102.5°C. **HRMS-ESI$^-$ (m/z)**: $[M]^-$ calculated for $C_{27}H_{20}NO_5^-$ 438.1347, found 438.1347. **HPLC analysis** (Lux-Cellulose-4, Heptane/Ethanol (80/20), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **94% ee**, **t_r1**: 6.35 min, **t_r2**: 7.50 min

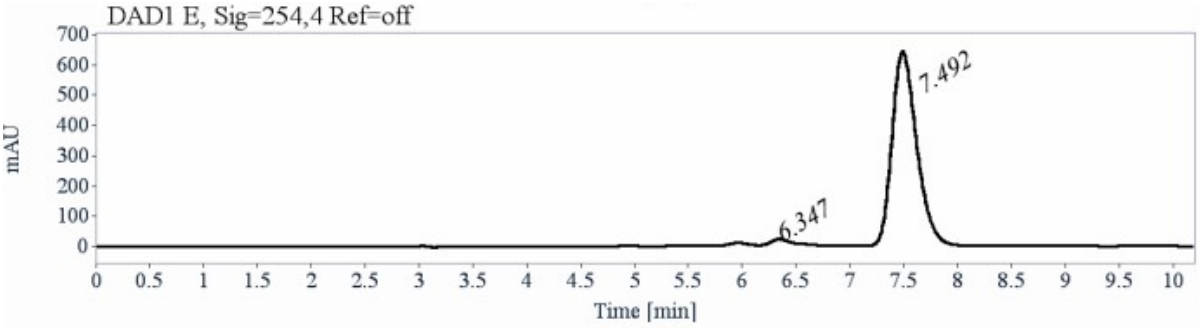
Chiral HPLC spectrum of *rac*-**8**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.35	2388	49.98	1.15		
7.50	2390	50.02	1.54	1.34	3.13
Sum	4778	100.00			

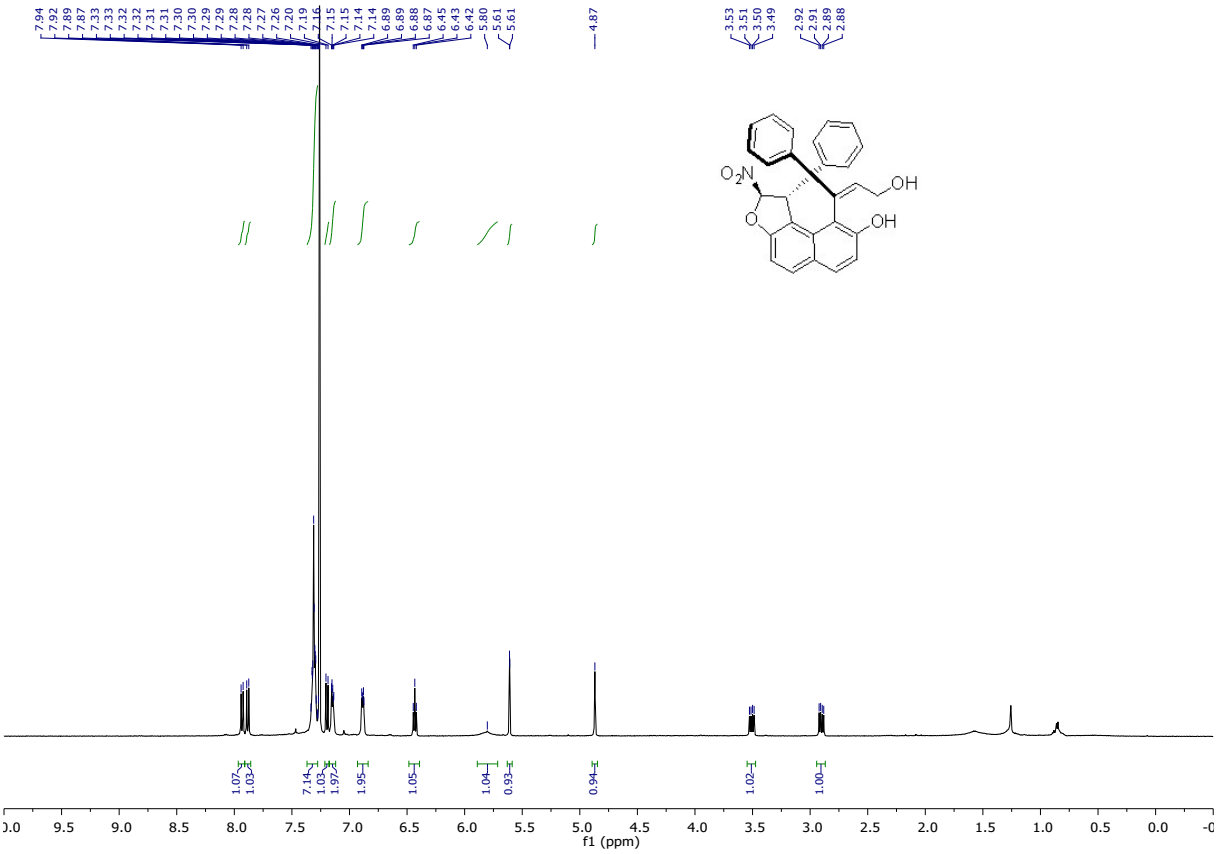
Chiral HPLC spectrum of **8**



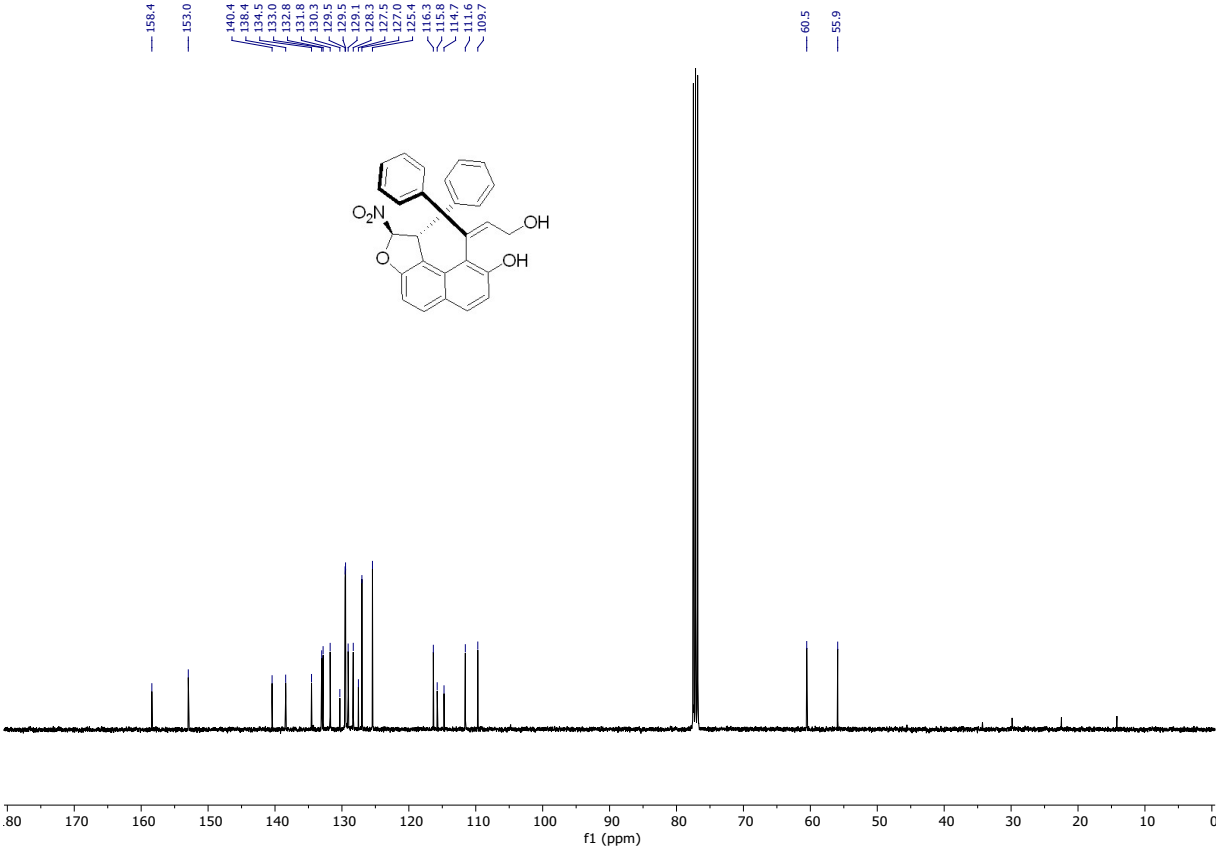
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.35	287	2.74	1.15		
7.49	10200	97.26	1.54	1.34	3.12
Sum	10487	100.00			

^{1}H NMR spectrum of **8** in $CDCl_3$

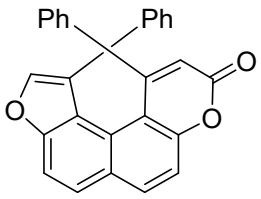


^{13}C NMR spectrum of **8** in $CDCl_3$



d) Elimination reaction

*1,11-diphenyl-9H-benzofuro[4,5-f]chromen-9-one (**7**)*



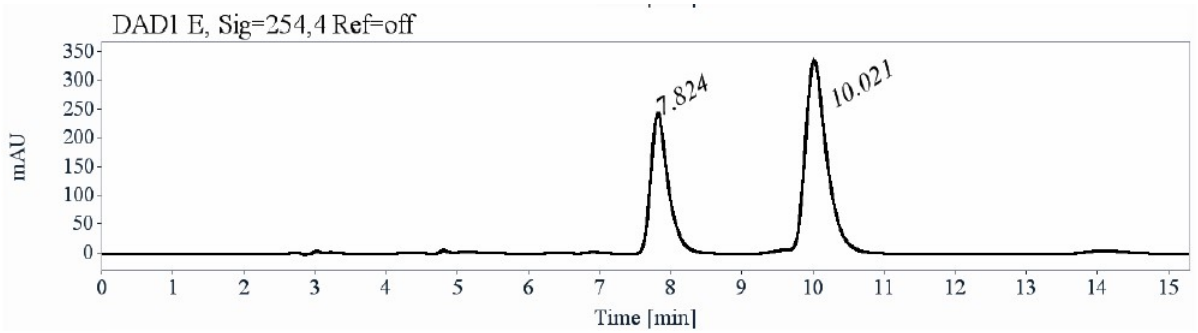
Molecular Weight: 388,4220

In a microwave G4 tube, a solution of **4ga** (21 mg, 0.05 mmol) and DBU (75 µL, 0.50 mmol) in dry THF (500 µL) was heated at 110°C for 45 min. After cooling at room temperature, the solvent was removed *in vacuo*. The crude mixture was purified by silica gel column chromatography (gradient from 100% pentane to 95:5 pentane/EtOAc) to afford the desired compound as a pale-yellow solid (5.5 mg, 0.015 mmol, 30% yield)

R_f = 0.42 (P.E./EtOAc 8:2), **$[\alpha]_D^{25}$** ($CHCl_3$, *c* = 0.25) = -314°, **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.40 (s, 1H), 7.35 – 7.28 (m, 1H), 7.25 – 7.14 (m, 3H), 6.97 – 6.82 (m, 4H), 6.31 (d, *J* = 7.7 Hz, 2H), 6.01 (s, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.1, 156.8, 155.6, 142.3, 136.4, 134.1, 132.6, 129.4, 129.1, 128.5, 128.5, 127.6, 127.3, 126.9, 126.3, 125.9, 125.4, 124.9, 121.2, 115.8, 113.6, 113.2, 112.7, 109.3, 90.9. **MP** decomposition >220°C, **HRMS-ESI$^+$ (m/z)**: $[M+Ag]^+$ calculated for $C_{27}H_{16}O_3Ag^+$ 495.0145, found 495.0144. **HPLC analysis**

(Lux-Cellulose-4, Heptane/Ethanol (80/20), Flow: 1 mL/min, Temp: 25 °C, UV detection: 254 nm) indicated **78% ee**, t_r**1**: 7.50 min, t_r**2**: 9.6 min

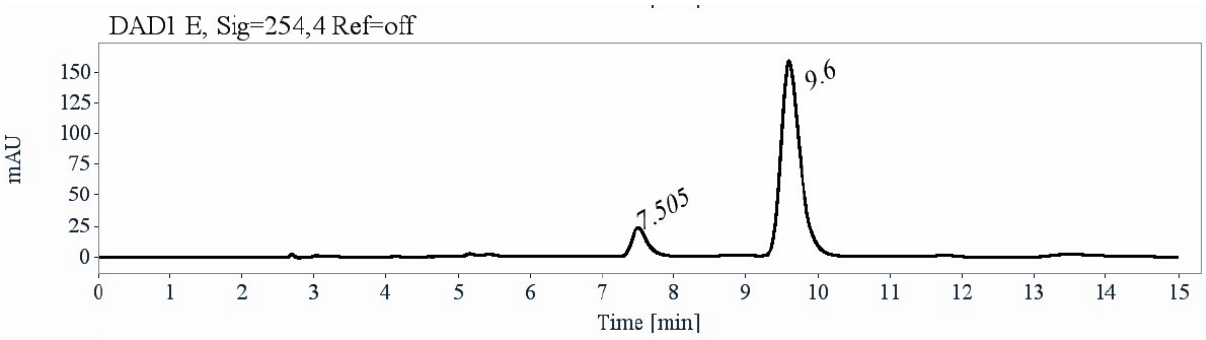
Chiral HPLC spectrum of *rac*-**7**



Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.82	4186	36.68	1.65		
10.02	7228	63.32	2.40	1.45	4.54
Sum	11414	100.00			

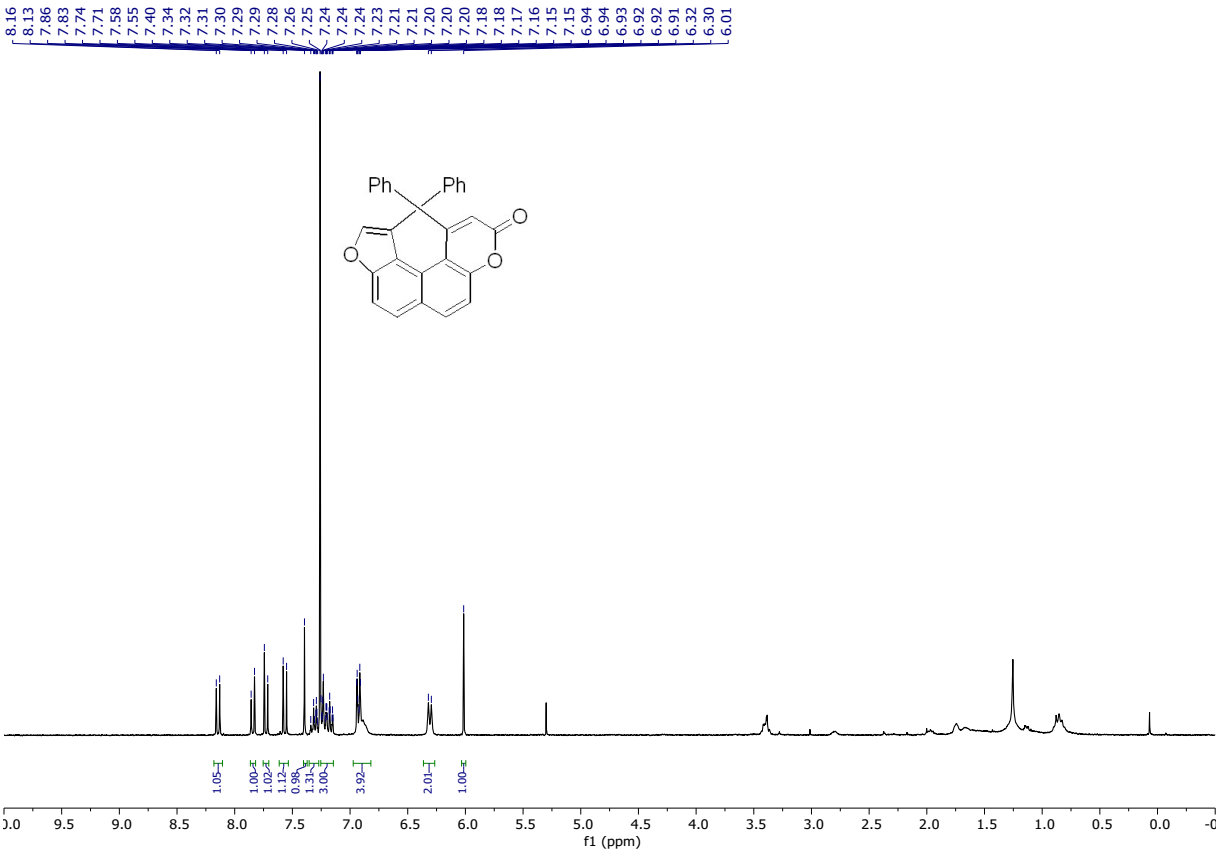
Chiral HPLC spectrum of **7**



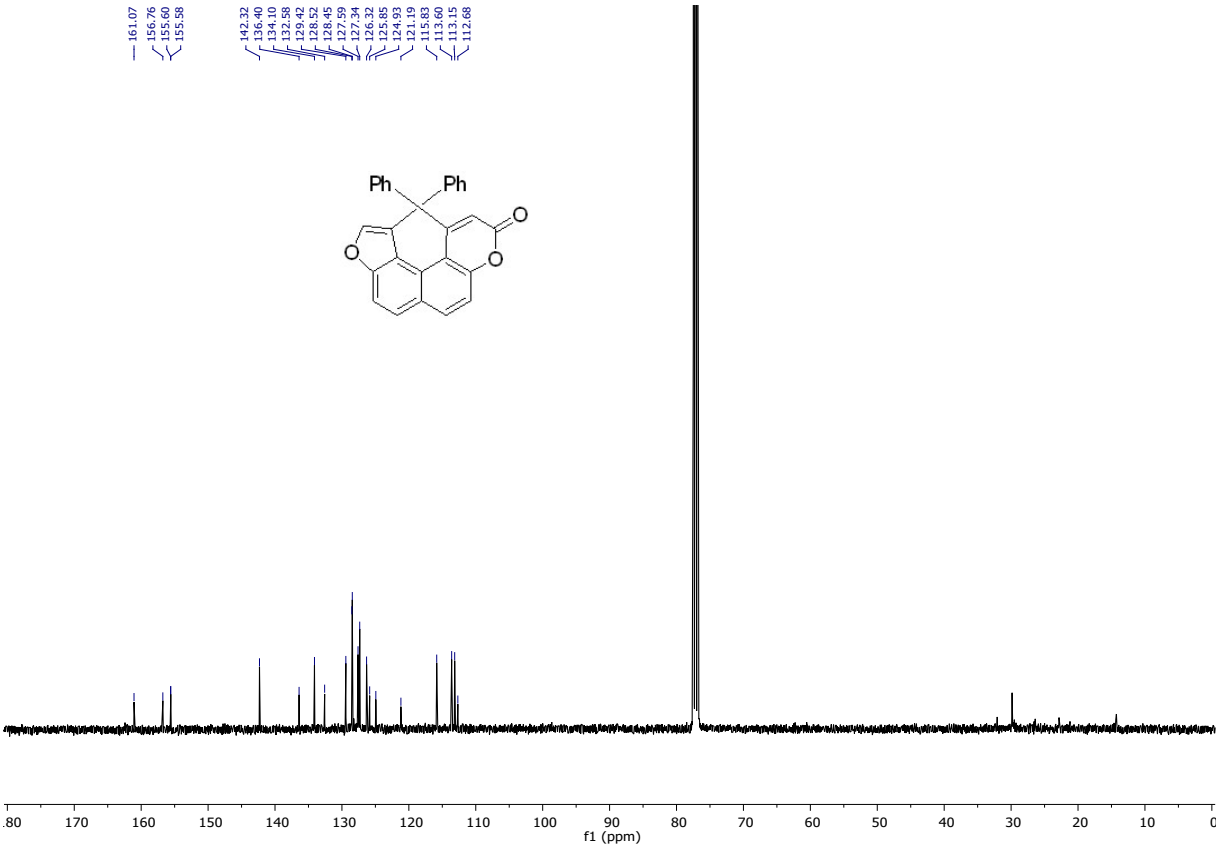
Signal: DAD1 E, Sig=254,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.51	360	10.96	1.54		
9.60	2925	89.04	2.25	1.46	4.92
Sum	3285	100.00			

^{1}H NMR spectrum of **7** in $CDCl_3$



^{13}C NMR spectrum of **7** in $CDCl_3$



8. Computational studies

All the structures were optimized at the PBE0/def2-SVP level[19,20] with Grimme correction for the dispersion "GD3" as implemented in Gaussian 16.[21,22]

a) ***Compound 1***

Min1 E[hartree] = -1148.742317 G[hartree] = -1148.442496

O	5.190002	9.766448	-0.317216
O	3.767516	8.175614	6.430951

[19] C. Adamo, V. Barone, *J. Chem. Phys.*, **1999**, *110*, 6158–6170.

[20] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.*, **2005**, *7*, 3297–3305.

[21] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 16 Rev. C.01. Wallingford, CT, **2016**.

[22] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.*, **2010**, *132*, 154104.

C 4.643234 6.025940 2.334636
H 5.362086 6.558006 2.961136
C 4.363756 4.684777 2.580249
H 4.860557 4.173192 3.408432
C 3.461491 3.994454 1.771031
H 3.242364 2.941584 1.964988
C 2.839374 4.657786 0.713811
H 2.121876 4.129160 0.081445
C 3.109785 6.001230 0.472453
H 2.590686 6.526617 -0.332369
C 4.014542 6.704401 1.279950
C 4.381407 8.093585 0.969020
C 4.629084 8.538380 -0.299478
H 4.516713 8.047701 -1.263228
C 4.804360 9.180362 1.835452
C 5.342797 10.139104 0.970827
C 6.057709 11.273126 1.379654
H 6.463215 11.972243 0.647169
C 6.279239 11.398314 2.728905
H 6.894180 12.219372 3.105370
C 5.716617 10.492035 3.676375
C 4.851496 9.429354 3.243495
C 6.025148 10.655704 5.059719
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H 5.730803 9.945559 7.086028
C 4.524306 8.920474 5.598060
C 4.132168 8.736670 4.267991
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C 1.943026 7.554685 3.333445
C 1.549467 8.520473 2.395168
H 2.053716 9.488895 2.379092
C 0.520922 8.255925 1.495580
H 0.229970 9.019107 0.769414
C -0.140452 7.028238 1.524159
H -0.947566 6.821345 0.817098
C 0.236937 6.065707 2.460048
H -0.266753 5.096211 2.482676
C 1.271567 6.324282 3.353870
H 1.589444 5.552798 4.058855
44
TS E[hartree] = -1148.710575 G[hartree] = -1148.410569
O 1.679347 3.602742 0.089752
O 1.677209 -3.603894 -0.090409
C -1.985505 1.973099 -1.287879
H -1.409133 2.242993 -2.176212

C -3.378337 2.019474 -1.315027
H -3.895142 2.306219 -2.234442
C -4.105023 1.718974 -0.166350
H -5.196782 1.766001 -0.177234
C -3.433334 1.346224 0.998601
H -3.998471 1.098974 1.900023
C -2.042890 1.299077 1.025142
H -1.519872 1.043045 1.949017
C -1.299986 1.625540 -0.115851
C 0.146099 1.953143 -0.028633
C 0.379040 3.297245 0.011041
H -0.323042 4.127682 -0.000492
C 1.468965 1.318251 0.029885
C 2.338259 2.431866 0.092072
C 3.732408 2.420650 0.123908
H 4.291543 3.355311 0.174232
C 4.311344 1.189486 0.068648
H 5.398671 1.089944 0.074237
C 3.533711 -0.001132 -0.000134
C 2.081161 -0.000697 -0.000275
C 4.310645 -1.192214 -0.068769
H 5.398032 -1.093323 -0.074143
C 3.730982 -2.423031 -0.124152
H 4.289568 -3.358026 -0.174374
C 2.336821 -2.433413 -0.092589
C 1.468181 -1.319278 -0.030559
C 0.144925 -1.953380 0.027702
C 0.377069 -3.297620 -0.011943
H -0.325511 -4.127637 -0.000551
C -1.300980 -1.624915 0.114666
C -1.986912 -1.972073 1.286571
H -1.410856 -2.242317 2.175003
C -3.379776 -2.017619 1.313475
H -3.896912 -2.304063 2.232798
C -4.106081 -1.716679 0.164674
H -5.197870 -1.763057 0.175366
C -3.433966 -1.344322 -1.000158
H -3.998798 -1.096730 -1.901677
C -2.043490 -1.298003 -1.026455
H -1.520157 -1.042276 -1.950237
44
Min2 E[hartree] = -1148.742320 G[hartree] = -1148.442504
O 1.317118 3.459734 -0.712289
O 1.453582 -3.446279 0.830747
C -2.393889 1.638295 0.714956
H -2.615040 2.236974 -0.171567
C -3.429777 1.199490 1.533862
H -4.460173 1.474630 1.295668

C	-3.158824	0.393264	2.639027
H	-3.973731	0.042266	3.276931
C	-1.840714	0.036484	2.923243
H	-1.616727	-0.590947	3.789611
C	-0.802002	0.482393	2.111224
H	0.229770	0.213386	2.346716
C	-1.065733	1.285117	0.991381
C	0.041379	1.827611	0.190719
C	0.105194	3.130975	-0.216042
H	-0.618117	3.939242	-0.140202
C	1.349122	1.275195	-0.118138
C	2.087408	2.356278	-0.610940
C	3.468402	2.339285	-0.849293
H	3.982397	3.226769	-1.220690
C	4.129056	1.183452	-0.513387
H	5.216834	1.132672	-0.603874
C	3.438496	0.021261	-0.057246
C	2.003807	0.011079	0.024051
C	4.192556	-1.130654	0.317037
H	5.282762	-1.064424	0.284008
C	3.590494	-2.295407	0.724597
H	4.155667	-3.175227	1.034839
C	2.191783	-2.332125	0.643819
C	1.387294	-1.262056	0.238332
C	0.061026	-1.833232	0.078619
C	0.188861	-3.135204	0.474647
H	-0.526777	-3.953772	0.480283
C	-1.136649	-1.307485	-0.592339
C	-2.420287	-1.679589	-0.169254
H	-2.532217	-2.280879	0.735823
C	-3.547626	-1.256301	-0.866520
H	-4.540750	-1.546111	-0.514574
C	-3.413855	-0.447057	-1.994334
H	-4.300066	-0.108202	-2.536549
C	-2.141133	-0.071807	-2.424264
H	-2.024679	0.557929	-3.309873
C	-1.011657	-0.502213	-1.734223
H	-0.016800	-0.218949	-2.084057

b) ***Compound 3ma***

35

Min1 E[hartree] = -1340.609453 G[hartree] = -1340.385365

O	1.353254	4.541682	2.432321
O	6.756432	6.066895	6.767309
C	2.078539	4.159477	3.524659
C	1.897725	2.921592	4.148137
H	1.113927	2.240797	3.815132

C	2.777047	2.608995	5.159707
H	2.707358	1.637282	5.655161
C	3.794794	3.503036	5.581807
C	4.730589	3.067868	6.567869
H	4.611311	2.064277	6.982988
C	5.775621	3.857780	6.972191
H	6.517313	3.530054	7.701689
C	5.833271	5.147591	6.423825
C	6.438467	7.220798	6.125845
C	5.320540	7.062360	5.349506
C	4.919572	5.676439	5.508683
C	3.902180	4.811576	4.982986
C	3.035206	5.084826	3.895507
C	7.314910	8.387807	6.392375
H	6.819874	9.281341	5.984520
H	7.386376	8.529047	7.484565
C	4.635869	8.184232	4.679658
C	5.203556	8.836538	3.579489
H	6.151836	8.474369	3.175310
C	4.546171	9.909310	2.976881
H	4.995442	10.399507	2.109700
C	3.311209	10.336660	3.459422
H	2.787212	11.163351	2.974263
C	2.739025	9.698435	4.561816
H	1.765999	10.021850	4.937883
C	3.400502	8.637103	5.172307
H	8.337159	8.273715	5.960714
H	0.642344	3.920659	1.878167
Cl	2.681286	7.822632	6.556852
H	3.121605	6.008043	3.361553

35

TS1 E[hartree] = -1340.568464 G[hartree] = -1340.341123

O	0.688387	4.564800	3.359428
O	6.351902	6.163872	7.198655
C	1.912311	4.191760	3.791021
C	2.383223	2.869068	3.643651
H	1.766607	2.120115	3.137266
C	3.593644	2.523945	4.196203
H	3.933105	1.485823	4.149117
C	4.406157	3.467898	4.869083
C	5.540079	3.020824	5.608390
H	5.808524	1.962538	5.565980
C	6.219040	3.878478	6.431814
H	7.028703	3.559556	7.089376
C	5.829661	5.227375	6.390867
C	5.824809	7.366593	6.855760
C	5.013531	7.247846	5.732989
C	4.884891	5.787792	5.536885

C	3.998425	4.848139	4.886845
C	2.703927	5.148690	4.399918
C	6.106557	8.381328	7.906060
H	7.106095	8.830901	7.811618
H	5.364239	9.183276	7.914507
C	4.554199	8.298657	4.790375
C	3.809603	7.900270	3.658134
H	3.673849	6.839834	3.482745
C	3.266178	8.771877	2.725994
H	2.689947	8.367348	1.890908
C	3.469385	10.141038	2.859538
H	3.035002	10.855633	2.157208
C	4.306882	10.577654	3.875385
H	4.577077	11.631550	3.960389
C	4.876265	9.681345	4.785357
H	6.067922	7.853091	8.871012
H	0.226635	3.798161	3.004894
Cl	6.121191	10.406251	5.762761
H	2.265568	6.134598	4.540664

35

TS2 E[hartree] = -1340.555950 G[hartree] = -1340.329157

O	1.499047	3.645082	2.378600
O	6.763473	6.067091	6.264583
C	2.112060	3.626381	3.583375
C	1.847902	2.621986	4.538442
H	1.098050	1.851860	4.331996
C	2.599883	2.577385	5.689660
H	2.470618	1.748176	6.390287
C	3.590886	3.548181	5.967443
C	4.538816	3.313352	7.006444
H	4.408928	2.439808	7.649882
C	5.653672	4.099768	7.113819
H	6.465454	3.895234	7.813066
C	5.705788	5.234801	6.285630
C	6.435637	7.124391	5.494575
C	5.118196	7.051316	5.048669
C	4.697915	5.686341	5.434172
C	3.719024	4.678778	5.085979
C	3.033207	4.621293	3.857516
C	7.597657	8.013176	5.225700
H	7.849662	8.664887	6.079503
H	8.473449	7.370853	5.044427
C	4.440137	8.319241	4.635518
C	5.075785	9.516523	5.061539
H	5.900576	9.441469	5.763426
C	4.687044	10.794789	4.692842
H	5.251342	11.653690	5.063074
C	3.565320	10.968943	3.888768

H 3.236697 11.960612 3.570846
C 2.825170 9.845337 3.559921
H 1.889085 9.937241 3.006657
C 3.221832 8.561154 3.955009
H 7.429809 8.641751 4.343371
H 0.931845 2.871633 2.298368
Cl 2.021913 7.355720 3.644633
H 3.247646 5.339680 3.073059
35
Min2 E[hartree] = -1340.609328 G[hartree] = -1340.385373
O 1.148804 4.845997 2.661842
O 6.713263 6.087166 6.904829
C 2.020040 4.386837 3.585959
C 1.979840 3.048832 4.042127
H 1.225016 2.363291 3.643787
C 2.890964 2.612679 4.976147
H 2.860280 1.574641 5.317981
C 3.878834 3.476125 5.507107
C 4.833931 3.002090 6.456612
H 4.775954 1.956770 6.770314
C 5.814785 3.817265 6.965997
H 6.558374 3.465888 7.682580
C 5.822075 5.148586 6.517441
C 6.393614 7.239865 6.264026
C 5.299202 7.067550 5.458759
C 4.910181 5.683865 5.611875
C 3.903177 4.836714 5.052110
C 2.967423 5.261688 4.085220
C 7.247322 8.415345 6.535451
H 6.791556 9.317171 6.107247
H 7.381617 8.559273 7.618437
C 4.651388 8.123946 4.661295
C 3.351574 8.546792 4.981361
H 2.848331 8.068112 5.824800
C 2.706469 9.540078 4.252931
H 1.693893 9.845105 4.525910
C 3.358158 10.143668 3.177411
H 2.862088 10.925074 2.597009
C 4.648015 9.749421 2.837322
H 5.174049 10.205621 1.997042
C 5.283514 8.747539 3.572808
H 8.244776 8.289818 6.083622
H 0.560306 4.132372 2.395507
Cl 6.883736 8.272235 3.097055
H 2.977873 6.283394 3.707259

c) ***Compound 3n***

36

Min1 E[hartree] = -956.365701 G[hartree] = -956.126152

O	0.790380	4.922669	3.439940
O	7.077907	5.883366	6.621511
H	2.804245	6.288719	4.193621
H	0.142210	4.232104	3.268207
C	1.849369	4.391142	4.088217
C	1.909107	3.015072	4.405819
H	1.084854	2.355033	4.117123
C	2.995796	2.515051	5.085524
H	3.031351	1.452880	5.342159
C	4.074070	3.345297	5.473328
C	5.171539	2.814268	6.217059
H	5.162982	1.749044	6.461548
C	6.208740	3.606637	6.639579
H	7.044483	3.221310	7.225188
C	6.151123	4.963998	6.278668
C	6.676273	7.057843	6.088835
C	5.508583	6.939375	5.391668
C	5.134006	5.545552	5.523093
C	4.021487	4.736022	5.122478
C	2.889047	5.231892	4.442388
C	4.858848	8.016808	4.624504
C	4.553012	7.838359	3.272145
H	4.807373	6.883115	2.806467
C	3.935858	8.837405	2.521346
H	3.705320	8.668207	1.467617
C	3.620173	10.047044	3.131035
H	3.133267	10.842049	2.560820
C	3.925711	10.261618	4.474945
H	3.674035	11.217919	4.933958
C	4.549731	9.258321	5.224755
O	4.888176	9.398727	6.523547
C	4.552084	10.578738	7.196483
H	3.461482	10.754577	7.200812
H	4.894316	10.456390	8.232237
H	5.051703	11.461772	6.758809
H	7.315830	7.916467	6.273492

36

TS1 E[hartree] = -956.346185 G[hartree] = -956.104921

O	3.516507	3.682836	1.581339
O	3.851151	6.239414	8.243103
H	3.276775	5.453261	3.294699
H	3.620262	2.854996	1.101406
C	3.867460	3.499351	2.873474
C	4.339661	2.261435	3.351148
H	4.467419	1.415658	2.668760

C 4.585687 2.126815 4.696363
H 4.897088 1.157335 5.093945
C 4.423354 3.199565 5.604606
C 4.562150 2.937912 6.998157
H 4.829725 1.927583 7.316467
C 4.317739 3.916748 7.917678
H 4.368866 3.754928 8.995075
C 4.031853 5.196690 7.415451
C 3.749852 7.331732 7.474057
C 3.853243 7.064349 6.129568
C 3.978150 5.586924 6.071418
C 4.054435 4.503651 5.107001
C 3.730050 4.573950 3.733960
C 3.952584 8.155743 5.128329
C 3.836303 7.932828 3.751825
H 3.655024 6.925733 3.412102
C 3.956112 8.925517 2.783480
H 3.849978 8.664600 1.728567
C 4.211927 10.230179 3.176305
H 4.307849 11.033644 2.442306
C 4.352030 10.510787 4.532471
H 4.559249 11.534464 4.842428
C 4.230691 9.507907 5.499292
O 4.382765 9.793419 6.812346
C 4.785742 11.071769 7.216398
H 4.031853 11.840771 6.971852
H 4.904170 11.029359 8.307203
H 5.750619 11.360519 6.764071
H 3.619022 8.265829 8.001548
36
TS2 E[hartree] = -956.337265 G[hartree] = -956.09495
O 3.325738 3.209022 1.730128
O 3.702928 6.274620 8.113845
H 3.102936 5.133908 3.376819
H 3.447469 2.351478 1.310148
C 3.755408 3.145439 3.015874
C 4.338449 1.979128 3.549358
H 4.475719 1.091542 2.923889
C 4.677441 1.959474 4.882646
H 5.064823 1.039917 5.329198
C 4.506211 3.090217 5.715659
C 4.697023 2.953961 7.121536
H 5.041117 1.994641 7.515486
C 4.381485 3.981576 7.963856
H 4.442077 3.906870 9.050364
C 4.000610 5.196613 7.367698
C 3.532327 7.289521 7.259580
C 3.730934 6.953335 5.939165

C 3.945742 5.486523 5.998632
C 4.043100 4.324261 5.134144
C 3.603129 4.273305 3.798934
C 3.863714 8.091794 4.967885
C 3.990750 9.386497 5.518392
H 4.044587 9.500314 6.598890
C 4.095075 10.551596 4.770107
H 4.185058 11.513400 5.279184
C 4.114847 10.470920 3.383509
H 4.203100 11.366982 2.764915
C 4.048860 9.219357 2.788131
H 4.088260 9.143623 1.702278
C 3.936975 8.047848 3.552030
O 3.909485 6.846609 2.956344
C 4.107039 6.718780 1.573825
H 5.092421 7.111330 1.268559
H 4.058792 5.643259 1.355281
H 3.319217 7.232035 0.995113
H 3.275409 8.231224 7.731894
36
Min2 E[hartree] = -956.365707 G[hartree] = -956.126138
O 1.032924 4.823233 3.046424
O 7.131166 5.825060 6.565745
H 3.039241 6.180326 3.836052
H 0.380983 4.137529 2.869567
C 1.975079 4.339362 3.884545
C 1.914624 3.018248 4.383568
H 1.083911 2.366389 4.094805
C 2.904780 2.555081 5.219022
H 2.861954 1.527905 5.591058
C 3.991349 3.374527 5.606618
C 5.031493 2.859803 6.438920
H 4.955174 1.824525 6.780864
C 6.115506 3.621558 6.795019
H 6.928145 3.237958 7.413366
C 6.137033 4.945208 6.322268
C 6.787584 6.979199 5.953895
C 5.583584 6.890481 5.316636
C 5.141686 5.528396 5.539452
C 4.032145 4.724234 5.120237
C 3.016862 5.172978 4.249218
C 4.895485 7.999805 4.632872
C 3.587791 8.346700 4.984766
H 3.095952 7.773852 5.774696
C 2.909967 9.388507 4.353945
H 1.887380 9.634439 4.647124
C 3.552420 10.106781 3.351010
H 3.037458 10.925188 2.841811

C	4.862284	9.794864	2.987053
H	5.350248	10.372079	2.201400
C	5.541804	8.751489	3.625678
O	6.812973	8.402115	3.337308
C	7.488909	9.063045	2.305560
H	7.616206	10.140043	2.517224
H	8.480376	8.597667	2.232842
H	6.971649	8.951231	1.335872
H	7.488381	7.803999	6.048565

d) ***Compound 4na***

52

Min1 E[hartree] = -1468.421999 G[hartree] = -1468.071228

O	1.391377	4.363848	2.602794
O	6.897943	6.059399	6.747747
O	-0.127597	5.966134	3.959709
O	0.573131	7.710172	2.906113
N	0.570885	6.525749	3.157701
C	2.996100	6.058408	2.989795
H	2.933279	7.054928	3.435518
C	1.618317	5.705502	2.392462
H	1.478774	5.979380	1.340026
C	2.196392	3.978153	3.641648
C	2.117887	2.712579	4.227741
H	1.357757	1.997403	3.912427
C	3.062987	2.423682	5.186697
H	3.071058	1.436981	5.656707
C	4.046816	3.363372	5.589813
C	5.038932	2.959354	6.533502
H	4.991612	1.941427	6.927690
C	6.045586	3.801082	6.925092
H	6.827508	3.504656	7.625354
C	6.012228	5.104018	6.403980
C	6.500411	7.190823	6.131994
C	5.374928	7.011369	5.379332
C	5.045956	5.602248	5.523963
C	4.058661	4.689479	5.022752
C	3.120155	4.942193	3.995565
C	4.084072	6.095193	1.934850
C	4.895330	4.991922	1.660644
H	4.772037	4.073682	2.239966
C	5.867172	5.062667	0.662449
H	6.498971	4.194167	0.460573
C	6.035360	6.234969	-0.071800
H	6.799132	6.289725	-0.851490
C	5.227022	7.340490	0.196907
H	5.357552	8.266885	-0.368030
C	4.259003	7.270645	1.194682

H 3.637650 8.142614 1.418559
C 4.711481 8.157387 4.732418
C 5.421540 8.997278 3.872208
H 6.444573 8.720136 3.607773
C 4.844028 10.149083 3.336658
H 5.417290 10.785715 2.659640
C 3.529202 10.464003 3.661970
H 3.056177 11.355992 3.244009
C 2.792728 9.643648 4.518514
H 1.757788 9.895012 4.748294
C 3.377263 8.495191 5.060231
O 2.737615 7.635730 5.875135
C 1.420969 7.914587 6.283458
H 0.725310 7.964912 5.429183
H 1.119603 7.084712 6.934042
H 1.368093 8.859700 6.851594
H 7.077718 8.087900 6.342951
52
TS E[hartree] = -1468.388213 G[hartree] = -1468.035914
O 2.809454 3.265558 1.976204
O 4.086420 7.119567 7.760753
O 0.205866 3.872722 2.200619
O 0.476830 5.060429 0.419039
N 0.872723 4.474699 1.396484
C 2.623490 5.473514 2.876334
H 1.661119 5.567306 3.409279
C 2.369307 4.540467 1.662872
H 2.798302 4.888640 0.715338
C 3.294997 3.276210 3.248582
C 3.509042 2.085708 3.955341
H 3.412634 1.122536 3.453249
C 3.698784 2.200934 5.312352
H 3.758222 1.301382 5.930306
C 3.770153 3.465244 5.952943
C 3.746074 3.534182 7.379628
H 3.703939 2.596326 7.938693
C 3.714079 4.732976 8.045886
H 3.639888 4.804185 9.131755
C 3.881780 5.884436 7.259059
C 4.486282 7.896955 6.731277
C 4.537666 7.208978 5.547788
C 4.038401 5.883864 5.872080
C 3.772339 4.667698 5.161675
C 3.423677 4.541312 3.788580
C 2.994831 6.870145 2.438946
C 3.943867 7.108191 1.437540
H 4.539392 6.282658 1.039938
C 4.141593 8.391258 0.940455

H 4.884868 8.558676 0.158126
C 3.398739 9.461274 1.442218
H 3.544981 10.465755 1.036809
C 2.475301 9.241591 2.459956
H 1.895298 10.072434 2.868444
C 2.273014 7.952041 2.949019
H 1.530945 7.779527 3.733037
C 5.354881 7.615209 4.393000
C 6.134102 6.658885 3.731367
H 6.025332 5.610393 4.014903
C 7.056073 7.012661 2.748722
H 7.652602 6.240562 2.258069
C 7.219873 8.352789 2.416844
H 7.944928 8.651739 1.655952
C 6.457526 9.329398 3.056265
H 6.590194 10.375843 2.781863
C 5.526903 8.971190 4.035695
H 4.773563 8.914169 6.977142
O 4.770091 9.868050 4.705790
C 4.852991 11.223348 4.366604
H 4.134155 11.751198 5.006679
H 5.862202 11.633869 4.549091
H 4.583005 11.394680 3.309996
52
Min2 E[hartree] = -1468.390709 G[hartree] = -1468.038484
O 2.949143 3.294047 2.051787
O 4.554610 7.129080 7.792482
O 0.800339 4.578209 0.911344
O 2.300393 5.176053 -0.517613
N 1.933345 4.808873 0.573288
C 2.749593 5.481935 2.849093
H 1.663307 5.343423 3.026027
C 3.011296 4.623504 1.619010
H 3.961281 4.827665 1.101551
C 3.199789 3.295546 3.392650
C 3.191266 2.125322 4.158782
H 3.050710 1.153503 3.684263
C 3.277019 2.281434 5.525532
H 3.187338 1.408887 6.177500
C 3.494070 3.548811 6.123659
C 3.513802 3.669176 7.547383
H 3.326355 2.771459 8.141488
C 3.737747 4.870078 8.171064
H 3.729645 4.982031 9.256034
C 4.085183 5.948983 7.340133
C 5.016064 7.804546 6.717011
C 4.851436 7.104159 5.552236
C 4.152683 5.892287 5.947725

C	3.667745	4.713088	5.291795
C	3.356361	4.567094	3.917352
C	2.903186	6.973132	2.709401
C	3.396569	7.574057	1.548622
H	3.794307	6.970942	0.731097
C	3.361187	8.960630	1.401309
H	3.744062	9.411212	0.482713
C	2.836072	9.763247	2.409926
H	2.793139	10.847994	2.283252
C	2.351623	9.172610	3.577484
H	1.942498	9.791286	4.379314
C	2.373428	7.790235	3.718049
H	1.969539	7.330594	4.623531
C	5.519151	7.400293	4.276142
C	6.002219	6.354161	3.481162
H	5.844101	5.328063	3.816399
C	6.686132	6.588199	2.290461
H	7.049950	5.747583	1.695336
C	6.915468	7.897619	1.881597
H	7.450212	8.102812	0.951114
C	6.474471	8.961993	2.665877
H	6.666294	9.983197	2.337206
C	5.785621	8.724352	3.858910
H	5.486892	8.761817	6.913704
O	5.354185	9.710569	4.674391
C	5.555172	11.045391	4.303890
H	5.106070	11.660672	5.094345
H	6.628631	11.292967	4.224276
H	5.060948	11.280447	3.345565

e) ***Compound 7***

46

Min1 E[hartree] = -1261.880656 G[hartree] = -1261.573853

O	-1.832477	-2.331733	-1.655994
O	4.196800	0.665570	0.831234
C	-1.983026	-0.994912	-1.757877
H	-2.899456	-0.651350	-2.231211
C	-0.600855	-2.543350	-1.151361
C	-0.005999	-3.809600	-1.066962
H	-0.565058	-4.707634	-1.332417
C	1.322292	-3.831187	-0.724670
H	1.873943	-4.774221	-0.723428
C	2.021350	-2.642615	-0.362961
C	3.416067	-2.703798	-0.099276
H	3.924865	-3.666094	-0.196453
C	4.129110	-1.581112	0.224032
H	5.209953	-1.591066	0.370517
C	3.436022	-0.374087	0.451539

C 3.670964 1.904857 1.158681
C 2.240443 1.899962 1.377323
H 1.851615 2.755242 1.930169
C 1.435912 0.859327 1.017212
C 2.042257 -0.284041 0.343602
C 1.347439 -1.381095 -0.278885
C 0.032669 -1.332320 -0.847221
C -0.891310 -0.306887 -1.308176
C 0.037388 0.851133 1.508938
C -0.519080 -0.313746 2.057934
H 0.060617 -1.238742 2.064121
C -1.795987 -0.296194 2.611171
H -2.211473 -1.212075 3.038067
C -2.539124 0.883865 2.625011
H -3.543528 0.895270 3.055419
C -1.992266 2.049055 2.088493
H -2.569546 2.976709 2.084786
C -0.714839 2.033264 1.537996
H -0.307876 2.938755 1.082106
C -0.722838 1.140831 -1.500407
C 0.523590 1.685006 -1.838528
H 1.389205 1.026733 -1.934666
C 0.666788 3.053312 -2.059750
H 1.650358 3.458821 -2.308860
C -0.436845 3.899755 -1.968969
H -0.323150 4.972552 -2.142033
C -1.688768 3.365253 -1.658641
H -2.560590 4.019955 -1.583190
C -1.828555 2.002254 -1.421191
H -2.800868 1.599131 -1.128674
O 4.429454 2.820663 1.308453
46
TS E[hartree] = -1261.828569 G[hartree] = -1261.521527
O -2.074422 -1.761411 -0.463826
O 2.928060 2.795612 -2.420256
C -1.220277 -2.019642 0.534410
H -1.410965 -2.917682 1.117545
C -1.757395 -0.537116 -0.922869
C -2.617343 0.134750 -1.797331
H -3.534880 -0.340862 -2.144846
C -2.255888 1.411825 -2.109482
H -2.894660 2.034636 -2.739222
C -0.972779 1.912887 -1.746452
C -0.586638 3.103971 -2.414387
H -1.355640 3.683786 -2.930344
C 0.726744 3.436354 -2.547229
H 1.075803 4.265182 -3.164076
C 1.680337 2.585205 -1.963288

C 3.971670 1.930121 -2.164123
C 3.746509 1.122965 -0.987981
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C 2.538851 1.036915 -0.358847
C 1.352521 1.594927 -1.014907
C -0.041676 1.183415 -0.918612
C -0.598801 -0.020658 -0.305382
C -0.322399 -1.009557 0.747310
C 2.628381 0.656921 1.065615
C 2.162830 1.576258 2.013031
H 1.554837 2.423243 1.685268
C 2.514000 1.439934 3.352345
H 2.155129 2.168592 4.082875
C 3.313545 0.375950 3.763363
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C -0.112157 -0.285138 4.426199
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C -0.505829 -1.773329 -1.527845
C 0.176175 -2.966257 -1.803788
H -0.271929 -3.731109 -2.439148
C 1.375418 -3.138990 -1.160344
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C 1.945499 -2.112662 -0.351730
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C 3.174698 -0.116940 1.170535

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H	2.534259	3.614648	0.777357
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C	2.074520	0.235311	0.378161
C	1.319335	-0.829863	-0.229238
C	-0.025269	-0.738134	-0.716760
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f) ***Compound 4aa***

54

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C 5.775621 3.857780 6.972191
H 6.517313 3.530054 7.701689
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C 6.438467 7.220798 6.125845
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C 5.238142 8.888463 3.631102
H 6.216825 8.568147 3.265944
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N 0.941454 4.426717 1.286897

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H	3.217447	10.443360	0.941981
C	2.227984	9.180448	2.388169
H	1.587620	9.978749	2.771295
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H	6.623453	8.703686	8.485776
C	5.318045	7.639137	4.331518
C	6.167608	6.700926	3.718680
H	6.152057	5.663762	4.060518
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H	7.707401	6.340315	2.259929
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H	7.804189	8.720570	1.514248
C	6.250403	9.349721	2.878270
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54
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N 0.879962 6.385439 1.416686
C 2.591769 6.350105 3.251160
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C	6.526868	8.396283	3.173944
H	6.578773	9.202575	3.906404

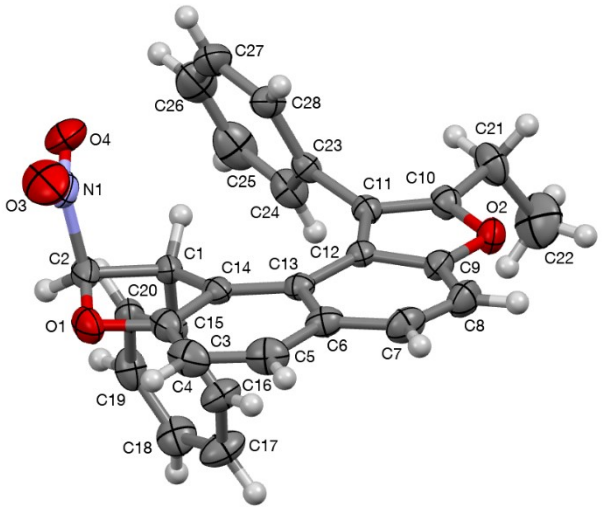
9. Single crystal X-Ray diffraction

Crystals suitable for single crystal X-ray diffraction analysis were obtained by slow evaporation from cyclohexane for **4aa**, from a CH_2Cl_2/n-hexane mixture for **4na**, from CH_2Cl_2 for **4ma** and **4oa**, from a CH_2Cl_2/cyclohexane mixture for **5fa** and from $CHCl_3$ for **4ha**. They were measured on a Rigaku Oxford Diffraction SuperNova diffractometer at room temperature at the CuKα radiation (λ=1.54184 Å). Data collection reduction and multiscan ABSPACK correction were performed with CrysAlisPro (Rigaku Oxford Diffraction). Using Olex2[1] the structures were solved by intrinsic phasing methods with SHELXT[2] and SHELXL[3] was used for full matrix least squares refinement. H-atoms were found experimentally for all compounds except for **5na** where they were introduced at geometrical positions. All hydrogens were refined as riding atoms with their Uiso parameters constrained to 1.2Ueq(parent atom) for the CH and CH_2 groups and to 1.5Ueq(parent atom) for the CH_3.
5na crystallized with the two enantiomers in the asymmetric unit but not related by a crystallographic symmetry as they are also conformers.

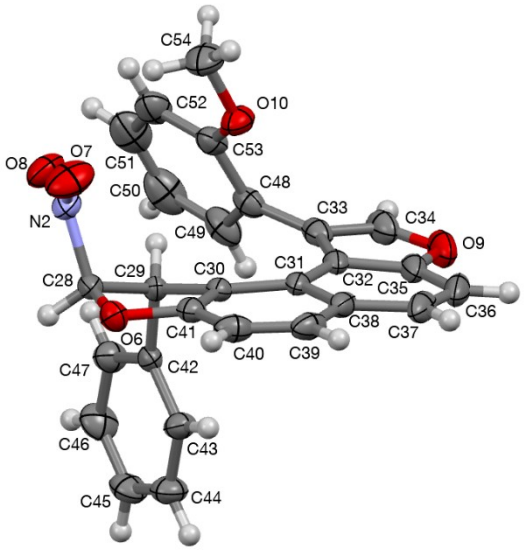
1- Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.
2- Sheldrick, G. M. *Acta Cryst.* **2015**, A71, 3-8.
3- Sheldrick, G. M. *Acta Cryst.* **2015**, C71, 3-8.

Table A. Crystal data and structure refinement for **4aa**, **4na**, **4ma**, **4fa**, **4ha**, **4oa** and **7**.

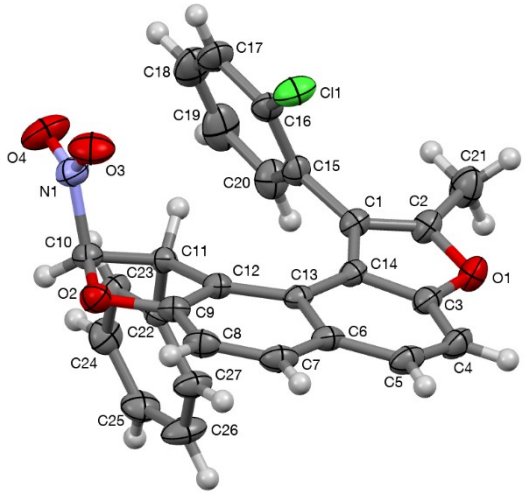
Compound	**4aa**	**4na**	**4ma**	**4fa**	**4ha**	**4oa**	**7**
Formula	$C_{28}H_{21}N_1O_4$	$C_{54}H_{38}N_2O_{10}$	$C_{27}H_{18}Cl_1N_1O_4$	$C_{27}H_{20}N_2O_3$	$C_{27}H_{19}N_1O_4$	$C_{27}H_{17}N_1O_5$	$C_{27}H_{16}O_3$
M_w	435.46	874.86	455.87	420.45	421.43	435.42	388.40
Crystal system	orthorhombic	orthorhombic	monoclinic	orthorhombic	triclinic	orthorhombic	monoclinic
Space group	P $2_12_12_1$	P n$a2_1$	P 2_1/c	P $2_12_12_1$	P -1	P b c a	P 2_1/n
a/ Å	12.28419(14)	15.4716(8)	15.3160(5)	9.18760(10)	8.7947(2)	10.9082(6)	10.93381(14)
b/ Å	13.47791(17)	10.1507(8)	9.2552(2)	11.14520(10)	9.7683(2)	13.4620(7)	15.53317(18)
c/ Å	13.83030(17)	27.2357(19)	16.7635(5)	20.9565(2)	13.6750(3)	28.2100(13)	11.17806(14)
α/ °					78.591(2)		
β/ °			112.958(4)		74.221(2)		92.8746(12)
γ/ °					66.162(2)		
V/ Å^3	2289.82(5)	4277.3(5)	1421.4(2)	2145.90(4)	1028.93(5)	4142.5(4)	1896.06(4)
Z	4	4	4	4	2	8	4
Dc/g.cm^{-3}	1.266	1.359	1.384	1.301	1.360	1.396	1.361
Crystal colour	colorless	colorless	colorless	colorless	colorless	colorless	yellow
Crystal size/mm^3	0.08*0.1*0.22	0.04*0.16*0.3	0.05*0.12*0.2	0.24*0.28*0.3	0.1*0.1*0.12	0.12*0.26*0.3	0.12*0.18*0.2
μ(Mo-Kα)/mm^{-1}	0.685	0.773	1.841	0.689	0.744	0.798	0.707
N° of refl. measured	17009	29242	14184	22277	18898	12209	14711
N° of unique refl.	4475	7959	4174	4452	4028	3947	3710
N° of obs. refl.[$F^2 > 4\sigma F^2$]	4184	6706	3074	4332	3629	2964	3365
N° parameters refined	300	598	299	291	290	300	272
R_1 [$F^2>4\sigma F^2$]	0.0371	0.0706	0.0473	0.0404	0.0435	0.0661	0.0347
wR_1 [$F^2>4\sigma F^2$]	0.0991	0.1815	0.1342	0.1123	0.1221	0.2311	0.0957
R_2 [all refl.]	0.04	0.0792	0.0671	0.0419	0.0469	0.0970	0.0378
wR_2 [all refl.]	0.1031	0.1946	0.1692	0.1142	0.1260	0.2936	0.0992
Goodness of fit [all refl.]	1.026	1.04	1.132	1.069	1.039	1.132	1.043
Residual Fourier/e. Å^{-3}	-0.155; 0.127	-0.248; 0.569	-0.385; 0.288	-0.174; 0.14	-0.25; 0.24	-0.341; 0.404	-0.151; 0.172
Flack	0.0(3)			-0.06(8)			



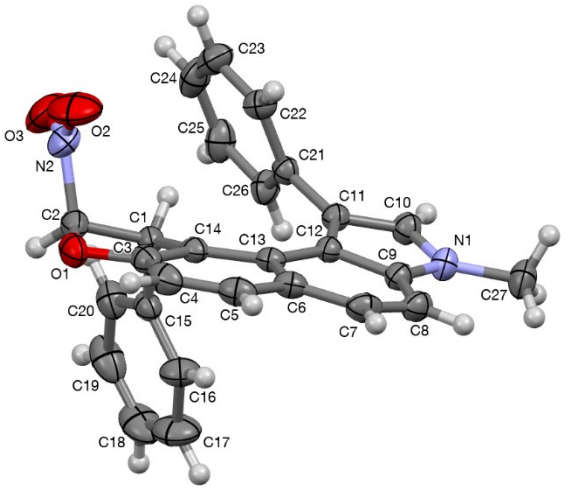
4aa



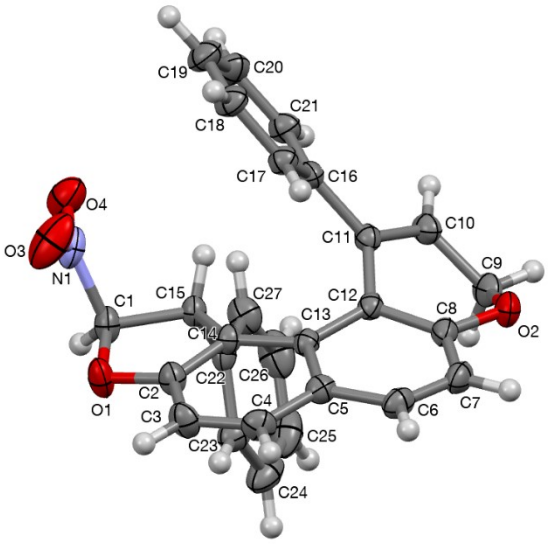
4na



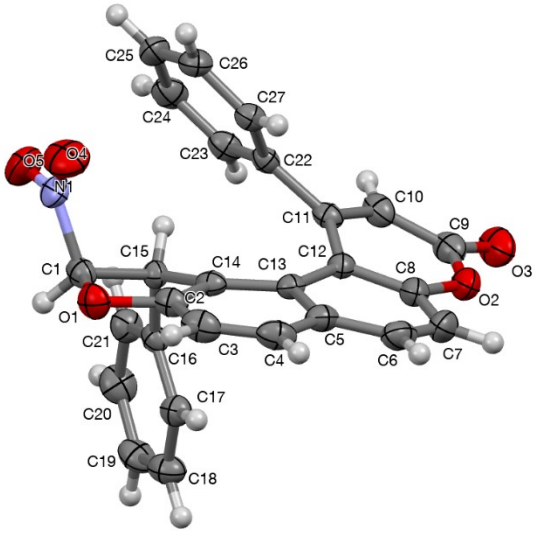
4ma



4fa

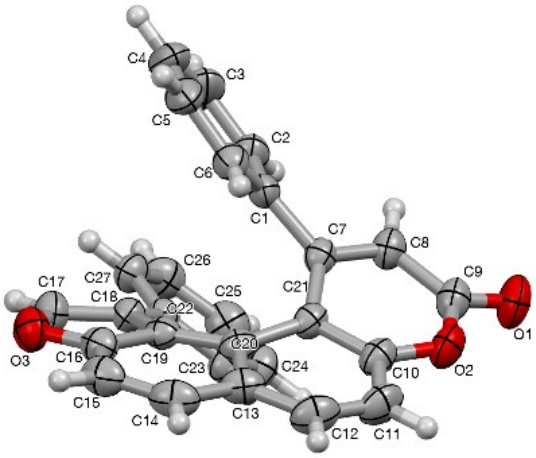


4ha



4oa

7



oa and **8**. Atomic displacement parameters
ıantiomer for **4na** is presented for clarity.

10. Virbational Circular Dichroism (VCD) and Electronic Circular Dichroism (ECD)

Goal: Elucidation of the absolute configuration of the two enantiomers of **4aa** using VCD and ECD spectroscopies combined with quantum chemistry calculations.

a) Measurments

VCD measurements: Infrared (IR) and vibrational circular dichroism (VCD) spectra were recorded on a Bruker PMA 50 accessory coupled to a Vertex70 Fourier transform infrared spectrometer. A photoelastic modulator (Hinds PEM 90) set at l/4 retardation was used to modulate the handedness of the circular polarized light at 50 kHz. Demodulation was performed by a lock-in amplifier (SR830 DSP). An optical low-pass filter (< 1800 cm-1) before the photoelastic modulator was used to enhance the signal/noise ratio. A transmission cell equipped with CaF2 windows and of 200 µm of optical pathlength was used. Solutions with a concentration of 0.06 mol L^{-1} were prepared by dissolving the solid samples in CD_2Cl_2. The VCD spectra of the pure enantiomers (1st eluted)-**4aa** and (2nd eluted)-**4aa** were measured at room temperature and the baseline of the spectra were corrected using the standard procedure of the half-subtraction of the spectra of each enantiomer. For each individual spectrum, about 12000 scans were averaged at 4 cm^{-1} resolution (corresponding to 3 hours measurement time). For IR absorption spectra, the cell filled with CD_2Cl_2 served as a reference. The spectra are presented without smoothing and further data processing.

ECD measurements:

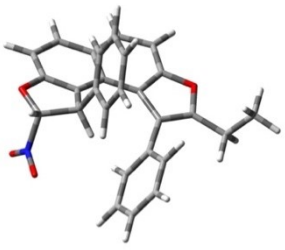
UV-vis and electronic circular dichroism (ECD) spectra were measured on a JASCO J-815 spectrometer equipped with a JASCO Peltier cell holder PTC-423 to maintain the temperature at 20.0 °C. A quartz photoelastic modulator set at l/4 retardation was used to modulate the handedness of the circular polarized light at 50 kHz. A quartz cell of 1 mm of optical path length was used. Solutions with a concentration of 0.22 mmol.L^{-1} for both enantiomers were prepared in acetonitrile (HPLC grade). The ECD spectrometer was purged with nitrogen during the recording of spectra. The UV absorption and ECD spectra were recorded using acetonitrile as a reference and are presented without smoothing and further data processing. Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 2 nm, and 3 accumulations per sample.

MOLECULAR MODELING

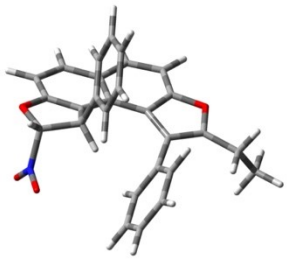
1- Conformational study.

The IR and VCD spectra of molecule **4aa** were calculated for the enantiomer of absolute configuration (1*R,*2*R,P*). For the conformational analysis of this molecule, the geometries have been optimized using density functional theory (DFT) with B3LYP functional and TZVP basis set. Solvent effects were considered using the implicit polarizable dielectric continuum solvation model SMD. Dichloromethane (DCM) and acetonitrile (ACN) were chosen in analogy respectively with the VCD and ECD experiments. By systematically exploring the conformational space regardless of the selected solvent, we were able to establish that there are only two conformations for the molecule (1*R*,2*R*,*P*)-**4aa** (Figure 1).

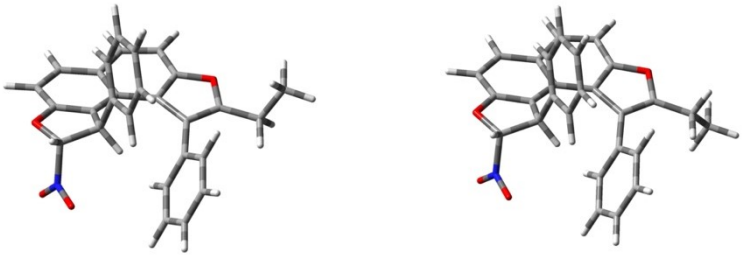
(a) in CD_2Cl_2



A_1 (60%)



A_2 (40%)



B_1 (61%)

B_2 (39%)

*Figure 1- Geometries of the two conformations of (1R,2R,P)-**4aa** optimized with (a) SMD(DCM)/B3LYP/TZVP and (b) SMD(ACN)/B3LYP/TZVP level. The Boltzmann populations calculated at the same theoretical level as for the geometry optimizations are given in brackets.*

2- Calculation of averaged IR, VCD, UV and ECD spectra

The vibrational frequencies, IR absorption and VCD intensities were calculated using the same theoretical level as for geometry optimizations, SMD(DCM)/B3LYP/TZVP. The frequencies calculations allow to establish that the conformations found are minima (no imaginary frequency). For the calculation of IR/VCD spectra, computed harmonic frequencies are generally larger than those experimentally observed. Thus, a scaling factor of 0.985 has been applied homogenously to all calculated frequencies in order to calibrate the spectra. IR absorption and VCD spectra were constructed respectively from calculated dipole and rotational strengths assuming Lorentzian band shape with half-width of 8 cm^{-1}.

Based on the SMD(ACN)/B3LYP/TZVP optimized geometries, the ECD and UV-vis spectra were calculated using time dependent density functional theory (TD-DFT) with CAM-B3LYP functional and 6-31++G(d,p) basis set. Calculations were performed for vertical 1A singlet excitation using 60 states. In order to compare theoretical and experimental spectra, the calculated UV and ECD spectra have been modeled using a gaussian function, with a half-width of 0.37 eV. Due to the approximations of the theoretical model used, an offset almost constant was observed between measured and calculated frequencies. Using UV spectra, all calculated frequencies were calibrated by a factor of 1.02. All calculations were performed using Gaussian 16 package.[21]

RESULTS

IR AND VCD ANALYSIS

Figure 2 shows the IR and VCD spectra measured for the two enantiomers (1st eluted)-**4aa** (green curve) and (2nd eluted)-**4aa** (red curve) and calculated for the enantiomer (1*R*,2*R*,*P*)-**4aa** (blue curve). It can be observed that the IR and VCD spectra calculated for (1*R*,2*R*,*P*)-**4aa** gives the best correlation (signs and intensities of bands) with the spectra measured for the (1st eluted)-**4aa** enantiomer.

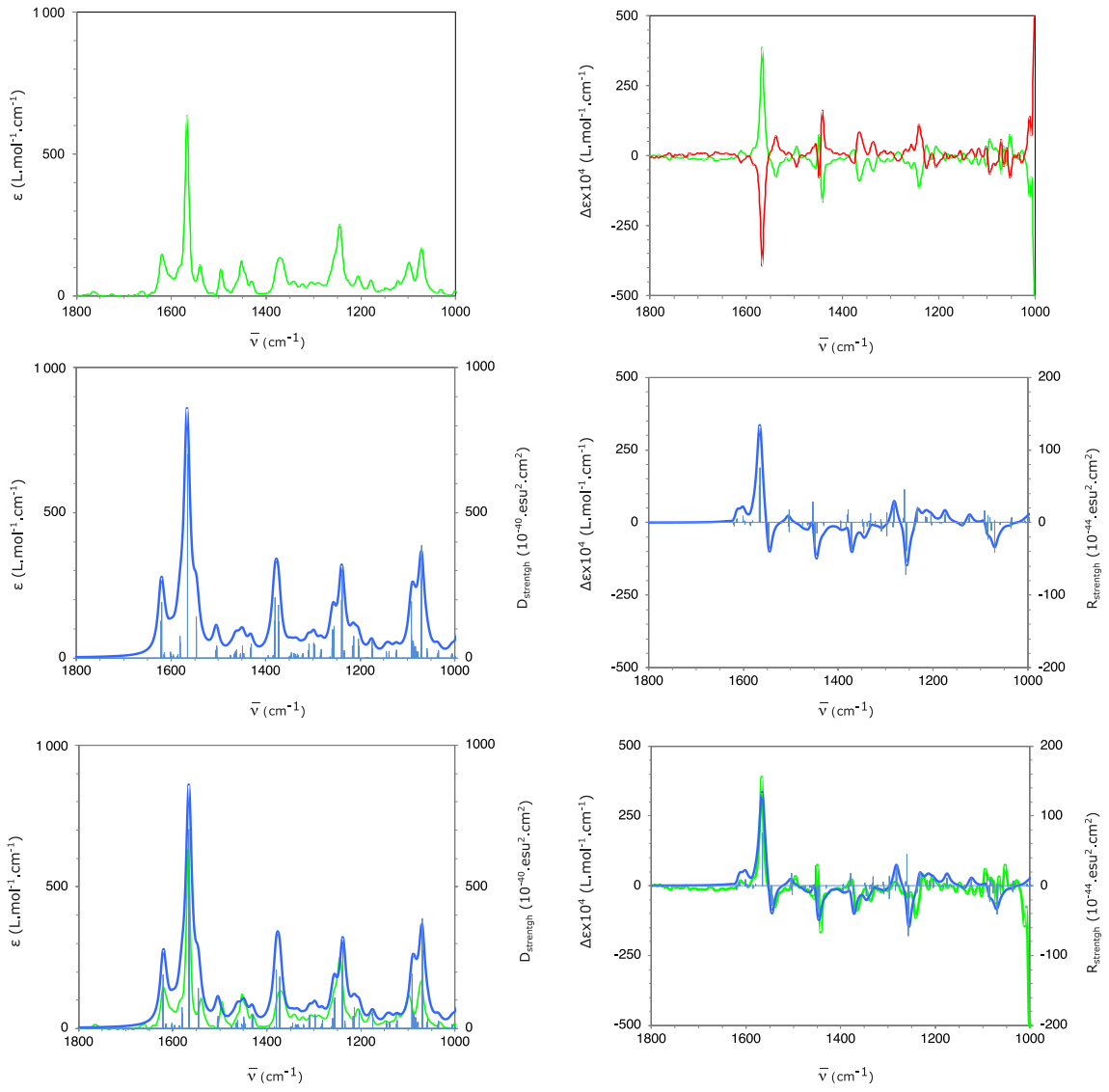


*Figure 2 - IR (left) and VCD (right) spectra measured in CD_2Cl_2 for (1st eluted)-**4aa** (green) and (2nd eluted)-**4aa** (red), and calculated using SMD(DCM)/B3LYP/TZVP for (1R,2R,P)-**4aa*** (Lorentzian shape in dark blue, Dipole and Rotational strength in clear blue).

UV AND ECD ANALYSIS

Figure 3 shows the UV and ECD spectra measured for the two enantiomers (1st eluted)-**4aa** (green curve) and (2nd eluted)-**4aa** (red curve) and calculated for the enantiomer (1*R*,2*R*,*P*)-**4aa** (blue curve). It can be observed that the UV and ECD spectra calculated for (1*R*,2*R*,*P*)-**4aa** gives the best correlation (signs and intensities of bands) with the spectra measured for the (1st eluted)-**4aa** enantiomer.

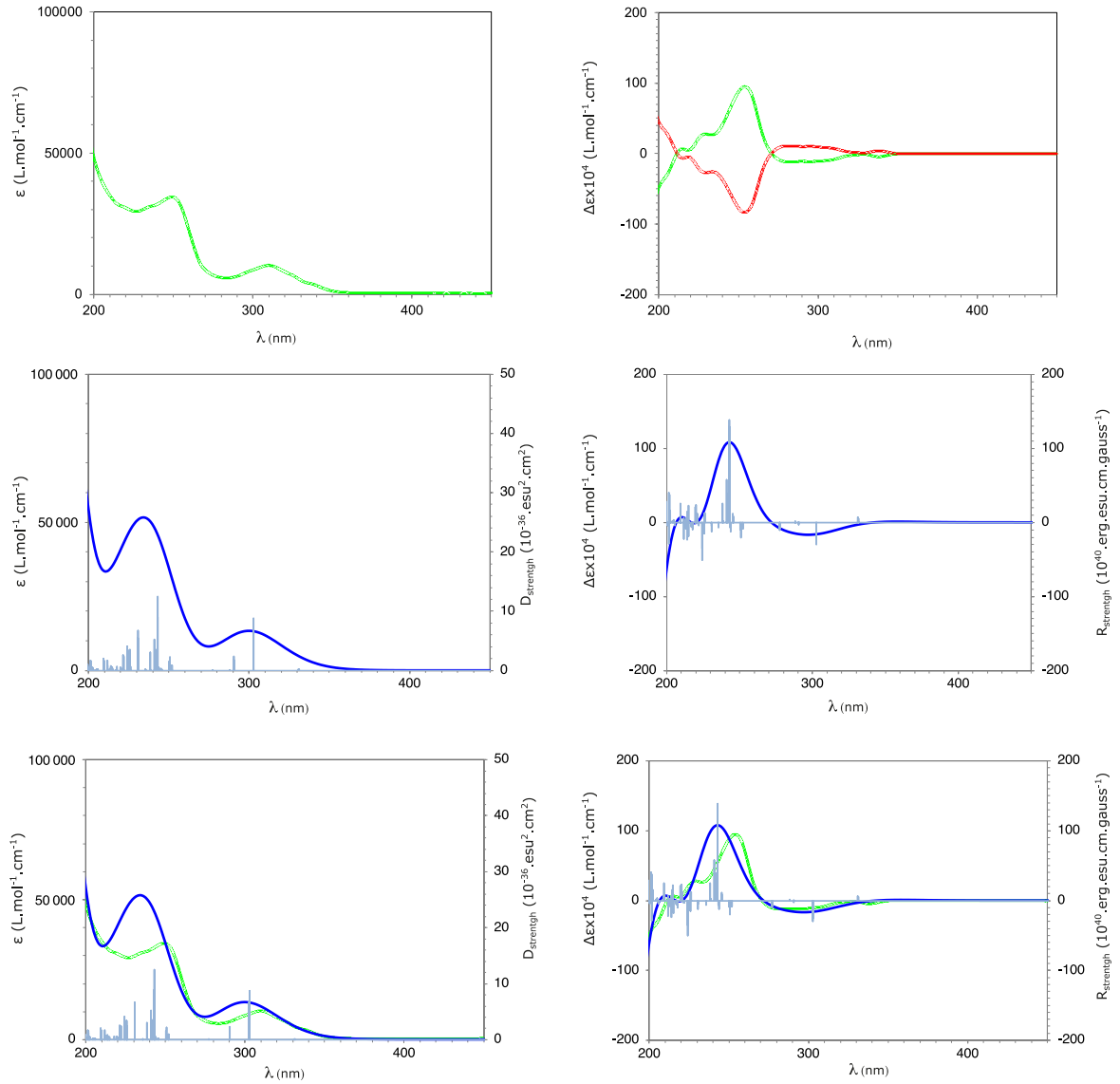


*Figure 3 - UV (left) and ECD (right) spectra measured in CH_3CN for (1st eluted)-**4aa** (green) and (2nd eluted)-**4aa** (red), and calculated using TD(60)-SMD(ACN)/CAM-B3LYP/6-31++G(d,p)//SMD(ACN)/B3LYP/TZVP for (1R,2R,P)-**4aa*** (Gaussian shape in dark blue, Dipole and Rotational strength in clear blue).

CONCLUSION

The absolute configuration of the **4aa** molecule was established by comparing measured and calculated IR/VCD and UV/ECD spectra. DFT conformational analysis of the molecule at the SMD(DCM)/B3LYP/TZVP (VCD) and SMD(ACN)/B3LYP/TZVP (ECD) levels established that two conformations are required to model the various spectra : IR, VCD, UV and ECD (Figure 1-3). For both the IR/VCD and UV/ECD analyses, excellent agreement between measured and calculated spectra unambiguously establishes that the 1st eluted enantiomer of the **4aa** molecule is of absolute configuration (1*R*,2*R*,*P*). Consequently, the 2nd eluted enantiomer will be (1*S*,2*S*,*M*).

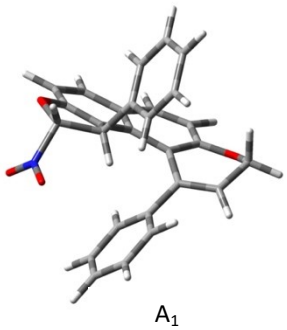
Goal: Elucidation of the absolute configuration of the two enantiomers of molecule **4ha** using VCD and ECD spectroscopies combined with quantum chemistry calculations.

MOLECULAR MODELING

1- Conformational study.

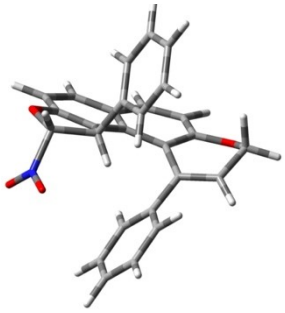
The IR and VCD spectra of molecule **4ha** were calculated for the enantiomer of absolute configuration (1*R*,2*R*,*P*). For the conformational analysis of this molecule, the geometries have been optimized using density functional theory (DFT) with B3LYP functional and TZVP basis set. Solvent effects were considered using the implicit polarizable dielectric continuum solvation model SMD. Dichloromethane (DCM) and acetonitrile (ACN) were chosen in analogy respectively with the VCD and ECD experiments. By systematically exploring the conformational space regardless of the selected solvent, we were able to establish that there is only one conformation for the molecule (1*R*,2*R*,*P*)-**4ha** (Figure 1).

(a) in CD_2Cl_2



A_1

(b) in CH_3CN



B_1

*Figure 1- Single conformation geometry of (1R,2R,P)-**4ha** optimized with (a) SMD(DCM)/B3LYP/TZVP and (b) SMD(ACN)/B3LYP/TZVP level.*

2- Calculation of averaged IR, VCD, UV and ECD spectra

The vibrational frequencies, IR absorption and VCD intensities were calculated using the same theoretical level as for geometry optimization, SMD(DCM)/B3LYP/TZVP. The frequencies calculations allow to establish that the conformation found is a minimum (no imaginary frequency). For the calculation of IR/VCD spectra, computed harmonic frequencies are generally larger than those experimentally observed. Thus, a scaling factor of 0.985 has been applied homogenously to all calculated frequencies in order to calibrate the spectra. IR absorption and VCD spectra were constructed

respectively from calculated dipole and rotational strengths assuming Lorentzian band shape with half-width of 8 cm^{-1}.

Based on the SMD(ACN)/B3LYP/TZVP optimized geometry, the ECD and UV-vis spectra were calculated using time dependent density functional theory (TD-DFT) with CAM-B3LYP functional and 6-31++G(d,p) basis set. Calculations were performed for vertical 1A singlet excitation using 60 states. In order to compare theoretical and experimental spectra, the calculated UV and ECD spectra have been modeled using a gaussian function, with a half-width of 0.37 eV. Due to the approximations of the theoretical model used, an offset almost constant was observed between measured and calculated frequencies. Using UV spectra, all calculated frequencies were calibrated by a factor of 1.02. All calculations were performed using Gaussian 16 package.[21]

RESULTS

IR AND VCD ANALYSIS

Figure 2 shows the IR and VCD spectra measured for the two enantiomers (1st eluted)-**4ha** (green curve) and (2nd eluted)-**1** (red curve) and calculated for the enantiomer (1*R*,2*R*,*P*)-**4ha** (blue curve). It can be observed that the IR and VCD spectra calculated for (1*R*,2*R*,*P*)-**4ha** gives the best correlation (signs and intensities of bands) with the spectra measured for the (1st eluted)-**4ha** enantiomer.

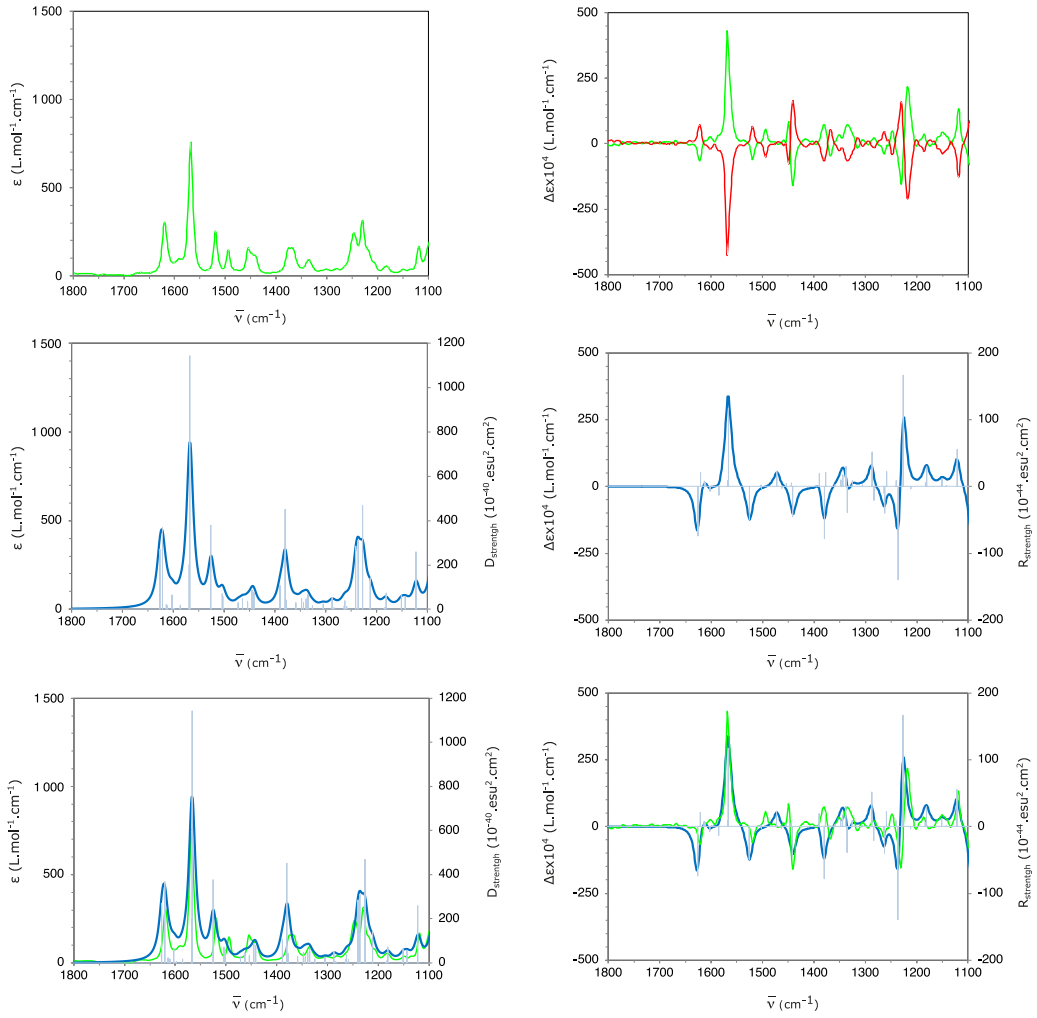


*Figure 2 - IR (left) and VCD (right) spectra measured in CD_2Cl_2 for (1st eluted)-**4ha** (green) and (2nd eluted)-**4ha** (red), and calculated using SMD(DCM)/B3LYP/TZVP for (1R,2R,P)-**4ha*** (Lorentzian shape in dark blue, Dipole and Rotational strength in clear blue).

UV AND ECD ANALYSIS

Figure 3 shows the UV and ECD spectra measured for the two enantiomers (1st eluted)-**4ha** (green curve) and (2nd eluted)-**1** (red curve) and calculated for the enantiomer (1*R*,2*R*,*P*)-**4ha** (blue curve). It can be observed that the UV and ECD spectra calculated for (1*R*,2*R*,*P*)-**4ha** gives the best correlation (signs and intensities of bands) with the spectra measured for the (1st eluted)-**4ha** enantiomer.

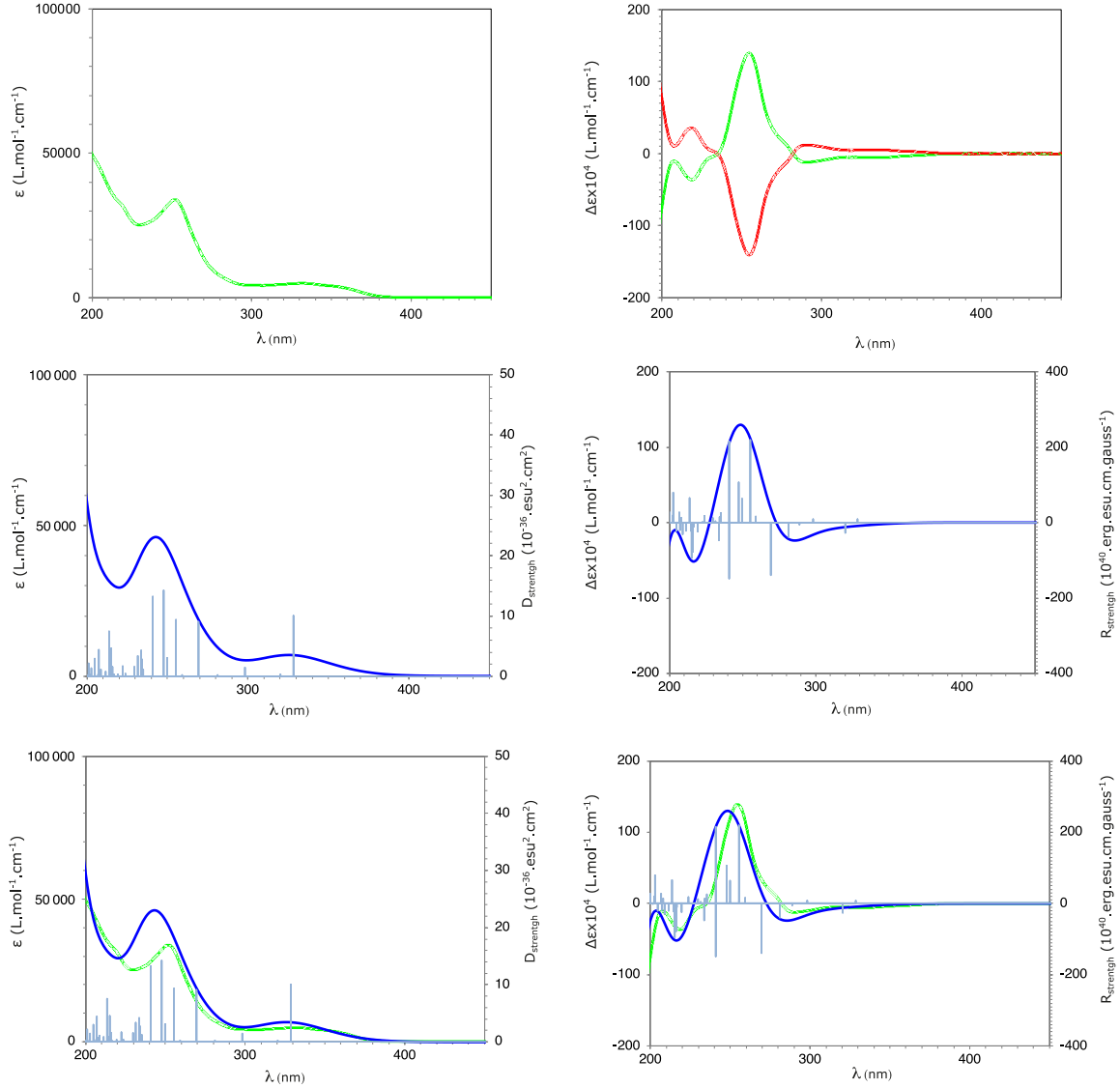


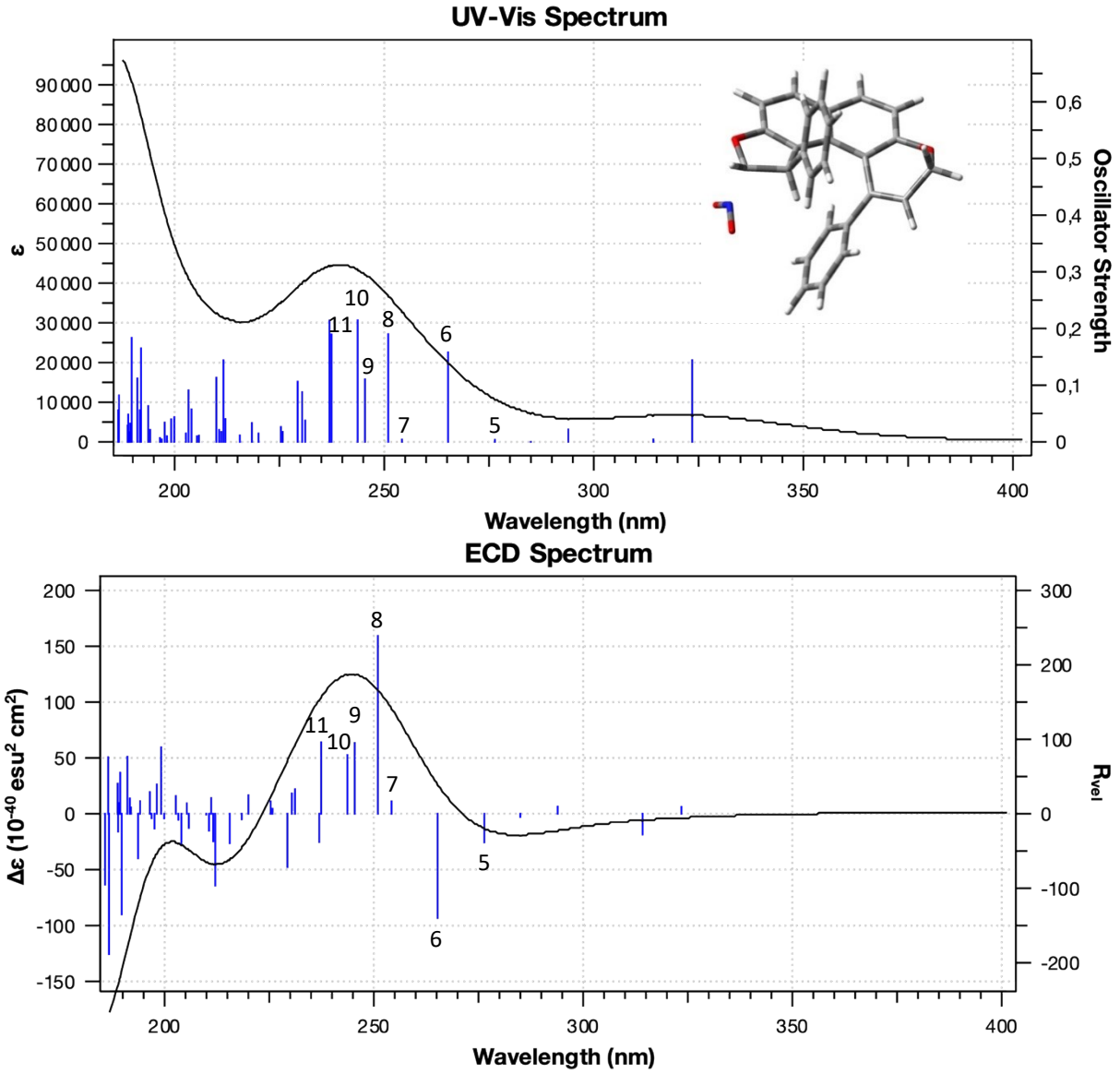
*Figure 3 - UV (left) and ECD (right) spectra measured in CH_3CN for (1st eluted)-**4ha** (green) and (2nd eluted)-**4ha** (red), and calculated using TD(60)-SMD(ACN)/CAM-B3LYP/6-31++G(d,p)//SMD(ACN)/B3LYP/TZVP for (1R,2R,P)-**4ha*** (Gaussian shape in dark blue, Dipole and Rotational strength in clear blue).

CONCLUSION

The absolute configuration of the EYP1-116 molecule was established by comparing measured and calculated IR/VCD and UV/ECD spectra. DFT conformational analysis of the molecule at the SMD(DCM)/B3LYP/TZVP (VCD) and SMD(ACN)/B3LYP/TZVP (ECD) levels established that only one conformation is required to model the various spectra: IR, VCD, UV and ECD (Figure 1-3). For both the IR/VCD and UV/ECD analyses, excellent agreement between measured and calculated spectra unambiguously establishes that the 1st eluted enantiomer of the **4ha** molecule is of absolute configuration (1*R*,2*R*,*P*). Consequently, the 2nd eluted enantiomer will be (1*S*,2*S*,*M*).

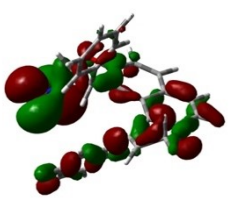
*Rotatory Strengths (R) in cgs (10**-40 erg-esu-cm/Gauss)*
*All frontier MOs of R,R,P)-**4aa** and (R,R,P)-**4ha** are given with isosurfaces of 0.02 a.u*

*Analysis of MO-pair contributions to notable excitations of the UV and ECD simulated spectra of (R,R,P)-**4ha***

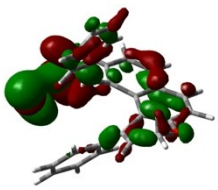


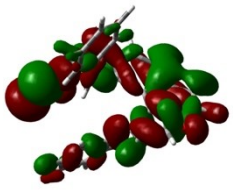
Excited State 5: Singlet-A 4.4854 eV 276.41 nm f=0.0035 R_{vel} = -38.3071

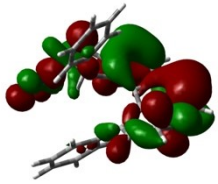
98 ->111	0.11342
99 ->111	-0.13964
100 ->111	0.36022
101 ->111	-0.13073
103 ->111	-0.18023
107 ->111	-0.16330
109 ->111	0.23818
110 ->111	0.39140

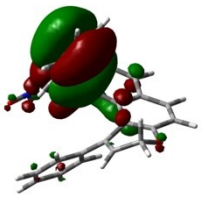

HOMO-12 (MO98)

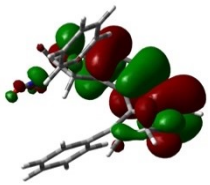

HOMO-11 (MO99)

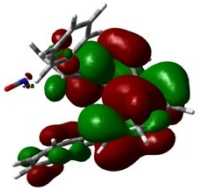

HOMO-10 (MO100)

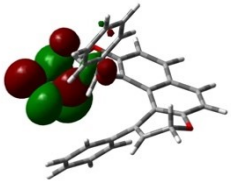

HOMO-9 (MO101)


HOMO-7 (MO103)


HOMO-3 (MO107)

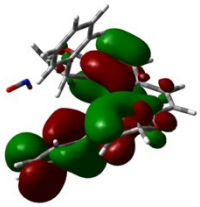

HOMO-1 (MO109)

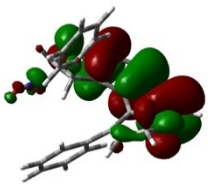

HOMO (MO110)

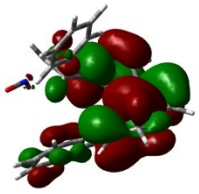

LUMO (MO111)

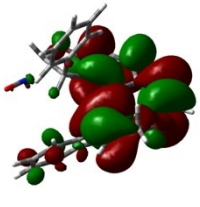
Excited State 6: Singlet-A 4.6743 eV 265.24 nm f=0.1578 R_{vel} = -139.9312

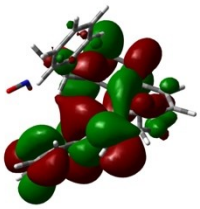
108 ->112	0.19407
109 ->113	0.16215
110 ->113	0.54885
110 ->115	-0.26110
110 ->126	0.10551

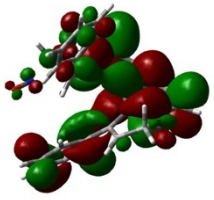

HOMO-2 (MO108)

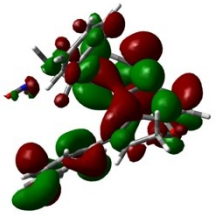

HOMO-1 (MO109)


HOMO (MO110)


LUMO+1 (MO112)


LUMO+2 (MO113)


LUMO+4 (MO115)


LUMO+15 (MO126)

Excited State 7: Singlet-A 4.8769 eV 254.23 nm f=0.0040 R_{vel} = 16.5872

99 ->111	0.12567
101 ->111	0.17537
107 ->111	0.10151
108 ->111	0.49522
109 ->111	0.35863
110 ->111	0.11688

HOMO-9 (MO101) HOMO-3 (MO107) HOMO-2 (MO108) HOMO-1 (MO109) HOMO-11 (MO99)

HOMO (MO110) LUMO (MO111)

Excited State 8: Singlet-A 4.9403 eV 250.96 nm f=0.1900 R_{vel} = 236.8566

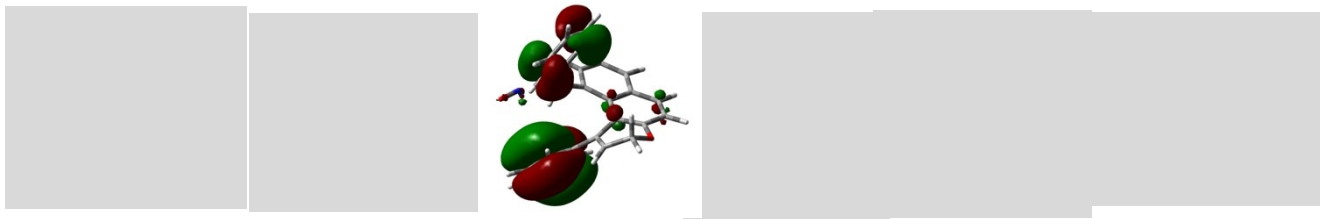
108 ->112	0.42576
108 ->113	0.16621
109 ->112	0.36038
110 ->113	-0.24191
110 ->115	-0.14806

HOMO-2 (MO108) **HOMO-1 (MO109)** HOMO (MO110) LUMO+1 (MO112) LUMO+2 (MO113) LUMO+4 (MO115)

Excited State 9: Singlet-A 5.0521 eV 245.41 nm f=0.1103 R_{vel} = 95.1526

99 ->111	-0.10106
101 ->111	-0.12109
106 ->113	0.10928
107 ->111	-0.11208
108 ->111	0.39209
108 ->112	0.10940
109 ->111	-0.33926

109 ->112 -0.15171
110 ->115 0.22758

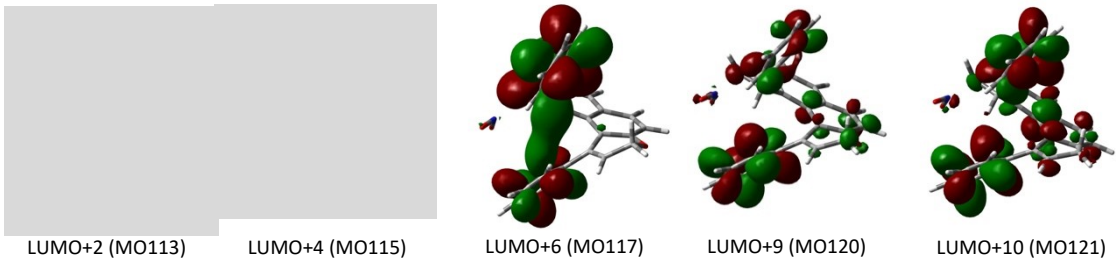


HOMO-11 (MO99) HOMO-9 (MO101) HOMO-4 (MO106) HOMO-3 (MO107) HOMO-2 (MO108) HOMO-1 (MO109)

HOMO (MO110) LUMO (MO111) LUMO+1 (MO112) LUMO+2 (MO113) LUMO+4 (MO115)

Excited State 10: Singlet-A 5.0881 eV 243.67 nm f=0.2145 R_{vel} = 78.8083
106 ->113 -0.16617
108 ->111 0.29830
108 ->112 -0.18809
108 ->117 -0.13336
108 ->120 0.11841
108 ->121 0.12829
109 ->111 -0.21320
109 ->112 0.18260
110 ->115 -0.29540
110 ->117 -0.12114

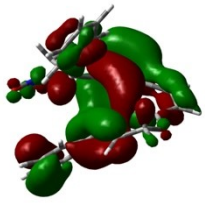
HOMO-4 (MO106) HOMO-2 (MO108) HOMO-1 (MO109) HOMO (MO110) LUMO (MO111) LUMO+1 (MO112)



LUMO+2 (MO113) LUMO+4 (MO115) LUMO+6 (MO117) LUMO+9 (MO120) LUMO+10 (MO121)

Excited State 11: Singlet-A 5.2224 eV 237.41 nm f=0.1895 R_{vel} = 96.9768
104 ->112 -0.15025

108 ->113	0.34883
109 ->113	-0.27644
109 ->115	-0.21286
110 ->113	0.11233
110 ->115	-0.10663
110 ->116	0.20306
110 ->120	-0.14517
110 ->121	-0.13706
110 ->126	-0.14354



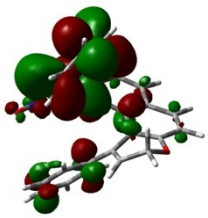
HOMO-6 (MO104)

HOMO-2 (MO108) **HOMO-1 (MO109)** HOMO (MO110)

LUMO+1 (MO112)

LUMO+2 (MO113)

LUMO+4 (MO115)

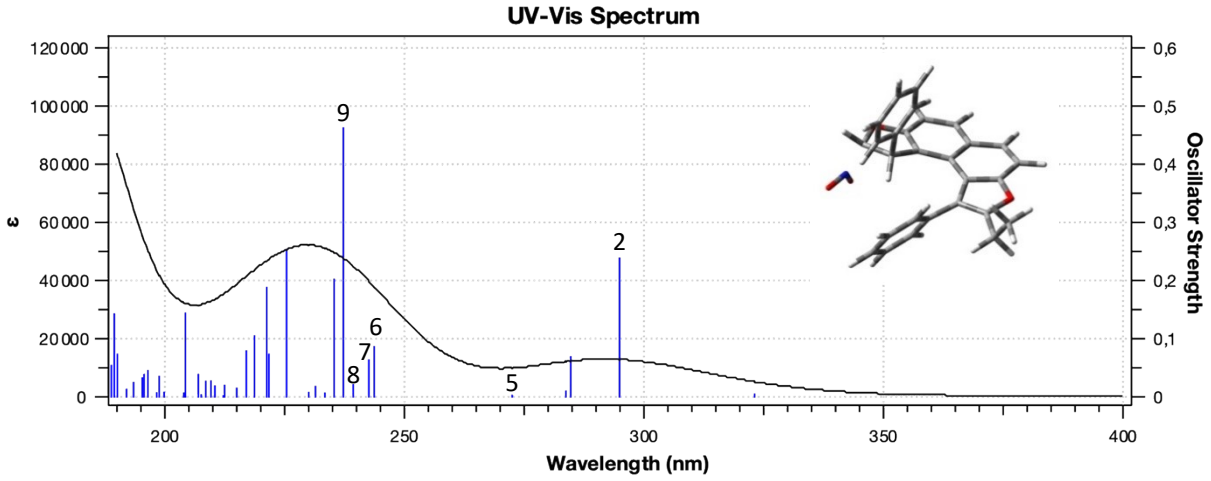


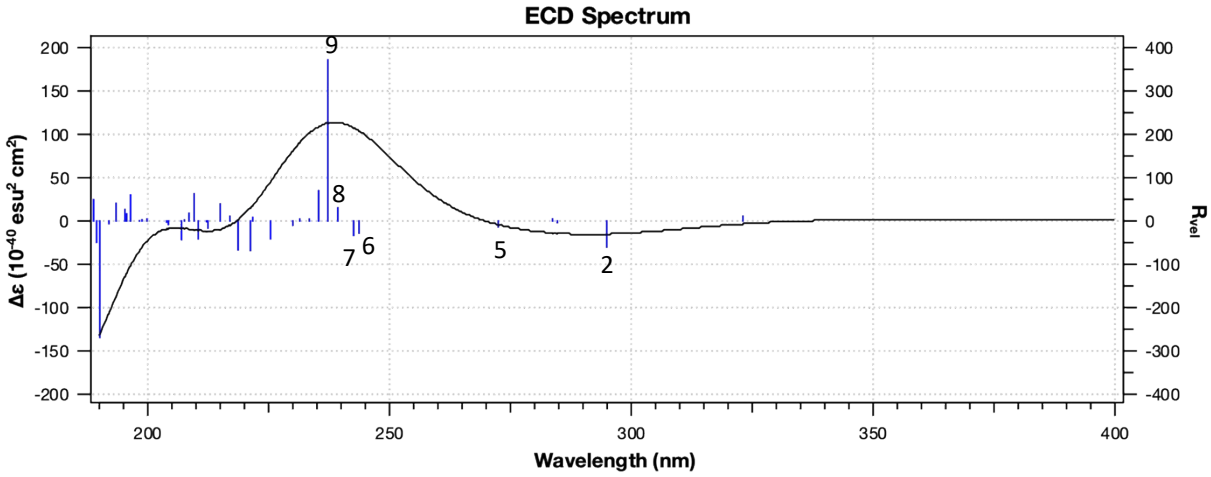
LUMO+5 (MO116)

LUMO+9 (MO120)

LUMO+10 (MO121)

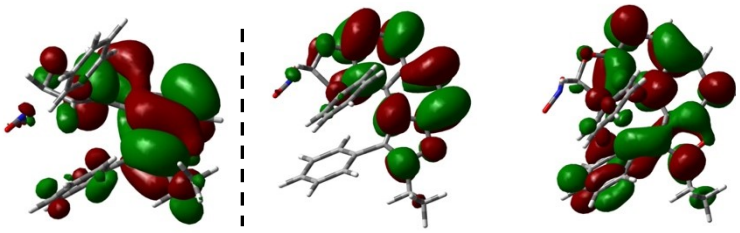
*Analysis of MO-pair contributions to notable excitations of the UV and ECD simulated spectra of (R,R,P)-**4aa***





Excited State 2: Singlet-A 4.2041 eV 294.91 nm f=0.2383 R_{vel} = -60.413

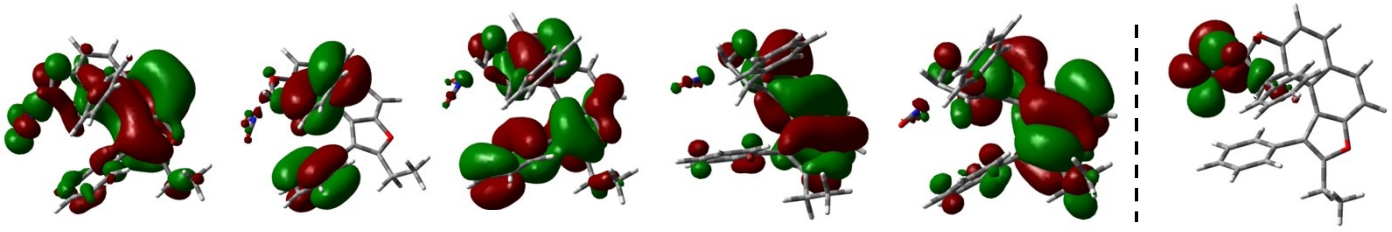
114 ->116	0.66125
114 ->117	-0.10298



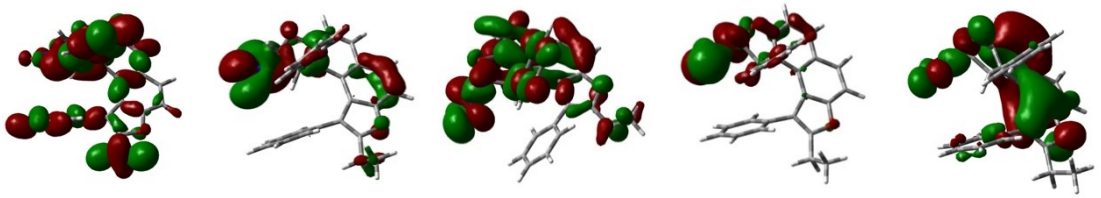
HOMO (MO114) LUMO+1 (MO116) LUMO+2 (MO117)

Excited State 5: Singlet-A 4.5500 eV 272.49 nm f=0.0022 R_{vel} = -13.7218

98 ->115	-0.14150
103 ->115	-0.18122
104 ->115	0.32651
105 ->115	0.16996
106 ->115	0.19347
107 ->115	0.19926
111 ->115	0.16843
112 ->115	0.11287
113 ->115	0.19682
114 ->115	0.32278



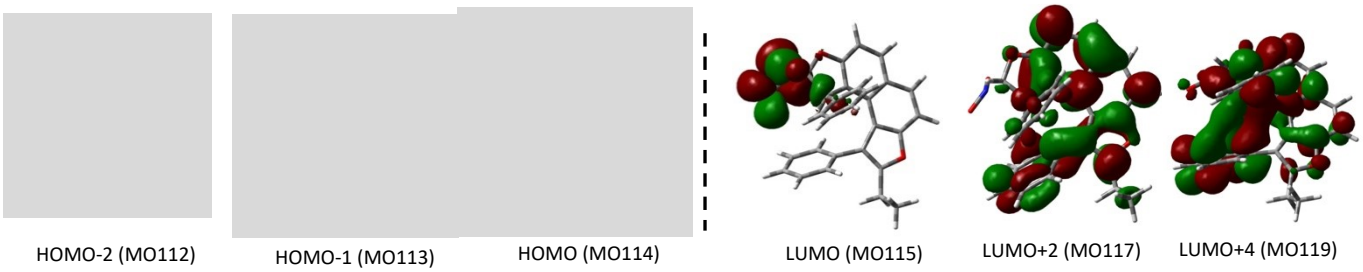
HOMO-7 (MO107) HOMO-3 (MO111) HOMO-2 (MO112) HOMO-1 (MO113) HOMO (MO114) LUMO (MO115)



HOMO-16 (MO98) HOMO-11 (MO103) HOMO-10 (MO104) HOMO-9 (MO105) HOMO-8 (MO106)

Excited State 6: Singlet-A 5.0876 eV 243.70 nm f=0.0861 R_{vel} = -28.2188

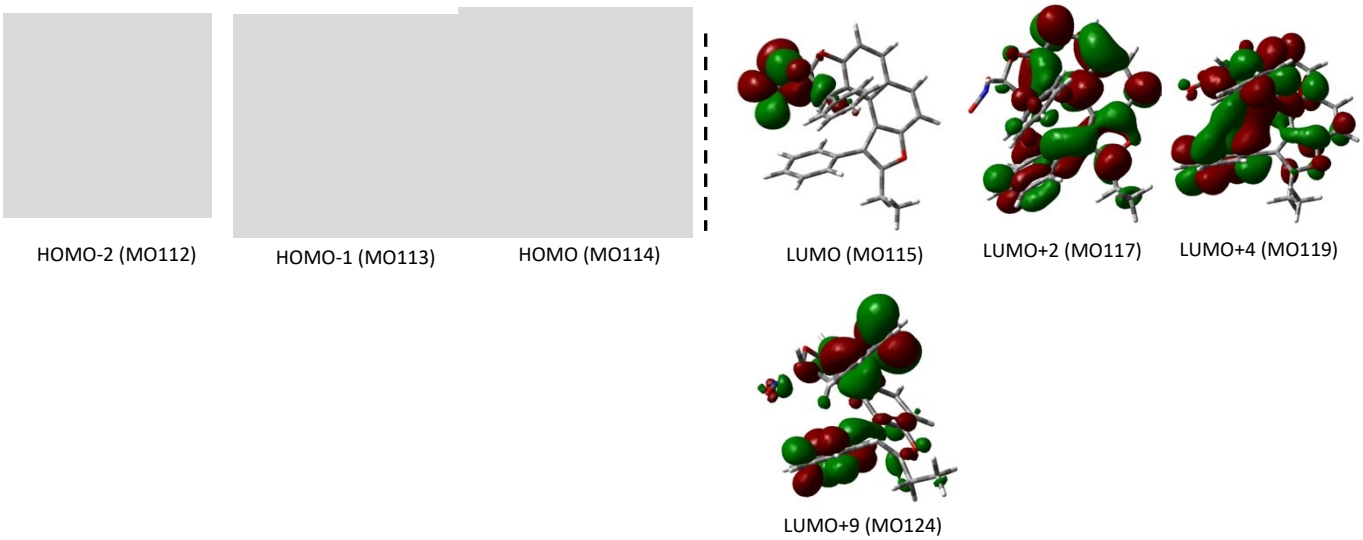
112 ->115	-0.35000
113 ->115	0.43515
114 ->117	0.27410
114 ->119	-0.19334



HOMO-2 (MO112) HOMO-1 (MO113) HOMO (MO114) LUMO (MO115) LUMO+2 (MO117) LUMO+4 (MO119)

Excited State 7: Singlet-A 5.1111 eV 242.58 nm f=0.0629 R_{vel} = -33.1522

112 ->115	-0.25331
112 ->117	-0.10690
113 ->115	0.28741
114 ->117	-0.34347
114 ->119	0.38740
114 ->124	0.13654



HOMO-2 (MO112) HOMO-1 (MO113) HOMO (MO114) LUMO (MO115) LUMO+2 (MO117) LUMO+4 (MO119)

LUMO+9 (MO124)

Excited State 8: Singlet-A 5.1808 eV 239.31 nm f=0.0206 R_{vel} = 30.2842

103 ->115	0.11691
104 ->115	-0.19497
111 ->115	-0.14359
112 ->115	0.39164
113 ->115	0.36540
114 ->115	0.10520
114 ->122	0.11834

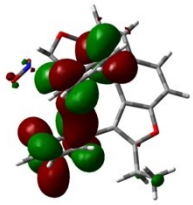
HOMO-3 (MO111)

HOMO-2 (MO112)

HOMO-1 (MO113)

HOMO (MO114)

LUMO (MO115)



LUMO+7 (MO122)

HOMO-11 (MO103)

HOMO-10 (MO104)

Excited State 9: Singlet-A 5.2260 eV 237.25 nm f=0.4621 R_{vel} = 371.717

112 ->115	-0.21206
112 ->116	-0.11365
113 ->116	0.40877
113 ->117	-0.12027
114 ->117	-0.17592
114 ->118	-0.12562
114 ->119	-0.22229
114 ->121	0.11326
114 ->124	-0.21033

HOMO-2 (MO112)

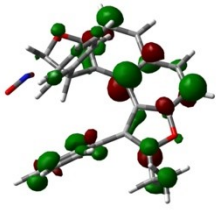
HOMO-1 (MO113)

HOMO (MO114)

LUMO (MO115)

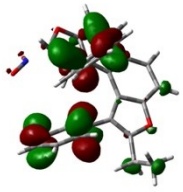
LUMO+1 (MO116)

LUMO+2 (MO117)



LUMO+3 (MO118)

LUMO+4 (MO119)



LUMO+6 (MO121)

LUMO+9 (MO124)