1. General information

All reactions, unless noted, were performed in oven-dried (120 °C) glassware with magnetic stirring under an inert atmosphere of dry nitrogen. Analytical thin layer chromatography (TLC) was carried out using EM Science silica gel 60 F254 plates; visualization was accomplished with UV light (254 nm). Column chromatography was performed on CombiFlash® RF200 and RF+ purification systems using normal phase disposable columns. $^1$H, $^{13}$C, $^{19}$F NMR spectra were recorded on a Bruker spectrometer (300 or 500 MHz). Chemical shifts were reported in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard (CDCl$_3$, $\delta = 7.26$). Spectra were reported as follows: chemical shift ($\delta$ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite of magnetically non-equivalent protons, dd = doublet of doublets), coupling constants (Hz), integration and assignment. $^{13}$C NMR spectra were collected on Bruker instruments (75 or 126 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl$_3$, $\delta = 77.0$). High-resolution mass spectra (HRMS) were performed on a Bruker MicroTOF-ESI mass spectrometer with an ESI resource using CsI or LTQ ESI positive ion calibration solution as the standard. Enantioselectivities were determined by HPLC analysis at 25 °C using an Agilent 1260 Infinity HPLC System equipped with an G1311B quaternary pump, G1315D diode array detector, G1329B auto-sampler, G1316A thermostated column compartment and G1170A valve drive. For instrument control and data processing, Agilent OpenLAB CDS ChemStation Edition for LC & LC/MS Systems (Rev. C.01.07 [26]) software was used. The Chiralpak AD-H column was obtained from Daicel Chiral Technologies. Tetrahydrofuran, dichloromethane, chloroform, and toluene were purified using a JC-Meyer solvent purification system. Optical rotations were reported as follows: $[\alpha]_D^{23}$ (c: g/100 mL, in DCM).
2. Preparation of Reactants

1H-Isochromene acetals (1)\(^1\), donor-acceptor cyclobutenes (2)\(^2\), donor-acceptor cyclopropenes (4)\(^3\), siloxyalkynes (6)\(^4\), donor-acceptor azetine (9)\(^5\) and other metallo-vinyl carbenes cycloaddition products (10 and 11)\(^6\) were prepared by reported methods.

Figure 1. General procedure for the synthesis of Donor-Acceptor Cyclobutenes.

The modified procedure for the synthesis of donor-acceptor cyclobutenes (2a-2f) is described: To a solution of sulfur ylide (S1a-S1f, 3.0 mmol) and Cu(CH\(_3\)CN)\(_4\)BF\(_4\) (94.3 mg, 0.3 mmol, 10 mol% ) in 10 mL CH\(_2\)Cl\(_2\) at 40 °C was slowly added a solution of enoldiazo compounds S2 (3.6 mmol, 1.2 equiv.) in 3 mL CH\(_2\)Cl\(_2\) over 5 minutes. The resulting solution was stirred at 40 °C for 10 min, after which the crude product was purified by flash chromatography (hexane/ethyl acetate = 19/1) to give donor-acceptor cyclobutenes (2a-2f) in excellent yield.


Figure 2. General procedure for the catalyzed [4+4]-cycloaddition reactions.

The donor-acceptor cyclobutene (2a-2h) (0.13 mmol, 1.3 equiv.) was dissolved in dry CH\(_2\)Cl\(_2\) (1 mL), after which a solution of HNTf\(_2\) (10 mol%) in dry CH\(_2\)Cl\(_2\) (0.1 mL) was added slowly. The mixture was stirred at 35 °C for 5 min, then a solution of acetal compounds (1a-1I) (0.1 mmol, 1.0 equiv.) in 1 mL CH\(_2\)Cl\(_2\) was added over 30 minutes. The reaction solution was stirred at the same temperature for 24 h, and the progress of the reaction was monitored by TLC. After complete reaction of the acetal substrate, the reaction solution was subjected to flash chromatography on silica gel with a 5:1 (v/v) mixture of hexane:ethyl acetate as the eluent to afford the desired products 3aa-3gg.

Figure 3. General procedure for the catalyzed [4+3]-cycloaddition reactions.
The acetal compound (1a-1j) (0.2 mmol, 1.0 equiv.) and 4 Å molecular sieves (50 mg) were dissolved in dry CH₂Cl₂ (1 mL), and a solution of HNTf₂ (20 mol%) in dry CH₂Cl₂ (0.4 mL) was added slowly, after which a solution of donor-acceptor cyclopropene (4a-4d) (0.24 mmol, 1.2 equiv.) in dry CH₂Cl₂ (1.0 mL) was added over 5 min. The reaction solution was stirred at room temperature for 2 h, and the progress of the reaction was monitored by TLC. After complete reaction of the acetal substrate, the reaction solution was subjected to flash chromatography on silica gel with a 9:1 (v/v) mixture of hexane:ethyl acetate as the eluent to afford the desired product (5aa-5ad).

**Figure 4.** General procedure for the catalyzed [4+2]-cycloaddition reactions.

Acetal compound (1a-1d, 1f, 1h and 1i) (0.2 mmol, 1.0 equiv.) and siloxyalkynes 6a-6d (0.3 mmol, 1.5 equiv.) were dissolved in dry CH₂Cl₂ (2 mL), and a solution of HNTf₂ (20 mol%) in dry CH₂Cl₂ (0.4 mL) was added slowly, after which another solution of siloxyalkynes (6a-6d) (0.1 mmol, 0.5 equiv.) in dry CH₂Cl₂ (0.5 mL) was added in the reaction solution, then HNTf₂ (10 mol%) was slowly added to the reaction solution. The progress of the reaction was monitored by TLC. After complete reaction of the acetal substrate (<10 min), the reaction solution was cooled to 0 °C, and TBAF (0.4 mmol, 2.0 equiv., 1.0 M in THF) was added. The reaction solution was then stirred at 0 °C for 1-3 h, and the progress of the reaction was monitored by TLC. Upon completion of the reaction the solvent was removed, and the residue was subjected to flash chromatography on silica gel with a 9:1 (v/v) mixture of hexane:ethyl acetate as the eluent to afford the desired products 7aa-7ad.

**Figure 5.** General procedure for the catalyzed [4+2]-cycloaddition reaction of 1m with 6a.

Acetal compound 1m (36 mg, 0.2 mmol, 1.0 equiv.) and siloxyalkyne 6a (76.2 mg, 0.3 mmol, 1.5 equiv.) were dissolved in dry CH₂Cl₂ (2 mL), and a solution of HNTf₂ (20 mol%) in dry CH₂Cl₂ (0.4 mL) was added slowly. Then another solution of siloxyalkyne 6a (25.4 mg, 0.1 mmol, 0.5 equiv.) in dry CH₂Cl₂ (0.5 mL) was added in the reaction solution, after which HNTf₂ (10 mol%) was slowly added. The progress of the reaction was monitored by TLC. After complete reaction of the acetal substrate (<10...
min), the reaction solution was subjected to flash chromatography on silica gel with a 10:1 (v/v) mixture of hexane: CH₂Cl₂ as the eluent to afford the desired products 7ma.

**Figure 6.** General procedure for the catalyzed [4+2]-cycloaddition reactions of 1n with siloxyalkynes 6a-6d.

Acetal compound 1n (43.6 mg, 0.2 mmol, 1.0 equiv.) and siloxyalkynes 6a-6d (0.3 mmol, 1.5 equiv.) were dissolved in dry CH₂Cl₂ (2 mL), and a solution of HNTf₂ (10 mol%) in dry CH₂Cl₂ (0.2 mL) was added slowly. The progress of the reaction was monitored by TLC. After complete reaction of acetal substrate (<10 min), the reaction solution was subjected to flash chromatography on silica gel with a 19:1 (v/v) mixture of hexane: ethyl acetate as the eluent to afford the desired products 7na-7nd.

4. Constraints of these Brønsted acid catalyzed cycloadditions of benzopyrylium.

**Figure 7.** Constraints of these Brønsted acid catalyzed cycloadditions.
Acetal compounds 1m and 1n were employed in [4+4]-cycloaddition reactions with 2a but did not produce any of the desired products. Spectral analysis showed that mostly starting material remained [Eq(1-2)]. The isopropyl acetal substrate 1j, which forms the bulky 2-propanol nucleophile, failed to suppress the competing desilylation pathway [Eq(3)]. When CHCl$_3$ and CH$_2$ClCH$_2$Cl were used as solvent, the [4+4] cycloaddition reaction was inefficient, and the desired product was isolated in only 7% and 12% yields [Eq(4-5)]. The reaction between acetal compounds 1m and 1n and donor-acceptor cyclopropene 4a did not produce any of the desired products. Spectral analysis showed that mostly starting material remained [Eq(6-7)].

Other constraints were noted in our evaluation of this methodology (Figure 1). As expected, nitrogen-containing donor-acceptor azetine (9) and other metallovinylcarbenes cycloaddition products (10 and 11) were unreactive, and the reactants were recovered. In addition, compound 12 reacted with acetal (1a), giving only the direct addition product 13 in good yield, which suggests unfavorable competition for cycloaddition from desilylation.

**Figure 8.** Observed other reaction constraints.

![Figure 8](image)

5. General procedure for large scale reaction, further transformations and discussion.

**Figure 9.** General procedure for large scale reaction of 1d with 2a.

![Figure 9](image)

Donor-acceptor cyclobutene 2a (756.6 mg, 1.95 mmol, 1.3 equiv.) was dissolved in dry CH$_2$Cl$_2$ (10 mL), after which a solution of HNTf$_2$ (10 mol%) in dry CH$_2$Cl$_2$ (1.5 mL) was added slowly. The solution was stirred at 35 °C for 5 min, then a solution of acetal compounds 1d (384 mg, 1.5 mmol, 1.0 equiv.) in 5 mL CH$_2$Cl$_2$ was added over 30 minutes. The reaction solution was stirred at same temperature for 24 h, and the progress of the reaction was monitored by TLC. After complete reaction of the acetal
substrate, the reaction solution was subjected to flash chromatography on silica gel with a 5:1 (v/v) mixture of hexane:ethyl acetate as the eluent to afford the desired product 3da in 87% yield.

**Figure 10.** General procedure for further transformation of 3da with Hydrazine.

A screw-capped 25-mL vial equipped with a magnetic stirring bar was loaded with compound 3da (0.15 mmol) and anhydrous ethanol (2.5 mL). Hydrazine hydrate (45 wt. % N₂H₄, 0.225 mmol, 1.5 equiv.) in anhydrous ethanol (2.5 mL) was added in one portion at room temperature, and the reaction solution was stirred at 90 °C for 1 h. The progress of the reaction was monitored by TLC. After complete conversion of starting material 3da, the solvent was evaporated, and the residue was purified by column chromatography on silica gel with a 2:1 (v/v) mixture of hexane:ethyl acetate as the eluent to afford pyrazole 14da.

**Methyl (E)-5-Benzylox-10-fluoro-1-phenyl-4,5-dihydro-2H-benzo[3,4]-cycloocta[1,2-c]pyrazole-6-carboxylate.**

White solid (60 mg, 89% yield), 0.2 mmol scale reaction. m.p. 138 – 139 °C.

Major rotamer:

\(^1H\) NMR (500 MHz, chloroform-\(d\)) \(\delta 11.57\) (s, 1H), 8.05 (s, 1H), 7.60 (d, \(J = 7.5\) Hz, 2H), 7.51 – 7.48 (comp., 2H), 7.58 (t, \(J = 7.5\) Hz, 2H), 7.28 – 7.23 (comp., 3H), 7.18 – 7.13 (comp., 3H), 6.81 (dd, \(J = 10.0\), 2.5 Hz, 1H), 4.51 (dd, \(J = 10.0\), 6.0, 6.0 Hz, 1H), 3.61 – 3.53 (comp., 5H).

\(^13C\) NMR (126 MHz, chloroform-\(d\)) \(\delta 197.98, 165.46, 162.55\) (d, \(J = 254\) Hz, 1C), 142.14, 136.63, 135.95 (d, \(J = 9\) Hz, 1C), 132.66, 131.17, 129.05, 128.98, 128.49, 128.39, 128.00, 127.89, 119.93 (d, \(J = 21\) Hz, 1C), 114.62 (d, \(J = 21\) Hz, 1C), 114.63, 52.04, 44.54, 25.91.

\(^19F\) NMR (470.5 MHz, chloroform-\(d\)) \(\delta -112.2\) (m, 1F).

Minor rotamer:

\(^1H\) NMR (500 MHz, chloroform-\(d\)) \(\delta 7.90\) (s, 1H), 7.65 – 7.58 (m, 1H), 7.52 – 7.48 (comp, 2H), 7.39 – 7.36 (m, 1H), 7.33 – 7.23 (comp, 3H), 7.19 – 7.13 (comp, 3H), 6.73 (t, \(J = 8.5\) Hz, 1H), 6.61 (d, \(J = 8.5\) Hz, 2H), 4.92 (t, \(J = 5.5\) Hz, 1H), 3.88 (s, 3H), 3.45 (dd, \(J = 15.5\), 5.5 Hz, 1H), 3.03 (dd, \(J = 15.5\), 5.5 Hz, 1H).

\(^13C\) NMR (126 MHz, chloroform-\(d\)) \(\delta 197.76, 167.37, 162.38\) (d, \(J = 250\) Hz, 1C), 142.28, 135.53, 133.37, 131.83, 130.13, 128.30, 128.18, 128.09, 118.16 (d, \(J = 21\) Hz, 1C), 113.89 (d, \(J = 21\) Hz, 1C), 52.78, 45.76, 25.47.
**19F NMR** (470.5 MHz, chloroform-d) δ -112.6 (m, 1F).

**HRMS (ESI)** scaled for [M+H]+: C_{28}H_{22}FN_{2}O_{3}, m/z: 453.1609, observed: 453.1598.

**Figure 11.** General procedure for further transformation of 3da with Hydroxylamine.

A screw-capped 25 mL vial equipped with a magnetic stirring bar was loaded with compound 3da (0.1 mmol), p-toluenesulfonic acid monohydrate (PTSA·H_{2}O, 0.1 mmol) and anhydrous ethanol (2.5 mL). Hydroxylamine (50% wt. in water, 0.3 mmol) in anhydrous ethanol (2.5 mL) was added in one portion at room temperature, and the reaction solution was stirred at 90 °C for 3 days. After that, hydroxylamine (50% wt. in water, 0.3 mmol) in anhydrous ethanol (2.5 mL) was added again, and the reaction solution was stirred at 90 °C for an additional 3 days. Solvents were evaporated, and the residue was purified by column chromatography on silica gel with a 3:1 (v/v) mixture of hexane:ethyl acetate as the eluent to afford pyrazole 15da.

**Methyl (E)-5-Benzoyl-10-fluoro-1-phenyl-4,5-dihydrobenzo[3,4]-cycloocta[1,2-c]isoxazole-6-carboxylate.**

White solid (30 mg, 66% yield), 0.1 mmol scale reaction. m.p. 218 – 219 °C.

**Major rotamer:**

**1H NMR** (500 MHz, chloroform-d) δ 7.97 (s, 1H), 7.64 (d, J = 7.2 Hz, 1H), 7.59 – 7.53 (comp., 2H), 7.51 (t, J = 7.0 Hz, 2H), 7.56 – 7.54 (comp., 3H), 7.36 – 7.29 (comp, 3H), 7.51 (t, J = 7.0 Hz, 2H), 7.56 – 7.54 (comp., 3H), 7.36 – 7.29 (comp, 3H), 7.51 (t, J = 7.0 Hz, 2H), 7.56 – 7.54 (comp., 3H), 7.36 – 7.29 (comp, 3H), 7.51 (t, J = 7.0 Hz, 2H), 7.56 – 7.54 (comp., 3H), 7.36 – 7.29 (comp, 3H), 7.51 (t, J = 7.0 Hz, 2H), 7.56 – 7.54 (comp., 3H), 7.36 – 7.29 (comp, 3H), 7.51 (t, J = 7.0 Hz, 2H), 7.56 – 7.54 (comp., 3H), 7.36 – 7.29 (comp, 3H), 7.51 (t, J = 7.0 Hz, 2H), 7.56 – 7.54 (comp., 3H), 7.36 – 7.29 (comp, 3H).

**13C NMR** (126 MHz, chloroform-d) δ 197.07, 167.20, 164.92, 162.80 (d, J = 9 Hz, 1C), 160.53, 141.02, 136.67, 135.70, 133.08, 132.66, 131.38 (d, J = 9 Hz, 1C), 130.13, 128.39, 127.82, 127.51, 119.26 (d, J = 21 Hz, 1C), 116.25 (d, J = 21 Hz, 1C), 113.36, 52.10, 44.16, 25.10.

**19F NMR** (470.5 MHz, chloroform-d) δ -110.9 (m, 1F).

**Minor rotamer:**

**1H NMR** (500 MHz, chloroform-d) δ 7.86 (s, 1H), 6.93 (td, J = 8.5, 2.5 Hz, 1H), 6.88 (dd, J = 8.5, 2.5 Hz, 1H), 6.77 (dd, J = 8.5, 5.5 Hz, 1H), 5.11 (dd, J = 7.0, 5.0 Hz, 1H), 3.86 (s, 3H), 3.55 (dd, J = 16.0, 5.0 Hz, 1H), 3.35 (dd, J = 16.0, 5.0 Hz, 1H).

**13C NMR** (126 MHz, chloroform-d) δ 197.36, 166.91, 165.97, 162.60 (d, J = 254 Hz, 1C), 161.09, 141.23, 135.21, 133.21, 130.88, 128.39, 128.34, 127.16, 117.78, 117.69 (d, J = 22 Hz, 1C), 115.49 (d, J = 22 Hz, 1C), 114.00, 52.88, 45.45, 23.25.
$^{19}$F NMR (470.5 MHz, chloroform-$d$) $\delta$ -111.5 (m, 1F).

HRMS (ESI) scaled for [M+H]$^+$: C$_{28}$H$_{21}$FNO$_4$, m/z: 454.1449, observed: 454.1431.

Figure 12. NMR spectra of compound 15da in different deuterated solvents.

Discussion 1. The ratio of the proton NMR signals are different in different deuterated solvents, indicating that rotamers exists in solution of product 15da.
Figure 13. The NMR spectra of compound 15da in different temperatures.

Discussion 2. The ratio of the proton NMR spectra reversibly change at different temperatures, indicating the existence of rotamers.

Figure 14. The 1D gradient NOE spectra experiment of 15da.

6. General procedure for the synthesis of salen type ligands L1 and L2

Figure 15. General procedure for the synthesis of salen type ligand L1.

1,1'-(1E,1′E)-(((1S,2S)-Cyclohexane-1,2-diyl)bis(azanylylidene))bis(methanylylidene)bis(3-butyl-7-fluoronaphthalen-2-ol)

To a solution of (S,S)-1,2-cyclohexanedi-amine (57 mg, 0.5 mmol, 1.0 equiv.) in EtOH (5 mL) was added a solution of 7ma (270.6, 1.1 mmol, 2.1 equiv.) in EtOH (5 mL). The suspension was refluxed for 12 h at which time a yellow solution was evident. The mixture was cooled to room temperature, and the solvent was removed. The reaction mixture was purified by flash chromatography on silica gel (15% EtOAc/hexanes) to give L1 (151 mg, 53%) as an amorphous yellow solid: mp 60 – 61 °C.

$^1$H NMR (500 MHz, chloroform-d) δ 14.63 (s, 2H), 8.46 (s, 2H), 7.32 (dd, $J = 8.5, 6.0$ Hz, 2H), 7.26 (s, 2H), 7.22 (dd, $J = 11.5, 2.5$ Hz, 2H), 6.83 (td, $J = 8.5, 2.5$ Hz, 2H), 3.45 – 3.29 (m, 2H), 2.71 – 2.65 (m, 2H), 2.57 – 2.51 (m, 2H), 2.24 (d, $J = 14.0$ Hz, 2H), 1.96 (d, $J = 8.5$ Hz, 2H), 1.85 – 1.70 (m, 2H), 1.66 – 1.55 (m, 4H), 1.55 – 1.39 (comp., 6H), 0.97 (t, $J = 7.5$ Hz, 6H).
**13C NMR** (126 MHz, chloroform-d) δ 174.27, 161.92 (d, \( J = 245 \) Hz, 1C), 158.76, 134.84, 134.00, 133.92, 130.19 (d, \( J = 9 \) Hz, 1C), 123.04, 111.35 (d, \( J = 24 \) Hz, 1C), 106.04 (d, \( J = 3.9 \) Hz, 1C), 102.90 (d, \( J = 24 \) Hz, 1C), 68.55, 32.44, 31.04, 29.53, 24.38, 22.81, 14.02.

**19F NMR** (470.5 MHz, chloroform-d) δ -113.1 (m, 1F).

**HRMS (ESI)** scaled for [M+H]+: C_{36}H_{41}F_{2}N_{2}O_{2}, m/z: 571.3131, observed: 571.3114.

\([\alpha]_D^{23} = +460.98 \) (c 0.31, CH2Cl2).

**Figure 16.** General procedure for the synthesis of salen type ligand L2.

\(1,1'-(1E,1'E)-(1S,2S)-1,2-diphenylethane-1,2-diyl)bis(azanylylidene)bis(methanylylidene)-bis(3-buty1-7-fluoronaphthalen-2-ol)\)

To a solution of \((S,S)-1,2\)-diphenylethlenediaine (40.3 mg, 0.19 mmol, 1.0 equiv.) in EtOH (5 mL) was added a solution of \(7\text{ma}\) (93.5 mg, 0.38 mmol, 2 equiv.) in EtOH (5 mL). The suspension was refluxed for 12 h at which time a yellow solution was evident. The mixture was cooled to room temperature, and the solvent was removed. The crude mixture was purified by flash chromatography on silica gel (35% EtOAc/hexanes) to give L2 (94 mg, 74%) as an amorphous yellow solid: mp 65 – 66 °C.

**1H NMR** (500 MHz, chloroform-d) δ 15.41 (s, 2H), 8.82 (s, 2H), 7.45 – 7.38 (comp., 4H), 7.34 (s, 2H), 7.32 – 7.25 (comp., 10H), 6.93 (td, \( J = 8.5, 2.5 \) Hz, 2H), 4.85 (s, 2H), 2.73 – 2.57 (m, 4H), 1.69 – 1.52 (m, 4H), 1.47 – 1.40 (m, 4H), 0.99 (t, \( J = 7.5 \) Hz, 6H).

**13C NMR** (126 MHz, chloroform-d) δ 169.12, 161.76 (d, \( J = 245 \) Hz, 1C), 158.84, 137.97, 133.43, 133.34, 133.16, 130.33 (d, \( J = 9.7 \) Hz, 1C), 128.72, 128.09, 127.76, 123.63, 111.96 (d, \( J = 24 \) Hz, 1C), 107.07 (d, \( J = 4 \) Hz, 1C), 103.31 (d, \( J = 24 \) Hz, 1C), 77.95, 30.96, 29.41, 22.74, 14.05.

**19F NMR** (470.5 MHz, chloroform-d) δ -113.1 (m, 1F).

**HRMS (ESI)** scaled for; [M+H]+: C_{44}H_{43}F_{2}N_{2}O_{2}, m/z: 669.3293, observed:669.3284.

\([\alpha]_D^{23} = +134.44 \) (c 0.30, CH2Cl2).

7. Analytical and spectral characterization data for reaction products

**Methyl (5E, 9Z)-7,10-Dibenzoyl-9-hydroxy-7,8-dihydrobenzo[8]-annulene-6-carboxylate.**

Colorless oil (33 mg, 76% yield), 0.1 mmol scale reaction.

**1H NMR** (500 MHz, chloroform-d) δ 8.32 (s, 1H), 8.11 (d, \( J = 7.5 \) Hz, 2H), 7.62 (t, \( J = 7.5 \) Hz, 1H), 7.53 – 7.52 (comp, 3H), 7.34 – 7.31 (comp, 2H), 7.25 – 7.20 (comp, 4H), 7.04 (t, \( J = 7.5 \) Hz, 1H), 6.77
(d, J = 7.5 Hz, 1H), 5.27 (dd, J = 12.5, 4.5 Hz, 1H), 3.74 (s, 3H), 2.95 (t, J = 12.5 Hz, 1H), 2.50 (dd, J = 12.5, 4.5 Hz, 1H).

$^{13}$C NMR (126 MHz, chloroform-$d$) δ 198.2, 192.2, 186.7, 167.6, 142.3, 135.9, 135.8, 135.1, 133.9, 133.5, 132.2, 131.1, 130.7, 129.9, 129.3, 128.9, 128.8, 128.0, 127.8, 127.7, 52.5, 46.9, 37.0.

HRMS (ESI) scaled for [M+H]$^+$: C$_{28}$H$_{23}$O$_5$, m/z: 439.1540, observed: 439.1541.


Colorless oil (29.4 mg, 65% yield), 0.1 mmol scale reaction.

$^1$H NMR (500 MHz, chloroform-$d$) δ 8.31 (s, 1H), 8.12 (d, J = 8.0 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.5 Hz, 2H), 7.43 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 7.0 Hz, 1H), 7.28 – 7.19 (comp, 4H), 7.15 (d, J = 8.0 Hz, 1H), 6.59 (s, 1H), 5.26 (dd, J = 12.5, 4.5 Hz, 1H), 3.73 (s, 3H), 2.98 (t, J = 12.5 Hz, 1H), 2.50 (dd, J = 12.5, 4.5 Hz, 1H), 2.10 (s, 3H).

$^{13}$C NMR (126 MHz, chloroform-$d$) δ 198.3, 192.2, 186.6, 167.8, 142.5, 138.0, 135.9, 135.1, 133.7, 133.4, 132.9, 132.7, 131.0, 130.2, 129.9, 129.3, 128.9, 128.8, 128.6, 127.8, 112.8, 52.5, 47.0, 37.0, 20.9.

HRMS (ESI) scaled for [M+H]$^+$: C$_{29}$H$_{25}$O$_6$, m/z: 453.1697, observed: 453.1698.

Methyl ($5E$, 9Z)-7,10-Dibenzoyl-9-hydroxy-3-methoxy-7,8-dihydrobenzo[8]annulene-6-carboxylate.

Colorless oil (26 mg, 55% yield), 0.1 mmol scale reaction.

$^1$H NMR (500 MHz, chloroform-$d$) δ 8.29 (s, 1H), 8.12 (d, J = 7.5 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 7.0 Hz, 1H), 7.29 – 7.22 (comp, 5H), 7.06 (s, 1H), 6.67 (d, J = 8.5 Hz, 1H), 6.61 (d, J = 8.5 Hz, 1H), 5.28 (dd, J = 12.5, 4.5 Hz, 1H), 3.85 (s, 3H), 3.75 (s, 3H), 3.00 (t, J = 12.5 Hz, 1H), 2.51 (dd, J = 12.5, 4.5 Hz, 1H).

$^{13}$C NMR (126 MHz, chloroform-$d$) δ 198.2, 192.5, 186.4, 167.7, 158.9, 142.1, 136.8, 136.0, 135.1, 133.5, 133.3, 130.7, 129.4, 129.0, 128.8, 127.9, 126.2, 114.8, 113.9, 112.3, 55.4, 52.5, 47.1, 37.0.

HRMS (ESI) scaled for [M+H]$^+$: C$_{29}$H$_{25}$O$_6$, m/z: 469.1646, observed: 469.1651.

White solid (64 mg, 81% yield, 80% ee), 0.2 mmol scale reaction. m.p. 171 – 172 °C.

Optical purity determined by HPLC analysis [Daicel chiralpak ADH, n-hexane/i-PrOH = 75/25, 1.0 mL/min, λ = 254 nm, t₁ = 9.10 min, t₂ = 19.63 min].

1H NMR (500 MHz, chloroform-d) δ 8.27 (s, 1H), 8.11 (d, J = 8.5 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.56 – 7.49 (comp, 3H), 7.42 – 7.36 (m, 1H), 7.28 – 7.19 (comp, 4H), 7.06 (td, J = 8.5, 2.5 Hz, 1H), 6.49 (dd, J = 9.5, 2.5 Hz, 1H), 5.28 (dd, J = 13.5, 4.5 Hz, 1H), 3.74 (s, 3H), 2.92 (t, J = 12.0 Hz, 1H), 2.53 (dd, J = 12.0, 4.5 Hz, 1H).

13C NMR (126 MHz, chloroform-d) δ 198.02, 192.00, 187.00, 167.49, 161.70 (d, J = 254 Hz, 1C), 141.27, 136.31 (d, J = 8.4 Hz, 1C), 135.48, 134.99, 133.58, 131.81, 131.74, 131.42, 131.03, 129.20, 128.98, 128.78, 128.03, 118.74 (d, J = 21 Hz, 1C), 115.21 (d, J = 21 Hz, 1C), 112.06, 52.57, 46.75, 46.75, 37.04.

19F NMR (470.5 MHz, chloroform-d) δ -113.0 (m, 1F).


[α]D23 = +55.4 (c 0.43, CH2Cl2).


Colorless oil (25.3 mg, 50% yield), 0.1 mmol scale reaction.

1H NMR (500 MHz, chloroform-d) δ 8.30 (s, 1H), 8.11 (d, J = 8.0 Hz, 2H), 7.82 (s, 1H), 7.64 (t, J = 7.5 Hz, 2H), 7.55 (t, J = 7.5 Hz, 2H), 7.26 - 7.20 (m, 5H), 6.90 (d, J = 8.0 Hz, 1H), 5.30 (dd, J = 12.5, 4.5 Hz, 1H), 3.76 (s, 3H), 2.87 (t, J = 12.5 Hz, 1H), 2.55 (dd, J = 12.5, 4.5 Hz, 1H).

13C NMR (126 MHz, chloroform-d) δ 198.71, 191.69, 187.58, 167.22, 140.47, 137.85, 136.39, 135.47, 134.86, 133.65, 132.85, 132.28, 131.48, 130.00 (q, J = 32 Hz, 1C), 129.23, 129.00, 128.80, 128.07, 126.91 (q, J = 3.6 Hz, 1C), 123.62 (q, J = 271 Hz, 1C), 124.50 (q, J = 3.6 Hz, 1C), 111.89, 52.69, 46.75, 36.81.

19F NMR (470.5 MHz, chloroform-d) δ -63.2 (s, 1F).


Methyl (5E, 9Z)-7-Benzoyl-2-fluoro-9-hydroxy-10-(4-methyl-benzoyl)-7,8-dihydrobenzo[8]annulene-6-carboxylate.
Colorless oil (40 mg, 85% yield), 0.1 mmol scale reaction.

H NMR (500 MHz, chloroform-d) δ 8.26 (s, 1H), 8.11 (d, J = 7.5 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.58 – 7.47 (comp, 3H), 7.14 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.0 Hz, 3H), 6.52 (dd, J = 9.5 Hz, 4.5, 1H), 5.26 (dd, J = 12.5, 4.5 Hz, 1H), 3.74 (s, 3H), 2.91 (t, J = 12.5 Hz, 1H), 2.51 (dd, J = 12.5, 4.5 Hz, 1H), 2.34 (s, 3H).

C NMR (126 MHz, chloroform-d) δ 198.11, 191.63, 186.97, 167.52, 161.69 (d, J = 254 Hz, 1C), 142.17, 141.30, 136.56 (d, J = 8.4 Hz, 1C), 135.00, 133.55, 132.62, 131.94, 131.75, 131.68, 130.99, 129.38, 128.96, 128.78, 128.75, 118.75 (d, J = 21 Hz, 1C), 115.14 (d, J = 21 Hz, 1C), 111.79, 52.54, 46.77, 37.01, 21.55.

F NMR (470.5 MHz, chloroform-d) δ -113.1 (m, 1F).


Methyl (5E, 9Z)-7-Benzoyl-2-fluoro-9-hydroxy-10-(4-methoxy-benzoyl)-7,8-dihydrobenzo[8]annulene-6-carboxylate.

Colorless oil (41 mg, 84% yield), 0.1 mmol scale reaction.

H NMR (500 MHz, chloroform-d) δ 8.25 (s, 1H), 8.11 (d, J = 7.5 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.58 – 7.50 (comp, 3H), 7.23 (d, J = 8.5 Hz, 2H), 7.08 (td, J = 8.5, 2.5 Hz, 1H), 6.75 (d, J = 9.0 Hz, 2H), 6.56 (dd, J = 9.0, 2.5 Hz, 1H), 5.26 (dd, J = 12.5, 4.5 Hz, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 2.90 (t, J = 12.5 Hz, 1H), 2.50 (dd, J = 12.5, 4.5 Hz, 1H).

C NMR (126 MHz, chloroform-d) δ 198.14, 190.80, 186.52, 167.52, 162.21, 161.75 (d, J = 254 Hz, 1C), 141.21, 136.80 (d, J = 8.4 Hz, 1C), 135.01, 133.53, 131.92, 131.81, 131.74, 131.60, 131.06, 128.95, 128.77, 127.74, 118.74 (d, J = 21 Hz, 1C), 115.17 (d, J = 21 Hz, 1C), 113.40, 111.34, 55.34, 52.52, 46.80, 36.88.

F NMR (470.5 MHz, chloroform-d) δ -113.0 (m, 1F).

HRMS (ESI) scaled for [M+H]+: C29H24FO6, m/z: 487.1551, observed: 487.1553.

Methyl (5E, 9Z)-7-Benzoyl-2-fluoro-9-(4-fluorobenzoyl)-10-(4-hydroxy-benzoyl)-7,8-dihydrobenzo[8]annulene-6-carboxylate.

Colorless oil (37 mg, 78% yield), 0.1 mmol scale reaction.

H NMR (500 MHz, chloroform-d) δ 8.25 (s, 1H), 8.10 (d, J = 7.5 Hz, 2H), 7.64 (t, J = 7.5 Hz, 1H), 7.55 - 7.51 (comp, 3H), 7.26 - 7.24 (comp, 2H), 7.09 (td, J = 8.0, 2.5 Hz, 1H), 6.95 (t, J = 9.0 Hz, 2H), 6.51 (dd, J = 9.0, 2.5 Hz, 1H), 5.27 (dd, J = 12.5, 4.5 Hz, 1H), 3.74 (s, 3H), 2.91 (t, J = 12.5 Hz, 1H), 2.53 (dd, J = 12.5, 4.5 Hz, 1H).

C NMR (126 MHz, chloroform-d) δ 197.94, 191.64, 185.92, 167.44,165.39 (d, J = 254 Hz, 1C),
161.75 (d, J = 254 Hz, 1C), 141.06, 136.15 (d, J = 8.4 Hz, 1C), 134.93, 133.61, 131.97, 131.91, 131.78, 131.70, 131.14, 128.98, 128.77, 118.67 (d, J = 21 Hz, 1C), 115.41 (d, J = 21 Hz, 1C), 115.30 (d, J = 21 Hz, 1C), 52.59, 46.71, 36.93.

19F NMR (470.5 MHz, chloroform-d) δ -106.8 (m, 1F), -112.7 (m, 1F).

HRMS (ESI) scaled for [M+H]+: C28H21F2O5, m/z: 475.1352, observed: 475.1350.


![Chemical Structure](image)

Colorless oil (40 mg, 87% yield), 0.1 mmol scale reaction.

1H NMR (500 MHz, chloroform-d) δ 8.17 (s, 1H), 8.09 (d, J = 7.5 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.60 – 7.49 (comp, 4H), 7.22 (td, J = 8.5, 2.5 Hz, 1H), 6.96 (d, J = 8.5 Hz, 3H), 5.24 (dd, J = 12.5, 4.5 Hz, 1H), 3.70 (s, 3H), 2.85 (t, J = 12.5 Hz, 1H), 2.51 (dd, J = 12.5, 4.5 Hz, 1H).

13C NMR (126 MHz, chloroform-d) δ 198.05, 188.64, 160.93, 167.48, 161.92 (d, J = 254 Hz, 1C), 141.09, 139.86, 135.27 (d, J = 8.4 Hz, 1C), 133.97, 133.81, 133.57, 132.54, 131.97, 131.90, 130.84, 128.96, 128.77, 127.80, 119.18 (d, J = 21 Hz, 1C), 116.16 (d, J = 21 Hz, 1C), 110.47, 56.70, 46.80, 36.59.

19F NMR (470.5 MHz, chloroform-d) δ -112.6 (m, 1F).

HRMS (ESI) scaled for [M+H]+: C26H20FO5S, m/z: 463.1010, observed: 463.1011.


![Chemical Structure](image)

Colorless oil (38 mg, 81% yield), 0.1 mmol scale reaction.

1H NMR (500 MHz, chloroform-d) δ 8.25 (s, 1H), 8.01 (d, J = 8.5 Hz, 2H), 7.51 (dd, J = 8.5, 6.0 Hz, 1H), 7.39 – 7.36 (m, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.28 – 7.22 (comp, 4H), 7.05 (td, J = 8.5, 2.5 Hz, 1H), 6.49 (dd, J = 9.0, 3.0 Hz, 1H), 5.25 (dd, J = 13.5, 4.5 Hz, 1H), 3.73 (s, 3H), 2.92 (t, J = 12.0 Hz, 1H), 2.52 (dd, J = 12.0, 4.5 Hz, 1H), 2.45 (s, 3H).

13C NMR (126 MHz, chloroform-d) δ 197.59, 192.12, 186.97, 167.50, 161.67 (d, J = 254 Hz, 1C), 144.53, 141.19, 136.30 (d, J = 8.4 Hz, 1C), 135.50, 132.38, 132.03, 132.01, 131.79, 131.72, 131.39, 131.13, 129.66, 129.20, 128.93, 128.02, 118.71 (d, J = 21 Hz, 1C), 115.19 (d, J = 21 Hz, 1C), 112.07, 52.54, 46.59, 37.20, 21.72.

19F NMR (470.5 MHz, chloroform-d) δ -113.2 (m, 1F).


Colorless oil (33 mg, 67% yield), 0.1 mmol scale reaction.

\(^1\text{H NMR}\) (500 MHz, chloroform-\(d\)) \(\delta\) 8.26 (s, 1H), 8.05 (d, \(J = 8.5\) Hz, 2H), 7.52 (d, \(J = 8.5\) Hz, 3H), 7.38 (d, \(J = 8.5\) Hz, 1H), 7.29 – 7.21 (comp, 5H), 7.06 (td, \(J = 8.5, 2.5\) Hz, 1H), 6.50 (dd, \(J = 9.5, 2.5\) Hz, 1H), 5.20 (dd, \(J = 12.5, 4.5\) Hz, 1H), 3.75 (s, 3H), 2.93 (t, \(J = 12.5\) Hz, 1H), 2.47 (dd, \(J = 12.5, 4.5\) Hz, 1H).

\(^{13}\text{C NMR}\) (126 MHz, chloroform-\(d\)) \(\delta\) 196.92, 191.76, 187.01, 167.43, 161.73 (\(d, J = 254\) Hz, 1C), 141.37, 140.12, 136.29 (\(d, J = 8.4\) Hz, 1C), 135.40, 133.33, 131.80, 131.73, 131.46, 130.76, 130.20, 129.30, 129.20, 128.04, 118.79 (d, \(J = 21\) Hz, 1C), 115.26 (d, \(J = 21\) Hz, 1C), 52.60, 46.72, 36.94.

\(^{19}\text{F NMR}\) (470.5 MHz, chloroform-\(d\)) \(\delta\) -112.8 (m, 1F).

HRMS (ESI) scaled for [M+H]\(^+\): C\(_{28}\)H\(_{21}\)ClFO\(_5\), m/z: 491.1056, observed: 491.1063.


Colorless oil (38 mg, 72% yield), 0.1 mmol scale reaction.

\(^1\text{H NMR}\) (500 MHz, chloroform-\(d\)) \(\delta\) 8.26 (s, 1H), 7.97 (d, \(J = 8.5\) Hz, 2H), 7.68 (d, \(J = 8.5\) Hz, 2H), 7.50 (dd, \(J = 8.5, 6.0\) Hz, 1H), 7.39 (t, \(J = 7.0\) Hz, 1H), 7.27 – 7.22 (comp, 5H), 7.06 (td, \(J = 8.5, 3.0\) Hz, 1H), 6.50 (dd, \(J = 9.0, 3.0\) Hz, 1H), 5.19 (dd, \(J = 12.5, 4.5\) Hz, 1H), 3.75 (s, 3H), 2.93 (t, \(J = 12.5\) Hz, 1H), 2.47 (dd, \(J = 12.5, 4.5\) Hz, 1H).

\(^{13}\text{C NMR}\) (126 MHz, chloroform-\(d\)) \(\delta\) 197.14, 191.74, 187.01, 167.43, 161.73 (\(d, J = 254\) Hz, 1C), 141.39, 136.29 (d, \(J = 8.4\) Hz, 1C), 135.39, 133.74, 132.31, 131.80, 131.74, 131.48, 130.73, 130.29, 129.20, 128.90, 128.05, 118.80 (d, \(J = 21\) Hz, 1C), 115.26 (d, \(J = 21\) Hz, 1C), 52.60, 46.72, 36.91.

\(^{19}\text{F NMR}\) (470.5 MHz, chloroform-\(d\)) \(\delta\) -112.8 (m, 1F).

HRMS (ESI) scaled for [M+H]\(^+\): C\(_{28}\)H\(_{21}\)BrFO\(_5\), m/z: 535.0551, observed: 535.0561.

Colorless oil (43 mg, 85% yield), 0.1 mmol scale reaction.

\(^1\)H NMR (500 MHz, chloroform-\(d\)) \(\delta\) 8.29 (s, 1H), 8.27 - 8.23 (comp, 2H), 8.04 (d, \(J = 8.0\) Hz, 1H), 7.95 - 7.86 (m, 1H), 7.61 (t, \(J = 8.0\) Hz, 1H), 7.58 - 7.50 (comp, 3H), 7.39 (t, \(J = 7.0\) Hz, 1H), 7.31 - 7.21 (comp, 5H), 7.11 (td, \(J = 8.0, 2.5\) Hz, 1H), 6.51 (dd, \(J = 9.5, 2.5\) Hz, 1H), 5.25 (dd, \(J = 12.5, 4.5\) Hz, 1H), 3.78 (s, 3H), 2.99 (t, \(J = 12.5\) Hz, 1H), 2.49 (dd, \(J = 12.5, 4.5\) Hz, 1H).

\(^1^3\)C NMR (126 MHz, chloroform-\(d\)) \(\delta\) 200.92, 192.34, 186.66, 167.60, 161.76 (d, \(J = 254\) Hz, 1C), 141.33, 136.42 (d, \(J = 8.4\) Hz, 1C), 135.43, 134.57, 133.90, 132.82, 132.03, 132.01, 131.76, 131.69, 131.41, 130.92, 130.63, 129.19, 128.48, 128.03, 127.91, 127.57, 126.52, 125.26, 124.67, 118.78 (d, \(J = 21\) Hz, 1C), 115.26 (d, \(J = 21\) Hz, 1C), 112.12, 52.61, 50.81, 50.31, 36.67.

\(^1^9\)F NMR (470.5 MHz, chloroform-\(d\)) \(\delta\) -112.9 (m, 1F).

HRMS (ESI) scaled for [M+H]\(^+\): C\(_{32}\)H\(_{24}\)FO\(_5\), m/z: 507.1602, observed: 507.1608.


Colorless oil (47 mg, 51% yield), 0.2 mmol scale reaction.

\(^1\)H NMR (500 MHz, chloroform-\(d\)) \(\delta\) 8.17 (s, 1H), 8.08 (d, \(J = 8.5\) Hz, 2H), 7.64 - 7.48 (comp, 5H), 7.21 (td, \(J = 8.5, 2.5\) Hz, 1H), 7.00 - 6.86 (comp, 3H), 5.25 (dd, \(J = 13.5, 4.5\) Hz, 1H), 3.69 (s, 3H), 2.85 (t, \(J = 12.5\) Hz, 1H), 2.51 (dd, \(J = 12.0, 4.5\) Hz, 1H).

\(^1^3\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 198.02, 188.66, 179.43, 167.47, 161.91 (d, \(J = 254\) Hz, 1C), 141.07, 139.85, 135.27 (d, \(J = 8.4\) Hz, 1C), 134.98, 133.97, 133.84, 133.57, 132.52, 131.98, 131.91, 130.86, 128.96, 128.77, 127.81, 119.18 (d, \(J = 21\) Hz, 1C), 116.15 (d, \(J = 21\) Hz, 1C), 110.47, 52.52, 46.81, 36.58.

\(^1^9\)F NMR (470.5 MHz, chloroform-\(d\)) \(\delta\) -113.0 (m, 1F).

HRMS (ESI) scaled for [M+H]\(^+\): C\(_{26}\)H\(_{20}\)FO\(_5\)S, m/z: 463.1010, observed: 463.1021.

Methyl (5\(E\), 7\(S\), 8\(S\), 9\(Z\))-7,10-Dibenzoyl-2-fluoro-9-hydroxy-8-methyl-7,8-dihydrobenzo[8]annulene-6-carboxylate.

Colorless oil (21 mg, 45% yield), >19:1 dr, 97% ee), 0.1 mmol scale reaction.

Optical purity determined by HPLC analysis [Daicel chiralpak ADH, n-hexane/i-PrOH = 80/20, 1.0 mL/min, \(\lambda = 254\) nm, \(t_1 = 4.67\) min, \(t_2 = 5.44\) min].

\(^1\)H NMR (500 MHz, chloroform-\(d\)) \(\delta\) 8.11 (d, \(J = 7.5\) Hz, 2H), 8.08 (s, 1H), 7.59 (t, \(J = 7.5\) Hz, 1H), 7.50 (t, \(J = 7.5\) Hz, 2H), 7.42 (dd, \(J = 8.5, 6.0\) Hz, 1H), 7.37 - 7.32 (m, 1H), 7.25 - 7.17 (comp, 4H),
7.07 (td, J = 8.5, 2.5 Hz, 1H), 6.50 (dd, J = 9.5, 2.5 Hz, 1H), 5.02 (d, J = 11.5 Hz, 1H), 3.67 (s, 3H), 3.46 (dq, J = 11.5, 6.5 Hz, 1H), 0.95 (d, J = 6.5 Hz, 3H).

13C NMR (126 MHz, chloroform-d) δ 199.32, 197.86, 184.12, 167.35, 161.93 (d, J = 254 Hz, 1C), 141.75, 137.41, 136.08 (d, J = 8.4 Hz, 1C), 135.32, 133.53, 133.03, 131.99, 131.13, 130.75, 130.68, 129.13, 129.10, 128.70, 127.98, 118.44 (d, J = 21 Hz, 1C), 115.18 (d, J = 21 Hz, 1C), 52.45, 51.26, 41.30, 15.52.

19F NMR (470.5 MHz, chloroform-d) δ -113.0 (m, 1F).

HRMS (ESI) scaled for [M+H]+: C29H24FO5, m/z: 471.1602, observed: 471.1616.

[a]D23 = +146.3 (c 0.61, CH2Cl2).

Methyl (5E, 7S, 8S, 9Z)-7,10-Dibenzoyl-8-ethyl-2-fluoro-9-hydroxy-7,8-dihydrobenzo[8]annulene-6-carboxylate.

Colorless oil (17 mg, 35% yield, >19:1 dr, 90% ee), 0.1 mmol scale reaction.

Optical purity determined by HPLC analysis [Daicel chiralpak ADH, n-hexane/i-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t1 = 4.93 min, t2 = 6.90 min].

1H NMR (500 MHz, chloroform-d) δ 8.13 (d, J = 7.5 Hz, 2H), 8.10 (s, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H), 7.45 (dd, J = 8.5, 6.0 Hz, 1H), 7.38 (t, J = 7.3 Hz, 1H), 7.28 – 7.19 (comp, 4H), 7.10 (td, J = 8.5, 2.5 Hz, 1H), 6.53 (dd, J = 9.5, 2.5 Hz, 1H), 5.07 (d, J = 11.5 Hz, 1H), 3.68 (s, 3H), 3.35 (td, J = 11.5, 3.0 Hz, 1H), 1.85 – 1.77 (m, 1H), 1.08 – 1.03 (m, 1H), 0.67 (t, J = 7.5 Hz, 3H).

13C NMR (126 MHz, chloroform-d) δ 200.26, 198.40, 184.74, 167.35, 162.02 (d, J = 254 Hz, 1C), 141.73, 137.30, 136.25 (d, J = 8.4 Hz, 1C), 135.38, 133.53, 133.07, 132.03, 131.14, 130.77, 130.70, 129.08, 128.70, 127.96, 118.15 (d, J = 21 Hz, 1C), 115.18 (d, J = 21 Hz, 1C), 52.43, 50.16, 48.74, 23.66, 12.09.

19F NMR (470.5 MHz, chloroform-d) δ -113.0 (m, 1F).


[a]D23 = +327.7 (c 0.14, CH2Cl2).

Methyl (5E, 7S, 8S, 9Z)-7-Benzoyl-2-fluoro-9-hydroxy-10-(4-methoxybenzoyl)-8-methyl-7,8-dihydrobenzo[8]annulene-6-carboxylate.

Colorless oil (25 mg, 50% yield, >19:1 dr, 97% ee), 0.1 mmol scale reaction.

Optical purity determined by HPLC analysis [Daicel chiralpak ADH, n-hexane/i-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t1 = 13.59 min, t2 = 17.50 min].

1H NMR (500 MHz, chloroform-d) δ 8.13 (d, J = 8.5 Hz, 2H), 8.09 (s, 1H), 7.61 (t, J = 7.5 Hz, 1H),
7.52 (t, J = 7.5 Hz, 2H), 7.46 (dd, J = 8.5, 6.0 Hz, 1H), 7.20 – 7.18 (comp, 2H), 7.11 (td, J = 8.5, 2.5 Hz, 1H), 6.76 – 6.73 (comp, 2H), 6.60 (dd, J = 9.5, 2.5 Hz, 1H), 5.04 (d, J = 11.5 Hz, 1H), 3.82 (s, 3H), 3.68 (s, 3H), 3.50 – 3.39 (m, 1H), 0.96 (d, J = 6.5 Hz, 3H).

\(^{13}\)C NMR (126 MHz, chloroform-d) δ 199.50, 196.55, 183.96, 167.39, 161.99 (d, J = 254 Hz, 1C), 161.96, 141.69, 137.46, 136.53 (d, J = 8.4 Hz, 1C), 133.49, 133.00, 132.06, 131.41, 130.79, 130.72, 129.12, 128.67, 127.62, 118.42 (d, J = 21 Hz, 1C), 115.14 (d, J = 21 Hz, 1C), 113.36, 110.99, 55.32, 52.40, 51.25, 41.07, 15.53.

\(^{19}\)F NMR (470.5 MHz, chloroform-d) δ -112.9 (m, 1F).

HRMS (ESI) scaled for [M+H]+: C\(_{30}\)H\(_{26}\)FO\(_6\), m/z: 501.1708, observed: 501.1686.

[\(\alpha\)]\(_{D}^{23}\) = +384.0 (c 0.30, CH\(_2\)Cl\(_2\)).

Methyl 9-Benzoyl-7-ethyl-8-hydroxy-7H-benzo-[7]annulene-6-carboxylate.

![Methyl 9-Benzoyl-7-ethyl-8-hydroxy-7H-benzo-[7]annulene-6-carboxylate](image)

Pale yellow oil (49.5 mg, 71% yield), 0.2 mmol scale reaction.

\(^1\)H NMR (300 MHz, chloroform-d) δ 7.99 (s, 1H), 7.42 (d, J = 7.5 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.22 – 7.11 (comp, 5H), 6.92 (t, J = 7.0 Hz, 1H), 6.78 (d, J = 7.8 Hz, 1H), 4.13 – 4.03 (m, 1H), 3.89 (s, 3H), 1.32 – 1.13 (m, 2H), 0.82 (t, J = 7.5 Hz, 3H).

\(^{13}\)C NMR (75 MHz, Chloroform-d) δ 196.3, 189.0, 166.9, 138.8, 133.2, 132.0, 130.7, 129.7, 129.6, 127.8, 127.7, 126.1, 52.5, 49.9, 17.7, 12.2.

HRMS (ESI) scaled for [M+H]+: C\(_{22}\)H\(_{21}\)O\(_4\), m/z: 349.1434, observed: 349.1437.

Methyl 9-Benzoyl-7-ethyl-8-hydroxy-2-methyl-7H-benzo[7]-annulene-6-carboxylate.

![Methyl 9-Benzoyl-7-ethyl-8-hydroxy-2-methyl-7H-benzo[7]-annulene-6-carboxylate](image)

Pale yellow oil (58 mg, 80% yield), 0.2 mmol scale reaction.

\(^1\)H NMR (500 MHz, chloroform-d) δ 7.95 (s, 1H), 7.33 – 7.28 (comp, 2H), 7.18 (t, J = 7.5 Hz, 2H), 7.12 (d, J = 7.5 Hz, 2H), 6.99 (d, J = 7.5 Hz, 1H), 6.56 (s, 1H), 4.13 – 4.03 (m, 1H), 3.88 (s, 3H), 1.98 (s, 3H), 1.33 – 1.28 (m, 1H), 1.20 – 1.17 (m, 1H), 0.82 (t, J = 7.5 Hz, 3H).

\(^{13}\)C NMR (126 MHz, chloroform-d) δ 195.9, 189.5, 167.0, 138.9, 137.8, 134.0, 130.8, 130.5, 129.8, 129.4, 127.7, 127.0, 52.4, 49.9, 21.0, 17.7, 12.2.

HRMS (ESI) scaled for [M+H]+: C\(_{23}\)H\(_{23}\)O\(_4\), m/z: 363.1591, observed: 363.1594.
Methyl 9-Benzoyl-7-ethyl-8-hydroxy-3-methoxy-7H-benzo[7]-annulene-6-carboxylate.

Pale yellow oil (60 mg, 79% yield), 0.2 mmol scale reaction.

$^1$H NMR (500 MHz, chloroform-d) δ 7.93 (s, 1H), 7.33 – 7.29 (m, 1H), 7.20 (t, $J = 7.5$ Hz, 2H), 7.15 (d, $J = 7.5$ Hz, 2H), 6.92 (s, 1H), 6.68 (d, $J = 8.6$ Hz, 1H), 6.51 (dd, $J = 8.5$, 3.0 Hz, 1H), 4.09 – 4.06 (m, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 1.32 – 1.27 (m, 1H), 1.25 – 1.17 (m, 1H), 0.82 (t, $J = 7.5$ Hz, 3H).

$^{13}$C NMR (126 MHz, chloroform-d) δ 196.6, 188.0, 166.9, 157.5, 138.7, 134.4, 132.2, 130.5, 129.6, 127.8, 114.6, 113.5, 55.3, 52.5, 50.2, 20.9, 12.3.

HRMS (ESI) scaled for [M+H]$^+$: C$_{23}$H$_{23}$O$_5$, m/z: 379.1540, observed: 379.1540.

Methyl 9-Benzoyl-7-ethyl-8-hydroxy-2,3-dimethoxy-7H-benzo[7]annulene-6-carboxylate.

Pale yellow oil (66 mg, 81% yield), 0.2 mmol scale reaction.

$^1$H NMR (500 MHz, chloroform-d) δ 7.90 (s, 1H), 7.32 (t, $J = 7.5$ Hz, 1H), 7.22 (t, $J = 7.5$ Hz, 2H), 7.16 (d, $J = 7.5$ Hz, 2H), 6.86 (s, 1H), 6.17 (s, 1H), 4.11 – 4.06 (m, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 3.26 (s, 3H), 1.36 – 1.29 (m, 1H), 1.23 (s, 1H), 0.83 (t, $J = 7.5$ Hz, 3H).

$^{13}$C NMR (126 MHz, chloroform-d) δ 195.5, 189.5, 167.0, 148.1, 138.6, 130.5, 129.7, 129.2, 128.0, 116.37, 111.6, 55.8, 55.4, 49.8, 20.5, 17.9, 12.2.

HRMS (ESI) scaled for [M+H]$^+$: C$_{24}$H$_{25}$O$_6$, m/z: 409.1646, observed: 409.1645.


Pale yellow oil (57 mg, 78% yield), 0.2 mmol scale reaction.

$^1$H NMR (500 MHz, chloroform-d) δ 7.94 (s, 1H), 7.39 (t, $J = 7.5$ Hz, 1H), 7.35 (d, $J = 7.5$ Hz, 1H), 7.23 (t, $J = 7.5$ Hz, 2H), 7.15 (d, $J = 7.5$ Hz, 2H), 6.89 (t, $J = 7.5$ Hz, 1H), 6.47 (d, $J = 10.0$ Hz, 1H), 4.15 – 4.03 (m, 1H), 3.89 (s, 3H), 1.30 – 1.27 (m, 1H), 1.23 – 1.16 (m, 1H), 0.83 (t, $J = 7.5$ Hz, 3H).

$^{13}$C NMR (126 MHz, chloroform-d) δ 195.89, 191.57, 166.76, 161.32 (d, $J = 254$ Hz, 1C), 137.73, 131.74, 131.65, 131.09, 129.40, 128.03, 119.57 (d, $J = 22$ Hz, 1C), 113.61 (d, $J = 22$ Hz, 1C), 52.54, 49.73, 20.89, 12.18.
**Methyl 7-Ethyl-2-fluoro-8-hydroxy-9-(4-methylbenzoyl)-7H-benzo[7]annulene-6-carboxylate.**

Pale yellow oil (57 mg, 75% yield), 0.2 mmol scale reaction.

**1H NMR** (500 MHz, chloroform-d) δ 7.94 (s, 1H), 7.43 – 7.36 (m, 1H), 7.03 (comp, 4H), 6.90 (t, J = 8.0 Hz, 1H), 6.51 (d, J = 11.5 Hz, 1H), 4.13 – 4.02 (m, 1H), 3.88 (s, 3H), 2.33 (s, 3H), 1.30 – 1.24 (m, 1H), 1.23 – 1.16 (m, 1H), 0.83 (t, J = 7.5 Hz, 3H).

**13C NMR** (126 MHz, chloroform-d) δ 195.43, 189.85, 166.78, 161.31 (d, J = 250 Hz, 1C), 141.76, 137.72, 131.71, 131.68, 131.61, 129.56, 128.73, 119.57 (d, J = 22 Hz, 1C), 113.51 (d, J = 22 Hz, 1C), 52.51, 49.65, 21.50, 20.90, 12.18.

**19F NMR** (470.5 MHz, chloroform-d) δ -111.7 (m, 1F).


**Methyl 7-Ethyl-2-fluoro-8-hydroxy-9-(4-methoxybenzoyl)-7H-benzo[7]annulene-6-carboxylate.**

Pale yellow oil (61 mg, 78% yield), 0.2 mmol scale reaction.

**1H NMR** (500 MHz, chloroform-d) δ 7.93 (s, 1H), 7.44 – 7.38 (m, 1H), 7.12 (d, J = 8.5 Hz, 2H), 6.91 (t, J = 8.5 Hz, 1H), 6.72 (d, J = 9.0 Hz, 2H), 6.55 (d, J = 10.0 Hz, 1H), 4.11 – 4.01 (m, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 1.27 – 1.22 (m, 1H), 1.21 – 1.15 (m, 1H), 0.82 (t, J = 7.5 Hz, 3H).

**13C NMR** (126 MHz, chloroform-d) δ 194.66, 189.52, 166.78, 161.37 (d, J = 250 Hz, 1C), 137.63, 131.88, 131.69, 119.51 (d, J = 22 Hz, 1C), 113.50 (d, J = 22 Hz, 1C), 113.36, 55.31, 52.50, 49.40, 20.90, 12.17.

**19F NMR** (470.5 MHz, chloroform-d) δ -111.8 (m, 1F).

**HRMS (ESI)** scaled for [M+H]+: C23H22FO5, m/z: 381.1497, observed: 381.1499.

**Methyl 7-Ethyl-2-fluoro-9-(4-fluorobenzoyl)-8-hydroxy-7H-benzo[7]annulene-6-carboxylate.**

Pale yellow oil (61 mg, 78% yield), 0.2 mmol scale reaction.

**1H NMR** (500 MHz, chloroform-d) δ 7.92 (s, 1H), 7.44 – 7.38 (m, 1H), 7.12 (d, J = 8.5 Hz, 2H), 6.91 (t, J = 8.5 Hz, 1H), 6.72 (d, J = 9.0 Hz, 2H), 6.55 (d, J = 10.0 Hz, 1H), 4.11 – 4.01 (m, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 1.27 – 1.22 (m, 1H), 1.21 – 1.15 (m, 1H), 0.82 (t, J = 7.5 Hz, 3H).

**13C NMR** (126 MHz, chloroform-d) δ 194.66, 189.52, 166.78, 161.37 (d, J = 250 Hz, 1C), 137.63, 131.88, 131.69, 119.51 (d, J = 22 Hz, 1C), 113.50 (d, J = 22 Hz, 1C), 113.36, 55.31, 52.50, 49.40, 20.90, 12.17.

**19F NMR** (470.5 MHz, chloroform-d) δ -111.7 (m, 1F).

**HRMS (ESI)** scaled for [M+H]+: C23H22FO5, m/z: 397.1446, observed: 397.1449.
Pale yellow oil (46 mg, 60% yield), 0.2 mmol scale reaction.

\[ \text{\textsuperscript{1}H NMR (500 MHz, chloroform-d) } \delta 7.93 (s, 1H), 7.44 - 7.37 (m, 1H), 7.20 - 7.12 (comp, 2H), 6.95 - 6.88 (comp, 3H), 6.48 (d, J = 9.5 Hz, 1H), 4.15 - 4.02 (m, 1H), 3.88 (s, 3H), 1.29 - 1.23 (m, 1H), 1.22 - 1.15 (m, 1H), 0.82 (t, J = 7.5 Hz, 3H). \]

\[ \text{\textsuperscript{13}C NMR (126 MHz, chloroform-d) } \delta 195.52, 188.64, 166.68, 164.17 \text{ (d, } J = 254 \text{ Hz, 1C), 161.36 \text{ (d, } J = 254 \text{ Hz, 1C), 137.58, 131.92, 131.84, 119.48 \text{ (d, } J = 22 \text{ Hz, 1C), 115.26 \text{ (d, } J = 22 \text{ Hz, 1C), 113.78 \text{ (d, } J = 22 \text{ Hz, 1C), 52.55, 49.54, 20.92, 12.15.}} \]

\[ \text{\textsuperscript{19}F NMR (470.5 MHz, chloroform-d) } \delta -107.2 \text{ (m, 1F), -111.5 \text{ (m, 1F).}} \]

\[ \text{HRMS (ESI) scaled for } [\text{M+H}]^+: \text{C}_{22}\text{H}_{19}\text{F}_{2}O_4, \text{ m/z: 385.1246, observed: 385.1249.} \]

**Methyl 7-Ethyl-2-fluoro-8-hydroxy-9-(thiophene-2-carbonyl)-7H-benzo[7]annulene-6-carboxylate.**

Pale yellow oil (33.5 mg, 45% yield), 0.2 mmol scale reaction.

\[ \text{\textsuperscript{1}H NMR (500 MHz, chloroform-d) } \delta 7.92 (s, 1H), 7.49 (d, J = 5.0 Hz, 1H), 7.48 - 7.44 (m, 1H), 7.03 \text{ (t, } J = 8.5 \text{ Hz, 1H), 6.95 \text{ (d, } J = 8.5 \text{ Hz, 1H), 6.90 - 6.85 \text{ (m, 1H), 6.76 \text{ (d, } J = 5.0 \text{ Hz, 1H), 4.06 - 3.99 \text{ (m, 1H), 3.87 (s, 3H), 1.28 - 1.22 (m, 1H), 1.17 - 1.12 (m, 1H), 0.82 (t, } J = 7.5 \text{ Hz, 3H).}} \]

\[ \text{\textsuperscript{13}C NMR (126 MHz, chloroform-d) } \delta 192.19, 182.51, 166.69, 164.17 \text{ (d, } J = 250 \text{ Hz, 1C), 137.43, 133.51, 132.81, 132.43, 131.68 \text{ (d, } J = 9 \text{ Hz, 1C), 127.42, 119.70 \text{ (d, } J = 21 \text{ Hz, 1C), 114.32 \text{ (d, } J = 21 \text{ Hz, 1C), 109.61, 52.52, 48.69, 20.87, 12.16.}} \]

\[ \text{\textsuperscript{19}F NMR (470.5 MHz, chloroform-d) } \delta -111.5 \text{ (m, 1F).}} \]

\[ \text{HRMS (ESI) scaled for } [\text{M+H}]^+: \text{C}_{20}\text{H}_{18}\text{F}_{3}O_S, \text{ m/z: 373.0904, observed: 373.0907.} \]

**Methyl 9-Benzoyl-8-hydroxy-3-methoxy-7-methyl-7H-benzo[7]annulene-6-carboxylate.**

Pale yellow oil (59 mg, 81% yield), 0.2 mmol scale reaction.
$^1$H NMR (500 MHz, chloroform-$d$) δ 7.88 (s, 1H), 7.31 (t, $J = 7.5$ Hz, 1H), 7.20 (t, $J = 7.5$ Hz, 2H), 7.16 (d, $J = 7.5$ Hz, 2H), 6.93 (d, $J = 2.5$ Hz, 1H), 6.70 (d, $J = 9.0$ Hz, 1H), 6.53 (dd, $J = 9.0, 2.5$ Hz, 1H), 4.35 – 4.15 (m, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 1.03 – 0.68 (m, 3H).

$^{13}$C NMR (126 MHz, chloroform-$d$) δ 191.10, 188.02, 166.68, 157.57, 134.47, 130.54, 129.61, 127.84, 114.70, 55.28, 52.42.

HRMS (ESI) scaled for [M+H]$^+$: C$_{22}$H$_{21}$O$_5$, m/z: 365.1384, observed: 365.1388.

Methyl 9-Benzoyl-8-hydroxy-3-methoxy-7-phenyl-7H-[7]-annulene-6-carboxylate.

Pale yellow oil (58.8 mg, 69% yield), 0.2 mmol scale reaction.

$^1$H NMR (300 MHz, chloroform-$d$) δ 8.19 (s, 1H), 7.32 – 7.28 (m, 1H), 7.23 – 7.10 (comp, 4H), 7.04 – 6.89 (comp, 5H), 6.81 (d, $J = 2.5$ Hz, 1H), 6.38 (d, $J = 8.5$ Hz, 1H), 6.25 (dd, $J = 8.5, 2.5$ Hz, 1H), 3.94 (s, 3H), 3.71 (s, 3H).

$^{13}$C NMR (75 MHz, chloroform-$d$) δ 196.5, 186.7, 166.9, 157.4, 140.9, 136.4, 135.2, 134.4, 134.2, 130.7, 130.6, 129.6, 127.9, 126.7, 126.5, 126.2, 114.5, 112.9, 55.2, 52.8.

HRMS (ESI) scaled for [M+H]$^+$: C$_{27}$H$_{23}$O$_5$, m/z: 427.1540, observed: 427.1545.

Methyl 9-Benzoyl-8-hydroxy-3-methoxy-7-octyl-7H-[7]-annulene-6-carboxylate.

Pale yellow oil (58 mg, 63% yield), 0.2 mmol scale reaction.

$^1$H NMR (500 MHz, chloroform-$d$) δ 7.93 (s, 1H), 7.31 (t, $J = 7.5$ Hz, 1H), 7.23 – 7.12 (comp, 4H), 6.92 (s, 1H), 6.67 (d, $J = 8.5$ Hz, 1H), 6.51 (d, $J = 11.0$ Hz, 1H), 4.17 – 4.11 (m, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 1.26 – 1.11 (m, 14H), 0.86 (t, $J = 7.5$ Hz, 3H).

$^{13}$C NMR (126 MHz, chloroform-$d$) δ 196.73, 187.81, 166.90, 157.52, 138.72, 137.04, 134.51, 134.41, 132.42, 130.52, 129.58, 127.81, 126.78, 114.56, 113.47, 110.75, 55.25, 52.51, 48.69, 31.79, 29.14, 29.09, 29.03, 27.68, 27.47, 22.60, 14.08.

HRMS (ESI) scaled for [M+H]$^+$: C$_{29}$H$_{35}$O$_5$, m/z: 463.2479, observed: 463.2488.

(3-Butyl-2-hydroxynaphthalen-1-yl)(phenyl)methanone.

Yellow oil (52 mg, 86% yield), 0.2 mmol scale reaction.
**1H NMR** (500 MHz, chloroform-\textit{d}) \(\delta\) 11.84 (s, 1H), 7.81 (s, 1H), 7.72 (d, \(J = 7.5\) Hz, 1H), 7.69 – 7.63 (m, 2H), 7.61 – 7.54 (m, 1H), 7.43 (t, \(J = 8.0\) Hz, 2H), 7.27 (t, \(J = 7.5\) Hz, 2H), 7.15 – 7.09 (m, 1H), 2.94 – 2.83 (m, 2H), 1.85 – 1.73 (m, 2H), 1.55 – 1.47 (m, 2H), 1.04 (t, \(J = 7.5\) Hz, 3H).

**13C NMR** (126 MHz, chloroform-\textit{d}) \(\delta\) 200.9, 161.2, 140.7, 135.0, 132.5, 129.4, 128.5, 128.0, 126.1, 125.7, 123.6, 113.7, 31.5, 30.1, 22.7, 14.1.

**HRMS (ESI)** scaled for [M+H]+: C_{21}H_{21}O_{2}, \(m/z\): 305.1536, observed: 305.1538.

(3-Butyl-2-hydroxy-7-methylnaphthalen-1-yl)(phenyl)methanone.

Yellow oil (60 mg, 94% yield), 0.2 mmol scale reaction.

**1H NMR** (500 MHz, chloroform-\textit{d}) \(\delta\) 11.92 (s, 1H), 7.76 (s, 1H), 7.65 (d, \(J = 7.5\) Hz, 2H), 7.61 (d, \(J = 8.0\) Hz, 1H), 7.58 (t, \(J = 7.5\) Hz, 1H), 7.43 (t, \(J = 7.5\) Hz, 2H), 7.10 (d, \(J = 8.0\) Hz, 1H), 7.01 (s, 1H), 2.91 – 2.82 (m, 2H), 2.16 (s, 3H), 1.83 – 1.73 (m, 2H), 1.54 – 1.46 (h, \(J = 7.5\) Hz, 2H), 1.03 (t, \(J = 7.4\) Hz, 3H).

**13C NMR** (126 MHz, chloroform-\textit{d}) \(\delta\) 201.0, 161.4, 140.7, 135.4, 134.9, 132.3, 131.5, 131.3, 129.4, 128.4, 127.8, 126.3, 125.8, 125.5, 113.3, 31.5, 30.0, 22.7, 21.9, 14.1.

**HRMS (ESI)** scaled for [M+H]+: C_{22}H_{23}O_{2}, \(m/z\): 319.1693, observed: 319.1706.

(3-Butyl-2-hydroxy-6-methoxynaphthalen-1-yl)(phenyl)methanone.

Yellow oil (64 mg, 96% yield), 0.2 mmol scale reaction.

**1H NMR** (500 MHz, chloroform-\textit{d}) \(\delta\) 11.53 (s, 1H), 7.71 (s, 1H), 7.64 (d, \(J = 9.0\) Hz, 2H), 7.57 (t, \(J = 8.0\) Hz, 1H), 7.42 (t, \(J = 8.0\) Hz, 2H), 7.16 (d, \(J = 9.0\) Hz, 1H), 7.08 (d, \(J = 3.0\) Hz, 1H), 6.79 (dd, \(J = 9.0, 2.5\) Hz, 1H), 3.89 (s, 3H), 2.91 – 2.82 (m, 2H), 1.81 – 1.70 (m, 2H), 1.51 – 1.47 (m, 2H), 1.02 (t, \(J = 7.5\) Hz, 3H).

**13C NMR** (126 MHz, chloroform-\textit{d}) \(\delta\) 200.8, 159.3, 155.7, 140.7, 133.9, 132.9, 132.5, 129.4, 129.2, 128.6, 127.5, 126.1, 117.4, 114.0, 106.8, 55.2, 31.5, 30.1, 22.7, 14.1.

**HRMS (ESI)** scaled for [M+H]+: C_{22}H_{25}O_{3}, \(m/z\): 335.1642, observed: 335.1629.

(3-Butyl-7-fluoro-2-hydroxynaphthalen-1-yl)(phenyl)methanone.
Yellow oil (48.3 mg, 75% yield), 0.2 mmol scale reaction.

\[ ^1H \text{NMR (500 MHz, chloroform-}d\text{)} \delta 12.00 \text{ (s, 1H), 7.77 (s, 1H), 7.69 (dd, } J = 9.0, 6.0 \text{ Hz, 1H), 7.66 – 7.62 (m, 2H), 7.60 (t, } J = 7.5 \text{ Hz, 1H), 7.45 (t, } J = 7.5 \text{ Hz, 2H), 7.03 (td, } J = 7.5, 2.5 \text{ Hz, 1H), 6.85 (dd, } J = 12.0, 2.5 \text{ Hz, 1H), 2.92 – 2.80 (m, 2H), 1.78 – 1.72 (m, 2H), 1.51 – 1.48 (m, 2H), 1.02 (t, } J = 7.5 \text{ Hz, 3H).} \]

\[ ^13C \text{NMR (126 MHz, chloroform-}d\text{)} \delta 200.67, 162.26, 160.39 (d, } J = 245 \text{ Hz, 1C), 140.12, 134.80, 132.76, 132.51 (d, } J = 9 \text{ Hz, 1C), 131.79, 130.23, 130.16, 129.30, 128.70, 125.05, 113.31 (d, } J = 21 \text{ Hz, 1C), 110.51 (d, } J = 21 \text{ Hz, 1C), 31.43, 29.90, 22.68, 14.03.} \]

\[ ^19F \text{NMR (470.5 MHz, chloroform-}d\text{)} \delta -112.6 \text{ (m, 1F).} \]

HRMS (ESI) scaled for \([M+H]^+\): C_{21}H_{20}FO_2, m/z: 323.1442, observed: 323.1441.

(3-Butyl-7-fluoro-2-hydroxynaphthalen-1-yl)(p-tolyl)methanone.

Yellow oil (53 mg, 79% yield), 0.2 mmol scale reaction.

\[ ^1H \text{NMR (500 MHz, chloroform-}d\text{)} \delta 11.75 \text{ (s, 1H), 7.76 (s, 1H), 7.69 (dd, } J = 9.0, 6.0 \text{ Hz, 1H), 7.55 (d, } J = 8.0 \text{ Hz, 2H), 7.24 (d, } J = 8.0 \text{ Hz, 2H), 7.03 (td, } J = 8.5, 2.5 \text{ Hz, 1H), 6.92 (dd, } J = 12.0, 2.5 \text{ Hz, 1H), 2.90 – 2.80 (m, 2H), 2.46 (s, 3H), 1.80 – 1.70 (m, 2H), 1.52 – 1.44 (m, 2H), 1.01 (t, } J = 7.5 \text{ Hz, 3H).} \]

\[ ^13C \text{NMR (126 MHz, chloroform-}d\text{)} \delta 200.28, 161.63, 160.46 (d, } J = 245 \text{ Hz, 1C), 143.77, 137.30, 134.39, 132.53 (d, } J = 9 \text{ Hz, 1C), 131.72, 130.14, 130.06, 129.61, 129.37, 125.04, 113.26 (d, } J = 21 \text{ Hz, 1C), 110.49 (d, } J = 21 \text{ Hz, 1C), 31.44, 29.92, 22.67, 21.75, 14.02.} \]

\[ ^19F \text{NMR (470.5 MHz, chloroform-}d\text{)} \delta -111.8 \text{ (m, 1F).} \]

HRMS (ESI) scaled for \([M+H]^+\): C_{22}H_{22}FO_2, m/z: 337.1598, observed: 337.1613.

(3-Butyl-7-fluoro-2-hydroxynaphthalen-1-yl)(4-fluorophenyl)methanone.
Yellow oil (56 mg, 83% yield), 0.2 mmol scale reaction.

\[ ^1H \text{NMR} \ (500 \text{ MHz, chloroform-}d) \delta 11.68 \ (s, 1H), 7.77 \ (s, 1H), 7.72 - 7.65 \ (m, 3H), 7.13 \ (t, J = 8.5 \text{ Hz}, 2H), 7.05 \ (dd, J = 12.0, 8.5, 2.5 \text{ Hz}, 1H), 6.87 \ (dd, J = 12.0, 2.5 \text{ Hz}, 1H), 2.89 - 2.78 \ (comp, 2H), 1.77 - 1.71 \ (m, 2H), 1.52 - 1.44 \ (m, 2H), 1.01 \ (t, J = 7.5 \text{ Hz}, 3H). \]

\[ ^13C \text{NMR} \ (126 \text{ MHz, chloroform-}d) \delta 198.87, 165.52 \ (d, J = 255 \text{ Hz}, 1C), 161.87, 160.56 \ (d, J = 245 \text{ Hz}, 1C), 136.11, 134.76, 132.35, 132.28, 132.16, 132.09, 131.80, 130.32 \ (d, J = 9 \text{ Hz}, 1C), 125.07, 115.92 \ (d, J = 21 \text{ Hz}, 1C), 113.44 \ (d, J = 21 \text{ Hz}, 1C), 110.34 \ (d, J = 21 \text{ Hz}, 1C), 31.42, 29.89, 22.66, 14.01. \]

\[ ^19F \text{NMR} \ (470.5 \text{ MHz, chloroform-}d) \delta -112.3 \ (m, 1F). \]

\[ \text{HRMS (ESI) scaled for [M+H]}^+ : \text{C}_{21}\text{H}_{19}\text{F}_2\text{O}_2, \text{m/z: 341.1348, observed: 341.1363.} \]

\( \text{(3-Butyl-7-fluoro-2-hydroxynaphthalen-1-yl)(thiophen-2-yl)methanone.} \)

Yellow oil (40.6 mg, 62% yield), 0.2 mmol scale reaction.

\[ ^1H \text{NMR} \ (500 \text{ MHz, chloroform-}d) \delta 10.41 \ (s, 1H), 7.76 \ (dd, J = 9.0, 6.0 \text{ Hz}, 1H), 7.41 \ (dd, J = 4.0, 1.0 \text{ Hz}, 1H), 7.37 \ (dd, J = 12.0, 2.5 \text{ Hz}, 1H), 7.10 - 7.06 \ (comp, 2H), 2.88 - 2.79 \ (m, 2H), 1.80 - 1.67 \ (m, 2H), 1.50 - 1.43 \ (m, 2H), 1.00 \ (t, J = 7.5 \text{ Hz}, 3H). \]

\[ ^13C \text{NMR} \ (126 \text{ MHz, chloroform-}d) \delta 190.81, 160.40 \ (d, J = 245 \text{ Hz}, 1C), 159.16, 144.51, 135.59, 134.91, 133.73, 132.0 \ (d, J = 9 \text{ Hz}, 1C), 131.59, 130.00 \ (d, J = 9 \text{ Hz}, 1C), 128.16, 125.28, 113.64 \ (d, J = 21 \text{ Hz}, 1C), 110.15 \ (d, J = 21 \text{ Hz}, 1C), 31.46, 29.99, 22.65, 14.01. \]

\[ ^19F \text{NMR} \ (470.5 \text{ MHz, chloroform-}d) \delta -110.5 \ (m, 1F). \]

\[ \text{HRMS (ESI) scaled for [M+H]}^+ : \text{C}_{19}\text{H}_{18}\text{FO}_2\text{S, m/z: 329.1006, observed: 329.1021.} \]

\( \text{(3-Cyclopropyl-2-hydroxynaphthalen-1-yl)(phenyl)methanone.} \)
Yellow oil (46 mg, 80% yield), 0.2 mmol scale reaction.

$^1$H NMR (500 MHz, chloroform-d) $\delta$ 11.48 (s, 1H), 7.70 – 7.66 (comp, 3H), 7.61 – 7.55 (comp, 2H), 7.43 (t, $J$ = 8.0 Hz, 2H), 7.31 – 7.23 (comp, 2H), 7.12 (ddd, $J$ = 8.4, 6.9, 1.4 Hz, 1H), 2.38 – 2.33 (m, 1H), 1.15 – 1.08 (m, 2H), 0.89 – 0.84 (m, 2H).

$^{13}$C NMR (126 MHz, chloroform-d) $\delta$ 200.7, 160.8, 140.4, 133.1, 132.6, 131.0, 130.7, 129.5, 128.5, 128.2, 128.0, 125.9, 125.8, 123.7, 114.0, 10.0, 7.5.

HRMS (ESI) scaled for [M+H]$^+$: C$_{20}$H$_{17}$O$_2$, m/z: 289.1223, observed: 289.1237.

(3-benzyl-2-hydroxynaphthalen-1-yl)(phenyl)methanone.

Yellow solid (57 mg, 85% yield), 0.2 mmol scale reaction.

$^1$H NMR (500 MHz, chloroform-d) $\delta$ 11.79 (s, 1H), 7.70 (s, 1H), 7.68 (d, $J$ = 8.0 Hz, 1H), 7.66 – 7.62 (comp., 2H), 7.58 (t, $J$ = 7.5 Hz, 1H), 7.43 (t, $J$ = 7.5 Hz, 2H), 7.39 – 7.34 (comp., 4H), 7.26 (dd, $J$ = 15.0, 8.0 Hz, 3H), 7.12 (t, $J$ = 7.5 Hz, 1H), 4.23 (s, 2H).

$^{13}$C NMR (126 MHz, chloroform-d) $\delta$ 200.8, 160.7, 140.5, 139.7, 135.7, 132.6, 131.5, 131.1, 129.4, 129.2, 128.5, 128.52, 128.2, 128.1, 126.3, 126.1, 126.0, 123.7, 36.1.

HRMS (ESI) scaled for [M+H]$^+$: C$_{24}$H$_{19}$O$_2$, m/z: 339.1380, observed: 339.1387.

(2-Hydroxy-3-phenyl-naphthalen-1-yl)(phenyl)methanone.

Yellow oil (22 mg, 35% yield), 0.2 mmol scale reaction.

$^1$H NMR (500 MHz, chloroform-d) $\delta$ 11.11 (s, 1H), 8.00 (s, 1H), 7.82 (d, $J$ = 8.0 Hz, 1H), 7.76 – 7.70 (comp, 4H), 7.61 (t, $J$ = 7.5 Hz, 1H), 7.55 – 7.51 (comp, 2H), 7.46 (td, $J$ = 7.5, 1.5 Hz, 3H), 7.38 – 7.31 (m, 2H), 7.23 – 7.20 (m, 1H).

$^{13}$C NMR (126 MHz, chloroform-d) $\delta$ 200.5, 158.3, 140.2, 136.8, 135.8, 132.8, 132.0, 131.6, 129.6, 128.6, 128.5, 128.3, 128.0, 126.7, 125.9, 124.0, 115.2.

HRMS (ESI) scaled for [M+H]$^+$: C$_{23}$H$_{17}$O$_2$, m/z: 325.1223, observed: 325.1234.

3-butyl-7-fluoro-2-hydroxy-1-naphthaldehyde.
White solid (31 mg, 61% yield), 0.2 mmol scale reaction.

\textbf{\textsuperscript{1}H NMR} (500 MHz, chloroform-\textit{d}) \(\delta\) 13.61 (s, 1H), 10.64 (s, 1H), 7.89 (dd, \(J = 11.0, 2.5\) Hz, 1H), 7.78 (s, 1H), 7.73 (dd, \(J = 9.0, 6.0\) Hz, 1H), 7.17 (td, \(J = 8.0, 2.5\) Hz, 1H), 2.83 – 2.69 (m, 2H), 1.76 – 1.65 (m, 2H), 1.48 – 1.41 (m, 2H), 0.99 (t, \(J = 7.5\) Hz, 3H).

\textbf{\textsuperscript{13}C NMR} (126 MHz, chloroform-\textit{d}) \(\delta\) 192.79, 165.20, 162.40 (d, \(J = 245\) Hz, 1C), 137.16, 133.2 (d, \(J = 9\) Hz, 1C), 131.74, 131.19, 131.11, 124.52, 113.90 (d, \(J = 21\) Hz, 1C), 110.60, 103.12 (d, \(J = 21\) Hz, 1C), 31.25, 29.17, 22.58, 13.96.

\textbf{\textsuperscript{19}F NMR} (470.5 MHz, chloroform-\textit{d}) \(\delta\) -113.0 (m, 1F).

\textbf{HRMS (ESI)} scaled for [M+H]\(^+\) \(\text{C}_{15}\text{H}_{16}\text{FO}_2\), \(m/z\): 247.1129, observed: 247.1133.

\((3\text{-butynaphthalen}-2\text{-yl})\text{oxy} \text{triisopropylsilane.}

\begin{center}
\includegraphics[width=0.2\textwidth]{7ma}
\end{center}

Colorless oil (65 mg, 91% yield), 0.2 mmol scale reaction.

\textbf{\textsuperscript{1}H NMR} (500 MHz, chloroform-\textit{d}) \(\delta\) 7.76 (dd, \(J = 8.0, 1.0\) Hz, 1H), 7.69 (dd, \(J = 8.0, 1.0\) Hz, 1H), 7.63 (s, 1H), 7.40 (ddd, \(J = 8.0, 7.0, 1.0\) Hz, 1H), 7.34 (ddd, \(J = 8.0, 7.0, 1.0\) Hz, 1H), 7.17 (s, 1H), 2.89 – 2.81 (m, 2H), 1.78 – 1.69 (m, 2H), 1.51 – 1.42 (m, 5H), 1.22 (d, \(J = 7.5\) Hz, 18H), 1.02 (t, \(J = 7.5\) Hz, 3H).

\textbf{\textsuperscript{13}C NMR} (126 MHz, chloroform-\textit{d}) \(\delta\) 153.0, 135.0, 133.3, 129.1, 128.2, 127.0, 126.1, 123.4, 112.4, 32.3, 31.2, 22.8, 18.2, 13.2. The spectra is consist with previous report.\(^4\)

\((3\text{-cyclopropynaphthalen}-2\text{-yl})\text{oxy} \text{triisopropylsilane.}

\begin{center}
\includegraphics[width=0.2\textwidth]{7nb}
\end{center}

Colorless oil (62.5 mg, 92% yield), 0.2 mmol scale reaction.

\textbf{\textsuperscript{1}H NMR} (500 MHz, chloroform-\textit{d}) \(\delta\) 7.72 (d, \(J = 8.0\) Hz, 1H), 7.68 (d, \(J = 8.0\) Hz, 1H), 7.39 (ddd, \(J = 8.0, 7.0, 1.0\) Hz, 1H), 7.35 (s, 1H), 7.34 – 7.31 (m, 1H), 7.18 (s, 1H), 2.42 – 2.32 (m, 1H), 1.53 – 1.43 (m, 3H), 1.23 (d, \(J = 7.5\) Hz, 18H), 1.07 – 1.01 (m, 2H), 0.85 – 0.77 (m, 2H).
\[^{13}C\text{ NMR}\] (126 MHz, chloroform-\(d\)) \(\delta\) 153.8, 135.9, 132.9, 129.1, 127.1, 126.0, 125.1, 123.7, 123.5, 112.4, 18.2, 13.1, 10.9, 8.0. The spectra is consist with previous report.\(^4\)

\((3\text{-Benzylnaphthalen-2-yl)oxy})\text{triisopropylsilane.}\)

\[
\begin{align*}
\text{Colorless oil (74mg, 96\% yield), 0.2 mmol scale reaction.}
\end{align*}
\]

\[^{1}H\text{ NMR}\] (500 MHz, chloroform-\(d\)) \(\delta\) 7.76 – 7.71 (m, 2H), 7.52 (s, 1H), 7.44 (t, \(J = 7.5\) Hz, 1H), 7.39 – 7.33 (comp, 3H), 7.32 – 7.28 (comp, 3H), 7.24 (s, 1H), 4.26 (s, 2H), 1.51 – 1.40 (m, 3H), 1.22 – 1.19 (m, 18H).

\[^{13}C\text{ NMR}\] (126 MHz, chloroform-\(d\)) \(\delta\) 152.9, 140.7, 133.2, 129.4, 129.1, 129.0, 128.4, 127.3, 126.1, 126.0, 125.5, 123.6, 112.5, 36.9, 18.2, 13.2.

\[^{7}R\text{MS (ESI)}\] scaled for [M+H]\(^{+}\): C\(_{26}\)H\(_{35}\)OSi, \(\text{m/z}\): 391.2452, observed: 391.2448.

\[^{3}\text{Triisopropyl(3-phenylnaphthalen-2-yl)oxy)silane.}\)

\[
\begin{align*}
\text{Colorless oil (18.8 mg, 25\% yield), 0.2 mmol scale reaction.}
\end{align*}
\]

\[^{1}H\text{ NMR}\] (300 MHz, chloroform-\(d\)) \(\delta\) 7.85 – 7.78 (comp, 2H), 7.73 (s, 1H), 7.64 – 7.59 (comp, 2H), 7.50 – 7.42 (comp, 3H), 7.41 – 7.33 (comp, 2H), 7.29 (s, 1H), 1.33 – 1.20 (m, 3H), 1.04 (d, \(J = 7.5\) Hz, 18H).

\[^{13}C\text{ NMR}\] (75 MHz, chloroform-\(d\)) \(\delta\) 151.8, 139.1, 135.0, 134.0, 130.0, 129.1, 127.8, 127.0, 126.2, 126.0, 123.9, 113.9, 17.9, 13.0. The spectra is consist with previous report.\(^4\)

\[^{3}\text{Methyl 2-Benzoyl-1-(6-fluoro-3-phenyl-1H-isochromen-1-yl)-3-methyl-4-oxocyclobutane-1-carboxylate.}\)

\[
\begin{align*}
\text{Colorless oil (10.8 mg, 23\% yield, 5:1 dr).}
\end{align*}
\]

Major isomer: \[^{1}H\text{ NMR}\] (500 MHz, chloroform-\(d\)) \(\delta\) 8.05 (d, \(J = 7.5\) Hz, 2H), 7.78 – 7.71 (comp., 2H),
7.52 (t, J = 7.5 Hz, 2H), 7.44 - 7.39 (comp., 2H), 7.24 (s, 1H), 7.09 – 7.01 (comp., 2H), 6.96 – 6.85 (comp., 2H), 6.47 (s, 1H), 6.08 (s, 1H), 4.45 (d, J = 8.8 Hz, 1H), 4.20 – 4.05 (m, 1H), 3.63 (s, 3H), 0.90 (d, J = 7.5 Hz, 3H).

**13C NMR** (126 MHz, Chloroform-d) δ 201.67, 197.10, 167.26, 163.20 (d, J = 245 Hz), 151.18, 137.09, 133.64, 133.22, 129.45, 128.87, 128.71, 128.46, 128.3, 128.30, 127.84, 127.14, 127.06, 124.90, 124.43, 113.78 (d, J = 21 Hz), 111.22 (d, J = 21 Hz), 102.39, 76.10, 55.11, 52.93, 45.50, 12.63.

**HRMS (ESI)** scaled for [M+H]+: C_{29}H_{24}FO_{5}, m/z: 471.1608, observed: 471.191607.

**Methyl 2-Benzyol-1-(6-fluoro-3-phenyl-1H-isochromen-1-yl)-3-methyl-4-oxocyclobutane-1-carboxylate.**

Colorless oil (8.4 mg, 18% yield, 5:1 dr).
Major isomer: **1H NMR** (500 MHz, Chloroform-d) δ 8.06 (d, J = 7.5 Hz, 2H), 7.74 – 7.72 (comp, 2H), 7.66 – 7.61 (m, 1H), 7.53 – 7.50 (comp, 2H), 7.44 – 7.39 (comp, 3H), 7.25 – 7.22 (m, 1H), 7.09 – 7.07 (m, 1H), 6.93 – 6.85 (m, 2H), 6.45 (s, 1H), 6.07 (s, 1H), 4.49 (d, J = 9.0 Hz, 1H), 4.12 – 4.04 (m, 1H), 3.62 (s, 3H), 1.51 – 1.43 (m, 1H), 1.17 – 1.07 (m, 1H), 0.71 (t, J = 7.5 Hz, 3H).

**13C NMR** (126 MHz, Chloroform-d) δ 201.16, 197.37, 162.26, 160.42 (d, J = 245 Hz), 129.42, 128.85, 128.66, 128.46, 128.35, 127.84, 124.90, 124.42, 113.74(d, J = 21 Hz), 111.18 (d, J = 21 Hz), 102.26, 76.20, 61.85, 52.93, 46.94, 43.57, 21.45, 11.19.

**HRMS (ESI)** scaled for [M+H]+: C_{30}H_{26}FO_{5}, m/z: 485.1764, observed: 485.1760.

**Methyl 2-Benzoyl-1-(6-fluoro-3-(4-methoxyphenyl)-1H-isochromen-1-yl)-3-methyl-4-oxocyclobutane-1-carboxylate.**

Colorless oil (6 mg, 12% yield).
Major isomer: **1H NMR** (500 MHz, chloroform-d) δ 8.04 (d, J = 7.5 Hz, 2H), 7.68 (d, J = 9.0 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H), 7.45 – 7.38 (m, 1H), 7.01 (dd, J = 8.4, 5.5 Hz, 1H), 6.96 – 6.92 (comp, 2H), 6.91 – 6.82 (comp, 2H), 6.34 (s, 1H), 6.07 (s, 1H), 4.43 (d, J = 8.5 Hz, 1H), 4.19 – 4.07 (m, 1H), 3.86 (s, 3H), 3.63 (s, 3H), 0.90 (d, J = 7.5 Hz, 3H).

**13C NMR** (126 MHz, chloroform-d) δ 201.71, 200.06, 164.20, 162.55 (d, J = 245 Hz), 151.24, 137.12,
133.57, 128.82, 128.34, 126.04, 114.09, 113.29 (d, J = 21 Hz), 110.85 (d, J = 21 Hz), 100.67, 76.13, 55.35; 55.16; 52.89; 45.50; 12.68.

HRMS (ESI) scaled for [M+H]+: C_{30}H_{26}FO_6, m/z: 501.1708, observed: 501.1686.

Methyl 1-oxo-2-(3-phenyl-1H-isochromen-1-yl)-2,3-dihydro-1H-indene-2-carboxylate.

![Methyl 1-oxo-2-(3-phenyl-1H-isochromen-1-yl)-2,3-dihydro-1H-indene-2-carboxylate](image)

Colorless oil (17 mg, 45% yield, 1:1 dr), 0.1 mmol scale reaction.

13 was reported as 1:1 mixture spectrum:

\[ \text{H NMR (500 MHz, chloroform-d)} \delta 7.91 \,(d, \, J = 7.5 \text{ Hz}, \, 1H), \, 7.73 \,(d, \, J = 7.5 \text{ Hz}, \, 1H), \, 7.66 – 7.62 \,(\text{comp., } 2H), \, 7.57 \,(td, \, J = 7.5, \, 1.0 \text{ Hz}, \, 1H), \, 7.52 – 7.47 \,(m, \, 1H), \, 7.45 \,(d, \, J = 7.5 \text{ Hz}, \, 1H), \, 7.43 – 7.37 \,(\text{comp., } 4H), \, 7.35 – 7.29 \,(\text{comp., } 5H), \, 7.25 – 7.19 \,(\text{comp., } 4H), \, 7.16 \,(tt, \, J = 7.5, \, 2.5 \text{ Hz}, \, 2H), \, 7.07 \,(d, \, J = 7.5 \text{ Hz}, \, 1H), \, 7.01 \,(d, \, J = 7.5 \text{ Hz}, \, 1H), \, 6.99 – 6.95 \,(\text{comp, } 2H), \, 6.70 \,(s, \, 1H), \, 6.40 \,(s, \, 1H), \, 6.37 \,(s, \, 1H), \, 6.35 \,(s, \, 1H), \, 4.04 \,(d, \, J = 17.5 \text{ Hz}, \, 1H), \, 3.92 \,(d, \, J = 17.5 \text{ Hz}, \, 1H), \, 3.92 \,(s, \, 3H), \, 3.84 \,(s, \, 3H), \, 3.69 \,(d, \, J = 17.3 \text{ Hz}, \, 1H), \, 3.42 \,(d, \, J = 17.3 \text{ Hz}, \, 1H). \]

\[ \text{C NMR (126 MHz, chloroform-d)} \delta 199.22, \, 198.48, \, 168.88, \, 168.12, \, 154.48, \, 154.37, \, 153.45, \, 151.99, \, 135.5, \, 135.4, \, 134.85, \, 134.75, \, 133.83, \, 133.04, \, 131.49, \, 129.02, \, 128.85, \, 128.76, \, 128.53, \, 128.37, \, 128.15, \, 127.63, \, 127.44, \, 127.00, \, 126.78, \, 126.33, \, 126.18, \, 125.79, \, 125.08, \, 124.84, \, 124.67, \, 124.39, \, 123.34, \, 123.50, \, 101.01, \, 99.89, \, 80.14, \, 79.77, \, 70.24, \, 65.15, \, 53.43, \, 53.32, \, 33.24, \, 31.68. \]

HRMS (ESI) scaled for [M+H]+: C_{26}H_{21}O_4, m/z: 419.1254, observed: 419.1261.

8. X-ray crystal structure of the product 3fa, 7ma and 15da

![X-ray crystal structure of the product 3fa, 7ma and 15da](image)

Single crystals of C_{26}H_{22}FO_5 were prepared by slow evaporation of a EA/hexane solution. A suitable colorless plate-like crystal with dimensions of 0.021 mm × 0.107 mm × 0.141 mm, was mounted in paratone oil onto a nylon loop. All data were collected at 100.0(1) K, using a XtaLAB Synergy/ Dualflex, HyPix fitted with CuKα radiation (λ = 1.54184 Å). Data collection and unit cell refinement were performed using CrysAlisPro software.[1] The total number of data were measured in the 6.76° < 2θ < 144.8°, using θ scans. Data processing and absorption correction, giving minimum and maximum
transmission factors (0.769, 1.000) were accomplished with CrysAlisPro\textsuperscript{[1]} and SCALE3 ABSPACK\textsuperscript{[2]}, respectively. The structure, using Olex2\textsuperscript{[3]}, was solved with the ShelXT\textsuperscript{[4]} structure solution program using direct methods and refined (on \(F^2\)) with the ShelXL\textsuperscript{[5]} refinement package using full-matrix, least-squares techniques. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atom positions were determined by geometry and refined by a riding model.

\textsuperscript{[1]} CrysAlisPro 1.171.40.63a (Rigaku Oxford Diffraction, 2019)
\textsuperscript{[2]} SCALE3 ABSPACK – An Oxford Diffraction program(1.0.4,gui:1.0.3) (C) 2005 Oxford Diffraction Ltd.
\textsuperscript{[4]} G. M. Sheldrick, \textit{Acta Cryst.} 2015, \textbf{A71}, 3.
\textsuperscript{[5]} G. M. Sheldrick, \textit{Acta Cryst.} 2008, \textbf{A64}, 112.
Table S1: Crystallographic data and structure refinement for 3fa

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$wR_2 = \left\{ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \right\}^{1/2}$

$R_1 = \sum |F_o| - |F_c| / \sum |F_o|$
Single crystals of C₁₅H₁₅FO₂ were prepared by slow evaporation of a dichloromethane and hexane solution. A suitable colorless block-like crystal, with dimensions of 0.175 mm × 0.104 mm × 0.072 mm, was mounted in paratone oil onto a nylon loop. All data were collected at 100.0(1) K, using a XtaLAB Synergy/ Dualflex, HyPix fitted with CuKα radiation (λ = 1.54184 Å). Data collection and unit cell refinement were performed using CrysAlisPro software[1]. The total number of data were measured in the 9.27° < 2θ < 152.5°, using ω scans. Data processing and absorption correction, giving minimum and maximum transmission factors (0.600, 1.000) were accomplished with CrysAlisPro[6] and SCALE3 ABSPACK[7], respectively. The structure, using Olex2[8], was solved with the ShelXT[9] structure solution program using direct methods and refined (on F²) with the ShelXL[10] refinement package using full-matrix, least-squares techniques. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atom positions were determined by geometry and refined by a riding model.

[7] SCALE3 ABSPACK - An Oxford Diffraction program(1.0.4,gui:1.0.3) (C) 2005 Oxford Diffraction Ltd.
Table S2: Crystallographic data and structure refinement for 7ma

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\[
\begin{align*}
    wR_2 &= \left\{ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2 - 2)\right\}^{1/2} \\
    R_1 &= \frac{\sum |F_o| - |F_c|}{\sum |F_o|}
\end{align*}
\]
Single crystals of C$_{28}$H$_{21}$FNO$_4$ were prepared by slow evaporation of a dichloromethane and hexane solution. A suitable colorless plank-like crystal, with dimensions of 0.369 mm × 0.180 mm × 0.058 mm, was mounted in paratone oil onto a nylon loop. All data were collected at 100.0(1) K, using a XtaLAB Synergy/ Dualflex, HyPix fitted with CuKα radiation (λ = 1.54184 Å). Data collection and unit cell refinement were performed using CrysAlisPro software.[1] The total number of data were measured in the $7.29^\circ < 2\theta < 153.4^\circ$, using $\omega$ scans. Data processing and absorption correction, giving minimum and maximum transmission factors (0.437, 1.000) were accomplished with CrysAlisPro[11] and SCALE3 ABSPACK[12], respectively. The structure, using Olex2[13], was solved with the ShelXT[14] structure solution program using direct methods and refined (on $F^2$) with the ShelXL[15] refinement package using full-matrix, least-squares techniques. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atom positions were determined by geometry and refined by a riding model.

[12] SCALE3 ABSPACK - An Oxford Diffraction program (1.0.4, gui:1.0.3) (C) 2005 Oxford Diffraction Ltd.
Table S3: Crystallographic data and structure refinement for 15da

<table>
<thead>
<tr>
<th>Identification code</th>
<th>15da</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{28}H_{21}FNO_{4}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>454.46</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_{1}/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>12.28538(14)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>20.3181(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>8.91344(10)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>99.0372(11)</td>
</tr>
<tr>
<td>γ (°)</td>
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</tr>
<tr>
<td>Volume (Å³)</td>
<td>2197.31(4)</td>
</tr>
<tr>
<td>Z</td>
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</tr>
<tr>
<td>ρ (calc.)</td>
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</tr>
<tr>
<td>λ</td>
<td>1.54184</td>
</tr>
<tr>
<td>Temp. (K)</td>
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</tr>
<tr>
<td>F(000)</td>
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</tr>
<tr>
<td>μ (mm⁻¹)</td>
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</tr>
<tr>
<td>T_{min}, T_{max}</td>
<td>0.437, 1.000</td>
</tr>
<tr>
<td>2θ range (°)</td>
<td>7.29 to 153.4</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>21382</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>4485 [R(int) = 0.0402]</td>
</tr>
<tr>
<td>Completeness</td>
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</tr>
<tr>
<td>Data / restraints / parameters</td>
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<tr>
<td>Observed data [I &gt; 2σ(I)]</td>
<td>4040</td>
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<tr>
<td>wR(F² all data)</td>
<td>0.1051</td>
</tr>
<tr>
<td>R(F obsd data)</td>
<td>0.0383</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.05</td>
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<tr>
<td>largest diff. peak and hole (e Å⁻³)</td>
<td>0.29 / -0.78</td>
</tr>
</tbody>
</table>

\[ wR_2 = \left\{ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)} \right\}^{1/2} \]

\[ R_t = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \]
9. References


10. NMR spectrum of products

PhOC
OH

3aa

CO2CH3

PhOC
OH

3aa

CO2CH3
15da in acetone-D6

15da in CD2Cl2
11. HPLC spectra of products

**Chiral HPLC of racemic 3da**

![HPLC spectrum of racemic 3da](image)

<table>
<thead>
<tr>
<th>#</th>
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<td>295.3</td>
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<td>46.779</td>
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**Chiral HPLC of chiral 3da**

![HPLC spectrum of chiral 3da](image)

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**Chiral HPLC of racemic 3dg**

![HPLC spectrum of racemic 3dg](image)

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Chiral HPLC of racemic 3dh

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Chiral HPLC of chiral 3dh

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Chiral HPLC of racemic 3gg

![Chiral HPLC of racemic 3gg](image)

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<td>2</td>
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Chiral HPLC of chiral 3gg

![Chiral HPLC of chiral 3gg](image)