# Mechanistic studies of fluoride-promoted silicon elimination in β-benzotriazolyl-β-aryl-γ-ketosilanes

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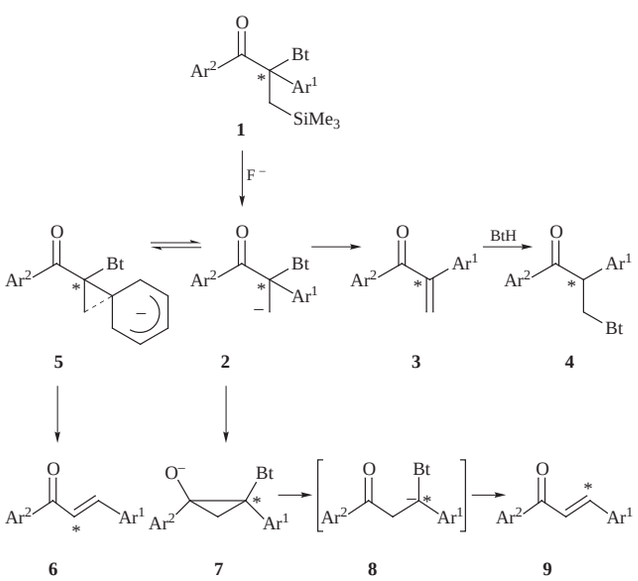
Vicinal elimination of trimethylsilyl and benzotriazolyl groups from 2-benzotriazolyl-2-aryl-3-ketopropylsilanes forms, along with the expected 1,1-disubstituted ethylenes, significant amounts of the corresponding chalcones. A study of this transformation by carbon labeling suggests the intermediate formation of cyclopropanes. Stabilizing/destabilizing (electron-donor/acceptor) *para*-substituents on the aryl group affect the product distribution of the elimination in a manner consistent with the proposed mechanism.

## Introduction

The formation of an alkene by vicinal elimination of silicon is a well documented process.[1a,b] Recently, we have shown that a wide variety of 1,1-disubstituted ethylenes are available from 2-benzotriazolyl-2-arylethylsilanes upon vicinal elimination of trimethylsilyl and benzotriazolyl groups in the presence of fluoride ion.[2] While establishing the scope of this methodology an unusual rearrangement of β-benzotriazolyl-γ-ketosilanes **1** was observed. Along with the expected product **3** the corresponding *E*-chalcones **9** were obtained (Scheme 1).[2,3a,b]



**Scheme 1** Rearrangement of **1** into the chalcone **9** upon vicinal elimination of trimethylsilyl and benzotriazolyl groups.

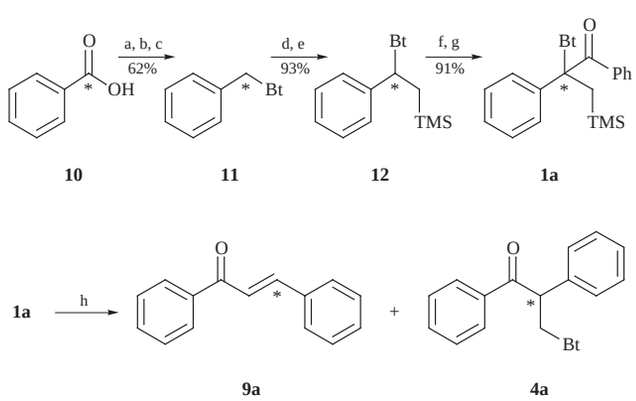
Two possible mechanisms which involve carbanion **2** have been proposed to explain this unusual rearrangement.[2] Carbanion **2**, generated upon treatment of 2-benzotriazolyl-2-arylethylsilanes **1** with caesium fluoride at elevated temperature, yields either intermediate **5** or **7**. Intermediate **5** could arise from stabilization of the carbanion by a bridged phenonium anion perhaps *via* a Grovenstein–Zimmerman rearrangement.[4] Alternatively, formation of cyclopropyl species **7**, formed by intramolecular addition of the primary anion to the carbonyl, can ring-open to carbanion **8** which is energetically favorable due to formation of carbonyl, double stabilized anion and release of three-membered ring strain.[5] While the alternative ring opening of such species is documented in the literature[6] we believe that under the reaction conditions carbanion **8** is formed exclusively. Consecutive protonation of **8** and β-elimination of benzotriazole leads to the chalcone **9**. However, no support for either of the proposed mechanisms was offered in our earlier paper.

Labeling the quaternary carbon in **1** should establish the mechanism of this unexpected rearrangement. Depending on the mechanism operating the labeled carbon should end up in position 2 in the resulting chalcone **6** or position 3 of chalcone **9**.

## Results and discussion

### Carbon labeling experiment

Compound **1a** was prepared from commercial labeled benzoic acid **10** in a straightforward manner (Scheme 2).



**Scheme 2** Carbon labeling experiment. *Reagents and conditions*: a: 1.1 equiv. $TiCl_4$, 3 equiv. $NaBH_4$, glyme, 16 h, RT; b: 1.3 equiv. $Ph_3PCl_2$, $CH_2Cl_2$, 24 h, RT; c: 1.1 equiv. BtH, 0.05 equiv. $Et_4NI$, toluene, 24 h, reflux; d: 1.1 equiv. *n*-BuLi, THF, −78 °C; e: 1.1 equiv. $TMSCH_2Cl$, 10 h, −78 °C to RT; f: 1.1 equiv. *n*-BuLi, THF, −78 °C; g: 1.1 equiv. BzCl, 10 h, −78 °C to RT; h: 1.5 equiv. CsF, DMF, 1 h, 100 °C.

When **1a** was heated in the presence of CsF formation of **4a** and **9a** was observed.[7] The $^{13}C$ NMR spectra of chalcone **9a** showed an intense peak at 144.9 ppm which corresponds to the β-position. To ensure that no **6a** was formed during the rearrangement, we investigated the appearance of carbon signals at the α- and β-positions of the rearranged product. The signal for the α-position in **9a** was a doublet at 122.1 ppm and $J = 70.5$ Hz. The $^{13}C$ NMR spectra of the rearranged product

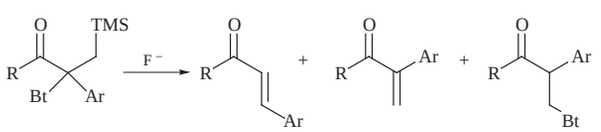
**Table 1** Influence of *para* substitution on the rearrangement of compounds **1a**–**f**

| Entry | Ar | R | Percentage of **9** in the mixture | Isolated yield **3** + **4** + **9** (%) |
|---|---|---|---|---|
| **1a** | Ph | Ph | 75 | 91 |
| **1b** | *p*-$FC_6H_4$ | Ph | 50 | 56 |
| **1c** | Ph | *p*-$FC_6H_4$ | 100 | 79 |
| **1d** | *p*-$FC_6H_4$ | *p*-$MeOC_6H_4$ | 29 | 67 |
| **1e** | *p*-$MeC_6H_4$ | *p*-$MeOC_6H_4$ | 25 | 93 |
| **1f** | *p*-$Me_2NC_6H_4$ | $Me_2N$ | 0 | 96 |

revealed no singlet in this area which would have indicated the presence of **6a**. Thus, it appears that **9a** was formed exclusively and no Grovenstein–Zimmerman rearrangement took place. Therefore, the labeling experiment supports the existence of a cyclopropyl intermediate **7**.

### Influence of *para*-substituents on the rearrangement

By stabilizing/destabilizing intermediate **7**, electron donating and electron withdrawing *para*-substituents should influence the product distribution between the expected **3** and the rearranged **9**. Substrates **1b**–**f** were prepared similarly to **1a** in good yields (Table 1). These substrates were subjected to vicinal elimination of trimethylsilyl and benzotriazolyl groups in the presence of CsF in DMF at reflux (Scheme 3). The product




**1** **9** **3** **4**

**Scheme 3**

distribution was monitored by GC and is summarized in Table 1.

According to these results the substituent, R, attached to the carbonyl has a greater influence on the outcome of the reaction than the nature of the aryl substituent, Ar, in the 2-position of **1**. Furthermore, if R is electron withdrawing as is the case with **1c**, then mostly rearranged product **9c** is formed with only traces of **3** and **4**. In other words these groups favor cyclopropyl species **7** by enhancing the electrophilicity of the adjacent carbonyl and lead to the formation of the rearranged product **9**. Alternatively, when R is an electron donating group (**1d**, **1e**, **1f**) the cyclopropyl species are less favorable and only minor amounts, if any, of rearranged product are observed. Thus the influence of substituents on the mechanism further corroborates the results of the carbon labeling experiment.

## Conclusions

Our experimental findings are consistent with formation of a cyclopropyl intermediate **7** in the vicinal elimination of trimethylsilyl and benzotriazolyl groups in β-benzotriazolyl-β-aryl-γ-ketosilanes **1**, which leads to the formation of chalcones **9**.

## Experimental

### General methods

Melting points were determined with a MEL-TEMP capillary melting point apparatus. NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as internal standard for $^1H$ (300 MHz) or solvent as internal standard for $^{13}C$ (75 MHz). Tetrahydrofuran (THF) was distilled under nitrogen immediately before use over sodium–benzophenone. Chloromethyltrimethylsilane was purchased from Gelest, Inc. Column chromatography was conducted with silica gel 230–400 mesh. All organometallic reactions were carried out under argon in oven-dried glassware. All other reagents were reagent grade and were used without purification.

**[1-$^{13}$C]Benzyl-1*H*-1,2,3-benzotriazole (11a).** Labeled benzyl chloride (0.75 g, 6 mmol) was mixed with benzotriazole (0.72 g, 6 mmol) in toluene (50 $cm^3$). A catalytic amount of $Et_4NI$ (0.037 g, 0.1 mmol) was added and the reaction mixture was heated at reflux for 12 h. The reaction mixture was cooled to room temperature, diluted with diethyl ether (100 $cm^3$), sequentially washed with aqueous sodium hydroxide solution (1 M, 50 $cm^3$) and water (100 $cm^3$), dried over magnesium sulfate, and concentrated to yield desired product **11a** (1.2 g, 83%). Found: C, 74.37; H, 5.25; N, 20.12. $C_{13}H_{11}N_3$ required: C, 74.26; H, 5.28; N, 19.99%; $\delta_H$ 5.78 (2H, d, $J$ = 141.2 Hz), 7.25–7.52 (7H, m), 7.67 (1H, m), 8.02 (1H, d, $J$ = 8.5 Hz); $\delta_C$ 52.1, 109.5, 119.5, 123.6, 128.4, 128.6, 128.6, 132.5, 131.8, 134.5 (d, $J$ = 45.8 Hz), 145.9.

### General procedure for synthesis of compounds 12

The corresponding arylbenzotriazole (4 mmol) was dissolved in THF (40 $cm^3$) and cooled to −78 °C. *n*-BuLi (2.5 $cm^3$, 1.6 M) solution in hexanes was added dropwise over 5 min. After stirring for 15 min at −78 °C, chloromethyltrimethylsilane (0.56 $cm^3$, 4 mmol) was added and the stirred reaction mixture was brought to room temperature overnight. The reaction mixture was diluted with ethyl acetate (40 $cm^3$) and quenched with saturated aqueous ammonium chloride solution (50 $cm^3$). The organic layer was washed with brine, separated, dried over magnesium sulfate, and concentrated. The resulting residue was subjected to column chromatography (hexanes–ethyl acetate = 3 : 1) to yield the corresponding product.

**{[1-$^{13}$C]-1-Phenyl-2-(1,1,1-trimethylsilyl)ethyl}-1*H*-1,2,3-benzotriazole (12a).** Yellow prisms (93%), mp 120–121 °C. Found: C, 68.85; H, 7.13; N, 14.26. $C_{17}H_{21}N_3Si$ required: C, 68.87; H, 7.15; N, 14.18%; $\delta_H$ 0.09 (9H, s), 2.18 (1H, m), 2.23 (1H, m), 6.24 (1H, dt, $J$ = 141.5 Hz, $J$ = 8.0 Hz), 7.48–7.70 (8H, m), 8.25 (1H, d, $J$ = 8.0 Hz); $\delta_C$ −1.8, 23.5 (d, $J$ = 33.6 Hz), 60.1, 109.8, 119.7, 123.6, 126.6, 128.0, 128.6, 132.1, 140.4 (d, $J$ = 45.8 Hz), 146.2.

**1-[1-(4-Fluorophenyl)-2-(1,1,1-trimethylsilyl)ethyl]-1*H*-1,2,3-benzotriazole (12b).** White prisms (59%), mp 91.0 °C (lit.[3] mp 89.0–90.0 °C); $\delta_H$ 0.01 (9H, s), 2.06–2.13 (1H, m), 2.18–2.34 (1H, m), 3.74 (s, 3H), 6.12 (1H, t, $J$ = 8.2 Hz), 7.13 (2H, t, $J$ = 8.0 Hz), 7.38–7.66 (5H, m), 8.16 (1H, d, $J$ = 8.3 Hz); $\delta_C$ −1.7, 23.7, 60.4, 109.7, 115.5 (d, $J$ = 21.5 Hz), 119.9, 123.7, 126.9, 128.4 (d, $J$ = 8.5 Hz), 132.0, 136.7 (d, $J$ = 3.2 Hz), 146.3, 162.2 (d, $J$ = 247.5 Hz).

**1-[1-Phenyl-2-(1,1,1-trimethylsilyl)ethyl]-1*H*-1,2,3-benzotriazole (12c).** White needles (88%), mp 123.0 °C. Found: C, 69.47; H, 7.35; N, 14.26. $C_{17}H_{21}N_3Si$ required: C, 69.10; H, 7.18; N, 14.23%; $\delta_H$ 0.14 (9H, s), 2.21–2.28 (1H, m), 2.41–2.49 (1H, m), 6.24–6.31 (1H, t, $J$ = 8.0 Hz), 7.57–7.71 (8H, m), 8.31 (1H, d, $J$ = 7.9 Hz); $\delta_C$ −1.6, 29.6, 61.3, 109.9, 119.9, 123.7, 126.8, 126.9, 128.2, 128.8, 132.3, 140.9, 146.4.

**1-[1-(4-Methylphenyl)-2-(1,1,1-trimethylsilyl)ethyl]-1*H*-1,2,3-benzotriazole (12e).** Colorless prisms (66%), mp 91.0 °C (lit.[3] mp 90.0–91.0 °C); $\delta_H$ 0.04 (9H, s), 2.06 (1H, dd, $J$ = 8.0 Hz, $J$ = 14.5 Hz), 2.25 (1H, dd, $J$ = 8.0 Hz, $J$ = 14.5 Hz), 2.42 (3H, s), 6.12 (1H, t, $J$ = 8.0 Hz), 7.23 (2H, d, $J$ = 8.1 Hz), 7.41–7.58 (5H, m), 8.13 (1H, d, $J$ = 8.1 Hz); $\delta_C$ −1.7, 20.9, 23.4, 61.1, 109.9, 119.8, 123.6, 126.6, 126.7, 129.4, 132.1, 137.8, 137.8, 146.2.

**1-[1-(4-*N*,*N*-Dimethylaminophenyl)-2-(1,1,1-trimethylsilyl)-ethyl]-1*H*-1,2,3-benzotriazole (12f).** Orange solid (67%), mp 107–108 °C. Found: C, 67.81; H, 7.98; N, 16.33. $C_{19}H_{26}N_4Si$ required: C, 67.41; H, 7.76; N, 16.55%; $\delta_H$ 0.06 (9H, s), 2.21 (2H, dd, $J$ = 8.3 Hz, $J$ = 14.4 Hz), 3.03 (6H, s), 6.15 (1H, t, $J$ = 8.3 Hz), 6.82 (2H, d, $J$ = 8.6 Hz), 7.48–7.59 (4H, m), 7.65 (1H, d, $J$ = 8.2 Hz), 8.17 (1H, d, $J$ = 8.2 Hz); $\delta_C$ −1.7, 23.1, 40.0, 60.9, 110.2, 111.9, 119.5, 123.3, 126.4, 127.5, 127.8, 131.9, 146.2, 149.9.

### General procedure for synthesis of compounds 1a–f

The corresponding starting material **12** (1 mmol) was dissolved in THF (25 cm$^3$) and cooled to −78 °C. *n*-BuLi (0.61 cm$^3$, 1.53 M in hexanes) was added to the mixture over 5 min. After stirring for 30 min, the corresponding benzoyl chloride (1.1 mmol) was added and the reaction mixture was brought to room temperature overnight. The reaction mixture was diluted with ethyl acetate (100 cm$^3$) and quenched with a saturated aqueous solution of ammonium sulfate (50 cm$^3$). The organic layer was separated, dried over magnesium sulfate and concentrated. The resulting residue was subjected to column chromatography (hexanes–ethyl acetate, 4 : 1) to yield the corresponding product.

**[2-$^{13}$C]-(1*H*-1,2,3-Benzotriazol-1-yl)-1,2-diphenyl-3-(1,1,1-trimethylsilyl)propan-1-one (1a).** Colorless oil (91%), $\delta_H$ 0.12 (9H, s), 2.44 (2H, br s), 7.28 (1H, d, $J$ = 8.0 Hz), 7.46–7.84 (12H, m), 8.31 (1H, d, $J$ = 8.0 Hz); $\delta_C$ 1.2, 32.5 (d, $J$ = 35.0 Hz), 79.4, 114.8, 121.9, 126.3, 128.0, 130.1, 131.0, 132.0, 134.1, 140.6 (d, $J$ = 47.8 Hz), 148.4, 198.0 (d, $J$ = 42.7 Hz); HRMS Calc. for $C_{24}H_{25}N_3OSi$: 282.1845. Found: 282.1455.

**2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-phenyl-2-(4-fluorophenyl)-3-(1,1,1-trimethylsilyl)propan-1-one (1b).** Colorless oil (67%). Found: C, 68.66; H, 5.98; N, 9.80. $C_{24}H_{24}FN_3OSi$ required: C, 69.03; H, 5.81; N, 10.07%; $\delta_H$ −0.03 (9H, s), 2.61 (2H, q, $J$ = 7.1 Hz), 7.11–7.51 (m, 10H), 7.62 (2H, d, $J$ = 7.2 Hz), 8.17 (1H, d, $J$ = 8.0 Hz); $\delta_C$ 0.2, 30.9, 77.0, 112.0, 115.5 (d, $J$ = 21.5 Hz), 120.1, 123.9, 127.4, 128.4 (d, $J$ = 8.5 Hz), 129.9, 130.0, 132.7, 133.2, 134.8 (d, $J$ = 3.2 Hz), 146.7, 162.2 (d, $J$ = 249.5 Hz), 196.0.

**2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-(4-fluorophenyl)-2-phenyl-3-(1,1,1-trimethylsilyl)propan-1-one (1c).** Oil (89%), $\delta_H$ −0.02 (9H, s), 2.58 (2H, d, $J$ = 7.1 Hz), 7.04 (2H, t, $J$ = 8.5 Hz), 7.17 (1H, d, $J$ = 8.5 Hz), 7.35–7.52 (7H, m), 7.71–7.76 (2H, m), 8.22 (1H, d, $J$ = 7.1 Hz); $\delta_C$ 0.1, 30.8, 77.5, 112.2, 115.1 (d, $J$ = 21.5 Hz), 120.1, 123.9, 127.3, 127.8 (d, $J$ = 8.5 Hz), 128.3, 128.4, 129.4, 132.1, 132.2 (d, $J$ = 3.2 Hz), 138.84, 146.63, 163.27, (d, $J$ = 249.5 Hz), 194.50; HRMS Calc. for $C_{24}H_{24}FN_3OSi$: 417.1673. Found: 417.1693.

**2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-(4-methoxyphenyl)-2-(4-fluorophenyl)-3-(1,1,1-trimethylsilyl)propan-1-one (1d).** Glassy oil (88%). Found: C, 67.27; H, 6.03; N, 9.30; $C_{25}H_{26}FN_3O_2Si$ required: C, 67.08; H, 5.87; N, 9.39%; $\delta_H$ −0.09 (9H, s), 2.26 (1H, d, $J$ = 2.8 Hz), 2.54 (1H, d, $J$ = 2.8 Hz), 3.88 (3H, s), 6.74 (2H, d, $J$ = 8.9 Hz), 7.08–7.14 (3H, m), 7.28–7.41 (m, 4H), 7.62 (2H, d, $J$ = 8.9 Hz), 8.13 (1H, d, $J$ = 8.5 Hz); $\delta_C$ 0.2, 31.1, 55.3, 76.9, 112.1, 113.5, 114.9 (d, $J$ = 21.4 Hz), 120.1, 123.9, 127.4, 130.0 (d, $J$ = 8.2 Hz), 133.9 (d, $J$ = 3.4 Hz), 134.4, 146.4, 160.1 (d, $J$ = 247.5 Hz), 164.3, 196.1.

**2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-(4-methoxyphenyl)-2-(4-methylphenyl)-3-(1,1,1-trimethylsilyl)propan-1-one (1e).** Oil (93%). Found: C, 70.02; H, 6.65; N, 9.43. $C_{26}H_{29}N_3OSi$ required: C, 70.39; H, 6.59; N, 9.47%; $\delta_H$ −0.20 (9H, s), 2.33 (3H, s), 2.36 (1H, d, $J$ = 14.8 Hz), 2.54 (1H, d, $J$ = 14.8 Hz), 3.74 (3H, s), 6.68 (2H, d, $J$ = 9.0 Hz), 6.98–7.01 (1H, m), 7.13 (2H, d, $J$ = 8.0 Hz), 7.19–7.25 (4H, m), 7.55 (2H, d, $J$ = 9.0 Hz), 8.00 (1H, d, $J$ = 7.0 Hz); $\delta_C$ 0.2, 21.0, 31.0, 55.3, 77.5, 112.5, 113.4, 119.9, 123.7, 127.0, 128.0, 128.1, 128.9, 132.1, 133.5, 136.5, 138.2, 146.7, 163.0, 194.5.

### General procedure for synthesis of compounds 3, 4 and 9

The corresponding starting material **1** (1 mmol) was dissolved in dry DMF (2 cm$^3$), CsF (0.18 g, 1.5 mmol) added and the reaction mixture heated at reflux. The reaction was monitored by GC and the reaction time varied between 40 min and 3 h. Upon completion, the reaction mixture was diluted with ethyl acetate (30 cm$^3$), washed with water, dried over magnesium sulfate, and concentrated to yield crude product as a mixture of isomers. The mixture was subjected to column chromatography (hexanes–ethyl acetate, 9 : 1) to afford the corresponding mixture of isomers.

**1-Phenyl-2-(4-fluorophenyl)prop-2-en-1-one (3b).** Oil (28%), $\delta_H$ 5.64 (1H, s), 6.05 (1H, s), 7.04 (2H, m), 7.31 (4H, m), 7.44 (1H, m), 7.88 (2H, d, $J$ = 7.4 Hz); $\delta_C$ 115.43 (d, $J$ = 21.8 Hz), 121.32, 128.45, 128.72 (d, $J$ = 8.8 Hz), 129.00, 129.96, 133.16, 137.06, 147.14, 161.21 (d, $J$ = 246.8 Hz), 190.35; HRMS Calc. for $C_{15}H_{11}FO$: 226.0793. Found: 226.0730.

**1-(4-Methoxyphenyl)-2-(4-fluorophenyl)prop-2-en-1-one (3d).** Oil (47 %), $\delta_H$ 3.79 (3H, s), 5.48 (1H, s), 5.89 (1H, s), 6.83-6.98 (4H, m), 7.31–7.36 (2H, m), 7.83 (2H, d, $J$ = 8.7 Hz); $\delta_C$ 55.4, 113.7, 115.4 (d, $J$ = 21.7 Hz), 119.2, 128.5 (d, $J$ = 8.3 Hz), 132.4, 133.3, 147.3, 161.2 (d, $J$ = 246.8 Hz), 163.8, 196.0; HRMS Calc. for $C_{16}H_{13}FO_2$: 257.0977. Found: 257.0975.

**1-(4-Methoxyphenyl)-2-(4-methylphenyl)prop-2-en-1-one (3e).** Colorless oil (72%), $\delta_H$ 2.31 (3H, s), 3.80 (3H, s), 5.48 (1H, s), 5.93 (1H, s), 6.87 (2H, d, $J$ = 8.8 Hz), 7.12 (2H, d, $J$ = 8.0 Hz), 7.30 (2H, d, $J$ = 8.2 Hz), 7.90 (2H, d, $J$ = 8.8 Hz); $\delta_C$ 21.0, 55.3, 113.5, 117.6, 126.5, 129.2 (2C), 129.8, 132.2, 134.2, 138.1, 148.3, 163.6, 196.3; HRMS Calc. for $C_{17}H_{16}O_2$: 252.1150. Found: 252.1135.

**1-(Dimethylamino)-2-(4-*N*,*N*-dimethylaminophenyl)propan-1-one (3f).** Orange solid (96%), mp 64–65 °C. Found: C, 71.26; H, 8.33; N, 12.84. $C_{13}H_{18}N_2O$ required: C, 71.52; H, 8.33; N, 12.84%; $\delta_H$ 2.89 (3H, s), 2.94 (6H, s), 3.05 (3H, s), 5.09 (1H, s), 5.53 (1H, s), 6.65 (2H, d, $J$ = 8.2 Hz), 7.27 (2H, d, $J$ = 8.2 Hz); $\delta_C$ 34.27, 38.25, 40.02, 109.05, 111.93, 123.12, 126.30, 144.77, 150.25, 171.37.

**[2-$^{13}$C]-1,2-Diphenyl-3-(1*H*-1,2,3-benzotriazol-1-yl)propan-1-one (4a).** White solid (24%), $\delta_H$ 4.85–4.92 (1H, m), 5.36–5.44 (1H, m), 5.55 (1H, dt, $J$ = 132.5 Hz, $J$ = 7.0 Hz), 7.21–7.48 (10H, m), 7.83–8.01 (4H, m); $\delta_C$ 53.9, 54.2 (d, $J$ = 18.8 Hz), 109.7, 119.6, 123.6, 127.2, 128.1, 128.5, 128.8, 129.4, 129.4, 133.4, 135.5 (d, $J$ = 41.0 Hz), 145.4, 196.8 (d, $J$ = 40.2 Hz); HRMS Calc. for $C_{21}H_{17}N_3O$: 329.1483. Found: 329.1491.

**(*E*)-[3-$^{13}$C]-1,3-Diphenylprop-2-en-1-one (9a).** Yellow solid (72%), mp 50–51 °C, $\delta_H$ 7.26 (1H, s), 7.39–7.65 (9H, m), 8.03 (2H, d, $J$ = 8.2 Hz); $\delta_C$ 122.1 (d, $J$ = 70.5 Hz), 128.4, 128.5, 128.6, 128.9, 129.0, 130.7, 132.1, 134.3, 135.2, 137.5 (d, $J$ = 73.5 Hz), 144.8, 190.6; HRMS Calc. for $C_{15}H_{12}O + H^+$: 210.1044. Found: 210.1023.

**(*E*)-1-Phenyl-3-(4-fluorophenyl)prop-2-en-1-one (9b).** White solid (56%), mp 82–83 °C, $\delta_H$ 7.11 (2H, t, $J$ = 8.5 Hz), 7.43–7.66 (6H, m), 7.78 (1H, d, $J$ = 15.8 Hz), 8.03 (2H, d, $J$ = 7.5 Hz); $\delta_C$ 115.9 (d, $J$ = 21.8 Hz), 121.9, 128.5, 128.6, 130.3 (d, $J$ = 8.8 Hz), 131.2 (d, $J$ = 3.5 Hz), 132.8, 138.2, 143.5, 164.4 (d, $J$ = 249.7 Hz), 190.3.

**(*E*)-1-(4-Fluorophenyl)-3-phenylprop-2-en-1-one (9c).** Oil (79%). Found: C, 79.61; H, 4.68. $C_{15}H_{11}FO$ required: C, 79.62; H, 4.91%; $\delta_H$ 7.05–7.44 (6H, m), 7.52 (2H, br s), 7.68 (1H, d, $J$ = 14.5 Hz), 7.93 (2H, br s); $\delta_C$ 115.58 (d, $J$ = 21.8 Hz), 121.62, 128.25, 128.45 (d, $J$ = 8.8 Hz), 130.63, 131.02 (d, $J$ = 3.5 Hz), 134.78, 145.03, 163.53 (d, $J$ = 256.8 Hz), 167.28, 188.82.

**(*E*)-1-(4-Methoxyphenyl)-3-(4-fluorophenyl)prop-2-en-1-one (9d).** White solid (19%), $\delta_H$ 3.89 (3H, s), 6.97 (2H, d, $J$ = 8.7 Hz), 7.14 (2H, t, $J$ = 8.5 Hz), 7.45 (1H, d, $J$ = 15.5 Hz), 7.61–7.66 (2H, m), 7.75 (1H, d, $J$ = 15.5 Hz), 8.03 (2H, d, $J$ = 8.7 Hz); $\delta_C$ 55.5, 113.9, 115.9 (d, $J$ = 21.8 Hz), 121.7, 130.3 (d, $J$ = 8.8 Hz), 131.4 (d, $J$ = 3.5 Hz), 137.3, 142.7, 163.9 (d, $J$ = 243.5 Hz), 165.7, 188.6.

**(*E*)-1-(4-Methoxyphenyl)-3-(4-methylphenyl)prop-2-en-1-one (9e).** White needles (22%), mp 125.8–126.7 °C (lit.[3] mp 126 °C), $\delta_H$ 2.39 (3H, s), 3.89 (3H, s), 6.98 (2H, d, $J$ = 8.8 Hz), 7.22 (2H, d, $J$ = 8.0 Hz), 7.51 (1H, d, $J$ = 15.5 Hz), 7.54 (2H, d, $J$ = 8.0 Hz), 7.79 (1H, d, $J$ = 15.5 Hz), 8.03 (2H, d, $J$ = 8.8 Hz); $\delta_C$ 21.4, 55.4, 113.8, 120.9, 128.3, 129.6, 130.7, 131.2, 132.3, 140.7, 143.9, 163.3, 188.7.

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