A denitrogenative palladium-catalyzed cascade for regioselective synthesis of fluorenes

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S1
1. General considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All arylation reactions were performed in resealable screw-capped Schlenk tube (approx. 20 mL volume) in the presence of Teflon-coated magnetic stirrer bar (4 mm × 10 mm). 1,4-Dioxane was distilled from sodium benzophenone ketyl under nitrogen. DPPF, PPh2, K2CO3, Na2CO3 and Cs2CO3 were purchased from Aldrich. XPhos, cataCXium A, PPh2-DavePhos and Pd(OAc)2 were purchased from Strem. PPh3, P(4-OMePh)3 and PCy3 were purchased from Acros. Hydrazones were prepared using a general procedure as described in the literature.1 Commercially available aryl halides and benzoic acid derivatives were used as received. Thin layer chromatography was performed on Merck precoated silica gel 60 F254 plates. Silica gel (Merck, 70-230 and 230-400 mesh) was used for column chromatography. Melting points were recorded on an uncorrected Büchi Melting Point B-545 instrument. 1H NMR spectra were recorded on a Bruker (500 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in CDCl3 (δ 7.26 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. 13C NMR spectra were referenced to CDCl3 (δ 77.00 ppm, the middle peak). 31P NMR spectra were referenced to 85% H3PO4 externally. Coupling constants (J) were reported in Hertz (Hz). Mass spectra (EI-MS and ES-MS) were recorded on a HP 5989B Mass Spectrometer. High-resolution mass spectra (HRMS) were obtained on a Brüker APEX 47e FTICR mass spectrometer (ESIMS). GC-MS analysis was conducted on a HP 5973 GCD system using a HP5MS column (30 m × 0.25 mm). The products described in GC yield were accorded to the authentic samples/dodecane calibration standard from HP 6890 GC-FID system. All yields reported refer to isolated yield of compounds estimated to be greater than 95% purity as determined by capillary gas chromatography (GC) or 1H NMR. Compounds described in the literature were characterized by comparison of their 1H, and or 13C NMR spectra to the previously reported data. The procedures in this section are representative, and thus the yields may differ from those reported in tables.
2. General procedures and data for ligand and reaction condition screenings

General procedure for reaction optimization (Table 1, S1-3): (2-Bromobenzylidene)hydrazine (47.8 mg, 0.24 mmol), Pd(OAc)$_2$ (4.5 mg, 0.02 mmol), ligand (0.05 mmol) and base (0.6 mmol) were loaded to a Schlenk tube equipped with a Teflon-coated stir bar and screw cap. The tube was carefully evacuated and backfilled with nitrogen for three cycles. Norbornene (28 mg, 0.3 mmol) was added under a stream of nitrogen purging from the Schlenk line and 2-Iodotoluene (26 µL, 0.2 mmol), solvent (0.1 M, 2.0 mL) were added by syringe. The tube was placed into a preheated oil bath (130 °C) and stirred for 18 h. After completion of reaction, the reaction tube was allowed to reach room temperature. Ethyl acetate (~3 mL), dodecane (45 µL, internal standard), water (~2 mL) were added. The organic layer was subjected to GC analysis. The GC yield was previously calibrated by authentic sample/dodecane calibration curve.

A benchmarking reaction has been shown in Table S1 and we initiated the optimization with a survey of phosphine ligands. PCyPh$_2$ (Table S1, entry 2) was found to have the optimal balance of electron richness and steric hindrance, giving the highest yield in this comparison. More electron rich (Table S1, entry 1, 6) and electron-deficient ligands (Table S1, entry 7, 11) were poor performers in this survey. Bulky (Table S1, entry 4, 12-15) or bidentate (Table S1, entry 16) ligands gave low yields (13-45%) in general. A wild range of strong and mild bases promoted the reaction (Table S2, entry 1, 3-6, 9-10) while K$_2$CO$_3$ has been chosen due to its economic attractiveness and ease of handling. Na$_2$CO$_3$, Na$_3$PO$_4$ and K$_2$HPO$_4$ gave low yields (5-10%, Table S2, entry 2, 7-8), which is presumably due to their low solubility in toluene. Several solvents with a high boiling point were screened and DMF proved to be the best solvent (Table S2, entry 12). The stoichiometries of reagents were also optimized as shown in Table S3. 1.5 equiv of norbornene and 1.2 equiv of hydrazone 2a was found to provide the highest product yield (80%, Table S3, entry 1).
**Table S1. Phosphine ligand screening**

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<th>Entry</th>
<th>Ligand</th>
<th>% Yield</th>
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<tr>
<td>1</td>
<td>PCy$_3$</td>
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<tr>
<td>2</td>
<td>PCyPh$_2$</td>
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<tr>
<td>3</td>
<td>PPh$_3$</td>
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<td>5</td>
<td>P(2-pyridyl)Ph$_2$</td>
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</tr>
<tr>
<td>6</td>
<td>P(4-OMePh)$_3$</td>
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<td>9</td>
<td>P(2-MePh)$_3$</td>
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<tr>
<td>10</td>
<td>P(2-furyl)$_3$</td>
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<tr>
<td>14</td>
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<td>16</td>
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*Reaction conditions: 10 mol% Pd(OAc)$_2$, 25 mol% ligand, 2-iodotoluene (0.2 mmol), (2-bromobenzylidene)hydrazine (0.24 mmol), norbornene (0.3 mmol), K$_2$CO$_3$ (0.6 mmol), toluene (0.1 M, 2 mL), 130 °C for 18 h under N$_2$. DPPF = 1,1’-bis(diphenylphosphino)ferrocene, cataCXium A = di(1-adamantyl)-n-butylphosphine, XPhos = 2-Dicyclohexylphosphino-2’,4’,6’-triisopropylbiphenyl, PPh$_2$-DavePhos = 2-dicyclohexylphosphino-2’-(N,N-dimethylamino)biphenyl, cataCXium ABn = Di(1-adamantyl)benzylphosphine. Calibrated GC-FID yields were reported.*
Table S2. Screening of solvent and base\textsuperscript{a}

![Chemical structure](image)

<table>
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<td>1,4-dioxane</td>
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\textsuperscript{a}Reaction conditions: \(\text{Pd(OAc)}\textsubscript{2}\) (10 mol\%), PCyPh\textsubscript{2} (25 mol\%), 2-iodotoluene (0.2 mmol), (2-bromobenzylidene)hydrazine (0.24 mmol), norbornene (0.3 mmol), base (0.6 mmol), solvent (0.1 M, 2 mL), 130 °C for 18 h under \(\text{N}_2\). \textsuperscript{b}Calibrated GC-FID yields were reported.
Table S3. Stoichiometry screening of reagentsa

<table>
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<th>Entry</th>
<th>Equiv of norbornene</th>
<th>Equiv of 2a</th>
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<td>6</td>
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<td>79</td>
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aReaction conditions: Pd(OAc)2 (10 mol%), PCyPh2 (25 mol%), 2-iodotoluene (0.2 mmol), (2-bromobenzylidene)hydrazine, norbornene, K2CO3 (0.6 mmol), DMF (0.1 M, 2 mL), 130 °C for 18 h under N2. bCalibrated GC-FID yields were reported. cReaction at 110 °C.

3. General procedures for regioselective synthesis of fluorenes

General procedure for regioselective synthesis of fluorenes: Norbornene (141 mg, 1.5 mmol), Pd(OAc)2 (22.5 mg, 0.1 mmol) and PCyPh2 (67.1 mg, 0.25 mmol) were dissolved in DMF (10.0 mL, 5.0 mol% Pd per 2.0 mL stock solution) under N2 and stirred for 5 minutes to give a light yellow milky solution. 2-Bromoaryl aldehyde hydrazone derivatives (0.24 mmol), aryl halide (if solid, 0.2 mmol) and K2CO3 (82.8 mg, 0.6 mmol) were loaded to a Schlenk tube equipped with a Teflon-coated stir bar and screw cap. The tube was carefully evacuated and backfilled with nitrogen for three cycles. Aryl halide (if liquid, 0.2 mmol) and stock solution (0.1 M, 2.0 mL) were added by syringe and the tube was placed into a preheated oil bath (130 °C) and stirred for 18 h. After completion of reaction, the reaction tube was allowed to reach room temperature. Ethyl acetate (~4 mL) and water (~3 mL) were added. The organic layer was separated and the aqueous layer was washed with ethyl acetate. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford the desired product.
4. Procedure for gram-scale reaction

General procedure for gram-scale synthesis: Pd(OAc)$_2$ (224.5 mg, 1 mmol), PCyPh$_2$ (670 mg, 2.5 mmol), (2-bromobenzylidene)hydrazine (2388 mg, 12 mmol) and K$_2$CO$_3$ (4140 mg, 30 mmol) were loaded to a Schlenk flask (500 mL) equipped with a Teflon-coated stir bar and screw cap. The tube was carefully evacuated and backfilled with nitrogen for three cycles. Norbornene (1410 mg, 15 mmol) was then added under a stream of nitrogen purging from the Schlenk line. 2-Iodotoluene (1300 µL, 10 mmol) and DMF (0.1 M, 100 mL) were added by syringe. The mixture was stirred for 2 minutes at room temperature and placed into a preheated oil bath (130 °C) and stirred for 18 h. After completion of reaction, the reaction tube was allowed to reach room temperature. Ethyl acetate (~3 mL), and water (~2 mL) were added. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford the desired product.

5. Procedure for three-component reaction

General procedure for three-component synthesis of fluorenes: Pd(OAc)$_2$ (4.5 mg, 0.02 mmol), PCyPh$_2$ (13.4 mg, 0.05 mmol), 2-bromobenzaldehyde (31 µL, 0.26 mmol) and K$_2$CO$_3$ (82.8 mg, 0.6 mmol) were loaded to a Schlenk tube equipped with a Teflon-coated stir bar and screw cap. The tube was carefully evacuated and backfilled with nitrogen for three cycles. Norbornene (28 mg, 0.3 mmol) was then added under a stream of nitrogen purging from the Schlenk line. 2-Iodotoluene (26 µL, 0.2 mmol), hydrazine hydrate (13 mg, 0.26 mmol) and DMF (0.1 M, 2.0 mL) were added by syringe. The tube was stirred for 5 minutes at room temperature and placed into a preheated oil bath (130 °C) and stirred for 18 h. After completion of reaction, the reaction tube was allowed to reach room temperature. Ethyl acetate (~3 mL), and water (~2 mL) were added. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford the desired product.
6. Procedure and NMR data for deuterium labelling study

Procedure for deuterium labelling study (Scheme S1A): Deuterium-labelled 2-bromobenzaldehyde was prepared according to reported literature procedure. Deuterium labelled 2-bromobenzaldehyde hydrazone (48 mg, 0.24 mmol) and K$_2$CO$_3$ (82.8 mg, 0.6 mmol) were loaded to a Schlenk tube equipped with a Teflon-coated stir bar and screw cap. The tube was carefully evacuated and backfilled with nitrogen for three cycles. Norbornene (28 mg, 0.3 mmol) was then added under a stream of nitrogen purging from the Schlenk line. 2-Iodotoluene (26 μL, 0.2 mmol) and DMF (0.1 M, 2.0 mL) were added by syringe. The tube was stirred for 5 minutes at room temperature and placed into a preheated oil bath (130 °C) and stirred for 18 h. After completion of reaction, the reaction tube was allowed to reach room temperature. Ethyl acetate (~3 mL), and water (~2 mL) were added. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford a white powder (17.0 mg, 47% yield).

When deuterium labelled hydrazone A was tested under the standard reaction conditions, less than 10% deuterium was incorporated at the methylene position (Scheme S1A). The decreased yield of 47% might indicate a more difficult C-D activation of the hydrazone carbon at palladacycle C. However, the C9-proton of fluorene is weakly acidic and could undergo H/D exchange under basic conditions. We have prepared deuterium-labelled fluorene B by adding 20 equiv of D$_2$O into the standard reaction mixture (Scheme S1B). Treating B with 3 equiv of water and K$_2$CO$_3$ gave 3a with less than 15% deuterium incorporation (Scheme S1C). When the reaction was carried out in DMF-d$_7$, no H/D exchange was observed at C9-H (Scheme S1D).

Scheme S1 Deuterium labelling study
7. Characterization data for coupling products

1-Methyl-9H-fluorene (Table 2, entry 3a)

Yield: 81% (29.2 mg); \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 2.45 (s, 3H), 3.81 (s, 2H), 7.16 (d, \(J = 7.4\) Hz, 1H), 7.30 – 7.38 (m, 2H), 7.40 (t, \(J = 7.4\) Hz, 1H), 7.59 (d, \(J = 7.4\) Hz, 1H), 7.67 (d, \(J = 7.6\) Hz, 1H), 7.81 (d, \(J = 7.5\) Hz, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 19.0, 35.9, 117.4, 120.0, 125.0, 126.6, 126.7, 127.1, 127.8, 134.3, 141.4, 142.1, 142.1, 143.1.

1,3-Dimethyl-9H-fluorene (Table 2, entry 3b)

Yield: 80% (31.0 mg); White solid; Melting point 86.6 – 88.6 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 2.42 (s, 3H), 2.47 (s, 3H), 3.77 (s, 2H), 6.99 (s, 1H), 7.32 (t, \(J = 7.4\) Hz, 1H), 7.40 (t, \(J = 7.4\) Hz, 1H), 7.49 (s, 1H), 7.58 (d, \(J = 7.4\) Hz, 1H), 7.79 (d, \(J = 7.4\) Hz, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 18.8, 21.4, 35.4, 117.9, 119.8, 125.0, 126.4, 126.6, 128.7, 133.8, 136.6, 139.1, 141.5, 142.0, 143.5; HRMS: calcd. for C\(_{15}\)H\(_{14}\) [M+H]\(^+\): 195.1168 found 195.1169.

1-Methoxy-9H-fluorene (Table 2, entry 3c)

Yield: 76% (29.8 mg); Light yellow solid; Melting point 47.8 – 49.4 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 3.88 (s, 2H), 3.97 (s, 3H), 6.87 (d, \(J = 8.0\) Hz, 1H), 7.34 (t, \(J = 7.4\) Hz, 1H), 7.37 – 7.43 (m, 2H), 7.46 (d, \(J = 7.5\) Hz, 1H), 7.60 (d, \(J = 7.4\) Hz, 1H), 7.81 (d, \(J = 7.5\) Hz, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 34.3, 55.3, 108.6, 112.7, 120.1, 125.1, 126.6, 126.7, 128.4, 130.5, 141.8, 143.4, 143.4, 156.3; HRMS: calcd. for C\(_{14}\)H\(_{13}\)O [M+H]\(^+\): 197.0961 found 197.0961.
1,3-Dimethoxy-9H-fluorene (Table 2, entry 3d)

Yield: 70% (31.6 mg); Light yellow solid; Melting point 64.5 – 66.0 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 3.77 (s, 2H), 3.90 (s, 3H), 3.91 (s, 3H), 6.46 (d, $J = 1.8$ Hz, 1H), 6.96 (d, $J = 1.8$ Hz, 1H), 7.32 (t, $J = 7.4$ Hz, 1H), 7.38 (t, $J = 7.4$ Hz, 1H), 7.56 (d, $J = 7.4$ Hz, 1H), 7.74 (d, $J = 7.5$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 33.7, 55.4, 55.7, 96.3, 97.5, 119.9, 123.2, 125.1, 126.5, 126.7, 141.7, 143.6, 144.1, 156.8, 161.0; HRMS: calcd. for C$_{15}$H$_{15}$O$_2$ [M+H]$^+$: 227.1067 found 227.1067.

1-Isopropyl-9H-fluorene (Table 2, entry 3e)

Yield: 79% (32.9 mg); White solid; Melting point 47.8 – 49.4 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 1.39 (s, 3H), 1.40 (s, 3H), 3.25 (hept, $J = 6.9$ Hz, 1H), 3.94 (s, 2H), 7.29 (d, $J = 7.4$ Hz, 1H), 7.35 (t, $J = 7.4$ Hz, 1H), 7.39 – 7.48 (m, 2H), 7.61 (d, $J = 7.4$ Hz, 1H), 7.70 (d, $J = 7.4$ Hz, 1H), 7.84 (d, $J = 7.5$ Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 23.1, 31.1, 35.5, 117.5, 119.9, 123.2, 124.9, 126.6, 126.7, 127.5, 140.7, 141.5, 142.2, 143.0, 145.1; HRMS: calcd. for C$_{16}$H$_{17}$ [M+H]$^+$: 209.1325 found 209.1324.

1-Trifluoromethyl-9H-fluorene (Table 2, entry 3f)

Yield: 48% (22.5 mg); Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) δ 4.09 (s, 2H), 7.32 – 7.45 (m, 2H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.53 – 7.63 (m, 2H), 7.82 (d, $J = 7.4$ Hz, 1H), 7.95 (d, $J = 7.5$ Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 36.1, 120.1, 123.1, 123.3, 125.0, 125.6, 127.0, 127.2, 127.7, 140.1, 140.6, 142.9, 143.4; HRMS: calcd. for C$_{14}$H$_8$F$_3$ [M-H]$^-$: 233.0584 found 233.0584.
1-Phenyl-9H-fluorene (Table 2, entry 3g)

Yield: 58% (28.1 mg); \(^1^H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 3.99 (s, 2H), 7.29 – 7.38 (m, 2H), 7.38 – 7.46 (m, 2H), 7.46 – 7.56 (m, 4H), 7.59 (d, \(J = 7.2\) Hz, 2H), 7.83 (d, \(J = 7.5\) Hz, 1H), 7.85 (d, \(J = 7.7\) Hz, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 36.8, 118.9, 120.0, 124.8, 126.7, 126.8, 127.2, 127.3, 127.4, 128.5, 128.5, 139.1, 140.9, 141.1, 141.5, 142.1, 143.2.

3-Fluoro-1-methyl-9H-fluorene (Table 2, entry 3h)

Yield: 76% (30.1 mg); White solid; Melting point 68.7 – 71.0 °C; \(^1^H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.40 (s, 3H), 3.72 (s, 2H), 6.85 (dd, \(J = 10.2, 2.4\) Hz, 1H), 7.29 (dd, \(J = 8.7, 2.4\) Hz, 1H), 7.34 (td, \(J = 7.4, 1.2\) Hz, 1H), 7.39 (t, \(J = 7.5\) Hz, 1H), 7.56 (d, \(J = 7.4\) Hz, 1H), 7.73 (d, \(J = 7.5\) Hz, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 18.9 (d, \(J = 1.7\) Hz), 35.2, 104.2 (d, \(J = 22.9\) Hz), 114.4 (d, \(J = 22.7\) Hz), 120.2, 125.0, 126.8, 127.1, 135.7 (d, \(J = 8.6\) Hz), 137.2 (d, \(J = 2.2\) Hz), 141.3 (d, \(J = 3.3\) Hz), 142.9 (d, \(J = 9.4\) Hz), 143.8, 162.7 (d, \(J = 242.5\) Hz); HRMS: calcd. for C\(_{14}\)H\(_{12}\)F \([M+H]^+\): 199.0918 found 199.0918.

2-Fluoro-1-methyl-9H-fluorene (Table 2, entry 3i)

Yield: 70% (26.9 mg); White solid; Melting point 93.0 – 95.1 °C; \(^1^H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.35 (d, \(J = 1.7\) Hz, 3H), 3.78 (s, 2H), 7.07 (t, \(J = 9.1\) Hz, 1H), 7.29 (t, \(J = 7.4\) Hz, 1H), 7.38 (t, \(J = 7.4\) Hz, 1H), 7.51 – 7.59 (m, 2H), 7.72 (d, \(J = 7.5\) Hz, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 11.4 (d, \(J = 4.0\) Hz), 35.9 (d, \(J = 3.1\) Hz), 113.8 (d, \(J = 24.2\) Hz), 117.9 (d, \(J = 9.1\) Hz), 119.5, 121.4 (d, \(J = 18.7\) Hz), 124.9, 126.1, 126.8, 137.0 (d, \(J = 2.6\) Hz), 141.4, 142.9 (d, \(J = 2.0\) Hz), 144.5 (d, \(J = 5.8\) Hz), 160.6 (d, \(J = 243.3\) Hz); HRMS: calcd. for C\(_{14}\)H\(_{12}\)F \([M+H]^+\): 199.0918 found 199.0918.
**11H-Benz[a]fluorene (Table 2, entry 3j)**

![11H-Benz[a]fluorene](image)

Yield: 59% (25.5 mg); \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 4.18 (s, 2H), 7.35 (t, \(J = 7.4\) Hz, 1H), 7.43 (t, \(J = 7.4\) Hz, 1H), 7.48 (t, \(J = 7.5\) Hz, 1H), 7.56 (t, \(J = 7.5\) Hz, 1H), 7.64 (d, \(J = 7.4\) Hz, 1H), 7.85 (d, \(J = 7.4\) Hz, 1H), 7.89 (d, \(J = 8.4\) Hz, 1H), 7.91 – 7.98 (m, 2H), 8.02 (d, \(J = 8.2\) Hz, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 35.6, 118.7, 119.6, 124.0, 124.9, 125.3, 126.3, 126.4, 126.8, 127.8, 128.9, 130.7, 132.8, 138.9, 139.8, 142.6, 143.3.

**11H-Indeno[2,1-f]quinoline (Table 2, entry 3k)**

![11H-Indeno[2,1-f]quinoline](image)

Yield: 48% (20.8 mg); Light brown solid; Melting point 125.4 – 128.3 °C; \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.13 (s, 2H), 7.34 (t, \(J = 7.4\) Hz, 1H), 7.40 – 7.43 (m, 2H), 7.61 (d, \(J = 7.5\) Hz, 1H), 7.83 (d, \(J = 7.5\) Hz, 1H), 8.09 – 8.13 (m, 2H), 8.28 (dd, \(J = 8.5\), 1.2 Hz, 1H), 8.89 (dd, \(J = 4.3\), 1.5 Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 35.2, 119.9, 121.3, 122.0, 124.9, 125.7, 126.7, 127.0, 129.2, 132.2, 139.5, 139.6, 141.8, 143.3, 147.9, 149.6; HRMS: calcd. for C\(_{16}\)H\(_{12}\)N [M+H]\(^{+}\): 218.0964 found 218.0964.

**11H-Indeno[2,1-a]pyrene (Table 2, entry 3l)**

![11H-Indeno[2,1-a]pyrene](image)

Yield: 62% (36.0 mg); Yellow solid; Melting point 209.8 – 213.3 °C; \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.54 (s, 3H), 4.35 (s, 2H), 7.22 (d, \(J = 7.9\) Hz, 1H), 7.58 (d, \(J = 7.5\) Hz, 1H), 7.87 (s, 1H), 7.97 (t, \(J = 7.6\) Hz, 1H), 8.04 (d, \(J = 8.9\) Hz, 1H), 8.09 – 8.20 (m, 5H), 8.50 (s, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 21.6, 35.3, 116.1, 120.9, 123.8, 124.0, 124.9, 125.1, 125.1, 125.2, 125.5, 126.8, 127.4, 127.9, 127.9, 128.1, 130.9, 131.0, 131.1, 136.6, 138.3, 139.7, 140.7, 142.4; HRMS: calcd. for C\(_{24}\)H\(_{17}\) [M+H]\(^{+}\): 305.1324 found 305.1323.
1,3,6,7-Tetramethoxy-9H-fluorene (Table 2, entry 3m)

Yield: 58% (33.2 mg); Light yellow solid; Melting point 139.6 – 141.3 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 3.67 (s, 2H), 3.89 (s, 3H), 3.90 (s, 3H), 3.94 (s, 3H), 3.99 (s, 3H), 6.39 (d, $J = 2.0$ Hz, 1H), 6.83 (d, $J = 2.0$ Hz, 1H), 7.08 (s, 1H), 7.22 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 33.6, 55.3, 55.7, 56.1, 56.2, 95.7, 96.4, 103.0, 108.3, 122.9, 134.2, 136.6, 144.0, 148.5, 148.8, 156.5, 161.0; HRMS: calcd. for C$_{17}$H$_{18}$O$_4$Na [M+Na]$^+$: 309.1097 found 309.1095.

1,3,7-Trimethoxy-9H-fluorene (Table 2, entry 3n)

Yield: 65% (33.3 mg); Light yellow solid; Melting point 140.1 – 143.0 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 3.73 (s, 2H), 3.87 (s, 3H), 3.90 (s, 3H), 3.90 (s, 3H), 6.39 (d, $J = 2.0$ Hz, 1H), 6.86 (d, $J = 2.0$ Hz, 1H), 6.92 (dd, $J = 8.4$, 2.4 Hz, 1H), 7.10 (d, $J = 2.5$ Hz, 1H), 7.62 (d, $J = 8.4$ Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 33.8, 55.3, 55.5, 55.6, 95.8, 110.6, 112.7, 120.4, 122.3, 134.7, 143.5, 145.9, 156.6, 159.3, 161.0; HRMS: calcd. for C$_{16}$H$_{17}$O$_3$ [M+H]$^+$: 257.1172 found 257.1174.

1-Isopropyl-6-methyl-9H-fluorene (Table 2, entry 3o)

Yield: 90% (40.0 mg); White solid; Melting point 88.2 – 90.5 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 1.31 (s, 3H), 1.32 (s, 3H), 2.44 (s, 3H), 3.16 (hept, $J = 6.9$ Hz, 1H), 3.81 (s, 2H), 7.09 (d, $J = 7.6$, 1H), 7.20 (d, $J = 7.2$ Hz, 1H), 7.34 (t, $J = 7.6$ Hz, 1H), 7.40 (d, $J = 7.6$ Hz, 1H), 7.53 – 7.64 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 21.5, 23.0, 31.0, 35.0, 117.3, 120.4, 122.9, 124.5, 127.3, 127.5, 136.2, 140.0, 141.1, 141.5, 142.2, 145.0; HRMS: calcd. for C$_{17}$H$_{19}$ [M+H]$^+$: 223.1481 found 223.1481.
1-Isopropyl-6-(trifluoromethyl)-9H-fluorene (Table 2, entry 3p)

Yield: 60% (33.1 mg); Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 1.34, 1.35 (s, 3H), 3.20 \text{ (hept, } J = 6.9 \text{ Hz, } 1H), 7.31 \text{ (d, } J = 7.6 \text{ Hz, } 1H), 7.42 \text{ (t, } J = 7.6 \text{ Hz, } 1H), 7.63 \text{ (d, } J = 7.9 \text{ Hz, } 1H), 7.69 \text{ (d, } J = 7.6 \text{ Hz, } 1H), 7.80 \text{ (s, } 1H), 7.85 \text{ (d, } J = 8.0 \text{ Hz, } 1H\); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 22.9, 31.1, 35.5, 118.2, 119.9, 121.8, 124.0, 124.4, 125.7, 127.8, 128.5, 140.1, 141.3, 143.2, 145.3, 145.5\); HRMS: calcd. for C\(_{17}\)H\(_{15}\)F\(_3\)[M+H]\(^+\): 276.1120 found 276.1122.

1-(Cyclobutylmethoxy)-7-fluoro-9H-fluorene (Table 2, entry 3q)

Yield: 67% (30.1 mg); Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 1.90 – 2.00 \text{ (m, } 4H), 2.14 – 2.19 \text{ (m, } 2H), 2.78 – 2.87 \text{ (m, } 1H), 3.83 \text{ (s, } 2H), 4.05 \text{ (d, } J = 6.3 \text{ Hz, } 2H), 6.80 \text{ (dd, } J = 6.4, 2.5 \text{ Hz, } 1H), 7.06 \text{ (td, } J = 8.8, 2.1 \text{ Hz, } 1H), 7.23 – 7.25 \text{ (m, } 1H), 7.31 – 7.35 \text{ (m, } 2H), 7.68 \text{ (dd, } J = 8.6, 5.1 \text{ Hz, } 1H\); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 18.7, 24.8, 34.4 \text{ (d, } J = 2.3 \text{ Hz), 34.8, 71.9, 109.5, 112.2, 112.3 \text{ (d, } J = 22.7 \text{ Hz), 113.7 \text{ (d, } J = 22.9 \text{ Hz), 120.8 \text{ (d, } J = 8.8 \text{ Hz), 128.5, 130.7, 137.9, 142.5, 145.6 \text{ (d, } J = 8.6 \text{ Hz), 155.9, 162.5 \text{ (d, } J = 245.0 \text{ Hz); HRMS: calcd. for C}_{18}\text{H}_{18}\text{F}[M+H]^+: 269.1336 found 269.1340.}

8-Fluoro-1,3-dimethyl-9H-fluorene (Table 2, entry 3r)

Yield: 83% (35.2 mg); White solid; Melting point 76.4 – 77.8 \(^\circ\)C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 2.40 \text{ (s, } 3H), 2.45 \text{ (s, } 3H), 3.76 \text{ (s, } 2H), 6.93 – 7.05 \text{ (m, } 2H), 7.35 \text{ (td, } J = 7.8, 5.0 \text{ Hz, } 1H), 7.45 \text{ (s, } 1H), 7.53 \text{ (d, } J = 7.5 \text{ Hz, } 1H\); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 18.7, 21.4, 31.9, 113.0 \text{ (d, } J = 20.7 \text{ Hz), 115.7 \text{ (d, } J = 3.2 \text{ Hz), 118.4, 128.7 \text{ (d, } J = 6.9 \text{ Hz), 128.8, 129.4, 134.1, 136.9, 138.8, 140.7 \text{ (d, } J = 2.5 \text{ Hz), 145.4 \text{ (d, } J = 6.5 \text{ Hz), 159.7 \text{ (d, } J = 246.3 \text{ Hz); HRMS: calcd. for C}_{15}\text{H}_{14}\text{F}[M+H]^+: 213.1074 found 213.1074.}

S16
7-Fluoro-1,3-dimethyl-9H-fluorene (Table 2, entry 3s)

Yield: 80% (33.9 mg); Light yellow solid; Melting point 105.5 – 107.2°C; $^1$H NMR (500 MHz, CDCl$_3$) δ 2.38 (s, 3H), 2.44 (s, 3H), 3.71 (s, 2H), 6.95 (s, 1H), 7.07 (td, $J = 8.9$, 2.4 Hz, 1H), 7.24 (dd, $J = 9.0$, 2.3 Hz, 1H), 7.40 (s, 1H), 7.67 (dd, $J = 8.3$, 5.1 Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 18.7, 21.4, 35.5 (d, $J = 2.5$ Hz), 112.2 (d, $J = 22.7$ Hz), 113.7 (d, $J = 22.9$ Hz), 117.7, 120.6 (d, $J = 8.9$ Hz), 128.4, 133.8, 136.9, 138.0 (d, $J = 2.3$ Hz), 138.9 (d, $J = 2.1$ Hz), 140.6, 145.5 (d, $J = 8.4$ Hz), 162.2 (d, $J = 243.9$ Hz); HRMS: calcd. for C$_{15}$H$_{14}$F$^+$: 213.1074 found 213.1073.

8-Isopropyl-9H-fluoreno[2,3-d][1,3]dioxole (Table 2, entry 3t)

Yield: 80% (40.3 mg); Light yellow solid; Melting point 113.2 – 115.2°C; $^1$H NMR (500 MHz, CDCl$_3$) δ 1.33 (s, 3H), 1.34 (s, 3H), 3.16 (hept, $J = 6.9$ Hz, 1H), 3.77 (s, 2H), 6.01 (s, 2H), 7.02 (s, 1H), 7.17 (d, $J = 7.6$ Hz, 1H), 7.22 (s, 1H), 7.35 (t, $J = 7.6$ Hz, 1H), 7.49 (d, $J = 7.4$ Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 23.0, 30.9, 35.3, 100.5, 101.1, 105.6, 116.4, 122.0, 127.4, 135.9, 136.7, 140.7, 141.5, 144.7, 147.0, 147.1; HRMS: calcd. for C$_{17}$H$_{17}$O$_2$$^+$: 253.1223 found 253.1223.

7,9-Dimethyl-10H-fluoreno[1,2-d][1,3]dioxole (Table 2, entry 3u)

Yield: 80% (38.1 mg); Light yellow solid; Melting point 166.4 – 169.4°C; $^1$H NMR (500 MHz, CDCl$_3$) δ 2.37 (s, 3H), 2.42 (s, 3H), 3.69 (s, 2H), 6.02 (s, 2H), 6.87 (d, $J = 7.9$ Hz, 1H), 6.92 (s, 1H), 7.25 (d, $J = 7.9$ Hz, 1H), 7.36 (s, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 18.7, 21.4, 31.7, 101.0, 107.2, 112.7, 117.6, 123.2, 128.2, 133.9, 136.8, 138.1, 138.2, 141.1, 143.5, 146.6; HRMS: calcd. for C$_{16}$H$_{15}$O$_2$$^+$: 239.1067 found 239.1068.
6-Fluoro-7-methoxy-1,3-dimethyl-9H-fluorene (Table 2, entry 3v)

![Image of 6-Fluoro-7-methoxy-1,3-dimethyl-9H-fluorene](image)

Yield: 63% (38.1 mg); White solid; Melting point 136.1 – 138.3 ºC; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.36 (s, 3H), 2.42, (s, 3H), 3.66 (s, 2H), 3.94 (s, 3H), 6.92, (s, 1H), 7.14 (d, \(J = 7.8\) Hz, 1H), 7.30 (s, 1H), 7.41 (d, \(J = 11.1\) Hz, 1H); \(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 18.7, 21.4, 35.4, 55.5, 107.5 (d, \(J = 19.8\) Hz), 110.1 (d, \(J = 1.7\) Hz), 117.4, 128.1, 133.7, 134.9 (d, \(J = 7.6\) Hz), 136.9, 139.1, 139.1 (d, \(J = 3.3\) Hz), 140.9 (d, \(J = 2.6\) Hz), 146.7 (d, \(J = 11.8\) Hz), 152.3 (d, \(J = 243.2\) Hz); HRMS: calcd. for C\(_{16}\)H\(_{16}\)FO [M+Na]\(^+\): 243.1180 found 243.1183.

1-Isopropyl-7-((3-methylbenzyl)oxy)-9H-fluorene (Table 2, entry 3w)

Yield: 66% (43.3 mg); Light yellow solid; Melting point 68.0 – 69.5 ºC; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.35 (s, 3H), 1.37 (s, 3H), 2.42 (s, 3H), 3.19 (hept, \(J = 6.9\) Hz, 1H), 3.87 (s, 2H), 5.11 (s, 2H), 7.03 (dd, \(J = 8.4, 2.4\) Hz, 1H), 7.14 – 7.24 (m, 3H), 7.30 – 7.37(m, 3H), 7.37 (s, 1H), 7.57 (dd, \(J = 7.5, 1.0\) Hz, 1H), 7.69 (d, \(J = 8.3\) Hz, 1H); \(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 21.4, 23.0, 31.0, 35.6, 70.3, 111.5, 113.7, 116.7, 120.5, 122.1, 124.6, 127.4, 128.2, 128.5, 128.7, 135.4, 137.0, 138.2, 140.1, 141.4, 144.7, 144.8, 158.4; HRMS: calcd. for C\(_{24}\)H\(_{25}\)O [M+H]\(^+\): 329.1900 found 329.1905.

6-Chloro-1-methyl-9H-fluorene (Table 2, entry 3x)

Yield: 48% (20.6 mg); White solid; Melting point 85.5 – 89.0 ºC; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.42 (s, 3H), 3.75 (s, 2H), 7.16 (d, \(J = 7.5\) Hz, 1H), 7.24 – 7.28 (m, 1H), 7.32 (t, \(J = 7.5\) Hz, 1H), 7.46 (d, \(J = 8.0\) Hz, 1H), 7.60 (d, \(J = 7.6\) Hz, 1H), 7.73 (d, \(J = 1.9\) Hz, 1H); \(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 18.9, 35.5, 117.6, 120.2, 126.0, 126.5, 127.3, 128.4, 132.7, 134.4, 140.2, 141.2, 142.5, 143.8; HRMS: calcd. for C\(_{14}\)H\(_{10}\)Cl [M-H]: 213.0477 found 213.0478.
2-(2-((6,8-Dimethyl-9\textit{H}-fluoren-2-yl)oxy)ethyl)-1,3-dioxane (Table 2, entry 3y)

Yield: 74\% (48.0 mg); Yellow solid; Melting point 149.5 – 152.2 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.30 – 1.50 (m, 1H), 2.07 – 2.20 (m, 3H), 2.37 (s, 3H), 2.43 (s, 3H), 3.70 (s, 2H), 3.82 (td, \(J = 12.3, 2.4\) Hz, 2H), 4.10 – 4.24 (m, 4H), 4.84 (t, \(J = 5.2\) Hz, 1H), 6.90 (s, 1H), 6.93 (dd, \(J = 8.3, 2.4\) Hz, 1H), 7.12 (d, \(J = 2.3\) Hz, 1H), 7.36 (s, 1H), 7.63 (d, \(J = 8.2\) Hz, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 18.8, 21.4, 25.8, 35.2, 35.5, 63.5, 66.9, 99.5, 111.2, 113.3, 117.2, 120.4, 127.6, 133.6, 135.0, 136.6, 138.5, 141.4, 145.2, 158.3; HRMS: calcd. for C\(_{21}\)H\(_{24}\)O\(_3\)Na [M+Na]\(^+\): 347.1618 found 347.1616.

(8\textit{R},9\textit{S},13\textit{S},14\textit{S})-3-((9\textit{H}-fluoren-1-yl)methoxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[\textit{a}]phenanthrene-17,2'-[1,3]dioxolane] (Table 2, entry 3z)

Yield: 76\% (45.3 mg); Light orange solid; Melting point 96.7 – 102.6 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 0.89 (s, 3H), 1.27 – 1.49 (m, 5H), 1.61 – 1.67 (m, 1H), 1.75 – 1.87 (m, 3H), 1.88 – 1.92 (m, 1H), 2.00 – 2.06 (m, 1H), 2.23 – 2.27 (m, 1H), 2.31 – 2.34 (m, 1H), 2.85 – 2.88 (m, 2H), 3.88 – 3.98 (m, 6H), 5.18, (s, 2H), 6.76 (d, \(J = 2.6\) Hz, 1H), 6.82 (dd, \(J = 8.0\) Hz, 1H), 7.23 (d, \(J = 8.6\) Hz, 1H), 7.31 (td, \(J = 7.4, 0.9\) Hz, 1H), 7.36 – 7.43 (m, 3H), 7.55 (d, \(J = 7.4\) Hz, 1H), 7.78 (dd, \(J = 7.1, 1.2\) Hz, 1H), 7.80, (d, \(J = 7.5\)Hz, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 14.1, 14.4, 22.4, 22.7, 26.2, 27.0, 29.9, 30.7, 31.6, 34.3, 35.6, 39.1, 43.7, 46.2, 49.4, 64.6, 65.3, 68.6, 112.2, 114.7, 119.5, 119.7, 120.0, 125.0, 126.3, 126.4, 126.8, 126.9, 127.3, 133.1, 133.4, 138.2, 141.5, 141.8, 142.2, 143.1, 156.7; HRMS: calcd. for C\(_{34}\)H\(_{37}\)O\(_3\) [M+H]\(^+\): 493.2737 found 493.2740.
8,8’-(Oxybis(methylene))bis(3-methyl-9H-fluorene) (Scheme 1, compound 4)

Yield: 51% (41.1 mg); Light orange solid; Melting point 174.0 – 176.6 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.47 (s, 6H), 3.84 (s, 4H), 4.75 (s, 4H), 7.13 (d, $J = 7.6$ Hz, 1H), 7.4 (d, $J = 7.3$ Hz, 1H), 7.38 – 7.43 (m, 4H), 7.62 (s, 2H), 7.74 (d, $J = 7.3$ Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 21.5, 35.1, 70.4, 119.3, 120.5, 124.7, 126.3, 127.1, 127.7, 134.3, 136.3, 140.2, 141.7, 142.0, 142.2; HRMS: calcd. for C$_{30}$H$_{26}$ONa [M+Na]$^+$: 425.1876 found 425.1876.

8. References


9. $^1$H and $^{13}$C NMR spectra
$^1$H NMR and $^{13}$C NMR spectra for 1-Methyl-9$H$-fluorene (Table 2, entry 3a)
$[^1]H$ NMR and $[^13]C$ NMR spectra for 1,3-Dimethyl-9H-fluorene (Table 2, entry 3b)
$^1$H NMR and $^{13}$C NMR spectra for 1-Methoxy-9H-fluorene (Table 2, entry 3c)
$^1$H NMR and $^{13}$C NMR spectra for 1,3-Dimethoxy-9H-fluorene (Table 2, entry 3d)
$^1$H NMR and $^{13}$C NMR spectra for 1-Isopropyl-9H-fluorene (Table 2, entry 3e)
$^1$H NMR and $^{13}$C NMR spectra for 1-Trifluoromethyl-9$H$-fluorene (Table 2, entry 3f)
$^1$H NMR and $^{13}$C NMR spectra for 1-Phenyl-9H-fluorene (Table 2, entry 3g)
$^{1}$H NMR and $^{13}$C NMR spectra for 3-Fluoro-1-methyl-9H-fluorene (Table 2, entry 3h)
$^{1}$H NMR and $^{13}$C NMR spectra for 2-Fluoro-1-methyl-9H-fluorene (Table 2, entry 3i)
$^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra for $11H$-Benzo[a]fluorene (Table 2, entry 3j)
¹H NMR and ¹³C NMR spectra for 11H-Indeno[2,1-f]quinoline (Table 2, entry 3k)
$^{1}H$ NMR and $^{13}$C NMR spectra for $11H$-Indeno[2,1-a]pyrene (Table 2, entry 3)
$^{1}$H NMR and $^{13}$C NMR spectra for 1,3,6,7-Tetramethoxy-9H-fluorene (Table 2, entry 3m)
$^1$H NMR and $^{13}$C NMR spectra for 1,3,7-Trimethoxy-9$H$-fluorene (Table 2, entry 3n)
H NMR and $^{13}$C NMR spectra for 1-Isopropyl-6-methyl-9$H$-fluorene (Table 2, entry 3o)
$^1$H NMR and $^{13}$C NMR spectra for 1-Isopropyl-6-(trifluoromethyl)-9H-fluorene (Table 2, entry 3p)
$^1$H NMR and $^{13}$C NMR spectra for 1-(Cyclobutylmethoxy)-7-fluoro-9H-fluorene (Table 2, entry 3q)
$^1$H NMR and $^{13}$C NMR spectra for 8-Fluoro-1,3-dimethyl-9H-fluorene (Table 2, entry 3r)
\(^1\)H NMR and \(^{13}\)C NMR spectra for 7-Fluoro-1,3-dimethyl-9\(H\)-fluorene (Table 2, entry 3s)
$^{1}$H NMR and $^{13}$C NMR spectra for 8-Isopropyl-9H-fluoreno[2,3-d][1,3]dioxole (Table 2, entry 3t)
$^1$H NMR and $^{13}$C NMR spectra for 7,9-Dimethyl-10H-fluoreno[1,2-d][1,3]dioxole (Table 2, entry 3u)
\(^1\)H NMR and \(^{13}\)C NMR spectra for 6-Fluoro-7-methoxy-1,3-dimethyl-9H-fluorene (Table 2, entry 3v)
$^1$H NMR and $^{13}$C NMR spectra for 1-Isopropyl-7-((3-methylbenzyl)oxy)-9H-fluorene (Table 2, entry 3w)
\(^1\)H NMR and \(^{13}\)C NMR spectra for 6-Chloro-1-methyl-9\(H\)-fluorene (Table 2, entry 3x)
$^{\text{1}}$H NMR and $^{\text{13}}$C NMR spectra for 2-(2-((6,8-Dimethyl-9H-fluoren-2-yl)oxy)ethyl)-1,3-dioxane (Table 2, entry 3y)
$^1$H NMR and $^{13}$C NMR spectra for (8\textit{R},9\textit{S},13\textit{S},14\textit{S})-3-((9\textit{H}-fluoren-1-yl)methoxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[\textit{a}]phenanthrene-17,2'-[1,3]dioxolane] (Table 2, entry 3z)
$^1$H NMR and $^{13}$C NMR spectra for 8,8'-(Oxybis(methylene))bis(3-methyl-9H-fluorene) (Scheme 1, compound 4)