Novel Preparation of Polymer-Supported Iodobenzene and Its Synthetic Utility as a Recyclable Reagent with *m*-Chloroperbenzoic Acid

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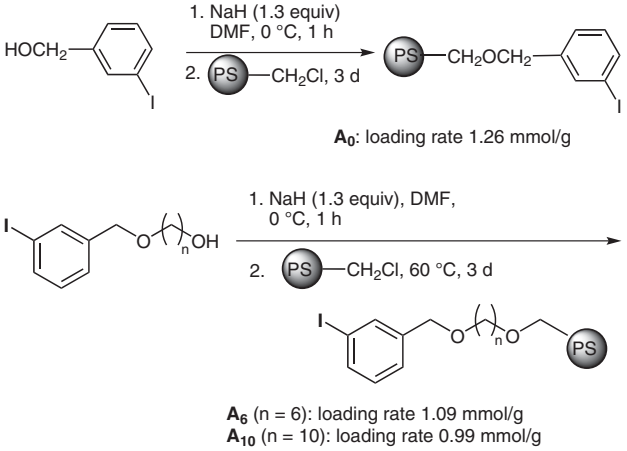
Abstract: Three novel polymer-supported iodobenzene compounds A_0, A_6, and A_{10} were prepared from the reaction of commercially available cross-linked poly(*p*-chloromethyl)styrene with *m*-iodobenzylalcohol, 6-(*m*-iodobenzyloxy)-1-hexanol, and 10-(*m*-iodobenzyloxy)-1-decanol. Their catalytic reactivity and reusability for the oxidative α-tosyloxylation of ketones and the cyclization of *N*-methoxy-2-arylethanesulfonamides in the presence of *m*-chloroperbenzoic acid (*m*CPBA) were confirmed to provide α-tosyloxyketones and *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxides, respectively, in good yields.

Key words: polymer-supported PhI, recycle *m*CPBA, α-tosyloxyketone, ketone, *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxide, catalyst

Many synthetic studies of hypervalent iodines have been undertaken.[1] Among them, [(hydroxy)(tosyloxy)iodo]benzene is highly efficient and is, so far, the sole reagent capable of direct α-tosyloxylation of ketones.[2a,b] α-Tosyloxyketones are very important strategic precursors for the preparation of various heteroaromatics, such as thiazoles, imidazoles, oxazoles, selenazoles, pyrazoles, and benzofurans.[2] Therefore, we have been studying the synthetic uses of [(hydroxy)(tosyloxy)iodo]arenes, 1-(arenesulfonyloxy)benziodoxolones, and poly[4-(hydroxy)(tosyloxy)iodo]styrenes for the construction of thiazoles, imidazoles, imidazo[1.2-*a*]pyridines, and 2,1-benzothiazines.[3] On the other hand, the aromatic iodide-catalyzed oxidative conversions of substrates such as ketones, hydroquinones, and alcohols with *m*-chloroperbenzoic acid (*m*CPBA) or Oxone® has become very popular[4] because it is a metal-free oxidative reaction and is thus environmentally benign. Recently, we also reported an efficient method to prepare various [(hydroxy)(sulfonyloxy)iodo]arenes directly from iodoarenes with *m*CPBA and sulfonic acids at room temperature.[5] Such methods include the iodobenzene-catalyzed and the ion-supported iodobenzene-catalyzed α-tosyloxylation of ketones with *m*CPBA and *p*-toluenesulfonic acid monohydrate, and the iodobenzene-catalyzed and the ion-supported iodobenzene-catalyzed preparation of 3,4-dihydro-1*H*-2,1-benzothiazine 2,2-dioxides from *N*-methoxy-2-arylethanesulfonamides with *m*CPBA.[6] Here, as part of our study on the catalytic use of iodoarenes for organic synthesis,[6] we would like to report the polymer-supported iodobenzene-catalyzed α-tosyloxylation of ketones and the cyclization of *N*-methoxy-2-arylethanesulfonamides to *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxides.

First, *m*-iodobenzylalcohol was selected as the iodoaryl group for the polymer-supported iodobenzene, because *m*-iodobenzylalcohol could be efficiently prepared by the reduction of methyl *m*-iodobenzoate with diisobutylaluminum hydride (DIBAL-H). Methyl *m*-iodobenzoate was quantitatively obtained from commercially available *m*-iodobenzoic acid. Then, three novel polymer-supported iodobenzene compounds $\mathbf{A_0}$, $\mathbf{A_6}$, and $\mathbf{A_{10}}$ were prepared by the reactions of commercially available cross-linked poly(*p*-chloromethyl)styrene (loading rate: 1.87 mmol/g) with *m*-iodobenzylalcohol, 6-(*m*-iodobenzyloxy)-1-hexanol, and 10-(*m*-iodobenzyloxy)-1-decanol, respectively, as shown in Scheme 1. The loading rates of the iodobenzene group in the three polymer-supported materials $\mathbf{A_0}$ (1.26 mmol/g), $\mathbf{A_6}$ (1.09 mmol/g), and $\mathbf{A_{10}}$ (0.99 mmol/g) were estimated from both the recovery of *m*-iodobenzylalcohol, 6-(*m*-iodobenzyloxy)-1-hexanol, and 10-(*m*-iodobenzyloxy)-1-decanol from the reactions with cross-linked poly(*p*-chloromethyl)styrene, respectively, and by the elemental analysis of $\mathbf{A_0}$, $\mathbf{A_6}$, and $\mathbf{A_{10}}$. Peaks assignable to the iodobenzene groups in $\mathbf{A_0}$, $\mathbf{A_6}$, and $\mathbf{A_{10}}$ were readily observed by ^{1}H NMR measurement in $CDCl_3$. In particular, peaks of the iodobenzene group of $\mathbf{A_6}$ and $\mathbf{A_{10}}$ were clearly observed. This indicates that the iodobenzene groups in $\mathbf{A_0}$, $\mathbf{A_6}$, and $\mathbf{A_{10}}$ are flexible and freely soluble in organic solvents. This observation suggests that $\mathbf{A_0}$, $\mathbf{A_6}$,



Scheme 1 Preparation of polymer-supported iodobenzene

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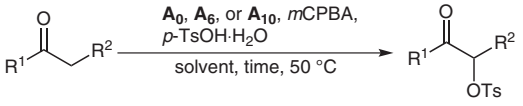
and $\mathbf{A_{10}}$ may not only have reactivities that are comparable to iodobenzene, but should also be reusable, unlike volatile iodobenzene.

Entry 1 in Table 1 shows the effect of $\mathbf{A_0}$, $\mathbf{A_6}$, and $\mathbf{A_{10}}$ on the yield of α-tosyloxyacetophenone in the reaction of acetophenone with *m*CPBA and *p*-toluenesulfonic acid monohydrate in chloroform or acetonitrile at 50 °C. As shown in entries 1, 7, and 8, $\mathbf{A_6}$ and $\mathbf{A_{10}}$ showed better reactivity than $\mathbf{A_0}$. Propiophenone, *m*-nitroacetophenone, 3-pentanone, 6-undecanone, ethyl benzoylacetate, and methyl acetoacetate were treated with *m*CPBA and *p*-toluenesulfonic acid monohydrate in the presence of $\mathbf{A_6}$ and $\mathbf{A_{10}}$ to provide the corresponding α-tosyloxyketones in good to moderate yields under the same conditions (entries 9–14). After the reaction, $\mathbf{A_6}$ and $\mathbf{A_{10}}$ were recovered quantitatively and could be reused for the same α-tosyloxylation of *p*-nitroacetophenone, maintaining good to moderate yields of the product (entries 2–5). The reason why the yields of α-tosyloxy-*p*-nitroacetophenone from *p*-nitroacetophenone decreased using polymer-supported material $\mathbf{A_6}$ and $\mathbf{A_{10}}$ that was recovered after the second and third run, was that the iodobenzene groups of $\mathbf{A_6}$ and $\mathbf{A_{10}}$ were partly oxidized to inert PhI(V) groups by *m*CPBA. Practically, the yield of α-tosyloxy-*p*-nitroacetophenone from *p*-nitroacetophenone could be markedly increased when the PhI(V) groups of polymer-supported material $\mathbf{A_{10}}$ recovered after the third run were reduced to PhI(I) groups by treatment with $NaBH_4$, before the reaction with *p*-nitroacetophenone, *m*CPBA, and *p*-toluenesulfonic acid (entry 6). The advantages of using polymer-supported iodobenzene are the simple isolation of α-tosyloxyketones by filtration, and the reusability of the polymer-supported material. Thus, when the filtrate from the reaction mixture was poured into chloroform and washed with aqueous sodium bicarbonate, α-tosyloxylketones were obtained in high purity (>90%) after removal of the solvent. The cyclization of *N*-methoxy-2-phenylethanesulfonamide with $\mathbf{A_0}$, $\mathbf{A_6}$, and $\mathbf{A_{10}}$, in the presence of *m*CPBA, was carried out to provide *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxide in good yields, as shown in Table 2 (entries 1–4). Although the reactivities of $\mathbf{A_0}$, $\mathbf{A_6}$, and $\mathbf{A_{10}}$ were the same, the polymer-supported material could be recovered quantitatively and reused for the same reaction, maintaining good yields of the product. The same treatment of other *N*-methoxy-2-arylethanesulfonamides with $\mathbf{A_0}$, $\mathbf{A_6}$ and $\mathbf{A_{10}}$ in the presence of *m*CPBA provided the corresponding 7-substituted *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxides in good to moderate yields, depending on the substrates (entries 5–8).

In conclusion, various α-tosyloxyketones were prepared in good yields from the reaction of ketones with *m*CPBA and *p*-toluenesulfonic acid monohydrate in the presence of polymer-supported iodobenzene compounds $\mathbf{A_0}$, $\mathbf{A_6}$, and $\mathbf{A_{10}}$, especially the latter two. The cyclization of *N*-methoxy-2-arylethanesulfonamides with $\mathbf{A_0}$, $\mathbf{A_6}$, and $\mathbf{A_{10}}$ in the presence of *m*CPBA and *p*-toluenesulfonic acid monohydrate occurred efficiently to provide *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxides in good to moderate yields. The advantages of using these polymer-supported iodobenzene compounds are easy isolation of the products by filtration and their reusability in the same reactions.

Table 1 α-Tosyloxylation of Ketones with *m*CPBA and *p*-TsOH·H_2O in the Presence of $\mathbf{A_0}$, $\mathbf{A_6}$, or $\mathbf{A_{10}}$



Ar-I	$\mathbf{A_0}$ (1.3 equiv)	$\mathbf{A_6}$ (0.5 equiv)	$\mathbf{A_{10}}$ (0.5 equiv)
*m*CPBA	1.1	2.5	2.5
p-TsOH·H_2O	1.1	5.0	3.0
time	16 h	9 h	9 h
solvent	$CHCl_3$	MeCN	MeCN

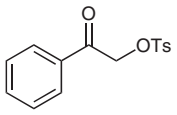
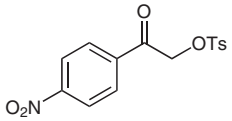
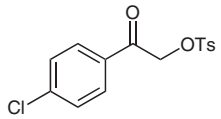
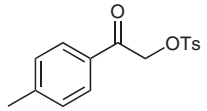
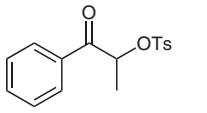
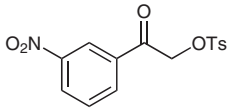
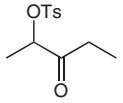
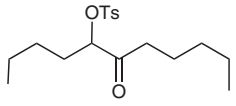
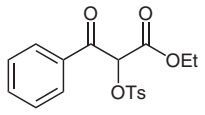
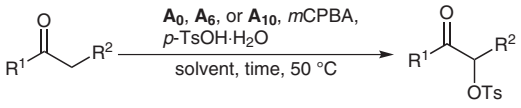
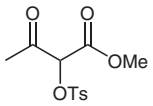
Entry	Product	Yields (%)		
		$\mathbf{A_0}$	$\mathbf{A_6}$	$\mathbf{A_{10}}$
1		28	71	85
2		–	77	88
3		–	77[a]	80[a]
4		–	69[b]	73[b]
5		–	64[c]	51[c]
6		–	–	86[d]
7		30	72	85
8		29	64	70
9		–	81	83
10		–	77	86
11		–	46	68[e]
12		–	54	77[e]
13		–	70[f]	75[f]

Table 1 α-Tosyloxylation of Ketones with *m*CPBA and *p*-TsOH·H_2O in the Presence of $\mathbf{A_0}$, $\mathbf{A_6}$, or $\mathbf{A_{10}}$ (continued)

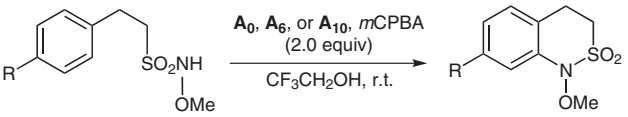


Ar-I	$\mathbf{A_0}$ (1.3 equiv)	$\mathbf{A_6}$ (0.5 equiv)	$\mathbf{A_{10}}$ (0.5 equiv)
*m*CPBA	1.1	2.5	2.5
p-TsOH·H_2O	1.1	5.0	3.0
time	16 h	9 h	9 h
solvent	$CHCl_3$	MeCN	MeCN

Entry	Product	Yields (%)		
		$\mathbf{A_0}$	$\mathbf{A_6}$	$\mathbf{A_{10}}$
14		–	70[g]	63[g]

[a] Yield with the first recovered polymer.
[b] Yield with the second recovered polymer.
[c] Yield with the third recovered polymer.
[d] Yield with the fourth recovered polymer, which was reduced by $NaBH_4$ in dioxane, before reuse.
[e] Reaction time was 1.5 h.
[f] Reaction time was 3 h.
[g] Reaction time was 1 h.

Table 2 Cyclization of *N*-Methoxy-2-arylethanesulfonamides with *m*CPBA in the Presence of $\mathbf{A_0}$, $\mathbf{A_6}$, or $\mathbf{A_{10}}$



$\mathbf{A_0}$ (1.5 equiv), 16 h
$\mathbf{A_6}$ (1.3 equiv), 9 h
$\mathbf{A_{10}}$ (1.0 equiv), 6 h

Entry	R	Yields		
		$\mathbf{A_0}$	$\mathbf{A_6}$	$\mathbf{A_{10}}$
1	H	75	74	75
2	H	–	79[a]	82[a]
3	H	–	76[b]	85[b]
4	H	–	82[c]	89[c]
5	CH_2Cl	–	61	65
6	Me	51[d]	62	67
7	Br	53	39	38
8	Cl	39	45	45

[a] Yield with the first recovered polymer.
[b] Yield with the second recovered polymer.
[c] Yield with the third recovered polymer.
[d] Reaction time was 24 h.

^1H and ^{13}C NMR spectra were obtained with Jeol JNM-GSX-400, Jeol JNM-LA-400, and Jeol JNM-LA-500 spectrometers. Chemical shifts (δ) are expressed in ppm downfield from TMS. Mass spectra were recorded with Jeol HX-110 or Jeol JMS-ATII15 spectrometers. IR spectra were measured with a Jasco FT/IR-4100 spectrometer. Melting points were determined with a Yamato melting point apparatus model MP-21. Silica gel 60 (Kanto Kagaku Co.) was used for column chromatography and Wakogel B-5F was used for preparative TLC. Cross-linked poly(*p*-chloromethyl)styrene (loading rate: 1.87 mmol/g) was obtained from Argonaut Technologies Co.

6-(*m*-Iodobenzyloxy)-1-hexanol and 10-(*m*-Iodobenzyloxy)-1-decanol; Typical Procedure

A solution of 6-(2′-tetrahydropyranyloxy)-1-hexanol (50 mmol, 10.11 g) in THF (25 mL) was stirred for 1 h with Na_2SO_4. After removal of Na_2SO_4 from the solution, NaH (1.3 equiv, 55% purity, 65 mmol, 2.83 g) was added at 0 °C and the obtained mixture was stirred for 2 h under an argon atmosphere. Then, *m*-iodobenzyl bromide (1.1 equiv, 55 mmol, 16.27 g) was added and the mixture was stirred at r.t. for 12 h. After the reaction, the mixture was quenched with H_2O (30 mL) and poured into Et_2O (50 mL). The organic layer was dried over Na_2SO_4. After filtration and removal of the solvent under reduced pressure, MeOH (100 mL) and *p*-TsOH·H_2O (0.4 equiv, 3.80 g) were added and the obtained mixture was stirred at r.t. for 3 h. After the reaction and removal of the solvent under reduced pressure, 6-(*m*-iodobenzyloxy)-1-hexanol was obtained in a crude state. Pure 6-(*m*-iodobenzyloxy)-1-hexanol was obtained in 95% yield by column chromatography on silica gel (EtOAc–hexane, 1:2).

6-(*m*-Iodobenzyloxy)-1-hexanol

^1H NMR (500 MHz, $CDCl_3$): δ = 1.34–1.44 (m, 4 H), 1.54–1.66 (m, 4 H), 3.46 (t, *J* = 6.5 Hz, 2 H), 3.62–3.68 (br s, 2 H), 4.44 (s, 2 H), 7.08 (t, *J* = 7.9, 7.6 Hz, 1 H), 7.29 (d, *J* = 7.6 Hz, 1 H), 7.61 (d, *J* = 7.9 Hz, 1 H), 7.69 (s, 1 H).

10-(*m*-Iodobenzyloxy)-1-decanol

^1H NMR (500 MHz, $CDCl_3$): δ = 1.25–1.39 (m, 12 H), 1.54–1.65 (m, 4 H), 3.46 (t, *J* = 6.5 Hz, 2 H), 3.61–3.67 (br s, 2 H), 4.42 (s, 2 H), 7.07 (t, *J* = 7.9, 7.6 Hz, 1 H), 7.29 (d, *J* = 7.6 Hz, 1 H), 7.60 (d, *J* = 7.9 Hz, 1 H), 7.70 (s, 1 H).

Polymer-Supported PhI $\mathbf{A_0}$, $\mathbf{A_6}$, and $\mathbf{A_{10}}$; Typical Procedure

A solution of 6-(*m*-iodobenzyloxy)-1-hexanol (1.42 equiv, 61 mmol, 20.4 g) in DMF (20 mL) was stirred for 1 h with Na_2SO_4. After removal of Na_2SO_4 from the solution, NaH (1.3 equiv, 80 mmol, 55% purity, 3.84 g) was added at 0 °C and the obtained mixture was stirred for 2 h under an argon atmosphere. Then, cross-linked poly(*p*-chloromethyl)styrene (loading rate: 1.87 mmol/g, 22.9 g) was added and the obtained mixture was stirred for 3 d at 60 °C. When the reaction was complete, H_2O was added and the precipitates were collected by filtration and washed with H_2O and then EtOH. The obtained solids were dried by vacuum pump to provide polymer-supported PhI $\mathbf{A_6}$ in 91% yield. Unreacted 6-(*m*-iodobenzyloxy)-1-hexanol (7.38 g) was recovered by removal of the solvent from the filtrate.

Polymer-Supported PhI $\mathbf{A_0}$

^1H NMR (500 MHz, $CDCl_3$): δ = 7.74 (s, 1 H), 7.63 (d, *J* = 8.0 Hz, 1 H), 7.33 (d, *J* = 7.6 Hz, 1 H), 7.10 (dd, *J* = 8.0, 7.6 Hz, 1 H), 4.66 (s, 2 H).

Anal. found: C, 75.55; H, 6.47; I, 16.01; loading rate: 1.26 mmol/g.

Polymer-Supported PhI $\mathbf{A_6}$

^1H NMR (500 MHz, $CDCl_3$): δ = 7.69 (s, 1 H), 7.60 (d, *J* = 8.0 Hz, 1 H), 7.28 (d, *J* = 7.6 Hz, 1 H), 7.07 (dd, *J* = 8.0, 7.6 Hz, 1 H), 4.42 (s, 2 H), 3.52 (t, *J* = 6.6 Hz, 2 H), 3.45 (t, *J* = 6.6 Hz, 2 H).

Anal. found: C, 77.28; H, 7.27; I, 11.62; loading rate: 1.09 mmol/g.

Polymer-Supported PhI A_{10}

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.69 (s, 1 H), 7.60 (d, *J* = 7.7 Hz, 1 H), 7.29 (d, *J* = 7.0 Hz, 1 H), 7.07 (dd, *J* = 7.7, 7.0 Hz, 1 H), 4.43 (s, 2 H), 3.52 (t, *J* = 6.7 Hz, 2 H), 3.45 (t, *J* = 6.4 Hz, 2 H).

Anal. found: C, 78.91; H, 7.45; I, 9.41; loading rate: 0.99 mmol/g.

α-Tosyloxylation of Ketones; Typical Procedure

To a solution of acetophenone (120 mg, 1 mmol) in MeCN (5 mL) were added polymer-supported PhI $\mathbf{A_{10}}$ (0.5 equiv, 444 mg), *p*-TsOH·H_2O (3.0 equiv, 570 mg), and *m*CPBA (65% purity, 2.5 equiv, 664 mg). The mixture was stirred for 9 h at 50 °C under an argon atmosphere. After the reaction, MeOH (5 mL) was added and the precipitated polymer-reagent was obtained by filtration and washed with Et_2O. The filtrate was poured into sat. aq $NaHCO_3$ and extracted with $CHCl_3$ (3 × 15 mL). The organic layer was dried over Na_2SO_4 and, after removal of the solvent under reduced pressure, α-tosyloxyacetophenone was obtained in a crude state (purity >90%). Pure α-tosyloxyacetophenone was obtained by short column chromatography on silica gel (EtOAc–hexane, 1:4) in 85% yield. Polymer-supported iodobenzene was recovered in 87% yield (386 mg).

α-Tosyloxyacetophenone

Mp 90 °C (Lit.[2h] 90–91 °C).

IR (KBr): 1180, 1360, 1715 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3 H), 5.27 (s, 2 H), 7.35 (d, *J* = 8.5 Hz, 2 H), 7.47 (t, *J* = 8.2 Hz, 2 H), 7.61 (t, *J* = 8.2 Hz, 1 H), 7.84 (d, *J* = 8.2 Hz, 2 H), 7.85 (d, *J* = 8.2 Hz, 2 H).

α-Tosyloxy-*p*-methylacetophenone

Mp 105 °C (Lit.[7] 82–83 °C).

IR (KBr): 1170, 1350, 1700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 2.45 (s, 3 H), 5.24 (s, 2 H), 7.26 (d, *J* = 8.1 Hz, 2 H), 7.35 (d, *J* = 8.2 Hz, 2 H), 7.74 (d, *J* = 8.1 Hz, 2 H), 7.86 (d, *J* = 8.2 Hz, 2 H).

α-Tosyloxy-*p*-chloroacetophenone

Mp 123 °C (Lit.[7] 125 °C).

IR (KBr): 1190, 1360, 1710 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3 H), 5.21 (s, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 7.45 (d, *J* = 8.6 Hz, 2 H), 7.80 (d, *J* = 8.6 Hz, 2 H), 7.84 (d, *J* = 8.4 Hz, 2 H).

α-Tosyloxy-*p*-nitroacetophenone

Mp 137 °C (Lit.[7] 130–131 °C).

IR (KBr): 1180, 1340, 1710 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 3 H), 5.25 (s, 2 H), 7.37 (d, *J* = 8.3 Hz, 2 H), 7.83 (d, *J* = 8.3 Hz, 2 H), 8.03 (d, *J* = 8.9 Hz, 2 H), 8.32 (d, *J* = 8.9 Hz, 2 H).

α-Tosyloxypropiophenone

Mp 68 °C (Lit.[7] 68–69 °C).

IR (KBr): 1170, 1370, 1700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.60 (d, *J* = 7.0 Hz, 3 H), 2.41 (s, 3 H), 5.79 (q, *J* = 7.0 Hz, 1 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 7.46 (t, *J* = 7.2 Hz, 2 H), 7.75 (d, *J* = 7.2 Hz, 2 H), 7.88 (d, *J* = 8.1 Hz, 2 H).

α-Tosyloxy-3-pentanone

Mp 45–46 °C (Lit.[2k] 43–44 °C).

IR (neat): 1190, 1360, 1720 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (t, *J* = 7.3 Hz, 3 H), 1.35 (d, *J* = 7.0 Hz, 3 H), 2.47 (s, 3 H), 2.60 (m, 2 H), 4.80 (q, *J* = 7.0 Hz, 1 H), 7.37 (d, *J* = 8.0 Hz, 2 H), 7.81 (d, *J* = 8.0 Hz, 2 H).

α-Tosyloxy-6-undecanone

Mp 72 °C (Lit.[3d] 72 °C).

IR (neat): 1190, 1380, 1720 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.70–0.80 (m, 3 H), 0.86–1.75 (m, 15 H), 2.46 (s, 3 H), 2.51 (t, *J* = 7.5 Hz, 2 H), 4.64 (dd, *J* = 8.0, 4.6 Hz, 1 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.80 (d, *J* = 8.0 Hz, 2 H).

Methyl α-Tosyloxyacetoacetate

Oil.

IR (neat): 1180, 1320, 1720 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 2.48 (s, 3 H), 3.71 (s, 3 H), 5.20 (s, 1 H), 7.38 (d, *J* = 8.5 Hz, 2 H), 7.83 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.66, 26.53, 53.27, 80.34, 128.18, 129.98, 132.02, 145.90, 163.86, 196.98.

HRMS (FAB): *m*/*z* [M + 1] calcd for $C_{12}H_{15}O_6S$: 287.0589; found: 287.0596.

Ethyl α-Tosyloxybenzoylacetate

Oil.

IR (neat): 1440, 1590, 1690 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (t, *J* = 7.0 Hz, 3 H), 2.85 (s, 3 H), 4.18 (m, 2 H), 5.59 (s, 1 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 7.46 (t, *J* = 7.5 Hz, 2 H), 7.61 (t, *J* = 7.5 Hz, 1 H), 7.79 (d, *J* = 8.5 Hz, 2 H), 7.93 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.75, 21.63, 62.80, 78.03, 128.24, 128.71, 129.34, 129.82, 132.34, 133.28, 134.36, 145.68, 164.12, 188.19.

HRMS (FAB): *m*/*z* [M + 1] calcd for $C_{18}H_{19}O_6S$: 363.0902; found: 363.0920.

α-Tosyloxy-*m*-nitroacetophenone

Mp 129–130 °C.

IR (KBr): 1615, 1375, 1348, 1188 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3 H), 5.25 (s, 2 H), 7.37 (d, *J* = 8.0 Hz, 2 H), 7.72 (t, *J* = 8.0 Hz, 1 H), 7.84 (d, *J* = 8.0 Hz, 2 H), 8.21 (dt, *J* = 8.0, 1.2 Hz, 1 H), 8.46 (dt, *J* = 8.0, 1.2 Hz, 1 H), 8.63 (t, *J* = 1.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.38, 69.87, 123.05, 128.15, 128.25, 130.03, 130.25, 132.35, 133.72, 135.29, 144.70, 145.88, 188.82.

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{15}H_{13}O_6NSNa$: 358.0356; found: 358.0347.

Benzosultams; Typical Procedure

To a solution of *N*-methoxy-2-phenylethanesulfonamide (0.5 mmol, 107.5 mg) and polymer-supported PhI $\mathbf{A_{10}}$ (1.0 equiv, 444 mg) in CF_3CH_2OH (3 mL) was added *m*CPBA (2.0 equiv, 1.0 mmol, 65% purity, 265 mg). The mixture was stirred for 6 h at r.t. under an argon atmosphere. After the reaction, MeOH (5 mL) was added and the precipitates were filtered and washed with Et_2O. The filtrate was poured into sat. aq $NaHCO_3$ and extracted with $CHCl_3$ (3 × 15 mL). The organic layer was dried over Na_2SO_4 and, after removal of the solvent under reduced pressure, *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxide was obtained in a crude state (purity >90%). Pure product was obtained by preparative TLC (silica gel; hexane–$CHCl_3$, 1:5) in 75% yield. Polymer-supported iodobenzene was recovered in 92% yield (409 mg).

***N*-Methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxide**
Mp 104.0–106.0 °C.

IR (KBr): 3000, 2950, 2815, 1580, 1480, 1360, 1170 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.42 (t, *J* = 6.4 Hz, 2 H), 3.50 (td, *J* = 6.4, 1.5 Hz, 2 H), 4.08 (s, 3 H), 7.20–7.23 (m, 1 H), 7.31–7.34 (m, 2 H), 7.36–7.40 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.86 (s), 40.20 (s), 65.57 (p), 126.72 (q), 127.88 (t), 128.03 (t), 128.90 (t), 129.41 (t), 141.88 (q).

MS (EI): *m*/*z* = 213 $[M]^+$.

Anal. Calcd for $C_9H_{11}NO_3S$: C, 50.69; H, 5.20; N, 6.57. Found: C, 50.76; H, 5.32; N, 6.58.

***N*-Methoxy-7-methyl-3,4-dihydro-2,1-benzothiazine-2,2-dioxide**
Mp 119.0–121.0 °C.

IR (KBr): 3000, 2950, 2815, 1620, 1500, 1360, 1170 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 3 H), 3.36 (t, *J* = 6.6 Hz, 2 H), 3.47 (t, *J* = 6.6 Hz, 2 H), 4.07 (s, 3 H), 7.08 (d, *J* = 7.9 Hz, 1 H), 7.12 (d, *J* = 7.9 Hz, 1 H), 7.18 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.99 (p), 27.56 (s), 40.20 (s), 65.68 (p), 123.61 (q), 128.27 (t), 129.32 (t), 130.07 (t), 138.22 (q), 141.63 (q).

MS (EI): *m*/*z* = 227 $[M]^+$.

Anal. Calcd for $C_{10}H_{13}NO_3S$: C, 52.85; H, 5.77; N, 6.16. Found: C, 52.80; H, 5.69; N, 6.14.

***N*-Methoxy-7-chloromethyl-3,4-dihydro-2,1-benzothiazine-2,2-dioxide**
Mp 120.0–122.5 °C.

IR (paraffin oil): 1360, 1280, 1236, 1170 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.40 (t, *J* = 6.5 Hz, 2 H), 3.49 (t, *J* = 6.5 Hz, 2 H), 4.09 (s, 3 H), 4.58 (s, 2 H), 7.21 (d, *J* = 8.0 Hz, 1 H), 7.34 (dd, *J* = 8.0, 1.9 Hz, 1 H), 7.39 (d, *J* = 1.9 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.61 (s), 40.11 (s), 44.92 (s), 65.69 (p), 126.69 (q), 127.44 (t), 128.80 (t), 129.84 (t), 137.59 (q), 141.96 (q).

MS (FAB): *m*/*z* = 261 $[M + 1]^+$.

Anal. Calcd for $C_{10}H_{12}ClNO_3S \cdot 1/5H_2O$: C, 45.44; H, 4.69; N, 5.30. Found: C, 45.44; H, 4.62; N, 5.24.

***N*-Methoxy-7-bromo-3,4-dihydro-2,1-benzothiazine-2,2-dioxide**
Mp 138.0–139.5 °C.

IR (paraffin oil): 1360, 1292, 1167 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.35 (t, *J* = 6.6 Hz, 2 H), 3.48 (t, *J* = 6.6 Hz, 2 H), 4.08 (s, 3 H), 7.08 (d, *J* = 8.4 Hz, 1 H), 7.42 (dd, *J* = 8.4, 2.0 Hz, 1 H), 7.52 (d, *J* = 2.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.50 (s), 40.24 (s), 65.86 (p), 120.94 (q), 125.51 (q), 130.00 (t), 130.73 (t), 131.71 (t), 142.94 (q).

MS (FAB): *m*/*z* = 291[M + 1]$^+$.

Anal. Calcd for $C_9H_{10}BrNO_3S$: C, 37.00; H, 3.45; N, 4.79. Found: C, 36.87; H, 3.43; N, 4.75.

***N*-Methoxy-7-chloro-3,4-dihydro-2,1-benzothiazine-2,2-dioxide**
Mp 123.0–125.0 °C.

IR (KBr): 3000, 2950, 2815, 1600, 1480, 1360, 1160 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.37 (t, *J* = 6.5 Hz, 2 H), 3.48 (t, *J* = 6.5 Hz, 2 H), 4.08 (s, 3 H), 7.14 (d, *J* = 8.2 Hz, 1 H), 7.27 (dd, *J* = 8.2, 2.2 Hz, 1 H), 7.36 (d, *J* = 2.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.55 (s), 40.42 (s), 65.95 (p), 125.08 (q), 127.14 (t), 128.92 (t), 130.60 (t), 133.53 (q), 142.90 (q).

MS (EI): *m*/*z* = 247 $[M]^+$.

Anal. Calcd for $C_9H_{10}ClNO_3S$: C, 43.64; H, 4.07; N, 5.65. Found: C, 43.39; H, 4.08; N, 5.52.

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