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One-pot synthesis of cyclohexenes bearing quaternary trifluoromethylated carbon via Diels-Alder reaction

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ABSTRACT

The Diels-Alder reactions of a variety of α, β unsaturated carbonyls trifluoromethylated have been investigated. These compounds were found to undergo the cycloaddition readily with dienes to give cyclohexenes bearing quaternary trifluoromethylated carbon (6-7-8) (a-b-c) and (6-7-8) (a'-b'-c') in moderate to good yields.

KEYWORDS

Organofluorine compounds;
Diels–alder reactions;
Cyclohexenes trifluoromethylated.

INTRODUCTION

The Formation of quaternary carbons bearing a trifluoromethyl group is of great interest for the preparation of analogues of natural products and bioactive molecules[1-3]. The Diels-Alder reactions are among the most widely used reactions in organic synthesis[4-8] and such reactions with trifluomethlated α, β -insaturated carbonyls is very attractive for the construction of cyclic compounds bearing CF_3 quaternary carbons[9-13].

Usually cycloaddition must be carried out via polar mechanism characterized by nucleophilic/ electrophilic interactions to occur under mild conditions[14-16]. Most butadiene and dipoles are good nucleophiles, but ethylene must be electrophilically activated for the reaction to be of experimentally interest. In addition the multiple substitution with electron-withdrawing (EW) groups accelerates the cycloaddition to increase the electrophilic character of ethylene[17-18].

Particularly trifluoromethyl is an EW group, but it alone is not sufficient to activate ethylene efficiently. In fact, Iwa ojima and al have showed that the introduction of the substituted phenyl group in the olefin is interesting not only because it increases the reactivity of dienophile but also because it may them to estimate the relative magnitude of the effect of trifluoromethyl group on regioselectivity[19].

As a continuation of our research program focused on the reactivity study of trifluoromethyl derivatives prepared from vilsmeir methods[20-22], we report in this paper a straightforward access to substituted cyclohexenes by Diels-Alder cycloaddition of a variety of symmetrical dienes, i.e., butadiene, 2,3-dimethylbutadiene and cyclopentadiene with a multisubstituted carbonyls bearing CF_3 groups and other EW groups such as ph and CO.

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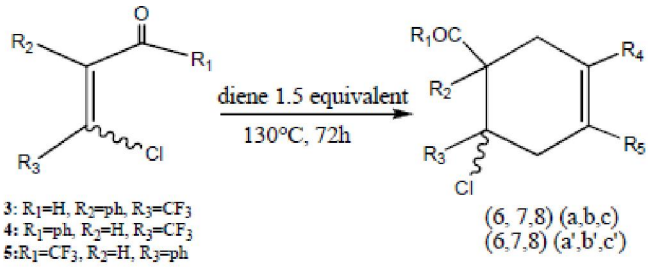
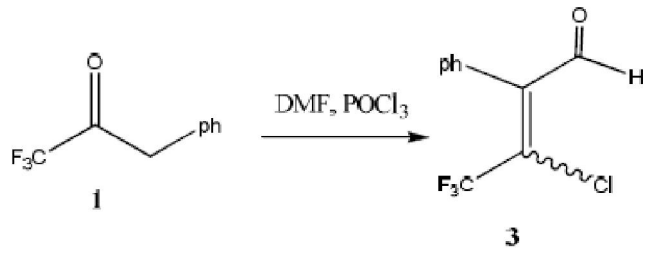
RESULTS AND DISCUSSION

The synthesis of trifluoromethylated carbonyls (3-4-5) was already described[23-24] by Vilsmeier reaction on trifluoromethylketone (1) and 4.4.4-trifluoro-1-phenylbutane-1.3-diene (2) (Scheme 1 and 2).

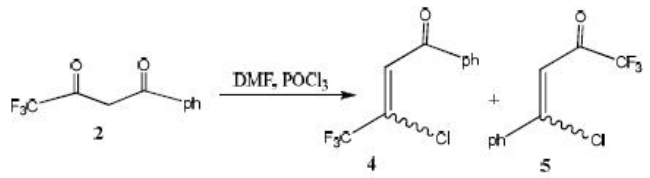
The Diels-Alder reactions of these multisubstituted olefins, used as a mixture of isomers Z and E, with symmetrical dienes, such as: butadiene, 1,2-dimethylbutadiene and cyclopentadiene, are carried out at 130°C for 72 hours in a sealed pyrex ampoule. These reactions give a mixture of diasterioisomeres of cyclohexenes: (6-7-8) (a-b-c) and (6-7-8) (a'-b'-c') in moderate to good yield (Scheme 3, TABLE 1).

As shown in TABLE 1, cyclohexenes (6-7-8) were obtained as a mixture of cis and trans diastereoisomeres which could be separated by further column chromatography. The stereochemistry of the major cis and the minor trans isomers was confirmed by ^{19}F NMR and NOE experiments. These isomers could be differentiated by chemical shifts CF_3. The NOE spectra of separated diastereoisomers showed, after irradiation of CF_3 group, a 4% enhancement of the proton H-2 for the cis isomer 7a. Figure

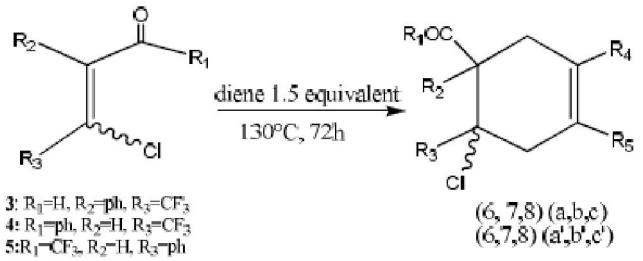




Scheme 1



Scheme 2



Scheme 3

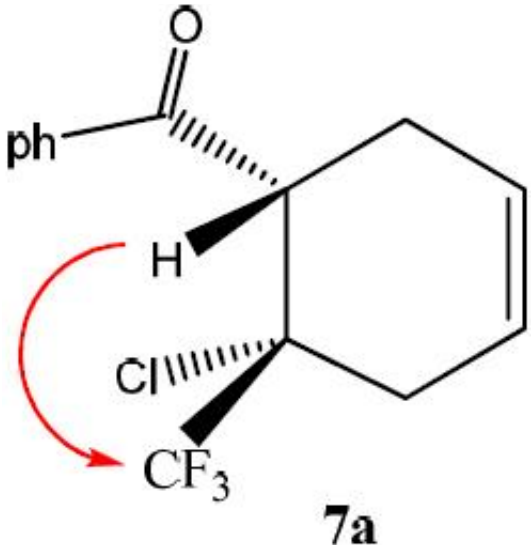


Figure 1 : NOE correlation of 7a

In summary, we have described a simple and direct cycloaddition of unsaturated carbonyls trifluoromethylated with various dienes via Diels-Alder reaction. We have obtained a CF_3 substituted cyclohexenes.

EXPERIMENTAL SECTION

All reactions progress was monitored by thin-layer chromatography (TLC) analysis (Merck Kieselgel 60 F_{254}). All compounds were purified by chromatography column (Silica gel 60, 70-230 mesh ASTM). IR spectra were obtained on Perkin-Elmer Paragon 1000 PC. ^1H NMR spectra were recorded on a Bruker AC-300 (300 MHz) spectrometer using tetramethylsilane (TMS, $\delta_H = 0$) as internal standard. ^{13}C NMR spectra were recorded on a Bruker AC-300 (75 MHz) spectrometer with proton decoupling. For ^{19}F spectra, C_6F_6 was used as reference and they were performed on a Bruker AC-300

TABLE 1 : Diels–Alder reactions of dienes and trifluoromethylated, α, β-unsaturated carbonyls

Entry	R1	R2	R3	R4	R5	Cycloadducts	%Cis/trans	Yiel(%)
1	H	ph	CF3	H	H	6 (a, a')	75/25	65
1	-	-	-	CH3	CH3	6 (b, b')	58/42	60
1	-	-	-	cyclopentadiene		6 (c, c')	63/37	58
2	ph	H	CF3	H	H	7 (a, a')	76/24	72
2	-	-	-	CH3	CH3	7 (b, b')	68/32	78
2	-	-	-	cyclopentadiene		7 (c, c')	65/35	68
3	CF3	H	ph	H	H	8 (a, a')	70/30	75
3	-	-	-	CH3	CH3	8 (b, b')	82/18	72
3	-	-	-	cyclopentadiene		8 (c, c')	67/33	70

(282.36 MHz). Mass spectra were carried out on a Hewlett-Packard model (70 eV) under electronic impact (EI). Elemental analyses were carried out with a Perkin-Elmer CHN, Analyser. Coupling constants (J values) are given in Hertz and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).

General procedure for the synthesis of cycloadducts

A mixture of the dienes (1.5 equivalent) and multisustituted olefins (1 equivalent) (3-4-5) was sealed in a pyrex tube and heated at 130°C for 72h to give trifluoromethylated cyclohexenes (6-7-8). The reaction mixture was submitted to column chromatography on silica gel with (petroleum ether/ether 90:10) as the eluent.

Cis-6-chloro,6-trifluoromethyl,1-phenyl cyclohex-3-enecarbanal 6a

Colorless oil, IR ν cm^{-1}: 1710 (CO), 1181.42-1179.58 (CF_3); ^{1}H NMR (300MHz, $CDCl_3$): δ 2.4 (m, 4H), 6.07 (m, 2H), 9.8 (s, 1H), 7.1 (m,5H); CNMR (75MHz, $CDCl_3$): δ 190.92, 132.7, 131.8(q,CF_3,$^1J_{CF}$=276Hz),1130.6, 129.6(q, C-CF_3, $^2J_{CF}$=18.8Hz), 128.1, 32.6, 32.1; ^{19}F NMR (282.4 MHz; $CDCl_3$): δ 101.53; MS(m/z): 288.5 (M^+, 2), 253 (35), 231.5 (45), 211 (33), 189 (22), 77 (80), 57 (40), 35 (14) Anal. Calcd for $C_{14}H_{12}OF_3Cl$: C, 58.23; H, 4.15 found: C, 58.29; H, 4.16%

Trans-6-chloro,6-trifluoromethyl,1-phenyl cyclohex-3-ene carbanal 6a'

Colorless oil, IR ν cm^{-1}: 1710 (CO), 1181.42-1179.58 (CF_3) ; ^{1}H NMR (300MHz, $CDCl_3$): δ 3.25 (m, 4H), 6.25 (m, 2H), 10.2 (s, 1H), 7.3 (m,5H); ^{13}C NMR (75MHz, $CDCl_3$):δ 191.78, 132.9, 131.8(q,CF_3,$^1J_{CF}$=276Hz), 130.8, 129.7(q, C-CF_3, $^2J_{CF}$=18.8Hz), (128.1-131.3) (m, C_6H_5), 33.1, 32.4; ^{19}F NMR (282.4 MHz; $CDCl_3$): δ 102.65; MS(m/z): 288.5 (M^+, 20), 253 (50), 231.5 (25), 211 (32), 189 (25), 77 (70), 57 (30), 35 (15) ; Anal. Calcd for $C_{14}H_{12}OF_3Cl$: C, 58.23; H, 4.15 found: C, 58.27; H, 4.15%.

Cis-6-chloro,6-trifluoromethyl,1-phenyl, 3,4-dimethylcyclohex-3-ene carbanal 6b

Colorless oil, IR ν cm^{-1}: 1700.68(CO), 1171.32-1168.93(CF_3) ; ^{1}H NMR (300MHz, $CDCl_3$): δ 1.5 (s, 3H), 1.69 (s, 3H), 2.23 (m, 4H), 9.8 (s, 1H), 7.1-7.4 (m,5H); ^{13}C NMR (75MHz,$CDCl_3$):δ 192.7, 152.7, 133.2, 131, 130.6, 129, 128.7 (q,CF_3,$^1J_{CF}$=273Hz), 130.8(q, C-CF_3, $^2J_{CF}$=18.6Hz), 32.6, 31.8; ^{19}F NMR (282.4 MHz; $CDCl_3$): δ 102.59; MS(m/z): 316.5 (M^+, 40), 281 (35), 259 (66), 239 (34), 77 (40), 57 (60), 35 (26); Anal. Calcd for $C_{16}H_{16}OF_3Cl$: C, 60.66; H, 5.05; found: C, 60.74; H, 5.06%.

Trans-6-chloro,6-trifluoromethyl,1-phenyl,3,4-dimethylcyclohex-3-ene carbanal 6b'

Colorless oil, IR ν cm^{-1}: 1700.68(CO), 1171.32-1168.93(CF_3); ^{1}H NMR (300MHz, $CDCl_3$): δ 1.7 (s, 3H), 1.85(s, 3H), 2.5 (m, 4H), 10.1 (s, 1H), 7.1-7.4 (m,5H); ^{13}C NMR(75MHz,$CDCl_3$):δ 193.8, 152.8, 133.4, 131.1, 130.6, 129, 128.8 (q,CF_3,$^1J_{CF}$=273Hz), 130.6(q, C-CF_3, $^2J_{CF}$=18.5Hz), 33.6, 32.7; ^{19}F NMR (282.4 MHz; $CDCl_3$): δ 102.97; MS(m/z): 316.5 (M^+, 10), 281 (55), 259 (60), 239

(28), 77 (60), 57 (40), 35 (25) ; Anal. Calcd for $C_{16}H_{16}OF_3Cl$: C, 60.66; H, 5.05; found: C, 60.58; H, 5.06%.

Cis-6-chloro,6-trifluoromethyl,1-phenyl, bicyclo[2,2,1]hep-3-ene carbanal 6c

Colorless oil, IR ν cm^{-1}: 1706(CO), 1172.17-1170.34(CF_3); ^{1}H NMR (300MHz, $CDCl_3$): δ 2.5(m, 2H), 3.1 (m, 1H), 3.3 (m, 1H), 6.17 (m, 1H), 6.31 (m, 1H), 7.1-7.4 (m, 5H), 9.8 (s, 1H); ^{13}C NMR (75MHz, $CDCl_3$):δ 191.28, 132.8 (q,C-CF_3, $^2J_{CF}$=28.6Hz), 130.1(q,CF_3,$^1J_{CF}$=273Hz), 127.2-132.3 (m, 5H), 129.2, 128.7, 57.5, 45.6, 37.6; ^{19}F NMR (282.4 MHz; $CDCl_3$): δ 101.67; MS(m/z): 300 (M^+, 70), 265 (45), 243 (56), 223 (34), 77 (47), 57 (66), 35 (22); Anal. Calcd for $C_{15}H_{12}OF_3Cl$: C, 59.90; H, 3.99; found: C, 59.94; H, 4.01%..

Trans-6-chloro,6-trifluoromethyl,1-phenyl bicyclo[2,2,1]hep-3-ene carbanal 6c'

Colorless oil, IR ν cm^{-1}: 1706(CO), 1172.17-1170.34(CF_3); ^{1}H NMR (300MHz, $CDCl_3$): δ 2.6(m, 2H), 3.2 (m, 1H), 3.5 (m, 1H), 6.2 (m, 1H), 6.35 (m, 1H), 7.1-7.4 (m, 5H), 10.1 (s, 1H); ^{13}C NMR (75MHz, $CDCl_3$):δ 192.41, 133 (q,C-CF_3, $^2J_{CF}$=28.6Hz), 131.2(q,CF_3,$^1J_{CF}$=273Hz), 127.1-132.3 (m, 5H), 129.4, 128.9, 57.7, 45.7, 37.9; ^{19}F NMR (282.4 MHz; $CDCl_3$): δ 103.48; MS(m/z): 300 (M^+, 30), 265 (49), 243 (66), 223 (24), 77 (44), 57 (53), 35 (20) ; Anal. Calcd for $C_{15}H_{12}OF_3Cl$: C, 59.90; H, 3.99; found: C, 59.96; H, 3.99%.

Cis-6-chloro,6-trifluoromethylcyclohex-3-ene phenone 7a

Colorless oil, IR ν cm^{-1}: 1720(CO), 1140-1168(CF_3); ^{1}H NMR (300MHz, $CDCl_3$): δ 2.2 (m, 2H), 2.5 (m, 2H), 3.3 (t, J= 16.6 Hz, 1H), 6.05 (m, 1H), 6.17 (m, 1H), 7.2-7.4(m,5H); ^{13}CNMR(75MHz,$CDCl_3$):δ 197, 132.3, 131.2, 130.4, 129, 128.8 (q,CF_3,$^1J_{CF}$=291Hz),127.6(q,C-CF_3,$^2J_{CF}$=20.1Hz),126, 125.7, 46.7, 37.6, 35.1; ^{19}F NMR (282.4 MHz; $CDCl_3$): δ 85.48; MS(m/z): 288.5 (M^+, 10), 253 (60), 231 (28), 77 (60), 57 (40), 35 (25); Anal. Calcd for $C_{14}H_{12}OF_3Cl$: C, 58.23; H, 4.15; found: C, 58.27; H, 4.16%.

Trans-6-chloro,6-trifluoromethylcyclohex-3-ene phenone 7a'

Colorless oil, IR ν cm^{-1}: 1720(CO), 1140-1168(CF_3); ^{1}H NMR (300MHz, $CDCl_3$): δ 2.3 (m, 2H), 2.6 (m, 2H), 3.4 (t, J= 16.6 Hz, 1H), 6.1 (m, 1H), 6.2 (m, 1H), 7.2-7.4(m, 5H); ^{13}CNMR(75MHz,$CDCl_3$):δ 199, 132.2, 131.3, 130.4, 130, 128.8 (q, CF_3, $^1J_{CF}$=291Hz), 127.7(q,C-CF_3,$^2J_{CF}$=20.1Hz),126.1, 125.7, 46.8, 37.9, 35.3; ^{19}F NMR (282.4 MHz; $CDCl_3$): δ 86.35; MS(m/z): 288.5 (M^+, 30), 253 (70), 231 (28), 77 (65), 57 (30), 35 (24) Anal. Calcd for $C_{14}H_{12}OF_3Cl$: : C, 58.23; H, 4.15; found: C, 58.31; H, 4.16%.

Cis-6-chloro, 6-trifluoromethyl,3,4-dimethylcyclohex-3-ene phenone 7b

Colorless oil, IR ν cm^{-1}: 1725(C0), 1145-1230(CF_3); ^{1}H NMR (300MHz, $CDCl_3$): δ 1.3 (s, 3H), 1.6 (s, 3H), 3.2 (t, J= 16.5 Hz, 1H), 2.5 (d, J=16.5, 2H), 2.7 (s, 2H),7.4-7.8(m,5H); ^{13}CNMR(75MHz,$CDCl_3$):δ 196.4, 133.4, 133.2, 131.2, 129.8, 127 (q,CF_3,$^1J_{CF}$=290.3Hz),128.6(q,C-CF_3,$^2J_{CF}$=20.1Hz),46.2, 39.8, 37.4, 29.6, 19.2; ^{19}F NMR (282.4 MHz; $CDCl_3$): δ 86.75; MS(m/z): 316.5 (M^+), 287(20), 281 (80), 259 (57), 239(51), 211 (12) 77 (42), 57 (10); Anal. Calcd for $C_{16}H_{16}OF_3Cl$: C, 60.66; H, 5.05; found: C, 60.64; H, 5.06%.

Trans-6-chloro,6-trifluoromethyl,3,4-dimethylcyclohex-3-ene phenone 7b'

Colorless oil, IR ν cm^{-1}: 1725(C0), 1145-1230(CF_3); ^{1}H NMR (300MHz, $CDCl_3$): δ 1.5 (s, 3H), 1.8 (s, 3H), 3.3 (t, J= 16.5 Hz, 1H), 2.8 (d, J=16.5 Hz, 2H), 2.9 (s, 2H),7.3-7.8(m,5H); ^{13}CNMR(75MHz,$CDCl_3$):δ 198, 133.6, 133, 132, 130, 127.5 (q,CF_3,$^1J_{CF}$=290.3Hz),128.7 (q,C-CF_3,$^2J_{CF}$=20.1Hz),46.5, 39, 37.6, 30, 19.5; ^{19}F NMR (282.4 MHz; $CDCl_3$): δ 89.74; MS(m/z): 316.5 (M^+), 287(30), 281 (60), 259 (54), 239(43), 211 (15) 77 (52), 57 (26); Anal. Calcd for $C_{16}H_{16}OF_3Cl$: C, 60.66; H, 5.05; found: C, 60.65; H, 5.05%.

Cis-6-chloro, 6-trifluoromethyl bicyclo[2,2,1]hep-3-ene phenone 7c

Colorless oil, IR ν cm^{-1}: 1721.13(C0), 1159.6(CF_3); ^{1}H NMR (300MHz, $CDCl_3$): δ 3.8 (m, 1H), 3.7 (m, 2H), 2.2 (m, 2H), 6.2 (m, 1H), 6.4 (m, 1H), 7.2-7.7 (m, 5H); ^{13}C NMR (75MHz, $CDCl_3$):δ 197, 128 (q,C-CF_3, $^2J_{CF}$=28.6Hz), 128.5-131.1 (m,

C_6H_5), 127.2, 126.4, 55.3, 46.4, 32.2; ^{19}F NMR (282.4 MHz; $CDCl_3$): δ 87.34; MS(m/z): 300.5 (M^+), 265 (59), 243 (62), 223 (14), 77 (24), 57 (51); Anal. Calcd for $C_{15}H_{12}OF_3Cl$: C, 59.9O; H, 3.99; found: C, 59.96; H, 3.98%.

Trans-6-chloro,6-trifluoromethyl bicyclo[2,2,1]hep-3-ene phenone 7c'

Colorless oil, IR ν cm^{-1}: 1721.13(C0), 1159.6(CF_3); ^{1}H NMR (300MHz, $CDCl_3$): δ 3.9 (m, 1H), 3.8 (m, 2H), 2.4 (m, 2H), 6.5 (m, 1H), 6.7 (m, 1H), 7.2-7.8 (m, 5H); ^{13}C NMR (75MHz, $CDCl_3$):δ 199, 129.6 (q,C-CF_3, $^2J_{CF}$=28.6Hz), 129.2-132.4 (m, C_6H_5), 127.5, 126.7, 55.6, 46.7, 32.4; ^{19}F NMR (282.4 MHz; $CDCl_3$): δ 89.52; MS(m/z): 300.5 (M^+), 265 (28), 243 (41), 223 (63), 77 (42), 57 (52) ; Anal. Calcd for $C_{15}H_{12}OF_3Cl$: C, 59.90; H, 3.99; found: C, 59.98; H, 3.99%.

Cis-3-[6-chloro,6-phenylcyclohex-3-enyl],1,1,1-trifluoroethanone 8a

Colorless oil, IR ν cm^{-1}: 1710(CO), 1164-1158(CF_3); ^{1}H NMR (300MHz, $CDCl_3$): δ 2.1(m, 2H), 2.9 (m,2H), 4.2 (m, 1H), 5.89 (m, 1H), 6.15 (m, 1H), 7.1-7.3 (m, 5H); ^{13}C NMR (75MHz, $CDCl_3$):δ 199,130.2–132.4 (C_6H_5), 129.1 (q,CF_3,$^1J_{CF}$=288.7Hz), 128.3, 127.1, 47.5, 46.1, 38.4; ^{19}F NMR (282.4 MHz; $CDCl_3$): δ 99.97 ; MS(m/z): 288.5 (M^+), 253 (41), 231 (53), 211 (34), 191 (38), 97 (44), 77 (47), 57 (26), 35 (40); Anal. Calcd for $C_{14}H_{12}OF_3Cl$: C, 58.23; H, 4.16; found: C, 58.25; H, 4.15%.

Trans-3-[6-chloro,6-phenylcyclohex-3-enyl],1,1,1-trifluoroethanone 8a'

Colorless oil, IR ν cm^{-1}: 1710(CO), 1164-1158(CF_3); ^{1}H NMR (300MHz, $CDCl_3$): δ 2.2(m, 2H), 2.9 (m,2H), 4.3 (m, 1H), 5.92 (m, 1H), 6.3 (m, 1H), 7.1-7.4 (m, 5H); ^{13}C NMR (75MHz, $CDCl_3$):δ 199.5, 131–132.6 (C_6H_5), 129.8(q,CF_3,$^1J_{CF}$=289Hz), 128.5, 127.6, 47.9, 46.5, 38.7; ^{19}F NMR (282.4 MHz; $CDCl_3$): δ 101.03 ; MS(m/z): 288.5 (M^+), 253 (20), 231 (33), 211 (44), 191 (18), 97 (51), 77 (41), 57 (36), 35 (40) ; Anal. Calcd for $C_{14}H_{12}OF_3Cl$: C, 58.23; H, 4.16; found: C, 58.25; H, 4.15%.

Cis-3-[6-chloro, 3,4-dimethyl, 6-phenylcyclohex-3-enyl]-1,1,1-trifluoroethanone 8b

Colorless oil, IR ν cm^{-1}: 1711(CO), 1232-1159(CF_3); ^{1}H NMR (300MHz, $CDCl_3$): δ 1.4(s, 3H), 1.7 (s, 3H), 2.6 (m, 2H), 2.7 (m, 2H), 3.39 (t, 1H), 7.3-7.9 (m, 5H); ^{13}C NMR (75MHz, $CDCl_3$):δ 200.8, 130–134 (C_6H_5), 128.2(q,CF_3,$^1J_{CF}$=290.8Hz), 47.1, 39.7, 38.1, 25.8, 19.7; ^{19}F NMR (282.4 MHz; $CDCl_3$): δ 99.63 ; MS(m/z): 316.5 (M^+), 281 (48), 239 (17) 219 (63), 97 (24), 77 (47) ; Anal. Calcd for $C_{16}H_{16}OF_3Cl$: C, 60.66; H, 5.05; found: C, 60.74; H, 5.06%.

Trans-3-[6-chloro,3,4-dimethyl,6-phenylcyclohex-3-enyl]-1,1,1-trifluoroethanone 8b'

Colorless oil IR ν cm^{-1}: 1711(CO), 1232-1159(CF_3); ^{1}H NMR (300MHz, $CDCl_3$): δ 1.5(s, 3H), 1.9 (s, 3H), 2.8 (m, 2H), 3 (m, 2H), 3.7 (t, 1H), 7.2-7.9 (m, 5H); ^{13}C NMR (75MHz, $CDCl_3$):δ 202, 130–134 (C_6H_5), 128.6(q,CF_3,$^1J_{CF}$=291Hz), 47.6, 39.9, 38.5, 26.1, 20.6; ^{19}F NMR (282.4 MHz; $CDCl_3$): δ 100.51 ; MS(m/z): 316.5 (M^+), 281 (33), 239 (36) 219 (28), 77 (41) ; Anal. Calcd for $C_{16}H_{16}OF_3Cl$: C, 60.66; H, 5.05; found: C, 60.70; H, 5.06%.

Cis-3-[6-chloro,6-phenyl bicyclo[2,2,1]hep-3-enyl]-1,1,1-trifluoroethanone 8c

Colorless oil, IR ν cm^{-1}: 171O(CO), 1143-1142(CF_3); ^{1}H NMR (300MHz, $CDCl_3$): δ 2.2 (m, 2H), 2.8(m, 1H), 3.4 (m, 1H), 3.8 (m, 1H), 6.3 (m, 1H), 6.5 (m, 1H), 7.3-7.8 (m, 5H); ^{13}C NMR (75MHz, $CDCl_3$):δ 199, 130–132.5 (C_6H_5), 129.7(q,CF_3,$^1J_{CF}$=286.6Hz),126.7, 127.9, 55.9, 47.1, 32.7, 26.1; ^{19}F NMR (282.4 MHz; $CDCl_3$): δ 101.53 ; MS(m/z): 300.5 (M^+), 262 (58), 243 (31), 220 (13), 75 (40) ; Anal. Calcd for $C_{15}H_{12}OF_3Cl$: C, 59.90; H, 3.99; found: C, 59.99; H, 4.12%.

Trans-3-[6-chloro,6-phenyl bicyclo[2,2,1]hep-3-enyl]-1,1,1-trifluoroethanone 8c'

Colorless oil, IR ν cm^{-1}: 171O(CO), 1143-1142(CF_3); ^{1}H NMR (300MHz, $CDCl_3$): δ 2.4 (m, 2H), 2.9(m, 1H), 3.6 (m, 1H), 3.9 (m, 1H), 6.6 (m, 1H), 6.8 (m, 1H), 7.3-7.8 (m, 5H); ^{13}C NMR (75MHz, $CDCl_3$):δ 200, 130.5–133 (C_6H_5), 129.9(q,CF_3,$^1J_{CF}$=286.9Hz),127, 127.9, 56, 47.4, 32.9, 26.3; ^{19}F NMR (282.4 MHz; $CDCl_3$): δ 103.06 ; MS(m/z): 300.5 (M^+, 40), 260 (29), 243 (30), 222

(37), 75 (41) ; Anal. Calcd for $C_{15}H_{12}OF_3Cl$: C, 59.90; H, 3.99; found: C, 59.98; H, 4.01.

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