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1. General Information

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in pre-heated glassware under an argon atmosphere using standard Schlenk techniques. Solvents used in reactions were either freshly distilled or obtained in extra-dry grade from commercial sources. All commercially available reagents were purchased from TCI, Sigma-Aldrich, Alfa Aesar, Acros or ABCR in the highest purity grade and used directly without further purification. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F-254 plates and visualized by fluorescence quenching under UV light or staining with the standard solution of KMnO₄. Column chromatography was performed on Merck or Fluka silica gel 60 (40-63 μm) using a forced flow of 0.5 bar. ¹H NMR (300 MHz, 400 MHz and 600 MHz), ¹³C NMR (75 MHz, 100 MHz and 150 MHz) and ¹⁹F NMR (282 MHz, 376 MHz and 564 MHz) spectra were measured on a Bruker DPX 300, Agilent DD2 500 or an Agilent DD2 600 spectrometer. Spectra were calibrated relative to solvent’s residual proton and carbon chemical shift: CHCl₃ δ (ppm) = 7.26 for ¹H NMR and δ (ppm) = 77.0 for ¹³C NMR or C₆H₆ δ (ppm) = 7.16 for ¹H and δ (ppm) = 128.0 for ¹³C NMR. Coupling constants were reported as Hertz (Hz), signal shapes and splitting patterns were indicated as follows: s, singlet; brs, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra were recorded on a Finnigan MAT 4200S, a Bruker Daltonics Micro Tof, a Waters-Micromass Quatro LCZ (ESI); peaks are given in m/z (% of basis peak). Melting points were measured on a Stuart SMP10 and are uncorrected.

X-Ray diffraction: Data sets for compounds 6 and 11c were collected with a Bruker D8 Venture Photon III Diffractometer. Programs used: data collection: APEX3 V2019.1-0¹ (Bruker AXS Inc., 2019); cell refinement: SAINT V8.40A (Bruker AXS Inc., 2019); data reduction: SAINT V8.40A (Bruker AXS Inc., 2019); absorption correction, SADABS V2016/2 (Bruker AXS Inc., 2019); structure solution SHELXT-2015² (Sheldrick, G. M. Acta Cryst., 2015, A71, 3-8); structure refinement SHELXL-2015² (Sheldrick, G. M. Acta Cryst., 2015, C71 (1), 3-8) and graphics, XP⁵ (Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, 1998). R-values are given for observed reflections, and wR² values are given for all reflections.

Cyclic voltammograms were recorded in an air-tight measuring cell (rhd instruments, TSC 1600 closed) equipped with a platinum disc working electrode (0.25 mm), platinum crucible counter electrode, and an Ag/Ag⁺ pseudo-reference electrode (rhd instruments, Ag wire MicroPseudo reference). Measurements were performed using a Metrohm Autolab potentiostat (Metrohm, PGSTAT204) and data were collected and analysed using the Autolab Nova 2.1 program. Additional voltammograms were measured with the addition of ferrocene as an internal reference, and all potentials were then referenced to the Fe/Fe⁺ redox couple. The potentials of irreversible redox events were determined by finding the inflection point of the curve.

Acetonitrile was obtained from Acros Organics in extra-dry grade. Tetrabutylammonium hexafluorophosphate (>99.0%, for electrochemical analysis) was purchased from Sigma Aldrich. Ferrocene was purchased from Merck. All chemicals were used without further purification.
2. Synthesis of Starting Materials

3-Methylbenzofuran 1a was purchased from commercial sources and used as received. Benzofurans 1b-e, 1g, 1i-1l and 1p were synthesized according to the literature procedures. The other benzofurans 1f, 1h, 1m and 1n-o were synthesized as detailed below.

Benzofuran substrates

Benzoyl fluoride 2a was purchased from commercial source and distilled before use. Other acyl fluorides 2b-q were synthesized according to literature procedures.13

Acyl fluorides

The photocatalyst [Ir{dF(CF3)2ppy}2(dtbbpy)]PF6 (Ir-F) and triazolium salts A were prepared following known literature procedures.13,14 1-Acetyl-3-methylindole 5 was synthesized using a literature procedure.15 Anhydrides were also prepared following a literature report.16
General procedure A:\(^{17}\):

**Step 1:** 2-Hydroxyketone \( S_1 \) (10 mmol, 1.0 equiv), ethylbromoacetate (14 mmol, 1.4 equiv) and \( K_2 CO_3 \) (40 mmol, 4.0 equiv) were added to 10 mL of dry acetone in a round-bottom flask. The mixture was refluxed for 48 h. After cooling down to rt, the reaction mixture was filtered, the filter cake was washed with EtOAc and the filtrate was concentrated under reduced pressure to afford the crude alkylated product \( S_2 \).

**Step 2:** To the solution of this compound in EtOH (4 mL), 6 mL of aqueous 3.0 N NaOH solution was added and the resulting mixture was stirred at rt overnight. The solvents were removed under reduced pressure and 2N aqueous HCl solution was added to adjust the pH to 1-2. The resulting precipitate was collected by filtration and washed with water. The obtained crude product \( S_3 \) was used without further purification.

**Step 3:** A solution of the obtained carboxylic acid \( S_3 \) (1.0 equiv), and NaOAc (6.08 equiv) in Ac₂O (6.08 equiv) was refluxed for 24 h. After cooling down to rt, the reaction mixture was poured onto ice and extracted with EtOAc (three times). The combined organic layers were dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated under reduced pressure and purified by flash column chromatography to afford the title compound 1.

**N-Acetyl-N-(3-methylbenzofuran-5-yl)acetamide 1f**

![Chemical structure](image)

The title product was synthesized on a 10.0 mmol scale using \( N-(3\text{-acetyl-4-hydroxyphenyl})\text{acetamide} \) (CAS: 7298-67-1) using the General Procedure A. The product was purified by silica gel chromatography using a gradient of pentane/EtOAc (50:1 to 30:1, \( v/v \)) and was obtained as a white solid (400 mg, 17% over three steps), m.p. = 98-100 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm) 7.52 (dd, \( J = 8.6, 0.6 \) Hz, 1H), 7.47 (q, \( J = 1.4 \) Hz, 1H), 7.31 (d, \( J = 1.7 \) Hz, 1H), 7.04 (dd, \( J = 8.6, 2.2 \) Hz, 1H), 2.32 (s, 6H), 2.23 (d, \( J = 1.4 \) Hz, 3H). \(^{13}\)C NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm) 173.4, 154.7, 143.0, 134.0, 130.3, 124.4, 119.7, 115.9, 112.5, 27.1, 7.8. HRMS (ESI): m/z [M + Na]^+ calc for \( C_{13}H_{13}NNaO_3 \): 254.0788, found: 254.0786.

**5-Chloro-3,6-dimethylbenzofuran 1h**

![Chemical structure](image)

The title product was synthesized on a 10.0 mmol scale using \( 1\text{-}(5\text{-chloro-2-hydroxy-4-methylphenyl})\text{ethan-1-one} \) (CAS: 28480-70-8) using the General Procedure A. The product was purified by silica gel chromatography using pentane and was obtained as light yellow solid (620 mg, 34% over three steps), m.p. = 45-48 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm) 7.49 (s, 1H), 7.35 (d, \( J = 1.3 \) Hz, 1H), 7.31 (t, \( J = 0.7 \) Hz, 1H), 2.46 (s, 3H), 2.20 (s, 3H). \(^{13}\)C NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm) 173.4, 154.7, 143.0, 134.0, 130.3, 124.4, 119.7, 115.9, 112.5, 27.1, 7.8. HRMS (EI): Exact mass calculated for \( C_{10}H_{11}ClO \): 180.0342, found: 180.0337.
General procedure B:
Step 1: Lithium aluminum hydride (5 mmol) was suspended in anhydrous THF (10 mL) and cooled to 0 °C under nitrogen atmosphere. 2-(Benzofuran-3-yl)acetic acid S4 (CAS: 64175-51-5, 2.0 mmol, 352.3 mg) in THF (5 mL) was added dropwise. The mixture was stirred for 1 h at the same temperature and then warmed to room temperature. Upon completion, the reaction was quenched with 10% aqueous HCl solution at 0 °C and then extracted with EtOAc (three times). The combined organic phases were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The obtained crude product S5 was used without further purification.

Step 2: To a solution of this compound S5 in dichloromethane (10 mL), triethylamine (0.55 mL, 4 mmol), dimethylaminopyridine (DMAP, 24 mg, 0.2 mmol) and acetic anhydride (0.28 mL, 3 mmol) were added under nitrogen atmosphere at 0 °C. After the reaction solution was stirred at room temperature overnight, a saturated aqueous NH₄Cl solution was added and the mixture was extracted with dichloromethane (three times). The combined organic layer was dried over MgSO₄ and filtered and concentrated under reduced pressure. The residue was subjected to silica gel column chromatography (pentane:EtOAc = 20:1) to obtain the product 1m (283 mg, 69% over two steps) as pale yellow oil.

2-(Benzofuran-3-yl)ethyl acetate 1m

![Chemical structure](image)

1H NMR (400 MHz, CDCl₃) δ (ppm) 7.60 – 7.57 (m, 1H), 7.49 – 7.47 (m, 2H), 7.33 – 7.27 (m, 1H), 7.26 – 7.23 (m, 1H), 4.36 (t, J = 6.9 Hz, 2H), 3.03 (td, J = 6.9, 1.1 Hz, 2H), 2.06 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 171.0, 155.3, 141.9, 127.9, 124.3, 122.5, 119.5, 116.4, 111.5, 63.4, 23.3, 21.0. HRMS (ESI): m/z [M + Na]⁺ calcld for C₁₂H₁₂NaO₃: 227.0679, found: 227.0676.

General procedure C:
Step 1: To a cooled (-10 °C) solution of methyl salicylate S6 (30 mmol) and Me(OMe)NH•HCl (2.93g, 30 mmol) in anhydrous THF (30 mL) PrMgCl (2 M in THF, 45 mL, 90 mmol) was slowly added under nitrogen atmosphere. The solution was stirred for 1 h at the same temperature and then warmed to room temperature. Upon completion, the reaction was quenched with saturated NH₄Cl aqueous solution (30 mL) and extracted with EtOAc (three times). The combined organic phases were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (pentane:EtOAc = 20:1) to afford the Weinreb amide S7 as colorless oil (5.0 g, 92%).

Step 2: To a cooled (-78 °C) solution of the Weinreb amide S7 (10 mmol) in anhydrous THF (8 mL) NaH (60% dispersion in mineral oil, 480 mg, 12 mmol) was slowly added under nitrogen atmosphere. The solution was stirred for...
10 min. Then alkyl magnesium bromide (12 mmol) in THF was added. The mixture was slowly warmed to room temperature and stirred for 4 h. Upon completion, the reaction was quenched with saturated NH₄Cl aqueous solution and extracted with EtOAc (three times). The combined organic phases were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (pure pentane) to afford the corresponding ketone.

3-Isobutylbenzofuran 1n

![3-Isobutylbenzofuran 1n](image)

1n was prepared from the Weinreb amide S7 and isobutylmagnesium bromide following general procedure C then cyclized following general procedure A. Purified by flash column chromatography purification (pure pentane) led to 3-isobutylbenzofuran 1n as colorless oil (600 mg, 34%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.60 – 7.57 (m, 1H), 7.32 (d, J = 8.1 Hz, 1H), 7.26 (s, 1H), 7.16 – 7.06 (m, 2H), 2.40 (dd, J = 7.1, 1.0 Hz, 2H), 1.93 – 1.82 (m, 1H), 0.83 (d, J = 6.7 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 155.3, 141.6, 128.6, 123.9, 122.1, 119.8, 119.4, 111.3, 32.7, 28.2, 22.6. HRMS (EI): Exact mass calculated for C₁₂H₁₄O⁺ (M⁺): 174.1045, found: 174.1036.

3-Pentylbenzofuran 1o

![3-Pentylbenzofuran 1o](image)

1o was prepared from the Weinreb amide S7 and pentylmagnesium bromide following general procedure C then cyclized following general procedure A. Purified by flash column chromatography (pure pentane) led to 3-pentylbenzofuran 1o as colorless oil (720 mg, 38%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.43 – 7.41 (m, 1H), 7.33 – 7.31 (m, 1H), 7.26 (d, J = 1.2 Hz, 1H), 7.16 – 7.07 (m, 2H), 2.52 (td, J = 7.6, 1.2 Hz, 2H), 1.58 (p, J = 7.4 Hz, 2H), 1.24 (dt, J = 7.2, 3.6 Hz, 4H), 0.76 (d, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 155.3, 141.0, 128.4, 124.0, 122.1, 120.7, 119.6, 111.4, 31.7, 28.7, 23.5, 22.5, 14.0. HRMS (EI): Exact mass calculated for C₁₃H₁₆O⁺ (M⁺): 188.1201, found: 188.1196.

3. Detailed Optimization of Reaction Conditions

**Table S1. Screening of the photocatalyst and solvent**

| Entry | Photocatalyst | Solvent | Base | Yield |
|-------|---------------|---------|------|-------|
| 1     | [Ir{dF(CF₃)ppy}₂(dtbbpy)]PF₆ (Ir-F) | CH₃Cl₂ | Cs₂CO₃ | 14    |
| 2     | [Ir{dF(CF₃)ppy}₂(dtbbpy)]PF₆ (Ir-F) | CH₃CN | Cs₂CO₃ | 32    |
| 3     | [Ir{dF(CF₃)ppy}₂(dtbbpy)]PF₆ (Ir-F) | Acetone | Cs₂CO₃ | 16    |
|   | Reaction Conditions                        | Product Yields (%) |
|---|-------------------------------------------|--------------------|
| 4 | [Ir\{dF(CF\textsubscript{3})ppy\}_2(dtbbpy)]PF\textsubscript{6} (Ir-F) | DMSO Cs\textsubscript{2}CO\textsubscript{3} 8 |
| 5 | [Ir\{dF(CF\textsubscript{3})ppy\}_2(dtbbpy)]PF\textsubscript{6} (Ir-F) | DMF Cs\textsubscript{2}CO\textsubscript{3} 15 |
| 6 | [Ir\{dF(CF\textsubscript{3})ppy\}_2(dtbbpy)]PF\textsubscript{6} (Ir-F) | 1.4-dioxane Cs\textsubscript{2}CO\textsubscript{3} 9 |
| 7 | [Ir\{dF(CF\textsubscript{3})ppy\}_2(dtbbpy)]PF\textsubscript{6} (Ir-F) | CH\textsubscript{3}CN K\textsubscript{2}CO\textsubscript{3} 18 |
| 8 | [Ir\{dF(CF\textsubscript{3})ppy\}_2(dtbbpy)]PF\textsubscript{6} (Ir-F) | CH\textsubscript{3}CN K\textsubscript{3}PO\textsubscript{4} 31 |
| 9 | [Ir\{dF(CF\textsubscript{3})ppy\}_2(dtbbpy)]PF\textsubscript{6} (Ir-F) | CH\textsubscript{3}CN K\textsubscript{2}HPO\textsubscript{4} 50 |
| 10 | [Ir\{dF(CF\textsubscript{3})ppy\}_2(dtbbpy)]PF\textsubscript{6} (Ir-F) | CH\textsubscript{3}CN KO\textsubscript{t}Bu 0 |
| 11 | [Ir\{dF(CF\textsubscript{3})ppy\}_2(dtbbpy)]PF\textsubscript{6} (Ir-F) | CH\textsubscript{3}CN/DMF (10/1) K\textsubscript{2}HPO\textsubscript{4} 73(70) |
| 12 | [Ir\{dF(CF\textsubscript{3})ppy\}_2(dtbbpy)]PF\textsubscript{6} (Ir-F) | CH\textsubscript{3}CN/DMSO (10/1) K\textsubscript{2}HPO\textsubscript{4} 66 |
| 13 | [Ir\{dF(CF\textsubscript{3})ppy\}_2(dtbbpy)]PF\textsubscript{6} (Ir-F) | CH\textsubscript{3}CN/Acetone (10/1) K\textsubscript{2}HPO\textsubscript{4} 61 |
| 14 | [Ir\{dF(CF\textsubscript{3})ppy\}_2(dtbbpy)]PF\textsubscript{6} (Ir-F) | CH\textsubscript{3}CN/DMF (10/1) K\textsubscript{2}HPO\textsubscript{4} 57 |
| 15 | [Ir\{dF(CF\textsubscript{3})ppy\}_2(dtbbpy)]PF\textsubscript{6} (Ir-F) | CH\textsubscript{3}CN/DMF (10/1) Cs\textsubscript{2}CO\textsubscript{3} 40 |
| 16 | Ru(bpy)(PF\textsubscript{6})\textsubscript{2} | CH\textsubscript{3}CN/DMF (10/1) K\textsubscript{2}HPO\textsubscript{4} ND |
| 17 | Ir(dFCF\textsubscript{3}ppy)_2(bpy)PF\textsubscript{6} | CH\textsubscript{3}CN/DMF (10/1) K\textsubscript{2}HPO\textsubscript{4} 44 |
| 18 | 9-Mesityl-10-methylacridinium | CH\textsubscript{3}CN/DMF (10/1) K\textsubscript{2}HPO\textsubscript{4} ND |
| 19 | 4-CzIPN | CH\textsubscript{3}CN/DMF (10/1) K\textsubscript{2}HPO\textsubscript{4} 34 |
| 20 | EosinY Na | CH\textsubscript{3}CN/DMF (10/1) K\textsubscript{2}HPO\textsubscript{4} ND |

*Unless otherwise noted, 1a (0.1 mmol), 2a (0.4 mmol), PC (2 mol%), NHC A (20 mol%) and base (2.0 equiv) in solvent (1 mL) at rt under irradiation with 5 W blue LEDs for 24 h, 15:1 d.r.*

*Yields were determined by \textsuperscript{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. *Isolated yield in brackets. ND = no detected.

4. General Procedure and Spectral Data of Products

4.1 General Procedure D for the Reaction of Benzofuran Derivatives with Acyl Fluorides
To a Schlenk tube carbene catalyst A (6.3 mg, 0.02 mmol), Ir-F (2.2 mg, 0.002 mmol) and K₂HPO₄ (34.8 mg, 0.2 mmol) were added. Then the reaction tube was evacuated and backfilled with argon two times. Subsequently, benzofuran derivative 1 (0.10 mmol, if solid, it should be added at the beginning), freshly prepared acyl fluoride 2 (0.4 mmol, if solid, it should be added at the beginning), CH₃CN (1 mL) and DMF (0.1 mL) were added. The resulting mixture was degassed under vacuum two times and then irradiated with 5 W blue LEDs at room temperature for 24 hours. Then, the residue was purified by silica gel chromatography using a mixture of n-pentane and ethyl acetate as an eluent to get the desired product 3. Each reaction was carried out twice and the average value was used as the final yield. The diastereoselectivity was determined by ¹H NMR on the crude product.

4.2 Spectral Data of Products

(2-Fluoro-3-methyl-2,3-dihydrobenzofuran-3-yl)(phenyl)methanone (3a)

![Chemical structure of 3a](image)

The reaction was performed according to General Procedure D with 1a (0.1 mmol, 13.2 mg) and 2a (0.4 mmol, 43 uL). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3a was obtained as a colorless oil (18.0 mg, 70% yield), d.r. = 15:1. ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.56 – 7.52 (m, 2H), 7.51 – 7.48 (m, 1H), 7.41 – 7.35 (m, 2H), 7.30 (td, J = 7.8, 1.4 Hz, 1H), 7.22 (dd, J = 7.5, 1.4 Hz, 1H), 7.07 – 6.99 (m, 2H), 6.65 (d, J = 64.3 Hz, 1H), 1.80 (d, J = 4.0 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 199.5 (d, J = 8.7 Hz), 156.8 (d, J = 3.2 Hz), 136.1, 132.4, 129.9, 128.5, 128.4, 125.3, 122.8, 115.0 (d, J = 241.3 Hz), 110.6, 62.9 (d, J = 20.2 Hz), 18.9 (d, J = 15.7 Hz). ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm) -113.9 (minor), -129.3 (major). HRMS (ESI): m/z [M + Na]+ calcd for C₁₆H₁₃FNaO₂: 279.0792, found: 279.0793.

(2-Fluoro-6-methoxy-3-methyl-2,3-dihydrobenzofuran-3-yl)(phenyl)methanone (3b)

![Chemical structure of 3b](image)

The reaction was performed according to General Procedure D with 1b (0.1 mmol, 16.2 mg) and 2a (0.4 mmol, 43 uL). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3b was obtained as a colorless oil (16.8 mg, 59% yield), d.r. = 26:1. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.54 – 7.48 (m, 3H), 7.40 – 7.36 (m, 2H), 7.09 – 7.07 (m, 1H), 6.62 (d, J = 64.1 Hz, 1H), 6.59 – 6.56 (m, 2H), 3.80 (s, 3H), 1.75 (d, J = 3.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 199.9 (d, J = 8.7 Hz), 161.6, 158.1 (d, J = 3.0 Hz), 136.3, 132.3, 128.5, 128.3, 125.9, 120.3, 115.6 (d, J = 241.4 Hz), 108.5, 97.1, 62.3 (d, J = 20.0 Hz), 55.6, 18.8 (d, J = 15.7 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm) -114.0 (minor), -129.4 (major). HRMS (ESI): m/z [M + Na]+ calcd for C₁₇H₁₅FNaO₃: 309.0897, found: 309.0897.

3-Benzoyl-2-fluoro-3-methyl-2,3-dihydrobenzofuran-6-yl acetate (3c)

![Chemical structure of 3c](image)
The reaction was performed according to General Procedure D with 1c (0.1 mmol, 19.0 mg) and 2a (0.4 mmol, 43 uL). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3c was obtained as a colorless oil (23.3 mg, 74% yield), d.r. = 15:1. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.57 (dt, \(J = 8.5, 1.7\) Hz, 2H), 7.54 – 7.50 (m, 1H), 7.42 – 7.38 (m, 2H), 7.20 (d, \(J = 8.7\) Hz, 1H), 6.79 – 6.76 (m, 2H), 6.67 (d, \(J = 63.8\) Hz, 1H), 2.30 (s, 3H), 1.79 (d, \(J = 3.8\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 199.1 (d, \(J = 8.6\) Hz), 169.1, 157.4 (d, \(J = 3.0\) Hz), 151.9, 135.8, 132.5, 128.6, 128.4, 125.9, 125.6, 115.9, 115.4 (d, \(J = 240.8\) Hz), 62.4 (d, \(J = 19.9\) Hz), 21.1, 19.0 (d, \(J = 15.7\) Hz). \(^19\)F NMR (283 MHz, CDCl\(_3\)) \(\delta\) (ppm) -114.2 (minor), -129.2 (major). HRMS (ESI): m/z [M + Na]+ calcd for C\(_{13}\)H\(_{15}\)FNaO\(_2\): 337.0847, found: 337.0846.

(6-Chloro-2-fluoro-3-methyl-2,3-dihydrobenzofuran-3-yl)(phenyl)methanone (3d)

The reaction was performed according to General Procedure D with 1d (0.1 mmol, 16.7 mg) and 2a (0.4 mmol, 43 uL). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3d was obtained as a colorless oil (18.0 mg, 62% yield), d.r. = 13:1. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.57 (t, \(J = 7.7\) Hz, 2H), 7.53 (d, \(J = 6.8\) Hz, 1H), 7.42 (t, \(J = 7.7\) Hz, 2H), 7.14 (d, \(J = 8.0\) Hz, 1H), 7.04 – 7.00 (m, 2H), 6.68 (d, \(J = 63.7\) Hz, 1H), 1.79 (d, \(J = 3.8\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 198.8 (d, \(J = 8.3\) Hz), 157.4 (d, \(J = 3.0\) Hz), 135.6, 135.3, 132.7, 128.7, 128.4, 127.2, 126.1, 123.0, 115.28 (d, \(J = 242.8\) Hz), 111.4, 62.47 (d, \(J = 20.1\) Hz), 19.03 (d, \(J = 15.6\) Hz). \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) (ppm) -114.3 (minor), -129.4 (major). HRMS (ESI): m/z [M + Na]+ calcd for C\(_{16}\)H\(_{18}\)FNaO\(_2\): 313.0402, found: 313.0402.

2-Fluoro-3,5-dimethyl-2,3-dihydrobenzofuran-3-yl)(phenyl)methanone (3e)

The reaction was performed according to General Procedure D with 1e (0.1 mmol, 56.2 mg) and 2a (0.4 mmol, 43 uL). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3e was obtained as a colorless oil (8.5 mg, 31% yield), d.r. = 8:1. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.57 – 7.47 (m, 3H), 7.41 – 7.35 (m, 2H), 7.09 (d, \(J = 8.2\) Hz, 1H), 7.02 (s, 1H), 6.89 (d, \(J = 8.1\) Hz, 1H), 6.61 (d, \(J = 64.6\) Hz, 1H), 2.31 (s, 3H), 1.77 (d, \(J = 4.1\) Hz, 3H). \(^{13}\)C NMR (75 MHz, CD\(_2\)CN) \(\delta\) (ppm) 199.5 (d, \(J = 8.7\) Hz), 154.7 (d, \(J = 3.1\) Hz), 136.1, 132.4, 132.3, 130.3, 128.5, 128.4, 125.6, 115.1 (d, \(J = 241.1\) Hz), 110.1, 62.9 (d, \(J = 20.1\) Hz), 20.9, 18.8 (d, \(J = 15.8\) Hz). \(^19\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) (ppm) -113.9 (minor), -128.8 (major). HRMS (ESI): m/z [M + Na]+ calcd for C\(_{15}\)H\(_{17}\)FNaO: 293.0948, found: 293.0950.

N-Acetyl-N-(3-benzoyl-2-fluoro-3-methyl-2,3-dihydrobenzofuran-5-yl)acetamide (3f)

The reaction was performed according to General Procedure D with 1f (0.1 mmol, 23.1 mg) and 2a (0.4 mmol,43 uL). After purification by flash chromatography (n-pentane/ethyl acetate = 30/1), the desired compound 3f was obtained as a
colorless oil (14.9 mg, 42% yield), d.r. = 15:1. The diastereoselectivity was determined by \(^1\)H NMR on the crude product, and only major isomer was obtained after flash chromatography. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.62 – 7.59 (m, 2H), 7.54 (t, \(J = 7.4\ Hz, 1H\)), 7.42 (t, \(J = 7.5\ Hz, 2H\)), 7.03 (dd, \(J = 12.5, 1.2\ Hz, 3H\)), 6.74 (d, \(J = 63.5\ Hz, 1H\)), 2.25 (s, 6H), 1.84 (d, \(J = 3.5\ Hz, 3H\)). \(^1^3\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm) 198.8 (d, \(J = 8.8\ Hz\)), 173.0, 156.7 (d, \(J = 2.9\ Hz\)), 135.5, 134.0, 130.3, 128.7, 128.3, 126.5, 115.3 (d, \(J = 243.2\ Hz\)), 111.4, 63.0 (d, \(J = 20.3\ Hz\)), 26.9, 19.2 (d, \(J = 15.1\ Hz\)). \(^1^9\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) (ppm) -129.8. HRMS (ESI): m/z [M + Na]^+ calcd for C\(_{20}\)H\(_{18}\)F\(_2\)NaO\(_2\): 378.1112, found: 378.1111.

(5-Bromo-2-fluoro-3-methyl-2,3-dihydrobenzofuran-3-yl)(phenyl)methanone (3g)

![Structure of 3g](image)

The reaction was performed according to General Procedure D with 1g (0.1 mmol, 21.1 mg) and 2a (0.4 mmol, 43 uL). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3g was obtained as a colorless oil (10.2 mg, 30% yield), d.r. = 30:1. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.62 – 7.57 (m, 2H), 7.56 – 7.53 (m, 1H), 7.45 – 7.38 (m, 3H), 7.35 (d, \(J = 2.0\ Hz, 1H\)), 6.89 (d, \(J = 8.5\ Hz, 1H\)), 6.56 (d, \(J = 63.8\ Hz, 1H\)), 1.80 (d, \(J = 3.8\ Hz, 3H\)). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 198.4 (d, \(J = 8.6\ Hz\)), 155.8 (d, \(J = 3.0\ Hz\)), 135.4, 132.8, 132.7, 130.9, 128.7, 128.6, 128.4, 115.1 (d, \(J = 242.8\ Hz\)), 114.8, 112.1, 62.9 (d, \(J = 20.1\ Hz\)), 19.2 (d, \(J = 15.6\ Hz\)). \(^1^9\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) (ppm) -114.6 (minor), -129.1 (major). HRMS (ESI): m/z [M + Na]^+ calcd for C\(_{19}\)H\(_{12}\)BrFNaO\(_2\): 356.9897, found: 356.9896.

(5-Chloro-2-fluoro-3,6-dimethyl-2,3-dihydrobenzofuran-3-yl)(phenyl)methanone (3h)

![Structure of 3h](image)

The reaction was performed according to General Procedure D with 1h (0.1 mmol, 18.1 mg) and 2a (0.4 mmol, 43 uL). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3h was obtained as a yellow oil (18.3 mg, 60% yield), d.r. = 10:1. \(^1\)H NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.61 – 7.59 (m, 2H), 7.56 – 7.51 (m, 1H), 7.44 – 7.40 (m, 2H), 7.20 (s, 1H), 6.88 (s, 1H), 6.64 (d, \(J = 64.0\ Hz, 1H\)), 2.37 (s, 3H), 1.78 (d, \(J = 3.8\ Hz, 3H\)). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 198.7 (d, \(J = 8.6\ Hz\)), 155.4 (d, \(J = 3.0\ Hz\)), 137.9, 135.6, 132.7, 128.6, 128.4, 127.8, 127.7, 125.8, 115.3 (d, \(J = 242.3\ Hz\)), 112.6, 62.8 (d, \(J = 20.1\ Hz\)), 20.6, 19.1 (d, \(J = 15.6\ Hz\)). \(^1^9\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) (ppm) -114.6 (minor), -129.3 (major). HRMS (ESI): m/z [M + Na]^+ calcd for C\(_{17}\)H\(_{14}\)ClFNaO\(_2\): 327.0559, found: 327.0559.

(2-Fluoro-6,7-dimethoxy-3-methyl-2,3-dihydrobenzofuran-3-yl)(phenyl)methanone (3i)

![Structure of 3i](image)
The reaction was performed according to General Procedure D with 1i (0.1 mmol, 19.2 mg) and 2a (0.4 mmol, 43 uL). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3i was obtained as a colorless oil (10.0 mg, 32% yield), d.r. = 15:1. The diastereoselectivity was determined by 1H NMR on the crude product, and only major isomer was obtained after flash chromatography. 1H NMR (400 MHz, CDCl3) δ (ppm) δ 7.52 – 7.47 (m, 3H), 7.40 – 7.36 (m, 2H), 6.82 (d, J = 8.3 Hz, 1H), 6.65 (d, J = 44.5 Hz, 1H), 6.56 (d, J = 11.0 Hz, 1H), 4.00 (s, 3H), 3.87 (s, 3H), 1.76 (d, J = 3.8 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ (ppm) 199.7 (d, J = 11.0 Hz), 148.6 (d, J = 2.9 Hz), 153.4, 153.4, 153.4, 153.4, 133.9, 133.9, 133.9, 133.9, 128.5, 128.5, 128.3, 128.3, 122.6, 118.6, 115.6 (d, J = 242.5 Hz), 106.6, 62.5 (d, J = 19.9 Hz), 60.8, 56.4, 18.7 (d, J = 15.2 Hz). 19F NMR (376 MHz, CDCl3) δ (ppm) -128.7. HRMS (ESI): m/z [M + Na]+ calcd for C18H17FNaO3: 339.1003, found: 339.1003.

(2-Fluoro-1-methyl-1,2-dihyronaphtho[2,1-b]furan-1-yl)(phenyl)methanone (3j)

The reaction was performed according to General Procedure D with 1j (0.1 mmol, 18.2 mg) and 2a (0.4 mmol, 43 uL). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3j was obtained as a colorless oil (22.6 mg, 74% yield), d.r. = 20:1. 1H NMR (300 MHz, CDCl3) δ (ppm) δ 7.88 (t, J = 7.5 Hz, 2H), 7.70 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 7.4 Hz, 2H), 7.48 – 7.42 (m, 2H). 7.39 – 7.26 (m, 4H), 6.73 (d, J = 65.9 Hz, 1H), 1.96 (d, J = 5.7 Hz, 3H). 13C NMR (75 MHz, CDCl3) δ (ppm) 199.08 (d, J = 7.8 Hz), 154.47 (d, J = 2.7 Hz), 136.3, 132.7, 131.6, 130.6, 129.7, 129.2, 128.6, 128.4, 127.6, 124.0, 122.0, 121.4, 115.57 (d, J = 242.6 Hz), 111.8, 63.68 (d, J = 18.4 Hz), 17.28 (d, J = 19.5 Hz). 19F NMR (282 MHz, CDCl3) δ (ppm) -110.9 (minor), -125.8 (major). HRMS (ESI): m/z [M + Na]+ calcd for C20H16FNaO2: 329.0948, found: 329.0948.

(3-Ethyl-2-fluoro-2,3-dihydrobenzofuran-3-yl)(phenyl)methanone (3k)

The reaction was performed according to General Procedure D with 1k (0.1 mmol, 14.6 mg) and 2a (0.4 mmol, 43 uL). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3k was obtained as a colorless oil (12.8 mg, 47% yield), d.r. = 15:1. The diastereoselectivity was determined by 1H NMR on the crude product, and only major isomer was obtained after flash chromatography. 1H NMR (500 MHz, CDCl3) δ (ppm) 7.51 – 7.47 (m, 3H), 7.39 – 7.36 (m, 2H), 7.28 – 7.25 (m, 2H), 7.21 (dd, J = 7.7, 1.3 Hz, 1H), 7.00 – 6.97 (m, 2H), 6.77 (d, J = 63.2 Hz, 1H), 2.57 – 2.50 (m, 1H), 2.26 – 2.17 (m, 1H), 1.08 (t, J = 7.4 Hz, 3H). 13C NMR (125 MHz, CDCl3) δ (ppm) 200.2 (d, J = 9.1 Hz), 157.2 (d, J = 3.1 Hz), 137.4 (d, J = 1.1 Hz), 131.9, 129.9, 128.4, 127.6, 126.6, 125.9, 122.5, 115.2 (d, J = 238.8 Hz), 110.8, 67.5 (d, J = 20.0 Hz), 25.8 (d, J = 11.8 Hz), 10.4 (d, J = 2.6 Hz). 19F NMR (470 MHz, CDCl3) δ -135.2. HRMS (ESI): m/z [M + Na]+ calcd for C19H15FNaO2: 293.0948, found: 293.0950.

(2-Fluoro-3-phenethyl-2,3-dihydrobenzofuran-3-yl)(phenyl)methanone (3l)
The reaction was performed according to General Procedure D with 1H (0.1 mmol, 22.2 mg) and 2a (0.4 mmol, 43 uL). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3l was obtained as a colorless oil (22.3 mg, 64% yield), d.r. = 15:1. 1H NMR (300 MHz, CDCl3) δ (ppm) 7.59 – 7.56 (m, 2H), 7.51 (d, J = 8.2 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.32 – 7.25 (m, 4H), 0.721 (d, J = 5.9 Hz, 1H), 7.16 (d, J = 6.9 Hz, 2H), 7.01 (t, J = 7.9 Hz, 2H), 6.85 (d, J = 63.2 Hz, 1H), 2.84 – 2.71 (m, 3H), 2.48 – 2.40 (m, 1H). 13C NMR (75 MHz, CDCl3) δ (ppm) 199.7 (d, J = 9.2 Hz), 157.2 (d, J = 3.0 Hz), 141.2, 137.1, 132.1, 130.0, 129.0, 128.5, 128.2, 127.7, 126.2, 125.8, 122.6, 115.2 (d, J = 238.6 Hz), 110.9, 67.0, 35.0 (d, J = 10.8 Hz), 32.2 (d, J = 2.3 Hz). 19F NMR (282 MHz, CDCl3) δ (ppm) -115.0 (minor), -133.8 (major). HRMS (ESI): m/z [M + Na]+ calcd for C23H19FNO2: 369.1261, found: 369.1261.

2-(3-Benzoyl-2-fluoro-2,3-dihydrobenzofuran-3-yl)ethyl acetate (3m)

The reaction was performed according to General Procedure D with 1m (0.1 mmol, 20.4 mg) and 2a (0.4 mmol, 43 uL). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3m was obtained as a colorless oil (18.2 mg, 55% yield), d.r. = 20:1. 1H NMR (400 MHz, CDCl3) δ (ppm) 7.54 – 7.47 (m, 3H), 7.40 – 7.36 (m, 2H), 7.31 – 7.27 (m, 1H), 7.23 (dd, J = 7.8, 1.3 Hz, 1H), 7.03 – 6.99 (m, 2H), 6.76 (d, J = 62.9 Hz, 1H), 4.35 – 4.29 (m, 1H), 4.22 – 4.16 (m, 1H), 2.96 – 2.88 (m, 1H), 2.55 – 2.48 (m, 1H), 1.93 (s, 3H). 13C NMR (100 MHz, CDCl3) δ (ppm) 198.8 (d, J = 9.1 Hz), 170.7, 157.0 (d, J = 2.9 Hz), 136.8 (d, J = 0.6 Hz), 132.2, 130.3, 128.5, 127.9, 125.9, 125.7, 122.8, 115.0 (d, J = 239.2 Hz), 111.0, 65.1 (d, J = 19.7 Hz), 61.1 (d, J = 3.4 Hz), 31.3 (d, J = 10.6 Hz), 20.7. 19F NMR (376 MHz, CDCl3) δ (ppm) -115.8 (minor), -131.4 (major). HRMS (EI): m/z [M + Na]+ calcd for C19H17FNaO2: 351.1003, found: 351.1001.

(2-Fluoro-3-isobutyl-2,3-dihydrobenzofuran-3-yl)(phenyl)methane (3n)

The reaction was performed according to General Procedure D with 1n (0.1 mmol, 18.8 mg) and 2a (0.4 mmol, 43 uL). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3n was obtained as a colorless oil (16.8 mg, 56% yield), d.r. = 13:1. 1H NMR (400 MHz, CDCl3) δ (ppm) 7.62 – 7.60 (m, 2H), 7.48 (tt, J = 6.7, 1.1 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.25 – 7.19 (m, 2H), 6.97 – 6.81 (m, 3H), 2.66 – 2.61 (m, 1H), 2.15 – 2.08 (m, 1H), 1.93 – 1.85 (m, 1H), 1.00 – 0.97 (m, 6H). 13C NMR (100 MHz, CDCl3) δ (ppm) 199.49 (d, J = 8.9 Hz), 156.95 (d, J = 3.1 Hz), 137.30 (d, J = 1.4 Hz), 132.0, 129.8, 128.3, 127.9, 126.4, 126.1, 122.5, 115.06 (d, J = 238.7 Hz), 110.9, 66.95 (d, J = 21.1 Hz), 40.31 (d, J = 9.0 Hz), 26.1, 24.2, 22.61 (d, J = 1.3 Hz). 19F NMR (376 MHz, CDCl3) δ (ppm) -116.1 (minor), -133.3 (major). HRMS (EI): m/z [M + Na]+ calcd for C19H19FNaO2: 321.1261, found: 321.1262.

(2-Fluoro-3-pentyl-2,3-dihydrobenzofuran-3-yl)(phenyl)methane (3o)
The reaction was performed according to General Procedure D with 1o (0.1 mmol, 18.8 mg) and 2a (0.4 mmol, 43 uL). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3o was obtained as a colorless oil (21.5 mg, 69% yield), d.r. = 15:1. 1H NMR (400 MHz, CDCl3) δ (ppm) 7.46 – 7.43 (m, 2H), 7.06 (dd, J = 7.5, 1.3 Hz, 1H), 7.00 – 6.80 (m, 6H), 6.69 (td, J = 7.5, 1.1 Hz, 1H), 2.49 – 2.41 (m, 1H), 2.20 – 2.12 (m, 1H), 1.52 – 1.42 (m, 2H), 1.19 – 1.13 (m, 4H), 0.81 – 0.77 (m, 3H). 13C NMR (100 MHz, CDCl3) δ (ppm) 199.4 (d, J = 9.0 Hz), 157.9 (d, J = 2.9 Hz), 138.0 (d, J = 1.1 Hz), 131.6, 130.0, 128.2, 128.0, 127.8, 126.2, 122.6, 115.8 (d, J = 238.8 Hz), 111.0, 67.5 (d, J = 20.0 Hz), 33.0 (d, J = 10.9 Hz), 32.5, 25.9 (d, J = 2.2 Hz), 22.4, 12.0. 19F NMR (376 MHz, CDCl3) δ (ppm) -115.0 (minor), -134.2 (major). HRMS (EI): m/z [M + Na]+ calcd for C30H21FNaO2: 335.1418, found: 335.1418.

(3-Cyclohexyl-2-fluoro-2,3-dihydrobenzofuran-3-yl)(phenyl)methanone (3p)

The reaction was performed according to General Procedure D with 1p (0.1 mmol, 20.0 mg) and 2a (0.4 mmol, 43 uL). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3p was obtained as a colorless oil (21.0 mg, 69% yield), d.r. = 20:1. The diastereoselectivity was determined by 1H NMR on the crude product, and only major isomer was obtained after flash chromatography. 1H NMR (400 MHz, CDCl3) δ (ppm) 7.58 – 7.55 (m, 2H), 7.32 (dd, J = 7.5, 1.3 Hz, 1H), 7.03 – 6.97 (m, 1H), 6.96 – 6.91 (m, 3H), 6.82 – 6.64 (m, 3H), 2.73 (tt, J = 11.4, 2.9 Hz, 1H), 1.98 (d, J = 11.3 Hz, 1H), 1.64 (d, J = 13.1 Hz, 1H), 1.55 – 1.51 (m, 2H), 1.49 – 1.42 (m, 2H), 1.24 – 1.07 (m, 2H), 1.05 – 0.87 (m, 2H). 13C NMR (100 MHz, CDCl3) δ (ppm) 199.2 (d, J = 9.8 Hz), 157.8 (d, J = 1.5 Hz), 137.7, 131.9, 129.8, 128.6, 128.2, 128.0, 125.8, 122.1, 117.0 (d, J = 238.9 Hz), 110.5, 70.8 (d, J = 17.4 Hz), 42.9 (d, J = 6.5 Hz), 30.2 (d, J = 3.9 Hz), 28.5 (d, J = 4.0 Hz), 27.5, 27.1, 26.5. 19F NMR (376 MHz, CDCl3) δ (ppm) -135.4. HRMS (EI): m/z [M + Na]+ calcd for C21H23FNaO2: 347.1418, found: 347.1418.

(2-Fluoro-1-methyl-1,2-dihydronaphtho[2,1-b]furan-1-yl)(p-tolyl)methanone (3q)

The reaction was performed according to General Procedure D with 1j (0.1 mmol, 18.2 mg) and 2b (0.4 mmol, 55.2 mg). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3q was obtained as a colorless oil (23.6 mg, 74% yield), d.r. = 20:1. 1H NMR (400 MHz, CDCl3) δ (ppm) 7.84 (t, J = 8.2 Hz, 2H), 7.67 (d, J = 8.2 Hz, 1H), 7.49 (d, J = 8.3 Hz, 2H), 7.44 – 7.40 (m, 1H), 7.35 – 7.29 (m, 2H), 7.07 (d, J = 8.2 Hz, 2H), 6.73 (d, J = 66.2 Hz, 1H), 2.29 (s, 3H), 1.92 (d, J = 5.7 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ (ppm) 198.3 (d, J = 7.6 Hz), 154.3 (d, J = 2.5 Hz), 143.7, 133.4, 131.4, 130.6, 129.7, 129.3, 129.2, 128.8, 127.6, 124.0, 122.1, 121.9, 115.8 (d, J = 242.5 Hz), 111.8, 63.5 (d, J = 18.2 Hz), 21.5, 17.4 (d, J = 19.8 Hz). 19F NMR (376 MHz, CDCl3) δ (ppm) -110.9 (minor), -125.9 (major). HRMS (EI): m/z [M + Na]+ calcd for C21H27FNaO2: 343.1105, found: 343.1104.
The reaction was performed according to General Procedure D with 1j (0.1 mmol, 18.2 mg) and 2c (0.4 mmol, 61.6 mg). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3r was obtained as a colorless oil (24.9 mg, 74% yield), d.r. > 20:1. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) ppm: 7.84 (dd, \(J = 8.6, 5.7\) Hz, 2H), 7.67 – 7.62 (m, 3H), 7.44 – 7.39 (m, 1H), 7.35 – 7.29 (m, 2H), 6.78 – 6.73 (m, 2H), 6.75 (d, \(J = 66.3\) Hz, 1H), 3.76 (s, 3H), 1.90 (d, \(J = 5.8\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) ppm: 196.9 (d, \(J = 7.3\) Hz), 163.2, 154.1 (d, \(J = 2.5\) Hz), 131.4, 131.2, 130.6, 129.7, 129.2, 128.5, 127.6, 124.0, 122.4, 122.1, 116.0 (d, \(J = 242.6\) Hz), 113.9, 111.7, 63.3 (d, \(J = 18.0\) Hz), 55.4, 17.5 (d, \(J = 20.1\) Hz). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) ppm: -125.8. HRMS (EI): m/z [M + Na]\(^+\) calcd for C\(_{21}\)H\(_{17}\)FNaO\(_3\): 359.1054, found: 359.1053.

(2-Fluoro-1-methyl-1,2-dihydronaphtho[2,1-b]furan-1-yl)(4-fluorophenyl)methanone (3s)

The reaction was performed according to General Procedure D with 1j (0.1 mmol, 18.2 mg) and 2d (0.4 mmol, 56.8 mg). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3s was obtained as a colorless oil (25.0 mg, 77% yield), d.r. = 15:1. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm: 7.86 (t, \(J = 9.4\) Hz, 2H), 7.64 – 7.57 (m, 3H), 7.45 – 7.41 (m, 1H), 7.37 – 7.30 (m, 2H), 6.97 – 6.91 (m, 2H), 6.68 (d, \(J = 65.8\) Hz, 1H), 1.91 (d, \(J = 5.8\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) ppm: 197.4 (d, \(J = 7.7\) Hz), 165.2 (d, \(J = 255.7\) Hz), 154.4 (d, \(J = 2.4\) Hz), 132.4 (d, \(J = 3.1\) Hz), 131.7, 131.3 (d, \(J = 9.2\) Hz), 130.6, 129.6, 129.3, 127.7, 124.1, 121.9, 121.5, 115.8 (d, \(J = 21.8\) Hz), 115.5 (d, \(J = 243.1\) Hz), 111.8, 63.5 (d, \(J = 18.4\) Hz), 17.3 (d, \(J = 19.7\) Hz). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) ppm: -104.8 (major), -105.5 (minor), -110.7 (minor), -125.7 (major). HRMS (EI): m/z [M + Na]\(^+\) calcd for C\(_{20}\)H\(_{14}\)F\(_2\)NaO\(_2\): 347.0854, found: 347.0855.

(4-Chlorophenyl)( 2-fluoro-1-methyl-1,2-dihydronaphtho[2,1-b]furan-1-yl)methanone (3t)

The reaction was performed according to General Procedure D with 1j (0.1 mmol, 18.2 mg) and 2e (0.4 mmol, 63.4 mg). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3t was obtained as a
colorless oil (21.5 mg, 63% yield), d.r. = 13:1. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 7.86 (t, $J = 9.3$ Hz, 2H), 7.62 (d, $J = 8.2$ Hz, 1H), 7.49 – 7.46 (m, 2H), 7.43 (ddd, $J = 8.4$, 6.9, 1.3 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.30 (d, $J = 8.8$ Hz, 1H), 7.25 – 7.21 (m, 2H), 6.66 (d, $J = 65.7$ Hz, 1H), 1.91 (d, $J = 5.9$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 197.9 (d, $J = 7.8$ Hz), 154.4 (d, $J = 2.6$ Hz), 139.3, 134.4, 131.8, 130.6, 129.5, 129.3, 128.9, 127.8, 124.1, 121.8, 121.3, 115.3 (d, $J = 243.3$ Hz), 111.8, 63.6 (d, $J = 18.6$ Hz), 17.2 (d, $J = 19.5$ Hz). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ (ppm) -110.6 (minor), -125.7 (major). HRMS (EI): m/z [M + Na]$^+$ calcld for C$_{20}$H$_{14}$ClFNaO$_2$: 363.0559, found: 363.0559.

(2-Fluoro-1-methyl-1,2-dihydronaphtho[2,1-b]furan-1-yl)(4-iodophenyl)methanone (3u)

The reaction was performed according to General Procedure D with 1j (0.1 mmol, 18.2 mg) and 2f (0.4 mmol, 100.0 mg). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3u was obtained as a colorless oil (16.0 mg, 37% yield), d.r. = 10:1. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm) 7.85 – 7.83 (m, 1H), 7.63 – 7.60 (m, 3H), 7.44 – 7.41 (m, 1H), 7.36 – 7.33 (m, 1H), 7.29 (d, $J = 8.8$ Hz, 1H), 7.23 – 7.21 (m, 2H), 6.64 (d, $J = 65.7$ Hz, 1H), 1.90 (d, $J = 5.7$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm) 198.4 (d, $J = 7.8$ Hz), 154.5 (d, $J = 2.6$ Hz), 137.9, 135.4, 131.8, 130.6, 129.8, 129.6, 129.3, 127.8, 124.1, 121.8, 121.2, 115.3 (d, $J = 243.2$ Hz), 111.8, 100.7, 63.6 (d, $J = 18.5$ Hz), 17.1 (d, $J = 19.5$ Hz). $^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ (ppm) -110.7 (minor), -125.8 (major). HRMS (EI): m/z [M + Na]$^+$ calcld for C$_{22}$H$_{16}$FNaO$_2$: 454.9915, found: 454.9914.

(2-Fluoro-1-methyl-1,2-dihydronaphtho[2,1-b]furan-1-yl)(4-(trifluoromethoxy)phenyl)methanone (3v)

The reaction was performed according to General Procedure D with 1j (0.1 mmol, 18.2 mg) and 2g (0.4 mmol, 83.2 mg). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3v was obtained as a colorless oil (24.2 mg, 62% yield), d.r. = 14:1. The diastereoselectivity was determined by $^1$H NMR on the crude product, and only major isomer was obtained after flash chromatography. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm) 7.87 (dd, $J = 16.8$, 8.5 Hz, 2H), 7.64 (d, $J = 7.8$ Hz, 1H), 7.59 – 7.57 (m, 2H), 7.45 – 7.42 (m, 1H), 7.35 (t, $J = 7.2$ Hz, 1H), 7.31 (d, $J = 8.8$ Hz, 1H), 7.08 (d, $J = 8.9$ Hz, 2H), 6.67 (d, $J = 65.6$ Hz, 1H), 1.93 (d, $J = 5.6$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm) 197.6 (d, $J = 7.8$ Hz), 154.5 (d, $J = 2.6$ Hz), 152.1 (q, $J = 1.8$ Hz), 134.9, 131.9, 130.7, 130.6, 129.6, 129.3, 127.8, 124.2, 121.8, 121.1, 120.3 (d, $J = 1.4$ Hz), 120.1 (q, $J = 257.9$ Hz), 115.3 (d, $J = 243.1$ Hz), 111.8, 63.7 (d, $J = 18.6$ Hz), 17.1 (d, $J = 19.4$ Hz). $^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ (ppm) -57.7, -125.8. HRMS (EI): m/z [M + Na]$^+$ calcld for C$_{22}$H$_{14}$F$_3$NaO$_2$: 413.0771, found: 413.0771.

4-(2-Fluoro-1-methyl-1,2-dihydronaphtho[2,1-b]furan-1-carbonyl)benzonitrile (3w)
The reaction was performed according to General Procedure D with 1j (0.1 mmol, 18.2 mg) and 2h (0.4 mmol, 59.6 mg). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3w was obtained as a colorless oil (10.0 mg, 30% yield), d.r. = 10:1. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.87 (dd, \(J = 10.1, 8.2\) Hz, 2H), 7.60 – 7.29 (m, 8H), 6.57 (d, \(J = 64.9\) Hz, 1H), 1.93 (d, \(J = 5.6\) Hz, 3H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 198.6 (d, \(J = 8.3\) Hz), 154.9 (d, \(J = 2.9\) Hz), 140.0, 132.3, 132.2, 130.7, 129.5, 128.5, 128.0, 124.3, 121.5, 117.6, 115.8, 114.8 (d, \(J = 244.1\) Hz), 111.9, 64.0 (d, \(J = 19.2\) Hz), 16.8 (d, \(J = 18.8\) Hz). \(^19\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) (ppm) -110.3 (minor), -125.6 (major). HRMS (EI): m/z [M + Na]\(^+\) calcd for C\(_{21}\)H\(_{14}\)FNaO\(_2\): 354.0901, found: 354.0902.

\((2\text{-Fluoro-1-methyl-1,2-dihydronaphtho[2,1-b]furan-1-yl}(m\text{-tolyl})\text{methanone (3x)})\)

The reaction was performed according to General Procedure D with 1j (0.1 mmol, 18.2 mg) and 2i (0.4 mmol, 55.2 mg). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3x was obtained as a colorless oil (20.8 mg, 65% yield), d.r. = 25:1. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.83 – 7.77 (m, 2H), 7.63 (d, \(J = 8.5\) Hz, 1H), 7.40 – 7.29 (m, 3H), 7.23 – 7.16 (m, 3H), 7.07 (t, \(J = 7.6\) Hz, 1H), 6.64 (d, \(J = 66.0\) Hz, 1H), 2.19 (s, 3H), 1.87 (d, \(J = 5.7\) Hz, 3H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 199.3 (d, \(J = 7.9\) Hz), 154.6 (d, \(J = 2.6\) Hz), 138.5, 136.3, 133.4, 131.6, 130.6, 129.8, 129.23, 129.19, 128.4, 127.6, 125.4, 124.0, 122.1, 121.5, 115.7 (d, \(J = 242.5\) Hz), 111.7, 63.7 (d, \(J = 18.3\) Hz), 21.3, 17.3 (d, \(J = 19.5\) Hz). \(^19\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) (ppm) -110.8 (minor), -125.9 (major). HRMS (EI): m/z [M + Na]\(^+\) calcd for C\(_{21}\)H\(_{14}\)FNaO\(_2\): 343.1105, found: 343.1105.

\((2\text{-Fluoro-1-methyl-1,2-dihydronaphtho[2,1-b]furan-1-yl}(3\text{-methoxyphenyl})\text{methanone (3y)})\)

The reaction was performed according to General Procedure D with 1j (0.1 mmol, 18.2 mg) and 2j (0.4 mmol, 61.6 mg). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3y was obtained as a colorless oil (26.9 mg, 80% yield), d.r. = 20:1. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.87 – 7.82 (m, 2H), 7.70 – 7.67 (m, 1H), 7.46 – 7.42 (m, 1H), 7.36 – 7.32 (m, 1H), 7.30 (d, \(J = 8.9\) Hz, 1H), 7.17 (t, \(J = 7.9\) Hz, 1H), 7.10 (dt, \(J = 7.8, 1.3\) Hz, 1H), 7.04 (dd, \(J = 2.6, 1.6\) Hz, 1H), 6.97 – 6.94 (m, 1H), 6.70 (d, \(J = 66.0\) Hz, 1H), 3.62 (s, 3H), 1.93 (d, \(J = 5.8\) Hz, 3H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 198.9 (d, \(J = 7.7\) Hz), 159.5, 154.5 (d, \(J = 2.6\) Hz), 137.4, 131.6, 130.6, 129.7,
129.6, 129.2, 127.7, 124.0, 122.0, 121.6, 120.8, 119.5, 115.6 (d, J = 242.7 Hz), 112.7, 111.7, 63.7 (d, J = 18.3 Hz), 55.1, 17.2 (d, J = 19.5 Hz). $^{19}$F NMR (282 MHz, CDCl$_3$) δ (ppm) -110.9 (minor), -125.8 (major). HRMS (EI): m/z [M + Na]$^+$ calcd for C$_2$I$_2$F$_3$NaO$_2$: 359.105, found: 359.1054.

(2-Fluoro-1-methyl-1,2-dihydronaphtho[2,1-b]furan-1-yl)(3-fluorophenyl)methanone (3z)

The reaction was performed according to General Procedure D with 1j (0.1 mmol, 18.2 mg) and 2k (0.4 mmol, 56.8 mg). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3z was obtained as a colorless oil (26.6 mg, 82% yield), d.r. = 13:1. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 7.91 – 7.87 (m, 2H), 7.67 (d, J = 8.2 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.40 – 7.32 (m, 2H), 7.29 – 7.22 (m, 3H), 7.17 – 7.12 (m, 1H), 6.69 (d, J = 65.6 Hz, 1H), 1.95 (d, J = 5.7 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 197.9 (d, J = 6.4 Hz), 162.4 (d, J = 248.6 Hz), 154.6 (d, J = 2.7 Hz), 138.1 (d, J = 6.4 Hz), 131.9, 130.6, 130.3 (d, J = 7.7 Hz), 129.6, 129.3, 127.8, 124.1, 124.0 (d, J = 3.2 Hz), 121.8, 121.0, 119.8 (d, J = 21.3 Hz), 115.6 (d, J = 23.3 Hz), 115.2 (d, J = 243.1 Hz), 111.8, 63.7 (d, J = 18.7 Hz), 17.1 (d, J = 19.4 Hz). $^{19}$F NMR (282 MHz, CDCl$_3$) δ (ppm) -110.8 (major), -112.5 (minor), -125.7 (major), -125.8 (minor). HRMS (EI): m/z [M + Na]$^+$ calcd for C$_{29}$H$_{14}$F$_2$NaO$_2$: 347.085, found: 347.0856.

(3-Chlorophenyl)(2-fluoro-1-methyl-1,2-dihydronaphtho[2,1-b]furan-1-yl)methanone (3aa)

The reaction was performed according to General Procedure D with 1j (0.1 mmol, 18.2 mg) and 2l (0.4 mmol, 63.4 mg). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3aa was obtained as a colorless oil (23.2 mg, 68% yield), d.r. = 13:1. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.87 (dd, J = 11.5, 8.5 Hz, 2H), 7.63 (d, J = 8.2 Hz, 1H), 7.53 (t, J = 1.9 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.39 – 7.33 (m, 2H), 7.31 (d, J = 8.8 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.16 (t, J = 7.9 Hz, 1H), 6.64 (d, J = 65.6 Hz, 1H), 1.93 (d, J = 5.7 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 197.99 (d, J = 8.1 Hz), 154.67 (d, J = 2.7 Hz), 137.8, 134.9, 132.6, 131.9, 130.7, 129.9, 129.6, 129.4, 128.7, 127.8, 126.2, 124.1, 121.8, 120.8, 115.17 (d, J = 243.3 Hz), 111.8, 63.80 (d, J = 18.7 Hz), 17.06 (d, J = 19.3 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) δ (ppm) -110.7 (minor), -125.7 (major). HRMS (EI): m/z [M + Na]$^+$ calcd for C$_{29}$H$_{14}$ClFNaO$_2$: 363.0559, found: 363.0660.

(3-Bromophenyl)(2-fluoro-1-methyl-1,2-dihydronaphtho[2,1-b]furan-1-yl)methanone (3ab)
The reaction was performed according to General Procedure D with 1j (0.1 mmol, 18.2 mg) and 2m (0.4 mmol, 81.2 mg). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3ab was obtained as a colorless oil (14.2 mg, 37% yield), d.r. = 14:1. 1H NMR (300 MHz, CDCl3) δ (ppm) 7.87 (t, J = 8.7 Hz, 2H), 7.68 (t, J = 1.7 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.47 – 7.41 (m, 1H), 7.38 – 7.35 (m, 1H), 7.31 (d, J = 8.9 Hz, 2H), 7.09 (t, J = 7.9 Hz, 1H), 6.63 (d, J = 65.4 Hz, 1H), 1.92 (d, J = 5.7 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ (ppm) 197.9 (d, J = 8.0 Hz), 154.7 (d, J = 2.7 Hz), 138.1, 135.5, 131.9, 131.6, 130.7, 129.6, 129.4, 127.8, 126.5, 124.2, 122.9, 121.8, 120.8, 115.2 (d, J = 243.4 Hz), 111.8, 63.8 (d, J = 18.7 Hz), 17.0 (d, J = 19.1 Hz). 19F NMR (282 MHz, CDCl3) δ (ppm) -110.6 (minor), -125.7 (major). HRMS (EI): m/z [M + Na]+ calcd for C20H13BrFNaO5: 407.0053, found: 407.0053.

(3,4-Dimethylphenyl)(2-fluoro-1-methyl-1,2-dihydronaphtho[2,1-b]furan-1-yl)methane (3ac)

![Chemical structure of 3ac](image)

The reaction was performed according to General Procedure D with 1j (0.1 mmol, 18.2 mg) and 2n (0.4 mmol, 60.9 mg). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3ac was obtained as a colorless oil (28.4 mg, 85% yield), d.r. = 15:1. 1H NMR (400 MHz, CDCl3) δ (ppm) 7.87 (t, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.37 – 7.27 (m, 3H), 7.02 (d, J = 8.0 Hz, 1H), 6.75 (d, J = 66.3 Hz, 1H), 2.22 (s, 3H), 2.17 (s, 3H), 1.94 (d, J = 5.8 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ (ppm) 198.5 (d, J = 19.1 Hz), 154.4 (d, J = 2.6 Hz), 142.5, 137.1, 133.7, 131.4, 130.6, 130.0, 129.7, 129.2, 127.6, 126.1, 123.9, 122.1, 122.0, 122.0, 121.8, 120.8, 115.2 (d, J = 243.4 Hz), 111.7, 63.5 (d, J = 18.1 Hz), 19.8, 19.7, 17.4 (d, J = 19.8 Hz). 19F NMR (376 MHz, CDCl3) δ (ppm) -110.9 (minor), -125.8 (major). HRMS (EI): m/z [M + Na]+ calcd for C22H19FNaO5: 357.1261, found: 357.1262.

(2-Fluoro-1-methyl-1,2-dihydronaphtho[2,1-b]furan-1-yl)(naphthalen-2-yl)methane (3ad)

![Chemical structure of 3ad](image)

The reaction was performed according to General Procedure D with 1j (0.1 mmol, 18.2 mg) and 2o (0.4 mmol, 69.7 mg). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3ad was obtained as a colorless oil (22.1 mg, 62% yield), d.r. > 20:1. 1H NMR (400 MHz, CDCl3) δ (ppm) 8.00 (s, 1H), 7.90 (d, J = 8.8 Hz, 1H), 7.85 (dd, J = 8.1, 1.2 Hz, 1H), 7.77 – 7.65 (m, 5H), 7.55 – 7.51 (m, 1H), 7.47 – 7.40 (m, 2H), 7.37 – 7.31 (m, 2H), 6.80 (d, J = 66.0 Hz, 1H), 1.99 (d, J = 5.8 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ (ppm) 198.8 (d, J = 7.8 Hz), 154.6 (d, J = 2.7 Hz), 135.0, 133.3, 132.1, 131.7, 130.7, 130.1, 129.7, 129.6, 129.3, 128.6, 128.5, 127.7, 127.5, 126.8, 124.5, 124.0, 122.0, 121.9, 115.7 (d, J = 242.9 Hz), 111.7, 63.8 (d, J = 18.4 Hz), 17.4 (d, J = 19.7 Hz). 19F NMR (282 MHz, CDCl3) δ (ppm) -110.5 (minor), -125.6 (major). HRMS (EI): m/z [M + Na]+ calcd for C24H17FNaO5: 379.1105, found: 379.1105.
(2-Fluoro-1-methyl-1,2-dihyronaphtho[2,1-b]furan-1-yl)(furan-2-yl)methanone (3ae)

The reaction was performed according to General Procedure D with 1j (0.1 mmol, 18.2 mg) and 2p (0.4 mmol, 45.6 mg). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3ae was obtained as a colorless oil (14.8 mg, 50% yield), d.r. > 20:1. The diastereoselectivity was determined by 1H NMR on the crude product, and only major isomer was obtained after flash chromatography. 1H NMR (300 MHz, CDCl3) δ (ppm) 7.85 – 7.82 (m, 2H), 7.65 (d, J = 8.4 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.36 – 7.28 (m, 2H), 6.89 (d, J = 3.7 Hz, 1H), 6.71 (d, J = 65.6 Hz, 1H), 6.36 (dd, J = 3.6, 1.7 Hz, 1H), 1.92 (d, J = 5.6 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ (ppm) 186.1 (d, J = 8.6 Hz), 154.8 (d, J = 2.7 Hz), 150.6, 146.9, 131.5, 130.6, 129.9, 129.2, 127.6, 123.9, 122.0, 120.6, 119.5, 115.3 (d, J = 242.9 Hz), 112.4, 111.8, 62.7 (d, J = 18.8 Hz), 15.8 (d, J = 19.1 Hz). 19F NMR (282 MHz, CDCl3) δ (ppm) -125.2. HRMS (EI): m/z [M + Na]+ calcld for C18H13FNaO3: 319.0741, found: 319.0741.

(2-Fluoro-1-methyl-1,2-dihyronaphtho[2,1-b]furan-1-yl)(thiophen-2-yl)methanone (3af)

The reaction was performed according to General Procedure D with 1j (0.1 mmol, 18.2 mg) and 2q (0.4 mmol, 52.0 mg). After purification by flash chromatography (n-pentane/ethyl acetate = 50/1), the desired compound 3af was obtained as a colorless oil (21.2 mg, 68% yield), d.r. > 20:1. The diastereoselectivity was determined by 1H NMR on the crude product, and only major isomer was obtained after flash chromatography. 1H NMR (400 MHz, CDCl3) δ (ppm) 7.86 (dd, J = 14.5, 8.5 Hz, 2H), 7.64 (d, J = 8.4 Hz, 1H), 7.49 (dd, J = 4.9, 1.1 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.36 – 7.35 (m, 1H), 7.31 (d, J = 8.8 Hz, 1H), 7.27 (dd, J = 4.0, 1.1 Hz, 1H), 6.88 (dd, J = 5.0, 3.9 Hz, 1H), 6.70 (d, J = 65.7 Hz, 1H), 1.91 (d, J = 5.7 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ (ppm) 190.9 (d, J = 7.9 Hz), 154.8 (d, J = 2.5 Hz), 141.3, 134.7, 132.7, 131.8, 130.6, 129.8, 129.3, 128.3, 127.8, 124.1, 122.0, 121.6, 115.9 (d, J = 244.1 Hz), 111.8, 63.1 (d, J = 18.7 Hz), 16.5 (d, J = 19.3 Hz). 19F NMR (282 MHz, CDCl3) δ (ppm) -125.1. HRMS (EI): m/z [M + Na]+ calcld for C18H13FNaO2S: 335.0512, found: 335.0513.
5. Less Successful and Failed Examples

![Chemical Structures and Reaction Scheme]

6. Synthetic Utility

6.1 The Reaction of Indole with Benzoyl Fluoride

To a Schlenk tube, compound 4a (17.3 mg, 0.1 mmol), carbene catalyst A (6.3 mg, 0.02 mmol), 4-CzIPN (4.0 mg, 0.005 mmol) and K$_2$HPO$_4$ (34.8 mg, 0.2 mmol) were added. Then the reaction tube was evacuated and backfilled with argon two times. Subsequently, freshly prepared benzoyl fluoride 2a (0.4 mmol, 43 uL), CH$_3$CN (1 mL) and DMF (0.1 mL) were added. The resulting mixture was degassed under vacuum two times and then irradiated with 2x45 W blue LEDs at room temperature for 24 hours. After that, the residue was purified by silica gel chromatography using a mixture of
n-pentane and ethyl acetate as an eluent (n-pentane/ethyl acetate = 10/1) to get the desired product 5a (14.9 mg, 50% yield) as a colorless oil with >20:1 d.r. (Note: the product 5a is not very stable during column chromatography, so it must be purified very quickly) 1H NMR (300 MHz, CDCl3) δ (ppm) 8.18 (d, J = 8.6 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.38 – 7.33 (m, 3H), 7.30 (d, J = 6.7 Hz, 1H), 7.19 – 7.09 (m, 2H), 6.61 (d, J = 64.7 Hz, 1H), 2.34 (s, 3H), 1.80 (d, J = 4.3 Hz, 3H). 13C NMR (75 MHz, CDCl3) δ (ppm) 200.6, 169.3, 141.0, 136.8, 131.8, 130.0, 129.6, 128.4, 128.3, 127.6, 124.6, 117.1, 102.2 (d, J = 220.4 Hz), 61.7 (d, J = 1.8 Hz), 23.2, 18.0 (d, J = 15.1 Hz). 19F NMR (282 MHz, CDCl3) δ (ppm) -144.0. HRMS (EI): m/z [M + Na]+ calcd for C18H18FNNaO2: 336.0797, found: 336.0796.

To a Schlenk tube compound 4b (23.5 mg, 0.1 mmol), carbene catalyst A (6.3 mg, 0.02 mmol), 4-CzIPN (4.0 mg, 0.005 mmol) and K2HPO4 (34.8 mg, 0.2 mmol) were added. Then the reaction tube was evacuated and backfilled with argon two times. Subsequently, freshly prepared benzoyl fluoride 2a (0.4 mmol, 43 uL), CH3CN (1 mL) and DMF (0.1 mL) were added. The resulting mixture was degassed under vacuum two times and then irradiated with 2x45 W blue LEDs at room temperature for 24 hours. After that, the residue was purified by silica gel chromatography using a mixture of n-pentane and ethyl acetate as an eluent (n-pentane/ethyl acetate = 10/1) to get the desired product 5b (18.9 mg, 53% yield) as a colorless oil with >20:1 d.r. (Note: the product 5b is not very stable during column chromatography, so it must be purified very quickly) 1H NMR (600 MHz, CDCl3) δ (ppm) 8.33 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 7.7 Hz, 2H), 7.06 (t, J = 7.7 Hz, 1H), 7.02 (d, J = 7.0 Hz, 1H), 6.99 (t, J = 7.9 Hz, 4H), 6.92 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H), 6.81 (q, J = 7.4 Hz, 3H), 6.43 (d, J = 60.9 Hz, 1H), 1.60 (d, J = 3.7 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ (ppm) 200.0 (d, J = 8.7 Hz), 169.3 (d, J = 3.1 Hz), 142.2 (d, J = 3.1 Hz), 138.1, 135.9, 132.2, 131.2, 130.8, 129.7, 128.5, 128.3, 127.6, 125.2, 124.9, 118.5, 103.3 (d, J = 219.9 Hz), 62.1 (d, J = 22.3 Hz), 16.8 (d, J = 13.2 Hz). 19F NMR (282 MHz, CDCl3) δ (ppm) -140.3. HRMS (EI): m/z [M + Na]+ calcd for C23H18FNNaO2: 382.1214, found: 382.1212.

6.2 1 mmol Scale Reaction

To a Schlenk tube 1-methylnaphtho[2,1-b]furan 1j (182.2 mg, 1.0 mmol), carbene catalyst A (63 mg, 0.2 mmol), Ir-F (22 mg, 0.02 mmol) and K2HPO4 (348 mg, 2.0 mmol) were added. Then the reaction tube was evacuated and backfilled with argon two times. Subsequently, freshly prepared benzoyl fluoride 2a (4.0 mmol, 0.43 mL), CH3CN (10 mL) and DMF (1 mL) were added. The resulting mixture was degassed under vacuum two times and then irradiated with 2x45 W blue LEDs at room temperature for 36 hours. After that, the residue was purified by silica gel chromatography using a mixture of n-pentane and ethyl acetate as an eluent (n-pentane/ethyl acetate = 50/1) to get the desired product 3j (253.4 mg, 83% yield) as a colorless oil with 20:1 d.r..
6.3 Formation of 2-Isoxazoline Ring Systems

To a stirred solution of (2-fluoro-1-methyl-1,2-dihyronaphtho[2,1-b]furan-1-yl)(phenyl)methanone 3j (0.1 mmol, 30.6 mg) in EtOH (2 mL), hydroxylamine hydrochloride (0.5 mmol, 5.0 equiv), NaOAc (1 mmol, 10.0 equiv) was added at rt. The mixture was stirred at 70 °C in an oil bath for 24 h. Then, the solvent was removed and the residue was purified by flash column chromatography using a mixture of n-pentane and ethyl acetate as an eluent (n-pentane/ethyl acetate = 5/1) to give compound 6 as a white solid (18.3 mg, 57% yield), m.p. = 128-130 °C. 1H NMR (600 MHz, CDCl3) δ (ppm) 7.84 (dd, J = 15.2, 8.4 Hz, 2H), 7.78 (d, J = 8.8 Hz, 1H), 7.46 – 7.44 (m, 1H), 7.38 – 7.35 (m, 1H), 7.28 – 7.26 (m, 2H), 7.20 (t, J = 7.6 Hz, 2H), 7.11 (d, J = 8.8 Hz, 1H), 6.70 (d, J = 7.1 Hz, 2H), 6.40 (d, J = 64.8 Hz, 1H), 1.97 (d, J = 5.0 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ (ppm) 159.8 (d, J = 9.8 Hz), 155.3 (d, J = 3.1 Hz), 131.4, 131.2, 130.6, 130.2, 129.3, 128.8, 128.2, 127.5, 127.1, 123.7, 122.2, 119.8, 115.7 (d, J = 242.1 Hz), 112.0, 57.6 (d, J = 21.4 Hz), 16.7. 19F NMR (564 MHz, CDCl3) δ (ppm) -128.0. HRMS (EI): m/z [M + Na]+ calcd for C20H16FNNaO2: 344.1057, found: 344.1057.

To a stirred solution of compound 6 (0.05 mmol, 16.1 mg) in toluene (2 mL), p-TsOH (0.2 mmol, 4.0 equiv) was added at rt. The mixture was stirred at 70 °C in an oil bath for 12 h. Then, the solvent was removed and the residue was purified by flash column chromatography using a mixture of n-pentane and ethyl acetate as an eluent (n-pentane/ethyl acetate = 10/1) to give compound 7 as a colorless oil (8.1 mg, 54% yield). 1H NMR (600 MHz, CDCl3) δ (ppm) 7.76 (dd, J = 8.5, 4.6 Hz, 2H), 7.44 – 7.41 (m, 1H), 7.31 – 7.28 (m, 2H), 7.23 – 7.20 (m, 4H), 7.09 – 7.03 (m, 2H), 6.62 (s, 1H), 2.05 (s, 3H). 13C NMR (150 MHz, CDCl3) δ (ppm) 161.8, 156.3, 151.1, 130.2, 129.7, 129.2, 129.1, 128.5, 128.2, 126.5, 123.3, 122.6, 117.5, 117.2, 112.2, 68.2, 19.9. HRMS (EI): m/z [M + Na]+ calcd for C20H15NNaO2: 324.0995, found: 324.0995.

6.4 Carbonyl Reduction

To a dry Schlenk tube under argon (2-fluoro-1-methyl-1,2-dihyronaphtho[2,1-b]furan-1-yl)(phenyl)- methanone 3j (0.1 mmol, 30.6 mg) and MeOH/THF (1:1, 2 mL) were added. Then the reaction mixture was cooled to 0 °C and NaBH₄ (7.4 mg, 0.20 mmol) was added. After the starting material was consumed completely (monitored by TLC), the reaction was quenched by adding saturated NH₄Cl solution (5.0 mL). The mixture was extracted with ethyl acetate (15 mL × 3). The
combined organic extracts were washed with brine, dried over anhydrous MgSO₄ and filtrated. Then the solvent was concentrated under reduced pressure to give the desired product 8 with 99% yield and 1:1 d.r.

(2-Fluoro-1-methyl-1,2-dihyronaphtho[2,1-b]furan-1-yl)(phenyl)methanol 8

![Chemical Structure](image)

1H NMR (400 MHz, CDCl₃) δ (ppm) (both isomers) 7.88 – 7.79 (m, 4H), 7.71 (d, J = 8.7 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.39 – 7.35 (m, 2H), 7.31 – 7.27 (m, 2H), 7.25 – 7.13 (m, 5H), 7.12 – 7.04 (m, 4H), 6.99 (d, J = 8.8 Hz, 1H), 6.86 (d, J = 7.4 Hz, 2H), 6.45 (d, J = 36.0 Hz, 1H), 6.29 (d, J = 35.9 Hz, 1H), 5.17 (t, J = 3.0 Hz, 1H), 4.99 (d, J = 2.7 Hz, 1H), 2.21 (d, J = 3.0 Hz, 1H), 1.98 (d, J = 2.8 Hz, 1H), 1.91 (d, J = 4.5 Hz, 3H), 1.73 (d, J = 4.3 Hz, 3H). 13C NMR (100 MHz, CDCl₃) δ (ppm) 155.7 (d, J = 3.3 Hz), 155.6 (d, J = 3.6 Hz), 139.4 (d, J = 7.3 Hz), 131.0, 130.71, 130.68, 130.65, 129.6, 129.3, 128.4, 128.2, 128.0, 127.7, 127.5, 126.9, 126.51, 126.49, 123.4, 123.3, 122.7, 122.5, 120.7, 120.0, 115.8 (d, J = 238.9 Hz), 115.1 (d, J = 238.0 Hz), 57.8 (d, J = 18.7 Hz), 57.6 (d, J = 18.8 Hz), 16.0 (d, J = 15.2 Hz), 14.0 (d, J = 14.8 Hz). 19F NMR (376 MHz, CDCl₃) δ (ppm) -130.3, -131.2. HRMS (EI): m/z [M + Na]+ calcd for C₂₀H₁₇FNaO₂: 331.1105, found: 331.1105.

7. Mechanism Study

7.1 Reaction in the Presence of TEMPO

![Reaction Scheme](image)

To a Schlenk tube carbene catalyst A (6.3 mg, 0.02 mmol), Ir-F (2.2 mg, 0.002 mmol), K₂HPO₄ (34.8 mg, 0.2 mmol), 1-methylnaphtho[2,1-b]furan 1j (18.2 mg, 0.1 mmol) and TEMPO (2.0 equiv) were added. Then the reaction tube was evacuated and backfilled with argon two times. Subsequently, freshly prepared benzoyl fluoride 2a (0.4 mmol, 43 μL), CH₃CN (1 mL) and DMF (0.1 mL) were added. The resulting mixture was degassed under vacuum two times and then irradiated with 2x45 W blue LEDs at room temperature for 24 hours. After that, we did not observe the desired product 3j and starting material unreacted.

7.2 The Acyl Azolium Salt as a Competent Substrate

![Reaction Scheme](image)

To a Schlenk tube Ir-F (2.2 mg, 0.002 mmol), 1-methylnaphtho[2,1-b]furan 1j (18.2 mg, 0.1 mmol) and 2-benzoyl-1,3-dimethyl-1H-imidazol-3-ium trifluoromethanesulfonate 9 (1.0 equiv) were added. Then the reaction tube was evacuated and backfilled with argon two times. Subsequently, NEt₃·3HF (0.1 mmol, 16.1 mg), CH₃CN (1 mL) and
DMF (0.1 mL) were added. The resulting mixture was degassed under vacuum two times and then irradiated with 2x45 W blue LEDs at room temperature for 24 hours. The yield was determined by $^1$H NMR using 1,3,5-trimethoxybenzene as internal standard.

7.3 Experiments with a Chiral NHC Catalyst

![Chemical Structures]

To a Schlenk tube chiral carbene catalyst (4.7 mg, 0.01 mmol), Ir-F (2.2 mg, 0.002 mmol), K$_2$HPO$_4$ (34.8 mg, 0.2 mmol) and 1-methylnaphtho[2,1-b]furan 1j (18.2 mg, 0.1 mmol) were added. Then the reaction tube was evacuated and backfilled with argon two times. Subsequently, freshly prepared benzoyl fluoride 2a (0.4 mmol, 43 μL), CH$_3$CN (1 mL) and DMF (0.1 mL) were added. The resulting mixture was degassed under vacuum two times and then irradiated with 2x45 W blue LEDs at room temperature for 24 hours. After that, the residue was purified by silica gel chromatography using a mixture of n-pentane and ethyl acetate as an eluent (n-pentane/ethyl acetate = 50/1) to get the desired product 3j (16.2 mg, 53% yield) as a colorless oil with > 20:1 and 30% ee.
7.4 Emission Quenching Experiments (Stern–Volmer Studies)

Emission intensities were recorded using a Jasco FP-8300 spectrofluorometer. All [Ir(dF(CF₃)ppy)₂(dtbbpy)]PF₆ solutions were excited at 400 nm and the emission intensity was recorded at 460 nm. In a typical experiment, to a certain amount of solution with [Ir(dF(CF₃)ppy)₂(dtbbpy)]PF₆ in CH₃CN (5 mL) was added the appropriate amount of quencher (1j or 9) in a screw-top quartz cuvette. After degassing the solution by bubbling argon for 5 minutes, the emission of the sample was recorded.
7.5 Cyclic Voltammetry

Benzofuran 1j exhibits an irreversible oxidation at +0.90 V vs Fc/Fc⁺ in acetonitrile (Figure 1). Using a value of +0.380 V for the Fc/Fc⁺ redox couple vs SCE in acetonitrile, this corresponds to an oxidation potential of +1.28 V vs SCE. Figure S2 shows the first scan; on subsequent scans a significantly greater peak current was observed, and a second oxidation peak appeared at a slightly lower potential (approx. +0.75 V vs Fc/Fc⁺, +1.13 V vs SCE), as can be seen in Figure S3. Scanning to higher potentials than those in Figures 1 and 2 resulted in higher currents in the return direction, towards more negative potentials, than the peak potential in the forward scanning direction (not shown). Furthermore, a green solid was observed to be deposited on the electrode. This points to the formation, upon oxidation of 1j, of a species that is more easily oxidized than 1j itself, possibly in part due to the observed adhesion to the Pt surface. The reactivity of the oxidation product was also visible in the voltammograms measured in the presence of internal ferrocene, where a great number of small redox events was observed (Figure S4). The reduction of Fc⁺ is not discernible, and thus the inflection point of the Fc oxidation peak was used as the best estimate of \( E_{1/2} \) (Fc).

Figure S2: Cyclic voltammogram (100 mV s⁻¹) of 1j (0.01 M) in acetonitrile with [Bu₄N⁺][PF₆⁻] (0.1 M) as the supporting electrolyte.
Figure S3: Cyclic voltammogram (100 mV s\(^{-1}\)) of 1j (0.01 M) in acetonitrile with \([\text{Bu}_4\text{N}]^+\)[PF\(_6\)] (0.1 M) as the supporting electrolyte. Here, the third cycle of three is shown.

Figure S4: Cyclic voltammogram (100 mV s\(^{-1}\)) of 1j (0.01 M) in acetonitrile with added ferrocene (~0.01M) and \([\text{Bu}_4\text{N}]^+\)[PF\(_6\)] (0.1 M) as the supporting electrolyte.
8. General Procedure E for the Reaction of Benzofuran with Anhydrides

To a Schlenk tube carbene catalyst A (6.3 mg, 0.02 mmol), Ir-F (2.2 mg, 0.002 mmol) and K2HPO4 (34.8 mg, 0.2 mmol), 1-methylnaphtho[2,1-b]furan 1j (18.2 mg, 0.1 mmol) and an anhydride 10 (2.0 equiv) were added. Then the reaction tube was evacuated and backfilled with argon two times. Subsequently, CH3CN (1 mL) and DMF (0.1 mL) were added. The resulting mixture was irradiated with 2x45 W blue LEDs at room temperature for 24 hours. After that, the residue was purified by silica gel chromatography using a mixture of n-pentane and ethyl acetate as an eluent to get the desired product 11.

1-Benzoyl-1-methyl-1,2-dihydronaphtho[2,1-b]furan-2-yl benzoate (11a)

The reaction was performed according to General Procedure E with 1j (0.1 mmol, 18.2 mg) and benzoic anhydride 10a (0.2 mmol, 69.7 mg). After purification by flash chromatography (n-pentane/ethyl acetate = 30/1), the desired compound 11a was obtained as a colorless oil (22.5 mg, 55% yield), d.r. > 20:1. 1H NMR (400 MHz, CDCl3) δ (ppm) 8.11 – 8.07 (m, 2H), 7.87 – 7.82 (m, 2H), 7.67 (d, J = 8.5 Hz, 1H), 7.64 – 7.59 (m, 3H), 7.49 – 7.45 (m, 3H), 7.43 – 7.39 (m, 2H), 7.35 – 7.28 (m, 3H), 1.94 (s, 3H). 13C NMR (100 MHz, CDCl3) δ (ppm) 200.0, 164.9, 154.7, 136.4, 133.9, 132.6, 131.4, 130.4, 130.1, 129.6, 129.2, 128.9, 128.7, 128.6, 128.6, 127.7, 123.8, 122.2, 121.7, 111.9, 103.8, 62.5, 18.2. HRMS (EI): m/z [M + Na]⁺ calcd for C27H20NaO4: 431.1254, found: 431.1252.

1-Methyl-1-(4-(trifluoromethyl)benzoyl)-1,2-dihydronaphtho[2,1-b]furan-2-yl4-(trifluoro- methyl)benzoate (11b)

The reaction was performed according to General Procedure E with 1j (0.1 mmol, 18.2 mg) and 4-(trifluoromethyl)benzoic anhydride 10b (0.2 mmol, 72.4 mg). After purification by flash chromatography (n-pentane/ethyl acetate = 30/1), the desired compound 11b was obtained as a colorless oil (25.0 mg, 46% yield), d.r. > 20:1. 1H NMR (400 MHz, CDCl3) δ (ppm) 8.22 – 8.21 (m, 2H), 7.91 – 7.86 (m, 2H), 7.75 (d, J = 8.3 Hz, 2H), 7.66 – 7.64 (m, 3H), 7.53 (d, J = 8.3 Hz, 2H), 7.46 – 7.43 (m, 1H), 7.38 – 7.35 (m, 2H), 7.31 (d, J = 8.8 Hz, 1H), 1.92 (s, 3H).
\[ ^{13}C \text{ NMR (100 MHz, CDCl}_3 \delta \text{ (ppm)} \text{ 199.3, 163.8, 154.7, 139.5, 135.4 (q, } J = 32.9 \text{ Hz ), 133.8 (q, } J = 32.8 \text{ Hz), 132.0, 131.67, 131.66, 130.5, 130.4, 129.48, 129.46, 129.1, 128.1, 125.7 (p, } J = 3.6 \text{ Hz), 124.2, 123.4 (q, } J = 271.2 \text{ Hz), 123.1 (q, } J = 271.3 \text{ Hz), 121.3, 121.1, 111.9, 103.9, 62.7, 17.8. \]
\[ ^{19}F \text{ NMR (376 MHz, CDCl}_3 \delta \text{ (ppm)} \text{ -63.3, -63.4. \] HRMS (EI): m/z [M + Na]\text{] calcd for C}_{29}H_{18}F_6NaO_4: 567.1001, found: 567.1002.

1-(3-Methoxybenzoyl)-1-methyl-1,2-dihyronaphtho[2,1-b]furan-2-yl 3-methoxybenzoate (11c)

The reaction was performed according to General Procedure E with 1j (0.1 mmol, 18.2 mg) and 3-methoxybenzoic anhydride 10c (0.2 mmol, 57.3 mg). After purification by flash chromatography (n-pentane/ethyl acetate = 30/1), the desired compound 11c was obtained as a white solid (30.0 mg, 64% yield), d.r. > 20:1, m.p. = 100-102 °C. \[ ^1H \text{ NMR (400 MHz, CDCl}_3 \delta \text{ (ppm)} \text{ 7.87 – 7.83 (m, 2H), 7.71 – 7.66 (m, 2H), 7.60 (dd, } J = 2.7, 1.5 \text{ Hz, 1H), 7.45 (s, 1H), 7.44 – 7.40 (m, 1H), 7.39 – 7.29 (m, 3H), 7.20 – 7.13 (m, 4H), 6.97 – 6.94 (m, 1H), 3.84 (s, 3H), 3.62 (s, 3H), 1.94 (s, 3H). \]
\[ ^{13}C \text{ NMR (100 MHz, CDCl}_3 \delta \text{ (ppm)} \text{ 199.7, 164.8, 159.6, 159.4, 154.7, 137.5, 131.4, 130.3, 129.9, 129.64, 129.62, 129.2, 127.8, 123.9, 122.4, 122.3, 121.7, 121.3, 120.4, 119.5, 114.4, 113.1, 111.8, 103.9, 62.5, 55.4, 55.1, 18.1. \]
HRMS (EI): m/z [M + Na]\text{] calcd for C}_{29}H_{24}NaO_6: 491.1465, found: 491.1464.
9. X-ray Structure Data of 6 and 11c

X-ray crystal structure analysis of 6 (STU10250): A colorless, prism-like specimen of C_{20}H_{16}FNO_2, approximate dimensions 0.060 mm x 0.100 mm x 0.206 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1764 frames were collected. The total exposure time was 21.95 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 33214 reflections to a maximum θ angle of 66.68° (0.84 Å resolution), of which 2706 were independent (average redundancy 12.274, completeness = 99.4%, R_{int} = 5.99%, R_{sig} = 2.58%) and 2394 (88.47%) were greater than 2σ(F^2). The final cell constants of a = 13.9630(4) Å, b = 7.2473(2) Å, c = 15.2346(4) Å, β = 93.8710(10)°, volume = 1538.13(7) Å^3, are based upon the refinement of the XYZ-centroids of 9958 reflections above 2σ(I) with 13.53° < 2θ < 133.3°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.911. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8520 and 0.9530. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P2_1/c, with Z = 4 for the formula unit, C_{20}H_{16}FNO_2. The final anisotropic full-matrix least-squares refinement on F^2 with 222 variables converged at R1 = 3.66%, for the observed data and wR2 = 9.26% for all data. The goodness-of-fit was 1.043. The largest peak in the final difference electron density synthesis was 0.223 e/Å^3 and the largest hole was -0.302 e/Å^3 with an RMS deviation of 0.040 e/Å^3. On the basis of the final model, the calculated density was 1.388 g/cm^3 and F(000), 672 e^-. CCDC Nr.: 2150837.
Figure S5: Crystal structure of compound 6. Thermal ellipsoids are shown at 30% probability.

X-ray crystal structure analysis of 11c (STU10262): A colorless, prism-like specimen of C_{29}H_{24}O_{6}, approximate dimensions 0.103 mm x 0.162 mm x 0.229 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Mo ImS (MoKα, λ = 0.71073 Å) and a MX mirror monochromator. A total of 704 frames were collected. The total exposure time was 3.91 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 25697 reflections to a maximum θ angle of 27.50° (0.77 Å resolution), of which 5265 were independent (average redundancy 4.881, completeness = 99.5%, R_{int} = 4.18%, R_{sig} = 2.94%) and 4435 (84.24%) were greater than 2σ(F²). The final cell constants of a = 8.4379(3) Å, b = 9.3205(2) Å, c = 15.1745(4) Å, α = 93.4920(10)°, β = 104.5430(10)°, γ = 90.5840(10)°, volume = 1152.62(6) Å³, are based upon the refinement of the XYZ-centroids of 7614 reflections above 20 σ(I) with 5.559° < 2θ < 54.95°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.953. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9790 and 0.9900. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P-1, with Z = 2 for the formula unit, C_{29}H_{24}O_{6}. The final anisotropic full-matrix least-squares refinement on F² with 319 variables converged at R1 = 3.94%, for the observed data and wR2 = 10.34% for all data. The goodness-of-fit was 1.055. The largest peak in the final difference electron density synthesis was 0.372 e/Å³ and the largest hole was -0.224 e/Å³ with an RMS deviation of 0.045 e/Å³. On the basis of the final model, the calculated density was 1.350 g/cm³ and F(000), 492 e⁻. CCDC Nr.: 2150839.
Figure S6: Crystal structure of compound 11c. Thermal ellipsoids are shown at 30% probability.
10. NMR Spectra of Products

$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 1f
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 1h
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 1m
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 1n
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 1o
\(^1\)H NMR (300 MHz, CDCl\(_3\)), \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) and \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) spectra of product 3a
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of product 3b
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of product 3c
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of product 3d
$^1$H NMR (300 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (282 MHz, CDCl$_3$) spectra of product 3e
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of product 3f
$^{1}$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of product 3g
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of product 3h
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of product 3i
$^1$H NMR (300 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (282 MHz, CDCl$_3$) spectra of product 3j
$^1$H NMR (500 MHz, CDCl$_3$), $^{13}$C NMR (125 MHz, CDCl$_3$) and $^{19}$F NMR (470 MHz, CDCl$_3$) spectra of product 3k
$^1$H NMR (300 MHz, CDCl$_3$), $^{13}$C NMR (75 MHz, CDCl$_3$) and $^{19}$F NMR (282 MHz, CDCl$_3$) spectra of product 3l
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of product 3m
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of product 3n

3m

3n
$^1$H NMR (400 MHz, C$_6$D$_6$), $^{13}$C NMR (100 MHz, C$_6$D$_6$) and $^{19}$F NMR (376 MHz, C$_6$D$_6$) spectra of product 3o
$^1$H NMR (400 MHz, $C_6D_6$), $^{13}$C NMR (100 MHz, $C_6D_6$) and $^{19}$F NMR (376 MHz, $C_6D_6$) spectra of product 3p
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of product 3q
**1H NMR (300 MHz, CDCl₃), 13C NMR (100 MHz, CDCl₃) and 19F NMR (282 MHz, CDCl₃) spectra of product 3r**
1H NMR (400 MHz, CDCl₃), 13C NMR (100 MHz, CDCl₃) and 19F NMR (282 MHz, CDCl₃) spectra of product 3s
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (282 MHz, CDCl$_3$) spectra of product 3t
$^1$H NMR (600 MHz, CDCl$_3$), $^{13}$C NMR (150 MHz, CDCl$_3$) and $^{19}$F NMR (564 MHz, CDCl$_3$) spectra of product 3u
$^1$H NMR (600 MHz, CDCl$_3$), $^{13}$C NMR (150 MHz, CDCl$_3$) and $^{19}$F NMR (564 MHz, CDCl$_3$) spectra of product 3v
$^1$H NMR (300 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (282 MHz, CDCl$_3$) spectra of product 3w
1H NMR (300 MHz, CDCl₃), 13C NMR (100 MHz, CDCl₃) and 19F NMR (282 MHz, CDCl₃) spectra of product 3x.
$^{1}$H NMR (300 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (282 MHz, CDCl$_3$) spectra of product 3y
$\text{H NMR (300 MHz, CDCl}_3$, $^{13}\text{C NMR (100 MHz, CDCl}_3$ and $^{19}\text{F NMR (282 MHz, CDCl}_3$ spectra of product 3z}
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of product 3aa
$^1$H NMR (300 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (282 MHz, CDCl$_3$) spectra of product 3ab
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of product 3ac
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (282 MHz, CDCl$_3$) spectra of product 3ad
$^{1}$H NMR (300 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (282 MHz, CDCl$_3$) spectra of product 3ae
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (282 MHz, CDCl$_3$) spectra of product 3af
3af

3af
$^1$H NMR (300 MHz, CDCl$_3$), $^{13}$C NMR (75 MHz, CDCl$_3$) and $^{19}$F NMR (282 MHz, CDCl$_3$) spectra of product 5a
\(^1\)H NMR (600 MHz, \(\text{C}_6\text{D}_6\)), \(^13\)C NMR (150 MHz, \(\text{C}_6\text{D}_6\)) and \(^19\)F NMR (282 MHz, \(\text{C}_6\text{D}_6\)) spectra of product 5b
$^1$H NMR (600 MHz, CDCl$_3$), $^{13}$C NMR (150 MHz, CDCl$_3$) and $^{19}$F NMR (564 MHz, CDCl$_3$) spectra of product 6
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (150 MHz, CDCl$_3$) spectra of product 7
$^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of product 8
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 11a
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) and $^{19}$F NMR (376 MHz, CDCl$_3$) spectra of product 11b.
$^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 11c
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