SUPPORTING INFORMATION: PART B

Iridium-catalyzed enantioselective olefinic C(sp²)–H allylic alkylation

Rahul Sarkar, and Santanu Mukherjee*

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, INDIA

*Corresponding author: E-mail: sm@iisc.ac.in
Enantioselective Olefin $C(sp^2)$–H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-2
Enantioselective Olefinic C\((sp^2)\)‒H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-4
Enantioselective Olefinic C(sp²)‒H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-5
Enantioselective Olefinic C(sp$^2$)‒H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-7

Phenomenex Cellulose-1 column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

| Peak# | Ret. Time | Area  | Area % |
|-------|-----------|-------|--------|
| 1     | 4.806     | 18096 | 2.693  |
| 2     | 5.310     | 653800| 97.307 |
| Total |           | 671896| 100.000|

PeakTable

PDA Ch1 290nm 4nm

mAU

PDA Multi 1

min
Enantioselective Olefinic C(sp²)‒H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-8
Enantioselective Olefinic C\( \text{sp}^2 \)-H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-9

Phenomenex Cellulose-2 column (75:25 \( n \)-Hexane/EtOH, 1.0 mL/min, 20 °C)

| Peak# | Ret. Time | Area  | Area % |
|-------|-----------|-------|--------|
| 1     | 5.115     | 338222| 50.076 |
| 2     | 5.664     | 337192| 49.924 |
| Total |           | 675414| 100.000|

Phenomenex Cellulose-2 column (75:25 \( n \)-Hexane/EtOH, 1.0 mL/min, 20 °C)

| Peak# | Ret. Time | Area  | Area % |
|-------|-----------|-------|--------|
| 1     | 5.153     | 1834359| 97.015 |
| 2     | 5.710     | 56438 | 2.985  |
| Total |           | 1890797| 100.000|
Enantioselective Olefinic $C(s^p)$–H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-11

Phenomenex Cellulose-2 column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)
Enantioselective Olefinic C(spinor)-H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-12
Daicel Chiralpak IB column (95:5 n-Hexane/EtOH, 0.5 mL/min, 20 °C)

PeakTable

| Peak# | Ret. Time | Area   | Area % |
|-------|-----------|--------|--------|
| 1     | 12.717    | 349177 | 49.648 |
| 2     | 13.277    | 354135 | 50.352 |
| Total |           | 703313 | 100.00 |

Daicel Chiralpak IB column (95:5 n-Hexane/EtOH, 0.5 mL/min, 20 °C)

PeakTable

| Peak# | Ret. Time | Area   | Area % |
|-------|-----------|--------|--------|
| 1     | 12.729    | 25060  | 4.180  |
| 2     | 13.277    | 574465 | 95.820 |
| Total |           | 599526 | 100.00 |
Enantioselective Olefin C(sp²)‒H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-14
Enantioselective Olefinic C(sp²)‒H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-15

Phenomenex Cellulose-2 column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)
Phenomenex Cellulose-2 column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

Peak Table

| Peak# | Ret. Time | Area   | Area % |
|-------|-----------|--------|--------|
| 1     | 10.459    | 575144 | 52.646 |
| 2     | 11.734    | 517326 | 47.354 |
| Total |           | 1092470| 100.000|

Phenomenex Cellulose-2 column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

Peak Table

| Peak# | Ret. Time | Area   | Area % |
|-------|-----------|--------|--------|
| 1     | 10.441    | 1097237| 95.681 |
| 2     | 11.710    | 49533  | 4.319  |
| Total |           | 1146770| 100.000|
**Enantioselective Olefinic C(sp)^2^-H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-19**

Phenomenex Cellulose-2 column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

| Peak# | Ret. Time | Area   | Area % |
|-------|-----------|--------|--------|
| 1     | 5.544     | 150239 | 50.140 |
| 2     | 6.189     | 149395 | 49.859 |
| Total |           | 299633 | 100.000|

**PeakTable**
Enantioselective Olefinic C(sp²)‒H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-20

**RHS-IV-252-01**

![Chemical Structure](image)

**3bj**

NMR spectra are shown, with peak assignments and chemical shifts indicated.

![NMR Spectrum](image)

**RHS-IV-252-01**

![NMR Spectrum](image)

**3bj**

Chemical shifts and assignments are provided for the NMR spectra.
Enantioselective Olefinic C(sp$^3$)−H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-21

Phenomenex Cellulose-2 column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

| Peak# | Ret. Time | Area   | Area % |
|-------|-----------|--------|--------|
| 1     | 5.356     | 236066 | 50.054 |
| 2     | 5.937     | 255511 | 49.946 |
| Total |           | 511577 | 100.000|

Phenomenex Cellulose-2 column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

| Peak# | Ret. Time | Area   | Area % |
|-------|-----------|--------|--------|
| 1     | 5.364     | 346423 | 97.665 |
| 2     | 5.946     | 8282   | 2.335  |
| Total |           | 354704 | 100.000|
Enantioselective Olefinic $C(sp^2)$–H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-23

Phenomenex Cellulose-2 column (75:25 $n$-Hexane/EtOH, 1.0 mL/min, 20 °C)

Phenomenex Cellulose-2 column (75:25 $n$-Hexane/EtOH, 1.0 mL/min, 20 °C)
Enantioselective Olefinic C(sp²)‒H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-24
Enantioselective Olefinic C(sp$^2$)–H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-25

Phenomenex Cellulose-2 column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

| Peak# | Ret. Time | Area   | Area %  |
|-------|-----------|--------|---------|
| 1     | 5.694     | 150302 | 50.347  |
| 2     | 6.414     | 148233 | 49.653  |
| Total |           | 298535 | 100.000 |

Phenomenex Cellulose-2 column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

| Peak# | Ret. Time | Area   | Area %  |
|-------|-----------|--------|---------|
| 1     | 5.676     | 1322456| 97.805  |
| 2     | 6.394     | 29673  | 2.195   |
| Total |           | 1352129| 100.000 |
Enantioselective Olefinic $C(sp^2)$–H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-27

Phenomenex Cellulose-2 column (75:25 $n$-Hexane/EtOH, 1.0 mL/min, 20 °C)
Phenomenex Cellulose-2 column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

PeakTable

| Peak# | Ret. Time | Area  | Area % |
|-------|-----------|-------|--------|
| 1     | 6.762     | 4941660 | 49.662 |
| 2     | 7.294     | 5008911 | 50.338 |
| Total |           | 9950580 | 100.000 |

mAU

Phenomenex Cellulose-2 column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

PeakTable

| Peak# | Ret. Time | Area  | Area % |
|-------|-----------|-------|--------|
| 1     | 6.759     | 8230090 | 98.040 |
| 2     | 7.291     | 164571  | 1.960  |
| Total |           | 8394661 | 100.000 |
Enantioselective Olefinic C(sp^2)‒H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-31

Phenomenex Cellulose-2 column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

Peak Table

| Peak# | Ret. Time | Area   | Area % |
|-------|-----------|--------|--------|
| 1     | 5.257     | 228296 | 51.144 |
| 2     | 6.258     | 218081 | 48.856 |
| Total |           | 446377 | 100.000|

Phenomenex Cellulose-2 column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

Peak Table

| Peak# | Ret. Time | Area   | Area % |
|-------|-----------|--------|--------|
| 1     | 5.255     | 1714566| 97.563 |
| 2     | 6.253     | 42835  | 2.437  |
| Total |           | 1757401| 100.000|
Daicel Chiralpak IG column (60:40 \(n\)-Hexane/EtOH, 1.0 mL/min, 20 °C)

| Peak# | Ret. Time | Area  | Area % |
|-------|-----------|-------|--------|
| 1     | 7.802     | 205394| 49.849 |
| 2     | 8.488     | 206636| 50.151 |
| Total |           | 412030| 100.000|

PDA Ch1 288nm 4nm

| Peak# | Ret. Time | Area  | Area % |
|-------|-----------|-------|--------|
| 1     | 7.806     | 245141| 95.989 |
| 2     | 8.489     | 10243 | 4.011  |
| Total |           | 255384| 100.000|
Phenomenex Cellulose-1 column (75:25 n-Hexane/EtOH, 0.5 mL/min, 20 °C)
Enantioselective Olefinic C(sp)³–H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-36
Daicel Chiralpak IB column (95:5 n-Hexane/i-PrOH, 0.4 mL/min, 20 °C)

| Peak# | Ret. Time | Area   | Area % |
|-------|-----------|--------|--------|
| 1     | 17.035    | 2111970| 48.442 |
| 2     | 17.763    | 2247789| 51.558 |
| Total |           | 4359759| 100.000|

Daicel Chiralpak IB column (95:5 n-Hexane/i-PrOH, 0.4 mL/min, 20 °C)

| Peak# | Ret. Time | Area   | Area % |
|-------|-----------|--------|--------|
| 1     | 16.903    | 234749 | 1.798  |
| 2     | 17.597    | 12824734| 98.202 |
| Total |           | 13059483| 100.000|
Phenomenex Cellulose-2 column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

| Peak# | Ret. Time | Area   | Area %  |
|-------|-----------|--------|---------|
| 1     | 5.586     | 407797 | 49.298  |
| 2     | 6.166     | 419411 | 50.702  |
| Total |           | 827209 | 100.000 |

Phenomenex Cellulose-2 column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

| Peak# | Ret. Time | Area    | Area %  |
|-------|-----------|---------|---------|
| 1     | 5.574     | 1681799 | 95.591  |
| 2     | 6.142     | 77563   | 4.409   |
| Total |           | 1759361 | 100.000 |
Enantioselective Olefin C\(^{sp^2}\)‒H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-40

RHS-IV-306-01

3bt

CO\(_2\)Bu

RHS-IV-306-01

3bt

CO\(_2\)Bu

RHS-IV-306-01
Enantioselective Olefinic $C(sp^3)\text{‒H}$ Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-41

Phenomenex Cellulose-2 column (85:15 $n$-Hexane/EtOH, 1.0 mL/min, 20 °C)
Enantioselective Olefinic $C(sp^3)$‒H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-42
Phenomenex Cellulose-1 column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

**Peak Table**

| Peak# | Ret. Time | Area   | Area % |
|-------|-----------|--------|--------|
| 1     | 7.006     | 27140  | 49.992 |
| 2     | 7.829     | 27148  | 50.008 |
| Total |           | 54287  | 100.000|

**Peak Table**

| Peak# | Ret. Time | Area   | Area % |
|-------|-----------|--------|--------|
| 1     | 7.022     | 11407  | 3.095  |
| 2     | 7.785     | 357118 | 96.905 |
| Total |           | 368524 | 100.000|
Enantioselective Olefinic $C(sp^2)$–H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-44
Phenomenex Cellulose-1 column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

**Peak Table**

| Peak# | Ret. Time | Area     | Area %  |
|-------|-----------|----------|---------|
| 1     | 5.265     | 367205   | 50.182  |
| 2     | 5.950     | 364539   | 49.818  |
| Total |           | 731744   | 100.000 |

**Peak Table**

| Peak# | Ret. Time | Area     | Area %  |
|-------|-----------|----------|---------|
| 1     | 5.213     | 41646    | 3.088   |
| 2     | 6.006     | 1306936  | 96.912  |
| Total |           | 1348582  | 100.000 |
Enantioselective Olefinic $C(sp^2)$–H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-46
Enantioselective Olefinic C(sp²)–H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-47

Phenomenex Cellulose-1 column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

| Peak# | Ret. Time | Area       | Area %  |
|-------|-----------|------------|---------|
| 1     | 11.232    | 420984     | 49.477  |
| 2     | 15.693    | 429890     | 50.523  |
| Total |           | 850875     | 100.000 |

Phenomenex Cellulose-1 column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

| Peak# | Ret. Time | Area       | Area %  |
|-------|-----------|------------|---------|
| 1     | 11.305    | 54009      | 3.210   |
| 2     | 15.694    | 1628304    | 96.790  |
| Total |           | 1682312    | 100.000 |
Enantioselective Olefinic \( C(\text{sp}^2) \)-H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-48
Phenomenex Cellulose-1 column (95:5 n-Hexane/EtOH, 0.5 mL/min, 20 °C)
Enantioselective Olefinic $C(sp^2)$–H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-50
Enantioselective Olefinic $C(sp^3)$–H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-51
Enantioselective Olefinic $C(sp^2)$–H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-52

**Phenomenex Cellulose-2 column (60:40 $n$-Hexane/EtOH, 1.0 mL/min, 20 °C)**

| Peak# | Ret. Time | Area   | Area % |
|-------|-----------|--------|--------|
| 1     | 11.213    | 189592 | 49.506 |
| 2     | 17.299    | 193379 | 50.494 |
| Total |           | 382971 | 100.000 |

**PeakTable**

| Peak# | Ret. Time | Area   | Area % |
|-------|-----------|--------|--------|
| 1     | 11.197    | 222965 | 96.904 |
| 2     | 17.299    | 7124   | 3.096  |
| Total |           | 230089 | 100.000 |

PDA Ch1 300nm 4nm

mAU

mAU
Enantioselective Olefinic $C(sp^2)$–H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-53

![Chemical Structure]

Obtained using literature method:
*Angew. Chem. Int. Ed.* 2018, 57, 9505-9509

| Peak# | Ret. Time | Area | Area % |
|-------|-----------|------|--------|
| 1     | 11.201    | 16674| 86.940 |
| 2     | 17.266    | 25052| 13.060 |
| Total |           | 191825| 100.000|

PDA Ch1 300nm 4nm
Enantioselective Olefinic C(sp²)‒H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-54
Enantioselective Olefinic $C(sp^2)$–H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-55

Daicel Chiralpak IG column (75:25 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

| Peak# | Ret. Time | Area   | Area % |
|-------|-----------|--------|--------|
| 1     | 14.239    | 94647  | 51.026 |
| 2     | 15.444    | 90839  | 48.974 |
| Total |           | 185485 | 100.000|

PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area   | Area % |
|-------|-----------|--------|--------|
| 1     | 14.212    | 1582134| 97.285 |
| 2     | 15.429    | 44154  | 2.715  |
| Total |           | 1626288| 100.000|
Enantioselective Olefinic C(sp²)‒H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-57

Phenomenex Cellulose-1 column (90:10 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

| Peak# | Ret. Time | Area   | Area % |
|-------|-----------|--------|--------|
| 1     | 5.652     | 208250 | 50.605 |
| 2     | 6.732     | 203267 | 49.395 |
| Total |           | 411517 | 100.000|

Phenomenex Cellulose-1 column (90:10 n-Hexane/EtOH, 1.0 mL/min, 20 °C)

| Peak# | Ret. Time | Area   | Area % |
|-------|-----------|--------|--------|
| 1     | 5.666     | 73015  | 2.871  |
| 2     | 6.740     | 2470410| 97.129 |
| Total |           | 2543426| 100.000|
Enantioselective Olefinic C(sp^3)–H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-58
Enantioselective Olefinic C(sp²)–H Allylic Alkylation, Sarkar & Mukherjee, SI-Part B, Page S-59

Phenomenex Cellulose-3 column (99:1 n-Hexane/i-PrOH, 0.3 mL/min, 20 °C)

| Peak# | Ret. Time | Area   | Area %  |
|-------|-----------|--------|---------|
| 1     | 13.148    | 2301732| 49.667  |
| 2     | 18.299    | 2332590| 50.333  |
| Total |           | 4634322| 100.000 |

Phenomenex Cellulose-3 column (99:1 n-Hexane/i-PrOH, 0.3 mL/min, 20 °C)

| Peak# | Ret. Time | Area   | Area %  |
|-------|-----------|--------|---------|
| 1     | 13.253    | 2109072| 97.266  |
| 2     | 18.601    | 59284  | 2.734   |
| Total |           | 2168356| 100.000 |