Supplementary Material (ESI) for Chemical Communications

Supporting Information

Thiocarbonyl induced heterocumulenic Pauson-Khand type reaction: Expedient synthetic method for thieno[2,3-*b*]indol-2-ones

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Table of Contents

Experimental Procedures

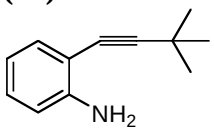
General.

All melting points were determined on a Yanaco MP-52502 apparatus and are uncorrected. Infrared spectra were recorded on Hitachi Model 270-30 or Horiba FT-710 model spectrophotometers. ^{1}H and ^{13}C NMR data were obtained with JEOL JNM-EX 500, JEOL JNM-EX 300, JEOL JNM-EX 270, or Bruker AV-600 instruments and chemical shifts are reported as δ values relative to tetramethylsilane (0.00 ppm for ^{1}H NMR) and chloroform-*d* (77.0 ppm for ^{13}C NMR). Mass spectra were measured on a Bruker Daltonics microTOF spectrometer or a Hitachi double-focusing spectrometer M-80B model spectrometer. Elemental analyses were performed with a YANACO CHN-CODER MT-6 model analyzer or a Perkin Elmer 2400 II analyzer. Acetylenes **1a–h** were purchased from Aldrich Chemical Co., Tokyo Chemical Industry Co., or Wako Pure Chemical Industries.

Typical Procedure for the Synthesis of Alkynylaniline.

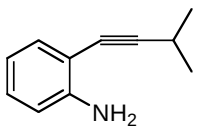
To a mixture of 2-iodoaniline (2.0 g, 9.1 mmol), $Pd(PPh_3)_2Cl_2$ (130 mg, 0.18 mmol), and copper(I) iodide (17 mg, 0.091 mmol) in Et_3N (20 mL) was added slowly 3,3-dimethyl-1-butyne (**1a**) (1.3 mL, 11 mmol). After being stirred for 2 h at room temperature, 50 mL of saturated aqueous ammonium chloride and 50 mL of CH_2Cl_2 were added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (90 mL). The combined organic layers were washed with water and brine, dried over anhydrous $MgSO_4$, and concentrated. Purification of the residue by column chromatography (*n*-hexane/AcOEt = 4/1) afforded **2a** as a yellow oil (1.6 g, 99% yield).

2-(3,3-Dimethyl-1-butynyl)aniline (2a).[1]



Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 1.34 (s, 9H), 4.06 (br s, 2H), 6.62–6.67 (m, 2H), 7.02–7.08 (m, 1H), 7.21–7.24 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 147.3 (C), 131.8 (CH), 128.7 (CH), 117.8 (CH), 114.0 (CH), 108.8 (C), 104.1 (C), 75.3 (C), 31.2 (CH_3), 28.2 (C).

2-(3-Methyl-1-butynyl)aniline (2b).[2]



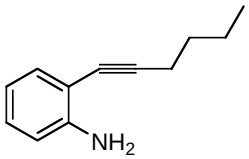
Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 1.31 (d, J = 6.9 Hz, 6H), 2,86 (sextet, J = 6.9

[1] Hiroya, K.; Itoh, S.; Sakamoto, T. *J. Org. Chem.* **2004**, *69*, 1126.

[2] Kuyper, L. F.; Baccanari, D. P.; Jones, M. L.; Hunter, R. N.; Tansik, R. L.; Joyner, S. S.; Boytos, C. M.; Rudolph, S. K.; Knick, V.; et al. *J. Med. Chem.* **1996**, *39*, 892.

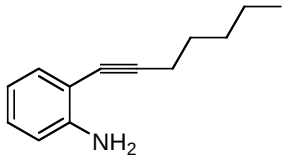
Hz, 1H), 4.17 (br s, 2H), 6.65–6.71 (m, 2H), 7.06–7.12 (m, 1H), 7.24–7.27 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 21.4 (CH), 23.3 (CH_3), 76.0 (C), 101.3 (C), 108.8 (C), 114.1 (CH), 117.8 (CH), 128.8 (CH), 131.9 (CH), 147.4 (C).

2-(1-Hexynyl)aniline (2c).[1]



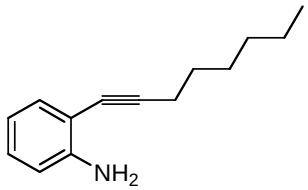
Yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$, δ) 0.95 (t, J = 7.2 Hz, 3H), 1.42–1.66 (m, 4H), 2.46 (t, J = 7.0 Hz, 2H), 4.15 (br s, 2H), 6.62–6.68 (m, 2H), 7.03–7.10 (m, 1H), 7.22–7.25 (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$, δ) 13.6 (CH_3), 19.3 (CH_2), 22.0 (CH_2), 31.0 (CH_2), 76.9 (C), 95.7 (C), 109.0 (C), 114.1 (CH), 117.8 (CH), 128.7 (CH), 132.0 (CH), 147.6 (C).

2-(1-Heptynyl)aniline (2d).[3]



Yellow oil; IR (neat) 3381, 2929, 1612, 1493 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 0.92 (t, J = 7.1 Hz, 3H), 1.30–1.50 (m, 4H), 1.63 (tt, J = 7.1, 7.1 Hz, 2H), 2.46 (t, J = 7.1 Hz, 2H), 4.16 (br s, 2H), 6.63–6.69 (m, 2H), 7.04–7.10 (m, 1H), 7.22–7.25 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 14.0 (CH_3), 19.6 (CH_2), 22.2 (CH_2), 28.6 (CH_2), 31.1 (CH_2), 76.9 (C, acetylene), 95.8 (C, acetylene), 109.0 (C), 114.1 (CH), 117.8 (CH), 128.8 (CH), 132.0 (CH), 147.5 (C); MS (EI) *m/z* 187 (M^+, 95), 130 (100); HRMS–EI calcd for $C_{13}H_{17}N$ 187.1361 (M^+), found 187.1370.

2-(1-Octynyl)aniline (2e).[4]

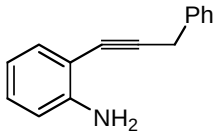


Yellow oil; IR (neat) 3381, 2931, 1614, 1493 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 0.89 (t, J = 6.9 Hz, 3H), 1.28–1.33 (m, 4H), 1.40–1.47 (m, 2H), 1.56–1.66 (m, 2H), 2.45 (t, J = 7.1 Hz, 2H), 4.14 (br s, 2H), 6.62–6.68 (m, 2H), 7.03–7.08 (m, 1H), 7.21–7.24 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 14.1 (CH_3), 19.6 (CH_2), 22.6 (CH_2), 28.6 (CH_2), 28.9 (CH_2), 31.3 (CH_2), 76.9 (C, acetylene), 95.8 (C, acetylene), 109.0 (C), 114.1 (CH), 117.8 (CH), 128.7 (CH), 132.0 (CH), 147.6 (C); MS (EI) *m/z* 201 (M^+, 60), 130 (100); HRMS–EI calcd

[3] Woodgate, P. D.; Sutherland, H. S. *J. Organomet. Chem.* **2001**, *629*, 131.
[4] Vasilevsky, S. F.; Tretyakov, E. V.; Verkruijsse, H. D. *Synth. Commun.* **1994**, *24*, 1733.

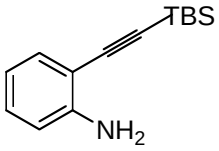
for $C_{14}H_{19}N$ 201.1517 (M^+), found 201.1517.

2-(3-Phenyl-1-propynyl)aniline (2f).[5]



Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 3.87 (s, 2H), 4.14 (brs, 2H), 6.64–6.68 (m, 2H), 7.08 (dd, J = 8.0, 7.5 Hz, 1H), 7.20–7.35 (m, 4H), 7.39–7.42 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 25.9 (CH_2), 79.2 (C, acetylene), 92.8 (C, acetylene), 108.3 (C), 114.1 (CH), 117.8 (CH), 126.6 (CH), 127.8 (CH), 128.5 (CH), 129.1 (CH), 132.1 (CH), 136.8 (C), 147.8 (C).

2-[2-(1,1-dimethylethyl)dimethylsilyl]ethynyl]aniline (2h).

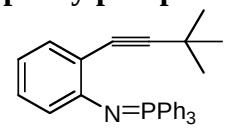


Yellow oil; IR (neat) 3386, 2931, 1612, 1488, 1465, 1311, 748 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 0.22 (s, 6H), 1.03 (s, 3H), 4.25 (br, 2H), 6.61–6.74 (m, 2), 7.13 (t, J = 7.7 Hz, 1H), 7.32 (d, J = 7.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) -4.4 (CH_3), 16.6 (C), 26.2 (CH_3), 97.9 (C), 102.4 (C), 107.9 (C), 114.1 (CH), 117.7 (CH), 129.8 (CH), 132.3 (CH), 148.3 (C); HRMS-ESI (m/z): $[M + Na]^+$ calcd for $C_{14}H_{21}NNaSi$: 254.1335, found: 254.1326.

Typical Procedure for the Synthesis of Iminophosphoranes 3.

A mixture of aniline **2a** (1.6 g, 9.2 mmol), PPh_3 (2.9 g, 11 mmol), C_2Cl_6 (2.7 g, 11 mmol), Et_3N (3.2 mL, 23 mmol), and benzene (15 mL) was stirred at room temperature for 4 h. The resulting colorless precipitate was removed by filtration, and the filtrate was concentrated. The residue was purified by column chromatography (*n*-hexane/AcOEt = 4/1) to furnish **3a** as a colorless solid (3.4 g, 85% yield).

2-(3,3-Dimethyl-1-butynyl)-*N*-(triphenylphosphonylidene) benzeneamine (3a).[6]

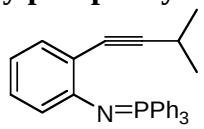


Colorless solid (*n*-hexane/AcOEt); mp 109–110 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 1.38 (s, 9H), 6.42 (d, J = 6.2 Hz, 1H), 6.54 (dd, J = 7.5, 7.0 Hz, 1H), 6.77 (dd, J = 7.5, 7.0 Hz,

[5] Lu, X.; Petersen, J. L.; Wang, K. K. *Org. Lett.* **2003**, *5*, 3277.
[6] Shi, C.; Wang, K. K. *J. Org. Chem.* **1998**, *63*, 3517.

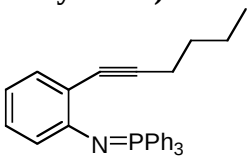
1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.41–7.50 (m, 9H), 7.81–7.87 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 28.2 (C), 31.5 (CH_3), 79.8 (C, acetylene), 100.3 (C, acetylene), 117.0 (CH, d, *J* = 1.1 Hz), 119.4 (C, d, *J* = 22.6 Hz), 121.3 (CH, d, *J* = 9.0 Hz), 127.6 (CH), 128.4 (CH, d, *J* = 12.5 Hz), 131.46 (C, d, *J* = 100.0 Hz), 131.48 (CH, d, *J* = 2.7 Hz), 132.7 (CH, d, *J* = 9.5 Hz), 133.2 (CH, d, *J* = 1.3 Hz), 152.1 (C).

2-(3-Methyl-1-butynyl)-*N*-(triphenylphosphonylidene)benzenamine (3b).



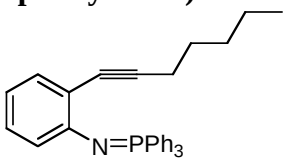
Colorless solid (*n*-hexane/AcOEt); mp 128–129 °C; IR (KBr) 2964, 1580, 682 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 1.328 (d, *J* = 6.9 Hz, 3H) 1.331 (d, *J* = 6.9 Hz, 3H), 2.90 (sextet, *J* = 6.9 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 6.55 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.75–6.81 (m, 1H), 7.28–7.32 (m, 1H), 7.38–7.53 (m, 9H), 7.80–7.87 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 21.6 (CH_3), 23.4 (CH), 80.6 (C, acetylene), 97.6 (C, acetylene), 117.0 (CH, d, *J* = 1.1 Hz), 119.3 (C, d, *J* = 22.4 Hz), 121.3 (CH, d, *J* = 9.3 Hz), 127.6 (CH), 128.4 (CH, d, *J* = 11.8 Hz), 131.4 (C, d, *J* = 100.1 Hz), 131.5 (CH, d, *J* = 3.0 Hz), 132.7 (CH, d, *J* = 10.0 Hz), 133.0 (CH, d, *J* = 1.7 Hz), 152.3 (C); MS (EI) *m/z* 419 (M^+, 100), 418 (40), 183 (42); HRMS–EI calcd for $C_{29}H_{26}NP$ 419.1804 (M^+), found 419.1811.

2-(1-Hexynyl)-*N*-(triphenylphosphonylidene)benzenamine (3c).



Yellow solid (*n*-hexane/AcOEt); mp 111–112 °C; IR (KBr) 3052, 2945, 1475, 1446, 1357, 1106, 694 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 0.91 (t, *J* = 7.2 Hz, 3H), 1.50 (dq, *J* = 7.4, 7.2 Hz, 2H), 1.66 (tt, *J* = 7.1, 7.4 Hz, 2H), 2.51 (t, *J* = 7.1 Hz, 2H), 6.46 (d, *J* = 8.0 Hz, 1H), 6.55 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.76–6.81 (m, 1H), 7.28–7.32 (m, 1H), 7.38–7.52 (m, 9H), 7.79–7.85 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 13.7 (CH_3), 19.8 (CH_2), 22.2 (CH_2), 31.3 (CH_2), 81.4 (C, acetylene), 92.3 (C, acetylene), 117.0 (CH, d, *J* = 1.3 Hz), 119.4 (C, d, *J* = 21.8 Hz), 121.5 (CH, d, *J* = 9.3 Hz), 127.6 (CH), 128.4 (CH, d, *J* = 12.3 Hz), 131.4 (C, d, *J* = 100.1 Hz), 131.5 (CH, d, *J* = 2.5 Hz), 132.7 (CH, d, *J* = 10.0 Hz), 132.9 (CH, d, *J* = 1.3 Hz), 152.4 (C); MS (EI) *m/z* 433 (M^+, 100), 432 (23), 262 (45), 183 (63); HRMS–EI calcd for $C_{30}H_{28}NP$ 433.1960 (M^+), found 433.1974.

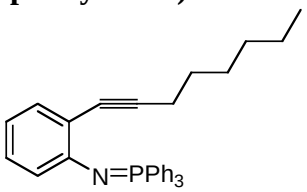
2-(1-Heptynyl)-*N*-(triphenylphosphonylidene)benzenamine (3d).



Yellow solid (*n*-hexane/AcOEt); mp 91–93 °C; IR (KBr) 2927, 2358, 1583, 1436, 1114, 692 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 0.87 (t, *J* = 7.2 Hz, 3H), 1.29–1.50 (m, 4H),

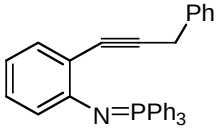
1.63–1.72 (m, 2H), 2.50 (t, *J* = 7.3 Hz, 2H), 6.46 (d, *J* = 8.0 Hz, 1H), 6.56 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.76–6.81 (m, 1H), 7.28–7.32 (m, 1H), 7.39–7.45 (m, 6H), 7.47–7.53 (m, 3H), 7.78-7.85 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 14.0 (CH_3), 20.1 (CH_2), 22.3 (CH_2), 29.0 (CH_2), 31.4 (CH_2), 81.4 (C, acetylene), 92.4 (C, acetylene), 117.1 (CH), 119.4 (C, d, *J* = 22.0 Hz), 121.5 (CH, d, *J* = 9.5 Hz), 127.6 (CH), 128.4 (CH, d, *J* = 11.8 Hz), 131.4 (C, d, *J* = 100.0 Hz), 131.5 (CH, d, *J* = 2.6 Hz), 132.7 (CH, d, *J* = 9.7 Hz), 132.9 (CH, d, *J* = 1.2 Hz), 152.4 (C); MS (EI) *m/z* 447 (M^+, 100), 262 (40), 183 (53); HRMS–EI calcd for $C_{31}H_{30}NP$ 447.2116 (M^+), found 447.2122.

2-(1-Octynyl)-*N*-(triphenylphosphonylidene)benzenamine (3e).



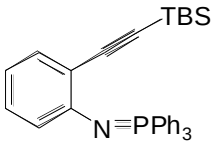
Yellow solid (*n*-hexane/AcOEt); mp 102–104 °C; IR (KBr) 2927, 2312, 1477, 1436, 1340, 1106, 692 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 0.86 (t, *J* = 7.3 Hz, 3H), 1.26–1.31 (m, 4H), 1.42–1.51 (m, 2H), 1.67 (tt, *J* = 7.3, 7.3 Hz, 2H), 2.50 (t, *J* = 7.3 Hz, 2H), 6.46 (d, *J* = 8.0 Hz, 1H), 6.56 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.76–6.81 (m, 1H), 7.28–7.32 (m, 1H), 7.39–7.45 (m, 6H), 7.48–7.53 (m, 3H), 7.79–7.85 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 14.1 (CH_3), 20.1 (CH_2), 22.5 (CH_2), 28.9 (CH_2), 29.3 (CH_2), 31.5 (CH_2), 81.4 (C, acetylene), 92.4 (C, acetylene), 117.1 (CH), 119.4 (C, d, *J* = 21.9 Hz), 121.5 (CH, d, *J* = 9.3 Hz), 127.6 (CH), 128.4 (CH, d, *J* = 12.3 Hz), 131.4 (CH, d, *J* = 100.0 Hz), 131.5 (CH, d, *J* = 2.7 Hz), 132.7 (CH, d, *J* = 9.5 Hz), 132.9 (C, d, *J* = 1.2 Hz), 152.4 (C); MS (EI) *m/z* 461 (M^+, 100), 262 (48), 183 (50); HRMS–EI calcd for $C_{32}H_{32}NP$ 461.2272 (M^+), found 461.2264.

2-(3-Phenyl-1-propynyl)-*N*-(triphenylphosphonylidene)benzenamine (3f).



Orange solid (*n*-hexane/AcOEt); mp 154–155 °C; IR (KBr) 3008, 2360, 1581, 1437, 1346, 1109, 692 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 3.94 (s, 2H), 6.48 (d, *J* = 7.7 Hz, 1H), 6.58 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.82 (dd, *J* = 7.7, 7.4 Hz, 1H), 7.15–7.26 (m, 3H), 7.32–7.38 (m, 7H), 7.44-7.49 (m, 5H), 7.79–7.83 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 26.3 (CH_2), 83.8 (C, acetylene), 89.2 (C, acetylene), 117.0 (CH), 119.0 (C, d, *J* = 22.0 Hz), 121.6 (CH, d, *J* = 9.0 Hz), 126.2 (CH), 127.95 (CH), 128.04 (CH), 128.3 (CH), 128.4 (CH, d, *J* = 11.8 Hz), 131.3 (C, d, *J* = 100.0 Hz), 131.5 (CH, d, *J* = 2.7 Hz), 132.6 (CH, d, *J* = 9.8 Hz), 133.0 (CH, d, *J* = 1.3 Hz), 137.5 (C), 152.7 (C); MS (EI) *m/z* 467 (M^+, 100), 262 (58), 183 (62); HRMS–EI calcd for $C_{33}H_{26}NP$ 467.1804 (M^+), found 467.1801.

2-[2-(1,1-dimethylethyl)dimethylsilyl]ethynyl]-*N*-(triphenylphosphonylidene)benzena mine (3h).

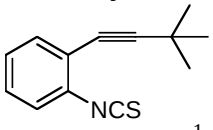


Colorless solid, mp 125.4–127.2 °C; IR (KBr) 2946, 1581, 1349, 694 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, δ) 0.26 (s, 6H), 1.01 (s, 9H), 6.41 (d, J = 8.1 Hz, 1H), 6.57 (t, J = 7.5 Hz, 1H), 6.82 (dt, J = 1.9, 8.3 Hz, 1H), 7.39 (ddd, J = 2.0, 7.5, 1.9 Hz, 1H), 7.44 (dt, J = 2.7, 7.7 Hz, 6H), 7.52 (dt, J = 1.4, 7.2 Hz, 3H), 7.82–7.87 (m, 6H); ^{13}C NMR (125.65 MHz, $CDCl_3$, δ) –4.1 (CH_3), 16.8 (C), 26.3 (CH_3), 93.6 (C), 107.5 (C), 116.9 (CH), 118.6 (CH, d, J = 22.8 Hz), 121.6 (CH, d, J = 9.6 Hz), 128.5 (CH, d, J = 12.1 Hz), 128.6 (C), 130.9 (CH), 131.6 (CH, d, J = 2.2 Hz), 132.5 (CH, d, J = 9.6 Hz), 133.9 (C), 153.2 (C); HRMS-ESI (m/z): $[M + H]^+$ calcd for $C_{32}H_{35}NPSi$: 492.2271, found : 492.2261.

Typical Procedure for the Synthesis of 2-Alkynylphenyl Isothiocyanates 4.

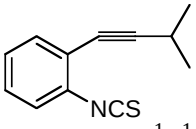
A mixture of iminophosphorane **3a** (971 mg, 2.24 mmol) and CS_2 (20 mL) was stirred at room temperature for 12 h. The reaction mixture was concentrated, and the residue was purified by column chromatography (*n*-hexane/AcOEt = 30/1) to furnish **4a** as a colorless liquid (556 mg, 96 % yield).

2-(3,3-Dimethyl-1-butynyl)phenyl Isothiocyanate (4a).



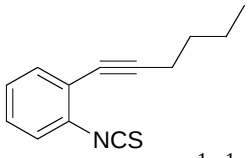
Colorless oil; IR (neat) 2900, 2028, 1440, 746 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, δ) 1.35 (s, 9H), 7.07–7.09 (m, 1H), 7.14–7.20 (m, 2H), 7.37 (dd, J = 7.7, 7.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, δ) 28.3 (C), 30.6 (CH_3), 74.7 (C, acetylene), 106.5 (C, acetylene), 123.6 (C), 124.5 (CH), 126.8 (CH), 128.2 (CH), 132.2 (C), 132.7 (CH), 136.4 (C, NCS); MS (EI) *m/z* 215 (M^+, 99), 200 (100); HRMS–EI calcd for $C_{13}H_{13}NS$ 215.0769 (M^+), found 215.0771.

2-(3-Methyl-1-butynyl)phenyl Isothiocyanate (4b).



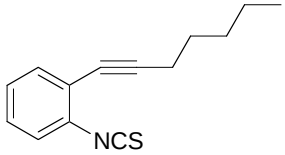
Colorless oil; IR (neat) 2969, 2069, 1450, 757 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, δ) 1.33 (d, J = 7.0 Hz, 6H), 2.87 (sextet, J = 7.0 Hz, 1H), 7.12 (dd, J = 7.7, 7.7 Hz, 1H), 7.18–7.24 (m, 2H), 7.41 (dd, J = 7.7, 7.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, δ) 21.5 (CH), 22.5 (CH_3), 75.5 (C, acetylene), 104.1 (C, acetylene), 123.6 (C), 124.5 (CH), 126.8 (CH), 128.2 (CH), 132.5 (CH), 132.6 (C), 137.4 (C, NCS); MS (EI) *m/z* 200 (M^+, 100), 186 (90); HRMS–EI calcd for $C_{12}H_{11}NS$ 201.0613 (M^+), found 201.0612.

2-(1-Hexynyl)phenyl Isothiocyanate (4c).



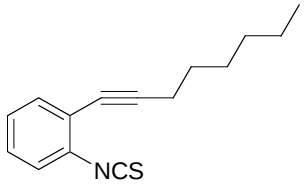
Colorless oil; IR (neat) 2916, 2022, 1562, 686 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, δ) 0.98 (t, J = 7.4 Hz, 3H), 1.52 (tq, J = 7.5, 7.4 Hz, 2H), 1.66 (tt, J = 7.5, 7.2 Hz, 2H), 2.51 (t, J = 7.2 Hz, 2H), 7.12 (d, J = 7.9 Hz, 1H), 7.18–7.25 (m, 2H), 7.41 (dd, J = 7.6, 7.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, δ) 13.7 (CH_3), 19.5 (CH_2), 22.1 (CH_2), 30.3 (CH_2), 76.4 (C, acetylene), 99.2 (C, acetylene), 123.5 (C), 124.5 (CH), 126.8 (CH), 128.2 (CH), 132.4 (CH), 132.9 (C), 138.0 (C, NCS); MS (EI) *m/z* 215 (M^+, 75), 186 (100); HRMS–EI calcd for $C_{13}H_{13}NS$ 215.0769 (M^+), found 215.0762.

2-(1-Heptynyl)phenyl Isothiocyanate (4d).



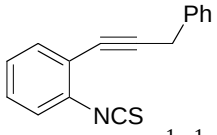
Colorless oil; IR (neat) 2931, 2042, 1594, 1481, 933, 754 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, δ) 0.95 (t, J = 6.9 Hz, 3H) 1.36–1.42 (m, 2H), 1.50–1.45 (m, 2H), 1.60–1.70 (m, 2H), 2.50 (t, J = 7.2 Hz, 2H), 7.12 (d, J = 7.9 Hz, 1H), 7.18-7.24 (m, 2H), 7.41 (dd, J = 7.7, 7.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, δ) 14.0 (CH_3), 19.8 (CH_2), 22.3 (CH_2), 28.0 (CH_2), 31.2 (CH_2), 76.4 (C, acetylene), 99.3 (C, acetylene) 123.5 (C), 124.5 (CH), 126.8 (CH), 128.2 (CH), 132.4 (CH), 132.9 (C), 138.1 (C, NCS); MS (EI) *m/z* 229 (M^+, 83), 186 (100); HRMS–EI calcd for $C_{14}H_{15}NS$ 229.0925 (M^+), found 229.0916.

2-(1-Octynyl)phenyl Isothiocyanate (4e).



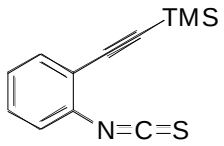
Colorless oil; IR (neat) 2929, 2048, 1594, 1481, 941, 754 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, δ) 0.92 (t, J = 6.9 Hz, 3H), 1.31–1.39 (m, 4H), 1.45–1.52 (m, 2H), 1.60–1.69 (m, 2H), 2.50 (t, J = 7.2 Hz, 2H), 7.12 (d, J = 7.9 Hz, 1H), 7.18-7.25 (m, 2H), 7.41 (dd, J = 7.7, 7.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, δ) 14.1 (CH_3), 19.8 (CH_2), 22.6 (CH_2), 28.2 (CH_2), 28.7 (CH_2), 31.4 (CH_2), 76.4 (C, acetylene), 99.3 (C, acetylene), 123.5 (C), 124.5 (CH), 126.8 (CH), 128.2 (CH), 132.4 (CH), 132.9 (C), 138.0 (C, NCS); MS (EI) *m/z* 243 (M^+, 95), 186 (100); HRMS–EI calcd for $C_{15}H_{17}NS$ 243.1082 (M^+), found 243.1082.

2-(3-Phenyl-1-propynyl)phenyl isothiocyanate (4f).



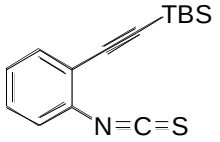
Colorless oil; IR (neat) 3029, 2030, 1452, 755 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, δ) 3.94 (s, 2H), 7.16 (d, J = 7.9 Hz, 1H), 7.22 (dd, J = 7.9, 7.4 Hz, 1H), 7.26–7.31 (m, 2H) , 7.39 (dd, J = 7.9, 7.4 Hz, 2H), 7.46–7.48 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, δ) 26.2 (CH_2), 78.4 (C, acetylene), 96.2 (C, acetylene), 122.9 (C), 124.7 (CH), 126.8 (CH) 126.9 (CH), 128.2 (CH), 128.65 (CH), 128.67 (CH), 132.5 (CH), 133.2 (C), 136.0 (C), 138.4 (C, NCS); MS (EI) *m/z* 249 (M^+, 100), 217 (26); HRMS–EI calcd for $C_{16}H_{11}NS$ 249.0613 (M^+), found 249.0617.

2-[2-(trimethylsilyl)ethynyl]phenyl isothiocyanate (4g).



Colorless oil; IR (neat) 3070, 2960, 2898, 2537, 2038, 1592, 1477, 1444, 1409, 1249, 1103, 935, 844, 756 cm^{-1}; ^1H NMR (600.0 MHz, $CDCl_3$, δ) 0.30(s, 9H), 7.09–7.12 (m, 1H), 7.16–7.28 (m, 2H), 7.43–7.46 (m, 1H); ^{13}C NMR (75.45 MHz, $CDCl_3$, δ) 0.2 (CH_3), 100.3 (C), 103.5 (C), 123.0 (C), 125.2 (CH), 127.3 (CH), 129.8 (CH), 133.4 (C), 133.5 (CH), 137.9 (C); MS (EI) m/z 231 (M^+, 32), 216 (100); HRMS–EI calcd for $C_{12}H_{13}NSSi$ 231.0538 (M^+), found 231.0540.

2-[2-(1,1-dimethylethyl)dimethylsilyl]ethynyl]phenyl isothiocyanate (4h).



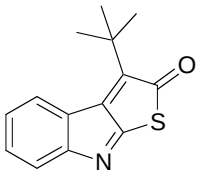
Colorless oil; IR (KBr) 2931, 2067, 1411, 1365, 732 cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$, δ) 0.25 (s, 6H), 1.03 (s, 9H), 7.13 (dd, J =1.0, 8.0 Hz, 1H), 7.19 (dt, J =1.3, 7.6 Hz, 1H), 7.27 (dt, J =1.5, 7.8 Hz, 1H), 7.46 (dd, J =1.5, 7.8 Hz, 1H); ^{13}C NMR (125.65 MHz, $CDCl_3$, δ) -4.8 (CH_3), 16.8 (C), 26.1 (CH_3), 100.5 (C), 101.0 C), 122.0 (C), 125.1 (CH), 126.7 (CH), 129.2 (CH), 132.8 (C), 133.1 (CH), 136.8 (C); HRMS-ESI calcd for $C_{15}H_{19}NNaSSi$ 196.0900 $[M + Na]^+$, found 296.0911.

The Pauson-Khand Type Reaction of the 2-Alkynylphenyl Isothiocyanate 4 Promoted by $Co_2(CO)_8$ and NMO.

To a solution of isothiocyanate **4a** (50 mg, 0.23 mmol) in CH_2Cl_2 (0.5 mL) was added $Co_2(CO)_8$ (87 mg, 0.26 mmol). After being stirred at room temperature for 0.5 h, NMO (160 mg, 1.4 mmol) was added. The mixture was stirred for additional 5 min, and

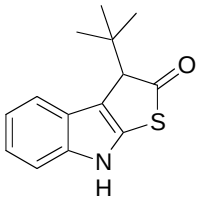
evaporated. Column chromatography (*n*-hexane/CH_2Cl_2 = 1/2) of the residue gave **5a** as a red solid (5 mg, 2% yield) and **6a** as a colorless solid (22 mg, 46% yield).

3-*tert*-Butyl-1-thia-8-aza-cyclopenta[*a*]inden-2-one (5a).



Red solid; mp 112–113 °C; IR (KBr) 2864, 1690, 1418, 1356, 718 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, δ) 1.52 (s, 9H), 7.00–7.09 (m, 1H), 7.30–7.34 (m, 2H), 7.78 (d, J = 7.8 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$, δ) 30.3 (CH_3), 36.2 (C), 120.7 (CH), 125.1 (C), 125.6 (CH), 128.0 (CH), 132.7 (CH), 151.3 (C), 152.1 (C), 159.9 (C), 174.2 (C), 194.1 (C, C=O); MS (EI) *m/z* 243 (M^+, 100), 228 (60), 200 (80); HRMS–EI calcd for $C_{14}H_{13}NOS$ 243.0718 (M^+), found 243.0705.

3-*tert*-Butyl-3,8-dihydro-1-thia-8-aza-cyclopenta[*a*]inden-2-one (6a).



Colorless solid; mp 144–146 °C; IR (KBr) 3380, 2960, 2360, 1731, 1434, 997, 750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, δ) 1.52 (s, 9H), 3.62 (s, 1H), 7.12–7.15 (m, 2H), 7.35–7.38 (m, 1H), 7.44–7.47 (m, 1H), 8.30 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 27.7 (CH_3) 38.0 (C), 64.4 (CH), 109.5 (C), 111.2 (CH), 119.3 (CH), 120.7 (CH), 121.0 (CH), 125.7 (C), 130.7 (C), 138.2 (C), 206.1 (C, C=O); MS (EI) *m/z* 245 (M^+, 25), 189 (100); HRMS–EI calcd for $C_{14}H_{15}NOS$ 245.0875 (M^+), found 245.0871.

Conversion of 5a to 6a by $Co_2(CO)_8$ and NMO.

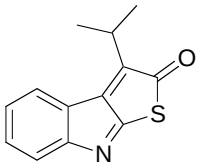
To a solution of **5a** (122 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) was added $Co_2(CO)_8$ (170 mg, 0.5 mmol). After stirring at room temperature for 0.5 h, NMO (355 mg, 3.0 mmol) was added. The mixture was stirred for additional 3 h and evaporated. Column chromatography (*n*-hexane/CH_2Cl_2 = 1/2) of the residue gave **6a** as a colorless solid (54 mg, 44% yield).

The Pauson-Khand Type Reaction Promoted by $Mo(CO)_6$ and Dimethyl Sulfoxide.

A mixture of $Mo(CO)_6$ (290 mg, 1.1 mmol), DMSO (0.35 mL, 5.0 mmol), and toluene (5 mL) was heated at 115 ^oC for 5 min, and the original colorless solution turned to bright yellow. A toluene solution (1 mL) of **4a** (107 mg, 0.5 mmol) was added to the mixture using a syringe pump (2 mL/1 h). The mixture was further heated until the starting material had been completely consumed. The crude reaction mixture was filtered through a plug of Celite with the aid of CH_2Cl_2. The filtrate was evaporated, and the residue was purified by flash chromatography (*n*-hexane:CH_2Cl_2 = 1:2) to afford **5a** as a brown powder (92 mg,

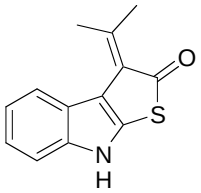
75 %).

3-Isopropyl-1-thia-8-aza-cyclopenta[*a*]inden-2-one (5b).



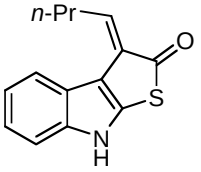
Red solid; mp 95–96 °C; IR (KBr) 3384, 2965, 1712, 1533, 1432, 1201, 943, 788, 734 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, δ) 1.40 (d, J = 7.1 Hz, 6H), 3.33 (sextet, J = 7.1 Hz, 1H), 7.08–7.12 (m, 1H), 7.35 (d, J = 4.4 Hz, 2H), 7.59 (d, J = 7.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.3 (CH_3) 27.1 (CH), 120.7 (CH), 125.1 (C), 125.6 (CH), 125.8 (CH), 133.0 (CH), 147.6 (C), 151.8 (C), 159.7 (C), 174.7 (C), 194.1 (C, C=O); MS (EI) *m/z* 229 (M^+, 100), 200 (52); HRMS–EI calcd for $C_{13}H_{11}NOS$ 229.0562 (M^+), found 229.0551.

3-Isopropylidene-3,8-dihydro-1-thia-8-aza-cyclopenta[*a*]inden-2-one (7b).



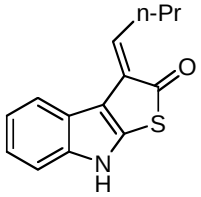
Yellow solid (*n*-hexane/CH_2Cl_2); mp 171–173 °C; IR (KBr) 3218, 2362, 2360, 1716, 1654, 1457, 1089, 753 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, δ) 2.42 (s, 3H), 2.61 (s, 3H), 7.15–7.20 (m, 2H), 7.38–7.39 (m, 1H), 7.80 (d, J = 7.2 Hz, 1H), 8.41 (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, δ) 23.0 (CH_3), 28.6 (CH_3), 110.5 (C), 111.4 (CH), 120.2 (CH), 120.8 (CH), 121.4 (CH), 123.6 (C), 129.2 (C), 132.3 (C), 138.7 (C), 148.1 (C), 193.5 (C, C=O); MS (EI) *m/z* 229 (M^+, 95), 200 (100), 186 (63); HRMS–EI calcd for $C_{13}H_{11}NOS$ 229.0562 (M^+), found 229.0558.

(*E*)-3-Butylidene-3,8-dihydro-1-thia-8-aza-cyclopenta[*a*]inden-2-one (*E*-7c).



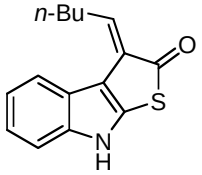
Yellow solid (*n*-hexane/CH_2Cl_2); mp 116–117 °C; IR (KBr) 3384, 1690, 1622, 1460 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, δ) 1.08 (t, J = 7.4 Hz, 3H), 1.71 (tq, J = 7.4, 7.4 Hz, 2H), 2.86 (dt, J = 7.7, 7.4 Hz, 2H), 6.68 (t, J = 7.7 Hz, 1H), 7.15–7.22 (m, 2H), 7.34–7.40 (m, 1H), 7.76–7.82 (m, 1H), 8.46 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 13.9 (CH_3), 22.7 (CH_2), 33.1 (CH_2), 109.3 (C), 111.6 (CH), 117.3 (CH), 121.3 (CH), 121.7 (CH), 122.9 (C), 132.3 (C), 134.5 (C), 135.3 (CH), 138.7 (C), 195.6 (C, C=O); MS (EI) *m/z* 243 (M^+, 56), 186 (100); HRMS–EI calcd for $C_{14}H_{13}NOS$ 243.0718 (M^+), found 243.0720; Anal Calcd for $C_{14}H_{13}NOS$: C, 69.10; H, 5.39; N,5.76. Found: C, 68.88; H, 5.58; N, 5.80.

(*Z*)-3-Butylidene-3,8-dihydro-1-thia-8-aza-cyclopenta[*a*]inden-2-one (*Z*-7c).



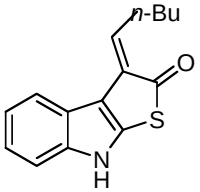
Yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 1.03 (t, J = 7.6 Hz, 3H), 1.59–1.65 (m, 2H), 2.84 (q, J = 7.6 Hz, 2H), 6.75 (dd, J = 7.6, 7.6 Hz, 1H), 7.17–7.22 (m, 2H), 7.37 (dd, J = 1.5, 7.6 Hz, 1H), 7.63 (dd, J = 1.5, 7.2 Hz, 1H), 8.22 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 14.0 (CH_3), 22.7 (CH_2), 30.5 (CH_2), 110.1 (C), 111.5 (CH), 117.3 (CH), 121.3 (CH), 121.7 (CH), 122.8 (C), 131.4 (C), 132.3 (C), 138.4 (C), 140.0 (CH), 195.6 (C, C=O).

(*E*)-3-Pentylidene-3,8-dihydro-1-thia-8-aza-cyclopenta[*a*]inden-2-one (*E*-7d).



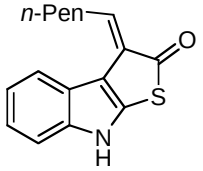
Yellow solid (*n*-hexane/CH_2Cl_2); mp 125–126 °C; IR (KBr) 3280, 1672, 1600, 1436 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 0.96 (t, J = 7.2 Hz, 3H), 1.49 (tq, J = 7.2, 7.2 Hz, 2H), 1.65 (tt, J = 7.2, 7.2 Hz, 2H), 2.85 (dt, J = 7.7, 7.2 Hz, 2H), 6.67 (t, J = 7.7 Hz, 1H), 7.15–7.21 (m, 2H), 7.33–7.38 (m, 1H), 7.75–7.81 (m, 1H), 8.42 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 14.0 (CH_3), 22.5 (CH_2), 31.0 (CH_2), 31.6 (CH_2), 109.4 (C), 111.6 (CH), 119.8 (CH), 121.4 (CH), 121.8 (CH), 123.0 (C), 132.9 (C), 134.5 (C), 135.7 (CH), 138.7 (C), 195.4 (C, C=O); MS (EI) *m/z* 257 (M^+, 60), 186 (100); HRMS–EI calcd for $C_{15}H_{15}NOS$ 257.0874 (M^+), found 257.0877.

(*Z*)-3-Pentylidene-3,8-dihydro-1-thia-8-aza-cyclopenta[*a*]inden-2-one (*Z*-7d).



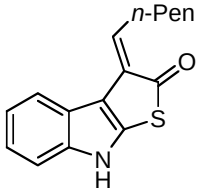
Yellow solid; mp 121–122 °C; ^{1}H NMR (600 MHz, $CDCl_3$, δ) 0.96 (t, J = 7.3 Hz, 3H), 1.41–1.47 (m, 2H), 1.54–1.59 (m, 2H), 2.86 (dd, J = 7.3, 7.8 Hz, 2H), 6.74 (dd, J = 7.8, 7.8 Hz, 1H), 7.16–7.21 (m, 2H), 7.35 (dd, J = 1.7, 7.5 Hz, 1H), 7.62 (dd, J = 1.7, 7.5 Hz, 1H), 8.20 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 13.9 (CH_3), 22.5 (CH_2), 28.3 (CH_2), 31.6 (CH_2), 110.3 (C), 111.4 (CH), 117.4 (CH), 121.4 (CH), 121.8 (CH), 122.9 (C), 131.3 (C), 132.3 (C), 138.5 (C), 140.3 (CH), 193.8 (C, C=O); HRMS–ESI calcd for $C_{15}H_{15}NNaOS$ 280.0767 $[M + Na]^+$, found 280.0764.

(*E*)-3-Hexylidene-3,8-dihydro-1-thia-8-aza-cyclopenta[*a*]inden-2-one (*E*-7e).



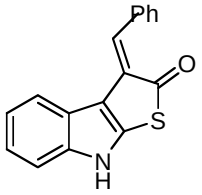
Yellow solid (*n*-hexane/CH_2Cl_2); mp 125–128 °C; IR (KBr) 3284, 1674, 1602, 1434 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, δ) 0.91 (t, J = 7.3 Hz, 3H), 1.33–1.39 (m, 4H), 1.65 (tt, J = 7.6, 7.3 Hz, 2H), 2.85 (dt, J = 7.7, 7.3 Hz, 2H), 6.66 (t, J = 7.7 Hz, 1H), 7.15–7.19 (m, 2H), 7.33–7.35 (m, 1H), 7.77 (dd, J = 7.7, 7.7 Hz, 1H), 8.52 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 14.0 (CH_3), 22.5 (CH_2), 29.1 (CH_2), 31.2 (CH_2), 31.5 (CH_2), 109.2 (C), 111.6 (CH), 119.7 (CH), 121.3 (CH), 121.7 (CH), 122.9 (C), 132.8 (C), 134.5 (C), 135.6 (CH), 138.7 (C), 195.8 (C, C=O); MS (EI) *m/z* 271 (M^+, 68), 186 (100); HRMS–EI calcd for $C_{16}H_{17}NOS$ 271.1031 (M^+), found 271.1033.

3-Hexylidene-3,8-dihydro-1-thia-8-aza-cyclopenta[*a*]inden-2-one (*Z*-7e).



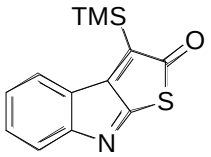
Yellow solid; mp 96–99 °C; IR (KBr) 3394, 1689, 1612, 1450 cm^{-1}; (300 MHz, $CDCl_3$, δ) 0.84 (t, J = 7.1Hz, 3H), 1.26–1.33 (m, 4H), 1.50 (tt, J = 7.6, 7.4 Hz, 2H), 2.77 (dt, J = 7.6, 7.6 Hz, 2H), 6.66 (t, J = 7.6 Hz, 1H), 7.07–7.12 (m, 2H), 7.26 (d, J = 6.9 Hz, 1H), 7.54 (dd, J = 6.9, 6.9 Hz, 1H), 8.15 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 14.0 (CH_3), 22.5 (CH_2), 29.1 (CH_2), 31.2 (CH_2), 31.5 (CH_2), 109.2 (C), 111.6 (CH), 119.7 (CH), 121.3 (CH), 121.7 (CH), 122.9 (C), 132.8 (C), 134.5 (C), 135.6 (CH), 135.7 (C), 195.8 (C, C=O); HRMS–ESI calcd for $C_{16}H_{17}NNaOS$ 294.0923 $[M + Na]^+$, found 294.0919.

(*E*)-3-Benzylidene-3,8-dihydro-1-thia-8-aza-cyclopenta[*a*]inden-2-one (*E*-7f).



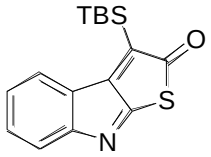
Pale orange solid (*n*-hexane/CH_2Cl_2); mp 155–156 °C; IR (KBr) 3382, 2360, 1731, 1434, 997 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, δ) 6.34 (d, J = 8.1 Hz, 1H), 6.89 (dd, J = 7.7, 7.1 Hz, 1H), 7.09 (dd, J = 8.1, 7.1 Hz, 1H), 7.28 (d, J = 8.1 Hz, 1H), 7.39–7.45 (m, 5H), 7.51 (s, 1H), 8.55 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 109.2 (C), 111.2 (CH), 120.8 (CH), 121.7 (CH), 122.0 (CH), 128.3 (CH), 122.7 (C), 129.0 (CH), 130.2 (CH), 130.3 (CH), 131.1 (C), 136.1 (C), 137.0 (C), 138.8 (C), 196.1 (C, C=O); MS (EI) *m/z* 277 (M^+, 82), 249 (100); HRMS calcd for $C_{17}H_{11}NOS$ 277.0562 (M^+), found 277.0558.

3-Trimethylsily-1-thia-8-aza-cyclopenta[*a*]inden-2-one (5g).



Brown solid; mp 128.4–129.9 °C; IR (KBr) 2854, 1704, 1434, 1342, 1295, 709 cm^{-1}; ^{1}H NMR (500.0 MHz, $CDCl_3$, δ) 0.44 (s, 9H), 7.05 (dt, J =1.2, 7.4 Hz, 1H), 7.24–7.36 (m, 2H), 7.56 (d, J =7.6 Hz, 1H); ^{13}C NMR (75.45 MHz, $CDCl_3$, δ) -0.8 (CH_3), 120.5 (CH), 125.6 (C), 125.7 (CH), 126.4 (CH), 143.1 (C), 160.1 (C), 177.1 (C), 197.5 (C). HRMS–ESI calcd for $C_{13}H_{13}NNaOSSi$: 282.0379 $[M + Na]^+$, found :282.1379.

3-[(1,1-dimethylethyl)dimethylsilyl]-1-thia-8-aza-cyclopenta[*a*]inden-2-one (5h).



Brown solid; mp 116.0–117.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 0.42 (s, 6H), 0.96 (s, 9H), 7.02 (dt, J =1.3, 7.5 Hz, 1H), 7.21–7.37 (m, 2H), 7.61 (d, J = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) -4.0 (CH_3), 19.0 (C), 26.6 (CH_3), 120.5 (CH), 125.6 (CH), 125.7 (C), 126.7 (CH), 133.8 (CH), 142.5 (C), 160.3 (C), 166.9 (C), 177.7 (C), 197.7 (C); IR (KBr) 2854, 1704, 1434, 1357, 717 cm^{-1}; HRMS–ESI calcd for $C_{16}H_{20}NOSSi$: 302.1029 $[M + H]^+$, found: 302.1027.

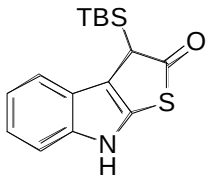
A Typical Procedure for the Catalytic Pauson-Khand Type Reaction.

In a 10 mL flask fitted with a reflux condenser were placed $[RhCl(cod)]_2$ (11 mg, 0.022 mmol), 1,3-bis(diphenylphosphino)propane (dppp) (12 mg, 0.047 mmol), and toluene (0.5 mL). After the mixture was stirred at room temperature for 15 min, 2-alkynylphenyl isothiocyanate **4e** (105 mg, 0.43 mmol) in toluene (1.5 mL) was added. The mixture was degassed, charged with CO, and heated at reflux for 3 h. The reaction mixture was concentrated *in vacuo*, and residue was purified by column chromatography (*n*-hexane/CH_2Cl_2 = 1/2) to give **7e** (*E, Z* mixture, *E*/*Z* = 69/31) as a yellow solid (58 mg, 50%).

3-[(1,1-dimethylethyl)dimethylsilyl]-3,8-dihydro-1-thia-8-aza-cyclopenta[*a*]inden-2-one (6h).

To a solution of **5h** (347.7 mg, 1.02 mmol) in MeOH (15 mL) at 0 °C was added sodium borohydride (47.3 mg, 1.12 mmol). After being stirred for 10 min, the reaction was quenched by the addition of 1N HCl aq. (10 mL). The mixture was extracted with AcOEt, washed with brine, dried over $MgSO_4$, and evaporated. The residue was purified by column

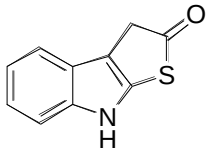
chromatography on silica gel (*n*-hexane/AcOEt = 9/1) to furnish **6h** as a colorless solid (245 mg, 79%).



Colorless solid; mp 147.8–150.1 °C; IR (KBr) 3278, 2931, 1758, 1673, 1442, 995, 740 cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$, δ) 0.14 (s, 3H), 0.21 (s, 3H), 0.96 (s, 9H), 3.97 (s, 1H), 7.09–7.16 (m, 2H), 7.11–7.39 (m, 2H), 8.22 (br, 1H); ^{13}C NMR (125.65 MHz, $CDCl_3$, δ) -5.4 (CH_3), -5.1 (CH_3), 18.5 (C), 26.8 (CH_3), 40.9 (CH), 109.6 (C), 111.2 (CH), 118.6 (CH), 120.3 (CH), 120.9 (CH), 124.3 (C), 128.3 (C), 138.2 (C), 205.8 (C); HRMS-ESI calcd for $C_{16}H_{21}NNaOSSi$: 326.1005 $[M + Na]^+$, found 326.1015.

3,8-Dihydro-2H-thieno[2,3-*b*]indol-2-one (8).

To a mixture of **6h** (92.0 mg, 0.30 mmol), AcOH (0.17 mL, 3.00 mmol), and THF (10 mL) at 0 °C was added 1M THF solution of TBAF (0.60 mL, 0.30 mmol). After being stirred for 10 min, the reaction was quenched by the addition of water. The mixture was extracted with AcOEt, washed with brine, dried over $MgSO_4$, and evaporated. The residue was purified by flash chromatography on silica gel (*n*-hexane/AcOEt = 9/1) to furnish **8** (56.7 mg, 99%) as a colorless solid.



Colorless solid; mp 147.8–150.1 °C; IR (KBr) 3270, 2908, 1704, 1450, 1025, 910, 748 cm^{-1}; ^1H NMR (500.0 MHz, $CDCl_3$, δ) 3.93 (s, 2H), 7.14–7.19 (m, 2H), 7.37–7.41 (m, 2H), 8.24 (br, 1H); ^{13}C NMR (125.65 MHz, $CDCl_3$, δ) 42.3 (CH_2), 105.6 (C), 117.8 (CH), 120.9 (CH), 121.4 (CH), 124.4 (C), 130.0 (C), 138.2 (C), 204.4 (C); HRMS-ESI calcd for $C_{10}H_7NNaOS$: 212.0141 $[M + Na]^+$, found 212.0136.