Supporting Information for:

Nickel-Catalyzed Intermolecular Codimerization of Acrylates and Alkynes

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Contents

Instrumentation and Chemicals

All manipulations of oxygen- and moisture-sensitive materials were conducted in a dry box or with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on Varian UNITY INOVA 500 (^{1}H, 500 MHz; ^{13}C, 125.7 MHz) spectrometer using tetramethylsilane (^{1}H) as an internal standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), integration, and identification. GC-MS analyses and High-resolution mass spectra were obtained with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. Preparative recycling gel permeation chromatography (GPC) was performed with JAI LC-908 equipped with JAIGEL-1H and -2H columns (toluene as an eluent). Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at Kyoto University Elemental Analysis Center. Infrared spectra (IR) spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. In-situ IR spectra were obtained with Mettler Toledo ReactIR 45M equipped with AgX Fiber (9.5 mm). Melting points were determined using a YANAKO MP-500D. TLC analyses were performed by means of Merck Kieselgel 60 F_{254} (0.25 mm) Plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline $KMnO_4$ solution followed by heating. Flash column chromatography was carried out using Kanto Chemical silica gel (spherical, 40–50 mm). Unless otherwise noted, commercially available reagents were used without purification. Toluene was purchased from Wako Pure Chemical Co. stored over slices of sodium. Bis(1,5-cyclooctadiene)nickel and ligands were purchased from Strem Chemicals, Inc.

Experimental Procedure and Characterization Data

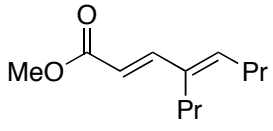
Synthesis of *N*-phenyl-2-aminopyridine (3b).[1]

The reaction was performed in a 20 mL sealed tube equipped with a Teflon-coated magnetic stirrer tip. A mixture of 2-bromopyridine (1.58 g, 10 mmol) and aniline (1.83 mL, 20 mmol) was heated at 160 °C for 2 h. Saturated $NaHCO_3$ aq. was added slowly to the reaction mixture and the mixture was extracted with ethyl acetate (3 × 40 mL). The combined organic layers were washed with brine, dried over sodium sulfate and concentrated *in vacuo*. Aniline was removed by distillation under reduced pressure. The residue was recrystallized from hexane to give *N*-phenylaminopyridine (1.40 g, 82%). Another 2-aminopyridine derivatives were also synthesized in this method.

Experimental Procedure for the Nickel-catalyzed Codimerization of Acrylates and Alkynes.

General procedure. The reaction was performed in a 5 mL sealed vessel equipped with a Teflon-coated magnetic stirrer tip. An acrylate (0.60 or 1.0 mmol) and an alkyne (0.50 mmol) were added to a solution of bis(1,5-dicyclooctadiene)nickel (14 mg, 0.050 mmol), tricyclohexylphosphine (14 mg, 0.050 mmol) and *N*-aryl-2-aminopyridine (0.10 mmol) in toluene (5 mL) in a dry box. The VIAL was taken outside the dry box and heated at 100 °C for 24 h. The reaction mixture was poured into 0.5N HCl aq. (30 mL) and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine, dried over sodium sulfate and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (hexane/AcOEt = 40/1) to give the corresponding conjugated diene.

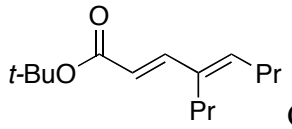
Methyl (2*E*,4*E*)-4-propyl-2,4-octadienoate (4aa).[2]



Colorless oil. TLC: R_f 0.46 (hexane/AcOEt = 10/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (d, *J* = 15.5 Hz, 1H), 5.88 (t, *J* = 7.5 Hz, 1H), 5.80 (d, *J* = 15.5 Hz, 1H), 3.75 (s, 3H), 2.21 (t, *J* = 9.5 Hz, 2H), 2.16 (q, *J* = 7.5 Hz, 2H), 1.43 (m, 4H), 0.93 (t, *J* = 7.0 Hz, 3H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.15, 149.28, 142.78, 137.35, 114.58, 51.42, 30.79, 28.57, 22.41, 21.90, 14.19, 13.88. IR (neat): 2960, 2873, 1722, 1625, 1464, 1434, 1378, 1307, 1265, 1191, 1168, 1043,

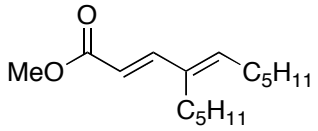
985, 858 cm^{-1}. MS (EI): *m/z* (%): 196 ($[M]^+$, 40), 167 ($[M–Et]^+$, 36), 153 ([M–Pr], 100), 137 ([M–CO_2Me], 31). HRMS calcd for $C_{12}H_{20}O_2$: 196.1463. Found: 196.1462. Anal calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.18; H, 10.51.

***tert*-Butyl (2*E*,4*E*)-4-propyl-2,4-octadienoate (4ba).**



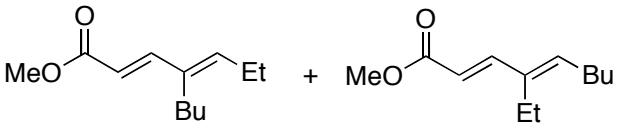
Colorless oil. TLC: R_f 0.66 (hexane/AcOEt = 10/1). ^1H NMR (500 MHz, $CDCl_3$): δ 7.14 (d, *J* = 15.5 Hz, 1H), 5.83 (t, *J* = 7.0 Hz, 1H), 5.72 (d, *J* = 15.5 Hz, 1H), 2.20 (t, *J* = 8.0 Hz, 2H), 2.15 (q, *J* = 7.0 Hz, 2H), 1.49 (s, 9H), 1.43 (m, 4H), 0.92 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.13, 147.96, 141.77, 137.38, 116.94, 79.93, 30.74, 28.65, 28.21, 22.47, 21.94, 14.20, 13.87. IR (neat): 2961, 2872, 1709, 1624, 1456, 1368, 1308, 1285, 1256, 1152, 1086, 984, 858 cm^{-1}. MS (EI): *m/z* (%): 238 ($[M]^+$, 27), 182 ($[M–CH_2=C(CH_3)_2]^+$, 38), 165 ($[M–(CH_3)_3CO]^+$, 35), 153 ($[M–CH_2=C(CH_3)_2–Et]^+$, 50), 139 ($[M–CH_2=C(CH_3)_2–Pr]^+$, 100). HRMS calcd for $C_{15}H_{26}O_2$: 238.1933. Found: 238.1935.

Methyl (2*E*,4*E*)-4-pentyl-2,4-decadienoate (4ab).



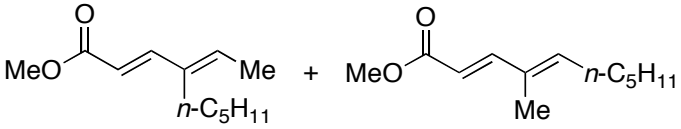
Colorless oil. TLC: R_f 0.53 (hexane/AcOEt = 10/1). ^1H NMR (500 MHz, $CDCl_3$): δ 7.24 (d, *J* = 16.0 Hz, 1H), 5.86 (t, *J* = 7.5 Hz, 1H), 5.80 (d, *J* = 16.0 Hz, 1H), 3.75 (s, 3H), 2.21 (t, *J* = 7.5 Hz, 2H), 2.17 (q, *J* = 7.5 Hz, 2H), 1.46-1.25 (m, 12H), 0.89 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.14, 149.27, 142.74, 137.52, 114.58, 51.37, 32.02, 31.57, 28.86, 28.71, 28.44, 26.62, 22.52, 22.50, 13.99, 13.96. IR (neat): 2956, 2860, 1722, 1622, 1467, 1435, 1379, 1308, 1268, 1166, 1096, 1044, 985, 851 cm^{-1}. MS (EI): *m/z* (%): 252 ($[M]^+$, 35), 195 ($[M–Bu]^+$, 36), 181 ($[M–C_5H_{11}]^+$, 100). HRMS calcd for $C_{16}H_{28}O_2$: 252. 2089. Found: 252.2084.

Methyl (2*E*,4*E*)-4-propylidene-2-octenoate and
methyl (2*E*,4*E*)-4-ethyl-2,4-nonadienoate (1:1 mixture) (4ac).



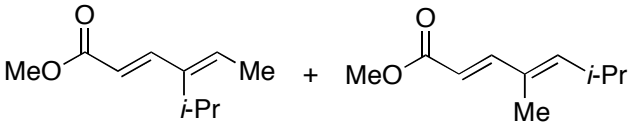
Colorless oil. TLC: R_f 0.46 (hexane/AcOEt = 10/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (d, *J* = 16.0 Hz, 0.5H), 7.23 (d, *J* = 16.0 Hz, 0.5H), 5.85 (t, *J* = 7.5 Hz, 0.5H), 5.84 (t, *J* = 7.5 Hz, 0.5H), 5.82 (d, *J* = 16.0 Hz, 0.5H), 5.81 (d, *J* = 16.0 Hz, 0.5H), 3.75 (s, 3H), 2.28-2.16 (m, 4H), 1.44-1.29 (m, 4H), 1.03 (t, *J* = 7.5 Hz, 1.5H), 1.01 (t, *J* = 7.5 Hz, 1.5H), 0.91 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.14, 149.24, 148.79, 144.05, 142.22, 138.91, 137.01, 114.69, 114.50, 51.40, 31.35, 30.98, 28.25, 26.32, 22.89, 22.44, 22.02, 19.67, 13.94, 13.91, 13.67, 13.31. IR (neat): 2959, 2874, 1721, 1624, 1458, 1435, 1296, 1265, 1167, 1086, 984, 845 cm^{-1}. MS (EI): *m/z* (%): 196 ($[M]^+$, 71), 167 ([M–Et], 88), 139 ([M–Bu], 100), 137 ([M–CO_2Me], 50). HRMS calcd for $C_{12}H_{20}O_2$: 196.1463. Found: 196.1458.

Methyl (2*E*,4*E*)-4-ethylidene-2-nonenoate and
methyl (2*E*,4*E*)-4-methyl-2,4-decadienoate (5:1 mixture) (4ad). [2]



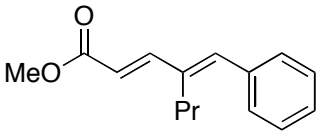
Colorless oil. TLC: R_f 0.48 (hexane/AcOEt = 10/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (d, *J* = 15.5 Hz, 0.17H), 7.24 (d, *J* = 16.0 Hz, 0.83H), 5.96 (q, *J* = 7.0 Hz, 0.83H), 5.91 (t, *J* = 7.0 Hz, 0.17H), 5.80 (d, *J* = 16.0 Hz, 0.83H), 5.78 (d, *J* = 15.5 Hz, 0.17H), 3.75 (s, 3H), 2.23 (t, *J* = 8.0 Hz, 1.67H), 2.19 (q, *J* = 7.0 Hz, 0.33H), 1.80 (d, *J* = 7.0 Hz, 2.5H), 1.76 (s, 0.50H), 1.45-1.27 (m, 6H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.17, 149.04, 138.63, 136.58, 114.43, 51.42, 31.95, 28.10, 26.21, 22.54, 14.48, 14.02. IR (neat): 2959, 2873, 1721, 1624, 1435, 1308, 1269, 1192, 1167, 984, 818 cm^{-1}. MS (EI): *m/z* (%): 196 ($[M]^+$, 56), 181 ([M–Me], 40), 139 ($[M–Bu]^+$, 87), 125 ($[M–C_5H_{11}]^+$, 100). HRMS calcd for $C_{12}H_{20}O_2$: 196.1463. Found: 196.1454.

Methyl (2*E*,4*E*)-4-isopropyl-2,4-hexadienoate and
methyl (2*E*,4*E*)-4,6-dimethyl-2,4-heptadienoate (10:1 mixture) (4ae).



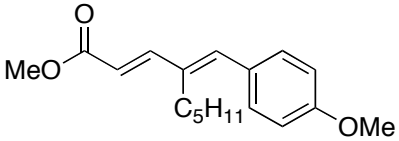
Colorless oil. TLC: R_f 0.43 (hexane/AcOEt = 10/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, *J* = 15.5 Hz, 0.09H), 7.24 (d, *J* = 16.0 Hz, 0.91H), 5.96 (d, *J* = 16.0 Hz, 0.91H), 5.89 (q, *J* = 7.0 Hz, 0.91H), 5.78 (d, *J* = 15.5 Hz, 0.09H), 5.71 (d, *J* = 9.0 Hz, 0.09H), 3.74 (s, 3H), 2.92 (sept, *J* = 7.0 Hz, 0.91H), 2.68 (dsept, *J* = 9.0, 7.0 Hz, 0.09H), 1.78 (d, *J* = 7.0 Hz, 0.91H), 1.77 (s, 0.09H), 1.11 (d, *J* = 7.0 Hz, 5.45H), 1.01 (d, *J* = 7.0 Hz, 0.55H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.91, 146.99, 143.05, 130.93, 115.98, 51.39, 27.23, 20.76, 14.10. IR (neat): 2963, 2874, 1722, 1621, 1435, 1300, 1270, 1173, 1045, 985, 865, 821 cm^{-1}. MS (EI): *m/z* (%): 168 ($[M]^+$, 50), 153 ($[M–Me]^+$, 100), 109 ($[M–CO_2Me]^+$, 72). HRMS calcd for $C_{10}H_{16}O_2$: 168.1150. Found: 168.1158.

Methyl (2*E*,4*E*)-4-benzylidene-2-heptenoate (4af). [2]



Colorless oil. TLC: R_f 0.35 (hexane/AcOEt = 10/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (d, *J* = 16.0 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.31 (m, 3H), 6.81 (s, 1H), 5.99 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H), 2.45 (t, *J* = 8.0 Hz, 2H), 1.56 (m, 2H), 0.99 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.82, 149.44, 138.99, 138.83, 136.63, 129.04, 128.45, 127.78, 116.74, 51.54, 29.36, 22.18, 14.28. IR (neat): 2957, 2873, 1717, 1619, 1435, 1309, 1266, 1168, 1084, 1031, 983, 851, 696 cm^{-1}. MS (EI): *m/z* (%): 230 ($[M]^+$, 26), 201 ($[M–Et]^+$, 28), 171 ($[M–CO_2Me]^+$, 66), 141 (76), 129 ($[M–PhCH_2]^+$, 100). HRMS calcd for $C_{15}H_{18}O_2$: 230.1307. Found: 230.1301.

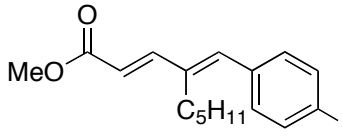
Methyl (2*E*,4*E*)-4-(4-methoxybenzylidene)-2-nonenoate (4ag).



White solid, mp. 35-37 °C (hexane-AcOEt). TLC: R_f 0.30 (hexane/AcOEt = 10/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, *J* = 15.5 Hz, 1H), 7.29 (d, *J* = 9.0 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.73 (s, 1H), 5.94 (d, *J* = 15.5 Hz,

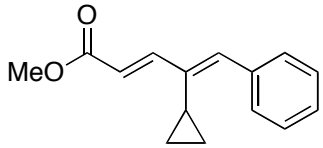
1H), 3.83 (s, 3H), 3.78 (s, 3H), 2.46 (t, J = 7.5 Hz, 2H), 1.56 (m, 2H), 1.37 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.98, 159.34, 149.98, 138.60, 137.44, 130.65, 129.24, 115.67, 113.98, 55.29, 51.47, 32.17, 28.38, 27.31, 22.44, 14.04. IR (neat): 2954, 2871, 1717, 1618, 1601, 1509, 1435, 1306, 1255, 1165, 1035, 982, 851, 824, 730 cm^{-1}. MS (EI): *m/z* (%): 288 ([M]$^+$, 68), 229 ([M–CO_2Me]$^+$, 65), 171 (73), 159 (62), 121 ([MeO-C_6H_4-CH_2]$^+$, 100). HRMS calcd for $C_{18}H_{24}O_3$: 288.1725. Found: 288.1728. Anal calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 74.98; H, 8.68.

Methyl (2*E*,4*E*)-4-(4-fluorobenzylidene)-2-nonenoate (4ah).



Colorless oil. TLC: R_f 0.36 (hexane/AcOEt = 10/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, J = 16.0 Hz, 1H), 7.29 (dd, J_{HH} = 9.0 Hz, J_{HF} = 5.0 Hz, 2H), 7.07 (dd, J_{HH} = 9.0 Hz, J_{HF} = 9.0 Hz, 2H), 6.75 (s, 1H), 5.98 (d, J = 16.0 Hz, 1H), 3.79 (s, 3H), 2.43 (t, J = 8.0 Hz, 2H), 1.53 (m, 2H), 1.34 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.76, 162.20 (d, J_{CF} = 247 Hz), 149.18, 139.04, 137.36, 132.75 (d, J_{CF} = 3.4 Hz), 130.75 (d, J_{CF} = 7.8 Hz), 116.89, 115.49 (d, J_{CF} = 21.5 Hz), 51.55, 32.08, 28.48, 27.23, 22.37, 13.98. IR(neat): 2954, 2872, 1706, 1622, 1598, 1506, 1435, 1312, 1269, 1235, 1167, 1091, 981, 855, 826, 728 cm^{-1}. MS (EI): *m/z* (%): 276 ([M]$^+$, 56), 219 ([M–Bu]$^+$, 85), 159 (100), 109 ([F-C_6H_4-CH_2]$^+$, 60). HRMS calcd for $C_{17}H_{21}FO_2$: 276.1526. Found: 276.1521. Anal calcd for $C_{17}H_{21}FO_2$: C, 73.89; H, 7.66. Found: C, 73.63; H, 7.66.

Methyl (2*E*,4*E*)-4-cyclopropyl-5-phenyl-2,4-pentadienoate (4ai).



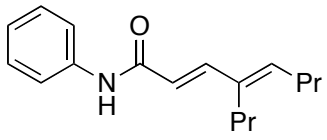
White powder, mp. 62-65 °C (Et_2O). TLC: R_f 0.41 (hexane/AcOEt = 10/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (d, J = 7.5 Hz, 2H), 7.41 (d, J = 15.5 Hz, 1H), 7.35 (t, J = 7.5 Hz, 2H), 7.28 (t, J = 7.5 Hz, 1H), 6.84 (s, 1H), 6.36 (d, J = 15.5 Hz, 1H), 3.79 (s, 3H), 1.61 (m, 1H), 0.89 (m, 2H), 0.25 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.92, 149.56, 140.07, 138.53, 136.11, 130.06, 127.94, 127.89, 117.99, 51.47, 9.71, 8.89. IR (KBr): 3026, 2988, 2949, 1709, 1615, 1447, 1429, 1309, 1292, 1195, 1162, 1006, 857, 694 cm^{-1}. MS (EI): *m/z* (%): 228 ([M]$^+$, 71), 169

([M–CO_2Me]$^+$, 100), 168 (62). HRMS calcd for $C_{15}H_{16}O_2$: 228.1150. Found: 228.1156. Anal calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.85; H, 7.20.

Experimental Procedure for the Nickel-catalyzed Reaction of Acrylamides and Alkynes.

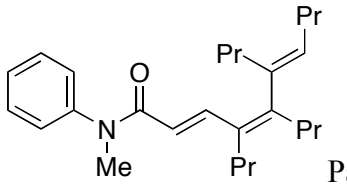
General procedure. The reaction was performed in a 5 mL sealed vessel equipped with a Teflon-coated magnetic stirrer tip. An acrylamide (0.50 mmol) and an alkyne (0.60 mmol) were added to a solution of bis(1,5-dicyclooctadiene)nickel (14 mg, 0.050 mmol) and tricyclohexylphosphine (14 mg, 0.050 mmol) in 1,4-dioxane (5 mL) in a dry box. The VIAL was taken outside the dry box and heated at 80 °C for 24 h. The resulting reaction mixture was cooled to ambient temperature and filtered through a silica gel pad, concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (hexane/AcOEt = 10/1) to give the corresponding conjugated diene.

(2*E*,4*E*)-*N*-Phenyl-4-propyl-2,4-octadienamide (7aa).



White powder, mp. 107-108 °C (CH_2Cl_2). TLC: R_f 0.39 (hexane/AcOEt = 5/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.5 Hz, 2H), 7.46 (br, 1H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 15.5 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 5.92 (d, *J* = 15.5 Hz, 1H), 5.87 (t, *J* = 7.5 Hz, 1H), 2.23 (t, *J* = 8.0 Hz, 2H), 2.16 (q, *J* = 7.5 Hz, 2H), 1.44 (m, 4H), 0.93 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.89, 146.64, 142.09, 138.29, 137.04, 128.96, 124.07, 119.82, 117.57, 30.79, 28.80, 22.44, 21.96, 14.20, 13.87. IR (KBr): 3254, 2959, 2870, 1655, 1599, 1541, 1499, 1441, 1339, 1246, 1182, 1087, 901, 866, 754, 690 cm^{-1}. MS (EI): *m*/*z* (%): 257 ([M]$^+$, 84), 165 ([M–PhNH]$^+$, 100). HRMS calcd for $C_{17}H_{23}NO$: 257.1780. Found: 257.1786. Anal calcd for $C_{17}H_{23}NO$: C, 79.33; H, 9.01; N, 5.44. Found: C, 79.42; H, 9.13; N, 5.43.

(2*E*,4*Z*,6*E*)-*N*-Methyl-*N*-phenyl-4,5,6-tripropyldeca-2,4,6-trienamide (8ba).



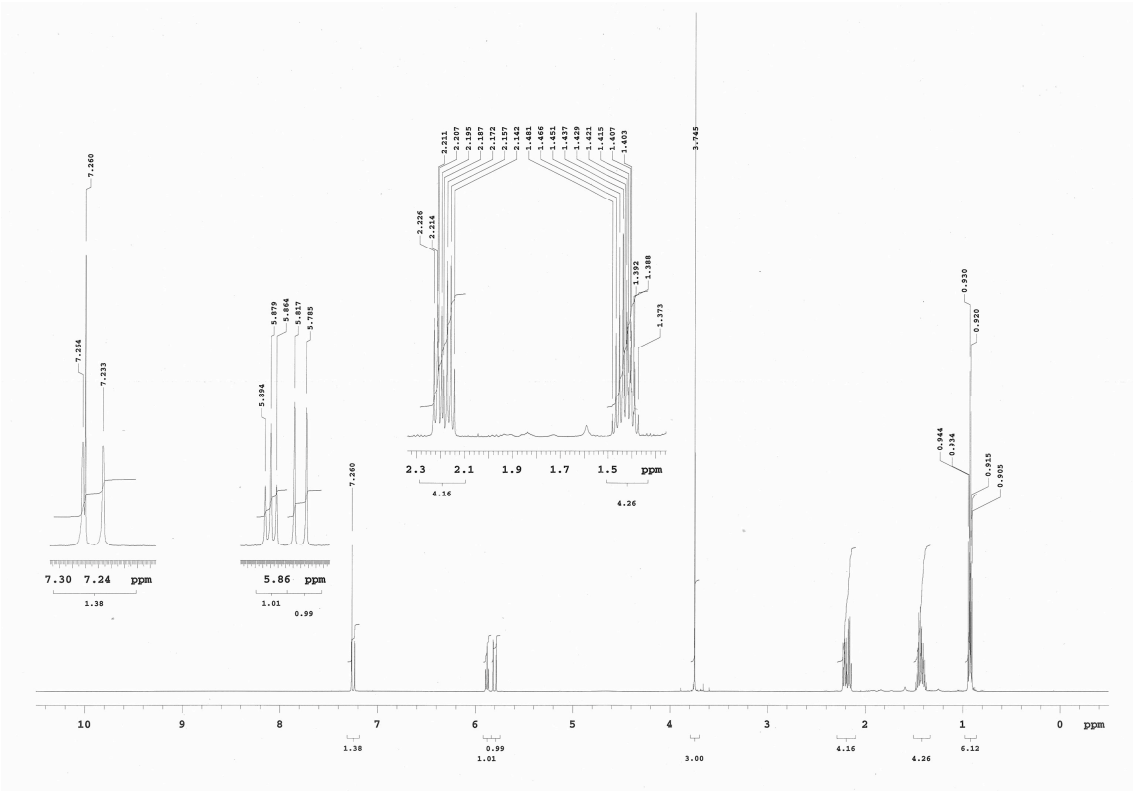
Pale yellow oil. R_f = 0.45 (hexane/AcOEt = 10/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, *J* = 15.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 2H), 5.66 (d, *J* = 15.5 Hz, 1H), 5.03 (t, *J* = 7.5 Hz, 1H), 3.35 (s, 3H), 2.12 (m, 6H), 1.94 (t, *J* = 7.5 Hz, 2H), 1.46 (m, 2H), 1.38 (m, 4H), 1.18 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H), 0.90 (t, *J* = 7.5 Hz, 3H), 0.85 (t, *J* = 7.5 Hz, 3H), 0.67 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.37, 152.32, 144.30, 142.75, 138.69, 132.63, 131.78, 129.29, 127.39, 127.07, 115.86, 37.12, 33.26, 31.87, 30.16, 30.14, 23.03, 22.20, 21.81, 21.37, 14.52, 14.13, 14.06, 13.99. IR (neat): 2958, 2871, 1657, 1596, 1496, 1362, 1289, 1122, 990, 898, 857, 772, 700 cm^{-1}. MS (EI): *m/z* (%): 381 ($[M]^+$, 44), 275 ($[M–NMePh]^+$, 100), 247 ($[M–C(O)NMePh]^+$, 75), 205 (82). HRMS calcd for $C_{26}H_{39}NO$: 381.3032. Found: 381.3031.

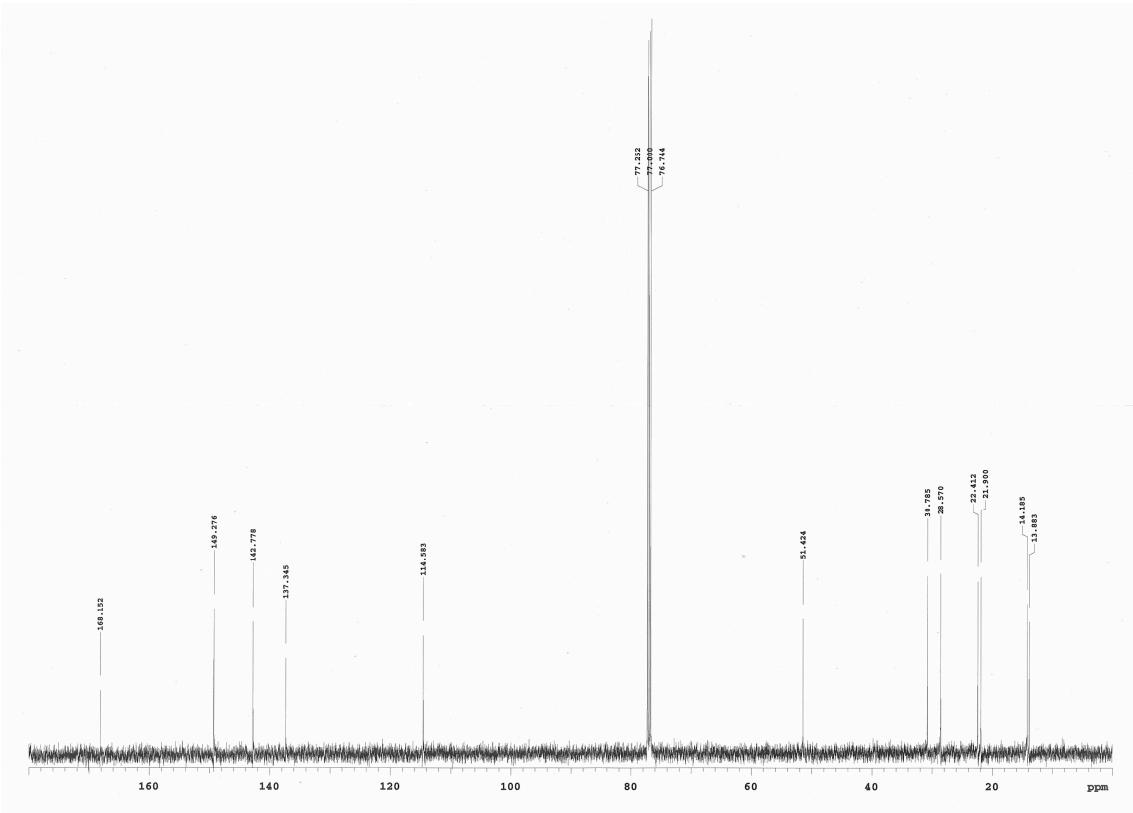
[References]

1. T. Hisano, T. Matsuoka, K. Tsutsumi, K. Muraoka, M. Ichikawa, *Chem. Pharm. Bull.* 1981, **29**, 3706.
2. N. M. Neisius, B. Plietker, *Angew. Chem., Int. Ed.* 2009, **48**, 5752.

^{1}H NMR and ^{13}C NMR Spectra

4aa





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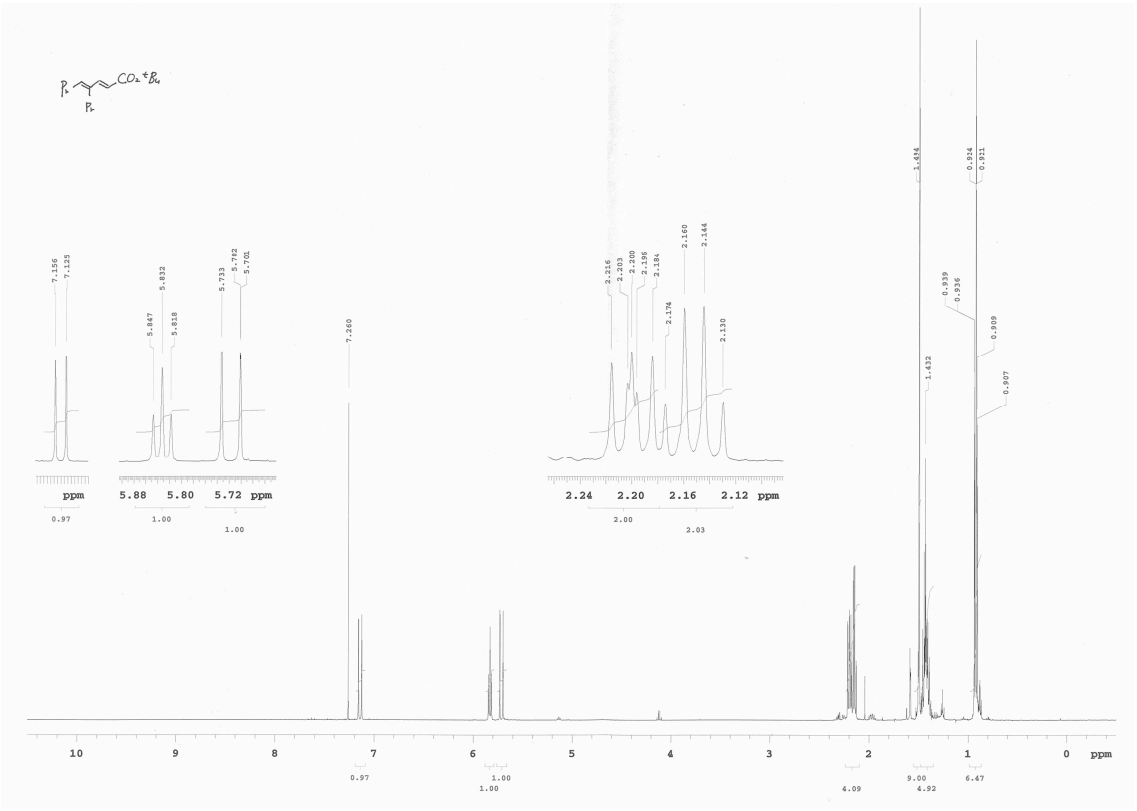
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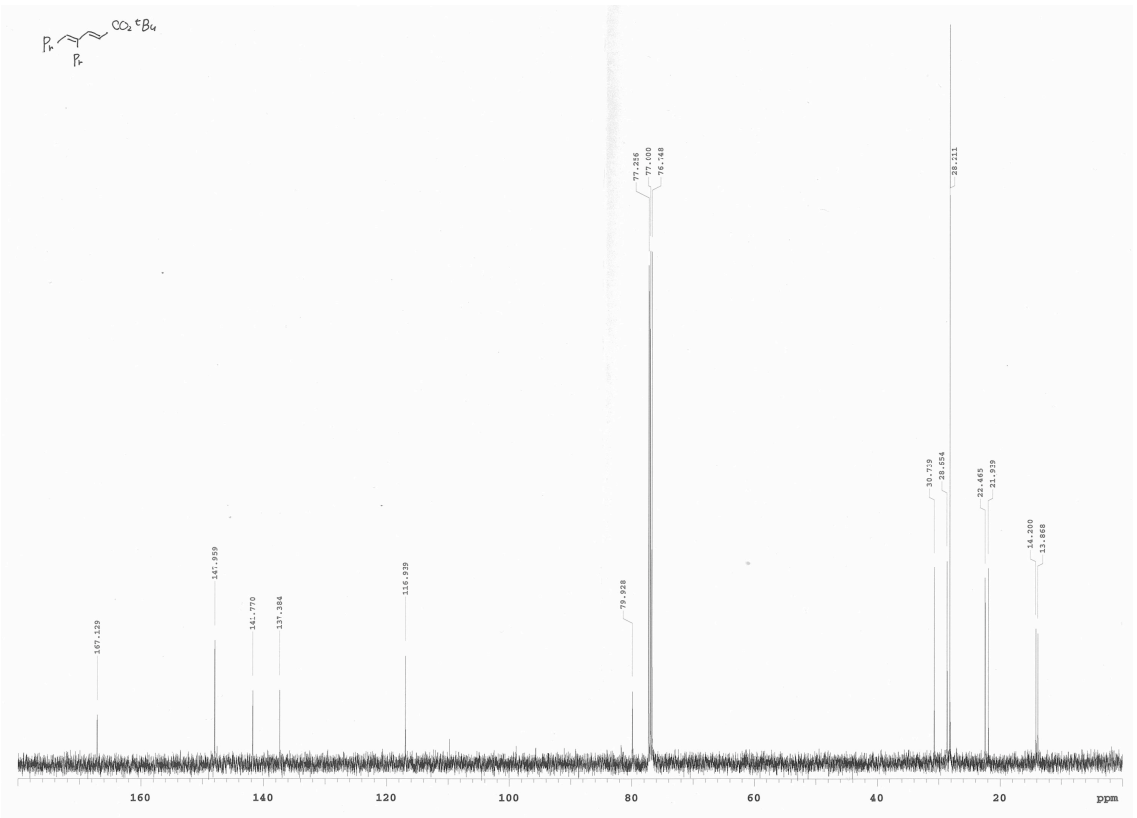
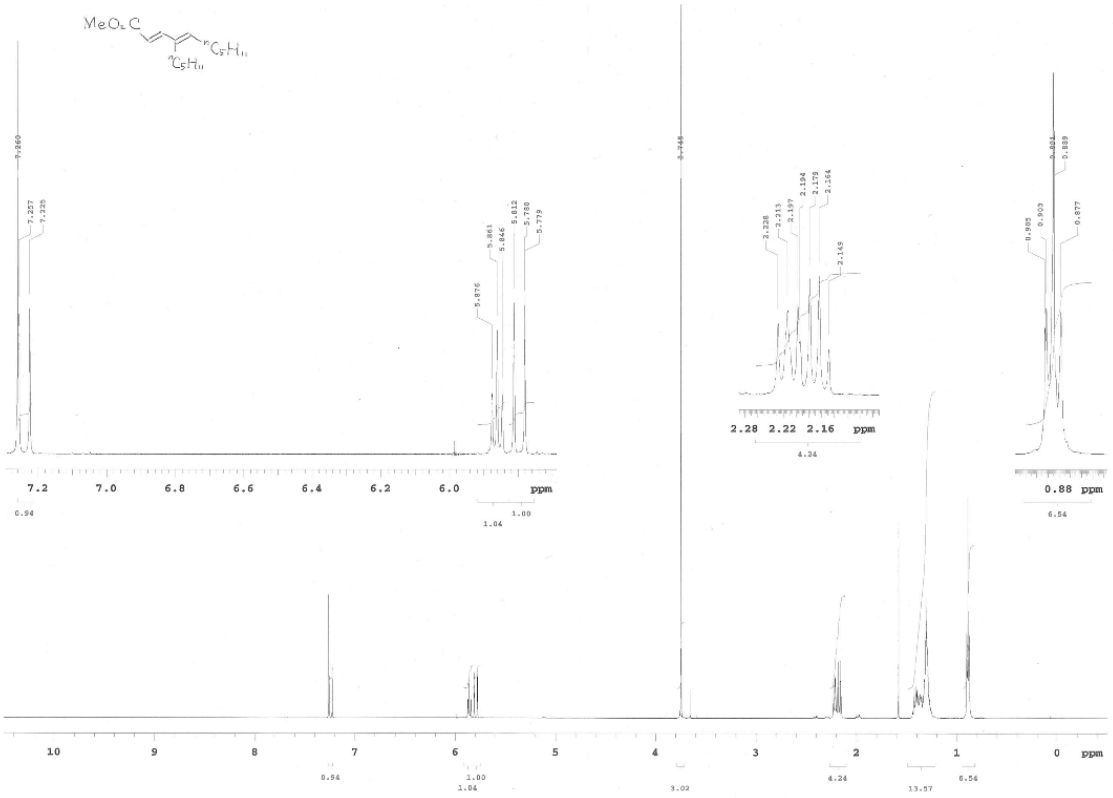
2.24 2.20 2.16 2.12 ppm
10 9 8 7 6 5 4 3 2 1 0 ppm


160 140 120 100 80 60 40 20 ppm

4ab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nC5H11
nC5H11
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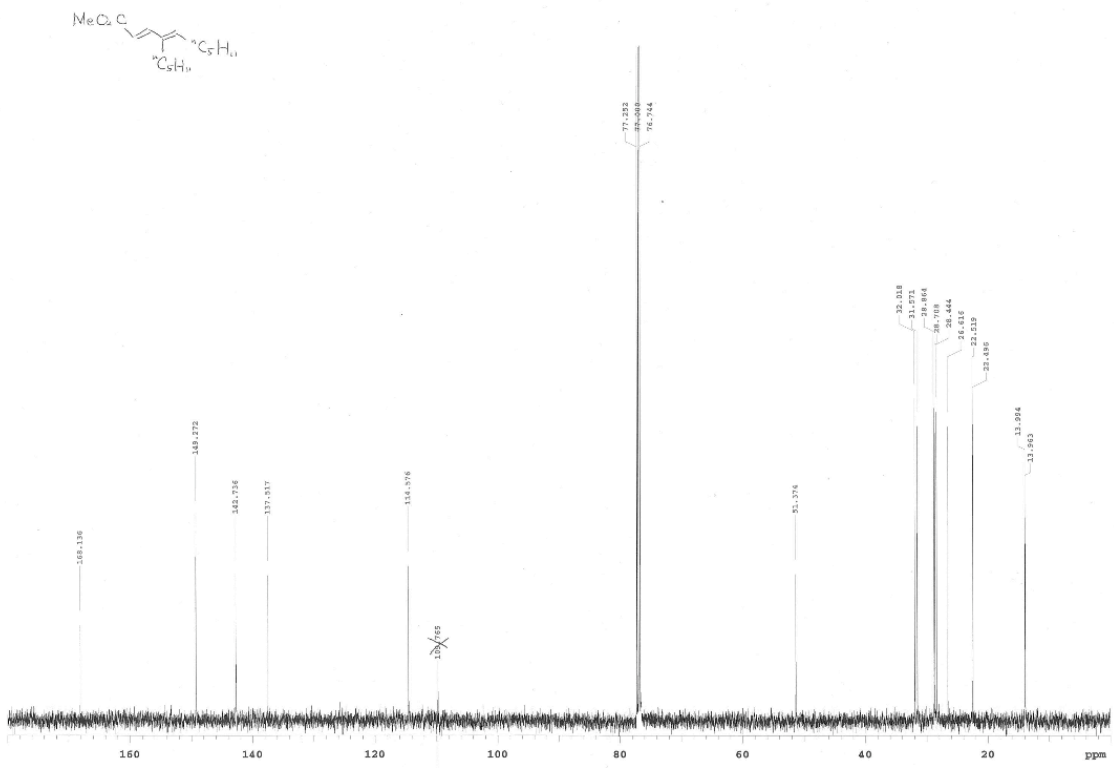
2.28 2.22 2.16 ppm
0.88 ppm
10 9 8 7 6 5 4 3 2 1 0 ppm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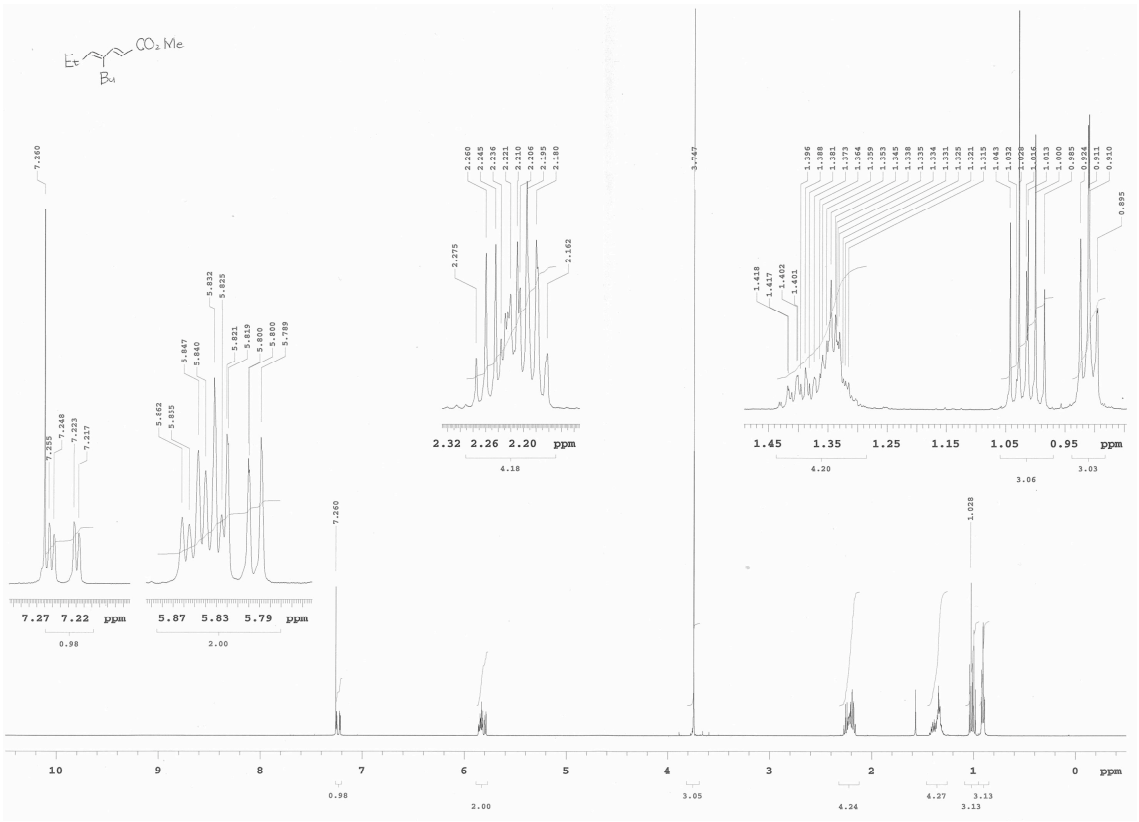
nC5H11
nC5H11
160 140 120 100 80 60 40 20 ppm

4ac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CO2Me
Bu
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7.255
7.248
7.223
7.217
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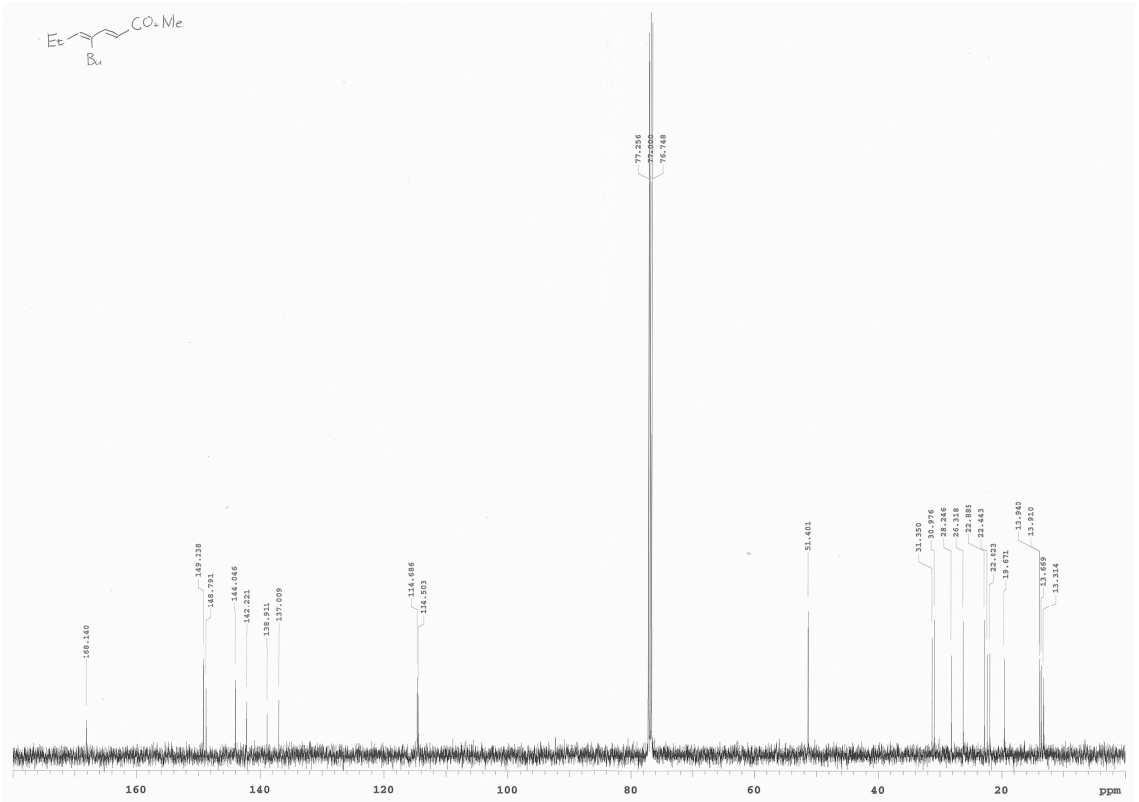
5.855
5.847
5.840
5.832
5.825
5.821
5.819
5.800
5.800
5.789
2.275
2.260
2.245
2.236
2.221
2.210
2.206
2.195
2.180
2.162
3.747
1.418
1.417
1.402
1.401
1.396
1.388
1.381
1.373
1.364
1.359
1.353
1.345
1.338
1.335
1.334
1.331
1.325
1.321
1.315
1.443
1.432
1.428
1.016
1.013
1.000
0.985
0.924
0.911
0.910
0.895
7.27 7.22 ppm
0.98
5.87 5.83 5.79 ppm
2.00
2.32 2.26 2.20 ppm
4.18
1.45 1.35 1.25 1.15 1.05 0.95 ppm
4.20
3.06
3.03
7.260
1.028
10 9 8 7 6 5 4 3 2 1 0 ppm
0.98
2.00
3.05
4.24
4.27
3.13
3.13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Bu
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142.221
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137.009
114.686
114.503
51.401
31.350
30.976
28.246
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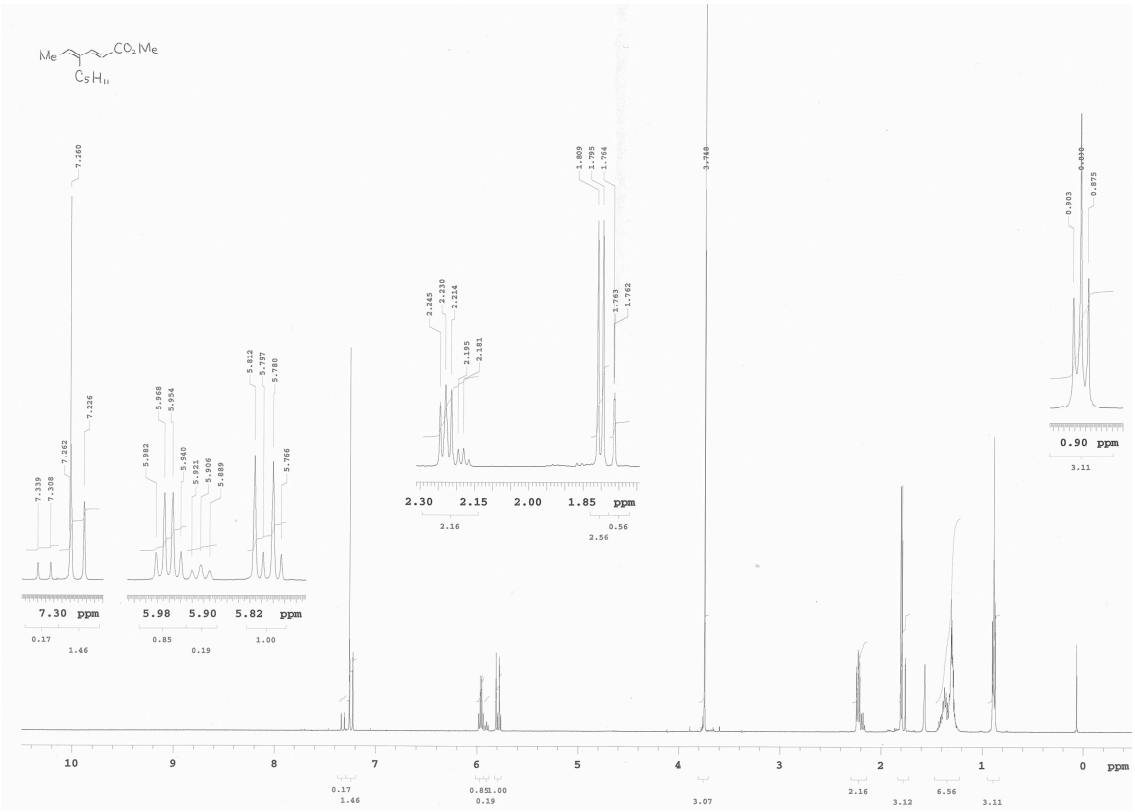
22.885
22.443
22.163
19.671
13.940
13.910
13.669
13.314
160 140 120 100 80 60 40 20 ppm

4ad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CO2Me
C5H11
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7.339
7.308
7.262
7.226
5.982
5.968
5.954
5.840
5.826
5.812
5.797
5.780
5.766
2.245
2.230
2.214
2.195
2.181
1.809
1.795
1.764
1.762
3.748
0.903
0.890
0.875
7.30 ppm
5.98
5.90
5.82 ppm
2.30
2.15
2.00
1.85 ppm
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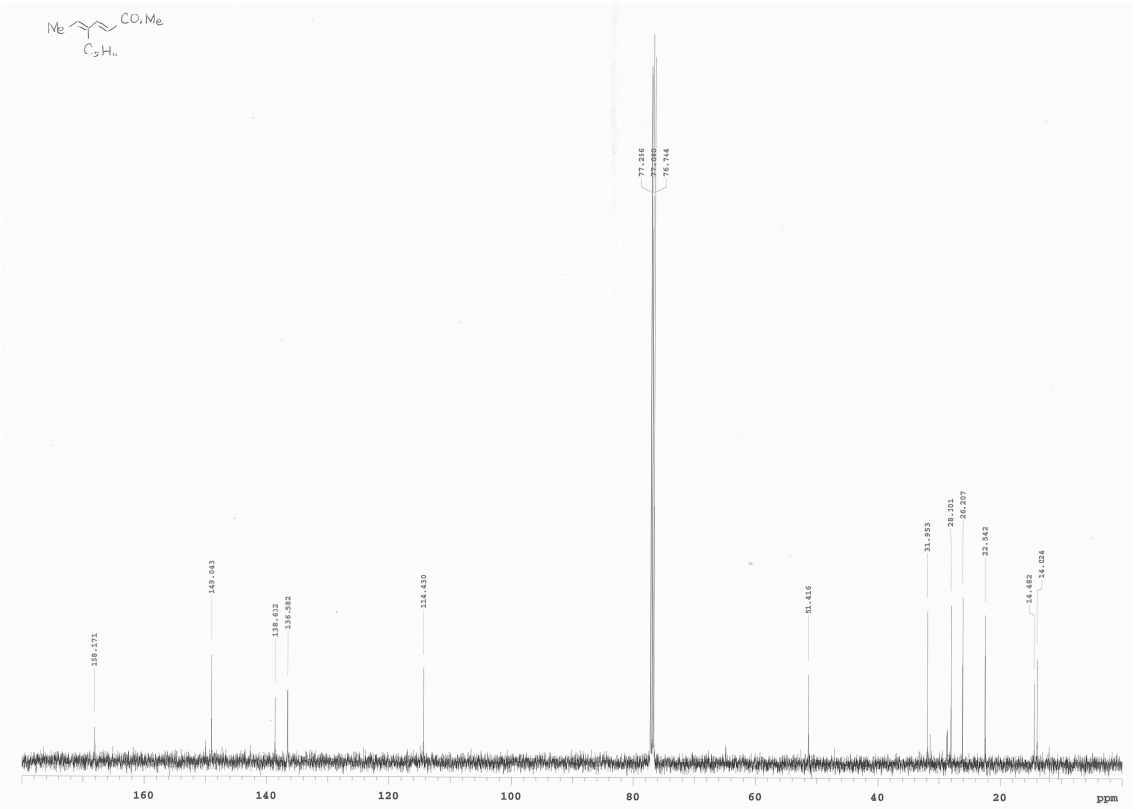
10
9
8
7
6
5
4
3
2
1
0 ppm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C5H11
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76.744
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149.043
138.632
136.582
114.430
51.416
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28.301
26.257
22.542
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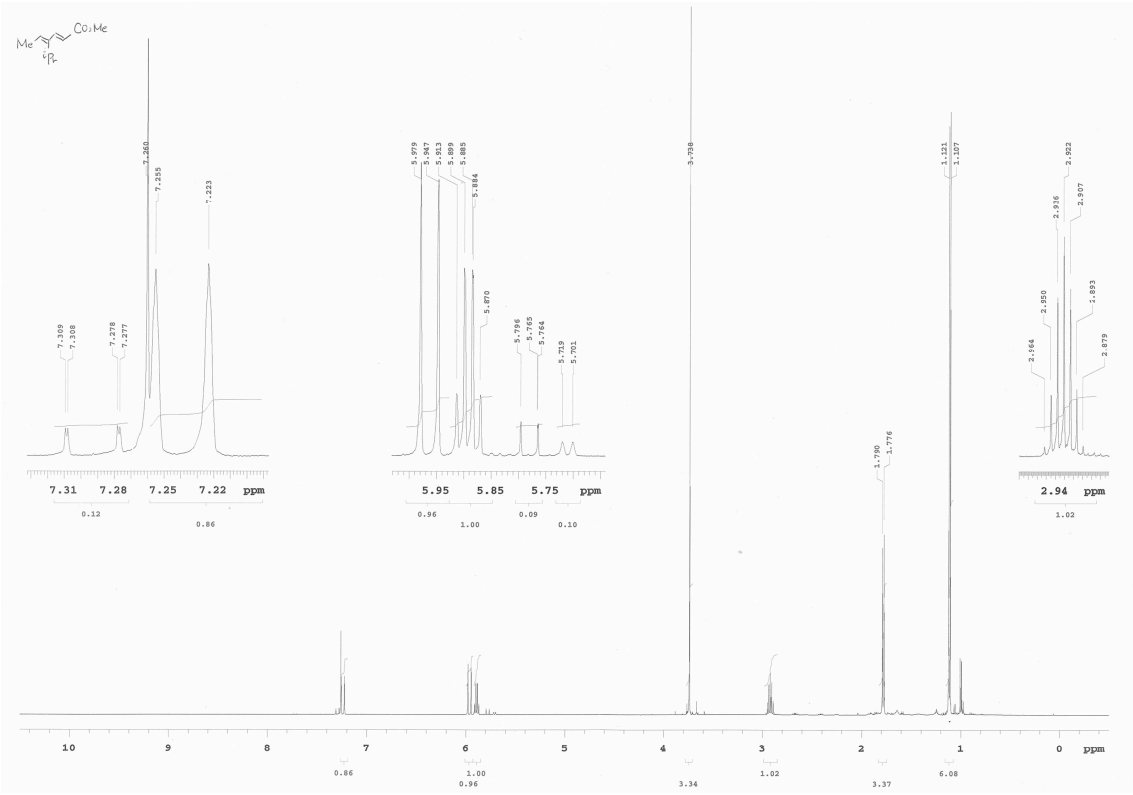
14.024
160
140
120
100
80
60
40
20
ppm

4ae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CO2Me
iPr
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7.223
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5.947
5.913
5.899
5.885
5.864
5.870
5.796
5.765
5.764
5.719
5.701
3.708
1.790
1.776
1.121
1.107
2.952
2.916
2.907
2.893
2.879
2.850
2.664
7.31
7.28
7.25
7.22
ppm
0.12
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5.85
5.75
ppm
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0.09
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ppm
1.02
10
9
8
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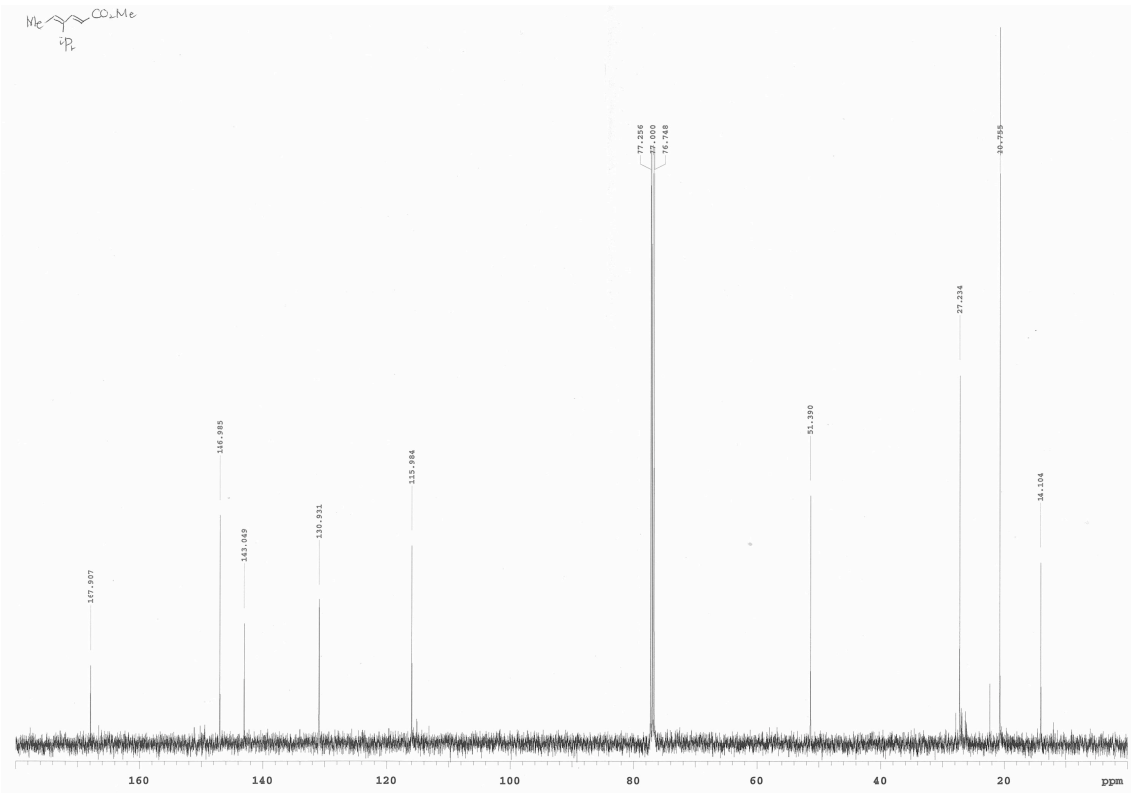
3.37
6.08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120
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80
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40
20
ppm

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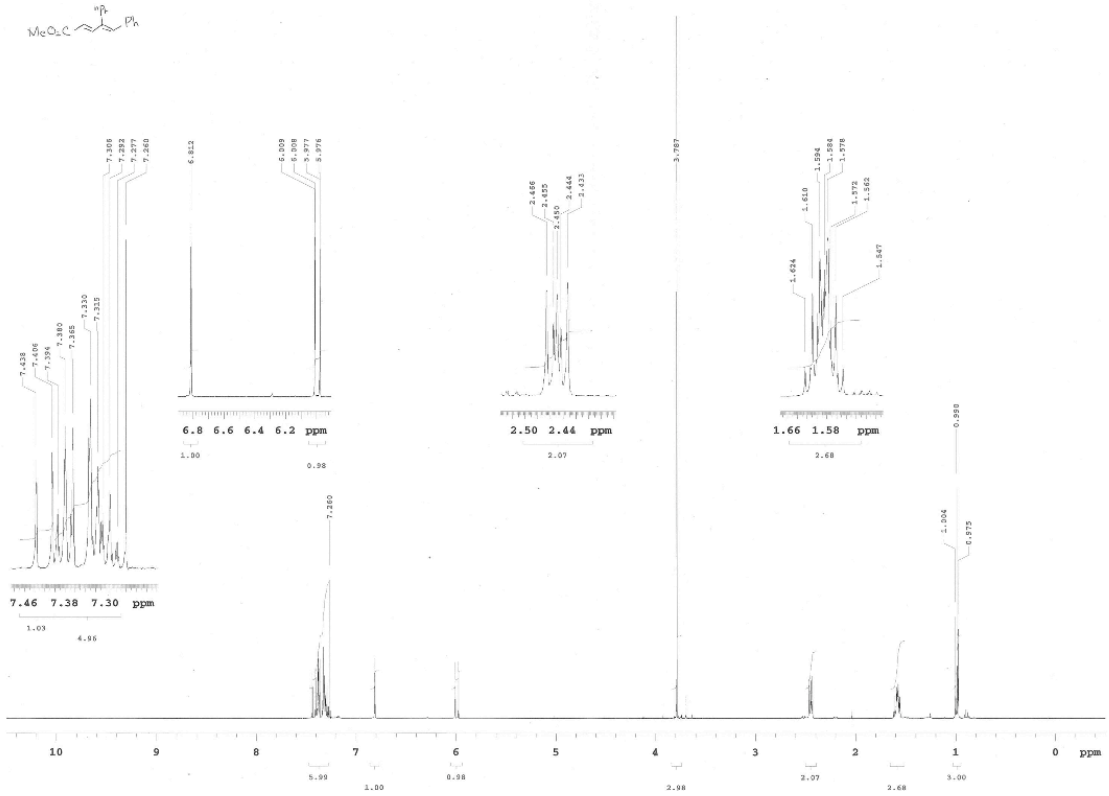
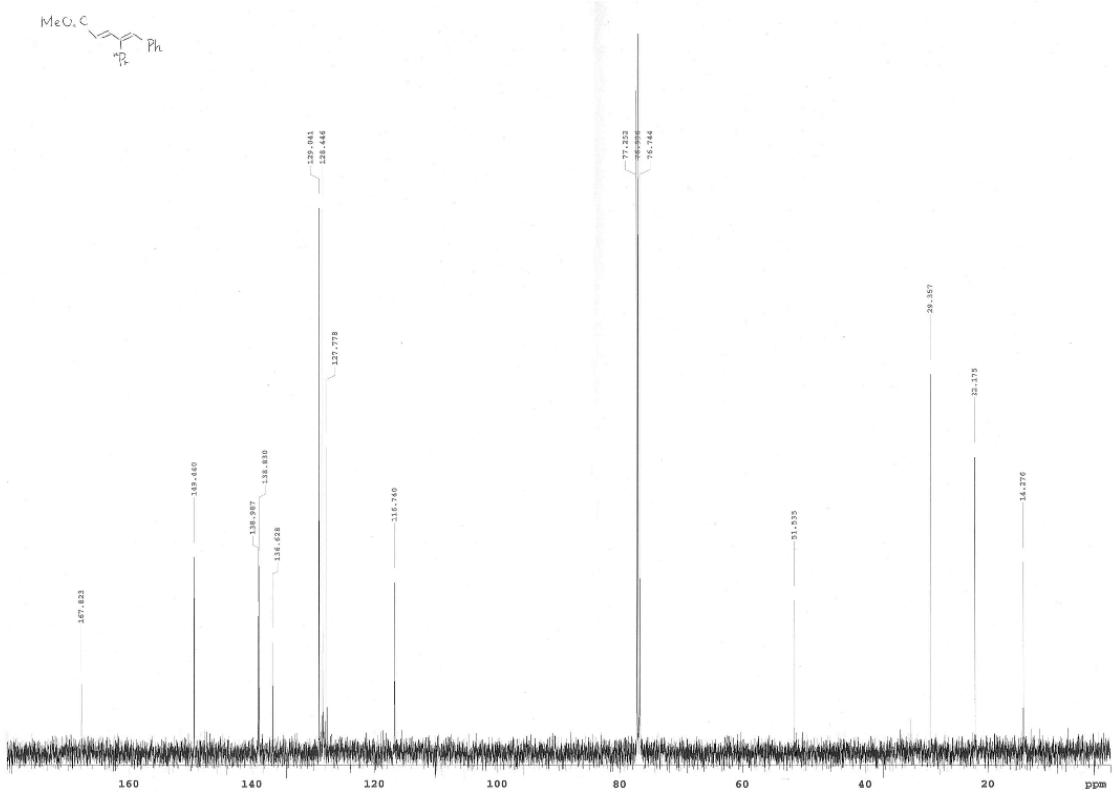
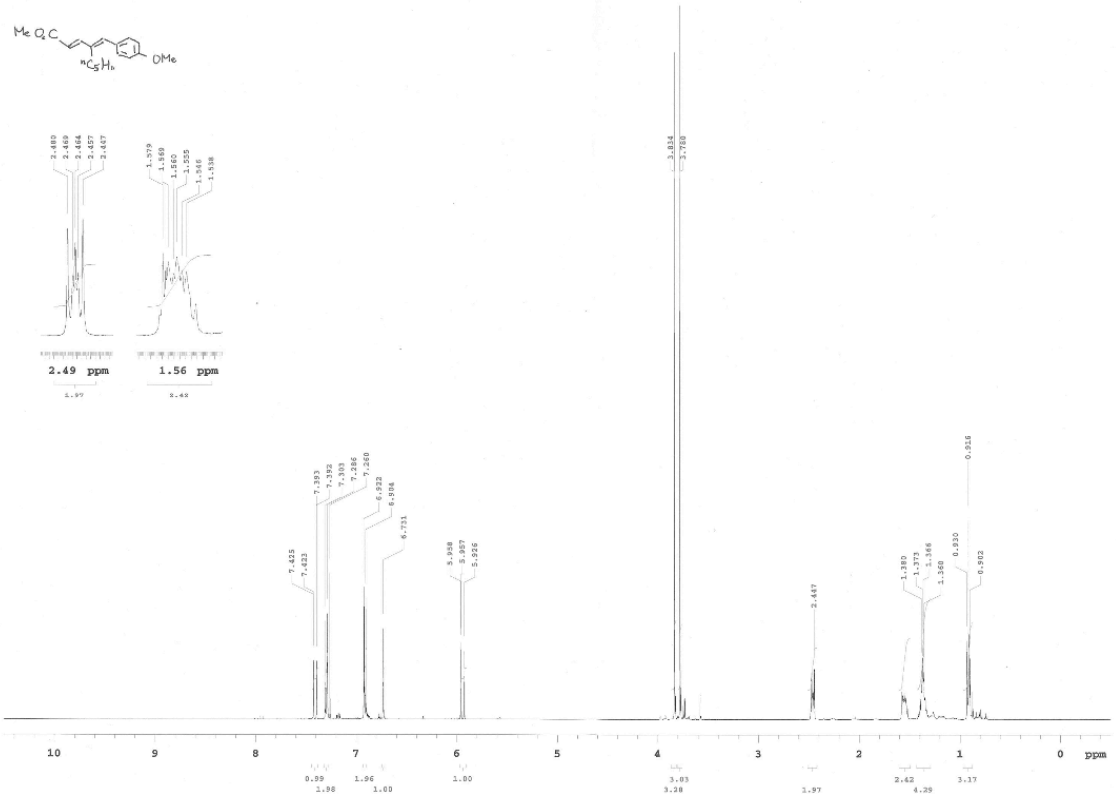
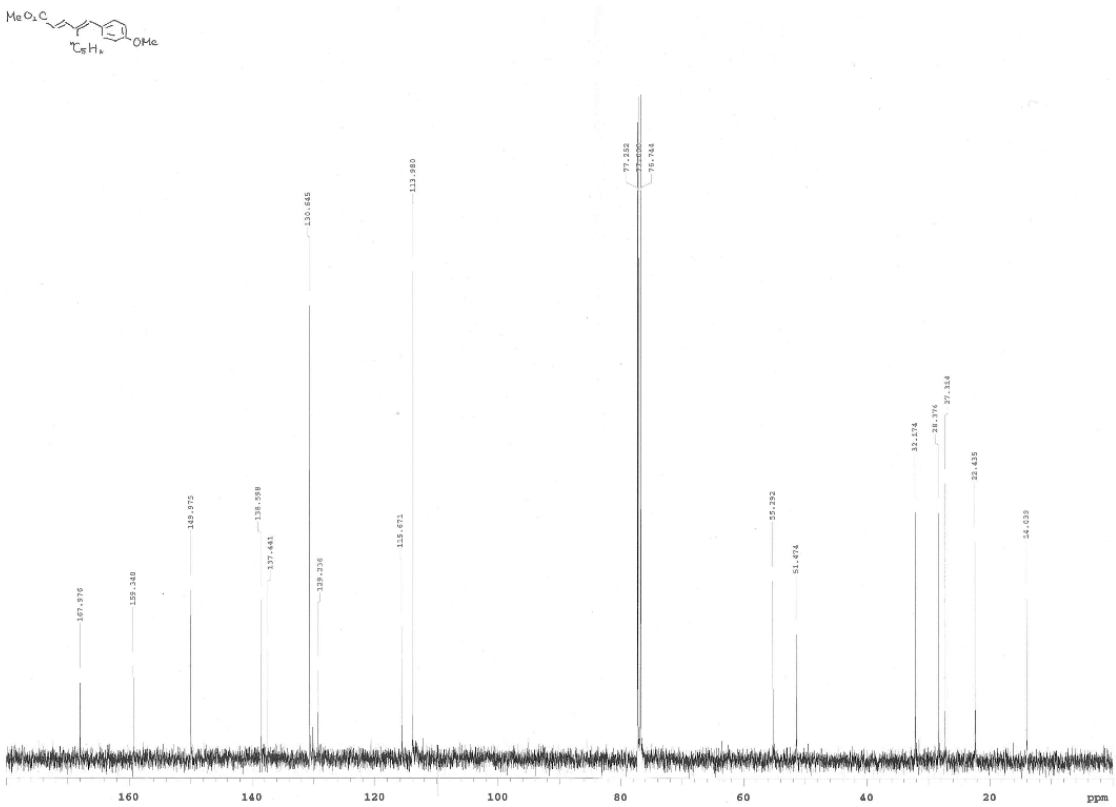

MeO2C
Ph
iPr
7.46 7.38 7.30 ppm
6.8 6.6 6.4 6.2 ppm
2.50 2.44 ppm
1.66 1.58 ppm
10 9 8 7 6 5 4 3 2 1 0 ppm


MeO2C
Ph
iPr
160 140 120 100 80 60 40 20 ppm

4ag





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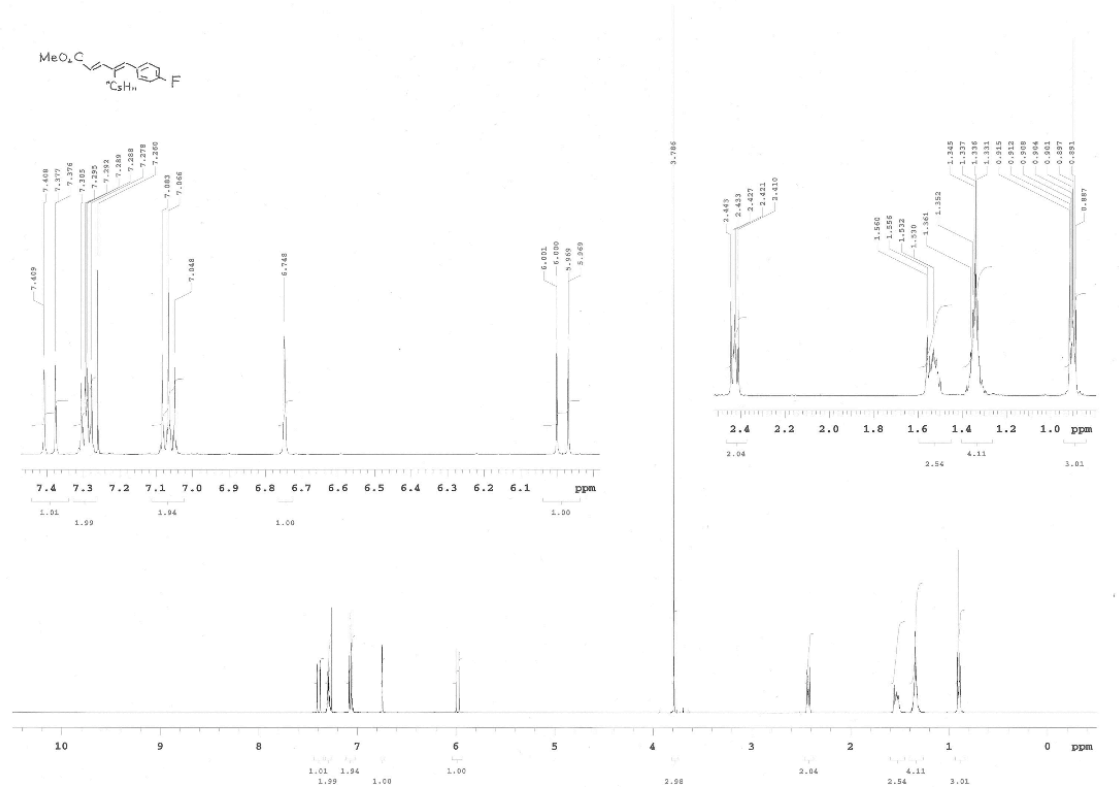

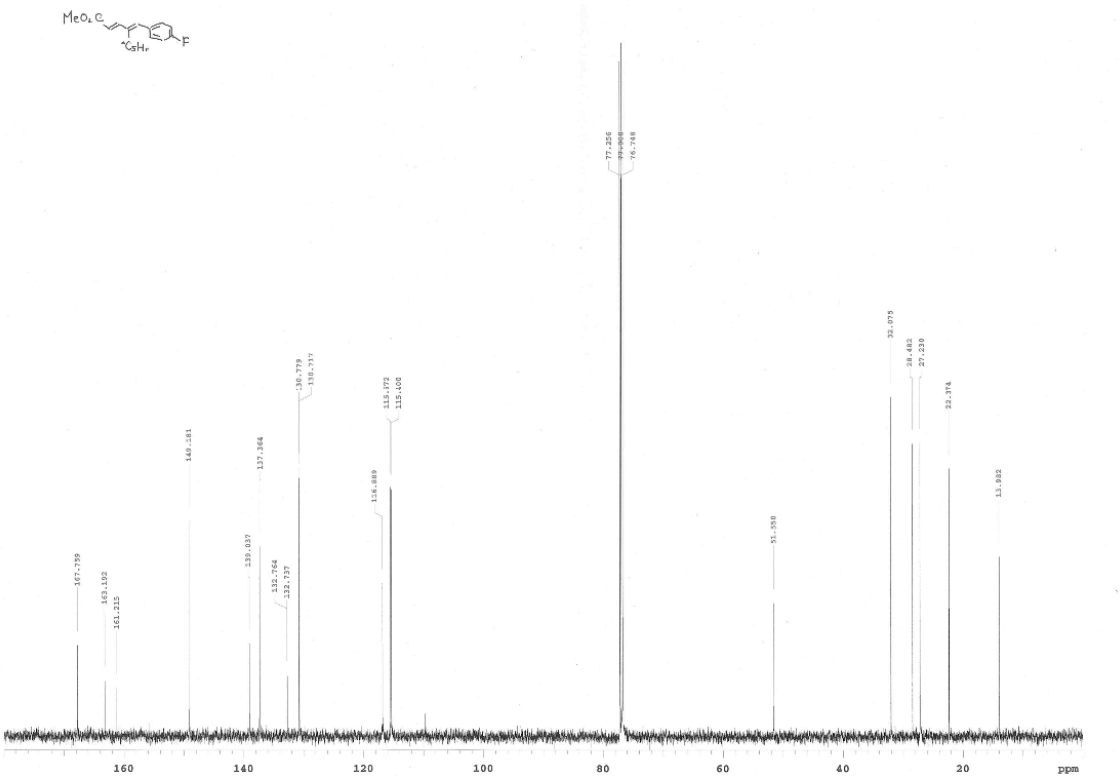

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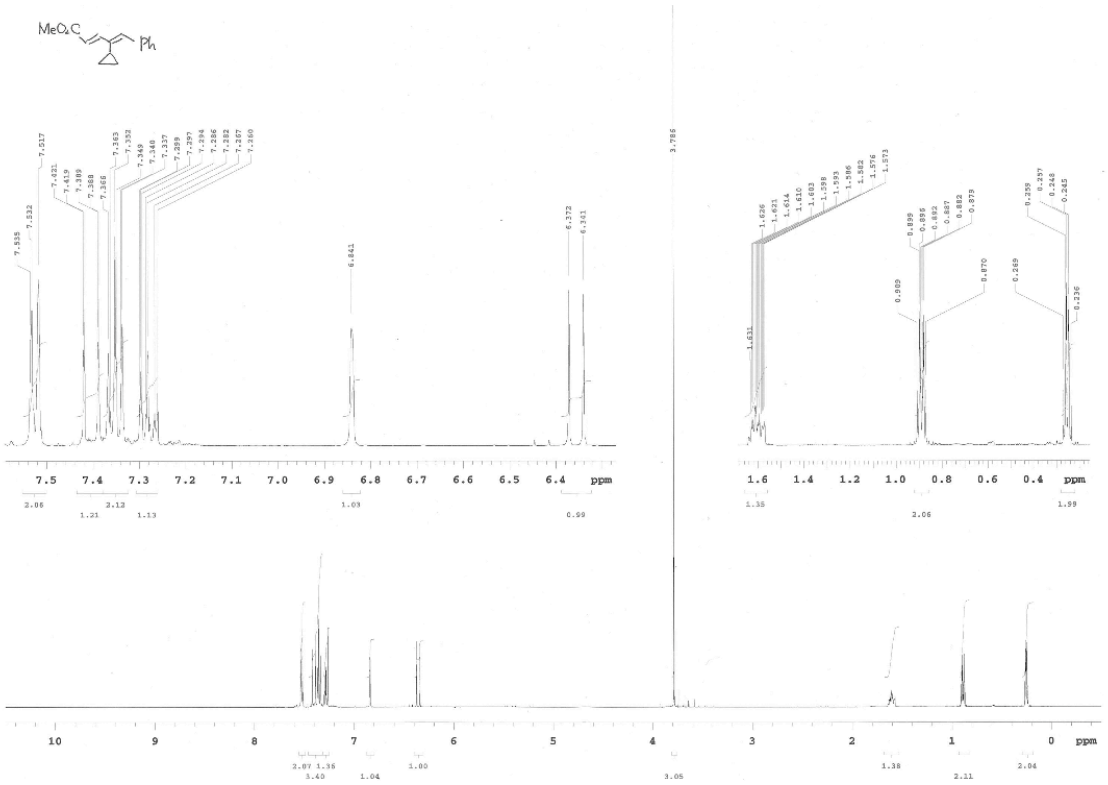

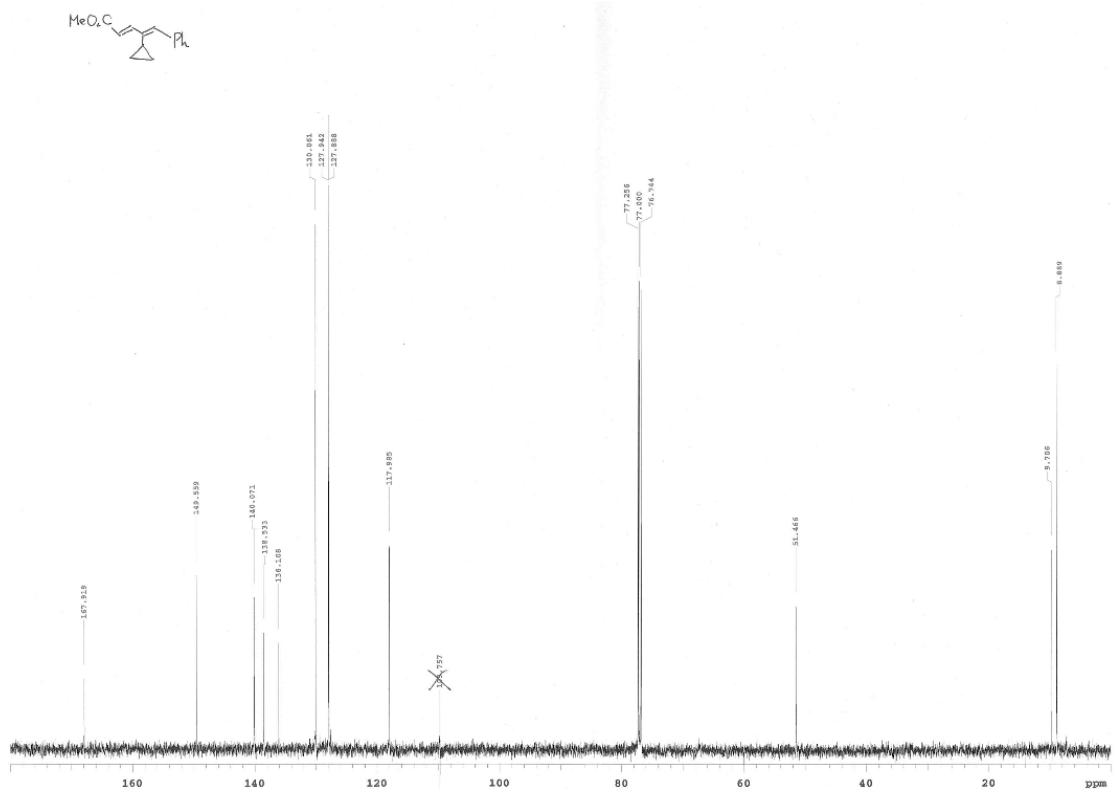

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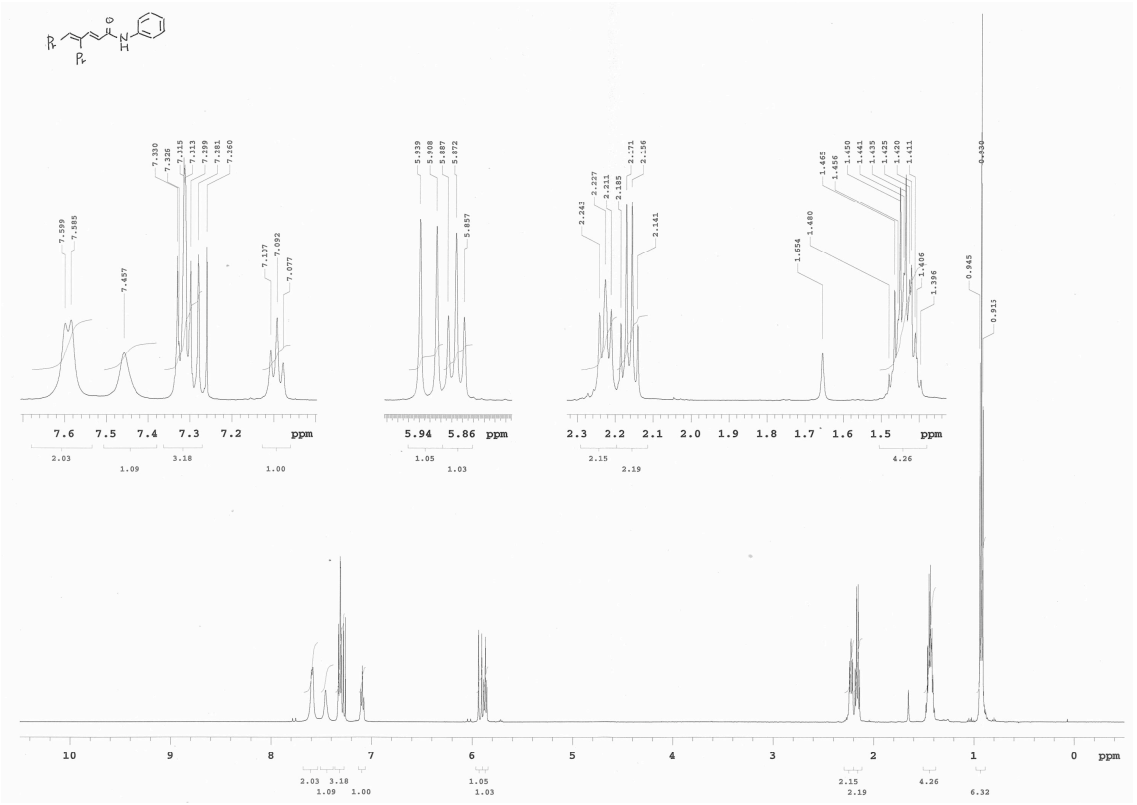

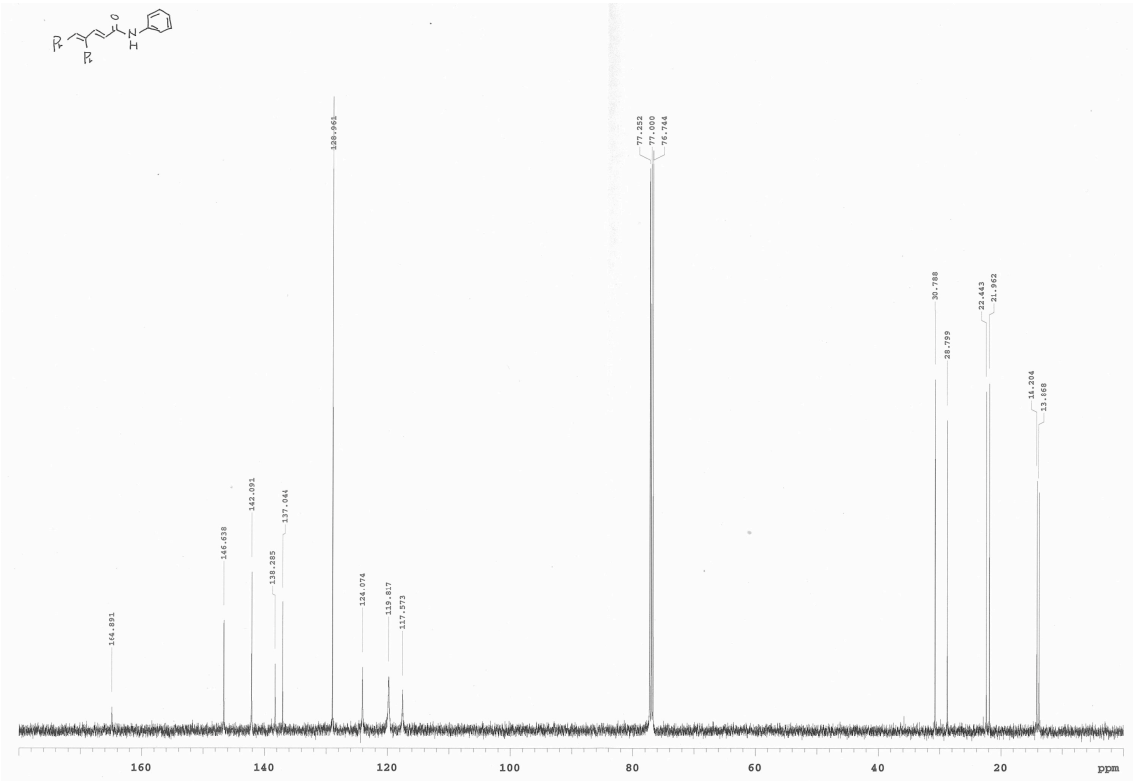

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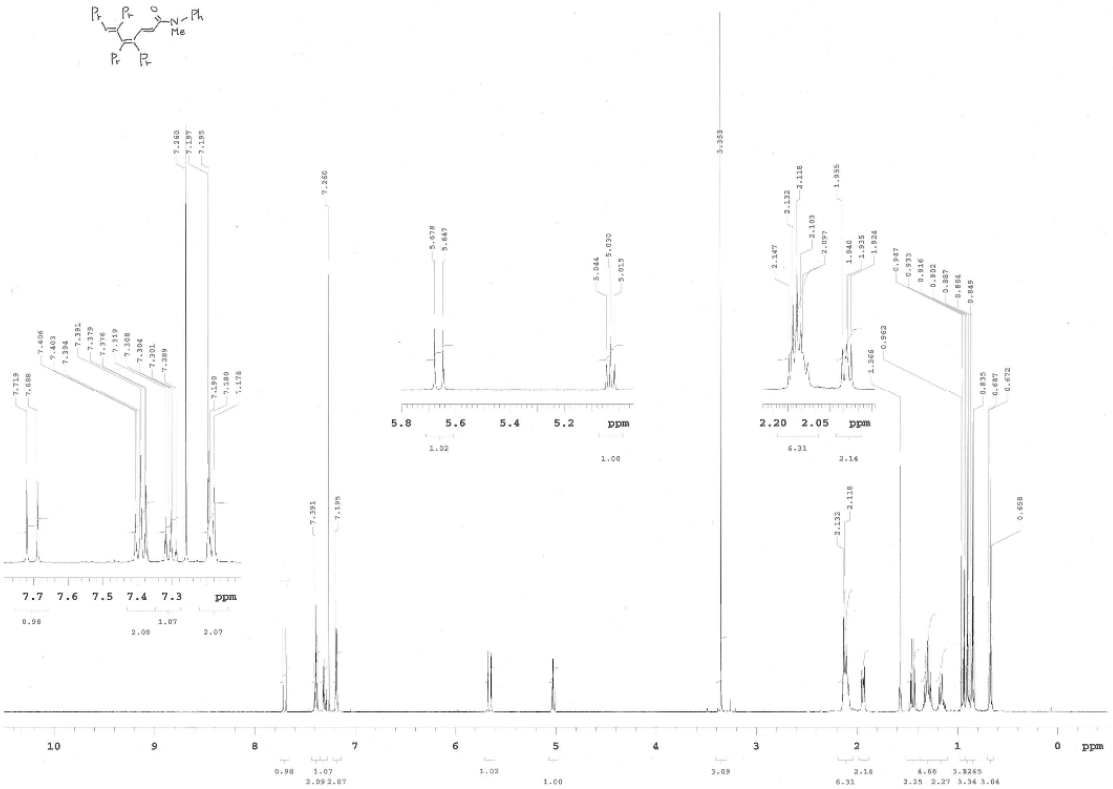
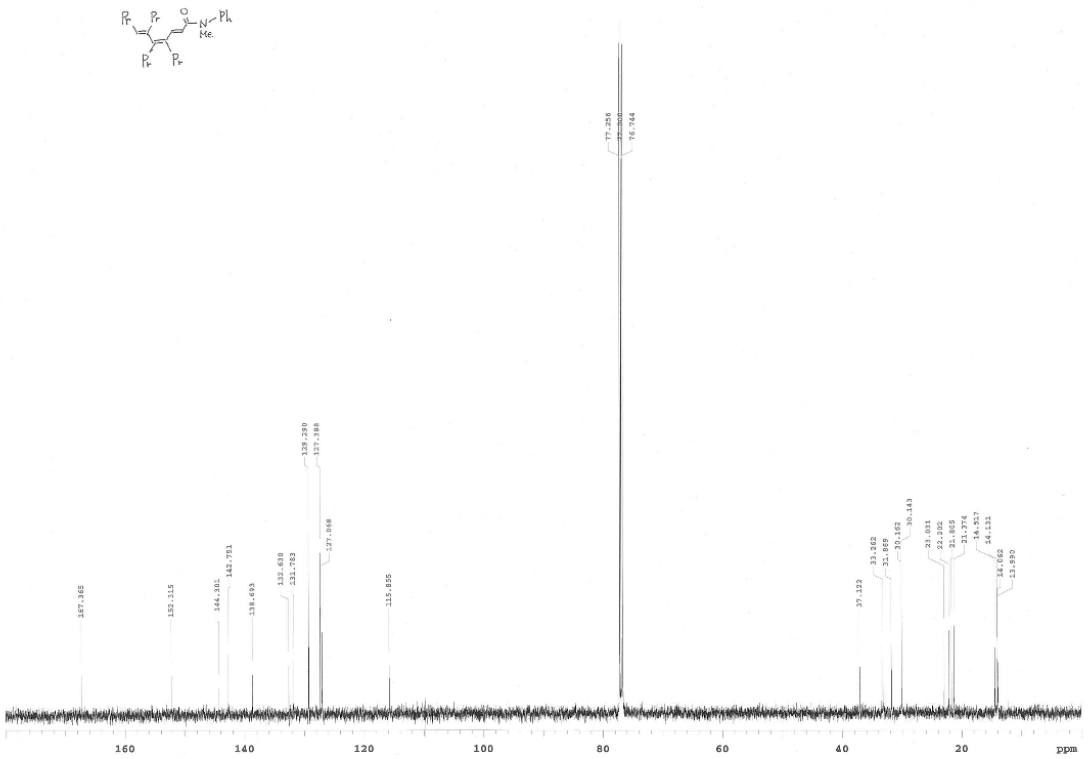
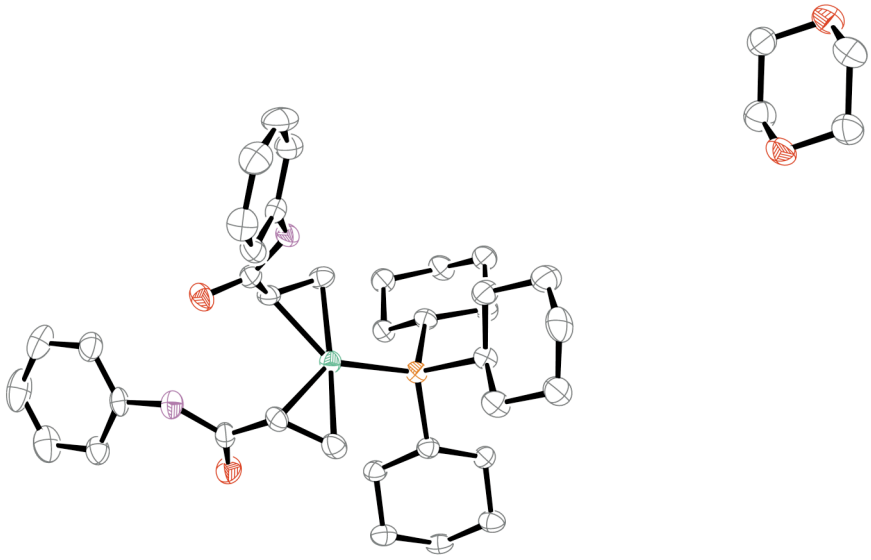




ORTEP Drawing of A'



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Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.20 X 0.20 X 0.20 mm
Crystal System	triclinic
Lattice Type	Primitive
Detector Position	49.95 mm
Pixel Size	0.068 mm
Lattice Parameters	a = 9.847(3) Å b = 10.050(3) Å c = 19.516(6) Å α = 96.441(5)° β = 99.758(7)° γ = 94.550(3)° *V* = 1881.8(11) Å^3
Space Group	P-1 (#2)
Z value	2
D_{calc}	1.273 g/cm^3
F_{000}	776.00
m(MoKa)	6.001 cm^{-1}
Detector	Rigaku Saturn
Goniometer	Rigaku AFC10
Radiation	MoKa (l = 0.71070 Å)

	graphite monochromated
Detector Aperture	70 mm x 70 mm
Data Images	720 exposures
w oscillation Range (c=45.0, f=0.0)	-110.0 - 70.0°
Exposure Rate	80.0 sec./ °
Detector Swing Angle	-19.93°
w oscillation Range (c=45.0, f=90.0)	-110.0 - 70.0°
Exposure Rate	80.0 sec./°
Detector Swing Angle	-19.93°
Detector Position	49.95 mm
Pixel Size	0.068 mm
$2q_{max}$	54.9°
No. of Reflections Measured	Total: 14217
	Unique: 8099 (R_{int} = 0.063)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.761 - 0.887)
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F^2
Function Minimized	S w (Fo^2 - Fc^2)^2
Least Squares Weights	1/[0.8500s(Fo^2)]/(4Fo^2)
$2q_{max}$ cutoff	54.9°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	8099
No. Variables	492
Reflection/Parameter Ratio	16.46
Residuals: R1 (I>2.00s(I))	0.0644
Residuals: R (All reflections)	0.1184
Residuals: wR2 (All reflections)	0.1037
Goodness of Fit Indicator	1.024
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	1.03 e/Å^3
Minimum peak in Final Diff. Map	-0.85 e/Å^3