Gold-Catalyzed [2+2+2+2]-Cycloaddition of 1,3,5-Hexahydro-1,3,5-triazines with Alkoxyallenes

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**General information**

All the reactions were carried out under argon atmosphere in a flame-dried schlenk tube. Solvents were dried prior to use. For column chromatography, 200-300 mesh silica gel was used. NMR spectra were recorded on Bruker 300MHz, 400MHz or 500 MHz spectrometer in CDCl₃ or Acetone-d₆. High resolution mass spectra (HRMS) were performed on Agilent 6540 Q-TOF mass spectrometer. Melting points were determined on a SGW X-4B melting point apparatus.

Compounds 1[¹] and 2[²] were prepared according to related literatures. Ph₃PAuCl[³] and NaBArF[⁴] were prepared according to literature procedures.

**General procedure for table 2**

Under an argon atmosphere, triazine 1a (0.20 mmol), alkoxyallenes 2 (0.60 mmol), Ph₃PAuCl (3 mol %), NaBArF (3 mol %) and DCE (2.0 mL) were added into a 10 mL flame-dried sealed tube. The resulting solution was stirred at rt for 12 h. Then solvent was removed under vacuum and the residue was purified by silica gel flash column purification to afford products 3.

3a was prepared via general procedure, purified by silica gel flash column purification (eluent: EA/DCM/PE = 1:1:6) and obtained as white solid in 97% yield (163.7 mg);
m.p.: 153-154 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.43-7.32 (m, 10H), 6.76-6.67 (m, 4H), 6.64-6.51 (m, 4H), 6.31-6.25 (m, 2H), 4.88 (s, 4H), 4.07-3.94 (m, 4H), 3.77-3.64 (m, 10H); ¹³C NMR (100 MHz, CDCl₃): δ 150.63, 150.56, 150.44, 142.84, 142.70, 142.45, 142.22, 137.61, 128.73, 128.17, 127.65, 127.63, 116.58, 116.43, 114.94, 114.85, 114.81, 112.14, 112.07, 111.58, 74.20, 55.96, 53.86, 53.34, 49.94, 49.62; HRMS (ESI+): calcd. for C₃₆H₃₉N₂O₄ [M+H]+: 563.2904; found: 563.2904.

3a' was isolated as minor product via general procedure using tBuXPhosAuCl/NaBArF as catalyst, purified by silica gel flash column purification and obtained as colorless oil in 35% yield (29 mg); ¹H NMR (400 MHz, Acetone-d₆): δ 7.40-7.29 (m, 5H), 7.02 (d, J = 8.5 Hz, 2H), 6.95 (d, J = 8.5 Hz, 2H), 6.83-6.76 (m, 4H), 6.30 (s, 1H), 4.85 (s, 2H), 4.61 (s, 2H), 3.99 (s, 2H), 3.72 (s, 3H), 3.71 (s, 3H), 3.69 (s, 2H); ¹³C NMR (100 MHz, Acetone-d₆): δ 154.63, 154.48, 144.71, 144.61, 142.02, 138.77, 129.30, 128.65, 128.43, 119.64, 119.46, 115.09, 115.05, 109.35, 74.42, 72.28, 55.63, 52.75, 47.92; HRMS (ESI+): calcd. for C₂₆H₂₉N₂O₃ [M+H]+: 417.2173; found: 417.2175.

3b was prepared via general procedure, purified by silica gel flash column purification (eluent: DCM/PE = 1:1 with 1% EA) and obtained as white solid in 81% yield (175.1 mg); m.p.: 154-155 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.56-7.48 (m, 4H), 7.29-7.20 (m, 4H), 6.77-6.67 (m, 4H), 6.63-6.45 (m, 4H), 6.27-6.21 (m, 2H), 4.85-4.79 (m, 4H), 4.05-3.91 (m, 4H), 3.78-3.74 (m, 6H), 3.73-3.63 (m, 4H); ¹³C NMR (75 MHz, CDCl₃): δ 150.78, 150.73, 150.61, 142.58, 142.53, 142.50, 142.39, 142.15, 136.62, 136.60, 131.90, 131.88, 129.37, 129.35, 122.18, 122.16, 117.27,
3c was prepared via general procedure, purified by silica gel flash column purification (eluent: DCM/PE = 1:1 with 1% EA) and obtained as white solid in 98% yield (183.1 mg); m.p.: 188-189 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.34-7.27 (m, 4H), 6.96-6.88 (m, 4H), 6.76-6.65 (m, 4H), 6.63-6.46 (m, 4H), 6.26 (s, 2H), 4.80 (s, 4H), 4.02-3.90 (m, 4H), 3.83 (s, 6H), 3.76-3.63 (m, 10H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.66, 159.65, 150.57, 142.74, 142.51, 129.69, 129.44, 129.43, 116.58, 116.44, 114.92, 114.84, 114.81, 114.13, 112.18, 112.10, 111.61, 73.98, 55.95, 55.43, 53.88, 53.35, 49.91, 49.62; HRMS (ESI+): calcd. for C$_{38}$H$_{43}$N$_{2}$O$_{6}$ [M+H]$^+$: 623.3116; found: 623.3117.

3d was prepared via general procedure, purified by silica gel flash column purification (eluent: DCM/PE = 1:1 with 1% EA) and obtained as white solid in 92% yield (197.3 mg); m.p.: 142-143 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.45-7.21 (m, 20H), 6.70-6.46 (m, 8H), 6.33 (s, 2H), 5.77 (s, 2H), 4.20-4.00 (m, 4H), 3.78-3.58 (m, 10H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.56, 150.49, 142.61, 142.43, 142.27, 141.74, 141.64, 141.45, 128.71, 128.70, 128.02, 128.00, 127.04, 127.01, 117.16, 117.06, 114.98, 114.87, 114.78, 112.07, 111.65, 85.29, 85.25, 55.98, 53.97, 53.49, 50.31, 49.93; HRMS (ESI+): calcd. for C$_{48}$H$_{47}$N$_{2}$O$_{4}$ [M+H]$^+$: 715.3530; found: 715.3532.
**3e** was prepared via general procedure, purified by silica gel flash column purification (eluent: DCM/PE = 1:1 with 1% EA) and obtained as white solid in 91% yield (112.0 mg); m.p.: 120-121 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.87-6.76 (m, 4H), 6.74-6.61 (m, 4H), 6.16 (s, 2H), 4.04-3.90 (m, 4H), 3.81-3.62 (m, 16H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.74, 150.66, 150.55, 144.66, 144.63, 142.91, 142.60, 142.30, 115.43, 115.27, 115.00, 114.91, 114.86, 112.23, 112.14, 111.64, 60.08, 55.99, 53.72, 53.22, 49.62, 49.32; HRMS (ESI+): calcd. for C$_{24}$H$_{31}$N$_2$O$_4$ [M+H]$^+$: 411.2278; found: 411.2276.

**3f** was prepared via general procedure, purified by silica gel flash column purification (eluent: DCM/PE = 1:1 with 1% EA) and obtained as white solid in 87% yield (187.6 mg); m.p.: 191-192 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.22-8.09 (m, 2H), 7.98-7.74 (m, 4H), 7.59-7.43 (m, 8H), 6.78-6.37 (m, 8H), 6.26-6.13 (m, 2H), 5.40-5.27 (m, 2H), 4.34-3.90 (m, 4H), 3.85-3.40 (m, 10H), 2.20-1.98 (m, 4H), 1.12-0.97 (m, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 150.44, 142.62, 142.48, 142.37, 142.24, 137.35, 134.07, 130.75, 129.39, 128.91, 128.62, 128.11, 126.61, 126.07, 125.95, 125.87, 125.42, 125.22, 125.03, 124.36, 123.58, 123.24, 115.69, 115.61, 115.52, 114.78, 112.07, 112.01, 83.44, 83.26, 56.28, 55.69, 54.01, 53.54, 50.11, 30.36, 30.10, 29.84, 10.75, 10.46; HRMS (ESI+): calcd. for C$_{48}$H$_{51}$N$_2$O$_4$ [M+H]$^+$: 719.3843; found: 719.3840.
3g was prepared via general procedure, purified by silica gel flash column purification (eluent: DCM/PE = 1:1 with 1% EA) and obtained as white solid in 88% yield (145.4 mg); m.p.: 162-163 °C; ¹H NMR (400 MHz, CDCl₃): δ 6.92-6.58 (m, 8H), 6.28 (s, 2H), 4.13 (s, 2H), 4.05-3.60 (m, 22H), 2.10-1.68 (m, 8H); ¹³C NMR (75 MHz, CDCl₃): δ 150.58, 143.92, 142.62, 115.17, 115.03, 114.95, 114.86, 114.82, 112.23, 112.18, 111.73, 77.87, 77.84, 74.79, 68.78, 56.01, 53.71, 53.22, 49.70, 49.40, 27.97, 26.05; HRMS (ESI+): calcd. for C₃₂H₄₃N₂O₆ [M+H]⁺: 551.3116; found: 551.3115.

3h was prepared via general procedure, purified by silica gel flash column purification (eluent: DCM/PE = 1:1 with 1% EA) and obtained as white solid in 89% yield (177.0 mg); m.p.: 189-190 °C; ¹H NMR (400 MHz, CDCl₃): δ 6.87-6.61 (m, 8H), 6.21 (s, 2H), 4.06-3.89 (m, 4H), 3.87-3.67 (m, 14H), 1.74-1.61 (m, 4H), 1.46-1.16 (m, 28H), 0.95-0.78 (m, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 150.58, 143.78, 142.66, 114.84, 114.65, 112.22, 72.88, 55.99, 53.31, 49.49, 32.05, 30.11, 29.77, 29.75, 29.60, 29.48, 26.06, 22.84, 14.27; HRMS (ESI+): calcd. for C₄₂H₆₇N₂O₄ [M+H]⁺: 663.5095; found: 663.5093.

3i was prepared via general procedure, purified by silica gel flash column purification (eluent: EA/PE = 1:9) and obtained as white solid in 86% yield (153.4 mg); m.p.: 115-116 °C; ¹H NMR (400 MHz, Acetone-d₆): δ 7.13-7.04 (m, 4H), 6.99-6.71 (m,
14H), 4.22-4.12 (m, 4H), 4.03-3.94 (m, 4H), 3.79 (s, 6H), 3.69 (s, 6H); ¹³C NMR (75 MHz, Acetone-\textit{d₆}): δ 156.45, 152.19, 151.94, 142.97, 141.08, 121.19, 121.03, 118.17, 115.60, 115.46, 115.40, 113.38, 113.27, 112.50, 55.89, 55.74, 53.87, 53.16, 50.49, 49.82; HRMS (ESI+): calcd. for C₃₆H₃₉N₂O₆ [M+H]⁺: 595.2803; found: 595.2807.

3j was prepared via general procedure, purified by silica gel flash column purification (eluent: EA/PE = 1:200 to 1:100) and obtained as white solid in 87% yield (224.3 mg); m.p.: 175-176 °C; ¹H NMR (400 MHz, Acetone-\textit{d₆}): δ 7.81-7.74 (m, 8H), 7.56-7.44 (m, 12H), 6.77-6.71 (m, 8H), 6.68 (s, 2H), 4.18 (s, 4H), 3.83 (s, 4H), 3.71 (s, 6H), 1.12 (s, 18H); ¹³C NMR (125 MHz, Acetone-\textit{d₆}): δ 151.79, 151.56, 143.27, 143.05, 138.81, 136.15, 133.39, 131.12, 128.95, 119.70, 115.64, 115.26, 113.25, 112.71, 55.85, 55.81, 53.84, 49.75, 26.96, 19.79; HRMS (ESI+): calcd. for C₅₄H₆₃N₂O₄Si₂ [M+H]⁺: 859.4321; found: 859.4323.

**General procedure for table 3**

Under an argon atmosphere, triazines 1 (0.20 mmol), alkoxyallene 2i (0.60 mmol), Ph₃PAuCl (3 mol %), NaBArF (3 mol %) and DCE (2.0 mL) were added into a 10 mL flame-dried sealed tube. The resulting solution was stirred at rt for 12 h. Then solvent was removed under vacuum and the residue was purified by silica gel flash column purification to afford products 4.
4a was prepared via general procedure, purified by silica gel flash column purification (eluent: EA/PE = 1:30) and obtained as white solid in 72% yield (115.5 mg); m.p.: 182-183 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.30-7.16 (m, 4H), 7.06-6.97 (m, 4H), 6.95-6.67 (m, 10H), 6.63 (s, 2H), 4.29-4.15 (m, 4H), 4.02-3.89 (m, 4H), 3.81 (s, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 155.54, 151.49, 147.75, 147.62, 147.53, 140.02, 139.99, 129.41, 129.29, 129.23, 120.32, 120.21, 117.70, 116.21, 116.15, 116.00, 114.87, 111.47, 111.45, 111.01, 55.86, 53.81, 53.11, 50.13, 49.64; HRMS (ESI+): calcd. for C₃₄H₃₅N₂O₄ [M+H]⁺: 535.2591; found: 535.2590.

4b was prepared via general procedure, purified by silica gel flash column purification (eluent: EA/PE = 1:30) and obtained as white solid in 79% yield (133.4 mg); m.p.: 177-178 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.10-6.96 (m, 8H), 6.93-6.86 (m, 4H), 6.79-6.65 (m, 4H), 6.60 (s, 2H), 4.24-4.12 (m, 4H), 3.98-3.87 (m, 4H), 3.82 (s, 6H), 2.25 (s, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 155.51, 151.56, 145.51, 139.91, 139.88, 129.95, 129.83, 129.77, 125.04, 120.64, 120.52, 117.72, 114.87, 111.45, 110.99, 55.88, 53.75, 53.05, 50.06, 49.56, 20.37; HRMS (ESI+): calcd. for C₃₆H₃₉N₂O₄ [M+H]⁺: 563.2904; found: 563.2906.

4c was prepared via general procedure, purified by silica gel flash column purification (eluent: EA/PE = 1:30) and obtained as white solid in 63% yield (107.9 mg); m.p.:
135-136 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.02-6.94 (m, 5H), 6.94-6.86 (m, 7H), 6.77-6.60 (m, 6H), 4.24-4.12 (m, 4H), 3.96-3.86 (m, 4H), 3.81 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 156.75, 156.73, 156.67, 155.67, 153.64, 153.62, 153.57, 151.37, 144.30, 144.28, 144.09, 144.07, 143.90, 143.88, 140.35, 119.79, 119.68, 117.69, 115.89, 115.82, 115.80, 115.60, 115.53, 115.51, 114.93, 112.08, 112.04, 111.99, 111.94, 111.59, 111.50, 55.87, 53.92, 53.34, 50.16, 49.74; HRMS (ESI+): calcd. for C$_{34}$H$_{33}$F$_2$N$_2$O$_4$ [M+H]$^+$: 571.2403; found: 571.2401.

$^{4d}$ was prepared via general procedure, purified by silica gel flash column purification (eluent: EA/PE = 1:30) and obtained as white solid in 60% yield (124.6 mg); m.p.: 153-154 °C; $^1$H NMR (300 MHz, Acetone-$d_6$): $\delta$ 7.33-7.22 (m, 4H), 7.14-7.07 (m, 4H), 7.00-6.88 (m, 8H), 6.75-6.67 (m, 2H), 4.29-4.20 (m, 4H), 4.01 (s, 4H), 3.79 (s, 6H); $^{13}$C NMR (75 MHz, Acetone-$d_6$): $\delta$ 156.62, 152.04, 147.78, 147.47, 142.00, 132.52, 132.28, 118.96, 118.32, 115.65, 114.54, 113.77, 108.25, 108.12, 55.90, 53.86, 49.80; HRMS (ESI+): calcd. for C$_{34}$H$_{33}$Br$_2$N$_2$O$_4$ [M+H]$^+$: 691.0802; found: 691.0806.

$^{4e}$ was prepared via general procedure, purified by silica gel flash column purification (eluent: EA/PE = 1:30 to 1:20) and obtained as white solid in 44% yield (79.7 mg); m.p.: 223-224 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.18-7.00 (m, 6H), 6.95-6.76 (m, 6H), 6.74-6.59 (m, 6H), 4.26-4.13 (m, 4H), 3.98-3.88 (m, 4H), 3.81 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 155.77, 151.37, 148.74, 148.58, 148.49, 141.10, 135.35, 135.15, 135.04, 130.34, 130.26, 130.21, 118.43, 118.29, 117.94, 116.29, 116.26, 116.17,
4f was prepared via general procedure, purified by silica gel flash column purification (eluent: EA/PE = 1:100) and obtained as white solid in 57% yield (108.0 mg); m.p.: 213-214 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.10-6.98 (m, 6H), 6.95-6.78 (m, 6H), 6.67-6.54 (m, 4H), 4.21-4.10 (m, 4H), 3.94-3.84 (m, 4H), 3.81 (s, 6H), 2.32-2.20 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.70, 151.43, 146.78, 146.66, 146.61, 140.95, 135.22, 135.03, 134.93, 131.41, 131.32, 131.26, 123.01, 122.94, 122.79, 118.84, 118.71, 117.92, 114.91, 112.20, 112.13, 111.65, 110.21, 109.81, 55.85, 53.56, 53.06, 49.73, 49.40, 18.89; HRMS (ESI+): calcd. for C$_{36}$H$_{37}$Cl$_2$N$_2$O$_4$ [M+H]$^+$: 631.2125; found: 631.2125.

**Deuterium labeling and control experiments for Scheme 2**

1. **Scheme 2a**

Under an argon atmosphere, triazine 1a (0.10 mmol), D-1a (0.10 mmol), alkoxyallene 2a (0.60 mmol), Ph$_3$PAuCl (3 mol %), NaBAR$_3$ (3 mol %) and DCE (2.0 mL) were
added into a 10 mL flame-dried sealed tube. The resulting solution was stirred at rt for 12 h. The solvent was removed under vacuum to give a mixture of 3a, D2-3a and D4-3a. The crude product was purified by silica gel flash column purification (eluent: EA/DCM/PE = 1:1:15) to afford a mixture of 3a, D2-3a and D4-3a as a white solid, m.p.: 152-154 °C; 1H NMR (300 MHz, CDCl3): δ 7.52-7.30 (m, 10H), 6.78-6.66 (m, 4H), 6.65-6.50 (m, 4H), 6.33-6.24 (m, 2H), 4.88 (s, 4H), 4.07-3.94 (m, 2H), 3.75-3.65 (m, 10H); 13C NMR (100 MHz, CDCl3): δ 150.63, 150.56, 150.44, 142.84, 142.70, 142.45, 142.21, 137.61, 128.73, 128.17, 127.65, 127.63, 116.58, 116.43, 114.94, 114.85, 114.80, 112.13, 112.07, 111.58, 74.20, 55.96, 53.86, 53.34, 49.93, 49.62; HRMS (ESI+): calcd. for C36H37D2N2O4 [M+H]+: 565.3030; found: 565.3028. calcd. for C36H35D4N2O4 [M+H]+: 567.3155; found: 567.3149. calcd. for C36H39N2O4 [M+H]+: 563.2904; found: 563.2905.

2. Scheme 2b

Under an argon atmosphere, 3a′ (21 mg, 0.05 mmol), 2a (22 mg, 0.15 mmol), Ph3PAuCl (0.74 mg, 0.0015 mmol), NaBArF (1.3 mg, 0.0015 mmol) and DCE (2.0 mL) were added into a 10 mL flame-dried sealed tube. The resulting solution was stirred at rt for 12 h. Then solvent was removed under vacuum and the residue was purified by
silica gel flash column purification (eluent: EA/DCM/PE = 1:1:6) to give 3a as a white solid in 97% yield (27.2 mg).

3. Scheme 2c

![Diagram](image)

Under an argon atmosphere, 5\(^{[5]}\) (55.5 mg, 0.1 mmol), 2a (43.8 mg, 0.3 mmol), Ph\(_3\)PAuCl (1.5 mg, 0.003 mmol), NaBAr\(_F\) (2.6 mg, 0.003 mmol) and DCE (2.0 mL) were added into a 10 mL flame-dried sealed tube. The resulting solution was stirred at rt for 12 h. Then solvent was removed under vacuum and the residue was purified by silica gel flash column purification (eluent: EA/DCM/PE = 1:20:20) to give 6 as a white solid in 95% yield (66.7 mg); m.p.: 96-98 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): δ 7.56-7.48 (m, 2H), 7.41-7.10 (m, 12H), 6.80-6.50 (m, 6H), 6.47-6.18 (m, 4H), 4.85 (s, 2H), 3.99-3.57 (m, 14H), 2.45 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): δ 150.85, 150.76, 150.66, 144.12, 142.29, 142.01, 141.92, 141.80, 141.68, 141.60, 141.25, 141.01, 140.94, 137.51, 137.50, 134.29, 134.25, 129.63, 129.16, 129.11, 128.66, 128.13, 128.01, 127.53, 127.41, 127.35, 123.88, 123.84, 116.65, 116.50, 115.01, 114.88, 114.82, 114.77, 112.01, 111.61, 111.11, 74.13, 74.11, 56.16, 55.89, 55.84, 55.49, 54.66, 53.68, 52.51, 51.99, 51.07, 50.27, 21.70; HRMS (ESI+): calcd. for C\(_{42}\)H\(_{44}\)N\(_3\)O\(_5\)S [M+H]\(^+\): 702.2996; found: 702.2999.

4. Scheme 2d

![Diagram](image)

Under an argon atmosphere, 3a' (21 mg, 0.05 mmol), 4-methyl-N-phenyl-N-1,2-
propadien-1-ylbenzenesulfonamide (43 mg, 0.15 mmol), Ph₃PAuCl (0.74 mg, 0.0015 mmol, NaBArF (1.3 mg, 0.0015 mmol) and DCE (2.0 mL) were added into a 10 mL flame-dried sealed tube. The resulting solution was stirred at rt for 12 h. Then solvent was removed under vacuum and the residue was purified by silica gel flash column purification (eluent: EA/DCM/PE = 1:1:6) to give 6 as a white solid in 90% yield (31.5 mg).

5. Scheme 2e

Under an argon atmosphere, 5[5] (55.5 mg, 0.1 mmol), 4-methyl-N-phenyl-N-1,2-propadien-1-ylbenzenesulfonamide (85.5 mg, 0.3 mmol), Ph₃PAuCl (1.5 mg, 0.003 mmol, NaBArF (2.6 mg, 0.003 mmol) and DCE (2.0 mL) were added into a 10 mL flame-dried sealed tube. The resulting solution was stirred at rt for 12 h. Then solvent was removed under vacuum and the residue was purified by silica gel flash column purification (eluent: EA/DCM/PE = 1:20:20) to give 7 as a white solid in 81% yield (68.1 mg); m.p.: 240-242 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.50 (d, J = 7.9 Hz, 4H), 7.34-7.20 (m, 10H), 7.13 (d, J = 7.9 Hz, 4H), 6.81-6.47 (m, 5H), 6.43-6.03 (m, 5H), 3.95-3.45 (m, 14H), 2.44 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 151.13, 148.81, 144.21, 141.30, 141.14, 140.87, 140.68, 134.16, 129.66, 129.22, 129.16, 127.97, 127.56, 127.45, 127.42, 127.39, 115.12, 114.95, 114.86, 111.69, 111.63, 110.93, 56.91, 55.91, 55.86, 55.81, 53.24, 52.34, 21.70; HRMS (ESI+): calcd. for C₄₈H₄₉N₄O₆S₂ [M+H]⁺: 841.3088; found: 841.3082.

6. Scheme 2f
Under an argon atmosphere, 1a (81 mg, 0.2 mmol), 2a (29.2 mg, 0.2 mmol), Ph₃PAuCl (2.96 mg, 0.006 mmol), NaBArF (5.3 mg, 0.006 mmol) and DCE (2.0 mL) were added into a 10 mL flame-dried sealed tube. The resulting solution was stirred at rt for 12 h. Then solvent was removed under vacuum and the residue was purified by silica gel flash column purification (eluent: EA/DCM/PE = 1:20:20) to give 3a′ in 56% yield (46.6 mg) and 3a in 43% yield (24.2 mg).

**X-ray structure of 3j**

The crystal structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC 1517337, 3j). The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**References**


2013, 135, 3550.


Retention Time: 12.93 minutes
Extraction Mass: 841.31
Fit (%) N/A  RFit (%) N/A

Analyte Name: 840.301529392

Collision Energy = 35 ± 15 eV

<table>
<thead>
<tr>
<th>Compound Name (Library Hit)</th>
<th>Score</th>
<th>Formula</th>
<th>Intensity</th>
<th>Threshold</th>
<th>Expected m/z</th>
<th>Found at m/z</th>
<th>Error (ppm)</th>
<th>Expected RT (min)</th>
<th>Found RT (min)</th>
<th>RT Delta (min)</th>
<th>Isotope Diff (%)</th>
<th>Library Score (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>840.301529392 (No data for Library Hit Name xcm)</td>
<td>57%</td>
<td>C48H48N4O6S2</td>
<td>31379</td>
<td>50</td>
<td>841.3088</td>
<td>841.3082</td>
<td>-0.7</td>
<td>0.00</td>
<td>12.93</td>
<td>12.93</td>
<td>4.6%</td>
<td>N/A</td>
</tr>
</tbody>
</table>
3d

CDCl₃
$3e$

![Chemical structure](image)
decyl-n-O
PMP
N
O
PMP
O-n-decyl
CDCl₃
3h
Acetone-$d_6$

3i
Acetone-$d_6$
**4a**

![Chemical Structure](image)

**NMR Spectrum**

- **Chemical Shifts:**
  - 49.64 ppm
  - 50.13 ppm
  - 53.11 ppm
  - 53.81 ppm
  - 55.86 ppm
  - 111.01 ppm
  - 111.45 ppm
  - 111.47 ppm
  - 114.87 ppm
  - 115.00 ppm
  - 116.15 ppm
  - 116.47 ppm
  - 117.70 ppm
  - 120.21 ppm
  - 120.32 ppm
  - 129.23 ppm
  - 129.29 ppm
  - 129.41 ppm
  - 139.99 ppm
  - 140.02 ppm
  - 147.53 ppm
  - 147.62 ppm
  - 147.75 ppm
  - 151.49 ppm
  - 155.54 ppm

**Solvent:** CDCl₃
Me

PMPO

N

Me

OPMP

CDCl₃

4b
4c

![Diagram of a chemical structure with peaks at various ppm values.](image)
Acetone-\textit{d}_6

4d
Acetone-\textit{d}_6

4d
4e

\[
\text{PMPO} \quad \text{N} \quad \text{OPMP} \\
\text{Cl} \quad \text{N} \quad \text{OPMP} \\
\text{Cl} \quad \text{CDCl}_3
\]
The image contains a chemical structure labeled as 4f. The chemical structure is drawn with various atoms and bonds, indicating a molecule with specific functional groups such as Me, Cl, and a ring system. The spectrum below the structure shows a series of peaks at various chemical shifts, denoted in parts per million (ppm). The peaks are labeled with their corresponding chemical shifts, such as 5.87, 5.96, 3.91, etc., indicating the position and intensity of the signals in the spectrum.