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Copper Acetate Mediated α-Oxysulfonylation of α-Diazo β-Ketosulfones

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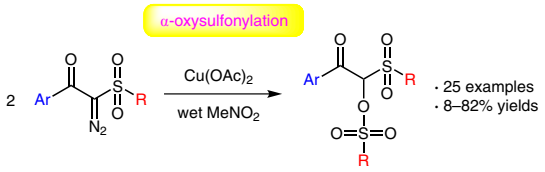

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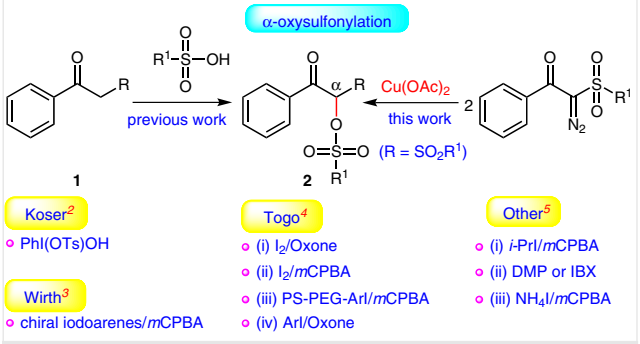
Abstract Copper acetate mediated α-oxysulfonylation of α-diazo β-ketosulfones in wet nitromethane under nitrogen provides α-oxysulfonyl β-ketosulfones. The use of different copper salts is investigated for the development of a facile and efficient transformation. A plausible mechanism is proposed herein.

Key words diazo compounds, β-ketosulfones, oxysulfonylation, copper acetate, bond formation

α-Functionalization of carbonyl synthons has attracted considerable interest among synthetic organic researchers because the method leads to the formation of carbon–carbon or carbon–heteroatom bonds, and the resulting products can be transformed into diversified molecules under a variety of reaction conditions.[1] Among a number of α-functionalized hetero substituents, such as halo (C–X bond formation),[1a] alkoxy or hydroxy (C–O bond formation),[1b] amino, diazo or azido (C–N bond formation),[1c,d] mercapto (C–S bond formation),[1e] or boron (C–B bond formation),[1f] the development of new synthetic strategies for α-functionalization of carbonyl synthons is still in high demand. Therefore, compared to reported work on the establishment of an oxy substituent (e.g., hydroxy, alkyloxy, aryloxy, aminooxy, or carbonyloxy) on the α-position of carbonyl compounds, we found that the introduction of an α-oxysulfonyl group is less documented.[2–5] Furthermore, we observed that the α-oxysulfonylation of carbonyl synthons has almost been exclusively focused on the use of the Koser-type indane (a hypervalent iodine reagent), as shown in Scheme 1.

In 1982, α-oxysulfonylation with [hydroxy(tosyloxy)iodo]benzene [HTIB, PhI(OTs)OH] was first demonstrated by the Koser group.[2] Subsequently, Wirth et al. developed a

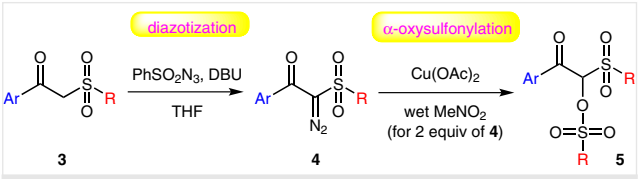


Scheme 1 Synthesis of α-oxysulfonyl ketones

catalytic chiral-iodoarene-mediated enantioselective α-oxysulfonylation of ketones **1**.[3] The Togo group investigated non-metallic oxidants (Oxone or *m*CPBA) for the α-oxysulfonylation of ketones **1** with iodo-containing reagents (e.g., iodoarenes or iodine) under acidic (*p*-TsOH or AcOH) conditions.[4] Similarly, the efficient utilization of different iodoarene derivatives has been successfully reported for synthesizing α-sulfonyloxy ketones **2**.[5]

In our ongoing research program on the formation of sulfonyl skeletons by α-functionalization of β-ketosulfones,[6] we modified our synthetic aim to introducing the diazo group on the α-position of β-ketosulfones. α-Diazo β-ketosulfones are of great interest because of the ambiphilic intermediates. Accordingly, many synthetic applications of α-diazo β-ketosulfones exist for the preparation of functionalized sulfonyl skeletons.[7] Herein, we wanted to describe the synthetic route for substituted α-oxysulfonyl β-ketosulfones **5** via the $Cu(OAc)_2$-mediated self-dimerizative debenzoylation of α-diazo β-ketosulfones **4** (2 equiv), as shown in Scheme 2. This two-step procedure for the α-diazotization of β-ketosulfones **3** with benzenesulfonyl azide

and $Cu(OAc)_2$ promoted the α-oxysulfonylation of α-diazo β-ketosulfones **4**, and established carbon–nitrogen (C–N) and carbon–oxygen (C–O) bond formation.



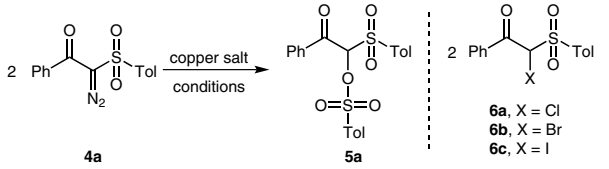
Scheme 2 Two-step synthetic route to α-oxysulfonyl β-ketosulfones **5**

α-Diazo β-ketosulfones **4** were easily prepared in good yields (74–88%) by DBU-mediated diazotization of β-ketosulfones **3** (Ar = Ph, Tol, 4-FC_6H_4, 4-$MeOC_6H_4$, 4-$F_3CC_6H_4$, 4-$O_2NC_6H_4$, 3-$O_2NC_6H_4$, 4-PhC_6H_4, 2-naphthyl, 3,4-$Cl_2C_6H_3$; R = Tol, Ph, Me, 3-MeC_6H_4, 4-FC_6H_4, 4-$MeOC_6H_4$, 4-EtC_6H_4, 4-*i*-PrC_6H_4, 4-*n*-BuC_6H_4, 4-*t*-BuC_6H_4, *n*-Bu) with $PhSO_2N_3$ in THF at room temperature. The structure of **4n** was determined by single-crystal X-ray crystallography.[8] With compounds **4** in hand, the next step was to examine the conversion from α-diazo β-ketosulfones **4** (2 equiv) into α-oxysulfonyl β-ketosulfones **5** (1 equiv). We employed two equivalents of **4a** (Ar = Ph, R = Tol) as the model substrate to investigate a range of copper salts in promoting the α-oxysulfonylation reaction. Regarding the control conditions [reflux, $MeNO_2$ (5 mL), 20 h], the use of commercially available copper salts (1.2 equiv) [$Cu(OAc)_2$, $Cu(NO_3)_2$, $CuSO_4$, $Cu(OTf)_2$, CuF_2, $CuCl_2$, $CuBr_2$, CuI, CuO and CuCN] was initially studied for the formation of **5a** (Table 1, entries 1–10).

Among these screened copper salts, both $Cu(OAc)_2$ and $Cu(OTf)_2$ provided **5a** in moderate yields (71% and 60%) under refluxing $MeNO_2$ conditions (Table 1, entries 1 and 4). In contrast, the use of $Cu(NO_3)_2$ and $CuSO_4$ resulted in the formation of complex mixtures (Table 1, entries 2 and 3). On using copper halides, 10% of **5a** (for CuF_2) and three α-halo-β-ketosulfones (**6a–c**) with yields of 61% (X = Cl, for $CuCl_2$), 51% (X = Br, for $CuBr_2$) and 22% (X = I, for CuI) were obtained under the above-stated condition (Table 1, entries 5–8).[9] Although the isolated yields of **6a–c** are low, the novel copper halide mediated α-halogenation of **4a** has been reported.[6b] A plausible mechanism for the formation of **6b** is illustrated in Scheme 3. The initial coordination of **4a** gives **I** by the complexation of $CuBr_2$ and the nitrogen atom of the diazo group. Through subsequent intramolecular migration, the tertiary copper complex **II** is formed. Following the removal of molecular nitrogen, intermediate **III** is afforded. After the involvement of H_2O, **IV** is produced along with in situ generated HBr. Finally, the hydroxy group in **IV**, via a six-membered ring, promotes the removal of CuO and HBr to produce **6b** via intramolecular rearrangement.

The structures of **5a**, **6a** and **6b** were determined by single-crystal X-ray crystallography.[8] No reactions were observed when using CuO and CuCN (Table 1, entries 9 and 10). From the results in hand, $Cu(OAc)_2$ proved to be the most reactive copper complex compared to the other derivatives. After changing the amounts of $Cu(OAc)_2$ (1.2 → 2.5 and 5.0; 1.2 → 0.5 equivalents) (Table 1, entries 11–13), lower yields (60% and 40%; 35%) of **5a** were detected. Next, we found that $Cu(OAc)_2$ produced different yields of **5a** under concentrated (48% for 1.0 mmol/1 mL) and dilute (66% for 1.0 mmol/10 mL) conditions (Table 1, entries 14 and 15).

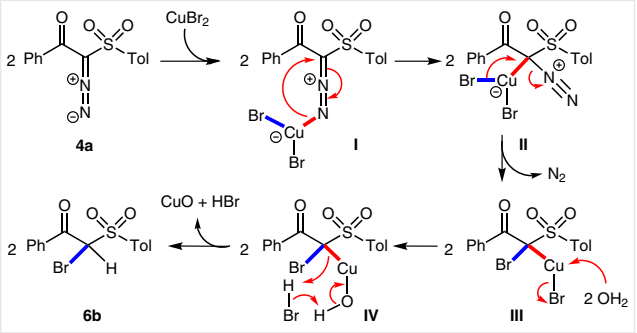
Table 1 Reaction Conditions[a]



4a 5a

Entry	Cu salt (equiv)	Solvent (mL)	Time (h)	Yield of **5a** (%)[b]
1	$Cu(OAc)_2$ (1.2)	$MeNO_2$ (5)	20	71
2	$Cu(NO_3)_2$ (1.2)	$MeNO_2$ (5)	20	–[c]
3	$CuSO_4$ (1.2)	$MeNO_2$ (5)	20	–[c]
4	$Cu(OTf)_2$ (1.2)	$MeNO_2$ (5)	20	60
5	CuF_2 (1.2)	$MeNO_2$ (5)	20	10
6	$CuCl_2$ (1.2)	$MeNO_2$ (5)	20	–[d]
7	$CuBr_2$ (1.2)	$MeNO_2$ (5)	20	–[d]
8	CuI (1.2)	$MeNO_2$ (5)	20	–[d]
9	CuO (1.2)	$MeNO_2$ (5)	20	–[c]
10	CuCN (1.2)	$MeNO_2$ (5)	20	–[c]
11	$Cu(OAc)_2$ (2.5)	$MeNO_2$ (5)	20	60
12	$Cu(OAc)_2$ (5.0)	$MeNO_2$ (5)	20	40
13	$Cu(OAc)_2$ (0.5)	$MeNO_2$ (5)	20	35
14	$Cu(OAc)_2$ (1.2)	$MeNO_2$ (1)	20	48
15	$Cu(OAc)_2$ (1.2)	$MeNO_2$ (10)	20	66
16	$Cu(OAc)_2$ (1.2)	AcOH (5)	20	58
17	$Cu(OAc)_2$ (1.2)	DMF (5)	20	35
18	$Cu(OAc)_2$ (1.2)	CH_2Cl_2 (5)	20	–[c]
19	$Cu(OAc)_2$ (1.2)	$EtNO_2$ (5)	20	56
20	$Cu(OAc)_2$ (1.2)	$MeNO_2$ (5)	50	50
21	$Cu(OAc)_2$ (1.2)	$MeNO_2$ (5)	20	20[e]
22	–	$MeNO_2$ (5)	20	–[f]
23	$Cu(OAc)_2$ (1.2)	$MeNO_2$ (aq)[g] (5)	20	70
24	$Cu(OAc)_2$ (1.2)	$MeNO_2$ (dry)[h] (5)	20	–[f]

[a] The reactions were run on a 1.0 mmol scale with **4a** at reflux under N_2.
[b] Yield of isolated product.
[c] Complex mixture.
[d] Compounds **6a** (61%), **6b** (51%) and **6c** (22%) were obtained.
[e] Room temperature.
[f] No reaction.
[g] $MeNO_2/H_2O$ = 10:1.
[h] Anhydrous $MeNO_2$ and 4 Å MS (100 mg) were added.

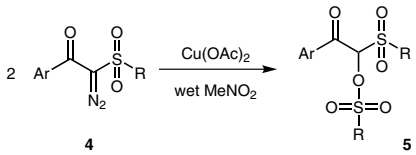


Scheme 3 Proposed mechanism for the formation of **6b**

Furthermore, three other factors: solvent, time and temperature, were studied. After changing the solvent (from $MeNO_2$ to AcOH, DMF, CH_2Cl_2 or $EtNO_2$), the results showed no observed formation of **5a** in CH_2Cl_2, whilst AcOH and $EtNO_2$ provided better yields of **5a** (58% and 56%) than DMF (35%) (Table 1, entries 16–19). For an extended reaction time (10 h → 50 h), the isolated yield of **5a** was 50% (Table 1, entry 20), while a 20% yield was isolated when the temperature was decreased (101 °C → 25 °C) (Table 1, entry 21). In the absence of $Cu(OAc)_2$, no reaction was observed (Table 1, entry 22). Using a mixed solvent comprising $MeNO_2$ and H_2O (10:1, 5 mL), **5a** was isolated in a 70% yield (Table 1, entry 23). However, the use of anhydrous $MeNO_2$ in the presence of molecular sieves did not result in the formation of **5a** (Table 1, entry 24). The results showed that water is a key factor affecting the formation of **5a**. According to the experimental results, the optimum conditions for the synthesis of **5a** are: $Cu(OAc)_2$ (2 equiv), wet $MeNO_2$ (5 mL), reflux, 20 hours. Aside from the present α-oxysulfonylation reaction, $Cu(OAc)_2$ has also been reported as a promoter for different functional group transformations.[10]

Using the optimized conditions (Table 1, entry 1), we further explored the substrate scope of the reaction; the results of the α-oxysulfonylations are shown in Table 2. For the formation of α-oxysulfonyl β-ketosulfones **5a–y**, different Ar and R substituents on the β-ketosulfones **4a–y** (2 equiv), including an electron-donating aryl group (for Ar = 4-$MeOC_6H_4$), an electron-neutral aryl group (for Ar = Ph, Tol, biphenyl, 2-naphthyl; R = Ph, Tol, 3-MeC_6H_4, 4-EtC_6H_4, 4-*i*-PrC_6H_4, 4-*n*-BuC_6H_4, 4-*t*-BuC_6H_4), an electron-withdrawing aryl group (for Ar = 4-$O_2NC_6H_4$, 3-$O_2NC_6H_4$, 4-$F_3CC_6H_4$) and an alkyl group (for R = Me, *n*-Bu) performed differently providing a range of distributed yields of the desired products. However, the conditions were slightly inappropriate for compounds **4c**, **4o** and **4t** with a strong electron-donating 4-methoxyphenyl group (Ar or R), which gave **5c** and **5o** in 60% and 45% yields, respectively. However, **5t** was isolated in only 8% yield. For stronger electron-withdrawing groups, the conditions were also inappropriate. Lower yields of **5e** (47%), **5f** (49%) and **5g** (54%) were observed for the α-oxysulfonylation of **4e**, **4f** and **4g** having 4-trifluoromethylphenyl and 3- or 4-nitrophenyl groups. For the synthesis of **5y** (R = *n*-Bu), only a 12% yield was obtained. A mixture of five- and six-membered cyclic sulfones was formed by the $Cu(OAc)_2$-mediated intramolecular C–H insertion process with **4y**. The phenomenon is similar to Maguire's report.[11] The structures of **5d** and **5t** were determined by single-crystal X-ray crystallography.[8] Although our synthetic route is not an atom-economic method, we have developed a novel $Cu(OAc)_2$-mediated route for preparing the structural framework of α-oxysulfonyl β-ketosulfones.

Table 2 Synthesis of α-Oxysulfonyl β-Ketosulfones **5**[a]

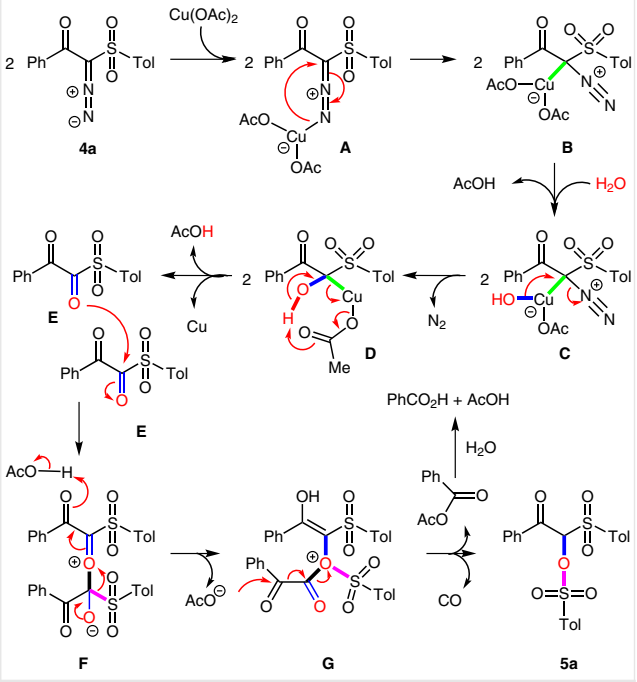


4 **5**

Entry	β-Ketosulfone	Ar	R	Product, yield (%)[b]
1	**4a**	Ph	Tol	**5a**, 71
2	**4b**	4-FC_6H_4	Tol	**5b**, 73
3	**4c**	4-$MeOC_6H_4$	Tol	**5c**, 60
4	**4d**	Tol	Tol	**5d**, 82
5	**4e**	4-$F_3CC_6H_4$	Tol	**5e**, 47
6	**4f**	4-$O_2NC_6H_4$	Tol	**5f**, 49
7	**4g**	3-$O_2NC_6H_4$	Tol	**5g**, 54
8	**4h**	4-PhC_6H_4	Tol	**5h**, 65
9	**4i**	2-naphthyl	Tol	**5i**, 66
10	**4j**	3,4-$Cl_2C_6H_3$	Tol	**5j**, 67
11	**4k**	Ph	Ph	**5k**, 72
12	**4l**	4-FC_6H_4	Ph	**5l**, 74
13	**4m**	4-PhC_6H_4	Ph	**5m**, 63
14	**4n**	Ph	Me	**5n**, 56
15	**4o**	4-$MeOC_6H_4$	Me	**5o**, 45
16	**4p**	4-MeC_6H_4	Me	**5p**, 72
17	**4q**	4-PhC_6H_4	Me	**5q**, 67
18	**4r**	Ph	3-MeC_6H_4	**5r**, 70
19	**4s**	Ph	4-FC_6H_4	**5s**, 72
20	**4t**	Ph	4-$MeOC_6H_4$	**5t**, 8
21	**4u**	Ph	4-EtC_6H_4	**5u**, 73
22	**4v**	Ph	4-*i*-PrC_6H_4	**5v**, 72
23	**4w**	Ph	4-*n*-BuC_6H_4	**5w**, 74
24	**4x**	Ph	4-*t*-BuC_6H_4	**5x**, 76
25	**4y**	Ph	*n*-Bu	**5y**, 12[c]

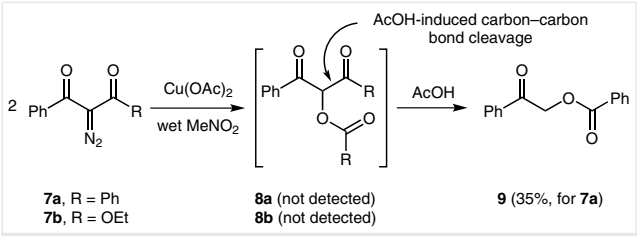
[a] The reactions were run on a 1.0 mmol scale with **4**, $Cu(OAc)_2$ (220 mg, 1.2 mmol), and wet $MeNO_2$ (95%, 5 mL) under N_2 at reflux for 20 h.
[b] Yield of isolated product.
[c] A mixture of cyclic sulfones was isolated.

A plausible mechanism for the formation of **5a** is illustrated in Scheme 4 via the $Cu(OAc)_2$-mediated one-pot self-dimerizative debenzoylation of two equivalents of **4a**. On the basis of the preliminary experience for copper triflate mediated reactions of diazo β-ketosulfones,[6b] we think that the initial coordination of **4a** could provide two equivalents of **A** by the complexation of $Cu(OAc)_2$ and the nitrogen atom of the diazo group. Through subsequent intramolecular migration, two equivalents of **B**, containing a tertiary copper complex, are formed. Following the involvement of water (from $MeNO_2$)[12] and acetate/water exchange, two equivalents of **C** are afforded along with AcOH. The hydroxy group then promotes the removal of molecular nitrogen from **C** leading to **D**. Next, intramolecular rearrangement via a seven-membered ring produces **E**. As reported by Luo and Deng,[13a] adduct **E** (an α,β-diketosulfone) was found quite unstable to isolation.[13b,c] Subsequently, intermolecular self-coupling of two equivalents of **E** occurs to afford one equivalent of **F**. After a cascade two-step route for the protonation of the carbonyl group and sulfonyl migration, intermediate **G** is formed. Finally, **5a** is produced by an in situ acetate ion mediated debenzoylative route along with the removal of CO. Hydrolysis of the anhydride leads to the isolation of $PhCO_2H$ and AcOH. Looking at the proposed mechanism, we can understand that the obtained yield should be halved because one molecule of the product **5a** is formed from two molecules of diazo compound **4a**.



Scheme 4 A plausible mechanism for the synthesis of **5a**

Changing the 1,3-dicarbonyl synthons from α-diazo β-ketosulfones **4a** to β-diketone **7a** and β-ketoester **7b**, the $Cu(OAc)_2$-mediated reactions of **7a**,**b** (2 equiv) were investigated (Scheme 5). However, the formation of compounds **8a**,**b** was not observed, and ester **9** was generated in only a 35% yield (from **7a**). A possible explanation for the reaction of **7a** with $Cu(OAc)_2$ would involve the initial formation of **8a**. Subsequent debenzoylation mediated by in situ formed AcOH (see Scheme 4) leads to the generation of **9** via carbon–carbon bond cleavage.[14] The structure of **9** was determined by single-crystal X-ray crystallography.[8]

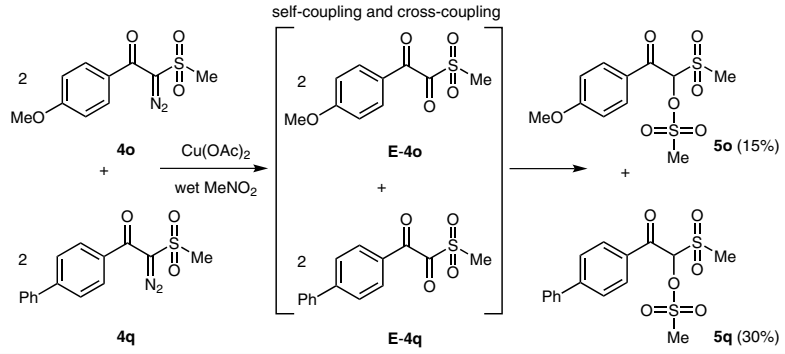


Scheme 5 Reaction of compounds **7** with $Cu(OAc)_2$

To extend this one-pot domino protocol, the $Cu(OAc)_2$-mediated α-oxysulfonylation of a mixture of **4o** and **4q** (1:1) was examined (Scheme 6). Unexpectedly, we observed that the isolated yields of **5o** (45% → 15%) and **5q** (67% → 30%) were decreased compared with the individual $Cu(OAc)_2$-mediated α-oxysulfonylations of **4o** or **4q**. According to the plausible mechanism (Scheme 4), we believe that the competition of intermediates **E-4o** and **E-4q** is the key factor affecting the product yields and distribution via intermolecular cross-coupling (4-methoxyphenyl versus biphenyl) and self-coupling (4-methoxyphenyl versus 4-methoxyphenyl or biphenyl versus biphenyl). From the results, we understand that the control experiment demonstrated that a stronger electron-donating 4-methoxyphenyl group (for **E-4o**) could trigger electrophilic instability easily such that the formation of an α-oxysulfonylated product is inhibited.

In summary, we have developed a synthetic method for the preparation of α-oxysulfonyl β-ketosulfones **5a–y** in good yields via $Cu(OAc)_2$-mediated α-oxysulfonylation of two equivalents of substituted α-diazo β-ketosulfones **4a–y** in $MeNO_2$ at reflux. The use of different copper salts was investigated for a facile conversion. A plausible mechanism has been proposed. The structures of the key products were confirmed by X-ray crystallography. Further investigations regarding the synthetic applications of β-ketosulfones are ongoing in our laboratory.

All reagents and solvents were obtained from commercial sources and were used without further purification. Reactions were routinely carried out under an atmosphere of dry nitrogen with magnetic stirring. Products in organic solvents were dried with anhydrous $MgSO_4$ before concentration in vacuo. Melting points were determined with an SMP3 melting point apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 400 and at 100 MHz, respectively. High-resolution mass spectrometry (HRMS)



Scheme 6 $Cu(OAc)_2$-mediated reaction of a 1:1 mixture of **4o** and **4q**

was performed using a Finnigan/Thermo Quest MAT 95XL mass spectrometer. X-ray crystal structures were obtained with an Enraf-Nonius FR-590 diffractometer (CAD4, Kappa CCD). Scanned copies of NMR ($CDCl_3$) spectroscopic data for all compounds and X-ray crystal structure analysis data of compounds **4n**, **5a**, **5d**, **5t**, **6a**, **6b** and **9** are available.

α-Diazo β-Ketosulfones 4a–y; General Procedure

DBU (182 mg, 1.2 mmol) was added to a solution of compound **3** (1.0 mmol) in THF (10 mL) at r.t. The reaction mixture was stirred at r.t. for 10 min. Benzenesulfonyl azide (200 mg, 1.1 mmol) was added to the reaction mixture at r.t. The resulting mixture was stirred at r.t. for 20 h. The solvent was concentrated, the residue diluted with H_2O (10 mL) and the mixture extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated under reduced pressure to afford the crude product. Purification on silica gel (hexanes/EtOAc = 8:1–4:1) afforded compounds **4a–y**.

2-Diazo-1-phenyl-2-(toluene-4-sulfonyl)ethanone (4a)[7b]

Yield: 264 mg (88%); colorless solid; mp 76–78 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.0 Hz, 2 H), 7.56–7.51 (m, 3 H), 7.44–7.40 (m, 2 H), 7.33 (d, *J* = 8.8 Hz, 2 H), 2.43 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.6, 145.3 (×2), 138.5, 135.7, 132.9, 129.7 (×2), 128.8 (×2), 128.1 (×2), 127.3 (×2), 21.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{13}N_2O_3S$: 301.0647; found: 301.0657.

2-Diazo-1-(4-fluorophenyl)-2-(toluene-4-sulfonyl)ethanone (4b)

Yield: 254 mg (80%); colorless solid; mp 95–97 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.4 Hz, 2 H), 7.62–7.57 (m, 2 H), 7.34 (d, *J* = 7.6 Hz, 2 H), 7.15–7.09 (m, 2 H), 2.44 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.4, 165.4 (d, *J* = 253.9 Hz), 145.5 (×2), 138.5, 132.0 (d, *J* = 3.0 Hz), 130.2 (d, *J* = 9.1 Hz, ×2), 129.8 (×2), 128.1 (×2), 116.1 (d, *J* = 22.0 Hz, ×2), 21.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}FN_2O_3S$: 319.0553; found: 319.0558.

2-Diazo-1-(4-methoxyphenyl)-2-(toluene-4-sulfonyl)ethanone (4c)[7g]

Yield: 271 mg (82%); colorless solid; mp 140–142 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.8 Hz, 2 H), 7.55 (d, *J* = 8.8 Hz, 2 H), 7.22 (d, *J* = 8.8 Hz, 2 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 3.82 (s, 3 H), 2.41 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.2, 163.4, 145.2, 138.6, 131.6, 129.7 (×2), 129.6 (×2), 128.1 (×2), 114.0 (×2), 62.4, 55.4, 21.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}N_2O_4S$: 331.0753; found: 331.0748.

2-Diazo-2-(toluene-4-sulfonyl)-1-*p*-tolylethanone (4d)[7g]

Yield: 264 mg (84%); colorless solid; mp 118–120 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.4 Hz, 2 H), 7.46 (d, *J* = 8.4 Hz, 2 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 2 H), 2.43 (s, 3 H), 2.38 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.3, 145.2, 143.9 (×2), 138.6, 133.2, 129.6 (×2), 129.4 (×2), 128.1 (×2), 127.5 (×2), 21.62, 21.55.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}N_2O_3S$: 315.0803; found: 315.0809.

2-Diazo-2-(toluene-4-sulfonyl)-1-(4-trifluoromethylphenyl)ethanone (4e)

Yield: 294 mg (80%); colorless solid; mp 121–122 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.4 Hz, 2 H), 7.69 (d, *J* = 8.4 Hz, 2 H), 7.64 (d, *J* = 8.8 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 2.44 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.8, 145.7, 138.9, 138.4, 134.2 (q, *J* = 32.6 Hz), 129.8 (×2), 128.1 (×2), 127.9 (×2), 125.8 (q, *J* = 3.0 Hz), 124.6, 123.3 (q, *J* = 271.4 Hz), 121.9, 21.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{12}F_3N_2O_3S$: 369.0521; found: 369.0530.

2-Diazo-1-(4-nitrophenyl)-2-(toluene-4-sulfonyl)ethanone (4f)[7h]

Yield: 279 mg (81%); colorless solid; mp 136–138 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 8.8 Hz, 2 H), 7.83 (d, *J* = 8.4 Hz, 2 H), 7.70 (d, *J* = 8.8 Hz, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 2.45 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.4, 150.0, 145.9, 140.9, 138.3, 132.7, 129.9 (×2), 128.7 (×2), 128.0 (×2), 123.9 (×2), 21.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}N_3O_5S$: 346.0498; found: 346.0502.

2-Diazo-1-(3-nitrophenyl)-2-(toluene-4-sulfonyl)ethanone (4g)

Yield: 283 mg (82%); colorless solid; mp 114–116 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33–8.26 (m, 2 H), 7.88–7.85 (m, 1 H), 7.79 (d, *J* = 8.4 Hz, 2 H), 7.65–7.61 (m, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 2.39 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.5, 147.9, 145.7 (×2), 138.1, 137.0, 132.9, 130.0, 129.7 (×2), 127.8 (×2), 126.8, 122.3, 21.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}N_3O_5S$: 346.0498; found: 346.0508.

1-Biphenyl-4-yl-2-diazo-2-(toluene-4-sulfonyl)ethanone (4h)

Yield: 278 mg (74%); colorless solid; mp 133–135 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.8 Hz, 2 H), 7.65 (br s, 4 H), 7.59 (d, *J* = 8.8 Hz, 2 H), 7.49–7.40 (m, 3 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 2.45 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.2, 145.9, 145.4, 139.4, 138.6, 134.5, 130.0, 129.7 (×2), 129.0 (×2), 128.4, 128.2 (×2), 128.1 (×2), 127.4 (×2), 127.2 (×2), 21.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{17}N_2O_3S$: 377.0960; found: 377.0967.

2-Diazo-1-naphthalen-2-yl-2-(toluene-4-sulfonyl)ethanone (4i)

Yield: 263 mg (75%); colorless solid; mp 104–106 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (s, 1 H), 7.82 (d, *J* = 8.4 Hz, 2 H), 7.89–7.85 (m, 3 H), 7.63–7.54 (m, 3 H), 7.35 (d, *J* = 8.8 Hz, 2 H), 2.44 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.6, 145.4, 138.6, 135.2, 133.0, 132.0, 129.7 (×2), 129.1, 128.9, 128.7, 128.6, 128.2 (×2), 127.9, 127.4, 127.2, 123.3, 21.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{15}N_2O_3S$: 351.0803; found: 351.0812.

2-Diazo-1-(3,4-dichlorophenyl)-2-(toluene-4-sulfonyl)ethanone (4j)

Yield: 286 mg (78%); colorless solid; mp 118–120 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.4 Hz, 2 H), 7.57 (d, *J* = 2.0 Hz, 1 H), 7.50 (d, *J* = 8.4 Hz, 1 H), 7.39 (dd, *J* = 2.0, 8.4 Hz, 1 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 2.44 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.4, 145.6 (×2), 138.3, 137.4, 135.3, 133.4, 130.8, 129.8 (×2), 129.5, 128.0 (×2), 126.4, 21.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{11}Cl_2N_2O_3S$: 368.9868; found: 368.9871.

2-Benzenesulfonyl-2-diazo-1-phenylethanone (4k)[7c]

Yield: 246 mg (86%); colorless solid; mp 125–127 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07–8.04 (m, 2 H), 7.68–7.63 (m, 1 H), 7.58–7.54 (m, 5 H), 7.45–7.41 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.6, 141.4, 135.8, 134.1, 133.0, 129.1 (×2), 128.9, 128.8 (×2), 128.1 (×2), 127.4 (×2).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{11}N_2O_3S$: 287.0490; found: 287.0498.

2-Benzenesulfonyl-2-diazo-1-(4-fluorophenyl)ethanone (4l)

Yield: 255 mg (84%); colorless solid; mp 78–79 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03–8.01 (m, 2 H), 7.68–7.53 (m, 5 H), 7.14–7.09 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.3, 165.4 (d, *J* = 253.2 Hz), 141.4, 134.2, 132.0 (d, *J* = 3.8 Hz), 130.2 (d, *J* = 9.1 Hz, ×2), 129.2 (×2), 128.0 (×3), 116.1 (d, *J* = 22.7 Hz, ×2).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{10}FN_2O_3S$: 305.0396; found: 305.0405.

2-Benzenesulfonyl-1-biphenyl-4-yl-2-diazoethanone (4m)

Yield: 290 mg (80%); colorless solid; mp 134–136 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10–8.07 (m, 2 H), 7.65 (br s, 4 H), 7.60–7.55 (m, 4 H), 7.49–7.45 (m, 3 H), 7.43–7.39 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.1, 145.9, 141.5, 139.4, 134.4, 134.1, 131.1, 129.1 (×2), 129.0 (×2), 128.4, 128.14 (×2), 128.08 (×2), 127.4 (×2), 127.2 (×2).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{15}N_2O_3S$: 363.0803; found: 363.0810.

2-Diazo-2-methanesulfonyl-1-phenylethanone (4n)[7h]

Yield: 184 mg (82%); colorless solid; mp 120–122 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.65 (m, 2 H), 7.62–7.58 (m, 1 H), 7.51–7.47 (m, 2 H), 3.41 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.3, 135.5, 133.3 (×2), 129.1 (×2), 127.3 (×2), 44.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_9H_9N_2O_3S$: 225.0334; found: 225.0330.

Single-crystal X-ray analysis: Slow diffusion of EtOAc into a solution of compound **4n** in CH_2Cl_2 yielded colorless prisms. The compound crystallizes in the triclinic crystal system, space group *P*-1, *a* = 5.0953(5) Å, *b* = 9.0098(8) Å, *c* = 11.5067(11) Å, *V* = 492.80(8) Å^3, *Z* = 2, d_{calcd} = 1.518 mg/cm^3, *F*(000) = 234, 2θ range 1.876–26.414°; *R* indices (all data): *R*1 = 0.0348, *wR*2 = 0.0822.

2-Diazo-2-methanesulfonyl-1-(4-methoxyphenyl)ethanone (4o)

Yield: 198 mg (78%); colorless solid; mp 93–95 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.8 Hz, 2 H), 6.96 (d, *J* = 8.8 Hz, 2 H), 3.87 (s, 3 H), 3.41 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.9, 163.7, 129.8 (×2), 128.1 (×2), 114.3 (×2), 55.6, 45.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{11}N_2O_4S$: 255.0440; found: 255.0443.

2-Diazo-2-methanesulfonyl-1-*p*-tolylethanone (4p)

Yield: 188 mg (79%); colorless solid; mp 118–120 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 8.4 Hz, 2 H), 7.29 (d, *J* = 8.4 Hz, 2 H), 3.40 (s, 3 H), 2.41 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.0, 144.4 (×2), 132.9, 129.7 (×2), 127.5 (×2), 45.0, 21.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{11}N_2O_3S$: 239.0490; found: 239.0498.

1-Biphenyl-4-yl-2-diazo-2-methanesulfonylethanone (4q)

Yield: 240 mg (80%); colorless solid; mp 139–141 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.4 Hz, 2 H), 7.71 (d, *J* = 8.4 Hz, 2 H), 7.62–7.60 (m, 2 H), 7.50–7.46 (m, 2 H), 7.44–7.39 (m, 1 H), 3.44 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.7, 146.2, 139.2, 134.1 (×2), 129.0 (×2), 128.5, 128.0 (×2), 127.6 (×2), 127.2 (×2), 45.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{13}N_2O_3S$: 301.0647; found: 301.0653.

2-Diazo-1-phenyl-2-(toluene-3-sulfonyl)ethanone (4r)

Yield: 243 mg (81%); colorless solid; mp 104–106 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.82 (m, 1 H), 7.81 (s, 1 H), 7.56–7.53 (m, 3 H), 7.46–7.40 (m, 4 H), 2.43 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.7, 141.3, 139.4 (×2), 135.8, 134.9, 132.9, 128.9, 128.8 (×2), 128.3, 127.4 (×2), 125.2, 21.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{13}N_2O_3S$: 301.0647; found: 301.0643.

2-Diazo-2-(4-fluorobenzenesulfonyl)-1-phenylethanone (4s)

Yield: 243 mg (80%); colorless solid; mp 101–103 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12–8.08 (m, 2 H), 7.58–7.54 (m, 3 H), 7.46–7.42 (m, 2 H), 7.25–7.19 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.5, 166.0 (d, *J* = 255.4 Hz), 137.3 (d, *J* = 3.0 Hz), 135.6 (×2), 133.1, 131.3 (d, *J* = 9.9 Hz, ×2), 128.9 (×2), 127.4 (×2), 116.4 (d, *J* = 22.7 Hz, ×2).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{10}FN_2O_3S$: 305.0396; found: 305.0408.

2-Diazo-2-(4-methoxybenzenesulfonyl)-1-phenylethanone (4t)

Yield: 256 mg (81%); colorless solid; mp 104–106 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.8 Hz, 2 H), 7.55 (d, *J* = 8.4 Hz, 2 H), 7.54–7.52 (m, 1 H), 7.44–7.40 (m, 2 H), 6.99 (d, *J* = 9.2 Hz, 2 H), 3.87 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.7, 164.1 (×2), 135.9, 133.0, 132.9 (×2), 130.5 (×2), 128.8 (×2), 127.4 (×2), 114.2, 55.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{13}N_2O_4S$: 317.0596; found: 317.0602.

2-Diazo-2-(4-ethylbenzenesulfonyl)-1-phenylethanone (4u)

Yield: 264 mg (84%); colorless gum.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.0 Hz, 2 H), 7.57–7.53 (m, 3 H), 7.45–7.41 (m, 2 H), 7.37 (d, *J* = 8.4 Hz, 2 H), 2.74 (q, *J* = 7.6 Hz, 2 H), 1.27 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.7, 151.4, 138.8, 135.9, 133.0, 129.7, 128.8 (×2), 128.6 (×2), 128.3 (×2), 127.5 (×2), 29.0, 15.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}N_2O_3S$: 315.0803; found: 315.0805.

2-Diazo-2-(4-isopropylbenzenesulfonyl)-1-phenylethanone (4v)

Yield: 272 mg (83%); colorless solid; mp 74–76 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.4 Hz, 2 H), 7.57–7.53 (m, 3 H), 7.45–7.41 (m, 2 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 3.03–2.96 (m, 1 H), 1.27 (d, *J* = 6.8 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.7, 155.9 (×2), 138.8, 135.9, 132.9, 128.8 (×2), 128.3 (×2), 127.4 (×2), 127.2 (×2), 34.3, 23.6 (×2).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{17}N_2O_3S$: 329.0960; found: 329.0966.

2-(4-*n*-Butylbenzenesulfonyl)-2-diazo-1-phenylethanone (4w)

Yield: 280 mg (82%); colorless gum.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95–7.93 (m, 2 H), 7.56–7.52 (m, 3 H), 7.44–7.40 (m, 2 H), 7.35–7.33 (m, 2 H), 2.69 (t, *J* = 7.6 Hz, 2 H), 1.65–1.58 (m, 2 H), 1.40–1.31 (m, 2 H), 0.93 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.7, 150.2, 138.7, 135.9, 132.9, 129.6, 129.1 (×2), 128.8 (×2), 128.2 (×2), 127.4 (×2), 35.6, 33.0, 22.2, 13.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{19}N_2O_3S$: 343.1116; found: 343.1118.

2-(4-*tert*-Butylbenzenesulfonyl)-2-diazo-1-phenylethanone (4x)

Yield: 294 mg (86%); colorless solid; mp 92–94 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99–7.95 (m, 2 H), 7.58–7.53 (m, 5 H), 7.46–7.41 (m, 2 H), 1.35 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.7, 158.2, 138.5, 135.9, 133.0, 130.0, 128.8 (×2), 128.0 (×2), 127.5 (×2), 126.1 (×2), 35.3, 31.0 (×3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{19}N_2O_3S$: 343.1116; found: 343.1118.

2-(*n*-Butane-1-sulfonyl)-2-diazo-1-phenylethanone (4y)

Yield: 223 mg (84%); colorless solid; mp 94–96 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68–7.65 (m, 2 H), 7.62–7.58 (m, 1 H), 7.51–7.48 (m, 2 H), 3.55–3.51 (m, 2 H), 1.86–1.79 (m, 2 H), 1.53–1.44 (m, 2 H), 0.95 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.3, 135.6, 133.3, 129.0 (×3), 127.4 (×2), 56.5, 24.6, 21.3, 13.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{15}N_2O_3S$: 267.0803; found: 267.0807.

α-Oxysulfonyl β-Ketosulfones 5a–y; General Procedure

$Cu(OAc)_2$ (220 mg, 1.2 mmol) was added to a solution of **4** (1.0 mmol) in $MeNO_2$ (5 mL) at r.t. The reaction mixture was stirred at r.t. for 10 min and then at reflux for 20 h. The mixture was cooled to r.t. and the solvent was concentrated. The residue was diluted with H_2O (10 mL)

and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated under reduced pressure to afford the crude product. Purification on silica gel (hexanes/EtOAc = 8:1–4:1) afforded compounds **5a–y**.

Toluene-4-sulfonic Acid 2-Oxo-2-phenyl-1-(toluene-4-sulfonyl)ethyl Ester (5a)[5e]

Yield: 158 mg (71%); colorless solid; mp 180–182 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95–7.93 (m, 2 H), 7.68 (d, *J* = 8.4 Hz, 2 H), 7.65–7.60 (m, 1 H), 7.59 (d, *J* = 8.4 Hz, 2 H), 7.49–7.45 (m, 2 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 6.36 (s, 1 H), 2.47 (s, 3 H), 2.39 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.5, 146.6, 146.0, 134.6, 134.3, 131.8, 131.7, 130.1 (×2), 129.9 (×4), 129.8 (×2), 128.6 (×2), 128.2 (×2), 89.5, 21.8, 21.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{21}O_6S_2$: 445.0780; found: 445.0788.

Single-crystal X-ray analysis: Slow diffusion of EtOAc into a solution of compound **5a** in CH_2Cl_2 yielded colorless prisms. The compound crystallizes in the monoclinic crystal system, space group *P*21/*c*, *a* = 5.8538(6) Å, *b* = 17.3655(19) Å, *c* = 20.225(2) Å, *V* = 2041.4(4) Å^3, *Z* = 4, d_{calcd} = 1.446 mg/cm^3, *F*(000) = 928, 2θ range 1.550–26.624°; *R* indices (all data): *R*1 = 0.0623, *wR*2 = 0.1046.

Toluene-4-sulfonic Acid 2-(4-Fluorophenyl)-2-oxo-1-(toluene-4-sulfonyl)ethyl Ester (5b)

Yield: 169 mg (73%); colorless solid; mp 144–146 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03–7.99 (m, 2 H), 7.68 (d, *J* = 8.4 Hz, 2 H), 7.59 (d, *J* = 8.4 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.4 Hz, 2 H), 7.17–7.12 (m, 2 H), 6.24 (s, 1 H), 2.47 (s, 3 H), 2.40 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 185.1, 166.6 (d, *J* = 256.9 Hz), 146.7, 146.1, 132.8 (d, *J* = 9.8 Hz, ×2), 132.3, 132.2, 131.7, 129.98 (×2), 129.95 (×2), 129.91 (×2), 128.2 (×2), 116.0 (d, *J* = 22.7 Hz, ×2), 89.9, 21.9, 21.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{20}FO_6S_2$: 463.0685; found: 463.0684.

Toluene-4-sulfonic Acid 2-(4-Methoxyphenyl)-2-oxo-1-(toluene-4-sulfonyl)ethyl Ester (5c)

Yield: 142 mg (60%); colorless solid; mp 131–133 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.8 Hz, 2 H), 7.67 (d, *J* = 8.4 Hz, 2 H), 7.63 (d, *J* = 8.4 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.4 Hz, 2 H), 6.94 (d, *J* = 8.8 Hz, 2 H), 6.32 (s, 1 H), 3.90 (s, 3 H), 2.46 (s, 3 H), 2.40 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.3, 164.8, 146.4, 145.9, 132.4 (×2), 132.0, 131.9, 130.1 (×2), 129.8 (×4), 128.2 (×2), 127.4, 114.0 (×2), 89.6, 55.6, 21.9, 21.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{23}O_7S_2$: 475.0885; found: 475.0887.

Toluene-4-sulfonic Acid 2-Oxo-1-(toluene-4-sulfonyl)-2-*p*-tolylethyl Ester (5d)[5e]

Yield: 188 mg (82%); colorless solid; mp 176–178 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.4 Hz, 2 H), 7.66 (d, *J* = 8.4 Hz, 2 H), 7.62 (d, *J* = 8.4 Hz, 2 H), 7.32 (d, *J* = 8.8 Hz, 2 H), 7.27 (d, *J* = 8.4 Hz, 2 H), 7.20 (d, *J* = 8.4 Hz, 2 H), 6.36 (s, 1 H), 2.45 (s, 3 H), 2.43 (s, 3 H), 2.39 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 185.8, 146.5, 146.0, 145.9, 131.9 (×2), 131.7, 130.0 (×2), 129.9 (×2), 129.84 (×2), 129.82 (×2), 129.4 (×2), 128.2 (×2), 89.3, 21.8 (×2), 21.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{23}O_6S_2$: 459.0936; found: 459.0938.

Slow diffusion of EtOAc into a solution of compound **5d** in CH_2Cl_2 yielded colorless prisms. The compound crystallizes in the monoclinic crystal system, space group *Cc*, *a* = 16.0826(13) Å, *b* = 12.8002(11) Å, *c* = 11.0923(9) Å, *V* = 2146.9(3) Å^3, *Z* = 4, d_{calcd} = 1.419 mg/cm^3, *F*(000) = 960, 2θ range 2.085–26.440°; *R* indices (all data): *R*1 = 0.0849, *wR*2 = 0.2038.

Toluene-4-sulfonic Acid 2-Oxo-1-(toluene-4-sulfonyl)-2-(4-trifluoromethylphenyl)ethyl Ester (5e)

Yield: 120 mg (47%); colorless solid; mp 155–158 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 8.0 Hz, 2 H), 7.72 (d, *J* = 8.4 Hz, 2 H), 7.70 (d, *J* = 8.4 Hz, 2 H), 7.57 (d, *J* = 8.4 Hz, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 6.23 (s, 1 H), 2.48 (s, 3 H), 2.40 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.4, 146.9, 146.3, 136.7, 135.5 (q, *J* = 32.6 Hz), 131.6, 130.2 (×2), 130.04 (×2), 129.98 (×6), 128.2 (×2), 125.6 (q, *J* = 3.8 Hz), 123.3 (q, *J* = 271.4 Hz), 90.2, 21.9, 21.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{20}F_3O_6S_2$: 513.0653; found: 513.0657.

Toluene-4-sulfonic Acid 2-(4-Nitrophenyl)-2-oxo-1-(toluene-4-sulfonyl)ethyl Ester (5f)

Yield: 120 mg (49%); colorless solid; mp 198–200 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 9.2 Hz, 2 H), 8.15 (d, *J* = 8.8 Hz, 2 H), 7.69 (d, *J* = 8.4 Hz, 2 H), 7.57 (d, *J* = 8.8 Hz, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 2 H), 6.18 (s, 1 H), 2.49 (s, 3 H), 2.42 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.2, 150.8, 147.0, 146.4, 138.4, 131.6, 131.4, 131.0 (×2), 130.1 (×2), 130.0 (×2), 129.9 (×2), 128.2 (×2), 123.7 (×2), 90.4, 21.9, 21.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{20}NO_8S_2$: 490.0630; found: 490.0633.

Toluene-4-sulfonic Acid 2-(3-Nitrophenyl)-2-oxo-1-(toluene-4-sulfonyl)ethyl Ester (5g)

Yield: 132 mg (54%); colorless solid; mp 180–182 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (s, 1 H), 8.45 (dd, *J* = 1.6, 7.6 Hz, 1 H), 8.37 (d, *J* = 7.6 Hz, 1 H), 7.73–7.71 (m, 1 H), 7.70 (d, *J* = 8.0 Hz, 2 H), 7.56 (d, *J* = 8.0 Hz, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 6.20 (s, 1 H), 2.47 (s, 3 H), 2.39 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 185.6, 148.2, 147.0, 146.5, 135.4, 135.2, 135.0, 131.5, 131.3, 130.1 (×2), 130.0 (×2), 129.9 (×2), 128.3, 128.1 (×2), 124.5, 90.4, 21.8, 21.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{20}NO_8S_2$: 490.0630; found: 490.0631.

Toluene-4-sulfonic Acid 2-Biphenyl-4-yl-2-oxo-1-(toluene-4-sulfonyl)ethyl Ester (5h)

Yield: 169 mg (65%); colorless solid; mp 93–95 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.4 Hz, 2 H), 7.71–7.68 (m, 4 H), 7.65–7.62 (m, 4 H), 7.51–7.42 (m, 3 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 6.38 (s, 1 H), 2.47 (s, 3 H), 2.39 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 185.9, 147.3, 146.6, 146.0, 139.4, 132.8, 131.9, 131.8, 130.4 (×2), 130.0 (×2), 129.9 (×4), 129.1 (×2), 128.7, 128.2 (×2), 127.3 (×2), 127.2 (×2), 89.6, 21.9, 21.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{25}O_6S_2$: 521.1093; found: 521.1096.

Toluene-4-Sulfonic Acid 2-Naphthalen-2-yl-2-oxo-1-(toluene-4-sulfonyl)ethyl Ester (5i)

Yield: 163 mg (66%); colorless solid; mp 162–164 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (40 MHz, $CDCl_3$): δ = 8.49 (s, 1 H), 7.99 (d, *J* = 7.6 Hz, 1 H), 7.91–7.87 (m, 3 H), 7.72–7.58 (m, 6 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 8.4 Hz, 2 H), 6.49 (s, 1 H), 2.46 (s, 3 H), 2.33 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.3, 146.6, 146.0, 136.1, 132.7, 131.9, 131.8, 131.7, 130.2, 130.1 (×2), 129.90 (×2), 129.85 (×2), 129.8, 129.6, 128.5, 128.2 (×2), 127.8, 127.1, 124.2, 89.8, 21.8, 21.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{23}O_6S_2$: 495.0936; found: 495.0932.

Toluene-4-sulfonic Acid 2-(3,4-Dichlorophenyl)-2-oxo-1-(toluene-4-sulfonyl)ethyl Ester (5j)

Yield: 172 mg (67%); colorless solid; mp 174–176 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (40 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 2.0 Hz, 1 H), 7.85 (dd, *J* = 2.0, 8.4 Hz, 1 H), 7.70 (d, *J* = 8.0 Hz, 2 H), 7.58 (d, *J* = 8.4 Hz, 2 H), 7.56 (d, *J* = 8.4 Hz, 1 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 2 H), 6.13 (s, 1 H), 2.48 (s, 3 H), 2.42 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 185.2, 146.9, 146.4, 139.4, 133.5, 131.59, 131.56, 131.4, 130.7, 130.1 (×2), 130.0 (×4), 129.9, 129.0, 128.2 (×2), 90.3, 21.9, 21.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{19}Cl_2O_6S_2$: 513.0000; found: 513.0002.

Benzenesulfonic Acid 1-Benzenesulfonyl-2-oxo-2-phenylethyl Ester (5k)[5e]

Yield: 150 mg (72%); colorless solid; mp 166–168 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96–7.93 (m, 2 H), 7.83–7.80 (m, 2 H), 7.76–7.70 (m, 3 H), 7.66–7.41 (m, 8 H), 6.42 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.2, 135.2, 134.89, 134.87, 134.7 (×2), 134.2, 130.0 (×2), 129.8 (×2), 129.33 (×2), 129.25 (×2), 128.7 (×2), 128.1 (×2), 89.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{17}O_6S_2$: 417.0467; found: 417.0463.

Benzenesulfonic Acid 1-Benzenesulfonyl-2-(4-fluorophenyl)-2-oxoethyl Ester (5l)

Yield: 161 mg (74%); colorless solid; mp 145–147 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03–8.00 (m, 2 H), 7.83–7.80 (m, 2 H), 7.75–7.71 (m, 3 H), 7.64–7.54 (m, 3 H), 7.46–7.42 (m, 2 H), 7.18–7.13 (m, 2 H), 6.30 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.7, 166.6 (d, *J* = 257.0 Hz), 135.3, 134.8, 134.7, 132.9, 132.8 (d, *J* = 9.8 Hz, ×2), 130.6 (d, *J* = 3.0 Hz), 129.9 (×2), 129.4 (×2), 129.3 (×2), 128.1 (×2), 116.1 (d, *J* = 22.0 Hz, ×2), 89.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{16}FO_6S_2$: 435.0372; found: 435.0378.

Benzenesulfonic Acid 1-Benzenesulfonyl-2-biphenyl-4-yl-2-oxoethyl Ester (5m)

Yield: 155 mg (63%); colorless solid; mp 176–178 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05–8.02 (m, 2 H), 7.85–7.82 (m, 2 H), 7.78–7.42 (m, 15 H), 6.45 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 185.6, 147.4, 139.4, 135.2, 135.1, 135.0, 134.7, 132.9, 130.4 (×2), 130.1 (×2), 129.34 (×2), 129.28 (×2), 129.1 (×2), 128.7, 128.2 (×2), 127.3 (×4), 89.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{21}O_6S_2$: 493.0780; found: 493.0787.

Methanesulfonic Acid 1-Methanesulfonyl-2-oxo-2-phenylethyl Ester (5n)

Yield: 82 mg (56%); colorless solid; mp 184–186 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08–8.05 (m, 2 H), 7.72–7.67 (m, 1 H), 7.58–7.53 (m, 2 H), 6.56 (s, 1 H), 3.31 (s, 3 H), 3.08 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.3, 135.4, 129.8 (×2), 129.6, 129.1 (×2), 87.0, 40.0, 37.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{13}O_6S_2$: 293.0154; found: 293.0155.

Methanesulfonic Acid 1-Methanesulfonyl-2-(4-methoxyphenyl)-2-oxoethyl Ester (5o)

Yield: 72 mg (45%); colorless solid; mp 196–198 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 9.2 Hz, 2 H), 7.01 (d, *J* = 8.8 Hz, 2 H), 6.52 (s, 1 H), 3.91 (s, 3 H), 3.30 (s, 3 H), 3.07 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 185.0, 165.6, 132.5 (×2), 126.5, 114.5 (×2), 114.3, 87.0, 55.7, 40.0, 37.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{15}O_7S_2$: 323.0259; found: 323.0261.

Methanesulfonic Acid 1-Methanesulfonyl-2-oxo-2-*p*-tolylethyl Ester (5p)

Yield: 110 mg (72%); colorless solid; mp 167–169 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 6.55 (s, 1 H), 3.30 (s, 3 H), 3.06 (s, 3 H), 2.45 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.6, 147.0, 131.7, 129.9 (×2), 129.8 (×2), 87.0, 40.0, 37.7, 21.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{15}O_6S_2$: 307.0310; found: 307.0315.

Methanesulfonic Acid 2-Biphenyl-4-yl-1-methanesulfonyl-2-oxo-ethyl Ester (5q)

Yield: 123 mg (67%); colorless solid; mp 176–178 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, *J* = 8.4 Hz, 2 H), 7.77 (d, *J* = 8.4 Hz, 2 H), 7.65–7.63 (m, 2 H), 7.51–7.42 (m, 3 H), 6.60 (s, 1 H), 3.33 (s, 3 H), 3.10 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.7, 148.2, 139.2, 132.7, 130.4 (×2), 129.1, 128.8 (×2), 127.7 (×2), 127.4 (×2), 87.1, 40.0, 37.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{17}O_6S_2$: 369.0467; found: 369.0462.

Toluene-3-sulfonic Acid 2-Oxo-2-phenyl-1-(toluene-3-sulfonyl)ethyl Ester (5r)

Yield: 155 mg (70%); colorless solid; mp 112–114 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96–7.94 (m, 2 H), 7.65–7.61 (m, 3 H), 7.53–7.37 (m, 7 H), 7.30 (d, *J* = 7.6 Hz, 1 H), 6.35 (s, 1 H), 2.41 (s, 3 H), 2.29 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.3, 139.8, 139.6, 136.0, 135.5, 134.7, 134.63, 134.57, 134.3, 130.2, 129.8 (×2), 129.13, 129.06, 128.7 (×2), 128.4, 127.2, 125.2, 89.7, 21.3, 21.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{21}O_6S_2$: 445.0780; found: 445.0783.

4-Fluorobenzenesulfonic Acid 1-(4-Fluorobenzenesulfonyl)-2-oxo-2-phenylethyl Ester (5s)

Yield: 163 mg (72%); colorless solid; mp 218–220 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96–7.93 (m, 2 H), 7.83–7.78 (m, 3 H), 7.69–7.65 (m, 2 H), 7.53–7.49 (m, 2 H), 7.25–7.21 (m, 2 H), 7.15–7.11 (m, 2 H), 6.47 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.1, 135.5, 135.1 (d, *J* = 3.6 Hz), 134.2 (d, *J* = 3.0 Hz), 133.2 (d, *J* = 10.6 Hz, ×2), 131.2 (d, *J* = 9.9 Hz, ×2), 130.3 (d, *J* = 3.0 Hz), 129.7 (×2), 129.1, 129.0, 128.9 (×2), 116.8 (d, *J* = 22.7 Hz, ×2), 116.8 (d, *J* = 22.7 Hz, ×2), 89.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{15}F_2O_6S_2$: 453.0278; found: 453.0277.

4-Methoxybenzenesulfonic Acid 1-(4-Methoxybenzenesulfonyl)-2-oxo-2-phenylethyl Ester (5t)

Yield: 19 mg (8%); colorless solid; mp 166–168 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94–7.92 (m, 2 H), 7.74–7.72 (m, 2 H), 7.68–7.61 (m, 3 H), 7.52–7.46 (m, 3 H), 7.39–7.35 (m, 1 H), 6.98–6.94 (m, 2 H), 6.13 (s, 1 H), 3.90 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.9, 164.8, 163.9, 135.1, 134.5, 133.3, 132.3 (×2), 129.8 (×2), 129.1 (×2), 128.8 (×2), 127.0 (×2), 126.0, 114.4 (×2), 74.5, 55.7 (×2).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{21}O_8S_2$: 477.0678; found: 477.0684.

Single-crystal X-ray analysis: Slow diffusion of EtOAc into a solution of compound **5t** in CH_2Cl_2 yielded colorless prisms. The compound crystallizes in the monoclinic crystal system, space group *P*21/*c*, *a* = 5.7476(7) Å, *b* = 18.106(2) Å, *c* = 20.945(3) Å, *V* = 2167.4(5) Å^3, *Z* = 4, d_{calcd} = 1.460 mg/cm^3, *F*(000) = 992, 2θ range 1.490–26.616°; *R* indices (all data): *R*1 = 0.1974, *wR*2 = 0.3067.

4-Ethylbenzenesulfonic Acid 1-(4-Ethylbenzenesulfonyl)-2-oxo-2-phenylethyl Ester (5u)

Yield: 172 mg (73%); colorless solid; mp 138–140 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94–7.91 (m, 2 H), 7.71 (d, *J* = 8.4 Hz, 2 H), 7.65–7.60 (m, 3 H), 7.48–7.44 (m, 2 H), 7.36 (d, *J* = 8.4 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 2 H), 6.35 (s, 1 H), 2.76 (q, *J* = 7.6 Hz, 2 H), 2.68 (q, *J* = 7.6 Hz, 2 H), 1.29 (t, *J* = 7.6 Hz, 3 H), 1.22 (d, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.6, 152.6, 152.1, 134.5, 134.3, 131.9, 130.2 (×2), 129.8 (×2), 128.8 (×2), 128.74 (×3), 128.65 (×2), 128.4 (×2), 89.5, 29.0, 28.9, 14.92, 14.86.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{25}O_6S_2$: 473.1093; found: 473.1096.

4-Isopropylbenzenesulfonic Acid 1-(4-Isopropylbenzenesulfonyl)-2-oxo-2-phenylethyl Ester (5v)

Yield: 180 mg (72%); colorless solid; mp 114–116 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.89 (m, 2 H), 7.73 (d, *J* = 8.4 Hz, 2 H), 7.64 (d, *J* = 8.4 Hz, 2 H), 7.63–7.59 (m, 1 H), 7.47–7.43 (m, 2 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 7.24 (d, *J* = 8.4 Hz, 2 H), 6.35 (s, 1 H), 3.05–2.96 (m, 1 H), 2.96–2.89 (m, 1 H), 1.29 (d, *J* = 7.2 Hz, 6 H), 1.22 (d, *J* = 7.2 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.6, 157.1, 156.9, 134.51, 134.47, 132.0, 130.3 (×2), 129.7 (×2), 128.7 (×2), 128.5, 128.4 (×2), 127.4 (×4), 89.6, 34.4, 34.3, 23.53 (×2), 23.48 (×2).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{29}O_6S_2$: 501.1406; found: 501.1412.

4-*n*-Butylbenzenesulfonic Acid 1-(4-*n*-Butylbenzenesulfonyl)-2-oxo-2-phenylethyl Ester (5w)

Yield: 195 mg (74%); colorless solid; mp 95–96 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.91 (m, 2 H), 7.71 (d, *J* = 8.4 Hz, 2 H), 7.62 (d, *J* = 8.0 Hz, 2 H), 7.62–7.60 (m, 1 H), 7.48–7.44 (m, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.20 (d, *J* = 8.4 Hz, 2 H), 6.35 (s, 1 H), 2.71 (t, *J* = 7.6 Hz, 2 H), 2.63 (t, *J* = 7.6 Hz, 2 H), 1.67–1.52 (m, 4 H), 1.42–1.27 (m, 4 H), 0.95 (t, *J* = 7.6 Hz, 3 H), 0.93 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.5, 151.4, 150.9, 134.5, 134.3, 131.94, 131.91, 130.1 (×2), 129.8 (×2), 129.3 (×4), 128.6 (×2), 128.3 (×2), 89.5, 35.8, 35.6, 33.0 (×2), 22.3, 22.2, 13.84, 13.81.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{33}O_6S_2$: 529.1719; found: 529.1723.

4-*tert*-Butylbenzenesulfonic Acid 1-(4-*tert*-Butylbenzenesulfonyl)-2-oxo-2-phenylethyl Ester (5x)

Yield: 200 mg (76%); colorless solid; mp 154–156 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.88 (m, 2 H), 7.74 (d, *J* = 8.8 Hz, 2 H), 7.64 (d, *J* = 8.0 Hz, 2 H), 7.62–7.58 (m, 1 H), 7.56 (d, *J* = 8.4 Hz, 2 H), 7.45–7.41 (m, 2 H), 7.39 (d, *J* = 8.8 Hz, 2 H), 6.36 (s, 1 H), 1.36 (s, 9 H), 1.28 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.6, 159.4, 158.9, 134.5, 134.3, 131.8, 131.6, 130.0 (×2), 129.7 (×2), 128.6 (×2), 128.1 (×2), 126.29 (×2), 126.27 (×2), 89.6, 35.4, 35.3, 31.0 (×3), 30.9 (×3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{33}O_6S_2$: 529.1719; found: 529.1724.

n-Butane-1-sulfonic Acid 1-(Butane-1-sulfonyl)-2-oxo-2-phenylethyl Ester (5y)

Yield: 23 mg (12%); colorless gum.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07–8.05 (m, 2 H), 7.69–7.66 (m, 2 H), 7.56–7.53 (m, 1 H), 6.54 (s, 1 H), 3.54 (t, *J* = 8.0 Hz, 2 H), 3.36 (t, *J* = 7.6 Hz, 2 H), 1.95–1.91 (m, 2 H), 1.91–1.85 (m, 2 H), 1.54–1.40 (m, 4 H), 0.99 (t, *J* = 7.6 Hz, 3 H), 0.96 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.5, 134.5, 133.4, 129.8 (×2), 127.4 (×2), 87.0, 56.6, 52.6, 25.2, 24.7, 21.3, 21.3, 13.4, 13.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{25}O_6S_2$: 377.1093; found: 377.1098.

α-Halo-β-Ketosulfones 6a–c; General Procedure

$CuCl_2$ (80 mg, 0.6 mmol), $CuBr_2$ (134 mg, 0.6 mmol) or CuI (114 mg, 0.6 mmol) was added to a solution of **4a** (150 mg, 0.5 mmol) in $MeNO_2$ (5 mL) at r.t. The reaction mixture was stirred at r.t. for 10 min and then at reflux for 20 h. The reaction mixture was cooled to r.t. and the solvent was concentrated. The residue was diluted with H_2O (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated under reduced pressure to afford the crude product. Purification on silica gel (hexanes/EtOAc = 8:1 to 4:1) afforded compounds **6a–c**.

2-Chloro-1-phenyl-2-(toluene-4-sulfonyl)ethanone (6a)[15]

Yield: 94 mg (61%); colorless solid; mp 136–138 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.0 Hz, 2 H), 7.78 (d, *J* = 8.4 Hz, 2 H), 7.70–7.66 (m, 1 H), 7.56–7.52 (m, 2 H), 7.38 (d, *J* = 8.0 Hz, 2 H), 6.19 (s, 1 H), 2.48 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.4, 146.6, 134.8, 134.6, 131.2, 130.8 (×2), 129.68 (×2), 129.65 (×2), 129.0 (×2), 72.0, 21.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{14}ClO_3S$: 309.0352; found: 309.0356.

Single-crystal X-ray analysis: Slow diffusion of EtOAc into a solution of compound **6a** in CH_2Cl_2 yielded colorless prisms. The compound crystallizes in the monoclinic crystal system, space group *P*21/*c*, *a* = 14.5323(19) Å, *b* = 9.7603(13) Å, *c* = 10.0176(15) Å, *V* = 1379.6(3) Å^3, *Z* = 4, d_{calcd} = 1.487 mg/cm^3, *F*(000) = 640, 2θ range 1.443–25.274°; *R* indices (all data): *R*1 = 0.0523, *wR*2 = 0.1110.

2-Bromo-1-phenyl-2-(toluene-4-sulfonyl)ethanone (6b)[15]

Yield: 90 mg (51%); colorless solid; mp 163–165 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.4 Hz, 2 H), 7.84 (d, *J* = 8.0 Hz, 2 H), 7.67–7.63 (m, 1 H), 7.53–7.49 (m, 2 H), 7.37 (d, *J* = 8.4 Hz, 2 H), 6.23 (s, 1 H), 2.46 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.7, 146.4, 134.7, 134.3, 131.8, 130.9 (×2), 129.52 (×2), 129.48 (×2), 129.0 (×2), 60.1, 21.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{14}BrO_3S$: 352.9847; found: 352.9852.

Single-crystal X-ray analysis: Slow diffusion of EtOAc into a solution of compound **6b** in CH_2Cl_2 yielded colorless prisms. The compound crystallizes in the monoclinic crystal system, space group *P*21/*c*, *a* = 14.6837(12) Å, *b* = 9.7540(8) Å, *c* = 10.0220(8) Å, *V* = 1393.5(2) Å^3, *Z* = 4, d_{calcd} = 1.684 mg/cm^3, *F*(000) = 712, 2θ range 1.428–26.357°; *R* indices (all data): *R*1 = 0.0245, *wR*2 = 0.0501.

2-Iodo-1-phenyl-2-(toluene-4-sulfonyl)ethanone (6c)[15]

Yield: 44 mg (22%); colorless solid; mp 150–152 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92–7.87 (m, 4 H), 7.64–7.60 (m, 1 H), 7.49–7.45 (m, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 6.52 (s, 1 H), 2.44 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.2, 146.1, 134.5, 133.6, 132.2, 130.9 (×2), 129.5 (×2), 129.2 (×2), 129.0 (×2), 37.8, 21.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{14}IO_3S$: 400.9708; found: 400.9715.

Benzoic Acid 2-Oxo-2-phenylethyl Ester (9)[16]

$Cu(OAc)_2$ (220 mg, 1.2 mmol) was added to a solution of **7a** (250 mg, 1.0 mmol) in $MeNO_2$ (5 mL) at r.t. The reaction mixture was stirred at r.t. for 10 min and then at reflux for 20 h. The reaction mixture was cooled to r.t. and the solvent was concentrated. The residue was diluted with H_2O (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated under reduced pressure to afford the crude product. Purification on silica gel (hexanes/EtOAc = 8:1 to 4:1) afforded **9**.

Yield: 42 mg (35%); colorless solid; mp 118–120 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17–8.14 (m, 2 H), 7.99–7.96 (m, 2 H), 7.65–7.58 (m, 2 H), 7.53–7.45 (m, 4 H), 5.58 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.1, 166.0, 134.3, 133.9, 133.3, 130.0 (×2), 129.4, 128.9 (×2), 128.4 (×2), 127.8 (×2), 66.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{13}O_3$: 241.0865; found: 241.0866.

Single-crystal X-ray analysis: Slow diffusion of EtOAc into a solution of compound **9** in CH_2Cl_2 yielded colorless prisms. The compound crystallizes in the monoclinic crystal system, space group *P*21/*c*, *a* = 9.0669(3) Å, *b* = 14.1271(5) Å, *c* = 9.6077(3) Å, *V* = 1230.53(7) Å^3, *Z* = 4, d_{calcd} = 1.297 mg/cm^3, *F*(000) = 504, 2θ range 2.246–26.418°; *R* indices (all data): *R*1 = 0.0683, *wR*2 = 0.1854.

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Supporting Information

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