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Supporting Information

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Palladium-Catalyzed α-Arylation of Trimethylsilyl Enol Ethers with Aryl Bromides and Chlorides. A Synergistic Effect of Two Metal Fluorides as Additives[**]

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Table of Contents

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General Methods. Trimethylsiloxy-4-phenyl-2-butene and 3-methyl-1-(trimethylsiloxy)cyclohexene were prepared as described previously [1]. Aryl bromides, aryl chlorides, tributyltin fluoride, MnF_2, ZnF_2, $Pd(OAc)_2$, $P(t\text{-}Bu)_3$, and DMF solvent (anhydrous, sure-seal) were purchased from Aldrich Chemical Co. and used as received. THF and toluene were distilled under argon from sodium / benzophenone prior to use. CsF (Aldrich Chemical Co.) was ground to a fine powder using a mortar and pestle and then dried under vacuum at 100 °C overnight. All other chemicals were used as received from commercial sources. ^1H NMR spectra were obtained on a 300-, 400- or 500-MHz spectrometer, and chemical shifts were recorded relative to residual protiated solvent. ^{13}C NMR spectra were obtained at 75.5, 100.6 or 125.8 MHz on a 300-, 400- or 500-MHz instrument, and chemical shifts were recorded relative to the solvent resonance. Both ^1H NMR and ^{13}C NMR chemical shifts are reported in parts per million downfield from tetramethylsilane. The purity of products was determined by NMR spectroscopy, HRMS or CHN microanalysis.

Method A. In a glove box, a Schlenk tube equipped with a stir bar was charged with $Pd(OAc)_2$ (0.015 mmol), CsF (0.700 mmol) and Bu_3SnF (0.700 mmol). The tube was fitted with a rubber septum and removed from the glove box. Two mL of toluene, $P(t\text{-}Bu)_3$ (0.027 mmol) in a stock solution of toluene (0.3-0.4 mL), a solution of aryl halide (0.50 mmol) in a stock solution of toluene (0.5-0.6 mL) and silyl enol ether (0.700 mmol) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced by a Teflon screw cap under an argon flow. The reaction mixture was heated to the indicated temperature over 30 minutes with stirring and allowed to stir at that temperature for the indicated time. After cooling to room temperature, the reaction mixture was diluted with 10 mL of ether or ethyl acetate, filtered through a pad of silica gel and then the filtrate was concentrated in vacuo after washing the pad of silica gel with the same solvent. The crude product was purified by column chromatography on silica gel.

Method B. In a glove box, to a mixture of Pd(dba)$_2$ (0.012mmol), P(*t*-Bu)$_3$ (0.022 mmol), ZnF$_2$ (0.560 mmol) and CsF (0.160 mmol) were added DMF (2.0 mL) in an oven-dried 4 mL vial. The corresponding aryl halides (0.400 mmol) and silyl enol ether (0.560 mmol) were added to the solution, and then the vial was sealed with a cap containing a PTFE septum. The reaction mixture was stirred at 85 °C for the indicated time. After cooling to room temperature, the reaction mixture was diluted with 20 mL of ether or ethyl acetate and then quenched with 2 mL of water. The organic layer was extracted with H_2O (4 × 2mL) and then washed with brine and dried (Na_2SO_4). The solvent was removed under reduced pressure to afford the crude product, which was purified by chromatography on silica gel (eluent: 5-10% ethyl acetate in hexanes).

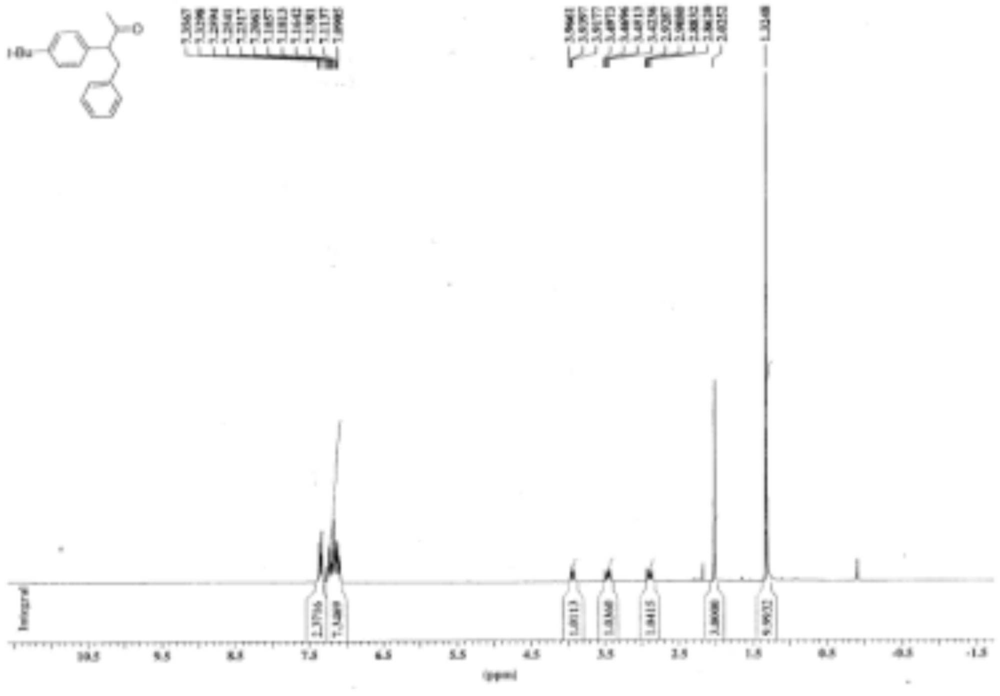
Method C. In a glove box, to a mixture of Pd(dba)$_2$ (0.0080 mmol), P(*t*-Bu)$_3$ (0.016 mmol), ZnF$_2$ (0.400 mmol) and MnF$_2$ (0.160 mmol) were added DMF (2.0 mL) in an oven-dried 4 mL vial. The corresponding aryl halide (0.400 mmol) and silyl enol ether (0.600 mmol) were added to the solution, and then the vial was sealed with a cap containing a PTFE septum. The reaction mixture was stirred at 70 °C for the indicated time. Work up was conducted as for method B.

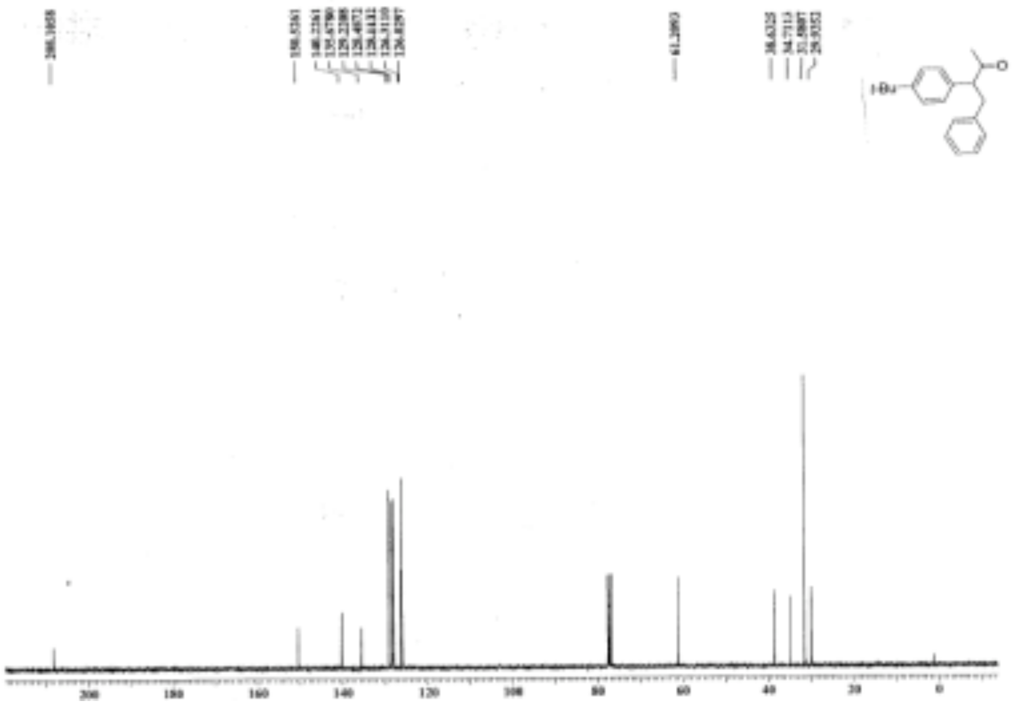
Method D. In a glove box, to a mixture of Pd(dba)$_2$ (0.012mmol), P(*t*-Bu)$_3$ (0.022 mmol), ZnF$_2$ (0.560 mmol) and MnF$_2$ (0.560 mmol) were added DMF (2.0 mL) in an oven-dried 4 mL vial. The corresponding aryl halides (0.400 mmol) and silyl enol ether (0.560 mmol) were added to the solution, and then the vial was sealed with a cap containing a PTFE septum. The reaction mixture was stirred at 60 °C for the indicated time. Work up was conducted as for method B.

Method E. This method was identical to method D, except that the reaction mixture was stirred at 70 °C for the indicated time.

3-(4-*tert*-Butylphenyl)-4-phenyl-2-butanone (Table 1, entry 8). Method A was followed using 2-trimethylsiloxy-4-phenyl-2-butene (154 mg, 0.699 mmol), 1-bromo-4-*tert*-butylbenzene (109 mg, 0.501 mmol), CsF (107 mg, 0.703 mmol), Bu_3SnF (216 mg, 0.699 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), and P(*t*-Bu)$_3$ (5.45 mg, 0.027 mmol). The reaction mixture was purified by column chromatography on silica gel (2 % ethyl acetate in hexanes) to afford 137 mg (98%) of the desired product as a colorless liquid. This product was also formed using Method B, as shown in **Table 3, entry 1**.

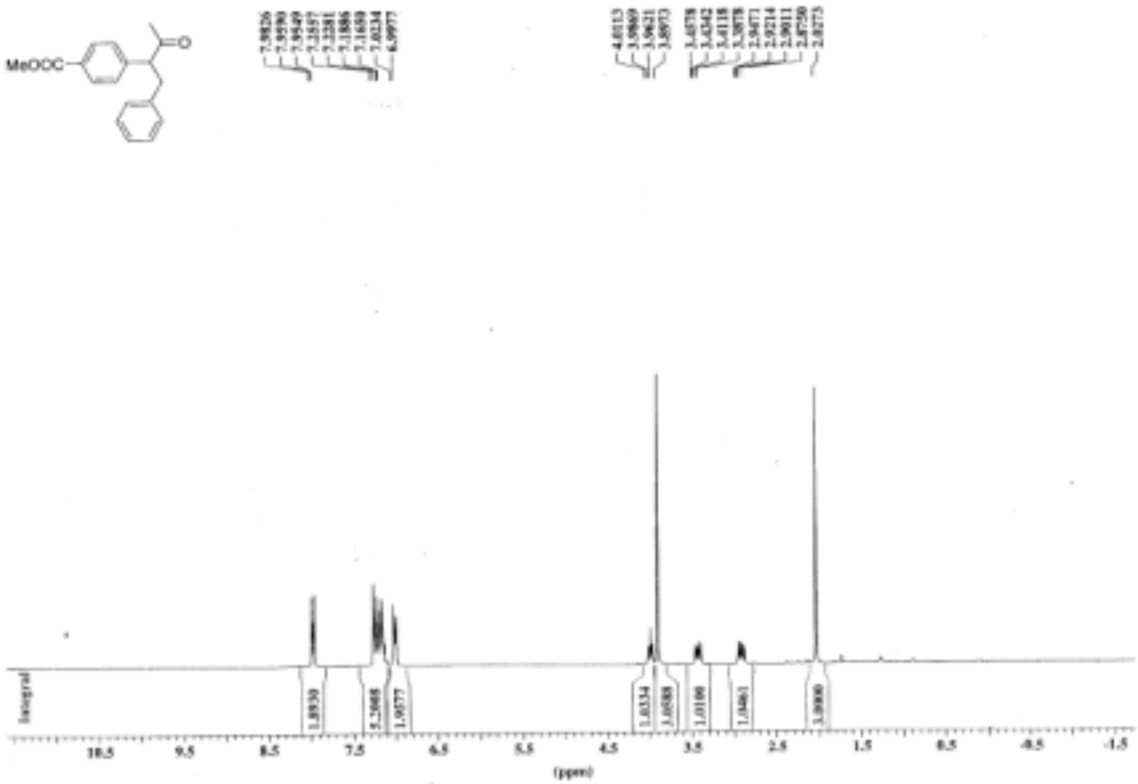
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (d, J = 8.07 Hz, 2H), 7.25-7.09 (m, 7H), 3.94 (t, J = 7.26 Hz, 1H), 3.46(dd, J = 13.8 Hz, J=8.31 Hz, 1H), 2.89 (dd, J = 13.7Hz, J=6.21 Hz, 1H), 2.02 (s, 3H) 1.32 (s, 9 H). ^{13} C NMR (75.5 MHz, $CDCl_3$): δ 208.1, 150.5, 140.2, 135.6, 129.2, 128.5, 128.1, 126.3, 126.0, 61.2, 38.6, 34.7, 31.6, 29.9. HR MS (EI) Calcd for $C_{20}H_{24}O$: 280.18272. Found m/e $(M)^+$ 280.18328.





Methyl 4-(3-oxo-1-phenylbutan-2-yl)benzoate (Table 2, entry 1). Method A was followed using 2-trimethylsiloxy-4-phenyl-2-butene (154 mg, 0.699 mmol), methyl-4-chlorobenzoate (86 mg, 0.499 mmol), CsF (107mg, 0.703 mmol), Bu_3SnF (216 mg, 0.699 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), and $P(t\text{-}Bu)_3$ (5.45 mg, 0.027 mmol). The reaction was conducted at 90 °C for 17 h. The reaction mixture was purified by column chromatography on silica gel (5-10 % ethyl acetate in hexanes) to afford 126 mg (89%) of the desired product as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, J = 8.31 Hz, 2H), 7.25-7.16 (m, 5H), 7.01(d, J = 7.71 Hz, 2H), 3.98 (t, J = 7.44 Hz, 1H), 3.89 (s, 3H), 3.42(dd, J = 13.8 Hz, J = 7.2 Hz, 1H), 2.92 (dd, J = 13.8Hz, J = 7.71 Hz, 1H), 2.03 (s, 3H). ^{13} C NMR (75.5 MHz, $CDCl_3$): δ 207.1, 166.9, 143.7, 139.2, 130.3, 129.5, 129.1, 128.6, 128.5, 126.5, 61.7, 52.3, 38.5, 29.9. HR MS (EI) Calcd for $C_{18}H_{18}O_3$: 282.12559. Found m/e $(M)^+$ 282.12587.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2.0273
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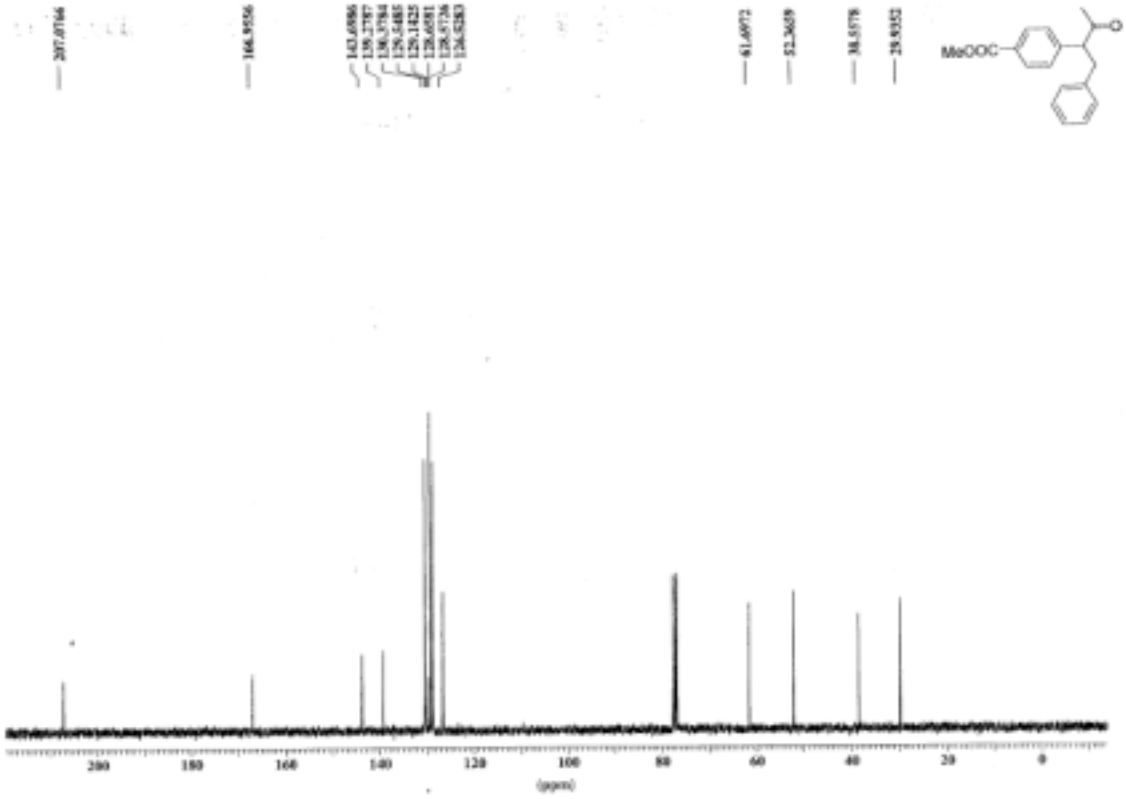
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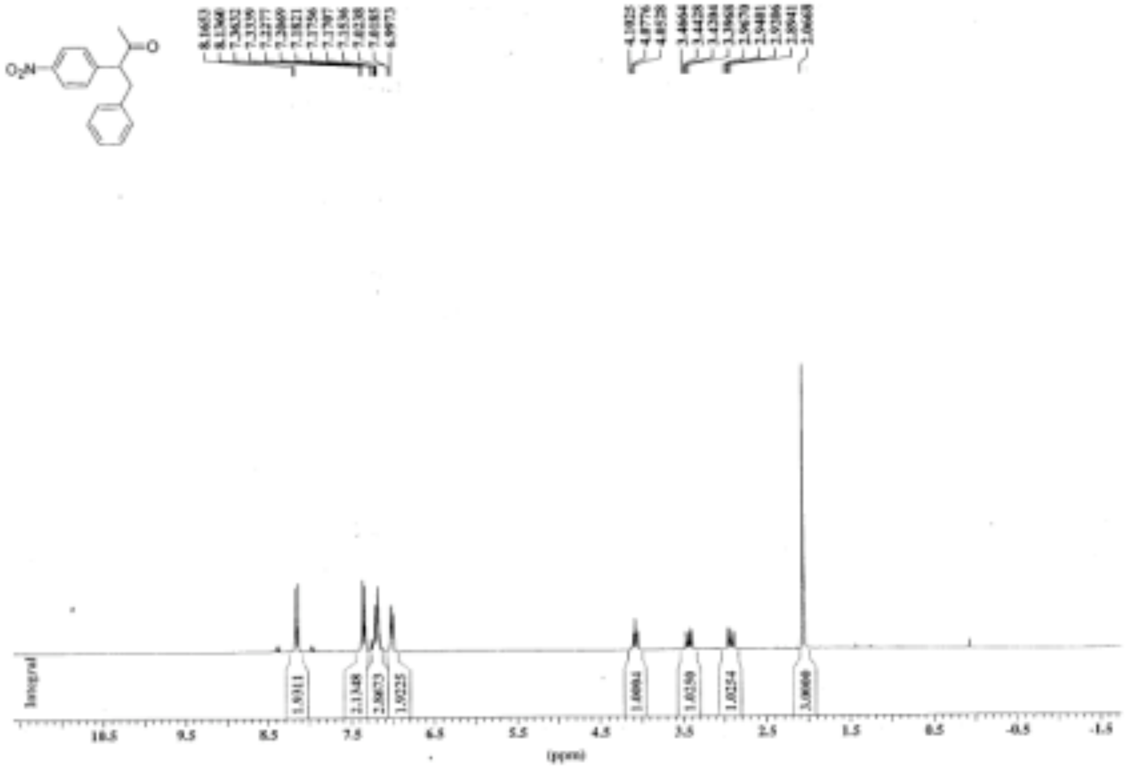
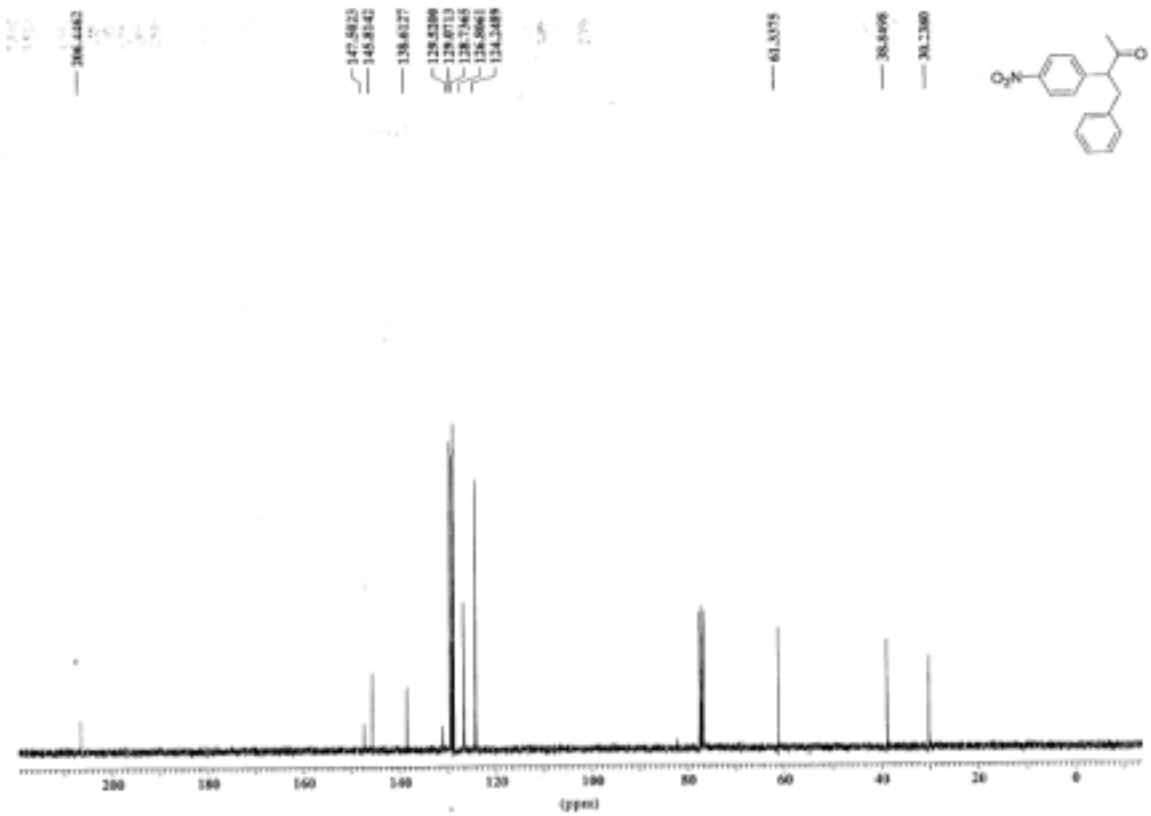
29.9352
MeOOC
O
200
180
160
140
120
100
80
60
40
20
0
(ppm)

3-(4-Nitrophenyl)-4-phenyl-2-butanone (Table 2, entry 2). Method A was followed using 2-trimethylsiloxy-4-phenyl-2-butene (154 mg, 0.699 mmol), 1-bromo-4-nitrobenzene (102 mg, 0.500 mmol), CsF (107mg, 0.703 mmol), Bu_3SnF (216 mg, 0.699 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), and $P(t\text{-}Bu)_3$ ((5.45 mg, 0.027 mmol). The reaction was conducted at 85 °C for 14 h. The reaction mixture was purified by column chromatography on silica gel (5-10 % ethyl acetate in hexanes) to afford 113 mg (84%) of the desired product as a pale yellow solid.

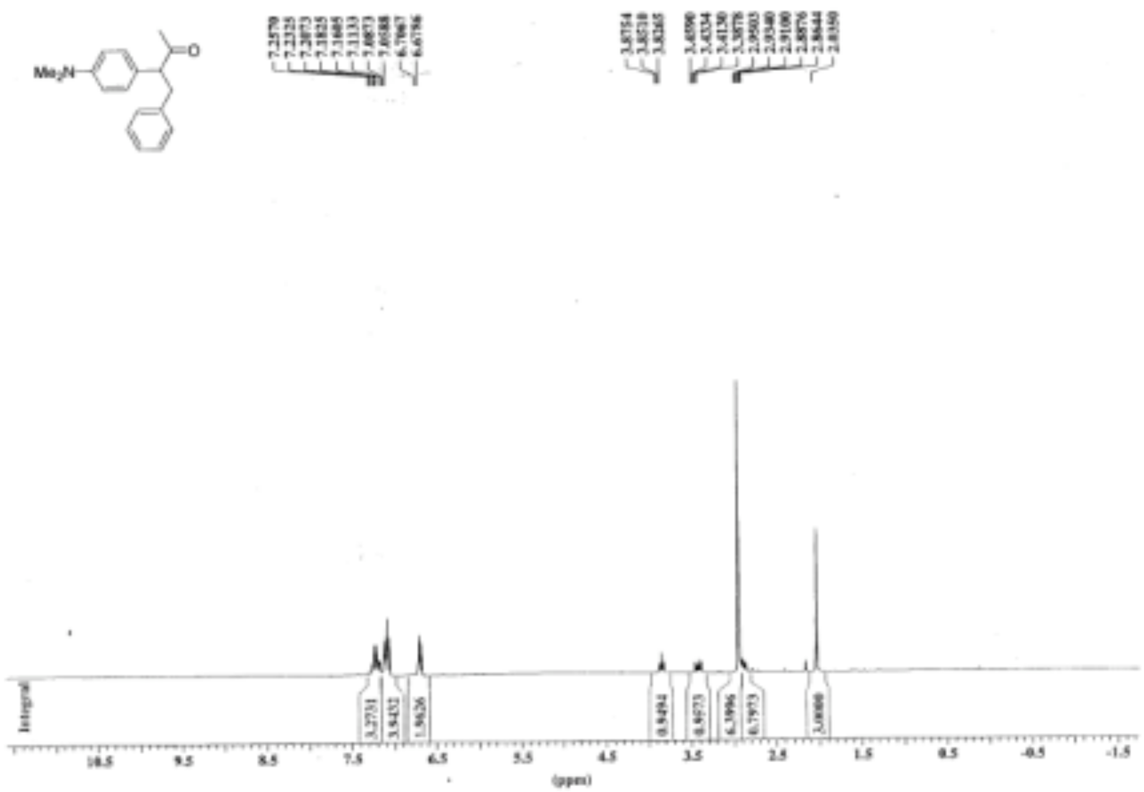
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15 (d, J = 8.79 Hz, 2H), 7.34 (d, J = 8.79 Hz, 2H), 7.22-7.15 (m, 3H), 7.02-6.99(m, 2H), 4.07 (t, J = 7.47 Hz, 1H), 3.43 (dd, J = 13.8 Hz, J = 7.08Hz, 1H), 2.93(dd, J = 13.92 Hz, J = 8.07 Hz, 1H), 2.06 (s, 3H). ^{13} C NMR (75.5 MHz, $CDCl_3$): δ 206.4, 147.5, 145.8, 138.6, 129.5, 129.0, 128.7, 126.8, 124.2, 61.3, 38.8, 30.2 HR MS (EI) Calcd for $C_{16}H_{15}NO_2$: 269.101519. Found m/e $(M)^+$ 269.10545.





3-(4-N,N-dimethylaminophenyl)-4-phenyl-2-butanone (Table 2, entry 3). Method A was followed using 2-trimethylsiloxy-4-phenyl-2-butene (154 mg, 0.699 mmol), 4-bromo-N,N-dimethylaniline (103 mg, 0.499 mmol), CsF (107 mg, 0.703 mmol), Bu_3SnF (216 mg, 0.699 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), and P(*t*-Bu)$_3$ (5.45 mg, 0.027 mmol). The reaction was conducted at 85 °C for 12 h. The reaction mixture was purified by column chromatography on silica gel (5 % ethyl acetate in hexanes) to afford 129 mg (96%) of the desired product as an off-white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25-7.16 (m, 3H), 7.11-7.05 (m, 4H), 6.69 (d, J = 8.43 Hz, 2H), 3.85 (t, J = 7.35 Hz, 1H), 3.42 (dd, J = 13.8 Hz, J=7.68Hz, 1H), 2.95-2.86(overlap, 7H), 2.03 (s, 3H). ^{13} C NMR (75.5 MHz, $CDCl_3$): δ 208.4, 150.0, 140.4, 129.28, 129.24, 128.4, 126.2, 113.0, 60.7, 40.7, 38.5, 29.5. HR MS (EI) Calcd for $C_{18}H_{21}NO$: 267.16231. Found m/e $(M)^+$ 267.16265.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2.0350
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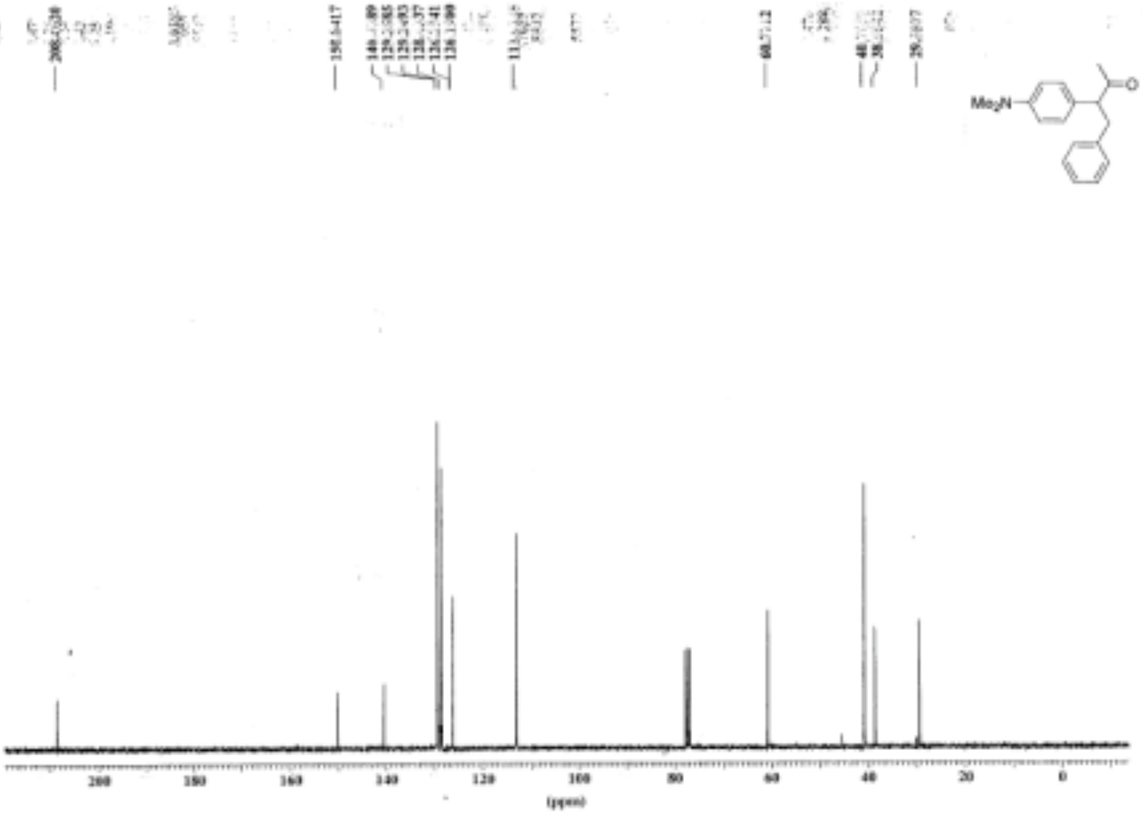
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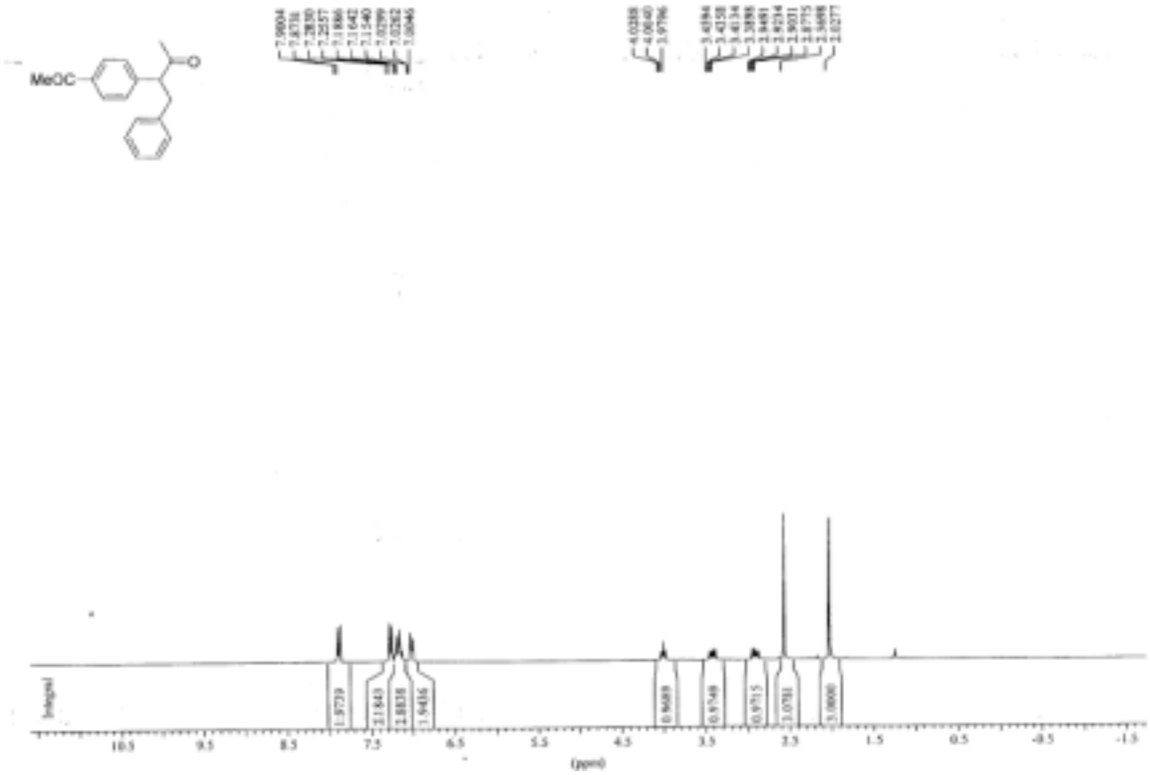
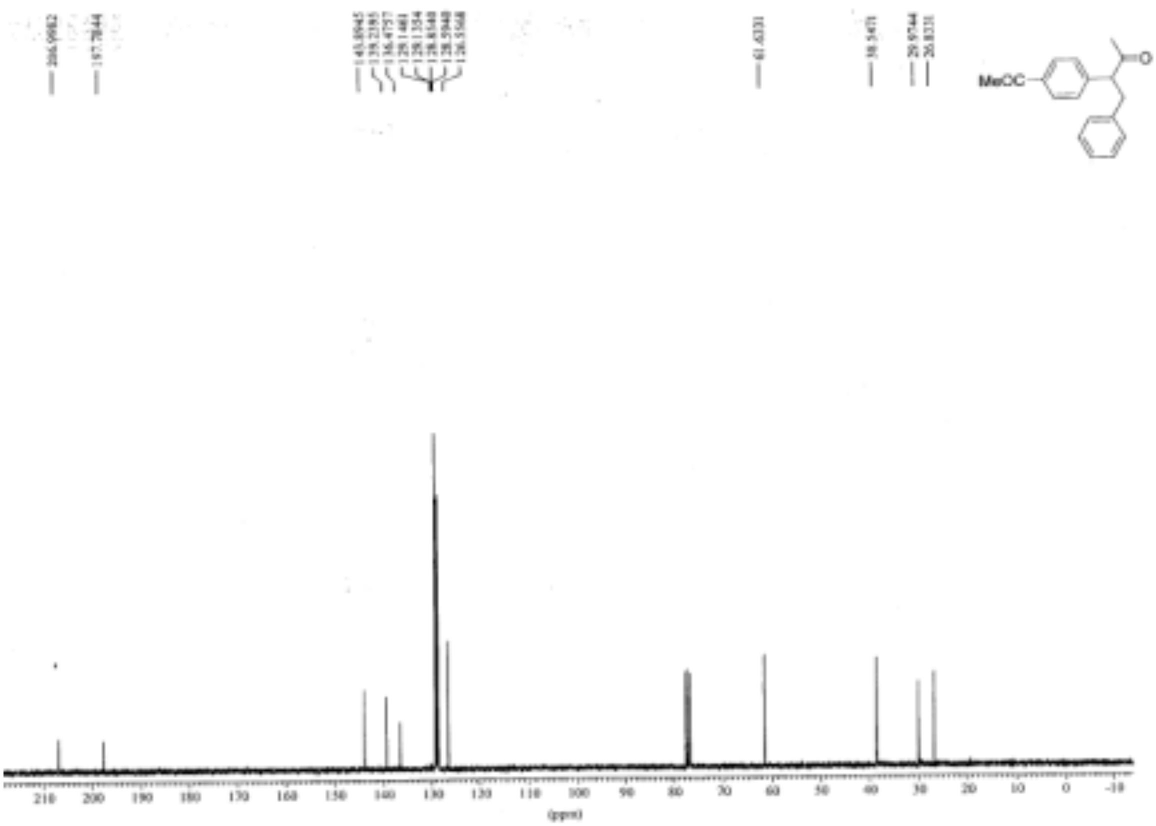
180
160
140
120
100
80
60
40
20
0
(ppm)

3-(4-Acetylphenyl)-4-phenyl-2-butanone (Table 2, entry 4). Method A was followed using 2-trimethylsiloxy-4-phenyl-2-butene (154 mg, 0.699 mmol), 4'-bromoacetophenone (101 mg, 0.497 mmol), CsF (107 mg, 0.703 mmol), Bu_3SnF (216 mg, 0.699 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), and P(*t*-Bu)$_3$ (5.45 mg, 0.027 mmol). The reaction was conducted at 85 °C for 12 h. The reaction mixture was purified by column chromatography on silica gel (10 % ethyl acetate in hexanes) to afford 129 mg (97%) of the desired product as a white solid. **(Table 3, entry 3).** Method B.

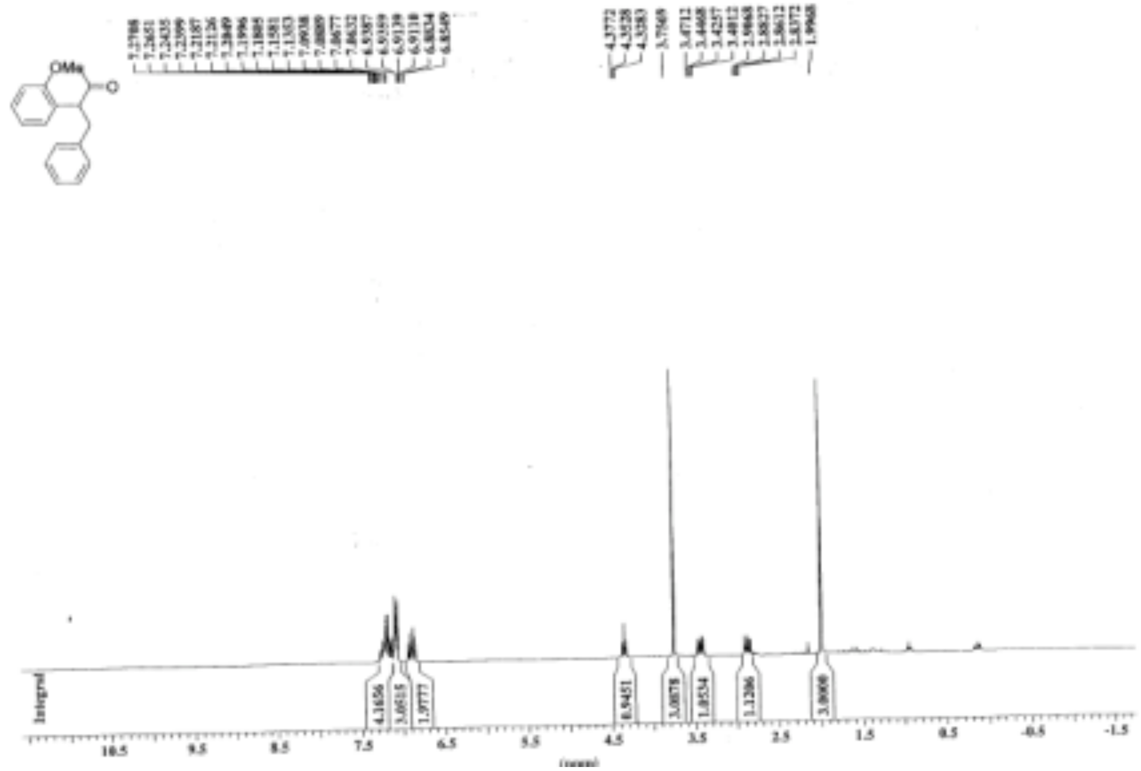
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (d, J = 9.27 2H), 7.27 (d, J = 8.19 Hz, 2H), 7.18-7.15 (m, 3), 7.02-7.00 (m, 2H), 4.00 (t, J = 7.44 Hz, 1H), 3.42 (dd, J = 13.8 Hz, J = 7.08Hz, 1H), 2.91 (dd, J = 13.8 Hz, J=7.71, 1H), 2.57 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.9, 197.8, 143.9, 139.2, 136.4, 129.15, 129.13, 128.8, 128.6, 126.6 61.6, 38.5, 29.9, 26.8. HR MS (EI) Calcd for $C_{18}H_{18}O_2$: 266.13068. Found m/e $(M)^+$ 266.13117.





3-(2-Methoxyphenyl)-4-phenyl-2-butanone (Table 2, entry 5). Method A was followed using 2-trimethylsiloxy-4-phenyl-2-butene (154 mg, 0.699 mmol), 2-bromoanisole (96 mg, 0.498 mmol), CsF (107 mg, 0.703 mmol), Bu_3SnF (216 mg, 0.699 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), $P(t\text{-}Bu)_3$ (5.45 mg, 0.027 mmol). The reaction was conducted at 85 °C for 19 h. The reaction mixture was purified by column chromatography on silica gel (5 % ethyl acetate in hexanes) to afford 124 mg (97%) of the desired product as a colorless liquid. **(Table 3, entry 2).** Method B.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27-7.13 (m, 4H), 7.09-7. 06 (m, 3H), 6.93-6.85 (m, 2H), 4.35 (t, J = 7.35 Hz, 1H), 3.75 (s, 3H), 3.43 (dd, J = 13.65 Hz, J = 7.32Hz, 1H), 2.87 (dd, J = 13.68 Hz, J = 7.2, 1H), 1.99 (s, 3H). ^{13} C NMR (75.5 MHz, $CDCl_3$): 208.5, 157.1, 140.5, 129.3, 129.1, 128.6, 128.2, 127.6, 126.1, 121.1, 111.1, 55.6, 54.4, 37.1, 29.6. δ. . HR MS (EI) Calcd for $C_{17}H_{19}O_2$: 254.13068. Found m/e $(M)^+$ 254.13112.



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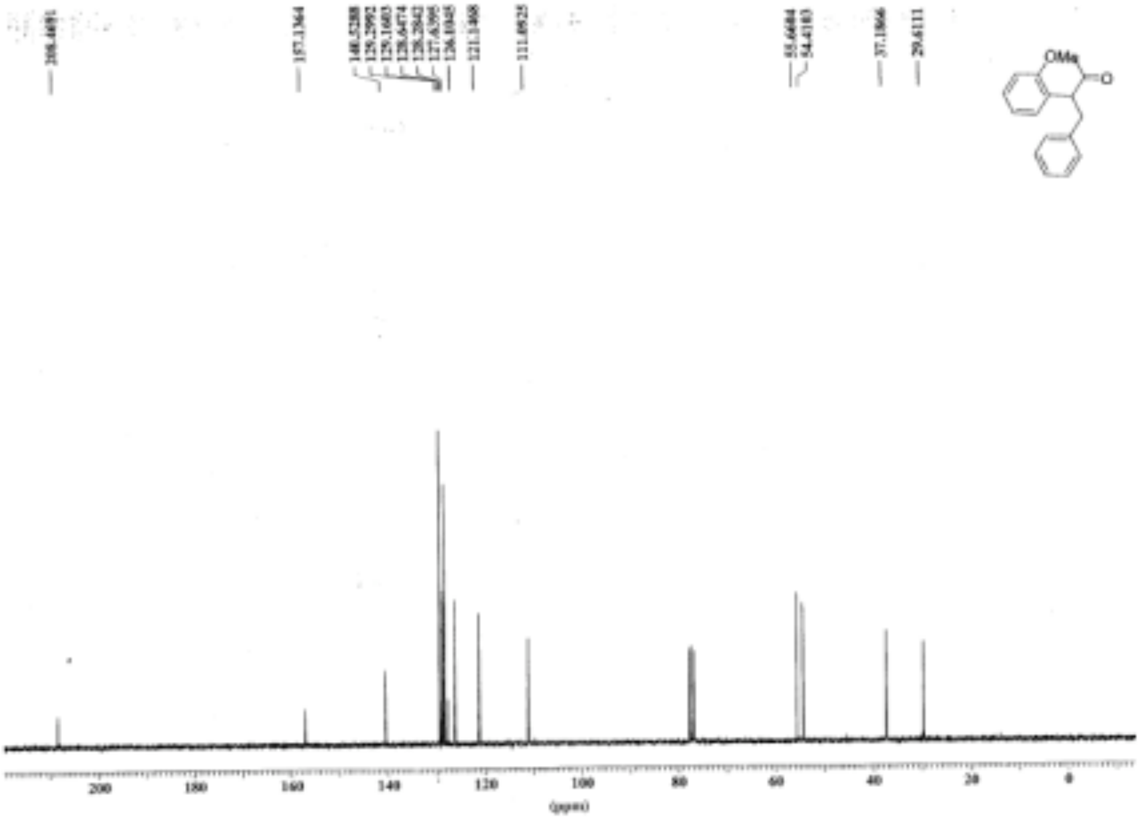

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29.6111
OMe
O
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180
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140
120
100
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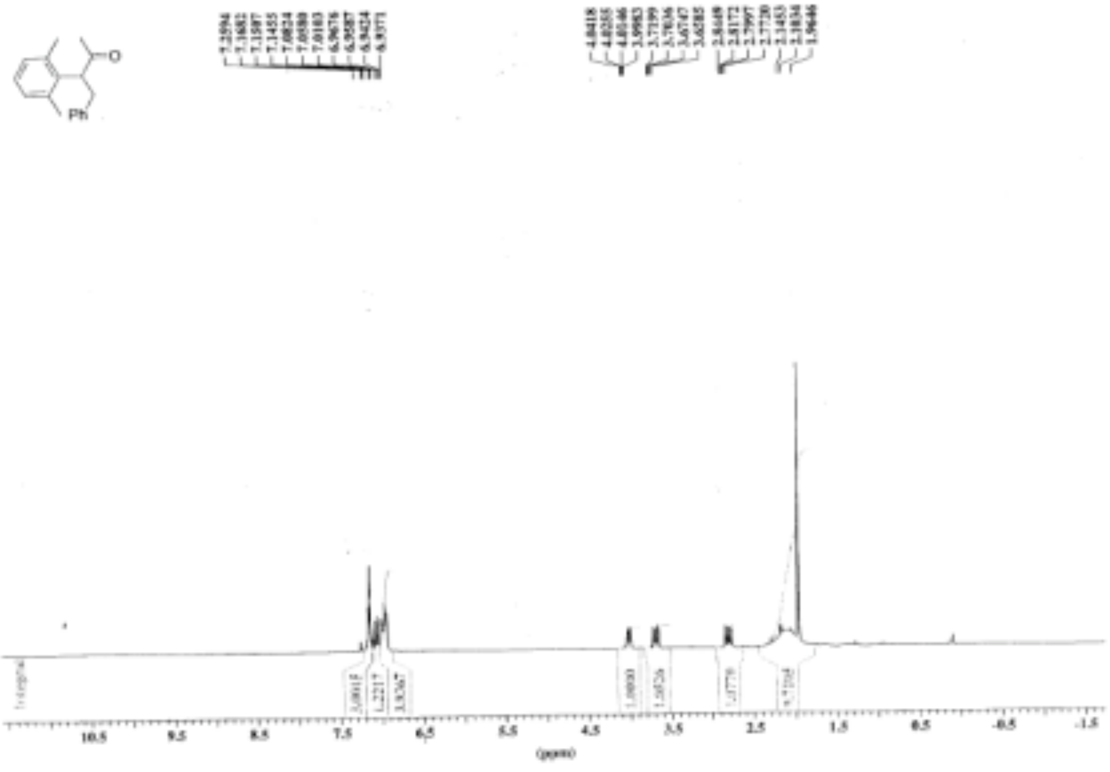
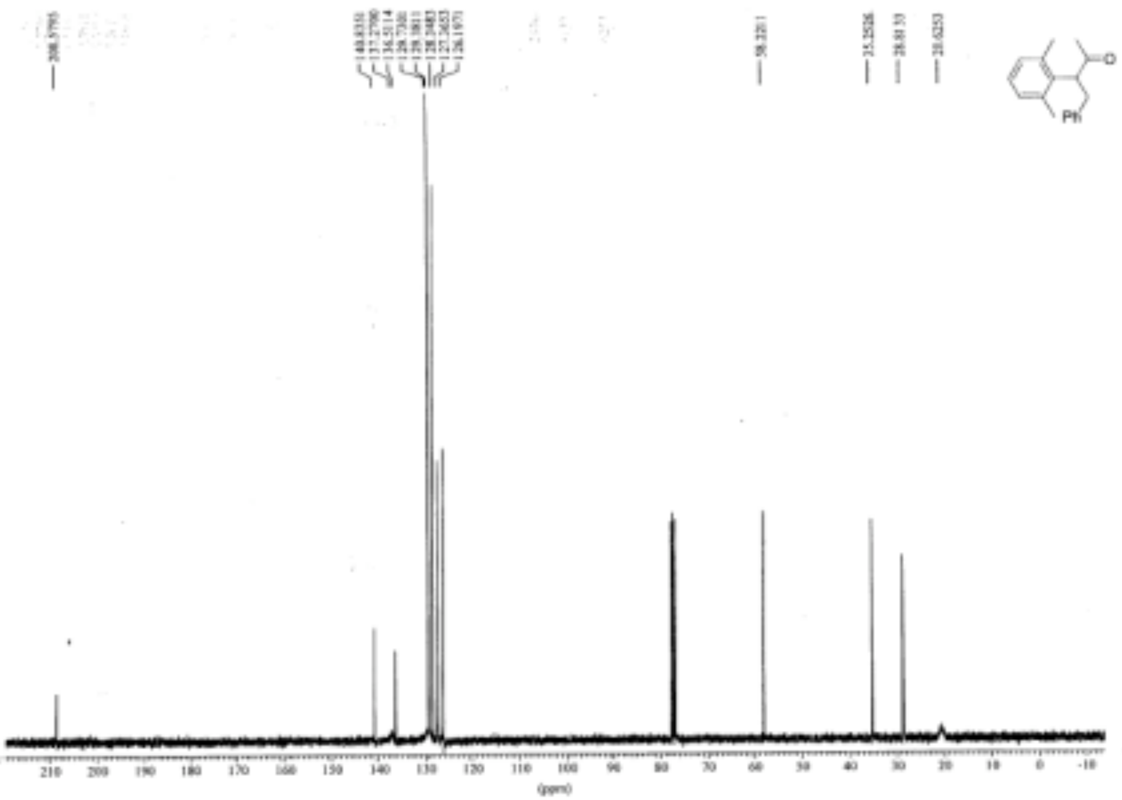
60
40
20
0
(ppm)

3-(2,6-Dimethylphenyl)-4-phenyl-2-butanone (Table 2, entry 6). Method A was followed using 2-trimethylsiloxy-4-phenyl-2-butene (154 mg, 0.699 mmol), 2-bromo-*m*-xylene (94 mg, 0.492 mmol), CsF (107 mg, 0.703 mmol), Bu_3SnF (216 mg, 0.699 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), and P(*t*-Bu)$_3$ (5.45 mg, 0.027 mmol). The reaction was conducted at 85 °C for 20 h. The reaction mixture was purified by column chromatography on silica gel (3 % ethyl acetate in hexanes) to afford 117 mg (93%) of the desired product as a colorless liquid.

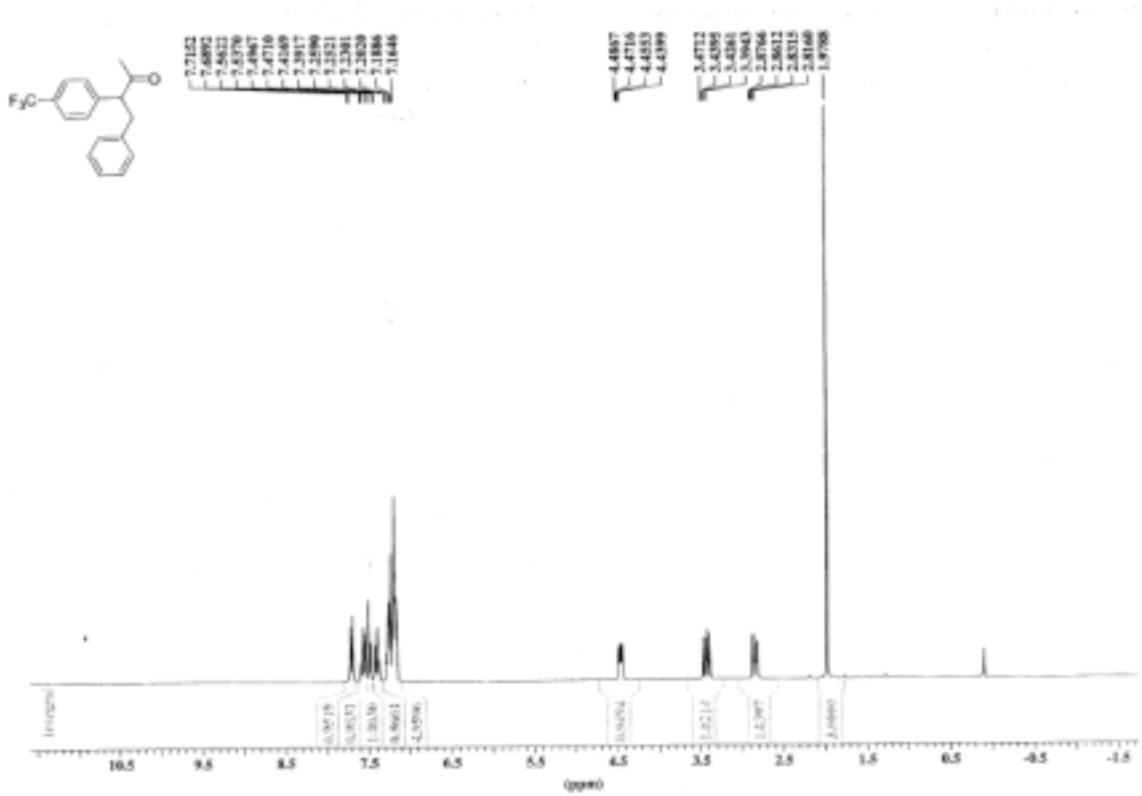
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16-7.14 (m, 3H), 7.08-7. 01 (m, 1H), 6.96-6.93 (m, 4H), 4.02 (dd, J = 8.16 Hz, J = 4.89 Hz, 1H), 3.69 (dd, J = 13.56 Hz, J = 4.89 Hz, 1H), 2.80 (dd, J = 13.65 Hz, J = 8.31Hz, 1H), 2.1 (b, 6H), 1.96 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 208.5, 140.8, 136.5, 129.3, 128.3, 127.3, 126.2, 58.2, 35.2, 28.81. HR MS (EI) Calcd for $C_{18}H_{20}O$: 252.15142. Found m/e $(M)^+$ 252.15174.





3-(4-Trifluoromethylphenyl)-4-phenyl-2-butanone (Table 2, entry 7). Method A was followed using 2-trimethylsiloxy-4-phenyl-2-butene (154 mg, 0.699 mmol), 4-bromobenzotrifluoride (114 mg, 0.502 mmol), CsF (107 mg, 0.703 mmol), Bu_3SnF (216 mg, 0.699 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), and $P(t\text{-}Bu)_3$ (5.45 mg, 0.027 mmol). The reaction was conducted at 85 °C for 16 h. The reaction mixture was purified by column chromatography on silica gel (3 % ethyl acetate in hexanes) to afford 133 mg (91%) of the desired product as a pale yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, J = 7.8 Hz, 1H), 7.56-7.49 (m, 1H), 7.47-7.39 (m, 3H), 7.25-7.16 (m, 5H), 4.46 (dd, J = 9.45 Hz, J = 4.89 Hz, 1H), 3.43 (dd, J = 13.53 Hz, J = 9.51 Hz, 1H), 2.84 (dd, J = 13.53 Hz, J = 4.62 Hz, 1H), 1.97 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.7, 139.6, 137.62, 137.60, 132.59, 132.57, 129.37, 129.33, 129.04, 128.65, 128.57, 127.59, 126.68, 126.61, 126.57, 126.53, 126.45, 122.81, 56.17, 56.14, 39.58, 30.39. HR MS (EI) Calcd for $C_{17}H_{15}F_3O$: 292.10750. Found m/e $(M)^+$ 292.10793.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7.1886
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4.4716
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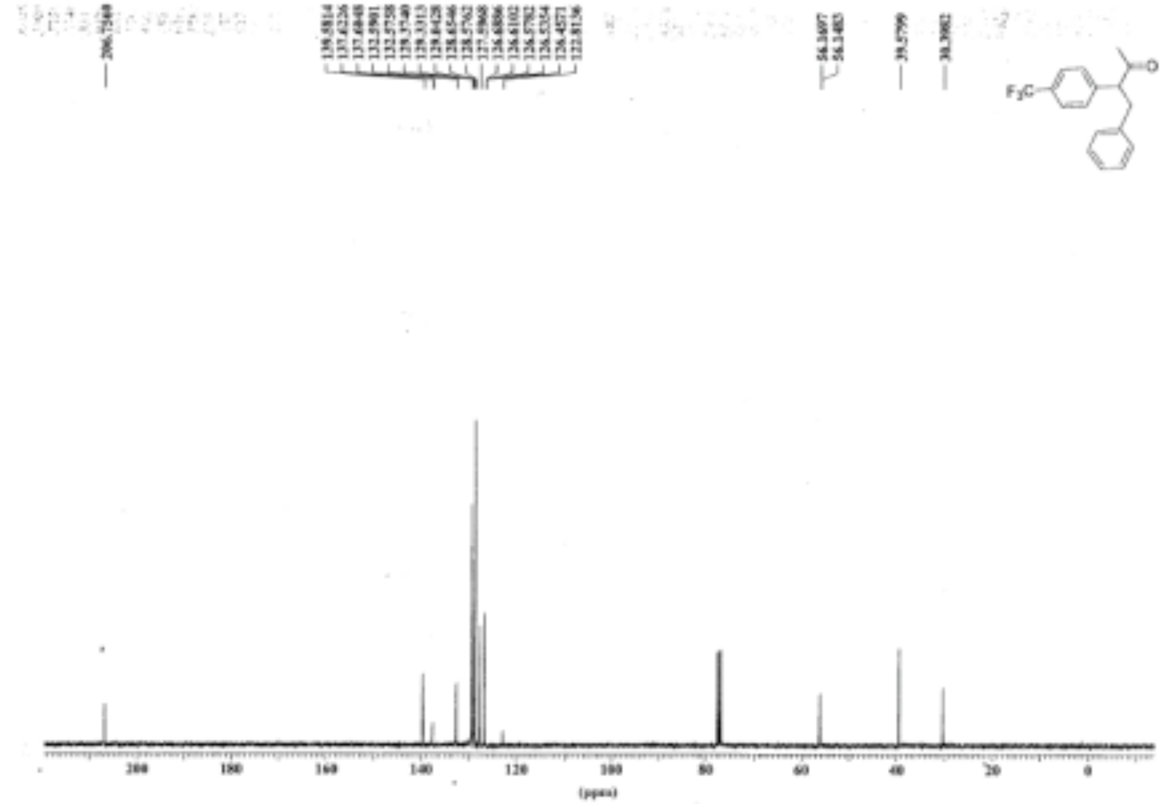
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
(ppm)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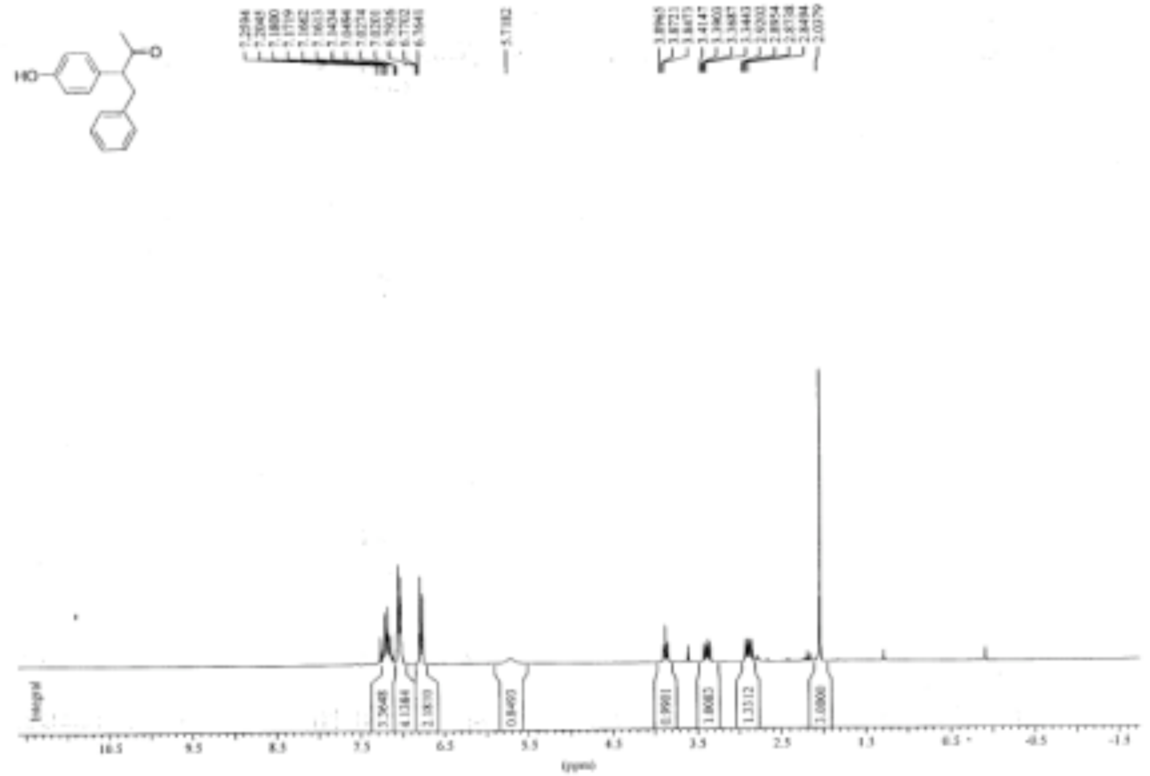
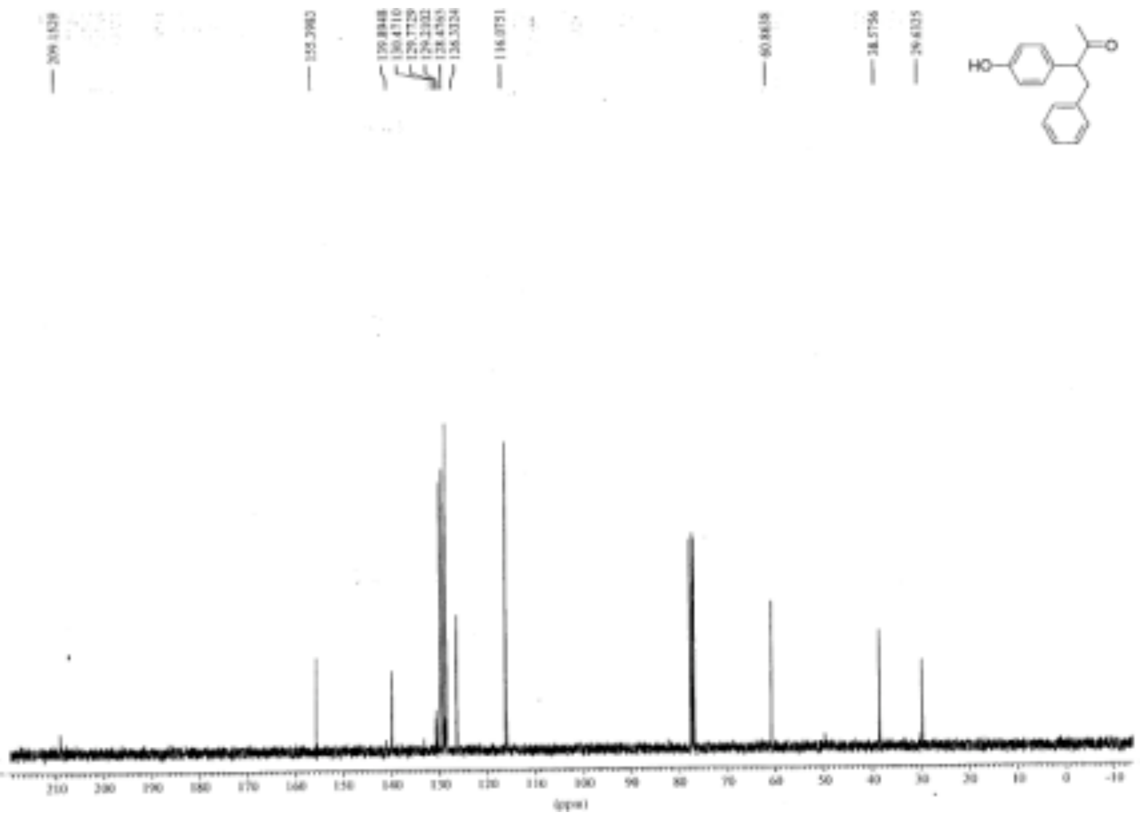
126.6886
126.6102
126.5782
126.5354
126.4571
123.8136
56.3497
56.3483
39.5799
30.3982
F3C
O
200
180
160
140
120
100
80
60
40
20
0
(ppm)

3-(4-Hydroxyphenyl)-4-phenyl-2-butanone (Table 2, entry 8). Method A was followed using 2-trimethylsiloxy-4-phenyl-2-butene (154 mg, 0.699 mmol), 4-bromophenol (87 mg, 0.498 mmol), CsF (107 mg, 0.703 mmol), Bu_3SnF (216 mg, 0.699 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), and P(*t*-Bu)$_3$ (5.45 mg, 0.027 mmol). The reaction was conducted at 85 °C for 19 h. The reaction mixture was purified by column chromatography on silica gel (chloroform) to afford 66 mg (55 %) of the desired product as a white solid. **(Table 3, entry 4).** Method B.

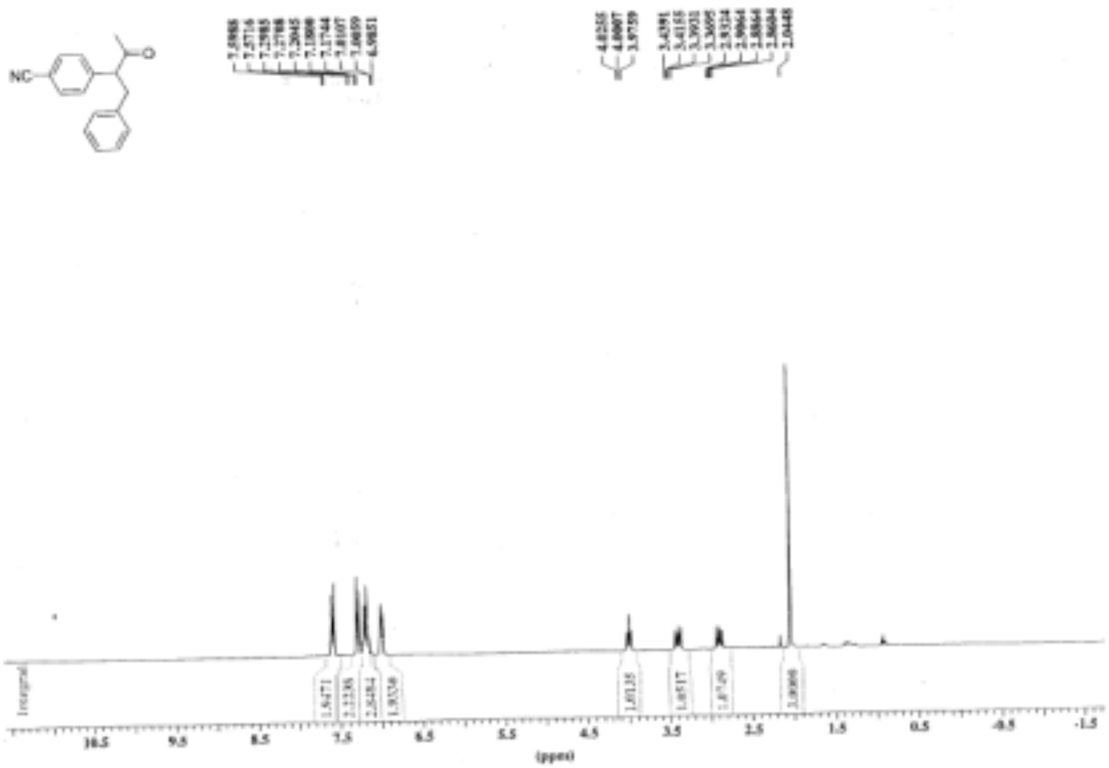
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20-7.14 (m, 3H), 7.05-7.02 (m, 4H), 6.79-6.76 (m, 2H), 5.72 (b, 1H), 3.87(t, J = 7.44 Hz, 1H), 3.38 (dd, J = 14.76 Hz, 7.32 Hz 1H), 2.88 (dd, J = 13.92 Hz, J = 7.44 Hz, 1H), 2.03 (s, 3H). ^{13} C NMR (75.5 MHz, $CDCl_3$): δ 209.1, 155.39, 139.9, 130.4, 129.7, 129.2, 128.4, 126.3, 116.1, 60.8, 38.5, 29.6. HR MS (EI) Calcd for $C_{16}H_{16}O_2$: 240.11503. Found m/e $(M)^+$ 240.11528.





3-(4-Cyanophenyl)-4-phenyl-2-butanone (Table 2, entry 9). Method A was followed using 2-trimethylsiloxy-4-phenyl-2-butene (154 mg, 0.699 mmol), 4-chlorobenzonitrile (67 mg, 0.482 mmol) , CsF (107 mg, 0.703 mmol), Bu_3SnF (216 mg, 0.699 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), and P(*t*-Bu)$_3$ (5.45 mg, 0.027 mmol). The reaction was conducted at 90 °C for 16 h. The reaction mixture was purified by column chromatography on silica gel (5-10 % ethyl acetate in hexanes) to afford 99 mg (80 %) of the desired product as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, J = 8.19 Hz, 2H), 7.56-7.49 (m, 1H), 7.28 (d, J = 8.19, 2H), 7.20-7.17 (m, 3H), 7.01-6.98 (m, 2H), 3.99 (d, J = 7.44 Hz, 1H), 3.40 (dd, J = 13.8 Hz, J = 7.2 Hz, 1H), 2.89 (dd, J = 13.92 Hz, J = 7.92 Hz, 1H), 2.04 (s, 3H). ^{13} C NMR (75.5 MHz, $CDCl_3$): δ 206.5, 143.8, 138.7, 132.8, 129.4, 129.0, 128.7, 126.7, 118.7, 111.6, 61.6, 38.7, 30.2. HR MS (EI) Calcd for $C_{17}H_{15}NO$: 249.11536. Found m/e $(M)^+$ 249.11576.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4.0007
3.9759
3.4391
3.4155
3.3931
3.3695
2.9324
2.9064
2.8864
2.8604
2.0448
Integral
1.8471
2.1238
2.0454
1.9338
1.0125
1.0517
1.0729
3.0000
10.5
9.5
8.5
7.5
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5.5
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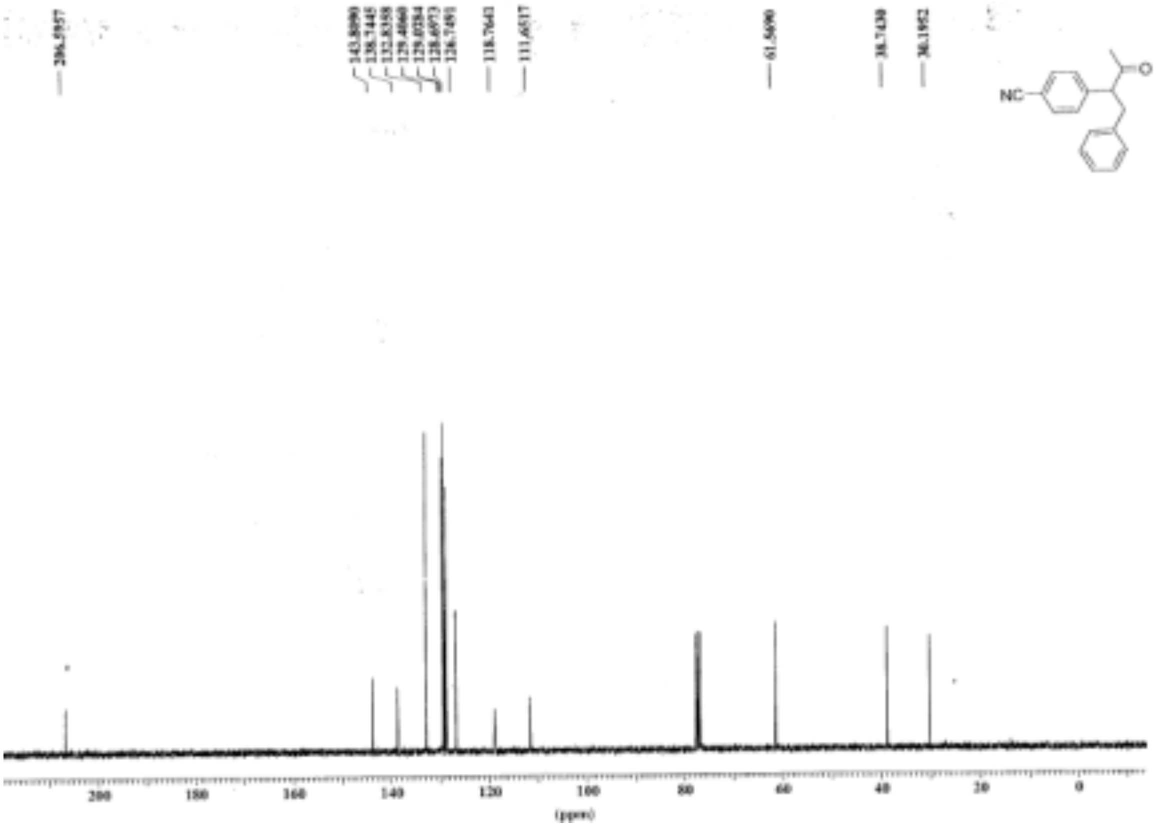
(ppm)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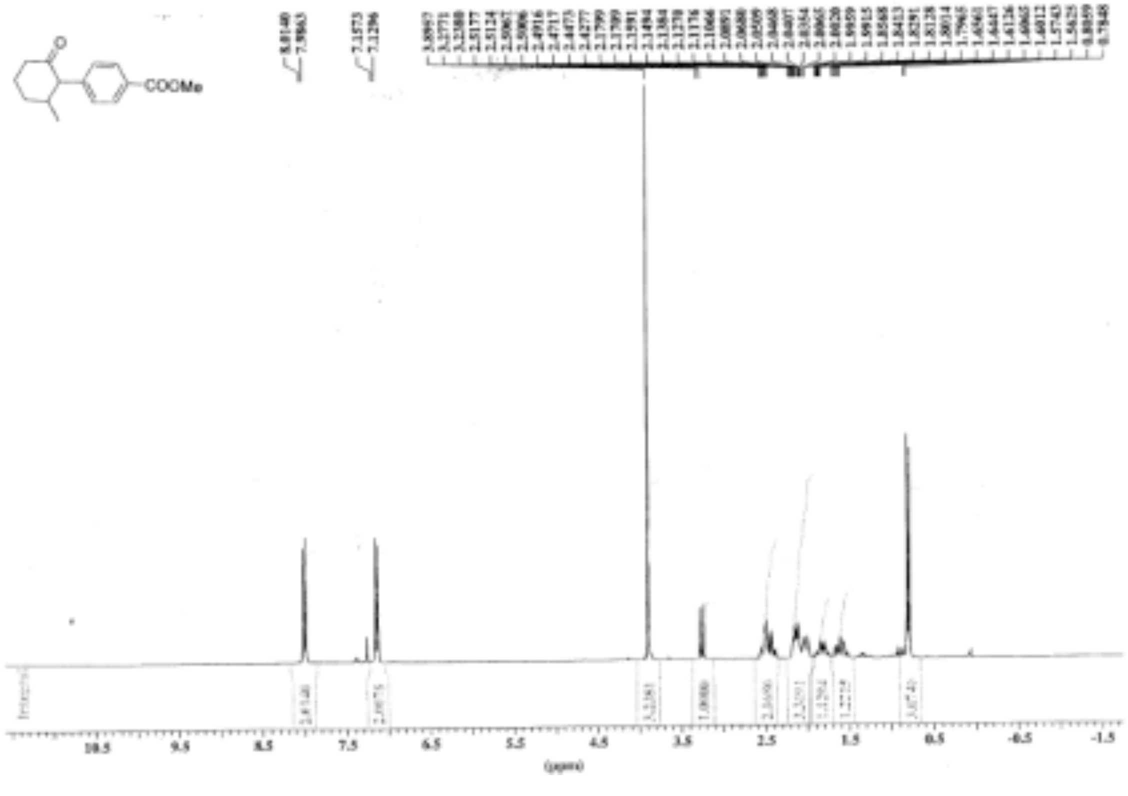
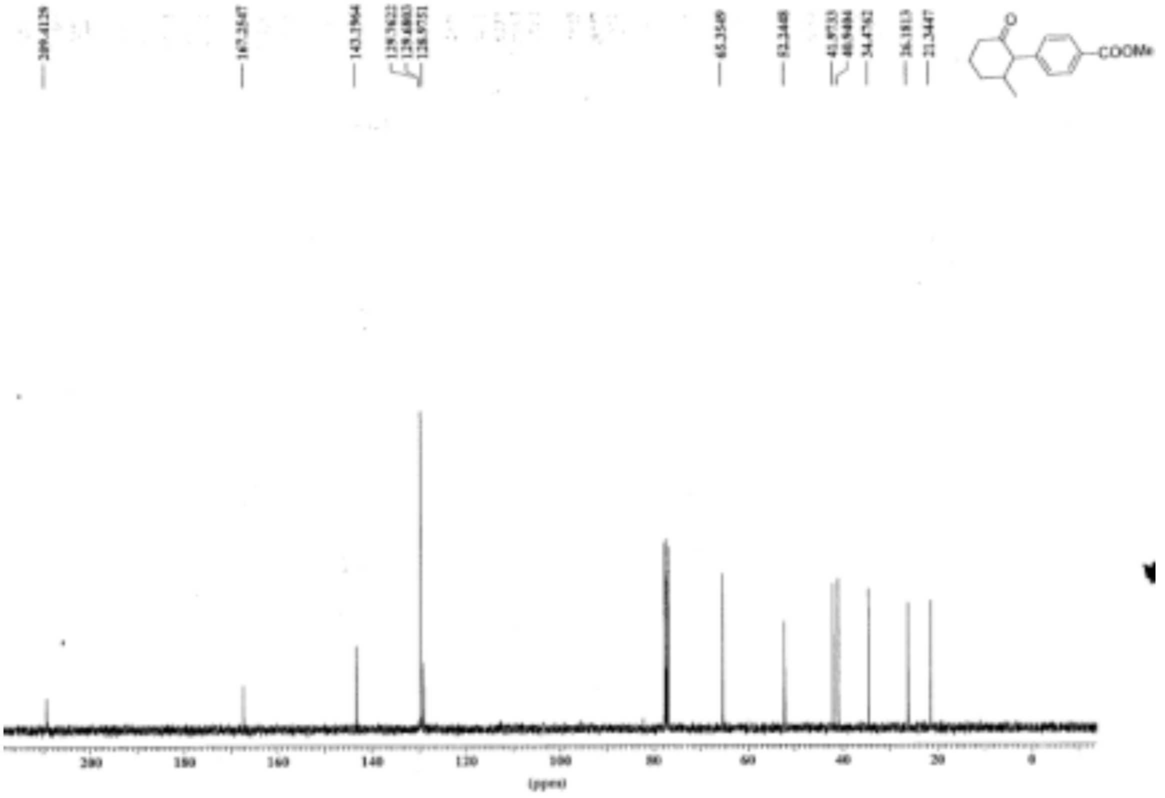
38.7430
30.1952
NC
O
200
180
160
140
120
100
80
60
40
20
0
(ppm)

2-(4-Carboxyphenyl)-3-methyl-1-cyclohexanone (Table 2, entry 10). Method A was followed using 1-trimethylsiloxy-3-methyl-1-cyclohexene (129 mg, 0.700 mmol), methyl-4-chlorobenzoate (86 mg, 0.499 mmol), CsF (107 mg, 0.703 mmol), Bu_3SnF (216 mg, 0.699 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), and P(*t*-Bu)$_3$ (5.45 mg, 0.027 mmol) (5.45 mg, 0.027 mmol). The reaction was conducted at 90 °C for 16 h. The reaction mixture was purified by column chromatography on silica gel (10 % ethyl acetate in hexanes) to afford 99 mg (80 %) of the desired product as a white solid.

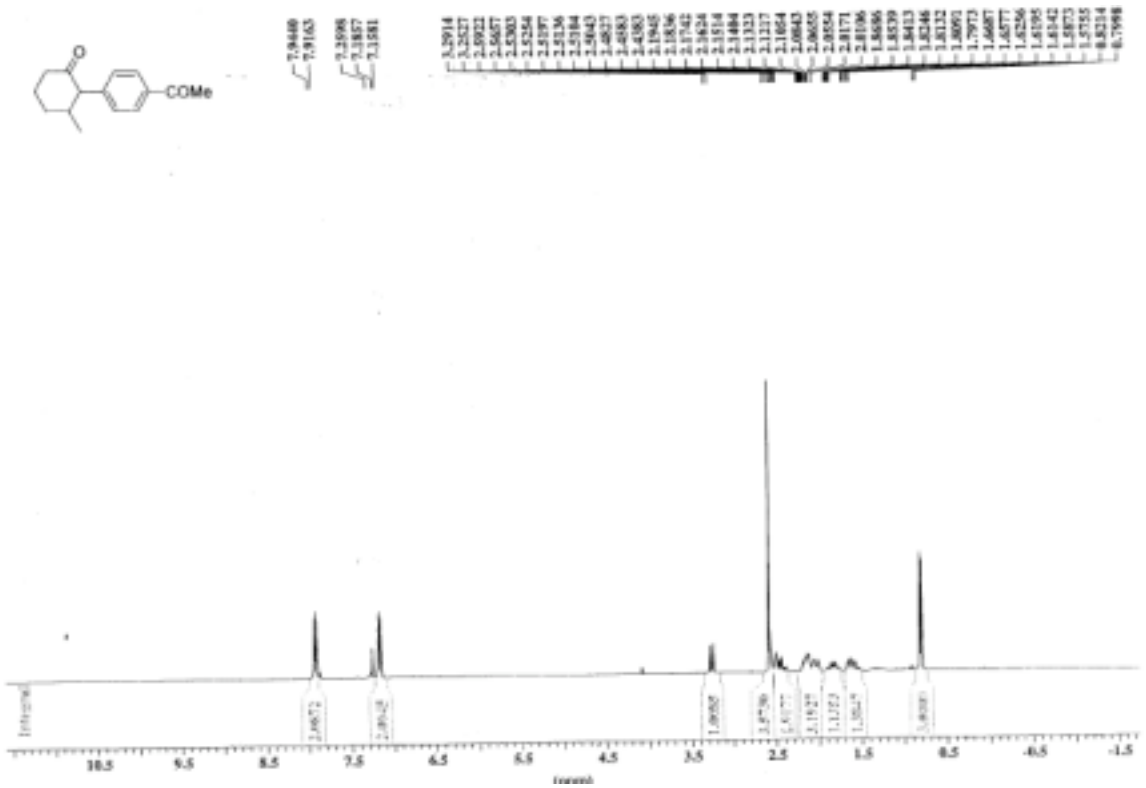
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (d, J = 8.31 Hz, 2H), 7.14 (d, J = 8.31, 2H), 3.89 (s, 3H), 3.25 (d, J = 11.73 Hz, 1H), 2.51-2.42 (m, 2H), 2.18-1.99 (m, 3H), 1.85-1.79 (m, 1H), 1.65-1.56 (m, 1H), 0.79 (d, J = 6.33 Hz, 3H). ^{13} C NMR (75.5 MHz, $CDCl_3$): δ 209.4, 167.2, 143.1, 129.7, 129.6, 128.9, 65.3, 52.2, 41.9, 40.9, 34.4, 26.1, 21.3. HR MS (EI) Calcd for $C_{15}H_{18}O_3$: 246.12559. Found m/e $(M)^+$ 246.12606.





2-(4-Acetylphenyl)-3-methyl-1-cyclohexanone (Table 2, entry 11). Method A was followed using 1-trimethylsiloxy-3-methyl-1-cyclohexene (129 mg, 0.700 mmol), 4'-chloroacetophenone (80 mg, 0.502 mmol), CsF (107 mg, 0.703 mmol), Bu_3SnF (216 mg, 0.699 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), $P(t\text{-}Bu)_3$ (5.45 mg, 0.027 mmol). The reaction was conducted at 90 °C for 17 h. The reaction mixture was purified by column chromatography on silica gel (10 % ethyl acetate in hexanes) to afford 81 mg (70 %) of the desired product as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (d, J = 8.31 Hz, 2H), 7.17 (d, J = 8.31, 2H), 3.27 (d, J = 11.61 Hz, 1H), 2.59 (s, 3H), 2.56-2.43 (m, 2H), 2.19-2.01 (m, 3H), 1.86-1.79 (m, 1H), 1.66-1.57 (m, 1H), 0.81 (d, J = 6.48 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 209.4, 198.1, 143.4, 136.1, 129.8, 128.6, 65.36, 41.9, 40.9, 34.4, 26.8, 26.1, 21.3. HR MS (EI) Calcd for $C_{15}H_{18}O_2$: 230.13068. Found m/e $(M)^+$ 230.13110.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2.4583
2.4383
2.1945
2.1836
2.1742
2.1624
2.1514
2.1484
2.1333
2.1217
2.1054
2.0843
2.0655
2.0554
2.0171
2.0106
1.8686
1.8539
1.8413
1.8246
1.8132
1.8091
1.7973
1.6687
1.6577
1.6256
1.6195
1.6142
1.5873
1.5755
0.8214
0.7998
2.0672
2.0948
1.0000
3.0730
1.0177
1.1927
1.1373
1.3847
3.0000
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9.5
8.5
7.5
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3.5
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0.5
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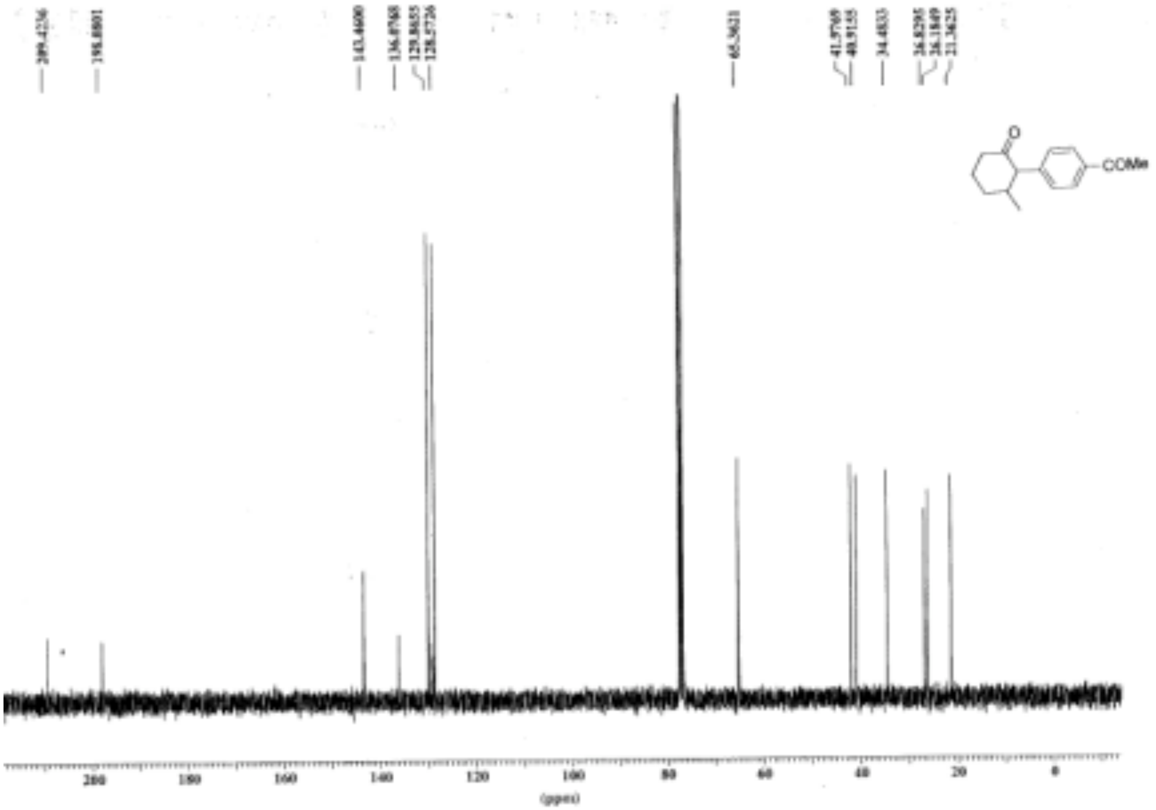
-1.5
(ppm)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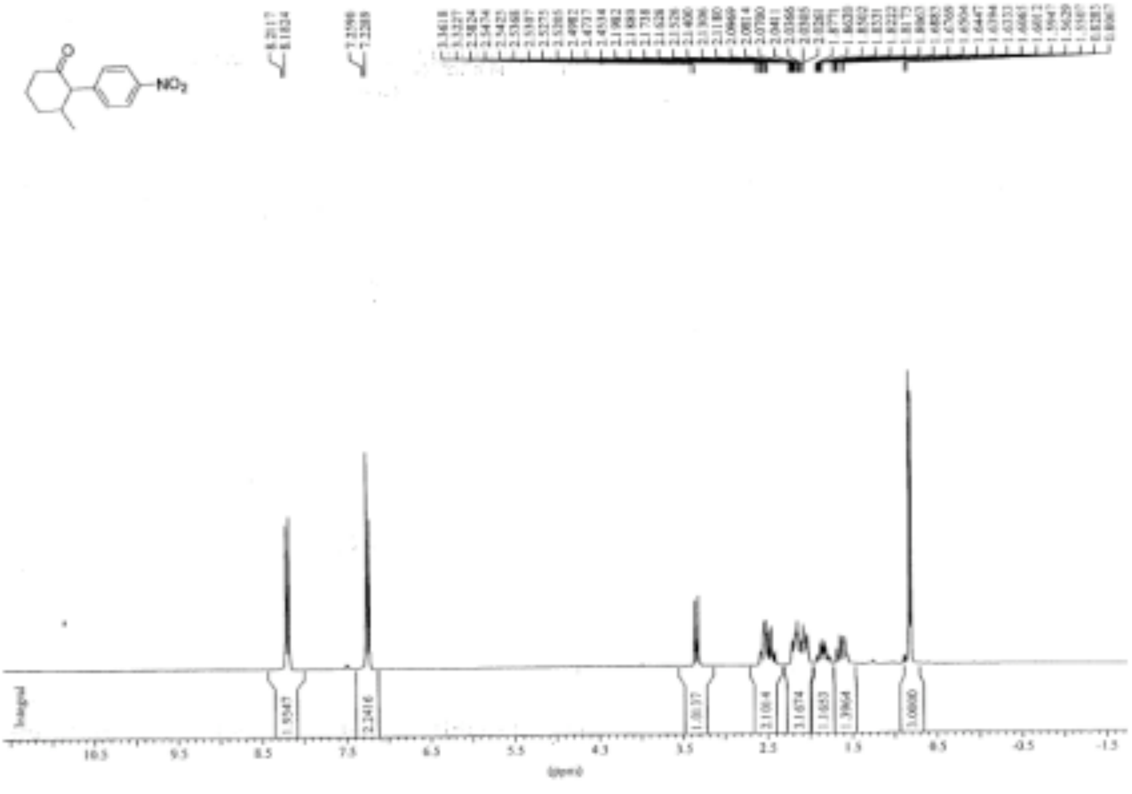
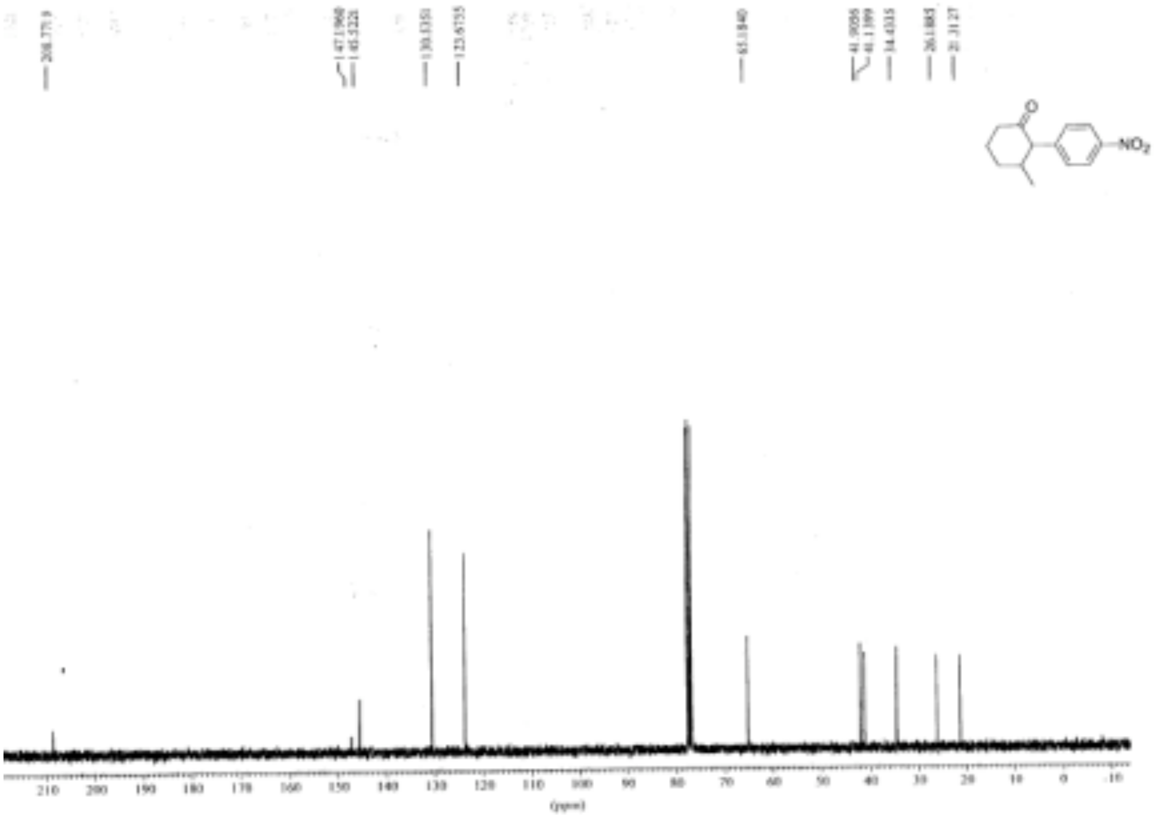
26.8295
26.1849
21.3625
COMe
200
180
160
140
120
100
80
60
40
20
0
(ppm)

2-(4-Nitrophenyl)-3-methyl-1-cyclohexanone (Table 2, entry 12). Method A was followed using 1-trimethylsiloxy-3-methyl-1-cyclohexene (129 mg, 0.700 mmol), 1-chloro-4-nitrobenzene (80 mg, 0.502 mmol), CsF (107mg, 0.703 mmol), Bu_3SnF (216 mg, 0.699 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), P(*t*-Bu)$_3$ (5.45 mg, 0.027 mmol). The reaction was conducted at 90 °C for 15 h. The reaction mixture was purified by column chromatography on silica gel (10 % ethyl acetate in hexanes) to afford 98 mg (84 %) of the desired product as a white solid.

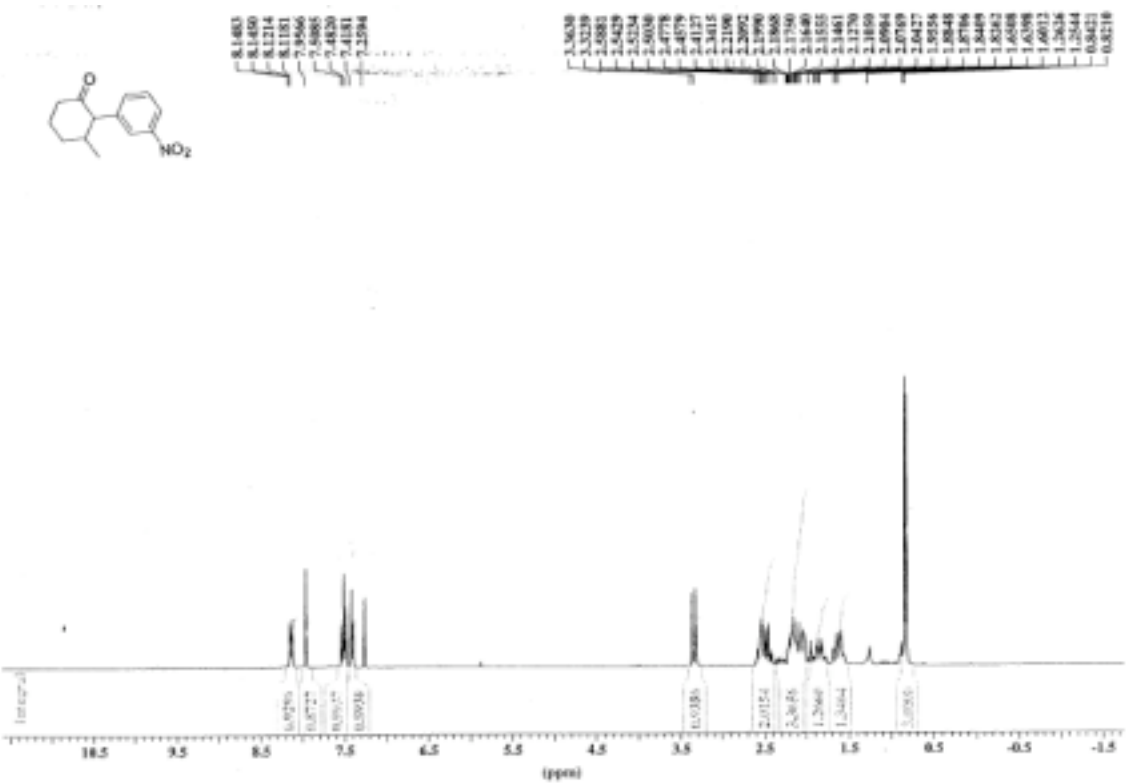
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19 (d, J = 8.79 Hz, 2H), 7.23 (d, J = 8.79, 2H), 3.34 (d, J = 11.73 Hz, 1H), 2.59 (s, 3H), 2.58-2.45 (m, 2H), 2.19-2.02 (m, 3H), 1.87-1.80 (m, 1H), 1.68-1.55 (m, 1H), 0.81 (d, J=6.48 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 208.7, 147.2, 145.5, 130.5, 123.6, 65.1, 41.9, 41.1, 34.4, 26.1, 21.3. HR MS (EI) Calcd for $C_{13}H_{15}NO_3$: 233.10519. Found m/e $(M)^+$ 233.10548.





2-(3-Nitrophenyl)-3-methyl-1-cyclohexanone (Table 2, entry 13). Method A was followed using 1-trimethylsiloxy-3-methyl-1-cyclohexene (129 mg, 0.700 mmol), 1-chloro-3-nitrobenzene (80 mg, 0.498 mmol), CsF (107 mg, 0.703 mmol), Bu_3SnF (216 mg, 0.699 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), and P(*t*-Bu)$_3$ (5.45 mg, 0.027 mmol). The reaction was conducted at 90 °C for 17 h. The reaction mixture was purified by column chromatography on silica gel (10 % ethyl acetate in hexanes) to afford 90 mg (77 %) of the desired product as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14-8.11 (m, 1H), 7.95 (s, 1H), 7.50-7.41 (m, 2H), 3.34 (d, J = 11.73 Hz, 1H), 2.58-2.43 (m, 2H), 2.19-2.07 (m, 3H), 1.88-1.82 (m, 1H), 1.65-1.60 (m, 1H), 0.83 (d, J = 6.33 Hz, 3H). ^{13} C NMR (75.5 MHz, $CDCl_3$): δ 208.8, 148.4, 139.8, 135.9, 129.3, 124.6, 122.2, 64.9, 41.8, 41.0, 34.4, 26.1, 21.3. HR MS (EI) Calcd for $C_{13}H_{15}NO_3$: 233.10519. Found m/e $(M)^+$ 233.10548.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3.3239
2.5881
2.5429
2.5234
2.5030
2.4778
2.4579
2.4127
2.3415
2.2198
2.2092
2.1990
2.1868
2.1750
2.1640
2.1555
2.1461
2.1270
2.1050
2.0964
2.0769
2.0427
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1.8848
1.8786
1.8449
1.8262
1.6588
1.6398
1.6012
1.2636
1.2544
0.8421
0.8210
1.0042
0.9296
0.8727
0.9937
0.8938
1.0386
2.0154
2.3616
1.2660
1.3464
3.0959
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9.5
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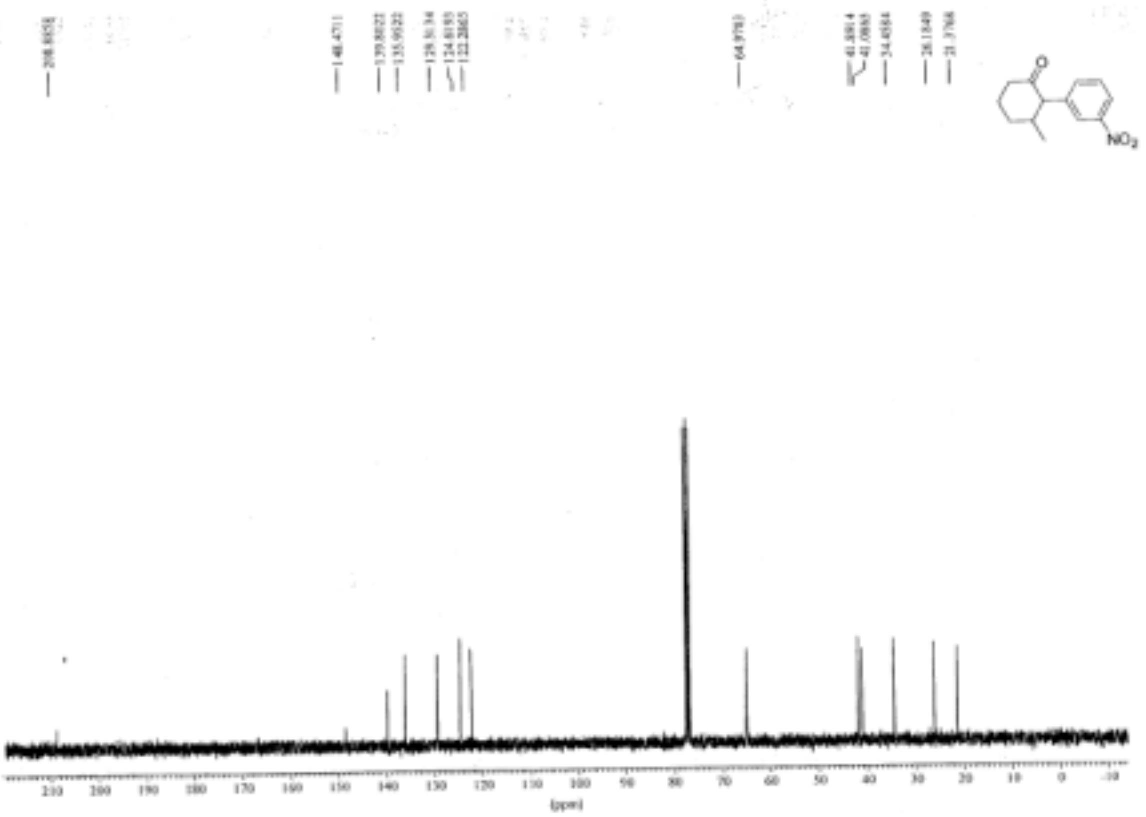
(ppm)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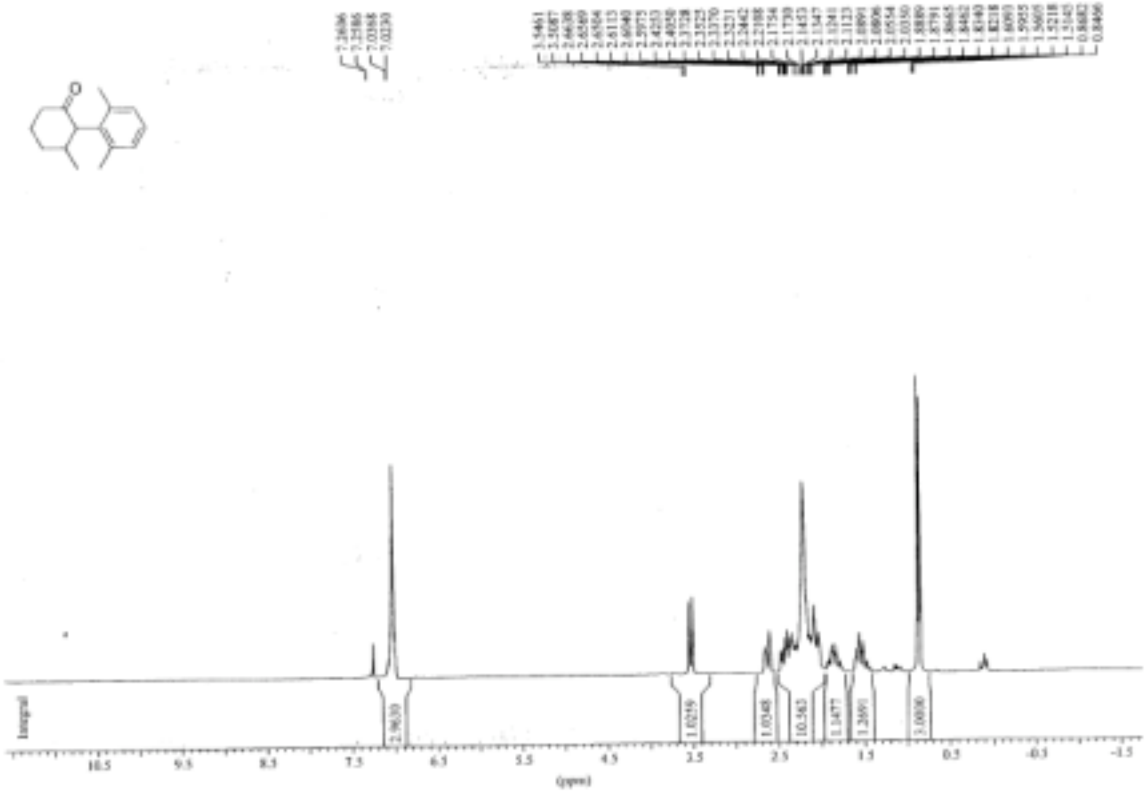
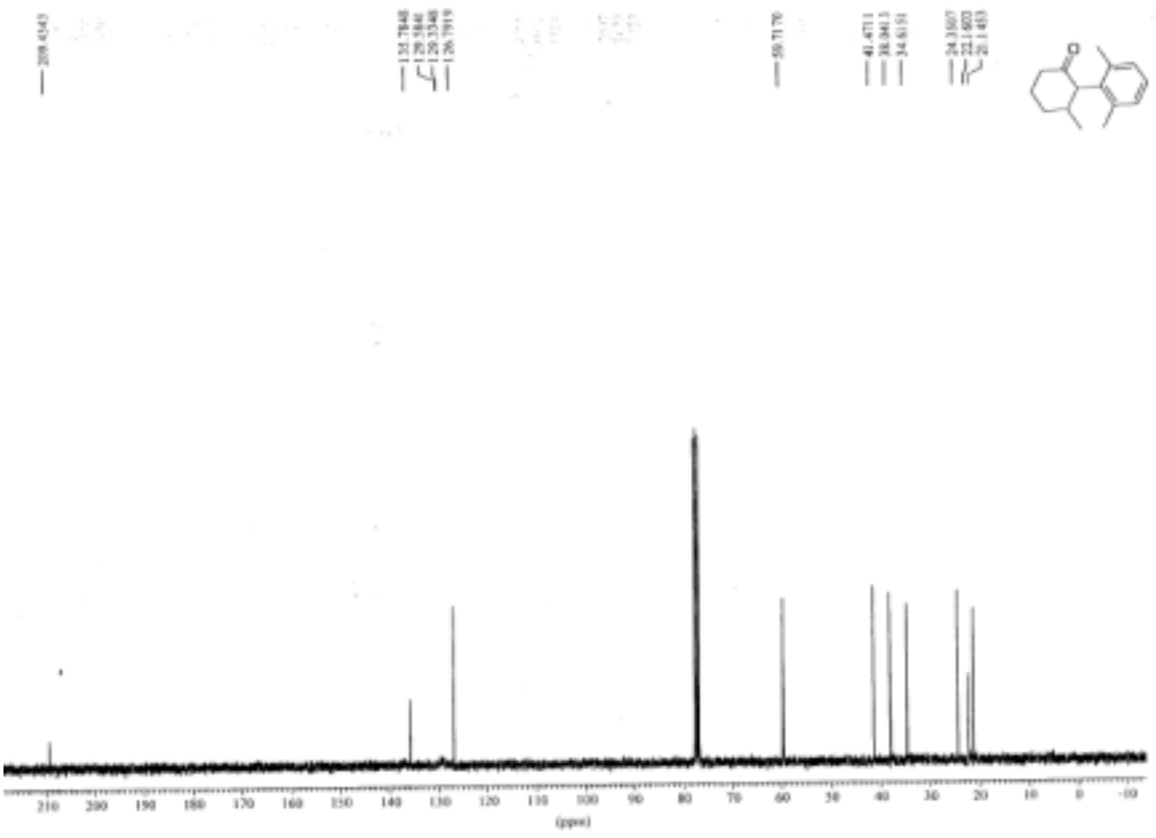
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

2-(2,6-Dimethylphenyl)-3-methyl-1-cyclohexanone (Table 2, entry 14). Method A was followed using 1-trimethylsiloxy-3-methyl-1-cyclohexene (129 mg, 0.700 mmol), 2-bromo-*m*-xylene (94 mg, 0.492 mmol), CsF (107 mg, 0.703 mmol), Bu_3SnF (216 mg, 0.699 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), and $P(t\text{-}Bu)_3$ (5.45 mg, 0.027 mmol). The reaction was conducted at 85 °C for 20 h. The reaction mixture was purified by column chromatography on silica gel (2-4 % ethyl acetate in hexanes) to afford 92 mg (85 %) of the desired product as a colorless liquid.

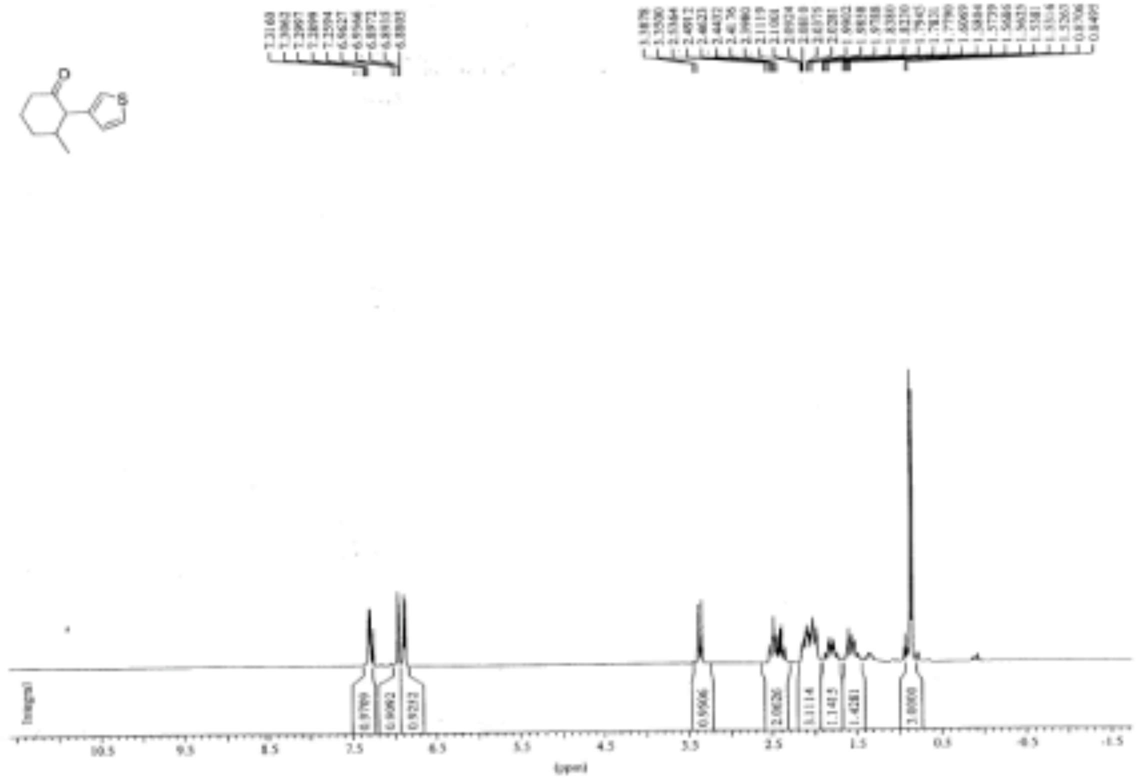
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.03-7.02 (m, 3H), 3.52 (d, J = 11.22 Hz, 1H), 2.66-2.59 (m, 1H), 2.42-2.03 (overlap, 10H), 1.88-1.82 (m, 1H), 1.60-1.51 (m, 1H), 0.85 (d, J = 6.48 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 209.4, 135.7, 129.5, 129.3, 126.8, 59.7, 41.4, 38.0, 34.6, 24.3, 22.1, 21.1. HR MS (EI) Calcd for $C_{15}H_{20}O$: 216.15142. Found m/e $(M)^+$ 216.15174.





2-(3-thienyl)-3-methyl-1-cyclohexanone (Table 2, entry 15). Method A was followed using 1-trimethylsiloxy-3-methyl-1-cyclohexene (129 mg, 0.700 mmol), 3-bromothiophene (84 mg, 0.500 mmol), CsF (107 mg, 0.703 mmol), Bu_3SnF (216 mg, 0.699 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), and P(*t*-Bu)$_3$ (5.45 mg, 0.027 mmol). The reaction was conducted at 85 °C for 20 h. The reaction mixture was purified by column chromatography on silica gel (2-4 % ethyl acetate in hexanes) to afford 76 mg (78 %) of the desired product as a colorless liquid

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31-7.28 (m, 1H), 6.96 (s, 1H), 6.89-6.88 (m, 1H), 3.37 (d, J = 11.34 Hz, 1H), 2.53-2.39 (m, 2H), 2.11-1.97 (m, 3H), 1.84-1.78 (m, 1H), 1.60-1.52 (m, 1H), 0.86 (d, J = 6.33 Hz, 3H). ^{13} C NMR (75.5 MHz, $CDCl_3$): δ 210.0, 138.2, 127.9, 125.4, 122.7, 60.2, 41.9, 41.0, 34.2, 26.1, 21.4. HR MS (EI) Calcd for $C_{11}H_{14}OS$: 194.07654. Found m/e $(M)^+$ 194.07684.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9.5
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7.5
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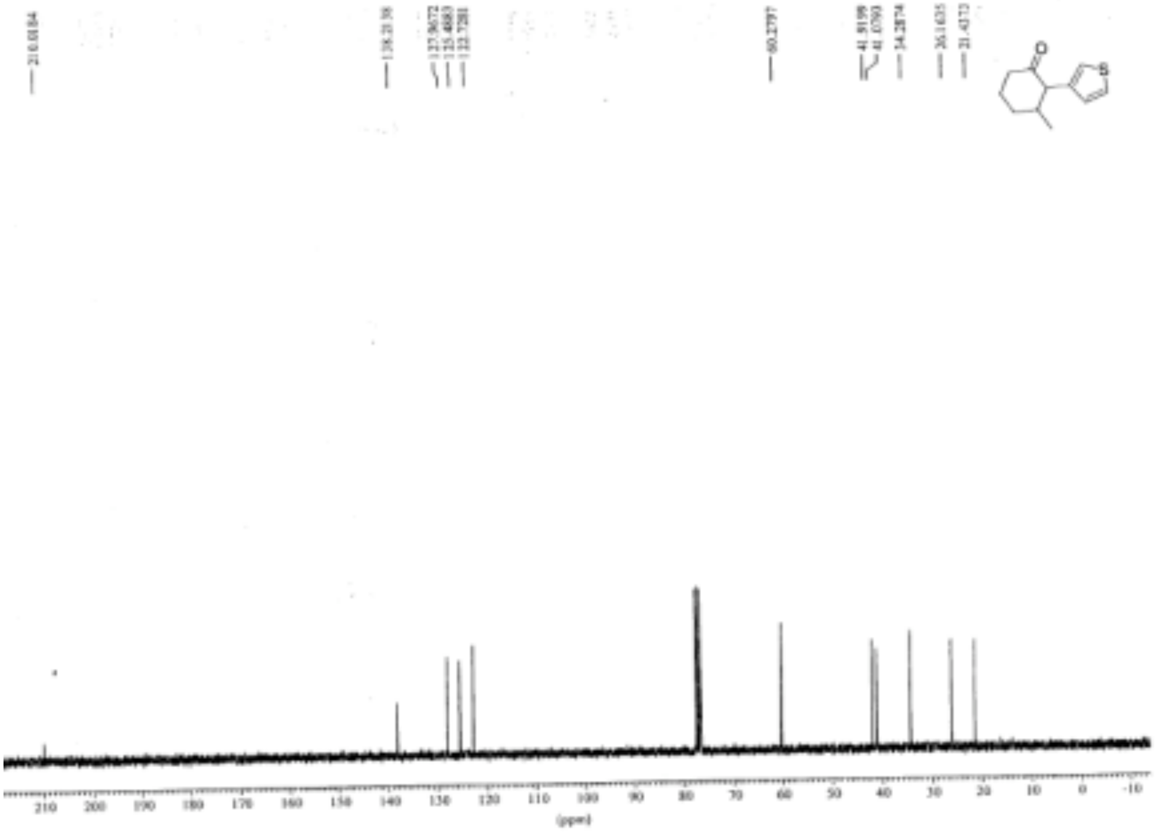
-0.5
-1.5
(ppm)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200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

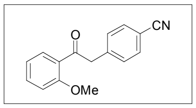
3-(4-Nitrophenyl)-4-phenyl-2-butanone (Reaction 1). Method A was followed using 2-trimethylsiloxy-4-phenyl-2-butene (154 mg, 0.699 mmol), 1-bromo-4-nitrobenzene (102 mg, 0.500 mmol), CsF (107mg, 0.703 mmol), Bu_3SnF (216 mg, 0.699 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), and P(*t*-Bu)$_3$ (5.45 mg, 0.027 mmol) and 2 mL of THF. The reaction was conducted at 85 °C for 19 h. The reaction mixture was purified by column chromatography on silica gel (5-10 % ethyl acetate in hexanes) to afford 105 mg (78%) of the desired product as a pale yellow solid.

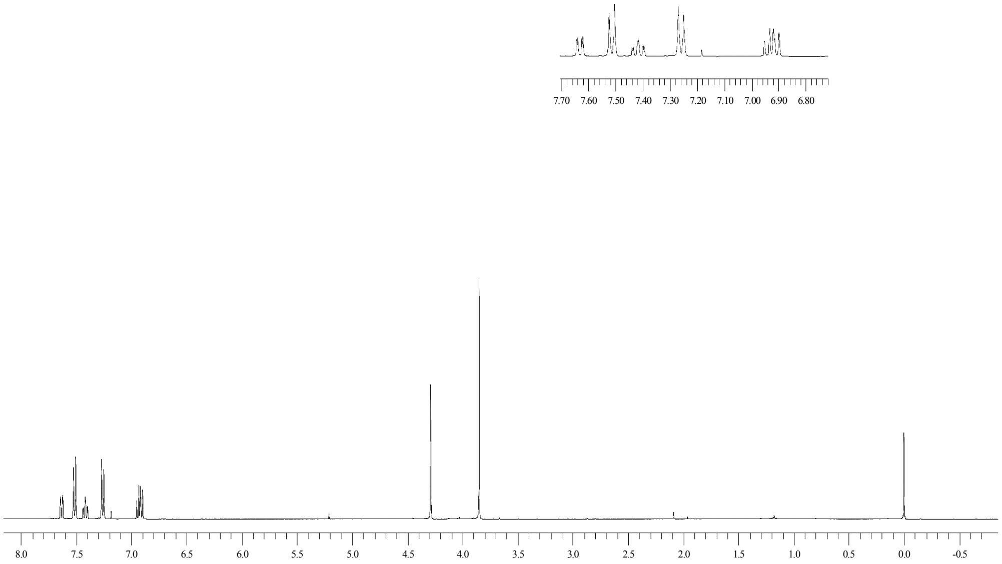
3-(4-Acetylphenyl)-4-phenyl-2-butanone (Reaction 1). Method A was followed using 2-trimethylsiloxy-4-phenyl-2-butene (154 mg, 0.699 mmol), 4'-bromoacetophenone (101 mg, 0.497 mmol), CsF (107 mg, 0.703 mmol), Bu_3SnF (216 mg, 0.699 mmol), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol), and P(*t*-Bu)$_3$ (5.45 mg, 0.027 mmol) and 2mL THF. The reaction was conducted at 85 °C for 12 h. The reaction mixture was purified by column chromatography on silica gel (10 % ethyl acetate in hexanes) to afford 80 mg (60%) of the desired product as a white solid.

Xuebin: Procedures need to be given for Table 3 entries 1-4.

You need to format the pictures in this version. The other version had the method numbers wrong.

4-(2-(2-Methoxyphenyl)-2-oxoethyl)benzonitrile. (Table 3, entry 5). Method C was followed. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H), 4.29 (s, 2H), 6.90-6.95 (m, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.40-7.44 (m, 1H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.63 (dd, *J* = 7.3, 1.8 Hz, 1H); ^{13}C NMR(100.6 MHz, $CDCl_3$) δ 49.08, 54.48, 109.44, 110.58, 117.98, 119.86, 126.35, 129.57, 129.74, 131.02, 133.20, 139.90, 157.60, 197.24.


O
CN
OMe


7.70 7.60 7.50 7.40 7.30 7.20 7.10 7.00 6.90 6.80
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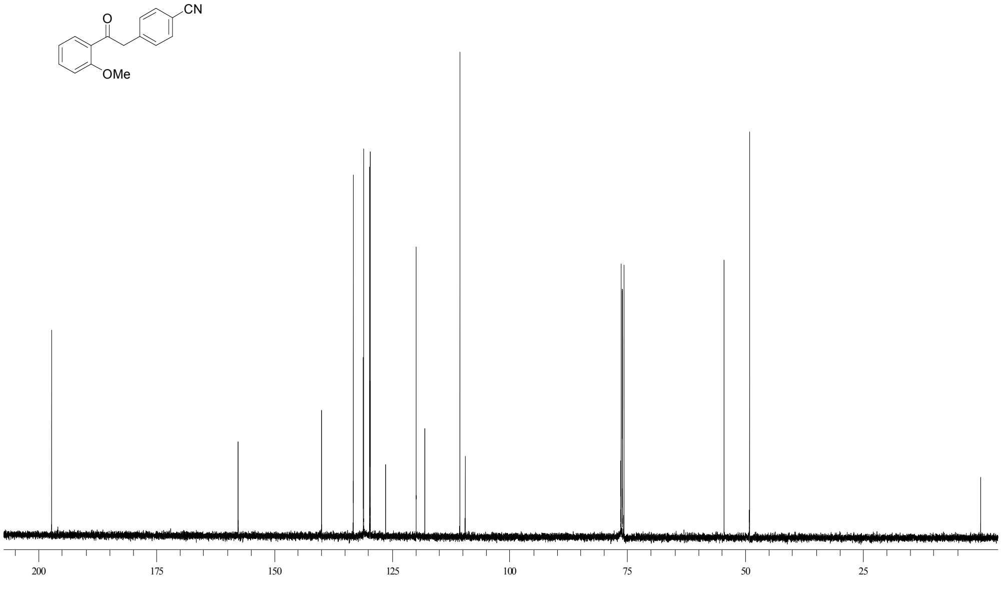
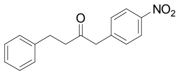
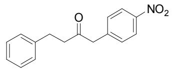
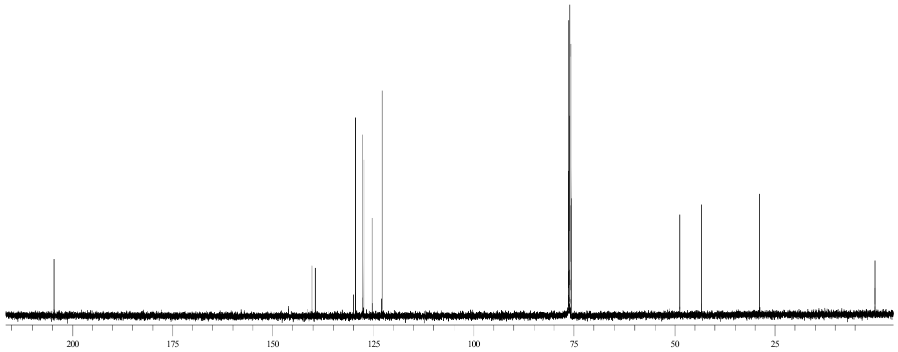

O
CN
OMe
200 175 150 125 100 75 50 25

1-(4-Acetylphenyl)-4-phenyl-2-butanone. (Table 3, entry 6). Method C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52 (s, 3H), 2.71-2.88 (m, 4H), 3.66 (s, 2H), 7.06-7.21 (m, 7H), 7.83 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR(100.6 MHz, $CDCl_3$) δ 26.66, 29.78, 43.94, 50.13, 126.24, 128.35, 128.55, 128.77, 129.74, 135.96, 139.39, 140.69, 197.72, 206.36; Anal. Calcd. For $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.96; H, 6.86.

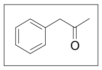
1-(4-Nitrophenyl)-4-phenyl-2-butanone. (Table 3, entry 7). Method D. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.74-2.86 (m, 4H), 3.70 (s, 2H), 7.06-7.22 (m, 7H), 8.09 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR(100.6 MHz, $CDCl_3$) δ 28.74, 43.19, 48.58, 122.75, 125.30, 127.31, 127.56, 129.39, 129.83, 139.43, 140.21, 204.45; Anal. Calcd. For $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 70.96; H, 5.66; N, 5.25.

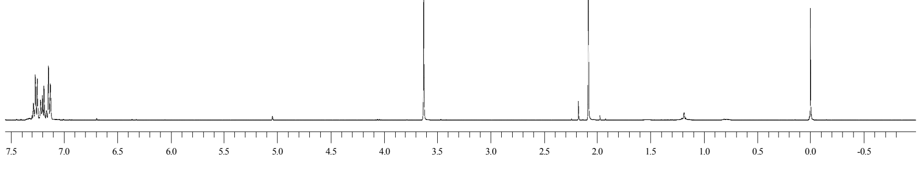


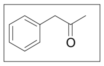




1-Phenylpropan-2-one. (Table 3, entry 8). Method E. ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.08 (s, 3H), 3.63 (s, 2H), 7.13-7.27 (m, 5H); ^{13}C NMR(100.6 MHz, CDCl$_3$) δ 28.62, 50.02, 126.05, 127.74, 128.37, 133.21, 205.42.



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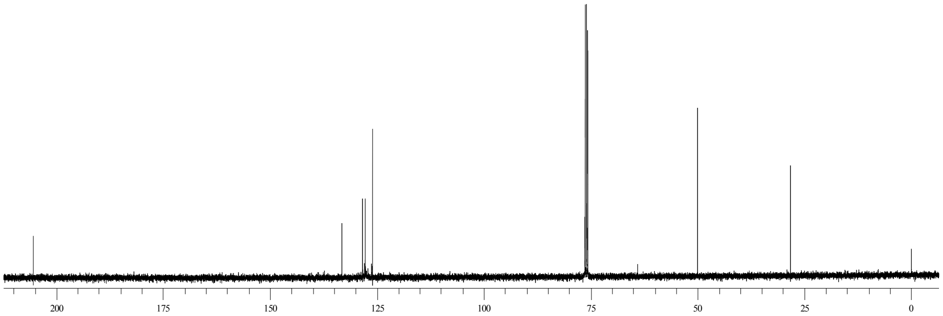
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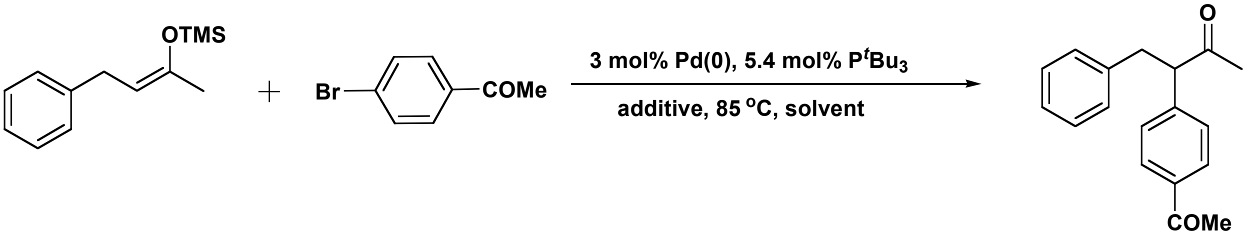
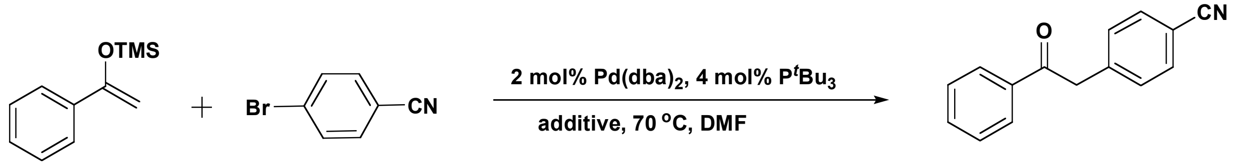
Table S1. Effect of combinations of CsF, MnF_2 and ZnF_2 on the coupling of silyl enol ethers with an aryl bromide.



Entry	Pd source	solvent	additive (equiv)	yield (%)
1	$Pd(OAc)_2$	toluene	$CsF(1.4)/MnF_2(1.4)$	no product
2	$Pd(OAc)_2$	DMF	$CsF(1.4)/MnF_2(1.4)$	10%
3	$Pd(OAc)_2$	DMF	$ZnF_2(1.4)/MnF_4(1.4)$	10% conversion
4	$Pd(dba)_2$	DMF	$ZnF_2(1.4)/MnF_4(1.4)$	83%
5	$Pd(dba)_2$	DMF	ZnF_2 (1.4)/CsF (1.4)	65%
6	$Pd(dba)_2$	DMF	ZnF_2 (1.4)/CsF (0.4)	90%

Reaction conditions: 1.0 equiv aryl halide, 1.4 equiv silyl enol ether, 1 mL solvent was added per 0.2 mmol of aryl halide.

Table S2. Effect of combinations of CsF, MnF_2 and ZnF_2 on the coupling of silyl enol ethers with an aryl bromide.



Entry	additive (equiv)	yield (%)
1	ZnF_2 (1.0)	*74
2	CsF (1.0)	only diarylation
3	MnF_2 (1.0)	30 % conversion
4	ZnF_2 (1.0)/CsF (0.2)	60 %diarylation
5	MnF_2 (1.0)/CsF (0.2)	20 % diarylation
6	ZnF_2 (1.0)/MnF_2 (0.4)	80 (diarylation< 5%)

* enol ether product

Reaction conditions: 1.0 equiv aryl halide, 1.5 equiv silyl enol ether, 1 mL DMF was added per 0.2 mmol of aryl halide.

References:

(1) Matsuzawa, S.; Horiguchi, Y. Nakamura, E. Kuwajima, I. *Tetrahedron*, **1989**, *45*, 349.