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Chromatography-Free and Eco-Friendly Synthesis of Aryl Tosylates and Mesylates

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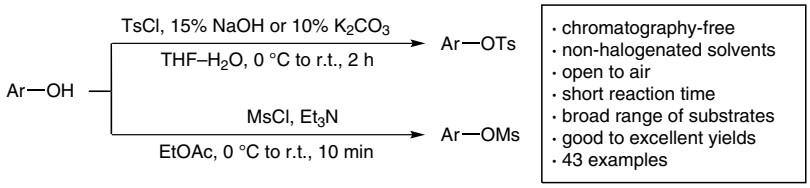

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Abstract Two chromatography-free and eco-friendly protocols have been developed to synthesize aryl tosylates and mesylates by the tosylation and mesylation of the corresponding hydroxyarenes, respectively. These protocols are superior to other known ones regarding the simplicity, reaction time and conditions, the range of substrates, yields, and environmental friendliness.

Key words aryl tosylates, aryl mesylates, tosylation, mesylation, green chemistry

Introduction

Aryl tosylates and mesylates are important intermediates in organic synthesis.[1] Recently, they have attracted considerable attention as the alternative electrophiles to aryl halides in the transition-metal-catalyzed cross-coupling reactions.[2] Substitution of aryl halides with aryl tosylates and mesylates can make chemical processes more environmentally friendly by reducing the production of halide waste.

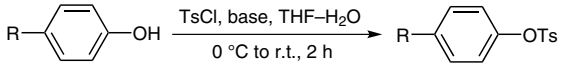
Various methods have been reported to prepare aryl tosylates and mesylates. The methods for the synthesis of aryl tosylates include transition-metal-catalyzed sulfonylation,[3] solvent-free synthesis with[4] or without[5] microwave activation, heteropolyacid-catalyzed tosylation,[6] reaction of phenols with thiols using H_2O_2/$POCl_3$ system,[7] and tosyloxylation of anilides.[8] Aryl mesylates have been synthesized via one-pot demethylation–mesylation of aryl methyl ethers[9] and thermal decomposition of dry arenediazonium *o*-benzenedisulfonimides in methanesulfonic acid.[10] However, these methods have one or more drawbacks, such as long reaction time, high temperature, low reactivity for phenols bearing electron-withdrawing groups, and requirement for special equipment or reagent. Currently, the sulfonation of hydroxyarenes with tosyl chloride (TsCl) or mesyl chloride (MsCl) in the presence of an amine base such as pyridine and triethylamine in an anhydrous organic solvent such as dichloromethane is the prevailing method to prepare aryl tosylates[1b,2d,11] and mesylates,[1a,c,d,2c,12] respectively. Although this conventional method is mostly simple and efficient, it involves halogenated solvent, anhydrous conditions, and inert atmosphere, and the products need to be purified by recrystallization or column chromatography in most cases. Herein, we report the chromatography-free, environmentally friendly, and economically viable methods for the synthesis of aryl tosylates and mesylates.

Scope and Limitations

In order to optimize the tosylation conditions, ethyl 4-hydroxybenzoate (**A**), whose ester group is subject to hydrolysis under basic conditions, and 4-methoxyphenol (**B**), whose methoxy group is inert under basic conditions, were chosen as model substrates (Table 1). During this study the reactions were monitored by thin-layer chromatography. Generally, both substrates **A** and **B** were completely consumed within two hours, so the reaction time was set as two hours for all reactions. In order to reduce organic waste, only readily available and inexpensive inorganic bases, including NaOH, KOH, Na_2CO_3, and K_2CO_3, were examined. It has been reported that water is an efficient solvent for the tosylation of alkanols.[13] However, using water as the sole solvent, the reactions of phenols **A** and **B** with TsCl, respectively, in the presence of 5% NaOH were sluggish because of their poor solubility in water. According to the solvent selection guide,[14] THF is an usable solvent while ethyl acetate is a preferred solvent for organic reactions and workup. Therefore, THF was chosen, in which most hy-

droxyarenes are soluble, as solvent for the tosylation reactions and ethyl acetate for the subsequent workup. TsCl is subject to hydrolysis under basic conditions at ambient temperature, so it is critical to control the reaction temperature at 0 °C during its addition. After the bases, solvent, and reaction temperature were selected, the use of TsCl and bases was optimized and tested at different concentrations of strong bases to obtain pure aryl tosylates in high yields. In order to compensate for its loss due to hydrolysis, extra TsCl was needed, but too much TsCl might result in impure product with TsCl as impurity. As shown in Table 1, an amount of 1.20 equivalents of TsCl was needed when NaOH or KOH was used as base (entries 1–3 and 6–8). Due to its slower hydrolysis in weaker bases such as 10% Na_2CO_3 and 10% K_2CO_3, an amount of 1.01 equivalents of TsCl were enough (entries 4, 5, 9, and 10). For the tosylation of substrate **A**, when 5% NaOH was used as the base, an amount of 3.30 equivalents of base gave a higher yield (entries 1 and 2). The increase of the concentration of NaOH solution resulted in lower yields (entries 2 and 3), which is probably due to the faster hydrolysis of the ethyl ester group in the more concentrated NaOH solution. Pleasingly, substitution of strong bases with relatively weaker base 10% Na_2CO_3 or 10% K_2CO_3 gave almost quantitative yields (entries 4 and 5). For substrate **B**, which is a weaker acid than substrate **A**, among all bases examined, 15% NaOH gave the best yield (entries 6–10). Therefore, for phenols with functional groups that are reactive under basic conditions, the optimal tosylation conditions were set as entry 5 in Table 1, while for phenols with functional groups that are inert under basic conditions, the optimal tosylation conditions were set as entry 7 in Table 1.

Table 1 Optimization of Tosylation Conditions[a]



A: R = CO_2Et
B: R = OMe

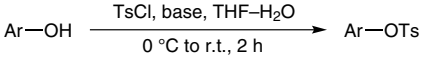
Entry	Substrate	Base	Molar ratio (phenol/TsCl/base)	Yield (%)[b]
1	**A**	5% NaOH	1.00:1.20:2.40	85
2	**A**	5% NaOH	1.00:1.20:3.30	91
3	**A**	10% NaOH	1.00:1.20:3.30	83
4	**A**	10% Na_2CO_3	1.00:1.01:1.88	98
5	**A**	10% K_2CO_3	1.00:1.01:1.88	99
6	**B**	10% NaOH	1.00:1.20:3.30	89
7	**B**	15% NaOH	1.00:1.20:3.30	96
8	**B**	10% KOH	1.00:1.20:3.30	87
9	**B**	10% Na_2CO_3	1.00:1.01:1.88	93
10	**B**	10% K_2CO_3	1.00:1.01:1.88	94

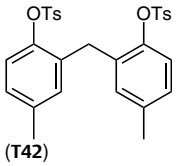
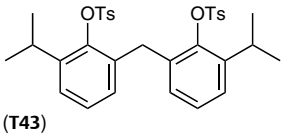
[a] Reaction conditions: phenol (25.0 mmol), base (aq solution in wt%), and THF (15 mL to dissolve phenol and 35 mL to dissolve TsCl).
[b] Isolated yields.

With the optimized reaction conditions in hand, the scope of these new tosylation protocol was explored. A wide range of commercially available or readily prepared hydroxyarenes with various steric and electronic properties were examined, and the results are summarized in Table 2. With 15% NaOH as base, the tosylation of monohydric phenols bearing electron-donating groups, which are stable under basic conditions, and unsubstituted phenols and naphthalenols gave the corresponding aryl tosylates in excellent yields (entries 1–14). For the same substrates, substitution of 15% NaOH with 10% K_2CO_3 as base generally resulted in lower yields of aryl tosylates (entries 5–7 and 9–11). The yield difference is particularly notable for substrates bearing a bulky allyl (entry 5) or *tert*-butyl group (entries 6 and 7) and for the one with methoxy groups on both *ortho*-positions (entry 11). These results confirm that 15% NaOH is a better choice as base for substrates that are relatively weaker acids. Monohydric phenols bearing electron-withdrawing groups are stronger acids than those unsubstituted and those with electron-donating groups. With 10% K_2CO_3 as base, their tosylation yielded the corresponding tosylates in excellent yields (entries 15–31), which demonstrates that our tosylation method is superior to others that gave somewhat lower yields of tosylates for phenols bearing electron-withdrawing groups.[3,5] The tosylation protocol with 15% NaOH as base worked efficiently for the synthesis of heteroaryl tosylates (entries 32–36) that have potential applications in the synthesis of biologically active molecules. With 15% NaOH as base, the tosylation of dihydric phenols and naphthalenols and bisphenols also gave good to excellent yields (entries 37–43). Slight steric effects were observed as the substrates with substituents at the *ortho*-position(s) generally have lower yields than their isomers with substituents on the *para*- or *meta*-position(s) under the same reaction conditions (entries 8, 11, 16, 21, 28, and 30). Notably, for all these tosylation reactions, the workup procedure was very simple and straight-forward. After the reaction was complete, a two-phase mixture was obtained with the organic layer on the top and the aqueous layer at the bottom. Since an excess of base was used in the procedure, any unreacted hydroxyarene would stay in the aqueous phase as its sodium or potassium salt during extraction with ethyl acetate. Pure tosylates were obtained without further purification, and many of these aryl tosylates in Table 2 have been successfully used in the nickel-catalyzed cross-coupling reactions in our laboratory.[2a] However, this tosylation method did not work efficiently on several substrates (not shown in Table 2). Thus, the tosylation of 1,5-dihydroxynaphthalene did not yield the pure ditosylate due to its poor solubility under the optimal reaction conditions. With 2-hydroxypyridine as substrate, the product is a mixture resulting from O-tosylation and N-to-

sylation due to the presence of two tautomers and therefore two reactive sites.[15] For the extremely bulky substrate such as 2,6-di-*tert*-butyl-4-methylphenol, a mixture of the starting phenol and the desired tosylate was obtained when 15% NaOH was used as base under the optimal reaction conditions. For these substrates, no further study was carried out to optimize their tosylation conditions.

Table 2 Scope of the Tosylation Protocol[a]



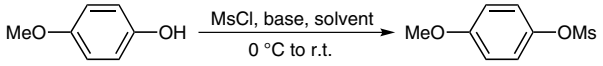
Entry	ArOTs	Yield (%)[b]
1	4-MeC_6H_4OTs (**T1**)	99[c]
2	3-MeC_6H_4OTs (**T2**)	99[c]
3	2-MeC_6H_4OTs (**T3**)	99[c]
4	2,5-$Me_2C_6H_3OTs$ (**T4**)	98[c]
5	2-$AllylC_6H_4OTs$ (**T5**)	100[c], 76[d]
6	4-*t*-BuC_6H_4OTs (**T6**)	99[c], 71[d]
7	3-*t*-BuC_6H_4OTs (**T7**)	99[c], 83[d]
8	2,4-(*t*-Bu)$_2C_6H_3OTs$ (**T8**)	97[c]
9	4-$MeOC_6H_4OTs$ (**T9**)	96[c], 94[d]
10	2-$MeOC_6H_4OTs$ (**T10**)	99[c], 98[d]
11	2,6-$(MeO)_2C_6H_3OTs$ (**T11**)	90[c], 62[d]
12	PhOTs (**T12**)	100[c]
13	1-TsO-naphthalene (**T13**)	96[c]
14	2-TsO-naphthalene (**T14**)	100[c]
15	4-ClC_6H_4OTs (**T15**)	94[d]
16	2,4-$Cl_2C_6H_3OTs$ (**T16**)	98[d]
17	4-$CHOC_6H_4OTs$ (**T17**)	96[d]
18	1-CHO-2-TsO-naphthalene (**T18**)	94[d]
19	4-AcC_6H_4OTs (**T19**)	100[d]
20	3-AcC_6H_4OTs (**T20**)	99[d]
21	2-AcC_6H_4OTs (**T21**)	95[d]
22	4-$AcNHC_6H_4OTs$ (**T22**)	99[d]
23	4-$CO_2EtC_6H_4OTs$ (**T23**)	99[d]
24	3,5-$(CO_2Me)_2C_6H_3OTs$ (**T24**)	95[d]
25	4-CNC_6H_4OTs (**T25**)	99[d]
26	3,5-$F_2C_6H_3OTs$ (**T26**)	96[d]
27	3-$F_3CC_6H_4OTs$ (**T27**)	100[d]
28	2-$F_3CC_6H_4OTs$ (**T28**)	97[d]
29	4-$O_2NC_6H_4OTs$ (**T29**)	96[d]
30	2-$O_2NC_6H_4OTs$ (**T30**)	96[d]
31	4-$F_3COC_6H_4OTs$ (**T31**)	99[d]
32	3-TsO-pyridine (**T32**)	93[c]
33	8-TsO-quinoline (**T33**)	98[c]
34	1-Me-5-TsO-pyrazole (**T34**)	88[c]
35	2,4-Me_2-3-TsO-thiophene (**T35**)	93[c]
36	4-TsO-coumarin (**T36**)	77[c]
37	1,2-$(TsO)_2$-benzene (**T37**)	84[e]
38	1,3-$(TsO)_2$-benzene (**T38**)	82[e]
39	1,4-$(TsO)_2$-benzene (**T39**)	75[e]
40	2,3-$(TsO)_2$-naphthalene (**T40**)	96[e]
41	2,7-$(TsO)_2$-naphthalene (**T41**)	72[e]
42	 (**T42**)	94[e]
43	 (**T43**)	94[e]

[a] Reaction conditions: ArOH (25.0 mmol), TsCl (5.72 g, 30.0 mmol when 15% NaOH was used as base or 4.81 g, 25.2 mmol when 10% K_2CO_3 was used as base), and THF (15 mL to dissolve ArOH and 35 mL to dissolve TsCl).
[b] Isolated yields.
[c] Base: 15% NaOH (22.00 g, 82.5 mmol).
[d] Base: 10% K_2CO_3 (65.00 g, 47.0 mmol).
[e] TsCl (11.44 g, 60.0 mmol), 15% NaOH (44.00 g, 165.0 mmol), and THF (15 mL to dissolve ArOH and 70 mL to dissolve TsCl).

For the mesylation of hydroxyarenes, the mesylation of 4-methoxyphenol with MsCl was chosen as a model reaction to optimize the reaction conditions. As shown in Table 3, initially the above tosylation methods that use THF as solvent and inorganic 5% NaOH or 10% K_2CO_3 as base were attempted. Unfortunately, a mixture of the starting phenol and its mesylate was obtained in each case (entries 1, 2). Since MsCl is more reactive to water than TsCl, solid K_2CO_3 powder was used as base to reduce the hydrolysis of MsCl. Again, however, a mixture was obtained (entry 3), which was probably due to the poor solubility of K_2CO_3 in THF. In order to facilitate the mesylation reaction, the organic base, triethylamine, was chosen because it is readily available and superior to pyridine in the sulfonylation reactions.[16] With triethylamine as the base and THF as the solvent, the mesylation reaction was complete within 10 minutes after MsCl was added in one portion into the reaction mixture at 0 °C (entry 4). The same reaction in ethyl acetate also gave an excellent yield in 10 minutes (entry 5). For both reactions, good stirring was needed because thick slurry was formed right after the addition of MsCl. Since the solvents THF and ethyl acetate were used as received and may contain a trace amount of water, an excess amount of MsCl was used to compensate for its hydrolysis by residual water in

the solvent. Between THF and ethyl acetate, ethyl acetate is preferred because it is more eco-friendly than THF.[14] In addition, with ethyl acetate as solvent, it is not necessary to use additional solvent in the workup step, and the separation is generally easier and faster. Therefore, the optimal reaction conditions for mesylation were set as entry 5 in Table 3.

Table 3 Optimization of Mesylation Conditions[a]



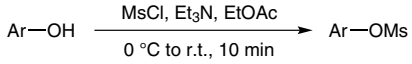
Entry	Solvent	Base	Molar ratio (phenol/MsCl/base)	Time	Yield (%)[b]
1	THF	5% NaOH	1.00:1.25:2.00	2 h	–[c]
2	THF	10% K_2CO_3	1.00:1.45:2.40	2 h	–[c]
3	THF	K_2CO_3	1.00:1.25:2.00	24 h	–[c]
4	THF	Et_3N	1.00:1.25:2.00	10 min	99
5	EtOAc	Et_3N	1.00:1.25:2.00	10 min	99

[a] Reaction conditions: 4-methoxyphenol (25.0 mmol) and solvent (75 mL).
[b] Isolated yields.
[c] Not isolated.

In order to define the scope of the mesylation protocol, a wide range of commercially available or readily prepared hydroxyarenes with various steric and electronic properties were examined, and the results are summarized in Table 4. No obvious electronic effects were observed as all substrates bearing electron-donating (entries 1–11) or electron-withdrawing (entries 15–31) groups and unsubstituted substrates (entries 12–14) gave excellent yields. This method is also applicable to the synthesis of heteroaryl mesylates (entries 32–36) and dimesylates (entries 37–43), giving good to excellent yields. Only slight steric effects were observed in several cases (entries 8 and 11). In all cases aryl mesylates were obtained in high purity without further purification, as side product triethylamine hydrochloride salt and any remaining MsCl and triethylamine were removed by washing with water in the workup step. Again, many of these aryl mesylates have been successfully used in the Ni-catalyzed cross-coupling reactions in our laboratory, and the manuscript is in preparation for publication. Similar to the tosylation protocol, however, the mesylation of 1,5-dihydroxynaphthalene, 2-hydroxypyridine, and 2,6-di-*tert*-butyl-4-methylphenol did not yield pure mesylate under the optimal reaction conditions.

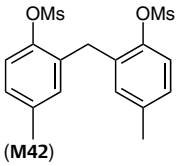
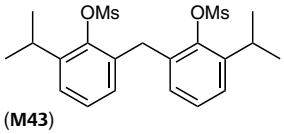
In conclusion, we have developed two efficient and practical protocols to synthesize aryl tosylates and mesylates, respectively, in good to excellent yields. All reactions were carried out in nonhalogenated solvents in open air with short reaction times. These protocols are simple, chromatography-free, environmentally friendly, economically viable, and applicable to a wide range of substrates. This first systematic investigation of tosylation and mesylation of hydroxyarenes provides a useful catalogue to the synthetic chemistry community as both aryl tosylates and mesylates are important substrates in a variety of organic reactions.

Table 4 Scope of the Mesylation Protocol[a]



Entry	ArOMs	Yield (%)[b]
1	4-MeC_6H_4OMs (**M1**)	100
2	3-MeC_6H_4OMs (**M2**)	100
3	2-MeC_6H_4OMs (**M3**)	100
4	2,5-$Me_2C_6H_3OMs$ (**M4**)	98
5	2-$AllylC_6H_4OMs$ (**M5**)	98
6	4-*t*-BuC_6H_4OMs (**M6**)	100
7	3-*t*-BuC_6H_4OMs (**M7**)	98
8	2,4-*t*-$Bu_2C_6H_3OMs$ (**M8**)	94
9	4-$MeOC_6H_4OMs$ (**M9**)	99
10	2-$MeOC_6H_4OMs$ (**M10**)	97
11	2,6-$(MeO)_2C_6H_3OMs$ (**M11**)	90
12	PhOMs (**M12**)	97
13	1-MsO-naphthalene (**M13**)	99
14	2-MsO-naphthalene (**M14**)	94
15	4-ClC_6H_4OMs (**M15**)	97
16	2,4-$Cl_2C_6H_3OMs$ (**M16**)	97
17	4-$CHOC_6H_4OMs$ (**M17**)	96
18	1-CHO-2-MsO-naphthalene (**M18**)	96
19	4-AcC_6H_4OMs (**M19**)	99
20	3-AcC_6H_4OMs (**M20**)	98
21	2-AcC_6H_4OMs (**M21**)	97
22	4-$AcNHC_6H_4OMs$ (**M22**)	88
23	4-$CO_2EtC_6H_4OMs$ (**M23**)	99
24	3,5-$(CO_2Me)_2C_6H_3OMs$ (**M24**)	97
25	4-CNC_6H_4OMs (**M25**)	98
26	3,5-$F_2C_6H_3OMs$ (**M26**)	99
27	3-$CF_3C_6H_4OMs$ (**M27**)	97
28	2-$CF_3C_6H_4OMs$ (**M28**)	96
29	4-$NO_2C_6H_4OMs$ (**M29**)	97
30	2-$NO_2C_6H_4OMs$ (**M30**)	94
31	4-$CF_3OC_6H_4OMs$ (**M31**)	98
32	3-MsO-pyridine (**M32**)	71
33	8-MsO-quinoline (**M33**)	85
34	1-Me-5-MsO-pyrazole (**M34**)	74
35	2,4-Me_2-3-MsO-thiophene (**M35**)	99
36	4-MsO-coumarin (**M36**)	92
37	1,2-$(MsO)_2$-benzene (**M37**)	98[c]

Table 4 (continued)

Entry	ArOMs	Yield (%)[b]
38	1,3-$(MsO)_2$-benzene (**M38**)	99[c]
39	1,4-$(MsO)_2$-benzene (**M39**)	70[c]
40	2,3-$(MsO)_2$-naphthalene (**M40**)	88[c]
41	2,7-$(MsO)_2$-naphthalene (**M41**)	91[c]
42	 (**M42**)	96[c]
43	 (**M43**)	92[c]

[a] Reaction conditions: ArOH (25.0 mmol), MsCl (3.72 g, 32.5 mmol), Et_3N (5.06 g, 50.0 mmol), and EtOAc (75 mL).
[b] Isolated yields.
[c] MsCl (7.44 g, 65.0 mmol), Et_3N (10.12 g, 100.0 mmol), and EtOAc (150 mL).

All reactions were carried out in open air. Except for two phenols (entries 42 and 43 in Tables 2 and 4) that were synthesized by literature procedures,[17] reagents and solvents were purchased from commercial suppliers and used as received. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer, and chemical shifts were reported in ppm relative to TMS at δ = 0.00 as an internal reference. Melting points were determined using a Mel-Temp melting point apparatus and are uncorrected. TLC was carried out on precoated silica gel plates with PF254 indicator. High-resolution mass spectra (HRMS) were obtained using a quadrupole instrument using either electron ionization (EI) or electrospray ionization (ESI) as the ionization method. Characterization data of new aryl tosylates and mesylates and those known, but not fully characterized are shown below.

Aryl Tosylates T1–T43; General Procedure

To a solution of hydroxyarene (25.0 mmol) in THF (15 mL) was added 10% K_2CO_3 (65.00 g, 47.1 mmol) or 15% NaOH (22.00 g, 82.5 mmol) as an aq solution (wt%). After the resulting solution was cooled to 0 °C with an ice-water bath, a solution of TsCl (4.82 g, 25.3 mmol for 10% K_2CO_3 or 5.72 g, 30.0 mmol for 15% NaOH) in THF (35 mL) was slowly added over 15 min at 0 °C. After the addition of TsCl, the ice-water bath was removed and the reaction mixture was stirred for 2 h. To the mixture was then added EtOAc (100 mL; more was needed when aryl tosylate had poor solubility in EtOAc). The two-phase mixture was separated. The organic layer was washed with H_2O (50 mL) and dried ($MgSO_4$). Removal of solvent under reduced pressure gave the corresponding pure aryl tosylate. Any trace amount of TsCl, if present, can be removed by simply washing the product with hexanes (Table 2).

Aryl Mesylates M1–M43; General Procedure

To a solution of hydroxyarene (25.0 mmol) in EtOAc (75 mL) at 0 °C was added Et_3N (5.06 g, 50.0 mmol) followed by MsCl (3.72 g, 32.5 mmol). After the addition of MsCl, the ice-water bath was removed and the resulting thick slurry was vigorously stirred for 10 min. To the slurry was then added H_2O (50 mL). The two-phase mixture was separated. The organic layer was washed with H_2O (25 mL) and dried ($MgSO_4$). Removal of solvent under reduced pressure gave the corresponding pure aryl mesylate (Table 4).

3-*tert*-Butylphenyl Tosylate (T7)

Yield: 7.56 g (99%); pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 7.6 Hz, 2 H), 7.32 (d, *J* = 7.5 Hz, 2 H), 7.30–7.20 (m, 2 H), 6.88 (d, *J* = 7.5 Hz, 1 H), 6.83 (s, 1 H), 2.46 (s, 3 H), 1.20 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.2, 149.6, 145.3, 132.5, 129.6, 129.1, 128.7, 123.9, 119.6, 119.5, 34.7, 31.0, 21.8.

HRMS (EI): *m*/*z* (M^+) calcd for $C_{17}H_{20}O_3S$: 304.1133; found: 304.1135.

2,4-Di-*tert*-butylphenyl Tosylate (T8)

Yield: 8.78 g (97%); white solid; mp 56–58 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.3 Hz, 2 H), 7.39–7.35 (m, 3 H), 7.16–7.11 (m, 2 H), 2.46 (s, 3 H), 1.35 (s, 9 H), 1.28 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.5, 147.3, 145.1, 140.2, 134.9, 129.9, 128.0, 124.9, 123.9, 119.8, 34.9, 34.6, 31.4, 30.5, 21.7.

HRMS (ESI): *m*/*z* (M + Na)$^+$ calcd for $C_{21}H_{28}O_3SNa$: 383.1657; found: 383.1654.

2,6-Dimethoxyphenyl Tosylate (T11)

Yield: 6.92 g (90%); white solid; mp 95–97 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.3 Hz, 2 H), 7.32 (d, *J* = 8.5 Hz, 2 H), 7.12 (t, *J* = 8.4 Hz, 1 H), 6.54 (d, *J* = 8.5 Hz, 2 H), 3.66 (s, 6 H), 2.45 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.6, 144.4, 135.0, 129.1, 128.4, 128.3, 127.4, 105.0, 55.9, 21.6.

HRMS (ESI): *m*/*z* (M + H)$^+$ calcd for $C_{15}H_{17}O_5S$: 309.0797; found: 309.0794.

1-Formylnaphthalen-2-yl Tosylate (T18)

Yield: 7.70 g (94%); white solid; mp 130–132 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.39 (s, 1 H), 9.15 (d, *J* = 8.5 Hz, 1 H), 8.05 (d, *J* = 8.8 Hz, 1 H), 7.86 (d, *J* = 8.1 Hz, 1 H), 7.73 (d, *J* = 8.6 Hz, 2 H), 7.68–7.64 (m, 1 H), 7.58–7.55 (m, 1 H), 7.36 (d, *J* = 8.7 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 1 H), 2.46 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.9, 153.2, 146.5, 136.5, 132.1, 131.3, 130.7, 130.3, 129.9, 128.6, 128.4, 127.2, 125.8, 123.0, 121.4, 21.8.

HRMS (ESI): *m*/*z* (M + H)$^+$ calcd for $C_{18}H_{15}O_4S$: 327.0691; found: 327.0692.

3,5-Difluorophenyl Tosylate (T26)

Yield: 6.84 g (96%); white solid; mp 60–62 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.3 Hz, 2 H), 7.35 (d, *J* = 8.3 Hz, 2 H), 6.73 (tt, *J* = 6.5, 2.3 Hz, 1 H), 6.60 (dd, *J* = 7.1, 2.0 Hz, 2 H), 2.47 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.8 (dd, *J* = 250.6, 14.4 Hz), 150.6 (t, *J* = 13.9 Hz), 146.1, 131.8, 130.1, 128.5, 106.7 (m), 103.0 (t, *J* = 25.7Hz), 21.8.

HRMS (EI): *m*/*z* (M^+) calcd for $C_{13}H_{10}F_2O_3S$: 284.0319; found: 284.0323.

1-Methyl-1*H*-pyrazol-5-yl Tosylate (T34)

Yield: 5.55 g (88%); white solid; mp 69–71 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.3 Hz, 2 H), 7.37 (d, *J* = 8.1 Hz, 2 H), 7.31 (d, *J* = 2.2 Hz, 1 H), 5.69 (d, *J* = 2.3 Hz, 1 H), 3.56 (s, 3 H), 2.48 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.6, 143.1, 138.1, 131.2, 130.1, 128.8, 95.2, 34.8, 21.8.

HRMS (ESI): *m*/*z* (M + H)$^+$ calcd for $C_{11}H_{13}N_2O_3S$: 253.0647; found: 253.0647.

2,4-Dimethylthiophen-3-yl Tosylate (T35)

Yield: 6.57 g (93%); off-white solid; mp 60–62 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.6 Hz, 2 H), 7.35 (d, *J* = 8.8 Hz, 2 H), 6.62 (s, 1 H), 2.46 (s, 3 H), 2.04 (s, 3 H), 1.89 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.5, 141.0, 133.2, 131.7, 129.9, 128.6, 128.5, 116.5, 21.7, 13.3, 12.0.

HRMS (ESI): *m*/*z* (M + H)$^+$ calcd for $C_{13}H_{15}O_3S_2$: 283.0463; found: 283.0461.

2,3-Ditosyloxynaphthalene (T40)

Yield: 11.20 g (96%); white solid; mp 182–184 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.76 (dd, *J* = 6.3, 3.3 Hz, 2 H), 7.72 (s, 2 H), 7.66 (d, *J* = 8.5 Hz, 4 H), 7.53–7.51 (dd, *J* = 6.3, 3.3 Hz, 2 H), 7.26 (d, *J* = 8.6 Hz, 4 H), 2.44 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.7, 139.4, 132.2, 131.6, 129.7, 128.6, 127.8, 127.3, 122.4, 21.8.

HRMS (ESI): *m*/*z* (M + H)$^+$ calcd for $C_{24}H_{21}O_6S_2$: 469.0780; found: 469.0780.

2,2′-Methylenebis(4-methylphenyl) Ditosylate (T42)

Yield: 12.60 g (94%); white solid; mp 115–117 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.3 Hz, 4 H), 7.31 (d, *J* = 8.0 Hz, 4 H), 6.95–6.91 (m, 4 H), 6.65 (s, 2 H), 3.52 (s, 2 H), 2.45 (s, 6 H), 2.20 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.9, 145.4, 136.8, 133.0, 132.5, 131.8, 129.9, 128.4, 128.1, 121.9, 29.3, 21.7, 20.9.

HRMS (ESI): *m*/*z* (M + H)$^+$ calcd for $C_{29}H_{29}O_6S_2$: 537.1406; found: 537.1404.

2,2′-Methylenebis[6-(1-methylethyl)phenyl] Ditosylate (T43)

Yield: 13.91 g (94%); white solid; mp 158–160 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.2 Hz, 4 H), 7.32 (d, *J* = 8.0 Hz, 4 H), 7.17 (dd, *J* = 7.8, 1.7 Hz, 2 H), 7.09 (dd, *J* = 7.8, 7.8 Hz, 2 H), 6.72 (dd, *J* = 7.6, 1.6 Hz, 2 H), 3.84 (s, 2 H), 3.30 (sept, *J* = 6.8 Hz, 2 H), 1.15 (d, *J* = 6.8 Hz, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.5, 145.2, 142.9, 134.3, 134.0, 129.9, 128.8, 128.0, 127.2, 125.3, 31.5, 27.5, 23.6, 21.7.

HRMS (ESI): *m*/*z* (M + H)$^+$ calcd for $C_{33}H_{37}O_6S_2$: 593.2032; found: 593.2030.

2-Allylphenyl Mesylate (M5)

Yield: 5.19 g (98%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.22 (m, 4 H), 5.99–5.89 (m, 1 H), 5.13–5.08 (m, 2 H), 3.49 (d, *J* = 6.6 Hz, 2 H), 3.17 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.4, 135.6, 133.0, 131.1, 127.8, 127.3, 122.0, 116.8, 38.2, 34.2.

HRMS (EI): *m*/*z* (M$^+$) calcd for $C_{10}H_{12}O_3S$: 212.0507; found: 212.0506.

3-*tert*-Butylphenyl Mesylate (M7)

Yield: 5.59 g (98%); pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.27 (m, 3 H), 7.10 (dd, *J* = 6.8, 2.2 Hz, 1 H), 3.12 (s, 3 H), 1.32 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.9, 149.3, 129.5, 124.4, 119.2, 118.8, 37.2, 34.9, 31.2.

HRMS (EI): *m*/*z* (M$^+$) calcd for $C_{11}H_{16}O_3S$: 228.0820; found: 228.0822.

2,4-Di-*tert*-butylphenyl Mesylate (M8)

Yield: 6.67 g (94%); white solid; mp 58–60 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.41 (m, 2 H), 7.22 (dd, *J* = 8.4, 2.5 Hz, 1 H), 3.23 (s, 3 H), 1.42 (s, 9 H), 1.31 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.9, 146.6, 139.8, 125.1, 124.3, 119.9, 39.1, 34.9, 34.7, 31.4, 30.5.

HRMS (EI): *m*/*z* (M$^+$) calcd for $C_{15}H_{24}O_3S$: 284.1446; found: 284.1447.

2,4-Dichlorophenyl Mesylate (M16)

Yield: 5.85 g (97%); pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 2.5 Hz, 1 H), 7.40–7.37 (d, *J* = 8.8 Hz, 1 H), 7.31–7.28 (dd, *J* = 8.8, 2.5 Hz, 1 H), 3.25 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.9, 133.4, 130.6, 128.4, 127.8, 125.4, 38.8.

HRMS (EI): *m*/*z* (M$^+$) calcd for $C_7H_6Cl_2O_3S$: 239.9415; found: 239.9417.

4-Ethoxycarbonylphenyl Mesylate (M23)[18]

Yield: 6.06 g (99%); white solid; mp 40–42 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 6.8 Hz, 2 H), 7.36 (d, *J* = 6.8 Hz, 2 H), 4.36 (q, *J* = 7.3 Hz, 2 H), 3.19 (s, 3 H), 1.40 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.4, 152.4, 131.6, 129.6, 121.9, 61.4, 37.8, 14.3.

HRMS (ESI): *m*/*z* (M + H)$^+$ calcd for $C_{10}H_{13}O_5S$: 245.0484; found: 245.0481.

Dimethyl 5-Mesyloxyisophthalate (M24)

Yield: 7.01 g (97%); white solid; mp 143–145 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (t, *J* = 1.5 Hz, 1 H), 8.12 (d, *J* = 1.5 Hz, 2 H), 3.97 (s, 6 H), 3.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.9, 149.0, 132.7, 129.4, 127.4, 52.8, 38.0.

HRMS (ESI): *m*/*z* (M + H)$^+$ calcd for $C_{11}H_{13}O_7S$: 289.0382; found: 289.0378.

2-(Trifluoromethyl)phenyl Mesylate (M28)

Yield: 5.80 g (96%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 7.8 Hz, 1 H), 7.62–7.57 (m, 2 H), 7.38 (dd, *J* = 7.2, 7.2 Hz, 1 H), 3.22 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.6 (q, *J* = 2.2 Hz), 133.8, 127.7 (q, *J* = 5.2 Hz), 127.0, 123.1, 122.8 (q, *J* = 272.0 Hz), 122.6 (q, *J* = 32.0 Hz), 33.9.

HRMS (EI): *m*/*z* (M$^+$) calcd for $C_8H_7F_3O_3S$: 240.0068; found: 240.0063.

4-Trifluoromethoxyphenyl Mesylate (M31)

Yield: 6.29 g (98%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 9.0 Hz, 2 H), 7.27 (d, *J* = 9.1 Hz, 2 H), 3.17 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8, 147.2, 123.7, 122.7, 120.5 (q, *J* = 258.2 Hz), 37.6.

HRMS (EI): *m*/*z* (M^+) calcd for $C_8H_7F_3O_4S$: 256.0017; found: 256.0016.

1-Methyl-1*H*-pyrazol-5-yl Mesylate (M34)

Yield: 3.25 g (74%); pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 2.1 Hz, 1 H), 6.08 (d, *J* = 2.2 Hz, 1 H), 3.79 (s, 3 H), 3.26 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.6, 138.4, 94.7, 37.5, 35.1.

HRMS (ESI): *m*/*z* (M + H)$^+$ calcd for $C_5H_9N_2O_3S$: 177.0334; found: 177.0336.

2,4-Dimethylthiophen-3-yl Mesylate (M35)

Yield: 5.12 g (99%); off-white solid; mp 54–56 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.70 (s, 1 H), 3.20 (s, 3 H), 2.41 (s, 3 H), 2.17 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.2, 131.2, 128.4, 116.9, 38.4, 13.6, 12.4.

HRMS (ESI): *m*/*z* (M + H)$^+$ calcd for $C_7H_{11}O_3S_2$: 207.0150; found: 207.0146.

1,3-Dimesyloxybenzene (M38)

Yield: 6.60 g (99%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (t, *J* = 8.3 Hz, 1 H), 7.31–7.26 (m, 3 H), 3.24 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.5, 131.0, 121.2, 116.7, 37.6.

HRMS (ESI): *m*/*z* (M + H)$^+$ calcd for $C_8H_{11}O_6S_2$: 266.9997; found: 266.9996.

2,2′-Methylenebis(4-methylphenyl) Dimesylate (M42)

Yield: 9.23 g (96%); white solid; mp 112–114 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (d, *J* = 8.5 Hz, 2 H), 7.07 (d, *J* = 8.3 Hz, 2 H), 6.94 (s, 2 H), 4.09 (s, 2 H), 3.11 (s, 6 H), 2.29 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.2, 137.3, 132.1, 132.0, 128.7, 121.9, 38.1, 30.6, 21.0.

HRMS (ESI): *m*/*z* (M + H)$^+$ calcd for $C_{17}H_{21}O_6S_2$: 385.0780; found: 385.0773.

2,2′-Methylenebis[6-(1-methylethyl)phenyl] Dimesylate (M43)

Yield: 10.13 g (92%); white solid; mp 136–138 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (dd, *J* = 7.8, 1.5 Hz, 2 H), 7.18 (dd, *J* = 7.5, 7.5 Hz, 2 H), 6.83 (dd, *J* = 7.5, 1.5 Hz, 2 H), 4.29 (s, 2 H), 3.49 (sept, *J* = 6.8 Hz, 2 H), 3.25 (s, 6 H), 1.26 (d, *J* = 7.0 Hz, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.1, 143.0, 133.3, 128.6, 127.6, 125.8, 39.0, 32.0, 27.5, 23.7.

HRMS (ESI): *m*/*z* (M + H)$^+$ calcd for $C_{21}H_{29}O_6S_2$: 441.1406; found: 441.1406.

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Supporting Information

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