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Direct synthesis of methyl 2-diazo-4-aryl-3-butenoates and their application to the enantioselective synthesis of 4-aryl-4-(1-naphthyl)-2-butenoates

Huw M. L. Davies,* Jaemoon Yang and James R. Manning

Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, NY 14260-3000, USA

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Dedicated to Jack Halpern on the occasion of his 80th birthday

Abstract—An improved one-flask synthesis of various methyl 2-diazo-4-aryl and 4-heteroaryl-3-butenoates, precursors to donor/acceptor substituted carbenoids, is described. Their Rh_2(*S*-DOSP)$_4$ catalyzed reaction with 1-acetoxy-3,4-dihydronaphthalene, via a combined C–H activation/Cope rearrangement pathway followed by elimination of acetic acid affords a highly enantioselective (98–99% ee) entry to methyl 4-aryl- and 4-heteroaryl-4-(1-naphthyl)-2-butenoates.

1. Introduction

Recently, carbenoid chemistry has become an attractive means for intermolecular functionalization of unactivated C–H bonds.[1–3] The metal-catalyzed decomposition of diazo compounds generates reactive carbenoid intermediates that are capable of undergoing insertions into C–H bonds.[1] A major challenge of such transformations is controlling the reactivity of the carbenoid species, such that selective functionalization of the substrate can occur. An effective way to accomplish this is through the use of diazo compounds that contain both electron donating and electron accepting substituents.[1] On metal-catalyzed decomposition they generate donor/acceptor-substituted carbenoids that are highly chemoselective. Methyl arylvinyldiazoacetates are a very useful class of precursors to these donor/acceptor carbenoids. Their importance has been further increased by the discovery of the combined C–H activation/Cope rearrangement as a highly diastereoselective and enantioselective transformation.[4] An example of the utilization of this chemistry is the dirhodium tetrakis-(*N*-(dodecylbenzenesulfonyl)prolinate) [Rh_2(*S*-DOSP)$_4$] catalyzed reaction of methyl styryldiazoacetate **1** with 1-acetoxy-3,4-dihydronaphthalene **2** to form methyl 4-phenyl-4-(1-naphthyl)-3-butenoate **3** (Scheme 1).[4d] In order to broaden the utility of this chemistry to potential pharmaceutical targets, the ready availability of a range of aryl- and heteroarylvinyldiazoacetates would be highly desirable. Herein, we report a one-flask synthesis of a series of arylvinyldiazoacetates, the majority of which have not been prepared before. Furthermore, we illustrate through the synthesis of 4-aryl-4-(1-naphthyl)-2-butenoates the range of functionality that is compatible with the combined C–H activation/Cope rearrangement chemistry.

2. Results and discussion

The existing protocol for the synthesis of arylvinyldiazoacetates usually begins from the arylcarboxaldehyde and requires three discrete steps, a Wittig reaction to generate the 4-arylbutenoic acid, an esterification step and a diazo transfer step.[5] In addition, tedious extractions and chromatographic purifications at two stages are required. The synthesis of the arylvinyldiazoacetates would be much more convenient if a one-flask procedure was developed and only a single chromatographic purification was required in the final step. In order to explore the possibility of developing a one-flask procedure, 3,4-dimethoxybenzaldehyde **4a** was used as a model substrate. After considerable experimentation, THF was found to be the optimum solvent for compatibility

* Corresponding author. Tel.: +1 716 645 6800x2186; fax: +1 716 645 6547; e-mail: hdavies@acsu.buffalo.edu

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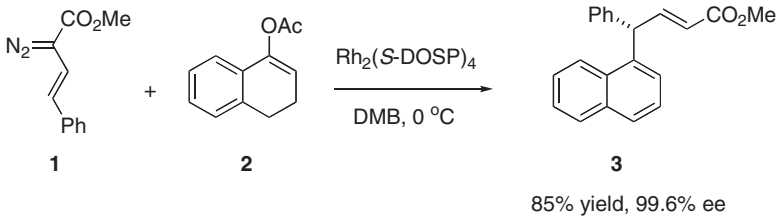


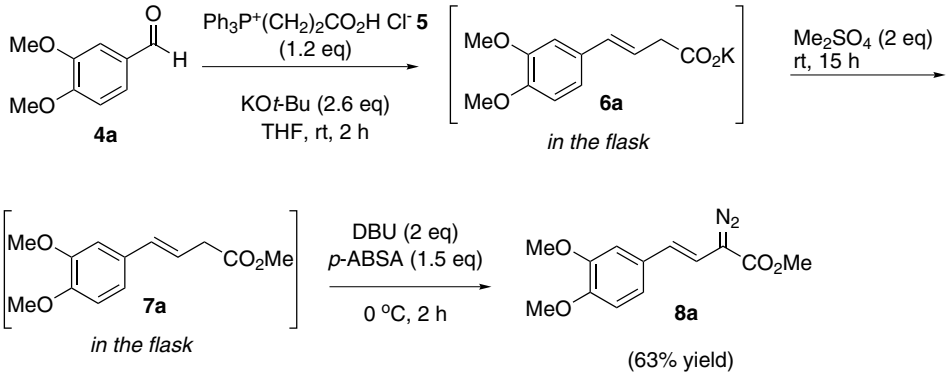
Scheme 1. Previous example of the enantioselective synthesis of methyl 4-(1-naphthyl)-4-phenylbutenoate.

with the three reaction steps. The reaction of **4a** with Wittig reagent **5** using an excess of potassium *t*-butoxide as base generated the potassium butenoate **6a**, which was then directly methylated with dimethyl sulfate to form the methyl butenoate **7a**. *p*-Acetamidobenzenesulfonyl azide (*p*-ABSA)[6] and DBU were then added to the reaction mixture to form the arylvinyldiazoacetate **8a**. The overall yield for the three step sequence was 63% and **8a** was formed in a >20:1 *E*:*Z* isomer ratio (Scheme 2).

Having established that the one-flask protocol was effective, the synthesis of various methyl arylvinyldiazoacetate derivatives was undertaken (Table 1). Styryldiazoacetates **8a–e** with a range of phenyl substituents were formed in 46–65% yield. The reaction could also be extended to naphthyl **8f**, indole **8g** and **8h**, furan **8i** and **8j**, thiophene **8k–m**, pyridine **8n**, benzofuran **8o**, and benzothiophene **8p** derivatives to form the arylvinyldiazoacetates in 17–64% yield. In all cases, a high preference for the formation of the (*E*)-isomer was observed, and in cases where significant traces of the (*Z*)-isomer were present, it was readily removed by column chromatography.

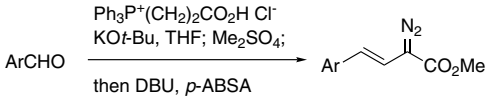
With a variety of arylvinyldiazoacetates in hand, the next step was to test their reactivity in the C–H activation/Cope rearrangement reaction with 1-acetoxy-3,4-dihydronaphthalene (Table 2). This reaction was very favorable with the majority of substrates resulting in the formation of the 4-aryl-4-(1-naphthyl)butenoates in high yield (79–90%) and exceptionally high enantioselectivity (⩾98% ee). Exceptions to this general trend were in the case of heterocycles containing very nucleophilic heteroatoms such as the thiophene **8k–m**, pyridine **8n**, and benzothiophene **8p** derivatives. Even so, if the heteroatom is reasonably protected as in the case of the 5-substituted thiophenes **8l** and **8m**, butenoates **9l** and **9m** can be formed in good yield and very high enantioselectivity. Furan derivative **8i** failed to form any of the butenoate **9i**, but this is unsurprising because furans are highly reactive toward carbenoid intermediates.[7] Once again, if the furan is sterically protected as in the 5-chloro derivative **8j**, the corresponding butenoate **9j** can be formed in 45% yield. Striking examples that illustrate the selectivity of the combined C–H activation/Cope rearrangement are the successful reactions with the indole derivatives **8g** and **8h**.

The mechanism of the transformation is considered to be a combined C–H activation/Cope rearrangement to form **10**, followed by elimination of acetic acid and generation of butenoate **9** (Fig. 1). The combined C–H activation/Cope rearrangement has been shown to be highly enantioselective (generally, >96% ee)[4] and the stereochemical outcome has been consistent with the model shown in Figure 1.[4d] In this model, the catalyst is configured in a D_2-symmetric arrangement with two blocking groups as shown. The substrate approaches from the front and over the vinyl part of the carbenoid to give the initial C–H activation/Cope rearrangement intermediate **10**. In our previous studies, aryl compounds related to **10** were prone to a retro-Cope rearrangement,[4d,e] but in this case elimination of acetic acid occurs preferentially to form **9**. The current studies show that the enantioselectivity in the combined C–H activation/Cope rearrangement is virtually independent of the nature of the aryl substituent in the methyl arylvinyldi-



Scheme 2. One-pot synthesis of arylvinyldiazoacetate.

Table 1. One-flask, three-step synthesis of methyl arylvinyldiazoacetates



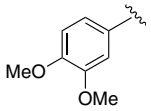
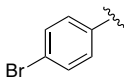
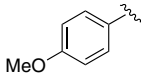
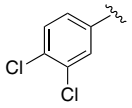
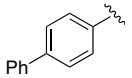
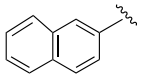
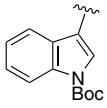
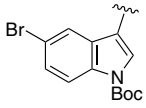
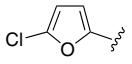
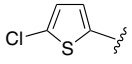
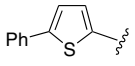
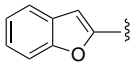
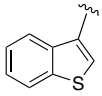
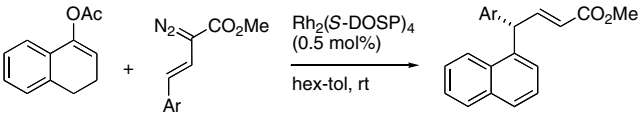
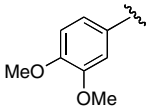
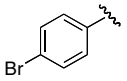
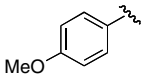
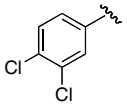
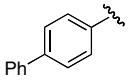
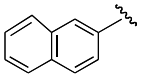
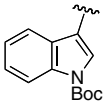
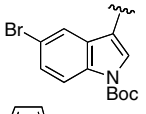
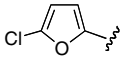
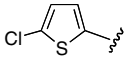
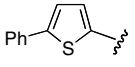
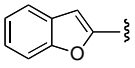
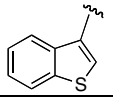
Product	Ar	Yield (%)
8a		63
8b		59
8c		65
8d		46
8e		49
8f		55
8g		49
8h		17
8i		69
8j		46
8k		62
8l		54
8m		50
8n		33
8o		30
8p		30

Table 2. C–H Activation chemistry of arylvinyldiazoacetates



2 **8** **9**

Product[a]	Ar	Yield (%)	ee (%)
9a		92	99.5
9b		79	99.4
9c		82	99.1
9d		79	>98
9e		90	98.5
9f		89	>98
9g		82	>98
9h		82	>98
9i		0	
9j		45	99.6
9k		14	ND
9l		88	99.5
9m		66	99.3
9n		0	
9o		60	99.1
9p		20	ND

[a] Reaction conducted at 23 °C with **8** (2 equiv) added over 1 h to a stirred solution of **2** (1 equiv) and Rh_2(*S*-DOSP)$_4$ (0.5 mol %) and then stirred overnight. The yield represents isolated yield after chromatography except for **9k**, which represents an NMR determined conversion. The enantiomeric excess for some of the products could not be reported to three significant figures due to excessive peak broadening during the chiral HPLC analysis.

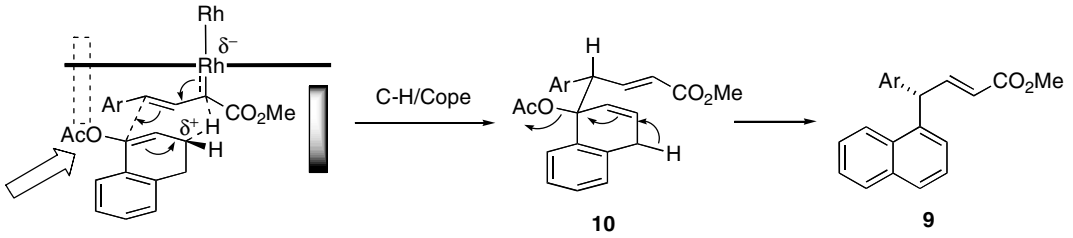


Figure 1. Predictive stereochemical model for Rh_2(*S*-DOSP)$_4$-catalyzed reaction.

azoacetates because **9** is formed in ⩾98% ee in all cases. On the basis of this model, the predicted configuration for **9** is as drawn. Supporting evidence that this prediction was correct was obtained by comparing the specific rotation of **3** derived from the reactions of **1** and **2** with the material obtained from the reaction of **8f** with 1,3-cyclohexadiene.[4a]

3. Conclusion

In conclusion, we have developed a very convenient one-flask protocol for the synthesis of a wide variety of aryl and heteroarylvinyldiazoacetates, which requires only one purification step. The reactivity of these diazo compounds with 1-acetoxy-3,4-dihydronaphthalene through a combined C–H activation/Cope rearrangement pathway has been explored. The corresponding 4-aryl-4-(1-naphthyl)butenoates were obtained in ⩾98% ee. These studies demonstrate that a variety of heterocyclic systems are compatible with the chemistry of the donor/acceptor substituted rhodium carbenoids.

4. Experimental

4.1. General procedure for preparation of the vinyldiazoacetates 8

A solution of potassium *tert*-butoxide (1.46 g, 13 mmol) in THF (14 mL) was added at 0 °C via syringe into a mixture of the aldehyde (5 mmol) and 2-carboxyethyltriphenylphosphonium chloride (2.22 g, 6.0 mmol)[4a] in THF (12 mL) over 15 min. The reaction mixture was stirred for a further 15 min at 0 °C and then 2 h at ambient temperature under argon. Dimethyl sulfate (1.26 g, 10 mmol) was then added at ambient temperature and the mixture stirred for a further 15 h under argon. The mixture was then cooled in an ice bath and DBU (1.52 g, 10 mmol) slowly added followed by *p*-ABSA (1.80 g, 7.5 mmol), which was added in several portions at 0 °C over 5 min. After stirring for 2 h at 0 °C under argon, the solvent was removed in vacuo and the residue diluted with cold water (10 mL), CH_2Cl_2 (20 mL), and saturated NH_4Cl (20 mL). The organic layer was washed once with saturated NH_4Cl, dried over $MgSO_4$, filtered, and then concentrated. Purification of product **8** was performed by flash chromatography on silica gel or neutral alumina using a pentane/diethyl ether solvent system.

4.2. (*E*)-Methyl 2-diazo-4-(3,4-dimethoxyphenyl)but-3-enoate 8a

Purified via flash chromatography (silica gel, pentane–diethyl ether, 2:1) to give **8a** as a red solid (0.825 g, 63% yield), R_f 0.29 (pentane–diethyl ether, 2:1); FTIR (neat): 2079, 1702, 1514, 1246 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 6.91 (d, $J = 2.0$ Hz, 1H), 6.88 (dd, $J = 8.2$, 2.0 Hz, 1H), 6.82 (d, $J = 8.2$ Hz, 1H), 6.30 (d, $J = 16.5$ Hz, 1H), 6.14 (d, $J = 16.5$ Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.2 (C), 148.7 (C), 148.0 (C), 129.5 (C), 122.6 (CH), 118.5 (CH), 110.7 (CH), 108.2 (CH), 107.8 (CH), 55.31 (CH_3), 55.27 (CH_3), 51.7 (CH_3), missing carbon attributed to C=N_2; LC–MS (ESI) *m*/*z* (relative intensity): 235.0 (100), 263.1 ($[M+H]^+$, 81). Anal. Calcd for $C_{13}H_{14}N_2O_4$: C, 59.54; H, 5.38. Found: C, 59.60; H, 5.37.

4.3. (*E*)-Methyl 2-diazo-4-(4-bromophenyl)but-3-enoate 8b

Purified via flash chromatography (silica gel, pentane–diethyl ether, 10:1) to give **8b** as a red solid (0.829 g, 59% yield), R_f 0.36 (petroleum ether–diethyl ether, 9:1); FTIR (neat): 3010, 2953, 2845, 2078, 1705, 1626 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, $J = 8.5$ Hz, 2H), 7.21 (d, $J = 8.5$ Hz, 2H), 6.48 (d, $J = 16.5$ Hz, 1H), 6.13 (d, $J = 16.5$ Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.2 (C), 135.6 (C), 131.7 (CH), 127.2 (CH), 121.6 (CH), 120.6 (C), 112.1 (CH), 52.2 (CH_3), missing carbon attributed to C=N_2; HRMS (EI) calcd for $C_{11}H_9N_2O_2Br$ 279.9847, found 279.9824.

4.4. (*E*)-Methyl 2-diazo-4-(4-methoxyphenyl)but-3-enoate 8c

Purified via flash chromatography (silica gel, pentane–diethyl ether, 7:1) to give **8c** as a red solid (0.754 g, 65% yield), R_f 0.23 (pentane–diethyl ether, 9:1); FTIR (neat): 3041, 3009, 2956, 2834, 2072, 1694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.29 (d, $J = 8.8$ Hz, 2H), 6.86 (d, $J = 8.8$ Hz, 2H), 6.29 (d, $J = 16.0$ Hz, 1H), 6.14 (d, $J = 16.0$ Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.8 (C), 158.8 (C), 129.6 (C), 127.0 (CH), 122.7 (CH), 114.1 (CH), 108.5 (CH), 55.2 (CH_3), 52.2 (CH_3), missing carbon attributed to C=N_2; HRMS (EI) calcd for $C_{12}H_{12}N_2O_3$ 232.0848, found 232.0867.

4.5. (*E*)-Methyl 2-diazo-4-(3,4-dichlorophenyl)but-3-enoate 8d

Purified via flash chromatography (silica gel, pentane–diethyl ether, 10:1) to give **8d** as a red solid (0.623 g, 46% yield), R_f 0.30 (petroleum ether–diethyl ether, 9:1); FTIR (neat): 3051, 3000, 2954, 2149, 2086, 1697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, $J = 2.0$ Hz, 1H), 7.35 (d, $J = 8.5$ Hz, 1H), 7.16 (dd, $J = 8.5$, 2.0 Hz, 1H), 6.48 (d, $J = 16.5$ Hz, 1H), 6.10 (d, $J = 16.5$ Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.9 (C), 136.8 (C), 132.6 (C), 130.35 (CH), 130.28 (C), 127.2 (CH), 124.7 (CH), 120.1 (CH), 113.6 (CH), 52.3 (CH_3), missing carbon attributed to C=N_2; HRMS (EI) calcd for $C_{11}H_8N_2O_2Cl_2$ 269.9963, found 269.9972.

4.6. (*E*)-Methyl 2-diazo-4-(4-biphenyl)but-3-enoate 8e

Purified via flash chromatography (silica gel, pentane–diethyl ether, 7:1) to give **8e** as a red solid (0.677 g, 49% yield), R_f 0.32 (pentane–diethyl ether, 5:1); FTIR (neat): 3020, 2947, 2072, 1699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.61–7.56 (m, 4H), 7.46–7.43 (m, 4H), 7.36–7.33 (m, 1H), 6.53 (d, $J = 16.3$ Hz, 1H), 6.24 (d, $J = 16.3$ Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.3 (C), 140.4 (C), 139.5 (C), 135.7 (C), 128.6 (CH), 127.2 (CH), 126.7 (CH), 126.1 (CH), 122.4 (CH), 111.1 (CH), 52.2 (CH_3), one missing carbon attributed to C=N_2, the other to accidental equivalence; HRMS (EI) m/z calcd for $[C_{17}H_{14}N_2O_2]^+$ (M^+): 278.1050, found 278.1053.

4.7. (*E*)-Methyl 2-diazo-4-(naphthalen-3-yl)but-3-enoate 8f

Purified via flash chromatography (silica gel, pentane–diethyl ether, 9:1–7:1) to give **8f** as a red solid (0.697 g, 55% yield), R_f 0.31 (pentane–diethyl ether, 9:1); FTIR (neat): 3057, 3020, 2946, 2120, 2093, 1705 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.80–7.78 (m, 3H), 7.69 (s, 1H), 7.60 (dd, $J = 9.0$, 1.8 Hz, 1H), 7.47–7.41 (m, 2H), 6.60 (d, $J = 16.5$ Hz, 1H), 6.36 (d, $J = 16.5$ Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.4 (C), 134.2 (C), 133.5 (C), 132.5 (C), 128.2 (CH), 127.8 (CH), 127.5 (CH), 126.2 (CH), 125.6 (CH), 125.3 (CH), 122.99 (CH), 122.95 (CH), 111.3 (CH), 52.1 (CH_3), missing carbon attributed to C=N_2; HRMS (EI) calcd for $C_{15}H_{12}N_2O_2$ 252.0899, found 252.0899.

4.8. *tert*-Butyl 3-((*E*)-3-(methoxycarbonyl)-3-diazoprop-1-enyl)-1*H*-indole-1-carboxylate 8g

Purified via flash chromatography (silica gel, pentane–diethyl ether, 7:1) to give **8g** as a red solid (0.840 g, 49% yield), R_f 0.26 (pentane–diethyl ether, 9:1); FTIR (neat) 2079, 1734 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.17 (m, 1H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.60 (s, 1H), 7.35 (t, $J = 7.5$ Hz, 1H), 7.29 (t, $J = 7.5$ Hz, 1H), 6.52 (d, $J = 16.5$ Hz, 1H), 6.32 (d, $J = 16.5$ Hz, 1H), 3.87 (s, 3H), 1.67 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.4 (C), 149.2 (C), 135.7 (C), 128.1 (C), 124.6 (CH), 122.8 (CH), 122.6 (CH), 119.4 (CH), 118.3 (C), 115.2 (CH), 114.4 (CH), 110.5 (CH), 83.6 (C), 52.0 (CH_3), 27.9 (CH_3), missing carbon attributed to C=N_2; HRMS (EI) calcd for $C_{18}H_{19}N_3O_4$ 341.1370, found 341.1369. Anal. Calcd for $C_{18}H_{19}N_3O_4$: C, 63.33; H, 5.61. Found: C, 63.57; H, 5.77.

4.9. *tert*-Butyl-3-((*E*)-3-(methoxycarbonyl)-3-diazoprop-1-enyl)-5-bromo-1*H*-indole-1-carboxylate 8h

Purified via flash chromatography (neutral alumina, pentane–diethyl ether, 9:1) to give **8h** as a pink solid (0.357 g, 17% yield), R_f 0.37 (pentane–diethyl ether, 5:1); FTIR (CH_2Cl_2): 2079, 1736, 1710, 1450, 1371 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.05 (m, 1H), 7.85 (d, $J = 2.0$ Hz, 1H), 7.59 (s, 1H), 7.43 (dd, $J = 8.5$, 2.0 Hz, 1H), 6.46 (d, $J = 16.5$ Hz, 1H), 6.27 (d, $J = 16.5$ Hz, 1H), 3.88 (s, 3H), 1.67 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.4 (C), 149.0 (C), 134.5 (C), 129.9 (C), 127.5 (CH), 123.3 (CH), 122.1 (CH), 117.8 (C), 116.7 (CH), 116.3 (C), 113.5 (CH), 111.5 (CH), 84.2 (C), 52.2 (CH_3), 28.1 (CH_3), missing carbon attributed to C=N_2; LC–MS (ESI) m/z (relative intensity): 447.9 (100), 441.9 ($[M+Na]^+$, 57.1); HRMS (ESI) calcd for $C_{18}H_{18}NaBrN_3O_4$ 442.0373, found 442.0375.

4.10. (*E*)-Methyl 2-diazo-4-(furan-2-yl)but-3-enoate 8i

Purified via flash chromatography (silica gel, pentane–diethyl ether, 19:1) to give **8i** as a red oil (0.662 g, 69% yield); R_f 0.54 (pentane–diethyl ether, 9:1); FTIR (neat) 2080, 1707 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, $J = 1.5$ Hz, 1H), 6.39–6.35 (m, 2H), 6.16 (d, $J = 3.5$ Hz, 1H), 6.12 (d, $J = 16$ Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.3 (C), 152.7 (C), 141.9 (CH), 111.7 (CH), 111.4 (CH), 109.6 (CH), 106.8 (CH), 52.2 (CH_3), missing carbon attributed to C=N_2; HRMS (EI) calcd for $C_9H_8N_2O_3$ 192.0535, found 192.0529.

4.11. (*E*)-Methyl 2-diazo-4-(5-chlorofuran-2-yl)but-3-enoate 8j

Purified via flash chromatography (neutral alumina, pentane–diethyl ether, 19:1) to give **8j** as a red solid (0.522 g, 46% yield), R_f 0.47 (pentane–diethyl ether, 9:1); FTIR (neat) 2954, 2084, 1708, 1632, 1339 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 6.36 (d, $J = 16.2$ Hz, 1H), 6.14 (s, 2H), 6.06 (d, $J = 16.2$ Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.2 (C), 152.3 (C), 135.8 (C), 110.7 (CH), 110.2 (CH), 108.6 (CH), 108.0 (CH), 52.2 (CH_3), missing carbon attributed to C=N_2; HRMS (EI) calcd for $C_9H_7ClN_2O_3$ 226.0140, found 226.0141.

4.12. (*E*)-Methyl 2-diazo-4-(thiophen-2-yl)but-3-enoate 8k

Purified via flash chromatography (silica gel, pentane–diethyl ether, 19:1) to give **8k** as a red solid (0.644 g, 62% yield), R_f 0.41 (pentane–diethyl ether, 9:1); FTIR (neat) 2080, 1703 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.15 (d, $J = 5.0$ Hz, 1H), 6.95 (dd, $J = 5.0$, 3.5 Hz, 1H), 6.90 (d, $J = 3.5$ Hz, 1H), 6.42 (d, $J = 16$ Hz, 1H),

6.27 (d, $J = 16$ Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.3 (C), 142.1 (C), 127.4 (CH), 124.5 (CH), 124.1 (CH), 116.7 (CH), 110.4 (CH), 52.2 (CH_3), missing carbon attributed to C=N_2; HRMS (EI) calcd for $C_9H_8N_2O_2S$ 208.0301, found 208.0307.

4.13. (*E*)-Methyl 2-diazo-4-(5-chlorothiophen-2-yl)but-3-enoate (8l)

Purified via flash chromatography (neutral alumina, pentane–diethyl ether, 20:1) to give **8l** as an orange solid (0.656 g, 54% yield), R_f 0.36 (pentane–diethyl ether, 9:1); FTIR (neat): 2083, 1705 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.75 (d, $J = 3.5$ Hz, 1H), 6.65 (d, $J = 3.5$ Hz, 1H), 6.29 (d, $J = 16$ Hz, 1H), 6.14 (d, $J = 16$ Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.9 (C), 140.9 (C), 128.2 (C), 126.4 (CH), 123.5 (CH), 116.0 (CH), 110.7 (CH), 52.1 (CH_3), missing carbon attributed to C=N_2; HRMS (EI) calcd for $C_9H_7ClN_2O_2S$ 241.9911, found 241.9908.

4.14. (*E*)-Methyl 2-diazo-4-(5-phenylthiophen-2-yl)but-3-enoate 8m

Purified via flash chromatography (silica gel, pentane–diethyl ether, 7:1) to give **8m** as a pink solid (0.714 g, 50% yield), R_f 0.33 (pentane–diethyl ether, 5:1); FTIR (neat): 2090, 1708, 1437, 1260 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, $J = 7.5$ Hz, 2H), 7.37 (appt. t, $J = 8.0$ Hz, 2H), 7.27 (t, $J = 8.0$ Hz, 1H), 7.17 (d, $J = 4.0$ Hz, 1H), 6.85 (d, $J = 4.0$ Hz, 1H), 6.38 (d, $J = 16.0$ Hz, 1H), 6.28 (d, $J = 16.0$ Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.2 (C), 142.7 (C), 141.5 (C), 134.0 (C), 128.7 (CH), 127.3 (CH), 125.7 (CH), 125.3 (CH), 123.3 (CH), 116.7 (CH), 110.1 (CH), 52.2 (CH_3), missing carbon attributed to C=N_2; HRMS (EI) m/z calcd for $[C_{15}H_{12}N_2O_2S]^+$ (M^+): 284.0614, found 284.0619.

4.15. (*E*)-Methyl 2-diazo-4-(pyridin-3-yl)but-3-enoate 8n

Purified via flash chromatography (neutral alumina, pentane–diethyl ether, 2:1) to give **8n** as a red solid (0.335 g, 33% yield), R_f 0.20 (pentane–diethyl ether, 2:1 × 2); FTIR (neat): 2085, 1702, 1252 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD): δ 8.42 (d, $J = 2.4$ Hz, 1H), 8.23 (dd, $J = 4.8$, 0.8 Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.29 (dd, $J = 8.0$, 4.8 Hz, 1H), 6.63 (d, $J = 16.8$ Hz, 1H), 6.34 (d, $J = 16.8$ Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.3 (C), 147.4 (CH), 147.2 (CH), 132.0 (C), 131.3 (CH), 122.9 (CH), 118.5 (CH), 113.3 (CH), 51.8 (CH_3), missing carbon attributed to C=N_2; HRMS (ESI) m/z calcd for $[C_{10}H_{10}N_3O_2]^+$ $(M+H)^+$: 204.0768, found 204.0761. Anal. Calcd for $C_{10}H_9N_3O_2$: C, 59.11; H, 4.46. Found: C, 58.90; H, 4.48.

4.16. (*E*)-Methyl 2-diazo-4-(benzofuran-2-yl)but-3-enoate 8o

Purified via flash chromatography (silica gel, pentane–diethyl ether, 8:1) to give **8o** as a red solid (0.363 g, 30% yield), R_f 0.31 (pentane–diethyl ether, 5:1); FTIR (neat): 2083, 1709, 1688, 1339 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, $J = 7.6$ Hz, 1H), 7.43 (d, $J = 7.9$ Hz, 1H), 7.24 (t, $J = 7.0$ Hz, 1H), 7.18 (t, $J = 7.0$ Hz, 1H), 6.72 (d, $J = 16.0$ Hz, 1H), 6.50 (s, 1H), 6.28 (d, $J = 16.0$ Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.0 (C), 154.8 (C), 154.5 (C), 129.1 (C), 124.2 (CH), 122.8 (CH), 120.6 (CH), 113.3 (CH), 111.3 (CH), 110.7 (CH), 103.3 (CH), 52.3 (CH_3), missing carbon attributed to C=N_2; LRMS (EI) m/z (relative intensity): 155.0 (100), 242.0 ($[M]^+$, 28.5); HRMS (EI) m/z calcd for $[C_{13}H_{10}N_2O_3]^+$ (M^+): 242.0686, found 242.0691. Anal. Calcd for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16. Found: C, 64.74; H, 4.17.

4.17. (*E*)-Methyl 2-diazo-4-(benzo[*b*]thiophen-3-yl)but-3-enoate (8p)

Purified via flash chromatography (silica gel, pentane–diethyl ether, 7:1) to give **8p** as a red solid (0.382 g, 30% yield), R_f 0.30 (pentane–diethyl ether, 5:1); FTIR (neat): 2080, 1699, 1230 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89–7.85 (m, 2H), 7.43–7.36 (m, 3H), 6.57–6.48 (m, 2H), 3.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.3 (C), 140.2 (C), 137.0 (C), 133.2 (C), 124.4 (CH), 124.1 (CH), 122.7 (CH), 121.5 (CH), 120.7 (CH), 115.1 (CH), 112.3 (CH), 52.1 (CH_3), missing carbon attributed to C=N_2; HRMS (EI) m/z calcd for $[C_{13}H_{10}N_2O_2S]^+$ (M^+): 258.0457, found 258.0466.

4.18. General procedure for preparation of the 4-aryl-4-(1-naphthyl)butenoates 9

A solution of **8** (1.0 mmol) in toluene (14 mL) and hexanes (1 mL) was added via a syringe pump over 30 min into a green solution of 3,4-dihydro-1-naphthalenyl acetate **2** (0.094 g, 0.5 mmol) and Rh_2(*S*-DOSP)$_4$ (10 mg, 0.005 mmol) in toluene (0.5 mL) and hexanes (1.5 mL). After stirring for at least 12 h at rt under argon, the crude reaction mixture was concentrated in vacuo and purified by flash chromatography on silica gel using a pentane/diethyl ether solvent system to give **9**.

4.19. (*S*,*E*)-Methyl 4-(3,4-dimethoxyphenyl)-4-(naphthalen-5-yl)but-2-enoate 9a

Purified via flash chromatography (silica gel, pentane–diethyl ether, 3:2) to give **9a** as a solid (0.166 g, 92% yield); mp 47–55 °C; R_f 0.33 (pentane–diethyl ether, 2:1); $[\alpha]_D^{25} = +33.6$ (c 1.80, $CHCl_3$); FTIR (neat): 1719, 1515, 1265 cm^{-1}; ^{1}H NMR (500 MHz, CD_3OD): δ 7.91 (m, 1H), 7.78 (m, 1H), 7.71 (d, $J = 8.5$ Hz, 1H), 7.44 (dd, $J = 16.5$, 6.5 Hz, 1H), 7.38–7.32 (m, 3H), 7.20 (d, $J = 7.0$ Hz, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 6.69 (d, $J = 2.0$ Hz, 1H), 6.61 (dd, $J = 8.0$, 2.0 Hz, 1H), 5.59 (d, $J = 6.0$ Hz, 1H), 5.53 (dd, $J = 16.0$, 1.5 Hz, 1H), 3.70 (s, 3H), 3.615 (s, 3H), 3.612 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.9 (C), 150.6 (CH), 149.2 (C), 148.0 (C), 137.2 (C), 134.1 (C), 133.4 (C), 131.5 (C), 128.9 (CH), 127.9 (CH), 126.35 (CH), 126.26 (CH), 125.6 (CH), 125.3 (CH), 123.8 (CH), 122.9 (CH), 121.0 (CH), 112.1 (CH), 111.2 (CH), 55.8

(CH_3), 51.5 (CH_3), 49.0 (CH), missing carbon attributed to accidental equivalence of two of the methoxy groups; HRMS (EI) calcd for $C_{23}H_{22}O_4$ 362.1513, found 362.1520; HPLC analysis: 99.5% ee (Chiralcel OD-H, 10% *i*-PrOH in hexanes, 1.0 mL/min, $\lambda = 254$ nm, $t_R = 13.8$ min, major; $t_R = 21.2$ min, minor). Anal. Calcd for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12. Found: C, 75.83; H, 6.33.

4.20. (*S*,*E*)-Methyl 4-(4-bromophenyl)-4-(naphthalen-5-yl)but-2-enoate 9b

Purified via flash chromatography (silica gel, pentane–diethyl ether, 9:1) to give **9b** as a yellow solid (0.151 g, 79% yield); mp 45–47 °C; R_f 0.36 (pentane–diethyl ether, 9:1); $[\alpha]_D^{25} = +24.5$ (*c* 0.80, $CHCl_3$); FTIR (neat): 1719 cm^{-1}; ^1H NMR (500 MHz, CD_3OD): δ 7.88–7.86 (m, 1H), 7.80–7.78 (m, 1H), 7.23 (d, $J = 7.5$ Hz, 1H), 7.43 (dd, $J = 15.5$, 6.5 Hz, 1H), 7.38–7.33 (m, 5H), 7.19 (d, $J = 7.5$ Hz, 1H), 7.03 (d, $J = 8.5$ Hz, 2H), 5.65 (d, $J = 6.5$ Hz, 1H), 5.55 (dd, $J = 15.5$, 1.5 Hz, 1H), 3.62 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7 (C), 149.7 (CH), 140.0 (C), 136.4 (C), 134.1 (C), 131.8 (CH), 131.2 (C), 130.5 (CH), 129.0 (CH), 128.2 (CH), 126.5 (CH), 126.4 (CH), 125.7 (CH), 125.3 (CH), 123.6 (CH), 123.4 (CH), 121.0 (C), 51.6 (CH_3), 48.8 (CH); HRMS (EI) calcd for $C_{21}H_{17}BrO_2$ 380.0406, found 380.0402; HPLC analysis: 99.4% ee (Chiralcel OD-H, 5% *i*-PrOH in hexanes, 0.8 mL/min, $\lambda = 254$ nm, $t_R = 12.1$ min, major; $t_R = 27.0$ min, minor). Anal. Calcd for $C_{21}H_{17}BrO_2$: C, 66.16; H, 4.49. Found: C, 65.94; H, 4.49.

4.21. (*S*,*E*)-Methyl 4-(4-methoxyphenyl)-4-(naphthalen-5-yl)but-2-enoate 9c

Purified via flash chromatography (silica gel, pentane–diethyl ether, 9:1) to give **9c** as an oil (0.136 g, 82% yield); R_f 0.15 (9:1 pentane–diethyl ether); $[\alpha]_D^{25} = +35.1$ (*c* 1.51, $CHCl_3$); FTIR (neat): 1722, 1510, 1251 cm^{-1}; ^1H NMR (500 MHz, CD_3OD): δ 7.89 (d, $J = 7.5$ Hz, 1H), 7.77 (m, 1H), 7.71 (d, $J = 8.5$ Hz, 1H), 7.44 (dd, $J = 16.5$, 6.5 Hz, 1H), 7.36–7.31 (m, 3H), 7.18 (d, $J = 8.0$ Hz, 1H), 7.00 (d, $J = 8.5$ Hz, 2H), 6.76 (d, $J = 8.5$ Hz, 2H), 5.58 (d, $J = 6.5$ Hz, 1H), 5.50 (dd, $J = 16$, 1.5 Hz, 1H), 3.66 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.9 (C), 158.5 (C), 150.8 (CH), 137.4 (C), 134.1 (C), 132.9 (C), 131.4 (C), 129.8 (CH), 128.8 (CH), 127.8 (CH), 126.3 (CH), 126.2 (CH), 125.6 (CH), 125.3 (CH), 123.8 (CH), 122.8 (CH), 114.1 (CH), 55.2 (CH_3), 51.5 (CH_3), 48.6 (CH); HRMS (EI) calcd for $C_{22}H_{20}O_3$ 332.1407, found 332.1411; HPLC analysis: 99.1% ee (Chiralcel OD-H, 10% *i*-PrOH in hexanes, 0.8 mL/min, $\lambda = 254$ nm, $t_R = 11.1$ min, major; $t_R = 19.9$ min, minor). Anal. Calcd for $C_{22}H_{20}O_3$: C, 79.50; H, 6.06. Found: C, 79.64; H, 6.23.

4.22. (*S*,*E*)-Methyl 4-(3,4-dichlorophenyl)-4-(naphthalen-5-yl)but-2-enoate 9d

Purified via flash chromatography (silica gel, pentane–diethyl ether, 9:1) to give **9d** as an oil (0.146 g, 79% yield); R_f 0.24 (pentane–diethyl ether, 9:1); $[\alpha]_D^{25} = +37.7$ (*c* 4.88, $CHCl_3$); FTIR (neat): 1723 cm^{-1}; ^1H NMR (500 MHz, CD_3OD): δ 7.98 (m, 1H), 7.92 (m, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.56–7.46 (m, 5H), 7.36 (d, $J = 2.0$ Hz, 1H), 7.34 (d, $J = 7.0$ Hz, 1H), 7.15 (dd, $J = 8.5$, 2.0 Hz, 1H), 5.81 (d, $J = 6.5$ Hz, 1H), 5.70 (dd, $J = 16.0$, 1.5 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4 (C), 148.9 (CH), 141.2 (C), 135.8 (C), 134.0 (C), 132.8 (C), 131.1 (C), 131.0 (C), 130.6 (CH), 130.5 (CH), 129.0 (CH), 128.4 (CH), 128.1 (CH), 126.5 (CH), 126.4 (CH), 125.8 (CH), 125.3 (CH), 123.6 (CH), 123.3 (CH), 51.6 (CH_3), 48.4 (CH); HRMS (EI) calcd for $C_{21}H_{16}Cl_2O_2$ 370.0522, found 370.0528; HPLC analysis: >98% ee (Chiralcel OD-H, 5% *i*-PrOH in hexanes, 0.8 mL/min, $\lambda = 254$ nm, $t_R = 14.3$ min, major; 34.0 min, minor). Anal. Calcd for $C_{21}H_{16}Cl_2O_2$: C, 67.94; H, 4.34. Found: C, 68.07; H, 4.51.

4.23. (*S*,*E*)-Methyl 4-(4-biphenyl)-4-(naphthalen-5-yl)but-2-enoate 9e

Purified via flash chromatography (silica gel, pentane–diethyl ether, 7:1) to give **9e** as a yellow solid (0.125 g, 66% yield), mp 53–55 °C; R_f 0.21 (pentane–diethyl ether, 5:1); $[\alpha]_D^{25} = +2.4$ (*c* 3.02, $CHCl_3$); FTIR ($CDCl_3$): 3028, 2948, 1721, 1652 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.04 (m, 1H), 7.93–7.85 (m, 2H), 7.69–7.29 (m, 14H), 5.80–5.73 (m, 2H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.8 (C), 150.3 (CH), 140.5 (C), 139.9 (C), 139.8 (C), 137.0 (C), 134.1 (C), 131.4 (C), 129.1 (CH), 128.9 (CH), 128.7 (CH), 127.9 (CH), 127.4 (CH), 127.2 (CH), 126.9 (CH), 126.5 (CH), 126.3 (CH), 125.6 (CH), 125.3 (CH), 123.7 (CH), 123.0 (CH), 51.5 (CH_3), 49.0 (CH); LRMS (ESI) *m*/*z* (relative intensity): 379.1 ($[M+H]^+$, 70); HPLC analysis: 98.5% ee (Chiralcel OD-H, 10% *i*-PrOH in hexanes, 0.9 mL/min, $\lambda = 254$ nm, $t_R = 13.0$ min, major; $t_R = 21.9$ min, minor). Anal. Calcd for $C_{27}H_{22}O_2$: C, 85.69; H, 5.86. Found: C, 85.46; H, 5.89.

4.24. (*S*,*E*)-Methyl 4-(naphthalen-3-yl)-4-(naphthalen-5-yl)but-2-enoate 9f

Purified via flash chromatography (silica gel, pentane–diethyl ether, 9:1) to give **9f** as a solid (0.156 g, 89% yield); mp 85–86 °C; R_f 0.27 (pentane–diethyl ether, 9:1); $[\alpha]_D^{25} = +6.9$ (*c* 0.64, $CHCl_3$); FTIR (neat): 1722 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, $J = 8.0$ Hz, 1H), 7.88–7.74 (m, 5H), 7.67–7.63 (m, 2H), 7.48–7.41 (m, 5H), 7.33–7.29 (m, 2H), 5.81 (d, $J = 6.0$ Hz, 1H), 5.67 (dd, $J = 16.0$, 1.6 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.9 (C), 150.2 (CH), 138.5 (C), 136.9 (C), 134.1 (C), 133.5 (C), 132.4 (C), 131.5 (C), 128.9 (CH), 128.4 (CH), 128.0 (CH), 127.8 (CH), 127.6 (CH), 127.4 (CH), 127.1 (CH), 126.7 (CH), 126.3 (CH), 126.2 (CH), 125.9 (CH), 125.7 (CH), 125.4 (CH), 123.8 (CH), 123.3 (CH), 51.5 (CH_3), 49.5 (CH); HRMS (EI) calcd for $C_{25}H_{20}O_2$ 352.1458, found 352.1463; HPLC analysis: >98% ee (Chiralcel OD-H, 5% *i*-PrOH in hexanes, 0.8 mL/min, $\lambda = 254$ nm, $t_R = 14.9$ min, major; $t_R = 21.4$ min, minor).

4.25. *tert*-Butyl 3-((*R*,*E*)-3-(methoxycarbonyl)-1-(naphthalen-5-yl)allyl)-1*H*-indole-1-carboxylate 9g

Purified via flash chromatography (silica gel, pentane–diethyl ether, 7:1) to give **9g** as a white solid (0.181 g, 82% yield), mp 91–94 °C; R_f 0.19 (pentane–diethyl ether, 5:1); $[\alpha]_D^{25} = +2.3$ (*c* 3.02, $CHCl_3$); FTIR (neat): 2980, 1728, 1371, 1157 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.12 (m, 1H), 8.02 (m, 1H), 7.89 (m, 1H), 7.79 (d, $J = 8.0$ Hz, 1H), 7.57–7.47 (m, 3H), 7.39 (m, 1H), 7.32–7.24 (m, 4H), 7.16–7.12 (m, 1H), 5.82 (d, $J = 6.4$ Hz, 1H), 5.74 (dd, $J = 15.8$, 1.4 Hz, 1H), 3.70 (s, 3H), 1.65 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.8 (C), 149.7 (C), 148.6 (CH), 135.7 (C), 134.1 (C), 131.3 (C), 129.5 (C), 129.0 (CH), 128.0 (CH), 126.4 (CH), 126.2 (CH), 125.7 (CH), 125.4 (CH), 124.6 (CH), 123.2 (CH), 123.0 (CH), 122.6 (CH), 120.9 (C), 119.4 (CH), 115.3 (CH), 83.9 (C), 51.5 (CH_3), 40.3 (CH), 28.1 (CH_3), two missing carbons attributed to accidental equivalence; LCMS (ESI) *m*/*z* (relative intensity): 464.0 ($[M+Na]^+$, 100.0); HPLC analysis: >98% ee (Chiralcel OD-H, 20% *i*-PrOH in hexanes, 0.8 mL/min, $\lambda = 254$ nm, $t_R = 6.5$ min, major; 17.5 min, minor). Anal. Calcd for $C_{28}H_{27}NO_4$: C, 76.17; H, 6.16; N, 3.17. Found: C, 75.83; H, 6.23; N, 3.08.

4.26. *tert*-Butyl 3-((*R*,*E*)-3-(methoxycarbonyl)-1-(naphthalen-5-yl)allyl)-5-bromo-1*H*-indole-1-carboxylate 9h

Purified via flash chromatography (silica gel, pentane–diethyl ether, 9:1) to give **9h** as a yellow solid (0.213 g, 82% yield), mp 94–96 °C; R_f 0.13 (pentane–diethyl ether, 10:1); $[\alpha]_D^{25} = +27.9$ (*c* 4.14, $CHCl_3$); FTIR (neat): 1729, 1450, 1372 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.94 (m, 2H), 7.89 (m, 1H), 7.80 (d, $J = 7.9$ Hz, 1H), 7.49 (m, 3H), 7.40 (m, 3H), 7.27 (d, $J = 7.3$ Hz, 1H), 7.19 (s, 1H), 5.73 (d, $J = 5.8$ Hz, 1H), 5.68 (dd, $J = 15.6$, 1.2 Hz, 1H), 3.70 (s, 3H), 1.61 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7 (C), 149.3 (C), 148.2 (CH), 135.2 (C), 134.5 (C), 134.2 (C), 131.3 (C), 129.1 (CH), 128.3 (CH), 127.6 (CH), 126.5 (CH), 126.1 (CH), 125.9 (C), 125.8 (CH), 125.4 (CH), 123.3 (CH), 123.2 (CH), 122.0 (CH), 120.2 (C), 116.9 (CH), 116.1 (C), 84.5 (C), 51.6 (CH_3), 40.1 (CH), 28.1 (CH_3), missing carbon attributed to accidental equivalence; LCMS (ESI) *m*/*z* (relative intensity): 541.9 ($[M+Na]^+$, 85.6); HRMS (ESI) calcd for $C_{28}H_{26}BrNO_4Na$ 542.0937, found 542.0940; HPLC analysis: >98% ee (Chiralcel OD-H, 15% *i*-PrOH in hexanes, 0.9 mL/min, $\lambda = 254$ nm, $t_R = 5.9$ min, major; 15.6 min, minor). Anal. Calcd for $C_{28}H_{26}BrNO_4$: C, 64.62; H, 5.04. Found: C, 64.88; H, 5.27.

4.27. (*R*,*E*)-Methyl 4-(5-chlorofuran-2-yl)-4-(naphthalen-5-yl)but-2-enoate 9j

Purified via flash chromatography (silica gel, pentane–diethyl ether, 9:1) to give **9j** as a yellow solid (0.073 g, 45% yield); R_f 0.26 (pentane–diethyl ether, 9:1); $[\alpha]_D^{25} = +26.9$ (*c* 0.87, $CHCl_3$); FTIR (neat): 1719 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.94–7.87 (m, 2H), 7.82 (d, $J = 7.6$ Hz, 1H), 7.53–7.43 (m, 3H), 7.39 (dd, $J = 16.0$, 6.0 Hz, 1H), 7.30 (d, $J = 7.6$ Hz, 1H), 6.08 (d, $J = 3.6$ Hz, 1H), 6.00 (d, $J = 3.6$ Hz, 1H), 5.77 (dd, $J = 16.0$, 1.6 Hz, 1H), 5.63 (d, $J = 6.0$ Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.6 (C), 153.3 (C), 146.5 (CH), 135.8 (C), 134.1 (C), 134.0 (C), 131.1 (C), 129.0 (CH), 128.5 (CH), 126.5 (CH), 126.3 (CH), 125.8 (CH), 125.4 (CH), 123.6 (CH), 123.1 (CH), 110.6 (CH), 107.0 (CH), 51.6 (CH_3), 43.2 (CH); HRMS (EI) calcd for $C_{19}H_{15}ClO_3$ 326.0704, found 326.0705; HPLC analysis: 99.6% ee (Chiralcel OD-H, 5% *i*-PrOH in hexanes, 0.8 mL/min, $\lambda = 254$ nm, $t_R = 8.8$ min, major; $t_R = 14.6$ min, minor).

4.28. (*R*,*E*)-Methyl 4-(5-chlorothiophen-2-yl)-4-(naphthalen-5-yl)but-2-enoate 9l

Purified via flash chromatography (silica gel, pentane–diethyl ether, 9:1) to give **9l** as an oil (0.151 g, 88% yield); R_f 0.24 (pentane–diethyl ether, 9:1); $[\alpha]_D^{25} = +69.8$ (*c* 1.25, $CHCl_3$); FTIR (neat): 1723 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.97–7.87 (m, 2H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.51–7.44 (m, 4H), 7.36 (d, $J = 6.8$ Hz, 1H), 6.75 (d, $J = 4.0$ Hz, 1H), 6.59 (d, $J = 4.0$ Hz, 1H), 5.83 (dd, $J = 15.6$, 1.6 Hz, 1H), 5.73 (d, $J = 6.0$ Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5 (C), 148.5 (CH), 143.1 (C), 136.0 (C), 134.1 (C), 131.0 (C), 129.2 (C), 129.0 (CH), 128.6 (CH), 126.6 (CH), 126.0 (CH), 125.9 (CH), 125.8 (CH), 125.5 (CH), 125.3 (CH), 123.3 (CH), 123.2 (CH), 51.6 (CH_3), 44.6 (CH); HRMS (EI) calcd for $C_{19}H_{15}ClO_2S$ 342.0476, found 342.0471; HPLC analysis: 99.5% ee (Chiralcel OD-H, 5% *i*-PrOH in hexanes, 0.8 mL/min, $\lambda = 254$ nm, $t_R = 10.4$ min, major; $t_R =$ 22.6 min, minor). Anal. Calcd for $C_{19}H_{15}ClO_2S$: C, 66.56; H, 4.41. Found: C, 66.34; H, 4.69.

4.29. (*R*,*E*)-Methyl 4-(naphthalen-5-yl)-4-(5-phenylthiophen-2-yl)but-2-enoate 9m

Purified via flash chromatography (silica gel, pentane–diethyl ether, 7:1) to give **9m** as an oily brown solid (0.126 g, 66% yield), R_f 0.20 (pentane–diethyl ether, 5:1); $[\alpha]_D^{25} = +18.9$ (*c* 1.32, $CHCl_3$); FTIR ($CHCl_3$): 3061, 2951, 1719, 1271 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.04–8.02 (m, 1H), 7.90–7.88 (m, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.58–7.46 (m, 6H), 7.43–7.41 (m, 1H), 7.33 (t, $J = 8.0$ Hz, 2H), 7.25–7.22 (m, 1H), 7.16 (d, $J = 3.5$ Hz, 1H), 6.79 (d, $J = 3.5$ Hz, 1H), 5.88–5.83 (m, 2H), 3.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.7 (C), 149.1 (CH), 143.77 (C), 143.75 (C), 136.6 (C), 134.1 (C), 134.0 (C), 131.1 (C), 128.9 (CH), 128.8 (CH), 128.4 (CH), 127.3 (CH), 127.2 (CH), 126.5 (CH), 126.1 (CH), 125.8 (CH), 125.5 (CH), 125.4 (CH), 123.4 (CH), 123.0 (CH), 122.7 (CH), 51.6 (CH_3), 44.6 (CH); LRMS (EI) *m*/*z* (relative intensity): 385.1 ($[M+H]^+$, 100.0); HRMS (ESI) *m*/*z* calcd for $[C_{25}H_{20}O_2SNa]^+$ $(M+Na)^+$: 407.1076, found 407.1082; HPLC analysis: 99.3% ee (Chiralcel OD-H, 5% *i*-PrOH in hexanes, 0.9 mL/min, $\lambda = 254$ nm, $t_R = 14.8$ min, major; $t_R = 27.9$ min, minor).

4.30. (*R*,*E*)-Methyl 4-(benzofuran-2-yl)-4-(naphthalen-5-yl)but-2-enoate 9o

Purified via flash chromatography (silica gel, pentane–diethyl ether, 9:1) to give **9o** as a yellow oily solid (0.102 g, 60% yield), R_f 0.15 (pentane–diethyl ether, 10:1); $[\alpha]_D^{25} = -33.5$ (*c* 0.94, $CHCl_3$); FTIR (neat): 1723, 1655, 1454, 1272, 1170 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.00 (m, 1H), 7.90 (m, 1H), 7.84 (d, $J = 8.2$ Hz, 1H), 7.54–7.43 (m, 6H), 7.36 (d, $J = 7.3$ Hz, 1H), 7.25 (m, 1H), 7.20 (m, 1H), 6.44 (s, 1H), 5.83 (m, 2H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.6 (C), 156.9 (C), 155.0 (C), 146.4 (CH), 134.2 (C), 134.1 (C), 131.2 (C), 129.0 (CH), 128.5 (CH), 128.3 (C), 126.6 (CH), 126.5 (CH), 125.8 (CH), 125.5 (CH), 124.0 (CH), 123.8 (CH), 123.2 (CH), 122.8 (CH), 120.8 (CH), 111.2 (CH), 105.4 (CH), 51.6 (CH_3), 43.7 (CH); LRMS (EI) *m*/*z* (relative intensity): 342.2 ($[M]^+$, 100.0); HRMS (EI) *m*/*z* calcd for $[C_{23}H_{18}O_3]^+$ 342.1250, found 342.12509; HPLC analysis: 99.1% ee (Chiralcel OD-H, 15% *i*-PrOH in hexanes, 0.8 mL/min, $\lambda = 254$ nm, $t_R = 12.7$ min, major; $t_R = 11.3$ min, minor). Anal. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30. Found: C, 80.44; H, 5.37.

4.31. (*R*,*E*)-Methyl 4-(benzo[*b*]thiophen-3-yl)-4-(naphthalen-5-yl)but-2-enoate 9p

Purified via flash chromatography (silica gel, pentane–diethyl ether, 7:1) to give **9p** as a yellow oil (0.036 g, 20% yield), R_f 0.23 (pentane–diethyl ether, 5:1); $[\alpha]_D^{25} = +4.0$ (*c* 1.70, $CHCl_3$); FTIR (neat): 3061, 2948, 1720, 1269 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, $J = 8.0$ Hz, 1H), 7.91–7.87 (m, 2H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.59–7.54 (m, 2H), 7.51–7.46 (m, 2H), 7.40–7.33 (m, 2H), 7.29 (t, $J = 7.50$ Hz, 1H), 7.23 (d, $J = 7.0$ Hz, 1H), 7.02 (s, 1H), 5.97 (d, $J = 6.0$ Hz, 1H), 5.66 (dd, $J = 15.8$, 1.3 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7 (C), 148.6 (CH), 140.7 (C), 137.9 (C), 135.80 (C), 135.76 (C), 134.1 (C), 131.4 (C), 129.0 (CH), 128.1 (CH), 126.6 (CH), 126.3 (CH), 125.8 (CH), 125.5 (CH), 124.9 (CH), 124.5 (CH), 124.2 (CH), 123.4 (CH), 123.2 (CH), 122.9 (CH), 122.0 (CH), 51.6 (CH_3), 43.0 (CH); LRMS (EI) *m*/*z* (relative intensity): 359.1 ($[M+H]^+$, 30); HRMS (ESI) *m*/*z* calcd for $[C_{23}H_{18}O_2SNa]^+$ $(M+Na)^+$: 381.0920, found 381.0934.

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