Supporting Information

Pd(0)-Catalyzed Iodoalkynylation of Norbornene Scaffolds: The Remarkable Solvent Effect on Reaction Pathway

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I. General information

Unless otherwise noted, all reagents were obtained commercially and used without further purification.

NMR spectrum: ^1H and ^{13}C spectra were recorded on Bruker AVANCE spectrometer, operating at 400 or 300 MHz for ^1H NMR, 100 MHz or 75 MHz for ^{13}C NMR. For ^1H NMR, chemical shifts were reported downfield from CDCl_3 (δ : 7.28 ppm). For ^{13}C NMR, chemical shifts were reported in the scale relative to the solvent of CDCl_3 (δ : 77.0 ppm) used as an internal reference.

Mass spectroscopy: Mass spectra were in general recorded on AMD 402/3 or HP 5989A or LCT Premier XE mass selective detector.

Chromatography: Column chromatography was performed with silica gel (200-300 mesh ASTM).

II. The Procedure for Substrate Synthesis and Iodoalkynylation

Procedure A: substrates **1** synthesis

To a solution of DMAP (5.5 mmol) and iodine (5.5 mmol) in dry CH₂Cl₂ (30 mL) was added **S-1** (5 mmol). The resulting mixture was refluxed for 6h. The contents were then cooled to room temperature, washed with sodium thiosulfate to remove unreacted iodine, and extracted with diethyl ether (3 x 30 mL). Subsequently, the extract was washed with brine (30 mL), dried over NaSO₄, and concentrated. The residue was purified by silica-gel chromatography to afford product **1**.

Procedure B: Pd(OAc)₂-catalyzed iodoalkynylation

In a 25 mL Schlenk tube, the mixture of **1** (0.3 mmol), Pd(OAc)₂ (0.03mmol, 6.8 mg) and norbornene (33.8 mg, 0.36 mmol) were dissolved in CCl₄ or MeCN (3 mL). Then, the mixture was heated to 50 °C for 12 hours. The reaction mixture was cooled to room temperature and directly subjected to silica gel column chromatography (petroleum ether) to give the product **4** or **3**.

III. The data for Compounds 3 and 4.

4a (73 mg, white solid)

^1H NMR (400 MHz, CDCl_3): δ 1.29-1.39 (m, 3H), 1.59-1.62 (m, 2H), 2.17 (d, $J = 10.4$ Hz, 2H), 2.54 (s, 1H), 2.77-2.79 (m, 2H), 4.26 (dd, $J = 8.0$ Hz, $J = 2.0$ Hz, 1H), 7.30-7.32 (m, 3H), 7.50-7.52 (m, 2H); ^{13}C -NMR (100 MHz, CDCl_3): 28.7, 29.0, 35.1, 37.7, 42.5, 45.6, 49.3, 84.8, 95.4, 123.8, 127.8, 128.2, 131.5; HRMS EI (m/z): calcd for $\text{C}_{15}\text{H}_{15}\text{I}$ 322.0219, found 322.0217.

4d (62 mg, white solid)

¹H NMR (400 MHz, CDCl₃): δ 1.29-1.38 (m, 3H), 1.57-1.62 (m, 2H), 2.16 (d, *J* = 10.4 Hz, 1H), 2.51 (s, 1H), 2.74-2.76 (m, 2H), 3.82 (s, 3H), 4.26 (dd, *J* = 8.0 Hz, *J* = 2.4 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H); ¹³C-NMR (100 MHz, CDCl₃): 28.6, 28.9, 35.0, 38.1, 42.4, 45.5, 49.2, 55.2, 84.4, 93.8, 113.7, 115.8, 132.6, 132.7, 159.1; HRMS ESI (*m/z*) [*M*+H]⁺: calcd for C₁₆H₁₈OI 353.0397, found 353.0401.

4e (116 mg, white solid)

¹H NMR (400 MHz, CDCl₃): δ 1.32-1.38 (m, 3H), 1.59-1.65 (m, 2H), 2.22 (dt, *J* = 10.4 Hz, *J* = 1.6 Hz, 1H), 2.77 (d, *J* = 3.6 Hz, 1H), 2.87 (d, *J* = 7.6 Hz, 1H), 4.25 (dd, *J* = 8.0 Hz, *J* = 2.4 Hz, 1H), 7.15 (dt, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 7.26 (dt, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 7.55-7.59 (m, 2H); ¹³C-NMR (100 MHz, CDCl₃): 22.2, 26.9, 31.0, 40.5, 43.9, 44.4, 51.0, 84.0, 94.1, 125.3, 126.0, 126.9, 128.8, 132.2, 133.3; HRMS ESI (*m/z*) [M+H]⁺: calcd for C₁₅H₁₅BrI 400.9396, found 400.9401.

4f (78mg, white solid)

¹H NMR (400 MHz, CDCl₃): δ 1.28-1.39 (m, 3H), 1.58-1.63 (m, 2H), 2.14 (d, *J* = 10.4 Hz, 1H), 2.52 (s, 1H), 2.75-2.76 (m, 2H), 4.25 (dd, *J* = 7.6 Hz, *J* = 2.0 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H); ¹³C-NMR (100 MHz, CDCl₃): 28.7, 29.0, 35.1, 37.4, 42.4, 45.5, 49.2, 83.8, 96.6, 121.9, 122.7, 131.4, 132.9; HRMS ESI

(m/z) [M+H]⁺: calcd for C₁₅H₁₅BrI 400.9396, found 400.9401.

4g (75 mg, white solid)

¹H NMR (400 MHz, CDCl₃): δ 1.28-1.39 (m, 3H), 1.58-1.62 (m, 2H), 2.14 (d, *J* = 10.4 Hz, 1H), 2.52 (s, 1H), 2.76-2.77 (m, 2H), 4.25 (d, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 2H); ¹³C-NMR (100 MHz, CDCl₃): 28.7, 29.0, 35.1,

37.4, 42.4, 45.6, 49.3, 83.7, 96.4, 122.3, 128.5, 132.7, 133.8; HRMS EI (m/z): calcd for C₁₅H₁₄ClI 355.9829, found 355.9831.

4h (53 mg, white solid)

¹H NMR (400 MHz, CDCl₃): δ 1.28-1.39 (m, 3H), 1.58-1.64 (m, 2H), 2.15 (d, *J* = 10.4 Hz, 1H), 2.52 (s, 1H), 2.75-2.77 (m, 2H), 4.26 (d, *J* = 6.4 Hz, 1H), 7.01 (t, *J* =

8.4 Hz, 2H), 7.47 (dd, $J = 8.4$ Hz, $J = 5.6$ Hz, 2H); ^{13}C -NMR (100 MHz, CDCl_3): 28.7, 29.0, 35.1, 37.6, 42.4, 45.6, 49.3, 83.7, 95.0, 115.4 (d, $J = 21.9$ Hz), 119.8 (d, $J = 3.6$ Hz), 133.3 (d, $J = 8.3$ Hz), 162.2 (d, $J = 247.0$ Hz); HRMS EI (m/z): calcd for $\text{C}_{15}\text{H}_{14}\text{FI}$ 340.0124, found 340.0122.

4i (65 mg, yellow oil)

^1H NMR (400 MHz, CDCl_3): δ 1.28-1.39 (m, 3H), 1.57-1.63 (m, 2H), 2.16 (dt, $J = 10.4$ Hz, $J = 1.6$ Hz, 1H), 2.53 (s, 1H), 2.76 (d, $J = 2.4$ Hz, 1H), 2.80 (d, $J = 7.6$ Hz, 1H), 4.24 (dd, $J = 7.6$ Hz, $J = 2.0$ Hz, 1H), 6.98 (dd, $J = 5.2$ Hz, $J = 3.6$ Hz, 1H),

7.20-7.23 (m, 2H); ^{13}C -NMR (100 MHz, CDCl_3): 28.7, 29.0, 35.2, 37.0, 42.7, 45.5, 49.2, 78.0, 99.0, 123.8, 126.3, 126.8, 131.1; HRMS ESI (m/z) $[\text{M}+\text{H}]^+$: calcd for $\text{C}_{13}\text{H}_{14}\text{SI}$ 328.9855, found 328.9861.

4c (63 mg, off white solid)

^1H NMR (400 MHz, CDCl_3): δ 1.30-1.39 (m, 3H), 1.59-1.63 (m, 2H), 2.17 (dt, $J = 10.4$ Hz, $J = 1.6$ Hz, 1H), 2.34 (s, 3H), 2.53 (s, 1H), 2.76-2.78 (m, 2H), 4.26 (dd, $J = 7.6$ Hz, $J = 2.0$ Hz, 1H), 7.11 (d, $J = 7.6$ Hz, 1H), 7.20 (t, $J = 7.6$ Hz, 1H), 7.29-7.35

(m, 2H); ^{13}C -NMR (100 MHz, CDCl_3): 21.2, 28.7, 29.0, 35.1, 37.7, 42.5, 45.6, 49.3, 84.9, 95.0, 123.5, 128.1, 128.6, 128.7, 132.0, 137.8; HRMS EI (m/z): calcd for $\text{C}_{16}\text{H}_{17}\text{I}$ 336.0375, found 336.0371.

4j (28 mg, yellow oil)

^1H NMR (400 MHz, CDCl_3): δ 0.93 (t, $J = 5.4$ Hz, 3H), 1.23-1.32 (m, 3H), 1.44-1.56 (m, 6H), 2.07 (dt, $J = 10.0$ Hz, $J = 2.0$ Hz, 1H), 2.24 (td, $J = 6.8$ Hz, $J = 3.0$ Hz, 2H), 2.37-2.38 (m, 1H), 2.52 (dd, $J = 7.6$ Hz, $J = 1.6$ Hz, 1H), 2.70 (d, $J = 2.0$ Hz, 1H), 4.17 (dd, $J = 7.6$ Hz, $J = 2.4$ Hz, 1H); ^{13}C -NMR (100 MHz, CDCl_3): 13.6, 18.6, 22.0,

28.6, 29.0, 31.0, 34.8, 38.5, 42.1, 45.7, 49.3, 84.9, 85.4; HRMS ESI (m/z) [M+H]⁺: calcd for C₁₃H₂₀I 303.0604, found 303.0609.

¹H NMR (400 MHz, CDCl₃): δ 1.31-1.36 (m, 3H), 1.55-1.59 (m, 2H), 2.11 (d, J = 10.8 Hz, 1H), 2.47 (s, 1H), 2.64-2.66 (m, 1H), 2.74 (s, 1H), 4.19 (dd, J = 8.0 Hz, 2.0

Hz, 1H), 4.27 (d, $J = 2.4$ Hz, 2H), 4.70 (s, 2H), 7.31-7.42 (m, 5H); ^{13}C -NMR (100 MHz, CDCl_3): 28.6, 29.0, 35.0, 36.7, 42.2, 45.6, 49.3, 57.6, 71.4, 80.4, 91.7, 127.7, 127.8, 128.2, 128.4; HRMS EI (m/z): calcd for $\text{C}_{17}\text{H}_{19}\text{IO}$ 366.0481, found 366.0478.

4i (56 mg, colorless oil)

^1H NMR (400 MHz, CDCl_3): δ 0.20 (s, 3H), 1.24-1.34 (m, 3H), 1.55-1.58 (m, 2H), 2.09 (d, $J = 10.4$ Hz, 1H), 2.45 (s, 1H), 2.56 (d, $J = 8.4$ Hz, 1H), 2.71 (s, 1H), 4.13 (dd,

$J = 7.6$ Hz, 2.0 Hz, $1H$); ^{13}C -NMR (100 MHz, $CDCl_3$): 0.04 , 28.7 , 29.0 , 35.0 , 36.3 , 42.8 , 45.7 , 49.2 , 88.8 , 111.0 ; HRMS EI (m/z): calcd for $C_{12}H_{19}ISi$ 318.0301 , found 318.0303 .

8 (104 mg, off white solid)

1H NMR (400 MHz, $CDCl_3$): δ 1.71 (d, $J = 11.1$ Hz, $1H$), 2.44 - 2.49 (m, $2H$), 2.94 - 2.96 (m, $2H$), 3.04 - 3.09 (m, $1H$), 3.13 - 3.19 (m, $2H$), 3.90 (dd, $J = 7.8$ Hz, $J =$

2.1 Hz, 1H), 4.63 (s, 2H), 7.27-7.34 (m, 6H), 7.41-7.43 (m, 4H); ^{13}C -NMR (100 MHz, CDCl_3): 28.5, 37.7, 39.0, 42.4, 47.4, 47.6, 48.3, 51.2, 85.4, 93.2, 122.9, 128.1, 128.4, 128.8, 128.9, 131.4, 135.6, 175.8, 176.1; HRMS ESI (m/z) $[\text{M}+\text{H}]^+$: calcd for $\text{C}_{24}\text{H}_{21}\text{NO}_2\text{I}$ 482.0611, found 482.0615.

3a (79 mg, yellow oil)

^1H NMR (400 MHz, CDCl_3): δ 1.21-1.29 (m, 1H), 1.36 (td, $J = 8.8$ Hz, $J = 2.8$ Hz, 1H), 1.56-1.73 (m, 2H), 2.21 (dd, $J = 14.0$ Hz, $J = 8.0$ Hz, 1H), 2.44 (t, $J = 4.0$ Hz,

1H), 2.69-2.76 (m, 2H), 2.82 (d, $J = 4.0$ Hz, 1H), 3.96 (ddd, $J = 8.0$ Hz, $J = 5.2$ Hz, $J = 0.8$ Hz, 1H), 7.30-7.34 (m, 3H), 7.53-7.56 (m, 2H); ^{13}C -NMR (100 MHz, CDCl_3): 22.2, 26.9, 30.9, 40.3, 43.9, 44.2, 50.7, 85.1, 89.2, 123.9, 127.6, 128.1, 131.3; HRMS EI (m/z): calcd for $\text{C}_{15}\text{H}_{15}\text{I}$ 322.0219, found, 322.0217.

3b (76 mg, yellow oil)

^1H NMR (400 MHz, CDCl_3): δ 1.21-1.27 (m, 1H), 1.32-1.38 (td, $J = 8.8$ Hz, $J = 2.8$ Hz, 1H), 1.56-1.72 (m, 2H), 2.20 (dd, $J = 13.6$ Hz, $J = 8.8$ Hz, 1H), 2.36 (s, 3H), 2.42 (t, $J = 4.0$ Hz, 1H), 2.69-2.72 (m, 1H), 2.72-2.75 (m, 1H), 2.80 (d, $J = 4.0$ Hz, 1H), 3.96 (ddd, $J = 8.0$ Hz, $J = 4.8$ Hz, $J = 0.8$ Hz, 1H), 7.12 (d, $J = 7.6$ Hz, 2H), 7.43 (d, $J = 8.4$ Hz, 2H); ^{13}C -NMR (100 MHz, CDCl_3): 21.5, 22.3, 26.9, 30.9, 40.4, 44.0, 44.3, 50.8, 85.2, 88.4, 120.9, 128.9, 131.2, 137.6; HRMS EI (m/z): calcd for $\text{C}_{16}\text{H}_{17}\text{I}$ 336.0375, found 336.0371.

3d (65 mg, yellow oil)

^1H NMR (400 MHz, CDCl_3): δ 1.20-1.26 (m, 1H), 1.32-1.38 (m, 1H), 1.56-1.71 (m, 2H), 2.19 (dd, $J = 13.6$ Hz, $J = 8.0$ Hz, 1H), 2.41 (t, $J = 4.0$ Hz, 1H), 2.68-2.73 (m, 2H), 2.79 (d, $J = 4.0$ Hz, 1H), 3.82 (s, 3H), 3.95 (dd, $J = 7.6$ Hz, $J = 5.6$ Hz, 1H), 6.84 (d, $J = 8.8$ Hz, 2H), 7.47 (d, $J = 8.8$ Hz, 2H); ^{13}C -NMR (100 MHz, CDCl_3): 22.4, 26.9, 30.9, 40.4, 44.0, 44.2, 50.8, 55.3, 84.9, 87.6, 113.8, 113.9, 116.2, 132.7, 132.9, 159.2; HRMS ESI (m/z) [$\text{M}+\text{H}$] $^+$: calcd for $\text{C}_{16}\text{H}_{18}\text{OI}$ 353.0397, found 353.0401.

3e (114 mg, yellow oil)

^1H NMR (400 MHz, CDCl_3): δ 1.22-1.28 (m, 1H), 1.34-1.40 (m, 1H), 1.57-1.73 (m, 2H), 2.21 (dd, $J = 13.6$ Hz, $J = 8.0$ Hz, 1H), 2.49 (s, 1H), 2.75-2.79 (m, 1H), 2.82 (s, 1H), 2.84 (d, $J = 3.6$ Hz, 1H), 3.96 (dd, $J = 7.2$ Hz, $J = 6.0$ Hz, 1H), 7.14 (t, $J = 7.6$ Hz, 1H), 7.26 (t, $J = 7.6$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.63 (d, $J = 7.6$ Hz, 1H); ^{13}C -NMR (100 MHz, CDCl_3): 22.2, 26.9, 31.0, 40.5, 43.9, 44.4, 51.0, 84.0, 94.1, 125.3, 126.0, 126.9, 128.8, 132.2, 133.3; HRMS ESI (m/z) $[\text{M}+\text{H}]^+$: calcd for $\text{C}_{15}\text{H}_{15}\text{BrI}$ 400.9396, found 400.9401.

3f (77 mg, yellow oil)

^1H NMR (400 MHz, CDCl_3): δ 1.21-1.28 (m, 1H), 1.33-1.39 (m, 1H), 1.59-1.73 (m, 2H), 2.20 (dd, $J = 13.6$ Hz, $J = 8.0$ Hz, 1H), 2.43 (t, $J = 4.0$ Hz, 1H), 2.65-2.70 (m, 1H), 2.72 (s, 1H), 2.80 (d, $J = 4.0$ Hz, 1H), 3.96 (ddd, $J = 8.0$ Hz, $J = 5.6$ Hz, $J = 0.8$ Hz, 1H), 7.38 (d, $J = 8.8$ Hz, 2H), 7.40 (d, $J = 8.8$ Hz, 2H); ^{13}C -NMR (75 MHz, CDCl_3): 22.2, 26.8, 30.8, 40.2, 43.9, 44.1, 50.7, 84.1, 90.5, 121.7, 122.8, 131.3, 132.7; HRMS ESI (m/z) [$\text{M}+\text{H}$] $^+$: calcd for $\text{C}_{15}\text{H}_{15}\text{BrI}$ 400.9396, found 400.9401.

3g (92 mg, yellow oil)

^1H NMR (400 MHz, CDCl_3): δ 1.21-1.27 (m, 1H), 1.32-1.38 (m, 1H), 1.55-1.71 (m, 2H), 2.20 (dd, $J = 14.0$ Hz, $J = 8.4$ Hz, 1H), 2.42 (s, 1H), 2.66-2.70 (m, 1H), 2.73 (s, 1H), 2.80 (d, $J = 3.6$ Hz, 1H), 3.95 (dd, $J = 7.6$ Hz, $J = 5.6$ Hz, 1H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 2H); ^{13}C -NMR (100 MHz, CDCl_3): 22.3, 26.9, 30.9, 40.3, 44.0, 44.2, 50.8, 84.1, 90.4, 122.5, 128.5, 132.6, 133.6; HRMS EI (m/z): calcd for $\text{C}_{15}\text{H}_{14}\text{ClI}$ 355.9829, found 355.9831.

3h (59 mg, yellow oil)

^1H NMR (400 MHz, CDCl_3): δ 1.21-1.27 (m, 1H), 1.32-1.39 (m, 1H), 1.55-1.72 (m, 2H), 2.20 (dd, $J = 13.6$ Hz, $J = 8.0$ Hz, 1H), 2.42 (s, 1H), 2.66-2.71 (m, 1H), 2.73 (s, 1H), 2.80 (d, $J = 4.0$ Hz, 1H), 3.96 (dd, $J = 7.6$ Hz, $J = 5.6$ Hz, 1H), 7.00 (t, $J = 8.8$ Hz, 2H), 7.51 (dd, $J = 8.4$ Hz, $J = 5.6$ Hz, 2H); ^{13}C -NMR (100 MHz, CDCl_3): 22.3, 26.8, 30.8, 40.2, 43.9, 44.1, 50.7, 84.0, 88.8 (d, $J = 1.4$ Hz), 115.3 (d, $J = 29.1$ Hz), 119.9 (d, $J = 4.8$ Hz), 133.0 (d, $J = 10.9$ Hz), 162.1 (d, $J = 329.1$ Hz); HRMS EI (m/z): calcd for $\text{C}_{15}\text{H}_{14}\text{FI}$ 340.0124, found 340.0122.

3i (72 mg, yellow oil)

^1H NMR (400 MHz, CDCl_3): δ 1.22-1.28 (m, 1H), 1.33-1.39 (m, 1H), 1.58-1.73 (m, 2H), 2.20 (dd, $J = 13.6$ Hz, $J = 8.0$ Hz, 1H), 2.44 (t, $J = 4.0$ Hz, 1H), 2.65-2.72 (m, 1H), 2.75 (s, 1H), 2.82 (d, $J = 4.0$ Hz, 1H), 3.95 (ddd, $J = 8.0$ Hz, $J = 5.2$ Hz, $J = 0.8$ Hz, 1H), 6.97 (dd, $J = 5.2$ Hz, $J = 3.6$ Hz, 1H), 7.20-7.24 (m, 2H); ^{13}C -NMR (100 MHz, CDCl_3): 22.1, 27.0, 30.9, 40.5, 44.0, 44.2, 50.9, 79.0, 93.3, 124.1, 126.2, 126.7, 130.8; HRMS ESI (m/z) [$\text{M}+\text{H}$] $^+$: calcd for $\text{C}_{13}\text{H}_{15}\text{SI}$ 328.9855, found 328.9861.

3c (58 mg, yellow oil)

^1H NMR (400 MHz, CDCl_3): δ 1.21-1.28 (m, 1H), 1.33-1.39 (m, 1H), 1.59-1.72 (m, 2H), 2.20 (dd, $J = 13.6$ Hz, $J = 8.0$ Hz, 1H), 2.34 (s, 3H), 2.43 (t, $J = 4.0$ Hz, 1H), 2.69-2.73 (m, 1H), 2.75 (s, 1H), 2.80 (d, $J = 4.0$ Hz, 1H), 3.96 (ddd, $J = 8.0$ Hz, $J = 5.6$ Hz, $J = 1.2$ Hz, 1H), 7.11 (d, $J = 7.6$ Hz, 1H), 7.20 (t, $J = 7.6$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 1H), 7.35 (s, 1H); ^{13}C -NMR (100 MHz, CDCl_3): 21.2, 22.2, 26.9, 30.9, 40.4, 44.0, 44.3, 50.8, 85.3, 88.8, 123.8, 128.0, 128.4, 128.6, 131.9, 137.8; HRMS EI (m/z): calcd for $\text{C}_{16}\text{H}_{17}\text{I}$ 336.0375, found 336.0371.

^1H NMR (400 MHz, CDCl_3): δ 0.93 (t, $J = 7.2$ Hz, 3H), 1.14-1.20 (m, 1H), 1.25-1.31 (m, 1H), 1.45-1.57 (m, 6H), 2.12 (dd, $J = 14.0$ Hz, $J = 8.4$ Hz, 1H), 2.23 (td, $J = 6.8$ Hz, $J = 2.4$ Hz, 2H), 2.26-2.28 (m, 1H), 2.50 (s, 1H), 2.58-2.63 (m, 1H), 2.65 (d, $J = 4.4$ Hz, 1H), 3.89 (ddd, $J = 8.0$ Hz, $J = 5.2$ Hz, $J = 0.8$ Hz, 1H); ^{13}C -NMR (100 MHz, CDCl_3): 13.6, 18.8, 22.1, 22.5, 26.7, 30.6, 30.8, 39.9, 43.8, 44.1, 50.5, 78.9, 85.6; HRMS ESI (m/z) [$\text{M}+\text{H}$] $^+$: calcd for $\text{C}_{13}\text{H}_{20}\text{I}$ 303.0604, found 303.0609.

3l (62 mg, colorless oil)

^1H NMR (400 MHz, CDCl_3): δ 0.20 (s, 9H), 1.18 (dt, $J = 11.6$ Hz, 4.4 Hz, 1H), 1.30-1.33 (m, 1H), 1.48-1.64 (m, 2H), 2.14 (dd, $J = 14.0$ Hz, 8.4 Hz, 1H), 2.35 (t, $J = 4.0$ Hz, 1H), 2.54 (s, 1H), 2.60-2.67 (m, 1H), 2.73 (d, $J = 4.0$ Hz, 1H), 3.87 (dd, $J = 7.2$ Hz, 5.6 Hz, 1H); ^{13}C -NMR (100 MHz, CDCl_3): -0.09, 22.0, 26.8, 31.0, 40.6, 43.8, 44.3, 50.6, 90.1, 105.9; HRMS EI (m/z): calcd for $\text{C}_{12}\text{H}_{19}\text{ISi}$ 318.0301, found 318.0303.

6 (66 mg, yellow oil)

^1H NMR (300 MHz, CDCl_3): δ 1.20-1.33 (m, 2H), 1.63-1.74 (m, 2H), 2.21 (dd, $J = 13.8$ Hz, $J = 8.1$ Hz, 1H), 2.50 (t, $J = 3.9$ Hz, 1H), 2.62-2.64 (m, 1H), 2.67 (s, 1H), 2.75 (d, $J = 3.9$ Hz, 1H), 3.98 (ddd, $J = 7.8$ Hz, $J = 4.8$ Hz, $J = 0.6$ Hz, 1H), 7.26-7.28 (m, 3H), 7.44-7.48 (m, 2H); ^{13}C -NMR (75 MHz, CDCl_3): 26.9, 29.5, 40.0, 42.8, 44.0, 49.8, 50.6, 84.5, 89.2, 124.0, 127.6, 128.1, 131.3; HRMS EI (m/z): calcd for $\text{C}_{15}\text{H}_{15}\text{Br}$, 274.0357, found, 274.0351.

IV. X-ray Crystallography of Compound 4a

Crystal data and structure refinement

Identification code	mo_dm11200_0m	
Empirical formula	C ₁₅ H ₁₅ I	
Formula weight	322.17	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, P2(1)/c	
Unit cell dimensions	a = 8.0942(10) Å	alpha = 90 deg.
	b = 34.437(4) Å	beta = 90.491(2) deg.
	c = 9.1647(11) Å	gamma = 90 deg.
Volume	2554.5(5) Å ³	
Z, Calculated density	8, 1.675 Mg/m ³	
Absorption coefficient	2.478 mm ⁻¹	
F(000)	1264	

Crystal size	0.35 x 0.28 x 0.02 mm
Theta range for data collection	2.30 to 25.02 deg.
Limiting indices	-9<=h<=9, -40<=k<=32, -10<=l<=10
Reflections collected / unique	15388 / 4407 [R(int) = 0.0821]
Completeness to theta = 25.02	97.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9521 and 0.4776
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4407 / 36 / 289
Goodness-of-fit on F ²	1.241
Final R indices [I>2sigma(I)]	R1 = 0.0958, wR2 = 0.2388
R indices (all data)	R1 = 0.1035, wR2 = 0.2431
Largest diff. peak and hole	3.412 and -1.927 e.A ⁻³