Supporting Information 2 for

Sulfinyl-Mediated Stereoselective Overman Rearrangements and Diels- Alder Cycloadditions

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¹H NMR (CDCl₃, 400 MHz) **2e**

2e

¹³C NMR (CDCl₃, 100 MHz) **2e**

2e

S4

¹H NMR (CDCl₃, 400 MHz) **3e**

3e

^{13}C NMR (CDCl_3 , 100 MHz) **3e**

3e

¹H NMR (CDCl₃, 400 MHz) **2f**

2f

^{13}C NMR (CDCl_3 , 100 MHz) **2f**

2f

^1H NMR (CDCl_3 , 400 MHz) **3f**

3f

^{13}C NMR (CDCl_3 , 100 MHz) **3f**

3f

S11
¹H NMR (CDCl₃, 500 MHz) **2g**

2g

^{13}C NMR (CDCl_3 , 125 MHz) **2g**

2g

^1H NMR (CDCl_3 , 400 MHz) **3g** **3g**

3g

S15
¹H NMR (CDCl₃, 400 MHz) **2h**

2h

S16
¹³C NMR (CDCl₃, 100 MHz) **2h**

2h

3h

S18
¹³C NMR (CDCl₃, 100 MHz) **3h**

3h

¹H NMR (CDCl₃, 400 MHz) (±)-**22h**

(±)-**22h**

S20
¹³C NMR (CDCl₃, 100 MHz) (±)-**22h**

(±)-**22h**

^1H NMR (CDCl_3 , 400 MHz) ($\pm$)-**23h** ($\pm$)-**23h**

¹³C NMR (CDCl₃, 100 MHz) (±)-**23h**

(±)-**23h**

^1H NMR (CDCl_3 , 400 MHz) ($\pm$)-**24h** **($\pm$)-24h**

¹³C NMR (CDCl₃, 100 MHz) (±)-^{S24}**24h**

(±)-**24h**

^1H NMR (CDCl_3 , 400 MHz) **4a** **4a**

^{13}C NMR (CDCl_3 , 100 MHz) **4a** **4a**

¹H NMR (CDCl₃, 400 MHz) **5a:5a'** (73:27)

^1H NMR (CDCl_3 , 400 MHz) **5a:5a'** (73:27) expansion

^{13}C NMR (CDCl_3 , 100 MHz) **5a**:**5a'** (73:27)

^1H NMR (CDCl_3 , 400 MHz) **4b** **4b**

^{13}C NMR (CDCl_3 , 100 MHz) **4b** **4b**

¹H NMR (CDCl₃, 400 MHz) **5b:5b'** (93:7)

^1H NMR (CDCl_3 , 400 MHz) **5b:5b'** (93:7) expansion

^{13}C NMR (CDCl_3 , 100 MHz) **5b:5b'** (93:7)

^1H NMR (CDCl_3 , 400 MHz) **4c** **4c**

¹³C NMR (CDCl₃, 100 MHz) **4c**

4c

^1H NMR (CDCl_3 , 400 MHz) **5c** **5c**

¹³C NMR (CDCl₃, 100 MHz) ^{S38}**5c**

^1H NMR (CDCl_3 , 400 MHz) **4d** **4d**

S40
¹³C NMR (CDCl₃, 100 MHz) **4d**

4d

^1H NMR (CDCl_3 , 400 MHz) **5d** **5d**

S42
¹³C NMR (CDCl₃, 100 MHz) **5d**

5d

^1H NMR (CDCl_3 , 400 MHz) **4e** **4e**

S44
¹³C NMR (CDCl₃, 100 MHz) **4e**

4e

¹H NMR (CDCl₃, 400 MHz) **5e:5e'** (85:15)

^1H NMR (CDCl_3 , 400 MHz) **5e:5e'** (85:15) expansion

^{13}C NMR (CDCl_3 , 100 MHz) **5e:5e'** (85:15)

S48
¹H NMR (CDCl₃, 400 MHz) **4f**

4f

S49
¹³C NMR (CDCl₃, 100 MHz) **4f**

4f

S50
¹H NMR (CDCl₃, 400 MHz) **5f**

5f

¹³C NMR (CDCl₃, 100 MHz) **5f**

5f