

Biaryl and atropisomeric biaryl aldehyde synthesis by one-step, metal-free benzannulation of aryl enals and propiolates

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Contents

General experimental information.....	S1
General process for the synthesis of biaryl aldehydes 3 and 5	S1-S2
Characterization data for all products.....	S2-S11
Reference.....	S1
1	
¹ H and ¹³ C NMR spectra.....	S12-S36

General experimental information

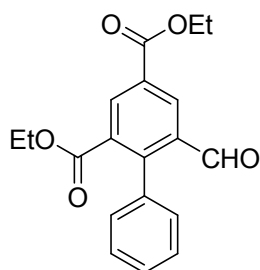
All experiments were carried out under open atmosphere. All chemicals and solvents used in the experiments were obtained from commercial sources and used directly without further treatment. ¹H and ¹³C NMR were recorded in 400 MHz apparatus. The frequencies for ¹H NMR and ¹³C NMR test were 400 MHz and 100 MHz, respectively. The chemical shifts of were reported in ppm with TMS as internal standard. Melting points were tested in X-4A instrument without correcting temperature, and the HRMS were obtained under ESI model with TOF analyzer.

General process for the synthesis of biaryl aldehydes **3** and **5**

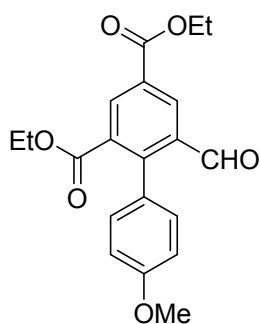
To a 25 mL round bottom flask equipped with stirring bar was charged ethyl propiolate **2** (0.4 mol). The dimethyl amine (40 wt.% aqueous solution) was then added dropwise. Afterwards, the enal **1** or **4** (0.2 mmol) and AcOH (1 mL) were successively employed. The vessel was then heated at 80 °C for 12 h with stirring (TLC). After cooling down to room temperature, 10 mL was added, and Na₂CO₃ was slowly added to the resulting mixture until no bubble occur. After filtration, the solid

was washed with a small amount of ethyl acetate (EA) for several times. The liquid phase was extracted with EA (3×8 mL). The organic phases were combined and dried with anhydrous Na_2SO_4 . The solid was filtered out, and the solution was subjected to reduced pressure to remove the solvent. The residue was employed to silica gel chromatography to provide pure products with the elution of mixed petroleum ether and EA ($v/v = 10 : 1$).

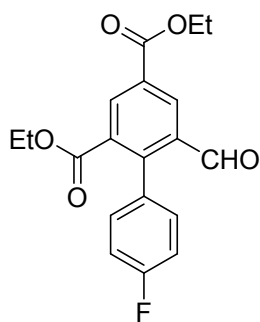
Characterization data for all products



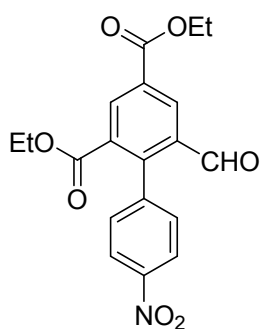
Diethyl 6-formylbiphenyl-2,4-dicarboxylate (3a).¹ Yellow liquid; ^1H NMR (400 MHz, CDCl_3): 9.77 (s, 1 H), 8.75 (d, $J = 2.0$ Hz, 1 H), 8.69 (d, $J = 2.0$ Hz, 1 H), 7.48-7.46 (m, 3 H), 7.30-7.27 (m, 2 H), 4.46 (q, $J = 7.2$ Hz, 2 H), 4.07 (q, $J = 7.2$ Hz, 2 H), 1.44 (t, $J = 7.2$ Hz, 3 H), 0.99 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 190.8, 166.7, 164.8, 148.6, 135.2, 135.1, 134.9, 133.9, 130.9, 130.5, 129.4, 128.6, 128.2, 61.8, 61.5, 14.3, 13.6.



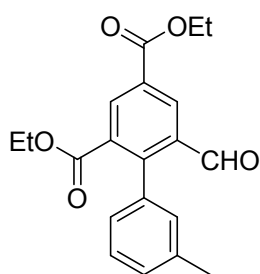
Diethyl 6-formyl-4'-methoxybiphenyl-2,4-dicarboxylate (3b).¹ Yellow liquid; ^1H NMR (400 MHz, CDCl_3): 9.81 (s, 1 H), 8.71 (d, $J = 1.6$ Hz, 1 H), 8.63 (d, $J = 2.0$ Hz, 1 H), 7.21 (d, $J = 8.4$ Hz, 2 H), 6.99 (d, $J = 8.8$ Hz, 2 H), 4.45 (q, $J = 7.2$ Hz, 2 H), 4.12 (q, $J = 7.2$ Hz, 2 H), 3.88 (s, 3 H), 1.44 (t, $J = 7.2$ Hz, 3 H), 1.06 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 191.0, 166.9, 164.8, 159.9, 148.4, 135.3, 134.7, 134.2, 130.9, 130.8, 130.2, 127.1, 113.7, 61.7, 61.5, 55.4, 14.3, 13.8.



Diethyl 4'-fluoro-6-formylbiphenyl-2,4-dicarboxylate (3c). Yellow liquid; ^1H NMR (400 MHz, CDCl_3): 9.77 (s, 1 H), 8.74 (d, $J = 2.0$ Hz, 1 H), 8.69 (d, $J = 2.0$ Hz, 1 H), 7.28 (d, $J = 8.0$ Hz, 2 H), 7.17 (t, $J = 8.4$ Hz, 2 H), 4.46 (q, $J = 7.2$ Hz, 2 H), 4.11 (q, $J = 7.2$ Hz, 2 H), 1.44 (t, $J = 7.2$ Hz, 3 H), 1.07 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 190.4, 166.4, 164.7, 162.9 (d, $J = 257.8$ Hz), 147.5, 135.3, 135.1, 133.9, 131.2, 131.1 (d, $J = 1.2$ Hz), 130.7, 115.5, 115.2, 61.8, 61.6, 14.3, 13.8; ESI-HRMS Calcd for $\text{C}_{19}\text{H}_{18}\text{FO}_5$ $[\text{M} + \text{H}]^+$ 345.1133, found 345.1123.

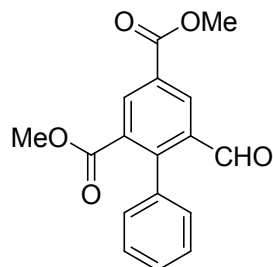


Diethyl 6-formyl-4'-nitrobiphenyl-2,4-dicarboxylate (3d).¹ Yellow liquid; ^1H NMR (400 MHz, CDCl_3): 9.73 (s, 1 H), 8.81 (d, $J = 1.6$ Hz, 1 H), 8.78 (d, $J = 1.6$ Hz, 1 H), 8.35 (d, $J = 8.4$ Hz, 2 H), 7.51 (d, $J = 8.4$ Hz, 2 H), 4.49 (q, $J = 7.2$ Hz, 2 H), 4.15 (q, $J = 7.2$ Hz, 2 H), 1.46 (t, $J = 7.2$ Hz, 3 H), 1.11 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 189.3, 165.4, 164.4, 147.9, 146.2, 142.7, 135.7, 134.9, 132.7, 132.0, 131.6, 130.2, 123.3, 62.1, 61.9, 14.3, 13.8.

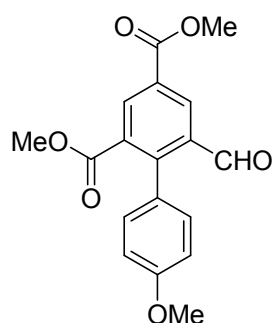


Diethyl 6-formyl-3'-methylbiphenyl-2,4-dicarboxylate (3e). Yellow liquid; ^1H NMR (400 MHz, CDCl_3): 9.78 (s, 1 H), 8.73 (d, $J = 1.6$ Hz, 1 H), 8.66 (d, $J = 2.0$ Hz, 1 H), 7.34 (t, $J = 7.6$ Hz, 1 H), 7.28 (s, 1 H), 7.09 (d, $J = 8.8$ Hz, 2 H), 4.45 (q, $J = 7.2$ Hz, 2 H), 4.08 (q, $J = 7.2$ Hz, 2 H), 2.41 (s,

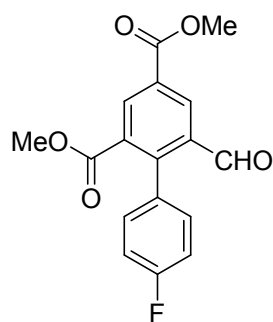
3 H), 1.44 (t, $J = 7.2$ Hz, 3 H), 1.00 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 190.9, 166.8, 164.8, 148.8, 137.9, 135.09, 135.06, 134.8, 133.9, 130.8, 130.3, 130.0, 129.3, 128.0, 126.6, 61.7, 61.5, 21.4, 14.3, 13.6; ESI-HRMS Calcd for $\text{C}_{20}\text{H}_{21}\text{O}_5$ $[\text{M} + \text{H}]^+$ 341.1384, found 341.1374.



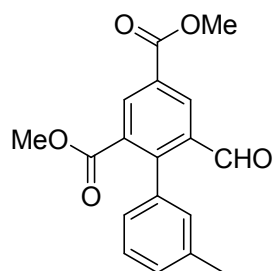
Dimethyl 6-formylbiphenyl-2,4-dicarboxylate (3f). Yellow solid, m.p. 87 °C; ^1H NMR (400 MHz, CDCl_3): 9.75 (s, 1 H), 8.74 (d, $J = 2.0$ Hz, 1 H), 8.69 (d, $J = 2.0$ Hz, 1 H), 7.47 (t, $J = 3.2$ Hz, 3 H), 7.30-7.27 (m, 2 H), 3.99 (s, 3 H), 3.65 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 190.6, 166.7, 165.2, 149.0, 135.2, 134.9, 133.3, 131.1, 130.1, 129.3, 128.6, 128.2, 126.8, 52.6, 52.4; ESI-HRMS Calcd for $\text{C}_{17}\text{H}_{15}\text{O}_5$ $[\text{M} + \text{H}]^+$ 299.0914, found 299.0910.



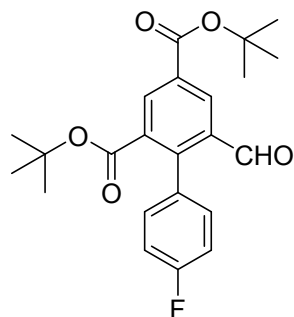
Dimethyl 6-formyl-4'-methoxybiphenyl-2,4-dicarboxylate (3g). Yellow solid, m.p. 113 °C; ^1H NMR (400 MHz, CDCl_3): 9.79 (s, 1 H), 8.72 (d, $J = 2.0$ Hz, 1 H), 8.64 (d, $J = 2.0$ Hz, 1 H), 7.20 (d, $J = 8.4$ Hz, 2 H), 7.00 (d, $J = 8.8$ Hz, 2 H), 3.99 (s, 3 H), 3.89 (s, 3 H), 3.68 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 190.9, 167.0, 165.3, 159.9, 148.7, 135.5, 134.8, 133.6, 131.1, 130.7, 129.8, 126.8, 113.7, 55.3, 52.6, 52.4; ESI-HRMS Calcd for $\text{C}_{18}\text{H}_{16}\text{O}_6\text{Na}$ $[\text{M} + \text{Na}]^+$ 351.0839, found 351.0835.



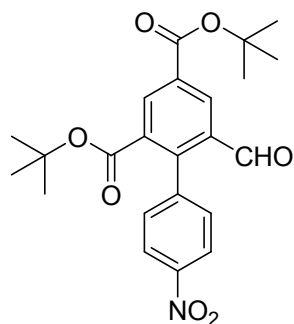
Dimethyl 4'-fluoro-6-formylbiphenyl-2,4-dicarboxylate (3h). Yellow solid, m.p. 95 °C; ¹H NMR (400 MHz, CDCl₃): 9.76 (s, 1 H), 8.75 (d, *J* = 2.0 Hz, 1 H), 8.71 (d, *J* = 1.6 Hz, 1 H), 7.28-7.25 (m, 2 H), 7.18 (t, *J* = 8.4 Hz, 2 H), 4.00 (s, 3 H), 3.68 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): 190.2, 166.5, 165.1, 162.9 (d, *J* = 248.3 Hz), 147.9, 135.3, 133.3, 131.4, 131.1, 131.0, 130.8 (d, *J* = 3.5 Hz), 130.4, 115.4 (d, *J* = 21.1 Hz), 52.7, 52.5; ESI-HRMS Calcd for C₁₇H₁₄FO₅ [M + H]⁺ 317.0820, found 317.0817.



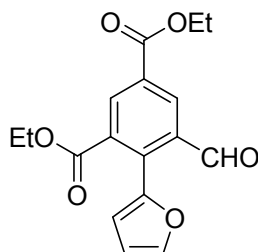
Dimethyl 6-formyl-3'-methylbiphenyl-2,4-dicarboxylate (3i). White solid, m.p. 112 °C; ¹H NMR (400 MHz, CDCl₃): 9.76 (s, 1 H), 8.74 (d, *J* = 1.6 Hz, 1 H), 8.68 (d, *J* = 1.6 Hz, 1 H), 7.35 (t, *J* = 8.0 Hz, 1 H), 7.28 (s, 1 H), 7.08 (d, *J* = 6.8 Hz, 2 H), 3.99 (s, 3 H), 3.66 (s, 3 H), 2.41 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): 190.8, 166.8, 165.3, 149.2, 137.9, 135.3, 134.90, 134.86, 133.3, 131.0, 129.98, 129.96, 129.4, 128.1, 126.4, 52.6, 52.4, 21.4; ESI-HRMS Calcd for C₁₈H₁₆O₅Na [M + Na]⁺ 335.0890, found 335.0881.



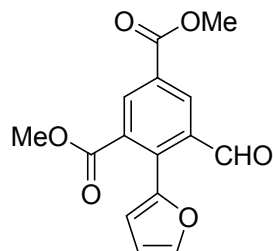
Di-tert-butyl 4'-fluoro-6-formylbiphenyl-2,4-dicarboxylate (3j). Yellow solid, m.p. 85 °C; ¹H NMR (400 MHz, CDCl₃): 9.76 (s, 1 H), 8.63 (d, *J* = 2.0 Hz, 1 H), 8.53 (d, *J* = 2.0 Hz, 1 H), 7.30-7.27 (m, 2 H), 7.18 (t, *J* = 8.8 Hz, 2 H), 1.64 (s, 9 H), 1.27 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃): 190.6, 166.1, 164.1, 162.7 (d, *J* = 223.0 Hz), 146.2, 135.7, 134.9, 134.5, 132.2, 131.5 (d, *J* = 2.8 Hz), 131.3 (d, *J* = 7.8 Hz), 130.4, 115.3 (d, *J* = 21.6 Hz), 82.6, 82.4, 28.2, 27.6; ESI-HRMS Calcd for C₂₃H₂₅FO₅Na [M + Na]⁺ 423.1578, found 423.1571.



Di-tert-butyl 6-formyl-4'-nitrophenyl-2,4-dicarboxylate (3k). White solid, m.p. 191 °C; ¹H NMR (400 MHz, CDCl₃): 9.71 (s, 1 H), 8.67 (d, *J* = 2.0 Hz, 1 H), 8.64 (d, *J* = 1.6 Hz, 1 H), 8.35 (d, *J* = 8.4 Hz, 2 H), 7.48 (d, *J* = 8.4 Hz, 2 H), 1.65 (s, 9 H), 1.28 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃): 189.5, 165.1, 163.4, 147.9, 144.9, 143.0, 135.2, 134.6, 133.0, 131.4, 130.4, 123.3, 83.1, 82.7, 28.1, 27.7; ESI-HRMS Calcd for C₂₃H₂₅NO₇Na [M + Na]⁺ 450.1523, found 450.1527.

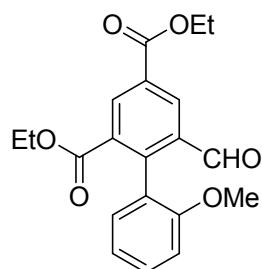


Diethyl 5-formyl-4-(furan-2-yl)isophthalate (3l). Brown solid, m.p. 68 °C; ¹H NMR (400 MHz, CDCl₃): 10.03 (s, 1 H), 8.71 (d, *J* = 2.0 Hz, 1 H), 8.61 (d, *J* = 2.0 Hz, 1 H), 7.63 (t, *J* = 1.6 Hz, 1 H), 6.61 (d, *J* = 1.2 Hz, 2 H), 4.45 (q, *J* = 7.2 Hz, 2 H), 4.26 (q, *J* = 7.2 Hz, 2 H), 1.44 (t, *J* = 7.2 Hz, 3 H), 1.23 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): 190.4, 166.8, 164.5, 146.3, 144.3, 135.9, 135.4, 134.7, 134.1, 131.1, 131.0, 114.2, 111.8, 61.9, 61.8, 14.3, 14.0; ESI-HRMS Calcd for C₁₇H₁₇O₆ [M + H]⁺ 317.1020, found 317.1016.

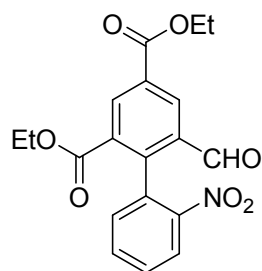


Dimethyl 5-formyl-4-(furan-2-yl)isophthalate (3m). Brown solid, m.p. 115 °C; ¹H NMR (400 MHz, CDCl₃): 10.02 (s, 1 H), 8.71 (d, *J* = 1.6 Hz, 1 H), 8.61 (d, *J* = 2.0 Hz, 1 H), 7.64 (d, *J* = 0.8 Hz, 1 H), 6.63-6.60 (m, 2 H), 3.99 (s, 3 H), 3.82 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): 190.3, 166.9, 164.9, 146.1, 144.5, 136.2, 135.5, 134.7, 133.6, 131.3, 130.7, 114.3, 111.8, 52.8, 52.7; ESI-

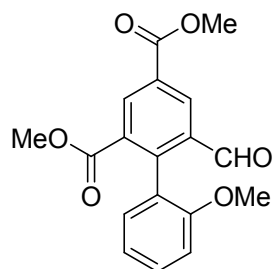
HRMS Calcd for $C_{15}H_{13}O_6$ $[M + H]^+$ 289.0707, found 289.0704.



Diethyl 6-formyl-2'-methoxybiphenyl-2,4-dicarboxylate (3n). Yellow liquid; 1H NMR (400 MHz, $CDCl_3$): 9.73 (s, 1 H), 8.75 (d, $J = 2.0$ Hz, 1 H), 8.73 (d, $J = 2.0$ Hz, 1 H), 7.47-7.42 (m, 1 H), 7.13-7.10 (m, 1 H), 7.07-7.03 (m, 1 H), 6.99 (d, $J = 8.0$ Hz, 1 H), 4.45 (q, $J = 7.2$ Hz, 2 H), 4.09 (q, $J = 7.2$ Hz, 2 H), 3.73 (s, 3 H), 1.43 (t, $J = 7.2$ Hz, 3 H), 1.02 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 191.2, 166.5, 164.9, 156.6, 145.6, 135.2, 135.1, 134.0, 130.8, 130.7, 130.4, 130.3, 124.2, 120.6, 110.5, 61.6, 61.3, 55.5, 14.3, 13.7; ESI-HRMS Calcd for $C_{20}H_{21}O_6$ $[M + H]^+$ 357.1333, found 357.1324.

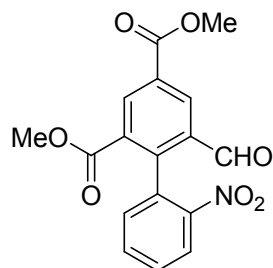


Diethyl 6-formyl-2'-nitrobiphenyl-2,4-dicarboxylate (3o). Yellow liquid; 1H NMR (400 MHz, $CDCl_3$): 9.71 (s, 1 H), 8.89 (d, $J = 2.0$ Hz, 1 H), 8.79 (d, $J = 2.0$ Hz, 1 H), 8.31-8.29 (m, 1 H), 7.73-7.64 (m, 2 H), 7.23-7.21 (m, 1 H), 4.48 (q, $J = 7.2$ Hz, 2 H), 4.10 (q, $J = 6.0$ Hz, 2 H), 1.46 (t, $J = 7.2$ Hz, 3 H), 1.08 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 189.4, 164.9, 164.5, 148.3, 145.7, 136.1, 134.9, 133.24, 133.21, 132.4, 131.1, 131.09, 131.01, 129.6, 124.6, 61.9, 61.7, 14.3, 13.8; ESI-HRMS Calcd for $C_{19}H_{18}NO_7$ $[M + H]^+$ 372.1078, found 372.1068.

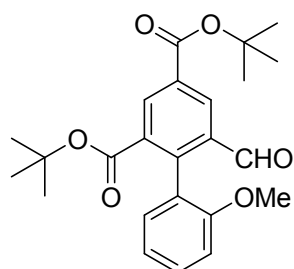


Dimethyl 6-formyl-2'-methoxybiphenyl-2,4-dicarboxylate (3p). White solid, m.p. 128 °C; 1H NMR (400 MHz, $CDCl_3$): 9.72 (s, 1 H), 8.75 (d, $J = 1.6$ Hz, 1 H), 8.73 (d, $J = 2.0$ Hz, 1 H), 7.47-

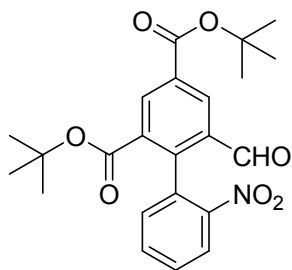
7.43 (m, 1 H), 7.12-7.09 (m, 1 H), 7.06 (t, $J = 7.2$ Hz, 1 H), 7.00 (d, $J = 8.4$ Hz, 1 H), 3.99 (s, 3 H), 3.73 (s, 3 H), 3.66 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 191.1, 166.6, 165.4, 156.5, 145.9, 135.4, 135.2, 133.4, 131.0, 130.8, 130.5, 129.9, 123.9, 120.6, 110.6, 55.5, 52.6, 52.2; ESI-HRMS Calcd for $\text{C}_{18}\text{H}_{17}\text{O}_6$ $[\text{M} + \text{H}]^+$ 329.1020, found, 329.1019.



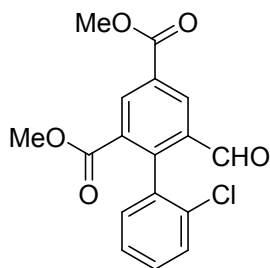
Dimethyl 6-formyl-2'-nitrobiphenyl-2,4-dicarboxylate (3q). Yellow solid, m.p. 127 °C; ^1H NMR (400 MHz, CDCl_3): 9.71 (s, 1 H), 8.89 (d, $J = 2.0$ Hz, 1 H), 8.80 (d, $J = 1.6$ Hz, 1 H), 8.32-8.29 (m, 1 H), 7.73-7.64 (m, 2 H), 7.23-7.20 (m, 1 H), 4.02 (s, 3 H), 3.68 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 189.2, 165.1, 164.9, 148.2, 146.3, 136.1, 134.9, 133.3, 133.2, 132.1, 131.0, 130.7, 130.4, 129.7, 124.6, 52.8, 52.6; ESI-HRMS Calcd for $\text{C}_{17}\text{H}_{14}\text{NO}_7$ $[\text{M} + \text{H}]^+$ 344.0765, found 344.0760.



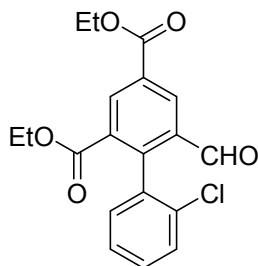
Di-tert-butyl 6-formyl-2'-methoxybiphenyl-2,4-dicarboxylate (3r). Yellow liquid; ^1H NMR (400 MHz, CDCl_3): 9.70 (s, 1 H), 8.63 (d, $J = 1.6$ Hz, 1 H), 8.57 (d, $J = 2.0$ Hz, 1 H), 7.46-7.42 (m, 1 H), 7.12-7.10 (m, 1 H), 7.05 (t, $J = 7.2$ Hz, 1 H), 3.72 (s, 3 H), 1.62 (s, 9 H), 1.23 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3): 191.4, 166.2, 164.1, 156.6, 144.4, 135.7, 134.9, 134.8, 131.8, 131.0, 130.2, 130.1, 124.7, 120.6, 110.5, 82.1, 81.9, 55.4, 28.2, 27.5; ESI-HRMS Calcd for $\text{C}_{24}\text{H}_{28}\text{O}_6\text{Na}$ $[\text{M} + \text{Na}]^+$ 435.1778, found 435.1771.



Di-tert-butyl 6-formyl-2'-nitrobiphenyl-2,4-dicarboxylate (3s). Yellow liquid; ^1H NMR (400 MHz, CDCl_3): 9.70 (s, 1 H), 8.72 (d, $J = 1.6$ Hz, 1 H), 8.67 (d, $J = 2.0$ Hz, 1 H), 8.30-8.27 (m, 1 H), 7.73-7.64 (m, 2 H), 7.23 (dd, $J_1 = 7.2$ Hz, $J_2 = 1.6$ Hz, 1 H), 1.65 (s, 9 H), 1.23 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3): 189.7, 164.7, 163.7, 148.2, 143.9, 135.7, 134.6, 133.2, 133.1, 132.9, 132.7, 132.5, 131.2, 129.4, 124.7, 82.7, 82.5, 28.2, 27.6; ESI-HRMS Calcd for $\text{C}_{23}\text{H}_{25}\text{NO}_7\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 450.1523, found 450.1510.

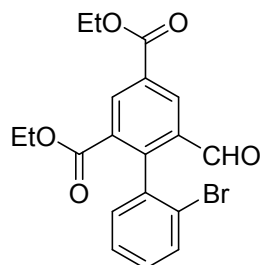


Dimethyl 2'-chloro-6-formyl-[1,1'-biphenyl]-2,4-dicarboxylate (3t). Yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 9.67 (s, 1 H), 8.84 (d, $J = 26.4$ Hz, 2 H), 7.54 – 7.51 (m, 1 H), 7.44 (dd, $J = 7.6, 1.6$ Hz, 1 H), 7.38 (dd, $J = 7.4, 1.2$ Hz, 1 H), 7.23 (dd, $J = 7.4, 1.6$ Hz, 1 H), 4.01 (s, 3 H), 3.71 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 189.8, 165.5, 165.1, 146.5, 135.9, 135.2, 134.5, 133.1, 132.2, 131.7, 130.8, 130.6, 130.1, 129.4, 126.7, 52.7, 52.5; ESI-HRMS Calcd for $\text{C}_{17}\text{H}_{13}\text{ClO}_5\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 355.0344, found 355.0337.

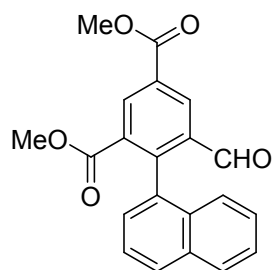


Diethyl 2'-chloro-6-formyl-[1,1'-biphenyl]-2,4-dicarboxylate (3u). Yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 9.67 (s, 1H), 8.83 (d, $J = 24.0$ Hz, 2H), 7.52 (dd, $J = 8.0, 1.2$ Hz, 0H), 7.43 (dd, $J = 7.8, 1.6$ Hz, 1H), 7.37 (dd, $J = 7.4, 1.2$ Hz, 1H), 7.23 (dd, $J = 7.6, 1.6$ Hz, 1H), 4.47 (d, $J = 7.2$ Hz, 2H), 4.12 (d, $J = 7.2$ Hz, 2H), 1.45 (d, $J = 7.2$ Hz, 3H), 1.05 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR

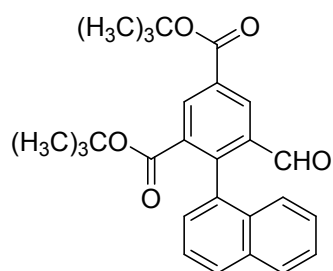
(100 MHz, CDCl₃) δ 190.0, 165.5, 164.7, 146.1, 135.9, 135.0, 134.8, 133.3, 132.9, 131.5, 131.2, 130.7, 130.0, 129.3, 126.6, 61.8, 61.6, 14.3, 13.7; ESI-HRMS Calcd for C₁₉H₁₈ClO₅ [M + H]⁺ 361.0837, found 361.0839.



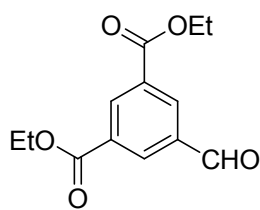
Diethyl 2'-bromo-6-formyl-[1,1'-biphenyl]-2,4-dicarboxylate (3v). Yellow liquid; ¹H NMR (400 MHz, CDCl₃) δ 9.67 (s, 1 H), 8.83 (dd, *J* = 25.6, 2.0 Hz, 2 H), 7.70 (d, *J* = 7.6 Hz, 1 H), 7.43 (dd, *J* = 7.6, 1.0 Hz, 1 H), 7.35 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.23 (dd, *J* = 7.6, 1.6 Hz, 1 H), 4.47 (d, *J* = 7.0 Hz, 2 H), 4.12 (dd, *J* = 7.2, 1.2 Hz, 2 H), 1.45 (d, *J* = 7.2 Hz, 3 H), 1.05 (d, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 190.0, 165.4, 164.7, 147.7, 136.8, 135.9, 134.9, 132.6, 132.4, 131.5, 131.2, 130.6, 130.1, 127.2, 123.3, 61.8, 61.6, 14.3, 13.7; ESI-HRMS Calcd for C₁₉H₁₇BrO₅Na [M + Na]⁺ 427.0152, found 427.0146.



Dimethyl 5-formyl-4-(naphthalen-1-yl)isophthalate (3w). Yellow liquid; ¹H NMR (400 MHz, CDCl₃) δ 9.46 (s, 1 H), 8.86 (s, 2 H), 7.95 (d, *J* = 9.2 Hz, 3 H), 7.58-7.48 (m, 2 H), 7.40 (d, *J* = 7.6 Hz, 1 H), 7.33 (d, *J* = 7.2 Hz, 1 H), 7.27 (d, *J* = 8.4 Hz, 1 H), 4.03 (s, 3 H), 3.44 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 190.4, 166.0, 165.3, 147.9, 136.2, 135.6, 133.7, 133.0, 132.8, 132.5, 131.2, 130.6, 129.1, 128.6, 127.3, 127.0, 126.3, 125.2, 124.9, 52.7, 52.3; ESI-HRMS Calcd for C₂₁H₁₆O₅Na [M + Na]⁺ 371.0890 found 371.0886.



Di-tert-butyl 5-formyl-4-(naphthalen-1-yl)isophthalate (3x). Yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 9.49 (s, 1 H), 8.76 (d, $J = 1.6$ Hz, 1 H), 8.70 (d, $J = 1.6$ Hz, 1 H), 7.98 – 7.90 (m, 2 H), 7.56 – 7.48 (m, 2 H), 7.40 (d, $J = 7.6$ Hz, 1 H), 7.33 (t, $J = 7.2, 4.0$ Hz, 2 H), 1.66 (s, 9 H), 0.80 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.8, 166.0, 164.0, 146.1, 136.2, 135.6, 135.0, 133.5, 133.2, 132.8, 132.5, 130.3, 128.9, 128.3, 127.5, 126.9, 126.4, 125.7, 124.9, 82.3, 81.9, 28.2, 27.0; ESI-HRMS Calcd for $\text{C}_{27}\text{H}_{28}\text{O}_5\text{Na}$ $[\text{M} + \text{Na}]^+$ 455.1829, found 455.1825.

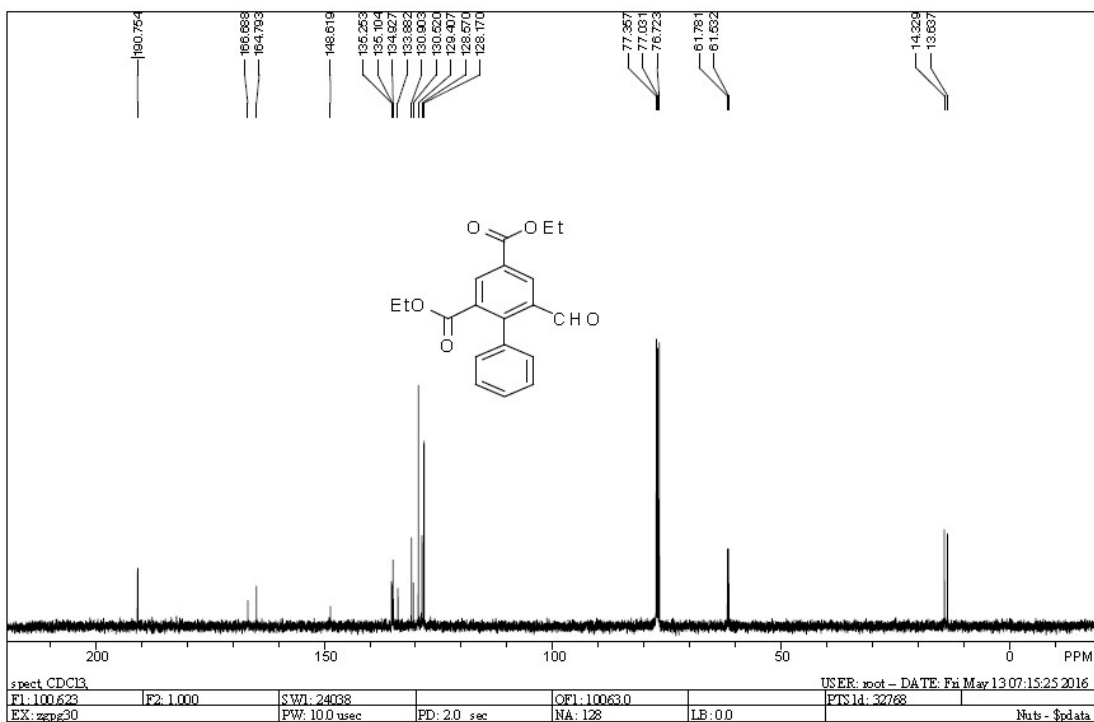
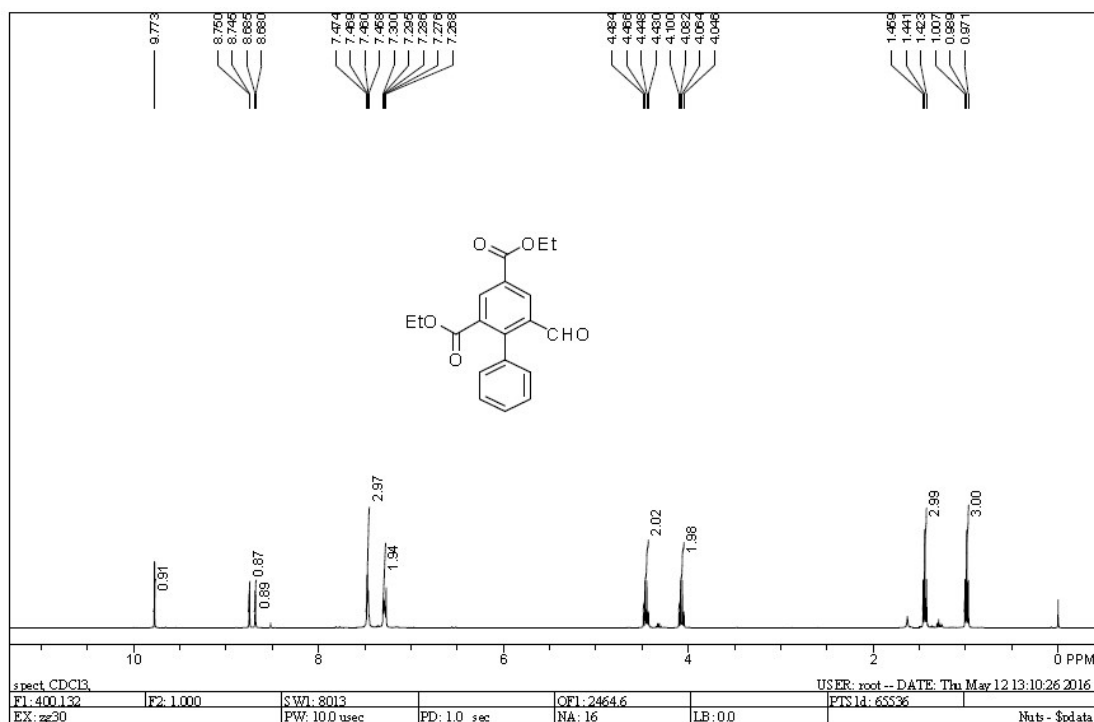


Diethyl 5-formylisophthalate (5). White solid, m.p. 84 °C; ^1H NMR (400 MHz, CDCl_3): 10.14 (s, 1 H), 8.92 (t, $J = 1.6$ Hz, 1 H), 8.71 (d, $J = 1.6$ Hz, 1 H), 4.46 (q, $J = 7.2$ Hz, 4 H), 1.44 (t, $J = 7.2$ Hz, 6 H); ^{13}C NMR (100 MHz, CDCl_3): 190.5, 164.7, 136.8, 135.7, 134.1, 132.2, 61.9, 14.3; ESI-HRMS Calcd for $\text{C}_{13}\text{H}_{15}\text{O}_5$ $[\text{M} + \text{H}]^+$ 251.0914, found 251.0915.

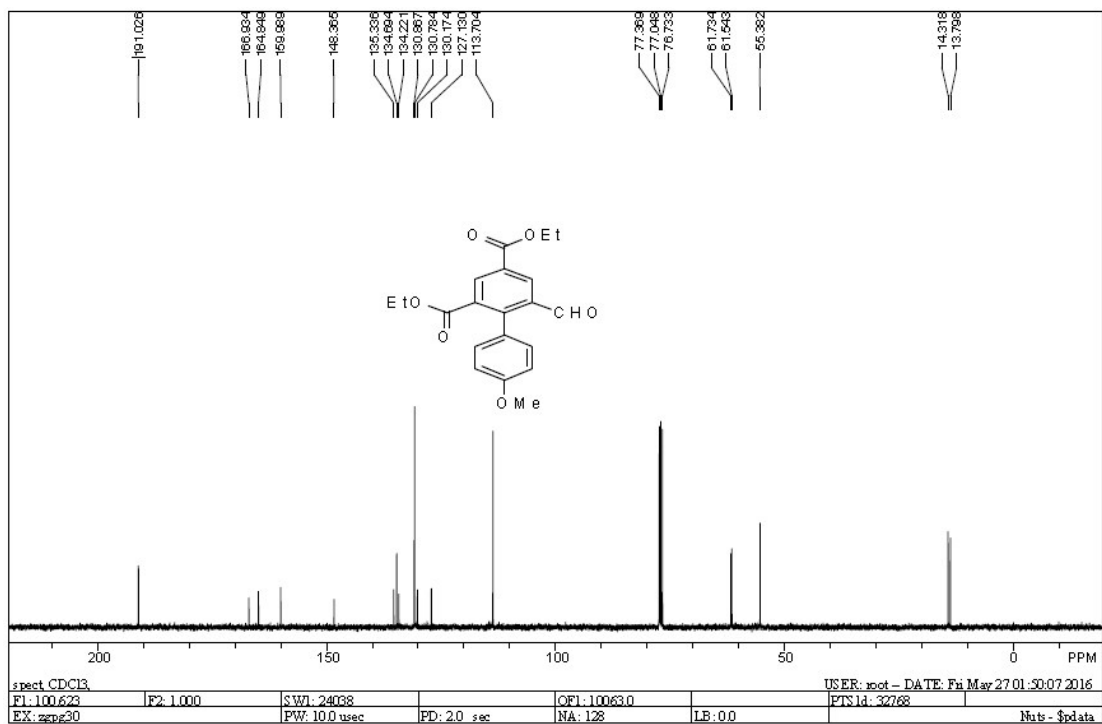
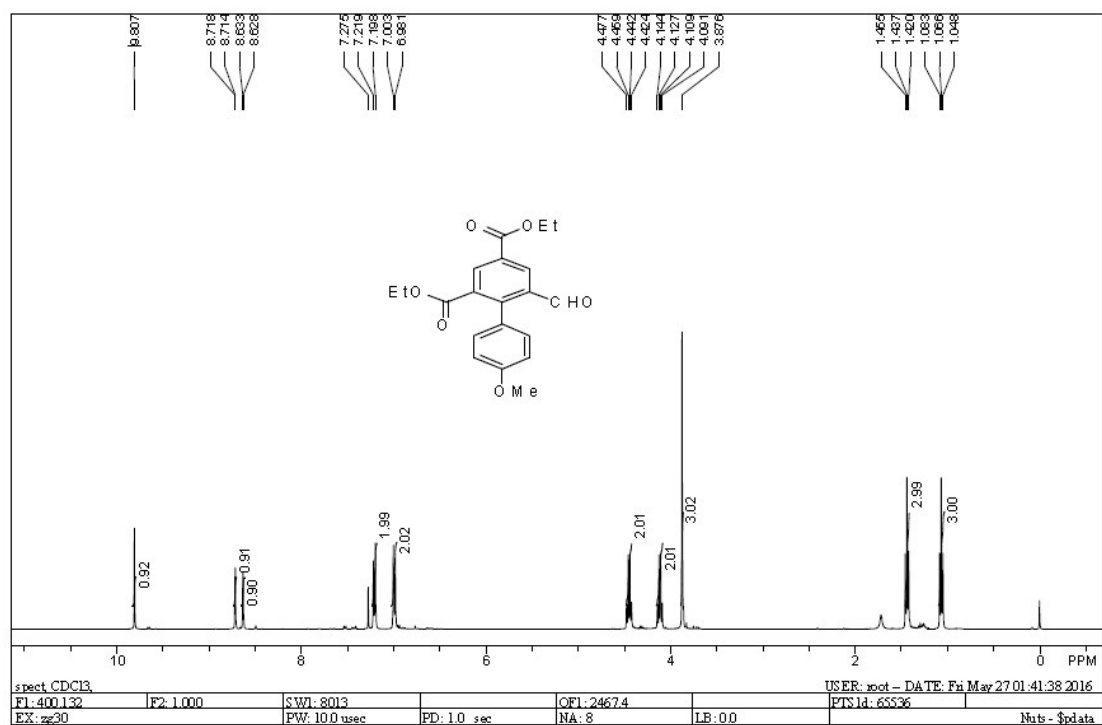
References

1. C. Challa, J. Vellekkatt, J. Ravindran and R. S. Lankalapall, *Org. Biomol. Chem.*, 2014, **12**, 8588-8592.

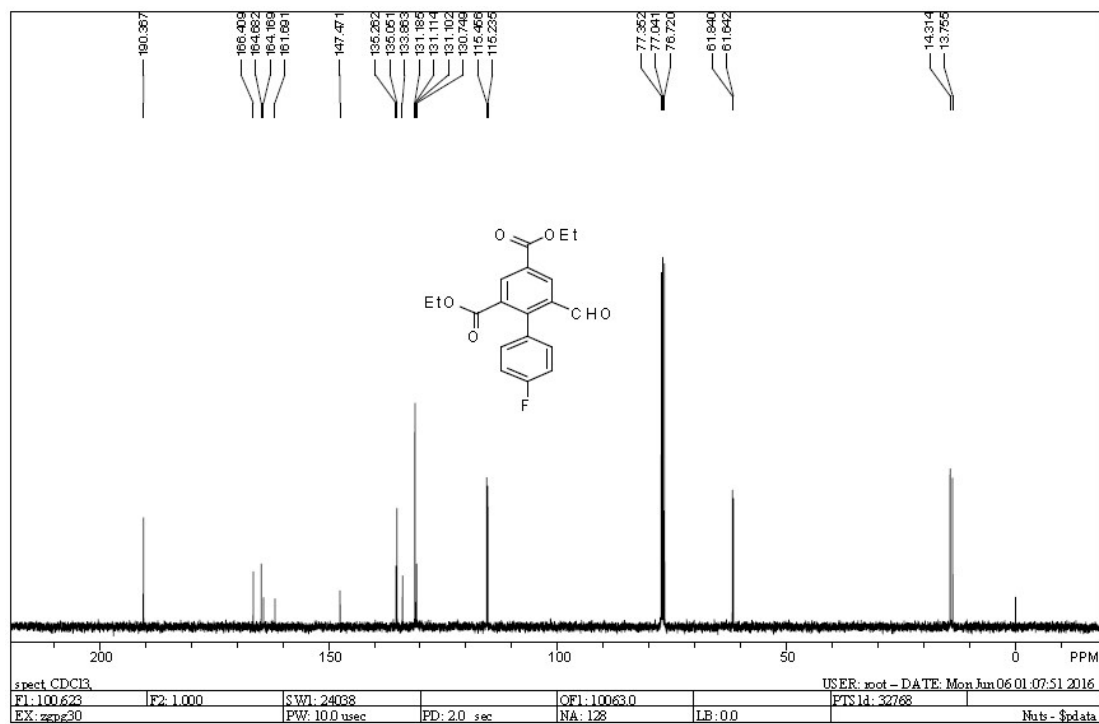
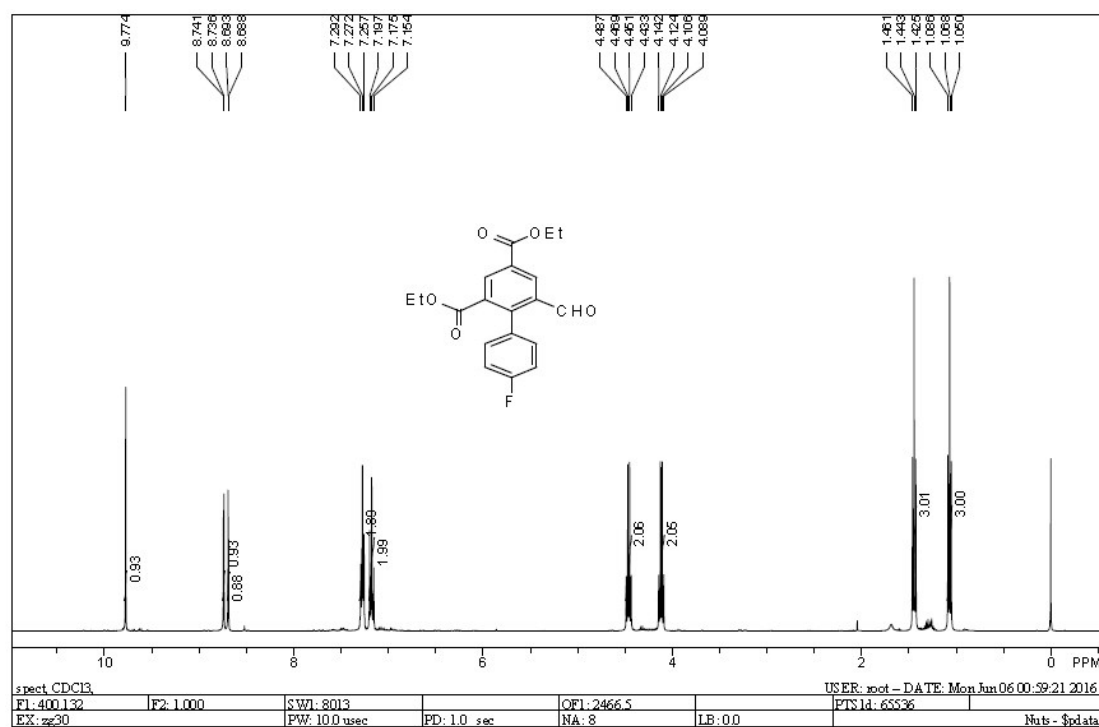
^1H and ^{13}C NMR of **3a**



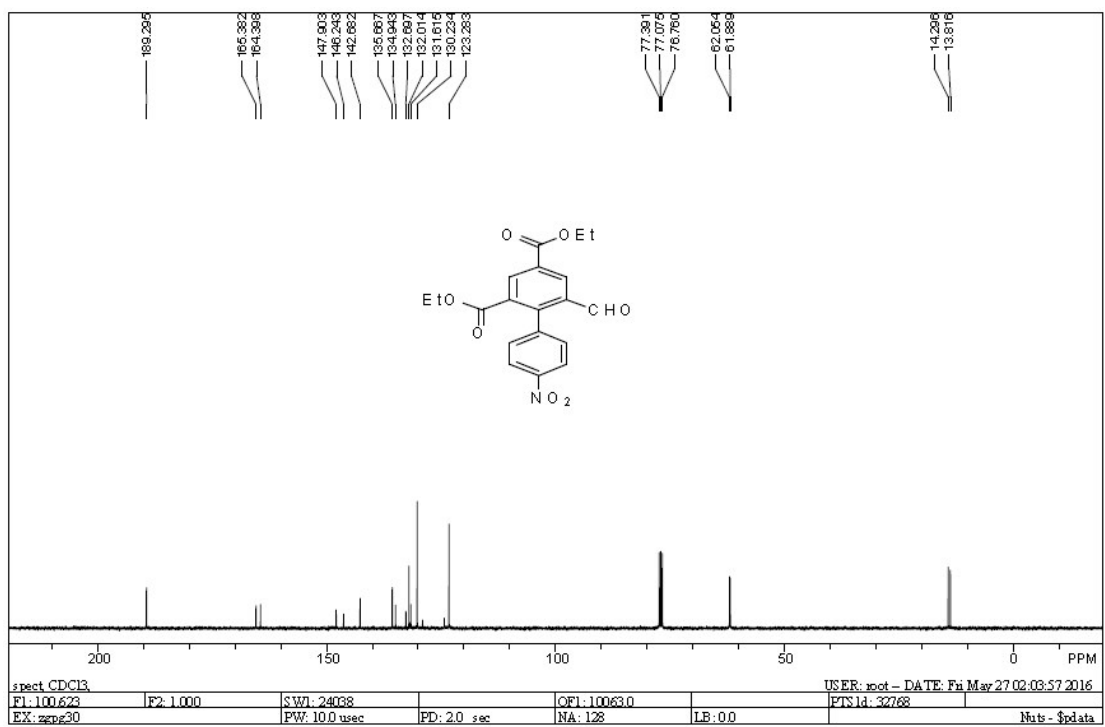
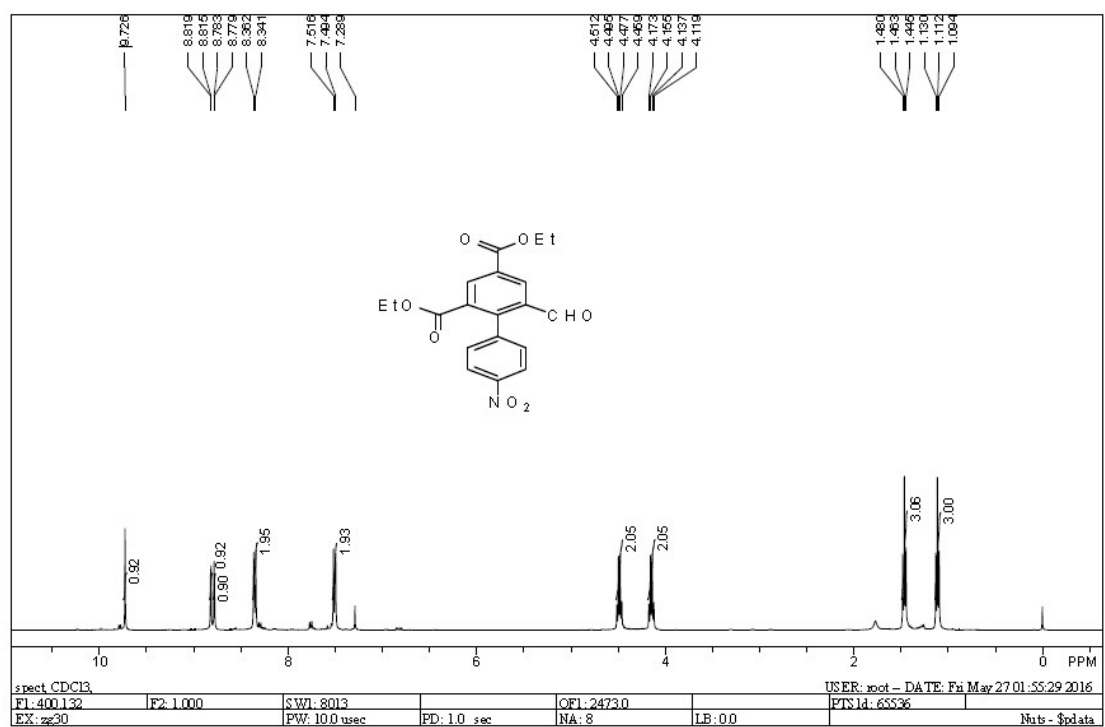
¹H and ¹³C NMR of **3b**



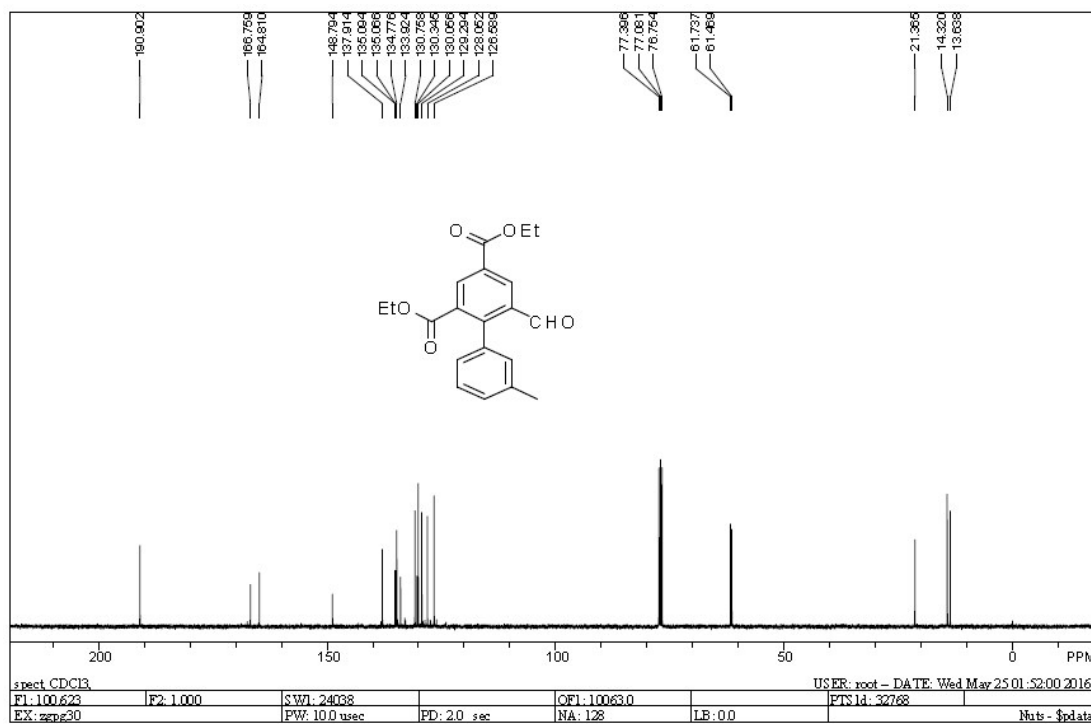
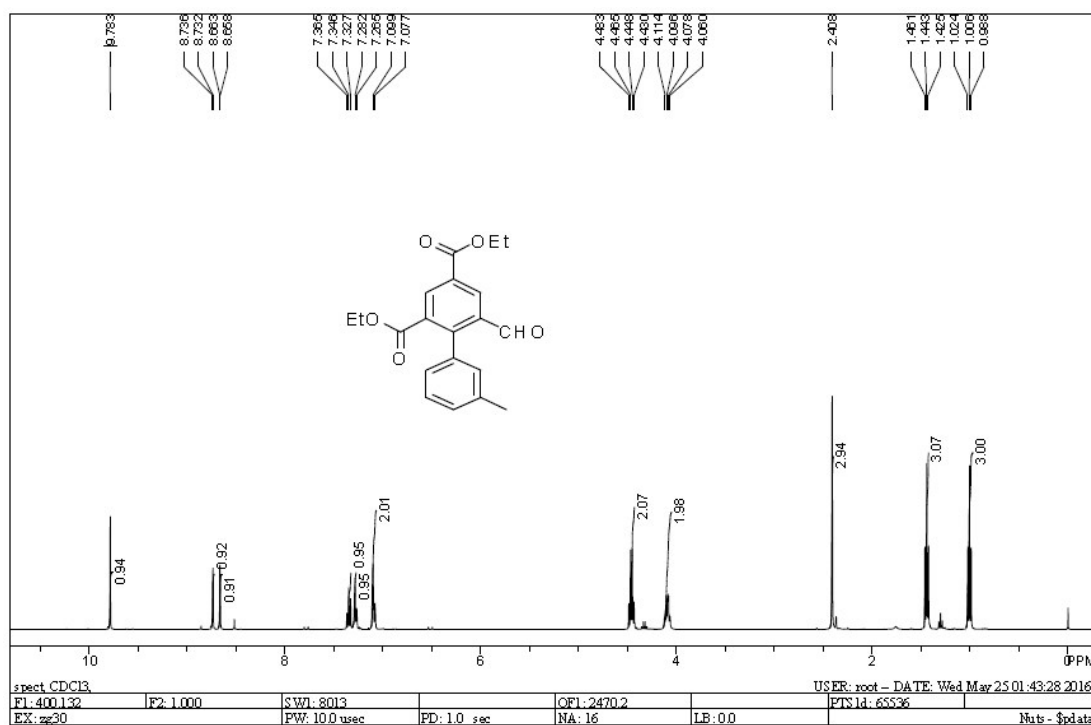
¹H and ¹³C NMR of 3c



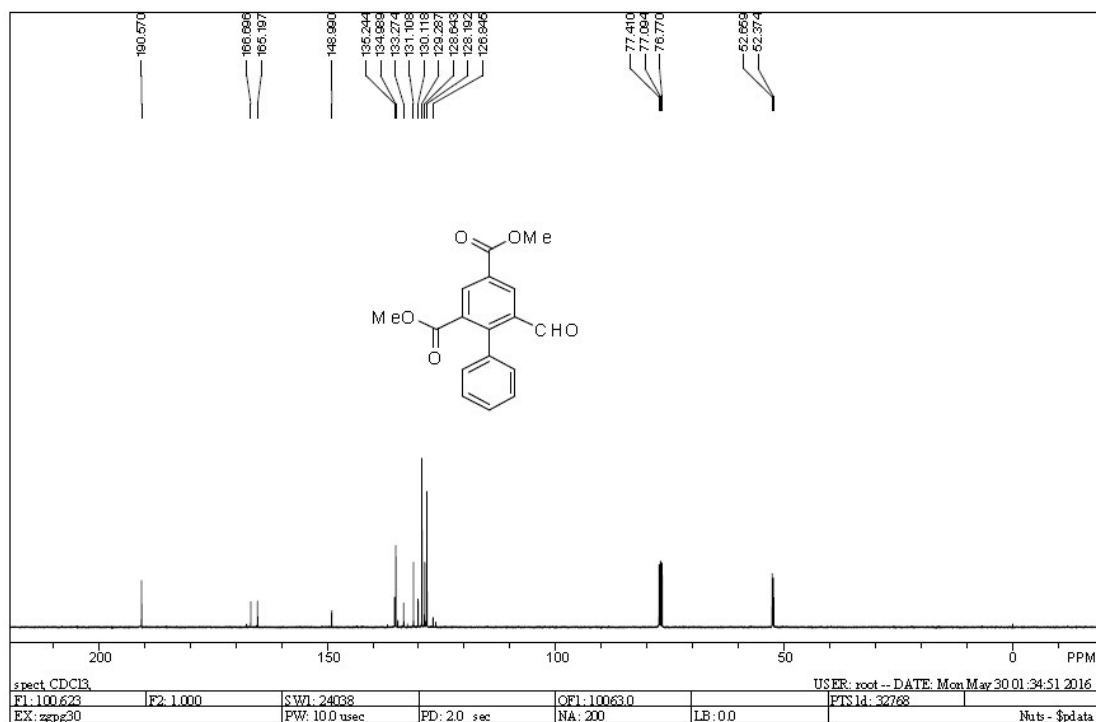
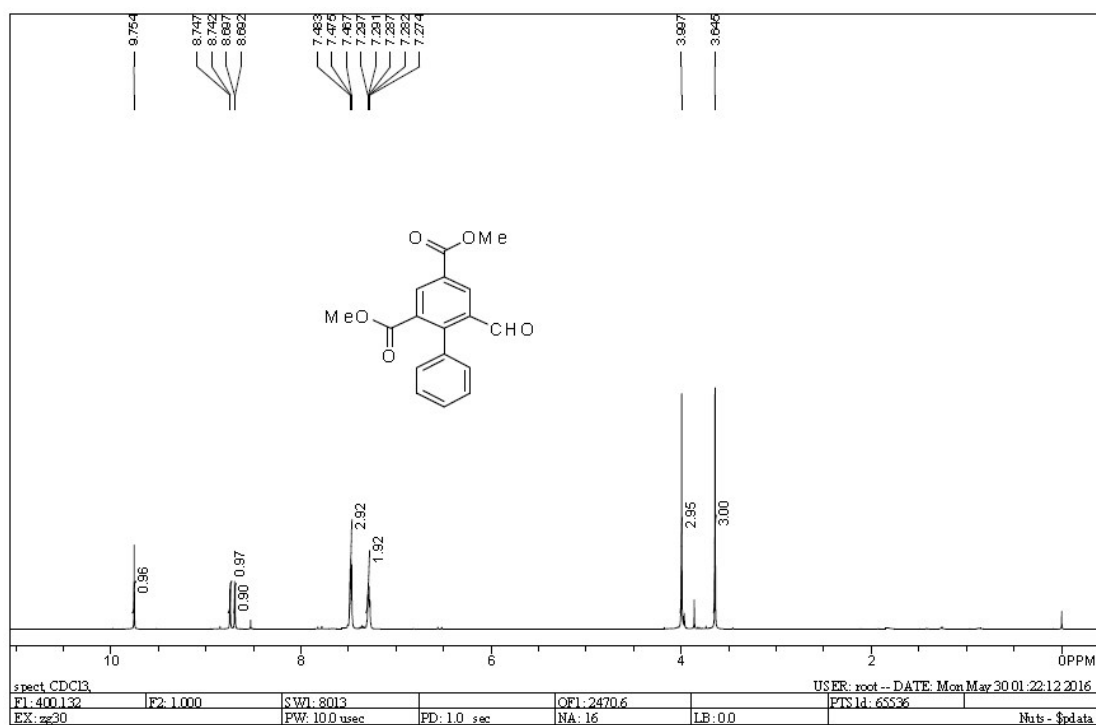
¹H and ¹³C NMR of **3d**



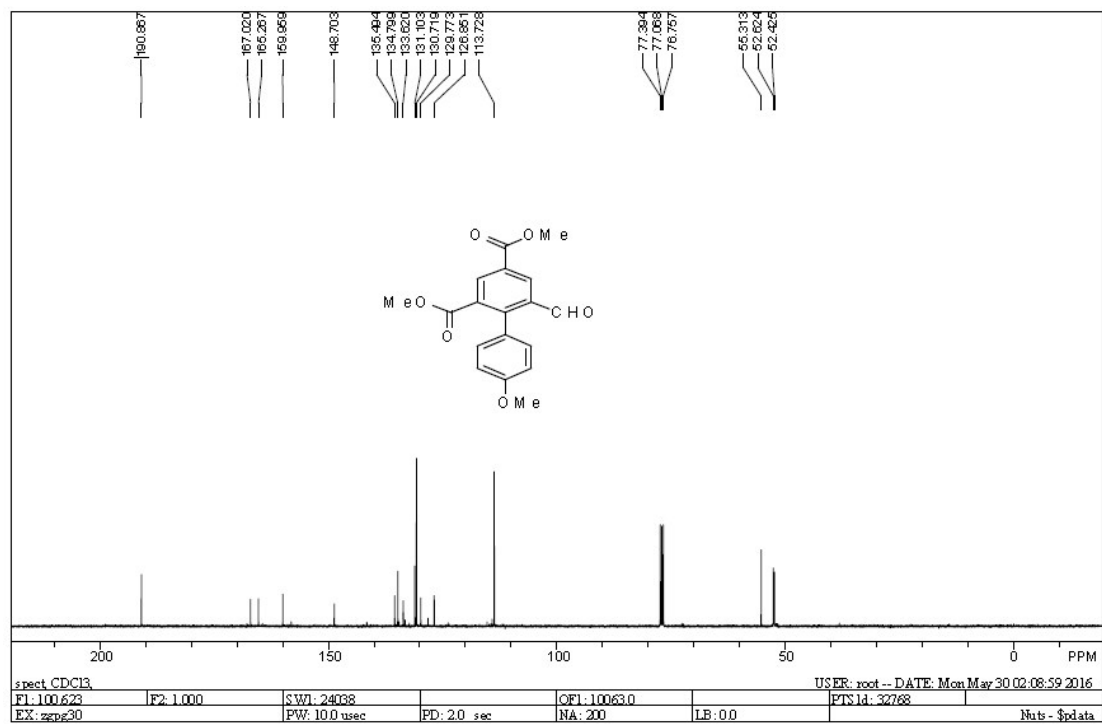
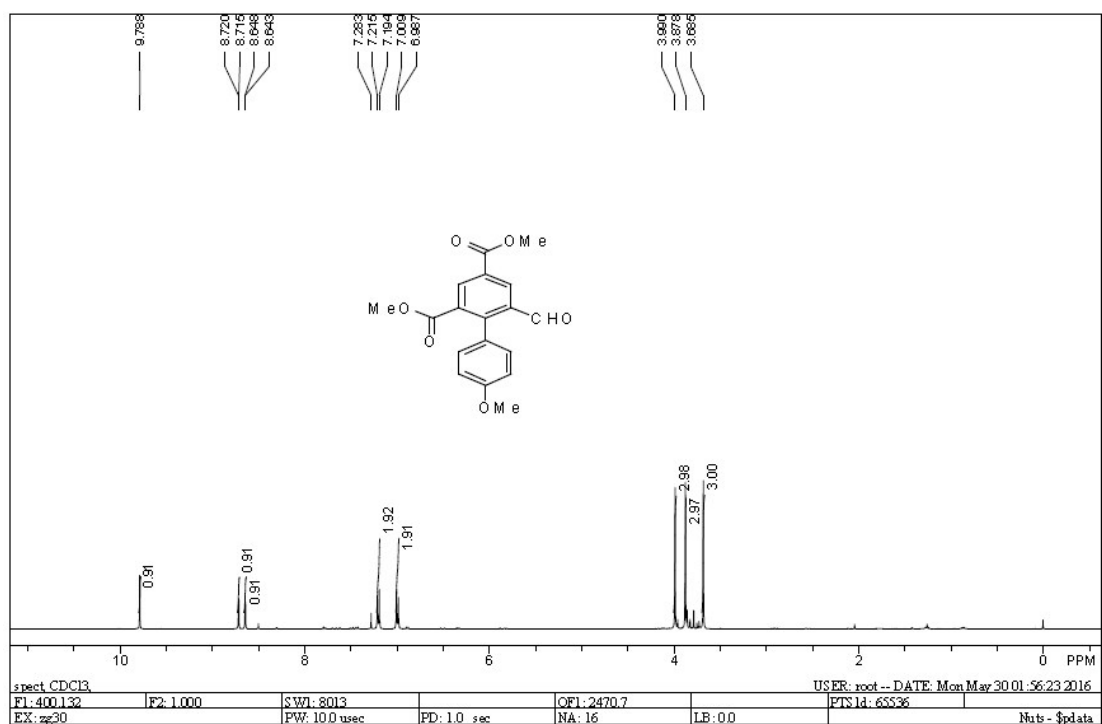
¹H and ¹³C NMR of 3e



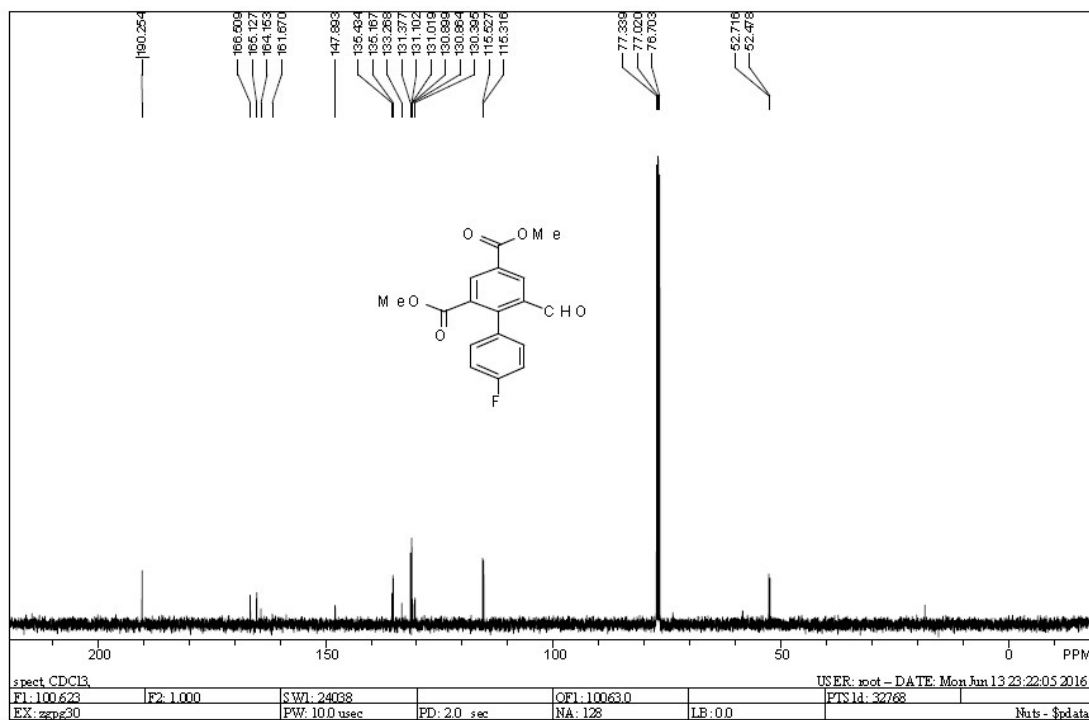
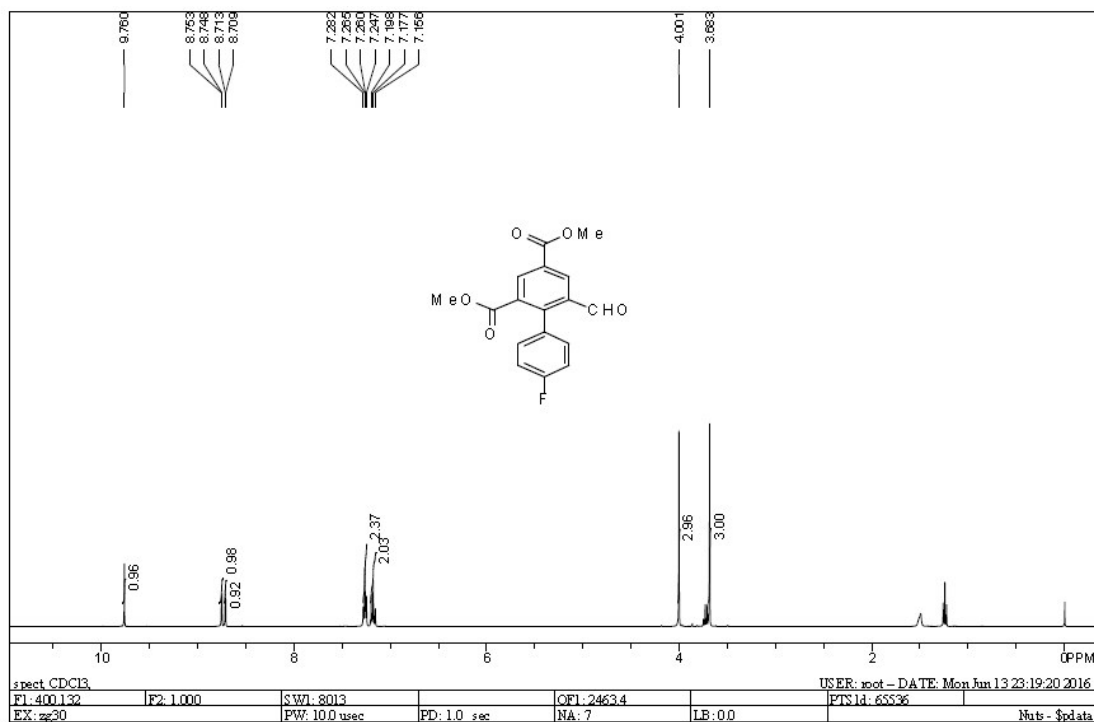
^1H and ^{13}C NMR of **3f**



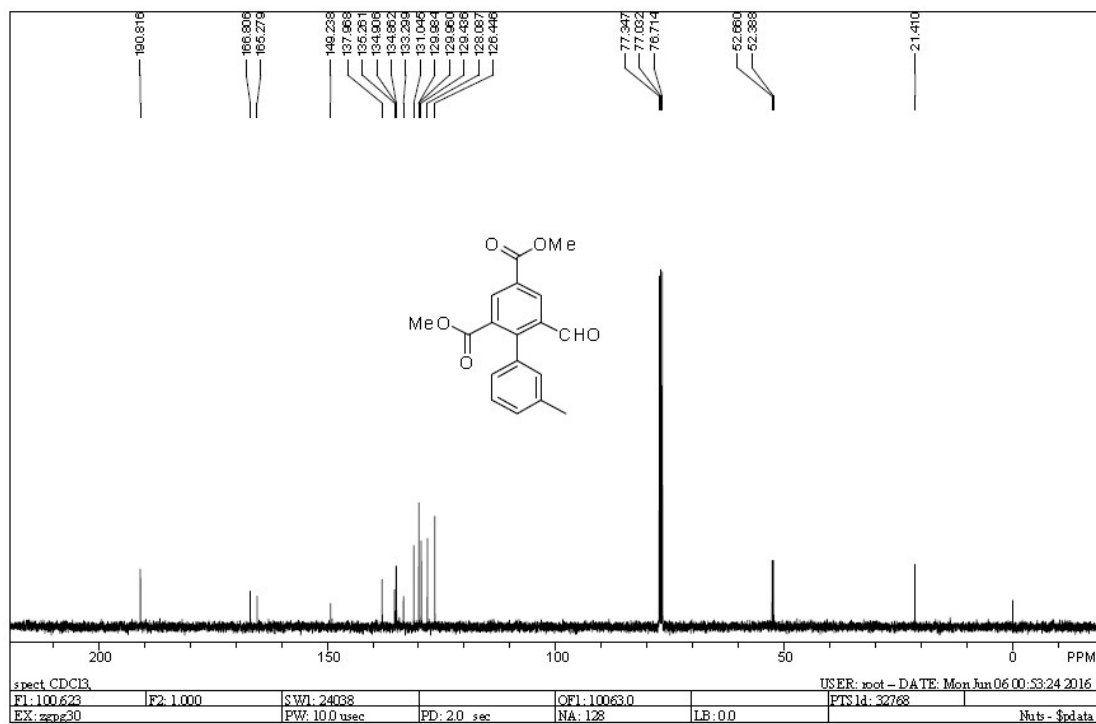
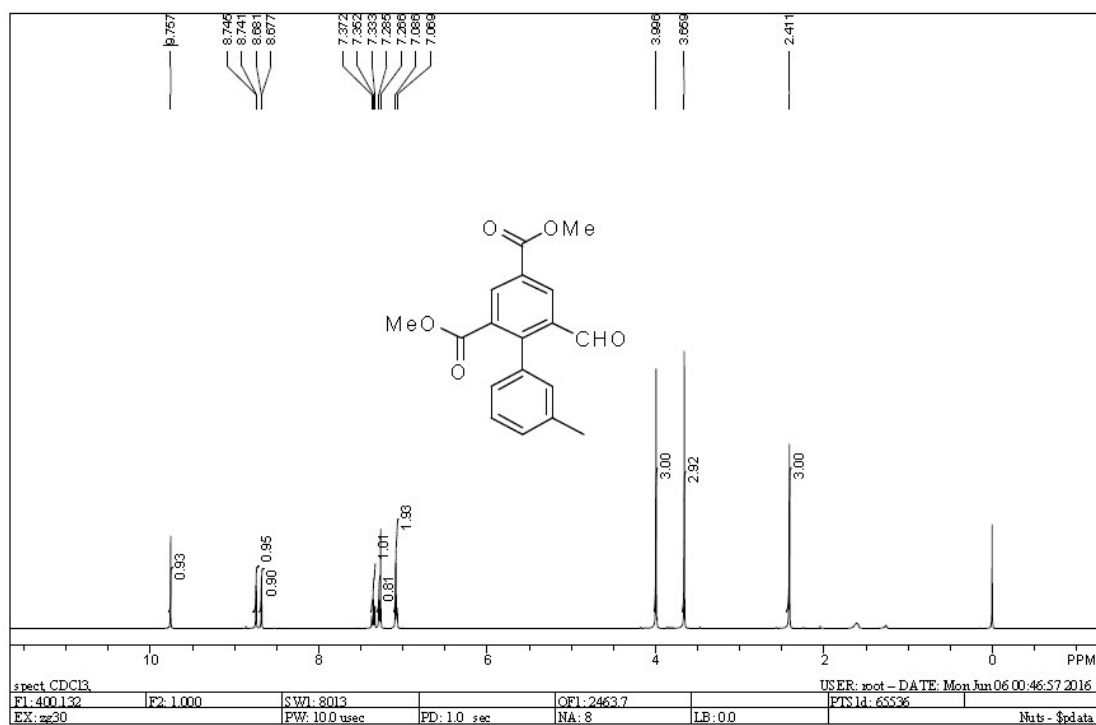
¹H and ¹³C NMR of **3g**



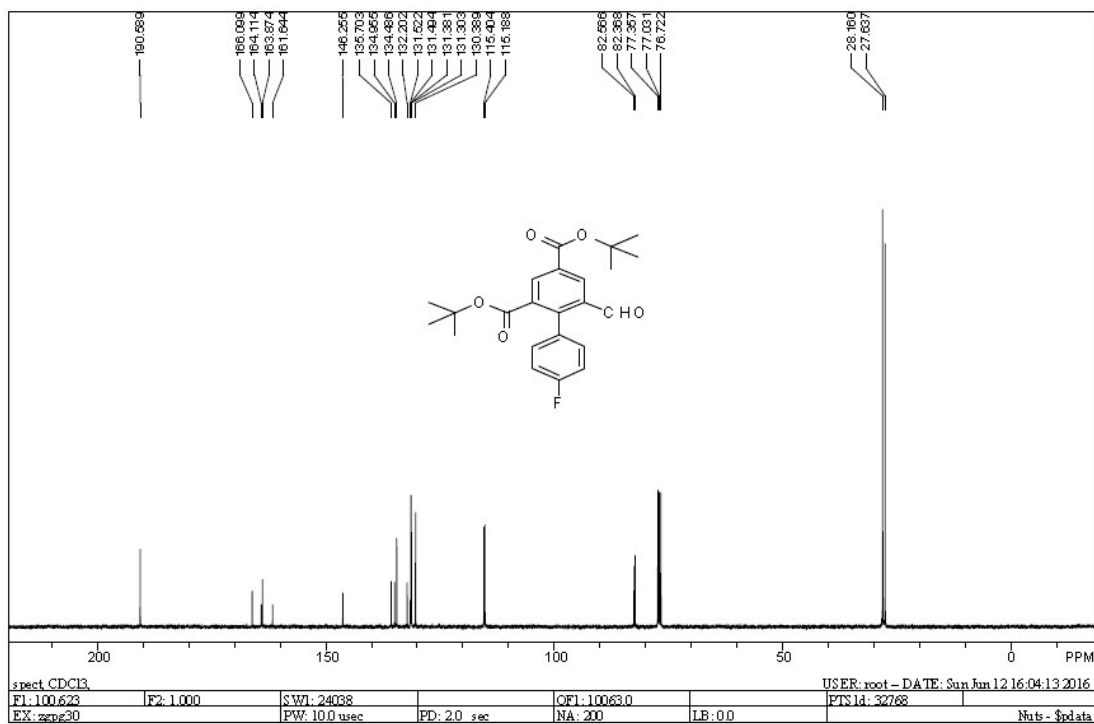
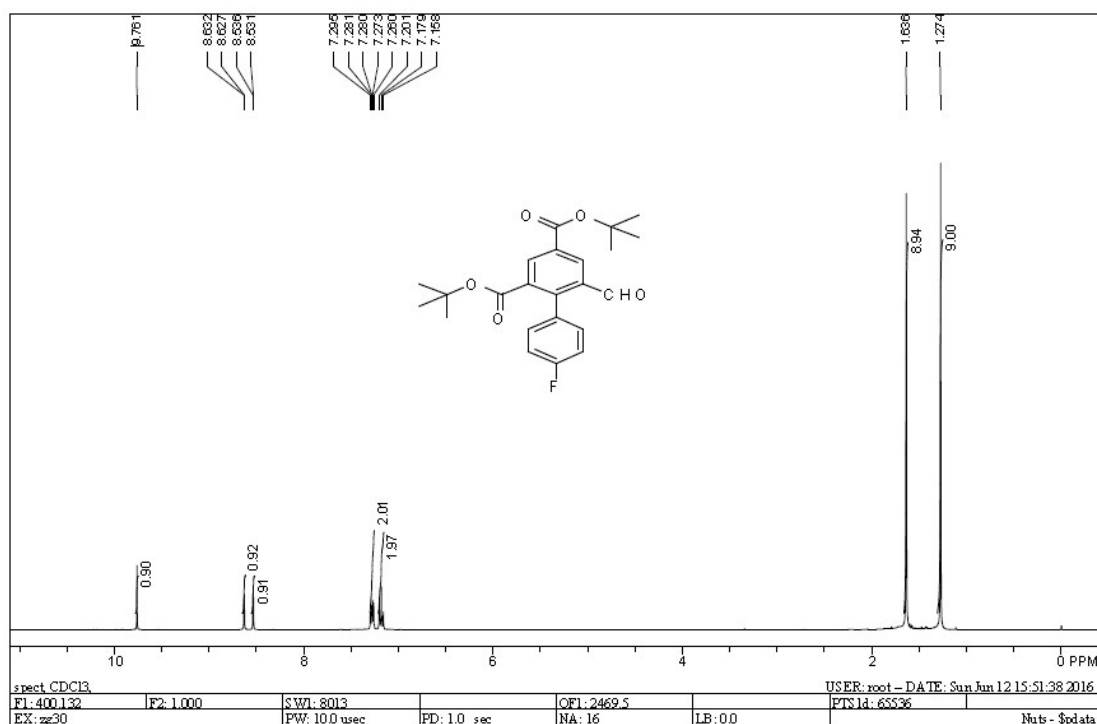
¹H and ¹³C NMR of **3h**



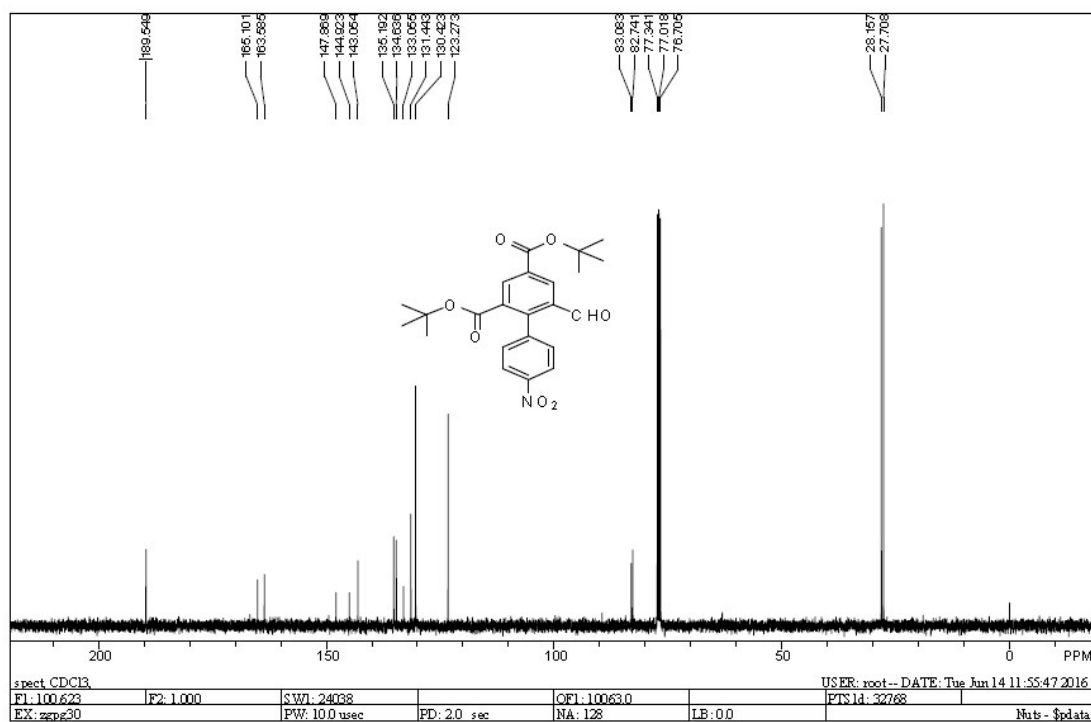
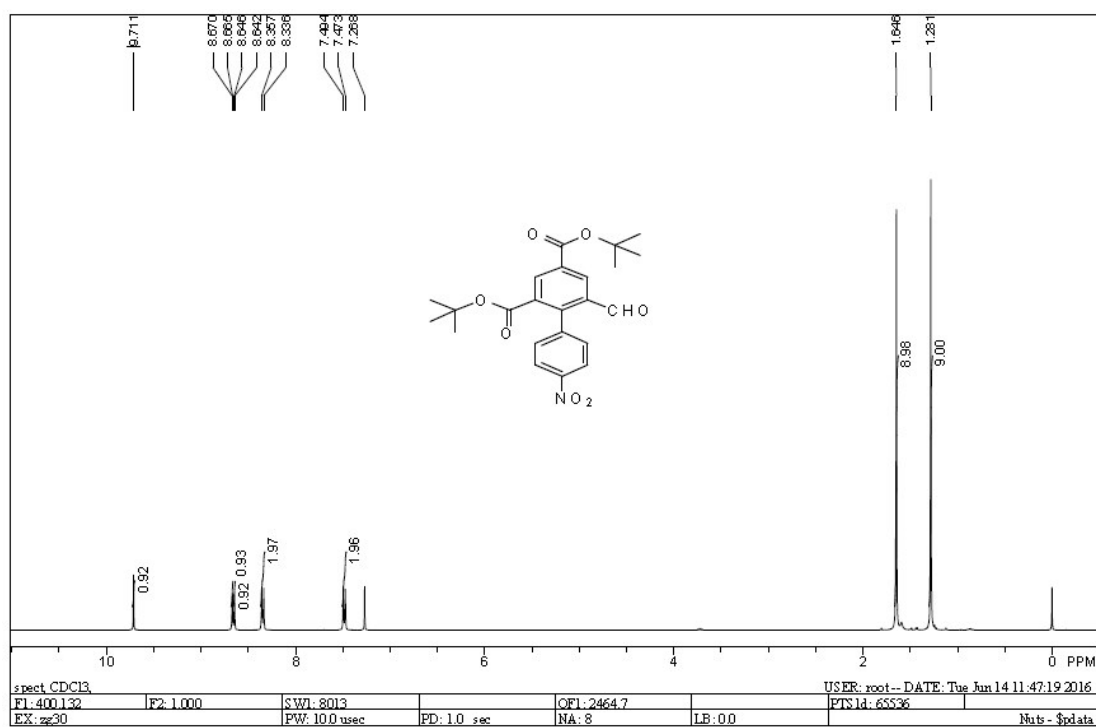
¹H and ¹³C NMR of **3i**



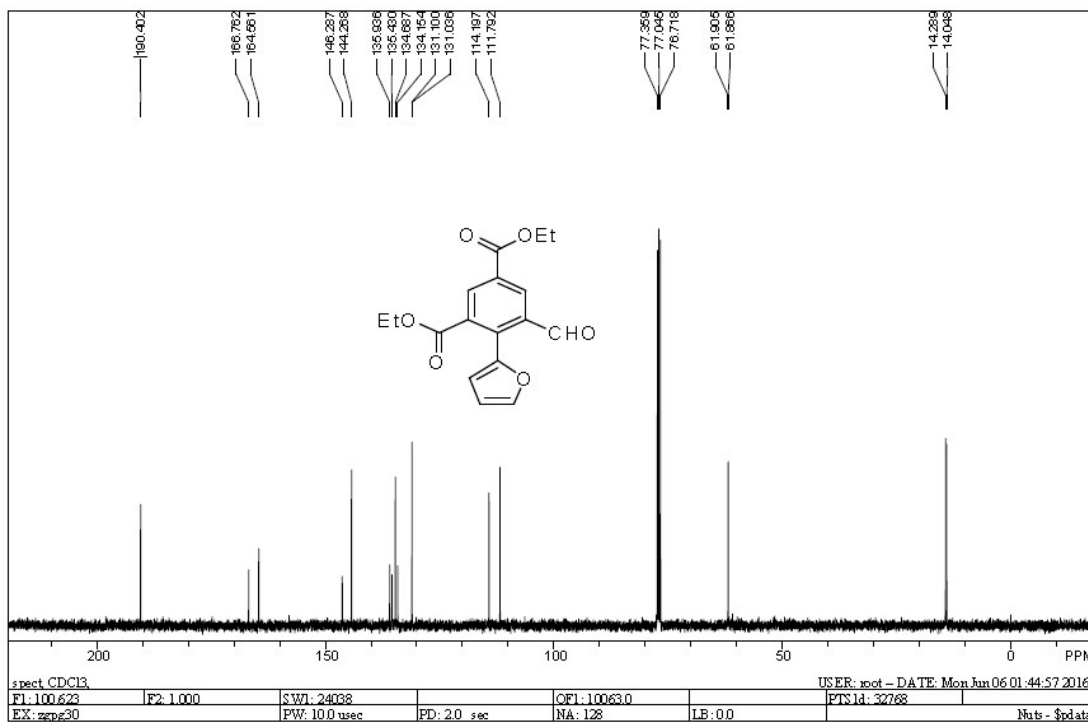
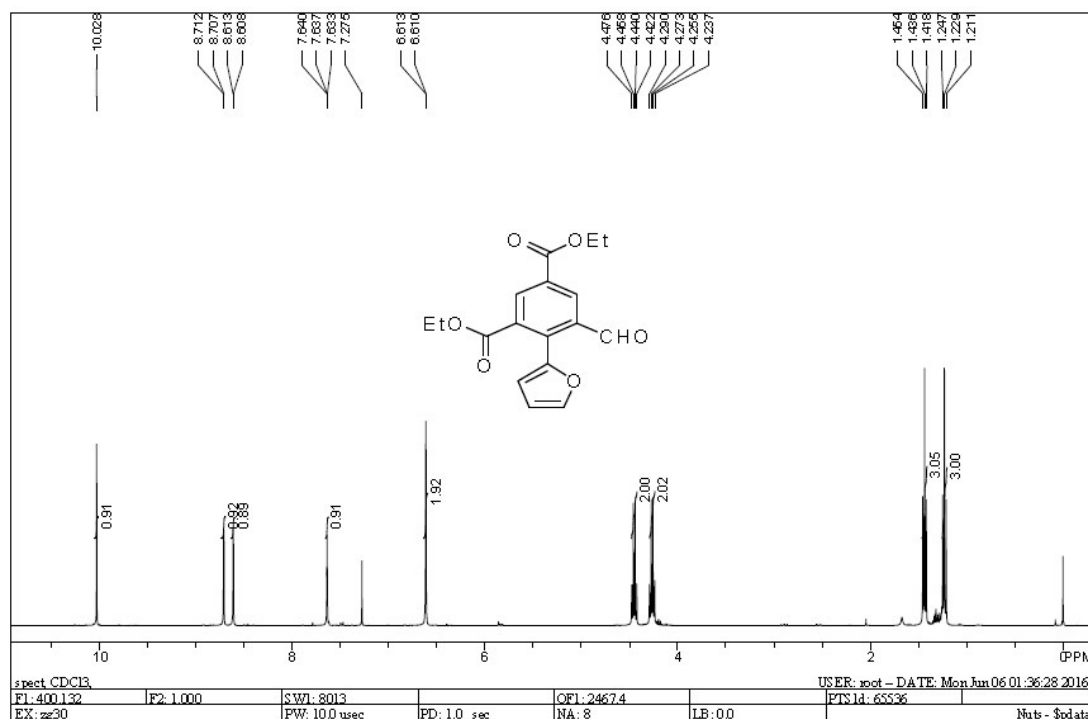
¹H and ¹³C NMR of **3j**



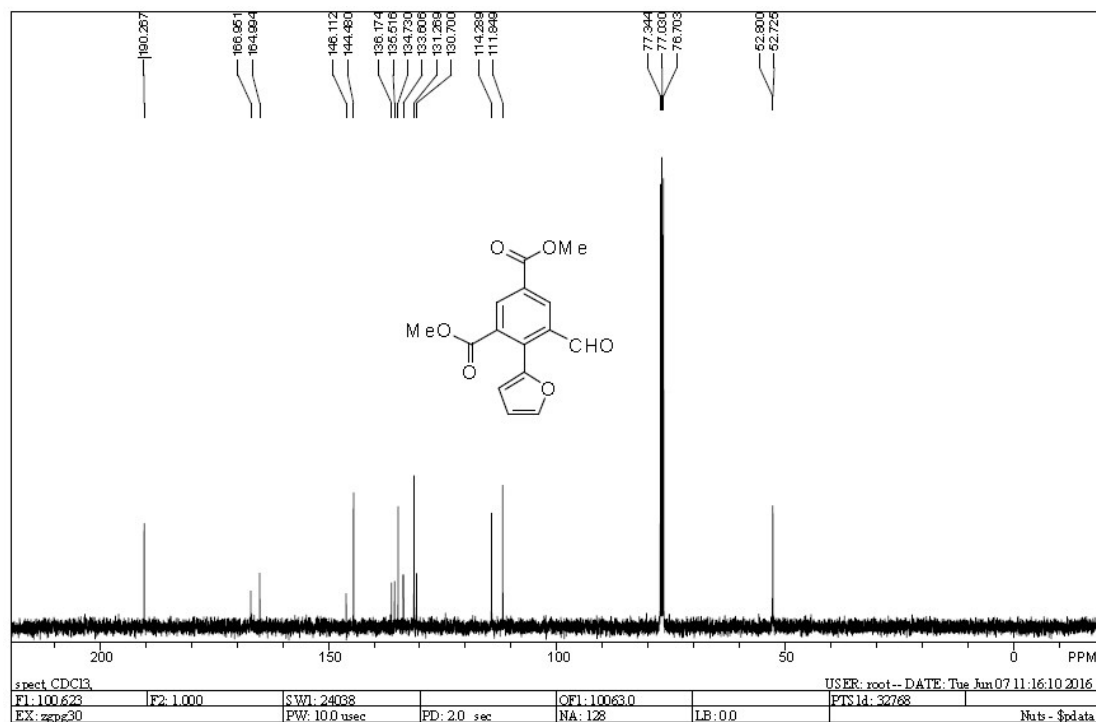
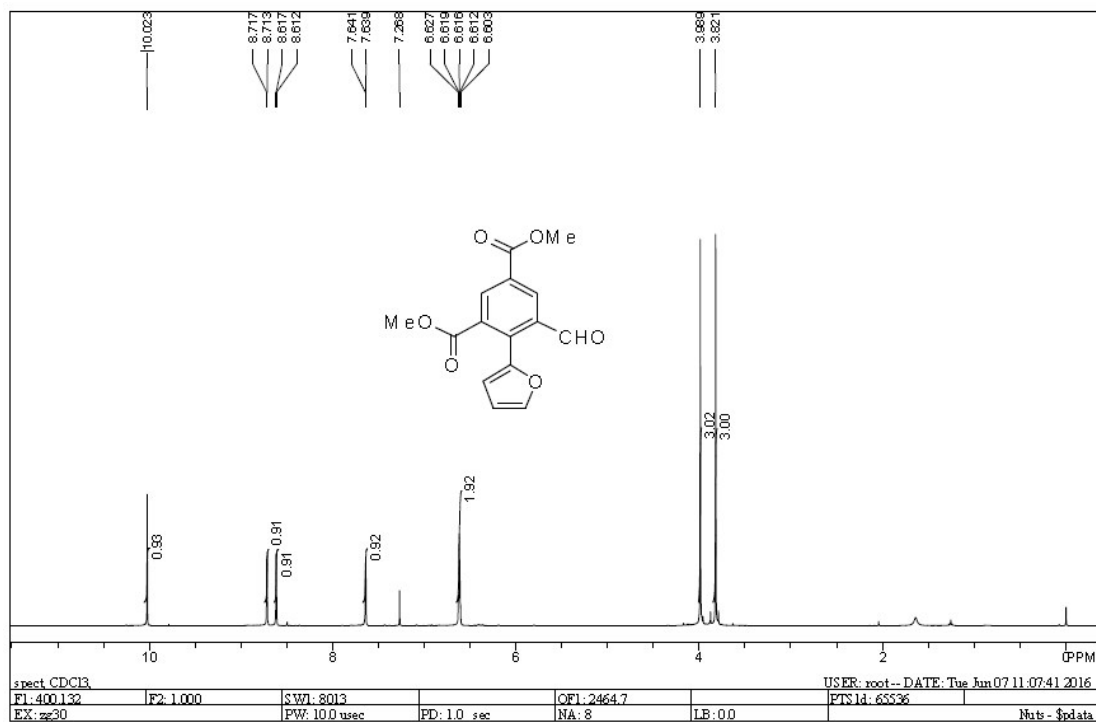
¹H and ¹³C NMR of **3k**



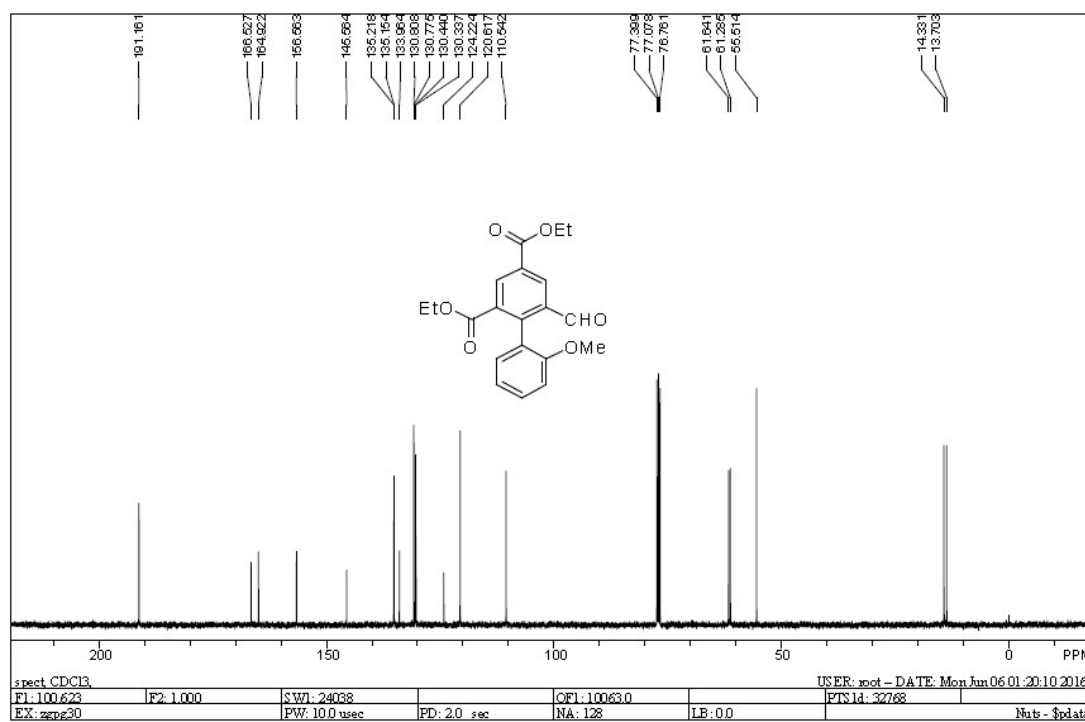
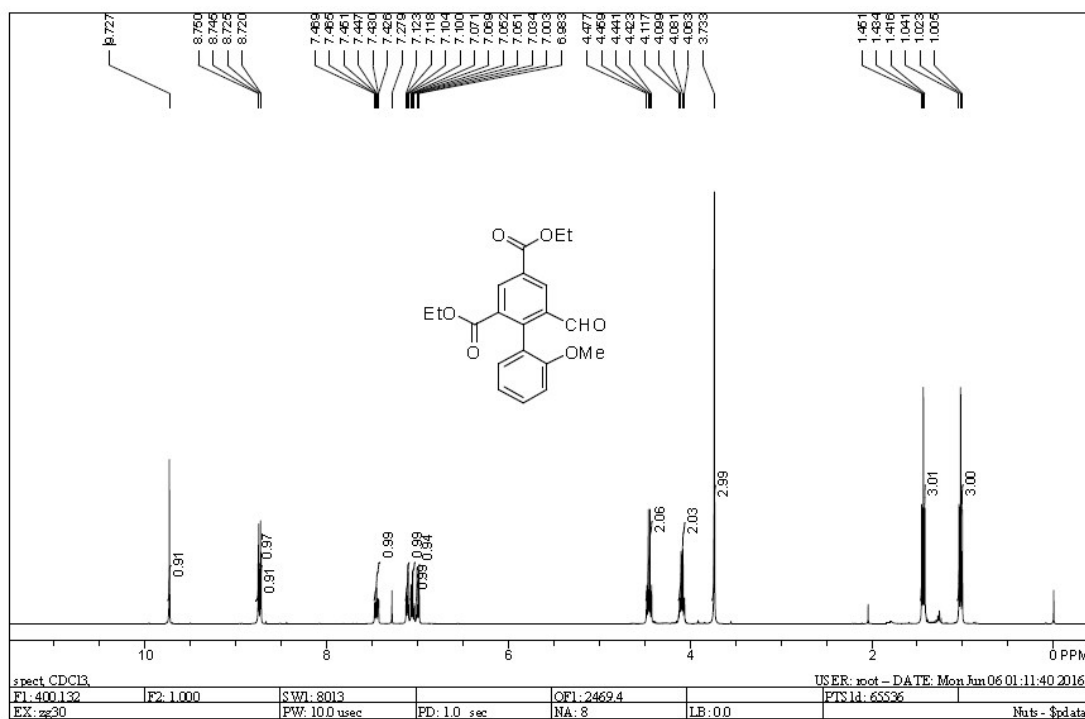
^1H and ^{13}C NMR of **31**



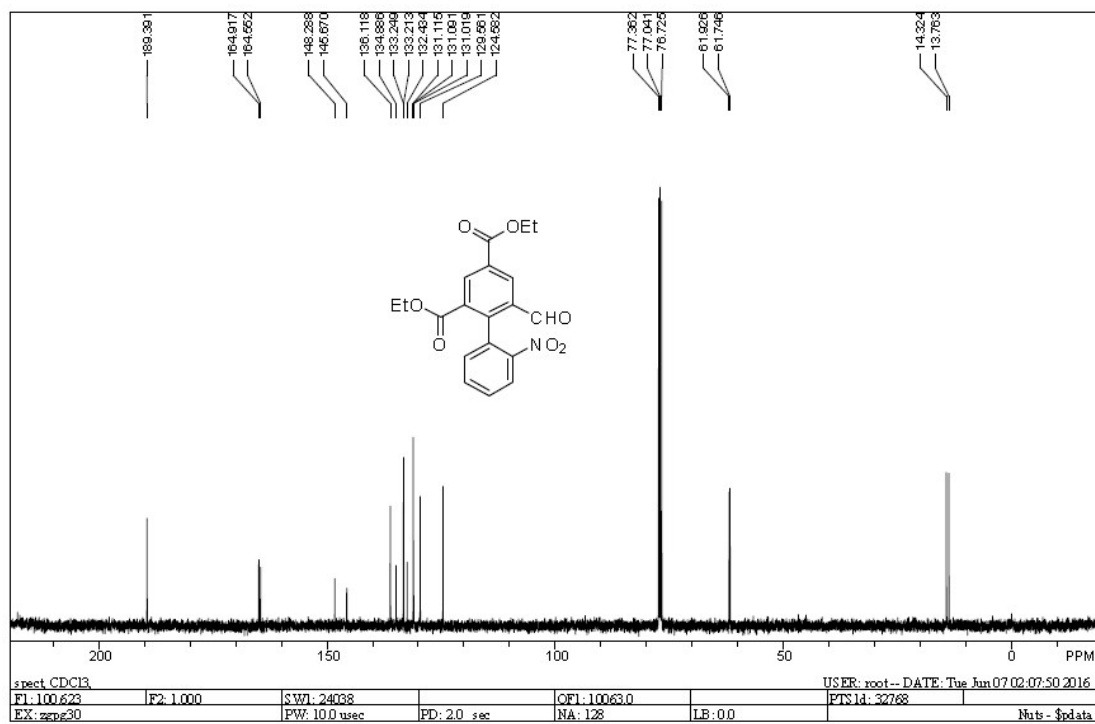
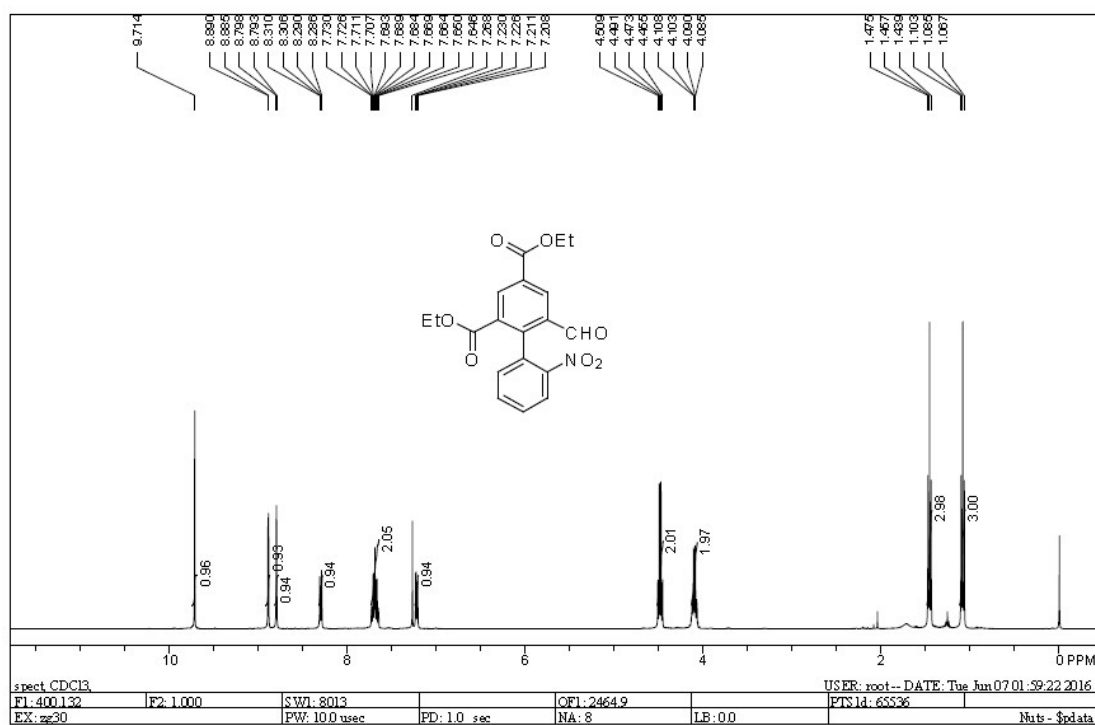
¹H and ¹³C NMR of **3m**



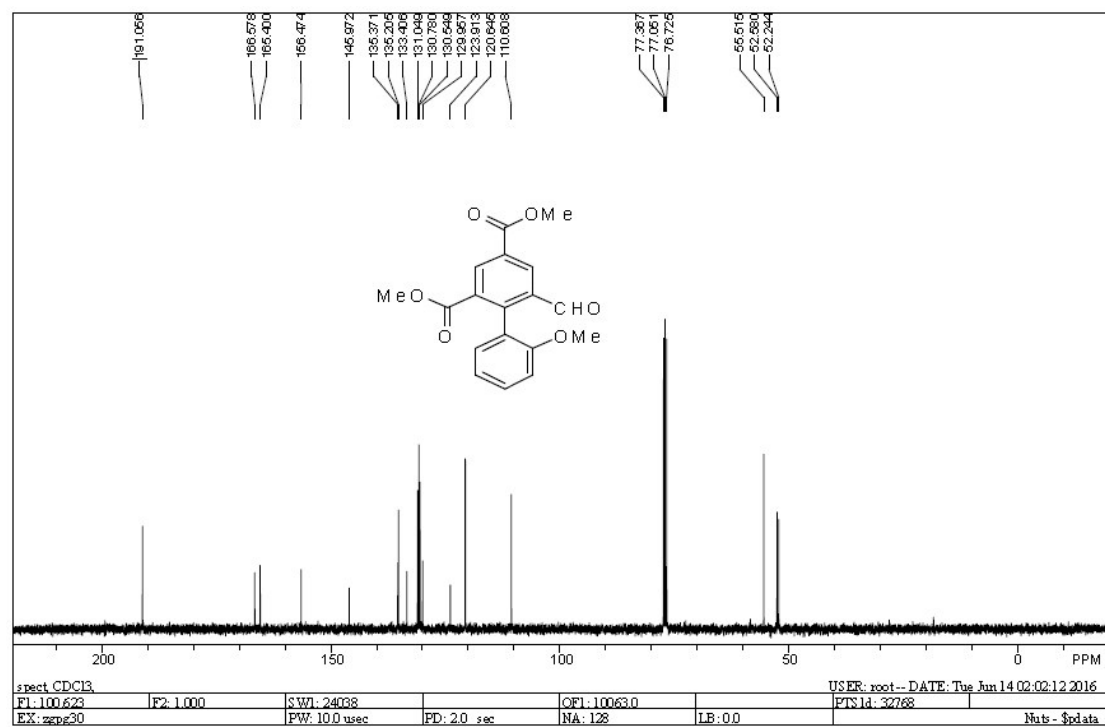
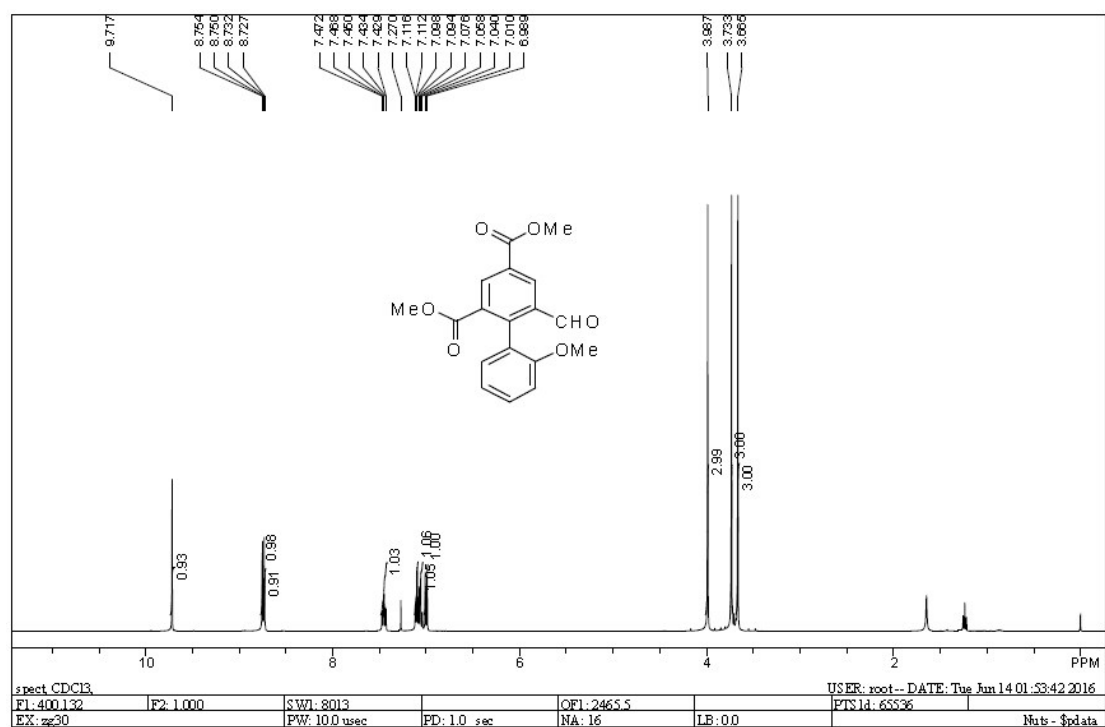
¹H and ¹³C NMR of **3n**



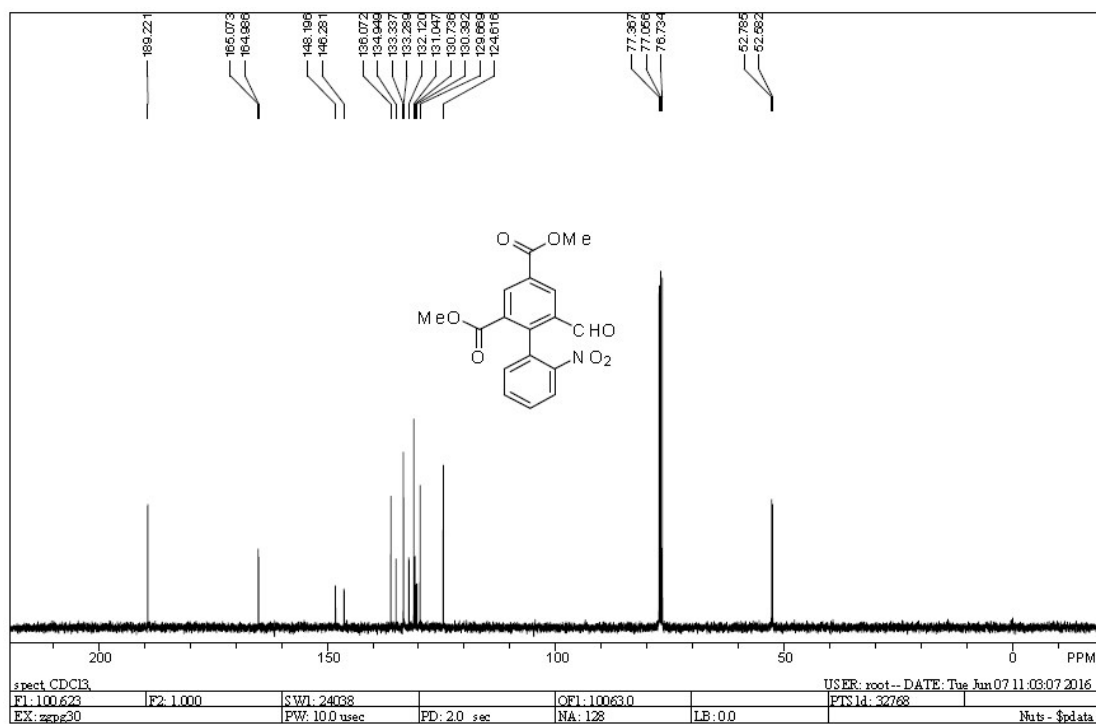
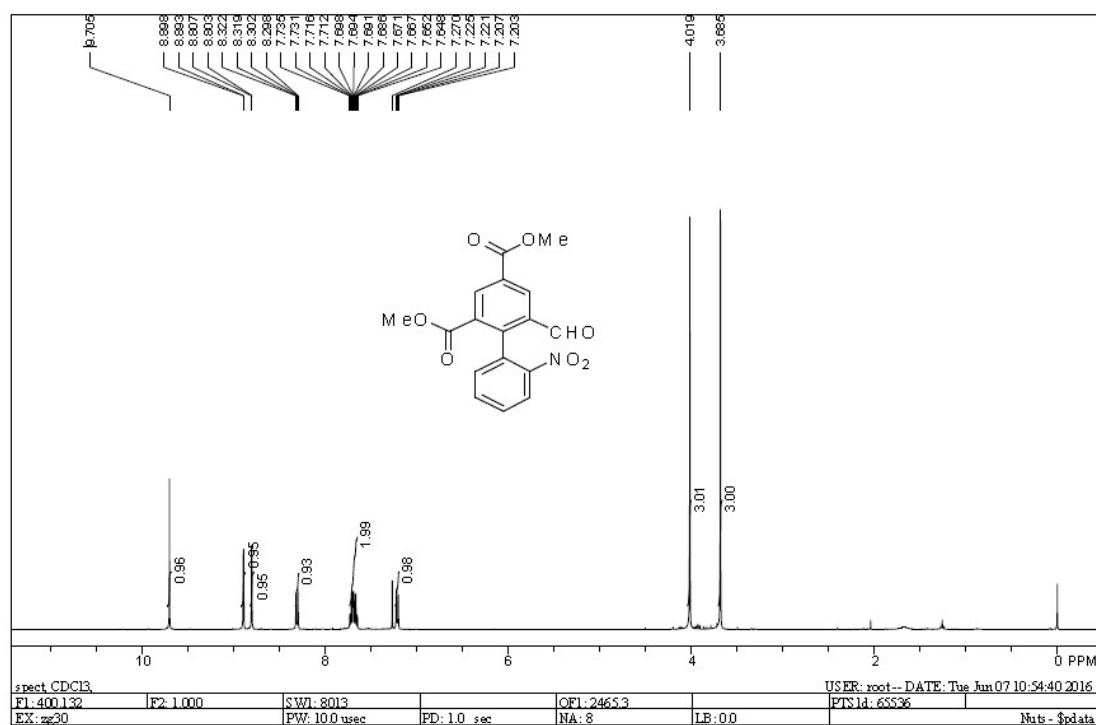
¹H and ¹³C NMR of **3o**



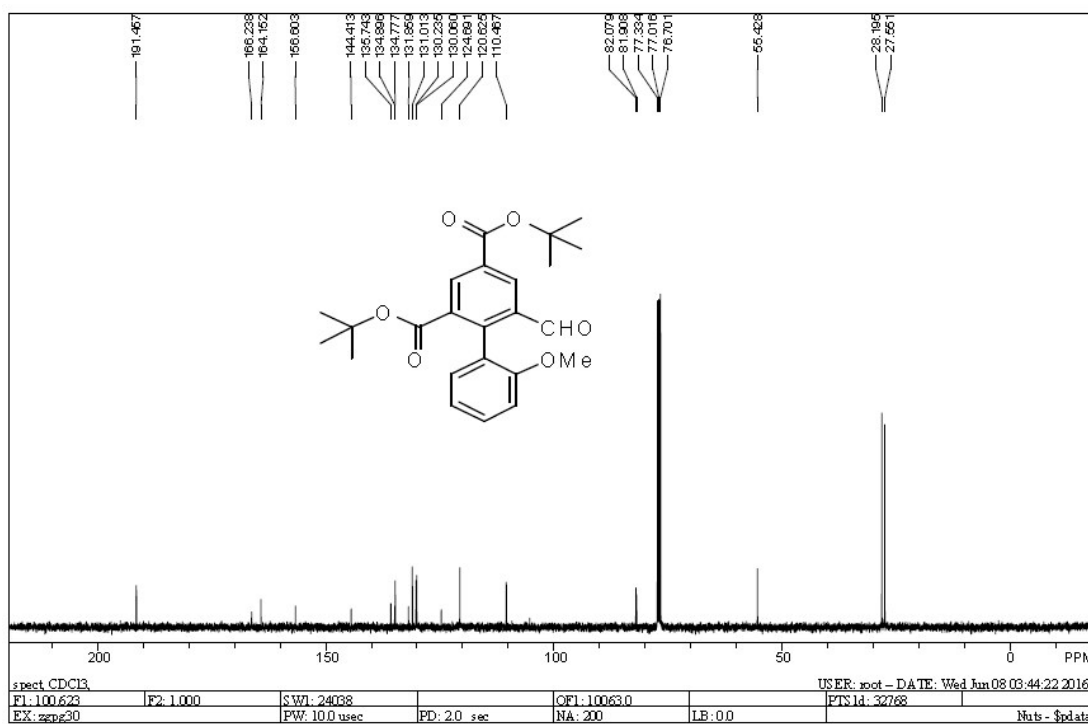
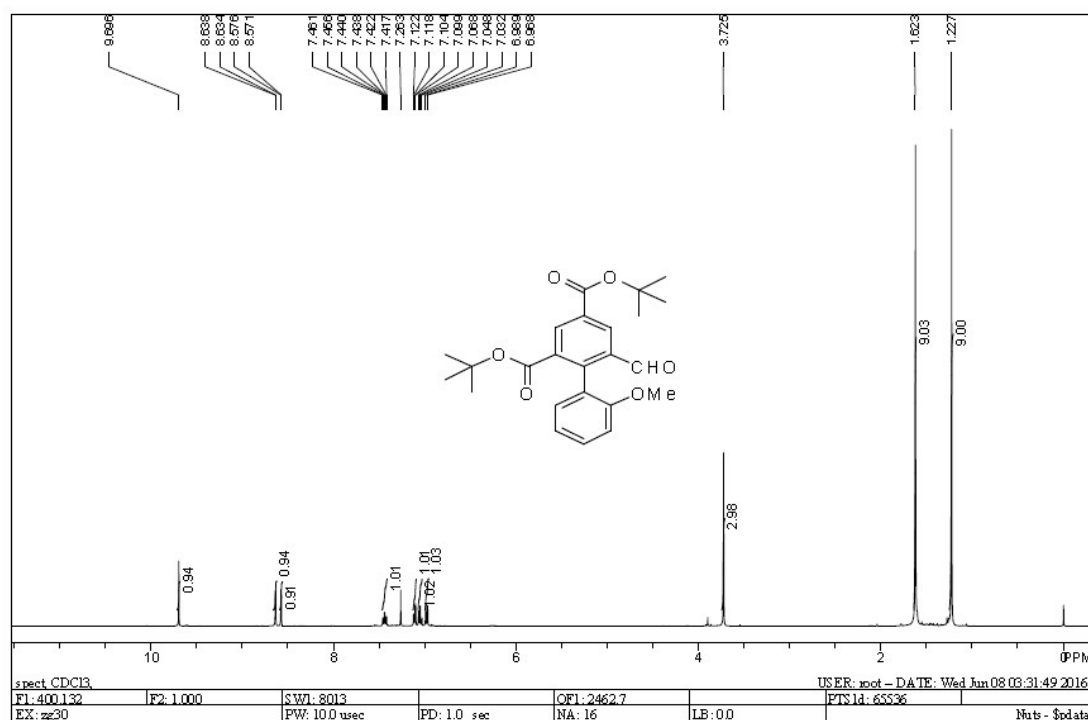
^1H and ^{13}C NMR of **3p**



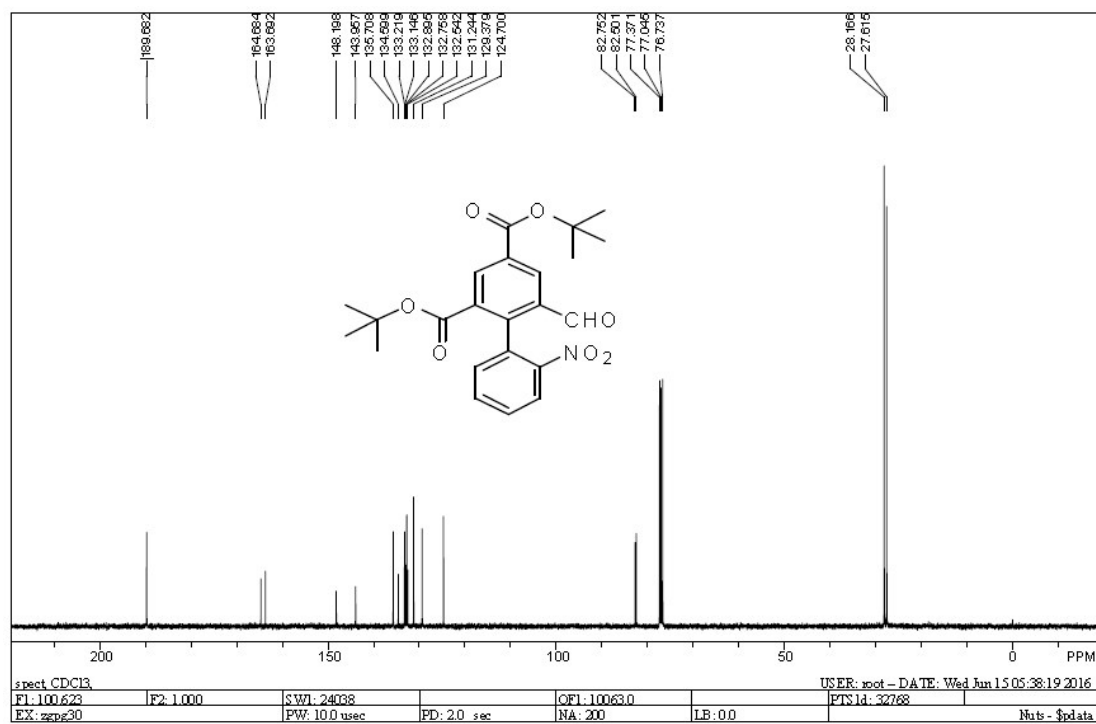
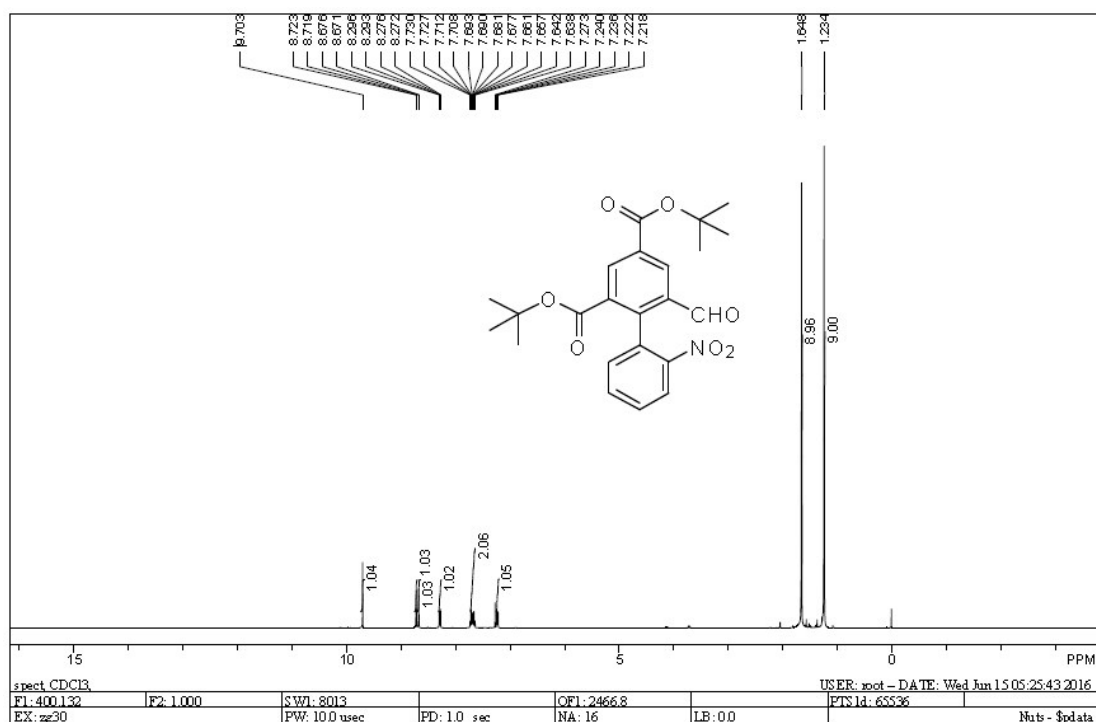
¹H and ¹³C NMR of 3q



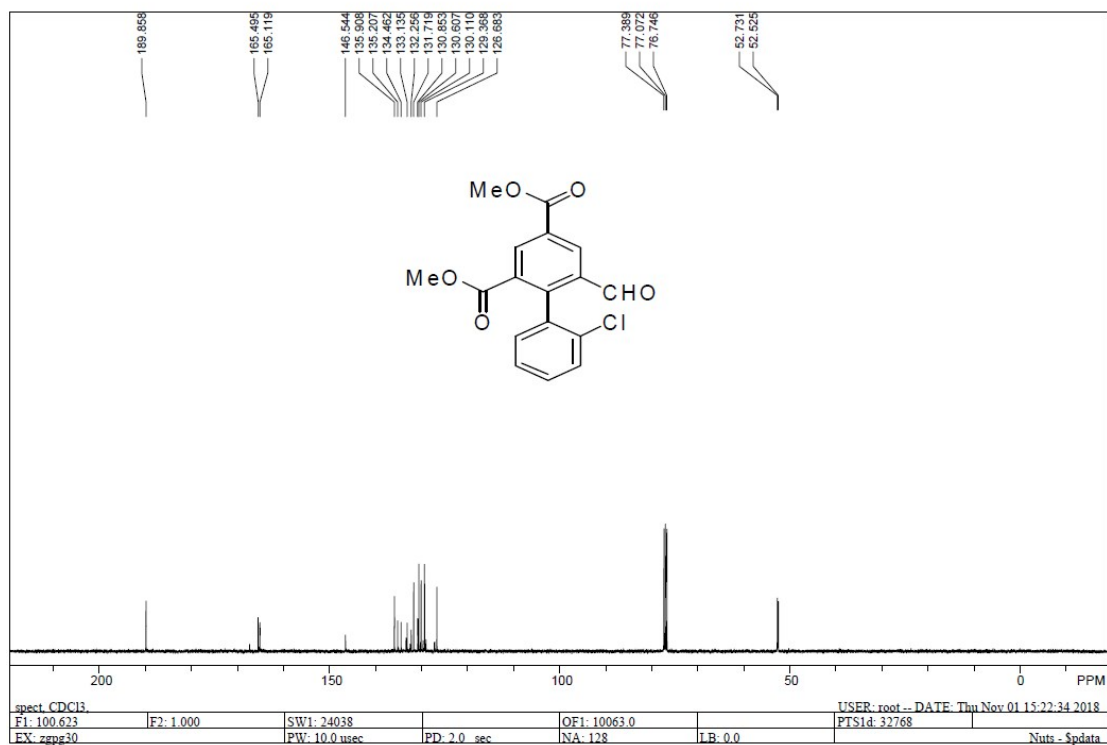
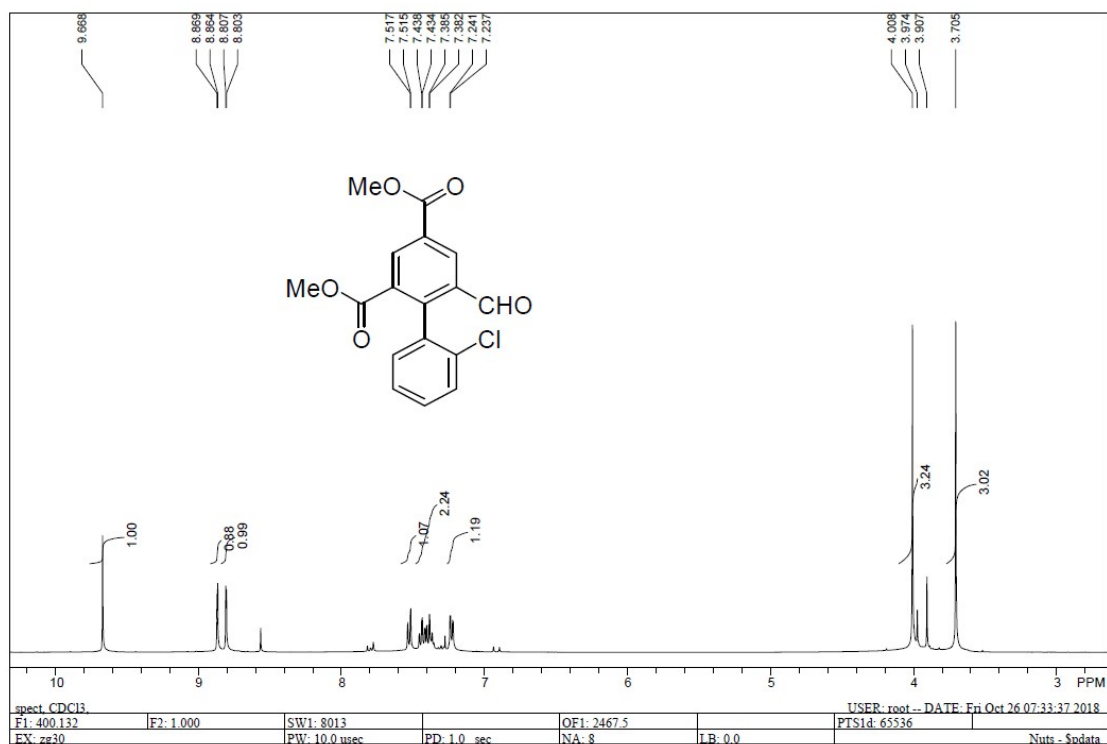
¹H and ¹³C NMR of **3r**



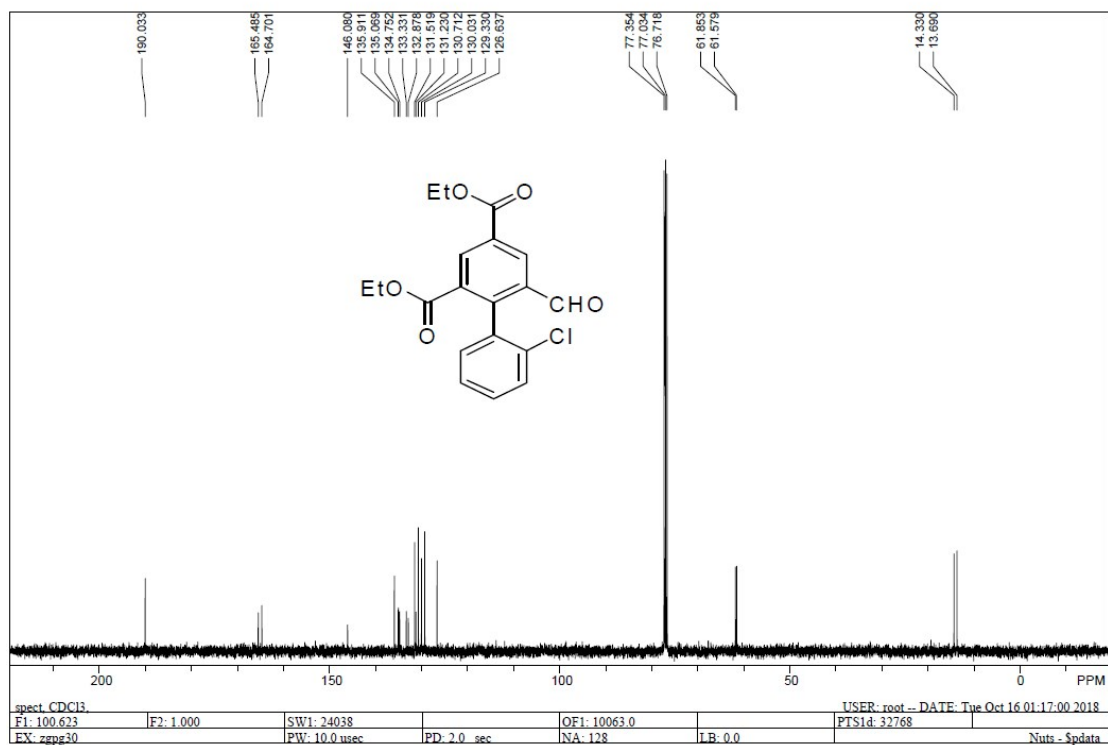
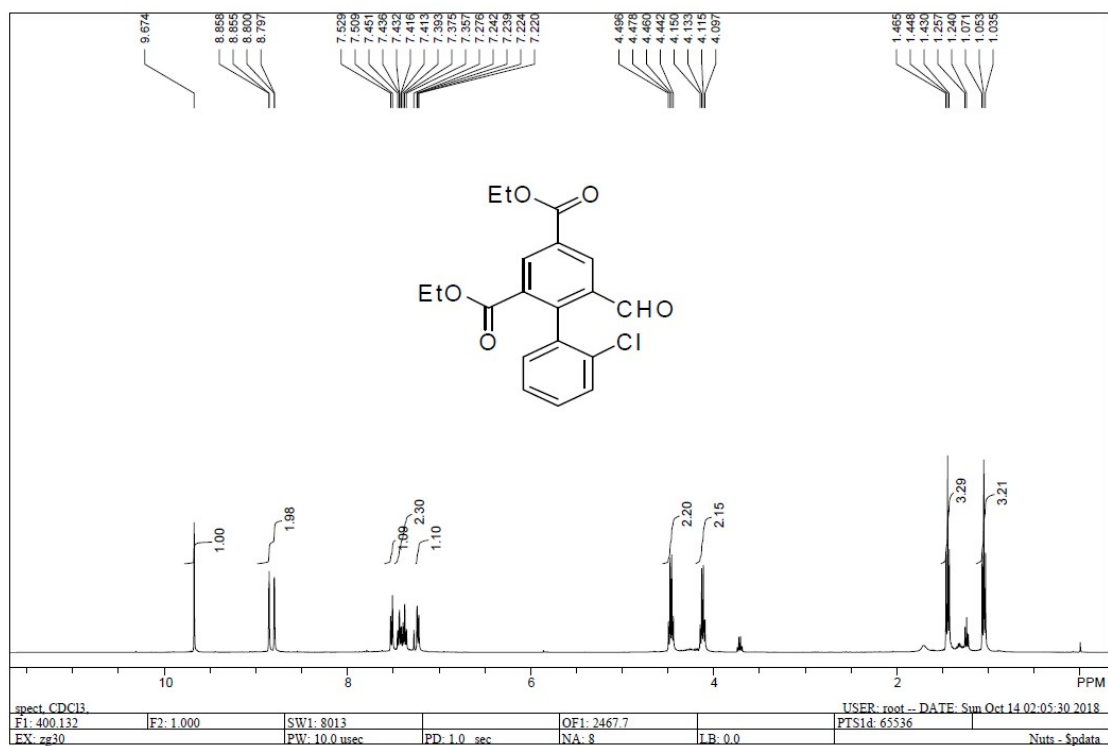
¹H and ¹³C NMR of **3s**



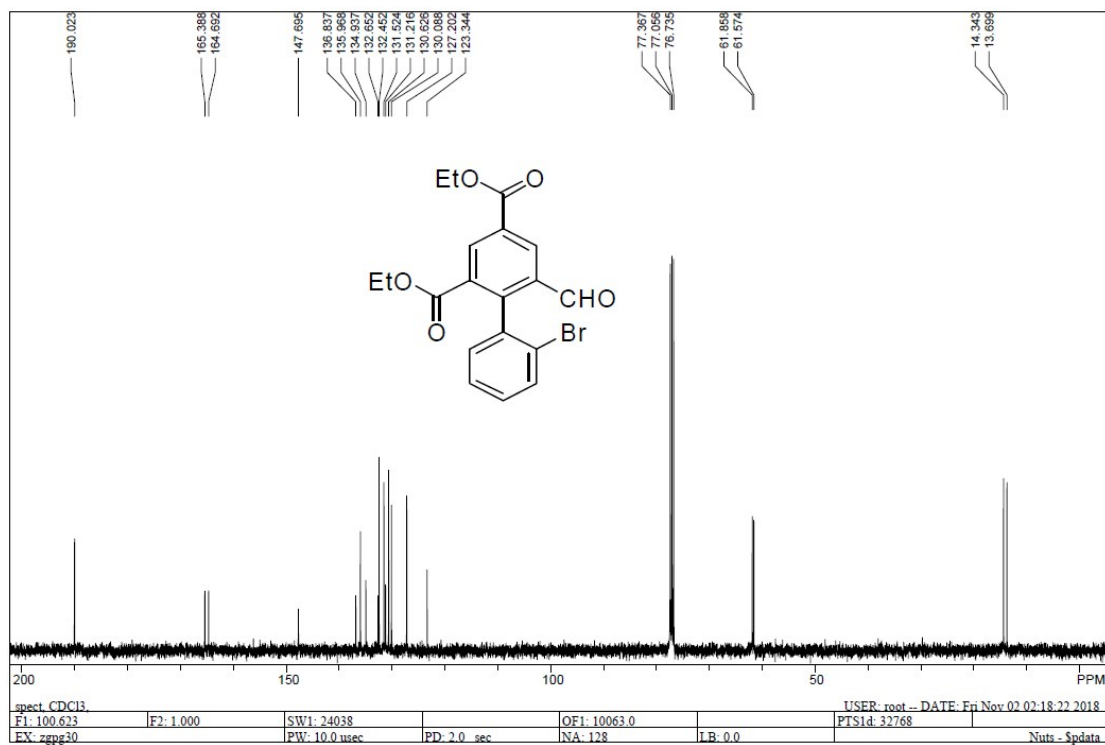
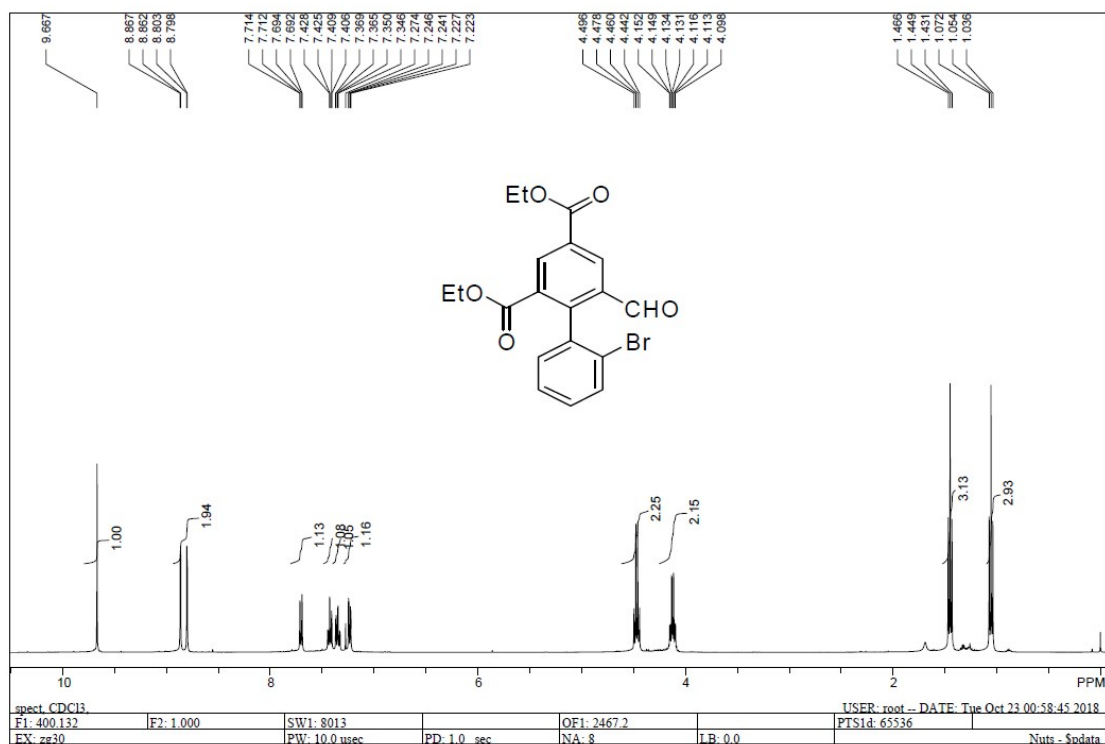
¹H and ¹³C NMR of 3t



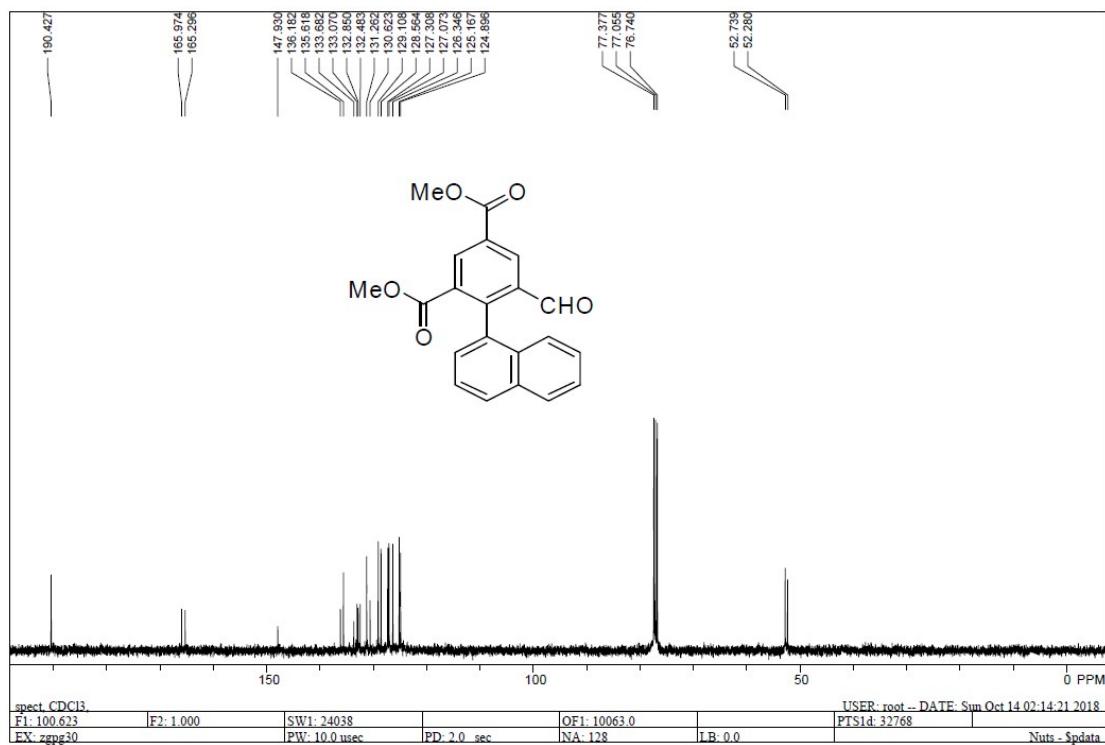
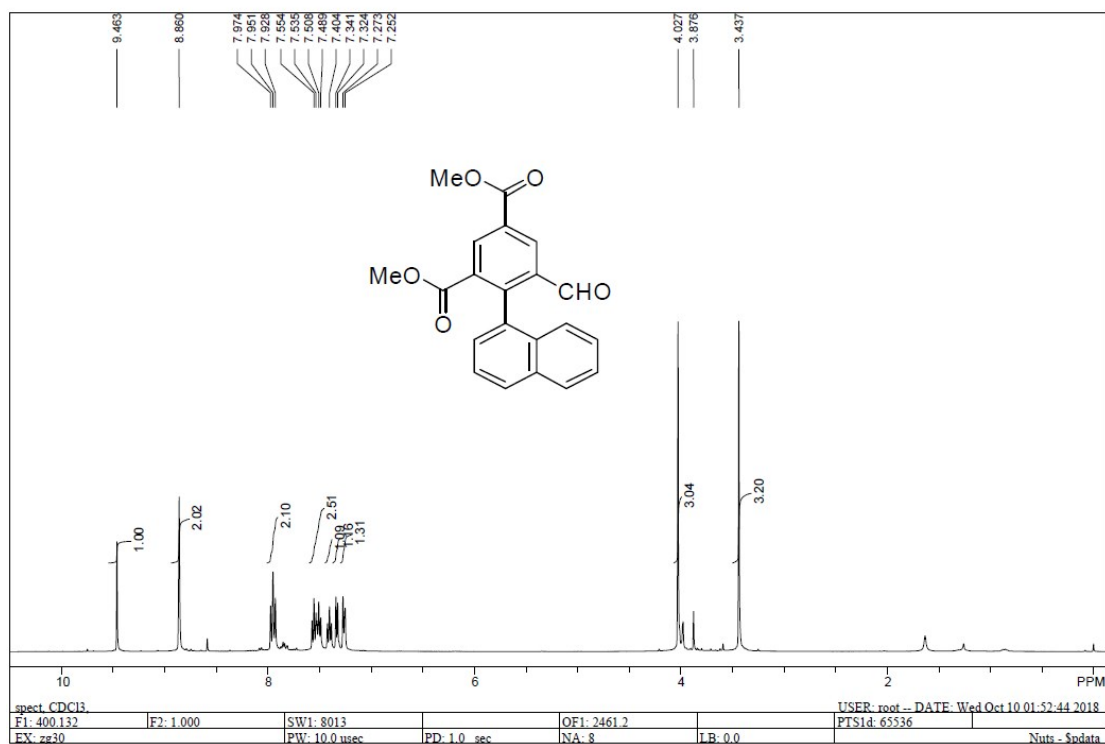
¹H and ¹³C NMR of **3u**



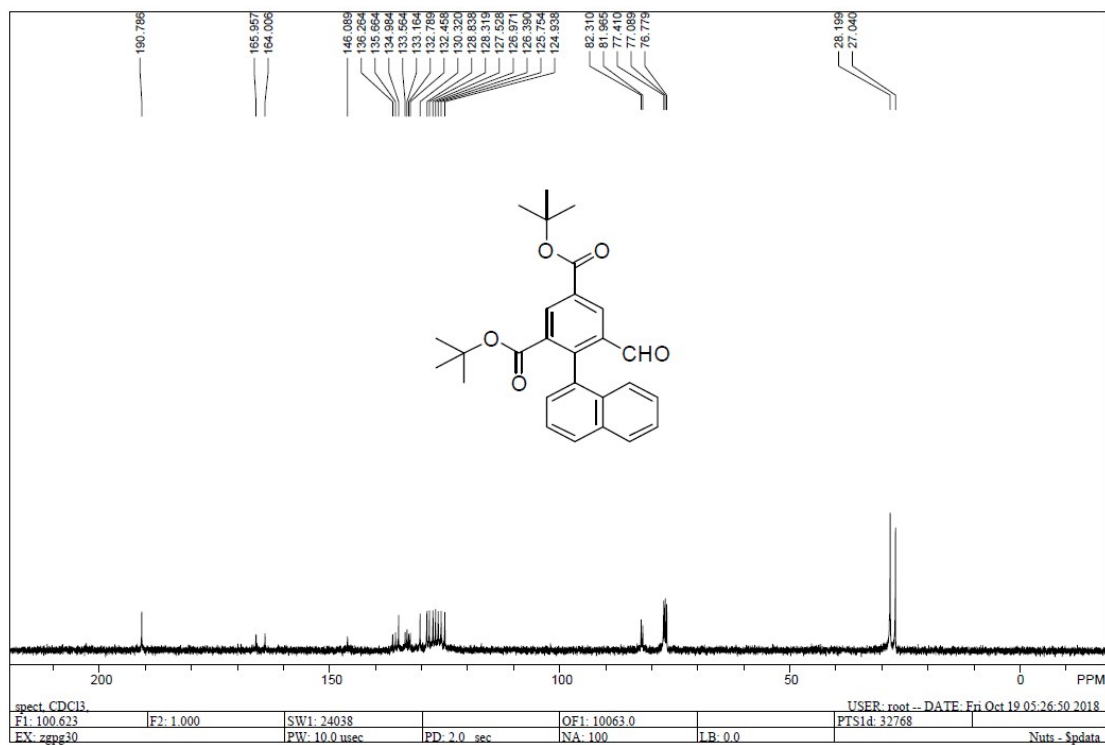
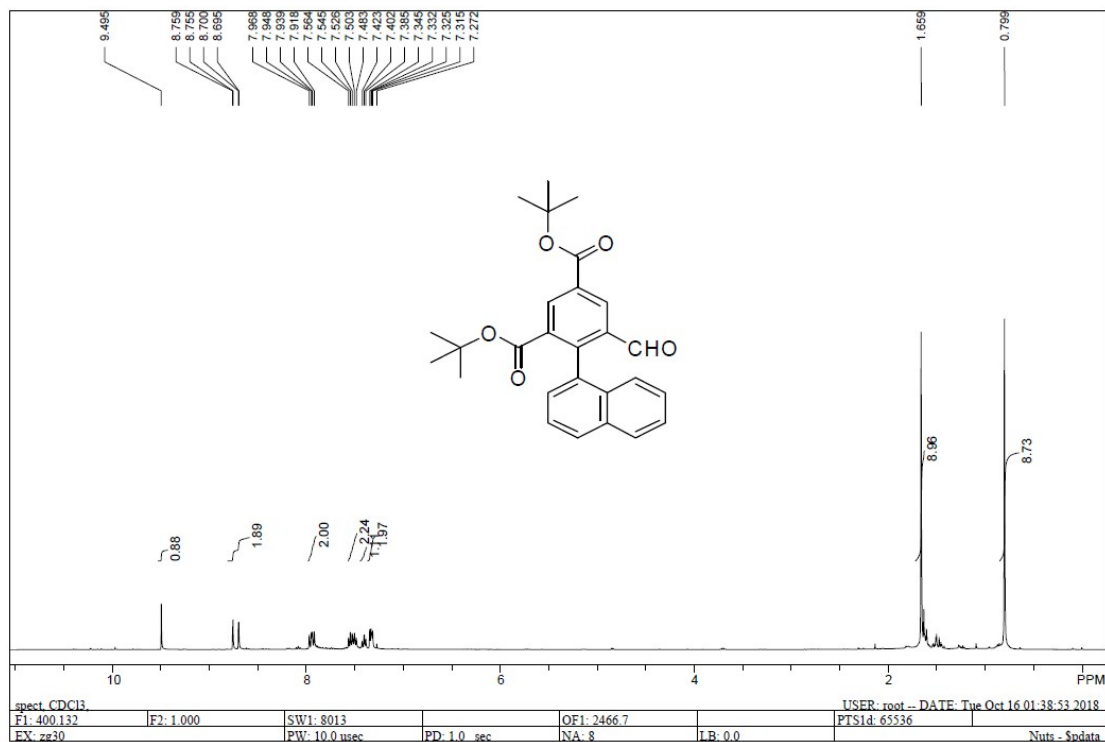
¹H and ¹³C NMR of **3v**



^1H and ^{13}C NMR of **3w**



^1H and ^{13}C NMR of **3x**



¹H and ¹³C NMR of 5

