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Palladium-Catalyzed Cross-Coupling of Cyclopropanol-Derived Ketone Homoenolates with Aryl Bromides

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Supporting Information

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General Experimental

Reactions were conducted in flame- or oven-dried glassware under an atmosphere of argon using freshly distilled solvents unless specified otherwise. Commercial reagents were used as received. Toluene was distilled from CaH₂ prior to use. Tetrahydrofuran was distilled from sodium/benzophenone.

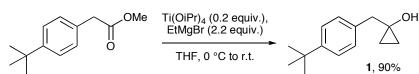
Thin-layer chromatography was performed on Merck silica gel 60 F254 plates. Visualization was carried out using UV light and/or KMnO₄, anisaldehyde or $(NH_4)_2Ce(NO_3)_6$ solutions. Hexanes (ACS grade), ethyl acetate (EtOAc, CHROMASOLV[®] for HPLC), diethyl ether (ACS grade) and pentane (ACS grade) were used as received. Flash column chromatographyⁱ was carried out using Aldrich silica gel (60 Å, 230 - 400 mesh).

¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker 400 AV or Bruker 300 AV spectrometer in chloroform-d (99.8% deuterated). Spectra recorded using chloroform were calibrated to 7.28 ppm ¹H and 77.23 ppm ¹³C. Chemical shifts (δ) are reported in ppm and multiplicities are indicated by s (singlet), d (doublet), q (quartet), t (triplet), quint (quintet), m (multiplet), br (broad). Coupling constants *J* are reported in Hertz (Hz). Infrared (IR) spectra were recorded as thin films (neat) in NaCl cells using a Mattson Genesis II FT-IR instrument. Mass Spectrometry was conducted at the Mass Spectrometry Facility of Queen's University on either a Waters/Micromass GC-TOF instrument with an EI source or an Applied Biosystems/MDS Sciex QStar XL QqTOF instrument with and ESI source.

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General procedure 1: Synthesis of Cyclopropanols Using the Kulinkovich Reaction - 1

Cyclopropanol 1



An oven dried 100 mL round-bottomed flask equipped with a stir bar was charged with methyl *ptert*-butylphenylacetate (2.0 g, 2.0 mL, 9.7 mmol, 1.0 equiv.), capped with a rubber septum and flushed with argon for 10 minutes. To the flask was added freshly distilled tetrahydrofuran (THF, 30 mL) and the resulting solution cooled to 0 °C with an ice bath. Once cold, neat titanium(IV) isopropoxide (0.551 g, 0.600 mL, 1.9 mmol, 0.2 equiv.) was added via a syringe. Freshly prepared ethylmagnesium bromide (21.0 mmol, 0.7 M in THF, 2.2 equiv.) was then added drop wise via a cannula over a period of 40 minutes, and the reaction was allowed to warm to ambient temperature. The progress of the reaction was monitored by thin-layer chromatography (TLC). Once complete, the reaction was quenched with aqueous 1M HCl, diluted with EtOAc and the phases were separated. The organic phase was washed with brine, dried using MgSO₄ and concentrated *in vacuo*. The crude product was purified by flash column chromatography using a 17% solution of EtOAc in hexanes. Cyclopropanol **1** (1.780 g, 8.7 mmol) was isolated as a white solid in 90% yield.

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Data for 1
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 $\frac{1}{1}$ H NMR (400 MHz, CDCl₃)

δ 7.39 (d, J = 8.0 Hz, 2 H), 7.27 (d, J = 8.0 Hz, 2 H), 2.82 (s, 2 H),
2.07 (bs, 1 H), 1.36 (s, 9 H), 0.85 (dd, J = 6.8, 5.2 Hz, 2 H),
0.68 (dd, J = 6.8, 5.2 Hz, 2 H).

 $\frac{13}{C NMR}$ (100 MHz, CDCl₃)

 $\delta \ 149.3, \ 135.4, \ 129.0, \ 125.4, \ 56.0, \ 43.5, \ 34.3, \ 31.3, \ 13.1.$

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

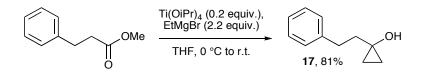
 $v = 3364, 2920, 2860, 1673, 1462, 1376, 722 \text{ cm}^{-1}$

- <u>m.p.</u> 43 °C
- HRMS EI

Calculated for $C_{14}H_{20}O[M^+] = 204.1514$, found = 204.1522

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Cyclopropanol 17



Following *General Procedure 1*, methyl 3-phenylpropanoate (1.08 g, 6.6 mmol, 1.0 equiv.) was converted to cyclopropanol **17**. Purification by flash column chromatography using a 20% solution of EtOAc in hexanes afforded the product (0.396 g, 5.3 mmol) as a clear oil in 81% yield.

Data for 17

¹<u>H NMR</u> (400 MHz, CDCl₃)

δ 7.32 (t, J = 7.2 Hz, 2 H), 7.25 (d, J = 7.2 Hz, 2 H), 7.22 (t, J = 7.2 Hz, 1 H),

2.88 (dd, J = 9.2, 6.8 Hz, 2 H), 1.91 (dd, J = 9.2, 6.4 Hz, 2 H),

0.79 (dd, *J* = 6.4, 5.2 Hz, 2 H), 0.49 (dd, *J* = 6.8, 5.2 Hz, 2 H).

 $\frac{13}{C}$ NMR (100 MHz, CDCl₃)

δ 142.1, 128.4, 128.3, 125.8, 55.7, 40.3, 32.4, 13.6.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

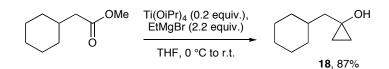
 υ = 3355, 3083, 3006, 2925, 1603, 1454, 1243, 1010, 747 cm⁻¹

<u>HRMS</u> EI

Calculated for $C_{11}H_{14}O[M^+] = 162.1045$, found = 162.1042

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Cyclopropanol 18



Following *General Procedure 1*, methyl 2-cyclohexylacetate (0.970 g, 6.2 mmol, 1.0 equiv.) was converted to cyclopropanol **18**. Purification by flash column chromatography using a 20% solution of EtOAc in hexanes afforded the product (0.827 g, 5.4 mmol) as a white solid in 87% yield.

Data for 18

¹<u>H NMR</u> (400 MHz, CDCl₃)

δ 1.88 (dd, J = 8.4, 1.2 Hz, 2 H), 1.81-1.65 (m, 5 H), 1.47 (d, J = 7.2 Hz, 2 H),

1.30 (dq, J = 12.0, 2.8 Hz, 2 H), 1.18 (tquint, J = 12.0, 2.8 Hz, 1 H),

0.97 (dq, J = 12.0, 2.8 Hz, 2 H), 0.75 (dd, J = 6.8, 5.6 Hz, 2 H),

0.44 (dd, *J* = 6.8, 5.6 Hz, 2 H).

$\frac{13}{C}$ NMR (100 MHz, CDCl₃)

δ 54.0, 45.6, 35.1, 33.7, 26.5, 26.2, 13.6.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

 υ = 3310, 2897, 1643, 1461, 1378, 724 cm⁻¹

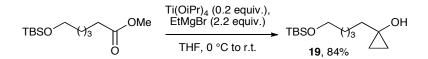
<u>m.p.</u> 34-36 °C

HRMS EI

Calculated for $C_{10}H_{18}O[M^+] = 154.1358$, found = 154.1365

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Cyclopropanol 19



Following *General Procedure* 1, methyl 6-(*tert*-butyldimethylsilyloxy)hexanoate (1.65 g, 6.3 mmol, 1.0 equiv.) was converted to cyclopropanol **19**. Purification by flash column chromatography using a 14% solution of EtOAc in hexanes afforded the product (1.37 g, 5.3 mmol) as a clear oil in 84% yield.

Data for 19

¹<u>H NMR</u> (400 MHz, CDCl₃)

δ 3.64 (t, J = 6.4 Hz, 2 H), 1.56 (m, 6 H), 1.41 (m, 2 H), 0.91 (s, 9 H),

0.75 (t, *J* = 6.0 Hz, 2 H), 0.46 (t, *J* = 6.0 Hz, 2 H), 0.07 (s, 6 H).

 $\frac{13}{C}$ NMR (100 MHz, CDCl₃)

δ 63.1, 55.7, 38.2, 32.7, 25.9, 25.7, 25.6, 18.3, 13.4, -5.4.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

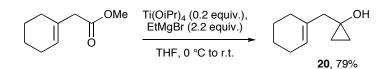
 $v = 3014, 2935, 2854, 1635, 1463, 1388, 1101, 835 \text{ cm}^{-1}$

HRMS EI

Calculated for $C_{14}H_{30}O_2Si [M^+] = 258.2015$, found = 258.2027

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Cyclopropanol 20



Following *General Procedure 1*, methyl 2-cyclohexenylacetate (0.500 g, 3.3 mmol, 1.0 equiv.) was converted to cyclopropanol **20**. Purification by flash column chromatography using a 20% solution of EtOAc in hexanes afforded the product (0.396 g, 2.6 mmol) as a clear oil in 79% yield.

	Data	for	20
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 $\frac{1}{1}$ H NMR (400 MHz, CDCl₃)

δ 5.64 (bs, 1 H), 2.20 (s, 2 H), 2.07 (m, 5 H), 1.68-1.59 (m, 4 H),

0.79 (dd, *J* = 6.8, 5.2 Hz, 2 H), 0.48 (dd, *J* = 6.8, 5.2 Hz, 2 H).

 $\frac{13}{C}$ NMR (100 MHz, CDCl₃)

 δ 135.0, 124.4, 53.6, 46.4, 29.0, 25.2, 22.8, 22.3, 12.6.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

 $v = 3382, 3002, 2928, 2862, 1660, 1448, 1012 \text{ cm}^{-1}$

HRMS EI

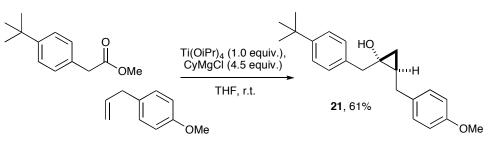
Calculated for $C_{10}H_{16}O[M^+] = 152.1201$, found = 152.1208

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General procedure 2: Synthesis of Cyclopropanols Using the Chaⁱⁱ modification of the

Kulinkovich Reaction





An oven dried 50 mL round-bottomed flask equipped with a stir bar was charged with methyl *ptert*-butylphenylacetate (0.500 g, 0.500 mL, 2.4 mmol, 1.0 equiv.), 4-allylanisole (0.533 g, 0.553 mL, 3.6 mmol, 1.5 equiv.), capped with a rubber septum and flushed with argon for 10 minutes at ambient temperature. To the flask was added freshly distilled THF (18 mL) and the resulting solution was stirred vigorously. Neat titanium(IV) isopropoxide (0.682 g, 0.741 mL, 2.4 mmol, 1.0 equiv.) was added *via* syringe. With the aid of a syringe pump, commercial grade cyclohexylmagnesium chloride (11.0 mmol, 5.4 mL, 2.0 M in diethylether, 4.5 equiv.) was added dropwise over a period of 90 minutes. The progress of the reaction was monitored by TLC analysis. Once complete, the reaction was quenched with aqueous 1M HCl, diluted with EtOAc and the phases were separated. The organic phase was washed with brine, dried using MgSO₄ and concentrated *in vacuo*. The crude product was purified by flash column chromatography using a 12% solution of EtOAc in hexanes. Cyclopropanol **21** (0.476 g, 1.5 mmol) was isolated as a clear oil in 61% yield. Rosa and Orellana

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Data for 21
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 $\frac{1}{1}$ MMR (400 MHz, CDCl₃)

δ 7.40 (d, *J* = 8.0 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.23 (d, *J* = 8.4 Hz, 2 H), 6.90 (d, *J* = 8.4 Hz, 2 H), 3.84 (s, 3 H), 3.10 (d, *J* = 14.4 Hz, 1 H),

2.92 (dd, *J* = 15.2, 6.4 Hz, 1 H), 2.84 (d, *J* = 14.4 Hz, 1 H),

2.56 (dd, J = 15.2, 8.8 Hz, 1 H), 2.04 (bs, 1 H), 1.50 (m, 1 H), 1.36 (s, 9 H),

1.03 (dd, *J* = 10.0, 6.0 Hz, 1 H), 0.57 (t, *J* = 6.0 Hz, 1 H).

 $\frac{13}{C}$ NMR (100 MHz, CDCl₃)

δ 157.8, 149.4, 135.1, 133.3, 129.0, 129.0, 125.5, 113.7, 59.1, 55.2, 39.4, 34.7,
34.3, 31.3, 25.9, 19.8.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

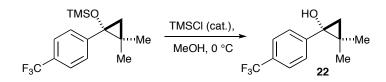
 υ = 3404, 2961, 2868, 1612, 1513, 1462, 1248, 1036, 815 cm⁻¹

HRMS EI

Calculated for $C_{22}H_{28}O_2$ [M⁺] = 324.2089, found = 324.2103

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Cyclopropanol 22



A dry 10 mL roundbottomed flask equipped with a stir bar was charged with the corresponding siloxycyclopropane (0.100 g, 0.33 mmol, 1.0 equiv.), capped with a rubber septum and flushed with argon for 10 minutes at ambient temperature. To the flask was added dry methanol (4 mL) and the resulting solution was cooled to 0 °C. Once cold, a single drop of chlorotrimethylsilane was added. Consumption of the siloxycyclopropane was monitored using TLC. Once complete, the reaction was concentrated to dryness *in vacuo*. Crude cyclopropanol **22** (0.75 g, 0.33 mmol) was obtained as a yellow oil in nearly quantitative yield.

Data for 22

¹<u>H NMR</u> (400 MHz, CDCl₃)

δ 7.61 (d, J = 8.0 Hz, 2 H), 7.51 (d, J = 8.0 Hz, 2 H), 2.00 (bs, 1 H), 1.42 (s, 3 H),

1.15 (d, *J* = 6.0 Hz, 2 H), 0.84 (d, *J* = 6.0 Hz, 2 H), 0.78 (s, 3 H).

 $\frac{13}{C}$ NMR (100 MHz, CDCl₃)

δ 145.4, 129.2 (q, ${}^{2}J_{C-F}$ = 32.0 Hz), 128.2, 125.0 (q, ${}^{3}J_{C-F}$ = 4.0 Hz),

123.1 (q, ${}^{1}J_{C-F}$ = 270.0 Hz), 64.0, 24.7, 24.1, 22.6, 20.0.

 $\frac{19}{\text{F}}$ NMR (376 MHz, CDCl₃)

-62.7

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

 υ = 3389, 2923, 2864, 1648, 1454, 871,759 cm⁻¹

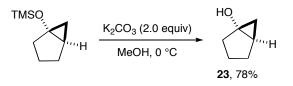
HRMS EI

Calculated for $C_{11}H_{13}OF_3$ [M⁺] = 230.0918, found = 230.0927

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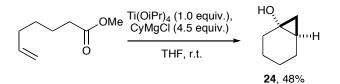
General procedure 3: <u>Deprotection of siloxycyclopropanes</u>

Cyclopropanol 23



A dry 25 mL round bottom flask equipped with a stir bar was charged the (bicyclo[3.1.0]hexan-1yloxy)trimethylsilane (0.400 g, 2.3 mmol, 1.0 equiv.), capped with a rubber septum and flushed with argon for 10 minutes at ambient temperature. To the flask was added dry methanol (MeOH, 10 mL) and the resulting solution was cooled to 0 °C. Once cold, solid potassium carbonate (0.636 g, 4.6 mmol, 2.0 equiv.) was added in one portion. Consumption of the siloxycyclopropane was monitored using TLC. Once complete, the reaction was quenched with a saturated aqueous solution of NH₄Cl, diluted with EtOAc and the phases separated. The organic phase was washed with brine, dried over anhydrous MgSO₄ and concentrated *in vacuo*. The crude product was purified by flash column chromatography using a 33% solution of ether in pentane. Cyclopropanol **23** (0.176 g, 1.8 mmol) was isolated as a clear oil in 78% yield. Spectral data obtained for this compound is consistent with that reported by Murai and coworkers.³

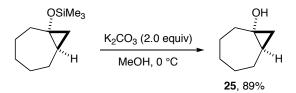
Cyclopropanol 24



Following *General Procedure 2*, methyl hept-6-enoate (0.200 g, 1.4 mmol, 1.0 equiv.) was converted to cyclopropanol **24**. Purification by flash column chromatography using an 11% solution of EtOAc in hexanes afforded the desired product (0.075 g, 0.67 mmol) as a clear oil in 48% yield. Spectral data obtained for this compound is consistent with that reported by Narasaka and co-workers.ⁱⁱⁱ

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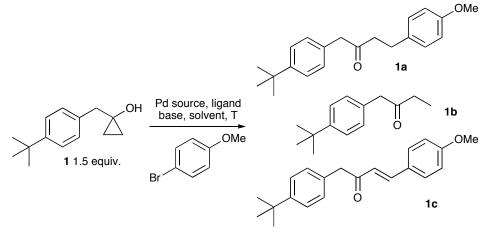
Cyclopropanol 25



Following *General Procedure* 3, the (bicyclo[3.1.0]hexan-1-yloxy)trimethylsilane (bicyclo[5.1.0]octan-1-yloxy)trimethylsilane (0.200 g, 1.0 mmol, 1.0 equiv.), was converted to cyclopropanol **25**. Purification by flash column chromatography using a 33% solution of ether in pentane afforded the product (0.112 g, 0.89 mmol) as a powdery white solid in 89% yield. Spectral data is consistent with those reported by Murai and co-workers.^{iv}

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Reaction Development



Pd source (equiv.) ^a	Ligand (equiv.)	Base (equiv.)	Solvent	Temp. (°C)	1a ^b	1b ^b	1c ^b
Pd(OAc) ₂ (0.1)	dppp (0.2)	K ₂ CO ₃ (2.0)	Toluene	80	59%	16%	5%
Pd(OAc) ₂ (0.1)	Xantphos (0.2)	Cs_2CO_3 (2.0)	Toluene	80	46%	22%	0%
Pd(OAc) ₂ (0.1)	dppp (0.2)	Cs ₂ CO ₃ (2.0)	Toluene	80	77%	0%	0%
Pd(OAc) ₂ (0.1)	PPh ₃ (0.4)	Cs ₂ CO ₃ (2.0)	Toluene	80	53%	18%	0%
Pd(OAc) ₂ (0.1)	DavePhos (0.2)	Cs ₂ CO ₃ (2.0)	Toluene	80	62%	15%	0%
Pd(OAc) ₂ (0.1)	dppe (0.2)	Cs ₂ CO ₃ (2.0)	Toluene	80	73%	0%	0%
Pd(OAc) ₂ (0.1)	dppf (0.2)	Cs ₂ CO ₃ (2.0)	Toluene	80	77%	0%	0%
Pd(OAc) ₂ (0.1)	S-Phos (0.2)	Cs ₂ CO ₃ (2.0)	Toluene	80	64%	18%	0%
Pd(OAc) ₂ (0.1)	X-Phos (0.2)	Cs ₂ CO ₃ (2.0)	Toluene	80	49%	36%	0%
Pd(OAc) ₂ (0.1)	P(tBu) ₃ (0.4)	Cs ₂ CO ₃ (2.0)	Toluene	80	46%	36%	0%
Pd(OAc) ₂ (0.1)	P(Cy) ₂ buP(Cy) ₂ (0.2)	Cs ₂ CO ₃ (2.0)	Toluene	80	79%	<5%	0%
Peppsi-IPr (0.1)	n/a	Cs ₂ CO ₃ (2.0)	Toluene	80	0%	86%	0%
Pd(OAc) ₂ (0.1)	P(Cy) ₂ buP(Cy) ₂ (0.2)	Ag ₂ CO ₃ (2.0)	Toluene	80	21%	62%	0%
Pd(OAc) ₂ (0.1)	P(Cy) ₂ buP(Cy) ₂ (0.2)	K ₂ CO ₃ (2.0)	Toluene	80	8%	82%	0%
Pd(OAc) ₂ (0.1)	P(Cy) ₂ buP(Cy) ₂ (0.2)	Na ₂ CO ₃ (2.0)	Toluene	80	0%	0%	0%

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Reaction Development – Continued

Pd source	Ligand	Base		Temp.	- b	h	- b
(equiv.) ^a	(equiv.)	(equiv.)	Solvent	(°C)	1a ^b	1b ^b	1 c ^b
Pd(OAc) ₂ (0.1)	P(Cy) ₂ buP(Cy) ₂ (0.2 equiv)	K ₃ PO ₄ (2.0)	Toluene	80	86%	<5%	0%
Pd(OAc) ₂ (0.1)	P(Cy) ₂ buP(Cy) ₂ (0.2 equiv)	KOtBu (2.0)	Toluene	80	0%	90%	0%
Pd(OAc) ₂ (0.1)	P(Cy) ₂ buP(Cy) ₂ (0.2 equiv)	CsOAc (2.0)	Toluene	80	24%	60%	0%
Pd(OAc) ₂ (0.1)	P(Cy) ₂ buP(Cy) ₂ (0.2 equiv)	KOAc (2.0)	Toluene	80	8%	74%	0%
Pd(OAc) ₂ (0.1)	P(Cy) ₂ buP(Cy) ₂ (0.2 equiv)	K ₃ PO ₄ (2.0)	DMA	80	60%	26%	0%
Pd(OAc) ₂ (0.1)	P(Cy) ₂ buP(Cy) ₂ (0.2 equiv)	K ₃ PO ₄ (2.0)	NMP	80	65%	24%	0%
Pd(OAc) ₂ (0.1)	P(Cy) ₂ buP(Cy) ₂ (0.2 equiv)	K ₃ PO ₄ (2.0)	DME	80	81%	<5%	0%
Pd(OAc) ₂ (0.1)	P(Cy) ₂ buP(Cy) ₂ (0.2 equiv)	K ₃ PO ₄ (2.0)	MeCN	80	56%	32%	0%
Pd(OAc) ₂ (0.1)	P(Cy) ₂ buP(Cy) ₂ (0.2 equiv)	K ₃ PO ₄ (2.0)	THF	60	67%	12%	0%
Pd(OAc) ₂ (0.05)	P(Cy) ₂ buP(Cy) ₂ (0.10 equiv)	K ₃ PO ₄ (2.0)	Toluene	80	81%	8%	0%
Pd(OAc) ₂ (0.025)	P(Cy) ₂ buP(Cy) ₂ (0.05 equiv)	K ₃ PO ₄ (2.0)	Toluene	80	71%	16%	0%
Pd(OAc) ₂ (0.01)	P(Cy) ₂ buP(Cy) ₂ (0.02)	K ₃ PO ₄ (2.0)	Toluene	80	64%	18%	0%
Pd(OAc) ₂ (0.1)	dppb (0.2)	K ₃ PO ₄ (2.0)	Toluene	80	83%	0%	0%
Pd(OAc) ₂ (0.1)	P(Ph) ₂ pentP(Ph) ₂ (0.2)	K ₃ PO ₄ (2.0)	Toluene	80	79%	9%	0%
Pd(OAc) ₂ (0.1)	P(Cy) ₂ etP(Cy) ₂ (0.2)	K ₃ PO ₄ (2.0)	Toluene	80	82%	<5%	0%
Pd(OAc) ₂ (0.1)	P(Cy) ₂ prP(Cy) ₂ (0.2)	K ₃ PO ₄ (2.0)	Toluene	80	0%	0%	0%
Pd(OAc) ₂ (0.1)	dppe (0.2)	K ₃ PO ₄ (2.0)	Toluene	80	79%	<1%	<7%
Pd(OAc) ₂ (0.1)	dppf (0.2)	K ₃ PO ₄ (2.0)	Toluene	80	77%	<3%	0%
Pd₂dba ₃ (0.05)	P(Cy) ₂ buP(Cy) ₂ (0.2)	K ₃ PO ₄ (2.0)	Toluene	80	71%	18%	0%

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Pd source (equiv.) ^a	Ligand (equiv.)	Base (equiv.)	Solvent	Temp. (°C)	1a ^b	1b ^b	1c ^b
PdCl ₂ (0.1)	P(Cy) ₂ buP(Cy) ₂ (0.2)	K ₃ PO ₄ (2.0)	Toluene	80	68%	21%	0%
Pd(OAc) ₂ (0.1)	P(Cy) ₂ buP(Cy) ₂ (0.3)	K ₃ PO ₄ (2.0)	Toluene	80	83%	8%	0%
Pd(OAc) ₂ (0.05)	dppb (0.1)	K ₃ PO ₄ (2.0)	Toluene	80	81%	10%	0%
Pd(OAc) ₂ (0.1)	P(Ph) ₂ pentP(Ph) ₂ (0.2)	K ₃ PO ₄ (2.0)	Toluene	80	79%	9%	0%
Pd(OAc) ₂ (0.1)	P(Cy) ₂ etP(Cy) ₂ (0.2)	K ₃ PO ₄ (2.0)	Toluene	80	82%	<5%	0%
Pd(OAc) ₂ (0.1)	dppb (0.2)	K ₃ PO ₄ (2.0)	Toluene	60	72%	15%	0%
Pd(OAc) ₂ (0.1)	dppb (0.2)	K ₃ PO ₄ (2.0)	Toluene	21	11%	68%	0%
Pd(OAc) ₂ (0.1)	dppb (0.2)	K ₃ PO ₄ (2.0)	Toluene	80	79% ^c	0%	0%

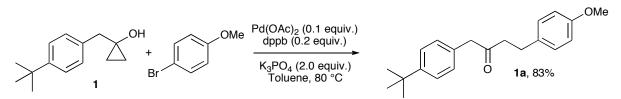
Reaction Development – Continued

^a All reactions conducted on a 0.24 mmol scale and 0.1 M concentration of starting material unless otherwise stated. ^b Isolated yields. ^c Reaction conducted on a 1.92 mmol scale and 0.1 M concentration of starting material.

Rosa and Orellana

General procedure 4: Cross-Coupling of Cyclopropanols with Aryl Bromides

Ketone 1a



An oven dried 15 mL test tube equipped with a stir bar was charged with cyclopropanol **1** (0.050 g, 0.24 mmol, 1.0 equiv.), palladium diacetate (Pd(OAc)₂, 0.005 g, 0.024 mmol, 0.10 equiv.), 1,4-bis(diphenylphosphino)butane (dppb) (0.020 g, 0.048 mmol, 0.20 equiv.) and K₃PO₄ (0.106 g, 0.48 mmol, 2.0 equiv.). The reaction vessel was capped with a rubber septum and flushed with argon for 10 minutes at ambient temperature prior to the addition of toluene (2.4 mL). The resulting mixture was stirred at room temperature for 5 minutes. Neat 4-bromoanisole (0.067 g, 0.045 mL, 0.36 mmol, 1.5 equiv.) was added *via* syringe. The resulting mixture was heated to 80 °C with the aid of an oil bath. Reaction progress was monitored using TLC. Once complete, the crude reaction mixture was diluted with ethyl acetate (EtOAc), filtered through a plug of silica and concentrated *in vacuo*. Flash column chromatography of the resulting crude product using a 7% solution of EtOAc in hexanes afforded ketone **1a** as a clear oil (0.062 g, 0.20 mmol) in 83% yield.

Rosa and Orellana

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Data for 1a
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¹<u>H NMR</u> (400 MHz, CDCl₃)

δ 7.35 (d, *J* = 8.0 Hz, 2 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 7.07 (d, *J* = 8.4 Hz, 2 H), 6.82 (d, *J* = 8.4 Hz, 2 H), 3.80 (s, 3 H), 3.65 (s, 2 H), 2.83 (t, *J* = 6.8 Hz, 2 H), 2.76 (t, *J* = 6.8 Hz, 2 H), 1.33 (s, 9 H).

¹³C NMR (100 MHz, CDCl₃)

 $\delta \ 207.8, \ 157.8, \ 149.8, \ 132.9, \ 130.9, \ 129.1, \ 128.9, \ 125.5, \ 113.7, \ 55.1, \ 49.8, \ 43.6,$

34.3, 31.2, 28.8.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

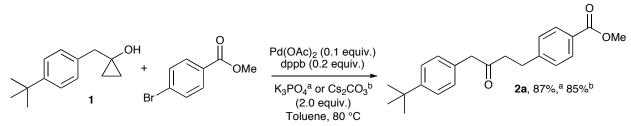
 $v = 2935, 2869, 1712, 1611, 1513, 1247, 1036, 823 \text{ cm}^{-1}$

<u>HRMS</u> EI

Calculated for $C_{21}H_{26}O_2$ [M⁺] = 310.1933, found = 310.1946

Rosa and Orellana

Ketone 2a



Following *General Procedure 4* cyclopropanol **1a** (0.050 g, 0.24 mmol, 1.0 equiv.) was coupled to methyl 4-bromobenzoate (0.077 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using an 11% solution of EtOAc in hexanes afforded the ketone **2a** (0.071 g, 0.21 mmol) as a white powdery solid in 87% yield. Using Cs_2CO_3 , ketone **2a** (0.066 g, 0.20 mmol) was prepared in 85% yield.

Data for 2a

 1 H NMR (400 MHz, CDCl₃)

 δ 7.93 (d, J = 8.0 Hz, 2 H), 7.34 (d, J = 8.0 Hz, 2 H), 7.20 (d, J = 8.0 Hz, 2 H),

7.11 (d, J = 8.0 Hz, 2 H), 3.92 (s, 3 H), 3.66 (s, 2 H), 2.94 (t, J = 7.2 Hz, 2 H),

2.81 (t, *J* = 7.2 Hz, 2 H), 1.33 (s, 9 H).

```
\frac{13}{C} NMR (100 MHz, CDCl<sub>3</sub>)
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δ 207.0, 166.9, 149.9, 146.4, 130.7, 129.7, 128.9, 128.3, 127.9, 125.6, 51.9, 49.8,
42.6, 34.3, 31.2, 29.5.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

 υ = 3068, 3023, 2926, 1727, 1711, 1460, 1232, 951 cm⁻¹

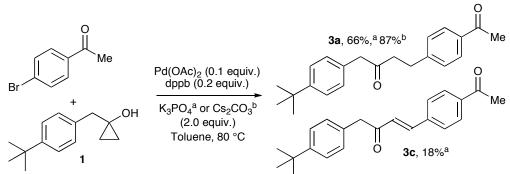
<u>m.p.</u> 47°C

HRMS EI

Calculated for $C_{22}H_{26}O_3$ [M⁺] = 338.1882, found = 338.1895

Rosa and Orellana

Ketones 3a and 3c



Following *General Procedure 4*, cyclopropanol **1** (0.050 g, 0.24 mmol, 1.0 equiv.) and using Cs_2CO_3 was coupled with 4'-bromoacetophenone (0.072 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 10% solution of EtOAc in hexanes afforded ketone **3a** (0.067 g, 0.21 mmol) as a clear oil in 87% yield. Using K_3PO_4 , ketone **3a** (0.051 g, 0.16 mmol) was isolated in 66% yield and was accompanied by ketone **3c** (0.014 g, 0.04 mmol) in 18% yield.

Data for 3a

 1 H NMR (400 MHz, CDCl₃)

δ 7.86 (d, J = 8.0 Hz, 2 H), 7.35 (d, J = 8.0 Hz, 2 H), 7.23 (d, J = 8.0 Hz, 2 H),

7.12 (d, *J* = 8.0 Hz, 2 H), 3.66 (s, 2 H), 2.94 (t, *J* = 7.2 Hz, 2 H),

2.82 (t, *J* = 7.2 Hz, 2 H), 2.59 (s, 3 H), 1.33 (s, 9 H).

 $\frac{13}{C}$ NMR (100 MHz, CDCl₃)

δ 206.9, 197.5, 149.9, 146.7, 135.2, 130.7, 128.9, 128.5, 125.6, 49.7, 42.6, 34.3, 31.2, 30.8, 29.5, 26.4.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

 υ = 2963, 2905, 2869, 1713, 1681, 1607, 1268, 823 cm⁻¹

<u>HRMS</u> EI

Calculated for $C_{22}H_{26}O_2$ [M⁺] = 322.1933, found = 322.1941

Rosa and Orellana

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Data for 3c
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¹<u>H NMR</u> (400 MHz, CDCl₃)

δ 7.97 (d, *J* = 8.4 Hz, 2 H), 7.65 (d, *J* = 16.0 Hz, 1 H), 7.62 (d, *J* = 8.0 Hz, 2 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 6.88 (d, *J* = 16.0 Hz, 1 H), 3.94 (s, 2 H), 2.63 (s, 3 H), 1.34 (s, 9 H).

 $\frac{13}{C}$ NMR (100 MHz, CDCl₃)

δ 197.1, 197.0, 149.9, 141.3, 138.8, 138.1, 130.8, 129.0, 128.7, 128.3, 127.2, 125.7, 48.1, 34.4, 31.2, 26.5.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

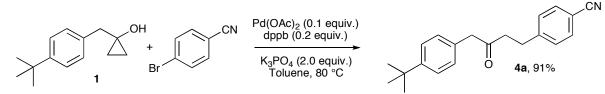
 $\upsilon = 2961, 1675, 1616, 1411, 1360, 1270, 1074 \text{ cm}^{-1}$

- <u>m.p.</u> 93 °C
- HRMS EI

Calculated for $C_{22}H_{24}O_2$ [M⁺] = 320.1776, found = 320.1784

Rosa and Orellana

Ketone 4a



Following *General Procedure* 4, cyclopropanol 1 (0.050 g, 0.24 mmol, 1.0 equiv.) was coupled with 4-bromobenzonitrile (0.066 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 10% solution of EtOAc in hexanes afforded ketone **4a** (0.067 g, 0.20 mmol) as a clear oil in 91% yield.

Data for 4a

 $\frac{1}{1}$ H NMR (400 MHz, CDCl₃)

δ 7.54 (d, J = 8.0 Hz, 2 H), 7.35 (d, J = 8.0 Hz, 2 H), 7.23 (d, J = 8.0 Hz, 2 H),

7.10 (d, J = 8.0 Hz, 2 H), 3.66 (s, 2 H), 2.94 (t, J = 7.2 Hz, 2 H),

2.82 (t, *J* = 7.2 Hz, 2 H), 1.33 (s, 9 H).

¹³C NMR (100 MHz, CDCl₃)

 δ 206.6, 150.0, 146.6, 132.1, 130.5, 129.1, 128.9, 125.6, 118.9, 109.8, 49.7,

42.2, 34.4, 31.2, 29.5.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

 $\upsilon = 2943, 2893, 2221, 1713, 1609, 936, 724 \text{ cm}^{-1}$

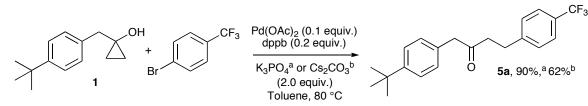
<u>m.p.</u> 64 °C

<u>HRMS</u> EI

Calculated for $C_{21}H_{23}ON [M^+] = 305.1780$, found = 305.1791

Rosa and Orellana

Ketone 5a



Following *General Procedure 4*, cyclopropanol **1a** (0.050 g, 0.24 mmol, 1.0 equiv.) was coupled to 4-bromo- α , α , α -trifluorotoluene (0.081 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 10% solution of EtOAc in hexanes afforded ketone **5a** (0.075 g, 0.22 mmol) as a white solid in 90% yield. Using Cs₂CO₃, ketone **5a** (0.052 g, 0.15 mmol) was prepared in 62% yield.

Data for 5a

 $\frac{1}{1}$ H NMR (400 MHz, CDCl₃)

δ 7.51 (d, J = 8.0 Hz, 2 H), 7.35 (d, J = 8.0 Hz, 2 H), 7.25 (d, J = 8.0 Hz, 2 H),

7.11 (d, J = 8.0 Hz, 2 H), 3.66 (s, 2 H), 2.92 (t, J = 7.2 Hz, 2 H),

2.82 (t, *J* = 7.2 Hz, 2 H), 1.33 (s, 9 H).

¹³C NMR (100 MHz, CDCl₃)

 δ 206.9, 149.9, 145.0, 130.6, 128.9, 128.6, 128.6 (q, ${}^{2}J_{C-F}$ = 32.0 Hz), 125.6, 125.2

(q, ${}^{3}J_{C-F}$ = 4.0 Hz), 124.1 (q, ${}^{1}J_{C-F}$ = 271.0.0 Hz), 49.8, 42.6, 34.3, 31.2, 29.3.

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\frac{19}{\text{F}} NMR (376 MHz, CDCl<sub>3</sub>)
```

-62.3

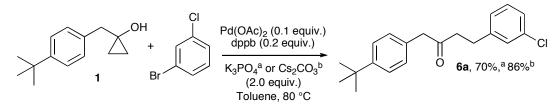
- <u>IR</u> Mattson Genesis II FT-IR instrument (thin film, NaCl) v = 3012, 2964, 1718, 1615, 1447, 962, 793 cm⁻¹
- <u>m.p.</u> 64 °C

<u>HRMS</u> EI

Calculated for $C_{21}H_{23}F_{3}O[M^{+}] = 348.1701$, found = 348.1715

Rosa and Orellana

Ketone 6a



Following *General Procedure 4* and utilizing Cs_2CO_3 as a base, cyclopropanol **1** (0.050 g, 0.24 mmol, 1.0 equiv.) was coupled with 3-bromochlorobenzene (0.069 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 7% solution of EtOAc in hexanes afforded ketone **6a** (0.067 g, 0.21 mmol) as a clear oil in 86% yield. Using K_3PO_4 , ketone **6a** (0.053 g, 0.17 mmol) was prepared in 70% yield.

Data for 6a

¹<u>H NMR</u> (400 MHz, CDCl₃)

δ 7.36 (d, J = 8.0 Hz, 2 H), 7.19 (m, 2 H), 7.12 (d, J = 8.0 Hz, 3 H),

7.03 (d, J = 6.4 Hz, 1 H), 3.66 (s, 2 H), 2.87 (dt, J = 6.8, 1.6 Hz, 2 H),

2.79 (dt, *J* = 6.8, 1.6 Hz, 2 H), 1.34 (s, 9 H).

 $\frac{13}{C}$ NMR (100 MHz, CDCl₃)

δ 207.1, 149.9, 142.9, 134.0, 130.7, 129.6, 128.9, 128.4, 126.5, 126.2, 125.6,
49.8, 42.8, 34.4, 31.2, 29.2.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

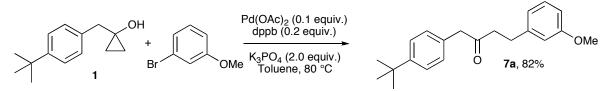
 υ = 3057, 2960, 2903, 1721, 1598, 1476, 1363, 1079, 781 cm⁻¹

<u>HRMS</u> EI

Calculated for $C_{20}H_{23}CIO [M^+] = 314.1437$, found = 314.1449

Rosa and Orellana

Ketone 7a



Following *General Procedure 4* and cyclopropanol **1** (0.050 g, 0.24 mmol, 1.0 equiv.) was coupled to 3-bromoanisole (0.067 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 3% solution of EtOAc in hexanes afforded ketone **7a** (0.063 g, 0.20 mmol) as a clear oil in 82% yield.

Data for 7a

¹<u>H NMR</u> (400 MHz, CDCl₃)

δ 7.36 (d, J = 8.0 Hz, 2 H), 7.20 (t, J = 8.0 Hz, 1 H),

7.13 (d, J = 8.0 Hz, 2 H), 6.75 (d, J = 8.0 Hz, 2 H), 6.72 (s, 1 H),

3.80 (s, 3 H), 3.67 (s, 2 H), 2.88 (dd, *J* = 7.2, 1.6 Hz, 2 H),

2.80 (dd, *J* = 7.2, 1.6 Hz, 2 H), 1.34 (s, 9 H).

¹³C NMR (100 MHz, CDCl₃)

δ 207.6, 159.6, 149.8, 142.5, 130.9, 129.3, 128.9, 125.6, 120.6, 114.0,

111.3, 55.0, 49.8, 43.2, 34.4, 31.2, 29.7.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

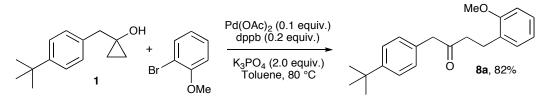
 $\upsilon = 2916, 2823, 1713, 1619, 1241, 1033, 817 \text{ cm}^{-1}$

<u>HRMS</u> EI

Calculated for $C_{21}H_{26}O_2$ [M⁺] = 310.1933, found = 310.1946

Rosa and Orellana

Ketone 8a



Following *General Procedure 4* cyclopropanol **1a** (0.050 g, 0.24 mmol, 1.0 equiv.) was coupled to 2-bromoanisole (0.067 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 4% solution of EtOAc in hexanes afforded ketone **8a** (0.061 g, 0.20 mmol) as a clear oil in 82% yield.

Data for 8a

¹<u>H NMR</u> (400 MHz, CDCl₃)

δ 7.36 (d, J = 8.0 Hz, 2 H), 7.21 (t, J = 8.0 Hz, 1 H), 7.14 (d, J = 8.0 Hz,

2 H), 7.12 (d, *J* = 8.0 Hz, 1 H), 6.88 (t, *J* = 8.0 Hz, 1 H),

6.85 (d, J = 8.0 Hz, 1 H), 3.81 (s, 3 H), 3.67 (s, 2 H),

2.90 (t, J = 7.6 Hz, 2 H), 2.78 (t, J = 7.6 Hz, 2 H), 1.34 (s, 9 H).

¹³C NMR (100 MHz, CDCl₃)

δ 208.3, 157.3, 149.6, 131.1, 130.0, 129.1, 129.0, 127.3, 125.5, 120.3,

110.1, 55.0, 49.6, 41.7, 34.3, 31.3, 25.0.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

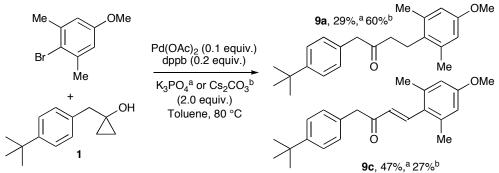
 $v = 3028, 2917, 1710, 1622, 1428, 1237, 1029, 766 \text{ cm}^{-1}$

<u>HRMS</u> EI

Calculated for $C_{21}H_{26}O_2$ [M⁺] = 310.1933, found = 310.1945

Rosa and Orellana

Ketones 9a and 9c



Following *General Procedure 4* and utilizing Cs_2CO_3 as a base, cyclopropanol **1** (0.050 g, 0.24 mmol, 1.0 equiv.) was coupled to 4-bromo-3,5-dimethylanisole (0.077 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 5% solution of EtOAc in hexanes afforded ketone **11a** (0.059 g, 0.14 mmol) as a clear oil in 60% yield, along with 27% of ketone **9c** (0.022 g, 0.07 mmol). Using K₃PO₄, ketones **9a** (0.024 g, 0.07 mmol) and **9c** (0.038 g, 0.11 mmol) were prepared in 29% and 47% yield, respectively.

Data for 9a

¹ H NMR	(400 MHz, CDCl ₃)
	δ 7.37 (d, J = 8.0 Hz, 2 H), 7.16 (d, J = 8.0 Hz, 2 H), 6.56 (s, 2 H), 3.77 (s, 3 H),
	3.68 (s, 2 H), 2.80 (dd, <i>J</i> = 10.8, 7.6 Hz, 2 H), 2.56 (dd, <i>J</i> = 10.8, 7.6 Hz, 2 H),
	2.20 (s, 6 H), 1.33 (s, 9 H).

¹³C NMR (100 MHz, CDCl₃)

δ 208.4, 157.3, 149.9, 137.3, 131.0, 129.7, 129.0, 125.6, 113.4, 55.0, 49.9, 40.8, 34.4, 31.2, 23.3, 19.9.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

 $v = 3015, 2982, 1712, 1513, 1235, 1043, 873 \text{ cm}^{-1}$

<u>HRMS</u> EI

Calculated for $C_{23}H_{30}O_2$ [M⁺] = 338.2246, found = 338.2234

Rosa and Orellana

- Data for 9c
- ¹<u>H NMR</u> (400 MHz, CDCl₃)

δ 7.78 (d, *J* = 16.4 Hz, 1 H), 7.39 (d, *J* = 8.0 Hz, 2 H), 7.23 (d, *J* = 8.0 Hz, 2 H), 6.62 (s, 2 H), 6.38 (d, *J* = 16.4 Hz, 1 H), 3.92 (s, 2 H), 3.81 (s, 3 H), 2.29 (s, 6 H), 1.34 (s, 9 H).

 $\frac{13}{C}$ NMR (100 MHz, CDCl₃)

δ 197.8, 159.4, 149.7, 141.4, 139.2, 131.6, 129.3, 129.0, 126.3, 125.6, 113.8,

55.0, 48.0, 34.4, 31.2, 21.5.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

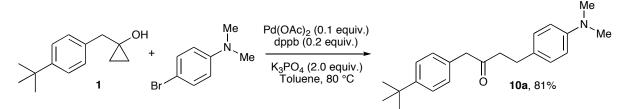
 υ = 2954, 1681, 1623, 1243, 1020, 985, 814 cm⁻¹

- <u>m.p.</u> 74 °C
- HRMS EI

Calculated for $C_{23}H_{28}O_2$ [M⁺] = 336.2089, found = 336.2103

Rosa and Orellana

Ketone 10a



Following *General Procedure 4*, cyclopropanol **1** (0.050 g, 0.24 mmol, 1.0 equiv.) was coupled to 4-bromo-*N*,*N*-dimethylaniline (0.072 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 10% solution of EtOAc in hexanes afforded ketone **10a** (0.063 g, 0.20 mmol) as a yellow oil in 81% yield.

Data for 10a

 $\frac{1}{1}$ H NMR (400 MHz, CDCl₃)

δ 7.37 (d, J = 8.4, 2 H), 7.15 (d, J = 8.4 Hz, 2 H), 7.06 (d, J = 8.4 Hz, 2 H),

6.71 (d, J = 8.4 Hz, 2 H), 3.67 (s, 2 H), 2.94 (s, 6 H),

2.83 (dt, J = 6.4, 2.4 Hz, 2 H), 2.77 (dt, J = 6.4, 2.4 Hz, 2 H), 1.35 (s, 9 H).

 $\frac{13}{C}$ NMR (100 MHz, CDCl₃)

δ 208.2, 149.7, 149.1, 131.1, 129.0, 128.8, 125.6, 125.5, 113.0, 49.8, 43.9, 40.8,

34.4, 31.3, 28.8.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

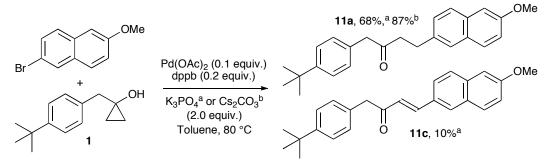
 υ = 2955, 2922, 2802, 1711, 1650, 1613, 1516, 1362, 812 cm⁻¹

HRMS EI

Calculated for $C_{22}H_{29}NO[M^+] = 323.2249$, found = 323.2238

Rosa and Orellana

Ketones 11a and 11c



Following *General Procedure 4* and utilizing Cs_2CO_3 as a base, cyclopropanol **1** (0.050 g, 0.24 mmol, 1.0 equiv.) was coupled to 6-methoxy-2-bromonaphthalene (0.085 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 7% solution of EtOAc in hexanes afforded ketone **11a** (0.075 g, 0.21 mmol) as a white solid in 87% yield. Using K₃PO₄, ketone **11a** was prepared in 68% (0.059 g, 0.16 mmol) yield, along with unsaturated ketone **11c** in 10% yield (0.007 g, 0.02 mmol).

Data for 11a

 1 H NMR (400 MHz, CDCl₃)

δ 7.69 (dd, J = 8.0, 2.0 Hz, 2 H), 7.52 (s, 1 H), 7.35 (d, J = 8.0 Hz, 2 H),

7.27 (d, J = 8.0 Hz, 1 H), 7.17 (d, J = 2.0 Hz, 1 H), 7.14 (m, 3 H), 3.94 (s, 3 H),

3.68 (s, 2 H), 3.04 (t, J = 7.6 Hz, 2 H), 2.88 (t, J = 7.6 Hz, 2 H), 1.35 (s, 9 H).

 $\frac{13}{C}$ NMR (100 MHz, CDCl₃)

 δ 207.7, 157.2, 149.8, 136.0, 133.0, 130.9, 129.0, 128.9, 128.8, 127.5, 126.8,

126.2, 125.6, 118.7, 105.5, 55.2, 49.8, 43.3, 34.4, 31.2, 29.6.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

 $v = 3008, 2942, 1716, 1628, 1233, 1040, 866 \text{ cm}^{-1}$

<u>m.p.</u> 79-80 °C

<u>HRMS</u> EI

Calculated for $C_{25}H_{28}O_2$ [M⁺] = 360.2089, found = 360.2102.

Rosa and Orellana

Data for 11c

 1 H NMR (400 MHz, CDCl₃)

δ 7.89 (s, 1 H), 7.80 (d, J = 16.0 Hz, 1 H), 7.77 (d, J = 8.8 Hz, 1 H),
7.73 (d, J = 8.8 Hz, 1 H), 7.64 (dd, J = 8.8, 1.2 Hz, 1 H), 7.40 (d, J = 8.0 Hz, 2 H),
7.26 (d, J = 8.0 Hz, 2 H), 7.19 (dd, J = 8.8, 2.4 Hz, 1 H), 7.14 (d, J = 2.4 Hz, 1 H),
6.89 (d, J = 16.0 Hz, 1 H), 3.97 (s, 2 H), 3.95 (s, 3 H), 1.35 (s, 9 H).

 $\frac{13}{C}$ NMR (100 MHz, CDCl₃)

δ 197.4, 158.8, 149.7, 143.5, 135.7, 131.4, 130.3, 130.1, 129.7, 129.0, 128.6,
127.4, 125.6, 124.4, 124.2, 119.4, 105.9, 55.3, 47.8, 34.4, 31.2.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

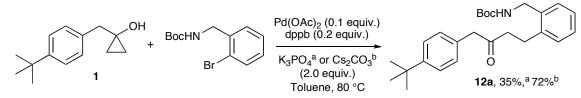
 $\upsilon = 3114, 2908, 1685, 1627, 1241, 1027, 952, 836 \text{ cm}^{-1}$

- <u>m.p.</u> 136-138 °C
- HRMS EI

Calculated for $C_{25}H_{26}O_2$ [M⁺] = 358.1933, found = 358.1946.

Rosa and Orellana

Ketone 12a



Following *General Procedure 4* and utilizing $Cs_2CO_3^{b}$ as a base, cyclopropanol **1** (0.050 g, 0.24 mmol, 1.0 equiv.) was coupled to *N*-Boc-2-bromobenzylamine (0.103 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 13% solution of EtOAc in hexanes afforded ketone **12a** (0.071 g, 0.17 mmol) as a white solid in 72% yield. Using K_3PO_4 ,^a ketone **12a** (0.069 g, 0.17 mmol) was prepared in 70% yield.

Data for 12a

 $\frac{1}{1}$ H NMR (400 MHz, CDCl₃)

 δ 7.34 (d, J = 8.0 Hz, 2 H), 7.26 (m, 1 H) 7.19 (m, 2 H), 7.10 (d, J = 8.0 Hz, 3 H),

4.81 (bs, 1 H), 4.30 (s, 2 H), 3.66 (s, 2 H), 2.91 (t, J = 7.2 Hz, 2 H),

2.78 (t, J = 7.2 Hz, 2 H), 1.48 (s, 9 H), 1.33 (s, 9 H).

¹³C NMR (100 MHz, CDCl₃)

δ 207.4, 155.6, 149.8, 138.8, 136.1, 130.7, 129.2, 128.9, 128.6, 127.6, 126.5,

125.6, 79.4, 49.8, 42.4, 42.0, 34.3, 31.2, 28.3, 26.1.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

 υ = 3002, 2953, 1728, 1712, 1455, 1024, 769 cm⁻¹

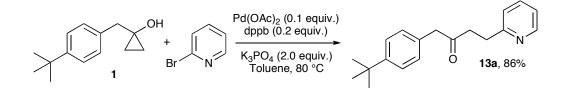
<u>m.p.</u> 77 °C

HRMS EI

Calculated for $C_{26}H_{35}NO_3$ [M⁺] = 409.2617, found = 409.2632

Rosa and Orellana

Ketone 13a



Following *General Procedure 4*, cyclopropanol **1** (0.050 g, 0.24 mmol, 1.0 equiv.) was coupled to 2-bromopyridine (0.057 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 40% solution of EtOAc in hexanes afforded ketone **13a** (0.058 g, 0.21 mmol) as a clear oil in 86% yield.

Data for 13a

 $\frac{1}{1}$ H NMR (400 MHz, CDCl₃)

δ 8.50 (d, *J* = 4.0 Hz, 1 H), 7.57 (t, *J* = 8.0 Hz, 1 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.09-7.17 (m, 4 H), 3.71 (s, 2 H), 3.07 (t, *J* = 6.8 Hz, 2 H), 2.99 (t, *J* = 6.8 Hz, 2 H), 1.32 (s, 9 H).

¹³C NMR (100 MHz, CDCl₃)

δ 207.6, 160.3, 149.6, 149.0, 136.2, 131.0, 129.0, 125.5, 123.1, 121.1, 49.6, 40.8, 34.3, 31.7, 31.2.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

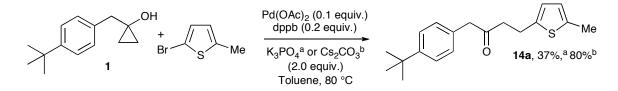
 $v = 3055, 3009, 2961, 2903, 2868, 1712, 1592, 1435, 1079 \text{ cm}^{-1}$

<u>HRMS</u> EI

Calculated for $C_{19}H_{23}NO[M^+] = 281.1780$, found = 281.1775

Rosa and Orellana

Ketone 14a



Following *General Procedure 4* and utilizing Cs_2CO_3 as a base, cyclopropanol **1** (0.050 g, 0.24 mmol, 1.0 equiv.) was coupled to 2-bromo-5-methylthiophene (0.064 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 5% solution of EtOAc in hexanes afforded ketone **14a** (0.058 g, 0.19 mmol) as a slightly yellow oil in 80% yield. Using K_3PO_4 , ketone **14a** (0.027 g, 0.09 mmol) was prepared in 37% yield.

Data for 14a

¹<u>H NMR</u> (400 MHz, CDCl₃)

δ 7.37 (d, J = 8.0 Hz, 2 H), 7.15 (d, J = 8.0 Hz, 2 H), 6.54 (s, 2 H), 3.68 (s, 2 H),

3.03 (t, *J* = 7.2 Hz, 2 H), 2.83 (t, *J* = 7.2 Hz, 2 H), 2.44 (s, 3 H), 1.35 (s, 9 H).

¹³C NMR (100 MHz, CDCl₃)

δ 207.2, 149.8, 141.2, 137.6, 130.8, 129.0, 125.6, 124.6, 124.2, 49.7, 43.5, 34.4, 31.2, 24.0, 15.2.

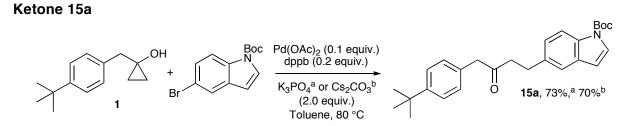
IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

 υ = 3100, 2961, 2921, 2869, 1714, 1515, 1462, 1363, 1079, 796 cm⁻¹

HRMS EI

Calculated for $C_{19}H_{24}SO[M^+] = 300.1548$, found = 300.1559

Rosa and Orellana



Following *General Procedure 4*, cyclopropanol **1a** (0.050 g, 0.24 mmol, 1.0 equiv.) was coupled to *N*-Boc-5-bromoindole (0.107 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 5% solution of EtOAc in hexanes afforded ketone **15a** (0.074 g, 0.18 mmol) as a slightly yellow oil in 73% yield. Using Cs_2CO_3 , ketone **15a** (0.070 g, 0.17 mmol) was prepared in 70% yield.

Data for 15a

¹<u>H NMR</u> (400 MHz, CDCl₃)

δ 8.04 (d, J = 7.6 Hz, 1 H), 7.59 (d, J = 3.2 Hz, 1 H), 7.34 (m, 3 H),

7.12 (d, J = 8.0 Hz, 3 H), 6.52 (d, J = 4.0 Hz, 1 H), 3.65 (s, 2 H),

2.99 (t, J = 7.2 Hz, 2 H), 2.83 (t, J = 7.2 Hz, 2 H), 1.69 (s, 9 H), 1.33 (s, 9 H).

 $\frac{13}{C}$ NMR (100 MHz, CDCl₃)

δ 207.8, 149.7, 149.7, 135.2, 133.6, 130.9, 130.7, 129.0, 126.0, 125.5, 124.7,

120.2, 114.9, 107.0, 83.5, 49.8, 43.9, 34.3, 31.2, 29.7, 28.1.

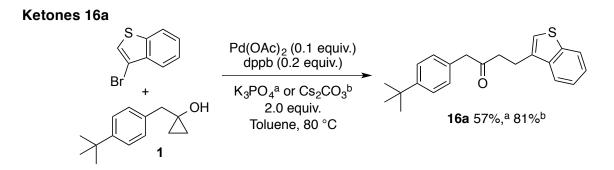
IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

 $v = 2956, 2924, 2868, 1730, 1714, 1469, 1376, 1256, 1013 \text{ cm}^{-1}$

<u>HRMS</u> EI

Calculated for $C_{27}H_{33}NO_3$ [M⁺] = 419.2460, found = 419.2472

Rosa and Orellana



Following *General Procedure 4* and utilizing Cs_2CO_3 as a base, cyclopropanol **1** (0.050 g, 0.24 mmol, 1.0 equiv.) coupled to 3-bromobenzothiophene (0.077 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 4% solution of EtOAc in hexanes afforded ketone **16a** (0.065 g, 0.19 mmol) as a yellow oil in 81% yield. Using K₃PO₄, ketone **16a** (0.046 g, 0.14 mmol) was prepared in 57% yield.

Data for 16a

¹<u>H NMR</u> (400 MHz, CDCl₃)

δ 7.86 (dd, J = 8.0, 2.0 Hz, 1 H), 7.69 (dd, J = 8.0, 2.0 Hz, 1 H) 7.39-7.35 (m, 4 H),

7.12 (d, *J* = 8.0 Hz, 2 H), 7.02 (s, 1 H), 3.69 (s, 2 H), 3.13 (t, *J* = 7.6 Hz, 2 H),

2.92 (t, *J* = 7.6 Hz, 2 H), 1.34 (s, 9 H).

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    <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)
    δ 207.4, 149.9, 140.4, 138.5, 135.1, 130.8, 128.9, 125.6, 124.1, 123.8, 122.8, 121.5, 121.4, 49.8, 40.9, 34.3, 31.2, 22.4.
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IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

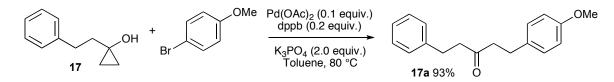
 υ = 3076, 3021, 2959, 1713, 1542, 1378, 953 cm⁻¹

HRMS EI

Calculated for $C_{22}H_{24}SO [M^+] = 336.1548$, found = 336.1561

Rosa and Orellana

Ketone 17a



Following *General Procedure 4* cyclopropanol **17** (0.050 g, 0.24 mmol, 1.0 equiv.) was coupled to 4-bromoanisole (0.067 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 10% solution of EtOAc in hexanes afforded ketone **17a** (0.060 g, 0.22 mmol) as a clear oil in 93% yield.

Data for 17a

¹<u>H NMR</u> (400 MHz, CDCl₃)

δ 7.31 (t, J = 7.6 Hz, 2 H), 7.22 (t, J = 7.6 Hz, 1 H) 7.19 (d, J = 7.6 Hz, 2 H),

7.10 (d, J = 8.4 Hz, 2 H), 6.85 (d, J = 8.4 Hz, 2 H), 3.81 (s, 3 H),

2.91 (t, *J* = 7.6 Hz, 2 H), 2.86 (t, *J* = 7.6 Hz, 2 H), 2.73 (t, *J* = 7.6 Hz, 2 H),

2.71 (t, *J* = 7.6 Hz, 2 H).

¹³C NMR (100 MHz, CDCl₃)

δ 209.2, 157.9, 140.9, 132.9, 129.1, 128.4, 128.2, 126.0, 113.8, 55.2, 44.7, 44.4, 29.6, 28.8.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

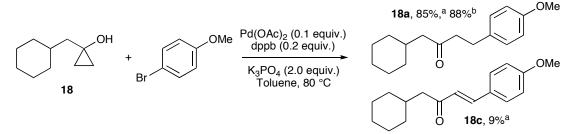
 $v = 3061, 3027, 2932, 2835, 1712, 1611, 1512, 1247, 1035, 823, 700 \text{ cm}^{-1}$

<u>HRMS</u> EI

Calculated for $C_{18}H_{20}O_2$ [M⁺] = 268.1463, found = 268.1475

Rosa and Orellana

Ketones 18a and 18c



Following *General Procedure 4* and utilizing $Cs_2CO_3^{b}$ as a base, cyclopropanol **18** (0.037 g, 0.24 mmol, 1.0 equiv.) was coupled to 4-bromoanisole (0.067 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 10% solution of EtOAc in hexanes afforded the product (0.055 g, 0.21 mmol) as a clear oil in 88% yield. Using K_3PO_4 , ketones **18a** (0.053 g, 0.20 mmol) and **18c** (0.006 g, 0.02 mmol) were prepared in 85% and 9% yield respectively.

Data for 18a

 1 H NMR (400 MHz, CDCl₃)

δ 7.12 (d, J = 8.4 Hz, 2 H), 6.84 (d, J = 8.4 Hz, 2 H), 3.80 (s, 3 H),

2.85 (t, J = 7.6 Hz, 2 H), 2.69 (t, J = 7.6 Hz, 2 H), 2.27 (d, J = 6.8 Hz, 2 H),

1.83 (m, 1 H), 1.70-1.61 (m, 5 H), 1.24 (tq, *J* = 12.4, 2.8 Hz, 2 H), 1.16 (m, 1 H),

0.91 (dq, J = 12.0, 3.2 Hz, 2 H)

$\frac{13}{C}$ NMR (100 MHz, CDCl₃)

δ 210.1, 157.8, 133.1, 129.1, 113.7, 55.2, 50.7, 45.1, 33.8, 33.1, 28.8, 26.1, 26.0.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

 υ = 2920, 2851, 1711, 1612, 1513, 1247, 1037, 826 cm⁻¹

<u>HRMS</u> EI

Calculated for $C_{17}H_{24}O_2$ [M⁺] = 260.1776, found = 260.1784

Rosa and Orellana

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Data for 18c
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 1 H NMR (400 MHz, CDCl₃)

δ 7.53 (d, *J* = 8.8 Hz, 2 H), 7.52 (d, *J* = 16.0 Hz, 1 H), 6.93 (d, *J* = 8.0 Hz, 2 H), 6.65 (d, *J* = 16.0 Hz, 1 H), 3.86 (s, 3 H), 2.52 (d, *J* = 6.8 Hz, 2 H), 1.91 (m, 1 H), 1.77-1.66 (m, 5 H), 1.32 (m, 2 H), 1.19 (m, 1 H), 0.91 (dq, *J* = 12.0, 2.8 Hz, 2 H)

 $\frac{13}{C}$ NMR (100 MHz, CDCl₃)

δ 200.3, 161.4, 142.1, 129.9, 127.2, 124.5, 114.3, 55.3, 48.5, 34.6, 33.3, 26.2, 26.1.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

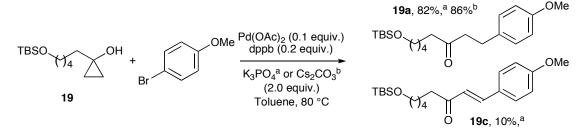
 υ = 2921, 2850, 1648, 1602, 1488, 1255, 1027 cm⁻¹

- <u>m.p.</u> 61 °C
- <u>HRMS</u> EI

Calculated for $C_{17}H_{22}O_2$ [M⁺] = 258.1620, found = 258.1610

Rosa and Orellana

Ketones 19a and 19b



Following *General Procedure 4* and utilizing Cs_2CO_3 as a base, cyclopropanol **19** (0.062 g, 0.24 mmol, 1.0 equiv.) was coupled to 4-bromoanisole (0.067 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 5% solution of EtOAc in hexanes afforded ketone **19a** (0.076 g, 0.21 mmol) as a clear oil in 86% yield. Using K_3PO_4 , ketones **19a** (0.072 g, 0.20 mmol) and **19c** (0.007 g, 0.02 mmol) were prepared in 82% and 10% yield, respectively.

- Data for 19a
- $\frac{1}{1}$ H NMR (400 MHz, CDCl₃)

8 7.11 (d, J = 8.4 Hz, 2 H), 6.84 (d, J = 8.4 Hz, 2 H), 3.80 (s, 3 H),
3.60 (t, J = 6.4 Hz, 2 H), 2.85 (t, J = 7.6 Hz, 2 H), 2.71 (t, J = 7.6 Hz, 2 H),
2.40 (t, J = 7.6 Hz, 2 H), 1.57 (quint, J = 7.6 Hz, 2 H), 1.52 (quint, J = 7.6 Hz, 2 H),
1.31 (quint, J = 7.6 Hz, 2 H), 0.91 (s, 9 H), 0.06 (s, 6 H).

 $\frac{13}{C}$ NMR (100 MHz, CDCl₃)

δ 210.3, 157.8, 133.1, 129.1, 113.8, 62.9, 55.1, 44.4, 42.9, 32.5, 28.8, 25.9, 25.4, 23.5, 18.2, -5.4.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

 υ = 2926, 2873, 1711, 1604, 1363, 1251, 1102, 1007, 776 cm⁻¹

HRMS ESI

Calculated for $C_{21}H_{37}O_3Si [M+H^+] = 365.2507$, found = 365.2507

Rosa and Orellana

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Data for 19c
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 $\frac{1}{1}$ H NMR (400 MHz, CDCl₃)

δ 7.54 (d, J = 16.0 Hz, 1 H), 7.53 (d, J = 8.4 Hz, 2 H), 6.94 (d, J = 8.4 Hz, 2 H),
6.65 (d, J = 16.0 Hz, 1 H), 3.87 (s, 3 H), 3.64 (t, J = 6.4 Hz, 2 H),
2.67 (t, J = 7.6 Hz, 2 H), 1.71 (quint, J = 7.6 Hz, 2 H), 1.56 (m, 3 H), 1.31 (m, 2 H),
0.91 (s, 9 H), 0.07 (s, 6 H).

¹³C NMR (100 MHz, CDCl₃)

δ 200.4, 161.4, 142.0, 129.8, 127.1, 124.0, 114.3, 62.9, 55.3, 40.7, 32.6, 25.9, 25.5, 24.2, 18.3, -5.4.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

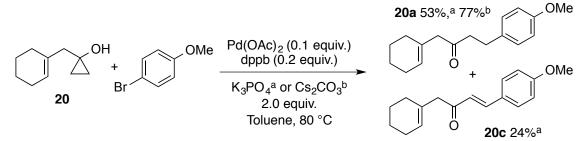
 $\upsilon = 2942, 1673, 1624, 1422, 1251, 1083, 1034, 842 \text{ cm}^{-1}$

HRMS ESI

Calculated for $C_{21}H_{35}O_3Si [M+H^+] = 363.2350$, found = 363.2351

Rosa and Orellana

Ketones 20a and 20c



Following *General Procedure 4* and utilizing Cs_2CO_3 as a base, cyclopropanol **20** (0.037 g, 0.24 mmol, 1.0 equiv.) was coupled to 4-bromoanisole (0.067 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 5% solution of EtOAc in hexanes afforded ketone **20a** (0.048 g, 0.19 mmol) as a clear oil in 77% yield. Using K_3PO_4 , ketones **20a** (0.033 g, 0.13 mmol) and **20c** (0.015 g, 0.06 mmol) were prepared in 53% and 24% yield, respectively.

Data for 20a

 $\frac{1}{1}$ H NMR (400 MHz, CDCl₃)

δ 7.11 (d, J = 8.4 Hz, 2 H), 6.84 (d, J = 8.4 Hz, 2 H), 5.53 (bs, 1 H), 3.80 (s, 3 H),
2.99 (s, 2 H), 2.84 (t, J = 7.2 Hz, 2 H), 2.74 (t, J = 7.2 Hz, 2 H), 2.03 (m, 2 H),
1.87 (m, 2 H), 1.57 (m, 4 H).

- ¹³C NMR (100 MHz, CDCl₃)
 δ 208.3, 157.8, 133.1, 131.5, 129.2, 126.2, 113.7, 55.2, 52.7, 43.3, 28.8, 28.5, 25.3, 22.6, 21.8.
 - IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

 υ = 3021, 2928, ,2835, 1712, 1612, 1246, 1036, 824 cm⁻¹

HRMS EI

Calculated for $C_{17}H_{22}O_2$ [M⁺] = 258.1620, found = 258.1631

Rosa and Orellana

- Data for 20c
- $\frac{1}{1}$ MMR (400 MHz, CDCl₃)

δ 7.58 (d, *J* = 16.0 Hz, 1 H), 7.52 (d, *J* = 8.4 Hz, 2 H), 6.93 (d, *J* = 8.4 Hz, 2 H), 6.71 (d, *J* = 16.0 Hz, 1 H), 5.64 (bs, 1 H), 3.86 (s, 3 H), 3.24 (s, 2 H), 2.07 (m, 2 H), 1.99 (m, 2 H), 1.68-1.57 (m, 4 H).

 $\frac{13}{C}$ NMR (100 MHz, CDCl₃)

δ 198.6, 161.4, 142.4, 132.1, 129.9, 127.2, 126.0, 123.0, 114.3, 55.3, 50.8,
28.6, 25.4, 22.7, 21.9.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

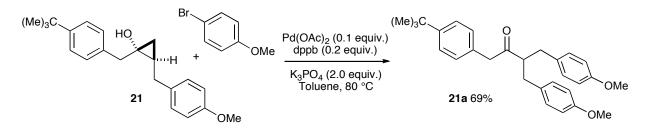
 υ = 2930, 2837, 1682, 1661, 1599, 1254, 1030 cm⁻¹

- <u>m.p.</u> 74 °C
- HRMS EI

Calculated for $C_{17}H_{20}O_2$ [M⁺] = 256.1463, found = 256.1474

Rosa and Orellana

Ketone 21a



Following *General Procedure 4*, cyclopropanol **21** (0.078 g, 0.24 mmol, 1.0 equiv.) was coupled to 4-bromoanisole (0.067 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 5% solution of EtOAc in hexanes afforded ketone **21a** (0.071 g, 0.16 mmol) as a clear oil in 69% yield.

Data for 21a

 1 H NMR (400 MHz, CDCl₃)

δ 7.25 (d, *J* = 8.0 Hz, 2 H), 7.10 (d, *J* = 8.4 Hz, 4 H), 6.83 (d, *J* = 8.4 Hz, 4 H), 6.75 (d, *J* = 8.0 Hz, 2 H), 3.82 (s, 6 H), 3.17 (m, 1 H), 3.15 (s, 2 H),

2.85 (dd, *J* = 13.6, 9.2 Hz, 2 H), 2.68 (dd, *J* = 13.6, 6.0 Hz, 2 H), 1.33 (s, 9 H).

¹³C NMR (100 MHz, CDCl₃)

δ 211.7, 158.0, 149.4, 131.3, 130.3, 129.8, 129.2, 125.2, 113.8, 55.1, 51.7, 37.7, 34.3, 31.2, 31.2.

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

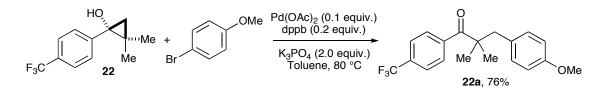
 $\upsilon = 3021, 2972, 2835, 1713, 1248, 1037, 836 \text{ cm}^{-1}$

HRMS EI

Calculated for $C_{29}H_{34}O_3$ [M⁺] = 430.2508, found = 430.2493

Rosa and Orellana

Ketone 22a



Following *General Procedure 4*, cyclopropanol **22** (0.055 g, 0.24 mmol, 1.0 equiv.) was coupled to 4-bromoanisole (0.067 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 3% solution of EtOAc in hexanes afforded ketone **22a** (0.061 g, 0.18 mmol) as a clear oil in 76% yield.

Data for 22a

¹<u>H NMR</u> (400 MHz, CDCl₃)

δ 7.64 (d, J = 8.0 Hz, 2 H), 7.49 (d, J = 8.0 Hz, 2 H), 7.03 (d, J = 8.0 Hz, 2 H),

6.83 (d, J = 8.0 Hz, 2 H), 3.81 (s, 3 H), 3.01 (s, 2 H), 1.30 (s, 6 H).

 $\frac{13}{C}$ NMR (100 MHz, CDCl₃)

δ 209.5, 158.2, 142.9, 131.9 (q, ${}^{2}J_{C-F}$ = 32.0 Hz), 131.3, 130.1, 127.2, 125.0 (q, ${}^{3}J_{C-F}$ = 4.0 Hz), 123.6 (q, ${}^{1}J_{C-F}$ = 271.0.0 Hz), 113.4, 55.1, 50.0, 45.2, 25.8.

¹⁹F NMR (376 MHz, CDCl₃)

-62.9

IR Mattson Genesis II FT-IR instrument (thin film, NaCl)

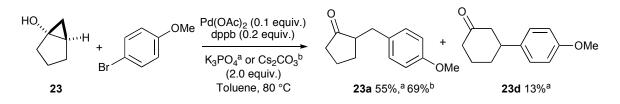
 $\upsilon = 3015, 2983, 2869, 1711, 1601, 1433, 1138, 780 \text{ cm}^{-1}$

HRMS EI

Calculated for $C_{19}H_{19}F_3O_2$ [M⁺] = 336.1337, found = 336.1349

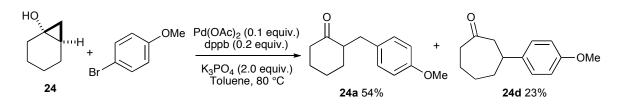
Rosa and Orellana

Ketones 23a and 23d



Following *General Procedure 4* and utilizing Cs_2CO_3 as a base, cyclopropanol **23** (0.024 g, 0.24 mmol, 1.0 equiv.) was coupled to 4-bromoanisole (0.067 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using an 8% solution of EtOAc in hexanes afforded ketone **23a** (0.034 g, 0.17 mmol) as a clear oil in 69% yield. Using K_3PO_4 , ketones **23a** (0.027 g, 0.13 mmol) and **23d** (0.006 g, 0.03 mmol) were prepared in 55% and 13 % yield, respectively.

Spectral data for **23a** is consistent with those reported by Ricankova and co-workers.⁴ Spectral data for **23d** is consistent with those reported by Yu and co-workers.^v



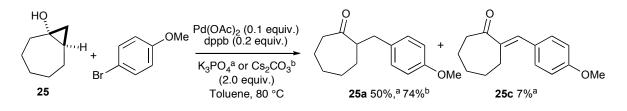
Ketones 24a and 24d

Following *General Procedure* – and utilizing K_3PO_4 as a base, cyclopropanol **24** (0.027 g, 0.24 mmol, 1.0 equiv.) was coupled to 4-bromoanisole (0.067 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 13% solution of EtOAc in hexanes afforded ketone **24a** (0.028 g, 0.13 mmol) as a clear oil in 54% yield along with the corresponding ring-expanded ketone **24d** (0.012 g, 0.05 mmol) in 23% yield.

Spectral data for **24a** is consistent with those reported by Bolm and co-workers.^{vi} Spectral data for **24d** is consistent with those reported by Minnaard and co-workers.^{vii}

Rosa and Orellana

Ketones 25a and 25c



Following *General Procedure 4* and utilizing Cs_2CO_3 as a base, cyclopropanol **25** (0.030 g, 0.24 mmol, 1.0 equiv.) was coupled to 4-bromoanisole (0.067 g, 0.36 mmol, 1.5 equiv.). Purification by flash column chromatography using a 7% solution of EtOAc in hexanes afforded ketone **25a** (0.041 g, 0.18 mmol) as a clear oil in 74% yield. Using K_3PO_4 , ketones **25a** (0.028 g, 0.12 mmol) and **25c** (0.013 g, 0.06 mmol) were prepared in 50% and 23 % yield, respectively.

Spectral data for **25a** is consistent with those reported by Ricankova and co-workers.^{viii} Spectral data for **25c** is consistent with those reported by Zhang and co-workers.^{ix}

ⁱ Still, W.C.; Kahn, M.; Mitra. A. *J. Org. Chem.* **1978**, *43*, 2923 – 2925.

ⁱⁱ Lee, J.; Kim, Heejin; Cha, J. K. *J. Am. Chem. Soc.* **1996**, *118*, 4198 – 4199.

^{III} Iwasawa, N.; Hayakawa, S.; Funahashi, M.; Isobe, K.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **1996**, *66*, 819 – 827.

^{iv} Murai,S.; Aya, T.; Sonoda, N. *J. Org. Chem.* **1973**, *38*, 4354 – 4356.

^v Li, Q.; Dong, Z.; Yu, Z-X. *Org. Lett.*, **2011**, *13*, 1122 – 1125.

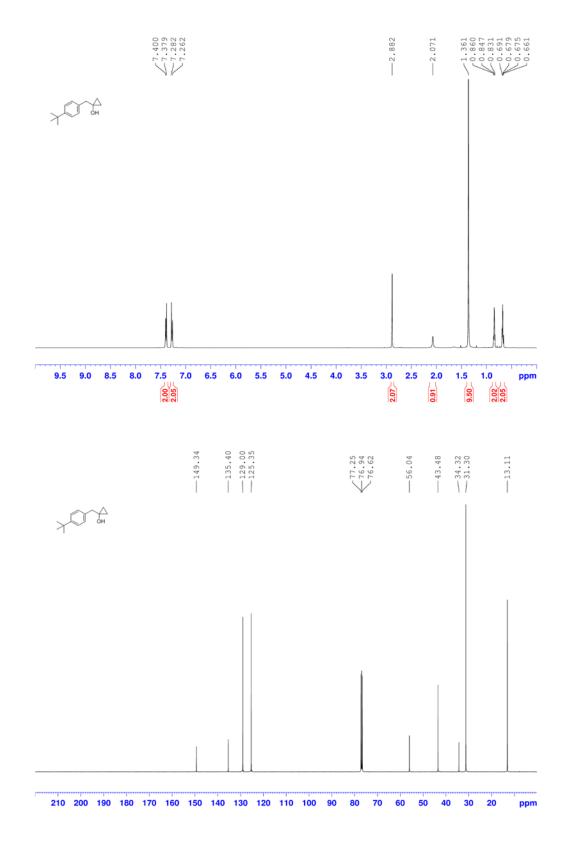
^{vi} Lu, S-M.; Bolm, C. Angew. Chem. Int. Ed. **2008**, 47, 8920 – 8923.

^{vii} Gottumukkala, A.; Devries, J.; Minnaard, A. Chem. Eur. J., **2011**, *17*, 3091 – 3095.

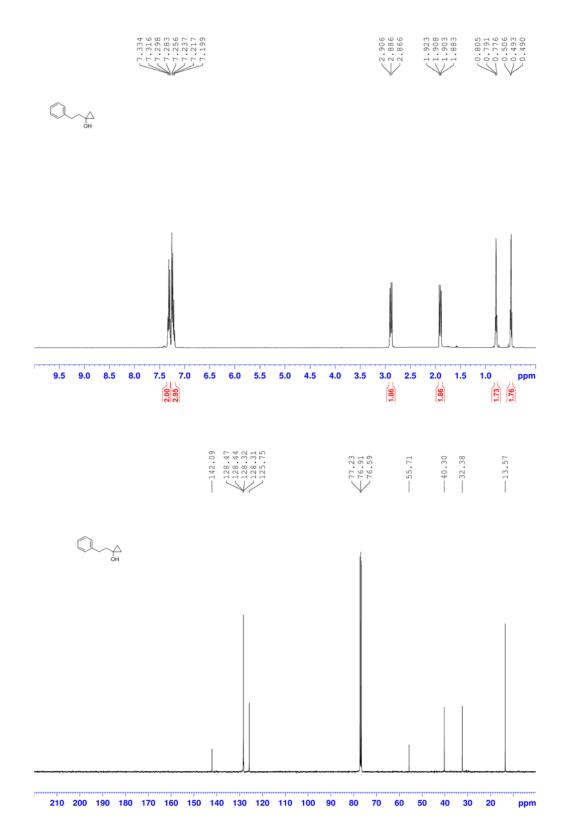
^{viii} Rejzek, M.; Wimmer, Z.; Saman, D.; Ricankova. M. *Helv. Chim. Acta.* **1994**, *77*, 1241-1255.

^{ix} Tian, F.; Yao, D.; Liu, Y.; Xie, F.; Zhang, W. Adv. Syn. and Cat. 2010, 352, 1841 – 1845.

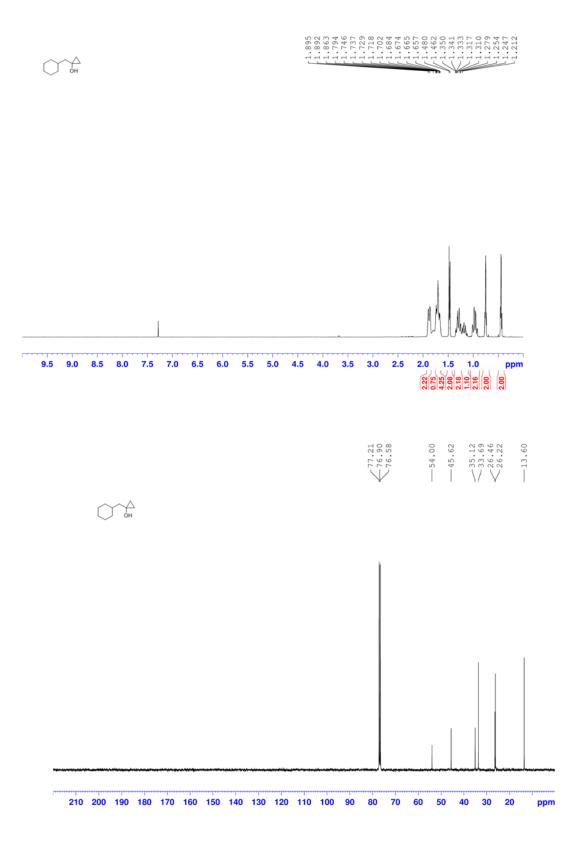
Rosa and Orellana



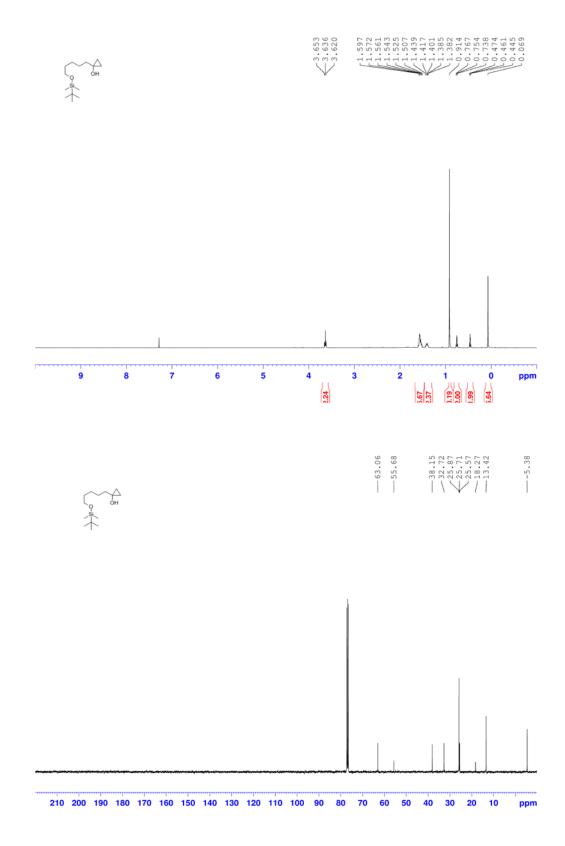
Rosa and Orellana



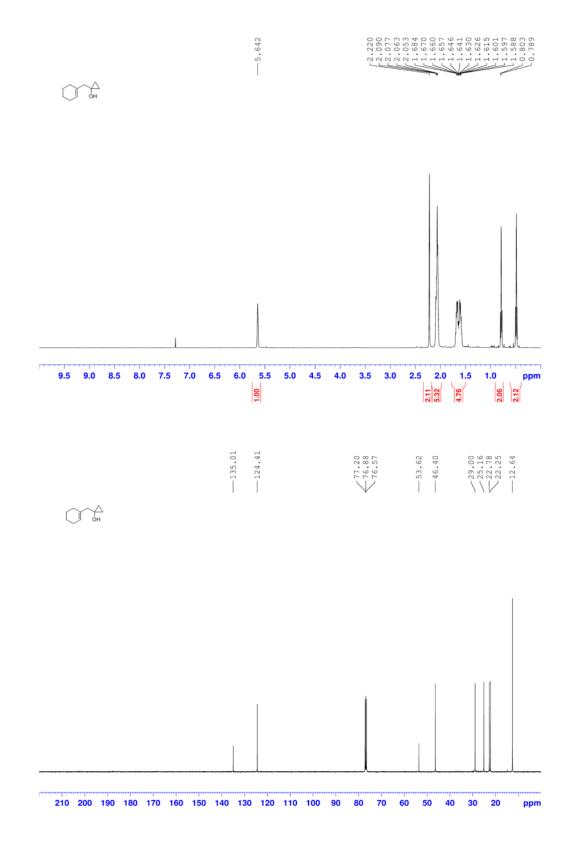
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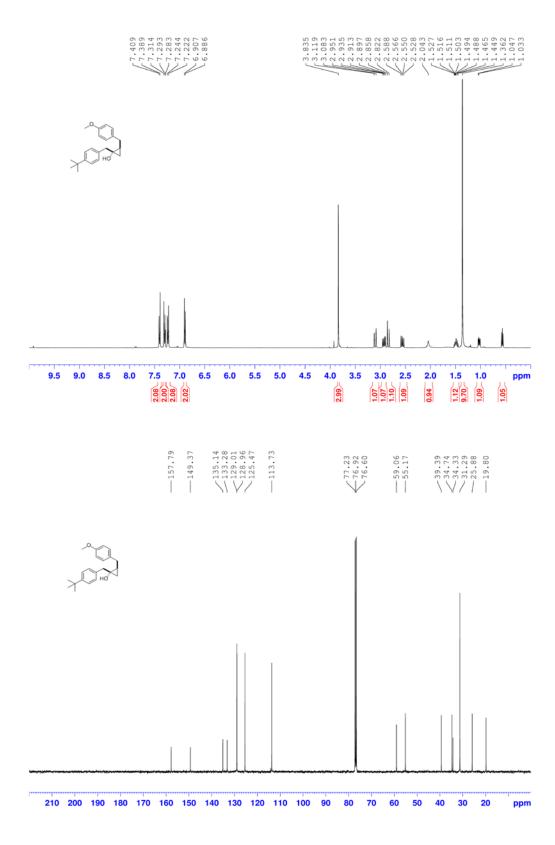
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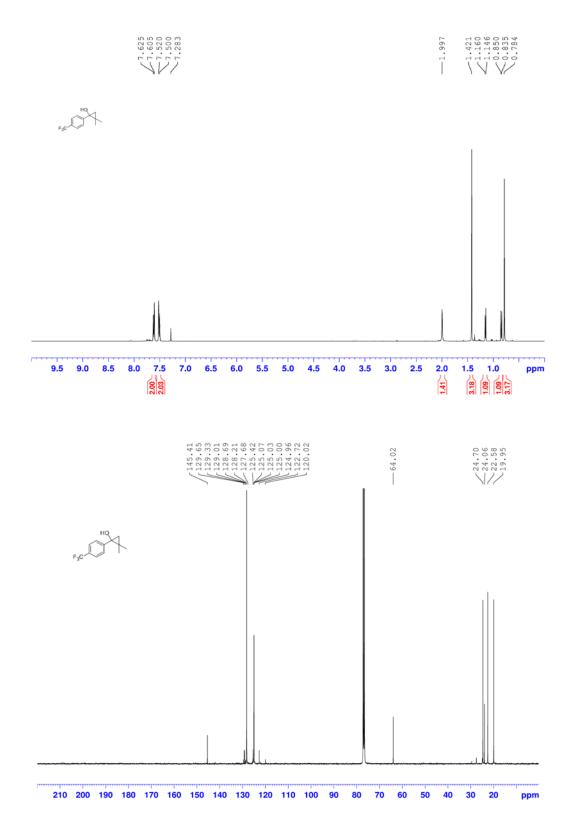
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Rosa and Orellana

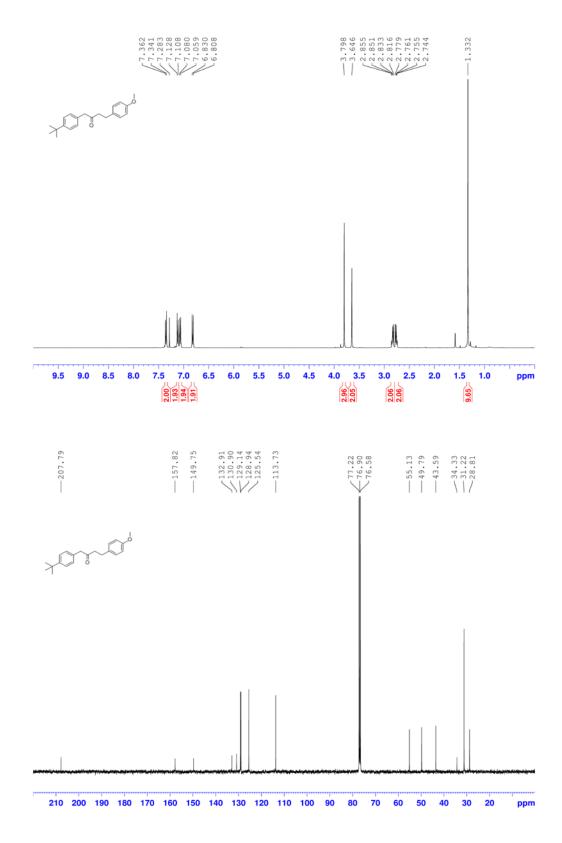


Rosa and Orellana



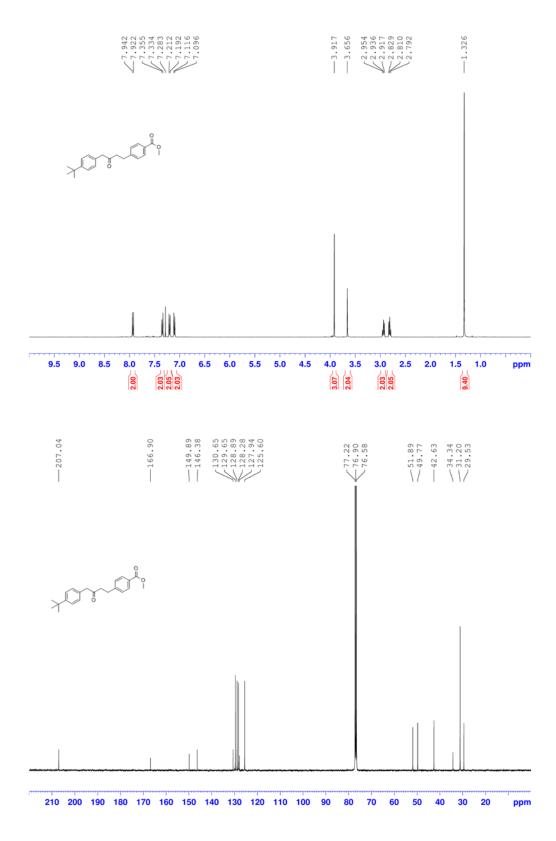
Rosa and Orellana

¹H- and ¹³C-NMR data for ketone 1a



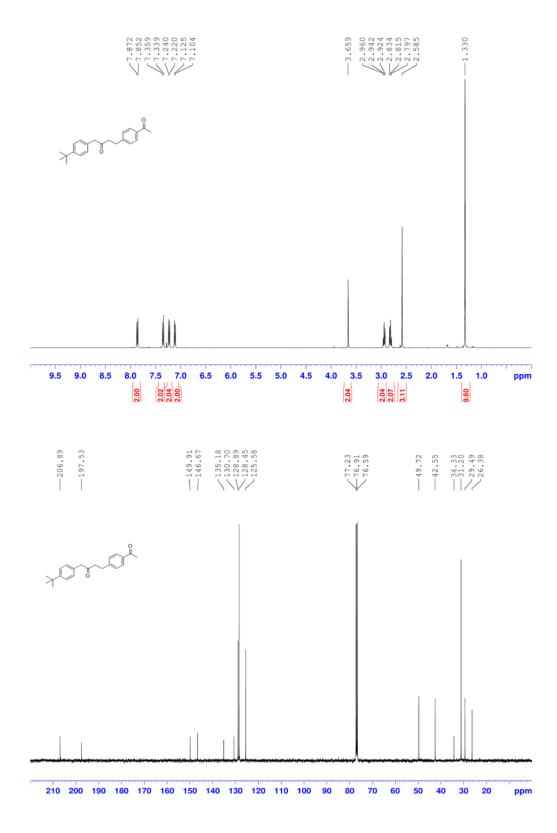
Rosa and Orellana

¹H- and ¹³C-NMR data for ketone 2a



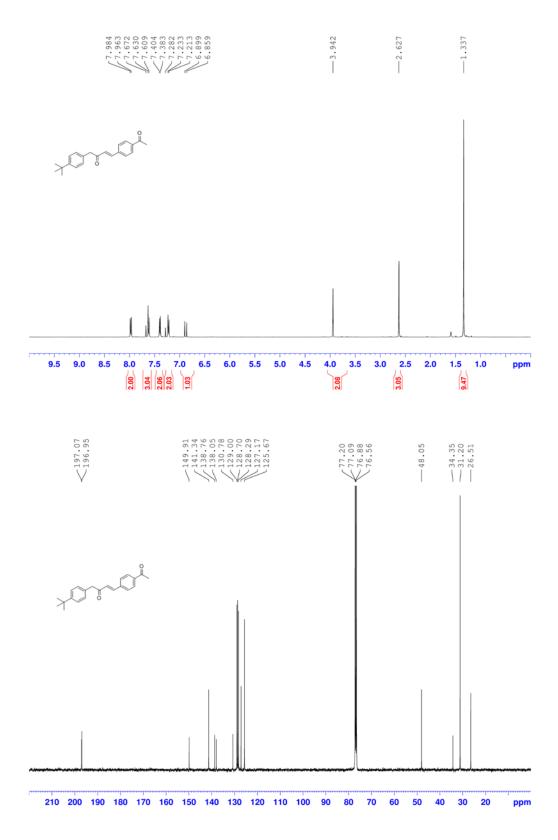
Rosa and Orellana

¹H- and ¹³C-NMR data for ketone 3a



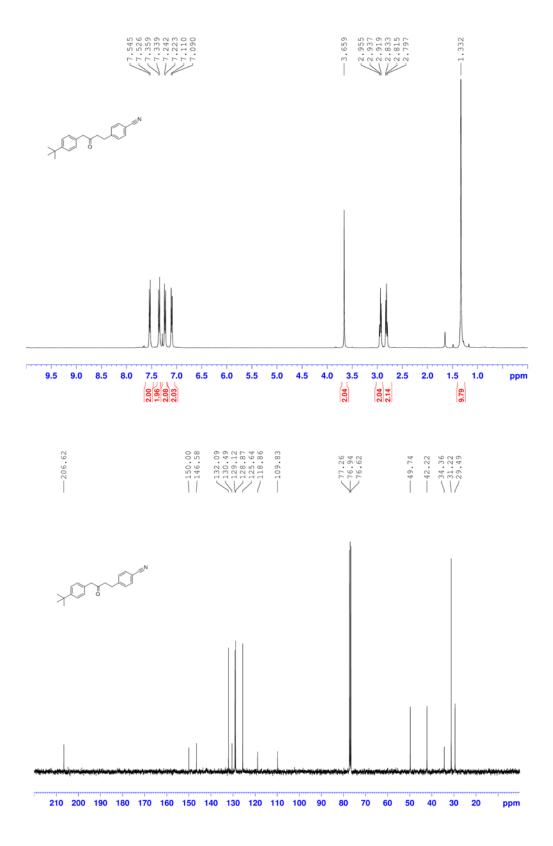
Rosa and Orellana

¹H and ¹³C NMR data for α , β -unsaturated ketone 3c



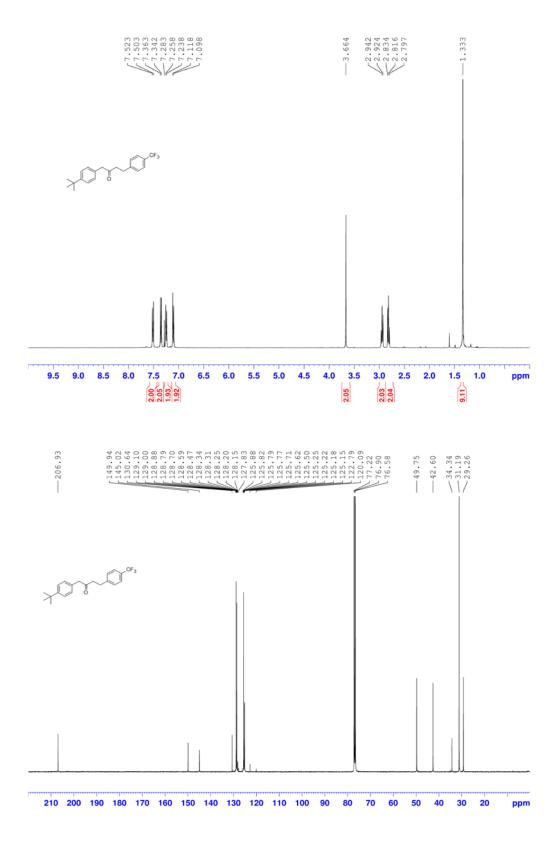
Rosa and Orellana

¹H and ¹³C NMR data for ketone 4a



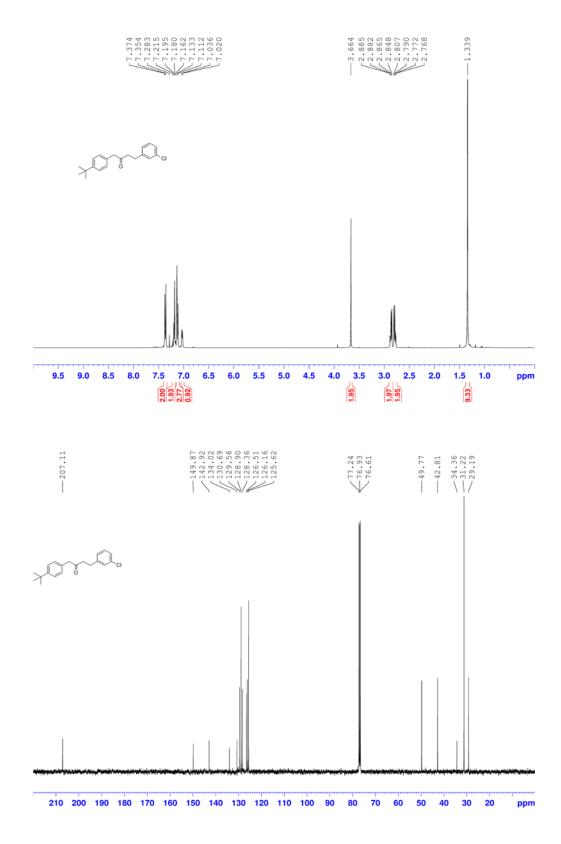
Rosa and Orellana

¹H- and ¹³C-NMR data for ketone 5a



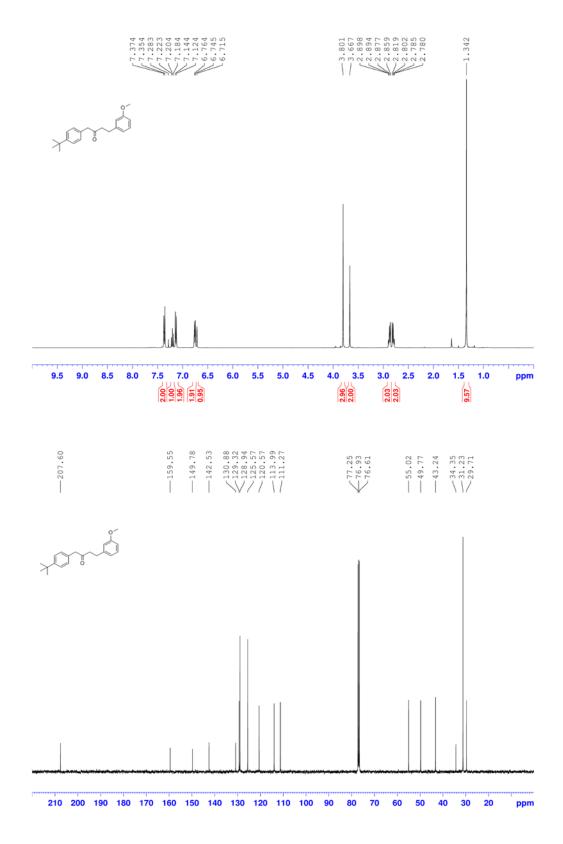
Rosa and Orellana

¹H- and ¹³C-NMR data for ketone 6a



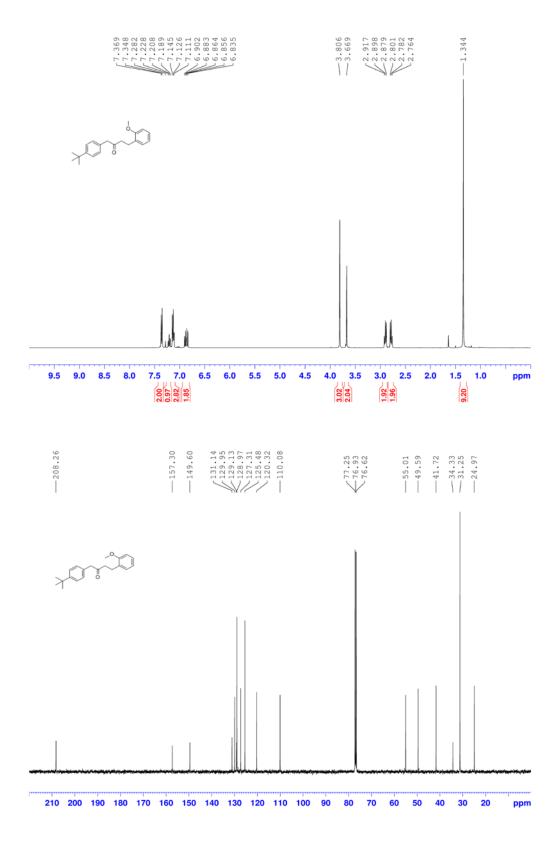
Rosa and Orellana

¹H and ¹³C NMR data for ketone 7a



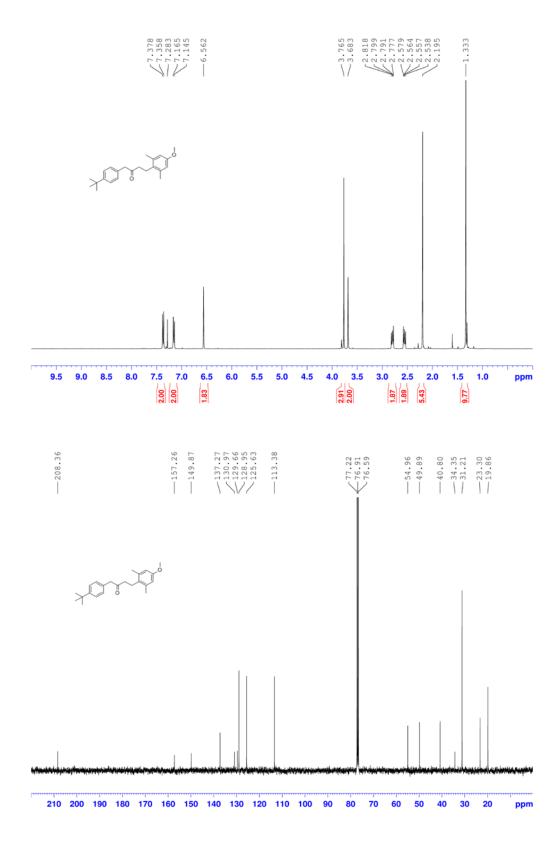
Rosa and Orellana

¹H- and ¹³C-NMR data for ketone 8a



Rosa and Orellana

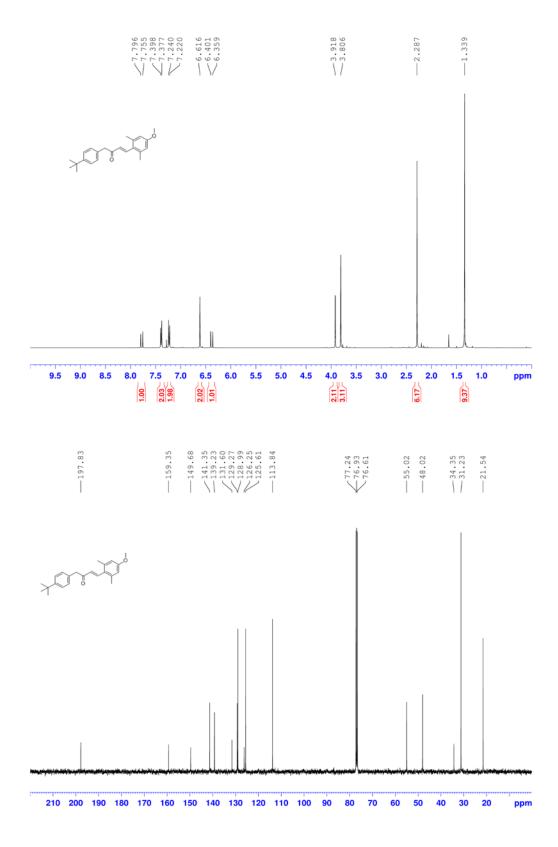
¹H- and ¹³C-NMR data for ketone 9a



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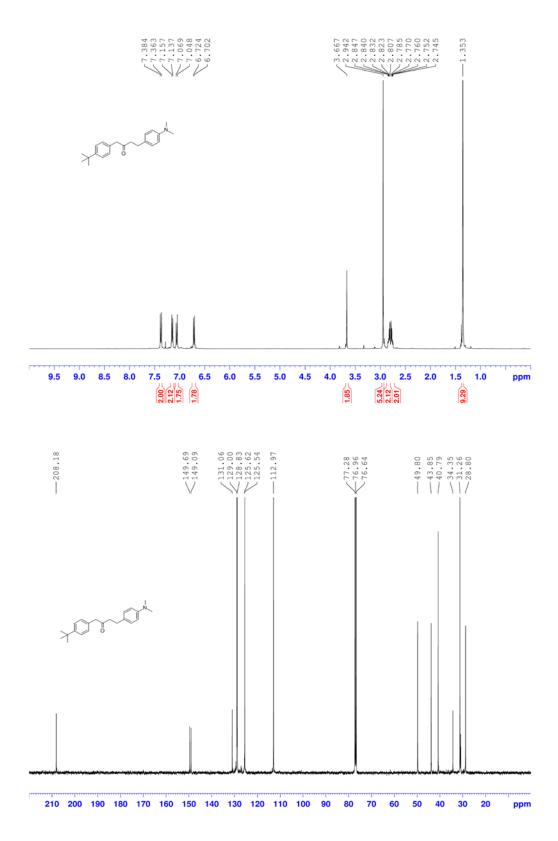
Rosa and Orellana

¹H- and ¹³C-NMR data for α , β -unsaturated ketone 9c

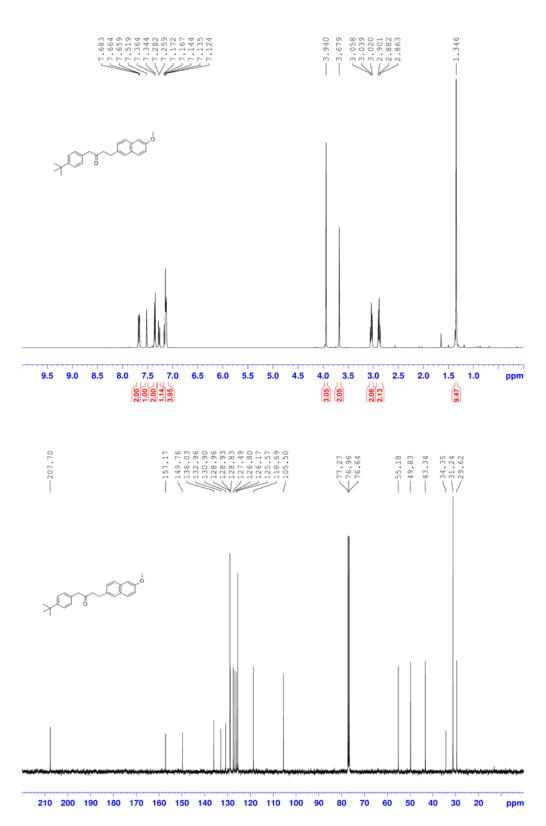


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¹H- and ¹³C-NMR data for ketone 10a

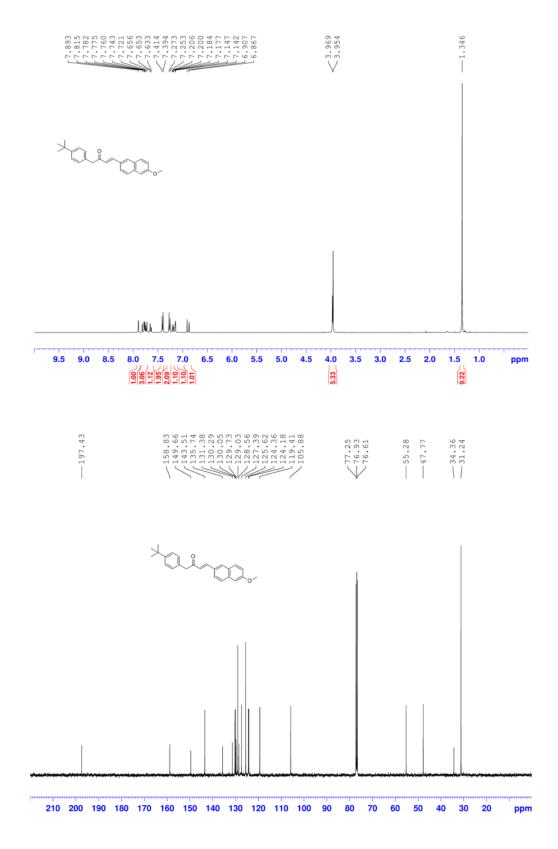


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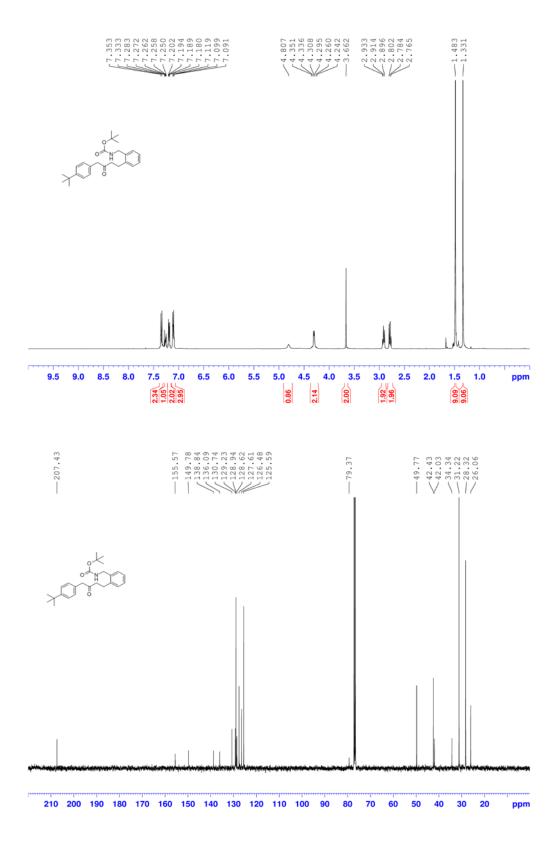
Rosa and Orellana

¹H- and ¹³C-NMR data for α , β -unsaturated ketone 11c



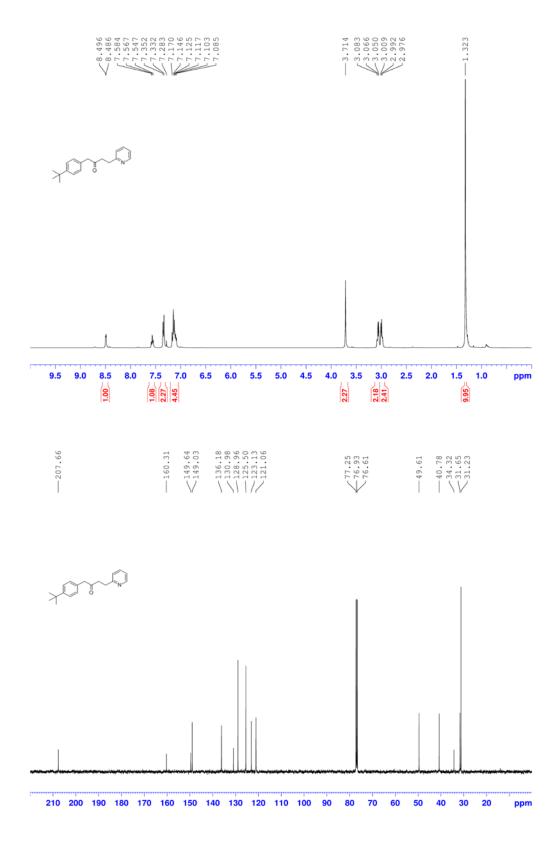
Rosa and Orellana

¹H- and ¹³C-NMR data for ketone 12a



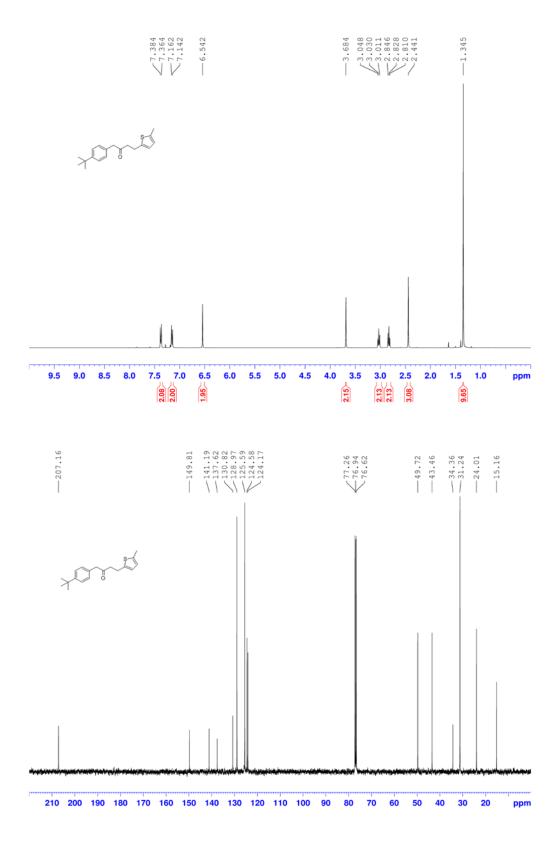
Rosa and Orellana

¹H- and ¹³C-NMR data for ketone 13a



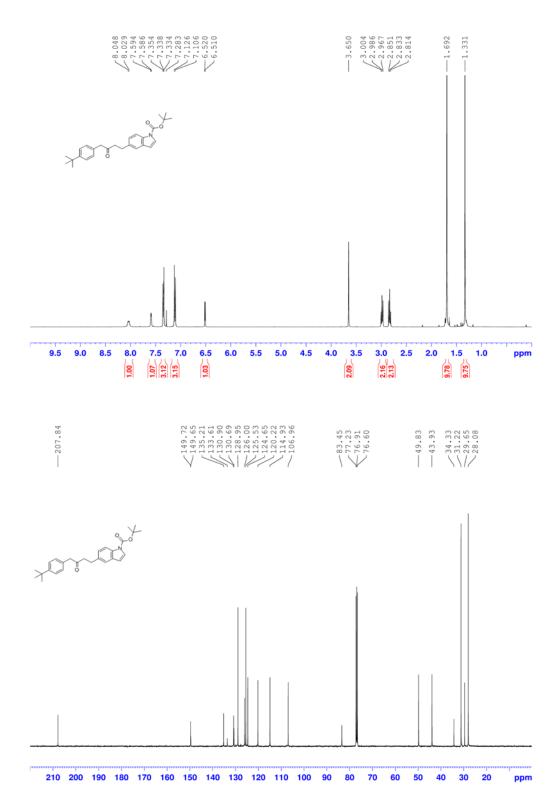
Rosa and Orellana

¹H- and ¹³C-NMR data for ketone 14a



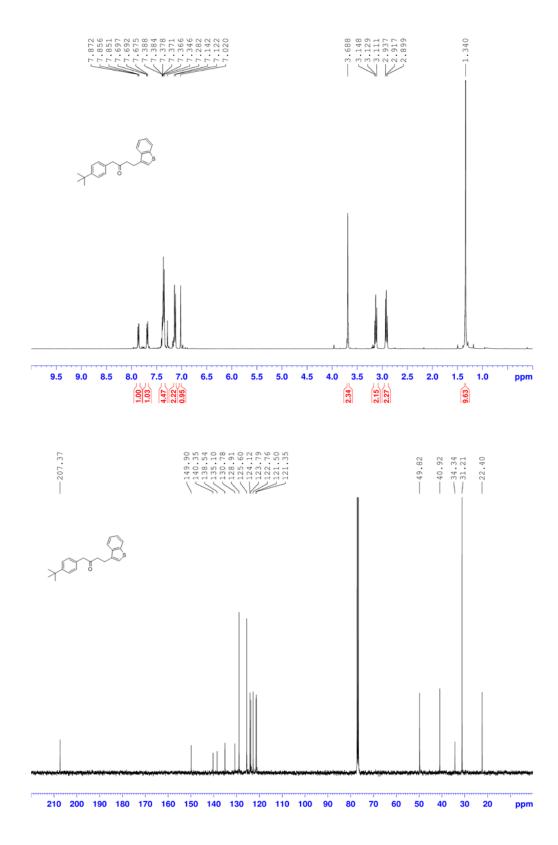
Rosa and Orellana

¹H- and ¹³C-NMR data for ketone 15a



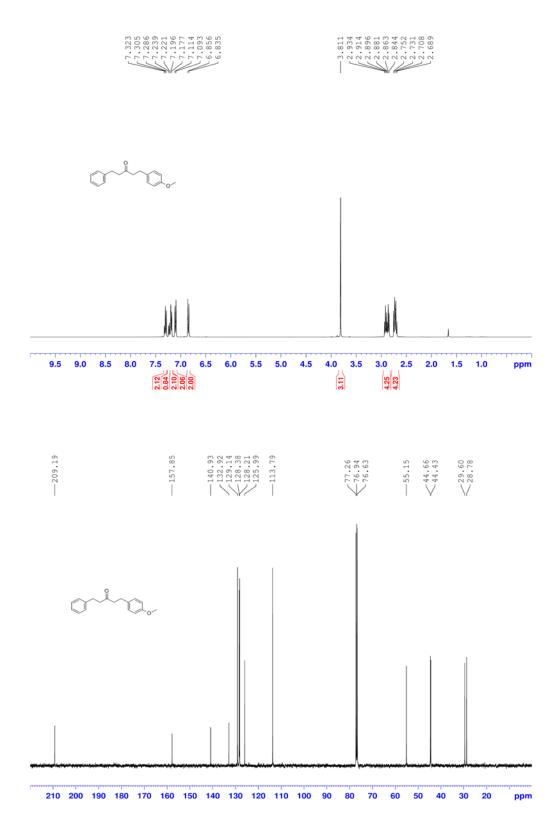
Rosa and Orellana

¹H- and ¹³C-NMR data for ketone 16a



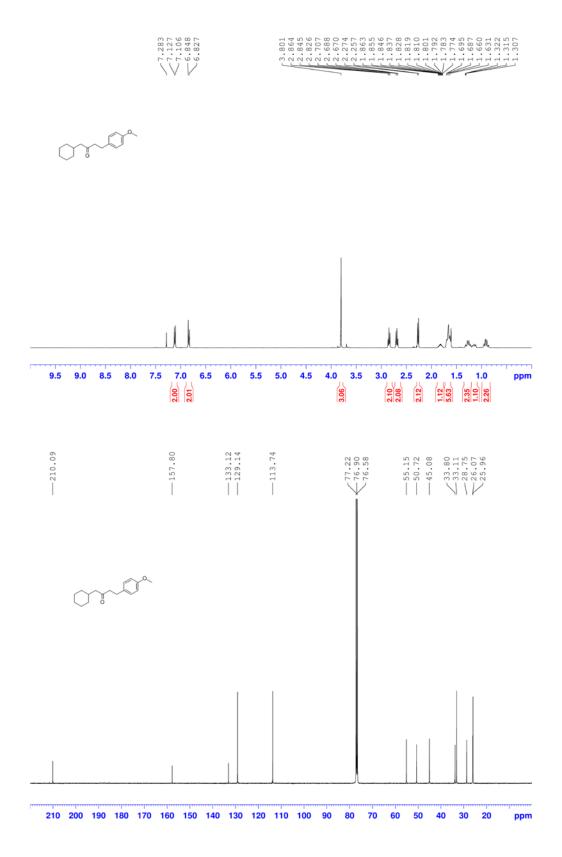
Rosa and Orellana

¹H- and ¹³C-NMR data for ketone 17a



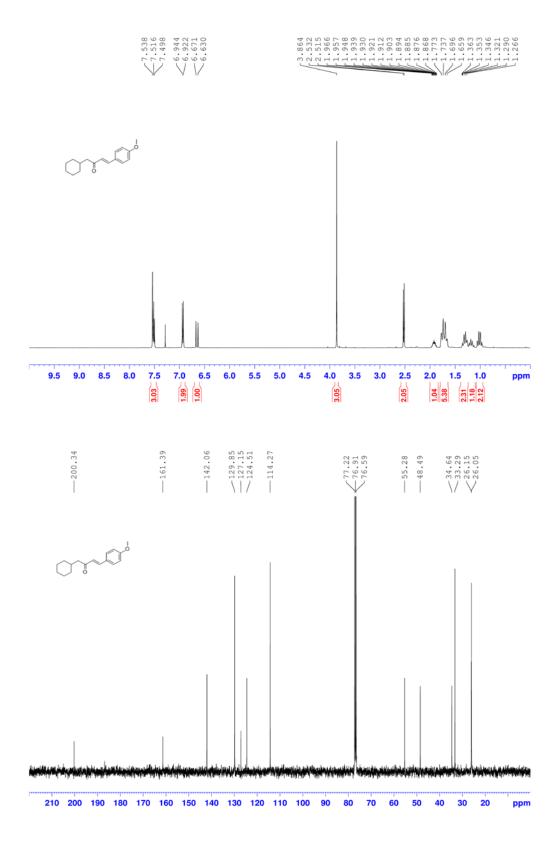
Rosa and Orellana

¹H- and ¹³C-NMR data for ketone 18a



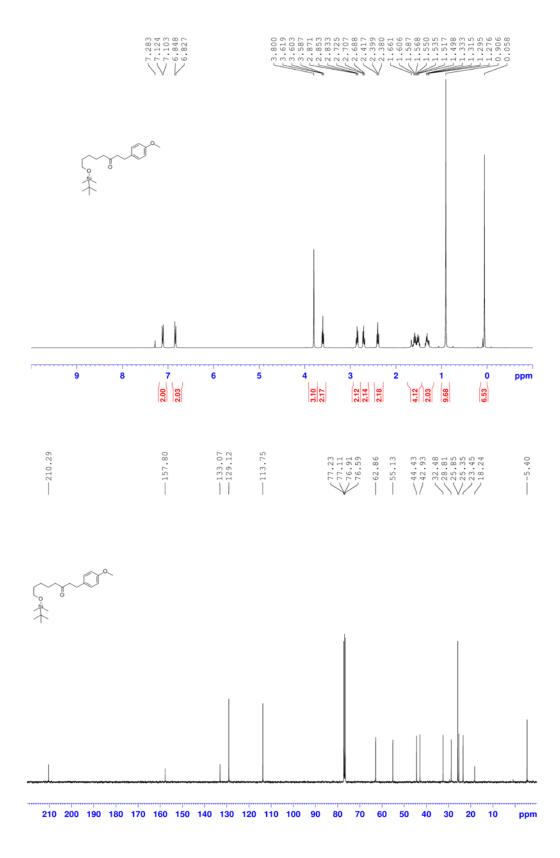
Rosa and Orellana

$^1\text{H-}$ and $^{13}\text{C-NMR}$ data for $\alpha,\beta\text{-unsaturated}$ ketone 18c



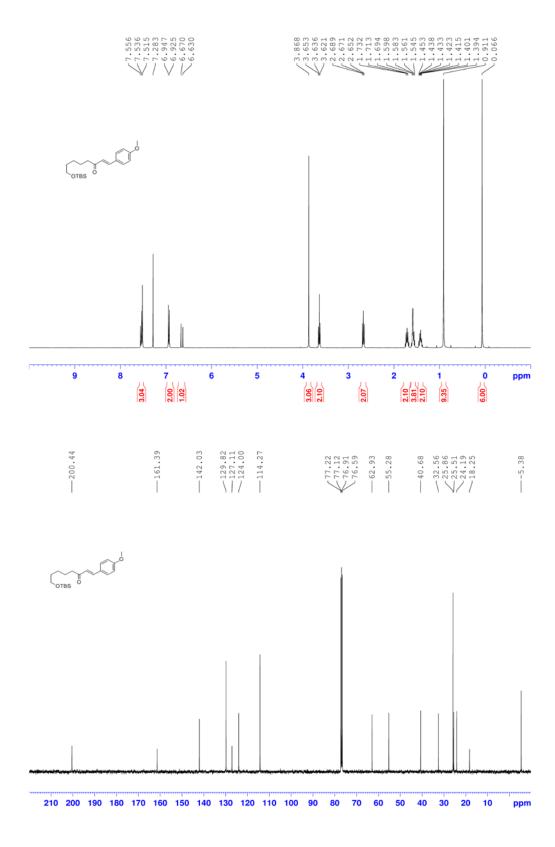
Rosa and Orellana

¹H- and ¹³C-NMR data for ketone 19a



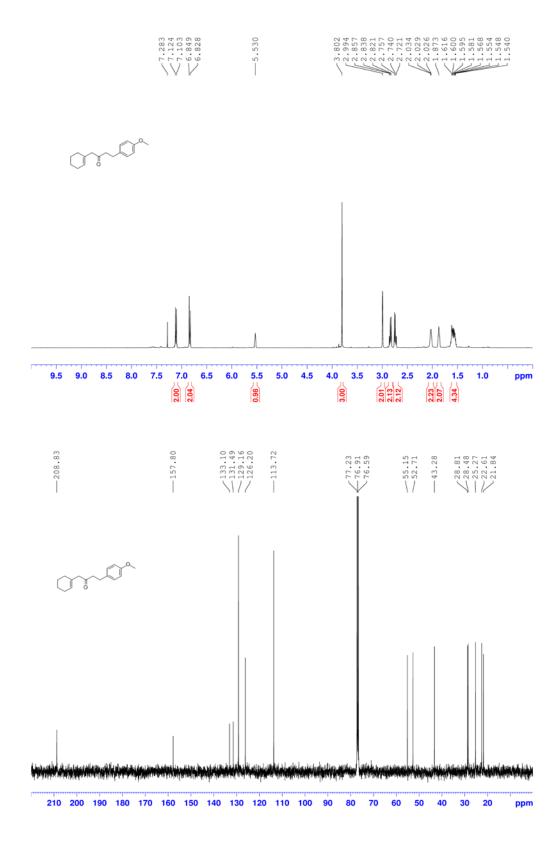
Rosa and Orellana

¹H- and ¹³C-NMR data for α , β -unsaturated ketone 19c



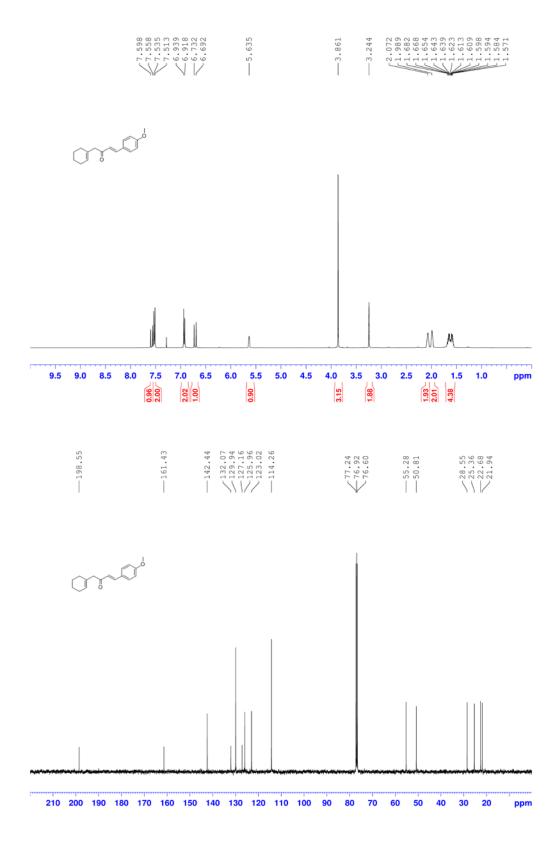
Rosa and Orellana

¹H- and ¹³C-NMR data for ketone 20a



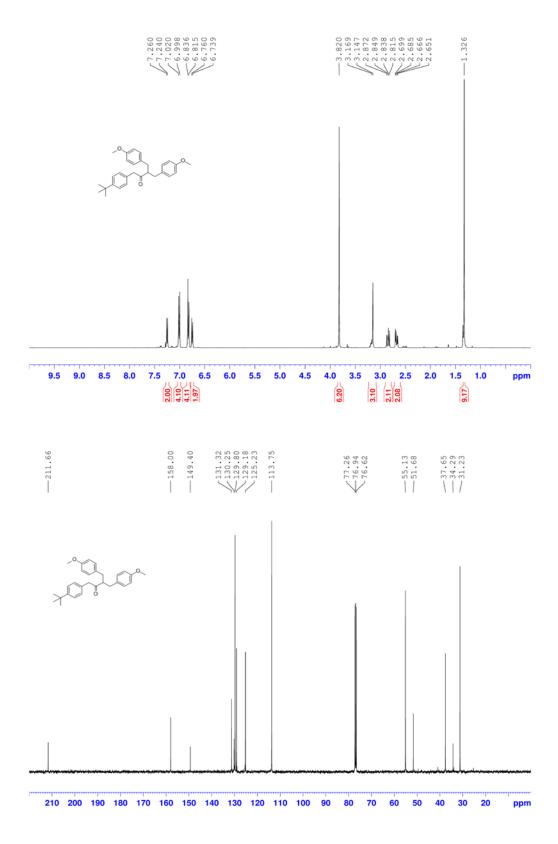
Rosa and Orellana

¹H- and ¹³C-NMR data for α , β -unsaturated ketone 20c



Rosa and Orellana

¹H- and ¹³C-NMR data for ketone 21a



Rosa and Orellana

¹H- and ¹³C-NMR data for ketone 22a

