

Supporting Information for:

Nickel-catalyzed [4+2] cycloaddition for highly substituted arenes

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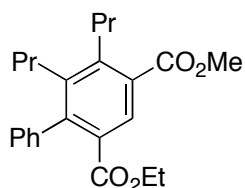
Instrumentation and Chemicals

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. ^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on Varian UNITY INOVA 500 spectrometer and were recorded in CDCl_3 . Chemical shifts (δ) are in parts per million relative to CHCl_3 at 7.26 ppm for ^1H and relative to CDCl_3 at 77.0 ppm for ^{13}C unless otherwise noted. Elemental analyses were performed by Elemental Analysis Center of Kyoto University. High-resolution mass spectra were obtained with a JEOL JMS-MS700 (EI) or a Thermo Fisher SCIENTIFIC EXACTIVE (ESI, APCI) spectrometer. Infrared spectra (IR) spectra were determined on a SHIMADZU IR Affinity-1 spectrometer. 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. and stored in a dry box under a purified argon atmosphere. Triphenylphosphine was purchased from Wako Pure Chemical Co. and purified by recrystallization from ethanol. Dienes **1a–h**,^[1] cyclododecyne (**2d**), and cyclopentadecyne (**2e**)^[2] were prepared according to the literature. 1-(4-Methoxyphenyl)-1-heptyne (**2i**) and 1-(4-fluorophenyl)-1-heptyne (**2j**) were prepared by Sonogashira cross-coupling reaction of 1-heptyne with corresponding aryl iodides. All reactions were performed in WHEATON 5.0 mL V-vial with 20–400 screw cap.

Experimental procedure and characterization data for nickel-catalyzed [4+2] cycloaddition of diens with alkynes and sequential aromatization

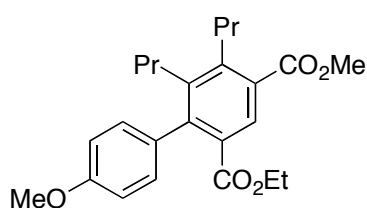
General procedure. The reaction was performed in a 5 mL sealed vessel equipped with a Teflon-coated magnetic stirrer tip. An diene **1** (0.50 mmol) and an alkyne **2** (1.5 mmol) were added to a solution of bis(1,5-cyclooctadiene)nickel (7 mg, 0.025 mmol) and triphenylphosphine (8 mg, 0.030 mmol) in toluene (1 mL) in a dry box. The VIAL was taken outside the dry box and heated at 100 °C for 6 h. After cooled to ambient temperature, DBU (0.15 mL, 1.0 mmol) was added to the mixture, and this was stirred vigorously under air at room temperature for 2 h. The resulting reaction mixture was filtered through a silica gel pad and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (hexane/ethyl acetate = 10:1) to give the corresponding arene **3**.

2-Ethyl 4-methyl 5,6-dipropyl-[1,1'-biphenyl]-2,4-dicarboxylate (**3aa**).



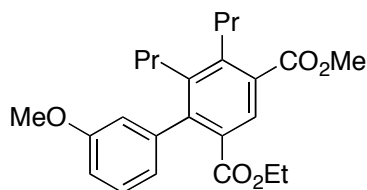
Colorless oil. ¹H NMR (500 MHz, CDCl₃): δ 8.08 (s, 1H), 7.36 (m, 3H), 7.16 (m, 2H), 3.95 (q, *J* = 7.0 Hz, 2H), 3.92 (s, 3H), 2.95 (t, *J* = 8.0 Hz, 2H), 2.42 (t, *J* = 8.0 Hz, 2H), 1.59 (m, 2H), 1.31 (m, 2H), 1.04 (t, *J* = 7.0 Hz, 3H), 0.92 (t, *J* = 7.5 Hz, 3H), 0.72 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 168.33, 167.83, 145.50, 144.89, 141.64, 140.18, 130.27, 130.07, 128.80, 128.74, 127.59, 127.02, 60.75, 52.13, 32.18, 32.04, 25.12, 24.38, 14.71, 14.51, 13.64. IR (neat): 2962, 1728, 1232, 703 cm⁻¹. HRMS (APCI) calcd for C₂₃H₂₉O₄ ([M+H]⁺): 369.2060. Found: 360.2053. Anal calcd for C₂₃H₂₈O₄: C, 74.97; H, 7.66. Found: C, 74.91; H, 7.67.

2-Ethyl 4-methyl 4'-methoxy-5,6-dipropyl-[1,1'-biphenyl]-2,4-dicarboxylate (**3ba**).



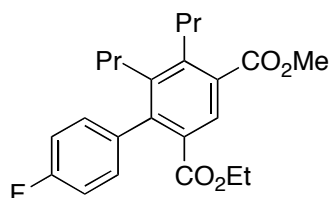
White powder, mp. 66–67 °C (hexane-AcOEt). ¹H NMR (500 MHz, CDCl₃): δ 8.04 (s, 1H), 7.07 (d, *J* = 9.0 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 3.98 (q, *J* = 7.0 Hz, 2H), 3.91 (s, 3H), 3.85 (s, 3H), 2.93 (t, *J* = 8.0 Hz, 2H), 2.43 (t, *J* = 8.0 Hz, 2H), 1.58 (m, 2H), 1.30 (m, 2H), 1.03 (t, *J* = 7.5 Hz, 3H), 0.98 (t, *J* = 7.0 Hz, 3H), 0.74 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 168.31, 167.99, 158.58, 145.38, 144.56, 142.07, 132.30, 130.43, 129.99, 129.80, 128.53, 113.02, 60.77, 55.19, 52.15, 32.19, 31.97, 25.10, 24.38, 14.75, 14.59, 13.79. IR (KBr): 2961, 1727, 1707, 1516, 1250, 1028, 841 cm⁻¹. HRMS (APCI) calcd for C₂₄H₃₁O₅ ([M+H]⁺): 399.2166. Found: 399.2154. Anal calcd for C₂₄H₃₀O₅: C, 72.34; H, 7.59. Found: C, 72.49; H, 7.75.

2-Ethyl 4-methyl 3'-methoxy-5,6-dipropyl-[1,1'-biphenyl]-2,4-dicarboxylate (3ca).



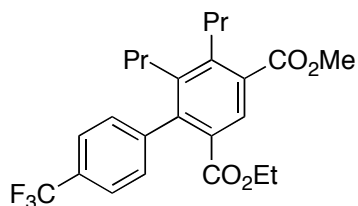
Pale yellow oil. ^1H NMR (500 MHz, CDCl_3): δ 8.07 (s, 1H), 7.28 (dd, $J = 8.0, 7.0$ Hz, 1H), 6.90 (ddd, $J = 8.0, 2.5, 1.0$ Hz, 1H), 6.76 (ddd, $J = 7.0, 1.5, 1.0$ Hz, 1H), 6.71 (dd, $J = 2.5, 1.5$ Hz, 1H), 3.97 (q, $J = 7.0$ Hz, 2H), 3.92 (s, 3H), 3.80 (s, 3H), 2.94 (t, $J = 8.5$ Hz, 2H), 2.43 (t, $J = 8.0$ Hz, 2H), 1.57 (m, 2H), 1.34 (m, 2H), 1.04 (t, $J = 7.0$ Hz, 3H), 0.96 (t, $J = 7.0$ Hz, 3H), 0.75 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 168.27, 167.78, 158.93, 145.59, 144.58, 141.55, 141.44, 130.17, 129.93, 128.72, 128.62, 121.42, 114.36, 112.67, 60.79, 55.24, 52.20, 32.15, 32.05, 25.12, 24.61, 14.78, 14.63, 13.69. IR (neat): 2960, 1727, 1589, 1465, 1233, 790, 708 cm^{-1} . HRMS (APCI) calcd for $\text{C}_{24}\text{H}_{31}\text{O}_5$ ($[\text{M}+\text{H}]^+$): 399.2166. Found: 399.2154.

2-Ethyl 4-methyl 4'-fluoro-5,6-dipropyl-[1,1'-biphenyl]-2,4-dicarboxylate (3da).



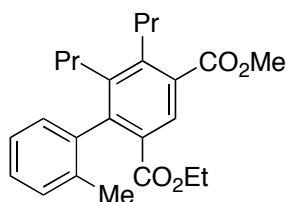
Pale yellow oil. ^1H NMR (500 MHz, CDCl_3): δ 8.09 (s, 1H), 7.14–7.06 (m, 4H), 3.99 (q, $J = 7.0$ Hz, 2H), 3.92 (s, 3H), 2.93 (t, $J = 8.0$ Hz, 2H), 2.39 (t, $J = 8.0$ Hz, 2H), 1.58 (m, 2H), 1.29 (m, 2H), 1.04 (t, $J = 7.0$ Hz, 3H), 0.99 (t, $J = 7.0$ Hz, 3H), 0.74 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 168.23, 167.56, 161.98 (d, $J_{\text{CF}} = 245$ Hz), 145.66, 143.84, 141.84, 135.99 (d, $J_{\text{CF}} = 3.3$ Hz), 130.46, 130.33 (d, $J_{\text{CF}} = 7.6$ Hz), 129.93, 128.87, 114.62 (d, $J_{\text{CF}} = 21.5$ Hz), 60.87, 52.23, 32.18, 32.02, 25.11, 24.34, 14.75, 14.57, 13.76. IR (neat): 2963, 1727, 1513, 838 cm^{-1} . HRMS (APCI) calcd for $\text{C}_{27}\text{H}_{28}\text{FO}_4$ ($[\text{M}+\text{H}]^+$): 387.1966. Found: 387.1951.

2-Ethyl 4-methyl 5,6-dipropyl-4'-(trifluoromethyl)-[1,1'-biphenyl]-2,4-dicarboxylate (3ea).



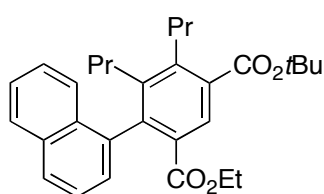
White powder, mp. 55–56 $^{\circ}\text{C}$ (hexane-AcOEt). ^1H NMR (500 MHz, CDCl_3): δ 8.16 (s, 1H), 7.66 (d, $J = 8.5$ Hz, 2H), 7.30 (d, $J = 8.5$ Hz, 2H), 3.97 (q, $J = 7.0$ Hz, 2H), 3.93 (s, 3H), 2.94 (t, $J = 8.0$ Hz, 2H), 2.36 (t, $J = 8.5$ Hz, 2H), 1.59 (m, 2H), 1.29 (m, 2H), 1.04 (t, $J = 7.0$ Hz, 3H), 0.93 (t, $J = 7.5$ Hz, 3H), 0.72 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 168.14, 167.10, 146.02, 144.24, 143.50, 141.35, 130.86, 129.31 (q, $J_{\text{CF}} = 32.4$ Hz), 129.30, 129.21, 129.16, 124.58 (q, $J_{\text{CF}} = 3.9$ Hz), 124.22 (q, $J_{\text{CF}} = 271$ Hz), 60.94, 52.30, 32.14, 32.03, 25.11, 24.38, 14.75, 14.53, 13.54. IR (KBr): 2969, 1730, 1701, 1324, 1237, 1163, 1126, 842 cm^{-1} . HRMS (APCI) calcd for $\text{C}_{24}\text{H}_{28}\text{F}_3\text{O}_4$ ($[\text{M}+\text{H}]^+$): 437.1934. Found: 437.1926. Anal calcd for $\text{C}_{24}\text{H}_{27}\text{F}_3\text{O}_4$: C, 66.04; H, 6.24. Found: C, 66.32; H, 6.26.

2-Ethyl 4-methyl 2'-methyl-5,6-dipropyl-[1,1'-biphenyl]-2,4-dicarboxylate (3fa).



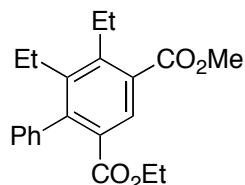
Colorless oil. ^1H NMR (500 MHz, CDCl_3): δ 8.14 (s, 1H), 7.26–7.15 (m, 3H), 6.99 (dd, $J = 7.5, 1.0$ Hz, 1H), 3.96 (q, $J = 7.0$ Hz, 2H), 3.92 (s, 3H), 3.07 (m, 1H), 2.84 (m, 1H), 2.47 (m, 1H), 2.16 (m, 1H), 1.97 (s, 3H), 1.63 (m, 1H), 1.56 (m, 1H), 1.34–1.18 (m, 2H), 1.03 (t, $J = 7.5$ Hz, 3H), 0.93 (t, $J = 7.0$ Hz, 3H), 0.69 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 168.38, 167.48, 145.84, 144.41, 141.54, 139.52, 135.66, 130.08, 129.41, 129.32, 129.19, 128.63, 127.35, 125.04, 60.71, 52.19, 32.09, 32.02, 25.17, 23.83, 19.97, 14.69, 14.67, 13.61. IR (neat): 2961, 1728, 1233, 730 cm^{-1} . HRMS (APCI) calcd for $\text{C}_{24}\text{H}_{31}\text{O}_4$ ($[\text{M}+\text{H}]^+$): 383.2217. Found: 383.2204.

1-tert-Butyl 3-ethyl 4-(naphthalen-1-yl)-5,6-dipropylisophthalate (3ga)



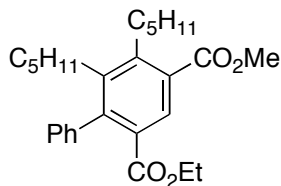
Pale yellow viscous oil. ^1H NMR (500 MHz, CDCl_3): δ 8.04 (s, 1H), 7.86 (m, 2H), 7.46 (m, 2H), 7.31 (m, 2H), 7.21 (dd, $J = 7.0, 1.0$ Hz, 1H), 3.68 (q, $J = 7.5$ Hz, 2H), 3.03 (m, 1H), 2.85 (m, 1H), 2.39 (m, 1H), 2.07 (m, 1H), 1.65 (m, 2H), 1.65 (s, 9H), 1.23 (m, 2H), 1.04 (t, $J = 7.5$ Hz, 3H), 0.56 (t, $J = 7.5$ Hz, 3H), 0.47 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 167.98, 167.60, 144.38, 142.25, 142.08, 138.00, 133.43, 133.13, 132.60, 130.47, 128.50, 128.03, 127.47, 126.34, 125.90, 125.84, 125.59, 124.83, 81.78, 60.39, 32.57, 32.07, 28.18, 25.24, 24.60, 14.71, 14.52, 13.04. IR (neat): 2964, 1722, 1251, 1153, 1028, 851, 802, 781 cm^{-1} . HRMS (EI) calcd for $\text{C}_{30}\text{H}_{36}\text{O}_4$ ($[\text{M}]^+$): 460.2614. Found: 460.2607.

2-Ethyl 4-methyl 5,6-diethyl-[1,1'-biphenyl]-2,4-dicarboxylate (3ab).



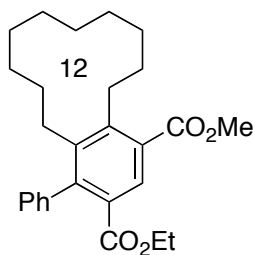
White powder, mp. 41–42 °C (hexane-AcOEt). ^1H NMR (500 MHz, CDCl_3): δ 8.09 (s, 1H), 7.37 (m, 3H), 7.18 (m, 2H), 3.95 (q, $J = 7.5$ Hz, 2H), 3.93 (s, 3H), 3.03 (q, $J = 7.5$ Hz, 2H), 2.52 (q, $J = 7.5$ Hz, 2H), 1.24 (t, $J = 7.5$ Hz, 3H), 0.93 (t, $J = 7.5$ Hz, 3H), 0.92 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 168.25, 167.75, 146.76, 144.90, 142.62, 140.07, 130.17, 130.01, 128.80, 128.75, 127.62, 127.03, 60.78, 52.20, 23.17, 22.64, 15.87, 15.32, 13.65. IR (KBr): 2984, 1725, 1711, 1244, 707 cm^{-1} . HRMS (APCI) calcd for $\text{C}_{21}\text{H}_{25}\text{O}_4$ ($[\text{M}+\text{H}]^+$): 341.1747. Found: 341.1733. Anal calcd for $\text{C}_{21}\text{H}_{24}\text{O}_4$: C, 74.09; H, 7.11. Found: 74.17; H, 7.27.

2-ethyl 4-methyl 5,6-dipentyl-[1,1'-biphenyl]-2,4-dicarboxylate (**3ac**).



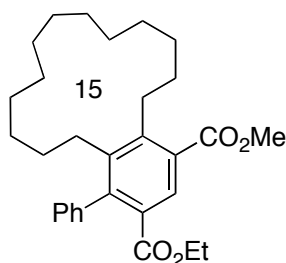
Colorless oil. ^1H NMR (500 MHz, CDCl_3): δ 8.07 (s, 1H), 7.35 (m, 3H), 7.16 (d, $J = 8.0$ Hz, 2H), 3.95 (q, $J = 7.0$ Hz, 2H), 3.92 (s, 3H), 2.95 (t, $J = 8.0$ Hz, 2H), 2.43 (t, $J = 8.0$ Hz, 2H), 1.56 (m, 2H), 1.45–1.34 (m, 4H), 1.27 (m, 2H), 1.08 (m, 4H), 0.92 (t, $J = 7.0$ Hz, 6H), 0.75 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 168.34, 167.81, 145.68, 144.89, 141.72, 140.11, 130.19, 129.87, 128.77, 128.70, 127.57, 127.00, 60.76, 52.18, 32.49, 32.07, 31.52, 30.49, 30.11, 29.71, 22.41, 21.87, 14.05, 13.82, 13.64. IR (neat): 2956, 1727, 1234, 1031, 703 cm^{-1} . HRMS (APCI) calcd for $\text{C}_{27}\text{H}_{37}\text{O}_4$ ($[\text{M}+\text{H}]^+$): 425.2686. Found: 425.2675.

3-Ethyl 1-methyl 4-phenyl-5,6,7,8,9,10,11,12,13,14-decahydrobenzo[12]annulene-1,3-dicarboxylate (**3ad**).



White powder, mp. 83–85 °C (hexane-AcOEt). ^1H NMR (500 MHz, CDCl_3): δ 8.06 (s, 1H), 7.35 (m, 3H), 7.16 (d, $J = 8.0$ Hz, 2H), 3.94 (q, $J = 7.0$ Hz, 2H), 3.92 (s, 3H), 3.09 (t, $J = 8.5$ Hz, 2H), 2.55 (t, $J = 8.5$ Hz, 2H), 1.72 (m, 2H), 1.56 (m, 4H), 1.44 (m, 6H), 1.38 (m, 2H), 1.23 (m, 2H), 0.92 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 168.53, 167.81, 145.50, 145.18, 141.75, 140.17, 130.72, 129.93, 128.76, 128.55, 127.53, 127.02, 60.77, 52.22, 29.16, 28.79, 28.58, 28.44, 28.29, 27.88, 27.39, 22.86, 22.65, 13.66. IR (KBr): 2934, 1723, 1705, 1296, 1154, 1028, 702 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{35}\text{O}_4$ ($[\text{M}+\text{H}]^+$): 423.2530. Found: 423.2525. Anal calcd for $\text{C}_{27}\text{H}_{34}\text{O}_4$: C, 76.74; H, 8.11. Found: C, 76.72; H, 7.99.

3-Ethyl 1-methyl 4-phenyl-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-5H-benzo[15]annulene-1,3-dicarboxylate (**3ae**).

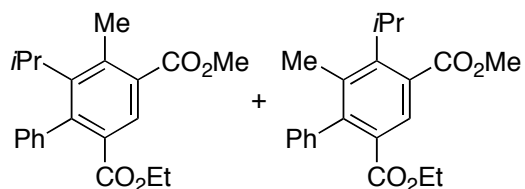


White powder, mp. 104–105 °C (hexane-AcOEt). ^1H NMR (500 MHz, CDCl_3): δ 8.10 (s, 1H), 7.36 (m, 3H), 7.15 (d, $J = 8.0$ Hz, 2H), 3.95 (q, $J = 7.5$ Hz, 2H), 3.92 (s, 3H), 2.93 (t, $J = 8.0$ Hz, 2H), 2.42 (t, $J = 8.5$ Hz, 2H), 1.67–1.55 (m, 4H), 1.45–1.23 (m, 16H), 1.10 (m, 2H), 0.92 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 168.28, 167.76, 145.84, 145.13, 141.83, 140.17, 130.26, 129.90, 128.85, 128.61, 127.60, 126.98, 60.76, 52.20, 30.08, 29.66, 29.30, 28.45, 27.92, 27.56, 26.56, 26.30, 26.27, 26.03, 24.94, 24.92, 13.64. IR (KBr): 2925, 1730, 1705, 1239, 1029, 709 cm^{-1} . HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{41}\text{O}_4$ ($[\text{M}+\text{H}]^+$): 465.2999. Found: 465.2996. Anal calcd for $\text{C}_{30}\text{H}_{40}\text{O}_4$: C, 77.55; H, 8.68. Found: C,

77.29; H, 8.88.

2-Ethyl 4-methyl 6-isopropyl-5-methyl-[1,1'-biphenyl]-2,4-dicarboxylate and

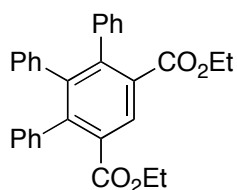
2-ethyl 4-methyl 5-isopropyl-6-methyl-[1,1'-biphenyl]-2,4-dicarboxylate (1:1 mixture) (3af).



Colorless oil. ^1H NMR (500 MHz, CDCl_3): δ 7.98 (s, 0.5H), 7.78 (s, 0.5H), 7.36 (m, 3H), 7.13 (m, 2H), 3.95 (q, $J = 7.0$ Hz, 2H), 3.92 (s, 3H), 3.46 (sept, $J = 7.0$ Hz, 0.5H), 3.20 (sept, $J = 7.0$ Hz, 0.5H), 2.65 (s, 1.5H),

2.11 (s, 1.5H), 1.37 (d, $J = 7.0$ Hz, 3H), 1.19 (d, $J = 7.0$ Hz, 3H), 0.92 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 170.49, 168.58, 168.04, 167.61, 148.06, 146.20, 144.54, 140.70, 136.57, 132.14, 132.03, 129.51, 128.64, 128.58, 127.92, 127.75, 127.69, 127.46, 127.04, 126.96, 60.81, 60.75, 52.39, 52.19, 31.11, 30.57, 21.10, 20.93, 18.65, 17.92, 13.65, 13.64. IR (neat): 2959, 1728, 1257, 1235, 1030, 703 cm^{-1} . HRMS (APCI) calcd for $\text{C}_{21}\text{H}_{25}\text{O}_4$ ($[\text{M}+\text{H}]^+$): 341.1747. Found: 341.1735.

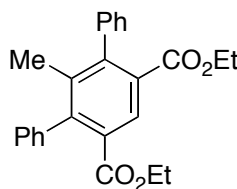
Diethyl 6'-phenyl-[1,1':2',1''-terphenyl]-3',5'-dicarboxylate (3hg).



Pale red powder, mp. 128–130 °C (hexane-AcOEt). ^1H NMR (500 MHz, CDCl_3): δ 8.25 (s, 1H), 7.10 (m, 6H), 6.97 (m, 4H), 6.87 (m, 3H), 6.68 (m, 2H), 4.02 (q, $J = 7.0$ Hz, 4H), 0.93 (t, $J = 7.0$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3): δ 167.94, 143.77, 142.76, 139.29, 138.01, 131.95, 131.03, 129.43,

129.06, 127.17, 126.78, 126.62, 125.93, 61.15, 13.61. IR (KBr): 1730, 1318, 1200, 1085, 761, 699 cm^{-1} . HRMS (APCI) calcd for $\text{C}_{30}\text{H}_{27}\text{O}_4$ ($[\text{M}+\text{H}]^+$): 451.1904. Found: 451.1893. Anal calcd for $\text{C}_{30}\text{H}_{26}\text{O}_4$: C, 79.98; H, 5.82. Found: C, 79.98; H, 5.96.

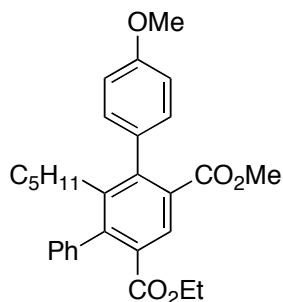
Diethyl 2'-methyl-[1,1':3',1''-terphenyl]-4',6'-dicarboxylate (3hh).



Pale red powder, mp. 68–72 °C (hexane-AcOEt). ^1H NMR (500 MHz, CDCl_3): δ 8.15 (s, 1H), 7.39 (m, 6H), 7.19 (d, $J = 8.0$ Hz, 4H), 4.01 (q, $J = 7.0$ Hz, 4H), 1.81 (s, 3H), 0.96 (t, $J = 7.0$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3): δ 167.73, 144.68, 140.11, 136.71, 131.32, 128.54, 128.03, 127.60,

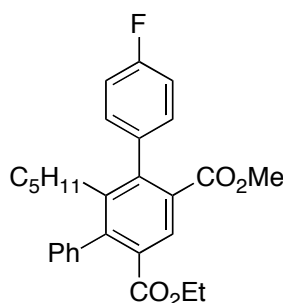
127.19, 60.96, 18.83, 13.66. IR (KBr): 1719, 1251, 1026, 765, 707 cm^{-1} . HRMS (APCI) calcd for $\text{C}_{25}\text{H}_{25}\text{O}_4$ ($[\text{M}+\text{H}]^+$): 389.1747. Found: 389.1736.

4'-Ethyl 6'-methyl 4-methoxy-2'-pentyl-[1,1':3',1''-terphenyl]-4',6'-dicarboxylate (3ai).



Pale yellow viscous oil. ^1H NMR (500 MHz, CDCl_3): δ 8.08 (s, 1H), 7.36 (m, 3H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.13 (d, $J = 8.5$ Hz, 2H), 6.93 (d, $J = 8.5$ Hz, 2H), 3.99 (q, $J = 7.0$ Hz, 2H), 3.85 (s, 3H), 3.60 (s, 3H), 2.25 (t, $J = 8.0$ Hz, 2H), 1.03 (m, 2H), 0.95 (t, $J = 7.0$ Hz, 3H), 0.82 (m, 2H), 0.70 (m, 2H), 0.57 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 168.04, 167.75, 158.64, 144.47, 144.42, 142.41, 139.55, 131.59, 131.53, 129.88, 128.89, 127.65, 127.30, 127.14, 113.14, 60.93, 55.18, 52.05, 31.62, 30.31, 29.80, 21.49, 13.67, 13.61. IR (neat): 2956, 1728, 1515, 1247, 1032, 833, 704 cm^{-1} . HRMS (APCI) calcd for $\text{C}_{29}\text{H}_{33}\text{O}_5$ ($[\text{M}+\text{H}]^+$): 461.2323. Found: 461.2310. Anal calcd for $\text{C}_{29}\text{H}_{32}\text{O}_5$: C, 75.63; H, 7.00. Found: C, 75.72; H, 7.02.

4'-Ethyl 6'-methyl 4-fluoro-2'-pentyl-[1,1':3',1''-terphenyl]-4',6'-dicarboxylate (3ah).

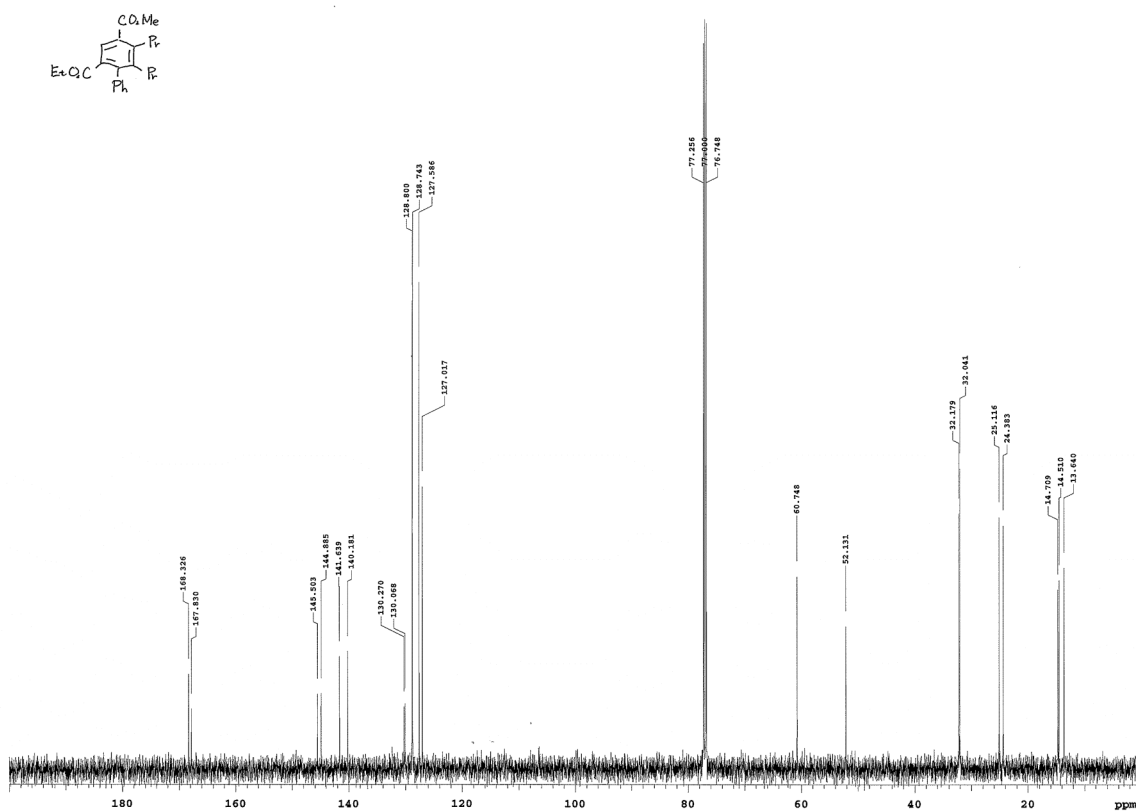
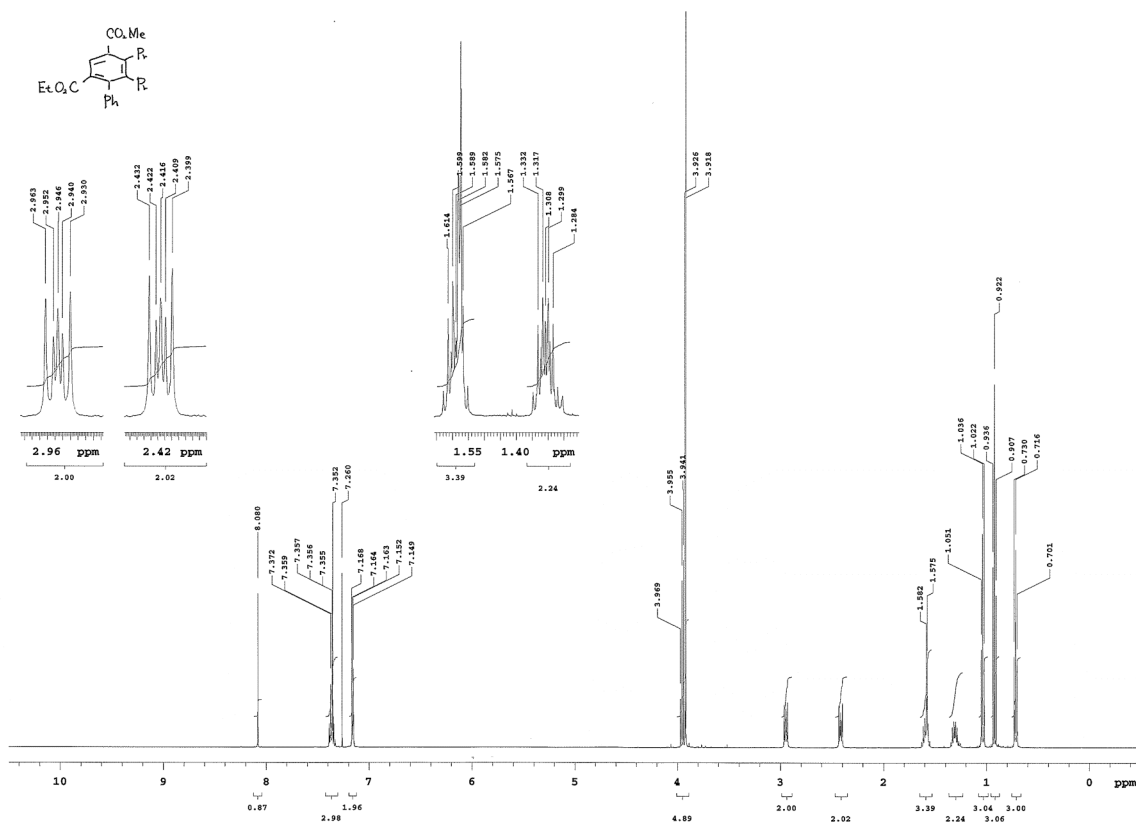


Pale yellow viscous oil. ^1H NMR (500 MHz, CDCl_3): δ 8.13 (s, 1H), 7.37 (m, 3H), 7.23–7.17 (m, 4H), 7.10 (m, 2H), 3.99 (q, $J = 7.0$ Hz, 2H), 3.61 (s, 3H), 2.22 (t, $J = 8.0$ Hz, 2H), 1.02 (m, 2H), 0.95 (t, $J = 7.0$ Hz, 3H), 0.81 (m, 2H), 0.70 (m, 2H), 0.57 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 167.66, 167.60, 162.01 (d, $J_{\text{CF}} = 245$ Hz), 144.71, 143.71, 142.19, 139.29, 135.24 (d, $J_{\text{CF}} = 3.3$ Hz), 132.06, 131.09, 130.42 (d, $J_{\text{CF}} = 7.6$ Hz), 128.84, 127.70, 127.61, 127.27, 114.75 (d, $J_{\text{CF}} = 21.0$ Hz), 61.02, 52.07, 31.60, 30.33, 29.78, 21.44, 13.66, 13.59. IR (neat): 2956, 1733, 1512, 838, 703 cm^{-1} . HRMS (APCI) calcd for $\text{C}_{28}\text{H}_{30}\text{FO}_4$ ($[\text{M}+\text{H}]^+$): 449.2123. Found: 449.2110. Anal calcd for $\text{C}_{28}\text{H}_{29}\text{FO}_4$: C, 74.98; H, 6.52. Found: C, 75.07; H, 6.38.

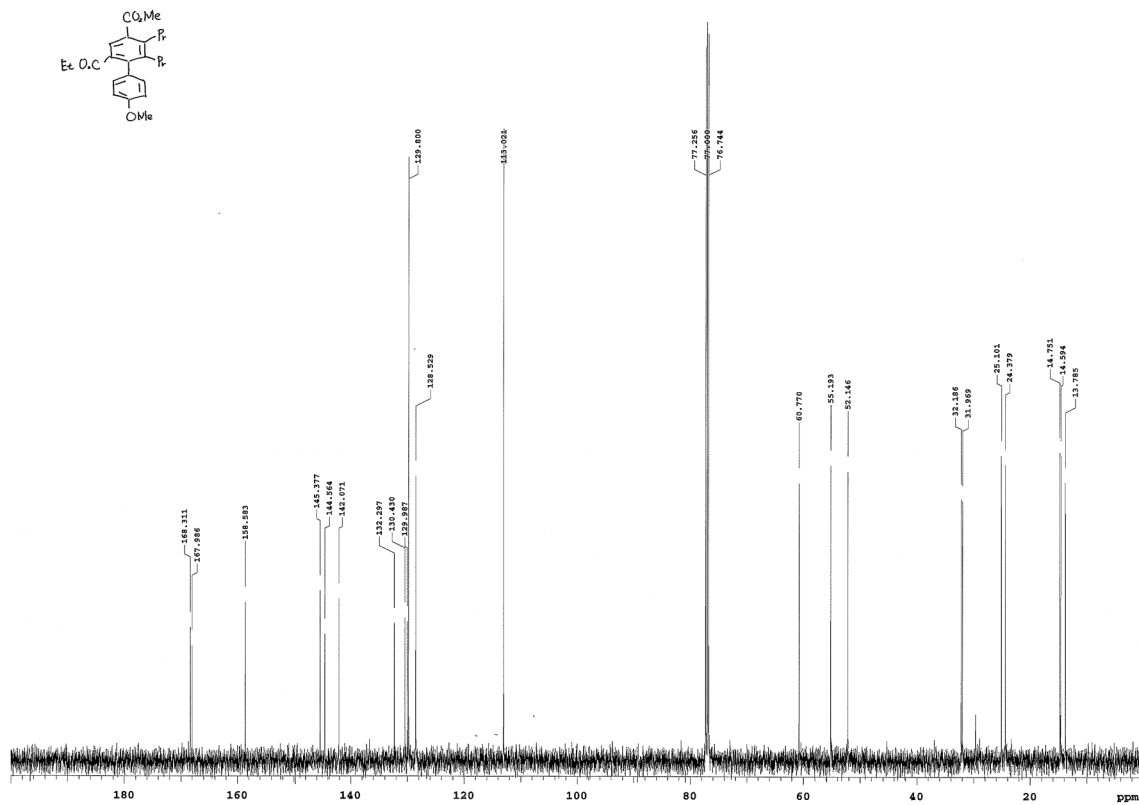
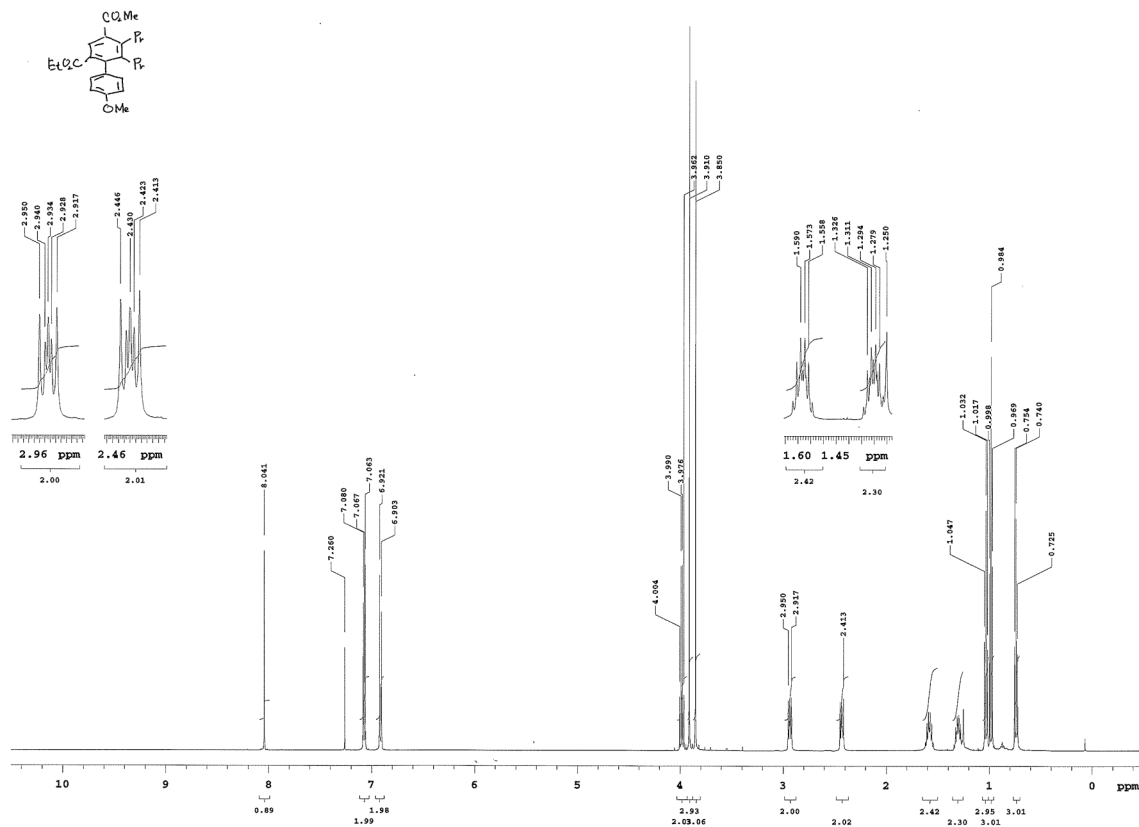
References

- [1] C. Dockendorff, S. Sahli, M. Olsen, L. Milhau, M. Lautens, *J. Am. Chem. Soc.* **2005**, *127*, 15028.
- [2] K. M. Brummond, K. D. Gesenberg, J. L. Kent, A. D. Kerekes, *Tetrahedron Lett.* **1998**, *39*, 8613.

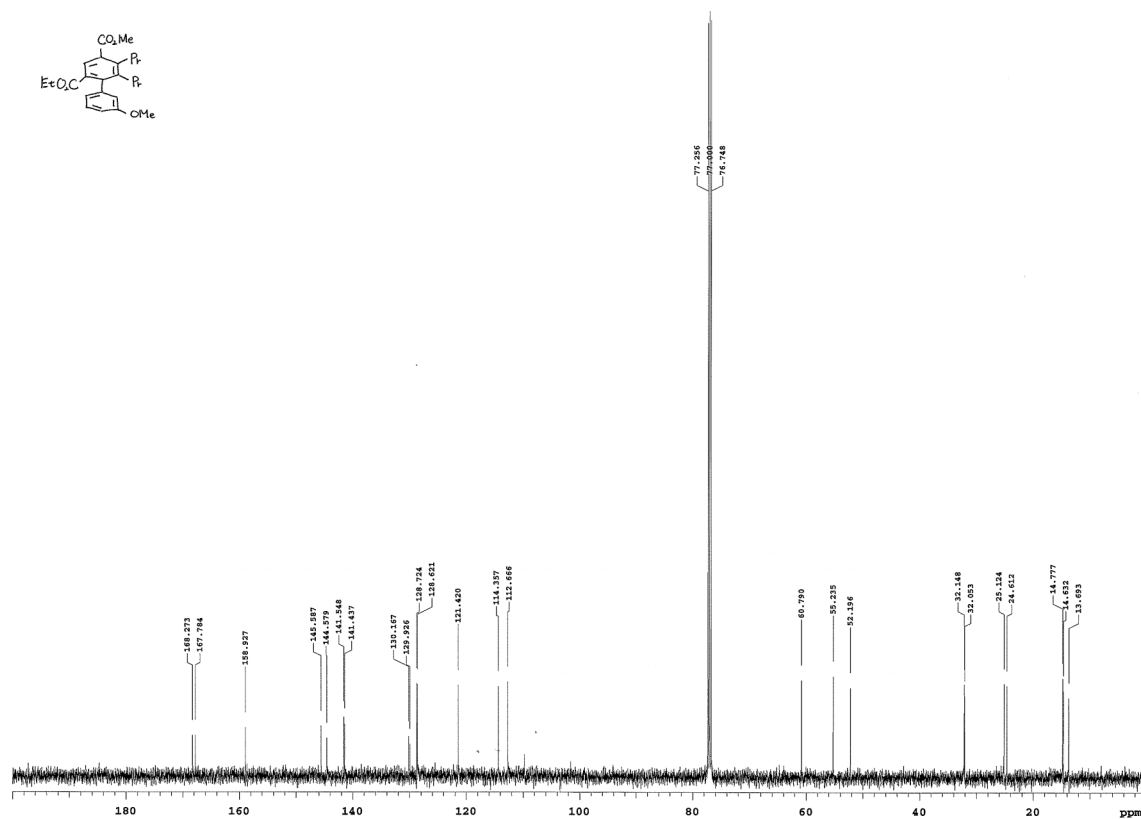
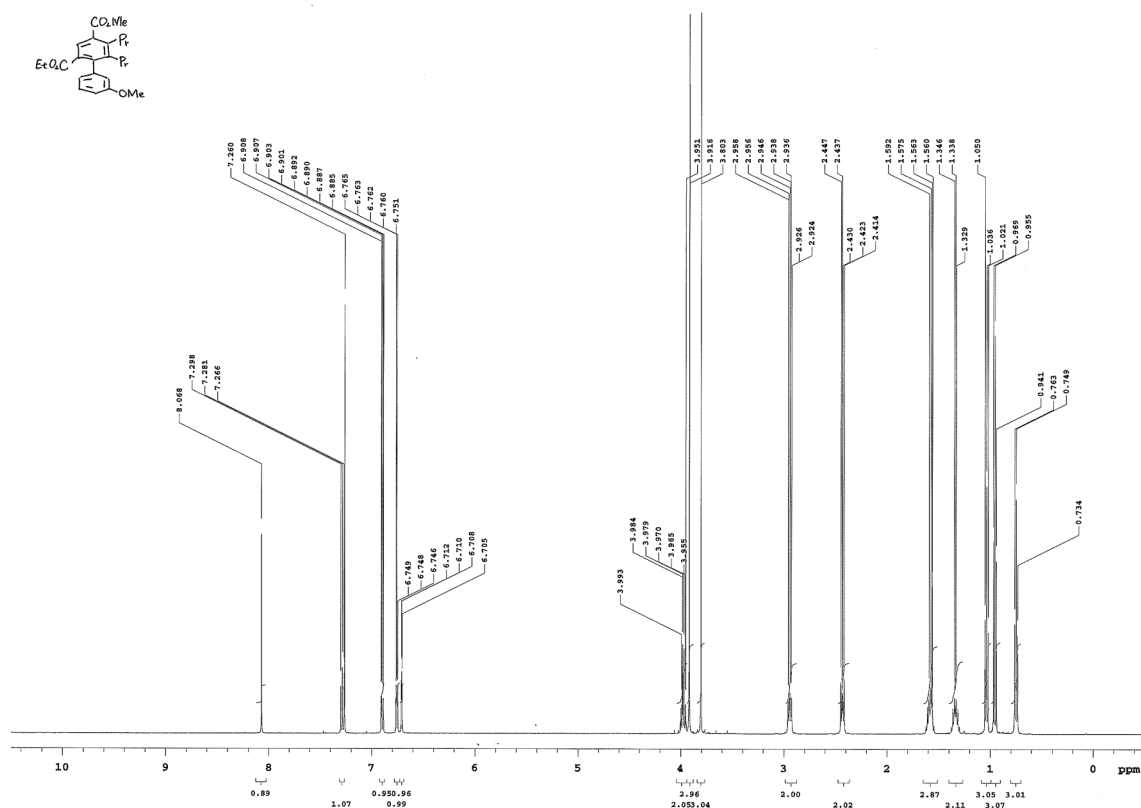
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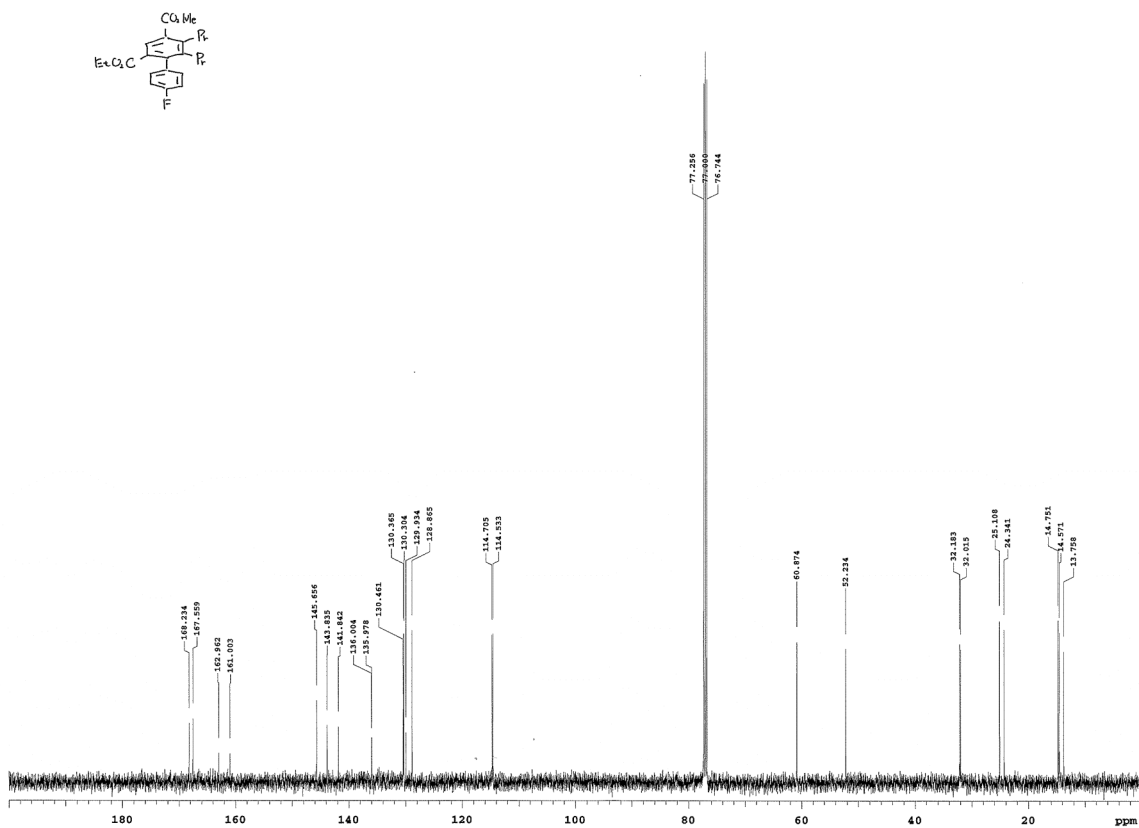
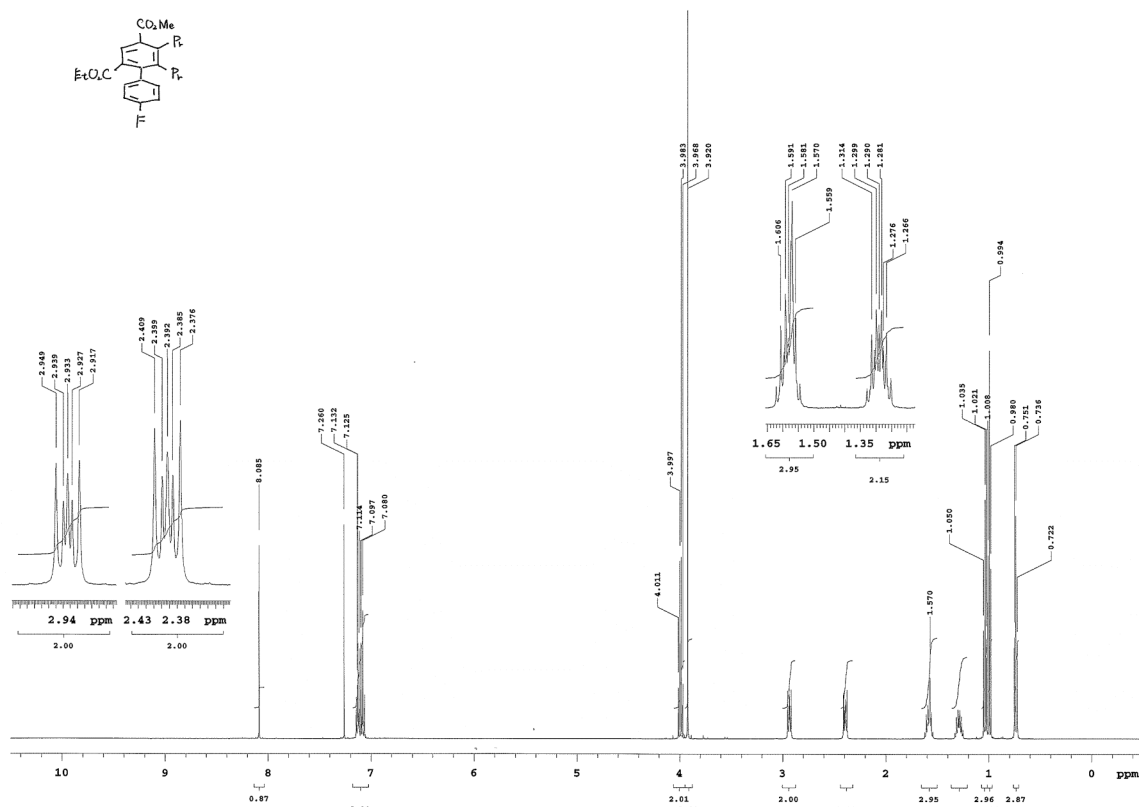
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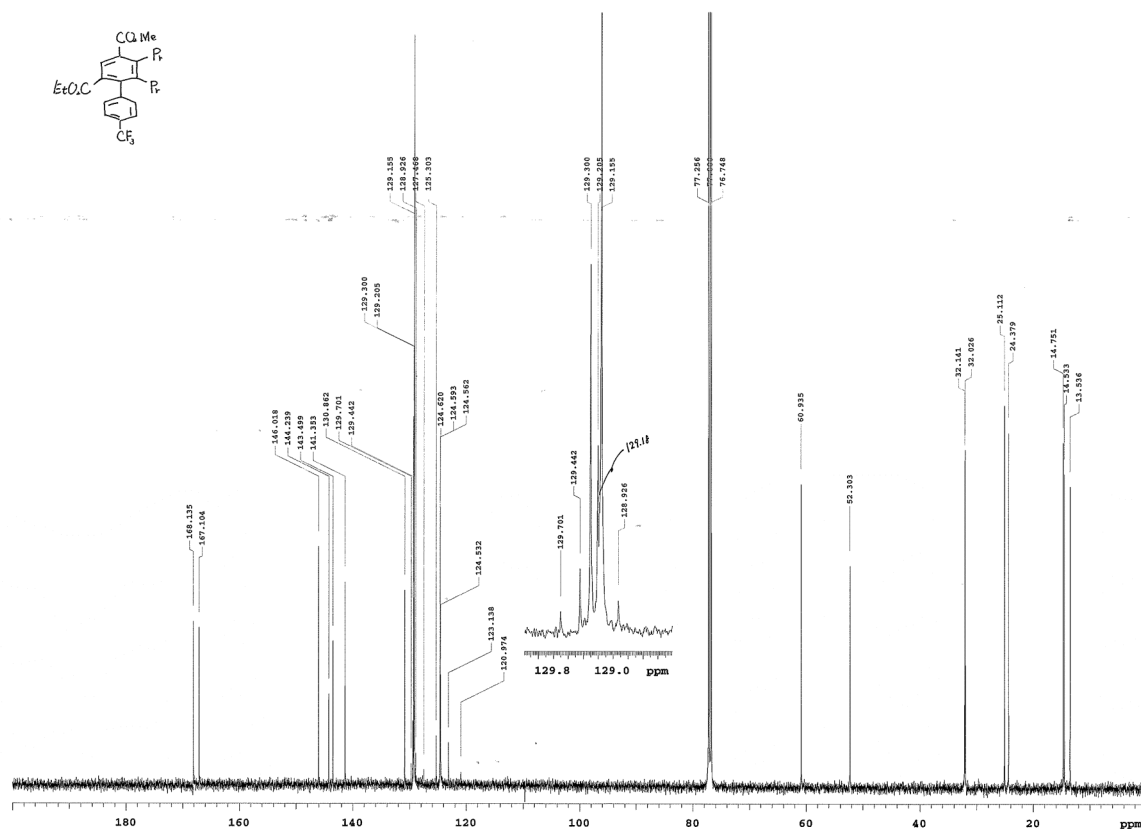
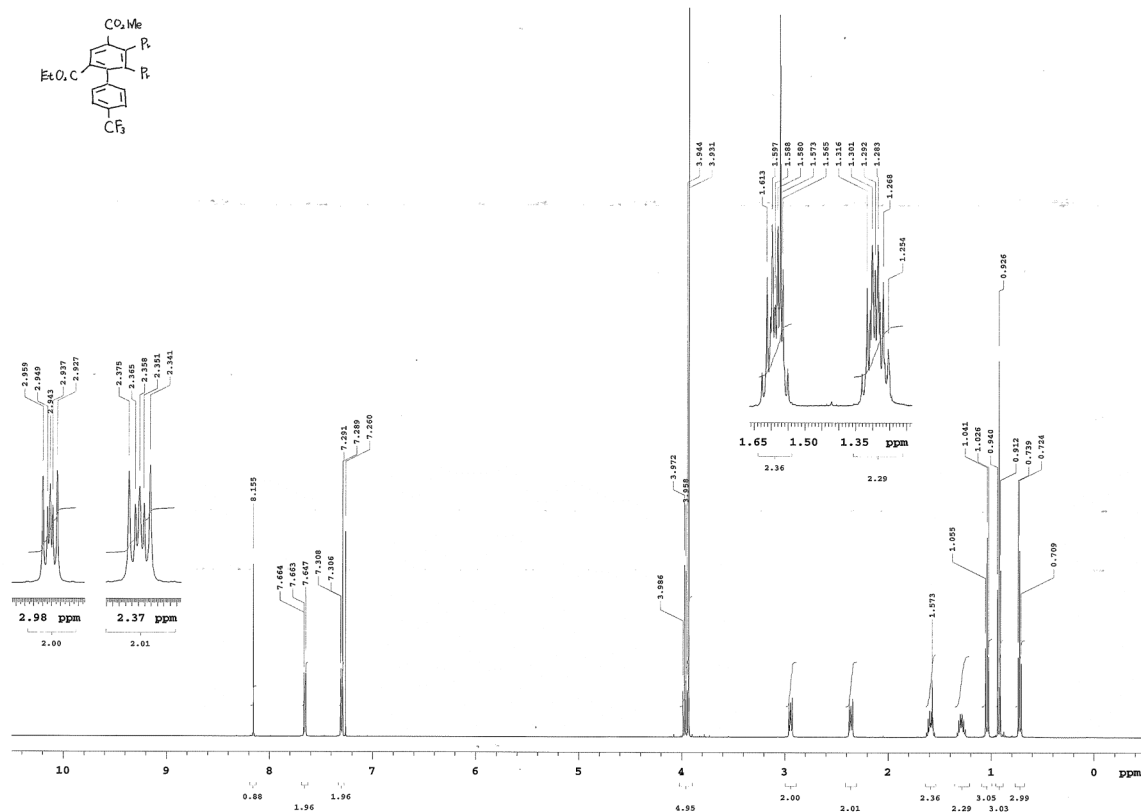
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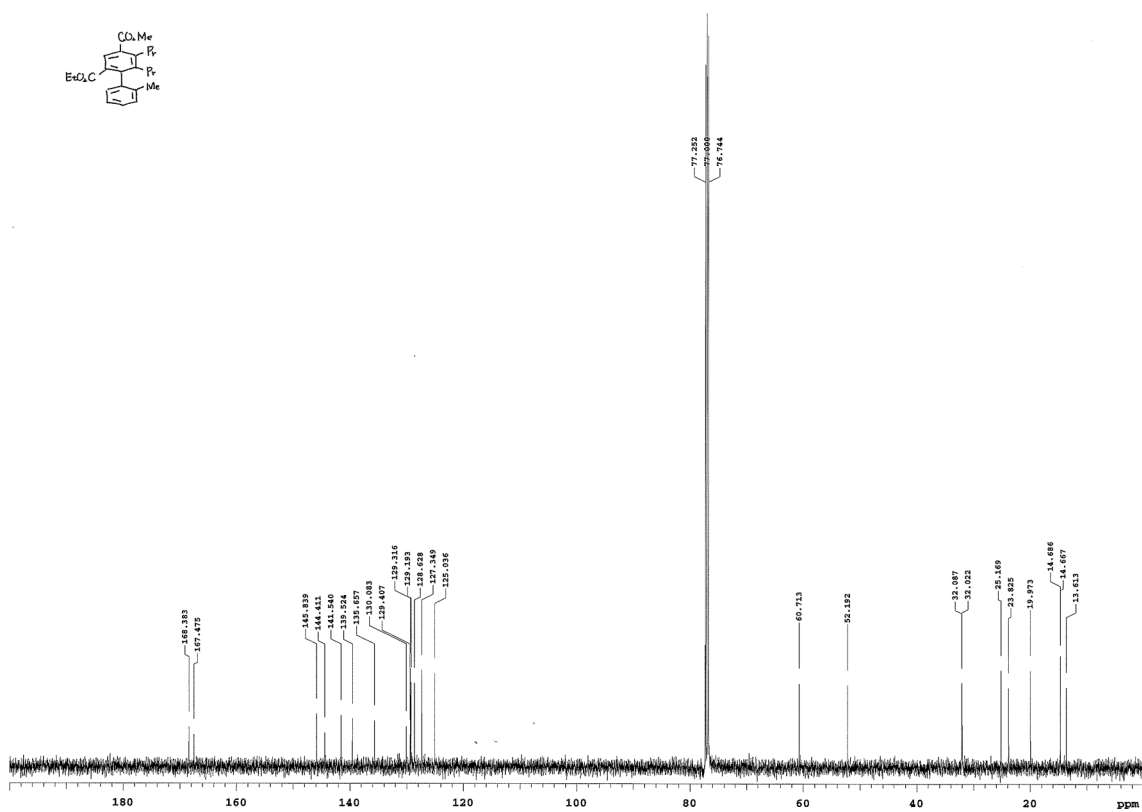
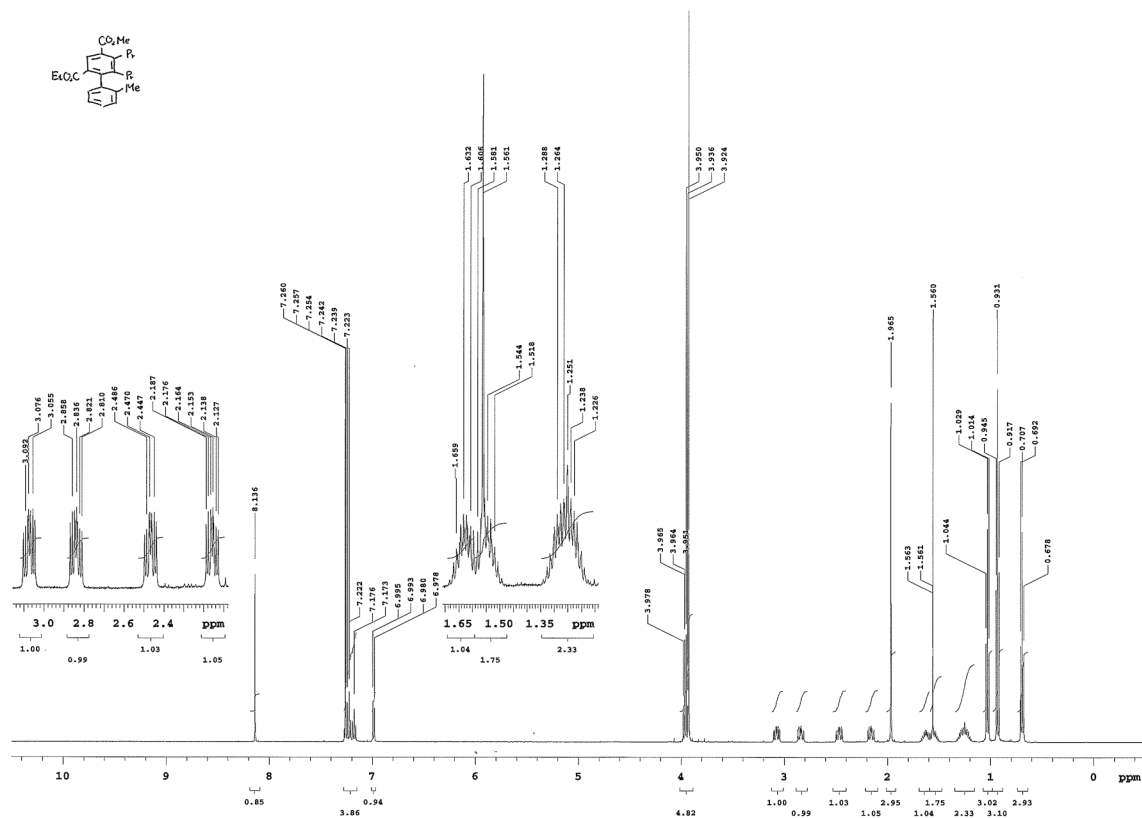
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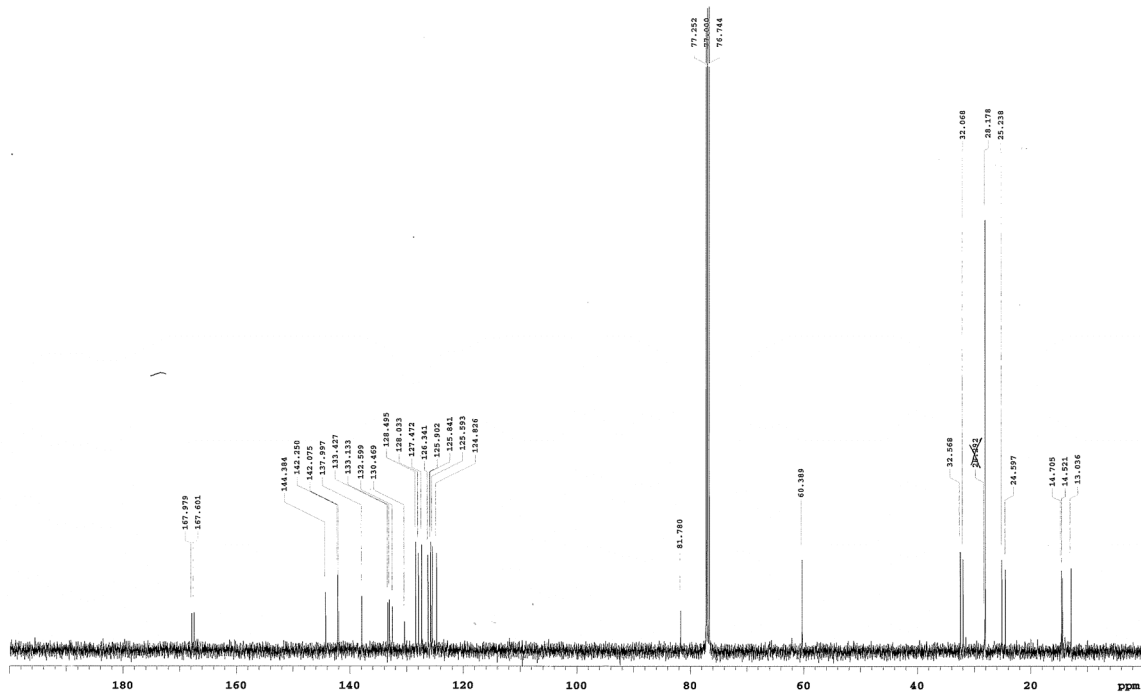
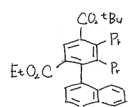
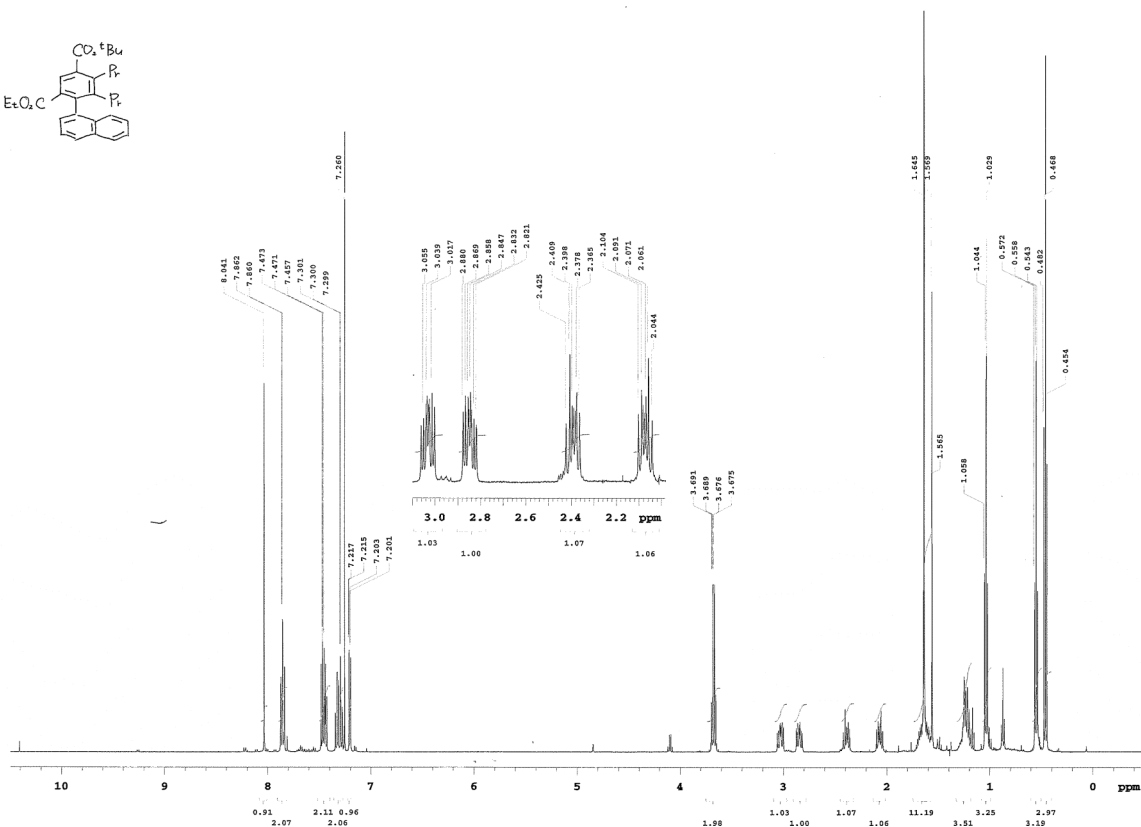
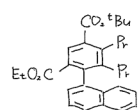
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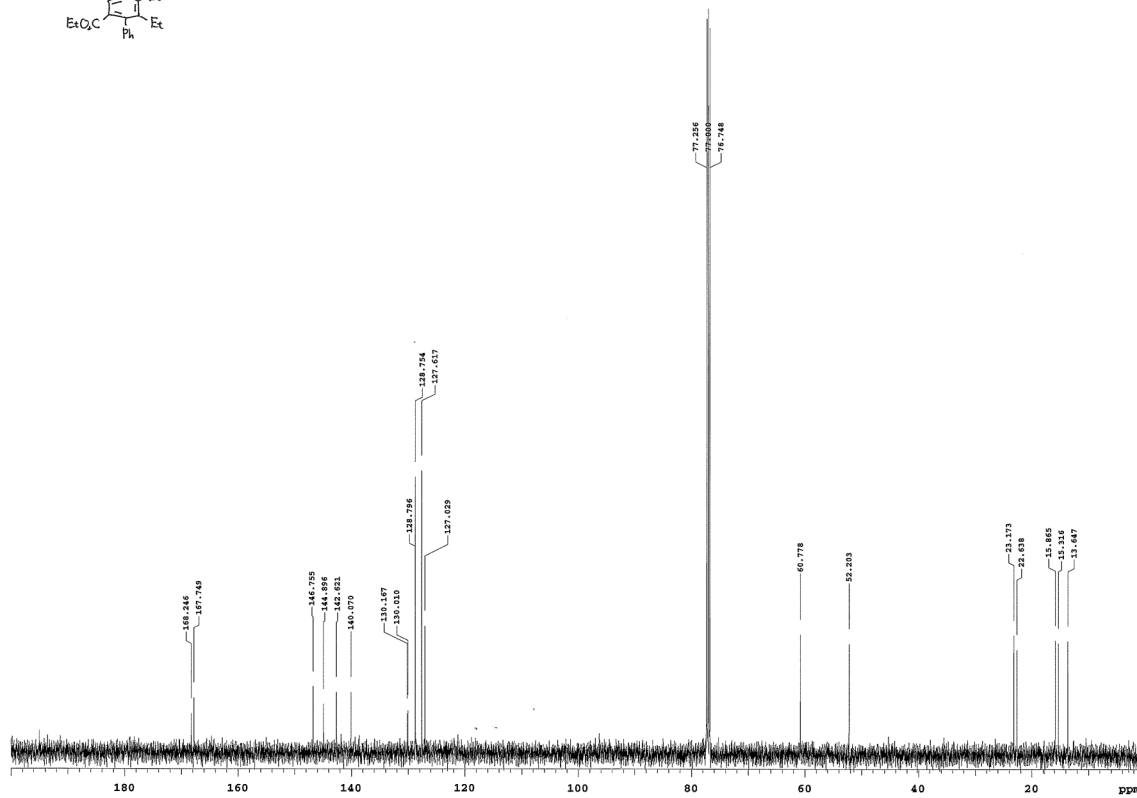
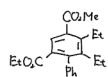
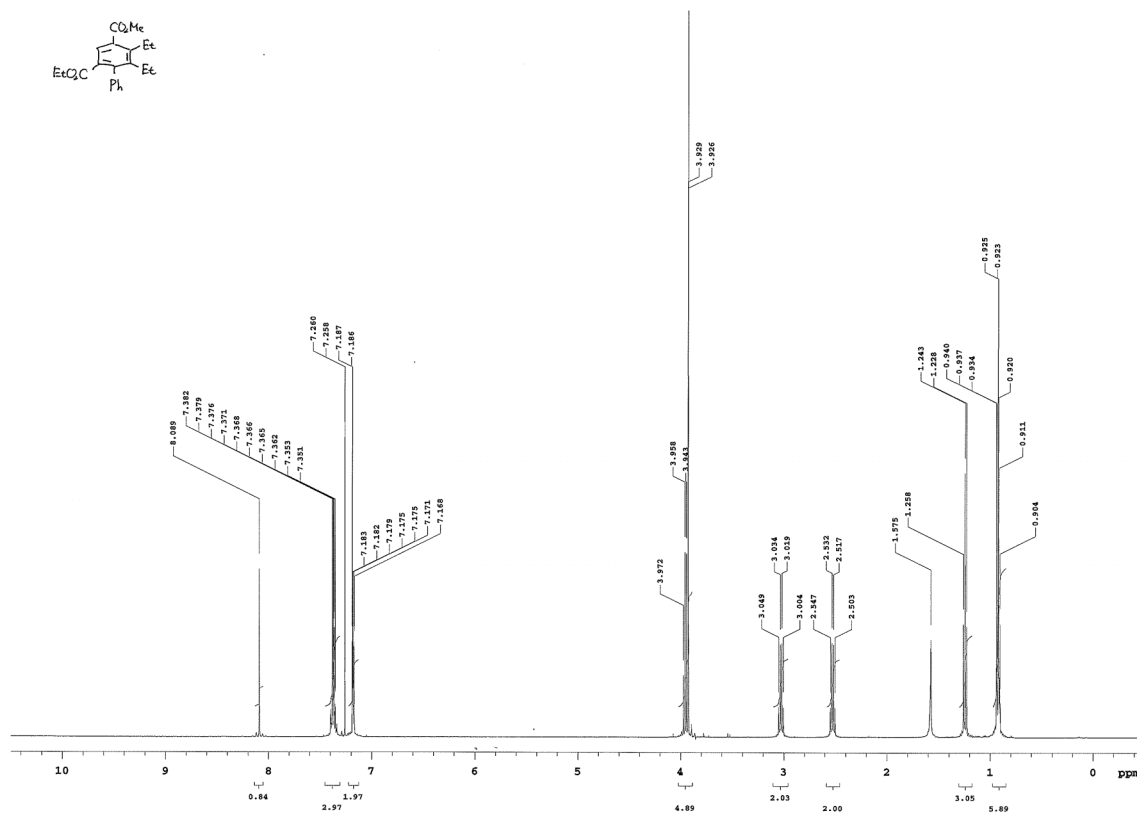
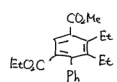
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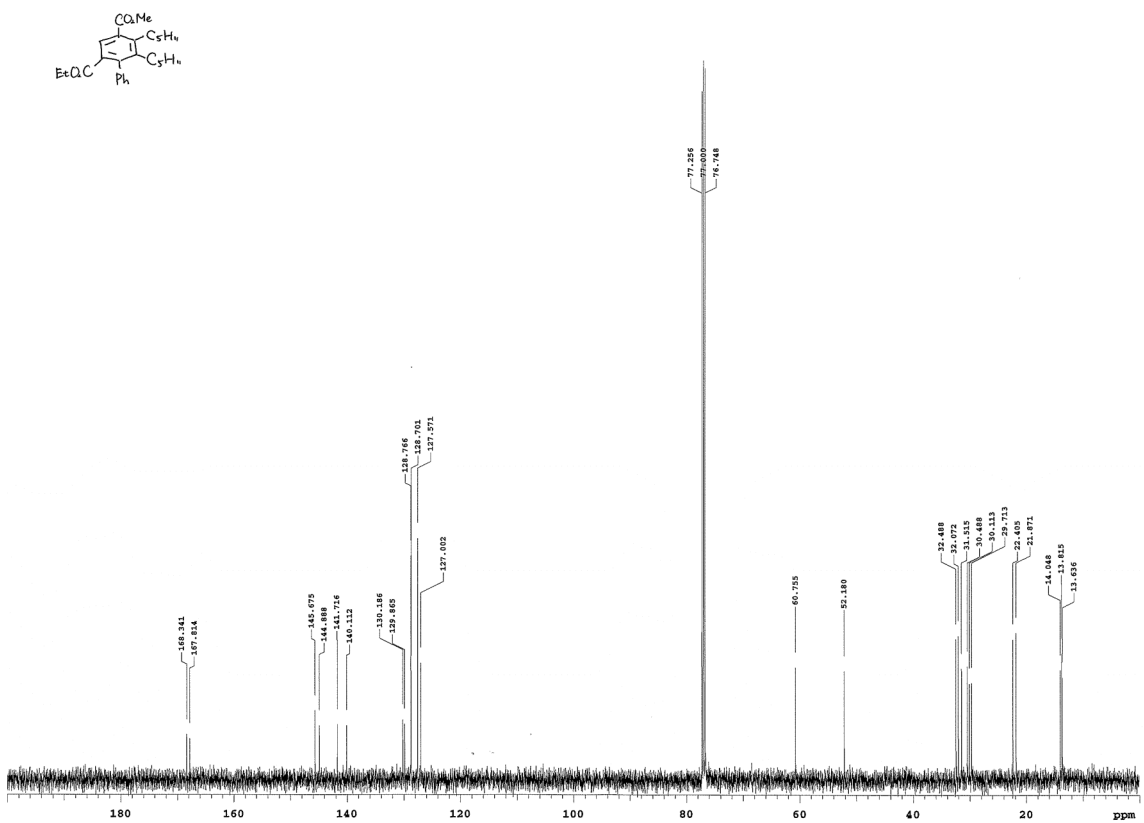
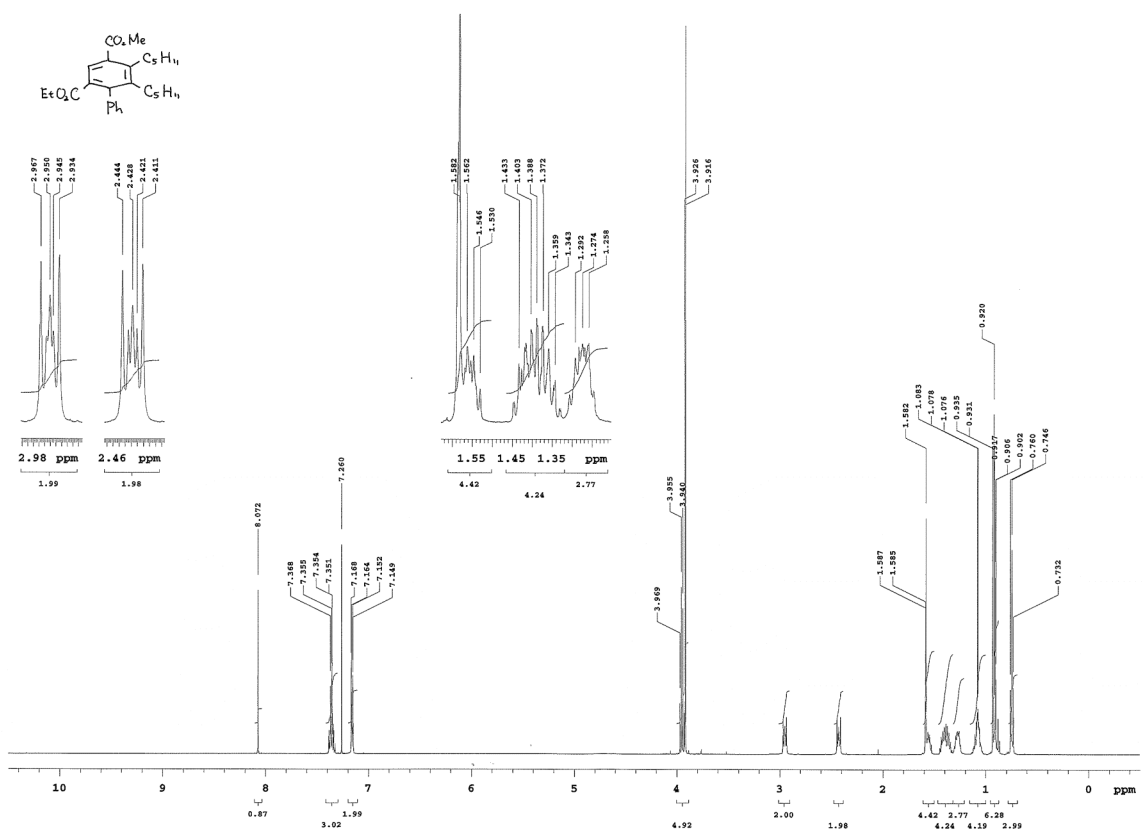
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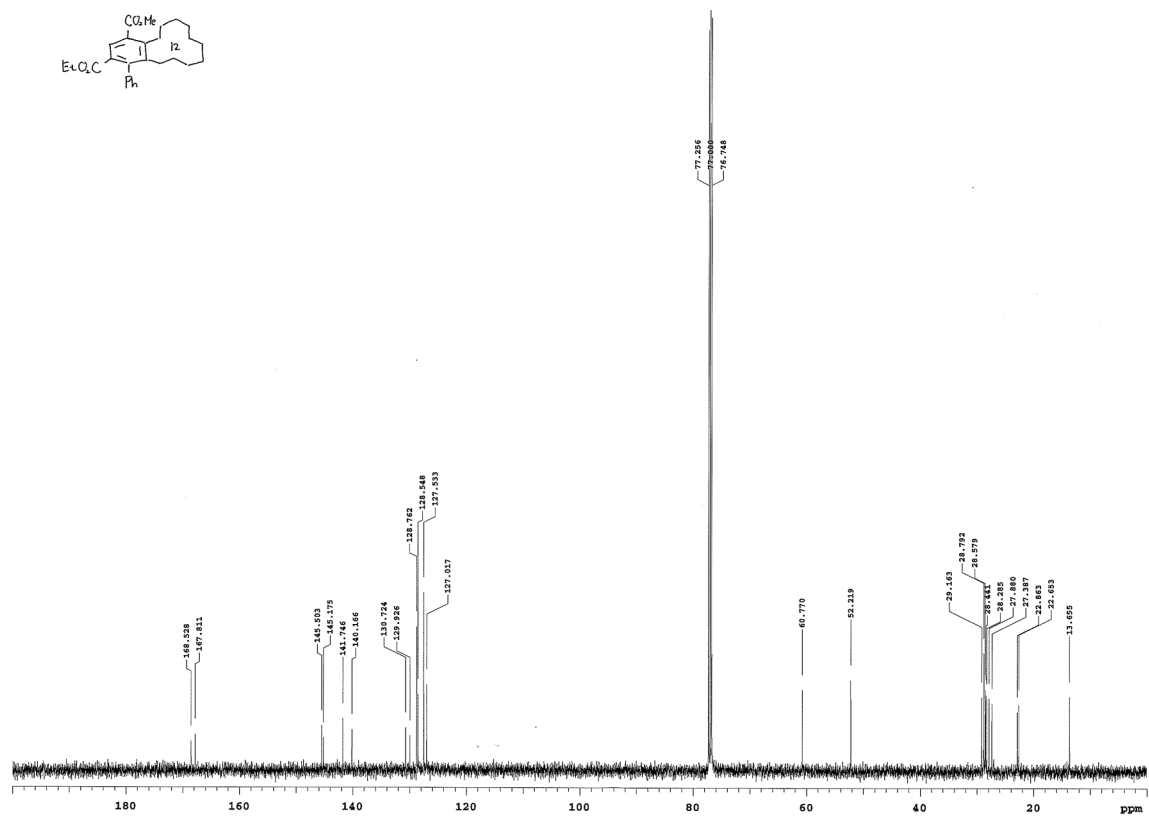
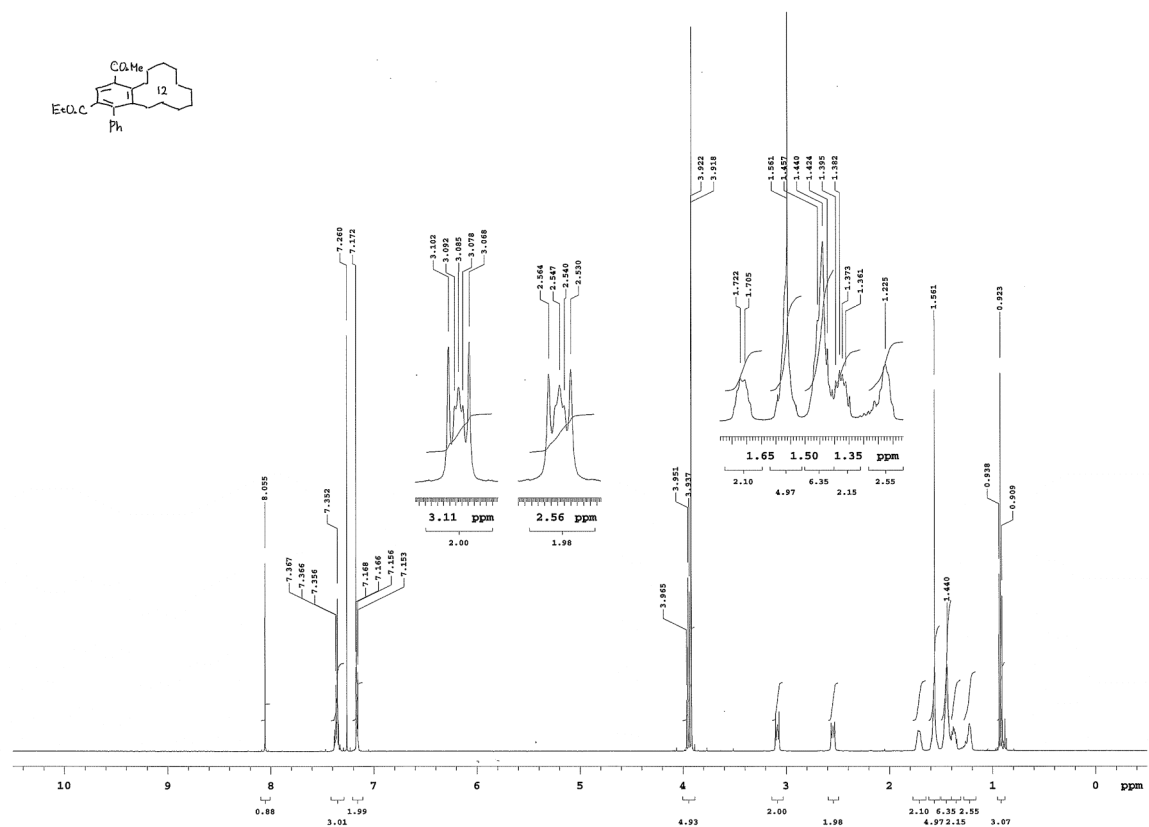
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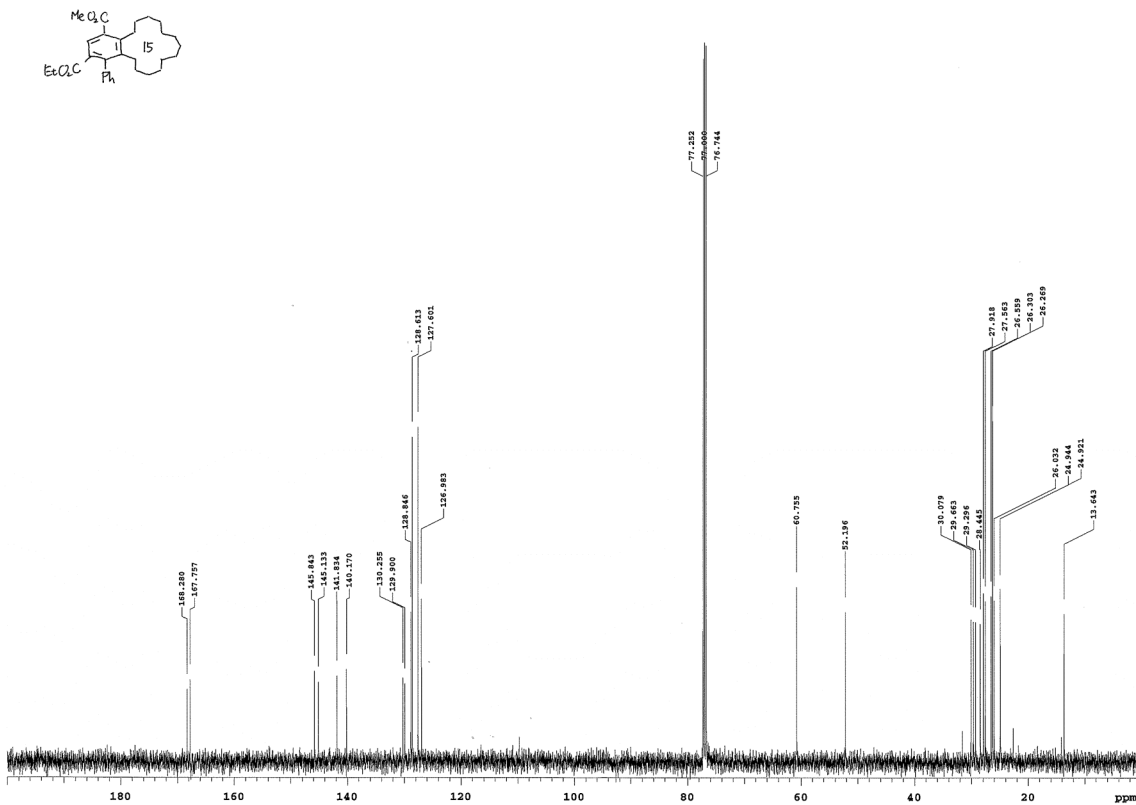
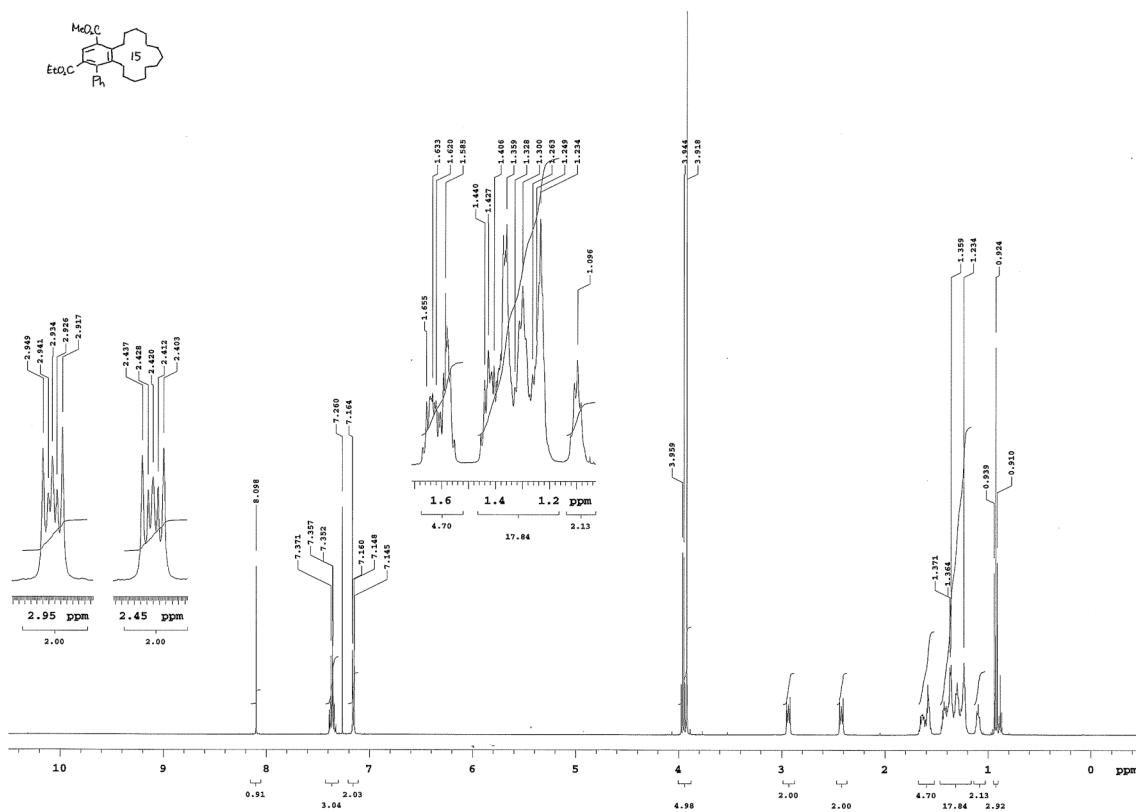
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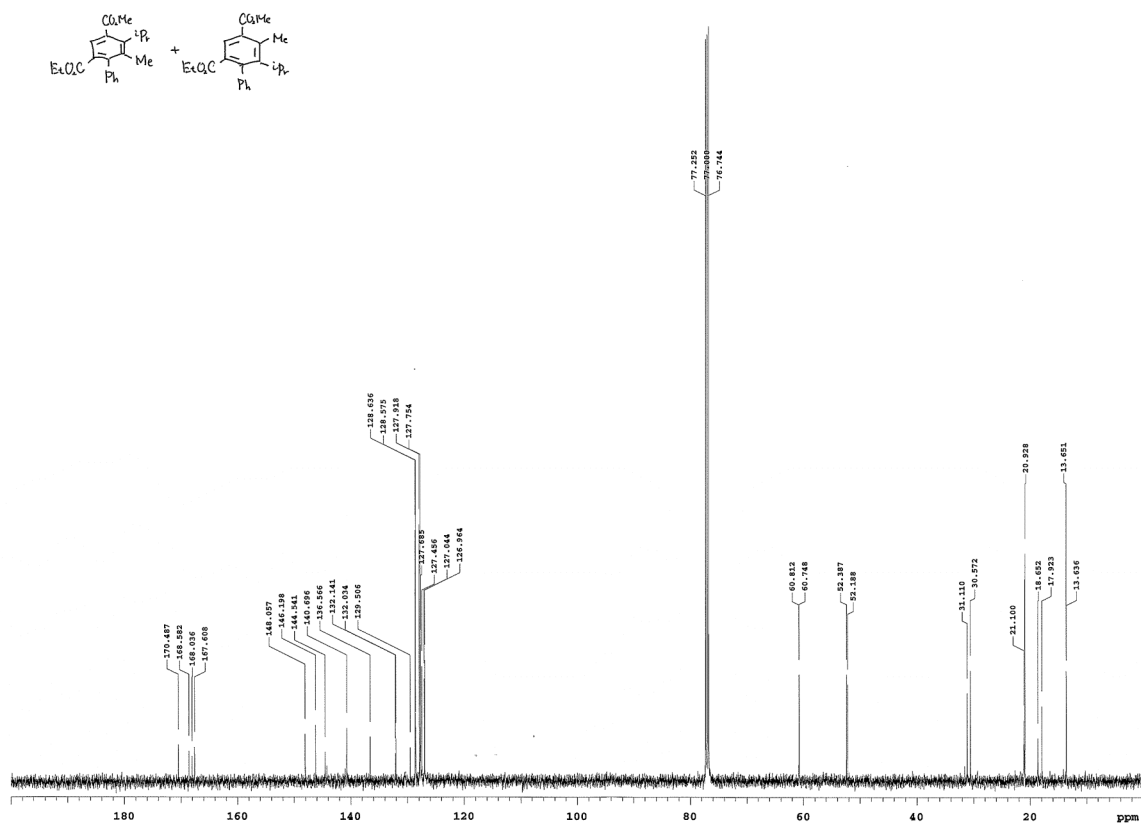
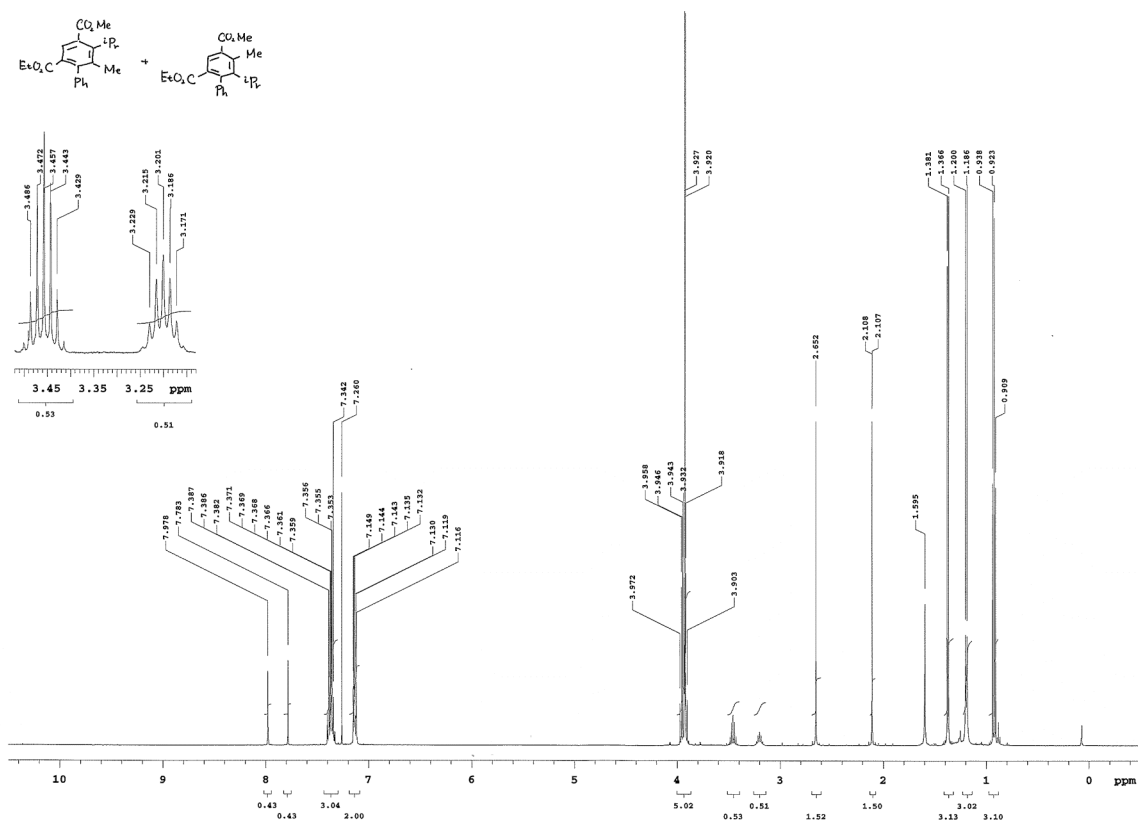
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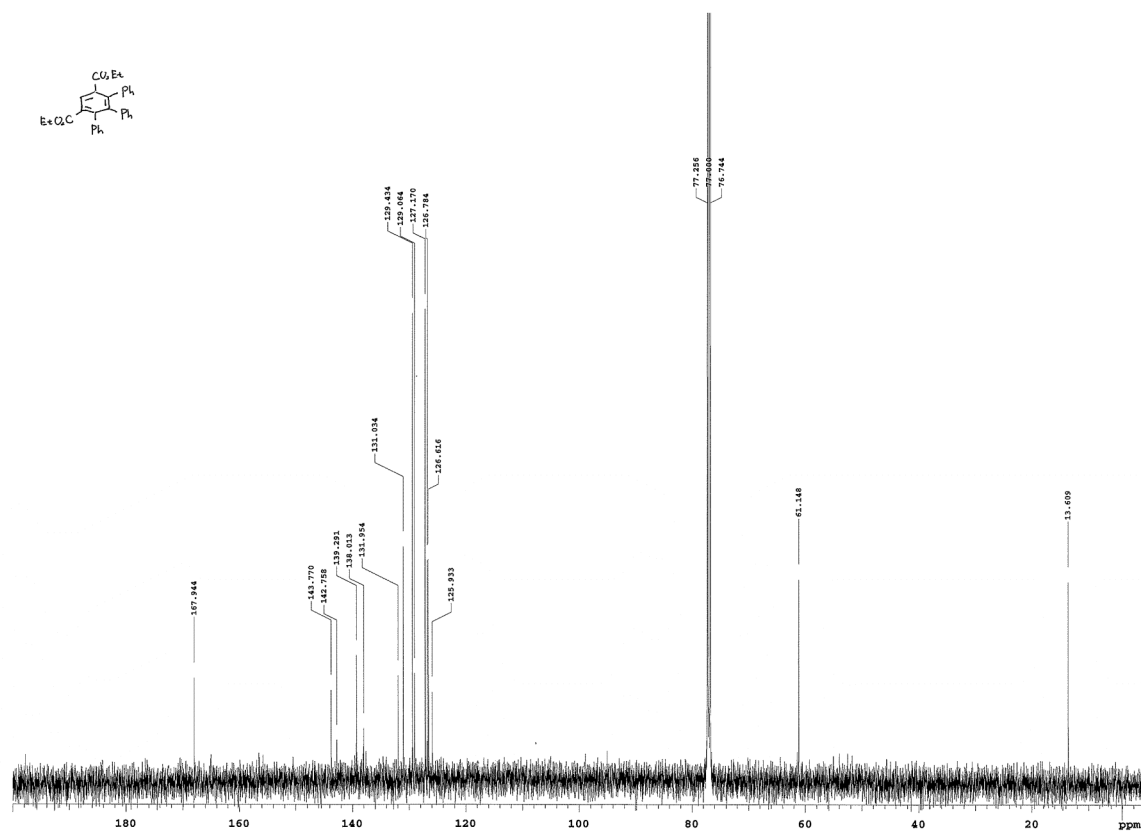
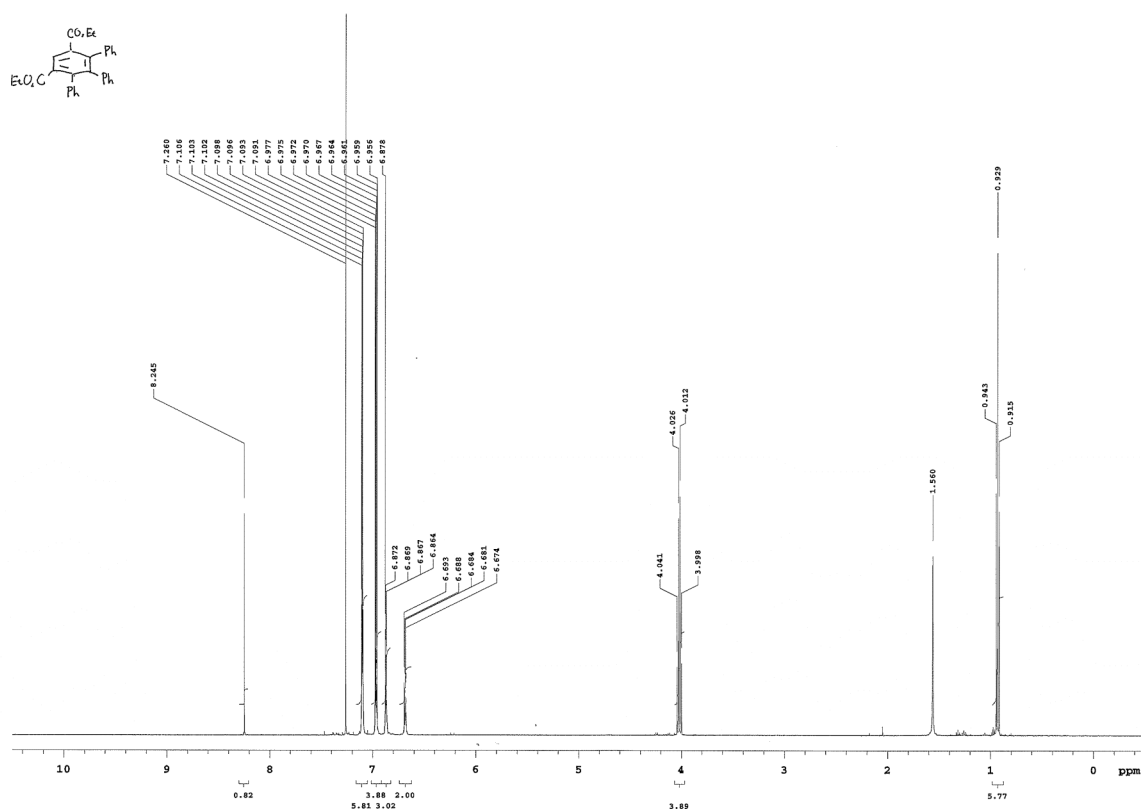
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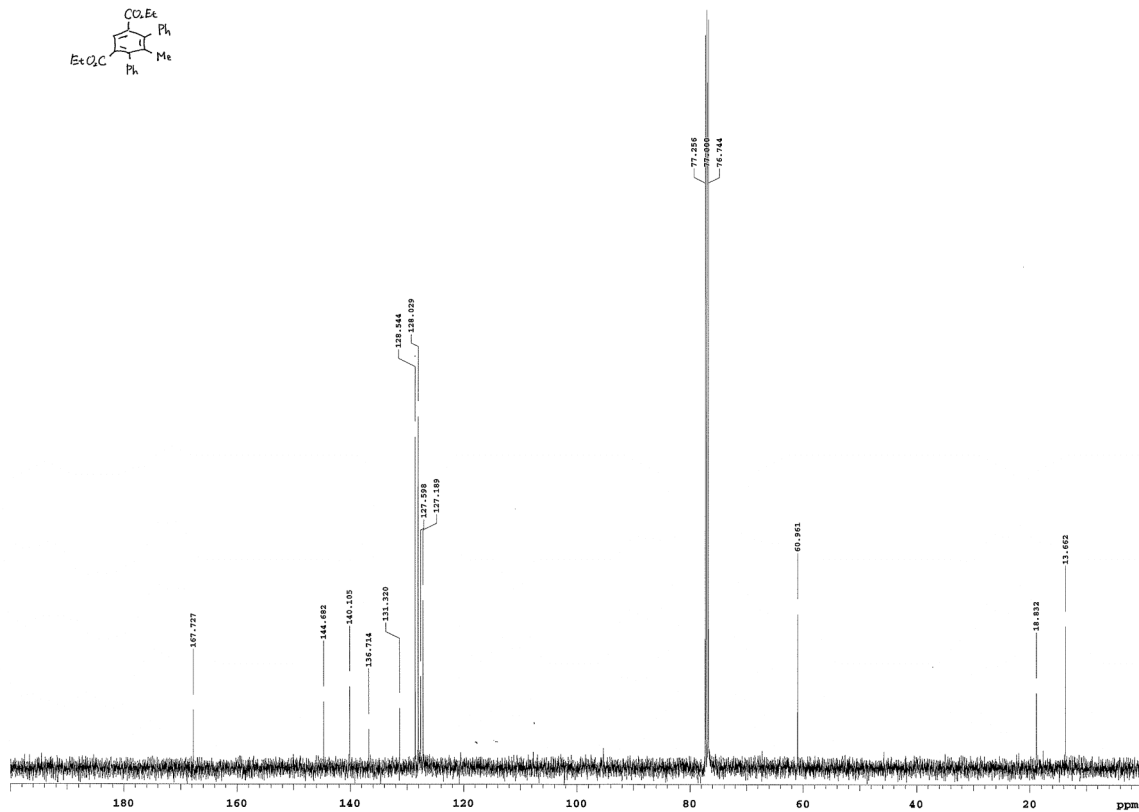
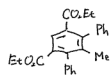
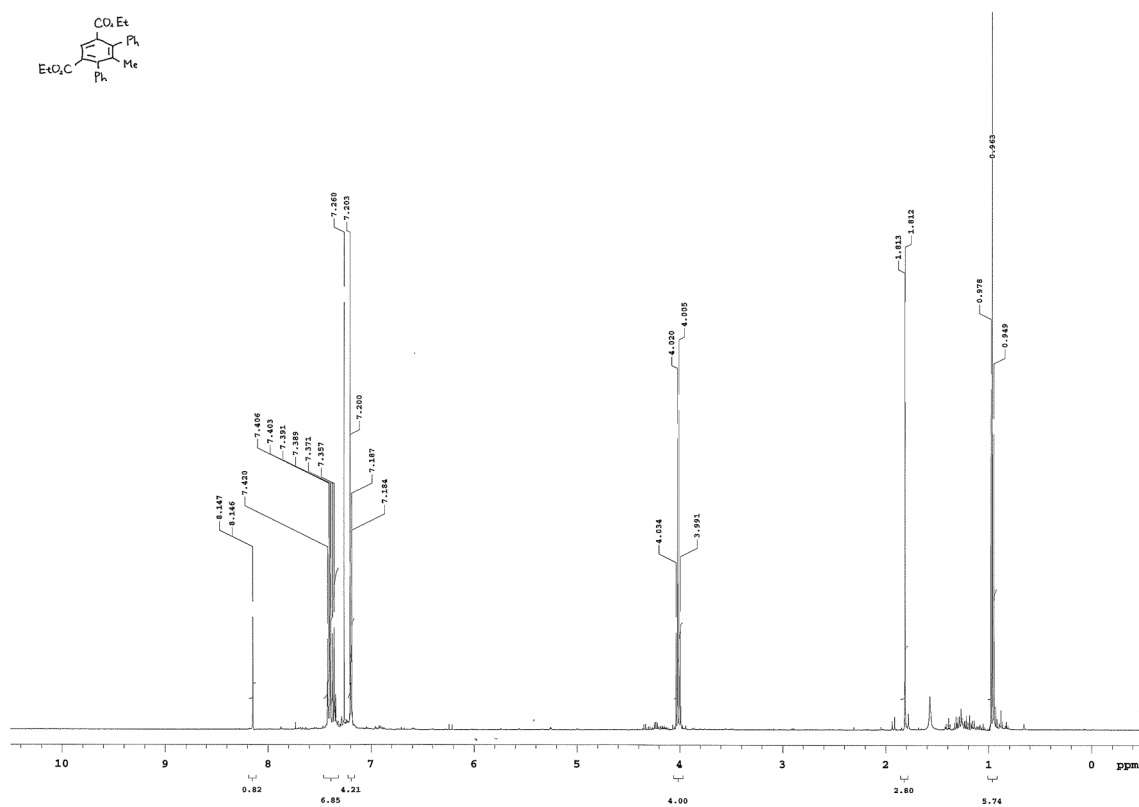
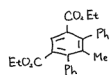
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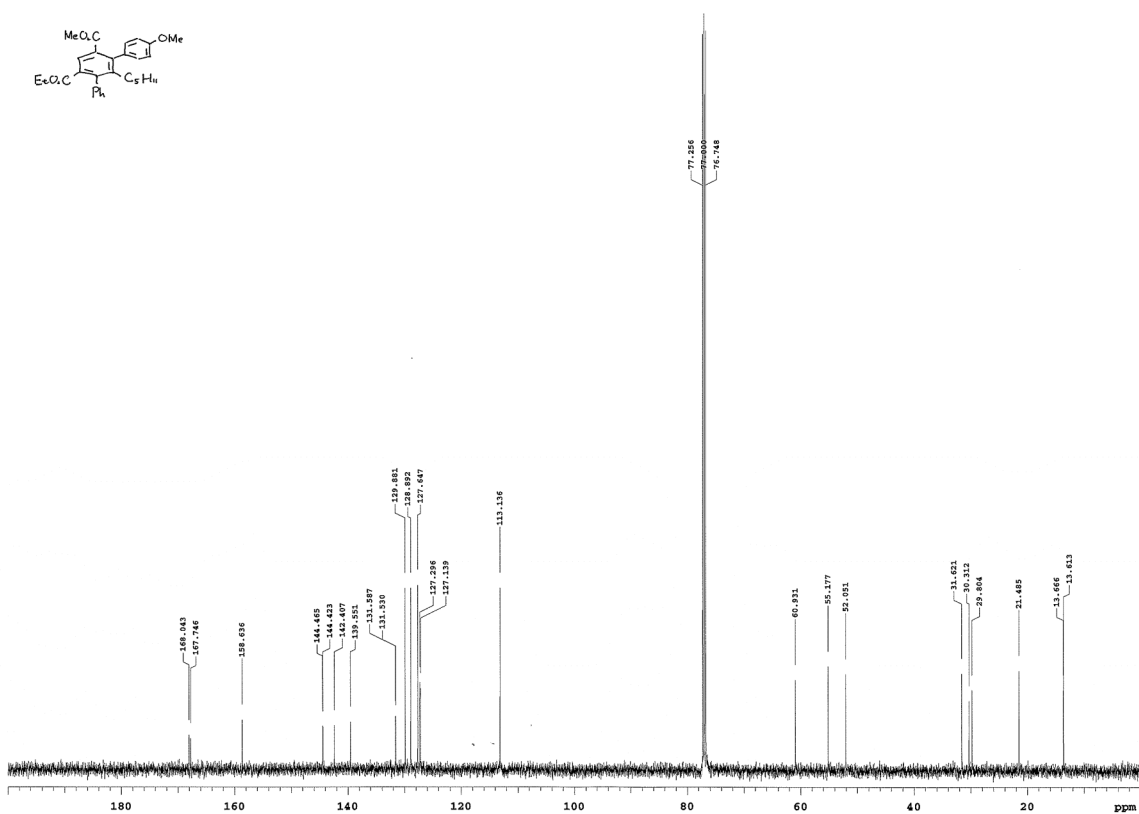
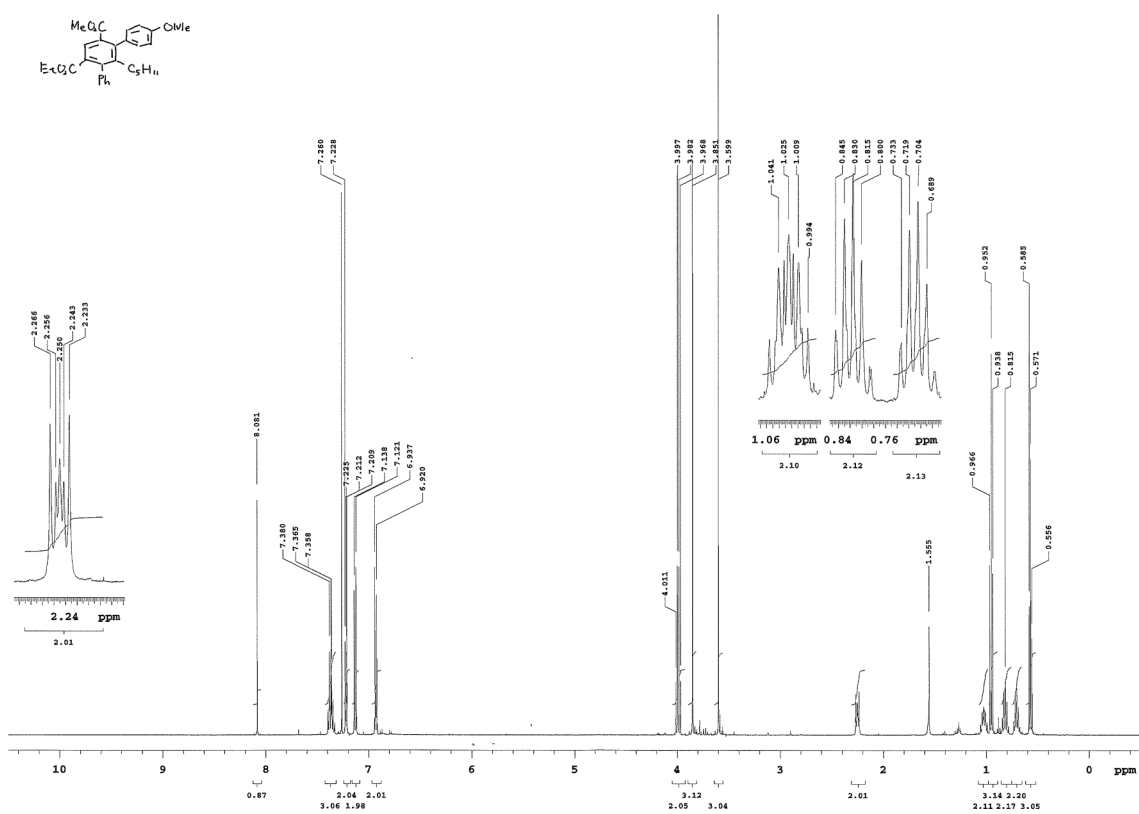
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3hh



3ai



3aj

