Fluorenes and Styrenes by Au(I)-Catalyzed Annulation of Enynes and Alkynes

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Supporting Information

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I. General Information

Unless otherwise noted, all reagents were obtained commercially and used without further purification. HPLC grade dichloromethane (CH₂Cl₂), ACS grade pentane, ACS grade hexanes, ACS grade toluene, ACS grade ethyl acetate and ACS grade diethyl ether were obtained from Fischer Scientific. The catalyst, $(2,4-(t-Bu)_2C_6H_3O)_3PAuCl$, was prepared according to the method of Sawamura.¹ TLC analysis of reaction mixtures was performed on Merck silica gel 60 F254 TLC plates using I₂ stain and UV light to visualize the reaction components. Column chromatography was carried out on ICN SiliTech 32-63 D 60 Å silica gel.

¹H and ¹³C NMR spectra were recorded with Bruker AV-300, AVQ-400, AVB-400, DRX-500, and AV-500 spectrometers referenced to chloroform, unless otherwise noted. Product ratios were determined by ¹H NMR unless otherwise noted. Mass spectral data were obtained via the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley.

II. Mechanistic Experiments

The mechanism by which styrene and fluorene products arise from the *cis*-cyclopropanes was investigated through a number of experiments. In particular, three questions were addressed. Are there any isolable intermediates *en route* to styrene and fluorene products from the cyclopropanes? Are all steps in the syntheses of the styrenes and fluorenes necessarily gold-catalyzed? Might the formation of the styrenes and fluorenes be reversible; might one form more rapidly than the other and then isomerize under the reaction condition? For these investigations *cis*-cyclopropane *cis*-5 was used as the model substrate, involving the formation of styrene **3** or fluorene **4**.

Isolation and Reactivity of Arene Intermediate 89

Isolation: The following experiments permitted the identification of arene **89** as a possible intermediate in the transformation of **cis-5** to styrene **3** and fluorene **4**.

¹ Ochida, A.; Ito, H.; Sawamura, M. J. Am. Chem. Soc. 2006, 128, 16486.



By treating the *cis*-cyclopropane (*cis*-5) with 5% AuCl at -10 $^{\circ}$ C and quenching the reaction after 30 min, a low yield of arene **89** was obtained (equation S1, see experimental procedure below). Treatment of *cis*-5 with 5% AgOTf at -10 $^{\circ}$ C, in the absence of Au(I) produced no reaction over the course of 16 h. Treatment of *cis*-5 with 10% TfOH at -10 $^{\circ}$ C also produced no reaction within 45 min, and no further reaction was observed overnight at room temperature.



A stirred suspension of AuCl (0.05 equiv) in CH₂Cl₂ (0.2 M based on cyclopropane) was cooled to -10 °C. A solution of cyclopropane *cis*-5 in CH₂Cl₂ (0.2 M based on cyclopropane) was added to the catalyst mixture, and the resulting solution was stirred at -10 °C for 30 min, at which point TLC indicated complete consumption of starting material. The reaction mixture was filtered through silica and washed with excess Et₂O, and **89** was isolated in 20% yield following silica column chromotography (5% Et₂O in hexanes). A mixture of fluorene **4** and styrene **3** (3.8:1) was also isolated in 52% yield. ¹H NMR (CDCl₃, 400 MHz) δ 7.32 (m, 6 H), 7.12 (dd, 1 H, *J* = 8.0, 1.2 Hz), 6.87 (d, 1 H, *J* = 1.2 Hz), 5.04 (s, 1 H), 2.31 (s, 3 H), 1.48 (s, 6 H), 1.13 (s, 9 H); ¹³C NMR (CDCl₃, 100 MHz) δ 176.8, 144.0, 140.1, 139.1, 135.5, 132.8, 129.4, 128.1, 127.4, 126.7, 125.4, 82.1, 39.0, 30.4, 27.0, 20.7; HRMS (FAB) Calcd. for [C₂₁H₂₆O₂] 310.1933, Found 310.1927.

Reactivity: The following experiments were designed to test whether arene **89** was an intermediate *en route* to **3** and **4** and whether those transformations were necessarily catalyzed by gold.



Arene **89** was subjected to the standard reaction conditions for styrene synthesis $(5\% (ArO)_3PAuCl, AgOTf)$, and the product yield and distribution were evaluated by ¹H NMR against an internal standard. After 10 min, there was 98% conversion to styrene **3**. No further reaction was observed at extended timepoints.

Arene **89** was then subjected to the standard reaction conditions for fluorene synthesis (5% (ArO)₃PAuCl, AgSbF₆), and the product yield and distribution were evaluated by ¹H NMR against an internal standard. After 10 min, 55% conversion to fluorene **4** and 40% conversion to styrene **3** was observed. After 45 min, at -10 °C, no further change was observed (equation S2).

Arene **89** was re-subjected to the fluorene conditions, except that the reaction was run at room temperature. After 15 min, 66% conversion to fluorene **4** and 34% conversion to styrene **3** was observed. After 30 min, 69% conversion to **4** and 31% conversion to **3** was observed. After 6 h, there was 79% conversion to **4** and 21% conversion to **3** and after 9 h, 91% conversion to **4** and 9% conversion to **3** was observed (equation S2).



Reactions were performed on arene **89** using only silver salts to test whether gold was necessary for the transformations to styrenes and fluorenes. Arene **89** was reacted with 5% AgOTf, the silver salt used for styrene synthesis. After 15 min, there was 10% conversion to styrene **3** and 88% of the starting material remained. After 12 h, 87% conversion to styrene **3** was observed (equation S3). The arene **89** was then reacted with 5% AgSbF₆, the silver salt for fluorene synthesis. After 15 min, 53% conversion to fluorene **4** and 42% conversion to styrene **3** was observed. No further conversion was observed at extended reaction times (equation S3).



The chemoselectivities achievable in this reaction by simply switching the counterion of the gold catalyst is remarkable and represents a further example of the ability of counterions to effect selectivity in catalysis.^{2,3}

Stability of Styrene and Fluorene Products

Experiments were performed in order to test whether the formation of the styrene and/or fluorene products was reversible under the reaction conditions.



² For a review of counterion effects in catalysis see: Fagnou, K.; Lautens, M. Angew. Chem. Int. Ed. 2002, 41, 26.
³ For various counterion effects in gold catalysis see the following; Reactivity effects: (a) Kang, J.-E.; Kim, H.-B.; Lee, J.-W.; Shin, S. Org. Lett. 2006, 8, 3537. Regioselectivity effects: (b) Zhang, Z.; Liu, C.; Kinder, R. E.; Han, X.; Qian, H.; Widenhoefer, R. A. J. Am. Chem. Soc. 2006, 128, 9066. (c) Lian, J.-J.; Chen, P.-C.; Lin, Y.-P.; Ting, H.-C.; Liu, R.-S. J. Am. Chem. Soc. 2006, 128, 11372. Enantioselectivity effects: (d) LaLonde, R. L.; Sherry, B. D.; Kang, E. J.; Toste, F. D. J. Am. Chem. Soc. 2007, 129, 2452. (e) Hamilton, G. L.; Kang, E. J.; Mba, M.; Toste, F. D. Science 2007, 317, 496.

These experiments will address the possibility that elimination (E1) proceeds more rapidly than annulation (SN1) under the reaction conditions, and therefore that formation of styrene **3** precedes formation of fluorene **4** under the conditions for fluorene synthesis. Although both products would arise from a common intermediate, these experiments address questions of reversibility and relative rates of product formation.

In order to test whether a catalytic amount of acid would catalyze the formation of fluorene from styrene, styrene **3** was treated with 10% HBF₄. By ¹H NMR, quantitative conversion to fluorene **4** was observed at 2 h (equation S5). A 9:1 mixture of styrene **3** to fluorene **4** was then treated with 10% TfOH, and the reaction was monitored by ¹H NMR. At 30 min, there was quantitative conversion to fluorene, such that only **4** was observed (equation S6).



The preceding experiments established that styrene **3** can isomerization to fluorene **4** under acidic conditions. The same tests were performed in the presence of the gold catalyst. Styrene **3** was subjected to the standard reaction conditions for fluorene synthesis (5% (ArO)₃PAuCl, AgSbF₆), and the product yield and distribution were evaluated by ¹H NMR against an internal standard. No reaction was observed in 2 h, but after 16 h there was 45% conversion to fluorene **4** (equation S7).



Since pivalic acid is liberated during the reaction conditions the preceding experiment does not absolutely reproduce the reaction conditions. The following experiments were devised to test whether styrene was converted to fluorene under the actual reaction conditions. The results suggest that the rate of isomerization of styrene to fluorene is highly dependent upon the reaction temperature.

A 63:37 mixture of *cis*-5 and 3 was subjected to the standard reaction conditions for fluorene synthesis (5% (ArO)₃PAuCl, AgSbF₆) at -10 $^{\circ}$ C, and the product yield and distribution were

evaluated by ¹H NMR against an internal standard. After 15 min, *cis*-5 was completely consumed, and 47% **3** and 47% **4** were observed.⁴ After 45 min, no further reaction had occurred. The reaction mixture was warmed to room temperature and left overnight. After 16 h, 33% **3** and 63% **4** were observed, indicating slow conversion of **3** to **4** at room temperature. The overnight experiment was repeated at -10 °C, and no isomerization of **3** was observed (equation S8).



The experiment was repeated at room temperature with the same catalyst system. After 10 min, *cis*-5 was completely consumed, and 12% **3** ansd 85% **4** were observed.⁴ After 20 min, there was 7% **3** and 89% **4**, while after 30 min, 3% **3** and 97% **4** were observed (equation S9).



These experiments imply that at room temperature, two pathways operate for fluorene formation: direct SN1 reaction from arene **89** and acid-catalyzed isomerization of styrene to fluorene. The isomerization pathway appears particularly relevant at room temperature, and may explain the higher fluorene yields attained in some cases at room temperature compared with the reaction run at -10 $^{\circ}$ C.

Labeling Experiment

In order to test the amount of fluorene that was arising through styrene, the following labeling experiments were performed. The results imply that little fluorene arises from styrene at either 10 °C or room temperature, although the styrene isomerization pathway is more active at elevated temperatures.

The deuterated *cis*-cyclopropane (d^6 -*cis*-5) was prepared from d^6 -acetone and was subjected to the standard reaction conditions for fluorene synthesis (5% (ArO)₃PAuCl, AgSbF₆) at -10 °C.

⁴ 100% represents the sum total of *cis*-5 and 3 that constituted the starting material.

The fluorene product was isolated in 75% yield and was determined to have retained 96% of the deuterium label (equation S10).



The experiment was repeated at room temperature, and the expected fluorene product was isolated in 78% yield. Increased scrambling of the deuterium label was observed: 90% deuterium incorporation remained (equation S11).



Summary

Given the data presented above, the following conclusions may be drawn regarding the transformation of *cis*-cyclopropane *cis*-5 into styrene 3 and fluorene 4:

- Arene **89** is a plausible intermediate *en route* to styrene and fluorene products from the cyclopropanes.
- Simply changing the counterion dramatically alters the ratio of **3**:4 obtained either from *cis*-**5** or **89** under otherwise identical reaction conditions. Experiments with **89** demonstrate that even when AgX is used without additional gold, the product selectivity is still altered.
- Although the cycloisomerization of *cis*-5 to **89** is Au-catalyzed, the subsequent elimination/annulation steps may be catalyzed by other Brønsted and Lewis acids.
- It is likely that two pathways for the synthesis of **4** are operative: direct SN1 reaction from **89** and isomerization of some initially formed **3**. Although the latter pathway is probably not the major one under the reaction conditions, it may be more relevant to reactions run at elevated temperatures.
- The fluorene:styrene ratio and the rate of isomerization of styrene to fluorene are apparently highly sensitive to the precise Brønsted acid present *in situ*.

III. Optimization Data

Following our initial result (entry 1, below), extensive efforts were devoted to optimizing the one-pot synthesis of fluorene **4** from **1** and **2**. In contrast to the results obtained in the two-pot synthesis of styrene **3**, poor conversion and yield were observed when AgOTf was used. Initial reactions on NMR scale were promising, as switching the catalyst counterion provided a dramatic increase in selectivity for **4** over **3** (entries 2-3). In all cases, significant quantities of cyclopropane *trans*-**5** were also present.

Upon scale up of the reaction, decreased yields were obtained, and lower temperatures proved optimal (entries 5-8). Additionally, significant quantities of complex decomposition products were inseperable from *trans-5* upon column chromotography, and although lower temperatures did not eliminate the presence of these contaminants, the crude reaction mixtures were far cleaner by NMR when the reaction was run at low temperature. It is noteworthy that although a BINAP-derived catalyst performed similarly to monophosphine and monophosphite gold complexes, use of dppm(AuCl)₂ resulted in a dramatically altered product distribution under otherwise identical conditions.

In the end, the highest isolated yield of fluorene 4 obtained from the one-pot reaction (52%) compared unfavorably to that obtained for the two-pot synthesis (61%). Additionally, no one-pot conditions were identified to compare with the two-pot synthesis of styrene 3, which proceeded in 71% yield over two steps. Attempts to develop a one-pot styrene synthesis of *n*-pentyl-substituted enyne 58 maximally resulted in 25% yield of styrene 60 by NMR.

| | Piv + 1 5% | 6 Catalyst | Ph 3 | + | 4 | / } |
|----------------|--|------------|---------------------|-----|-----------------|--------|
| entry | catalyst | Piv:Enyne | Т | 3 | 4 | |
| 1 ^a | PPh ₃ AuNTf ₂ | 1.5:1 | 23 °C | 21% | 23% | |
| 2 ^a | PPh ₃ AuCl/AgSbF ₆ | 2:1 | 23 °C | 0% | 52% | |
| 3 ^a | PPh ₃ AuCl/AgOTf | 1.5:1 | 23 °C | 15% | 10% | |
| 4 ^a | PPh ₃ AuOBz | 1.5:1 | 23 °C | 0% | 0% ^c | |
| 5 ^b | PPh ₃ AuCl/AgSbF ₆ | 1.5:1 | -10 °C ^d | 0% | 49% | |
| 6 ^b | PPh ₃ AuCl/AgSbF ₆ | 1.5:1 | -20 °C | 0% | 45% | |
| 7 ^b | BINAP(AuCl) ₂ /AgSbF ₆ | 1.5:1 | -10 °C | 5% | 47% | |
| 8 ^b | dppm(AuCl) ₂ /AgSbF ₆ | 1.5:1 | -10 °C | 24% | 32% | |
| 9 ^b | (ArO) ₃ PAuCl/AgSbF ₆ | 1.5:1 | -10 °C | 0% | 52% | |
| 10 | AgSbF ₆ | 1.5:1 | 23 °C | 0% | 0% ^e | |

a) Yields determined by NMR. b) Isolated yields. c) No reaction observed. d) Decreased temperature resulted in slightly higher isolated yield and cleaner crude reaction mixtures.
e) Slow conversion of 1 to the corresponding allene and subsequen hydrolysis of the pivaloate ester was observed.

Optimization of the carbene precursor showed that the pivaloate ester provided the best selectivity in differentiating between the styrene and fluorene pathways (see table below). The

acetate and benzoate esters were particularly poor for forming fluorene products, providing mixtures of **3** and **4** under fluorene conditions (B conditions). The success of the propargyl pivaloate ester substrates in gold chemistry is well precedented⁵ and has previously been attributed to the greater stability of pivalate esters to hydrolysis. In this chemistry, the origin of the enhanced selectivity with pivalate esters is unclear. However, we expect that the nature of the conjugate acid (pK_A, sterics) produced during the reaction has an effect on the product selectivity.

| = | OR Ph | 1) 5% A 2) Cond | uCl, CH ₂ Cl ₂ | Ph 3 | or | 4 |
|-------|------------------|-----------------------|--------------------------------------|--------------------|----------------------------------|-----------------------|
| entry | propargyl ester | cp yield ^a | conditions A ^b | yield ^c | conditions B ^t | o yield ^c |
| 1 | R = Piv 1 | 5 80% | | 89% | | 76% |
| 2 | Bz 67 | 68 82% | 3 | 79% | 4 | 19% (+ 53% 3) |
| 3 | Ac 69 | 70 60% | | 81% | | 57% (+ 32% 3) |

^a Isolated yields of *cis*-cyclopropane. Reactions run with 3:1 ratio of propargyl ester:**2** ^b **A**: 5% AgOTf, 5% (ArO)₃PAuCl, CH₂Cl₂. **B**: 5% AgSbF₆, 5% (ArO)₃PAuCl, CH₂Cl₂. ^c Isolated yields

IV. Cyclopropanes

General procedure for the synthesis of 1-alkynyl-2-vinyl-cyclopropanes from enynes and propargyl esters:

A solution of the appropriate enyne (1 equiv) and propargyl ester (3 equiv) in CH_2Cl_2 (0.2 M based on enyne) was added to an externally cooled 1 dram vial containing a stirred suspension of AuCl (0.05 equiv) in CH_2Cl_2 (0.2 M based on enyne) at -25 °C. The resulting mixture (0.1 M based on enyne) was carefully maintained at -25 °C, and the reaction monitored by TLC. Upon consumption of the enyne (15 – 60 min), the reaction mixture was filtered through a silica plug and washed with excess Et_2O . The resulting solution was concentrated under vacuum and purified by silica column chromatography (hexanes/Et₂O).

Compound 5

Enyne 2 and propargyl ester 1 were reacted according to the general procedure. The reaction was quenched after 20 min, and *cis*-5 was isolated as a clear oil in 79% yield following silica column chromatography (2% Et_2O in hexanes). Cyclopropane *trans*-5 was also isolated in 5% yield.



Cycopropane *cis*-5: ¹H NMR (CDCl₃, 500 MHz) δ 7.35 (d, J = 8.0 Hz), 7.27 (m, 3 H), 1.98 (t, 1 H, J = 8.0 Hz), 1.85 (s, 3 H), 1.65 (s, 3 H), 1.42 (s, 3 H), 1.28 (s, 9 H), 1.07 (dd, 1 H, J = 6.5, 4.5 Hz), 0.99 (dd, 1 H, J = 8.5, 4.5 Hz); ¹³C NMR

⁵ (a) Shi, X.; Gorin, D. J.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 5802. (b) Johansson, M. J.; Gorin, D. J.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 18002.

 $(CDCl_3, 100 \text{ MHz}) \delta 176.9, 139.1, 131.6, 128.2, 127.4, 14.2, 122.8, 93.1, 78.6, 39.0, 28.4, 27.3, 24.5, 21.4, 19.1, 17.6, 16.3; HRMS (FAB) Calcd. for [C₂₁H₂₆O₂] 310.1933, Found 310.1934. Important observed ¹H nOe correlations are indicated below:$





Cyclopropane *trans*-5: ¹H NMR (CDCl₃, 400 MHz) δ 7.36 (m, 2 H), 7.25 (m, 3 H), 2.29 (t, 1 H, *J* = 7.5 Hz), 1.85 (s, 3 H), 1.61 (s, 3 H), 1.27 (m, 13 H), 0.71 (dd, 1 H, *J* = 6.5, 5.0 Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 176.4, 137.9, 131.6, 128.1, 127.4, 123.8, 123.6, 95.5, 76.2, 38.9, 28.1, 27.3, 20.8, 19.6, 18.9, 17.5, 14.4; HRMS (FAB) Calcd. for [C₂₁H₂₆O₂] 310.1933, Found 310.1928. Important observed ¹H nOe correlations are indicated below:



Compound 7

Enyne **6** and propargyl ester **1** were reacted according to the general procedure at -25 °C. The reaction was quenched after 30 min, and cyclopropane **7** was isolated as a clear oil in 94% yield following silica column chromatography (2% Et₂O in hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 7.41-7.38 (m, 2H), 7.34-7.27 (m, 3H), 2.02 (m, 1H), 1.89 (s, 3H), 1.68 (d, 3H, J = 1.2 Hz), 1.57 (q, 2H, J = 7.4 Hz), 1.33 (s, 9H), 1.19 (t, 3H, J = 7.4 Hz), 1.10 (dd, 1H, J = 6.4, 4.6 Hz), 1.02 (dd, 1H, J = 8.9, 4.6 Hz); ¹³C NMR (CDCl₃, 100 MHz): δ 177.0, 139.3, 131.7, 128.3, 127.5, 124.5, 122.6, 92.0, 79.9, 39.1, 31.9, 27.5, 22.6, 20.6, 19.2, 17.9, 12.1. HRMS (EI) Calcd. for [C₂₂H₂₈O₂] 324.2089, Found 324.2083.

Compound 11



Enyne **10** and propargyl ester **1** were reacted according to the general procedure. The reaction was quenched after 60 min, and cyclopropane **11** was isolated as a clear oil in 83% yield following silica column chromatography (2% Et₂O in hexanes). ¹H NMR (CDCl₃, 400 MHz) δ 7.37 (d, 1 H, *J* = 7.6 Hz), 7.18 (m, 3 H), 2.41 (s, 3 H), 2.03 (t, 1 H, *J* = 8 Hz), 1.87 (s, 3 H), 1.48 (s,

3 H), 1.39 (s, 3 H), 1.32 (s, 9 H), 1.11 (dd, 1 H, J = 6.4, 4.8 Hz), 1.01 (dd, 1 H, J = 8.8, 4.8 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 176.9, 139.9, 139.1, 131.8, 129.2, 127.3, 125.4, 123.9, 122.8, 97.0, 77.6, 39.0, 28.6, 27.3, 24.6, 21.6, 20.5, 19.0, 17.6, 16.7; HRMS (FAB) Calcd. for [C₂₂H₂₈O₂] 324.2089, Found 324.2085.



Enyne 14 and propargyl ester 1 were reacted according to the general procedure. The reaction was quenched after 30 min, and cyclopropane 15 was isolated as a clear oil in 82% yield following silica column chromatography (5% Et₂O in hexanes). ¹H NMR (CDCl₃, 500 MHz) δ 7.18 (t, 1 H, *J* = 7.5 Hz), 6.93 (d, 1 H, *J* = 7.5 Hz), 6.88 (s, 1 H), 6.81 (d,

1 H, J = 8.0 Hz), 3.78 (s, 3 H), 1.97 (t, 1 H, J = 7.5 Hz), 1.84 (s, 3 H), 1.64 (s, 3 H), 1.42 (s, 3 H), 1.28 (s, 9 H), 1.11 (dd, 1 H, J = 5.5, 5.5 Hz), 1.01 (dd, 1 H, J = 9.0, 4.5 Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 176.8, 159.2, 139.0, 129.1, 125.1, 124.0, 122.7, 116.4, 113.9, 92.9, 78.5, 55.1, 38.9, 28.3, 27.3, 24.3, 21.3, 19.1, 17.6, 16.1; HRMS (FAB) Calcd. for [C₂₂H₂₈O₃] 340.2038, Found 340.2045.

Compound 19



Enyne **18** and propargyl ester **1** were reacted according to the general procedure. The reaction was quenched after 50 min, and cyclopropane **19** was isolated as a clear oil in 72% yield following silica column chromatography (2% Et₂O in hexanes). ¹H NMR (CDCl₃, 400 MHz) δ 7.63 (s, 1 H), 7.52 (m, 2 H), 7.43 (t, 1 H, *J* = 7.6 Hz), 2.04 (t, 1 H, *J* = 8.0

Hz), 1.88, (s, 3 H), 1.68 (s, 3 H), 1.46 (s, 3 H), 1.32 (s, 9 H), 1.28 (dd, 1 H, J = 6.4, 4.8 Hz), 1.06 (dd, 1 H, J = 8.8, 4.8 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 176.8, 139.0, 134.4, 131.0 (q, J = 32 Hz), 128.7, 128.4 (q, J = 4 Hz), 125.1, 123.9 (q, J = 16 Hz), 123.8 (q, J = 260 Hz), 123.0, 95.1, 39.0, 28.6, 27.3, 24.1, 21.5, 19.1, 17.6, 16.1; HRMS (FAB) Calcd. for [C₂₂H₂₅O₂F₃] 378.1807, Found 378.1812.

Compound 23



Enyne **22** and propargyl ester **1** were reacted according to the general procedure. The reaction was quenched after 50 min, and cyclopropane **23** was isolated as a clear oil in 75% yield following silica column chromatography (2% Et₂O in hexanes). ¹H NMR (CDCl₃, 400 MHz) δ 7.25 (m, 3 H), 7.16 (m, 1 H), 2.41 (s, 3 H), 2.07 (t, 1 H, *J* = 8.0 Hz), 1.94 (s, 3 H),

1.74 (s, 3 H), 1.51 (s, 3 H), 1.38 (s, 9 H), 1.15 (dd, 1 H, J = 6.4, 4.8 Hz), 1.08 (dd, 1 H, J = 9.0, 4.8 Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 176.9, 139.1, 137.7, 132.1, 128.5, 128.2, 128.0, 123.9, 122.7, 92.6, 78.7, 38.9, 28.3, 27.2, 24.4, 21.3, 21.2, 19.1, 17.6, 16.2; HRMS (FAB) Calcd. for [C₂₂H₂₈O₂] 324.2089, Found 324.2083.

Compound 27



Enyne **26** and propargyl ester **1** were reacted according to the general procedure at -25 °C. The reaction was quenched after 75 min, and cyclopropane **27** was isolated as a clear oil in 41% yield following silica column chromatography (2% Et₂O in hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 7.20 (d, 1H, *J* = 8.0 Hz), 7.05 (d, 1H, *J* = 8.0 Hz), 2.31 (s, 3H),

1.94 (m, 1H), 1.82 (s, 3H), 1.61 (s, 3H), 1.39 (s, 3H), 1.25 (s, 9H), 1.03 (dd, 1H, *J* = 6.4, 4.7 Hz),

0.95 (dd, 1H, J = 8.9, 4.6 Hz); ¹³C NMR (CDCl₃, 100 MHz): δ 177.1, 139.4, 137.5, 131.6, 129.1, 122.9, 121.3, 92.4, 78.8, 39.2, 28.5, 27.5, 24.7, 21.6, 19.3, 17.8, 16.5. HRMS (EI) Calcd. for [C₂₂H₂₈O₂] 324.2089, Found 324.2079.

Compound 31



Enyne **30** and propargyl ester **1** were reacted according to the general procedure at -25 °C. The reaction was quenched after 30 min, and cyclopropane **31** was isolated as a clear oil in 62% yield following silica column chromatography (2% Et₂O in hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 7.35-7.30 (m, 4H), 2.00 (m, 1H), 1.88 (s, 3H), 1.68 (s, 3H), 1.46

(s, 3H), 1.34 (s, 9H), 1.32 (s, 9H), 1.08 (m, 1H), 1.01 (dd, 1H, J = 8.9, 4.5 Hz); ¹³C NMR (CDCl₃, 100 MHz): δ 177.1, 150.7, 139.4, 131.4, 125.3, 122.9, 121.4, 92.4, 78.8, 39.2, 34.9, 31.4, 28.5, 27.5, 24.7, 21.5, 19.3, 17.8, 16.5. HRMS (EI) Calcd. for [C₂₅H₃₄O₂] 366.2558, Found 366.2561.

Compound 35



Enyne **34** and propargyl ester **1** were reacted according to the general procedure. The reaction was quenched after 40 min, and cyclopropane **35** was isolated as a clear oil in 79% yield following silica column chromatography (2% Et₂O in hexanes). ¹H NMR (CDCl₃, 500 MHz) δ 7.59 (d, 2 H, *J* = 8.0 Hz), 7.05 (d, 2 H, *J* = 8.0 Hz), 1.98 (t, 1 H, *J* = 7.5 Hz), 1.84

(s, 3 H), 1.62 (s, 3 H), 1.40 (s, 3 H), 1.27 (s, 9 H), 1.05 (dd, 1 H, J = 6.0, 4.5 Hz), 0.99 (dd, 1 H, J = 9.0, 4.5 Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 176.7, 138.9, 137.2, 133.0, 123.6, 122.8, 94.7, 92.9, 77.7, 38.9, 28.4, 27.2, 24.2, 21.4, 19.0, 17.6, 16.1; HRMS (FAB) Calcd. for [C₂₁H₂₅O₂I] 436.0899, Found 436.0895.

Compound 39



Enyne **38** and propargyl ester **1** were reacted according to the general procedure. The reaction was quenched after 40 min, and cyclopropane **39** was isolated as a clear oil in 79% yield following silica column chromatography (2% Et₂O in hexanes). ¹H NMR (CDCl₃, 400 MHz) δ 7.46 (d, 2 H, *J* = 8.0 Hz), 7.35 (d, 2 H, *J* = 8.0 Hz), 2.01 (t, 1 H, *J* = 8.0

Hz), 1.88 (s, 3 H), 1.68 (s, 3 H), 1.46 (s, 3 H), 1.32 (s, 9 H), 1.15 (dd, 1 H, J = 6.4, 4.8 Hz), 1.08 (dd, 1 H, J = 8.8, 4.8 Hz), 0.29 (s, 9 H); ¹³C NMR (CDCl₃, 100 MHz) δ 176.9, 139.8, 139.1, 133.1, 130.7, 124.6, 122.8, 93.5, 78.7, 39.0, 28.5, 27.3, 24.4, 21.4, 19.1, 17.6, 16.4, -1.2; HRMS (FAB) Calcd. for [C₂₄H₃₄O₂Si] 282.2328, Found 282.2335.

Compound 43



Enyne 42 and propargyl ester 1 were reacted according to the general procedure at -10 °C with 10% AuCl. The reaction was quenched after 30 min, and cyclopropane 43 was isolated as a clear oil in 87% yield following silica column chromatography (20% EtOAc in hexanes).

¹H NMR (CDCl₃, 400 MHz) δ 7.64 (d, 2H, J = 8.1 Hz), 7.19 (d, 2H, J = 8.1 Hz), 7.15 (d, 2H, J = 8.3 Hz), 6.97 (d, 2H, J = 8.4 Hz), 2.35 (s, 3H), 1.92 (m, 1H), 1.78 (s, 3H), 1.58 (s, 3H), 1.35 (s, 3H), 1.23 (s, 9H), 1.10-0.98 (m, 1H), 0.94 (dd, 1H, J = 8.9, 4.6 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 177.1, 171.5, 144.2, 139.2, 136.1, 132.7, 129.9, 127.4, 123.0, 121.0, 39.1, 28.5, 27.5, 27.2, 24.6, 21.7, 21.5, 21.3, 19.3, 17.8, 16.3, 14.4. HRMS (EI) Calcd. for [C₂₈H₃₃NO₄S] 479.2130, Found 479.2130.

Compound 47



Enyne **42** and propargyl ester **1** were reacted according to the general procedure. The reaction was quenched after 60 min, and cyclopropane **47** was isolated as a clear oil in 73% yield following silica column chromatography (5% Et₂O in hexanes). ¹H NMR (CDCl₃, 400 MHz) δ 8.11 (d, 2 H, *J* = 8.0 Hz), 7.61 (t, 1 H, *J* = 7.6 Hz), 7.49 (t, 2 H, *J* =

7.6 Hz), 7.39 (s, 4 H), 2.02 (t, 1 H, J = 7.6 Hz), 1.88 (s, 3 H), 1.67 (s, 3 H), 1.46 (s, 3 H), 1.32 (s, 9 H), 1.10 (dd, 1 H, J = 6.4, 4.8 Hz), 1.03 (dd, 1 H, J = 8.8, 4.8 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 176.9, 166.4, 139.1, 135.2, 133.1, 131.8, 131.7, 130.1, 129.7, 128.4, 128.0, 124.2, 122.8, 93.7, 78.3, 66.4, 39.0, 28.5, 27.3, 24.4, 21.4, 19.1, 17.6, 16.3; HRMS (EI) Calcd. [C₂₉H₃₂O₄] 444.2301, Found 444.2294.

Compound 51



Enyne **50** and propargyl ester **1** were reacted according to the general procedure. The reaction was quenched after 60 min, and cyclopropane **51** was isolated as a clear oil in 74% yield following silica column chromatography (5% Et₂O in hexanes). ¹H NMR (CDCl₃, 400 MHz) δ 7.32 (m, 4 H), 2.01 (t, 1 H, *J* = 7.6 Hz), 1.89 (s,

3 H), 1.68 (s, 3 H), 1.46 (s, 3 H), 1.32 (s, 9 H), 1.22 (m, 3 H), 1.25 (d, 18 H, J = 6.4 Hz), 1.10 (m, 1 H), 1.03 (dd, 1 H, J = 8.8, 4.8 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 176.9, 141.0, 139.2, 131.4, 125.5, 122.7, 122.5, 92.5, 78.7, 64.8, 39.0, 28.4, 27.3, 24.5, 21.4, 19.1, 18.1, 17.6, 16.3, 12.0; HRMS (EI) Calcd. for [C₃₁H₄₈O₃Si] 496.3373, Found 496.3366.

Compound 55



Enyne **54** and propargyl ester **1** were reacted according to the general procedure at -25 °C. The reaction was quenched after 60 min, and cyclopropane **55** was isolated as a clear oil in 77% yield following silica column chromatography (2% Et₂O in hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 8.29 (d, 1H, *J* = 7.0 Hz), 7.80 (m, 1H), 7.74 (d, 1H, *J* = 8.2 Hz), 7.58 (d, 1H, *J* = 7.1 Hz), 7.49 (m, 2H), 7.38 (t, 1H, *J* = 7.7 Hz), 2.06 (m, 1H), 1.86 (s, 3H),

1.69 (s, 3H), 1.51 (s, 3H), 1.28 (s, 9H), 1.19 (m, 1H), 1.08 (dd, 1H, J = 8.9, 4.7 Hz); ¹³C NMR (CDCl₃, 100 MHz): δ 177.1, 139.4, 133.6, 133.4, 130.1, 128.3, 127.9, 126.7, 126.6, 126.4, 125.4, 123.4, 122.0, 98.2, 39.2, 28.9, 27.5, 24.7, 22.0, 19.3, 17.9, 17.0. HRMS (EI) Calcd. for [C₂₅H₂₈O₂] 360.2089, Found 360.2085.

Enyne **58** and propargyl ester **1** were reacted according to the general procedure. The reaction was quenched after 20 min, and *cis*-**59** was isolated as a clear oil in 50% yield following silica column chromatography (2% Et_2O in hexanes). Cyclopropane *trans*-**59** was also isolated as a clear oil in 12% yield.

PivO n-Pen

Cyclopropane *cis*-**59**: ¹H NMR (C₆D₆, 500 MHz) δ 2.00 (t, 1 H, *J* = 7.0 Hz), 1.82 (t, 1 H, *J* = 8.0 Hz), 1.72 (s, 3 H), 1.66 (s, 3 H), 1.32 (m, 2 H), 1.23 (s, 9 H), 1.19 (s, 3 H), 1.3-1.1 (m, 6 H), 1.05 (dd, 1 H, *J* = 6.0, 4.5 Hz), 0.82 (t, 3 H, *J* = 7.0 Hz), 0.64 (q, 1 H, *J* = 4.5 Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 176.8,

139.4, 122.1, 82.6, 78.5, 38.9, 30.7, 28.7, 27.6, 27.2, 24.8, 22.2, 20.8, 19.0, 18.7, 17.5, 15.8, 13.9; HRMS (FAB) Calcd. for $[C_{20}H_{31}O_2]$ 303.2324, Found 303.2313.





Cyclopropane *trans*-**59**: ¹H NMR (CDCl₃, 400 MHz) δ 2.15 (t, 2 H, J = 7.2 Hz), 2.12 (m, 1 H), 1.89 (s, 3 H), 1.62 (s, 3 H), 1.48 (m, 2 H), 1.38 (m, 6 H), 1.30 (s, 9 H), 1.19 (s, 3 H), 1.12 (dd, 1 H, J = 5.2, 4,4 Hz), 0.93 (t, 3 H, J = 7.2 Hz), 0.59 (dd, 1 H, J = 6.4, 4.4 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 176.5, 138.4, 123.1, 85.8, 76.2, 38.9, 31.0, 28.8, 27.7, 27.3, 22.6, 22.2, 20.4, 20.1, 18.9, 18.7, 17.5, 14.0; HRMS (FAB) Calcd. for [C₂₀H₃₁O₂] 303.2324, Found

303.2317. Important observed ¹H nOe correlations are indicated below:



Compound 62



Enyne **61** and propargyl ester **1** were reacted according to the general procedure at -10° C. The reaction was quenched after 30 min, and cyclopropane **62** was isolated as a clear oil in 74% yield following silica column chromatography (2% Et₂O in hexanes). ¹H NMR (CDCl₃, 400 MHz) δ 2.35 (m, 1H), 1.83-1.76 (m, 1H), 1.78 (s, 3H), 1.65-1.61 (m, 4H), 1.58 (s,

3H), 1.41-1.31 (m, 6H), 1.27 (s, 3H), 1.25 (s, 9H), 0.88-0.79 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 177.0, 139.6, 122.4, 82.5, 82.9, 39.1, 33.0, 28.9, 28.1, 27.5, 26.3, 24.9, 24.4, 21.2, 19.2, 17.7, 16.2. HRMS (EI) Calcd. for [C₂₁H₃₂O₂] 316.2402, Found 316.2401.



Envne 64 and propargyl ester 1 were reacted according to the general procedure. The reaction was quenched after 60 min, and cyclopropane 65 was isolated as a clear oil in 58% yield following silica column chromatography (2% Et₂O in hexanes). ¹H NMR (CDCl₃, 500 MHz) δ 7.28 (d, 2 H, J = 8.0 Hz), 7.18 (m, 3 H), 2.70 (t, 2 H, J = 8.0 Hz), 2.14 (t, 2 H, J =

6.5 Hz), 1.84 (m, 1 H), 1.82 (s, 3 H), 1.74 (pentet, 2 H, J = 7.0 Hz), 1.60 (s, 3 H), 1.33 (s, 3 H), 1.27 (s, 9 H), 0.91 (t, 1 H, J = 5 Hz), 0.86 (dd, 1 H, J = 8.0, 4.5 Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 176.7, 141.8, 139.4, 128.5, 128.2, 125.7, 122.3, 83.4, 77.9, 38.9, 34.3, 30.5, 27.7, 27.2, 24.9, 20.8, 19.0, 18.0, 17.6, 15.9; HRMS (EI) Calcd. for [C₂₄H₃₂O₂] 352.2402, Found 352.2406.

Compound 68



Envne 2 and propargyl ester 67 were reacted according to the general procedure at -25 °C. The reaction was quenched after 30 min, and cyclopropane 68 was isolated as a clear oil in 82% yield following silica column chromatography (2% Et₂O in hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 8.09 (d, 2H, J = 7.2 Hz), 7.54 (t, 1H, J = 7.4 Hz), 7.41-7.34 (m, 4H), 7.30-7.24 (m, 3H), 2.08 (m, 1H), 1.91 (s,

3H), 1.70 (s, 3H), 1.44 (s, 3H), 1.12 (dd, 1H, J = 6.3, 4.8 Hz), 1.00 (dd, 1H, J = 8.9, 4.8 Hz); ¹³C NMR (CDCl₃, 100 MHz): δ 165.1, 139.4, 133.3, 131.8, 130.2, 130.0, 128.6, 128.4, 127.6, 124.3, 123.6, 93.2, 79.0, 28.7, 24.7, 21.8, 19.3, 18.2, 16.6. HRMS (EI) Calcd. for [C₂₃H₂₂O₂] 330.1619, Found 330.1614.

Compound 70



Envne 2 and propargyl ester 69 were reacted according to the general procedure at -10 °C. The reaction was quenched after 15 min, and cyclopropane 70 was isolated as a clear oil in 60% yield following silica column chromatography (2% Et₂O in hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 7.38-7.36 (m, 2H), 7.33-7.29 (m, 3H), 2.01 (m, 1H), 1.89 (s, 3H), 1.71 (s, 3H), 1.47 (s, 3H), 1.12 (dd, 1H, J =

6.3, 4.7 Hz), 1.04 (dd, 1H, J = 9.0, 4.7 Hz); ¹³C NMR (CDCl₃, 100 MHz): δ 169.7, 139.3, 131.7, 128.3, 127.6, 124.2, 123.4, 93.0, 78.9, 28.5, 24.6, 21.5, 20.8, 19.2, 18.0, 16.7. HRMS (EI) Calcd. for [C₁₈H₂₀O₂] 268.1463, Found 268.1463.

Compound 72



Envne 2 and propargyl ester 71 were reacted according to the general procedure at -5 °C. The reaction was quenched after 20 min, and cyclopropane 72 was isolated as a clear oil in 80% yield following silica column chromatography (2% Et₂O in hexanes). ¹H NMR (CDCl₃, 500 MHz) δ 7.36 (d, 2 H, J = 7.5 Hz), 7.27 (m, 3 H), 2.5 (m, 1 H), 2.41 (m, 1 H), 2.31 (m, 1 H), 2.19 (m, 1 H), 1.94 (t, 1 H, J = 7.5 Hz), 1.8-1.6 (m, 4 H), 1.43 (s, 3 H), 1.27 (s, 9 H), 1.13 (t, 1 H, J = 5.0 Hz), 1.00 (dd, 1 H, J = 8.5, 5.0 Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 177.0, 136.8, 134.1, 132.0, 128.5, 127.8, 124.6, 93.6, 79.0, 39.4, 30.0, 29.7, 29.6, 27.7, 27.4, 26.7, 25.2, 21.5, 15.9; HRMS (FAB) Calcd. for [C₂₃H₂₈O₂] 336.2089, Found 336.2086.



Enyne **2** and propargyl ester **75** were reacted according to the general procedure at -25 °C. The reaction was quenched after 15 min, and cyclopropane **76** was isolated as a clear oil in 83% yield following silica column chromatography (2% Et₂O in hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 7.39-7.36 (m, 2H), 7.32-7.28 (m, 3H), 2.38 (m, 2H), 2.24-2.10 (m, 2H), 2.03 (t, 1H, *J* = 7.7 Hz), 1.77 (m, 2H), 1.69-1.52 (m, 6H), 1.51-1.45 (m, 2H), 1.46 (s, 3H), 1.32 (s, 9H), 1.13 (dd, 1H, *J* =

6.5, 4.7 Hz), 1.06 (dd, 1H, J = 8.9, 4.7 Hz); ¹³C NMR (CDCl₃, 100 MHz): δ 177.0, 139.3, 131.9, 131.6, 128.2, 127.5, 124.4, 93.4, 78.9, 39.1, 30.4, 29.0, 28.8, 27.8, 27.5, 26.9, 25.8, 25.2, 24.7, 21.7, 16.0. HRMS (EI) Calcd. for [C₂₆H₃₄O₂Li (M⁺ + Li)] 385.2718, Found 385.2726.

Compound 80



Enyne **2** and propargyl ester **79** were reacted according to the general procedure at -10 °C. The reaction was quenched after 50 min, and cyclopropane **80** was isolated as a clear oil in 59% yield following silica column chromatography (1% Et₂O in hexanes). ¹H NMR (CDCl₃, 500 MHz) δ 7.4-7.2 (m, 5 H), 2.24 (m, 1 H), 2.15 (m, 1 H), 1.95 (m, 3 H), 1.55-1.21 (m, 8 H), 1.42 (s, 3 H), 1.27 (s, 9 H), 1.04 (dd, 1 H, *J* = 6.5, 4.5 Hz), 0.99 (dd, 1 H, *J* = 9.0, 4.5 Hz), 0.93 (t, 3 H, *J* = 7.0 Hz), 0.76 (t, 3 H, *J* = 7.0 Hz); ¹³C NMR (z) δ 176 9 139 5 131 5 131 3 128 0 127 3 124 1 92 9 78 9 38 9 30 5 30 4

 $(CDCl_3, 125 \text{ MHz}) \delta 176.9, 139.5, 131.5, 131.3, 128.0, 127.3, 124.1, 92.9, 78.9, 38.9, 30.5, 30.4, 30.2, 29.2, 28.3, 27.3, 24.4, 22.8, 21.2, 16.3, 14.1, 14.0; HRMS (FAB) Calcd. for <math>[C_{27}H_{38}O_2]$ 394.2872, Found 394.2876.

Compound 84



Enyne 2 and propargyl ester 83 were reacted according to the general procedure. The reaction was quenched after 50 min, and cyclopropane 84 was isolated as a clear oil in 79% yield following silica column chromatography (2% Et_2O in hexanes) as an inseperable 1.2:1 mixture of olefin isomers. ¹H NMR (CDCl₃, 400

MHz) δ The following resonances could be resolved for the major isomer: 2.16 (t, 1 H, J = 7.2 Hz), 1.72 (m, 1 H), 1.58 (s, 3 H), The following resonances could be resolved for the minor isomer: 2.04 (t, 1 H, J = 7.6 Hz), 1.83 (m, 1 H), 1.39 (s, 3 H), The following resonances could not be resolved: 7.5-7.2 (m, 10 H), 1.48 (s, 6 H), 1.31 (s, 18 H), 1.2-1.0 (m, 4 H), 0.8-0.5 (m, 8 H), ; ¹³C NMR (CDCl₃, 100 MHz) δ The following resonances could not be resolved: 177.0, 176.7, 140.3, 140.2, 131.6, 128.1, 127.4, 127.3, 126.5, 126.4, 124.3, 124.2, 93.2, 93.0, 78.8, 78.7, 39.0, 29.1, 28.6, 27.4, 27.3, 24.6, 24.4, 21.6, 21.4, 16.6, 16.3, 12.9, 12.5, 11.4, 11.3, 4.9, 4.3; HRMS (FAB) Calcd. for [C₂₃H₂₈O₂] 336.2089, Found 336.2086.

V. Styrenes

General procedure for the synthesis of styrenes from 1-alkynyl-2-vinyl-cyclopropanes.

The gold catalyst was generated in a 1 dram vial with a threaded cap by addition of AgOTf (0.05) equiv), (2,4-(t-Bu)₂C₆H₃O)₃PAuCl (0.05 equiv), and CH₂Cl₂ (0.2 M based cyclopropane). After stirring for 5 min, the catalyst mixture was cooled to -10 °C, and a solution of the cyclopropane (1 equiv.) in CH₂Cl₂ (0.2 M) was added. The resulting mixture (0.1 M) was maintained at -10 °C. Analysis by TLC generally indicated complete consumption of starting material within minutes, and the reaction mixture was then filtered through a silica plug and washed with excess Et₂O. The resulting solution was concentrated under vacuum and purified by column chromatography (pentane/toluene).

Compound 3



Cyclopropane *cis*-5 was reacted according to the general procedure. The reaction was quenched after 15 min, and styrene 3 was isolated as a clear oil in 89% yield following silica column chromatography (pentane). ¹H NMR (CDCl₃, 500 MHz) δ 7.45 (d, 2 H, J = 8.0 Hz), 7.38 (m, 3 H), 7.24 (d, 1 H, J = 8.5 Hz), 7.12 (s, 2 H), 5.04 (s, 1 H), 4.96 (s, 1 H), 2.38 (s, 3 H), 1.64 (s, 3 H); ¹³C NMR (CDCl₃, 125 MHz) δ 146.3, 142.1, 139.9, 139.5, 136.8, 130.8, 129.0, 128.8, 127.9, 127.8, 126.7, 115.9, 23.6, 21.0; HRMS (FAB) Calcd. for [C₁₆H₁₆] 208.1252, Found 208.1249.

Compound 8



Cyclopropane 7 was reacted according to the general procedure. The reaction was quenched after 15 min, and styrene 8 was isolated as a clear oil in 81% yield following silica column chromatography (hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 7.41 (m, 2H), 7.37-7.28 (m, 3H), 7.24-7.21 (m, 2H), 7.13 (m, 2H), 5.03 (s, 1H), 4.96 (s, 1H), 2.67 (q, 2H, J = 7.6 Hz), 1.64 (s, 3H), 1.26 (t, 3H, J = 7.6 Hz); ¹³C NMR

(CDCl₃, 100 MHz): δ 146.7, 143.4, 142.5, 140.4, 139.7, 129.9, 129.3, 129.1, 128.2, 126.9, 126.8, 116.2, 28.7, 23.8, 15.7. HRMS (EI) Calcd. for [C₁₇H₁₈] 222.1408, Found 222.1408.

Compound 12



Cyclopropane 11 was reacted according to the general procedure. The reaction was quenched after 15 min, and styrene 12 was isolated as a clear oil in 72% yield following silica column chromatography (pentane). ¹H NMR (CDCl₃, 500 MHz) δ 7.18 (m, 6 H), 6.99 (s, 1 H), 4.94 (s, 1 H), 4.82 (s, 1 H), 2.38 (s, 3 H), 2.14 (s, 3 H), 1.67 (s, 3 H); ¹³C NMR (CDCl₃, 125 MHz) δ 45.7, 141.9, 140.1, 139.3, 136.3,

135.7, 130.9, 129.9, 129.7, 128.4, 127.7, 127.0, 125.2, 115.4, 23.3, 21.0, 20.2; HRMS (FAB) Calcd. for [C₁₇H₁₈] 222.1409, Found 222.1406.



Cyclopropane 15 was reacted according to the general procedure. The reaction was quenched after 15 min, and styrene 16 was isolated as an inseperable mixture with the fluorene 17 as a vellow oil in 85% combined yield (31% 16, 54% 17) following silica column chromatography (2% Et₂O in hexanes). The following resonances could be identified for 19: ¹H NMR

 $(CDCl_3, 500 \text{ MHz}) \delta 7.28 \text{ (t. 1 H, } J = 8.0 \text{ Hz}), 7.21 \text{ (d. 1 H, } J = 8.0 \text{ Hz}), 7.15 \text{ (m. 2 H)}, 7.01 \text{ (m$ 2 H), 6.89 (m, 1 H), 5.07 (s, 1 H), 5.0 (s, 1 H), 3.68 (s, 3 H), 2.37 (s, 3 H), 1.68 (s, 3 H); The following resonances could be identified for 19: 13 C NMR (CDCl₃, 125 MHz) δ 146.6, 143.5, 139.9, 139.3, 136.8, 130.7, 129.1, 129.0, 127.9, 121.4, 115.8, 114.4, 112.4, 55.2, 23.6, 21.0; HRMS (FAB) Calcd. for [C₁₇H₁₈O] 238.1358, Found 238.1358.

Compound 20



Cyclopropane **19** was reacted according to the general procedure. The reaction was quenched after 15 min, and styrene 20 was isolated as a clear oil in 93% yield following silica column chromatography (pentane). ¹H NMR (CDCl₃, 500 MHz) δ 7.70 (s, 1 H), 7.61 (d, 1 H, J = 7.5 Hz), 7.57 (d, 1 H, J = 8.0 Hz), 7.48 (t, 1 H, J = 8.0 Hz), 7.22 (d, 1 H, J = 8.0 Hz), 7.17 (d, 1 H, J = 8.0 Hz), 7.13 (s, 1 H), 5.08 (s, 1 H), 4.95 (s, 1 H), 2.37 (s, 3 H), 1.66 (s, 3 H); ¹³C NMR (CDCl₃, 125 MHz) δ 145.6, 142.8, 140.0, 137.8, 137.1, 132.2, 130.6, 130.3 (q, J = 32 Hz), 129.2, 128.5, 128.4, 125.6 (q, J = 4 Hz), 123.4 (q, J = 4 Hz), 124.2 (q, J = 262 Hz), 116.7, 23.7, 21.0; HRMS

Compound 24



Cyclopropane 23 was reacted according to the general procedure. The reaction was quenched after 15 min, and styrene 24 was isolated as a clear oil in 60% yield following silica column chromatography (pentane). Fluorene 25 was also isolated in 19% yield (full characterization below). ¹H NMR (CDCl₃, 500 MHz) δ 7.26 (m, 4 H), 7.14 (m, 3 H), 5.05 (s, 1 H), 4.98 (s, 1 H), 2.39 (s, 3 H), 2.14 (s,

3 H), 1.67 (s, 3 H); ¹³C NMR (CDCl₃, 125 MHz) δ 146.5, 142.0, 139.9, 139.5, 137.5, 136.8, 130.8, 129.5, 129.0, 127.8, 127.7, 127.4, 126.0, 115.8, 23.6, 21.3, 21.0; HRMS (FAB) Calcd. for [C₁₇H₁₈] 222.1409, Found 222.1407.

Compound 28

 CH_3

Cyclopropane 27 was reacted according to the general procedure. The reaction was quenched after 15 min, and styrene 28 was isolated as a clear oil in 58% yield following silica column chromatography (hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 7.29 (d, 2H, J = 8.0), 7.16 (m, 3H), 7.09 (m, 2H), 2.37 (s, 3H), CH₃ 2.36 (s, 3H), 1.63 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 146.9, 140.2, 139.6, 139.4, 137.0, 136.6, 131.1, 129.3, 127.8, 116.0, 23.8, 21.4, 21.3. HRMS (EI) Calcd. for

[C₁₇H₁₈] 222.1408, Found 222.1409.

(FAB) Calcd. for [C₁₇H₁₅F₃] 276.1126, Found 276.1123.



Cyclopropane **31** was reacted according to the general procedure. The reaction was quenched after 15 min, and styrene **32** was isolated as a clear oil in 86% yield following silica column chromatography (hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 7.40-7.34 (m, 4H), 7.20 (d, *J* = 7.6 Hz), 7.14-7.11 (m, 2H), 5.05 (s, 1H), 5.00 (s, 1H), 2.38 (s, 3H), 1.65 (s, 3H), 1.36 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz): δ 149.9, 147.0, 140.2, 139.6, 139.3, 137.0, 131.2, 129.3,

128.6, 127.8, 125.1, 115.9, 34.7, 31.6, 23.8, 21.3, 19.5. HRMS (EI) Calcd. for $[C_{20}H_{24}]$ 264.1878, Found 264.1877.

Compound 36



Cyclopropane **35** was reacted according to the general procedure. The reaction was quenched after 15 min, and styrene **36** was isolated as a clear oil in 83% yield following silica column chromatography (pentane). ¹H NMR (CDCl₃, 400 MHz) δ 7.73 (d, 2 H, *J* = 8.4 Hz), 7.23 (m, 4 H), 7.12 (s, 1 H), 5.10 (s, 1 H), 4.99 (s, 1 H), 2.43 (s, 3 H), 1.72 (s, 3 H); ¹³C NMR (CDCl₃, 100 MHz) δ 146.0,

141.7, 139.9, 138.2, 137.2, 137.1, 130.9, 130.6, 129.2, 128.3, 116.4, 92.6, 23.8, 21.1; HRMS (FAB) Calcd. for $[C_{16}H_{15}I]$ 334.0219, Found 334.0210.

Compound 40



Cyclopropane **39** was reacted according to the general procedure. The reaction was quenched after 15 min, and styrene **40** was isolated as a yellow oil in 95% yield following silica column chromatography (5% toluene in pentane). ¹H NMR (CDCl₃, 400 MHz) δ 7.56 (d, 2 H, *J* = 8.0 Hz), 7.46 (d, 2 H, *J* = 8.0 Hz), 7.23 (m, 1 H), 7.18 (m, 2 H), 5.11 (s, 1 H), 5.03 (s, 1 H), 2.43

(s, 3 H), 1.71 (s, 3 H), 0.35 (s, 9 H); 13 C NMR (CDCl₃, 100 MHz) δ 146.5, 142.5, 140.0, 139.5, 138.6, 136.9, 133.1, 131.0, 129.2, 128.2, 127.9, 116.0, 23.7, 21.1, -1.0; HRMS (FAB) Calcd. for [C₁₉H₂₄Si] 280.1647, Found 280.1644.

Compound 44



Cyclopropane **43** was reacted according to the general procedure. The reaction was quenched after 15 min, and styrene **44** was isolated as a white solid in 71% yield following silica column chromatography (20% EtOAc in hexanes). ¹H NMR (CDCl₃, 500 MHz) δ 7.69 (d, 2 H, *J* = 8.0 Hz), 7.28 (d, 2 H, *J* = 8.5 Hz), 7.22 (d, 2 H, *J* = 8.0 Hz), 7.2-7.1 (m, 5 H), 5.00 (s, 1 H), 4.92

(s, 1 H), 2.38 (s, 3 H), 2.36 (s, 3 H), 1.56 (s, 3 H); 13 C NMR (CDCl₃, 100 MHz) δ 146.2, 143.9, 139.9, 139.4, 138.4, 137.0, 136.0, 135.3, 130.6, 129.8, 129.6, 129.2, 128.0, 127.4, 121.5, 116.2, 23.5, 21.6, 21.0; HRMS (FAB) Calcd. for [C₂₃H₂₂NO₂S] 377.1450, Found 377.1448.



Cyclopropane 47 was reacted according to the general procedure. The reaction was guenched after 15 min, and styrene 48 was isolated as a clear oil in 89% yield following silica column chromatography (2% Et₂O in hexanes). ¹H NMR (CDCl₃, 400 MHz) δ 8.16 (d, 2 H, J = 8.0 Hz), 7.63 (t, 1 H, J = 7.2 Hz), 7.5 (m, 6 H), 7.3-7.1 (m, 3 H), 5.46 (s, 2 H), 5.10 (s, 1 H),

5.02 (s, 1 H), 2.43 (s, 3 H), 1.72 (s, 3 H); ¹³C NMR (CDCl₃, 125 MHz) δ 166.5, 146.2, 142.1, 139.9, 138.9, 136.9, 134.4, 133.0, 130.8, 130.1, 129.7, 129.1, 129.0, 128.4, 128.0, 127.8, 116.1, 66.5, 23.7, 21.0; HRMS (EI) Calcd. for [C₂₄H₂₂O₂] 342.1620, Found 342.1620.

Compound 52



Cyclopropane 51 was reacted according to the general procedure. The reaction was quenched after 15 min, and styrene 52 was isolated as a clear oil in 64% yield following silica column chromatography (1% Et₂O in hexanes). ¹H NMR (CDCl₃, 400 MHz) δ 7.43 (d, 2 H, J = 8.4 Hz), 7.38 (d, 2 H, J = 8.4 Hz), 7.23 (d, 1 H, J = 8.0 Hz), 7.15 (m, 2 H), 5.08 (s, 1 H),

5.01 (s, 1 H), 4.92 (s, 2 H), 2.42 (s, 3 H), 1.69 (s, 3 H), 1.24 (m, 3 H), 1.20 (d, 18 H, *J* = 5.6 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 146.6, 140.6, 140.2, 140.0, 139.4, 136.8, 131.0, 129.1, 128.7, 127.7, 125.4, 115.9, 65.0, 23.6, 21.1, 18.1, 12.1; HRMS (EI) Calcd. for [C₂₆H₃₈OSi] 394.2692, Found 394.2687.

Compound 56



Cyclopropane 55 was reacted according to the general procedure. The reaction was quenched after 15 min, and styrene 56 was isolated as a white solid in 69% yield following silica column chromatography (pentane). Fluorene 57 was also isolated in 7% yield (full characterization below). ¹H NMR (CDCl₃, 400 MHz): δ 7.86 (dd, 2H, J = 16.8, 8.2 Hz), 7.65 (d, 1H, J = 8.4 Hz), 7.50-7.46 (m, 2H),

7.41-7.37 (m, 2H), 7.32 (d, 1H, J = 7.8 Hz), 7.23 (d, 1H, J = 7.8 Hz), 7.14 (s, 1H), 4.82 (s, 2H), 2.41 (s, 3H), 1.55 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 145.8, 141.3, 140.2, 138.2, 136.5, 133.7, 132.4, 132.1, 128.7, 128.4, 128.2, 127.5, 127.4, 126.8, 125.9, 125.8, 125.3, 115.8, 23.8, 21.3. HRMS (EI) Calcd. for [C₂₀H₁₈] 258.1408, Found 258.1408.

Compound 60



Cyclopropane *cis*-59 was reacted according to the general procedure. The reaction was quenched after 15 min, and styrene 60 was isolated as a clear oil in 65% yield following silica column chromatography (pentane). ¹H NMR (CDCl₃, 500 MHz) δ 6.97 (m, 3 H), 5.16 (s, 1 H), 4.92 (s, 1 H), 2.57 (t, 2 H, J = 8.0 Hz), 2.32 (s, 3 H), 2.02 (s, 3 H), 1.55 (m, 2 H), 1.33 (m, 4 H), 0.89 (t, 3 H, J = 7.0 Hz); ¹³C NMR (CDCl₃, 125 MHz) & 145.6, 140.7, 139.3, 136.2, 129.7, 128.0, 126.1, 114.5, 32.9, 32.0, 31.5. 25.3, 22.5, 21.1, 14.0; HRMS (FAB) Calcd. for [C₁₅H₂₂] 202.1722, Found 202.1726.



Cyclopropane **62** was reacted according to the general procedure. The reaction was quenched after 15 min, and styrene **63** was isolated as a clear oil in 53% yield following silica column chromatography (hexanes). ¹H NMR (CDCl₃, 400 MHz) δ 7.12 (s, 1 H), 7.01 (m, 2 H), 5.20 (s, 1 H), 4.84 (s, 1 H), 2.77 (m, 1 H), 2.38 (s, 3 H), 2.07 (s, 3 H), 1.83 (m, 5 H), 1.42 (m, 5 H); ¹³C NMR (CDCl₃, 100 MHz)

δ 146.0, 144.5, 140.3, 136.4, 128.0, 126.9, 126.1, 114.6, 40.3, 34.9, 27.1, 26.3, 25.9, 21.3; HRMS (FAB) Calcd. [C₁₆H₂₂] 214.1722, Found 214.1724.

Compound 66



Cyclopropane **65** was reacted according to the general procedure. The reaction was quenched after 15 min, and styrene **66** was isolated as a clear oil in 66% yield following silica column chromatography (1% Et₂O in hexanes). ¹H NMR (CDCl₃, 400 MHz) δ 7.28 (m, 2 H), 7.19 (m, 3 H), 6.99 (m, 3 H), 5.15 (s, 1 H), 4.82 (s, 1 H), 2.67 (m, 4 H), 2.33 (s, 3 H), 2.02 (s, 3 H), 1.92 (m, 2 H); ¹³C

NMR (CDCl₃, 100 MHz) δ 145.5, 142.4, 140.8, 138.7, 136.3, 129.8, 128.4, 128.2, 128.1, 126.3, 125.7, 114.7, 36.0, 33.3, 32.7, 25.2, 21.1; HRMS (EI) Calcd. for [C₁₉H₂₂] 250.1722, Found 250.1722.

Compound 73



Cyclopropane **72** was reacted according to the general procedure. The reaction was quenched after 15 min, and styrene **73** was isolated as a clear oil in 89% yield following silica column chromatography (5% toluene in pentane). ¹H NMR (CDCl₃, 400 MHz) δ 7.40 (m, 6 H), 7.18 (d, 2 H, *J* = 6.4 Hz), 5.63 (s, 1 H), 2.44 (s, 3 H), 2.39 (m, 2 H), 2.22 (m, 2 H), 1.83 (quintet, 2 H, *J* = 7.2 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 144.1, 142.7, 140.2, 136.6, 134.7, 131.0, 129.6, 129.0, 128.9,

127.9, 127.8, 126.7, 35.7, 33.2, 24.2, 21.2; HRMS (FAB) Calcd. for [C₁₈H₁₈] 234.1409, Found 234.1405.

Compound 77



Cyclopropane **76** was reacted according to the general procedure. The reaction was quenched after 15 min, and styrene **77** was isolated as a white solid in 91% yield following silica column chromatography (hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 7.45 (m, 2H), 7.34 (m, 2H), 7.30-7.26 (m, 1H), 7.15-7.09 (m, 3H), 5.72 (t, 1H, *J* = Hz), 2.38 (s, 3H), 2.19 (m, 2H), 1.92 (m, 2H), 1.54 (m, 2H), 1.51-1.43 (m, 4H), 1.28-1.19 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 142.8, 142.5, 141.0, 139.4, 136.6, 131.0, 130.4, 130.3, 129.2, 128.1, 127.8, 126.8, 30.2, 28.4, 27.1,

26.8, 26.6, 21.3. HRMS (EI) Calcd. for [C₂₁H₂₄] 276.1878, Found 276.1878.



Cyclopropane **80** was reacted according to the general procedure. The reaction was quenched after 15 min, and styrene **81** was isolated as a clear oil in 77% yield (8.3:1 (E:Z) mixture of olefin isomers) following silica column chromatography (5% toluene in pentane). ¹H NMR (CDCl₃, 500 MHz) δ The following resonances could be resolved for the major isomer: 7.43 (m, 2 H), 7.33 (m, 4 H), 7.15 (m, 2 H), 5.45 (t, 1 H, *J* = 7.0 Hz), 2.40 (s, 3 H), 2.08 (q, 2 H, *J* = 7.0 Hz), 1.83 (t, 2 H, *J* = 7.0 Hz), 1.43 (t, 2 H, *J* = 7.0 Hz), 1.10 (m, 4 H), 0.95 (t, 3 H, *J* = 7.5 Hz), 0.75

(t, 3 H, J = 7.0 Hz); ¹³C NMR (CDCl₃, 125 MHz) δ The following resonances could be resolved for the major isomer: 142.2, 141.6, 140.7, 139.5, 136.1, 131.1, 130.7, 130.2, 129.0, 127.8, 127.6, 126.5, 30.5, 30.4, 30.3, 22.8, 22.6, 21.0, 13.9, 13.8; HRMS (FAB) Calcd. for [C₂₂H₂₈] 292.2191, Found 292.2201. Important observed ¹H nOe correlations for the major olefin isomer are indicated below:



Compound 85

Cyclopropane **84** was reacted according to the general procedure at room temperature. The reaction was quenched after 100 min, and styrene **85** was isolated as a clear oil in 72% yield following silica column chromatography (5% toluene in pentane). Fluorene x was also isolated in 16% yield. ¹H NMR (CDCl₃, 500 MHz) δ 7.69 (d, 2 H, *J* = 7.5 Hz), 7.43 (m, 2 H), 7.32 (m, 1 H), 7.16 (m, 3 H), 4.88 (s, 1 H), 4.87 (s, 1 H), 2.44 (s, 3 H), 1.19 (m, 1 H), 0.49 (m, 2 H), 0.37 (m, 2 H); ¹³C NMR (CDCl₃, 100 MHz) δ 151.9, 142.3, 139.8, 139.2, 136.9, 130.9, 129.6, 129.4, 127.8, 127.7, 126.6, 111.2, 21.1 17.0, 7.8; HRMS (FAB) Calcd. for [C₁₈H₁₈] 234.1409, Found 234.1407.

VI. Fluorenes

General procedure for the synthesis of fluorenes from 1-alkynyl-2-vinyl-cyclopropanes.

The gold catalyst was generated in a 1 dram vial with a threaded cap by addition of $AgSbF_6$ (0.05 equiv), ((2,4-(*t*-Bu)₂C₆H₃)O)₃PAuCl (0.05 equiv.), and CH₂Cl₂ (0.2 M based cyclopropane). After stirring for 5 min, a solution of the cyclopropane (1 equiv) in CH₂Cl₂ (0.2 M) was added. The resulting mixture (0.1 M) was maintained at room temperature unless otherwise noted. Analysis by TLC generally indicated complete consumption of starting material within minutes, and the reaction mixture was then filtered through a silica plug and washed with excess Et₂O. The resulting solution was concentrated under vacuum and purified by column chromatography (pentane/toluene).



Cyclopropane *cis*-5 was reacted according to the general procedure at -10 °C. The reaction was quenched after 20 min, and fluorene 4 was isolated as a clear oil in 76% yield following silica column chromatography (5% toluene in pentane). ¹H NMR (CDCl₃, 500 MHz) δ 7.22 (d, 1 H, *J* = 6.5 Hz), 7.57 (s, 1 H), 7.44 (d, 1 H, *J* = 6.5 Hz), 7.33 (m, 3 H), 7.15 (d, 1 H, *J* = 7.5 Hz), 2.46 (s, 3 H), 1.49 (s, 6 H);

 13 C NMR (CDCl₃, 125 MHz) δ 153.9, 150.1, 139.3, 139.2, 136.5, 128.0, 127.0, 126.8, 122.5, 122.2, 120.5, 119.8, 46.4, 27.2, 21.5; HRMS (FAB) Calcd. for [C₁₆H₁₆] 208.1252, Found 208.1252.

Compound 9



Cyclopropane 7 was reacted according to the general procedure at room temperature. The reaction was quenched after 15 min, and fluorene 9 was isolated as a clear oil in 79% yield following silica column chromatography (5% toluene in pentane). Styrene 8 was also isolated in 9% yield. ¹H NMR

(CDCl₃, 400 MHz): δ 7.71-7.69 (m, 1H), 7.55 (s, 1H), 7.41-7.40 (m, 1H), 7.34-7.26 (m, 3H), 7.14 (d, 1H, *J* = 7.6 Hz), 2.72 (q, 2H, *J* = 7.6 Hz), 1.46 (s, 6H), 1.29 (t, 3H, *J* = 7.6 Hz); ¹³C NMR (CDCl₃, 100 MHz): δ 154.2, 151.3, 143.3, 139.5, 127.3, 127.2, 127.1, 122.8, 122.6, 120.1, 119.6, 46.7, 29.2, 27.4, 16.1. HRMS (EI) Calcd. for [C₁₇H₁₈] 222.1408, Found 222.1409.

Compound 13



Cyclopropane **11** was reacted according to the general procedure at -10 °C. The reaction was quenched after 20 min, and fluorene **13** was isolated as a white solid in 66% yield following silica column chromatography (5% toluene in pentane). ¹H NMR (CDCl₃, 400 MHz) δ 7.75 (s, 1 H), 7.41 (d, 1 H, *J* = 7.6 Hz), 7.35 (d, 1 H, *J* = 7.6 Hz), 7.28 (t, 1 H, *J* = 7.2 Hz), 7.21 (d, 1 H, *J* = 7.6 Hz), 7.17 (d, 1 H, *J*

= 7.2 Hz); 2.79 (s, 3 H), 2.53 (s, 3 H), 1.53 (s, 6 H); ¹³C NMR (CDCl₃, 125 MHz) δ 154.5, 151.3, 140.4, 137.2, 136.4, 133.2, 129.2, 127.4, 126.8, 124.0, 122.2, 120.1, 46.0, 27.6, 21.8, 21.2; HRMS (FAB) Calcd. for [C₁₇H₁₈] 222.1409, Found 222.1406.

Compound 17



Cyclopropane **15** was reacted according to the general procedure at -10 °C. The reaction was quenched after 20 min, and fluorene **17** was isolated as a clear oil in 75% yield following silica column chromatography (2% Et₂O in hexanes). ¹H NMR (CDCl₃, 400 MHz) δ 7.58 (s, 1 H), 7.37 (d, 2 H, *J* = 8.0 Hz), 7.30 (s, 1 H), 7.19 (d, 1 H, *J* = 7.6 Hz), 6.92 (dd, 1 H, *J* = 8.0, 2.8 Hz),

3.94 (s, 3 H), 2.50 (s, 3 H), 1.51 (s, 6 H); 13 C NMR (CDCl₃, 125 MHz) δ 159.2, 151.7, 146.3, 140.5, 139.1, 136.5, 128.2, 123.1, 122.3, 120.5, 113.2, 104.9, 55.5, 45.9, 27.3, 21.5; HRMS (FAB) Calcd. for [C₁₇H₁₈O] 238.1358, Found 238.1351. The regioisomer was assigned based on the coupling constants of the aromatic protons.



The minor regioisomer could also be isolted by silica column chromatography (2% Et₂O in hexanes). ¹H NMR (CDCl₃, 500 MHz) δ 7.53 (s, 1 H), 7.33 (m, 3 H), 7.15 (d, 1 H, *J* = 7.5 Hz), 6.82 (d, 1 H, *J* = 8.5 Hz), 3.93 (s, 3 H), 2.45 (s, 3 H), 1.57 (s, 6 H); ¹³C NMR (CDCl₃, 125 MHz) δ 156.7, 151.7, 141.0, 139.6, 139.2, 136.3, 128.3, 128.1, 121.9, 120.6, 112.4, 109.4, 55.1, 47.3, 24.5, 21.4; HRMS for [C] U O O 228 1258. Found 228 1255.

(FAB) Calcd. for $[C_{17}H_{18}O]$ 238.1358, Found 238.1355. The regioisomer was assigned based on the coupling constants of the aromatic protons.

Compound 21



Cyclopropane **19** was reacted according to the general procedure at -10 °C. The reaction was quenched after 20 min, and fluorene **21** was isolated as a mixture with styrene **20** (2.5:1 styrene:fluorene) in 87% combined yield following silica column chromatography (5% toluene in pentane). The

fluorene was formed as a 1:1 mixture of regioisomers. In order to obtain analytically pure **21** for characterization purposes, the product mixture was subjected to the oxidative cleavage conditions of Shing⁶ to functionalize the styrene **20**. Pure fluorene was thus obtained as a 1:1 mixture of regioisomers. ¹H NMR (CDCl₃, 400 MHz) δ The following resonances could not be assigned to either isomer: 7.97 (d, 1 H, *J* = 5.6 Hz), 7.95 (d, 1 H, *J* = 7.2 Hz), 7.65-7.45 (m, 6 H), 7.38 (m, 2 H), 7.24 (m, 2 H), 2.50 (s, 6 H), 1.63 (s, 9 H), 1.53 (s, 3 H); ¹³C NMR (CDCl₃, 100 MHz) δ The following resonances could not be assigned to either isomers could not be assigned to either isomers. 157.5, 152.0, 150.9, 150.2, 142.2, 140.0, 138.0, 137.1, 136.8, 129.3, 129.1, 127.4, 127.1, 126.8, 126.1, 125.2 (q, *J* = 6 Hz), 124.0 (q, *J* = 4 Hz), 123.4, 122.9, 122.5, 122.1, 121.0, 120.2, 116.8 (q, *J* = 3 Hz), 48.9, 46.8, 27.0, 26.1, 26.0, 21.5, 21.4; HRMS (FAB) Calcd. for [C₁₇H₁₅F₃] 276.1126, Found 276.1121.

Compound 25



Cyclopropane 23 was reacted according to the general procedure at -10 °C. The reaction was quenched after 20 min, and fluorene 25 was isolated as a 1.6:1 mixture of regioisomers (meso:not) in 85% yield following silica column chromatography (5% toluene in pentane). ¹H NMR (CDCl₃,

500 MHz) δ The following resonances could be resolved for the major (meso) isomer: 7.55 (m, 2 H), 7.33 (m, 2 H), 7.16 (m, 2 H), 2.47 (s, 6 H), 1.49 (s, 6 H), The following resonances could be resolved for the minor isomer: 7.59 (d, 1 H, J = 7.5 Hz), 7.55 (m, 1 H), 7.33 (m, 1 H), 7.26 (t, 1 H, J = 7.5 Hz), 7.16 (m, 1 H), 7.08 (d, 1 H, J = 7.5 Hz), 2.70 (s, 3 H), 2.47 (s, 3 H), 1.60 (s, 6 H); ¹³C NMR (CDCl₃, 125 MHz) δ The following resonances could be resolved for the major (meso) isomer: 151.2, 139.3, 136.5, 127.9, 122.2, 120.5, 46.1, The following resonances could be resolved for the minor isomer: 151.5, 150.4, 139.8, 139.1, 134.1, 129.7, 128.1, 127.0, 121.9, 120.3, 117.5, 114.5, 47.6, The following resonances could not be resolved: 27.3, 24.5, 21.5, 19.0; HRMS (FAB) Calcd. for [C₁₇H₁₈] 222.1409, Found 222.1409.

⁶ Shing, T. K. M.; Tam, E. K. W.; Tai, V. W.-F.; Chung, I. H. F.; Jiang Q. Chem. Eur. J. 1996, 2, 50.



Cyclopropane 27 was reacted according to the general procedure at room temperature. The reaction was quenched after 15 min, and fluorene 29 was isolated as a clear oil in 76% yield following silica column chromatography (5% toluene in pentane). ¹H NMR (CDCl₃, 400 MHz): δ

7.57 (d, 1H, J = 7.7 Hz), 7.49 (s, 1H), 7.29 (d, 1H, J = 7.6 Hz), 7.22 (s, 1H), 7.12 (d, 1H, J = 7.7 Hz), 7.09 (d, 1H, J = 7.6 Hz), 2.42 (s, 6H), 1.44 (s, 6H); ¹³C NMR (CDCl₃, 125 MHz): δ 154.4, 150.9, 139.6, 137.2, 136.8, 136.7, 127.9, 127.8, 123.5, 122.4, 120.5, 119.8, 46.5, 27.5, 22.0, 21.7. HRMS (EI) Calcd. for [C₁₇H₁₈] 222.1408, Found 222.1412.

Compound 33



Cyclopropane 31 was reacted according to the general procedure at room temperature. The reaction was quenched after 15 min, and fluorene 33 was isolated as a clear oil in 93% yield following silica column chromatography (5% toluene in pentane). ¹H NMR (CDCl₃, 400 MHz): δ

7.61 (d, 1H, J = 8.0 Hz), 7.50 (s, 1H), 7.43 (s, 1H), 7.36 (d, 1H, J = 8.0 Hz), 7.30 (d, 1H, J = 7.6Hz), 7.09 (d, 1H, J = 7.6 Hz), 2.43 (s, 3H), 1.47 (s, 6H), 1.38 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz): 8 154.0, 151.3, 150.7, 139.6, 136.8, 136.6, 127.8, 125.1, 124.2, 122.4, 120.6, 119.5, 46.7, 35.2, 31.9, 27.6, 21.7. HRMS (EI) Calcd. for [C₂₀H₂₄] 264.1878, Found 264.1876.

Compound 37



Cyclopropane 35 was reacted according to the general procedure at room temperature. The reaction was quenched after 20 min, and fluorene 37 was isolated as a clear oil in 63% yield following silica column chromatography (5% toluene in pentane). Styrene **36** was also isolated in 17% yield. ¹H NMR $(CDCl_3, 500 \text{ MHz}) \delta 7.75 \text{ (s, 1 H)}, 7.65 \text{ (d, 1 H, } J = 8.0 \text{ Hz}), 7.51 \text{ (s, 1 H)}, 7.44$ (d, 1 H, J = 8.0 Hz), 7.31 (d, 1 H, J = 7.5 Hz), 7.17 (d, 1 H, J = 8.0 Hz), 2.44 (s, 3 H), 1.45 (s, 6 H); ¹³C NMR (CDCl₃, 125 MHz) δ 156.2, 150.2, 138.8, 138.3, 136.8, 135.9, 132.0, 128.7, 122.3, 121.6, 120.6, 92.3, 46.7, 27.0, 21.5; HRMS (FAB) Calcd. for [C16H15I] 334.0219, Found 334.0219.

Compound 41



Cyclopropane 39 was reacted according to the general procedure at room temperature. The reaction was quenched after 20 min, and fluorene 41 was isolated as a clear oil in 59% yield following silica column chromatography (5% toluene in pentane). The desilvlated fluorene 4 was isolated in 14% yield. ¹H NMR (CDCl₃, 500 MHz) δ 7.69 (d, 1 H, J = 7.5 Hz), 7.55 (s, 2 H),

7.49 (d, 1 H, J = 7.0 Hz), 7.32 (d, 1 H, J = 8.0 Hz), 7.14 (d, 1 H, J = 8.0 Hz), 2.44 (s, 3 H), 1.46 (s, 6 H), 0.32 (s, 9 H); ¹³C NMR (CDCl₃, 125 MHz) δ 153.1, 151.0, 140.1, 139.1, 139.0, 136.5, 132.0, 128.2, 127.2, 122.2, 120.7, 119.2, 46.4, 27.2, 21.5, -0.9; HRMS (FAB) Calcd. for [C₁₉H₂₄Si] 280.1647, Found 280.1650.



Cyclopropane **43** was reacted according to the general procedure at -10 °C. The reaction was quenched after 20 min, and fluorene **45** was isolated as a white solid in 60% yield following silica column chromatography (10% EtOAc in hexanes). ¹H NMR (CDCl₃, 400 MHz) δ 7.64 (d, 1H, *J* = 8.2 Hz), 7.48 (d, 1H, *J* = 8.1), 7.24-7.22 (m, 1H), 7.16-7.12 (m, 3H), 7.03 (d, 1H, *J* =

8.3 Hz), 6.80 (s, 1H), 6.58 (broad s, 1H), 2.38 (s, 3H), 2.29 (s, 3H), 1.36 (s, 6H); 13 C NMR (CDCl₃, 100 MHz) δ 144.2, 143.6, 141.5, 139.1, 136.2, 136.0, 135.6, 132.9, 130.7, 129.9, 128.5, 127.5, 126.1, 121.3, 74.0, 32.8, 21.8, 20.8. HRMS (EI) Calcd. for [C₂₃H₂₄NO₂S] 378.1527, Found 378.1537.

Compound 49



Cyclopropane **47** was reacted according to the general procedure at -10 °C. The reaction was quenched after 20 min, and fluorene **49** was isolated as a clear oil in 71% yield following silica column chromatography (2% Et₂O in hexanes). ¹H NMR (CDCl₃, 500 MHz) δ 8.13 (d, 2 H, *J* = 7.0 Hz), 7.73 (d, 1 H, *J* = 8.0 Hz), 7.59 (m, 2 H), 7.52 (s, 1 H), 7.45 (m, 3 H), 7.35 (d, 1 H, *J*

= 7.5 Hz), 7.17 (d, 1 H, J = 8.0 Hz), 2.47 (s, 3 H), 1.51 (s, 6 H); ¹³C NMR (CDCl₃, 125 MHz) δ 167.0, 154.8, 151.5, 139.9, 139.3, 137.1, 135.2, 133.5, 130.7, 130.2, 128.8, 128.7, 127.8, 123.2, 122.8, 121.2, 120.4, 67.6, 47.0, 27.7, 22.0; HRMS (EI) Calcd. for [C₂₄H₂₂O₂] 342.1620, Found 342.1617.

Compound 53



Cyclopropane **51** was reacted according to the general procedure at -10 °C. The reaction was quenched after 20 min, and fluorene **53** was isolated as a clear oil in 90% yield following silica column chromatography (1% Et₂O in hexanes). ¹H NMR (CDCl₃, 500 MHz) δ 7.68 (d, 2 H, *J* = 7.5 Hz), 7.56 (s, 1 H), 7.47 (s, 1 H), 7.34 (d, 2 H, *J* = 7.5

Hz), 7.14 (d, 1 H, J = 8.0 Hz), 2.47 (s, 3 H), 1.53 (s, 6 H), 1.24 (m, 3 H), 1.15 (d, 18 H, J = 5.6 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 154.1, 151.0, 140.9, 139.4, 138.0, 136.5, 127.8, 124.6, 122.3, 120.5, 120.3, 119.6, 65.5, 46.4, 27.3, 23.4, 21.6, 18.1, 12.2; HRMS (EI) Calcd. for [C₂₆H₃₈OSi] 394.2692, Found 394.2689.

Compound 57



Cyclopropane **55** was reacted according to the general procedure at room temperature. The reaction was quenched after 15 min, and fluorene **57** was isolated as white solid in 79% yield following silica column chromatography (5% toluene in pentane). ¹H NMR (CDCl₃, 400 MHz): δ 8.76 (d, 1H, *J* = 8.4 Hz), 8.16 (s, 1H), 7.94 (d, 1H, *J* = 8.1 Hz), 7.84 (d, 1H, *J* = 8.3 Hz), 7.66-

7.59 (m, 2H), 7.51 (m, 1H), 7.42 (d, 1H, *J* = 7.6 Hz), 7.18 (d, 1H, *J* = 7.4 Hz), 2.54 (s, 3H), 1.52 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 152.7, 151.9, 140.5, 136.6, 133.6, 133.3, 129.7, 129.2,

128.2, 127.1, 126.5, 124.9, 124.0, 123.9, 122.1, 120.9, 46.3, 26.8, 21.9. HRMS (EI) Calcd. for [C₂₀H₁₈] 258.1408, Found 258.1409.

Compound 74



Cyclopropane 72 was reacted according to the general procedure at room temperature. The reaction was quenched after 20 min, and fluorene 74 was isolated as a white solid in 63% yield following silica column chromatography (5% toluene in pentane). Styrene **73** was also isolated in 24% yield. ¹H NMR $(CDCl_3, 400 \text{ MHz}) \delta 7.74 \text{ (d, 1 H, } J = 6.4 \text{ Hz}), 7.58 \text{ (s, 1 H)}, 7.48 \text{ (d, 1 H, } J = 6.8 \text{ Hz})$ Hz), 7.36 (m, 3 H), 7.17 (d, 1 H, J = 7.2 Hz), 2.50 (s, 3 H), 2.15 (m, 8 H); ¹³C NMR (CDCl₃, 100

MHz) & 154.6, 151.4, 139.7, 139.6, 136.3, 128.3, 127.3, 126.7, 122.9, 122.6, 120.2, 119.5, 57.4, 40.0, 26.9, 21.5; HRMS (FAB) Calcd. for [C₁₈H₁₈] 234.1409, Found 234.1405.

Compound 78



Cyclopropane 76 was reacted according to the general procedure at room temperature. The reaction was quenched after 15 min, and fluorene 78 was isolated as a white solid in 66% yield following silica column chromatography (5% toluene in pentane). Styrene 77 was also isolated in 21% yield. ¹H NMR (CDCl₃, 400 MHz): δ 7.68 (d, 1H, J = 7.2 Hz), 7.54-7.52 (m, 2H), 7.43 (d, 1H, J = 7.7 Hz), 7.31 (dt, 1H, J = 7.3, 1.2 Hz), 7.26 (dd, 1H, J = 7.3, 1.2 Hz),

7.09 (d, 1H, J = 7.7 Hz), 2.42 (s, 3H), 1.92 (m, 8H), 1.85 (m, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 154.5, 151.3, 139.6, 139.4, 136.6, 128.0, 127.0, 126.9, 124.1, 123.9, 120.7, 120.0, 53.3, 34.2, 29.4, 26.4, 25.3, 21.6. HRMS (EI) Calcd. for [C₂₁H₂₄] 276.1878, Found 276.1876.

Compound 82



Cyclopropane 80 was reacted according to the general procedure at room temperature. The reaction was quenched after 20 min, and fluorene 82 was isolated as a clear oil in 84% yield following silica column chromatography (5% toluene in pentane). ¹H NMR (CDCl₃, 500 MHz) δ 7.68 (d, 1 H, J = 7.0 Hz), 7.53 (s, 1 H), 7.31 (m, 3 H), 7.22 (d, 1 H, J = 7.5 Hz), 7.12 (d, 1 H, J = 8.0 Hz), 2.57 (s, 3 H), 1.94 (dd, 4 H, J = 9.5, 7.5 Hz), 1.97 (sextet, 4 H, J = 7.5

Hz), 0.68 (t, 6 H, J = 7.5 Hz), 0.62 (m, 4 H); ¹³C NMR (CDCl₃, 100 MHz) δ 151.0, 147.7, 141.2, 141.1, 136.2, 127.9, 126.8, 126.6, 122.8, 122.5, 120.2, 119.4, 54.5, 40.2, 25.9, 23.1, 21.5, 13.8; HRMS (FAB) Calcd. for [C₂₂H₂₈] 292.2191, Found 292.2196.

Compound 86



Cyclopropane 84 was reacted according to the general procedure at room temperature. The reaction was quenched after 20 min, and fluorene 86 was isolated as a clear oil in 84% yield following silica column chromatography (5% toluene in pentane). ¹H NMR (CDCl₃, 400 MHz) δ 7.74 (d, 1 H, J = 7.2 Hz), 7.59 (s, 1 H), 7.47 (d, 1 H, J = 7.2 Hz), 7.35 (m, 3 H), 7.16 (d, 1 H, J = 7.6 Hz), 2.50 (s,

3 H), 1.45 (s, 3 H), 1.18 (m, 1 H), 0.43 (m, 2 H), 0.28 (m, 2 H); ¹³C NMR (CDCl₃, 100 MHz) δ

VII. Experimental procedures for reactions with any proparyl esters 90 and 94

Compound 91



Enyne 2 and propargyl ester 90 were reacted according to the general procedure at -5 °C. The reaction was quenched after 30 min, and cyclopropane 91 was isolated as a clear oil in 91% yield (1:2 (E:Z) mixture of olefin isomers) following silica column chromatography (2% Et₂O in hexanes). The

olefin isomers were used as a mixture in the subsequent steps, although they could be separated chromatographically for characterization purposes.

(*E*)-ISOMER: ¹H NMR (CDCl₃, 500 MHz) δ 7.42 (d, 2 H, *J* = 7.5 Hz), 7.34 (m, 4 H), 7.25 (m, 4 H), 6.46 (s, 1 H), 2.16 (t, 1 H, *J* = 7.5 Hz), 1.48 (s, 3 H), 1.29 (s, 9 H), 1.17 (t, 1 H, *J* = 5.5 Hz), 1.06 (dd, 1 H, *J* = 8.5, 5.0 Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 176.9, 147.0, 134.7, 131.7, 128.9, 128.1, 128.9, 127.5, 126.9, 123.8, 120.9, 91.9, 79.2, 39.0, 29.1, 27.2, 24.4, 21.7, 16.9; HRMS (FAB) Calcd. for [C₂₅H₂₆O₂] 358.1933, Found 358.1930. Important observed ¹H nOe correlations are indicated below:



(*Z*)-ISOMER: ¹H NMR (CDCl₃, 500 MHz) δ 7.40 (d, 2 H, *J* = 7.5 Hz), 7.28 (m, 4 H), 7.22 (m, 4 H), 6.18 (s, 1 H), 2.17 (t, 1 H, *J* = 7.5 Hz), 1.44 (s, 3 H), 1.33 (t, 1 H, *J* = 6.0 Hz), 1.30 (s, 9 H), 1.16 (dd, 1 H, *J* = 8.5, 5.0 Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 176.2, 147.4, 134.3, 131.5, 128.6, 138.1, 127.4, 127.0, 123.8, 117.8, 92.3, 79.2, 39.0, 30.6, 27.1, 24.7, 22.1, 16.1; HRMS (FAB) Calcd. for [C₂₅H₂₆O₂] 358.1933, Found 358.1941.



Compounds 92 and 93

Cyclopropane **91** was reacted according to the general procedure for fluorene synthesis at room temperature. The reaction was quenched after 60 min, and two products were isolated following silica column chromatography (2% Et_2O :hexanes). Fluorene **93** was isolated as a white solid in 20% yield, while cycloheptatriene **92**, was isolated in 79% yield.



Ph

The spectral data for fluorene **93** matched those reported in the literature': ¹H NMR (CDCl₃, 300 MHz) δ 7.76 (d, 1 H, *J* = 7.8 Hz), 7.61 (s, 1 H), 7.4-7.2 (m, 7 H), 7.07 (m, 3 H), 5.0 (s, 1 H), 2.45 (s, 3 H); ¹³C NMR (CDCl₃, 100 MHz) δ 148.3, 145.2, 141.9, 141.2, 141.1, 137.0, 128.7, 128.3, 127.3, 127.2, 126.8, 125.3, 125.0, 120.5, 119.8, 54.1, 21.6; HRMS (FAB) Calcd. for [C₂₀H₁₆O] 256.1252,

Found 256.1248.

Compound 95



Enyne 2 and propargyl ester 94 were reacted according to the general procedure at -5 °C. The reaction was quenched after 50 min, and cyclopropane 95 was isolated as a clear oil in 63% yield as a single olefin isomer following silica column chromatography (5% EtOAc in hexanes). ¹H NMR (CDCl₃, 500 MHz) δ 7.37 (d, 2 H, *J* = 8.0 Hz), 7.32 (m, 2 H),

7.24 (m, 3 H), 6.84 (d, 2 H, J = 8.0 Hz), 6.13 (s, 1 H), 3.81 (s, 3 H), 2.09 (t, 1 H, J = 7.5 Hz), 1.45 (s, 3 H), 1.33 (s, 9 H), 1.31 (m, 1 H), 1.15 (dd, 1 H, J = 8.0, 5.0 Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 176.7, 159.0, 146.4, 132.0, 130.2, 128.5, 127.9, 127.4, 124.3, 117.8, 114.0, 93.0, 79.6, 55.6, 39.5, 31.1, 27.6, 25.1, 22.6, 16.4; HRMS (FAB) Calcd. for [C₂₆H₂₈O₃] 388.2038, Found 388.2034.

Compounds 96 and 97

Cyclopropane **95** was reacted according to the general procedure for fluorene synthesis at room temperature. The reaction was quenched after 40 min, and two products were isolated following silica column chromatography (2% Et_2O in hexanes). Fluorene **97** was isolated as a white solid in 69% yield, while cycloheptatriene **96** was isolated in 23% yield.



Cycloheptatriene **96**: ¹H NMR (CDCl₃, 500 MHz) δ 7.51 (d, 2 H, *J* = 7.5 Hz), 7.4-7.2 (m, 5 H), 6.72 (d, 2 H, *J* = 8.5 Hz), 6.53 (s, 1 H), 6.06 (d, 1 H, *J* = 7.0 Hz), 5.92 (d, 1 H, *J* = 7.0 Hz), 4.77 (s, 1 H), 3.76 (s, 3 H), 1.91 (s, 3 H), 1.23 (s, 9 H); ¹³C NMR (CDCl₃, 125 MHz) δ 176.6, 158.0, 143.0, 142.8, 137.2, 136.1, 130.8, 128.5, 128.0, 127.6, 127.5, 127.1, 121.6, 113.7, 112.8, 55.1, 50.6, 38.8, 27.0, 24.4; HRMS (EI) Calcd. for [C₂₆H₂₈O₃] 388.2038, Found

388.2035.

⁷ Bordwell, F. G.; Bausch, M. J. J. Am. Chem. Soc. **1986**, 108, 1979.



Fluorene **97**: ¹H NMR (CDCl₃, 500 MHz) δ 7.78 (d, 1 H, *J* = 7.5 Hz), 7.63 (s, 1 H), 7.38 (t, 1 H, *J* = 7.5 Hz), 7.31 (d, 1 H, *J* = 7.0 Hz), 7.26 (m, 1 H), 7.20 (d, 1 H, *J* = 7.5 Hz), 7.09 (s, 1 H, *J* = 8.0 Hz), 7.02 (d, 2 H, *J* = 8.5 Hz), 6.81 (d, 2 H, *J* = 8.5 Hz), 4.98 (s, 1 H), 3.78 (s, 3 H), 2.49 (s, 3 H); ¹³C NMR (CDCl₃, 125 MHz) δ 158.4, 148.6, 145.4, 141.0, 140.9, 136.9, 133.8, 129.2, 128.2, 127.2, 127.1, 125.2, 124.9, 120.4, 119.7, 114.0, 55.2, 53.3, 21.5; HRMS (EI) Calcd. for [C₂₁H₁₈O] 286.1358, Found 286.1358.







S33














210 200 190 180 170 160 150 140 130 120 110 100



90

80 70 60 50 40 30 20 10

ppm









AVB-400 ZBO Proton starting parameters. 6/11/03 RN







230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70













1H starting parameters (zg30) DRX-500 zBBO probe 080804 HvH

















230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



















DRX-500 5mm ZBO probe 13C starting parameters. Rev 10/15/07 RN With CPD proton decoupling. Use ns*td0 scans



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
































210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



























210 200 190 180 170 160 150 140 130 120 110 100 ppm





AVB-400 ZBO Carbon Starting paramters 6/11/03 RN









CH₃

Current Data Parameters NAME IW13110F2-5_H2 EXPNO 1 PROCNO 1 DU /u USER iain

/u iain



AVB-400 ZBO Proton starting parameters. 6/11/03 RN



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



1H starting parameters (zg30) DRX-500 zBBO probe 080804 HvH













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230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm









230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



