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Diselenide- and Disulfide-Mediated Synthesis of Isocoumarins

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Cyclizations of stilbenecarboxylic acids to the corresponding isocoumarin derivatives using diselenide or disulfide reagents have been developed. By employing bis(triflouroacetoxy)iodobenzene as oxidant for the 6-*endo*-*trig* cyclizations a variety of dihydroisocoumarins have been prepared in good yields. This method is capable of forming isocoumarins and dihydroisocoumarin derivatives by a cyclization–elimination route.

Introduction

Selenium-based reagents have established themselves as powerful tools for the functionalizations of alkenes allowing a high degree of selectivity under extremely mild experimental reaction conditions.[1] Organoselenium compounds are utilized as convenient reagents in a variety of organic transformations, promoting a wide range of reactivities including cationic, anionic, radical, oxidative, as well as elimination and rearrangement pathways.[2] Numerous selenium-catalyzed reactions have been developed in organic synthesis,[3] but the use of catalytic selenocyclizations in the synthesis of heterocycles are rare.[4] Perhaps the most important contribution is represented by butenolide synthesis from β,γ-unsaturated acids by using selenium catalysis.[5] More recently, the reaction of β,γ-unsaturated acids to butenolides with hypervalent iodine reagents in the presence of catalytic amounts of diphenyl diselenide has been described by us.[6] Inspired by the reactivity and the subsequent functionalization of selenium electrophiles in cyclization reactions, we focused on the synthesis of isocoumarins.[7] Isocoumarins are natural products exhibiting a broad spectrum of pharmacological activities, such as antifungal,[8] antiallergic,[9] antimicrobial,[10] phytotoxic,[11] Anti-inflammatory,[12] immunomodulatory,[13] cytotoxic,[14] and antiangiogenic effects.[15] The broad range of activities has led to a continued interest in the synthesis of this class of lactones, especially isocoumarins substituted in the 3-position. Considerable efforts have been directed toward the synthesis of isocoumarins via either traditional,[16] electrophilic[17] or transition-metal-catalyzed reactions.[18] Selenium also shares many chemical properties with its neighboring homologue sulfur. Therefore, we also decided to use diphenyl disulfide in the selective synthesis of dihydroisocoumarins. Several other routes to dihydroisocoumarins have already been reported together with some biologic activities.[19]

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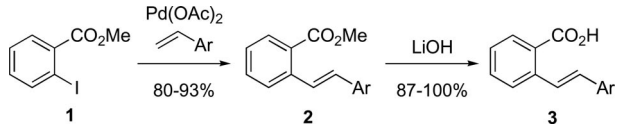
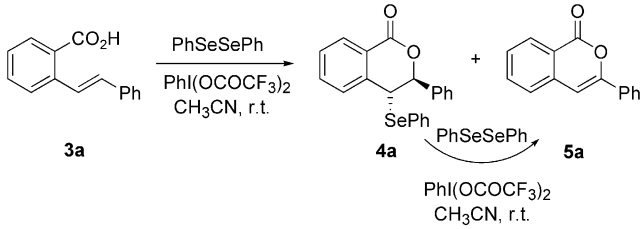
Results and Discussion

During the development of a new approach towards the synthesis of isocoumarins and dihydroisocoumarins, stilbenecarboxylic acids were synthesized by coupling of styrenes with methyl 2-iodobenzoate **1** using a Mizoroki–Heck reaction providing stilbene esters **2** in good yields.[1c,20] The subsequent hydrolysis with lithium hydroxide in the presence of aqueous methanol provided the corresponding carboxylic acids **3** in high yields (Scheme 1).



Scheme 1. Simple sequence for the preparation of carboxylic acids **3**.

We have already reported the use of hypervalent iodine compounds as oxidants for a facile in-situ formation of selenium electrophiles from diselenides,[6] but this protocol has not yet been applied to the synthesis of isocoumarins. The key difference in the previous and present examples is the elimination step because elimination was facilitated due to presence of acidic proton in β,γ-butenoic acids. In sharp contrast, there is no active methylene group in stilbenes **3** bearing a carboxylic acid functionality. Clive et al. reported that the reaction of 2-styrylbenzoic acid **3a** (Ar = Ph) with phenylselenenyl chloride afforded a mixture of dihydroisocoumarin **4a** and a five-membered lactone resulting from a 5-*exo* cyclization onto the stilbene double bond (Scheme 2).[21]



Scheme 2. Cyclization of stilbenecarboxylic acid **3a**.

The cyclization of **3a** using an excess (2.4 equiv.) of *N*-phenylselenosuccinimide (*N*-PSS) as a different selenium electrophile was reported to give a mixture of **4a** and **5a**, compound **4a** was converted into **5a** by oxidative elimination using *m*CPBA.[22] Because of the overstoichiometric amounts of *N*-PPS as an expensive reagent, we developed a rapid catalytic method for the synthesis of isocoumarins from precursors **3**. Employing the reaction conditions developed previously, 2-styrylbenzoic acid **3a** was cyclized using 5 mol-% of diphenyl diselenide and 1.2 equiv. of [bis-(triflouroacetoxy)iodo]benzene as oxidant leading to lactones **5a** along with traces of **4a** but the rate of the reaction was low (Table 1, entry 1). If the reaction is stopped after 5 min, small amounts of dihydroisocoumarin **4a** can be identified with isocoumarin **5a** being the main product as determined by ^{1}H NMR spectroscopy. In order to improve the yield of cyclized products, the amount of the catalyst was examined. An increase to 10 mol-% is sufficient to obtain the reaction product in 92% yield (Table 1, entry 3) while larger amounts could not increase the yields further. No reaction was observed in the absence of diphenyl diselenide (Table 1, entry 5).

Table 1. Optimization of reaction conditions.

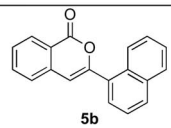
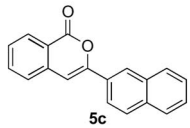
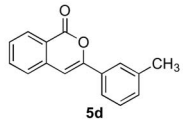
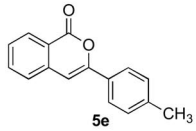
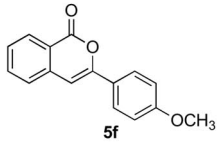
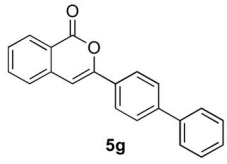
Entry	PhSeSePh	$PhI(OCOCF_3)_2$ [equiv.]	Time [h]	**5a** Yield [%]
1	5 mol-%	1.2	1	30
2	5 mol-%	2.1	1	30
3	10 mol-%	1.2	1	92
4	15 mol-%	1.2	1	92
5	–	2.1	10	0

Using the optimized conditions, the protocol was extended to other stilbene derivatives **3** as shown in Table 2. The reaction of stilbenecarboxylic acids bearing naphthyl **3b/3c**, tolyl **3d/3e**, 4-methoxyphenyl **3f** and biphenyl **3g** substituents gave the corresponding isocoumarins **5** in high yields. In some cases the dihydroisocoumarin derivatives **4** are obtained as minor side products.

Even with electron-rich substrates such as **3f** rapid conversion took place at room temperature and the corresponding isocoumarin **5f** as single product using only 10 mol-% diphenyl diselenide and the hypervalent iodine reagent (Table 2, entry 5).

Under the same reaction conditions conversion of initially formed dihydroisocoumarins **4b**, **4c**, and **4e** into isocoumarins **5b**, **5c**, and **5e** took place when the reaction time was extended up to 16 hours (Table 2, entries 1–2,4–6). It was found that quite long reaction times were required to

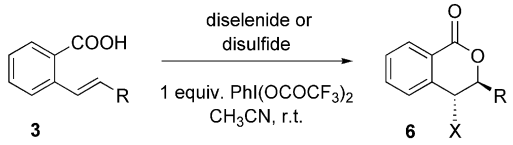
Table 2. Different substrates **3** for isocoumarin synthesis.

Entry	**3**	Product	Yield [%]
1	**3b** R = 1-naphthyl	 **5b**	99
2	**3c** R = 2-naphthyl	 **5c**	94[a]
3	**3d** R = 3-Me-C_6H_4	 **5d**	81[b]
4	**3e** R = 4-Me-C_6H_4	 **5e**	88
5	**3f** R = 4-MeO-C_6H_4	 **5f**	96
6	**3g** R = 4-Ph-C_6H_4	 **5g**	99

[a] 4% dihydroisocoumarin **4c** was also isolated. [b] Reaction time 1 h.

accomplish the synthesis of isocomarins. The corresponding dihydroisocoumarins can also be isolated by preparative TLC if the reaction is stopped after a short period (5–20 min). The dihydroisocoumarins **4a** and **4d** have an *anti* relation of the substituents due to the *anti* addition to the *E*-configured double bond.[21]

A selective reaction to dihydroisocoumarins can be performed by selecting different electrophiles while maintaining the hypervalent iodine reagent as oxidant. When the reaction was carried out using dimethyl diselenide instead of diphenyl diselenide the dihydroisocoumarin derivative **6a** (Scheme 3) is obtained as single product in almost quantitative yield under very mild reaction condition within five minutes (Table 3, entry 1). This indicates that the substituent on the selenium atom is strongly influencing the subsequent reactivity of the selenide. However, dimethoxymethyl diselenide and diphenyl ditelluride failed completely in this



Scheme 3. Selective synthesis of dihydroisocoumarins **6**.

reaction. The use of hypervalent iodine reagents as the only electrophile to activate the double bond was also unsuccessful and resulted in decomposition.

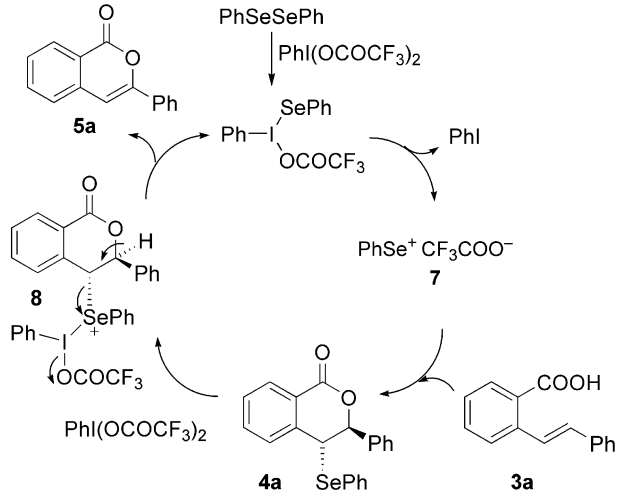
Table 3. Selective synthesis of dihydroisocoumarins **6**.

Entry	Reagent (1.2 equiv.)	Time [min]	**3**	X	Product yield [%]
1	MeSeSeMe	5	**3e** R = 4-Me-C_6H_4	SeMe	**6a** 97
2	PhSSPh	60	**3a** R = Ph	SPh	**6b** 75
3	PhSSPh	60	**3a** R = Ph	SPh	**6b** 5[a]
4	PhSSPh	60	**3b** R = 1-naphthyl	SPh	**6c** 66
5	PhSSPh	60	**3g** R = 4-Ph-C_6H_4	SPh	**6d** 57

[a] $PhI(OCOCF_3)_2$ (2.0 equiv.).

In order to extend the scope of this method and the structural variety of the dihydroisocoumarin derivatives **6**, we also investigated diphenyl disulfide and hypervalent iodine compounds as reagent combination to perform such cyclizations. Also the sulfur electrophiles led to a selective 6-*endo*-*trig* cyclization and formation of dihydroisocoumarins. The reaction of three stilbenecarboxylic acids **3a**, **3b** and **3g** was examined using diphenyl disulfide and [bis(trifluoroacetoxy)iodo]benzene and good yields of new dihydroisocoumarin derivatives **6** were obtained (Table 3, entries 2, 4, 5). Furthermore, the results in Table 3, entry 3 also suggest that an excess of hypervalent iodine is detrimental for the cyclization as the disulfide is further irreversibly oxidized, whereas an excess of hypervalent iodine reagent is tolerated using diphenyl diselenide as catalyst (Table 1, entries 1 and 2).

The catalytic cycle is initiated by the oxidation of diphenyl diselenide with the hypervalent iodine reagent to form phenylselenenyl trifluoroacetate **7** (Scheme 4). Electrophile **7** then reacts with the stilbenecarboxylic acid **3a** in a cyclization reaction to yield compound **4a**. The selenide in lactone **4a** is then activated by [bis(trifluoroacetoxy)iodo]-benzene and intermediate **8** eliminates by forming isocoumarin **5a**.



Scheme 4. Proposed catalytic cycle.

Conclusions

In conclusion, a simple and inexpensive catalytic method has been developed to effect the conversion of stilbenecarboxylic acids to the corresponding isocoumarins, seleno- as well as thio-dihydroisocoumarins. The use of hypervalent iodine compounds as oxidants to form selenium electrophiles has shown unique reactivity in the synthesis of isocoumarins. The cyclization is accomplished by mixing a solution of the substrate with diphenyl diselenide and [bis(trifluoroacetoxy)iodo]benzene. Several dihydroisocoumarin derivatives have also been synthesized. The methodology is straightforward, the reaction conditions are mild and the products are formed in good yields.

Experimental Section

1-Vinylnaphthalene: A mixture of CH_3PPh_3Br (12.9 mmol, 4.61 g) and KO*t*Bu (14 mmol, 1.57 g) in dry toluene (30 mL) stirred at 0 °C for 30 min and at room temp. for 4 h. The reaction mixture was cooled to 0 °C followed by addition of 1-naphthaldehyde (11.8 mmol, 1.84 g). The reaction mixture was stirred overnight at room temp. The solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography using hexane as eluent to yield (11.8 mmol, 1.81 g, quantitative) 1-vinylnaphthalene as colorless oil. The spectroscopic data are in agreement with literature data.[23]

GP1: General Procedure for the Synthesis of 2-Substituted Benzoates 2:[1c,20] A mixture of methyl 2-iodo benzoate (15 mmol, 4.0 g), styrene (18 mmol, 2.1 mL), triethylamine (32 mmol, 4.4 mL), palladium acetate (0.48 mmol, 323 mg) and triphenylphosphane (0.96 mmol, 251 mg) were heated under reflux at 100 °C for 5 h. Solid products were isolated by diluting the reaction mixtures with 10% hydrochloric acid (200 mL) with stirring to dissolve the salts and excess amine. Finally, the residue was purified by column chromatography (EtOAc/hexane, 1:12) to give products in good yields.

Methyl 2-[(*E*)-2-Phenylethenyl]benzoate (2a): According to GP1 compound **2a** was obtained as yellow oil in 87% yield (13.07 mmol, 3.11 g) after purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.04 (d, J = 16.2 Hz, 1 H, *CH*=CH-Ph), 7.98 (dd, J = 7.9, 1.3 Hz, 1 H, Ar-*H*), 7.76 (d, J = 7.9 Hz, 1 H, Ar-*H*), 7.60 (d, J = 7.8 Hz, 2 H, Ar-*H*), 7.55 (dt, J = 7.5, 1.1 Hz, 1 H, Ar-*H*), 7.41 (t, J = 7.8 Hz, 2 H, Ar-*H*), 7.36 (dt, J = 7.8, 1.1 Hz, 1 H, Ar-*H*), 7.33–7.32 (m, 1 H, Ar-*H*), 7.06 (d, J = 16.2 Hz, 1 H, CH=*CH*-Ph), 3.97 (s, 3 H, COO*CH*$_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.9, 139.3, 137.5, 132.2, 131.5, 130.7, 128.7 (2 × C), 128.6, 127.9, 127.5, 127.2, 127.0, 126.9 (2 × C), 52.2 ppm. IR (KBr): $\tilde{\nu}$ = 3061, 3024, 2949, 2839, 1718, 1598, 1584, 1565, 1495, 1480, 1447, 1433, 1293, 1271, 1250, 1189, 1131, 1077, 1016, 964, 761, 743, 705, 691 cm^{-1}. HRMS (ES): *m*/*z* [M + NH_4]$^+$ calcd. for $C_{16}H_{18}NO_2$: 256.1332; found 256.1331. The spectroscopic data are in agreement with literature data.[24]

Methyl 2-[(*E*)-2-(1-Naphthyl)ethenyl]benzoate (2b): According to GP1 compound **2b** was obtained as light yellow viscous oil in 93% yield (14 mmol, 4.03 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, J = 8.1 Hz, 1 H, Ar-*H*), 7.91 (d, J = 15.9 Hz, 1 H, *CH*=CH), 7.88 (dd, J = 8.1, 1.2 Hz, 1 H, Ar-*H*), 7.79–7.71 (m, 4 H, Ar-*H*), 7.68 (d, J = 15.9 Hz, 1 H, CH=*CH*), 7.49–7.40 (m, 4 H, Ar-*H*), 7.28 (t, J = 7.6 Hz, 1 H, Ar-*H*), 3.84 (s, 3 H, COO*CH*$_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.9 (C=O), 139.6 (C), 135.0 (C), 133.8

(C), 132.3 (CH), 131.5 (C), 130.7 (CH), 130.6 (CH), 128.8 (C), 128.7 (CH), 128.5 (2× CH), 128.3 (CH), 127.4 (CH), 127.3 (CH), 126.1 (CH), 125.8 (CH), 124.2 (CH), 123.8 (CH), 52.2 (OCH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3061, 2947, 1718, 1596, 1568, 1480, 1432, 1282, 1259, 1246, 1130, 1076, 963, 795, 775 cm^{-1}. HRMS (ES): *m/z* [M + NH_4]$^+$ calcd. for $C_{20}H_{20}NO_2$: 306.1489; found 306.1491.

Methyl 2-[(*E*)-2-(2-Naphthyl)ethenyl]benzoate (2c): According to GP1 compound **2c** was obtained as colourless crystals in 87% yield (13.06 mmol, 3.76 g); m.p. 77 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 16.2 Hz, 1 H, CH=CH-naph), 7.89 (dd, *J* = 7.9, 1.3 Hz, 1 H, Ar-H), 7.82 (s, 1 H, Ar-H), 7.78–7.71 (m, 5 H, Ar-H), 7.48 (dt, *J* = 7.7, 1.1 Hz, 1 H, Ar-H), 7.41–7.38 (m, 2 H, Ar-H), 7.28 (t, *J* = 7.7 Hz, 1 H, Ar-H), 7.12 (d, *J* = 16.2 Hz, 1 H, CH=CH-naph), 3.89 (s, 3 H, $COOCH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.9, 139.3, 135.0, 133.7, 133.2, 132.2, 131.6, 130.8, 128.6, 128.4, 128.1, 127.7 (2× C), 127.21, 127.05, 127.0, 126.3, 126.0, 123.9, 52.2 (O*CH*$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3055, 2949, 1717, 1627, 1596, 1566, 1482, 1432, 1266, 1242, 1130, 1077, 961, 814, 741 cm^{-1}. HRMS (ES): *m/z* [M + NH_4]$^+$ calcd. for $C_{20}H_{20}NO_2$: 306.1489; found 306.1493.

Methyl 2-[(*E*)-2-(3-Methylphenyl)ethenyl]benzoate (2d): According to GP1 compound **2d** was obtained as light yellow viscous oil in 79% yield (11.9 mmol, 3.0 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 16.2 Hz, 1 H, *CH*=CH-Ar), 7.85 (d, *J* = 7.9 Hz, 1 H, *Ar-H*), 7.64 (d, *J* = 7.9 Hz, 1 H, *Ar-H*), 7.43 (dt, *J* = 7.9, 1.0 Hz, 1 H, *Ar-H*), 7.29–7.22 (m, 3 H, *Ar-H*), 7.17 (t, *J* = 8.6 Hz, 1 H, *Ar-H*), 7.01 (d, *J* = 7.5 Hz, 1 H, *Ar-H*), 6.91 (d, *J* = 16.2 Hz, 1 H, *Ar-H*), 3.85 (s, 3 H, COOC*H*$_3$), 2.30 (s, 3 H, Ar-C*H*$_3$) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 167.9 (C=O), 139.4 (C), 138.2 (C), 137.4 (C), 132.2 (CH), 131.7 (CH), 130.7 (CH), 128.7 (CH), 128.6 (C & CH), 127.5 (CH), 127.2 (CH), 127.1 (CH), 127.0 (CH), 124.2 (CH), 52.2, 21.5 ppm. IR (KBr): $\tilde{\nu}$ = 3061, 3021, 2948, 1718, 1601, 1487, 1433, 1294, 1274, 1252, 1130, 1077, 962, 779 cm^{-1}. HRMS (AP): *m/z* [M + H]$^+$ calcd. for $C_{17}H_{17}O_2$: 253.1229; found 253.1236.

Methyl 2-[(*E*)-2-(4-Methylphenyl)ethenyl]benzoate (2e): According to GP1 compound **2e** was obtained as colourless crystals in 82% yield (12.3 mmol, 3.1 g) after purification; m.p. 79–80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 16.2 Hz, 1 H, *CH*=CH-Ar), 7.81 (d, *J* = 8.0 Hz, 1 H, *Ar-H*), 7.60 (d, *J* = 7.9 Hz, 1 H, *Ar-H*), 7.37 (t, *J* = 7.5 Hz, 1 H, *Ar-H*), 7.34 (d, *J* = 7.9 Hz, 2 H, *Ar-H*), 7.18 (t, *J* = 7.6, 7.6 Hz, 1 H, *Ar-H*), 7.05 (d, *J* = 7.9 Hz, 2 H, *Ar-H*), 6.88 (d, *J* = 16.2 Hz, 1 H, 1 H, CH=*CH*-Ar), 3.80 (s, 3 H, COO*CH*$_3$), 2.25 (s, 3 H, Ar*CH*$_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.0 (C=O), 139.5 (C), 137.8 (C), 134.8 (C), 132.2 (CH), 131.5 (CH), 130.7 (CH), 129.5 (2× CH), 128.5 (C), 127.0 (CH), 126.9 (3× CH), 126.4 (CH), 52.1 (OCH_3), 21.4 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3077, 2957, 2915, 2843, 1713, 1598, 1512, 1466, 1436, 1271, 1249, 1192, 1128, 1080, 964, 806, 797, 749, 710 cm^{-1}. HRMS (ESI): *m/z* [M + H]$^+$ calcd. for $C_{17}H_{17}O_2$: 253.1223; found 253.1224.

Methyl 2-[(*E*)-2-(4-Methoxyphenyl)ethenyl]benzoate (2f): According to GP1 compound **2f** was obtained as colourless crystal in 85% yield (12.8 mmol, 3.43 g); m.p. 80–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 7.9 Hz, 1 H, *Ar-H*), 7.90 (d, *J* = 16.3 Hz, 1 H, CH=C*H*), 7.74 (d, *J* = 7.9 Hz, 1 H, *Ar-H*), 7.54–7.50 (m, 3 H, *Ar-H*), 7.32 (t, *J* = 7.5, 7.5 Hz, 1 H, *Ar-H*), 7.01 (d, *J* = 16.3 Hz, 1 H, C*H*=CH), 6.93 (d, *J* = 8.4 Hz, 2 H, *Ar-H*), 3.95 (s, 3 H, CO-OC*H*$_3$), 3.85 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.0 (C=O), 159.6 (C), 139.5 (C), 132.1 (CH), 131.0 (CH), 130.7 (CH), 130.3 (C), 128.4 (C), 128.2 (2× CH), 126.7 (2× CH), 125.3 (CH), 114.2 (2× CH), 55.4 (OMe), 52.1 (OMe) ppm. IR (KBr): $\tilde{\nu}$ = 3065, 3000, 2950, 2905, 2833, 1717, 1603, 1592, 1512, 1432, 1301, 1277, 1250, 1176, 1129, 1078, 1030, 971, 767, 755, 721 cm^{-1}. HRMS (ESI): *m/z* [M + H]$^+$ calcd. for $C_{17}H_{17}O_3$: 269.1172; found 269.1175.

Methyl 2-[(*E*)-2-Biphenylethenyl]benzoate (2g): According to GP1 compound **2g** was obtained as colourless crystal in 84% yield (12.6 mmol, 3.96 g); m.p. 138 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 16.2 Hz, 1 H, *CH*=CH-Ar-Ar), 7.99 (d, *J* = 7.9 Hz, 1 H, *Ar-H*), 7.79 (d, *J* = 7.9 Hz, 1 H, *Ar-H*), 7.68–7.66 (m, 6 H, *Ar-H*), 7.56 (t, *J* = 7.5 Hz, 1 H, *Ar-H*), 7.50 (t, *J* = 7.5 Hz, 2 H, *Ar-H*), 7.41–7.36 (m, 2 H, *Ar-H*), 7.10 (d, *J* = 16.2 Hz, 1 H, CH=*CH*-Ar-Ar), 3.99 (s, 3 H, COO*Me*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.9 (C=O), 140.7 (C), 140.6 (C), 139.3 (C), 136.6 (C), 132.2 (CH), 131.0 (CH), 130.8 (CH), 128.9 (2× CH), 128.6 (C), 127.5 (CH), 127.4 (5× CH), 127.2 (CH), 127.0 (3× CH), 52.2 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3071, 3032, 2947, 1719, 1566, 1487, 1432, 1266, 1248, 1129, 1077, 971, 832, 765, 721, 700 cm^{-1}. HRMS (ESP): *m/z* [M + NH_4]$^+$ calcd. for $C_{22}H_{22}NO_2$: 332.1645; found 332.1647.

GP2: General Procedure for the Synthesis of Stilbene Carboxylic Acids 3: To a mixture of **2a** (2.0 g, 8.4 mmol) in 60 mL of THF/MeOH/H_2O (4:1:l) LiOH (600 mg, 25.2 mmol) was added at room temperature. The reaction mixture was then heated at 70 °C for 12 h. After the reaction mixture was allowed to cool to room temperature, reaction mixture was neutralised (pH = 6) using 1 M HCl. The product was extracted with ethyl acetate, washed with water and brine. The extract was dried with anhydrous $MgSO_4$, evaporated under reduced pressure and then recrystallized from ethanol to give the corresponding stilbenecarboxylic acids in very good yields.

2-[(*E*)-2-Phenylethenyl]carboxylic Acid (3a):[25] According to GP2 compound **3a** was obtained as colourless solid in 87% yield (7.2 mmol, 1.64 g); m.p. 154–155 °C (ref.[22] m.p. 159–161 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04–7.98 (m, 2 H, *CH*=CH-Ar & *Ar-H*), 7.66 (d, *J* = 7.8 Hz, 1 H, *Ar*-H), 7.49–7.47 (m, 3 H, *Ar-H*), 7.31–7.27 (m, 3 H, *Ar-H*), 7.22–7.16 (m, 1 H, *Ar-H*), 6.95 (d, *J* = 16.2 Hz, 1 H CH=*CH*-Ar) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.3 (C=O), 140.3 (C), 137.4 (C), 133.2 (C), 131.9 (CH), 131.7 (CH), 128.8 (3× CH), 128.0 (CH), 127.6 (CH), 127.4 (CH), 127.3 (CH), 127.0 (2× CH) ppm. IR (KBr): $\tilde{\nu}$ = 3330–2745, 3061, 1685, 1601, 1565, 1495, 1447, 1406, 1301, 1275, 1253, 1078, 963, 913, 759, 744 cm^{-1}. HRMS (ESP): *m/z* [M + H]$^+$ calcd. for $C_{15}H_{12}O_2H_1$: 225.0910; found 225.0912. The spectroscopic data are in agreement with literature data.[25]

2-[(*E*)-2-(1-Naphthyl)ethenyl]carboxylic Acid (3b): According to GP2 compound **3b** was obtained as colourless crystals in 98% yield (8.2 mmol, 2.25 g); m.p. 160–162 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.4 Hz, 1 H, *Ar-H*), 8.06 (dd, *J* = 7.9, 1.2 Hz, 1 H, *Ar-H*), 8.01 (d, *J* = 16.0 Hz, 1 H, *CH*=CH), 7.80–7.78 (m, 2 H, *Ar-H*), 7.74 (d, *J* = 7.4 Hz, 2 H, *Ar-H*), 7.70 (d, *J* = 16.0 Hz, 1 H, CH=*CH*), 7.55 (td, *J* = 7.5, 1.0 Hz, 1 H, *Ar-H*), 7.48–7.39 (m, 3 H, *Ar-H*), 7.33 (td, *J* = 8.5, 1.1 Hz, 1 H, *Ar-H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.6 (C=O), 140.6 (C), 134.9 (C), 133.8 (C), 133.2 (CH), 131.7 (CH), 131.4 (C), 130.7 (CH), 128.9 (CH), 128.7 (CH), 128.3 (CH), 127.8 (CH), 127.5 (CH), 127.4 (C), 126.2 (CH), 125.84 (CH), 125.80 (CH), 124.4 (CH), 123.8 (CH) ppm. IR (KBr): $\tilde{\nu}$ = 3223–2513, 1675, 1598, 1564, 1482, 1402, 1403, 1266, 1171, 1145, 1086, 964, 925, 794, 745, 664 cm^{-1}. HRMS (ESI): *m/z* [M + NH_4]$^+$ calcd. for $C_{19}H_{18}NO_2$: 292.1332; found 292.1335.

2-[(*E*)-2-(2-Naphthyl)ethenyl]carboxylic Acid (3c): According to GP2 compound **3c** was obtained as colourless crystals in 95% yield (7.9 mmol, 2.16 g); m.p. 219–220 °C (ref.[26] m.p. 211–212 °C). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.30 (d, *J* = 16.3 Hz, 1 H,

CH=CH), 8.06–8.04 (dd, *J* = 7.8, 1.2 Hz, 1 H, *Ar-H*), 8.02 (s, 1 H, *Ar-H*), 7.96–7.90 (m, 4 H, *Ar-H*), 7.87–7.85 (dd, *J* = 8.6, 1.7 Hz, 1 H, *Ar-H*), 7.64 (dt, *J* = 7.4, 1.0 Hz, 1 H, *Ar-H*), 7.55–7.49 (m, 2 H, *Ar-H*), 7.44 (dt, *J* = 7.7, 1.1 Hz, 1 H, *Ar-H*), 7.38 (d, *J* = 16.3 Hz, 1 H, CH=*CH*) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 168.8, 140.0, 136.2, 134.8, 134.2, 133.1, 131.9, 131.7, 130.0, 129.2, 128.9, 128.8, 128.6, 128.2, 127.8, 127.7, 127.3, 126.9, 124.6 ppm. IR (KBr): $\tilde{\nu}$ = 3103–2517, 1675, 1627, 1598, 1565, 1485, 1410, 1305, 1249, 1165, 1141, 1080, 964, 930, 903, 845, 822, 800, 742, 702, 663 cm^{-1}. HRMS (ESI): *m*/*z* [M + H]$^+$ calcd. for $C_{19}H_{15}O_2$: 275.1067; found 275.1071.

2-[(*E*)-2-(3-Methylphenyl)ethenyl]carboxylic Acid (3d): According to GP2 compound **3d** was obtained as colourless crystals in 81% yield (6.8 mmol, 1.62 g); m.p. 163–164 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (dd, *J* = 7.8, 1.3 Hz, 1 H, *Ar-H*), 7.97 (d, *J* = 16.2 Hz, 1 H, *CH*=CH-Ar), 7.67 (d, *J* = 7.8 Hz, 1 H, *Ar-H*), 7.50 (t, *J* = 7.6 Hz, 1 H, *Ar-H*), 7.30–7.27 (m, 3 H, *Ar-H*), 7.20–7.17 (m, 1 H, *Ar-H*), 7.03 (d, *J* = 7.6 Hz, 1 H, *Ar-H*), 6.93 (d, *J* = 16.2 Hz, 1 H, CH=*CH*-Ar), 2.30 (s, 3 H, Ar-*CH*$_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.6 (C=O), 140.3 (C), 138.3 (C), 137.3 (C), 133.1 (CH), 132.1 (CH), 131.7 (CH), 128.8 (CH), 128.6 (CH), 127.7 (CH), 127.4 (CH), 127.3 (CH), 127.2 (C & CH), 124.1 (CH), 21.5 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3069–2511, 1689, 1595, 1581, 1566, 1484, 1415, 1303, 1278, 1261, 1166, 1143, 1077, 957, 934, 777, 754, 733, 702 cm^{-1}. HRMS (ES): *m*/*z* [M + NH_4]$^+$ calcd. for $C_{16}H_{18}NO_2$: 256.1332; found 256.1334.

2-[(*E*)-2-(4-Methylphenyl)ethenyl]carboxylic Acid (3e): According to GP2 compound **3e** was obtained as colourless crystals in 88% yield (0.0074 mol, 1.76 g); m.p. 159–160 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.14 (dd, *J* = 5.9, 1.2 Hz, 1 H, *Ar-H*), 8.07 (d, *J* = 16.2 Hz, 1 H, *CH*=CH), 7.78 (d, *J* = 7.8 Hz, 1 H, *Ar-H*), 7.60 (dt, *J* = 8.5, 1.1 Hz, 1 H, *Ar-H*), 7.50 (d, *J* = 8.0 Hz, 2 H, *tolyl-H*), 7.39 (dt, *J* = 8.5, 1.1 Hz, 1 H, *Ar-H*), 7.22 (d, *J* = 8.0 Hz, 2 H, *tolyl-H*), 7.06 (d, *J* = 16.2 Hz, 1 H, CH=*CH*), 2.41 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.2 (C=O), 140.4 (C), 137.9 (C), 134.6 (C), 133.1 (CH), 131.8 (CH), 131.7 (CH), 129.5 (2× CH), 127.3 (CH), 127.2 (C), 127.1 (CH), 126.9 (2× CH), 126.5 (CH), 21.3 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3064–2647, 1682, 1594, 1570, 1511, 1481, 1412, 1306, 1277, 1253, 1079, 957, 934, 853, 802, 748 cm^{-1}. HRMS (ESI): *m*/*z* [M + H]$^+$ calcd. for $C_{16}H_{15}O_2$: 239.1067; found 239.1069.

2-[(*E*)-2-(4-Methoxyphenyl)ethenyl]carboxylic Acid (3f): According to GP2 compound **3f** was obtained as colourless crystals in 97% yield (8.4 mmol, 2.14 g); m.p. 192 °C. ^{1}H NMR (500 MHz, [D$_6$]-DMSO): δ = 7.85–7.82 (m, 2 H, *Ar-H*), 7.79 (d, *J* = 16.4 Hz, 1 H, CH=*CH*-Ar), 7.56 (t, *J* = 7.3, *J* = 7.3 Hz, 1 H, *Ar-H*), 7.50 (d, *J* = 8.7 Hz, 2 H, *Ar-H*), 7.36 (t, *J* = 7.3 Hz, 1 H, *Ar-H*), 7.13 (d, *J* = 16.4 Hz, 1 H, *CH*=CH-Ar), 3.79 (s, 1 H, OCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.7, 159.2, 138.1, 131.8, 130.3, 130.2, 129.8, 129.5, 127.9, 126.9, 126.3, 124.7, 114.3, 55.2 ppm. IR (KBr): $\tilde{\nu}$ = 3100–2517, 1688, 1604, 1562, 1508, 1405, 1298, 1076, 1026, 966, 901, 749 cm^{-1}. HRMS (ES): *m*/*z* [M + H]$^+$ calcd. for $C_{16}H_{15}O_3$: 255.1016; found 255.1018.

2-[(*E*)-2-(Biphenyl)ethenyl]carboxylic Acid (3g): According to GP2 compound **3g** was obtained as colourless crystals in 92% yield (7.7 mmol, 2.31 g); m.p. 180–183 °C. ^{1}H NMR (500 MHz, [D$_6$]-DMSO): δ = 7.99 (d, *J* = 16.4 Hz, 1 H, *CH*=CH-Ar-Ar), 7.88 (d, *J* = 8.0 Hz, 2 H, *Ar-H*), 7.72 (t, *J* = 8.0 Hz, 4 H, *Ar-H*), 7.66 (d, *J* = 8.3 Hz, 2 H, *Ar-H*), 7.60 (t, *J* = 8.0 Hz, 1 H, *Ar-H*), 7.49 (t, *J* = 7.9 Hz, 2 H, *Ar-H*), 7.42–7.37 (m, 2 H, *Ar-H*), 7.24 (d, *J* = 16.4 Hz, 1 H, CH=*CH*-Ar-Ar) ppm. ^{13}C NMR (125 MHz & DEPT 135, [D$_6$]DMSO): δ = 168.6 (C=O), 139.6 (C), 139.5 (C), 137.8 (C), 136.4 (C), 131.9 (CH), 130.3 (CH), 130.1 (CH), 129.8 (C), 129.0 (2× CH), 127.5 (CH), 127.4 (CH), 127.20 (2× CH), 127.15 (CH), 127.0 (2× CH), 126.6 (CH), 126.5 (2× CH) ppm. IR (KBr): $\tilde{\nu}$ = 3100–2540, 1683, 1627, 1602, 1565, 1485, 1452, 1409, 1305, 1272, 1247, 1139 1073, 965, 917, 823, 764, 744, 718, 697, 558 cm^{-1}. HRMS (ES): *m*/*z* [M + H]$^+$ calcd. for $C_{21}H_{17}O_2$: 301.1223; found 301.1225.

General Procedure GP3 for the Catalytic Reaction: Stilbenecarboxylic acid **3** (0.22 mmol) was added to a solution of diphenyl diselenide (0.022 mmol, 6.9 mg, 10 mol-%) in acetonitrile (5 mL) followed by [bis(trifluoroacetoxy)iodo]benzene (112 mg, 0.26 mmol) and the mixture was stirred under argon at room temperature until TLC showed no remaining starting material. The solvent was evaporated under reduced pressure and the residue purified immediately by flash chromatography eluting with ethyl acetate:hexane (1:4) to yield the cyclization products (first elution with hexane gave diphenyl diselenide, second elution with ethyl aetate/hexane gave cyclized product, and the seleno-substituted products **4** could be isolated on preparative TLC if the reaction was stopped after 5–20 min).

3,4-Dihydro-3-phenyl-4-(phenylseleno)isocoumarin (4a): According to GP3 compound **4a** was obtained as colourless crystals in 47% yield (0.1 mmol, 39 mg); m.p. 123–125 °C (ref.[21,22] m.p. 124–125 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.8 Hz, 1 H, *Ar-H*), 7.46–7.44 (m, 2 H, *Ar-H*), 7.37 (dt, *J* = 7.6, 1.4 Hz, 1 H, *Ar-H*), 7.30–7.25 (m, 2 H, *Ar-H*), 7.20 (t, *J* = 7.6 Hz, 2 H, *Ar-H*), 7.14–7.11 (m, 4 H, *Ar-H*), 7.02–7.00 (m, 2 H, *Ar-H*), 5.76 (d, *J* = 2.3 Hz, 1 H, CH-*CH*-O), 4.78 (d, *J* = 2.3 Hz, 1 H, *CH*-CH-O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.5 (C=O), 138.3 (C), 138.0 (C), 136.6 (2× CH), 133.9 (CH), 130.1 (CH), 129.4 (2× CH), 129.1 (CH), 128.6 (2× CH), 128.4 (CH), 128.2 (2× CH), 127.7 (C), 125.9 (2× CH), 124.9 (C), 82.3 (CH-O), 43.8 (CH) ppm. IR (KBr): $\tilde{\nu}$ = 3058, 2927, 1732, 1598, 1474, 1437, 1234, 1065, 767, 737, 689 cm^{-1}. HRMS (ESI): *m*/*z* [M + H]$^+$ calcd. for $C_{21}H_{17}O_2Se^{80}$: 381.0394; found 381.0402. The spectroscopic data are in agreement with literature data.[21,22]

3,4-Dihydro-3-(2′-naphthyl)-4-(phenylseleno)isocoumarin (4c): According to GP3 compound **4c** was obtained as white solid in 4% yield (9.3 μmol, 4 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98 (dd, *J* = 7.8, *J* = 1.2 Hz, 1 H, *Ar-H*), 7.67–7.65 (m, 1 H, *Ar-H*), 7.63 (br. d, *J* = 8.9 Hz, 2 H, *Ar-H*), 7.48–7.46 (m, 3 H, *Ar-H*), 7.37–7.35 (m, 3 H, *Ar-H*), 7.31–7.24 (m, 2 H, *Ar-H*), 7.20 (t, *J* = 7.6 Hz, 2 H, *Ar-H*), 7.13–7.10 (m, 2 H, *Ar-H*), 5.92 (d, *J* = 2.3 Hz, 1 H, CH-*CH*-O), 4.90 (d, *J* = 2.3 Hz, 1 H, *CH*-CH-O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.6 (C=O), 138.0 (C), 136.6 (2× CH), 135.5 (C), 133.9 (CH), 132.88 (C), 132.85 (C), 130.1 (CH), 129.4 (2× CH), 129.1 (CH), 128.6 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 127.6 (C), 127.5 (CH), 126.5 (2× CH), 125.3 (CH), 124.9 (C), 123.3 (CH), 82.4 (CH-*CH*-O), 43.8 (*CH*-CH-O) ppm. HRMS (ESI): *m*/*z* [M + H]$^+$ calcd. for $C_{25}H_{19}O_2Se$: 431.0545; found 431.0546.

3,4-Dihydro-3-(3′-methylphenyl)-4-(phenylseleno)isocoumarin (4d): According to GP3 compound **4d** was obtained as orange-yellow solid; m.p. 192–193 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 6.8 Hz, 1 H, *Ar-H*), 7.45–7.43 (m, 2 H, *Ar-H*), 7.38 (dt, *J* = 7.6, 1.4 Hz, 1 H, *Ar-H*), 7.31–7.25 (m, 2 H, *Ar-H*), 7.21 (t, *J* = 7.6 Hz, 2 H, *Ar-H*), 7.13 (d, *J* = 7.6 Hz, 1 H, *Ar-H*), 7.02 (t, *J* = 7.6 Hz, 1 H, *Ar-H*), 6.93 (d, *J* = 7.6 Hz, 1 H, *Ar-H*), 6.83 (s, 1 H, *Ar-H*), 6.79 (d, *J* = 7.6 Hz, 1 H, *Ar-H*), 5.73 (d, *J* = 2.4 Hz, 1 H, CH-*CH*-O), 4.79 (d, *J* = 2.4 Hz, 1 H, *CH*-CH-O), 2.16 (s, 3 H, Ar-*CH*$_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.6 (C=O), 138.4 (C), 138.2 (C), 138.1 (C), 136.6 (2× CH), 133.9 (C & CH), 130.1

(CH), 129.3 (2× CH), 129.1 (CH), 129.0 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 126.6 (CH), 124.9 (C), 122.9 (CH), 82.3 (CH-*CH*-O), 43.8 (*CH*-CH-O), 21.4 (CH_3) ppm. HRMS (EI): *m/z* $[M]^+$ calcd. for $C_{22}H_{18}O_2Se$: 392.0480; found 392.0493.

3-(Phenyl)isocoumarin (5a): According to GP3 compound **5a** was obtained as colourless soild in 92% yield (0.20 mmol, 45.1 mg); m.p. 90–92 °C (ref.[27] m.p. 90–91 °C). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.25 (d, *J* = 8.2 Hz, 1 H, *Ar-H*), 7.84–7.81 (m, 2 H, *Ar-H*), 7.66 (dt, *J* = 7.6, 1.3 Hz, 1 H, *Ar-H*), 7.46–7.36 (m, 5 H, *Ar-H*), 6.90 (s, 1 H, *CH*=C-O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.3 (C=O), 153.7 (C), 137.6 (C), 134.9 (CH), 132.0 (C), 130.0 (CH), 129.7 (CH), 128.9 (2× CH), 128.2 (CH), 126.0 (CH), 125.3 (2× CH), 120.6 (C), 101.8 (CH) ppm. IR (KBr): $\tilde{\nu}$ = 3062, 3030, 2962, 2922, 1732, 1635, 1483, 1234, 1066, 766 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd. for $C_{15}H_{11}O_2$: 223.0754; found 223.0753. The spectroscopic data are in agreement with literature data.[27]

3-(1-Naphthyl)isocoumarin (5b): According to GP3 compound **5b** was obtained as colourless crystals in 99% yield (0.22 mmol, 59 mg); m.p. 147 °C (ref.[28] m.p. 120–122 °C). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 7.9 Hz, 1 H, *Ar-H*), 8.16–8.14 (m, 1 H, *Ar-H*), 7.85 (d, *J* = 8.2 Hz, 1 H, *Ar-H*), 7.83–7.81 (m, 1 H, *Ar-H*), 7.68–7.65 (m, 2 H, *Ar-H*), 7.48–7.41 (m, 5 H, *Ar-H*), 6.71 (s, 1 H, *CH* of lactone ring) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.6 (C=O), 154.8 (C), 137.5 (C), 134.9 (CH), 133.8 (C), 130.84 (C), 130.77 (C), 130.6 (CH), 129.8 (CH), 128.6 (CH), 128.4 (CH), 127.7 (CH), 127.1 (CH), 126.3 (CH), 125.9 (CH), 125.2 (CH), 125.1 (CH), 120.6 (CH), 107.1 (CH) ppm. IR (KBr): $\tilde{\nu}$ = 3091, 3042, 1717, 1640, 1606, 1566, 1509, 1487, 1453, 1397, 1352, 1310, 1241, 1200, 1179, 1154, 1117, 1066, 1053, 1026, 993, 956, 922, 882, 847, 790, 770, 748, 690 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd. for $C_{19}H_{13}O_2$: 273.0910; found 273.0907. The spectroscopic data are in agreement with literature data.[28]

3-(Naphthalen-2-yl)isocoumarin (5c): According to GP3 a mixture of stilbenecarboxylic acid **3c** (60 mg, 0.22 mmol) and PhSeSePh (6.9 mg, 0.022 mmol) was treated with [bis(trifluoroacetoxy)iodo]-benzene (113 mg, 0.26 mmol). Product **5c** was obtained as colourless crystals in 94% yield (0.21 mmol, 57 mg); m.p. 157 °C (ref.[29] m.p. 161–163 °C). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.40 (s, 1 H, *Naph-H*), 8.28 (d, *J* = 7.9 Hz, 1 H, *Ar-H*), 7.89–7.78 (m, 4 H, *Ar-H*), 7.68 (dt, *J* = 7.9, 1.3 Hz, 1 H, *Ar-H*), 7.48–7.45 (m, 4 H, *Ar-H*), 7.03 (s, 1 H, lactone-*CH*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.4 (C=O), 153.6 (C), 137.6 (C), 134.9 (CH), 133.9 (C), 133.2 (C), 129.8 (CH), 129.0 (CH), 128.9 (CH), 128.6 (CH), 128.2 (CH), 127.7 (CH), 127.3 (CH), 126.9 (CH), 126.1 (CH), 125.4 (CH), 122.0 (CH), 120.7 (C), 102.3 (CH) ppm. IR (KBr): $\tilde{\nu}$ = 3108, 3058, 1717, 1635, 1608, 1562, 1367, 1331, 1221, 1191, 1074, 851, 818, 746, 682 cm^{-1}. HRMS (AP): *m/z* $[M + H]^+$ calcd. for $C_{19}H_{13}O_2$: 273.0916; found 273.0909 The spectroscopic data are in agreement with literature data.[29]

3-(3′-Methylphenyl)isocoumarin (5d): According to GP3 mixture of stilbenecarboxylic acid **3d** (5 mg, 0.021 mmol) and PhSeSePh (0.7 mg, 0.0021 mmol) was treated with [bis(trifluoroacetoxy)iodo]-benzene (10.8 mg, 0.0252 mmol). Product **5d** was obtained as colourless crystals in 81% yield (0.017 mmol, 4 mg); m.p. 90 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.25 (d, *J* = 8.2 Hz, 1 H, *Ar-H*), 7.68–7.64 (m, 2 H, *Ar-H*), 7.62 (d, *J* = 7.8 Hz, 1 H, *Ar-H*), 7.45–7.42 (m, 2 H, *Ar-H*), 7.29 (t, *J* = 7.8 Hz, 1 H, *Ar-H*), 7.19 (s, 1 H, *Ar-H*), 6.89 (s, 1 H, *CH* of lactone ring), 2.37 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.4 (C=O), 153.9 (C), 138.6 (C), 137.7 (C), 134.9 (CH), 132.0 (C), 130.8 (CH), 129.7 (CH), 128.7 (CH), 128.1 (CH), 125.9 (2× CH), 122.4 (CH), 120.6 (C), 101.7 (CH), 21.5 (CH_3) ppm. HRMS (AP): *m/z* $[M + H]^+$ calcd. for $C_{16}H_{13}O_2$: 237.0916; found 237.0917.

3-(4′-Methylphenyl)isocoumarin (5e): According to GP3 compound **5e** was obtained as colourless crystals in 95% yield (0.21 mmol, 49 mg); m.p. 114–115 °C (ref.[28] m.p. 108–110 °C). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 8.2 Hz, 1 H, *Ar-H*), 7.70 (d, *J* = 8.1 Hz, 2 H, *tolyl-H*), 7.63 (dt, *J* = 8.2, *J* = 1.3 Hz, 1 H, *Ar-H*), 7.41–7.38 (m, 2 H, *Ar-H*), 7.19 (d, *J* = 8.1 Hz, 2 H, *tolyl-H*), 6.83 (s, 1 H, *CH* of lactone ring), 2.33 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.4 (C=O), 153.9 (C), 140.3 (C), 137.8 (C), 134.8 (CH), 129.7 (CH), 129.6 (2× CH), 129.2 (C), 127.9 (CH), 125.9 (CH), 125.2 (2× CH), 120.5 (C), 101.1 (CH), 21.4 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3032, 2921, 1731, 1630, 1604, 1559, 1512, 1477, 1458, 1343, 1308, 1235, 1107, 1067, 1008, 847, 817, 751, 711, 688 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd. for $C_{16}H_{13}O_2$: 237.0910; found 237.0911. The spectroscopic data are in agreement with literature data.[28]

3-(4′-Methoxyphenyl)isocoumarin (5f): According to GP3 compound **5f** was obtained as colourless crystals in 96% yield (0.21 mmol, 53 mg); m.p. 112–113 °C (ref.[28] m.p. 111–113 °C). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 8.34 Hz, 1 H, *Ar-H*), 7.76 (d, *J* = 8.9 Hz, 2 H, *Ar-H*), 7.63 (dt, *J* = 7.6, *J* = 1.3 Hz, 1 H, *Ar-H*), 7.40–7.38 (m, 2 H, *Ar-H*), 6.90 (d, *J* = 8.9 Hz, 2 H, *Ar-H*), 6.76 (s, 1 H, latone-*H*), 3.80 (s, 3 H, OCH_3) ppm. ^{13}C & DEPT 90, 135 NMR (125 MHz, $CDCl_3$): δ = 162.5 (C=O), 161.1 (C), 153.8 (C), 137.9 (C), 134.8 (CH), 129.7 (CH), 127.7 (CH), 126.9 (2× CH), 125.7 (CH), 124.6 (C), 120.2 (C), 114.3 (2× CH), 100.3 (CH), 55.4 (OCH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3036, 2999, 2958, 2844, 1738, 1632, 1562, 1514, 1480, 1457, 1344, 1309, 1290, 1264, 1237, 1200, 1177, 1114, 1064, 1022, 925, 880, 837, 820, 790, 752, 687, 668 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd. for $C_{16}H_{13}O_3$: 253.0859; found 253.0858. The spectroscopic data are in agreement with literature data.[28]

3-(Biphenyl)isocoumarin (5g): According to GP3 mixture of stilbenecarboxylic acid **3g** (100 mg, 0.33 mmol) and PhSeSePh (10.3 mg, 0.033 mmol) was treated with [bis(trifluoroacetoxy)iodo]-benzene (170 mg, 0.4 mmol). Product **5g** was obtained as colourless crystals in 99% yield (0.325 mmol, 97 mg); m.p. 173 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.3 Hz, 1 H, *Ar-H*), 7.88 (d, *J* = 8.6 Hz, 2 H, *Ar-H*), 7.65–7.61 (m, 3 H, *Ar-H*), 7.57 (m, 2 H, *Ar-H*), 7.43 (d, *J* = 7.5 Hz, 2 H, *Ar-H*), 7.39 (t, *J* = 7.5 Hz, 2 H, *Ar-H*), 7.33–7.29 (m, 1 H, *Ar-H*), 6.92 (s, 1 H, lactone-*CH*) ppm. ^{13}C & DEPT 90, 135 NMR (125 MHz, $CDCl_3$): δ = 162.3 (C=O), 153.5 (C), 142.7 (C), 140.1 (C), 137.6 (C), 134.9 (CH), 130.8 (C), 129.7 (CH), 128.9 (2× CH), 128.2 (CH), 127.9 (CH), 127.5 (2× CH), 127.1 (2× CH), 126.0 (CH), 125.7 (2× CH), 120.6 (C), 101.8 (CH) ppm. IR (KBr): $\tilde{\nu}$ = 3098, 3061, 3032, 1719, 1639, 1602, 1486, 1408, 1239, 1071, 836, 764, 687 cm^{-1}. HRMS (ESP): *m/z* $[M + H]^+$ calcd. for $C_{21}H_{15}O_2$: 299.1067; found 299.1070.

3,4-Dihydro-3-(4′-methylphenyl)-4-(methylseleno)isocoumarin (6a): Stilbenecarboxylic acid **3e** (59.5 mg, 0.25 mmol), was added to a solution of dimethyl diselenide (2.65 mL, 5.2 mg, 0.028 mmol) in acetonitrile (5 mL), followed by [bis(trifluoroacetoxy)iodo]benzene (112 mg, 0.26 mmol) and the mixture stirred under argon at room temperature for 5 min. The solvent was then evaporated under reduced pressure and the residue was purified immediately by flash column chromatography eluting with ethyl acetate:light petroleum (1:4) to yield **6** in 97% yield (80 mg, 0.22 mmol) as light yellow viscous oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.05 (dd, *J* = 7.6, 1.3 Hz, 1 H, *Ar-H*), 7.47 (dt, *J* = 7.6, 1.3 Hz, 1 H, *Ar-H*), 7.36 (d, *J* = 7.6 Hz, 1 H, *Ar-H*), 7.31 (dt, *J* = 7.6, 1.0 Hz, 1 H, *Ar-H*), 7.09 (d, *J* = 8.1 Hz, 2 H, *tolyl-H*), 7.03 (d, *J* = 8.1 Hz, 2 H, *tolyl-H*),

5.73 (d, J = 4.3 Hz, 1 H, CH-*CH*-O), 4.46 (d, J = 4.3 Hz, 1 H, *CH*-CH-O), 2.22 (s, 3 H, CH_3), 1.85 (s, 3 H, SeCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.0 (C=O), 139.0 (C), 138.4 (C), 135.3 (C), 134.2 (CH), 130.2 (CH), 129.3 (2× CH), 128.3 (CH), 128.2 (CH), 126.3 (2× CH), 125.0 (C), 83.8 (CH), 39.6 (CH), 21.1 (CH_3) and 4.8 (SeCH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3030, 2924, 1726, 1634, 1601, 1515, 1455, 1371, 1282, 1259, 1234, 1109, 1088, 1047, 913, 817, 783, 760, 700 cm^{-1}. HRMS (ESI): *m*/*z* [M + H]$^+$ calcd. for $C_{17}H_{17}O_2Se$: 333.0405; found 333.0394.

GP 4 for Preparation of Thio-Substituted Dihydroisocoumarins 6b–d: To a stirred solution of **3** (0.45 mmol), PhSSPh (0.45 mmol, 98 mg) in CH_3CN (10 mL) bis(trifluoroacetoxy)iodobenzene (0.44 mmol, 189 mg) was added at room temperature. The mixture was stirred at room temperature for 1 h. The solvent was then evaporated under reduced pressure and the residue was purified immediately by flash column chromatography eluting with ethyl acetate:hexane (1:4) to yield the cyclization products **7**, **8** and **9** (first elution with hexane gave diphenyl disulfide, second elution with ethyl acetate:hexane gave the cyclized product).

3-Phenyl-4-(phenylthio)isochroman-1-one (6b): According to GP4 compound **6b** was obtained as colourless solid in 75% yield (0.34 mmol, 112.5 mg); m.p. 218 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13 (d, J = 7.6 Hz, 1 H, *Ar-H*), 7.53 (t, J = 7.6 Hz, 1 H, *Ar-H*), 7.45–7.41 (m, 3 H, *Ar-H*), 7.36–7.32 (m, 4 H, *Ar-H*), 7.25–7.24 (m, 3 H, *Ar-H*), 7.14–7.13 (m, 2 H, *Ar-H*), 5.78 (d, J = 3.2 Hz, 1 H, CH-*CH*-O), 4.72 (d, J = 3.2 Hz, 1 H, *CH*-CH-O) ppm. ^{13}C NMR & DEPT 135 (125 MHz, $CDCl_3$): δ = 163.6 (C=O), 137.7 (C), 137.2 (C), 134.5 (2× CH), 134.0 (CH), 132.4 (C), 130.2 (CH), 129.3 (2× CH), 128.9 (2× CH), 128.6 (2× CH), 128.5 (CH), 128.4 (CH), 126.1 (2× CH), 125.1 (C), 81.7 (CH-*CH*-O), 50.8 (*CH*-CH-O) ppm. IR (KBr): $\tilde{\nu}$ = 3059, 3027, 2988, 1708, 1601, 1461, 1439, 1377, 1331, 1302, 1241, 1113, 1098, 1077, 1029, 748, 742, 728, 715, 692 cm^{-1}. HRMS (ESP): *m*/*z* [M + H]$^+$ calcd. for $C_{21}H_{17}O_2S$: 333.0944; found 333.0935.

3-(1-Naphthyl)-4-(phenylthio)isochroman-1-one (6c): According to GP4 compound **6c** was obtained as colourless crystals in 66% yield (0.30 mmol, 114 mg); m.p. 179 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (dd, J = 7.4, 1.5 Hz, 1 H, *Ar-H*), 7.73 (d, J = 8.2 Hz, 1 H, *Ar-H*), 7.61 (d, J = 8.2 Hz, 1 H, *Ar-H*), 7.50–7.48 (m, 2 H, *Ar-H*), 7.39–7.35 (m, 4 H, *Ar-H*), 7.32–7.29 (m, 4 H, *Ar-H*), 7.14 (t, J = 7.5 Hz, 1 H, *Ar-H*), 7.07–7.04 (m, 1 H, *Ar-H*), 7.01 (d, J = 7.3 Hz, 1 H, *Ar-H*), 6.51 (d, J = 1.7 Hz, 1 H, CH-*CH*-O), 4.69 (d, J = 1.7 Hz, 1 H, *CH*-CH-O) ppm. ^{13}C NMR & DEPT 135 (125 MHz, $CDCl_3$): δ = 163.9 (C=O), 137.0 (C), 136.0 (2× CH), 134.1 (CH), 133.8 (C), 132.5 (C), 131.9 (C), 130.1 (CH), 129.8 (C), 129.5 (CH), 129.4 (2× CH), 129.2 (CH), 129.1 (CH), 128.9 (CH), 128.7 (CH), 126.8 (CH), 125.9 (CH), 124.9 (CH), 124.8 (C), 124.1 (CH), 122.2 (CH), 79.4 (CH-*CH*-O), 50.2 (*CH*-CH-O) ppm. IR (KBr): $\tilde{\nu}$ = 3065, 2970, 1714, 1598, 1460, 1439, 1389, 1329, 1290, 1243, 1120, 1092, 1023, 787, 774, 754, 748, 714, 693 cm^{-1}. HRMS (ESP): *m*/*z* [M + H]$^+$ calcd. for $C_{25}H_{19}O_2S$: 383.1100; found 383.1102.

3-Bisphenyl-4-(phenylthio)isochroman-1-one (6d): According to GP4 compound **6d** was obtained as colourless crystals in 57% yield (0.26 mmol, 106 mg); m.p. 132–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 7.6 Hz, 1 H, *Ar-H*), 7.46 (dt, J = 7.6, 1.4 Hz, 1 H, *Ar-H*), 7.41 (d, J = 7.1 Hz, 2 H, *Ar-H*), 7.37–7.30 (m, 8 H, *Ar-H*), 7.27–7.22 (m, 4 H, *Ar-H*), 7.11 (d, J = 8.3 Hz, 2 H, *Ar-H*), 5.72 (d, J = 3.6 Hz, 1 H, CH-*CH*-O), 4.66 (d, J = 3.6 Hz, 1 H, *CH*-CH-O) ppm. ^{13}C NMR & DEPT 135 (125 MHz, $CDCl_3$): δ = 163.6 (C=O), 141.3 (C), 140.2 (C), 137.3 (C), 136.6 (C), 134.4 (2× CH), 134.1 (CH), 132.4 (C), 130.3 (CH), 129.3 (2× CH), 128.8 (4× CH), 128.5 (CH), 127.6 (CH), 127.3 (2× CH), 127.0 (3× CH), 126.7 (CH), 125.2 (C), 81.7 (CH-*CH*-O), 50.8 (*CH*-CH-O) ppm. IR (KBr): $\tilde{\nu}$ = 3057, 3030, 2955, 2918, 1712, 1601, 1583, 1487, 1457, 1439, 1409, 1369, 1333, 1302, 1237, 1113, 1088, 1047, 1028, 757, 747, 742, 708, 687 cm^{-1}. HRMS (ESP): *m*/*z* [M + H]$^+$ calcd. for $C_{27}H_{21}O_2S$: 409.1257; found 409.1256.

Supporting Information (see also the footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra for compounds **2**–**6**.

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