Supplementary Methods

General Information

All reactions were performed under nitrogen. The reagents used for experiments were purchased from Sigma-Aldrich, Acros Organics, TCI, and Alfa Aesar and used as received unless otherwise noted. DMF, DCE, DCM, DCB and DMSO were distilled from CaH₂ under nitrogen and stored in glove box. ¹H, ¹³C and ¹⁹F NMR spectra were recorded at 400, 100.6 and 376.5 MHz respectively using Bruker Avance 400 MHz spectrometer. HPLC yields were measured on Waters ACQUITY. High resolution mass spectra (HRMS) were determined on Waters Micromass GCT Premier Mass Spectrometer at Shanghai institute of organic chemistry. Note that [NO][BF₄] should be stored in glove box and the freshly opened [NO]BF₄ chemical gives the best result.
Experimental Section

**Supplementary Table 1.** Optimization studies resulting in discovery of benefited effect of Iodide

| Entry | Additive | Solvent | Yield (%)$^b$ |
|-------|----------|---------|--------------|
| 1     | -        | DCE     | 40           |
| 2     | -        | DCM     | 12           |
| 3     | -        | PhCl    | 43           |
| 4     | -        | DCB     | 46           |
| 5     | -        | DMF     | 0            |
| 6     | -        | DMSO    | 0            |
| 7     | -        | CH$_3$CN| 0            |
| 8     | TBAC     | DCB     | 76           |
| 9$^c$ | TBAI     | DCB     | 73           |
| 10$^{d,e}$ | TBAI   | DCB     | 78           |
| 11$^e$ | TBAI     | DCB     | 62           |
| 12$^f$ | TBAI     | DCB     | 85           |
| 13$^g$ | TBAI     | DCB     | 90           |
| 14$^{e,h}$ | TBAI   | DCB     | 90           |
| 15$^{e,i}$ | TBAI   | DCB     | 89           |
| 16$^{e,j}$ | TBAI   | DCB     | 90           |
| 17$^{e,k}$ | TBAI   | DCB     | 89           |
| 18$^{e,l}$ | TBAI   | DCB     | 87           |
| 19$^{m}$ | TBAI     | DCB     | 82           |
| 20$^{n}$ | TBAI     | DCB     | 0            |

$^a$ Reaction conditions: azobenzene (0.2 mmol, 0.0364 g), [NO][BF$_4$] (0.4 mmol, 0.0468 g), Pd(OAc)$_2$ (10 mol%, 0.0045 g), additive (10 mol%), 1.5 mL of solvent, 80 °C, 24 h. $^b$ Isolated yields. $^c$ The reaction was conducted at 70 °C. $^d$ 5 mol% of TBAI was used. $^e$ 5 mol% of Pd(OAc)$_2$ was used. $^f$ 3 mol% Pd(OAc)$_2$ and 3 mol% TBAI were used. $^g$ 1 mol% Pd(OAc)$_2$ and 1 mol% TBAI were used. $^h$ 2 mol% TsOH was added. $^i$ 2 mol% HOAc was added. $^j$ 2 mol% PivOH was added. $^k$ 2 mol% benzoic acid was added. $^l$ 2 mol% 4-nitrobenzoic acid was added. $^m$ 0.4 mmol scale reaction was conducted with 0.5 mol% Pd(OAc)$_2$ and 0.5 mol% TBAI. $^n$ The reaction was conducted without Pd(OAc)$_2$. 

Identification of iodide-bridged binuclear palladium complex from catalytic reaction system:

![Reaction Scheme](image)

**Procedure:** In a glove box, 250 mL flask equipped with a stir bar was charged with 1a (20 mmol, 3.6440 g), Pd(OAc)$_2$ (0.2 mmol, 0.0449 g), TBAI (0.2 mmol, 0.0738 g), [NO][BF$_4$] (40 mmol, 4.6724 g) and DCB (50 mL). The flask was sealed and removed out of the glove box. The reaction mixture was stirred at 80 $^\circ$C for 2 h. After cooling to room temperature, the reaction mixture was added hexane (100 mL) and freeze-dried in refrigerator for 24 h to produce some red solid. Poured out the liquid and the solid residue was washed with Et$_2$O (2×15 mL), the red solid was then dissolved in CH$_2$Cl$_2$ and by diffusion of hexane to afford 4a as red needle crystals. The structure of 4a was established by single-crystal X-ray diffraction analysis (see below).

After the screening of methyl, ethyl and n-butyl substituents on azobenzenes, we found only (E)-bis(4-butylphenyl)diazene could be used to afford soluble iodide-bridged binuclear palladium complex, an analogue of 4a, and therefore (E)-bis(4-butylphenyl)diazene was used to prepare iodide-bridged binuclear palladium complex with cyclopalladated (E)-bis(4-butylphenyl)diazene for investigation of the reaction mechanism.

Preparation of iodide-bridged binuclear palladium complex with cyclopalladated (E)-bis(4-butylphenyl)diazene 4b.

![Reaction Scheme](image)

**Procedure:** In a glove box, a 25 mL of the Schlenk tube equipped with a stir bar was charged with Pd(OAc)$_2$ (0.2 mmol, 0.0449), TBAI (0.2 mmol, 0.0738 g), 1b (2 mmol, 0.5888 g) and DCB (50 mL). The tube was sealed and removed out of the glove box. The reaction mixture was stirred at 90 $^\circ$C for 12 h. The reaction mixture was cooled to room temperature, filtered and the filtrate was concentrated under reduced pressure. The residue was purified by chromatography on silica gel (eluent: 5-10% CH$_2$Cl$_2$/hexane) to provide the corresponding product 4b (Binuclear Pd$^{II}$-I complex, red solid, 68.2 mg, 65%) and [Pd$_2$I$_6$]([nBu$_4$N]$_2$ (black solid, 16.5 mg, 11%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.83 (d, J = 7.7 Hz, 1H), 7.69 (s, 1H), 7.64 (d, J = 6.2 Hz, 2H), 7.28-7.25 (m, 2H), 7.05 (d, J = 7.7 Hz, 1H), 2.70-2.59 (m, 4H), 1.73-1.57 (m, 4H), 1.41-1.36 (m, 4H), 0.97-0.92 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 162.7, 159.9, 149.4, 145.6, 137.6, 129.7, 128.2, 126.0, 123.6, 36.4, 35.4, 33.2, 33.1, 22.3, 22.2, 13.9. Anal. Calcd. for C$_{40}$H$_{50}$I$_2$N$_4$Pd$_2$: C, 45.60; H, 4.78; N, 5.32; Found: C, 45.54; H, 4.85; N, 5.31. The structure of 4b was established by single-crystal X-ray diffraction analysis (see below).
The reactivity and catalytic activity of iodide-bridged binuclear palladium complexes:

**Stoichiometric reaction of 4b with [NO][BF₄] to form 3b**

In a glove box, a 25 mL of the Schlenk tube equipped with a stir bar was charged with 4b (0.1 mmol, 0.1053 g), [NO][BF₄] (0.6 mmol, 0.0701 g) and DCB (5 mL). The tube was sealed and removed out of the glove box. The reaction mixture was stirred at room temperature for 24 h. Upon completion, the reaction mixture was purified directly by chromatography on silica gel (eluent: 5-10% ether/hexane) to provide the corresponding product 3b (yellow oil, 24.6 mg, 38%).

**Studies of the catalytic activity of 4b:**

**Procedure:** In a glove box, a 25 mL of the Schlenk tube equipped with a stir bar was charged with 4b (1.5 mol%, 0.0032 g), TBAOAc (3 mol%, 0.0019 g), anhydrous p-toluenesulfonic acid (6 mol%, 0.0021 g), 1b (0.2 mmol, 0.0589 g) or 1c (0.2 mmol, 0.0421 g), [NO][BF₄] (0.6 mmol, 0.0701 g) and DCB (1.5 mL). The tube was sealed and removed out of the glove box. The reaction mixture was stirred at 90 °C for 48 h. 3b and 3c were obtained with 47% and 66% yields respectively (yields given in parentheses were isolated yields under standard reaction conditions). 4b provided the similar yields to the combination of 3 mol% Pd(OAc)₂ and 3 mol% TBAI (see below).
Conversion of the acetate-bridged binuclear palladium complex to the corresponding iodide-bridged binuclear palladium complex and the regeneration of iodide-bridged binuclear palladium complex under the conditions mimicking catalytic reaction:

Preparation of the acetate-bridged binuclear palladium complex with cyclopalladated (E)-bis(4-butylphenyl)diazene

**Procedure:** In a glove box, a 25 mL of the Schlenk tube equipped with a stir bar was charged with Pd(OAc)$_2$ (0.2 mmol, 0.0449), anhydrous p-toluenesulfonic acid (0.4 mmol, 0.0689 g), 1b (0.6 mmol, 0.1766 g) and DCB (3 mL). The tube was sealed and removed out of the glove box. The reaction mixture was stirred at 90 °C for 12 h. Upon completion, the reaction mixture was purified directly by chromatography on silica gel (eluent: 1-5% MeOH/CH$_2$Cl$_2$) to provide the corresponding product 5b (Binuclear Pd$^{II}$-OAc complex, black red solid, trans : cis = 5.71 : 1, 71.7 mg, 78%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.56 (d, $J = 7.9$ Hz, 2H), 7.43 (d, $J = 7.9$ Hz, 0.35H), 7.39 (d, $J = 8.5$ Hz, 0.70H), 7.28 (d, $J = 8.5$ Hz, 4H), 7.04 (d, $J = 8.5$ Hz, 4H), 6.97 (d, $J = 8.5$, 0.69H), 6.93 (dd, $J = 7.9$ Hz, 1.5 Hz, 2H), 6.77 (dd, $J = 7.9$ Hz, 1.5 Hz, 0.33H), 6.50 (d, $J = 1.4$ Hz, 0.34H), 6.32 (d, $J = 1.4$ Hz, 2H), 2.65-2.61 (m, 4.83H), 2.45-2.36 (m, 3.30H), 2.30-2.20 (m, 2.15H), 2.06 (s, 6H), 1.65-1.57 (m, 5H), 1.52-1.43 (m, 4.88H), 1.42-1.27 (m, 10.15H), 0.98-0.89 (m, 14.53H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 180.6, 161.3, 155.1, 148.9, 146.8, 145.5, 132.9, 132.5, 128.1, 127.9, 127.6, 125.4, 125.2, 123.2, 123.3, 123.5, 36.5, 36.4, 35.4, 33.3, 32.9, 32.6, 24.4, 22.5, 22.2, 13.8. Anal. Calcd. for C$_{44}$H$_{56}$N$_4$O$_4$Pd$_2$: C, 57.58; H, 6.15; N, 6.10; Found: C, 57.59; H, 6.18; N, 6.14. The structure of 5b was established by single-crystal X-ray diffraction analysis (see below).

Conversion of 5b to 4b

**Procedure:** In a glove box, a 25 mL of the Schlenk tube equipped with a stir bar was charged with 5b (0.1 mmol, 0.0917 g), TBAI (0.4 mmol, 0.0738 g) and DCB (3 mL). The tube was sealed and removed out of the glove box. The reaction mixture was stirred at 90 °C for 12 h. Upon
completion, the reaction mixture was purified directly by chromatography on silica gel (eluent: 5-10% CH₂Cl₂/hexane) to provide the corresponding product 4b (77.9 mg, 74%).

**Experiment for the regeneration of 4b under the conditions mimicking catalytic reaction:**

![Chemical structure](image)

**Procedure:** In a glove box, a 50 mL of the Schlenk tube equipped with a stir bar was charged with 4b (0.1 mol, 0.1053 g), 1b (1.0 mmol, 0.2944 g), [NO][BF₄] (0.3 mmol, 0.0351 g) and DCB (10 mL). The tube was sealed and removed out of the glove box. The reaction mixture was stirred at 90 °C for 4 h. Upon completion, the reaction mixture was cooled down to room temperature, then NEt₃ (1.5 mmol, 0.1521 g) in 1 mL MeOH was injected by a syringe under N₂ atmosphere to neutralize the acid formed in the reaction and extra [NO][BF₄]. The mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (10 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to provide product 3b (43.5 mg, 133%), at the same time, 4b (22.1 mg, 21%) was also recovered.

**The catalytic activity and reactivity of [Pd₂I₆](nBu₄N)₂:**

**Catalytic activity of [Pd₂I₆](nBu₄N)₂**

![Chemical structure](image)

**Procedure:** In a glove box, a 25 mL of the Schlenk tube equipped with a stir bar was charged with [Pd₂I₆](nBu₄N)₂ (1.5 mol%, 0.0043 g), 1a (0.2 mmol, 0.0364 g), [NO][BF₄] (0.4 mmol, 0.0468 g) and DCB (1.5 mL). The tube was sealed and removed out of the glove box. The reaction mixture was stirred at 80 °C for 24 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (20 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to provide product 3a (34.9 mg, 82%).
Transformation of $[{\text{Pd}_2}{\text{I}_6}](^{t}{\text{Bu}_4}{\text{N}})_2$ to 4b

**Procedure:** In a glove box, a 100 mL of the Schlenk tube equipped with a stir bar was charged with $[{\text{Pd}_2}{\text{I}_6}](^{t}{\text{Bu}_4}{\text{N}})_2$ (0.1 mmol, 0.1433 g), [NO][BF₄] (0.7 mmol, 0.0818 g), 1b (1.0 mmol, 0.2944 g) and DCB (10 mL). The tube was sealed and removed out of the glove box. The reaction mixture was stirred at 90 °C for 4 h. Upon completion, the reaction mixture was cooled down to room temperature, and NEt₃ (1.5 mmol, 0.1521 g) in 1 mL MeOH was injected by a syringe under N₂ atmosphere to neutralize the acid formed in the reaction and extra [NO][BF₄]. The mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (10 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to provide product 3b (25.3 mg, 78%), at the same time, 4b was just detected by ¹H NMR, but no pure compound was isolated because of its small amount.

Stoichiometric reaction of acetate-bridged binuclear palladium 5a to generate 3a:

** Procedure:** In a glove box, a 50 mL of the Schlenk tube equipped with a stir bar was charged with 5a (0.1 mol, 0.0693 g), 1a-D₁₀ (0.2 mol, 0.0385 g), [NO][BF₄] (0.4 mmol, 0.0468 g) and DCB (5 mL). The tube was sealed and removed out of the glove box. The reaction mixture was stirred at 80 °C for 1 h. Upon completion, the reaction mixture was cooled down to room temperature, diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (20 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel, the yield of 3a was determined by ¹H NMR using dibromomethane as the internal standard.

Kinetic experiments to evaluate activity of catalyst systems and the order in 4b:

**Kinetic experiments to evaluate activity of catalyst systems**

**Procedure:** In a glove box, a 100 mL flask equipped with a stir bar was charged with Pd(OAc)₂ (3 mol%, 0.0134 g) or 4b (1.5 mol%, 0.0316 g), anhydrous p-toluenesulfonic acid (6 mol%, 0.0206 g), 1c (2 mmol, 0.4204 g), [NO][BF₄] (6 mmol, 0.7008 g), internal standard 3,4-dichlorotoluene (2
mmol, 0.3221 g) and DCB (15 mL). The flask was sealed and removed out of the glove box. The reaction mixture was stirred at room temperature for 5 min and then 90 °C. The samples were obtained at the indicated time using syringes with long needles which were filled with N₂ before use. Filtered the samples with a pad of silica gel and washed with 1.5 mL MeOH. The concentrations of 3c were determined by HPLC analysis. The reaction was monitored to approximately 10-15% conversion.

The Initial rate with Pd(OAc)₂ and TsOH catalyst system (Catalyst System A)

Following the above mentioned procedure: the reaction was carried out with Pd(OAc)₂ (3 mol%, 0.0134 g), anhydrous p-toluenesulfonic acid (6 mol%, 0.0206 g), 1c (2 mmol, 0.4204 g), [NO][BF₄] (6 mmol, 0.7008 g) and internal standard 3,4-dichlorotoluene (2 mmol, 0.3221 g) in DCB (15 mL).

Supplementary Table 2. Initial rate with catalytic system A

| Time (min) | 0.5  | 1    | 1.5  | 2    | 2.5  | 3    | 3.5  | 4    |
|------------|------|------|------|------|------|------|------|------|
| 3b (M)     | 0.001459 | 0.001847 | 0.002159 | 0.002806 | 0.003488 | 0.004124 | 0.004904 | 0.005503 |

| Time (min) | 5    | 6    | 7    | 8    | 9    | 10   | 12   | 14   |
|------------|------|------|------|------|------|------|------|------|
| 3b (M)     | 0.006506 | 0.007366 | 0.008263 | 0.008884 | 0.00935 | 0.010229 | 0.010909 | 0.012376 |

| Time (min) | 16   | 18   | 20   |      |      |      |      |      |
|------------|------|------|------|------|------|------|------|------|
| 3b (M)     | 0.01294 | 0.013631 | 0.014167 |      |      |      |      |      |
Supplementary Figure 1. Plot of the initial rate versus time with catalytic system A

The initial rate with Pd(OAc)$_2$, TBAI and TsOH catalyst system (Catalyst System B)

Following the above mentioned procedure: the reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0134 g), anhydrous p-toluenesulfonic acid (6 mol%, 0.0206 g), TBAI (3 mol%, 0.0222 g), 1c (2 mmol) and DCB (10 mL). The flask was sealed and removed out of the glove box. The reaction mixture was stirred at room temperature for 5 min and then 90 °C for 1 h. Put the flask into the glove box after evacuation. [NO][BF$_4$] (6 mmol, 0.7008 g), internal standard 3,4-dichlorotoluene (2 mmol, 0.3221 g) and DCB (5 mL) were added. The flask was sealed and removed out of the glove box. The reaction mixture was stirred at room temperature for 5 min and then 90 °C.
**Supplementary Table 3.** Initial rate with catalytic system B

| Time (min) | 0.5  | 1    | 1.5  | 2    | 2.5  | 3    | 3.5  | 4    |
|------------|------|------|------|------|------|------|------|------|
| 3b (M)     | 0.001308 | 0.001618 | 0.001902 | 0.002571 | 0.002827 | 0.003317 | 0.003931 | 0.004679 |
| Time (min) | 5    | 6    | 7    | 8    | 9    | 10   | 12   | 14   |
| 3b (M)     | 0.006619 | 0.00877 | 0.010437 | 0.01208 | 0.014246 | 0.015185 | 0.01813 | 0.019825 |
| Time (min) | 16   |      |      |      |      |      |      |      |
| 3b (M)     | 0.022124 |      |      |      |      |      |      |      |

**Supplementary Figure 2.** Plot of the initial rate versus time with catalytic system B

**The Initial rate with 4b catalyst system (Catalyst System C)**

\[
Y = 0.00188X - 0.00276 \\
R^2 = 0.998
\]

Following the above mentioned procedure: the reaction was carried out with 4b (1.5 mol%, 0.0316 g), 1c (2 mmol, 0.4204 g), [NO][BF₄] (6 mmol, 0.7008 g) and internal standard 3,4-dichlorotoluene (2 mmol, 0.3221 g) in DCB (15 mL). The flask was sealed and removed out of the glove box. The reaction mixture was stirred at room temperature for 5 min and then 90 °C.
**Supplementary Table 4. Initial rate with catalytic system C**

| Time (min) | 0.5  | 1    | 1.5  | 2    | 2.5  | 3    | 3.5  | 4    |
|------------|------|------|------|------|------|------|------|------|
| 3b (M)     | 0.000121 | 0.00034 | 0.000708 | 0.001343 | 0.00175 | 0.002467 | 0.00345 | 0.004413 |

| Time (min) | 5    | 6    | 7    | 8    | 9    | 10   | 12   |
|------------|------|------|------|------|------|------|------|
| 3b (M)     | 0.007094 | 0.009253 | 0.010807 | 0.013421 | 0.014722 | 0.0162 | 0.019485 |

Supplementary Figure 3. Plot of the initial rate versus time with catalytic system C

**The initial rate with 5b, TsOH and HOAc catalyst system (Catalyst System D)**

\[
Y = 0.00231X - 0.0046 \\
R^2 = 0.997
\]

Following the above mentioned procedure: the reaction was carried out with 5b (1.5 mol%, 0.0275 g), anhydrous p-toluenesulfonic acid (6 mol%, 0.0206 g), HOAc (3 mol%, 0.0036 g), 1c (2 mmol, 0.4204 g), [NO][BF₄] (6 mmol, 0.7008 g) and internal standard 3,4-dichlorotoluene (2 mmol, 0.3221 g) in DCB (15 mL).
**Supplementary Table 5.** Initial rate with catalytic system D

| Time (min) | 0.5  | 1    | 1.5  | 2    | 2.5  | 3    | 3.5  | 4    |
|------------|------|------|------|------|------|------|------|------|
| 3b (M)     | 0.000321 | 0.000526 | 0.000783 | 0.001483 | 0.002137 | 0.002485 | 0.003242 | 0.004335 |
| Time (min) | 5    | 6    | 7    | 8    | 9    | 10   | 12   | 14   |
| 3b (M)     | 0.005391 | 0.006487 | 0.007937 | 0.00848 | 0.010131 | 0.010971 | 0.012534 | 0.013543 |
| Time (min) | 16   | 18   | 20   |      |      |      |      |      |
| 3b (M)     | 0.014175 | 0.014794 | 0.016159 |      |      |      |      |      |

**Supplementary Figure 4.** Plot of the initial rate versus time with catalytic system D

\[ Y = 0.00117X - 0.000542 \]

\[ R^2 = 0.994 \]
Supplementary Figure 5. Kinetic profiles for the formation of 3b using different catalytic systems

The initial rates were 0.00117, 0.00188, 0.00231, and 0.00115 with regard to condition A, B, C, and D respectively. The initial rate of binuclear Pd-I species 4b is two times as fast as Pd(OAc)$_2$ and TsOH catalytic system and is more fast than Pd(OAc)$_2$, TBAI and TsOH catalytic system, therefore indicating that 4b is a kinetically competent catalyst for the reaction. The initial rate of binuclear Pd-OAc species 5b is almost the same as Pd(OAc)$_2$ and TsOH catalytic system, thus 5b is the kinetically competent catalyst when without the addition of TBAI.

Determination of the order in 4b

The order in 4b was obtained by determining the initial rate of reactions with different [4b].

Procedure: In a glove box, a 100 mL flask equipped with a stir bar was charged with 1.5 mol%, 1 mol%, 0.75 mol%, 0.5 mol% or 0.25 mol% of 4b, 1b (2 mmol, 0.4204 g), [NO][BF$_4$] (6 mmol, 0.7008 g), internal standard 3,4-dichlorotoluene (2 mmol, 0.3221 g) and DCB (15 mL). The flask was sealed and removed out of the glove box. The reaction mixture was stirred at room temperature for 5 min and then 90 ºC. The reactions were monitored to approximately 2-15% conversion.
Following the above mentioned procedure: the reaction was carried out with 4b (1.5 mol%, 0.0316 g), 1c (2 mmol, 0.4204 g), [NO][BF₄] (6 mmol, 0.7008 g) and internal standard 3,4-dichlorotoluene (2 mmol, 0.3221 g) in DCB (15 mL). The flask was sealed and removed out of the glove box. The reaction mixture was stirred at room temperature for 5 min and then 90 °C.

### Supplementary Table 6. Initial rate with 1.5 mol% of 4b

| Time (min) | 0.5  | 1    | 1.5  | 2    | 2.5  | 3    | 3.5  | 4    |
|-----------|------|------|------|------|------|------|------|------|
| 3b (M)    | 0.000121 | 0.00034 | 0.000708 | 0.001343 | 0.00175 | 0.002467 | 0.00345 | 0.004413 |

| Time (min) | 5  | 6  | 7  | 8  | 9  | 10 | 12 |
|-----------|----|----|----|----|----|----|----|
| 3b (M)    | 0.007094 | 0.009253 | 0.010807 | 0.013421 | 0.014722 | 0.0162 | 0.019485 |

Supplementary Figure 6. Plot of the initial rate versus time with 1.5 mol% of 4b

Following the above mentioned procedure: the reaction was carried out with 4b (1 mol%, 0.0211...
g), 1c (2 mmol, 0.4204 g), [NO][BF₄] (6 mmol, 0.7008 g) and internal standard 3,4-dichlorotoluene (2 mmol, 0.3221 g) in DCB (15 mL). The flask was sealed and removed out of the glove box. The reaction mixture was stirred at room temperature for 5 min and then 90 ºC.

**Supplementary Table 7. Initial rate with 1 mol% of 4b**

| Time (min) | 0.5  | 1   | 1.5  | 2   | 2.5  | 3   | 3.5  | 4   |
|------------|------|-----|------|-----|------|-----|------|-----|
| **3b (M)** | 0.000338 | 0.000514 | 0.000735 | 0.001038 | 0.00136 | 0.001912 | 0.002726 | 0.003626 |
| Time (min) | 5    | 6   | 7    | 8   | 9    | 10  | 12   | 14  |
| **3b (M)** | 0.006059 | 0.007707 | 0.009044 | 0.010985 | 0.012699 | 0.014104 | 0.016357 | 0.018258 |

**Supplementary Figure 7.** Plot of the initial rate versus time with 1 mol% of 4b

Following the above mentioned procedure: the reaction was carried out with 4b (0.75 mol%, 0.0158 g), 1c (2 mmol, 0.4204 g), [NO][BF₄] (6 mmol, 0.7008 g) and internal standard 3,4-dichlorotoluene (2 mmol, 0.3221 g) in DCB (15 mL). The flask was sealed and removed out of the glove box. The reaction mixture was stirred at room temperature for 5 min and then 90 ºC.
Supplementary Table 8. Initial rate with 0.75 mol% of 4b

| Time (min) | 0.5  | 1    | 1.5  | 2    | 2.5  | 3    | 3.5  | 4    |
|-----------|------|------|------|------|------|------|------|------|
| 3b (M)    | 0.000986 | 0.001027 | 0.001164 | 0.001351 | 0.001623 | 0.001851 | 0.002082 | 0.002423 |
| Time (min)| 5    | 6    | 7    | 8    | 9    | 10   | 12   | 14   |
| 3b (M)    | 0.003107 | 0.003965 | 0.005444 | 0.006571 | 0.007553 | 0.008467 | 0.009992 | 0.011466 |
| Time (min)| 16   |      |      |      |      |      |      |      |
| 3b (M)    | 0.012386 |      |      |      |      |      |      |      |

Supplementary Figure 8. Plot of the initial rate versus time with 0.75 mol% of 4b

Following the above mentioned procedure: the reaction was carried out with 4b (0.5 mol%, 0.0105 g), 1c (2 mmol, 0.4204 g), [NO][BF₄] (6 mmol, 0.7008 g) and internal standard 3,4-dichlorotoluene (2 mmol, 0.3221 g) in DCB (15 mL). The flask was sealed and removed out of the glove box. The reaction mixture was stirred at room temperature for 5 min and then 90 ºC.
**Supplementary Table 9.** Initial rate with 0.5 mol% of 4b

| Time (min) | 0.5  | 1    | 1.5  | 2    | 2.5  | 3    | 3.5  | 4    |
|------------|------|------|------|------|------|------|------|------|
| 3b (M)     | 0.000531 | 0.000761 | 0.001012 | 0.001238 | 0.001459 | 0.001857 | 0.002015 | 0.002343 |
| Time (min) | 5    | 6    | 7    | 8    | 9    | 10   | 12   | 14   |
| 3b (M)     | 0.003025 | 0.003725 | 0.004457 | 0.005097 | 0.005949 | 0.006632 | 0.007256 | 0.007948 |
| Time (min) | 16   | 18   | 20   |      |      |      |      |      |
| 3b (M)     | 0.008744 | 0.00927 | 0.010122 |      |      |      |      |      |

**Supplementary Figure 9.** Plot of the initial rate versus time with 0.5 mol% of 4b

Following the above mentioned procedure: the reaction was carried out with 4b (0.25 mol%, 0.0053 g), 1c (2 mmol, 0.4204 g), [NO][BF₄] (6 mmol, 0.7008 g) and internal standard 3,4-dichlorotoluene (2 mmol, 0.3221 g) in DCB (15 mL). The flask was sealed and removed out of the glove box. The reaction mixture was stirred at room temperature for 5 min and then 90 °C.
**Supplementary Table 10.** Initial rate with 0.25 mol% of 4b

| Time (min) | 0.5  | 1   | 1.5 | 2   | 2.5 | 3   | 3.5 | 4   |
|------------|------|-----|-----|-----|-----|-----|-----|-----|
| 3b (M)     | 0.000258 | 0.000352 | 0.000494 | 0.000555 | 0.000656 | 0.000767 | 0.000881 | 0.000974 |
| Time (min) | 5    | 6   | 7   | 8   | 9   | 10  | 12  | 14  |
| 3b (M)     | 0.00116 | 0.001337 | 0.001481 | 0.001641 | 0.001756 | 0.001879 | 0.002088 | 0.002222 |
| Time (min) | 16   | 18  | 20  |     |     |     |     |     |
| 3b (M)     | 0.002353 | 0.002526 | 0.002618 |     |     |     |     |     |

**Supplementary Figure 10.** Plot of the initial rate versus time with 0.25 mol% of 4b

A plot of initial rate ($\Delta [3b]/\Delta t$) versus [4b] proved to be linear indicating first order dependence on 4b (Figure S11). This observation would support that 4b could remain intact during the course of the reaction.
KIE Experiments

Intramolecular KIE experiments: In a glove box, a 25 mL of the Schlenk tube equipped with a stir bar was charged with Pd(OAc)$_2$ (1 mol%, 0.0005 g), 1a-$D_5$ (0.2 mmol, 0.00374 g), [NO][BF$_4$] (0.4 mmol, 0.0468 g), TBAI (1 mol%, 0.0007 g), and DCB (1.5 mL). The tube was sealed and removed out of the glove box. The reaction mixture was stirred at 80 °C for 2.5 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (20 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to give 1a-$D_5$ and the corresponding products 3a-$D_5$ and 3a-$D_4$ (10.1 mg, 23%, 3a-$D_5$:3a-$D_4$ = 5.4:1 (Figure S12)). The residue 1a-$D_5$ was subject to $^1$H NMR and $H-D$ exchange was not observed. This phenomenon indicates that C-H activation might be irreversible (Figure S13).
Intermolecular KIE experiments: In a glove box, a 25 mL of the Schlenk tube equipped with a stir bar was charged with Pd(OAc)$_2$ (1 mol%, 0.0005 g), TBAI (1 mol%, 0.0007 g), 1a (0.2 mmol, 0.0364 g) or 1a-D$_{10}$ (0.2 mmol, 0.0364 g), [NO][BF$_4$] (0.4 mmol, 0.0468 g) and DCB (1.5 mL). The tube was sealed and removed out of the glove box. The reaction mixture was stirred at 80 °C for indicated time. Upon completion, the reaction mixture was diluted with 10 mL of CH$_3$CN, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the CH$_3$CN
(20 mL). The filtrate was diluted with CH$_3$CN to 100 mL. The concentrations of 3b were determined by HPLC analysis.

**(b) Intermolecular KIE experiment from two parallel reactions**

![Chemical structure](image)

## Supplementary Table 11

| Time (min) | 10   | 20   | 30   | 40   | 50   | 60   | 70   | 80   |
|------------|------|------|------|------|------|------|------|------|
| 3a (M)     | 0.001984 | 0.007089 | 0.013317 | 0.020256 | 0.024633 | 0.032971 | 0.038553 | 0.044021 |
| 3a-D$_9$ (M)| 0.000403 | 0.001767 | 0.003437 | 0.004491 | 0.006301 | 0.007577 | 0.008508 | 0.010135 |

## Supplementary Figure 14.

Plot of Initial rates of 1a and 1a-D$_{10}$ versus time

KIE = 0.000613/0.000138 = 4.4

Intramolecular KIE and intermolecular KIE experiments, of values 5.4 and 4.4 respectively, suggest that the cleavage of C-H bond is the rate-determination step.
Preparation of azobene starting materials

Synthesis of symmetric azobenzenes \(^1\)

\[
\begin{array}{c}
\text{R-NH}_2 \\
6 \text{ mol}\% \text{ CuBr} \\
18 \text{ mol}\% \text{ Pyridine} \\
\text{Toluene, 60 °C}
\end{array}
\rightarrow
\begin{array}{c}
\text{R} \\
\text{N-N}
\end{array}
\]

A 100 mL round flask was equipped with a stir bar was charged with CuBr (6 mol%), pyridine (18 mol%), aniline (5 mmol) in toluene (20 mL). The reaction mixture was vigorously stirred at 60 °C for 20 h under air or O\(_2\) (1 atm). After cooling down to room temperature and concentrating in vacuum, the residue was purified by flash chromatography on silica gel.

Synthesis of unsymmetric azobenzenes \(^2-4\)

Substituted aniline (10 mmol) was dissolved in 30 mL of DCM. To this solution Oxone (15 mmol) dissolved in 30 ml of water was added. The solution was stirred under nitrogen at room temperature until TLC monitoring indicated complete consumption of the starting material. After separation of the layers, the aqueous layer was extracted with DCM twice. The combined organic layers were washed with 1N HCl twice, saturated sodium bicarbonate solution, water, brine and dried (sodium sulfate), filtered. The filtrate was concentrated under reduced pressure and the crude products were used without further purifications. To a round bottom flask equipped with a magnetic stir bar was combined the indicated aniline (6-10 mmol, 1.2-2 equiv) and the indicated nitrosobenzene (5 mmol) in glacial acetic acid (30 mL). The reaction solution was stirred at room temperature for 48 h. Upon completion, the reaction mixture was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel.

1a-1l, 1n-1q, 1t, 1ab, 1ad-1ae are known compounds, and the analytical data are consistent with previously reported data. \(^1-2, 5-11\)

Analytical data for new azobenzenes

(E)-1-(3-bromo-4-fluorophenyl)-2-phenyldiazene (1m) : \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.18 (d, \(J = 6.1\) Hz, 1H), 7.93 (d, \(J = 6.7\) Hz, 3H), 7.55-7.54 (m, 3H), 7.29 (t, \(J = 8.2\) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 160.4 (d, \(J = 252.8\) Hz), 152.2, 149.4 (d, \(J = 3.4\) Hz), 131.5, 129.1, 126.9, 124.9 (d, \(J = 7.9\) Hz), 123.0, 116.7 (d, \(J = 23.7\) Hz), 110.0 (d, \(J = 22.6\) Hz). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\): -103.8. HRMS (ESI): calcd for C\(_{12}\)H\(_8\)N\(_2\)BrF [M+H]\(^+\): 278.9928, found 278.9927.
(E)-(4-((3-methoxyphenyl)diazenyl)phenyl)(phenyl)methanone (1s): \(^1\text{H NMR (400 MHz, CDCl}_3\)) \(\delta\): 7.98 (q, \(J = 8.3\) Hz, 4H), 7.84 (d, \(J = 7.6\) Hz, 2H), 7.61 (d, \(J = 7.3\) Hz, 2H), 7.48 (m, 4H), 7.09 (d, \(J = 8.2\) Hz, 1H), 3.91 (s, 3H). \(^{13}\text{C NMR (100 MHz, CDCl}_3\)) \(\delta\): 195.96, 160.36, 154.56, 153.79, 139.16, 137.39, 132.64, 131.00, 129.85, 128.37, 122.59, 118.53, 117.62, 105.81, 55.48. \textbf{HRMS (ESI)}: calcd for C\(_{20}\)H\(_{16}\)O\(_2\)N\(_2\) [M+H\(^+\)]: 317.1285, found 317.1282.

(E)-1-(2,3,4,5,6-pentadeuterophenyl)-2-o-tolyldiazene (1u): \(^1\text{H NMR (400 MHz, CDCl}_3\)) \(\delta\): 7.67 (d, \(J = 7.9\) Hz, 1H), 7.43-7.36 (m, 2H), 7.33-7.26 (m, 1H), 2.77 (s, 3H). \(^{13}\text{C NMR (100 MHz, CDCl}_3\)) \(\delta\): 152.9, 150.7, 138.0, 131.2, 130.9, 130.2 (t, \(J = 24.2\) Hz), 129.9, 128.5 (t, \(J = 24.5\) Hz), 126.4, 122.5 (t, \(J = 24.7\) Hz) 115.4, 17.5. \textbf{HRMS (ESI)}: calcd for C\(_{13}\)H\(_7\)D\(_5\)N\(_2\) [M+H\(^+\)]: 202.1387, found 202.1386.

(E)-1-(4-fluorophenyl)-2-o-tolyldiazene (1v): \(^1\text{H NMR (400 MHz, CDCl}_3\)) \(\delta\): 7.97 (dd, \(J = 8.4\) Hz, 5.5 Hz, 2H), 7.65 (d, \(J = 8.0\) Hz, 1H), 7.43-7.35 (m, 2H), 7.32-7.26 (m, 1H), 7.22 (t, \(J = 8.5\) Hz, 2H), 2.75 (s, 3). \(^{13}\text{C NMR (100 MHz, CDCl}_3\)) \(\delta\): 164.2 (d, \(J = 251.6\) Hz), 150.5, 149.5, 138.1, 131.1 (d, \(J = 32.4\) Hz), 126.4, 124.9 (d, \(J = 8.9\) Hz), 115.9 (d, \(J = 22.9\) Hz), 115.4, 17.5. \(^{19}\text{F NMR (376 MHz, CDCl}_3\)) \(\delta\): -109.8. \textbf{HRMS (ESI)}: calcd for C\(_{13}\)H\(_{11}\)N\(_2\)F [M+H\(^+\)]: 215.0979, found 215.0978.

(E)-1-(4-chlorophenyl)-2-o-tolyldiazene (1w): \(^1\text{H NMR (400 MHz, CDCl}_3\)) \(\delta\): 7.89 (d, \(J = 8.6\) Hz, 2H), 7.66 (d, \(J = 8.0\) Hz, 1H), 7.51 (d, \(J = 8.6\) Hz, 2H), 7.44-7.34 (m, 2H), 7.33-7.25 (m, 1H), 2.75 (s, 3H). \(^{13}\text{C NMR (100 MHz, CDCl}_3\)) \(\delta\): 151.3, 150.5, 138.3, 136.6, 131.3, 131.2, 129.3, 126.4, 124.2, 115.4, 17.5. \textbf{HRMS (ESI)}: calcd for C\(_{13}\)H\(_{11}\)N\(_2\)Cl [M+H\(^+\)]: 231.0684, found 231.0682.
(E)-1-(4-bromophenyl)-2-o-tolyldiazene (1x) : $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.82 (d, $J = 8.2$ Hz, 2H), 7.70-7.62 (m, 3H), 7.44-7.35 (m, 2H), 7.33-7.24 (m, 1H), 2.75 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 151.7, 150.5, 138.4, 132.3, 131.3, 131.3, 126.45, 125.1, 124.4, 115.4, 17.5. HRMS (ESI): calcd for C$_{13}$H$_{11}$N$_2$Br [M+H]$^+$: 275.0178, found 275.0177.

(E)-methyl-4-(o-tolyldiazenyl)benzoate (1y) : $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.21 (d, $J = 8.3$ Hz, 2H), 7.97 (d, $J = 8.3$ Hz, 2H), 7.68 (d, $J = 8.0$ Hz, 1H), 7.44-7.35 (m, 2H), 7.33-7.27 (m, 1H), 3.98 (s, 3H), 2.77 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 166.5, 155.4, 150.6, 138.8, 131.6, 131.5, 131.3, 130.5, 126.4, 122.7, 115.3, 52.2, 17.5. HRMS (ESI): calcd for C$_{15}$H$_{14}$N$_2$O$_2$ [M+H]$^+$: 255.1128, found 255.1128.

(E)-phenyl(4-(o-tolyldiazenyl)phenyl)methanone (1z) : $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.98 (q, $J = 8.4$ Hz, 4H), 7.85 (d, $J = 7.6$ Hz, 2H), 7.68 (d, $J = 8.0$ Hz, 1H), 7.62 (t, $J = 7.3$ Hz, 1H), 7.52 (t, $J = 7.5$ Hz, 2H), 7.45-7.34 (m, 2H), 7.31-7.27 (m, 1H), 2.76 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 196.0, 154.9, 150.7, 138.9, 138.9, 137.5, 132.6, 131.7, 131.4, 131.0, 130.0, 128.4, 126.5, 122.7, 115.4, 17.5. HRMS (ESI): calcd for C$_{20}$H$_{16}$N$_2$O [M+H]$^+$: 301.1335, found 301.1334.

(E)-4-(o-tolyldiazenyl)benzaldehyde (1aa) : $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 10.11 (s, 1H), 8.03 (s, 4H), 7.68 (d, $J = 8.0$ Hz, 1H), 7.40 (dt, $J = 14.7$ Hz, 7.3 Hz, 2H), 7.31-7.26 (m, 1H), 2.76 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 191.6, 156.2, 150.6, 139.2, 137.3, 132.0, 131.5, 130.7, 126.5, 123.4, 115.4, 17.5. HRMS (ESI): calcd for C$_{14}$H$_{12}$N$_2$O [M+H]$^+$: 225.1022, found 225.1022.

(E)-methyl-4-((2-chlorophenyl)diazenyl)benzoate (1ac) : $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.20
(d, J = 8.5 Hz, 2H), 8.00 (d, J = 8.5 Hz, 2H), 7.72 (dd, J = 8.0 Hz, 1.5, 1H), 7.61-7.57 (m, 1H), 7.43 (td, J = 7.6 Hz, 1.6 Hz, 1H), 7.36 (dd, J = 11.1 Hz, 4.1 Hz, 1H), 3.96 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 166.3, 155.2, 148.4, 135.9, 132.4, 132.3, 130.8, 130.6, 127.3, 123.1, 117.5, 52.3. HRMS (ESI): calcd for C\(_{14}H_{11}N_2O_2Cl\) [M+H]\(^+\): 275.0582, found 275.0580.

(E)-methyl-4-((2-chlorophenyl)diazenyl)benzoate (1ad): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.20 (d, J = 8.6 Hz, 2H), 8.01 (d, J = 8.6 Hz, 2H), 7.78 (dd, J = 7.8 Hz, 1.2 Hz, 1H), 7.70 (dd, J = 7.9 Hz, 1.7 Hz, 1H), 7.42-7.33 (m, 2H), 3.96 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 166.3, 155.0, 149.5, 133.9, 132.6, 132.3, 130.7, 128.0, 123.2, 117.7, 52.3. HRMS (ESI): calcd for C\(_{14}H_{11}N_2O_2Br\) [M+H]\(^+\): 319.0077, found 319.0075.

(E)-Dipentadeuteroazobenzene (1a-D\(_{10}\)): \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 152.5, 130.4 (t, J = 24.1 Hz), 128.5 (t, J = 24.5 Hz), 122.4 (t, J = 24.6 Hz). HRMS (ESI): calcd for C\(_{12}D_{10}N_2\) [M+H]\(^+\): 193.1544, found 193.1544.

2,3,4,5,6-pentadeuteroazobenzene (1a-D\(_5\)): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.97-7.92 (m, 2H), 7.57-7.46 (m, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 152.6, 152.5, 130.9, 130.4 (t, J = 25.0 Hz), 129.0, 128.5 (t, J = 24.4 Hz), 122.8, 122.4 (t, J = 24.6 Hz). HRMS (ESI): calcd for C\(_{12}H_5D_5N_2\) [M+H]\(^+\): 188.1231, found 188.1230.

General procedure for the reaction of azobenzene with [NO][BF\(_4\)] with Pd(OAc)\(_2\) and TABI:
In a glove box, a 25 mL of the Schlenk tube equipped with a stir bar was charged with Pd(OAc)\(_2\) (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), p-toluenesulfonic acid (6 mol%, 0.0021 g), Azobenzene (0.2 mmol), [NO][BF\(_4\)] (0.6 mmol, 0.0701 g) and DCB (1.5 mL). The tube was sealed and removed out of the glove box. The reaction mixture was stirred at 90 °C for 48 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (20 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to provide the corresponding product.
Analytical data for products

2-Phenyl-2H-benzo[\textit{d}][1,2,3]triazole 1-oxide (3a): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (1 mol%, 0.0005 g), TBAI (1 mol%, 0.0007 g), 1a (0.2 mmol, 0.0364 g), [NO][BF$_4$] (0.4 mmol, 0.0468 g) in DCB (1.5 mL) at 80 °C for 24 h. 3a was obtained as white solid (38.3 mg, 90%; eluent: 10%-30% ether/hexane).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.17 (d, $J = 7.8$ Hz, 2H), 7.80 (d, $J = 8.7$ Hz, 1H), 7.76 (d, $J = 8.7$ Hz, 1H), 7.60-7.57 (m, 2H), 7.54-7.50 (m, 1H), 7.44 (t, $J = 7.8$ Hz, 1H), 7.34 (t, $J = 7.8$ Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 141.1, 135.3, 129.9, 129.2, 129.1, 126.5, 126.3, 123.5, 119.1, 114.0. HRMS (ESI): calcd for C$_{12}$H$_9$N$_3$O [M+H]$^+$: 212.0818, found 212.0818.

6-Butyl-2-(4-butylphenyl)-2H-benzo[\textit{d}][1,2,3]triazole 1-oxide (3b): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1b (0.2 mmol, 0.0589 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.5 mL) at 90 °C for 48 h. 3b was obtained as yellow oil (34.4 mg, 53%; eluent: 5-10% ether/hexane).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.02 (d, $J = 8.4$ Hz, 2H), 7.65 (d, $J = 8.9$ Hz, 2H), 7.54 (s, 1H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.28 (dd, $J = 8.9$, 1.0 Hz, 2H), 2.77-2.64 (m, 4H), 1.71-1.57 (m, 4H), 1.43-1.30 (m, 4H), 0.97-0.89 (m, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 145.0, 141.9, 140.1, 133.0, 131.4, 129.1, 126.6, 123.4, 118.5, 111.3, 35.7, 35.3, 33.3, 32.8, 22.2, 22.1, 13.8. HRMS (ESI): calcd for C$_{20}$H$_{26}$N$_3$O [M+H]$^+$: 324.2070, found 324.2072.

6-Methyl-2-p-tolyl-2H-benzo[\textit{d}][1,2,3]triazole 1-oxide (3c): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1c (0.2 mmol, 0.0421 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.5 mL) at 90 °C for 48 h. 3c was obtained as pale yellow solid (35.5 mg, 74%; eluent: 10%-30% ether/hexane).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.03 (d, $J = 7.9$ Hz, 2H), 7.65 (d, $J = 8.8$ Hz, 1H), 7.55 (s, 1H), 7.38 (d, $J = 7.8$ Hz, 2H), 7.27 (d, $J = 8.5$ Hz, 1H), 2.50 (s, 3H), 2.46 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 140.1, 139.9, 137.1, 132.88, 132.0, 129.7, 126.7, 123.4, 118.5, 111.9, 21.9, 21.30. HRMS (ESI): calcd for C$_{14}$H$_{13}$N$_3$O [M+H]$^+$: 240.1131, found 240.1131.

5-Methyl-2-m-tolyl-2H-benzo[\textit{d}][1,2,3]triazole 1-oxide (3d): The title compound was prepared
according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1d (0.2 mmol, 0.0421 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.5 mL) at 90 °C for 48 h. 3d was obtained as pale yellow solid (36.2 mg, 76%; eluent: 10%-30% ether/hexane). $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.94 (d, $J = 7.1$ Hz, 2H), 7.67 (d, $J = 8.9$ Hz, 1H), 7.47 (s, 1H), 7.43 (d, $J = 7.9$ Hz, 1H), 7.31 (d, $J = 7.6$ Hz, 1H), 7.16 (d, $J = 8.9$ Hz, 1H), 2.47 (s, 3H), 2.46 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ: 141.5, 139.5, 139.3, 135.2, 130.5, 129.3, 128.92, 125.3, 124.0, 120.7, 117.1, 113.4, 22.1, 21.4. HRMS (ESI): calcd for C$_{14}$H$_{13}$N$_3$O [M+H]$^+$: 240.1131, found 240.1130.

4-Methyl-2-(o-tolyl)-2H-benzo[d][1,2,3]triazole 1-oxide (3e): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1e (0.2 mmol, 0.0421 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.5 mL) at 90 °C for 48 h. 3e was obtained as pale yellow oil (10.2 mg, 21%; eluent: 10%-30% ether/hexane). $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.66 (d, $J = 8.5$ Hz, 1H), 7.54-7.39 (m, 5H), 7.30-7.22 (m, 3H), 2.65 (s, 3H), 2.22 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ: 142.0, 137.0, 133.8, 131.5, 131.3, 129.8, 127.9, 126.9, 126.5, 125.3, 111.4, 17.8, 15.9. HRMS (ESI): calcd for C$_{14}$H$_{13}$N$_3$O [M+H]$^+$: 240.1131, found 240.1130.

4-Fluoro-2-(2-fluorophenyl)-2H-benzo[d][1,2,3]triazole 1-oxide (3f): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1f (0.2 mmol, 0.0436 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.5 mL) at 90 °C for 48 h. 3f was obtained as pale yellow solid (8.5 mg, 17%; eluent: 1:1:9 ether/CH$_2$Cl$_2$/hexane). $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.71-7.58 (m, 3H), 7.41-7.35 (m, 2H), 7.32-7.25 (m, 1H), 7.16-7.10 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ: -116.67 (s, 1F), -127.10 (s, 1F).

13C NMR (100 MHz, CDCl$_3$) δ: 156.2 (d, $J = 228.5$ Hz), 153.6 (d, $J = 229.9$ Hz), 133.6 (d, $J = 21.4$ Hz), 133.6 (d, $J = 8.0$ Hz), 128.9, 127.3 (d, $J = 5.8$ Hz), 126.2 (d, $J = 6.1$ Hz), 124.9 (d, $J = 3.9$ Hz), 122.0 (d, $J = 12.4$ Hz), 117.2 (d, $J = 18.8$ Hz), 112.6 (d, $J = 16.1$ Hz), 110.3 (d, $J = 5.6$ Hz). HRMS (ESI): calcd for C$_{12}$H$_8$N$_3$OF$_2$ [M+H]$^+$: 248.0630, found 248.0629.

6-Cyclohexyl-2-(4-cyclohexylphenyl)-2H-benzo[d][1,2,3]triazole 1-oxide (3g): The title compound was prepared according to the general procedure. The reaction was carried out with
Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1g (0.2 mmol, 0.0693 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.5 mL) at 90 ºC for 48 h. 3g was obtained as pale yellow solid (54.4 mg, 72%; eluent: 1:1:9 ether/CH$_2$Cl$_2$/hexane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.01 (d, $J = 8.2$ Hz, 2H), 7.65 (d, $J = 9.0$ Hz, 1H), 7.56 (s, 1H), 7.40 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 9.0$ Hz, 1H), 2.62-2.59 (m, 2H), 1.96-1.75 (m, 10H), 1.50-1.25 (m, 10H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 150.0, 147.1, 140.2, 133.0, 130.5, 127.5, 126.7, 123.5, 118.5, 109.6, 44.6, 44.4, 34.2, 33.9, 26.7, 26.6, 26.0, 26.0. HRMS (ESI): calcd for C$_{24}$H$_{29}$N$_3$O $[\text{M+H}]^+$: 376.2383, found 376.2382.

6-Chloro-2-(4-chlorophenyl)-2$^H$-benzo[d][1,2,3]triazole 1-oxide (3h): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1h (0.2 mmol, 0.0502 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.5 mL) at 90 ºC for 48 h. 3h was obtained as white solid (38.6 mg, 69%; eluent: 1:1:9 ether/CH$_2$Cl$_2$/hexane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.17 (d, $J = 8.6$ Hz, 2H), 7.79 (s, 1H), 7.70 (d, $J = 9.2$ Hz, 1H), 7.56 (d, $J = 8.6$ Hz, 2H), 7.39 (d, $J = 9.1$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 139.6, 136.1, 133.6, 132.7, 131.2, 129.5, 126.6, 124.4, 120.4, 113.1. HRMS (ESI): calcd for C$_{12}$H$_7$N$_3$OCl$_2$ $[\text{M+H}]^+$: 280.0039, found 280.0038.

5-Bromo-2-(3-bromophenyl)-2$^H$-benzo[d][1,2,3]triazole 1-oxide (3i): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1i (0.2 mmol, 0.0680 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.5 mL) at 100 ºC for 24 h. 3i was obtained as brown solid (57.0 mg, 77%; eluent: 1:1:9 ether/CH$_2$Cl$_2$/hexane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.38 (s, 1H), 8.19 (d, $J = 7.9$ Hz, 1H), 7.95 (s, 1H), 7.67 (t, $J = 7.4$ Hz, 2H), 7.48-7.40 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 141.7, 135.9, 133.1, 130.5, 130.5, 126.1, 125.3, 123.60, 122.7, 121.6, 121.4, 115.4. HRMS (ESI): calcd for C$_{12}$H$_7$N$_3$OBr$_2$ $[\text{M+H}]^+$: 367.9029, found 367.9027.

6-Iodo-2-(4-iodophenyl)-2$^H$-benzo[d][1,2,3]triazole 1-oxide (3j): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1j (0.2 mmol, 0.0868 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.5 mL) at 90 ºC for 48 h. 3j was obtained as brown solid (82.4 mg, 89%; eluent: 1:1:9 ether/CH$_2$Cl$_2$/hexane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.22 (s, 1H), 7.98-7.91 (m, 4H), 7.67 (d, $J = 9.1$ Hz, 1H), 7.51 (d, $J = 9.1$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 140.0, 138.5, 138.4, 134.7, 127.7, 124.5, 123.0, 120.4, 96.0, 90.9. HRMS (ESI): calcd for C$_{12}$H$_7$N$_3$OI$_2$ $[\text{M+H}]^+$: 463.8751, found 463.8749.
6-(Methoxycarbonyl)-2-(4-(methoxycarbonyl)phenyl)-2H-benzo[d][1,2,3]triazole 1-oxide (3k):

The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)₂ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1k (0.2 mmol, 0.0596 g), [NO][BF₄] (3 equiv, 0.0701 g) in DCB (1.5 mL) at 90 °C for 48 h. 3k was obtained as pale yellow solid (57.9 mg, 88%; eluent: 1:2:5 ether/CH₂Cl₂/hexane). ¹H NMR (400 MHz, CDCl₃) δ: 8.54 (s, 1H), 8.37 (d, J = 8.1 Hz, 2H), 8.24 (d, J = 7.5 Hz, 2H), 8.05 (d, J = 9.2 Hz, 1H), 7.77 (d, J = 9.1 Hz, 1H), 3.97 (s, 3H), 3.96 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 165.7, 165.5, 142.4, 138.4, 131.2, 130.6, 129.4, 128.3, 126.4, 122.5, 119.2, 117.7, 52.7, 52.5. HRMS (ESI): calcd for C₁₆H₁₃N₃O₅ [M+H]+: 328.0928, found 328.0926.

2-(4-(Trifluoromethyl)phenyl)-2H-benzo[d][1,2,3]triazole 1-oxide (3l):

The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)₂ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1l (0.2 mmol, 0.0501 g), [NO][BF₄] (3 equiv, 0.0701 g) in DCB (1.5 mL) at 90 °C for 48 h. 3l was obtained as white solid (41.2 mg, 74%; eluent: 10%-30% ether/hexane). ¹H NMR (400 MHz, CDCl₃) δ: 8.44 (d, J = 8.5 Hz, 2H), 7.85 (d, J = 8.6 Hz, 2H), 7.80-7.75 (m, 2H), 7.49-7.45 (m, 1H), 7.38-7.34 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 165.7, 165.5, 142.4, 138.4, 131.2, 130.6, 129.4, 128.3, 126.4, 122.5, 119.2, 117.7, 52.7, 52.5. ¹⁹F NMR (376 MHz, CDCl₃) δ: -62.8. HRMS (ESI): calcd for C₁₃H₈N₃OF₃ [M+H]+: 280.0692, found 280.0691.

2-Phenyl-6-(trifluoromethyl)-2H-benzo[d][1,2,3]triazole 1-oxide (3l'):

The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)₂ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1l (0.2 mmol, 0.0501 g), [NO][BF₄] (3 equiv, 0.0701 g) in DCB (1.5 mL) at 90 °C for 48 h. 3l' was obtained as white solid (6.6 mg, 12%; eluent: 10% ether/hexane). ¹H NMR (400 MHz, CDCl₃) δ: 8.18 (d, J = 7.7 Hz, 3H), 7.90 (d, J = 9.1 Hz, 1H), 7.63-7.55 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ: 141.4, 135.0, 130.5, 129.4, 128.3 (q, J = 33.3 Hz), 125.6, 125.3 (q, J = 2.7 Hz), 123.5, 123.5 (q, J = 270.8 Hz), 120.6, 113.3 (q, J = 5.1 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ: -62.8. HRMS (ESI): calcd for C₁₃H₈N₃OF₃ [M+H]+: 280.0692, found 280.0691.

2-(3-Bromo-4-fluorophenyl)-2H-benzo[d][1,2,3]triazole 1-oxide (3m):

The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)₂ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1l (0.2 mmol, 0.0501 g), [NO][BF₄] (3 equiv, 0.0701 g) in DCB (1.5 mL) at 90 °C for 48 h. 3m was obtained as white solid (6.6 mg, 12%; eluent: 10% ether/hexane). ¹H NMR (400 MHz, CDCl₃) δ: 8.18 (d, J = 7.7 Hz, 3H), 7.90 (d, J = 9.1 Hz, 1H), 7.63-7.55 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ: 141.4, 135.0, 130.5, 129.4, 128.3 (q, J = 33.3 Hz), 125.6, 125.3 (q, J = 2.7 Hz), 123.5, 123.5 (q, J = 270.8 Hz), 120.6, 113.3 (q, J = 5.1 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ: -62.8. HRMS (ESI): calcd for C₁₃H₈N₃OF₃ [M+H]+: 280.0692, found 280.0691.
prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1m (0.2 mmol, 0.0558 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in chlorobenzene (1.5 mL) at 100 °C for 48 h. 3m was obtained as white solid (45.0 mg, 73%; eluent: 10%-30% ether/hexane). $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.49 (dd, $J$ = 6.0 Hz, 2.6 Hz, 1H), 8.22 (ddd, $J$ = 9.0 Hz, 4.1 Hz, 2.6 Hz, 1H), 7.75 (dd, $J$ = 12.4 Hz, 8.8 Hz, 2H), 7.48-7.44 (m, 1H), 7.37-7.30 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 159.4 (d, $J$ = 252.4 Hz), 141.3, 131.9, 129.6, 128.6, 126.7, 126.5, 124.1 (d, $J$ = 8.0 Hz), 119.1, 116.9 (d, $J$ = 24.1 Hz), 114.0, 109.7 (d, $J$ = 22.7 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) δ: -103.9. HRMS (ESI): calcd for C$_{12}$H$_7$N$_3$OBrF [M+H]$^+$: 307.9829, found 307.9828.

5-Bromo-6-fluoro-2-phenyl-2H-benzo[d][1,2,3]triazole 1-oxide (3m'): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1m (0.2 mmol, 0.0558 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in chlorobenzene (1.5 mL) at 100 °C for 48 h. 3m' was obtained as white solid (7.5 mg, 12%; eluent: 10% ether/hexane). $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.15-8.12 (m, 2H), 8.08 (d, $J$ = 5.9 Hz, 1H), 7.63-7.55 (m, 3H), 7.53 (d, $J$ = 6.7 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 156.7 (d, $J$ = 252.6 Hz), 138.3, 135.0, 130.3, 129.4, 125.1 (d, $J$ = 11.6 Hz), 124.0, 123.5, 114.8 (d, $J$ = 27.1 Hz), 99.1 (d, $J$ = 30.0 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) δ: -104.3. HRMS (ESI): calcd for C$_{12}$H$_7$N$_3$OBrF [M+H]$^+$: 307.9829, found 307.9828.

2-(3,5-Difluorophenyl)-2H-benzo[d][1,2,3]triazole 1-oxide (3n): The title compound was prepared as a inseperable mixture of 3n and 3n' according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1n (0.2 mmol, 0.0436 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in chlorobenzene (1.5 mL) at 100 °C for 48 h. The mixture of 3n and 3n' was obtained as white solid (32.0 mg, 65%; 3n: 3n' = 11.1, eluent: 10-20% ether/hexane). $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.02-7.97 (m, 2H), 7.75 (dd, $J$ = 12.1 Hz, 8.8 Hz, 2H), 7.49-7.45 (m, 1H), 7.36 (dd, $J$ = 8.3 Hz, 7.2 Hz, 1H), 6.97 (tt, $J$ = 8.6 Hz, 2.3 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 162.8 (dd, $J$ = 249.7 Hz, 13.6 Hz), 141.4, 136.8 (t, $J$ = 13.3 Hz), 129.9, 126.9, 126.8, 119.2, 114.1, 106.3 (dd, $J$ = 15.7 Hz, 5.8 Hz), 105.1 (t, $J$ = 25.3 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) δ: -106.5. HRMS (ESI): calcd for C$_{12}$H$_7$N$_3$OF$_2$ [M+H]$^+$: 248.0630, found 248.0630.

2-(4-(Methylsulfonyl)phenyl)-2H-benzo[d][1,2,3]triazole 1-oxide (3o): The title compounds was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3
mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1o (0.2 mmol, 0.0436 g), [NO][BF₄] (3 equiv, 0.0701 g) in nitrobenzene (1.5 mL) at 100 °C for 24 h. 3o was obtained as white solid (38.5 mg, 67%; eluent: 10-20% ether/hexane then CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ: 8.56-8.54 (m, 2H), 8.16-8.14 (m, 2H), 7.75 (t, J = 7.6 Hz, 2H), 7.49-7.45 (m, 1H), 7.38-7.34 (m, 1H), 3.11 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 141.7, 140.9, 139.20, 130.0, 128.6, 127.1, 126.7, 123.3, 119.2, 114.0, 44.5. HRMS (ESI): calcd for C₁₃H₁₁N₃O₃S [M+H]+: 290.0594, found 290.0593.

6-(Methylsulfonyl)-2-phenyl-2H-benzo[d][1,2,3]triazole 1-oxide (3o’): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)₂ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1o (0.2 mmol, 0.0436 g), [NO][BF₄] (3 equiv, 0.0701 g) in nitrobenzene (1.5 mL) at 100 °C for 24 h. 3o’ was obtained as white solid (6.0 mg, 10%; eluent: 10-20% ether/hexane). ¹H NMR (400 MHz, CDCl₃) δ: 8.57 (s, 1H), 8.19 (d, J = 7.3 Hz, 2H), 7.97-7.91 (m, 2H), 7.65-7.58 (m, 3H), 3.14 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 141.7, 138.1, 134.9, 130.7, 129.4, 126.0, 125.7, 123.4, 121.1, 117.2, 44.4. HRMS (ESI): calcd for C₁₃H₁₁N₃O₃S [M+H]+: 290.0594, found 290.0593.

2-(4-(Methoxycarbonyl)phenyl)-2H-benzo[d][1,2,3]triazole 1-oxide (3p): The title compounds were prepared according to the general procedure. The reaction was carried out with Pd(OAc)₂ (0.5 mol%, 0.0007 g), TBAI (0.5 mol%, 0.0011 g), 1p (0.6 mmol, 0.1441 g), [NO][BF₄] (2 equiv, 0.1402 g) in DCB (1.5 mL) at 80 °C for 24 h. 3p was obtained as pale yellow solid (122.9 mg, 76%; eluent: 10-30% ether/hexane then CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ: 8.39 (d, J = 8.7 Hz, 2H), 8.24 (d, J = 8.7 Hz, 2H), 7.77 (dd, J = 11.6 Hz, 9.0 Hz, 2H), 7.46 (t, J = 8.2 Hz, 2H), 7.37-7.34 (m, 1H), 3.96 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 165.8, 141.5, 138.7, 130.9, 130.6, 129.7, 126.74, 122.6, 119.2, 114.1, 52.4. HRMS (ESI): calcd for C₁₄H₁₁N₃O₃ [M+H]+: 270.0873, found 270.0872.

6-(Methoxycarbonyl)-2-phenyl-2H-benzo[d][1,2,3]triazole 1-oxide (3p’): The title compounds were prepared according to the general procedure. The reaction was carried out with Pd(OAc)₂ (0.5 mol%, 0.0007 g), TBAI (0.5 mol%, 0.0011 g), 1p (0.6 mmol, 0.1441 g), [NO][BF₄] (2 equiv, 0.1402 g) in DCB (1.5 mL) at 80 °C for 24 h. 3p’ was obtained as white solid (17.5 mg, 11%; eluent: 10-20% ether/hexane). ¹H NMR (400 MHz, CDCl₃) δ: 8.59 (s, 1H), 8.18 (d, J = 7.5 Hz, 2H), 8.07 (d, J = 9.1 Hz, 1H), 7.80 (d, J = 9.1 Hz, 1H), 7.62-7.55 (m, 3H), 3.98 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 165.8, 142.2, 135.1, 130.3, 129.3, 129.0, 128.0, 126.3, 123.4, 119.1, 117.8, 52.6. HRMS (ESI): calcd for C₁₄H₁₁N₃O₃
2-(4-Nitrophenyl)-2H-benzo[d][1,2,3]triazole 1-oxide (3q): The title compounds were prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1q (0.2 mmol, 0.0454 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in nitrobenzene (1.5 mL) at 100 °C for 24 h. 3q was obtained as yellow solid (44.3 mg, 86%; eluent: 10-30% ether/hexane then CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.61 (d, $J$ = 9.2 Hz, 2H), 8.45 (d, $J$ = 9.2 Hz, 2H), 7.78 (t, $J$ = 8.7 Hz, 2H), 7.52-7.48 (m, 1H), 7.41-7.37 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 147.4, 141.9, 139.9, 130.2, 127.2, 126.9, 124.7, 123.1, 119.3, 114.1. HRMS (ESI): calcd for C$_{12}$H$_8$N$_4$O$_3$ [M+H]$^+$: 257.0669, found 257.0668.

6-Nitro-2-phenyl-2H-benzo[d][1,2,3]triazole 1-oxide (3q’): The title compounds were prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1q (0.2 mmol, 0.0454 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in nitrobenzene (1.5 mL) at 100 °C for 24 h. 3q’ was obtained as yellow solid (3.5 mg, 7%; eluent: 10-20% ether/hexane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.85 (d, $J$ = 2.0 Hz, 1H), 8.28 (dd, $J$ = 9.5 Hz, 2.1 Hz, 1H), 8.21-8.19 (m, 2H), 7.91 (d, $J$ = 9.5 Hz, 1H), 7.64-7.61 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 145.4, 141.8, 134.9, 130.8, 129.5, 125.4, 123.4, 120.5, 113.0. HRMS (ESI): calcd for C$_{12}$H$_8$N$_4$O$_3$ [M+H]$^+$: 257.0669, found 257.0668.

5-Methoxy-2-(4-(methoxycarbonyl)phenyl)-2H-benzo[d][1,2,3]triazole 1-oxide (3r): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1r (0.2 mmol, 0.0541 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.5 mL) at 90 °C for 48 h. 3r was obtained pale yellow solid (40.6 mg, 68%; eluent: 1:2:5 ether/CH$_2$Cl$_2$/hexane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.34 (d, $J$ = 8.5 Hz, 2H), 8.20 (d, $J$ = 8.5 Hz, 2H), 7.62 (d, $J$ = 9.4 Hz, 1H), 6.99 (d, $J$ = 9.4 Hz, 1H), 6.87 (s, 1H), 3.94 (s, 3H), 3.88 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.9, 161.0, 142.6, 138.8, 130.5, 130.3, 123.0, 122.5, 122.1, 114.7, 95.0, 55.7, 52.4. HRMS (ESI): calcd for C$_{15}$H$_{13}$N$_3$O$_4$ [M+H]$^+$: 300.0979, found 300.0977.

2-(4-Benzoylphenyl)-5-methoxy-2H-benzo[d][1,2,3]triazole 1-oxide (3s): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3
mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1s (0.2 mmol, 0.0633 g), [NO][BF₄] (3 equiv, 0.0701 g) in DCB (1.5 mL) at 90 °C for 48 h. 3s was obtained as white solid (50.0 mg, 72%; eluent: 1:2:5 ether/CH₂Cl₂/hexane). ¹H NMR (400 MHz, CDCl₃) δ: 8.38 (d, J = 8.7 Hz, 2H), 7.98 (d, J = 8.7 Hz, 2H), 7.83-7.81 (m, 2H), 7.65-7.59 (m, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.01 (dd, J = 9.4 Hz, 2.1 Hz, 1H), 6.89 (d, J = 1.9 Hz, 1H), 3.89 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 195.2, 161.0, 142.6, 138.2, 137.6, 137.0, 132.7, 130.9, 130.0, 128.4, 123.0, 122.5, 122.1, 114.7, 95.0, 55.7. HRMS (ESI): calcd for C₂₀H₁₅N₃O₃ [M+H]⁺: 346.1186, found 346.1186.

4-Methyl-2-phenyl-2H-benzo[d][1,2,3]triazole 1-oxide (3t): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)₂ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1t (0.2 mmol, 0.0392 g), [NO][BF₄] (3 equiv, 0.0701 g) in DCB (1.5 mL) at 90 °C for 48 h. 3t was obtained orange oil (31.0 mg, 69%; eluent: 10%-30% ether/hexane). ¹H NMR (400 MHz, CDCl₃) δ: 8.18 (d, J = 8.1 Hz, 2H), 7.62 (dd, J = 16.0 Hz, 8.5 Hz, 3H), 7.55 (d, J = 7.4 Hz, 1H), 7.31-7.20 (m, 2H), 2.66 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 141.4, 135.3, 129.8, 129.7, 129.2, 128.0, 126.6, 126.4, 123.7, 111.2, 15.8. HRMS (ESI): calcd for C₁₃H₁₁N₃O [M+H]⁺: 226.0975, found 226.0974.

4-Methyl-2-(2,3,4,5,6-pentadeuterophenyl)-2H-benzo[d][1,2,3]triazole 1-oxide (3u): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)₂ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1u (0.2 mmol, 0.0402 g), [NO][BF₄] (3 equiv, 0.0701 g) in DCB (1.5 mL) at 90 °C for 48 h. 3u was obtained as orange oil (30.0 mg, 65%; eluent: 10%-30% ether/hexane). ¹H NMR (400 MHz, CDCl₃) δ: 7.65 (d, J = 8.5 Hz, 1H), 7.29-7.26 (m, 1H), 7.23-7.21 (m, 1H), 2.67 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 141.5, 135.2, 129.7, 129.3 (t, J = 25.2 Hz), 128.7 (t, J = 24.8 Hz), 128.0, 126.6, 126.4, 123.3 (t, J = 25.3 Hz), 111.2, 15.8. HRMS (ESI): calcd for C₁₃H₆D₅N₃O [M+H]⁺: 231.1289, found 231.1288.

2-(4-Fluorophenyl)-4-methyl-2H-benzo[d][1,2,3]triazole 1-oxide (3v): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)₂ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1v (0.2 mmol, 0.0428 g), [NO][BF₄] (3 equiv, 0.0701 g) in DCB (1.0 mL) and nitrobenzene (0.5 mL). 3v was obtained as
orange solid (29.9 mg, 62%; eluent: 1:1:8 ether/CH$_2$Cl$_2$/hexane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.21 (dd, $J = 8.5$ Hz, 4.8 Hz, 2H), 7.63 (d, $J = 8.5$ Hz, 1H), 7.32-7.22 (m, 4H), 2.66 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 162.9 (d, $J = 251.4$ Hz), 141.5, 131.4 (d, $J = 3.1$), 129.7, 128.2, 126.8, 126.3, 125.9 (d, $J = 8.9$ Hz, 2H), 116.3 (d, $J = 23.3$ Hz), 111.2, 15.8. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$: 109.6. HRMS (ESI): calcd for C$_{13}$H$_{10}$N$_3$OF [M+H]$^+$: 244.0881, found 244.0880.

2-(4-Chlorophenyl)-4-methyl-2H-benzo[d][1,2,3]triazole 1-oxide (3w): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1w (0.2 mmol, 0.0461 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.0 mL) and nitrobenzene (0.5 mL). 3w was obtained as orange solid (30.8 mg, 59%; eluent: 1:1:8 ether/CH$_2$Cl$_2$/hexane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.22 (d, $J = 8.8$ Hz, 2H), 7.62 (d, $J = 8.5$ Hz, 1H), 7.57 (d, $J = 8.8$ Hz, 2H), 7.27-7.23 (m, 2H), 2.66 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 141.6, 135.7, 133.9, 129.7, 129.4, 128.3, 126.8, 124.6, 111.2, 15.8. HRMS (ESI): calcd for C$_{13}$H$_{10}$N$_3$OCl [M+H]$^+$: 260.0585, found 260.0584.

2-(4-Bromophenyl)-4-methyl-2H-benzo[d][1,2,3]triazole 1-oxide (3x): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1x (0.2 mmol, 0.0550 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.0 mL) and nitrobenzene (0.5 mL). 3x was obtained as pale yellow solid (33.2 mg, 55%; eluent: 1:1.8 ether/CH$_2$Cl$_2$/hexane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.17-8.15 (m, 1H), 7.74-7.72 (m, 1H), 7.61 (d, $J = 8.5$ Hz, 1H), 7.29-7.21 (m, 2H), 2.65 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 141.6, 134.4, 132.3, 129.7, 128.3, 126.8, 124.6, 111.2, 15.8. HRMS (ESI): calcd for C$_{13}$H$_{10}$N$_3$OBr [M+H]$^+$: 304.0080, found 304.0079.

2-(4-(Methoxycarbonyl)phenyl)-4-methyl-2H-benzo[d][1,2,3]triazole 1-oxide (3y): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1y (0.2 mmol, 0.0508 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.5 mL). 3y was obtained as pale yellow solid (46.4 mg, 82%; eluent: 10-30% ether/hexane then CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.41 (d, $J = 8.5$ Hz, 2H), 8.26 (d, $J = 8.5$ Hz, 2H), 7.61 (d, $J = 8.5$ Hz, 1H), 7.28-7.25 (m, 1H), 7.22 (d, $J = 6.7$ Hz, 1H), 3.98 (s, 3H), 2.66 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.9, 141.8, 138.8, 130.7, 130.5, 129.8, 128.5, 127.0, 126.6, 122.7, 111.2, 52.4, 15.8. HRMS (ESI): calcd for C$_{13}$H$_{10}$N$_3$OCl [M+H]$^+$: 304.0080, found 304.0079.
C_{15}H_{13}N_{3}O_{3} [M+H]^+ : 284.1030, found 284.1028.

2-(4-Benzoylphenyl)-4-methyl-2H-benzo[d][1,2,3]triazole 1-oxide 1-oxide (3z): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1z (0.2 mmol, 0.0601 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.5 mL). 3z is obtained as pale yellow solid (54.7 mg, 83%; eluent: 1:1:3 ether/CH$_2$Cl$_2$/hexane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.45 (d, $J = 8.6$ Hz, 2H), 8.03 (d, $J = 8.6$ Hz, 2H), 7.87-7.84 (m, 2H), 7.63 (t, $J = 8.1$ Hz, 2H), 7.52 (t, $J = 7.7$ Hz, 2H), 7.30-7.22 (m, 2H), 2.67 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 195.2, 141.9, 138.2, 138.0, 137.0, 132.8, 130.9, 130.0, 129.8, 128.5, 128.4, 127.1, 126.6, 122.7, 111.2, 15.8. HRMS (ESI): calcd for C$_{20}$H$_{15}$N$_3$O$_2$ [M+H]$^+$: 330.1237, found 330.1234.

2-(4-Formylphenyl)-4-methyl-2H-benzo[d][1,2,3]triazole 1-oxide (3aa): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1aa (0.2 mmol, 0.0449 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.5 mL). 3aa was obtained as pale yellow solid (27.4 mg, 54%; eluent: 1:1:3 ether/CH$_2$Cl$_2$/hexane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 10.12 (s, 1H), 8.55 (d, $J = 8.5$ Hz, 2H), 8.11 (d, $J = 8.4$ Hz, 2H), 7.62 (d, $J = 8.5$ Hz, 1H), 7.30-7.22 (m, 2H), 2.66 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 190.8, 142.0, 139.7, 136.2, 130.5, 129.8, 128.6, 127.2, 111.2, 15.8. HRMS (ESI): calcd for C$_{14}$H$_{11}$N$_3$O$_2$ [M+H]$^+$: 254.0924, found 254.0923.

4-Chloro-2-phenyl-2H-benzo[d][1,2,3]triazole 1-oxide (3ab): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1ab (0.2 mmol, 0.0433 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.5 mL). 3ab was obtained as pale yellow solid (20.0 mg, 41%; eluent: 10%-30% ether/hexane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.17 (d, $J = 8.0$, 2H), 7.74 (d, $J = 8.7$, 1H), 7.62-7.53 (m, 3H), 7.48 (d, $J = 7.3$, 1H), 7.29-7.26 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 139.0, 135.0, 130.3, 129.3, 128.5, 127.5, 126.2, 124.6, 123.8, 112.9. HRMS (ESI): calcd for C$_{12}$H$_8$N$_3$OCl [M+H]$^+$: 246.0429, found 246.0428.
4-Chloro-2-(4-(methoxycarbonyl)phenyl)-2H-benzo[d][1,2,3]triazole 1-oxide (3ac): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1ac (0.2 mmol, 0.0548 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.0 mL) and nitrobenzene (0.5 mL). 3ac was obtained as pale yellow solid (37.0 mg, 61%; eluent: 1:3:96-1:3:60 ether/CH$_2$Cl$_2$/hexane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.41 (d, $J$ = 8.8 Hz, 2H), 8.27 (d, $J$ = 8.8 Hz, 2H), 7.73 (d, $J$ = 8.7 Hz, 1H), 7.51 (d, $J$ = 7.2 Hz, 1H), 7.31-7.27 (m, 1H), 3.99 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.7, 139.3, 138.3, 131.2, 130.6, 128.9, 127.7, 126.5, 124.6, 122.9, 112.8, 52.5. HRMS (ESI): calcd for C$_{14}$H$_{10}$N$_3$O$_3$Cl [M+H]$^+$: 304.0483, found 304.0483.

2-(2-Chlorophenyl)-6-(methoxycarbonyl)-2H-benzo[d][1,2,3]triazole 1-oxide (3ac'): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1ac (0.2 mmol, 0.0548 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.0 mL) and nitrobenzene (0.5 mL). 3ac' was obtained as pale yellow solid (4.9 mg, 8%; eluent: 1:3:100-1:3:10 ether/CH$_2$Cl$_2$/hexane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.62 (s, 1H), 8.09 (dd, $J$ = 9.2 Hz, 1.4 Hz, 1H), 7.82 (d, $J$ = 9.2 Hz, 1H), 7.69-7.66 (m, 1H), 7.64-7.61 (m, 2H), 7.55-7.53 (m, 1H), 3.99 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.7, 139.3, 138.3, 131.2, 130.6, 128.9, 127.7, 126.5, 124.6, 122.9, 112.8, 52.7. HRMS (ESI): calcd for C$_{14}$H$_{10}$N$_3$O$_3$Cl [M+H]$^+$: 304.0483, found 304.0482.

4-Bromo-2-(4-(methoxycarbonyl)phenyl)-2H-benzo[d][1,2,3]triazole 1-oxide (3ad): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1ad (0.2 mmol, 0.0638 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.0 mL) and nitrobenzene (0.5 mL). 3ad was obtained as pale yellow solid (51.9 mg, 74%; eluent: 1:3:96-1:3:60 ether/CH$_2$Cl$_2$/hexane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.38 (d, $J$ = 8.7 Hz, 2H), 8.25 (d, $J$ = 8.7 Hz, 2H), 7.76 (d, $J$ = 8.7 Hz, 1H), 7.68 (d, $J$ = 7.2 Hz, 1H), 7.24-7.20 (m, 1H), 3.97 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.7, 140.4, 138.3, 132.3, 131.2, 130.6, 127.4, 126.9, 122.9, 113.4, 112.7, 52.5. HRMS (ESI): calcd for C$_{14}$H$_{10}$N$_3$O$_3$Br [M+H]$^+$: 347.9978, found 347.9977.
2-(2-Bromophenyl)-6-(methoxycarbonyl)-2H-benzo[d][1,2,3]triazole 1-oxide (3ad’): The title compound was prepared according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1ad (0.2 mmol, 0.0638 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.0 mL) and nitrobenzene (0.5 mL). 3ad’ was obtained as pale yellow solid (6.7 mg, 10%; eluent: 1:3:10 ether/CH$_2$Cl$_2$/hexane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.62 (s, 1H), 8.09 (dd, $J = 9.2$ Hz, 1.4 Hz, 1H), 7.84 (t, $J = 7.8$ Hz, 2H), 7.60-7.56 (m, 3H), 3.99 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.7, 142.9, 134.0, 133.9, 133.2, 130.0, 129.1, 128.5, 128.2, 124.8, 122.2, 119.5, 118.0, 52.7. HRMS (ESI): calcd for C$_{14}$H$_{10}$N$_3$O$_3$Br [M+H]$^+$: 347.9978, found 347.9977.

2-(3,5-Dimethylphenyl)-2H-benzo[d][1,2,3]triazole 1-oxide (3ae): The title compound was prepared as an inseparable mixture of 3ae and 3ae’ according to the general procedure. The reaction was carried out with Pd(OAc)$_2$ (3 mol%, 0.0014 g), TBAI (3 mol%, 0.0022 g), TsOH (6 mol%, 0.0021 g), 1ae (0.2 mmol, 0.0421 g), [NO][BF$_4$] (3 equiv, 0.0701 g) in DCB (1.5 mL). The mixture of 3ae and 3ae’ was obtained as light yellow oil (29.4 mg, mixture of 3ae and 3ae’, 3ae : 3ae’ = 18.5, eluent: 10-30% ether/hexane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.81-7.76 (m, 2H), 7.74 (s, 2H), 7.46-7.42 (m, 1H), 7.34 (t, $J = 7.7$ Hz, 1H), 7.15 (s, 1H), 2.42 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 140.9, 139.1, 135.0, 131.7, 129.0, 126.5, 126.2, 121.3, 119.0, 114.0, 21.3. HRMS (ESI): calcd for C$_{14}$H$_{13}$N$_3$O [M+H]$^+$: 240.1131, found 240.1131.

**Computational Section**

**Computational methods.** All geometry optimizations were carried out with the hybrid density functional theory (DFT) at the level of M06$^{12}$ using DZP basis sets. Here, the DZP stands for a basis set that employs 6-31G(d) all-electron basis set$^{13}$ for H, C, N, and O atoms, and the corresponding basis sets with the Stuttgart/Dresden effective-core potential (SDD)$^{14-16}$ for the palladium and iodine atoms. Analytical frequencies were calculated to confirm the correctness of the structure of either a local minimum or a transition state (TS). The solvation effects were considered using the IEF-PCM model$^{17}$ with 1,2-dichlorobenzene as the model solvent. A step size of 0.1 amu$^{1/2}$ bohr was used in the IRC (intrinsic reaction coordinate) procedure$^{18}$ to check the connectivity between a transition state and the reactant as well as the product.

The optimized structures are then adopted to calculate the free energies at the level of M06 functional$^{12}$ with TZP basis sets. Here TZP stands for a basis set that employs a 6-311++G(2d,2p) all-electron basis set$^{19}$ for the main group elements (6-311G(d) for iodine atom)$^{20}$ and the corresponding basis sets with the Stuttgart/Dresden effective-core potential (SDD)$^{14-16}$ for the
palladium atom. The free energy at M06/TZP level in solution phase was calculated according to
Eq. 1:²¹-²³

\[
G_{\text{soln}}^{\text{M06/TZP}} = E_{\text{gas}}^{\text{M06/TZP}} + \Delta G_{\text{thermo(soln)}}^{\text{M06/DZP}} + \Delta G_{\text{solv}} + RT \ln \left( \frac{RT}{P} \right)
\]  \hspace{1cm} (1)

The first term in the right-hand side is the electronic energy computed at M06/TZP level in gas
phase. The second term is the thermal correction to the free energy of the solute in the solution
phase at M06/DZP level. The third term is the solvation free energy. The last term denotes the free
energy correction from the gas-phase standard state (1 atm) to the solution phase standard state of
1 M. It should be noted that the solvation free energy \( \Delta G_{\text{solv}} \) was obtained by using SMD model²⁴
at the level of B3LYP/6-31G(d) to make it consistent with the specific methods used in the
development of such solvation model.²¹-²³ All calculations were carried out using the Gaussian 09
program.²⁵

Supplementary Figure 15. Computed free energy changes for [BF₄]⁻ and azobenezene 1a
coordinate to the unoccupied axial site of (a) Pd(III)-Pd(III) intermediate LM1, and (b)
Pd(II)-Pd(IV) intermediate LM1’. As shown, all of the considered coordination steps are
endothermic. It is worthy to note the distances between Pd center and azobenezene 1a are too long
for an effective chemical interaction. We suggest the steric repulsion between the axial
azobenezene 1a and equatorial ligands hinders the coordination.
Supplementary Figure 16. Optimized structures for (a) acetate-bridged bipalladium species 5a and LM1, and (b) iodide-bridged bipalladium species 4a and LM1'. LM1 could be considered as a Pd(III)-Pd(III) species with a direct chemical interaction between the two palladium atoms. However, LM1’ should be a Pd(II)-Pd(IV) species without the direct Pd-Pd interaction.

X-ray Crystallographic Analysis

Supplementary Table 12. Crystal data and structure refinement for 3a (CCDC 1428672)

| Identification code | Compound-1 |
|---------------------|------------|
| Empirical formula   | C12 H9 N3 O |
| Formula weight      | 211.22     |
| Temperature         | 100(2) K   |
| Wavelength          | 1.54184 Å  |
| Crystal system      | Monoclinic |
Space group Cc
Unit cell dimensions a = 6.4226(2) Å \( \alpha = 90^\circ \).
b = 23.1159(8) Å \( \beta = 107.696(4)^\circ \).
c = 6.9516(3) Å \( \gamma = 90^\circ \).

Volume 983.23(7) Å³
Z 4
Density (calculated) 1.427 Mg/m³
Absorption coefficient 0.776 mm⁻¹
F(000) 440
Crystal size 0.320 x 0.220 x 0.080 mm³
Theta range for data collection 3.824 to 72.787°.
Index ranges -6 ≤ h ≤ 7, -27 ≤ k ≤ 27, -7 ≤ l ≤ 8
Reflections collected 1658
Independent reflections 1119 \[ R(int) = 0.0124 \]
Completeness to theta = 67.684° 99.7 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 1.00000 and 0.76102
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 1119 / 2 / 146
Goodness-of-fit on F² 1.092
Final R indices [I>2sigma(I)] R1 = 0.0243, wR2 = 0.0633
R indices (all data) R1 = 0.0248, wR2 = 0.0638
Absolute structure parameter 0.0(3)
Extinction coefficient 0.0049(6)
Largest diff. peak and hole 0.226 and -0.126 e.Å⁻³

Supplementary Table 13. Crystal data and structure refinement for complex 4a (CCDC 1858247)

Identification code complex 4a
| Property                              | Value                                      |
|--------------------------------------|--------------------------------------------|
| Empirical formula                    | C24 H18 I2 N4 Pd2                          |
| Formula weight                       | 829.02                                     |
| Temperature                          | 100(2) K                                  |
| Wavelength                           | 1.54178 Å                                 |
| Crystal system                       | Triclinic                                  |
| Space group                          | P-1                                        |
| Unit cell dimensions                 | a = 4.18530(10) Å, b = 10.9291(3) Å, c = 13.2771(3) Å |
|                                     | α = 110.318(2)°, β = 90.072(2)°, γ = 96.088(2)° |
| Volume                               | 565.84(2) Å³                              |
| Z                                    | 1                                          |
| Density                              | 2.433 Mg/m³                                |
| Absorption coefficient               | 34.402 mm⁻¹                                |
| F(000)                               | 388                                        |
| Crystal size                         | 0.18 x 0.05 x 0.02 mm³                     |
| Theta range for data collection      | 3.55 to 69.95°                             |
| Index ranges                         | -5<=h<=4, -13<=k<=13, -16<=l<=16           |
| Reflections collected                | 19939                                      |
| Independent reflections              | 2125 [R(int) = 0.0430]                     |
| Completeness to theta = 69.95°       | 99.6 %                                     |
| Absorption correction                | Semi-empirical from equivalents           |
| Max. and min. transmission           | 0.5462 and 0.0629                          |
| Refinement method                    | Full-matrix least-squares on F²            |
| Data / restraints / parameters       | 2125 / 0 / 145                             |
| Goodness-of-fit on F²                | 1.079                                      |
| Final R indices [I>2sigma(I)]        | R1 = 0.0268, wR2 = 0.0678                  |
| R indices (all data)                 | R1 = 0.0289, wR2 = 0.0690                  |
| Largest diff. peak and hole          | 1.220 and -1.169 e.Å⁻³                    |
**Supplementary Table 14.** Crystal data and structure refinement for complex 4b (CCDC 1858251)

| Parameter                        | Value                                      |
|----------------------------------|--------------------------------------------|
| Identification code              | complex 4b                                 |
| Empirical formula                | C40 H50 I2 N4 Pd2                           |
| Formula weight                   | 1053.44                                    |
| Temperature                      | 100(2) K                                   |
| Wavelength                       | 1.54178 Å                                  |
| Crystal system                   | Triclinic                                  |
| Space group                      | P-1                                        |
| Unit cell dimensions             | a = 4.63200(10) Å, b = 13.8323(5) Å, c = 16.6380(6) Å |
|                                  | α = 65.897(2)°, β = 85.801(2)°, γ = 81.030(2)° |
| Volume                           | 961.12(5) Å³                               |
| Z                                | 1                                          |
| Density (calculated)             | 1.820 Mg/m³                                 |
| Absorption coefficient           | 20.405 mm⁻¹                                 |
| F(000)                           | 516                                        |
| Crystal size                     | 0.22 x 0.20 x 0.05 mm³                      |
| Theta range for data collection  | 3.53 to 69.99°                             |
| Index ranges                     | -5≤h≤3, -16≤k≤16, -19≤l≤20                  |
| Reflections collected            | 6474                                       |
| Independent reflections          | 3630 [R(int) = 0.0302]                     |
Completeness to theta = 69.99° 99.2 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.4285 and 0.0939
Refinement method Full-matrix least-squares on F^2
Data / restraints / parameters 3630 / 0 / 217
Goodness-of-fit on F^2 1.044
Final R indices [I>2sigma(I)]
R1 = 0.0387, wR2 = 0.1041
R indices (all data) R1 = 0.0394, wR2 = 0.1047
Largest diff. peak and hole 1.738 and -1.924 e.Å^-3

**Supplementary Table 15.** Crystal data and structure refinement for complex 5b (CCDC 1858266)

| Identification code | complex 5b |
|---------------------|------------|
| Empirical formula   | C44 H56 N4 O4 Pd2 |
| Formula weight      | 917.73 |
| Temperature         | 100(2) K |
| Wavelength          | 1.54184 Å |
| Crystal system      | Triclinic |
| Space group         | P-1 |
| Unit cell dimensions| a = 10.9439(3) Å  α = 85.362(2)°. |
|                     | b = 11.2900(3) Å  β = 75.755(2)°. |
|                     | c = 17.5270(5) Å  γ = 81.146(2)°. |
| Volume              | 2071.89(9) Å³ |
| Z                   | 2 |
| Density (calculated)| 1.471 Mg/m³ |
| Absorption coefficient| 7.365 mm⁻¹ |
| F(000)              | 944 |
| Crystal size        | 0.40 x 0.20 x 0.12 mm³ |
| Theta range for data collection | 3.97 to 70.00°. |
| Index ranges        | -13<=h<=13, -13<=k<=13, -21<=l<=21 |
| Reflections collected| 37130 |
Independent reflections 7858 [R(int) = 0.0382]
Completeness to theta = 70.00° 99.9 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.4719 and 0.1566
Refinement method Full-matrix least-squares on F^2
Data / restraints / parameters 7858 / 0 / 506
Goodness-of-fit on F^2 1.051
Final R indices [I>2sigma(I)] R1 = 0.0277, wR2 = 0.0756
R indices (all data) R1 = 0.0301, wR2 = 0.0772
Largest diff. peak and hole 0.634 and -0.942 e.Å^-3

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Supplementary Figure 17. $^1$H NMR spectra of 3a.

Supplementary Figure 18. $^{13}$C NMR spectra of 3a.
Supplementary Figure 19. $^1$H NMR spectra of 3b.

Supplementary Figure 20. $^{13}$C NMR spectra of 3b.
Supplementary Figure 21. $^1$H NMR spectra of 3c.

Supplementary Figure 22. $^{13}$C NMR spectra of 3c.
Supplementary Figure 23. $^1$H NMR spectra of 3d.

Supplementary Figure 24. $^{13}$C NMR spectra of 3d.
Supplementary Figure 25. $^1$H NMR spectra of 3e.

Supplementary Figure 26. $^{13}$C NMR spectra of 3e.
Supplementary Figure 27. $^1$H NMR spectra of 3f.

Supplementary Figure 28. $^{13}$C NMR spectra of 3f.
Supplementary Figure 29. $^{19}$F NMR spectra of $3f$.

Supplementary Figure 30. $^1$H NMR spectra of $3g$. 
Supplementary Figure 31. $^{13}$C NMR spectra of 3g.

Supplementary Figure 32. $^1$H NMR spectra of 3h.
Supplementary Figure 33. $^{13}$C NMR spectra of 3h.

Supplementary Figure 34. $^1$H NMR spectra of 3i.
Supplementary Figure 35. $^{13}\text{C}$ NMR spectra of 3i.

Supplementary Figure 36. $^1\text{H}$ NMR spectra of 3j.
Supplementary Figure 37. $^{13}$C NMR spectra of 3j.

Supplementary Figure 38. $^1$H NMR spectra of 3k.
Supplementary Figure 39. $^{13}$C NMR spectra of 3k.

Supplementary Figure 40. $^1$H NMR spectra of 3l.
Supplementary Figure 41. $^{13}$C NMR spectra of 3l.

Supplementary Figure 42. $^{19}$F NMR spectra of 3l.
Supplementary Figure 43. $^1$H NMR spectra of 31'.

Supplementary Figure 44. $^{13}$C NMR spectra of 31'.
Supplementary Figure 45. $^{19}$F NMR spectra of $3l'$.

Supplementary Figure 46. $^1$H NMR spectra of $3m$. 
Supplementary Figure 47. $^{13}$C NMR spectra of $3m$.

Supplementary Figure 48. $^{19}$F NMR spectra of $3m$. 
Supplementary Figure 49. $^1$H NMR spectra of $3m'$. 

Supplementary Figure 50. $^{13}$C NMR spectra of $3m'$. 
Supplementary Figure 51. $^{19}$F NMR spectra of 3m'.

Supplementary Figure 52. $^1$H NMR spectra of 3n.
Supplementary Figure 53. $^{13}$C NMR spectra of 3n.

Supplementary Figure 54. $^{19}$F NMR spectra of 3n.
Supplementary Figure 55. $^1$H NMR spectra of 3o.

Supplementary Figure 56. $^{13}$C NMR spectra of 3o.
Supplementary Figure 57. $^1$H NMR spectra of 3o'.

Supplementary Figure 58. $^{13}$C NMR spectra of 3o'.
Supplementary Figure 59. $^1$H NMR spectra of 3p.

Supplementary Figure 60. $^{13}$C NMR spectra of 3p.
Supplementary Figure 61. $^1$H NMR spectra of 3p’.

Supplementary Figure 62. $^{13}$C NMR spectra of 3p’.
Supplementary Figure 63. $^1$H NMR spectra of 3q.

Supplementary Figure 64. $^{13}$C NMR spectra of 3q.
Supplementary Figure 65. $^1$H NMR spectra of 3q$^\prime$.

Supplementary Figure 66. $^{13}$C NMR spectra of 3q$^\prime$. 
Supplementary Figure 67. $^1$H NMR spectra of 3r.

Supplementary Figure 68. $^{13}$C NMR spectra of 3r.
Supplementary Figure 69. $^1$H NMR spectra of 3s.

Supplementary Figure 70. $^{13}$C NMR spectra of 3s.
Supplementary Figure 71. $^1$H NMR spectra of 3t.

Supplementary Figure 72. $^{13}$C NMR spectra of 3t.
Supplementary Figure 73. $^1$H NMR spectra of 3u.

Supplementary Figure 74. $^{13}$C NMR spectra of 3u.
Supplementary Figure 75. $^1$H NMR spectra of $3v$.

Supplementary Figure 76. $^{13}$C NMR spectra of $3v$. 
Supplementary Figure 77. $^{19}$F NMR spectra of 3v.

Supplementary Figure 78. $^1$H NMR spectra of 3w.
Supplementary Figure 79. $^{13}$C NMR spectra of 3w.

Supplementary Figure 80. $^1$H NMR spectra of 3x.
Supplementary Figure 81. $^{13}$C NMR spectra of 3x.

Supplementary Figure 82. $^1$H NMR spectra of 3y.
Supplementary Figure 83. $^{13}$C NMR spectra of 3y.

Supplementary Figure 84. $^1$H NMR spectra of 3z.
Supplementary Figure 85. $^{13}$C NMR spectra of 3z.

Supplementary Figure 86. $^1$H NMR spectra of 3aa.
Supplementary Figure 87. $^{13}$C NMR spectra of 3aa.

Supplementary Figure 88. $^1$H NMR spectra of 3ab.
Supplementary Figure 89. $^{13}$C NMR spectra of 3ab.

Supplementary Figure 90. $^1$H NMR spectra of 3ac.
Supplementary Figure 91. $^{13}$C NMR spectra of 3ac.

Supplementary Figure 92. $^1$H NMR spectra of 3ac'. 
Supplementary Figure 93. $^{13}$C NMR spectra of 3ac'.

Supplementary Figure 94. $^1$H NMR spectra of 3ad.
Supplementary Figure 95. $^{13}$C NMR spectra of 3ad.

Supplementary Figure 96. $^1$H NMR spectra of 3ad'.
Supplementary Figure 97. $^{13}$C NMR spectra of 3ad$^\dagger$.

Supplementary Figure 98. $^1$H NMR spectra of 3ae.
Supplementary Figure 99. $^{13}$C NMR spectra of 3ae.

Supplementary Figure 100. $^1$H NMR spectra of 4b.
Supplementary Figure 101. $^{13}$C NMR spectra of 4b.

Supplementary Figure 102. $^1$H NMR spectra of 5b.
Supplementary Figure 103. $^{13}$C NMR spectra of 5b.