Design and Synthesis of (E)-1- ((3-Ethyl-2, 4,4-trimethylcyclohex-2-enylidene)methyl-4- Substituted Benzenes from 1-(2,6,6-Trimethylcyclohex-1-enyl) ethanol

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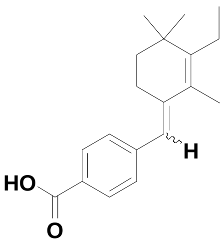
Supporting Information

I. General

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 °C at 300 MHz and 75 MHz, respectively, with TMS as internal standard. Mass spectra were recorded on Varian MS mass spectrometer.

II. Analytical data of unusual 1,3-dienes

2



White solid: mp 185-187 °C; Yield: 0.147 G; 85%; ^{1}H NMR (300 MHz, DMSOd$_6$): δ = 1.03 (t, *J* = 8 Hz, 3H), 1.05 (s, 6H), 1.44 (m, 2H), 1.86 (s, 3H), 2.19 (q, 2H), 2.55 (m, 2H), 6.47 (s, 1H), 7.40 (d, *J* = 8 Hz, 2H), 7.40 (d, J = 8 Hz, 2H), 7.90–7.82 (d, *J* = 8.0 Hz, 2H), 13.0–12.6 (br s, 1H); ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 14.6, 22.3, 23.7, 27.3, 35.4, 38.1, 67.1, 120.5, 126.6, 127.8, 129.0, 141.2, 142.8, 148.1. HR FT-ICR MS: calcd for $C_{19}H_{24}O_2$ ($[M+H]^+$) 285.1848; found: 285.1856.

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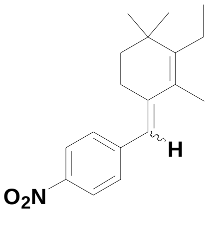

Syrup; Yield: 0.150 G; 80%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03-1.14 (m, 15H), 1.52-1.56 (m, 7H), 1.70-1.75 (m, 2H), 1.94 (s, 3H), 2.15 (q, 2H), 2.25 (q, 4H), 2.34-2.42 (m, 2H), 2.58-2.67 (m, 4H), 6.16 (s, 1H), 6.47 (s, 2H), 7.29-7.32 (d, *J* = 12 Hz, 2H), 7.39-7.42 (d, *J* = 12 Hz, 4H), 8.12-8.15 (d, *J* = 12 Hz, 2H), 8.17-8.20 (d, *J* = 12 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 15.1, 15.6, 19.4, 22.8, 23.4, 24.8, 27.9, 28.9, 33.5, 36.4, 37.5, 39.0, 41.2, 119.9, 123.45, 123.7, 127.3, 130.1, 144.4, 146.5, 147.5, 150.7. HR-MS: ($C_{18}H_{23}NO_2$) calculated ($[M+H]^+$) 286.1828 found 286.1824.

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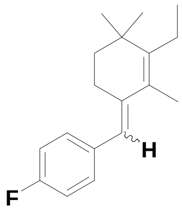
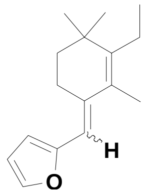


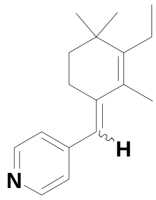
Syrup; Yield: 0.162 G; 78%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06-1.13 (m, 9H), 1.49-1.54 (m, 2H), 1.93 (s, 3H), 2.22-2.25 (q, *J* = 12 Hz, 2H), 2.53-2.62 (m, 2H), 6.42 (s, 1H), 7.00-7.06 (m, 2H), 7.21-7.29 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.2, 15.5, 23.2, 24.5, 28.1, 36.2, 39.3, 115.0, 115.3, 120.5, 127.3, 131.1, 135.3, 140.5, 147.8, 159.1, 160.2.

9



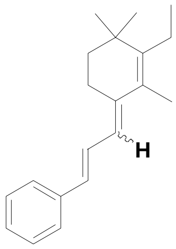
Syrup; Yield: 0.189 G; 79%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06-1.10 (m, 12H), 1.57-1.61 (m, 2H), 1.90 (s, 3H), 2.20-2.27 (q, *J* = 12 Hz, 2H), 2.70-2.75 (m, 2H), 6.29-6.31 (m, 2H), 6.43-6.45 (m, 1H), 7.39-7.40 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.2, 15.3, 23.2, 24.9, 27.9, 35.9, 38.5, 108.7, 110.3, 111.8, 127.2, 138.9, 141.2, 148.5, 154.9. HR-MS: ($C_{16}H_{22}O$) calculated ($[M+H]^+$) 231.1460 found 231.1467.

10



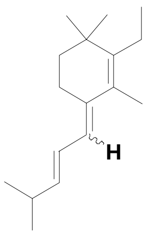
Syrup; Yield: 0.186 G; 83%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.07-1.12 (m, 9H), 1.50-1.53 (m, 2H), 1.92 (s, 3H), 2.20-2.27 (q, *J* = 12 Hz, 2H), 2.58-2.70 (m, 2H), 6.34 (s, 1H), 7.16-7.18 (m, 2H), 8.50-8.62 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.1, 15.5, 23.4, 24.7, 27.9, 36.3, 39.0, 119.1, 124.4, 127.2, 144.4, 147.1, 149.7, 150.3. HR-MS: ($C_{16}H_{22}O$) calculated ($[M+H]^+$) 242.1909 found 242.1918.

11



Syrup; Yield: 0.173 G; 86%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05-1.10 (m, 9H), 1.56-1.62 (m, 2H), 1.89 (s, 3H), 2.19-2.25 (q, *J* = 12 Hz, 2H), 2.60-2.64 (m, 2H), 6.24-6.30 (m, 1H), 6.56-6.61 (m, 1H), 7.17-7.25 (m, 2H), 7.28-7.35 (m, 2H), 7.43-7.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.2, 23.3, 23.5, 28.1, 36.3, 38.9, 121.6, 126.5, 127.3, 127.6, 128.9, 131.2, 139.0, 140.4, 148.3.

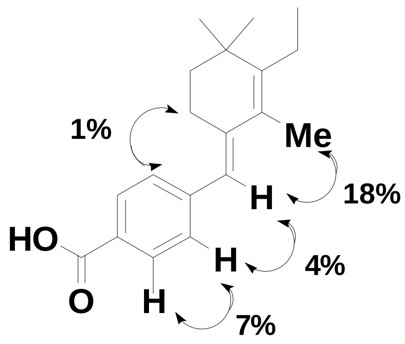
12



Syrup; Yield: 0.192 G; 81%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00-1.10 (m, 15H), 1.52-1.60 (m, 2H), 1.82 (s, 3H), 2.14-2.23 (q, *J* = 12 Hz, 2H), 2.35-2.46 (m, 1H), 2.46-2.53 (m, 2H), 5.65-5.75 (m, 1H), 6.01-6.09 (m, 1H), 6.32-6.43 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.0, 15.2, 23.1, 23.2, 28.2, 28.9, 32.1, 33.1, 36.1, 38.9, 40.5, 121.4, 124.5, 127.4, 137.5, 141.3, 146.6.

NOE experiments of compound 2

NOE experiments clearly indicate that the phenyl ring is trans in **2** (1H-1H NOEs: 6.46 ppm->7.38 ppm-4%, 6.46 ppm->1.85 ppm-18%, 7.39 ppm->7.90 ppm-7%, 7.39 ppm >6.46 ppm-4%, 7.39 ppm -> 2.55 ppm -1%.

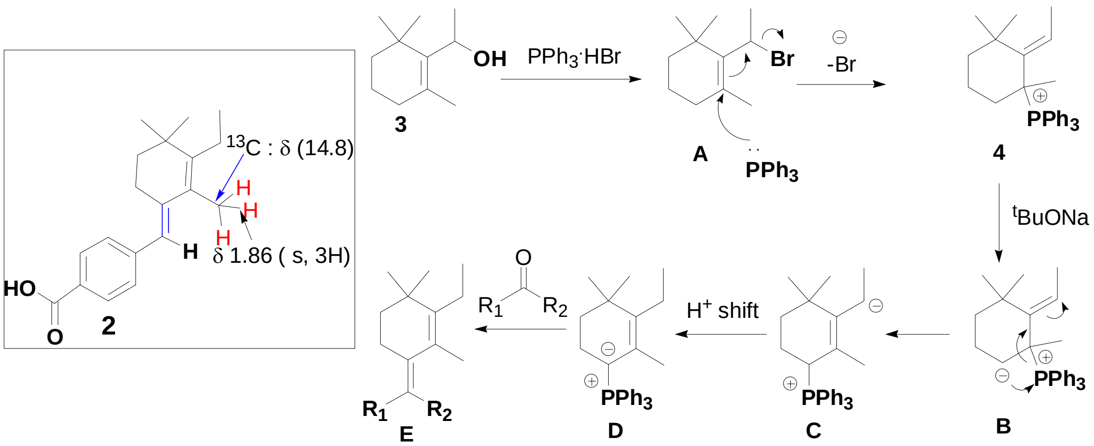


2: *E*

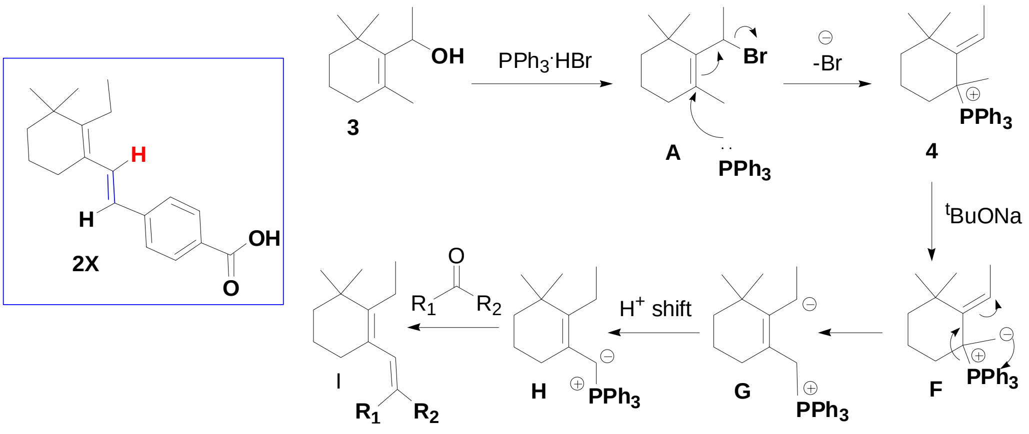
Proposed Mechanism:

Based our final product analytical data's: mainly ^{1}H NMR δ 1. 86 (s, 3H) and ^{13}C NMR δ 14.8) clearly demonstrates that deprotonation occur at methylene in the ring (**mechanism A**). Had it been deprotected from methyl group, we would have gotten final product **2X** (having 2 vinylic proton peaks – δ 6.8 region) (**mechanism B)** written below.

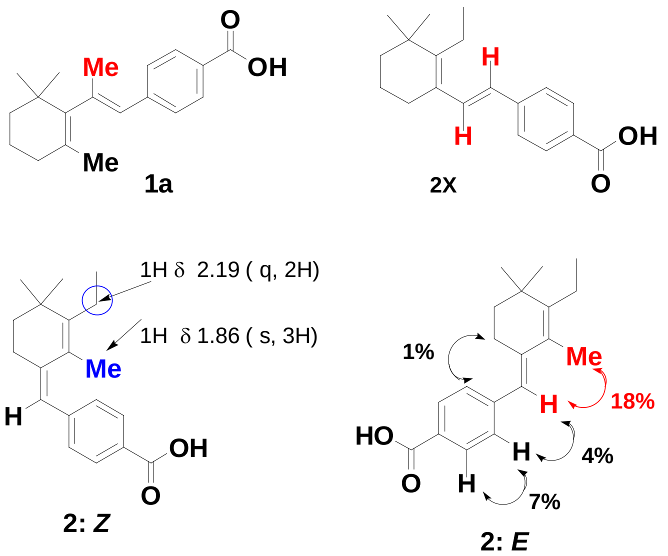
(A) Proposed Mechanism for Unusal Wittig Reaction: deprotonation at methylene carbon



(B) Proposed Mechanism for Unusal Wittig Reaction: deprotonation at methyl carbon



Had deprotonation occurred in the methyl proton outside the ring system, we would have expected the final product **2X** which contains two vinylic protons. But our NMR data's clearly indicates one vinylic proton and proton NMR of our final compound contains **one** singlet at δ 1.86 (s, 3H) for three protons that co-relate to methyl proton outside the ring. This clearly corroborate with our proposed mechanism where deprotonation occur at methylene proton inside the cyclohexene ring not outside methyl ring.



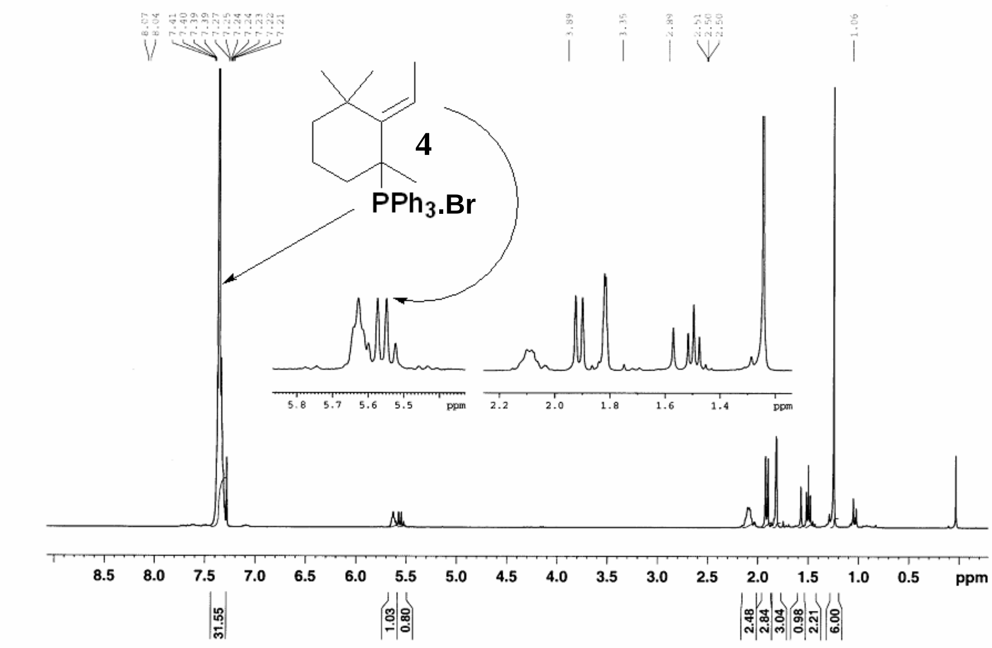
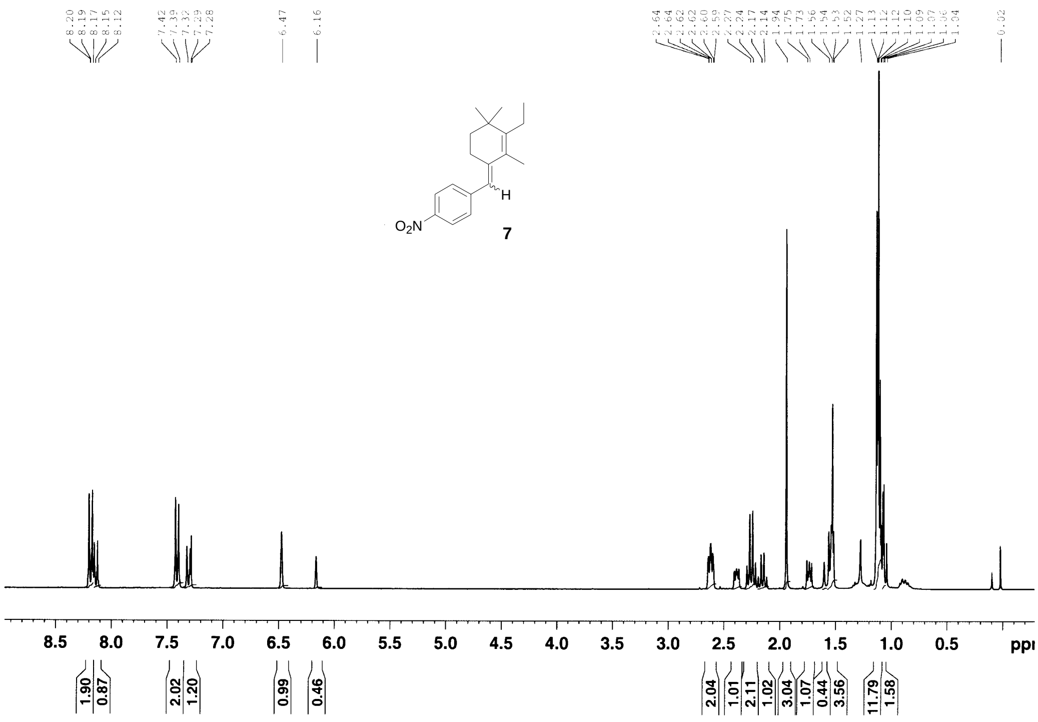
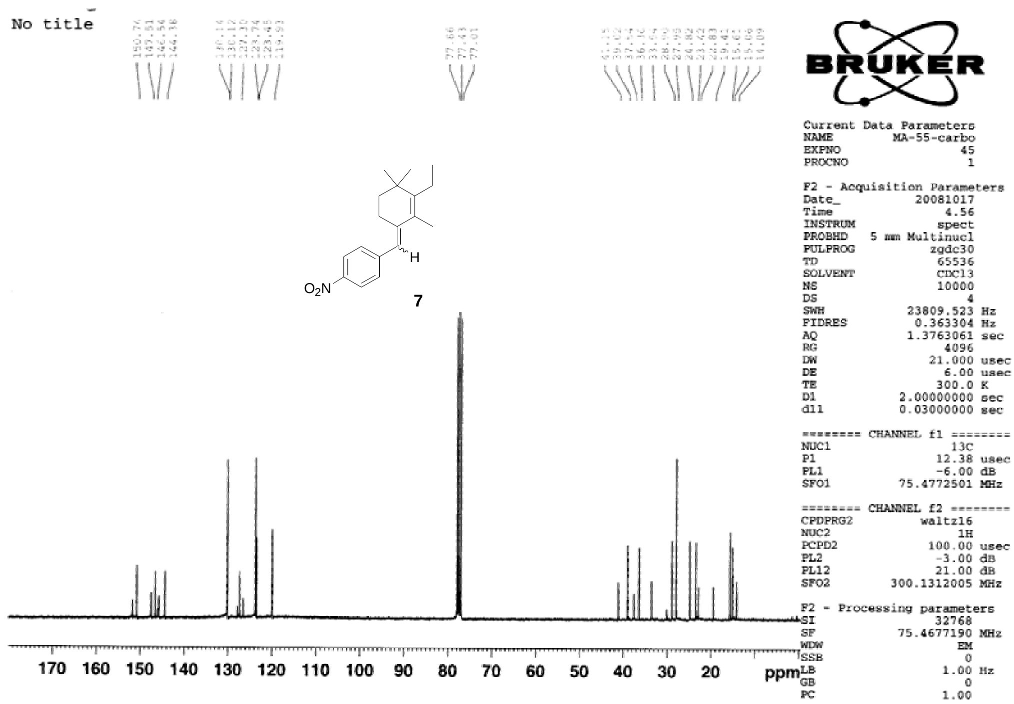


Figure 3

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F2 - Acquisition Parameters
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Time 4.56
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TD 65536
SOLVENT CDCl3
NS 10000
DS 4
SWH 23809.523 Hz
FIDRES 0.363304 Hz
AQ 1.3763061 sec
RG 4096
DW 21.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
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P1 12.38 usec
PL1 -6.00 dB
SFO1 75.4772501 MHz
======== CHANNEL f2 ========
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NUC2 1H
PCPD2 100.00 usec
PL2 -3.00 dB
PL12 21.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
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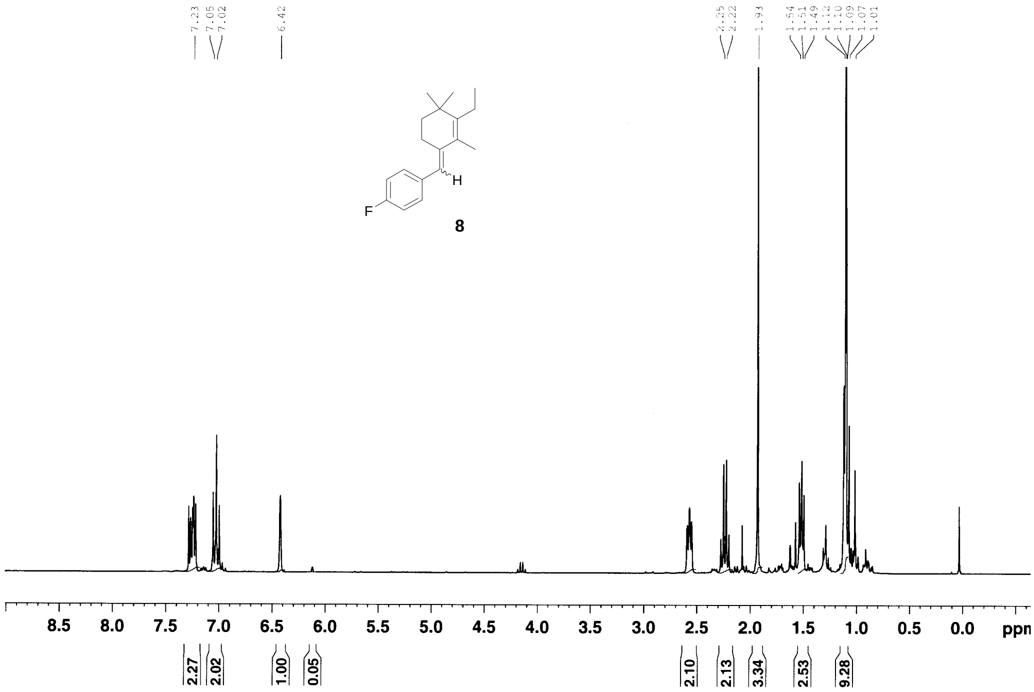
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6.42
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2.22
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F
H
8
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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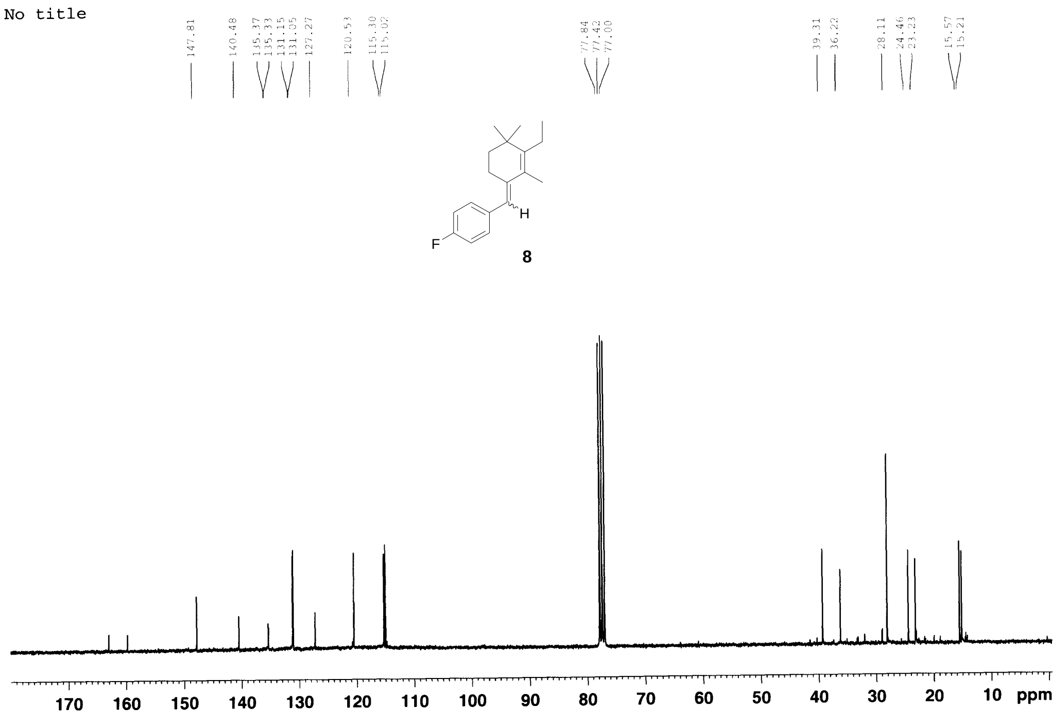
2.10
2.13
3.34
2.53
9.28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77.00
39.31
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23.23
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15.21
H
F
8
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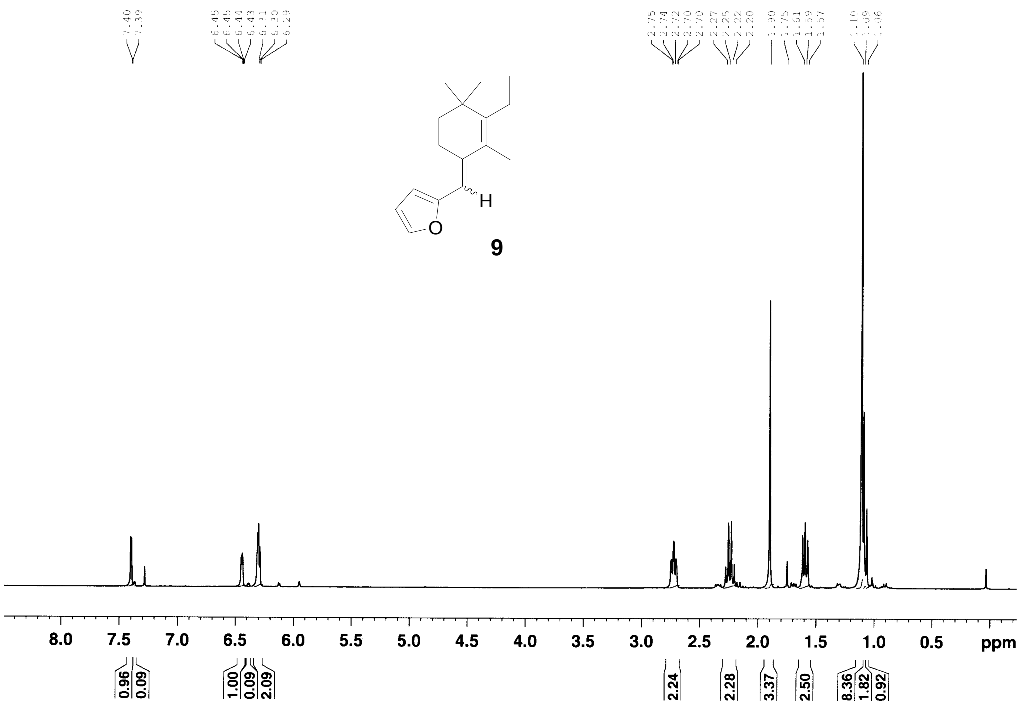
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2.70
2.27
2.25
2.22
2.20
1.90
1.75
1.61
1.59
1.57
1.10
1.09
1.06
H
O
9
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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0.09
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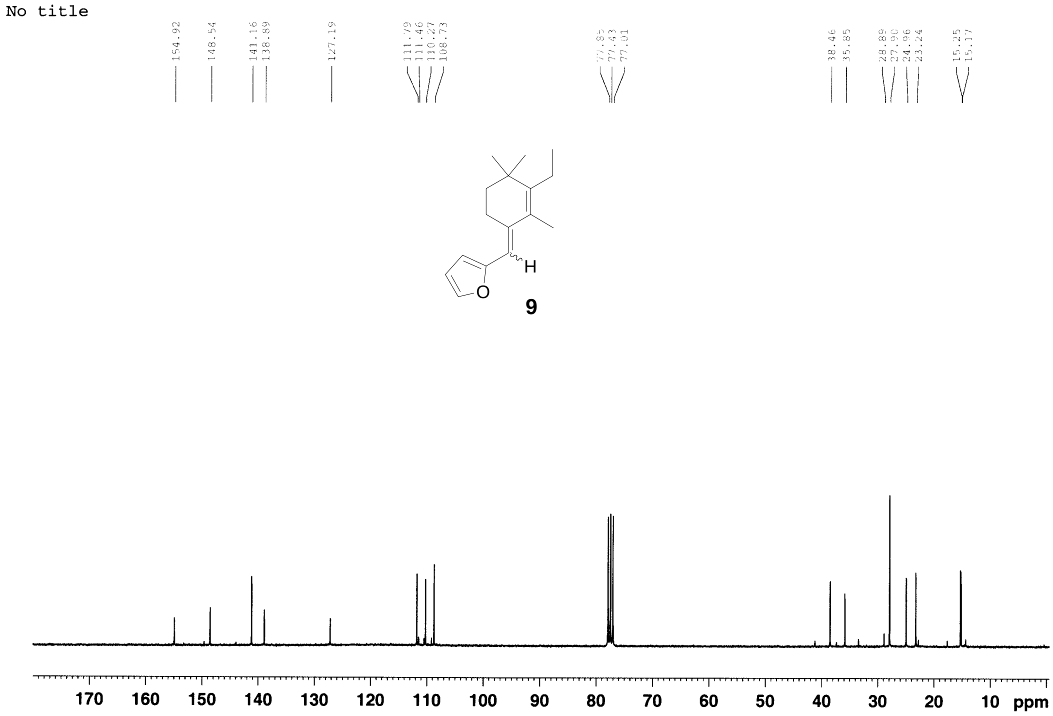
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O
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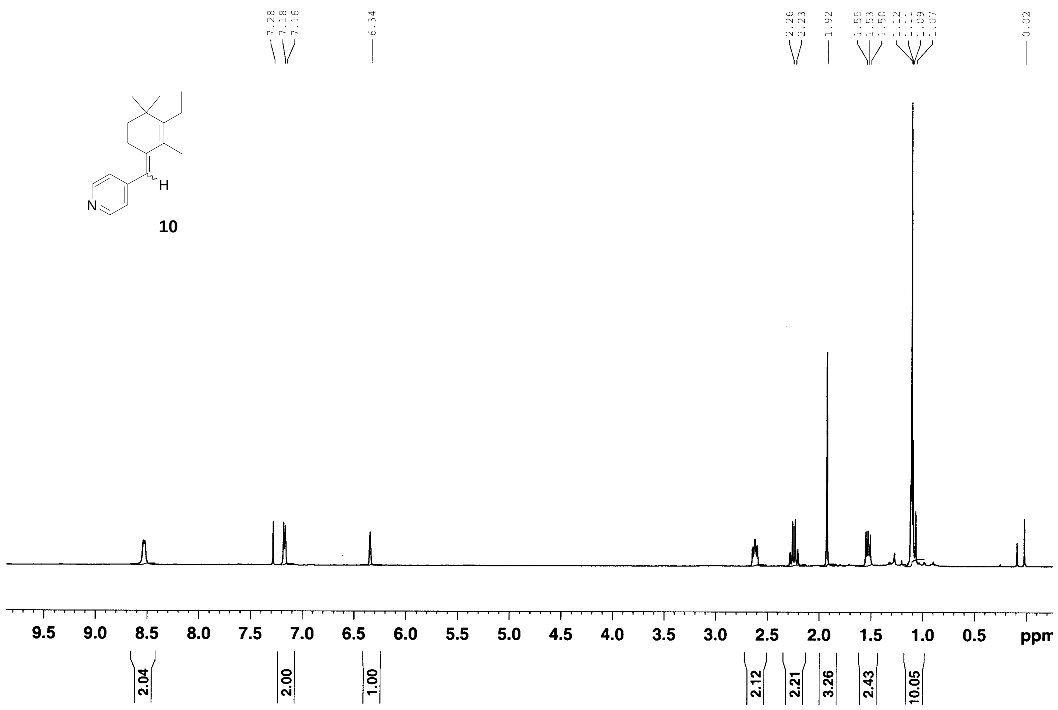
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0.02
H
N
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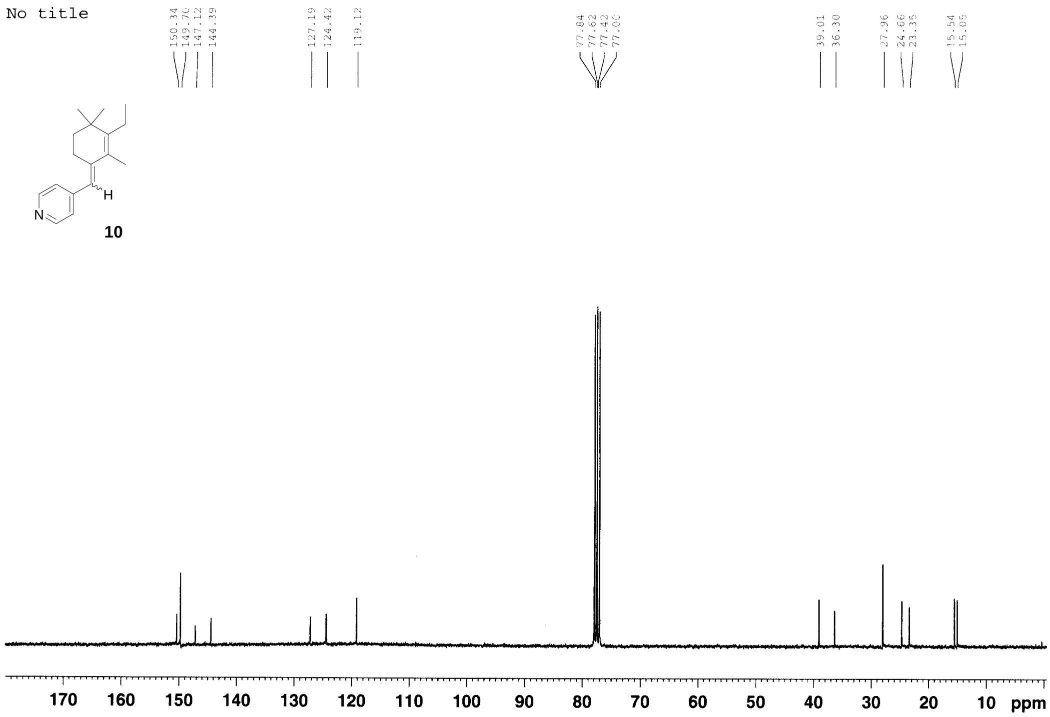
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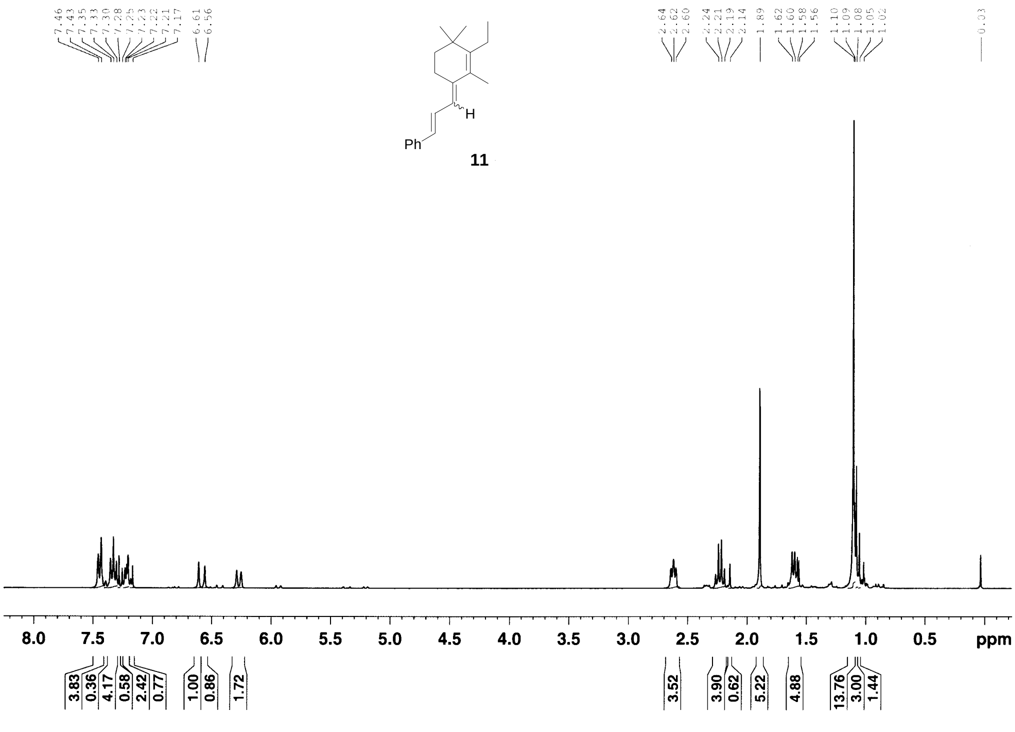
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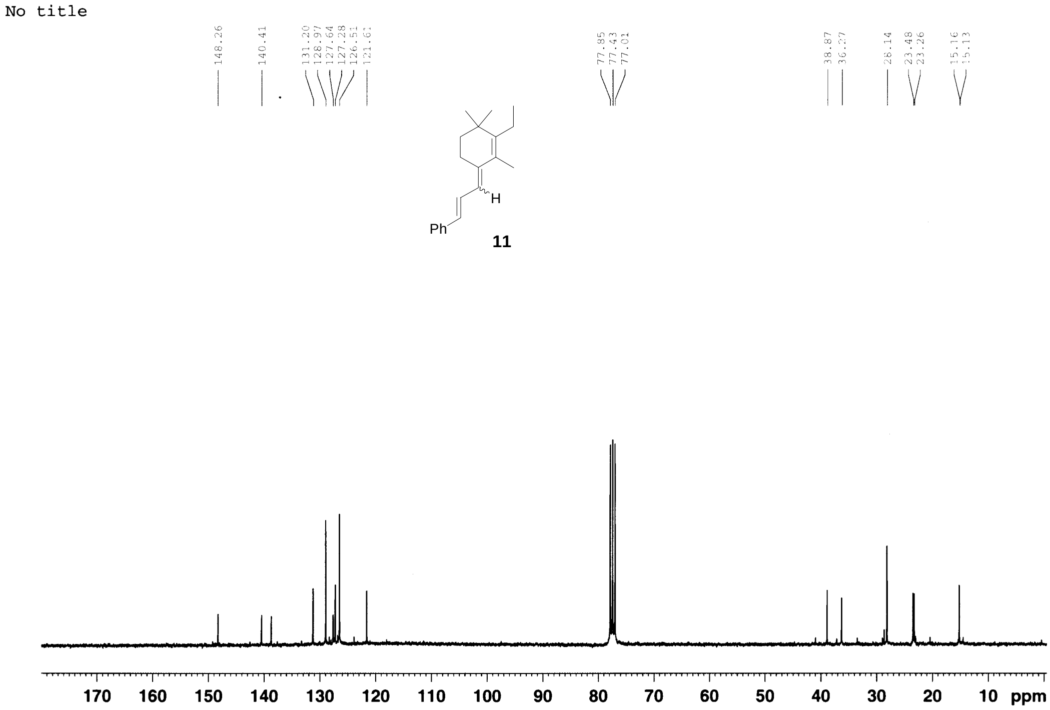
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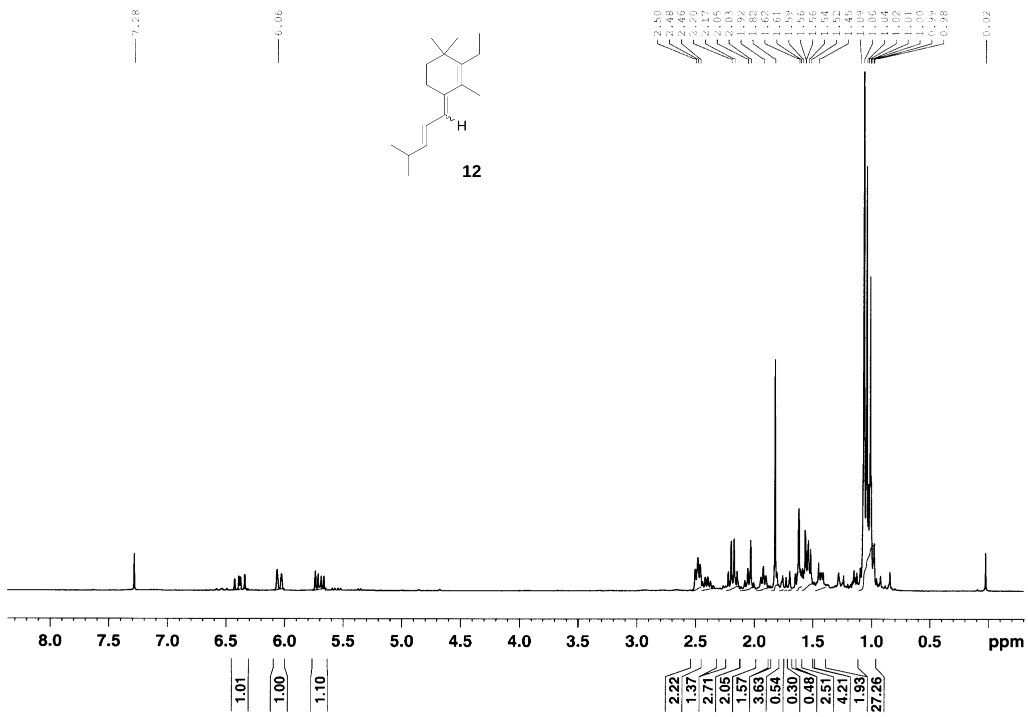
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1.00
1.10
2.22
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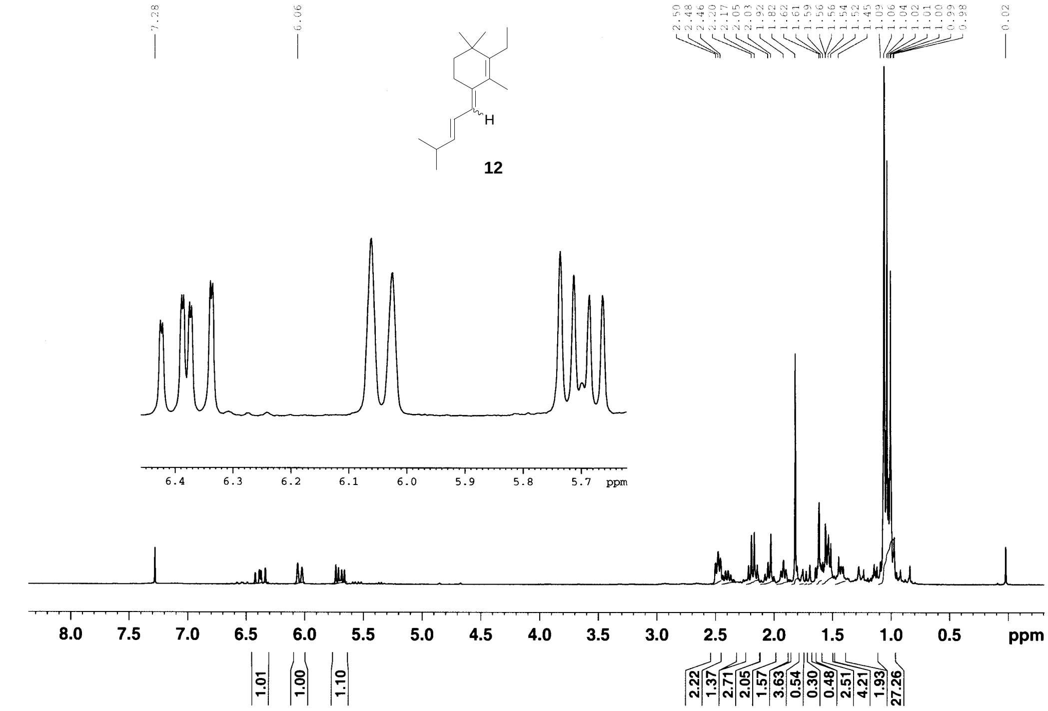

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