

Electronic Supplementary Information (ESI) for

**(NHC)Ni(II)-Catalyzed Regioselective Hydroalkenylation of Norbornene Derivatives:  
Fine-Tuning of NHC Ligands and Donor Alkene Substrates.**

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## General Aspects

Unless otherwise indicated, all reactions were performed under a nitrogen atmosphere from which oxygen and moisture were rigidly excluded from reagents and glassware. Ni(cod)<sub>2</sub> [Bis(1,5-cyclooctadiene)nickel(0)] were purchased from bide or J&K, stored in a glovebox and used without further purification. KHMDs [Potassium hexamethyldisilazane] was purchased from bide, stored in a glovebox and used without further purification. NHC and NHC-HCl were purchased from TCI or bide, and stored in a glove box before use. NaBARF [Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate] were purchased from Ark or Bide, vacuumized for 12 h under 100°C and then stored in a glove box before use. Toluene was distilled over sodium and CaH<sub>2</sub> before use. Both commercially available and synthesized alkenes were dried with CaH<sub>2</sub> or CaCl<sub>2</sub> before use.

Product analysis was assisted by SUSTech Core Research Facilities. <sup>1</sup>H and <sup>13</sup>C NMR were recorded on Bruker spectrometers in CDCl<sub>3</sub> (400 or 500 MHz for <sup>1</sup>H and 100 or 125 MHz for <sup>13</sup>C). Chemical shifts in <sup>1</sup>H NMR spectra are reported in ppm on the δ scale from an internal standard of TMS. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in hertz (Hz), and integration. Chemical shifts of <sup>13</sup>C NMR spectra are reported in ppm from the central peak of CDCl<sub>3</sub> (77.16 ppm) or C<sub>6</sub>D<sub>6</sub> (128.06 ppm) on the δ scale. High resolution mass spectra (HRMS) were obtained on a Finnigan MAT 95XL GC Mass Spectrometer. GCMS and peaks assignment were recorded on Agilent Technologies 7890B GC system and 5977A MSD. Column: Agilent Techs HP-5MS UI, 30 m \* 0.250 mm, 0.25 micron. Programming method:

	Rate (°C/min)	Value (°C)	Hold time (min)	Run time (min)
Initial		50	2	2
Ramp 1	30	200	1	8
Ramp 2	40	280	15	25

Purification of product was performed by using Silica Gel (230–400 mesh, 0.040-0.063 mm) coarse fritted glass column. Analytical thin layer chromatography (TLC) was performed using EM Science silica gel 60 F254 plates. The developed chromatogram was analyzed by UV lamp (254 nm), ethanolic phosphomolybdic acid (PMA) or potassium permanganate (KMnO<sub>4</sub>). Yield and selectivity of products were determined either by GC-MS or crude <sup>1</sup>H

NMR integration of areas of selected peaks with relaxation time  $d1 = 10$  seconds and  $\text{CH}_3\text{NO}_2$  or Mesitylene as internal standard.

## Substrate Preparation

Except otherwise indicated, all the alkene substrates, **1** and **2**, employed in this work are obtained from commercial source or synthesized according to literature procedures (known compounds).

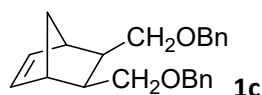
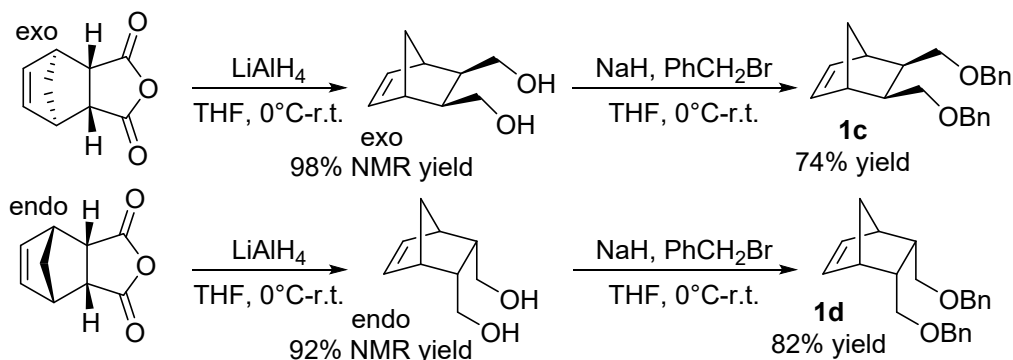
### A) Preparation of substituted norbornene derivatives

#### A1) Symmetrically substituted norbornene derivatives **1a-1d**

**1a**, **1b** were commercially available.

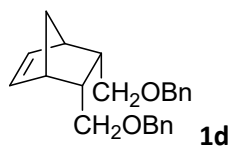
**1c** and **1d** were prepared by corresponding anhydride.<sup>1</sup>

Relative configuration



**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.27 (m, 10H), 6.15 (t,  $J = 1.8$  Hz, 2H), 4.47 (d,  $J = 1.5$  Hz, 4H), 3.68 – 3.58 (m, 2H), 3.40 – 3.28 (m, 2H), 2.79 (p,  $J = 1.7$  Hz, 2H), 1.45 (d,  $J = 8.9$  Hz, 1H), 1.27 (dt,  $J = 9.2, 1.8$  Hz, 1H).

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.7, 137.5, 128.5, 127.8, 127.7, 73.3, 71.9, 45.1, 42.9, 40.8.



**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.26 (m, 10H), 6.04 (t,  $J = 1.9$  Hz, 2H), 4.49 – 4.36 (m, 4H), 3.36 – 3.24 (m, 2H), 3.10 – 3.00 (m, 2H), 2.96 (hept,  $J = 1.7$  Hz, 2H), 2.58 – 2.44 (m, 2H), 1.47

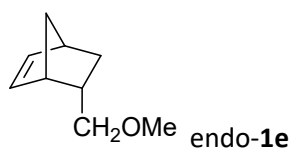
(dt,  $J = 8.3, 1.9$  Hz, 1H), 1.32 (dt,  $J = 8.3, 1.5$  Hz, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.8, 135.5, 128.5, 127.8, 127.6, 73.1, 70.6, 49.2, 45.8, 41.7.

## A2) Asymmetrically substituted norbornene derivatives

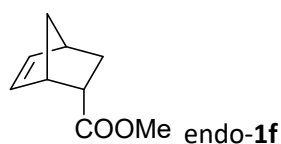
**Endo-1e**<sup>2</sup>, **Endo-1f**<sup>3</sup> and **1g**<sup>4</sup> were synthesized by reported literature.

**Exo-1f** was obtained from commercially available **1f** (endo : exo = 4 : 1) by silica gel column chromatography.



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.12 (dd,  $J = 5.8, 3.0$  Hz, 1H), 5.93 (dd,  $J = 5.8, 2.9$  Hz, 1H), 3.30 (s, 3H), 3.08 (dd,  $J = 9.2, 6.7$  Hz, 1H), 3.01 (t,  $J = 9.0$  Hz, 1H), 2.89 (s, 1H), 2.79 (d,  $J = 4.1$  Hz, 1H), 2.34 (dh,  $J = 12.8, 3.9$  Hz, 1H), 1.81 (ddd,  $J = 11.7, 9.2, 3.8$  Hz, 1H), 1.42 (dq,  $J = 8.4, 2.1$  Hz, 1H), 1.24 (d,  $J = 8.3$  Hz, 1H), 0.49 (ddd,  $J = 11.6, 4.5, 2.6$  Hz, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.3, 132.6, 58.9, 49.6, 44.1, 42.3, 38.8, 29.3.



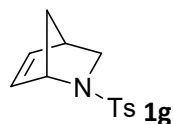
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.19 (dd,  $J = 5.7, 3.1$  Hz, 1H), 5.92 (dd,  $J = 5.7, 2.9$  Hz, 1H), 3.62 (s, 3H), 3.19 (ddq,  $J = 4.0, 2.8, 1.3$  Hz, 1H), 2.99 – 2.93 (m, 1H), 2.92 – 2.86 (m, 1H), 1.90 (ddd,  $J = 11.8, 9.3, 3.7$  Hz, 1H), 1.42 (ddt,  $J = 11.5, 7.0, 2.2$  Hz, 2H), 1.27 (dt,  $J = 7.9, 1.5$  Hz, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.4, 137.9, 132.5, 51.6, 49.8, 45.8, 43.3, 42.7, 29.4.



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.23 – 5.97 (m, 2H), 3.69 (s, 3H), 3.11 – 3.01 (m, 1H), 2.92 (t,  $J = 2.8$  Hz, 1H), 2.31 – 2.19 (m, 1H), 1.92 (dt,  $J = 11.8, 4.0$  Hz, 1H), 1.52 (dt,  $J = 8.2, 1.5$  Hz, 1H), 1.41 – 1.32 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.9, 138.2, 135.9, 51.9, 46.7, 46.5, 43.1, 41.8, 30.5.



**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.65 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 6.08 (dd, *J* = 5.8, 3.1 Hz, 1H), 5.97 (dd, *J* = 5.7, 2.4 Hz, 1H), 4.62 (s, 1H), 3.40 – 3.32 (m, 1H), 3.12 (s, 1H), 2.52 (d, *J* = 8.4 Hz, 1H), 2.40 (s, 3H), 1.51 – 1.34 (m, 2H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 143.3, 136.9, 136.2, 133.6, 129.6, 127.8, 64.3, 48.1, 47.2, 43.9, 21.7.

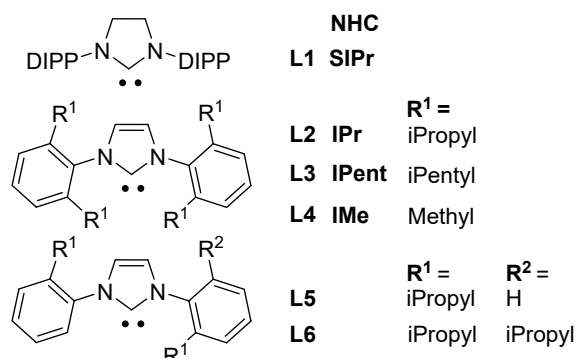
#### B) Terminal olefin **2a-t**.

**2a-2h**, **2m-2n**, **2s**, **2t** were obtained from commercial source and dried before use.

**2i-2l**, **2o-2r** were synthesized according to reported literature.<sup>5-7</sup>

## Ligand Preparation

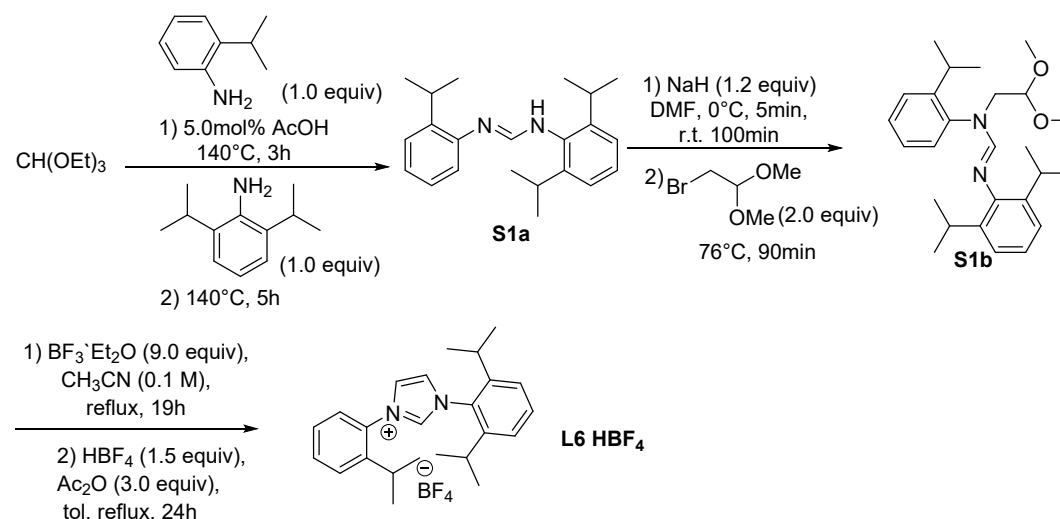
NHC employed in this work is shown below:



**L1-3** were obtained from commercial source.

**L4**·HCl and **L5**·HCl were synthesized according to the reported literature.<sup>8,9</sup>

**L6**·HBF<sub>4</sub> was synthesized by a modified procedure.<sup>10,11</sup>



### **S1a**, *N*-(2,6-diisopropylphenyl)-*N'*-(2-isopropylphenyl)formamidine

2-isopropylaniline (4.05 g, 30 mmol, 1 equiv.), triethyl orthoformate (5.0 mL, 30 mmol, 1 equiv.) and acetic acid (86  $\mu$ L, 1.5 mmol, 0.05 equiv.) were heated at 140 °C for 3 h. 2, 6-diisopropylaniline (5.31 g, 30 mmol, 1 equiv.) was added and the mixture was heated to 140 °C for 5 h, then cooled to r.t.. The crude material was triturated with hexane (20 mL) at -18 °C and filtered. The resulting solid was recrystallized in acetone to give a white solid (3.4 g, 35% yield).

The formamidine exist in two isomeric forms in a 2:1 ratio, and the data matched well with the literature report. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (d, *J* = 11.4 Hz, 0.3H), 7.65 (s,

0.7H), 7.24 – 7.04 (m, 7H), 6.16 (d,  $J = 11.9$  Hz, 0.3H), 3.35-3.17 (m, 2H), 3.11 (hept,  $J = 6.7$  Hz, 0.7H), 2.64-2.50 (m, 0.3H), 1.32 – 1.15 (m, 16H), 1.05 (d,  $J = 6.8$  Hz, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  151.0, 148.9, 146.2, 145.8, 144.4, 142.7, 142.6, 141.4, 140.9, 139.0, 137.5, 136.3, **133.5**, 128.0, 127.0, 127.0, 126.9, 126.7, 126.7, 126.6, 126.5, 126.4, 126.3, 125.8, 125.5, 125.2, 124.4, 124.2, 124.1, 123.9, 123.8, 123.8, 123.6, 123.4, 122.9, 121.0, 119.1, 118.7, 118.1, 115.9, 28.4, 28.2, 28.2, 28.0, 28.0, 27.9, 27.8, 27.7, 27.7, 23.9, 23.8, 23.7, 23.5, 23.2, 23.0, 22.6, 22.6, 22.4.

### **S1a to L6·HBF<sub>4</sub>**

Formamidine **S1a** (3.4 g, 10.5 mmol, 1 equiv.) was dissolved in DMF (100 mL, 0.1 M) and the solution was cooled to 0 °C. After adding NaH (60% dispersion in mineral oil, 756 mg, 19 mmol, 1.8 equiv.), the mixture was stirred for 5 min at 0 °C, warmed to r.t., and stirred for 100 min. Bromoacetaldehyde dimethyl acetal (3.55 g, 21 mmol, 2 equiv.) was added and the mixture was heated at 76 °C for 90 min. All the volatiles were removed in vacuo and acetonitrile (20 mL) was added to the resulting yellow solid. The mixture was filtered and the colorless precipitate was washed with acetonitrile. The solvent of the filtrate was removed in vacuo and the resulting yellow oil was purified by flash column chromatography ( $\text{CH}_2\text{Cl}_2$  to  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 95:5) on silica gel to yield **S1b** (2.4g, 55% yield).

**S1b** (2.4 g, 5.8 mmol, 1 equiv.) was dissolved in acetonitrile (58 mL, 0.1 M) and  $\text{BF}_3\cdot\text{Et}_2\text{O}$  (4.41 mL, 34.8 mmol, 6 equiv.) was added to the solution. After stirring the mixture at 70 °C for 3 h, additional  $\text{BF}_3\cdot\text{Et}_2\text{O}$  (3 equiv.) was added. The mixture was stirred at 70 °C for 16 h. After cooling to room temperature all the volatiles were removed in vacuo and  $\text{HBF}_4$  (757mg, 8.7 mmol, 1.5 equiv.),  $\text{Ac}_2\text{O}$  (1.6 mL, 17.4 mmol, 3 equiv.) and toluene (30 mL) were added to the residue. The mixture was heated at reflux for 24 h and subsequently all the volatiles were removed in vacuo. The residue was purified by flash column chromatography (EA) on silica gel to gray solid. The solid was put in EA and then filtered after ultrasonication, and repeated several times to obtain **L6·HBF<sub>4</sub>** (1.1g, 43% yield).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (t,  $J = 1.7$  Hz, 1H), 7.79 (t,  $J = 1.8$  Hz, 1H), 7.61 (d,  $J = 1.7$  Hz, 1H), 7.61 – 7.49 (m, 4H), 7.46 – 7.39 (m, 1H), 7.34 (d,  $J = 7.8$  Hz, 2H), 2.66 (hept,  $J = 6.8$  Hz, 1H), 2.40 (hept,  $J = 6.8$  Hz, 2H), 1.29 – 1.17 (m, 19H).



**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 145.3, 144.0, 137.2, 132.2, 132.1, 132.0, 129.9, 127.8, 127.3, 127.1, 125.9, 125.9, 124.8, 29.0, 28.5, 24.3, 24.2, 23.8.

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -152.276, -152.326, -152.332.

**HRMS**–ESI (m/z): [M]<sup>+</sup> calcd for C<sub>24</sub>H<sub>31</sub>N<sup>+</sup> 347.2482; found 347.2472.

## General Procedure for Preparation of [NHC-Ni(allyl)Cl]

All the [NHC-Ni(allyl)Cl] were prepared similarly and [L1-Ni(allyl)Cl], [L2-Ni(allyl)Cl], [L3-Ni(allyl)Cl] are characterized in our recent report.<sup>12</sup>

For NHC = L1-L3,

In a glove box, 0.05 mmol Ni(cod)<sub>2</sub> were added to an oven-dried test tube. 0.2 mL cod followed by two drops of allyl chloride were added and the mixture was stirred until Ni(cod)<sub>2</sub> was dissolved completely. The solution was then dried by vacuo. NHC (0.05 mmol) and 1 mL toluene was added and the mixture was stirred at r.t. for 1 h.

For NHC = L4-L6,

The procedure is similar to the above, except NHC was generated in situ by using NHC·HCl or NHC·HBF<sub>4</sub> (0.05mmol), deprotonated by KHMDS (0.06 mmol) and 1 mL toluene were added and the mixture was stirred at r.t. for 1 h.

[L4-Ni(allyl)Cl]

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.06 (t, *J* = 7.5 Hz, 2H), 7.01 (d, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 7.5 Hz, 2H), 6.08 (s, 2H), 4.58 (tt, *J* = 13.8, 7.1 Hz, 1H), 3.32 (dd, *J* = 7.5, 2.7 Hz, 1H), 2.45 (d, *J* = 14.1 Hz, 1H), 2.31 (s, 6H), 2.26 (d, *J* = 6.8 Hz, 1H), 2.14 (s, 6H), 1.38 (dd, *J* = 13.4, 7.8 Hz, 1H), 1.08 (d, *J* = 12.8 Hz, 1H).

<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 186.1, 139.0, 136.4, 129.3, 122.7, 107.6, 69.9, 43.5, 28.4, 18.8, 18.7.

[L5-Ni(allyl)Cl]

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.16 – 7.04 (m, 8H), 6.48 (s, 2H), 5.71 – 5.42 (m, 2H), 4.56 (s, 1H), 3.45 – 3.33 (m, 1H), 2.88 (d, *J* = 47.3 Hz, 1H), 2.45 (d, *J* = 14.1 Hz, 1H), 2.25-2.12 (m, 2H), 1.38 (dd, *J* = 15.6, 8.1 Hz, 1H), 1.10 (s, 13H).

<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 188.0, 138.3, 129.9, 128.8, 128.4, 123.3, 107.5, 68.5, 43.7, 35.7, 28.4, 28.1.

[L6-Ni(allyl)Cl]

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.26 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.3 Hz, 4H), 6.52 (d, *J* = 1.8 Hz, 2H), 4.66 – 4.43 (m, 1H), 3.41 – 3.31 (m, 1H), 3.24 – 2.68 (m, 2H), 2.45 (d, *J* = 14.0 Hz, 1H), 2.23 (s, 1H), 1.68 – 0.95 (m, 22H).

<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 188.4, 138.5, 136.2, 130.4, 130.1, 129.8, 128.8, 126.6, 124.6, 123.9, 123.0, 107.5, 68.9, 43.7, 35.7, 28.8, 28.7, 28.4, 28.1, 26.6.

## **General procedure for Cross-Hydroalkenylation of Norbornene Derivatives**

### **General Procedure for the in situ Generation of [NHC-Ni(allyl)]BARF Catalyst**

In a glove box, 0.05 mmol [NHC-Ni(allyl)Cl] complex solution was filtered to an oven-dried test tube with 1.0 equiv. of NaBARF, and then the residue was filter by toluene (3\*0.2 mL). Next, 0.2 mmol of 1-octene was added, and the mixture was stirred at r.t. for 1 h before use.

### **General Procedure for the Cross-Hydroalkenylation:**

In a glove box, a toluene solution of norbornene derivatives and terminal olefin (1:1.2 or indicated ratio, 1 mL) were added in one-pot into the above in situ generated [NHC-Ni(allyl)]BARF catalyst solution, unless otherwise indicated. This solution was allowed to stir at r.t. for indicated time.

### **General workup procedure:**

After stirring for the indicated time at r.t., the reaction mixture was added a spatula of K<sub>2</sub>CO<sub>3</sub>(s), diluted with 2 mL of hexane, and was stirred in open air for 1 h. The mixture was equipped with nitromethane as standard and was stirred for another 5 min. After standing for 5 min, it was sampled out for substrate conversion analysis by <sup>1</sup>H NMR analysis. The whole mixture was then filtered through a short plug of silica gel and rinsed with 75 mL eluent (Hexane: ethyl acetate = 1:1). The solvent was removed on rotavap and was subjected to <sup>1</sup>H NMR analysis using mesitylene as standard. The product structure was then confirmed by chromatography and isolation except otherwise indicated.

### Representative Procedure for Cross-Hydroalkenylation of **1a** and **2a** to give **3aa**

A toluene solution of **1a** and **2a** (1:1.2, 2 mL) was added in one-pot to the above in situ generated [IPr-Ni(allyl)]BARF catalyst (0.05 mmol) in toluene (2 mL) (For Table 1, entry 1). After stirring at r.t. for 12 h in glovebox, the reaction mixture was added a spatula of K<sub>2</sub>CO<sub>3</sub>(s), diluted with 2 mL of hexane, and was stirred in open air for 1 h. The mixture was equipped with nitromethane as standard and was stirred for another 5 min. After standing for 5 min, it was sampled out to <sup>1</sup>H NMR and GCMS analysis. The mixture was then filtered through a short plug of silica gel and rinsed with 75 mL hexane/EA (1:1). The solvent was removed on rotary evaporation, and the residual was collected for analysis. Yield: 76%, **3:4** = 12:1. *E/Z* > 20:1, (**3+4**):**5** = 4.3:1. After column chromatography, the cross product was collected using hexane as eluent.

## Determination of the Cross-Hydroalkenylation C5/C6-Selectivity

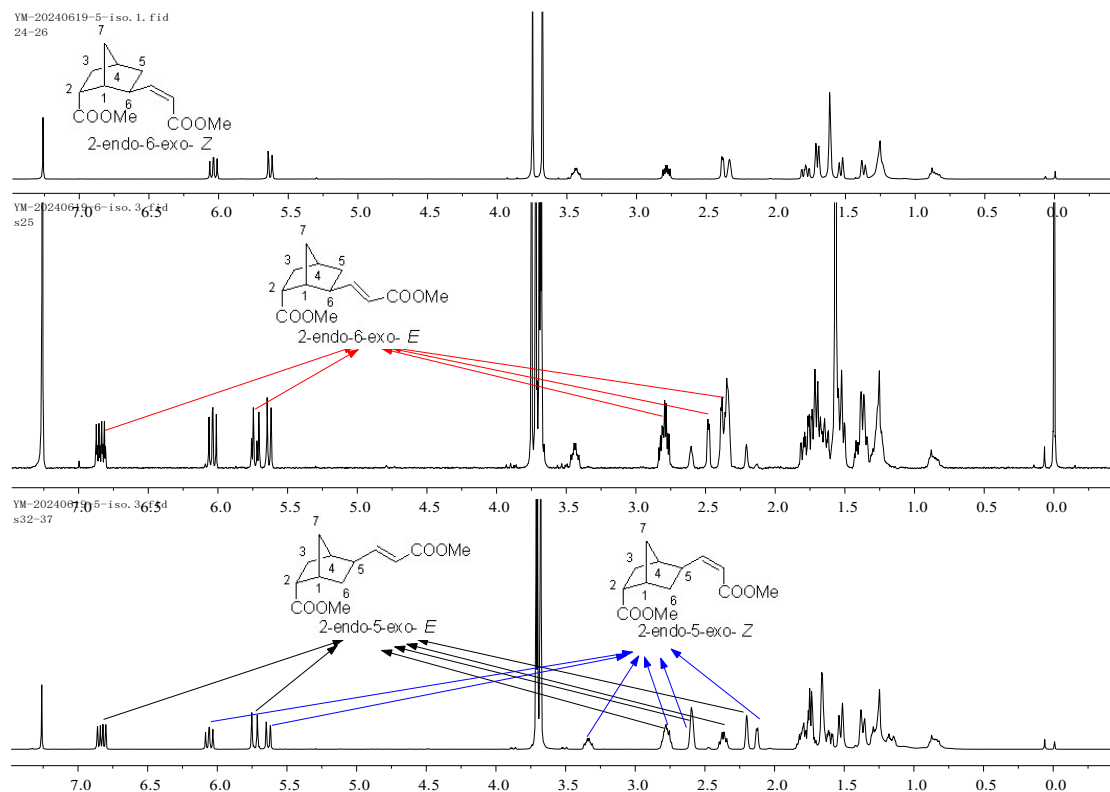
The C5/C6-product structures were determined by  $^1\text{H}$ ,  $^{13}\text{C}$ , 135 DEPT, COSY, HSQC and NOSEY NMR, and comparison of a set of isolated products.

However, in some cases with activated donors, a relatively lower *E/Z* selectivity than usual was observed and resulted in product identification problems in crude NMR. And their *E*- and *Z*-products at C5/C6-positions respectively share very similar chemical shift at the olefin region. As a consequent, their ratios were determined by other characteristic peaks and integration analysis after deduced the product structure via more detailed 2D NMR (See isolated products in the spectrum section).

Here below shown some complicated examples:

A) C5/C6-Selectivity of cross hydroalkenylation products **3fs** of **endo-1f** with methyl acrylate **2s**.

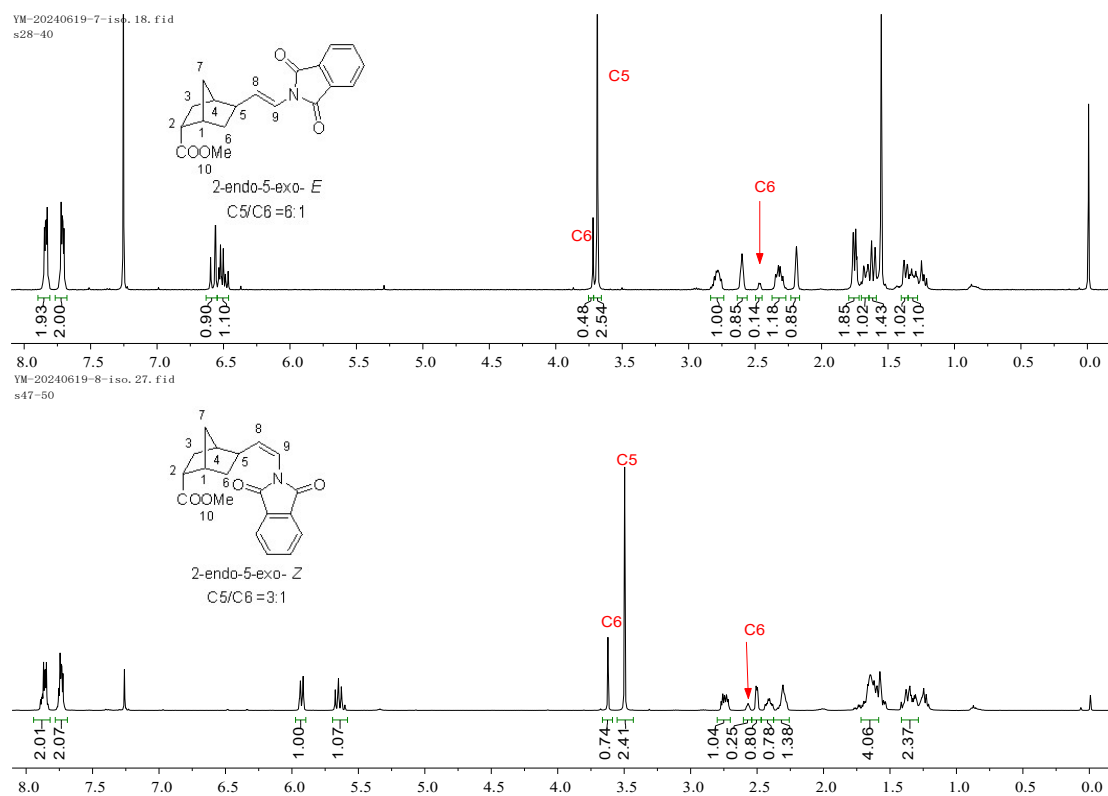
Isolated 2-endo-6-exo-*Z*-**3fs** and a *E/Z* mixture of 2-endo-5-exo-**3fs** were used to deduce the characteristic peaks of 2-endo-6-exo-*E*-**3fs**, as shown below:



The key differences between 2-endo-5-exo-*E*-**3fs** and 2-endo-6-exo-*E*-**3fs** are the chemical shift of -COOMe, H(1), H(2), H(4), H(5/6).

B) C5/C6-Selectivity of cross hydroalkenylation products **3ft** of **endo-1f** with vinylphthalimide **2t**

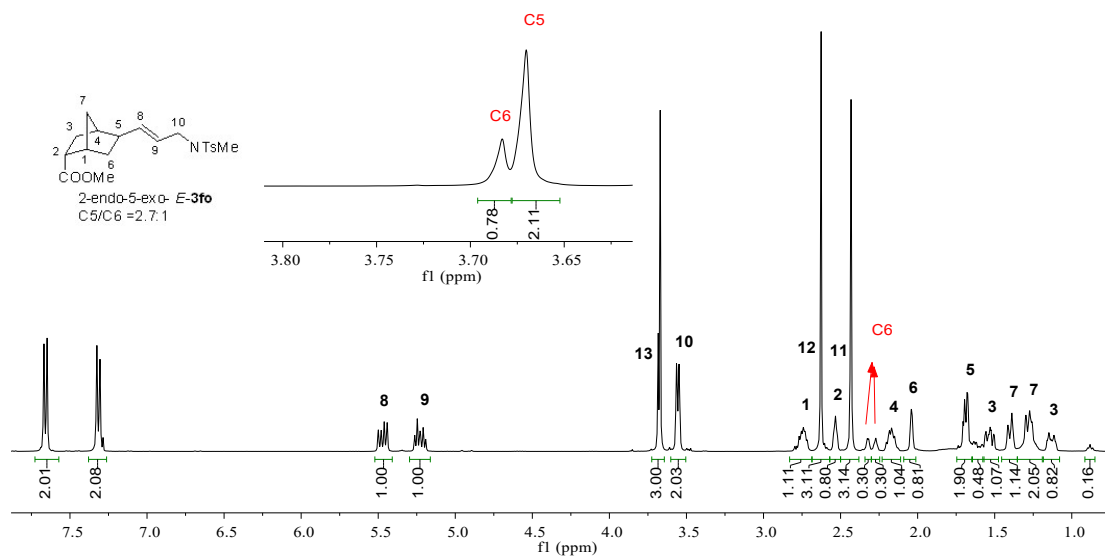
The characteristic peaks of 2-endo-6-exo-*E*-**3ft** and 2-endo-6-exo-*Z*-**3ft** in <sup>1</sup>H NMR (at 3.7 and 3.0-2.0 ppm) were determined by a comparison with the isolated 2-endo-5-exo-*Z*-**3ft** and 2-endo-5-exo-*E*-**3ft**.



C) C5/C6-Selectivity of cross hydroalkenylation products **3fo** of **endo-1f** with allylINTsMe **2o**.

No *Z* pdt was observed by NMR, 2-endo-5-exo-*E*-**3fo** and 2-endo-6-exo-*E*-**3fo** were assigned by 2D NMR. Their characteristic peaks were back deduced and can be observed in <sup>1</sup>H NMR.

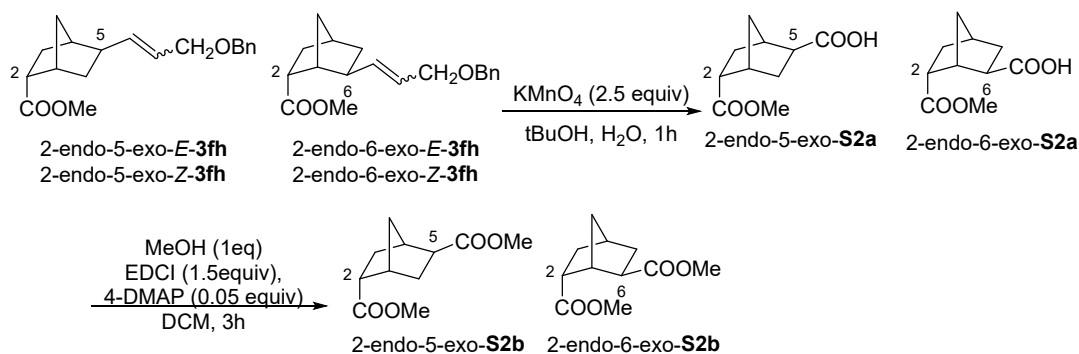
Below is a spectrum with lower product selectivity for demonstration purpose:



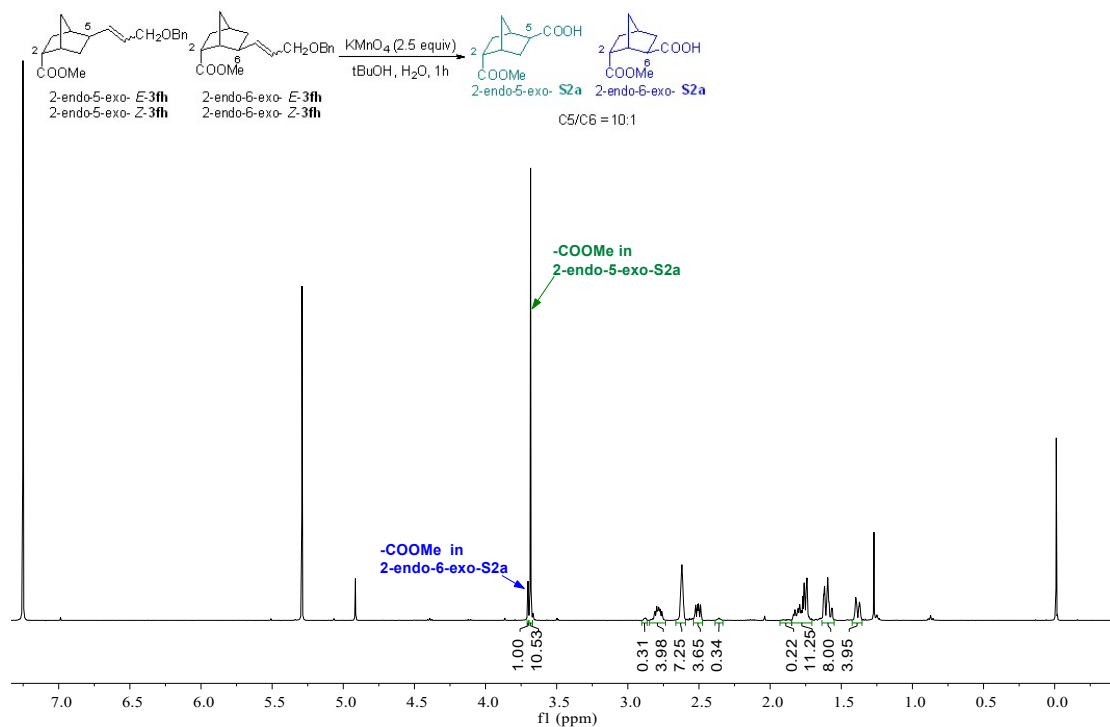
#### D) C5/C6-Selectivity of cross-HA products **3fh** of **endo-1f** with allylOBn **2h**.

The *E/Z*-product is not fully separated by column chromatography, and they have similar chemical shift at the following regions: (Alkene and allylic region at ~5.5 and ~4.0ppm, and H(1) and H(4) at 3.0-2.0 ppm).

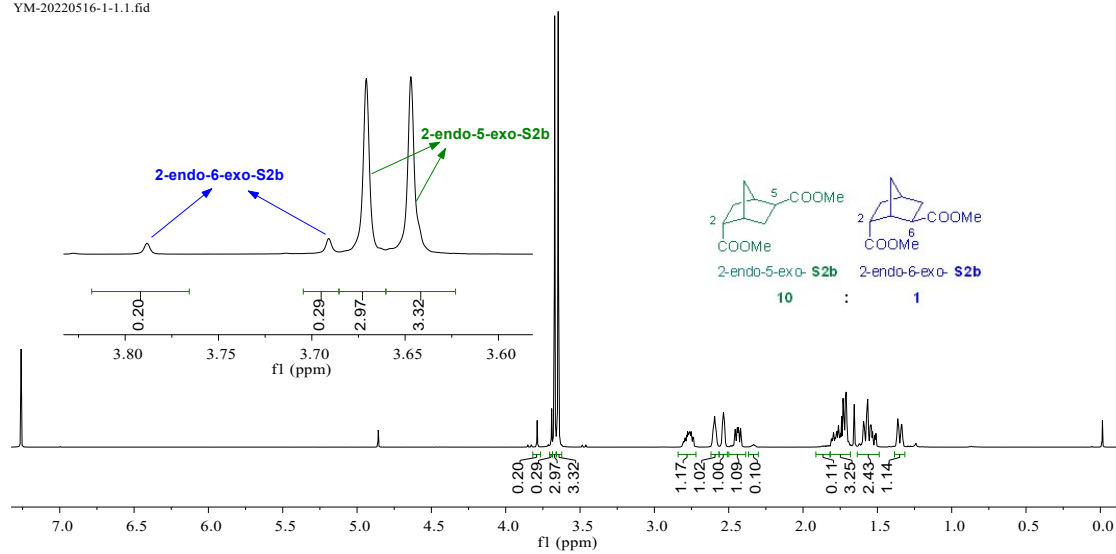
We deduced the product structure by post-oxidation of the products to the corresponding acid and ester as shown below:<sup>13</sup>



YM-20220515-1-B.1.fid



YM-20220516-1-1.1.fid

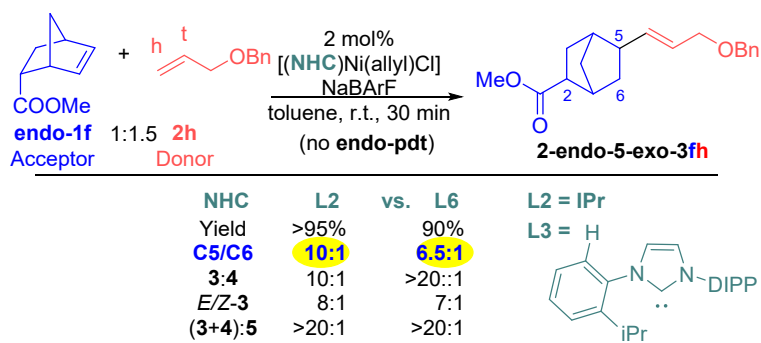


This method is also applicable for **3eh**, **3fa** and **3fo** selectivity determination.



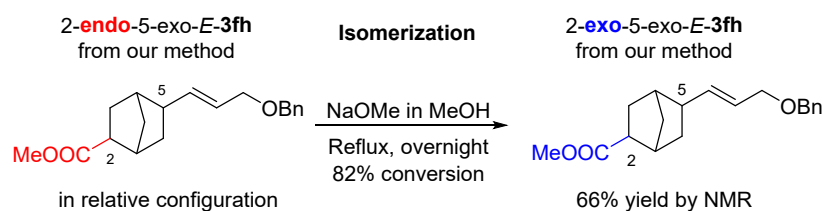
## Ligand Effect on C5/C6 Selectivity.

The ligand effect on C5/C6-selectivity was examined by using **L2** and **L6** as ligand under Table 3 condition (as showed in Fig 1). As implied by our hypothesis in the manuscript, the use of smaller NHC resulted in a significant drop of C5/C6-selectivity (from 10:1 to 6.5:1).



**ESI Table 1:** Ligand effect on C5/C6-selectivity in cross-hydroalkenylation of asymmetric substituted norbornene derivatives

## Endo-to-Exo Isomerization of the C2-Ester Stereocenter.



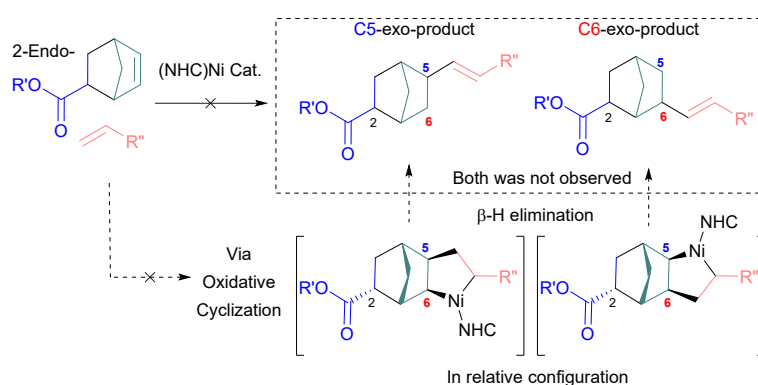
Although the exo-COOMe substituted norbornene is an efficient cross-HA acceptor, the C5-selectivity is not as good as the corresponding endo acceptor at this stage. To address this issue, we applied the isomerization literature procedure to fulfill that demand.<sup>14</sup>

The C2-endo ester (0.25 mmol) product obtained from the C5-selective cross-HA was added to a solution of NaOMe (0.25 mmol, 1 equiv.) in 2 mL MeOH. This mixture was heated overnight at reflux temperature under nitrogen atmosphere. The solution was then allowed to cool to r.t., After removed the solvent by rotary evaporation, and the residue was acidified with ice-cold 3 M HCl aqueous solution. This mixture was then quickly extracted twice with ethyl ether. The ethereal extracts were washed with brine, dried (MgSO<sub>4</sub>) and concentrated to yield a pale yellow oil. Isolated product spectra are provided in the spectra section.

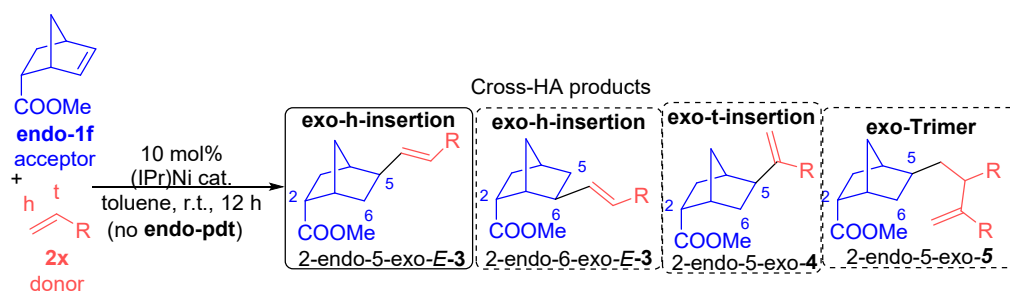
## Mechanistic discussion of C5/C6 selectivity in hydroalkenylation of norbornene derivatives

### A) Attempts to use NHC-Ni(0) and Ni(I) as catalyst in cross-hydroalkenylation of norbornene derivatives

As the Ni(II) catalyst may undergo unintended reduction and make the redox-active cross-dimerization of substrate possible (e.g. oxidative cyclization as shown below), we further tested the system by more electron-rich Ni(0) and Ni(I) catalyst directly:



However, the experimental result showed that they are not responsible for our desired reactivity and selectivity (by using 2 sets of substrates). < 5% Conversion of substrate was observed by  $^1\text{H}$  NMR.



Ni cat.	Donor	Conv. 1/2%	Yield%	3:4	E/Z-3	C5/C6
1	<b>2h</b> allylOBn <sup>[c]</sup>	< 5%	< 5%	-	-	-
(IPr)/Ni(cod) <sub>2</sub> <sup>[a]</sup>						
2	<b>2s</b> vinyl-CO <sub>2</sub> Me	< 5%	< 5%	-	-	-
3	<b>2h</b> allylOBn <sup>[c]</sup>	< 5%	< 5%	-	-	-
[Ni( $\mu$ -Cl)(IPr)] <sub>2</sub> <sup>[b]</sup>						
4	<b>2s</b> vinyl-CO <sub>2</sub> Me	< 5%	< 5%	-	-	-

Procedure: Basically the same as the cross-HA general procedure, except used different

catalysts. Olefin acceptor endo-**1f** (0.25 mmol) and olefin donor **2h** or **2s** (0.375 mmol) were added to the Ni cat. in toluene (2 mL) at r.t. and stirred for 12 h.

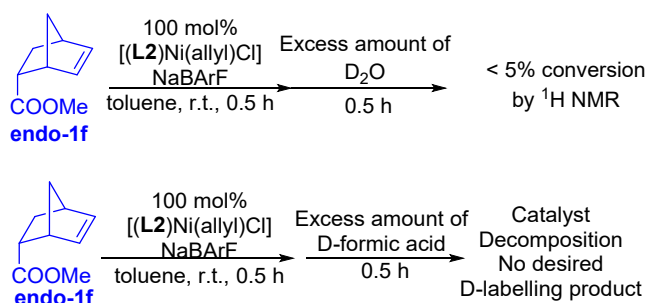
[a] (IPr)/Ni(cod)<sub>2</sub> catalyst: IPr (0.025mmol), Ni(cod)<sub>2</sub> (0.025mmol), 1 mL toluene were added to an oven-dried test tube, the mixture was stirred for 1 h.

[b] [Ni(μ-Cl)(IPr)]<sub>2</sub> was synthesized according to a reported procedure and used directly:<sup>15</sup> In a N<sub>2</sub>-filled glove box, an oven-dried test tube equipped with a magnetic stir bar was charged with Ni(dme)Cl<sub>2</sub> (50.6 mg, 0.23 mmol, 1.0 equiv.), Ni(cod)<sub>2</sub> (63 mg, 0.23 mmol, 1.0 equiv.), IPr (176 mg, 0.45 mmol, 1.97 equiv.) and toluene (4 mL) was added. The resulting mixture was stirred at r.t. inside the glovebox for 18 h. The obtained mixture was filtered through a small pad of Celite and the filtrate concentrated to 1 mL under reduced pressure. Hexane (9 mL) was added to and the mixture was cooled at -25 °C overnight, which were then filtered and washed with cold hexane (122 mg, 0.126 mmol, 54% yield). NMR data are essentially the same as reported. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.15 – 7.06 (m, 12H), 6.69 (s, 4H), 3.18-3.03 (m, 8H), 2.51 (d, *J* = 6.6 Hz, 24H), 1.17 (d, *J* = 6.7 Hz, 24H). <sup>13</sup>C NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>) δ 146.3, 139.3, 130.6, 129.6, 123.5, 29.7, 24.9, 24.4.

[c] 2 mol%, 30mins.

## B) D-labeling experiment by D<sub>2</sub>O and D-formic acid

Trapping the endo-**1f** with the our (NHC)Ni(II) catalyst was attempted by using D<sub>2</sub>O or D-formic acid as follow. However, no desired D-labeled product was observed in case of using D<sub>2</sub>O, while the catalyst and substrate decomposition were observed in the case of using D-formic acid.



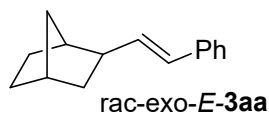
## Compound Characterization Data

All the cross-HA products were obtained as **exo-alkenyl products**.

Products were purified by normal phase silica gel column chromatography, 230-400 mesh.

See the R<sub>f</sub> information and isolated yield next to specific compounds. Some inseparable *E/Z*-products were isolated as a mixture.

### A) Table 1



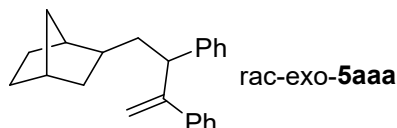
(purified by Hex, R<sub>f</sub> = 0.86 in Hex, 42% isolated yield)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.34 – 7.22 (m, 4H), 7.20 – 7.10 (m, 1H), 6.28 (d, *J* = 15.8 Hz, 1H), 6.11 (dd, *J* = 15.8, 8.0 Hz, 1H), 2.29 – 2.20 (m, 2H), 2.12 (d, *J* = 3.7 Hz, 1H), 1.58 – 1.55 (m, 1H), 1.52 (m, 2H), 1.43 (dt, *J* = 9.8, 2.0 Hz, 1H), 1.35 (dtd, *J* = 12.1, 4.5, 2.6 Hz, 1H), 1.25 (dd, *J* = 7.8, 2.1 Hz, 1H), 1.22 – 1.17 (m, 1H), 1.17 – 1.11 (m, 1H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 138.2, 136.6, 128.6, 127.4, 126.8, 126.1, 45.6, 42.9, 38.1, 36.8, 36.0, 29.9, 29.2.

**HRMS**–ESI (*m/z*): [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>19</sub><sup>+</sup> 199.1481; found 199.1475.

The minor product **4aa** was identified in the <sup>1</sup>H NMR.



(purified by Hex, R<sub>f</sub> = 0.65 in Hex, 8% isolated yield)

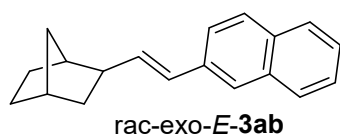
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.25 – 7.10 (m, 10zH), 5.38 (d, *J* = 1.1 Hz, 1H), 5.20 (d, *J* = 1.2 Hz, 1H), 3.83 (t, *J* = 7.5 Hz, 1H), 2.15 (d, *J* = 4.3 Hz, 1H), 2.06 (d, *J* = 3.7 Hz, 1H), 1.86 (dt, *J* = 14.1, 7.2 Hz, 1H), 1.49 – 1.24 (m, 6H), 1.04 (m, 4H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 151.9, 144.0, 143.0, 128.4, 128.3, 128.1, 127.2, 126.9, 126.2, 113.3, 48.6, 42.6, 40.9, 39.7, 38.6, 36.7, 35.6, 30.2, 28.9.

**HRMS**–ESI (*m/z*): [M+H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>27</sub><sup>+</sup> 303.2107; found 303.2096.

## B) Major products from Table 2

### B1) Vinylarenes

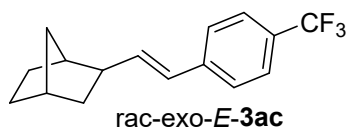


(purified by Hex,  $R_f = 0.76$  in Hex, 32% isolated yield)

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 – 7.76 (m, 3H), 7.69 (d,  $J = 1.6$  Hz, 1H), 7.60 (dd,  $J = 8.5, 1.7$  Hz, 1H), 7.51 – 7.38 (m, 2H), 6.49 (d,  $J = 15.8$  Hz, 1H), 6.29 (dd,  $J = 15.8, 8.1$  Hz, 1H), 2.35 (dt,  $J = 13.7, 4.6$  Hz, 2H), 2.21 (d,  $J = 3.7$  Hz, 1H), 1.67 – 1.60 (m, 1H), 1.58 – 1.54 (m, 1H), 1.52 (dt,  $J = 9.9, 2.0$  Hz, 1H), 1.48 – 1.42 (m, 1H), 1.36 – 1.28 (m, 2H), 1.26 (dt,  $J = 9.2, 2.0$  Hz, 1H), 1.22 (dt,  $J = 9.8, 1.9$  Hz, 1H).

$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  137.1, 135.6, 128.1, 127.9, 127.7, 127.5, 126.2, 125.5, 125.4, 123.7, 45.7, 42.9, 38.1, 36.8, 36.0, 29.9, 29.2.

**HRMS**–ESI ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{21}^+$  249.1638; found 249.1628.



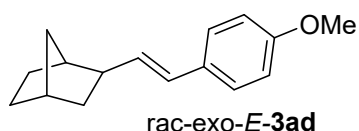
(purified by Hex,  $R_f = 0.90$  in Hex, 18% isolated yield)

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J = 8.1$  Hz, 2H), 7.41 (d,  $J = 8.1$  Hz, 2H), 6.33 (d,  $J = 15.8$  Hz, 1H), 6.22 (dd,  $J = 15.8, 7.8$  Hz, 1H), 2.29 (dt,  $J = 8.3, 3.9$  Hz, 2H), 2.15 (d,  $J = 3.6$  Hz, 1H), 1.55 – 1.33 (m, 3H), 1.33 – 1.15 (m, 5H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.3, 126.3, 126.2, 125.7, 125.6, 125.5, 45.6, 42.8, 37.9, 36.8, 36.0, 29.9, 29.1.

$^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.4.

**HRMS**–ESI ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{16}\text{H}_{18}\text{F}_3^+$  267.1355; found 267.1344.



(purified by 1:20 DCM/Hex,  $R_f = 0.45$  in 1:10 DCM/Hex, 47% isolated yield)

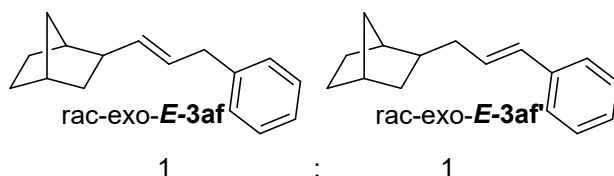
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.21 (m, 2H), 6.87 – 6.79 (m, 2H), 6.24 (d,  $J = 15.8$  Hz, 1H), 5.98 (dd,  $J = 15.8, 8.1$  Hz, 1H), 3.79 (s, 3H), 2.24 (dq,  $J = 16.7, 4.3$  Hz, 2H), 2.11 (d,  $J = 3.6$  Hz, 1H), 1.56 – 1.49 (m, 3H), 1.43 (dp,  $J = 9.8, 2.3$  Hz, 1H), 1.40 – 1.31 (m, 1H), 1.26 (dt,  $J = 6.2, 4.5$  Hz, 1H), 1.23 – 1.19 (m, 1H), 1.19 – 1.12 (m, 1H).

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.7, 134.6, 131.0, 127.1, 126.7, 114.0, 55.4, 45.6, 42.9, 38.2, 36.8, 36.0, 29.9, 29.2.

**HRMS**–ESI ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{16}\text{H}_{21}\text{O}^+$  229.1587, found 229.1579.

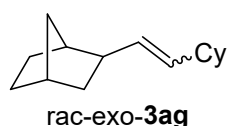
## B2) Alkyl olefins as donors (Set 2)

The products were obtained as an inseparable mixture, and were assigned based on the crude  $^1\text{H NMR}$ , a comparison with related compounds in Set 3-4, and reported literature with similar structure.<sup>16</sup>



(purified by Hex,  $R_f = 0.88$  in Hex, 25% isolated yield)

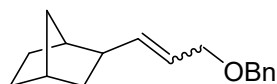
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (ddd,  $J = 8.1, 6.5, 1.4$  Hz, 2H), 7.32 – 7.26 (m, 4H), 7.19 (ddd,  $J = 7.8, 5.4, 1.5$  Hz, 4H), 6.47 – 6.29 (m, 1H, **3af'**), 6.27 – 6.14 (m, 1H, **3af'**), 5.59 – 5.37 (m, 2H, **3af**), 3.39 – 3.23 (m, 2H, **3af**), 2.22–1.92 (m, 8H), 1.54–1.07 (m, 16H).



(purified by Hex,  $R_f = 0.96$  in Hex, 11% isolated yield)

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.32–5.25 (m, 2H), 2.40–0.97 (m, 22H).

B3) Heterosubstituted olefins as donors (Set 3, O-substituted)



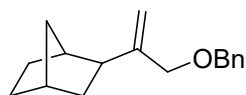
**rac-exo-3ah**  
*E/Z*=4.7:1

(purified by 1:15 DCM/Hex, *R<sub>f</sub>* = 0.21 in 1:10 DCM/Hex, 68% isolated yield)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.37 – 7.26 (m, 5H), 5.66 – 5.56 (m, 0.83H, *E*), 5.54 – 5.38 (m, 1.17H, *E+Z*), 4.46 (d, *J* = 6.5 Hz, 2H), 4.12 – 4.03 (m, 0.34H, *Z*), 3.97 – 3.91 (m, 1.66H, *E*), 2.32 – 2.26 (m, 0.17H, *Z*), 2.20 – 2.26 (m, 1H), 2.16 – 2.09 (m, 0.83H, *E*), 2.08 – 2.04 (m, 0.83H, *E*), 1.98 – 1.94 (m, 0.17H, *Z*), 1.53 – 1.42 (m, 2H), 1.37 – 1.32 (m, 1H), 1.31 – 1.26 (m, 1H), 1.26 – 1.22 (m, 1H), 1.21 (dd, *J* = 5.2, 2.6 Hz, 1H), 1.18 – 1.13 (m, 1H), 1.13 – 1.06 (m, 1H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 140.5, 128.5, 128.0, 127.7, 123.7, 72.0, 71.2, 44.8, 42.5, 37.8, 36.7, 35.8, 29.8, 29.1.

**HRMS**–ESI (*m/z*): [*M*+*H*]<sup>+</sup> calcd for C<sub>17</sub>H<sub>23</sub>O<sup>+</sup> 243.1743; found 243.1734.



**rac-exo-4ah**

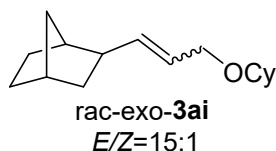
(purified by 1:15 DCM/Hex, *R<sub>f</sub>* = 0.24 in 1:10 DCM/Hex, 3% isolated yield)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.40 – 7.27 (m, 5H), 5.04 (s, 1H), 4.90 (s, 1H), 4.50 (d, *J* = 1.6 Hz, 2H), 4.00 – 3.89 (m, 2H), 2.25 (q, *J* = 4.0 Hz, 2H), 2.16 – 2.06 (m, 1H), 1.55 – 1.45 (m, 3H), 1.42 (dddd, *J* = 12.2, 6.1, 4.0, 2.5 Hz, 1H), 1.37 (dp, *J* = 9.6, 2.0 Hz, 1H), 1.24 – 1.15 (m, 2H), 1.11 (dp, *J* = 9.6, 1.6 Hz, 1H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 150.2, 138.6, 128.5, 127.8, 127.6, 108.9, 73.4, 72.1, 44.2, 40.4, 36.8, 36.7, 36.1, 30.4, 29.0.

**HRMS**–ESI (*m/z*): [*M*+*H*]<sup>+</sup> calcd for C<sub>17</sub>H<sub>23</sub>O<sup>+</sup> 243.1743; found 243.1737.



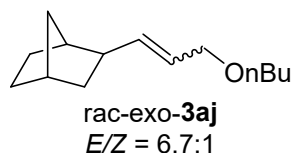


(purified by 1:15 DCM/Hex, Rf = 0.23 in 1:10 DCM/Hex, 60% isolated yield)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 5.61 – 5.54 (m, 0.94H, *E*), 5.52 – 5.35 (m, 1.06H, *E+Z*), 4.06 (d, *J* = 6.0 Hz, 0.06H, *Z*), 3.95 – 3.88 (m, 1.94H, *E*), 3.25 (tq, *J* = 9.2, 4.0 Hz, 1H), 2.22 (d, *J* = 3.9 Hz, 1H), 2.10 (td, *J* = 8.1, 4.9 Hz, 1H), 2.07 – 2.03 (m, 1H), 1.91 (dt, *J* = 7.8, 4.5 Hz, 2H), 1.73 (qt, *J* = 6.1, 4.0, 3.6 Hz, 2H), 1.57 – 1.51 (m, 1H), 1.51 – 1.42 (m, 3H), 1.34 (dp, *J* = 9.7, 2.0 Hz, 1H), 1.30 – 1.26 (m, 2H), 1.25 – 1.11 (m, 6H), 1.09 (dp, *J* = 9.7, 1.7 Hz, 1H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 139.4, 124.6, 77.1, 68.8, 44.7, 42.5, 37.8, 36.7, 35.8, 32.5, 29.8, 29.1, 26.0, 24.4.

**HRMS**–ESI (m/z): [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>27</sub>O<sup>+</sup> 235.2056; found 235.2045.

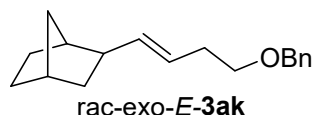


(purified by 1:15 DCM/Hex, Rf = 0.23 in 1:10 DCM/Hex, 66% isolated yield)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 5.58 (ddt, *J* = 15.3, 7.6, 1.2 Hz, 0.87H, *E*), 5.52 – 5.27 (m, 1H, *E+Z*), 4.06 – 3.98 (m, 0.26H, *Z*), 3.88 (dd, *J* = 6.3, 1.0 Hz, 1.74H, *E*), 3.40 (dt, *J* = 9.5, 6.7 Hz, 2H), 2.32 (td, *J* = 9.0, 4.6 Hz, 0.13H, *Z*), 2.22 (dd, *J* = 5.2, 3.1 Hz, 1H), 2.10 (td, *J* = 8.2, 4.9 Hz, 0.87H, *E*), 2.06 – 2.02 (m, 0.87H, *E*), 1.99 – 1.93 (m, 0.13H), 1.55 (dq, *J* = 9.0, 6.9 Hz, 2H), 1.51 – 1.42 (m, 3H), 1.41 – 1.31 (m, 3H), 1.27 (dtd, *J* = 12.3, 4.6, 2.7 Hz, 1H), 1.19 (dd, *J* = 7.7, 2.2 Hz, 1H), 1.17 – 1.12 (m, 1H), 1.09 (ddq, *J* = 9.7, 3.0, 1.6 Hz, 1H), 0.91 (t, *J* = 7.4 Hz, 3H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 139.9, 124.0, 71.8, 70.0, 44.7, 42.5, 37.8, 36.7, 35.8, 32.0, 29.8, 29.1, 19.5, 14.1.

**HRMS**–ESI (m/z): [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>25</sub>O<sup>+</sup> 209.1900; found 209.1891.



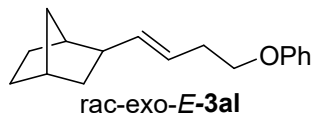
(purified by 1:15 DCM/Hex, Rf = 0.20 in 1:10 DCM/Hex, 48% isolated yield)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.37 – 7.26 (m, 5H), 5.49 – 5.25 (m, 2H), 4.51 (s, 2H), 3.47 (t, *J* = 6.9 Hz, 2H), 2.30 (q, *J* = 6.7 Hz, 2H), 2.22 (q, *J* = 5.6, 4.1 Hz, 1H), 2.05 (td, *J* = 7.8, 4.9 Hz, 1H),

2.01 (t,  $J = 2.3$  Hz, 1H), 1.46 (ddd,  $J = 14.9, 7.6, 2.8$  Hz, 3H), 1.33 (dt,  $J = 9.8, 2.1$  Hz, 1H), 1.25 – 1.21 (m, 1H), 1.21 – 1.13 (m, 2H), 1.10 – 1.05 (m, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.7, 138.4, 128.5, 127.8, 127.6, 123.7, 73.0, 70.5, 45.1, 42.8, 38.0, 36.8, 35.8, 33.2, 29.9, 29.2.

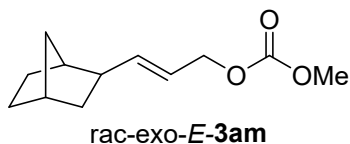
**HRMS**–ESI ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{25}\text{O}^+$  257.1900; found 257.1889.



(purified by 1:20 DCM/Hex,  $R_f = 0.60$  in 1:10 DCM/Hex, 30% isolated yield)

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.21 (m, 3H), 7.00 – 6.84 (m, 3H), 5.48 (dd,  $J = 15.4, 7.4$  Hz, 1H), 5.40 (dt,  $J = 15.3, 6.4$  Hz, 1H), 3.96 (t,  $J = 6.9$  Hz, 2H), 2.46 (q,  $J = 6.8$  Hz, 2H), 2.22 (d,  $J = 4.1$  Hz, 1H), 2.07 (td,  $J = 7.8, 4.8$  Hz, 1H), 2.04 – 2.00 (m, 1H), 1.52 – 1.43 (m, 3H), 1.35 (dt,  $J = 9.6, 2.0$  Hz, 1H), 1.27 (td,  $J = 4.6, 2.6$  Hz, 1H), 1.23 – 1.19 (m, 1H), 1.16 (dd,  $J = 6.6, 2.2$  Hz, 1H), 1.10 (dt,  $J = 9.6, 1.9$  Hz, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 139.0, 129.5, 122.9, 120.7, 114.7, 67.9, 45.1, 42.8, 38.0, 36.8, 35.8, 32.7, 29.9, 29.2.

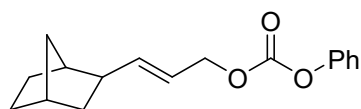


(purified by 1:10 DCM/Hex,  $R_f = 0.16$  in 1:10 DCM/Hex, 61% isolated yield)

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.70 (m, 1H), 5.48 (m, 1H), 4.55 (d,  $J = 6.5$  Hz, 2H), 3.77 (s, 3H), 2.22 (s, 1H), 2.10 (td,  $J = 8.1, 4.9$  Hz, 1H), 2.05 (d,  $J = 3.6$  Hz, 1H), 1.47 (m, 3H), 1.33 (m, 1H), 1.30 – 1.22 (m, 2H), 1.22 – 1.18 (m, 1H), 1.16 (m, 1H), 1.14 – 1.07 (m, 1H).

$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.8, 142.8, 120.7, 69.0, 54.8, 44.7, 42.3, 37.6, 36.7, 35.8, 29.8, 29.1.

**HRMS**–ESI ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{12}\text{H}_{19}\text{O}_3^+$  211.1329; found 211.1302.



rac-exo-*E*-**3an**

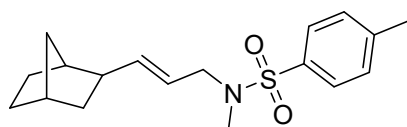
(purified by 1:10 DCM/Hex, R<sub>f</sub> = 0.18 in 1:10 DCM/Hex, 44% isolated yield)

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.38 (dd, *J* = 8.5, 7.4 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.19 – 7.16 (m, 2H), 5.78 (dd, *J* = 15.3, 7.9 Hz, 1H), 5.57 (dtd, *J* = 15.1, 6.7, 1.1 Hz, 1H), 4.67 (d, *J* = 6.8 Hz, 2H), 2.25 (d, *J* = 4.3 Hz, 1H), 2.15 (td, *J* = 8.3, 5.0 Hz, 1H), 2.08 (d, *J* = 3.8 Hz, 1H), 1.54 – 1.45 (m, 3H), 1.35 (dt, *J* = 9.8, 2.0 Hz, 1H), 1.29 (dtd, *J* = 12.3, 4.5, 2.8 Hz, 1H), 1.24 – 1.20 (m, 1H), 1.18 (dt, *J* = 9.3, 2.1 Hz, 1H), 1.13 (dt, *J* = 9.7, 1.9 Hz, 1H).

**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 153.7, 151.3, 143.5, 129.6, 126.1, 121.2, 120.3, 69.7, 44.7, 42.3, 37.6, 36.7, 35.8, 29.8, 29.1.

**HRMS**–ESI (*m/z*): [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>21</sub>O<sub>3</sub><sup>+</sup> 273.1485; found 273.1474.

B4) Heterosubstituted olefins as donors (Set 4, N-substituted)



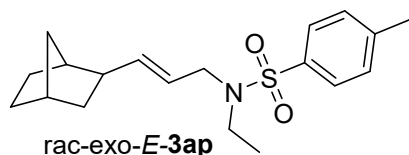
rac-exo-*E*-**3ao**

(purified by 1:20 EA/Hex, R<sub>f</sub> = 0.44 in 1:15 EA/Hex, 57% isolated yield)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.71 – 7.61 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 5.49 – 5.39 (m, 7.8 Hz, 1H), 5.20 (dt, *J* = 14.6, 6.7 Hz, 1H), 3.53 (d, *J* = 6.7 Hz, 2H), 2.62 (s, 3H), 2.42 (s, 3H), 2.19 (t, *J* = 4.5 Hz, 1H), 2.04 (td, *J* = 8.2, 4.7 Hz, 1H), 1.99 (s, 1H), 1.55 – 1.39 (m, 4H), 1.23 (m, 1H), 1.21 – 1.09 (m, 4H), 1.06 (dt, *J* = 9.6, 1.8 Hz, 1H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 143.4, 141.7, 134.6, 129.7, 127.6, 121.3, 52.6, 44.5, 42.4, 37.7, 36.7, 35.7, 34.0, 29.7, 29.0, 21.6.

**HRMS**–ESI (*m/z*): [M+H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>26</sub>NO<sub>2</sub>S<sup>+</sup> 320.1679; found 320.1666.

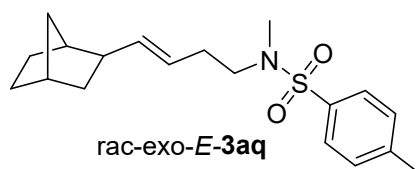


(purified by 1:20 EA/Hex, R<sub>f</sub> = 0.47 in 1:15 EA/Hex, 59% isolated yield)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.28 (s, 2H), 5.52 – 5.37 (m, 1H), 5.23 – 5.08 (m, 1H), 3.73 (d, *J* = 6.6 Hz, 2H), 3.18 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 2.19 (d, *J* = 4.0 Hz, 1H), 2.01 (q, *J* = 7.6 Hz, 1H), 1.98 – 1.92 (m, 1H), 1.50 – 1.38 (m, 3H), 1.22 (dt, *J* = 9.7, 2.0 Hz, 1H), 1.19 – 1.12 (m, 3H), 1.07 (t, *J* = 7.1 Hz, 4H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 143.0, 140.9, 137.7, 129.7, 127.3, 122.0, 49.3, 44.5, 42.4, 41.6, 37.6, 36.7, 35.7, 29.8, 29.1, 21.6, 13.9.

**HRMS**–ESI (*m/z*): [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>28</sub>NO<sub>2</sub>S<sup>+</sup> 334.1835; found 334.1817.

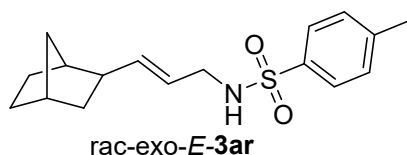


(purified by 1:20 EA/Hex, R<sub>f</sub> = 0.43 in 1:15 EA/Hex, 38% isolated yield)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.71 – 7.59 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.44 – 5.32 (m, 1H), 5.28 – 5.17 (m, 1H), 3.00 (dd, *J* = 8.5, 6.6 Hz, 2H), 2.71 (s, 3H), 2.41 (s, 3H), 2.25– 2.11 (m, 3H), 2.02 (dd, *J* = 8.4, 5.0 Hz, 1H), 1.99 – 1.95 (m, 1H), 1.54 – 1.39 (m, 3H), 1.33 – 1.26 (m, 1H), 1.24 – 1.16 (m, 2H), 1.16 – 1.12 (m, 1H), 1.12 – 1.04 (m, 1H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 143.3, 139.0, 135.0, 129.7, 127.5, 123.2, 50.3, 45.0, 42.7, 37.9, 36.7, 35.7, 34.9, 31.4, 29.8, 29.1, 21.6.

**HRMS**–ESI (*m/z*): [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>28</sub>NO<sub>2</sub>S<sup>+</sup> 334.1835; found 334.1821.



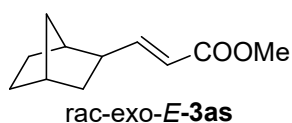
(purified by 1:20 EA/Hex, Rf = 0.16 in 1:15 EA/Hex, 58% isolated yield)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.83 – 7.69 (m, 2H), 7.34 – 7.26 (m, 2H), 5.44 – 5.33 (m, 1H), 5.22 – 5.14 (m, 1H), 4.22 (s, 1H), 3.53 – 3.45 (m, 2H), 2.40 (s, 3H), 2.16 (s, 1H), 1.96 (dd, *J* = 8.4, 4.9 Hz, 1H), 1.90 – 1.85 (m, 1H), 1.52 – 1.41 (m, 2H), 1.41 – 1.33 (m, 1H), 1.23 – 1.17 (m, 1H), 1.17 – 1.08 (m, 3H), 1.08 – 1.02 (m, 1H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 143.7, 140.5, 137.3, 129.8, 127.3, 121.9, 45.6, 44.5, 42.4, 37.6, 36.7, 35.7, 29.7, 29.0, 21.7.

**HRMS**–ESI (*m/z*): [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>24</sub>NO<sub>2</sub>S<sup>+</sup> 306.1522; found 306.1510.

#### B5) Activated olefins as donors (Set 5)

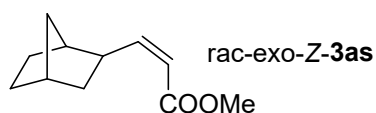


(purified by 1:5 DCM/Hex, Rf = 0.21 in 1:5 DCM/Hex, 52% isolated yield)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 6.83 (dd, *J* = 15.6, 8.2 Hz, 1H), 5.70 (dd, *J* = 15.6, 1.3 Hz, 1H), 3.69 (s, 3H), 2.28 – 2.24 (m, 1H), 2.24 – 2.18 (m, 1H), 2.14 – 2.09 (m, 1H), 1.56 – 1.45 (m, 3H), 1.41 – 1.30 (m, 2H), 1.27 – 1.13 (m, 3H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 167.7, 154.3, 118.4, 51.5, 44.8, 42.0, 37.1, 36.7, 35.9, 29.8, 29.0.

**HRMS**–ESI (*m/z*): [M+H]<sup>+</sup> calcd for C<sub>11</sub>H<sub>17</sub>O<sub>2</sub><sup>+</sup> 181.1223; found 181.1217.

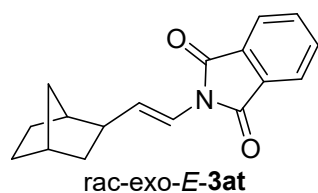


(purified by 1:5 DCM/Hex, Rf = 0.27 in 1:5 DCM/Hex, 15% isolated yield)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 6.06 (dd, *J* = 11.4, 9.9 Hz, 1H), 5.59 (dd, *J* = 11.4, 1.2 Hz, 1H), 3.67 (s, 3H), 3.27 (td, *J* = 9.2, 4.7 Hz, 1H), 2.24 (s, 1H), 2.03 (d, *J* = 1.6 Hz, 1H), 1.74 – 1.66 (m, 1H), 1.54 – 1.45 (m, 2H), 1.42 – 1.31 (m, 2H), 1.22 – 1.14 (m, 3H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 167.0, 156.4, 116.5, 51.1, 43.1, 41.0, 38.9, 36.6, 36.2, 29.7, 28.9.

**HRMS**–ESI (*m/z*): [M+H]<sup>+</sup> calcd for C<sub>11</sub>H<sub>17</sub>O<sub>2</sub><sup>+</sup> 181.1223; found 181.1216.



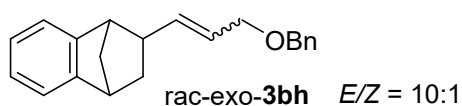
(purified by 1:20 EA/Hex, R<sub>f</sub> = 0.42 in 1:15 EA/Hex, 53% isolated yield)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.84 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.79 – 7.66 (m, 2H), 6.61 – 6.42 (m, 2H), 2.28 (s, 1H), 2.20 (td, *J* = 8.3, 4.8 Hz, 1H), 2.13 (s, 1H), 1.53 – 1.42 (m, 3H), 1.40-1.33 (m, 1H), 1.31 – 1.23 (m, 2H), 1.23 – 1.14 (m, 2H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 166.9, 134.4, 131.9, 128.2, 123.5, 116.0, 44.1, 42.9, 38.2, 36.8, 35.9, 29.9, 29.1.

**HRMS**–ESI (*m/z*): [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>18</sub>NO<sub>2</sub><sup>+</sup> 268.1332; found 268.1321.

#### B6) Symmetrically substituted norbornene derivatives (Set 6)

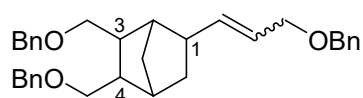


(purified by 1:100 EA/Hex, R<sub>f</sub> = 0.20 in 1:100 EA/Hex, 67% isolated yield)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.39 – 7.32 (m, 4H), 7.32 – 7.26 (m, 1H), 7.15 (ddd, *J* = 9.3, 5.2, 3.2 Hz, 2H), 7.05 (dt, *J* = 5.3, 2.4 Hz, 2H), 5.82 (ddt, *J* = 15.4, 8.2, 1.4 Hz, 1H, *E*), 5.67 – 5.58 (m, 1.2H, *E+Z*), 4.52 (s, 2H, *E*), 4.49 (s, 0.2H, *Z*), 4.13-4.00 (m, 0.2H, *Z*), 4.00 (dd, *J* = 6.2, 1.3 Hz, 2H, *E*), 3.36 – 3.31 (m, 1.1H, *E+Z*), 3.13 (s, 1H, *E*), 3.07 (s, 0.1H, *Z*), 2.44-2.36 (m, 0.1H, *Z*), 2.19 (td, *J* = 8.4, 4.3 Hz, 1H, *E*), 1.78 – 1.68 (m, 2H), 1.64 (dt, *J* = 12.1, 4.2 Hz, 1H), 1.54 (d, *J* = 2.3 Hz, 1H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 148.6, 148.3, 139.1, 138.6, 128.5, 128.0, 127.7, 125.8, 125.7, 125.5, 120.8, 120.7, 72.2, 71.1, 49.9, 46.4, 44.2, 43.1, 35.3.

**HRMS**–ESI (*m/z*): [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>22</sub>O<sup>+</sup> 291.1743; found 291.1730.



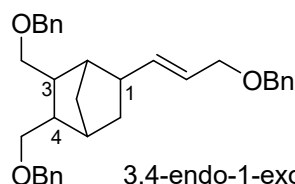
3,4-exo-1-exo-3ch  $E/Z = 12:1$

(purified by 1:40 EA/Hex,  $R_f = 0.39$  in 1:10 EA/Hex, 64% isolated yield)

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 – 7.27 (m, 15H), 5.70 – 5.57 (m, 1H, *E*), 5.57 – 5.41 (m, 1.15H, *E+Z*), 4.49 (s, 2H), 4.44 (s, 4H), 4.07 (d,  $J = 6.4$  Hz, 0.15H, *Z*), 3.95 (d,  $J = 6.4$  Hz, 2H, *E*), 3.48 (ddd,  $J = 9.2, 5.7, 3.4$  Hz, 2H), 3.28 (t,  $J = 8.4$  Hz, 2H), 2.27 – 2.16 (m, 2H), 2.11 – 2.06 (m, 1H), 2.02 – 1.92 (m, 2H), 1.36 (q,  $J = 3.9, 3.3$  Hz, 1H), 1.29 – 1.22 (m, 1H), 1.23 – 1.15 (m, 1H).

$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9, 138.8, 128.6, 128.5, 128.1, 128.0, 127.9, 127.8, 127.8, 124.4, 73.4, 73.3, 72.1, 71.2, 70.7, 70.5, 46.0, 45.7, 45.1, 44.8, 40.3, 37.6, 31.3.

**HRMS**–ESI ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{33}\text{H}_{39}\text{O}_3^+$  483.2894; found 483.2879.



3,4-endo-1-exo-*E*-3dh

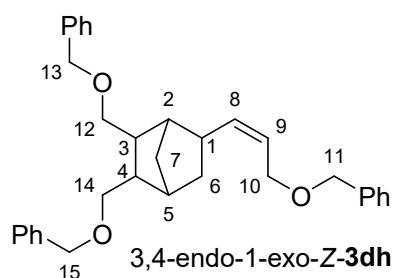
(purified by 1:40 EA/Hex,  $R_f = 0.38$  in 1:10 EA/Hex, 12% isolated yield)

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 – 7.24 (m, 15H), 5.62 (ddt,  $J = 15.3, 7.2, 1.3$  Hz, 1H), 5.46 (dtd,  $J = 15.4, 6.3, 1.2$  Hz, 1H), 4.50 – 4.38 (m, 6H), 3.94 (dd,  $J = 6.2, 1.0$  Hz, 2H), 3.56 – 3.47 (m, 2H), 3.45 – 3.39 (m, 1H), 3.34 (t,  $J = 8.8$  Hz, 1H), 2.38 – 2.31 (m, 1H), 2.29 – 2.23 (m, 2H), 2.20 – 2.16 (m, 1H), 1.66 (ddd,  $J = 13.1, 8.5, 2.6$  Hz, 1H), 1.48 (dt,  $J = 9.9, 1.8$  Hz, 1H), 1.28 (ddd,  $J = 9.9, 2.7, 1.4$  Hz, 1H), 1.25 – 1.21 (m, 1H), 1.19 – 1.10 (m, 1H).

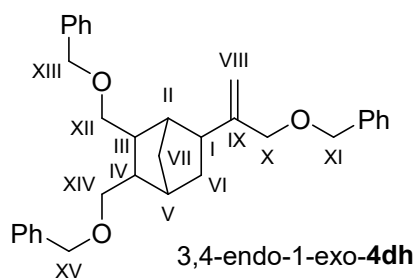
$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  140.1, 138.7, 128.5, 128.5, 128.0, 127.8, 127.8, 127.7, 127.7, 127.6, 124.3, 73.3, 72.0, 71.1, 68.5, 68.0, 45.9, 40.9, 40.3, 39.6, 37.0, 36.5, 30.7.

**HRMS**–ESI ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{33}\text{H}_{39}\text{O}_3^+$  483.2894; found 483.2881

Minor products separated from the above:



3,4-endo-1-exo-*Z*-3dh



3,4-endo-1-exo-4dh

(purified by 1:40 EA/Hex,  $R_f = 0.42$  in 1:10 EA/Hex, 11% isolated yield)

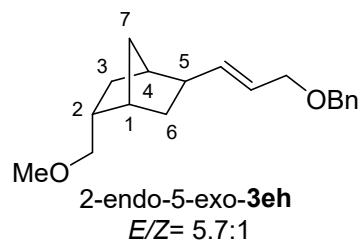
Mixture of 3,4-endo-1-exo-**Z-3dh** and 3,4-endo-1-exo-**4dh**, and **Z-3dh** : **4dh**=1 : 0.65.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.38 – 7.26 (m, 25.5H), 5.53 (dd, *J* = 10.7, 9.0 Hz, 1H, H(8)), 5.48 – 5.41 (m, 1H, H(9)), 5.10 (s, 0.63H, H(VIII)), 4.93 (s, 0.65H, H(VIII)), 4.52 – 4.37 (m, 10.2H), 4.07 (ddd, *J* = 12.1, 6.9, 1.4 Hz, 1H, H(10)), 4.01 – 3.96 (m, 1H, H(10)), 3.93 (q, *J* = 12.7, 11.7 Hz, 1.37H, H(V)), 3.61 – 3.32 (m, 6.9H, H(12), H(14), H(XII), V(XIV), 2.51 (td, *J* = 8.7, 4.7 Hz, 1H, H(1)), 2.42 – 2.20 (m, 6.53H, H(5), H(3), H(4), H(I-V) ), 2.10 (s, 1H, H(2)), 1.75 (ddd, *J* = 13.3, 8.5, 2.6 Hz, 1H, H(6)), 1.66 (ddd, *J* = 11.6, 8.8, 2.6 Hz, 0.82H, H(VI)), 1.56 – 1.49 (m, 1.84H, H(7), H(VII)), 1.38 – 1.24 (m, 3.65H, H(7), H(VII), H(VI)), 1.10 (dt, *J* = 13.1, 4.6 Hz, 1H, H(6))

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 149.7 (C(IX)), 140.2 (C(8)), 138.6, 138.6, 138.6, 128.5, 128.5, 128.5, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 124.4 (C(9)), 109.3 (C(VIII)), 73.3 (C(V)), 73.3, 73.3, 72.1, 71.9, 68.7, 68.5, 68.0, 67.9, 66.0 (C(10)), 46.9 (C(2)), 43.9 (C(5)), 41.2, 40.8, 40.2, 40.2, 39.5, 39.5, 37.2 (C(7), C(VII)), 35.9, 32.4 (C(6)), 32.1 ((C(1)), 29.5 (C(VI)).

**HRMS**–ESI (*m/z*): [M+H]<sup>+</sup> calcd for C<sub>33</sub>H<sub>39</sub>O<sub>3</sub><sup>+</sup> 483.2894; found 483.2879.

### C) Major products from Table 3



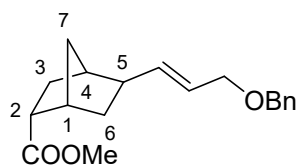
(purified by 1:40 EA/Hex, R<sub>f</sub> = 0.21 in 1:20 EA/Hex, 55% isolated yield of a mixture of 2-endo-5-exo-**3eh** and 2-endo-6-exo-**3eh**, C5/C6 ratio was determined by derivatization)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.40 – 7.27 (m, 5H), 5.62 (dd, *J* = 15.4, 7.4 Hz, 0.85H, *E*), 5.57 – 5.41 (m, 1.15H, *E+Z*), 4.52 (s, 0.35H, *Z*), 4.49 (s, 1.74H, *E*), 4.09 – 4.06 (m, 0.30H, *Z*), 3.96 (d, *J* = 6.0 Hz, 1.77H, *E*), 3.36 – 3.22 (m, 5.2H), 2.27 (d, *J* = 4.2 Hz, 1H), 2.20 – 2.06 (m, 1H), 2.06 – 1.98 (m, 2H), 1.83 – 1.67 (m, 2H), 1.51 – 1.40 (m, 1H), 1.27 (dtq, *J* = 7.3, 4.2, 1.5 Hz, 1H), 1.18 (dddd, *J* = 13.0, 5.4, 4.2, 1.6 Hz, 0.85H, *E*), 1.12 – 1.01 (m, 0.17H, *Z*), 0.75-0.62 (m, 1H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 140.1, 138.5, 128.5, 128.0, 127.7, 124.0, 75.1, 72.0, 71.1, 59.0, 45.1, 42.9, 39.1, 38.8, 37.3, 34.1, 30.9.

**HRMS**–ESI (*m/z*): [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>27</sub>O<sub>2</sub><sup>+</sup> 287.2006; found 287.1998.





2-endo-5-exo-**3fh**  
*E/Z*=10:1

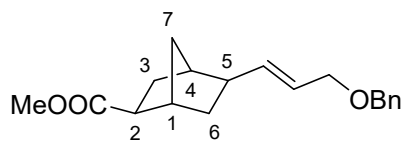
(purified by 1:40 EA/Hex, *R<sub>f</sub>* = 0.21 in 1:20 EA/Hex, 69% isolated yield of a mixture of 2-endo-5-exo-**3fh** and 2-endo-6-exo-**3fh**, C5/C6 ratio was determined by derivatization)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.34 (d, *J* = 5.0 Hz, H), 5.61 (ddt, *J* = 15.3, 7.5, 1.1 Hz, 0.9H, *E*), 5.56 – 5.44 (m, 1.1H, *E+Z*), 4.50 (d, *J* = 9.0 Hz, 2H), 4.13 – 4.03 (m, 0.18H, *Z*), 3.95 (dd, *J* = 6.2, 1.0 Hz, 1.8H, *E*), 3.68 (d, *J* = 1.7 Hz, 4H), 2.80 – 2.72 (m, 1H), 2.55 (td, *J* = 4.3, 1.2 Hz, 1H), 2.24 (td, *J* = 8.3, 4.8 Hz, 1H), 2.13 (dt, *J* = 3.4, 1.5 Hz, 1H), 1.74 – 1.67 (m, 2H), 1.57 (ddd, *J* = 13.1, 8.5, 2.5 Hz, 1H), 1.52 – 1.48 (m, 1H), 1.31 (ddt, *J* = 11.6, 3.1, 1.6 Hz, 1H), 1.27 – 1.19 (m, 1H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.5, 139.4, 138.5, 128.5, 127.9, 127.7, 124.3, 72.0, 71.0, 51.7, 45.3, 44.0, 43.0, 40.8, 37.6, 33.0, 32.2.

**HRMS**–ESI (*m/z*): [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>25</sub>O<sub>3</sub><sup>+</sup> 301.1798; found 301.1792.

2-exo-5-exo-*E*-**3fh** and 2-exo-6-exo-*E*-**3fh** were obtained from a cross-HA with an **exo-1f** as substrate:

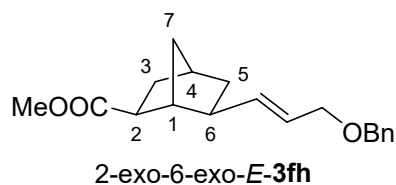


2-exo-5-exo-*E*-**3fh**

(purified by 1:40 EA/Hex, *R<sub>f</sub>* = 0.21 in 1:20 EA/Hex, 48% isolated yield of a mixture of 2-exo-5-exo-*E*-**3fh** and 2-exo-6-exo-*E*-**3fh**)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.40 – 7.27 (m, 5H), 5.66 – 5.58 (m, 1H), 5.58 – 5.43 (m, 1H), 4.49 (s, 2H), 3.96 (dd, *J* = 6.3, 1.3 Hz, 2H), 3.66 (s, 3H), 2.51 (d, *J* = 4.2 Hz, 1H), 2.35-2.30 (m, 1H), 2.16-2.11 (d, *J* = 4.9 Hz, 2H), 1.90-1.82 (m, 1H), 1.57-1.46 (m, 2H), 1.42-1.30 (m, 3H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 176.6, 139.4, 138.5, 128.5, 127.9, 127.7, 124.5, 72.1, 71.0, 51.8, 46.0, 43.9, 42.2, 41.3, 37.4, 34.3, 34.0.

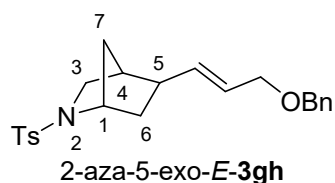


(purified by 1:40 EA/Hex, R<sub>f</sub> = 0.21 in 1:20 EA/Hex, 48% isolated yield of a mixture of 2-exo-5-exo-*E*-3fh and 2-exo-6-exo-*E*-3fh)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.40 – 7.27 (m, 5H), 5.66 – 5.58 (m, 1H), 5.58 – 5.43 (m, 1H), 4.49 (s, 2H), 3.96 (dd, *J* = 6.3, 1.3 Hz, 2H), 3.66 (s, 3H), 2.40 – 2.35 (m, 2H), 2.35-2.30 (m, 1H), 2.23-2.17 (m, 1H), 1.90-1.82 (m, 1H), 1.57-1.46 (m, 2H), 1.42-1.30 (m, 3H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 176.3, 138.9, 138.5, 128.5, 127.9, 127.7, 124.8, 72.1, 71.0, 51.9, 46.7, 46.6, 44.5, 36.8, 36.4, 34.0, 33.6.

**HRMS**–ESI (m/z): [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>25</sub>O<sub>3</sub><sup>+</sup> 301.1798; found 301.1789.

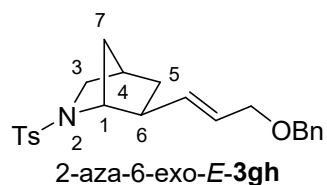


(purified by 1:20 EA/Hex, R<sub>f</sub> = 0.28 in 1:5 EA/Hex, 31% isolated yield)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.72 – 7.69 (m, 2H), 7.34 – 7.26 (m, 7H), 5.61 – 5.53 (m, 2H), 4.47 (s, 2H), 4.19 – 4.14 (m, 1H), 3.93 (d, *J* = 4.6 Hz, 2H), 3.07 (d, *J* = 2.4 Hz, 2H), 2.42 (d, *J* = 2.1 Hz, 3H), 2.39 – 2.33 (m, 1H), 2.30 (d, *J* = 1.5 Hz, 1H), 2.11 – 2.04 (m, 1H), 1.38 (ddd, *J* = 13.0, 5.0, 2.9 Hz, 1H), 1.33 (dd, *J* = 10.4, 2.3 Hz, 1H), 0.92 (dt, *J* = 10.2, 2.2 Hz, 1H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 143.4, 138.3, 137.0, 135.8, 129.8, 128.5, 127.9, 127.8, 127.6, 125.8, 72.4, 70.7, 60.3, 54.2, 43.3, 42.7, 39.0, 34.3, 21.7.

**HRMS**–ESI (m/z): [M+H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>28</sub>NO<sub>3</sub>S<sup>+</sup> 398.1784; found 398.1779.



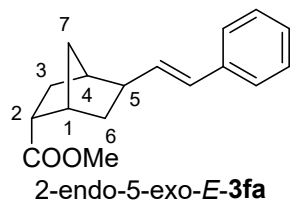
(purified by 1:20 EA/Hex, R<sub>f</sub> = 0.31 in 1:5 EA/Hex, 18% isolated yield)

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.71 – 7.68 (m, 2H), 7.38 – 7.28 (m, 7H), 5.58 (dtd, *J* = 15.5, 5.7, 1.2 Hz, 1H), 5.47 (dtd, *J* = 15.6, 7.3, 1.3 Hz, 1H), 4.49 (s, 2H), 3.98 – 3.96 (m, 1H), 3.95 (dq, *J* = 5.9, 1.2 Hz, 2H), 3.10 – 2.98 (m, 2H), 2.73 (q, *J* = 7.4, 6.8 Hz, 1H), 2.47 (d, *J* = 10.4 Hz, 1H),

2.42 (s, 3H), 1.68 (ddd,  $J = 12.9, 8.6, 2.3$  Hz, 1H), 1.42 (dtd,  $J = 12.9, 4.5, 2.5$  Hz, 1H), 1.33 – 1.28 (m, 1H), 0.85 (dp,  $J = 10.4, 2.4, 1.9$  Hz, 1H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  143.4, 138.3, 135.8, 135.0, 129.8, 128.5, 127.9, 127.8, 127.5, 127.0, 72.4, 70.7, 64.2, 53.8, 46.0, 37.6, 34.9, 34.1, 21.7.

HRMS–ESI (m/z):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{23}\text{H}_{28}\text{NO}_3\text{S}^+$  398.1784; found 398.1779.

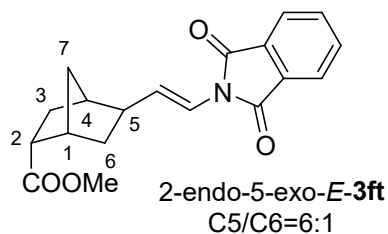


(purified by 1:100 EA/Hex,  $R_f = 0.20$  in 1:100 EA/Hex, 9% isolated yield)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (dd,  $J = 8.2, 6.9$  Hz, 3H), 7.24 – 7.15 (m, 2H), 6.31 (d,  $J = 15.7$  Hz, 1H), 6.10 (dd,  $J = 15.8, 8.1$  Hz, 1H), 3.70 (s, 3H), 2.85 – 2.73 (m, 1H), 2.60 (s, 1H), 2.37 (td,  $J = 13.2, 12.5, 7.8$  Hz, 1H), 2.20 (s, 1H), 1.79 – 1.71 (m, 2H), 1.65 (ddd,  $J = 13.3, 8.5, 2.5$  Hz, 1H), 1.39 – 1.29 (m, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  175.5, 137.9, 135.7, 128.6, 128.0, 127.0, 126.1, 51.7, 45.4, 44.8, 43.3, 40.9, 37.8, 33.3, 32.3.

HRMS–ESI (m/z):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{21}\text{O}_2^+$  257.1536; found 257.1532.

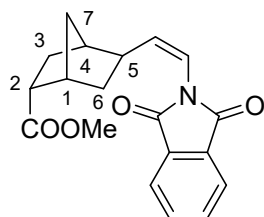


(purified by 1:20 EA/Hex,  $R_f = 0.27$  in 1:10 EA/Hex, 56% isolated yield of a mixture of 2-endo-5-exo-*E*-**3ft** and 2-endo-6-exo-*E*-**3ft**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (dd,  $J = 5.4, 3.0$  Hz, 2H), 7.72 (dt,  $J = 5.5, 2.3$  Hz, 2H), 6.59 (d,  $J = 14.7$  Hz, 1H), 6.55 – 6.47 (m, 1H), 3.73 (s, 0.42H, C6), 3.69 (s, 2.58H, C5), 2.84 – 2.74 (m, 1H), 2.61 (s, 0.86H, C5), 2.47 (d,  $J = 4.3$  Hz, 0.14H, C6), 2.38 – 2.28 (m, 1.14H, C5, C6), 2.20 (s, 0.86H, C5), 1.80 – 1.72 (m, 2H), 1.71 – 1.65 (m, 1H), 1.65 – 1.59 (m, 1H), 1.38 (dd,  $J = 10.0, 2.2$  Hz, 1H), 1.36 – 1.28 (m, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.4, 166.8, 134.4, 131.9, 127.2, 123.6, 116.5, 51.7, 45.3, 43.5, 43.4, 40.9, 37.8, 33.5, 32.3.

**HRMS**–ESI (m/z): [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>19</sub>NO<sub>4</sub><sup>+</sup> 326.1387; found 326.1376.

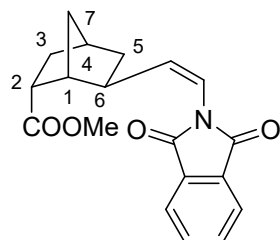


**2-endo-5-exo-Z-3ft**

(purified by 1:10 EA/Hex, R<sub>f</sub> = 0.15 in 1:10 EA/Hex, 19% isolated yield of a mixture of 2-endo-5-exo-Z-**3ft** and 2-endo-6-exo-Z-**3ft**)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.87 (ddd, *J* = 8.6, 5.4, 3.1 Hz, 2H), 7.78 – 7.69 (m, 2H), 5.93 (dd, *J* = 8.4, 2.9 Hz, 1H), 5.64 (td, *J* = 10.7, 10.2, 8.3 Hz, 1H), 3.50 (s, 3H), 2.74 (dt, *J* = 11.4, 4.9 Hz, 1H), 2.50 (d, *J* = 4.2 Hz, 1H), 2.41 (td, *J* = 9.1, 4.3 Hz, 1H), 2.36-2.23 (m, 1H), 1.71-1.52 (m, 4H), 1.40-1.29 (m, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.0, 167.0, 138.5, 134.3, 132.2, 123.6, 114.8, 51.5, 46.4, 46.0, 38.0, 37.9, 37.4, 35.1, 31.4.



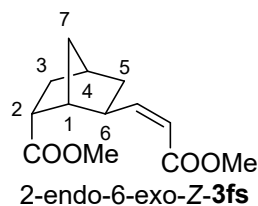
**2-endo-6-exo-Z-3ft**

(purified by 1:10 EA/Hex, R<sub>f</sub> = 0.15 in 1:10 EA/Hex, 19% isolated yield of a mixture of 2-endo-5-exo-Z-**3ft** and 2-endo-6-exo-Z-**3ft**)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.87 (ddd, *J* = 8.6, 5.4, 3.1 Hz, 2H), 7.78 – 7.69 (m, 2H), 5.93 (dd, *J* = 8.4, 2.9 Hz, 1H), 5.64 (td, *J* = 10.7, 10.2, 8.3 Hz, 1H), 3.62 (s, 3H), 2.74 (dt, *J* = 11.4, 4.9 Hz, 1H), 2.57 (d, *J* = 4.5 Hz, 1H), 2.36-2.23 (m, 2H), 1.79-1.52 (m, 3H), 1.40-1.24 (m, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.3, 167.3, 138.0, 134.3, 132.2, 123.8, 114.3, 51.7, 45.3, 43.3, 40.7, 40.3, 37.8, 33.4, 32.2.

**HRMS**–ESI (m/z): [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>19</sub>NO<sub>4</sub><sup>+</sup> 326.1387; found 326.1378.

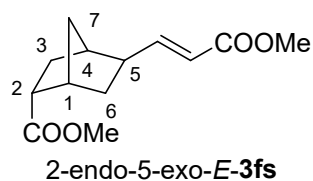


(purified by 1:40 EA/Hex, R<sub>f</sub> = 0.40 in 1:10 EA/Hex, 16% isolated yield)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.04 (dd, *J* = 11.4, 9.6 Hz, 1H), 5.63 (dd, *J* = 11.4, 1.3 Hz, 1H), 3.75 (s, 3H), 3.68 (s, 3H), 3.43 (td, *J* = 9.0, 4.4 Hz, 1H), 2.78 (td, *J* = 8.4, 4.3 Hz, 1H), 2.38 (dd, *J* = 4.4, 1.5 Hz, 1H), 2.33 (s, 1H), 1.79 (ddd, *J* = 12.5, 8.6, 2.5 Hz, 1H), 1.73 – 1.66 (m, 2H), 1.57 – 1.49 (m, 1H), 1.37 (ddq, *J* = 10.1, 3.1, 1.6 Hz, 1H), 1.28 – 1.18 (m, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.0, 166.4, 154.6, 117.6, 51.9, 51.1, 46.8, 46.1, 38.6, 37.8, 37.4, 35.8, 31.3.

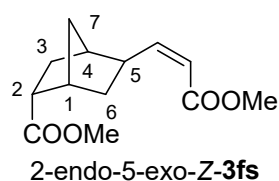
HRMS–ESI (*m/z*): [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>18</sub>O<sub>4</sub><sup>+</sup> 239.1278; found 239.1270.



(purified by 1:40 EA/Hex, R<sub>f</sub> = 0.35 in 1:10 EA/Hex, 39% isolated yield of a mixture of 2-endo-5-exo-*E*-**3fs** and 2-endo-5-exo-*Z*-**3fs**)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.83 (dd, *J* = 15.6, 8.2 Hz, 1H), 5.73 (dd, *J* = 15.5, 1.3 Hz, 1H), 3.71 (s, 3H), 3.68 (s, 3H), 2.78 (dq, *J* = 11.3, 6.3, 2.1 Hz, 1H), 2.60 (t, *J* = 4.2 Hz, 1H), 2.37 (td, *J* = 8.3, 5.2 Hz, 1H), 2.24 – 2.18 (m, 1H), 1.85 – 1.70 (m, 2H), 1.64 – 1.58 (m, 1H), 1.52 (dt, *J* = 10.1, 1.9 Hz, 1H), 1.37 (dtt, *J* = 10.3, 2.9, 1.5 Hz, 1H), 1.29 (td, *J* = 4.8, 3.6, 1.9 Hz, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.2, 167.6, 153.3, 119.0, 51.8, 51.6, 45.2, 43.9, 42.5, 40.8, 37.8, 32.4, 32.2.



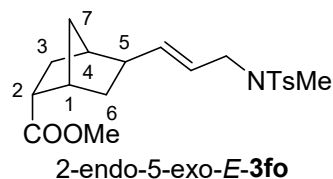
(purified by 1:40 EA/Hex, R<sub>f</sub> = 0.35 in 1:10 EA/Hex, 39% isolated yield of a mixture of 2-endo-5-exo-*E*-**3fs** and 2-endo-5-exo-*Z*-**3fs**)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.06 (dd, *J* = 11.5, 9.6 Hz, 1H), 5.63 (dd, *J* = 11.5, 1.3 Hz, 1H), 3.70

(s, 3H), 3.68 (s, 3H), 3.34 (td,  $J = 9.1, 4.8$  Hz, 1H), 2.78 (dq,  $J = 11.3, 6.3, 2.1$  Hz, 1H), 2.60 (t,  $J = 4.2$  Hz, 1H), 2.13 (d,  $J = 4.3$  Hz, 1H), 1.85 – 1.70 (m, 3H), 1.52 (dt,  $J = 10.1, 1.9$  Hz, 1H), 1.37 (dtt,  $J = 10.3, 2.9, 1.5$  Hz, 1H), 1.16 (dtd,  $J = 13.3, 4.5, 2.0$  Hz, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.0, 166.7, 155.2, 117.5, 51.7, 51.2, 45.4, 43.8, 40.6, 40.6, 37.9, 34.2, 32.0.

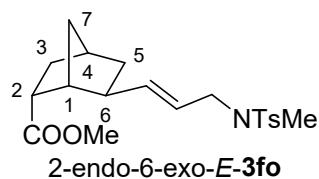
**HRMS**–ESI (m/z):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_{18}\text{O}_4^+$  239.1278; found 239.1268.



(purified by 1:20 EA/Hex,  $R_f = 0.21$  in 1:10 EA/Hex, 65% isolated yield of a mixture of 2-endo-5-exo- *E*-**3fo** and 2-endo-6-exo-*E*-**3fo**)

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 – 7.57 (m, 2H), 7.32 (d,  $J = 8.0$  Hz, 2H), 5.52 – 5.41 (m, 1H), 5.23 (dtd,  $J = 15.0, 6.6, 1.2$  Hz, 1H), 3.67 (s, 3H), 3.56 (d,  $J = 6.6$  Hz, 2H), 2.83 – 2.69 (m, 1H), 2.63 (s, 3H), 2.54 (d,  $J = 4.3$  Hz, 1H), 2.43 (s, 3H), 2.18 (td,  $J = 8.4, 5.6$  Hz, 1H), 2.09 – 2.01 (m, 1H), 1.75 – 1.64 (m, 2H), 1.58-1.49 (m, 1H), 1.45 – 1.35 (m, 1H), 1.32 – 1.26 (m, 1H), 1.13 (dtd,  $J = 13.0, 4.6, 1.9$  Hz, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.3, 143.4, 140.7, 134.6, 129.7, 127.5, 121.9, 52.4, 51.6, 45.2, 43.7, 42.9, 40.7, 37.5, 34.0, 32.8, 32.1, 21.6.



(purified by 1:20 EA/Hex,  $R_f = 0.21$  in 1:10 EA/Hex, 65% isolated yield of a mixture of 2-endo-5-exo- *E*-**3fo** and 2-endo-6-exo-*E*-**3fo**)

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 – 7.57 (m, 2H), 7.32 (d,  $J = 8.0$  Hz, 2H), 5.52 – 5.41 (m, 1H), 5.23 (dtd,  $J = 15.0, 6.6, 1.2$  Hz, 1H), 3.68 (s, 3H), 3.56 (d,  $J = 6.6$  Hz, 2H), 2.83 – 2.69 (m, 1H), 2.63 (s, 3H), 2.43 (s, 3H), 2.35 – 2.29 (m, 1H), 2.28 (d,  $J = 4.5$  Hz, 1H), 2.18 (td,  $J = 8.4, 5.6$  Hz, 1H), 1.64 – 1.57 (m, 2H), 1.58-1.49 (m, 1H), 1.45 – 1.35 (m, 1H), 1.35 – 1.21 (m, 2H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.1, 143.4, 140.4, 134.6, 129.7, 127.5, 122.3, 52.4, 51.7, 46.0, 45.8, 39.1, 37.3, 37.3, 37.1, 34.1, 31.4, 21.6.

HRMS–ESI (m/z): [M+H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>27</sub>NO<sub>4</sub>S<sup>+</sup> 378.1734; found 378.1722.

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