Supporting Information

Catalytic Ortho C-H Methylation and Trideuteromethylation of Arylthianthrenium Salts via the Catellani Strategy

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**General Information:**

The $^1$H NMR, $^{13}$C NMR, $^{19}$F NMR and $^{31}$P NMR were recorded with Bruker 400 MHz spectrometer instruments in CDCl$_3$. The chemical shifts ($\delta$) of $^1$H NMR, $^{13}$C NMR, $^{19}$F NMR and $^{31}$P NMR were measured in ppm, referenced to residual $^1$H and $^{13}$C signals of nondeuterated CDCl$_3$ ($\delta = 7.26$ and $77.00$) as internal standards. All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of products was accomplished by flash chromatography using silica gel (200–300 mesh). Thin layer chromatography (TLC) was performed on Merck silica gel GF254 plates and visualized by UV-light (254 nm). Melting points were obtained on a Yanaco-241 apparatus and are uncorrected. HRMS were recorded on Agilent 6520 Q-TOF mass spectrometer with ESI resource.

**General Procedure for the Synthesis of Substrates:**

1. **General Procedure for the Synthesis of Aryl Thianthrenes**

   (1)

   A 50 mL two-necked flask was charged with thianthrene S-oxide (TTSO, 5.0 mmol, 1.0 equiv), DCM (10.0 mL) and arenes (5.0 mmol, 1.0 equiv) under a nitrogen atmosphere. The reaction mixture was then cooled to -40 °C and stirred at this temperature. Tf$_2$O (6.0 mmol, 1.2 equiv) was added dropwise. The reaction mixture was stirred at -40 °C for 1 h, and then allowed to stir at room temperature for 12 h, neutralized by a saturated NaHCO$_3$ solution, and extracted with DCM. The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from DCM/MTBE system as a white solid.
A 50 mL two-necked flask was charged with thianthrene S-oxide (TTSO, 5.0 mmol, 1.0 equiv), DCM (10.0 mL) and arenes (5.0 mmol, 1.0 equiv) under a nitrogen atmosphere. The reaction mixture was then cooled to -40 °C and stirred at this temperature, trifluoroacetic anhydride (TFAA, 15.0 mmol, 3.0 equiv) and trifluoromethanesulfonic acid (TfOH, 7.5 mmol, 1.5 equiv) were added dropwise. The reaction mixture was stirred at 40 °C for 1 h, and then allowed to stir at room temperature for 12 h, neutralized by a saturated aqueous NaHCO₃ solution, and extracted with DCM. Drying of organic phase with anhydrous Na₂SO₄, and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from DCM/MTBE system as a white solid.
A 50 mL two-necked flask was charged with thianthrene S-oxide (TTSO, 5.0 mmol, 1.0 equiv), DCM (10.0 mL) and Flurbiprofen (5.0 mmol, 1.0 equiv) under a nitrogen atmosphere. The reaction mixture was then cooled to -40 °C and stirred at this temperature. Tf$_2$O (6.0 mmol, 1.2 equiv) was added dropwise. The reaction mixture was stirred at -40 °C for 1 h, and then allowed to stir at room temperature for 12 h, extracted with DCM. The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from DCM/MTBE system as a white solid.

In a 38 mL sealed tube, the mixture of (4-(methoxycarbonyl)phenyl)boronic acid (3.0 mmol, 1.0 equiv), thianthrene (TT, 4.5 mmol, 1.5 equiv), Cu(OTf)$_2$ (6.0 mmol, 2.0 equiv), H$_2$O (6.0 mmol, 2.0 equiv) were added in 3.0 mL MeCN. Then, the tube was purged with N$_2$ for three times and sealed with PTFE cap. The reaction mixture was heated to 100 °C for 3 h. After cooling to room temperature, the reaction mixture was added into ammonia solution (50 mL, 25%–28% solution in water), and the water phase was extracted with DCM (3 x 30 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from DCM/Et$_2$O system as a white solid.

2. General Procedure for the Synthesis of Activated Olefins

In a 50 mL round bottom flask, acryloyl chloride (6.0 mmol, 1.2 equiv) was added dropwise to a solution of corresponding alcohols and amines (5.0 mmol, 1.0 equiv) and Et$_3$N (7.5 mmol, 1.5 equiv) in DCM (10.0 mL) at 0 °C. After the addition was
complete, the ice bath was removed, and the reaction mixture was stirred at room temperature. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the reaction mixture was diluted with water and extracted with DCM. The combined organic layer was washed with saturated aqueous NaHCO$_3$. The organic extract was dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the activated olefins.

\[
\text{Indoline (5.0 mmol, 1.0 equiv) was dissolved in THF (10.0 mL) in a 50 mL two-necked flask, K}_2\text{CO}_3 (10.0 \text{ mmol, 2.0 equiv}) was added and the mixture was cooled to 0 \^\circ\text{C under a nitrogen atmosphere. Acryloyl chloride (5.5 mmol, 1.1 equiv) was added dropwise via syringe with rapid stirring. The formation of a white precipitate was immediately observed. After the addition was complete, the mixture was stirred vigorously for 20 min, then poured into a large beaker of water (100.0 mL) cooled in an ice-water bath. The aqueous mixture was stirred slowly for 1 h under an open atmosphere and solid NaCl (approximately 2.0 g) was added to enhance precipitation. When a large amount of white precipitate was visible, the solid was collected by filtration, air dried for 2 h and dried under vacuum overnight to give 1-(indolin-1-yl)prop-2-en-1-one as an off-white solid.}
\]

**Experimental Procedure:**

**General procedure A:** In a 38 mL sealed tube, the mixture of 1 (0.2 mmol, 1.0 equiv), 2 (0.4 mmol, 2.0 equiv), 3 (0.4 mmol, 2.0 equiv), Pd(OAc)$_2$ (10 mol%), P(4-CF$_3$-C$_6$H$_4$)$_3$ (25 mol%), N1 (0.2 mmol, 1.0 equiv), Cs$_2$CO$_3$ (0.6 mmol, 3.0 equiv) were added in 2.0 mL PhCF$_3$/MeCN (1:1). Then, the tube was purged with N$_2$ for
three times and sealed with PTEF cap. The reaction mixture was heated to 80 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give the products 4a-4e, 4g-4i, 40, 4q-4r, 4a-d3-4c-d3.

The same procedure as General procedure A except changing the amount of 3 to 0.2 mmol (1.0 equiv) give the products 4f, 4j-4n, 4p, 4s-4d3, 4af-4al, 4an-4d3, 4am-4d3.

General procedure B: In a 38 mL sealed tube, the mixture of 1 (0.2 mmol, 1.0 equiv), 2 (0.8 mmol, 4.0 equiv), 3 (0.4 mmol, 2.0 equiv), Pd(OAc)2 (10 mol%), P(4-CF3-C6H4)3 (25 mol%), N1 (0.4 mmol, 2.0 equiv), Cs2CO3 (0.6 mmol, 3.0 equiv) were added in 2.0 mL PhCF3/MeCN (1:1). Then, the tube was purged with N2 for three times and sealed with PTEF cap. The reaction mixture was heated to 80 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give the products 4a, 4t-4z, 4aa-4ae, 4m, 4n, 4a-d6, 4t-d6, 4ac-d6, 4u-d6, 4w-d6, 4aa-d6, 4ad-d6, 4ae-d6, 4al, 4ao, 4ap, 4as.

The same procedure as General procedure B except changing the amount of 3 to 0.2 mmol (1.0 equiv) give the products 4m, 4n, 4ag-d6, 4aq, 4ar-d6.

General procedure C: In a 38 mL sealed tube, the mixture of 1 (0.2 mmol, 1.0 equiv), 2 (0.4 mmol, 2.0 equiv), MeB(OH)2 (0.4 mmol, 2.0 equiv), Pd(OAc)2 (10 mol%), P(4-CF3-C6H4)3 (25 mol%), N1 (0.2 mmol, 1.0 equiv), Cs2CO3 (0.6 mmol, 3.0 equiv) were added in 2.0 mL PhCF3/MeCN (1:1). Then, the tube was purged with N2 for three times and sealed with PTEF cap. The reaction mixture was heated to 80 °C.
for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give the product 5.

The same procedure as General procedure C except changing the amount of 2 to 0.8 mmol (4.0 equiv) and N1 to 0.4 equiv (2.0 equiv) give the products 6, 4at, 4at-d9.

**General procedure D:** In a 38 mL sealed tube, the mixture of 1a (0.2 mmol, 1.0 equiv), 2-7 (0.3 mmol, 1.5 equiv), MeB(OH)2 (0.4 mmol, 2.0 equiv), Pd(OAc)2 (10 mol%), P(4-CF3-C6H4)3 (25 mol%), N1 (0.2 mmol, 1.0 equiv), Cs2CO3 (0.6 mmol, 3.0 equiv) were added in 2.0 mL PhCF3/MeCN (1:1). Then, the tube was purged with N2 for three times and sealed with PTFE cap. The reaction mixture was heated to 80 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give the product 7.

**General procedure E:** In a 38 mL sealed tube, the mixture of 1a (0.2 mmol, 1.0 equiv), nBuI (0.4 mmol, 2.0 equiv), MeB(OH)2 (0.4 mmol, 2.0 equiv), Pd(OAc)2 (10 mol%), P(4-CF3-C6H4)3 (25 mol%), N1 (0.2 mmol, 1.0 equiv), Cs2CO3 (0.6 mmol, 3.0 equiv) were added in 2.0 mL PhCF3/MeCN (1:1). Then, the tube was purged with N2 for three times and sealed with PTFE cap. The reaction mixture was heated to 80 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give the product 8.

**Control Experiments:**
1. One-pot C-H methylation:

A 25 mL two-necked flask was charged with thianthrene S-oxide (TTSO, 0.2 mmol, 1.0 equiv), DCM (1.0 mL) and 1,3-dimethylbenzene (0.2 mmol, 1.0 equiv) under a nitrogen atmosphere. The reaction mixture was then cooled to -40 °C and stirred at this temperature, trifluoroacetic anhydride (TFAA, 0.6 mmol, 3.0 equiv) and trifluoromethanesulfonic acid (TfOH, 0.3 mmol, 1.5 equiv) were added dropwise. The reaction mixture was stirred at 40 °C for 0.5 h, and then allowed to stir at room temperature for 12 h. The mixture was concentrated to dryness under reduced pressure to give the crude product of **1a**.

In a 38 mL sealed tube, the mixture of the crude product of **1a**, **2a** (0.4 mmol, 2.0 equiv), **3a** (0.4 mmol, 2.0 equiv), Pd(OAc)$_2$ (10 mol%), P(4-CF$_3$-C$_6$H$_4$)$_3$ (25 mol%), **N1** (0.2 mmol, 1.0 equiv), Cs$_2$CO$_3$ (1.0 mmol, 5.0 equiv) were added in 2.0 mL PhCF$_3$/MeCN (1:1). Then, the tube was purged with N$_2$ for three times and sealed with PTEF cap. The reaction mixture was heated to 80 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give product **4a** in 85% yield.

2. Competition experiments:

(1)

In a 38 mL sealed tube, the mixture of **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv), **2b** (0.4 mmol, 2.0 equiv), ethyl acrylate (0.4 mmol, 0.2 equiv), Pd(OAc)$_2$
(10 mol%), P(4-CF_3-C_6H_4)_3 (25 mol%), N_1 (0.2 mmol, 1.0 equiv), Cs_2CO_3 (0.6 mmol, 3.0 equiv) were added in 2.0 mL PhCF_3/MeCN (1:1). Then, the tube was purged with N_2 for three times and sealed with PTFE cap. The reaction mixture was heated to 80 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give a mixture of 4a and 4a-d_3. ^1H NMR was carried out by adding 1,3,5-trimethoxybenzene (0.2 mmol, 1.0 equiv) as an internal standard in a mixture of 4a and 4a-d_3. (the ^1H NMR spectrum of the crude product is shown below).

In a 38 mL sealed tube, the mixture of 1a (0.2 mmol, 1.0 equiv), 2a (0.4 mmol, 2.0 equiv), 3a (0.4 mmol, 0.2 equiv), 3r (0.4 mmol, 0.2 equiv), Pd(OAc)_2 (10 mol%),
P(4-CF₃-C₆H₄)₃ (25 mol%), N1 (1.0 equiv), Cs₂CO₃ (0.6 mmol, 3.0 equiv) were added in 2.0 mL PhCF₃/MeCN (1:1). Then, the tube was purged with N₂ for three times and sealed with PTFE cap. The reaction mixture was heated to 80 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give a mixture of 4a and 4r. ¹H NMR was carried out by adding 1,3,5-trimethoxybenzene (0.2 mmol, 1.0 equiv) as an internal standard in a mixture of 4a and 4r. (the ¹H NMR spectrum of the crude product is shown below).

Characterization of Products:

(E)-3-(2,4,6-trimethylphenyl) ethyl acrylate(4a)\[^{11}\]

\[
\text{CH}_3
\begin{array}{c}
\text{CH}_2
\end{array}
\text{CO}_2\text{Et}
\]

Yield: 96%, 41.9 mg; appearance: white solid, M.P.: 35-36 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 16.4 Hz, 1H), 6.90 (s, 2H), 6.06 (d, J = 16.4 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 2.33 (s, 6H), 2.29 (s, 3H), 1.35 (t, J = 6.8 Hz).
Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.91, 143.07, 138.15, 136.71, 130.85, 129.05, 123.08, 60.35, 20.99, 20.93, 14.24.

($E$)-3-(2,4-dimethoxy-6-methylphenyl) ethyl acrylate(4b)$^{[2]}$

\[
\text{OMe} \quad \text{MeO} \quad 4b \quad \text{CO}_2\text{Et}
\]

Yield: 71%, 35.5 mg; appearance: white solid, M.P.: 68-70 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 (d, $J = 16.0$ Hz, 1H), 6.61 (d, $J = 16.0$ Hz, 1H), 6.36 – 6.32 (m, 2H), 4.24 (q, $J = 6.8$ Hz, 2H), 3.84 (s, 3H), 3.80 (s, 3H), 2.43 (s, 3H), 1.32 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.51, 161.09, 160.93, 141.42, 138.25, 119.06, 115.18, 107.50, 96.17, 60.01, 55.29, 55.16, 21.45, 14.31.

($E$)-3-(8-methoxy-6-methylquinolin-5-yl) ethyl acrylate(4c)

\[
\text{MeO} \quad 4c \quad \text{CO}_2\text{Et}
\]

Yield: 75%, 40.7 mg; appearance: yellow solid, M.P.: 108-109 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.84 – 8.82 (m, 1H), 8.36 – 8.33 (m, 1H), 8.03 (d, $J = 16.0$ Hz, 1H), 7.40 – 7.36 (m, 1H), 6.85 (s, 1H), 6.11 (d, $J = 16.0$ Hz, 1H), 4.27 (q, $J = 7.2$ Hz, 2H), 4.04 (s, 3H), 2.49 (s, 3H), 1.32 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.54, 155.10, 148.28, 140.78, 138.94, 136.15, 132.82, 127.55, 124.67, 122.48, 121.90, 110.60, 60.58, 55.93, 21.46, 14.24.

ESI-MS: Calcd for C$_{16}$H$_{17}$NO$_3$: [M+H$^+$] 272.1281, found 272.1284.

($E$)-3-(2,4,6-trimethylphenyl) cyclohexyl acrylate(4d)

\[
\text{CO}_2\text{Cy} \quad 4d
\]
Yield: 83%, 45.2 mg; appearance: white solid, M.P.: 72-73 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.83 (d, $J$ = 16.4 Hz, 1H), 6.89 (s, 2H), 6.05 (d, $J$ = 16.4 Hz, 1H), 4.94 – 4.87 (m, 1H), 2.34 (s, 6H), 2.29 (s, 3H), 1.97 – 1.92 (m, 2H), 1.81 – 1.75 (m, 2H), 1.64 – 1.36 (m, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.45, 142.79, 138.13, 136.78, 130.99, 129.09, 123.67, 72.68, 31.73, 25.43, 23.80, 21.07, 20.99.

ESI-MS: Calcd for C$_{18}$H$_{24}$O$_2$: [M+H$^+$] 273.1849, found 273.1848.

(E)-3-(2,4,6-trimethylphenyl) tert butyl acrylate(4e)

Yield: 85%, 41.9 mg; appearance: colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.75 (d, $J$ = 16.4 Hz, 1H), 6.89 (s, 2H), 5.98 (d, $J$ = 16.0 Hz, 1H), 2.33 (s, 6H), 2.28 (s, 3H), 1.55 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.40, 142.00, 138.01, 136.79, 131.04, 129.05, 124.82, 80.41, 28.21, 21.13, 21.01.

(E)-3-(2,4,6-trimethylphenyl) phenyl acrylate(4f)

Yield: 94%, 50.1 mg; appearance: white solid, M.P.: 60-62 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.96 (d, $J$ = 16.4 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.18 – 7.08 (m, 3H), 6.83 (s, 2H), 6.19 (d, $J$ = 16.4 Hz, 1H), 2.30 (s, 6H), 2.21 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.34, 150.83, 145.11, 138.73, 137.06, 130.53, 129.35, 129.29, 125.68, 122.02, 121.61, 21.16, 21.03.

(E)-3-(2,4,6-trimethylphenyl) Benzyl acrylate(4g)
Yield: 66%, 37.0 mg; appearance: colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 16.4$ Hz, 1H), 7.35 – 7.22 (m, 5H), 6.79 (s, 2H), 6.02 (d, $J = 16.4$ Hz, 1H), 5.17 (s, 2H), 2.24 (s, 6H), 2.18 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.18, 143.75, 138.38, 136.87, 136.05, 130.75, 129.16, 128.55, 128.26, 128.20, 122.64, 66.29, 21.10, 21.01.

ESI-MS: Calcd for C$_{19}$H$_{20}$O$_2$: [M+H$^+$] 281.1536, found 281.1537.

(Z)-2-fluoro-3-(2,4,6-trimethylphenyl) methyl acrylate(4h)

Yield: 60%, 26.7 mg; appearance: yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.06 (d, $J = 35.6$ Hz, 1H), 6.91 (s, 2H), 3.91 (s, 3H), 2.29 (s, 3H), 2.24 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.46 (d, $J = 35.0$ Hz), 146.38 (d, $J = 262.0$ Hz), 138.33, 136.59, 128.35, 126.30, 116.98 (d, $J = 11.0$ Hz), 52.64, 21.02, 20.33 (d, $J = 3.0$ Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -121.82 (s).

ESI-MS: Calcd for C$_{13}$H$_{15}$FO$_2$: [M+H$^+$] 223.1129, found 223.1128.

(E)-3-(2,4,6-trimethylbenzylidene)dihydrofuran-2(3H)-one/3-(2,4,6-trimethylbenzyl)furan-2(5H)-one(4i)

Yield: 53%, 22.9 mg; appearance: white solid, M.P.: 98-99 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65 (s, 1H), 6.90 (s, 2H), 6.88 (s, 1.6H), 6.61 (s,
0.8H), 4.73 (s, 1.6H), 4.38 (t, J = 7.2 Hz, 2H), 3.55 (s, 1.6H), 2.68 (td, J = 7.2, 2.4 Hz, 2H), 2.29 (s, 3H), 2.28 (s, 2.4H), 2.20 (s, 4.8H), 2.18 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 174.07, 171.21, 144.73, 137.86, 137.19, 136.32, 136.19, 135.29, 133.04, 131.15, 131.04, 128.98, 128.36, 127.80, 70.33, 65.52, 26.52, 25.56, 20.96, 20.81, 20.00, 19.75.

ESI-MS: Calcd for C$_{14}$H$_{16}$O$_2$: [M+H$^+$] 217.1223, found 217.1224.

(E)-N,N-diethyl-3-(2,4,6-trimethylphenyl) acrylamide(4j)

Yield: 92%, 45.1 mg; appearance: colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.79 (d, J = 16.0 Hz, 1H), 6.90 (s, 2H), 6.42 (d, J = 16.0 Hz, 1H), 3.49 – 3.42 (m, 4H), 2.33 (s, 6H), 2.28 (s, 3H), 1.21 (t, J = 7.2 Hz, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.61, 140.71, 137.53, 136.41, 132.41, 128.88, 123.13, 42.18, 41.09, 21.04, 20.97, 15.06, 13.28.

ESI-MS: Calcd for C$_{16}$H$_{23}$NO: [M+H$^+$] 246.1852, found 246.1852.

(E)-1-(indolin-1-yl)-3-mesitylprop-2-en-1-one(4k)

Yield: 84%, 49.0 mg; appearance: yellow solid, M.P.: 152-154 ºC.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.44 (d, J = 6.4 Hz, 1H), 8.02 (d, J = 16.0 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.09 (t, J = 7.6 Hz, 1H), 6.98 (s, 2H), 6.53 (d, J = 15.6 Hz, 1H), 4.22 (t, J = 8.0 Hz, 2H), 3.25 (s, 2H), 2.44 (s, 6H), 2.36 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.16, 142.94, 141.51, 137.85, 136.52, 131.68, 129.00, 127.40, 124.39, 124.07, 123.69, 117.31, 47.88, 27.82, 21.04, 20.90.

ESI-MS: Calcd for C$_{20}$H$_{21}$NO: [M+H$^+$] 292.1696, found 292.1695.

(E)-N-((3s,5s,7s)-adamantan-1-yl)-3-mesitylacrylamide(4l)
Yield: 71%, 45.9 mg; appearance: white solid, M.P.: 219-220 ºC.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.68 (d, $J = 16.4$ Hz, 1H), 6.86 (s, 2H), 5.94 (d, $J = 16.0$ Hz, 1H), 5.45 (s, 1H), 2.30 (s, 6H), 2.27 (s, 3H), 2.10 (s, 9H), 1.71 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.90, 138.53, 137.40, 136.52, 131.53, 128.85, 126.78, 52.12, 41.65, 36.32, 29.40, 21.04, 22.09.

ESI-MS: Calcd for C$_{22}$H$_{29}$NO: [M+H$^+$] 324.2322, found 324.2318.

(E)-3-mesityl-N-phenylacrylamide(4m)

Yield: 77%, 40.9 mg; appearance: white solid, M.P.: 187-188 ºC.

$^1$H NMR (400 MHz, DMSO-d$_6$) δ 10.17 (s, 1H), 7.72 – 7.66 (m, 3H), 7.34 (t, $J = 8.0$ Hz, 2H), 7.07 (t, $J = 7.6$ Hz, 1H), 6.92 (s, 2H), 6.44 (d, $J = 16.0$ Hz, 1H), 2.31 (s, 6H), 2.23 (s, 3H).

$^{13}$C NMR (100 MHz, DMSO-d$_6$) δ 163.62, 139.32, 138.06, 137.35, 136.32, 130.96, 129.11, 128.86, 126.67, 123.39, 119.20, 20.95, 20.67.

ESI-MS: Calcd for C$_{18}$H$_{19}$NO: [M+H$^+$] 266.1539, found 266.1540.

(E)-1,3,5-trimethyl-2-(2-(phenylsulfonyl)vinyl) benzene(4n)

Yield: 61%, 34.9 mg; appearance: white solid, M.P.: 116-118 ºC.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.97 – 7.94 (m, 2H), 7.87 (d, $J = 16.0$ Hz, 1H), 7.65 – 7.60 (m, 1H), 7.58 – 7.54 (m, 2H), 6.88 (s, 2H), 6.54 (d, $J = 15.6$ Hz, 1H), 2.29 (s, 6H), 2.27 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.81, 140.76, 139.41, 137.06, 133.25, 131.51, 129.37, 129.28, 128.35, 127.47, 21.03, 20.99.

(E)-1-mesitylpent-1-en-3-one(4o)$^{[2]}$

![Image of 4o](image_url)

Yield: 97%, 39.2 mg; appearance: white solid, M.P.: 43-45 ºC.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J$ = 16.8 Hz, 1H), 6.90 (s, 2H), 6.36 (d, $J$ = 16.4 Hz, 1H), 2.70 (q, $J$ = 7.2 Hz, 2H), 2.33 (s, 6H), 2.29 (s, 3H), 1.19 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 200.97, 140.66, 138.29, 136.75, 131.12, 131.01, 129.13, 33.98, 21.04, 20.99, 8.18.

diethyl (E)-(2,4,6-trimethylstyryl) phosphonate(4p)$^{[6]}$

![Image of 4p](image_url)

Yield: 63%, 35.6 mg; appearance: yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (dd, $J$ = 23.6, 18.0 Hz, 1H), 6.88 (s, 2H), 5.86 (dd, $J$ = 20.4, 18.0, Hz, 1H), 4.18 – 4.10 (m, 4H), 2.31 (s, 6H), 2.27 (s, 3H), 1.36 (t, $J$ = 7.2 Hz, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 147.49 (d, $J$ = 6.0 Hz), 138.08, 136.04, 131.98 (d, $J$ = 22.0 Hz), 129.01, 119.96 (d, $J$ = 184.0 Hz), 61.72 (d, $J$ = 5.0 Hz), 20.95, 20.84, 16.38 (d, $J$ = 6.0 Hz).

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 18.77 (s).

1,3,5-trimethyl-2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl) benzene(4q)

![Image of 4q](image_url)

Yield: 62%, 30.8 mg; appearance: yellow oil.
1H NMR (400 MHz, CDCl3) δ 7.46 (d, J = 7.6 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.25 – 7.18 (m, 1H), 7.00 (dd, J = 15.2, 10.4 Hz, 1H), 6.90 (s, 2H), 6.71 (d, J = 16.0 Hz, 1H), 6.60 (d, J = 15.6 Hz, 1H), 6.48 (dd, J = 15.6, 10.4 Hz, 1H), 2.35 (s, 6H), 2.30 (s, 3H).

13C NMR (100 MHz, CDCl3) δ 137.38, 136.32, 136.05, 134.20, 133.62, 131.76, 131.06, 129.77, 128.80, 128.61, 127.39, 126.28, 21.17, 20.95.

ESI-MS: Calcd for C19H20: [M+H+] 249.1638, found 249.1635.

(E)-1,3,5-trimethyl-2-(3-phenylprop-1-en-1-yl) benzene(4r)[7]

Yield: 70%, 33.1 mg; appearance: colorless oil.

1H NMR (400 MHz, CDCl3) δ 7.38 – 7.30 (m, 4H), 7.26 – 7.21 (m, 1H), 6.94 (s, 2H), 6.37 – 6.26 (m, 2H), 3.58 (d, J = 4.0 Hz, 2H), 2.37 (s, 6H), 2.34 (s, 3H).

13C NMR (100 MHz, CDCl3) δ 137.60, 136.60, 135.51, 133.07, 129.81, 128.84, 128.39, 127.67, 126.85, 125.96, 32.55, 20.85, 19.88.

ESI-MS: Calcd for C19H20: [M+H+] 251.1794, found 251.1788.

ethyl (E)-3-(4-isopropyl-2,6-dimethylphenyl)acrylate(4t)

Yield: 53%, 26.5 mg; appearance: colorless oil.

1H NMR (400 MHz, CDCl3) δ 7.39 – 7.36 (m, 2H), 7.34 – 7.29 (m, 2H), 7.24 – 7.20 (m, 1H), 6.87 (s, 2H), 6.47 (d, J = 16.0 Hz, 1H), 6.33 (dt, J = 15.6, 6.8 Hz, 1H), 2.80 – 2.75 (m, 2H), 2.41 – 2.36 (m, 2H), 2.34 (s, 6H), 2.28 (s, 3H).

13C NMR (100 MHz, CDCl3) δ 137.65, 135.94, 135.42, 135.10, 130.34, 129.91, 128.90, 128.50, 126.92, 125.93, 32.62, 29.28, 20.80, 19.80.

ESI-MS: Calcd for C19H22O: [M+H+] 251.1794, found 251.1788.

ethy (E)-3-(4-isopropyl-2,6-dimethylphenyl)acrylate(4t)
Yield: 71%, 35.0 mg; appearance: yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J = 16.4$ Hz, 1H), 6.94 (s, 2H), 6.07 (d, $J = 16.4$ Hz, 1H), 4.28 (q, $J = 7.2$ Hz, 2H), 2.89 – 2.78 (m, 1H), 2.36 (s, 6H), 1.35 (t, $J = 7.2$ Hz, 3H), 1.25 (s, 3H), 1.23 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.02, 149.21, 143.21, 136.87, 131.41, 126.49, 123.23, 60.44, 33.78, 23.81, 21.26, 14.31.

ESI-MS: Calcd for C$_{16}$H$_{22}$O$_2$: [M+H$^+$] 247.1693, found 247.1692.

ethyl (E)-3-(4-cyclohexyl-2,6-dimethylphenyl)acrylate(4u)

Yield: 80%, 45.8 mg; appearance: pink solid, M.P.: 58-59 ºC.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 16.0$ Hz, 1H), 6.93 (s, 2H), 6.07 (d, $J = 16.4$ Hz, 1H), 4.28 (q, $J = 7.2$ Hz, 2H), 2.46 – 2.38 (m, 1H), 2.36 (s, 6H), 1.87 – 1.84 (m, 4H), 1.78 – 1.74 (m, 1H), 1.44 – 1.33 (m, 8H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.00, 148.44, 143.20, 136.80, 131.38, 126.90, 123.16, 60.40, 44.27, 34.25, 26.83, 26.11, 21.24, 14.29.

ESI-MS: Calcd for C$_{19}$H$_{26}$O$_2$: [M+H$^+$] 287.2006, found 287.2005.

ethyl (E)-3-(4-methoxy-2,6-dimethylphenyl)acrylate(4v)

Yield: 55%, 25.8 mg; appearance: white solid, M.P.: 63-64 ºC.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J = 16.4$ Hz, 1H), 6.62 (s, 2H), 6.07 (d, $J = 16.4$ Hz, 1H), 4.27 (q, $J = 7.2$ Hz, 2H), 3.79 (s, 3H), 2.37 (s, 6H), 1.34 (t, $J = 6.8$ Hz, 3H).
**ethyl (E)-3-(2,6-dimethyl-4-phenoxyphenyl)acrylate (4w)**

\[
\text{PhO} \quad 4w
\]

Yield: 61%, 36.2 mg; appearance: yellow oil.

**1H NMR (400 MHz, CDCl\textsubscript{3})** \(\delta 7.82 (d, J = 16.4 \text{ Hz}, 1\text{H}), 7.39 - 7.33 (m, 2\text{H}), 7.16 - 7.11 (m, 1\text{H}), 7.05 - 7.01 (m, 2\text{H}), 6.70 (s, 2\text{H}), 6.06 (d, J = 16.4 \text{ Hz}, 1\text{H}), 4.28 (q, J = 7.2 \text{ Hz}, 2\text{H}), 2.33 (s, 6\text{H}), 1.35 (t, J = 7.2 \text{ Hz}, 3\text{H}).

**13C NMR (100 MHz, CDCl\textsubscript{3})** \(\delta 166.98, 157.10, 156.53, 142.48, 139.07, 129.77, 128.68, 123.58, 123.09, 119.36, 118.00, 60.48, 21.20, 14.27.

**ESI-MS:** Calcd for C\textsubscript{14}H\textsubscript{18}O\textsubscript{3}: [M+H\textsuperscript{+}] 235.1329, found 235.1325.

**ethyl (E)-3-(4-(difluoromethoxy)-2,6-dimethylphenyl)acrylate (4x)**

\[
\text{HF}_2\text{CO} \quad 4x
\]

Yield: 53%, 28.6 mg; appearance: yellow oil.

**1H NMR (400 MHz, CDCl\textsubscript{3})** \(\delta 7.76 (d, J = 16.4 \text{ Hz}, 1\text{H}), 6.82 (s, 2\text{H}), 6.50 (t, J = 73.6 \text{ Hz}, 1\text{H}), 6.04 (d, J = 16.4 \text{ Hz}, 1\text{H}), 4.28 (q, J = 6.8 \text{ Hz}, 2\text{H}), 2.34 (s, 6\text{H}), 1.35 (t, J = 6.8 \text{ Hz}, 3\text{H}).

**13C NMR (100 MHz, CDCl\textsubscript{3})** \(\delta 166.61, 150.59 (t, J = 3.0 \text{ Hz}), 142.08, 138.87, 131.19, 124.25, 118.73, 115.78 (t, J = 258.0 \text{ Hz}), 60.61, 21.20, 14.27.

**19F NMR (376 MHz, CDCl\textsubscript{3})** \(\delta -80.66.

**ESI-MS:** Calcd for C\textsubscript{14}H\textsubscript{16}F\textsubscript{2}O\textsubscript{3}: [M+H\textsuperscript{+}] 271.1140, found 271.1140.

**ethyl (E)-3-(3,4',5-trimethyl-[1,1'-biphenyl]-4-yl)acrylate (4y)**
Yield: 60%, 35.3 mg; appearance: yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J$ = 16.4 Hz, 1H), 7.41 (d, $J$ = 8.0 Hz, 2H), 7.21 (s, 2H), 7.16 (d, $J$ = 7.6 Hz, 2H), 6.04 (d, $J$ = 16.4 Hz, 1H), 4.21 (q, $J$ = 7.2 Hz, 2H), 2.34 (s, 6H), 2.31 (s, 3H), 1.28 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.92, 142.88, 140.97, 137.56, 137.30, 132.59, 129.46, 126.84, 123.65, 60.54, 21.36, 21.11, 14.32.

ESI-MS: Calcd for C$_{20}$H$_{22}$O$_2$: [M+Na$^+$] 317.1512, found 317.1516.

ethyl (E)-3-(4-fluoro-2,6-dimethylphenyl)acrylate(4z)

Yield: 62%, 27.6 mg; appearance: yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J$ = 16.4 Hz, 1H), 6.77 (d, $J$ = 9.6 Hz, 2H), 6.03 (d, $J$ = 16.4 Hz, 1H), 4.28 (q, $J$ = 7.2 Hz, 2H), 2.34 (s, 6H), 1.34 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.71, 161.98 (d, $J$ = 246.0 Hz), 142.23, 139.25 (d, $J$ = 8.0 Hz), 129.91, 123.98, 114.88 (d, $J$ = 20.0 Hz), 60.58, 21.23 (d, $J$ = 1.0 Hz), 14.29.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -114.17.

ESI-MS: Calcd for C$_{13}$H$_{15}$FO$_2$: [M+H$^+$] 223.1129, found 223.1130.

ethyl (E)-3-(4-chloro-2,6-dimethylphenyl)acrylate(4aa)

Yield: 60%, 35.3 mg; appearance: yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J$ = 16.4 Hz, 1H), 6.77 (d, $J$ = 9.6 Hz, 2H), 6.03 (d, $J$ = 16.4 Hz, 1H), 4.28 (q, $J$ = 7.2 Hz, 2H), 2.34 (s, 6H), 1.34 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.71, 161.98 (d, $J$ = 246.0 Hz), 142.23, 139.25 (d, $J$ = 8.0 Hz), 129.91, 123.98, 114.88 (d, $J$ = 20.0 Hz), 60.58, 21.23 (d, $J$ = 1.0 Hz), 14.29.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -114.17.

ESI-MS: Calcd for C$_{13}$H$_{15}$FO$_2$: [M+H$^+$] 223.1129, found 223.1130.
Yield: 70%, 33.4 mg; appearance: colorless oil.

**H NMR (400 MHz, CDCl₃)** δ 7.75 (d, J = 16.0 Hz, 1H), 7.06 (s, 2H), 6.04 (d, J = 16.4 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 2.32 (s, 6H), 1.34 (t, J = 7.2 Hz, 3H).

**C NMR (100 MHz, CDCl₃)** δ 166.55, 142.06, 138.42, 133.59, 132.41, 128.00, 124.38, 60.64, 20.93, 14.26.

**ESI-MS**: Calcd for C₁₃H₁₅IO₂: [M+H⁺] 331.0189, found 331.0190.

**ethyl (E)-3-(4-iodo-2,6-dimethylphenyl)acrylate (4ab)**

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\includegraphics[width=0.2\textwidth]{4ab.png}
\end{center}}
\]
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Yield: 68%, 44.9 mg; appearance: yellow oil.

**H NMR (400 MHz, CDCl₃)** δ 7.72 (d, J = 16.0 Hz, 1H), 7.43 (s, 2H), 6.04 (d, J = 16.4 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 2.29 (s, 6H), 1.34 (t, J = 6.8 Hz, 3H).

**C NMR (100 MHz, CDCl₃)** δ 166.51, 142.18, 138.57, 136.90, 133.63, 124.50, 94.35, 60.66, 20.61, 14.27.

**ESI-MS**: Calcd for C₁₃H₁₅IO₂: [M+H⁺] 331.0189, found 331.0190.

**ethyl (E)-3-(4-((N,4-dimethylphenyl)sulfonamido)-2,6-dimethylphenyl)acrylate (4ac)**

```
\[
\text{\begin{center}
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\end{center}}
\]
```

Yield: 70%, 54.2 mg; appearance: white solid, M.P.: 124-126 ºC.

**H NMR (400 MHz, CDCl₃)** δ 7.70 (d, J = 16.4 Hz, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 7.6 Hz, 2H), 6.74 (s, 2H), 5.98 (d, J = 16.4 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 3.05 (s, 3H), 2.35 (s, 3H), 2.21 (s, 6H), 1.27 (t, J = 6.8 Hz, 3H).

**C NMR (100 MHz, CDCl₃)** δ 166.62, 143.57, 142.28, 141.12, 137.47, 133.63, 132.90, 129.29, 127.86, 125.95, 124.23, 60.59, 37.93, 21.53, 21.11, 14.26.

**ESI-MS**: Calcd for C₂₁H₂₅NO₄S: [M+H⁺] 388.1577, found 388.1576.

**methyl (E)-4-(3-ethoxy-3-oxoprop-1-en-1-yl)-3,5-dimethylbenzoate (4ad)**
Yield: 83%, 43.5 mg; appearance: white solid, M.P.: 52-54 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.77 (d, \(J = 16.4\) Hz, 1H), 7.70 (s, 2H), 6.06 (d, \(J = 16.8\) Hz, 1H), 4.27 (q, \(J = 7.2\) Hz, 2H), 3.88 (s, 3H), 2.35 (s, 6H), 1.33 (t, \(J = 7.2\) Hz, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.79, 166.25, 142.25, 138.64, 136.63, 129.27, 128.96, 125.06, 60.63, 52.00, 20.85, 14.19.

ESI-MS: Calcd for C\(_{15}\)H\(_{18}\)O\(_4\): [M+H\(^+\)] 263.1278, found 263.1274.

\((E)\)-5-cyclohexyl-1,3-dimethyl-2-(3-phenylprop-1-en-1-yl)benzene(4ae)

Yield: 63%, 38.4 mg; appearance: yellow oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.39 – 7.29 (m, 4H), 7.24 (t, \(J = 7.2\) Hz, 1H), 6.97 (s, 2H), 6.38 – 6.29 (m, 2H), 3.59 (d, \(J = 2.8\) Hz, 2H), 2.53 – 2.46 (m, 1H), 2.40 (s, 6H), 1.96 – 1.89 (m, 4H), 1.84 – 1.80 (m, 1H), 1.55 – 1.44 (m, 4H), 1.37 – 1.34 (m, 1H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 145.86, 137.60, 136.49, 133.54, 129.88, 128.38, 127.70, 126.84, 126.59, 125.96, 44.12, 34.49, 32.79, 26.96, 26.20, 20.08.

ESI-MS: Calcd for C\(_{23}\)H\(_{28}\): [M–H\(^–\)] 303.2118, found 303.2124.

ethyl \((E)\)-3-(2,4-dimethyl-6-(methyl-d\(_3\))phenyl)acrylate(4a-d\(_3\))

Yield: 88%, 39.0 mg; appearance: yellow solid, M.P.: 33-35 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, \(J = 16.4\) Hz, 1H), 6.90 (s, 2H), 6.06 (d, \(J = 16.8\) Hz, 1H), 4.27 (q, \(J = 7.2\) Hz, 2H), 3.88 (s, 3H), 2.35 (s, 6H), 1.33 (t, \(J = 7.2\) Hz, 3H).
16.4 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 2.34 (s, 3H), 2.29 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H).

**13C NMR (100 MHz, CDCl₃)** δ 167.00, 143.13, 138.24, 136.80, 136.69, 130.95, 129.11, 123.13, 60.43, 21.05, 21.00, 14.29.

**ESI-MS**: Calcd for C₁₄H₁₅D₃O₂: [M+H⁺] 222.1568, found 222.1569.

**ethyl (E)-3-(2,4-dimethoxy-6-(methyl-d₃)phenyl)acrylate (4b-d₃)**

Yield: 65%, 32.9 mg; appearance: white solid, M.P.: 68-70 °C.

**1H NMR (400 MHz, CDCl₃)** δ 7.88 (d, J = 16.0 Hz, 1H), 6.61 (d, J = 16.4 Hz, 1H), 6.35 (dd, J = 12.0, 2.4 Hz, 2H), 4.25 (q, J = 6.8 Hz, 2H), 3.85 (s, 3H), 3.81 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H).

**13C NMR (100 MHz, CDCl₃)** δ 168.59, 161.15, 160.99, 141.41, 138.33, 119.15, 115.32, 107.53, 96.27, 60.09, 55.38, 55.25, 14.38.

**ESI-MS**: Calcd for C₁₄H₁₅D₃O₄: [M+H⁺] 254.1466, found 254.1465.

**ethyl (E)-3-(8-methoxy-6-(methyl-d₃)quinolin-5-yl)acrylate (4c-d₃)**

Yield: 70%, 38.4 mg; appearance: yellow solid, M.P.: 104-106 °C.

**1H NMR (400 MHz, CDCl₃)** δ 8.87 – 8.85 (m, 1H), 8.40 – 8.36 (m, 1H), 8.07 (d, J = 16.0 Hz, 1H), 7.43 – 7.39 (m, 1H), 6.89 (s, 1H), 6.14 (d, J = 16.4 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 4.08 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H).

**13C NMR (100 MHz, CDCl₃)** δ 166.58, 155.21, 148.35, 140.83, 139.06, 136.06, 132.82, 127.62, 124.71, 122.59, 121.93, 110.63, 60.60, 55.96, 14.28.

**ESI-MS**: Calcd for C₁₆H₁₄D₃NO₃: [M+H⁺] 275.1470, found 275.1469.

**ethyl (E)-3-(4-methyl-2,6-bis(methyl-d₃)phenyl)acrylate (4a-d₆)**
Yield: 71%, 31.9 mg; appearance: yellow solid, M.P.: 36-37 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J = 16.0$ Hz, 1H), 6.90 (s, 2H), 6.05 (d, $J = 16.4$ Hz, 1H), 4.28 (q, $J = 7.6$ Hz, 2H), 2.29 (s, 3H), 1.35 (t, $J = 7.6$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.03, 143.14, 138.27, 136.72, 130.98, 129.13, 123.11, 60.45, 21.02, 14.31.

ESI-MS: Calcd for C$_{14}$H$_{12}$D$_6$O$_2$: [M+H$^+$] 225.1756, found 225.1753.

ethyl (E)-3-(4-isopropyl-2,6-bis(methyl-$d_3$)phenyl)acrylate($4t-d_6$)

Yield: 69%, 34.8 mg; appearance: yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 16.4$ Hz, 1H), 6.94 (s, 2H), 6.07 (d, $J = 16.0$ Hz, 1H), 4.28 (q, $J = 7.2$ Hz, 2H), 2.88 – 2.80 (m, 1H), 1.35 (t, $J = 6.8$ Hz, 3H), 1.26 (s, 3H), 1.24 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.05, 149.22, 143.16, 136.79, 131.39, 126.49, 123.11, 60.45, 33.77, 23.81, 14.30.

ESI-MS: Calcd for C$_{16}$H$_{16}$D$_6$O$_2$: [M+H$^+$] 253.2069, found 253.2067.

ethyl (E)-3-(4-((N,4-dimethylphenyl)sulfonamido)-2,6-bis(methyl-$d_3$)phenyl) acrylate($4ac-d_6$)

Yield: 68%, 53.5 mg; appearance: yellow solid, M.P.: 124-125 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.70 (d, $J = 16.4$ Hz, 1H), 7.40 (d, $J = 8.0$ Hz, 2H),
7.18 (d, $J = 8.4$ Hz, 2H), 6.74 (s, 2H), 5.98 (d, $J = 16.4$ Hz, 1H), 4.20 (q, $J = 7.2$ Hz, 2H), 3.05 (s, 3H), 2.35 (s, 3H), 1.27 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.58, 136.54, 135.21, 134.09, 130.34, 126.57, 125.87, 122.26, 120.81, 118.91, 117.14, 53.55, 30.89, 14.48, 7.22.

ESI-MS: Calcd for C$_{21}$H$_{19}$D$_6$NO$_4$S: [M+H$^+$] 394.1954, found 394.1954.

ethyl (E)-3-(4-cyclohexyl-2,6-bis(methyl-d$_3$)phenyl)acrylate(4u-d$_6$)

Yield: 76%, 44.5 mg; appearance: pink solid, M.P.: 56-58 ºC.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.84 (d, $J = 16.0$ Hz, 1H), 6.92 (s, 2H), 6.06 (d, $J = 16.4$ Hz, 1H), 4.27 (q, $J = 7.2$ Hz, 2H), 2.47 – 2.39 (m, 1H), 1.86 – 1.84 (m, 4H), 1.77 – 1.73 (m, 1H), 1.44 – 1.32 (m, 8H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.04, 148.47, 143.19, 136.74, 131.42, 126.92, 123.11, 60.42, 44.28, 34.26, 26.84, 26.12, 14.31.

ESI-MS: Calcd for C$_{19}$H$_{20}$D$_6$O$_2$: [M+H$^+$] 293.2382, found 293.2380.

ethyl (E)-3-(2,6-bis(methyl-d$_3$)-4-phenoxyphenyl)acrylate(4w-d$_3$)

Yield: 62%, 37.5 mg; appearance: yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.18 (d, $J = 15.6$ Hz, 1H), 7.72 – 7.67 (m, 2H), 7.50 – 7.45 (m, 1H), 7.40 – 7.36 (m, 2H), 7.05 (s, 2H), 6.41 (d, $J = 16.4$ Hz, 1H), 4.63 (q, $J = 7.2$ Hz, 2H), 1.70 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.93, 157.07, 156.45, 142.39, 138.94, 129.72, 128.62, 123.53, 122.92, 119.31, 117.96, 60.42, 14.26.

ESI-MS: Calcd for C$_{19}$H$_{14}$D$_6$O$_3$: [M+H$^+$] 303.1862, found 303.1858.

ethyl (E)-3-(4-chloro-2,6-bis(methyl-d$_3$)phenyl)acrylate(4aa-d$_6$)
Yield: 66%, 32.3 mg; appearance: yellow solid, M.P.: 37-38 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J = 16.4$ Hz, 1H), 7.05 (s, 2H), 6.04 (d, $J = 16.4$ Hz, 1H), 4.27 (q, $J = 7.2$ Hz, 2H), 1.34 (t, $J = 6.8$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.50, 141.97, 138.28, 133.57, 132.38, 127.98, 124.27, 60.58, 14.23.

ESI-MS: Calcd for C$_{13}$H$_8$D$_6$ClO$_2$: [M+H$^+$] 245.1210, found 245.1209.

methyl (E)-4-(3-ethoxy-3-oxoprop-1-en-1-yl)-3,5-bis(methyl-d$_3$)benzoate (4ad-d$_6$)

Yield: 81%, 43.5 mg; appearance: white solid, M.P.: 50-52 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.77 (d, $J = 16.4$ Hz, 1H), 7.70 (s, 2H), 6.06 (d, $J = 16.4$ Hz, 1H), 4.27 (q, $J = 7.2$ Hz, 2H), 3.88 (s, 3H), 1.33 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.79, 166.26, 142.23, 138.67, 136.54, 129.29, 128.99, 125.03, 60.63, 51.99, 14.19.

ESI-MS: Calcd for C$_{15}$H$_{12}$D$_6$O$_4$: [M+H$^+$] 269.1654, found 269.1656.

( E)-5-cyclohexyl-1,3- bis(methyl-d$_3$)-2-(3-phenylprop-1-en-1-yl)benzene(4ae-d$_6$)

Yield: 57%, 35.4 mg; appearance: yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 – 7.26 (m, 4H), 7.22 – 7.17 (m, 1H), 6.92 (s, 2H), 6.34 – 6.26 (m, 2H), 3.55 – 3.53 (m, 2H), 2.48 – 2.41 (m, 1H), 1.92 – 1.85 (m, 4H), 1.80 – 1.75 (m, 1H), 1.53 – 1.42 (m, 4H), 1.40 – 1.35 (m, 1H).
\[^{13}\text{C NMR (100 MHz, CDCl}_3\] \(\delta\) 145.86, 137.61, 136.38, 133.60, 129.87, 128.39, 127.74, 126.84, 126.59, 125.96, 44.13, 34.49, 32.78, 26.96, 26.21.

**ESI-MS:** Calcd for C\(_{23}\)H\(_{22}\)D\(_6\): [M–H\(^+\)] 309.2495, found 309.2500.

\((E)-1,5\text{-dimethyl-3-(methyl-}\text{-d}_3\text{-)}\text{-2-(4-phenylbut-1-en-1-yl)benzene(4s-d}_3\text{)}\)

Yield: 47%, 23.8 mg; appearance: yellow oil.

\[^1\text{H NMR (400 MHz, CDCl}_3\] \(\delta\) 7.37 (d, \(J\) = 7.6 Hz, 2H), 7.31 (t, \(J\) = 7.2 Hz, 2H), 7.21 (t, \(J\) = 7.2 Hz, 1H), 6.87 (s, 2H), 6.46 (d, \(J\) = 16.0 Hz, 1H), 6.37 – 6.29 (m, 1H), 2.80 – 2.75 (m, 2H), 2.40 – 2.35 (m, 2H), 2.33 (s, 3H), 2.27 (s, 3H).

\[^{13}\text{C NMR (100 MHz, CDCl}_3\] \(\delta\) 137.66, 135.96, 135.45, 135.10, 130.35, 129.92, 128.90, 128.50, 126.92, 125.94, 32.64, 29.28, 20.80, 19.79.

**ESI-MS:** Calcd for C\(_{19}\)H\(_{19}\)D\(_3\): [M+H\(^+\)] 254.1983, found 254.1979.

\((1R,2S,5R)-2\text{-isopropyl-5-methylcyclohexyl (E)-3-mesitylacrylate(4af)}\)

Yield: 94%, 61.8 mg; appearance: colorless oil.

\[^1\text{H NMR (400 MHz, CDCl}_3\] \(\delta\) 7.85 (d, \(J\) = 16.4 Hz, 1H), 6.90 (s, 2H), 6.06 (d, \(J\) = 16.0 Hz, 1H), 4.88 – 4.80 (m, 1H), 2.35 (s, 6H), 2.29 (s, 3H), 2.14 – 2.10 (m, 1H), 1.99 – 1.89 (m, 1H), 1.74 – 1.70 (m, 2H), 1.61 – 1.44 (m, 2H), 1.15 – 1.02 (m, 2H), 0.96 – 0.92 (m, 7H), 0.83 (d, \(J\) = 7.2 Hz, 3H).

\[^{13}\text{C NMR (100 MHz, CDCl}_3\] \(\delta\) 166.58, 142.82, 138.16, 136.81, 130.89, 129.12, 123.41, 74.22, 47.12, 41.01, 34.28, 31.39, 26.49, 23.71, 22.02, 21.11, 21.00, 20.66, 16.63.

**ESI-MS:** Calcd for C\(_{22}\)H\(_{32}\)O\(_2\): [M–H\(^+\)] 327.2330, found 327.2335.

\(\text{benzo[d][1,3]dioxol-5-yl (E)-3-mesitylacrylate(4ag)}\)
Yield: 81%, 50.3 mg; appearance: white solid, M.P.: 89-91 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.06 (d, \(J = 16.4\) Hz, 1H), 6.95 (s, 2H), 6.83 (d, \(J = 8.4\) Hz, 1H), 6.75 (d, \(J = 2.4\) Hz, 1H), 6.66 (dd, \(J = 8.4, 2.0\) Hz, 1H), 6.27 (d, \(J = 16.4\) Hz, 1H), 6.01 (s, 2H), 2.41 (s, 6H), 2.33 (s, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.60, 147.93, 145.23, 145.12, 145.09, 138.73, 137.04, 130.46, 129.27, 121.81, 113.91, 107.87, 103.77, 101.61, 21.13, 21.00.

ESI-MS: Calcd for C\(_{19}\)H\(_{18}\)O\(_4\): [M+H\(^+\)] 311.1278, found 311.1277.

(R)-2,5,7,8-tetramethyl-2-((4\(R\),8\(R\))-4,8,12-trimethyltridecyl)chroman-6-yl (E)-3-mesitylacrylate(4ah)

Yield: 75%, 90.4 mg; appearance: colorless oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.13 (d, \(J = 16.4\) Hz, 1H), 6.97 (s, 2H), 6.37 (d, \(J = 16.4\) Hz, 1H), 2.66 (t, \(J = 6.4\) Hz, 2H), 2.45 (s, 6H), 2.35 (s, 3H), 2.17 (s, 3H), 2.13 (s, 3H), 2.09 (s, 3H), 1.92 – 1.78 (m, 2H), 1.65 – 1.52 (m, 4H), 1.49 – 1.40 (m, 4H), 1.31 – 1.26 (m, 7H), 1.22 – 1.10 (m, 7H), 0.93 – 0.89 (m, 14H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.45, 149.32, 144.58, 140.48, 138.54, 136.92, 130.60, 129.26, 126.80, 125.01, 122.97, 121.96, 117.30, 74.94, 39.32, 37.40, 37.24, 32.74, 32.65, 31.07, 27.92, 24.77, 24.41, 22.68, 22.59, 21.16, 21.02, 20.98, 20.58, 19.71, 19.62, 12.97, 12.13, 11.80.

ESI-MS: Calcd for C\(_{41}\)H\(_{62}\)O\(_3\): [M+H\(^+\)] 603.4772, found 603.4767.

5-formyl-2-methoxyphenyl (E)-3-mesitylacrylate(4ai)
Yield: 73%, 47.4 mg; appearance: red solid, M.P.: 130-131 °C.

^1^H NMR (400 MHz, CDCl₃) δ 9.89 (s, 1H), 8.08 (d, J = 16.4 Hz, 1H), 7.79 (dd, J = 8.4, 1.6 Hz, 1H), 7.70 (d, J = 2.0 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H), 6.93 (s, 2H), 6.32 (d, J = 16.4 Hz, 1H), 3.94 (s, 3H), 2.41 (s, 6H), 2.31 (s, 3H).

^1^3^C NMR (100 MHz, CDCl₃) δ 189.97, 164.57, 156.44, 145.60, 140.22, 138.87, 137.14, 130.23, 129.93, 129.86, 129.30, 123.57, 120.89, 111.94, 56.17, 21.18, 20.99.

ESI-MS: Calcd for C₂₀H₂₀O₄: [M+H⁺] 325.1434, found 325.1432.

5-chloro-2-(2,4-dichlorophenoxy)phenyl (E)-3-mesitylacrylate(4aj)

Yield: 83%, 76.7 mg; appearance: colorless oil.

^1^H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 16.4 Hz, 1H), 7.40 (d, J = 2.4 Hz, 1H), 7.33 (d, J = 2.4 Hz, 1H), 7.22 (dd, J = 8.8, 2.4 Hz, 1H), 7.16 (dd, J = 8.8, 2.4 Hz, 1H), 6.95 (d, J = 8.8 Hz, 1H), 6.91 (s, 2H), 6.87 (d, J = 8.8 Hz, 1H), 6.13 (d, J = 16.4 Hz, 1H), 2.32 (s, 6H), 2.29 (s, 3H).

^1^3^C NMR (100 MHz, CDCl₃) δ 164.04, 151.36, 146.42, 146.09, 142.07, 139.06, 137.20, 130.31, 130.24, 129.58, 129.35, 129.09, 128.00, 126.93, 125.47, 124.71, 120.94, 120.62, 119.65, 21.12, 21.08.

ESI-MS: Calcd for C₂₄H₁₉Cl₃O₃: [M–H⁻] 459.0327, found 459.0337.

1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl (E)-3-mesitylacrylate(4ak)
Yield: 89%, 58.1 mg; appearance: yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.87 (d, $J = 16.4$ Hz, 1H), 6.90 (s, 2H), 6.09 (d, $J = 16.4$ Hz, 1H), 4.52 (d, $J = 1.6$ Hz, 1H), 2.35 (s, 6H), 2.29 (s, 3H), 1.88 – 1.80 (m, 1H), 1.77 – 1.71 (m, 2H), 1.66 – 1.63 (m, 1H), 1.53 – 1.44 (m, 1H), 1.30 – 1.21 (m, 2H), 1.17 (s, 3H), 1.11 (s, 3H), 0.85 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.39, 142.80, 138.20, 136.76, 130.89, 129.13, 123.17, 86.12, 48.40, 48.38, 41.42, 39.70, 29.73, 28.70, 25.85, 21.07, 21.02, 20.14, 19.44.

ESI-MS: Calcd for C$_{22}$H$_{30}$O$_2$: [M–H$^-$] 325.2173, found 325.2179.

(3S,4R,6R,6aS)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl (E)-3-mesitylacrylate(4al)

Yield: 89%, 77.0 mg; appearance: white solid, M.P.: 114-116 ºC.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.90 (d, $J = 16.0$ Hz, 1H), 6.90 (s, 2H), 6.27 (s, 1H), 6.02 (d, $J = 16.0$ Hz, 1H), 4.91 (dd, $J = 6.4$, 2.0 Hz, 1H), 4.81 (d, $J = 6.4$ Hz, 1H), 4.46 – 4.41 (m, 1H), 4.14 – 4.07 (m, 3H), 2.34 (s, 6H), 2.29 (s, 3H), 1.52 (s, 3H), 1.47 (s, 3H), 1.39 (s, 3H), 1.36 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.28, 144.83, 138.70, 137.04, 130.41, 129.24, 121.81, 113.19, 103.30, 101.00, 85.14, 82.27, 79.29, 72.90, 66.81, 26.97, 25.90, 25.08, 24.59, 21.16, 21.02.

ESI-MS: Calcd for C$_{24}$H$_{32}$O$_2$: [M+H$^+$] 433.2221, found 433.2220.

(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-
2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl (E)-3-mesitylacrylate(4am)

Yield: 95%, 106.2 mg; appearance: white solid, M.P.: 109-111 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 16.0$ Hz, 1H), 6.89 (s, 2H), 6.05 (d, $J = 16.4$ Hz, 1H), 5.42 (d, $J = 4.4$ Hz, 1H), 4.82 – 4.73 (m, 1H), 2.44 – 2.41 (m, 2H), 2.35 (s, 6H), 2.29 (s, 3H), 2.06 – 1.87 (m, 5H), 1.71 – 1.47 (m, 8H), 1.41 – 1.29 (m, 4H), 1.21 – 1.10 (m, 7H), 1.07 (s, 3H), 1.04 – 0.97 (m, 2H), 0.94 (d, $J = 6.4$ Hz, 3H), 0.91 – 0.88 (m, 6H), 0.70 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.31, 142.86, 139.62, 138.08, 136.75, 130.86, 129.09, 123.37, 122.57, 73.97, 56.60, 56.06, 49.94, 42.22, 39.65, 39.46, 38.18, 36.97, 36.53, 36.13, 35.75, 31.84, 31.78, 28.18, 27.95, 27.83, 24.22, 23.80, 22.78, 22.53, 21.09, 20.98, 19.27, 18.66, 11.78.

ESI-MS: Calcd for C$_{39}$H$_{58}$O$_2$: [M+Na$^+$] 581.4329, found 581.4336.

(E)-N-(((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-3-mesitylacrylamide(4an)

Yield: 83%, 76.0 mg; appearance: yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.77 (d, $J = 16.0$ Hz, 1H), 7.20 (d, $J = 8.4$ Hz, 1H), 7.03 – 7.00 (m, 1H), 6.92 (s, 1H), 6.88 (s, 2H), 6.01 (d, $J = 15.6$ Hz, 1H), 5.72 (t, $J = 6.0$ Hz, 1H), 3.39 – 3.26 (m, 2H), 3.02 – 2.92 (m, 1H), 2.89 – 2.79 (m, 2H), 2.31
(s, 6H), 2.29 (s, 3H), 1.99 – 1.93 (m, 1H), 1.79 – 1.73 (m, 2H), 1.72 – 1.69 (m, 1H), 1.51 – 1.34 (m, 5H), 1.26 (s, 3H), 1.25 (s, 3H), 1.24 (s, 3H), 1.00 (s, 3H).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (d, $J$ = 16.0 Hz, 1H), 7.23 (d, $J$ = 8.0 Hz, 1H), 7.07 – 7.04 (m, 1H), 6.95 (s, 1H), 6.90 (s, 2H), 6.13 – 6.05 (m, 2H), 3.42 – 3.27 (m, 2H), 3.01 – 2.84 (m, 3H), 2.34 (s, 3H), 2.31 (s, 3H), 2.01 – 1.95 (m, 1H), 1.84 – 1.68 (m, 3H), 1.56 – 1.49 (m, 2H), 1.48 – 1.38 (m, 2H), 1.30 – 1.27 (m, 10H), 1.01 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.18, 147.03, 145.40, 139.19, 137.38, 136.44, 136.32, 134.69, 131.28, 128.83, 126.76, 125.53, 124.02, 123.65, 49.90, 45.15, 38.14, 37.44, 37.29, 36.08, 33.28, 30.06, 25.16, 23.88, 21.02, 20.88, 18.82, 18.61, 18.48.

ESI-MS: Calcd for C$_{32}$H$_{40}$D$_3$NO: [M+Na$^+$] 483.3425, found 483.3430.

(E)-3-(2,4-dimethyl-6-(methyl-$d_3$)phenyl)-N-((1R,4aS,10aR)-7-isopropyl-1,4-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)acrylamide(4an-$d_3$)

Yield: 79%, 72.8 mg; appearance: yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (d, $J$ = 16.0 Hz, 1H), 7.23 (d, $J$ = 8.0 Hz, 1H), 7.07 – 7.04 (m, 1H), 6.95 (s, 1H), 6.90 (s, 2H), 6.13 – 6.05 (m, 2H), 3.42 – 3.27 (m, 2H), 3.01 – 2.84 (m, 3H), 2.34 (s, 3H), 2.31 (s, 3H), 2.01 – 1.95 (m, 1H), 1.84 – 1.68 (m, 3H), 1.56 – 1.49 (m, 2H), 1.48 – 1.38 (m, 2H), 1.30 – 1.27 (m, 10H), 1.01 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.18, 147.03, 145.40, 139.19, 137.38, 136.44, 136.32, 134.69, 131.28, 128.83, 126.76, 125.53, 124.02, 123.65, 49.90, 45.15, 38.14, 37.44, 37.29, 36.08, 33.28, 30.06, 25.16, 23.88, 21.02, 20.88, 18.82, 18.61, 18.48.

ESI-MS: Calcd for C$_{32}$H$_{40}$D$_3$NO: [M+Na$^+$] 483.3425, found 483.3430.

(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl (E)-3-(2,4-dimethyl-6-(methyl-$d_3$)phenyl)acrylate(4am-$d_3$)
Yield: 87%, 97.8 mg; appearance: yellow solid, M.P.: 117-119 ºC.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J = 16.0$ Hz, 1H), 6.89 (s, 2H), 6.04 (d, $J = 16.4$ Hz, 1H), 5.41 (d, $J = 3.6$ Hz, 1H), 4.80 - 4.72 (m, 1H), 2.47 - 2.40 (m, 2H), 2.34 (s, 3H), 2.29 (s, 3H), 2.04 - 1.81 (m, 5H), 1.67 - 1.44 (m, 8H), 1.35 - 1.25 (m, 4H), 1.22 - 1.08 (m, 7H), 1.05 (s, 3H), 0.92 (d, $J = 6.4$ Hz, 3H), 0.88 - 0.86 (m, 6H), 0.69 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.53, 143.02, 139.78, 138.28, 136.93, 136.81, 131.02, 129.19, 123.50, 122.70, 74.13, 56.72, 56.15, 50.05, 42.35, 39.76, 39.56, 38.28, 37.07, 36.22, 35.84, 31.97, 31.90, 28.29, 28.07, 27.93, 24.34, 23.87, 22.88, 22.62, 21.20, 21.10, 19.41, 18.76, 11.90.

ESI-MS: Calcd for C$_{39}$H$_{55}$D$_3$O$_2$: [M+H$^+$] 562.4698, found 562.4696.

benzo[d][1,3]dioxol-5-yl (E)-3-(4-methyl-2,6-bis(methyl-d$_3$)phenyl)acrylate

(4ag-d$_6$)

Yield: 76%, 48.1 mg; appearance: colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 16.0$ Hz, 1H), 6.94 (s, 2H), 6.82 (d, $J = 7.6$ Hz, 1H), 6.74 (d, $J = 2.4$ Hz, 1H), 6.65 (dd, $J = 8.4$, 2.4 Hz, 1H), 6.26 (d, $J = 16.4$ Hz, 1H), 6.01 (s, 2H), 2.32 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.67, 147.92, 145.23, 145.11, 145.04, 138.78, 136.99, 130.46, 129.29, 121.70, 113.92, 107.90, 103.78, 101.62, 21.03.
ESI-MS: Calcd for C_{19}H_{12}D_{6}O_{4}: [M+H^+] 317.1654, found 317.1657.

ethyl (E)-3-(4,6-dimethylbenzo[d][1,3]dioxol-5-yl)acrylate(4ao)

Yield: 76%, 37.7 mg; appearance: yellow oil.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.76 (d, \(J = 16.4\) Hz, 1H), 6.55 (s, 1H), 6.00 (d, \(J = 16.4\) Hz, 1H), 5.92 (s, 2H), 4.26 (q, \(J = 7.2\) Hz, 2H), 2.29 (s, 3H), 2.23 (s, 3H), 1.33 (t, \(J = 7.2\) Hz, 3H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 167.00, 146.72, 144.73, 142.30, 131.52, 127.17, 122.40, 117.99, 108.32, 100.73, 60.38, 21.22, 14.26, 13.23.

ESI-MS: Calcd for C_{14}H_{16}O_{4}: [M+H^+] 249.1121, found 249.1121.

8-methoxy-5-methyl-6-(methyl-d\textsubscript{3})quinoline(5)

Yield: 78%, 29.7 mg; appearance: yellow solid, M.P.: 88-89 °C.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.85 (dd, \(J = 4.0, 1.2\) Hz, 1H), 8.29 (dd, \(J = 8.4, 1.2\) Hz, 1H), 7.41 (dd, \(J = 8.4, 4.0\) Hz, 1H), 6.86 (s, 1H), 4.05 (s, 3H), 2.47 (s, 3H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 152.91, 147.62, 139.15, 133.67, 132.01, 128.52, 122.47, 121.17, 110.68, 55.73, 13.51.

ESI-MS: Calcd for C_{12}H_{10}D_{3}NO: [M+H^+] 191.1258, found 191.1258.

\(\text{N,4-dimethyl-N-}(3,4,5\text{-trimethylphenyl})\text{benzenesulfonamide}(6)\)

Yield: 65%, 39.4 mg; appearance: red solid, M.P.: 93-95 °C.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.53 (d, \(J = 8.0\) Hz, 2H), 7.29 (d, \(J = 7.6\) Hz, 2H),
6.76 (s, 2H), 3.14 (s, 3H), 2.47 (s, 3H), 2.25 (s, 6H), 2.17 (s, 3H).

\[ ^{13}C\text{ NMR (100 MHz, CDCl}_3\] \( \delta \) 143.26, 138.50, 136.99, 134.51, 134.02, 129.17, 128.00, 125.77, 38.38, 21.52, 20.54, 15.14.

**ESI-MS:** Calcd for C_{17}H_{21}NO_{2}S: [M+Na]^{+} 326.1185, found 326.1189.

**4-(2,3,5-trimethylphenyl)morpholine(7)**

Yield: 52%, 21.4 mg; appearance: yellow oil.

\[ ^{1}H\text{ NMR (400 MHz, CDCl}_3\] \( \delta \) 6.78 (s, 1H), 6.75 (s, 1H), 3.89 – 3.87 (m, 4H), 2.89 (t, \( J = 4.0 \) Hz, 4H), 2.31 (s, 3H), 2.26 (s, 3H), 2.21 (s, 3H).

\[ ^{13}C\text{ NMR (100 MHz, CDCl}_3\] \( \delta \) 151.20, 137.85, 135.35, 127.89, 125.98, 117.23, 67.44, 52.61, 21.09, 20.53, 13.59.

**ESI-MS:** Calcd for C_{13}H_{19}NO: [M+H]^{+} 206.1539, found 206.1536.

**6-butyl-8-methoxy-5-methylquinoline(8)**

Yield: 86%, 39.4 mg; appearance: yellow oil.

\[ ^{1}H\text{ NMR (400 MHz, CDCl}_3\] \( \delta \) 8.84 – 8.83 (m, 1H), 8.29 – 8.23 (m, 1H), 7.41 – 7.36 (m, 1H), 6.83 (s, 1H), 4.04 (s, 3H), 2.76 (t, \( J = 8.0 \) Hz, 2H), 2.48 (s, 3H), 1.62 – 1.54 (m, 2H), 1.46 – 1.36 (m, 2H), 0.94 (t, \( J = 7.2 \) Hz, 3H).

\[ ^{13}C\text{ NMR (100 MHz, CDCl}_3\] \( \delta \) 153.30, 147.58, 139.14, 138.64, 132.17, 128.71, 121.77, 121.07, 109.97, 55.67, 34.41, 33.16, 22.65, 13.93, 13.18.

**ESI-MS:** Calcd for C_{15}H_{19}NO: [M+H]^{+} 230.1539, found 230.1538.

**ethyl (E)-3-(2,6-dimethyl-4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl)acrylate(4ap)**

S35
Yield: 50%, 44.8 mg; appearance: yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 (dd, $J = 5.2$, 1.6 Hz, 1H), 7.82 (d, $J = 16.4$ Hz, 1H), 7.59 – 7.54 (m, 1H), 6.99 – 6.92 (m, 4H), 6.88 – 6.84 (m, 1H), 6.75 (d, $J = 8.4$ Hz, 1H), 6.63 (s, 2H), 6.05 (d, $J = 16.4$ Hz, 1H), 5.64 – 5.56 (m, 1H), 4.27 (q, $J = 7.2$ Hz, 2H), 4.20 (dd, $J = 9.6$, 5.2 Hz, 1H), 4.09 (dd, $J = 10.0$, 4.8 Hz, 1H), 2.32 (s, 6H), 1.49 (d, $J = 6.4$ Hz, 3H), 1.34 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.00, 163.02, 158.29, 155.37, 149.40, 146.66, 142.45, 139.01, 138.66, 127.83, 122.69, 121.13, 116.79, 116.71, 115.68, 111.60, 70.87, 69.17, 60.40, 21.43, 16.93, 14.27.

ESI-MS: Calcd for C$_{27}$H$_{29}$NO$_5$: [M+H$^+$] 448.2118, found 448.2113.

(3a$S$,4$R$,6$R$,6a$S$)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl (E)-3-(2,6-dimethyl-4-(4-(2-(pyridin-2-yloxy)propoxy)phenyl)acrylate (4aq)

Yield: 50%, 66.2 mg; appearance: yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 – 8.13 (m, 1H), 7.59 – 7.54 (m, 1H), 7.62 – 7.52 (m, 1H), 6.98 – 6.92 (m, 4H), 6.88 – 6.84 (m, 1H), 6.74 (d, $J = 8.4$ Hz, 1H), 6.62 (s, 2H), 6.27 (s, 1H), 6.01 (d, $J = 16.4$ Hz, 1H), 5.63 – 5.55 (m, 1H), 4.90 (dd, $J = 6.4$, 3.6 Hz, 1H), 4.80 (d, $J = 6.4$ Hz, 1H), 4.46 – 4.40 (m, 1H), 4.19 (dd, $J = 9.6$, 5.2 Hz, 1H), 4.14 – 4.06 (m, 4H), 2.33 (s, 6H), 1.51 (s, 3H), 1.48 (d, $J = 6.4$ Hz,
3H), 1.47 (s, 3H), 1.38 (s, 3H), 1.36 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.34, 163.02, 158.65, 155.45, 149.22, 146.66, 144.13, 139.40, 138.67, 127.28, 121.22, 116.84, 116.72, 115.70, 113.17, 111.61, 109.28, 100.95, 85.10, 82.22, 79.26, 72.87, 70.87, 69.16, 66.79, 26.86, 25.06, 24.57, 21.58, 16.93.

ESI-MS: Calcd for C$_{37}$H$_{43}$NO$_{10}$: [M+H$^+$] 662.2960, found 662.2957.

benzo[d][1,3]dioxol-5-yl (E)-3-(2,6-bis(methyl-d$_3$)-4-(4-(2-(pyridin-2-yloxy)pro- poxy)phenoxy)phenyl)acrylate (4ar-d$_6$)

![Chemical Structure](image)

Yield: 48%, 52.4 mg; appearance: yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.16 (dd, $J$ = 4.8, 1.6 Hz, 1H), 8.01 (d, $J$ = 16.0 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.01 – 6.94 (m, 4H), 6.89 – 6.85 (m, 1H), 6.81 (d, $J$ = 8.4 Hz, 1H), 6.76 (d, $J$ = 8.0 Hz, 1H), 6.72 (d, $J$ = 2.0 Hz, 1H), 6.66 (s, 2H), 6.63 (dd, $J$ = 8.4, 2.4 Hz, 1H), 6.23 (d, $J$ = 16.4 Hz, 1H), 6.00 (s, 2H), 5.65 – 5.57 (m, 1H), 4.21 (dd, $J$ = 10.0, 5.2 Hz, 1H), 4.10 (dd, $J$ = 9.6, 4.8 Hz, 1H), 1.50 (d, $J$ = 6.4 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.76, 163.03, 158.74, 155.47, 149.23, 147.92, 146.67, 145.23, 145.05, 144.45, 139.38, 138.68, 127.37, 121.25, 121.15, 116.90, 116.73, 115.72, 113.92, 111.61, 107.91, 103.79, 101.63, 70.87, 69.17, 16.94.

ESI-MS: Calcd for C$_{32}$H$_{23}$D$_6$NO$_7$: [M+H$^+$] 546.2393, found 546.2394.

ethyl (E)-3-(2'-fluoro-4'-(1-methoxy-1-oxopropan-2-yl)-3,5-dimethyl-[1,1'-biphenyl]-4-yl)acrylate (4as)

![Chemical Structure](image)
Yield: 59%, 45.4 mg; appearance: colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 (d, $J = 16.4$ Hz, 1H), 7.38 (t, $J = 8.4$ Hz, 1H), 7.24 (s, 2H), 7.16 – 7.09 (m, 2H), 6.12 (d, $J = 16.4$ Hz, 1H), 4.29 (q, $J = 7.2$ Hz, 2H), 3.76 (q, $J = 7.2$ Hz, 1H), 3.70 (s, 3H), 2.41 (s, 6H), 1.53 (d, $J = 7.2$ Hz, 3H), 1.36 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.39, 166.80, 159.68 (d, $J = 247.0$ Hz), 142.77, 141.94 (d, $J = 7.0$ Hz), 136.92, 135.34, 133.38, 130.65 (d, $J = 4.0$ Hz), 128.72 (d, $J = 2.0$ Hz), 127.23 (d, $J = 14.0$ Hz), 124.05, 123.51 (d, $J = 3.0$ Hz), 115.23 (d, $J = 23.0$ Hz), 60.59, 52.22, 44.88, 21.25, 18.40, 14.30.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -117.11.

ESI-MS: Calcd for C$_{23}$H$_{25}$FO$_4$: [M+H$^+$] 385.1810, found 385.1807.

methyl 2-(2-fluoro-3',4',5'-trimethyl-[1,1'-biphenyl]-4-yl)propanoate(4at)

Yield: 85%, 51.1 mg; appearance: yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (t, $J = 8.4$ Hz, 1H), 7.20 (s, 2H), 7.15 – 7.09 (m, 2H), 3.77 (q, $J = 7.2$ Hz, 1H), 3.72 (s, 3H), 2.36 (s, 6H), 2.23 (s, 3H), 1.55 (d, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.47, 159.67 (d, $J = 246.0$ Hz), 141.24 (d, $J = 7.0$ Hz), 136.51, 134.76, 132.32, 130.74 (d, $J = 4.0$ Hz), 128.04 (d, $J = 3.0$ Hz), 127.91, 123.32 (d, $J = 3.0$ Hz), 115.06 (d, $J = 24.0$ Hz), 52.15, 44.86, 20.64, 18.40, 15.22.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -117.35.

ESI-MS: Calcd for C$_{19}$H$_{25}$FO$_2$: [M–H$^-$] 299.1453, found 299.1455.

methyl-$_d_2$ 2-(2-fluoro-4'-methyl-3',5'-bis(methyl-$_d_3$)-[1,1'-biphenyl]-4-yl)propanoate(4at-$_d_9$)
Yield: 80%, 49.5 mg; appearance: yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.41 (t, $J = 8.4$ Hz, 1H), 7.22 (s, 2H), 7.17 – 7.12 (m, 2H), 3.78 (q, $J = 7.2$ Hz, 1H), 2.25 (s, 3H), 1.57 (d, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 174.46, 159.67 (d, $J = 246.0$ Hz), 141.24 (d, $J = 8.0$ Hz), 136.36, 134.76, 132.32, 130.72 (d, $J = 4.0$ Hz), 128.03 (d, $J = 1.0$ Hz), 127.92, 123.30 (d, $J = 4.0$ Hz), 115.05 (d, $J = 24.0$ Hz), 44.85, 18.37, 15.16.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -117.30.

ESI-MS: Calcd for C$_{19}$H$_{12}$D$_9$FO$_2$: [M+Na$^+$] 332.1983, found 332.1986.
References:


X-ray Date:

Figure S1. ORTEP drawing for the product 4ag.

Table 1 Crystal data and structure refinement for N240104A.

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Radiation MoKα (λ = 0.71073)

2θ range for data collection/°4.994 to 50.016

Index ranges  -15 ≤ h ≤ 16, -8 ≤ k ≤ 8, -20 ≤ l ≤ 20

Reflections collected  8941

Independent reflections  2836 [Rint = 0.0180, Rsigma = 0.0180]

Data/restraints/parameters  2836/0/208

Goodness-of-fit on F2   1.054

Final R indexes [I>=2σ(I)]  R1 = 0.0399, wR2 = 0.1088

Final R indexes [all data]  R1 = 0.0489, wR2 = 0.1172

Largest diff. peak/hole / e Å⁻³  0.16/-0.15

Table 2 Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å²×103) for N240104A. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

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Table 3 Anisotropic Displacement Parameters (Å²×10³) for N240104A. The Anisotropic
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**Table 4 Bond Lengths for N240104A.**

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**Table 5 Bond Angles for N240104A.**
C4  C3  O4  128.61(15)  C13  C12  C18  118.16(15)
C4  C3  C2  121.46(15)  C14  C13  C12  122.50(15)
C3  C4  C5  117.29(14)  C13  C14  C15  117.62(15)
C6  C5  C4  120.45(14)  C13  C14  C19  121.30(17)
C5  C6  O2  118.35(14)  C15  C14  C19  121.08(18)
C5  C6  C7  122.38(14)  C14  C15  C16  122.67(15)
C7  C6  O2  119.16(14)  C11  C16  C17  121.74(14)
C2  C7  C6  115.82(14)  C15  C16  C11  118.90(14)
O1  C8  O2  122.42(14)  C15  C16  C17  119.35(14)
O1  C8  C9  126.81(14)

Table 6 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å²×103) for N240104A.

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NMR Spectra:

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**^13C NMR (100 MHz, CDCl₃)**
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$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
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$^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3)$

$\text{CO}_2\text{Ph}$

$^1\text{C NMR} \ (100 \text{ MHz, CDCl}_3)$
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$^{13}C$ NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{19}$F NMR (376 MHz, CDCl$_3$)
^1H NMR (400 MHz, CDCl₃)

^13C NMR (100 MHz, CDCl₃)
$^1$H NMR (400 MHz, CDCl$_3$)

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$^{13}$C NMR (100 MHz, CDCl$_3$)
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$^{13}C\text{ NMR (100 MHz, CDCl}_3$)
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PO(OEt)$_2$

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$^{13}$C NMR (100 MHz, CDCl$_3$)
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$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{19}$F NMR (376 MHz, CDCl$_3$)
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$\text{O}$

$\text{O}$

$\text{4aa}$

$\text{H}$

$\text{NMR (400 MHz, CDCl}_3)$

$\text{Cl}$

$\text{O}$

$\text{O}$

$\text{4aa}$

$\text{C}$

$\text{NMR (100 MHz, CDCl}_3)$
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$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
\[ \text{Cy} \quad \text{Ph} \]

4ae

\(^1\text{H NMR} (400 \text{ MHz}, \text{CDCl}_3)\)

\[ \text{Cy} \quad \text{Ph} \]

4ae

\(^{13}\text{C NMR} (100 \text{ MHz}, \text{CDCl}_3)\)
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$^13$C NMR (100 MHz, CDCl$_3$)
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^1H NMR (400 MHz, CDCl₃)

^13C NMR (100 MHz, CDCl₃)
$^1$H NMR (400 MHz, CDCl$_3$)

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$\text{C NMR (100 MHz, CDCl}_3\) $
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\[ \text{Bu}_\text{N} \text{MeO} \]

\[ \text{C NMR (100 MHz, CDCl}_3\text{)} \]

\[ \text{MeO} \]

\[ \text{Bu}_\text{N} \]

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\[ \text{C NMR (100 MHz, CDCl}_3\text{)} \]
$\text{H NMR (400 MHz, CDCl}_3\text{)}$

$\text{C NMR (100 MHz, CDCl}_3\text{)}$
**$^1$H NMR (400 MHz, CDCl$_3$)**

**$^{13}$C NMR (100 MHz, CDCl$_3$)**
S113

4ar-\textit{d}$_6$

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