Heck Reaction

Fujiwara–Moritani Reaction of Weinreb Amides using a Ruthenium-Catalyzed C–H Functionalization Reaction

Riki Das and Manmohan Kapur^{*[a]}

Abstract: The ruthenium-catalyzed Fujiwara–Moritani reaction (oxidative-Heck reaction) of Weinreb amides is reported herein. The reaction affords exclusively *ortho*-C–H olefination products, has excellent substrate scope and tolerates halogen functionalities, which increase the synthetic utility of the method. A variety of activated olefins as well as styrenes can be employed as coupling partners.

Introduction

Over the past few years, the Fujiwara–Moritani reaction^[1,2] or the oxidative Heck reaction has become one of the most versatile and widely utilized reactions in the field of C–H functionalization.^[3] Known initially to be catalyzed by palladium, the scope of this important transformation has been extended successfully to catalysis by several other transition metals.^[2] The only notable drawback of the oxidative Heck reaction is the need to employ electron-deficient (activated) olefins so as to ensure a good transformation. However, there have been reports in which electron-neutral olefins have successfully been employed in this transformation. This reaction has been widely used on a variety of arenes and quite often Lewis-basic directing groups^[4] have been employed to direct the site-selectivity, invariably involving metallacycles^[5] in the process (Scheme 1).

A variety of directing groups have been employed; these include amides, *O*-alkylhydroxamic acids, and Weinreb amides.^[6] In the case of *O*-alkylhydroxamic acids or simple aryl hydroxamic acids, such transformations invariably result in cleavage of the sensitive N–O bond. There are very few reports in which the N–O bond survives the oxidative-C–H olefination reaction conditions, and most of the research groups deliberately sacrifice the N-alkoxyl group as an internal oxidant so as to eliminate the need for an external oxidant.^[7–9] Wang and co-workers reported an efficient catalytic system for the rhodium catalyzed C–H olefinations of aryl Weinreb amides in which they used acrylates as the coupling partners.^[7c] In continuation to our efforts in the area of site-selective C–H functionalization,^[10] we report herein, the *ortho*-selective ruthenium-catalyzed Fuji-

 [a] R. Das, Dr. M. Kapur Department of Chemistry Indian Institute of Science Education and Research Bhopal Academic Building II, Indore Bypass Road, Bhauri, Bhopal 462066, MP (India) E-mail: mk@iiserb.ac.in
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Scheme 1. Directed Fujiwara–Moritani or oxidative-Heck reaction of arenes.

wara–Moritani reaction of aryl Weinreb amides in which we have successfully employed a variety of activated olefins as well as styrenes as coupling partners. The reaction worked very well with both the coupling partners possessing halogen functionalities, thereby enhancing the synthetic utility of the method (Scheme 2).

Results and Discussion

Our efforts were initiated with the optimization of different reaction conditions for the oxidative Heck-reaction. A variety of catalyst systems were tested. As we were more interested in styrenes as coupling partners, the optimization reactions were carried out with styrene as the olefin source. The palladium catalyzed combinations did not result in any notable reactions. With the other reaction conditions that were attempted, either the reaction was unsuccessful or simply resulted in cleavage of the N–O bond of the starting material. Only the ruthenium-catalyzed reactions resulted in notable conversions and the best transformation was obtained with the in situ-generated cationic ruthenium catalyst using the acetate-assisted C–H function-

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Scheme 2. Previously reported methods and our approach.



alization^[11] (Table 1, entry 15). Under these optimized reaction conditions, the products were obtained in moderate-to-excellent yields with very good substrate scope (Table 2). The site-

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selectivity was as expected and exclusively, the *ortho*olefinated products. In all the substrates attempted, the reaction afforded olefinated products with *E*-stereochemistry and in some of the substrates **2i**–**j** and **2q**, the di-olefinated product was the major product.

Barring styrenes, the reaction was unsuccessful with electron-neutral olefins. In almost all the cases, the N-alkoxyl group was lost in the product. The observed outcome, however, was not unexpected as several reports were available in literature where such catalytic systems resulted in the loss of the N–O bond. An exception was observed in **2r** where the Weinreb amide functionality was found to be intact. At this moment, we are not sure whether the cleavage of the N–O bond is because it acts as an internal oxidant, as when a control reaction was carried out without any coupling partner (the olefin), it simply resulted in the starting material without the N-alkoxyl group.

In an attempt to check whether modifying the structure of the Weinreb amide would prevent the N–O bond cleavage, we synthesized a new Weinreb amide of the type **3** in which we incorporated a five-membered cyclic structure (Table 3). The Fujiwara-Moritani reactions of this cyclic Weinreb amide, however, were not very different. As shown in Table 3, in almost all cases, the product obtained was of the type **4**, in which the isoxazolidine ring had opened up.

An exception was found in the case of 4g, the N– O bond survived the reaction conditions. As depicted in Table 3, these substrates also resulted in similar transformations as the acyclic ones with fair substrate scope and moderate-to-good yields.

Similar to that of acyclic Weinreb amides, in this case too, a control experiment when conducted under the reaction conditions, without the olefin partner, resulted in about 50% of the ring-opened starting material. The products of the type **4** may have good synthetic utility as a new hydroxyl functionality has been created that can serve as a handle for further synthetic manipulations.

A plausible mechanism for the transformation is shown in Scheme 3. The initial coordination of the carbonyl oxygen to the Ru^{II} metal is followed by cyclometallation via C–H activation of the *ortho* C–H. This is followed by coordination of the metal to the olefin and subsequent carbometallation. *Syn*- β -hydride elimination followed by removal of a proton leads to Ru⁰, which is then converted into Ru^{II} by the oxidant Cu^{II}.

In this particular transformation, it is postulated by several research groups that this oxidation to regenerate the active catalyst is actually carried out by the

N-alkoxyl group, thus resulting in its cleavage. However, our control experiments show that even in absence of the olefin coupling partner, this N–O bond cleavage is feasible and that

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the N–O bond reduction might actually be proceeding by an alternative mechanism. It is quite possible that the $[Ru^{II}-H]^+$ species formed after the β -hydride elimination could play a role in this N–O bond reduction. At this moment though, we do not have conclusive proof for this.

Conclusions

In summary, we have carried out the directed Fujiwara–Moritani or the oxidative-Heck reaction of Weinreb amides using an acetate-assisted ruthenium catalyzed C–H functionalization reaction. The reaction affords exclusively *ortho*-olefinated products with good substrate scope and moderate-to-good yields. The transformation works very well with styrenes as well as activated olefins and tolerates halogen functionalities in both the coupling partners.

Experimental Section

General Methods: All commercially available compounds (Acros, Aldrich, Fluka, Merck etc.,) were used without purification. Unless otherwise noted, all reactions were performed in oven-dried glassware. All reactions were run under an atmosphere of argon or nitrogen. All solvents used in the reactions were purified before use. Tetrahydrofuran, 1,4-dioxane and toluene were distilled from sodium and benzophenone, whereas dry dichloromethane, N,N-dimethylformamide (DMF) and triethylamine were distilled from CaH₂. Petroleum ether with a boiling range of 40-60°C was used. Melting points are uncorrected. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer and a Bruker Avance III 500 MHz NMR spectrometer; spectra were recorded at 295 K in CDCl₃; chemical shifts are calibrated to the residual proton and carbon resonance of the solvent: CDCl₃ (¹H: δ = 7.25; ¹³C: δ = 77.0). HRMS: Bruker Daltonics MicroTOF-Q-II with electron spray ionization (ESI) or atmospheric pressure chemical ionization (APCI). GC-HRMS: Performed on Agilent 7200 GC-QToF (with Electron Impact (EI), 70 eV) with 7890 A GC using DB-5 column. GC-LRMS: Performed on Agilent 7890 A GC with Agilent 5975C MS (EI 70 eV) using DB-5 column. IR: PerkinElmer Spectrum BX FTIR, Shimadzu IRAffinity-1 FTIR and were recorded as thin films between KBr plates.

The acyclic Weinreb amides were prepared according to procedures reported in the literature.^[13] Hydroxamic acids used for preparation of the 5-membered cyclic Weinreb amides were also prepared according to procedures reported in the literature.^[14]

General Procedures for the Preparation of Cyclic Weinreb Amides:

Hydroxamic acid (1 equiv) was dissolved in MeOH/H₂O (3:2) and then Cs₂CO₃ (3 equiv), KI (0.2 equiv), and 1,3-dibromopropane (1.2 equiv) were added. The reaction mixture was allowed to stir at room temperature for 48 h. This was then concentrated under vacuum and extracted twice with EtOAc. The organic layer was washed with brine, dried over anhydrous NaSO₄, filtered, and concentrated under vacuum. The crude mixture was purified by silica-gel column chromatography.

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Scheme 3. Plausible mechanism for the transformation.

Oxazolidin-2-yl(phenyl)methanone (3 a):^[15]

Prepared according to the general procedure and the title compound was isolated a colourless gel (43% yield). ¹H NMR (400 MHz, CDCl₃): δ =7.74 (d, J=7.2 Hz, 2 H), 7.43 (t, J=7.3 Hz, 1 H), 7.36 (t, J=7.4 Hz, 2 H), 3.92 (t, J=6.8 Hz, 2 H), 3.84 (t, J=7.3 Hz, 2 H), 2.29 ppm (q, J=7.2 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃): δ =169.56, 133.49, 131.19, 128.99, 127.90, 69.48, 44.89, 27.37 ppm; ESI-HRMS: Calculated for C₁₀H₁₁NO₂ [*M*+H]⁺ 178.0863, found 178.0862.

Oxazolidin-2-yl(p-tolyl)methanone (3b):

Prepared according to the general procedure and the title compound was isolated as a yellow gel (64% yield). ¹H NMR (400 MHz, CDCl₃): δ = 7.68 (d, J = 8.1 Hz, 2 H), 7.19 (d, J = 8.0 Hz, 2 H), 3.93 (t, J = 6.9 Hz, 2 H), 3.86 (t, J = 7.4 Hz, 2 H), 2.36 (s, 3 H), 2.30 ppm (q, J = 7.37 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃): δ = 170.04, 141.68, 130.55, 129.16, 128.59, 69.42, 44.86, 27.40, 21.52 ppm; ESI-HRMS: Calculated for C₁₁H₁₃NO₂ [*M*+H]⁺ 192.1019, found 192.1039.

Oxazolidin-2-yl(4-methoxyphenyl)methanone (3 c):

Prepared according to the general procedure and the title compound was isolated as a yellow gel (64% yield). ¹H NMR (400 MHz, CDCl₃): δ = 7.80 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 3.93 (t, *J* = 6.9 Hz, 2H), 3.87 (t, *J* = 7.6 Hz, 2H), 3.82 (s, 3 H), 2.30 ppm (q, *J* = 7.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 169.77, 162.03, 131.29, 125.46, 113.16, 69.43, 55.36, 44.91, 27.36 ppm; ESI-HRMS: Calculated for C₁₁H₁₃NO₃ [*M*+H]⁺ 208.0968, found 208.0991.

General Procedure for the Ru-Catalyzed Oxidative Olefination Reaction:

In a pressure tube equipped with a stirrer bar, Weinreb amide (0.303 mmol) was dissolved in dry 1,4-dioxane (1.5 mL). The reaction mixture was degassed with argon for about 10 min, followed by the addition of $[RuCl_2(p-cymene)]_2$ (4 mol%), AgSbF₆ (20% mmol), Cu(OAc)_2·H_2O (0.666 mmol), and the olefin partner (0.909 mmol). The tube was fitted with a Teflon screw cap under an argon flow. The reaction mixture was heated to 100°C and stirred at that temperature. The reaction was followed either by

GCMS or by TLC. Upon completion of the reaction and subsequent cooling to room temperature, the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite. The filtrate was concentrated under reduced pressure and the crude product was purified by silica-gel column chromatography.

(E)-2-(4-chlorostyryl)-N-methylbenzamide (2a):

Yield: 95 %, yellowish-white solid, m.p. 148–150 °C, TLC $R_{\rm f}$ 0.30 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ = 7.67 (d, J = 8.1 Hz, 1 H), 7.47–7.39 (m, 5 H), 7.31–7.24 (m, 3 H), 6.98 (d, J = 16.2 Hz, 1 H), 5.82 (bs, 1 H), 2.99 ppm (d, J=5.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ = 170.14, 135.67, 135.64, 135.29, 133.57, 130.24, 129.92, 128.87, 127.98, 127.67, 127.52, 126.56, 126.16, 26.87 ppm; IR (KBr): \hat{v} =3598, 3342, 2354, 2328, 1638, 1535, 1169, 959, 850, 748, 672 cm⁻¹; ESI-HRMS: Calculated for C₁₆H₁₄CINO [*M*+H]⁺ 272.0837, found 272.0842.

(E)-2-(4-bromostyryl)-N-methylbenzamide (2b):

Yield: 82%, white solid, m.p. 139–142 °C; TLC $R_{\rm f}$ 0.30 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ =7.71 (d, J=7.9 Hz, 1 H), 7.53–7.42 (m, 5 H), 7.41–7.36 (m, 2 H), 7.32 (t, J=7.6 Hz, 1 H), 7.01 (d, J=16.3 Hz, 1 H), 5.83 (bs, 1 H), 3.04 ppm (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ =170.15, 136.08, 135.65, 135.26, 131.81, 130.24, 129.92, 128.29, 127.69, 127.52, 126.67, 126.14, 121.73, 26.87 ppm; IR (KBr): \ddot{v} =3593, 2848, 2355, 2337, 1658, 1520, 1167, 801, 751, 687 cm⁻¹; ESI-HRMS: Calculated for C₁₆H₁₄BrNO [*M*+H]⁺ 316.0332 and 318.0312, found 316.0349 and 318.0330.

(E)-N-methyl-2-(4-methylstyryl)benzamide (2 c):

Yield: 75%, white solid, m.p. 156–158°C, TLC $R_{\rm f}$ 0.30 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ =7.71 (d, J=7.9 Hz, 1 H), 7.50 (dd, J=7.6, 1.1 Hz, 1 H), 7.45–7.42 (m, 4 H), 7.31 (dd, J=7.5, 1.1 Hz, 1 H), 7.20 (d, J=7.9 Hz, 2 H), 7.06 (d, J=16.3 Hz, 1 H), 5.83 (bs, 1 H), 3.04 (d, J=4.9 Hz, 3 H), 2.30 ppm (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ =170.26, 138.00, 135.62, 135.55, 134.31, 131.39, 130.16, 129.43, 127.66, 127.30, 126.73, 126.14, 124.89, 26.85, 21.28 ppm; IR (KBr): \hat{v} =3231, 2367, 2343, 1674, 1522, 1053, 744, 670 cm⁻¹; ESI-HRMS: Calculated for C₁₇H₁₇NO [*M*+H]⁺ 252.1383, found 252.1389.

(E)-N-methyl-2-styrylbenzamide (2d):

Yield: 68%, white solid, m.p. 133–136 °C, TLC $R_{\rm f}$ 0.30 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ =7.67 (d, J=7.87 Hz, 1 H), 7.50–7.46 (m, 3 H), 7.45–7.38 (m, 2 H), 7.34 (t, J=7.3 Hz, 2 H), 7.29–7.25 (m, 2 H), 7.04 (d, J=16.3 Hz, 1 H), 5.82 (s, 1 H), 2.97 ppm (d, J=4.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ =170.23, 137.08, 135.65, 135.48, 131.39, 130.19, 128.72, 128.00, 127.62, 127.49, 126.81, 126.20, 125.93, 26.86 ppm; IR (KBr): $\tilde{\nu}$ =3592, 3310, 2355, 2325, 1649, 1632, 1539, 1315, 1154, 962, 761, 691 cm⁻¹; ESI-HRMS: Calculated for C₁₆H₁₅NO [M+H]⁺ 238.1226, found 238.1212.

(E)-2-(4-methoxystyryl)-N-methylbenzamide (2e):

Yield: 61 %, white solid, m.p. 102–105 °C; TLC $R_{\rm f}$ 0.30 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ = 7.79–7.68 (m, 1 H), 7.53–7.42 (m, 4 H), 7.34 (d, J = 16.8 Hz, 1 H), 7.31–7.28 (m, 1 H), 7.03 (d, J = 16.8 Hz, 1 H), 6.92 (d, J = 8.4 Hz, 2 H), 5.84 (bs, 1 H), 3.86 (s, 3 H), 3.50 ppm (d, J = 4.8 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ = 170.34, 159.60, 135.75, 135.42, 131.34, 130.94, 130.14, 129.92 128.55, 128.07, 127.63, 127.10, 126.82, 125.99, 123.74, 114.16, 55.35,

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26.84 ppm; IR (KBr): $\tilde{\nu}$ = 3352, 3063, 2953, 2843, 2357, 2334, 1648, 1633, 1555, 1537, 1517,1414, 1303, 1251, 1176, 1112, 1032, 964, 853, 821, 751, 702, 668 cm⁻¹; ESI-HRMS: Calculated for C₁₇H₁₇NO₂ [*M*+H]⁺ 268.1332, found 268.1343.

(E)-N-methyl-2-(2-(naphthalene-1-yl)vinyl)benzamide (2 f):

Yield: 57%, white solid, M.p. 195–197°C; TLC $R_{\rm f}$ 0.30 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ =8.23 (d, J=8.3 Hz, 1H), 7.91–7.89 (m, 1H), 7.86–7.85 (m, 3H), 7.79 (d, J=7.2 Hz, 1H), 7.57–7.49 (m, 6H), 7.36 (td, J=7.5, 1.1 Hz, 1H), 5.87 (bs, 1H), 3.03 ppm (d, J=4.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ =170.26, 135.82, 135.75, 134.62, 133.70, 131.35, 130.28, 128.89, 128.49, 128.40, 127.68, 126.55, 126.20, 125.87, 125.78, 124.10, 123.64, 26.90 ppm; IR (KBr): $\tilde{\nu}$ =3665, 3606, 2355, 2325, 1629, 1538, 1164, 950, 779, 762, 665 cm⁻¹; ESI-HRMS: Calculated for C₂₀H₁₇NO [*M*+Na]⁺ 310.1202, found 310.1214.

(E)-2-(4-fluorostyryl)-N-methylbenzamide (2g):

Yield: 54%, yellowish white solid, m.p. 118–120 °C, TLC $R_{\rm f}$ 0.30 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ = 7.69 (d, J = 7.9 Hz, 1 H), 7.51–7.40 (m, 5 H), 7.31–7.28 (m, 1 H), 7.09–7.01 (m, 3 H), 5.93 (bs, 1 H), 3.02 ppm (d, J=4.8 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ = 170.24, 162.53 (d, J=247.8 Hz, 1C), 135.49 (d, J= 18.6 Hz, 2C), 133.33, 130.22, 130.03, 128.35 (d, J=8.1 Hz, 2C), 127.53, 127.50, 126.09, 125.72, 125.70, 115.66 (d, J=21.8 Hz, 2C), 26.87 ppm; IR (KBr): $\tilde{\nu}$ =3575, 2865, 2391, 2334, 1661, 1542, 1186, 973, 863, 693 cm⁻¹; ESI-HRMS: Calculated for C₁₆H₁₄FNO [*M*+H]⁺ 256.1132, found 256.1152.

(2*E*, 2'*E*)-dibenzyl-3,3,-(2-(methylcarbamoyl)-1,3-phenylene) diacrylate (2 i):

Yield: 87%, white solid, M.p. 85–87 °C, TLC $R_{\rm f}$ 0.30 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ =7.72 (d, J=15.9 Hz, 2H), 7.58 (d, J=7.9 Hz, 2H), 7.38–7.30 (m, 11H), 6.42 (d, J=15.9 Hz, 2H), 5.92 (d, J=4.8 Hz, 1H), 5.20 (s, 2H), 2.99 ppm (d, J=4.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ =168.05, 166.00, 141.19, 138.51, 135.86, 132.39, 129.62, 128.61, 128.33, 128.24, 127.85, 121.16, 66.51, 26.86 ppm; IR (KBr): $\tilde{\nu}$ =3591, 3306, 3063, 2949, 2355, 2329, 1713, 1697, 1647, 1555, 1539, 1454, 1414, 1375, 1314, 1264, 1164, 1013, 976, 805, 751, 697 cm⁻¹; ESI-HRMS: Calculated for C₂₈H₂₅NNaO₅ [*M*+Na]⁺ 478.1625, found 478.1626.

(2*E*,2*E*')-diethyl- 3,3'-(2-methylcarbamoyl)-1,3-phenylene)diacrylate (2j):

Yield: 67%, white solid, m.p. 127–129 °C, TLC $R_{\rm f}$ 0.30 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCI₃): δ =7.70 (d, J=15.9 Hz, 2H), 7.62 (d, J=7.9 Hz, 2H), 7.41(t, J=7.9 Hz, 1H), 6.42 (d, J=15.9 Hz, 2H), 5.73 (bs, 1H), 4.23 (q, J=7.1 Hz, 4H), 3.06 (d, J=4.9 Hz, 3H), 1.31 ppm (t, J=7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCI₃): δ =168.18, 166.22, 140.58, 138.25, 132.58, 129.65, 127.79, 121.72, 60.74, 26.89, 14.27 ppm; IR (KBr): $\tilde{\nu}$ =3361, 2354, 1713, 1644, 1367, 1315, 1264, 1174, 1037, 982, 869, 802 cm⁻¹; ESI-HRMS: Calculated for C₁₈H₂₁NO₅ [*M*+H]⁺ 332.1492, found 332.1503.

(E)-2-(4-Bromostyryl)-4-methoxy-N-methylbenzamide (2k):

Yield: 82%, white solid, m.p. 186–188 °C; TLC $R_{\rm f}$ 0.20 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ = 7.53 (d, J = 16.4 Hz, 1 H), 7.47–7.42 (m, 3 H), 7.36 (d, J = 9.3 Hz, 2 H), 7.14 (d, J = 2.4 Hz, 1 H), 6.94 (d, J = 16.2 Hz, 1 H), 6.81 (dd, J = 8.6, 2.4 Hz, 1 H), 5.75 (bs,

1 H), 3.88 (s, 3 H), 2.98 ppm (3 H, s); ¹³C NMR (100 MHz, CDCl₃): δ = 169.77, 160.96, 137.43, 136.00, 131.82, 130.09, 129.38, 128.33, 127.02, 121.80, 113.19, 111.38, 55.44, 26.90 ppm; IR (KBr): $\tilde{\nu}$ = 3565, 2354, 2320, 1620, 1520, 1395, 1286, 1217, 1170, 1039, 961, 854, 803, 703 cm⁻¹; ESI-HRMS: Calculated for C₁₇H₁₆BrNO₂ [*M*+H]⁺ 346.0437 and 348.0417, found 346.0457 and 348.0436.

(E)-2-(4-chlorostyryl)-4-methoxy-N-methylbenzamide (21):

Yield: 78%, white solid, m.p. 183–187 °C; TLC $R_{\rm f}$ 0.20 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ =7.52 (d, J=16.1 Hz, 1 H), 7.44–7.41 (m, 3 H), 7.30 (d, J=8.6 Hz, 2 H), 7.14 (d, J=2.2 Hz, 1 H), 6.95 (d, J=16.3 Hz, 1 H), 6.81 (dd, J=8.4, 2.3 Hz, 1 H), 5.75 (bs, 1 H), 3.85 (s, 3 H), 2.98 ppm (3 H, s); ¹³C NMR (100 MHz, CDCl₃): δ = 169.78, 160.96, 137.45, 135.56, 133.63, 130.04, 129.38, 128.88, 128.28, 128.02, 126.91 113.15, 111.38, 55.44, 26.90 ppm; IR (KBr): $\hat{\nu}$ =3393, 2359, 2334, 1638, 1525, 1040, 956, 849, 803, 687, 667 cm⁻¹; ESI-HRMS: Calculated for C₁₇H₁₆CINO₂ [*M*+H]⁺ 302.0942, found 302.0961.

(E)-4-Methoxy-N-methyl-2-styrylbenzamide (2 m):

Yield: 74%, white solid, m.p. 120–123 °C, TLC $R_{\rm f}$ 0.30 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCI₃): δ =7.57–7.53 (m, 3 H), 7.49 (d, J=8.4 Hz, 1 H), 7.39 (t, J=7.6 Hz, 2 H), 7.31 (d, J=7.6 Hz, 1 H), 7.18 (d, J=2.3 Hz, 1 H), 7.05 (d, J=16.0 Hz, 1 H), 6.85 (dd, J= 8.4 Hz, 2.8 Hz, 1 H), 5.8 (bs, 1 H), 3.88 (s, 3 H), 3.02 ppm (s, 3 H); ¹³C NMR (100 MHz, CDCI₃): δ =169.87, 160.91, 137.60, 136.99, 131.49, 129.53, 128.73, 128.29, 128.05, 126.85, 126.27, 113.02, 111.36, 55.41, 26.88 ppm; IR (KBr): $\tilde{\nu}$ =3567, 2362, 2342, 1521, 1149, 1162, 1037, 952, 827, 748, 682 cm⁻¹; ESI-HRMS: Calculated for C₁₇H₁₇NNaO₂ [*M*+Na]⁺ 290.1151, found 290.1166.

(*E*)-4-methoxy-*N*-methyl-2-(2-(naphthalene-1-yl)vinyl)benzamide (2 n):

Yield: 71%, white solid, m.p. 185–186 °C; TLC $R_{\rm f}$ 0.30 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ =8.19 (d, J=8.1 Hz, 1 H), 7.87–7.74 (m, 4 H), 7.55–7.45 (m, 5 H), 7.26–7.24 (m, 1 H), 6.85 (dd, J=8.6 Hz, 2.15, 1 H), 5.83 (bs, 1 H), 3.89 (s, 3 H), 2.96 ppm (d, J=4.7 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ =169.86, 160.98, 137.86, 134.50, 133.71, 131.34, 129.60, 129.21, 128.69, 128.59, 128.46, 128.44, 126.21, 125.87, 125.77, 124.17,123.61, 112.97, 111.92, 55.48, 26.90 ppm; IR (KBr): $\tilde{\nu}$ =3566, 2355, 2325, 1618, 1539, 1285, 1157, 1112, 1040, 950, 768 cm⁻¹; ESI-HRMS: Calculated for C₂₁H₁₉NO₂ [*M*+H]⁺ 318.1489, found 318.1486.

(E)-4-methoxy-N-methyl-2-(4-methylstyryl)benzamide (2 o):

Yield: 58%, white solid, m.p. 138–140 °C; TLC $R_{\rm f}$ 0.30 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCI₃): δ =7.45 (d, J=3.2 Hz, 1 H), 7.42 (d, J=4.4 Hz, 1 H), 7.39 (d, J=8.0 Hz, 2 H), 7.16–7.12 (m, 3 H), 6.97 (d, J=16.2 Hz, 1 H), 6.79 (dd, J=8.5, 2.5 Hz, 1 H), 5.76 (bs, 1 H), 3.84 (s, 3 H), 2.96 (d, J=4.9 Hz, 3 H), 2.34 ppm (s, 3 H); ¹³C NMR (100 MHz, CDCI₃): δ =169.91, 160.91, 138.06, 137.73, 134.21, 131.51, 129.58, 129.45, 128.20, 126.77, 125.22, 112.90, 111.25, 55.40, 26.87, 21.28 ppm; IR (KBr): $\tilde{\nu}$ =3548, 2364, 2342, 1656, 1523, 1158, 1138, 1048, 942, 826, 758, 686 cm⁻¹; ESI-HRMS: Calculated for C₁₈H₁₉NO₂ [*M*+H]⁺ 282.1489, found 282.1489.

(E)-2-(4-fluorostyryl)-4-methoxy-N-methylbenzamide (2p):

Yield: 53%, white solid, m.p. 135–140 °C; TLC $R_{\rm f}$ 0.30 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ = 7.52–7.46 (m, 4H),

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7.17 (d, J=2.6 Hz, 1H), 7.07 (t, J=8.6 Hz, 2H), 7.00 (d, J=16.1 Hz, 1H), 6.84 (dd, J=8.6, 2.6 Hz, 1H), 5.84 (bs, 1H), 3.89 (s, 3H), 3.02 ppm (d, J=5.4 Hz, 3H); ¹³C NMR (100 MHz, CDCI₃): $\delta = 169.88$, 162.25 (d, J=261.7 Hz, 1C), 137.58, 133.23 (d, J=25.0 Hz, 2C), 130.18, 129.41, 128.41(d, J=64 Hz, 2C), 128.19, 126.06, 126.05, 115.68 (d, J=17.3 Hz, 2C), 112.99, 111.32, 55.43, 26.90 ppm; IR (KBr): $\tilde{\nu} = 3276$, 2364, 2338, 1654, 1515, 1224, 1035, 952, 842, 680, 667 cm⁻¹; ESI-HRMS: Calculated for C₁₇H₁₆FNO₂ [*M*+H]⁺ 286.1238, found 286.1263.

Dimethyl 4,4'-((1*E*,1*E*')-(2-(methylcarbamoyl)-1,3-phenylene)bis (ethane-2,1-diyl))dibenzoate (2q):

Yield: 86%, white solid, m.p. 127–129 °C; TLC $R_{\rm f}$ 0.30 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ =8.04 (d, J=8.4 Hz, 4H), 7.66 (d, J=7.3 Hz, 2H), 7.55 (d, J=7.9 Hz, 4H), 7.44 (t, J=8.6 Hz, 1H), 7.30 (d, J=16.0 Hz, 2H), 7.12 (d, J=16.0 Hz, 2H), 5.87 (bm, 1H), 3.94 (s, 6H), 3.10 ppm (d, J=5.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ =169.77, 166.83, 141.32, 136.20, 134.49, 130.42, 130.05, 129.47, 129.32, 127.64, 126.65, 125.08, 52.17, 26.82 ppm; IR (KBr): $\tilde{\nu}$ =3402, 2359, 2356, 2331, 1647, 1540, 1278, 1174, 955, 693, 666 cm⁻¹; ESI-HRMS: Calculated for C₂₈H₂₅NNaO₅ [*M*+Na]⁺ 478.1625, found 478.1629.

(E)-2-(2-cyanovinyl)-N-methoxy-N-methylbenzamide (2r):

Yield: 69%, white solid, m.p. 70–74 °C, TLC $R_{\rm f}$ 0.30 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ = 7.56–7.54 (m, 1 H), 7.47 (d, J= 16.6 Hz, 1 H), 7.43–7.40 (m, 2 H), 7.38–7.36 (m, 1 H), 5.87 (d, J= 16.6 Hz, 1 H), 3.40–3.33 ppm (m, 6 H); ¹³C NMR (100 MHz, CDCl₃): δ = 168.86, 147.62, 135.53, 130.86, 130.52, 129.87, 127.53, 125.65, 117.83, 98.60, 61.27, 32.64 ppm; IR (KBr): $\tilde{\nu}$ = 3545, 3022, 2219, 1644, 1487, 1447, 980, 774, 639, 570 cm⁻¹; ESI-HRMS: Calculated for C₁₂H₁₂N₂O₂ [*M*+H]⁺ 217.0972, found 217.0987.

(*E*)-Benzyl 3-(5-bromo-2-(methylcarbamoyl)phenyl)acrylate (2 s):

Yield: 66%, white solid, m.p. 123–126 °C; TLC $R_{\rm f}$ 0.30 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCI₃): δ = 7.99 (d, J = 16.0 Hz, 1H), 7.77 (d, J = 2 Hz, 1H), 7.64–7.55 (m, 1H), 7.42–7.34 (m, 6H), 6.45 (d, J = 16.2 Hz, 1H), 5.79 (bs, 1H), 5.26 (s, 2H), 3.02 ppm (s, 3H); ¹³C NMR (100 MHz, CDCI₃): δ = 168.30, 165.84, 140.99, 135.84, 134.72, 132.70, 131.78, 130.07, 129.18, 128.61, 128.47, 128.28, 124.62, 121.67, 66.56, 26.96 ppm; IR (KBr): $\tilde{\nu}$ = 3295, 2364, 2343, 1693, 1652, 1555, 1313, 1167, 1007, 974, 748 cm⁻¹; ESI-HRMS: Calculated for C₁₈H₁₆BrNO₃ [*M*+H]⁺ 374.0386 and 376.0367, found 374.0387 and 376.0370.

(*E*)-benzyl 3-(3-methyl-2-(methylcarbomyl)phenyl)acrylate (2t):

Yield: 61 %, white solid, m.p. 78–80 °C; TLC $R_{\rm f}$ 0.30 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ =7.74 (d, J=16.0 Hz, 1H), 7.44–7.33 (m, 6H), 7.29–7.26 (m, 1H), 7.21 (d, J=7.8 Hz, 1H), 6.43 (d, J=15.9 Hz, 1H), 5.91 (bs, 1H), 5.22 (s, 2H), 3.01 (d, J=5.2 Hz, 3H), 2.33 ppm (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 169.58, 166.33, 142.17, 138.23, 135.98, 135.42, 131.92, 131.33, 129.11, 128.58, 128.25, 128.19, 123.80, 120.04, 66.35, 26.55, 19.13 ppm; IR (KBr): $\tilde{\nu}$ =3289, 3067, 2949, 2365, 2343, 1716, 1650, 1591, 1542, 1458, 1409, 1376, 1313, 1262, 1233, 1164, 1088, 979, 866, 791, 739, 648 cm⁻¹; ESI-HRMS: Calculated for C₁₉H₁₉NO₃ [*M*+H]⁺ 310.1438, found 310.1447.

(*E*)-*N*,2-dimethyl-6-(2-(naphthalene-1-yl)vinyl)benzamide (2u):

Yield: 54%, white solid, m.p. 210–213 °C; TLC $R_{\rm f}$ 0.30 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ =8.17 (d, J=8.1 Hz, 1H), 7.87–7.78 (m, 3H), 7.68 (d, J=7.1 Hz, 1H), 7.61 (d, J=7.8 Hz, 1H), 7.54–7.44 (m, 3H), 7.31(t, J=7.6 Hz, 1H), 7.18–7.12 (m, 2H), 5.7 (bs, 1H), 2.99 (d, J=5.2 Hz, 3H), 2.36 ppm (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ =170.68, 136.78, 135.08, 134.74, 134.68, 133.67, 131.33, 129.49, 129.10, 128.67, 128.66, 128.33, 128.26, 126.20, 125.88, 125.74, 123.97, 123.69, 123.12, 26.63, 19.27 ppm; IR (KBr): $\hat{\nu}$ =3366, 2358, 2338, 1649, 1517, 1031, 796, 770, 739, 667 cm⁻¹; ESI-HRMS: Calculated for C₂₁H₁₉NNaO [*M*+Na]⁺ 324.1359, found 324.1347.

(*E*)-benzyl 3-(2-((3-hydroxypropyl)carbamoyl)-5-methoxyphenyl) acrylate (4a):

Yield: 72%, white solid, m.p. 109–110 °C, TLC $R_{\rm f}$ 0.20 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCI₃): δ =8.09 (d, J=15.9 Hz, 1H), 7.48 (d, J=8.5 Hz, 1H), 7.45–7.31 (m, 5H), 7.06 (d, J=2.5 Hz, 1H), 6.91 (dd, J=8.5, 2.5 Hz, 1H), 6.47 (bs, 1H), 6.40 (d, J=15.9 Hz, 1H), 5.25 (s, 2H), 3.72 (t, J=5.6 Hz, 2H), 3.59 (q, J=6.0 Hz, 2H), 1.76 ppm (qt, J=5.8 Hz, 2H); ¹³C NMR (100 MHz, CDCI₃): δ =169.10, 166.50, 160.96, 142.82, 135.82, 134.40, 129.79, 129.44, 128.70, 128.63, 128.38, 120.43, 115.63, 111.88, 66.61, 60.12, 55.47, 37.59, 31.97 ppm; IR (KBr): $\bar{\nu}$ =3428, 3318, 2334, 2355, 1866, 1731, 1714, 1696, 1647, 1539, 1455, 1315 cm⁻¹; ESI-HRMS: Calculated for C₂₁H₂₃NO₅ [M+H]⁺ 370.1649, found 370.1665.

(2*E*,2'*E*)-dibenzyl 3,3'-(2-((3-hydroxypropyl)carbamoyl)-5methyl-1,3-phenylene)diacrylate (4 b):

Yield: 73%, white solid, m.p. 113–114°C, TLC R_f 0.20 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ =7.80 (d, J=15.9 Hz, 2H), 7.44 (s, 2H), 7.45–7.33 (m, 10H), 6.46 (d, J=15.9 Hz, 2H), 6.33 (t, J=5.9 Hz, 1H), 5.24 (s, 4H), 3.70 (t, J=5.8 Hz, 2H), 3.62 (q, J=5.9 Hz, 2H), 2.38 (s, 3H), 1.80 ppm (qt, J=5.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ =168.04, 166.36, 141.54, 139.57, 136.06, 135.77, 132.20, 128.63, 128.49, 128.38, 128.36, 120.67, 66.63, 60.46, 37.78, 31.74, 21.32 ppm; IR (KBr): \hat{v} =3441, 2355, 2329, 1712, 1634, 1596, 1539, 1454, 1376, 1314, 1264, 1167, 1070, 974, 856, 751, 699, 575 cm⁻¹; ESI-HRMS: Calculated for C₃₁H₃₁NNaO₆ [*M*+Na]⁺ 536.2044, found 536.2070.

(*E*)-methyl-3-(2-((3-hydroxypropyl)carbamoyl)-3-methylphenyl) acrylate (4c):

Yield: 68 %, viscous pale yellow gel, TLC $R_{\rm f}$ 0.20 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ = 7.72 (d, J = 15.9 Hz, 1 H), 7.41 (d, J = 7.7 Hz, 1 H), 7.25 (t, J = 8.1 Hz, 1 H), 7.18 (d, J = 7.5 Hz, 1 H), 6.38 (d, J = 15.9 Hz, 1 H), 6.37 (bs, 1 H), 3.85–3.70 (m, 5 H), 3.63–3.53 (m, 2 H), 2.31 (s, 3 H) 1.81 ppm (qt, J = 6.1 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ = 169.57, 167.32, 141.99, 138.03, 135.42, 131.99, 131.21, 129.18, 123.65, 119.82, 60.17, 51.85, 37.27, 31.94, 19.18 ppm; IR (KBr): $\tilde{\nu}$ = 3434, 2334, 2318, 1742, 1714, 1685, 1643, 1539, 1456, 1317, 1064, 965, 864, 782, 658 cm⁻¹; ESI-HRMS: Calculated for C₁₅H₁₉NNaO₄ [*M*+Na]⁺ 300.1206, found 300.1209.

(2*E*,2'*E*)-diethyl 3,3'-(2-((3-hydroxypropyl)carbomoyl)-5-methoxy-1,3-phenylene)diacrylate (4 d):

Yield: 63%, white solid, m.p. 102–108°C, TLC $R_{\rm f}$ 0.20 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ = 7.76 (d, *J* = 15.9 Hz,

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2H), 7.13 (s, 2H), 6.40 (d, J = 15.9 Hz, 2H), 6.34 (t, J = 5.9 Hz, 1H), 4.27 (q, J = 7.1 Hz, 4H), 3.88 (s, 3H), 3.82 (t, J = 5.8 Hz, 2H), 3.67 (q, J = 6.8 Hz, 2H), 1.89 (quintet, J = 5.8 Hz, 2H), 1.75 (bs, 1H), 1.34 ppm (t, J = 7.1 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 168.07$, 166.42, 159.77, 140.84, 133.79, 131.60, 121.26, 112.89, 60.84, 60.11, 55.51, 37.48, 31.83, 14.21 ppm; IR (KBr): $\ddot{\nu} = 3356$, 2982, 2940, 2359, 1714, 1646, 1596, 1541, 1458, 1368, 1272, 1178, 1038, 974, 859 cm⁻¹; ESI-HRMS: Calculated for C₂₁H₂₇NNaO₇ [*M*+Na]⁺ 428.1680, found 428.1654.

(2*E*,2'*E*)-diethyl-3,3'-(2-((3-hydroxypropyl)carbamoyl)-5methyl-1,3-phenylene)diacrylate (4e):

Yield: 61 %, white solid, m.p. 149–154 °C, TLC $R_{\rm f}$ 0.20 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ =7.74 (d, J = 15.9 Hz, 2H), 7.44 (s, 2 H), 6.45 (t, J = 6.0 Hz, 1H), 6.40 (d, J = 15.9 Hz, 2H), 4.25 (q, J = 7.1 Hz, 4H), 3.80 (t, J = 5.8 Hz, 2H), 3.66 (q, J = 5.9 Hz, 2H), 2.40 (s, 3 H), 1.88 (qt, J = 5.9 Hz, 2H), 1.33 (t, J = 7.1 Hz, 6H), 1.27 ppm (bs, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 168.21, 166.62, 140.96, 139.47, 135.94, 132.25, 128.34, 121.00, 60.83, 60.35, 37.67, 31.84, 21.34, 14.26 ppm; IR (KBr): $\tilde{\nu}$ = 3361, 3296, 2359, 2334, 1699, 1635, 1557, 1541, 1368, 1316, 1268, 1181, 1040, 985, 864, 693 cm⁻¹; ESI-HRMS: Calculated for C₂₁H₂₇NO₆ [*M*+H]⁺ 390.1911, found 390.1920.

(*E*)-2-(4-chlorostyryl)-*N*-(3-hydroxypropyl)-4-methylbenzamide (4 f):

Yield: 58%, white solid, m.p. 124–127 °C, TLC $R_{\rm f}$ 0.20 (3:2, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCI₃): δ =7.55–7.47 (m, 2H), 7.45 (d, J=8.5 Hz, 2H), 7.40 (d, J=7.8 Hz, 1H), 7.34 (d, J=8.5 Hz, 2H), 7.40 (d, J=16.3 Hz, 1H), 6.26 (bs, 1H), 3.74 (t, J=5.3 Hz, 2H), 3.63 (q, J=6.3 Hz, 2H), 2.42 (s, 3 H), 1.79 (qt, J=5.8 Hz, 2H), 1.68 ppm (bs, 1H); ¹³C NMR (100 MHz, CDCI₃): δ = 170.75, 140.62, 135.62, 135.42, 133.55, 132.42, 129.84, 128.94, 128.51, 127.90, 127.66, 126.87, 126.61, 59.47, 36.87, 32.34, 21.48 ppm; IR (KBr): $\tilde{\nu}$ =3670, 3593, 2918, 2852, 2650, 2549, 2354, 2325, 1673, 1515, 1153, 1044, 958, 812, 684, 663 cm⁻¹; ESI-HRMS: Calculated for C₁₉H₂₀CINNaO₂ [*M*+Na]⁺ 352.1075, found 352.1047.

(*E*)-isoxazolidin-2-yl(4-methyl-2-(2-(phenylsulfonyl)vinyl)phenyl) methanone (4g):

Yield: 48%, white solid, m.p. 158–160 °C, TLC R_f 0.30 (2:3, Petroleum ether/EtOAc); ¹H NMR (400 MHz, CDCI₃): δ =7.92–7.90 (m, 2H), 7.82 (d, J=15.4 Hz, 1 H), 7.60–7.56 (m, 1H), 7.53–7.49 (m, 2H), 7.36 (d, J=7.9 Hz, 1 H), 7.32 (s, 1 H), 7.24–7.21 (m, 1 H), 6.82 (d, J=15.4 Hz, 1 H), 4.91–3.68 (m, 4H), 2.73–2.15 ppm (m, 5H); ¹³C NMR (100 MHz, CDCI₃): δ =166.49, 140.52, 140.48, 133.42, 133.07, 131.33, 130.25, 129.32, 128.98, 128.61, 127.73, 127.59, 69.70, 44.04, 27.41, 21.30 ppm; IR (KBr): $\tilde{\nu}$ =3430, 3054, 3021, 2351, 1631, 1447, 1305, 1147, 1081, 974, 838, 746, 627 cm⁻¹; ESI-HRMS: Calculated for C₁₉H₁₉SNO₄ [*M*+K]⁺ 396.0666, found 396.0687.

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