Supporting Information for Nickel-Catalyzed Formation of Cyclopentenone Derivatives via the Unique Cycloaddition of α,β-Unsaturated Phenylesters with Alkynes

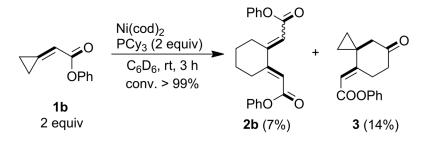
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Experimental Section

General: All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or dry box techniques. ¹H, ³¹P, and ¹³C nuclear magnetic resonance spectra were recorded on Brucker Avance III 400 and Varian Unity Inova 600 spectrometers. The chemical shifts in ¹H NMR spectra were recorded relative to either Me₄Si or residual protiated solvent (C₆D₅H (δ 7.16), CHCl₃ (δ 7.27), or toluene-*d*₇ (δ 2.09)). The chemical shifts in the ¹³C NMR spectra were recorded relative to Me₄Si. The chemical shifts in the ³¹P NMR spectra were recorded using 85% H₃PO₄ as external standard. Elemental analyses were performed at Instrumental Analysis Center, Faculty of Engineering, Osaka University. X-ray crystal data were collected by a Rigaku RAXIS-RAPID Imaging Plate diffractometer.

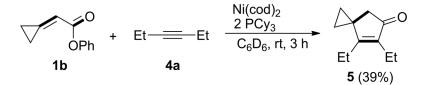
Materials: The degassed and distilled solvents (toluene and hexane) used in this work were commercially available. THF, C_6D_6 , and toluene- d_8 were distilled from sodium benzophenone ketyl. ^{*i*}PrOH was distilled from sodium. ^{*i*}PrOD (>98% D) was purchased from Merck and used as received. All commercially available reagents were distilled and degassed prior to use.



Stoichiometric reaction of 1b with Ni(cod)₂ in the presence of PCy₃: To a C_6D_6 solution of Ni(cod)₂ (11.1 mg, 0.04 mmol) and PCy₃ (22.7 mg, 0.08 mmol) was added a C_6D_6 solution of 1b (17.6 mg, 0.10 mmol), resulting in change of the color from orange to dark brown. The reaction mixture was stirred for 3 h at ambient temperature, and then insoluble was filtered to remove by passing through a pad of celite. The filtrate was concentrated *in vacuo* to give brown residue. NMR analysis using 2-methoxynaphthalene as internal standard revealed the formation of 2b and 3 in 7% and 14% yield, respectively. Isolation of the products was conducted with 0.20 mmol of 1b, and purification of the crude product by HPLC gave 2b and 3 in 4 mg and 13 mg yield, respectively.

Spectral data of **3**: ¹H NMR (400 MHz, C₆D₆, rt): δ 0.14 (dd, J = 4.4, 6.4 Hz, 2H, CH₂ of C³-ring), 0.42 (dd, J = 4.4, 6.4 Hz, 2H, CH₂ of C³-ring), 1.81 (s, 2H, -COCH₂C), 2.11 (t, J = 6.8 Hz, 2H, -CH₂CH₂CO), 3.09 (m, 2H, -CH₂CH₂CO), 5.55 (s, 1H, =CHCO₂Ph), 6.94 (t, J = 7.2 Hz, 1H, -Ph), 7.10 (t, J = 8.0 Hz, 2H, -Ph), 7.18 (m, 2H, -Ph). ¹³C NMR (100 MHz, C₆D₆, rt): δ 15.8 (C³), 22.8 (C³), 27.0 (-CH₂CH₂CO) 37.9 (-CH₂CH₂CO), 47.4 (-COCH₂C-), 110.0 (-C=CHCO₂Ph), 122.1 (-Ph), 125.7 (-Ph), 129.6 (-Ph), 151.4 (*ipso-Ph*), 164.5 (-CO₂Ph), 165.8 (-C=CHCO₂Ph), 207.1 (-CO). HRMS (CI) Calcd for C₁₆H₁₇O₃ 257.1178 (M + H), Found m/z 257.1180.

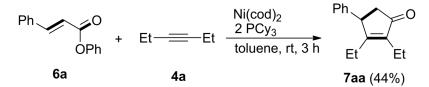
Spectral data for **2b**: ¹H NMR (400 MHz, C₆D₆, rt): δ 1.21 (br s, 4H, -CH₂CH₂C-), 2.96 (br s, 4H, -CH₂CH₂C-), 6.01 (s, 2H, C=CH-), 6.94 (t, J = 7.2 Hz, 2H, -OPh), 7.00-7.16 (m, 8H, -OPh). ¹³C NMR (100 MHz, C₆D₆, rtm): δ 25.6 (CH₂CH₂C), 30.4 (CH₂CH₂C), 114.9 (-C=CH-), 122.0 (-OPh), 125.8 (-OPh), 129.6 (-OPh), 151.3 (ipso-Ph), 162.5 (-C=CH-), 164.0 (-CO). HRMS (CI) Calcd for C₂₂H₂₁O₄ 349.1440 (M + H), Found m/z .349.1443.



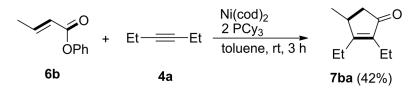
Stoichiometric reaction of 1b with 4a in the presence of Ni(cod)₂ and PCy₃: To a C_6D_6 solution of Ni(cod)₂ (11.1 mg, 0.04 mmol) and PCy₃ (21.8 mg, 0.08 mmol) was added a C_6D_6 solution of 1b (25.0

mg, 0.12 mmol), resulting in change of the color from orange to dark brown. Then, 3-hexyne (4a, 3.3 mg, 0.04 mmol) was added to the solution, and the reaction mixture was transferred into a J-Young NMR tube. Monitoring of the reaction by NMR spectroscopy demonstrated that all of 1b were consumed after 3 hours. The yield of 5 (3.4 mg, 52%) was determined by GC analysis using tetradecane as an internal standard. Following the aforementioned procedure, isolation of 5 was conducted with 0.20 mmol of Ni(cod)₂. After the reaction mixture was stirred for 3 h at room temperature, insoluble was filtered to remove by passing through a pad of silica, and then the filtrate was concentrated *in vacuo*. To the residue was added 1.0 M aqueous sodium hydroxide (30 mL). The organic layer was extracted with diethyl ether (20 mL x 3). The combined organic layer was dried over magnesium sulfate, filtered and concentrated *in vacuo*. Further purification by silica gel chromatography (hexane/ethyl acetate = 98/2) afforded **5** as colorless oil (13.8 mg, 39%).

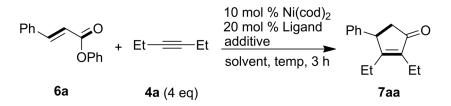
¹H NMR (400 MHz, CDCl₃, rt): δ 0.94 (m, 2H, -CH₂ of C³-ring), 1.02-1.08 (m, 8H, -CH₂ of C³-ring and two -CH₃ groups), 1.98 (q, *J* = 7.6 Hz, 2H, -CH₂CH₃), 2.21 (q, *J* = 7.6 Hz, 2H, -CH₂CH₃), 2.43 (s, 2H, -CH₂-). ¹³C NMR (100 MHz, CDCl₃, rt): δ 12.1 (-CH₂ of C³-ring), 13.2 (-CH₂CH₃), 13.8 (-CH₂CH₃), 17.1 (-CH₂CH₃), 18.1 (-CH₂CH₃), 24.7 (-CH₂C-), 45.1(C³-ring), 141.5 (-C=C-C=O), 176.9 (-C=C-C=O), 208.1 (-C=C-C=O). HRMS (EI) Calcd for C₁₁H₁₆O 164.1201, Found m/z 164.1198.



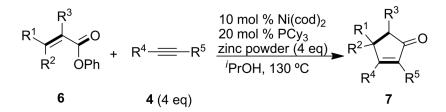
Stoichiometric reaction of 6a with 4a in the presence of $Ni(cod)_2$ and PCy_3 : To a C_6D_6 solution of $Ni(cod)_2$ (11.6 mg, 0.04 mmol) and PCy_3 (21.8 mg, 0.08 mmol) was added a C_6D_6 solution of 6a (9.0 mg, 0.04 mmol), resulting in change of the color from orange to deep red. Then, 4a (3.6 mg, 0.04 mmol) was added to the solution, and the reaction mixture was transferred into a J-Young NMR tube. Monitoring of the reaction by NMR spectroscopy demonstrated that all of 6a were consumed after 3 hours. The yield of 7aa (3.7 mg, 44%) was determined by GC analysis using tetradecane as an internal standard.



Stoichiometric reaction of 6b with 4a in the presence of $Ni(cod)_2$ and PCy_3 : To a C_6D_6 solution of $Ni(cod)_2$ (11.6 mg, 0.04 mmol) and PCy_3 (21.8 mg, 0.08 mmol) was added a C_6D_6 solution of 6b (6.5 mg, 0.04 mmol), resulting in change of the color from orange to deep red. Then, 4a (3.6 mg, 0.04 mmol) was added to the solution, and the reaction mixture was transferred into a J-Young NMR tube. Monitoring of the reaction by NMR spectroscopy demonstrated that all of 6b were consumed after 3 hours. The yield of 7ba (3.0 mg, 42%) was determined by GC analysis using tetradecane as an internal standard.



Optimization for Ni(0)-catalyzed dephenoxylative [3 + 2] cycloaddition of 6a with 4a: All catalytic reactions listed in Table 1, in which 0.10 mmol of **6a** (22.4 mg) was served in 5.0 mL of solvent, were conducted by using a pressure-tight test-tube. After the reaction mixture was thermostated at a given temperature for 3 hours, the yield of **7aa** was determined by GC analysis using tetradecane as an internal standard.



Ni(0)-Catalyzed Dephenoxylative Cycloaddition Reaction of 6 with 4:

All catalytic reactions listed in Table 2 were conducted by using a pressure-tight test-tube. Ni(cod)₂ (0.10 mmol), PCy₃ (0.20 mmol), Zn powder (4.0 mmol), and α,β -Unsaturated Phenyl Ester **6** (1.0 mmol) were charged into the test-tube, and then 15.0 mL of ^{*i*}PrOH and alkyne **4** (4.0 mmol) were added to the mixture in this order. The test-tube was tightly sealed up and thermostated at 130 °C for 3 hours. After the reaction mixture was cooled down to room temperature, insoluble was filtered to remove by passing

through a pad of celite, and then the filtrate was concentrated *in vacuo*. The resulting crude product was further purified by the method hereinafter described separately.



Table 1, run 3, 2,3-diethyl-4-phenylcyclopenten-2-one (7aa): The resulting crude product was further purified by passing through a pad of SiO₂ (eluent: hexane) followed by HPLC (eluent: CHCl₃), yielding **7aa** as colorless oil (194.5 mg, 91%). ¹H NMR (400 MHz, CDCl₃, rt): δ 0.99 (t, J = 7.6 Hz, 3H, 2-CH₂CH₃), 1.07 (t, J = 7.6 Hz, 3H, 3-CH₂CH₃), 1.99 (dq, J = 7.6, 7.6 Hz, 1H, 3-CHHCH₃), 2.30 (q, J = 7.6 Hz, 2H, 2-CH₂CH₃), 2.33 (dd, J = 2.4, 18.8 Hz, 1H, -CHH-), 2.46 (dq, J = 7.6, 7.6 Hz, 1H, 3-CHHCH₃), 2.88 (dd, J = 6.8, 18.8 Hz, 1H, -CHH-), 3.96 (d, J = 6.8 Hz, 1H, -CH₂C(Ph)H-), 7.07 (d, J = 6.8 Hz, 2H, *o-Ph*), 7.20 (t, J = 6.8 Hz, 1H, *p-Ph*), 7.28 (t, J = 6.8 Hz, 2H, *m-Ph*). ¹³C{¹H} NMR (100 MHz, CDCl₃, rt): δ 12.1 (-CH₂CH₃), 13.5 (-CH₂CH₃), 16.5 (-CH₂CH₃), 22.1 (-CH₂CH₃), 44.9 (5-C), 46.2 (4-C), 127.0 (-Ph), 127.4 (-Ph), 128.9 (-Ph), 142.2 (-Ph), 142.2 (2-C), 176.1 (3-C), 209.1 (1-CO). HRMS (EI) Calcd for C₁₅H₁₈O 214.1358, Found m/z 214.1365.



Table 2, run 1, 2,3-dimethyl-4-phenylcyclopenten-2-one (7ab): The resulting crude product was further purified by passing through a pad of SiO₂ (eluent: hexane) followed by HPLC (eluent: CHCl₃), yielding **7ab** as colorless oil (156.5 mg, 84%). ¹H NMR (400 MHz, CDCl₃, rt): δ 1.78 (dd, J = 0.8, 2.0 Hz, 3H, 2-CH₃), 1.81 (s, 3H, 3-CH₃), 2.35 (dd, J = 2.0, 19.2 Hz, 1H, -CHH-), 2.88 (dd, J = 6.8, 19.2 Hz, 1H, -CHH-), 3.81 (m, J = 6.8 Hz, 1H, -CH₂C(Ph)H-), 7.08 (d, J = 7.2 Hz, 2H, *o-Ph*), 7.24 (t, J = 7.2 Hz, 1H, *p-Ph*), 7.33 (t, J = 7.2 Hz, 2H, *m-Ph*). ¹³C{¹H} NMR (100 MHz, CDCl₃, rt): δ 8.3 (-CH₃), 15.6 (-CH₃), 44.6 (5-C), 49.2 (4-C), 127.1 (-Ph), 127.4 (-Ph), 128.9 (-Ph), 137.1 (2-C), 142.1 (-Ph), 171.6 (3-C), 209.1 (1-CO). HRMS (EI) Calcd for C₁₃H₁₄O 186.1045, Found m/z 186.1037.

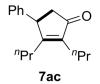


Table 2, run 2, 4-phenyl-2,3-dipropylcyclopenten-2-one (7ac): The resulting crude product was further purified by passing through a pad of SiO₂ (eluent: hexane) followed by HPLC (eluent: CHCl₃), yielding **7ac** as colorless oil (160.0 mg, 66%). ¹H NMR (400 MHz, CDCl₃, rt): δ 0.84 (t, *J* = 7.2 Hz, 3H, 2-CH₂CH₂CH₃), 0.92 (t, *J* = 7.2 Hz, 3H, 3-CH₂CH₂CH₃), 1.35 (m, 1H, 3-CH₂CHHCH₃), 1.50 (dt, *J* = 7.2, 7.2 Hz, 2H, 2-CH₂CH₂CH₃), 1.48-1.56 (m, 1H, 3-CH₂CHHCH₃), 1.94 (ddd, *J* = 5.2, 9.2, 14.0 Hz, 1H, 3-CHHCH₂CH₃), 2.18-2.31, (m, 2H, 2-CH₂CH₂CH₃), 2.32 (dd, *J* = 2.0, 18.8 Hz, 1H, -CHH-), 2.39 (ddd, *J* = 7.2, 9.2, 14.9 Hz, 1H, 3-CHHCH₂CH₃), 2.88 (dd, *J* = 7.2, 18.8 Hz, 1H, -CHH-), 3.91 (m, *J* = 7.2 Hz, 1H, -CH₂CH₂CH-), 7.06 (d, *J* = 6.8 Hz, 2H, *o-Ph*), 7.20 (t, *J* = 6.8 Hz, 1H, *p-Ph*), 7.28 (t, *J* = 6.8 Hz, 2H, *m-Ph*). ¹³C{¹H} NMR (100 MHz, CDCl₃, rt): δ 14.2 (-CH₂CH₂CH₃), 14.2 (-CH₂CH₂CH₃), 20.8 (-CH₂CH₂CH₃), 22.0 (-CH₂CH₂CH₃), 25.3 (-CH₂CH₂CH₃), 31.0 (-CH₂CH₂CH₃), 44.9 (5-C), 46.5 (4-C), 127.0 (*-Ph*), 127.3 (*-Ph*), 128.9 (*-Ph*), 141.4 (*-Ph*), 142.4 (2-C), 175.3 (3-C), 209.2 (1-CO). HRMS (EI) Calcd for C₁₇H₂₂O 242.1671, Found m/z .242.1672.



Table 2, run 3, 2,3-dibutyl-4-phenylcyclopenten-2-one (7ad): An authentic sample was prepared by using a stoichiometric amount of Ni(cod)₂ (0.20 mmol). To the resulting crude product was added NaOH*aq* (1.0 M, 50 mL), and then the organic layer was extracted with diethyl ether (50 mL x 3). The combined organic layer was dried over magnesium sulfate, filtered and concentrated *in vacuo*. Further purification by silica gel chromatography (eluent: hexane/AcOEt = 95/5) gave **7ad** as colorless oil (55.4 mg, 98%). ¹H NMR (400 MHz, CDCl₃, rt): δ 0.77 (t, *J* = 6.8 Hz, 3H, 2-(CH₂)₃CH₃), 0.87 (t, *J* = 6.8 Hz, 3H, 3-(CH₂)₃CH₃), 1.12-1.38 (m, 8H, -CH₂- x 4), 1.88 (m, 1H, 3-CHH(CH₂)₂CH₃), 2.17 (m, 2H, 2-CH₂(CH₂)₂CH₃), 2.25 (dd, *J* = 1.6, 18.8 Hz, 1H, -CHH-), 2.33 (m, 1H, 3-CHH(CH₂)₂CH₃), 2.79 (dd, *J* = 6.8, 18.8 Hz, 1H, -CH*H*-), 3.85 (d, *J* = 6.8 Hz, 1H, -CH₂C(Ph)*H*-), 7.01 (d, *J* = 7.2 Hz, 2H, *o*-*Ph*), 7.19 (m, 1H, *p*-*Ph*), 7.24 (t, *J* = 7.2 Hz, 2H, *m*-*Ph*). ¹³C {¹H</sup>} NMR (100 MHz, CDCl₃, rt): δ 13.9 (-CH₃), 14.1 (-CH₃), 22.8 (-CH₂-), 22.9 (-CH₂-), 23.2 (-CH₂-), 28.7 (-CH₂-), 29.6 (-CH₂-), 31.0 (-CH₂-), 44.9 (5-C), 46.5 (4-C), 127.0 (-*Ph*), 127.4 (-*Ph*), 128.5 (-*Ph*), 141.4 (-*Ph*), 142.4 (2-C), 175.4 (3-C), 209.3 (1-CO). HRMS (EI) Calcd for C₁₉H₂₆O 270.1984, Found m/z 270.1982.

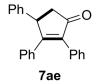


Table 2, run 4, 2,3,4-triphenylcyclopenten-2-one (7ae): To the resulting crude product was added NaOH*aq* (1.0 M, 50 mL), and then the organic layer was extracted with diethyl ether (50 mL x 3). The combined organic layer was dried over magnesium sulfate, filtered and concentrated *in vacuo*. Recrystallization of the residue from hexane at -15 °C gave **7ae** as white microcrystalline (198.2 mg, 64%). ¹H NMR (400 MHz, CDCl₃, rt): δ 2.62 (dd, *J* = 2.0, 18.8 Hz, 1H, -C*H*H-), 3.23 (dd, *J* = 7.2, 18.8 Hz, 1H, -C*H*H-), 4.57 (dd, *J* = 2.0, 7.2 Hz, 1H, -CH₂C(Ph)*H*-), 7.03-7.29 (m, 15H, *Ph*). ¹³C{¹H} NMR (100 MHz, CDCl₃, rt): δ 46.0 (5-*C*), 47.2 (4-*C*), 126.9 (-*Ph*), 127.4 (-*Ph*), 128.0 (-*Ph*), 128.2 (-*Ph*), 128.4 (-*Ph*), 128.7 (-*Ph*), 128.9 (-*Ph*), 129.2 (-*Ph*), 129.6 (-*Ph*), 131.8 (*ipso-Ph*), 134.8 (*ipso-Ph*), 140.8 (*ipso-Ph*), 142.2 (2-*C*), 177.0 (3-*C*), 207.5 (1-*CO*). HRMS (EI) Calcd for C₂₃H₁₈O 310.1358, Found m/z 310.1352.

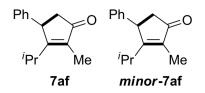


Table 2, run 5, 3-isopropyl-2-methyl-4-phenylcyclopenten-2-one (7af): To the resulting crude product was added NaOH*aq* (1.0 M, 50 mL), and then the organic layer was extracted with diethyl ether (50 mL x 3). The combined organic layer was dried over magnesium sulfate, filtered and concentrated *in vacuo*. Further purification by silica gel chromatography (eluent: hexane/AcOEt = 95/5) gave **7af** as colorless oil (97.9 mg, 46%,) and its regioisomer as colorless oil (52.3 mg, 24%). ¹H NMR (400 MHz, CDCl₃, rt): δ 0.79 (d, *J* = 6.0 Hz, 3H, -CH(CH₃)₂), 1.06 (d, *J* = 6.0 Hz, 3H, -CH(CH₃)₂), 1.82 (s, 3H, -CH₃), 2.29 (d, *J* = 18.8 Hz, 1H, -CHH-), 2.77 (m, 1H, -CH(CH₃)₂), 2.85 (dd, *J* = 6.8, 18.8 Hz, 1H, -CH*H*-), 3.96 (m, 1H, -CH₂C(Ph)*H*-), 7.10 (d, *J* = 6.8 Hz, 2H, *o*-*Ph*), 7.20-7.28 (m, 3H, *Ph*). ¹³C{¹H} NMR (100 MHz, CDCl₃, rt): δ 8.4 (-CH(CH₃)₂), 19.8 (-CH₃), 20.9 (-CH(CH₃)₂), 30.4 (-CH(CH₃)₂), 45.3 (5-C), 46.5 (4-C), 126.9 (-*Ph*), 127.6 (-*Ph*), 128.6 (-*Ph*), 136.0 (-*Ph*), 142.8 (2-C), 179.4 (3-C), 209.8 (1-CO). HRMS (EI) Calcd for C₁₅H₁₈O 214.1358, Found m/z 214.1360. Spectral data of the regioisomer of **7af**: ¹H NMR (400 MHz, CDCl₃, rt): δ 1.15 (d, *J* = 7.2 Hz, 3H, -CH(CH₃)₂), 1.17 (d, *J* = 7.2 Hz, 3H, -CH(CH₃)₂), 1.75 (s, 3H, -CH₃), 2.20 (dd, *J* = 6.8 Hz, 1H, -CH₄-), 2.76 (dd, *J* = 6.8, 18.8 Hz, 1H, -CH₄-), 2.75 (m, 1H, -CH(CH₃)₂), 3.67 (d, *J* = 6.8 Hz, 1H, -CH₄-), 7.00 (d, *J* = 7.2 Hz, 3H, -CH(CH₃)₂), 1.75 (s, 3H, -CH₃), 2.20 (dd, *J* = 2.0, 18.8 Hz, 1H, -CH₄-), 7.00 (d, *J* = 7.2 Hz, 3H, -CH(*C*-), 7.00 (d, *J* = 7.2 Hz, 3Hz, 1H, -CH-3.

2H, *o-Ph*), 7.17 (m, 1H, *p-Ph*), 7.23 (t, J = 7.2 Hz, 2H, *m-Ph*). ¹³C{¹H} NMR (100 MHz, CDCl₃, rt): δ 15.6 (-CH₃), 20.1 (-CH(CH₃)₂), 20.4 (-CH(CH₃)₂), 25.0 (-CH(CH₃)₂), 44.9 (5-C), 48.9 (4-C), 126.9 (-*Ph*), 127.2 (-*Ph*), 128.9 (-*Ph*), 142.3 (2-C), 145.4 (-*Ph*), 170.3 (3-C), 208.5 (1-CO). HRMS (EI) Calcd for C₁₅H₁₈O 214.1358, Found m/z 214.1355.

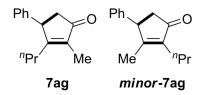


Table 2, run 6, 2-methyl-4-phenyl-3-propylcyclopenten-2-one (7ag): The resulting crude product was further purified by passing through a pad of SiO₂ (eluent: hexane) followed by HPLC (eluent: CHCl₃), yielding a mixture of the isomers of **7ag** as yellow oil (111.3 mg, 52%, major/minor = 72/28) The ratio of products was determined by NMR analysis. ¹H NMR (400 MHz, CDCl₃, rt): δ 0.77 (t, J = 7.2 Hz, 3H, -CH₂CH₂CH₃), 1.32-1.38 (m, 1H, -CH₂CHHCH₃), 1.45-1.52 (m, 1H, -CH₂CHHCH₃), 1.73 $(d, J = 1.2 \text{ Hz}, 3H, -CH_3), 1.90 \text{ (m, 1H, -CHHCH}_2\text{CH}_3), 2.22 \text{ (m, 1H, -CHHCH}_2\text{CH}_3), 2.23-2.37 \text{ (m, 2H, -CH}_3), 2.$ -CHH-), 2.85 (dd, J = 2.0, 18.8 Hz, 1H, -CHH-), 3.84 (m, J = 7.2 Hz, 1H, -CH₂C(Ph)H-), 6.80 (d, J = 6.8 Hz, 2H, *o-Ph*), 7.14-7.23 (m, 3H, *Ph*). ¹³C{¹H} NMR (100 MHz, CDCl₃, rt): δ 8.3 (-CH₂CH₂CH₃), 14.1 (-CH₃), 20.5 (-CH₂CH₂CH₃), 31.1 (-CH₂CH₂CH₃), 44.7 (5-C), 46.9 (4-C), 127.0 (-Ph), 127.3 (-Ph), 127.4 (-Ph), 128.9 (-Ph), 142.2 (2-C), 175.2 (3-C), 209.4 (1-CO). HRMS (EI) Calcd for C₁₅H₁₈O 214.1358, Found m/z 214.1358. Spectral data of minor product: ¹H NMR (400 MHz, CDCl₃, rt): δ 0.83 $-CH_2CH_2CH_3$), 2.23-2.37 (m, 1H, $-CHH_2$), 2.85-2.93 (m, 1H, $-CHH_2$), 3.60 (m, J = 7.2 Hz, 1H, -CH₂C(Ph)*H*-), 7.04 (d, J = 6.8 Hz, 2H, *o*-Ph), 7.18-7.29 (m, 3H, Ph). ¹³C{¹H} NMR (100 MHz, CDCl₃, rt): δ 14.0 (-CH₂CH₂CH₃), 15.5 (-CH₃), 21.7 (-CH₂CH₂CH₃), 25.2 (-CH₂CH₂CH₃), 44.7 (5-C), 49.1 (4-C), 127.0 (-Ph), 127.0 (-Ph), 128.9 (-Ph), 137.2 (-Ph), 141.3 (2-C), 171.9 (3-C), 208.9 (1-CO).



Table 2, run 7, 3-methyl-2,4-diphenylcyclopenten-2-one (7ah): Monitoring of the crude product by GC revealed the formation of the cycloaddition product as a mixture of regioisomers mixture (major/minor = 97/3). The resulting crude product was further purified by passing through a pad of SiO₂ (eluent: hexane) followed by HPLC (eluent: CHCl₃), yielding the major regioisomer **7ah** as colorless oil (159.7 mg, 64%). ¹H NMR (400 MHz, CDCl₃, rt): δ 1.93 (s, 3H, -CH₃), 2.52 (dd, *J* = 2.0, 19.2 Hz, 1H, -CHH-), 3.03 (dd, *J* = 7.2, 19.2 Hz, 1H, -CHH-), 3.92 (br d, *J* = 7.2 Hz, 1H, -CH₂C(Ph)H), 7.13 (d, *J* = 7.2 Hz, 2H, *Ph*), 7.14-7.40 (m, 8H, *Ph*). ¹³C{¹H} NMR (100 MHz, CDCl₃, rt): δ 16.8 (-CH₃), 45.1 (5-C), 49.2 (4-C), 127.3 (-*Ph*), 127.5 (-*Ph*), 127.9 (-*Ph*), 128.4 (-*Ph*), 129.2 (-*Ph*), 129.3 (-*Ph*), 131.7 (-*Ph*), 140.8 (-*Ph*), 141.9 (2-C), 173.3 (3-C), 206.8 (1-CO). HRMS (EI) Calcd for C₁₈H₁₆O 248.1201, Found m/z 248.1197.

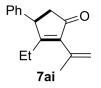


Table 2, Entry 8, 3-ethyl-4-phenyl-2-(1-propen-2-yl)cyclopenten-2-one (7ai): Monitoring of the crude product by GC revealed the formation of the cycloaddition product as a mixture of regioisomers mixture (major/minor = >99/1). To the resulting crude product was added NaOH*aq* (1.0 M, 50 mL), and then the organic layer was extracted with diethyl ether (50 mL x 3). The combined organic layer was dried over magnesium sulfate, filtered and concentrated *in vacuo*. Further purification by silica gel chromatography (eluent: hexane/AcOEt = 95/5) gave the major regioisomer **7ai** as colorless oil (43.0 mg, 19%). ¹H NMR (400 MHz, CDCl₃, rt): δ 1.18 (t, *J* = 7.6 Hz, 3H, -CH₃), 2.17 (dq, 1H, 3-CHHCH₃), 2.17 (s, 3H, -CH₃), 2.57 (dd, *J* = 2.0, 18.8 Hz, 1H, -CHHC(Ph)H-), 2.75 (dq, *J* = 7.6, 14.0 Hz, 1H, 3-CHHCH₃), 3.11 (dd, *J* = 6.8, 18.8 Hz, 1H, -CHHC(Ph)H-), 4.20 (br d, *J* = 6.8 Hz, 1H, -CH₂C(Ph)H-), 5.05 (s, 1H, =CHH), 5.43 (s, 1H, =CHH), 7.30 (d, *J* = 6.8 Hz, 2H, -*Ph*), 7.45 (m, 1H, -*Ph*), 7.51 (m, 2H, -*Ph*). ¹³C{¹H} NMR (100 MHz, CDCl₃, rt): δ 12.3 (-CH₃), 22.5 (-CH₃), 22.6 (-CH₂CH₃), 45.0 (5-*C*), 46.2 (4-*C*), 116.7 (-C=*C*H₂), 127.1 (-*Ph*), 127.4 (-*Ph*), 129.0 (-*Ph*), 137.4 (2-*C*), 141.9 (-*Ph*), 143.3 (-C=CH₂), 177.0 (3-*C*), 207.5 (1-CO). HRMS (EI) Calcd for C₁₆H₁₈O 226.1358, Found m/z 226.1361.



Table 2, Entry 9, 3-butyl-4-phenylcyclopenten-2-one (7aj): Monitoring of the crude product by GC revealed the formation of the cycloaddition product as a mixture of regioisomers mixture (42% yield, major/minor = 76/24). The resulting crude product was further purified by passing through a pad of SiO₂ (eluent: hexane) followed by HPLC (eluent: CHCl₃), yielding the major regioisomer **7aj** as colorless oil (64.2 mg, 30%). ¹H NMR (400 MHz, CDCl₃, rt): δ 0.79 (t, *J* = 7.2 Hz, 3H, -CH₂ CH₂CH₂CH₃), 1.22 (m, 2H, -CH₂ CH₂CH₂CH₃), 1.41 (m, 2H, -CH₂CH₂CH₂CH₃), 2.05 (m, 2H, -CH₂CH₂CH₂CH₃), 2.32 (d, *J* = 18.8 Hz, 1H, -CHHCH-), 2.84 (dd, *J* = 6.4, 18.8 Hz, 1H, -CHHCH-), 3.88 (m, *J* = 6.4Hz., 1H, -CH₂CH₂-CH₂), 6.02 (s, 1H, -CH=C-), 7.04 (m, *J* = 6.8 Hz, 2H, *o*-*Ph*), 7.17-7.24 (m, 3H, *Ph*). ¹³C {¹H} NMR (100 MHz, CDCl₃, rt): δ 13.8 (-CH₂CH₂CH₂CH₃), 22.3 (-CH₂CH₂CH₂CH₃), 29.1 (-CH₂CH₂CH₂CH₂), 31.2 (-CH₂CH₂CH₃), 45.7 (-CH₂CHPh), 49.6 (-CH₂CHPh), 126.9 (-*Ph*), 127.2 (-*Ph*), 128.9 (-*Ph*), 129.8 (-C=*C*-CO), 141.5 (-*Ph*), 184.6 (-*C*=C-CO), 209.1 (-CO). C₁₅H₁₈O 214.1358, Found m/z 214.1355.



Table 2, Entry 14, 2,3-diethyl-4-methylcyclopenten-2-one (7ba): To the resulting crude product was added NaOH*aq* (1.0 M, 50 mL), and then the organic layer was extracted with diethyl ether (50 mL x 3). The combined organic layer was dried over magnesium sulfate, filtered and concentrated *in vacuo*. Further purification by silica gel chromatography (eluent: hexane/AcOEt = 95/5) gave **7ba** as colorless oil (260.0 mg, 86%). ¹H NMR (400 MHz, CDCl₃, rt): δ 0.93 (t, *J* = 7.2 Hz, 3H, 2-CH₂CH₃), 1.05 (t, *J* = 7.2 Hz, 3H, 3-CH₂CH₃), 1.08 (d, *J* = 7.2 Hz, 3H, -CH₃), 1.90 (dd, *J* = 2.0, 18.4 Hz, 1H, 3-CHHCH-), 2.09 (q, *J* = 7.2 Hz, 2H, 2-CH₂CH₃), 2.25 (m, 1H, 3-CHHCH₃), 2.45 (m, 1H, -CHHCH₃), 2.60 (dd, *J* = 7.2 ,18.4 Hz, 1H, -CHH-), 2.81 (m, 1H, -CH₂C(Me)H-). ¹³C{¹H} NMR (100 MHz, CDCl₃, rt): δ 12.2 (-CH₂CH₃), 13.4 (-CH₂CH₃), 16.3 (-CH₂CH₃), 19.1 (-CH₃), 21.4 (-CH₂CH₃), 34.4 (5-C), 43.2 (4-C), 140.1 (2-C), 178.5 (3-C), 209.0 (1-CO). HRMS (EI) Calcd for C₁₀H₁₆O 152.1201, Found m/z .152.1194.

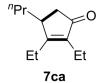


Table 2, Entry 15, 2,3-diethyl-4-propylcyclopenten-2-one (7ca): To the resulting crude product was added NaOH*aq* (1.0 M, 50 mL), and then the organic layer was extracted with diethyl ether (50 mL x 3). The combined organic layer was dried over magnesium sulfate, filtered and concentrated *in vacuo*. Further purification by silica gel chromatography (eluent: hexane/AcOEt = 95/5) gave **7ca** as colorless oil (141.2 mg, 79%). ¹H NMR (400 MHz, CDCl₃, rt): δ 0.86 (t, *J* = 7.2 Hz, 3H, 2-CH₂CH₃), 0.86 (t, *J* = 7.6 Hz, 3H, 3-CH₂CH₃), 1.00 (t, *J* = 7.6 Hz, 3H, -CH₂CH₂CH₃), 1.00-1.09 (m, 1H, -CHHCH₂CH₃), 1.09-1.27 (m, 2H, -CH₂CH₂CH₃), 1.58-1.67 (m, 1H, -CHHCH₂CH₃), 1.93 (dd, *J* = 2.0 ,18.4 Hz, 1H, -CHH-), 2.04 (q, *J* = 7.6 Hz, 2H, 2-CH₂CH₃), 2.21 (m, 1H, 3-CHHCH₃), 2.40 (dd, *J* = 6.8, 18.8 Hz, 1H, -CHH-), 2.48 (m, 1H, -CHHCH₃), 2.67 (m, 1H, -CH₂C(ⁿPr)H-). ¹³C {¹H} NMR (100 MHz, CDCl₃, rt): δ 12.3 (-CH₃), 13.4 (-CH₃), 14.1 (-CH₃), 16.3 (-CH₂-), 20.4 (-CH₂CH₃), 21.6 (-CH₂CH₃), 35.1 (-CH₂C₂H₅), 39.6 (5-*C*), 40.7 (4-*C*), 141.3 (2-*C*), 177.6 (3-*C*), 209.1 (1-CO). HRMS (EI) Calcd for C₁₂H₂₀O ,180.1514, Found m/z 180.1514.

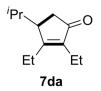


Table 2, Entry 16, 2,3-diethyl-4-isopropylcyclopenten-2-one (7da): To the resulting crude product was added NaOH*aq* (1.0 M, 50 mL), and then the organic layer was extracted with diethyl ether (50 mL x 3). The combined organic layer was dried over magnesium sulfate, filtered and concentrated *in vacuo*. Further purification by silica gel chromatography (eluent: hexane/AcOEt = 95/5) gave **7da** as colorless oil (151.3 mg, 84%). ¹H NMR (400 MHz, CDCl₃, rt): δ 0.53 (d, *J* = 6.8 Hz, 3H, -CH(CH₃)₂), 0.91 (t, *J* = 7.6 Hz, 3H, 2-CH₂CH₃), 0.94 (d, *J* = 6.8 Hz, 3H, -CH(CH₃)₂), 1.06 (t, *J* = 7.6 Hz, 3H, 3-CH₂CH₃), 2.01-2.23, (m, 6H, 2-CH₂CH₃, 3-CHHCH₃, -CH₂CH-, -CH(CH₃)₂), 2.49 (dq, *J* = 7.6, 15.2 Hz 1H, 3-CHHCH₃), 2.81 (m, 1H, -CH₂C(ⁱPr)H-). ¹³C{¹H} NMR (100 MHz, CDCl₃, rt): δ 12.1 (-CH₃), 13.4 (-CH₃), 14.4 (-CH(CH₃)₂), 16.1 (-CH(CH₃)₂), 21.4 (-CH₂CH₃), 21.7 (-CH₂CH₃), 27.3 (-CH(CH₃)₂), 34.8 (5-*C*), 44.9 (4-*C*), 142.1 (2-*C*), 176.7 (3-*C*), 209.2 (1-CO). HRMS (EI) Calcd for C₁₂H₂₀O 180.1514, Found m/z 180.1514.

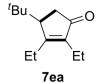


Table 2, Entry 17, 2,3-diethyl-4-isopropylcyclopenten-2-one (7ea): To the resulting crude product was added NaOH*aq* (1.0 M, 50 mL), and then the organic layer was extracted with diethyl ether (50 mL x 3). The combined organic layer was dried over magnesium sulfate, filtered and concentrated *in vacuo*. Further purification by silica gel chromatography (eluent: hexane/AcOEt = 95/5) gave **7ea** as colorless oil (110.6 mg, 57%). ¹H NMR (400 MHz, CDCl₃, rt): δ 0.88 (s, 9H, -C(CH₃)₃), 0.90 (t, *J* = 7.6 Hz, 3H, 2-CH₂CH₃), 1.06 (t, *J* = 7.6 Hz, 3H, 3-CH₂CH₃), 2.13 (q, 2H, 2-CH₂CH₃), 2.17 (dd, *J* = 2.0, 18.8 Hz, 1H, -CHHCH-), 2.27 (dd, *J* = 6.4 ,18.8 Hz, 1H, -CHHCH-), 2.38 (dq, *J* = 7.6, 11.6 Hz, 1H, 3-CHHCH₃), 2.66 (br d, *J* = 6.4 Hz, 1H, -CH₂CH-). ¹³C{¹H} NMR (100 MHz, CDCl₃, rt): δ 12.7 (-CH₂CH₃), 13.5 (-CH₂CH₃), 16.4 (-CH₂CH₃), 24.2 (-CH₂CH₃), 28.3 (-C(CH₃)₃), 34.4 (-C(CH₃)₃), 39.6 (5-C), 49.8 (4-C), 143.7 (2-C), 176.7 (3-C), 209.1 (1-CO). HRMS (EI) Calcd for C₁₃H₂₂O 1941671, Found m/z .194.1669.



Table 2, Entry 18, 4-cyclohexyl-2,3-diethylcyclopenten-2-one (7fa): To the resulting crude product was added NaOH*aq* (1.0 M, 50 mL), and then the organic layer was extracted with diethyl ether (50 mL x 3). The combined organic layer was dried over magnesium sulfate, filtered and concentrated *in vacuo*. Further purification by silica gel chromatography (eluent: hexane/AcOEt = 95/5) gave **7fa** as colorless oil (113.9 mg, 49%). ¹H NMR (400 MHz, CDCl₃, rt): δ 0.74 (m, 1H, -*Cy*), 0.92 (t, *J* = 7.6 Hz, 3H, 2-CH₂CH₃), 1.07 (t, *J* = 7.6 Hz, 3H, 3-CH₂CH₃), 1.00-1.28 (m, 5H, -*Cy*), 1.55-1.75 (m, 5H, -*Cy*), 2.09-2.25 (m, 5H, -*CH*₂C(Cy)H-, 2-CH₂CH₃, 3-CHHCH₃), 2.51 (dq, *J* = 7.6, 14.0 Hz 1H, 3-CH*H*CH₃), 2.78 (m, 1H, -CH₂C(Cy)*H*-). ¹³C{¹H} NMR (100 MHz, CDCl₃, rt): δ 12.3 (-CH₃), 13.5 (-CH₃), 16.2 (-Cy), 21.7 (-CH₂CH₃), 25.2 (-CH₂CH₃), 26.1 (-Cy), 26.4 (-Cy), 26.8 (-Cy), 32.5 (-Cy), 36.2 (5-*C*), 38.2 (-Cy), 44.8 (4-*C*), 142.2 (2-*C*), 176.4 (3-*C*), 209.4 (1-*C*O). HRMS (EI) Calcd for C₁₅H₂₄O 220.1827, Found m/z 220.1819.



Table 2, Entry 19, 2,3-diethylcyclopenten-2-one (7ga): An authentic sample was prepared by using a stoichiometric amount of Ni(cod)₂ (0.50 mmol). To the resulting crude product was added NaOH*aq* (1.0 M, 50 mL), and then the organic layer was extracted with diethyl ether (50 mL x 3). The combined organic layer was dried over magnesium sulfate, filtered and concentrated *in vacuo*. Further purification by silica gel chromatography (eluent: hexane/AcOEt = 95/5) and HPLC (eluent: CHCl₃) gave **7ga** as colorless oil (15.6 mg, 23%). ¹H NMR (400 MHz, CDCl₃, rt): δ 0.97 (t, *J* = 7.6 Hz, 3H, 2-CH₂CH₃), 1.14 (t, *J* = 7.6 Hz, 3H, 3-CH₂CH₃), 2.17 (q, *J* = 7.6 Hz, 2H, 2-CH₂CH₃), 2.34 (m, 2H, 4-CH₂-), 2.43 (q, *J* = 7.6 Hz, 2H, 3-CH₂CH₃), 2.48 (m, 2H, 5-CH₂-). ¹³C{¹H} NMR (100 MHz, CDCl₃, rt): δ 12.1 (-CH₃), 13.3 (-CH₃), 16.2 (-CH₂CH₃), 24.1 (-CH₂CH₃), 28.5 (5-C) 34.3 (4-C), 141.3 (2-C), 174.8 (3-C), 210.1 (CO). HRMS (EI) Calcd for C₉H₁₄O 138.1045, Found m/z 138.1048..

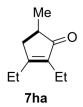
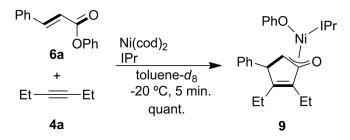
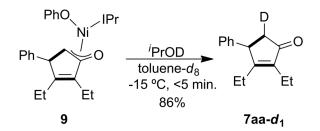


Table 2, Entry 20, 2,3-diethyl-5-methylcyclopenten-2-one (7ha): To the resulting crude product was added NaOH*aq* (1.0 M, 50 mL), and then the organic layer was extracted with diethyl ether (50 mL x 3). The combined organic layer was dried over magnesium sulfate, filtered and concentrated *in vacuo*. Further purification by silica gel chromatography (eluent: hexane/AcOEt = 95/5) gave **7ha** as colorless oil (94.2 mg, 62%). ¹H NMR (400 MHz, CDCl₃, rt): δ 0.96 (t, *J* = 7.2 Hz, 3H, 2-CH₂CH₃), 1.12 (t, *J* = 7.2 Hz, 3H, 3-CH₂CH₃), 1.14 (d, *J* = 7.2 Hz, 3H, -CH₃), 2.07 (br d, *J* = 18.0 Hz, 1H, -CHH-), 2.19 (q, *J* = 7.2 Hz, 2H, 3-CH₂CH₃), 2.33 (ddq, *J* = 2.4, 7.2, 7.2 Hz, 1H, -CH₂C(Me)*H*), 2.42 (q, *J* = 7.2 Hz, 2H, 2-CH₂CH₃), 2.75 (dd, *J* = 7.2 ,18.0 Hz, 1H, -CHH-). ¹³C{¹H} NMR (100 MHz, CDCl₃, rt): δ 12.1 (-CH₂CH₃), 13.4 (-CH₂CH₃), 16.3 (-CH₂CH₃), 16.6 (-CH₃), 23.9 (-CH₂CH₃), 37.7 (4-C), 39.5 (5-C), 139.9 (2-C), 172.9 (3-C), 212.4 (1-CO). HRMS (EI) Calcd for C₁₀H₁₆O 152.1201, Found m/z .152.1193.

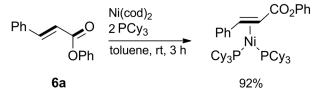


Observation of a reaction intermediate of 6a and 4a in the presence of Ni(cod)₂ **and IPr:** To a toluene-*d*₈ solution of Ni(cod)₂ (22.0 mg, 0.08 mmol) and IPr (31.3 mg, 0.08 mmol) was added a toluene-*d*₈ solution of **6a** (18.0 mg, 0.08 mmol) and **4a** (6.6 mg, 0.08 mmol) at -35 °C. The color of the solution turned into deep red. NMR observation at -20 °C revealed the quantitative formation of **9**. ¹H NMR (600 MHz, toluene-*d*₈, -20 °C): δ 0.89–0.98 (m, 6H, -*CH*₃), 1.07 (d, *J* = 6.0 Hz, 6H, -*CH*₃ groups of IPr), 1.13 (d, *J* = 6.0 Hz, 6H, -*CH*₃ groups of IPr), 1.14 (m, 1H, -*CH*HCH₃), 1.20 (d, *J* = 6.0 Hz, 6H, -*CH*₃ groups of IPr), 1.75 (m, 1H, -*CH*HCH₃), 1.86 (m, 1H, -*CH*HCH₃), 2.20 (m, 1H, -*CH*HCH₃), 2.54 (m, 2H, -*CH*(CH₃)₂), 2.58 (s, 1H, -*CH*HCh₃), 1.86 (m, 2H, -*CH*(CH₃)₂), 5.03 (s, 1H, -*CH*HCH₃), 2.54 (m, 2H, -*CH*(CH₃)₂), 2.58 (s, 1H, -*CH*HCh₃), 1.65 (d, *J* = 7.2 Hz, 2H, o-Ph), 6.66 (t, *J* = 6.6 Hz, 1H, *p*-Ph), 6.94 (m, 1H, *p*-Ph), 7.00 (m, 4H, *m*-Ph), 7.12 (m, 4H, *m*-Ph (IPr)), 7.38 (m, 2H, *p*-Ph (IPr)). ¹³C{¹H</sup>} NMR (150 MHz, toluene-*d*₈, -20 °C): δ 13.9 (-*C*H₂*C*H₃), 14.1 (-*C*H₂*C*H₃), 16.1 (-*C*H₂-), 20.0 (-*C*H₂-), 22.6 (-*C*H₃), 23.9 (-*C*H₃), 25.4 (-*C*H₃), 26.0 (-*C*H₃), 28.9 (-*C*H(CH₃)₂), 52.6 (*c*(Ph)H-), 81.8 (-*C*HC(O)-), 124.1 (=*C*H-), 124.3 (*m*-Ph), 124.4 (*m*-Ph), 129.8 (*p*-Ph), 136.5 (*ipso*-Ph), 137.6 (C(CO)=C), 139.7 (*ipso*-Ph), 146.4 (*o*-Ph (IPr)), 146.5 (*o*-Ph (IPr)), 157.0 (C(CO)=C), 162.9 (CHCO), 170.7 (*ipso*-OPh), 176.9 (NCN).



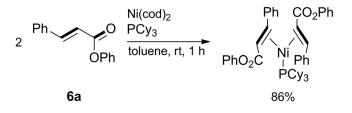
Reaction of 9 with ^{*i*}**PrOD-***d*₁**:** Treatment of 9 with ^{*i*}**PrOD** (>98% D) at -15 °C gave 7aa-*d*₁ (98% D) in 86% yield. ¹H (and ²D) NMR observation of the reaction mixture revealed that deuterium was selectively incorporated at the 5-position.

Isolation of $(\eta^2 - (E) - PhCH = CHCO_2Ph)Ni(PCy_3)_2$



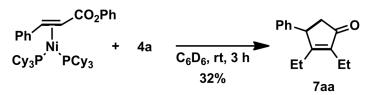
To toluene solution (5 mL) of Ni(cod)₂ (128.3 mg, 0.50 mmol) and PCy₃ (281.0 mg, 1.00 mmol) was added **6a** (128.3 mg, 0.53 mmol) at room temperature. The solution changed from yellow to red. The reaction mixture was stirred for 3 h and then concentration in vacuo. The residue was dissolved in toluene followed by the concentration in *vacuo* again. All volatiles were removed under reduced pressure, and then the deep red residue was purified by recrystallization from toluene/hexane at -35 °C, affording $(\eta^2 - (E) - PhCH = CHCO_2Ph)Ni(PCy_3)_2$ (248.9 mg, 60%) as a red solid. The resulting supernatant was concentrated again, and then the recrystallization procedure was repeated twice, yielding another title complex (130.5 mg, 31%). The title compound was found to be intact in solution at room temperature. ¹H NMR (400 MHz, C_6D_6 , rt): δ 1.00 (m, 2H, -*Cy*), 1.16–1.41 (m, 20H, -*Cy*), 1.56–1.92 (m, 32H, -*Cy*), 1.96-2.10 (m, 4H, -*Cy*), 2.16-2.33 (m, 8H, -*Cy*), 3.40 (m, J = 9.2 Hz, 1H, C(Ph)H=C(CO₂Ph)H), 4.17(m, 1H, C(Ph)H=C(CO₂Ph)H), 6.94 (m, 1H, *p*-Ph), 7.06 (m, 1H, *p*-Ph), 7.18 (m, 4H, *m*-Ph x 2), 7.40 (d, J = 7.2 Hz, 2H, o-Ph), 7.64 (d, J = 6.8 Hz, 2H, o-Ph). ¹³C{¹H} NMR (100 MHz, C₆D₆, rt): δ 30.3 (-Cv), 30.5 (-Cy), 31.2 (d, J = 9.9 Hz, -Cy), 31.4 (d, J = 7.6 Hz, -Cy), 31.6 (d, J = 8.6 Hz, -Cy), 31.9 (d, J = 6.9 Hz, -Cy), Hz, -Cy), 33.3 (-Cy), 34.5 (-Cy), 39.3 (-Cy), 40.3 (-Cy), 48.5 (d, J = 12.2 Hz, $C(Ph)H=C(CO_2Ph)H)$, 51.9 (d, *J* = 19.2 Hz, C(Ph)H=*C*(CO₂Ph)H), 122.5 (-*Ph*), 123.5 (-*Ph*), 124.2 (-*Ph*), 128.7 (-*Ph*), 129.0 (-*Ph*), 129.3 (-*Ph*), 148.2 (ipso-*Ph*), 152.3 (*ipso-OPh*), 169.8 (*CO*). ³¹P{¹H} NMR (109 MHz, C₆D₆, rt): δ 31.9 (m). Anal. Calcd for C₅₁H₇₈NiO₂P₂: C, 72.59; H, 9.32. Found: C, 72.94; H, 9.49. X-ray data for $(\eta^2 - (E) - PhCH = CHCO_2Ph)Ni(PCy_3)_2$. M = 843.78, yellow, Monoclinic, $P2_1/n$ (No. 14), a = 13.9259(12)Å, b = 18.0957(14) Å, c = 18.4593(17) Å, β = 90.150(3)°, V = 4651.7(7) Å³, Z = 4, D_{calcd} = 1.205 g/cm³, $T = -150 (2)^{\circ}C$, $R_1(wR_2) = 0.061 (0.131)$. Figure S1 shows an ORTEP drawing of the title complex.

Isolation of $(\eta^2 - (E) - PhCH = CHCO_2Ph)_2Ni(PCy_3)$



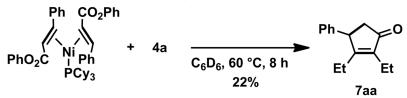
To toluene solution (5 mL) of $Ni(cod)_2$ (276.3 mg, 1.00 mmol) and PCy_3 (286.4 mg, 1.02 mmol) was added **6a** (452.3 mg, 2.02 mmol) at room temperature. The solution changed from yellow to bright red. The reaction mixture was stirred for 1 h and then concentration in *vacuo*. The residue was washed by hexane followed by the concentration in *vacuo* again. All volatiles were removed under reduced pressure, and then the orange residue was purified by recrystallization from toluene/hexane at -35 °C, affording $(\eta^2 - (E) - PhCH = CHCO_2Ph)_2Ni(PCy_3)$ (675.5 mg, 86%) as an orange microcrystalline. The title compound was found to be intact in solution at room temperature. ¹H NMR (400 MHz, C₆D₆, rt): $\delta 0.78 - 1.04$ (m, 2H, -Cy), 1.04-1.50 (m, 14H, -Cy), 1.50-1.84 (m, 11H, -Cy), 1.90-2.14 (m, 4H, -Cy), 2.27-2.46 (m, 2H, -Cy), 3.93 (d, J = 9.6 Hz, 1H, C(Ph) $H=C(CO_2Ph)H$), 4.45 (dd, J = 10.0, 10.0 Hz, 1H, C(Ph)H=C(CO₂Ph)*H*), 5.33 (dd, *J* = 10.4, 10.4 Hz, 1H, C(Ph)H=C(CO₂Ph)*H*), 6.21 (d, *J* = 10.8 Hz, 1H, C(Ph)H=C(CO₂Ph)H), 6.21 (m, 1H, -Ph), 6.74-7.05 (m, 10H, -Ph), 7.21 (m, 5H, -Ph), 7.29 (d, J = 8.0 Hz, 2H, o-Ph), 7.60 (d, J = 7.2 Hz, 2H, o-Ph). ¹³C{¹H} NMR (100 MHz, C₆D₆, rt): δ 26.9 (-Cy), 27.5 (d, J = 9.9 Hz, -Cy), 28.0 (d, J = 9.1 Hz, -Cy), 30.3 (-Cy), 30.7 (-Cy), 34.4 (d, J = 15.3 Hz, -Cy), 55.1 $(C(Ph)H=C(CO_2Ph)H)$, 69.1 ($C(Ph)H=C(CO_2Ph)H$), 70.1 (d, J = 6.9 Hz, $C(Ph)H=C(CO_2Ph)H$), 75.1 (d, J = 7.2 Hz, $C(Ph)H=C(CO_2Ph)H)$, 122.6 (-Ph), 123.0 (-Ph), 124.8 (-Ph), 125.0 (-Ph), 125.4 (-Ph), 126.6 (-Ph), 126.7 (-Ph), 128.5 (-Ph), 128.8 (-Ph), 129.0 (-Ph), 129.4 (-Ph), 140.2 (ipso-Ph), 142.6 (ipso-Ph), 151.7 (ipso-OPh), 151.9 (ipso-OPh), 167.4 (CO), 169.8 (CO), one peak attributed Phenyl unit might be obscured by the solvent signal. ${}^{31}P{}^{1}H$ NMR (109 MHz, C₆D₆, rt): δ 27.8 (s). Anal. Calcd for C48H57NiO4P: C, 73.20; H, 7.29. Found: C, 72.92; H, 7.58. X-ray data for $(\eta^2 - (E) - PhCH = CHCO_2Ph)_2Ni(PCy_3)$. M = 787.62, yellow, Triclinic, P-1 (No. 2), a = 11.9158(9) Å, b = 12.1881(9) Å, c = 14.9957(10) Å, $\alpha = 87.464(3)^\circ$, $\beta = 83.542(3)^\circ$, $\gamma = 69.604(2)^\circ$, V = 2028.3(2) Å³, Z = 12.1881(9) Å, $\alpha = 14.9957(10)$ Å, $\alpha = 14.9957(10)$ Å, $\alpha = 14.9957(10)$ Å, $\beta = 12.1881(9)^\circ$, $\gamma = 14.9957(10)$ Å, $\alpha = 14.9957(10)$ Å, $\beta = 12.1881(9)^\circ$, $\gamma = 14.9957(10)$ Å, $\alpha = 14.9957(10)$ Å, $\alpha = 14.9957(10)$ Å, $\beta = 12.1881(9)^\circ$, $\gamma = 14.9957(10)^\circ$, $V = 2028.3(2)^\circ$, $\gamma = 14.9957(10)^\circ$, $\gamma =$ 2, $D_{calcd} = 1.290 \text{ g/cm}^3$, $T = -150 (2)^{\circ}C$, $R_1(wR_2) = 0.072 (0.152)$. Figure S2 shows an ORTEP drawing of the title complex.

Reaction of $(\eta^2 - (E) - PhCH = CHCO_2Ph)Ni(PCy_3)_2$ with 3-hexyne



To a C₆D₆ solution of $(\eta^2 - (E)$ -PhCH=CHCO₂Ph)Ni(PCy₃)₂ (34.0 mg, 0.04 mmol) was added 3-hexyne at room temperature. The reaction mixture was transferred into a J-Young NMR tube. Monitoring of the reaction by NMR spectroscopy demonstrated that all of $(\eta^2 - (E)$ -PhCH=CHCO₂Ph)Ni(PCy₃)₂ were consumed within 3 hours, whereas no significant intermediates were observed. The yield of **7aa** (2.7 mg, 32%) was determined by GC analysis using tetradecane as an internal standard.

Reaction of $(\eta^2 - (E) - PhCH = CHCO_2Ph)_2Ni(PCy_3)$ with 3-hexyne



To a C₆D₆ solution of $(\eta^2 - (E) - PhCH = CHCO_2Ph)_2Ni(PCy_3)$ (31.0 mg, 0.04 mmol) was added 3-hexyne at room temperature. The reaction mixture was transferred into a J-Young NMR tube and kept at 60 °C. Monitoring of the reaction by NMR spectroscopy demonstrated that all of $(\eta^2 - (E) - PhCH = CH - CO_2Ph)_2Ni(PCy_3)$ was consumed after 8 hours, whereas no significant intermediates were observed. The reaction did not proceed at room temperature. The yield of **7aa** (2.0 mg, 22%) was determined by GC analysis using tetradecane as an internal standard.

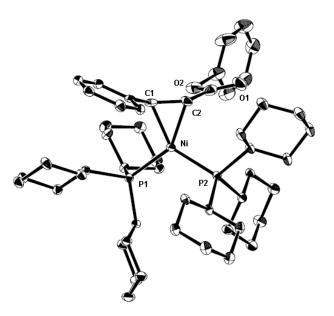


Figure S1. ORTEP drawing of $(\eta^2 - (E) - PhCH = CHCO_2Ph)Ni-(PCy_3)_2$ with thermal ellipsoids at the 30% probability level. H atoms are omitted for clarity.

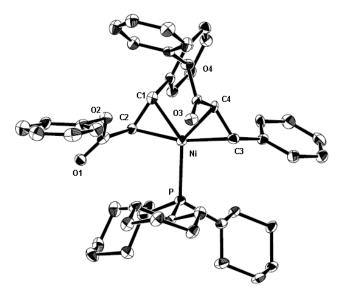
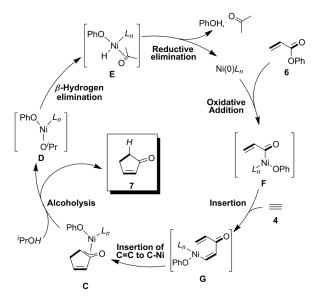
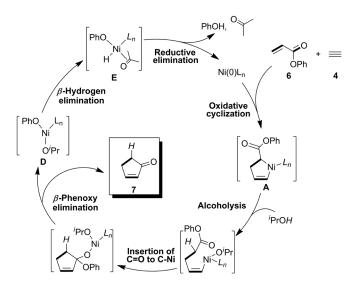


Figure S2. ORTEP drawing of $(\eta^2 - (E) - PhCH = CHCO_2Ph)_2Ni-(PCy_3)$ with thermal ellipsoids at the 30% probability level. H atoms are omitted for clarity.



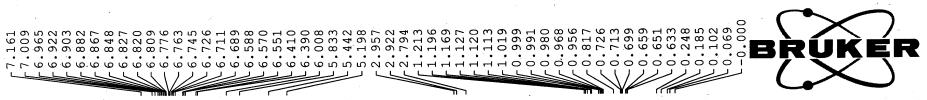
Scheme S1. An alternative reaction mechanism, involving a C–O bond activation of phenylester, for the Ni-catalyzed dephenoxylative cycloaddition reaction



Scheme S2. An alternative reaction mechanism, involving alcoholysis of A followed by ester carbonyl insertion into the Ni–C bond and β -phenoxy elimination, for the Ni-catalyzed dephenoxylative cycloaddition reaction

References

[1] Takahashi, T.; Xi, Z.; Nishihara, Y.; Huo, S.; Kasai, K; Aoyagi, K.; Denisov, V.; Negishi, E. *Tetrahedron*, **1997**, *53*, 9123.



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-	Current I NAME EXPNO PROCNO	Data Parame 00_PhCPA_[Dimer
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	NUC1 P1 PL1 PL1W SFO1 F2 - Proc SI SF WDW SSB LB GB PC	13.3448 400.132 cessing par	1H 4.00 1.00 1144 4710 camete 2768	usec dB W MHz ers MHz

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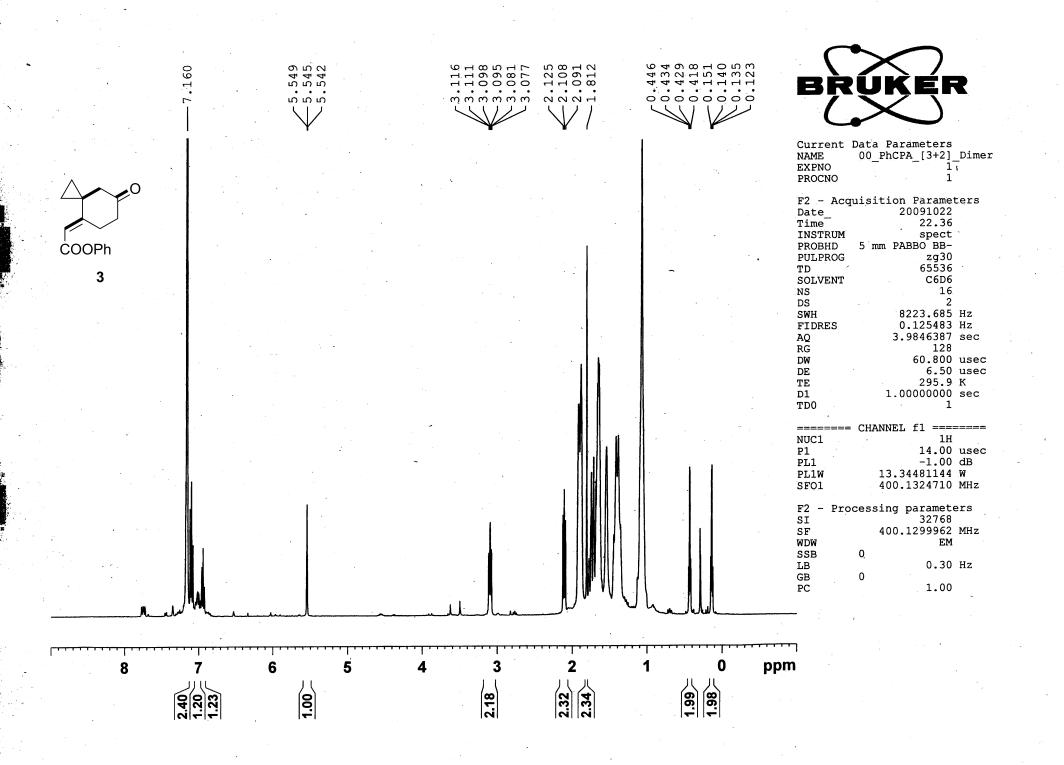
Ph0 ____O PhO 0

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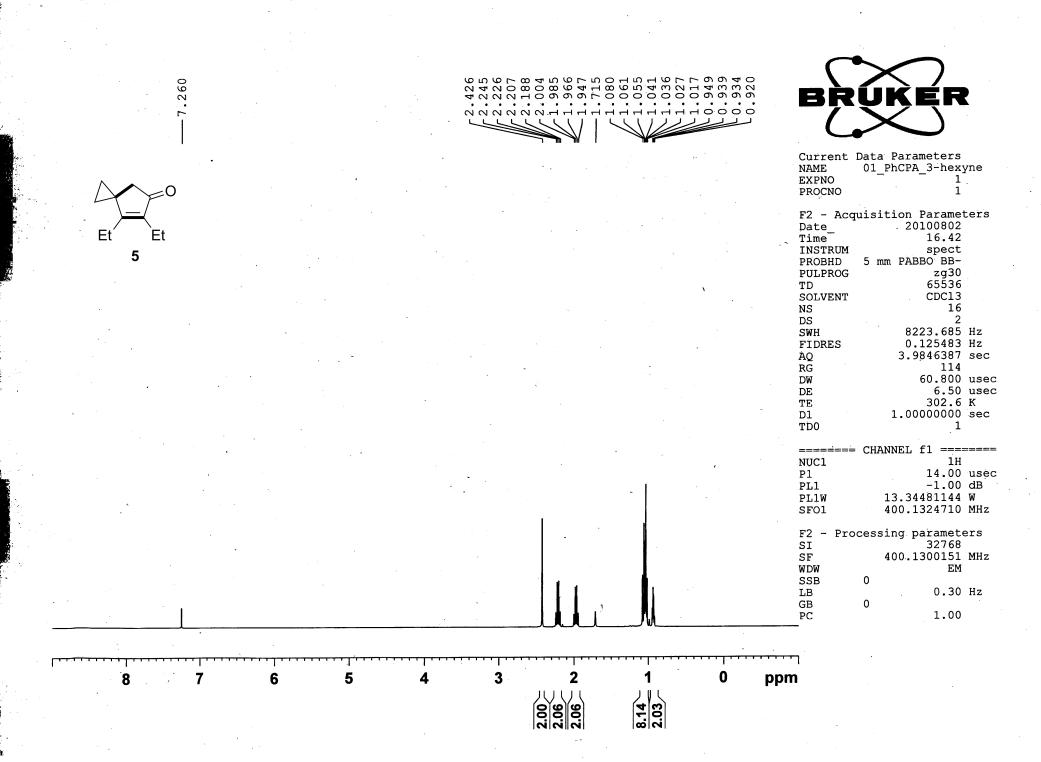
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PROCNO 1 Fine 20091021 Fine 23.44 INSTRUM apect PROBUD 5 m PABBO BB- PPULPROG 2009310 TOLVENT 6036 DS 20, 94 SWH 25252.235 Hz SWH 25252.235 Hz FIDERS 0.365323 Hzc AC 1.299330 Hzc AC 1.299330 Hzc AC 1.299330 Hzc AC 1.299330 Hzc AC 1.299330 Hzc AC 1.29930 Hzc TE 227.5 K D1 2.0000000 sec TE 227.5 K D1 2.0000000 sec TD 0 0.00000 sec TD 0 0.00000 Hzc TD 0 0.000000 Hzc TD 0 0.00000 Hzc TD 0 0.000000 Hzc TD 0 0.000000000000000000000000000000000	PhOO	164.01 	128.00 127.76 125.77 125.77 115.54			30.37 25.60	•	Current NAME EXPNO	Data Parameters 00_PhCPA_[3+3]_Dimer 13
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				PROČNO 1 F2 - Acquisition Parameters Date_ 20100802 Time 16.47 INSTRUM spect PROBHD 5 mm PABBO BB- PULPROG zgpg30 TD 65536 SOLVENT CDC13 NS 165 DS 4 SWH 24038.461 Hz FIDRES 0.366798 Hz AQ 1.3631988 sec RG 203 DW 20.800 usec DE 6.50 usec TE 303.7 K D1 2.00000000 sec D1 2.00000000 sec D1 0.03000000 sec D1 2.000 I1 0.03000000 sec D1 2.20 dB PL1 10.00 usec PL1 2.20 dB PL1W 21.94663811 W SF01 100.6228298 MHz ====== CHANNEL f2 ===== CPDPRG2 waltz16 NUC2 1H PCPD2 75.00 usec
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Ph. 🔿 o		Current Data Parameters NAME 02_PhCi_3-hexyne EXPNO 1 PROCNO 1
Ti to C Et Et 7aa		$\begin{array}{ccccc} F2 & - \ Acquisition \ Parameters\\ Date_ 20100226\\ Time 18.14\\ INSTRUM spect\\ PROBHD 5 mm \ PABBO \ BB-\\ PULPROG 2g30\\ TD 65536\\ SOLVENT CDC13\\ NS 16\\ DS 2\\ SWH 8223.685\ Hz\\ FIDRES 0.125483\ Hz\\ AQ 3.9846387\ sec\\ RG 28.5\\ DW 60.800\ usec\\ DE 6.50\ usec\\ TE 295.8\ K\\ D1 1.0000000 \ sec\\ TD0 1\\ \end{array}$
		$\begin{array}{c cccc} & = & = & = & \\ \text{NUC1} & & 1\text{H} \\ \text{P1} & & 14.00 \text{ usec} \\ \text{PL1} & & -1.00 \text{ dB} \\ \text{PL1W} & 13.34481144 \text{ W} \\ \text{SFO1} & 400.1324710 \text{ MHz} \\ \end{array}$ $\begin{array}{c ccccccccccccccccccccccccccccccccccc$
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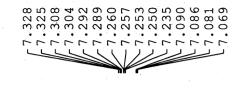
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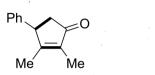
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Current NAME EXPNO PROCNO	Data Parameters 03_PhCi_2-butyr 1 1	ie
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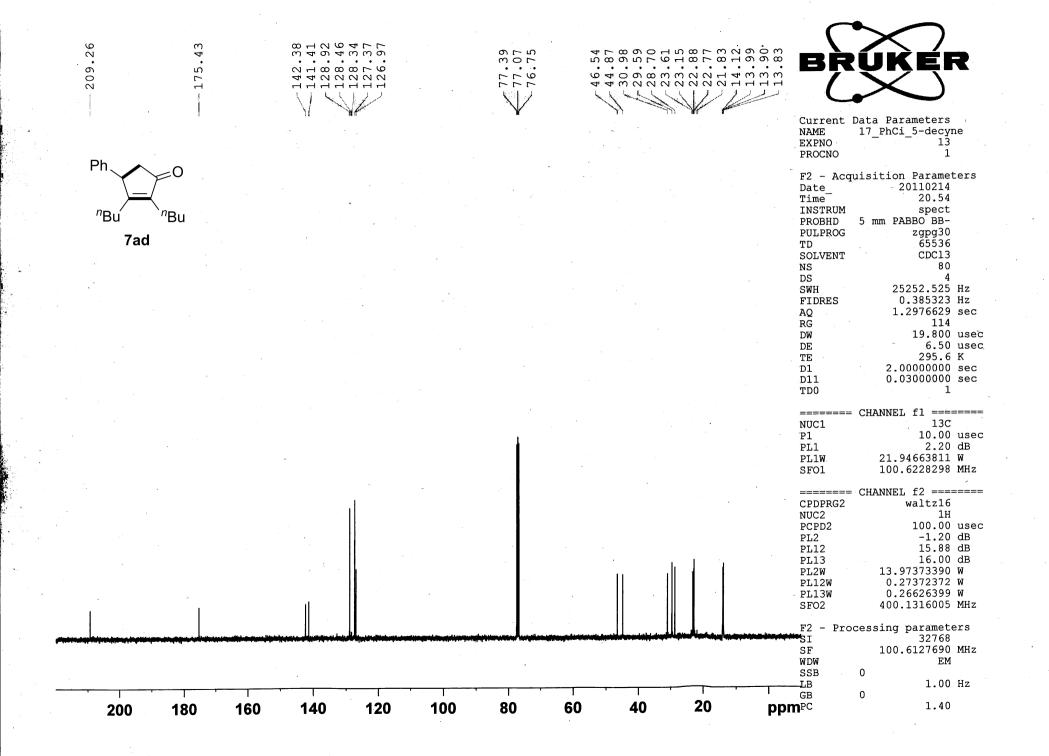
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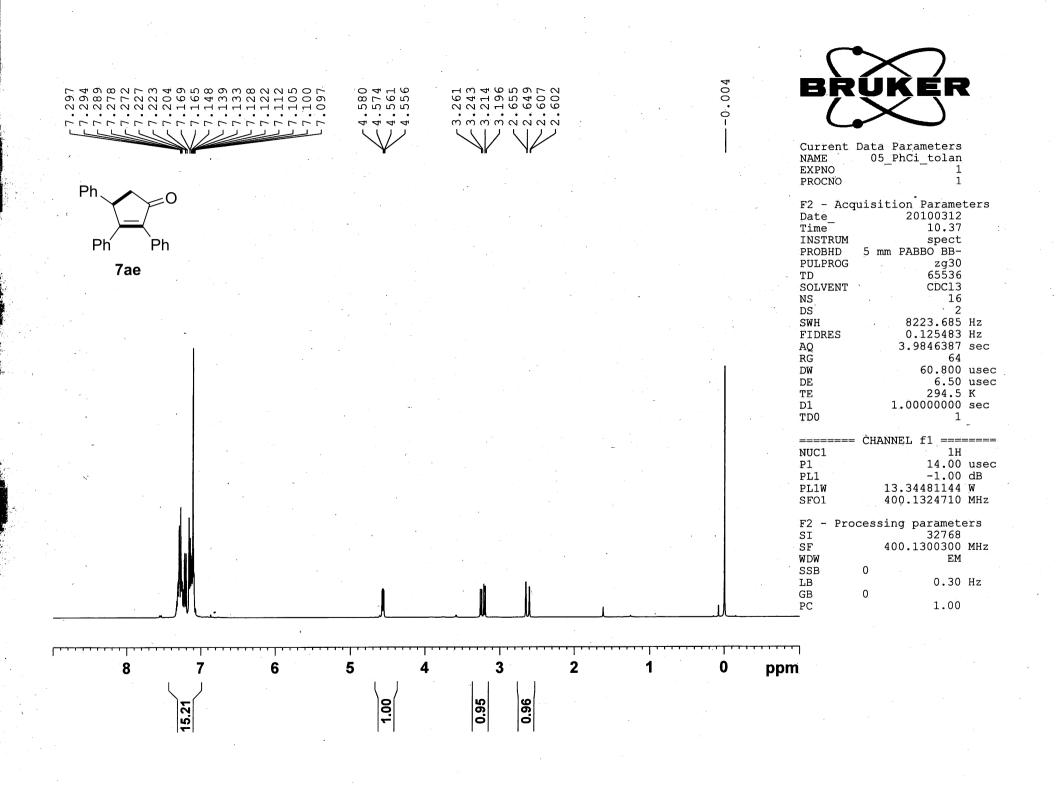
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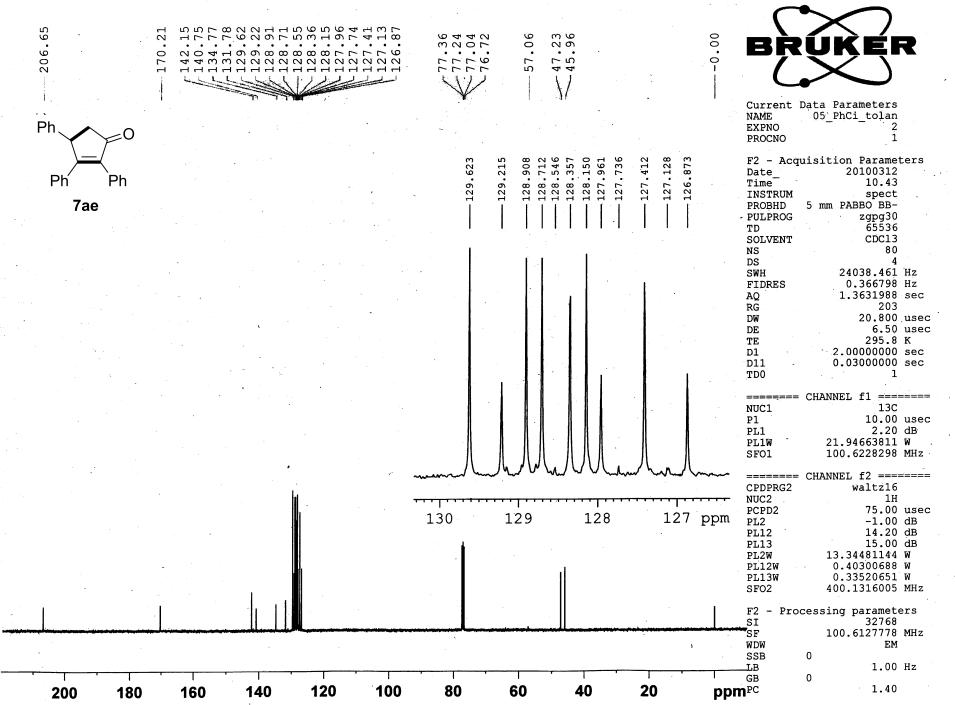
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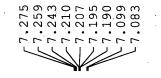
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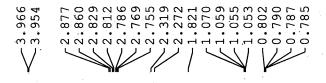
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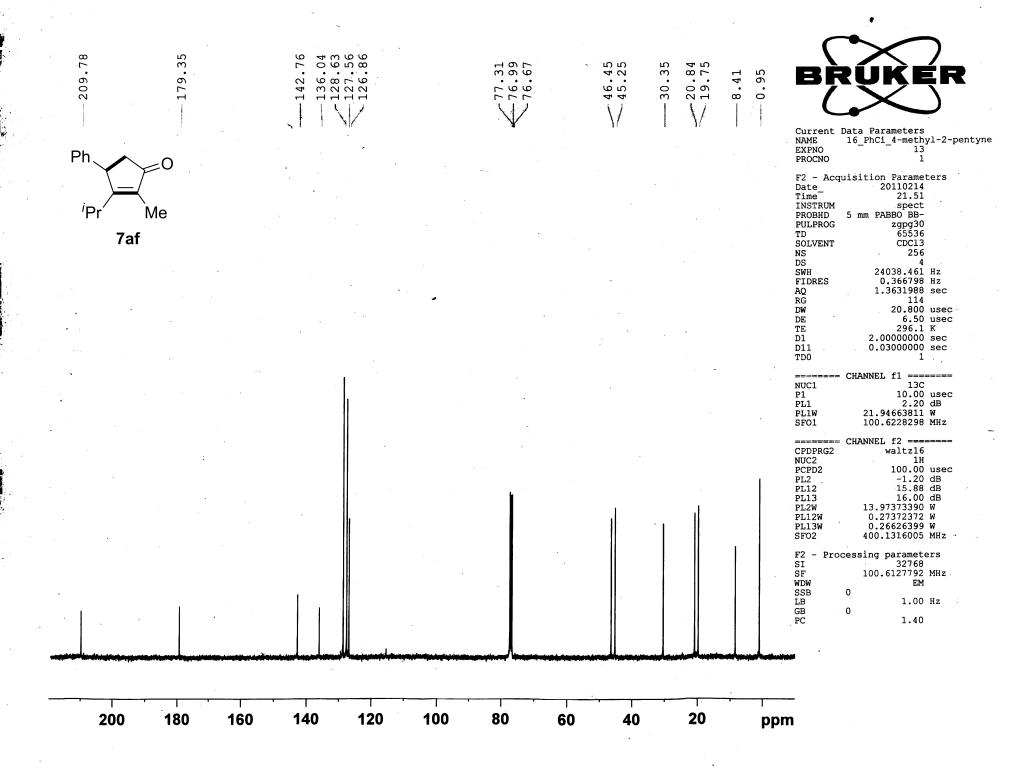


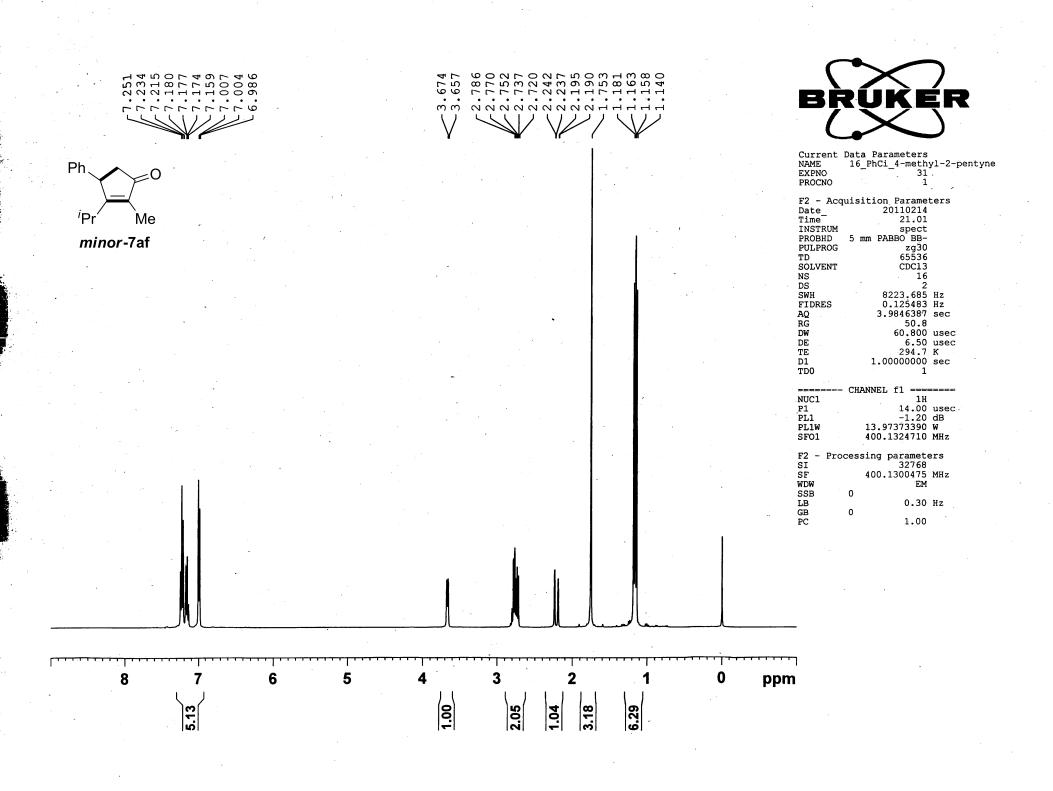


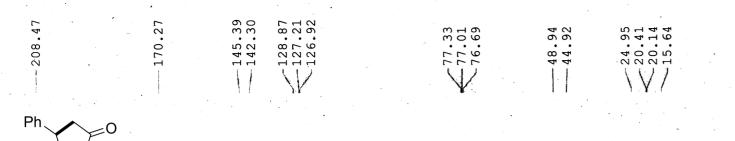
Current Data Parameters NAME 16_PhCi_4-methyl-2-pentyne EXPNO PROCNO 1 1

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	F2 - Acq	1110	ition	Daramo	tore
		urs.			LEIS
	Date		20	110214	
	Time			21.37	
	INSTRUM			spect	
		-		BO BB-	
	PROBHD	51	nm PAE		
	PULPROG			zq30	
	TD			65536	
	SOLVENT			CDC13	
	NS			16	
	DS			. 2	
	SWH		82	23.685	Hz
	FIDRES			125483	
	AQ		3.9	846387	
	RG			50.8	
	DW		•	60.800	usec
	DE				usec
	TE			294.9	
	D1 .		1.00	000000	sec
	TD0			1	
	100			-	
		~ ~ ~ ~		c 1	
		CH	ANNEL		====
	NUC1			1H	
	P1			14.00	usec
	PL1			-1.20	
			10.07		
	PL1W			373390	
	SF01		400.1	324710	MHz
			, ·		
	F2 - Pro	~~~~	ing n	aramot	ore
		cess	pring P	32768	613
	SI				
	SF		400.1	300251	MHz
	WDW			EM	
	SSB	0.			
		0			
	LB			0.30	HZ
	GB	0	-		
	PC			1.00	
				1.00	

8 3 2 7 6 5 4 1 0 ppm 3.09 3.05 1.0 1.16 2.07 5.17 3.27







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*minor-*7af

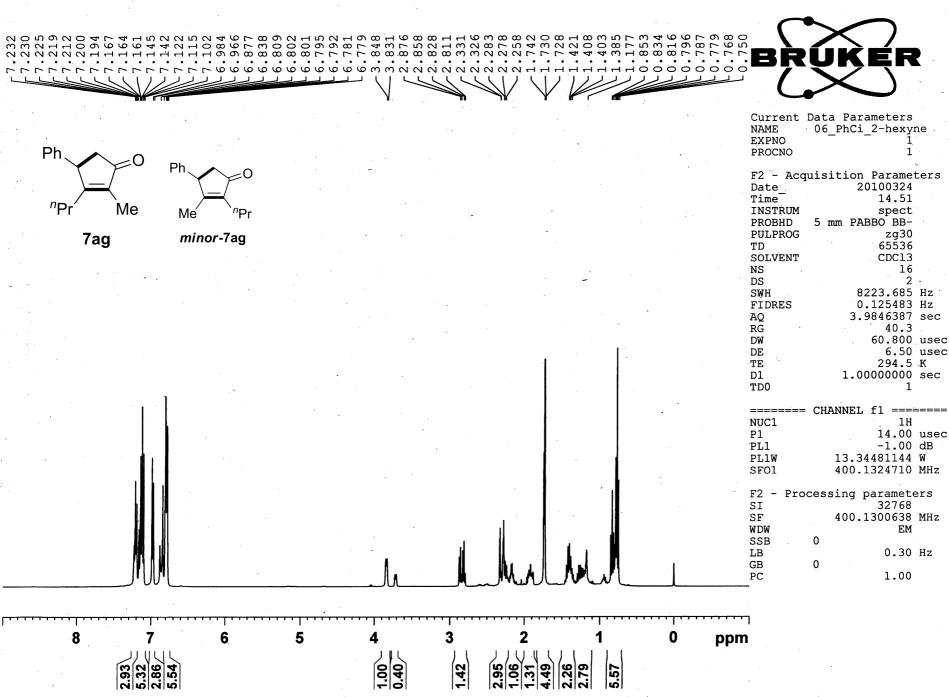
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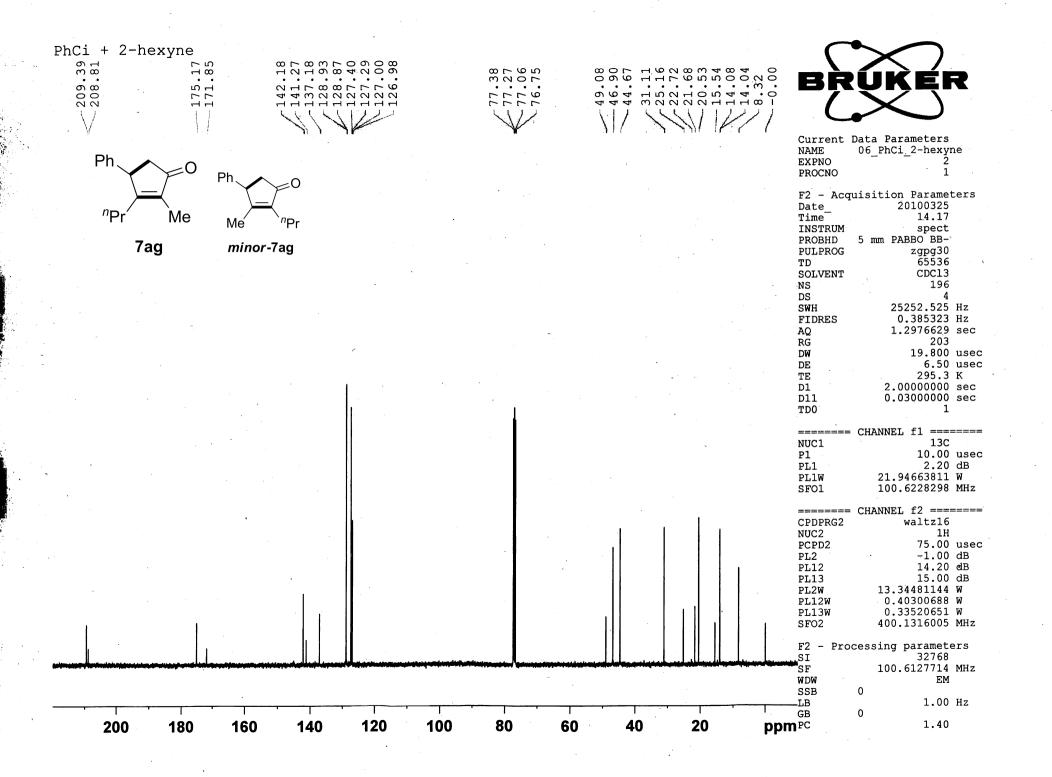


Current Data Parameters NAME 16_PhCi_4-methyl-2-pentyne EXPNO 313 PROCNO 1

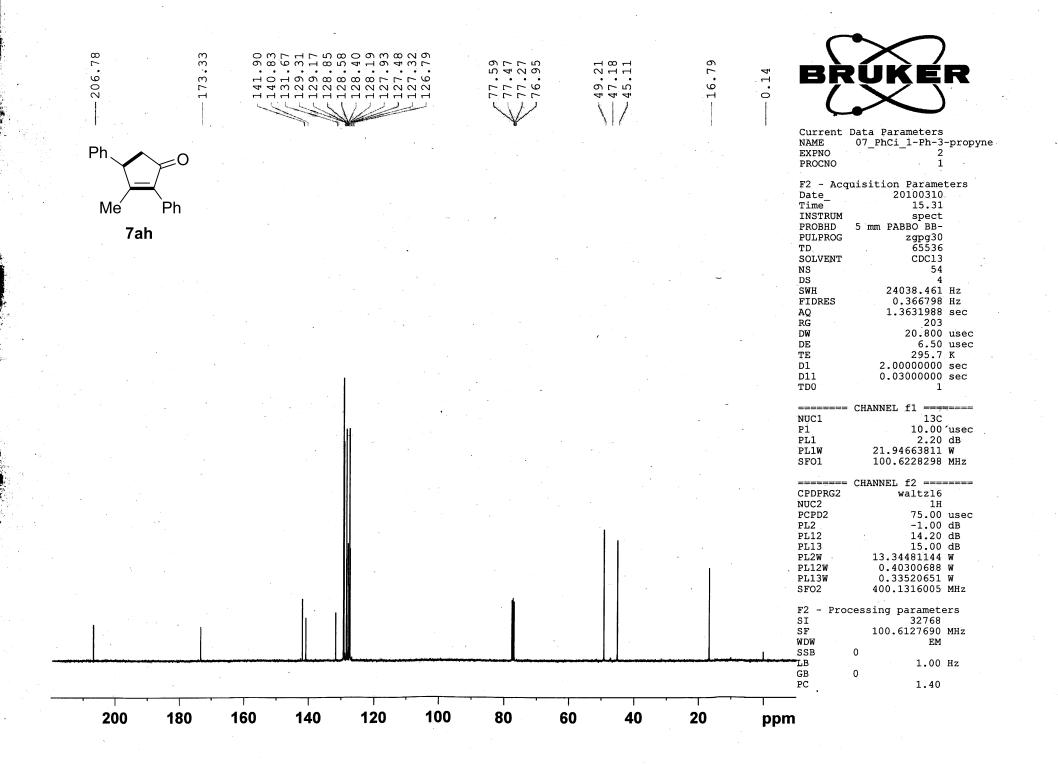
F2 - Acq	uisition Parameters
Date_	20110214
Time_	21.30
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDC13
NS	476
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AO	1.3631988 sec
RG	114
DW	20.800 usec
DE	6.50 usec
TE	295.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
NUC1 P1 PL1 PL1W SF01	CHANNEL f1 13C 10.00 usec 2.20 dB 21.94663811 W 100.6228298 MHz
CPDPRG2	CHANNEL f2 =======
NUC2	waltz16
PCPD2	1H
PL2	100.00 usec
PL12	-1.20 dB
PL13	15.88 dB
PL2W	16.00 dB
PL12W	13.97373390 W
PL12W	0.27372372 W
PL13W	0.26626399 W
SFO2	400.1316005 MHz
F2 - Prov SI SF WDW SSB LB GB GB PC	cessing parameters 32768 100.6127778 MHz EM 0 1.00 Hz 0 1.40

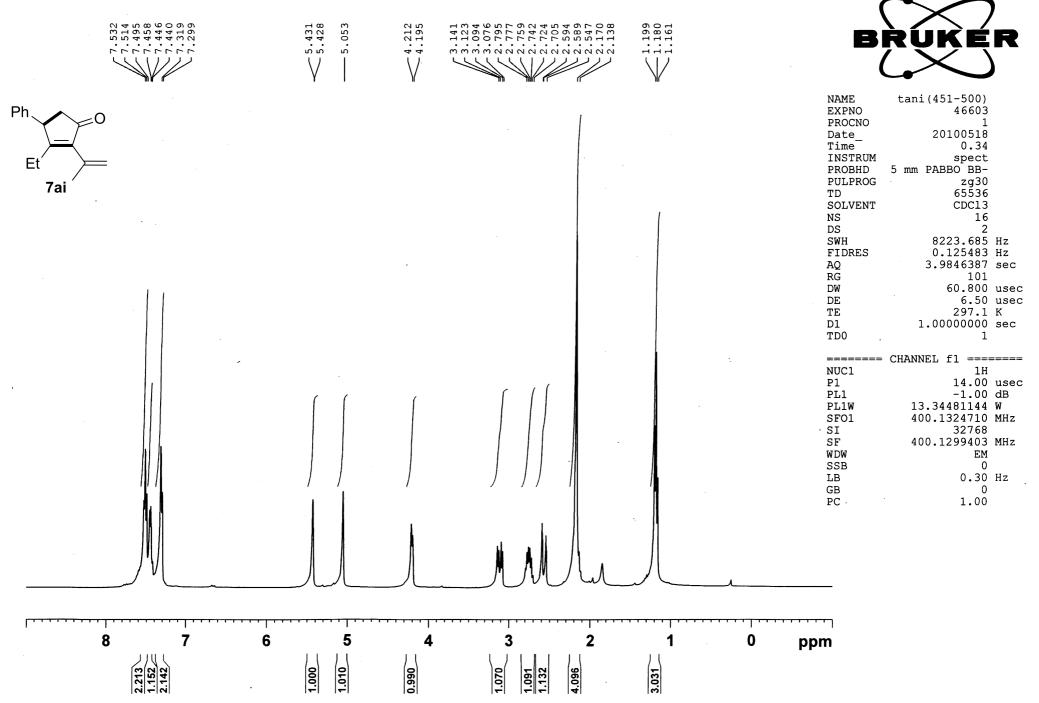
200 180 160 140 120 100 80 60 40 20 ppm

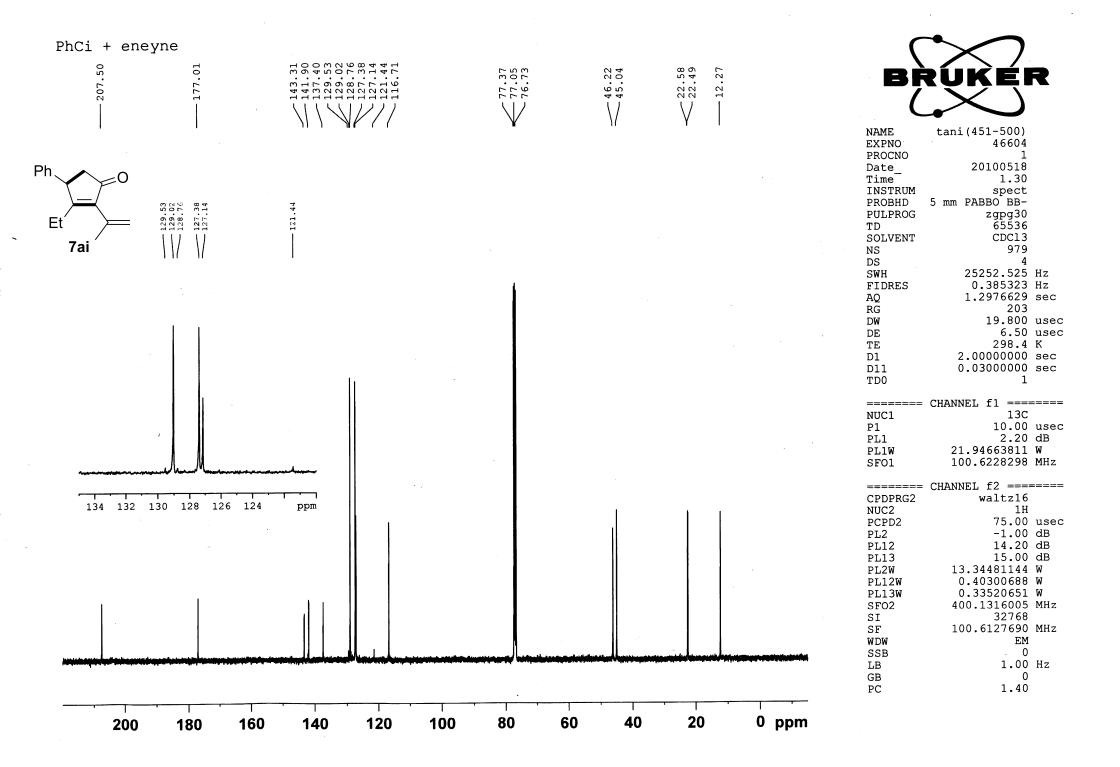


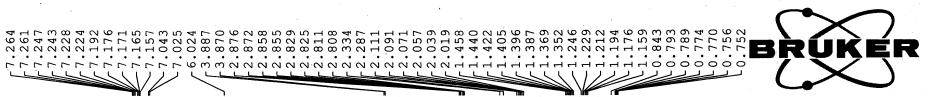


7.431 7.431 7.394 7.374 7.374 7.376 7.370 7.355 7.355	7.257 252 252 252 252 252 252 252 252 252	-7.236 -7.236 -7.233 -7.215 -7.176 -7.176 -7.155 -7.155 -7.155 -7.064 -7.064 -7.064				BRUKER
Ph	≓ 0		-		N F F	Current Data Parameters NAME 07_PhCi_1-Ph-3-propyne EXPNO 1 PROCNO 1 F2 - Acquisition Parameters
Me 7ah	`Ph			1	ם ת א ק ק ק ק ק ק ק ק ק ק ק ק ק ק ק ק ק ק	Date 20100310 Time 15.35 INSTRUM spect PROBHD 5 mm PABBO BB- PULPROG zg30 TD 65536 SOLVENT CDC13
					1 5 7 7 8 8 8 8 9 8 9 8 9 9 9 9 9 9 9 9 9 9	NS 16 DS 2 SWH 8223.685 Hz FIDRES 0.125483 Hz AQ 3.9846387 sec RG 32 DW 60.800 usec DE 6.50 usec TE 294.7 K
					[7 	D1 1.0000000 sec TD0 1
					F S S M S S S S S S S S S S S S S S S S	SF01 400.1324710 MHz F2 - Processing parameters 32768 SF 400.1300346 MHz WDW EM SSB 0 LB 0.30 Hz GB 0
				l		PC 1.00
8 	7.12 7.12 7.12 7.12 7.13 7.13 7.14 7.14 7.14 7.14 7.14 7.14 7.14 7.14		2 3.00 2	1	0 ppm	









F2 - Acquisition Parameter Date 20100623 Time 23.22 INSTRUM spect PROBHD 5 mm PABBO BB- PULPROG 2g30 TD 65536 SOLVENT CDC13	Data Parameters 09_PhCi_1-hexyne 1 1
NS 16 DS 2 SWH 8223.685 Hz FIDRES 0.125483 Hz AQ 3.9846387 se RG 50.8 DW 60.800 us DE 6.50 us TE 298.2 K	20100623 23.22 spect 5 mm PABBO-BB- zg30 65536 CDC13 16 2 8223.685 Hz 0.125483 Hz 3.9846387 sec 50.8 60.800 usec 6.50 usec 298.2 K 1.00000000 sec
PL1 -1.00 dE PL1W 13.34481144 W SF01 400.1324710 MH F2 - Processing parameters SI 32768 SF 400.1300452 MH WDW EM SSB 0 LB 0.30 Hz	1H 14.00 used -1.00 dB 13.34481144 W 400.1324710 MHz cessing parameters 32768 400.1300452 MHz EM 0 0.30 Hz
GB 0 PC 1.00	

8 7 6 5 3 2 0 ppm 4 IJП 3.00 2.01 1.20 1.00 1.04 1.16 3.56 <u>]5</u>

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209.07	184.64	41.4 79.7	127.20	77.47 77.15 76.84	45.65		Current Data Parameters
Ph	¥0						NAME 09_PhCi_1-hexyne EXPNO 2 PROCNO 1
ⁿ Bu	_ <н				•		F2 - Acquisition Parameters Date_ 20100623 Time 22.33 INSTRUM spect
7aj	j				-		PROBHD 5 mm PABBO BB- PULPROG zgpg30 TD 65536 SOLVENT CDC13 NS 64
					• • • • • • • •	н.	DS 4 SWH 25252.525 Hz FIDRES 0.385323 Hz AQ 1.2976629 sec
					•		RG 203 DW 19.800 usec DE 6.50 usec TE 299.4 K D1 2.0000000 sec
· · · · ·				•			D11 0.03000000 sec TD0 1 ======== CHANNEL f1 ========
· ·	•					•	NUC1 13C P1 10.00 usec PL1 2.20 dB PL1W 21.94663811 W SF01 100.6228298 MHz
				u			===== CHANNEL f2 f2 second
•				-			PL12 14.20 dB PL13 15.00 dB PL2W 13.34481144 W PL12W 0.40300688 W PL13W 0.33520651 W SFO2 400.1316005 MHz
							F2 - Processing parameters SI 32768 SF 100.6127690 MHz
200) 180	160 140	120 100	80	60 40	20	WDW EM SSB 0 LB 1.00 Hz GB 0 ppm ^{PC} 1.40

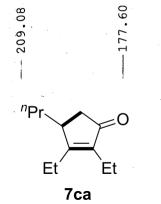
		Current Data Parameters NAME 10_PhCr_3-hexyne EXPNO 45511
Me Et Tba		PROCNO1 $F2$ - Acquisition Parameters $Date_$ 20100506Time22.17INSTRUMspectPROBHD5 mm PABBO BB-PULPROGzg30TD65536SOLVENTCDC13NS16DS2SWH8223.685 HzFIDRES0.125483 HzAQ3.9846387 secRG57DW60.800 usecDE6.50 usecTE296.8 K
		$\begin{array}{cccccccccccccccccccccccccccccccccccc$
۲۰۰۰۰۰۰۰۰۲۰۰۰۰ 8 7 6	5 4 3 2 1 0 p 33.12 33.00 33.12 33.00 1.13.12 3.00 1.13.12 5.00 1.13.12 5.00 1.13.1	opm

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	Me Et 7ba	Et								F2 - Acc Date	quisition Parameters 20100506 22.22 spect 5 mm PABBO BB- zgpg30 65536 CDCl3 48 4 24038.461 Hz 0.366798 Hz 1.3631988 sec 203 20.800 usec 6.50 usec 298.1 K 2.0000000 sec
	•									NUC1 P1 PL1 PL1W SF01	0.03000000 sec 1 = CHANNEL f1 ====== 13C 10.00 usec 2.20 dB 21.94663811 W 100.6228298 MHz = CHANNEL f2 ===== Waltz16 1H 75.00 usec -1.00 dB 14.20 dB 15.00 dB 13.34481144 W 0.40300688 W 0.33520651 W 400.1316005 MHz
	200	180	160	140	120 1	1	30	 40	20 pr	F2 - Pro WHMSI WDW SSB LB GB WMPC	Ocessing parameters 32768 100.6127690 MHz EM 0 1.00 Hz 0 1.40



ⁿ Pr 0	• • • • • • • • •	-			Current Data Parameters NAME 11_PhHex_3-hexyne EXPNO 1 PROCNO 1
Et Et					F2 - Acquisition Parameters Date20100423 Time17.39 INSTRUMspect
7ca				· · · ·	PROBHD5 mmPABBOBB-PULPROGzg30TD65536SOLVENTCDC13NS16
•			· · · · ·		DS 2 SWH 8223.685 Hz FIDRES 0.125483 Hz AQ 3.9846387 sec RG 36
					DW 60.800 use DE 6.50 use TE 294.8 K D1 1.0000000 sec TD0 1 1
					====== CHANNEL f1 f1 ===== f1 f1
					PL1W 13.34481144 W SF01 400.1324710 MHz F2 - Processing parameters
					SI 32768 SF 400.1300170 MHz WDW EM SSB 0 LB 0.30 Hz GB 0
	· · · · · · · · · · · · · · · · · · ·			J	PC 1.00
8 7	6 5	4 3	L 2 2.19 5.19 6.02 5.19 6.02 5.19 6.02 5.19 1.10 6.02 5.19 5.05 7.00 7.00 7.00 7.00 7.00 7.00 7.00	0 ppn	n



77.42 77.10 76.79





NAME EXPNO	11_PhHex	_3-hex 2 1	yne
PROCNO		1	
F2 - Acqu Date_ Time INSTRUM PROBHD PULPROG	20 5 mm PAB	100423 17.42 spect	ters
TD SOLVENT NS		65536 CDC13 31	
DS SWH FIDRES	0.	4 38.461 366798	Hz Hz
AQ RG DW		631988 203 20.800	usec
DE TE D1	2.00	6.50 295.9 000000	к
D11 TD0	0.03	000000	sec
======= NUC1 P1 PL1	CHANNEL	f1 === 13C 10.00 2.20	usec
PL1W SFO1		663811 228298	W
CPDPRG2	CHANNEL	f2 ==== altz16 1H	
NUC2 PCPD2 PL2 PL12	•	75.00 -1.00 14.20	dB dB
PL13 PL2W PL12W PL13W SF02	0.40	15.00 481144 300688 520651 316005	พ พ พ
•	essing p		

MHz

Hz

 200	180	160	140	120	100	80	60	40	20	PPm ^{PC}	0	1.40
						·				SSB	.0	1.00 1
									· · · · · · · · · · · · · · · · · · ·	SF WDW		100.6127690 I EM
										F2 -	Proces	sing parameter 32768
										PL13V SFO2		0.33520651 V 400.1316005 M
a A		•		•						PL2W PL12V	7	13.34481144 0.40300688
						1				PL12 PL13		14.20 (15.00 (
		×		· •						PCPD2 PL2	2	75.00
			•							NUC2		1H

Спрининала в страна R B R

Current	Data Parameters
NAME	12_PhMPen_3-hexyne
EXPNO	1
PROCNO	1
F2 - Acc	uisition Parameters
Date_	20100512
Time	18.30
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDC13
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	25.4
DW	60.800 usec
DE	6.50 usec
TE	295.5 K
D1	1.00000000 sec
TD0	1
NUC1 P1 PL1 PL1W SF01	= CHANNEL f1 ======= 1H 14.00 usec -1.00 dB 13.34481144 W 400.1324710 MHz
F2 - Pro SI SF WDW SSB LB GB PC	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0

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ppm

Et Et PROBUS 5 mm PABBO BB- PULPROG 229930 TO 65536 SOLVENT CDC13 NS 7 25 DS 4 SWH 25252.525 H: FIDRES 0.335323 H: AQ 203 DW 19.800 u: DE 6.50 u: D1 2.0000000 sc TD0 1 	د. 208.37 الم	175.78	 76.45 75.81	3 7	26.44 20.85 15.22 11.19 11.19 -0.00	Current Data Parameters NAME 12_PhMPen_3-hexy EXPNO 1 PROCNO 1 F2 - Acquisition Paramete Date 20100512 Time 18.33
NUC1 13C P1 10.00 ux PL1 2.20 dl PL1W 21.94663811 W SF01 100.6228298 MI ====== CHANNEL f2 ====== CPDPRG2 waltz16 NUC2 1H PCPD2 75.00 ux PL2 -1.00 dl PL12 14.20 dl PL13 15.00 dl PL2W 13.34481144 W PL12W 0.40300688 W						PROBHD 5 mm PABBO BB- PULPROG zgpg30 TD 65536 SOLVENT CDC13 NS 25 DS 4 SWH 25252.525 H FIDRES 0.385323 H AQ 1.2976629 s RG 203 DW 19.800 u DE 6.50 u TE 296.5 K D1 2.0000000 s D11 0.03000000 s
PL13W 0.33520651 W						NUC1 13C P1 10.00 u PL1 2.20 d PL1W 21.94663811 W SF01 100.6228298 M ====== CHANNEL f2 ===== CPDPRG2 waltz16 NUC2 1H PCPD2 75.00 u PL2 14.20 d PL13 15.00 d PL2W 13.34481144 W PL12W 0.40300688 W

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Current Data Parameters

14_PhDMPen_3-hexyne NAME EXPNO 1 PROCNO 1 F2 - Acquisition Parameters Date_ Time 20100513 12.57 INSTRUM spect PROBHD 5 mm PABBO BBzg30 PULPROG TD 65536 CDC13 SOLVENT NS 16 2 DS 8223.685 Hz SWH 0.125483 Hz FIDRES 3.9846387 sec AQ 40.3 RG DW 60.800 usec 6.50 usec DE 295.1 K ΤE D1 1.00000000 sec 1 TD0 ====== CHANNEL f1 ======= NUC1 1H P1 14.00 usec PL1 -1.00 dB PL1W 13.34481144 W SF01 400.1324710 MHz F2 - Processing parameters SI

 SI
 32768

 SF
 400.1300316
 MHz

 WDW
 EM

 SSB
 0

 LB
 0.30
 Hz

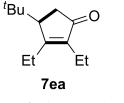
 GB
 0
 1.00

7 5 3 2 0 8 ppm 6 1 3.31 10.58 2.00 1.20 2.76

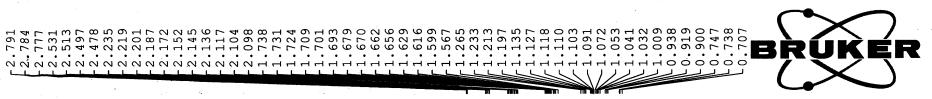
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$ \begin{array}{c} {}^{t}\text{Bu} \longrightarrow 0 \\ {}^{t}\text{Et} \\ {}^{t}\text{Et} \\ {}^{t}\text{Et} \\ {}^{t}\text{Et} \\ {}^{t}\text{Time} \\ {}^{t}\text{Ta} \\ \end{array} \\ \begin{array}{c} {}^{t}\text{PROCNO} \\ {}^{t}\text{I} \\ {}^{t}\text{I} \\ {}^{t}\text{e} \\ {}^{t}\text{2} \\ {}^{t}\text{2} \\ {}^{t}\text{Acquisition Parameters} \\ {}^{t}\text{Date} \\ {}^{t}\text{200513} \\ {}^{t}\text{I} \\ {}^{t}\text{I} \\ {}^{t}\text{I} \\ {}^{t}\text{e} \\ {}^{t}\text{2} \\ {}^{t}\text{2} \\ {}^{t}\text{Acquisition Parameters} \\ {}^{t}\text{Date} \\ {}^{t}\text{200513} \\ {}^{t}\text{I} \\ {}^{t}\text{I} \\ {}^{t}\text{I} \\ {}^{t}\text{RoBH 5 mm PABBO BB-} \\ {}^{t}\text{PULPROG } \\ {}^{t}\text{2} \\ {}^{c}\text{2} \\ {}^{t}\text{CO13} \\ {}^{t}\text{NS } \\ {}^{t}\text{S} \\ {}^{t}\text{SOUVENT } \\ {}^{t}\text{CO213} \\ {}^{t}\text{NS } \\ {}^{t}\text{SOUVENT } \\ {}^{t}\text{CO213} \\ {}^{t}\text{NS } \\ {}^{t}\text{SOUVENT } \\ {}^{t}\text{CO213} \\ {}^{t}\text{SOU0 usec} \\ {}^{t}\text{C1 } \\ \\ {}^{t}C$	•	176.65		143.70	•	$\overbrace{76.77}^{77.40}$		0 0 0 0 0 0 0 0 0 0 0	23.73 23.73 16.41 15.77 13.48	0.9	BR	UKER
F2 - Acquisition Parameters Time - 13.05 Time - 10.05 Time - 10.05 <th>^tBu.</th> <th></th> <th></th> <th></th> <th>•</th> <th></th> <th></th> <th></th> <th></th> <th></th> <th>NAME EXPNO</th> <th>14_PhDMPen_3-hexyne 13</th>	^t Bu.				•						NAME EXPNO	14_PhDMPen_3-hexyne 13
NUC1 13C P1 10:00 used PLW 21.94663811 W SF01 100.622828 MHz CPDPRG2 waltz16 NUC2 1H PCPD 75:00 used PL12 14:20 dB PL13 15:00 dB PL13 10:00 dB PL13 3:2765 SF02 400.1316005 MHz SF2 Processing parameters SF 100.6127690 MHz WDW EM SSB 0 SSB 0 SB 0 GB 0											Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 D1 D11	20100513 13.05 spect 5 mm PABBO BB- zgpg30 65536 CDC13 53 4 24038.461 Hz 0.366798 Hz 1.3631988 sec 203 20.800 usec 6.50 usec 296.4 K 2.0000000 sec 0.03000000 sec
CPDPRG2 waltz16 NUC2 1H PCPD2 75.00 usec PL2 -1.00 dB PL13 15.00 dB PL13 15.00 dB PL2W 13.34481144 W PL13W 0.40300688 W PL13W 0.33520651 W SFO2 400.1316005 MHz F2 - Processing parameters SI 32768 SF 100.6127690 MHz WDW EM SSB 0 LB 1.00 Hz GB 0		<u>.</u>	•		2		•				NUC1 P1 PL1 PL1W	13C 10.00 usec 2.20 dB 21.94663811 W
SI 32768 SF 100.6127690 MHz WDW EM SSB 0 LB 1.00 Hz GB 0		-									CPDPRG2 NUC2 PCPD2 PL2 PL12 PL13 PL2W PL12W PL12W PL13W SF02	waltz16 1H 75.00 usec -1.00 dB 14.20 dB 15.00 dB 13.34481144 W 0.40300688 W 0.33520651 W 400.1316005 MHz
			<u>ner 4 11 von fit plantation</u>			 ,				<u>hannada (</u> 1990) 1	SI WDW SSB 	32768 100.6127690 MHz EM 0 1.00 Hz



Current 1 NAME EXPNO PROCNO	Data Parame 13_PhCy_3-		ne
Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS	2 5 mm PABBC 6 C	00518 23.07 pect 2g30 55536 2DC13 16 2	
SWH FIDRES AQ RG DW DE TE D1 TD0	0.12 3.984 60	28.5 .800 6.50 97.0	Hz sec usec usec K
NUC1 P1 PL1 PL1W SFO1		1H 4.00 1.00 1144	dB W
F2 - Proc SI SF WDW SSB LB GB PC	cessing par 3 400.130 0 0	2768	MHz

5 4	2:34 1.04 2:34 2:34 2:34	5.39 1.67 1.06 1.06	0 рр	רי m
	_u	Malla	I	SSB LB GB PC
				F2 - SI SF WDW SSB LB GB GB PC
				NUC1 P1 PL1 PL1W SF01
· · ·				DW DE TE D1 TD0
				AQ
				NS DS SWH FIDR

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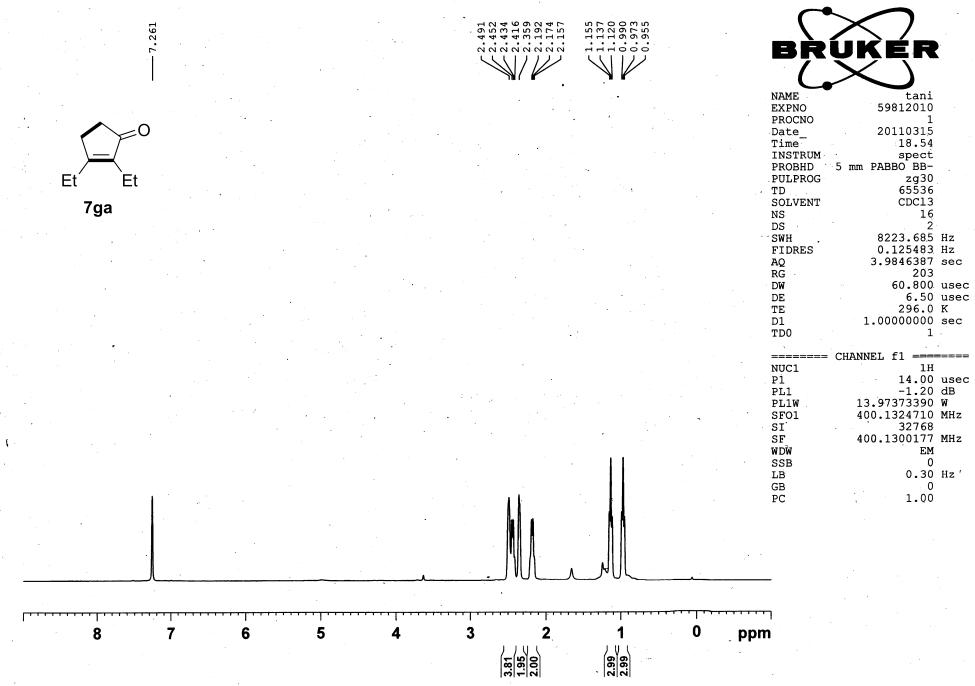
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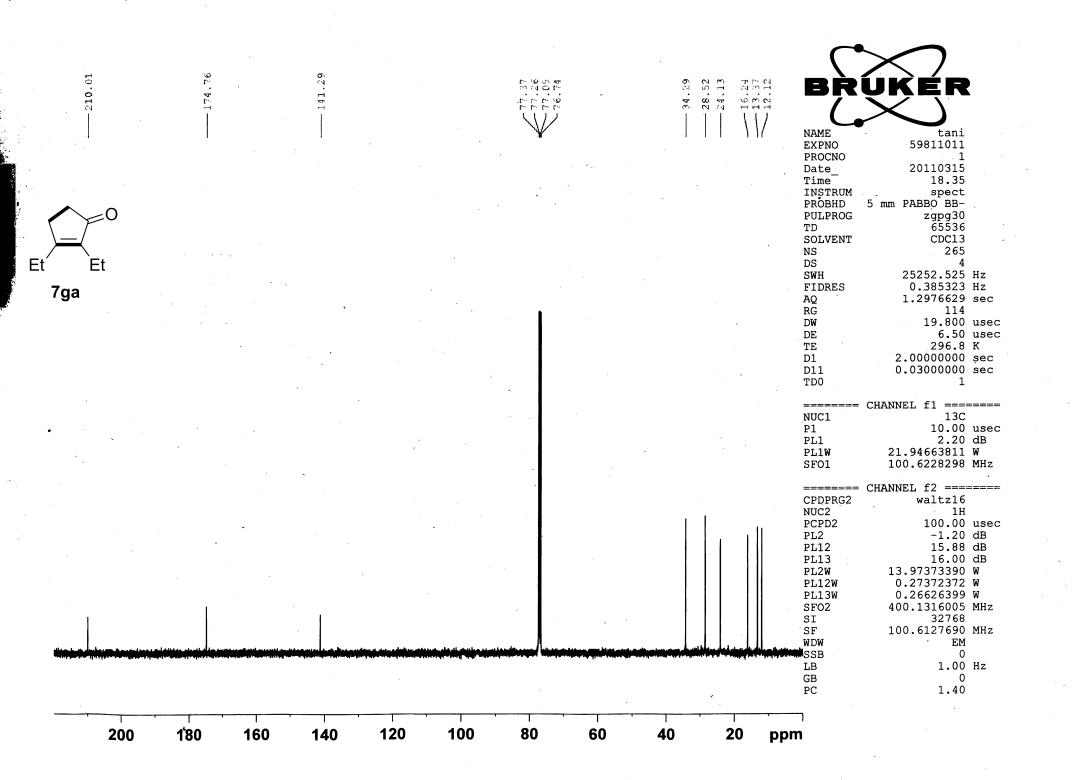
209.	142.	····	21.88 255.99 21.88 255.99 255.	
Et Et 7fa				F2 - Acquisition Parameters Date 20100518 Time 23.10 INSTRUM spect PROBHD 5 mm PABBO BB- PULPROG zgpg30 TD 65536 SOLVENT CDC13 NS 49 DS 4 SWH 24038.461 FIDRES 0.366798 AQ 1.3631988 RG 203
				DW 20.800 usec DE 6.50 usec TE 297.9 K D1 2.0000000 sec D11 0.03000000 sec TD0 1 ==== NUC1 13C P1 10.00 usec
				PL1 2.20 dB PL1W 21.94663811 W SF01 100.6228298 MHz ====== CHANNEL f2 ====== CPDPRG2 waltz16 NUC2 1H PCPD2 75.00 usec PL2 -1.00 dB
				PL12 14.20 dB PL13 15.00 dB PL2W 13.34481144 W PL12W 0.40300688 W PL13W 0.33520651 W SFO2 400.1316005 MHz

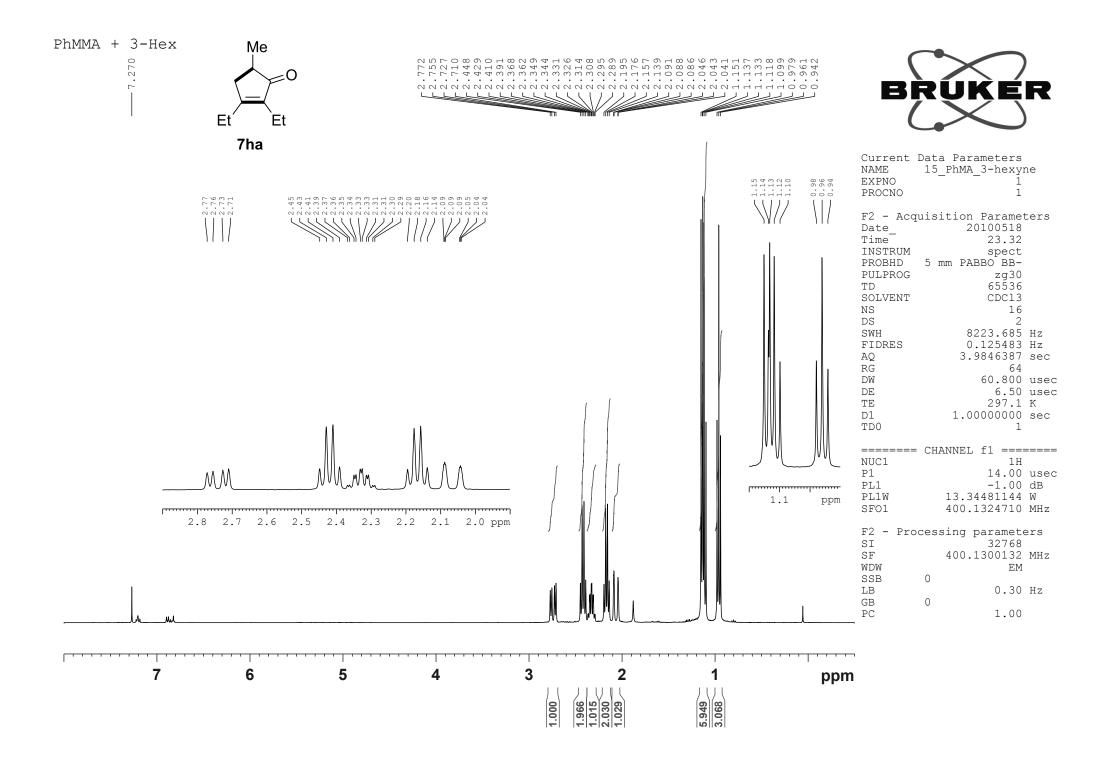
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I	Et Et 7ha					•			-		F2 - Acquisition ParametersDate20100518Time23.35INSTRUM
		•									FIDRES 0.366798 Hz AQ 1.3631988 sec RG 203 DW 20.800 usec DE 6.50 usec TE 298.1 K D1 2.00000000 sec D11 0.03000000 sec TD0 1
		· ·	• •		· .						NUC1 13C P1 10.00 usec PL1 2.20 dB PL1W 21.94663811 W SF01 100.6228298 MHz ====== CHANNEL f2 ======= CPDPRG2 waltz16 NUC2 1H PCPD2 75.00 usec
	l den ka general men ferstersettet der		la al la cal dans la la su da perpensione por que segu	al ha bei anny tajam da	and an an allowed a fine		Rear Aller State	ette a star a stalana stala star da 1911 - a star star star star star star	to the state of th	un appende het en termen tit en	PL2 -1.00 dB PL12 14.20 dB PL13 15.00 dB PL2W 13.34481144 W PL12W 0.40300688 W PL13W 0.33520651 W SFO2 400.1316005 MHz
	200	180	160	140	120	100	80	60	40	20	SF 100.6127690 MHz WDW EM SSB 0 LB 1.00 Hz GB 0 ppmPC 1.40