Supporting Information
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Supporting Information

Consecutive Aminolithiation–Carbolithiation of Linear Aminoalkene Bearing Terminal Vinyl Sulfide Moiety Giving Hydroindolizine

Yasutomo Yamamoto\textsuperscript{a}\textsuperscript{*}, Tatsuya Yamaguchi\textsuperscript{b}, Atsunori Kaneshige\textsuperscript{b}, Aiko Hashimoto\textsuperscript{a}, Sachiko Kaibe\textsuperscript{a}, Akari Miyawaki\textsuperscript{a}, Ken-ichi Yamada\textsuperscript{b}, and Kiyoshi Tomioka\textsuperscript{a,b}\textsuperscript{*}

\textsuperscript{a} Faculty of Pharmaceutical Sciences, Doshisha Women’s College of Liberal Arts, Kodo, Kyotanabe 610-0395, Japan

\textsuperscript{b} Graduate School of Pharmaceutical Sciences, Kyoto University, Yoshida Sakyo Kyoto 601-8502, Japan

yayamamo@dwc.doshisha.ac.jp; tomioka@pharm.kyoto-u.ac.jp

General
All melting points are uncorrected. Silica gel was used for column chromatography. \textsuperscript{1}H NMR (500 MHz) and \textsuperscript{13}C NMR (125 MHz) were measured in CDCl\textsubscript{3} unless otherwise mentioned, and chemical shift values and coupling constants are presented in ppm \( \delta \) relative to tetramethylsilane and Hz, respectively. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. \textsuperscript{13}C peak multiplicity assignments were made based on DEPT data. IR spectroscopy was measured as neat liquid films. The wave numbers of maximum absorption peaks of IR spectroscopy are presented in cm\(^{-1}\).

6-(Phenylthio)hex-5-en-1-ol (5)

A mixture of 5-hexyn-1-ol (981 mg, 10 mmol), thiophenol (1.21 g, 11 mmol), and AIBN (0.49 g, 3 mmol) in benzene (10 mL) was stirred at 80 °C for 1 h. Concentration followed by column chromatography (hexane/EtOAc 3/1) gave 6-(phenylthio)hex-5-en-1-ol\textsuperscript{1} (1.93 g, 93\%, \( E/Z \) 52/48) as a yellow oil.

\textsuperscript{1}H-NMR: 1.46-1.65 (5H, m), 2.20 (1.04H, dt, \( J = 7.3, 7.3 \)), 2.23 (0.96H, dt, \( J = 7.3, 7.3 \)), 3.66 (2H, dt, \( J = 6.3, 6.3 \)), 5.82 (0.48H, dt, \( J = 9.7, 7.3 \)), 5.97 (0.52H, dt, \( J = 14.9, 7.3 \)), 6.15 (0.52H, d, \( J = 14.9 \)), 6.21 (0.48H, d, \( J = 9.7 \)), 7.16-7.22 (1H, m), 7.25-7.36 (4H, m).

\textsuperscript{13}C NMR: 25.12 (CH\textsubscript{2}), 25.19 (CH\textsubscript{2}), 30.16 (CH\textsubscript{2}), 50.22 (CH\textsubscript{2}), 124.13 (CH), 128.52 (CH), 132.72 (CH), 137.40 (CH), 148.14 (CH), 151.20 (C).  

28.7 (CH$_2$), 32.1 (CH$_2$), 32.2 (CH$_2$), 32.7 (CH$_2$), 62.6 (CH$_2$), 62.7 (CH$_2$), 121.3 (CH), 123.1 (CH), 126.1 (CH), 126.2 (CH), 128.5 (CH), 128.8 (CH), 128.90 (CH), 128.93 (CH), 132.9 (CH), 136.28 (C), 136.35 (C), 136.6 (CH). IR (neat): 3341, 2932, 1582, 1481, 1443, 1065, 741. EIMS m/z: 208 (M$^+$).

Anal. Calcd for C$_{12}$H$_{16}$OS: C, 69.19; H, 7.74. Found: C, 68.96; H, 7.60.

2-Nitro-N-((phenylthio)hex-5-en-1-yl)benzenesulfonamide (6)

To a stirred solution of 2-nitrobenzenesulfonamide (3.64 g, 18.0 mmol), alcohol 5 (1.23 g, 6.0 mmol) and PPh$_3$ (2.68 g, 10.2 mmol) in toluene (10.6 mL) and THF (1.4 mL) was added DEAD (40% in toluene, 4.67 mL, 10.2 mmol) dropwise at 0 °C under argon atmosphere. After stirring for 3 h at room temperature, AcOEt (15 mL) and brine (15 mL) were added. The mixture was extracted with AcOEt (3 x 50 mL), and the combined organic layers were dried over K$_2$CO$_3$ and concentrated. Column chromatography (benzene, then acetone) gave 6 (1.80 g, 77%, E/Z 5:4). R$_f$ = 0.4 (benzene). $^1$H NMR: 1.41–1.50 (2H, m), 1.53–1.61 (2H, m), 2.13 (1.08H, ddt, $J = 1.2$, 7.3, 7.3), 2.21 (0.92H, ddt, $J = 1.2$, 7.3, 7.3), 3.10-3.15 (2H, m), 5.27 (1H, t, $J = 5.8$), 5.71 (0.46H, dt, $J = 9.2$, 7.3), 5.86 (0.4H, dt, $J = 14.7$, 7.3), 6.09 (0.54H, d, $J = 14.7$), 6.19 (0.46H, d, $J = 9.2$), 7.21 (1H, m), 7.28-7.32 (4H, m), 7.68-7.74 (2H, m), 7.83 (1H, m), 8.13 (1H, m). $^{13}$C NMR: 25.7 (CH$_2$), 25.8 (CH$_2$), 28.3 (CH$_2$), 28.91 (CH$_2$), 28.96 (CH$_2$), 32.3 (CH$_2$), 43.6 (CH$_2$), 122.0 (CH), 123.8 (CH), 125.4 (CH), 126.25 (CH), 126.31 (CH), 128.3 (CH), 128.6 (CH), 128.8 (CH), 128.98 (CH), 129.00 (CH), 131.02 (CH), 131.07 (CH), 132.0 (CH), 132.73 (CH), 132.76 (CH), 133.47 (CH), 133.55 (CH), 133.7 (C), 135.5 (CH), 136.05 (C), 136.10 (C) 148.0 (C). IR (neat): 3348, 2939, 1743, 1543, 1358, 1165. EIMS m/z: 392 (M$^+$). Anal. Calcd for C$_{18}$H$_{20}$N$_2$O$_4$S$_2$: C, 55.08; H, 5.14; N, 7.14. Found: C, 55.29; H, 5.29; N, 6.91.

3-(Phenylthio)prop-2-en-1-ol (7)$^{2a}$

A mixture of propargylalcohol (5.6 g, 100 mmol), thiophenol (10.3 mL, 100 mmol), and AIBN (4.93 g, 30 mmol) in benzene (100 mL) was strried at 80 °C for 1 h. Concentration followed by column chromatography (hexane/EtOAc 2/1) gave 3-(phenylthio)prop-2-en-1-ol$^2$ (14.3 g, 86%, E/Z 70/30) as

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a yellow oil.

$^1$H NMR: 4.21 (1.4H, dd, $J = 4.6, 4.6$), 4.38 (0.6H, dd, $J = 4.6, 4.6$), 5.93-6.00 (1H, m), 6.37 (0.3H, dt, $J = 9.8, 1.2$), 6.47 (0.7H, dt, $J = 15.0, 1.2$), 7.20-7.40 (5H, m).

2-Nitro-N-(3-(phenylthio)allyl)-N-(6-(phenylthio)hex-5-en-1-yl)benzenesulfonamide (8a) and 6-(Phenylthio)-N-(3-(phenylthio)allyl)hex-5-en-1-amine (1a)

To a stirred solution of 6 (1.18 g, 3.0 mmol), alcohol 7 (540 mg, 3.3 mmol), PPh$_3$ (1.18 g, 4.5 mmol) in benzene (25 mL) was added DEAD (40% in toluene, 2.1 mL, 4.5 mmol) dropwise at 0 °C under argon atmosphere. After stirring for 2.5 h at room temperature, AcOEt (20 mL) and brine (50 mL) were added. The mixture was extracted with AcOEt (50 + 25 + 25 mL) and the combined organic layers were dried over K$_2$CO$_3$, and concentrated. Column chromatography (benzene/hexane 1/2) gave a mixture (1.22 g) of 8a and inseparable byproducts including A, generated by S$_2$’ Mitsunobu reaction, as a colorless oil. $R_f = 0.2$ (benzene/hexane 1/2). 8a: $^1$H NMR: 1.36-1.47 (2H, m), 1.53-1.74 (2H, m), 2.10-2.17 (2H, m), 2.19-2.26 (2H, m), 3.29-3.36 (2H, m), 3.98 (1H, d, $J = 6.7$), 4.14 (1H, d, $J = 6.7$), 5.69-5.79 (1H, m), 5.84-5.99 (1H, m), 6.05-6.21 (1H, m), 6.35-6.41 (1H, m), 7.17-7.67 (14H, m). Characteristic signals of regioisomer A: 3.40-3.54 (2H, m, NsNH$_2$), 5.25 (1H, dd, $J = 3.7, 10.3$), 5.43 (1H, d, $J = 16.5$, CH=CH$_2$), 7.85 (1H, m, Ns), 7.98-8.06 (3H, m, Ns). Inseparable byproducts were presumably isomers of 8a because the elemental analysis of this mixture was agree with the chemical formula of 8a: Anal. Calcd for C$_{27}$H$_{28}$N$_2$O$_4$S$_3$: C, 59.97; H, 5.22; N, 5.18. Found: C, 60.12; H, 5.29; N, 5.06.

To a stirred solution of crude 8a obtained above (1.22 g), K$_2$CO$_3$ (622 mg, 4.5 mmol) in DMF (9 mL) was added thiophenol (0.40 mL, 3.9 mmol). After stirring for 7 h, AcOEt (40 mL) and water (40 mL) were added. The separated aqueous layer was extracted with AcOEt (3 x 40 mL), and the combined organic layers were washed with water (40 mL), brine (40 mL), dried over K$_2$CO$_3$, and concentrated. Column chromatography (AcOEt/Et$_3$N 40/1) gave 1a (639 mg, 60% in 2 steps) as a colorless oil. $R_f = 0.2$ (AcOEt/Et$_3$N 40/1). $^1$H NMR: 1.44-1.60 (4H, m), 2.19 (1.14H, dt, $J = 7.0$, 1.14).
7.0), 2.28 (0.86H, dt, J = 7.0, 7.0), 2.61-2.70 (2H, m), 3.32 (1.1H, d, J = 6.4), 3.45 (0.9H, dd, J = 1.2, 6.4), 5.79-6.00 (2H, m), 6.15 (0.57H, d, J = 15.0), 6.21 (0.43H, d, J = 9.5), 6.30-6.35 (1H, m), 7.16-7.23 (2H, m), 7.27-7.36 (8H, m). 13C NMR: 26.72 (CH₂), 26.78 (CH₂), 28.9 (CH₂), 29.6 (CH₂), 32.9 (CH₂), 47.7 (CH₂), 49.1 (CH₂), 49.2 (CH₂), 51.7 (CH₂), 121.1 (CH), 121.2 (CH), 121.3 (CH), 123.0 (CH), 123.1 (CH), 124.1 (CH), 124.2 (CH), 125.1 (CH), 125.2 (CH), 126.06 (CH), 126.09 (CH), 126.46 (CH), 126.48 (CH), 126.61 (CH), 126.65 (CH), 128.52 (CH), 128.54 (CH), 128.7 (CH), 128.91 (CH), 128.93 (CH), 129.0 (CH), 129.1 (CH), 129.53 (CH), 129.56 (CH), 130.6 (CH), 130.7 (CH), 132.3 (CH), 132.5 (CH), 133.0 (CH), 133.1 (CH), 135.3 (C), 135.92 (C), 135.96 (C), 136.4 (C), 136.8 (CH), 136.9 (CH). IR (neat): 3317, 2924, 1582, 1474. EIMS m/z: 355 [M]+. Anal. Calcd for C₂₁H₂₂NS₂: C, 70.94; H, 7.09; N, 3.94. Found: C, 71.17; H, 7.06; N, 3.87.

E/Z ratio of each olefins was determined by the integration ratio of allylic methylene protons and vinyl proton in ¹H NMR as shown below.

tert-Butyl (E)-(3-(phenylthio)allyl)carbamate (10)

A solution of tert-butyl prop-2-yn-1-ylcarbamate (1.55 g, 10 mmol), thiophenol (1.03 mL, 10 mmol), and AIBN (0.49 g, 3 mmol) in benzene (10 mL) were stirred at 80 °C for 1.5 h. Concentration followed by column chromatography (hexane/AcOEt 2/1) gave 10 (2.16 g, 82%) as yellow oil.

¹H NMR (rotamer was observed): 1.45-1.46 (9H, m), 3.82-3.93 (2H, m), 4.65 (1H, m), 5.83 (1H, m), 6.34 (1H, m), 7.26-7.35 (5H, m). ¹³C NMR (rotamer was observed): 28.5 (CH₃), 60.5 (CH₂), 79.7 (C), 125.2 (CH), 126.8 (CH), 126.9 (CH), 129.2 (CH), 129.3 (CH), 129.6 (CH), 129.8 (CH), 135.0 (C), 155.7 (C), 155.9 (C). IR (neat): 3350, 2977, 2932, 1698, 1509. HRMS-ESI m/z: [M + Na]+ calcd for C₁₄H₁₄NO₂S, 288.1034; found, 288.1032.

tert-Butyl hex-5-en-1-yl(3-(phenylthio)allyl)carbamate (12)
Under Ar atmosphere, to a stirred solution of N-Boc amide 10 (0.87 g, 3.2 mmol) in DMF (10 mL) was added NaH (0.15 g, 60% in mineral oil, 3.8 mmol) at 0 ºC. After the mixture was stirred for 30 min, 6-bromohex-1-ene (0.64 mL, 4.8 mmol) was added. After stirred for 18 h at room temperature, the reaction mixture was quenched with saturated NH₄Cl aq (5 mL). The mixture was poured into AcOEt (20 mL) and water (20 mL), and extracted with AcOEt (20 + 20 mL). The combined organic layers were washed with water (20 mL), brine (20 mL), dried over Na₂SO₄, and concentrated. Column chromatography (hexane/AcOEt 3/1) gave 12 (0.23 g, 21%) as yellow oil.

\[ \text{N-H NMR: } 1.34-1.40 (2H, m), 1.45-1.47 (9H, m), 1.55 (2H, s), 2.01-2.09 (2H, m), 3.12-3.19 (2H, m), 3.89-4.13 (2H, m), 4.94-5.02 (2H, m), 6.29 (1H, m), 7.26-7.35 (5H, m). \]

N-(3-(Phenylthio)allyl)hex-5-en-1-amine (1c)

To a stirred solution of N-Boc amide 12 (40 mg, 0.12 mmol) in CH₂Cl₂ (1 mL) was added TFA (0.5 mL) at room temperature and the mixture was stirred for 20 min. After concentration, the residue was basified with 10% NaOH aq. The mixture was extracted with Et₂O (10 mL), and the combined organic layers were washed with brine (10 mL), dried over Na₂SO₄, and concentrated. Column chromatography (hexane/AcOEt 3/1) gave 1c (9.1 mg, 31%, E/Z 1/1) as yellow oil.

\[ \text{¹H NMR: } 1.43-1.53 (5H, m), 2.05-2.09 (2H, m), 2.63 (1H, t, J = 7.4), 2.66 (1H, t, J = 7.4), 3.32 (1H, m), 3.45 (1H, m), 4.95 (1H, m), 5.00 (1H, m), 5.76-5.97 (2H, m), 6.33 (1H, m), 7.20-7.36 (5H, m). \]

HRMS-DART \( m/z \): [M + H]⁺ calcd for C₁₅H₂₁NS, 248.1473; found, 248.1482.

N-Allyl-2-nitrobenzenesulfonamide (13)

Allylamine (8.6 g, 151 mmol) was added dropwise to a stirred mixture of K₂CO₃ (21 g, 152 mmol), o-nitrobenzenesulfonyl chloride (33 g, 149 mmol) in CH₂Cl₂ (185 mL) at room temperature. The mixture was stirred for 2 h at room temperature, and then 10% HCl (30 mL) and water (40 mL) were

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successively added dropwise. The separated organic layer was washed with 10% HCl (30 mL), saturated NaHCO₃ (30 mL), brine (30 mL), dried over Na₂SO₄, and concentrated. Recrystallization from toluene gave titled compound as pale yellow prisms (29.5 g, 82%).

\[\text{Recrystallization from toluene gave titled compound as pale yellow prisms (29.5 g, 82%).}\]

\[\text{1H NMR: 3.78 (2H, t, } J = 5.5\text{), 5.11 (1H, d, } J = 10.3\text{), 5.21 (1H, d, } J = 17.2\text{), 5.38 (1H, br s), 5.74 (1H, m), 7.73-7.76 (2H, m), 7.88 (1H, m), 8.14 (1H, m).}\]

4-(Allyl(6-(phenylthio)hex-5-en-1-yl)amino)-3-nitrobenzenesulfonic acid (8b)

\[\text{DIAD (3.66 mL, 18.56 mmol) was added to a stirred solution of 6-(phenylthio)hex-5-en-1-ol (1.93 g, 9.3 mmol), } N\text{-allyl-2-nitro-benzenesulfonamide (4.49 g, 18.6 mmol) and } PPh_3 (4.86 g, 18.6 mmol) \text{ in THF (40 mL) at 0 °C. The reaction mixture was warmed room temperature, stirred for 1 h, and the solvent was removed under reduced pressure to give a residue, which was purified by column chromatography (hexane/acetone = 4/1) gave a mixture (4.24 g) of 4-(allyl(6-(phenylthio)hex-5-en-1-yl)amino)-3-nitrobenzenesulfonic acid (E/Z 53/47) and unidentified byproduct as a yellow oil.}\]

\[\text{1H-NMR: 1.35-1.61 (4H, m), 2.14 (1.06H, dt, } J = 7.5, 7.5\text{), 2.22 (0.94H, dt, } J = 7.5, 7.5\text{), 3.28-3.32 (1H, m), 3.93-3.95 (2H, m), 5.17-5.26 (2H, m), 5.67-5.76 (1.47H, m), 5.87 (0.53H, dt, } J = 14.9, 6.9\text{), 6.09 (0.53H, d, } J = 14.9\text{), 6.20 (0.47H, d, } J = 9.2\text{), 7.20-7.33 (5H, m), 7.58-7.70 (3H, m), 8.02-8.06 (1H, m).}\]

N-Allyl-6-(phenylthio)hex-5-en-1-amine (1b)

To a stirred suspension of crude 4-(allyl(6-(phenylthio)hex-5-en-1-yl)amino)-3-nitrobenzenesulfonic acid (4.24 g), K₂CO₃ (1.88 g, 13.6 mmol) in DMF (30 mL) was added thiophenol (1.2 mL, 11.7 mmol). The mixture was stirred for 2 h at room temperature, and then diluted with EtOAc (70 mL) and water (90 mL). The separated aqueous layer was extracted with EtOAc (2 x 90 mL), and the combined organic layers were washed with brine (2 x 45 mL), dried over Na₂SO₄, and concentrated. Column chromatography (hexane/EtOAc 1/1) gave N-allyl-6-(phenylthio)hex-5-en-1-amine (1.66 g, 72% in 2 steps, E/Z 52/48) as yellow oil.

\[\text{1H-NMR: 1.45-1.61 (4H, m), 2.19 (1.04H, ddt, } J = 1.2, 7.5, 7.5\text{), 2.28 (0.96H, ddt, } J = 1.2, 7.5, 7.5\text{), }\]
2.65 (2H, dt, J = 7.5, 7.5), 3.27 (2H, td, J = 1.2, 6.3), 5.11 (1H, d, J = 10.3), 5.19 (1H, d, J = 17.2), 5.81 (0.48H, dt, J = 9.2, 6.9), 5.92 (1H, tdd, J = 6.3, 10.3, 17.2), 5.97 (0.52H, dt, J = 14.9, 6.9), 6.15 (0.52H, td, J = 1.2, 14.9), 6.21 (0.48H, td, J = 1.2, 9.2), 7.18-7.21 (1H, m), 7.26-7.36 (4H, m).

13C-NMR: 26.66 (CH$_2$), 26.73 (CH$_2$), 28.9 (CH$_2$), 29.30 (CH$_2$), 29.33 (CH$_2$), 32.9 (CH$_2$), 49.0 (CH$_2$), 52.31 (CH$_2$), 52.33 (CH$_2$), 116.30 (CH$_2$), 116.33 (CH$_2$), 121.2 (CH), 123.0 (CH), 126.08 (CH), 126.14 (CH), 128.5 (CH), 128.7 (CH), 128.92 (CH), 128.94 (CH), 133.0 (CH), 136.28 (CH), 136.34 (CH), 136.4 (C), 136.8 (CH), 139.9 (C). IR (KBr) 3309, 3073, 2928, 2855, 1584, 1478, 1440. EIMS m/z: 247 (M$^+$).

HRMS-ESI m/z: [M+H]$^+$ calcd for C$_{15}$H$_{22}$NS, 248.1473; found, 248.1478.

N-allyl-N-(hex-5-enyl)-2-nitrobenzenesulfonamide (8d)$^4$

![Diagram of the reaction](image)

DEAD (6.5 mL, 15 mmol) was added to a stirred solution of 5-hexen-1-ol (1.2 mL, 10 mmol), N-allyl-2-nitrobenzenesulfonamide (2.42 g, 10 mmol) and triphenylphosphine (3.93 g, 15 mmol) in THF (30 mL) at 0 °C. The reaction mixture was warmed to room temperature and was stirred for 1 h. Concentration followed by column chromatography (hexane/AcOEt 4/1) gave 8d as a colorless oil (3.45 g, quant).

$^1$H NMR: 1.34 (2H, tt, J = 7.9, 7.9), 1.50-1.57 (2H, m), 2.02 (2H, dt, J = 7.3, 7.3), 3.28 (2H, t, J = 7.7), 3.93 (2H, d, J = 6.4), 4.92-4.99 (2H, m), 5.17 (1H, dq, J = 10.2, 1.2), 5.22 (1H, dq, J = 17.1, 1.5), 5.65-5.77 (2H, m), 7.60-7.70 (3H, m), 8.03 (1H, m). $^{13}$C NMR: 25.7 (CH$_2$), 27.0 (CH$_2$), 33.1 (CH$_2$), 46.8 (CH$_2$), 49.8 (CH$_2$), 114.8 (CH$_2$), 119.1 (CH$_2$), 124.1 (CH), 130.9 (CH), 131.6 (CH), 132.8 (CH), 133.3 (CH), 133.9 (C), 138.2 (CH), 148.0 (C). IR (neat): 2936, 1545, 1352, 1163, 914. EIMS m/z: 324 (M$^+$).

N-alllylhex-5-en-1-amine (1d)

![Diagram of the reaction](image)

To a stirred suspension of 8d (1.62 g, 5 mmol), K$_2$CO$_3$ (1.05 g, 7.5 mmol) in DMF (17 mL) was added thiophenol (0.67 mL, 6.5 mmol). The solution was stirred for 2 h at room temperature, and Et$_2$O (15 mL) and water (20 mL) were added. The separated aqueous layer was extracted with Et$_2$O (3 x 20

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mL). The combined organic layers were washed with water (3 x 40 mL), brine (20 mL), dried over Na₂SO₄, and concentrated. The residue was diluted with Et₂O (40 mL), extracted with 10% HCl (3 x 20 mL). The combined aqueous layers were basified with 10% NaOH. The basic aqueous layer was extracted with Et₂O (3 x 30 mL), brine (20 mL), dried over Na₂SO₄, and concentrated to give 1d (0.68 g, 98%) as a yellow oil.

1H NMR: 1.39-1.54 (5H, m), 2.07 (2H, t, J = 6.9), 3.25 (2H, dt, J = 6.3, 1.5), 4.94 (1H, dq, J = 10.3, 1.2), 5.01 (1H, dq, J = 17.2, 1.7), 5.08 (1H, dq, J = 10.3, 1.2), 5.17 (1H, dq, J = 17.2, 1.7), 5.81 (1H, ddt, J = 17.2, 10.3, 6.9), 5.91 (1H, ddt, J = 17.2, 10.3, 6.3).

13C NMR: 26.6 (CH₂), 29.5 (CH₂), 33.6 (CH₂), 49.2 (CH₂), 52.5 (CH₂), 114.4 (CH₂), 115.7 (CH₂), 137.0 (CH), 138.7 (CH). IR (neat): 3300, 3077, 2928, 2857, 1641, 1456. HRMS-DART m/z: [M+H]+ calcd for C₉H₁₇N, 140.1439; found, 140.1450.

1-(Phenylthio)-2-((phenylthio)methyl)octahydroindolizine (3a)

Under Ar atmosphere, to the solution of n-BuLi (1.62 M in hexane, 0.19 mL, 0.3 mmol) in THF (1.5 mL) was added the solution of 1a (71 mg, 0.2 mmol) in THF (0.5 mL) dropwise at –20 °C. The mixture was stirred for 2 h at room temperature, and then quenched with water (5 mL). The mixture was extracted with Et₂O (20 + 10 + 10 mL), and the combined organic layers were washed with brine (20 mL), dried over K₂CO₃ and concentrated. Column chromatography (hexane/AcOEt 5/1 to 0/1, then AcOEt/Et₃N 1/1) gave 3a (42 mg, 60%). The diastereomers of 3a were partially separated by column chromatography to give tc-3a, tt-3a and ct-3a.

**tt-3a**

Rf = 0.65 (hexane/AcOEt 1/1). 1H NMR (CDCl₃): 1.09-1.21 (m, 2H), 1.50 (1H, m), 1.59 (1H, m), 1.76 (m, 1H), 1.81 (m, 1H), 1.88 (m, 1H), 1.93 (ddd, 1H, J = 3.0, 11.5, 11.5), 2.21 (m, 1H), 2.32 (dd, 1H, J = 9.0, 9.0), 2.84 (dd, 1H, J = 6.0, 9.4), 2.87 (dd, 1H, J = 10.3, 12.6), 2.97 (br d, 1H, J = 10.5), 3.01 (dd, 1H, J = 2.0, 9.4), 3.15 (dd, 1H, J = 4.3, 12.6), 7.17 (m, 1H), 7.23-7.28 (m, 7H), 7.38-7.42 (m, 2H). 13C NMR (CDCl₃): 24.0 (CH₂), 25.1 (CH₂), 29.7 (CH₂), 38.7 (CH₂), 43.2 (CH), 53.0 (CH₂), 57.2 (CH), 57.8 (CH₂), 70.8 (CH), 125.9 (CH), 127.4 (CH), 128.9 (CH x 2), 129.3 (CH), 133.0 (CH), 134.4 (C), 136.0 (C). IR, MS and elemental analysis data were taken as a mixture of diastereomers. IR (neat): 2932, 1582, 1481. EIMS m/z: 355 [M]+. Anal. Calcd for C₂₁H₂₅NS₂: C, 70.94; H, 7.09;
N, 3.94. Found: C, 71.12; H, 7.23; N, 3.70.

The relative stereochemistry of $tt$-3a was determined by $^1$H NOESY correlation (red arrow) in toluene-$d_8$ as shown below.

$^1$H NMR (toluene-$d_8$): 0.99 (m, 1H), 1.12 (m, 1H), 1.35 (m, 1H), 1.43 (m, 1H), 1.57 (m, 1H), 1.69 (ddd, 1H, $J = 2.9, 10.9, 10.9$), 1.76 (m, 1H), 1.87 (m, 1H), 2.13 (dd, 1H, $J = 8.9, 8.9$), 2.24 (m, 1H), 2.71 (dd, 1H, $J = 10.3, 12.6$), 2.75 (br d, 1H, $J = 10.9$), 2.83 (dd, 1H, $J = 6.0, 9.2$), 2.93 (dd, 1H, $J = 1.4, 8.9$), 3.00 (dd, 1H, $J = 4.0, 12.6$), 6.87-7.34 (m, 10H). $^{13}$C NMR (toluene-$d_8$): 24.5 (CH$_2$), 25.6 (CH$_2$), 30.4 (CH$_2$), 39.0 (CH$_2$), 44.2 (CH), 53.0 (CH$_2$), 57.8 (CH), 58.1 (CH$_2$), 71.0 (CH$_2$), 125.8 (CH), 127.4 (CH), 129.0 (CH x 2), 129.3 (CH), 133.2 (CH), 135.6 (C), 137.0 (C).

$tc$-3a

$^1$H NMR (CDCl$_3$): 1.20-1.27 (m, 2H), 1.53 (m, 1H), 1.66 (m, 1H), 1.78-1.84 (m, 2H), 1.98-2.04 (m, 2H), 2.07 (dd, 1H, $J = 9.0, 9.0$), 2.71 (m, 1H), 2.83 (dd, 1H, $J = 12.0, 12.0$), 3.08 (br d, 1H, $J = 10.9$), 3.31 (dd, 1H, $J = 4.0, 12.0$), 3.45 (dd, 1H, $J = 10.0, 10.0$), 3.47 (dd, 1H, $J = 7.2, 9.4$), 7.14-7.18 (m, 2H), 7.21-7.28 (m, 8H). $^{13}$C NMR (CDCl$_3$): 24.1 (CH$_2$), 25.3 (CH$_2$), 30.1 (CH$_2$), 36.6 (CH$_2$), 37.4 (CH), 53.2 (CH$_2$), 53.5 (CH), 61.3 (CH$_2$), 68.2 (CH), 125.5 (CH), 126.1 (CH), 127.8 (CH), 128.8 (CH), 129.0 (CH), 129.5 (CH), 135.9 (C), 137.4 (C).

The relative stereochemistry of $tc$-3a was determined by $^1$H NOESY correlation (red arrow) in acetone-$d_6$ as shown below.

$^1$H NMR (acetone-$d_6$): 1.12-1.22 (m, 2H), 1.44 (m, 1H), 1.56 (m, 1H), 1.70-1.78 (m, 2H), 1.89-2.04
The relative stereochemistry of \( \text{ct-3a} \) was determined by \(^1\)H NOESY correlation (red arrow) in CDCl\(_3\) as shown below.

\( (E)\)-2a and \( (Z)\)-2a (Table 2, entry 2)

\( (E)\)-2a was obtained as a mixture of \( (E)\)-2a, \( tc\)-3a and \( ct\)-3a (1/0.1/0.27). \(^1\)H and \(^{13}\)C NMR of \( (E)\)-2a were assigned by the comparing the NMR data of a mixture of \( (E)\)-2a, \( tc\)- and \( ct\)-3a with those of pure \( tc\)- and \( ct\)-3a.

\(^1\)H NMR: 1.33 (1H, m), 1.49-1.71 (4H, m), 1.78 (1H, m), 2.30 (1H, ddd, \( J = 3.4, 9.8, 11.5 \)), 2.64 (1H, m), 2.85 (1H, dt, \( J = 11.5, 4.5 \)), 3.10 (1H, dd, \( J = 7.0, 12.3 \)), 3.15 (1H, dd, \( J = 3.2, 12.3 \)), 3.21 (1H, dd, \( J = 7.3, 14.3 \)), 3.43 (1H, ddd, \( J = 1.2, 6.1, 14.3 \)), 5.95 (1H, ddd, \( J = 6.1, 7.3, 15.0 \)), 6.32 (1H, d, \( J = 15.0 \)), 7.14-7.34 (10H, m). \(^{13}\)C NMR: 23.1 (CH\(_2\)), 25.4 (CH\(_2\)), 30.5 (CH\(_2\)), 36.1 (CH\(_2\)), 51.7 (CH\(_2\)), 56.0 (CH\(_2\)), 58.9 (CH), 125.4 (CH), 125.7 (CH), 126.6 (CH), 128.8 (CH), 128.9 (CH), 129.0 (CH), 129.4 (CH), 130.3 (CH), 135.4 (C), 137.4 (C). IR (neat): 2932, 1582, 1481. EIMS \( m/z \): 355 \([M]^+\).

\( (Z)\)-2a was obtained as a mixture of \( (E)\)-2a, \( (Z)\)-2a and \( tt\)-3a (1/1/0.64). \(^1\)H and \(^{13}\)C NMR of \( (Z)\)-2a
were assigned by the comparing the NMR data of a mixture of \((E)-2a\), \((Z)-2a\) and \(\eta-3a\) with those of \((E)-2a\) (assigned as above) and pure \(\eta-3a\).

\(\text{\textsuperscript{1}H NMR:}\) 1.33 (1H, m), 1.45-1.71 (4H, m), 1.80 (1H, m), 2.36 (1H, ddd, \(J = 3.7, 9.2, 11.6\)), 2.67 (1H, m), 2.91 (1H, dt, \(J = 11.6, 4.3\)), 3.11 (1H, ddd, \(J = 12.5, 7.5\)), 3.19 (1H, dd, \(J = 3.0, 12.5\)), 3.38 (1H, ddd, \(J = 0.9, 7.3, 15.0\)), 3.49 (1H, ddd, \(J = 1.5, 5.8, 15.0\)), 5.91 (1H, ddd, \(J = 5.8, 7.3, 9.5\)), 6.34 (1H, d, \(J = 9.5\)), 7.10-7.33 (10H, m).

\(\text{\textsuperscript{13}C NMR:}\) 23.1 (CH\(_2\)), 25.4 (CH\(_2\)), 30.3 (CH\(_2\)), 36.1 (CH\(_2\)), 52.0 (CH\(_2\)), 52.1 (CH\(_2\)), 59.2 (CH), 125.6 (CH), 126.5 (CH), 126.86 (CH), 128.74 (CH), 128.78 (CH), 128.99 (CH), 129.04 (CH), 135.9 (C), 137.4 (C). IR (KBr): 2924, 1574, 1474. EIMS \(m/\text{z}\): 355 [M]. Anal. Calcd for C\(_{21}\)H\(_{25}\)NS: C, 70.94; H, 7.09; N, 3.94. Found: C, 71.20; H, 7.05; N, 3.92.

1-\textsuperscript{Allyl}-2-((phenylthio)methyl)piperidine (2b)

\[
\begin{center}
\text{\textsuperscript{1}H NMR:}\ 1.32 (1H, m), 1.50-1.70 (4H, m), 1.80 (1H, m), 2.25 (1H, ddd, \(J = 12.6, 9.2, 3.5\)), 2.61 (1H, m), 2.85 (1H, dt, \(J = 12.6, 4.6\)), 3.04 (1H, dd, \(J = 13.8, 8.0\)), 3.09 (1H, dd, \(J = 12.6, 7.5\)), 3.16 (1H, dd, \(J = 12.6, 3.4\)), 3.39 (1H, dd, \(J = 13.8, 5.7\)), 5.13 (1H, d, \(J = 10.4\)), 5.17 (1H, dd, \(J = 17.2, 1.7\)), 5.89 (1H, m), 7.16 (1H, t, \(J = 7.5\)), 7.27 (2H, dd, \(J = 7.5, 7.5\)), 7.33 (2H, d, \(J = 7.5\)). \text{\textsuperscript{13}C NMR:}\ 23.1 (CH\(_2\)), 25.4 (CH\(_2\)), 30.3 (CH\(_2\)), 35.9 (CH\(_2\)), 51.5 (CH\(_2\)), 57.2 (CH\(_2\)), 59.0 (CH), 117.6 (CH\(_2\)), 125.6 (CH), 128.8 (CH x 2), 135.0 (CH), 137.5 (C). IR (KBr): 3037, 2933, 2855, 1584, 1480, 1439. EIMS \(m/\text{z}\): 247 (M\(^+\)). HRMS-ESI \(m/\text{z}\): [M+H]\(^+\) calcd for C\(_{15}\)H\(_{22}\)NS, 248.1473; found, 248.1464.

2-Methyl-1-(phenylthio)octahydroindolizine (3b)

\(\text{\textsuperscript{1}H NMR:}\ 1.04 (3H, d, \(J = 7.5\)), 1.16-1.29 (2H, m), 1.55-1.67 (2H, m), 1.78-1.87 (3H, m), 1.97-2.05 (2H, m), 2.66 (1H, m), 3.07 (1H, br d, \(J = 11.5\)), 3.35 (1H, dd, \(J = 8.0, 8.0\)), 3.47 (1H, dd, \(J = 10.3, 10.3\)), 7.13 (1H, m), 7.24-7.29 (4H, m). \text{\textsuperscript{13}C NMR:}\ 16.4 (CH\(_3\)), 23.9 (CH\(_2\)), 25.0 (CH\(_2\)), 29.7 (CH\(_2\)), 117.6 (CH\(_2\)), 125.6 (CH), 128.8 (CH x 2), 135.0 (CH), 137.5 (C). IR (KBr): 3037, 2933, 2855, 2788, 1584, 1480, 1439. EIMS \(m/\text{z}\): 247 (M\(^+\)). HRMS-ESI \(m/\text{z}\): [M+H]\(^+\) calcd for C\(_{16}\)H\(_{25}\)NS, 248.1473; found, 248.1464.
32.8 (CH), 53.1 (CH₂), 53.7 (CH), 62.4 (CH₂), 68.7 (CH), 125.4 (CH), 128.1 (CH), 128.9 (CH), 137.4 (C). IR (KBr) 2932, 2780, 1585, 1479, 1439. EIMS m/z: 247 (M⁺). HRMS-ESI m/z: [M+H]⁺ calcd for C₁₅H₂₂NS, 248.1473; found, 248.1458.

The relative stereochemistry of 3b was determined to be trans-cis by nOe correlation (red arrow) in C₆D₆ as shown below.

The reaction was quenched by an addition of water (350 mL) at 0 °C, and the whole was extracted with Et₂O (3 x 200 mL). The combined organic layers were washed successively with water (2 x 100 mL), brine (100 mL), dried over Na₂SO₄ and concentrated. Column chromatography (hexane-AcOEt 10/1 to 0/1) gave 16 (17.5 g, 74%) as a colorless oil.

1³C-NMR: 17.8 (CH₃), 25.3 (CH₃), 26.7 (CH₂), 28.1 (CH₃), 35.5 (CH₂), 45.5 (CH₂), 68.4 (CH), 71.0 (C), 79.5 (CH), 79.7 (C), 83.7 (C), 154.7 (C). IR (neat): 3301, 2978, 2939, 2870, 2114, 1697. EIMS m/z: 134 (M-Boc)⁺. Anal. Calcd for C₁₄H₂₁NO₂: C, 71.46; H, 8.99, N, 5.95. Found: C, 71.22; H, 8.96, N, 5.96.
tert-Butyl (6-(phenythio)hex-5-yn-1-yl)(3-(phenythio)prop-2-yn-1-yl)carbamate (17)

To a solution of diyne 16 (8.0 g, 34 mmol) in THF (180 mL) was added n-BuLi (1.66 M in hexane, 41 mL, 68 mmol) dropwise at –78 °C. After stirring for 30 min, a solution of diphenyl disulfide (14.8 g, 68 mmol) and MeI (4.23 mL, 68 mmol) in THF (250 mL) was added, and the mixture was stirred at room temperature for 2 h. The reaction was quenched by an addition of satd. NH₄Cl aq (500 mL), and the whole was extracted with Et₂O (3 x 200 mL). The combined organic layers were dried over Na₂SO₄ and concentrated. Column chromatography (toluene, then hexane/AcOEt 3/1) gave 17 (10.1 g, 66%) as a yellow oil.

1H-NMR: 1.48 (s, 9H), 1.61 (m, 2H), 1.74 (m, 2H), 2.48 (t, 2H, J = 7.0), 3.39 (t, 2H, J = 7.0), 4.27 (br, s, 2H), 7.17-7.23 (m, 2H), 7.29-7.34 (m, 4H), 7.38-7.42 (m, 4H). 13C-NMR: 19.9 (CH₂), 25.7 (CH₂), 27.2 (CH₂), 28.3 (CH₃), 37.3 (CH₂), 45.9 (CH₂) 60.3 (C), 65.2 (C), 69.5 (C), 80.2 (C), 95.2 (C), 99.2 (C), 125.8 (CH), 126.06 (CH), 126.11 (CH), 126.5 (CH), 129.0 (CH), 129.1 (CH), 132.5 (C), 133.5 (C), 154.9 (C). IR (neat): 3063, 2978, 2932, 2183, 1697, 1582. EIMS m/z: 350 (M-Boc)+.


tert-Butyl ((E)-3-(phenythio)allyl)((E)-6-(phenythio)hex-5-en-1-yl)carbamate (18)

A solution of 17 (2.26 g, 5 mmol) in THF (30 mL) was added to a suspension of LiAlH₄ (95%, 0.80 g, 20 mmol) in THF (20 mL) at room temperature, and the mixture was stirred at 40 °C for 1 h. After cooled to 0 °C, the reaction was quenched by an addition of water (0.8 mL), 15% NaOH (0.8 mL) and water (2.4 mL), and the whole was filtrated. The filtrate was dried over Na₂SO₄ and concentrated. Column chromatography (hexane/Et₂O 5/1) gave 18 (1.81 g, 80%) as a yellow oil.

1H-NMR: 1.39-1.57 (m, 4H), 1.45 (9H, s), 2.19 (dt, 2H, J = 7.0, 7.0), 3.20 (br s, 2H), 3.87 (br s, 2H), 5.80 (m, 1H), 5.95 (dt, 1H, J = 15.0, 7.0), 6.15 (d, 1H, J = 15.0), 6.27 (d, 1H, H, J = 15.0), 7.17-7.35 (m, 10H). 13C-NMR: 26.4 (CH₂), 28.0 (CH₃), 28.5 (CH₃), 32.8 (CH₂), 46.6 (CH₂), 49.1 (CH₂) 79.1 (C), 122.2 (CH), 125.2 (CH), 126.3 (CH), 126.9 (CH), 128.3 (CH), 128.5 (CH), 129.0 (CH), 129.2 (CH), 129.3 (CH), 130.2 (CH), 136.7 (C), 155.1 (C). IR (neat): 3063, 2962, 2932, 2169, 1582. EIMS m/z: 354 (M-Boc)+. Anal. Calcd for C₂₆H₃₃NO₂S₂: C, 68.53; H, 7.30, N, 3.07. Found: C, 68.49; H, 7.31, N, 3.04.
(E)-6-(Phenylthio)-N-((E)-3-(phenylthio)allyl)hex-5-en-1-amine (E,E-1a)

To a solution of **18** (0.91 g, 2 mmol) in CH$_2$Cl$_2$ (25 mL) was added ZnBr$_2$ (2.25 g, 10 mmol) at room temperature, and the mixture was stirred for 7 h. After an addition of water (25 mL) and satd. NaHCO$_3$ aq (100 mL), the whole was extracted with Et$_2$O (3 x 100 mL). The combined organic layers were dried over Na$_2$SO$_4$ and concentrated. Column chromatography (NH$_2$ silicagel, hexane/AcOEt 4/1 to 1/1) gave E,E-1a (0.51 g, 1.4 mmol) as a pale yellow oil.

$^1$H-NMR: 1.37 (1H, br s), 1.44-1.57 (4H, m), 2.19 (2H, ddt, $J = 1.2, 7.0, 7.0$), 2.63 (2H, t, $J = 7.0$), 3.33 (dd, 2H, $J = 1.2, 6.3$), 5.94 (1H, dt, $J = 15.0, 6.3$), 5.97 (1H, dt, $J = 15.0, 7.0$), 6.14 (1H, dt, $J = 15.0, 1.2$), 6.33 (1H, dt, $J = 15.0, 1.2$), 7.17-7.24 (2H, m), 7.27-7.36 (8H, m). $^{13}$C-NMR (C$_6$D$_6$): 26.9 (CH$_2$), 29.9 (CH$_2$), 33.2 (CH$_2$), 49.2 (CH$_2$), 51.7 (CH$_2$), 121.8 (CH), 123.5 (CH), 126.3 (CH), 126.6 (CH), 128.9 (CH), 129.21 (CH), 129.27 (CH), 129.6 (CH), 134.0 (CH), 136.4 (C), 137.0 (CH), 137.2 (C). IR (neat): 3310, 3063, 3009, 2924, 2855, 1581. EIMS m/z: 356 (M$^+$). Anal. Calcd for C$_{21}$H$_{25}$NS$_2$: C, 70.94; H, 7.09, N, 3.94. Found: C, 70.64; H, 7.16, N, 3.93.
$^1$H NMR, CDCl$_3$
$^1$H NMR, CDCl$_3$
6 (1H NMR, CDCl₃)
6 (\textsuperscript{13}C NMR, CDCl\textsubscript{3})
crude 8a ($^1$H NMR, CDCl$_3$)
1a-EZ mix (\(^1\)H NMR, CDCl\(_3\))
1a-EZ mix (\(^{13}\text{C}\) NMR, CDCl\(_3\))
10 (\(^1\)H NMR, CDCl\(_3\))
1c ('H NMR, CDCl₃)

X : parts per Million : 1H
1b (1H NMR, CDCl₃)

X: parts per Million: 1H
1b \((^{13}\text{C NMR, CDCl}_3)\)

\[
\begin{array}{llllllllllllllllll}
\text{X : parts per Million : } ^{13}\text{C} & 220.0 & 210.0 & 200.0 & 190.0 & 180.0 & 170.0 & 160.0 & 150.0 & 140.0 & 130.0 & 120.0 & 110.0 & 100.0 & 90.0 & 80.0 & 70.0 & 60.0 & 50.0 & 40.0 & 30.0 & 20.0 & 10.0 & 0 & -10.0 & -20.0 \\
\end{array}
\]

\[
\begin{array}{llllllllllllllllll}
\text{X : parts per Million : } ^{13}\text{C} & 220.0 & 210.0 & 200.0 & 190.0 & 180.0 & 170.0 & 160.0 & 150.0 & 140.0 & 130.0 & 120.0 & 110.0 & 100.0 & 90.0 & 80.0 & 70.0 & 60.0 & 50.0 & 40.0 & 30.0 & 20.0 & 10.0 & 0 & -10.0 & -20.0 \\
\end{array}
\]
8d (1H NMR, CDCl₃)

X : parts per Million : 1H
$8d$ (\textsuperscript{13}C NMR, CDCl$_3$)
1d (1H NMR, CDCl₃)
1d ($^{13}$C NMR, CDCl$_3$)
tt-3a \((^1\text{H NMR, CDCl}_3)\)
tt-3a (13C NMR, CDCl3)
**tt-3a (1H NMR, toluene-d₈)**

![1H NMR spectrum of tt-3a in toluene-d₈](image)

- Parts per Million (ppm) range from 0.4 to 10.0
- Key peaks at 7.3476, 7.3448, 7.3402, 7.3350, 7.3316, 7.3287, 7.3236, 7.0860, 6.9646, 6.8071, 6.0793, 6.0702, 3.9962, 3.4282, 3.4231, 3.3183, 2.9364, 2.9180, 2.8293, 2.7308, 2.7102, 2.5436, 2.4102, 2.0803, 2.0763, 1.8553, 1.7626, 1.5547, 1.4201, 1.3606, 1.1338, 1.0016, 0.9758, 0.4565, 0.4450.

X: parts per million: 1H
$tt-3a$ ($^{13}$C NMR, toluene-$d_8$)
**tc-3a** (\(^1\)H NMR, CDCl\(_3\))

X : parts per Million : 1H

Legend:
- 6.3398, 6.3094, 5.9767, 5.9641, 5.9619, 5.9493, 5.9344, 5.9195
- 4.3065, 4.2950, 4.2773, 4.1278, 4.1135, 3.4705, 3.4659, 3.4510, 3.4304
- 3.2959, 3.0874, 3.0657, 2.8498, 2.8258, 2.8011, 2.4885, 2.3013, 2.1696, 2.0676, 2.0442
- 1.8231, 1.6766, 1.6502, 1.2580, 1.2162, 1.0994, 0.8938, 0.8801, 0.7135
- 0.0704, 0.0063, 0.0000, -0.0069
tc-3a ($^{13}$C NMR, CDCl$_3$)
tc-3a (1H NMR, acetone-d_6)
$t\text{c-3a}$ ($^{13}\text{C NMR, acetone-d}_6$)
ct-3a (1H NMR, CDCl3)
ct-3a (\textsuperscript{13}C NMR, CDCl\textsubscript{3})
E-2a, tc-3a and ct-3a (1/0.1/0.27)
(1H NMR, CDCl₃)
$^{13}$C NMR, CDCl$_3$
E-2a, Z-2a and tt-3a (1/1/0.64)
(1H NMR, CDCl₃)

X : parts per Million : 1H
$E$-2a, $Z$-2a and $tt$-3a (1/1/0.64)

($^{13}$C NMR, CDCl$_3$)
2b (1H NMR, CDCl₃)
2b (\textsuperscript{13}C NMR, CDCl\textsubscript{3})

X : parts per Million : \textsuperscript{13}C
$3b\ (^{1}H\text{ NMR, CDCl}_{3})$
$^{13}$C NMR, CDCl$_3$
$3b \ (^{1}H \ NMR, \ C_{6}D_{6})$
16 ($^{13}$C NMR, CDCl$_3$)
17 (\textsuperscript{13}C NMR, CDCl\textsubscript{3})
18 (1H NMR, CDCl₃)
$^{13}$C NMR, C$_6$D$_6$
$E,E$-1a ($^1$H NMR, CDCl$_3$)
$E,E-1a$ ($^{13}$C NMR, CDCl$_3$)