Supporting Information

Cationic Rhodium(I) Complex-Catalyzed Cotrimerization of Propargyl Esters and Arylacetylenes Leading to Substituted Dihydropentalenes

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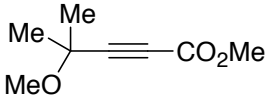
I. General

Anhydrous CH_2Cl_2 (No. 27,099-7), toluene (No. 24,451-1), Et_2O (No. 29,608-2), DME (No. 25,952-7), dioxane (No. 29,630-9), THF (No. 18,656-2), acetone (No. 27,072-5), and CH_3CN (No. 27,100-4) were obtained from Aldrich and used as received. Solvents for the synthesis of substrates were dried over Molecular Sieves 4A (Wako) or KOH prior to use. Propargyl esters **1a**,[1] **1b**,[2] **1c**,[2] **1d**,[2] and **1f**[2] were already reported. All other reagents were obtained from commercial sources and used as received unless otherwise noted. All reactions were carried out under nitrogen or argon with magnetic stirring. Infrared spectra were obtained on a JASCO A-302. NMR spectra were recorded on a JEOL AL 300 spectrometer. HRMS data were obtained on a BRUKER micrOTOF Focus II.

II. Synthesis of Propargyl Ether

4-Methoxy-4-methylpent-2-ynoic acid methyl ester (1e)



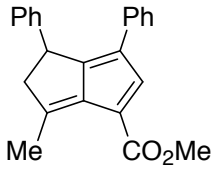
To a solution of 3-methoxy-3-methyl-1-butyne[3] (327 mg, 2.29 mmol) in THF was added a solution of *n*-butyllithium in hexane (7.0 mL, 1.57 M, 11.0 mmol) at –78 °C and the mixture was stirred for 30 minutes. To the resulting mixture was added a solution of methyl chloroformate (1.19 g, 11.0 mmol) in THF (10 mL) and the mixture was warmed to room temperature. After stirring for 1 hour, the reaction was quenched with aqueous saturated NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by a silica gel column chromatography (hexane/EtOAc = 10:1) to give **1e** (187 mg, 1.20 mmol, 52% yield) as a colorless oil.

IR (neat) 1757, 1715, 1436, 1261, 1176 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.79 (s, 3H), 3.38 (s, 3H), 1.50 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.8, 89.1, 75.9, 70.4, 52.7, 52.1, 27.5; HRMS (ESI) calcd for $C_8H_{12}O_3Na$ $[M+Na]^+$ 179.0679, found 179.0684.

III. Rhodium-Catalyzed Cotrimerization

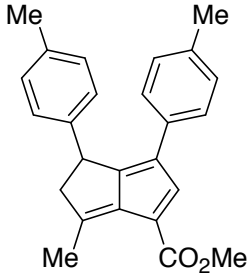
Representative procedure for rhodium-catalyzed cotrimerization (Table 2, entry 1, 4aa): $[Rh(cod)_2]BF_4$ (24.4 mg, 0.0600 mmol), **1a** (55.3 mg, 0.300 mmol), and cyclooctadiene (cod, 162.3 mg, 1.500 mmol) were dissolved in THF (1.0 mL). To this solution was added **2a** (153.2 mg, 1.500 mmol) in THF (1.0 mL). The solution was stirred at 40 °C for 16 hours. The resulting solution was concentrated and purified by a preparative TLC (hexane/toluene/Et_2O = 5:4:1), which furnished **4aa** (58.6 mg, 0.178 mmol, 59% yield) as an orange solid.

6-Methyl-3,4-diphenyl-4,5-dihydropentalene-1-carboxylic acid methyl ester (4aa)



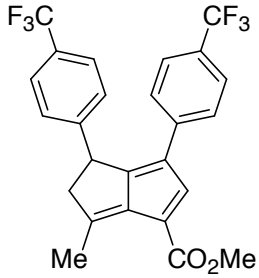
Mp 169.5–171.0 °C; IR (KBr) 1696, 1621, 1483, 1288, 1250 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.15 (s, 1H), 7.37–7.27 (m, 2H), 7.25–7.00 (m, 8H), 4.44 (d, J = 6.0 Hz, 1H), 3.85 (s, 3H), 3.73 (dd, J = 20.2, 6.0 Hz, 1H), 3.03 (d, J = 20.2 Hz, 1H), 2.59 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.7, 164.3, 154.7, 148.4, 145.8, 143.1, 134.3, 128.7, 128.4, 128.2, 127.1, 126.4, 126.3, 126.2, 117.7, 58.0, 51.1, 43.6, 18.1; HRMS (ESI) calcd for $C_{23}H_{20}O_2Na$ $[M+Na]^+$ 351.1356, found 351.1355.

6-Methyl-3,4-di-*p*-tolyl-4,5-dihydropentalene-1-carboxylic acid methyl ester (4ab)



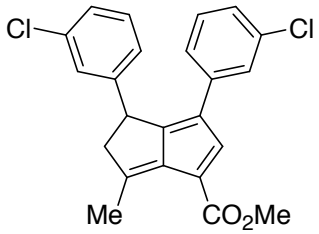
Orange solid; Mp 135.1–136.5 °C; IR (KBr) 1703, 1512, 1436, 1235, 1125 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.15 (s, 1H), 7.27–7.18 (m, 2H), 7.04–6.94 (m, 6H), 4.40 (d, J = 6.0 Hz, 1H), 3.85 (s, 3H), 3.72 (dd, J = 20.2, 6.0 Hz, 1H), 3.00 (d, J = 20.2 Hz, 1H), 2.58 (s, 3H), 2.25 (s, 3H), 2.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.3, 164.1, 154.2, 148.6, 145.8, 140.3, 135.93, 135.87, 131.6, 129.4, 129.0, 128.4, 126.9, 126.1, 117.6, 58.2, 51.0, 43.2, 21.03, 20.97, 18.1; HRMS (ESI) calcd for $C_{25}H_{24}O_2Na$ $[M+Na]^+$ 379.1669, found 379.1666.

6-Methyl-3,4-bis(4-trifluoromethylphenyl)-4,5-dihydropentalene-1-carboxylic acid methyl ester (4ac)



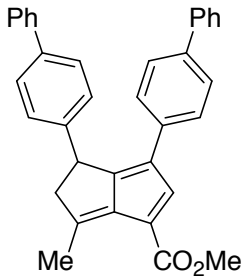
Orange amorphous; IR (KBr) 1708, 1328, 1123, 1069, 825 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.13 (s, 1H), 7.48 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.6 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 4.55 (d, J = 6.0 Hz, 1H), 3.88 (s, 3H), 3.84 (dd, J = 20.3, 6.0 Hz, 1H), 3.05 (d, J = 20.3 Hz, 1H), 2.65 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.4, 164.1, 155.1, 147.6, 146.7 (q, J = 1.2 Hz), 145.9, 137.6 (q, J = 1.2 Hz), 129.2 (q, J = 32.5 Hz), 128.3 (q, J = 32.5 Hz), 127.5, 127.4, 126.1, 125.9 (q, J = 3.7 Hz), 125.4 (q, J = 3.7 Hz), 124.13 (q, J = 271.7 Hz), 124.05 (q, J = 271.9 Hz), 118.7, 57.8, 51.3, 43.4, 18.3; HRMS (ESI) calcd for $C_{25}H_{18}O_2F_6Na$ $[M+Na]^+$ 487.1103, found 487.1102.

3,4-Bis(3-chlorophenyl)-6-methyl-4,5-dihydropentalene-1-carboxylic acid methyl ester (4ad)



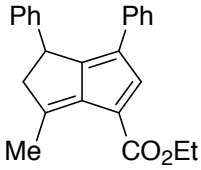
Orange solid; Mp 123.5–125.0 °C; IR (KBr) 1707, 1595, 1434, 1130, 1586 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.05 (s, 1H), 7.28–7.24 (m, 1H), 7.17–7.02 (m, 6H), 7.01–6.95 (m, 1H), 4.39 (d, J = 6.2 Hz, 1H), 3.86 (s, 3H), 3.74 (dd, J = 20.3, 6.2 Hz, 1H), 3.04 (d, J = 20.3 Hz, 1H), 2.62 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.8, 164.0, 154.8, 147.7, 145.7, 144.7, 136.0, 134.6, 134.3, 130.0, 129.5, 127.4, 127.2, 126.9, 126.4, 126.3, 125.3, 124.2, 118.3, 57.7, 51.2, 43.2, 18.2; HRMS (ESI) calcd for $C_{23}H_{18}O_2Cl_2Na$ $[M+Na]^+$ 419.0576, found 419.0582.

3,4-Bis(biphenyl-4-yl)-6-methyl-4,5-dihydropentalene-1-carboxylic acid methyl ester (4ae)



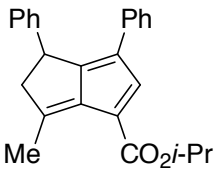
Orange solid; Mp 177.5–178.9 °C; IR (KBr) 1702, 1487, 1233, 1126, 764 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.21 (s, 1H), 7.57–7.11 (m, 18H), 4.51 (d, J = 6.0 Hz, 1H), 3.87 (s, 3H), 3.78 (dd, J = 20.2, 6.0 Hz, 1H), 3.08 (d, J = 20.2 Hz, 1H), 2.62 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.8, 164.3, 154.6, 148.3, 145.9, 142.2, 140.6, 140.5, 139.3, 138.9, 133.3, 128.6, 128.1, 127.5, 127.4, 127.1, 126.94, 126.86, 126.7, 126.6, 117.9, 58.1, 51.1, 43.3, 18.2; HRMS (ESI) calcd for $C_{35}H_{28}O_2Na$ $[M+Na]^+$ 503.1982, found 503.1992.

6-Methyl-3,4-diphenyl-4,5-dihydropentalene-1-carboxylic acid ethyl ester (4ba)



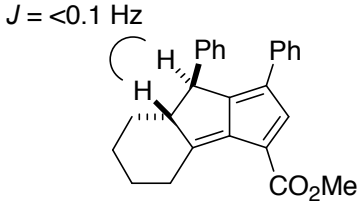
Orange solid; Mp 114.4–116.4 °C; IR (KBr) 1685, 1631, 1479, 1277, 767 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.16 (s, 1H), 7.35–7.00 (m, 10H), 4.44 (d, J = 5.9 Hz, 1H), 4.38–4.27 (m, 2H), 3.74 (dd, J = 20.2, 5.9 Hz, 1H), 3.03 (d, J = 20.2 Hz, 1H), 2.59 (s, 3H) 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.5, 163.9, 154.6, 148.3, 145.8, 143.2, 134.4, 128.6, 128.4, 128.2, 127.1, 126.4, 126.23, 126.19, 118.2, 59.8, 58.0, 43.6, 18.2, 14.5; HRMS (ESI) calcd for $C_{24}H_{22}O_2Na$ $[M+Na]^+$ 365.1512, found 365.1523.

6-Methyl-3,4-diphenyl-4,5-dihydropentalene-1-carboxylic acid isopropyl ester (4ca)



Orange solid; Mp 129.1–130.3 °C; IR (KBr) 1687, 1474, 1294, 1129, 1105 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.14 (s, 1H), 7.37–7.01 (m, 10H), 5.22 (septet, J = 6.3 Hz, 1H), 4.45 (d, J = 5.9 Hz, 1H), 3.76 (dd, J = 20.2, 5.9 Hz, 1H), 3.04 (d, J = 20.2 Hz, 1H), 2.60 (s, 3H), 1.38 (d, J = 6.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.3, 163.5, 154.4, 148.3, 145.8, 143.2, 134.4, 128.6, 128.4, 128.2, 127.1, 126.4, 126.2, 118.7, 67.0, 58.0, 43.6, 22.1, 18.2; HRMS (ESI) calcd for $C_{25}H_{24}O_2Na$ $[M+Na]^+$ 379.1669, found 379.1680.

1,8-Diphenyl-4,5,6,7,7a,8-hexahydrocyclopenta[a]indene-3-carboxylic acid methyl ester (4fa)

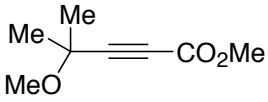


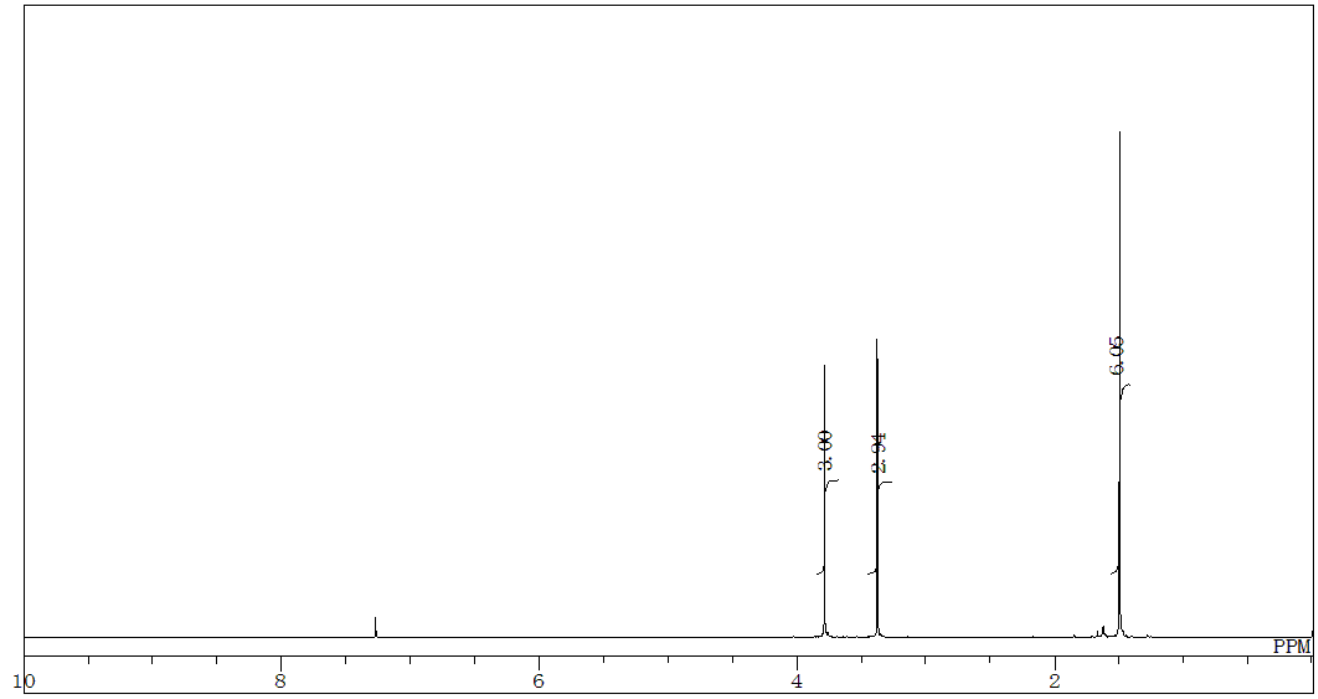
The relative configuration of this compound was determined by a coupling constant between two *trans*-protons on ^1H NMR. Orange solid; Mp 113.4–114.6 °C; IR (KBr) 1703, 1479, 1119, 764, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.18 (s, 1H), 7.36–6.98 (m, 10H), 4.07 (d, J = 14.5 Hz, 1H), 3.94 (s, 1H), 3.85 (s, 3H), 3.08–2.92 (m, 1H), 2.58–2.45 (m, 1H), 2.45–2.29 (m, 1H), 2.12–1.98 (m, 1H), 1.94–1.78 (m, 1H), 1.56–1.34 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.7, 164.3, 153.0, 148.9, 142.4, 142.3, 134.3, 128.7, 128.6, 128.2, 127.0, 126.5, 126.2, 118.0, 67.0, 51.7, 51.1, 34.8, 30.2, 27.1, 25.5; HRMS (ESI) calcd for $C_{26}H_{24}O_2Na$ $[M+Na]^+$ 391.1669, found 391.1677.

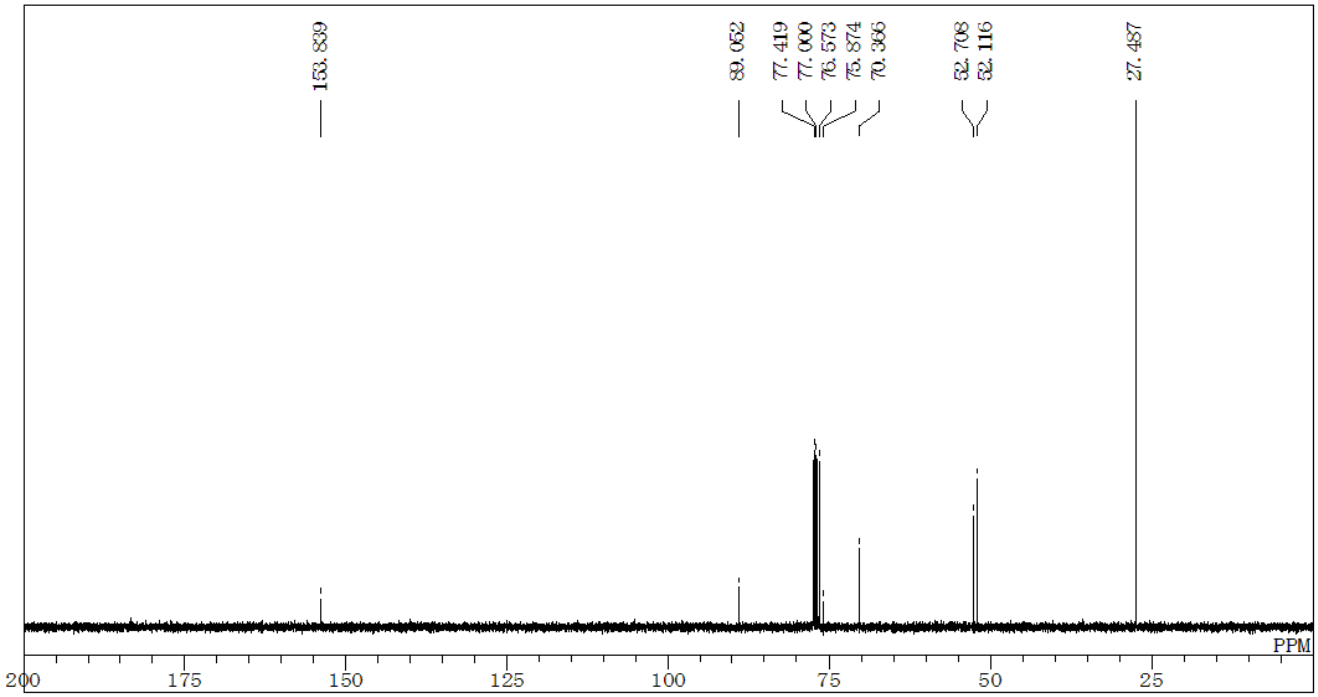
IV. References

(1) Matsumura, S.; Maeda, Y.; Nishimura, T.; Uemura, S. *J. Am. Chem. Soc*. **2003**, *125*, 8862.
(2) Shibata, Y.; Noguchi, K.; Tanaka, K. *J. Am. Chem. Soc.* **2010**, *132*, 7896.
(3) Pinkerton, D. M.; Banwell, M. G.; Willis, A. C. *Org. Lett.* **2009**, *11*, 4290.

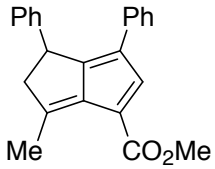
4-Methoxy-4-methylpent-2-ynoic acid methyl ester (1e)

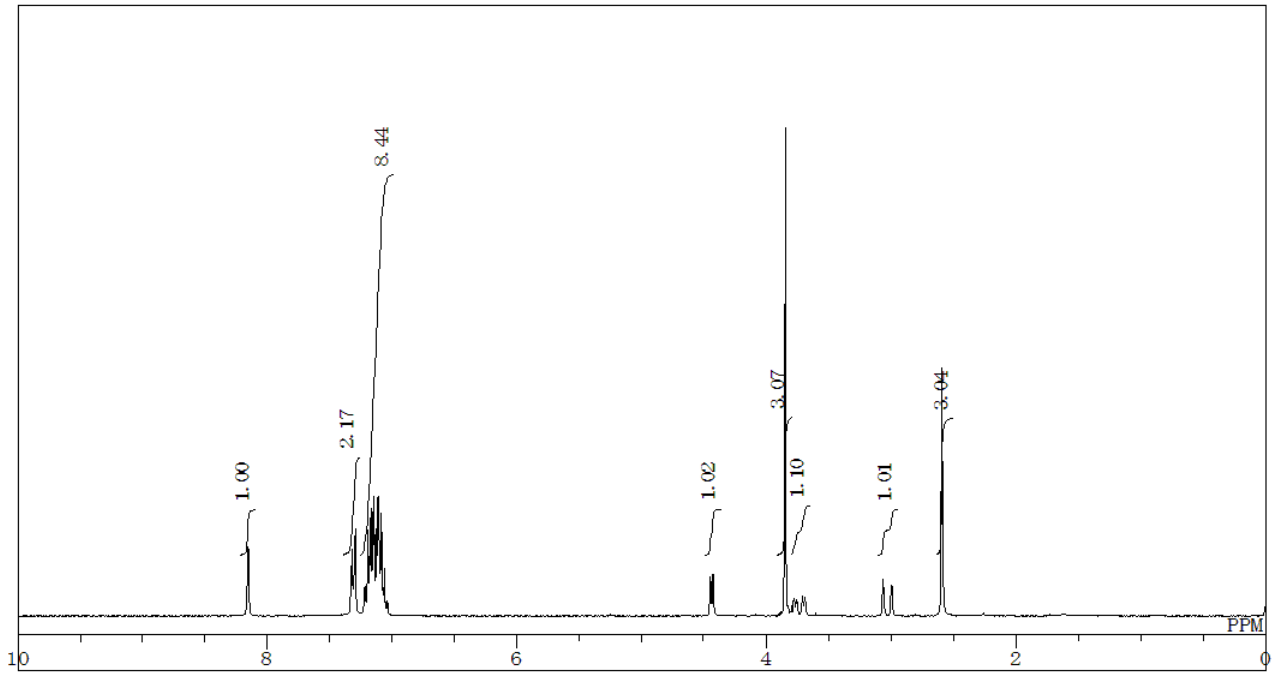


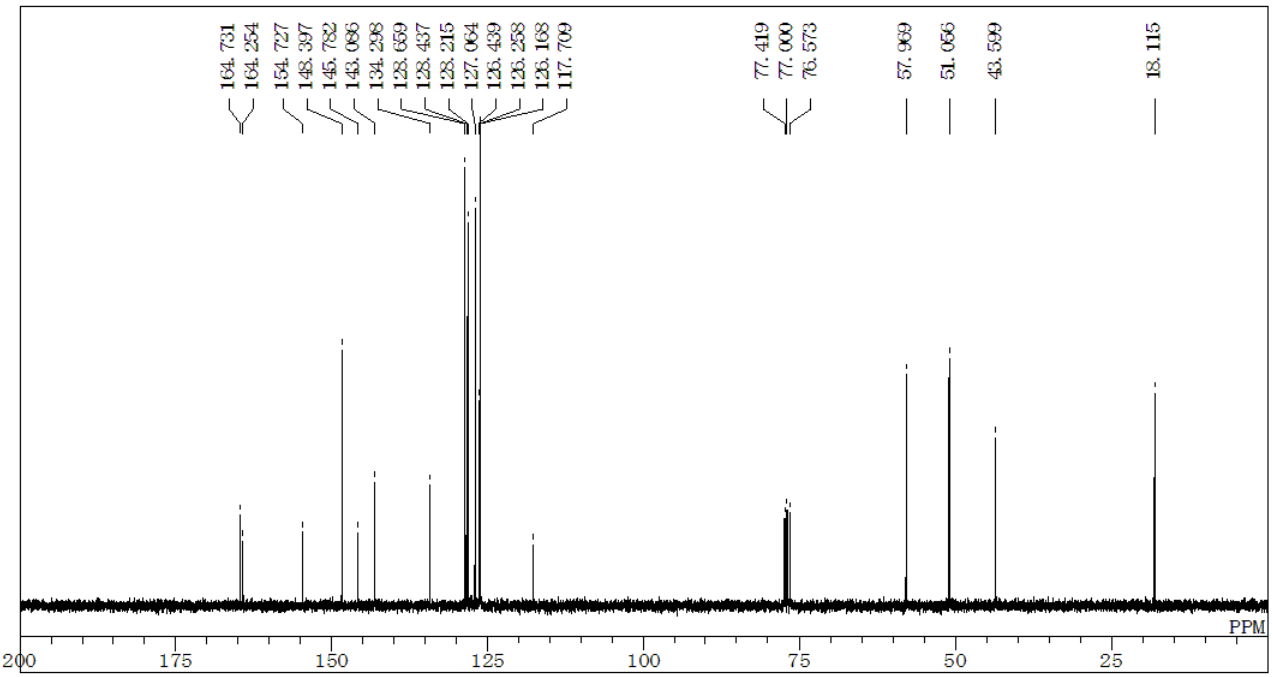




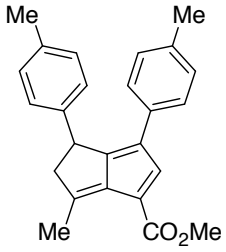
6-Methyl-3,4-diphenyl-4,5-dihydropentalene-1-carboxylic acid methyl ester (4aa)

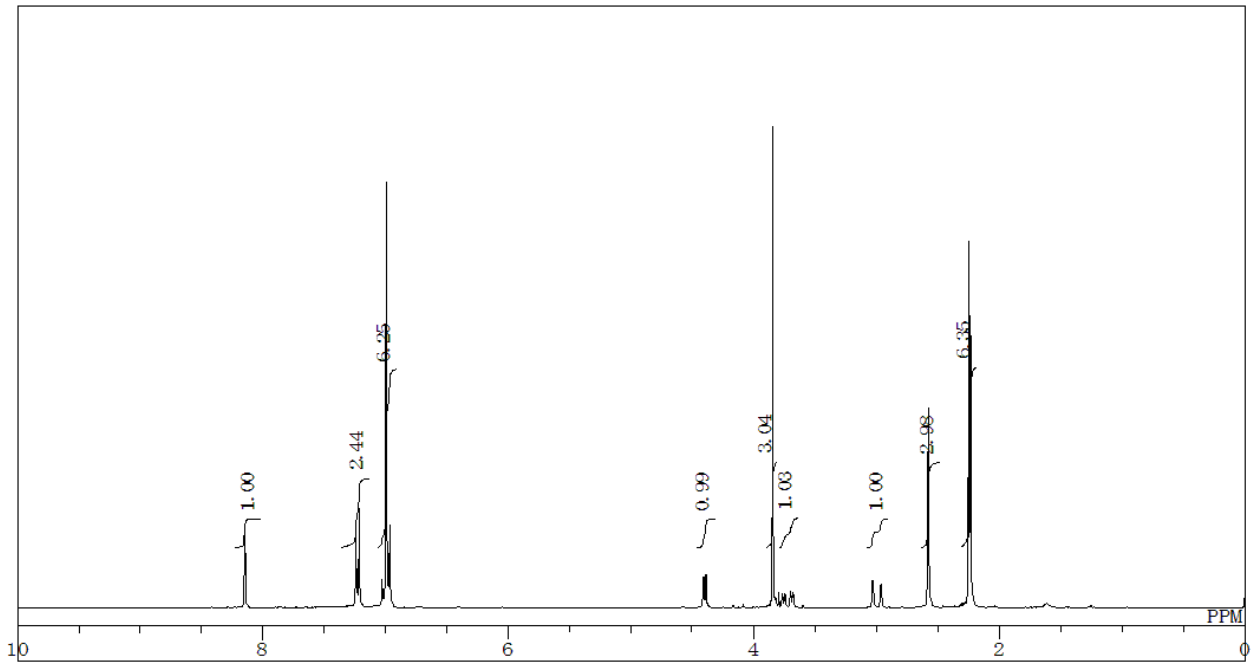


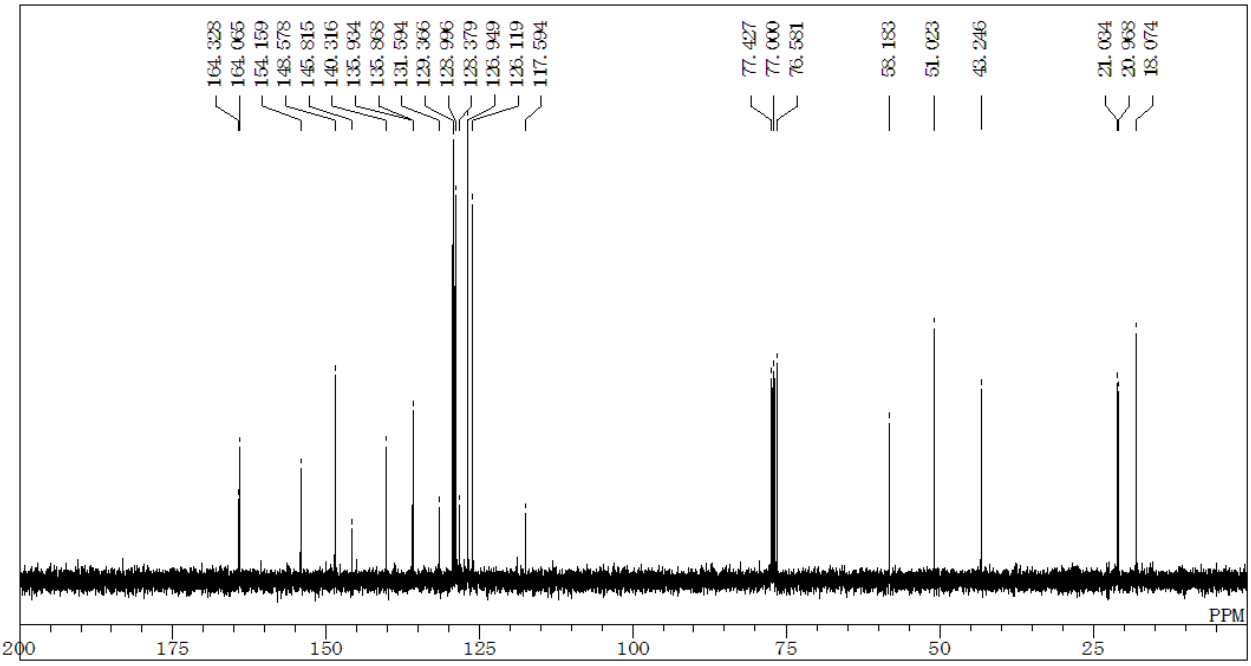




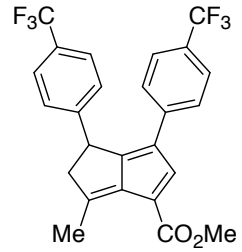
6-Methyl-3,4-di-*p*-tolyl-4,5-dihydropentalene-1-carboxylic acid methyl ester (4ab)

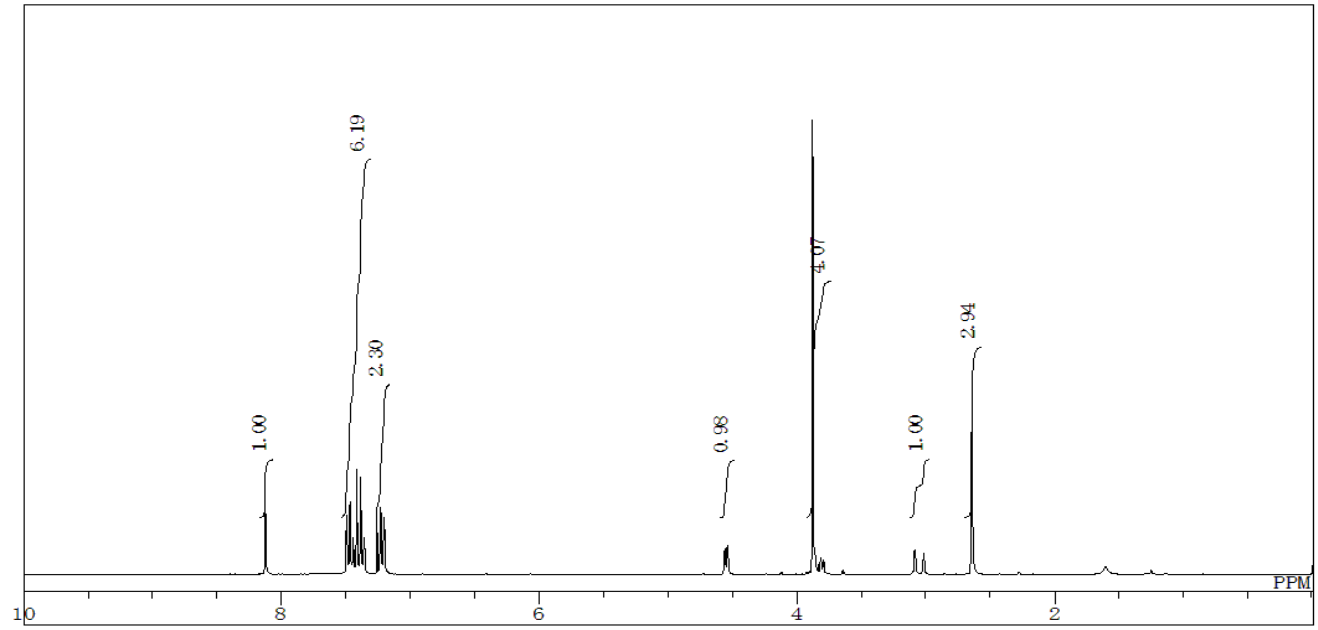


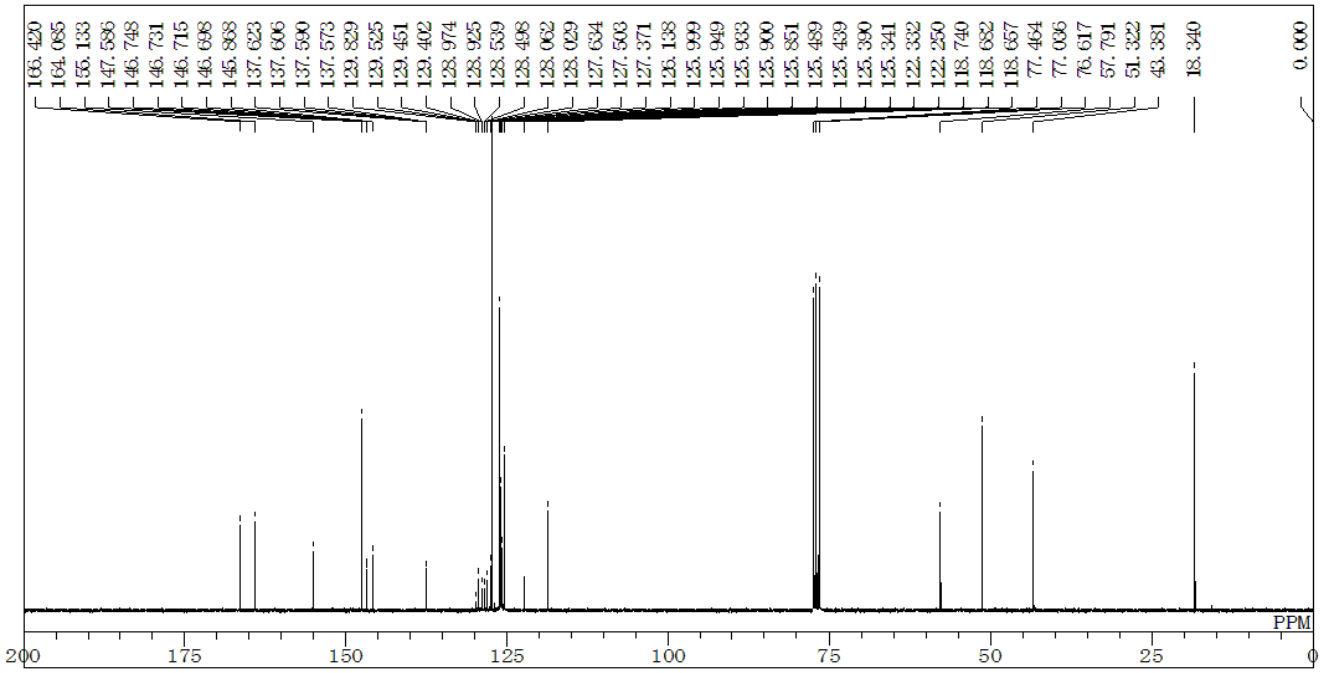




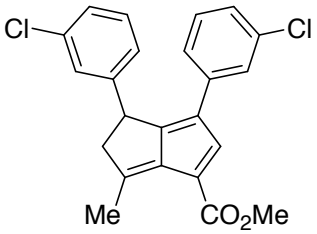
6-Methyl-3,4-bis(4-trifluoromethylphenyl)-4,5-dihydropentalene-1-carboxylic acid methyl ester (4ac)

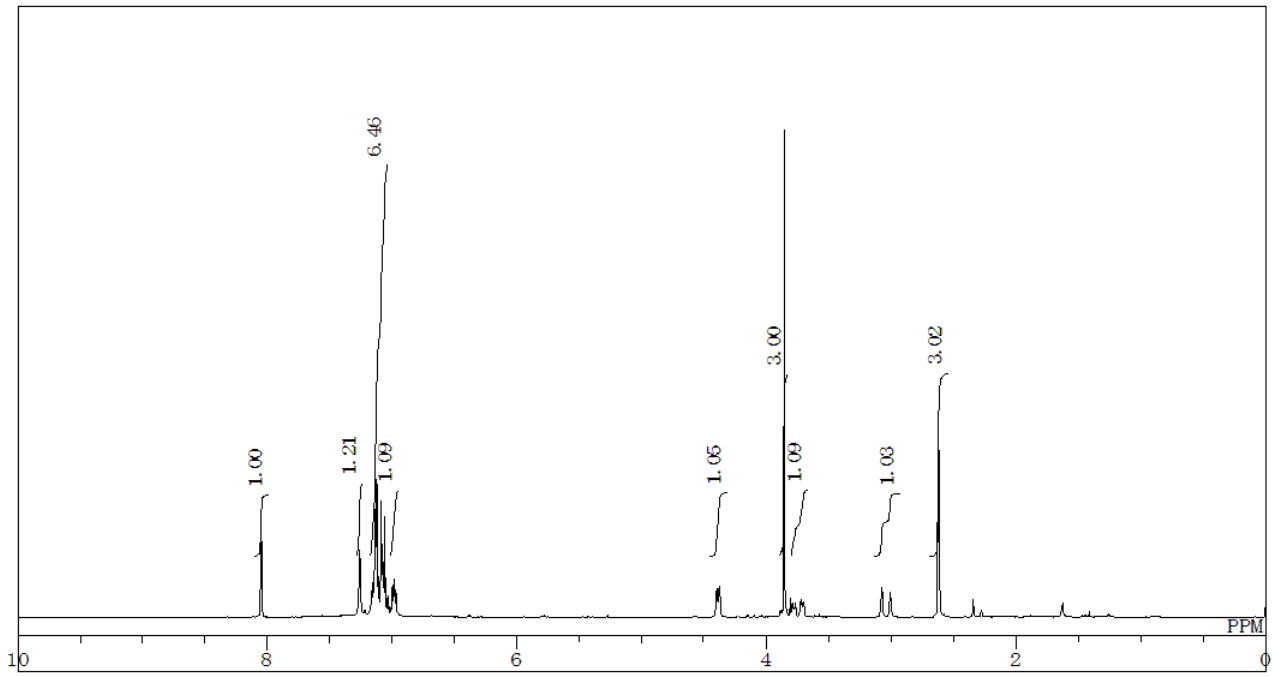


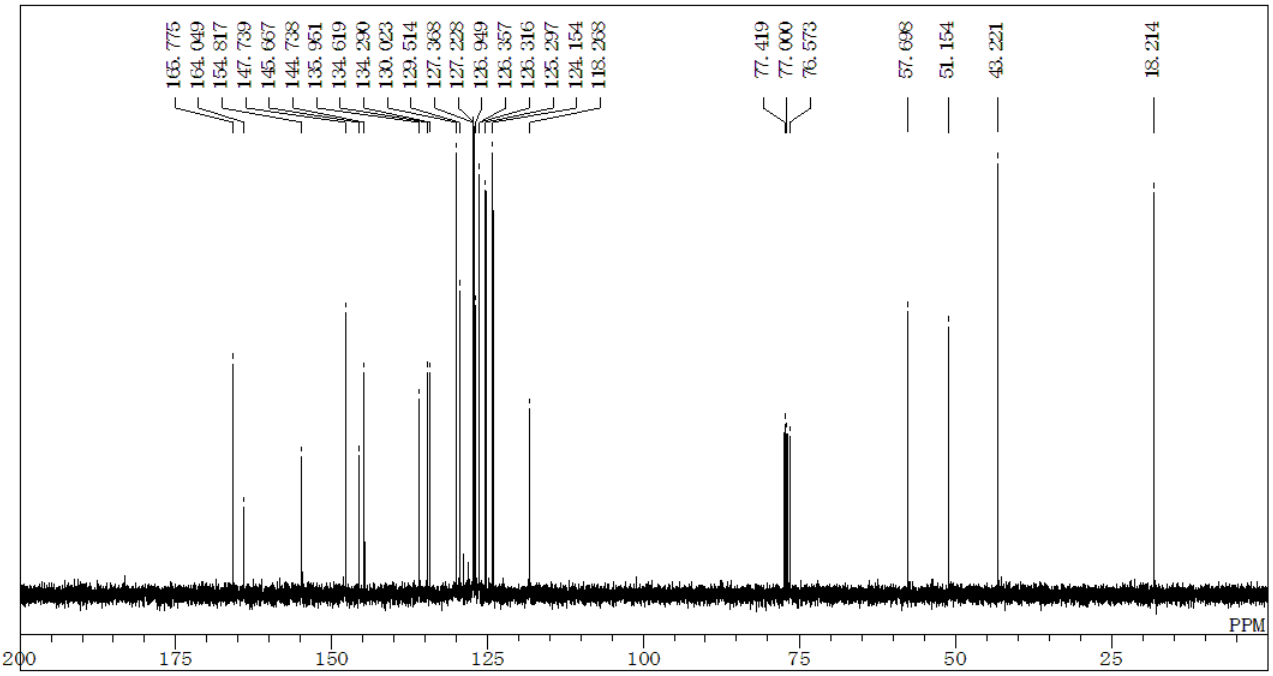




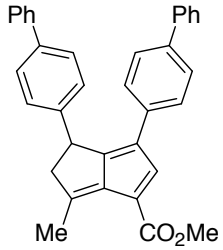
3,4-Bis(3-chlorophenyl)-6-methyl-4,5-dihydropentalene-1-carboxylic acid methyl ester (4ad)

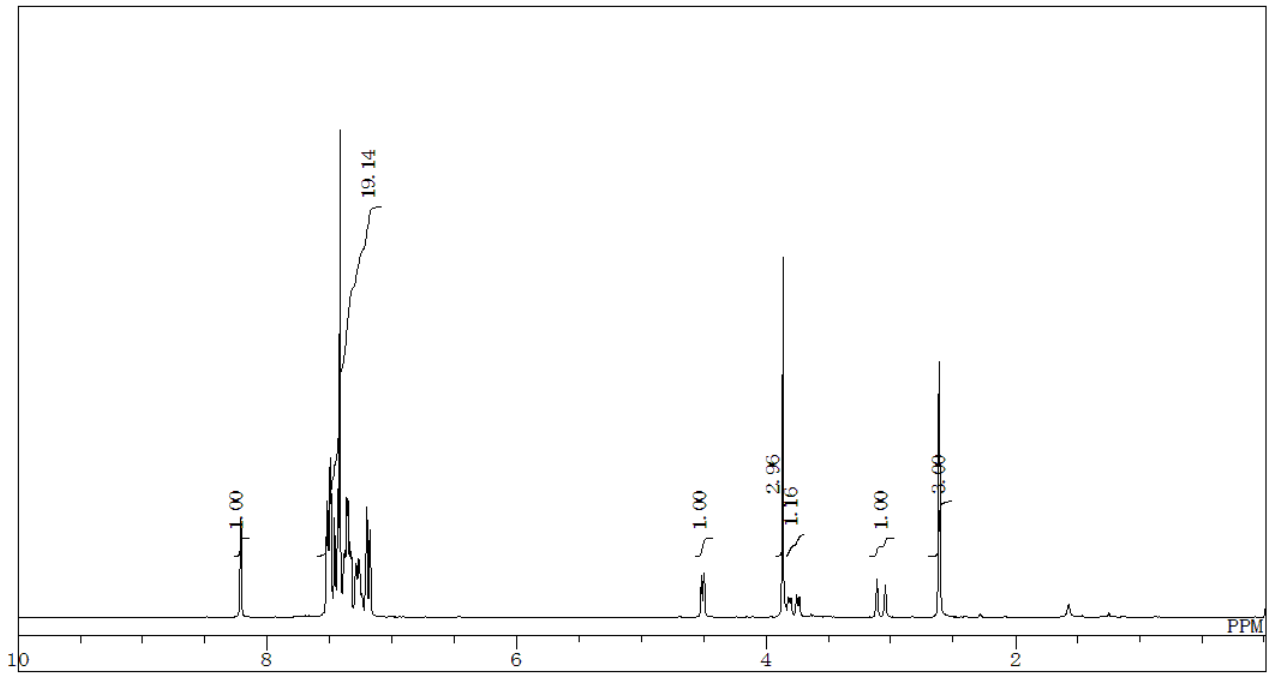


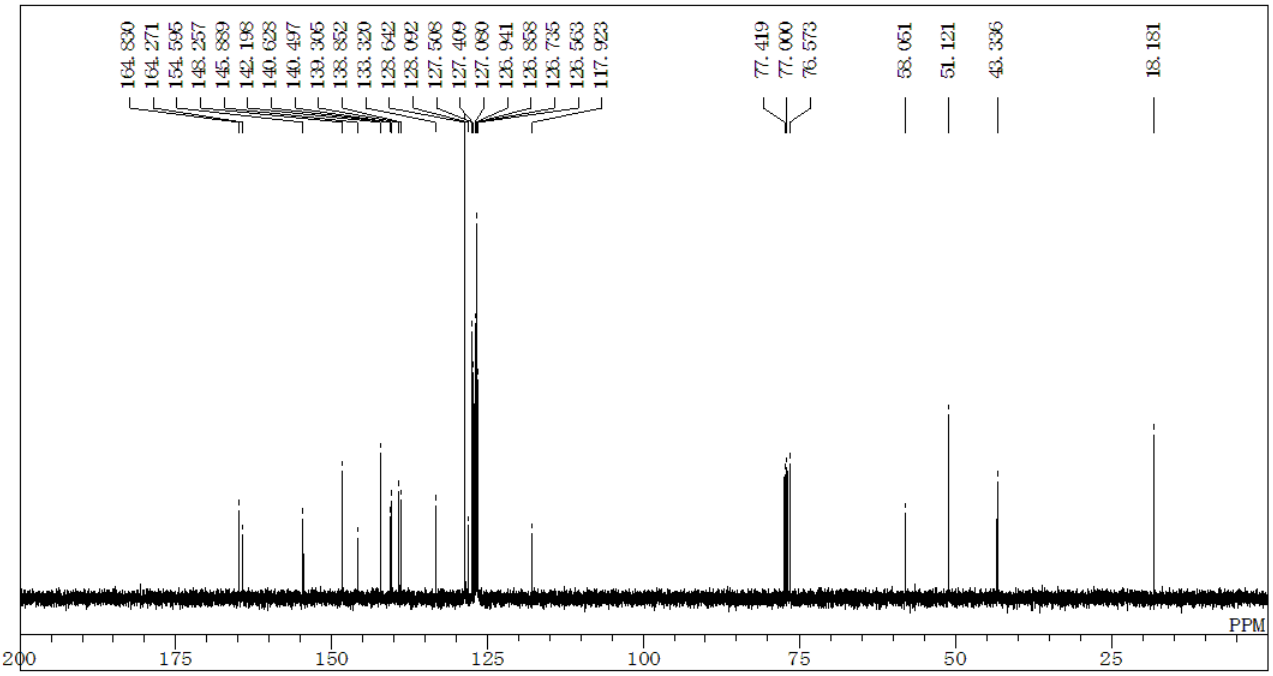




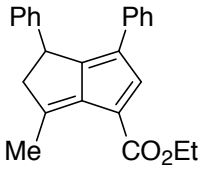
3,4-Bis(biphenyl-4-yl)-6-methyl-4,5-dihydropentalene-1-carboxylic acid methyl ester (4ae)

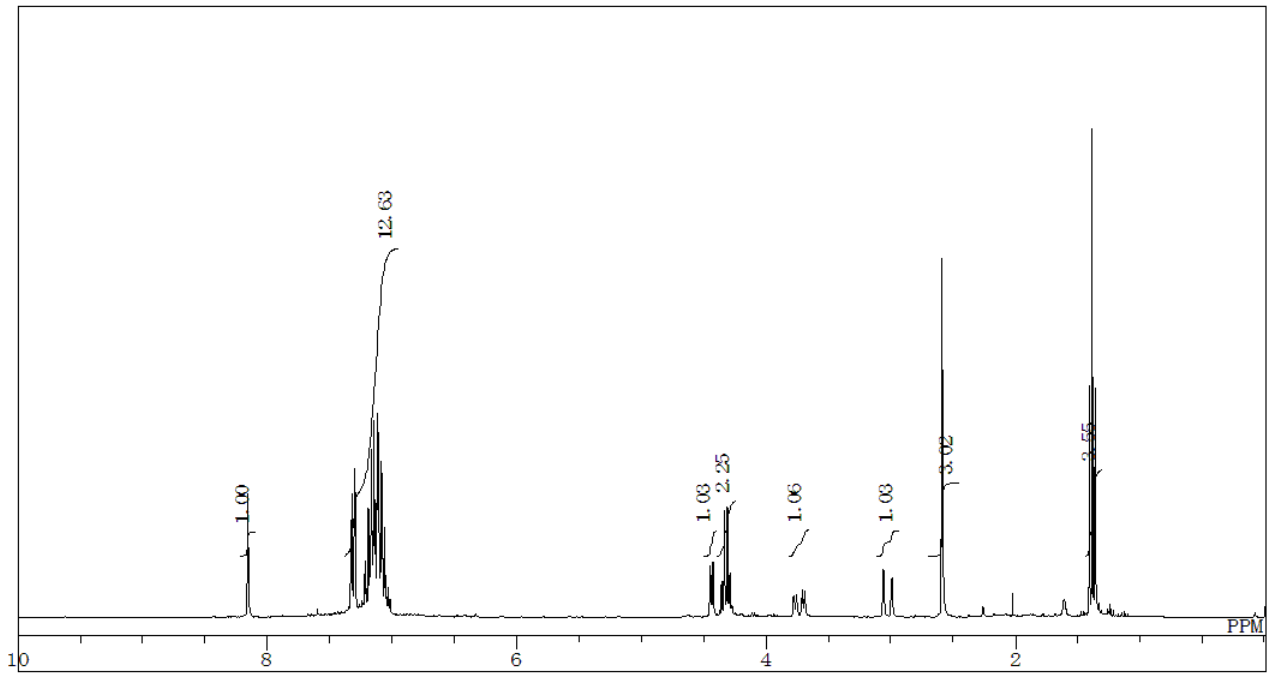


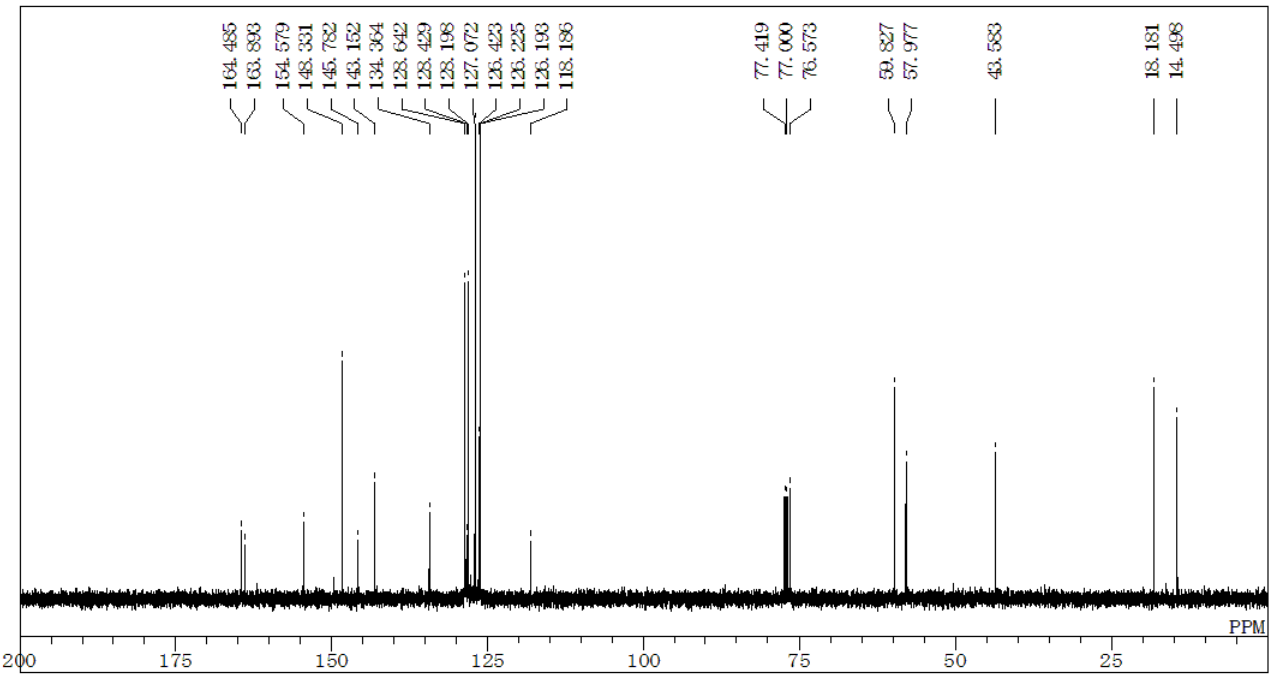




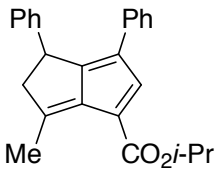
6-Methyl-3,4-diphenyl-4,5-dihydropentalene-1-carboxylic acid ethyl ester (4ba)

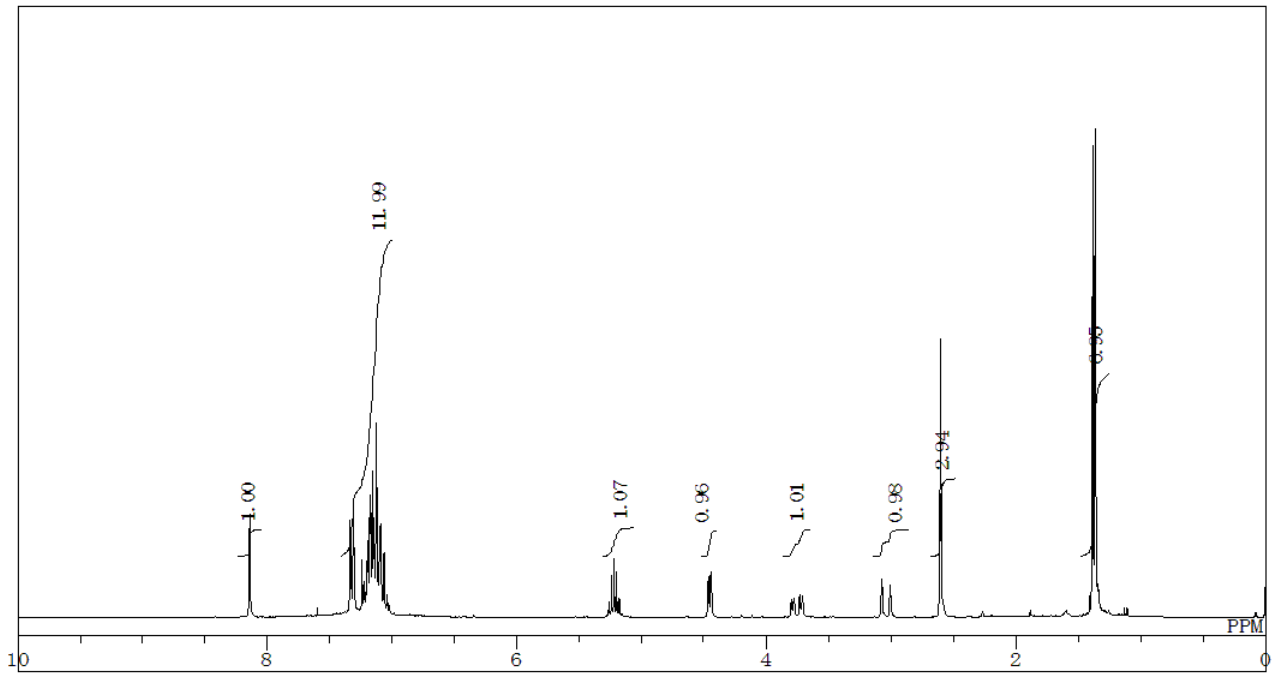


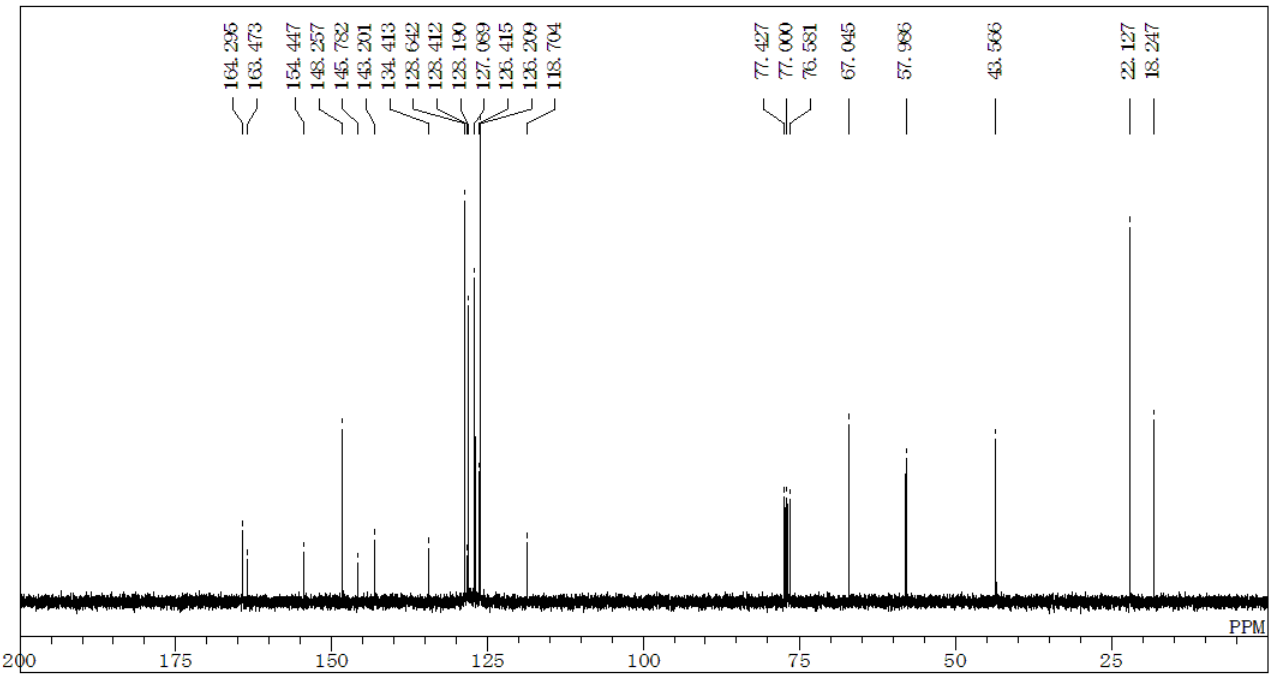




6-Methyl-3,4-diphenyl-4,5-dihydropentalene-1-carboxylic acid isopropyl ester (4ca)







1,8-Diphenyl-4,5,6,7,7a,8-hexahydrocyclopenta[a]indene-3-carboxylic acid methyl ester (4fa)