Supporting Information for

**One-pot Synthesis of Versatile Buckle Units for Click Chemistry:**

4,8-Diazacyclononynes (DACNs)

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**Table of Contents:**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>General Information</td>
<td>S2</td>
</tr>
<tr>
<td>Detailed Reaction Procedures and Analytical Data</td>
<td>S3-S12</td>
</tr>
<tr>
<td>¹H, and ¹³C NMR Spectra</td>
<td>S13-S20</td>
</tr>
</tbody>
</table>
1. General Information

All reactions were carried out in heat-gun-dried glassware under an argon atmosphere unless otherwise noted. Dry CH$_2$Cl$_2$, THF, toluene and CH$_3$CN were purchased from Kanto Chemical Co., Inc. and used without further purification. Silica-gel 60N (spherical neutral, particle size 63-210 µm) and aminopropylated silica-gel [60 (spherical) NH$_2$, particle size 40-50 µm] were purchased from Kanto Chemical Co., Inc. $^1$H NMR, $^{13}$C NMR spectra were recorded on a Varian Mercury ($^1$H: 300 MHz, $^{13}$C: 75 MHz) at ambient temperature using CDCl$_3$, CD$_3$CN and toluene-$d_8$ as solvents. Chemical shifts $\delta$ of $^1$H NMR in ppm are referenced to the protonated solvent peak as an internal standard and $^{13}$C NMR in ppm are referenced to the solvent peak as an internal standard CDCl$_3$ (77.1 ppm), and C$_6$D$_5$CD$_3$ (21.1 ppm). The peak multiplicities were given as followed: s, singlet; d, doublet; q, quartet; quin, quintet; m, multiplet; br, broad. Infrared spectra were recorded on a Fourier transfer infrared spectrophotometer (Perkin Elmer SpectrumOne) as neat liquid on NaCl plates. Melting points (m.p.) were measured on a Yanaco Micro Melting Point Apparatus. Analytical thin-layer chromatography (TLC) was carried out on silica gel 60 F$_{254}$ (Merck 5715) plates and developed plates were visualized by UV (254 nm) and by heating on a hot plate after staining with a 4% solution of phosphomolybdic acid in ethanol or a 2.5% solution of $p$-anisaldehyde in ethanol. Silica-gel column chromatography was performed using silica-gel 60N (Kanto Chemical Co., Inc.) unless otherwise noted. X-ray crystallographic data was collected using a Rigaku R-AXIS RAPID diffractometer with Cu-K$\alpha$ radiation ($\lambda = 1.5418$ Å) at 123 K. HRMS analyses were performed at the Analytical Center in IMCE, Kyushu University.
**Detailed Reaction Procedures and Analytical Data**

Spectroscopic data of Cycloalkynes 1a, 1b, 1c, 1d, 7, 9, 11, diamine derivatives 4a, 4b, 4c, 8, 8', 10, and aminoalcohol derivative 6 were reported. The cycloalkynes were synthesized by the presented one-pot procedure. The other known compounds were prepared by the reported procedures with slight modifications. The 1H and 13C NMR spectra of the products were consistent with the report data.

**General Procedures for One-pot Synthesis of DACN**

![Chemical Diagram](attachment:image.png)

0.25 mmol scale procedure: To a solution of 2 (25.8 mg, 0.300 mmol) in CH₂Cl₂ (10 mL) was added Co₃(O)₆ (107 mg, 0.313 mmol) at 30 °C and stirred for 1.5 h, and then the reaction mixture was diluted with additional CH₂Cl₂ (25 mL). The diamine derivative 4a (95.2 mg, 0.250 mmol) and BF₃·OEt₂ (130 µL, 1.00 mmol) were sequentially added to the reaction mixture at 30 °C. After confirmation of the consumption of 4a by TLC analysis, silica-gel 60N (2.1 g) was added to the mixture. CAN (412 mg, 0.754 mmol) was added to the mixture, and stirred at 30 °C for 1.5 h. After confirmation of the consumption of 4a by TLC analysis, to the mixture was added pyridine (80 µL, 1.0 mmol) and aminopropylated silica-gel (2.5 g). After stirring for 30 minutes, the mixture was filtered with filter paper using AcOEt, and the solvent was removed by rotary evaporator, then CH₂Cl₂ (10 mL), silica-gel 60N (300 mg), and aminopropylated silica-gel (300 mg) were added to the residue. Filtration using CH₂Cl₂ and evaporation of the mixture afforded crystalline 1a in 83% yield, determined by 1H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard.

10 mmol scale procedure: To a solution of 2 (1.03 g, 12.0 mmol) in CH₂Cl₂ (400 mL) was added Co₃(O)₆ (4.27 g, 12.5 mmol) at 30 °C and stirred for 1.5 h, and then the reaction mixture was diluted with additional CH₂Cl₂ (1 L). The diamine derivative 4a (3.83 g, 10.0 mmol) and BF₃·OEt₂ (5.2 mL, 41 mmol) were sequentially added to the reaction mixture at 30 °C. After confirmation of the consumption of 4a by TLC analysis, silica-gel 60N (84 g) was added to the mixture. CAN (16.4 g, 30.0 mmol) was added to the mixture, and stirred at 30 °C for 1.5 h. After confirmation of the consumption of 5a by TLC analysis, to the mixture was added pyridine (3.2 mL, 40 mmol) and aminopropylated silica-gel (100 g). After stirring for 1 h, the mixture was filtered with filter paper using AcOEt, and the solvent was removed by rotary evaporator, then CH₂Cl₂ (400 mL), silica-gel 60N (12 g), and aminopropylated silica-gel (12 g) were added to the residue. The mixture was filtered using CH₂Cl₂ and the solvent was removed under reduced pressure. The crude product was purified by recrystallization from CH₂Cl₂ (10 mL) with slow addition of hexane (100 mL) to afford 3.33 g (77%) of 1a as a colorless crystal.

---

Preparation of \( \text{1b} \)

\[
\begin{array}{c}
\text{Ns} - \equiv - \text{Ts} \\
^{1b}
\end{array}
\]

Cycloalkyne \( \text{1b} \) was afforded in 79\% yield (0.25 mmol scale) as a colorless crystal by the general procedure.

10 mmol scale: To a solution of 2 (1.03 g, 12.0 mmol) in CH\(_2\)Cl\(_2\) (400 mL) was added Co\(_2\)(CO)\(_8\) (4.27 g, 12.5 mmol) at 30 °C and stirred for 1.5 h, and then the reaction mixture was diluted with additional CH\(_2\)Cl\(_2\) (1 L). The diamine derivative \( \text{4b} \) (4.13 g, 10.0 mmol) and BF\(_3\)·OEt\(_2\) (5.2 mL, 41 mmol) were sequentially added to the reaction mixture at 30 °C. After confirmation of the consumption of \( \text{4b} \) by TLC analysis, silica-gel 60N (84 g) was added to the mixture. CAN (16.4 g, 30.0 mmol) was added to the mixture, and stirred at 30 °C for 1.5 h. After confirmation of the consumption of \( \text{5b} \) by TLC analysis, to the mixture was added pyridine (3.2 mL, 40 mmol) and aminopropylated silica-gel (100 g). After stirring for 1 h, the mixture was filtered with filter paper using AcOEt, and the solvent was removed by rotary evaporator, then CH\(_2\)Cl\(_2\) (400 mL), silica-gel 60N (12 g), and aminopropylated silica-gel (12 g) were added to the residue. The mixture was filtered using CH\(_2\)Cl\(_2\) and the solvent was removed under reduced pressure. The crude product was purified by recrystallization from CH\(_2\)Cl\(_2\) (120 mL) to afford 3.12 g (72\%) of \( \text{1b} \) as a colorless crystal.

Preparation of \( \text{7} \)

\[
\begin{array}{c}
\text{Ts} - \equiv - \text{O} \\
^{7}
\end{array}
\]

Cycloalkyne \( \text{7} \) was afforded in 59\% yield (0.25 mmol scale) as a colorless crystal by the general procedure.

Preparation of \( \text{9} \)

\[
\begin{array}{c}
\text{Ns} - \equiv - \text{Ts} \\
^{9}
\end{array}
\]

Cycloalkyne \( \text{9} \) was afforded in 83\% yield (0.25 mmol scale) as a colorless crystal by the general procedure.

Preparation of \( \text{11} \)

\[
\begin{array}{c}
\text{Ns} - \equiv - \text{Ts} \\
^{11}
\end{array}
\]

Cycloalkyne \( \text{11} \) was afforded in 59\% yield (0.25 mmol scale) as a colorless crystal by the general procedure.
Preparation of 1c

Cycloalkyne 1c was afforded in 69% yield (0.25 mmol scale) as a colorless crystal by the general procedure.

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.69 (d, \(J = 8.1\) Hz, 4H), 7.36 (d, \(J = 8.1\) Hz, 4H), 4.18-4.08 (m, 1H), 3.94 (d, \(J = 4.5\) Hz, 1H), 3.83 (d, \(J = 15.3\) Hz, 2H), 3.78 (d, \(J = 15.3\) Hz, 2H), 3.43-3.30 (m, 4H), 2.45 (s, 6H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 144.6, 133.0, 130.2, 127.7, 88.0, 71.3, 49.5, 41.4, 21.7.

IR (film, cm\(^{-1}\)): 3508, 1598, 1336, 1291, 1159, 1088, 1020, 921, 857, 711, 770, 740, 706, 661.

HRMS (FAB, matrix: 3-Nitrobenzyl alcohol, positive): Exact mass calc. for C\(_{21}\)H\(_{18}\)N\(_2\)O\(_5\)S\(_2\) [M+H]\(^+\), requires \(m/z\): 449.1205, found \(m/z\): 449.1200.

m.p.: 209-210 °C (decomposition; colorless crystal turn to clear amorphous)

Preparation of 1d

To a solution of 1b (5.15 g, 11.1 mmol) in acetonitrile (50 mL) was added Cs\(_2\)CO\(_3\) (4.67 g, 14.4 mmol) and \(p\)-toluene thiol (1.77 g, 14.3 mmol) at room temperature. After stirring for 1.5 h at that temperature, the reaction was quenched with 1 M aq. HCl (30 mL) and diluted with Et\(_2\)O (30 mL). The mixture was extracted with 1 M aq. HCl (15 mL \(\times 5\)) and the combined aqueous phase was washed with Et\(_2\)O (20 mL \(\times 2\)). To the aqueous phase was added NaOH (4.0 g, 100 mmol) at 0 °C and the pH was adjusted to around 13 with 1 M aq. NaOH. The solution was extracted with CH\(_2\)Cl\(_2\) (20 mL \(\times 4\)) and the combined organic phase was washed with water (20 mL \(\times 1\)), dried over Na\(_2\)SO\(_4\), filtered, and the solvent was removed under reduced pressure. The crystalline crude product was washed with a mixed solvent (hexane/Et\(_2\)O = 1/1), and the residual solvent was removed under reduced pressure to afford 2.56 g (83%) of 1d as a colorless crystal.

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.64 (d, \(J = 8.1\) Hz, 2H), 7.29 (d, \(J = 8.1\) Hz, 2H), 3.82 (t, \(J = 2.4\) Hz, 2H), 3.34 (t, \(J = 2.4\) Hz, 2H), 2.92 (t, \(J = 5.7\) Hz, 2H), 2.40 (s, 3H), 1.85 (tt, \(J = 6.0, 5.7\) Hz, 2H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 143.6, 135.0, 129.9, 127.4, 94.2, 85.9, 44.6, 44.0, 41.0, 39.4, 33.8, 21.6.

IR (film, cm\(^{-1}\)): 3334, 2925, 1598, 1329, 1095, 957, 893, 814, 691, 546.

HRMS (EI, positive): Exact mass calc. for C\(_{14}\)H\(_{10}\)N\(_2\)O\(_7\)S\(_2\) [M]\(^+\), requires \(m/z\): 278.1089, found \(m/z\): 278.1089.

m.p.: 104.3-104.9 °C

Preparation of 1e

To a solution of 1d (55.7 mg, 0.200 mmol) in CH\(_2\)Cl\(_2\) (2 mL) was added succinic anhydride (40.0 mg, 0.400 mmol) at room temperature. The mixture was stirred for 30 min at that temperature, then concentrated under reduced pressure. The crude product was purified by silica gel chromatography (CHCl\(_3\)/MeOH = 30/1) to afford 76.5 mg of 1e (quant.) as a colorless crystal.

The rotamers of 1e were observed in NMR spectroscopic analysis (ratio 65:35, determined by \(^1\)H NMR analysis), which cause partial peak separation and peak broadening.

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 10.25-9.00 (br, 1H), 7.66 (d, \(J = 8.1\) Hz, 2H), 7.334 (d, \(J = 8.1\) Hz, 1.3H), 7.326 (d, \(J = 8.1\) Hz, 0.7H), 4.22 (t, \(J = 2.4\) Hz, 1.3H), 4.05 (t, \(J = 2.4\) Hz, 0.7H), 3.87 (t, \(J = 2.7\) Hz, 2H), 3.62 (t, \(J = 5.4\) Hz, 1.3H), 3.59 (t, \(J = 5.4\) Hz, 0.7H), 3.27 (t, \(J = 5.7\) Hz, 1.3H),
3.16 (t, J = 5.7 Hz, 0.7H), 2.71-2.54 (m, 4H), 2.44 (s, 1.95H), 2.43 (s, 1.05H), 2.13-2.02 (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ 177.4, 177.3, 172.3, 171.1, 144.0, 143.9, 134.5, 134.4, 130.0, 129.9, 127.3, 127.2, 88.9, 88.5, 88.1, 86.9, 45.3, 43.9, 43.8, 40.9, 40.7, 39.5, 36.8, 32.0, 29.9, 29.4, 29.1, 28.5, 21.5.

IR (film, cm$^{-1}$): 2917, 1735, 1580, 813, 752, 715, 664, 567, 495.

HRMS (EI, positive): Exact mass calc. for C$_{18}$H$_{22}$N$_2$O$_5$S [M]$^+$, requires m/z: 378.1249, found m/z: 378.1249.

m.p.: 155.1-155.5 °C

One-pot synthesis of 1e from 1b

To a solution of 1b (1.74 g, 4.00 mmol) in acetonitrile (38 mL) was added Cs$_2$CO$_3$ (2.60 g, 8.00 mmol) and p-toluene thiol (993 mg, 8.00 mmol) at room temperature. After stirring for 1 h at that temperature, to this solution was added succinic anhydride (800 mg, 8.00 mmol). The mixture was stirred for 2 h at that temperature, followed by quenching of the reaction with aqueous NH$_3$ (8wt%, 25 mL) and diluted with Et$_2$O (20 mL). The mixture was extracted with water (20 mL $\times$ 2) and washed with Et$_2$O (20 mL $\times$ 2). To the combined aqueous phase added 1 M aq. HCl to adjusted the pH around 1. The solution was extracted with CH$_2$Cl$_2$ (20 mL $\times$ 3) and washed with water (10 mL) and brine (10 mL), the combined organic phase was dried over Na$_2$SO$_4$. After filtration, the solvent of residue was removed under reduced pressure. The solid residue was purified by recrystallization from CH$_2$Cl$_2$ (100 mL) with slow addition of hexane (150 mL) to afford 1.11 g (78%) of 1e as a colorless crystal.
Kinetic Study on Huisgen reaction of 1 with benzyl azide

The reactions were carried out between DACNs 1 and benzyl azide in mixed with molar ration of 1:1 at concentration of 50 mM in CD$_2$CN in NMR tubes with 1,3,5-trimethoxybenzene as an internal standard. The all reaction temperatures were controlled to 25 °C in incubator. Conversion of 1 was monitored by $^1$H NMR spectroscopic analysis. No other products were observed by the NMR. Second order rate constants for the reaction were determined by plotting the 1/[1] versus time and analysis by linear regression. All reactions were repeated in four times and the second order rate constants were averaged with standard error.

![Reaction diagram]

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average k = (3.23 ± 0.04) × 10$^{-3}$ M$^{-1}$ s$^{-1}$
HN
N–Ts

CD3CN, 25 °C
5 mM

Ph
N3

HN
N–Ts

1d
13d
13d'

run 1

\[
\begin{array}{ccc}
\text{time (sec)} & t/\text{[d]} & k \\
\hline
0 & 200 & k = 0.00329 \\
3720 & 217.510 & \\
16500 & 253.004 & k = 0.00328 \\
\end{array}
\]

run 2

\[
\begin{array}{ccc}
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\hline
0 & 200 & k = 0.00328 \\
4140 & 221.117 & \\
16920 & 253.646 & k = 0.00328 \\
\end{array}
\]

run 3

\[
\begin{array}{ccc}
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\hline
0 & 200 & k = 0.00328 \\
4560 & 223.214 & \\
17340 & 254.615 & \\
\end{array}
\]

run 4

\[
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\hline
0 & 200 & k = 0.00327 \\
4980 & 223.964 & \\
17760 & 255.918 & \\
\end{array}
\]

average \( k = (3.28 \pm 0.01) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1} \)
$\text{Su-N} \rightarrow \text{Ph$\text{N}_3$}$

$\text{CD}_2\text{CN}, \text{25 \textdegree C}$

$5 \text{mM}$

$\text{average } k = (5.08 \pm 0.09) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$
Preparation of 13c

To a solution of 1c (44.7 mg, 99.7 µmol) in CH$_2$Cl$_2$ (3 mL) was added benzyl azide (15 µL, 120 µmol) at room temperature. After stirring for 20 h at that temperature, the mixture was concentrated under reduced pressure. The crude product was purified by silica gel chromatography (CHCl$_3$/MeOH = 40/1) to afford 58.4 mg of 13c (quant.) as a colorless amorphous.

$^1$H NMR (300 MHz, CDCl$_3$): δ 7.74 (d, $J = 8.4$ Hz, 2H), 7.59 (d, $J = 8.4$ Hz, 2H), 7.41-7.29 (m, 7H), 7.20-7.14 (m, 2H), 5.86 (d, $J = 15.9$ Hz, 1H), 5.80 (d, $J = 15.9$ Hz, 1H), 4.54 (d, $J = 15.3$ Hz, 1H), 4.47 (d, $J = 15.3$ Hz, 1H), 4.31 (d, $J = 15.9$ Hz, 1H), 4.20 (d, $J = 15.9$ Hz, 1H), 4.16-4.04 (m, 1H), 3.60 (d, $J = 6.9$ Hz, 1H), 3.51 (dd, $J = 15.3$, 3.0 Hz, 1H), 3.29 (dd, $J = 15.3$, 6.9 Hz, 1H), 3.16 (dd, $J = 15.3$, 5.1 Hz, 1H), 2.45 (s, 3H), 2.44 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ 144.72, 144.66, 142.2, 135.2, 133.8, 132.6, 130.7, 130.2, 129.1, 128.5, 127.8, 127.4, 127.1, 69.3, 55.3, 52.4, 48.1, 44.5, 21.64, 21.62 (one aliphatic carbon is overlapping).

IR (film, cm$^{-1}$): 1598, 1454, 1341, 1162, 1089, 912, 816, 735, 656, 548.

HRMS (FAB, matrix: 3-nitrobenzyl alcohol, positive): Exact mass calc. for C$_{28}$H$_{32}$N$_5$O$_5$S$_2$ [M+H]$^+$, requires m/z: 582.1845, found m/z: 582.1845.

Preparation of 13d and 13d’

To a solution of 1d (55.5 mg, 199 µmol) in CH$_2$Cl$_2$ (2 mL) was added benzyl azide (30 µL, 240 µmol) at room temperature. After stirring for 20 h at that temperature, the mixture was concentrated under reduced pressure. The crude product was purified by silica gel chromatography (CHCl$_3$/MeOH = 40/1 to 20/1) to afford 58.2 mg of 13d (71%) and 29.4 mg of 13d’ (36%).

Spectroscopic data of 13d

$^1$H NMR (300 MHz, CDCl$_3$): δ 7.73 (d, $J = 8.4$ Hz, 2H), 7.36-7.28 (m, 5H), 7.17-7.11 (m, 2H), 5.51 (s, 2H), 4.54 (s, 2H), 3.97 (s, 2H), 3.19 (t, $J = 6.0$ Hz, 2H), 2.62 (t, $J = 5.7$ Hz, 2H), 2.42 (s, 3H), 1.67 (tt, $J = 6.0$, 5.7 Hz, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ 143.5, 143.2, 135.3, 134.9, 133.3, 129.8, 129.0, 128.4, 127.4, 127.2, 52.0, 50.9, 48.5, 45.6, 41.0, 31.0, 21.6.

IR (film, cm$^{-1}$): 2926, 1454, 1336, 1157, 1091, 979, 817, 753, 717, 549.

HRMS (FAB, matrix: 3-nitrobenzyl alcohol, positive): Exact mass calc. for C$_{21}$H$_{26}$N$_5$O$_2$S [M+H]$^+$, requires m/z: 412.1807, found m/z: 412.1806.

Colorless crystal, m.p.: 117-118 °C
The rotamers of colorless crystal requires HRMS (FAB, matrix: 3 \begin{equation} \text{IR (51.8, 50.4, 46.2, 46.1, 43.2, 29.7, 21.6.} \end{equation} \text{13C NMR (75 MHz, CDCl}_3): \delta 146.7, 143.8, 135.9, 135.8, 129.9, 129.0, 128.2, 127.3, 127.1, 77.3, 51.8, 50.4, 46.2, 46.1, 43.2, 29.7, 21.6.} \end{equation} \text{IR (film, cm}^{-1}): 2927, 1733, 1645, 1440, 1343, 1090, 818, 755, 715, 549.\text{HRMS (FAB, matrix: 3-nitrobenzyl alcohol, positive): Exact mass calc. for C}_{25}H_{36}N_2O_5S [M+H]^+, requires m/z: 412.1807, found m/z: 412.1806.\text{colorless crystal, m.p.: 119-120 °C} \end{equation} \text{Preparation of 13e and 13e'}}

To a solution of 1e (37.8 mg, 99.9 \mu mol) in CH_2Cl_2 (3 mL) was added benzyl azide (30 \mu L, 240 \mu mol) at room temperature. After stirring for 15 h at that temperature, the mixture was concentrated under reduced pressure. The crude product was purified by silica gel chromatography (FL100D, CHCl_3/MeOH = 35/1 to 30/1) to afford 8.2 mg of 13e (16\%) as a colorless crystal, 25.7 mg of 13e' (50\%) a colorless crystal and 12.9 mg of mixture (25\%).

\text{Spectroscopic data of 13e} \end{equation} \text{The rotamers of 13e were observed in NMR spectroscopic analysis (ratio 5:95, determined by ^1H NMR analysis), which cause partial peak separation and peak broadening.} \begin{equation} \text{^1H NMR (300 MHz, CDCl}_3): \delta 10.32 (br, 1H), 7.71 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.33-7.23 (m, 3H), 7.12 (m, 2H), 5.86 (s, 1.9H), 5.55 (s, 0.1H), 4.66 (s, 0.1H), 4.59 (s, 1.9H), 4.39 (s, 0.1H), 4.31-4.33 (m, 2H), 3.02 (t, J = 5.7 Hz, 1.9H), 2.98-2.92 (m, 0.1H), 2.73-2.55 (m, 2.1H), 2.50 (t, J = 5.7 Hz, 1.9H), 2.44 (s, 3H), 2.05-1.91 (m, 2H).} \end{equation} \text{^1C NMR (75 MHz, CDCl}_3): \delta 177.0, 172.8, 172.4, 144.4, 142.4, 135.6, 132.8, 130.9, 130.0, 128.9, 128.2, 127.8, 127.2, 52.2, 52.0, 47.9, 47.7, 46.8, 41.5, 29.7, 29.4, 28.9, 28.7, 28.3, 21.6. IR (film, cm}^{-1}): 2927, 1733, 1645, 1440, 1343, 1090, 818, 755, 715, 549. \text{HRMS (FAB, matrix: 3-nitrobenzyl alcohol, positive): Exact mass calc. for C}_{25}H_{36}N_2O_5S [M+H]^+, requires m/z: 512.1968, found m/z: 512.1968.\text{colorless crystal, m.p.: 199-200 °C (decomposition; colorless crystal turn to colorless amorphous)} \end{equation} \text{S11}
7.09 (m, 1.7H), 5.69 (s, 0.3H), 5.23 (s, 1.7H), 4.79 (s, 2H), 4.11 (s, 0.3H), 4.04 (s, 1.7H), 3.59 (t, \( J = 4.5 \) Hz, 1.7H), 3.29 (t, \( J = 4.5 \) Hz, 0.3H), 3.11 (t, \( J = 5.7 \) Hz, 0.3H), 2.95 (t, \( J = 5.7 \) Hz, 1.7H), 2.79 (m, 1.7H), 2.64 (m, 0.3H), 2.58 (m, 1.7H), 2.50 (m, 0.3H), 2.43 (s, 3H), 1.87-1.76 (m, 2H).

\[^{13}\text{C} \text{ NMR}\ (75 \text{ MHz, CDCl}_3): \delta 176.7, 173.5, 172.4, 144.5, 143.1, 142.4, 134.8, 134.2, 134.1, 133.5, 131.0, 130.9, 130.2, 130.1, 129.3, 129.2, 128.7, 128.6, 127.4, 127.3, 52.5, 52.3, 48.9, 48.1, 47.1, 44.2, 42.4, 30.1, 29.6, 28.9, 28.4, 27.8, 21.7.

IR (film, \( \text{cm}^{-1} \)): 2930, 1728, 1645, 1344, 1090, 912, 817, 768, 549, 471.

HRMS (FAB, matrix: 3-nitrobenzyl alcohol, positive): Exact mass calc. for \( \text{C}_{25}\text{H}_{30}\text{N}_{5}\text{O}_{5}\text{S} \ [\text{M+H}]^+ \), requires \( m/z \): 512.1968, found \( m/z \): 512.1968.

colorless crystal, m.p.: 78-79 °C
3. $^1$H, and $^{13}$C NMR Spectra

$^1$H NMR chart of 1c (CDCl$_3$, 300 MHz)

$^{13}$C NMR chart of 1c (CDCl$_3$, 75 MHz)
$^1$H NMR chart of 1d (CDCl$_3$, 300 MHz)

$^{13}$C NMR chart of 1d (CDCl$_3$, 75 MHz)
$^1$H NMR chart of 1e (CDCl$_3$, 300 MHz)

$^{13}$C NMR chart of 1e (CDCl$_3$, 75 MHz)
\(^1\text{H NMR chart of 13c (CDCl} _3, 300 \text{ MHz)}\)

\(^{13}\text{C NMR chart of 13c (CDCl} _3, 75 \text{ MHz)}\)
$^1$H NMR chart of 13d (CDCl$_3$, 300 MHz)

$^{13}$C NMR chart of 13d (CDCl$_3$, 75 MHz)
$^1$H NMR chart of $13d'$ (CDCl$_3$, 300 MHz)

$^{13}$C NMR chart of $13d'$ (CDCl$_3$, 75 MHz)
$^1$H NMR chart of 13e (CDCl$_3$, 300 MHz)

$^{13}$C NMR chart of 13e (CDCl$_3$, 75 MHz)
$^1$H NMR chart of 13e' (CDCl$_3$, 300 MHz)

$^{13}$C NMR chart of 13e' (CDCl$_3$, 75 MHz)