Supporting Information

A Switch to Vinylogous Reactivity of Vinyl Diazo Esters for the C–H Allylation of Benzamides by Merging Cobalt and Photoredox Catalysis

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Table of contents

General methods S2
General procedures and analytical data of starting materials S3
Optimization details for C–H allylation of benzamides S14
General procedures and analytical data of allylated products S16
Control experiments and mechanistic studies S32
References S42
^1H, ^13C-Spectra of all new compounds S43
ESI-HRMS of cobaltacycle intermediate S112
X-ray diffraction data S115
Experimental:

(1) General Methods:

All commercially available compounds were used without purification. Unless otherwise noted, all reactions were performed in oven-dried glassware. All reactions were run under an argon or nitrogen atmosphere. All solvents used in the reactions were purified before use. Dry tetrahydrofuran and toluene were distilled from sodium and benzophenone, whereas dichloroethane was distilled from CaH₂.¹ Petroleum ether with a boiling range of 40−60 °C were used. Melting points are uncorrected. ¹H, ¹³C and ¹⁹F NMR: Recorded on Bruker Avance III 400 MHz NMR Spectrometer, Bruker Avance III 500 MHz NMR Spectrometer and Bruker Avance III 700 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 7.26; ¹³C δ 77.0). HRMS: Bruker Daltonics MicroTOF Q-II with electron spray ionization (ESI) and Atmospheric Pressure Chemical Ionization (APCI). Single-crystal X-ray diffraction data were collected using a Bruker SMART APEX II CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation at different low temperatures for each crystal.
(1) General procedures and analytical data of starting materials:

1. Synthesis of N-(quinolin-8-yl) benzamides:

**Procedure:** To an oven-dried round bottom flask charged with a magnetic stir bar, were added the benzoic acid (1.5 equiv.), DMF (3 drops) and DCM (15 mL) under an N₂ atmosphere. Oxalyl chloride (3 equiv.) was added dropwise under ice-cold conditions. The ice bath was removed, and the reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure under an atmosphere of nitrogen.

To another oven-dried round bottom flask charged with a magnetic stir bar was added 8-aminoquinoline (1 equiv.), Et₃N (1.5 equiv.) and DCM (15 mL) under N₂ atmosphere. To this, was added dropwise, the solution of acid chloride (1.5 equiv.) in DCM (5 mL) under ice-cold conditions and the mixture was stirred overnight at room temperature. Then the reaction mixture was quenched with water and extracted with DCM (3 x 10 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (1:20 EtOAc: Petroleum ether) to afford the product in good yield.

2-methyl-N-(quinolin-8-yl)benzamide (1a):

Prepared by following the general procedure and the title compound was isolated in 78% (306 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.

4-bromo-2-methyl-N-(quinolin-8-yl)benzamide (1b):

Prepared by following the general procedure and the title compound was isolated in 72% (368 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.
4-fluoro-2-methyl-N-(quinolin-8-yl)benzamide (1c):\textsuperscript{1b}

Prepared by following the general procedure and the title compound was isolated in 80% (336 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.\textsuperscript{1b}

4'-methoxy-3-methyl-N-(quinolin-8-yl)-[1,1'-biphenyl]-4-carboxamide (1d):\textsuperscript{1c}

Prepared by following the general procedure and the title compound was isolated in 71% (390 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.\textsuperscript{1c}

2,4-dimethyl-N-(quinolin-8-yl)benzamide (1e):\textsuperscript{1b}

Prepared by following the general procedure and the title compound was isolated in 81% (336 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.\textsuperscript{1c}

2,3-dimethyl-N-(quinolin-8-yl)benzamide (1f):\textsuperscript{1b}

Prepared by following the general procedure and the title compound was isolated in 81% (336 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.\textsuperscript{1c}

3-methoxy-2-methyl-N-(quinolin-8-yl)benzamide (1g):\textsuperscript{1b}

Prepared by following the general procedure and the title compound was isolated in 73% (321 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.\textsuperscript{1b}

3-bromo-2-methyl-N-(quinolin-8-yl)benzamide (1h):\textsuperscript{1d}

Prepared by following the general procedure and the title compound was isolated in 75% (383 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.\textsuperscript{1d}
3-chloro-2-methyl-N-(quinolin-8-yl)benzamide (1i):\(^ {1c}\)

Prepared by following the general procedure and the title compound was isolated in 82% (365 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.\(^ {1c}\)

2-methyl-3-(quinolin-8-ylcarbamoyl)phenyl acetate (1j):\(^ {1a}\)

Prepared by following the general procedure and the title compound was isolated in 70% (335 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.\(^ {1a}\)

2,5-dimethyl-N-(quinolin-8-yl)benzamide (1k):\(^ {1b}\)

Prepared by following the general procedure and the title compound was isolated in 88% (364 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.\(^ {1b}\)

2-ethyl-N-(quinolin-8-yl)benzamide (1l):\(^ {1a}\)

Prepared by following the general procedure and the title compound was isolated in 82% (340 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.\(^ {1a}\)

N-(quinolin-8-yl)-1-naphthamide (1m):\(^ {1a}\)

Prepared by following the general procedure and the title compound was isolated in 75% (334 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.\(^ {1a}\)

N-(quinolin-8-yl)-5,6,7,8-tetrahydronaphthalene-1-carboxamide (1n):\(^ {1d}\)

Prepared by following the general procedure and the title compound was isolated in 82% (381 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.\(^ {1d}\)
4-cyano-2-methyl-N-(quinolin-8-yl)benzamide (1o):\(^{1a}\)

Prepared by following the general procedure and the title compound was isolated in 78% (224 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.\(^{1d}\)

2-Methyl-4-nitro-N-(quinoline-8-yl)benzamide (1p):\(^{1g}\)

Prepared by following the general procedure and the title compound was isolated in 64% (196 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.\(^{1d}\)

Synthesis of 3-methyl-2-(3-oxobutyl)-N-(quinolin-8-yl)benzamide (1q):\(^{1f}\)

To an oven-dried sealed tube charged with a magnetic stir-bar, 3-methyl-N-(quinolin-8-yl)benzamide (0.50 mmol, 130 mg), methyl vinyl ketone (MVK) (1.00 mmol, 110 µL), RuCl\(_2\)(PPh\(_3\))\(_2\) (0.05 mmol, 63.5 mg), sodium pivalate (13.5 mg, 0.12 mmol) and toluene (1 mL) were added under N\(_2\) atmosphere. The tube was capped and introduced into an oil bath preheated to 105 °C. After stirring for 4h at that temperature, the mixture was cooled and filtered through a Celite pad and concentrated under reduced pressure. The resulting residue was purified by silica gel flash column chromatography (eluent: Petroleum ether/EtOAc = 19/1) to obtain the desired alkylated product (83 mg, 50% yield). Spectral data obtained were in good agreement with those reported in the literature.\(^{1f}\)

2. Preparation of vinyl diazoesters:

(A) General Procedure:

(i) Synthesis of p-toluenesulfonylazide:

To a solution of p-toluenesulfonylchloride (10 g, 52.45 mmol, 1 equiv.) in a mixture of acetone (158 mL) and H\(_2\)O (158 mL), was added sodium azide (3.41 g, 52.45 mmol, 1 equiv.) portion-wise
over 15 min at 0 °C. After stirring for 3 h at room temperature, the reaction mixture was concentrated under reduced pressure until all the acetone was evaporated. The concentrated reaction mixture was extracted thrice with diethyl ether which is dried over Na$_2$SO$_4$ and the solvent was evaporated under reduced pressure maintaining the bath temperature at 30 °C, resulting in $p$-toluenesulfonylazide (10.25 g, 99% crude yield) as a colorless oil.

(II) Synthesis of vinyl diazo esters:

To a solution of the alkyl acetoacetate (A) (1 equiv., 20 mmol) in anhydrous THF (30 mL) was added DBU (1.2 equiv., 24.0 mmol) at 0 °C. The resulting solution was stirred for 5 minutes, and to this, a solution of tosyl azide (1.1 equiv., 22 mmol) in THF (10 mL) was added over 5 minutes. The resulting solution was warmed to room temperature and stirred for 4 h. The solvent was evaporated, and the resulting residue was diluted with water (100 mL) and extracted with ethyl acetate (100 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (hexane/ethyl acetate = 6/1) to give alkyl diazo acetoacetate (B) as a yellow oil.

<table>
<thead>
<tr>
<th>R = t-Bu</th>
<th>R = Bu, 82%</th>
<th>R = t-Bu, 88%</th>
<th>2a, R = t-Bu, 89%</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = Me</td>
<td>R = Me, 85%</td>
<td>R = Me, 86%</td>
<td>2b, R = Me, 78%</td>
</tr>
<tr>
<td>R = Et</td>
<td>R = Et, 86%</td>
<td>R = Et, 89%</td>
<td>2c, R = Et, 78%</td>
</tr>
<tr>
<td>R = i-Pr</td>
<td>R = i-Pr, 88%</td>
<td>R = i-Pr, 82%</td>
<td>2d, R = i-Pr, 79%</td>
</tr>
<tr>
<td>R = Bn</td>
<td>R = Bn, 84%</td>
<td>R = Bn, 86%</td>
<td>2e, R = Bn, 82%</td>
</tr>
<tr>
<td>R = isoamy</td>
<td>R = isoamy, 81%</td>
<td>R = isoamy, 89%</td>
<td>2f, R = isoamy, 70%</td>
</tr>
<tr>
<td>R = n-Octane</td>
<td>R = n-Octane, 80%</td>
<td>R = n-Octane, 88%</td>
<td>2g, R = n-Octane, 74%</td>
</tr>
</tbody>
</table>

To a solution of (B) (1 equiv., 16.1 mmol) in MeOH (20 mL) cooled to 0 °C, was slowly added NaBH$_4$ (1.5 equiv., 24 mmol). The resulting solution was warmed to room temperature and stirred for 30 minutes following which the solvent was removed under reduced pressure and the residue was diluted with water (50 mL) and extracted with ethyl acetate (50 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (petroleum ether/ethyl acetate = 4/1) to give C as a yellow oil.

To a solution of C (1 equiv., 10 mmol) and Et$_3$N (4.0 equiv., 40 mmol) in DCM (100 mL) at 0 °C was slowly added a solution of POCl$_3$ (1.5 equiv.) in DCM (10 mL) over 25 minutes. The resulting
solution was warmed to room temperature and stirred for 4 h. The solution was quenched with water (20 mL) and transferred to a separatory funnel and the layers were separated. The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate = 50/1) to give the vinyl diazo esters (2a–2g) as red oils.

**tert-butyl 2-diazo-3-enoate (2a):**

Reaction performed by following the general procedure (II), using ethyl tert-butyl acetoacetate (3.16 g, 20 mmol); Yield: 80%, (2.36 g); Physical appearance: red oil; TLC $R_f$ 0.3 (50:1 Petroleum ether: EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.15 (dd, $J$ = 17.4, 11.0 Hz, 1H), 5.10 (d, $J$ = 11.0 Hz, 1H), 4.84 (d, $J$ = 17.4 Hz, 1H), 1.52 (s, 9H). Spectral data obtained were in good agreement with those reported in the literature.$^{2a}$

**Methyl 2-diazo-3-enoate (2b):**

Reaction performed by following the general procedure (II), using ethyl methyl acetoacetate (2.32 g, 20 mmol); Yield: 78%, (1.69 g); Physical appearance: red oil; TLC $R_f$ 0.3 (50:1 Petroleum ether: EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.18 (dd, $J$ = 17.4, 11.0 Hz, 1H), 5.15 (d, $J$ = 11.9 Hz, 1H), 4.89 (d, $J$ = 17.4 Hz, 1H), 3.83 (s, 3H). Spectral data obtained were in good agreement with those reported in the literature.$^{2b}$

**Ethyl 2-diazo-3-enoate (2c):**

Reaction performed by following the general procedure (II), using ethyl acetoacetate (1.30 g, 10 mmol); Yield: 78%, (1.09 g); Physical appearance: red oil; TLC $R_f$ 0.3 (50:1 Petroleum ether: EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.19 (dd, $J$ = 17.4, 11.0 Hz, 1H), 5.13 (d, $J$ = 11.0 Hz, 1H), 4.88 (d, $J$ = 17.4 Hz, 1H), 4.29 (q, $J$ = 7.1 Hz, 2H), 1.32 (t, $J$ = 7.1 Hz, 3H). Spectral data obtained were in good agreement with those reported in the literature.$^{2a}$
**Isopropyl 2-diazobut-3-enoate (2d):** \(^{2b}\)

Reaction performed by following the general procedure (II), using ethyl acetoacetate (2.88 g, 20 mmol); Yield: 79%, (2.00 g); Physical appearance: red oil; TLC \( R_f \) 0.3 (50:1 Petroleum ether: EtOAc); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 6.19 (dd, \( J = 17.4, 11.0 \) Hz, 1H), 5.20 – 5.14 (m, 1H), 5.12 (d, \( J = 11.0 \) Hz, 1H), 4.86 (d, \( J = 17.4 \) Hz, 1H), 1.31 (s, 3H), 1.29 (s, 4H). Spectral data obtained were in good agreement with those reported in the literature.\(^{2b}\)

**Benzyl 2-diazobut-3-enoate (2e):** \(^{2a}\)

Reaction performed by following the general procedure (II), using benzyl acetoacetate (3.84 g, 20 mmol); Yield: 82%, (2.85 g); Physical appearance: red oil; TLC \( R_f \) 0.3 (50:1 Petroleum ether: EtOAc); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.46 – 7.31 (m, 5H), 6.22 (dd, \( J = 17.4, 11.0 \) Hz, 1H), 5.29 (s, 2H), 5.15 (d, \( J = 11.0 \) Hz, 1H), 4.90 (d, \( J = 17.4 \) Hz, 1H). Spectral data obtained were in good agreement with those reported in the literature.\(^{2a}\)

**Isopentyl 2-diazobut-3-enoate (2f):** \(^{2a}\)

Reaction performed by following the general procedure (II), using isoamyl acetoacetate (3.44 g, 20 mmol); Yield: 90%, (2.27 g); Physical appearance: red oil; TLC \( R_f \) 0.3 (50:1 Petroleum ether: EtOAc); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 6.19 (dd, \( J = 17.4, 11.0 \) Hz, 1H), 5.13 (d, \( J = 11.0 \) Hz, 1H), 4.88 (d, \( J = 17.4 \) Hz, 1H), 4.27 (t, \( J = 6.8 \) Hz, 2H), 1.78 – 1.67 (m, 1H), 1.63 – 1.53 (m, 3H), 0.96 (s, 3H), 0.95 (s, 3H). Spectral data obtained were in good agreement with those reported in the literature.\(^{2a}\)

**Octyl 2-diazobut-3-enoate (2g):**

Reaction performed by following the general procedure (II), using octyl acetoacetate (4.28 g, 20 mmol); Yield: 74%, (2.92 g); Physical appearance: red oil; TLC \( R_f \) 0.3 (50:1 Petroleum ether: EtOAc); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 6.24 – 6.03 (m, 1H), 5.11 (d, \( J = 11.0 \) Hz, 1H), 4.85 (d, \( J = 17.4 \) Hz, 1H), 4.25 – 4.16 (m, 2H), 1.71 – 1.58 (m, 2H), 1.41 – 1.17 (m, 10H), 0.95 – 0.81 (m, 3H); \(^{13}\)C NMR (126
MHz, CDCl3) δ 164.86, 120.51, 107.24, 65.26, 31.74, 29.15, 28.75, 25.80, 22.60, 14.02;

HRMS (ESI-ToF) m/z: [M+Na]+ Calcd. for C12H20N2O2 247.1417; Found 247.1394.

(i) General Procedure for the synthesis of vinyl diazo esters:

In an oven-dried round bottom flask equipped with a magnetic stir bar, the alcohol (10 mmol, 1 equiv.) and 2,2,6-trimethyl-1,3-dioxene-4-one (12 mmol, 1.2 equiv.) were dissolved in xylene (6 mL) and the resulting mixture was refluxed at 140 °C for 2 h under argon. The solvent was then evaporated by vacuum distillation, leaving behind a black oil. The crude mixture was purified by silica gel flash column chromatography (PE/EA = 10:1) to give the acetoacetate.

To a solution of the acetoacetate synthesized above (1 equiv., 12 mmol) in MeCN (25 mL), cooled to 0 °C, was added p-acetamidobenzenesulfonyl azide (1.1 equiv., 13.2 mmol), followed by triethylamine (1.5 equiv., 18 mmol), and the resulting reaction was allowed to warm to rt for 2 h. The resulting pale-yellow precipitate was filtered, and the residue was concentrated, which is dissolved in DCM, and washed with brine, after which the DCM layer was concentrated and then purified by silica gel flash column chromatography (PE/EA = 10:1) to give 2-diazo-3-oxobutanoate A.

To a solution of 2-diazo-3-oxobutanoate A (1 equiv., 10 mmol) in MeOH (30 mL) cooled to 0 °C, was added NaBH4 (1.5 equiv., 15 mmol), slowly, in portions. The resulting solution was warmed to room temperature and stirred for 1 h. Thereafter, the MeOH was evaporated under reduced pressure and the residue was diluted with water and the mixture was extracted with ethyl acetate. The resulting residue was dried over anhydrous Na2SO4 and filtered. After the solvent was removed under reduced pressure, the crude product was purified by silica gel flash column chromatography (PE/EA = 5:1) to give 2-diazo-3-hydroxybutanoate as a yellow oil.

To a solution of 2-diazo-3-hydroxybutanoate (8 mmol, 1 equiv.) and Et3N (4.0 equiv., 32 mmol) in DCM (40 mL) cooled to 0 °C, was slowly added a solution of POCl3 (1.5 equiv., 12.0 mmol) in
DCM (10 mL) over 20 minutes. The resulting solution was warmed to room temperature and stirred for 2 h. The solution was washed with water and dried over anhydrous Na₂SO₄. The crude product was purified by silica gel flash chromatography (PE/EA = 50:1) to afford the vinyl diazoesters (2h–2l).

Notes: (a) We have never observed any explosion during the preparation and manipulation of vinyl diazo compounds at the scales indicated here. (b) All the vinyl diazo ester were stored in the freezer at −20 °C.

(3aS,5S,6R,6aS)-5-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 2-diazobut-3-enoate (2h): ²c

Reaction performed by following above general procedure (II), using (3aS,5S,6R,6aS)-5-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 3-oxobutanoate (3.4 g, 10 mmol); Yield: 80%, (2.52 g); Physical appearance: red oil; TLC Rf 0.3 (50:1 Petroleum ether: EtOAc); 'H NMR (500 MHz, CDCl₃) δ 6.15 (dd, J = 17.4, 11.0 Hz, 1H), 5.91 (d, J = 3.6 Hz, 1H), 5.36 (d, J = 2.6 Hz, 1H), 5.18 (d, J = 11.0 Hz, 1H), 4.93 (d, J = 17.4 Hz, 1H), 4.61 (d, J = 3.6 Hz, 1H), 4.26 (dd, J = 8.0, 2.9 Hz, 1H), 4.22 – 4.16 (m, 1H), 4.16 – 4.07 (m, 1H), 4.03 (dd, J = 8.5, 4.9 Hz, 1H), 1.55 (s, 3H), 1.43 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H). Spectral data obtained were in good agreement with those reported in the literature. ²c

(4aR,6aR,6bS,8aS,12aS,12bS,14bR)-methyl 10-((2-diazobut-3-enoyl)oxy)-2,2,6a,6b,9,9,12a-heptamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydricene-4a-carboxylate (2i): ²c

Reaction performed by following above general procedure (II), using methyl (4aR,6aR,6bS,8aS,12aS,12bS,14bR)-2,2,6a,6b,9,9,12a-heptamethyl-10-((3-oxobutanoyl)oxy)-1,3,4,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-octadecahydricene-4a(2H)-carboxylate (2.77 g, 5 mmol); Yield: 71%, (1.20 g); Physical appearance: red solid; TLC Rf 0.3 (50:1 Petroleum ether: EtOAc); 'H NMR (500 MHz, CDCl₃) δ 6.19 (dd, J = 17.4, 11.0 Hz, 1H), 5.31 (t, J = 3.5 Hz, 1H), 5.13 (d, J = 11.0 Hz, 1H), 4.88 (d, J = 17.4 Hz, 1H), 4.63 (dd, J = 11.3, 5.0 Hz, 1H), 3.65 (s, 3H), 2.89 (dd, J = 13.9, 4.1 Hz, 1H), 2.04 – 1.95 (m, 1H), 1.95 –
1.87 (m, 2H), 1.77 – 1.59 (m, 10H), 1.51 – 1.24 (m, 5H), 1.24 – 1.02 (m, 7H), 0.96 (d, $J = 4.9$ Hz, 6H), 0.94 – 0.90 (m, 6H), 0.86 (d, $J = 8.8$ Hz, 3H), 0.75 (s, 3H). Spectral data obtained were in good agreement with those reported in the literature.\textsuperscript{2c}

(R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl 2-diazobut-3-enoate (2j): \textsuperscript{2c}

Reaction performed by following above general procedure (II), using (R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl 3-oxobutanoate (2.57 g, 5 mmol); Yield: 70\%, (1.52 g); Physical appearance: red oil; TLC $R_f$ 0.3 (50:1 Petroleum ether: EtOAc); \textsuperscript{1H NMR} (500 MHz, CDCl$_3$) δ 6.33 (dd, $J = 17.2$, 11.1 Hz, 1H), 5.22 (d, $J = 11.0$ Hz, 1H), 5.00 (d, $J = 17.4$ Hz, 1H), 2.63 (t, $J = 6.7$ Hz, 2H), 2.14 (d, $J = 10.7$ Hz, 3H), 2.08 (s, 3H), 2.05 (d, $J = 8.4$ Hz, 3H), 1.94 – 1.96 (m, 2H), 1.61 – 1.52 (m, 3H), 1.39 – 1.21 (m, 15H), 1.18 – 1.07 (m, 6H), 0.92 – 0.88 (m, 12H). Spectral data obtained were in good agreement with those reported in the literature.\textsuperscript{2}

(3R,8R,9R,10S,13S,14R)-3-((1-diazoallyl)oxy)-10,13-dimethyl-17-((S)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene (2k): \textsuperscript{2c}

Reaction performed by following above general procedure (II), using (3S,8S,9S,10R,13R,14S)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 3-oxobutanoate (2.35 g, 5 mmol); Yield: 66\%, (9.52 g); Physical appearance: red solid; TLC $R_f$ 0.3 (50:1 Petroleum ether: EtOAc); \textsuperscript{1H NMR} (500 MHz, CDCl$_3$) δ 6.20 (dd, $J = 17.4$, 11.0 Hz, 1H), 5.41 (d, $J = 4.9$ Hz, 1H), 5.13 (d, $J = 11.0$ Hz, 1H), 4.87 (d, $J = 17.4$ Hz, 1H), 4.75 (dt, $J = 10.6$, 5.5 Hz, 1H), 2.44 – 2.31 (m, 2H), 2.13 – 1.77 (m, 6H), 1.69 – 1.39 (m, 10H), 1.29 – 0.95 (m, 16H), 0.89 (dd, $J = 6.6$, 2.2 Hz, 6H), 0.70 (s, 3H). Spectral data obtained were in good agreement with those reported in the literature.\textsuperscript{2c}
(E)-3,7-dimethylocta-2,6-dien-1-yl 2-diazobut-3-enoate (2l):

Reaction performed by following above general procedure (II), using 3,7-dimethyloct-6-en-1-yl 3-oxobutanoate (2.38 g, 10 mmol); Yield: 60%, (1.48 g); Physical appearance: red oil; TLC $R_f$ 0.3 (50:1 Petroleum ether: EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.19 (dd, $J = 17.4$, 11.0 Hz, 1H), 5.39 (t, $J = 7.1$ Hz, 1H), 5.16 – 5.07 (m, 2H), 4.86 (d, $J = 17.3$ Hz, 1H), 4.72 (d, $J = 7.3$ Hz, 2H), 2.21 – 2.05 (m, 4H), 1.79 (s, 3H), 1.70 (s, 3H), 1.62 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 159.69, 137.75, 127.01, 118.29, 115.36, 113.85, 102.04, 56.47, 48.21, 26.96, 21.43, 20.45, 18.30, 12.44; ESI-HRMS: Calcd. for C$_{14}$H$_{20}$N$_2$O$_2$ [M+Na]$^+$ 271.1417; Found 271.1411.
(2) Optimization details for C–H bond allylation of benzamides:

**Table S1: Optimization of catalyst:**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Catalyst</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Co(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>28%</td>
</tr>
<tr>
<td>2.</td>
<td>Co(OAc)&lt;sub&gt;2&lt;/sub&gt;·4H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>26%</td>
</tr>
<tr>
<td>3.</td>
<td>Co(acac)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>45%</td>
</tr>
<tr>
<td>4.</td>
<td>Co(acac)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>NR</td>
</tr>
<tr>
<td>5.</td>
<td>CoCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>NR</td>
</tr>
<tr>
<td>6.</td>
<td>Ni(acac)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>NR</td>
</tr>
<tr>
<td>7.</td>
<td>Ni(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>NR</td>
</tr>
</tbody>
</table>

<sup>a</sup> Isolated yield; NR = No reaction

**Table S2: Optimization of base:**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Base</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>KOPiv</td>
<td>45%</td>
</tr>
<tr>
<td>2.</td>
<td>KOAc</td>
<td>26%</td>
</tr>
<tr>
<td>3.</td>
<td>CsOPiv</td>
<td>NR</td>
</tr>
<tr>
<td>4.</td>
<td>NaOPiv.H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>65%</td>
</tr>
<tr>
<td>5.</td>
<td>NaOAc</td>
<td>21%</td>
</tr>
<tr>
<td>6.</td>
<td>NaOPiv.H&lt;sub&gt;2&lt;/sub&gt;O (2 equiv.)</td>
<td>61%</td>
</tr>
<tr>
<td>7.</td>
<td>NaOPiv. H&lt;sub&gt;2&lt;/sub&gt;O (50 mol%)</td>
<td>56%</td>
</tr>
</tbody>
</table>

<sup>a</sup> Isolated yield; NR = No reaction
Table S3. Optimization of photocatalyst:

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Photocatalyst (PC)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Eosin blue</td>
<td>45%</td>
</tr>
<tr>
<td>2.</td>
<td>Ru(bpy)&lt;sub&gt;3&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>41%</td>
</tr>
<tr>
<td>3.</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;[Eosin Y]</td>
<td>65%</td>
</tr>
<tr>
<td>4.</td>
<td>Rose Bengal</td>
<td>NR</td>
</tr>
<tr>
<td>5.</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;[Eosin Y] (10 mol%)</td>
<td>40%</td>
</tr>
<tr>
<td>6.</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;[Eosin Y] (30 mol%)</td>
<td>63%</td>
</tr>
<tr>
<td>7.&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;[Eosin Y]</td>
<td>21%</td>
</tr>
</tbody>
</table>

<sup>a</sup> Isolated yield; <sup>b</sup> N<sub>2</sub> balloon were used; N.R. = No reaction

Table S4. Optimization of solvent:

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Solvent</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>DCE</td>
<td>NR</td>
</tr>
<tr>
<td>2.</td>
<td>MeOH</td>
<td>29%</td>
</tr>
<tr>
<td>3.</td>
<td>TFE</td>
<td>65%</td>
</tr>
<tr>
<td>4.</td>
<td>HFIP</td>
<td>34%</td>
</tr>
<tr>
<td>5.</td>
<td>MeCN</td>
<td>39%</td>
</tr>
<tr>
<td>6.</td>
<td>EtOH</td>
<td>21%</td>
</tr>
<tr>
<td>7.</td>
<td>DMF</td>
<td>NR</td>
</tr>
<tr>
<td>8.&lt;sup&gt;b&lt;/sup&gt;</td>
<td>TFE</td>
<td>41%</td>
</tr>
</tbody>
</table>

<sup>a</sup> Isolated yield; NR = No reaction; <sup>b</sup> 10 mol% of Co(acac)<sub>2</sub> was used.
(3) General procedure for the cobalt-catalyzed C–H allylation of benzamides:

In an oven-dried pressure tube equipped with a stir bar, the N-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol) and vinyl diazo ester (1.5 equiv., 0.15 mmol) were dissolved in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which Co(acac)$_2$ (20 mol%, 0.02 mmol), NaOPiv·H$_2$O (1 equiv., 0.1 mmol), and Na$_2$[Eosin Y] (20 mol%, 0.02 mmol) were added, the pressure tube was sealed with a septum cap. This reaction mixture was then stirred in a green LED (3W × 20) environment under an O$_2$ atmosphere using oxygen balloon. After 24 hours, the second portion of vinyl diazo ester (1.5 equiv., 0.15 mmol) was added and the reaction progress was further monitored by TLC. Upon completion of the reaction, the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite, and the filtrate was concentrated. The residue was dissolved in EtOAc and washed with saturated NaHCO$_3$ solution and brine. The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography.

**Figure 1:** Reaction Setup (0.1 mmol scale)
Analytical data of C–H allylated products:

**tert-butyl (E)-4-(3,5-dimethyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3a):**

Reaction performed on 0.1 mmol scale (28 mg); Yield: 61% (26 mg); Physical appearance: brown gel; TLC Rf 0.2 (4:1, Petroleum ether: EtOAc); \[^1H\text{NMR}\] (500 MHz, CDCl\(_3\)) \(\delta 9.95\) (s, 1H), \(8.99\) (dd, \(J = 7.5, 1.4\) Hz, 1H), \(8.75\) (dd, \(J = 4.2, 1.6\) Hz, 1H), \(8.20\) (dd, \(J = 8.1, 1.3\) Hz, 1H), \(7.66 - 7.56\) (m, 2H), \(7.46\) (dd, \(J = 8.3, 4.2\) Hz, 1H), \(7.03\) (s, 1H), \(7.02 - 6.96\) (m, 1H), \(6.95\) (s, 1H), \(5.71\) (d, \(J = 15.9\) Hz, 1H), \(3.60\) (d, \(J = 6.8\) Hz, 2H), \(2.44\) (s, 3H), \(2.38\) (s, 3H), \(1.37\) (s, 9H); \[^{13}C\text{NMR}\] (126 MHz, CDCl\(_3\)) \(\delta 168.43, 165.67, 148.34, 145.50, 139.25, 138.51, 136.27, 135.26, 134.96, 134.78, 134.29, 129.60, 128.03, 128.00, 127.40, 124.37, 121.97, 121.64, 116.73, 79.95, 35.88, 28.03, 21.22, 19.53; IR (KBr cm\(^{-1}\)): 2976, 2927, 1709, 1674, 1596, 1482, 1145, 982, 885, 851, 826; HRMS (ESI-ToF) m/z: [M+H]\(^+\) Calcd. for C\(_{26}\)H\(_{29}\)N\(_2\)O\(_3\) [M+H]\(^+\) 417.2173; found 417.2198.

**tert-butyl (E)-4-(5-bromo-3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3b):**

Reaction performed on 0.1 mmol scale (34 mg); Yield: 62% (30 mg); Physical appearance: colorless gel; TLC Rf 0.2 (4:1, Petroleum ether: EtOAc); \[^1H\text{NMR}\] (500 MHz, CDCl\(_3\)) \(\delta 9.95\) (s, 1H), \(8.94\) (dd, \(J = 6.9, 2.0\) Hz, 1H), \(8.77\) (dd, \(J = 4.2, 1.6\) Hz, 1H), \(8.21\) (dd, \(J = 8.3, 1.5\) Hz, 1H), \(7.67 - 7.58\) (m, 2H), \(7.47\) (dd, \(J = 8.3, 4.2\) Hz, 1H), \(7.38\) (s, 1H), \(7.30\) (s, 1H), \(6.95\) (dt, \(J = 15.5, 6.8\) Hz, 1H), \(5.72\) (d, \(J = 15.5\) Hz, 1H), \(3.60\) (d, \(J = 6.7\) Hz, 2H), \(2.45\) (s, 3H), \(1.38\) (s, 9H); \[^{13}C\text{NMR}\] (126 MHz, CDCl\(_3\)) \(\delta 167.17, 165.37, 148.48, 144.24, 138.43, 137.31, 137.00, 136.80, 136.35, 133.94, 131.77, 130.28, 128.00, 127.35, 125.05, 123.32, 122.32, 121.76, 116.86, 80.19, 35.61, 28.02, 19.42; IR (KBr cm\(^{-1}\)): 2976, 2954, 2131, 1708, 1672, 1481, 1143, 982, 896, 847, 791; HRMS (ESI-ToF) m/z: [M+H]\(^+\) Calcd. for C\(_{25}\)H\(_{29}\)BrN\(_2\)O\(_3\) 481.1121 and 483.1102; Found 481.1095 and 483.1074.
**tert-butyl (E)-4-(5-fluoro-3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3c):**

Reaction performed on 0.1 mmol scale (28 mg); Yield: 58% (24 mg); Physical appearance: yellowish gel; TLC $R_f$ 0.2 (4:1, Petroleum ether: EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 10.01 (s, 1H), 8.97 (dd, $J = 7.3$, 1.6 Hz, 1H), 8.78 (dd, $J = 4.2$, 1.6 Hz, 1H), 8.23 (d, $J = 8.2$ Hz, 1H), 7.68 – 7.59 (m, 2H), 7.49 (dd, $J = 8.2$, 4.2 Hz, 1H), 7.01 – 6.89 (m, 2H), 6.86 (dd, $J = 9.3$, 2.4 Hz, 1H), 5.73 (d, $J = 15.5$ Hz, 1H), 3.62 (d, $J = 6.1$ Hz, 2H), 2.47 (s, 3H), 1.38 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 167.52, 165.41, 162.75 (d, $J = 249.4$ Hz), 148.13, 144.31, 137.99 (d, $J = 8.4$ Hz), 137.60 (d, $J = 7.1$ Hz), 136.96, 133.95 (d, $J = 2.4$ Hz), 128.13, 127.58, 125.01, 122.35, 121.69, 117.41, 115.76, 115.59, 114.23, 114.05, 80.18, 35.80, 28.02, 19.75; $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ –111.94; IR (KBr cm$^{-1}$): 2954, 2925, 1714, 1608, 1483, 1286, 1199, 1049, 826, 791; HRMS (ESI-ToF) m/z: [M+H]$^+$ Calcd. for C$_{25}$H$_{26}$FN$_2$O$_4$ 421.1922; Found 421.1924.

**tert-butyl (E)-4-(4'-methoxy-5-methyl-4-(quinolin-8-ylcarbamoyl)-[1,1'-biphenyl]-3-yl)but 2-enoate (3d):** Reaction performed on 0.1 mmol scale (37 mg); Yield: 61% (31 mg); Physical appearance: yellow solid; M.p. 126–128 °C; TLC $R_f$ 0.2 (4:1, Petroleum ether: EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 10.02 (s, 1H), 9.01 (dd, $J = 7.2$, 1.7 Hz, 1H), 8.77 (dd, $J = 4.6$, 1.4 Hz, 1H), 8.20 (dd, $J = 8.5$, 1.8 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.59 – 7.55 (m, 2H), 7.46 (dd, $J = 8.5$, 4.6 Hz, 1H), 7.39 (s, 1H), 7.32 (s, 1H), 7.07 – 7.01 (m, 1H), 5.75 (d, $J = 15.7$ Hz, 1H), 3.90 (s, 3H), 3.70 (d, $J = 6.2$ Hz, 1H), 2.54 (s, 3H), 1.36 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 168.18, 165.58, 159.51, 148.39, 145.34, 141.94, 138.50, 136.30, 136.24, 135.54, 135.36, 134.22, 132.86, 128.28, 128.01, 127.39, 127.28, 125.83, 124.51, 122.08, 121.68, 116.80, 114.31, 80.00, 55.40, 36.14, 28.02, 19.80; IR (KBr cm$^{-1}$): 2976, 2925, 1709, 1674, 1488, 1178, 1034, 955, 906, 827, 791; HRMS (ESI-ToF) m/z: [M+H]$^+$ Calcd. for C$_{32}$H$_{33}$N$_2$O$_4$ 509.2435; Found 509.2432.
**tert-butyl (E)-4-(3,4-dimethyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3e):**

Reaction performed on 0.1 mmol scale (28 mg); Yield: 65% (27 mg); Physical appearance: colourless gel; TLC \( R_f \) 0.2 (4:1, Petroleum ether: EtOAc); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 9.95 (s, 1H), 8.99 (dd, \( J = 7.2, 1.5 \) Hz, 1H), 8.74 (dd, \( J = 4.2 \) Hz, 1.5 Hz, 1H), 8.19 (dd, \( J = 8.2, 1.6 \) Hz, 1H), 7.67 – 7.54 (m, 2H), 7.44 (dd, \( J = 8.2, 4.1 \) Hz, 1H), 7.20 (d, \( J = 7.8 \) Hz, 1H), 7.13 (d, \( J = 7.8 \) Hz, 1H), 6.96 (dt, \( J = 15.6, 6.2 \) Hz, 1H), 5.59 (dt, \( J = 15.6, 1.7 \) Hz, 1H), 3.62 (d, \( J = 6.0 \) Hz, 2H), 2.42 (s, 3H), 2.33 (s, 3H), 1.36 (s, 9H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 168.80, 165.70, 148.26, 144.76, 138.69, 138.33, 136.43, 134.84, 134.18, 132.43, 132.31, 131.20, 128.91, 128.03, 127.43, 123.91, 122.06, 121.60, 116.92, 79.92, 33.44, 28.05, 19.40, 19.27; IR (KBr cm\(^{-1}\)): 2975, 2923, 1708, 1674, 1456, 1273, 1144, 973, 907, 826, 791; HRMS (ESI-ToF) \( m/z \): [M+H]\(^+\) Calcd. For C\(_{26}\)H\(_{29}\)N\(_2\)O\(_4\) 417.2173; Found 417.2189.

**tert-butyl (E)-4-(4-methoxy-3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3f):**

Reaction performed on 0.1 mmol scale (29 mg); Yield: 62% (26 mg); Physical appearance: yellowish gel; TLC \( R_f \) 0.2 (4:1, Petroleum ether: EtOAc); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 9.97 (s, 1H), 8.99 (dd, \( J = 7.4, 1.6 \) Hz, 1H), 8.75 (dd, \( J = 4.2, 1.5 \) Hz, 1H), 8.20 (dd, \( J = 8.3, 1.7 \) Hz, 1H), 7.67 – 7.56 (m, 2H), 7.46 (dd, \( J = 8.3, 4.2 \) Hz, 1H), 7.11 (d, \( J = 8.4 \) Hz, 1H), 6.98 (dt, \( J = 15.6, 6.3 \) Hz, 1H), 6.92 (d, \( J = 8.5 \) Hz, 1H), 5.69 (dt, \( J = 15.5, 1.5 \) Hz, 1H), 3.89 (s, 3H), 3.57 (dd, \( J = 6.7, 1.2 \) Hz, 2H), 2.32 (s, 3H), 1.35 (s, 9H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 168.02, 165.68, 156.64, 148.26, 145.87, 139.04, 138.35, 136.45, 134.13, 128.21, 128.04, 127.44, 126.30, 124.11, 123.74, 122.09, 121.65, 116.95, 111.06, 79.88, 55.69, 35.33, 28.01, 13.09; IR (KBr cm\(^{-1}\)): 2975, 927, 1707, 675, 1325, 1145, 1095, 985, 847, 826; HRMS (ESI-ToF) \( m/z \): [M+H]\(^+\) Calcd. for C\(_{26}\)H\(_{29}\)N\(_2\)O\(_4\) 433.2122; Found 433.2143.
**tert-butyl (E)-4-(4-bromo-3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3g):**

Reaction performed on 0.1 mmol scale (34 mg); Yield: 61% (29 mg); Physical appearance: colourless gel; TLC $R_f$ 0.2 (4:1, Petroleum ether: EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) δ 9.95 (s, 1H), 8.96 (d, $J = 6.8$ Hz, 1H), 8.77 (d, $J = 4.2$ Hz, 1H), 8.21 (d, $J = 8.2$ Hz, 1H), 7.67 – 7.58 (m, 3H), 7.47 (dd, $J = 8.2$, 4.1 Hz, 1H), 7.03 (d, $J = 8.2$ Hz, 1H), 6.95 (dt, $J = 15.6$, 6.4 Hz, 1H), 5.69 (d, $J = 15.5$ Hz, 1H), 3.57 (d, $J = 6.5$ Hz, 2H), 2.52 (s, 3H), 1.37 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 167.13, 165.39, 148.48, 144.54, 139.42, 138.42, 136.34, 134.75, 134.75, 134.11, 133.89, 133.44, 128.92, 128.00, 127.33, 124.81, 124.25, 122.40, 121.77, 116.92, 80.12, 35.57, 28.02, 20.40; IR (KBr cm$^{-1}$): 2977, 2929, 1710, 1675, 1483, 1325, 1146, 983, 901, 826, 791; HRMS (ESI-ToF) m/z: [M+H]$^+$ Calcd. for C$_{25}$H$_{26}$BrN$_2$O$_3$ 481.1121 and 483.1102; Found 481.1140 and 483.1127.

**tert-butyl (E)-4-(4-chloro-3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3h):**

Reaction performed on 0.1 mmol scale (30 mg); Yield: 64% (28 mg); Physical appearance: yellowish gel; TLC $R_f$ 0.2 (4:1, Petroleum ether: EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) δ 9.95 (s, 1H), 8.96 (d, $J = 6.9$ Hz, 1H), 8.77 (d, $J = 4.4$ Hz, 1H), 8.21 (d, $J = 8.2$ Hz, 1H), 7.72 – 7.55 (m, 2H), 7.48 (dd, $J = 8.2$, 4.2 Hz, 1H), 7.44 (d, $J = 8.2$ Hz, 1H), 7.11 (d, $J = 8.2$ Hz, 1H), 6.95 (dt, $J = 15.5$, 6.5 Hz, 1H), 5.69 (d, $J = 15.5$ Hz, 1H), 3.59 (d, $J = 6.6$ Hz, 2H), 2.49 (s, 3H), 1.37 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 167.11, 165.42, 148.47, 144.65, 139.46, 138.43, 136.34, 133.89, 133.69, 133.39, 133.10, 130.12, 128.64, 128.00, 127.34, 124.77, 122.38, 121.76, 116.92, 80.12, 35.53, 28.01, 17.40; IR (KBr cm$^{-1}$): 2979, 2929, 1710, 1675, 1483, 1147, 1120, 984, 904, 826, 791; HRMS (ESI-ToF) m/z: [M+H]$^+$ Calcd. for C$_{25}$H$_{26}$ClN$_2$O$_3$ 437.1626; Found 437.1655.
**tert-butyl (E)-4-(4-acetoxy-3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3i):**

Reaction performed on 0.1 mmol scale (32 mg); Yield: 57% (26 mg); Physical appearance: Off-white solid; M.p. 112–114 °C; TLC Rf 0.2 (4:1, Petroleum ether: EtOAc); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 9.99 (s, 1H), 8.97 (d, J = 7.9 Hz, 1H), 8.76 (d, J = 2.0 Hz, 1H), 8.19 (d, J = 8.2 Hz, 1H), 7.72 (d, J = 7.7 Hz, 1H), 7.67 – 7.55 (m, 2H), 7.46 (dd, J = 7.9, 4.1 Hz, 2H), 7.25 (d, J = 8.3 Hz, 2H), 7.15 – 7.07 (m, 2H), 6.90 (dt, J = 15.4, 6.4 Hz, 1H), 5.67 (d, J = 15.5 Hz, 1H), 3.55 (d, J = 6.4 Hz, 2H), 2.46 (s, 3H), 2.33 (s, 3H), 1.33 (s, 9H); \(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 169.31, 167.05, 165.44, 148.44, 147.38, 143.72, 139.34, 138.45, 136.27, 134.02, 132.74, 127.98, 127.32, 126.81, 124.39, 123.49, 122.26, 121.72, 116.84, 79.96, 30.96, 27.98, 21.00, 19.24; \(\text{IR (KBr \, cm}^{-1}\text{): 2978, 2930, 2927, 276, 2757, 1708, 1674, 1482, 1474, 1431, 1391, 1384, 1362, 1340, 1327, 1312, 1307, 1274, 1272, 1261, 1242, 1211, 1170, 7992, 3579, 2803, 1998, 1672; \text{HRMS (ESI-ToF) m/z: [M+H]}^+ \text{ Calcd. for C}_{27}\text{H}_{29}\text{N}_{2}\text{O}_{5} 461.2071; \text{Found 461.2086.}}

**tert-butyl (E)-4-(3,6-dimethyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3j):**

Reaction performed on 0.1 mmol scale (28 mg); Yield: 64% (27 mg); Physical appearance: Off-white solid; M.p. 110–112 °C; TLC Rf 0.2 (4:1, Petroleum ether: EtOAc); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 9.97 (s, 1H), 9.01 (dd, J = 7.4, 1.4 Hz, 1H), 8.75 (dd, J = 4.2, 1.6 Hz, 1H), 8.21 (dd, J = 8.3, 1.6 Hz, 1H), 7.69 – 7.56 (m, 2H), 7.46 (dd, J = 8.3, 4.2 Hz, 1H), 7.23 (d, J = 7.8 Hz, 1H), 7.06 (d, J = 7.8 Hz, 1H), 6.98 (dt, J = 15.5, 6.8 Hz, 1H), 5.69 (dt, J = 15.5, 1.5 Hz, 1H), 3.59 (d, J = 6.7 Hz, 2H), 2.36 (s, 3H), 2.34 (s, 3H), 1.36 (s, 9H); \(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 168.85, 165.64, 148.23, 145.61, 138.32, 138.16, 136.52, 135.91, 134.16, 133.27, 132.13, 130.78, 128.06, 127.47, 127.24, 124.28, 122.11, 121.64, 117.01, 79.92, 35.79, 28.03, 19.98, 16.72; \(\text{IR (KBr \, cm}^{-1}\text{): 276, 2927, 1708, 1674, 1482, 1151, 1083, 982, 898, 849, 826; \text{HRMS (ESI-ToF) m/z: [M+Na]}^+ \text{ Calcd. for C}_{26}\text{H}_{28}\text{N}_{2}\text{O}_{3}\text{Na} 439.1992; \text{Found 439.2022.}}\)
**tert-butyl (E)-4-(3-ethyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enolate (3k):**

Reaction performed on 0.1 mmol scale (28 mg); Yield: 66% (28 mg); Physical appearance: colorless gel; TLC *R*ₚ 0.2 (4:1, Petroleum ether: EtOAc); **¹H NMR** (500 MHz, CDCl₃) δ 9.97 (s, 1H), 8.99 (dd, *J* = 7.4, 1.5 Hz, 1H), 8.75 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.69 – 7.57 (m, 2H), 7.46 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.00 (dt, *J* = 15.5, 6.9 Hz, 1H), 5.71 (dt, *J* = 15.5, 1.5 Hz, 1H), 3.63 (dd, *J* = 6.7, 1.2 Hz, 2H), 2.80 (q, *J* = 7.6 Hz, 2H), 1.36 (s, 9H), 1.30 (t, *J* = 7.2 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 168.18, 165.58, 148.37, 145.29, 141.22, 138.46, 137.43, 136.27, 134.69, 134.19, 129.54, 128.00, 127.40, 127.39, 127.24, 124.46, 122.08, 121.67, 116.79, 79.97, 35.92, 28.01, 26.55, 15.89; **IR** (KBr cm⁻¹): 2976, 2930, 1708, 1673, 1488, 1180, 1034, 955, 906, 827, 791, 764; **HRMS** (ESI-ToF) *m/z*: [M+H]^+^ Calcd. for C₂₆H₂₉N₂O₄ 417.2173; Found 417.2191.

**tert-butyl (E)-4-(4-methyl-3-(3-oxobutyl)-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enolate (3l):**

Reaction performed on 0.1 mmol scale (33 mg); Yield: 50% (23 mg); Physical appearance: colourless gel; TLC *R*ₚ 0.2 (4:1, Petroleum ether: EtOAc); **¹H NMR** (500 MHz, CDCl₃) δ 9.94 (s, 1H), 8.95 (dd, *J* = 7.1, 1.6 Hz, 1H), 8.73 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.19 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.45 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 6.95 (dt, *J* = 15.6, 6.0 Hz, 1H), 5.57 (d, *J* = 15.6 Hz, 1H), 3.61 (d, *J* = 5.8 Hz, 2H), 3.00 – 2.91 (m, 2H), 2.90 – 2.85 (m, 2H), 2.33 (s, 3H), 2.07 (s, 3H), 1.35 (m, 9H); **¹³C NMR** (126 MHz, CDCl₃) δ 207.86, 168.45, 165.63, 148.39, 144.52, 138.53, 138.43, 136.28, 135.76, 135.58, 134.06, 132.44, 131.49, 128.20, 128.00, 127.33, 123.98, 122.20, 121.65, 116.81, 79.98, 45.63, 33.47, 28.22, 28.04, 27.47, 19.44; **IR** (KBr cm⁻¹): 2977, 1711, 1678, 1520, 1488, 1180, 1034, 955, 906, 827, 791, 764; **HRMS** (ESI-ToF) *m/z*: [M+Na]^+^ Calcd. for C₂₉H₃₂N₂O₄Na 495.2254; Found 495.2276.
**tert-butyl (E)-4-(1-(quinolin-8-ylcarbamoyl)naphthalen-2-yl)but-2-enoate (3m):**

Reaction performed on 0.1 mmol scale (30 mg); Yield: 41% (18 mg); Physical appearance: brown gel; TLC $R_f$ 0.2 (4:1, Petroleum ether: EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) δ 10.18 (s, 1H), 9.12 (d, $J$ = 7.5 Hz, 1H), 8.69 (d, $J$ = 3.8 Hz, 1H), 8.20 (d, $J$ = 7.6 Hz, 1H), 8.09 – 8.02 (m, 1H), 7.95 (d, $J$ = 8.5 Hz, 1H), 7.93 – 7.90 (m, 1H), 7.69 (t, $J$ = 7.9 Hz, 1H), 7.63 (d, $J$ = 8.1 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.46 – 7.40 (m, 2H), 7.09 (dt, $J$ = 15.4, 6.6 Hz, 1H), 5.75 (d, $J$ = 15.6 Hz, 1H), 3.81 (d, $J$ = 6.2 Hz, 2H), 1.39 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 167.69, 165.55, 148.39, 145.01, 138.47, 136.26, 134.67, 134.29, 132.34, 132.32, 130.33, 129.78, 128.08, 128.02, 127.57, 127.39, 127.30, 126.20, 125.10, 124.77, 122.26, 121.70, 116.93, 80.10, 36.25, 28.05; IR (KBr cm$^{-1}$): 2976, 2923, 1710, 1674, 1481, 1090, 907, 830, 791; HRMS (ESI-ToF) $m/z$: [M+H]$^+$ Calcd. for C$_{28}$H$_{27}$N$_2$O$_3$ 439.2016; Found 439.2042.

**methyl (E)-4-(1-(quinolin-8-ylcarbamoyl)-5,6,7,8-tetrahydronaphthalen-2-yl)but-2-enoate (3n):** Reaction performed on 0.1 mmol scale (30 mg); Yield: 61% (24 mg); Physical appearance: Off-white solid; M.p. 118–120 °C; TLC $R_f$ 0.2 (4:1, Petroleum ether: EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) δ 9.93 (s, 1H), 8.99 (dd, $J$ = 7.3, 1.4 Hz, 1H), 8.73 (dd, $J$ = 4.2, 1.6 Hz, 1H), 8.20 (dd, $J$ = 8.3, 1.5 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.59 (dd, $J$ = 8.2, 1.4 Hz, 1H), 7.46 (dd, $J$ = 8.2, 4.0 Hz, 1H), 7.15 (d, $J$ = 7.6 Hz, 1H), 7.14 – 7.08 (m, 1H), 7.04 (d, $J$ = 8.0 Hz, 1H), 5.76 (d, $J$ = 15.7 Hz, 1H), 3.61 – 3.60 (m, 2H), 3.59 (s, 3H), 2.95 – 2.87 (m, 2H), 2.84 (t, $J$ = 5.8 Hz, 2H), 1.88 – 1.73 (m, 4H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 168.43, 166.66, 148.27, 147.34, 138.45, 137.86, 136.53, 136.30, 134.18, 134.08, 131.28, 130.44, 128.01, 127.38, 127.01, 122.11, 122.08, 121.64, 116.79, 51.25, 35.92, 29.55, 26.74, 22.88, 22.67; IR (KBr cm$^{-1}$): 2927, 2856, 1718, 1671, 1481, 1146, 984, 826, 791, 757; HRMS (ESI-ToF) $m/z$: [M+H]$^+$ Calcd. for C$_{25}$H$_{25}$N$_2$O$_3$ 401.1860; Found 401.1869.
**tert-butyl (E)-4-(1-(quinolin-8-ylcarbamoyl)-5,6,7,8-tetrahydronaphthalen-2-yl)but-2-enoate (3o):** Reaction performed on 0.1 mmol scale (30 mg); Yield: 59% (26 mg); Physical appearance: colorless gel; TLC $R_f$ 0.2 (4:1, Petroleum ether: EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.95 (s, 1H), 8.99 (dd, $J = 7.4, 1.3$ Hz, 1H), 8.76 (dd, $J = 4.2, 1.6$ Hz, 1H), 8.19 (dd, $J = 8.3, 1.4$ Hz, 1H), 7.66 – 7.56 (m, 2H), 7.46 (dd, $J = 8.3, 4.2$ Hz, 1H), 7.16 (d, $J = 7.9$ Hz, 1H), 7.06 (d, $J = 7.9$ Hz, 1H), 6.99 (dt, $J = 15.4, 6.8$ Hz, 1H), 5.70 (d, $J = 15.5$ Hz, 1H), 3.58 (d, $J = 6.6$ Hz, 2H), 2.94 – 2.87 (m, 2H), 2.84 (t, $J = 5.7$ Hz, 2H), 1.87 – 1.75 (m, 4H), 1.37 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 168.46, 165.62, 148.35, 145.61, 138.48, 137.80, 136.37, 136.28, 134.23, 133.97, 131.68, 130.39, 128.00, 127.38, 127.05, 124.28, 122.03, 121.65, 116.77, 79.92, 35.67, 29.55, 28.04, 26.78, 22.89, 22.68; IR (KBr cm$^{-1}$): 2976, 2931, 1708, 1672, 1481, 1143, 982, 908, 826, 791; HRMS (ESI-ToF) m/z: [M+H]$^+$ Calcd. for C$_{28}$H$_{31}$N$_2$O$_3$ 443.2329; Found 443.2348.

**tert-butyl (E)-4-(5-cyano-3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3p):**

Reaction performed on 0.1 mmol scale (29 mg); Yield: 56% (24 mg); Physical appearance: brown gel; TLC $R_f$ 0.2 (4:1, Petroleum ether: EtOAc); $^1$H NMR (700 MHz, CDCl$_3$) $\delta$ 9.98 (s, 1H), 8.93 (t, $J = 4.5$ Hz, 1H), 8.77 (d, $J = 4.1$ Hz, 1H), 8.22 (d, $J = 8.2$ Hz, 1H), 7.64 (d, $J = 4.1$ Hz, 2H), 7.52 (s, 1H), 7.49 (dd, $J = 8.2, 4.2$ Hz, 1H), 7.46 (s, 1H), 6.97 – 6.90 (m, 1H), 5.71 (dd, $J = 15.6, 1.6$ Hz, 1H), 3.65 (d, $J = 6.7$ Hz, 2H), 2.51 (s, 3H), 1.38 (s, 9H); $^{13}$C NMR (176 MHz, CDCl$_3$) $\delta$ 166.09, 165.13, 148.60, 143.42, 141.75, 138.36, 136.79, 136.74, 136.44, 133.57, 132.32, 131.05, 128.01, 127.32, 125.55, 122.70, 121.89, 118.23, 117.06, 113.35, 80.42, 35.45, 28.01, 22.36; IR (KBr cm$^{-1}$): 2978, 2925, 1709, 1676, 1523, 1484, 1258, 1148, 828, 759; HRMS (ESI-ToF) m/z: [M+H]$^+$ Calcd. for C$_{26}$H$_{26}$N$_3$O$_3$Na 428.1969; Found 428.1979.
**tert-butyl (E)-4-(3-methyl-5-nitro-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3q):**

Reaction performed on 0.1 mmol scale (30 mg); Yield: 51% (23 mg); Physical appearance: yellowish gel; TLC $R_f$ 0.2 (4:1, Petroleum ether: EtOAc); $^1$H NMR (700 MHz, CDCl$_3$) $\delta$ 10.01 (s, 1H), 8.93 (dd, $J = 4.9, 3.9$ Hz, 1H), 8.76 (dd, $J = 4.2, 1.7$ Hz, 1H), 8.22 (dd, $J = 8.3, 1.7$ Hz, 1H), 8.09 (d, $J = 2.2$ Hz, 1H), 8.02 (d, $J = 2.2$ Hz, 1H), 7.69 – 7.60 (m, 2H), 7.49 (dd, $J = 8.2, 4.2$ Hz, 1H), 6.99 – 6.93 (m, 1H), 5.72 (d, $J = 15.6$ Hz, 1H), 3.71 (d, $J = 6.8$ Hz, 2H), 2.58 (s, 3H), 1.37 (s, 9H); $^{13}$C NMR (176 MHz, CDCl$_3$) $\delta$ 166.00, 165.11, 160.98, 148.62, 148.10, 143.32, 139.03, 138.35, 137.46, 137.07, 136.45, 133.52, 128.01, 127.32, 125.58, 123.78, 122.77, 122.51, 121.91, 117.09, 80.42, 35.76, 28.00, 25.58; IR (KBr cm$^{-1}$): 2977, 1711, 1677, 1522, 1483, 1367, 1325, 1147, 827, 745; HRMS (ESI-ToF) $m/z$: [M+Na]$^+$ Calcd. for C$_{25}$H$_{25}$N$_3$O$_5$Na 470.1686; Found 470.1703.

**tert-butyl (E)-4-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (4a):**

Reaction performed on 0.1 mmol scale (26 mg); Yield: 65% (26 mg) and 1 mmol scale (260 mg)

Yield: 46% (185 mg); Physical appearance: colorless gel; TLC $R_f$ 0.2 (4:1, Petroleum ether: EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.96 (s, 1H), 8.98 (dd, $J = 7.8, 1.4$ Hz, 1H), 8.76 (dd, $J = 4.2, 1.5$ Hz, 1H), 8.20 (dd, $J = 8.3, 1.5$ Hz, 1H), 7.69 – 7.55 (m, 2H), 7.46 (dd, $J = 8.3, 4.2$ Hz, 1H), 7.34 (t, $J = 7.8$ Hz, 1H), 7.21 (d, $J = 7.6$ Hz, 1H), 7.15 (d, $J = 7.7$ Hz, 1H), 7.00 (dt, $J = 15.5, 6.8$ Hz, 1H), 5.71 (d, $J = 15.5$ Hz, 1H), 3.64 (d, $J = 6.7$ Hz, 2H), 2.48 (s, 3H), 1.36 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 168.19, 165.60, 148.40, 145.33, 138.50, 137.92, 136.31, 135.04, 134.80, 134.18, 129.38, 128.87, 128.01, 127.43, 127.39, 124.49, 122.11, 121.69, 116.82, 79.99, 35.90, 28.02, 19.59; IR (KBr cm$^{-1}$): 2980, 2923, 1715, 1670, 1479, 1150, 982, 908, 820, 795; HRMS (ESI-ToF) $m/z$: [M+Na]$^+$ Calcd. for C$_{35}$H$_{26}$N$_3$O$_5$Na 425.1836; Found 425.1813.
**Ethyl (E)-4-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (4b):**

Reaction performed on 0.1 mmol scale (26 mg); Yield: 66% (25 mg); Physical appearance: brown gel; TLC $R_f$ 0.2 (4:1, Petroleum ether: EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.95 (s, 1H), 8.98 (dd, $J = 7.4$, 1.5 Hz, 1H), 8.74 (dd, $J = 4.2$, 1.6 Hz, 1H), 8.20 (dd, $J = 8.3$, 1.6 Hz, 1H), 7.69 – 7.58 (m, 2H), 7.47 (dd, $J = 8.3$, 4.2 Hz, 1H), 7.34 (t, $J = 7.7$ Hz, 1H), 7.22 (d, $J = 7.7$ Hz, 1H), 7.15 (d, $J = 8.0$ Hz, 1H), 7.11 (dt, $J = 15.5$, 6.8 Hz, 1H), 5.77 (dt, $J = 15.6$, 1.6 Hz, 1H), 4.04 (q, $J = 7.1$ Hz, 2H), 3.65 (dd, $J = 6.7$, 1.6 Hz, 2H), 2.48 (s, 3H), 1.18 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 168.15, 166.23, 148.32, 146.66, 138.48, 136.30, 135.14, 134.50, 134.15, 129.42, 128.96, 128.07, 127.42, 127.39, 122.75, 122.14, 121.68, 116.85, 60.09, 36.11, 19.55, 14.14; IR (KBr cm$^{-1}$): 2980, 2921, 1720, 1689, 1510, 1120, 990, 885, 820, 751; HRMS (ESI-ToF) $m/z$: [M+H]$^+$ Calcd. for C$_{23}$H$_{23}$N$_2$O$_3$ 375.1703; Found 375.1723.

**tert-butyl (E)-4-(4-chloro-3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (4c):**

Reaction performed on 0.1 mmol scale (26 mg); Yield: 61% (29 mg); Physical appearance: yellowish gel; TLC $R_f$ 0.2 (4:1, Petroleum ether: EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.97 (s, 1H), 8.99 (dd, $J = 7.3$, 1.6 Hz, 1H), 8.74 (dd, $J = 4.3$, 1.6 Hz, 1H), 8.21 (dd, $J = 8.4$, 1.6 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.48 (dd, $J = 8.3$, 4.2 Hz, 1H), 7.34 (t, $J = 7.7$ Hz, 1H), 7.22 (d, $J = 7.6$ Hz, 1H), 7.16 – 7.14 (m, 1H), 7.13 – 7.08 (m, 1H), 5.77 (dt, $J = 15.6$, 1.4 Hz, 1H), 3.66 (dd, $J = 6.7$, 1.5 Hz, 2H), 3.59 (s, 3H), 2.48 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 168.19, 166.62, 148.13, 147.02, 138.20, 137.92, 136.63, 135.14, 134.39, 134.01, 129.44, 128.97, 128.07, 127.49, 127.37, 122.30, 122.20, 121.64, 117.15, 51.28, 36.17, 29.71, 19.55; IR (KBr cm$^{-1}$): 2980, 2852, 1718, 1672, 1481, 1153, 983, 896, 826, 791; HRMS (APCI-ToF) $m/z$: [M+Na]$^+$ Calcd. for C$_{22}$H$_{20}$N$_2$O$_3$Na 383.1366; Found 383.1394.
Isopropyl \((E)-4-(3\text{-methyl-2-}(\text{quinolin-8-ylcarbamoyl})\text{phenyl})\text{but-2-enoate (4d):}\)

Reaction performed on 0.1 mmol scale (26 mg); Yield: 64% (25 mg); Physical appearance: colorless gel; TLC \(R_f\) 0.2 (4:1, Petroleum ether: EtOAc); \(^1H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 9.96 (s, 1H), 8.99 (dd, \(J = 7.4\), 1.5 Hz, 1H), 8.75 (dd, \(J = 4.2\), 1.6 Hz, 1H), 8.20 (dd, \(J = 8.3\), 1.6 Hz, 1H), 7.68 – 7.57 (m, 2H), 7.46 (dd, \(J = 8.3\), 4.2 Hz, 1H), 7.34 (t, \(J = 7.7\) Hz, 1H), 7.22 (d, \(J = 7.6\) Hz, 1H), 7.15 (d, \(J = 7.7\) Hz, 1H), 7.09 (dt, \(J = 15.5\), 1.6 Hz, 1H), 5.76 (dt, \(J = 15.5\), 1.6 Hz, 1H), 4.94 (sep, \(J = 6.3\) Hz, 1H), 3.65 (dd, \(J = 6.7\), 1.4 Hz, 2H), 2.48 (s, 3H), 1.15 (d, \(J = 6.3\) Hz, 3H); \(^13C\) NMR (126 MHz, CDCl\(_3\)) \(\delta\) 168.22, 165.80, 148.33, 146.32, 138.42, 137.90, 136.43, 135.11, 134.59, 134.10, 129.42, 128.94, 128.04, 127.44, 127.42, 123.24, 122.19, 121.69, 117.00, 67.41, 36.04, 21.78, 19.57; IR (KBr cm\(^{-1}\)): 3054, 2924, 1720, 1667, 1457, 1131, 982, 898, 824, 790, 735; HRMS (ESI-ToF) \(m/z\): [M+Na]\(^+\) Calcd. for C\(_{24}\)H\(_{24}\)N\(_2\)O\(_3\)Na 411.1679; Found 411.1682.

Benzyl \((E)-4-(3\text{-methyl-2-}(\text{quinolin-8-ylcarbamoyl})\text{phenyl})\text{but-2-enoate (4e):}\)

Reaction performed on 0.1 mmol scale (26 mg); Yield: 61% (27 mg); Physical appearance: yellowish gel; TLC \(R_f\) 0.2 (4:1, Petroleum ether: EtOAc); \(^1H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 9.98 (s, 1H), 8.99 (d, \(J = 7.3\) Hz, 1H), 8.64 (d, \(J = 4.1\) Hz, 1H), 8.18 (d, \(J = 8.3\) Hz, 1H), 7.67 – 7.56 (m, 2H), 7.41 (dd, \(J = 8.3\), 4.3 Hz, 1H), 7.39 – 7.29 (m, 4H), 7.29 – 7.26 (m, 2H), 7.22 (d, \(J = 7.9\) Hz, 1H), 7.20 – 7.12 (m, 2H), 5.83 (d, \(J = 15.6\) Hz, 1H), 5.05 (s, 2H), 3.67 (d, \(J = 6.5\) Hz, 2H), 2.48 (s, 3H); \(^13C\) NMR (126 MHz, CDCl\(_3\)) \(\delta\) 168.14, 165.99, 148.24, 147.40, 138.30, 137.95, 136.43, 135.98, 135.18, 134.32, 134.05, 129.43, 128.99, 128.48, 128.15, 128.11, 128.02, 127.44, 127.42, 122.42, 122.18, 121.66, 117.02, 65.97, 36.15, 19.56; IR (KBr cm\(^{-1}\)): 3032, 2924, 1720, 1667, 1457, 1131, 982, 898, 824, 790, 735; HRMS (APCI-ToF) \(m/z\): [M+Na]\(^+\) Calcd. for C\(_{28}\)H\(_{24}\)N\(_2\)O\(_3\)Na 459.1679; Found 459.1708.
Isopentyl (E)-4-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (4f):
Reaction performed on 0.1 mmol scale (26 mg); Yield: 63% (26 mg); Physical appearance:
colorless gel; TLC Rf 0.2 (4:1, Petroleum ether: EtOAc); \(^1H NMR\) (500 MHz, CDCl\(_3\)) \(\delta\) 9.95 (s, 1H), 8.98 (dd, \(J = 7.3, 1.5\) Hz, 1H), 8.74 (dd, \(J = 4.2, 1.5\) Hz, 1H), 8.20 (dd, \(J = 8.3, 1.6\) Hz, 1H), 7.69 – 7.55 (m, 2H), 7.46 (dd, \(J = 8.3, 4.2\) Hz, 1H), 7.34 (t, \(J = 7.1\) Hz, 1H), 7.22 (d, \(J = 7.9\) Hz, 1H), 7.17 – 7.13 (m, 1H), 7.09 (dt, \(J = 15.6, 1.5\) Hz, 1H), 5.78 (d, \(J = 15.6\) Hz, 1H), 4.01 (t, \(J = 7.1\) Hz, 2H), 3.66 (dd, \(J = 6.7, 1.2\) Hz, 2H), 2.48 (s, 3H), 1.67 – 1.55 (m, 1H), 1.43 (q, \(J = 6.9\) Hz, 2H), 0.88 (d, \(J = 6.6\) Hz, 6H); \(^13C NMR\) (126 MHz, CDCl\(_3\)) \(\delta\) 168.15, 166.32, 148.34, 146.59, 138.49, 137.97, 136.31, 135.14, 134.52, 134.15, 129.42, 128.96, 128.01, 127.41, 127.38, 122.80, 122.14, 121.68, 116.85, 62.85, 37.26, 36.09, 24.99, 22.44, 19.56; IR (KBr cm\(^{-1}\)): 2955, 1714, 1674, 1423, 1126, 1089, 982, 895, 826, 790; HRMS (ESI-ToF) m/z: [M+H]\(^+\) Calcd. for C\(_{26}\)H\(_{29}\)N\(_2\)O\(_3\) 417.2173; Found 417.2164.

Octyl (E)-4-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (4g):
Reaction performed on 0.1 mmol scale (26 mg); Yield: 62% (28 mg); Physical appearance:
colorless gel; TLC Rf 0.2 (4:1, Petroleum ether: EtOAc \(^1H NMR\) (500 MHz, CDCl\(_3\)) \(\delta\) 9.95 (s, 1H), 8.99 (dd, \(J = 7.4, 1.5\) Hz, 1H), 8.74 (d, \(J = 4.2, 1.6\) Hz 1H), 8.20 (dd, \(J = 8.3, 1.6\) Hz, 1H), 7.68 – 7.56 (m, 2H), 7.46 (dd, \(J = 8.3, 4.2\) Hz, 1H), 7.34 (t, \(J = 7.7\) Hz, 1H), 7.22 (d, \(J = 7.6\) Hz, 1H), 7.15 (d, \(J = 7.7\) Hz, 1H), 7.09 (dt, \(J = 15.6, 1.6\) Hz, 1H), 5.78 (dt, \(J = 15.5, 1.5\) Hz, 1H), 3.97 (t, \(J = 6.8\) Hz, 2H), 3.66 (dd, \(J = 6.7, 1.2\) Hz, 2H), 2.48 (s, 3H), 1.58 – 1.47 (m, 2H), 1.30 – 1.25 (m, 10H), 0.90 (t, \(J = 6.1\) Hz, 3H); \(^13C NMR\) (126 MHz, CDCl\(_3\)) \(\delta\) 168.15, 166.33, 148.34, 146.59, 138.49, 137.97, 136.30, 135.14, 134.51, 134.15, 129.41, 128.95, 128.01, 127.41, 127.38, 122.81, 122.14, 121.68, 116.85, 64.38, 36.09, 31.79, 29.21, 29.15, 28.55, 25.88, 22.64, 19.56, 14.10; IR (KBr cm\(^{-1}\)): 2975, 29726, 1711, 1676, 1484, 1157, 899, 826, 791; HRMS (APCI-ToF) m/z: [M+H]\(^+\) Calcd. for C\(_{29}\)H\(_{35}\)N\(_2\)O\(_3\) 459.2642; Found 459.2665.
(Z)-3,7-dimethylocta-2,6-dien-1-yl (E)-4-(3-methyl-2-(quinolin-8-y1carbamoyl)phenyl)but-2-enoate (5a):

Reaction performed on 0.1 mmol scale (26 mg); Yield: 45% (21 mg);
Physical appearance: colorless gel; TLC Rf 0.2 (4:1, Petroleum ether: EtOAc); 

**H NMR** (500 MHz, CDCl3) δ 9.95 (s, 1H), 8.98 (dd, J = 7.3, 1.6 Hz, 1H), 8.74 (dd, J = 4.3, 1.5 Hz, 1H), 8.20 (dd, J = 8.3, 1.7 Hz, 1H), 7.66 – 7.57 (m, 2H), 7.46 (dd, J = 8.2, 4.2 Hz, 1H), 7.33 (t, J = 7.7 Hz, 1H), 7.21 (d, J = 7.6 Hz, 1H), 7.17 – 7.08 (m, 2H), 5.78 (dt, J = 15.5, 1.7 Hz, 1H), 5.28 (t, J = 7.2 Hz, 1H), 5.15 – 5.02 (m, 1H), 4.51 (d, J = 7.2 Hz, 2H), 3.65 (dd, J = 7.2 Hz, 2H), 2.47 (s, 3H), 2.13 – 2.03 (m, 4H), 1.76 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H); 

**C NMR** (126 MHz, CDCl3) δ 168.13, 166.23, 148.34, 146.81, 142.24, 138.48, 137.94, 136.27, 135.14, 134.42, 134.14, 132.14, 129.39, 128.93, 128.00, 127.37, 124.43, 123.82, 123.56, 122.73, 122.13, 121.66, 119.24, 116.85, 60.84, 36.06, 32.16, 26.62, 25.69, 23.49, 19.55, 17.66; 

IR (KBr cm⁻¹): 2980, 2929, 1720, 1675, 1522, 1483, 11120, 94, 904, 829, 791, 764; 

HRMS (ESI-ToF) m/z: [M+H]+ Calcd. for C₃₁H₃₄N₂O₄ 483.2642; Found 483.2666.

(3S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl (E)-4-(3-methyl-2-(quinolin-8-y1carbamoyl)phenyl)but-2-enoate (5b):

Reaction performed on 0.1 mmol scale (26 mg); Yield: 58% (41 mg); Physical appearance: colorless gel; TLC Rf 0.2 (4:1, Petroleum ether: EtOAc); 

**H NMR** (500 MHz, CDCl3) δ 9.96 (s, 1H), 8.99 (dd, J = 7.4, 1.4 Hz, 1H), 8.75 (dd, J = 4.2, 1.6 Hz, 1H), 8.20 (dd, J = 8.3, 1.5 Hz, 1H), 7.68 – 7.56 (m, 2H), 7.46 (dd, J = 8.3, 4.2 Hz, 1H), 7.34 (t, J = 7.7 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.15 (d, J = 7.7 Hz, 1H), 7.09 (dt, J = 15.5, 6.8 Hz, 1H), 5.76 (d, J = 15.6 Hz, 1H), 5.34 (d, J = 4.8 Hz, 1H), 4.69 – 4.39 (m, 1H), 3.67 (d, J = 6.7 Hz, 2H), 2.49 (s, 3H), 2.23 – 2.14 (m, 2H), 2.08 – 1.93 (m, 2H), 1.88 – 1.79 (m, 2H), 1.77 – 1.68 (m, 1H), 1.59 – 1.43 (m, 7H), 1.39 – 1.32 (m, 3H), 1.30 – 1.26 (m, 2H), 1.23 – 1.04 (m, 9H), 1.00 (s, 3H), 0.94 (d, J = 6.5 Hz, 3H), 0.90 (d, J = 2.2 Hz, 3H), 0.88 (d, J = 3.6 Hz, 3H), 0.70 (s, 3H); **C NMR** (126
MHz, CDCl$_3$) $\delta$ 168.15, 165.63, 148.37, 146.42, 139.71, 138.49, 137.95, 136.30, 135.11, 134.60, 134.16, 128.95, 128.01, 127.48, 127.40, 123.16, 122.54, 122.13, 121.69, 116.84, 73.70, 56.69, 56.14, 50.01, 42.32, 39.73, 39.53, 38.03, 36.96, 36.19, 36.09, 35.80, 31.90, 31.86, 28.24, 28.02, 27.67, 24.29, 23.83, 22.83, 22.57, 21.02, 19.58, 19.31, 18.72, 11.86; IR (KBr cm$^{-1}$): 2926, 2851, 1714, 1676, 1520, 1482, 1325, 1195, 1012, 790, 755; HRMS (ESI-ToF) $m/z$: $[\alpha]$$_D^{25}$ = -52.400 (c = 0.0025, CHCl$_3$); [M+H]$^+$ Calcd. for C$_{48}$H$_{63}$N$_2$O$_7$ 715.4833; Found 715.4855.

Methyl (4aS,6aS,6bR,8aR,10S,12aR,12bR,14bS)-2,2,6a,6b,9,9,12a-heptamethyl-10-(((E)-4-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoyl)oxy) 1,3,4,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-octadecahydropicene-4a(2H)-carboxylate (5c):

Reaction performed on 0.1 mmol scale (26 mg); Yield: 60% (48 mg); Physical appearance: Pale yellow gel; TLC $R_f$ 0.2 (4:1, Petroleum ether: EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.96 (s, 1H), 8.98 (d, $J$ = 7.1 Hz, 1H), 8.75 (d, $J$ = 2.9 Hz, 1H), 8.19 (d, $J$ = 7.8 Hz, 1H), 7.69 – 7.55 (m, 2H), 7.46 (d, $J$ = 8.2, 4.2 Hz, 1H), 7.34 (t, $J$ = 7.6 Hz, 1H), 7.22 (d, $J$ = 7.6 Hz, 1H), 7.16 (d, $J$ = 7.6 Hz, 1H), 7.13 – 7.04 (m, 1H), 5.80 (d, $J$ = 15.6 Hz, 1H), 5.30 (s, 1H), 4.44 (dd, $J$ = 11.1, 5.1 Hz, 1H), 3.70 – 3.66 (m, 2H), 2.88 (d, $J$ = 12.0 Hz, 1H), 2.48 (s, 3H), 2.03 – 1.95 (m, 1H), 1.91 – 1.86 (m, 2H), 1.74 – 1.64 (m, 2H), 1.58 – 1.54 (m, 3H), 1.49 – 1.43 (m, 3H), 1.38 – 1.32 (m, 3H), 1.31 – 1.27 (m, 2H), 1.24 – 1.18 (m, 2H), 1.14 (s, 3H), 1.10 – 1.01 (m, 3H), 0.95 (s, 3H), 0.92 (s, 3H), 0.89 (s, 3H), 0.74 – 0.72 (m, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 178.29, 168.11, 166.02, 148.42, 146.12, 143.79, 138.49, 137.91, 136.27, 135.07, 134.68, 134.14, 129.41, 128.94, 128.01, 127.39, 127.37, 123.27, 122.27, 122.10, 121.68, 116.80, 80.59, 55.25, 51.52, 47.51, 46.73, 45.85, 45.63, 41.30, 39.27, 38.05, 37.72, 36.88, 36.04, 33.86, 33.11, 32.58, 32.39, 30.70, 27.93, 27.68, 25.89, 23.65, 23.40, 23.07, 19.60, 18.17, 16.83, 16.66, 15.32; $[\alpha]$$_D^{25}$ = -52.400 (c = 0.0025, CHCl$_3$); IR (KBr cm$^{-1}$): 2925, 2853, 1715, 1676, 1596, 1199, 11161, 987, 825, 791, 752, 701, 667; HRMS (ESI-ToF) $m/z$: [M+H]$^+$ Calcd. for C$_{52}$H$_{67}$N$_2$O$_{5}$ 799.5044; Found 799.5028.
(3aS,5S,6R,6aS)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl (E)-4-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (5d): 

Reaction performed on 0.1 mmol scale (26 mg); Yield: 59% (35 mg); Physical appearance: brown gel; TLC Rf 0.2 (4:1, Petroleum ether: EtOAc); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.95 (s, 1H), 8.97 (dd, $J$ = 7.1, 1.3 Hz, 1H), 8.78 (dd, $J$ = 4.1, 1.2 Hz, 1H), 8.21 (dd, $J$ = 8.1, 1.5 Hz, 1H), 7.69 – 7.58 (m, 2H), 7.48 (dd, $J$ = 8.2, 4.2 Hz, 1H), 7.35 (t, $J$ = 7.6 Hz, 1H), 7.23 (d, $J$ = 7.5 Hz, 1H), 7.21 – 7.10 (m, 2H), 5.82 (d, $J$ = 15.6 Hz, 1H), 5.74 (d, $J$ = 3.6 Hz, 1H), 5.22 (d, $J$ = 2.7 Hz, 1H), 4.31 (d, $J$ = 7.6 Hz, 1H), 4.22 (dd, $J$ = 7.6, 2.8 Hz, 1H), 4.18 – 4.11 (m, 1H), 3.99 (d, $J$ = 5.5 Hz, 2H), 3.77 – 3.62 (m, 2H), 2.48 (s, 3H), 1.52 (s, 3H), 1.40 (s, 3H), 1.29 (s, 3H), 1.26 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 168.00, 164.70, 148.48, 148.34, 138.46, 137.91, 136.35, 135.22, 134.20, 134.10, 129.47, 129.12, 127.99, 127.40, 127.37, 122.18, 121.81, 121.75, 116.86, 112.16, 109.21, 104.94, 83.23, 79.69, 75.90, 72.36, 66.96, 36.16, 26.80, 26.71, 26.21, 25.22, 19.61; [$\alpha$]$_D^{25}$ = 111.600 (c = 0.0025, CHCl$_3$); IR (KBr cm$^{-1}$) 2986, 2923, 1725, 1675, 1152, 1036, 1021, 894, 844, 763; HRMS (ESI-ToF) m/z: [M+H]$^+$ Calcd. for C$_{33}$H$_{37}$N$_2$O$_8$ 589.2544; Found 589.2562.

(R)-2,5,8-trimethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl (E)-4-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (5e): 

Reaction performed on 0.1 mmol scale (26 mg); Yield: 41% (31 mg); Physical appearance: colorless gel; TLC Rf 0.2 (4:1, Petroleum ether: EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 10.02 (s, 1H), 9.00 (d, $J$ = 7.3 Hz, 1H), 8.73 (d, $J$ = 4.1 Hz, 1H), 8.19 (d, $J$ = 8.3 Hz, 1H), 7.68 – 7.57 (m, 2H), 7.43 (dd, $J$ = 8.3, 4.1 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.25 (d, $J$ = 7.7 Hz, 1H), 7.21 (d, $J$ = 7.7 Hz, 1H), 6.07 (d, $J$ = 15.5 Hz, 1H), 3.78 (d, $J$ = 6.6 Hz, 2H), 2.55 (t, $J$ = 7.7 Hz, 2H), 2.50 (s, 3H), 2.06 (s, 3H), 1.83 (s, 3H), 1.80 (s, 3H), 1.57 – 1.50 (m, 3H), 1.49 – 1.39 (m, 4H), 1.30 – 1.27 (m, 7H), 1.24 (s, 3H), 1.19 – 1.14 (m, 3H), 1.11 – 1.08 (m, 2H), 0.90 – 0.85 (m, 16H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 168.09, 164.74, 149.25, 148.53, 148.45, 140.26, 138.50, 137.97, 136.25, 135.20, 134.41, 134.13, 129.49, 129.08, 128.90, 128.00, 127.47, 127.36, 126.77, 124.99, 122.86, 122.17, 121.89, 121.71, 117.22,
116.85, 75.00, 39.38, 37.56, 37.46, 37.40, 37.30, 36.25, 32.79, 32.72, 29.71, 27.99, 24.82, 24.46, 22.73, 22.64, 21.05, 20.56, 19.76, 19.69, 19.64, 12.83, 11.99, 11.79; \([a]_{	ext{D}}^{23} = -170.000 \text{ (c = 0.0025, CHCl}_3\text{)}; \text{IR} \text{ (KBr cm}^{-1}\text{): 2989, 2930, 1730, 1675, 1482, 1030, 901, 763, 697;} ; \text{HRMS (ESI-} \text{ToF) } m/z: [M+H]^+ \text{ Calcd. For C}_{50}H_{67}N_2O_4 759.5095; \text{ Found 759.5083.}

(4) Control Experiments and Mechanistic Studies:

(A) Radical quenching experiment:

In an oven-dried pressure tube equipped with a stir bar, 2-methyl-N-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol) and tert-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) were dissolved in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which Co(acac)$_2$ (20 mol\%, 0.02 mmol), NaOPiv.H$_2$O (1 equiv., 0.1 mmol), and Na$_2$[Eosin Y] (20 mol\%, 0.02 mmol) along with TEMPO (1 equiv., 0.1 mmol) were added. This pressure tube was sealed with a septum cap and the reaction mixture was then stirred in a green LED (3W × 20) environment under an O$_2$ atmosphere using oxygen balloon. After 24 hours, a second portion of the tert-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) was added, and the reaction progress was monitored by TLC. It was observed that in the presence of TEMPO, the yield of the reaction was reduced to 14%. This result suggests that the reaction may proceed through a single electron transfer mechanism.

(B) DABCO experiment:

In an oven-dried pressure tube equipped with a stir bar, the 2-methyl-N-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol) and tert-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) were dissolved
in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which Co(acac)$_2$ (20 mol%, 0.02 mmol), NaOPiv.H$_2$O (1 equiv., 0.1 mmol), and Na$_2$[Eosin Y] (20 mol%, 0.02 mmol) along with DABCO (1 equiv., 0.1 mmol) were added. This pressure tube was sealed with a septum cap and the reaction mixture was then stirred in a green LED (3W × 20) environment under an O$_2$ atmosphere using oxygen balloon. After 24 hours, a second portion of the tert-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) was added, and the reaction progress was monitored by TLC. It was observed that in the presence of DABCO there is no effect on the reaction and a yield 61% was obtained after purification by a silica gel flash column chromatography. From this observation, we can eliminate the possibility of singlet oxygen being involved in the reaction.

(C) **Reversibility experiment:** To investigate the reversibility of the formation of the cobaltacycle, we performed D-quenching studies, both in the presence and absence of the coupling partner.

(I) **Reversibility experiment in absence of vinyl diazo ester:**

In an oven-dried pressure tube equipped with a stir bar, the 2-methyl-N-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol) and D$_2$O (10 equiv., 1 mmol) were dissolved in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which Co(acac)$_2$ (20 mol%, 0.02 mmol), NaOPiv.H$_2$O (1 equiv., 0.1 mmol), and Na$_2$[Eosin Y] (20 mol%, 0.02 mmol) were added. This pressure tube was sealed with a septum cap and the reaction mixture was then stirred in a green LED (3W × 20) environment under an O$_2$ atmosphere using oxygen balloon. After 24 hours the reaction mixture was diluted with EtOAc and washed with saturated NaHCO$_3$ solution and brine. The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography. $^1$H NMR analysis of the isolated compound shows no deuterium incorporation in the starting material.
(II) Reversibility experiment in the presence of vinyl diazo ester:

In an oven-dried pressure tube equipped with a stir bar, the 2-methyl-N-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol), tert-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) and D$_2$O (10 equiv., 1 mmol) was dissolved in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which Co(acac)$_2$ (20 mol%, 0.02 mmol), NaOPiv.H$_2$O (1 equiv., 0.1 mmol), and Na$_2$[Eosin Y] (20 mol%, 0.02 mmol), were added. This pressure tube was sealed with a septum cap and the reaction mixture was then stirred in a green LED (3W × 20) environment under an O$_2$ atmosphere using oxygen balloon. After 24 hours, the reaction mixture was diluted with EtOAc and washed with saturated NaHCO$_3$ solution and brine. The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography. $^1$H NMR of the isolated compound shows no deuterium incorporation in the starting material as well as in the product.

No D-incorporation into the starting material at the ortho position of benzamide, both, in the absence of the coupling partner as well as in the presence of the coupling partner suggests that the C–H activation is irreversible in nature.

(D) Studies to check for a Kinetic Isotopic Effect: To further investigate whether the C–H metalation step is rate-limiting, we carried out studies to check for a kinetic isotope effect.

(I) Competition Experiment (by NMR):

In an oven-dried pressure tube equipped with a stir bar, 2-methyl-N-(quinolin-8-yl)benzamide (1.0 equiv., 0.05 mmol) and 2-methyl-N-(quinolin-8-yl)benzamide-$d$ (1 equiv., 0.05 mmol) and tert-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) were dissolved in TFE (1 mL). The solution
was bubbled with oxygen for about 10 min, following which Co(acac)$_2$ (20 mol%, 0.02 mmol), NaOPiv.H$_2$O (1 equiv., 0.1 mmol), and Na$_2$[Eosin Y] (20 mol%, 0.02 mmol) were added. This pressure tube was sealed with a septum cap and the reaction mixture was then stirred in a green LED (3W × 20) environment under an O$_2$ atmosphere using oxygen balloon. The reaction was continued for 3 hours, after which, the reaction mixture was diluted with EtOAc and washed with saturated NaHCO$_3$ solution and brine. The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure and the crude material was purified by silica gel flash column chromatography. The recovered starting material was analyzed by $^1$H NMR. Relative integration of the peaks of the recovered starting materials indicated a value of 1.16 for $k_H/k_D$.

(II) Parallel Experiment (via GC):
Two parallel reactions for 2-methyl-N-(quinolin-8-yl)benzamide (1 equiv., 0.1 mmol) and 2-methyl-N-(quinolin-8-yl)benzamide-6-$d$ (1 equiv., 0.1 mmol) with tert-butyl 2-diazobut-3-enoate (2 equiv., 0.4 mmol) were performed according to the general procedure A, using dodecane (0.5 equiv., 0.1) as the internal standard. Aliquots were drawn at 40 minutes intervals and conversions were checked by GC-MS. The consumption starting material was plotted with time and $k_H/k_D$ was found to be 1.03 (average of 3 runs).
Plot A (Rate of reaction of 2-methyl-N-(quinolin-8-yl)benzamide):

![Graph](image)

Equation: \( y = a + b'x \)

<table>
<thead>
<tr>
<th>C1</th>
<th>Value</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.22947</td>
</tr>
<tr>
<td>Slope</td>
<td>-0.04643</td>
<td>0.00189</td>
</tr>
</tbody>
</table>

Adjusted R-Square: 0.99173

Plot B (Rate of reaction of 2-methyl-N-(quinolin-8-yl)benzamide-6-d):

![Graph](image)

Equation: \( y = a + b'x \)

<table>
<thead>
<tr>
<th>C1</th>
<th>Value</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
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<td>0.25683</td>
</tr>
<tr>
<td>Slope</td>
<td>-0.045</td>
<td>0.00212</td>
</tr>
</tbody>
</table>

Adjusted R-Square: 0.98899
A moderately low value of 1.16 and 1.03 obtained with competition and parallel experiments respectively, indicated that the C–H cleavage step is unlikely to be the rate-determining step. It is quite possible the allyl carbene migratory insertion step may be the rate-limiting step.

(E) Synthesis of the cobaltacycle intermediate (6a):³

To an oven-dried round bottom flask charged with a magnetic stir bar was added Co(acac)_2 (488.3 mg, 1.90 mmol, 1.0 equiv.) which is dissolved in 8 mL of 2,2,2-trifluoroethanol, to this solution 1a (497.8 mg, 1.90 mmol, 1.0 equiv.) was added under air, and the reaction mixture was kept at room temperature for 48 h. After completion of the reaction, the solvent was concentrated under reduced pressure to give a residue which was purified by silica gel column chromatography (10:90 PET ether: Ethyl acetate) to give the desired cobalt complex 6a as reported.

HRMS (ESI-ToF) m/z: [M+H]^+ Calcd. for C_{34}H_{26}CoN_{2}O_{4} 581.1382; Found 581.1411.

(F) Stoichiometric experiment:

In an oven-dried pressure tube equipped with a stir bar, the cobaltacycle (6a) (1.0 equiv., 0.1 mmol) and tert-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) were dissolved in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which NaOPiv.H_2O (1 equiv., 0.1 mmol), and Na_2[Eosin Y] (20 mol%, 0.02 mmol) were added. This pressure tube was sealed with a septum cap and the reaction mixture was then stirred in a green LED (3W × 20) environment.
under an O₂ atmosphere using oxygen balloon. After 24 hours, the second portion of the tert-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) was added, and the reaction progress was monitored by TLC. Upon completion of the reaction, the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite, and the filtrate was concentrated. The residue was re-dissolved in EtOAc and the solution was washed with saturated NaHCO₃ solution and brine. The organic extract was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography, giving the product in 43% yield.

(G) Cobaltacycle intermediate as a catalyst:

In an oven-dried pressure tube equipped with a stir bar, the cobaltacyle (6a) (1.0 equiv., 0.1 mmol) and tert-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) were dissolved in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which NaOPiv.H₂O (1 equiv., 0.1 mmol), and Na₂[Eosin Y] (20 mol%, 0.02 mmol) were added. This pressure tube was sealed with a septum cap and the reaction mixture was then stirred in a green LED (3W × 20) environment under an O₂ atmosphere using oxygen balloon. After 24 hours, the second portion of tert-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) was added, and the reaction progress was monitored by TLC. Upon completion of the reaction, the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite, and the filtrate was concentrated. The residue was re-dissolved in EtOAc and washed with saturated NaHCO₃ solution and brine. The organic extract was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography giving the product in 39% yield.

(H) Role of oxygen oxidant:

(I) reaction in presence of oxygen balloon:

In an oven-dried pressure tube equipped with a stir bar, the N-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol) and tert-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) were dissolved in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which Co(acac)₂
(1 equiv. 0.1 mmol), NaOPiv.H₂O (2 equiv. 0.2 mmol), were added, the pressure tube was sealed with a septum cap. This reaction mixture was then stirred in a dark environment under an O₂ atmosphere using oxygen balloon. After 24 hours, the second portion of vinyl diazo ester (1.5 equiv., 0.15 mmol) was added and the reaction progress was further monitored by TLC. After which, the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite, and the filtrate was concentrated. The residue was dissolved in EtOAc and washed with saturated NaHCO₃ solution and brine. The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography giving the allylated product in 24% yield.

(II) reaction in presence of nitrogen balloon:
In an oven-dried pressure tube equipped with a stir bar, the N-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol) and tert-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) were dissolved in TFE (1 mL). The solution was bubbled with nitrogen for about 10 min, following which Co(acac)₂ (1 equiv. 0.1 mmol), NaOPiv.H₂O (2 equiv., 0.2 mmol), were added, the pressure tube was sealed with a septum cap. This reaction mixture was then stirred in a dark environment under inert conditions. After 24 hours, the second portion of vinyl diazo ester (1.5 equiv., 0.15 mmol) was added, and the reaction progress was further monitored by TLC. After which, the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite, and the filtrate was concentrated. The residue was dissolved in EtOAc and washed with saturated NaHCO₃ solution and brine. The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography giving the trace amount of allylated product.
A moderately low yield i.e. 24% was obtained in the presence of oxygen balloon, however, only trace amount of product was obtained under the inert conditions, indicating that oxygen is necessary for this transformation.

(I) Role of additive:

(I) reaction in presence of NaOPiv.H₂O

In an oven-dried pressure tube equipped with a stir bar, the cobaltacyle (6a) (1.0 equiv., 0.1 mmol) and tert-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) were dissolved in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which NaOPiv.H₂O (1 equiv., 0.1 mmol) was added. This pressure tube was sealed with a septum cap and the reaction mixture was then stirred in dark environment under an O₂ atmosphere using oxygen balloon. After 24 hours, the second portion of tert-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) was added, and the reaction progress was monitored by TLC. Upon completion of the reaction, the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite, and the filtrate was concentrated. The residue was re-dissolved in EtOAc and washed with saturated NaHCO₃ solution and brine. The organic extract was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography giving the allylated product in 14% yield, however recovered starting material in 21% yield.

(II) reaction in presence of PivOH

In an oven-dried pressure tube equipped with a stir bar, the cobaltacyle (6a) (1.0 equiv., 0.1 mmol) and tert-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) were dissolved in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which PivOH (1 equiv., 0.1 mmol) was added. This pressure tube was sealed with a septum cap and the reaction mixture was then stirred in dark environment under an O₂ atmosphere using oxygen balloon. After 24 hours, the second portion of tert-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) was added, and the
reaction progress was monitored by TLC. Upon completion of the reaction, the reaction mixture was diluted with EtOAc and filtered through a short pad of Celite, and the filtrate was concentrated. The residue was re-dissolved in EtOAc and washed with saturated NaHCO$_3$ solution and brine. The organic extract was dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography giving the allylated product in 20% yield, however recovered starting material in 30% yield.

These results indicating that role of additive may be for the facilitation of protodemetalation step in this transformation.

(X) Mass Spectrometry Experiment:

**Procedure:** In an oven-dried pressure tube equipped with a stir bar, the 2-methyl-N-(quinolin-8-yl)benzamide (1.0 equiv., 0.1 mmol) and tert-butyl 2-diazobut-3-enoate (1.5 equiv., 0.15 mmol) were dissolved in TFE (1 mL). The solution was bubbled with oxygen for about 10 min, following which Co(acac)$_2$ (20 mol%, 0.02 mmol), NaOPiv.H$_2$O (1 equiv., 0.1 mmol), and Na$_2$[Eosin Y] (20 mol%, 0.02 mmol) were added. This pressure tube was sealed with a septum cap and the reaction mixture was then stirred in a green LED (3W × 20) environment under an O$_2$ atmosphere using
oxygen balloon for 30 minutes. An aliquot was drawn, passed through a frit, and subjected immediately to mass analysis

(5) References:


(2g)
ND-01-231-1H-500MHz-CDCl3

ND-01-231-13C-500MHz-CDCl3
## Display Report

### Analysis Info
- **Analysis Name**: D:/Data/NEW USER DATA 2022\April-2022/01-April/Dr.M.Kapur-NK-06-400.d
- **Method**: tune mix_iow.New.021117.m
- **Sample Name**: NK-06-400
- **Comment**: 
- **Acquisition Date**: 4/1/2022 3:54:31 PM
- **Operator**: RUCHI
- **Instrument**: micrOTOF-Q II 10330

### Acquisition Parameter
- **Source Type**: ESI
- **Focus**: Not active
- **Scan Begin**: 50 m/z
- **Scan End**: 3000 m/z
- **Ion Polarity**: Positive
- **Set Capillary**: 4600 V
- **Set End Plate Offset**: -500 V
- **Set Collision Cell RF**: 100.0 Vpp
- **Set Nebulizer**: 0.4 Bar
- **Set Dry Heater**: 180 °C
- **Set Dry Gas**: 4.0 l/min
- **Set Divert Valve**: Source

---

![Graph and molecule images](image-url)

**Dr.M.Kapur-NK-06-400.d: TIC +All MS**

**Molecule (3b)**

---

**Bruker Compass Data Analysis 4.0**

**Printed**: 4/1/2022 3:55:40 PM

Page 1 of 1
Display Report

Analysis Info
- Analysis Name: D:\Data\NEW USER DATA 2022\April-2022\01-April\Dr.M.Kapur-NK-06334-LS_1-B,7,01_11625.d
- Method: hrlcms-20 sept.m
- Sample Name: Dr.M.Kapur-NK-06334-LS
- Comment:
- Acquisition Date: 4/1/2022 3:02:03 PM
- Operator: RUCHI
- Instrument: micrOTOF-Q II 10330

Acquisition Parameter
- Source Type: ESI
- Focus: Active
- Scan Begin: 50 m/z
- Scan End: 3000 m/z
- Ion Polarity: Positive
- Set Capillary: 4500 V
- Set End Plate Offset: -500 V
- Set Collision Cell RF: 130.0 Vpp
- Set Nebulizer: 1.2 Bar
- Set Dry Heater: 200 °C
- Set Dry Gas: 6.0 l/min
- Set Divert Valve: Waste

![Graphs and Spectra]

Dr.M.Kapur-NK-06334-LS_1-B,7,01_11625.d: TIC + All MS
Dr.M.Kapur-NK-06334-LS_1-B,7,01_11625.d: UV Chromatogram, 200-400 nm
UV, 4.4-4.5min #2(2595-2890),
+MS, 4.4-4.5min #2(261-270)
+MS, 4.0-4.1min #2(236-242)

Bruker Compass DataAnalysis 4.0
printed: 4/1/2022 3:18:49 PM
Page 1 of 1
Display Report

Analysis Info
Analysis Name: D:\Data\NEW USER DATA 2022\April-2022\01-April\Dr.M.Kapur-NK-06289-LS_1-B5_01_11623.d
Method: hrlcms-20 sept.m
Sample Name: Dr.M.Kapur-NK-06289-LS
Comment

Acquisition Parameter
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Set Capillary: 4500 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 130.0 Vpp
Set Dry Gas: 6.0 l/min
Set Dry Heater: 200 °C
Set Divert Valve: Waste

Intens.
[mAUI] 10^7

Dr. M.Kapur-NK-06289-LS_1-B5_01_11623.d: TIC +All MS

10^6

Dr. M.Kapur-NK-06289-LS_1-B5_01_11623.d: UV Chromatogram, 200-400 nm

10^5

Dr. M.Kapur-NK-06289-LS_1-B5_01_11623.d: EIC 433.2132 +All MS

10^4

UV, 4.3-4.5min #(2529-2560)
+MS, 4.3-4.5min #(254-266)
+MS, 4.3-4.5min #(254-266)

10^3

233.0807
377.1515
543.2490

10^2

433.2143
434.2176

435.2203

C26H28N2O4, M+nH 433.21

433.2122
434.2155

435.2189

10^0

433.0
433.5
434.0
434.5
435.0
435.5

m/z

Bruker Compass DataAnalysis 4.0
printed: 4/1/2022 3:05:00 PM
Page 1 of 1
Display Report

Analysis Info
Analysis Name: D:\Data\NEW USER DATA 2022\April-2022\01-April\Dr.M.Kapur-NK-06-388_1-B,2_01_11620.d
Method: hrlcms-20 sept.m
Sample Name: Dr.M.Kapur-NK-06-388
Comment:

Acquisition Date: 4/1/2022 2:26:07 PM
Operator: RUCHI
Instrument: micrOTOF-Q II 10330

Acquisition Parameter
Source Type: ESI
Focus: Active
Scan Begin: 50 m/z
Scan End: 3000 m/z
Ion Polarity: Positive
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Set Collision Cell RF: 130.0 Vpp
Set Nebulizer: 1.2 Bar
Set Dry Heater: 200 °C
Set Dry Gas: 6.0 l/min
Set Divert Valve: Waste

Graphs and Data Analysis:
- TIC + All MS
- UV Chromatogram, 200-400 nm
- +MS, 4.0-4.2min #238-249
- +MS, 4.0-4.2min #238-249
- C29H32N2O4, M+Na 495.23
**Display Report**

**Analysis Info**
- **Analysis Name**: D:\Data\NEW USER DATA 2022\April-2022\18-april\Dr.M.Kapur-NK-06-303-LS_1-A,8_01_11772.d
- **Method**: hrlcms-20 sept.m
- **Sample Name**: Dr.M.Kapur-NK-06-303-LS
- **Comment**

**Acquisition Parameter**
- **Source Type**: ESI
- **Ion Polarity**: Positive
- **Scan Begin**: 50 m/z
- **Scan End**: 3000 m/z
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- **Set End Plate Offset**: -500 V
- **Set Collision Cell RF**: 130.0 Vpp
- **Set Nebulizer**: 1.2 Bar
- **Set Dry Gas**: 6.0 l/min
- **Set Divert Valve**: Waste

---

**Graphs**

1. Dr.M.Kapur-NK-06-303-LS_1-A,8_01_11772.d: TIC + All MS
   - Intensity over Time [min]

2. Dr.M.Kapur-NK-06-303-LS_1-A,8_01_11772.d: UV Chromatogram, 200-400 nm
   - Intensity [mAU] over Wavelength [nm]

3. Dr.M.Kapur-NK-06-303-LS_1-A,8_01_11772.d: EIC 401.1788 + All MS
   - Intensity [mAU] over m/z

4. Molecular Structure (3n)

---

**Bruker Compass DataAnalysis 4.0**

**printed**: 4/18/2022 2:48:00 PM

Page 1 of 1
Display Report

Analysis Info
Analysis Name: G:\HRMS-DATA-27-04-22\LC-HRMS-2022\NEW USER DATA
Method: RUCI
Sample Name: Dr.M.Kapur-NK-06-335-LS
Comment: Operated by Dr.M.Kapur-NK-06-335-LS
Instrument: microTOF-Q II 10330
Acquisition Date: 01-04-2022 14:40:27

Acquisition Parameter
Source Type: ESI
Focus: Active
Scan Begin: 50 m/z
Scan End: 3000 m/z
Ion Polarity: Positive
Set Capillary: 4600 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 130.0 Vpp
Set Nebulizer: 1.2 Bar
Set Dry Heater: 200 °C
Set Dry Gas: 6.0 l/min
Set Divert Valve: Waste

Graphs and Diagrams:
1. Intensity vs. Time [min]
2. UV Chromatogram: 200-400 nm
3. Mass Spectrogram: +MS, 3.5-4.0 min #208-241
4. Mass Spectrogram: +MS, 3.5-4.0 min #208-241
Display Report

Analysis Info
Analysis Name: D:\Data\USER DATA 2022\Nov-2022\21-11-2022\Prof.M.Kapur-NK_06_711.d
Method: tune_wide.m
Sample Name: NK_06_711
Comment:

Acquisition Date: 21-11-2022 09:56:32
Operator: Bruker
Instrument: micrOTOF-Q 10330

Acquisition Parameter
Source Type: ESI
Focus: Not active
Scan Begin: 50 m/z
Scan End: 3000 m/z
Ion Polarity: Positive
Set Capillary: 4600 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 600.0 Vpp
Set Nebulizer: 0.4 Bar
Set Dry Heater: 180 °C
Set Dry Gas: 4.0 l/min
Set Divert Valve: Source

Prof.M.Kapur-NK_06_711.d: TIC +All MS

(3p)

NC
Me
O
CO₂Bu

C26H25N3O3, M+nH, 428.20
Display Report

Analysis Info
Analysis Name: D:\Data\NEW USER DATA 2022\March-2022\31\March\Prof.M.Kapur-NK-06-286-LS.d
Method: tune_wide_APCI_23.06.m
Sample Name: NK-06-286-LS
Comment:

Acquisition Parameter
Source Type: Multi Mode
Ion Polarity: Positive
Set Nebulizer: 2.0 Bar
Focus: Not active
Set Capillary: 2500 V
Set Dry Heater: 200 °C
Scan Begin: 50 m/z
Set End Plate Offset: -500 V
Set Dry Gas: 5.0 l/min
Scan End: 3000 m/z
Set Collision Cell RF: 600.0 Vpp
Set Divert Valve: Source

---

Prof.M.Kapur-NK-06-286-LS.d: TIC +All MS

---

+MS, 0.4 min #2B

---

Me

C=O

NH

CO₂Me

---

C₂H₂O₂N₂O₃, M+Na, 383.14

---

Bruker Compass DataAnalysis 4.0
Display Report

Analysis Info
Analysis Name: D:\Data\NEW USER DATA 2022\March-2022\31MarchiProf.M.Kapur-NK-06-287-LS.d
Method: tune_wide_APCI_23.06.m
Sample Name: NK-06-287-LS
Comment:

Acquisition Parameter
Source Type: Multi Mode
Focus: Not active
Scan Begin: 50 m/z
Scan End: 3000 m/z
Ion Polarity: Positive
Set Capillary: 2500 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 600.0 Ypp
Set Nebulizer: 2.0 Bar
Set Dry Heater: 200 °C
Set Dry Gas: 5.0 l/min
Set Divert Valve: Source

Operator: RUCHI
Instrument: micrOTOF-Q II 10330

Acquisition Date: 3/31/2022 2:40:40 PM

Bruker Compass DataAnalysis 4.0  printed: 3/31/2022 2:42:34 PM  Page 1 of 1

S96
Mixture of rotamers

(5a)

Mixture of rotamers

(5a)
Display Report

Analysis Info

Analysis Name: D:\Data\USER DATA 2022\AUG2022\30-08-2022\Prof.M.Kapur-NK_06_375_US_R_2.d
Method: tune mix_low_New.021117.m
Sample Name: NK_06_375_US_R_2
Comment

Acquisition Parameter

Source Type: ESI
Focus: Not active
Scan Begin: 50 m/z
Scan End: 3000 m/z

Ion Polarity: Positive
Set Capillary: 4600 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 100.0 Vpp
Set Nebulizer: 0.4 Bar
Set Dry Heater: 180 °C
Set Dry Gas: 4.0 l/min
Set Divert Valve: Waste

Chemical structure image

Chart with mass spectrometry data

[Graph showing mass spectrometry data with m/z values and ion intensities]
S111
(7) ESI-HRMS for Cobaltacycle Intermediate (6a):
Detection of intermediates by mass spectrometry

\[
\text{N}\text{H} \quad \text{O} \quad \text{Co(acac)}_2 \text{ (20 mol\%)} \quad \text{Na}_2[\text{Eosin Y}] \text{ (20 mol\%)} \quad \text{NaOPlv.H}_2\text{O} \text{ (1 equiv.)} \\
\text{TFE, 3W Green LED} \\
\text{O}_2 \text{ balloon, 30 min.}
\]

**ESI-HRMS for C**
- calcld. [M+H] 419.0800
- found [M+H] 419.0785

**ESI-HRMS for F**
- calcld. [M+H] 559.1638
- found [M+H] 559.1645
(9) X-ray diffraction structural analysis data of 3j:

Sample Preparation: 5 mg of 3j (white solid) was taken in a 10 mL beaker and dissolved in a minimum amount of chloroform. Hexane (3 mL) was added to the beaker along the wall. The beaker was capped loosely and kept at room temperature for slow evaporation. After 5 days single crystal was obtained which was subjected to X-ray diffraction.

Table S5: Crystal data and structure refinement for 3j.

<table>
<thead>
<tr>
<th>Identification code</th>
<th>3j</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{26}H_{28}N_{2}O_{3}</td>
</tr>
<tr>
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<td>416.52</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>290.0</td>
</tr>
<tr>
<td>Crystal system</td>
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<tr>
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<td>P-1</td>
</tr>
<tr>
<td>a/Å</td>
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</tr>
<tr>
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</tr>
<tr>
<td>α/°</td>
<td>104.537(6)</td>
</tr>
<tr>
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<td>91.863(6)</td>
</tr>
<tr>
<td>γ/°</td>
<td>98.368(5)</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>1137.3(3)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>ρ_{calc}/g/cm³</td>
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</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.080</td>
</tr>
<tr>
<td>F(000)</td>
<td>444.2</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>1 × 0.8 × 0.6</td>
</tr>
<tr>
<td>Radiation</td>
<td>Mo Kα (λ = 0.71073)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>4.7 to 57.4</td>
</tr>
</tbody>
</table>
Index ranges -7 ≤ h ≤ 7, -16 ≤ k ≤ 16, -24 ≤ l ≤ 24
Reflections collected 33092
Independent reflections 5871 [R_{int} = 0.0649, R_{sigma} = 0.0504]
Data/restraints/parameters 5871/0/285
Goodness-of-fit on F^2 1.029
Final R indexes [I>=2σ (I)] R_I = 0.0538, wR_2 = 0.1303
Final R indexes [all data] R_I = 0.0910, wR_2 = 0.1558
Largest diff. peak/hole / e Å

Fig. S1. X-ray structure of tert-butyl (E)-4-(3,6-dimethyl-2-(quinolin-8-ylcarbamoyl)phenyl)but-2-enoate (3j) (ORTEP view at 50% ellipsoidal probability).