Electronic Supplementary Information (ESI) for Environmental Science: Nano.

Ligand Directed Debromination of Tetrabromodiphenyl Ether Mediated by Nickel under Visible Irradiation

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Product analysis

2,2',4,4'-tetrabromodiphenyl ether (BDE47) was analyzed by Agilent HPLC 1260 system with DAD detector and a DIKMA C-18 column (250×3mm). The mobile phase was 10% H_2O and 90% CH_3CN (v/v%) at 0.2 $mL\cdot min^{-1}$. The retention time of BDE47 was 28.16 min.

The debromination products of BDE47 were analyzed by Agilent GC7890 gas chromatograph with a DB-5 column (15 m×320 μm×0.25 μm) and an μ-ECD detector. The column temperature was held at 100 °C for 2 min. Then column temperature was increased to 230 °C at 15 $°C\cdot min^{-1}$ and then to 270 °C at 5 $°C\cdot min^{-1}$. The temperature of injector was 300 °C, and the temperature of detector was 325 °C. The flow rate of argon carrier gas was 2.9 $mL\cdot min^{-1}$. The retention time of BDE47 was 11.423 min, the retention time of 2,4,4'-tribromodiphenyl ether (BDE28) was 9.988 min, the retention time of 2,2',4-tribromodiphenyl ether (BDE17) was 9.801 min, the retention time of 4,4'-dibromodiphenyl ether (BDE15) was 8.552 min, the retention time of 2,4'-dibromodiphenyl ether (BDE8) was 8.298 min, the retention time of 2,2'-bromodiphenyl ether (BDE4) or 2,4-bromodiphenyl ether (BDE7) was 8.128 min, the retention time of 4-bromodiphenyl ether (BDE3) was 6.47 min, and the retention time of 2-bromodiphenyl ether (BDE1) was 6.26 min.

Diphenyl ether (DE) was analyzed by an Agilent 7890 GC with an Agilent DB-VRX column (20 m×180 μm×1 μm) and a flame ionization detector (FID). The column temperature was held at 40 °C, keeping for 3 min. Then column temperature was increased to 160 °C at 10 °C·min^{-1} and kept at this temperature for 3 min. Then column temperature was increased to 200 °C at 10 °C·min^{-1}. The temperature of injector was 200 °C, and the temperature of detector was 325 °C. The flow rate of the nitrogen carrier gas was 5 mL·min^{-1}. The retention time of DE was 20.056 min.

4'-Bromoacetophenone was analyzed by an Agilent HPLC 1260 system with a Dikma Diamonsil C-18 column (250×2.1 mm, 3-μm film thickness). The mobile phase was 60% water and 40% acetonitrile (v/v%) at 0.2 mL·min^{-1}.

The concentration of Br^- was quantified by ion chromatography (DX-900) with an IonPac AS23 column. The eluent was 15 mM KOH aqueous solution at a flow rate of 0.7 mL·min^{-1}.

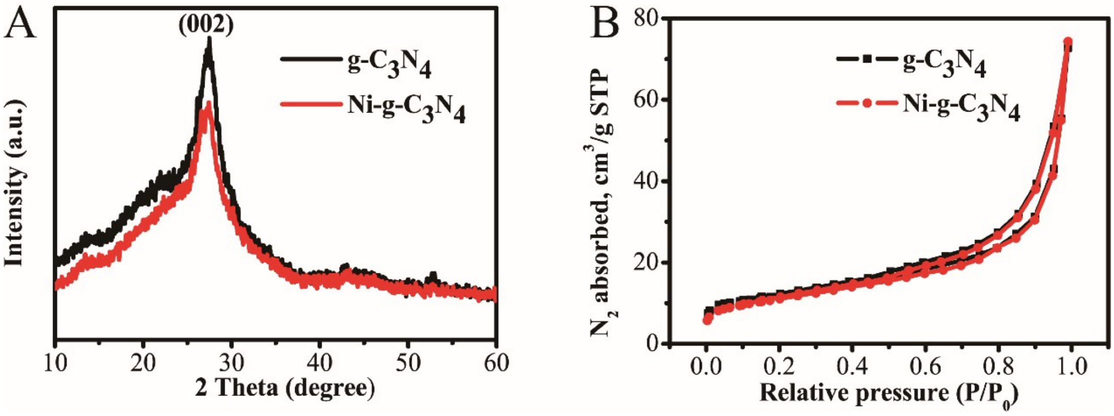


Fig. S1. (A) XRD patterns of g-C_3N_4 and Ni-g-C_3N_4. (B) N_2 adsorption/desorption isotherms of g-C_3N_4 and Ni-g-C_3N_4.

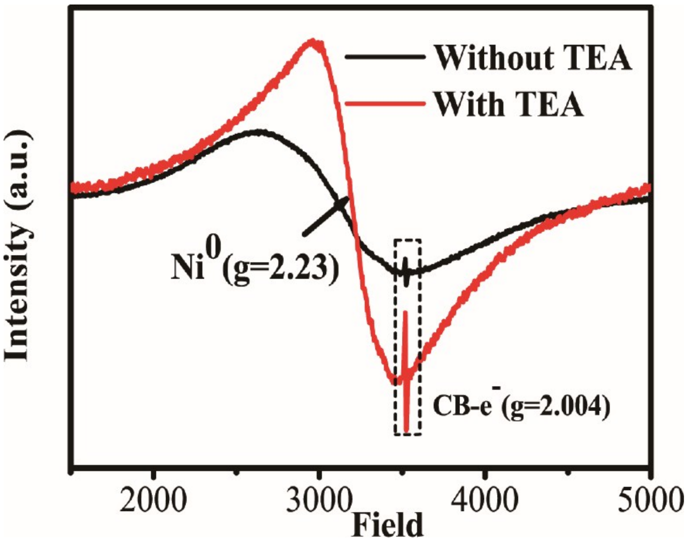


Fig. S2. Electron paramagnetic resonance (EPR) spectra of reaction suspension in methanol containing 2 g·L^{-1} g-C_3N_4 with 2 wt.% of $NiCl_2$ after 4 hours of irradiation in the absence or presence of trimethylamine (TEA).

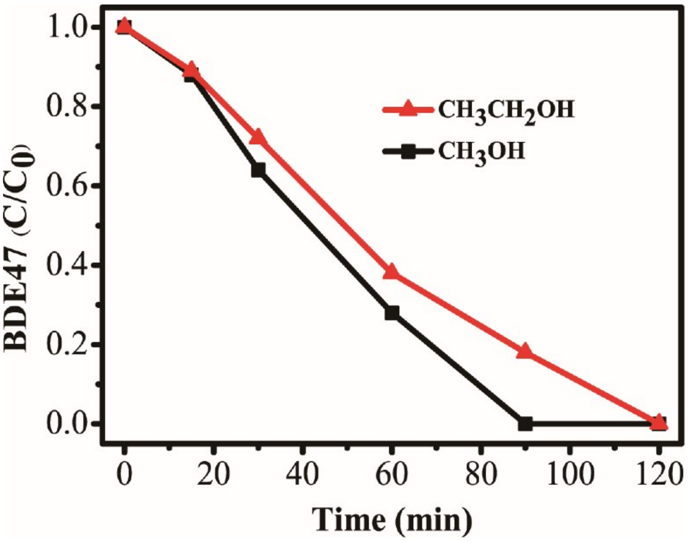


Fig. S3. Degradation of BDE47 catalyzed by *in-situ* formed Ni on g-C_3N_4 in the mixture of methanol and TEA (v/v=19:1) or the mixture of ethanol and TEA (v/v=19:1).

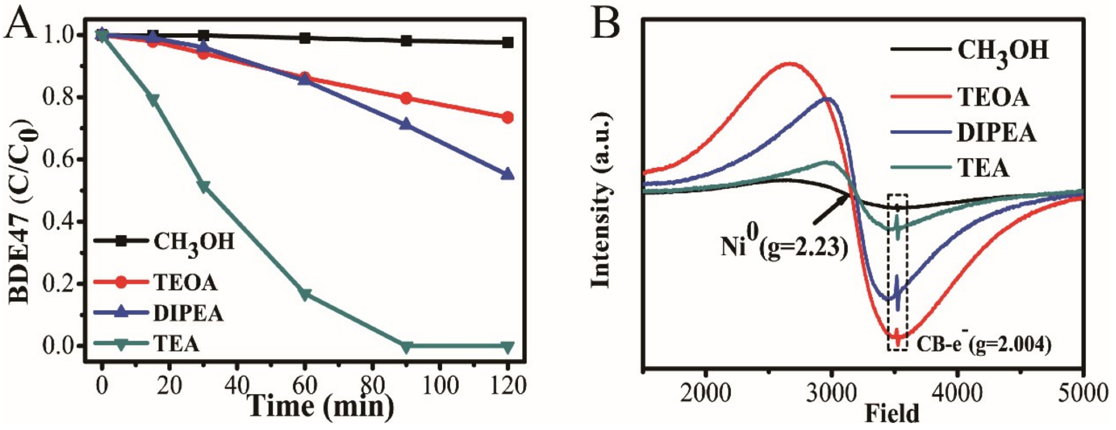


Fig. S4. (A) Degradation of BDE47 catalyzed by *in-situ* formed Ni on g-C_3N_4 with different sacrificial reagents. (B) Electron paramagnetic resonance (EPR) spectra of reaction suspension in methanol containing 2 g·L^{-1} g-C_3N_4 with 2 wt.% of $NiCl_2$ after 4 hours of irradiation with different sacrificial reagents.

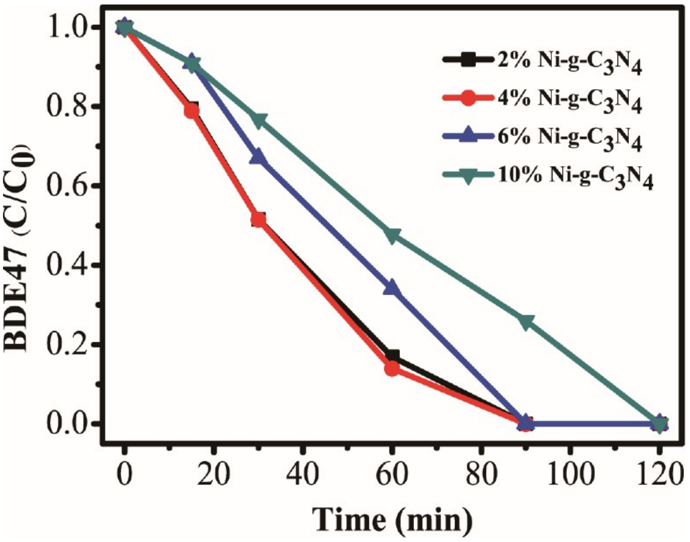


Fig. S5. Degradation of BDE47 in a suspension of g-C_3N_4 with 2 to 10wt.% of $NiCl_2$. Irradiation was provided by a 300 W Xe lamp with a 420 nm long pass filter. All experiments were conducted under Ar at 298K in a methanol/TEA mixture with 2 g·L^{-1} catalyst.

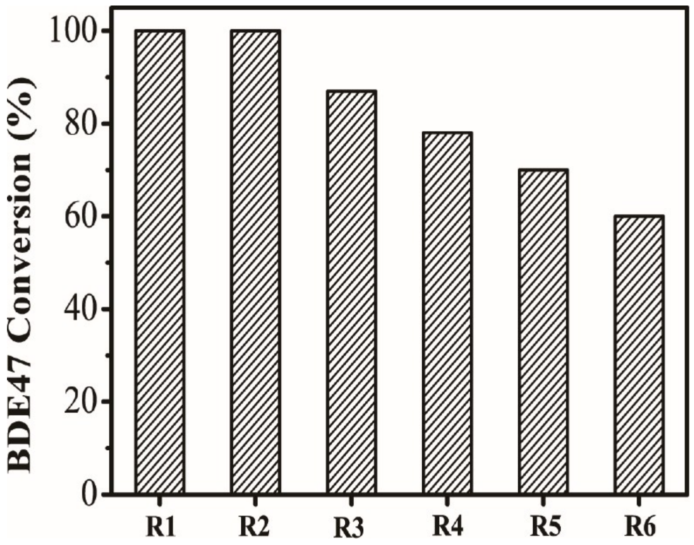


Fig. S6. Conversion of 10 μM BDE47 at 2 hours in three consecutive reactions by adding fresh BDE47 stock solution.

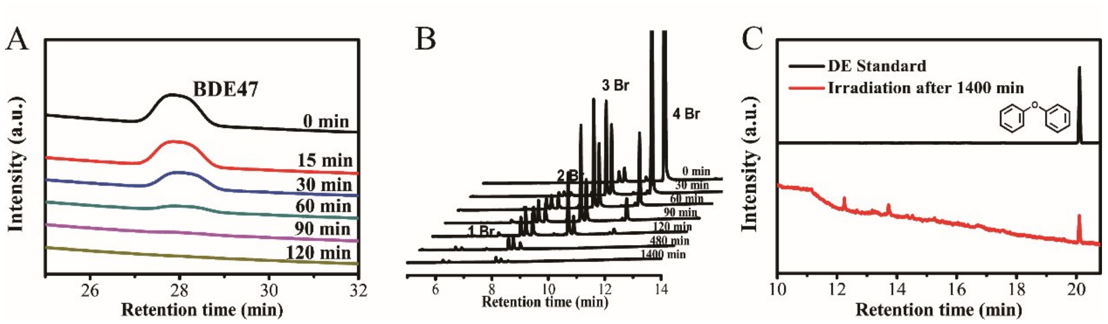


Fig. S7. (A) HPLC chromatograms of BDE47. (B) GC-μECD chromatograms of the debrominated products at various irradiation time. (C) Generation of DE detected by GC after 1400 min irradiation catalyzed by Ni-g-C_3N_4.

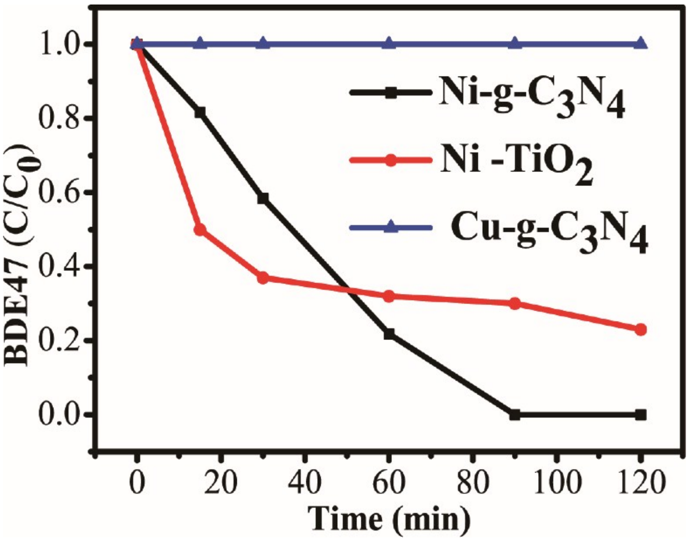


Fig. S8. Degradation of BDE47 catalyzed by Ni-g-C_3N_4, Cu-g-C_3N_4 (> 420 nm irradiation), and Ni-TiO_2 (> 360 nm irradiation) in methanol/TEA mixture.

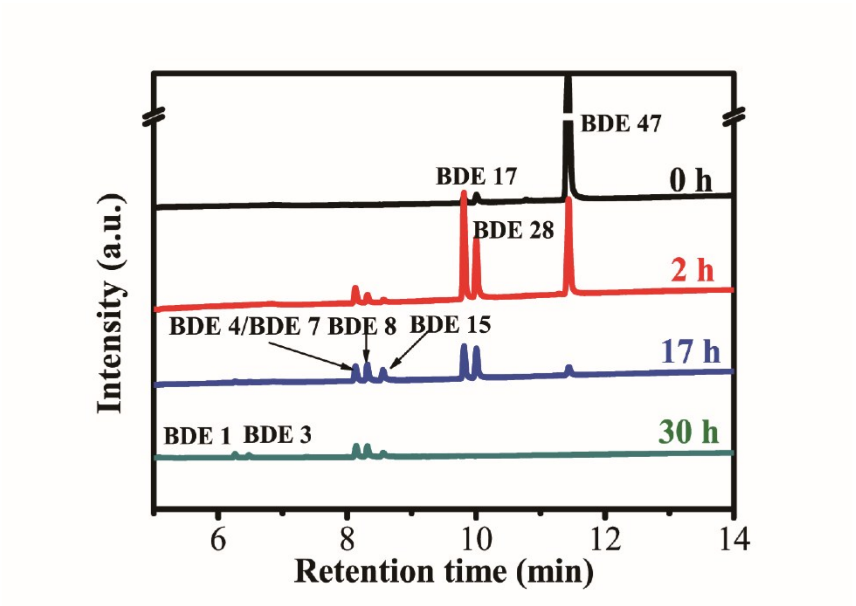


Fig. S9. GC-μECD chromatograms of the debrominated products of BDE47 catalyzed by Ni-TiO_2 at various irradiation time.

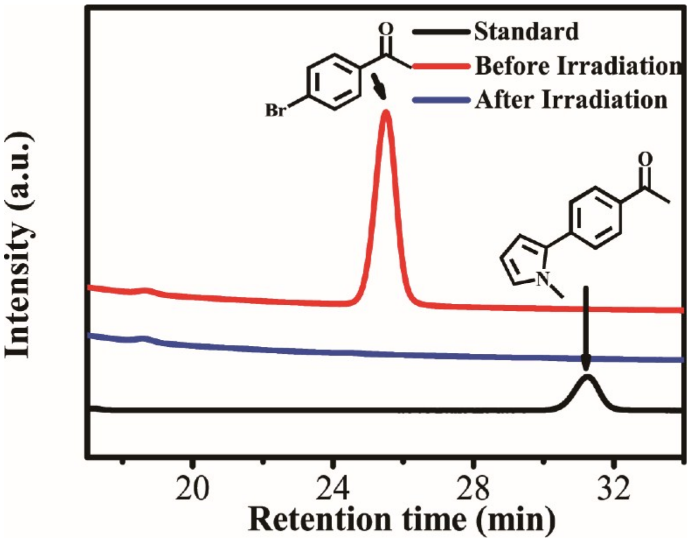
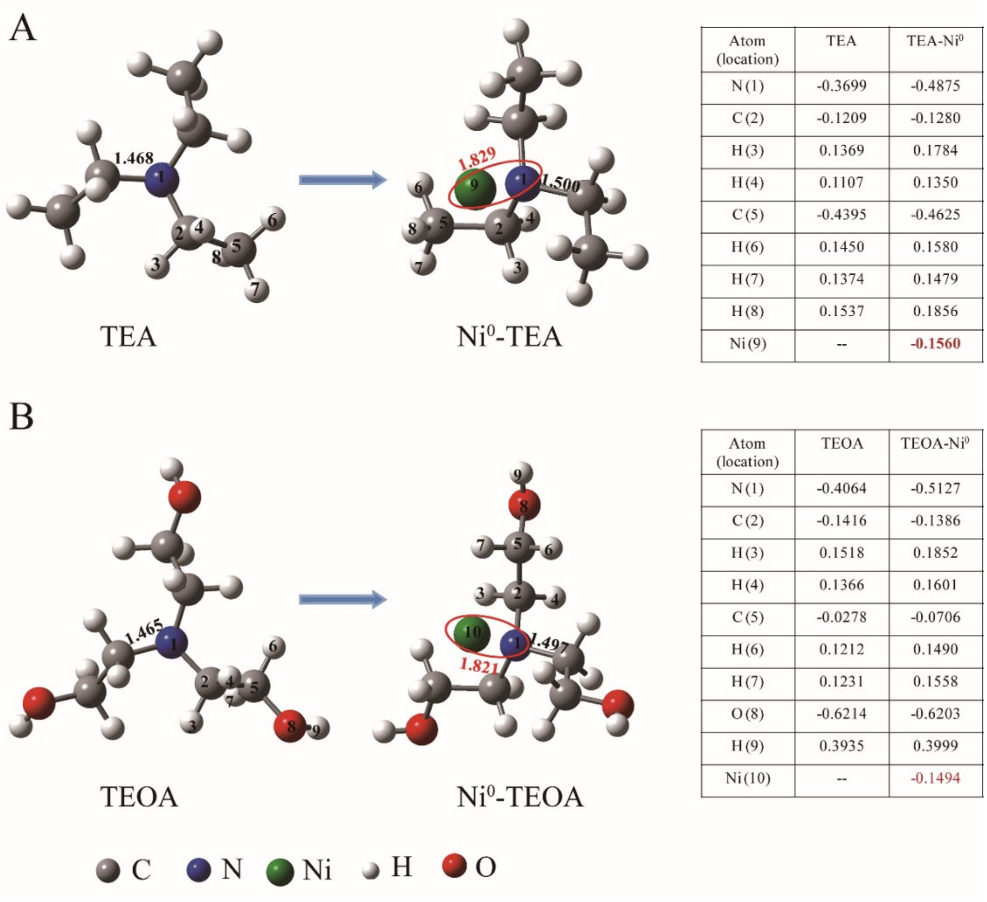


Fig. S10. HPLC chromatograms of product during debromination of 4'-bromoacetophenone with N-methylpyrrole as the aryl radical scavenger.



Atom (location)	TEA	TEA-Ni^0
N (1)	-0.3699	-0.4875
C (2)	-0.1209	-0.1280
H (3)	0.1369	0.1784
H (4)	0.1107	0.1350
C (5)	-0.4395	-0.4625
H (6)	0.1450	0.1580
H (7)	0.1374	0.1479
H (8)	0.1537	0.1856
Ni (9)	--	**-0.1560**

Atom (location)	TEOA	TEOA-Ni^0
N (1)	-0.4064	-0.5127
C (2)	-0.1416	-0.1386
H (3)	0.1518	0.1852
H (4)	0.1366	0.1601
C (5)	-0.0278	-0.0706
H (6)	0.1212	0.1490
H (7)	0.1231	0.1558
O (8)	-0.6214	-0.6203
H (9)	0.3935	0.3999
Ni (10)	--	-0.1494

Fig. S11. Calculated charge distributions of TEA and TEOA with or without the coordinated Ni^0 atom. The distance between Ni and N and the C-N bond lengths was indicated in the modeled configurations. Charge distributions was calculated by B3LYP/6-31G(d), Gaussian 09 Program.[1]

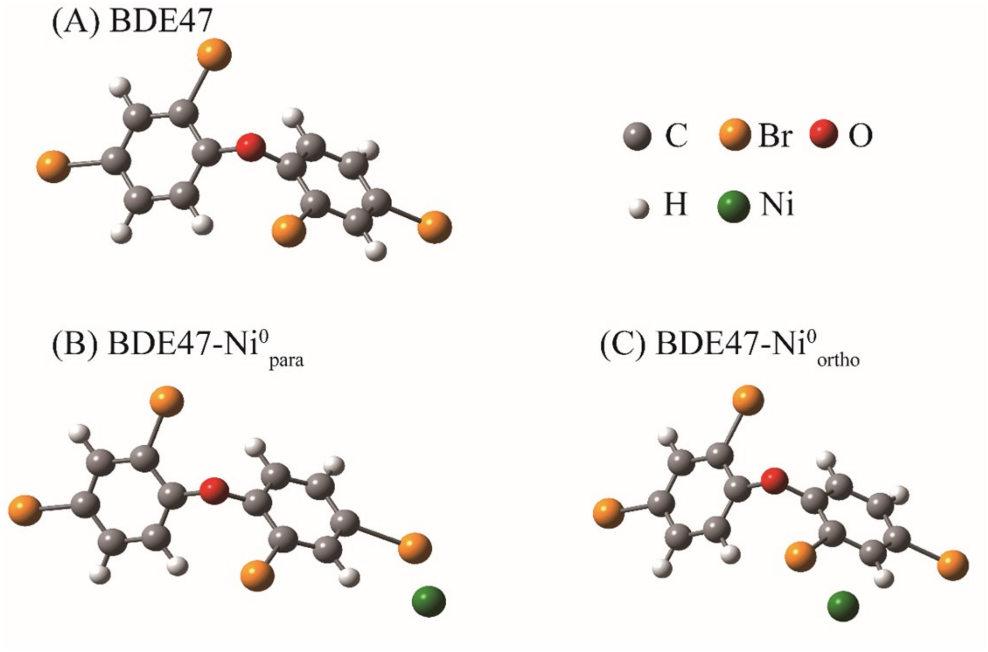


Fig. S12. Ball-and-stick models: (A) BDE47; Ni^0 next to (B) *para*-Br of BDE47 and (C) *ortho*-Br of BDE47.

Table S1. Concentration of Br$^-$ in debromination of BDE47 under different reaction conditions

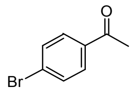
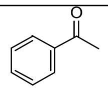
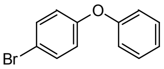
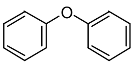
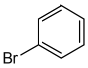
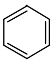
Irradiation	Time (h)	C [Br$^-$] (M)
>420 nm	1.5	1.8× 10^{-5}
>420 nm	23	3.2 × 10^{-5}
>360 nm[a]	24	3.9 × 10^{-5}

Reaction conditions: CH_3OH (19 mL), TEA (1 mL), BDE47 (10^{-5} M), catalyst (40 mg), Ar, under visible-light irradiation (> 420 nm) or ultraviolet light irradiation (> 360 nm).

[a]Yield of diphenyl ether at 16 h was 50% but decreased to 42.5% after 24 h of

irradiation. There might be pathways (e.g., carbon oxygen bond cleavage[2]) for DE decomposition under UV irradiation.

Table S2. Hydrodebromination of selected substrates catalyzed by Ni-g-C_3N_4.

Entry	Substrate	Product	Time (h)	yield (%)
1[a]			3	98%
2[b]			24	85%
3[a]			24	43%

Reaction conditions: CH_3OH (19 mL), TEA (1 mL), substrates ([a]100 μM, [b]10 μM), catalyst (40 mg), Ar, under visible-light irradiation (> 420 nm, 300 mW·cm^{-2})

Table S3. Amount of consumed BDE47 and generated H_2 at different time during irradiation with (A) TEA or (B) TEOA as the electron/hydrogen donor.

(A)

Time (min)	Conversion %	n1(BDE47) (μmol)	n2(H_2) (μmol)
0	0	0	0
30	44.8	0.09	0.08
60	84.5	0.17	0.20
90	100	0.20	0.33
120	100	0.20	0.42

(B)

Time (min)	Conversion %	n1(BDE47) (μmol)	n2(H_2) (μmol)
0	0	0	0
30	5.62	0.01	0.36
60	9.54	0.012	0.92
90	13.5	0.02	1.42
120	16.2	0.03	1.89

Table S4. Bond lengths of C-Br bonds in BDE47 obtained by DFT calculation shown in Fig. S12.

Adsorption state of BDE47	Bond length (Å)			
	Ortho-position		*Para*-position	
	$C\text{-}Br_2$	$C\text{-}Br_2'$	$C\text{-}Br_4$	$C\text{-}Br_4'$
Free	1.902	1.902	1.908	1.908
$Ni^0\text{-}Br_{para}$	1.901	1.902	1.990	1.908
$Ni^0\text{-}Br_{ortho}$	1.989	1.902	1.908	1.908

References

(1) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb. etc., Gaussian 09, Revision B.01, Gaussian, Inc.: Wallingford, CT, **2009**.

(2) M. Guo, J. Peng, Q. Yang and C. Li, Highly active and selective RuPd bimetallic NPs for the cleavage of the diphenyl ether C–O bond, *ACS. Catal.*, 2018, **8**, 11174-11183.