A Gold-Catalysed Fully Intermolecular Oxidation and Sulfur-Ylide Formation Sequence on Ynamides

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General Experimental
Starting Materials
Formation of Ynamides
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Crystal structure of 4eh
$^1$H and $^{13}$C NMR spectra of New Substrates
$^1$H and $^{13}$C NMR Spectra of Catalysis Products
General Experimental

All reactions were carried out under Ar in flame-dried glassware unless otherwise mentioned. The solvents used were purified using a Pure Solv-MD Solvent Purification System (alumina columns) from Innovative Technology and were transferred under Ar. Asynt DrySyn heating blocks on stirrer hotplates were employed with temperature control via external probe. Flash chromatography: Fluorochem silica gel 60 (43-63 μm). Thin layer chromatography (TLC): Macherey Nagel silica gel 60F254 analytical plates (plastic support) which were developed using standard visualizing agents: UV fluorescence (254 and 366 nm), phosphomolybdic acid /Δ, and potassium permanganate /Δ. IR: Perkin-Elmer Spectrum 100 FTIR spectrometer, only selected absorbencies (υmax) are reported in cm⁻¹. MS and HRMS (EI): VG ProSpec or VG-ZabSpec at 70 eV. High resolution EI spectra were measured using perfluorokerosene (PFK) as an internal calibrant. MS and HRMS (ES): Micromass LCT using a methanol mobile phase. HRMS was obtained using a lock-mass to adjust the calibrated mass scale. MS data are reported as m/z (relative intensity). Commercially available compounds were purchased from Aldrich, Fluka, Acros, Strem, Alfa Aesar and used without further purification. NMR: Spectra were recorded on Bruker AVIII300 (¹H = 300 MHz, ¹³C = 75.5 MHz), Bruker AVIII400 (¹H = 400 MHz, ¹³C = 101 MHz) in the solvents indicated; CDCl₃ was purchased from Aldrich (no TMS) and Cambridge Isotope Laboratory (0.05% v/v TMS); Chemical shifts (δ) are given in ppm relative to TMS. In the absence of TMS, solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl₃: δ_C = 77.0 ppm; residual CHCl₃ in CDCl₃: δ_H = 7.26 ppm). Coupling constants (J) are reported in Hz. Multiplicity is denoted in ¹H NMR by: s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet). 1D ¹³C NMR spectra were recorded using the JMOD or PENDANT pulse sequences from the Bruker standard pulse program library. JMOD were combined with DEPT 135 to assign quaternary carbons.
Starting Materials

The following compounds were prepared following literature procedures:

*N*-Phenylmethanesulfonamide (A)

(51% yield).\(^1\) Spectroscopic data were identical to those reported in literature.\(^2\)

*N*-Phenyl-4-methylbenzenesulfonamide (B)

(97% yield).\(^3\) Spectroscopic data were identical to those reported in literature.\(^2\)

*N*-Benzylmethanesulfonamide (C)

(88% yield).\(^1\) Spectroscopic data were identical to those reported in literature.\(^2\)

*N*-Benzyl-4-methylbenzenesulfonamide (D)

(83% yield).\(^1\) Spectroscopic data were identical to those reported in literature.\(^2\)

1-Ethynyl-4-fluorobenzene (E)

(44% yield over 2 steps).\(^4\) Spectroscopic data were identical to those reported in literature.\(^5\)

Methyl-4-ethynylbenzoate (F)

(88% yield over 2 steps).\(^6\) Spectroscopic data were identical to those reported in literature.\(^6\)

1-Ethynyl-4-methoxybenzene (G)

(96% yield over 2 steps).\(^7\) Spectroscopic data were identical to those reported in literature.\(^7\)

*(E)*-But-1-en-3-yn-1-ylbenzene (H)

(34% yield over 2 steps).\(^8\) Spectroscopic data were identical to those reported in literature.\(^9\)

Allyl(phenyl)sulfide (2a)

(Quant. yield).\(^10\) Spectroscopic data were identical to those reported in literature.\(^11\)

Allyl(\(p\)-tolyl)sulfide (2b)

(Quant. yield).\(^10\) Spectroscopic data were identical to those reported in literature.\(^12\)

Allyl(\(p\)-bromophenyl)sulfide (2c)

(Quant. yield).\(^10\) Spectroscopic data were identical to those reported in literature.\(^13\)

Allyl(benzyl)sulfide (2d)

(97% yield). Spectroscopic data were identical to those reported in literature.\(^14\)

Allyl(\(n\)-butyl)sulfide (2e)

(76% yield).\(^13\) Spectroscopic data were identical to those reported in literature.\(^15\)
Cinnamyl(phenyl)sulfide (2g)

(71% yield).\textsuperscript{13} Spectroscopic data were identical to those reported in literature.\textsuperscript{16}

2-Vinyltetrahydrothiophene (2h)

(70% yield over 2 steps).\textsuperscript{17} Spectroscopic data were identical to those reported in literature.\textsuperscript{16}

Methyl picolinate (I)

(97% yield).\textsuperscript{18} Spectroscopic data were identical to those reported in literature.\textsuperscript{19}

2-(Methoxycarbonyl)pyridine-1-oxide (3)

(97% yield).\textsuperscript{20} Spectroscopic data were identical to those reported in literature.\textsuperscript{21}

(E)-N-Phenyl-N-tosylhex-2-enamide (6)

Spectroscopic data were identical to those reported in literature.\textsuperscript{22}

Formation of Ynamides

General procedure 1 (GP1)

Following the method of Stahl,\textsuperscript{23} CuCl$_2$ (0.2 eq), amide (5 eq) and Na$_2$CO$_3$ (2 eq) were added to a flame-dried 500 mL three-necked round-bottomed flask. The flask was purged with oxygen for 15 min and a solution of freshly distillated pyridine (2 eq) in dry toluene (0.2 M) was added. A balloon filled with oxygen was connected to the flask and the stirred mixture was heated at 70 °C. After 15 min, a solution of alkyne (1.0 eq) in dry toluene (0.2 M) was added by syringe pump over 4 h. The mixture was allowed to stir at 70 °C for another 4 h and was then cooled to rt. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash chromatography to afford the desired product.

$\textit{N}$-Phenyl-$\textit{N}$-(phenylethynyl)methanesulfonyamide (1a)

Following GP1 using amide A (855 mg, 5 mmol) and phenylacetylene (0.11 mL, 1 mmol). After purification by flash chromatography [hexane:EtOAc (4:1)] ynamide 1a was isolated as a white solid (238.5 mg, 88%). Spectroscopic data were identical to those reported in literature.\textsuperscript{24}
**N-Methyl-N-(phenylethynyl)methanesulfonamide (1b)**

Following GP1 using amide A (855 mg, 5 mmol) and phenylacetylene (0.11 mL, 1 mmol). After purification by flash chromatography [hexane:EtOAc (4:1)] ynamide 1a was isolated as a white solid (238.5 mg, 88%). Spectroscopic data were identical to those reported in literature.24,25

**N-Benzyl-N-phenylethynyl-methanesulfonamide (1c)**

Following GP1 using amide C (1.9 g, 10 mmol) and phenylacetylene (0.22 mL, 2 mmol). After purification by flash chromatography [hexane:EtOAc (4:1)] ynamide 1c was isolated as a white solid (291 mg, 51%). Spectroscopic data were identical to those reported in literature.24

**N-Benzyl-4-methyl-N-phenylethynyl-benzenesulfonamide (1d)**

Following GP1 using amide D (2.6 g, 10 mmol) and phenylacetylene (0.22 mL, 2 mmol). After purification by flash chromatography [hexane:EtOAc (4:1)] ynamide 1d was isolated as a white solid (317.7 mg, 44%). Spectroscopic data were identical to those reported in literature.24

**4-Methyl-N-phenyl-N-(phenylethynyl)benzenesulfonamide (1e)**

Following GP1 using amide B (4.9 g, 20 mmol) and phenylacetylene (0.44 mL, 4 mmol). After purification by flash chromatography [hexane:EtOAc (4:1)] ynamide 1e was isolated as a white solid (1.1 g, 82%). Spectroscopic data were identical to those reported in literature.24

**3-(Phenylethynyl)oxazolidin-2-one (1f)**

Following GP1 using oxazolidinone (435 mg, 5 mmol) and phenylacetylene (0.11 mL, 1 mmol). After purification by flash chromatography [hexane:EtOAc (4:1)] ynamide 1f was isolated as a white solid (153.3 mg, 82%). Spectroscopic data were identical to those reported in literature.24
**N-((4-Methoxyphenyl)ethynyl)-4-methyl-N-phenylbenzenesulfonamide (1g)**

Following GP1 using amide B (1.8 g, 7.5 mmol) and alkyne G (200.0 mg, 1.5 mmol). After purification by flash chromatography [hexane:EtOAc (9:1)] ynamide 1g was isolated as a colourless solid (463.7 mg, 82%); mp: 100-102 °C; ¹H NMR (300 MHz, CDCl₃): δ = 7.62 (d, J = 8.3 Hz, 2H), 7.38-7.25 (m, 9H), 6.84 (d, J = 8.9 Hz, 2H), 3.81 (s, 3H), 2.45 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 159.8, 145.0, 139.3, 133.6 (2C), 133.2, 129.6 (2C), 129.2 (2C), 128.4 (2C), 128.2, 126.3 (2C), 114.7, 114.1 (2C), 81.7, 70.4, 55.4, 21.8; IR (neat): ν = 3065, 2936, 2838, 2241, 1370, 1172; HR-MS (ES-TOF): m/z: calcd for C₂₂H₁₉NO₃NaS: 400.0983, found 400.0985 [M+Na].

**Methyl 4-((4-methyl-N-phenylphenylsulfonamido)ethynyl)benzoate (1h)**

Following GP1 using amide B (2.96 g, 12.0 mmol) and alkyne F (384.3 mg, 2.4 mmol). After purification by flash chromatography [hexane:EtOAc (4:1)] ynamide 1h was isolated as a colourless solid (418.0 mg, 43%); mp: 96-98 °C; ¹H NMR (300 MHz, CDCl₃): δ = 7.96 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.38-7.34 (m, 3H), 7.33-7.27 (m, 4H), 3.92 (s, 3H), 2.44 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 166.7, 145.4, 138.8, 133.2, 130.9 (2C), 129.8 (2C), 129.6 (2C), 129.4 (2C), 129.1, 128.6, 128.4 (2C), 127.8, 126.5 (2C), 86.3, 70.5, 52.3, 21.9; IR (neat): ν = 3071, 2923, 2853, 2234, 1717, 1371, 1170; HR-MS (ES-TOF): m/z: calcd for C₂₃H₁₉NO₄NaS: 428.0932, found 428.0927 [M+Na].

**N-((4-Fluorophenyl)ethynyl)-4-methyl-N-phenylbenzenesulfonamide (1i)**

Following GP1 using amide B (547.4 g, 2.2 mmol) and alkyne E (53.2 mg, 0.44 mmol). After purification by flash chromatography [hexane:EtOAc (4:1)] ynamide 1i was isolated as a colourless solid (58.5 mg, 18%); mp: 80-82 °C; ¹H NMR (300 MHz, CDCl₃): δ = 7.61 (d, J = 8.3 Hz, 2H), 7.41-7.27 (m, 9H), 7.00 (t, J = 8.8 Hz, 2H), 2.46 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 162.7 (d,
$J = 249.7$ Hz, 1C), 145.3, 139.2, 133.9, 133.8, 133.4, 129.8 (2C), 129.4 (2C), 128.6 (3C), 126.5 (2C), 118.9, 115.8 (d, $J = 22.1$ Hz, 2C), 82.3, 69.7, 22.0; IR (neat): $\nu = 3057, 2982, 2243, 1680, 1374, 1174$; HR-MS (ES-TOF): $m/z$: calcd for $C_{21}H_{16}NO_2NaS$: 388.0783, found 388.0776 [M+Na].

**N-(Hex-1-ynyl)-N-phenylmethanesulfonamide (1j)**

Following GP1 using amide A (855 mg, 5.0 mmol) and hexyne (0.11 mL, 1.0 mmol). After purification by flash chromatography [hexane:EtOAc (4:1)] ynamide 1j was isolated as a colourless solid (188.5 mg, 75%). Spectroscopic data were identical to those reported in literature.\(^{22}\)

**{(E)-4-methyl-N-phenyl-N-(4-phenylbut-3-en-1-ynyl)benzenesulfonamide (1k)}**

Following GP1 using amide B (1.7 g, 7.0 mmol) and alkyne H (175.4 mg, 1.4 mmol). After purification by flash chromatography [hexane:EtOAc (4:1)] ynamide 1k was isolated as a yellow solid (386.3 mg, 75%); mp: 105-107 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.61$ (d, $J = 8.3$ Hz, 2H), 7.42-7.25 (m, 12H), 6.86 (d, $J = 16.2$ Hz, 1H), 6.27 (d, $J = 16.2$ Hz, 1H), 2.45 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 145.1, 140.1, 139.1, 136.5, 133.3, 129.7$ (2C), 129.3 (2C), 128.9 (2C), 128.6, 128.4 (3C), 126.4 (2C), 126.3 (2C), 107.5, 85.1, 70.3, 21.8; IR (neat): $\nu = 3067, 2970, 2847, 2249, 1607, 1368, 1172$; HR-MS (ES-TOF): $m/z$: calcd for $C_{23}H_{19}NO_2NaS$: 396.1034, found 396.1043 [M+Na].
## Study of Reaction Parameters

![Chemical反应图](image)

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<td>AuPPh3NTf2</td>
<td>1.0 eq.</td>
<td>CH2Cl2</td>
<td>1.2 eq.</td>
<td>23</td>
<td>24 h</td>
<td>17%</td>
<td>58%</td>
<td>24%</td>
</tr>
<tr>
<td>30</td>
<td>AuPPh3NTf2</td>
<td>1.0 eq.</td>
<td>CH2Cl2</td>
<td>1.2 eq.</td>
<td>23</td>
<td>24 h</td>
<td>23%</td>
<td>48%</td>
<td>26%</td>
</tr>
<tr>
<td>31</td>
<td>AuPPh3NTf2</td>
<td>1.0 eq.</td>
<td>CH2Cl2</td>
<td>1.2 eq.</td>
<td>23</td>
<td>24 h</td>
<td>28%</td>
<td>19%</td>
<td>51%</td>
</tr>
<tr>
<td>32</td>
<td>IPrAuNTf2</td>
<td>1.0 eq.</td>
<td>CH2Cl2</td>
<td>1.2 eq.</td>
<td>23</td>
<td>24 h</td>
<td>49%</td>
<td>-</td>
<td>50%</td>
</tr>
<tr>
<td>33</td>
<td>AuPPh3NTf2</td>
<td>1.0 eq.</td>
<td>CH2Cl2</td>
<td>1.2 eq.</td>
<td>23</td>
<td>24 h</td>
<td>22%</td>
<td>59%</td>
<td>16%</td>
</tr>
</tbody>
</table>

Yields determined from $^1$H NMR spectra against the addition of a known quantity of internal standard. Overlap of resonances and co-elution prevented accurate calculation of S5 yield.
Products of the Catalysis Reaction

**General procedure 2 (GP2)**

A solution of allyl sulfide 2 (1.2 eq) in CH$_2$Cl$_2$ (0.1 M) was added to a mixture of gold catalyst (5 mol% unless indicated in the main paper) and the corresponding ynamide 1 (1.0 eq). Pyridine N-oxide 3 (1.3 eq) was then added and the reaction mixture was stirred at room temperature until complete consumption of the starting material was observed (monitored by TLC). The mixture was filtered through a pad of silica and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography.

**N-(Methylsulfonyl)-N,2-diphenyl-2-(phenylthio)pent-4-enamide (4aa)**

Following GP2 using ynamide 1a (54.2 mg, 0.2 mmol) and allyl sulfide 2a (36.0 mg, 0.24 mmol) for 2 h. After purification by chromatography [hexane:EtOAc (4:1)] thioether 4aa was isolated as a colourless solid (62.4 mg, 71%); mp: 132-134 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.35$-$7.27$ (m, 1H), 7.24-7.07 (m, 8H), 6.97 (t, $J = 8.0$ Hz, 2H), 6.89 (d, $J = 7.2$ Hz, 2H), 6.72 (d, $J = 7.5$ Hz, 2H), 5.80-5.99 (m, 1H), 5.14 (dd, $J = 10.4$, 1.6 Hz, 1H), 5.01 (dd, $J = 17.2$, 1.6 Hz, 1H), 3.50 (s, 3H), 2.61 (ddt, $J = 15.8$, 5.9, 1.7 Hz, 1H), 2.48 (ddd, $J = 15.8$, 7.1, 1.2 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 173.1$, 138.8, 137.3 (2C), 133.5, 132.8, 132.0, 130.0, 129.7, 129.4, 128.8 (3C), 128.4 (2C), 128.0 (2C), 127.8, 127.2 (2C), 118.9, 66.2, 42.5, 39.4; IR (neat): $\nu = 3059$, 2927, 1681, 1355, 1158; HR-MS (ES-TOF): $m/z$: calcd for C$_{24}$H$_{23}$NO$_3$NaS$_2$: 460.1017, found 460.1021 [M+Na].

**N-Methyl-2-phenyl-2-(phenylthio)-N-tosylpent-4-enamide (4ba)**

Following GP2 using ynamide 1b (81.0 mg, 0.2 mmol) and allyl sulfide 2a (39.4 mg, 0.24 mmol) for 6 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether 4ba was isolated as a colourless solid (57.3 mg, 76%); mp: 95-97 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.56$-$7.19$ (m, 10H), 5.72 (ddt,
J = 17.2, 10.3, 6.9 Hz, 1H), 4.98 (dd, J = 10.3, 1.9 Hz, 1H), 4.80 (dd, J = 17.2, 1.9 Hz, 1H),
3.27 (s, 3H), 3.03 (s, 3H), 2.76 (d, J = 6.9 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ = 172.3,
137.8, 137.2 (2C), 132.7, 130.3, 129.3 (2C), 129.2, 129.1 (2C), 128.2, 126.4 (2C), 119.2,
64.0, 44.2, 42.3, 34.1; IR (neat): $\nu$ = 2947, 2869, 1700, 1679, 1360, 1168;
HR-MS (ES-TOF): m/z: calcd for C$_{19}$H$_{21}$NO$_3$NaS$_2$: 398.0861, found 398.0870 [M+Na].

$^{N}$-Benzyl-$^{N}$-(methylsulfonyl)-$^{2}$-phenyl-$^{2}$-(phenylthio)pent-$^{4}$-enamide (4ca)

Following GP2 using ynamide 1c (57.0 mg, 0.2 mmol) and allyl sulfide 2a
(36.0 mg, 0.24 mmol) for 5 h. After purification by chromatography
[toluene:EtOAc (16:1)] thioether 4ca was isolated as a colourless solid
(52.6 mg, 58%); mp: 127-129 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.54-7.47 (m, 2H), 7.46-
7.31 (m, 5H), 7.30-7.22 (m, 2H), 7.21-7.11 (m, 4H), 7.10-7.01 (m, 2H), 5.67 (ddt, J = 17.1,
10.3, 6.8 Hz, 1H), 4.96 (dd, J = 10.3, 1.9 Hz, 1H), 4.85 (d, J = 16.8 Hz, 1H), 4.75 (d, J = 17.1
Hz, 1H), 4.74 (d, J = 16.8 Hz, 1H), 3.19 (s, 3H), 2.85-2.69 (m, 2H); $^{13}$C NMR (101 MHz,
CDCl$_3$): $\delta$ = 173.8, 137.4, 136.8 (2C), 136.2, 132.4, 130.1, 129.5, 129.3 (2C), 129.0 (2C),
128.3, 128.2 (2C), 127.3, 127.1 (2C), 127.0 (2C), 119.2, 63.9, 51.0, 43.7, 43.2; IR (neat): $\nu$ =
3055, 3037, 2985, 1677, 1339, 1159; HR-MS (ES-TOF): m/z: calcd for C$_{25}$H$_{25}$NO$_3$NaS$_2$: 474.1174, found 474.1165 [M+Na].

$^{N}$-Benzyl-$^{2}$-phenyl-$^{2}$-(phenylthio)-$^{N}$-tosylpent-$^{4}$-enamide (4da)

Following GP2 using ynamide 1d (72.2 mg, 0.2 mmol) and allyl sulfide 2a
(36.0 mg, 0.24 mmol) for 5 h. After purification by chromatography
[toluene:EtOAc (49:1)] thioether 4da was isolated as a colourless solid
(64.2 mg, 61%); mp: 134-136 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.76 (d, J = 8.4 Hz, 2H),
7.34-7.27 (m, 3H), 7.22-7.12 (m, 10H), 7.12-7.03 (m, 4H), 5.52 (ddt, J = 17.1, 10.3, 6.8 Hz,
1H), 5.00 (d, J = 17.1 Hz, 1H), 4.85 (dd, J = 10.3, 1.8 Hz, 1H), 4.72 (d, J = 17.1 Hz, 1H), 4.57
(dd, J = 17.1, 1.8 Hz, 1H), 2.59-2.44 (m, 2H), 2.50 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ =
172.1, 144.7, 137.5, 136.7, 136.6 (2C), 136.5, 132.2, 129.8 (2C), 129.6 (2C), 129.3 (2C),
S-12
129.1 (2C), 129.0 (2C), 128.1, 128.0 (2C), 127.2 (2C), 127.0, 126.8 (2C), 118.9, 63.3, 52.0, 42.8, 21.8; IR (neat): $\nu = 3060, 3025, 2926, 2847, 1679, 1354, 1167$; HR-MS (ES-TOF): $m/z$: calcd for $\text{C}_{31}\text{H}_{29}\text{NO}_{3}\text{NaS}_{2}$: 550.1487, found 550.1480 [M+Na].

**N,2-Diphenyl-2-(phenylthio)-N-tosylpent-4-enamide (4ea)**

Following GP2 using ynamide 1e (69.4 mg, 0.2 mmol) and allyl sulfide 2a (36.0 mg, 0.24 mmol) for 2 h. After purification by chromatography [hexane:EtOAc (4:1)] thioether 4ea was isolated as a colourless solid (78.6 mg, 77%); mp: 137-139 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.98$ (d, $J = 8.2$ Hz, 2H), 7.40 (d, $J = 8.2$ Hz, 2H), 7.29-7.22 (m, 2H), 7.21-7.13 (m, 2H), 7.10-6.94 (m, 9H), 6.78 (d, $J = 7.5$ Hz, 2H), 5.68-5.55 (m, 1H), 4.97 (d, $J = 10.3$ Hz, 1H), 4.83 (d, $J = 17.1$ Hz, 1H), 2.53 (s, 3H), 2.50 (dd, $J = 15.8, 6.2$ Hz, 1H), 2.37 (dd, $J = 15.8, 6.8$ Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 171.3, 144.9, 138.8, 137.1$ (2C), 136.6, 134.3, 132.6 (2C), 130.0 (3C), 129.5, 129.4 (3C), 129.2, 128.7 (2C), 128.4 (2C), 127.8 (2C), 127.6, 127.1 (2C), 118.6, 65.2, 40.1, 21.9; IR (neat): $\nu = 2970, 2922, 2854, 1683, 1359, 1164$; HR-MS (ES-TOF): $m/z$: calcd for $\text{C}_{30}\text{H}_{27}\text{NO}_{3}\text{NaS}_{2}$: 536.1330, found 536.1332 [M+Na].

**3-(2-Phenyl-2-(phenylthio)pent-4-enoyl)oxazolidin-2-one (4fa)**

Following GP2 using ynamide 1f (18.7 mg, 0.1 mmol) and allyl sulfide 2a (30.0 mg, 0.2 mmol), and Au-II (7 mol%) for 24 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether 4fa was isolated as a yellow oil (22.5 mg, 64%); $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.39-7.21$ (m, 6H), 7.20-7.12 (m, 4H), 6.06-5.78 (m, 1H), 5.05 (d, $J = 10.2$ Hz, 1H), 4.94 (d, $J = 17.1$ Hz, 1H), 4.39-4.15 (m, 3H), 3.87-3.67 (m, 1H), 3.10 (dd, $J = 14.9, 8.2$ Hz, 1H), 2.74 (ddt, $J = 14.9, 5.7, 1.5$ Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 171.0, 151.5, 138.8, 137.6$ (2C), 133.4, 130.1, 129.8, 128.9 (2C), 128.3 (2C), 127.6, 126.9 (2C), 118.8, 66.7, 62.1, 44.8, 40.0; IR (neat): $\nu = 3065, 2923, 2850, 1787, 1678, 1383, 1180$; HR-MS (ES-TOF): $m/z$: calcd for $\text{C}_{20}\text{H}_{19}\text{NO}_{3}\text{NaS}$: 376.0983 found 376.0989 [M+Na].
**N,2-Diphenyl-2-(p-tolylthio)-N-tosylpent-4-enamide (4eb)**

Following GP2 using ynamide 1e (69.4 mg, 0.2 mmol) and allyl sulfide 2b (39.4 mg, 0.24 mmol) for 1 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether 4eb was isolated as a colourless solid (78.4 mg, 74%); mp: 163-165 ºC; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) = 7.98 (d, \(J = 8.2\) Hz, 2H), 7.40 (d, \(J = 8.2\) Hz, 2H), 7.22-7.12 (m, 2H), 7.11-7.03 (m, 2H), 6.95 (br s, 2H), 6.90-6.84 (m, 5H), 6.78 (d, \(J = 7.4\) Hz, 2H), 6.61 (br s, 1H), 5.60 (ddt, \(J = 17.1\), 10.4, 6.5 Hz, 1H), 4.95 (dd, \(J = 10.4\), 1.8 Hz, 1H), 4.82 (dd, \(J = 17.1\), 1.8 Hz, 1H), 2.53 (s, 3H), 2.51 (dd, \(J = 15.8\), 6.2 Hz, 1H), 2.37 (dd, \(J = 15.8\), 6.8 Hz, 1H), 2.27 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) = 171.3, 144.8, 139.7, 138.8, 137.1 (2C), 136.6 (2C), 134.3, 132.7, 130.0 (2C), 129.5 (2C), 129.4 (2C), 129.1 (2C), 128.3 (2C), 127.7 (2C), 127.5, 127.1 (2C), 126.2, 118.5, 64.9, 40.2, 21.9, 21.4; IR (neat): \(\nu\) = 3066, 3022, 2979, 2927, 1683, 1359, 1164; HR-MS (ES-TOF): m/z: calcd for C\(_{31}\)H\(_{29}\)NO\(_3\)NaS\(_2\): 550.1487, found 550.1479 [M+Na].

**2-(4-Bromophenylthio)-N,2-diphenyl-N-tosylpent-4-enamide (4ec)**

Following GP2 using ynamide 1e (69.4 mg, 0.2 mmol) and allyl sulfide 2c (55.0 mg, 0.24 mmol) for 4 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether 4ec was isolated as a colourless solid (66.4 mg, 56%); mp: 154-156 ºC; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) = 7.96 (d, \(J = 8.4\) Hz, 2H), 7.40 (d, \(J = 8.0\) Hz, 2H), 7.23-7.13 (m, 4H), 7.08 (app. t, \(J = 7.5\) Hz, 2H), 6.99 (app. t, \(J = 7.8\) Hz, 2H), 6.81-6.70 (m, 6H), 5.62 (ddt, \(J = 17.0\), 10.4, 6.4 Hz, 1H), 5.01 (dd, \(J = 10.4\), 1.6 Hz, 1H), 4.88 (dd, \(J = 17.0\), 1.6 Hz, 1H), 2.53 (s, 3H), 2.47 (dd, \(J = 15.9\), 6.1 Hz, 1H), 2.36 (dd, \(J = 15.9\), 6.8 Hz, 1H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) = 171.0, 145.0, 138.6, 138.5 (2C), 136.4, 134.0, 132.3 (2C), 131.8 (2C), 129.9 (2C), 129.4 (2C), 129.3, 129.2, 128.4 (2C), 127.9 (2C), 127.8 (2C), 127.1 (2C), 124.3, 118.9, 65.8, 39.6, 21.9; IR (neat): \(\nu\) = 3061, 2923, 2853, 1681, 1359, 1164; HR-MS (ES-TOF): m/z: calcd for C\(_{30}\)H\(_{26}\)NO\(_3\)NaS\(_2\)Br: 614.0435, found 614.0427 [M+Na].
2-(Benzylthio)-N,2-diphenyl-N-tosylpent-4-enamide (4ed)

Following GP2 using ynamide 1e (69.4 mg, 0.2 mmol) and allyl sulfide 2d (39.4 mg, 0.24 mmol) for 24 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether 4ed was isolated as a colourless solid (57.4 mg, 55%); mp: 124-126 °C; 1H NMR (300 MHz, CDCl₃): δ = 7.95 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.32-7.23 (m, 4H), 7.18-7.00 (m, 6H), 6.98-6.84 (m, 3H), 6.82 (dd, J = 8.2, 1.2 Hz, 2H), 5.49-5.22 (m, 1H), 4.89 (d, J = 16.6 Hz, 1H), 4.82 (dd, J = 10.7, 1.5 Hz, 1H), 3.55 (d, J = 11.1 Hz, 1H), 3.44 (d, J = 11.1 Hz, 1H), 3.03 (dd, J = 15.3, 7.7 Hz, 1H), 2.77 (dd, J = 15.3, 5.9 Hz, 1H), 2.48 (s, 3H); 13C NMR (101 MHz, CDCl₃): δ = 171.6, 144.9, 138.3, 136.8, 136.3, 134.5, 132.5 (3C), 129.8 (2C), 129.6 (2C), 129.5 (2C), 129.1, 128.8 (2C), 128.5 (2C), 127.8 (2C), 127.6, 127.5, 126.9 (2C), 118.4, 62.7, 42.1, 33.8, 21.9; IR (neat): ν = 3063, 3028, 2920, 1677, 1359, 1164; HR-MS (ES-TOF): m/z: calcd for C₃₁H₂₉NO₃NaS₂: 550.1487, found 550.1488 [M+Na].

2-(Butylthio)-N,2-diphenyl-N-tosylpent-4-enamide (4ee)

Following GP2 using ynamide 1e (69.4 mg, 0.2 mmol) and allyl sulfide 2e (31.3 mg, 0.24 mmol) for 4.5 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether 4ee was isolated as a yellow oil (60.1 mg, 61%); 1H NMR (300 MHz, CDCl₃): δ = 7.94 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.42-7.17 (m, 5H), 6.97 (br s, 3H), 6.83 (dd, J = 8.2, 1.4 Hz, 2H), 5.43-5.21 (m, 1H), 4.85 (d, J = 15.9 Hz, 1H), 4.84 (dd, J = 11.9, 1.8 Hz, 1H), 2.95 (dd, J = 15.3, 7.5 Hz, 1H), 2.74 (dd, J = 15.3, 6.1 Hz, 1H), 2.49 (s, 3H), 2.33 (dt, J = 11.0, 7.3 Hz, 1H), 2.22 (dt, J = 11.0, 7.3 Hz, 1H), 1.53-1.41 (m, 2H), 1.36-1.24 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H); 13C NMR (101 MHz, CDCl₃): δ = 171.7, 138.4, 136.8, 134.4, 132.6, 132.4 (3C), 129.7 (2C), 129.3 (2C), 128.9, 128.3 (2C), 127.6 (2C), 127.3, 126.8 (2C), 118.1, 61.4, 42.2, 30.6, 28.2, 22.4, 21.8, 13.8; IR (neat): ν = 3069, 2958, 2930, 2872, 1678, 1360, 1165; HR-MS (ES-TOF): m/z: calcd for C₂₈H₃₈NO₃NaS₂: 516.1643, found 516.1635 [M+Na].
2-(Allylthio)-N,2-diphenyl-N-tosylpent-4-enamide (4ef)

Following GP2 using ynamide 1e (69.4 mg, 0.2 mmol) and allyl sulfide 2f (27.4 mg, 0.24 mmol) for 6 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether 4ef was isolated as a yellow oil (64.8 mg, 68%); ^1H NMR (300 MHz, CDCl3): δ = 7.92 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.21-7.01 (m, 5H), 7.01-6.87 (m, 3H), 6.81 (dd, J = 8.2, 1.2 Hz, 2H), 5.66 (ddt, J = 17.0, 9.9, 7.1 Hz, 1H), 5.45-5.27 (m, 1H), 5.10 (dd, J = 17.0, 1.3 Hz, 1H), 5.03 (d, J = 9.9 Hz, 1H), 4.85-4.81 (m, 2H), 2.98 (dd, J = 12.1, 7.2 Hz, 1H), 2.92 (dd, J = 15.3, 7.5 Hz, 1H), 2.89 (dd, J = 12.1, 7.5 Hz, 1H), 2.75 (dd, J = 15.3, 6.1 Hz, 1H), 2.48 (s, 3H); ^13C NMR (101 MHz, CDCl3): δ = 171.6, 144.8, 138.2, 136.6, 134.3, 132.7, 132.4 (3C), 129.6 (2C), 129.3 (2C), 129.0, 128.4 (2C), 127.7 (2C), 127.4, 126.8 (2C), 118.6, 118.3, 62.2, 42.0, 32.1, 21.8; IR (neat): ν = 3070, 2924, 2860, 1678, 1359, 1164; HR-MS (ES-TOF): m/z: calcd for C_{27}H_{27}N_{2}O_{3}NaS_{2}: 500.1330, found 500.1327 [M+Na].

Methyl-4-(1-(4-methyl-N-phenylphenylsulfonamido)-1-oxo-2-(p-tolythio)pent-4-en-2-yl)benzoate (4hb)

Following GP2 using ynamide 1h (81.0 mg, 0.2 mmol) and allyl sulfide 2b (39.4 mg, 0.24 mmol) for 9 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether 4hb was isolated as a colourless solid (70.8 mg, 61%); mp: 193-195 °C; ^1H NMR (300 MHz, CDCl3): δ = 7.96 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 7.18 (t, J = 7.4 Hz, 1H), 7.08-6.92 (m, 3H), 6.91-6.79 (m, 7H), 5.61 (ddt, J = 17.1, 10.4, 6.5 Hz, 1H), 4.96 (dd, J = 10.4, 1.6 Hz, 1H), 4.83 (dd, J = 17.1, 1.6 Hz, 1H), 3.94 (s, 3H), 2.53 (s, 3H), 2.48 (dd, J = 15.8, 6.6 Hz, 1H), 2.39 (dd, J = 15.8, 6.6 Hz, 1H), 2.27 (s, 3H); ^13C NMR (101 MHz, CDCl3): δ = 170.6, 166.7, 145.0, 144.1, 140.1, 137.1 (2C), 136.4, 134.0, 132.7 (2C), 132.2, 130.0 (2C), 129.7 (2C), 129.5 (2C), 129.4 (3C), 129.1, 127.9 (2C), 127.2 (2C), 125.8, 118.0, 65.0, 52.4, 40.0, 21.9, 21.4; IR (neat): ν = 3075, 2985,
2953, 1720, 1684, 1361, 1164; HR-MS (ES-TOF): m/z: calcd for C$_{33}$H$_{31}$NO$_3$NaS$_2$: 608.1541, found 608.1543 [M+Na].

2-(4-Fluorophenyl)-N-phenyl-2-(p-tolylthio)-N-tosylpent-4-enamide (4ib)

Following GP2 using ynamide 1i (47.0 mg, 0.13 mmol) and allyl sulfide 2b (25.3 mg, 0.15 mmol) for 9 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether 4ib was isolated as a colourless solid (40.4 mg, 57%); mp: 174-176 ºC; $^1$H NMR (300 MHz, CDCl$_3$): δ = 7.96 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 7.05 (brd, 2H), 7.00-6.73 (m, 10H), 5.60 (ddt, J = 17.1, 10.4, 6.5 Hz, 1H), 4.96 (dd, J = 10.4, 1.7 Hz, 1H), 4.83 (dd, J = 17.1, 1.7 Hz, 1H), 2.53 (s, 3H), 2.46 (dd, J = 15.7, 6.3 Hz, 1H), 2.36 (dd, J = 15.7, 6.7 Hz, 1H), 2.28 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ = 171.1, 162.1 (d, J = 248.0 Hz, 1C), 144.9, 139.9, 137.1 (2C), 136.5, 134.8, 134.4, 132.4 (2C), 130.0 (2C), 129.6 (2C), 129.4 (2C), 129.3, 129.2, 128.8 (d, J = 8.1 Hz, 2C), 127.9 (2C), 126.1, 118.8, 115.2 (d, J = 21.5 Hz, 2C), 64.4, 40.2, 21.9, 21.4; $^{19}$F-NMR (282 MHz, CDCl$_3$): δ = -114.3 (ddd, J = 13.6, 7.6, 6.6 Hz, 1F); IR (neat): ν = 3072, 2985, 2927, 1683, 1360, 1165; HR-MS (ES-TOF): m/z: calcd for C$_{31}$H$_{28}$NO$_3$NaS$_2$F: 568.1392, found 568.1378 [M+Na].

(E)-N-Phenyl-2-(phenylthio)-2-styryl-N-tosylpent-4-enamide (4ka)

Following GP2 using ynamide 1k (74.6 mg, 0.2 mmol) and allyl sulfide 2a (36.0 mg, 0.24 mmol) for 3 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether 4ka was isolated as a colourless solid (56.7 mg, 53%); mp: 129-131 ºC; $^1$H NMR (300 MHz, CDCl$_3$): δ = 7.95 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.34-7.27 (m, 3H), 7.25-7.19 (m, 3H), 7.19-7.10 (m, 7H), 6.97 (dd, J = 7.4, 2.0 Hz, 2H), 5.85 (d, J = 16.2 Hz, 1H), 5.80-5.73 (m, 1H), 5.69 (d, J = 16.2 Hz, 1H), 5.06 (dd, J = 10.4, 1.4 Hz, 1H), 4.96 (dd, J = 17.2, 1.5 Hz, 1H), 2.51 (s, 3H), 2.47 (dd, J = 15.2, 6.0 Hz, 1H), 2.30 (dd, J = 15.2, 7.4 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ = 170.4, 144.9, 137.7 (2C), 136.3, 136.2, 135.2, 133.0, 132.6 (2C), 130.3, 130.1 (2C), 129.9, 129.8,
129.7, 129.4 (2C), 128.7 (2C), 128.5 (2C), 128.4 (2C), 127.9, 127.3, 126.6 (2C), 118.9, 62.3, 40.5, 21.9; IR (neat): ν = 3059, 2923, 2852, 1686, 1362, 1166; HR-MS (ES-TOF): m/z: calcd for C32H29NO3NaS2: 562.1487, found 562.1481 [M+Na].

(Z)-N,2-Diphenyl-N-tosyl-3,6,7,8-tetrahydro-2H-thiocine-2-carboxamide (4eg)

Following GP2 using ynamide 1e (69.4 mg, 0.2 mmol) and allyl sulfide 2g (27.4 mg, 0.24 mmol) for 8 h. After purification by chromatography [hexane:EtOAc (17:3)] product 4eg was isolated as a colourless solid (69.5 mg, 65%); mp: 174-176 °C; 1H NMR (300 MHz, CDCl3): δ = 7.88 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.20-7.06 (m, 2H), 6.92-6.87 (m, 5H), 6.71 (br s, 1H), 5.73 (dd, J = 18.4, 8.2 Hz, 1H), 5.52-5.42 (br s, 1H), 3.17 (br s, 1H), 2.72 (br s, 3H), 2.47 (s, 3H), 2.22 (br s, 2H), 1.86 (br s, 1H), 1.59 (br s, 1H); 13C NMR (101 MHz, CDCl3): δ = 172.4, 144.5, 138.8, 136.6, 134.7, 132.9, 132.4 (2C), 124.4 (2C), 129.3 (2C), 128.9, 128.4 (2C), 127.6 (2C), 127.5, 126.8 (2C), 126.5, 63.9, 38.9, 30.9, 29.5, 25.8, 21.8; IR (neat): ν = 2923, 2853, 1677, 1360, 1164; HR-MS (ES-TOF): m/z: calcd for C27H27NO3NaS2: 500.1330, found 500.1335 [M+Na].

N,2,3-Triphenyl-2-(phenylthio)-N-tosylpent-4-enamide (4eh)

Following GP2 using ynamide 1e (69.4 mg, 0.2 mmol) and allyl sulfide 2h (54.2 mg, 0.24 mmol) for 24 h. After purification by chromatography [hexane:EtOAc (17:3)] thioether 4eh was isolated as a colourless solid (70.7 mg, 60%) and a 10:1:1 mixture of two diastereoisomers; mp: 170-172 °C; 1H NMR (300 MHz, CDCl3): δ = 8.01 (d, J = 8.3 Hz, 2H), 7.62-7.32 (m, 4H), 7.31-7.14 (m, 6H), 7.13-6.99 (m, 5H), 6.95 (t, J = 7.4 Hz, 2H), 6.84-6.52 (m, 5H), 5.93 (dt, J = 17.1, 9.9 Hz, 1H), 4.99 (d, J = 10.3 Hz, 1H), 4.60 (d, J = 17.1 Hz, 1H), 4.15 (d, J = 9.4 Hz, 1H), 2.56 (s, 3H); 13C NMR (101 MHz, CDCl3): δ = 170.1, 144.6, 141.3, 137.2, 136.8, 136.1 (2C), 134.7, 133.6, 133.4 (2C), 132.0 (2C), 130.2 (3C), 130.0, 129.4, 129.2 (2C), 128.7 (4C), 128.2, 127.2 (4C), 126.8 (2C), 126.3, 117.2, 66.1, 53.7, 21.9; IR (neat): ν = 3060, 3034, 2964, 2925, 2853,
1686, 1360, 1162; HR-MS (ES-TOF): m/z: calcd for C_{36}H_{31}NO_{3}NaS_{2}: 612.1643, found 612.1632 [M+Na].

2-(4-Methoxyphenyl)-2-oxo-N-phenyl-N-tosylacetamide (5)

Following GP2 using ynamide 1g (75.4 mg, 0.2 mmol) and allyl sulfide 1b (39.4 mg, 0.24 mmol) for 24 h. After purification by chromatography [hexane:EtOAc (17:3)] keto imide 5 was isolated as a colourless solid (44.2 mg, 54%); mp: 148-150 °C; ¹H NMR (300 MHz, CDCl₃): δ = 7.88 (d, J = 8.9 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.49-7.29 (m, 5H), 7.13 (d, J = 6.8 Hz, 2H), 6.98 (d, J = 8.9 Hz, 2H), 3.89 (s, 3H), 2.47 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): 186.5, 167.1, 165.0, 146.0, 134.6, 133.9, 132.3 (2C), 130.9 (2C), 130.4, 130.0 (2C), 129.6 (2C), 129.3 (2C), 126.0, 114.6 (2C), 55.9, 22.0; IR (neat): ν = 3980, 2945, 2845, 1692, 1669, 1368, 1169; HR-MS (ES-TOF): m/z: calcd for C_{22}H_{19}NO_{5}NaS: 432.0882, found 432.0879 [M+Na].

Crystal structure of 4eh

Crystal Data for 4eh: C_{36}H_{31}NO_{3}S_{2}, M = 589.74, Monoclinic, a = 16.0175(3), b = 9.6290(2), c = 19.5279(5) Å, β = 98.570(1), U= 2978.2(1) Å³, T = 120(2) K, space group P2₁/c, Z = 4, 34108 reflections measured, 6813 unique (R_int = 0.0607) which were used in all calculations. The final R1 was 0.0458 (I>2σ(I)) and wR(F²) was 0.1150 (all data). The dataset was measured on a Bruker KappaCCD diffractometer at the window of a Bruker FR591 rotating anode (λ_{Mo-Kα} = 0.71073 Å). The data collection was driven by COLLECT and processed by DENZO. An absorption correction was applied using SADABS. The structure was solved using ShelXS-97 and refined by a full-matrix least-squares procedure on F² in ShelXL-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on the equivalent isotropic displacement parameter (U(eq)) of the parent atom. Figures were produced using OLEX2. The CIF has been deposited with the CCDC and has been given the deposition number 984457.
**Figure S1** Alternative views of the crystal structure of MDS_242 with ellipsoids drawn at the 50% probability level.

$^1$H and $^{13}$C NMR Spectra of New Substrates

Compound 1g
Compound 1h
Compound 1i
Compound 1k

Ph\(\rightarrow\)N
\(\downarrow\)Ts

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2H (ppm)

1H (ppm)

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200 180 160 140 120 100 80 60 40 20 0

Ts (ppm)
\( ^1H \) and \( ^{13}C \) NMR Spectra of Catalysis Products

Compound 4aa
Compound 4ba
Compound 4ca

\[
\begin{align*}
\text{Bn} & \quad \text{N} \\
\text{Ms} & \quad \text{S} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]
Compound 4da
Compound 4eb

![Structural formula of Compound 4eb]

![NMR spectrum of Compound 4eb]

![1H NMR spectrum of Compound 4eb]

![13C NMR spectrum of Compound 4eb]
Compound 4ec
Compound 4ed
Compound 4ee
Compound 4ib
Compound 4ka

Chemical structure and corresponding NMR spectra for Compound 4ka.
Compound 4eg
Compound 5