Visible-Light-Induced Intermolecular Atom-Transfer Radical Addition of Benzyl Halides to Olefins: Facile Synthesis of Tetrahydroquinolines

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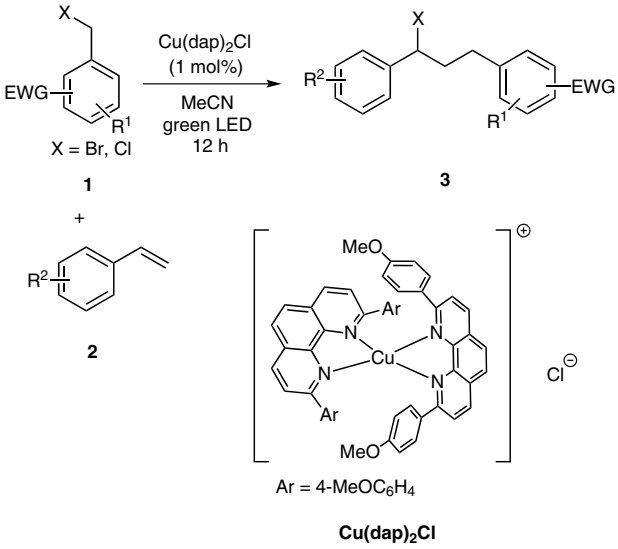
Abstract: $Cu(dap)_2Cl$ has been utilized as a visible-light photoredox catalyst for the atom-transfer radical addition (ATRA) of benzyl halides to styrenes and silyl enol ethers. The resulting ATRA products can be readily converted into tetrahydroquinolines.

Key words: visible-light photocatalysis, atom-transfer radical addition, benzyl halide, tetrahydroquinoline

The atom-transfer radical addition (ATRA) or Kharasch addition[1] of organic halides to olefins is a versatile tool for organic synthesis since it results in the formation of C–C and C–X bonds simultaneously. Commonly used initiators for ATRA reactions include peroxides,[1] triethylboron,[2] or organotin[3] reagents, which are not optimal with respect to operational safety, sensitivity, and environmental impact. Alternatively, transition-metal complexes of copper,[4] ruthenium,[5] iron,[6] or nickel[7] can be employed, nevertheless, the high catalyst loading necessary to achieve good yields leaves room for improvement. One solution to this problem has been proposed by adding reducing agents to regenerate the catalysts;[8] however, the reaction conditions necessary are generally quite harsh.

Visible-light-driven photocatalysis has been recognized as a versatile tool for a growing number of organic transformations.[9] Stephenson et al. reported intermolecular ATRA reactions between perhaloalkanes or α-halocarbonyl compounds and olefins using oxidative or reductive quenching of photoredoxcatalysts based on ruthenium and iridium complexes.[10,11] Likewise, our group recently succeeded in the use of $Cu(dap)_2Cl$ [dap = 2,9-bis(*p*-anisyl)-1,10-phenanthroline; Sauvage's catalyst][12] as visible-light photocatalyst for the same process utilizing the oxidative quenching pathway.[13] $Cu(dap)_2Cl$ is a stronger reductant ($^*Cu^+/Cu^{2+} = -1.43$ V) than commonly used photocatalysts $Ru(bpy)_3Cl_2$ or $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$ no matter if the latter are utilized in the oxidative ($^*Ru^{2+}/Ru^{3+} = -0.86$ V; $^*Ir^{3+}/Ir^{4+} = -0.89$ V) or reductive quenching pathway ($Ru^+/Ru^{2+} = -1.33$ V; $Ir^{2+}/Ir^{3+} = -1.21$ V). Thus, $^*Cu(dap)_2Cl$ can reduce substrates more effectively in the oxidative than $Ru(bpy)_3Cl_2$ or $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$ in the reductive quenching pathway with the additional advantage that no sacrificial electron donor has to be employed, making it an attractive alternative to ruthenium or iridium catalysts beside the economic advantage for visible-light-mediated ATRA reactions.[13] In this contribution, we demonstrate that also benzyl halides can be efficiently coupled with alkenes in ATRA reactions under visible-light catalysis (Scheme 1), offering a facile method for the synthesis of tetrahydroquinolines.



Scheme 1 Intermolecular atom-transfer radical addition of benzyl halides to styrenes

The activation of benzyl halides under visible-light photoredox conditions has only been shown in a few cases. Sauvage et al. demonstrated the dimerization of *p*-nitrobenzyl bromide under irradiation ($\lambda \geq 350$ nm) in the presence of triethylamine as an electron donor and $Cu(dap)_2Cl$,[12] while MacMillan developed the α-benzylation of aldehydes using *fac*-$Ir(ppy)_3$ (ppy = 2-phenylpyridine) as photoredox catalyst.[14] ATRA reactions of benzyl halides to alkenes under visible-light photoredox conditions are to the best of our knowledge not known, and only recently was it disclosed that under UV irradiation in the presence of Cu(II) complexes and AIBN this reaction proceeds, albeit only in low yields (0–35%).[15]

As a model system we investigated the ATRA between *p*-nitrobenzyl bromide (**1a**) and styrene (**2a**, Table 1). Employing 1 mol% of $Cu(dap)_2Cl$ and irradiating with a green light emitting diode (LED; $\lambda_{max} = 530$ nm) the desired ATRA product **3a** was smoothly obtained.

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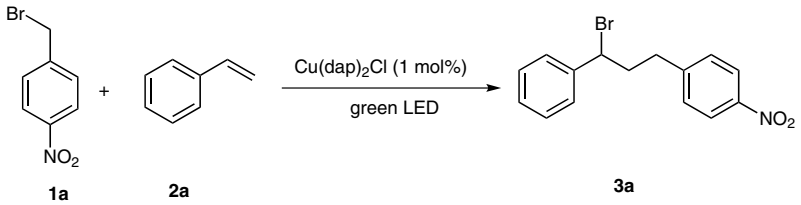
Table 1 ATRA Reaction between *p*-Nitrobenzyl Bromide and Styrene: Optimization of Reaction Conditions



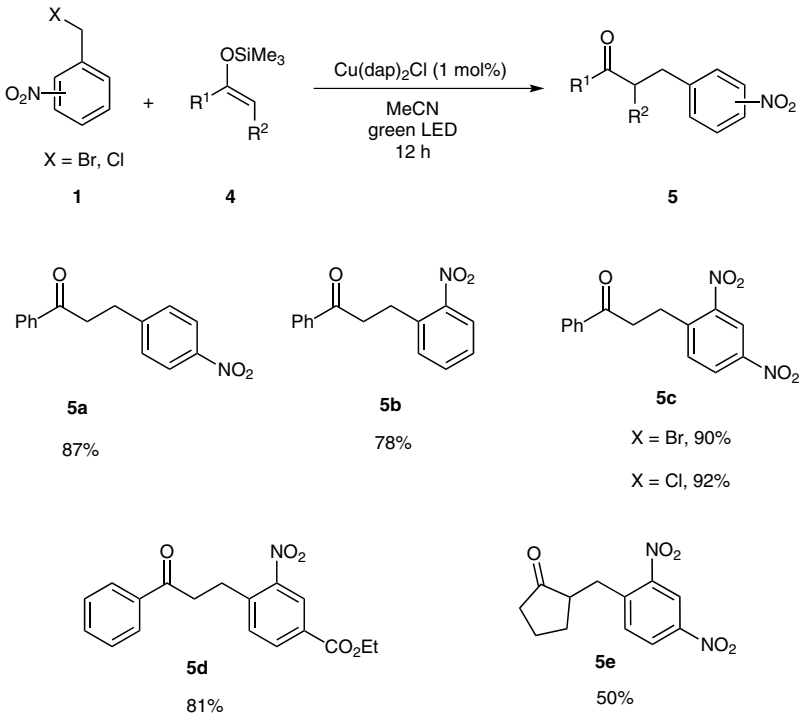
1a **2a** **3a**

Entry	Conditions	Yield (%)[a]
1	$Cu(dap)_2Cl$ (1 mol%), styrene (10 equiv), CH_2Cl_2, 530 nm, 24 h	60
2	$Cu(dap)_2Cl$ (1 mol%), styrene (10 equiv), MeCN, 530 nm, 24 h	85
3	$Cu(dap)_2Cl$ (1 mol%), styrene (5 equiv), MeCN, 530 nm, 12 h	85
4	$[Ir(ppy)_2(dtbbpy)](PF_6)$ (1 mol%), styrene (5 equiv), MeCN, 455 nm, 12 h	85
5	$Ru(bpy)_3Cl_2$ (1 mol%), styrene (5 equiv), MeCN, 455 nm, 12 h	69
6	no photocatalyst, 530 nm light, 24 h	no reaction
7	with $Cu(dap)_2Cl$, no light, 24 h	no reaction

[a] Isolated yield after purification on silica gel.

While the reaction was incomplete in dichloromethane as solvent after 24 hours, in acetonitrile full conversion was achieved already in 12 hours, allowing the isolation of **3a** in 85% yield (Table 1, entries 1–3). Styrene was initially employed in excess (5–10 equiv), but this amount can be reduced to 2 equivalents with equally good results (Table 2). $[Ir(ppy)_2(dtbbpy)](PF_6)$[16] (dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl, Table 1, entry 4) was also found to be a competent photocatalyst for this transformation with similar yield, but considering the economical advantage of Cu over Ir (cost per mol Cu/Ir = 1:10000) we decided to go forward with the former. $Ru(bpy)_3Cl_2$ was less efficient to give 69% of the desired product under otherwise identical reaction conditions (Table 1, entry 5). Control experiments established that both a photocatalyst as well as light are necessary for the reaction to proceed (Table 1, entries 6, 7).

Having established the optimum reaction conditions the scope of this ATRA reaction was evaluated (Table 2). Electron-poor benzyl bromides or chlorides are required



1 **4** **5**

5a 87%

5b 78%

5c X = Br, 90%; X = Cl, 92%

5d 81%

5e 50%

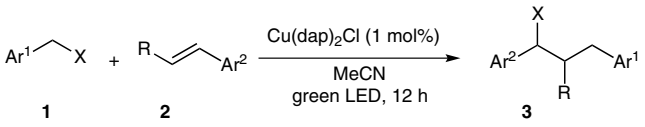
Scheme 2 ATRA reaction of benzyl halides with silyl enol ethers

calling for heteroarenes such as 4-quinolinyl (Table 2, entry 19) or nitro substitution in the phenyl ring of the benzyl moiety (entries 1–18). 2,4-Dinitrobenzyl chloride resulted in moderate yield when coupled with styrene (Table 2, entry 16), but gave excellent yields with substituted styrenes (Table 2, entries 17, 18). Attempts to use 4-cyano (entry 20), 4-trifluoromethylbenzyl bromide (entry 21) or benzyl bromide itself (entry 22) as reaction partner resulted in complete recovery of the starting material, being probably due to the high reduction potential of electroneutral or partially electron-deficient benzylic system to undergo the initial C–Br bond cleavage step ($E_{1/2} = -1.85$ V vs SCE for benzyl bromide in MeCN).[17]

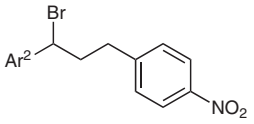
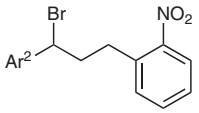
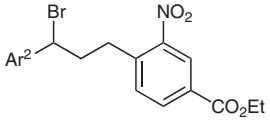
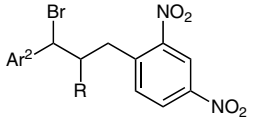
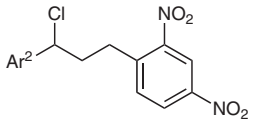
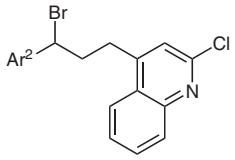
On the side of the alkenes, besides various styrenes, 2-vinylnaphthalene (Table 2, entries 4, 14) and 4-vinylbiphenyl (Table 2, entries 8, 15) proved to be good substrates for the title transformation.

Halide substitution at *para* (entries 2, 6, 12) or *meta* position is tolerated well (entries 3, 7, 13, 17), showing no cross reactivity with the benzyl halide. Methyl substitution in β-position of the styrene was possible, although a drop in the yield is observed (entry 11), while methyl substitution in α-position was not feasible, resulting besides the expected ATRA product in additional side products stemming from HBr elimination.

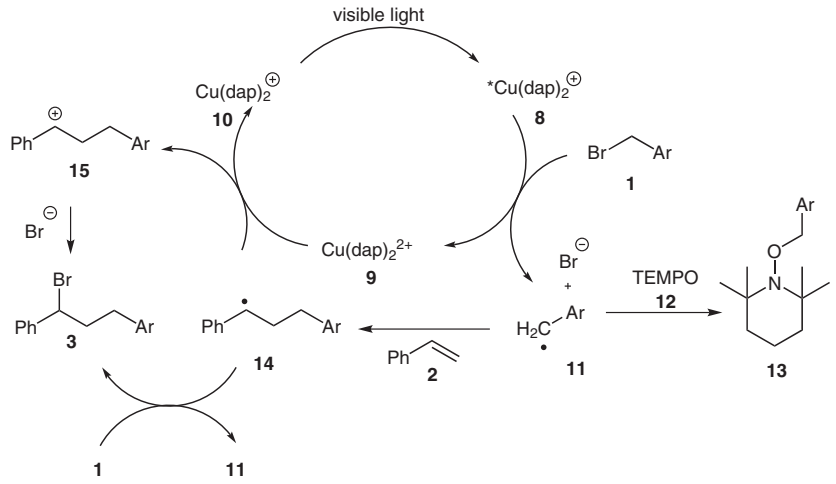
Table 2 Substrate Scope of the ATRA Reaction between Nitrobenzyl Halides and Styrenes[a]



1 **2** **3**

Entry	Ar^1	X	Product	Ar^2	Yield (%)[b]
1	4-$O_2NC_6H_4$	Br		Ph (**3a**)	85[c]
2				4-BrC_6H_4 (**3b**)	90
3				3-ClC_6H_4 (**3c**)	87 (84)[c]
4				2-naphthyl (**3d**)	85 (83)[c]
5	2-$O_2NC_6H_4$	Br		Ph (**3e**)	91 (80)[d]
6				4-BrC_6H_4 (**3f**)	87
7				3-ClC_6H_4 (**3g**)	80 (79)[c]
8				biphenyl (**3h**)	82
9	4-EtO_2C-2-$O_2NC_6H_3$	Br		Ph (**3i**)	70
10	2,4-$(O_2N)_2C_6H_3$	Br		Ph (**3j**, R = H)	89
11				Ph (**3k**, R = Me)	35[c,e,f]
12				4-BrC_6H_4 (**3l**, R = H)	86
13				3-ClC_6H_4 (**3m**, R = H)	95
14				2-naphthyl (**3n**, R = H)	81
15				biphenyl (**3o**, R = H)	90
16	2,4-$(O_2N)_2C_6H_3$	Cl		Ph (**3p**)	51
17				3-ClC_6H_4 (**3q**)	92
18				4-MeC_6H_4 (**3r**)	93
19	4-quinolinyl	Br		2-naphthyl (**3s**)	66
20	4-NCC_6H_4	Br		Ph	no reaction
21	4-$F_3CC_6H_4$	Br		Ph	no reaction
22	Ph	Br		Ph	no reaction

[a] Benzyl halide (0.2 mmol, 1 equiv), styrene (2-5 equiv), $Cu(dap)_2Cl$ (1 mol%) in degassed MeCN (1.0 mL), external irradiation at 530 nm for 12 h.
[b] Yield of isolated product.
[c] Benzyl bromide: 1 mmol.
[d] Benzyl bromide (2 mmol) with 0.5 mol% of catalyst loading.
[e] Internal irradiation at 60 °C for 20 h (see experimental section for details).
[f] Combined yield of two diastereoisomers (dr = 1.3:1).

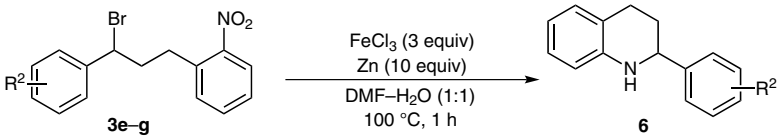


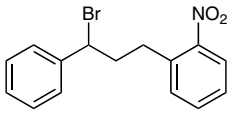
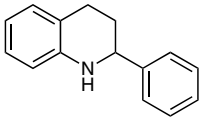
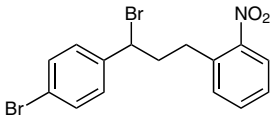
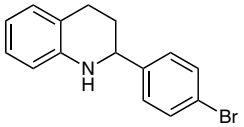
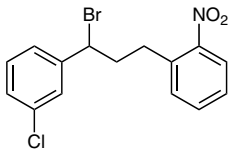
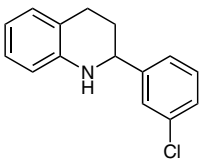
Scheme 3 Mechanistic discussion

Silyl enol ethers **4** also proved to be valuable coupling partners for the benzyl halides, affording the corresponding ketones **5** (Scheme 2). Excellent results were obtained when **4** contained an aromatic substituent (products **5a**–**d**), but also the silyl enol ether derived from cyclopentanone gave the ATRA product **5e** in acceptable yield. $Cu(dap)_2Cl$ was necessary for those transformations irrespective of the solvent used, contrasting the trifluoromethylation of enolsilanes with trifluoromethyl iodide that was recently reported to proceed by visible-light irradiation only when carried out in DMF.[18]

The product formation is consistent with an oxidative quenching cycle of the copper catalyst (Scheme 3). Excited $*Cu(dap)_2^+$ (**8**) is transformed to its Cu^{+2} state **9** by transferring an electron to the benzyl halide **1**, thus generating a benzyl radical **11**, which adds to the alkene **2** to give radical intermediate **14**. Product **3** can be formed by two possible pathways: through carbocation **15**, which is generated by a back electron transfer from **14** to $Cu(dap)_2^{+2}$ (**9**) (radical polar crossover), thus closing the catalytic cycle and regenerating the catalyst. This mechanistic proposal calls for the reaction of two components, **9**

Table 3 Application of ATRA Products to the Synthesis of Tetrahydroquinolines



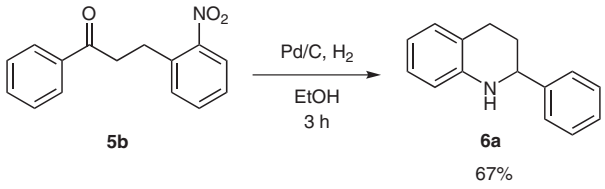
Starting material	Product	Yield (%)[a]
 **3e**	 **6a**	75
 **3f**	 **6b**	72
 **3g**	 **6c**	70

[a] Yield of isolated product.

and **14**, that are present only in low concentrations. Alternatively, a chain process can be initiated through electron transfer from **14** to **1**, which regenerates **11** (radical propagation). While both mechanistic pathways are viable, Stephenson et al. have elegantly shown that radical-polar crossover must clearly play a significant role in photoredox induced ATRA processes.[10] When the ATRA reaction was carried out in the presence of 2,2,6,6-tetramethylpiperidinoxyl (**12**, TEMPO), adduct **13** was detected by mass spectrometry, which supports the overall radical mechanism by either pathway of the process reported here (see Supporting Information for more details).

The ATRA products derived from *o*-nitrobenzyl bromide are valuable precursors for the synthesis of tetrahydroquinolines. Treatment of **3e–g** with $FeCl_3$/Zn in DMF–H_2O (1:1)[19] under reflux conditions smoothly resulted in the reduction of the nitro to the amino functionality with concurrent cyclization to 2-substituted tetrahydroquinolines **6** (Table 3).

Alternatively, **5** can be subjected to a catalytic hydrogenation with palladium/carbon,[20] to give tetrahydroquinolines **6** as exemplified for the transformation of **5b** to **6a** (Scheme 4).



Scheme 4

In conclusion, we have successfully developed the so far elusive visible-light-mediated ATRA between different electron deficient benzyl halides and styrenes or silyl enol ethers, applying $Cu(dap)_2Cl$ as an economic and highly efficient photoredox catalyst. The ATRA products derived from *o*-nitrobenzyl halides can be directly converted into 2-substituted tetrahydroquinolines.

All reactions were performed using common dry, inert atmosphere techniques. Reactions were monitored by TLC and visualized by a dual short/long wave UV lamp and stained with an ethanolic solution of vanillin. Column flash chromatography was performed using 230–400 mesh silica gel. NMR spectra were recorded on 300 MHz spectrometer. Chemical shifts for ^{1}H NMR were reported as δ (parts per million) relative to the signal of $CDCl_3$ at 7.26 ppm. Chemical shifts for ^{13}C NMR were reported as δ (parts per million) relative to the center line signal of the $CDCl_3$ triplet at 77 ppm. Proton and carbon assignments were established using spectral data of similar compounds. Standard abbreviations were used to denote signal multiplicities. Some of the ATRA products (**3a**, **3d**, **3e**, **3h**, **3j**, **3l**, **3m**, **3n**, **3o**) were unstable under mass spectrometric analysis. So HRMS of the corresponding methoxides has been obtained by converting the ATRA bromides into methoxides.

Photoredox Catalysis of ATRA Reaction; General Procedure A (GP-A)

An oven dried 10 mL vial equipped with a plastic septum and magnetic stir bar was charged with $Cu(dap)_2Cl$ (1 mol%) and the corresponding benzyl halide (1.0 equiv). The flask was purged with a stream of N_2 and MeCN (1.0 mL) was added. The resultant mixture was degassed for 5 min by N_2 sparging and the respective styrene (2–5 equiv) or silyl enol ether (3 equiv) was added to the vial. The vial was placed at a distance of 0.5–1.0 cm from a green LED lamp (530 nm) and stirred for 12 h. After the completion of the reaction (monitored by TLC), the mixture was directly concentrated in vacuo. The residue was purified by chromatography on silica gel, using hexane–EtOAc as the solvent system.

Bromide to Methoxide Transformation; General Procedure B (GP-B)

Since some of the ATRA products did not give molecular ion peaks in the MS analysis, they were converted into their corresponding methoxides for analytical purposes: The purified bromide (0.10 mmol) was dissolved in MeOH (1 mL) and refluxed at 60 °C for 2 h. After completion of the reaction (monitored by TLC), MeOH was removed in vacuo. The residue was purified by chromatography on silica gel, using hexane–EtOAc as the solvent system to afford the methoxides **3′** corresponding to the ATRA products **3**.

Tetrahydroquinolines;[19] General Procedure C (GP-C)

In a round-bottomed flask, $FeCl_3 \cdot 6H_2O$ (3 equiv) and Zn dust (10 equiv) were added to the ATRA product (0.46 mmol) in 1:1 DMF and H_2O (2.5 mL). The mixture was heated for 1 h in an oil bath at 100 °C. After completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was diluted with H_2O (5 mL) and basified with sat. aq Na_2CO_3. It was then extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried (Na_2SO_4), the solvent was removed in vacuo, and the residue was subjected to column chromatography on silica gel, using hexane–EtOAc as solvent system to obtain the pure product.

1-(3-Bromo-3-phenylpropyl)-4-nitrobenzene (3a)

According to general procedure GP-A, 4-nitrobenzyl bromide (0.216 g, 1.00 mmol, 1 equiv), $Cu(dap)_2Cl$ (8.8 mg, 1 mol%), and styrene (0.520 g, 5.00 mmol, 5 equiv) afforded **3a** (0.272 g, 85%) as a colorless liquid after column purification on silica gel; R_f = 0.45 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20–8.11 (m, 2 H), 7.42–7.27 (m, 7 H), 4.87 (dd, *J* = 8.6, 6.1 Hz, 1 H), 2.95 (ddd, *J* = 14.4, 9.1, 5.7 Hz, 1 H), 2.88–2.74 (m, 1 H), 2.71–2.55 (m, 1 H), 2.51–2.37 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.27, 146.67, 141.42, 129.38, 128.90, 128.69, 127.23, 123.85, 53.96, 40.79, 34.20.

MS (EI, 70 eV): *m*/*z* = 319 $[M]^+$, 275.1, 239.2, 44.1.

1-(3-Methoxy-3-phenylpropyl)-4-nitrobenzene (3a′)

General procedure GP-B afforded **3a′** (0.025 g, 74%) as a colorless liquid after column purification on silica gel; R_f = 0.53 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.16–8.10 (m, 2 H), 7.40–7.22 (m, 7 H), 4.07 (dd, *J* = 8.1, 5.1 Hz, 1 H), 3.22 (s, 3 H), 2.91–2.70 (m, 2 H), 2.21–2.05 (m, 1 H), 2.02–1.87 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.99, 141.59, 129.94, 129.26, 128.56, 127.84, 126.61, 123.67, 82.74, 56.68, 39.24, 32.01.

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{17}NO_3$ $[M]^+$: 271.1208; found: 271.1207.

1-[3-Bromo-3-(4-bromopropyl)propyl]-4-nitrobenzene (3b)

According to general procedure GP-A, 4-nitrobenzyl bromide (0.050 g, 0.23 mmol, 1 equiv), $Cu(dap)_2Cl$ (2 mg, 1 mol%), and 4-bromostyrene (0.126 g, 0.69 mmol, 3 equiv) afforded **3b** (0.082 g, 90%) as a colorless oil after column purification on silica gel; R_f = 0.45 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.21–8.13 (m, 2 H), 7.52–7.44 (m, 2 H), 7.38–7.29 (m, 2 H), 7.29–7.20 (m, 2 H), 4.80 (dd, *J* = 8.7, 6.1 Hz, 1 H), 2.94 (ddd, *J* = 14.4, 9.0, 5.7 Hz, 1 H), 2.87–2.75 (m, 1 H), 2.67–2.52 (m, 1 H), 2.47–2.31 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.96, 146.73, 140.48, 132.07, 129.36, 128.90, 123.91, 122.56, 52.67, 40.65, 34.09.

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{13}Br_2NO_2$ $[M]^+$: 396.9313; found: 396.9310.

1-[3-Bromo-3-(3-chlorophenyl)propyl]-4-nitrobenzene (3c)
According to general procedure GP-A, 4-nitrobenzyl bromide (0.216 g, 1.00 mmol, 1 equiv), $Cu(dap)_2Cl$ (8.8 mg, 1 mol%), and 3-chlorostyrene (0.415 g, 3.00 mmol, 3 equiv) afforded **3c** (0.298 g, 84%) as a colorless oil after column purification on silica gel; R_f = 0.30 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.21–8.11 (m, 2 H), 7.40–7.31 (m, 3 H), 7.31–7.19 (m, 3 H), 4.79 (dd, *J* = 8.8, 5.9 Hz, 1 H), 3.03–2.89 (m, 1 H), 2.88–2.75 (m, 1 H), 2.67–2.48 (m, 1 H), 2.48–2.29 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.93, 146.74, 143.38, 134.63, 130.17, 129.36, 128.82, 127.45, 125.44, 123.90, 52.44, 40.63, 34.08.

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{13}BrClNO_2$ $[M]^+$: 352.9818; found: 352.9817.

2-[1-Bromo-3-(4-nitrophenyl)propyl]naphthalene (3d)
According to general procedure GP-A, 4-nitrobenzyl bromide (0.216 g, 1.00 mmol, 1 equiv), $Cu(dap)_2Cl$ (8.8 mg, 1 mol%), and 2-vinylnapthalene (0.308 g, 2.00 mmol, 2 equiv) afforded **3d** (0.307 g, 83%) as a colorless liquid after column purification on silica gel; R_f = 0.30 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20–8.12 (m, 2 H), 7.90–7.73 (m, 4 H), 7.58–7.47 (m, 3 H), 7.35 (d, *J* = 8.7 Hz, 2 H), 5.05 (dd, *J* = 8.1, 6.5 Hz, 1 H), 3.04–2.91 (m, 1 H), 2.90–2.66 (m, 2 H), 2.62–2.46 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.23, 146.68, 138.56, 133.28, 133.02, 129.39, 129.06, 128.05, 127.76, 126.74, 126.69, 126.10, 124.85, 123.87, 54.35, 40.68, 34.22.

MS (EI, 70 eV): *m*/*z* = 370.0 $[M + H]^+$, 330.1, 290.1, 162.0, 141.0.

2-[1-Methoxy-3-(4-nitrophenyl)propyl]naphthalene (3d′)
General procedure GP-B afforded **3d′** (0.027 g, 78%) as a yellow liquid after column purification on silica gel; R_f = 0.43 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.17 (m, 2 H), 7.91–7.78 (m, 3 H), 7.70 (s, 1 H), 7.58–7.38 (m, 3 H), 7.38–7.23 (m, 2 H), 4.24 (dd, *J* = 7.9, 5.3 Hz, 1 H), 3.25 (s, 3 H), 2.96–2.70 (m, 2 H), 2.33–2.14 (m, 1 H), 2.13–1.95 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.92, 146.35, 138.96, 133.21, 129.27, 128.60, 127.80, 127.77, 127.69, 126.29, 126.00, 125.94, 124.17, 123.68, 82.88, 56.76, 39.05, 32.00.

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{19}NO_3$ $[M]^+$: 321.1365; found: 321.1367.

1-(3-Bromo-3-phenylpropyl)-2-nitrobenzene (3e)
According to general procedure GP-A, 2-nitrobenzyl bromide (0.050 g, 0.23 mmol, 1 equiv), $Cu(dap)_2Cl$ (2.0 mg, 1 mol%), and styrene (0.119 g, 1.15 mmol, 5 equiv) afforded **3e** (0.067 g, 91%) as a yellow liquid after column purification on silica gel; R_f = 0.44 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98–7.90 (m, 1 H), 7.54 (td, *J* = 7.7, 1.3 Hz, 1 H), 7.46–7.28 (m, 7 H), 4.99 (dd, *J* = 8.5, 6.4 Hz, 1 H), 3.12 (ddd, *J* = 13.4, 9.8, 5.3 Hz, 1 H), 2.93 (ddd, *J* = 13.3, 9.6, 6.1 Hz, 1 H), 2.71–2.44 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.51, 135.78, 133.20, 132.20, 128.83, 128.60, 127.54, 127.29, 125.83, 125.02, 54.59, 40.49, 32.10.

MS (EI, 70 eV): *m*/*z* = 321.0 $[M + H]^+$, 319.1, 239.2, 115.1, 44.1.

Large-Scale Reaction with Low Catalyst Loading: According to general procedure GP-A, 2-nitrobenzyl bromide (0.432 g, 2.0 mmol, 1 equiv), $Cu(dap)_2Cl$ (8.8 mg, 0.5 mol%), and styrene (1.04 g, 10.0 mmol, 5 equiv) in MeCN (5 mL) was irradiated for 12 h to obtain **3e** (0.510 g, 80%) as a yellow liquid after column purification on silica gel.

1-(3-Methoxy-3-phenylpropyl)-2-nitrobenzene (3e′)
General procedure GP-B afforded **3e′** (0.030 g, 89%) as a colorless oil after column purification on silica gel; R_f = 0.42 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93–7.85 (m, 1 H), 7.50 (t, *J* = 7.5 Hz, 1 H), 7.41–7.23 (m, 7 H), 4.14 (dd, *J* = 8.1, 5.1 Hz, 1 H), 3.23 (s, 3 H), 3.11–2.98 (m, 1 H), 2.98–2.84 (m, 1 H), 2.19–1.92 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.44, 141.74, 137.09, 132.87, 131.99, 128.48, 127.72, 127.00, 126.62, 124.71, 83.23, 56.67, 38.85, 29.56.

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{17}NO_3$ $[M]^+$: 271.1208; found: 271.1201.

1-[3-Bromo-3-(4-bromophenyl)propyl]-2-nitrobenzene (3f)
According to general procedure GP-A, 2-nitrobenzyl bromide (0.040 g, 0.18 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.5 mg, 1 mol%), and 4-bromostyrene (0.098 g, 0.54 mmol, 3 equiv) afforded **3f** (0.064 g, 87%) as a colorless liquid after column purification on silica gel; R_f = 0.44 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (dd, *J* = 8.1, 1.2 Hz, 1 H), 7.59–7.43 (m, 3 H), 7.42–7.33 (m, 2 H), 7.31–7.27 (m, 2 H), 4.93 (dd, *J* = 8.4, 6.5 Hz, 1 H), 3.10 (ddd, *J* = 13.3, 9.9, 5.3 Hz, 1 H), 2.92 (ddd, *J* = 13.3, 9.7, 6.1 Hz, 1 H), 2.66–2.41 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.55, 135.56, 133.28, 132.19, 131.99, 128.97, 127.65, 125.09, 122.23, 53.28, 40.37, 32.10.

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{13}Br_2NO_2$ $[M]^+$: 396.9313; found: 396.9314.

1-[3-Bromo-3-(3-chlorophenyl)propyl]-2-nitrobenzene (3g)
According to general procedure GP-A, 2-nitrobenzyl bromide (0.216 g, 1.00 mmol, 1 equiv), $Cu(dap)_2Cl$ (8.8 mg, 1 mol%), and 3-chlorostyrene (0.415 g, 3.00 mmol, 3 equiv) afforded **3g** (0.280 g, 79%) as a colorless liquid after column purification on silica gel; R_f = 0.48 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (dd, *J* = 7.8, 1.6 Hz, 1 H), 7.63–7.46 (m, 1 H), 7.44–7.33 (m, 3 H), 7.32–7.22 (m, 3 H), 4.91 (dd, *J* = 8.6, 6.2 Hz, 1 H), 3.13 (ddd, *J* = 13.4, 9.8, 5.2 Hz, 1 H), 2.93 (ddd, *J* = 13.3, 9.6, 6.1 Hz, 1 H), 2.66–2.39 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.12, 143.48, 135.53, 134.56, 133.29, 132.20, 130.12, 128.73, 127.68, 127.52, 125.51, 125.09, 53.08, 40.35, 32.07.

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{13}BrClNO_2$ $[M]^+$: 352.9818; found: 352.9818.

1-[3-Bromo-3-(biphenyl)propyl]-2-nitrobenzene (3h)
According to general procedure GP-A, 2-nitrobenzyl bromide (0.030 g, 0.13 mmol,1 equiv), $Cu(dap)_2Cl$ (1.1 mg, 1 mol%), and 4-vinylbiphenyl (0.046 g, 0.26 mmol, 2 equiv) afforded **3h** (0.045 g, 82%) as a colorless oil after column purification on silica gel; R_f = 0.36 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (dd, *J* = 8.5, 1.4 Hz, 1 H), 7.63–7.30 (m, 12 H), 5.05 (dd, *J* = 8.5, 6.5 Hz, 1 H), 3.21–3.08 (m, 1 H), 2.98 (ddd, *J* = 13.3, 9.5, 6.2 Hz, 1 H), 2.74–2.49 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.52, 140.47, 140.42, 135.78, 133.71, 133.23, 132.24, 129.63, 128.84, 127.74, 127.57, 127.13, 125.53, 125.05, 54.40, 40.41, 32.18.

MS (EI, 70 eV): *m*/*z* = 315.0 $[M – HBr]^+$, 281.1, 167.1, 133.1, 77.1.

1-(3-Methoxy-3-(biphenyl)propyl)-2-nitrobenzene (3h′)
General procedure GP-B afforded **3h′** (0.022 g, 63%) as a yellow gummy liquid after column purification on silica gel; R_f = 0.40 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.2 Hz, 1 H), 7.64–7.54 (m, 4 H), 7.48 (m, 3 H), 7.35 (m, 5 H), 4.20 (dd, *J* = 8.2, 5.0 Hz, 1 H), 3.27 (s, 3 H), 3.14–3.02 (m, 1 H), 3.02–2.92 (m, 1 H), 2.24–1.95 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.45, 140.86, 140.82, 140.63, 137.08, 132.89, 132.02, 128.77, 127.28, 127.24, 127.09, 127.07, 127.02, 124.73, 82.99, 56.74, 38.83, 29.61.

HRMS (ESI): *m*/*z* calcd for $C_{22}H_{21}ClNO_3$ + Na $[M + Na]^+$: 370.1414; found: 370.1412.

Ethyl 4-(3-Bromo-3-phenylpropyl)-3-nitrobenzoate (3i)
According to general procedure GP-A, ethyl 4-(bromomethyl)-3-nitrobenzoate (0.10 g, 0.34 mmol, 1 equiv), $Cu(dap)_2Cl$ (3 mg, 1 mol%), and styrene (0.176 g, 1.7 mmol, 5 equiv) afforded **3i** (0.093 g, 70%) as a light yellow liquid after column purification on silica gel; R_f = 0.67 (EtOAc–hexane, 1:8).

FT-IR (neat): 2981, 2360, 1720, 1532, 1455, 1262, 755 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.56 (d, *J* = 1.7 Hz, 1 H), 8.18 (dd, *J* = 8.0, 1.7 Hz, 1 H), 7.49–7.27 (m, 6 H), 4.98 (dd, *J* = 8.5, 6.3 Hz, 1 H), 4.41 (q, *J* = 7.13 Hz, 2 H), 3.17 (ddd, *J* = 13.4, 9.9, 5.2 Hz, 1 H), 2.98 (ddd, *J* = 13.3, 9.7, 6.1 Hz, 1 H), 2.70–2.44 (m, 2 H), 1.41 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.41, 149.14, 141.28, 140.33, 133.61, 132.44, 130.35, 128.89, 128.70, 127.26, 126.11, 125.79, 61.84, 54.26, 40.27, 32.20, 14.29.

HRMS (ESI): *m*/*z* calcd for $C_{18}H_{18}BrNO_4$ $[M]^+$: 391.0419; found: 391.0417.

1-(3-Bromo-3-phenylpropyl)-2,4-dinitrobenzene (3j)
According to general procedure GP-A, 2,4-dinitrobenzyl bromide (0.130 g, 0.5 mmol, 1 equiv), $Cu(dap)_2Cl$ (4.4 mg, 1 mol%), and styrene (0.260 g, 2.50 mmol, 5 equiv) afforded **3j** (0.162 g, 89%) as a yellow liquid after column purification on silica gel; R_f = 0.51 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (s, 1 H), 8.38 (dd, *J* = 8.5, 2.2 Hz, 1 H), 7.61 (d, *J* = 8.5 Hz, 1 H), 7.47–7.27 (m, 5 H), 4.98 (dd, *J* = 8.5, 6.3 Hz, 1 H), 3.25 (ddd, *J* = 13.5, 10.0, 5.2 Hz, 1 H), 3.05 (ddd, *J* = 13.4, 9.9, 6.1 Hz, 1 H), 2.72–2.45 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.06, 146.64, 142.78, 141.00, 133.54, 128.96, 128.84, 128.73, 127.22, 120.58, 53.92, 40.17, 32.27.

MS (EI, 70 eV): *m*/*z* = 285.0 $[M – HBr]^+$, 193.1, 179.0, 91.0.

1-(3-Methoxy-3-phenylpropyl)-2,4-dinitrobenzene (3j′)
General procedure GP-B afforded **3j′** (0.026 g, 75%) as a light yellow liquid after column purification on silica gel; R_f = 0.51 (EtOAc–hexane, 2:8).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.75 (d, *J* = 2.4 Hz, 1 H), 8.34 (dd, *J* = 8.5, 2.4 Hz, 1 H), 7.56 (d, *J* = 8.5 Hz, 1 H), 7.47–7.19 (m, 5 H), 4.15 (dd, *J* = 8.2, 4.8 Hz, 1 H), 3.21 (s, 3 H), 3.20–3.11 (m, 1 H), 3.11–2.96 (m, 1 H), 2.20–1.94 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.24, 146.28, 144.39, 141.19, 133.32, 128.63, 127.97, 126.86, 126.52, 120.30, 82.93, 56.69, 38.53, 29.75.

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{16}N_2O_5$ + Na $[M + Na]^+$: 339.0951; found: 339.0952.

1-(3-Bromo-2-methyl-3-phenylpropyl)-2,4-dinitrobenzene (3k)
An oven-dried Schlenk flask equipped with magnetic stir bar was charged with 2,4-dinitrobenzyl bromide (0.261 mg 1.00 mmol, 1.0 equiv), *trans*-β-methylstyrene (0.590 mg, 5.0 mmol, 5.0 equiv), and $Cu(dap)_2Cl$ (8.8 mg, 1 mol%). The flask was purged with a stream of N_2 and MeCN (10.0 mL) was added. The resultant mixture was degassed using freeze–pump–thaw cycles (5 ×) and flushed with N_2. The reaction mixture was internally irradiated using blue LED rods at 530 nm. After 20 h of irradiation, the solvent was evaporated under reduced pressure, and the crude reaction mixture was purified by chromatography on flash silica gel to afford **3k** (0.133 g, 35%) as a colorless oil in a diastereomeric ratio of 1.3:1; R_f = 0.63 (EtOAc–hexane, 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78* (d, *J* = 2.3 Hz, 1 H), 8.74 (d, *J* = 2.4 Hz, 1 H), 8.39–8.33 (m, 2 H), 7.60 (d, *J* = 8.5 Hz, 1 H), 7.55* (d, *J* = 8.5 Hz, 1 H), 7.34 (m, 10 H), 4.93* (d, *J* = 5.8 Hz, 1 H), 4.89 (d, *J* = 8.1 Hz, 1 H), 3.78 (dd, *J* = 13.5, 3.7 Hz, 1 H), 3.19* (dd, *J* = 13.4, 5.5 Hz, 1 H), 2.89 (dd, *J* = 12.3, 7.6 Hz, 1 H), 2.83 (dd, *J* = 12.4, 9.2 Hz, 1 H), 2.62–2.51 (m, 1 H), 2.43–2.35* (m, 1 H), 1.05* (d, *J* = 6.6 Hz, 3 H), 0.76 (d, *J* = 6.8 Hz, 2 H); * major diastereomer.

^{13}C NMR (100 MHz, CDCl3): δ = 146.67, 146.53, 142.30, 142.08, 140.05,139.96, 134.23, 133.98, 128.72, 128.58, 128.52, 128.37, 128.02, 127.86, 126.72, 126.58, 120.53, 120.30, 61.93, 61.59, 42.58, 42.25, 38.70, 37.80, 17.23, 16.61.

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{16}BrN_2O$ $[M]^+$: 379.0288; found: 379.0278.

1-[3-Bromo-3-(4-bromophenyl)propyl]-2,4-dinitrobenzene (3l)
According to general procedure GP-A, 2,4-dinitrobenzyl bromide (0.040 g, 0.15 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.3 mg, 1 mol%), and 4-bromostyrene (0.082 g, 0.45 mmol, 3 equiv) afforded **3l** (0.057 g, 86%) as a colorless oil after column purification on silica gel; R_f = 0.17 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.81 (d, *J* = 2.3 Hz, 1 H), 8.39 (dd, *J* = 8.5, 2.4 Hz, 1 H), 7.61 (d, *J* = 8.5 Hz, 1 H), 7.55–7.45 (m, 2 H), 7.29 (m, 2 H), 4.93 (dd, *J* = 8.6, 6.2 Hz, 1 H), 3.23 (ddd, *J* = 13.4, 10.1, 5.2 Hz, 1 H), 3.03 (ddd, *J* = 13.3, 10.0, 6.0 Hz, 1 H), 2.67–2.41 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.04, 146.72, 142.52, 140.05, 133.53, 132.13, 128.88, 127.28, 122.74, 120.65, 52.66, 40.06, 32.26.

MS (EI, 70 eV): *m*/*z* = 444.0 $[M]^+$, 422.0, 364.9, 350.2, 283.2.

1-[3-Methoxy-3-(4-bromophenyl)propyl]-2,4-dinitrobenzene (3l′)
General procedure GP-B afforded **3l′** (0.029 g, 82%) as a yellow oil after column purification on silica gel; R_f = 0.46 (EtOAc–hexane, 2:8).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.76 (d, *J* = 2.4 Hz, 1 H), 8.35 (dd, *J* = 8.5, 2.4 Hz, 1 H), 7.56 (d, *J* = 8.5 Hz, 1 H), 7.52–7.45 (m, 2 H), 7.20–7.13 (m, 2 H), 4.12 (dd, *J* = 8.2, 4.7 Hz, 1 H), 3.21 (s, 3 H), 3.18–2.96 (m, 2 H), 2.14–1.92 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.23, 146.34, 144.14, 140.31, 133.33, 131.79, 128.21, 126.93, 121.76, 120.35, 82.33, 56.78, 38.46, 29.69.

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{15}BrN_2O_5$ $[M]^+$: 394.0164; found: 394.0150.

1-[3-Bromo-3-(3-chlorophenyl)propyl]-2,4-dinitrobenzene (3m)
According to general procedure GP-A, 2,4-dinitrobenzyl bromide (0.040 g, 0.15 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.3 mg, 1 mol%), and 3-chlorostyrene (0.062 g, 0.45 mmol, 3 equiv) afforded **3m** (0.058 g, 95%) as a very light yellow oil after column purification on silica gel; R_f = 0.63 (EtOAc–hexane, 2:8).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.81 (d, *J* = 2.3 Hz, 1 H), 8.40 (dd, *J* = 8.5, 2.4 Hz, 1 H), 7.62 (d, *J* = 8.5 Hz, 1 H), 7.37 (d, *J* = 15.3 Hz, 1 H), 7.34–7.27 (m, 3 H), 4.91 (dd, *J* = 8.7, 6.0 Hz, 1 H), 3.26 (ddd,

J = 13.4, 10.0, 5.1 Hz, 1 H), 3.05 (ddd, J = 13.3, 9.9, 6.1 Hz, 1 H), 2.69–2.40 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.04, 146.73, 142.95, 142.50, 134.72, 133.53, 130.25, 128.97, 127.45, 127.27, 125.43, 120.65, 52.43, 40.03, 32.23.

MS (EI, 70 eV): m/z = 362.1 $[M – HCl]^+$, 358.0.

1-[3-Methoxy-3-(3-chlorophenyl)propyl]-2,4-dinitrobenzene (3m′)

General procedure GP-B afforded **3m′** (0.027 g, 77%) as a yellow gummy liquid after column purification on silica gel; R_f = 0.58 (EtOAc–hexane, 2:8).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.76 (d, J = 2.3 Hz, 1 H), 8.35 (dd, J = 8.5, 2.4 Hz, 1 H), 7.56 (d, J = 8.5 Hz, 1 H), 7.32–7.24 (m, 3 H), 7.19–7.13 (m, 1 H), 4.13 (dd, J = 8.1, 4.8 Hz, 1 H), 3.23 (s, 3 H), 3.20–2.98 (m, 2 H), 2.18–1.92 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.25, 146.36, 144.11, 143.53, 134.63, 133.34, 129.98, 128.12, 126.92, 126.56, 124.67, 120.35, 82.36, 56.91, 38.49, 29.68.

HRMS (ESI): m/z calcd for $C_{16}H_{15}ClN_2O_5$ + Na $[M + Na]^+$: 373.0562, found: 373.0561.

2-[1-Bromo-3-(2,4-dinitrophenyl)propyl]naphthalene (3n)

According to general procedure GP-A, 2,4-dinitrobenzyl bromide (0.040 g, 0.15 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.3 mg, 1 mol%), and 2-vinylnaphthalene (0.082 g, 0.30 mmol, 2 equiv) afforded **3n** (0.064 g, 81%) as a yellow liquid after column purification on silica gel; R_f = 0.23 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (d, J = 2.4 Hz, 1 H), 8.36 (dd, J = 8.5, 2.4 Hz, 1 H), 7.91–7.76 (m, 4 H), 7.64–7.46 (m, 4 H), 5.17 (dd, J = 8.3, 6.6 Hz, 1 H), 3.28 (ddd, J = 13.4, 10.0, 5.2 Hz, 1 H), 3.06 (ddd, J = 13.3, 9.8, 6.2 Hz, 1 H), 2.82–2.56 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.04, 146.61, 142.74, 138.12, 133.54, 133.31, 132.99, 129.13, 128.08, 127.76, 127.16, 126.83, 126.75, 126.17, 124.74, 120.58, 54.25, 40.05, 32.34.

MS (EI, 70 eV): m/z = 300.1, 254.2, 178.0, 156.1, 127.1.

2-[1-Methoxy-3-(2,4-dinitrophenyl)propyl]naphthalene (3n′)

General procedure GP-B afforded **3n′** (0.025 g, 71%) as a light yellow liquid after column purification on silica gel; R_f = 0.53 (EtOAc–hexane, 2:8).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.70 (d, J = 2.4 Hz, 1 H), 8.28 (dd, J = 8.5, 2.4 Hz, 1 H), 7.87–7.72 (m, 3 H), 7.67 (s, 1 H), 7.54–7.33 (m, 4 H), 4.28 (dd, J = 8.2, 4.9 Hz, 1 H), 3.21 (s, 3 H), 3.20–3.10 (m, 1 H), 3.02 (ddd, J = 13.4, 9.5, 6.3 Hz, 1 H), 2.25–1.99 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.20, 145.23, 143.30, 137.52, 132.29, 132.19, 127.63, 126.79, 126.73, 125.81, 125.29, 125.04, 124.85, 122.98, 121.16, 119.27, 82.05, 55.74, 37.30, 28.77.

HRMS (ESI): m/z calcd for $C_{20}H_{18}N_2O_5$ $[M]^+$: 366.1216; found: 366.1215.

2-[1-Bromo-3-(biphenyl)propyl]-2,4-dinitrobenzene (3o)

According to general procedure GP-A, 2,4-dinitrobenzyl bromide (0.040 g, 0.15 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.3 mg, 1 mol%), and 4-vinylbiphenyl (0.055 g, 0.30 mmol, 2 equiv) afforded **3o** (0.061 g, 90%) as a light yellow liquid after column purification on silica gel; R_f = 0.38 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.81 (d, J = 2.3 Hz, 1 H), 8.39 (dd, J = 8.5, 2.4 Hz, 1 H), 7.68–7.52 (m, 6 H), 7.51–7.31 (m, 6 H), 5.04 (dd, J = 8.5, 6.3 Hz, 1 H), 3.28 (ddd, J = 13.3, 10.0, 5.2 Hz, 1 H), 3.09 (ddd, J = 13.3, 9.8, 6.1 Hz, 1 H), 2.76–2.50 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.07, 146.66, 142.77, 141.79, 140.23, 139.93, 133.57, 128.89, 127.67, 127.60, 127.35, 127.22, 127.11, 120.62, 53.72, 40.10, 32.34.

MS (EI, 70 eV): m/z = 361.1 $[M – HBr]^+$, 280.2, 242.2.

2-(1-Methoxy-3-(biphenyl)propyl]-2,4-dinitrobenzene (3o′)

General procedure GP-B afforded **3o′** (0.021 g, 59%) as a yellow oil after column purification on silica gel; R_f = 0.42 (EtOAc–hexane, 2:8).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.76 (d, J = 2.3 Hz, 1 H), 8.35 (dd, J = 8.5, 2.4 Hz, 1 H), 7.59 (dd, J = 8.3, 2.6 Hz, 5 H), 7.49–7.39 (m, 2 H), 7.39–7.31 (m, 3 H), 4.21 (dd, J = 8.2, 4.8 Hz, 1 H), 3.26 (s, 3 H), 3.24–3.15 (m, 1 H), 3.14–3.01 (m, 1 H), 2.25–1.96 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.28, 146.29, 144.38, 140.92, 140.69, 140.22, 133.34, 128.82, 127.39, 127.37, 127.08, 126.97, 126.87, 120.32, 82.69, 56.77, 38.52, 29.80.

HRMS (ESI): m/z calcd for $C_{22}H_{20}N_2O_5$ + Na $[M + Na]^+$: 415.1264; found: 415.1266.

1-(3-Chloro-3-phenylpropyl)-2,4-dinitrobenzene (3p)

According to general procedure GP-A, 2,4-dinitrobenzyl chloride (0.049 g, 0.23 mmol, 1 equiv), $Cu(dap)_2Cl$ (2.0 mg, 1 mol%), and styrene (0.119 g, 1.15 mmol, 5 equiv) afforded **3p** (0.038 g, 51%) as a light yellow liquid after column purification on silica gel; R_f = 0.32 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (d, J = 2.3 Hz, 1 H), 8.38 (dd, J = 8.5, 2.4 Hz, 1 H), 7.62 (m, 1 H), 7.48–7.28 (m, 5 H), 4.91 (dd, J = 8.3, 5.9 Hz, 1 H), 3.26 (ddd, J = 13.5, 9.5, 5.7 Hz, 1 H), 3.07 (ddd, J = 13.4, 9.4, 6.6 Hz, 1 H), 2.59–2.30 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.10, 146.62, 142.98, 140.61, 133.53, 128.89, 128.75, 127.17, 126.86, 120.57, 62.63, 40.22, 31.12.

HRMS (ESI): m/z calcd for $C_{18}H_{13}ClN_2O_4$ $[M]^+$: 320.0522; found: 320.0524.

1-[3-Chloro-3-(3-chlorophenyl)propyl]-2,4-dinitrobenzene (3q)

According to general procedure GP-A, 2,4-dinitrobenzyl chloride (0.040 g, 0.18 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.5 mg, 1 mol%), and 3-chlorostyrene (0.074 g, 0.54 mmol, 3 equiv) afforded **3q** (0.060 g, 92%) as a light yellow oil after column purification on silica gel; R_f = 0.70 (EtOAc–hexane, 2:8).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.80 (d, J = 2.3 Hz, 1 H), 8.39 (dd, J = 8.5, 2.4 Hz, 1 H), 7.61 (d, J = 8.5Hz, 1 H), 7.39 (s, 1 H), 7.34–7.22 (m, 3 H), 4.87 (dd, J = 8.1, 6.0 Hz, 1 H), 3.27 (ddd, J = 13.4, 9.3, 6.0 Hz, 1 H), 3.08 (ddd, J = 13.4, 9.1, 6.9 Hz, 1 H), 2.48–2.37 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.08, 146.70, 142.68, 142.56, 134.73, 133.54, 130.18, 128.89, 127.24, 127.12, 125.06, 120.63, 61.62, 40.13, 31.05.

HRMS (ESI): m/z calcd for $C_{15}H_{12}Cl_2N_2O_4$ + Na $[M + Na]^+$: 377.0778; found: 377.0777.

1-(3-Chloro-3-*p*-tolylpropyl)-2,4-dinitrobenzene (3r)

According to general procedure GP-A, 2,4-dinitrobenzyl chloride (0.030 g, 0.13 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.1 mg, 1 mol%), and 4-methylstyrene (0.046 g, 0.39 mmol, 3 equiv) afforded **3r** (0.043 g, 93%) as a light yellow oil after column purification on silica gel; R_f = 0.25 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (d, J = 2.4 Hz, 1 H), 8.38 (dd, J = 8.4, 2.3 Hz, 1 H), 7.60 (d, J = 8.5 Hz, 1 H), 7.31–7.24 (m, 2 H), 7.21–7.14 (m, 2 H), 4.89 (dd, J = 8.3, 6.0 Hz, 1 H), 3.24 (ddd, J = 13.5, 9.6, 5.6 Hz, 1 H), 3.12–2.99 (m, 1 H), 2.51–2.38 (m, 2 H), 2.38–2.30 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.11, 146.59, 143.05, 138.71, 137.66, 133.53, 129.54, 127.15, 126.78, 120.55, 62.62, 40.13, 31.15, 21.18.

HRMS (ESI): m/z calcd for $C_{16}H_{16}ClN_2O_4$ $[M + H]^+$: 335.0793; found: 335.0797.

4-[3-Bromo-3-(naphthalen-6-yl)propyl]-2-chloroquinoline (3s)
According to general procedure GP-A, 4-(bromomethyl)-2-chloroquinoline (0.040 g, 0.11 mmol, 1 equiv), $Cu(dap)_2Cl$ (0.98 mg, 1 mol%), and 2-vinylnaphthalene (0.033 g, 0.22 mmol, 2 equiv) afforded **3s** (0.030 g, 66%) as a colorless oil after column purification on silica gel; R_f = 0.28 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06–8.01 (m, 1 H), 7.95 (d, *J* = 8.4 Hz, 1 H), 7.91–7.67 (m, 6 H), 7.61–7.47 (m, 4 H), 5.19 (dd, *J* = 8.5, 6.2 Hz, 1 H), 3.43–3.30 (m, 1 H), 3.17–3.04 (m, 1 H), 2.91–2.75 (m, 1 H), 2.64 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.61, 149.90, 148.13, 138.41, 133.32, 133.02, 130.44, 129.51, 129.11, 128.09, 127.77, 127.03, 126.79, 126.73, 126.18, 125.98, 124.81, 123.42, 121.86, 54.65, 39.66, 30.72.

MS (EI, 70 eV): *m*/*z* = 300.9, 222.0, 140.1, 44.0.

4-[3-Methoxy-3-(naphthalen-6-yl)propyl]-2-chloroquinoline (3s′)
General procedure GP-B afforded **3s′** (0.018 g, 83%) as a colorless oil after column purification on silica gel; R_f = 0.71 (EtOAc–hexane, 2:8).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (dd, *J* = 8.4, 0.6 Hz, 1 H), 7.98–7.91 (m, 1 H), 7.90–7.80 (m, 3 H), 7.76–7.66 (m, 2 H), 7.56–7.42 (m, 4 H), 7.24 (s, 1 H), 4.33 (dd, *J* = 8.0, 4.9 Hz, 1 H), 3.30 (s, 3 H), 3.27–3.18 (m, 1 H), 3.18–3.03 (m, 1 H), 2.40–2.23 (m, 1 H), 2.22–2.06 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.59, 150.64, 148.07, 138.82, 133.23, 130.23, 129.34, 128.64, 127.84, 127.78, 126.75, 126.32, 126.26, 126.04, 125.97, 124.14, 123.69, 121.68, 82.95, 56.85, 38.02, 28.22.

HRMS (ESI): *m*/*z* calcd for $C_{23}H_{21}ClNO$ $[M + H]^+$: 362.1306; found: 362.1309.

3-(4-Nitrophenyl)-1-phenylpropan-1-one (5a)[21]
According to general procedure GP-A, 4-nitrobenzyl bromide (0.040 g, 0.18 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.5 mg, 1 mol%), and (1-phenylvinyloxy)trimethylsilane (0.103 g, 0.54 mmol, 3 equiv) afforded 5a (0.041 g, 87%) as a yellow solid after column purification on silica gel; mp 157–159 °C (Lit.[21] mp 161–163 °C); R_f = 0.30 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (dd, *J* = 8.9, 2.2 Hz, 2 H), 7.95 (dd, *J* = 8.4, 1.3 Hz, 2 H), 7.60–7.41 (m, 5 H), 3.37 (dd, *J* = 10.8, 4.0 Hz, 2 H), 3.19 (t, *J* = 7.2 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.14, 149.21, 136.51, 133.42, 129.39, 128.74, 128.01, 124.34, 123.80, 39.42, 29.74.

MS (EI, 70 eV): *m*/*z* = 255.1 (24.7, $[M]^+$), 105.1 (100.0).

3-(2-Nitrophenyl)-1-phenylpropan-1-one (5b)[21]
According to general procedure GP-A, 2-nitrobenzyl bromide (0.216 g, 1.00 mmol, 1 equiv), $Cu(dap)_2Cl$ (8.8 mg, 1 mol%), and (1-phenylvinyloxy)trimethylsilane (0.576 g, 3.00 mmol, 3 equiv) afforded **5b** (0.198 g, 78%) as a light yellow solid after column purification on silica gel; mp 104–106 °C (Lit.[21] mp 111–112 °C); R_f = 0.40 (EtOAc–hexane, 1:9).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20–7.92 (m, 3 H), 7.75–7.36 (m, 6 H), 3.65–3.27 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.54, 149.34, 136.59, 136.57, 133.33, 133.27, 132.66, 128.67, 128.10, 127.49, 124.93, 39.46, 27.79.

MS (EI, 70 eV): *m*/*z* = 255.1 (24.7) $[M]^+$), 105.1 (100.0).

3-(2,4-Dinitrophenyl)-1-phenylpropan-1-one (5c)
According to general procedure GP-A, 2,4-dinitrobenzyl bromide (0.040 g, 0.15 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.3 mg, 1 mol%), and (1-phenylvinyloxy)trimethylsilane (0.086 g, 0.45 mmol, 3 equiv) afforded **5c** (0.040 g, 90%) as a yellow liquid after column purification on silica gel; R_f = 0.46 (EtOAc–hexane, 2:8).

FT-IR (neat): 3080, 2361, 1686, 1604, 1531, 1348, 748 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (d, *J* = 2.4 Hz, 1 H), 8.36 (dd, *J* = 8.5, 2.4 Hz, 1 H), 7.92 (dd, *J* = 5.2, 3.4 Hz, 2 H), 7.76 (d, *J* = 8.5 Hz, 1 H), 7.56 (ddd, *J* = 6.6, 3.8, 1.2 Hz, 1 H), 7.44 (dd, *J* = 10.4, 4.7 Hz, 2 H), 3.44 (s, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.54, 149.28, 146.57, 143.64, 136.20, 134.26, 133.61, 128.79, 128.05, 127.09, 120.42, 38.71, 27.54.

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{12}N_2O_5$ $[M]^+$: 300.0746; found: 300.0751.

Ethyl 3-Nitro-4-(3-oxo-3-phenylpropyl)benzoate (5d)
According to general procedure GP-A, ethyl 4-(bromomethyl)-3-nitrobenzoate (0.050 g, 0.17 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.5 mg, 1 mol%), and (1-phenylvinyloxy)trimethylsilane (0.098 g, 0.51 mmol, 3 equiv) afforded **5d** (0.046 g, 81%) as a yellow liquid after column purification on silica gel; R_f = 0.20 (EtOAc–hexane, 1:9).

FT-IR (neat): 2927, 2360, 1721, 1686, 1449, 1263, 743 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.54 (d, *J* = 1.7 Hz, 1 H), 8.13 (dd, *J* = 8.0, 1.8 Hz, 1 H), 7.94–7.88 (m, 2 H), 7.56–7.49 (m, 2 H), 7.45–7.37 (m, 2 H), 4.37 (q, *J* = 7.1 Hz, 2 H), 3.42–3.29 (m, 4 H), 1.37 (t, *J* = 7.13 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.04, 164.46, 149.33, 141.19, 136.41, 133.62, 133.40, 132.95, 130.25, 128.72, 128.07, 126.01, 61.79, 39.09, 27.72, 14.30.

HRMS (ESI): *m*/*z* calcd for $C_{18}H_{18}NO_5$ $[M + H]^+$: 328.1179; found: 328.1184.

2-(2,4-Dinitrobenzyl)cyclopentanone (5e)
According to general procedure GP-A, 2,4-dinitrobenzyl bromide (0.050 g, 0.19 mmol, 1 equiv), $Cu(dap)_2Cl$ (1.6 mg, 1 mol%), and (cyclopentenyloxy)trimethylsilane (0.089 g, 0.57 mmol, 3 equiv) afforded **5e** (0.025 g, 50%) as a yellow liquid after column purification on silica gel; R_f = 0.21 (EtOAc–hexane, 2:8).

FT-IR (neat): 3104, 2362, 1685, 1604, 1531, 1209, 835 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.78 (d, *J* = 2.3 Hz, 1 H), 8.37 (dd, *J* = 8.5, 2.4 Hz, 1 H), 7.65 (d, *J* = 8.5 Hz, 1 H), 3.47 (dd, *J* = 13.8, 6.1 Hz, 1 H), 2.99 (dd, *J* = 13.8, 7.6 Hz, 1 H), 2.59–2.25 (m, 2 H), 2.25–1.99 (m, 3 H), 1.91–1.70 (m, 1 H), 1.70–1.47 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 218.27, 149.29, 146.57, 142.45, 134.17, 126.88, 120.38, 49.90, 37.48, 32.61, 29.62, 20.44.

HRMS (ESI): *m*/*z* calcd for $C_{12}H_{13}N_2O_5$ $[M + H]^+$: 265.0819; found: 265.0819.

1,2,3,4-Tetrahydro-2-phenylquinoline (6a)[22]
According to general procedure GP-C, ATRA product **3e** (0.150 g, 0.46 mmol, 1 equiv), $FeCl_3·6H_2O$ (0.379 g, 1.40 mmol, 3 equiv), and Zn dust (0.305 g, 4.68 mmol, 10 equiv) afforded **6a** (0.075 g, 75%) as a colorless liquid after column purification on silica gel.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.24 (m, 5 H), 7.02 (t, *J* = 7.0 Hz, 2 H), 6.67 (td, *J* = 7.4, 1.0 Hz, 1 H), 6.60–6.53 (m, 1 H), 4.45 (dd, *J* = 9.3, 3.3 Hz, 1 H), 4.16 (br, 1 H), 2.94 (ddd, *J* = 16.2, 10.5, 5.5 Hz, 1 H), 2.75 (dt, *J* = 16.4, 4.8 Hz, 1 H), 2.20–1.93 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.65, 144.51, 129.33, 128.60, 127.49, 126.93, 126.60, 121.05, 117.36, 114.16, 56.30, 30.93, 26.39.

MS (ESI): *m*/*z* calcd for $C_{16}H_{17}N$ $[M + H]^+$: 210.1; found: 210.0

2-(4-Bromophenyl)-1,2,3,4-tetrahydroquinoline (6b)[22]
According to general procedure GP-C, ATRA product **3f** (0.053 g, 0.13 mmol, 1 equiv), $FeCl_3·6H_2O$ (0.107 g, 0.39 mmol, 3 equiv),

and Zn dust (0.086 g, 1.32 mmol, 10 equiv) afforded **6b** (0.027 g, 72%) as a colorless liquid after column purification on silica gel.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.44 (m, 2 H), 7.27 (d, *J* = 8.6 Hz, 2 H), 7.02 (t, *J* = 7.8 Hz, 2 H), 6.68 (t, *J* = 7.4 Hz, 1 H), 6.56 (d, *J* = 7.9 Hz, 1 H), 4.41 (dd, *J* = 9.1, 3.3 Hz, 1 H), 3.03–2.82 (m, 1 H), 2.72 (dt, *J* = 16.5, 4.9 Hz, 1 H), 2.22–2.04 (m, 1 H), 2.04–1.86 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.02, 143.58, 131.64, 129.31, 128.33, 126.98, 121.13, 121.03, 117.73, 114.33, 55.69, 30.78, 26.06.

MS (ESI): *m*/*z* calcd for $C_{15}H_{15}BrN$ $[M + H]^+$: 288.0; found: 288.0.

2-(3-Chlorophenyl)-1,2,3,4-tetrahydroquinoline (6c)[23]
According to general procedure GP-C, ATRA product **3g** (0.038 g, 0.10 mmol, 1 equiv), $FeCl_3 \cdot 6H_2O$ (0.086 g, 0.30 mmol, 3 equiv), and Zn dust (0.069 g, 1.0 mmol, 10 equiv) afforded **6c** (0.018 g, 70%) as a yellow oil after column purification on silica gel.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (s, 1 H), 7.27–7.18 (m, 3 H), 6.98 (m, 2 H), 6.65 (t, *J* = 7.4 Hz, 1 H), 6.54 (d, *J* = 7.8 Hz, 1 H), 4.38 (dd, *J* = 9.1, 3.4 Hz, 1 H), 2.87 (ddd, *J* = 16.0, 10.4, 5.5 Hz, 1 H), 2.68 (dt, *J* = 16.4, 4.9 Hz, 1 H), 2.08 (ddd, *J* = 10.1, 8.6, 5.1 Hz, 1 H), 2.02–1.86 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.79, 144.07, 134.45, 129.87, 129.34, 127.61, 127.02, 126.77, 124.80, 120.99, 117.69, 114.30, 55.82, 30.86, 26.12.

MS (ESI): *m*/*z* calcd for $C_{15}H_{15}ClN$ $[M + H]^+$: 244.0; found: 244.0.

Procedure for the Reduction of Ketone with Pd/C[20]
Ketone **5b** (150 mg, 0.58 mmol, 1 equiv) was dissolve in EtOH (3 mL) and of 5% Pd/C (23.2 mg) was added. H_2 gas was passed through the solution for 5 min and the mixture was stirred at r.t. for 3 h under H_2 atmosphere. After completion of the reaction (monitored by TLC), the mixture was filtered through a Celite bed, the filtrate was concentrated in vacuo, and the residue was subjected to column chromatography to obtain **6a** (81 mg, 67%) as a colorless liquid. For physical and spectral data see above.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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