Supporting Information

Strain-Induced Regioselectivities in Reactions of Benzyne Possessing Fused Four-membered Ring

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General Experimental Procedures

Ethereal solvents (anhydrous; *Kanto Chemical Co., Inc.*) were used as received. For thin-layer chromatography (TLC) analysis, Merck pre-coated plates (silica gel 60 F254, Art 5715, 0.25 mm) were used. For flash column chromatography, silica gel 60 (Merck Art 7734, 70–230 mesh) was used. Silica gel preparative TLC (PTLC) was performed on Merck silica gel 60 PF254 (Art 7747).

Melting point (mp) determinations were performed by using a Yanako MP-S3 instrument and are uncorrected. ¹H NMR and ¹³C NMR were measured on a JEOL JNM lambda-300, a JNM lambda-400, and a Bruker DRX-500 spectrometer. Infrared (IR) spectra were recorded on a Perkin Elmer 1600 FT/IR 200 spectrometer. High resolution mass spectra under electron impact conditions (HRMS) were obtained with a JEOL JMS 700 spectrometer.

Synthesis of hydroxy ketone 4:

To a mixture of triflate **1** (57.9 g, 118 mmol) and ketene silyl acetal **2a** (31.5 g, 156 mmol) in THF (490 mL) was added *n*-BuLi (1.59 M in hexane, 89 mL, 142 mmol) at $-78\text{ }^{\circ}\text{C}$. After 5 min, the reaction was stopped by adding sat. aq. NaHCO_3 . Extractive workup (Et_2O) followed by evaporation gave crude cycloadduct **3**. To a solution of cycloadduct **3** in MeCN (240 mL) was added 46% aq. HF (15 mL) at $0\text{ }^{\circ}\text{C}$. After warmed up to $40\text{ }^{\circ}\text{C}$, the reaction was further stirred for 13 h. After dilution with water, the products were extracted with Et_2O and the combined organic extracts were washed brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (hexane / EtOAc = 85 / 15) to afford **4** (12.8 g, 81.1%). Recrystallization from hexane–EtOAc gave **4** as colorless prisms. Mp $145.8\text{--}146.2\text{ }^{\circ}\text{C}$.

hydroxy ketone **4**

^1H NMR (acetone- d_6 , δ)

3.79 (s, 2H), 6.79 (d, 1H, $J = 8.3\text{ Hz}$), 7.02 (d, 1H, $J = 7.1\text{ Hz}$), 7.43 (dd, 1H, $J_1 = 7.1\text{ Hz}$, $J_2 = 8.3\text{ Hz}$), 9.74 (s, 1H);

^{13}C NMR (acetone- d_6 , δ)

51.8, 115.3, 116.3, 134.2, 138.4, 150.3, 152.2, 185.5;

IR (KBr)

3174, 1732, 1618, 1591, 1483, 1456, 1406, 1356, 1327, 1294, 1221, 1160, 1146, 1091, 1053, 1031, 972, 962, 875 cm^{-1} ;

Anal. Calcd for $\text{C}_8\text{H}_6\text{O}_2$: C, 71.64; H, 4.51. Found: C, 71.54; H, 4.67.

iodo-triflate

^1H NMR (CDCl_3 , δ)

4.07 (s, 2H), 7.32 (d, 1H, $J = 7.8\text{ Hz}$), 8.08 (d, 1H, $J = 7.8\text{ Hz}$);

^{13}C NMR (CDCl_3 , δ)

53.1, 89.3, 118.5 (q, $J_{\text{C-F}} = 321.3\text{ Hz}$), 125.0, 138.4, 140.1, 147.3, 151.9, 180.0;

IR (KBr)

1798, 1587, 1440, 1423, 1298, 1246, 1227, 1213, 1186, 1135, 1098, 1010, 954, 828 cm^{-1} ;

Anal. Calcd for $\text{C}_9\text{H}_4\text{O}_4\text{F}_3\text{IS}$: C, 27.57; H, 1.03; S, 8.18. Found: C, 27.76; H, 1.25; S, 8.48.

iodo-triflate **5**

^1H NMR (CDCl_3 , δ)

3.54 (s, 2H), 4.06–4.31 (m, 4H), 6.97 (d, 1H, $J = 7.8$ Hz), 7.89 (d, 1H, $J = 7.8$ Hz);

^{13}C NMR (CDCl_3 , δ)

48.2, 65.9, 86.8, 108.9, 118.4 (q, $J_{\text{C-F}} = 320.7$ Hz), 125.4, 139.3, 140.0, 143.6, 145.3;

IR (KBr)

3007, 2972, 2927, 2888, 1425, 1303, 1264, 1231, 1210, 1183, 1152, 1129, 1080, 1045, 1003, 949, 860, 824, 810 cm^{-1} ;

Anal. Calcd for $\text{C}_{11}\text{H}_8\text{O}_5\text{F}_3\text{I}$: C, 30.29; H, 1.85; S, 7.35. Found: C, 30.48; H, 1.83; S, 7.55.

[2+2] cycloaddition of cyclobutabenzyne **B** and KSA **2a**:

To a mixture of triflate **5** (131 mg, 0.301 mmol) and ketene silyl acetal **2a** (125 mg, 0.618 mmol) in THF (3.0 mL) was added *n*-BuLi (1.52 M in hexane, 0.30 mL, 0.46 mmol) at -78°C . After 5 min, the reaction was stopped by adding water. The products were extracted with EtOAc (X3) and the combined organic extracts were washed brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane / EtOAc = 8 / 2) to afford **6a** (77.7 mg, 71.2%) and **7a**. As the latter compound was still impure, repurification by PTLC (hexane / CH_2Cl_2 / Et_2O = 7 / 2 / 1) gave pure **7a** (2.5 mg, 2.3%).

cycloadduct **6a** (colorless oil)

^1H NMR (acetone- d_6 , δ)

0.12 (s, 3H), 0.13 (s, 3H), 0.90 (s, 9H), 1.15 (t, 3H, $J = 7.1$ Hz), 3.37 (d, 1H, $J = 13.4$ Hz), 3.41 (d, 1H, $J = 13.4$ Hz), 3.48 (s, 2H), 3.68 (qd, $J_1 = 7.1$, $J_2 = 8.9$ Hz), 3.88 (qd, $J_1 = 7.1$, $J_2 = 8.9$ Hz), 3.97–4.19 (m, 4H), 7.16 (d, 1H, $J = 7.5$ Hz), 7.18 (d, 1H, $J = 7.5$ Hz);

^{13}C NMR (acetone- d_6 , δ)

−3.6, −3.3, 15.5, 18.4, 26.0, 47.4, 49.3, 60.7, 65.6, 65.9, 103.4, 110.1, 124.8, 125.9, 140.6, 141.3, 141.4, 141.7;

IR (neat)

3061, 2930, 1609, 1472, 1435, 1390, 1347, 1242, 1133, 1058, 1014, 965, 900, 834, 782 cm^{-1} ;

Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{O}_4\text{Si}$: C, 66.25; H, 8.34. Found: C, 66.28; H, 8.60.

cycloadduct **7a** (colorless oil)

^1H NMR (acetone- d_6 , δ)

0.06 (s, 3H), 0.14 (s, 3H), 0.89 (s, 9H), 1.14 (t, 3H, $J = 7.0$ Hz), 3.33 (d, 1H, $J = 14.0$ Hz), 3.46 (d, 1H, $J = 14.0$ Hz), 3.47 (s, 2H), 3.66 (qd, 1H, $J_1 = 7.0$, $J_2 = 8.9$ Hz), 3.79 (qd, 1H, $J_1 = 7.0$, $J_2 = 8.9$ Hz), 4.06 (s, 4H), 7.11 (d, 1H, $J = 7.5$ Hz), 7.22 (d, 1H, $J = 7.5$ Hz);

^{13}C NMR (acetone- d_6 , δ)

−3.39, −3.37, 15.6, 18.5, 26.0, 47.1, 48.0, 60.5, 65.40, 65.44, 103.7, 109.9, 122.5, 123.6, 134.8, 143.0, 144.5, 149.5;

IR (neat)

3062, 2932, 1602, 1472, 1412, 1390, 1351, 1252, 1207, 1144, 1038, 982, 938, 905, 834, 780, 730 cm^{-1} ;

Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{O}_4\text{Si}$: C, 66.25; H, 8.34. Found: C, 66.33; H, 8.41.

*[2+2] cycloaddition of cyclobutabenzyne **B** and KSA **2b**:*

To a mixture of triflate **5** (77.7 mg, 0.177 mmol) and ketene silyl acetal **2b** (77.0 mg, 0.353 mmol) in THF (1.5 mL) was added *n*-BuLi (1.74 M in hexane, 0.15 mL, 0.26 mmol) at −78 °C. After 5 min, the reaction was stopped by adding water. The products were extracted with EtOAc (X3) and the combined organic extracts were washed brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane / CH_2Cl_2 / $\text{Et}_2\text{O} = 6 / 3 / 1$) to afford **6b-cis** (47.6 mg, 71.0%) and a mixture of **6b-trans**, and **7b**. These mixtures were again purified by PTLC (benzene / $\text{Et}_2\text{O} = 9 / 1$) to give **6b-trans** (1.7 mg, 2.5%) and **7b** (0.9 mg, 1.3%), respectively.

cycloadduct **6b-cis** (colorless oil)

^1H NMR (acetone- d_6 , δ)

−0.03 (s, 3H), 0.05 (s, 3H), 0.93 (s, 9H), 3.41 (d, 1H, $J = 13.8$ Hz), 3.45 (s, 3H), 3.46 (d, 1H, $J = 13.8$ Hz), 3.50 (s, 3H), 4.04–4.15 (m, 4H), 4.69 (s, 1H), 7.25 (d, 1H, $J = 7.6$ Hz), 7.39 (d, 1H, $J = 7.6$ Hz);

^{13}C NMR (acetone- d_6 , δ)

−4.0, −3.7, 18.6, 25.9, 48.1, 51.7, 57.3, 65.27, 65.32, 88.2, 106.1, 109.7, 125.1, 126.5, 140.1, 140.4, 143.7, 144.5;

IR (neat)

3061, 2928, 2828, 1602, 1472, 1418, 1389, 1362, 1334, 1244, 1204, 1141, 1087, 1012, 962, 898, 837, 782 cm^{-1} ;

Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{O}_5\text{Si}$: C, 63.46; H, 7.99. Found: C, 63.70; H, 8.05.

Key 2- and 3-bond HMBC correlations

position	δH (ppm)	carbon no. (ppm)
4	7.39	C-8 (88.2), C-6 (140.4), C-2 (144.5)
8	4.69	C-11 (57.3), C-7 (106.1), C-6 (140.4), C-5 (143.7)
3	7.25	C-1 (140.1), C-5 (143.7)

cycloadduct **6b-trans** (colorless oil)

^1H NMR (acetone- d_6 , δ)

0.13 (s, 3H), 0.15 (s, 3H), 0.91 (s, 9H), 3.47 (s, 3H), 3.48 (s, 3H), 3.49 (s, 2H), 4.00–4.18 (m, 4H), 4.84 (s, 1H), 7.26 (d, 1H, $J = 7.5$ Hz), 7.38 (d, 1H, $J = 7.5$ Hz);

^{13}C NMR (acetone- d_6 , δ)

−3.7, −3.3, 18.5, 26.1, 48.1, 52.7, 57.1, 65.7, 66.0, 90.0, 106.5, 110.1, 125.5, 126.7, 139.9, 141.4, 143.7, 144.7;

IR (neat)

2958, 2928, 2855, 1260, 1080, 1019, 840, 800 cm^{-1} ;

HRMS m/z 378.1852 (378.1863 calcd for $C_{20}H_{30}O_5Si$, M^+).

Key 2- and 3-bond HMBC correlations

position	δH (ppm)	carbon no. (ppm)
4	7.38	C-8 (90.0), C-6 (139.9), C-2 (144.7)
8	4.84	C-11 (57.1), C-7 (106.5), C-6 (139.9), C-5 (143.7)
3	7.26	C-1 (141.4), C-5 (143.7)
11	3.47	C-8 (90.0)

cycloadduct **7b** (colorless oil)

1H NMR (acetone- d_6 , δ)

−0.09 (s, 3H), 0.04 (s, 3H), 0.92 (s, 9H), 3.44 (s, 3H), 3.49 (d, 1H, $J = 14.5$ Hz), 3.51 (s, 3H), 3.52 (d, 1H, $J = 14.5$ Hz), 4.06–4.14 (m, 4H), 4.79 (s, 1H), 7.25 (d, 1H, $J = 7.7$ Hz), 7.35 (d, 1H, $J = 7.7$ Hz);

^{13}C NMR (acetone- d_6 , δ)

−3.20, −3.18, 19.0, 26.3, 47.4, 51.9, 57.3, 65.5, 65.6, 87.6, 106.2, 109.8, 124.84, 124.87, 136.9, 143.7, 145.2, 147.8;

IR (neat)

2956, 2928, 2855, 1460, 1420, 1358, 1258, 1208, 1152, 1115, 1073, 1043, 1006, 960, 912, 838, 815, 779 cm^{-1} ;

Anal. Calcd for $C_{20}H_{30}O_5Si$: C, 63.46; H, 7.99. Found: C, 63.74; H, 8.24.

Key 2- and 3-bond HMBC correlations

position	δ H (ppm)	carbon no. (ppm)
4	7.35	C-8 (106.2), C-6 (136.9), C-2 (145.2)
7	4.79	C-12 (57.3), C-8 (106.2), C-6 (136.9), C-5 (147.8)
3	7.25	C-1 (143.7), C-5 (147.8)
10	3.49, 3.52	C-9 (109.8), C-1 (143.7), C-2 (145.2)
11	3.44	C-8 (106.2)

*[2+2] cycloaddition of cyclobutabenzyne **B** and KSA **2c**:*

To a mixture of triflate **5** (403 mg, 0.924 mmol) and ketene silyl acetal **2c** (460 mg, 1.85 mmol) in THF (6.0 mL) was added *n*-BuLi (1.56 M in hexane, 1.3 mL, 2.0 mmol) at -78°C . After 5 min, the reaction was stopped by adding water. The products were extracted with EtOAc (X3) and the combined organic extracts were washed brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (hexane / EtOAc = 9 / 1) to afford **6c** (213 mg, 57%) and **7c**. As the latter compound was still impure, repurification by PTLC (hexane / EtOAc = 8 / 2) gave pure **7c** (1.8 mg, 0.5%).

cycloadduct **6c** (colorless oil)

^1H NMR (acetone- d_6 , δ)

0.00 (s, 3H), 0.06 (s, 3H), 0.92 (s, 9H), 3.38 (s, 3H), 3.41 (s, 3H), 3.44 (s, 2H), 3.45 (s, 3H), 4.05–4.16 (m, 4H), 7.27 (d, 1H, $J = 7.6$ Hz), 7.45 (d, 1H, $J = 7.6$ Hz);

^{13}C NMR (acetone- d_6 , δ)

−3.7, −3.3, 19.1, 26.4, 48.8, 51.1, 51.7, 52.4, 65.7, 65.9, 108.4, 110.1, 110.2, 125.1, 125.6, 140.8, 141.1, 144.8, 145.5;

IR (neat)

2956, 2930, 2856, 1602, 1472, 1418, 1358, 1257, 1200, 1145, 1113, 1084, 1030, 1010, 972, 948, 837, 817, 782 cm^{-1} ;

Anal. Calcd for $\text{C}_{21}\text{H}_{32}\text{O}_6\text{Si}$: C, 61.73; H, 7.89. Found: C, 61.80; H, 8.05.

Key 2- and 3-bond HMBC correlations

position	δH (ppm)	carbon no. (ppm)
4	7.45	C-8 (110.1), C-6 (141.1), C-2 (145.5)
11	3.38	C-8 (110.1)
12	3.41	C-8 (110.1)
13	3.45	C-7 (108.4)
3	7.27	C-10 (48.8), C-1 (140.8), C-5 (144.8)

cycloadduct **7c** (colorless oil)

^1H NMR (acetone- d_6 , δ)

−0.04 (s, 3H), 0.01 (s, 3H), 0.91 (s, 9H), 3.40 (s, 3H), 3.45 (s, 3H), 3.46 (s, 3H), 3.51 (s, 2H), 4.07–4.12 (m, 4H), 7.29 (d, 1H, $J = 7.6$ Hz), 7.43 (d, 1H, $J = 7.6$ Hz);

^{13}C NMR (acetone- d_6 , δ)

−3.9, −3.8, 18.5, 25.8, 47.8, 51.0, 51.6, 51.7, 65.46, 65.49, 107.7, 109.7, 110.7, 124.7, 124.9, 137.1, 141.8, 144.7, 147.2;

IR (neat)

2928, 2855, 1560, 1522, 1458, 1349, 1257, 1157, 1140, 1085, 1040, 946, 919, 837, 779 cm^{-1} ;
HRMS m/z 408.1952 (408.1968 calcd for $\text{C}_{21}\text{H}_{32}\text{O}_6\text{Si}$, M^+).

Key 2- and 3-bond HMBC correlations

position	δH (ppm)	carbon no. (ppm)
4	7.43	C-8 (107.7), C-6 (137.1), C-2 (144.7)
11	3.45	C-8 (107.7)
12	3.40	C-7 (110.7)
13	3.46	C-7 (110.7)
3	7.29	C-1 (141.8), C-5 (147.2)
10	3.51	C-9 (109.7), C-3 (124.7), C-1 (141.8), C-2 (144.7)

Synthesis of ketone **8**:

To a solution of cycloadduct **6a** (76.0 mg, 0.086 mmol) in MeCN (1.5 mL) was added sat. aq. KF (0.5 mL) and *n*-Bu₄NCl (70.0 mg, 0.25 mmol) at room temperature. After 7 h, the reaction was stopped by adding sat. aq. NaHCO₃. The products were extracted with Et₂O (X3), dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by silica-gel flash column (hexane / EtOAc = 7 / 3) to give ketone **8** (38.6 mg, 91.9%). Recrystallization from hexane–EtOAc gave **8** as colorless prisms. Mp 64.0–64.2 °C.

ketone **8**

¹H NMR (acetone-*d*₆, δ)

3.58 (s, 2H), 3.94 (s, 2H), 4.12 (s, 4H), 7.42 (d, 1H, J = 7.8 Hz), 7.58 (d, 1H, J = 7.8 Hz);

^{13}C NMR (acetone- d_6 , δ)

46.8, 53.0, 65.5, 109.3, 125.9, 129.8, 140.8, 141.5, 143.9, 152.0, 187.1;

IR (KBr)

2934, 2888, 1769, 1588, 1438, 1271, 1043, 1016, 1003, 956, 943, 809 cm^{-1} ;

Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{O}_3$: C, 71.28; H, 4.98. Found: C, 71.08; H, 5.24.

*Nucleophilic addition of piperidine to cyclobutabenzene **B**:*

To a mixture of triflate **5** (139 mg, 0.320 mmol) and piperidine (81 mg, 0.951 mmol) in THF (5.0 mL) was added *n*-BuLi (1.59 M in hexane, 0.75 mL, 1.2 mmol) at -78°C . After 5 min, the reaction was stopped by adding sat. aq. NaHCO_3 . The products were extracted with EtOAc (X3) and the combined organic extracts were washed brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane / Et_2O = 5 / 5) to afford **9a** (51.5 mg, 65.7%) and **10a**. As the latter compound was still impure, repurification by PTLC (hexane / CH_2Cl_2 / Et_2O = 7 / 2 / 1) gave pure **10a** (4.5 mg, 5.7%).

adduct **9a** (colorless oil)

^1H NMR (CDCl_3 , δ)

1.52–1.58 (m, 2H), 1.66–1.73 (m, 4H), 3.05–3.09 (m, 4H), 3.44 (s, 2H), 4.06–4.18 (m, 4H), 6.80 (d, 1H, J = 2.2 Hz), 6.97 (dd, 1H, J_1 = 2.2, J_2 = 8.1 Hz), 7.07 (d, 1H, J = 8.1 Hz);

^{13}C NMR (CDCl_3 , δ)

24.2, 25.9, 45.9, 51.9, 64.8, 109.0, 109.3, 121.3, 123.9, 132.6, 146.3, 153.1;

IR (neat)

2932, 2890, 2853, 2805, 1480, 1451, 1442, 1383, 1336, 1310, 1268, 1226, 1149, 1130, 1119, 1068, 1036, 1024, 1014, 981, 947, 926, 815 cm^{-1} ;

HRMS m/z 245.1426 (245.1416 calcd for $\text{C}_{15}\text{H}_{19}\text{O}_2\text{N}$, M^+).

adduct **10a** (colorless oil)

^1H NMR (CDCl_3 , δ)

1.59–1.67 (m, 6H), 3.27 (s, 2H), 3.27–3.31 (m, 4H), 4.03–4.15 (m, 4H), 6.53 (d, 1H, $J = 6.8$ Hz), 6.60 (d, 1H, $J = 8.5$ Hz), 7.21 (dd, 1H, $J_1 = 6.8$, $J_2 = 8.5$ Hz);

^{13}C NMR (CDCl_3 , δ)

24.5, 25.5, 46.7, 48.9, 64.5, 109.7, 111.7, 111.9, 127.1, 132.4, 143.7, 146.8;

IR (neat)

2924, 2852, 1740, 1603, 1571, 1486, 1466, 1451, 1416, 1392, 1341, 1257, 1230, 1086, 1032, 1015, 947 cm^{-1} ;

HRMS m/z 245.1437 (245.1416 calcd for $\text{C}_{15}\text{H}_{19}\text{O}_2\text{N}$, M^+).

Nucleophilic addition of 2,2,6,6-tetramethylpiperidine to cyclobutabenzyne B:

To a mixture of triflate **5** (552 mg, 1.27 mmol) and 2,2,6,6-tetramethylpiperidine (451 mg, 3.19 mmol) in THF (6.0 mL) was added *n*-BuLi (1.59 M in hexane, 1.2 mL, 1.9 mmol) at -78°C . After 5 min, the reaction was stopped by adding water. The products were extracted with EtOAc (X3) and the combined organic extracts were washed brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (hexane / EtOAc = 85 / 15) to afford **9b** (305 mg, 79.9%) and **10b**. As the latter compound was still impure, repurification by PTLC (hexane / CH_2Cl_2 / Et_2O = 90 / 5 / 5) gave pure **10b** (5.6 mg, 1.5%).

adduct **9b** (colorless oil)

^1H NMR (CDCl_3 , δ)

0.94 (s, 6H), 1.05 (s, 6H), 1.53–1.73 (m, 6H), 3.47 (s, 2H), 4.07–4.18 (m, 4H), 7.06 (d, 1H, $J = 1.6$ Hz), 7.08 (d, 1H, $J = 7.8$ Hz), 7.15 (dd, 1H, $J_1 = 1.6$, $J_2 = 7.8$ Hz);

^{13}C NMR (CDCl_3 , δ)

18.4, 29.0, 30.6, 42.4, 46.1, 54.1, 64.8, 109.1, 122.7, 125.9, 137.5, 138.9, 145.1, 146.3;

IR (neat)

2970, 2928, 1603, 1469, 1418, 1377, 1362, 1350, 1303, 1279, 1260, 1212, 1190, 1176, 1134, 1065, 1040, 1015, 973, 947, 924, 856, 827, 772, 726 cm^{-1} ;

HRMS m/z 301.2043 (301.2042 calcd for $\text{C}_{19}\text{H}_{27}\text{O}_2\text{N}$, M^+).

adduct **10b** (colorless oil)

^1H NMR (CDCl_3 , δ)

0.82 (s, 6H), 1.29 (s, 6H), 1.50–1.62 (m, 6H), 3.37 (s, 2H), 4.02–4.09 (m, 2H), 4.25–4.32 (m, 2H), 7.05 (d, 1H, $J = 7.0$ Hz), 7.23 (d, 1H, $J = 8.1$ Hz), 7.29 (d, 1H, $J_1 = 7.0$, $J_2 = 8.1$ Hz);

^{13}C NMR (CDCl_3 , δ)

19.2, 25.8, 33.7, 42.5, 46.8, 55.1, 66.1, 110.9, 121.4, 131.0, 131.6, 142.4, 143.3, 150.7;

IR (neat)

2969, 2927, 2883, 1600, 1584, 1472, 1381, 1365, 1319, 1281, 1258, 1244, 1225, 1176, 1148, 1133, 1017, 964, 949, 843, 766 cm^{-1} ;

HRMS m/z 301.2039 (301.2042 calcd for $\text{C}_{19}\text{H}_{27}\text{O}_2\text{N}$, M^+).

[2+2] cycloaddition of cyclobutabenzyne **12a** and KSA **2a**:

To a mixture of triflate **11a** (199 mg, 0.526 mmol) and ketene silyl acetal **2a** (538 mg, 2.66 mmol) in THF (3.0 mL) was added *n*-BuLi (1.74 M in hexane, 0.36 mL, 0.63 mmol) at -78°C . After 5 min, the reaction was stopped by adding water. The products were extracted with EtOAc (X3) and the combined organic extracts were washed brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane / EtOAc = 98 / 2) to afford a mixture of regioisomers (120 mg, 75.0%, **13a/14a** = 22 : 1).

Cycloadduct **13a** (including **14a**)

[#]the underlined data corresponds to the minor isomer's.

^1H NMR (acetone- d_6 , δ)

0.05 (s, 3H), 0.13 (s, 3H), 0.90 (s, 9H), 1.16 (t, 3H, $J = 7.1$ Hz), 3.11–3.22 (m, 4H), 3.28 (d, 1H, $J = 13.4$ Hz), 3.40 (d, 1H, $J = 13.4$ Hz), 3.62 (qd, 1H, $J_1 = 7.1$, $J_2 = 9.1$ Hz), 3.82 (qd, 1H,

$J_1 = 7.1$, $J_2 = 9.1$ Hz), 6.91 (d, 1H, $J = 7.4$ Hz), 6.97 (d, 1H, $J = 7.5$ Hz), 7.03 (d, 1H, $J = 7.5$ Hz), 7.08 (d, 1H, $J = 7.4$ Hz);

^{13}C NMR (acetone- d_6 , δ)

−4.01, −4.00, 15.2, 18.1, 25.6, 29.9, 30.0, 30.3, 47.4, 48.3, 59.8, 60.4, 103.1, 103.2, 120.0, 121.3, 122.2, 123.7, 135.1, 138.1, 139.9, 140.8, 142.4, 145.2, 147.9, 148.0;

IR (neat)

2929, 2857, 1472, 1463, 1414, 1388, 1361, 1249, 1198, 1146, 1099, 1056, 945, 885, 837, 779 cm^{-1} ;

Anal. Calcd for $\text{C}_{18}\text{H}_{28}\text{O}_2\text{Si}$: C, 71.00; H, 9.27. Found: C, 71.23; H, 9.30.

Key 2- and 3-bond HMBC correlations

position	δH (ppm)	carbon no. (ppm)
4	7.03	C-8 (48.3), C-6 (142.4), C-2 (145.2)
8	3.28, 3.40	C-7 (103.1), C-4 (122.2), C-5 (139.9), C-6 (142.4)
3	6.97	C-10 (30.0), C-1 (138.1), C-5 (139.9)

Hydrolysis of cycloadducts **13a** and **14a**:

To a solution of cycloadducts **13a** and **14a** (64.5 mg, 0.212 mmol) in MeCN (1.0 mL) was added 46% aq. HF (0.1 mL) at 0 °C. After warmed up to room temperature, the reaction was further stirred for 12 h. After dilution with water, the products were extracted with Et_2O and the combined organic extracts were washed brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane / CH_2Cl_2 / Et_2O = 7 / 2 / 1) to afford a mixture of regioisomers (27.0 mg, 88.5%, **19a/20a** = 22 : 1).

ketone **19a** (including minor regioisomer **20a**)

[#]the underlined data corresponds to the minor isomer's.

^1H NMR (CDCl_3 , δ)

3.23–3.28 (m, 4H), 3.90 (s, 2H), 7.10 (d, 1H, $J = 7.8$ Hz), 7.13 (d, 1H, $J = 7.5$ Hz), 7.23 (d, 1H, $J = 7.8$ Hz), 7.35 (d, 1H, $J = 7.5$ Hz);

^{13}C NMR (CDCl_3 , δ)

29.9, 31.02, 31.04, 31.7, 51.6, 52.3, 119.8, 122.1, 123.6, 128.3, 140.9, 141.0, 142.5, 145.4, 147.5, 148.2, 150.3, 155.1, 188.7, 189.3;

IR (neat)

2925, 1759, 1587, 1432, 1400, 1141, 1012, 1003, 890, 822, 770 cm^{-1} .

*[2+2] cycloaddition of cyclobutabenzene **12b** and KSA **2a**:*

To a mixture of triflate **11b** (164 mg, 0.419 mmol) and ketene silyl acetal **2a** (341 mg, 1.69 mmol) in THF (5.0 mL) was added *n*-BuLi (1.57 M in hexane, 0.40 mL, 0.62 mmol) at -78 °C. After 5 min, the reaction was stopped by adding water. The products were extracted with EtOAc (X3) and the combined organic extracts were washed brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane / $\text{Et}_2\text{O} = 97 / 3$) to afford a mixture of regioisomers (68.3 mg, 51.2%, **13b**/**14b** = 2.3 : 1).

cycloadduct **13b (including **14b**)**

#the underlined data corresponds to the minor isomer's.

^1H NMR (acetone- d_6 , δ)

0.05 (s, 3H), 0.07 (s, 3H), 0.12 (s, 3H), 0.14 (s, 3H), 0.89 (s, 9H), 0.90 (s, 9H), 1.14 (t, 3H, $J = 7.1$ Hz), 1.15 (t, 3H, $J = 7.1$ Hz), 1.96–2.12 (m, 2H), 2.75–2.94 (m, 4H), 3.27 (d, 1H, $J = 13.7$ Hz), 3.30 (d, 1H, $J = 13.4$ Hz), 3.39 (d, 1H, $J = 13.4$ Hz), 3.61 (qd, 1H, $J_1 = 7.1$, $J_2 = 9.0$ Hz), 3.67 (qd, $J_1 = 7.1$, $J_2 = 9.0$ Hz), 3.80 (qd, $J_1 = 7.1$, $J_2 = 9.0$ Hz), 3.90 (qd, 1H, $J_1 = 7.1$, $J_2 = 9.0$ Hz), 6.94 (d, 1H, $J = 7.4$ Hz), 6.98 (d, 1H, $J = 7.5$ Hz), 7.10 (d, 1H, $J = 7.5$ Hz), 7.17 (d, 1H, $J = 7.4$ Hz);

^{13}C NMR (acetone- d_6 , δ) *#one aromatic carbon signal of major isomer overlaps to the another one.*

–3.6, –3.4, –3.3, –3.2, 15.6, 15.7, 18.4, 18.5, 26.0, 26.1, 26.1, 26.3, 30.4, 31.9, 33.1, 33.4, 47.7, 48.5, 60.2, 61.0, 103.2, 103.6, 119.3, 121.5, 123.9, 126.4, 137.1, 137.3, 139.2, 139.8, 144.6, 144.8, 146.9;

IR (neat)

3060, 2951, 2857, 1616, 1593, 1471, 1436, 1390, 1360, 1343, 1278, 1248, 1143, 1058, 1006, 938, 885, 835, 779 cm^{-1} ;

Anal. Calcd for $\text{C}_{19}\text{H}_{30}\text{O}_2\text{Si}$: C, 71.64; H, 9.49. Found: C, 71.53; H, 9.62.

*Hydrolysis of cycloadducts **13b** and **14b**:*

To a solution of cycloadduct **13b** and **14b** (61.2 mg, 0.192 mmol) in MeCN (2.0 mL) was

added 46% aq. HF (0.1 mL) at 0 °C. After warmed up to room temperature, the reaction was further stirred for 8 h. After dilution with water, the products were extracted with Et₂O and the combined organic extracts were washed brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by PTLC (hexane / CH₂Cl₂ / Et₂O = 90 / 5 / 5) to afford ketone **19b** (18.6 mg, 61.2%) and **20b** (8.0 mg, 26.3%).

ketone **19b**

¹H NMR (CDCl₃, δ)

2.12 (tt, 2H, J₁ = J₂ = 7.5 Hz), 2.91 (t, 2H, J = 7.5 Hz), 2.96 (t, 2H, J = 7.5 Hz), 3.92 (s, 2H), 7.28 (d, 1H, J = 7.5 Hz), 7.38 (d, 1H, J = 7.5 Hz);

¹³C NMR (CDCl₃, δ)

25.4, 31.0, 32.2, 51.8, 120.6, 131.0, 138.7, 143.9, 145.9, 149.1, 189.1;

IR (neat)

2953, 2917, 2844, 1770, 1610, 1581, 1463, 1436, 1405, 1342, 1232, 1202, 1159, 1117, 1017, 966, 815, 748 cm⁻¹;

An_al. Calcd for C₁₁H₁₀O: C, 83.51; H, 6.37. Found: C, 83.37; H, 6.34.

Key 2- and 3-bond HMBC correlations

position	δH (ppm)	carbon no. (ppm)
4	7.28	C-8 (51.8), C-6 (143.9), C-2 (145.9)
8	3.92	C-4 (120.6), C-6 (143.9), C-5 (149.1), C-7 (189.1)
3	7.38	C-11 (32.2), C-1 (138.7), C-5 (149.1)
10	2.12	C-9 (31.0), C-11 (32.2), C-1 (138.7), C-2 (145.9)

ketone **20b**

^1H NMR (CDCl_3 , δ)

2.16 (tt, 2H, $J_1 = J_2 = 7.4$ Hz), 2.93 (t, 2H, $J = 7.4$ Hz), 2.97 (t, 2H, $J = 7.4$ Hz), 3.90 (s, 2H), 7.12 (d, 1H, $J = 7.7$ Hz), 7.28 (d, 1H, $J = 7.7$ Hz);

^{13}C NMR (CDCl_3 , δ)

25.2, 30.2, 33.6, 51.1, 118.2, 125.5, 139.4, 146.3, 146.9, 153.5, 188.7;

IR (neat)

2922, 1752, 1599, 1585, 1458, 1429, 1403, 1343, 1347, 1309, 1199, 1159, 1016, 964, 928, 831 cm^{-1} ;

Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{O}$: C, 83.51; H, 6.37. Found: C, 83.43; H, 6.23.

Key 2- and 3-bond HMBC correlations

position	δH (ppm)	carbon no. (ppm)
4	7.12	C-3 (125.5), C-6 (146.9), C-2 (153.5), C-8 (188.7)
7	3.90	C-5 (146.3), C-6 (146.9), C-8 (188.7)
3	7.28	C-11 (33.6), C-1 (139.4), C-5 (146.3)
10	2.16	C-9 (30.2), C-11 (33.6), C-1 (139.4), C-2 (153.5)

*[2+2] cycloaddition of cyclobutabenzyne **12c** and KSA **2a**:*

To a mixture of triflate **11c** (156 mg, 0.384 mmol) and ketene silyl acetal **2a** (361 mg, 1.78 mmol) in Et_2O (5.0 mL) was added $n\text{-BuLi}$ (1.56 M in hexane, 0.40 mL, 0.62 mmol) at -78°C . After 5 min, the reaction was stopped by adding water. The products were extracted with Et_2O (X3) and the combined organic extracts were washed brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLTLC (hexane / Et_2O = 98 / 2) to afford **13c** (46.3 mg, 36.3%) and **14c** (8.1 mg, 6.3%).

cycloadduct **13c** (colorless oil)

^1H NMR (acetone- d_6 , δ)

0.05 (s, 3H), 0.14 (s, 3H), 0.90 (s, 9H), 1.16 (t, 3H, $J = 7.1$ Hz), 1.64–1.85 (m, 4H), 2.69–2.83 (m, 4H), 3.22 (d, 1H, $J = 13.2$ Hz), 3.37 (d, 1H, $J = 13.2$ Hz), 3.60 (qd, 1H, $J_1 = 7.1$, $J_2 = 8.9$ Hz), 3.74 (qd, 1H, $J_1 = 7.1$, $J_2 = 8.9$ Hz), 6.89 (d, 1H, $J = 7.5$ Hz), 6.98 (d, 1H, $J = 7.5$ Hz);

^{13}C NMR (acetone- d_6 , δ)

–3.5, –3.0, 15.8, 18.6, 23.3, 24.0, 26.1, 26.7, 30.4, 47.6, 60.9, 103.8, 121.4, 131.5, 131.9, 136.5, 138.4, 147.2;

IR (neat)

2928, 2876, 1610, 1472, 1463, 1389, 1360, 1310, 1250, 1223, 1186, 1134, 1108, 1063, 1006, 990, 939, 907, 837, 812, 778 cm^{-1} ;

Anal. Calcd for $\text{C}_{20}\text{H}_{32}\text{O}_2\text{Si}$: C, 72.23; H, 9.70. Found: C, 72.20; H, 9.89.

Key 2- and 3-bond HMBC correlations

position	δH (ppm)	carbon no. (ppm)
4	6.89	C-8 (47.6), C-2 (136.5), C-6 (147.2)
8	3.22, 3.37	C-7 (103.8), C-4 (121.4), C-5 (138.4), C-6 (147.2)
3	6.98	C-12 (30.4), C-1 (131.9), C-5 (138.4)

cycloadduct **14c** (colorless oil)

^1H NMR (acetone- d_6 , δ)

0.04 (s, 3H), 0.13 (s, 3H), 0.88 (s, 9H), 1.13 (t, 3H, $J = 7.0$ Hz), 1.74–1.79 (m, 4H), 2.58–2.75 (m, 4H), 3.18 (d, 1H, $J = 13.3$ Hz), 3.31 (d, 1H, $J = 13.3$ Hz), 3.65 (qd, 1H, $J_1 = 7.0$, $J_2 = 9.1$ Hz), 3.78 (qd, 1H, $J_1 = 7.0$, $J_2 = 9.1$ Hz), 6.91 (d, 1H, $J = 7.7$ Hz), 6.94 (d, 1H, $J = 7.7$ Hz);

^{13}C NMR (acetone- d_6 , δ)

−3.4, −3.3, 15.6, 18.5, 23.4, 24.0, 25.6, 26.1, 30.6, 46.9, 60.4, 102.6, 119.1, 128.9, 133.6, 138.9, 140.3, 145.6;

IR (neat)

2928, 2857, 586, 1472, 1462, 1389, 1312, 1255, 1185, 1144, 1112, 1058, 1044, 964, 937, 835, 778 cm^{-1} .

Key 2- and 3-bond HMBC correlations

position	δH (ppm)	carbon no. (ppm)
4	6.91	C-8 (102.6), C-2 (138.9)
7	3.18, 3.31	C-8 (102.6), C-6 (140.3), C-5 (145.6)
3	6.94	C-12 (30.6), C-5 (145.6)

ketone **19c**

^1H NMR (CDCl_3 , δ)

1.75–1.83 (m, 4H), 2.76–2.88 (m, 4H), 3.86 (s, 2H), 7.21 (d, 1H, $J = 7.6$ Hz), 7.23 (d, 1H, $J = 7.6$ Hz);

^{13}C NMR (CDCl_3 , δ)

21.9, 22.8, 25.7, 29.2, 51.2, 120.4, 133.1, 136.3, 137.7, 146.2, 148.8, 189.1;

IR (neat)

2939, 2836, 1752, 1578, 1560, 1474, 1458, 1436, 1400, 1323, 1271, 1208, 1194, 1158, 1130, 1053, 972, 920, 840, 808, 732 cm^{-1} ;

Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{O}$: C, 83.69; H, 7.02. Found: C, 83.65; H, 7.02.

ketone **20c**

^1H NMR (CDCl_3 , δ)

1.81–1.88 (m, 4H), 2.73–2.85 (m, 4H), 3.80 (s, 2H), 7.05 (d, 1H, $J = 7.6$ Hz), 7.11 (d, 1H, $J = 7.6$ Hz);

^{13}C NMR (CDCl_3 , δ)

22.8, 23.2, 26.1, 30.9, 50.4, 118.0, 131.1, 133.8, 145.1, 146.1, 151.3, 188.4;

IR (KBr)

2937, 1756, 1596, 1578, 1474, 1460, 1431, 1405, 1316, 1206, 1165, 1134, 1052, 973, 957, 906, 891, 849, 836, 816 cm^{-1} ;

Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{O}$: C, 83.69; H, 7.02. Found: C, 83.39; H, 7.17.

*Nucleophilic addition of piperidine to cyclobutabenzynes **12a**:*

To a mixture of triflate **11a** (134 mg, 0.354 mmol) and piperidine (107 mg, 1.26 mmol) in THF (3.0 mL) was added *n*-BuLi (1.56 M in hexane, 0.6 mL, 0.9 mmol) at -78 °C. After 5 min, the reaction was stopped by adding water. The products were extracted with Et_2O (X3) and the combined organic extracts were washed brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (hexane / CH_2Cl_2 / $\text{Et}_2\text{O} = 90 / 5 / 5$) to afford **15a** (38.4 mg, 58.0%) and **16a** (8.0 mg, 12%).

adduct **15a** (colorless oil)

^1H NMR (CDCl_3 , δ)

1.51–1.57 (m, 2H), 1.68–1.73 (m, 4H), 3.04–3.12 (m, 8H), 6.71 (d, 1H, $J = 2.0$ Hz), 6.80 (dd, 1H, $J_1 = 2.0$, $J_2 = 8.0$ Hz), 6.92 (d, 1H, $J = 8.0$ Hz);

^{13}C NMR (CDCl_3 , δ)

24.3, 26.1, 28.8, 29.1, 52.2, 112.4, 116.8, 122.9, 136.9, 146.1, 152.7;

IR (neat)

2922, 2854, 2789, 1602, 1480, 1451, 1383, 1331, 1274, 1234, 1188, 1154, 1120, 1079, 1024,

944, 863, 838, 810, 734 cm^{-1} ;

Anal. Calcd for $\text{C}_{13}\text{H}_{17}\text{N}$: C, 82.82; H, 9.09, N, 7.43. Found: C, 82.66; H, 9.24; N, 7.23.

adduct **16a** (colorless oil)

^1H NMR (CDCl_3 , δ)

1.55–1.69 (m, 6H), 3.07–3.10 (m, 2H), 3.20–3.24 (m, 4H), 3.25–3.28 (m, 2H), 6.52 (d, 1H, $J = 7.2$ Hz), 6.59 (d, 1H, $J = 8.4$ Hz), 7.09 (dd, 1H, $J_1 = 7.2$, $J_2 = 8.4$ Hz);

^{13}C NMR (CDCl_3 , δ)

24.5, 25.6, 29.2, 31.6, 49.0, 111.7, 113.1, 128.3, 130.6, 146.0, 147.0;

IR (neat)

3059, 2928, 2852, 1600, 1573, 1482, 1541, 1384, 1346, 1248, 1227, 1129, 1034, 994, 857, 782, 756 cm^{-1} ;

HRMS m/z 187.1374 (187.1361 calcd for $\text{C}_{13}\text{H}_{17}\text{N}$, M^+).

*Nucleophilic addition of piperidine to cyclobutabenzynes **12b**:*

To a mixture of triflate **11b** (79.7 mg, 0.203 mmol) and piperidine (64 mg, 10.75 mmol) in THF (3.0 mL) was added *n*-BuLi (1.56 M in hexane, 0.35 mL, 0.55 mmol) at -78 °C. After 5 min, the reaction was stopped by adding water. The products were extracted with EtOAc (X3) and the combined organic extracts were washed brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane / CH_2Cl_2 / $\text{Et}_2\text{O} = 94 / 3 / 3$) to afford **15b** (15.4 mg, 37.6%) and **16b** (15.8 mg, 38.6%).

adduct **15b** (colorless oil)

^1H NMR (CDCl_3 , δ)

1.54–1.59 (m, 2H), 1.71–1.75 (m, 4H), 2.02–2.09 (m, 2H), 2.81–2.89 (m, 4H), 3.01–3.11 (m, 4H), 6.77 (dd, 1H, $J_1 = 2.2$, $J_2 = 8.2$ Hz), 6.87 (d, 1H, $J = 2.2$ Hz), 7.11 (d, 1H, $J = 8.2$ Hz);

^{13}C NMR (CDCl_3 , δ)

24.3 25.7, 26.0, 32.0, 33.2, 51.8, 113.4, 115.4, 124.4, 135.4, 145.1, 151.5;

IR (neat)

2933, 2845, 2789, 1615, 1574, 1495, 1464, 1442, 1382, 1335, 1241, 1215, 1121, 1092, 1027,

951, 862, 831, 805 cm^{-1} ;

Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{N}$: C, 82.98; H, 9.45, N, 6.91. Found: C, 82.72; H, 9.62; N, 6.62.

adduct **16b** (colorless oil)

^1H NMR (CDCl_3 , δ)

1.55–1.61 (m, 2H), 1.69–1.74 (m, 4H), 2.02–2.09 (m, 2H), 2.84–2.97 (m, 8H), 6.74 (d, 1H, $J = 7.8$ Hz), 6.90 (d, 1H, $J = 7.2$ Hz), 7.11 (d, 1H, $J_1 = 7.2$, $J_2 = 7.8$ Hz);

^{13}C NMR (CDCl_3 , δ)

24.4, 26.0, 26.5, 31.8, 33.4, 52.0, 114.6, 117.9, 127.0, 136.5, 145.8, 150.2;

IR (neat)

2932, 2844, 2790, 589, 1479, 1450, 1381, 1334, 1273, 1237, 1181, 1138, 1118, 1065, 1054, 1033, 981, 913, 858 cm^{-1} ;

HRMS m/z 201.1526 (201.1518 calcd for $\text{C}_{14}\text{H}_{19}\text{N}$, M^+).

Nucleophilic addition of piperidine to cyclobutabenzyne 12c:

To a mixture of triflate **11c** (206 mg, 0.508 mmol) and piperidine (130 mg, 1.53 mmol) in THF (3.2 mL) was added *n*-BuLi (1.56 M in hexane, 1.0 mL, 1.56 mmol) at -78 °C. After 5 min, the reaction was stopped by adding water. The products were extracted with EtOAc (X3) and the combined organic extracts were washed brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane / CH_2Cl_2 / $\text{Et}_2\text{O} = 90 / 5 / 5$) to afford **15c** (32.2 mg, 29.4%) and **16c** (60.7 mg, 55.5%).

adduct **15c** (colorless oil)

^1H NMR (CDCl_3 , δ)

1.52–1.58 (m, 2H), 1.68–1.79 (m, 8H), 2.68–2.73 (m, 4H), 3.06–3.09 (m, 4H), 6.66 (d, 1H, $J = 2.4$ Hz), 6.74 (dd, 1H, $J_1 = 2.4$, $J_2 = 8.3$ Hz), 6.95 (d, 1H, $J = 8.3$ Hz);

^{13}C NMR (CDCl_3 , δ)

23.4, 23.5, 24.3, 26.0, 28.5, 29.8, 51.4, 115.0, 117.3, 128.4, 129.5, 137.4, 150.3;

IR (neat)

2922, 1615, 1574, 1505, 1451, 1383, 1352, 1275, 1241, 1119, 1067, 1030, 990, 948, 904, 862,

826, 799 cm^{-1} ;

Anal. Calcd for $\text{C}_{15}\text{H}_{21}\text{N}$: C, 83.11; H, 9.76, N, 6.46. Found: C, 83.04; H, 9.99; N, 6.36

adduct **16c** (colorless oil)

^1H NMR (CDCl_3 , δ)

1.58–1.82 (m, 10H), 2.72–2.82 (m, 8H), 6.82 (d, 1H, $J = 7.5$ Hz), 6.87 (d, 1H, $J = 7.8$ Hz), 7.09 (dd, 1H, $J_1 = 7.5$, $J_2 = 7.8$ Hz);

^{13}C NMR (CDCl_3 , δ)

23.1, 23.2, 24.5, 25.0, 26.7, 29.7, 53.5, 116.3, 124.0, 125.6, 132.6, 138.0, 152.7;

IR (neat)

29232, 2855, 2793, 1582, 1460, 1379, 1336, 1271, 1235, 1116, 1090, 1033, 1008, 972, 929, 772, 721 cm^{-1} ;

Anal. Calcd for $\text{C}_{15}\text{H}_{21}\text{N}$: C, 83.11; H, 9.76, N, 6.46. Found: C, 82.95; H, 9.91; N, 6.16.

[2+4] cycloaddition of cyclobutabenzyne **12a** with 2-methoxyfuran:

To a mixture of triflate **11a** (85.5 mg, 0.226 mmol) and 2-methoxyfuran (114 mg, 1.16 mmol) in THF (2.0 mL) was added *n*-BuLi (1.57 M in hexane, 0.25 mL, 0.39 mmol) at -78°C . After 5 min, the reaction was stopped by adding water. The products were extracted with Et_2O (X3) and the combined organic extracts were washed brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (hexane / $\text{EtOAc} = 7 / 3$) to afford a mixture of regioisomers (32.6 mg, 72%, **17a/18a** = 4.0 : 1), which were separated by flash column chromatography (benzene / $\text{Et}_2\text{O} = 98 / 2$).

cycloadduct **17a**

^1H NMR (CDCl_3 , δ)

3.25–3.27 (m, 2H), 3.51–3.53 (m, 2H), 3.88 (s, 3H), 4.91 (s, 1H), 6.58 (d, 1H, $J = 8.1$ Hz), 6.62 (d, 1H, $J = 8.1$ Hz), 7.24 (d, 1H, $J = 8.3$ Hz), 7.96 (d, 1H, $J = 8.3$ Hz);

^{13}C NMR (CDCl_3 , δ)

30.4, 31.4, 55.8, 104.0, 107.0, 120.3, 121.5, 122.9, 124.6, 140.2, 143.1, 145.9, 150.0;

IR (KBr)

3206, 2952, 2916, 1635, 1595, 1456, 1390, 1352, 1322, 1249, 1198, 1172, 1131, 1092, 1010,

939, 914, 819, 797 cm^{-1} ;

Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_2$: C, 77.98; H, 6.04. Found: C, 77.78; H, 6.26.

Key 2- and 3-bond HMBC correlations

position	δH (ppm)	carbon no. (ppm)
4	7.96	C-9 (124.6), C-2 (143.1), C-5 (145.9)
OH	4.91	C-6 (107.0), C-10 (122.9), C-5 (145.9)
13	3.88	C-8 (150.0)
3	7.24	C-12 (31.4), C-10 (122.9), C-1 (140.2)

cycloadduct **18a**

^1H NMR (CDCl_3 , δ)

3.32–3.34 (m, 2H), 3.56–3.58 (m, 2H), 3.94 (s, 3H), 4.79 (s, 1H), 6.58 (d, 1H, $J = 8.1$ Hz), 6.73 (d, 1H, $J = 8.1$ Hz), 7.22 (d, 1H, $J = 8.4$ Hz), 8.10 (d, 1H, $J = 8.4$ Hz);

^{13}C NMR (CDCl_3 , δ)

30.3, 30.7, 55.8, 102.9, 108.5, 121.32, 121.33, 121.6, 125.6, 137.7, 143.0, 144.8, 150.6;

IR (KBr)

3272, 2920, 2831, 1636, 1600, 1578, 1479, 1426, 1405, 1368, 1307, 1250, 1207, 1133, 1028, 957, 826, 808, 769 cm^{-1} ;

Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_2$: C, 77.98; H, 6.04. Found: C, 77.78; H, 6.14.

Key 2- and 3-bond HMBC correlations

position	δ H (ppm)	carbon no. (ppm)
4	8.10	C-9 (121.6), C-2 (143.0), C-5 (150.6)
OH	4.79	C-7 (108.5), C-9 (121.6), C-8 (144.8)
13	3.94	C-5 (150.6)
3	7.22	C-12 (30.7), C-10 (125.6), C-1 (137.7)

*[2+4] cycloaddition of cyclobutabenzyne **12b** with 2-methoxyfuran:*

To a mixture of triflate **11b** (38.9 mg, 0.099 mmol) and 2-methoxyfuran (97.3 mg, 0.992 mmol) in THF (2.0 mL) was added *n*-BuLi (1.74 M in hexane, 0.1 mL, 0.17 mmol) at -78°C . After 5 min, the reaction was stopped by adding water. The products were extracted with Et_2O (X3) and the combined organic extracts were washed brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (hexane / CH_2Cl_2 / Et_2O = 82 / 12 / 8) to afford **17b** (9.8 mg, 46%) and **18b** (6.9 mg, 33%).

cycloadduct **17b**

^1H NMR (CDCl_3 , δ)

2.12 (tt, 2H, $J = 7.6$ Hz), 3.01 (t, 1H, $J = 7.6$ Hz), 3.57 (t, 1H, $J = 7.6$ Hz), 3.86 (s, 3H), 4.87 (s, 1H), 6.60 (d, 1H, $J = 8.2$ Hz), 6.64 (d, 1H, $J = 8.2$ Hz), 7.40 (d, 1H, $J = 8.4$ Hz), 7.93 (d, 1H, $J = 8.4$ Hz);

^{13}C NMR (CDCl_3 , δ)

24.8, 33.0, 35.3, 55.7, 104.5, 107.0, 119.8, 123.4, 124.4, 125.1, 138.6, 142.3, 145.5, 151.3;

IR (KBr)

3244, 2955, 2852, 1629, 1598, 1582, 1456, 1379, 1356, 1306, 1252, 1138, 1092, 1006, 887, 810, 800, 770 cm^{-1} ;

Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2$: C, 78.48; H, 6.59. Found: C, 78.40; H, 6.79.

Key 2- and 3-bond HMBC correlations

position	δH (ppm)	carbon no. (ppm)
4	7.93	C-9 (124.4), C-2 (142.3), C-5 (145.5)
14	3.86	C-8 (151.3)
3	7.40	C-13 (33.0), C-10 (125.1), C-1 (138.6)
13	3.01	C-12 (24.8), C-11 (35.3), C-3 (123.4), C-1 (138.6), C-2 (142.3)

cycloadduct **18b**

^1H NMR (CDCl_3 , δ)

2.18 (tt, 2H, $J = 7.6$ Hz), 3.03 (t, 1H, $J = 7.6$ Hz), 3.62 (t, 1H, $J = 7.6$ Hz), 3.94 (s, 3H), 4.80 (br-s, 1H), 6.57 (d, 1H, $J = 8.1$ Hz), 6.66 (d, 1H, $J = 8.1$ Hz), 7.38 (d, 1H, $J = 8.5$ Hz), 8.05 (d, 1H, $J = 8.5$ Hz);

^{13}C NMR (CDCl_3 , δ)

24.8, 32.9, 34.8, 55.8, 102.9, 108.8, 120.6, 123.1, 123.3, 126.2, 137.4, 142.2, 146.4, 150.2;

IR (KBr)

3317, 2959, 2854, 1631, 1595, 1461, 1440, 1412, 1363, 1315, 1302, 1272, 1255, 1228, 1170, 1141, 1077, 1031, 946, 823, 800, 770, 744, 720 cm^{-1} ;

Anal. Calcd for C₁₄H₁₄O₂: C, 78.48; H, 6.59. Found: C, 78.63; H, 6.61.

Key 2- and 3-bond HMBC correlations

position	δ H (ppm)	carbon no. (ppm)
4	8.05	C-9 (123.1), C-2 (142.2), C-5 (150.2)
14	3.94	C-5 (150.2)
3	7.40	C-13 (32.9), C-10 (126.2), C-1 (137.4)
13	3.03	C-13 (24.8), C-11 (34.8), C-3 (123.3), C-1 (137.4), C-2 (142.2)

[2+4] cycloaddition of cyclobutabenzene **12c** with 2-methoxyfuran:

To a mixture of triflate **11c** (248 mg, 0.611 mmol) and 2-methoxyfuran (600 mg, 6.12 mmol) in THF (4.0 mL) was added *n*-BuLi (1.74 M in hexane, 0.43 mL, 0.76 mmol) at -78°C . After 5 min, the reaction was stopped by adding water. The products were extracted with Et₂O (X3) and the combined organic extracts were washed brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by flash column chromatography (hexane / CH₂Cl₂ / Et₂O = 8 / 1 / 1) to afford **17c** (29.8 mg, 21%) and **18c** (39.7 mg, 29%).

cycloadduct **17c**

¹H NMR (CDCl₃, δ)

1.77–1.84 (m, 4H), 2.91 (br-s, 2H), 3.45 (br-s, 2H), 3.82 (s, 3H), 4.95 (s, 1H), 6.63 (d, 1H, J = 8.6 Hz), 6.65 (d, 1H, J = 8.6 Hz), 7.16 (d, 1H, J = 8.6 Hz), 7.88 (d, 1H, J = 8.6 Hz);

^{13}C NMR (CDCl_3 , δ)

22.3, 24.1, 29.9, 31.4, 56.2, 106.4, 107.3, 118.7, 125.0, 126.3, 128.5, 133.6, 135.2, 145.4, 152.6;

IR (KBr)

3334, 2936, 2855, 1624, 1611, 1575, 1517, 1460, 1364, 1298, 1270, 1248, 1180, 1148, 1099, 1067, 1038, 986, 961, 876, 828, 800, 768, 738 cm^{-1} ;

Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2$: C, 78.92; H, 7.06. Found: C, 78.89; H, 7.36.

Key 2- and 3-bond HMBC correlations

position	δH (ppm)	carbon no. (ppm)
4	7.88	C-9 (126.3), C-2 (135.2), C-5 (145.4)
15	3.82	C-8 (152.6)
3	7.16	C-14 (31.4), C-10 (125.0), C-1 (133.6)

cycloadduct **18c**

^1H NMR (CDCl_3 , δ)

1.80–1.84 (m, 4H), 2.89–2.92 (m, 2H), 3.50–3.53 (m, 2H), 3.91 (s, 3H), 4.89 (s, 1H), 6.56 (d, 1H, $J = 8.2$ Hz), 6.59 (d, 1H, $J = 8.2$ Hz), 7.14 (d, 1H, $J = 8.6$ Hz), 7.98 (d, 1H, $J = 8.6$ Hz);

^{13}C NMR (CDCl_3 , δ)

22.3, 23.9, 29.7, 31.2, 55.9, 103.2, 110.0, 119.2, 124.8, 126.2, 128.4, 132.9, 135.1, 147.5, 149.9;

IR (KBr)

3388, 2935, 2874, 1621, 1606, 1583, 1518, 1480, 1448, 1417, 1367, 1270, 1194, 1170, 1146, 1089, 1066, 1021, 1001, 966, 872, 812, 772, 739 cm^{-1} ;

Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2$: C, 78.92; H, 7.06. Found: C, 78.63; H, 7.36.

Key 2- and 3-bond HMBC correlations

position	δ H (ppm)	carbon no. (ppm)
4	7.98	C-9 (124.8), C-2 (135.1), C-5 (149.9)
15	3.91	C-5 (149.9)
3	7.14	C-14 (31.2), C-10 (126.2), C-1 (132.9)