

SUPPORTING INFORMATION

Cross Coupling of Sulfonyl Radical with Silver-Based Carbene: A Simple Approach to β -Carbonyl Arylsulfones

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List of Contents

General procedures for the preparation of starting materials.....	S2
Optimization of the Reaction Conditions	S3
Mechanistic studies.....	S4
Spectroscopic data for products.....	S8

General procedures for the preparation of starting materials

(a) The procedure for the synthesis of diazo compounds¹

The corresponding alcohol or dibenzylamine (20 mmol) and NaHCO₃ (5.0 g, 60 mmol) were dissolved in acetonitrile (50 mL) and bromoacetyl bromide (2.6 mL, 30 mmol) was added slowly at 0 °C. After stirring 30 min at the temperature, the reaction was quenched with H₂O. The solution was extracted with CH₂Cl₂ three times. The organic phase was washed with brine and dried over Na₂SO₄. The solvent was evaporated, and the residue was used in the next reaction without purification. The bromoacetate thus obtained and *N, N'*-ditosylhydrazine (13.6 g, 40 mmol) were dissolved in THF (50 mL) and cooled to 0 °C. DBU (6.0 mL, 40 mmol) was added dropwise and stirred at the temperature for 30 minutes. After the quenching of the reaction by the addition of saturated NaHCO₃ solution, it was extracted with Et₂O three times. The organic phase was washed with brine, dried over Na₂SO₄ and evaporated to give the crude product. The crude product thus obtained was purified by chromatography over a column of silica gel using petroleum and ethyl acetate as eluent to afford the desired product.

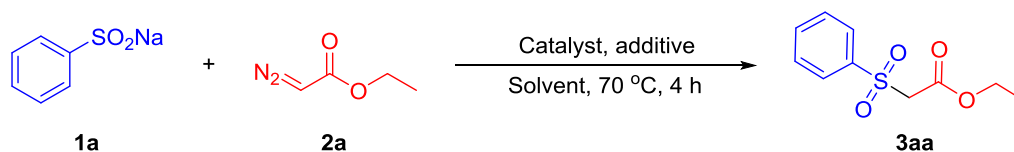
(b) The procedure for the synthesis of diazo compounds **2m** and **2n**²

To a stirred solution of methyl ethyl 2-methyl-3-oxobutanoate or ethyl 2-ethyl-3-oxobutanoate (10.0 mmol, 1.00 equiv) and *p*-acetamidobenzenesulfonyl azide (15.0 mmol, 1.50 equiv) in dry CH₃CN (20 mL) was added DBU (4.6 mL, 30 mmol, 3.0 equiv) at 0 °C. The reaction mixture was then allowed to warm to room temperature. After stirring for 12 h, the resulting mixture was quenched with 20 mL of 1 M HCl, and extracted with hexane (3 x 50 mL). The combined organic layers were washed with saturated solution of NaHCO₃ (50 mL), brine (50 mL), and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and purified by flash column chromatography using 1:20 ethyl acetate: petroleum as eluent to afford the corresponding diazo compounds **2m** or **2n** as a yellow oil.

(c) The procedure for the synthesis of sodium arylsulfonates³

Sodium sulfite (20 mmol, 2 equiv), sodium bicarbonate (20 mmol, 2 equiv) and the corresponding aryl sulfonyl chloride (10 mmol, 1 equiv.) were dissolved in distilled water (10 mL). The reaction mixture was stirred for 4 h at 80 °C. After cooling down to room temperature, water was removed in vacuo. 25 mL of ethanol was then added to this white residue and the resulting heterogeneous solution was filtered. The filtrate was concentrated under reduced pressure and the desired sodium aryl sulfonates were obtained as white crystalline powders.

Sodium arylsulfonates **1a**, **1b**, **1e** and **1f** are commercially available.

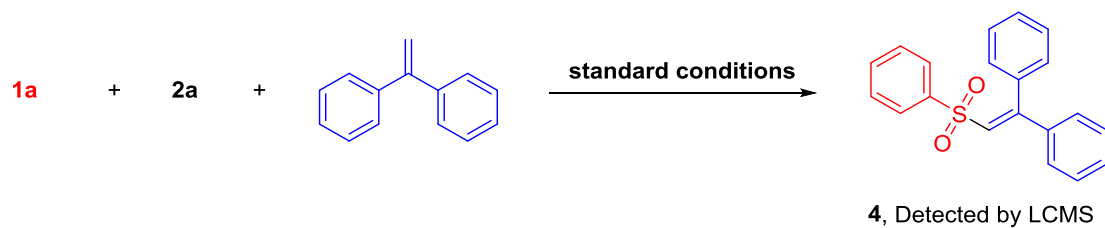
Table S1. Optimization of the Reaction Conditions^a

Entry	Catalyst (mol%)	Additive (equiv.)	Solvent	Ligand (mol%)	Yield [%] ^b
1	AgNO ₃ (20)	K ₂ S ₂ O ₈ (2.0)	DCE	—	n.d.
2	AgNO ₃ (20)	K ₂ S ₂ O ₈ (2.0)	EtOH	—	n.d.
3	AgNO ₃ (20)	K ₂ S ₂ O ₈ (2.0)	1,4-dioxane	—	n.d.
4	AgNO ₃ (20)	K ₂ S ₂ O ₈ (2.0)	MeCN	—	trace
5	AgNO ₃ (20)	K ₂ S ₂ O ₈ (2.0)	DMF	—	n.d.
6	AgNO ₃ (20)	K ₂ S ₂ O ₈ (2.0)	H ₂ O	—	n.d.
7	AgNO ₃ (20)	K ₂ S ₂ O ₈ (2.0)	MeCN/H ₂ O (1:1)	—	36
8	AgNO ₃ (20)	K ₂ S ₂ O ₈ (2.0)	MeCN/H ₂ O (5:1)	—	43
9	AgNO ₃ (20)	K ₂ S ₂ O ₈ (2.0)	MeCN/H ₂ O (7:1)	—	46
10	AgNO ₃ (20)	K ₂ S ₂ O ₈ (2.0)	MeCN/H ₂ O (10:1)	—	54
11	AgNO ₃ (20)	K ₂ S ₂ O ₈ (1.0)	MeCN/H ₂ O (10:1)	—	56
12	AgNO ₃ (20)	K ₂ S ₂ O ₈ (0.5)	MeCN/H ₂ O (10:1)	—	68
13	AgNO ₃ (20)	K ₂ S ₂ O ₈ (0.2)	MeCN/H ₂ O (10:1)	—	45
14	CF ₃ CO ₂ Ag (20)	K ₂ S ₂ O ₈ (0.5)	MeCN/H ₂ O (10:1)	—	62
15	AgOAc (20)	K ₂ S ₂ O ₈ (0.5)	MeCN/H ₂ O (10:1)	—	58
16	Ag ₂ CO ₃ (20)	K ₂ S ₂ O ₈ (0.5)	MeCN/H ₂ O (10:1)	—	63
17	AgF (20)	K ₂ S ₂ O ₈ (0.5)	MeCN/H ₂ O (10:1)	—	59
18	AgNO ₃ (20)	Na ₂ S ₂ O ₈ (0.5)	MeCN/H ₂ O (10:1)	—	65
19	AgNO ₃ (20)	(NH ₄) ₂ S ₂ O ₈ (0.5)	MeCN/H ₂ O (10:1)	—	48
20	AgNO ₃ (20)	K ₂ S ₂ O ₈ (0.5)	MeCN/H ₂ O (10:1)	L1(20)	76
21	AgNO ₃ (20)	K ₂ S ₂ O ₈ (0.5)	MeCN/H ₂ O (10:1)	L2(20)	73
22	AgNO ₃ (20)	K ₂ S ₂ O ₈ (0.5)	MeCN/H ₂ O (10:1)	L3(20)	68
23	AgNO ₃ (20)	K ₂ S ₂ O ₈ (0.5)	MeCN/H ₂ O (10:1)	L1(15)	77
24	AgNO ₃ (20)	K ₂ S ₂ O ₈ (0.5)	MeCN/H ₂ O (10:1)	L1(10)	77
25	AgNO₃ (10)	K₂S₂O₈ (0.5)	MeCN/H₂O (10:1)	L1(10)	80
26	AgNO ₃ (5)	K ₂ S ₂ O ₈ (0.5)	MeCN/H ₂ O (10:1)	L1(10)	72
27	AgNO ₃ (10)	K ₂ S ₂ O ₈ (0.5)	MeCN/H ₂ O (10:1)	L4(10)	68
28	AgNO ₃ (10)	K ₂ S ₂ O ₈ (0.5)	MeCN/H ₂ O (10:1)	L5(10)	70
29	AgNO ₃ (10)	K ₂ S ₂ O ₈ (0.5)	MeCN/H ₂ O (10:1)	L6(10)	57
30	—	K ₂ S ₂ O ₈ (0.5)	MeCN/H ₂ O (10:1)	L1(10)	< 5
31	AgNO ₃ (10)	—	MeCN/H ₂ O (10:1)	L1(10)	< 5

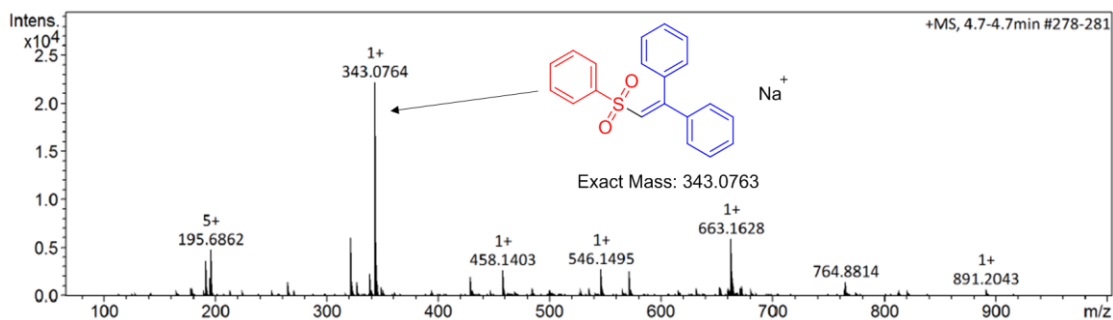
^a Unless otherwise noted, all the reactions were run with **1a** (0.5 mmol) and **2a** (1 mmol) in 2.0 mL solvent at 70 °C under air. ^b isolated yields. n.d. = not detected. **L1** = 1,10-phenanthroline, **L2** = 2,2'-bipyridine, **L3** = 2,2':6',2''-terpyridine, **L4** = 4,7-dimethoxy-1,10-phenanthroline, **L5** = 4,7-diphenyl-1,10-phenanthroline, **L6** = 3,8-dibromo-1,10-phenanthroline.

Mechanistic studies

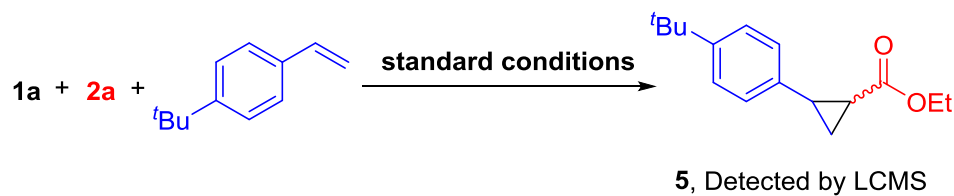
Scheme S1. Trapping of radical by 1,1-diphenylethylene



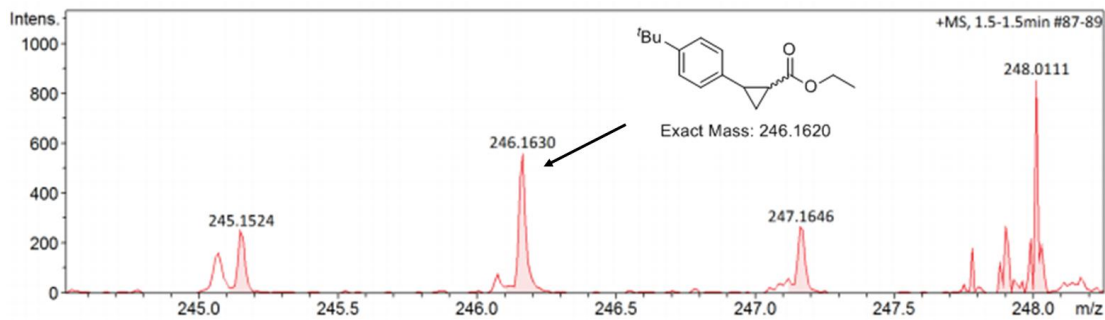
Adduct Detected by LCMS



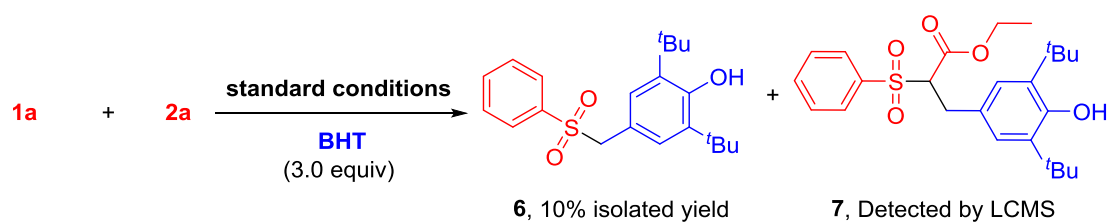
Scheme S2. Trapping of silver-based carbene



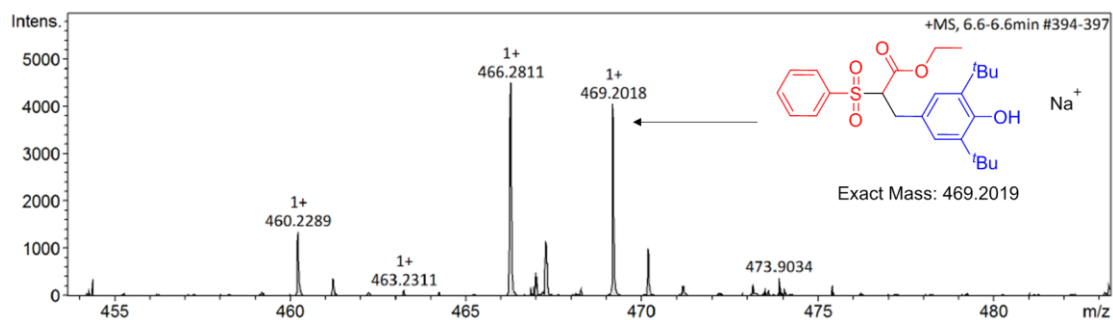
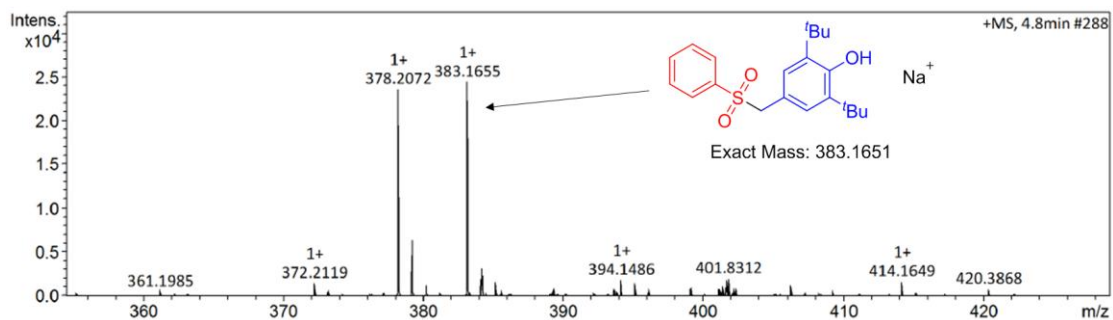
Adduct 7 Detected by LCMS



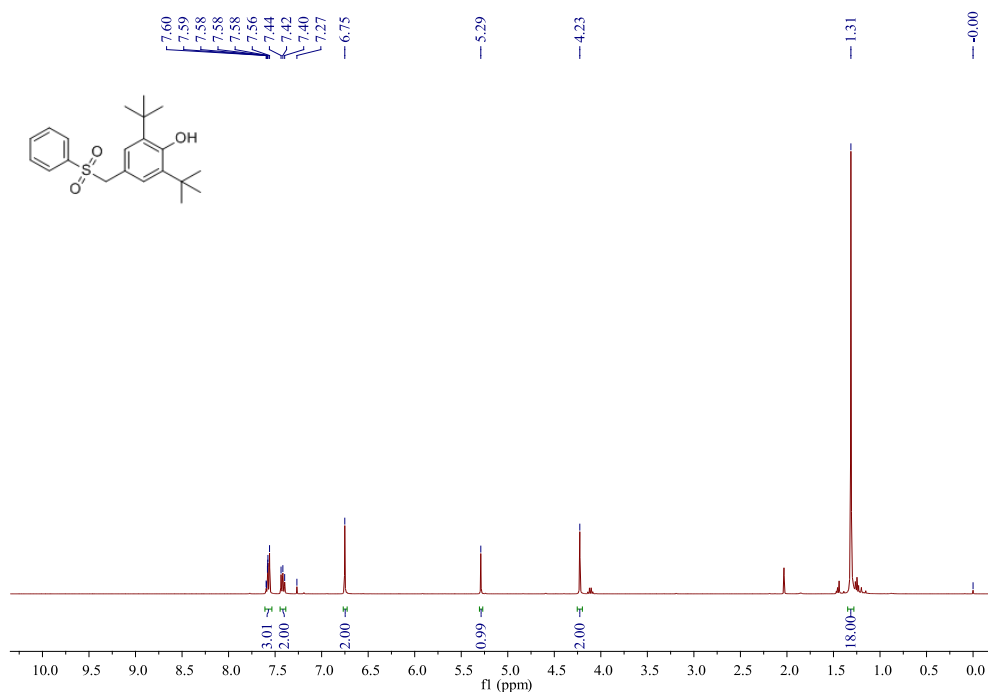
Scheme S3. Trapping of radicals by BHT

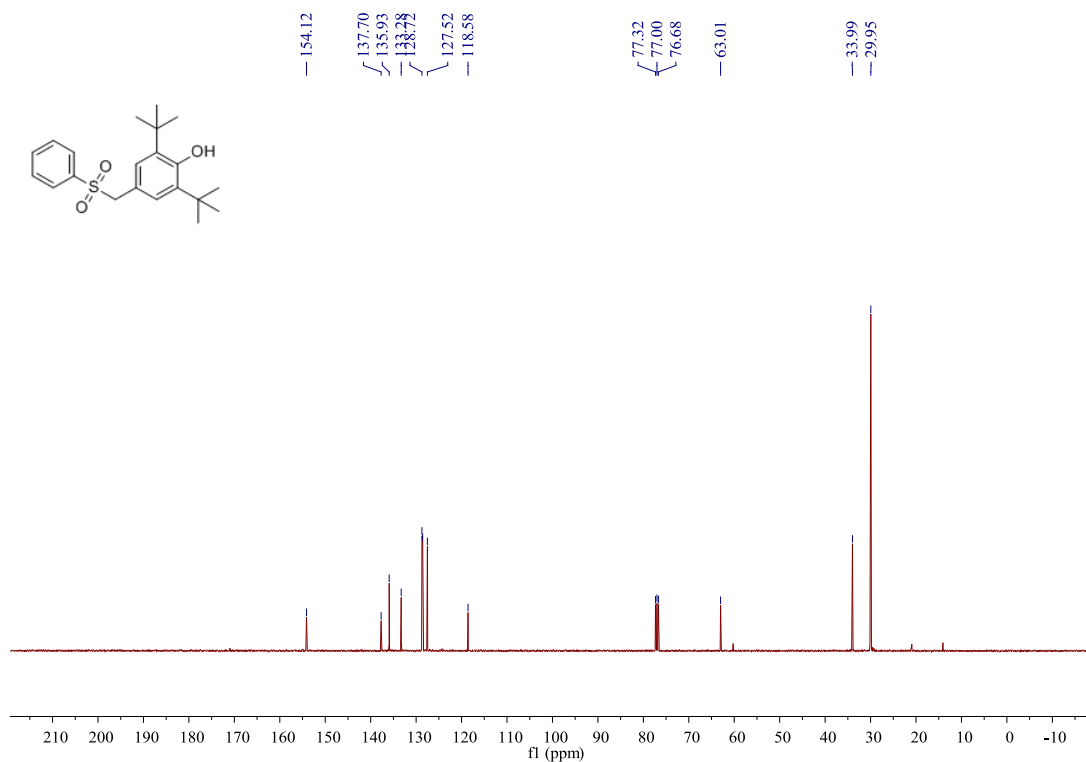


Adduct Detected by LCMS



NMR of 6





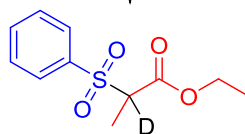
Scheme S4. Isotope labeling experiment



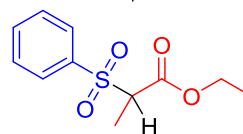
Reaction Medium $\text{CH}_3\text{CN}/\text{D}_2\text{O} = 10:1$ (2 mL)

Reaction Medium $\text{CD}_3\text{CN}/\text{H}_2\text{O} = 10:1$ (2 mL)

Product

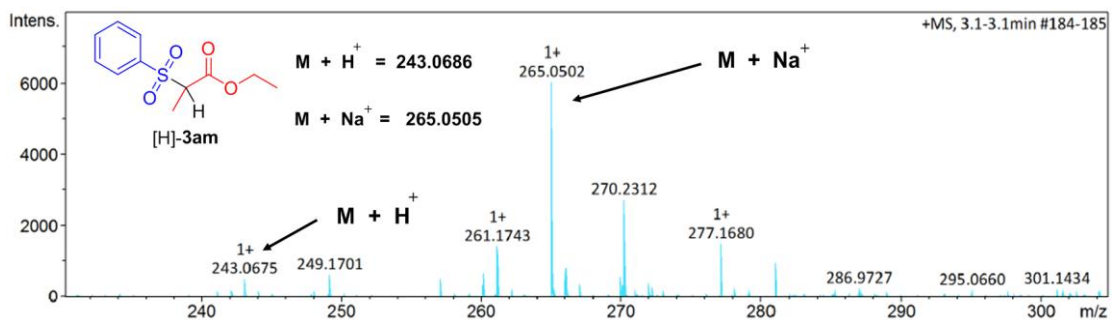
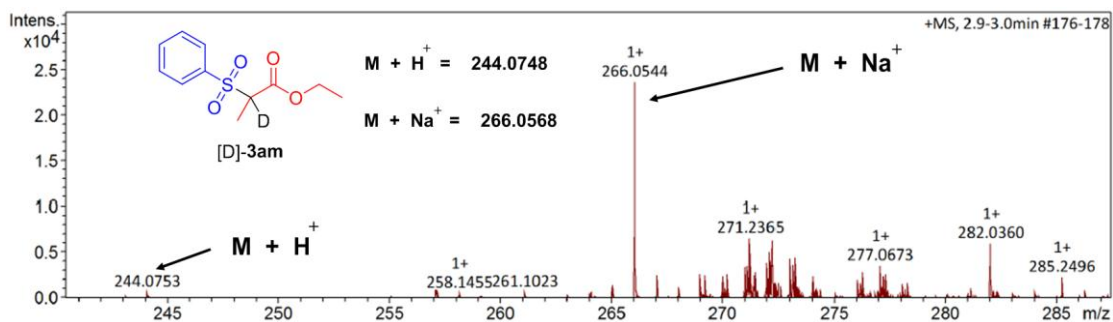


[D]-3am



[H]-3am

Product detected by LCMS



References:

- (1) T. Toma, J. Shimokawa and T. Fukuyama, *Org. Lett.*, 2007, **9**, 3195.
- (2) T. Hashimoto, Y. Naganawa and K. Maruoka, *J. Am. Chem. Soc.*, 2011, **133**, 8834.
- (3) (a) A. U. Meyer, S. Jager, D. Prasad Hari and B. Konig, *Adv. Synth. Catal.*, 2015, **357**, 2050. (b) G. Bogonda, D. V. Patil, H. Y. Kim and K. Oh, *Org. Lett.*, 2019, **21**, 3774.

Spectroscopic data for products

