

Supporting Information

Two Bird One Stone: Construction of Different Polysubstituted Benzenes from the Same Starting Material and Precatalyst by Switching the Active Sites of Catalyst with Different Additives

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General:

All reactions involving Grubbs' second generation catalyst were carried out under an atmosphere of ethylene (1 atm) using standard Schlenk techniques, and the solution of the catalytic reaction was degassed through freeze-pump-thaw cycle. Toluene was freshly distilled over sodium with the use of diphenyl ketone as an indicator under nitrogen. Grubbs' second generation catalyst was synthesized according to literature procedure^{1,2} and CuI, AgOTf were purchased from Alfa Company. Aliphatic internal alkyne **1n**³ was prepared by published sonogashira coupling reaction. Alkynes **1l**⁴ and **1o** were prepared by the acetylation of 2-butyne-1,4-diol and 1-(trimethylsilyl)-2-butyne-4-ol, respectively. Alkyne **1m** was prepared by reaction of 2-butyne-1,4-diol with benzyl bromide. Alkyne **1p** was prepared by reaction of trimethylsilyl chloride with 1-heptyne. Unsymmetrical diarylacetylenes were prepared by the palladium catalyzed coupling of the corresponding aryl iodides and arylacetylenes. Symmetrical diarylacetylenes were synthesized according to the literature procedures⁵. All other chemicals were purchased commercially and used as received unless indicated otherwise. ¹H NMR (300 MHz or 400 MHz) and ¹³C NMR (50 MHz, 75 MHz or 100 MHz) were registered on Varian 200 M, 300 M or Bruker 400 M spectrometers with CDCl₃ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ¹H spectrum as 0.00 ppm and CDCl₃ resonance in the ¹³C spectrum as 77.0 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). ³¹P NMR spectra were recorded on Varian 300 spectrometers at 121 MHz with H₃PO₄ (δ = 0 ppm) as external standard. Column chromatography was performed on silica gel 200-300 mesh. IR, MS, and HRMS were performed by the State-authorized Analytical Center in Peking University.

Typical procedure for the synthesis of 3a to 3i

A solution of diphenylacetylene (22.5 mg, 0.125 mmol), Grubbs' second generation catalyst, (10 mg, 0.0125 mmol, 10 mol %) and CuI (1.2 mg, 0.00625 mmol, 5 mol %) in dry toluene (2.5 mL) was stirred at 80 °C for 24 h under 1 atm ethylene pressure (using balloon). After cooling to room temperature, DMAD (89 mg, 0.625 mmol) was added under air conditions and the resulting mixture was stirred at 100 °C for another 24 h in sealed vessel. After cooling to room temperature, DDQ (35 mg, 0.15 mmol) was subsequently added and the reaction was stirred at 80 °C for a further 4 h. The reaction mixture was filtered through a short pad of silica gel eluting with CH₂Cl₂. The volatiles were removed in vacuo and the residue was purified by silica gel column chromatography (elution with petroleum ether: ethyl acetate = 10:1) to give the final product in 88% yield.

Typical procedure for the synthesis of 3j to 3r

A solution of 4-octyne (55 mg, 0.5 mmol) and Grubbs' second generation catalyst, (20 mg, 0.025 mmol, 5 mol %) in dry toluene (5 mL) was stirred at 80 °C for 24 h under 1 atm ethylene pressure (using balloon). After cooling to room temperature, DMAD (355 mg, 2.5 mmol) was added under air conditions and the resulting mixture was stirred at 100 °C for another 24 h in sealed vessel. After cooling to room temperature, DDQ (138 mg, 0.6 mmol) was subsequently added and the reaction was stirred at 80 °C for a further 4 h. The reaction mixture was filtered

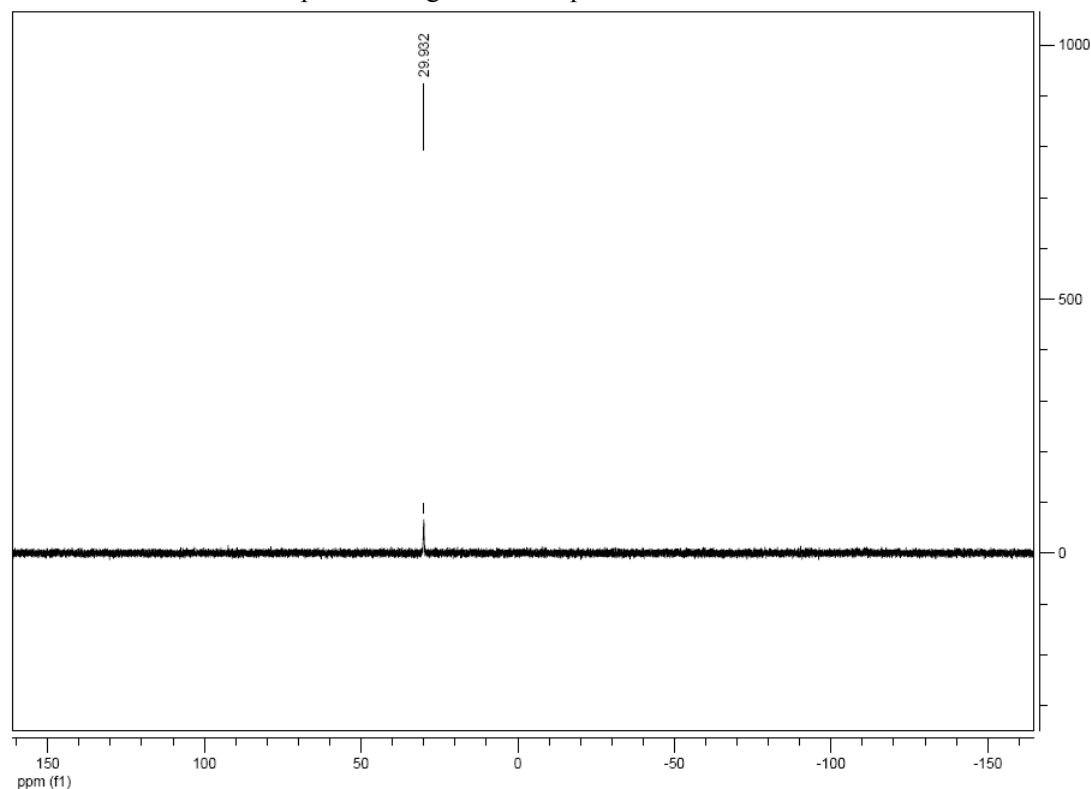
through a short pad of silica gel eluting with CH_2Cl_2 . The volatiles were removed in vacuo and the residue was purified by silica gel column chromatography (elution with petroleum ether: ethyl acetate = 30:1) to give the final product in 91% yield.

Typical procedure for the synthesis of 4a to 4l

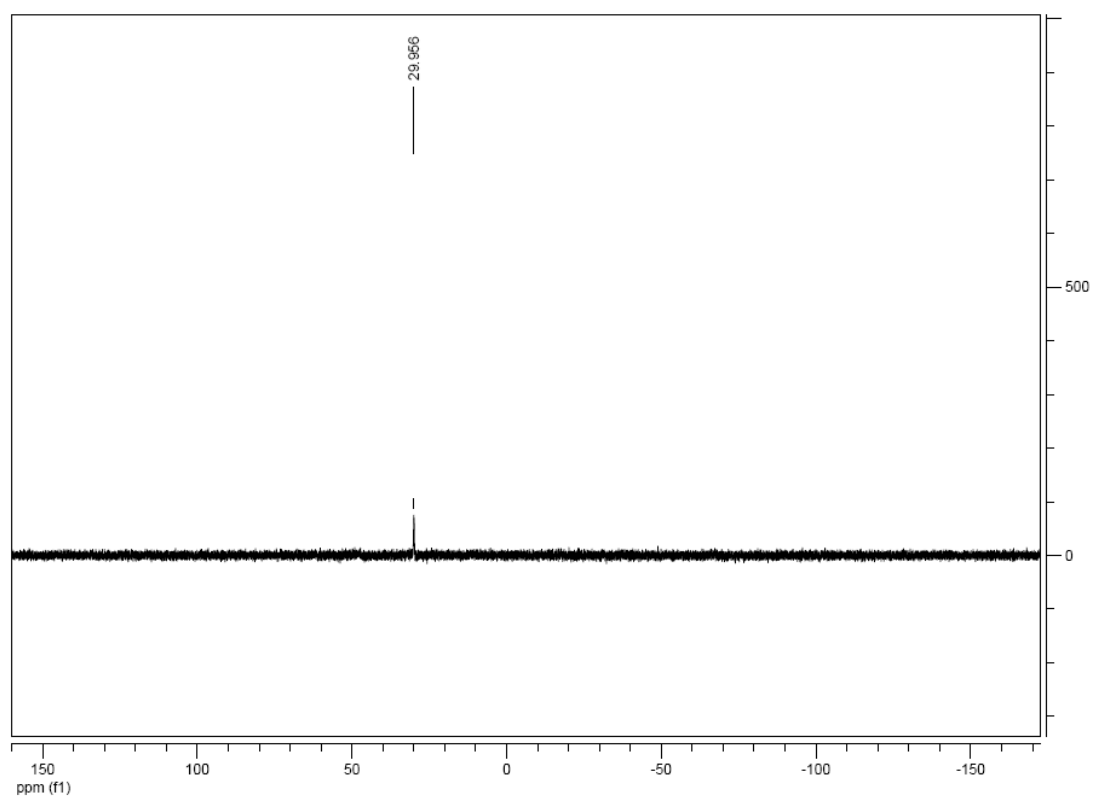
A solution of diphenylacetylene (22.5 mg, 0.125 mmol), Grubbs' second generation catalyst, (15.9 mg, 0.018 mmol, 15 mol %) and AgOTf (9.2 mg, 0.036 mmol, 30 mol %) in dry toluene (5 mL) was stirred at 110 °C for 12 h under 1 atm ethylene pressure (using balloon). After cooling to room temperature, DMAD (89 mg, 0.625 mmol) was added via syringe and the resulting mixture was stirred at 110 °C for another 24 h under ethylene conditions. After cooling to room temperature, DDQ (35 mg, 0.15 mmol) was subsequently added and the reaction was stirred at 80 °C for a further 4 h. The reaction mixture was filtered through a short pad of silica gel eluting with CH_2Cl_2 . The volatiles were removed in vacuo and the residue was purified by silica gel column chromatography (elution with petroleum ether: ethyl acetate = 10:1) to give the final product in 75% yield.

^{31}P NMR experiments

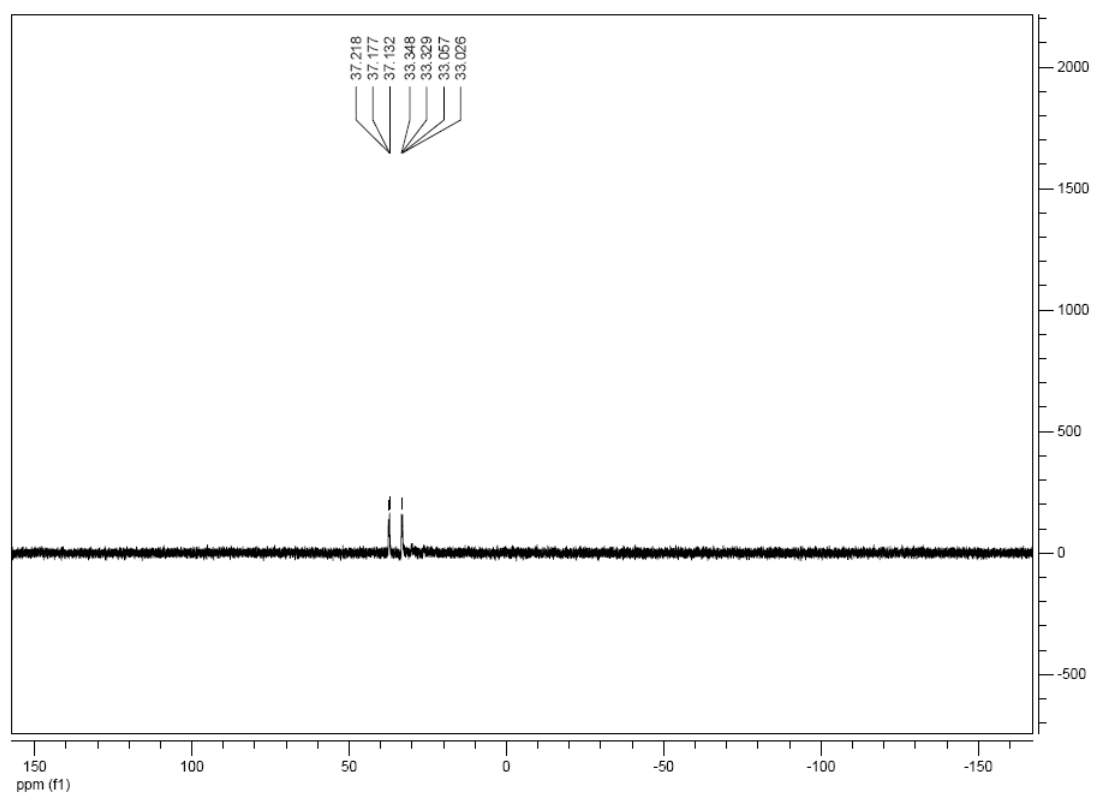
(a) The Grubbs' second generation catalyst (10 mg) was dissolved in toluene (0.5 mL) in an NMR tube fitted with a screw cap containing a rubber septum.



(b) The Grubbs' second generation catalyst (10 mg) and CuI (1.2 mg) were dissolved in toluene (0.5 mL) in an NMR tube fitted with a screw cap containing a rubber septum. The resulting solution was allowed to equilibrate in an oil bath preheated to 20 °C for 0.5 h before ^{31}P NMR experiments

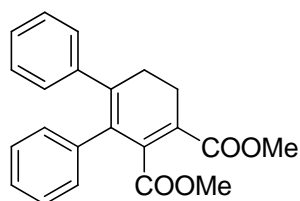


(c) The Grubbs' second generation catalyst (15.9 mg, 0.018 mmol) and AgOTf (9.2 mg, 0.036 mmol,) were dissolved in toluene (approximately 0.7 mL) in an NMR tube fitted with a screw cap containing a rubber septum. The resulting solution was allowed to equilibrate in an oil bath preheated to 90 °C for 0.5 h before ^{31}P NMR experiments.



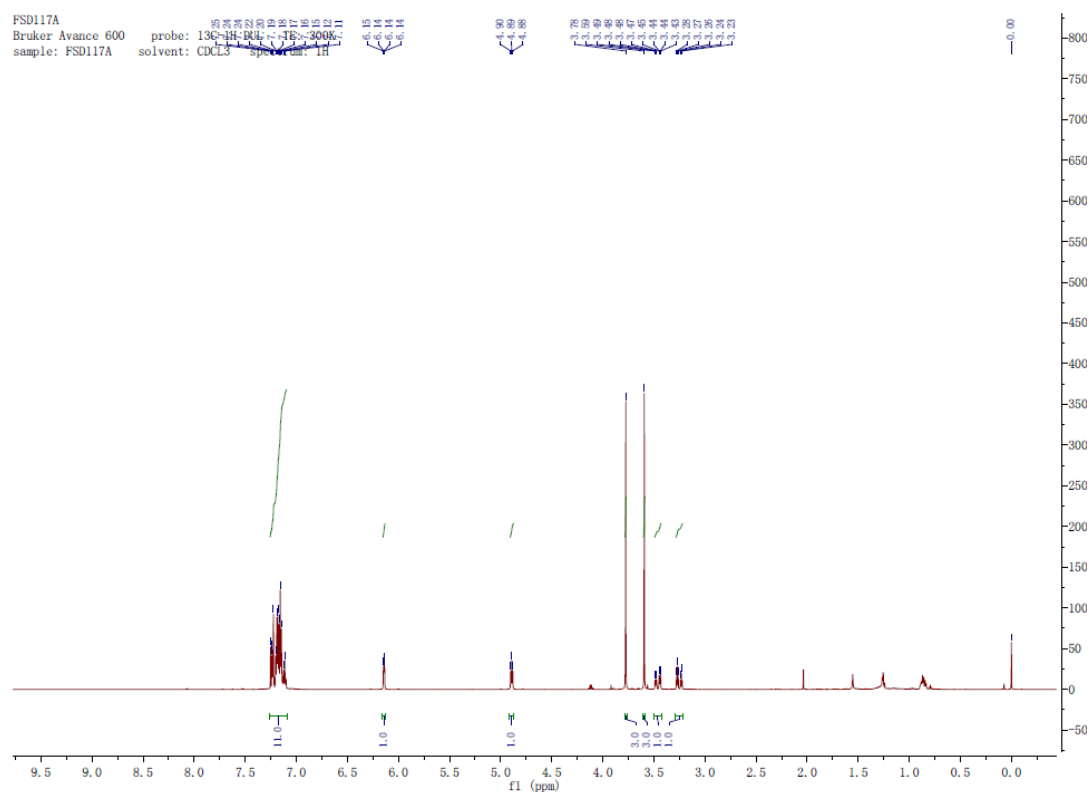
Investigation of mechanism in the presence of AgOTf as additive

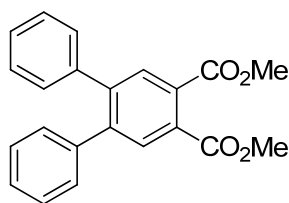
A solution of diphenylacetylene (22.5 mg, 0.125 mmol), Grubbs' second generation catalyst (31.8 mg, 0.036 mmol, 30 mol %) and AgOTf (18.4 mg, 0.072 mmol, 60 mol %) in dry toluene (5 mL) was stirred at 100 °C for 12 h under 1 atm ethylene pressure (using balloon). After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel eluting with petroleum ether. The volatiles were removed in vacuo and the residue was reacted with DMAD (89 mg, 0.625 mmol) in 5 mL toluene at 100 °C for 24 h under an atmosphere of nitrogen. After cooling to room temperature, the reaction mixture was removed in vacuo and the residue was purified by silica gel column chromatography (elution with petroleum ether: ethyl acetate = 10:1) to give the product in 81% yield.



Dimethyl 5',6'-dihydro-[1,1':2',1''-terphenyl]-3',4'-dicarboxylate

$^1\text{H-NMR}$ (CDCl_3 , 600 MHz): δ 7.24-7.09 (m, 10H), 6.14 (dd, $J = 4.6, 2.7$ Hz, 1H), 4.89 (t, $J = 6.2$ Hz, 1H), 3.78 (s, 3H), 3.59 (s, 3H), 3.46 (ddd, $J = 23.6, 6.9, 2.7$ Hz, 1H), 3.26 (m, 1H).



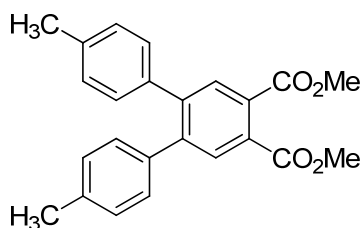


Dimethyl 4,5-di(phenyl)phthalate (**3a**)⁶

¹H-NMR (CDCl₃, 300 MHz): δ 7.79 (s, 2 H), 7.23-7.25 (m, 6 H), 7.12-7.15 (m, 4 H), 3.94 (s, 6 H);

¹³C NMR (CDCl₃, 50 MHz): δ 167.82, 143.38, 131.22, 130.69, 129.58, 128.12, 127.38, 52.70. MS

(ESI) m/z: 369.1 (M+Na⁺). IR (cm⁻¹): ν 2952, 1726, 1434, 1317, 1275, 1247, 1133, 1075.

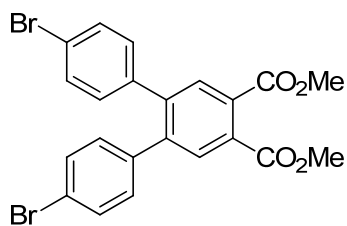


Dimethyl 4,5-di(4'-methylphenyl)phthalate (**3b**)

¹H-NMR (CDCl₃, 300 MHz): δ 7.75 (s, 2 H), 7.03 (s, 8 H), 3.92 (s, 6 H), 2.31 (s, 6H); ¹³C NMR

(CDCl₃, 50 MHz): δ 167.90, 143.30, 137.08, 136.76, 131.25, 130.43, 129.42, 128.85, 52.60, 21.11.

HRMS (ESI): Anal. Calcd. (M+H⁺) 375.15877, Found: 375.15909. IR (cm⁻¹): ν 2950, 1727, 1605, 1514, 1433, 1317, 1274, 1245, 1132.

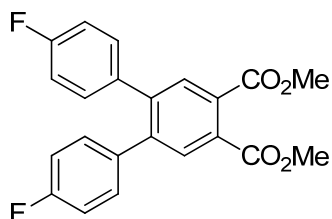


Dimethyl 4,5-di(4'-bromophenyl)phthalate (**3c**)

¹H-NMR (CDCl₃, 300 MHz): δ 7.75 (s, 2 H), 7.40 (d, *J* = 8.4 Hz, 4 H), 7.00 (d, *J* = 8.4 Hz, 4 H),

3.94 (s, 6 H); ¹³C NMR (CDCl₃, 50 MHz): δ 167.49, 141.97, 138.04, 131.57, 131.12, 122.09,

52.80. HRMS (ESI): Anal. Calcd. (M+H⁺) 502.94980, Found: 502.94881. IR (cm⁻¹): ν 2952, 1729, 1488, 1447, 1433, 1317, 1267, 1247, 1133, 1077.



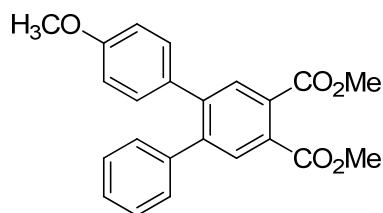
Dimethyl 4,5-di(4'-fluorophenyl)phthalate (**3d**)

¹H-NMR (CDCl₃, 300 MHz): δ 7.75 (s, 2 H), 7.05-7.12 (m, 4 H), 6.90-6.99 (m, 4 H), 3.94 (s, 6 H);

¹³C NMR (CDCl₃, 50 MHz): δ 167.58, 164.69, 159.76, 142.31, 135.34, 135.28, 131.30, 131.13,

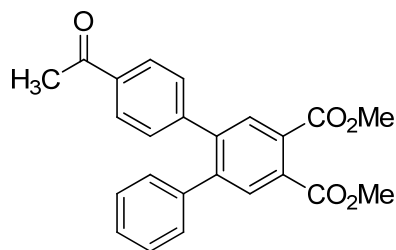
130.98, 115.53, 115.10, 52.70. HRMS (ESI): Anal. Calcd. (M+Na⁺) 405.09093, Found:

405.09089. IR (cm⁻¹): ν 2952, 1726, 1604, 1518, 1510, 1434, 1303, 1274, 1246, 1224, 1133.



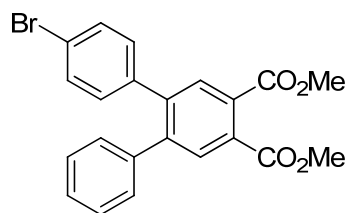
Dimethyl-4-(4'-methoxyphenyl),5-phenylphthalate (**3e**)

¹H-NMR (CDCl₃, 300 MHz): δ 7.78 (s, 1 H), 7.76 (s, 1 H), 7.24-7.27 (m, 3H), 7.13-7.16 (m, 2H), 7.06 (d, J = 8.7 Hz, 2 H), 6.77 (d, J = 9.0 Hz, 2 H), 3.95 (s, 3 H), 3.93 (s, 3 H), 3.78 (s, 3 H); ¹³C NMR (CDCl₃, 50 MHz): δ 167.98, 167.77, 158.97, 143.14, 139.80, 131.86, 131.80, 131.35, 131.04, 130.87, 130.78, 129.55, 128.85, 128.17, 127.30, 113.60, 55.18, 52.67. HRMS (ESI): Anal. Calcd. (M+H⁺) 399.12023, Found: 399.12029. IR (cm⁻¹): ν 2957, 1727, 1609, 1519, 1434, 1317, 1275, 1249, 1135.



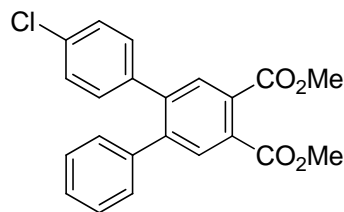
Dimethyl-4-(4'-acetylphenyl),5-phenylphthalate (**3f**)

¹H-NMR (CDCl₃, 300 MHz): δ 7.85 (s, 1 H), 7.82 (s, 1 H), 7.82 (d, J = 3.9 Hz, 2 H), 7.23-7.26 (m, 5 H), 7.10-7.14 (m, 2 H), 3.95 (s, 6 H), 2.58 (s, 3 H); ¹³C NMR (CDCl₃, 50 MHz): δ 197.65, 167.64, 167.53, 144.41, 143.53, 142.04, 139.00, 135.81, 131.45, 131.31, 131.02, 130.73, 129.85, 129.52, 128.33, 128.18, 127.70, 121.84, 52.78, 26.61. HRMS (ESI): Anal. Calcd. (M+H⁺) 389.13834, Found: 389.13835. IR (cm⁻¹): ν 2951, 1726, 1683, 1604, 1433, 1317, 1266, 1248, 1134, 1080.



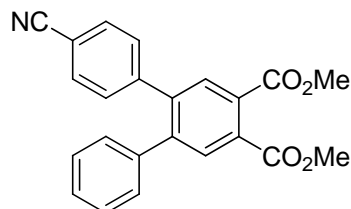
Dimethyl-4-(4'-bromophenyl),5-phenylphthalate (**3g**)

¹H-NMR (CDCl₃, 300 MHz): δ 7.78 (s, 1 H), 7.76 (s, 1 H), 7.37 (d, J = 8.7 Hz, 2 H), 7.25-7.28 (m, 3 H), 7.10-7.14 (m, 2 H), 7.01 (d, J = 8.4 Hz, 2 H), 3.94 (s, 3 H), 3.94 (s, 3 H); ¹³C NMR (CDCl₃, 50 MHz): δ 167.66, 167.61, 143.35, 142.02, 139.16, 138.45, 131.35, 131.18, 130.96, 129.53, 128.32, 127.61, 121.84, 52.73. HRMS (ESI): Anal. Calcd. (M+H⁺) 425.03809, Found: 425.03830. IR (cm⁻¹): ν 2950, 1727, 1433, 1317, 1272, 1247, 1133, 1077.



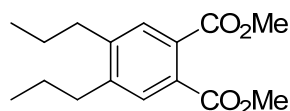
Dimethyl-4-(4'-chlorophenyl),5-phenylphthalate (**3h**)

¹H-NMR (CDCl₃, 300 MHz): δ 7.78 (s, 1 H), 7.76 (s, 1 H), 7.26-7.28 (m, 3 H), 7.21 (d, *J* = 8.4 Hz, 2 H), 7.10-7.14 (m, 2 H), 7.07 (d, *J* = 8.7 Hz, 2 H), 3.94 (s, 3 H), 3.94 (s, 3 H); ¹³C NMR (CDCl₃, 50 MHz): δ 167.64, 167.60, 143.37, 142.00, 139.16, 137.94, 133.58, 131.38, 131.29, 131.04, 130.99, 130.85, 129.50, 128.37, 128.28, 127.57, 52.70. HRMS (ESI): Anal. Calcd. (M+H⁺) 381.08903, Found: 381.08881. IR (cm⁻¹): ν 2951, 1727, 1433, 1317, 1267, 1276, 1247, 1133, 1091, 1075.



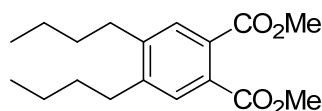
Dimethyl-4-(4'-cyanophenyl),5-phenylphthalate (**3i**)

¹H-NMR (CDCl₃, 300 MHz): δ 7.81 (s, 1 H), 7.79 (s, 1 H), 7.54 (d, *J* = 8.7 Hz, 4 H), 7.24-7.29 (m, 5 H), 7.08-7.11 (m, 2 H), 3.95 (s, 6 H); ¹³C NMR (CDCl₃, 50 MHz): δ 167.50, 167.27, 144.32, 143.58, 141.14, 138.61, 131.93, 131.33, 130.91, 130.30, 129.49, 128.44, 127.90, 118.49, 111.28, 52.80. HRMS (ESI): Anal. Calcd. (M+H⁺) 372.12297, Found: 372.12303. IR (cm⁻¹): ν 2951, 2227, 1729, 1606, 1428, 1318, 1275, 1248.



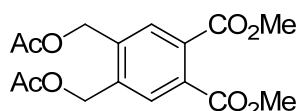
Dimethyl 4,5-dipropylphthalate (**3j**)

¹H-NMR (CDCl₃, 300 MHz): δ 7.49 (s, 2 H), 3.88 (s, 6 H), 2.59-2.65 (m, 4 H), 1.55-1.69 (m, 4H), 0.99 (t, *J* = 3.6 Hz, 6 H); ¹³C NMR (CDCl₃, 50 MHz): δ 168.29, 144.00, 129.60, 129.18, 52.37, 34.40, 23.85, 13.98. HRMS (ESI): Anal. Calcd. (M+H⁺) 279.15885, Found: 279.15909. IR (cm⁻¹): ν 2958, 2817, 1726, 1610, 1562, 1434, 1296, 1277, 1217, 1133.



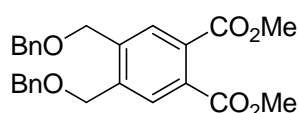
Dimethyl 4,5-di(n-butyl)phthalate (**3k**)⁷

¹H-NMR (CDCl₃, 300 MHz): δ 7.49 (s, 2 H), 3.88 (s, 6 H), 2.64 (t, *J* = 7.5 Hz, 4 H), 1.51-1.58 (m, 4 H), 1.35-1.43 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 6 H); ¹³C NMR (CDCl₃, 50 MHz): δ 168.29, 144.17, 129.57, 129.11, 52.38, 32.89, 32.12, 22.62, 13.84. MS (ESI): 329 (M+Na⁺). IR (cm⁻¹): ν 2954, 2872, 1726, 1434, 1292, 1264, 1215, 1132.



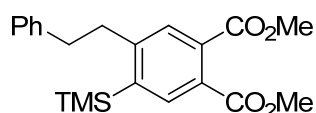
Dimethyl 4,5-bis(acetoxymethyl)phthalate (**3l**)

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ 7.77 (s, 2 H), 5.21 (s, 4H), 3.91 (s, 6 H), 2.12 (s, 6 H); $^{13}\text{C NMR}$ (CDCl_3 , 50 MHz): δ 170.20, 167.20, 137.46, 131.71, 129.45, 62.44, 52.61, 20.63. HRMS (ESI): Anal. Calcd. ($\text{M}+\text{H}^+$) 361.08886, Found: 361.08939. IR (cm^{-1}): ν 2953, 1728, 1435, 1375, 1309, 1216, 1133.



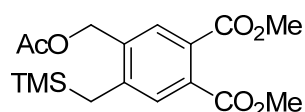
Dimethyl-4,5-di(benzyloxymethyl)phthalate (**3m**)

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ 7.82 (s, 2 H), 7.29-7.35 (m, 10 H), 4.59 (s, 4H), 4.52 (s, 4H), 3.90 (s, 6 H); $^{13}\text{C NMR}$ (CDCl_3 , 50 MHz): δ 167.87, 139.65, 137.48, 130.98, 128.67, 128.41, 127.79, 72.62, 68.67, 52.60. HRMS (ESI): Anal. Calcd. ($\text{M}+\text{H}^+$) 435.17982, Found: 435.18022. IR (cm^{-1}): ν 2951, 2860, 1725, 1453, 1434, 1305, 1270, 1212, 1131, 1091.



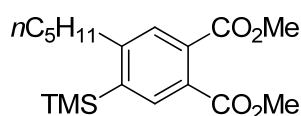
Dimethyl 4-phenethyl-5-(trimethylsilyl)phthalate (**3n**)

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ 7.84 (s, 1 H), 7.59 (s, 1 H), 7.31 (d, J = 6.9 Hz, 2 H), 7.22-7.24 (m, 1H), 7.23 (d, J = 7.2 Hz, 2 H), 3.92 (s, 3 H), 3.91 (s, 3 H), 3.04-3.10 (m, 2 H), 2.87-2.93 (m, 2 H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 168.30, 151.19, 142.50, 140.94, 135.05, 132.55, 128.66, 128.52, 128.22, 128.13, 126.19, 52.52, 52.47, 38.12, 37.85. HRMS (ESI): Anal. Calcd. ($\text{M}+\text{H}^+$) 371.16707, Found: 371.16731. IR (cm^{-1}): ν 2952, 1726, 1596, 1545, 1434, 1291, 1270, 1252, 1135, 838.



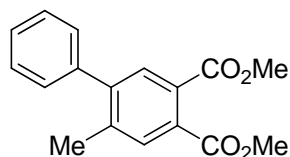
Dimethyl 4-(acetoxymethyl)-5-((trimethylsilyl)methyl)phthalate (**3o**)

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ 7.74 (s, 1 H), 7.28 (s, 1 H), 5.06 (s, 2 H), 3.89 (s, 3 H), 3.88 (s, 3 H), 2.22 (s, 2 H), 2.11 (s, 3 H), 0.016 (s, 9 H); $^{13}\text{C NMR}$ (CDCl_3 , 50 MHz): δ 170.62, 168.35, 167.53, 143.87, 134.97, 132.14, 129.88, 129.81, 129.77, 129.22, 127.06, 63.30, 52.62, 52.47, 23.93, 20.90, -1.54. HRMS (ESI): Anal. Calcd. ($\text{M}+\text{H}^+$) 353.14141, Found: 353.14149. IR (cm^{-1}): ν 2952, 1727, 1611, 1562, 1435, 1298, 1249, 1216, 1134.



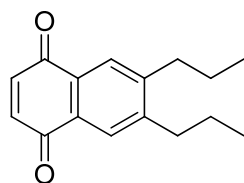
Dimethyl 4-pentyl-5-(trimethylsilyl)phthalate (**3p**)

¹H-NMR (CDCl₃, 300 MHz): δ 7.79 (s, 1 H), 7.49 (s, 1 H), 3.89 (s, 3 H), 3.88 (s, 3 H), 2.70-2.75 (m, 2 H), 1.54-1.62 (m, 2 H), 1.34-1.36 (m, 4 H), 0.90 (t, *J* = 6.9 Hz, 3 H), 0.33 (s, 9 H); ¹³C NMR (CDCl₃, 100 MHz): δ 168.47, 168.33, 152.56, 142.22, 134.93, 132.52, 128.33, 127.69, 52.47, 52.40, 36.12, 31.96, 31.78, 22.49, 13.94, 0.075. HRMS (ESI): Anal. Calcd. (M+H⁺) 337.18298, Found: 337.18296. IR (cm⁻¹): ν 2952, 1728, 1434, 1292, 1251, 1135, 838



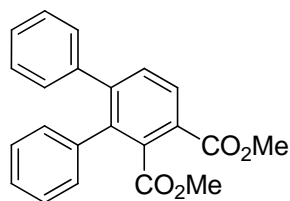
Dimethyl 5-methyl-4-phenylphthalate (**3q**)

¹H-NMR (CDCl₃, 300 MHz): δ 7.64 (s, 1 H), 7.61 (s, 1 H), 7.40-7.43 (m, 3 H), 7.30 (d, *J* = 8.4 Hz, 1 H), 7.29 (d, *J* = 7.8 Hz, 1 H), 3.93 (s, 3 H), 3.89 (s, 3 H), 2.32 (s, 3 H), 1.44-1.48 (m, 2 H), 1.16-1.25 (m, 6 H), 0.81 (t, *J* = 6.3 Hz, 3 H); ¹³C NMR (CDCl₃, 50 MHz): δ 168.28, 167.76, 144.63, 139.80, 139.36, 130.93, 130.84, 130.72, 130.47, 128.94, 128.82, 128.33, 127.65, 52.64, 52.54, 20.41. HRMS (ESI): Anal. Calcd. (M+Na⁺) 307.09385, Found: 307.09408. IR (cm⁻¹): ν 2954, 1726, 1434, 1310, 1247, 1132, 1072.



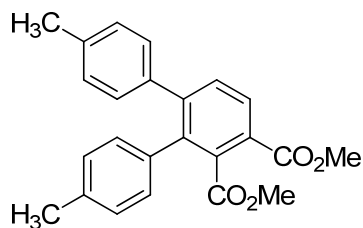
6, 7-dipropylnaphthalene-1,4-dione (**3r**)

¹H-NMR (CDCl₃, 300 MHz): δ 7.84 (s, 2 H), 6.91 (s, 2 H), 2.71 (t, *J* = 8.1 Hz, 4 H), 1.61-1.73 (m, 4 H), 1.01 (t, *J* = 7.5 Hz, 6 H); ¹³C NMR (CDCl₃, 50 MHz): δ 185.24, 147.51, 138.66, 138.53, 129.68, 126.99, 34.81, 23.75, 14.03. HRMS (ESI): Anal. Calcd. (M+H⁺) 243.13826, Found: 243.13796. IR (cm⁻¹): ν 2959, 2929, 2871, 1665, 1597, 1466, 1315, 1056.



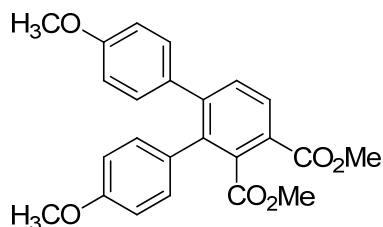
Dimethyl-3,4-diphenylphthalate (**4a**)⁸

¹H-NMR (CDCl₃, 300 MHz): δ 8.08 (d, *J* = 8.1 Hz, 1 H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.16-7.20 (m, 5 H), 7.03-7.12 (m, 5 H), 3.92 (s, 3 H), 3.57 (s, 3 H); ¹³C NMR (CDCl₃, 50 MHz): δ 169.09, 165.91, 146.20, 139.82, 138.74, 137.27, 136.55, 130.85, 130.81, 130.20, 129.50, 129.17, 127.77, 127.55, 127.29, 127.14, 126.22, 52.55, 52.12. MS (ESI) *m/z*: 369.1(M+Na⁺). IR (cm⁻¹): ν 2950, 1724, 1587, 1432, 1304, 1268, 1233, 1156, 1070



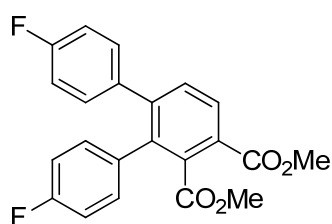
Dimethyl 3,4-di(4'-methylphenyl)phthalate (**4b**)

¹H-NMR (CDCl₃, 300 MHz): δ 8.04 (d, *J* = 8.1 Hz, 1 H), 7.50 (d, *J* = 8.1 Hz, 1H), 6.95-6.70 (m, 8 H), 3.91 (s, 3 H), 3.59 (s, 3 H), 2.28 (s, 3 H), 2.27 (s, 3 H); ¹³C NMR (CDCl₃, 50 MHz): δ 169.26, 165.99, 146.26, 138.72, 137.04, 136.82, 136.79, 134.37, 130.85, 130.00, 129.39, 128.98, 128.53, 128.33, 125.91, 52.50, 52.10, 21.22, 21.10. HRMS (ESI): Anal. Calcd. (M+H⁺) 397.14066, Found: 397.14103. IR (cm⁻¹): ν 2951, 1727, 1586, 1514, 1434, 1294, 1268, 1233, 1156, 1143, 1068.



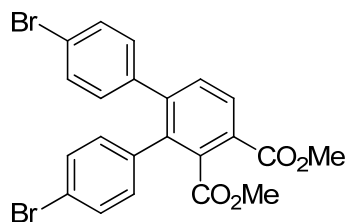
Dimethyl 3,4-di(4'-methoxyphenyl)phthalate (**4c**)

¹H-NMR (CDCl₃, 300 MHz): δ 8.03 (d, *J* = 8.1 Hz, 1 H), 7.49 (d, *J* = 8.1 Hz, 1H), 6.96-7.26 (m, 4 H), 6.70-6.75 (m, 4 H), 3.91 (s, 3 H), 3.76 (s, 3 H), 3.75 (s, 3 H), 3.61 (s, 3 H); ¹³C NMR (CDCl₃, 50 MHz): δ 169.32, 165.95, 158.62, 158.58, 146.07, 138.26, 136.85, 132.28, 131.34, 130.71, 129.67, 129.00, 125.70, 113.30, 113.09, 55.11, 55.04, 52.48, 52.15. HRMS (ESI): Anal. Calcd. (M+H⁺) 407.14854, Found: 407.14891. IR (cm⁻¹): ν 2950, 1727, 1609, 1517, 1434, 1296, 1247, 1179.



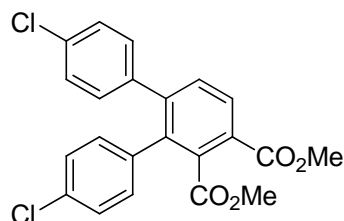
Dimethyl 3,4-di(4'-fluorophenyl)phthalate (**4d**)

¹H-NMR (CDCl₃, 300 MHz): δ 8.09 (d, *J* = 8.1 Hz, 1 H), 7.51 (d, *J* = 8.1 Hz, 1 H), 7.02-7.07 (m, 4 H), 6.86-7.00 (m, 4 H), 3.93 (s, 3 H), 3.60 (s, 3 H); ¹³C NMR (CDCl₃, 50 MHz): δ 168.89, 165.71, 163.67, 163.63, 160.39, 160.35, 145.27, 137.69, 136.74, 135.55, 133.04, 133.00, 131.98, 131.87, 131.18, 131.07, 130.76, 129.44, 126.47, 115.14, 114.96, 114.86, 114.68, 52.63, 52.25. HRMS (ESI): Anal. Calcd. (M+Na⁺) 405.09077, Found: 405.09089. IR (cm⁻¹): ν 2949, 1733, 1604, 1514, 1435, 1306, 1224, 1157.



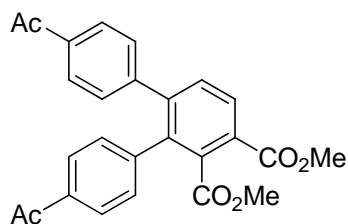
Dimethyl 3,4-di(4'-bromophenyl)phthalate (**4e**)

¹H-NMR (CDCl₃, 300 MHz): δ 8.09 (d, *J* = 8.1 Hz, 1 H), 7.49 (d, *J* = 8.1 Hz, 1 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 6.95 (d, *J* = 8.4 Hz, 2 H), 6.90 (d, *J* = 8.4 Hz, 2 H), 3.93 (s, 3 H), 3.61 (s, 3 H); ¹³C NMR (CDCl₃, 50 MHz): δ 168.70, 165.61, 144.77, 138.37, 137.33, 136.61, 135.90, 131.79, 131.25, 131.04, 130.74, 129.62, 126.76, 122.02, 121.90, 52.69, 52.36. HRMS (ESI): Anal. Calcd. (M+Na⁺) 524.93063, Found: 524.93076. IR (cm⁻¹): ν 2950, 1730, 1495, 1435, 1306, 1270, 1157.



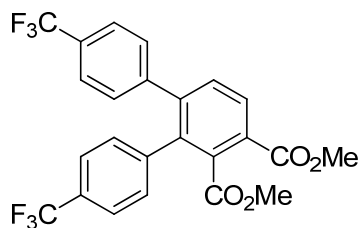
Dimethyl 3,4-di(4'-chlorophenyl)phthalate (**4f**)

¹H-NMR (CDCl₃, 300 MHz): δ 8.09 (d, *J* = 8.1 Hz, 1 H), 7.50 (d, *J* = 8.1 Hz, 1 H), 7.20 (d, *J* = 7.2 Hz, 2 H), 7.18 (d, *J* = 6.9 Hz, 2 H), 7.01 (d, *J* = 8.7 Hz, 2 H), 6.96 (d, *J* = 8.7 Hz, 2 H), 3.93 (s, 3 H), 3.61 (s, 3 H); ¹³C NMR (CDCl₃, 50 MHz): δ 168.74, 165.62, 144.84, 137.90, 137.39, 136.64, 135.43, 133.71, 133.61, 131.49, 130.72, 129.59, 128.27, 128.08, 126.68, 52.67, 52.33. HRMS (ESI): Anal. Calcd. (M+H⁺) 415.04997, Found: 415.04984. IR (cm⁻¹): ν 2950, 2916, 2848, 1727, 1595, 1492, 1434, 1306, 1292, 1269, 1233.



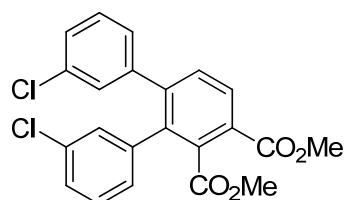
Dimethyl 3,4-di(4'-acetylphenyl)phthalate (**4g**)

¹H-NMR (CDCl₃, 300 MHz): δ 8.14 (d, *J* = 8.1 Hz, 1 H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2 H), 7.56 (d, *J* = 8.1 Hz, 1 H), 7.21 (d, *J* = 8.4 Hz, 2 H), 7.14 (d, *J* = 8.4 Hz, 2 H), 3.95 (s, 3 H), 3.59 (s, 3 H), 2.57 (s, 3 H), 2.55 (s, 3 H); ¹³C NMR (CDCl₃, 50 MHz): δ 197.57, 197.48, 168.55, 165.53, 144.72, 144.15, 141.98, 137.62, 136.42, 135.99, 135.83, 130.76, 130.46, 129.77, 129.68, 128.01, 127.76, 127.12, 52.75, 52.37, 26.57. HRMS (ESI): Anal. Calcd. (M+H⁺) 431.14883, Found: 431.14891. IR (cm⁻¹): ν 2951, 1727, 1683, 1606, 1434, 1304, 1265, 1158.



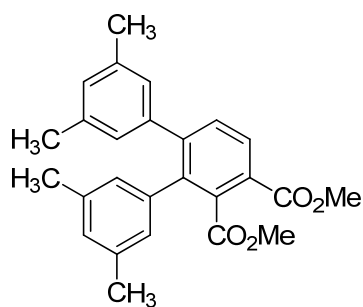
Dimethyl 3,4-di(4'-trifluoromethylphenyl)phthalate (**4h**)

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ 8.15 (d, $J = 8.4$ Hz, 1 H), 7.55 (d, $J = 8.1$ Hz, 1 H), 7.50 (d, $J = 8.4$ Hz, 2 H), 7.46 (d, $J = 8.4$ Hz, 2 H), 7.23 (d, $J = 8.1$ Hz, 2 H), 7.15 (d, $J = 8.1$ Hz, 2 H), 3.95 (s, 3 H), 3.59 (s, 3 H); $^{13}\text{C NMR}$ (CDCl_3 , 50 MHz): δ 168.47, 165.49, 144.43, 142.91, 140.60, 137.29, 136.63, 130.92, 130.59, 129.93, 129.76, 127.27, 126.55, 125.08, 125.00, 124.92, 124.82, 121.13, 52.79, 52.38. **HRMS (ESI)**: Anal. Calcd. ($\text{M}+\text{Na}^+$) 505.08539, Found: 505.08450. **IR** (cm^{-1}): ν 2955, 1731, 1324, 1307, 1270, 1162, 1123, 1109, 1061.



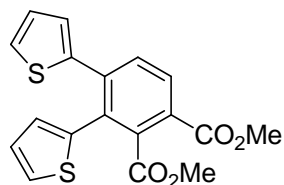
Dimethyl 3,4-di(3'-chlorophenyl)phthalate (**4i**)

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ 8.10 (d, $J = 8.1$ Hz, 1 H), 7.52 (d, $J = 8.1$ Hz, 1 H), 7.15-7.24 (m, 3H), 6.95-7.13 (m, 3 H), 6.68 (dt, $J = 7.5$, 1.5 Hz, 1 H), 6.67 (dt, $J = 7.8$, 1.5 Hz, 1 H), 3.94 (s, 3 H), 3.64 (s, 3 H); $^{13}\text{C NMR}$ (CDCl_3 , 50 MHz): δ 168.55, 165.56, 144.52, 141.10, 138.63, 137.22, 136.57, 133.94, 133.66, 130.73, 130.08, 129.69, 129.39, 129.16, 129.01, 128.49, 127.84, 127.70, 127.61, 126.91, 52.69, 52.27. **HRMS (ESI)**: Anal. Calcd. ($\text{M}+\text{Na}^+$) 437.03250, Found: 437.03179. **IR** (cm^{-1}): ν 2951, 1729, 1588, 1565, 1436, 1294, 1272, 1158.



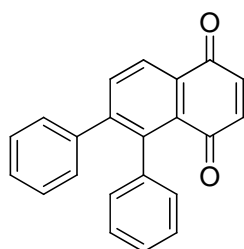
Dimethyl 3,4-di(3',5'-dimethylphenyl)phthalate (**4j**)

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ 8.02 (d, $J = 7.8$ Hz, 1 H), 7.49 (d, $J = 7.8$ Hz, 1H), 6.79 (s, 2 H), 6.68 (d, $J = 7.5$ Hz, 2 H), 6.67 (d, $J = 7.5$ Hz, 2 H), 3.91 (s, 3 H), 3.61 (s, 3 H), 2.17 (s, 6 H), 2.16 (s, 6 H); $^{13}\text{C NMR}$ (CDCl_3 , 50 MHz): δ 169.24, 166.04, 146.43, 139.76, 139.04, 137.13, 136.96, 136.60, 136.35, 130.65, 128.78, 128.72, 128.60, 127.97, 127.39, 125.87, 52.46, 51.93, 21.12. **HRMS (ESI)**: Anal. Calcd. ($\text{M}+\text{H}^+$) 403.19005, Found: 403.19039. **IR** (cm^{-1}): ν 2950, 1726, 1603, 1585, 1434, 1273, 1198, 1154, 1094.



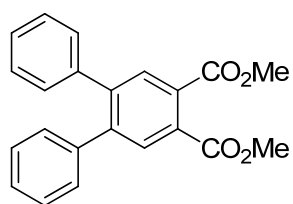
Dimethyl 3,4-di(thiophen-2-yl)phthalate (**4k**)

¹H-NMR (CDCl₃, 300 MHz): δ 8.07 (d, *J* = 8.4 Hz, 1 H), 7.71 (d, *J* = 8.1 Hz, 1 H), 7.38 (dd, *J* = 4.2, 2.1 Hz, 1 H), 7.29 (dd, *J* = 4.2, 2.1 Hz, 1 H), 7.02 (t, *J* = 1.8 Hz, 2 H), 6.92 (t, *J* = 2.1 Hz, 2 H), 3.92 (s, 3 H), 3.67 (s, 3 H); ¹³C NMR (CDCl₃, 50 MHz): δ 168.59, 165.35, 140.84, 140.23, 138.48, 136.94, 130.21, 130.11, 127.90, 127.83, 127.76, 126.98, 126.55, 125.81, 52.64, 52.30. HRMS (ESI): Anal. Calcd. (M+H⁺) 359.04038, Found: 359.04063. IR (cm⁻¹): ν 2949, 1724, 1584, 1432, 1289, 1199, 1156.

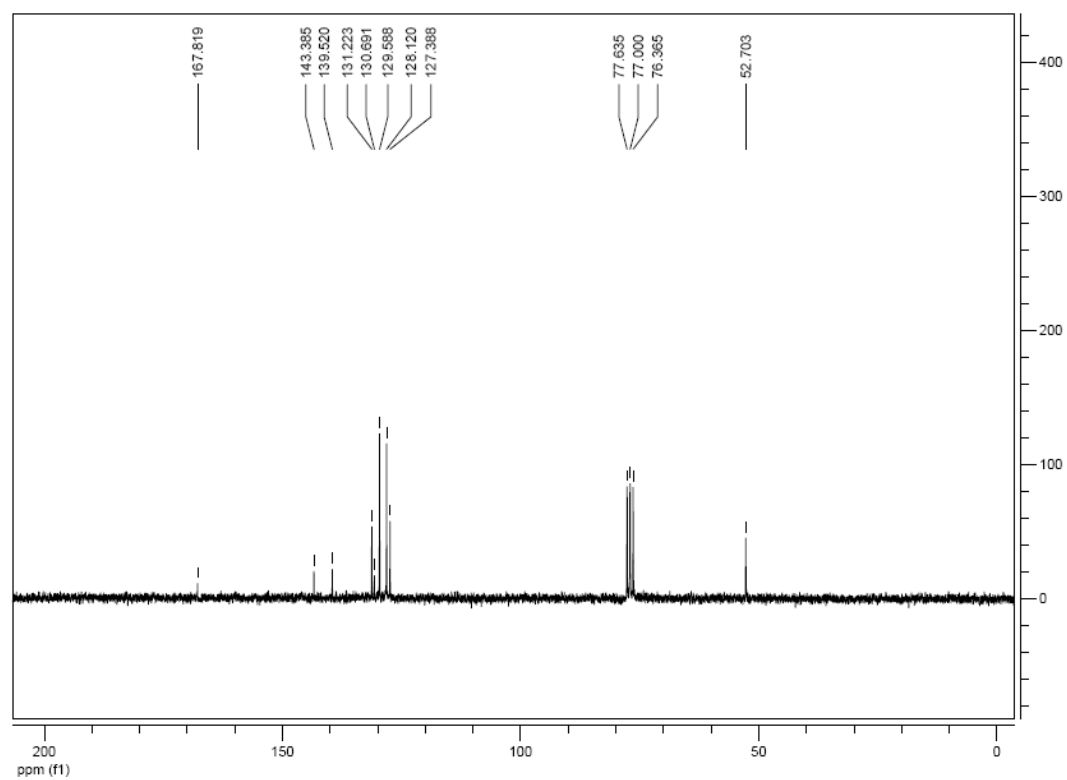
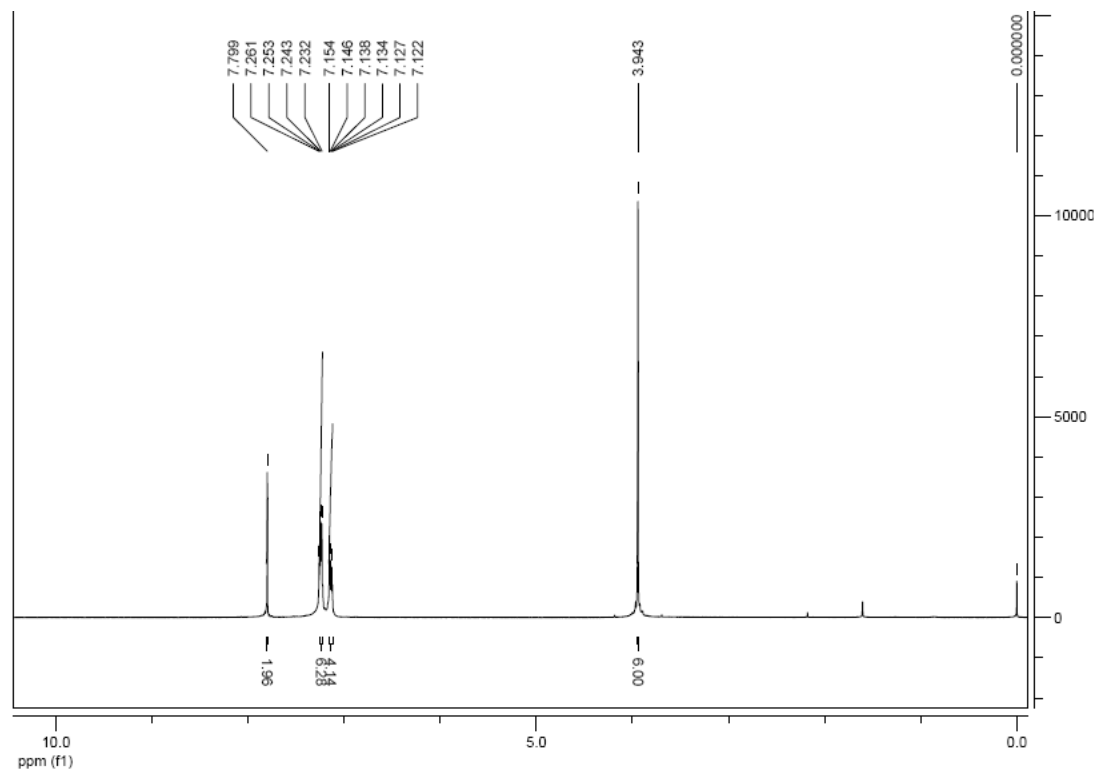


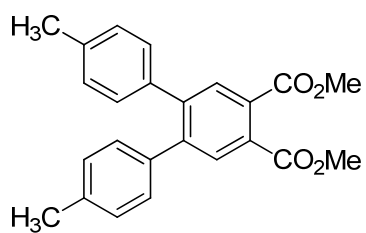
5, 6-diphenylnaphthalene-1,4-dione (**4l**)

¹H-NMR (CDCl₃, 300 MHz): δ 8.23 (d, *J* = 7.8 Hz, 1 H), 7.76 (d, *J* = 8.1 Hz, 1 H), 7.21-7.24 (m, 3 H), 7.16-7.18 (m, 3 H), 6.96-7.00 (m, 4 H), 6.95 (d, *J* = 10.2 Hz, 1 H), 6.81 (d, *J* = 10.2 Hz, 1 H); ¹³C NMR (CDCl₃, 50 MHz): δ 185.49, 185.11, 148.89, 141.62, 140.60, 139.78, 139.72, 138.75, 136.75, 134.98, 132.12, 129.70, 129.36, 129.20, 127.63, 127.12, 126.72, 126.35. HRMS (ESI): Anal. Calcd. (M+H⁺) 311.10654, Found: 311.10666. IR (cm⁻¹): ν 3054, 1660, 1615, 1555, 1310, 1260, 699.

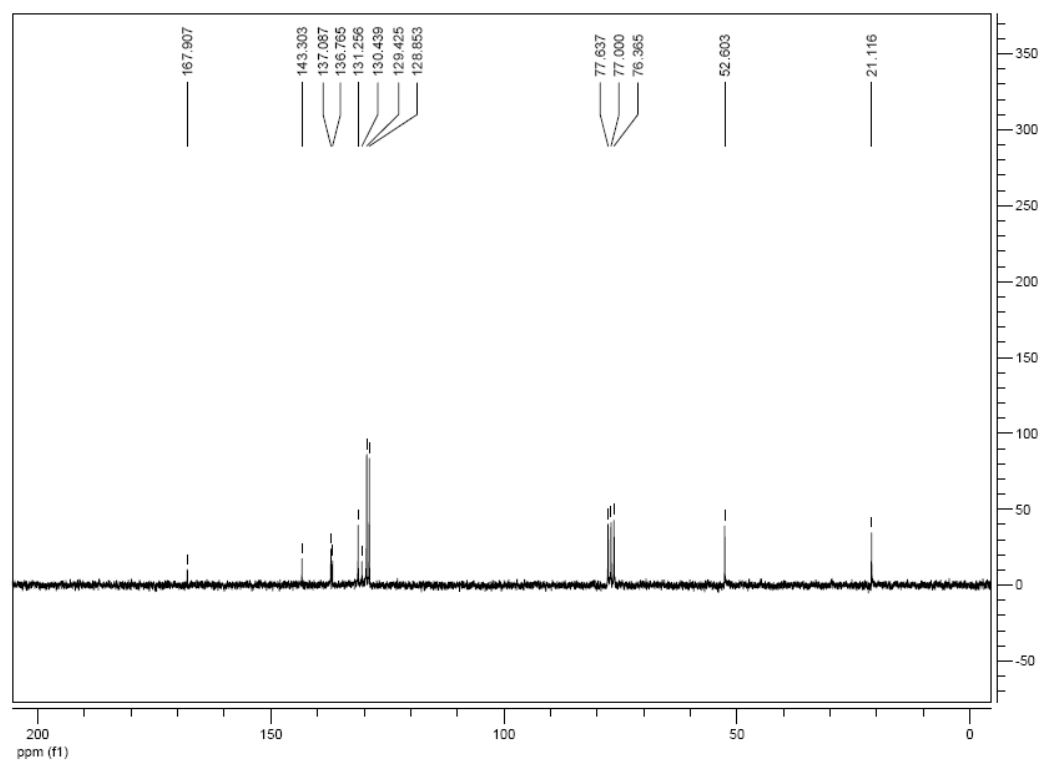
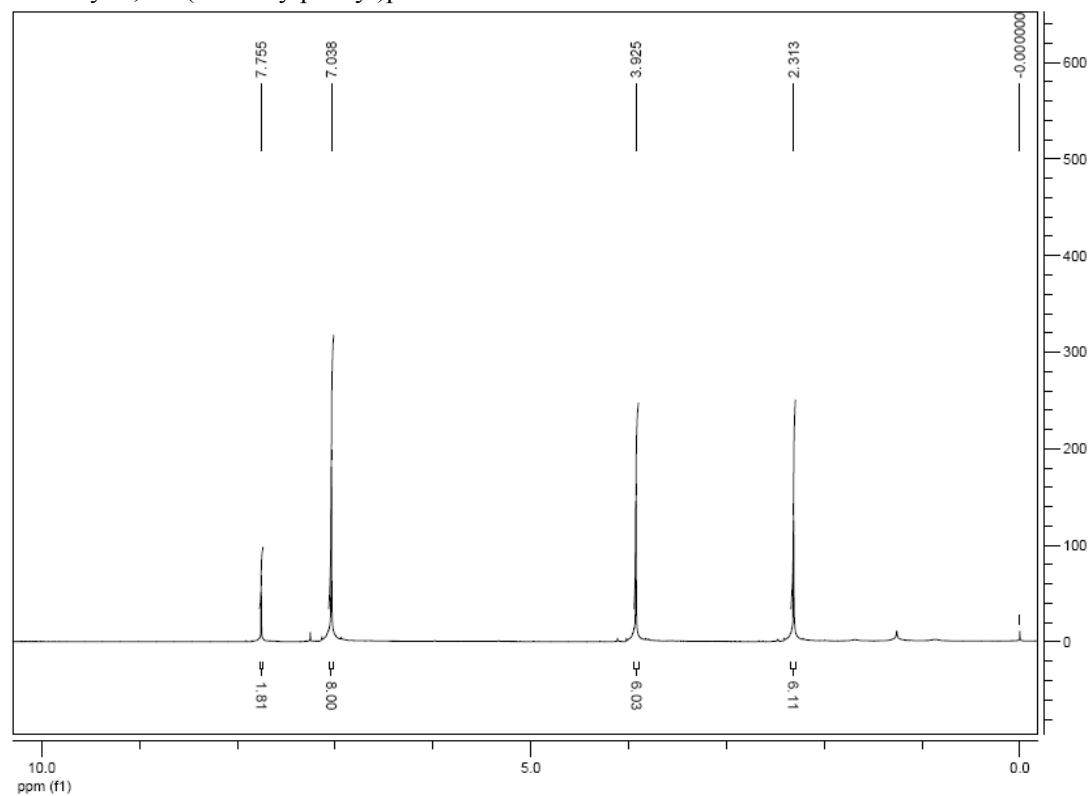


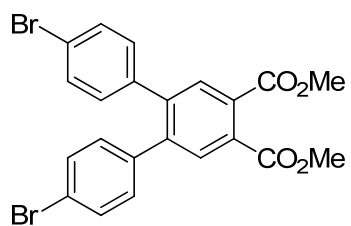
Dimethyl 4,5-di(phenyl)phthalate



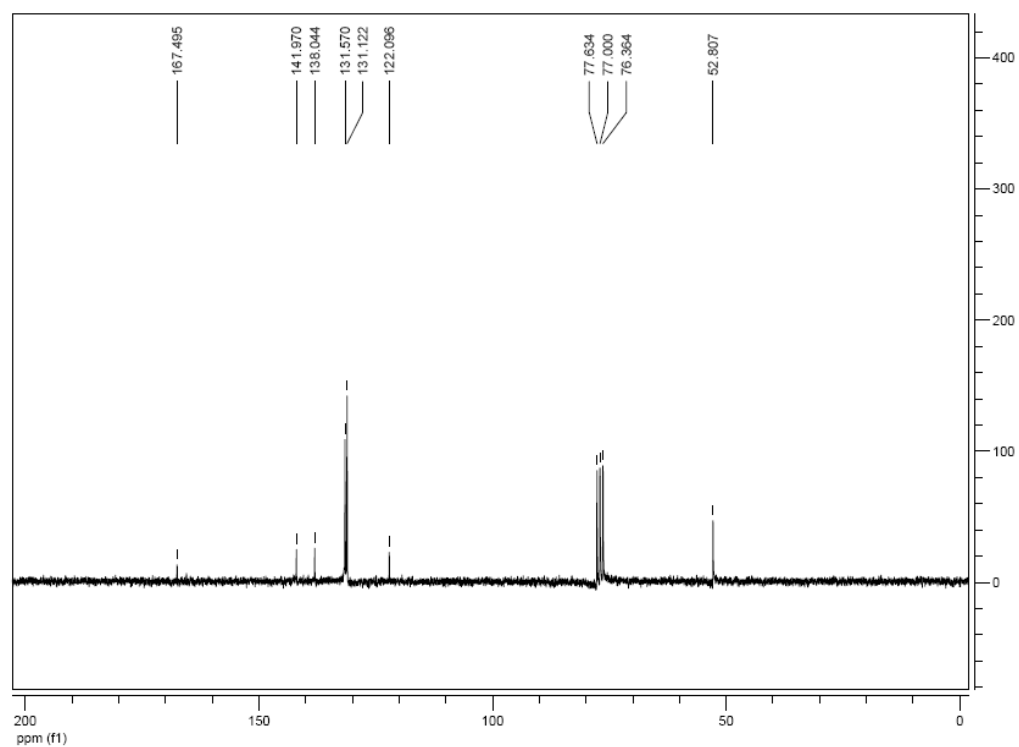
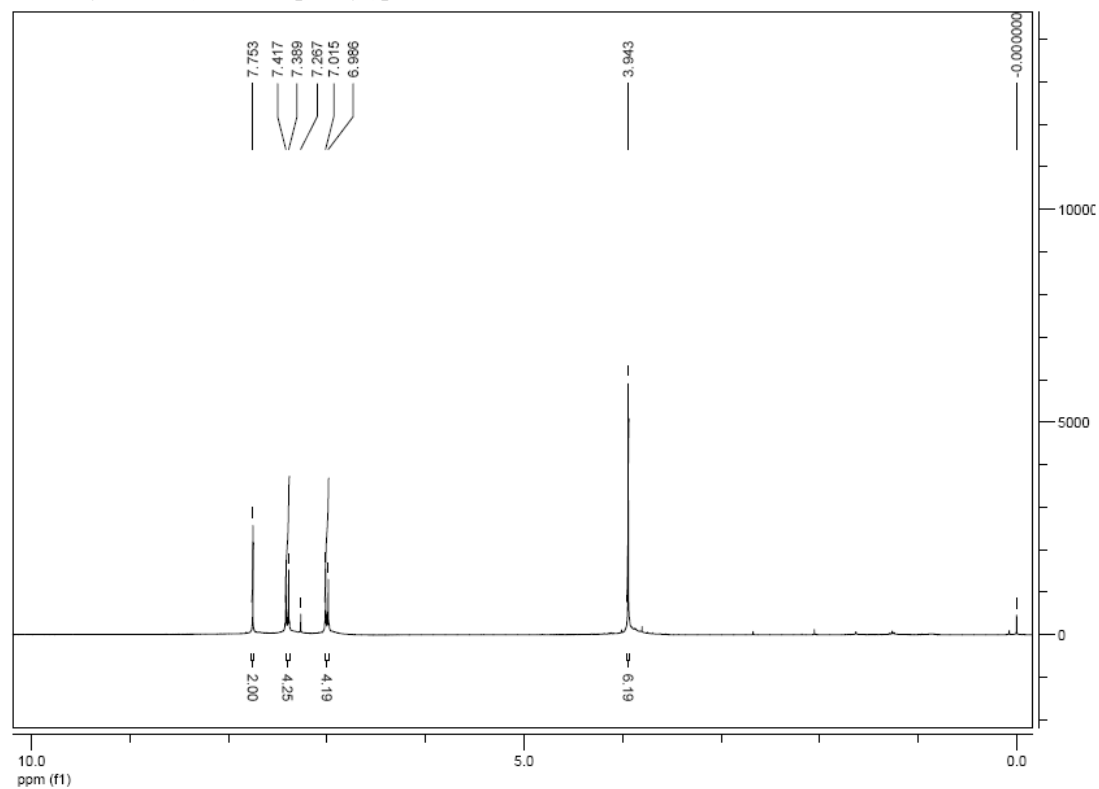


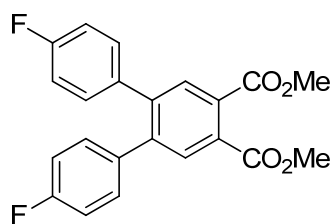
Dimethyl 4,5-di(4'-methylphenyl)phthalate



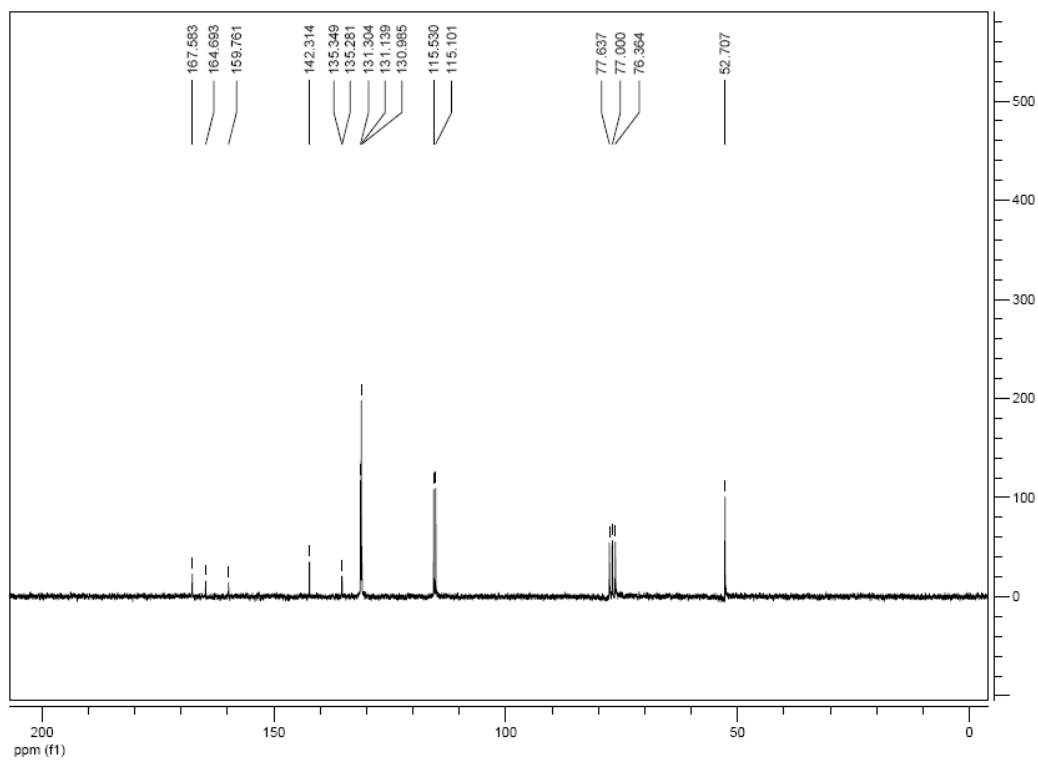
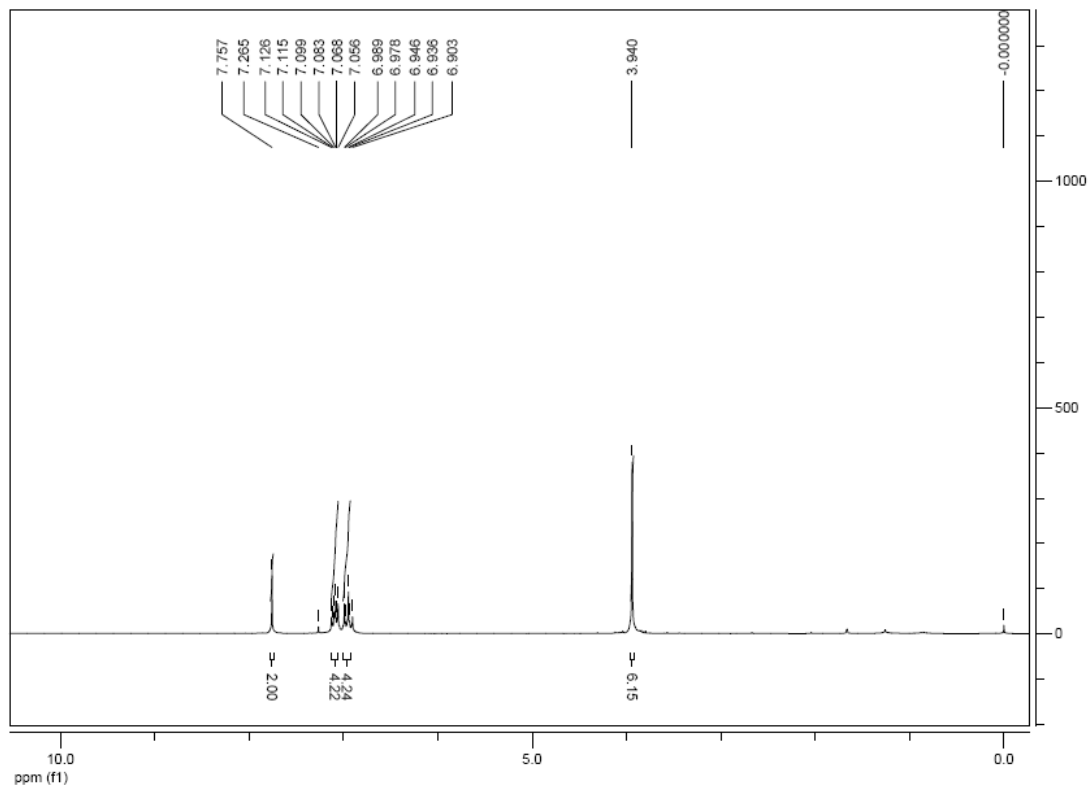


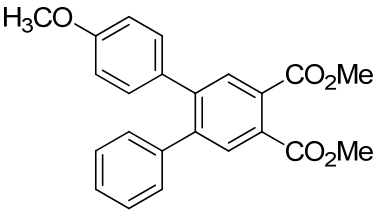
Dimethyl 4,5-di(4'-bromophenyl)phthalate



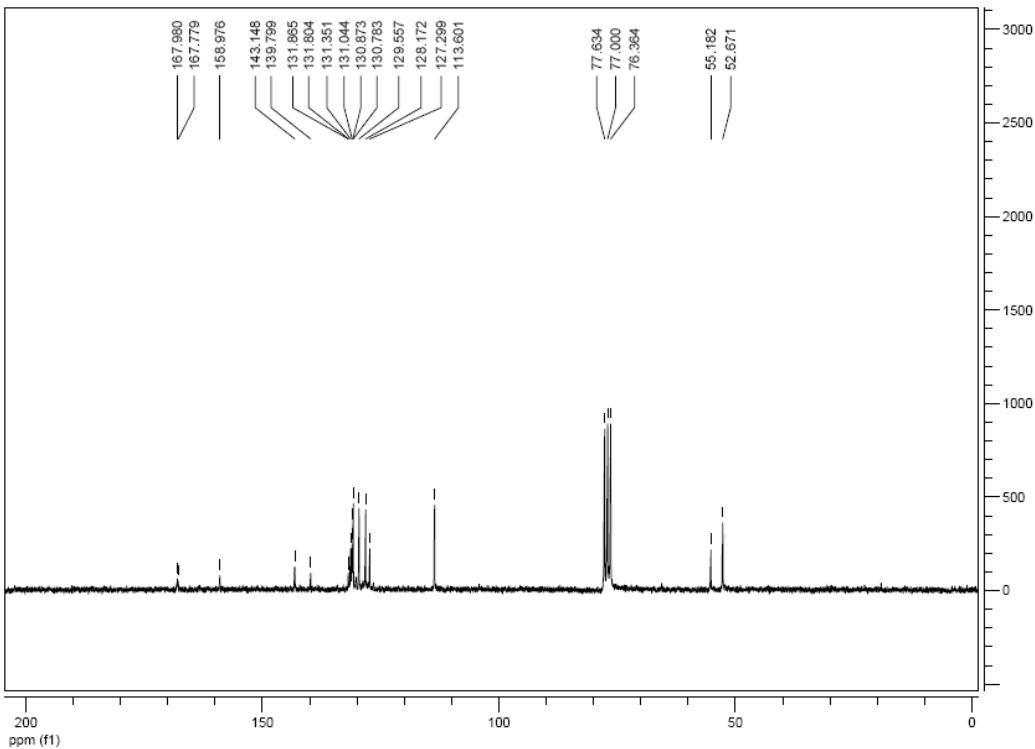
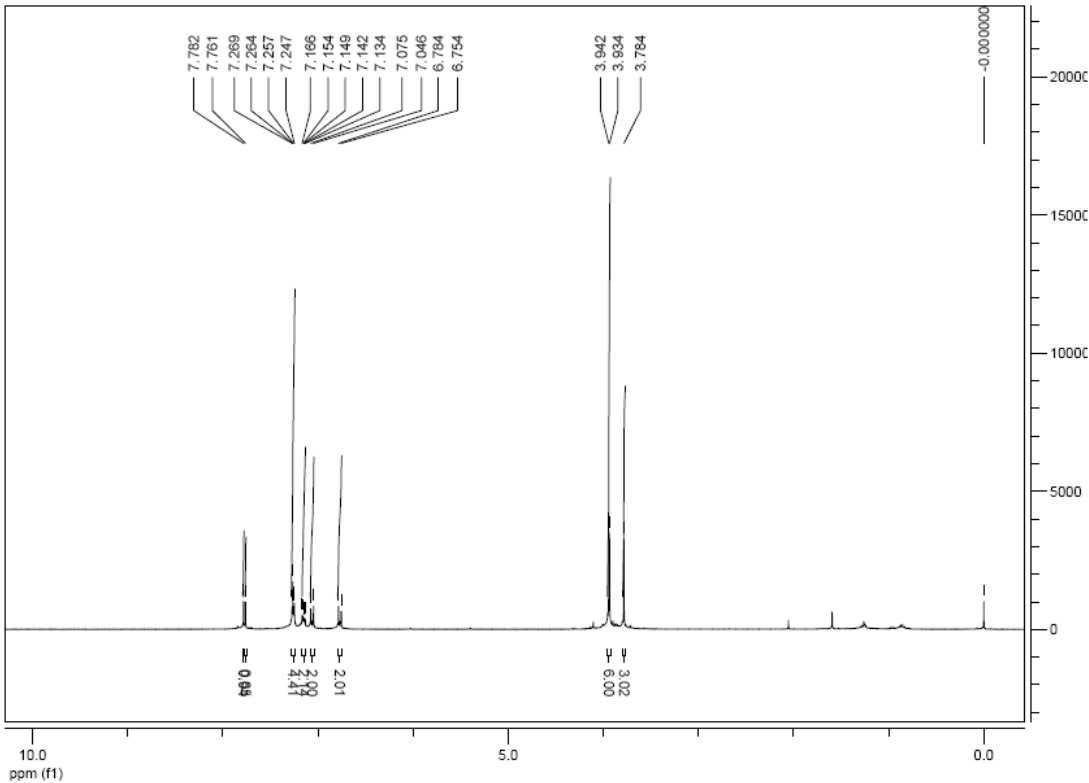


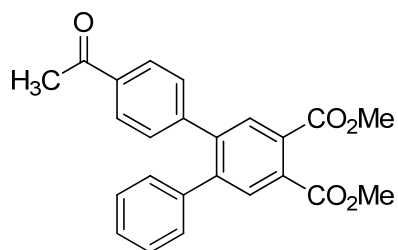
Dimethyl 4,5-di(4'-fluorophenyl)phthalate



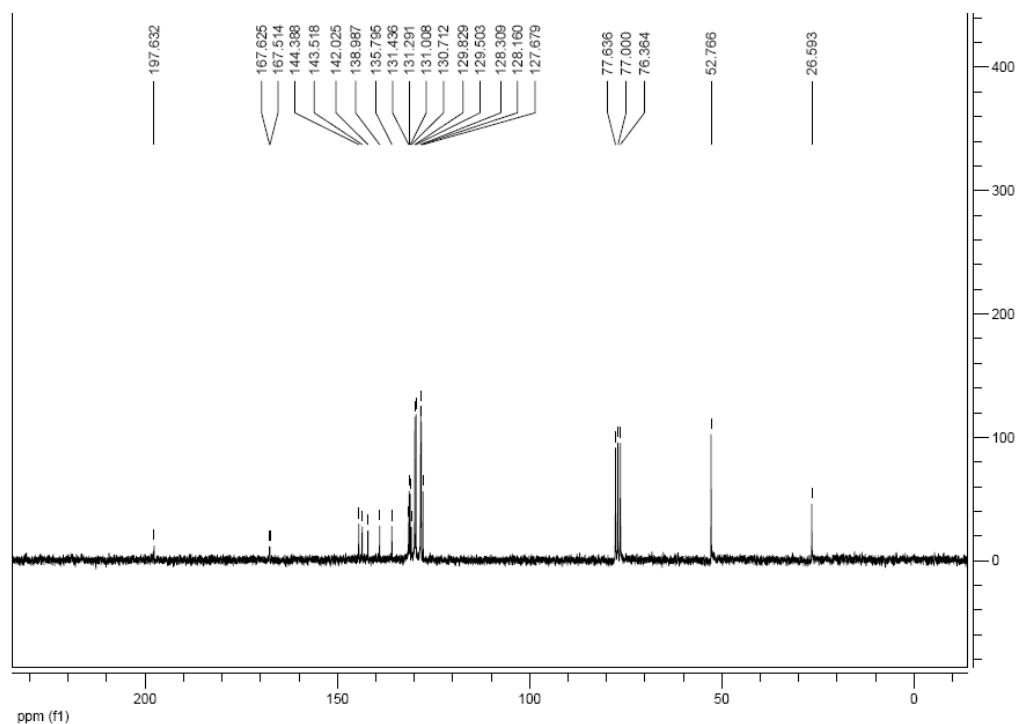
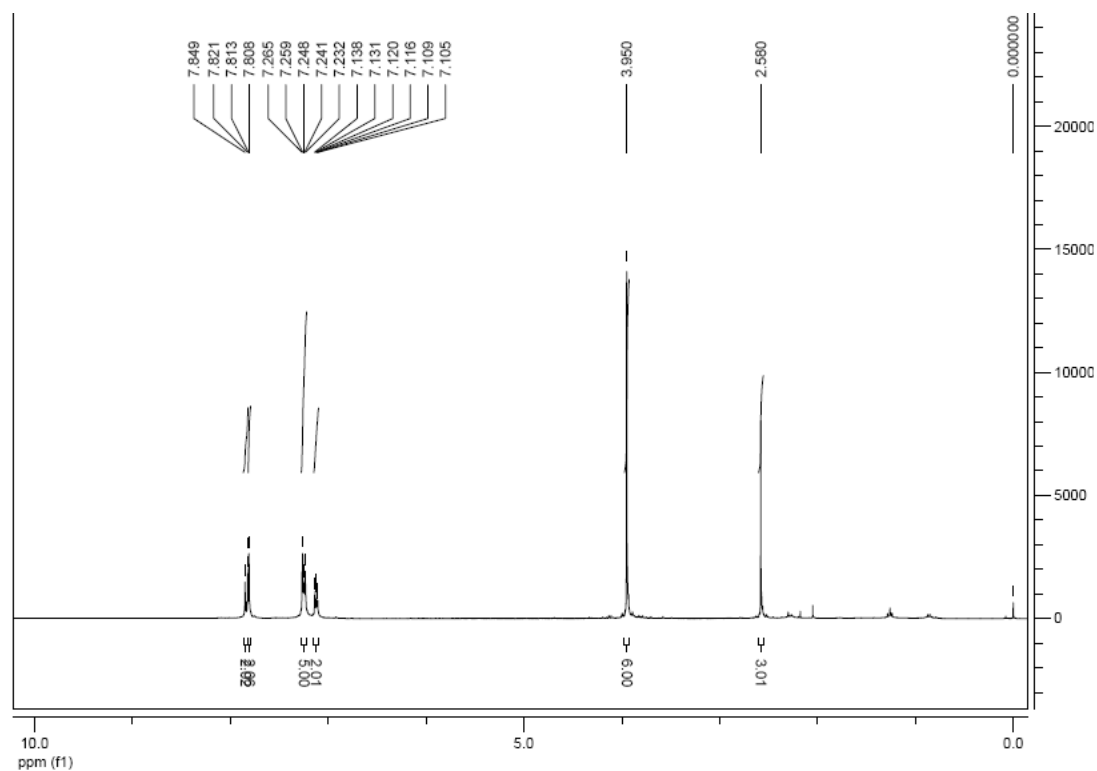


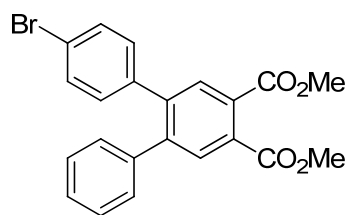
Dimethyl-4-(4'-methoxyphenyl),5-phenylphthalate



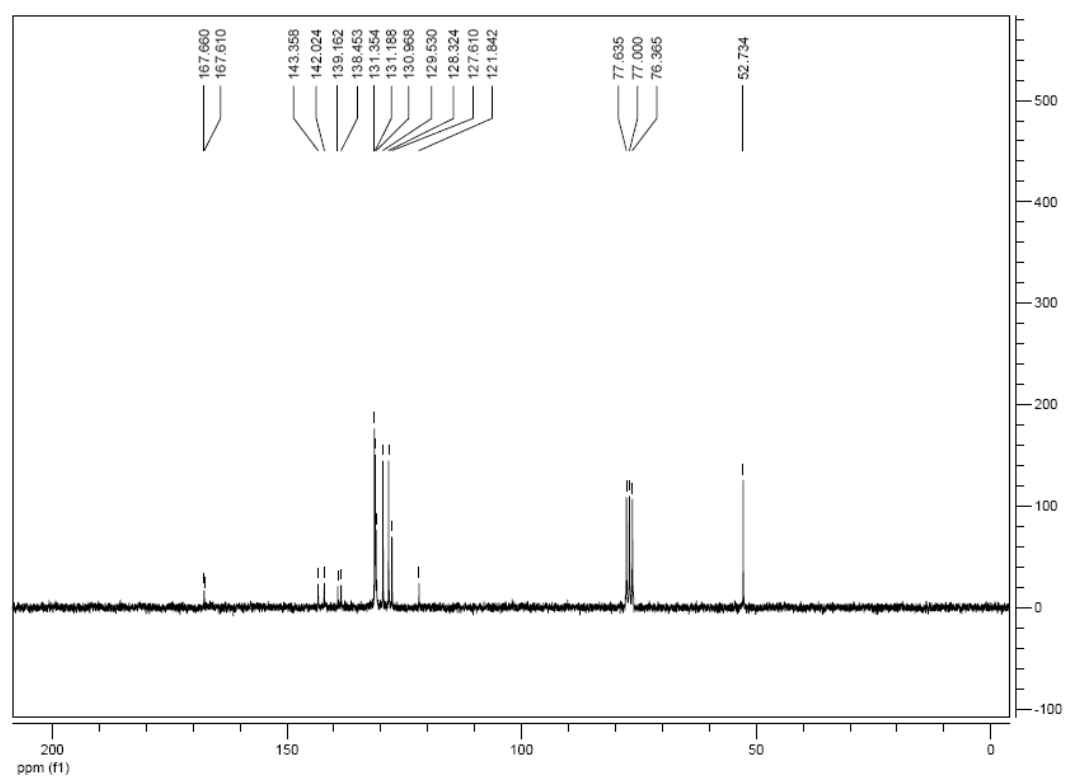
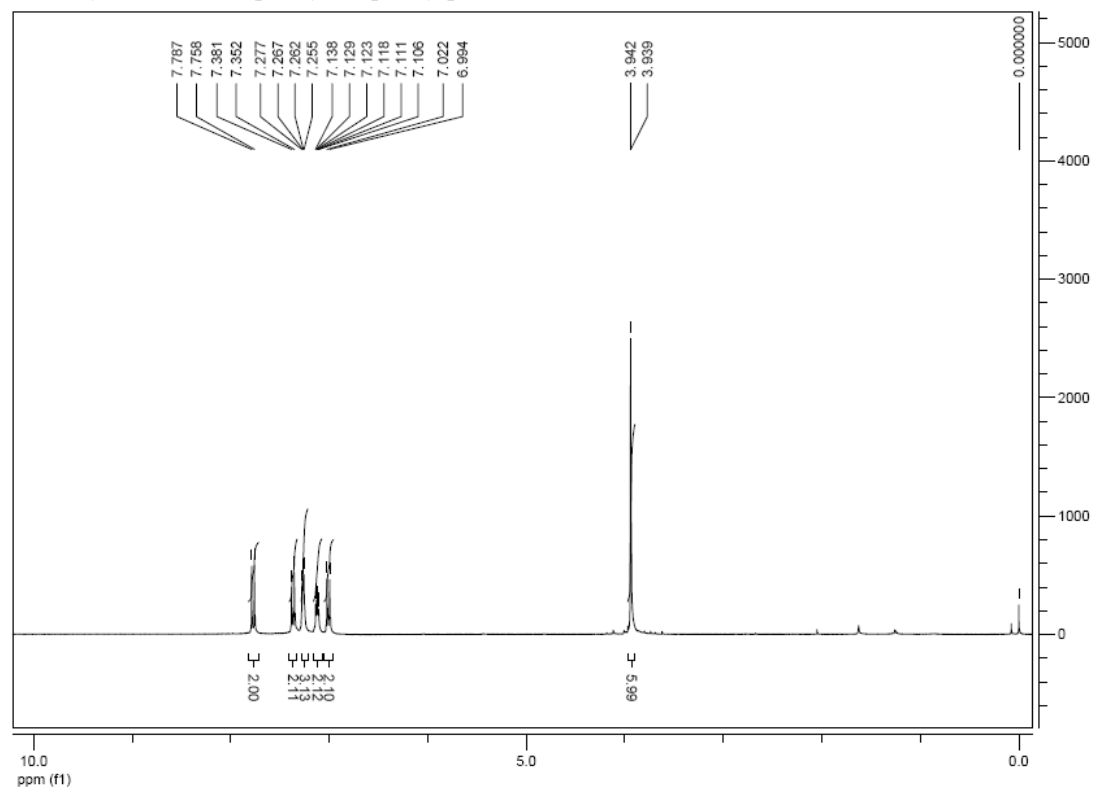


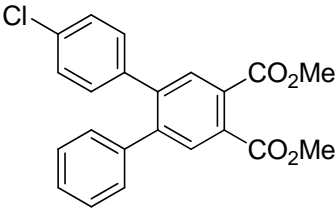
Dimethyl-4-(4'-acetylphenyl),5-phenylphthalate



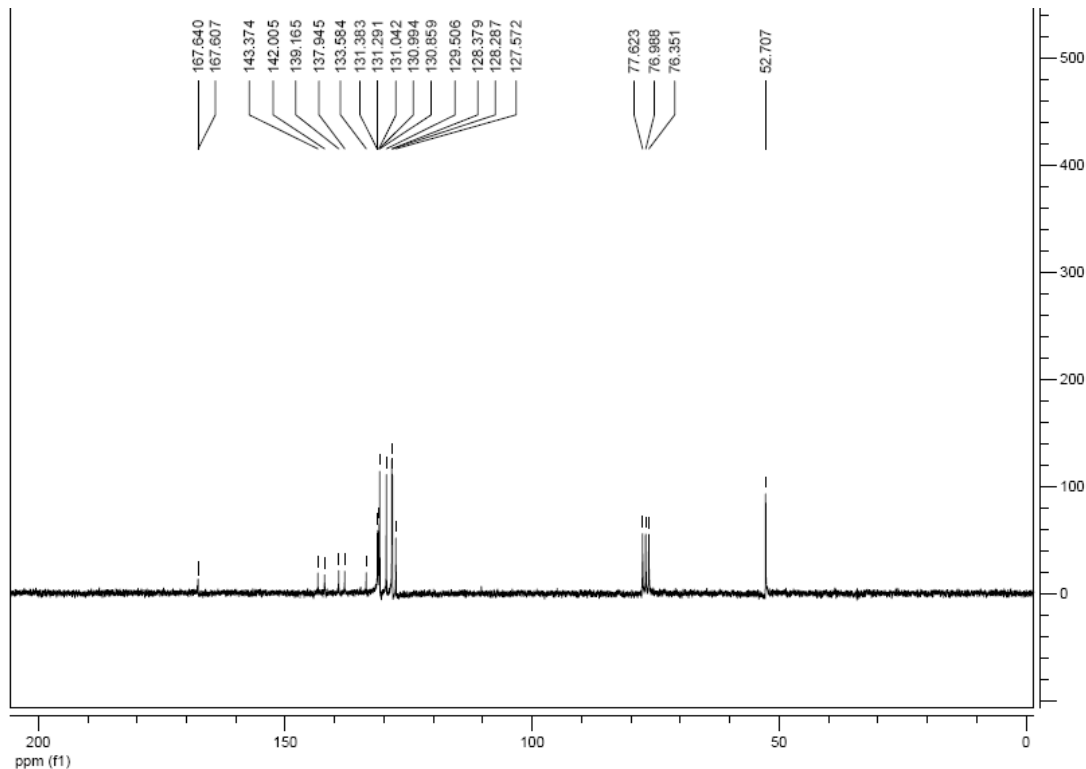
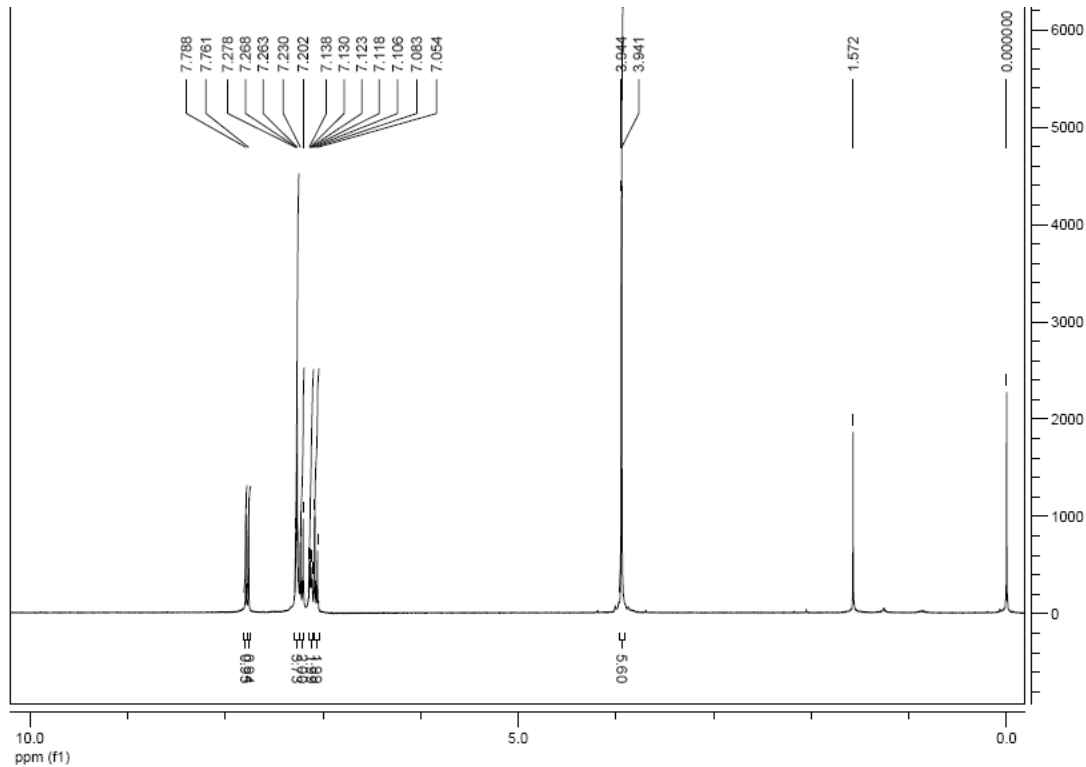


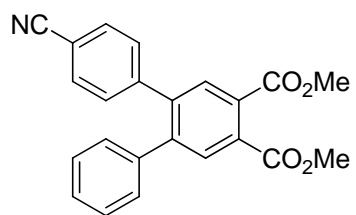
Dimethyl-4-(4'-bromophenyl),5-phenylphthalate



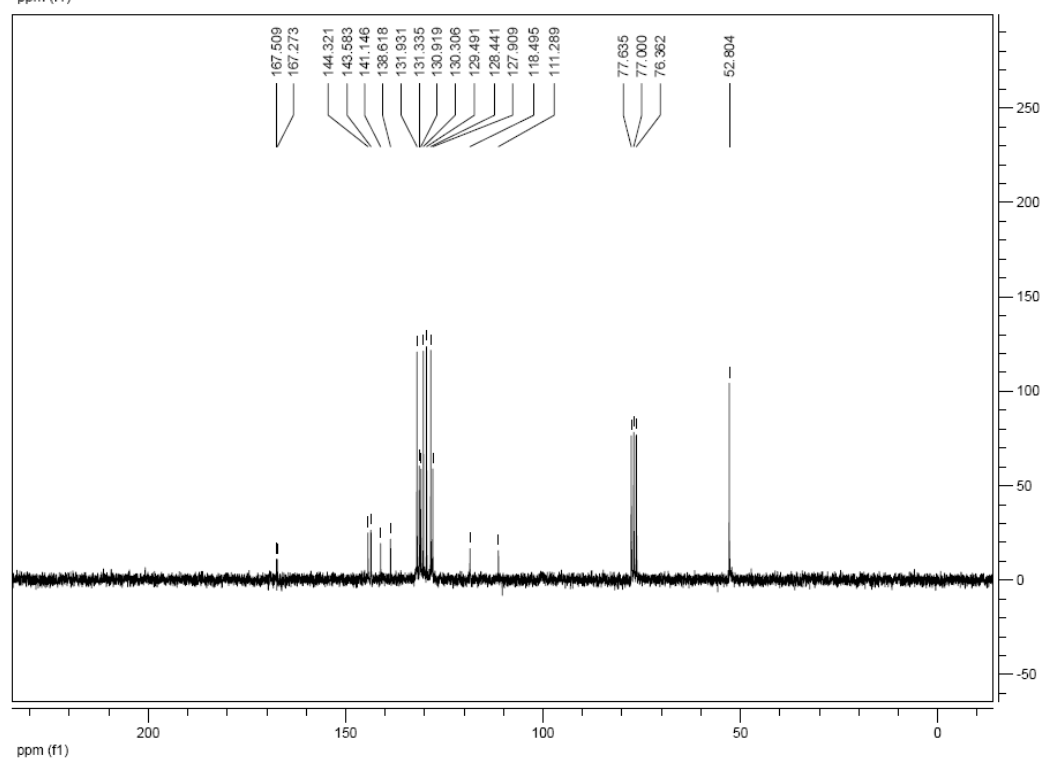
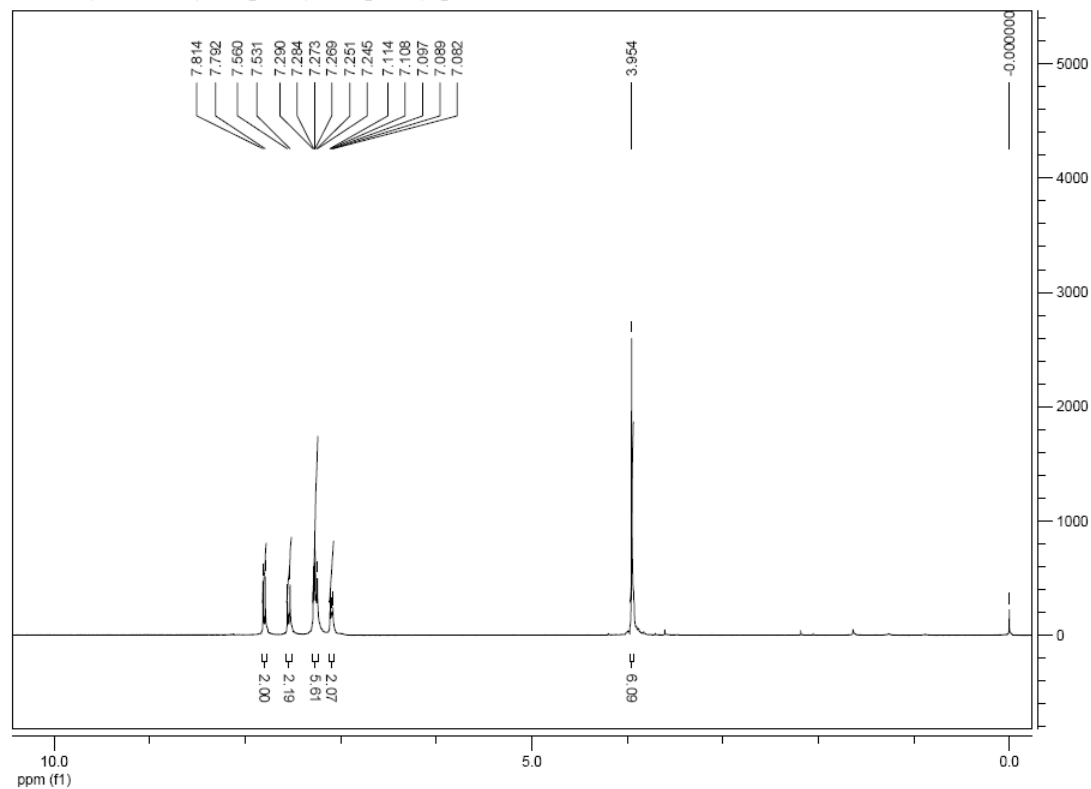


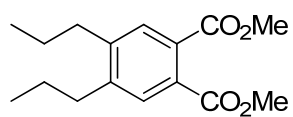
Dimethyl-4-(4'-chlorophenyl),5-phenylphthalate



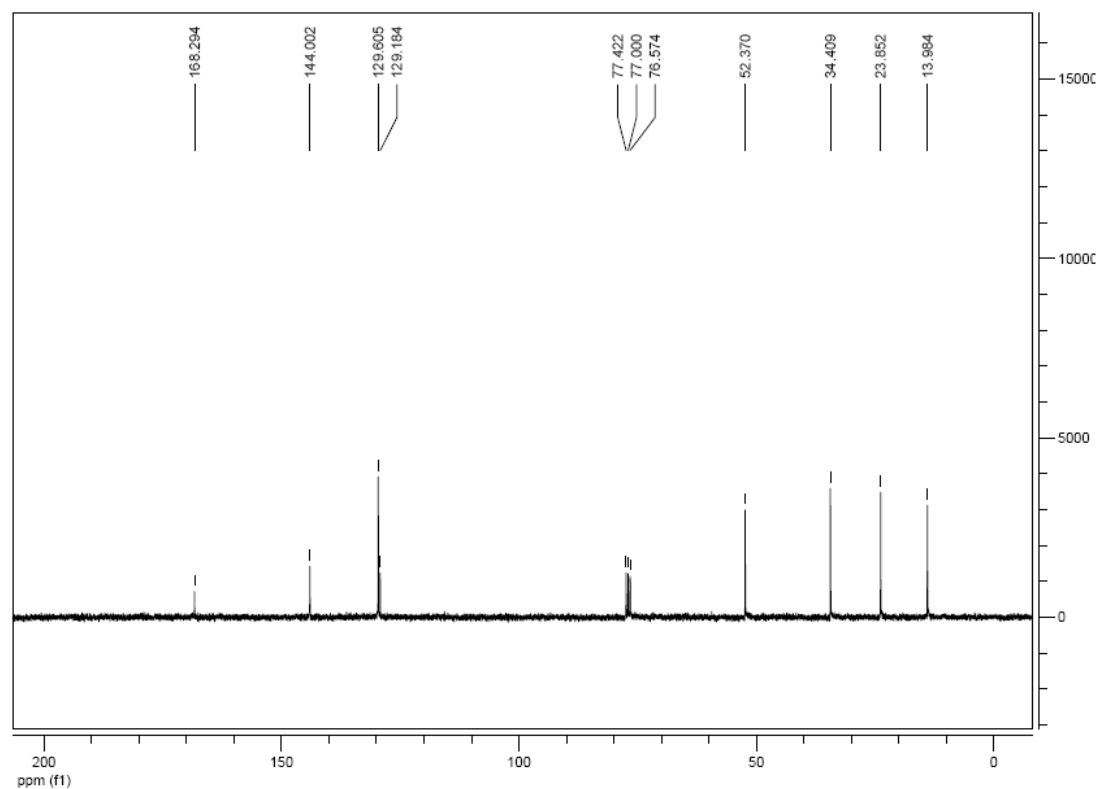
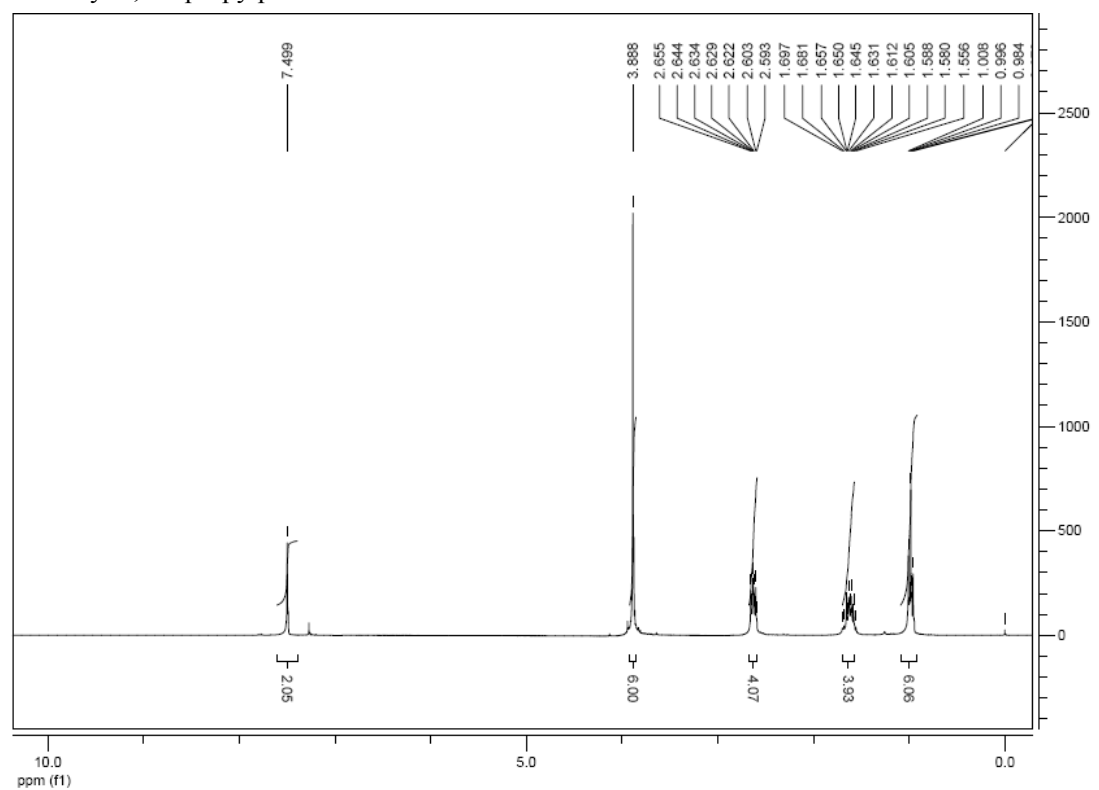


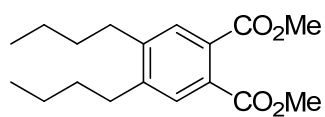
Dimethyl-4-(4'-cyanophenyl),5-phenylphthalate



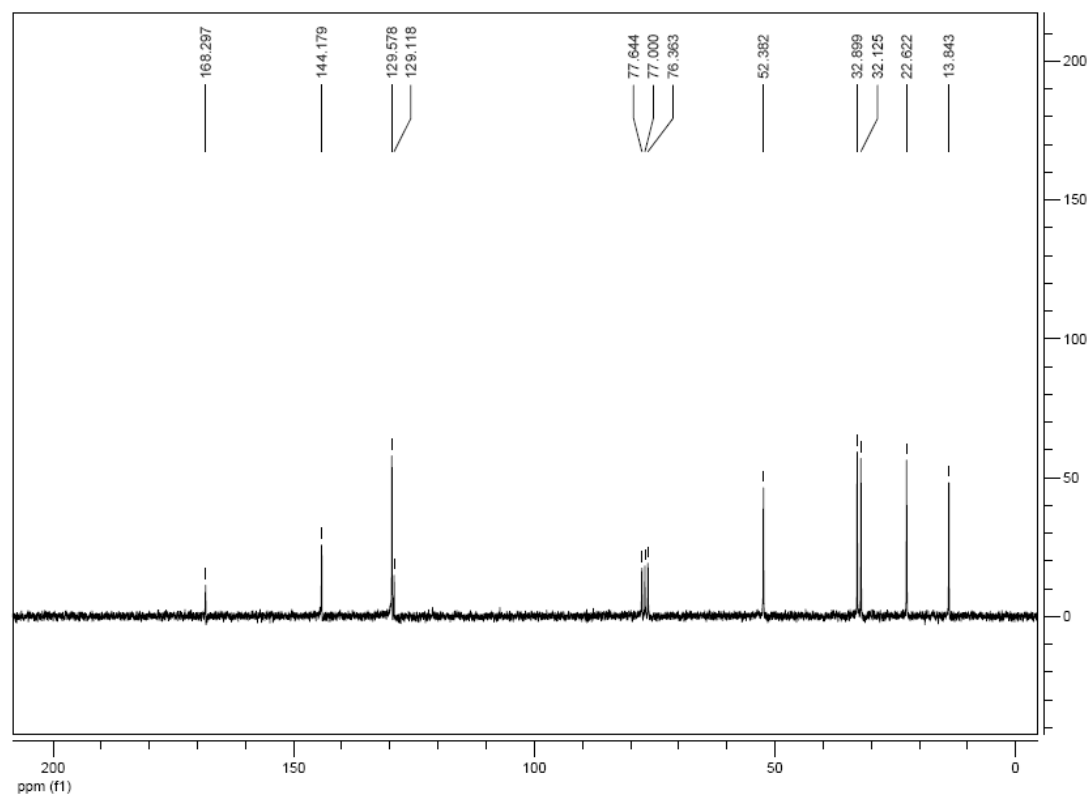
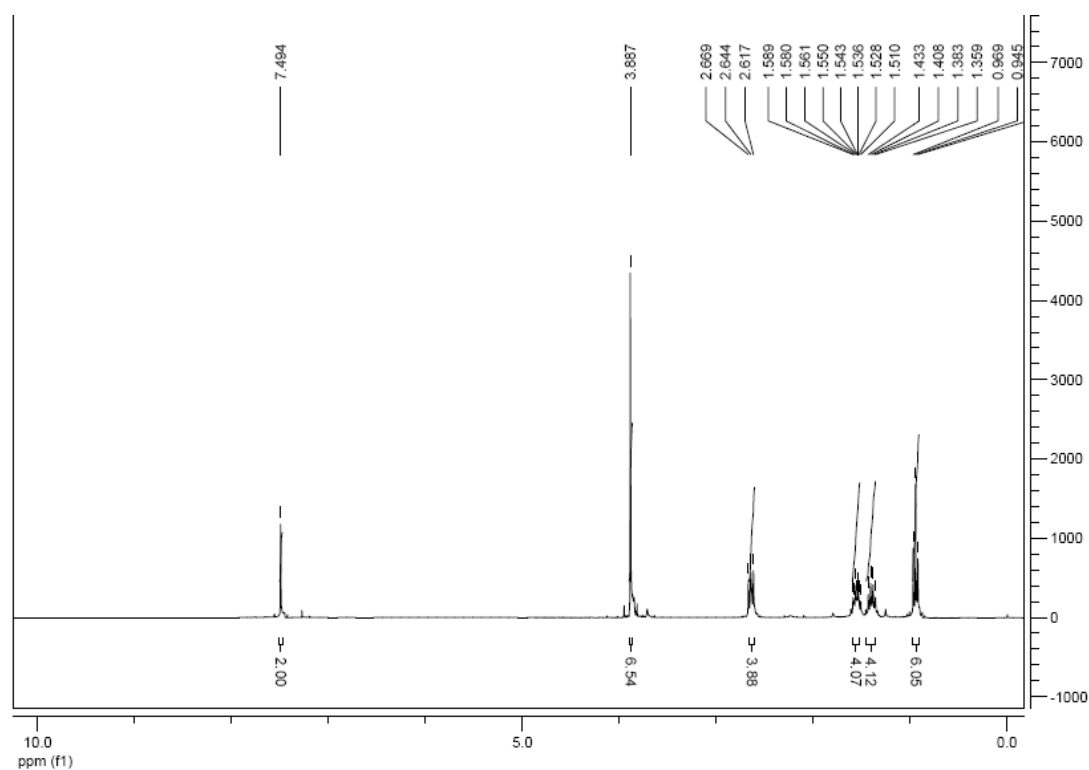


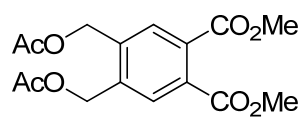
Dimethyl 4,5-dipropylphthalate



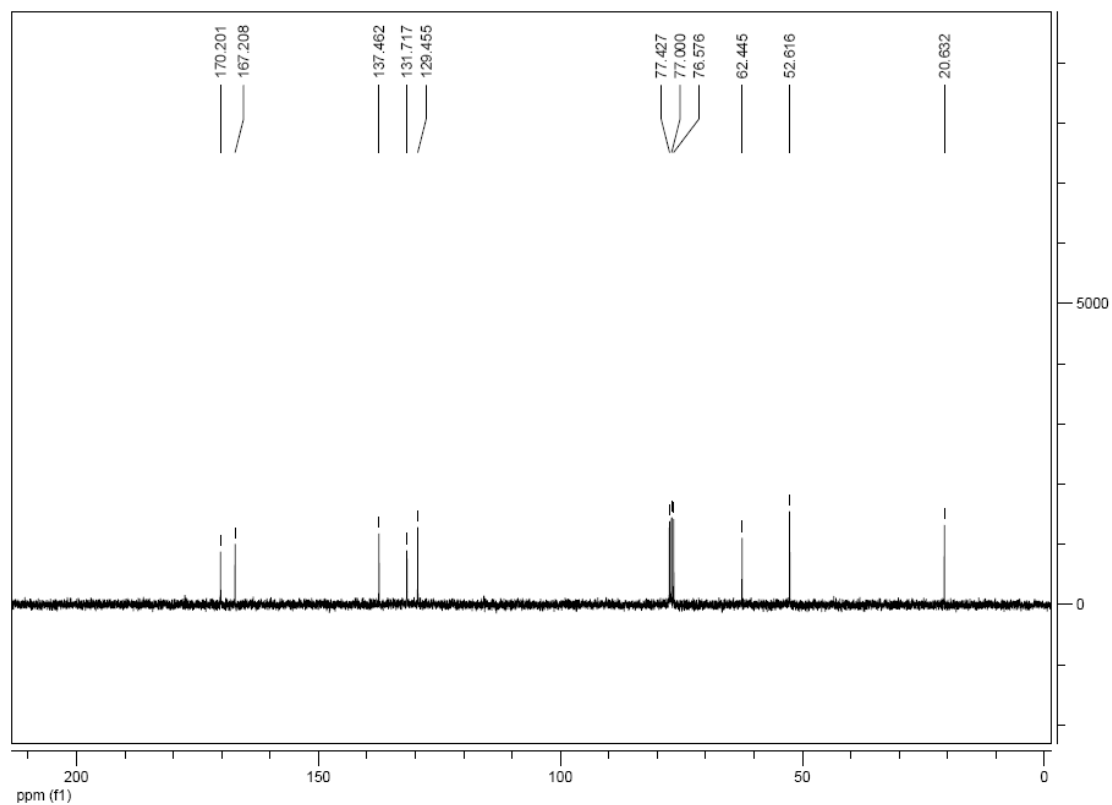
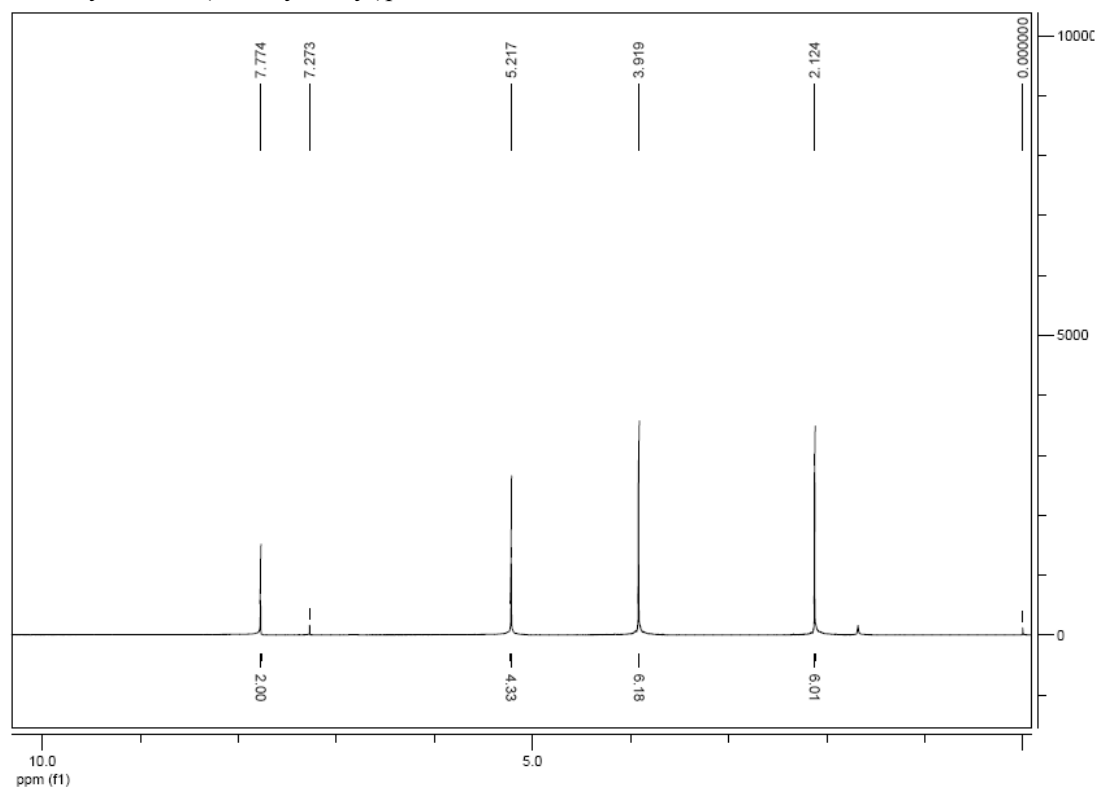


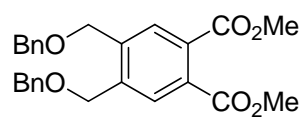
Dimethyl 4, 5-di(n-butyl)phthalate



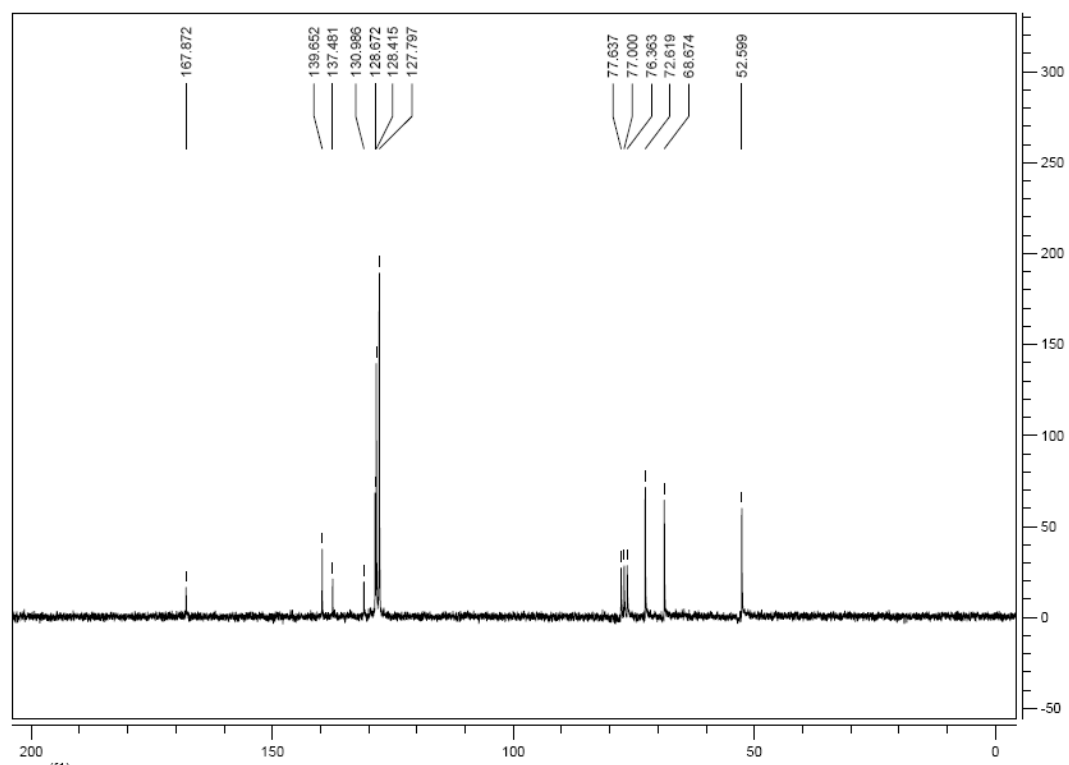
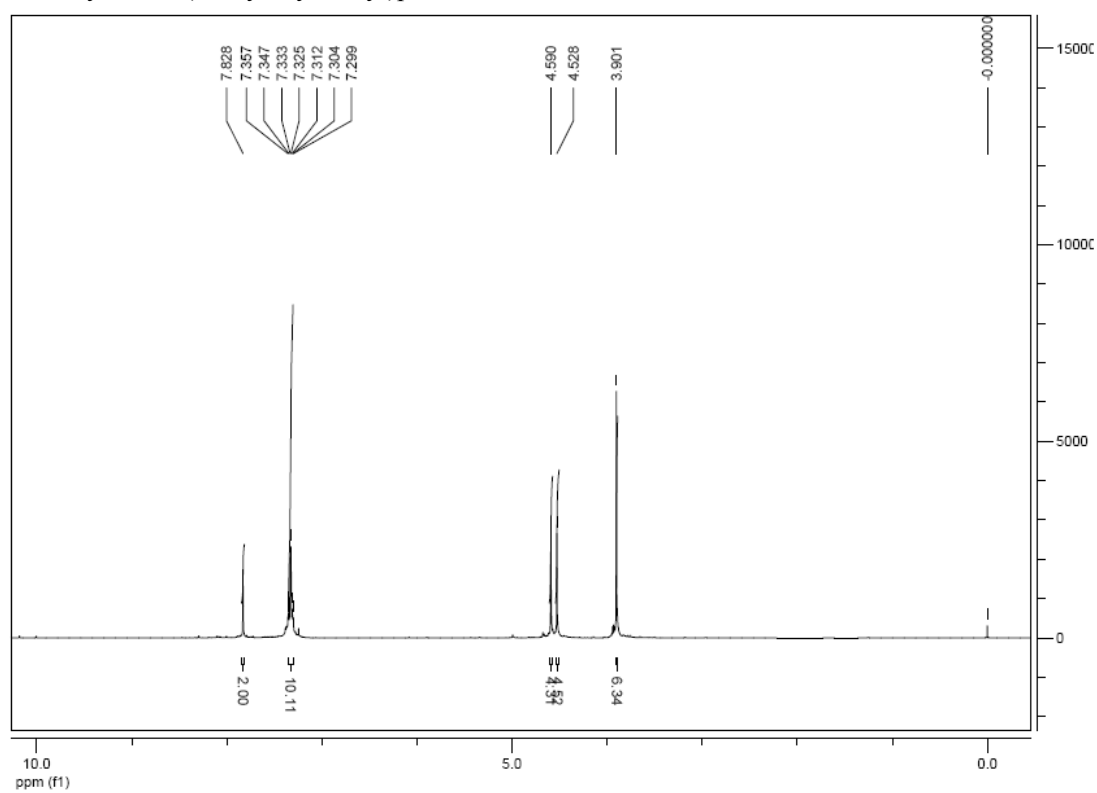


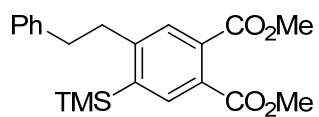
Dimethyl 4, 5-bis(acetoxymethyl)phthalate



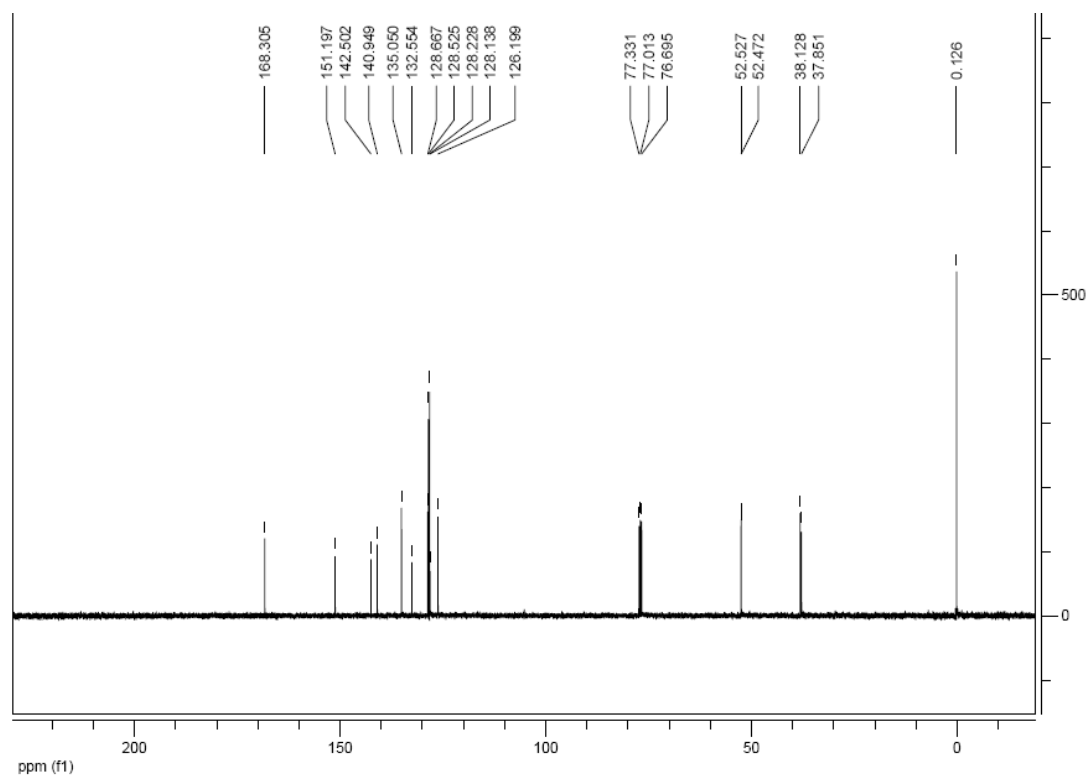
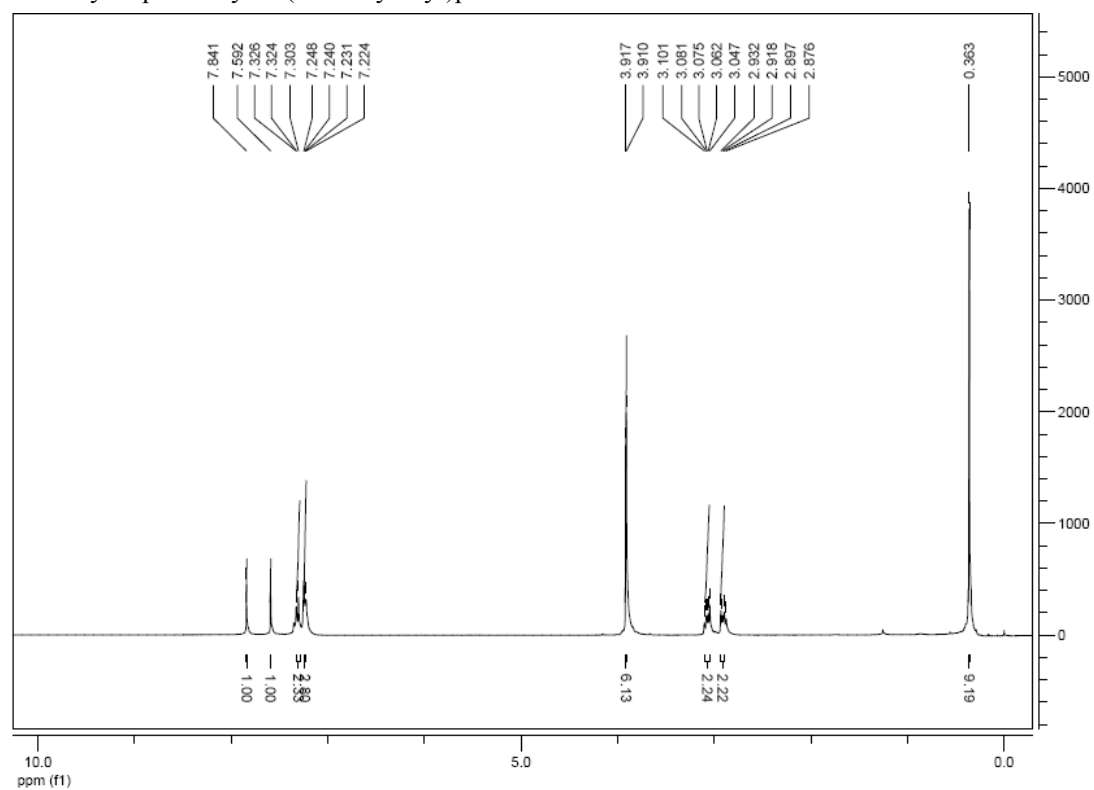


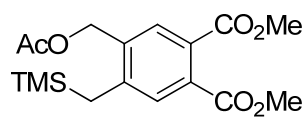
Dimethyl-4,5-di(benzyloxymethyl)phthalate



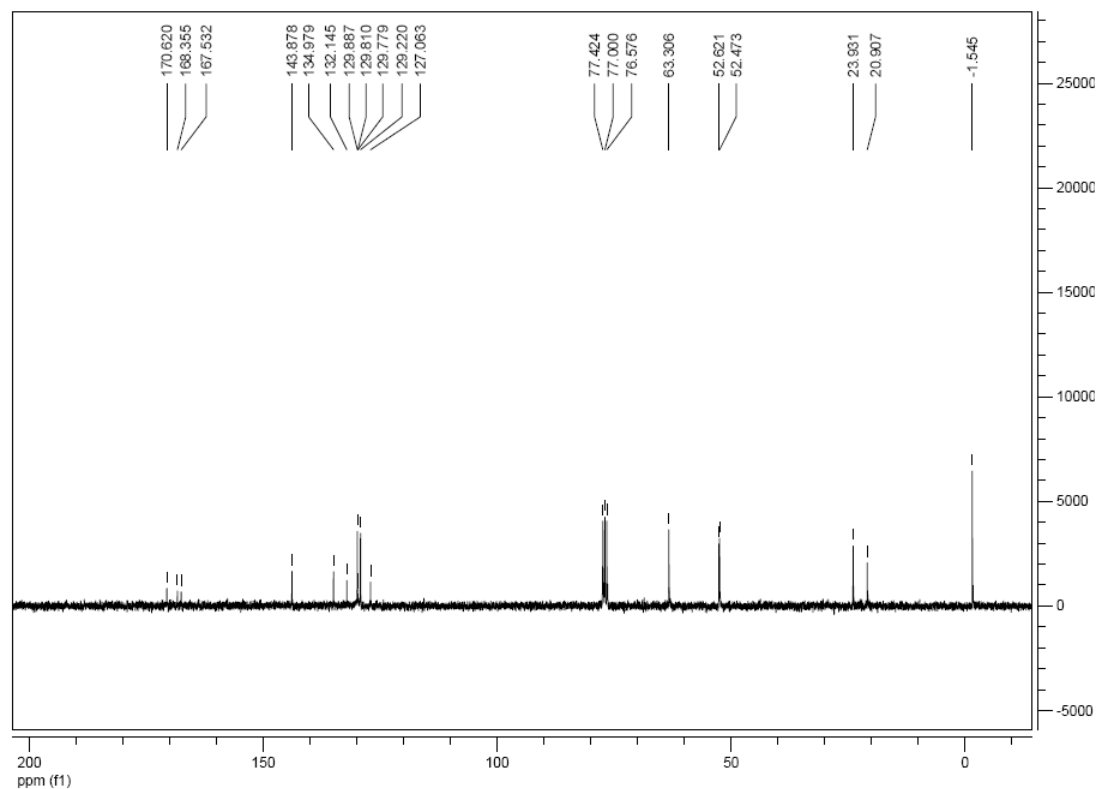
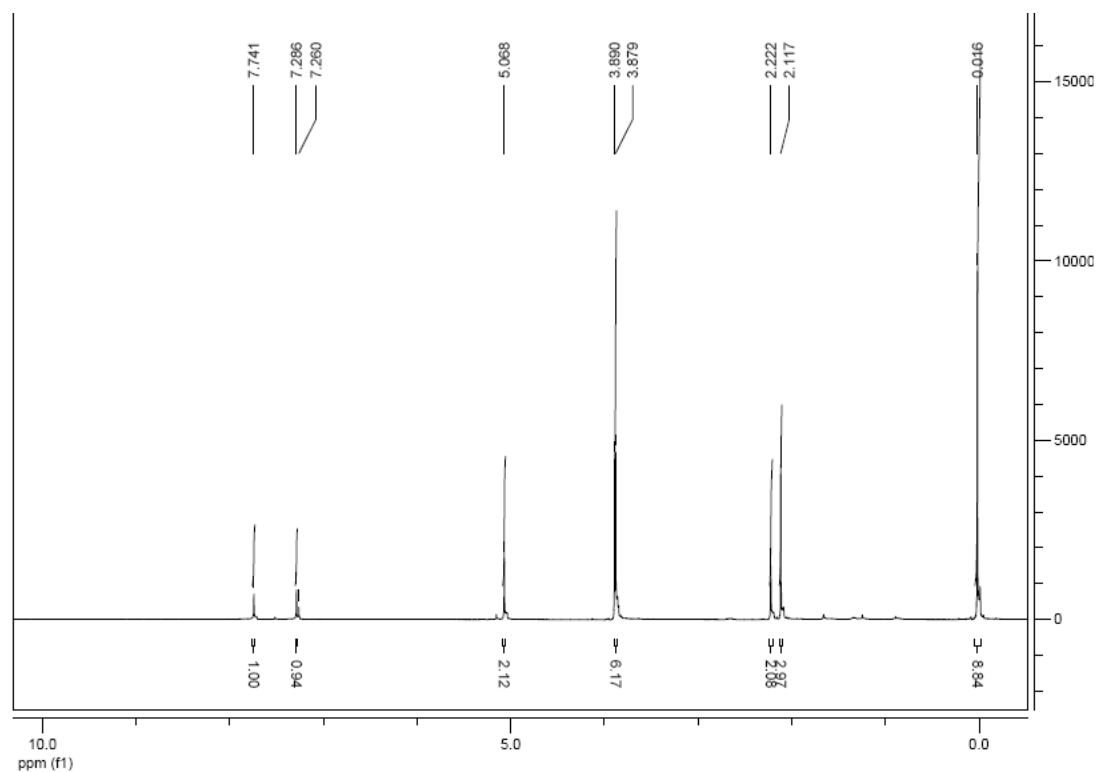


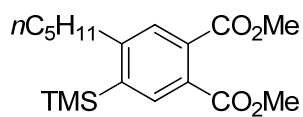
Dimethyl 4-phenethyl-5-(trimethylsilyl)phthalate



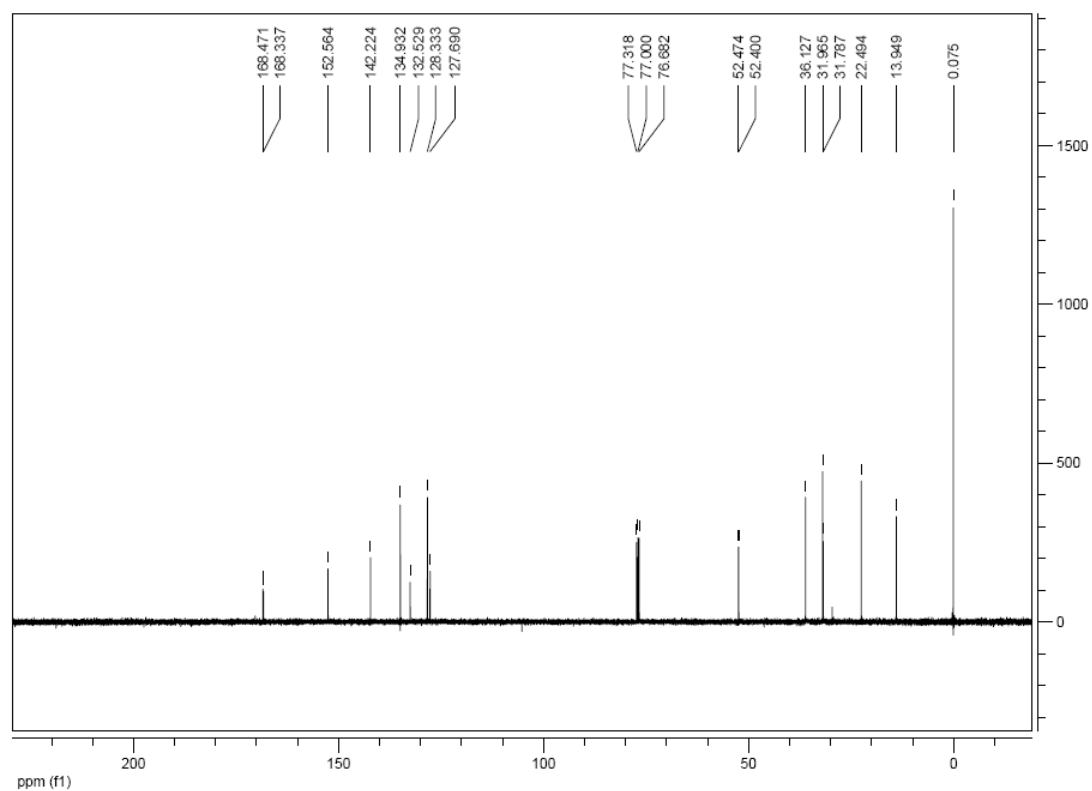
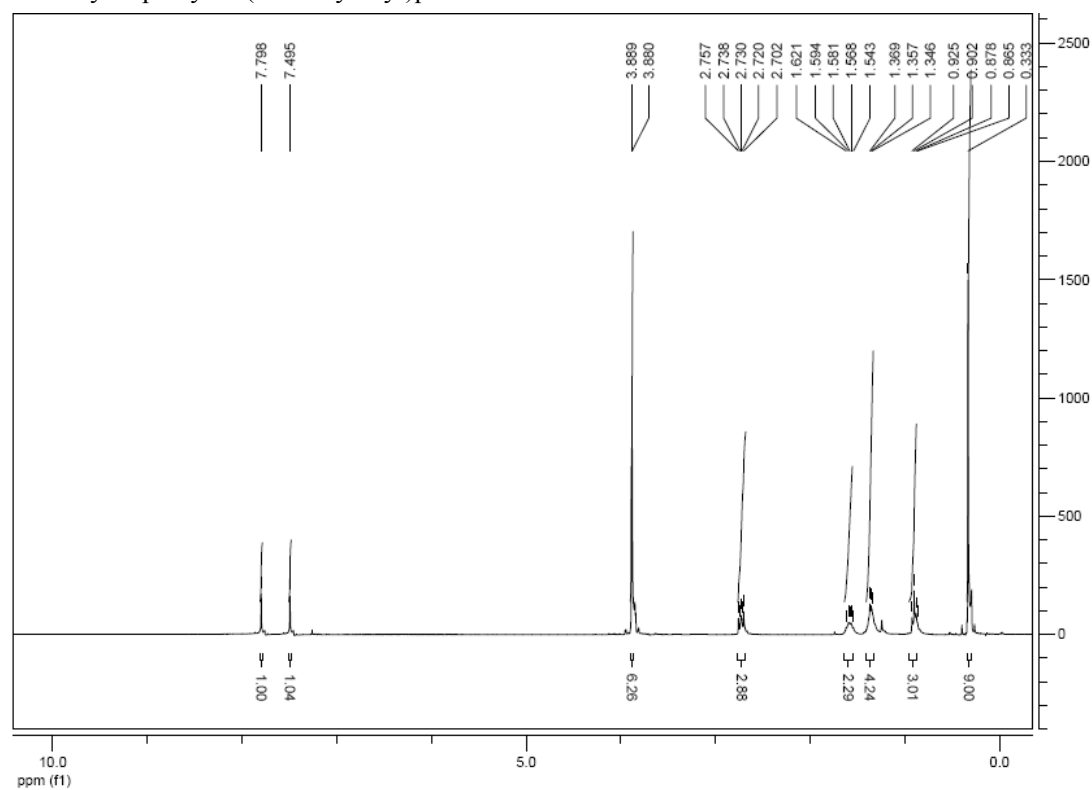


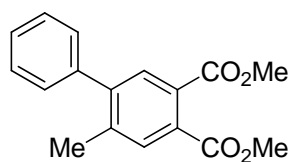
Dimethyl 4-(acetoxymethyl)-5-((trimethylsilyl)methyl)phthalate



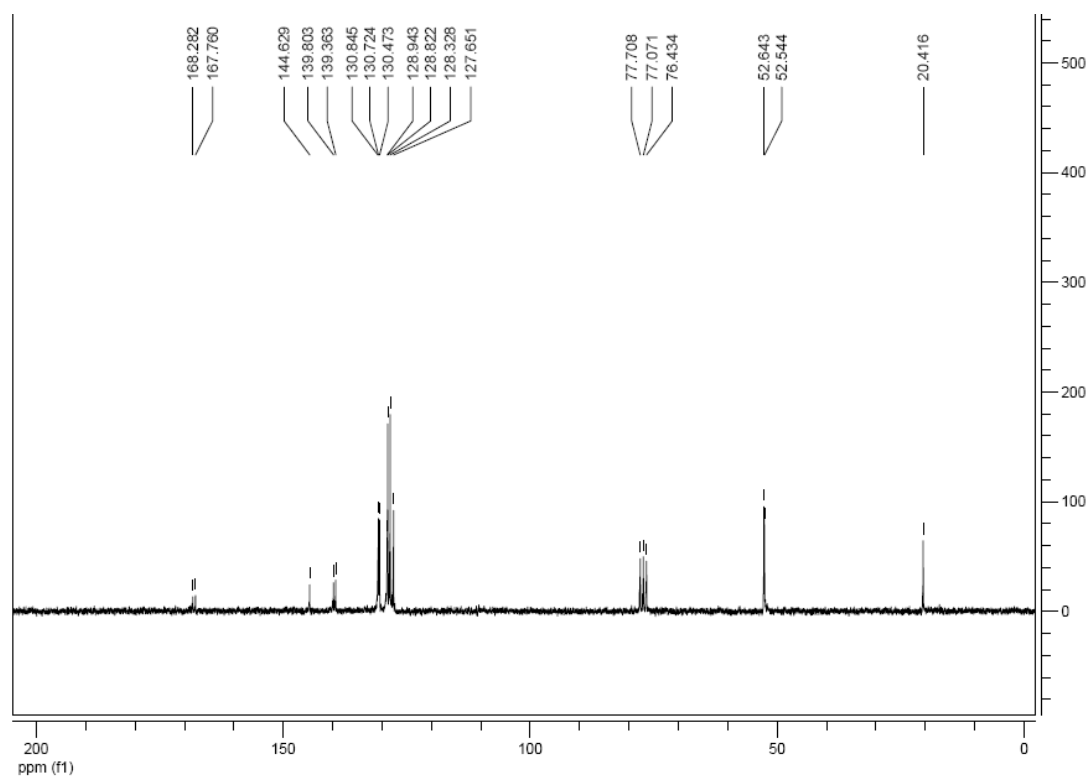
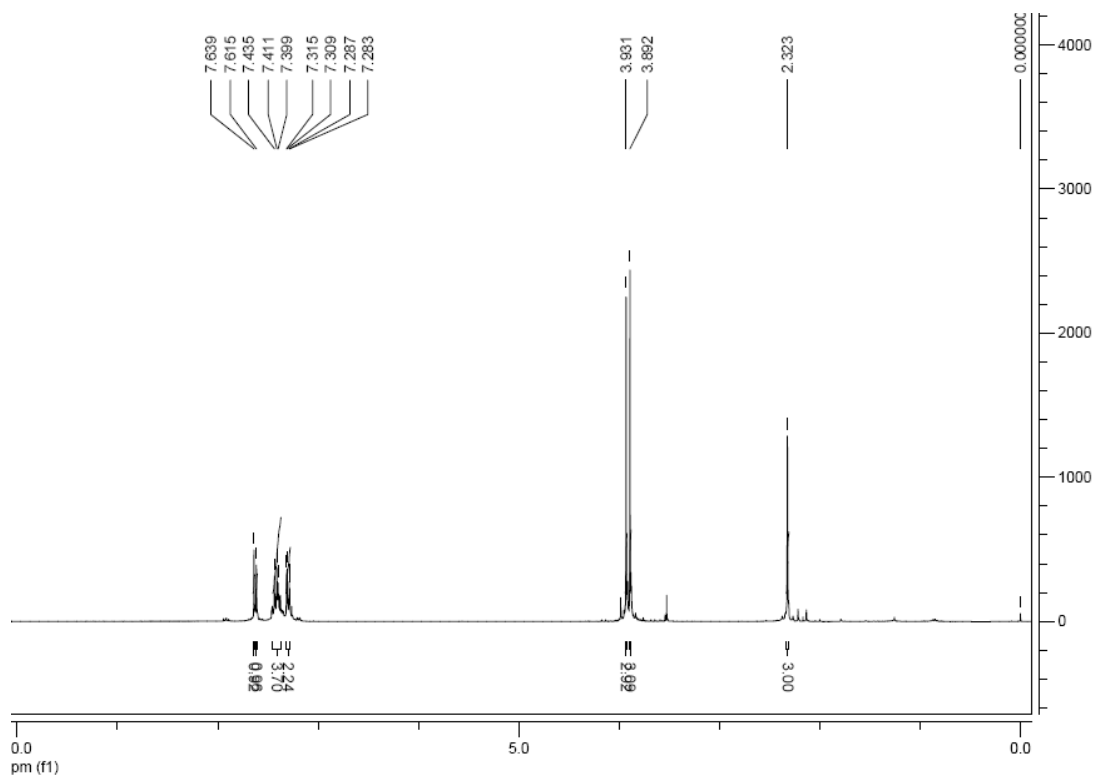


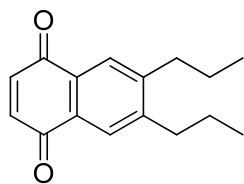
Dimethyl 4-pentyl-5-(trimethylsilyl)phthalate



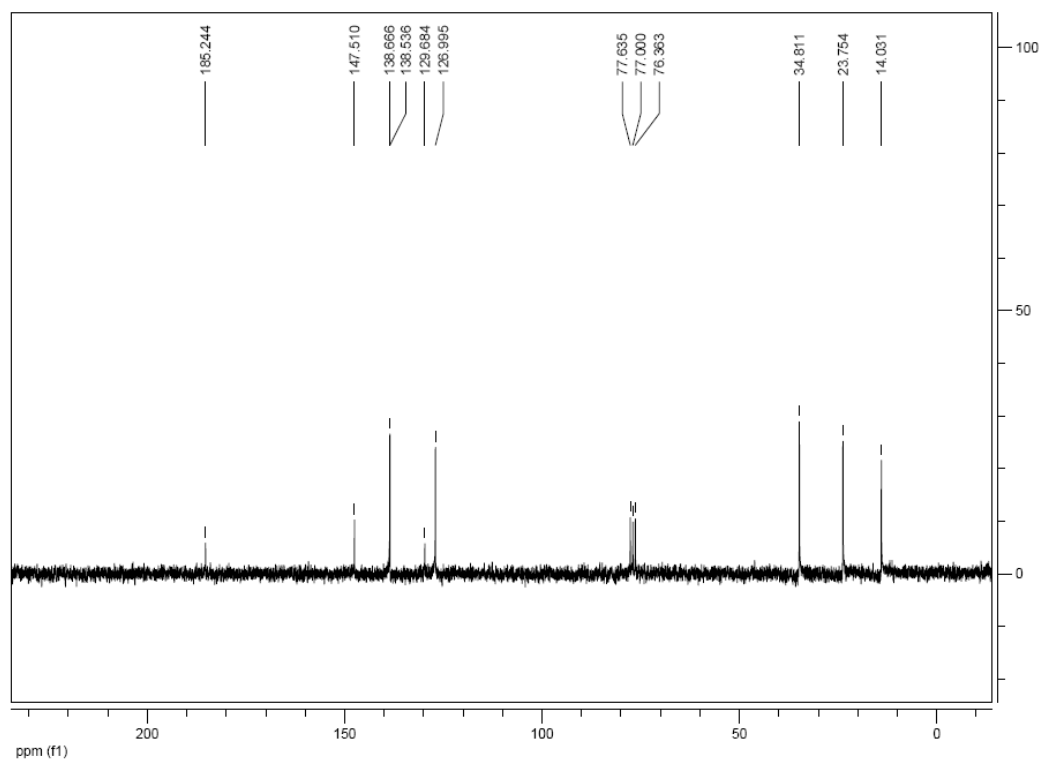
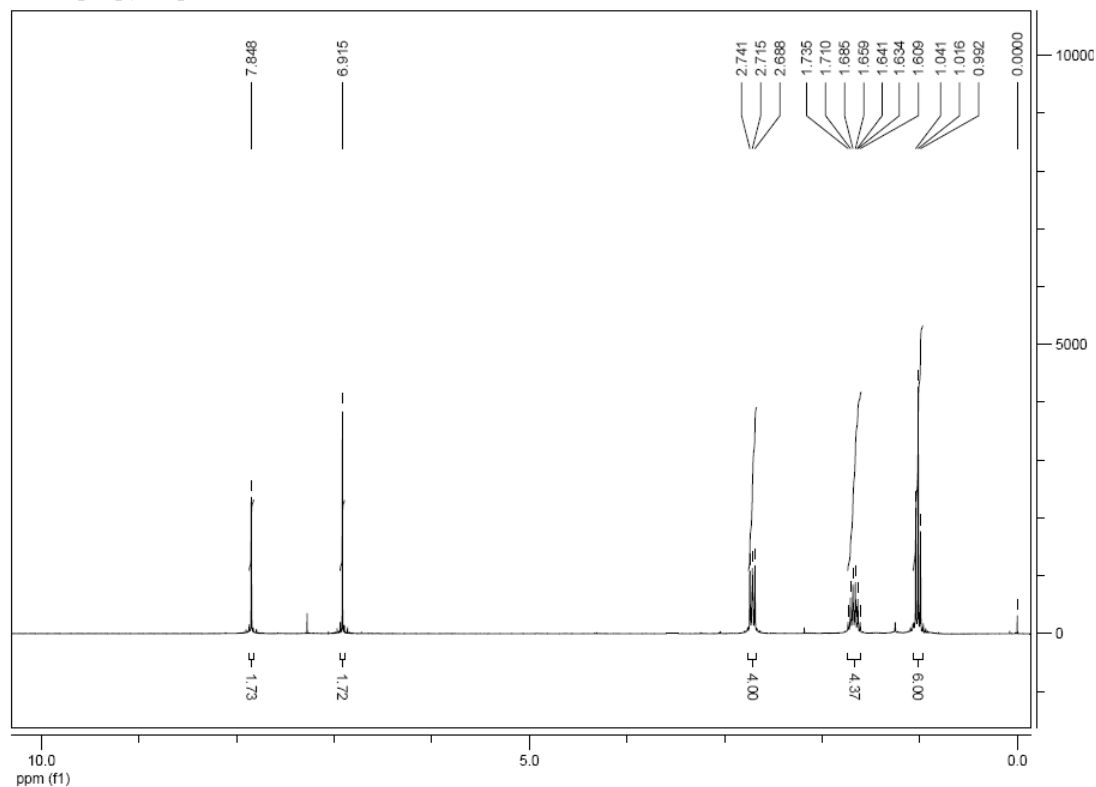


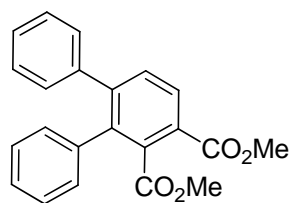
Dimethyl 5-methyl-4-phenylphthalate



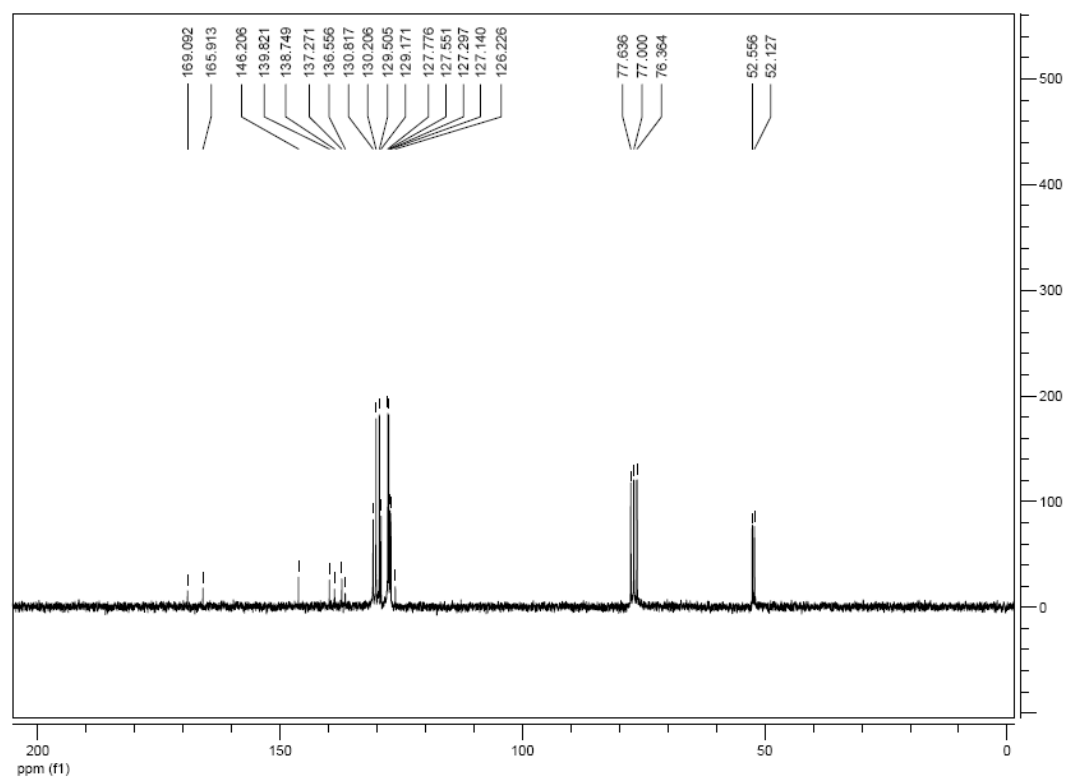
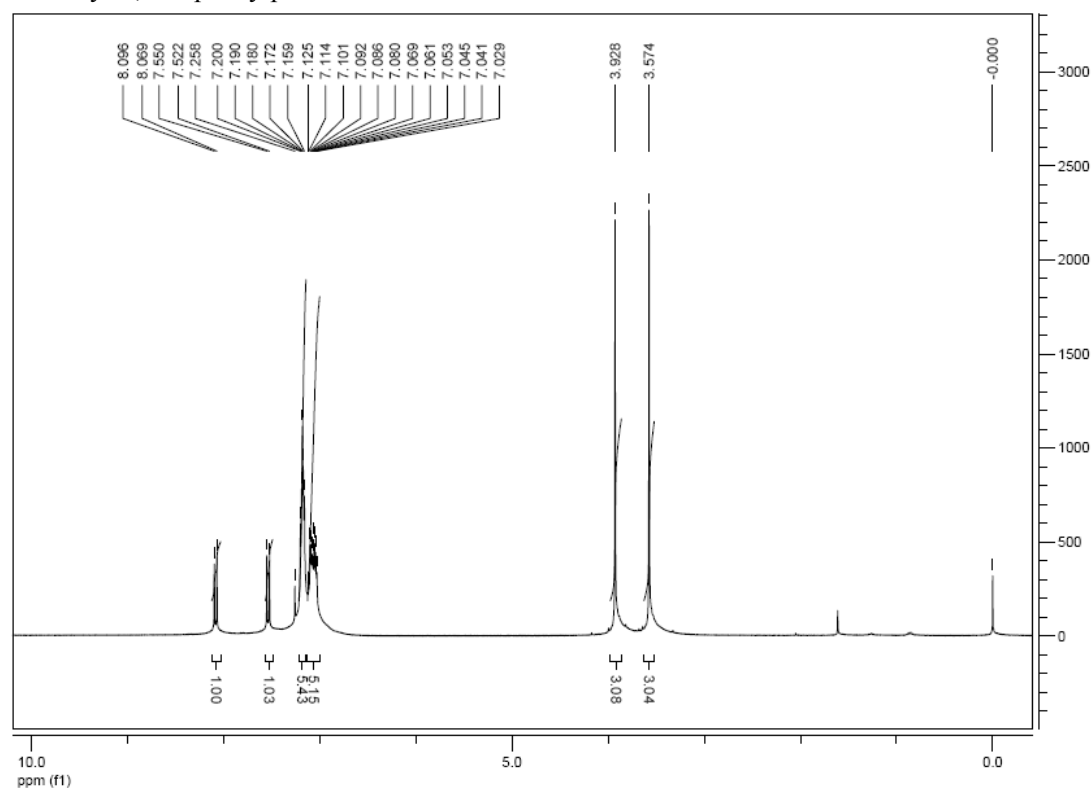


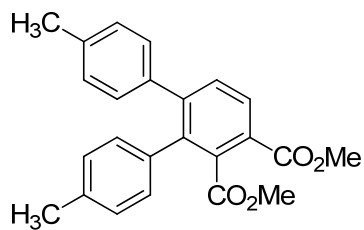
6, 7-dipropylnaphthalene-1,4-dione



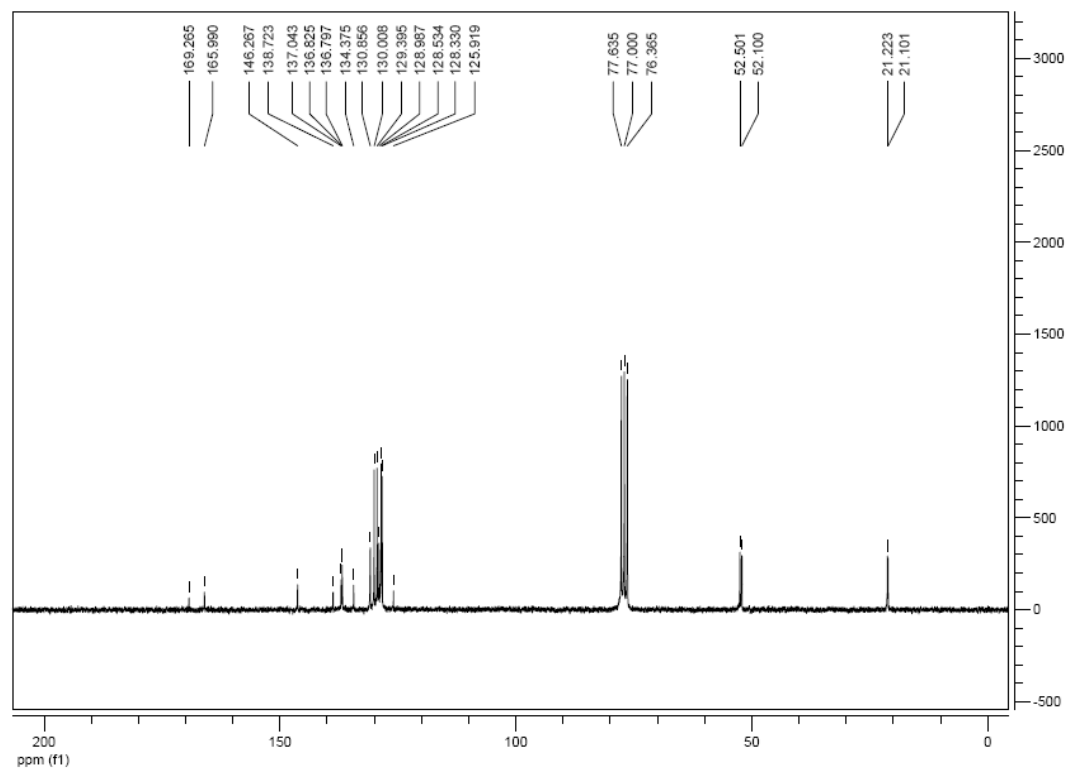
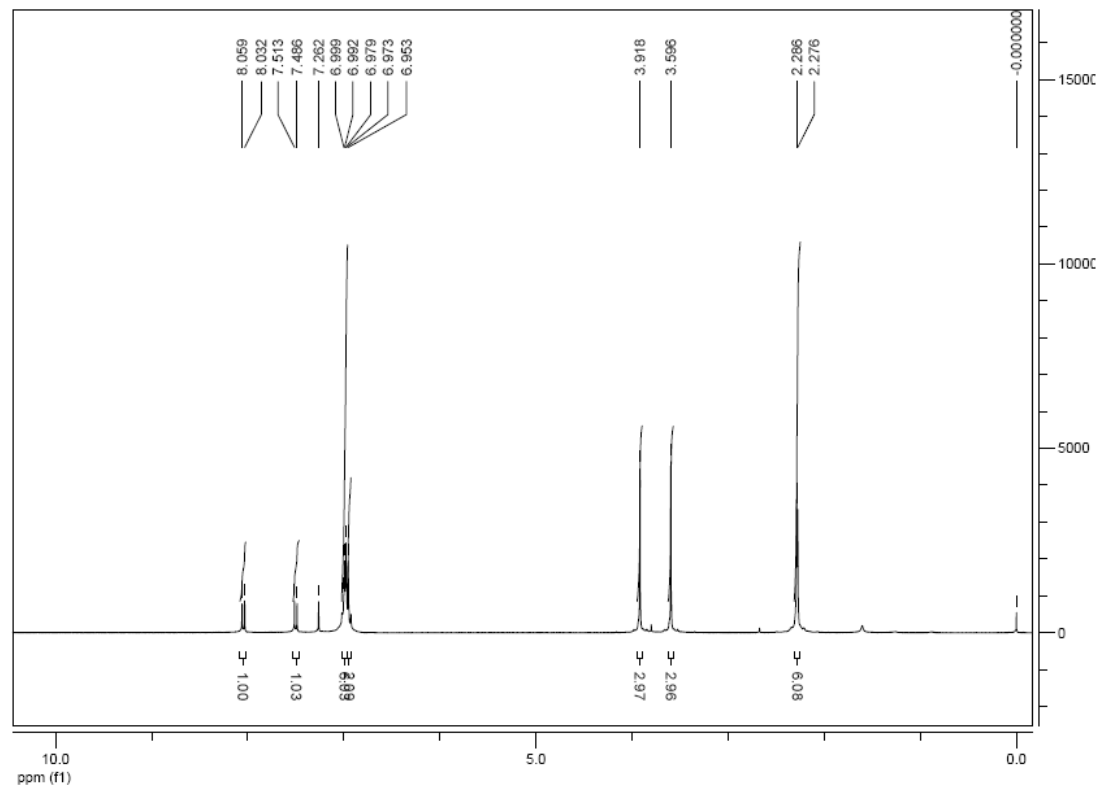


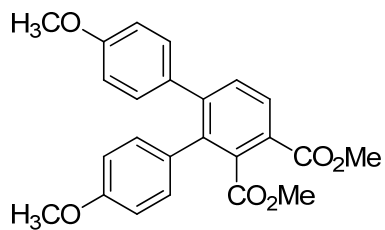
Dimethyl-3, 4-diphenylphthalate



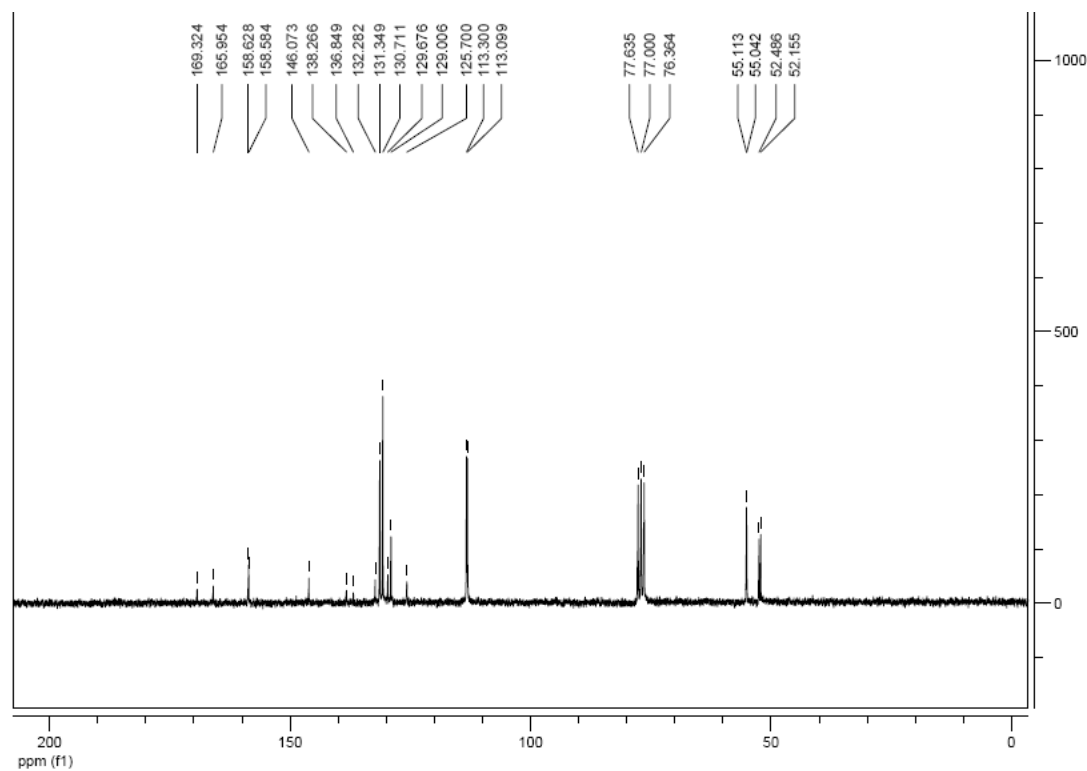
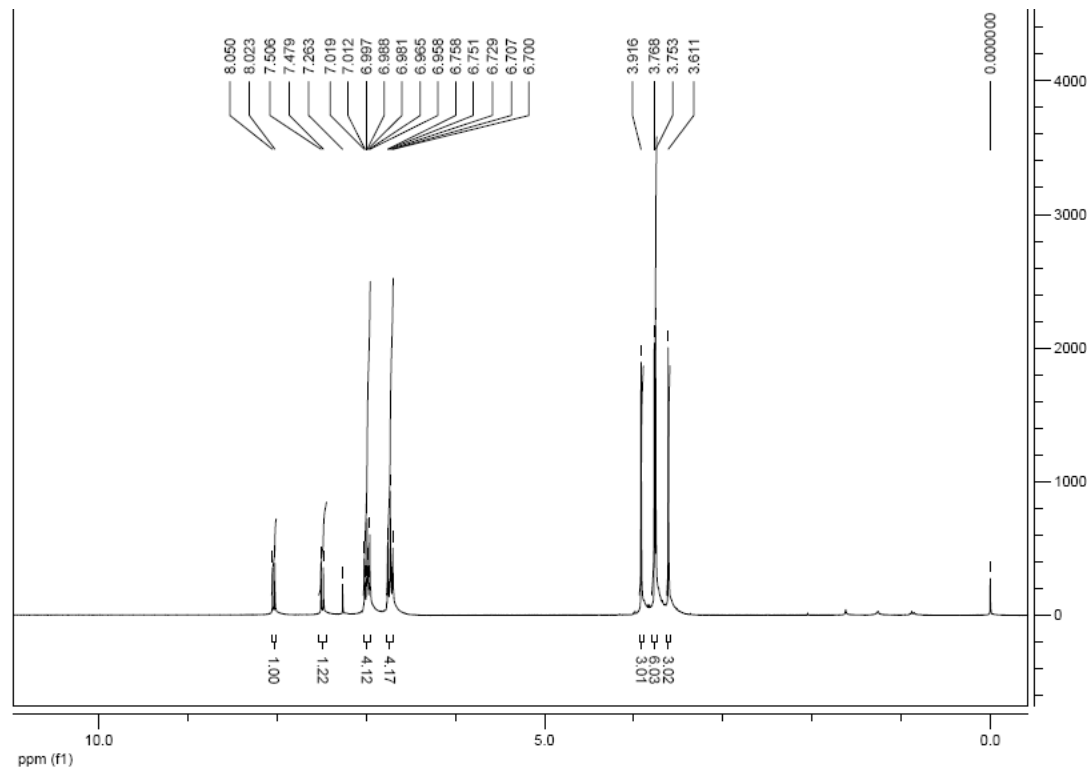


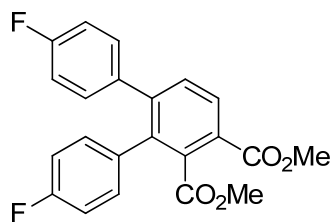
Dimethyl 3,4-di(4'-methylphenyl)phthalate



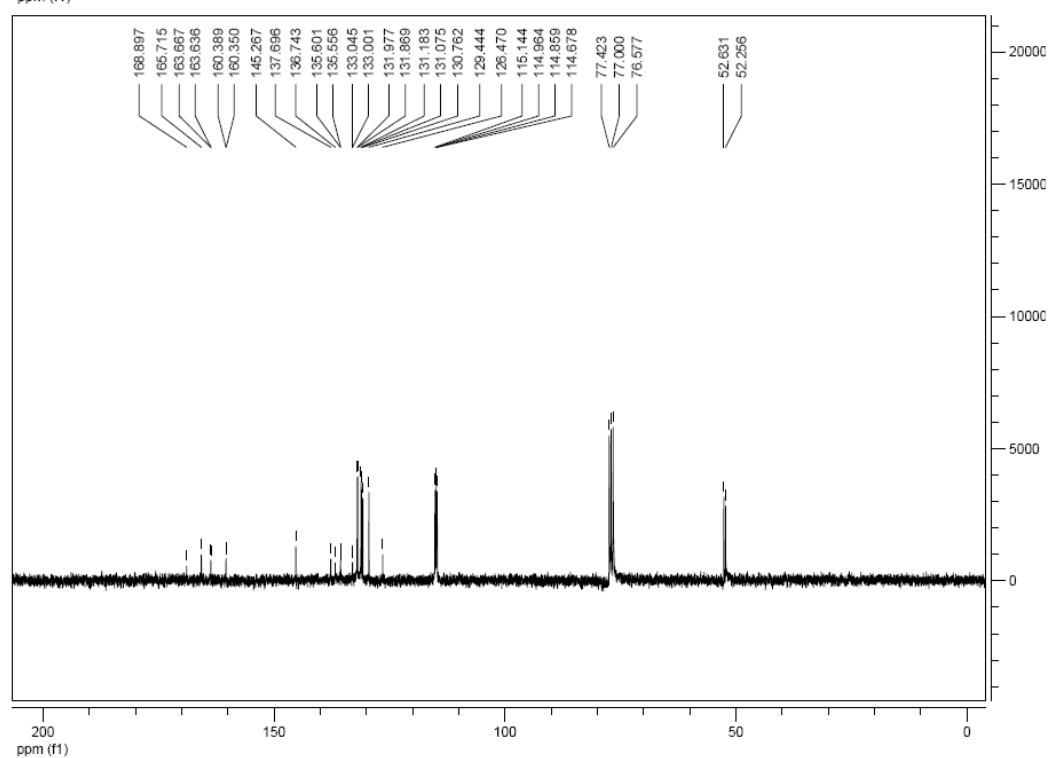
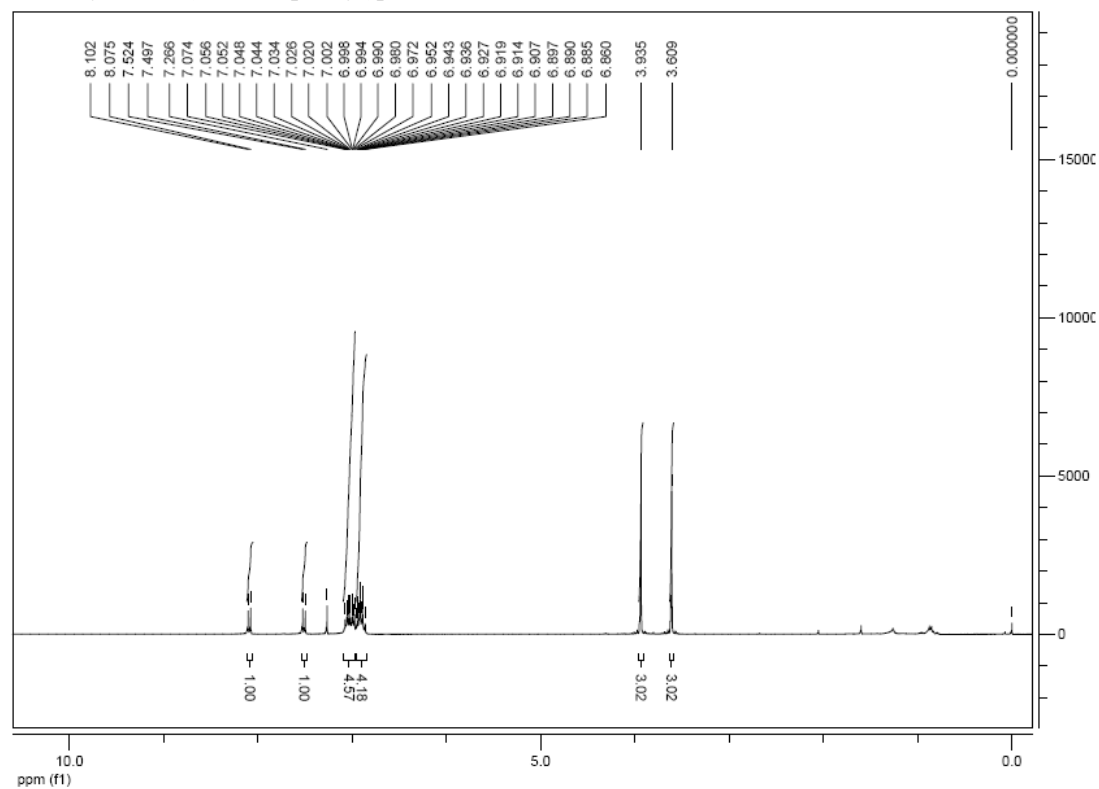


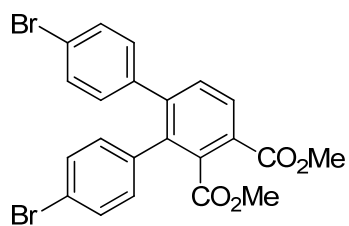
Dimethyl 3,4-di(4'-methoxyphenyl)phthalate



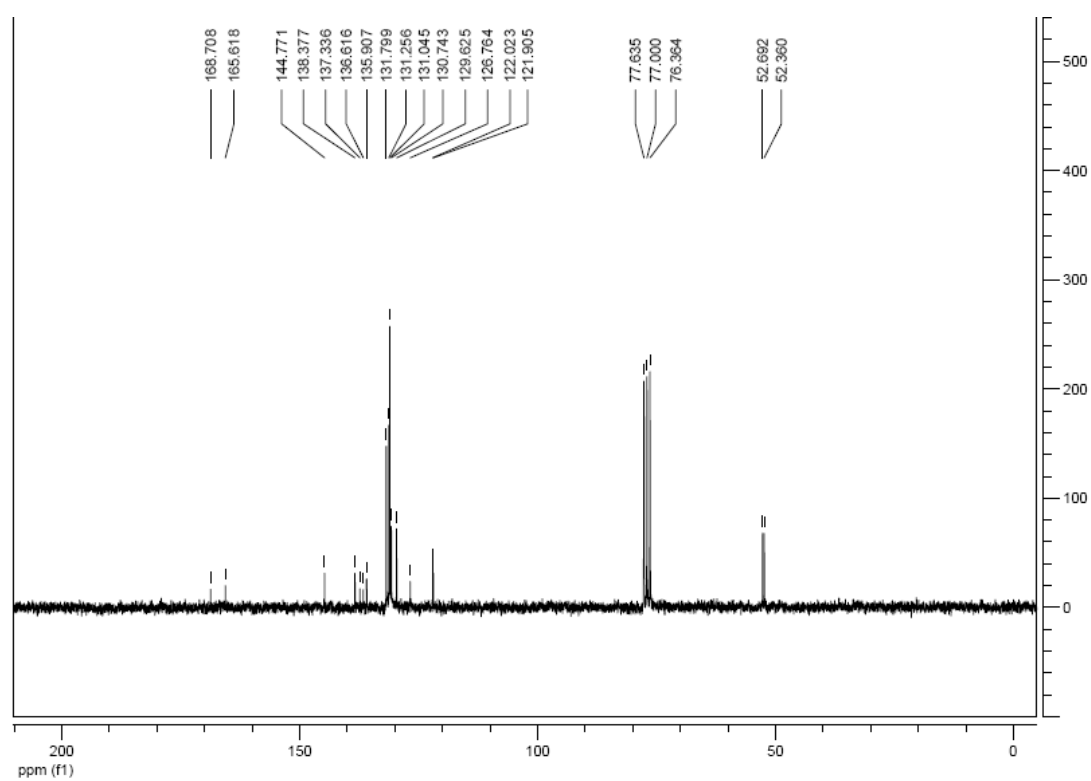
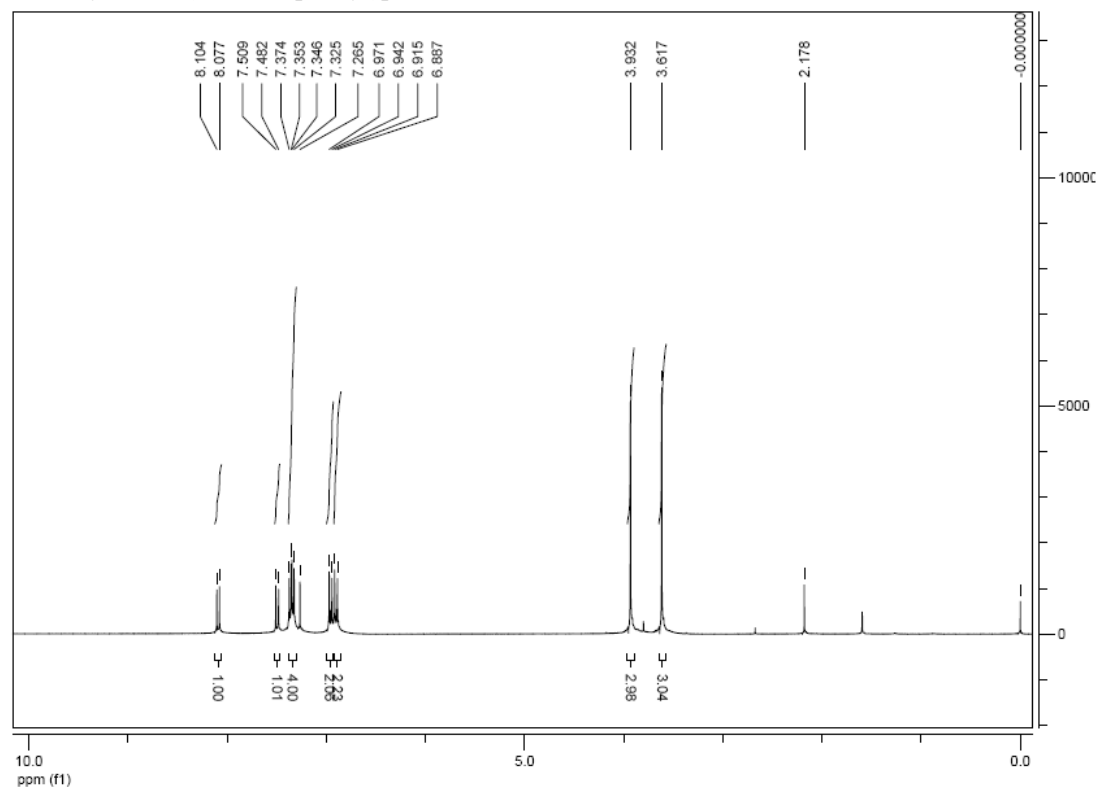


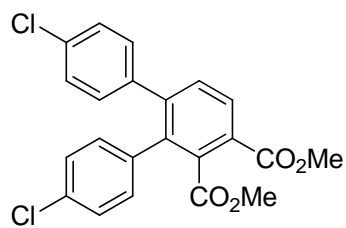
Dimethyl 3,4-di(4'-fluorophenyl)phthalate



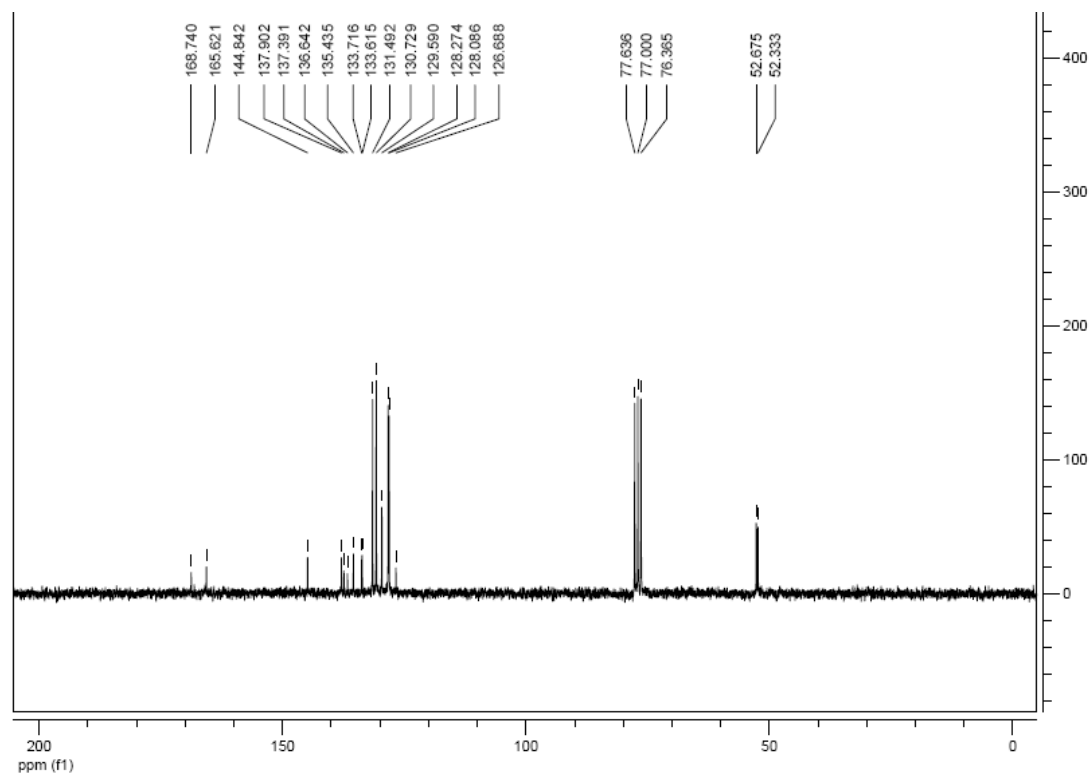
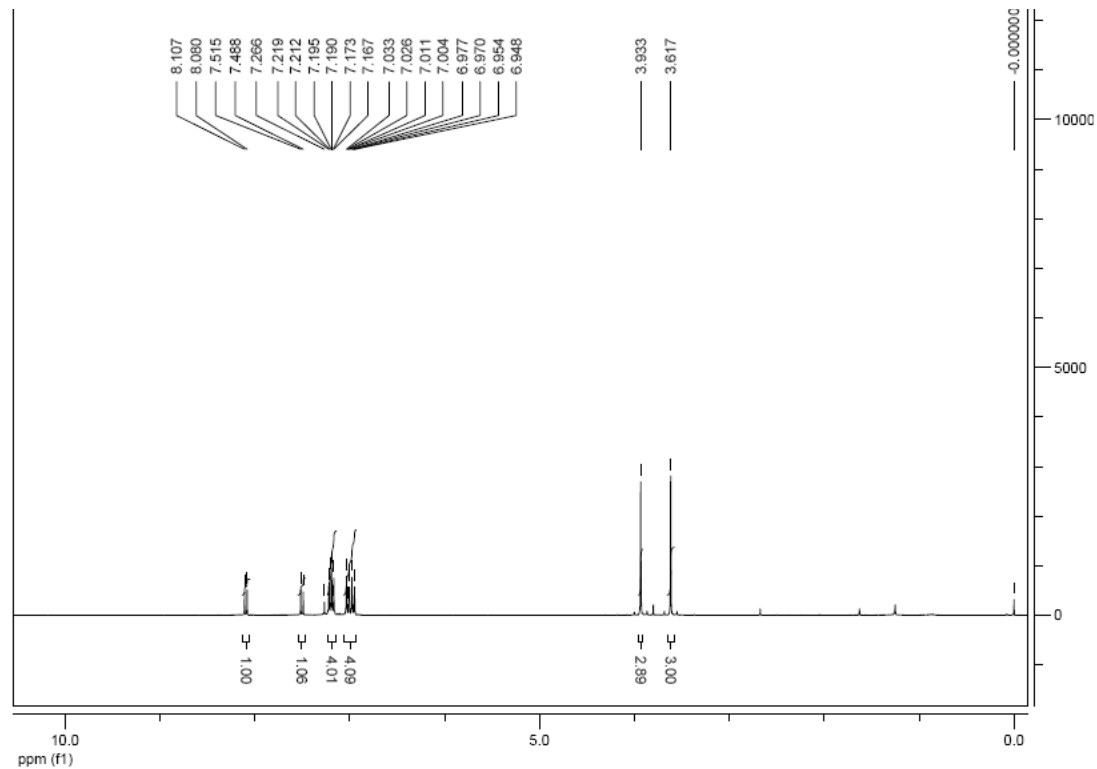


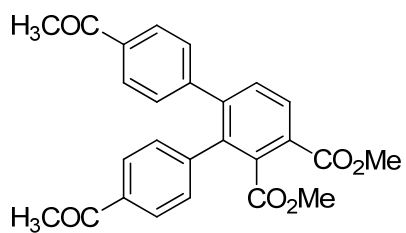
Dimethyl 3,4-di(4'-bromophenyl)phthalate



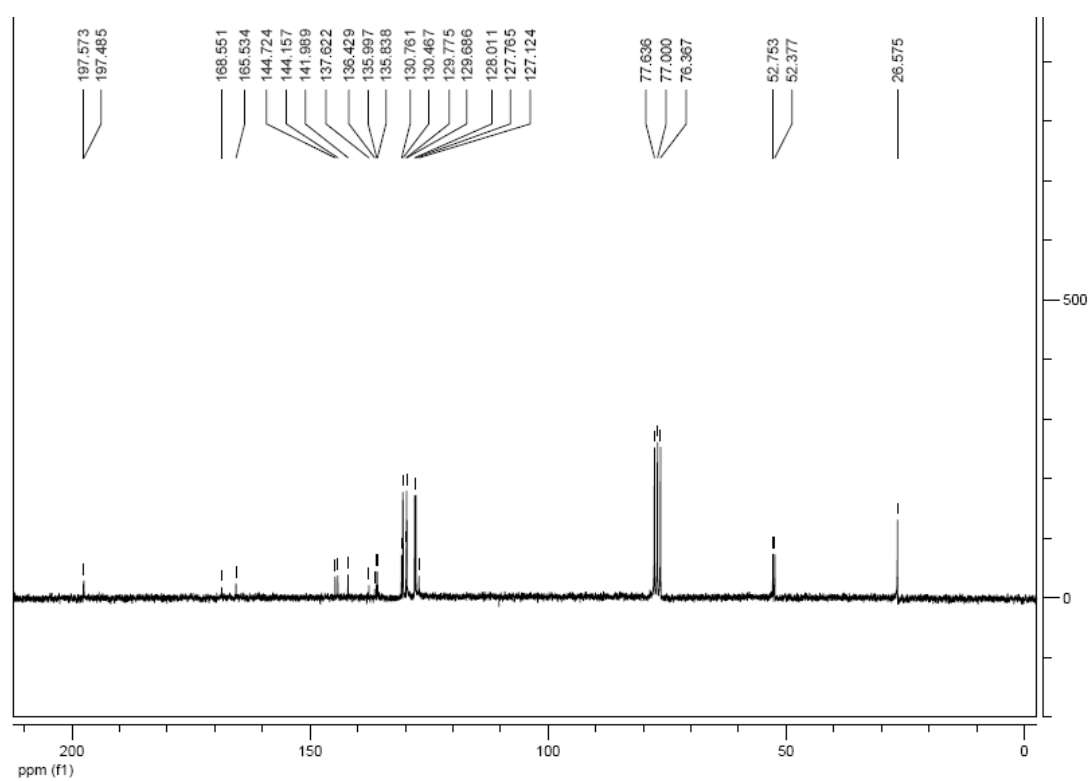
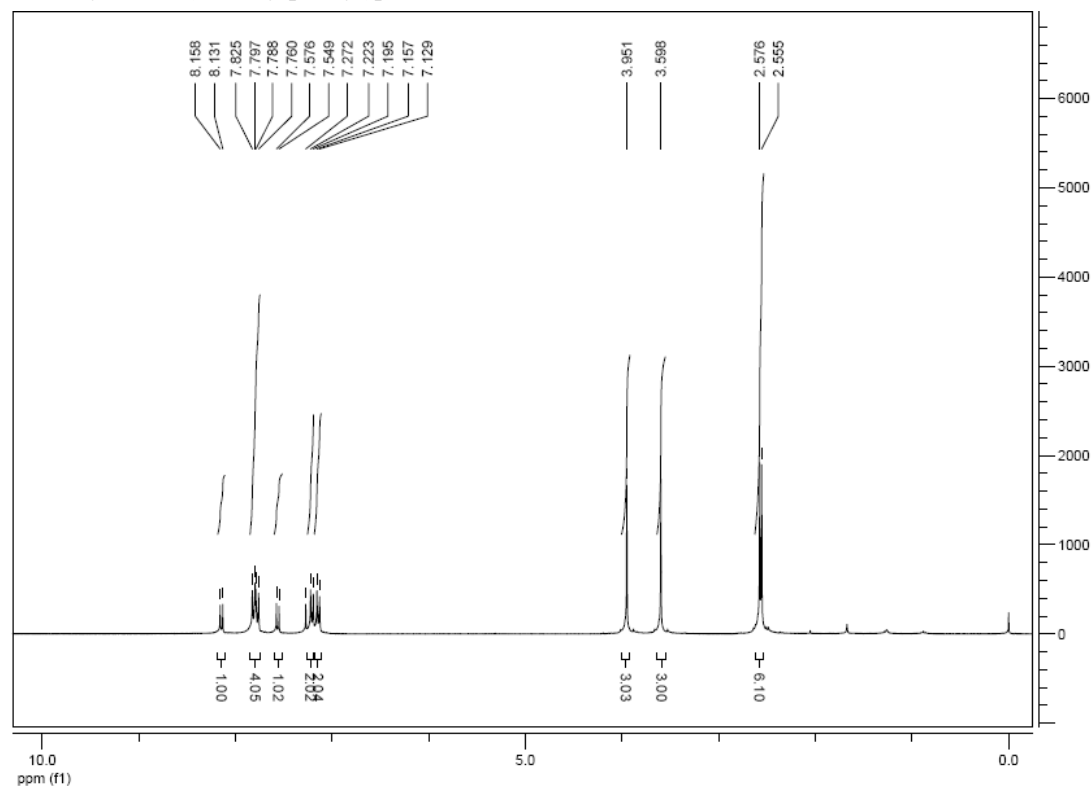


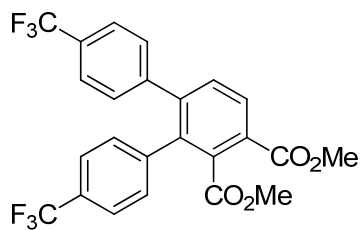
Dimethyl 3,4-di(4'-chlorophenyl)phthalate



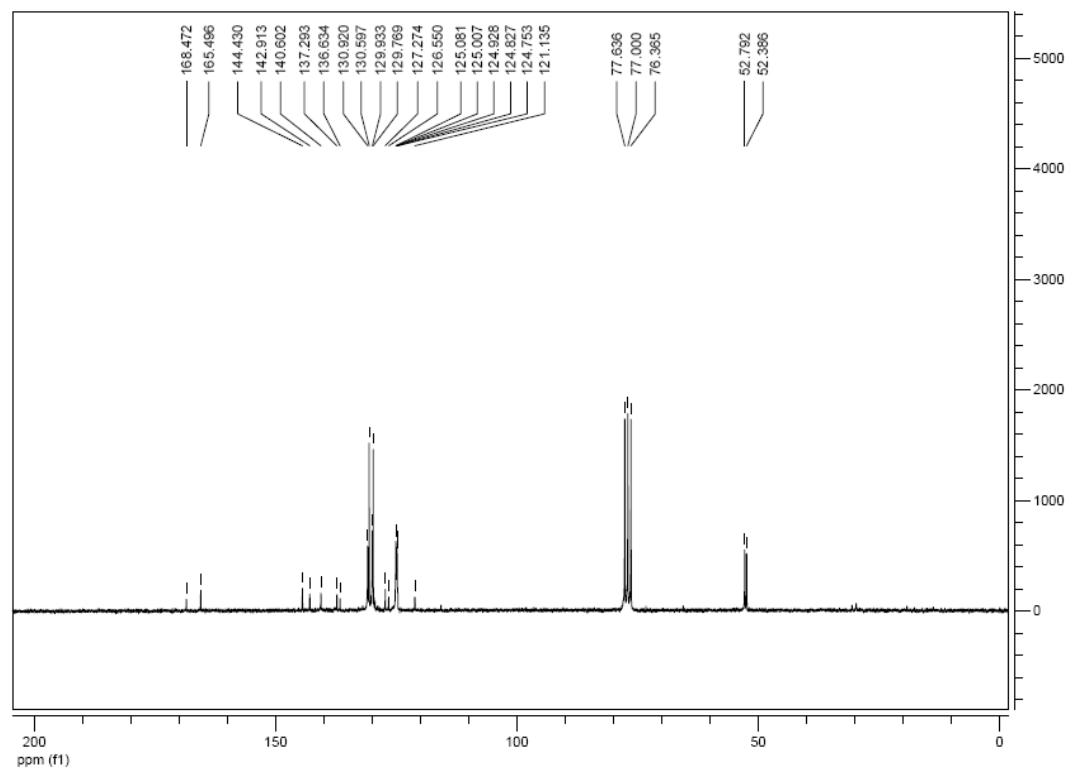
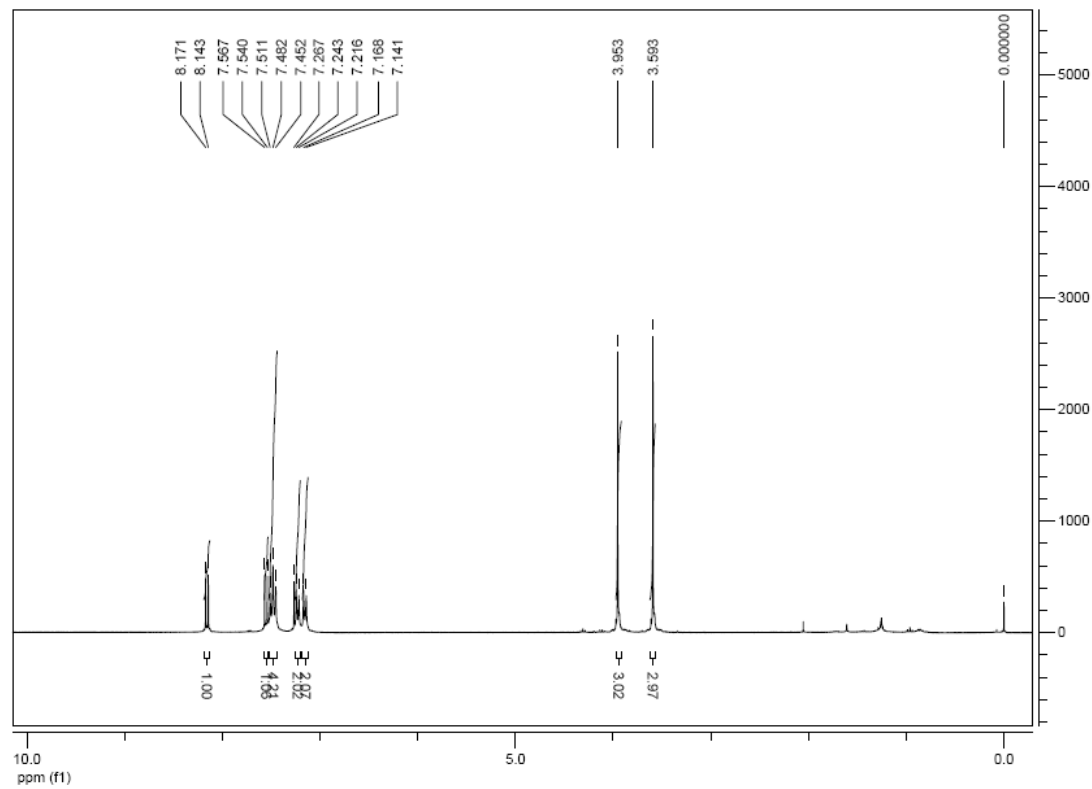


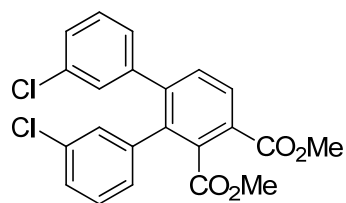
Dimethyl 3,4-di(4'-acetylphenyl)phthalate



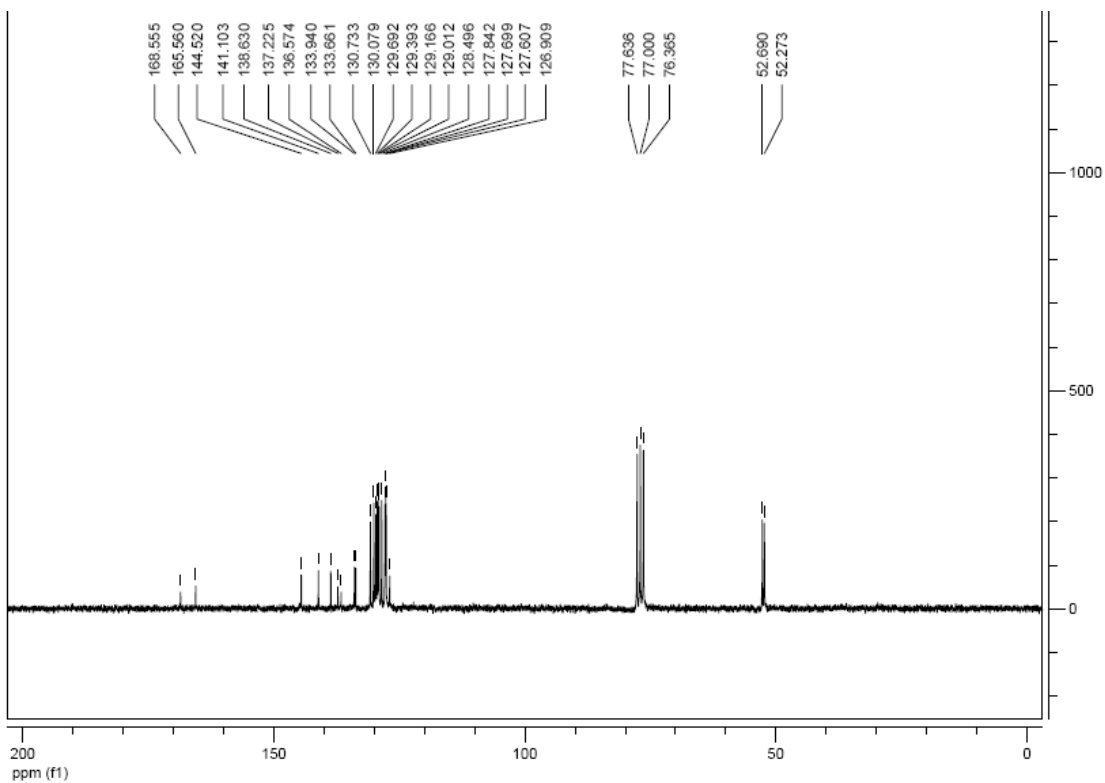
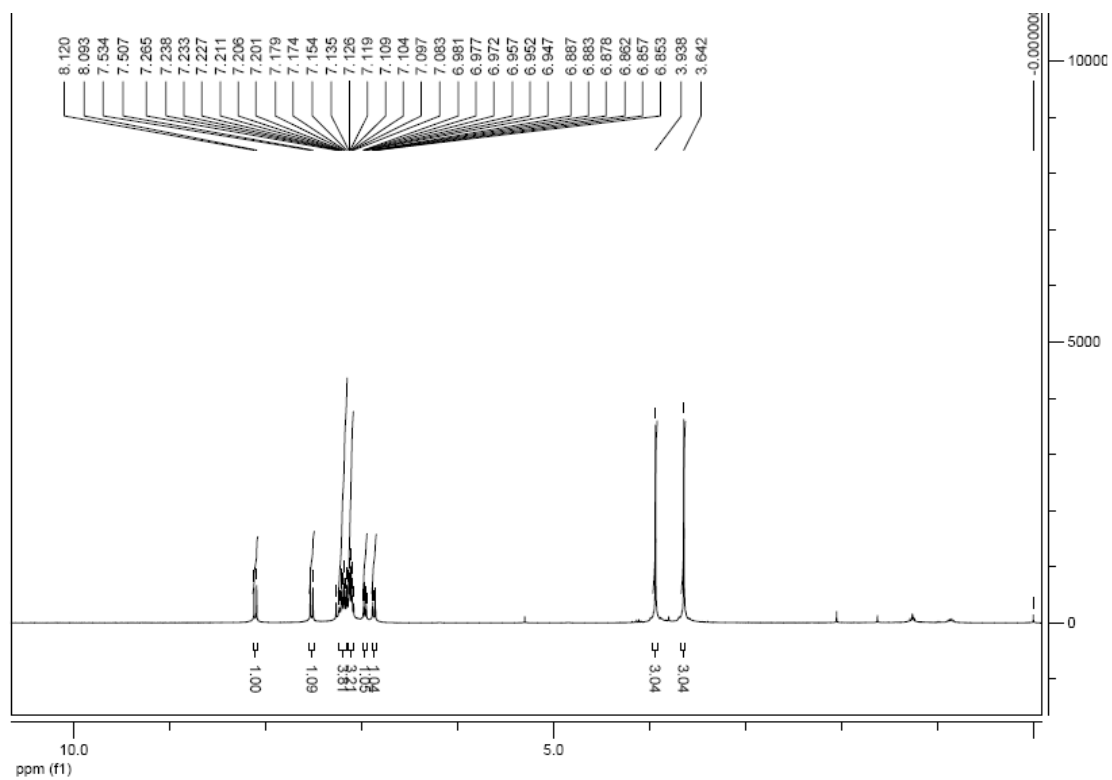


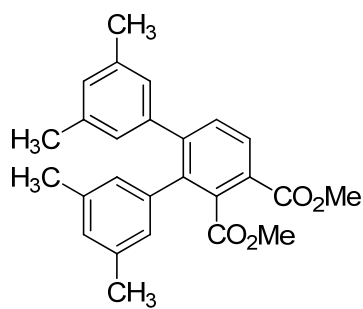
Dimethyl 3,4-di(4'-trifluoromethylphenyl)phthalate



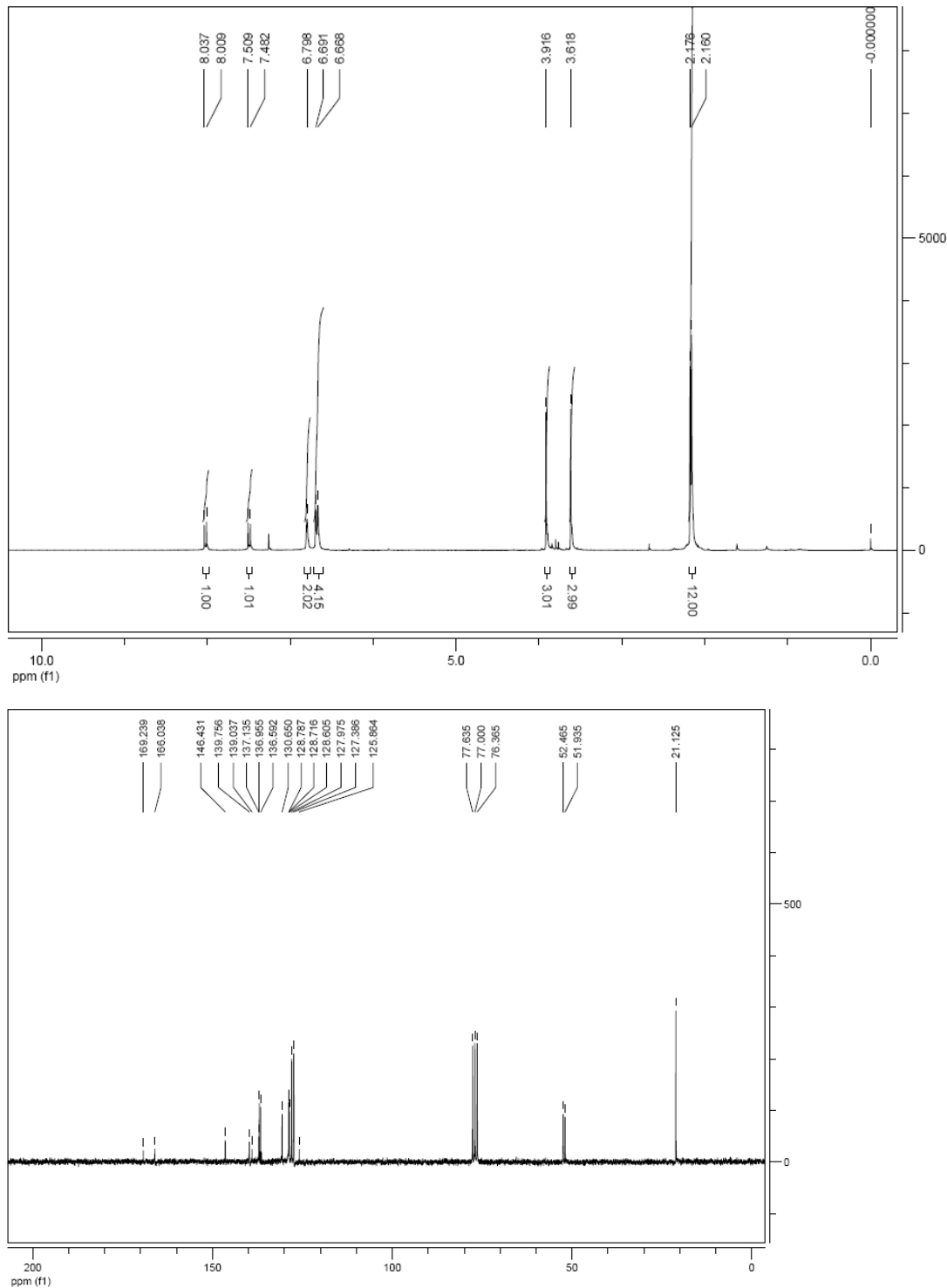


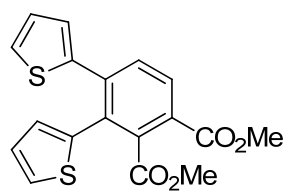
Dimethyl 3,4-di(3'-chlorophenyl)phthalate



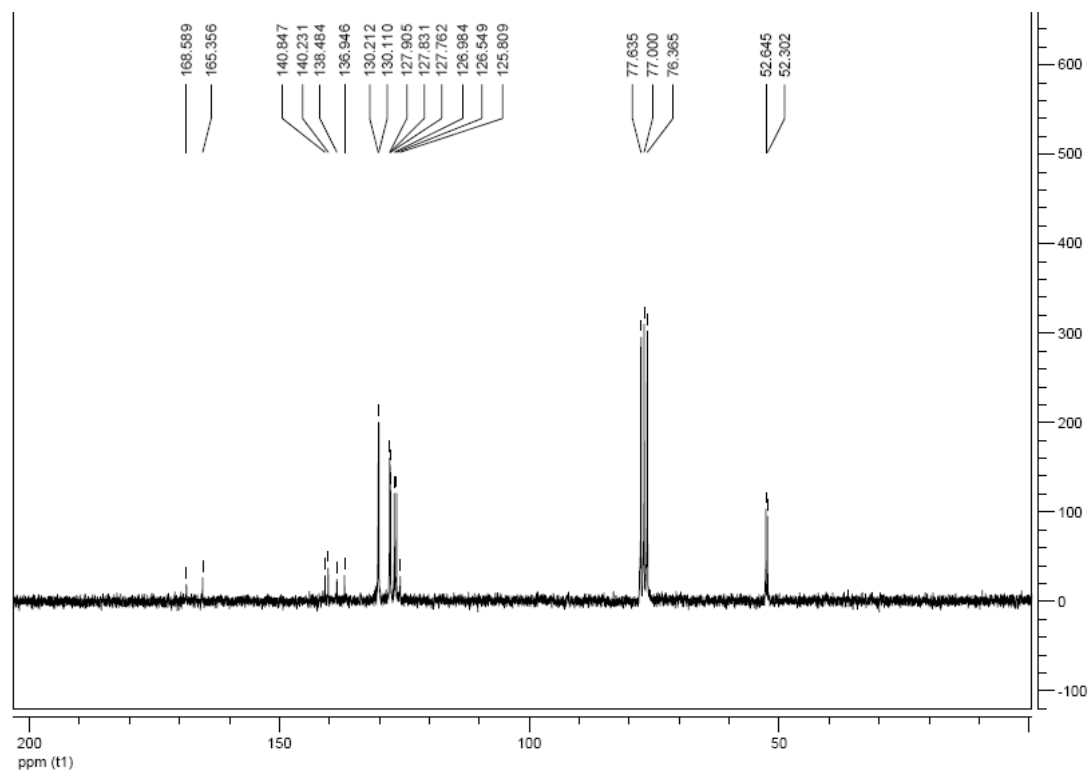
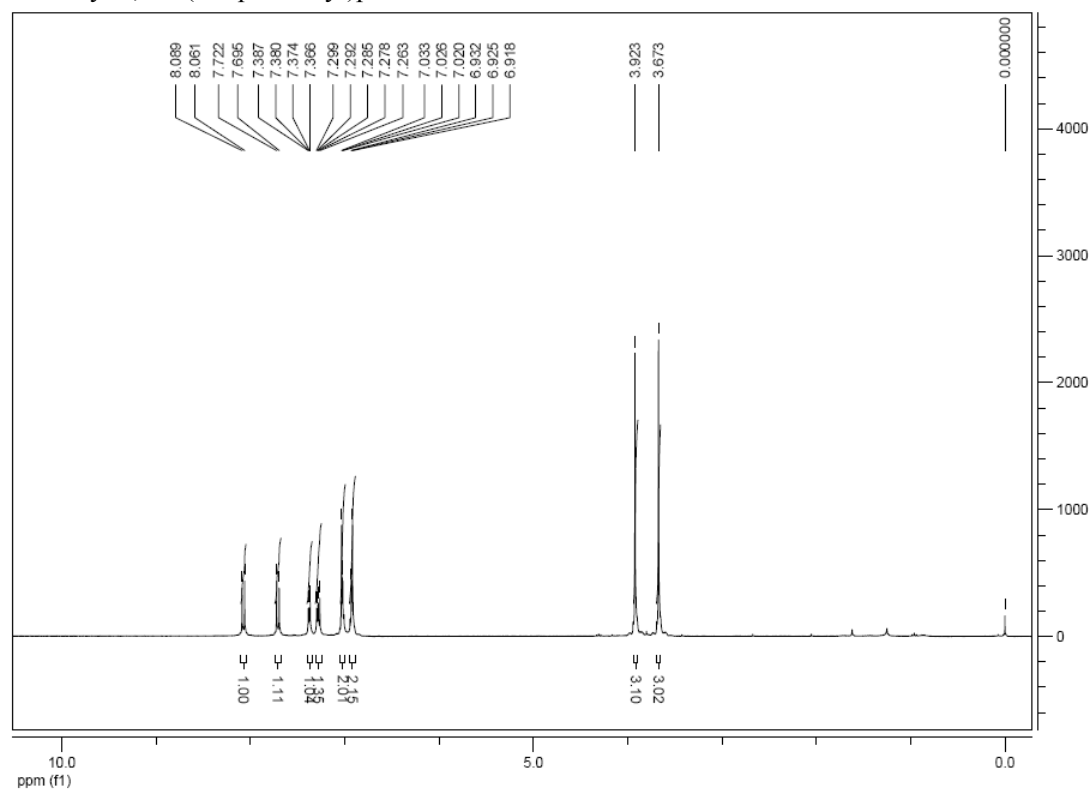


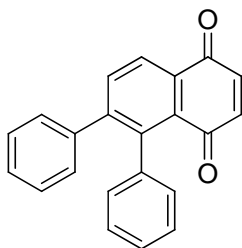
Dimethyl 3,4-di(3',5'-dimethylphenyl)phthalate



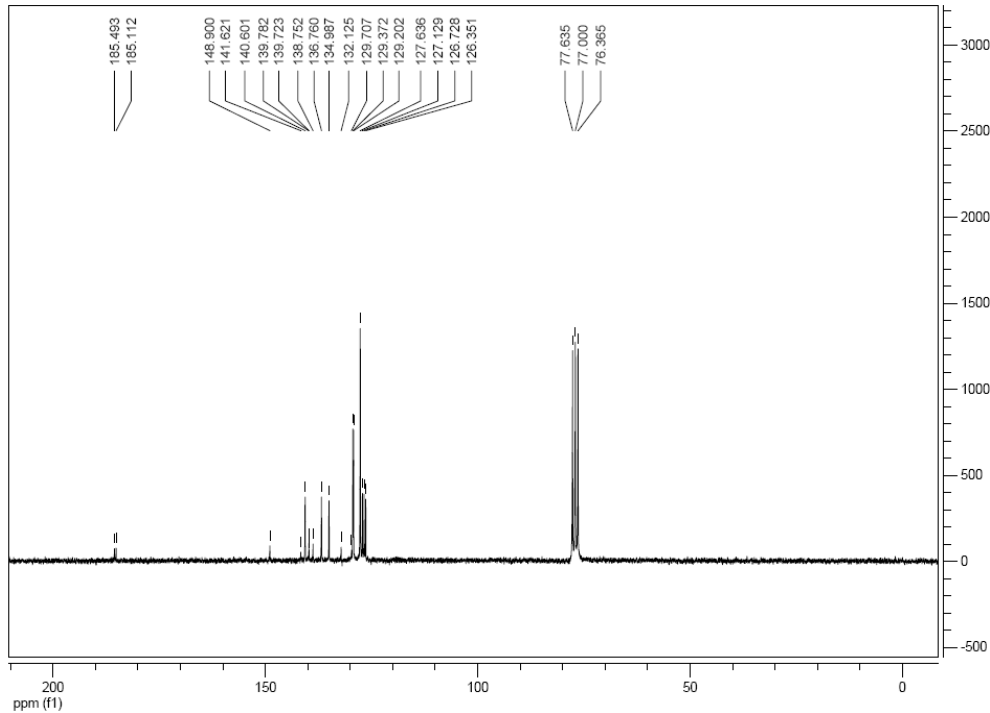
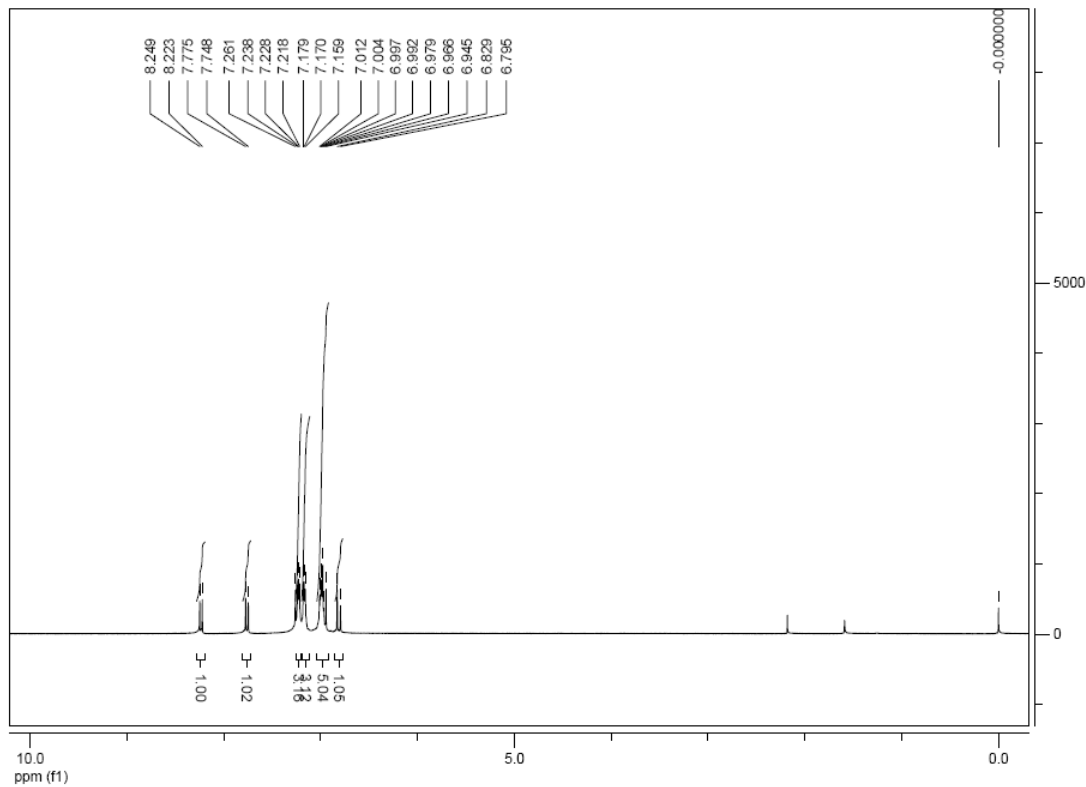


Dimethyl 3,4-di(thiophen-2-yl)phthalate





5, 6-diphenylnaphthalene-1,4-dione



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