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Highly regioselective tandem formal substitution and decarboxylation of 2-acyl-1-chlorocyclopropanecarboxylates with sodium sulfinates

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ABSTRACT

This article reported a highly regioselective tandem formal nucleophilic substitution and decarboxylation reaction of alkyl 2-acyl-1-chlorocyclopropanecarboxylates with sodium sulfinates under basic conditions. Actually, alkyl 2-acyl-1-chlorocyclopropanecarboxylates could be easily converted into cyclopropene intermediates by simple 1,2-elimination of hydrogen chloride, and this highly reactive cyclopropene quickly combines with sodium sulfinate via a regioselective 1,4-Michael addition. Subsequent esterolysis and decarboxylation of the 1,4-Michael adducts afforded 1-aroylsulfonyl-2-aroylcyclopropanes in high yields. This observation firstly demonstrates that direct Michael addition of sodium sulfinates with reactive cyclopropene is really workable.

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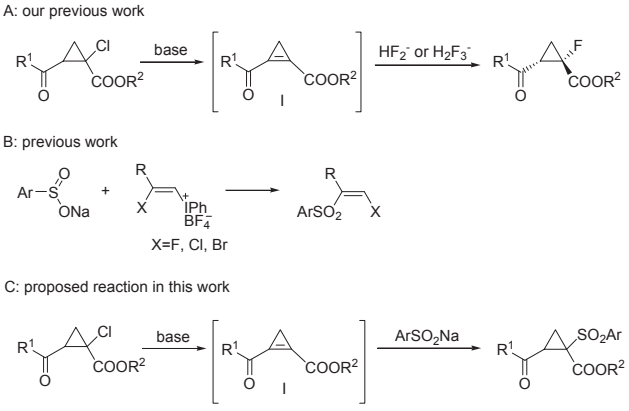
1. Introduction

Cyclopropenes, for their unique reactivity that extends far beyond chemical properties typical for common alkenes, has attracted increasing attention of chemists in the past decades.[1] Recently, a more reactive cyclopropene intermediate I (Scheme 1A) bearing two electron-withdrawing groups on its C=C bond was observed during our investigation in the formal fluorination reaction of ethyl 2-aroyl-1-chlorocyclopropanecarboxylates with HF_2^- or $H_2F_3^-$.[2] To our knowledge, this is one successful example for unique nucleophilic addition reaction of hydrogen fluoride with electro-deficient alkenes under weakly basic conditions.

Inspired by this observation, we want to evaluate nucleophilic addition reactions of other typical weak nucleophiles with the electron-deficient cyclopropenes generated in situ. Among them, sodium sulfinates as a kind of weaker nucleophile, to date, are rarely reported in direct Michael addition reaction with electron-deficient alkenes except with some special olefines such as alkenyliodonium salt (Scheme 1B).[3] For the wide applications of cyclopropyl sulfones in synthesis[4–8] and potential antimicrobial and pesticidal activities,[9] our attention was focused on the possibility to prepare cyclopropyl sulfones through direct Thia-Michael addition of sodium sulfinates with the reactive electron-deficient cyclopropenes (Scheme 1C).



Scheme 1. The additive reactions of weak nucleophiles with alkenes.

In general, cyclopropyl sulfones could be prepared from the cycloaddition of vinylic sulfones with active methylene compounds,[10] cyclization of sulfone-stabilized carbanions and electron-deficient alkenes,[11] or cycloisomerization of terminal epoxides with sodium salts of diethyl (phenylsulfonyl)-methylphosphonate.[12] Moreover, they could also be formed from further oxidation of

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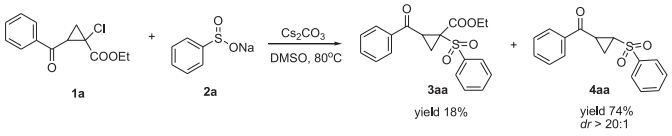
cyclopropyl sulfides.[13] There is still a great demand for a general and convenient procedure from readily available starting materials.

Based on the above idea and current research situation, we have tried the possible reaction between 2-aroyl-1-chlorocyclopropanecarboxylates and sodium sulfinates. As a consequence, a highly regioselective tandem reaction involving 1,2-elimination of HCl, 1,4-Michael addition of arylsulfinate, esterolysis and decarboxylation occurred smoothly, affording a variety of cyclopropyl sulfones in high yields with *dr*>20:1. In fact, it was the first instance reported hitherto about direct Michael addition of sodium arylsulfinate with cyclopropene intermediate I. Moreover, the introduction of sulfonyl group makes the subsequent esterolysis and decarboxylation proceed more easily in a tandem process.

2. Results and discussion

Initially, we began our study choosing ethyl 2-benzoyl-1-chlorocyclopropanecarboxylate **1a** and sodium benzenesulfinate **2a** as benchmark substrates. Fortunately, the product **4aa** in 74% yield with *dr*>20:1 was observed in the presence of 1 equiv Cs_2CO_3 in DMSO at 80 °C (Scheme 2). The structure of product for this process was carefully characterized by ^1H and ^{13}C NMR spectroscopy and HRMS, and the major isomer was assigned to be *trans*-**4aa**. This assignment was further supported by single crystal X-ray analysis of product **4bd** (see Supplementary data). It should be mentioned that product **3aa** (in 18% yield) yielded through simple sulfonate addition, which was hardly separated from **4aa** by silica gel column chromatography.



Scheme 2. Formal substitution reaction of **1a** with sodium sulfinate **2a**.

In order to get the optimal reaction conditions, several parameters including base, solvent and reaction temperature were screened using the above reaction of **1a** with **2a** as the model. The observed results are summarized in Table 1. Firstly, a variety of inorganic and organic bases were assessed. From the results listed in Table 1 (entries 2–11), we can conclude all of the inorganic bases can promote this reaction, but their property has a great influence on the reaction. Common bases like K_2CO_3 or Na_2CO_3 showed inferior catalytic activity, and gave only low conversions after 24 h (Table 1, entries 1–2). Strong base was conducive to the further decarboxylation of this reaction process. Among all the inorganic bases such as K_3PO_4, NaOH, KOH, and CH_3ONa, Cs_2CO_3 was the most suitable one, and the product **4aa** was produced in 89% yield with *dr*>20:1 possibly owing to its high solubility in DMSO (Table 1, entries 3–7). In contrast, strong base t-BuOK obviously accelerated the consumption rate of **1a**, but led to a significant decline in the yield of **4aa** (Table 1, entry 8). This decline could be attributed to much faster 1,2-elimination of **1a** and subsequent polymerization of the cyclopropene intermediate generated in situ under the strongly basic conditions. On the other hand, organic bases such as DIPEA, TEA and DBU also can promote the reaction, but the product yields were unsatisfied (Table 1, entries 9–11).Then, some commonly used solvents were screened. Strong polar aprotic solvents such as DMSO, DMF seems to be good choice for the high yields of **4aa** (Table 1, entries 4, 12–16). We realized that the solubility of base has a marked influence on the reaction in solvents, and DMSO was the most appropriate one. Decreasing the loading of base to 1.5 equiv or lowering reaction temperature resulted in the formation of **4aa** in relatively low yields (Table 1, entries 17–18). Based on the above observations, the optimized reaction conditions chosen for further investigation were as follows: substrate (1 equiv), sodium sulfinate (2 equiv), Cs_2CO_3 (2 equiv) in DMSO at 80 °C (Table 1, entry 4).

Table 1
Optimization of reaction conditions[a]

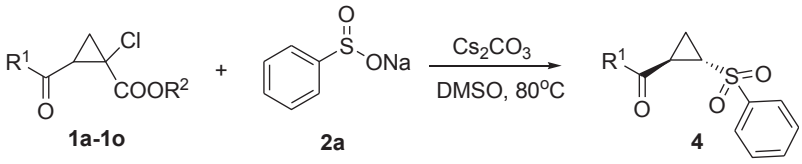
Entry	Base	Solvent	Time (h)[b]	Conversion (%)	Yield(%)[c]	
					3aa	**4aa**
1	K_2CO_3	DMSO	24	62	62(38)	16(10)
2	Na_2CO_3	DMSO	24	40	64(26)	12(5)
3	K_3PO_4	DMSO	10	100	19	70
4	Cs_2CO_3	DMSO	2	100	—	89
5	NaOH	DMSO	5	100	10	48
6	KOH	DMSO	4	100	4	48
7	CH_3ONa	DMSO	3	100	16	33
8	t-BuOK	DMSO	0.5	100	—	26
9	DIPEA	DMSO	24	26	27(7)	—
10	TEA	DMSO	24	44	51(22)	—
11	DBU	DMSO	2	100	16	43
12	Cs_2CO_3	DMF	4	100	11	74
13	Cs_2CO_3	CH_3CN	4	100	4	37
14	Cs_2CO_3	1,4-Dioxane	24	100	17	15
15	Cs_2CO_3	1,2-DCE	24	46	—	43(20)
16	Cs_2CO_3	Toluene	24	30	—	38(11)
17[d]	Cs_2CO_3	DMSO	10	100	9	81
18[e]	Cs_2CO_3	DMSO	24	100	34	5

[a] Unless otherwise noted, the reaction was performed with **1a** (0.2 mmol), **2a** (0.4 mmol), and the indicated base in solvent at 80 °C.
[b] Determined by TLC.
[c] Yields based on converted **1a**, and isolated yields in parentheses.
[d] Cs_2CO_3 (0.3 mmol).
[e] Reaction was performed at room temperature.

Under the optimized conditions, the reactions of sodium benzenesulfinate **2a** with a variety of alkyl 2-acyl-1-chlorocyclopropanecarboxylates **1a**–**1o** were studied. All the observed results were summarized in Table 2. In all the cases, the corresponding products **4ba**–**4ka** were respectively produced with excellent diastereoselectivities (*dr* up to 20:1). In contrast, the product yields obviously varied with the change of R^1 groups for **1**, though the effect of their electronic property seems to be irregular (entries 1–10). For example, both **1b** with electron-donating 4-Me group and **1d** with electron-withdrawing 4-Cl group gave the corresponding products **4ba** and **4da** in excellent yields, whereas **1c** with 4-MeO group and **1e** with 4-Br group provided moderate yields of **4ca** and **4ea**. Among them, the lowest yield was observed in the case of **1g** with a 4-Ph group (entry 7). In addition, substrates **1h**–**1k** with 2-furyl, 2-thienyl, 1-naphthyl or 1-pyrenyl groups were also tolerated in this process, affording almost the corresponding products **4ga**–**4ka** in moderate yields with high *dr* values (up to 20:1), respectively (Table 2, entries 8–11). Moreover, it should be noted that the electronic property of R^1 groups of **1** has an obvious influence on the reaction rates, and the electron-donating group decelerated the reaction. By the way, the steric effect of R^2 group on this reaction was also examined under the same conditions. According to the results listed in Table 2 (entries 12–15), we realized that the steric hindrance had a little influence on this cascade process. In fact, both small methyl ester **1l** and the bulky t-butyl ester **1m** gave the product **4aa** in highest yields in 89%, 87% with excellent *dr* value (entries 13–14). When R^2 is a functional group like $(CH_2)_2Cl$ or benzyl, substrates **1n** or **1o** were also adapted to the reaction, furnishing the expected product **4aa** in high yields (Table 2, entries 15–16).

Next, we examined the reaction of 2-benzoyl-1-chlorocyclopropaneformate **1a** with a group of sodium sulfinates. And the results were summarized in Table 3. The introduction of electronically different substituents such as Me, OMe and Cl groups

Table 2
Substrate scope for the reaction of **1** with **2aa**[a]

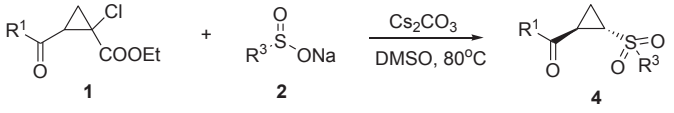


Entry	1	R^1	R^2	Time (h)[b] (h)[b]	Product	Yield (%)[c]	*dr*[d]
1	**1a**	C_6H_5	Et	2	**4aa**	89	>20:1
2	**1b**	4-MeC_6H_4	Et	6	**4ba**	80	>20:1
3	**1c**	4-$MeOC_6H_4$	Et	8	**4ca**	68	>20:1
4	**1d**	4-ClC_6H_4	Et	2	**4da**	88	>20:1
5	**1e**	4-BrC_6H_4	Et	2	**4ea**	60	>20:1
6	**1f**	2-BrC_6H_4	Et	2	**4fa**	48	>20:1
7	**1g**	4-PhC_6H_4	Et	3	**4ga**	33	>20:1
8	**1h**	2-Furyl	Et	2	**4ha**	78	>20:1
9	**1i**	2-Thienyl	Et	5	**4ia**	70	>20:1
10	**1j**	1-Naphthyl	Et	6	**4ja**	55	>20:1
11	**1k**	1-Pyrenyl	Me	4	**4ka**	72	>20:1
12	**1l**	C_6H_5	Me	2	**4aa**	89	>20:1
13	**1m**	C_6H_5	t-Bu	8	**4aa**	87	>20:1
14	**1n**	C_6H_5	$(CH_2)_2Cl$	4	**4aa**	79	>20:1
15	**1o**	C_6H_5	Benzyl	2	**4aa**	73	>20:1

[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol) and Cs_2CO_3 (0.4 mmol) in DMSO (2 mL) was stirred at 80 °C.
[b] Determined by TLC.
[c] Isolated by column chromatography.
[d] Diastereomeric ratios (trans:cis) determined by ^1H NMR of the crude product.

on the para position of benzene ring of sodium benzenesulfinate caused a marked decrease in the yields of the expected products **4ab**, **4ac** and **4ad**, despite of the high *dr* values (Table 3, entries 2–4). Sodium thiophene-2-sulfinate **2e** can also take reaction with **1a** smoothly to give the expected product **4ae** in 68% yield with *dr*>20:1 (Table 3, entry 5). In the case of sodium methanesulfinate **2f**, the reaction also underwent smoothly and afforded the formal substitution product **3af** with high *dr* value (Table 3, entry 6) rather than the desired decarboxylation product, indicative that the property of sulfonyl group has a big influence on the subsequent esterolysis. Sodium trifluoromethanesulfinate **2g**, a much weaker nucleophile, did not react with **1a** under the same conditions (Table 3, entry 7). Similar substituent effect of R^1 group of **1** on the reaction rate and the product yields was also observed in these cases (Table 3, entries 8–13).

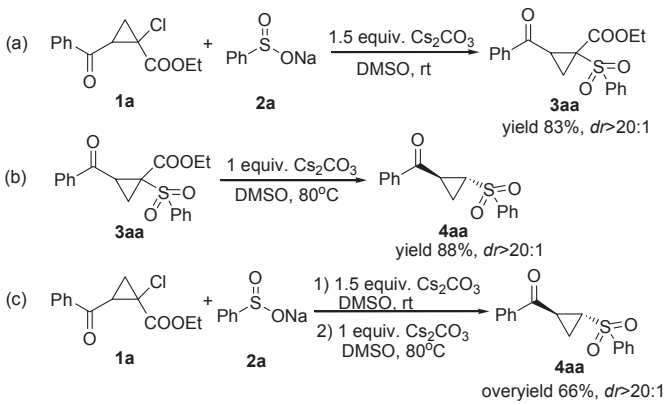
Table 3
Substrate scope for the reaction of **1** with **2**[a]



Entry	1	2	Time (h)[b]	Product	Yield (%)[c]	*dr*[d]
1	**1a**	**2a**(R^3=C_6H_5)	2	**4aa**	89	>20:1
2	**1a**	**2b**(R^3=4-MeC_6H_4)	9	**4ab**	50	>20:1
3[e]	**1a**	**2c**(R^3=4-$OMeC_6H_4$)	7	**4ac**	66	>20:1
4	**1a**	**2d**(R^3=4-ClC_6H_4)	9	**4ad**	51	>20:1
5[e]	**1a**	**2e**(R^3=2-thienyl)	6	**4ae**	68	>20:1
6	**1a**	**2f**(R^3=Me)	24	**3af**	53	>20:1
7	**1a**	**2g**(R^3=CF_3)	24	NR	—	—
8	**1b**	**2b**	12	**4bb**	51	>20:1
9	**1b**	**2d**	12	**4bd**	33	>20:1
10	**1d**	**2b**	5.5	**4db**	63	>20:1
11	**1d**	**2d**	6	**4dd**	43	>20:1
12[e]	**1i**	**2b**	12	**4ib**	51	>20:1
13[e]	**1i**	**2d**	12	**4id**	19	>20:1

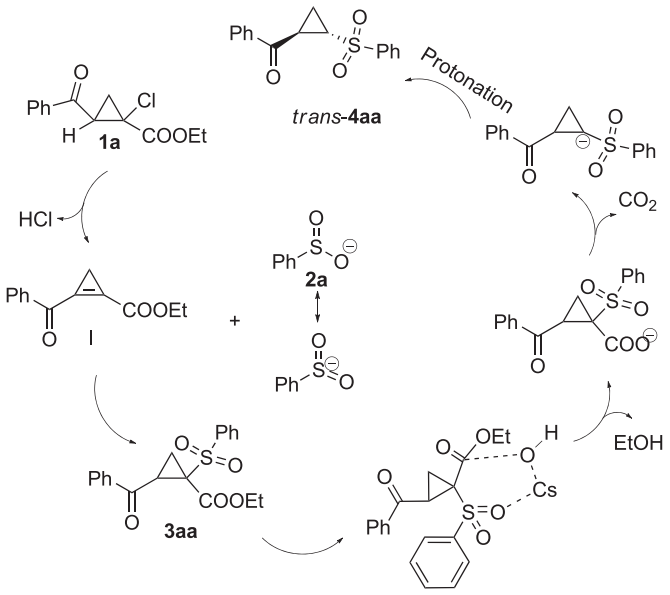
[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol) and Cs_2CO_3 (0.4 mmol) in DMSO (2 mL) was stirred at 80 °C.
[b] Determined by TLC.
[c] Isolated by column chromatography.
[d] Diastereomeric ratios (trans:cis) determined by ^1H NMR of the crude product.
[e] Cs_2CO_3 (0.5 mmol).

In order to further investigate the tandem process, we conducted some control experiments shown in Scheme 3. First, we found that only the formal substitution product **3aa** was generated and isolated in 83% yield when the reaction of **1a** and **2a** was performed in the presence of 1.5 equiv Cs_2CO_3 at room temperature (Scheme 3,a). When the isolated product **3aa** was treated with 1 equiv Cs_2CO_3 in DMSO at 80 °C, it was readily converted into **4aa** in 88% yield with *dr*>20:1 (Scheme 3,b). In this case, the total yield for **4aa** is 70%. When the crude product **3aa** was further treated with additional 1 equiv of Cs_2CO_3 in DMSO at 80 °C without isolation, the desired decarboxylation product **4aa** was obtained in total 66% yield (Scheme 3c). Compared with the 89% yield (Table 2, entry1), the relatively lower yields imply that the simultaneous esterolysis and decarboxylation would benefit the formal substitution reaction to some extent. In addition, the existence of arylsulfonyl group made the esterolysis and decarboxylation of **3aa** proceed more easily in basic media.



Scheme 3. Some control experiments.

According to the above investigation, a possible reaction mechanism was proposed and depicted in Scheme 4. The reaction was initiated by a simple 1,2-elimination of HCl, giving a highly reactive cyclopropene intermediate I. Next, sodium arylsulfinate attacked the intermediate I via Michael addition to furnish the formal substitution compound **3aa** under basic conditions. Subsequent esterolysis and decarboxylation of **3aa** provided the cyclopropyl aryl sulfone **4aa**. Though the activation role of arylsulfonyl group is still kept unclear, we presumed that its orientation and coordination ability with cesium ion plays a crucial role in the esterolysis process depicted in Scheme 4, since the analogous methylsulfonyl group did not have the role. In addition, we speculated that stereoelectronic and steric effects between aroyl and sulfonyl groups played the key role for the excellently diastereoselective formation of *trans*-**4aa** during the final protonation step as shown in Scheme 4.



Scheme 4. Proposed mechanism for the tandem reaction.

3. Conclusions

In summary, a novel and metal-free method for the high regioselective addition of the electron-deficient reactive cyclopropene intermediate generated in situ from 2-acyl-1-chlorocyclopropanecarboxylate with sodium sulfinate has been developed under mild conditions. A broad range of 1-aroylsulfonyl-2-aroylcyclopropane derivatives, which involves the 1,2-elimination/addition/esterolysis/decarboxylation pathway, was obtained in up to 89% yield with excellent *dr* value. In addition, the synthetically useful research of this special electron-deficient cyclopropene intermediate generated in situ is currently underway in our laboratory.

4. Experimental section

4.1. General information

All isolated compounds were characterized on the basis of ^{1}H NMR and ^{13}C NMR spectroscopic data, IR spectra, and HRMS data. All ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer with solvent resonances as the internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm). Infrared spectra were recorded with a FTIR spectrometer. High-resolution mass spectra (HRMS) were recorded with a Bruker TOF-Q spectrometer in the EI mode. Melting points were recorded with a melting point detector. All reactions were monitored by TLC analysis using silica gel 60 Å F-254 thin layer plates and visualized by UV. Flash column chromatography was performed on silica gel 60 Å, 10–40 μm. All reagents and solvents were of commercial grade and purified prior to use when necessary. Unless otherwise noted, 2-acyl-1-chlorocyclopropanecarboxylate were synthesized according to literature.[2]

4.2. Typical procedure for the synthesis of cyclopropyl aryl sulfones 4

Compounds 2-benzoyl-1-chlorocyclopropanecarboxylate **1a** (50 mg, 0.2 mmol), sodium benzenesulfinate **2a** (66 mg, 0.4 mmol) and Cs_2CO_3 (131 mg, 0.4 mmol) were putted into 2 mL of DMSO at room temperature, and then the reaction mixture was heated and stirred at 80 °C. The reaction was followed by TLC until all the substrate **1a** disappeared. The reaction was cooled to room temperature and was diluted with water (10 mL). Further treatment was followed by extraction with CH_2Cl_2 (2×20 mL). The combined organic extracts were washed with H_2O (20 mL) and brine (3×20 mL), dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether-EtOAc as eluent to afford the corresponding product **4aa**. Unless otherwise specified, all other products **3** and **4** were obtained according to this typical procedure. All the products **4** with trans configuration prepared in this work are racemic.

4.3. Phenyl((1*S*,2*R*)-2-(phenylsulfonyl)cyclopropyl)methanone (4aa)

White solid (51 mg, 89% yield). Mp 120.7–122.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.99 (d, *J*=7.7 Hz, 2H, ArH), 7.94 (d, *J*=7.7 Hz, 2H, ArH), 7.66 (dd, *J*=13.8, 6.2 Hz, 1H, ArH), 7.59 (dd, *J*=15.5, 7.5 Hz, 3H, ArH), 7.49 (t, *J*=7.7 Hz, 2H, ArH), 3.52 (ddd, *J*=9.7, 5.7, 4.2 Hz, 1H, CH-cyclo), 3.18 (ddd, *J*=9.8, 5.8, 4.2 Hz, 1H, CH-cyclo), 1.90–1.82 (m, 1H, CH_2-cyclo), 1.74 (dt, *J*=8.5, 5.3 Hz, 1H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ=195.2, 139.9, 136.49, 133.9, 129.5, 129.4, 128.8, 128.4, 127.7, 42.2, 23.0, 15.3. IR (neat): ν 3025, 2923, 1731, 1664, 1592, 1447, 1385, 1306, 1266, 1225, 1149, 1084, 1063, 1023, 981, 916, 861, 794 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{16}H_{15}O_3S$ $[M+H]^+$: 287.0742, found: 287.0745.

4.4. ((1*S*,2*R*)-2-(Phenylsulfonyl)cyclopropyl)(*p*-tolyl)methanone (4ba)

Light yellow solid (48 mg, 80% yield). Mp 129.3–131.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.97–7.86 (m, 4H, ArH), 7.68–7.62 (m, 1H, ArH), 7.56 (dd, *J*=10.5, 4.7 Hz, 2H, ArH), 7.30–7.26 (m, 2H, ArH), 3.55–3.44 (m, 1H, CH-cyclo), 3.17 (ddd, *J*=8.5, 5.8, 4.1 Hz, 1H, CH-cyclo), 2.42 (s, 3H, CH_3), 1.83 (tt, *J*=13.8, 6.4 Hz, 1H, CH_2-cyclo), 1.72 (ddd, *J*=8.5, 5.8, 4.7 Hz, 1H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ=194.6, 144.9, 139.89, 133.9, 133.9, 129.5, 129.5, 128.6, 127.7, 42.1, 22.9, 21.7, 15.2. IR (neat): ν 3027, 2922, 1734, 1662, 1603, 1447, 1418, 1383, 1307, 1233, 1209, 1178, 1148, 1086, 1061, 1033, 985, 920, 859, 817, 748 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{17}H_{17}O_3S$ $[M+H]^+$: 301.0898, found: 301.0888.

4.5. (4-Methoxyphenyl)((1*S*,2*R*)-2-(phenylsulfonyl)-cyclopropyl)methanone (4ca)

Light yellow solid (43 mg, 68% yield). Mp 85.6–87.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.97 (t, *J*=7.5 Hz, 2H, ArH), 7.93 (d, *J*=7.2 Hz, 2H, ArH), 7.65 (t, *J*=7.4 Hz, 1H, ArH), 7.57 (t, *J*=7.6 Hz, 2H,

ArH), 6.95 (d, *J*=8.9 Hz, 2H, ArH), 3.88 (s, 3H, OCH_3), 3.51–3.43 (m, 1H, CH-cyclo), 3.15 (ddd, *J*=8.6, 5.8, 4.2 Hz, 1H, CH-cyclo), 1.86–1.77 (m, 1H, CH_2-cyclo), 1.71 (dt, *J*=8.5, 5.2 Hz, 1H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): *δ*=193.3, 164.2, 139.9, 133.8, 130.9, 130.8, 129.5, 129.3, 129.1, 127.6, 114.0, 113.9, 55.6, 41.9, 22.7, 15.1. IR (neat): ν 3026, 2929, 1735, 1657, 1600, 1570, 1510, 1450, 1427, 1383, 1308, 1233, 1170, 1149, 1085, 1064, 1024, 980, 888, 856, 819, 762 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{17}H_{17}O_4S$ $[M+H]^+$: 317.0848, found: 317.0844.

4.6. (4-Chlorophenyl)((1*S*,2*R*)-2-(phenylsulfonyl)-cyclopropyl) methanone (4da)

Light yellow solid (56 mg, 88% yield). Mp 122.8–123.6 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): *δ*=7.93 (ddd, *J*=8.8, 6.2, 5.1 Hz, 4H, ArH), 7.72–7.61 (m, 1H, ArH), 7.57 (dd, *J*=17.0, 9.6 Hz, 2H, ArH), 7.51–7.41 (m, 2H, ArH), 3.54–3.41 (m, 1H, CH-cyclo), 3.17 (ddd, *J*=8.5, 5.9, 4.1 Hz, 1H, CH-cyclo), 1.85 (ddd, *J*=9.2, 5.8, 4.8 Hz, 1H, CH_2-cyclo), 1.74 (ddd, *J*=8.5, 5.7, 4.9 Hz, 1H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): *δ*=194.0, 140.5, 139.7, 134.7, 134.0, 129.8, 129.5, 129.2, 127.7, 42.3, 22.9, 15.4. IR (neat): ν 3095, 3039, 1676, 1584, 1483, 1446, 1402, 1374, 1310, 1287, 1258, 1212, 1148, 1083, 1022, 981, 915, 889, 866, 779, 754 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{16}H_{14}ClO_3S$ $[M+H]^+$: 321.0352, found: 321.0350.

4.7. (4-Bromophenyl)((1*S*,2*R*)-2-(phenylsulfonyl)-cyclopropyl) methanone (4ea)

White solid (43 mg, 60% yield). Mp 117.4–118.2 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): *δ*=7.96–7.90 (m, 2H, ArH), 7.84 (d, *J*=8.6 Hz, 2H, ArH), 7.71–7.55 (m, 5H, ArH), 3.45 (ddd, *J*=9.5, 5.8, 4.1 Hz, 1H, CH-cyclo), 3.17 (ddd, *J*=8.5, 5.9, 4.1 Hz, 1H, CH-cyclo), 1.90–1.81 (m, 1H, CH_2-cyclo), 1.78–1.70 (m, 1H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): *δ*=194.2, 139.7, 135.1, 133.9, 132.2, 129.9, 129.5, 129.3, 127.7, 42.3, 22.9, 15.4. IR (neat): ν 3029, 2924, 1734, 1671, 1583, 1481, 1447, 1422, 1402, 1382, 1308, 1226, 1175, 1148, 1069, 1035, 1009, 985, 921, 857, 826, 750 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{16}H_{14}BrO_3S$ $[M+H]^+$: 364.9847, found: 364.9841.

4.8. (2-Bromophenyl)((1*S*,2*R*)-2-(phenylsulfonyl)-cyclopropyl) methanone (4fa)

Yellowish oil (35 mg, 48% yield). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): *δ*=7.93 (d, *J*=7.3 Hz, 2H, ArH), 7.62 (dq, *J*=30.7, 7.6 Hz, 4H, ArH), 7.45–7.30 (m, 3H, ArH), 3.39–3.30 (m, 1H, CH-cyclo), 3.26 (ddd, *J*=8.8, 6.0, 4.2 Hz, 1H, CH-cyclo), 1.94–1.84 (m, 1H, CH_2-cyclo), 1.78 (dt, *J*=8.7, 5.2 Hz, 1H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): *δ*=198.7, 140.2, 139.7, 133.9, 133.9, 132.6, 129.5, 127.8, 127.6, 119.4, 43.4, 26.9, 16.7. IR (neat): ν 3062, 2923, 1690, 1586, 1468, 1445, 1430, 1379, 1315, 1287, 1213, 1188, 1152, 1087, 1069, 1026, 985, 952, 917, 861, 748 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{16}H_{14}BrO_3S$ $[M+H]^+$: 364.9847, found: 364.9833.

4.9. (4-Biphenyl)((1*S*,2*R*)-2-(phenylsulfonyl)cyclopropyl)-methanone (4ga)

Light yellow solid (24 mg, 33% yield). Mp 176.5–178.1 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): *δ*=8.06 (d, *J*=8.4 Hz, 2H, ArH), 7.95 (d, *J*=7.5 Hz, 2H, ArH), 7.74–7.69 (m, 2H, ArH), 7.65 (dd, *J*=8.7, 7.4 Hz, 3H, ArH), 7.57 (dd, *J*=15.1, 7.7 Hz, 2H, ArH), 7.49 (t, *J*=7.4 Hz, 2H, ArH), 7.42 (t, *J*=7.3 Hz, 1H, ArH), 3.56 (ddd, *J*=9.6, 5.7, 4.2 Hz, 1H, CH-cyclo), 3.20 (ddd, *J*=8.6, 5.8, 4.2 Hz, 1H, CH-cyclo), 1.88 (dt, *J*=9.3, 5.3 Hz, 1H, CH_2-cyclo), 1.80–1.72 (m, 1H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): *δ*=194.7, 146.6, 139.9, 139.6, 135.1, 133.9, 129.5, 129.1, 129.0, 128.5, 127.7, 127.5, 127.3, 42.2, 23.1, 15.4. IR (neat): ν 3027, 2923, 1733, 1663, 1601, 1559, 1516, 1481, 1448, 1406, 1381, 1307, 1267, 1227, 1207, 1183, 1150, 1085, 1067, 1028, 982, 920, 863, 839, 745 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{22}H_{19}O_3S$ $[M+H]^+$: 363.1055, found: 363.1051.

4.10. (Furan-2-yl)((1*S*,2*R*)-2-(phenylsulfonyl)cyclopropyl)-methanone (4ha)

White solid (43 mg, 78% yield). Mp 140.6–142.2 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): *δ*=7.95–7.91 (m, 2H, ArH), 7.70–7.62 (m, 2H, ArH), 7.57 (t, *J*=7.6 Hz, 2H, ArH), 7.31 (t, *J*=4.3 Hz, 1H, ArH), 6.59 (dd, *J*=3.6, 1.6 Hz, 1H, ArH), 3.43 (ddd, *J*=9.6, 5.7, 4.2 Hz, 1H, CH-cyclo), 3.15 (ddd, *J*=8.6, 5.9, 4.1 Hz, 1H, CH-cyclo), 1.89–1.78 (m, 1H, CH_2-cyclo), 1.78–1.66 (m, 1H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): *δ*=183.4, 152.2, 147.6, 139.8, 133.9, 129.4, 127.7, 118.6, 112.8, 41.8, 23.2, 14.9. IR (neat): ν 3039, 2924, 1735, 1664, 1568, 1466, 1403, 1381, 1308, 1286, 1234, 1196, 1153, 1084, 1039, 1015, 992, 920, 879, 855, 794, 755 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{14}H_{13}O_4S$ $[M+H]^+$: 277.0535, found: 277.0532.

4.11. ((1*S*,2*R*)-2-(Phenylsulfonyl)cyclopropyl)(thiophen-2-yl) methanone (4ia)

Yellow solid (43 mg, 78% yield). Mp 120.1–121.8 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): *δ*=7.95–7.90 (m, 2H, ArH), 7.88 (dd, *J*=3.8, 0.8 Hz, 1H, ArH), 7.72 (dd, *J*=4.9, 0.8 Hz, 1H, ArH), 7.66 (t, *J*=7.4 Hz, 1H, ArH), 7.57 (t, *J*=7.6 Hz, 2H, ArH), 7.18 (dd, *J*=4.7, 4.0 Hz, 1H, ArH), 3.43–3.33 (m, 1H, CH-cyclo), 3.18 (ddd, *J*=8.6, 5.9, 4.1 Hz, 1H, CH-cyclo), 1.84 (ddd, *J*=9.2, 5.8, 5.0 Hz, 1H, CH_2-cyclo), 1.74 (dt, *J*=8.6, 5.3 Hz, 1H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): *δ*=187.4, 143.4, 139.8, 135.2, 133.9, 133.2, 129.5, 128.6, 127.7, 41.9, 23.9, 15.1. IR (neat): ν 3022, 2924, 1731, 1652, 1515, 1447, 1413, 1381, 1353, 1305, 1246, 1223, 1194, 1147, 1086, 1065, 1022, 957, 920, 864, 843, 727 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{14}H_{13}O_3S_2$ $[M+H]^+$: 293.0306, found: 293.0301.

4.12. (Naphthalen-4-yl)((1*S*,2*R*)-2-(phenylsulfonyl)-cyclopropyl)methanone (4ja)

Yellow solid (59 mg, 72% yield). Mp 133.6–134.7 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): *δ*=8.42 (d, *J*=8.3 Hz, 1H, ArH), 7.94 (d, *J*=8.2 Hz, 1H, ArH), 7.92–7.85 (m, 3H, ArH), 7.79 (dd, *J*=9.3, 7.9 Hz, 1H, ArH), 7.60 (t, *J*=7.4 Hz, 1H, ArH), 7.47 (dddd, *J*=15.5, 11.5, 8.9, 5.9 Hz, 5H, ArH), 3.45–3.35 (m, 1H, CH-cyclo), 3.21 (ddd, *J*=8.5, 5.9, 4.1 Hz, 1H, CH-cyclo), 1.80 (ddt, *J*=10.5, 8.5, 4.7 Hz, 2H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): *δ*=198.27, 139.87, 134.94, 133.94, 133.86, 133.66, 129.96, 129.53, 129.04, 128.58, 128.28, 127.75, 126.72, 125.50, 124.49, 42.80, 26.28, 15.83. IR (neat): ν 3029, 2924, 1729, 1663, 1585, 1506, 1447, 1400, 1372, 1308, 1278, 1231, 1149, 1101, 1069, 1025, 960, 920, 889, 864, 809, 778, 733 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{20}H_{17}O_3S$ $[M+H]^+$: 337.0898, found: 337.0892.

4.13. (1,9-Dihydropyren-5-yl)((1*S*,2*R*)-2-(phenylsulfonyl)-cyclopropyl)methanone (4ka)

Yellow solid (59 mg, 72% yield). Mp 162.8–163.2 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): *δ*=8.77 (d, *J*=9.4 Hz, 1H, ArH), 8.35 (d, *J*=8.0 Hz, 1H, ArH), 8.21 (d, *J*=7.7 Hz, 2H, ArH), 8.18–8.07 (m, 3H, ArH), 8.06–7.96 (m, 4H, ArH), 7.69–7.62 (m, 1H, ArH), 7.58 (t, *J*=7.5 Hz, 2H, ArH), 3.67–3.60 (m, 1H, CH-cyclo), 3.38 (ddd, *J*=8.1, 6.2, 4.1 Hz, 1H, CH-cyclo), 2.01–1.92 (m, 2H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): *δ*=198.4, 134.0, 134.4, 133.9, 131.1, 131.0, 130.4, 130.03, 130.00, 129.5, 127.8, 127.1, 127.0, 126.6, 126.5, 126.4, 124.8, 124.4, 124.1, 43.0, 26.7, 16.0. IR (neat): ν 3043, 2957, 2922, 1735, 1659, 1587, 1537, 1502, 1446, 1381, 1311, 1259, 1214, 1184, 1145, 1116, 1080, 1021, 982, 959, 918, 889, 844, 782, 765, 747 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{26}H_{21}O_3S$ $[M+H]^+$: 413.1211, found: 413.1209.

4.14. Phenyl((1*S*,2*R*)-2-tosylcyclopropyl)methanone (4ab)

Light yellow solid (30 mg, 50% yield). Mp 117.4–118.6 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=8.04–7.95 (m, 2H, ArH), 7.79 (t, *J*=9.8 Hz, 2H, ArH), 7.61 (t, *J*=7.4 Hz, 1H, ArH), 7.48 (dd, *J*=17.0, 9.5 Hz, 2H, ArH), 7.36 (d, *J*=8.0 Hz, 2H, ArH), 3.55–3.45 (m, 1H, CH-cyclo), 3.16 (ddd, *J*=8.6, 5.8, 4.2 Hz, 1H, CH-cyclo), 2.45 (s, 3H, CH_3), 1.84 (ddd, *J*=9.3, 5.7, 4.8 Hz, 1H, CH_2-cyclo), 1.76–1.68 (m, 1H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ=195.3, 144.9, 136.9, 136.5, 133.8, 130.1, 128.8, 128.4, 127.7, 42.4, 23.1, 21.6, 15.3. IR (neat): ν 3046, 2923, 1734, 1682, 1593, 1456, 1383, 1317, 1268, 1217, 1145, 1086, 1025, 986, 917, 883, 815, 798, 746 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{17}H_{17}O_3S$ $[M+H]^+$: 301.0898, found: 301.0879.

4.15. ((1*S*,2*R*)-2-(4-Methoxyphenylsulfonyl)cyclopropyl) (phenyl)-methanone (4ac)

Yellow solid (42 mg, 66% yield). Mp 122.3–123.4 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.99 (d, *J*=7.4 Hz, 2H, ArH), 7.85 (d, *J*=8.9 Hz, 2H, ArH), 7.61 (t, *J*=7.4 Hz, 1H, ArH), 7.49 (t, *J*=7.7 Hz, 2H, ArH), 7.03 (t, *J*=7.4 Hz, 2H, ArH), 3.88 (s, 3H, OCH_3), 3.49 (ddd, *J*=9.5, 5.7, 4.2 Hz, 1H, CH-cyclo), 3.15 (ddd, *J*=8.6, 5.8, 4.2 Hz, 1H, CH-cyclo), 1.87–1.79 (m, 1H, CH_2-cyclo), 1.75–1.69 (m, 1H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ=195.3, 163.9, 136.5, 133.8, 131.4, 129.9, 128.8, 128.4, 114.7, 55.7, 42.6, 23.1, 15.4. IR (neat): ν 3044, 2936, 1734, 1672, 1594, 1497, 1387, 1297, 1262, 1222, 1146, 1089, 1024, 987, 858, 801, 741 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{16}H_{13}O_3S$ $[M+H]^+$: 285.0585, found: 285.0577.

4.16. ((1*S*,2*R*)-2-(4-Chlorophenylsulfonyl)cyclopropyl)(phenyl) -methanone (4ad)

Light yellow solid (33 mg, 51% yield). Mp 127.8–129.1 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.99 (d, *J*=7.5 Hz, 2H, ArH), 7.87 (d, *J*=8.5 Hz, 2H, ArH), 7.63 (t, *J*=7.6 Hz, 1H, ArH), 7.57–7.47 (m, 4H, ArH), 3.56–3.47 (m, 1H, CH-cyclo), 3.22–3.13 (m, 1H, CH-cyclo), 1.88–1.80 (m, 1H, CH_2-cyclo), 1.73 (dt, *J*=8.6, 5.3 Hz, 1H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ=194.9, 140.7, 138.3, 136.3, 133.9, 129.8, 129.2, 128.9, 128.4, 42.0, 23.1, 15.4. IR (neat): ν 3047, 2923, 1732, 1671, 1578, 1473, 1449, 1389, 1308, 1270, 1222, 1151, 1086, 1018, 984, 919, 887, 856, 830, 794, 760, 731 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{16}H_{14}ClO_3S$ $[M+H]^+$: 321.0352, found: 321.0350.

4.17. ((1*S*,2*R*)-2-(2-Thienylsulfonyl)cyclopropyl)(phenyl)-methanone (4ae)

Yellow solid (40 mg, 68% yield). Mp 113.4–114.2 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=8.04–7.98 (m, 2H, ArH), 7.73 (ddd, *J*=6.1, 4.3, 1.1 Hz, 2H, ArH), 7.62 (t, *J*=7.4 Hz, 1H, ArH), 7.50 (t, *J*=7.7 Hz, 2H, ArH), 7.16 (dd, *J*=4.8, 3.9 Hz, 1H, ArH), 3.54 (ddd, *J*=9.6, 5.8, 4.1 Hz, 1H, CH-cyclo), 3.30 (ddd, *J*=8.6, 5.8, 4.1 Hz, 1H, CH-cyclo), 1.95–1.86 (m, 1H, CH_2-cyclo), 1.82–1.75 (m, 1H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ=195.0, 140.5, 136.3, 134.2, 133.9, 128.9, 128.5, 128.0, 43.4, 23.7, 15.8. IR (neat): ν 3088, 3048, 1733, 1676, 1595, 1449, 1401, 1380, 1314, 1265, 1225, 1142, 1097, 1068, 1016, 984, 863, 736 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{14}H_{13}O_3S_2$ $[M+H]^+$: 293.0306, found: 293.0298.

4.18. *p*-Tolyl((1*S*,2*R*)-2-tosylcyclopropyl)methanone (4bb)

Light yellow solid (32 mg, 51% yield). Mp 143.7–145.2 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.89 (d, *J*=8.2 Hz, 2H, ArH), 7.80 (d, *J*=8.3 Hz, 2H, ArH), 7.35 (d, *J*=8.0 Hz, 2H, ArH), 7.28 (d, *J*=8.0 Hz, 2H, ArH), 3.51–3.44 (m, 1H, CH-cyclo), 3.14 (ddd, *J*=8.5, 5.8, 4.1 Hz, 1H, CH-cyclo), 2.44 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 1.81 (ddd, *J*=9.2, 5.8, 4.7 Hz, 1H, CH_2-cyclo), 1.73–1.69 (m, 1H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ=194.7, 144.9, 144.9, 137.0, 134.0, 130.1, 129.5, 128.6, 127.7, 42.2, 22.9, 21.7, 21.6, 15.2. IR (neat): ν 3028, 2923, 1732, 1661, 1602, 1491, 1455, 1419, 1383, 1305, 1271, 1232, 1210, 1178, 1145, 1085, 1064, 1032, 986, 919, 860, 818, 759, 716 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{18}H_{19}O_3S$ $[M+H]^+$: 315.1055, found: 315.1049.

4.19. ((1*S*,2*R*)-2-(4-Chlorophenylsulfonyl)cyclopropyl)(*p*-tolyl) methanone (4bd)

Light yellow solid (22 mg, 33% yield). Mp 156.2–157.1 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.96–7.80 (m, 4H, ArH), 7.59–7.51 (m, 2H, ArH), 7.29 (t, *J*=6.9 Hz, 2H, ArH), 3.49 (ddd, *J*=9.6, 5.8, 4.1 Hz, 1H, CH-cyclo), 3.15 (ddd, *J*=8.5, 5.8, 4.1 Hz, 1H, CH-cyclo), 2.44 (s, 3H, CH_3), 1.82 (ddd, *J*=9.3, 5.7, 4.8 Hz, 1H, CH_2-cyclo), 1.72 (ddd, *J*=8.5, 5.8, 4.8 Hz, 1H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ=194.4, 145.0, 140.7, 138.4, 133.9, 129.8, 129.6, 129.2, 128.6, 41.9, 22.9, 21.7, 15.3. IR (neat): ν 3039, 2920, 1733, 1663, 1604, 1574, 1470, 1423, 1386, 1322, 1269, 1232, 1205, 1177, 1147, 1086, 1035, 1012, 990, 861, 827, 761, 721 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{17}H_{16}ClO_3S$ $[M+H]^+$: 335.0509, found: 335.0504.

The procedure for crystal growth: Compound **4bd** was soluble in mixtures of chloroform and petroleum ether, crystal could be prepared by the slow volatilization of solvents at room temperature.

4.20. (4-Chlorophenyl)((1*S*,2*R*)-2-tosylcyclopropyl)methanone (4db)

Light yellow solid (42 mg, 63% yield). Mp 130.4–132.3 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.94 (dd, *J*=11.4, 9.6 Hz, 2H, ArH), 7.80 (d, *J*=8.3 Hz, 2H, ArH), 7.49–7.44 (m, 2H, ArH), 7.36 (d, *J*=8.0 Hz, 2H, ArH), 3.44 (ddd, *J*=9.5, 5.8, 4.1 Hz, 1H, CH-cyclo), 3.14 (ddd, *J*=8.5, 5.9, 4.1 Hz, 1H, CH-cyclo), 2.45 (s, 3H, CH_3), 1.83 (ddd, *J*=9.2, 5.8, 4.8 Hz, 1H, CH_2-cyclo), 1.79–1.67 (m, 1H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ=194.1, 145.0, 140.4, 136.8, 134.8, 130.1, 129.8, 129.2, 127.7, 42.5, 22.9, 21.6, 15.4. IR (neat): ν 3042, 2922, 1736, 1667, 1588, 1487, 1425, 1404, 1384, 1318, 1289, 1266, 1174, 1147, 1116, 1089, 1066, 1034, 986, 925, 862, 834, 814, 780, 755 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{17}H_{16}ClO_3S$ $[M+H]^+$: 335.0509, found: 335.0501.

4.21. ((1*S*,2*R*)-2-(4-Chlorophenylsulfonyl)cyclopropyl)(4-chlorophenyl)methanone (4dd)

Light yellow solid (30 mg, 43% yield). Mp 160.4–161.5 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.97–7.92 (m, 2H, ArH), 7.88–7.84 (m, 2H, ArH), 7.58–7.54 (m, 2H, ArH), 7.50–7.46 (m, 2H, ArH), 3.46 (ddd, *J*=9.5, 5.8, 4.1 Hz, 1H, CH-cyclo), 3.16 (ddd, *J*=8.5, 5.9, 4.1 Hz, 1H, CH-cyclo), 1.83 (ddd, *J*=9.2, 5.8, 4.8 Hz, 1H, CH_2-cyclo), 1.73 (ddd, *J*=8.5, 5.7, 4.9 Hz, 1H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ=193.8, 140.8, 140.6, 138.2, 134.6, 129.9, 129.8, 129.2, 129.2, 42.1, 22.9, 15.5. IR (neat): ν 3090, 2924, 1730, 1670, 1585, 1476, 1426, 1400, 1308, 1276, 1221, 1178, 1146, 1087, 1036, 991, 865, 766, 751 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{16}H_{13}Cl_2O_3S$ $[M+H]^+$: 354.9962, found: 354.9951.

4.22. (Thiophen-2-yl)((1*S*,2*R*)-2-tosylcyclopropyl)methanone (4ib)

Light yellow solid (31 mg, 51% yield). Mp 126.3–127.6 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.88 (dd, *J*=5.8, 4.9 Hz, 1H,

ArH), 7.79 (t, J=7.9 Hz, 2H, ArH), 7.74–7.71 (m, 1H, ArH), 7.36 (d, J=8.1 Hz, 2H, ArH), 7.18 (dd, J=4.8, 4.0 Hz, 1H, ArH), 3.40–3.33 (m, 1H, CH-cyclo), 3.16 (ddd, J=8.7, 5.9, 4.1 Hz, 1H, CH-cyclo), 2.44 (s, 3H, CH_3), 1.82 (ddd, J=9.2, 5.8, 4.9 Hz, 1H, CH_2-cyclo), 1.72 (dt, J=8.6, 5.2 Hz, 1H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ=187.5, 144.9, 143.5, 136.8, 135.1, 133.2, 130.1, 128.6, 127.7, 42.1, 23.9, 21.7, 15.1. IR (neat): ν 3022, 2923, 1724, 1645, 1594, 1515, 1454, 1416, 1382, 1293, 1247, 1222, 1189, 1142, 1109, 1084, 1065, 1020, 957, 921, 864, 842, 818, 758 cm^{-1}. HRMS (EI): m/z calcd for $C_{15}H_{15}O_3S_2$ $[M+H]^+$: 307.0463, found: 307.0461.

4.23. ((1*S*,2*R*)-2-(4-Chlorophenylsulfonyl)cyclopropyl)-(thiophen-2-yl)methanone (4id)

Light yellow solid (13 mg, 20% yield). Mp 170.4–171.8 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.89 (dd, J=3.8, 1.0 Hz, 1H, ArH), 7.88–7.83 (m, 2H, ArH), 7.74 (dd, J=5.0, 1.0 Hz, 1H, ArH), 7.58–7.52 (m, 2H, ArH), 7.20 (dd, J=4.9, 3.9 Hz, 1H, ArH), 3.44–3.33 (m, 1H, CH-cyclo), 3.21–3.12 (m, 1H, CH-cyclo), 1.83 (ddd, J=9.2, 5.8, 4.9 Hz, 1H, CH_2-cyclo), 1.78–1.71 (m, 1H, CH_2-cyclo). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ=187.2, 143.3, 140.8, 138.2, 135.3, 133.3, 129.9, 129.2, 128.6, 41.8, 23.9, 15.2. IR (neat): ν 3042, 2923, 1724, 1650, 1578, 1513, 1473, 1412, 1352, 1308, 1275, 1238, 1220, 1150, 1085, 1011, 957, 919, 861, 847, 831, 764, 740 cm^{-1}. HRMS (EI): m/z calcd for $C_{14}H_{12}ClO_3S_2$ $[M+H]^+$: 326.9916, found: 326.9911.

4.24. Ethyl 2-benzoyl-phenylsulfonylcyclopropanecarboxylate (3aa)

Yellowish oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=8.02–7.97 (m, 2H, ArH), 7.97–7.92 (m, 2H, ArH), 7.71 (t, J=7.5 Hz, 1H, ArH), 7.63–7.56 (m, 3H, ArH), 7.45 (t, J=7.7 Hz, 2H, ArH), 4.02–3.93 (m, 2H, COOEt), 3.66 (dd, J=9.4, 7.5 Hz, 1H, CH-cyclo), 2.36 (dd, J=7.4, 5.4 Hz, 1H, CH_2-cyclo), 2.24 (dd, J=9.5, 5.3 Hz, 1H, CH_2-cyclo), 0.97 (t, J=7.1 Hz, 3H, COOEt). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ=192.4, 163.3, 138.4, 136.4, 134.3, 133.8, 129.3, 129.1, 128.8, 128.6, 62.5, 53.3, 30.1, 18.4, 13.5. IR (neat): ν 3065, 2985, 1736, 1681, 1598, 1582, 1449, 1372, 1310, 1228, 1202, 1161, 1138, 1081, 1017, 933, 871, 856, 827, 756, 728 cm^{-1}. HRMS (EI): m/z calcd for $C_{19}H_{19}O_5S$ $[M+H]^+$: 359.0953, found: 359.0952.

4.25. Ethyl 2-benzoyl-1-methylsulfonylcyclopropanecarboxylate (3af)

Yellowish oil (32 mg, 53% yield). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=8.13–7.95 (m, 2H, ArH), 7.63 (t, J=7.4 Hz, 1H, ArH), 7.52 (t, J=7.7 Hz, 2H, ArH), 4.29–4.14 (m, 2H, COOEt), 3.51 (dd, J=9.7, 7.4 Hz, 1H, CH-cyclo), 3.25 (s, 3H, CH_3), 2.38–2.25 (m, 1H, CH_2-cyclo), 2.17 (dd, J=9.8, 5.3 Hz, 1H, CH_2-cyclo), 1.17 (t, J=7.1 Hz, 3H, COOEt). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ=192.3, 164.2, 136.2, 134.1, 128.9, 128.5, 62.9, 51.3, 40.8, 29.8, 17.4, 13.6. IR (neat): ν 2984, 2935, 1730, 1682, 1597, 1581, 1450, 1372, 1312, 1229, 1161, 1129, 1097, 1019, 965, 929, 856, 779, 763 cm^{-1}. HRMS (EI): m/z calcd for $C_{14}H_{17}O_5S$ $[M+H]^+$: 297.0797, found: 297.0793.

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Supplementary data

Supplementary data (Copies of ^1H and ^{13}C NMR spectra for all compounds; X-ray structure of **4bc**.) related to this article can be found at http://dx.doi.org/10.1016/j.tet.2016.04.062.

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