Supporting Information for:

Selective Synthesis of Dienes and Trienes via Nickel-Catalyzed Intermolecular Cotrimerization of Acrylates and Alkynes

Hiroaki Horie, Takuya Kurahashi*, and Seijiro Matsubara*

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto-daigaku Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

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 μm). 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.

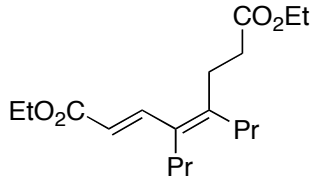
Experimental Procedure and Characterization Data for Products

General procedure for the nickel-catalyzed synthesis of conjugated diene.

Method A. The reaction was performed in a 5 mL sealed vessel equipped with a Teflon-coated magnetic stirrer tip. An acrylate (2.0 mmol, 2.0 equiv.) and an alkyne (0.50 mmol) were added to a solution of bis(1,5-dicyclooctadiene)nickel (6.8 mg, 0.025 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (21 mg, 0.050 mmol) and pottasium *tert*-butoxide (6.2 mg, 0.055 mmol) in 1,4-dioxane (2 mL) in a dry box. The VIAL was taken outside the dry box and heated at 100 ºC 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/ethyl acetate = 10:1) to give the corresponding conjugated diene.

Method B. The reaction was performed in a 15 mL sealed tube equipped with a Teflon-coated magnetic stirrer. An acrylate (2.0 mmol, 2.0 equiv.) was added to a solution of bis(1,5-dicyclooctadiene)nickel (14 mg, 0.050 mmol), 1,3-bis(2,6-diisopropylphenyl)-imidazolium chloride (43 mg, 0.10 mmol) and pottasium *tert*-butoxide (12 mg, 0.11 mmol) in 1,4-dioxane (0.5 mL) in a dry box and the VIAL was taken outside the dry box. To the mixture was added dropwise a solution of alkyne (0.50 mmol) in 1,4-dioxane (1.5 mL) at 100 ºC over a period of 20 h. The resulting mixture was stirred for 4 h and 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/ethyl acetate = 10:1) to give the corresponding conjugated diene.

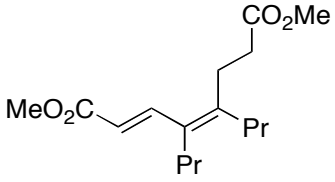
Diethyl (2*E*,4*Z*)-4,5-dipropyl-2,4-octadienedioate (3aa).



Yield: 82% (Method A), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, *J* = 15.5 Hz, 1H), 5.85 (d, *J* = 15.5 Hz, 1H), 4.21 (q, *J* = 7.0 Hz, 2H), 4.12 (q, *J* = 7.0 Hz, 2H), 2.62 (t, *J* = 8.0 Hz, 2H), 2.38 (t, *J* = 8.0 Hz, 2H), 2.21 (t, *J* = 8.0 Hz, 2H), 2.15 (t, *J* = 8.0 Hz, 2H), 1.44 (m, 2H), 1.38 (m, 2H), 1.31 (t, *J* = 7.0 Hz, 3H), 1.25 (t, *J* = 7.0 Hz, 3H), 0.95 (t, *J* = 7.0 Hz, 3H), 0.93 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.70, 167.88, 147.45, 142.00, 132.30, 116.71, 60.51, 60.18, 35.55, 34.31, 30.26, 27.28, 22.49, 21.97, 14.39, 14.35, 14.30, 14.18. IR (neat): 2961, 2907,

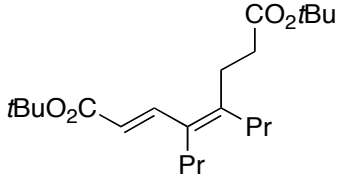
1732, 1712, 1614, 1466, 1300, 1261, 1177, 1040, 980, 860, 739 cm^{-1}. MS (EI): *m/z* (%): 310 ($[M]^+$, 38), 267 ($[M–Pr]^+$, 47), 264 (61), 236 ($[M–CO_2Et–H]^+$, 100), 219 (73), 189 (80), 163 (86). HRMS calcd for $C_{18}H_{30}O_4$: 310.2144. Found: 310.2140.

Dimethyl (2*E*,4*Z*)-4,5-dipropyl-2,4-octadienedioate (3ba).



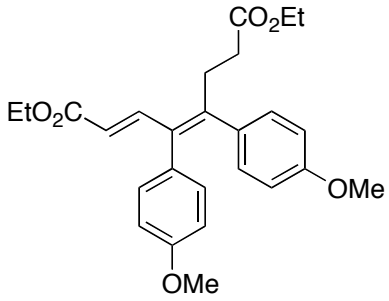
Yield: 71% (Method A), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 15.5 Hz, 1H), 5.84 (d, *J* = 15.5 Hz, 1H), 3.74 (s, 3H), 3.65 (s, 3H), 2.60 (t, *J* = 8.0 Hz, 2H), 2.38 (t, *J* = 8.0 Hz, 2H), 2.18 (t, *J* = 8.0 Hz, 2H), 2.12 (t, *J* = 8.0 Hz, 2H), 1.42 (m, 2H), 1.35 (m, 2H), 0.93 (t, *J* = 7.0 Hz, 3H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.03, 168.21, 147.50, 142.07, 132.30, 116.27, 51.60, 51.42, 35.50, 33.98, 30.17, 27.23, 22.42, 21.92, 14.35, 14.24. IR (neat): 2959, 2872, 1741, 1715, 1614, 1435, 1304, 1265, 1171, 1022, 860, 739 cm^{-1}. MS (EI): *m/z* (%): 282 ($[M]^+$, 16), 239 ($[M–Pr]^+$, 42), 222 ($[M–CO_2Me–H]^+$, 100), 189 (53), 163 (60). HRMS calcd for $C_{16}H_{26}O_4$: 282.1831. Found: 282.1842. Anal calcd for $C_{16}H_{26}O_4$: C, 68.06; H, 9.28. Found: C, 68.26; H, 9.27.

Di*tert*-butyl (2*E*,4*Z*)-4,5-dipropyl-2,4-octadienedioate (3ca).



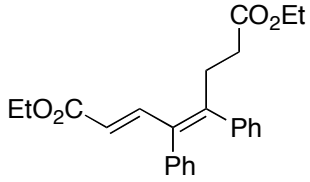
Yield: 49% (Method A), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 15.5 Hz, 1H), 5.76 (d, *J* = 15.5 Hz, 1H), 2.56 (t, *J* = 8.0 Hz, 2H), 2.30 (t, *J* = 8.0 Hz, 2H), 2.19 (t, *J* = 8.0 Hz, 2H), 2.13 (t, *J* = 8.0 Hz, 2H), 1.50 (s, 9H), 1.43 (s, 9H), 1.50-1.38 (m, 4H), 0.93 (t, *J* = 7.0 Hz, 3H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.08, 167.34, 147.22, 141.23, 132.05, 118.33, 80.42, 79.93, 35.48, 35.44, 30.24, 28.22, 28.07, 27.26, 22.48, 21.96, 14.37, 14.31. IR (neat): 2965, 1730, 1709, 1614, 1456, 1368, 1308, 1258, 1150, 982, 849, 754 cm^{-1}. MS (FAB): *m/z* (%): 367 ($[M+H]^+$, 15), 311 ($[M+H–H_2C=C(CH_3)_2]^+$, 10), 255 ($[M+H–H_2C=C(CH_3)_2]^+$, 100), 237 (50), 219(50). HRMS calcd for $C_{22}H_{38}O_4$: 366.2770. Found: 366.2764.

Diethyl (2*E*,4*Z*)-4,5-bis(4-methoxyphenyl)-2,4-octadienedioate (3ab).



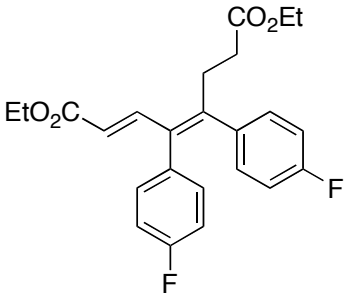
Yield: 82% (Method B), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, *J* = 15.5 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.82 (d, *J* = 9.0 Hz, 2H), 6.68 (d, *J* = 9.0 Hz, 2H), 6.62 (d, *J* = 9.0 Hz, 2H), 5.55 (d, *J* = 15.5 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 4.09 (q, *J* = 7.0 Hz, 2H), 3.73 (s, 3H), 3.71 (s, 3H), 3.11 (t, *J* = 8.0 Hz, 2H), 2.37 (t, *J* = 8.0 Hz, 2H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.24 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.52, 167.60, 158.26, 158.07, 146.94, 143.21, 135.90, 133.31, 131.81, 131.23, 130.37, 121.88, 113.38, 113.16, 60.50, 60.24, 55.06, 33.34, 29.55, 14.29, 14.18. IR (neat): 2980, 1732, 1712, 1607, 1508, 1292, 1248, 1175, 1034, 978, 868, 835, 600 cm^{-1}. MS (EI): *m/z* (%): 438 ($[M]^+$, 100), 346 (90), 277 (80). HRMS calcd for $C_{26}H_{30}O_6$: 438.2042. Found: 438.2032. Anal Calcd for $C_{26}H_{30}O_6$: C, 71.21; H, 6.90. Found: C, 71.10; H, 6.99.

Diethyl (2*E*,4*Z*)-4,5-diphenyl-2,4-octadienedioate (3ac).



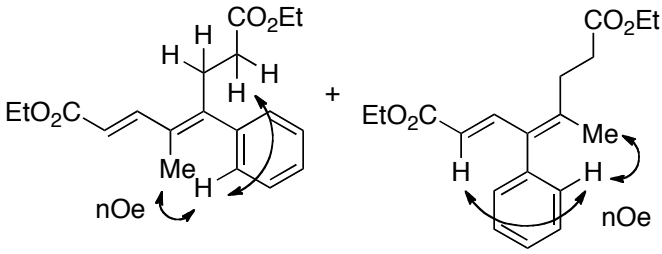
Yield: 68% (Method B), Yield: 49% (Method A), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, *J* = 15.5 Hz, 1H), 7.13-7.30 (m, 6H), 6.94-6.89 (m, 4H), 5.53 (d, *J* = 15.5 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 4.10 (q, *J* = 7.0 Hz, 2H), 3.15 (t, *J* = 8.0 Hz, 2H), 2.39 (t, *J* = 8.0 Hz, 2H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.24 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.43, 167.47, 147.48, 142.51, 140.95, 138.62, 136.82, 130.63, 129.00, 127.80, 127.67, 126.83, 126.60, 122.47, 60.55, 60.33, 33.16, 29.49, 14.27, 14.17. IR (neat): 2982, 1732, 1713, 1614, 1443, 1368, 1292, 1175, 1034, 978, 868, 770, 700, 598 cm^{-1}. MS (EI): *m/z* (%): 378 ($[M]^+$, 18), 332 ($[M–OEt–H]^+$, 89), 304 ([M–CO_2Et–H], 86), 286 (100), 258 (85), 217 (93). HRMS calcd for $C_{24}H_{26}O_4$: 378.1831. Found: 378.1828.

Diethyl (2*E*,4*Z*)-4,5-bis(4-fluorophenyl)-2,4-octadienedioate (3ad).



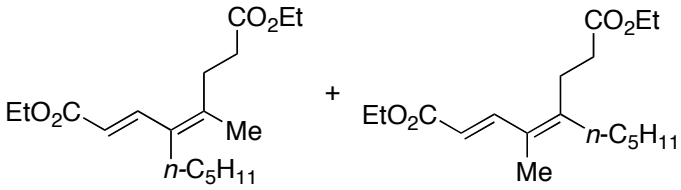
Yield: 30% (Method B), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, *J* = 15.5 Hz, 1H), 6.91-6.78 (m, 8H), 5.50 (d, *J* = 15.5 Hz, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 4.09 (q, *J* = 7.0 Hz, 2H), 3.12 (t, *J* = 8.0 Hz, 2H), 2.37 (t, *J* = 8.0 Hz, 2H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.24 (t, *J* = 7.0 Hz, 3H).). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.21, 167.22, 161.54 (d, J_{CF} = 245 Hz), 146.77, 142.20, 136.65, 136.25, 134.38, 132.17 (d, J_{CF} = 8.1 Hz), 130.67 (d, J_{CF} = 8.0 Hz), 122.83, 115.03 (d, J_{CF} = 21.0 Hz), 114.90 (d, J_{CF} = 21.0 Hz), 60.63, 60.44, 33.03, 29.55, 14.26, 14.16. IR (neat): 2983, 1733, 1713, 1615, 1602, 1506, 1292, 1223, 1178, 1159, 1046, 978, 838, 736 cm^{-1}. MS (EI): *m/z* (%): 414 ([M]$^+$, 8) 368 ([M–OEt–H]$^+$, 32), 340 ([M–CO_2Et–H]$^+$, 45), 322 ([M–2OEt–2H]$^+$, 100), 294 ([M–CO_2Et–OEt–2H]$^+$, 75). HRMS calcd for $C_{24}H_{24}F_2O_4$: 414.1643. Found: 414.1650.

Diethyl (2*E*,4*E*)-4-methyl-5-phenyl-2,4-octadienedioate and Diethyl (2*E*,4*E*)-5-methyl-4-phenyl-2,4-octadienedioate (1.4:1 mixture) (3ae).



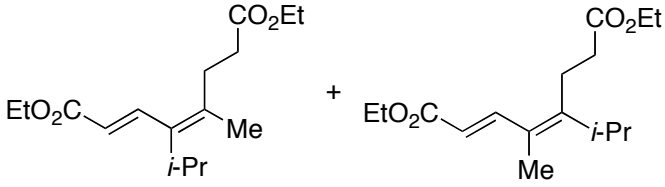
Yield: 53% (Method B), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (d, *J* = 16.0 Hz, 0.58H), 7.96 (d, *J* = 15.5 Hz, 0.42H), 7.36 (m, 2H), 7.30 (m, 1H), 7.10 (dd, *J* = 7.5, 1.5 Hz, 1.17H), 7.01 (dd, *J* = 8.0, 1.5 Hz, 0.83H), 5.99 (d, *J* = 16.0 Hz, 0.58H), 5.23 (d, *J* = 15.5 Hz, 0.42H), 4.25 (q, *J* = 7.0 Hz, 1.17H), 4.16 (q, *J* = 7.0 Hz, 0.83H), 4.15 (q, *J* = 7.0 Hz, 0.83H), 4.05 (q, *J* = 7.0 Hz, 1.17H), 2.97 (t, *J* = 8.0 Hz, 1.17H), 2.80 (t, *J* = 8.0 Hz, 0.83H), 2.54 (t, *J* = 8.0 Hz, 0.83H), 2.28 (t, *J* = 8.0 Hz, 1.17H), 1.68 (s, 1.75H), 1.63 (s, 1.25H), 1.34-1.19 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.52, 172.44, 167.61, 167.54, 146.95, 144.10, 142.29, 142.13, 141.74, 139.16, 135.85, 129.49, 128.89, 128.50, 128.32, 128.28, 127.24, 126.99, 120.39, 119.05, 60.63, 60.43, 60.31, 60.14, 33.49, 33.21, 29.54, 29.24, 21.36, 16.31, 14.34, 14.27, 14.20, 14.12. IR (neat): 2981, 1732, 1712, 1617, 1443, 1368, 1293, 1177, 1036, 976, 861, 772, 704 cm^{-1}. MS (EI): *m/z* (%): 316 ([M]$^+$, 11), 270 ([M–OEt–H]$^+$, 45), 242 ([M–CO_2Et–H], 70), 196 ([M–CO_2Et–OEt–2H]$^+$, 65), 169 ([M–2CO_2Et–H], 80), 155 ([M–2CO_2Et–Me]$^+$, 100). HRMS calcd for $C_{19}H_{24}O_4$: 316.1675. Found: 316.1683.

Diethyl (2*E*,4*Z*)-5-methyl-4-*n*-pentyl-2,4-octadienedioate and Diethyl (2*E*,4*Z*)-4-methyl-5-*n*-pentyl-2,4-octadienedioate (1:1 mixture) (3af).



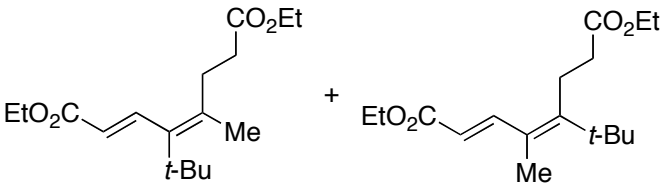
Yield: 50% (Method A), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 15.5 Hz, 0.5H), 7.75 (d, *J* = 15.5 Hz, 0.5H), 5.84 (d, *J* = 15.5 Hz, 1H), 4.21 (q, *J* = 7.0 Hz, 2H), 4.12 (q, *J* = 7.0 Hz, 1H), 4.11 (q, *J* = 7.0 Hz, 1H), 2.64 (m, 2H), 2.40 (m, 2H), 2.22 (t, *J* = 7.5 Hz, 1H), 2.17 (t, *J* = 8.0 Hz, 1H), 1.87 (s, 1.5H), 1.79 (s, 1.5H), 1.31 (m, 6H), 1.25 (m, 6H), 0.89 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.69, 172.62, 167.93, 167.77, 147.68, 142.80, 141.68, 132.54, 127.26, 116.95, 116.35, 60.51, 60.13, 34.13, 33.95, 33.64, 32.07, 32.05, 29.73, 28.56, 28.32, 28.14, 27.81, 22.54, 22.52, 19.87, 14.34, 14.17, 14.08, 14.03, 13.97. IR (neat): 2959, 2872, 1738, 1713, 1614, 1466, 1368, 1301, 1267, 1177, 1037, 978, 856, 731 cm^{-1}. HRMS calcd for $C_{18}H_{32}O_4$: 310.2144. Found: 310.2148. Anal calcd for $C_{18}H_{32}O_4$: C, 69.64; H, 9.74. Found: C, 69.77; H, 9.53.

Diethyl (2*E*,4*Z*)-4-isopropyl-5-methyl-2,4-octadienedioate and Diethyl (2*E*,4*E*)-5-isopropyl-4-methyl-2,4-octadienedioate (1:1 mixture) (3ag).



Yield: 60% (Method A), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 16.0 Hz, 0.5H), 7.75 (d, *J* = 16.0 Hz, 0.5H), 5.86 (d, *J* = 16.0 Hz, 0.5H), 5.85 (d, *J* = 16.0 Hz, 0.5H), 4.21 (q, 7.0 Hz, 2H), 4.14 (q, *J* = 7.0 Hz, 1H), 4.11 (q, *J* = 7.0 Hz, 1H), 3.03 (sept, *J* = 7.0 Hz, 0.5H), 2.92 (sept, *J* = 7.0 Hz, 0.5H), 2.59 (t, *J* = 8.0 Hz, 1H), 2.51 (t, *J* = 8.0 Hz, 1H), 2.37 (m, 2H). 1.29 (m, 6H), 1.04 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.86, 172.60, 167.66, 167.16, 151.90, 143.48, 142.56, 137.57, 135.97, 126.30, 120.42, 117.29, 60.48, 60.41, 60.21, 60.13, 35.85, 33.50, 31.71, 30.95, 29.48, 22.65, 20.91, 20.66, 18.65, 14.31, 14.19, 14.17, 13.63. IR (neat): 2976, 1738, 1712, 1614, 1460, 1368, 1290, 1177, 1038, 982, 858 cm^{-1}. MS (EI): *m/z* (%): 282 ([M]$^+$, 23), 239 ([M–CH(CH$_3$)$_2$]$^+$, 100), 208 ([M–CO$_2$Et–H], 88), 121 (79). HRMS calcd for $C_{16}H_{26}O_4$: 282.1831. Found: 282.1837. Anal calcd for $C_{16}H_{26}O_4$: C, 68.06; H, 9.28. Found: C, 68.29; H, 9.34.

Diethyl (2*E*,4*E*)-4-*tert*-butyl-5-methyl-2,4-octadienedioate and Diethyl (2*E*,4*E*)-5-*tert*-butyl-4-methyl-2,4-octadienedioate (3:1 mixture) (3ah).



Yield: 24% (Method A), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, *J* = 16.0 Hz, 0.25H), 7.34 (d, *J* = 16.0 Hz, 0.75H), 5.88 (d, *J* = 16.0 Hz, 0.25H), 5.59 (d, *J* = 16.0 Hz, 0.75H), 4.21 (q, *J* = 7.0 Hz, 0.5H), 4.20 (q, *J* = 7.0 Hz, 1.5 H), 4.13 (q, *J* = 7.0 Hz, 0.5H), 4.10 (q, *J* = 7.0 Hz, 1.5H), 2.73 (t, *J* = 8.5 Hz, 0.5H), 2.32 (m, 3.5H), 1.98 (s, 0.75H), 1.85 (s, 2.25H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.26 (s, 2.25H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.14 (s, 6.75H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.12, 172.43, 167.71, 166.53, 153.94, 148.53, 145.48, 140.19, 131.30, 128.43, 121.59, 117.17, 60.47, 60.29, 60.22, 60.13, 36.95, 35.80, 35.66, 33.54, 33.44, 31.04, 30.70, 26.06, 19.84, 17.45, 14.31, 14.26, 14.17. IR (neat): 2978, 1736, 1721, 1638, 1613, 1466, 1368, 1304, 1261, 1175, 1098, 1036, 988, 864 cm^{-1}. MS (FAB): *m/z* (%): 297 ($[M+H]^+$, 100), 296 ($[M]^+$, 22), 251 ($[M–OEt]^+$, 50), 205 (79). HRMS calcd for $C_{17}H_{28}O_4$: 296.1988. Found: 296.1978. Anal calcd for $C_{17}H_{28}O_4$: C, 68.89; H, 9.52. Found: C, 68.93; H, 9.56.

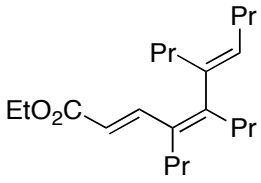
Procedure for the nickel-catalyzed synthesis of conjugated diene with IMes as a sterically less hindered ligand.

The reaction was performed in a 5 mL sealed vessel equipped with a Teflon-coated magnetic stirrer tip. Acrylate **1a** (2.0 mmol, 2.0 equiv.) and alkyne **2a** (0.50 mmol) were added to a solution of bis(1,5-dicyclooctadiene)nickel (6.8 mg, 0.025 mmol), 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (17 mg, 0.050 mmol) and pottasium *tert*-butoxide (6.2 mg, 0.055 mmol) in 1,4-dioxane (2 mL) in a dry box. The VIAL was taken outside the dry box and heated at 100 ºC 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 (eluted by hexane/ethyl acetate = 10:1) to give the corresponding conjugated diene **3aa** in 51% yield along with triene **4aa** in 21% yield.

General procedure for the nickel-catalyzed synthesis of conjugated triene.

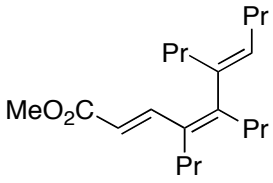
The reaction was performed in a 5 mL sealed vessel equipped with a Teflon-coated magnetic stirrer tip. An acrylate (0.75 mmol, 1.5 equiv.) and an alkyne (1.0 mmol) were added to a solution of bis(1,5-dicyclooctadiene)nickel (14 mg, 0.050 mmol), tris(4-methoxyphenyl)phophine (35 mg, 0.10 mmol) in MeCN (2 mL) in a dry box. The VIAL was taken outside the dry box and heated at 80 ºC 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 (eluted by hexane/ethyl acetate = 40:1) to give the corresponding conjugated triene.

Ethyl (2*E*,4*Z*,6*E*)-4,5,6-tripropyl-2,4,6-decatrienoate (4aa).



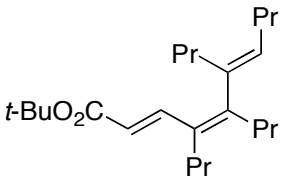
Yield: 92%, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, *J* = 16 Hz, 1H), 5.76 (d, *J* = 16 Hz, 1H), 5.00 (t, *J* = 7 Hz, 1H), 4.17 (q, *J* = 7.5 Hz, 2H), 2.25 (m, 2H), 2.20 (t, *J* = 8 Hz, 2H), 2.12 (m, 4H), 1.48-1.26 (m, 8H), 1.28 (t, *J* = 7.5 Hz, 3H), 0.96-0.88 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.15, 154.13, 146.16, 138.65, 132.58, 132.26, 114.71, 59.87, 33.13, 31.58, 30.09, 30.01, 22.99, 22.37, 21.83, 21.30, 14.41, 14.33, 14.17, 13.95. IR (neat): 2959, 2872, 1711, 1613, 1458, 1266, 1165, 1045, 991, 899, 853, 746 cm^{-1}. MS (EI): *m/z* (%): 320 ([M]$^+$, 100), 291 ([M–Et]$^+$, 86), 277 ([M–Pr]$^+$, 87), 247 ([M–CO_2Et]$^+$, 90). HRMS calcd for $C_{21}H_{36}O_2$: 320.2715. Found: 320.2708.

Methyl (2*E*,4*Z*,6*E*)-4,5,6-tripropyl-2,4,6-decatrienoate (4ba).



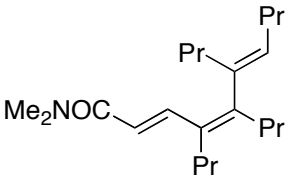
Yield: 94%, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 16 Hz, 1H), 5.77 (d, *J* = 16 Hz, 1H), 5.04 (t, *J* = 7.5 Hz, 1H), 3.71 (s, 3H), 2.25 (m, 2H), 2.20 (t, *J* = 7.5 Hz, 2H), 2.11 (m, 4H), 0.96-0.87 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.56, 154.34, 146.44, 138.72, 132.55, 132.31, 114.29, 51.19, 33.18, 31.65, 30.08, 30.02, 22.94, 22.36, 21.83, 21.33, 14.42, 14.30, 14.16, 13.86. IR (neat): 2957, 2872, 1722, 1614, 1456, 1433, 1267, 1165, 1045, 991, 898, 858, 748 cm^{-1}. MS (EI): *m/z* (%): 306 ([M]$^+$, 86), 263 ([M–Pr]$^+$, 100), 247 ([M–CO_2Me]$^+$, 65). HRMS calcd for $C_{20}H_{34}O_2$: 306.2559. Found: 306.2558.

***tert*-Butyl (2*E*,4*Z*,6*E*)-4,5,6-tripropyl-2,4,6-decatrienoate (4ca).**



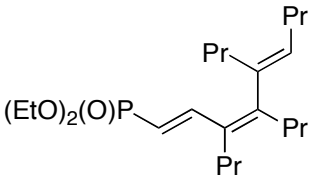
Yield: 75%, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, *J* = 16 Hz, 1H), 5.67 (d, *J* = 16 Hz, 1H), 5.04 (t, *J* = 7.5 Hz, 1H), 2.23 (m, 2H), 2.18 (t, *J* = 7 Hz, 2H), 2.11 (m, 4H), 1.47 (s, 9H), 1.45-1.24 (m, 8H), 0.95-0.87 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.48, 153.24, 145.06, 138.72, 132.60, 132.08, 116.77, 79.44, 33.14, 31.61, 30.05, 28.23, 23.05, 22.39, 21.83, 21.29, 14.45, 14.35, 14.16, 13.98. IR (neat): 2956, 2872, 1703, 1613, 1456, 1366, 1287, 1150, 988, 897, 856, 746 cm^{-1}. MS (EI): *m/z* (%): 348 ([M]$^+$, 14), 292 ([M–$(CH_3)_2C{=}CH_2$]$^+$, 100), 247 ([M–CO_2*t*-Bu]$^+$, 72). HRMS calcd for $C_{23}H_{40}O_2$: 348.3028.

(2*E*,4*Z*,6*E*)-*N*,*N*-Dimethyl-4,5,6-tripropyl-2,4,6-decatrienamide (4da).



Yield: 71%, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, *J* = 15 Hz, 1H), 6.17 (d, *J* = 15 Hz, 1H), 5.04 (t, *J* = 7.5 Hz, 1H), 3.08 (s, 3H), 3.00 (s, 3H), 2.27 (m, 2H), 2.18 (t, *J* = 8 Hz, 2H), 2.10 (m, 4H), 1.46-1.28 (m, 8H), 0.96-0.87 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.01, 152.33, 143.52, 138.64, 132.40, 131.76, 113.97, 37.34, 35.72, 33.24, 31.83, 30.20, 30.08, 22.99, 22.40, 21.80, 21.35, 14.52, 14.40, 14.18, 13.96. IR (neat): 2957, 2872, 1643, 1595, 1458, 1389, 1265, 1130, 990, 899, 844, 735 cm^{-1}. MS (EI): *m/z* (%): 319 ([M]$^+$, 80), 290 ([M–Et]$^+$, 46), 247 ([M–$CONMe_2$]$^+$, 74), 205 ([M–Pr–$CONMe_2$]$^+$, 100). HRMS calcd for $C_{21}H_{37}NO$: 319.2875. Found: 319.2873.

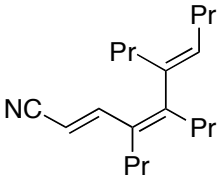
Diethyl (1*E*,3*Z*,5*E*)-3,4,5-tripropyl-1,3,5-nonatrienylphosphonate (4ea).



Yield: 83%, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (dd, *J* = 23.5, 17.5 Hz, 1H), 5.54 (dd, *J* = 20.5, 17.5 Hz, 1H), 5.03 (t, *J* = 7 Hz, 1H), 4.04 (m, 2H), 2.23 (m, 2H), 2.18 (t, *J* = 7.5 Hz, 2H), 2.09 (m, 4H), 1.43-1.24 (m, 8H), 1.30 (t, *J* = 7 Hz, 6H), 0.94-0.87 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.01, 149.19 (d, *J* = 7.6 Hz), 138.62, 132.79 (d, *J* = 22.5 Hz), 132.04, 109.44(d, *J* = 193 Hz), 61.39 (d, *J* = 5.3 Hz), 33.18, 31.65, 30.06, 29.66, 22.93, 22.28, 21.76, 21.33, 16.36 (d, *J* = 6.3 Hz), 14.46, 14.33, 14.15, 13.96. IR (neat): 2959, 2872, 1599, 1462, 1252, 1057, 1030, 961, 853, 818, 789, 735 cm^{-1}. MS (EI): *m/z* (%): 384 ([M]$^+$, 39), 355 ([M–Et]$^+$, 40), 341 ([M–Pr]$^+$, 58), 246 ([M–$P(OH)(OEt)_2$]$^+$, 99), 217 ([M–$P(OH)(OEt)_2$–Et]$^+$, 100), 203

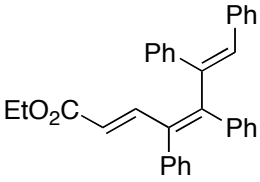
([M–P(OH)(OEt)$_2$–Pr]$^+$, 85). HRMS calcd for $C_{22}H_{41}O_3P$: 384.2793. Found: 384.2795. Anal calcd for $C_{22}H_{41}O_3P$: C, 68.72; H, 10.75. Found: C, 68.60; H, 10.79.

(2*E*,4*Z*,6*E*)-4,5,6-tripropyl-2,4,6-decatrienenitrile (4fa).



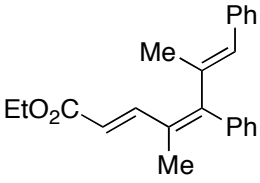
Yield: 22%, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (d, *J* = 16.5 Hz, 1H), 5.19 (d, *J* = 16.5 Hz, 1H), 5.02 (t, *J* = 7.5 Hz, 1H), 2.19 (m, 4H), 2.11 (m, 4H), 1.46-1.31 (m, 6H), 1.40 (sext, *J* = 8 Hz, 2H), 0.94 (t, *J* = 7.5 Hz, 6H), 0.90 (t, *J* = 7.5 Hz, 3H), 0.89 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.42, 151.60, 138.58, 132.96, 132.24, 119.93, 92.10, 33.12, 31.56, 30.00, 29.26, 22.86, 22.12, 21.77, 21.37, 14.44, 14.23, 14.12, 13.88. IR (neat): 2961, 2872, 2212, 1593, 1460, 1377, 1300, 972, 899, 812, 746 cm^{-1}. MS (EI): *m/z* (%): 273 ([M]$^+$, 25), 244 ([M–Et]$^+$, 24), 230 ([M–Pr]$^+$, 100). HRMS calcd for $C_{19}H_{31}N$: 273.2457. Found: 273.2446. Anal calcd for $C_{19}H_{31}N$: C, 83.45; H, 11.43; N, 5.12. Found: C, 83.16; H, 11.33; N, 4.98.

Ethyl (2*E*,4*Z*,6*E*)-4,5,6,7-tetraphenyl-2,4,6-heptatrienoate (4ac).



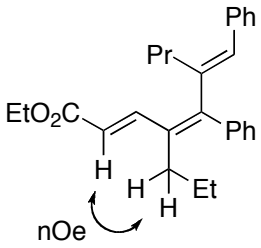
Yield: 77%, pale yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (d, *J* = 15.5 Hz, 1H), 7.19 (m, 8H), 7.13 (m, 7H), 7.00-6.94 (m, 5H), 6.89 (s, 1H), 6.82 (m, 1H), 5.69 (d, *J* = 15.5 Hz, 1H), 4.12 (q, *J* = 7 Hz, 2H), 1.18 (t, *J* = 7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.45, 151.69, 146.21, 141.32, 138.90, 138.75, 138.33, 136.44, 134.52, 131.10, 130.47, 129.68, 129.56, 128.19, 128.06, 128.03, 127.35, 127.32, 127.03, 127.00, 121.75, 60.11, 14.12. The configuration of triene **4ac** was unambiguously confirmed by an X-ray crystal structure analysis.

Ethyl (2*E*,4*E*,6*E*)-4,6-dimethyl-5,7-diphenyl-2,4,6-heptatrienoate (4ae).



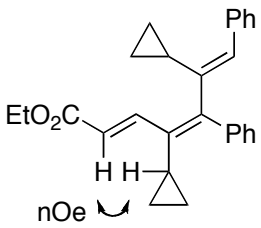
Yield: 86% (9/1), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (d, *J* = 15.5 Hz, 1H), 7.37 (m, 6H), 7.27 (m, 4H), 6.49 (s, 1H), 6.00 (d, *J* = 15.5 Hz, 1H), 4.21 (q, *J* = 7.5 Hz, 2H), 1.88 (s, 3H), 1.78 (s, 3H), 1.29 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.71, 153.74, 145.80, 139.67, 137.79, 137.38, 132.65, 129.38, 129.11, 128.87, 128.19, 128.14, 127.65, 126.81, 117.71, 60.14, 18.16, 16.32, 14.30.

Ethyl (2*E*,4*E*,6*E*)-6-benzylidene-5-phenyl-4-propyl-2,4-nonadienoate (4ai).



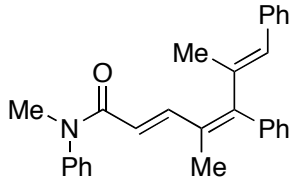
Yield: 81% (9/1), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 16 Hz, 1H), 7.38-7.31 (m, 8H), 7.26 (m, 2H), 6.47 (s, 1H), 5.98 (d, *J* = 16 Hz, 1H), 4.20 (q, *J* = 7 Hz, 2H), 2.24 (m, 2H), 2.05 (t, *J* = 7.5 Hz, 2H), 1.49 (sext, *J* = 7.5 Hz, 2H), 1.40 (sext, *J* = 7.5 Hz, 2H), 1.29 (t, *J* = 7 Hz, 3H), 0.83 (t, *J* = 7.5 Hz, 3H), 0.81 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.77, 152.71, 145.18, 143.01, 139.92, 137.41, 135.40, 132.55, 128.89, 128.79, 128.21, 128.12, 127.51, 126.80, 117.29, 60.12, 32.10, 31.79, 22.81, 21.35, 14.28, 14.25, 14.29. IR (neat): 2959, 2872, 1713, 1614, 1491, 1454, 1292, 1258, 1175, 1038, 860, 748, 700 cm^{-1}. MS (EI): *m/z* (%): 388 ($[M]^+$, 100), 359 ($[M–Et]^+$, 42), 345 ($[M–Pr]^+$, 25), 315 ($[M–CO_2Et]^+$, 73). HRMS calcd for $C_{27}H_{32}O_2$: 388.2402. Found: 388.2391.

Ethyl (2*E*,4*Z*,6*E*)-4,6-dicyclopropyl-5,7-diphenyl-2,4,6-heptatrienoate (4aj).



Yield: 60% (7/3), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (d, *J* = 15.5 Hz, 0.3H), 7.82 (d, *J* = 15.5 Hz, 0.7H), 7.60 (d, *J* = 7.5 Hz, 1.4H), 7.45-7.08 (m, 8.6H), 6.48 (d, *J* = 15.5 Hz, 0.3H), 6.44 (d, *J* = 15.5 Hz, 0.7H), 6.37 (s, 0.7H), 4.99 (d, *J* = 10 Hz, 0.3H), 4.25 (q, *J* = 7 Hz, 0.6H), 4.22 (q, *J* = 7 Hz, 1.4H), 1.82 (m, 1H), 1.58 (m, 1H), 1.33 (t, *J* = 7 Hz, 0.9H), 1.30 (t, *J* = 7 Hz, 2.1H), 0.84 (m, 0.6H), 0.70 (m, 1.4H), 0.65 (m, 0.6H), 0.59 (m, 2H), 0.36 (m, 1.4H), 0.02 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.90, 167.75, 153.34, 151.81, 146.99, 146.65, 142.19, 141.39, 139.74, 139.71, 139.09, 137.20, 135.98, 135.86, 133.13, 130.25, 129.91, 129.44, 129.33, 128.15, 128.09, 127.79, 127.71, 127.58, 127.26, 127.21, 126.77, 126.53, 118.26, 118.09, 60.09, 59.97, 14.36, 14.27, 14.06, 12.47, 11.93, 11.83, 9.45, 9.22, 8.11, 7.33. IR (neat): 3080, 3001, 1713, 1614, 1443, 1366, 1287, 1159, 1030, 986, 941, 864, 758, 700 cm^{-1}. MS (EI): *m/z* (%): 384 ($[M]^+$, 88), 355 ($[M–Et]^+$, 18), 311 ($[M–CO_2Et]^+$, 100), 269 ($[M–CO_2Et–C_3H_6]^+$, 63). HRMS calcd for $C_{27}H_{28}O_2$: 384.2089. Found: 384.2076.

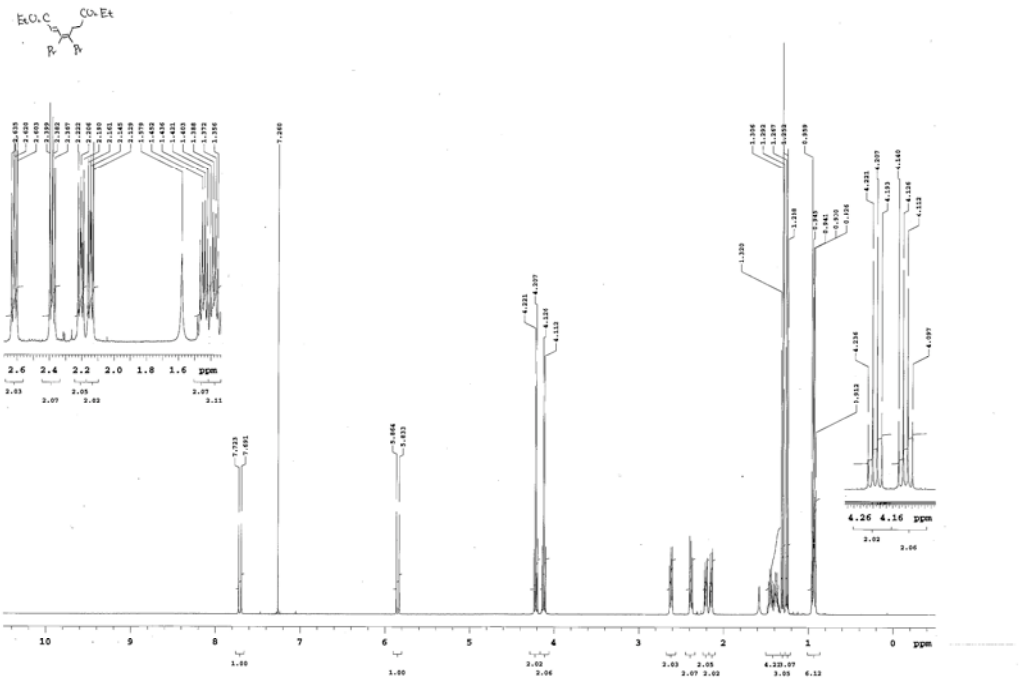
(2*E*,4*E*,6*E*)-*N*,4,6-trimethyl-*N*,5,7-triphenyl-2,4,6-heptatrienamide (4de).

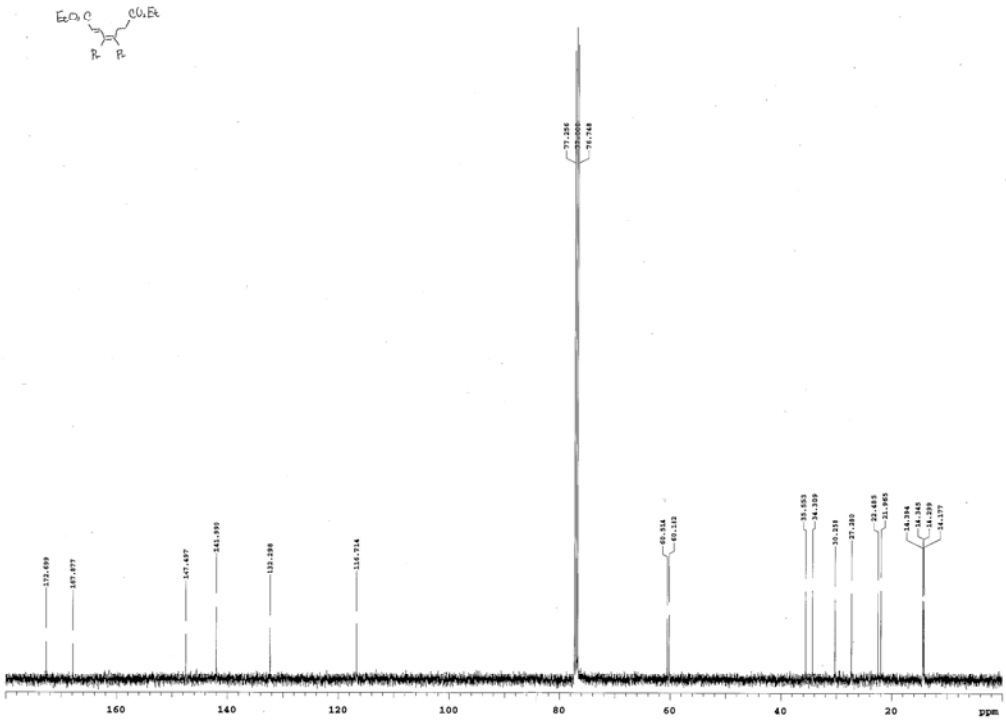


Yield: 49% (isolated as a single isomer), white powder, mp. 142-144 ºC (Hexane-CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, *J* = 15.5 Hz, 1H), 7.42-7.21 (m, 15H), 6.48 (s, 1H), 5.93 (d, *J* = 15.5 Hz, 1H), 3.37 (s, 3H), 1.78 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.99, 152.37, 144.03, 142.84, 140.13, 137.94, 137.56, 132.26, 129.44, 129.39, 129.26, 129.02, 128.15, 128.04, 127.37, 127.29, 126.67, 118.58, 37.43, 18.23, 16.24. IR (KBr): 1642, 1597, 1495, 1417, 1374, 1283, 1125, 773, 750, 698 cm^{-1}. MS (EI): *m/z* (%): 393 ($[M]^+$, 27), 287 ($[M–NPhMe]^+$, 19), 259 ($[M–CONPhMe]^+$, 100). HRMS calcd for $C_{28}H_{27}NO$: 393.2093. Found: 393.2088.

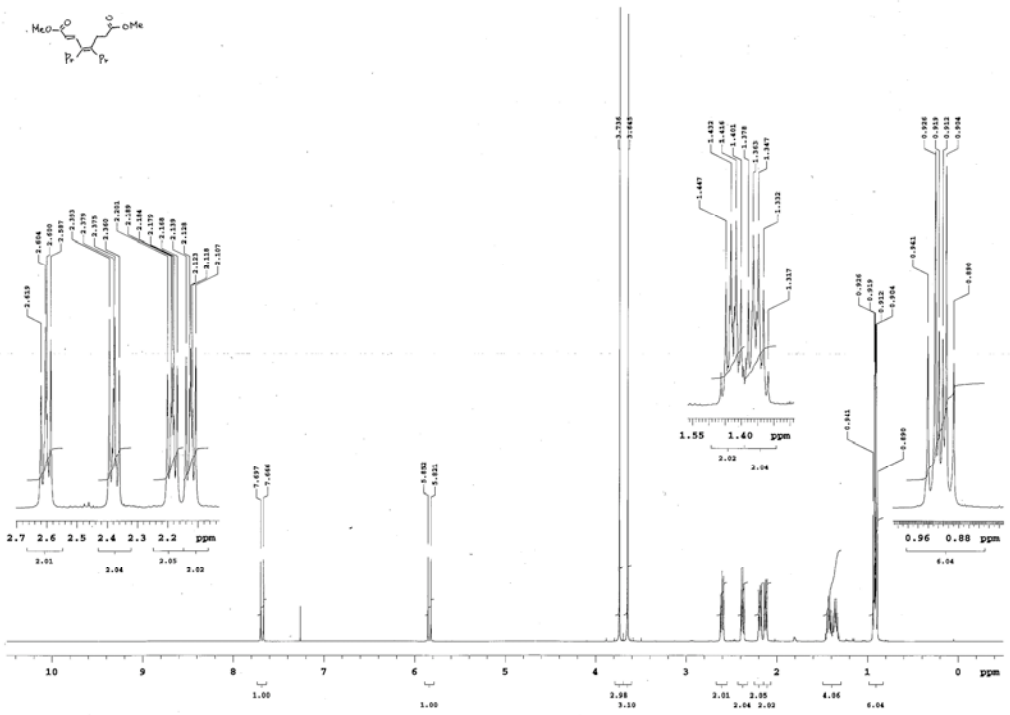
NMR Spectra of Products

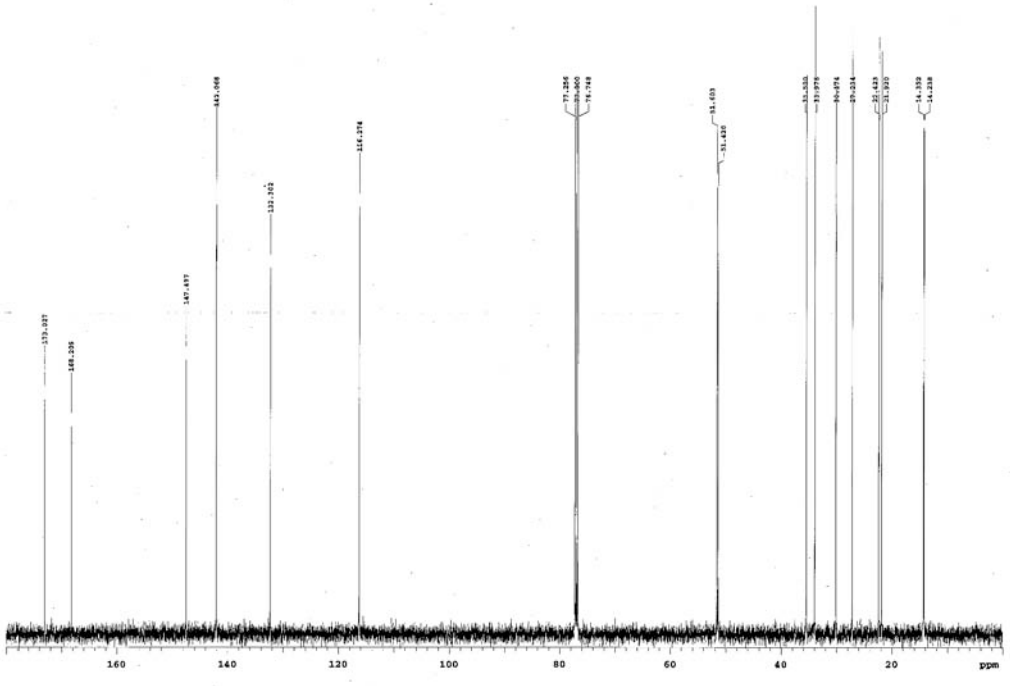
3aa



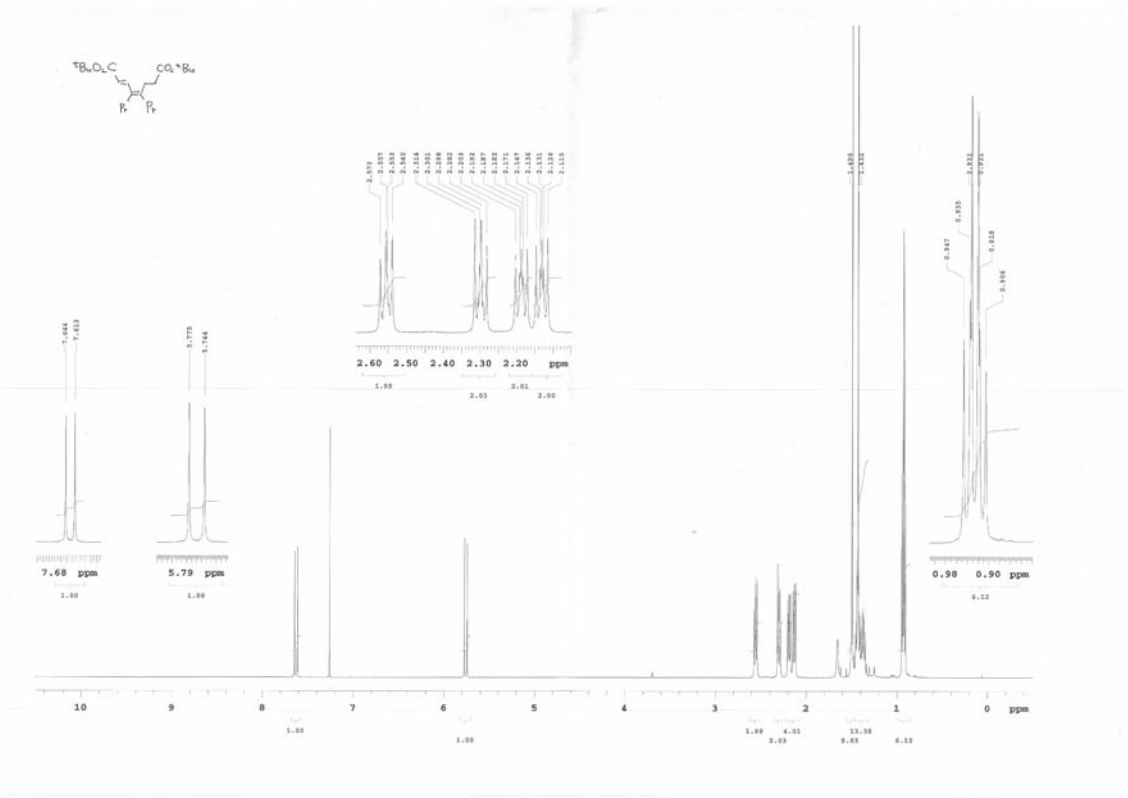


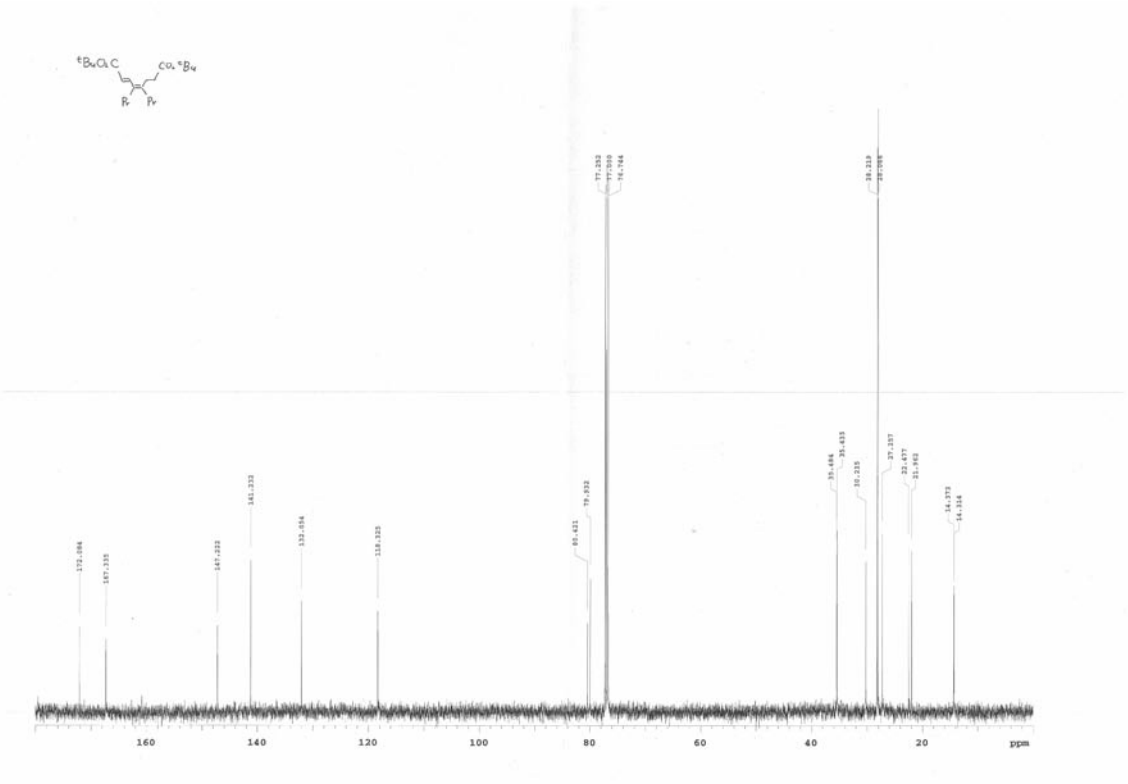
3ba



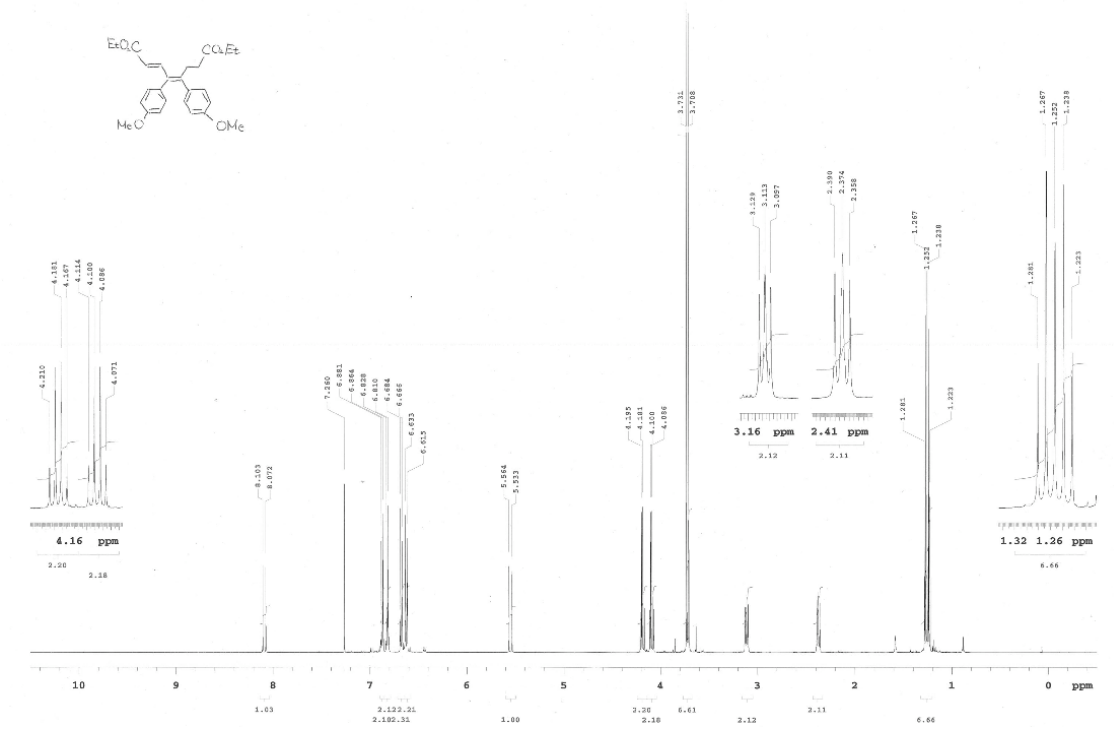


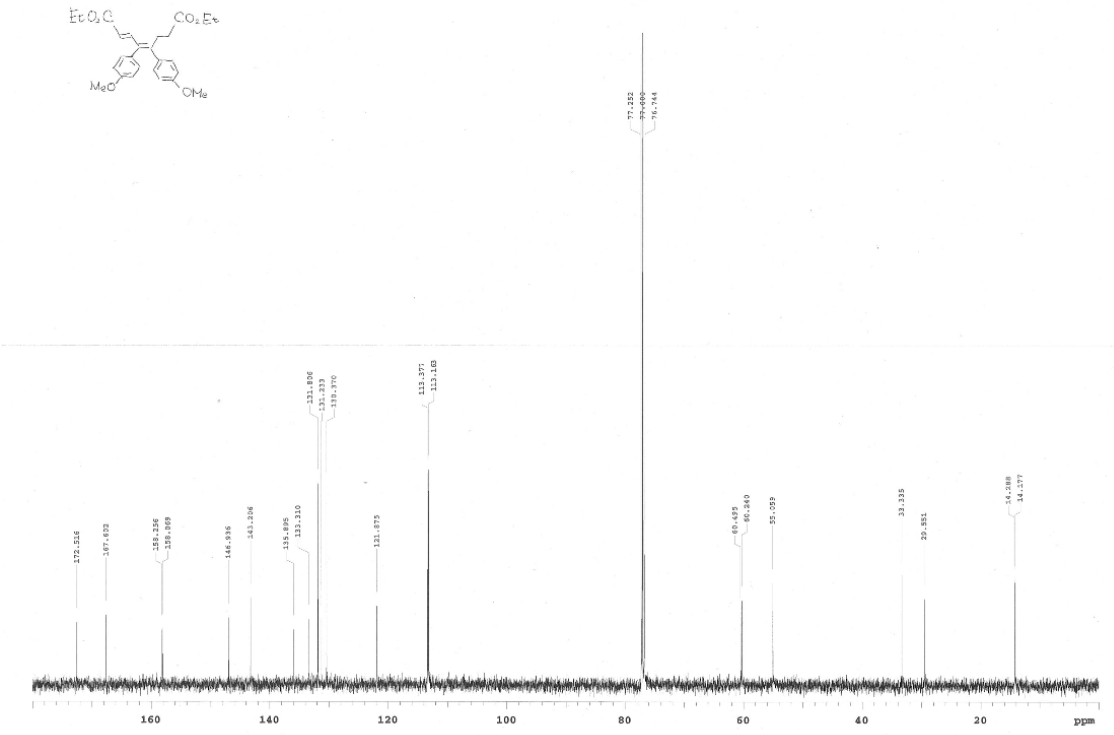
3ca


2.60 2.50 2.40 2.30 2.20 ppm
7.68 ppm
5.79 ppm
0.98 0.90 ppm
10 9 8 7 6 5 4 3 2 1 0 ppm

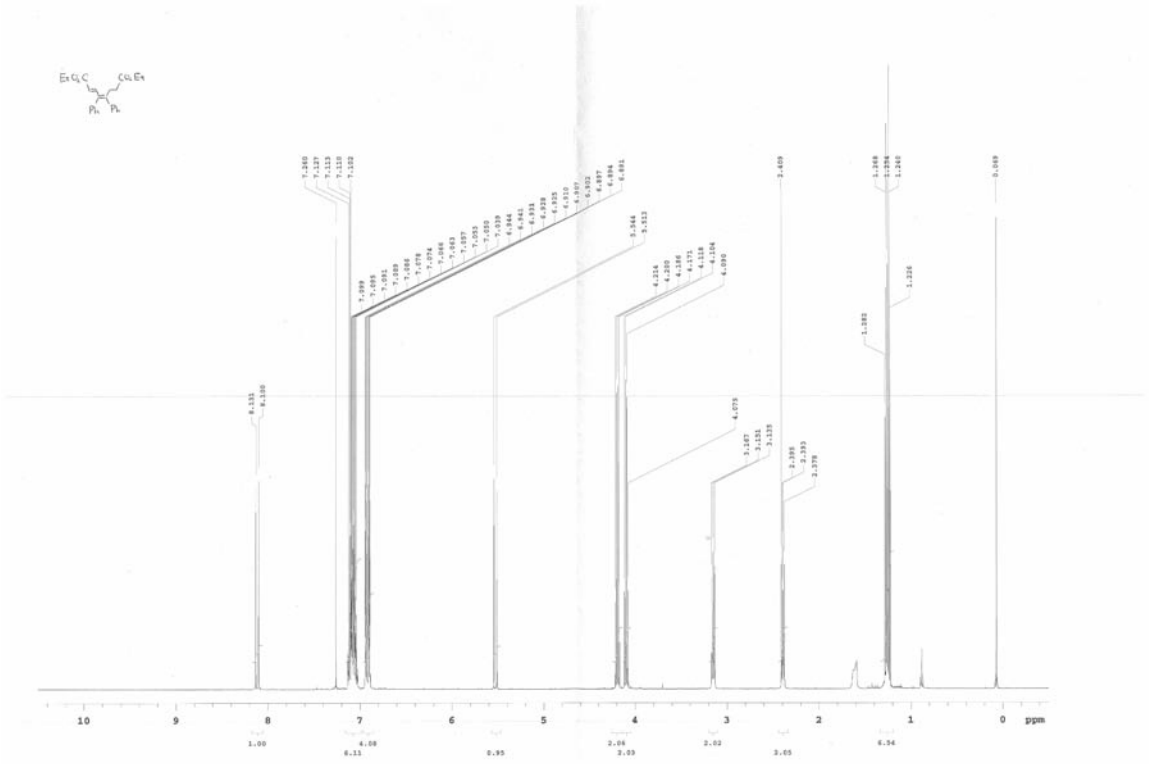

160 140 120 100 80 60 40 20 ppm

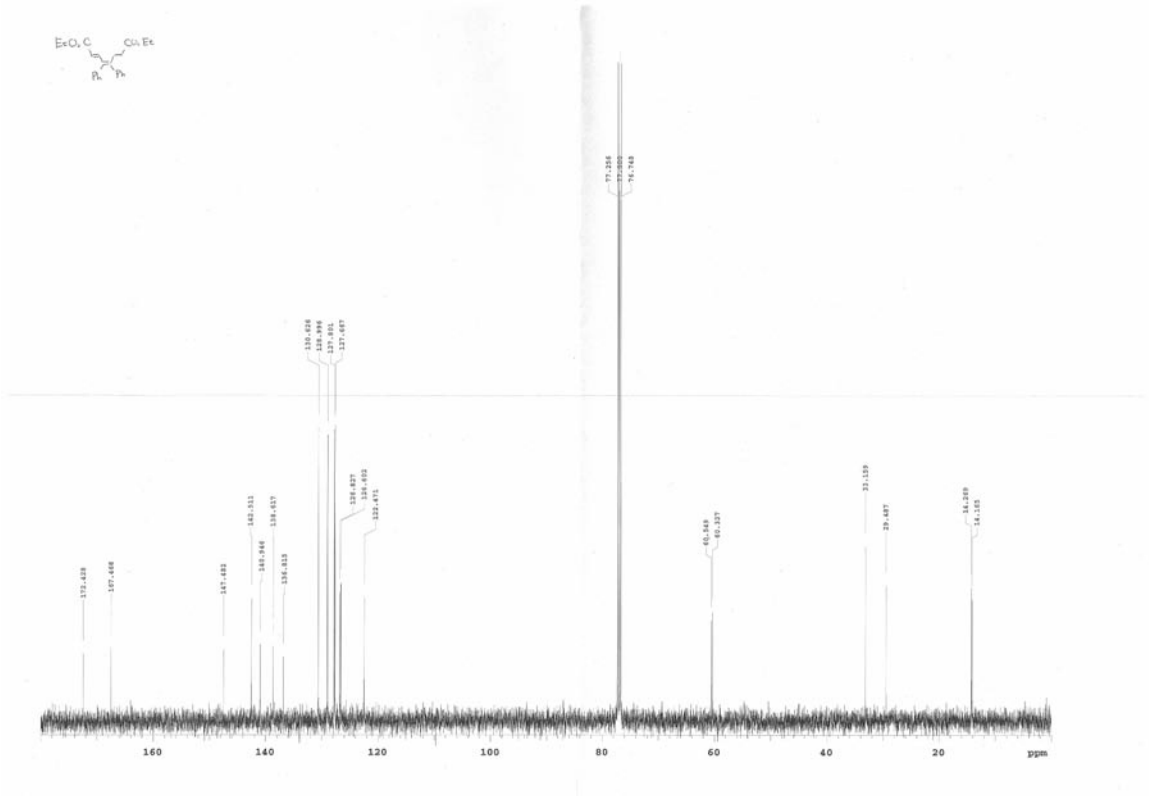
3ab


EtO2C
CO2Et
MeO
OMe
4.16 ppm
3.16 ppm
2.41 ppm
1.32 1.26 ppm
ppm

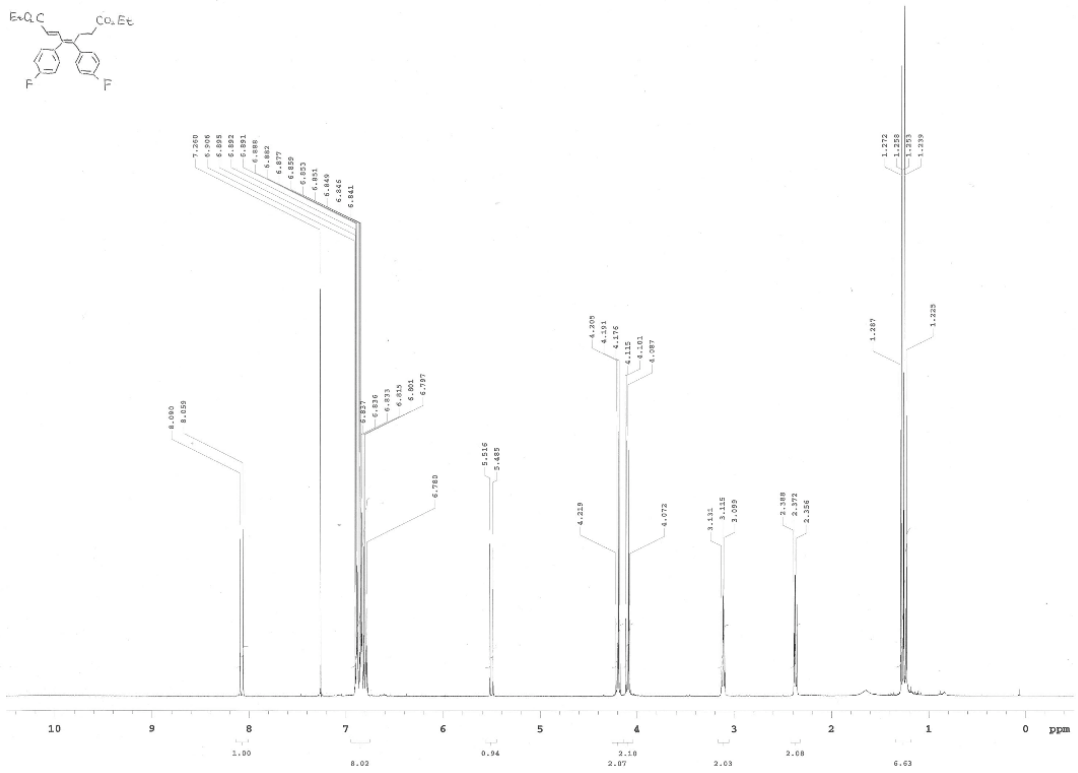

EtO2C
CO2Et
MeO
OMe
ppm

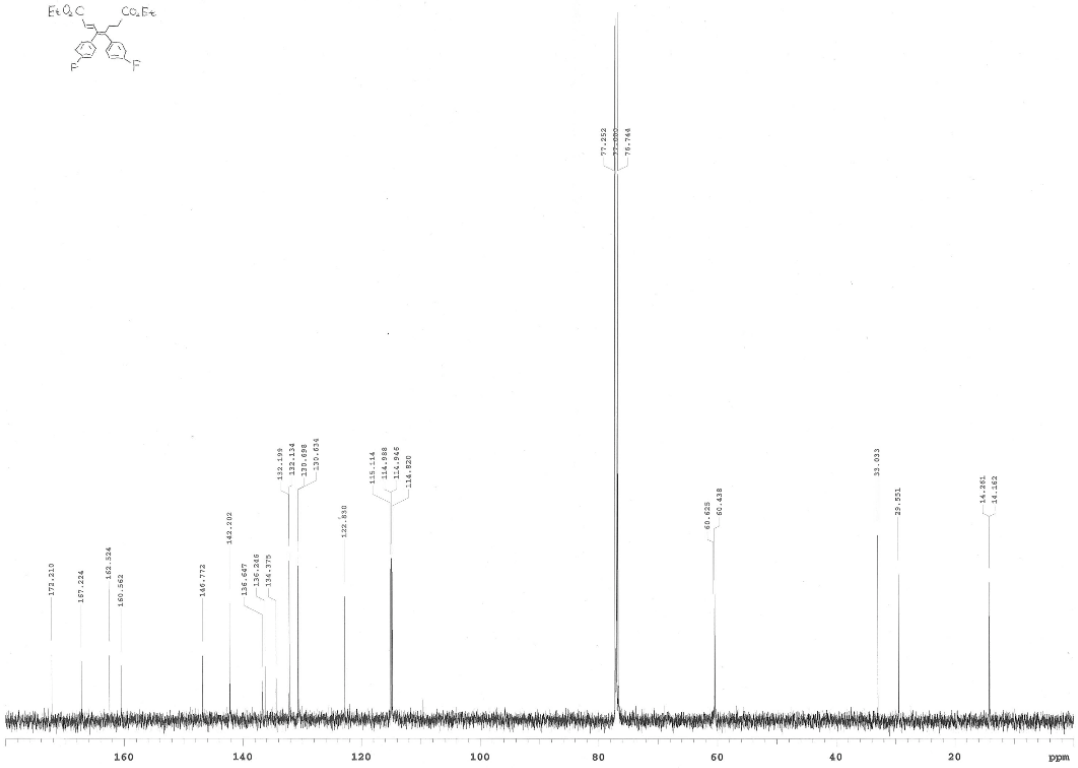
3ac



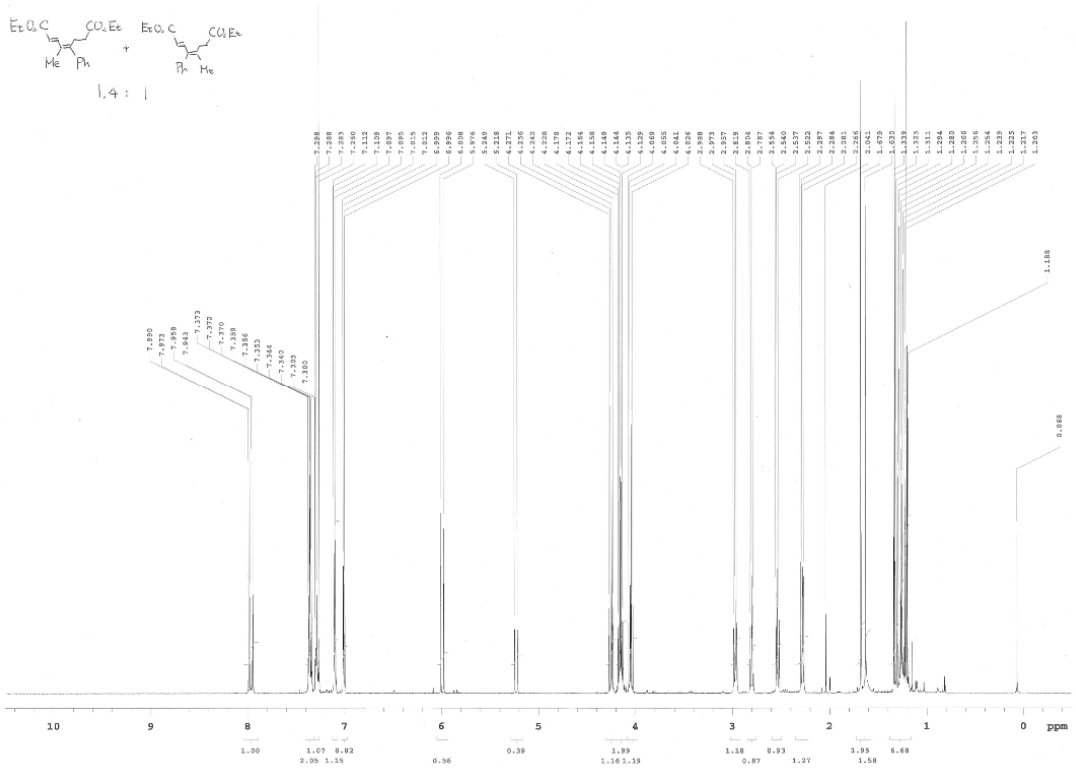


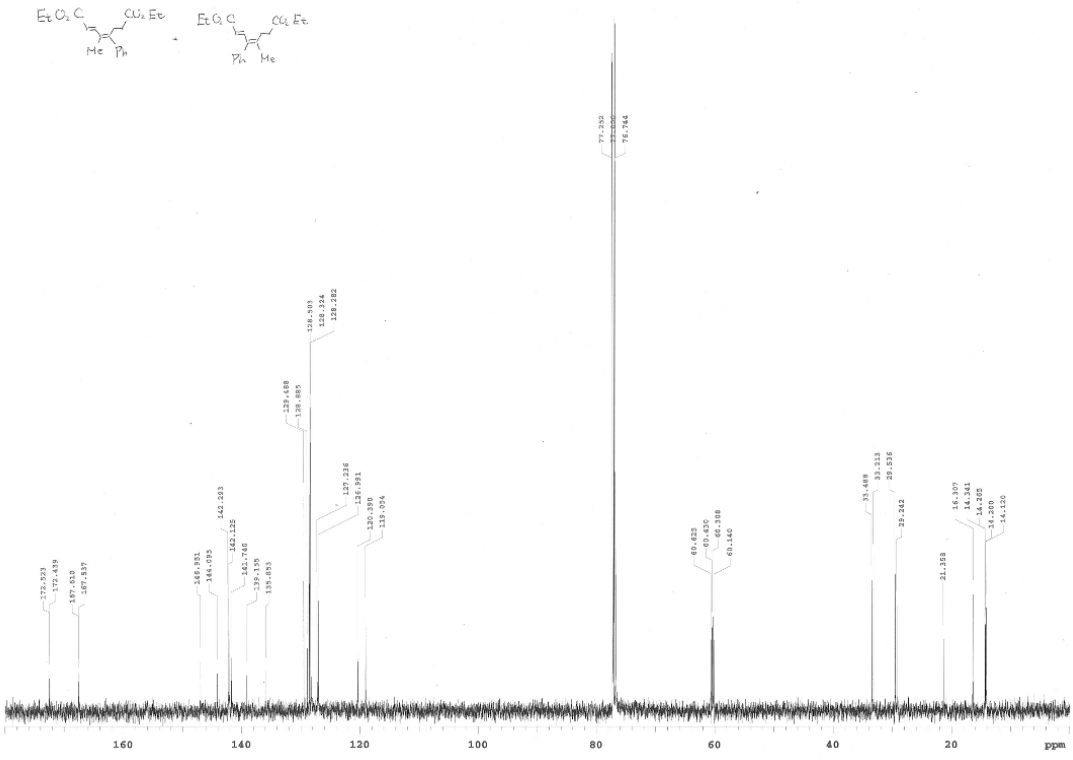
3ad


EtO2C
CO2Et
F
F
7.260
6.906
6.895
6.891
6.888
6.882
6.877
6.859
6.853
6.851
6.846
6.841
8.060
8.059
6.797
6.783
5.516
5.485
4.305
4.301
4.176
4.115
4.101
4.087
4.218
4.072
3.131
3.115
3.099
2.388
2.372
2.356
1.272
1.268
1.253
1.239
1.287
1.225
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
8.02
0.94
2.10
2.07
2.03
2.08
6.63

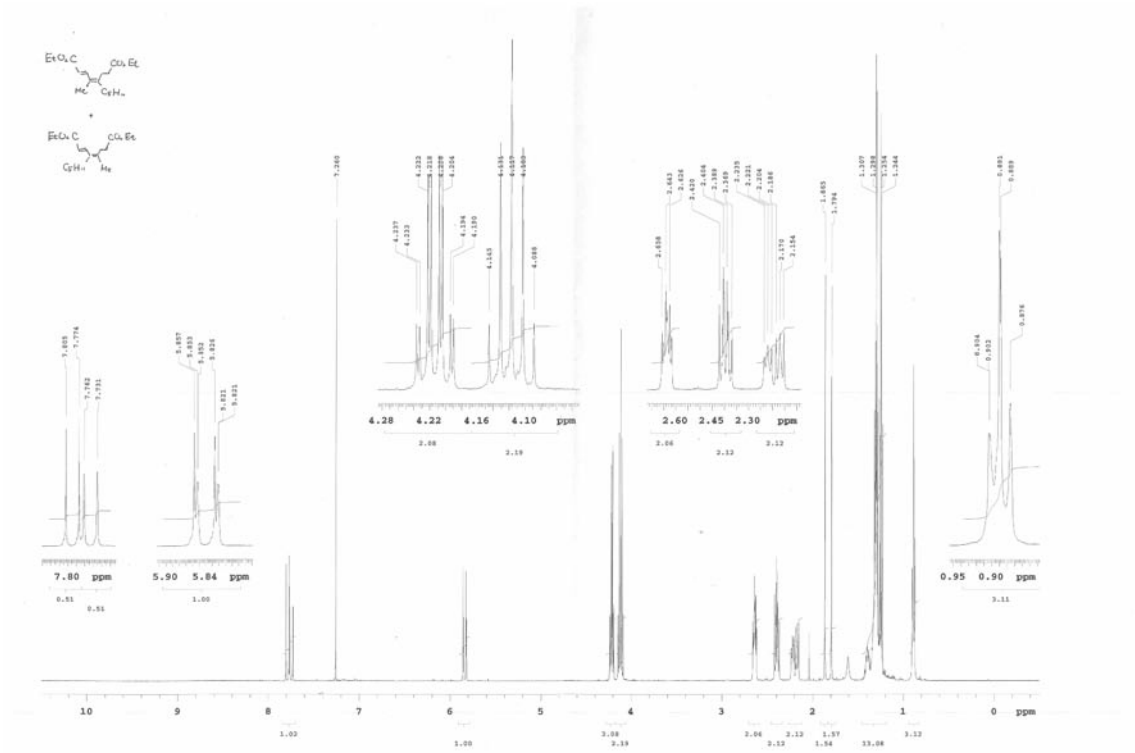

EtO2C
CO2Et
F
F
77.252
76.744
173.210
167.224
162.324
160.362
146.772
143.202
136.667
136.246
136.175
132.199
132.134
130.098
130.074
122.930
116.114
114.988
114.946
114.820
60.638
60.438
33.033
29.551
14.281
14.162
160
140
120
100
80
60
40
20
ppm

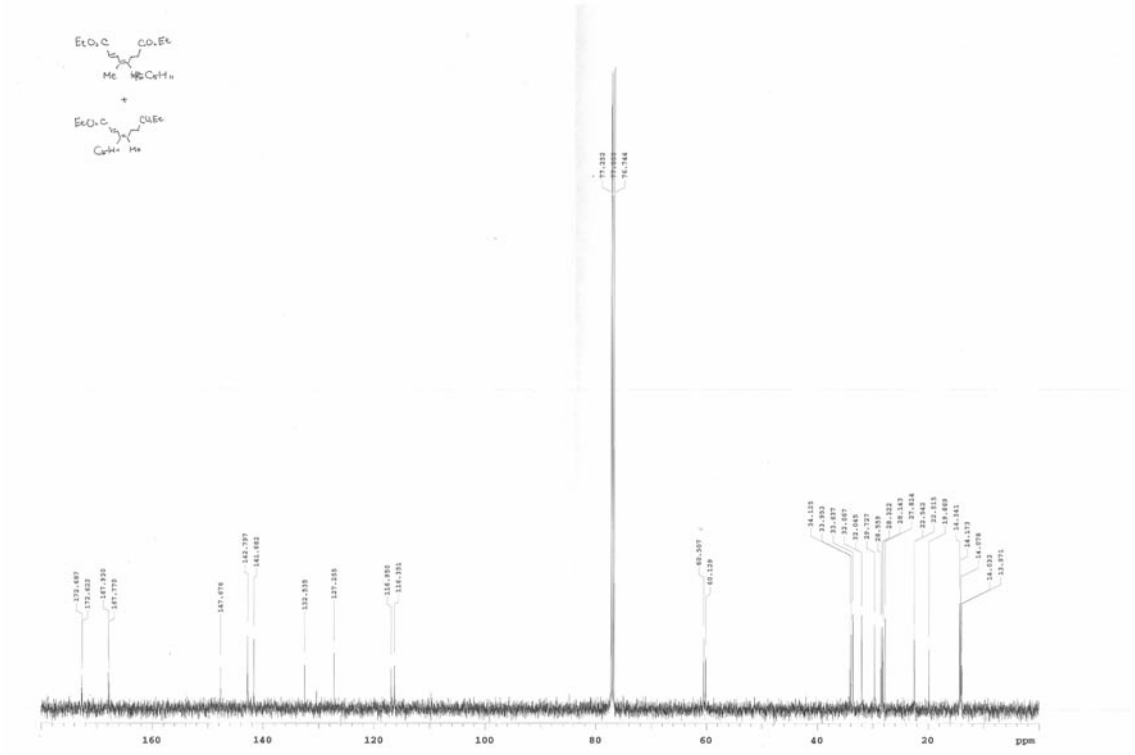
3ae



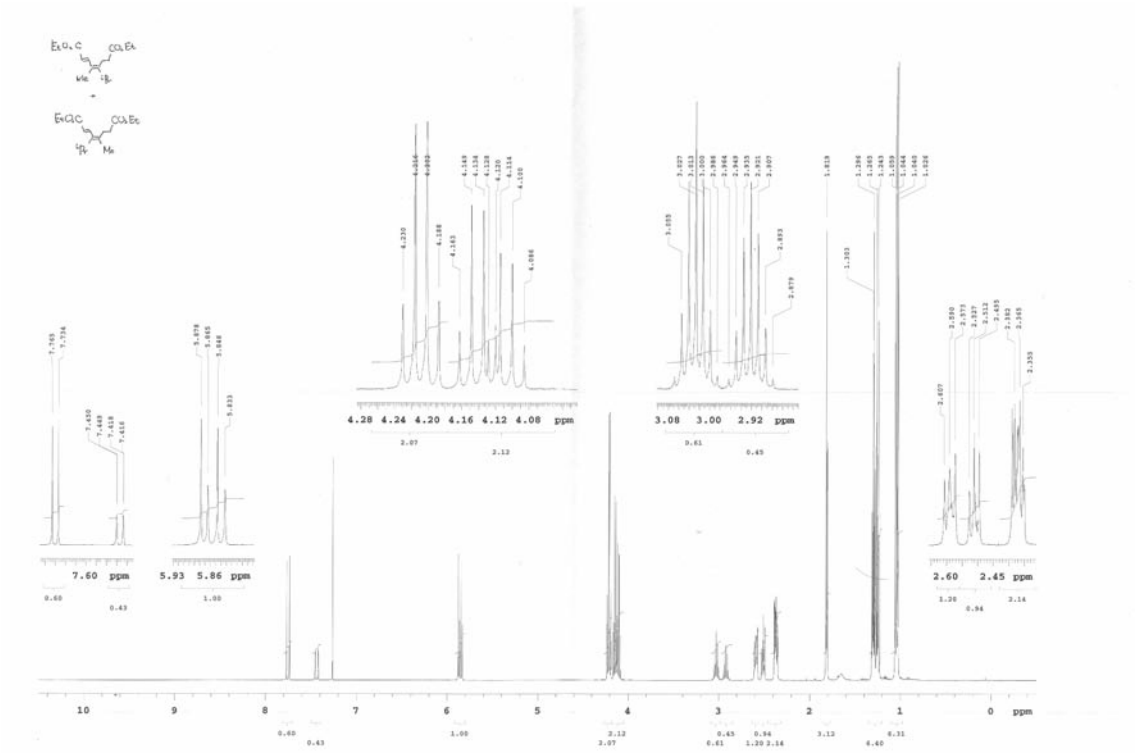


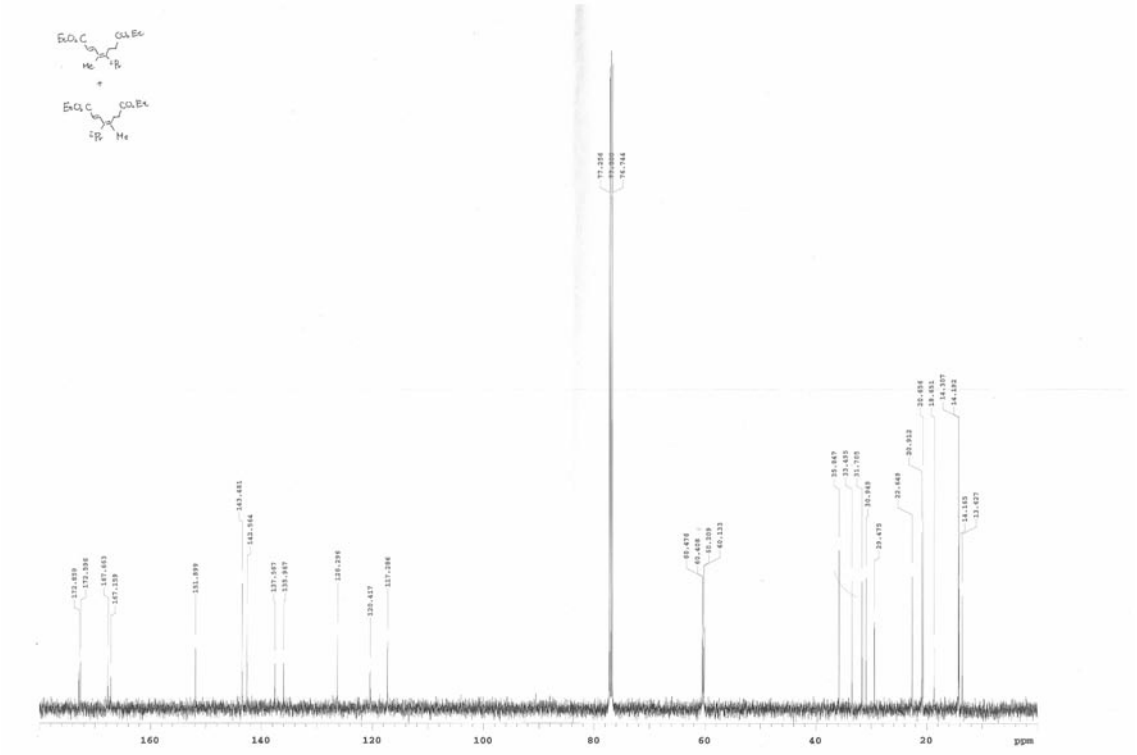
3af



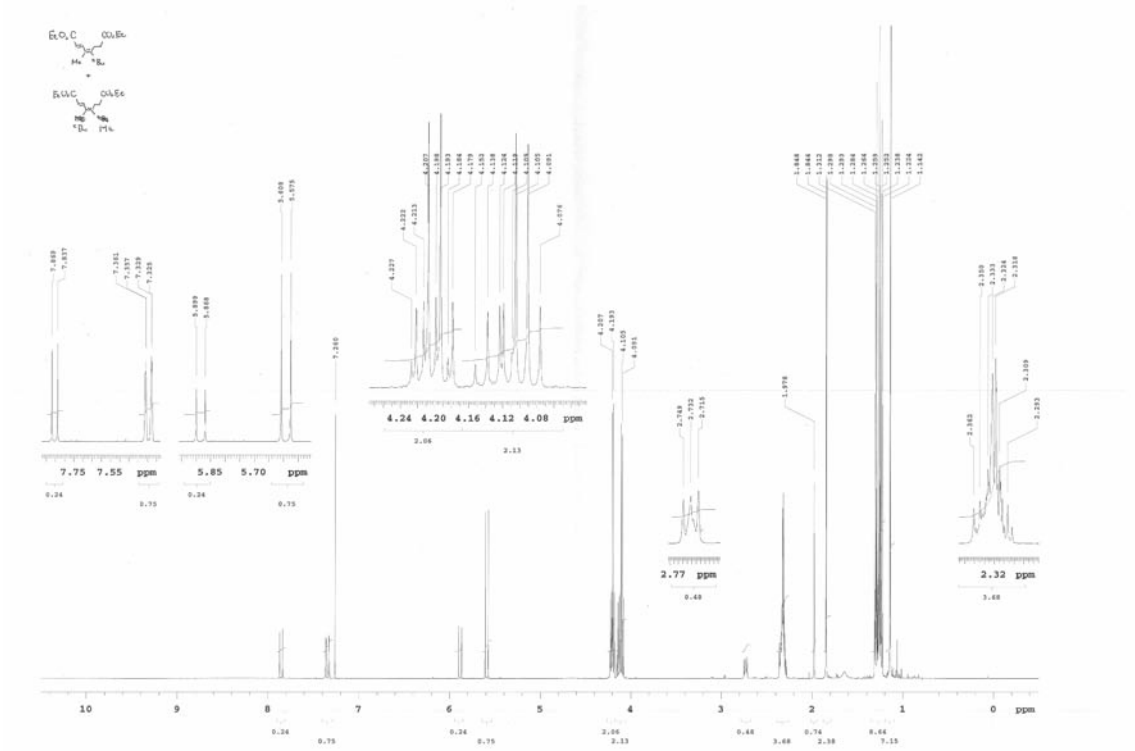


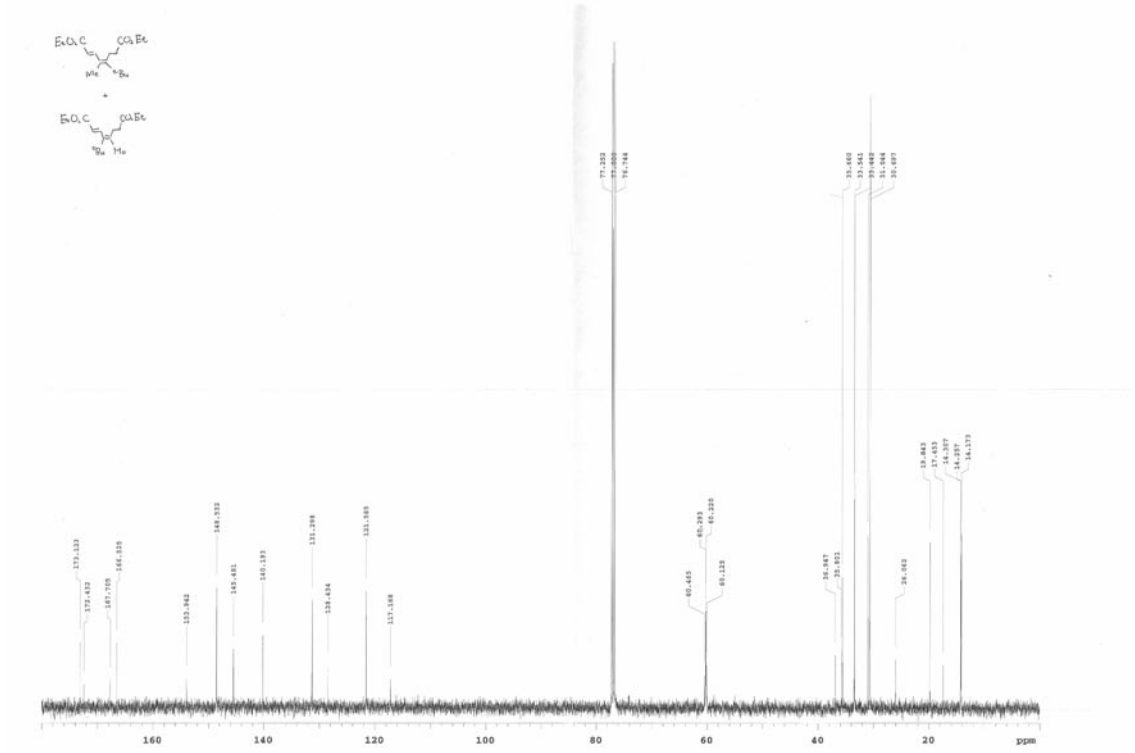
3ag



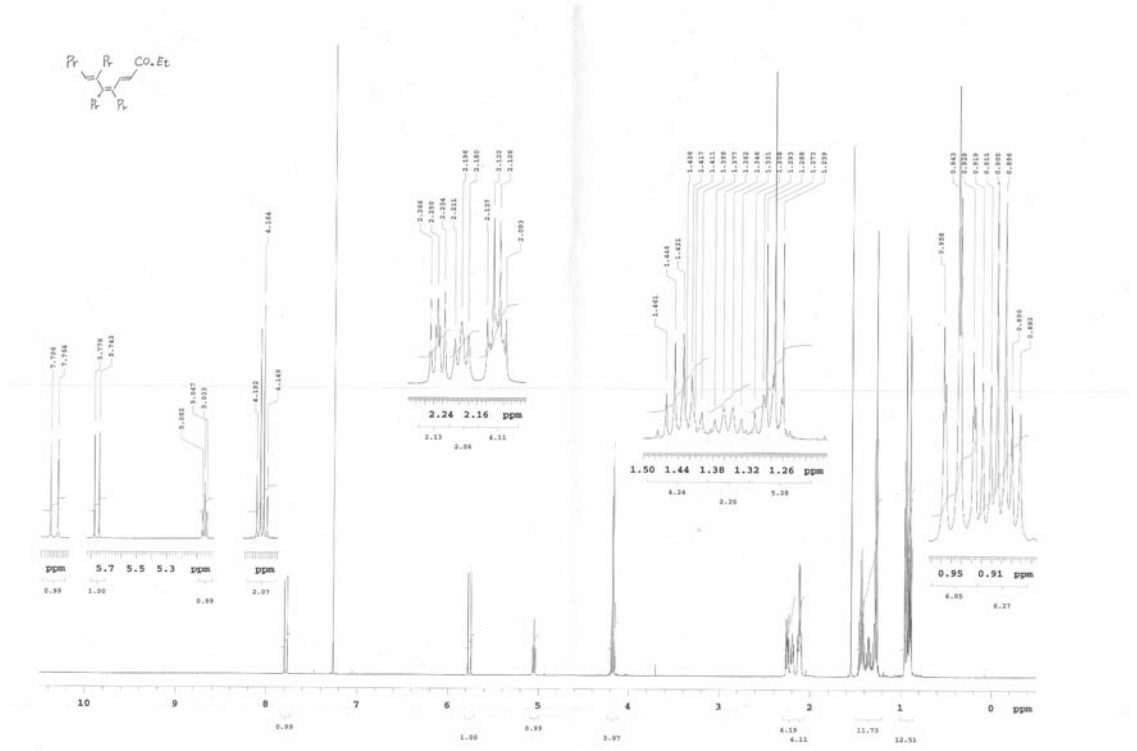


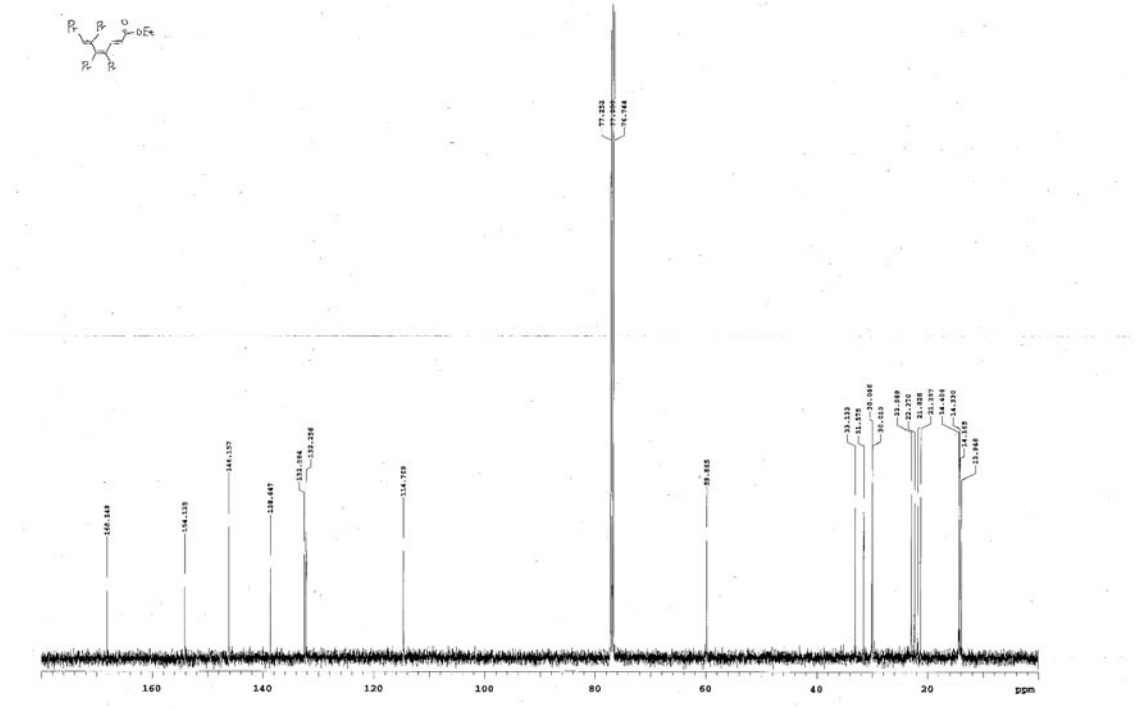
3ah


7.75 7.55 ppm
5.85 5.70 ppm
4.24 4.20 4.16 4.12 4.08 ppm
2.77 ppm
2.32 ppm
10 9 8 7 6 5 4 3 2 1 0 ppm

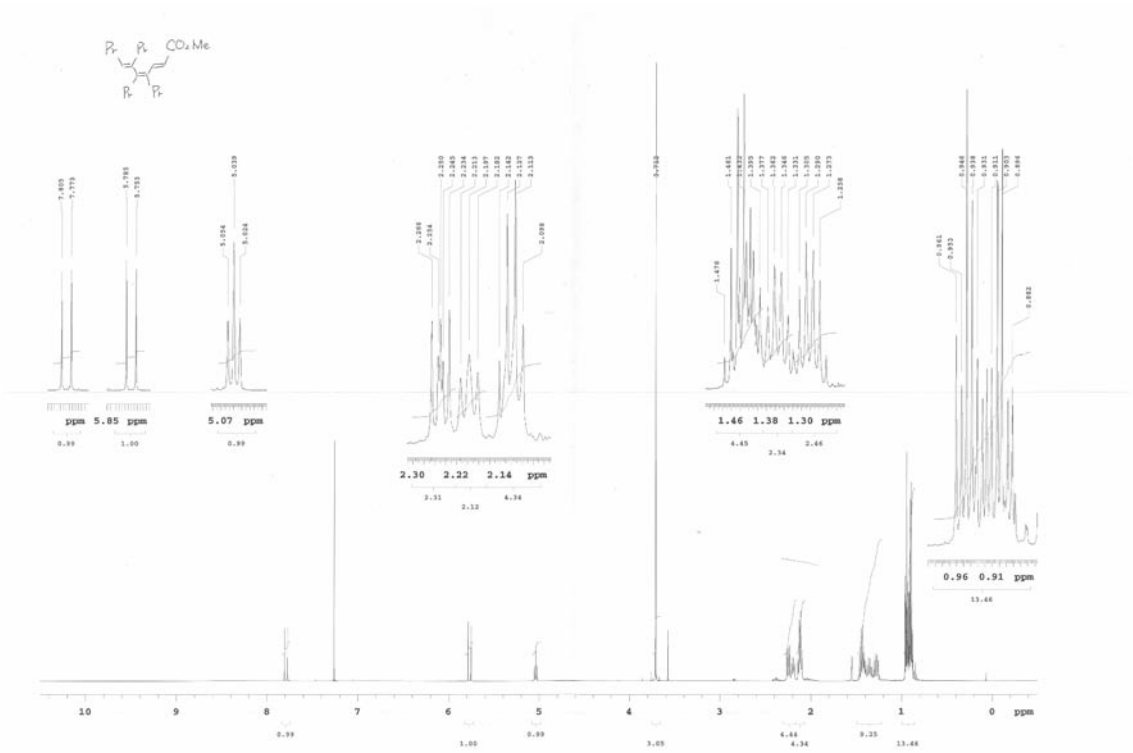

160 140 120 100 80 60 40 20 ppm

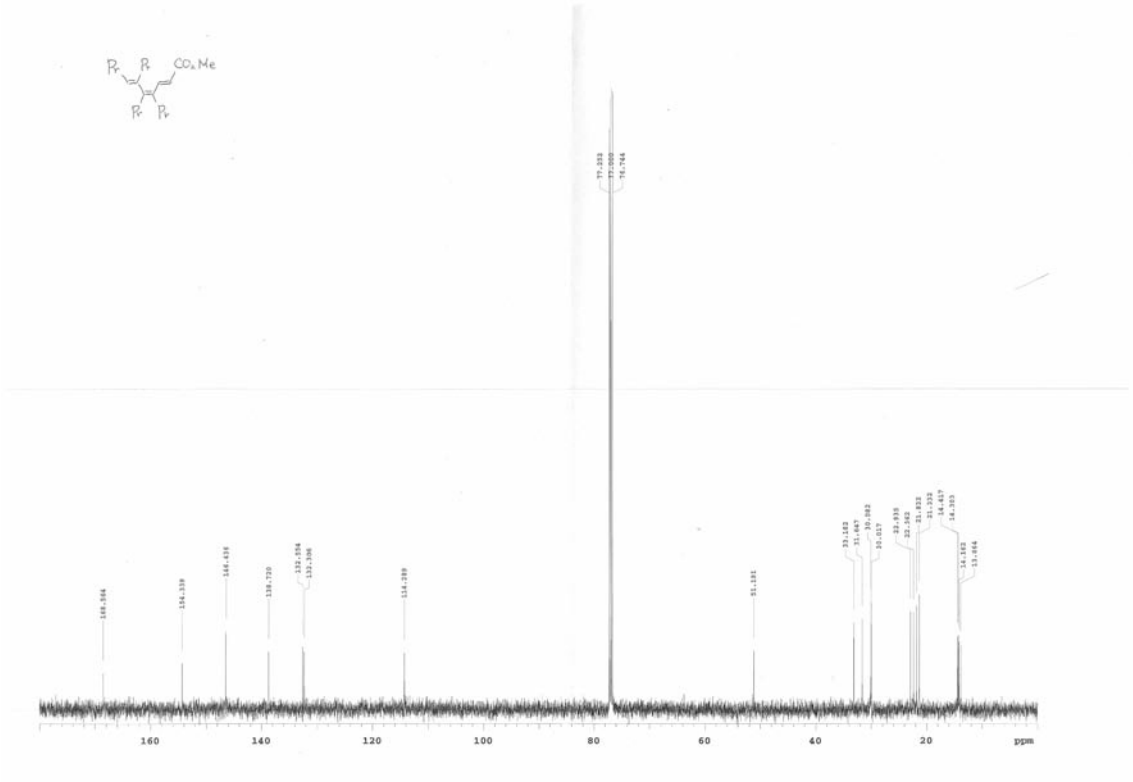
4aa



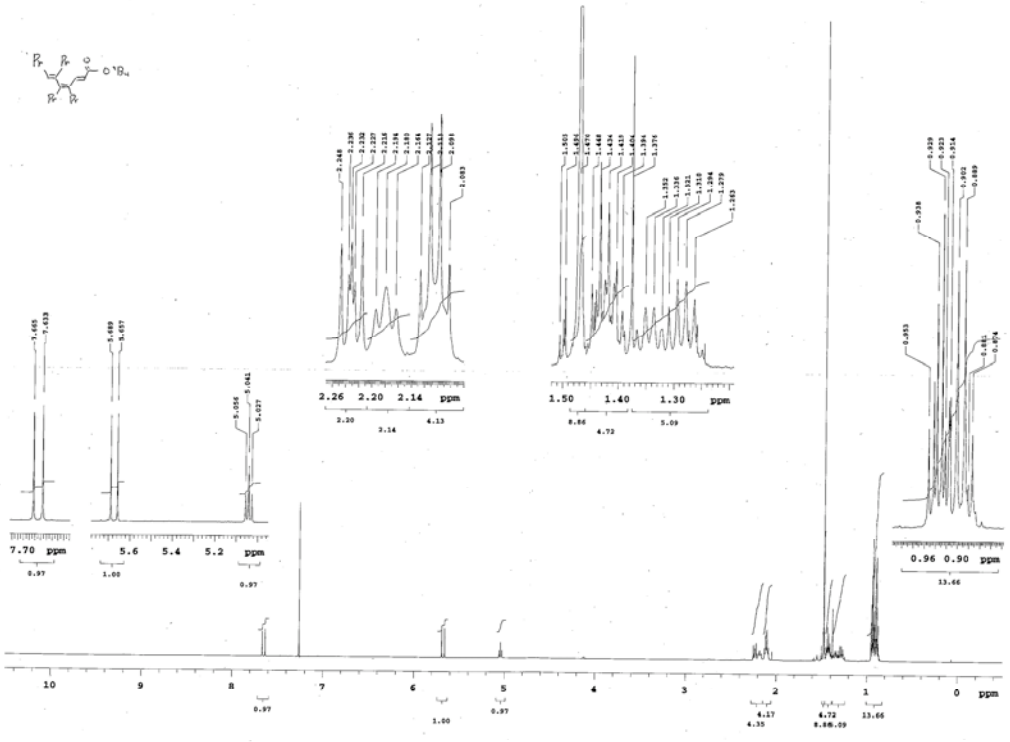


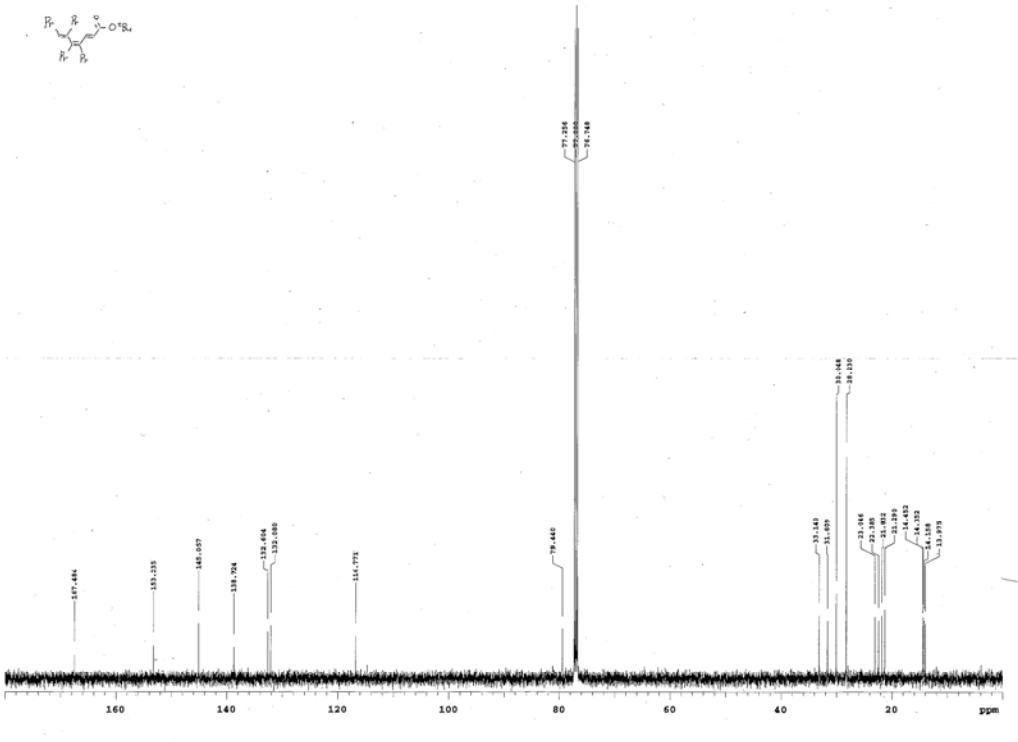
4ba


ppm 5.85 ppm
5.07 ppm
2.30 2.22 2.14 ppm
1.46 1.38 1.30 ppm
0.96 0.91 ppm
10 9 8 7 6 5 4 3 2 1 0 ppm

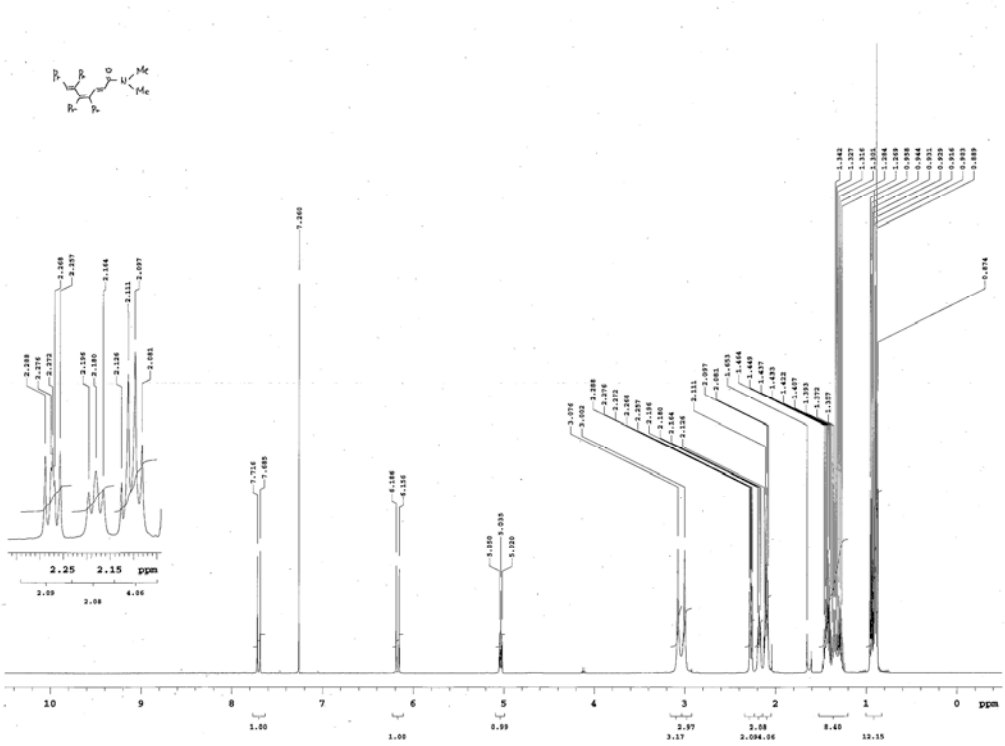

160 140 120 100 80 60 40 20 ppm

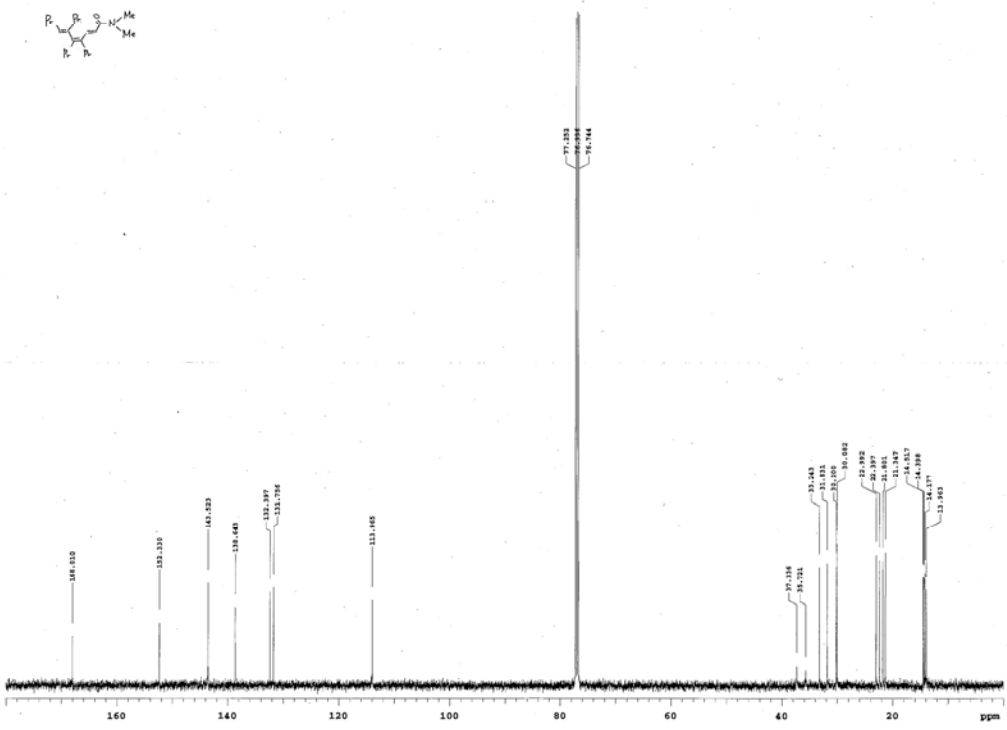
4ca



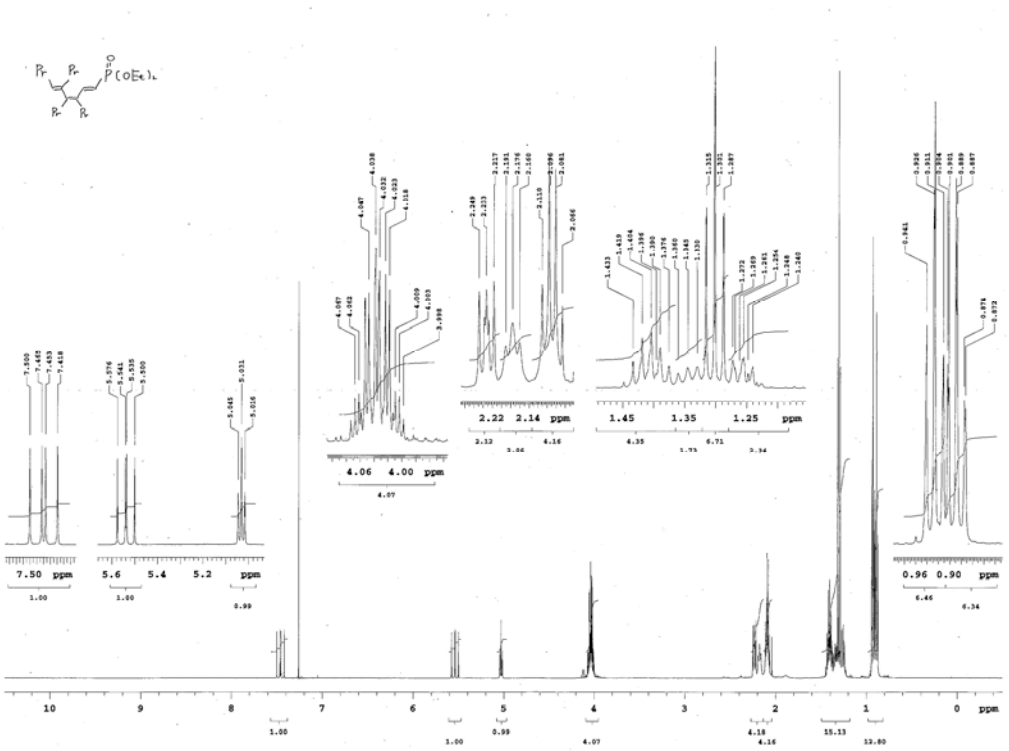


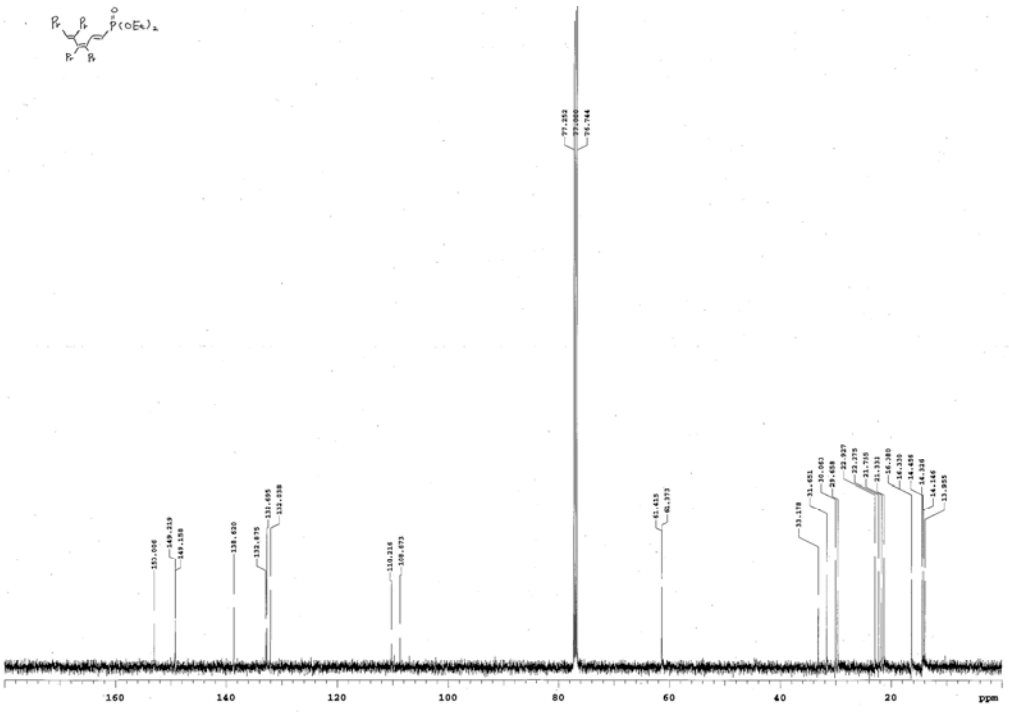
4da



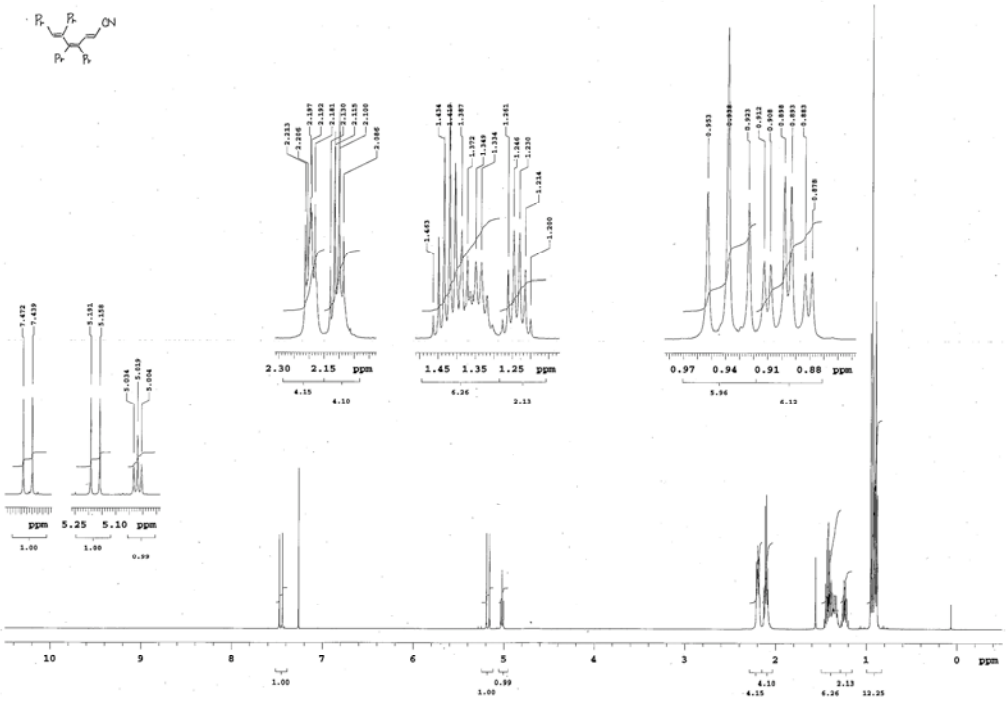


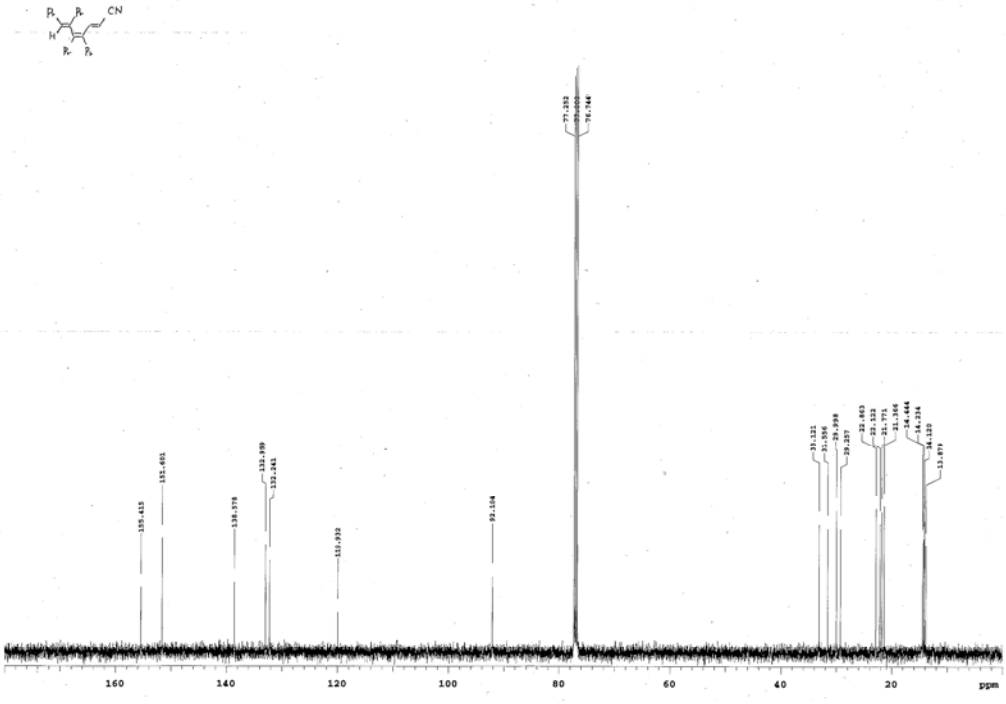
4ea



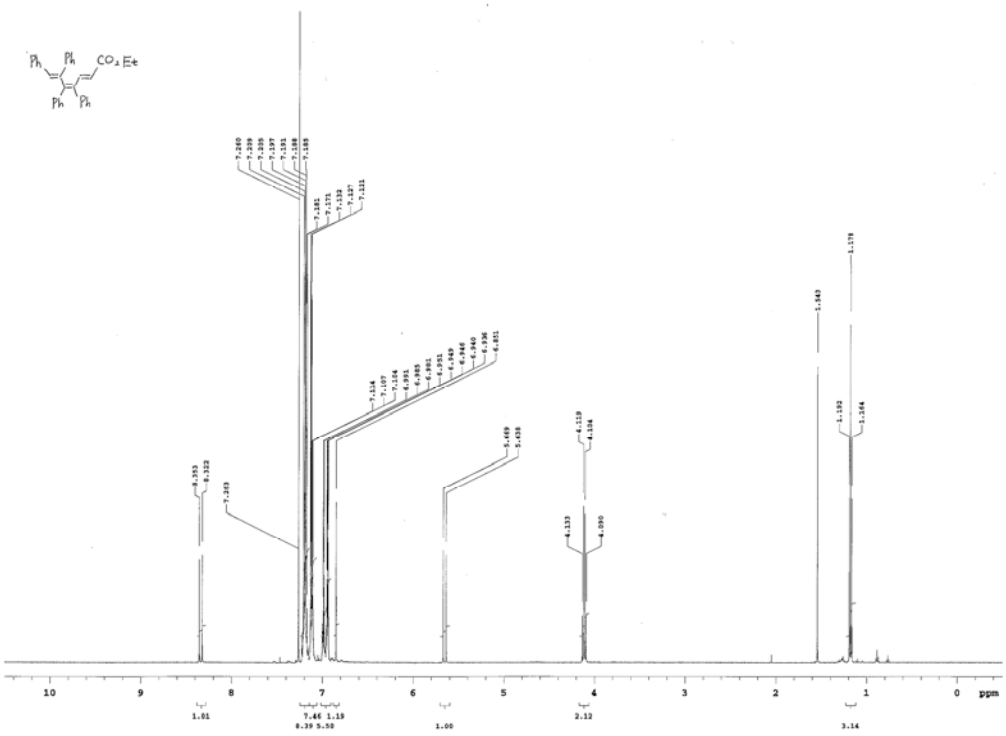


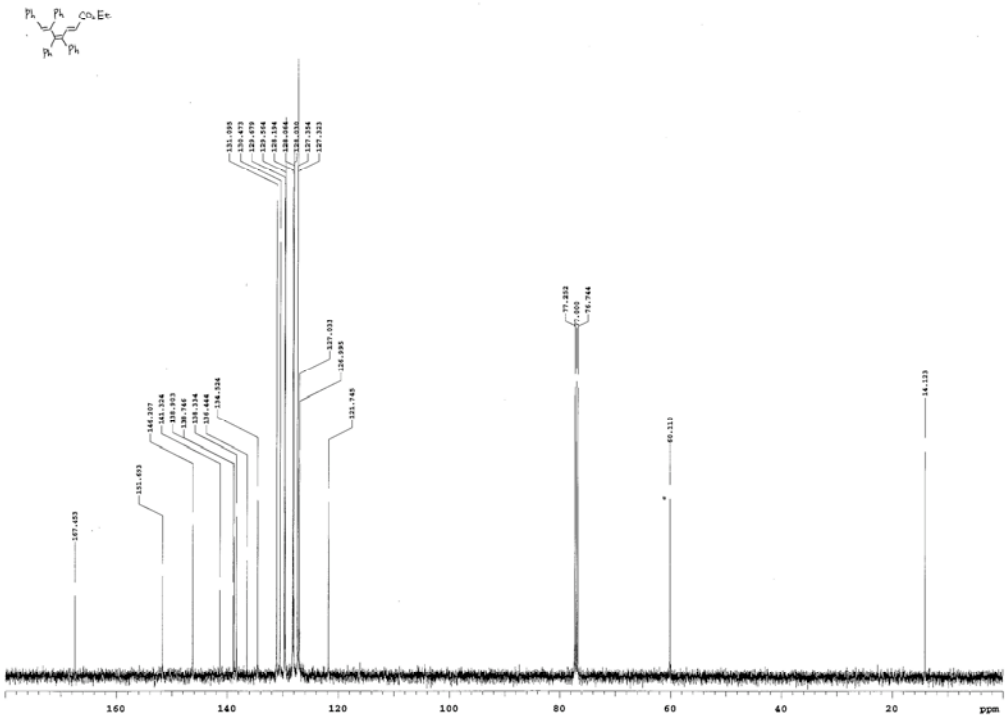
4fa



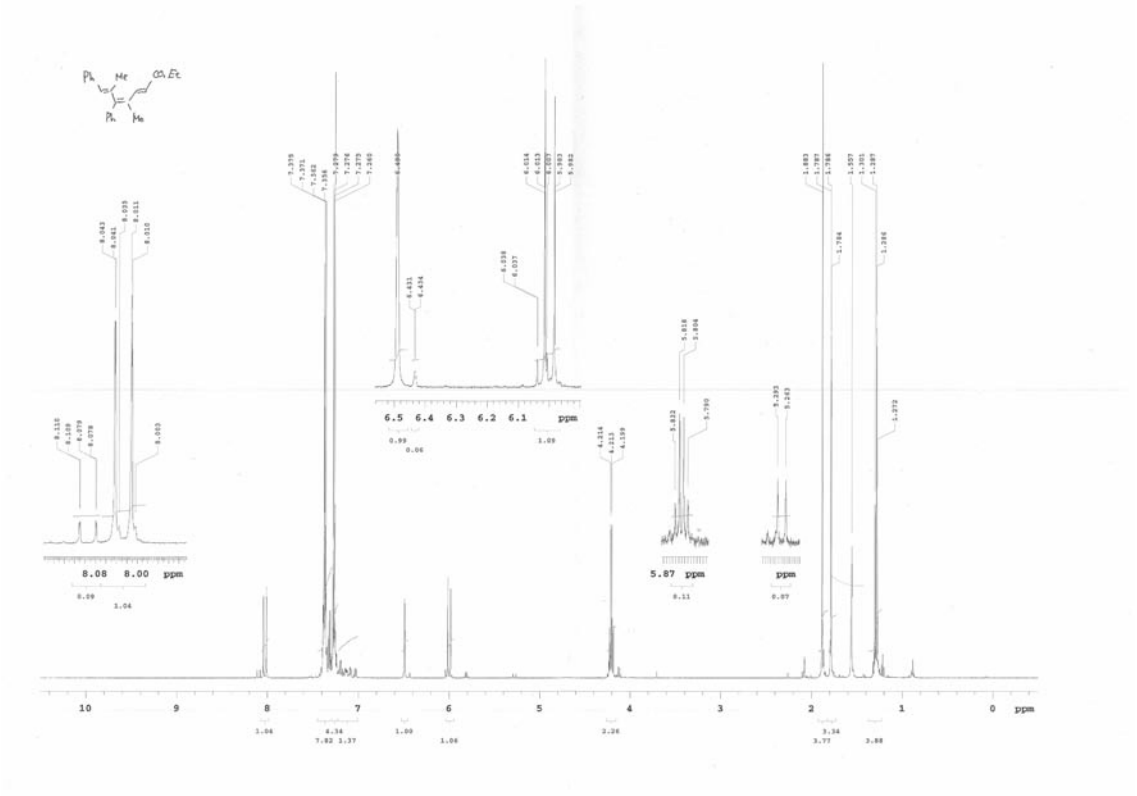


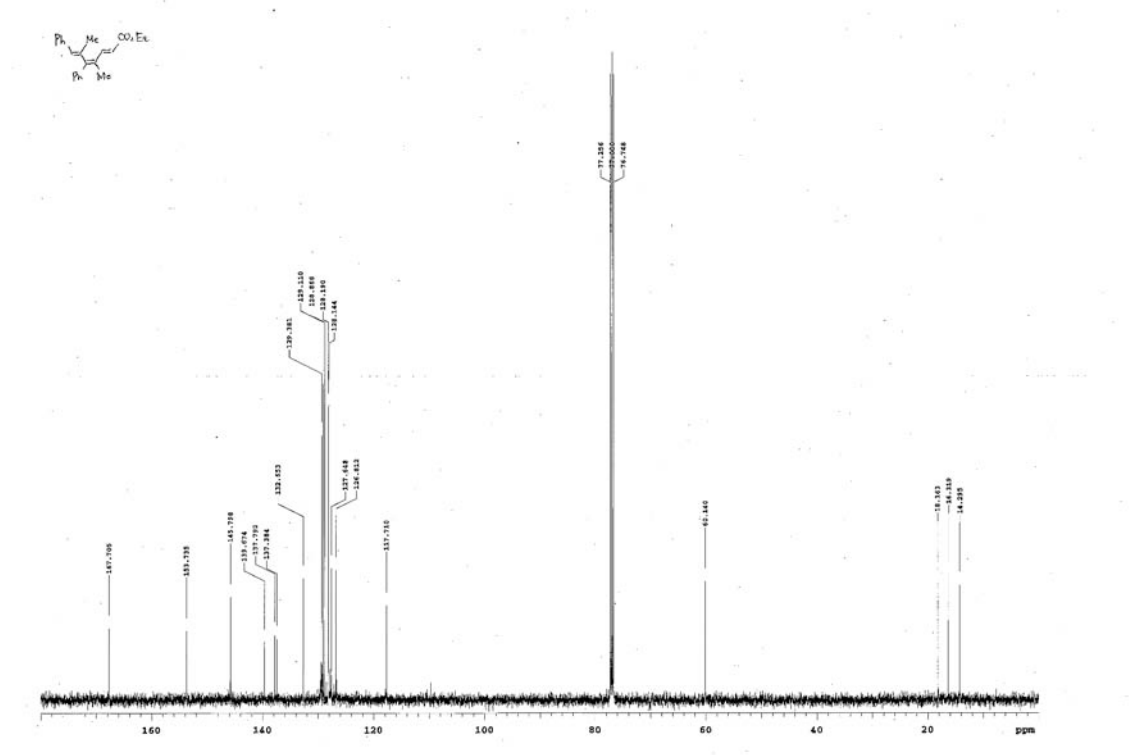
4ac



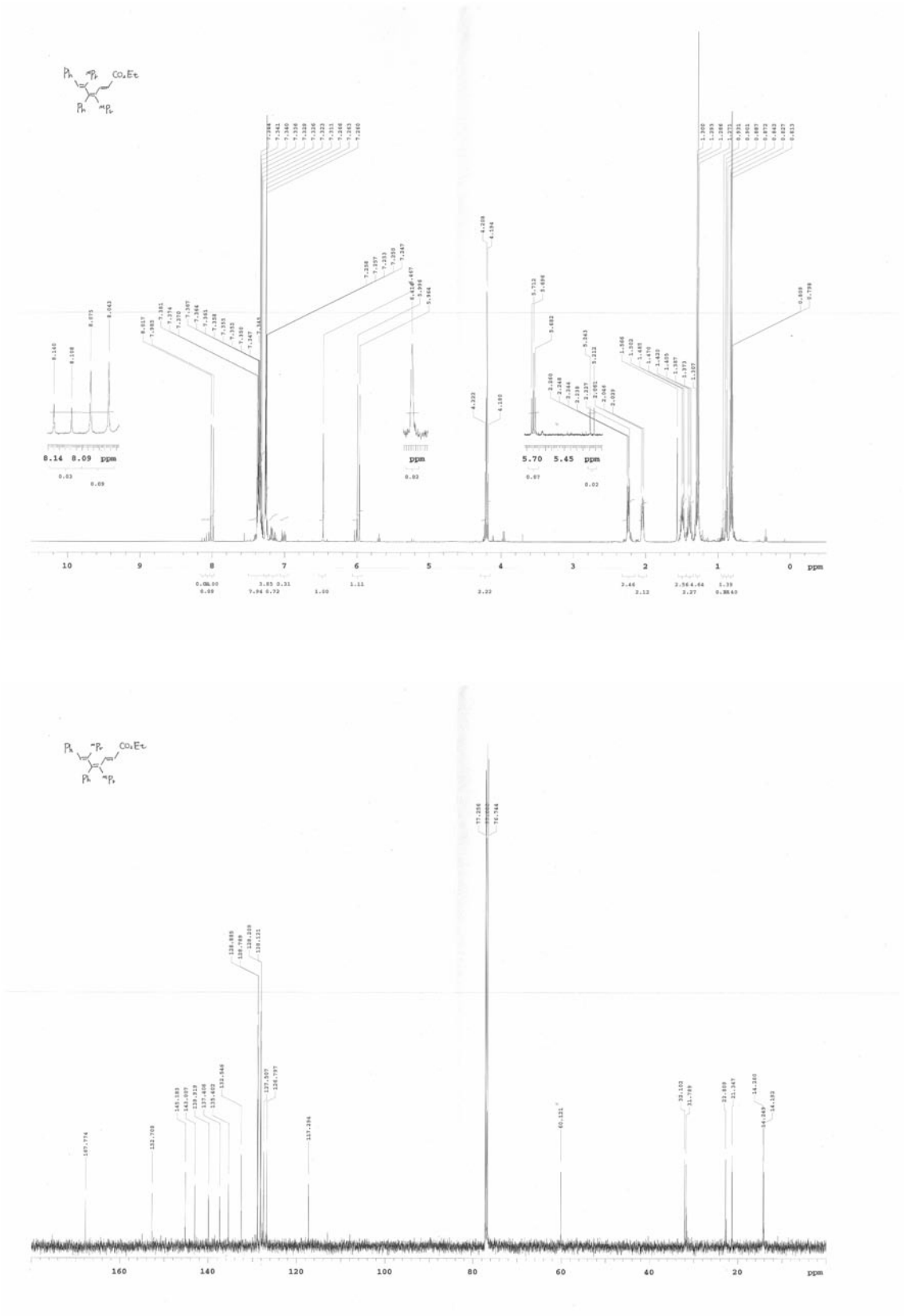


4ae

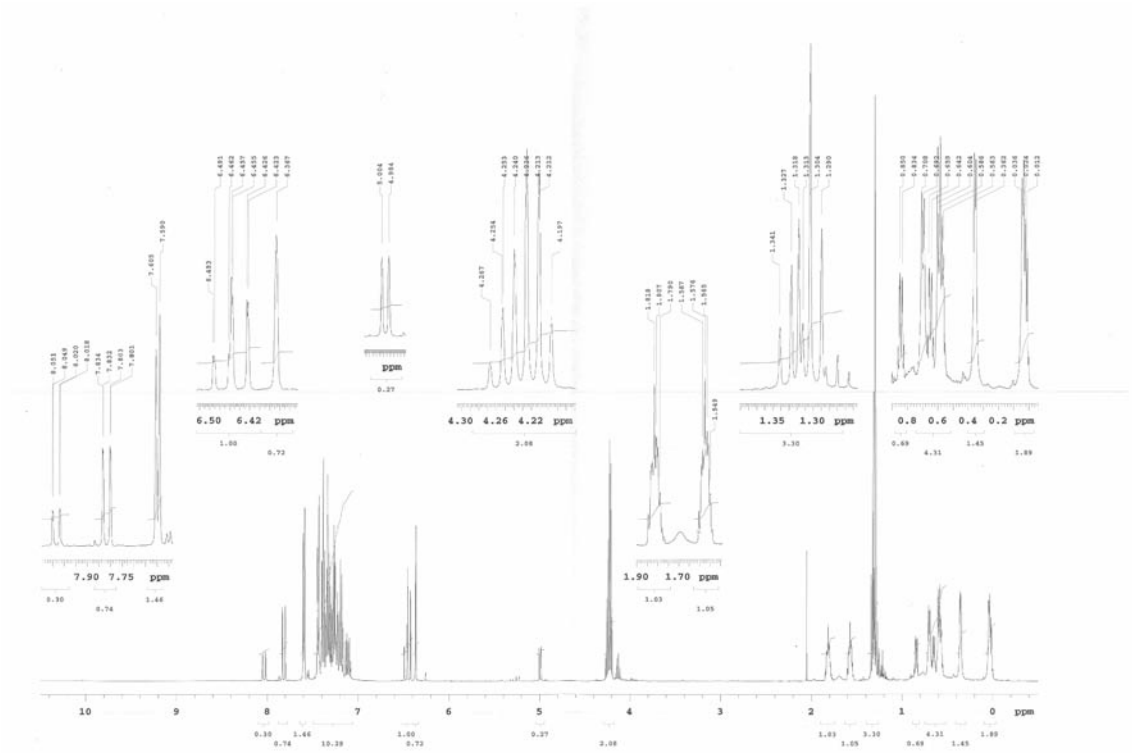


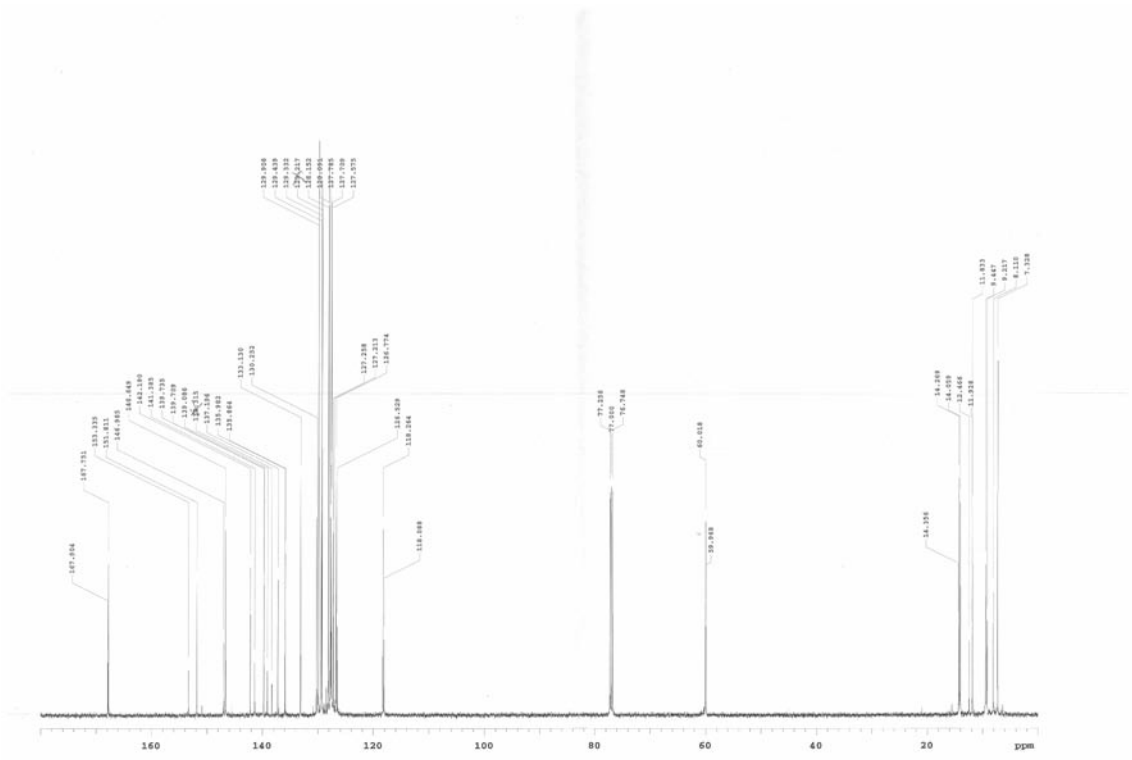


4ai

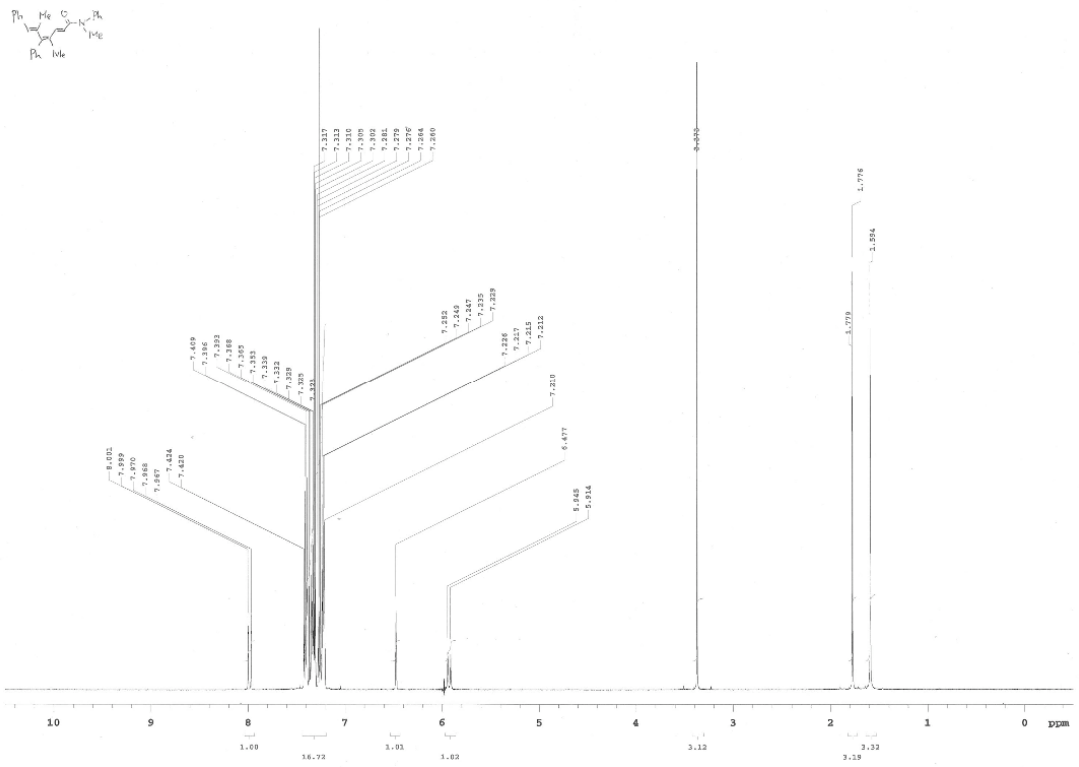


4aj





4de



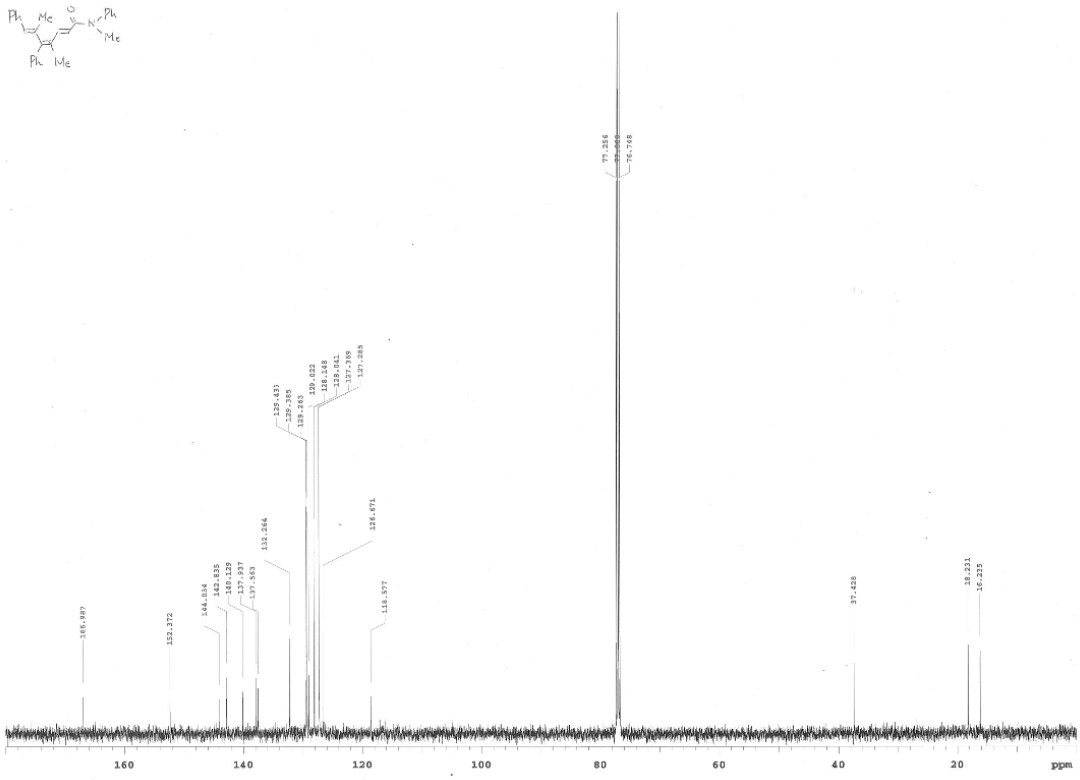
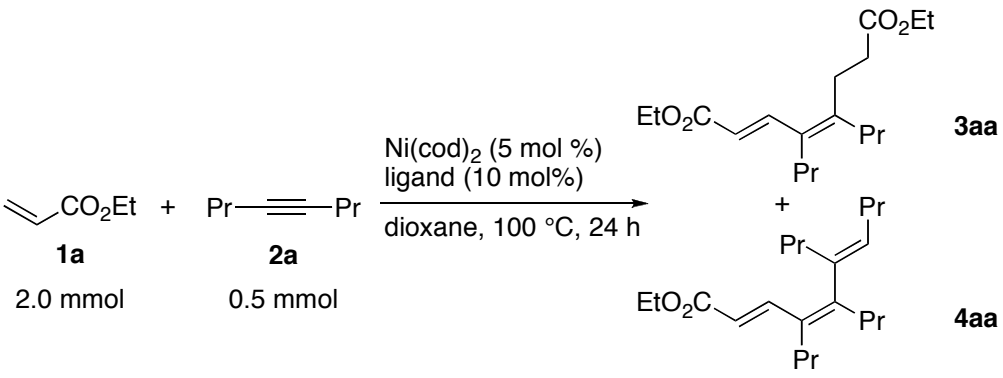
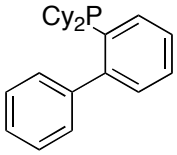
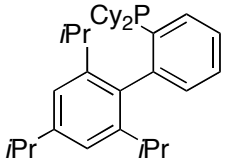
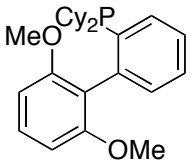


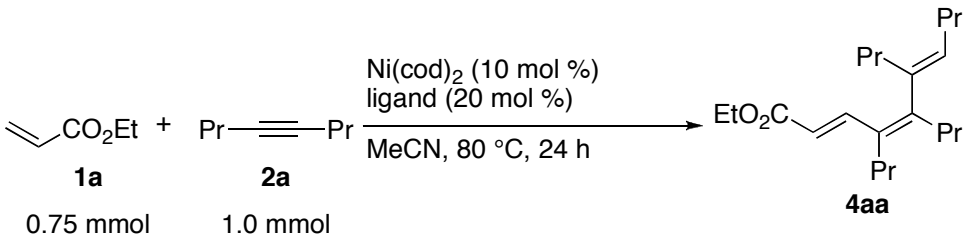
Table S1. Optimization of a Ligand for Cotrimerization between Two Molecules of Acrylates and One Alkyne to Afford 1,3-Diene **3**.[a]



entry	ligand	yield (%)	**3aa**[b]	**4aa**[c]
1	IPr (5 mol%)		19	6
2	IPr (7.5 mol%)		93	6
3	IPr (10 mol%)		99	<1
4	IPr (15 mol%)		98	<2
5	IMes		51	21
6			7	29
7			6	22
8			<1	23
9	PCy_3		19	68
10	PPh_3		8	78
11	$P(4\text{-MeO-}C_6H_4)_3$		12	70

[a]Reactions were carried out using $Ni(cod)_2$ (5 mol %), ligand (10 mol %), **1** (2.0 mmol, 2.0 equiv.), and **2** (0.5 mmol) in 2 mL of dioxane at 100 °C for 24 h. [b]Yields base on alkyne **2a**. [c]NMR yields.

Table S2. Optimization of a Ligand for Cotrimerization between an Acrylate and Two Molecules of Alkynes to Afford 1,3,5-Triene **4**.[a]



1a 0.75 mmol **2a** 1.0 mmol **4aa**

entry	ligand	yield (%) **4aa**[b]
1	PBu_3	45
2	PCy_3	79
3	$PtBu_3$	6
4	PPh_3	75
5	$P(4\text{-}MeO\text{-}C_6H_4)_3$	92
6	$P(4\text{-}MeO\text{-}C_6H_4)_3$	81[c]
7	$P(2\text{-}MeO\text{-}C_6H_4)_3$	24
8	$P(4\text{-}F\text{-}C_6H_4)_3$	15
9	dppe (10 mol%)	17
10	dppf (10 mol%)	13

[a]Reactions were carried out using $Ni(cod)_2$ (10 mol %), ligand (20 mol %), **1** (0.75 mmol, 1.5 equiv.), and **2** (1.0 mmol) in 2 mL of MeCN at 80 °C for 24 h. [b]Yields based on alkyne **2a**. [c]Reactions was carried out using **1** (4.0 mmol, 8 equiv.), and **2** (1.0 mmol).