Supplementary Information

Methylation Platform of Unconventional Inert Aryl Electrophiles: Trimethylboroxine as a Universal Methylating Reagent

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I. General remarks

NMR spectra were obtained on an Agilent 400-MR DD2 spectrometer. The $^1$H NMR (400 MHz) chemical shifts were measured relative to CDCl$_3$ as the internal reference (CDCl$_3$: $\delta$ = 7.26). The $^{13}$C NMR (100 MHz) chemical shifts were given using CDCl$_3$ as the internal standard (CDCl$_3$: $\delta$ = 77.16). High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-IT-TOF (ESI) or a Waters-Q-TOF-Premier (ESI). GC-MS spectra were recorded by Shimadzu GCMS-QP2010 SE. Infrared (IR) spectra were recorded on a Shimadzu IRTracer-100 FT-IR spectrophotometer.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. The solvents were purified and dried using Innovative Technology PS-MD-5 Solvent Purification System. Pd(acac)$_2$ were synthesized according to the literature procedures. PdCl$_2$ and Pd(OAc)$_2$ were purchased from Shanxi Kaida Chemical Engineering (China) CO., Ltd.. [Pd(allyl)Cl]$_2$ was purchased from Alfa Aesar. BrettPhos were purchased from Adamas-beta Ltd.. Dcype were purchased from Sigma-Aldrich. Trimethylboroxine (TMB, 3.5N in THF), 4-dimethylaminopyridine (4-DMAP), DavePhos, XPhos, aryl carboxylic acids and acyl chlorides were purchased from Energy Chemical. The yields of compound 2f, 2g and 2h were determined by GC analysis using calibration curves based on the data from authentic samples of the corresponding compounds. For all GC calibration curves, the ratio of molar concentration is taking as the horizontal axis and the ratio of GC area is taking as the vertical axis. Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of nitrogen in dried glassware with standard vacuum-line techniques.

II. Preparation of starting materials

2.1 Preparation of nitroaromatic substrates
Scheme S1. Nitroaromatic substrates.

Compound 1a, 1b, 1f, 1g, 1h and 1n were purchased and used without further purification. Compound 1c, 1d, 1e, 1i, 1j, 1k, 1l, 1m, and 1p were prepared according to literature. The 1H NMR and 13C NMR data were in accordance with the related literature. Compound 1o was prepared according to the follow procedure:

6-Methoxy-2,2-dimethyl-7-nitrochromane (1o) was prepared by the nitration of chromane derivative. A mixture of AcOH (1.5 mL), Ac₂O (1.5 mL) and chromane derivative (770 mg, 4 mmol) was cooled in ice bath. HNO₃ (0.35 mL) was added dropwise and stirred at 0 °C for 1 h. Then aqueous NaOH (1 mol/L) was added to neutralize the solution. The mixture was sequentially extracted with ethyl acetate (20 mL) and washed with brine (20 mL). The organic layer was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The resulting crude mixture was purified by column chromatography on silica gel (200-300 mesh, petroleum ether/ethyl acetate = 6/1) to afford the desired product as yellow oil (712 mg, 75% yield). 1H NMR (400 MHz, CDCl₃): δ = 1.36 (s, 6H), 1.86 (t, J = 6.8 Hz, 2H), 2.82 (t, J = 6.8 Hz, 2H), 3.78 (s, 3H), 6.87 (dt, J = 3.2, 1.2 Hz, 1H), 7.20 (d, J = 3.2 Hz, 1H) ppm. 13C NMR (100 MHz, CDCl₃) δ =
22.9, 26.8, 32.2, 56.1, 76.2, 107.9, 120.9, 125.4, 142.7, 151.3 ppm. HRMS (ESI') calcld for C_{12}H_{16}NO_{4} [M+H]^+ 238.1074, found 238.1075. IR (KBr): 2974, 2936, 2837, 1530, 1479, 1370, 1261, 1205, 1117, 1052, 924, 768 cm^{-1}.

2.2 Preparation of amide substrates

Scheme S2. Amide substrates.

General procedure: The amide substrates were prepared by a modified procedure according to the report. The corresponding benzoyl chloride (5 mmol, 1.0 equiv) was added to a mixture of aniline (0.51 g, 5.5 mmol, 1.1 equiv), triethylamine (1.4 mL, 10 mmol, 2 equiv), 4-DMAP (31 mg, 0.25 mmol, 0.05 equiv) and DCM (10 mL) at 0 °C. The reaction mixture was stirred at room temperature overnight, and then diluted with DCM (25 mL). The mixture was washed with 1 N HCl (15 mL), saturated aqueous NaHCO_{3} (15 mL), and brine (15 mL). Then the organic phase was dried over Na_{2}SO_{4}, filtered and concentrated under reduced pressure. The crude was recrystallized in ethanol. The resulting NH-free amide product (5 mmol) was dissolved in THF (25 mL). LiHMDS (1 mol/L in THF, 7.5 mL, 1.5 equiv) was added slowly at 0 °C. After stirring at 0 °C for 1 h, TsCl (1.14 g, 1.2 equiv) was added slowly. Then the reaction mixture was quenched by water after further stirring at room temperature for 15 h. The mixture was sequentially washed with 1 N HCl (15 mL), saturated aqueous NaHCO_{3} (15 mL), and brine (15 mL). The organic layer was dried over Na_{2}SO_{4}, filtered and concentrated under reduced pressure. The resulting crude mixture was purified by column chromatography on silica gel (200-300 mesh) to afford the desired product.
2.3 Preparation of benzoic phenyl ester substrates

Scheme S3. Benzoic phenyl ester substrates.

**General procedure:** The corresponding benzoyl chloride (5 mmol, 1.0 equiv) was added to a mixture of phenol (0.51 g, 5.5 mmol, 1.1 equiv), triethylamine (1.4 mL, 10 mmol, 2 equiv), 4-DMAP (31 mg, 0.25 mmol, 0.05 equiv) and DCM (10 mL) at 0 °C. The reaction mixture was stirred at room temperature overnight, and then diluted with DCM (25 mL). The mixture was washed with 1 N HCl (15 mL), saturated aqueous NaHCO₃ (15 mL), and brine (15 mL). The organic phase was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The product was further purified by recrystallization from ethanol.

III. Optimization of reaction conditions

**General procedure for reaction optimizations:**

An oven-dried vial equipped with a stirring bar was charged with substrate 1a/3a/4a (0.2 mmol, 1.0 equiv), TMB (100 μL, 3.5 N in THF, 3.5 mmol, 1.75 equiv), catalyst, ligand and base (0.4 mmol, 2 equiv) under N₂. Solvent (0.6 mL) was added at room temperature. The reaction mixture was placed in a preheated oil bath at indicated temperature, and stirred for the indicated time. Next, the reaction mixture was cooled down to room temperature, diluted with CH₂Cl₂ (10 mL), filtered through celite, and concentrated under reduced
pressure. Purification by column chromatography on silica gel (200-300 mesh, petroleum ether) afforded the product 2a.

**Table S1.** Examination of protecting group on amide.\(^a\)

![Diagram](image)

| Protecting group: | N−Ph | N−Ph | N−Ph | N−Ph | N−Ph | N−Ph | Yield of 2a: |
|-------------------|------|------|------|------|------|------|-------------|
|                   | H    | Ac   | Me   | Ts   | Ms   | Boc  |             |
| Yield of 2a:      | n.d. | <10% | trace| 85%  | n.d. | n.d. |

\(^a\)Reaction conditions: amide (0.2 mmol, 1 equiv), TMB (100 μL, 3.5N in THF, 3.5 mmol, 1.75 equiv), [Pd(allyl)Cl]2 (5 mol%), dpbb (20 mol%), CsF (2 equiv) in 1,4-dioxane (0.6 mL), 160 °C, 24 h. Isolated yields. dpbb = 1,4-diphenyl phosphinobutane.
Table S2. Optimization of the reaction conditions for palladium-catalyzed decarbonylative methylation of amides.\(^a\)

![Reaction scheme]

| Entry | Catalyst (10 mol%) | Ligand (20 mol%) | Base (2 equiv) | Yield (%)\(^b\) |
|-------|--------------------|------------------|---------------|----------------|
| 1     | Pd(OAc)\(_2\)      | Xantphos         | CsF           | 30             |
| 2     | Pd(OAc)\(_2\)      | dppp             | CsF           | 23             |
| 3     | Pd(OAc)\(_2\)      | dppf             | CsF           | 35             |
| 4     | Pd(OAc)\(_2\)      | dcype            | CsF           | 52             |
| 5     | Pd(OAc)\(_2\)      | dppb             | CsF           | 65             |
| 6     | Pd(OAc)\(_2\)      | DPEPPhos         | CsF           | 60             |
| 7     | Pd(OAc)\(_2\)      | IPr·HCl          | CsF           | Trace          |
| 8     | PdCl\(_2\)         | dppb             | CsF           | 32             |
| 9     | Pd(acac)\(_2\)     | dppb             | CsF           | 42             |
| 10    | Pd(en)(NO\(_3\))\(_2\) | dppb      | CsF           | 40             |
| 11    | Pd(COD)Cl\(_2\)    | dppb             | CsF           | 45             |
| 12    | [Pd(allyl)Cl]\(_2\) (5 mol%) | dppb    | CsF           | 85             |
| 13    | [Pd(allyl)Cl]\(_2\) (5 mol%) | dppb   | Cs\(_2\)CO\(_3\) | 10             |
| 14    | [Pd(allyl)Cl]\(_2\) (5 mol%) | dppb   | K\(_2\)PO\(_4\) | 35             |
| 15\(^c\) | [Pd(allyl)Cl]\(_2\) (5 mol%) | dppb   | CsF           | 38             |
| 16\(^d\) | [Pd(allyl)Cl]\(_2\) (5 mol%) | dppb   | CsF           | 55             |

\(^a\) Reaction conditions: amide 3\(a\) (0.2 mmol, 1 equiv), TMB (100 \(\mu\)L, 3.5\(\times\)\(N\) in THF, 3.5 mmol, 1.75 equiv), catalyst (10 mol%), ligand (20 mol%), base (2 equiv), solvent (0.6 mL) at 160 °C, 24 h. \(^b\) Isolated yield. \(^c\) Toluene was used as solvent. \(^d\) MeB(OH)\(_2\) (5 equiv) was used instead of TMB. Xantphos = \(4,5\)-bis(diphenylphosphino)-9,9-dimethylxanthene, dppb = \(1,4\)-diphenyl phosphinobutane, dppp = \(1,3\)-bis(diphenylphosphino)propane, dppf = \(1,1’\)-bis(diphenylphosphino)ferrocene, dcype = \(1,2\)-bis(dicyclohexylphosphino)ethane, DPEPPhos = bis[(2-diphenylphosphino)phenyl] ether, IPr·HCl = \(1,3\)-bis(2,6-diisopropylphenyl)imidazolium chloride, en = ethylenediamine, COD = 1,5-cyclooctadiene.
Table S3. Optimization of the reaction conditions for palladium-catalyzed decarbonylative methylation of benzoic phenyl esters. 

![Chemical structure](image)

| Entry | Catalyst (10 mol%) | Ligand (20 mol%) | Base   | Yield(%)\(^b\) |
|-------|-------------------|------------------|--------|---------------|
| 1     | Pd(OAc)\(_2\)     | DPEPhos          | CsF    | n.d.          |
| 2     | [Pd(allyl)Cl\(_2\)] (5 mol%) | dppb    | CsF    | n.d.          |
| 3     | Pd(OAc)\(_2\)     | dcype            | CsF    | 72            |
| 4     | Pd(OAc)\(_2\) (5 mol%) | dcype            | CsF    | 70            |
| 5     | Pd(OAc)\(_2\)     | dcype            | Cs\(_2\)CO\(_3\) | trace |
| 6\(^c\) | Pd(OAc)\(_2\)     | dcype            | CsF    | 45            |
| 7     | Ni(COD)\(_2\)     | dcype            | CsF    | 40            |
| 8     | Ni(COD)\(_2\)     | nBu\(_3\)P (40 mol%) | CsF    | 48            |
| 9     | Pd(OAc)\(_2\)     | dppp             | CsF    | n.d.          |
| 10    | Pd(en)(NO\(_3\))\(_2\) | dppb    | CsF    | 40            |
| 11    | PdCl\(_2\)        | dppb             | CsF    | 45            |
| 12    | Pd\(_2\)(dba)\(_3\) (5 mol%) | dppb    | CsF    | 28            |
| 13\(^c\) | Pd(OAc)\(_2\) (5 mol%) | dcype            | CsF    | 36            |
| 14\(^d\) | Pd(OAc)\(_2\)     | dcype            | CsF    | trace        |

\(^a\) Reaction conditions: ester 4a (0.2 mmol, 1 equiv), TMB (100 μL, 3.5 \(N\) in THF, 3.5 mmol, 1.75 equiv), catalyst (10 mol%), ligand (20 mol%), base (2 equiv), solvent (0.6 mL) at 160 °C, 24 h. 

\(^b\) Isolated yield. 

\(^c\) Toluene was used as solvent. 

\(^d\) MeB(OH)\(_2\) (5 equiv) was used instead of TMB. dppb = 1,4-diphenyl phosphinobutane, dppp = 1,3-bis(diphenylphosphino)propane, dcype = 1,2-bis(dicyclopentylphosphino)ethane, DPEPhos = bis[(2-diphenylphosphino)phenyl] ether, en = ethylenediamine, COD = 1,5-cyclooctadiene.
Table S4. Non-decarbonylative methylation of amide.\textsuperscript{a}

![Chemical Structure](image)

| Entry | Catalyst (10 mol%) | Ligand (20 mol%) | Temp (°C) | Yield of 2a (%)\textsuperscript{b} | Yield of 2a’(%)\textsuperscript{b} |
|-------|--------------------|------------------|-----------|-------------------------------------|-------------------------------|
| 1     | [Pd(allyl)Cl]\textsubscript{2} | dppb             | 110       | 40                                  | 24                            |
| 2     | [Pd(allyl)Cl]\textsubscript{2} | dppb             | 60        | n.d.                                | n.d.                          |
| 3     | [Pd(allyl)Cl]\textsubscript{2} | PCy\textsubscript{3} | 60        | n.d.                                | 30                            |
| 4     | Ni(COD)\textsubscript{2}       | PCy\textsubscript{3} | 60        | n.d.                                | n.d.                          |
| 5     | Ni(COD)\textsubscript{2}       | SIPr-HCl/KOtBu   | 60        | 18                                  | n.d.                          |

\textsuperscript{a} Reaction conditions: amide 3a (0.2 mmol, 1 equiv), TMB (100 μL, 3.5 N in THF, 3.5 mmol, 1.75 equiv), catalyst (10 mol%), ligand (20 mol%), CsF (2 equiv), solvent (0.6 mL), 24 h. \textsuperscript{b} Isolated yield. dppb = 1,4-diphenyl phosphinobutane, Cy = cyclohexyl, COD = 1,5-cyclooctadiene, SIPr = 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidine.

Table S5. Non-decarbonylative methylation of ester.\textsuperscript{a}

![Chemical Structure](image)

| Entry | Catalyst (10 mol%) | Ligand (20 mol%) | Temp (°C) | Yield of 2a (%)\textsuperscript{b} | Yield of 2a’(%)\textsuperscript{b} |
|-------|--------------------|------------------|-----------|-------------------------------------|-------------------------------|
| 1     | Pd(OAc)\textsubscript{2} | dcype           | 110       | 36                                  | <10                           |
| 2     | Pd(OAc)\textsubscript{2} | dcype           | 60        | n.d.                                | n.d.                          |
| 3     | Pd(OAc)\textsubscript{2} | PCy\textsubscript{3} | 60        | n.d.                                | 35                            |
| 4     | Ni(COD)\textsubscript{2} | PCy\textsubscript{3} | 60        | n.d.                                | n.d.                          |
| 5     | Ni(COD)\textsubscript{2} | SIPr-HCl/KOtBu | 60        | n.d.                                | n.d.                          |

\textsuperscript{a} Reaction conditions: ester 4a (0.2 mmol, 1 equiv), TMB (100 μL, 3.5 N in THF, 3.5 mmol, 1.75 equiv), catalyst (10 mol%), ligand (20 mol%), base (2 equiv), solvent (0.6 mL) at 160 °C, 24 h. \textsuperscript{b} Isolated yield. dcype = 1,2-bis(dicyclohexylphosphino)ethane, Cy = cyclohexyl, COD = 1,5-cyclooctadiene, SIPr = 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidine.
IV. General procedures for palladium- or nickel-catalyzed methylation of unconventional electrophiles

**Denitrative methylation of nitrobenzene 1**: An oven-dried vial equipped with a stirring bar was charged with nitroarene 1 (0.2 mmol, 1.0 equiv), TMB (100 μL, 3.5 N in THF, 3.5 mmol, 1.75 equiv), Pd(acac)₂ (3.1 mg, 5 mol%), BrettPhos (16.1 mg, 15 mol%), Cs₂CO₃ (130 mg, 2 equiv) and toluene (0.6 mL) under N₂ at room temperature. The reaction mixture was placed in a preheated oil bath at 150 °C, and stirred for the indicated time. Then the reaction mixture was cooled down to room temperature, diluted with CH₂Cl₂ (10 mL), filtered through celite, and concentrated under reduced pressure. Purification by column chromatography on silica gel (200-300 mesh) afforded the corresponding methylating product 2.

**Decarbonylative methylation of benzamide 3**: An oven-dried vial equipped with a stirring bar was charged with benzamide 3 (0.2 mmol, 1.0 equiv), TMB (100 μL, 3.5 N in THF, 3.5 mmol, 1.75 equiv), [Pd(allyl)Cl]₂ (3.9 mg, 5 mol%), dppb (17.1 mg, 20 mol%), CsF (61 mg, 2.0 equiv) and dioxane (0.6 mL) under N₂ at room temperature. The reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for the indicated time. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with CH₂Cl₂ (10 mL), filtered through celite, and concentrated under reduced pressure. Purification by column chromatography on silica gel (200-300 mesh) afforded the corresponding methylating product 2.

**Decarbonylative methylation of benzoic phenyl ester 4**: An oven-dried vial equipped with a stirring bar was charged with benzoic phenyl ester 4 (0.2 mmol, 1.0 equiv), TMB (100 μL, 3.5 N in THF, 3.5 mmol, 1.75 equiv), Pd(OAc)₂ (2.2 mg, 5 mol%), dcype (8.5 mg, 10 mol%), CsF (61 mg, 2 equiv) and dioxane (0.6 mL) under N₂ at room temperature. The reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for the indicated time. Then the reaction mixture was...
cooled down to room temperature, diluted with CH$_2$Cl$_2$ (10 mL), filtered through celite, and concentrated under reduced pressure. Purification by column chromatography on silica gel (200-300 mesh) afforded the corresponding methylating product 2.

**Methylation of 1-naphthyl methyl ether 5a and 1-naphthyl pivalate 5b:** An oven-dried vial equipped with a stirring bar was charged with 1-naphthyl methyl ether 5a or 1-naphthyl pivalate 5b (0.2 mmol, 1.0 equiv), TMB (100 μL, 3.5 N in THF, 3.5 mmol, 1.75 equiv), Ni(COD)$_2$ (5.5 mg, 10 mol%), dctype (17 mg, 20 mol%), CsF (61 mg, 2.0 equiv) and dioxane (0.6 mL) under N$_2$ at room temperature. The reaction mixture was placed in a preheated oil bath at 130 °C, and stirred for 24 h. The reaction mixture was then cooled down to room temperature, diluted with CH$_2$Cl$_2$ (10 mL), filtered through celite, and concentrated. Purification by column chromatography on silica gel (200-300 mesh, petroleum ether) afforded 2-methylnaphthalene (2b) as colorless liquid (R = Me, 14 mg, 48% yield; R = Piv, 23 mg, 82% yield).

**Defluoromethylation of 1-fluoro naphthalene 6:** An oven-dried vial equipped with a stirring bar was charged with 1-fluoro naphthalene 6 (0.2 mmol, 1.0 equiv), TMB (100 μL, 3.5 N in THF, 3.5 mmol, 1.75 equiv), Ni(COD)$_2$ (5.5 mg, 10 mol%), dctype (17 mg, 20 mol%), CsF (61 mg, 2.0 equiv) and toluene (0.6 mL) under N$_2$ at room temperature. The reaction mixture was placed in a preheated oil bath at 130 °C, and stirred for 24 h. The reaction mixture was then cooled down to room temperature, diluted with CH$_2$Cl$_2$ (10 mL), filtered through celite, and concentrated. Purification by column chromatography on silica gel (200-300 mesh, petroleum ether) afforded 1-methylnaphthalene (2a) as colorless liquid (20 mg, 70% yield).
Decyanative methylation of 2-naphthonitrile 7: An oven-dried vial equipped with a stirring bar was charged with 2-naphthonitrile 7 (0.2 mmol, 1.0 equiv), TMB (100 μL, 3.5N in THF, 3.5 mmol, 1.75 equiv), Ni(PCy₃)Cl₂ (13.8 mg, 10 mol%), PCy₃ (11.2 mg, 20 mol%), KOtBu (45mg, 2.0 equiv), CuF₂ (40.6 mg, 2.0 equiv) and toluene (0.6 mL) under N₂ at room temperature. The reaction mixture was placed in a preheated oil bath at 130 °C, and stirred for 24 h. The reaction mixture was then cooled down to room temperature, diluted with CH₂Cl₂ (10 mL), filtered through celite, and concentrated. Purification by column chromatography on silica gel (200-300 mesh) afforded 2-methylnaphthalene (2b) as colorless liquid (18 mg, 65% yield).

V. Characterization data of starting materials

\[ \text{N-Phenyl-N-tosyl-1-naphthamide (3a)} \]

According to the general procedure for amide synthesis, 3a was obtained as a white solid (petroleum ether/EtOAc = 8/1 to 4/1). \( ^1 \text{H NMR (400 MHz, CDCl₃):} \ \delta = 2.50 \text{ (s, 3H), 7.07 – 7.14 (m, 5H), 7.19 (t, } J = 7.7 \text{ Hz, 1H), 7.34 (dd, } J = 7.2, 1.2 \text{ Hz, 1H), 7.38 (d, } J = 8.6 \text{ Hz, 2H), 7.41 – 7.50 \text{ (m, 2H), 7.67 – 7.72 (m, 2H), 7.89 (d, } J = 8.4 \text{ Hz, 1H), 7.98 (d, } J = 8.4 \text{ Hz, 2H) ppm.} \)
\( ^{13} \text{C NMR (100 MHz, CDCl₃) \ \delta = 21.9, 124.2, 124.6, 126.5, 126.7, 127.4, 128.4, 129.0, 129.2, 129.6, 130.0, 130.1, 130.8, 132.2, 133.2, 135.7, 136.8, 145.2, 169.9 ppm.} \)
HRMS (ESI⁺) calcd for C₂₄H₂₀NO₃S [M+H]⁺ 402.1158, found 402.1162. IR (KBr): 3063, 3026, 2921, 1688, 1486, 1363, 1279, 1172, 1075, 944, 757, 696 cm⁻¹.

\[ \text{N-Phenyl-N-tosyl-2-naphthamide (3b)} \]

According to the general procedure for amide synthesis, 3b was obtained as a white solid (petroleum ether/EtOAc = 8/1 to 4/1). \( ^1 \text{H NMR (400 MHz, CDCl₃):} \ \delta = 2.46 \text{ (s, 3H), 7.20 – 7.26 (m, 5H), 7.33 (d, } J = 8.0 \text{ Hz, 2H), 7.41 – 7.52 (m, 3H), 7.60 (d, } J = 8.8 \text{ Hz, 1H), 7.71 (d, } J = 8.8 \text{ Hz, 2H), 7.85 (d, } J = 8.4 \text{ Hz, 2H), 8.04 (s, 1H) ppm.} \)
\( ^{13} \text{C NMR (100 MHz, CDCl₃) \ \delta = 21.9, 125.2, 126.8, 127.8, 127.9, 128.4, 129.1, 129.2, 129.3, 129.4, 129.7, 130.5, 131.0, 131.4, 132.2, 133.2, 135.3, 137.6, 145.0, 170.1 ppm.} \)
HRMS (ESI⁺) calcd for C₂₄H₂₀NO₃S [M+H]⁺ 402.1158, found 402.1159. IR (KBr): 3113, 2930, 2852, 1697, 1608, 1585, 1531, 1520, 1347, 1252, 1106, 814, 771, 742 cm⁻¹.
**N-Phenyl-N-tosyl-(1,1'-biphenyl)-4-carboxamide (3c)**

According to the general procedure for amide synthesis, 3c was obtained as a white solid (petroleum ether/EtOAc = 8/1 to 4/1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.46$ (s, 3H), 7.19 – 7.23 (m, 2H), 7.29 – 7.36 (m, 6H), 7.37 – 7.41 (m, 4H), 7.46 – 7.49 (m, 2H), 7.52 – 7.54 (m, 2H), 7.84 (d, $J = 8.4$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 21.9, 126.7, 127.2, 128.3, 129.0, 129.2, 129.3, 129.4, 129.6, 130.3, 130.5, 132.3, 135.3, 137.6, 139.6, 144.5, 144.9, 169.8$ ppm. HRMS (ESI$^+$) calcd for C$_{26}$H$_{22}$NO$_3$S [M+H]$^+$ 428.13, found 428.1324. IR (KBr): 3074, 2920, 2853, 1690, 1593, 1485, 1366, 1256, 1171, 1090, 745, 699 cm$^{-1}$.

**N-Phenyl-N-tosyl-(1,1'-biphenyl)-3-carboxamide (3d)**

According to the general procedure for amide synthesis, 3d was obtained as a white solid (petroleum ether/EtOAc = 8/1 to 4/1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.45$ (s, 3H), 7.18 – 7.23 (m, 2H), 7.23 – 7.26 (m, 1H), 7.29 – 7.43 (m, 11H), 7.50 (ddd, $J = 7.6, 2.0, 1.2$ Hz, 1H), 7.66 (t, $J = 1.6$ Hz, 1H), 7.85 (d, $J = 8.4$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 21.9, 126.7, 127.2, 128.3, 129.0, 129.2, 129.3, 129.4, 129.5, 129.6, 130.3, 130.5, 132.3, 135.3, 137.6, 139.6, 144.5, 144.9, 169.9$ ppm. HRMS (ESI$^+$) calcd for C$_{26}$H$_{22}$NO$_3$S [M+H]$^+$ 428.1315, found 428.1314. IR (KBr): 3072, 2921, 2865, 1699, 1594, 1494, 1376, 1162, 1086, 947, 886, 701 cm$^{-1}$.

**N-Phenyl-N-tosyl-(1,1'-biphenyl)-2-carboxamide (3e)**

According to the general procedure for amide synthesis, 3e was obtained as a white solid (petroleum ether/EtOAc = 8/1 to 4/1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.49$ (s, 3H), 6.39 (d, $J = 7.6$ Hz, 2H), 7.03 (t, $J = 7.6$ Hz, 2H), 7.10 – 7.16 (m, 2H), 7.16 – 7.23 (m, 3H), 7.23 – 7.29 (m, 1H), 7.29 – 7.37 (m, 5H), 7.38 – 7.43 (m, 1H), 7.83 (d, $J = 8.4$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 21.9, 126.9, 128.1, 128.3, 128.6, 128.9, 129.0, 129.4, 129.5, 129.7, 130.4, 130.6, 134.6, 135.2,
N-Phenyl-N-tosyl-4-methoxyl-1-benzamide (3f)

According to the general procedure for amide synthesis, 3f was obtained as a white solid (petroleum ether/EtOAc = 8/1 to 4/1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.44$ (s, 3H), $3.72$ (s, 3H), $6.65$ (d, $J = 8.8$ Hz, 2H), $7.16 - 7.19$ (m, 2H), $7.28 - 7.30$ (m, 5H), $7.47$ (d, $J = 8.8$ Hz, 2H), $7.78$ (d, $J = 8.4$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 21.8, 55.4, 113.4, 125.5, 129.0, 129.2, 129.3, 129.6, 130.3, 132.2, 135.4, 138.0, 144.7, 162.5, 169.5$ ppm. HRMS (ESI$^+$) calcd for C$_{26}$H$_{22}$NO$_3$S [M+H]$^+$ 428.1315, found 428.1325. IR (KBr): 3066, 2923, 2850, 1700, 1353, 1280, 1173, 1085, 958, 745, 692 cm$^{-1}$.

4-Fluoro-N-phenyl-N-tosylbenzamide (3g)

According to the general procedure for amide synthesis, 3g was obtained as a white solid (petroleum ether/Ether = 4/1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.45$ (s, 3H), $6.82 - 6.89$ (m, 2H), $7.12 - 7.17$ (m, 2H), $7.27 - 7.35$ (m, 5H), $7.45 - 7.50$ (m, 2H), $7.78 - 7.83$ (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 21.9, 55.4, 113.4, 125.5, 129.0, 129.2, 129.3, 129.6, 130.4, 132.26$ (d, $J = 9.3$ Hz), $135.1, 137.5, 145.1, 164.58$ (d, $J = 254.1$ Hz), $168.9$ ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -105.96$ ppm. HRMS (ESI$^+$) calcd for C$_{24}$H$_{17}$FNO$_3$S [M+H]$^+$ 370.0908, found 370.0913. The NMR spectra are in accordance with literature.$^{10}$

N-Phenyl-N-tosyl-4-(trifluoromethyl)benzamide (3h)

According to the general procedure for amide synthesis, 3h was obtained as a white solid (petroleum ether/ether = 8/1 to 4/1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.46$ (s, 3H), $7.11 - 7.16$ (m, 2H), $7.27 - 7.36$ (m, 5H), $7.43$ (d, $J = 8.3$ Hz, 2H), $7.52$ (d, $J = 8.2$ Hz, 2H), $7.84$ (d, $J = 8.4$ Hz, 2H) ppm.
ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 21.9, 123.4$ (q, $J = 271.0$ Hz), 125.2 (q, $J = 3.7$ Hz), 129.51, 129.53, 129.6, 129.7, 130.5, 133.1 (q, $J = 32.8$ Hz), 134.9, 136.9, 137.2 (q, $J = 1.0$ Hz), 145.4, 168.7 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -63.2$ ppm. HRMS (ESI$^+$) calcd for C$_{22}$H$_{16}$F$_3$NaO$_3$S [M+Na]$^+$ 442.0695, found 442.0695. The NMR spectra are in accordance with literature.$^{10}$

Methyl 4-(phenyl(tosyl)carbamoyl)benzoate (3q)

According to the general procedure for amide synthesis, 3q was obtained as a white solid (petroleum ether/EtOAc = 3/1 to 1/1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.46$ (s, 3H), 3.85 (s, 3H), 7.12 – 7.15 (m, 2H), 7.24 – 7.30 (m, 3H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.45 – 7.48 (m, 2H), 7.80 – 7.87 (m, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 21.9, 52.5, 129.3, 129.4, 129.48, 129.50, 129.6, 130.5, 132.6, 135.0, 137.0, 137.9, 145.3, 166.1, 169.2 ppm. HRMS (ESI$^+$) calcd for C$_{22}$H$_{20}$NO$_5$S [M+H]$^+$ 410.1057, found 410.1057. The NMR spectra are in accordance with literature.$^{10}$

$N$-Phenyl-$N$-tosylbenzo[b]thiophene-2-carboxamide (3r)

According to the general procedure for amide synthesis, 3r was obtained as a white solid (petroleum ether/EtOAc = 8/1 to 4/1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.46$ (s, 3H), 7.19 (s, 1H), 7.29 (d, $J = 8.0$ Hz, 1H), 7.32 – 7.38 (m, 4H), 7.39 (s, 1H), 7.47 (t, $J = 7.6$ Hz, 2H), 7.52 (m, 1H), 7.60 (d, $J = 8.0$ Hz, 1H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.91 (d, $J = 8.4$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 21.9, 122.4, 124.9, 125.8, 127.3, 129.5, 129.7, 129.8, 130.4, 131.1, 132.2, 135.5, 136.2, 136.7, 138.1, 142.4, 145.2, 162.9 ppm. HRMS (ESI$^+$) calcd for C$_{22}$H$_{18}$NO$_3$S$_2$ [M+H]$^+$ 408.0723, found 408.0727. IR (KBr): 3093, 3067, 3033, 2929, 1661, 1508, 1367, 1189, 1178, 753, 701, 679 cm$^{-1}$.

$N$-Phenyl-$N$-tosylbenzofuran-2-carboxamide (3s)

According to the general procedure for amide synthesis, 3s was obtained as a white solid (petroleum ether/EtOAc = 8/1 to 4/1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.45$ (s, 3H), 6.38 (s, 1H),
7.15 – 7.20 (m, 1H), 7.31 – 7.37 (m, 6H), 7.41 – 7.55 (m, 4H), 7.95 (d, J = 8.4 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 21.9, 112.1, 115.6, 123.0, 123.9, 126.6, 128.1, 129.5, 129.7, 129.8, 130.3, 130.6, 135.4, 136.6, 145.3, 146.2, 155.1, 159.1 ppm. HRMS (ESI$^+$) calcd for $C_{22}H_{18}NO_4S$ [M+H]$^+$ 392.0951, found 392.0956. IR (KBr): 3074, 3015, 2915, 1676, 1552, 1488, 1363, 1181, 1086, 938, 750, 701, 691 cm$^{-1}$.

Phenyl 1-naphthoate (4a)

According to the general procedure for ester synthesis, 4a was obtained as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.28 – 7.35 (m, 3H), 7.49 (t, J = 7.9 Hz, 2H), 7.55 – 7.62 (m, 2H), 7.63 – 7.68 (m, 1H), 7.94 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H), 8.49 (d, J = 7.3 Hz, 1H), 9.05 (d, J = 8.7 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 122.0, 124.7, 125.9, 126.0, 126.1, 126.5, 128.3, 128.8, 129.7, 131.4, 131.8, 134.0, 134.5, 151.1, 166.0 ppm. HRMS (ESI$^+$) calcd for $C_{17}H_{12}NaO_2$ [M+Na]$^+$ 271.073, found 271.0734. The NMR spectra are in accordance with literature.$^{11}$

Phenyl 2-naphthoate (4b)

According to the general procedure for ester synthesis, 4b was obtained as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 6.65 (dd, J = 8.0 Hz, 0.8 Hz, 1H), 7.18 – 7.20 (m, 2H), 7.24 – 7.29 (m, 1H) 7.40 – 7.44 (m, 5H), 7.59 – 7.61 (m, 2H), 7.89 (d, J = 16 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 117.4, 121.8, 125.9, 128.4, 129.1, 129.6, 130.8, 134.3, 146.7, 150.9, 165.5 ppm. HRMS (ESI$^+$) calcd for $C_{17}H_{13}O_2$ [M]$^+$ 248.0832, found 248.0827. The NMR spectra are in accordance with literature.$^{11}$

Phenyl (1,1'-biphenyl)-4-carboxylate (4c)

According to the general procedure for ester synthesis, 4c was obtained as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.24 – 7.26 (m, 2H), 7.27 – 7.31 (m, 1H), 7.41 – 7.52 (m, 5H), 7.66 – 7.68 (m, 2H), 7.75 (dd, J = 8.4, 1.5 Hz, 2H), 8.29 (dd, J = 8.4, 1.6 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 121.9, 126.0, 127.4, 127.5, 128.4, 128.5, 129.1, 129.6, 130.8, 130.9, 140.0, 146.4, 151.1, 165.2 ppm.
HRMS (ESI+) calcd for C_{19}H_{14}O_{2} [M+Na]^+ 297.0886, found 297.0891. The NMR spectra are in accordance with literature.\textsuperscript{12}

Phenyl (1,1'-biphenyl)-3-carboxylate (4d)

According to the general procedure for ester synthesis, 4d was obtained as a white solid. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ = 7.24 (d, J = 8.8 Hz, 2H), 7.29 (t, J = 7.6 Hz, 1H), 7.38 – 7.51 (m, 5H), 7.60 (t, J = 7.6 Hz, 1H), 7.66 (d, J = 7.2 Hz, 2H), 7.87 (d, J = 7.6 Hz, 1H), 8.19 (d, J = 7.6 Hz, 1H), 8.44 (s, 1H) ppm. \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ = 121.8, 126.1, 127.3, 128.0, 129.0, 129.07, 129.09, 129.2, 129.7, 130.2, 132.4, 140.1, 141.9, 151.1, 165.3 ppm. HRMS (ESI+) calcd for C_{19}H_{14}O_{2} [M+Na]^+ 297.0886, found 297.0893. The NMR spectra are in accordance with literature.\textsuperscript{13}

Phenyl (1,1'-biphenyl)-2-carboxylate (4e)

According to the general procedure for ester synthesis, 4e was obtained as a white solid. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ = 6.85 (d, J = 7.6 Hz, 2H), 7.17 (t, J = 7.6 Hz, 1H), 7.31 (t, J = 8.0 Hz, 2H), 7.38 – 7.52 (m, 7H), 7.61 (t, J = 7.6 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H) ppm. \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ = 121.4, 125.9, 127.5, 127.6, 128.4, 128.7, 129.4, 130.4, 130.6, 131.0, 131.9, 141.4, 142.9, 150.7, 167.4 ppm. HRMS (ESI+) calcd for C_{19}H_{14}O_{2} [M+Na]^+ 297.0886, found 297.0890. The NMR spectra are in accordance with literature.\textsuperscript{14}

Phenyl 4-methoxybenzoate (4f)

According to the general procedure for ester synthesis, 4f was obtained as a white solid. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ = 3.90 (s, 3H), 6.99 (d, J = 9.0 Hz, 2H), 7.19 – 7.23 (m, 2H), 7.22 – 7.32 (m, 1H), 7.40 – 7.46 (m, 2H), 8.17 (d, J = 9.0 Hz, 2H) ppm. \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ = 55.6, 113.9, 121.9, 122.0, 125.9, 129.6, 132.4, 151.2, 164.0, 165.1 ppm. HRMS (ESI+) calcd for C_{14}H_{13}O_{3} [M+H]^+ 229.0859, found 229.0860. The NMR spectra are in accordance with literature.\textsuperscript{11}
Phenyl 4-fluorobenzoate (4g)

According to the general procedure for ester synthesis, 4g was obtained as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.15 – 7.24$ (m, 4H), 7.26 – 7.32 (m, 1H), 7.39 – 7.48 (m, 2H), 8.18 – 8.28 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 115.92$ (d, $J = 22.0$ Hz), 121.8, 125.89 (d, $J = 2.9$ Hz), 126.1, 129.7, 132.92 (d, $J = 9.5$ Hz), 150.9, 164.68 (d, $J = 63.2$ Hz), 167.5 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -104.46$ ppm. HRMS (ESI$^+$) calcd for C$_{13}$H$_9$FNaO$_2$ [M+Na]$^+$ 239.0479, found 239.0484. The NMR spectra are in accordance with literature.$^{11}$

Phenyl 4-(trifluoromethyl)benzoate (4h)

According to the general procedure for ester synthesis, 4h was obtained as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.20 – 7.25$ (m, 2H), 7.28 – 7.34 (m, 1H), 7.41 – 7.50 (m, 2H), 7.79 (d, $J = 8.4$ Hz, 2H), 8.33 (d, $J = 8.4$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 121.7, 123.70$ (q, $J = 272.7$ Hz), 125.75 (q, $J = 3.7$ Hz), 126.4, 129.8, 130.7, 132.95 (q, $J = 1.2$ Hz), 135.14 (q, $J = 32.8$ Hz), 150.8, 164.1 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -63.16$ ppm. HRMS (ESI$^+$) calcd for C$_{14}$H$_9$F$_3$NaO$_2$ [M+Na]$^+$ 289.0447, found 289.0453. The NMR spectra are in accordance with literature.$^{14}$

Methyl phenyl terephthalate (4q)

According to the general procedure for ester synthesis, 4q was obtained as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 3.97$ (s, 3H), 7.21 – 7.24 (m, 2H), 7.28 – 7.32 (m, 1H), 7.42 – 7.47 (m, 2H), 8.16 – 8.19 (m, 2H), 8.26 – 8.29 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 52.7, 121.7, 126.3, 129.7, 129.8, 130.3, 133.4, 134.6, 150.8, 164.5, 166.3$ ppm. HRMS (ESI$^+$) calcd for C$_{15}$H$_{12}$NaO$_4$ [M+Na]$^+$ 279.0628, found 279.0635. The NMR spectra are in accordance with literature.$^{15}$

Phenyl benzo[b]thiophene-2-carboxylate (4r)
According to the general procedure for ester synthesis, 4r was obtained as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.25 – 7.32 (m, 3H), 7.42 – 7.48 (m, 3H), 7.51 (t, $J$ = 7.2 Hz, 1H), 7.90 – 7.95 (m, 2H), 8.26 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 121.7, 123.0, 125.2, 125.9, 126.3, 127.5, 129.7, 132.0, 132.8, 138.8, 142.8, 150.7, 161.4 ppm. HRMS (ESI$^+$) calcd for C$_{15}$H$_{10}$NaO$_2$ [M+Na]$^+$ 277.0294, found 277.0291. The NMR spectra are in accordance with literature.\textsuperscript{16}

Phenyl benzofuran-2-carboxylate (4s)

According to the general procedure for ester synthesis, 4s was obtained as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.26 – 7.32 (m, 3H), 7.34 – 7.38 (m, 1H), 7.43 – 7.47 (m, 2H), 7.48 – 7.53 (m, 1H), 7.65 (d, $J$ = 8.4 Hz, 1H), 7.73 – 7.76 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 112.6, 115.6, 121.7, 123.2, 124.1, 126.4, 127.0, 128.2, 129.7, 144.9, 150.3, 156.2, 158.0 ppm. HRMS (ESI$^+$) calcd for C$_{15}$H$_{10}$NaO$_3$ [M+Na]$^+$ 261.0522, found 261.0525. The NMR spectra are in accordance with literature.\textsuperscript{17}

Phenyl 6-(3-(1-adamantyl)-4-methoxyl phenyl)-2-naphthoate (4t)

According to the general procedure for ester synthesis, 4t was obtained as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.81 (s, 6H), 2.12 (s, 3H), 2.20 (s, 6 H), 3.92 (s, 3H), 7.01 (d, $J$ = 8.4 Hz, 1H), 7.28 – 7.31 (m, 3H), 7.45 – 7.49 (m, 2H), 7.57 (dd, $J$ = 8.0 Hz, 2.0 Hz, 1H), 7.63 (d, $J$ = 2.4 Hz, 1H), 7.84 (dd, $J$ = 8.4 Hz, 1.6 Hz, 1H), 7.99 (d, $J$ = 8.8 Hz, 1H), 8.05 (d, $J$ = 9.6 Hz, 2H), 8.21 (dd, $J$ = 8.8 Hz, 2.0 Hz, 1H), 8.80 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 29.2, 37.2, 37.4, 40.7, 55.3, 112.2, 121.9, 124.9, 125.9, 125.95, 126.03, 126.1, 126.3, 126.8, 128.6, 129.7, 130.0, 131.4, 131.8, 132.5, 136.4, 139.1, 141.9, 151.2, 159.1, 165.6 ppm. HRMS (ESI$^+$) calcd for C$_{34}$H$_{32}$NaO$_3$ [M+Na]$^+$ 511.2244, found 511.2243. IR (KBr): 2904, 2850, 1730, 1622, 1474, 1276, 1078, 814, 740, 691 cm$^{-1}$.

VI. Characterization data of methylated products
1-Methylnaphthalene (2a)

From nitro group: According to the general methylation method of nitrobenzene, 2a was obtained as colorless liquid starting from 1a (23 mg, 80% yield).

From amide: According to the general methylation procedure of amide, 2a was obtained as colorless liquid starting from 3a (24 mg, 85% yield).

From ester: According to the general methylation procedure of ester, 2a was obtained as colorless liquid starting from 4a (21 mg, 72% yield).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.72$ (s, 3H), 7.34 (d, $J = 6.8$ Hz, 1H), 7.36 – 7.42 (m, 1H), 7.48 – 7.57 (m, 2H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.83 – 7.89 (m, 1H), 8.02 (dd, $J = 8.4$, 1.2 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 19.5$, 124.2, 125.67, 125.70, 125.8, 126.5, 126.7, 128.6, 132.7, 133.7, 134.4 ppm. The NMR spectra are in accordance with literature.$^{18}$

2-Methylnaphthalene (2b)

From nitro group: According to the general methylation method of nitrobenzene, 2b was obtained as colorless liquid starting from 1b (19 mg, 68% yield).

From amide: According to the general methylation procedure of amide, 2b was obtained as colorless liquid starting from 3b (20 mg, 70% yield).

From ester: According to the general methylation procedure of ester, 2b was obtained as colorless liquid starting from 4b (21 mg, 75% yield).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.53$ (s, 3H), 7.33 (dd, $J = 8.4$ Hz, 1.6 Hz, 1H), 7.39 – 7.47 (m, 2H), 7.62 (s, 1H), 7.74 – 7.78 (m, 2H), 7.81 (d, $J = 7.6$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 21.9$, 125.1, 126.0, 127.0, 127.4, 127.7, 127.8, 128.2, 131.8, 133.8, 135.6 ppm. The NMR spectra are in accordance with literature.$^{18}$

4-Methyl-1,1'-biphenyl (2c)
From nitro group: According to the general methylation method of nitrobenzene, 2c was obtained as a white solid starting from 1c (22 mg, 65% yield).

From amide: According to the general methylation procedure of amide, 2c was obtained as a white solid starting from 3c (28 mg, 82% yield).

From ester: According to the general methylation procedure of ester, 2c was obtained as a white solid starting from 4c (22 mg, 66% yield).

\[ {}^1 H \text{NMR (400 MHz, CDCl}_3): \delta = 2.40 (s, 3H), 7.27 (d, J = 8.4 \text{ Hz, 2H}), 7.30 - 7.35 (m, 1H), 7.40 - 7.45 (m, 2H), 7.49 - 7.52 (m, 2H), 7.57 - 7.60 (m, 2H) \text{ ppm.} \]

\[ {}^{13} C \text{NMR (100 MHz, CDCl}_3): \delta = 21.2, 127.10, 127.11, 127.13, 128.8, 129.6, 137.2, 138.5, 141.3 \text{ ppm. The NMR spectra are in accordance with literature.} \]

3-Methyl-1,1'-biphenyl (2d)

From nitro group: According to the general methylation method of nitrobenzene, 2d was obtained as yellowish liquid starting from 1d (25 mg, 74% yield)

From amide: According to the general methylation procedure of amide, 2d was obtained as yellowish liquid starting from 3d (23 mg, 68% yield)

From ester: According to the general methylation procedure of ester, 2d was obtained as yellowish liquid starting from 4d (25 mg, 76% yield).

\[ {}^1 H \text{NMR (400 MHz, CDCl}_3): \delta = 2.45 (s, 3H), 7.18 - 7.21 (m, 1H), 7.34 - 7.38 (m, 2H), 7.41 - 7.48 (m, 4H), 7.60 - 7.63 (m, 2H) \text{ ppm.} \]

\[ {}^{13} C \text{NMR (100 MHz, CDCl}_3): \delta = 21.7, 124.4, 127.29, 127.31, 128.11, 128.12, 128.79, 128.82, 138.4, 141.4, 141.5 \text{ ppm. The NMR spectra are in accordance with literature.} \]

2-Methyl-1,1'-biphenyl (2e)

From nitro group: According to the general methylation method of nitrobenzene, 2e was obtained as yellowish liquid starting from 1e (18 mg, 53% yield)

\[ \]
From amide: According to the general methylation procedure of amide, 2e was obtained as yellowish liquid starting from 3e (20 mg, 60% yield).

From ester: According to the general methylation procedure of ester, 2e was obtained as yellowish liquid starting from 4e (17 mg, 52% yield).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.28 (s, 3H), 7.22 – 7.25 (m, 2H), 7.26 – 7.28 (m, 1H), 7.30 – 7.37 (m, 3H), 7.39 – 7.45 (m, 2H), 7.45 – 7.62 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 20.6, 125.9, 126.9, 127.3, 127.4, 128.2, 128.9, 129.3, 129.9, 130.4, 135.5 ppm. The NMR spectra are in accordance with literature.$^{18}$

4-Methylanisole (2f)

From nitrobenzene: The methylation of nitrobenzene 1f was conducted at 130 °C. Diphenylacetylene (35.6 mg, 0.2 mmol) was subjected as internal standard after the completion of reaction. The yield of 2f was determined by GC analysis using calibration curves based on data from the authentic sample of 2f and diphenylacetylene (84% yield).
From amide: According to the general methylation method of amide, the decarbonylative methylation of amide 3f was conducted with 2 equiv Et$_3$N added. Diphenylacetylene (35.6 mg, 0.2 mmol) was subjected as internal standard after the completion of reaction. The yields of 2f was determined by GC analysis using calibration curves based on data from the authentic sample of 2f and diphenylacetylene (47% yield).
**From ester:** According to the general methylation procedure of ester starting from 4f, diphenylacetylene (35.6 mg, 0.2 mmol) was subjected as internal standard after the completion of reaction. The yield of 2f were determined by GC analysis using calibration curves based on data from the authentic sample of 2f and diphenylacetylene (13% yield).

![Graph showing GC analysis results with calibration curve](image-url)

| Compound          | Retention Time | m/z   | Area  | Height | Conc. |
|-------------------|---------------|-------|-------|--------|-------|
| 1-p-methylanisole | 2.709         | 122.00| 47258 | 4886   | 0.128 |
| 2-diphenylacetylene| 7.390         | 177.90| 52154 | 30652  | 1.000 |

**Calibration Curve**

- ID: 1 m/z: 122.00 Name: p-methylanisole
- Eqn: y = 0.709808x + 0.000000
- r² = 0.999478
- MeanRF: 0.68 RFSDF: 0.06 RFRSD: 8.97
- CurveType: Least square
- ZeroThrough: Yes
- WeightedRegression: No
- Internal Standard

| #    | ConcRatio | GC Area Ratio | GC Area of Int Standard |
|------|-----------|---------------|-------------------------|
| 1    | 1.000     | 0.73          | 38485.00                |
| 2    | 0.800     | 0.56          | 280771.00               |
| 3    | 0.600     | 0.42          | 196416.00               |
| 4    | 0.400     | 0.27          | 113751.00               |
| 5    | 0.200     | 0.11          | 47479.00                |
1-Fluoro-4-methylbenzene (2g)

From nitro group: According to the general methylation method of nitrobenzene starting from 1g, mesitylene (27.8 μL, 0.2 mmol) was subjected as internal standard after the completion of reaction. The yield of 2g was determined by GC analysis using calibration curves based on data from the authentic sample of 2g and mesitylene (46% yield).
From amide: According to the general methylation procedure of amide starting from 3g, mesitylene (27.8 μL, 0.2 mmol) was subjected as internal standard after the completion of reaction. The yield of 2g was determined by GC analysis using calibration curves based on data from the authentic sample of 2g and mesitylene (47% yield).
From ester: According to the general methylation procedure of ester starting from 4g, mesitylene (27.8 μL, 0.2 mmol) was subjected as internal standard after the completion of reaction. The yield of 2g was determined by GC analysis using calibration curves based on data from the authentic sample of 2g and mesitylene (68% yield).
4-Methylbenzotrifluoride (2h)

From nitro group: According to the general methylation method of nitrobenzene starting from 1h, mesitylene (27.8 μL, 0.2 mmol) was subjected as internal standard after the completion of reaction. The yield of 2h was determined by GC analysis using calibration curves based on data from the authentic sample of 2h and mesitylene (62% yield).
**From amide:** According to the general methylation method of amide, the decarbonylative methylation of amide 3h was conducted with 2 equiv Et$_3$N added. Mesitylene (27.8 μL, 0.2 mmol) was subjected as internal standard after the completion of reaction. The yield of 2h was determined by GC analysis using calibration curves based on data from the authentic sample of 2h and mesitylene (55% yield).
From ester: According to the general methylation procedure of ester starting from 4h, mesitylene (27.8 μL, 0.2 mmol) was subjected as internal standard after the completion of reaction. The yield of 2h was determined by GC analysis using calibration curves based on data from the authentic sample of 2h and mesitylene (39% yield).
1-(4-Methoxy-3-methylphenyl)ethan-1-one (2i)

From nitro group: According to the general methylation method of nitrobenzene, 2i was obtained as colorless liquid starting from 1i (26 mg, 78% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.24 (s, 3H), 2.54 (s, 3H), 3.89 (s, 3H), 6.84 (d, $J = 8.4$ Hz, 1H), 7.62 – 7.77 (m, 1H), 7.80 – 7.83 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 16.4, 26.5, 55.6, 109.3, 126.9, 128.6, 129.9, 131.0, 161.9, 197.3 ppm. The NMR spectra are in accordance with literature.$^{19}$

4-(p-Tolyl)morpholine (2j)

From nitro group: According to the general methylation method of nitrobenzene, 2j was obtained as a white solid starting from 1j (14 mg, 40% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.28 (s, 3H), 3.10 – 3.14 (m, 4H), 3.85 – 3.88 (m, 4H), 6.84 (d, $J = 8.4$ Hz, 2H), 7.10 (d, $J = 8.4$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 20.6, 50.1, 67.1, 116.2, 129.7, 129.8, 149.3 ppm. The NMR spectra are in accordance with literature.$^{20}$

9-Methylphenanthrene (2k)

From nitro group: According to the general methylation method of nitrobenzene, 2k was obtained as a white solid starting from 1k (32 mg, 82% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.76 (s, 3H), 7.55 – 7.64 (m, 3H), 7.64 – 7.71 (m, 2H), 7.83 (dd, $J = 6.4$, 1.6 Hz, 1H), 8.06 – 8.11 (m, 1H), 8.67 (d, $J = 7.2$ Hz, 1H), 8.71 – 8.78 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 20.2, 122.6, 123.1, 124.8, 125.9, 126.3, 126.65, 126.72, 126.9, 128.0, 129.8, 130.5, 132.1, 132.2, 132.6 ppm. The NMR spectra are in accordance with literature.$^{21}$
1-Methylpyrene (2l)

From nitro group: According to the general methylation method of nitrobenzene, 2l was obtained as a white solid starting from 1l (33 mg, 76% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 3.00$ (s, 3H), 7.85 – 7.90 (m, 1H), 7.98 – 8.07 (m, 3H), 8.08 – 8.14 (m, 2H), 8.16 – 8.22 (m, 2H), 8.25 (d, $J = 9.2$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 20.0$, 123.8, 124.8, 124.87, 124.92, 124.93, 124.95, 125.9, 126.5, 127.2, 127.7, 128.0, 129.3, 129.8, 131.1, 131.5, 132.4 ppm. The NMR spectra are in accordance with literature.$^{21}$

3-Methylperylene (2m)

From nitro group: According to the general methylation method of nitrobenzene, 2m was obtained as a pale yellow solid starting from 1m (27 mg, 51% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.66$ (s, 3H), 7.34 (d, $J = 8.4$ Hz, 1H), 7.44 – 7.56 (m, 3H), 7.67 (t, $J = 8.0$ Hz, 2H), 7.83 (d, $J = 8.4$ Hz, 1H), 8.10 (d, $J = 7.6$ Hz, 1H), 8.13 – 8.24 (m, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 20.0$, 119.8, 120.1, 120.27, 120.29, 124.2, 126.4, 126.65, 126.71, 127.4, 127.6, 127.9, 128.6, 128.9, 129.6, 131.5, 131.6, 131.7, 133.8, 134.4, 134.8 ppm. IR (KBr): 3044, 2943, 2898, 2856, 1500, 1387, 1186, 817, 762 cm$^{-1}$.

5-Methylquinoline (2n)

From nitro group: According to the general methylation method of nitrobenzene, 2n was obtained as yellow liquid starting from 1n (24 mg, 84% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.68$ (s, 3H), 7.37 (d, $J = 7.2$ Hz, 1H), 7.40 – 7.45 (m, 1H), 7.58 – 7.62 (m, 1H), 7.96 (d, $J = 8.4$ Hz, 1H), 8.31 – 8.33 (m, 1H), 8.91 (d, $J = 4.0$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 18.7$, 120.8, 127.1,
The NMR spectra are in accordance with literature.\(^2\)

\[ \text{6-Methoxy-2,2,7-trimethylchromane (2o)} \]

**From nitro group:** According to the general methylation method of nitrobenzene, \(2o\) was obtained as a white solid starting from \(1o\) (19 mg, 45% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.31\) (s, 6H), 1.77 (t, \(J = 6.8\) Hz, 2H), 2.16 (s, 3H), 2.75 (t, \(J = 6.8\) Hz, 2H), 3.74 (s, 3H), 6.46 (d, \(J = 3.6\) Hz, 1H), 6.56 – 6.59 (m, 1H) ppm. \(^{13}\)C NMR (400 MHz, CDCl\(_3\)): \(\delta = 16.4, 23.2, 26.9, 27.1, 33.0, 55.8, 73.6, 111.1, 114.8, 120.8, 127.3, 146.3, 152.2\) ppm. HRMS (ESI\(^+\)) calcd for \(C_{13}H_{19}NO_2\) [M+H]\(^+\) 207.1380, found 207.1378. IR (KBr): 2954, 2922, 2850, 1479, 1457, 1423, 1250, 1203, 1049, 1020, 798, 711 cm\(^{-1}\).

\[ \text{2-Methylestrone-3-methyl ether (2p)} \]

**From nitro group:** According to the general methylation method of nitrobenzene, \(2p\) was obtained as yellow liquid starting from \(1p\) (37 mg, 62%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.91\) (s, 3H), 1.38 – 1.46 (m, 1H), 1.47 – 1.52 (m, 2H), 1.52 – 1.56 (m, 1H), 1.59 (d, \(J = 9.4\) Hz, 1H), 1.61 – 1.66 (m, 1H), 1.92 – 2.18 (m, 4H), 2.19 (s, 3H), 2.21 – 2.29 (m, 1H), 2.38 – 2.46 (m, 1H), 2.46 – 2.56 (m, 1H), 2.83 – 2.95 (m, 2H), 3.80 (d, \(J = 1.2\) Hz, 3H), 6.57 (s, 1H), 7.07 (s, 1H) ppm. \(^{13}\)C NMR (400 MHz, CDCl\(_3\)): \(\delta = 14.0, 16.2, 21.7, 26.1, 26.8, 29.7, 31.7, 36.0, 38.6, 44.1, 48.2, 50.5, 55.4, 110.5, 124.0, 127.8, 131.3, 134.8, 155.9, 221.2\) ppm. HRMS (ESI\(^+\)) calcd for \(C_{20}H_{27}O_2\) [M+H]\(^+\) 299.2006, found 299.2014. IR (KBr): 2994, 2874, 1739, 1612, 1508, 1256, 1214, 1098, 1053, 1024, 890, 830 cm\(^{-1}\).

\[ \text{Methyl 4-methylbenzoate (2q)} \]
From *amide*: According to the general methylation procedure of amide, 2q was obtained as a white solid starting from 3q (23 mg, 78% yield).

From *ester*: According to the general methylation procedure of ester, 2q was obtained as a white solid starting from 4q (23 mg, 80% yield).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.40 (s, 3H), 3.90 (s, 3H), 7.23 (d, $J = 8.0$ Hz, 2H), 7.93 (d, $J = 8.4$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 21.8, 52.1, 127.5, 129.2, 129.7, 143.7, 167.3 ppm. The NMR spectra are in accordance with literature.$^{23}$

![2-Methylbenzo[b]thiophene (2r)](image)

2-Methylbenzo[b]thiophene (2r)

From *amide*: According to the general methylation procedure of amide, 2r was obtained as a white solid starting from 3r (23 mg, 76% yield).

From *ester*: According to the general methylation procedure of ester, 2r was obtained as a white solid starting from 4r (21 mg, 70% yield).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.60 (d, $J = 1.2$ Hz, 3H), 6.97 – 7.00 (m, 1H), 7.26 (td, $J = 7.6, 1.4$ Hz, 1H), 7.29 – 7.34 (m, 1H), 7.66 (d, $J = 7.2$ Hz, 1H), 7.76 (dd, $J = 8.0, 1.2$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 16.3, 121.7, 122.1, 122.6, 123.5, 124.2, 139.8, 140.6, 141.0 ppm. The NMR spectra are in accordance with literature.$^{24}$

![2-Methylbenzofuran (2s)](image)

2-Methylbenzofuran (2s)

From *amide*: According to the general methylation procedure of amide, 2s was obtained as colorless liquid starting from 3s (14 mg, 54% yield).

From *ester*: According to the general methylation procedure of ester, 2s was obtained as colorless liquid starting from 4s (22 mg, 66% yield).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.46 (d, $J = 1.2$ Hz, 3H), 6.37 (penta, $J = 1.0$ Hz, 1H), 7.13 – 7.23 (m, 2H), 7.39 – 7.42 (m, 1H), 7.45 – 7.49 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 14.2, 102.7, 110.7, 120.2, 122.5, 123.2, 129.3, 154.8, 155.5 ppm. The NMR spectra are in accordance with literature.$^{24}$
2-Methyl-6-(3-(1-adamantyl)-4-methoxyphenyl)-naphthalene (2t)

From ester: According to the general methylation procedure of ester, 2t was obtained as a white solid starting from 4t (53 mg, 69% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.83 (s, 6H), 2.13 (s, 3H), 2.21 (s, 6H), 2.54 (s, 3H), 3.91 (s, 3H), 7.00 (d, $J$ = 8.4 Hz, 1H), 7.34 (dd, $J$ = 8.4, 1.3 Hz, 1H), 7.54 (dd, $J$ = 8.4, 2.3 Hz, 1H), 7.60 – 7.65 (m, 2H), 7.71 (dd, $J$ = 8.5, 1.6 Hz, 1H), 7.79 – 7.84 (m, 2H), 7.96 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 21.9, 29.3, 37.3, 37.3, 40.7, 55.3, 112.2, 124.9, 125.6, 125.8, 126.0, 126.7, 127.7, 128.0, 128.6, 132.1, 132.6, 133.4, 135.3, 138.2, 138.9, 158.5 ppm. HRMS (ESI$^+$) calcd for C$_{28}$H$_{31}$O $[\text{M+H}]^+$ 383.2369, found 383.2377. IR (KBr): 2956, 2905, 2850, 1602, 1498, 1460, 1235, 1140, 1032, 877, 807 cm$^{-1}$.

VII. Sequential methylation of 1-fluoro-4-nitronaphthalene.

1-Fluoro-4-nitronaphthalene (8) was prepared according to the literature.$^{25}$

An oven-dried vial equipped with a stirring bar was charged with 8 (76.4 mg, 0.4 mmol), TMB (200 $\mu$L, 3.5N in THF, 1.75 equiv), Pd(acac)$_2$ (6.2 mg, 5 mol%), BrettPhos (32.2 mg, 15 mol%), Cs$_2$CO$_3$ (260 mg, 2 equiv) and toluene (1.2 mL) under N$_2$ at room temperature. The reaction mixture was placed in a preheated oil bath at 150 °C, and stirred for 24 h. Then the reaction mixture was cooled down to room temperature, diluted with CH$_2$Cl$_2$ (20 mL), filtered through celite, and concentrated under reduced pressure. Purification by column chromatography on silica gel (200-300 mesh) afforded the corresponding product 9 as colorless oil (49 mg, 76% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.65 (s, 3H), 6.98 – 7.08 (m, 1H), 7.18 – 7.25 (m, 1H), 7.52 – 7.62 (m, 2H), 7.95 – 8.01 (m, 1H), 8.10 – 8.18 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 19.1, 108.92 (d, $J$ = 19.5 Hz), 121.15 (d, $J$ = 5.6 Hz), 123.85 (d, $J$ = 16.4 Hz), 124.34 (d, $J$ = 2.7 Hz), 125.9, 125.97 (d, $J$ = 5.6 Hz), 126.74 (d, $J$ = 1.0 Hz), 130.06 (d, $J$ = 4.8 Hz), 133.68 (d, $J$ = 4.4 Hz), 157.64 (d, $J$ = 249.1 Hz) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ = -126.50 ppm. HRMS (ESI$^+$) calcd for C$_{12}$H$_7$FNa $[\text{M+Na}]^+$ 183.0580, found 183.0581. IR (KBr): 2927, 2866, 1601, 1466, 1397, 1225, 1050, 819, 760, 731 cm$^{-1}$.
An oven-dried vial equipped with a stirring bar was charged with 9 (32 mg, 0.2 mmol), TMB (100 μL, 3.5N in THF, 1.75 equiv), Ni(COD)$_2$ (5.5 mg, 10 mol%), dctype (17 mg, 20 mol%), CsF (61 mg, 2.0 equiv) and toluene (0.6 mL) under N$_2$ at room temperature. The reaction mixture was placed in a preheated oil bath at 130 °C, and stirred for 24 h. The reaction mixture was then cooled down to room temperature, diluted with CH$_2$Cl$_2$ (10 mL), filtered through celite, and concentrated. Purification by column chromatography on silica gel (200-300 mesh, petroleum ether) afforded the corresponding product 10 colorless oil (17 mg, 55% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.67$ (s, 6H), 7.22 (s, 2H), 7.54 (dd, $J = 6.4, 3.2$ Hz, 2H), 8.02 (dd, $J = 6.4, 3.2$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 19.5, 124.8, 125.5, 126.4, 132.5, 132.8$ ppm. The NMR spectra are in accordance with literature.$^{26}$

VIII. Synthetic applications of catalytic methylation of unconventional aryl electrophiles

\[ \text{Ph} \xrightarrow{1 \text{LiHMDS (1.5 equiv)} \atop 2 \text{TsCl (1.2 equiv)}} \text{Ph} \]

$\text{N-phenyl-N-tosyl-(1,1'}$-biphenyl)-2-carboxamide (3e): N-phenyl-(1,1'-biphenyl)-2-carboxamide 11 (137 mg, 0.5 mmol) was dissolved in THF (2.5 mL). LiHMDS (1 mol/L in THF, 0.75 mL, 1.5 equiv) was added slowly at 0 °C under N$_2$. After stirring at 0 °C for 1 h, TsCl (114 mg, 1.2 equiv) was added slowly. Then the reaction mixture was quenched by water after further stirring at room temperature for 15 h. The mixture was sequentially washed with 1 N HCl (2 mL), saturated aqueous NaHCO$_3$ (2 mL), and brine (2 mL). The organic layer was dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The resulting crude mixture was purified by column chromatography on silica gel (200-300 mesh) to afford 3e as a white solid (182 mg, 85% yield).

\[ \text{Ph} \xrightarrow{\text{NaH, DMF}} \text{Ph} \]

$\text{N,4-dimethyl-N-(4-nitrophenyl)benzenesulfonamide (12):}$ An oven-dried vial equipped with a stirring bar was charged with $\text{N-methyl-p-toluenesulfonamide (1.85 g, 10 mmol)}$ and DMF (15 mL) under N$_2$. NaH (440 mg, 11 mmol) was added in portions at room temperature. The reaction mixture was stirred for 1 h. Then, $\text{p-fluoronitrobenzene (1.17 mL, 11 mmol)}$ was added and the reaction mixture was stirred for another 1 h. The reaction was then quenched with water (30 mL) and extracted with EtOAc (50 mL×2). Purification by chromatography on silica gel (200-300 mesh,
petroleum ether/CH₂Cl₂ = 2/1) afforded the corresponding product 12 as a yellowish solid (2.75 g, 90% yield). ¹H NMR (400 MHz, CDCl₃): δ = 2.42 (s, 3H), 3.22 (s, 3H), 7.24 – 7.28 (m, 2H), 7.31 – 7.35 (m, 2H), 7.39 – 7.44 (m, 2H), 8.14 – 8.20 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.7, 37.6, 124.4, 125.7, 127.7, 129.9, 132.9, 144.6, 145.7, 147.5 ppm. HRMS (ESI⁺) calcd for C₁₃H₁₄N₂O₄S [M+Na⁺] 329.0566, found 329.0566. IR (KBr): 3080, 2900, 1592, 1521, 1492, 1348, 1170, 1054, 872, 721, 665 cm⁻¹.

**N-(4'-methoxy-6-nitro-[1,1'-biphenyl]-3-yl)-N,4-dimethylbenzenesulfonamide (13):** Compound 13 was synthesized by a modified procedure of literature.²⁷ An oven-dried vial equipped with a stirring bar was charged with nitro aromatic 12 (4 mmol, 2.0 equiv), 4-bromoanisole (250 μL, 2 mmol, 1.0 equiv), [Pd(allyl)Cl]₂ (19 mg, 2.5 mol%), PCY₃-HBF₄ (55 mg, 7.5 mol%), 2,2-dimethylbutanoic acid (DMBA, 75 μL, 0.3 equiv) and K₂CO₃ (550 mg, 2.0 equiv) under N₂. Toluene (5 mL) was added at room temperature. The reaction mixture was placed in a preheated oil bath at 130 °C, and stirred for 24 h. The reaction mixture was then cooled down to room temperature, diluted with CH₂Cl₂ (50 mL), filtered through celite, and concentrated. Purification by chromatography on silica gel (200-300 mesh, petroleum ether/CH₂Cl₂/CH₂Cl₂/EtOAc = 20/4/1) afforded the corresponding product 13 as a yellowish solid. (594 mg, 72% yield) ¹H NMR (400 MHz, CDCl₃): δ = 2.43 (s, 3H), 3.20 (s, 3H), 3.84 (s, 3H), 6.91 – 6.96 (m, 2H), 7.15 – 7.22 (m, 4H), 7.29 (d, J = 7.9 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H), 7.75 – 7.79 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.8, 37.7, 55.5, 114.4, 124.4, 125.1, 127.9, 128.9, 128.9, 129.2, 129.8, 133.1, 137.0, 144.5, 145.0, 147.0, 160.0 ppm. HRMS (ESI⁺) calcd for C₂₁H₂₀N₂NaO₅S [M+Na⁺] 435.0985, found 435.0982. IR (KBr): 2926, 2853, 1612, 1515, 1347, 1255, 1169, 901, 746, 663 cm⁻¹.

**N-(4'-methoxy-6-methyl-[1,1'-biphenyl]-3-yl)-N,4-dimethylbenzenesulfonamide (14):** Compound 14 was synthesized according to the general methylation procedure of nitro group from 13. The reaction was conducted at 130 °C for 36 h. The corresponding product 14 was obtained as yellowish oil. (27 mg, 35% yield) ¹H NMR (400 MHz, CDCl₃) δ = 2.25 (s, 3H), 2.43 (s, 3H), 3.14 (s, 3H), 3.84 (s, 3H), 6.83 (d, J = 2.3 Hz, 1H), 6.92 (d, J = 8.8 Hz, 2H), 7.02 (dd, J = 8.0, 2.4
**1-(2,4-Dinitrophenyl)-4-methoxynaphthalene (15):** Compound 15 was synthesized by a modified procedure of literature. An oven-dried vial equipped with a stirring bar was charged with 1,3-dinitrobenzene (504 mg, 4 mmol, 2.0 equiv), 1-bromo-4-methoxynaphthalene (474 mg, 2 mmol, 1.0 equiv), [Pd(allyl)Cl]₂ (19 mg, 2.5 mol%), PCy₃·HBF₄ (55 mg, 7.5 mol%), 2,2-dimethylbutanoic acid (75 μL, 0.3 equiv) and K₂CO₃ (550 mg, 2.0 equiv) under N₂. Toluene (5 mL) was added at room temperature. The reaction mixture was placed in a preheated oil bath at 130 °C, and stirred for 24 h. The reaction mixture was then cooled down to room temperature, diluted with CH₂Cl₂ (50 mL), filtered through celite, and concentrated. Purification by chromatography on silica gel (200-300 mesh, petroleum ether/CH₂Cl₂ = 2/1) afforded the corresponding product 15 as a red solid (337 mg, 52% yield). ¹H NMR (400 MHz, CDCl₃): δ = 4.06 (s, 3H), 6.88 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.44 – 7.49 (m, 1H), 7.50 – 7.55 (m, 1H), 7.73 (d, J = 8.4 Hz, 1H), 8.37 (d, J = 8.4 Hz, 1H), 8.52 (dd, J = 8.4, 2.4 Hz, 1H), 8.86 (d, J = 2.4 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 55.8, 103.4, 119.9, 123.0, 124.0, 125.3, 125.8, 126.0, 126.6, 126.8, 127.8, 131.8, 135.0, 141.9, 147.2, 150.3, 156.8 ppm. HRMS (ESI⁺) calcd for C₁₇H₁₃N₂O₅ [M+H⁺] 325.0819, found 325.0818. IR (KBr): 3111, 2945, 2841, 1590, 1515, 1341, 1253, 1106, 1084, 815, 772, 740 cm⁻¹.

**1-Methoxy-4-(4-methyl-2-nitrophenyl)naphthalene (16):** Compound 16 was synthesized according to the general methylation procedure of nitro group from 15. The reaction was conducted at 130 °C for 36 h. The corresponding product 15 was obtained as a yellow solid (26 mg, 44% yield). ¹H NMR (400 MHz, CDCl₃) δ = 2.53 (s, 3H), 4.04 (s, 3H), 6.84 (d, J = 8.0 Hz, 1H), 7.23
(d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.39 – 7.44 (m, 2H), 7.44 – 7.51 (m, 2H), 7.83 (s, 1H), 8.33 (d, J = 8.4 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 21.1, 55.7, 103.4, 122.6, 124.6, 124.8, 125.4, 125.7, 126.4, 127.1, 127.7, 132.5, 132.7, 133.3, 133.4, 139.0, 150.2, 155.7 ppm. HRMS (ESI$^+$) calcd for $\text{C}_{18}\text{H}_{15}\text{NNO}_3$ [M$+$Na]$^+$ 316.0944, found 316.0947. IR (KBr): 2924, 2850, 1580, 1517, 1464, 1341, 1254, 1087, 817, 767 cm$^{-1}$.

5-Methoxy-9-methyl-7H-benzo[c]carbazole (17): Compound 17 was synthesized by Cadogentype reaction. An oven-dried vial equipped with a stirring bar was charged with nitroaromatic 16 (15 mg, 0.05 mmol, 1.0 equiv) under N$_2$. A mixture of P(OEt)$_3$ and 1,2-dichlorobenzene (v/v = 1/1, 0.3 mL) was added at room temperature. The reaction mixture was placed in a preheated oil bath at 150 °C, and stirred for 12 h. The reaction mixture was then cooled down to room temperature, diluted with CH$_2$Cl$_2$ (10 mL), filtered through celite, and concentrated. Purification by chromatography on silica gel (200-300 mesh, petroleum ether/CH$_2$Cl$_2$ = 2/1) afforded the corresponding product 17 as a white solid (13 mg, 98% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ = 2.55 (s, 3H), 4.03 (s, 3H), 6.83 (s, 1H), 7.18 (d, J = 8.1 Hz, 1H), 7.23 (s, 1H), 7.43 – 7.50 (m, 1H), 7.66 – 7.74 (m, 1H), 8.05 (br s, 1H), 8.31 (d, J = 8.1 Hz, 1H), 8.39 (d, J = 8.3 Hz, 1H), 8.66 (d, J = 8.3 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 22.0, 55.9, 91.6, 109.4, 111.1, 120.7, 121.8, 122.2, 122.3, 122.5, 123.2, 123.4, 127.5, 130.3, 133.0, 137.6, 138.8, 155.2 ppm. HRMS (ESI$^+$) calcd for $\text{C}_{18}\text{H}_{15}$NO$^+$ [M]$^+$ 261.1148, found 261.1156. IR (KBr): 3360, 2963, 2921, 2142, 1586, 1512, 1462, 1389, 1260, 1027, 968, 797, 766 cm$^{-1}$.

**IX. Mechanistic studies**

**8.1 General procedure for competition experiments**

An oven-dried vial equipped with a stirring bar was charged with two substrates (0.2 mmol, 1.0 equiv), TMB (100 μL, 3.5 N in THF, 3.5 mmol, 1.75 equiv), catalyst, ligand and base (0.4 mmol, 2.0 equiv), placed under a positive pressure of N$_2$. Solvent (0.6 mL) was added at room temperature. The reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for 4h. The reaction mixture was then cooled down to room temperature. Diphenylacetylene (35.6 mg, 0.2 mmol) and mesitylene (27.8 μL, 0.2 mmol) were subjected to the reaction mixture as the internal standard. The yields of 2f and 2h were separately
The yield of 2f was determined by GC analysis using diphenylacetylene and mesitylene as the internal standard, respectively.

Scheme S4 Competition experiments.

8.2 Competition experiment for denitrative methylation

The yield of 2f was determined by GC analysis using calibration curves based on data from the authentic sample of 2f and diphenylacetylene (1% yield).
**Compound**

1. p-methylanisole
2. diphenylisocyanate

| Compound       | R.Time | m/z  | Area  | Height | Conc. |
|----------------|--------|------|-------|--------|-------|
| p-methylanisole| 2.689  | 122.00 | 5934  | 760    | 0.013 |
| diphenylisocyanate| 7.312 | 177.90 | 633594 | 33388 | 1.000 |

**Calibration Curve**

- ID=1, m/z 122.00, Name=p-methylanisole
- Eq:x=0.705868x+0.000000
- r=0.999940, r2=0.999951
- MeanRF:0.68, RFSD:0.96, RFRSD:8.97
- CurveType:Least square
- ZeroThrough:Yes
- WeightedRegression:No
- Internal Standard

**GC Area Ratio**

| # | ConcRatio | GC AreaRatio | GC Area of Int Standard |
|---|-----------|--------------|-------------------------|
| 1 | 1.000     | 0.75         | 254855.00               |
| 2 | 0.800     | 0.56         | 280771.00               |
| 3 | 0.600     | 0.42         | 106416.00               |
| 4 | 0.400     | 0.27         | 113751.00               |
| 5 | 0.200     | 0.11         | 47479.00                |
The yield of 2h was determined by GC analysis using calibration curves based on data from the authentic sample of 2h and mesitylene (25% yield).
8.3 Competition experiment for decarbonylative methylation of amide

The yield of $2f$ was determined by GC analysis using calibration curves based on data from the authentic sample of $2f$ and diphenylacetylene (7% yield).

| Compound               | RT (min) | m/z   | Area  | Height | Conc. |
|------------------------|----------|-------|-------|--------|-------|
| p-methylanisole        | 2.677    | 122.00| 17771 | 2139   | 0.074 |
| diphenylacetylene      | 7.402    | 177.90| 339068| 24123  | 1.00  |

Calibration Curve

| # | ConcRatio | GC AreaRatio | GC Area of InternalStandard |
|---|-----------|--------------|-----------------------------|
| 1 | 1.000     | 0.73         | 384383.00                   |
| 2 | 0.800     | 0.58         | 280773.00                   |
| 3 | 0.600     | 0.42         | 196416.00                   |
| 4 | 0.400     | 0.27         | 113751.00                   |
| 5 | 0.200     | 0.11         | 47479.00                    |
The yield of 2h was determined by GC analysis using calibration curves based on data from the authentic sample of 2h and mesitylene (64% yield).
8.4 Competition experiment for decarbonylative methylation of ester

The yield of 2f was determined by GC analysis using calibration curves based on data from the authentic sample of 2f and diphenylacetylene (5% yield).

| Compound               | RTime | m/z  | Area   | Height | Conc. |
|------------------------|-------|------|--------|--------|-------|
| p-methylanisole        | 2.683 | 122.00 | 21925  | 2860   | 0.053 |
| diphenylacetylene      | 7.274 | 177.90 | 581143 | 36994  | 1.000 |

Calibration Curve

| ConcRatio | GCAreaRatio | GCArea of IntStandard |
|-----------|-------------|-----------------------|
| 1         | 1.000       | 364885.00              |
| 2         | 0.800       | 280771.00              |
| 3         | 0.600       | 196416.00              |
| 4         | 0.400       | 113751.00              |
| 5         | 0.200       | 47479.00               |
The yield of 2h was determined by GC analysis using calibration curves based on data from the authentic sample of 2h and mesitylene (9% yield).

X. References

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XI. Copies of NMR spectra

$^1$H NMR spectra of 1o:

$^{13}$C NMR spectra of 1o:
$^1$H NMR spectra of 2a:

$^{13}$C NMR spectra of 2a:
$^1$H NMR spectra of 2b:

$^{13}$C NMR spectra of 2b:
$^1$H NMR spectra of 2c:

$^{13}$C NMR spectra of 2c:
$^1$H NMR spectra of 2d:

$^{13}$C NMR spectra of 2d:
$^1$H NMR spectra of 2e:

$^{13}$C NMR spectra of 2e:
$^1$H NMR spectra of 2i:

$^{13}$C NMR spectra of 2i:
$^1$H NMR spectra of 2j:

$^{13}$C NMR spectra of 2j:
$^1$H NMR spectra of 2k:

$^{13}$C NMR spectra of 2k:
$^1$H NMR spectra of 2l:

$^{13}$C NMR spectra of 2l:
$^1$H NMR spectra of 2m:

$^{13}$C NMR spectra of 2m:
$^1$H NMR spectra of 2n:

$^{13}$C NMR spectra of 2n:
$^1$H NMR spectra of 2o:

$^{13}$C NMR spectra of 2o:
$^1$H NMR spectra of 2p:

$^{13}$C NMR spectra of 2p:
$^1$H NMR spectra of 2q:

$^{13}$C NMR spectra of 2q:
$^1$H NMR spectra of 2r:

$^{13}$C NMR spectra of 2r:
$^1$H NMR spectra of 2s:

$^{13}$C NMR spectra of 2s:
$^1$H NMR spectra of 2t:

$^{13}$C NMR spectra of 2t:
$^1$H NMR spectra of 3a:

$^{13}$C NMR spectra of 3a:
$^1$H NMR spectra of 3b:

$^{13}$C NMR spectra of 3b:
$^1$H NMR spectra of 3c:

$^{13}$C NMR spectra of 3c:
$^1$H NMR spectra of 3d:

$^{13}$C NMR spectra of 3d:
$^{1}H$ NMR spectra of 3e:

$^{13}C$ NMR spectra of 3e:
$^1$H NMR spectra of 3f:

$^{13}$C NMR spectra of 3f:
$^1$H NMR spectra of 3g:

$^{13}$C NMR spectra of 3g:
$^{19}$F NMR spectra of 3g:

$^1$H NMR spectra of 3h:
$^{13}$C NMR spectra of 3h:

$^{19}$F NMR spectra of 3h:
$^1$H NMR spectra of 3q:

$^{13}$C NMR spectra of 3q:
$^1$H NMR spectra of 3r:

$^{13}$C NMR spectra of 3r:
$^1$H NMR spectra of 3s:

$^{13}$C NMR spectra of 3s:
$^1$H NMR spectra of 4a:

$^{13}$C NMR spectra of 4a:
\(^1\)H NMR spectra of 4b:

\(^{13}\)C NMR spectra of 4b:
\(^1\)H NMR spectra of 4c:

\(^{13}\)C NMR spectra of 4c:
$^1$H NMR spectra of 4d:

$^{13}$C NMR spectra of 4d:
$^1$H NMR spectra of 4e:

$^{13}$C NMR spectra of 4e:
$^1$H NMR spectra of 4f:

$^{13}$C NMR spectra of 4f:
$^1$H NMR spectra of 4g:

$^{13}$C NMR spectra of 4g:
$^{19}\text{F NMR spectra of 4g:}$

$^{1}\text{H NMR spectra of 4h:}$
$^{13}$C NMR spectra of 4h:

![C NMR Spectrum](image)

$^{19}$F NMR spectra of 4h:

![F NMR Spectrum](image)
$^1$H NMR spectra of 4q:

$^{13}$C NMR spectra of 4q:
$^1$H NMR spectra of 4r:

$^{13}$C NMR spectra of 4r:
$^1$H NMR spectra of 4s:

$^{13}$C NMR spectra of 4s:
$^1$H NMR spectra of 4t:

$^{13}$C NMR spectra of 4t:
$^1$H NMR spectra of 9:

$^{13}$C NMR spectra of 9:
$^{19}$F NMR spectra of 9:

$^1$H NMR spectra of 10:
$^{13}$C NMR spectra of 10:

$^1$H NMR spectra of 12:
$^{13}$C NMR spectra of 12:

$^1$H NMR spectra of 13:
$^{13}$C NMR spectra of 13:

$^1$H NMR spectra of 14:
$^{13}$C NMR spectra of 14:

$^1$H NMR spectra of 15:
$^{13}$C NMR spectra of 15:

$^1$H NMR spectra of 16:
$^{13}$C NMR spectra of 16:

$^1$H NMR spectra of 17:
$^{13}$C NMR spectra of 17: