Supplementary Information

for

Deconstructive Functionalizations of Unstrained Carbon-Nitrogen Cleavage Enabled by Difluorocarbene

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1. General information

All chemicals were purchased from Admas Reagent, Energy chemical company, Bide Pharmatech Ltd (TMSCF₂Br), J&K SCIENTIFIC LTD (ICF₂COOEt) and Shang Fluoro Company (BrCF₂COOEt, ClCF₂H). Unless otherwise stated, all experiments were conducted in a sealed tube under ClCF₂H atmosphere. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh).

¹H-NMR and ¹³C-NMR spectra were recorded in CDCl₃ and DMSO-d₆ on a Bruker Avance 500 spectrometer (500 MHz ¹H, 125 MHz ¹³C (CPD), 470 MHz ¹⁹F) at room temperature. Chemical shifts were reported in ppm on the scale relative to CDCl₃ (δ = 7.26 for ¹H-NMR, δ = 77.00 for ¹³C-NMR) as an internal reference. Coupling constants (J) were reported in Hertz (Hz).
2. Optimization of the reaction conditions of the conversion of N-Phenylmorpholine

Table S1. The effects of additive

| Entry | Additive (3 equiv) | Yield (%)$^a$ |
|-------|--------------------|---------------|
| 1     | -                  | 31$^b$        |
| 2     | NaI                | 71            |
| 3     | ZnI                | 79            |
| 4     | TBAI               | 25            |
| 5     | KI                 | 78            |

$^a$ Reaction condition 1 : 1a (0.2 mmol), ICF$_2$COOEt (2, 0.6 mmol), Additive (3 equiv), K$_2$CO$_3$ (3 equiv.), H$_2$O (0.5 mL), MeCN (2 mL), for 10 h, N$_2$; GC yields.

Table S2. The effects of H$_2$O

| Entry | H$_2$O (X mL) | Yield (%)$^a$ |
|-------|---------------|---------------|
| 1     | 0.01          | Trace         |
| 2     | 0.1           | 63            |
| 3     | 0.3           | 77            |
| 4     | 0.5           | 78            |

$^a$ Reaction condition 1 : 1a (0.2 mmol), ICF$_2$COOEt (2, 0.6 mmol), KI (3 equiv), K$_2$CO$_3$ (3 equiv.), H$_2$O (0.5 mL), MeCN (2 mL), for 10 h, N$_2$; GC yields.
Table S3. The effects of Base

| Entry | Base (x equiv) | Yield (%)a |
|-------|----------------|------------|
| 1     | K₂CO₃ (3 equiv) | 77         |
| 2     | Na₂CO₃ (3 equiv) | 88 (84)b   |
| 3     | DBU (3 equiv)   | 68         |
| 4     | NaHCO₃ (3 equiv) | Trace     |
| 5     | Na₂CO₃ (1.2 equiv) | Trace   |
| 6     | Na₂CO₃ (1.8 equiv) | 50       |
| 7     | Na₂CO₃ (2.5 equiv) | 69       |
| 8     | Na₂CO₃ (2.5 equiv) | 87       |

a Reaction condition 1: 1a (0.2 mmol), ICF₂COOEt (2, 0.6 mmol), KI (3 equiv), Base (x equiv), H₂O (0.5 mL), MeCN (2 mL), for 10 h, N₂; GC yields.

Table S4. The effects of solvent

| Entry | Solvent (2 mL) | Yield (%)a |
|-------|----------------|------------|
| 1     | CH₃CN          | 88 (84)b   |
| 2     | DMF            | Trace      |
| 3     | Acetone        | 51         |
| 4     | CH₃OH          | 70         |

a Reaction condition 1: 1a (0.2 mmol), ICF₂COOEt (2, 0.6 mmol), KI (3 equiv), Na₂CO₃ (3 equiv.), H₂O (0.5 mL), Solvent (2 mL), for 10 h, N₂; GC yields.
### Table S5. The effects of temperature

| Entry | T °C | Yield (%)\(^a\) |
|-------|------|-----------------|
| 1     | 80   | 72              |
| 2     | 90   | 88 (84)\(^b\)  |
| 3     | 100  | 82              |

\(^{a}\) Reaction condition 1: 1a (0.2 mmol), ICF\(_2\)COOEt (2, 0.6 mmol), KI (3 equiv), Na\(_2\)CO\(_3\) (3 equiv.), H\(_2\)O (0.5 mL), MeCN (2 mL), for 10 h, N\(_2\); GC yields.

### Table S5. The effects of proportions of ICF\(_2\)COOEt

| Entry | ICF\(_2\)COOEt (x equiv) | Yield (%)\(^a\) |
|-------|--------------------------|-----------------|
| 1     | 1.2                      | 51              |
| 2     | 1.8                      | 64              |
| 3     | 2.5                      | 80              |
| 4     | 3                        | 88 (84)\(^b\)  |
| 5     | 4                        | 89              |

\(^{a}\) Reaction condition 1: 1a (0.2 mmol), ICF\(_2\)COOEt (2, x equiv), KI (3 equiv), Na\(_2\)CO\(_3\) (3 equiv.), H\(_2\)O (0.5 mL), MeCN (2 mL), for 10 h, N\(_2\); GC yields.
3. General process for the C(sp³)-N bond cleavage of the cyclic tertiary amines

3.1 For synthesis of alkyl iodides products (4a-4q)

In a dried Schlenk tube were placed the cyclic tertiary amines 1 (0.2 mmol), KI (0.6 mmol, 3 equiv), and Na₂CO₃ (0.6 mmol, 3 equiv), then the air was removed. N₂ was filled of Schleck tube and CH₃CN (2 mL), ICF₂COOEt (0.6 mmol, 3 equiv), H₂O (0.3 mL) is added the mixture. The resulting mixture was stirred at 90 °C for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc =20:1, v/v) to give the desired products.

3.2 For synthesis of alkyl iodides products (4r-4t)

In a dried Schlenk tube were placed the cyclic tertiary amines 1 (0.2 mmol), KI (0.6 mmol, 3 equiv) and KHF₂ (0.6 mmol, 3 equiv), then the air was removed. N₂ was filled of Schleck tube and CH₂Cl₂ (1 mL), TMSCF₂Br (0.6 mmol, 3 equiv), H₂O (0.3 mL) is added the mixture. The resulting mixture was stirred at rt for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc =20:1, v/v) to give the desired products.
3.3 For synthesis of alkyl bromide products (5a-5q)

In a dried Schlenk tube were placed the cyclic tertiary amines 1 (0.2 mmol), KBr (0.6 mmol, 3 equiv), and Na₂CO₃ (0.6 mmol, 3 equiv), then the air was removed. N₂ was filled of Schlenk tube and CH₃CN (2 mL), BrCF₂COOEt (0.6 mmol, 3 equiv), H₂O (0.3 mL) is added the mixture. The resulting mixture was stirred at 90 °C for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc = 20:1, v/v) to give the desired products.

3.4 For synthesis of alkyl bromide products (5r-5t)

In a dried Schlenk tube were placed the cyclic tertiary amines 1 (0.2 mmol) and KHF₂ (0.6 mmol, 3 equiv), then the air was removed. N₂ was filled of Schlenk tube and CH₂Cl₂ (1 mL), TMSCF₂Br (0.6 mmol, 3 equiv), H₂O (0.3 mL) is added the mixture. The resulting mixture was stirred at rt for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc = 20:1, v/v) to give the desired products.
4. Optimization of the reaction conditions of the \( N, N \)-dimethylamine react with \( \text{BrCF}_2\text{COOEt} \)

Table S6. The effects of additive and \( \text{XCF}_2\text{COOEt} \)

| Entry | Additive | \( \text{XCF}_2\text{COOEt} \) | Yield (\%)\(^a\) |
|-------|----------|-----------------|-----------------|
| 1     | KI       | ICF\(_2\)COOEt  | 85\(^b\)        |
| 2     | -        | ICF\(_2\)COOEt  | 83              |
| 3     | -        | BrCF\(_2\)COOEt | 84              |

\(^a\) Reaction condition 1 : 1a (0.2 mmol), \( \text{XCF}_2\text{COOEt} \) (2/3, 0.6 mmol), Additive (3 equiv), \( \text{K}_2\text{CO}_3 \) (3 equiv), \( \text{H}_2\text{O} \) (0.5 mL), MeCN (2 mL), for 10 h, \( \text{N}_2 \); GC yields.

Table S7. The effects of Base

| Entry | Base       | Yield (\%)\(^a\) |
|-------|------------|-----------------|
| 1     | \( \text{Na}_2\text{CO}_3 \) | 84              |
| 2     | \( \text{K}_2\text{CO}_3 \) | 95              |
| 3     | KOH        | 61              |
| 4     | \( \text{Na}_3\text{PO}_4 \) | 55              |

\(^a\) Reaction condition 1 : 1a (0.2 mmol), BrCF\(_2\)COOEt (3, 0.6 mmol), Base (3 equiv), \( \text{H}_2\text{O} \) (0.5 mL), MeCN (2 mL), for 10 h, \( \text{N}_2 \); GC yields.
Table S8. The effects of H$_2$O

| Entry | H$_2$O (X mL) | Yield (%)$^a$ |
|-------|---------------|---------------|
| 1     | 0.01          | Trace         |
| 2     | 0.05          | 43            |
| 3     | 0.1           | 79            |
| 4     | 0.3           | 95            |
| 5     | 0.5           | 99            |
| 6     | 1             | 97            |

$^a$ Reaction condition 1 : 1a (0.2 mmol), BrCF$_2$COOEt (3, 0.6 mmol), K$_2$CO$_3$ (3 equiv.), H$_2$O (X mL), MeCN (2 mL), for 10 h, N$_2$; GC yields.
5. General process for the C(spic)-N bond cleavage of the non-cyclic tertiary amines

5.1 For synthesis of formamide (7a-7o, 7t-7v, 7ad-7af)

In a dried Schlenk tube were placed the non-cyclic tertiary amines 6 (0.2 mmol), K$_2$CO$_3$ (0.6 mmol, 3 equiv), then the air was removed. N$_2$ was filled of Schleck tube and CH$_3$CN (2 mL), BrCF$_2$COOEt (0.6 mmol, 3 equiv), H$_2$O (0.5 mL) is added the mixture. The resulting mixture was stirred at 90 °C for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc =20:1, v/v) to give the desired products.

5.2 For synthesis of formamide (7p, 7r)

In a dried Schlenk tube were placed the non-cyclic tertiary amines 6 (0.2 mmol), K$_2$CO$_3$ (0.6 mmol, 3 equiv), then the air was removed. N$_2$ was filled of Schleck tube and CH$_3$CN (2 mL), BrCF$_2$COOEt (0.48 mmol, 2.4 equiv), H$_2$O (0.5 mL) is added the mixture. The resulting mixture was stirred at 90 °C for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc =20:1, v/v) to give the desired products.

5.3 For synthesis of formamide (7q, 7s)

In a dried Schlenk tube were placed the non-cyclic tertiary amines 6 (0.2 mmol), K$_2$CO$_3$ (0.6 mmol, 3 equiv), then the air was removed. N$_2$ was filled of Schleck tube and CH$_3$CN (2 mL), BrCF$_2$COOEt (0.8 mmol, 4 equiv), H$_2$O (0.7 mL) is added the mixture. The resulting mixture was stirred at 90 °C for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc =20:1, v/v) to give the desired products.
6. Crystal data of 7i

Crystallographic data for compound 7i (CCDC-1967215) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email: deposit@ccdc.cam.ac.uk).

Bond precision: C-C = 0.0030 Å  Wavelength=0.71073

| Bond         | Calculated | Reported |
|--------------|------------|----------|
| C-C          | 0.0030 Å   |          |
| Wavelength   | 0.71073    |          |

| Parameter     | Value      | Value      |
|---------------|------------|------------|
| Cell          | a=8.5597(14) | b=9.5439(15) | c=14.732(2)  |
|               | alpha=90    | beta=105.399(16) | gamma=90   |
| Temperature   | 293 K       |            |            |
| Volume        | 1160.3(3)   | 1160.3(3)  |            |
| Space group   | P 21/c      | P 1 21/c 1 |            |
| Hall group    | -P 2ybc     | -P 2ybc   |            |
| Moiety formula| C14 H12 F N O | C14 H12 F N O |           |
| Sum formula   | C14 H12 F N O | C14 H12 F N O |           |
| Mr            | 229.25      | 229.25    |            |
| Dχ, g cm⁻³    | 1.312       | 1.312     |            |
| Z              | 4           | 4         |            |
| Mρ (mm⁻¹)     | 0.094       | 0.094     |            |
| F000          | 480.0       | 480.0     |            |
| F000'         | 480.25      | 480.25    |            |
| h,k,l max     | 10,11,17    | 10,11,17  |            |
| Nref          | 2043        | 2037      |            |
| Tmin, Tmax    | 0.701,1.000 | 0.701,1.000 |            |
| Correction method | # Reported | T limits: Tmin=0.701 Tmax=1.000 |
| AbsCorr       | MULTI-SCAN  |            |            |
| Data completeness | 0.997     | Theta(max)= 24.998 |
| R(reflections) | 0.0499(1321) | WR2(reflections)= 0.1509(2037) |
| S             | 0.851       | Npar= 155  |            |
7. Optimization of the reaction conditions of the N, N-dimethylamine react with ClCF₂H

![Chemical Reaction Diagram]

| Entry | Base       | Additive | H₂O (X mL) | Solvent | T (°C) | Yield (%) |
|-------|------------|----------|------------|---------|--------|-----------|
| 1     | K₂CO₃      | -        | 0.5        | CH₃CN   | 90     | 33b       |
| 2     | K₂CO₃      | NCS      | 0.5        | CH₃CN   | 90     | NR        |
| 3     | K₂CO₃      | PhOH     | 0.5        | CH₃CN   | 90     | 33        |
| 4     | K₂CO₃      | Hydroquinone | 0.5   | CH₃CN   | 90     | Trace     |
| 5     | K₂CO₃      | S₈ (10 mol%) | 0.5       | CH₃CN   | 90     | 37        |
| 6     | K₂CO₃      | S₈ (20 mol%) | 0.5       | CH₃CN   | 90     | 61        |
| 7     | K₂CO₃      | S₈ (35 mol%) | 0.5       | CH₃CN   | 90     | 80(78)b   |
| 8     | K₂CO₃      | S₈ (50 mol%) | 0.5       | CH₃CN   | 90     | 65        |
| 9     | K₂CO₃      | S₈ (1 equiv) | 0.5      | CH₃CN   | 90     | 55        |
| 10    | K₂CO₃      | S₈ (35 mol%) | 0.01      | CH₃CN   | 90     | Trace     |
| 11    | K₂CO₃      | S₈ (35 mol%) | 0.05      | CH₃CN   | 90     | 30        |
| 12    | K₂CO₃      | S₈ (35 mol%) | 0.1       | CH₃CN   | 90     | 51        |
| 13    | K₂CO₃      | S₈ (35 mol%) | 1         | CH₃CN   | 90     | 80        |
| 14    | Na₂HPO₄    | S₈ (35 mol%) | 0.5       | CH₃CN   | 90     | NR        |
| 15    | tBuOK      | S₈ (35 mol%) | 0.5       | CH₃CN   | 90     | Trace     |
| 16    | MeONa      | S₈ (35 mol%) | 0.5       | CH₃CN   | 90     | Trace     |
| 17    | LiOH       | S₈ (35 mol%) | 0.5       | CH₃CN   | 90     | 45        |
| 18    | NaOH       | S₈ (35 mol%) | 0.5       | CH₃CN   | 90     | 53        |
| 19    | Na₂CO₃     | S₈ (35 mol%) | 0.5       | CH₃CN   | 90     | 77        |
| 20    | K₂CO₃      | S₈ (35 mol%) | 0.5       | DMF     | 90     | 70        |
| 21    | K₂CO₃      | S₈ (35 mol%) | 0.5       | C₂H₅OH  | 90     | 63        |
| 22    | K₂CO₃      | S₈ (35 mol%) | 0.5       | CH₃OH   | 90     | 41        |
| 23    | K₂CO₃      | S₈ (35 mol%) | 0.5       | 1.4-Dioxane | 90 | 53        |
| 24    | K₂CO₃      | S₈ (35 mol%) | 0.5       | CH₃CN   | 80     | 70        |
| 25    | K₂CO₃      | S₈ (35 mol%) | 0.5       | CH₃CN   | 100    | 77        |

* Reaction condition 1: 6v (0.2 mmol), the atmosphere of chlorodifluoromethane (ClCF₂H) (cat. 0.3 mmol), Additive (X equiv), base (X equiv.), H₂O (X mL), solvent (2 mL), for 10 h, N₂; GC yields; b isolated yields.

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8. General process for the non-cyclic tertiary amines react with ClCF₂H

8.1 For synthesis of formamide-d (7v-7ac)

In a dried Schlenk tube were placed the non-cyclic tertiary amines 6 (0.2 mmol), K₂CO₃ (0.6 mmol, 3 equiv), and S₈ (0.07 mmol, 0.35 equiv), then the air was removed. ClCF₂H was filled of Schleck tube and CH₃CN (2 mL), H₂O (0.5 mL) is added the mixture. The resulting mixture was stirred at 90 °C for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc =20:1, v/v) to give the desired products. The usage information of ClCF₂H is shown in the figure below.

1. Extract the air and keep the vacuum.
2. Inject ClCF₂H into a schlenk tube through a catheter.
3. Add solvent (2.5 mL) through disposable syringe.

25 mL schlenk tube
Density of ClCF₂H: 1.354 g/cm³
Cat. dosage of ClCF₂H: 0.3 mmol
9. General process for the C(sp³)-N bond cleavage of the tertiary amines (D₂O as the proton sources)

9.1 For synthesis of deuterated iodoalkanes products (8a-8l)

In a dried Schlenk tube were placed the cyclic tertiary amines 1 (0.2 mmol), KI (0.6 mmol, 3 equiv), and Na₂CO₃ (0.6 mmol, 3 equiv), then the air was removed. N₂ was filled of Schleck tube and CH₃CN (2 mL), ICF₂COOEt (0.6 mmol, 3 equiv), D₂O (0.3 mL) is added the mixture. The resulting mixture was stirred at 90 °C for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc =20:1, v/v) to give the desired products.

9.2 For synthesis of deuterated bromoalkanes products (8l-8y)

In a dried Schlenk tube were placed the cyclic tertiary amines 1 (0.2 mmol), KBr (0.6 mmol, 3 equiv), and Na₂CO₃ (0.6 mmol, 3 equiv), then the air was removed. N₂ was filled of Schleck tube and CH₃CN (2 mL), BrCF₂COOEt (0.6 mmol, 3 equiv), D₂O (0.3 mL) is added the mixture. The resulting mixture was stirred at 90 °C for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc =20:1, v/v) to give the desired products.
9.3 For synthesis of formamide-d (8z-8ae, 8al-8ak)

In a dried Schlenk tube were placed the non-cyclic tertiary amines 6 (0.2 mmol), K$_2$CO$_3$ (0.6 mmol, 3 equiv), then the air was removed. N$_2$ was filled of Schleck tube and CH$_3$CN (2 mL), BrCF$_2$COOEt (0.6 mmol, 3 equiv), D$_2$O (0.5 mL) is added the mixture. The resulting mixture was stirred at 90 °C for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc =20:1, v/v) to give the desired products.

9.4 For synthesis of formamide (8af, 8ah)

In a dried Schlenk tube were placed the non-cyclic tertiary amines 6 (0.2 mmol), K$_2$CO$_3$ (0.6 mmol, 3 equiv), then the air was removed. N$_2$ was filled of Schleck tube and CH$_3$CN (2 mL), BrCF$_2$COOEt (0.48 mmol, 2.4 equiv), D$_2$O (0.5 mL) is added the mixture. The resulting mixture was stirred at 90 °C for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc =20:1, v/v) to give the desired products.

9.5 For synthesis of formamide (8ag, 8ai)

In a dried Schlenk tube were placed the non-cyclic tertiary amines 6 (0.2 mmol), K$_2$CO$_3$ (0.6 mmol, 3 equiv), then the air was removed. N$_2$ was filled of Schleck tube and CH$_3$CN (2 mL), BrCF$_2$COOEt (0.8 mmol, 4 equiv), D$_2$O (0.7 mL) is added the mixture. The resulting mixture was stirred at 90 °C for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc =20:1, v/v) to give the desired product.
9.6 For synthesis of formamide-d (8al-8ao)

In a dried Schlenk tube were placed the non-cyclic tertiary amines 6 (0.2 mmol), K$_2$CO$_3$ (0.6 mmol, 3 equiv), and S$_8$ (0.07 mmol, 0.35 equiv), then the air was removed. ClCF$_2$H was filled of Schlenk tube and CH$_3$CN (2 mL), D$_2$O (0.5 mL) is added the mixture. The resulting mixture was stirred at 90 °C for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc =20:1, v/v) to give the desired products.
10. Optimization of the reaction conditions of synthesis of thioether

\[
\text{N} + \text{BrCF}_2\text{COOEt} + \text{SH} \rightarrow \text{N} + \text{S} \rightarrow 10a
\]

| Entry | Base     | Additive | H₂O (X mL) | Solvent | T (°C) | Yield (%)\(^a\) |
|-------|----------|----------|------------|---------|--------|-----------------|
| 1     | Na₂CO₃   | -        | 0.3        | CH₃CN   | 90     | 42\(^b\)       |
| 2     | Na₂CO₃   | KBr      | 0.3        | CH₃CN   | 90     | 91 (89)\(^b\)  |
| 3     | Na₂CO₃   | ZnBr     | 0.3        | CH₃CN   | 90     | 92             |
| 4     | Na₂CO₃   | KBr (2 equiv) | 0.3 | CH₃CN   | 90     | 65             |
| 5     | Na₂CO₃   | KBr (4 equiv) | 0.3 | CH₃CN   | 90     | 85             |
| 6     | Na₂CO₃   | KBr      | 0.01       | CH₃CN   | 90     | Trace          |
| 7     | Na₂CO₃   | KBr      | 0.1        | CH₃CN   | 90     | 70             |
| 8     | Na₂CO₃   | KBr      | 0.5        | CH₃CN   | 90     | 87             |
| 9     | K₂CO₃    | KBr      | 0.5        | CH₃CN   | 90     | 80             |
| 10    | KOH      | KBr      | 0.3        | CH₃CN   | 90     | 43             |
| 11    | DBU      | KBr      | 0.3        | CH₃CN   | 90     | Trace          |
| 12    | Na₂CO₃   | KBr      | 0.3        | DMF     | 90     | 66             |
| 13    | Na₂CO₃   | KBr      | 0.3        | Acetone | 90     | Trace          |
| 14    | Na₂CO₃   | KBr      | 0.3        | DMA     | 90     | 50             |
| 15    | Na₂CO₃   | KBr      | 0.3        | CH₃CN   | 80     | 79             |
| 16    | Na₂CO₃   | KBr      | 0.3        | CH₃CN   | 100    | 85             |

\(^a\) Reaction condition 1: 1d (0.2 mmol), BrCF₂COOEt (3, 0.6 mmol), thiols (9, 0.6 mmol). Additive (3 equiv), base (X equiv.), H₂O (X mL), solvent (2 mL), for 10 h, N₂; GC yields; \(^b\) isolated yields.
11. General process for the synthesis of thioether and ether

11.1 For synthesis of thioether (10a-10j)

In a dried Schlenk tube were placed the cyclic tertiary amines 1d (0.2 mmol), Na$_2$CO$_3$ (0.6 mmol, 3 equiv), thiol 9 (0.6 mmol, 3 equiv), and KBr (0.6 mmol, 3 equiv), then the air was removed. N$_2$ was filled of Schleck tube and CH$_3$CN (2 mL), BrCF$_2$COOEt 3 (0.6 mmol, 3 equiv), H$_2$O (0.5 mL) is added the mixture. The resulting mixture was stirred at 90 °C for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc =20:1, v/v) to give the desired products.

11.2 For synthesis of ether (12)

In a dried Schlenk tube were placed the cyclic tertiary amines 1d (0.2 mmol), Na$_2$CO$_3$ (0.6 mmol, 3 equiv), phenol 11 (0.6 mmol, 3 equiv), KBr (0.6 mmol, 3 equiv), and, then the air was removed. N$_2$ was filled of Schleck tube and CH$_3$CN (2 mL), DMF (2 mL), BrCF$_2$COOEt 3 (0.6 mmol, 3 equiv), H$_2$O (0.5 mL) is added the mixture. The resulting mixture was stirred at 90 °C for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc =20:1, v/v) to give the desired products.

12. General process for applications
12.1 For synthesis of 4d

In a dried Schlenk tube were placed the cyclic tertiary amines 1d (5 mmol), KBr (15 mmol, 3 equiv), and Na₂CO₃ (15 mmol, 3 equiv), then the air was removed. N₂ was filled of Schleck tube and CH₃CN (20 mL), BrCF₂COOEt (15 mmol, 3 equiv), H₂O (5 mL) is added the mixture. The resulting mixture was stirred at 90 °C for 20 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc =20:1, v/v) to give the desired products.

12.2 For synthesis of ether [1](12)

A mixture of N-(4-bromobutyl)-N-phenylformamide (4d) (0.2 mmol), phenol (0.24 mmol, 1.2 equiv) and K₂CO₃ (0.6 mmol, 3 equiv) in DMF (2 mL) was stirred for 90 °C for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc =5:1, v/v) to give the desired products.

12.3 For synthesis of alkylboronic ester [2](13)
In air, CuI (4.8 mg, 0.025 mmol), PPh₃ (8.6 mg, 0.033 mmol), LiOMe (20 mg, 0.5 mmol), and bis(pinacolato)diboron (96.5 mg, 0.38 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with N₂ (three cycles). DMF (0.5 mL), N-(4-bromobutyl)-N-phenylformamide (4d) (0.25 mmol) were added in turn by syringe under N₂ atmosphere. The resulting reaction mixture was stirred vigorously at 25 °C for 18 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc =10:1, v/v) to give the desired products.

12.4 For synthesis of 1, 4-diamine compounds (14)

A mixture of N-(4-bromobutyl)-N-phenylformamide (4d) (0.2 mmol), diethylamine (0.24 mmol, 1.2 equiv) and K₂CO₃ (0.6 mmol, 3 equiv) in DMF (2 mL) was stirred for 90 °C for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc =1:1, v/v) to give the desired product.

12.5 For synthesis of 15

A mixture of sertraline (0.2 mmol), diethylamine (0.24 mmol, 1.2 equiv) and K₂CO₃ (0.6 mmol, 3 equiv) in CH₃CN (2 mL) was stirred for 90 °C for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc =1:1, v/v) to give the desired product.

12.6 For synthesis of 16

A mixture of (S)-(+-)-Ibuprofen (0.2 mmol), diethylamine (0.24 mmol, 1.2 equiv) and K₂CO₃ (0.6 mmol, 3 equiv) in DMF (2 mL) was stirred for 90 °C for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether:
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EtOAc =1:1, v/v) to give the desired product.

12.7 For synthesis of 17

A mixture of benzoic acid (0.2 mmol), diethylamine (0.24 mmol, 1.2 equiv) and K$_2$CO$_3$ (0.6 mmol, 3 equiv) in DMF (2 mL) was stirred for 90 °C for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: EtOAc =1:1, v/v) to give the desired product.
13. Characterization data for products

**N-(2-(2-iodoethoxy)ethyl)-N-phenylformamide (4a)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (57 mg, 89%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.40 (s, 1H), 7.39 (t, $J = 7.9$ Hz, 2H), 7.28 (t, $J = 7.8$ Hz, 3H), 3.96 (t, $J = 5.6$ Hz, 2H), 3.67 (dt, $J = 9.7$, 6.1 Hz, 4H), 3.16 (t, $J = 6.6$ Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.6, 141.3, 129.6, 126.9, 126.4, 124.6, 71.4, 67.5, 45.7, 2.8.

HRMS (ESI, m/z) calcd for C$_{11}$H$_{15}$INO$_2$[M+H]$^+$: 320.0142; found: 320.0141.

**N-(2-(2-bromoethoxy)ethyl)-N-phenylformamide (5a)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (38 mg, 70%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.40 (s, 1H), 7.40 (dd, $J = 8.3$, 7.4 Hz, 2H), 7.32 – 7.25 (m, 3H), 3.97 (t, $J = 5.6$ Hz, 2H), 3.72 (t, $J = 6.0$ Hz, 2H), 3.69 (t, $J = 5.6$ Hz, 2H), 3.38 (t, $J = 6.0$ Hz, 2H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 162.7, 141.3, 129.6, 127.0, 124.6, 70.8, 67.8, 45.6, 30.3.

HRMS (ESI, m/z) calcd for C$_{11}$H$_{15}$BrNO$_2$[M+H]$^+$: 272.0281; found: 272.0283.

**N-(4-bromophenyl)-N-(2-(2-iodoethoxy)ethyl)formamide (4b)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (57 mg, 72%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.39 (s, 1H), 7.52 (d, $J = 8.8$ Hz, 2H), 7.20 (d, $J = 8.7$ Hz, 2H), 3.93 (t, $J = 5.3$ Hz, 2H), 3.68 (dt, $J = 10.3$, 5.9 Hz, 4H), 3.19 (t, $J = 6.4$ Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.2, 140.6, 132.7, 132.5, 127.8, 126.1, 120.4, 71.4, 67.6, 46.1, 2.8.
HRMS (ESI, m/z) calcd for C_{11}H_{14}BrINO_{2}[M+H]^+: 397.9247; found: 397.9248.

**N-(2-(2-bromoethoxy)ethyl)-N-(4-bromophenyl)formamide (5b)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (52 mg, 77%).

$^1$H NMR (500 MHz, Chloroform-$d$) δ 8.38 (s, 1H), 7.52 (d, $J = 8.7$ Hz, 2H), 7.19 (d, $J = 8.7$ Hz, 2H), 3.93 (t, $J = 5.3$ Hz, 2H), 3.73 (t, $J = 5.9$ Hz, 2H), 3.70 (t, $J = 5.3$ Hz, 2H), 3.44 – 3.36 (m, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) δ 162.3, 140.6, 132.7, 132.5, 127.9, 126.2, 120.5, 70.8, 67.8, 46.0, 30.4.

HRMS (ESI, m/z) calcd for C_{11}H_{14}BrINO_{2}[M+H]^+: 349.9386; found: 349.9385.

**N-(5-iodopentyl)-N-phenylformamide (4c)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (54 mg, 85%).

$^1$H NMR (500 MHz, Chloroform-$d$) δ 8.35 (s, 1H), 7.40 (dd, $J = 8.3$, 7.4 Hz, 2H), 7.32 – 7.25 (m, 1H), 7.16 (dd, $J = 8.4$, 1.2 Hz, 2H), 3.84 – 3.77 (m, 2H), 3.12 (t, $J = 6.9$ Hz, 2H), 1.83 – 1.73 (m, 2H), 1.58 – 1.49 (m, 2H), 1.44 – 1.34 (m, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) δ 162.4, 140.8, 129.7, 127.0, 124.3, 44.6, 32.9, 27.6, 26.5, 6.5.

HRMS (ESI, m/z) calcd for C_{12}H_{17}INO[M+H]^+: 318.0349; found: 318.0346.

**N-(5-bromopentyl)-N-phenylformamide (5c)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (50 mg, 84%).

$^1$H NMR (500 MHz, Chloroform-$d$) δ 8.31 (s, 1H), 7.36 (td, $J = 8.0$, 2.1 Hz, 2H), 7.27 – 7.22 (m, 1H), 7.14 – 7.07 (m, 2H), 3.77 (dd, $J = 8.3$, 6.4 Hz, 2H), 3.30 (t, $J = 6.7$ Hz, 2H), 1.81 – 1.75 (m, 2H), 1.55 – 1.48 (m, 2H), 1.42 – 1.36 (m, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) δ 162.4, 140.8, 129.7, 127.0, 126.0, 124.3, 44.6,
33.5, 32.2, 26.7, 25.3.
HRMS (ESI, m/z) calcd for C_{12}H_{17}BrNO[M+H]^+: 300.1417; found: 300.1418.

**N-(4-iodobutyl)-N-phenylformamide (4d)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (55 mg, 90%).

^1H NMR (500 MHz, Chloroform-d) δ 8.36 (s, 1H), 7.41 (t, J = 7.9 Hz, 2H), 7.30 (t, J = 7.5 Hz, 1H), 7.16 (d, J = 7.3 Hz, 2H), 3.84 (t, J = 7.2 Hz, 2H), 3.15 (t, J = 6.8 Hz, 2H), 1.85 – 1.76 (m, 2H), 1.64 (p, J = 7.5 Hz, 2H).

^13C NMR (125 MHz, Chloroform-d) δ 162.5, 140.6, 129.8, 127.1, 124.3, 43.6, 30.5, 28.5, 6.0.

HRMS (ESI, m/z) calcd for C_{11}H_{15}NO[M+H]^+: 304.0193; found: 304.0191.

**N-(4-bromobutyl)-N-phenylformamide (5d)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (43 mg, 84%).

^1H NMR (500 MHz, Chloroform-d) δ 8.37 (s, 1H), 7.46 – 7.38 (m, 2H), 7.31 (t, J = 7.0 Hz, 1H), 7.17 (d, J = 7.5 Hz, 2H), 3.86 (t, J = 6.8 Hz, 2H), 3.39 (t, J = 6.5 Hz, 2H), 1.86 (dt, J = 14.2, 6.8 Hz, 2H), 1.70 (p, J = 7.3 Hz, 2H).

^13C NMR (125 MHz, Chloroform-d) δ 162.4, 140.6, 129.8, 127.1, 124.2, 43.8, 33.0, 29.8, 26.2.

HRMS (ESI, m/z) calcd for C_{11}H_{15}BrNO[M+H]^+: 256.0332; found: 256.0333.

**N-(4-bromophenyl)-N-(4-iodobutyl)formamide (4e)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (65 mg, 85%).

^1H NMR (500 MHz, Chloroform-d) δ 8.32 (s, 1H), 7.52 (d, J = 8.7 Hz, 2H), 7.08 – 7.02 (m, 2H), 3.80 (t, J = 7.2 Hz, 2H), 3.14 (t, J = 6.8 Hz, 2H), 1.78 (m, J = 7.6 Hz, 2H), 1.62 (m, J = 6.2 Hz, 2H).
$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.0, 139.7, 132.9, 132.5, 127.4, 125.7, 120.5, 43.5, 30.4, 28.4, 5.8
HRMS (ESI, m/z) calcd for C$_{11}$H$_{14}$BrINO[M+H]$^+$: 381.9298; found: 381.9296.

N-(4-bromophenyl)-N-(4-bromobutyl)formamide (5e)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (55 mg, 83%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.32 (s, 1H), 7.58 – 7.46 (m, 2H), 7.09 – 7.00 (m, 2H), 3.81 (t, $J$ = 6.0 Hz, 2H), 3.40 – 3.32 (m, 2H), 1.83 (dq, $J$ = 9.1, 2.9 Hz, 2H), 1.70 – 1.61 (m, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.0, 139.7, 132.9, 132.5, 127.4, 125.7, 120.5, 43.7, 33.0, 29.7, 26.1.
HRMS (ESI, m/z) calcd for C$_{11}$H$_{14}$Br$_2$NO[M+H]$^+$: 333.9437; found: 333.9439.

N-(4-iodobutyl)-N-(4-methoxyphenyl)formamide (4f)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (63 mg, 95%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.24 (s, 1H), 7.07 (d, $J$ = 8.8 Hz, 2H), 6.91 (d, $J$ = 8.9 Hz, 2H), 3.80 (s, 3H), 3.75 (t, $J$ = 7.1 Hz, 2H), 3.14 (t, $J$ = 6.8 Hz, 2H), 1.85 – 1.74 (m, 2H), 1.60 (dq, $J$ = 9.7, 6.8 Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.6, 158.7, 133.4, 127.5, 126.5, 114.9, 55.6, 44.0, 30.4, 28.4, 6.0.
HRMS (ESI, m/z) calcd for C$_{12}$H$_{17}$INO$_2$[M+H]$^+$: 334.0298; found: 334.0297.

N-(4-bromobutyl)-N-(4-methoxyphenyl)formamide (5f)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (44 mg, 77%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.24 (s, 1H), 7.08 (d, $J$ = 8.8 Hz, 2H), 6.91 (d, $J$ = 8.8 Hz, 2H), 3.81 (s, 3H), 3.77 (t, $J$ = 7.1 Hz, 2H), 3.38 (t, $J$ = 6.6 Hz, 2H), 1.84 (dt,
$J = 14.0, 6.7 \text{ Hz, 1H, 1.65 (p, } J = 7.2 \text{ Hz, 2H).}$

$^{13}$C NMR (125 MHz, Chloroform- $d$) $\delta$ 162.6, 158.7, 133.4, 126.5, 114.9, 55.6, 44.2, 33.1, 29.7, 26.1.

HRMS (ESI, m/z) calcd for C$_{12}$H$_{17}$BrNO$_2$[M+H]$^+$: 286.0437; found: 286.0438.

$N$-(4-iodobutyl)$-N$-(3-chlorophenyl)formamide (4g)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (63 mg, 93%).

$^1$H NMR (500 MHz, Chloroform- $d$) $\delta$ 8.36 (s, 1H), 7.35 (t, $J = 8.0$ Hz, 1H), 7.29 – 7.25 (m, 1H), 7.18 (t, $J = 2.1$ Hz, 1H), 7.06 (d, $J = 7.9$ Hz, 1H), 3.82 (t, $J = 7.2$ Hz, 2H), 3.15 (t, $J = 6.8$ Hz, 2H), 3.15 (dt, $J = 8.5, 6.8$ Hz, 2H), 1.64 (tt, $J = 10.1, 6.8$ Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform- $d$) $\delta$ 162.0, 141.9, 135.4, 130.8, 127.2, 124.1, 122.0, 43.5, 30.4, 28.4, 5.8.

HRMS (ESI, m/z) calcd for C$_{11}$H$_{14}$ClINO[M+H]$^+$: 337.9803; found: 337.9806.

$N$-(4-bromobutyl)$-N$-(3-chlorophenyl)formamide (5g)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (38 mg, 65%).

$^1$H NMR (500 MHz, Chloroform- $d$) $\delta$ 8.37 (s, 1H), 7.35 (t, $J = 8.0$ Hz, 1H), 7.18 (t, $J = 2.1$ Hz, 1H), 7.07 (ddd, $J = 7.9, 2.2, 1.0$ Hz, 1H), 3.84 (t, $J = 7.2$ Hz, 2H), 3.39 (t, $J = 6.6$ Hz, 2H), 1.88 – 1.81 (m, 2H), 1.69 (p, $J = 7.5$ Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform- $d$) $\delta$ 162.1, 141.9, 135.4, 130.8, 127.2, 124.1, 122.1, 43.5, 32.9, 29.7, 26.2.

HRMS (ESI, m/z) calcd for C$_{11}$H$_{14}$BrClINO[M+H]$^+$: 289.9942; found: 289.9943.

$N$-(4-iodobutyl)$-N$-(4-isopropylphenyl)formamide (4h)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (66 mg, 96%).
$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.31 (s, 1H), 7.25 (d, $J = 8.4$ Hz, 2H), 7.07 (d, $J = 8.4$ Hz, 2H), 3.80 (t, $J = 7.2$ Hz, 2H), 3.15 (t, $J = 6.9$ Hz, 2H), 2.92 (p, $J = 6.9$ Hz, 1H), 1.85 – 1.77 (m, 2H), 1.64 (p, $J = 7.6$ Hz, 2H), 1.24 (d, $J = 6.9$ Hz, 6H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.5, 148.0, 138.3, 127.7, 127.4, 124.4, 43.7, 33.7, 30.5, 28.5, 24.0, 6.0.

HRMS (ESI, m/z) calcd for C$_{14}$H$_{21}$INO[M+H]$^+$: 346.0662; found: 346.0663.

$N$-$(4$-bromobutyl$)$-$N$-$(4$-isopropylphenyl)$formamide (5h)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (58 mg, 97%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.32 (s, 1H), 7.25 (d, $J = 8.4$ Hz, 2H), 7.08 (d, $J = 8.4$ Hz, 2H), 3.81 (t, $J = 7.2$ Hz, 2H), 3.38 (t, $J = 6.7$ Hz, 2H), 2.92 (p, $J = 6.9$ Hz, 1H), 1.89 – 1.80 (m, 2H), 1.68 (p, $J = 7.5$, 7.1 Hz, 2H), 1.24 (d, $J = 6.8$ Hz, 6H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.5, 148.0, 138.3, 127.7, 124.4, 43.9, 33.1, 29.8, 26.2, 23.9.

HRMS (ESI, m/z) calcd for C$_{14}$H$_{21}$BrNO[M+H]$^+$: 298.0801; found: 298.0806.

$N$-$(1,1$'-biphenyl$)-4$-yl-$N$-$(4$-iodobutyl)$formamide (4i)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (65 mg, 86%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.43 (s, 1H), 7.64 (d, $J = 8.5$ Hz, 2H), 7.59 (d, $J = 7.5$ Hz, 2H), 7.49 – 7.43 (m, 2H), 7.38 (t, $J = 7.5$ Hz, 1H), 7.24 (d, $J = 8.5$ Hz, 2H), 3.89 (t, $J = 7.2$ Hz, 2H), 3.18 (t, $J = 6.8$ Hz, 2H), 1.85 (p, $J = 6.9$ Hz, 2H), 1.70 (p, $J = 7.4$ Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.3 (t, $J = 31.3$ Hz), 140.0, 139.9, 139.8, 129.0, 128.4, 127.7, 127.0, 124.4, 43.5, 33.9, 30.5, 28.5.

HRMS (ESI, m/z) calcd for C$_{17}$H$_{18}$INO[M+H]$^+$: 380.0506; found: 380.0504.

$N$-$(1,1$'-biphenyl$)-4$-yl-$N$-$(4$-bromobutyl)$formamide (5i)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt
29 = 20:1, v/v) to give the product as a yellow oil (56 mg, 85%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.43 (s, 1H), 7.64 (d, $J = 8.5$ Hz, 2H), 7.58 (d, $J = 7.8$ Hz, 2H), 7.46 (dd, $J = 8.3$, 7.0 Hz, 2H), 7.40 – 7.36 (m, 1H), 7.27 – 7.23 (m, 2H), 3.90 (t, $J = 7.2$ Hz, 2H), 3.41 (t, $J = 6.5$ Hz, 1H), 1.93 – 1.86 (m, 2H), 1.74 (dt, $J = 14.2$, 7.3 Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.4, 140.1, 139.9, 139.8, 129.0, 128.4, 127.7, 127.0, 124.4, 43.8, 29.8, 28.5, 26.3.

HRMS (ESI, m/z) calcd for C$_{17}$H$_{19}$BrNO[M+H]$^+$: 332.0645; found: 332.0642.

$\text{N-(4-iodobutyl)-N-(naphthalen-2-yl)formamide (4j)}$

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (67 mg, 94%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.49 (s, 1H), 7.90 (d, $J = 8.7$ Hz, 1H), 7.88 – 7.81 (m, 2H), 7.59 (s, 1H), 7.57 – 7.47 (m, 2H), 7.32 (d, $J = 8.6$ Hz, 1H), 3.94 (t, $J = 7.2$ Hz, 2H), 3.15 (t, $J = 6.7$ Hz, 2H), 1.84 (p, $J = 6.9$ Hz, 2H), 1.69 (p, $J = 7.3$ Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.6, 138.0, 133.6, 132.0, 130.0, 127.8, 127.7, 127.2, 126.5, 122.5, 122.4, 43.5, 30.5, 28.5, 6.0.

HRMS (ESI, m/z) calcd for C$_{15}$H$_{17}$INO[M+H]$^+$: 354.0349; found: 354.0348.

$\text{N-(4-bromobutyl)-N-(naphthalen-2-yl)formamide (5j)}$

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (54 mg, 88%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.49 (s, 1H), 7.90 (d, $J = 8.7$ Hz, 1H), 7.88 – 7.81 (m, 2H), 7.58 (d, $J = 2.3$ Hz, 1H), 7.57 – 7.49 (m, 2H), 7.32 (dd, $J = 8.7$, 2.2 Hz, 1H), 3.95 (t, $J = 7.2$ Hz, 2H), 3.39 (t, $J = 6.6$ Hz, 2H), 1.93 – 1.84 (m, 2H), 1.73 (p, $J = 7.6$ Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.6, 138.0, 133.6, 132.0, 130.0, 127.8, 127.7, 127.2, 126.5, 122.5, 122.4, 43.8, 33.1, 29.8, 26.3.

HRMS (ESI, m/z) calcd for C$_{15}$H$_{17}$BrNO[M+H]$^+$: 306.0488; found: 306.0493.

$\text{N-(4-iodobutyl)-N-(p-tolyl)formamide (4k)}$

The reaction was performed following the general
Supporting Information

The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (55 mg, 86%).

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 8.30 (s, 1H), 7.20 (d, \(J = 8.2\) Hz, 2H), 7.04 (d, \(J = 8.3\) Hz, 2H), 3.80 (t, \(J = 7.1\) Hz, 2H), 3.14 (t, \(J = 6.8\) Hz, 2H), 2.35 (s, 3H), 1.80 (p, \(J = 6.9\) Hz, 2H), 1.62 (p, \(J = 7.4\) Hz, 2H).

\(^{13}\)C NMR (125 MHz, Chloroform-\(d\)) \(\delta\) 162.5, 138.0, 137.1, 130.3, 130.0, 124.4, 43.6, 30.5, 28.4, 21.0, 6.0.

HRMS (ESI, m/z) calcd for C\(_{12}\)H\(_{17}\)INO[M+H]\(^+\): 318.0349; found: 318.0351.

\(N\)-(4-bromobutyl)-\(N\)-(p-tolyl)formamide (5k)

\[\begin{array}{c}
\text{CHO} \\
\text{Br}
\end{array}\]

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (51 mg, 94%).

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 8.31 (s, 1H), 7.21 (d, \(J = 7.9\) Hz, 2H), 7.07 – 7.01 (m, 2H), 3.81 (t, \(J = 7.2\) Hz, 2H), 3.38 (t, \(J = 6.6\) Hz, 2H), 2.36 (s, 3H), 1.84 (dt, \(J = 15.0, 6.7\) Hz, 2H), 1.67 (dt, \(J = 14.4, 7.3\) Hz, 2H).

\(^{13}\)C NMR (125 MHz, Chloroform-\(d\)) \(\delta\) 162.5, 138.0, 137.1, 130.3, 125.9, 124.4, 43.9, 33.1, 29.8, 26.2, 21.0.

HRMS (ESI, m/z) calcd for C\(_{12}\)H\(_{17}\)BrNO[M+H]\(^+\): 270.0488; found: 270.0486.

\(N\)-(4-(tert-butyl)phenyl)-\(N\)-(4-iodobutyl)formamide (4l)

\[\begin{array}{c}
\text{CHO} \\
\text{I}
\end{array}\]

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (63 mg, 87%).

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 8.33 (s, 1H), 7.41 (d, \(J = 8.6\) Hz, 2H), 7.09 (d, \(J = 8.6\) Hz, 2H), 3.81 (t, \(J = 7.2\) Hz, 2H), 3.16 (t, \(J = 6.9\) Hz, 2H), 1.85 – 1.78 (m, 2H), 1.65 (p, \(J = 7.6\) Hz, 2H), 1.32 (s, 9H).

\(^{13}\)C NMR (125 MHz, Chloroform-\(d\)) \(\delta\) 162.5, 150.2, 137.8, 126.6, 124.0, 43.6, 34.6, 31.3, 30.5, 28.5, 5.9.

HRMS (ESI, m/z) calcd for C\(_{15}\)H\(_{23}\)INO[M+H]\(^+\): 360.0819; found: 360.0820.

\(N\)-(4-(tert-butyl)phenyl)-\(N\)-(4-bromobutyl)formamide (5l)

\[\begin{array}{c}
\text{CHO} \\
\text{Br}
\end{array}\]

The reaction was performed following the general procedure. The residue was purified by flash column
chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (59 mg, 95%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.36 (s, 1H), 7.43 (d, $J$ = 8.7 Hz, 2H), 7.11 (d, $J$ = 8.7 Hz, 2H), 3.84 (t, $J$ = 6.6 Hz, 2H), 3.41 (t, $J$ = 6.6 Hz, 2H), 1.88 (dt, $J$ = 15.0, 6.8 Hz, 2H), 1.71 (p, $J$ = 7.3 Hz, 2H), 1.34 (s, 9H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.5, 150.2, 138.0, 126.6, 124.0, 43.9, 34.6 33.1, 31.3, 29.8, 26.2.

HRMS (ESI, m/z) calcd for C$_{15}$H$_{23}$BrNO[M+H]$^+$: 312.0958; found: 312.0955.

$N$-(4-fluorophenyl)-$N$-(4-iodobutyl)formamide (4m)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (62 mg, 97%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.27 (s, 1H), 7.16 – 7.06 (m, 4H), 3.78 (t, $J$ = 7.2 Hz, 2H), 3.14 (t, $J$ = 6.8 Hz, 2H), 1.83 – 1.75 (m, 2H), 1.61 (p, $J$ = 7.3 Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.4 (d, $J$ = 123.1 Hz), 160.5, 136.7, 126.6 (d, $J$ = 4.2 Hz), 116.8 (d, $J$ = 12.5 Hz), 43.9, 30.4, 28.4, 5.9.

HRMS (ESI, m/z) calcd for C$_{11}$H$_{14}$FINO[M+H]$^+$: 322.0099; found:322.0098.

$N$-(4-bromobutyl)-$N$-(4-fluorophenyl)formamide (5m)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (52 mg, 95%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.28 (s, 1H), 7.16 – 7.08 (m, 4H), 3.80 (t, $J$ = 7.2 Hz, 2H), 3.38 (t, $J$ = 6.6 Hz, 2H), 1.84 (p, $J$ = 6.6 Hz, 2H), 1.66 (p, $J$ = 7.4 Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.4 (d, $J$ = 122.5 Hz), 160.5, 136.7, 126.6 (d, $J$ = 4.4 Hz), 116.8 (d, $J$ = 11.3 Hz), 116.6, 44.2, 33.0, 20.0, 26.1.

HRMS (ESI, m/z) calcd for C$_{11}$H$_{13}$BrFNO[M+H]$^+$: 274.0237; found: 274.0238.

$N$-(3,4-dimethoxyphenyl)-$N$-(4-iodobutyl)formamide (4n)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt
Supporting Information

= 20:1, v/v) to give the product as a yellow oil (66 mg, 90%).

\[ ^1H \text{ NMR (500 MHz, Chloroform-}d \text{) } \delta \]
\[ 8.40 (s, 1H), 6.88 (d, J = 8.5 Hz, 1H), 6.80 (dd, J = 8.4, 2.6 Hz, 1H), 6.75 (d, J = 2.5 Hz, 1H), 3.89 (d, J = 3.4 Hz, 6H), 3.86 (d, J = 7.1 Hz, 2H), 3.16 (t, J = 6.6 Hz, 2H), 1.81 (p, J = 6.7 Hz, 2H), 1.67 (p, J = 7.2 Hz, 2H). \]

\[ ^13C \text{ NMR (125 MHz, Chloroform-}d \text{) } \delta \]
\[ 167.1, 145.0, 149.6, 131.7, 117.9, 111.7, 108.9, 56.6, 56.3, 46.6, 30.1, 27.9, 6.2. \]

HRMS (ESI, m/z) calcd for C\(^{13}\)H\(^{19}\)INO\(^3\)[M+H]\(^+\): 364.0404; found: 364.0405.

\( N-(4\text{-bromobutyl})-N-(3,4\text{-dimethoxyphenyl})\text{formamide (5n)} \)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (61 mg, 97%).

\[ ^1H \text{ NMR (500 MHz, Chloroform-}d \text{) } \delta \]
\[ 8.36 (s, 1H), 6.86 (d, J = 8.5 Hz, 1H), 6.76 (dd, J = 8.4, 2.5 Hz, 1H), 6.72 (d, J = 2.5 Hz, 1H), 3.87 (d, J = 1.5 Hz, 6H), 3.83 (d, J = 7.1 Hz, 2H), 3.36 (td, J = 6.4, 1.7 Hz, 2H), 1.83 (dt, J = 14.7, 6.9 Hz, 2H), 1.68 (dt, J = 13.8, 7.2 Hz, 2H). \]

\[ ^13C \text{ NMR (125 MHz, Chloroform-}d \text{) } \delta \]
\[ 166.4, 149.9, 149.4, 132.0, 117.8, 111.6, 108.9, 56.4, 56.2, 46.2, 33.1, 29.5, 27.0, 25.6. \]

HRMS (ESI, m/z) calcd for C\(^{13}\)H\(^{19}\)BrNO\(^3\)[M+H]\(^+\): 316.0543; found: 316.0541.

\( 8-(3\text{-iodopropyl}-3,4\text{-dihydroquinoline-1(2H)-carbaldehyde (4o)} \)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (27 mg, 41%).

\[ ^1H \text{ NMR (500 MHz, Chloroform-}d \text{) } \delta \]
\[ 8.29 (d, J = 2.9 Hz, 1H), 7.18 – 7.10 (m, 2H), 7.05 (dd, J = 7.2, 1.9 Hz, 1H), 3.80 (t, J = 6.9 Hz, 2H), 3.11 (t, J = 6.8 Hz, 2H), 2.81 – 2.74 (m, 2H), 2.67 (t, J = 6.5 Hz, 2H), 2.09 (dt, J = 14.2, 6.9 Hz, 2H), 1.97 (p, J = 6.7 Hz, 2H). \]

\[ ^13C \text{ NMR (125 MHz, Chloroform-}d \text{) } \delta \]
\[ 163.4, 136.5, 135.8, 133.1, 128.5, 127.4, 127.0, 126.5, 126.2, 44.7, 40.1, 34.2, 32.5, 31.6, 27.0, 26.1, 23.6. \]

HRMS (ESI, m/z) calcd for C\(^{13}\)H\(^{17}\)INO[M+H]\(^+\): 330.0349; found: 330.0350.

\( N-(5\text{-bromopentan-2-yl})-N\text{-phenylformamide (5p)} \)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt
Supporting Information

= 20:1, v/v) to give the product as a yellow oil (44 mg, 82%).

$^1$H NMR (500 MHz, Methanol-$d_4$) $\delta$ 8.33 (s, 1H), 7.48 – 7.41 (m, 2H), 7.34 (d, $J$ = 7.5 Hz, 1H), 7.31 – 7.28 (m, 2H), 3.85 (t, $J$ = 7.3 Hz, 2H), 3.69 (h, $J$ = 6.2 Hz, 1H), 1.67 – 1.49 (m, 2H), 1.45 – 1.37 (m, 2H), 1.09 (d, $J$ = 6.2 Hz, 3H).

$^{13}$C NMR (125 MHz, Methanol-$d_4$) $\delta$ 163.4, 140.5, 129.6, 129.1, 127.1, 126.3, 124.29, 66.8, 44.7, 35.6, 23.5, 22.2.

$N$-(5-iodo-3-methylpentyl)-$N$-phenylformamide (4q)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (62 mg, 92%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.33 (s, 1H), 7.40 (t, $J$ = 7.9 Hz, 2H), 7.29 (d, $J$ = 7.6 Hz, 1H), 7.17 – 7.12 (m, 2H), 3.83 (ddd, $J$ = 14.2, 8.9, 5.8 Hz, 2H), 3.20 – 3.12 (m, 1H), 3.07 (dt, $J$ = 9.8, 7.5 Hz, 1H), 1.85 – 1.77 (m, 1H), 1.64 – 1.51 (m, 3H), 1.40 – 1.32 (m, 1H), 0.89 (d, $J$ = 6.1 Hz, 3H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.3, 140.8, 129.7, 127.0, 124.2, 42.8, 40.5, 33.8, 31.6, 18.5, 4.6.

$N$-(5-bromo-3-methylpentyl)-$N$-phenylformamide (5q)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (46 mg, 81%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.35 (s, 1H), 7.41 (t, $J$ = 7.9 Hz, 2H), 7.30 (t, $J$ = 7.5 Hz, 1H), 7.19 – 7.09 (m, 2H), 3.93 – 3.78 (m, 2H), 3.42 – 3.29 (m, 2H), 1.89 – 1.78 (m, 2H), 1.70 – 1.63 (m, 2H), 1.61 – 1.52 (m, 1H), 1.42 – 1.34 (m, 1H), 0.92 (d, $J$ = 6.2 Hz, 3H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.3, 140.8, 129.7, 127.0, 124.2, 42.8, 39.6, 34.0, 31.6, 29.4, 18.7.

$N$-(3-iodopropyl)-$N$-phenylformamide (4r)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt
= 20:1, v/v) to give the product as a yellow oil (52 mg, 90%).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.38 (s, 1H), 7.43 (t, $J = 7.9$ Hz, 2H), 7.32 (t, $J = 7.5$ Hz, 1H), 7.18 (d, $J = 7.3$ Hz, 2H), 3.90 (dd, $J = 7.8$, 6.5 Hz, 2H), 3.13 (t, $J = 7.0$ Hz, 2H), 2.11 (p, $J = 7.1$ Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-d) $\delta$ 162.6, 140.7, 129.9, 127.2, 124.1, 45.9, 31.7, 1.8.

$N$-($3$-bromopropyl)-$N$-phenylformamide ($5r$)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (40 mg, 83%).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.35 (s, 1H), 7.39 (t, $J = 7.7$ Hz, 2H), 7.27 (t, $J = 7.2$ Hz, 1H), 7.15 (d, $J = 7.8$ Hz, 2H), 3.93 (t, $J = 7.1$ Hz, 2H), 3.34 (t, $J = 6.7$ Hz, 2H), 2.10 (p, $J = 6.8$ Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-d) $\delta$ 162.5, 140.7, 129.8, 124.0, 43.9, 30.9, 30.3.

$N$-($3$-bromopropyl)-$N$-($4$-chlorophenyl)formamide ($5s$)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (38mg, 70%).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.36 (s, 1H), 7.40 (d, $J = 8.6$ Hz, 2H), 7.13 (d, $J = 8.7$ Hz, 2H), 3.94 (t, $J = 7.2$ Hz, 2H), 3.37 (t, $J = 6.5$ Hz, 2H), 2.13 (p, $J = 6.7$ Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-d) $\delta$ 162.2, 139.3, 132.8, 130.0, 126.9, 125.2, 44.0, 30.7, 30.0.

$N$-($3$,5-$d$imethylphenyl)-$N$-($3$-iodopropyl)formamide ($4t$)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (52 mg, 92%).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.34 (s, 1H), 6.93 (s, 1H), 6.77 (s, 2H), 3.91 (t, $J = 7.1$ Hz, 2H), 3.36 (t, $J = 6.7$ Hz, 2H), 2.33 (s, 6H), 2.12 (p, $J = 6.9$ Hz, 2H).
13C NMR (125 MHz, Chloroform-d) δ 162.5, 140.6, 139.6, 128.8, 121.8, 43.9, 30.9, 30.3, 21.3.

**N-(3,5-dimethylphenyl)-N-(3-bromopropyl)formamide (5t)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (45 mg, 83%).

1H NMR (500 MHz, Chloroform-d) δ 8.33 (s, 1H), 6.93 (s, 1H), 6.77 (s, 2H), 3.85 (t, \( J = 7.1 \) Hz, 2H), 3.11 (t, \( J = 7.1 \) Hz, 2H), 2.33 (s, 6H), 2.09 (p, \( J = 7.1 \) Hz, 2H).

13C NMR (125 MHz, Chloroform-d) δ 162.6, 140.5, 139.6, 128.8, 121.8, 45.8, 31.7, 21.3, 2.0.

**1H NMR (500 MHz, Chloroform-d) δ 9.68 (d, \( J = 7.6 \) Hz, 1H), 8.59 (s, 1H), 7.63 – 7.58 (m, 2H), 7.45 (d, \( J = 15.9 \) Hz, 1H), 7.24 (s, 2H), 6.67 (dd, \( J = 16.0, 7.7 \) Hz, 1H), 3.32 (s, 3H).

13C NMR (125 MHz, Chloroform-d) δ 193.4, 161.8, 151.2, 144.4, 131.1, 129.9, 128.6, 121.6, 31.6.

HRMS (ESI, m/z) calcd for C11H12NO2[M+H]+: 190.0863; found: 190.0866.

**hexyl 4-(N-methylformamido)benzoate (7b)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (36 mg, 69%).

1H NMR (500 MHz, Chloroform-d) δ 8.62 (s, 1H), 8.09 – 8.06 (m, 2H), 7.24 – 7.21 (m, 2H), 4.24 (p, \( J = 5.2 \) Hz, 2H), 3.35 (s, 3H), 1.72 (dd, \( J = 12.2, 6.2 \) Hz, 2H), 1.47 – 1.43 (m, 2H), 0.92 (dt, \( J = 22.3, 7.3 \) Hz, 7H).

13C NMR (125 MHz, Chloroform-d) δ 165.9, 162.0, 145.9, 131.2, 128.1, 120.7, 67.6, 38.9, 31.6, 30.6, 29.0, 24.0, 23.0, 14.1, 11.1.
Supporting Information

HRMS (ESI, m/z) calcd for C\textsubscript{15}H\textsubscript{22}NO\textsubscript{3}[M+H]\textsuperscript{+}: 264.1594; found: 264.1595.

\textit{N-methyl-N-(4-(thiophen-3-yl)phenyl)formamide (7c)}

\begin{center}
\includegraphics[width=0.2\textwidth]{structure_7c}
\end{center}

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (43 mg, 99%).

\textsuperscript{1}H NMR (500 MHz, Chloroform-\textit{d}) \(\delta\) 8.51 (s, 1H), 7.64 – 7.59 (m, 2H), 7.44 (d, \(J = 1.4\) Hz, 1H), 7.40 (dd, \(J = 5.1, 2.8\) Hz, 1H), 7.37 (dd, \(J = 5.0, 1.5\) Hz, 1H), 7.19 (d, \(J = 8.4\) Hz, 2H), 3.33 (d, \(J = 1.6\) Hz, 3H).

\textsuperscript{13}C NMR (125 MHz, Chloroform-\textit{d}) \(\delta\) 162.2, 141.1, 141.0, 134.1, 127.5, 126.6, 126.1, 122.6, 120.6, 32.0.

HRMS (ESI, m/z) calcd for C\textsubscript{12}H\textsubscript{12}NOS[M+H]\textsuperscript{+}: 218.0624; found: 218.0623.

\textit{N-(4-(hydrazinecarbonyl)phenyl)-N-methylformamide (7d)}

\begin{center}
\includegraphics[width=0.2\textwidth]{structure_7d}
\end{center}

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (21 mg, 53%).

\textsuperscript{1}H NMR (500 MHz, Chloroform-\textit{d}) \(\delta\) 8.64 (s, 1H), 8.49 (s, 1H), 8.13 (d, \(J = 8.8\) Hz, 2H), 7.35 – 7.31 (m, 2H), 3.37 (s, 3H).

\textsuperscript{13}C NMR (125 MHz, Chloroform-\textit{d}) \(\delta\) 164.0, 161.8, 152.7, 145.2, 128.6, 122.8, 121.5, 121.0, 31.6.

HRMS (ESI, m/z) calcd for C\textsubscript{9}H\textsubscript{12}N\textsubscript{3}O\textsubscript{2}[M+H]\textsuperscript{+}: 194.0924; found: 194.0923.

\textit{N-([1,1'-biphenyl]-4-yl)-N-methylformamide (7e)}

\begin{center}
\includegraphics[width=0.2\textwidth]{structure_7e}
\end{center}

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (42 mg, 99%).

\textsuperscript{1}H NMR (500 MHz, Chloroform-\textit{d}) \(\delta\) 8.54 (s, 1H), 7.63 (d, \(J = 8.6\) Hz, 2H), 7.58 (dd, \(J = 8.2, 1.3\) Hz, 2H), 7.46 (dd, \(J = 8.4, 6.9\) Hz, 2H), 7.39 – 7.35 (m, 1H), 7.24 (d, \(J = 8.5\) Hz, 2H), 3.35 (s, 3H).

\textsuperscript{13}C NMR (125 MHz, Chloroform-\textit{d}) \(\delta\) 162.3, 141.4, 139.9, 139.4, 129.0, 128.3, 127.6, 127.0, 122.5, 32.0.
HRMS (ESI, m/z) calcd for C_{14}H_{14}NO[M+H]^+: 212.1070; found: 212.1071.

\section*{Supporting Information}

\begin{flushright}
N-(4'-isopropyl-[1,1'-biphenyl]-4-yl)-N-methylformamide (7f)
\end{flushright}

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (50 mg, 99%).

\begin{flushright}
1^H NMR (500 MHz, Chloroform-d) \(\delta\) 8.53 (s, 1H), 7.62 (d, \(J = 8.5\) Hz, 2H), 7.52 (d, \(J = 8.2\) Hz, 2H), 7.33 (d, \(J = 8.0\) Hz, 2H), 7.23 (d, \(J = 8.7\) Hz, 2H), 3.35 (d, \(J = 1.3\) Hz, 3H), 2.97 (p, \(J = 6.9\) Hz, 1H), 1.31 (d, \(J = 6.9\) Hz, 6H).
\end{flushright}

\begin{flushright}
\textsuperscript{13}C NMR (125 MHz, Chloroform-d) \(\delta\) 162.3, 148.5, 141.1, 139.4, 137.4, 128.1, 127.1, 126.9, 122.5, 33.8, 32.1, 24.0.
\end{flushright}

HRMS (ESI, m/z) calcd for C_{17}H_{20}NO[M+H]^+: 254.1539; found: 254.1540.

\begin{flushright}
N-methyl-N-(4'-(trifluoromethoxy)-[1,1'-biphenyl]-4-yl)formamide
\end{flushright}

(7g)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a white solid (59 mg, 99%).

\begin{flushright}
1^H NMR (500 MHz, Chloroform-d) \(\delta\) 8.55 (s, 1H), 7.59 (dd, \(J = 8.7, 7.2\) Hz, 4H), 7.33 – 7.28 (m, 2H), 7.26 (d, \(J = 8.7\) Hz, 2H), 3.36 (s, 3H).
\end{flushright}

\begin{flushright}
\textsuperscript{13}C NMR (125 MHz, Chloroform-d) \(\delta\) 162.2, 148.9, 141.7, 138.7, 137.9, 128.3, 128.3, 122.52 121.4, 32.0.
\end{flushright}

HRMS (ESI, m/z) calcd for C_{15}H_{13}F_{3}DNO_{2}[M+H]^+: 296.0893; found: 296.0890.

\begin{flushright}
N-methyl-N-(4'-phenoxy-[1,1'-biphenyl]-4-yl)formamide (7h)
\end{flushright}

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a white solid (60 mg, 99%).
$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.54 (s, 1H), 7.60 (d, $J = 8.5$ Hz, 2H), 7.55 – 7.52 (m, 2H), 7.37 (dd, $J = 8.6$, 7.3 Hz, 2H), 7.24 (d, $J = 8.5$ Hz, 2H), 7.14 (s, 1H), 7.11 – 7.05 (m, 4H), 3.36 (s, 3H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.3, 157.2, 157.0, 141.1, 138.8, 134.9, 129.9, 128.3, 123.0, 123.6, 122.6, 119.2, 119.1, 32.1.

HRMS (ESI, m/z) calcd for $C_{20}H_{18}NO_2$[M+H]$^+$: 304.1332; found: 304.1333.

**N-(4'-fluoro-[1,1'-biphenyl]-4-yl)-N-methylformamide (7i)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a white solid (46 mg, 99%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.52 (s, 1H), 7.58 – 7.54 (m, 2H), 7.52 (dd, $J = 8.6$, 5.4 Hz, 2H), 7.23 (d, $J = 8.5$ Hz, 2H), 7.12 (t, $J = 8.7$ Hz, 2H), 3.34 (s, 3H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.2, 141.4, 138.4, 136.1, 136.1, 128.6, 128.5, 128.1, 122.5, 115.9, 115.7, 32.0.

HRMS (ESI, m/z) calcd for $C_{14}H_{13}FDNO$[M+H]$^+$: 230.0976; found: 230.0977.

**N-methyl-N-(4'-nitro-[1,1'-biphenyl]-4-yl)formamide (7j)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a red solid (32 mg, 63%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.59 (s, 1H), 8.30 (d, $J = 8.8$ Hz, 2H), 7.72 (d, $J = 8.8$ Hz, 2H), 7.68 (d, $J = 8.5$ Hz, 2H), 7.31 (d, $J = 8.5$ Hz, 2H), 3.37 (s, 3H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.1, 147.2, 146.3, 142.8, 136.6, 128.6, 127.6, 124.3, 122.4, 31.9.

HRMS (ESI, m/z) calcd for $C_{14}H_{13}N_2O_3$[M+H]$^+$: 257.0921; found: 257.0922.

**N-methyl-N-(3'-methyl-[1,1'-biphenyl]-4-yl)formamide (7k)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt =
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20:1, v/v) to give the product as a white solid (45 mg, 99%).

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 8.53 (s, 1H), 7.62 (d, \(J = 8.4\) Hz, 2H), 7.40 – 7.32 (m, 3H), 7.21 (dd, \(J = 18.6, 7.8\) Hz, 3H), 3.35 (s, 3H), 2.43 (s, 3H).

\(^1^3\)C NMR (125 MHz, Chloroform-\(d\)) \(\delta\) 162.3, 141.3, 134.0, 139.5, 138.6, 128.9, 128.4, 128.3, 127.8, 124.1, 122.5, 32.1, 21.6.

HRMS (ESI, m/z) calecd for C\(_{15}\)H\(_{16}\)NO\([\text{M+H}]^+\): 226.1226; found: 226.1224.

\((E)-N\text{-methyl-N-(4-(phenyldiazenyl)phenyl)}\text{formamide (7l)}\)

\[\text{CHO} \hspace{1cm} \overset{\text{N}}{\swarrow} \hspace{1cm} \overset{\text{N}}{\nwarrow} \hspace{1cm} \text{N}\]

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (35 mg, 73%).

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 8.63 (s, 1H), 7.98 (d, \(J = 8.7\) Hz, 2H), 7.93 – 7.90 (m, 2H), 7.51 (ddd, \(J = 13.8, 8.0, 6.3\) Hz, 3H), 7.30 (d, \(J = 8.7\) Hz, 2H), 3.37 (s, 3H).

\(^1^3\)C NMR (125 MHz, Chloroform-\(d\)) \(\delta\) 162.0, 152.5, 150.4, 144.2, 131.3, 129.2, 124.3, 122.9, 121.8, 31.8, 29.7.

HRMS (ESI, m/z) calecd for C\(_{14}\)H\(_{14}\)N\(_3\)O\([\text{M+H}]^+\): 240.1131; found:240.1133.

\(N\text{-methyl-N-(pyridin-2-yl)}\text{formamide (7m)}\)

\[\text{CHO} \hspace{1cm} \overset{\text{N}}{\nwarrow} \hspace{1cm} \text{N}\]

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (17 mg, 61%).

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 9.34 (s, 1H), 8.38 (dd, \(J = 5.1, 1.9\) Hz, 1H), 7.72 (td, \(J = 7.8, 2.0\) Hz, 1H), 7.11 (ddd, \(J = 7.5, 4.8\) Hz, 1H), 7.01 (d, \(J = 8.2\) Hz, 1H), 3.34 (s, 3H).

\(^1^3\)C NMR (125 MHz, Chloroform-\(d\)) \(\delta\) 162.3, 154.1, 148.6, 138.5, 120.2, 111.6, 28.8.

HRMS (ESI, m/z) calecd for C\(_7\)H\(_9\)N\(_2\)O\([\text{M+H}]^+\): 137.0709; found: 137.0714.

\(N\text{-}(2\text{-hydroxyethyl)}\text{-N-methylformamide (7n)}\)

\[\text{CHO} \hspace{1cm} \overset{\text{N}}{\nwarrow} \hspace{1cm} \overset{\text{HO}}{\swarrow} \hspace{1cm} \text{N}\]

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (21 mg, 99%).
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$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.07 (d, $J = 20.7$ Hz, 1H), 3.76 (dt, $J = 27.9$, 5.2 Hz, 2H), 3.51 (d, $J = 5.2$ Hz, 1H), 3.46 (d, $J = 1.4$ Hz, 1H), 3.37 (d, $J = 5.1$ Hz, 1H), 3.04 (s, 1H), 2.90 (s, 2H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 163.9, 163.6, 60.5, 58.9, 52.0, 47.8, 35.9, 29.9.

HRMS (ESI, m/z) calcd for C$_4$H$_{10}$NO$_2$[M+H]$^+$: 104.0706; found: 104.0708.

**piperidine-1-carbaldehyde (7o)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (21 mg, 90%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 9.25 (s, 1H), 4.11 – 4.05 (m, 2H), 3.75 (p, $J = 4.9$ Hz, 4H), 3.66 (q, $J = 5.2$ Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 186.9, 66.9, 66.0, 55.0, 45.5.

HRMS (ESI, m/z) calcd for C$_5$H$_{10}$NO$_2$[M+H]$^+$: 116.0706; found: 116.0708.

**pyrrolidine-1-carbaldehyde (7p) (CAS: 3760-54-1)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (19 mg, 55%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.20 (s, 1H), 3.44 (t, $J = 6.4$ Hz, 2H), 3.40 – 3.31 (m, 2H), 1.93 – 1.77 (m, 4H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 160.8, 46.0, 43.1, 24.9, 24.2.

**piperidine-1-carbaldehyde (7q) (CAS: 2591-86-8)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (9 mg, 39%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.00 (s, 1H), 3.48 (t, $J = 5.7$ Hz, 2H), 3.30 (t, $J = 5.6$ Hz, 2H), 1.69 (dd, $J = 7.4$, 4.6 Hz, 2H), 1.58 – 1.52 (m, 4H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 160.8, 46.8, 40.6, 26.6, 25.1, 24.7.
**N,N-dibutylformamide (7s) (CAS:761-65-9)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (7 mg, 20%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.98 (s, 1H), 3.31 – 3.12 (m, 4H), 1.47 (s, 4H), 1.32 – 1.21 (m, 4H), 0.89 (d, $J$ = 3.4 Hz, 6H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.7, 47.2, 41.9, 30.7, 29.4, 20.2, 19.6, 13.8, 13.6.

**4-(5-fluorobenzo[d]isoxazol-3-yl)piperidine-1-carbaldehyde (7t)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (22 mg, 45%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.09 (s, 1H), 7.63 (m, 1H), 7.25 (m, 1H), 7.08 (m, 1H), 4.47 – 4.39 (m, 1H), 3.86 – 3.76 (m, 1H), 3.43 – 3.36 (m, 1H), 3.31 (ddd, $J$ = 13.4, 11.4, 3.2 Hz, 1H), 2.97 (m, 1H), 2.16 (m, 2H), 2.03 – 1.84 (m, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 165.2, 164.0, 163.21, 160.9, 156.0, 122.18, 117.0, 112.8, 97.7, 97.5, 45.5, 39.4, 34.4, 30.7, 29.6.

**N-(4-(dimethylamino)phenyl)-N-methylformamide (7u)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (28 mg, 78%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 9.47 (d, $J$ = 0.8 Hz, 1H), 7.07 (d, $J$ = 9.0 Hz, 2H), 6.69 (d, $J$ = 9.0 Hz, 2H), 3.65 (d, $J$ = 0.7 Hz, 3H), 2.97 (s, 6H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 188.0, 149.8, 135.7, 123.1, 112.5, 40.5, 38.8. HRMS (ESI, m/z) calcd for C$_{10}$H$_{13}$N$_2$O[M+H]$^+$: 179.1179; found: 179.1176.

**N,N'-(1,4-phenylene)bis(N-methylformamide) (7v)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt =
20:1, v/v) to give the product as a yellow oil (37 mg, 96%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.46 (s, 2H), 7.21 (s, 4H), 3.31 (s, 6H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.3, 162.2, 162.0, 140.4, 124.7, 123.5, 122.9, 36.7, 32.1, 29.7.

HRMS (ESI, m/z) calcd for $\text{C}_{10}\text{H}_{13}\text{N}_{2}\text{O}_2$[M+H]$^+$: 193.0972; found: 193.0975.

$N$-($4$-($4$-(dimethylamino)benzyl)phenyl)-$N$-methylformamide (7w)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (40 mg, 75%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.43 (s, 1H), 7.22 (s, 2H), 7.07 (d, $J = 8.5$ Hz, 4H), 6.71 (d, $J = 8.7$ Hz, 2H), 3.90 (s, 2H), 3.29 (s, 3H), 2.93 (s, 6H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.4, 149.3, 140.7, 140.0, 129.9, 129.5, 128.6, 122.6, 113.0, 40.8, 40.4, 32.2.

HRMS (ESI, m/z) calcd for $\text{C}_{17}\text{H}_{21}\text{N}_{2}\text{O}_2$[M+H]$^+$: 269.1648; found: 269.1646.

$N$,$N'$-($\text{methylenebis(4,1-phenylene)})$bis($N$-methylformamide) (7x)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (55 mg, 97%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.41 (s, 2H), 7.20 (d, $J = 8.5$ Hz, 4H), 7.08 (d, $J = 8.4$ Hz, 4H), 3.95 (d, $J = 11.3$ Hz, 2H), 3.26 (s, 6H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.27, 140.47, 139.00, 130.00, 129.46, 122.61, 40.62, 32.09.

HRMS (ESI, m/z) calcd for $\text{C}_{17}\text{H}_{21}\text{N}_{2}\text{O}_2$[M+H]$^+$: 283.1441; found: 283.1445.

$N$-($2$-(benzhydryloxy)ethyl)-$N$-methylformamide (7y)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 1:1, v/v) to give the product as a yellow oil (49 mg, 90%).
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$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.08 (d, $J = 45.4$ Hz, 1H), 7.34 – 7.29 (m, 8H), 7.25 (ddd, $J = 5.9, 4.3, 2.4$ Hz, 2H), 5.35 (d, $J = 2.1$ Hz, 1H), 3.65 – 3.50 (m, 3H), 3.44 (t, $J = 5.0$ Hz, 1H), 3.05 (s, 1H), 2.85 (s, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 163.4, 162.7, 142.0, 141.7, 128.6, 128.5, 127.7, 127.6, 126.9, 126.8, 84.1, 84.0, 67.0, 65.6, 49.8, 44.6, 36.2, 30.1.

HRMS (ESI, m/z) calcd for C$_{17}$H$_{20}$NO$_2$[M+H]$^+$: 270.1489; found: 270.1490.

4-(5H-dibenzo[a,d][7]annulen-5-ylidene)piperidine-1-carbaldehyde (7z)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 1:1, v/v) to give the product as a yellow oil (46 mg, 76%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.99 (s, 1H), 7.38 – 7.32 (m, 4H), 7.26 (t, $J = 7.4$ Hz, 2H), 7.18 (d, $J = 4.3$ Hz, 2H), 6.93 (s, 2H), 3.78 (dt, $J = 12.9, 5.3$ Hz, 1H), 3.38 – 3.29 (m, 1H), 3.01 (td, $J = 8.8, 4.4$ Hz, 2H), 2.22 (dt, $J = 19.3, 6.6$ Hz, 4H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 160.8, 138.5, 138.4, 135.8, 134.7, 134.6, 133.8, 131.1, 130.9, 128.4, 128.4, 128.1, 128.1, 128.0, 126.7, 47.2, 41.2, 30.9, 29.4.

HRMS (ESI, m/z) calcd for C$_{20}$H$_{21}$N$_2$O[M+H]$^+$: 302.1539; found: 302.1541.

(1S,5S)-8-oxo-1,5,6,8-tetrahydro-2H-1,5-methanopyrido[1,2-a][1,5]diazocine-3(4H)-carbaldehyde (7aa)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 1:1, v/v) to give the product as a yellow oil (22 mg, 49%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.73 (d, $J = 118.4$ Hz, 1H), 7.27 – 7.20 (m, 1H), 6.40 (s, 1H), 6.02 (dd, $J = 26.6, 6.8$ Hz, 1H), 4.52 – 4.35 (m, 1H), 4.04 (d, $J = 15.7$ Hz, 1H), 3.82 (ddd, $J = 21.3, 15.7, 6.7$ Hz, 1H), 3.56 (dd, $J = 58.5, 13.0$ Hz, 1H), 3.40 (ddd, $J = 17.5, 12.7, 2.4$ Hz, 1H), 3.07 (d, $J = 3.7$ Hz, 1H), 2.95 – 2.82 (m, 1H), 2.55 – 2.46 (m, 1H), 2.27 (s, 1H), 2.05 (dd, $J = 6.7, 3.5$ Hz, 1H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 161.3, 161.2, 148.1, 148.0, 139.1, 138.7, 118.0, 117.6, 110.0, 105.2, 53.5, 52.5, 48.9, 48.7, 47.2, 46.1, 34.6, 33.9, 27.1, 26.8, 26.4, 26.3.
(R)-N-methyl-N-(3-phenyl-3-(o-tolyloxy)propyl)formamide (7ab)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 1:1, v/v) to give the product as a yellow oil (44 mg, 41%).

$\textbf{1}^H \text{ NMR (500 MHz, Chloroform-}d\text{)} \delta 8.03 (d, J = 20.1 \text{ Hz, 1H}), 7.39 – 7.22 (m, 5H), 7.15 (d, J = 7.3 \text{ Hz, 1H}), 7.02 – 6.93 (m, 1H), 6.86 – 6.75 (m, 1H), 6.63 – 6.55 (m, 1H), 5.18 (ddd, J = 21.1, 8.7, 4.1 Hz, 1H), 3.62 – 3.40 (m, 2H), 2.93 (d, J = 13.9 \text{ Hz, 3H}), 2.37 (d, J = 5.9 \text{ Hz, 3H}), 2.27 – 2.12 (m, 2H).

$\textbf{1}^C \text{ NMR (125 MHz, Chloroform-}d\text{)} \delta 162.8, 162.6, 140.9, 130.8, 130.7, 128.8, 128.7, 127.9, 127.7, 126.7, 126.7, 126.6, 125.7, 125.6, 120.7, 120.4, 112.7, 112.6, 76.3, 46.2, 41.8, 37.3, 36.0, 35.0, 29.6, 16.6.

N-methyl-N-(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)formamide (7ac)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 1:1, v/v) to give the product as a yellow oil (51 mg, 73%).

$\textbf{1}^H \text{ NMR (500 MHz, Chloroform-}d\text{)} \delta 8.01 (d, J = 16.6 \text{ Hz, 1H}), 7.43 (d, J = 8.9, 2.7 Hz, 2H), 7.39 – 7.31 (m, 3H), 7.31 – 7.26 (m, 2H), 6.88 (t, J = 7.9 \text{ Hz, 2H}), 5.16 (ddd, J = 31.2, 8.9, 4.0 Hz, 1H), 3.59 – 3.36 (m, 2H), 2.92 (d, J = 18.9 \text{ Hz, 3H}), 2.24 – 2.07 (m, 2H).

$\textbf{1}^C \text{ NMR (125 MHz, Chloroform-}d\text{)} \delta 162.8, 162.7, 159.9, 139.9, 129.1, 128.9, 128.3, 128.1, 127.0, 126.9, 126.9, 126.9, 126.8, 126.8, 125.7, 125.6, 115.8, 115.7, 77.0, 46.0, 41.57, 37.0, 35.9, 34. 9, 29.6.

4-(8-chloro-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carbaldehyde (7ad)

The reaction was performed following the general procedure. The residue was purified by flash column
chromatography (silica gel, petroleum ether: AcOEt = 1:1, v/v) to give the product as a yellow oil (27 mg, 41%).

$^{1}$H NMR (500 MHz, Chloroform-$d$) δ 8.38 (t, $J$ = 3.1 Hz, 1H), 8.04 (s, 1H), 7.43 (d, $J$ = 7.7 Hz, 1H), 7.21 – 7.04 (m, 4H), 3.88 (ddt, $J$ = 34.3, 11.0, 5.0 Hz, 1H), 3.52 (ddt, $J$ = 22.8, 10.8, 5.0 Hz, 1H), 3.41 – 3.29 (m, 2H), 3.18 (ddddd, $J$ = 21.8, 17.9, 9.1, 5.5 Hz, 2H), 2.82 – 2.77 (m, 1H), 2.47 (ddddd, $J$ = 17.4, 14.2, 9.1, 4.7 Hz, 1H), 2.38 – 2.21 (m, 4H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) δ 160.9, 156.7, 146.7, 139.5, 137.7, 137.4, 136.7, 135.2, 133.4, 133.1, 130.4, 129.1, 126.3, 122.5, 46.8, 40.8, 31.7, 30.2, 29.9.

(1R,3r,5S)-8-formyl-8-azabicyclo[3.2.1]octan-3-yl 1H-indole-3-carboxylate (7ae)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 1:1, v/v) to give the product as a yellow oil (41 mg, 68%).

$^{1}$H NMR (500 MHz, Chloroform-$d$) δ 10.12 (s, 1H), 8.24 – 8.12 (m, 2H), 7.85 (s, 1H), 7.43 (s, 1H), 7.27 (d, $J$ = 4.8 Hz, 1H), 5.39 (d, $J$ = 5.1 Hz, 1H), 4.66 (s, 1H), 4.10 (d, $J$ = 6.1 Hz, 1H), 2.26 (t, $J$ = 15.8 Hz, 3H), 2.16 (s, 1H), 2.06 – 1.99 (m, 3H), 1.25 (d, $J$ = 5.6 Hz, 1H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) δ 164.4, 157.6, 136.6, 131.3, 126.0, 123.2, 122.0, 120.9, 112.0, 108.2, 66.7, 53.8, 49.0, 38.8, 36.3, 28.3, 27.6, 14.2.

4-(3-chlorodibenzo[b,f][1,4]oxazepin-11-yl)piperazine-1-carbaldehyde (7af)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 1:1, v/v) to give the product as a yellow oil (40 mg, 59%).

$^{1}$H NMR (500 MHz, Chloroform-$d$) δ 8.10 (s, 1H), 7.40 (dd, $J$ = 8.7, 2.6 Hz, 1H), 7.31 (d, $J$ = 2.6 Hz, 1H), 7.19 (d, $J$ = 8.7 Hz, 1H), 7.15 (dd, $J$ = 7.8, 1.6 Hz, 1H), 7.12 – 7.08 (m, 2H), 7.04 – 7.00 (m, 1H), 3.73 – 3.35 (m, 8H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) δ 161.0, 159.4, 158.6, 151.7, 139.6, 133.0, 130.5, 129.0, 127.2, 125.9, 125.2, 124.7, 122.9, 120.2, 45.2, 39.8.
**N-methyl-N-phenylformamide (7ag) (CAS:93-61-8)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (21/27mg, 78% (99%)$^a$).

$^1$H NMR (500 MHz, Chloroform-$d$) δ 8.48 (s, 1H), 7.43 – 7.40 (m, 2H), 7.30 – 7.26 (m, 1H), 3.33 (s, 3H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) δ 162.4, 142.2, 129.7, 126.5, 122.4, 32.1.

**N-(4-bromophenyl)-N-methylformamide (7ah)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (30 mg, 71%).

$^1$H NMR (500 MHz, Chloroform-$d$) δ 8.45 (s, 1H), 7.53 (d, $J = 8.8$ Hz, 2H), 7.05 (d, $J = 8.7$ Hz, 2H), 3.29 (s, 3H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) δ 162.0, 141.2, 132.8, 132.1, 124.9, 123.8, 119.8, 32.0.

HRMS (ESI, m/z) calcd for C$_8$H$_9$BrNO[M+H]$^+$: 213.9862; found: 213.9865.

**N-(4-chlorophenyl)-N-methylformamide (7ai) (CAS:26772-93-0)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (26 mg, 75%).

$^1$H NMR (500 MHz, Chloroform-$d$) δ 8.44 (s, 1H), 7.38 (dd, $J = 8.7$, 0.9 Hz, 2H), 7.11 (dd, $J = 8.8$, 0.9 Hz, 2H), 3.29 (s, 3H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) δ 162.1, 140.3, 132.1, 129.8, 129.2, 124.6, 123.6, 32.1.

**N-methyl-N-(p-tolyl)formamide (7aj) (CAS:2739-04-0)**

The reaction was performed following the general procedure. The residue was purified by flash column
chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (26 mg, 88%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.41 (s, 1H), 7.23 – 7.17 (m, 2H), 7.08 – 7.02 (m, 2H), 3.28 (s, 3H), 2.35 (s, 3H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.4, 139.7, 136.4, 130.2, 129.7, 122.6, 32.3, 20.9.

$N$-(4-formylphenyl)-$N$-methylformamide (7ak) (CAS:79213-80-2)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (17 mg, 51%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 9.99 (s, 1H), 8.69 (s, 1H), 7.97 – 7.90 (m, 2H), 7.40 – 7.30 (m, 2H), 3.37 (s, 3H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 190.8, 161.8, 147.2, 133.7, 131.3, 120.9, 31.4.

$N$-(3-methoxyphenyl)-$N$-methylformamide (7al)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (27 mg, 80%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.51 (s, 1H), 7.33 (t, $J$ = 8.1 Hz, 1H), 6.83 (dd, $J$ = 8.4, 2.5 Hz, 1H), 6.80 – 6.76 (m, 1H), 6.72 (t, $J$ = 2.3 Hz, 1H), 3.85 (s, 3H), 3.32 (s, 3H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.4, 160.5, 143.4, 130.4, 114.5, 111.5, 108.6, 55.5, 32.1.

HRMS (ESI, m/z) calcd for C$_9$H$_{12}$NO$_2$[M+H]$^+$: 166.0863; found:166.0861.

$N$-(3-bromophenyl)-$N$-methylformamide (7am)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (33 mg, 78%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.51 (d, $J$ = 2.0 Hz, 1H), 7.36 (td, $J$ = 8.1, 2.1 Hz, 1H), 7.27 (dt, $J$ = 7.0, 1.8 Hz, 1H), 7.20 (q, $J$ = 2.1 Hz, 1H), 7.08 (dq, $J$ = 8.0, 1.6 Hz, 1H), 3.32 (d, $J$ = 2.0 Hz, 3H).
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$^{13}$C NMR (125 MHz, Chloroform-$d$) δ 162.0, 143.4, 135.3, 130.7, 126.5, 122.1, 120.2, 31.9.

HRMS (ESI, m/z) calcd for C$_8$H$_9$BrNO[M+H]$^+$: 213.9862; found: 213.9860.

$N$-methyl-$N$-($m$-tolyl)formamide (7an) (CAS:39970-42-8)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (25 mg, 83%).

$^1$H NMR (500 MHz, Chloroform-$d$) δ 8.45 (s, 1H), 7.30 – 7.26 (m, 1H), 7.09 – 7.04 (m, 1H), 7.01 – 6.87 (m, 2H), 3.29 (s, 3H), 2.38 (s, 3H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) δ 162.4, 142.2, 139.7, 129.4, 127.2, 123.1, 119.5, 32.1, 21.4.

$N$-ethyl-$N$-phenylformamide (7ao) (CAS:5461-49-4)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (19 mg, 63%).

$^1$H NMR (500 MHz, Chloroform-$d$) δ 8.35 (s, 1H), 7.41 (dd, $J = 8.4$, 7.3 Hz, 2H), 7.30 (d, $J = 7.4$ Hz, 1H), 7.16 (dd, $J = 8.5$, 1.2 Hz, 2H), 3.86 (q, $J = 7.2$ Hz, 2H), 1.16 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) δ 162.4, 142.2, 139.7, 129.4, 127.2, 123.1, 119.5, 32.1, 21.4.

$N$-phenyl-$N$-propylformamide (7ap)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (14 mg, 42%).

$^1$H NMR (500 MHz, Chloroform-$d$) δ 8.37 (s, 1H), 7.40 (t, $J = 7.8$ Hz, 2H), 7.29 (t, $J = 7.4$ Hz, 1H), 7.16 (d, $J = 7.3$ Hz, 2H), 3.80 – 3.75 (m, 2H), 1.55 (h, $J = 7.4$ Hz, 2H), 0.88 (t, $J = 7.4$ Hz, 3H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) δ 162.4, 144.1, 129.6, 129.2, 126.8, 126.8, 126.0, 124.3, 46.6, 20.9, 11.2.
HRMS (ESI, m/z) calcd for C_{10}H_{14}NO[M+H]^+: 164.1070; found: 164.1068.

**N-(2-(2-iodoethoxy)ethyl)-N-phenylformamide-d (8a)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (54 mg, 84%).

D incorporation by $^1$H NMR: 97%

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.40 (s, 0.03H), 7.40 (t, $J$ = 7.8 Hz, 2H), 7.27 (d, $J$ = 8.6 Hz, 3H), 3.97 (t, $J$ = 5.6 Hz, 2H), 3.67 (dt, $J$ = 9.8, 6.1 Hz, 4H), 3.16 (t, $J$ = 6.6 Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-d) $\delta$ 162.4 (t, $J$ = 28.8 Hz), 141.3, 129.6, 129.4, 127.0, 126.4, 124.5, 71.5, 67.5, 45.6, 2.7.

HRMS (ESI, m/z) calcd for C_{11}H_{14}DINO$_2$[M+H]$^+$: 321.0205; found: 321.0206.

**N-(4-bromophenyl)-N-(2-(2-iodoethoxy)ethyl)formamide-d (8b)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (60 mg, 75%).

D incorporation by $^1$H NMR: 97%

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.39 (s, 0.03H), 7.52 (d, $J$ = 8.7 Hz, 2H), 7.20 (d, $J$ = 8.7 Hz, 2H), 3.93 (t, $J$ = 5.3 Hz, 2H), 3.68 (dt, $J$ = 10.5, 5.9 Hz, 4H), 3.19 (t, $J$ = 6.4 Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-d) $\delta$ 162.0 (t, $J$ = 28.8 Hz), 140.6, 132.7, 132.5, 127.8, 126.1, 120.4, 71.4, 67.6, 46.0, 2.7.

HRMS (ESI, m/z) calcd for C_{11}H_{13}DBrINO$_2$[M+H]$^+$: 398.9310; found: 398.9312.

**N-(5-iodopentyl)-N-phenylformamide-d (8c)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (52 mg, 82%).

D incorporation by $^1$H NMR: 98%
$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.36 (s, 0.02H), 7.40 (t, $J$ = 7.9 Hz, 2H), 7.29 (t, $J$ = 7.5 Hz, 1H), 7.18 – 7.13 (m, 2H), 3.81 (t, $J$ = 7.4 Hz, 2H), 3.12 (t, $J$ = 6.9 Hz, 2H), 1.78 (p, $J$ = 7.0 Hz, 2H), 1.59 – 1.50 (m, 2H), 1.43 – 1.35 (m, 2H).
$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.2 (t, $J$ = 28.8 Hz), 140.8, 129.7, 127.0, 124.2, 44.5, 32.9, 27.59, 26.5, 6.6.
HRMS (ESI, m/z) calcd for C$_{12}$H$_{16}$DINO[M+H]$^+$: 319.0412; found: 319.0411.

N-(4-iodobutyl)-N-phenylformamide-$d$ (8d)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (56 mg, 91%).

D incorporation by $^1$H NMR: 97%

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.36 (s, 0.03H), 7.41 (t, $J$ = 7.9 Hz, 2H), 7.30 (t, $J$ = 7.5 Hz, 1H), 7.18 – 7.14 (m, 2H), 3.84 (t, $J$ = 7.2 Hz, 2H), 3.18 (t, $J$ = 6.8 Hz, 2H), 1.84 – 1.77 (m, 2H), 1.64 (p, $J$ = 7.5 Hz, 2H).
$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.2 (t, $J$ = 30.0 Hz), 140.6, 129.8, 127.1, 124.2, 43.5, 30.5, 28.5, 5.8.
HRMS (ESI, m/z) calcd for C$_{11}$H$_{14}$DINO[M+H]$^+$: 305.0256; found: 305.0257.

N-(4-iodobutyl)-N-(p-tolyl)formamide-$d$ (8e)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (57 mg, 89%).

D incorporation by $^1$H NMR: 97%

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.32 (s, 0.03H), 7.20 (d, $J$ = 8.1 Hz, 2H), 7.04 (d, $J$ = 8.3 Hz, 2H), 3.80 (t, $J$ = 7.1 Hz, 2H), 3.15 (t, $J$ = 6.9 Hz, 2H), 2.35 (s, 2H), 1.80 (dt, $J$ = 14.6, 6.9 Hz, 2H), 1.62 (p, $J$ = 7.6 Hz, 2H).
$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.7 (t, $J$ = 25.0 Hz), 138.0, 137.1, 130.3, 124.4, 43.6, 30.5, 28.4, 21.0, 6.0.
HRMS (ESI, m/z) calcd for C$_{12}$H$_{16}$DINO[M+H]$^+$: 319.0412; found: 319.0409.

N-(4-iodobutyl)-N-(4-isopropylphenyl)formamide-$d$ (8f)

The reaction was performed following the general procedure. The residue was purified by flash column
chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as
a yellow oil (67 mg, 97%).

D incorporation by $^1$H NMR: 97%

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.31 (s, 0.03H), 7.25 (d, $J = 8.3$ Hz, 2H), 7.07 (d, $J = 8.5$ Hz, 2H), 3.80 (t, $J = 7.2$ Hz, 2H), 3.15 (t, $J = 6.9$ Hz, 2H), 2.91 (p, $J = 6.9$ Hz, 1H), 1.85 – 1.76 (m, 2H), 1.63 (p, $J = 7.7$ Hz, 2H), 1.24 (d, $J = 6.9$ Hz, 6H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.7 (t, $J = 33.8$ Hz), 147.9, 138.3, 127.7, 124.4, 43.6, 33.7, 30.5, 28.5, 23.9, 5.9.

HRMS (ESI, m/z) calcd for C$_{14}$H$_{20}$DINO[M+H]$^+$: 347.0725; found: 347.0727.

$N$-$(4$-iodobutyl)$_-N$-$(4$-methoxyphenyl)formamide-$d$ (8g)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (54 mg, 81%).

D incorporation by $^1$H NMR: 98%

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.23 (s, 0.02H), 7.07 (d, $J = 8.9$ Hz, 2H), 6.91 (d, $J = 8.9$ Hz, 2H), 3.80 (s, 3H), 3.75 (t, $J = 7.1$ Hz, 2H), 3.14 (t, $J = 6.8$ Hz, 2H), 1.83 – 1.76 (m, 2H), 1.60 (p, $J = 7.5$ Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.3 (t, $J = 30.0$ Hz), 158.7, 133.4, 126.4, 114.9, 55.6, 43.9, 30.4, 28.4, 6.0.

HRMS (ESI, m/z) calcd for C$_{12}$H$_{16}$DINO$_2$[M+H]$^+$: 335.0361; found: 335.0360.

$N$-$(4$-iodobutyl)$_-N$-$(naphthalen$-2$-yl)formamide-$d$ (8h)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (60 mg, 85%).

D incorporation by $^1$H NMR: 95%

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.48 (s, 0.05H), 7.90 (d, $J = 8.7$ Hz, 1H), 7.87 – 7.81 (m, 2H), 7.57 – 7.48 (m, 2H), 7.32 (d, $J = 8.7$ Hz, 1H), 3.94 (t, $J = 7.1$ Hz, 2H), 3.15 (t, $J = 6.8$ Hz, 2H), 1.84 (dq, $J = 8.7$, 6.8 Hz, 2H), 1.72 – 1.65 (m, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.4 (t, $J = 27.5$ Hz), 137.9, 133.5, 132.0, 130.0, 127.8, 127.6, 127.2, 126.5, 122.5, 122.4, 43.5, 30.5, 28.5, 6.0.

HRMS (ESI, m/z) calcd for C$_{15}$H$_{16}$DINO$_2$[M+H]$^+$: 355.0412; found: 355.0413.

$N$-$(4$-bromophenyl)$_-N$-$(4$-iodobutyl)formamide-$d$ (8i)
The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (70 mg, 91%).

D incorporation by $^1$H NMR: 97%

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.33 (s, 0.03H), 7.54 (d, $J$ = 8.7 Hz, 2H), 7.05 (d, $J$ = 8.7 Hz, 2H), 3.81 (t, $J$ = 7.2 Hz, 2H), 3.15 (t, $J$ = 6.8 Hz, 2H), 1.87 – 1.72 (m, 2H), 1.63 (p, $J$ = 7.5 Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 161.8 (t, $J$ = 28.8 Hz), 139.7, 132.9, 132.5, 125.7, 120.5, 43.4, 30.4, 28.4, 5.7.

HRMS (ESI, m/z) calcd for C$_{11}$H$_{13}$DBrINO$[\text{M}+\text{H}]^+$: 382.9361; found: 382.9362.

$N$-(4-fluorophenyl)-$N$-(4-iodobutyl)formamide-$d$ (8j)

D incorporation by $^1$H NMR: 97%

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.27 (s, 0.03H), 7.17 – 7.05 (m, 4H), 3.79 (t, $J$ = 7.2 Hz, 2H), 3.15 (t, $J$ = 6.8 Hz, 2H), 1.83 – 1.75 (m, 2H), 1.61 (p, $J$ = 7.5 Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.4 (d, $J$ = 123.1 Hz), 162.1 (t, $J$ = 30.0 Hz), 160.5, 136.7, 126.5 (d, $J$ = 4.4 Hz), 126.5, 116.8 (d, $J$ = 10.6 Hz), 43.9, 30.4, 28.4, 5.8.

HRMS (ESI, m/z) calcd for C$_{11}$H$_{13}$DFINO$[\text{M}+\text{H}]^+$: 323.0161; found: 323.0164.

$N$-(3,4-dimethoxyphenyl)-$N$-(4-iodobutyl)formamide-$d$ (8k)

$D_a$ incorporation by $^1$H NMR: 99%

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.40 (s, 0.01H), 6.88 (s, 1H), 6.75 (s, 1H), 3.89 (t, $J$ = 2.9 Hz, 6H), 3.86 (d, $J$ = 7.0 Hz, 2H), 3.19 – 3.12 (m, 2H), 1.85 – 1.76 (m, 2H), 1.73 – 1.62 (m, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 166.8 (t, $J$ = 35.0 Hz), 150.0, 149.6, 131.7, 117.7 (t, $J$ = 36.3 Hz), 111.6, 108.9, 56.6, 56.3, 46.5, 30.1, 27.9, 6.1.

HRMS (ESI, m/z) calcd for C$_{13}$H$_{18}$DINO$_3$[M+H]$^+$: 365.0467; found: 365.0469.
8-(3-iodopropyl)-3,4-dihydroquinoline-1(2H)-carbaldehyde-d (8l)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (26 mg, 40%).

D incorporation by $^1$H NMR: 97%

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.29 (s, 0.03H), 7.14 (q, $J = 7.6$, 7.0 Hz, 2H), 7.05 (d, $J = 7.2$ Hz, 1H), 3.80 (t, $J = 6.9$ Hz, 2H), 3.11 (t, $J = 6.9$ Hz, 2H), 2.77 (t, $J = 7.5$ Hz, 2H), 2.67 (t, $J = 6.3$ Hz, 2H), 2.09 (p, $J = 7.0$ Hz, 2H), 1.97 (p, $J = 6.7$ Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-d) $\delta$ 163.2 (t, $J = 30.0$ Hz), 136.5, 135.7, 133.1, 128.5, 126.5, 126.2, 44.6, 40.1, 34.2, 33.6, 32.6, 31.6, 27.0, 26.1, 23.6.

HRMS (ESI, m/z) caleld for $\text{C}_{13}\text{H}_{16}\text{DINO}[\text{M+H}]^+$: 331.0412; found: 331.0413.

N-(2-(2-bromoethoxy)ethyl)-N-phenylformamide-d (8m)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (39 mg, 72%).

D incorporation by $^1$H NMR: 95%

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.40 (s, 0.05H), 7.40 (t, $J = 7.8$ Hz, 2H), 7.27 (d, $J = 8.6$ Hz, 3H), 3.97 (t, $J = 5.6$ Hz, 2H), 3.67 (dt, $J = 9.8$, 6.1 Hz, 4H), 3.16 (t, $J = 6.6$ Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-d) $\delta$ 162.4 (t, $J = 30.0$Hz), 141.3, 129.6, 129.4, 126.9, 126.4, 124.5, 70.8, 67.8, 45.6, 30.3.

HRMS (ESI, m/z) caleld for $\text{C}_{11}\text{H}_{14}\text{DBrNO}_2[\text{M+H}]^+$: 273.0343; found: 273.0342.

N-(2-(2-bromoethoxy)ethyl)-N-(4-bromophenyl)formamide-d (8n)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (51 mg, 73%).

D incorporation by $^1$H NMR: 95%
Supporting Information

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.38 (s, 0.05H), 7.52 (d, $J$ = 8.7 Hz, 2H), 7.19 (d, $J$ = 8.7 Hz, 2H), 3.94 (t, $J$ = 5.4 Hz, 2H), 3.72 (dt, $J$ = 16.0, 5.6 Hz, 4H), 3.44 – 3.38 (m, 2H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 162.0 (t, $J$ = 32.5 Hz), 140.6, 132.7, 132.5, 126.1, 120.4, 70.8, 67.9, 45.9, 30.3.

HRMS (ESI, m/z) calcd for C$_{11}$H$_{13}$DBr$_2$NO$_2$[M+H]$^+$: 350.9449; found: 350.9450.

$N$-(5-bromopentyl)-$N$-phenylformamide-$d$ (8o)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (44 mg, 81%).

D incorporation by $^1$H NMR: 95%

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.37 (s, 0.05H), 7.43 (t, $J$ = 7.9 Hz, 2H), 7.31 (t, $J$ = 7.5 Hz, 1H), 7.18 (d, $J$ = 7.3 Hz, 2H), 3.86 – 3.81 (m, 2H), 3.37 (t, $J$ = 6.7 Hz, 2H), 1.88 – 1.81 (m, 2H), 1.57 (p, $J$ = 7.3 Hz, 2H), 1.49 – 1.41 (m, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.1 (t, $J$ = 28.8 Hz), 140.8, 129.7, 127.0, 124.2, 44.5, 33.5, 32.2, 26.7, 25.3.

HRMS (ESI, m/z) calcd for C$_{12}$H$_{16}$DBrNO[M+H]$^+$: 270.0488; found: 270.0486.

$N$-(4-bromobutyl)-$N$-phenylformamide-$d$ (8p)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (41 mg, 81%).

D incorporation by $^1$H NMR: 96%

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.36 (s, 0.04H), 7.40 (d, $J$ = 7.6 Hz, 2H), 7.28 (q, $J$ = 9.0, 8.1 Hz, 1H), 7.16 (d, $J$ = 7.9 Hz, 2H), 3.84 (t, $J$ = 7.2 Hz, 2H), 3.37 (t, $J$ = 6.6 Hz, 2H), 1.89 – 1.80 (m, 2H), 1.69 (p, $J$ = 7.2, 6.6 Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.2 (t, $J$ = 27.5 Hz), 140.6, 129.8, 129.7, 127.0, 124.2, 43.7, 33.0, 29.8, 26.2.

HRMS (ESI, m/z) calcd for C$_{11}$H$_{14}$DBrNO[M+H]$^+$: 257.0394; found: 257.0392.

$N$-(4-bromobutyl)-$N$-(p-tolyl)formamide-$d$ (8q)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (41 mg, 81%).

D incorporation by $^1$H NMR: 95%

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.37 (s, 0.05H), 7.47 (d, $J$ = 7.9 Hz, 2H), 7.30 (t, $J$ = 7.9 Hz, 2H), 7.19 (d, $J$ = 7.8 Hz, 2H), 3.85 – 3.80 (m, 2H), 3.37 (t, $J$ = 6.7 Hz, 2H), 1.87 – 1.80 (m, 2H), 1.58 (p, $J$ = 7.3 Hz, 2H), 1.39 – 1.30 (m, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.1 (t, $J$ = 32.5 Hz), 140.6, 132.8, 132.5, 124.3, 44.3, 33.0, 29.9, 26.0.

HRMS (ESI, m/z) calcd for C$_{11}$H$_{14}$DBrNO[M+H]$^+$: 257.0394; found: 257.0392.
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chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (49 mg, 90%).

D incorporation by $^1$H NMR: 96%

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.31 (s, 0.04H), 7.20 (d, $J = 8.1$ Hz, 2H), 7.04 (d, $J = 8.4$ Hz, 2H), 3.81 (t, $J = 7.2$ Hz, 2H), 3.37 (t, $J = 6.6$ Hz, 2H), 2.35 (s, 3H), 1.88 – 1.80 (m, 2H), 1.67 (p, $J = 7.7$ Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-d) $\delta$ 162.5 (t, $J = 30.0$ Hz), 138.0, 137.1, 130.3, 124.4, 43.8, 33.1, 29.8, 26.2, 21.0, 20.9.

HRMS (ESI, m/z) calcd for C$_{12}$H$_{16}$DBrNO$^{[M+H]^+}$: 271.0551; found: 271.0550.

$N$-(4-bromobutyl)-$N$-(4-isopropylphenyl)formamide-d (8r)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (58 mg, 97%).

D incorporation by $^1$H NMR: 95%

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.32 (s, 0.05H), 7.26 (d, $J = 8.3$ Hz, 2H), 7.08 (d, $J = 8.4$ Hz, 2H), 3.81 (t, $J = 7.2$ Hz, 2H), 3.39 (t, $J = 6.6$ Hz, 2H), 2.92 (hept, $J = 7.0$ Hz, 1H), 1.89 – 1.81 (m, 2H), 1.68 (p, $J = 7.5$, 7.1 Hz, 2H), 1.25 (d, $J = 7.0$ Hz, 6H).

$^{13}$C NMR (125 MHz, Chloroform-d) $\delta$ 162.3 (t, $J = 31.3$ Hz), 148.0, 138.3, 127.7, 124.4, 43.9, 33.7, 29.8, 26.2, 24.0, 23.9.

HRMS (ESI, m/z) calcd for C$_{14}$H$_{20}$DBrNO$^{[M+H]^+}$: 299.0864; found: 299.0861.

$N$-(4-(tert-butyl)phenyl)-$N$-(4-bromobutyl)formamide-d (8s)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (50 mg, 80%).

D incorporation by $^1$H NMR: 96%

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.33 (s, 0.04H), 7.41 (d, $J = 8.6$ Hz, 2H), 7.08 (d, $J = 8.6$ Hz, 2H), 3.82 (t, $J = 7.2$ Hz, 2H), 3.39 (t, $J = 6.6$ Hz, 2H), 1.89 – 1.82 (m, 2H), 1.69 (p, $J = 7.5$ Hz, 2H), 1.32 (s, 9H).

$^{13}$C NMR (125 MHz, Chloroform-d) $\delta$ 162.3 (t, $J = 30.0$ Hz), 150.2, 138.0, 126.6, 123.9, 43.8, 34.6, 33.1, 31.3, 29.8, 26.2.

HRMS (ESI, m/z) calcd for C$_{15}$H$_{22}$DBrNO$^{[M+H]^+}$: 313.1220; found: 313.1222.

$N$-(4-bromobutyl)-$N$-(4-methoxyphenyl)formamide-d (8t)
The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (40 mg, 71%).

D incorporation by $^1$H NMR: 97%

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.25 (s, 0.04H), 7.08 (d, $J$ = 8.8 Hz, 2H), 6.92 (d, $J$ = 8.9 Hz, 2H), 3.81 (s, 3H), 3.77 (t, $J$ = 7.1 Hz, 2H), 3.38 (t, $J$ = 6.6 Hz, 2H), 1.89 – 1.79 (m, 2H), 1.65 (p, $J$ = 7.5 Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.4 (t, $J$ = 33.8 Hz), 158.7, 133.4, 126.5 126.4, 114.9, 55.6, 44.2, 33.1, 29.7, 26.1.

HRMS (ESI, m/z) calcd for C$_{12}$H$_{16}$DBrNO$_2$[M+H]$^+$: 287.0500; found: 287.0501.

\[
\text{N-[(1,1'-biphenyl)-4-yl]-N-(4-bromobutyl)formamide-d (8u)}
\]

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (58 mg, 87%).

D incorporation by $^1$H NMR: 95%

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.43 (s, 0.05H), 7.64 (d, $J$ = 8.5 Hz, 2H), 7.59 (d, $J$ = 7.0 Hz, 2H), 7.46 (t, $J$ = 7.7 Hz, 2H), 7.38 (t, $J$ = 7.4 Hz, 1H), 7.24 (d, $J$ = 8.6 Hz, 2H), 3.89 (t, $J$ = 7.2 Hz, 2H), 3.41 (t, $J$ = 6.6 Hz, 2H), 1.93 – 1.86 (m, 2H), 1.74 (p, $J$ = 7.7 Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.25 (t, $J$ = 28.8 Hz), 140.0, 139.9, 139.8, 129.0, 128.4, 127.7, 127.0, 124.4, 43.7, 33.1, 29.8, 26.3.

HRMS (ESI, m/z) calcd for C$_{17}$H$_{18}$DBrNO[M+H]$^+$: 333.0707; found: 333.0709.

\[
\text{N-(4-bromobutyl)-N-(4-fluorophenyl)formamide-d (8v)}
\]

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (52 mg, 94%).

D incorporation by $^1$H NMR: 95%

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.28 (s, 0.05H), 7.16 – 7.07 (m, 4H), 3.80 (t, $J$ = 7.2 Hz, 2H), 3.38 (t, $J$ = 6.6 Hz, 2H), 1.87 – 1.81 (m, 2H), 1.66 (p, $J$ = 7.7 Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.4 (d, $J$ = 123.1 Hz), 162.1 (t, $J$ = 30.0 Hz), 136.7, 126.5 (d, $J$ = 4.4 Hz), 116.8 (d, $J$ = 11.3 Hz), 44.1, 33.0 29.7, 26.19.

HRMS (ESI, m/z) calcd for C$_{11}$H$_{13}$DBrFNO[M+H]$^+$: 275.0300; found: 275.0302.
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**N-(4-bromophenyl)-N-(4-bromobutyl)formamide-d (8w)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (47 mg, 71%).

D incorporation by $^1$H NMR: 95%

$^1$H NMR (500 MHz, Chloroform-d) δ 8.33 (s, 0.05H), 7.53 (d, $J = 8.3$ Hz, 2H), 7.05 (d, $J = 8.6$ Hz, 2H), 3.82 (t, $J = 7.2$ Hz, 2H), 3.38 (t, $J = 6.5$ Hz, 2H), 1.88 – 1.79 (m, 2H), 1.67 (p, $J = 7.3$ Hz, 2H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 161.8 (t, $J = 31.3$ Hz), 139.70, 132.94, 132.50, 127.38, 125.65, 120.52, 43.66, 32.93, 29.66, 26.11.

HRMS (ESI, m/z) calcd for C$_{11}$H$_{13}$DBr$_2$NO$^{[M+H]^+}$: 334.9499; found: 334.9502.

**N-(4-bromobutyl)-N-(3,4-dimethoxyphenyl)formamide-d (8x)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (60 mg, 95%).

D$_a$ incorporation by $^1$H NMR: 95%

D$_b$ incorporation by $^1$H NMR: 81%

$^1$H NMR (500 MHz, Chloroform-d) δ 8.34 (s, 0.05H), 6.85 (d, $J = 1.6$ Hz, 1H), 6.80 – 6.68 (m, 1H), 3.86 (s, 6H), 3.84 – 3.79 (m, 2H), 3.36 (t, $J = 6.4$ Hz, 2H), 1.83 (p, $J = 6.4$ Hz, 2H), 1.67 (p, $J = 7.7$ Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-d) δ 168.3 (t, $J = 26.3$ Hz), 149.9, 149.2 132.4, 132.3, 117.4 (t, $J = 33.8$ Hz), 111.5, 108.9, 56.3, 56.2, 45.7, 33.1, 29.7, 25.8.

HRMS (ESI, m/z) calcd for C$_{13}$H$_{18}$DBr$_3$NO$_3$[M+H]$^+$: 317.0606; found: 317.0608.

**N-(4-bromobutyl)-N-(naphthalen-2-yl)formamide-d (8y)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (58 mg, 94%).

D incorporation by $^1$H NMR: 95%
$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.49 (s, 0.05H), 7.92 – 7.89 (m, 1H), 7.87 – 7.81 (m, 2H), 7.56 – 7.48 (m, 2H), 7.32 (d, $J$ = 8.7 Hz, 1H), 3.95 (t, $J$ = 7.2 Hz, 2H), 3.39 (t, $J$ = 6.6 Hz, 2H), 1.92 – 1.85 (m, 2H), 1.73 (p, $J$ = 7.7 Hz, 2H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.4 (t, $J$ = 27.5 Hz), 137.9, 133.6, 132.0, 1230.0, 127.8, 127.6, 127.2, 126.5, 122.4, 43.7, 33.0, 29.8, 26.3.

HRMS (ESI, m/z) calcd for C$_{15}$H$_{16}$DBrNO[M+H]$^+$: 307.0551; found: 307.0550.

$N$-methyl-$N$-(4-(thiophen-3-yl)phenyl)formamide-$d$ (8z)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (43 mg, 99%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.50 (s, 0.03H), 7.64 – 7.59 (m, 2H), 7.44 (dt, $J$ = 2.9, 1.4 Hz, 1H), 7.42 – 7.39 (m, 1H), 7.36 (dt, $J$ = 5.1, 1.3 Hz, 1H), 7.20 – 7.16 (m, 2H), 3.37 – 3.31 (m, 3H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.0 (t, $J$ = 30.0 Hz), 141.1, 141.0, 134.1, 127.6, 127.0, 126.6, 126.1, 122.5, 120.6, 32.0.

HRMS (ESI, m/z) calcd for C$_{12}$H$_{11}$DNOS[M+H]$^+$: 219.0697; found: 219.0699.

$N$-(4'-isopropyl-[1,1'-biphenyl]-4-yl)-$N$-methylformamide-$d$ (8aa)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (50 mg, 98%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.54 (s, 0.01H), 7.62 (d, $J$ = 8.6 Hz, 2H), 7.52 (d, $J$ = 8.2 Hz, 2H), 7.33 (d, $J$ = 8.2 Hz, 2H), 7.23 (d, $J$ = 8.5 Hz, 2H), 3.35 (s, 3H), 2.97 (p, $J$ = 6.9 Hz, 1H), 1.30 (d, $J$ = 7.0 Hz, 6H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 166.0 (t, $J$ = 28.8 Hz), 148.5, 141.1, 139.4, 137.4, 128.1, 127.0, 126.9, 122.5, 33.8, 32.0, 24.0.

HRMS (ESI, m/z) calcd for C$_{17}$H$_{19}$DNO[M+H]$^+$: 255.1602; found: 255.1603.

$N$-methyl-$N$-(4'-(trifluoromethoxy)-[1,1'-biphenyl]-4-yl)formamide-$d$

(8ab)
The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a white solid (50 mg, 85%).

D incorporation by $^1$H NMR: 97%

$^1$H NMR (500 MHz, Chloroform-$d$) δ 8.54 (s, 0.03H), 7.59 (dd, $J = 8.8, 7.2$ Hz, 4H), 7.31 – 7.27 (m, 2H), 7.25 (d, $J = 8.5$ Hz, 2H), 3.35 (s, 3H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) δ 162.0 (t, $J = 28.8$Hz), 148.9, 141.7, 138.7, 137.9, 128.3, 128.3, 127.7, 123.7, 122.5, 121.4, 119.5, 31.9.

HRMS (ESI, m/z) calcd for C$_{15}$H$_{12}$DF$_3$NO$_2$[M+H]$^+$: 297.0956; found: 297.0953.

$N$-methyl-$N$-(4'-fluoro-[1,1'-biphenyl]-4-yl)formamide-$d$ (8ac)

D incorporation by $^1$H NMR: 99%

$^1$H NMR (500 MHz, Chloroform-$d$) δ 8.52 (s, 0.02H), 7.59 – 7.55 (m, 2H), 7.54 – 7.50 (m, 2H), 7.25 – 7.20 (m, 2H), 7.13 (t, $J = 8.6$ Hz, 2H), 3.34 (s, 3H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) δ 163.6 (d, $J = 122.5$Hz), 162.2 (t, $J = 28.8$Hz), 161.6, 141.4, 138.4, 136.1 (d, $J = 1.9$Hz), 128.6, 128.5, 128.1, 122.5, 115.9 (d, $J = 16.9$Hz), 32.0.

HRMS (ESI, m/z) calcd for C$_{14}$H$_{12}$DFNO$_2$[M+H]$^+$: 231.1038; found: 231.1039.

$N$-methyl-$N$-(3'-methyl-[1,1'-biphenyl]-4-yl)formamide-$d$ (8ad)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a white solid (45 mg, 99%).

D incorporation by $^1$H NMR: 99%

$^1$H NMR (500 MHz, Chloroform-$d$) δ 8.53 (s, 0.02H), 7.62 (d, $J = 8.6$ Hz, 2H), 7.41 – 7.33 (m, 3H), 7.23 (d, $J = 8.6$ Hz, 2H), 7.19 (d, $J = 6.5$ Hz, 1H), 3.35 (s, 3H), 2.43 (s, 3H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) δ 162.0 (t, $J = 28.8$Hz), 141.3, 139.9, 139.5, 138.6, 128.9, 128.4, 128.3, 127.8, 124.1, 122.4, 32.0, 21.5.

HRMS (ESI, m/z) calcd for C$_{15}$H$_{13}$DNO[M+H]$^+$: 227.1289; found. 227.1293.
piperidine-1-carbaldehyde-\textit{d} (8ae)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (17 mg, 71%).

\( {}^1\text{H NMR} \) δ 8.07 (s, 0.02H), 3.73 – 3.69 (m, 1H), 3.69 – 3.65 (m, 1H), 3.60 – 3.57 (m, 1H), 3.43 – 3.39 (m, 1H).

HRMS (ESI, m/z) calcd for C_{5}H_{9}DNO_{2}[M+H]^+: 117.0769; found: 117.0770.

\( N\text{-(4-(dimethylamino)phenyl)-N-methylformamide-d} (8af) \)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (28 mg, 77%).

\( {}^1\text{H NMR} \) δ 8.30 (s, 0.04H), 7.04 (d, \( J = 9.0 \text{ Hz} \), 2H), 6.72 (d, \( J = 8.8 \text{ Hz} \), 2H), 3.25 (s, 3H), 2.96 (s, 6H).

HRMS (ESI, m/z) calcd for C_{10}H_{14}DN_{2}O[M+H]^+: 180.1242; found: 180.1243.

\( N,N\text{'-(1,4-phenylene)bis(N-methylformamide-d}_2 \) (8ag)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (38 mg, 97%).

\( {}^1\text{H NMR} \) δ 8.46 (s, 0.04H), 7.22 (s, 4H), 3.31 (s, 6H).

HRMS (ESI, m/z) calcd for C_{10}H_{11}D_{2}N_{2}O_{2}[M+H]^+: 195.1097; found: 195.1098.

\( N\text{-(4-(4-(dimethylamino)benzyl)phenyl)-N-methylformamide-d} (8ah) \)

The reaction was performed following the general procedure. The residue was purified by flash column
Supporting Information

chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (42 mg, 77%).

D incorporation by \( ^1H \) NMR: 96%

\( ^1H \) NMR (500 MHz, Chloroform-\( d \)) \( \delta \) 8.42 (s, 0.04H), 7.24 – 7.20 (m, 2H), 7.09 – 7.04 (m, 4H), 6.73 – 6.68 (m, 2H), 3.89 (s, 2H), 3.29 (s, 3H), 2.92 (s, 6H).

HRMS (ESI, m/z) calcd for C\(_{17}\)H\(_{20}\)DN\(_2\)O[M+H]\(^+\): 270.1711; found: 270.1709.

\( N,N'-(\text{methylenebis}(4,1\text{-phenylene}))\text{bis}(N\text{-methylformamide-}d_2) \) (8ai)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (51 mg, 90%).

D incorporation by \( ^1H \) NMR: 97%

\( ^1H \) NMR (500 MHz, Chloroform-\( d \)) \( \delta \) 8.44 (s, 0.06H), 7.22 (d, \( J = 8.5 \) Hz, 4H), 7.10 (d, \( J = 8.5 \) Hz, 4H), 3.99 (s, 2H), 3.29 (s, 6H).

HRMS (ESI, m/z) calcd for C\(_{11}\)H\(_{11}\)DNO\(_2\)[M+H]\(^+\): 285.1567; found: 285.1565.

\( N-(2\text{-}(\text{benzhydryl}oxy)\text{ethyl})\text{-}N\text{-methylformamide-}d \) (8aj)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (44 mg, 81%).

D incorporation by \( ^1H \) NMR: 97%

\( ^1H \) NMR (500 MHz, Chloroform-\( d \)) \( \delta \) 8.13 (s, 0.03H), 7.34 – 7.29 (m, 8H), 7.27 – 7.23 (m, 2H), 5.35 (d, \( J = 1.7 \) Hz, 1H), 3.62 – 3.52 (m, 3H), 3.45 (t, \( J = 5.0 \) Hz, 1H), 3.06 (s, 1H), 2.85 (s, 2H).

HRMS (ESI, m/z) calcd for C\(_{17}\)H\(_{10}\)DNO\(_2\)[M+H]\(^+\): 271.1551; found: 271.1552.

\( 4-(5H\text{-}\text{dibenzo}[a,d][7]\text{annulen-5-ylidene})\text{piperidine-}1\text{-carbaldehyde-}d \) (8ak)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (45mg, 75%).
D incorporation by $^1$H NMR: 95%

$^1$H NMR (500 MHz, Chloroform-$d$) δ 8.01 (s, 0.05H), 7.37 – 7.32 (m, 4H), 7.30 – 7.26 (m, 2H), 7.18 (dd, $J = 6.0$, 1.9 Hz, 2H), 6.93 (s, 2H), 3.79 (d, $J = 12.8$ Hz, 1H), 3.44 – 3.36 (m, 1H), 3.10 – 2.98 (m, 2H), 2.23 (ddt, $J = 21.1$, 12.3, 5.0 Hz, 4H).

HRMS (ESI, m/z) calcd for C$_{20}$H$_{20}$N$_2$O$[M+H]^+$: 303.1602; found:303.1605.

$N$-methyl-$N$-phenylformamide-$d$ (8al)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (19 mg, 71%).

D incorporation by $^1$H NMR: 97%

$^1$H NMR (500 MHz, Chloroform-$d$) δ 8.46 (s, 0.03H), 7.40 (t, $J = 7.8$ Hz, 2H), 7.29 – 7.24 (m, 1H), 7.16 (d, $J = 7.4$ Hz, 2H), 3.31 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) δ 162.1 (d, $J = 27.5$ Hz), 142.2, 129.6, 129.1, 126.4, 122.4, 32.0.

HRMS (ESI, m/z) calcd for C$_8$H$_9$DNO$[M+H]^+$: 137.0820; found: 137.0822.

$N$-methyl-$N$-(p-tolyl)formamide-$d$ (8am)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (24 mg, 81%).

D incorporation by $^1$H NMR: 98%

$^1$H NMR (500 MHz, Chloroform-$d$) δ 8.40 (s, 0.02H), 7.22 – 7.16 (m, 2H), 7.04 (d, $J = 8.4$ Hz, 2H), 3.28 (s, 3H), 2.35 (s, 3H).

HRMS (ESI, m/z) calcd for C$_9$H$_{11}$DNO$[M+H]^+$: 151.0976; found:151.0978.

$N$-(3-methoxyphenyl)-$N$-methylformamide-$d$ (8an)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (27 mg, 81%).

D incorporation by $^1$H NMR: 98%
Supporting Information

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.47 (s, 0.02H), 7.29 (t, $J = 8.1$ Hz, 1H), 6.79 (ddd, $J = 8.4$, 2.4, 0.9 Hz, 1H), 6.74 (ddd, $J = 8.0$, 2.1, 0.9 Hz, 1H), 6.68 (t, $J = 2.3$ Hz, 1H), 3.81 (d, $J = 1.2$ Hz, 3H), 3.28 (d, $J = 1.2$ Hz, 3H).

HRMS (ESI, m/z) calcd for C$_9$H$_{11}$DNO$_2$[M+H]$^+$: 167.0925; found: 167.0926.

**$N$-(3-bromophenyl)-$N$-methylformamide-$d$ (8ao)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (30 mg, 71%).

D incorporation by $^1$H NMR: 95%

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.48 (s, 0.05H), 7.40 (ddd, $J = 8.0$, 1.8, 0.9 Hz, 1H), 7.34 (t, $J = 2.0$ Hz, 1H), 7.30 – 7.24 (m, 1H), 7.11 (ddd, $J = 8.0$, 2.2, 0.9 Hz, 1H), 3.30 (s, 3H).

HRMS (ESI, m/z) calcd for C$_8$H$_8$DBrNO[M+H]$^+$: 214.9925; found: 214.9924.

**$N$-phenyl-$N$-(4-(p-tolylthio)butyl)formamide (10a)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (53 mg, 89%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.34 (s, 1H), 7.39 (t, $J = 7.8$ Hz, 2H), 7.29 (t, $J = 7.4$ Hz, 1H), 7.20 (d, $J = 8.2$ Hz, 2H), 7.09 (dd, $J = 20.2$, 7.7 Hz, 4H), 3.81 (t, $J = 7.1$ Hz, 2H), 2.84 (t, $J = 6.9$ Hz, 2H), 2.31 (s, 3H), 1.68 – 1.56 (m, 4H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.4, 140.8, 136.1, 132.5, 130.2, 130.2, 129.7, 129.7, 127.0, 124.3, 44.3, 34.0, 26.6, 26.4, 21.0.

HRMS (ESI, m/z) calcd for C$_{18}$H$_{22}$NOS[M+H]$^+$: 300.1417; found: 300.1415.

**$N$-(4-((4-isopropylphenyl)thio)butyl)-$N$-phenylformamide (10b)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (60 mg, 92%).
$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.34 (s, 1H), 7.39 (t, $J$ = 7.7 Hz, 2H), 7.29 (d, $J$ = 7.5 Hz, 1H), 7.23 (d, $J$ = 8.0 Hz, 2H), 7.12 (t, $J$ = 8.7 Hz, 4H), 3.82 (t, $J$ = 7.0 Hz, 2H), 2.85 (t, $J$ = 7.1 Hz, 2H), 1.69 – 1.56 (m, 5H), 1.23 (d, $J$ = 6.9 Hz, 6H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 162.39, 147.11, 140.75, 132.88, 130.09, 129.72, 127.07, 126.96, 124.26, 44.23, 33.83, 33.70, 26.62, 26.38, 23.98.

HRMS (ESI, m/z) calcd for C$_{20}$H$_{26}$NOS[M+H]$^+$: 328.1730; found: 328.1729.

**N-(4-(naphthalen-2-ylthio)butyl)-N-phenylformamide (10c)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (64 mg, 95%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.34 (s, 1H), 7.78 (d, $J$ = 8.0 Hz, 1H), 7.75 – 7.66 (m, 3H), 7.45 (dt, $J$ = 21.3, 7.1 Hz, 2H), 7.36 (dd, $J$ = 22.4, 8.0 Hz, 3H), 7.27 (t, $J$ = 7.1 Hz, 1H), 7.08 (d, $J$ = 7.8 Hz, 2H), 3.84 (t, $J$ = 6.6 Hz, 2H), 2.99 (t, $J$ = 6.5 Hz, 2H), 1.69 (dt, $J$ = 8.1, 4.3 Hz, 4H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.4, 140.7, 133.9, 133.8, 131.8, 129.7, 128.4, 127.8, 127.4, 127.1, 127.0, 126.6, 125.7, 124.2, 44.2, 33.1, 26.7, 26.3.

HRMS (ESI, m/z) calcd for C$_{21}$H$_{22}$NOS[M+H]$^+$: 336.1477; found: 336.1475.

**N-phenyl-N-(4-(pyridin-2-ylthio)butyl)formamide (10d)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (41 mg, 71%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.37 (d, $J$ = 4.9 Hz, 1H), 8.34 (s, 1H), 7.46 – 7.35 (m, 3H), 7.30 – 7.23 (m, 1H), 7.12 (dd, $J$ = 13.9, 7.9 Hz, 3H), 6.93 (dd, $J$ = 7.3, 5.0 Hz, 1H), 3.84 (t, $J$ = 6.7 Hz, 2H), 3.12 (t, $J$ = 6.6 Hz, 2H), 1.72 – 1.64 (m, 4H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.4, 159.0, 149.4, 140.8, 135.8, 129.7, 126.9, 124.3, 122.3, 119.3, 44.4, 29.5, 26.7.

HRMS (ESI, m/z) calcd for C$_{16}$H$_{19}$N$_{2}$OS[M+H]$^+$: 287.1213; found: 287.1211.

**N-(4-((6-bromopyridin-2-yl)thio)butyl)-N-phenylformamide (10e)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (37 mg, 95%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.34 (s, 1H), 8.04 (d, $J$ = 8.0 Hz, 1H), 7.84 (t, $J$ = 8.0 Hz, 2H), 7.30 – 7.23 (m, 1H), 6.95 (d, $J$ = 13.1 Hz, 3H), 6.92 (dd, $J$ = 7.3, 5.0 Hz, 3H), 3.84 (t, $J$ = 6.7 Hz, 2H), 3.12 (t, $J$ = 6.6 Hz, 2H), 1.72 – 1.47 (m, 4H).

$^{13}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.39, 149.4, 140.8, 135.8, 129.7, 126.9, 124.3, 119.3, 44.4, 29.5, 26.7.

HRMS (ESI, m/z) calcd for C$_{16}$H$_{19}$N$_{2}$OS[M+H]$^+$: 287.1213; found: 287.1211.
ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (62 mg, 85%).

\[ ^1 \text{H NMR (500 MHz, Chloroform-d)} \delta 8.34 (s, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.39 (t, J = 7.7 Hz, 2H), 7.28 (t, J = 7.4 Hz, 1H), 7.23 (t, J = 7.7 Hz, 1H), 7.17 (d, J = 7.9 Hz, 1H), 7.12 (d, J = 7.8 Hz, 1H), 6.99 (t, J = 7.6 Hz, 1H), 3.84 (t, J = 6.6 Hz, 2H), 2.89 (t, J = 6.6 Hz, 2H), 1.74 – 1.62 (m, 4H).
\]

\[ ^{13} \text{C NMR (125 MHz, Chloroform-d)} \delta 162.5, 140.6, 137.9, 133.0, 129.8, 127.8, 127.0, 126.5, 124.3, 123.5, 44.2, 32.4, 26.8, 25.6.
\]

HRMS (ESI, m/z) calcd for C_{16}H_{18}BrN_{2}O_{S}[M+H]^+:365.0318; found: 365.1320.

**N-(4-((5-methyl-1,3,4-thiadiazol-2-yl)thio)butyl)-N-phenylformamide (10f)**

[Diagram of the molecule]

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (59 mg, 95%).

\[ ^1 \text{H NMR (500 MHz, Chloroform-d)} \delta 8.42 (s, 1H), 7.41 (t, J = 7.7 Hz, 2H), 7.32 (t, J = 7.6 Hz, 1H), 7.20 – 7.14 (m, 2H), 3.93 (t, J = 6.8 Hz, 2H), 3.22 (t, J = 7.6 Hz, 2H), 2.89 (s, 3H), 1.76 (p, J = 7.2 Hz, 2H), 1.62 (p, J = 6.9 Hz, 2H).
\]

\[ ^{13} \text{C NMR (125 MHz, Chloroform-d)} \delta 169.8, 166.5, 164.8, 139.5, 123.0, 129.5, 127.9, 125.8, 124.6, 44.2, 33.5, 25.9, 25.8, 16.1.
\]

HRMS (ESI, m/z) calcd for C_{14}H_{18}N_{3}O_{S}[M+H]^+:308.0886; found: 308.0889.

**N-(4-(benzylthio)butyl)-N-phenylformamide (10g)**

[Diagram of the molecule]

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (55 mg, 92%).

\[ ^1 \text{H NMR (500 MHz, Chloroform-d)} \delta 8.35 (s, 1H), 7.40 (t, J = 7.7 Hz, 2H), 7.27 (s, 5H), 7.22 (d, J = 6.3 Hz, 1H), 7.14 (d, J = 7.9 Hz, 2H), 3.80 (t, J = 7.0 Hz, 2H), 3.65 (s, 2H), 2.39 (t, J = 6.9 Hz, 2H), 1.63 – 1.50 (m, 4H).
\]

\[ ^{13} \text{C NMR (125 MHz, Chloroform-d)} \delta 162.4, 140.8, 138.5, 129.7, 128.8, 128.5, 127.0, 124.2, 44.3, 36.2, 30.88, 26.7, 26.4.
\]

HRMS (ESI, m/z) calcd for C_{18}H_{22}N_{3}O_{S}[M+H]^+:300.1417; found: 300.1420.

**N-(4-(phenethylthio)butyl)-N-phenylformamide (10h)**
The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (69mg, 95%).

\[ ^1\text{H NMR (500 MHz, Chloroform-d)} \delta 8.37 (s, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.29 (q, J = 7.6 Hz, 3H), 7.23 – 7.13 (m, 5H), 3.83 (t, J = 7.0 Hz, 2H), 2.89 – 2.82 (m, 2H), 2.76 – 2.69 (m, 2H), 2.51 (t, J = 6.9 Hz, 2H), 1.66 – 1.56 (m, 4H).
\]

\[ ^{13}\text{C NMR (125 MHz, Chloroform-d)} \delta 162.4, 140.8, 129.7, 128.5, 127.0, 126.4, 124.2, 44.3, 36.3, 33.6, 31.8, 26.8, 26.7.
\]

HRMS (ESI, m/z) calcd for C\textsubscript{16}H\textsubscript{18}BrNOS[M+H]\textsuperscript{+}:365.0318; found: 365.0320.

**N-(4-(isopentylthio)butyl)-N-phenylformamide (10i)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (51 mg, 91%).

\[ ^1\text{H NMR (500 MHz, Chloroform-d)} \delta 8.36 (s, 1H), 7.41 (t, J = 7.9 Hz, 2H), 7.30 (d, J = 7.4 Hz, 1H), 7.17 (d, J = 7.2 Hz, 2H), 3.84 (t, J = 7.1 Hz, 2H), 2.50 – 2.43 (m, 4H), 1.66 – 1.56 (m, 5H), 1.42 (dd, J = 15.7, 6.7 Hz, 2H), 0.88 (d, J = 6.7 Hz, 6H).
\]

\[ ^{13}\text{C NMR (125 MHz, Chloroform-d)} \delta 162.35, 140.83, 129.69, 126.92, 124.21, 44.35, 38.64, 31.57, 30.06, 27.42, 26.80, 26.76, 22.29.
\]

HRMS (ESI, m/z) calcd for C\textsubscript{16}H\textsubscript{26}NOS[M+H]\textsuperscript{+}:280.1730; found: 280.1735.

**methyl 2-((4-(N-phenylformamido)butyl)thio)acetate (10j)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (26 mg, 46%).

\[ ^1\text{H NMR (500 MHz, Chloroform-d)} \delta 8.36 (s, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.30 (t, J = 7.5 Hz, 1H), 7.16 (d, J = 7.4 Hz, 2H), 3.83 (t, J = 6.9 Hz, 2H), 3.71 (s, 3H), 3.17 (s, 2H), 2.61 (t, J = 6.8 Hz, 2H), 1.65 – 1.57 (m, 4H).
\]

\[ ^{13}\text{C NMR (125 MHz, Chloroform-d)} \delta 170.9, 162.5, 140.7, 129.8, 127.0, 124.3, 52.4, 44.3, 33.4, 32.2, 26.6, 26.1.
\]

HRMS (ESI, m/z) calcd for C\textsubscript{14}H\textsubscript{20}NO\textsubscript{3}S[M+H]\textsuperscript{+}:282.1158; found: 282.1155.

**N-phenyl-N-(3-(p-tolylthio)propyl)formamide (10k)**
Supporting Information

N-(3-(naphthalen-2-ylthio)propyl)-N-phenylformamide (10l)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (59 mg, 92%).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.39 (s, 1H), 7.78 (d, $J = 7.9$ Hz, 1H), 7.74 – 7.68 (m, 3H), 7.47 (s, 2H), 7.38 – 7.32 (m, 3H), 7.27 (d, $J = 7.5$ Hz, 1H), 7.14 – 7.10 (m, 2H), 3.99 (t, $J = 7.2$ Hz, 2H), 3.00 (t, $J = 7.3$ Hz, 2H), 1.93 (p, $J = 7.2$ Hz, 2H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 162.5, 140.7, 133.7, 133.3, 131.9, 129.7, 128.5, 127.7, 127.7, 127.1, 127.0, 126.6, 125.8, 124.1, 43.9, 31.2, 27.3.

N-phenyl-N-(5-(p-tolylthio)pentyl)formamide (10m)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (57 mg, 91%).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.35 (s, 1H), 7.40 (t, $J = 7.8$ Hz, 2H), 7.29 (d, $J = 7.5$ Hz, 1H), 7.22 – 7.18 (m, 2H), 7.16 – 7.11 (m, 2H), 7.07 (d, $J = 7.9$ Hz, 2H), 3.79 (t, $J = 7.4$ Hz, 2H), 2.82 (t, $J = 7.3$ Hz, 2H), 2.30 (s, 3H), 1.60 (q, $J = 7.4$ Hz, 2H), 1.53 (p, $J = 7.5$, 6.7 Hz, 2H), 1.46 – 1.35 (m, 2H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 162.3, 140.9, 136.0, 132.8, 129.9, 129.7, 129.7, 126.9, 124.2, 44.8, 34.2, 28.8, 27.2, 25.9, 21.0.

N-(4-phenoxybutyl)-N-phenylformamide (12)
The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (52 mg, 97%).

\[ \text{1H NMR (500 MHz, Chloroform-d) } \delta \ 8.39 \ (s, 1H), 7.42 \ (t, J = 7.9 \ Hz, 2H), 7.32 \ (t, J = 7.7 \ Hz, 1H), 7.29 - 7.24 \ (m, 2H), 7.18 \ (d, J = 7.2 \ Hz, 2H), 6.93 \ (t, J = 7.4 \ Hz, 1H), 6.86 \ (d, J = 8.2 \ Hz, 2H), 3.93 \ (dt, J = 16.7, 6.2 \ Hz, 4H), 1.78 \ (dq, J = 14.4, 8.6, 8.0 \ Hz, 4H). \]

\[ \text{13C NMR (125 MHz, Chloroform-d) } \delta \ 162.6, 158.9, 140.8, 129.8, 129.6, 129.5, 127.1, 124.4, 120.7, 115.5, 114.5, 67.1, 44.6, 26.5, 24.4. \]

HRMS (ESI, m/z) calcd for C\textsubscript{17}H\textsubscript{20}NOS[M+H]\textsuperscript{+}:270.1489; found: 270.1491.

\[ N\text{-phenyl-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)formamide (13)} \]

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (33 mg, 55%).

\[ \text{1H NMR (500 MHz, Chloroform-d) } \delta \ 8.34 \ (s, 1H), 7.38 \ (t, J = 7.9 \ Hz, 2H), 7.28 \ (d, J = 7.4 \ Hz, 1H), 7.19 - 7.09 \ (m, 2H), 3.79 \ (t, J = 7.5 \ Hz, 2H), 1.57 - 1.46 \ (m, 2H), 1.40 \ (p, J = 7.6 \ Hz, 2H), 1.18 \ (s, 12H), 0.74 \ (t, J = 7.6 \ Hz, 2H). \]

\[ \text{13C NMR (125 MHz, Chloroform-d) } \delta \ 162.3, 141.1, 129.6, 126.8, 124.2, 83.0, 75.0, 44.8, 30.1, 24.8, 24.8, 21.3. \]

HRMS (ESI, m/z) calcd for C\textsubscript{17}H\textsubscript{27}BNO\textsubscript{3}[M+H]\textsuperscript{+}:304.2079; found: 304.2077.

\[ N\text{-}(4-(diethylamino)butyl)-N\text{- phenylformamide (14)} \]

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (49 mg, 99%).

\[ \text{1H NMR (500 MHz, Chloroform-d) } \delta \ 8.32 \ (s, 1H), 7.38 \ (t, J = 7.8 \ Hz, 2H), 7.29 - 7.24 \ (m, 1H), 7.14 \ (d, J = 7.2 \ Hz, 2H), 3.81 \ (t, J = 7.1 \ Hz, 2H), 2.81 \ (q, J = 7.2 \ Hz, 4H), 2.77 - 2.70 \ (m, 2H), 1.70 - 1.61 \ (m, 2H), 1.54 \ (p, J = 7.4 \ Hz, 2H), 1.18 \ (t, J = 7.3 \ Hz, 6H). \]

\[ \text{13C NMR (125 MHz, Chloroform-d) } \delta \ 162.6, 140.4, 129.8, 127.2, 124.3, 51.6, 46.6, 43.9, 25.1, 21.9, 9.8. \]

HRMS (ESI, m/z) calcd for C\textsubscript{15}H\textsubscript{25}N\textsubscript{2}O[M+H]\textsuperscript{+}:249.1961; found: 249.1963.
**N-(4-(((1R,4R)-4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)(methyl)amino)butyl)-N-phenylformamide (15)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (59 mg, 61%).

${^1}$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.38 (s, 1H), 7.69 (d, $J = 7.9$ Hz, 1H), 7.42 (t, $J = 7.8$ Hz, 2H), 7.30 (dd, $J = 11.3, 7.8$ Hz, 2H), 7.20 (d, $J = 11.5$ Hz, 3H), 7.12 (t, $J = 7.4$ Hz, 1H), 7.08 (d, $J = 2.1$ Hz, 1H), 6.87 (d, $J = 7.5$ Hz, 1H), 6.79 (dd, $J = 8.3, 2.1$ Hz, 1H), 4.10 (dd, $J = 5.7, 3.4$ Hz, 1H), 3.86 (t, $J = 7.3$ Hz, 3H), 2.44 (dt, $J = 11.6, 6.8$ Hz, 2H), 2.16 (s, 4H), 1.98 (d, $J = 2.7$ Hz, 1H), 1.67 – 1.58 (m, 4H), 1.56 – 1.47 (m, 2H).

${^{13}}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 162.4, 147.6, 138.1, 132.1, 130.8, 130.2, 130.0, 129.8, 129.7, 128.5, 128.2, 126.9, 126.7, 124.3, 62.1, 52.8, 44.8, 43.6, 37.0, 30.1, 25.4, 25.3, 15.4.

**4-(N-phenylformamido)butyl (S)-2-(4-isopropylphenyl)propanoate (16)**

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (66 mg, 90%).

${^1}$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.37 (s, 1H), 7.41 (t, $J = 7.7$ Hz, 2H), 7.31 (t, $J = 7.4$ Hz, 1H), 7.24 (d, $J = 7.8$ Hz, 1H), 7.18 – 7.13 (m, 3H), 7.10 (d, $J = 7.8$ Hz, 3H), 4.03 (d, $J = 2.6$ Hz, 1H), 3.79 (d, $J = 2.7$ Hz, 1H), 3.68 (dd, $J = 30.8, 7.2$ Hz, 2H), 2.45 (dd, $J = 7.2, 4.5$ Hz, 3H), 1.85 (td, $J = 6.8, 3.6$ Hz, 1H), 1.61 – 1.56 (m, 2H), 1.50 (d, $J = 7.4$ Hz, 3H), 1.46 (d, $J = 7.2$ Hz, 2H), 0.91 – 0.89 (m, 6H).

${^{13}}$C NMR (125 MHz, Chloroform-$d$) $\delta$ 174.7, 162.7, 140.7, 129.7, 129.4, 129.3, 127.3, 127.2, 127.1, 124.3, 64.1, 45.1, 45.1, 45.1, 44.5, 30.2, 25.9, 24.1, 22.4, 18.4, 18.3.
N-(4-(diethylamino)butyl)-N-phenylformamide (17)

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether: AcOEt = 20:1, v/v) to give the product as a yellow oil (49 mg, 99%).

\[
\begin{align*}
\text{CHO} & \quad \text{O} \\
\text{N} & \quad \text{O}
\end{align*}
\]

\begin{align*}
1^1\text{H NMR} & (500 \text{ MHz, Chloroform-}d) \delta 8.39 (s, 1H), 7.97 (dd, J = 8.1, 1.5 \text{ Hz, 2H}), 7.57 - 7.52 (m, 1H), 7.40 (q, J = 8.1 \text{ Hz, 4H}), 7.29 (t, J = 7.5 \text{ Hz, 1H}), 7.19 - 7.13 (m, 2H), 4.29 (t, J = 6.3 \text{ Hz, 2H}), 3.90 (t, J = 7.1 \text{ Hz, 2H}), 1.78 (dt, J = 12.6, 6.2 \text{ Hz, 2H}), 1.74 - 1.66 (m, 2H).
\end{align*}

\begin{align*}
1^{13}\text{C NMR} & (125 \text{ MHz, Chloroform-}d) \delta 166.5, 162.5, 140.7, 132.9, 130.3, 129.8, 129.5, 128.34, 127.0, 124.3, 64.3, 44.4, 26.0, 24.2.
\end{align*}

14. References

[1]. S. X. Huang, H. Y. Li, J. Med. Chem. 2010, 53, 8376.

[2]. C. T. Yang, Z. Q. Zhang. Angew. Chem. Int. Ed. 2012, 51, 528.
15. NMR spectroscopic data

\textit{N-(2-(2-iodoethoxy)ethyl)-N-phenylformamide (4a)}

\begin{center}
\includegraphics[width=\textwidth]{spectrum1.png}
\end{center}

\begin{center}
\includegraphics[width=\textwidth]{spectrum2.png}
\end{center}

\begin{center}
\includegraphics[width=\textwidth]{spectrum3.png}
\end{center}
Supporting Information

$N$-(2-(2-bromoethoxy)ethyl)$-N$-phenylformamide (5a)

![Chemical Structure](image)

![NMR Spectra](image)
$N$-(4-bromophenyl)$-N$-(2-(2-iodoethoxy)ethyl)formamide (4b)
Supporting Information

\[ N-(2-(2\text{-bromoethoxy})\text{ethyl})-N-(4\text{-bromophenyl})\text{formamide (5b)} \]

\[
\begin{align*}
\text{CHO} & \quad \text{Br} \\
\text{Br} & \quad \text{CHO} \\
\text{Br} & \quad \text{CHO}
\end{align*}
\]
Supporting Information

*N-(5-iodopentyl)-N-phenylformamide (4c)*

![Chemical structure of N-(5-iodopentyl)-N-phenylformamide (4c)](image)

![NMR spectrum of N-(5-iodopentyl)-N-phenylformamide (4c)](image)
Supporting Information

$N$-(5-bromopentyl)-$N$-phenylformamide (5c)

$$\begin{align*}
\text{CHO} & \quad \text{Br} \\
\text{N} & \quad \text{CHO} \\
\text{Br} & \quad \text{CHO}
\end{align*}$$
N-(4-iodobutyl)-N-phenylformamide (4d)
**Supporting Information**

\[ N\text{-}(4\text{-bromobutyl})\text{-}N\text{-}phenylformamide (5d) \]

![Chemical Structure](image)

![NMR Spectra](image)
Supporting Information

$N$-(4-bromophenyl)$-N$-(4-iodobutyl)formamide (4e)
N-(4-bromophenyl)-N-(4-bromobutyl)formamide (5e)
*N*-[4-iodobutyl]-*N*-[(4-methoxyphenyl)formamide (4f)
$N$-(4-bromobutyl)$-N$-(4-methoxyphenyl)formamide (5f)
N-(4-iodobutyl)-N-(3-chlorophenyl)formamide (4g)
$N\text{-}(4\text{-bromobutyl})\text{-}N\text{-}(3\text{-chlorophenyl})\text{formamide (5g)}$
Supporting Information

$N$-(4-iodobutyl)$-N$-(4-isopropylphenyl)formamide (4h)
$N$-(4-bromobutyl)-$N$-(4-isopropylphenyl)formamide (5h)
$N$-([1,1'-biphenyl]-4-yl)-$N$-(4-iodobutyl)formamide (4i)
Supporting Information

N-([1,1'-biphenyl]-4-yl)-N-(4-bromobutyl)formamide (5i)
N-(4-iodobutyl)-N-(naphthalen-2-yl)formamide (4j)
Supporting Information

\[N-(4\text{-bromobutyl})-N-(\text{naphthalen-2-yl})\text{formamide (5j)}\]

\[
\text{CHO} \quad \begin{array}{c}
\text{N} \\
\text{CHO} \\
\text{Br}
\end{array}
\]

\[
\text{CHO} \quad \begin{array}{c}
\text{N} \\
\text{CHO} \\
\text{Br}
\end{array}
\]

\[
\text{CHO} \quad \begin{array}{c}
\text{N} \\
\text{CHO} \\
\text{Br}
\end{array}
\]
$N$-(4-iodobutyl)-$N$-(p-tolyl)formamide (4k)
Supporting Information

\[ N-(4\text{-bromobutyl})-N-(p\text{-tolyl})\text{formamide (5k)} \]

\[
\begin{align*}
&\text{CHO} \\
&\text{Br} \\
&\text{N} \\
&\text{CHO} \\
&\text{Br}
\end{align*}
\]
Supporting Information

$N$-(4-(tert-butyl)phenyl)-$N$-(4-iodobutyl)formamide (4l)
Supporting Information

\n
\[ N-(4-(\text{tert-butyl})\text{phenyl})-N-(4\text{-bromobutyl})\text{formamide (5l)} \]
$N$-(4-fluorophenyl)-$N$-(4-iodobutyl)formamide (4m)
Supporting Information

\[ \text{N-}(4\text{-bromobutyl})\text{-N-}(4\text{-fluorophenyl})\text{formamide (5m)} \]

![Chemical structure of \( \text{N-}(4\text{-bromobutyl})\text{-N-}(4\text{-fluorophenyl})\text{formamide (5m)} \)]

![NMR spectra of \( \text{N-}(4\text{-bromobutyl})\text{-N-}(4\text{-fluorophenyl})\text{formamide (5m)} \)]

![Chemical structure of \( \text{N-}(4\text{-bromobutyl})\text{-N-}(4\text{-fluorophenyl})\text{formamide (5m)} \)]

![NMR spectra of \( \text{N-}(4\text{-bromobutyl})\text{-N-}(4\text{-fluorophenyl})\text{formamide (5m)} \)]
Supporting Information

$N$-(3,4-dimethoxyphenyl)-$N$-(4-iodobutyl)formamide (4n)
Supporting Information

\[ N-(4\text{-bromobutyl})-N-(3,4\text{-dimethoxyphenyl})\text{formamide (5n)} \]

\[
\begin{align*}
\text{CHO} & \quad \text{Br} \\
\text{O} & \quad \text{N} \\
\text{O} & \quad \text{H}
\end{align*}
\]
8-(3-iodopropyl)-3,4-dihydroquinoline-1(2H)-carbaldehyde (4o)
Supporting Information

\( N-(5\text{-bromopentan-2-yl})-N\text{-phenylformamide} (5p) \)
Supporting Information

\section*{N-(5-iodo-3-methylpentyl)-N-phenylformamide (4q)}

\begin{center}
\includegraphics[width=0.8\textwidth]{figure.png}
\end{center}
**Supporting Information**

**N-(5-bromo-3-methylpentyl)-N-phenylformamide (5q)**

![Chemical Structure of 5q](image)

![NMR Spectrum of 5q](image)

![Additional NMR Spectrum of 5q](image)
Supporting Information

\[ \text{\textit{N-(3-iodopropyl}-\textit{N-phenylformamide (4r)}} \]

![Chemical structure of N-(3-iodopropyl)-N-phenylformamide (4r)]

![NMR spectrum of N-(3-iodopropyl)-N-phenylformamide (4r)]

![Chemical structure of N-(3-iodopropyl)-N-phenylformamide (4r)]
Supporting Information

\(N\)-(3-bromopropyl)-\(N\)-phenylformamide (5r)
$N$-(3-bromopropyl)$-N$-(4-chlorophenyl)formamide (5s)
$N$-(3,5-dimethylphenyl)-$N$-(3-iodopropyl)formamide (4t)
$N$-(3,5-dimethylphenyl)-$N$-(3-bromopropyl)formamide (4t)
(E)-N-methyl-N-(4-(3-oxoprop-1-en-1-yl)phenyl)formamide (7a)
hexyl 4-(N-methylformamido)benzoate (7b)
$N$-methyl-$N$-(4-(thiophen-3-yl)phenyl)formamide (7c)
Supporting Information

\(N-(4-(\text{hydrazinecarbonyl})\text{phenyl})-N\text{-methylformamide (7d)}\)
(E)-N-methyl-N-(4-(phenyldiazenyl)phenyl)formamide (7e)
N-(4'-isopropyl-[1,1'-biphenyl]-4-yl)-N-methylformamide (7f)
N-methyl-N-(4′-(trifluoromethoxy)-[1,1'-biphenyl]-4-yl)formamide

(7g)
$N$-methyl-$N$-(4'-phenoxy-[1,1'-biphenyl]-4-yl)formamide (7h)
$N$-(4'-fluoro-[1,1'-biphenyl]-4-yl)-$N$-methylformamide (7i)
$N$-methyl-$N$-(4'-nitro-[1,1'-biphenyl]-4-yl)formamide (7j)
Supporting Information

*N*-methyl-*N*-(3'-methyl-[1,1'-biphenyl]-4-yl)formamide (7k)
(E)-N-methyl-N-(4-(phenyl diazenyl)phenyl)formamide (7l)
Supporting Information

*N*-methyl-*N*-(pyridin-2-yl)formamide (7m)
Supporting Information

\[ \text{N-(2-hydroxyethyl)-N-methylformamide (7n)} \]

\[ \text{HO} \quad \text{CHO} \]

\[ \text{HO} \quad \text{N} \]

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piperidine-1-carbaldehyde (7o)
Supporting Information

pyrrolidine-1-carbaldehyde (7p)

![NMR Spectra of pyrrolidine-1-carbaldehyde (7p)]
piperidine-1-carbaldehyde (7q)
$N,N$-dibutylformamide (7s)
Supporting Information

(7s)4-(5-fluorobenzo[d]isoxazol-3-yl)piperidine-1-carbaldehyde (7t)
Supporting Information

$N$-(4-(dimethylamino)phenyl)-$N$-methylformamide (7u)

![Chemical structure and NMR spectrum](image)

**NMR Spectra**

- **1H NMR (DMSO-d$_6$)**
  - δ (ppm): 9.47, 7.67, 7.0, 6.98, 3.85, 2.97

- **13C NMR (DMSO-d$_6$)**
  - δ (ppm): 188.01, 149.75, 135.74, 123.10, 112.51, 38.83
$N,N'-(1,4$-phenylene)$bis(N$-methylformamide)$ (7v)$
Supporting Information

*N-(4-(4-(dimethylamino)benzyl)phenyl)-N-methylformamide (7w)*

![Chemical structure of 7w]

![NMR spectrum of 7w]
$N,N'$-(methylenebis(4,1-phenylene))bis($N$-methylformamide) (7x)
$N$-(2-(benzhydryloxy)ethyl)-$N$-methylformamide (7y)
4-(5H-dibenzo[a,d][7]annulen-5-ylidene)piperidine-1-carbaldehyde (7z)
1S,5S)-8-oxo-1,5,6,8-tetrahydro-2H-1,5-methanopyrido[1,2-a][1,5]diazocine-3(4H)-carbaldehyde (7aa)
(R)-N-methyl-N-(3-phenyl-3-(o-tolyloxy)propyl)formamide (7ab)
Supporting Information

N-methyl-N-(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)formamide (7ac)
4-(8-chloro-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carbaldehyde (7ad)
(1R,3r,5S)-8-formyl-8-azabicyclo[3.2.1]octan-3-yl 1H-indole-3-carboxylate (7ae)
Supporting Information

4-(3-chlorodibenzo[b,f][1,4]oxazepin-11-yl)piperazine-1-carbaldehyde (7af)
Supporting Information

*N*-methyl-*N*-phenylformamide (7ag)

![Chemical Structure](image)

![NMR Spectrum](image)

![NMR Spectrum](image)
Supporting Information

N-(4-bromophenyl)-N-methylformamide (7ah)
$N$-(4-chlorophenyl)-$N$-methylformamide (7ai)
Supporting Information

*N*-methyl-*N*-(p-tolyl)formamide (7aj)
$N$-(4-formylphenyl)-$N$-methylformamide (7ak)
$N$-(3-methoxyphenyl)-$N$-methylformamide (7al)
Supporting Information

\textbf{N-(3-bromophenyl)-N-methylformamide (7am)}

\begin{center}
\includegraphics[width=0.4\textwidth]{N-(3-bromophenyl)-N-methylformamide.png}
\end{center}

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$N$-methyl-$N$-(m-tolyl)formamide (7an)
Supporting Information

$N$-ethyl-$N$-phenylformamide (7ao)

![Chemical Structure of N-ethyl-N-phenylformamide](image)

![NMR Spectra of N-ethyl-N-phenylformamide](image)
**Supporting Information**

**N-phenyl-N-propylformamide (7ap)**

![Chemical Structure](image1)

![NMR Spectrum](image2)

![Chemical Structure](image3)
$N$-(2-(2-iodoethoxy)ethyl)-$N$-phenylformamide-$d$ (8a)
Supporting Information

$N$-(4-bromophenyl)-$N$-(2-(2-iodoethoxy)ethyl)formamide-d (8b)

![Chemical structure image](image1)

![Chemical structure image](image2)

![Chemical structure image](image3)
Supporting Information

\[ N-(5-\text{iodopentyl})-N-\text{phenylformamide-d (8c)} \]

![Chemical Structure](image)

![NMR Spectra](image)
$N$-(4-iodobutyl)-$N$-phenylformamide-$d$ (8d)
$N$-(4-iodobutyl)-$N$-(p-tolyl)formamide-$d$ (8e)
Supporting Information

$N$-(4-iodobutyl)-$N$-(4-isopropylphenyl)formamide-$d$ (8f)

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$N$-(4-iodobutyl)-$N$-(4-methoxyphenyl)formamide-$d$ (8g)
$N$-(4-iodobutyl)-$N$-(naphthalen-2-yl)formamide-$d$ (8h)
$N$-(4-bromophenyl)-$N$-(4-iodobutyl)formamide-$d$ (8i)
$N$-(4-fluorophenyl)$-N$-(4-iodobutyl)formamide-$d$ (8j)
Supporting Information

$N$-(3,4-dimethoxyphenyl)-$N$-(4-iodobutyl)formamide-$d$ (8k)
8-(3-iodopropyl)-3,4-dihydroquinoline-1(2H)-carbaldehyde-d (8l)
$N$-(2-(2-bromoethoxy)ethyl)-$N$-phenylformamide-$d$ (8m)
Supporting Information

\[ \text{N-(2-(2-bromoethoxy)ethyl)-N-(4-bromophenyl)formamide-d (8n)} \]

![Chemical structure and NMR spectra](image_url)
$N$-(5-bromopentyl)-$N$-phenylformamide-$d$ (8o)
$N$-(4-bromobutyl)-$N$-(p-tolyl)formamide-$d$ (8p)
$N$-(4-bromobutyl)-$N$-(p-tolyl)formamide-$d$ (8q)
Supporting Information

$N$-(4-bromobutyl)$-N$-(4-isopropylphenyl)formamide-$d$ (8r)
**Supporting Information**

\(N\)-(4-(tert-butyl)phenyl)-\(N\)-(4-bromobutyl)formamide-\(d\) (8s)
Supporting Information

\[ \text{N-}(4\text{-bromobutyl})\text{-N-}(4\text{-methoxyphenyl})\text{formamide-}d \ (8t) \]
$N$-([1,1'-biphenyl]-4-yl)-$N$-(4-iodobutyl)formamide-$d$ (8u)
$N$-(4-bromobutyl)-$N$-(4-fluorophenyl)formamide-$d$ (8v)
Supporting Information

\[ \text{N-(4-bromophenyl)-N-(4-bromobutyl)formamide-d (8w)} \]
$N$-(4-bromobutyl)-$N$-(3,4-dimethoxyphenyl)formamide-$d$ (8x)
Supporting Information

$N$-(4-bromobutyl)$-N$-(naphthalen-2-yl)formamide-$_d$ (8y)

![Chemical Structure](image)

![NMR Spectra](image)
Supporting Information

\[ N\text{-methyl-}N\text{-}(4\text{-}(\text{thiophen-3-yl})\text{phenyl})\text{formamide-d} \quad (8z) \]

![Chemical Structure](image)

![NMR Spectra](image)
$N$-(4'-isopropyl-[1,1'-biphenyl]-4-yl)-$N$-methylformamide-$d$ (8aa)
$N$-methyl-$N$-(4'-(trifluoromethoxy)-[1,1'-biphenyl]-4-yl)formamide-$d$

(8ab)
Supporting Information

\[ N-(4'-\text{fluoro}-[1,1'-\text{biphenyl}]-4-\text{yl})-N-\text{methylformamide-d} \quad (8\text{ac}) \]
$N$-methyl-$N$-(3'-methyl-[1,1'-biphenyl]-4-yl)formamide-$d$ (8ad)
piperidine-1-carbaldehyde-$d$ (8ae)

$N$-(4-(dimethylamino)phenyl)-$N$-methylformamide-$d$ (8af)
$N,N'-(1,4$-phenylene)bis($N$-methylformamide-$d_2$) (8ag)

$N$-(4-(4-(dimethylamino)benzyl)phenyl)-$N$-methylformamide-$d$ (8ah)
$N,N'-(\text{methylenebis}(4,1\text{-phenylene}))\text{bis}(N\text{-methylformamide-$d_2$)} \ (8\text{ai})$

\[
\begin{align*}
\text{N-(2-(benzhydryloxy)ethyl)-N-methylformamide-$d$} \ (8\text{aj})
\end{align*}
\]
4-(5H-dibenzo[a,d][7]annulen-5-ylidene)piperidine-1-carbaldehyde - $d$ (8ak)

$N$-methyl-$N$-phenylformamide-$d$ (8al)
$N$-methyl-$N$-(p-tolyl)formamide-$d$ (8am)
Supporting Information

$N$-(3-methoxyphenyl)-$N$-methylformamide-$d$ (8an)

$N$-(3-bromophenyl)-$N$-methylformamide-$d$ (8ao)
Supporting Information

N-phenyl-N-(4-(p-tolylthio)butyl)formamide (10a)
$N$-(4-((4-isopropylphenyl)thio)butyl)-$N$-phenylformamide (10b)
$N$-(4-(naphthalen-2-ylthio)butyl)-$N$-phenylformamide (10c)
$N$-phenyl-$N$-(4-(pyridin-2-ylthio)butyl)formamide (10d)
Supporting Information

*N-(4-((6-bromopyridin-2-yl)thio)butyl)-N-phenylformamide (10e)*)

[Chemical structure diagram]

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Supporting Information

\[ \text{N-(4-((5-methyl-1,3,4-thiadiazol-2-yl)thio)butyl)-N-phenylformamide} \]

(10f)
$N$-(4-(benzylthio)butyl)-$N$-phenylformamide (10g)
Supporting Information

*N-(4-(phenethylthio)butyl)-N-phenylformamide (10h)*

![Chemical structure diagram](image)

![NMR spectrum](image)

![Chemical structure diagram](image)
N-(4-(isopentylthio)butyl)-N-phenylformamide (10i)

[Chemical structures and spectra images]

Supporting Information
methyl 2-((4-(N-phenylformamido)butyl)thio)acetate (10j)
Supporting Information

N-phenyl-N-(3-(p-tolylthio)propyl)formamide (10k)
$N$-(3-(naphthalen-2-ylthio)propyl)-$N$-phenylformamide (10l)
Supporting Information

\[ N\text{-phenyl}-N\text{-}(5\text{-(p-tolylthio)pentyl})\text{formamide (10m)}}]


Supporting Information

\[ N-(4\text{-phenoxybutyl})-N\text{-phenylformamide} (12) \]

\[
\text{CHO} \quad \begin{array}{c}
\text{N} \\
\text{CHO} \\
\text{O} \\
\text{N} \\
\text{CHO} \\
\text{O}
\end{array}
\]

\[
\begin{array}{c}
\text{CHO} \\
\text{N} \\
\text{O}
\end{array}
\]

\[
\begin{array}{c}
\text{CHO} \\
\text{N} \\
\text{O}
\end{array}
\]

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Supporting Information

$N$-(4-(diethylamino)butyl)-$N$-phenylformamide (13)

![Chemical Structure](image)

![NMR Spectrogram](image)
$N$-(4-(diethylamino)butyl)$-N$-phenylformamide (14)
$N$-(4-(((1R,4R)-4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)(methyl)amino)butyl)-$N$-phenylformamide (15)
4-(N-phenylformamido)butyl (S)-2-(4-isopropylphenyl)propanoate

(16)
$N$-(4-(diethylamino)butyl)-$N$-phenylformamide (17)