Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Copper-catalyzed cascade cyclization reaction of 3-aminocyclobutenones with electron-deficient internal alkynes: synthesis of fully substituted indoles

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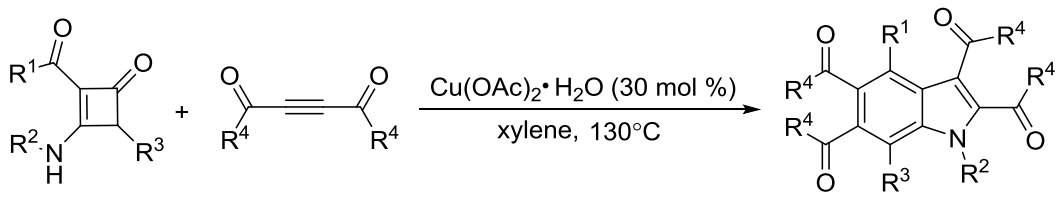
I. General Information:

Unless stated otherwise, all reactions were carried out in glassware under atmosphere. All glassware and stirrers were dried in an oven at 85 ℃ overnight. All reagents were commercially available without further purification. The substrates were prepared according to the previous method reported. Elevated temperatures were maintained by an IKA heating block for 1 dram vials. The chromatographic purification of the products was performed on silica gel 300–400 mesh. NMR-spectra were measured in the given solvent at room temperature on a Bruker Avance (600 MHz, ^{1}H; 151 MHz, ^{13}C) or Varian (500 MHz, ^{1}H; 126 MHz, ^{13}C) instrument. Data for ^{1}H NMR and ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI). The compound **3ea** was glued on a glass fiber. Data were collected at 293 Kusing graphite-monochromated Mo Kα radiation (λ = 0.71073Å) and IP technique inthe range 2.19° < θ < 27.48°. Empirical absorption correction was applied. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXS 97 crystallographic software package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps.

II. General Procedure for the Preparation of 3 (3ba as Example):

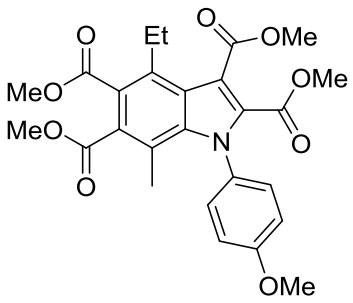


1 2 3

4-Methyl-2-propionyl-3-(p-tolylamino)cyclobut-2-enone **1b** (0.2 mmol, 0.0487 g), dimethyl acetylenedicarboxylate **2a** (0.4 mmol, 0.049 mL), $Cu(OAc)_2·H_2O$ (0.06 mmol, 0.0120 g) and xylene (2.0 mL) were added to a 10 mL Schlenk tube equipped with a magnetic stir bar. The reaction mixture was stirred for 6 h at 130 ℃. After **1b** was consumed (monitored by TLC), the reaction mixture was poured into saturated aqueous NaCl (5 mL), extracted with CH_2Cl_2 (2 mL × 3), washed with brine (10 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to yield the corresponding crude product, which was purified by silica gel chromatography (ethyl acetate/petroleum ether = 3/10, V/V) to give **3ba** (87.6 mg, 91%) as a white solid.

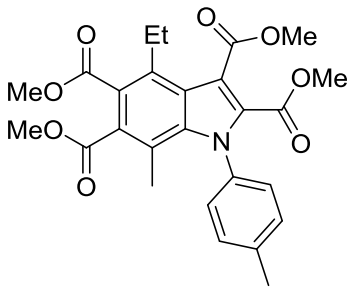
A scale-up reaction: 4-Methyl-2-propionyl-3-(phenylamino)cyclobut-2-enone **1e** (5 mmol, 1.15 g), dimethyl acetylenedicarboxylate **2a** (10 mmol, 1.23 mL), $Cu(OAc)_2·H_2O$ (1.5 mmol, 0.30 g) and xylene (20 mL) were added to a 50 mL Schlenk tube equipped with a magnetic stir bar. The reaction mixture was stirred for 12 h at 130 ℃. After **1e** was consumed (monitored by TLC), the reaction mixture was poured into saturated aqueous NaCl (50 mL), extracted with CH_2Cl_2 (20 mL × 3), washed with brine (100 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to yield the corresponding crude product, which was purified by silica gel chromatography (ethyl acetate/petroleum ether = 3/10, V/V) to give **3ea** (1.71 g, 73%) as a white solid.

Tetramethyl 4-ethyl-1-(4-methoxyphenyl)-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3aa):



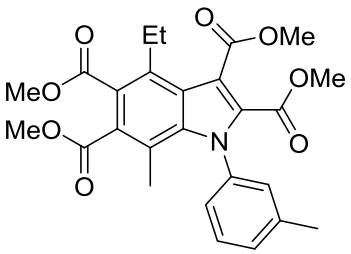
White solid; mp 118-120 ^{o}C, 80.6 mg, 81% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 3.96 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H), 3.83 (s, 3H), 3.71 (s, 3H), 3.01 (q, *J* = 7.3 Hz, 2H), 1.83 (s, 3H), 1.25 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.22, 169.00, 167.19, 160.39, 160.14, 137.79, 136.33, 131.59, 131.37, 131.23, 130.33, 125.47, 123.63, 120.41, 116.39, 113.61, 55.51, 52.71, 52.42, 52.40, 52.35, 23.66, 15.89, 15.85; HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{26}H_{28}NO_9^+$: 498.1759, found: 498.1761.

Tetramethyl 4-ethyl-7-methyl-1-(p-tolyl)-1*H*-indole-2,3,5,6-tetracarboxylate (3ba):



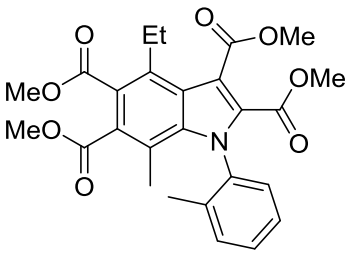
White solid; mp 140-142 ^{o}C, 87.6 mg, 91% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.24 – 7.20 (m, 2H), 3.96 (s, 3H), 3.86 (s, 3H), 3.82 (s, 3H), 3.70 (s, 3H), 3.02 (q, *J* = 7.5 Hz, 2H), 2.45 (s, 3H), 1.82 (s, 3H), 1.26 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.20, 168.98, 167.19, 160.34, 139.58, 137.65, 136.29, 136.23, 131.46, 131.22, 129.19, 129.07, 125.48, 123.67, 120.44, 116.43, 52.71, 52.40, 52.39, 52.35, 23.65, 21.36, 15.90, 15.86; HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{26}H_{27}NO_8Na^+$: 504.1629, found: 504.1633.

Tetramethyl 4-ethyl-7-methyl-1-(m-tolyl)-1*H*-indole-2,3,5,6-tetracarboxylate (3ca):



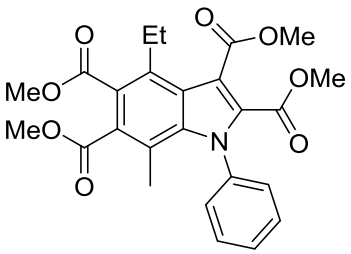
White solid; mp 109-111 °C, 81.9 mg, 85% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.13 (s, 1H), 3.96 (s, 3H), 3.87 (s, 3H), 3.82 (s, 3H), 3.70 (s, 3H), 3.05 – 2.98 (m, 2H), 2.40 (s, 3H), 1.80 (s, 3H), 1.26 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.22, 168.99, 167.18, 160.30, 138.77, 138.61, 137.57, 136.34, 131.37, 131.22, 130.22, 129.88, 128.25, 126.47, 125.46, 123.70, 120.41, 116.50, 52.71, 52.40, 52.39, 52.35, 23.66, 21.24, 15.86, 15.86; HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{26}H_{28}NO_8^+$: 482.1809, found: 482.1811.

Tetramethyl 4-ethyl-7-methyl-1-(o-tolyl)-1*H*-indole-2,3,5,6-tetracarboxylate (3da):



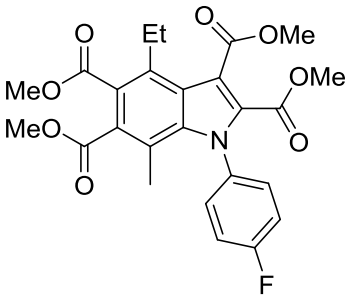
White solid; mp 108-110 °C, 84.7 mg, 88% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 3.97 (s, 3H), 3.87 (s, 3H), 3.83 (s, 3H), 3.69 (s, 3H), 3.08 – 2.94 (m, 2H), 1.99 (s, 3H), 1.76 (s, 3H), 1.27 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.23, 169.03, 167.18, 160.19, 138.14, 137.66, 136.76, 136.41, 131.18, 130.66, 130.24, 129.79, 129.29, 126.23, 125.53, 123.75, 120.23, 116.65, 52.73, 52.43, 52.39, 23.71, 17.51, 15.85, 14.80; HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{26}H_{27}NO_8Na^+$: 504.1629, found: 504.1636.

Tetramethyl 4-ethyl-7-methyl-1-phenyl-1*H*-indole-2,3,5,6-tetracarboxylate (3ea):



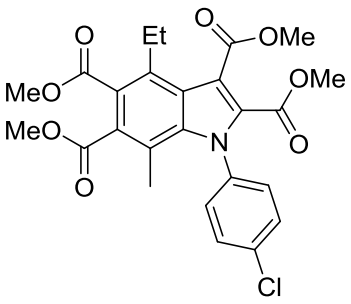
White solid; mp 121-123 ^{o}C, 81.3 mg, 87% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 7.7 Hz, 2H), 3.97 (s, 3H), 3.87 (s, 3H), 3.82 (s, 3H), 3.69 (s, 3H), 3.01 (q, *J* = 7.4 Hz, 2H), 1.79 (s, 3H), 1.26 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.12, 168.92, 167.11, 160.26, 138.93, 137.58, 136.30, 131.41, 131.33, 129.52, 129.40, 128.56, 125.60, 123.71, 120.33, 116.66, 52.74, 52.39, 52.36, 23.64, 15.87, 15.86; HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{25}H_{25}NO_8Na^+$: 490.1472, found: 490.1488.

Tetramethyl 4-ethyl-1-(4-fluorophenyl)-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3fa):



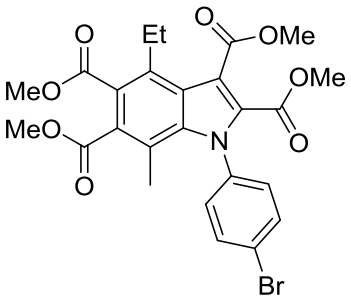
White solid; mp 111-113 ^{o}C, 74.8 mg, 77% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.33 (m, 2H), 7.15 (t, *J* = 8.2 Hz, 2H), 3.97 (s, 3H), 3.87 (s, 3H), 3.83 (s, 3H), 3.71 (s, 3H), 2.99 (q, *J* = 7.4 Hz, 2H), 1.82 (s, 3H), 1.26 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.06, 168.85, 167.13, 163.71, 161.10 (d, J_{CF} = 285.8 Hz), 137.77, 136.48, 134.91 (d, J_{CF} = 3.4 Hz), 131.58, 131.10 (d, J_{CF} = 8.7 Hz), 130.90, 125.69, 123.73, 120.08, 117.26, 115.60 (d, J_{CF} = 22.9 Hz), 52.80, 52.46, 52.39, 23.63, 16.05, 15.83; ^{19}F NMR (471 MHz, $CDCl_3$) δ -110.64 – -110.70 (m, 1F); HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{25}H_{24}NaFNO_8^+$: 508.1378, found: 508.1382.

Tetramethyl 1-(4-chlorophenyl)-4-ethyl-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3ga):



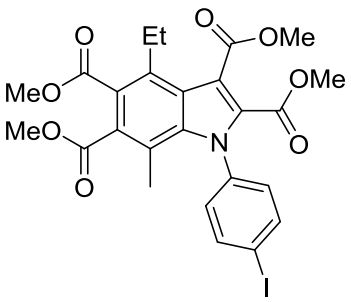
White solid; mp 124-126 ^{o}C, 83.3 mg, 83% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 3.97 (s, 3H), 3.87 (s, 3H), 3.83 (s, 3H), 3.72 (s, 3H), 2.98 (q, *J* = 7.4 Hz, 2H), 1.83 (s, 3H), 1.25 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.05, 168.83, 167.14, 160.10, 137.74, 137.56, 136.53, 135.56, 131.66, 130.69, 128.83, 125.75, 123.81, 120.07, 117.50, 52.83, 52.50, 52.49, 52.42, 23.63, 16.21, 15.84; HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{25}H_{24}ClNaNO_8^+$: 524.1083, found: 524.1089.

Tetramethyl 1-(4-bromophenyl)-4-ethyl-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3ha):



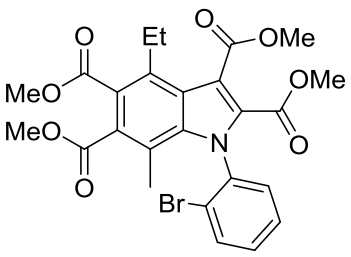
White solid; mp 121-123 ^{o}C, 85.2 mg, 78% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 3.97 (s, 3H), 3.87 (s, 3H), 3.83 (s, 3H), 3.72 (s, 3H), 2.98 (q, *J* = 7.3 Hz, 2H), 1.83 (s, 3H), 1.25 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.03, 168.81, 167.11, 160.08, 138.09, 137.69, 136.52, 131.82, 131.66, 130.98, 130.60, 125.76, 123.82, 123.61, 120.05, 117.52, 52.82, 52.51, 52.48, 52.41, 23.62, 16.24, 15.84; HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{25}H_{25}BrNO_8^+$: 546.0758, found: 546.0763.

Tetramethyl 4-ethyl-1-(4-iodophenyl)-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3ia):



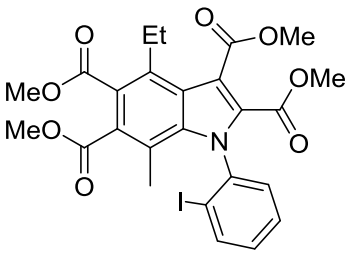
White solid; mp 123-125 ^{o}C, 92.6 mg, 78% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 3.96 (s, 3H), 3.87 (s, 3H), 3.83 (s, 3H), 3.72 (s, 3H), 2.98 (q, *J* = 7.5 Hz, 2H), 1.83 (s, 3H), 1.25 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.05, 168.83, 167.14, 160.09, 138.82, 137.82, 137.67, 136.52, 131.66, 131.20, 130.54, 125.74, 123.83, 120.09, 117.52, 95.18, 52.84, 52.53, 52.50, 52.43, 23.63, 16.28, 15.85; HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{25}H_{25}INO_8^+$: 594.0619, found: 594.0622.

Tetramethyl 1-(2-bromophenyl)-4-ethyl-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3ja):



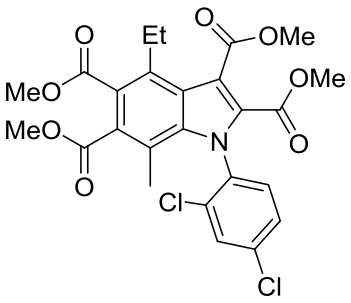
White solid; mp 94-96 ^{o}C, 79.8 mg, 73% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.65 (m, 1H), 7.45 – 7.37 (m, 3H), 3.98 (s, 3H), 3.87 (s, 3H), 3.83 (s, 3H), 3.71 (s, 3H), 3.02 – 2.93 (m, 2H), 1.82 (s, 3H), 1.27 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.11, 168.88, 167.32, 159.78, 138.74, 136.85, 136.46, 132.66, 131.55, 131.07, 130.98, 129.14, 127.64, 125.63, 124.93, 123.77, 120.07, 118.03, 52.81, 52.47, 52.45, 52.39, 23.63, 15.85, 15.04; HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{25}H_{25}BrNO_8^+$: 546.0758, found: 546.0761.

Tetramethyl 4-ethyl-1-(2-iodophenyl)-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3ka):



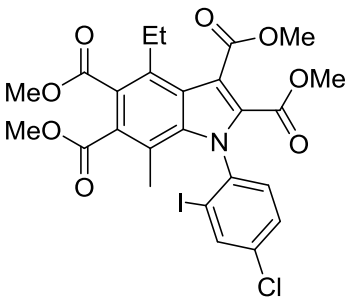
White solid; mp 95-97 ^{o}C, 89.0 mg, 75% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.42 – 7.35 (m, 1H), 7.26 – 7.19 (m, 1H), 3.98 (s, 3H), 3.87 (s, 3H), 3.83 (s, 3H), 3.71 (s, 3H), 3.02 – 2.94 (m, 2H), 1.80 (s, 3H), 1.27 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.14, 168.93, 167.32, 159.77, 142.21, 138.83, 136.50, 136.46, 131.55, 130.88, 130.36, 128.97, 128.51, 125.64, 123.83, 120.10, 118.10, 100.94, 52.82, 52.49, 52.46, 52.40, 23.65, 15.86, 15.34; HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{25}H_{25}INO_8^+$: 594.0619, found: 594.0625.

Tetramethyl 1-(2,4-dichlorophenyl)-4-ethyl-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3la):



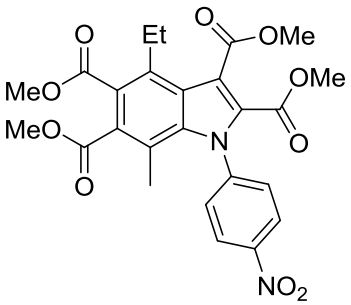
White solid; mp 160-162 ^{o}C, 86.9 mg, 81% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.5 Hz, 1H), 7.48 – 7.46 (m, 1H), 7.26 – 7.24 (m, 1H), 3.97 (s, 3H), 3.87 (s, 3H), 3.84 (s, 3H), 3.74 (s, 3H), 2.99 – 2.95 (m, 2H), 1.87 (s, 3H), 1.25 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.91, 168.69, 167.02, 159.89, 138.34, 137.75, 136.66, 134.07, 132.68, 131.94, 131.30, 130.15, 130.12, 128.89, 125.96, 123.87, 119.83, 118.11, 52.87, 52.59, 52.53, 52.44, 23.59, 16.43, 15.83; HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{25}H_{23}NaCl_2NO_8^+$: 558.0693, found: 558.0707.

Tetramethyl 1-(4-chloro-2-iodophenyl)-4-ethyl-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3ma):



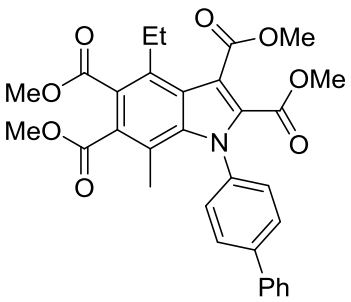
White solid; mp 175-177 ^{o}C, 100.4 mg, 80% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.92 (m, 1H), 7.45 – 7.43 (m, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 3.98 (s, 3H), 3.88 (s, 3H), 3.84 (s, 3H), 3.74 (s, 3H), 3.00 – 2.93 (m, 2H), 1.84 (s, 3H), 1.27 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.02, 168.81, 167.19, 159.69, 141.03, 138.24, 136.59, 136.55, 135.90, 131.78, 130.73, 128.76, 128.63, 125.85, 123.90, 119.85, 118.54, 101.20, 52.87, 52.59, 52.51, 52.44, 23.63, 15.85, 15.61; HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{25}H_{24}ClINO_8^+$: 628.0230, found: 628.0232.

Tetramethyl 4-ethyl-7-methyl-1-(4-nitrophenyl)-1*H*-indole-2,3,5,6-tetracarboxylate (3na):



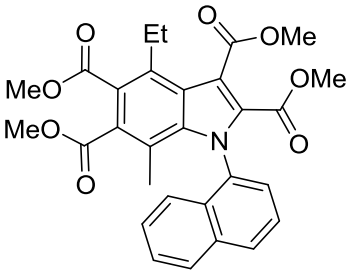
White solid; mp 119-121 ^{o}C, 68.7 mg, 67% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 3.99 (s, 3H), 3.88 (s, 3H), 3.84 (s, 3H), 3.73 (s, 3H), 2.97 (q, *J* = 7.5 Hz, 2H), 1.80 (s, 3H), 1.26 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.79, 168.62, 166.98, 159.86, 148.13, 144.92, 137.78, 136.81, 132.15, 130.65, 129.79, 126.19, 124.11, 123.87, 119.65, 118.67, 52.95, 52.65, 52.57, 52.50, 23.61, 16.56, 15.84; HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{25}H_{25}N_2O_{10}^+$: 513.1504, found: 513.1508.

Tetramethyl 1-([1,1'-biphenyl]-4-yl)-4-ethyl-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3oa):



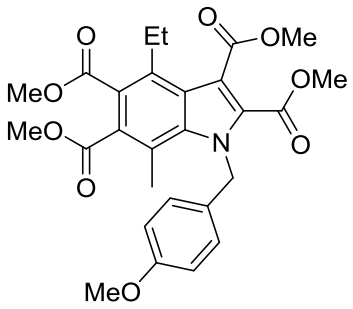
White solid; mp 95-97 ^{o}C, 84.8 mg, 78% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.66 (m, 4H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.35 (m, 1H), 3.97 (s, 3H), 3.87 (s, 3H), 3.82 (s, 3H), 3.71 (s, 3H), 3.04 (q, *J* = 6.5 Hz, 2H), 1.87 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.19, 168.97, 167.21, 160.33, 142.31, 139.63, 138.03, 137.79, 136.42, 131.42, 131.32, 129.75, 128.97, 128.01, 127.19, 127.05, 125.63, 123.81, 120.40, 116.90, 52.79, 52.47, 52.45, 52.40, 23.69, 16.09, 15.89; HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{31}H_{30}NO_8^+$: 544.1966, found: 544.1968.

Tetramethyl 4-ethyl-7-methyl-1-(naphthalen-1-yl)-1*H*-indole-2,3,5,6-tetracarboxylate (3pa):



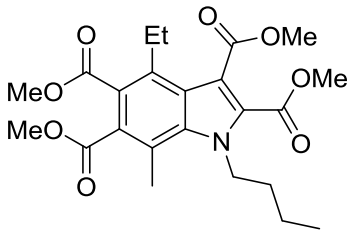
White solid; mp 176-178 ^{o}C, 80.7 mg, 78% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.50 (t, *J* = 6.3 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 3.99 (s, 3H), 3.87 (s, 3H), 3.76 (s, 3H), 3.53 (s, 3H), 3.17 – 2.97 (m, *J* = 7.1 Hz, 2H), 1.52 (s, 3H), 1.32 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.10, 168.94, 167.24, 159.95, 137.87, 136.41, 135.65, 133.35, 132.53, 131.35, 131.28, 129.96, 128.24, 127.86, 127.10, 126.82, 125.61, 124.62, 123.74, 122.46, 120.38, 52.72, 52.32, 52.30, 52.25, 23.69, 15.85, 14.85; HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{29}H_{27}NaNO_8^+$: 540.1629, found: 540.1635.

Tetramethyl 4-ethyl-1-(4-methoxybenzyl)-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3qa):



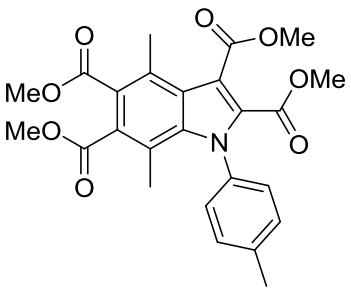
White solid; mp 65-67 ^{o}C, 82.9 mg, 81% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.80 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 5.96 (s, 2H), 3.94 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H), 3.82 (s, 3H), 3.75 (s, 3H), 2.96 (q, *J* = 7.4 Hz, 2H), 2.54 (s, 3H), 1.23 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.37, 168.99, 167.52, 160.87, 158.82, 137.65, 136.49, 131.51, 130.43, 129.94, 126.25, 125.32, 123.94, 119.50, 117.53, 114.35, 55.26, 52.70, 52.63, 52.53, 52.41, 49.61, 23.59, 16.55, 15.80; HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{27}H_{30}NO_9^+$: 512.1915, found: 512.1917.

Tetramethyl 1-butyl-4-ethyl-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3ra):



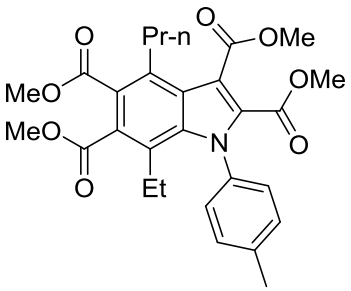
Colourless liquid; 64.4 mg, 72% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.77 – 4.61 (m, 2H), 3.92 (s, 3H), 3.92 (s, 3H), 3.89 (s, 3H), 3.86 (s, 3H), 2.93 (q, *J* = 7.5 Hz, 2H), 2.69 (s, 3H), 1.73 – 1.68 (m, 2H), 1.35 – 1.29 (m, 2H), 1.19 (t, *J* = 7.5 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.48, 169.02, 167.61, 161.13, 137.11, 136.52, 131.36, 129.89, 125.03, 124.02, 119.18, 117.12, 52.60, 52.58, 52.53, 52.34, 46.70, 34.42, 23.53, 19.74, 16.80, 15.74, 13.66; HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{23}H_{29}NaNO_8^+$: 470.1785, found: 470.1790.

Tetramethyl 4,7-dimethyl-1-(p-tolyl)-1*H*-indole-2,3,5,6-tetracarboxylate (3sa):



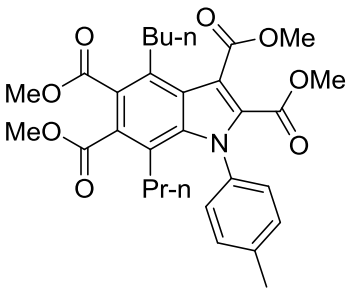
White solid; mp 127-129 ^{o}C, 86.0 mg, 92% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 3.96 (s, 3H), 3.87 (s, 3H), 3.82 (s, 3H), 3.70 (s, 3H), 2.58 (s, 3H), 2.45 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.24, 168.96, 167.13, 160.34, 139.61, 137.12, 136.18, 131.17, 131.02, 130.00, 129.22, 129.00, 125.80, 124.70, 120.32, 116.67, 52.71, 52.41, 52.38, 21.39, 16.37, 15.73; HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{25}H_{25}NaNO_8^+$: 490.1472, found: 490.1463.

Tetramethyl 7-ethyl-4-propyl-1-(p-tolyl)-1*H*-indole-2,3,5,6-tetracarboxylate (3ta):



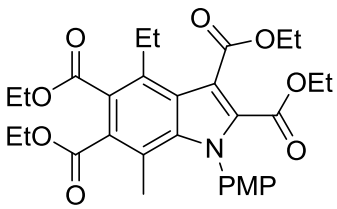
White solid; mp 92-94 ^{o}C, 91.7 mg, 90% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (s, 4H), 3.96 (s, 3H), 3.87 (s, 3H), 3.82 (s, 3H), 3.69 (s, 3H), 3.01 – 2.91 (m, 2H), 2.46 (s, 3H), 2.27 (q, *J* = 7.4 Hz, 2H), 1.71 – 1.59 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H), 0.78 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.27, 169.06, 167.11, 160.36, 139.69, 137.00, 136.06, 134.91, 131.95, 130.82, 129.28, 128.68, 126.86, 125.92, 124.50, 116.70, 52.75, 52.39, 52.36, 52.31, 32.41, 25.06, 21.40, 20.82, 16.02, 14.38; HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{28}H_{32}NO_8^+$: 510.2122, found: 510.2125.

Tetramethyl 4-butyl-7-propyl-1-(p-tolyl)-1*H*-indole-2,3,5,6-tetracarboxylate (3ua):



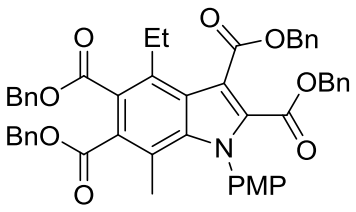
White solid; mp 80-82 ^{o}C, 94.6 mg, 88% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 4H), 3.95 (s, 3H), 3.86 (s, 3H), 3.81 (s, 3H), 3.69 (s, 3H), 3.03 – 2.93 (m, 2H), 2.46 (s, 3H), 2.22 – 2.14 (m, 2H), 1.64 – 1.54 (m, 2H), 1.43 – 1.35 (m, 2H), 1.26 – 1.17 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.45 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.30, 169.14, 167.20, 160.35, 139.61, 137.12, 136.00, 135.03, 131.72, 130.96, 129.28, 128.74, 125.80, 125.54, 124.40, 116.67, 52.73, 52.39, 52.35, 52.32, 33.99, 30.27, 29.71, 24.94, 23.13, 21.36, 13.95; HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{30}H_{35}NNaO_8^+$: 560.2255, found: 560.2263.

Tetraethyl 4-ethyl-1-(4-methoxyphenyl)-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3ab):



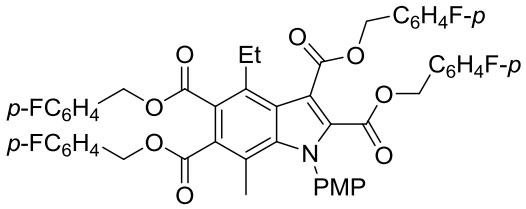
White solid; mp 98-100 ^{o}C, 102.9 mg, 93% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 4.43 (q, *J* = 7.2 Hz, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.29 (q, *J* = 7.2 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 3.04 (q, *J* = 7.5 Hz, 2H), 1.84 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.5 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.88, 168.69, 166.83, 160.11, 160.06, 137.65, 135.97, 131.67, 131.33, 130.45, 125.66, 123.60, 120.05, 116.61, 113.52, 61.88, 61.48, 61.44, 61.39, 55.52, 23.57, 16.05, 15.86, 14.10, 14.08, 13.99, 13.82; HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{30}H_{35}NNaO_9^+$: 576.2204, found: 576.2208.

Tetrabenzyl 4-ethyl-1-(4-methoxyphenyl)-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3ac):



White solid; mp 45-47 °C, 133.1 mg, 83% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 18H), 7.19 – 7.15 (m, 4H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.11 (s, 2H), 5.02 (s, 2H), 5.00 (s, 2H), 4.96 (s, 2H), 3.84 (s, 3H), 2.87 (q, *J* = 7.4 Hz, 2H), 1.75 (s, 3H), 1.03 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.59, 168.33, 166.27, 160.05, 159.86, 137.69, 136.43, 135.36, 135.24, 134.96, 134.61, 131.52, 131.37, 131.15, 130.32, 128.92, 128.87, 128.61, 128.54, 128.52, 128.50, 128.48, 128.44, 128.30, 128.30, 125.34, 123.73, 120.28, 116.38, 113.54, 67.71, 67.49, 67.28, 67.23, 55.43, 23.52, 15.97, 15.84; HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{50}H_{43}NaNO_9^+$: 824.2830, found: 824.2836.

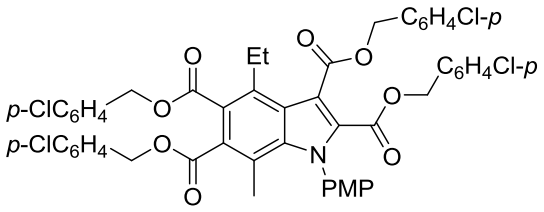
Tetrakis(4-fluorobenzyl) 4-ethyl-1-(4-methoxyphenyl)-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3ad):



White solid; mp 48-50 °C, 141.6 mg, 81% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 4H), 7.27 – 7.24 (m, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 7.12 – 7.09 (m, 2H), 7.05 – 6.93 (m, 8H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.09 (s, 2H), 5.06 (s, 2H), 5.01 (s, 2H), 4.93 (s, 2H), 3.83 (s, 3H), 2.83 (q, *J* = 7.4 Hz, 2H), 1.74 (s, 3H), 1.00 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.48, 168.26, 166.11, 163.61, 163.60, 163.55, 163.50, 161.97, 161.96, 161.91, 161.86, 160.13, 159.81, 137.64, 136.31, 131.77, 131.22, 131.19, 131.17, 131.07, 131.05, 131.01, 130.88, 130.86, 130.83, 130.77, 130.60, 130.54, 130.49, 130.47, 130.44, 130.26, 125.26, 123.71, 120.35, 116.22, 115.54, 115.47, 115.39, 115.33, 113.54, 66.93, 66.67, 66.52, 66.47, 55.41, 23.53, 15.93, 15.80; ^{19}F NMR (470 MHz, $CDCl_3$) δ -112.81 – -113.27 (m, 4F); HRMS(ESI-TOF): $[M + Na]^+$ calculated for

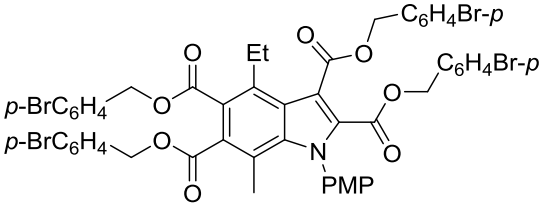
$C_{50}H_{39}NaF_4NO_9^+$: 896.2453, found: 896.2458.

Tetrakis(4-chlorobenzyl) 4-ethyl-1-(4-methoxyphenyl)-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3ae):



White solid; mp 55-57 °C, 142.8 mg, 76% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 – 7.21 (m, 4H), 7.21 – 7.15 (m, 8H), 7.12 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.3 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 5.00 (s, 2H), 5.00 (s, 2H), 4.91 (s, 2H), 4.84 (s, 2H), 3.76 (s, 3H), 2.80 (q, *J* = 7.4 Hz, 2H), 1.67 (s, 3H), 0.96 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.42, 168.19, 166.06, 160.18, 159.76, 137.66, 136.38, 134.52, 134.43, 134.32, 134.29, 133.75, 133.64, 133.44, 133.01, 131.82, 131.16, 130.97, 130.25, 130.11, 129.87, 129.77, 128.76, 128.74, 128.66, 125.22, 123.72, 120.45, 116.16, 113.57, 66.85, 66.57, 66.42, 66.39, 55.47, 23.61, 15.99, 15.87; HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{50}H_{39}NaCl_4NO_9^+$: 960.1271, found: 960.1273.

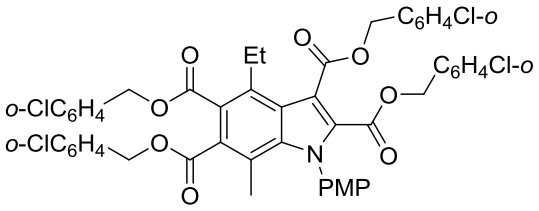
Tetrakis(4-bromobenzyl) 4-ethyl-1-(4-methoxyphenyl)-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3af):



White solid; mp 57-59 °C, 172.1 mg, 77% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.45 (m, 4H), 7.43 – 7.39 (m, 4H), 7.22 – 7.15 (m, 6H), 7.13 (d, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 5.06 (s, 4H), 4.97 (s, 2H), 4.89 (s, 2H), 3.85 (s, 3H), 2.88 (q, *J* = 7.4 Hz, 2H), 1.75 (s, 3H), 1.05 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.40, 168.17, 166.04, 160.19, 159.74, 137.66, 136.39, 134.25, 134.13, 133.94, 133.50, 131.82, 131.73, 131.71, 131.63, 131.15, 130.95, 130.36, 130.25, 130.14, 130.04, 125.21, 123.72, 122.69, 122.58, 122.47, 122.44,

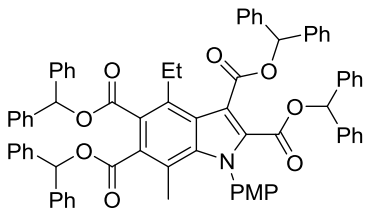
120.47, 116.15, 113.59, 66.87, 66.60, 66.44, 66.42, 55.52, 23.63, 16.00, 15.88; HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{50}H_{39}NaBr_4NO_9^+$: 1135.9251, found: 1135.9256.

Tetrakis(2-chlorobenzyl)4-ethyl-1-(4-methoxyphenyl)-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3ag):



White solid; mp 49-51 ^oC, 139.1 mg, 74% yield; ^1H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.36 – 7.32 (m, 3H), 7.32 – 7.27 (m, 2H), 7.24 – 7.14 (m, 11H), 6.85 – 6.80 (m, 2H), 5.28 (s, 2H), 5.22 (s, 2H), 5.20 (s, 2H), 5.11 (s, 2H), 3.82 (s, 3H), 2.95 (q, *J* = 7.4 Hz, 2H), 1.81 (s, 3H), 1.07 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.42, 168.17, 166.09, 160.06, 159.69, 137.78, 136.68, 133.83, 133.80, 133.64, 133.53, 133.10, 132.96, 132.87, 132.38, 131.62, 131.28, 131.13, 130.36, 130.28, 130.12, 130.06, 129.82, 129.65, 129.54, 129.45, 129.42, 129.41, 126.89, 126.87, 126.86, 126.80, 125.23, 123.84, 120.53, 116.34, 113.55, 64.81, 64.61, 64.57, 64.50, 55.41, 23.67, 15.95, 15.92; HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{50}H_{39}NaCl_4NO_9^+$: 960.1271, found: 960.1263.

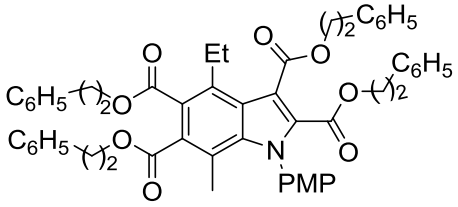
Tetrabenzhydryl 4-ethyl-1-(4-methoxyphenyl)-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3ah):



Colourless liquid; 181.4 mg, 82% yield; ^1H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.14 (m, 38H), 6.96 – 6.93 (m, 4H), 6.77 (s, 1H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.52 (s, 1H), 6.48 (s, 1H), 6.41 (s, 1H), 3.79 (s, 3H), 2.46 (q, *J* = 7.4 Hz, 2H), 1.57 (s, 3H), 0.54 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz,

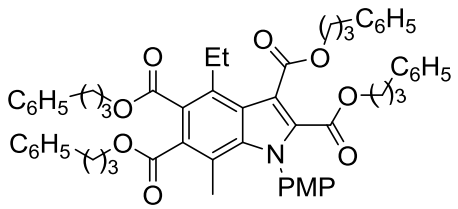
$CDCl_3$) δ 167.48, 167.30, 164.88, 160.02, 159.53, 139.90, 139.84, 139.54, 139.01, 137.50, 136.74, 133.24, 131.26, 130.93, 130.32, 128.22, 128.20, 127.80, 127.77, 127.69, 127.67, 127.37, 127.28, 127.18, 125.15, 123.94, 120.26, 116.00, 113.60, 78.75, 78.65, 78.23, 78.12, 55.40, 23.18, 15.65, 15.57; HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{74}H_{60}NO_9^+$: 1106.4263, found: 1106.4266.

Tetraphenethyl 4-ethyl-1-(4-methoxyphenyl)-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3ai):



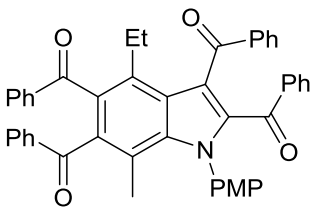
Colourless liquid; 137.3 mg, 80% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 6H), 7.25 – 7.17 (m, 14H), 7.10 (d, *J* = 7.1 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.46 (t, *J* = 7.2 Hz, 2H), 4.42 (t, *J* = 7.3 Hz, 2H), 4.35 (t, *J* = 7.3 Hz, 2H), 4.17 (t, *J* = 7.4 Hz, 2H), 3.87 (s, 3H), 3.04 – 2.99 (m, 4H), 2.95 (t, *J* = 7.3 Hz, 2H), 2.89 (q, *J* = 7.4 Hz, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 1.72 (s, 3H), 1.12 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.76, 168.60, 166.56, 160.07, 160.00, 137.67, 137.56, 137.50, 137.44, 137.03, 136.10, 132.00, 131.45, 131.24, 130.36, 128.93, 128.90, 128.78, 128.57, 128.54, 128.50, 126.66, 126.62, 126.59, 125.56, 123.62, 120.21, 116.28, 113.53, 66.49, 66.06, 66.01, 65.84, 55.51, 34.96, 34.91, 34.81, 34.60, 23.50, 15.95, 15.83; HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{54}H_{52}NO_9^+$: 858.3637, found: 858.3639.

Tetrakis(3-phenylpropyl) 4-ethyl-1-(4-methoxyphenyl)-7-methyl-1*H*-indole-2,3,5,6-tetracarboxylate (3aj):



Colourless liquid; 149.9 mg, 82% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 6H), 7.25 (d, *J* = 7.3 Hz, 4H), 7.20 – 7.13 (m, 10H), 7.09 (d, *J* = 7.3 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.37 (t, *J* = 6.7 Hz, 2H), 4.26 (t, *J* = 6.6 Hz, 2H), 4.22 (t, *J* = 6.7 Hz, 2H), 4.09 (t, *J* = 6.5 Hz, 2H), 3.81 (s, 3H), 3.07 (q, *J* = 7.4 Hz, 2H), 2.74 – 2.71 (m, 2H), 2.71 – 2.68 (m, 2H), 2.68 – 2.63 (m, 2H), 2.51 – 2.47 (m, 2H), 2.11 – 2.06 (m, 2H), 2.05 – 2.00 (m, 2H), 2.00 – 1.95 (m, 2H), 1.85 (s, 3H), 1.79 – 1.73 (m, 2H), 1.29 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.98, 168.78, 166.82, 160.28, 160.20, 141.09, 141.05, 141.03, 140.82, 137.68, 135.99, 131.93, 131.68, 131.51, 130.49, 128.49, 128.48, 128.47, 128.44, 128.41, 128.30, 126.10, 126.07, 125.73, 123.67, 120.10, 116.72, 113.65, 65.43, 65.11, 65.05, 64.99, 55.50, 32.25, 32.23, 32.19, 31.92, 30.26, 30.19, 30.06, 29.80, 23.71, 16.23, 15.99; HRMS(ESI-TOF): $[M + H]^+$ calculated for $C_{58}H_{60}NO_9^+$: 914.4263, found: 914.4266.

(4-Ethyl-1-(4-methoxyphenyl)-7-methyl-1*H*-indole-2,3,5,6-tetrayl)tetrakis(phenylmethanone) (3ak):



White solid; mp 86-88 ^{o}C, 58.6 mg, 43% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.4 Hz, 2H), 7.70 (d, *J* = 7.4 Hz, 2H), 7.48 (d, *J* = 7.1 Hz, 4H), 7.43 (q, *J* = 7.5 Hz, 2H), 7.39 – 7.32 (m, 8H), 7.22 – 7.19 (m, 4H), 6.82 (d, *J* = 8.9 Hz, 2H), 3.76 (s, 3H), 2.76 (q, *J* = 7.3 Hz, 2H), 1.72 (s, 3H), 0.82 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.17, 199.07, 193.15, 189.10, 160.03, 141.92, 139.44, 138.42, 138.28, 138.05, 137.92, 136.75, 135.01, 133.49, 133.38, 133.27, 133.16, 133.03, 131.06, 130.62, 130.03, 129.84, 129.71, 129.34, 128.40, 128.26, 128.23, 128.20, 124.44, 120.37, 118.48, 113.66, 55.43, 24.00, 16.58, 15.16; HRMS(ESI-TOF): $[M + Na]^+$ calculated for $C_{46}H_{35}NaNO_5^+$: 704.2407, found: 704.2410.

III. ORTEP Drawing of Compound 3ea:

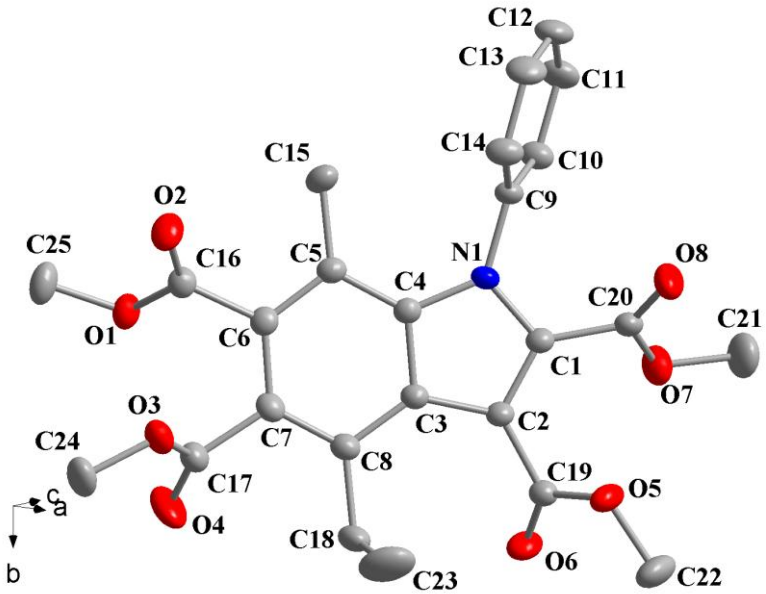


Figure 1. Crystal ORTEP drawing of compound 3ea

IV. Copies of ^{1}H NMR and ^{13}C NMR Spectra of 3:

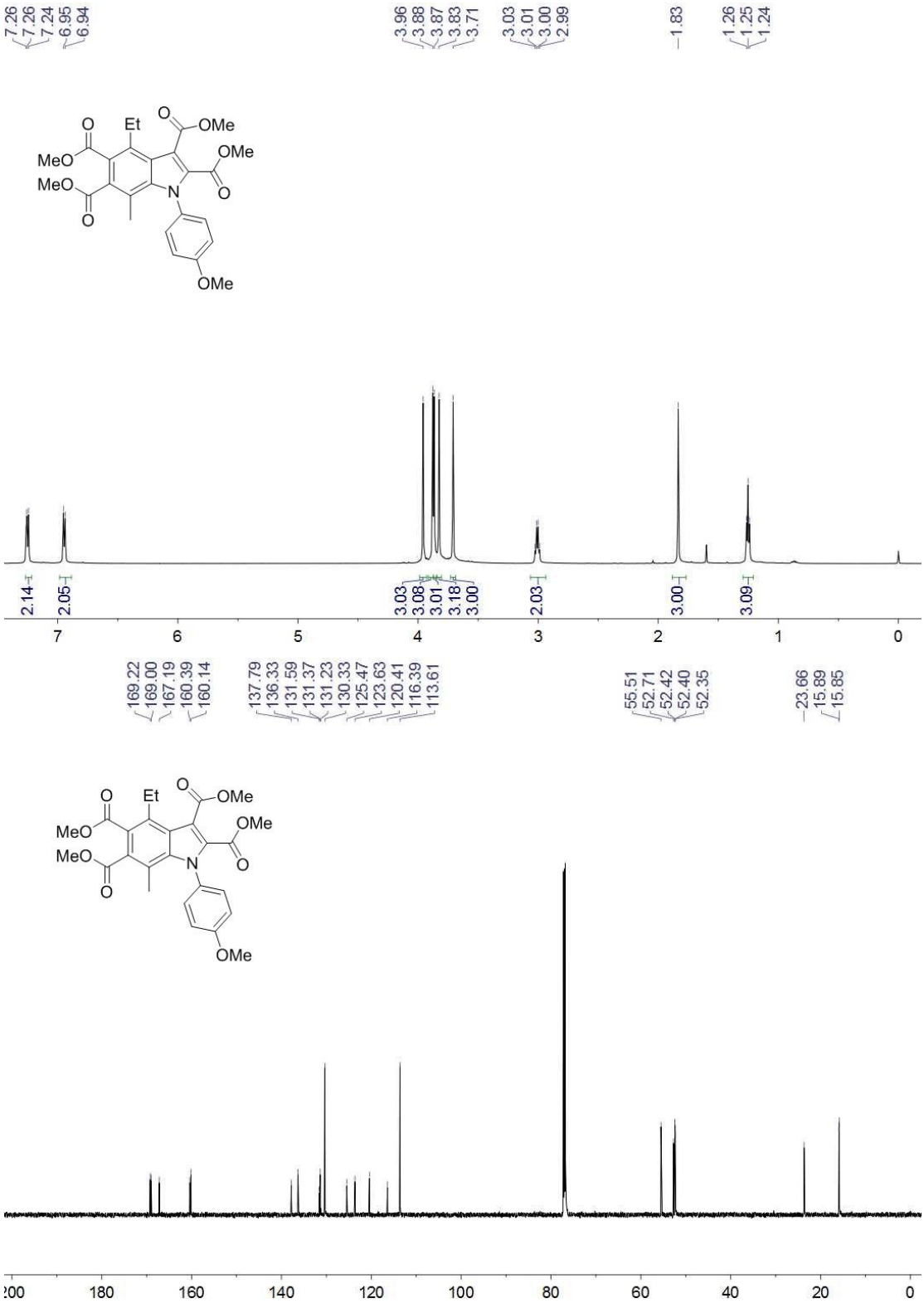


Figure 2. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3aa.**

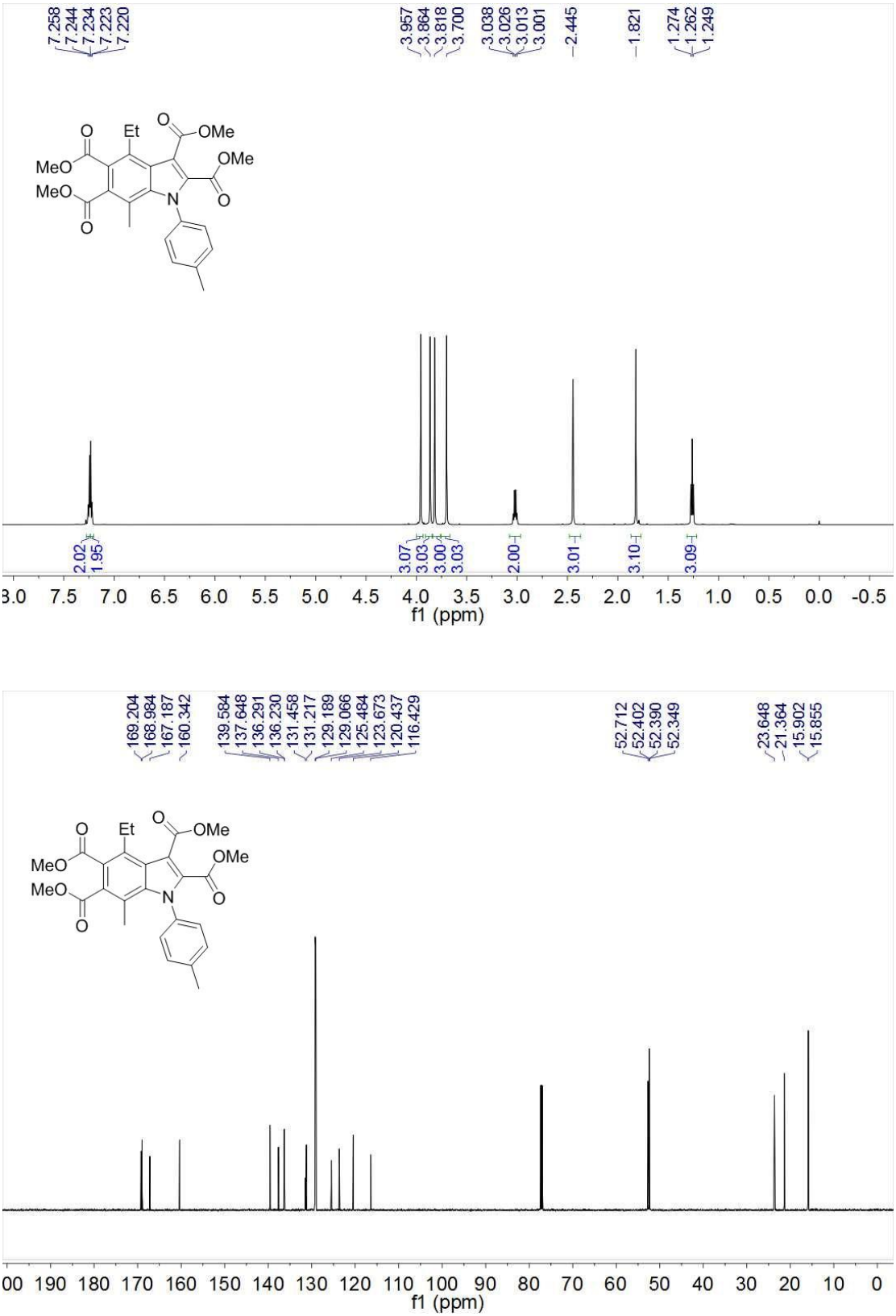


Figure 3. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3ba.**

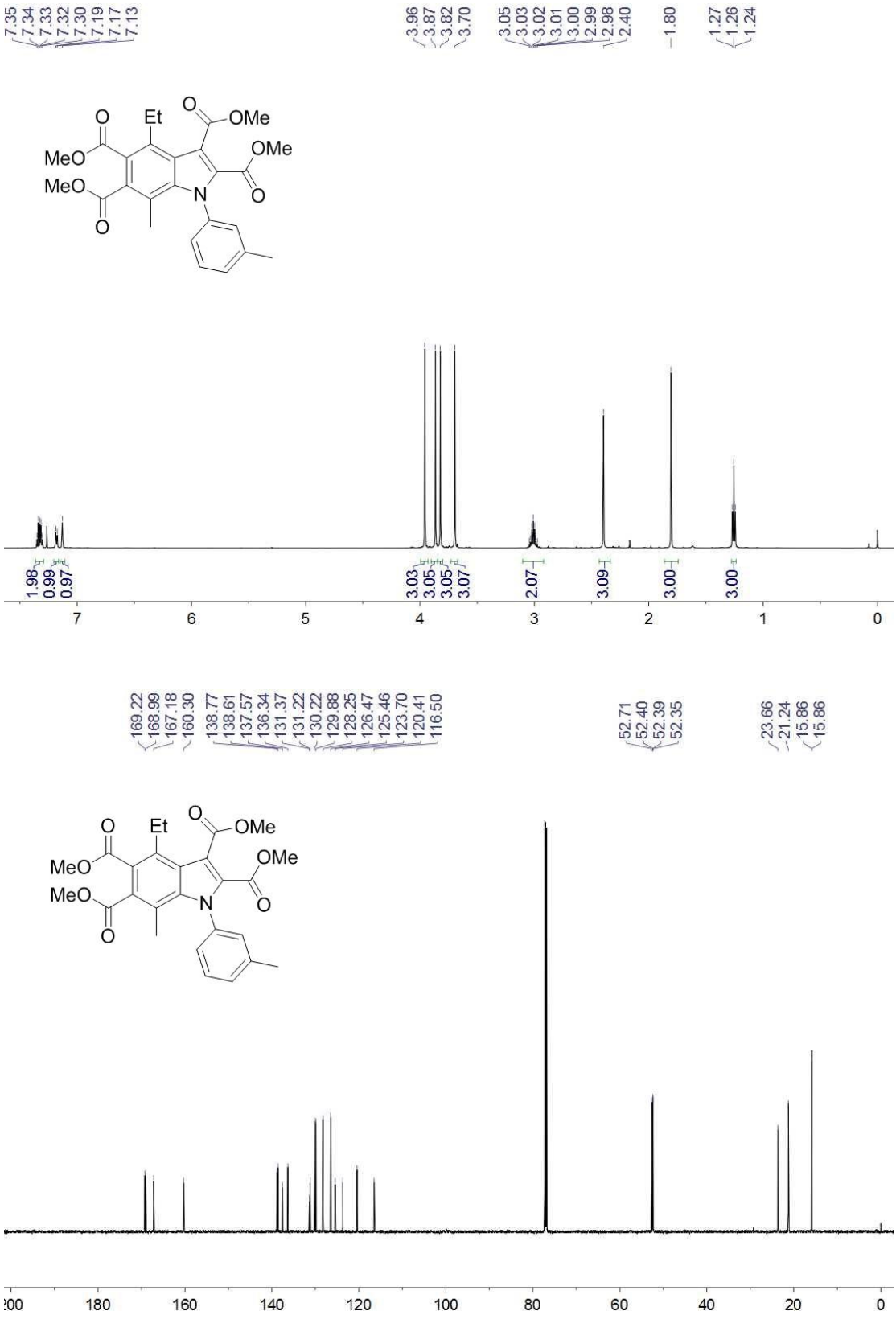


Figure 4. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3ca.**

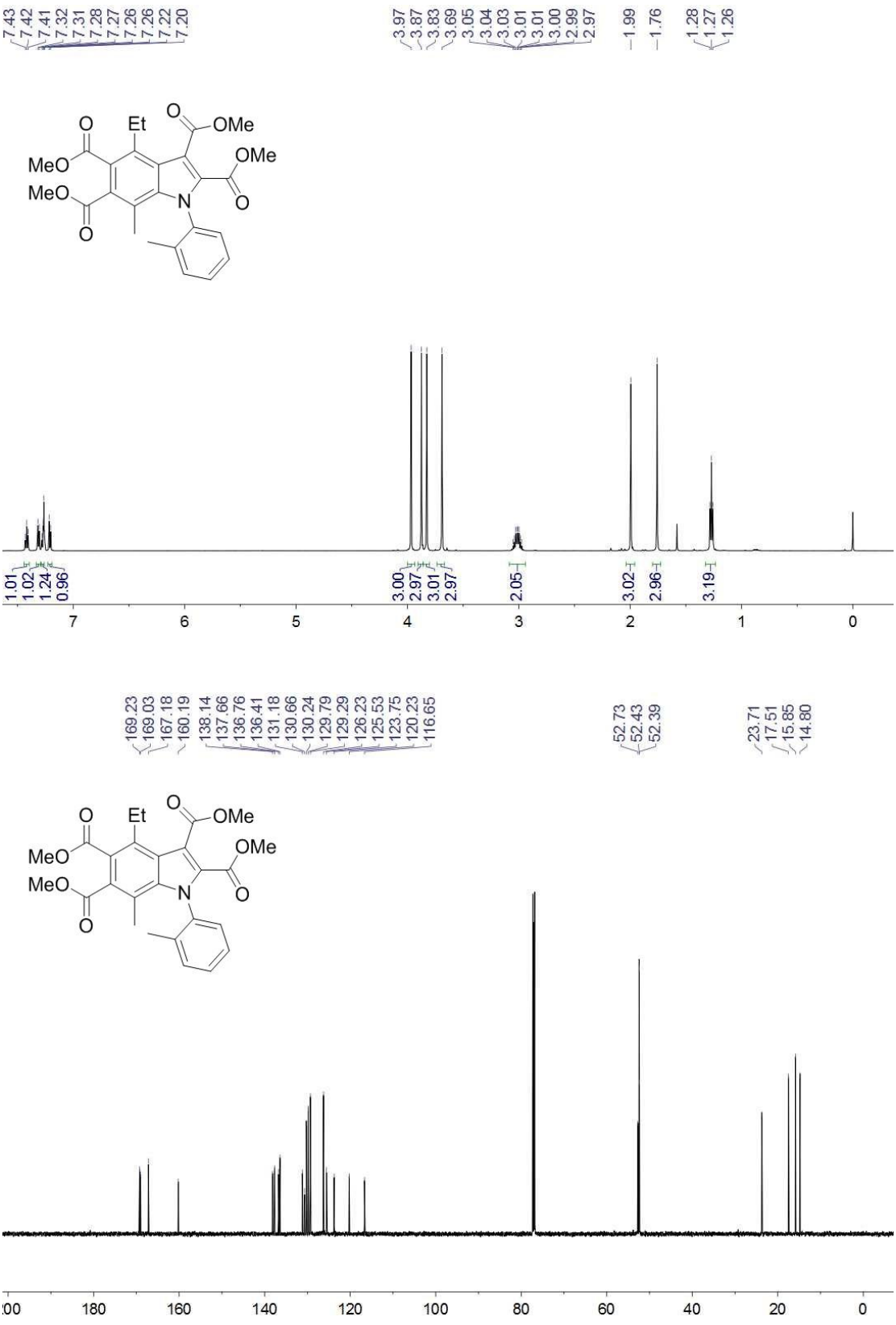


Figure 5. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3da.**

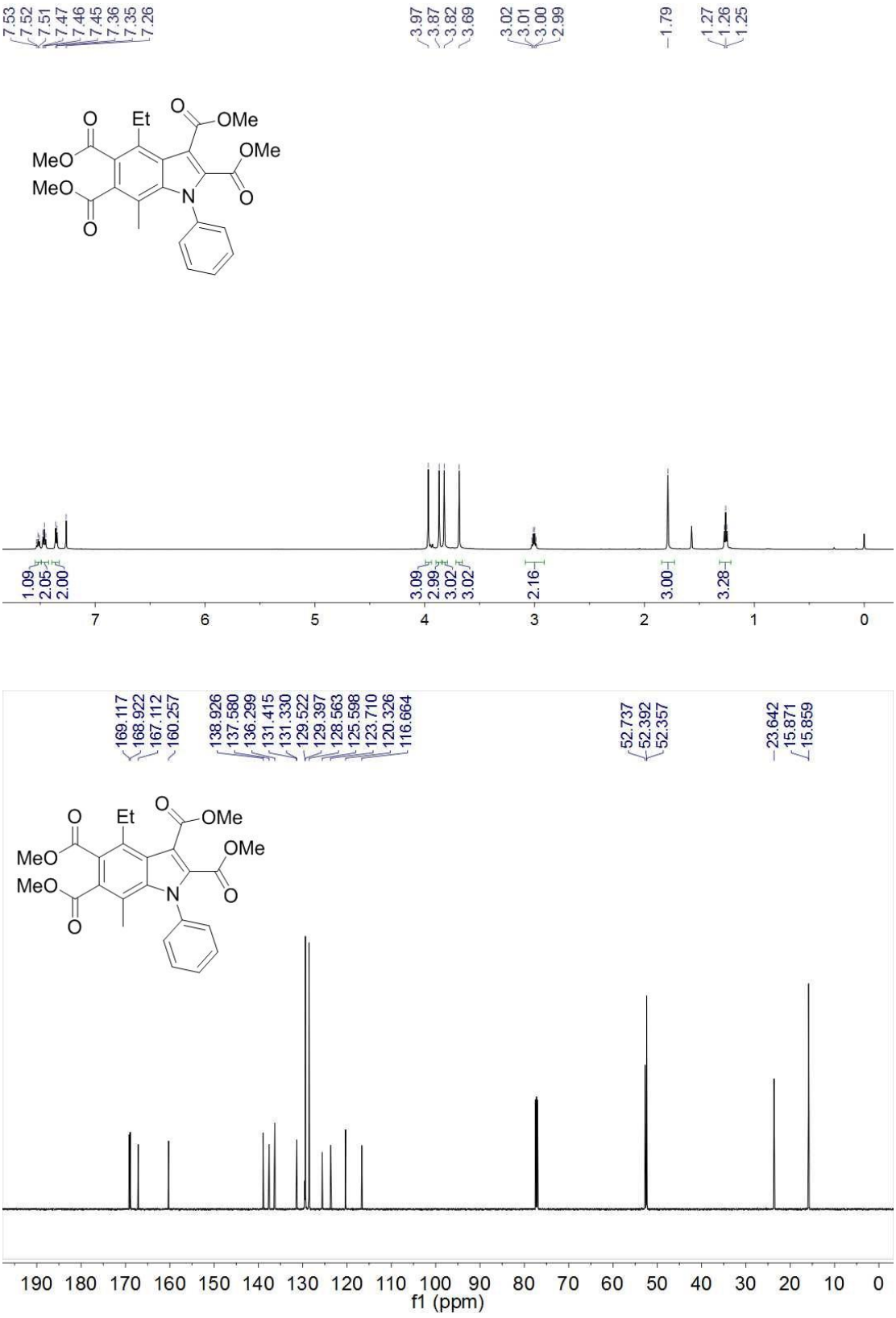
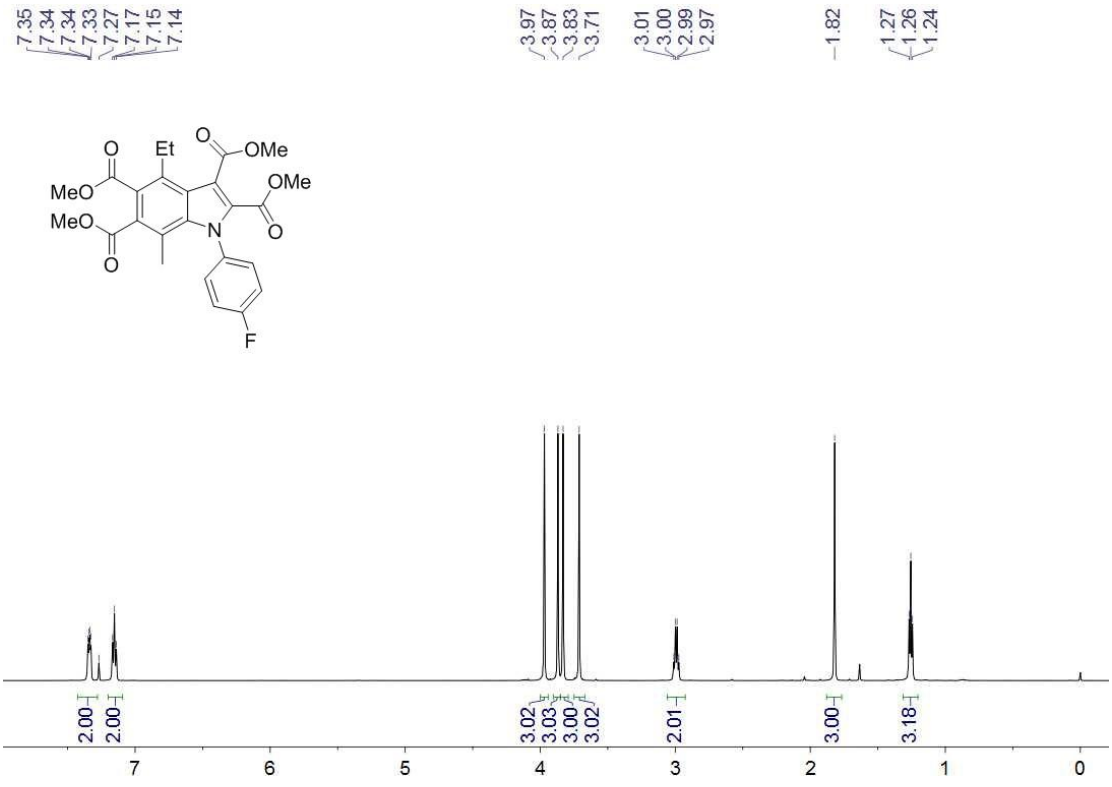
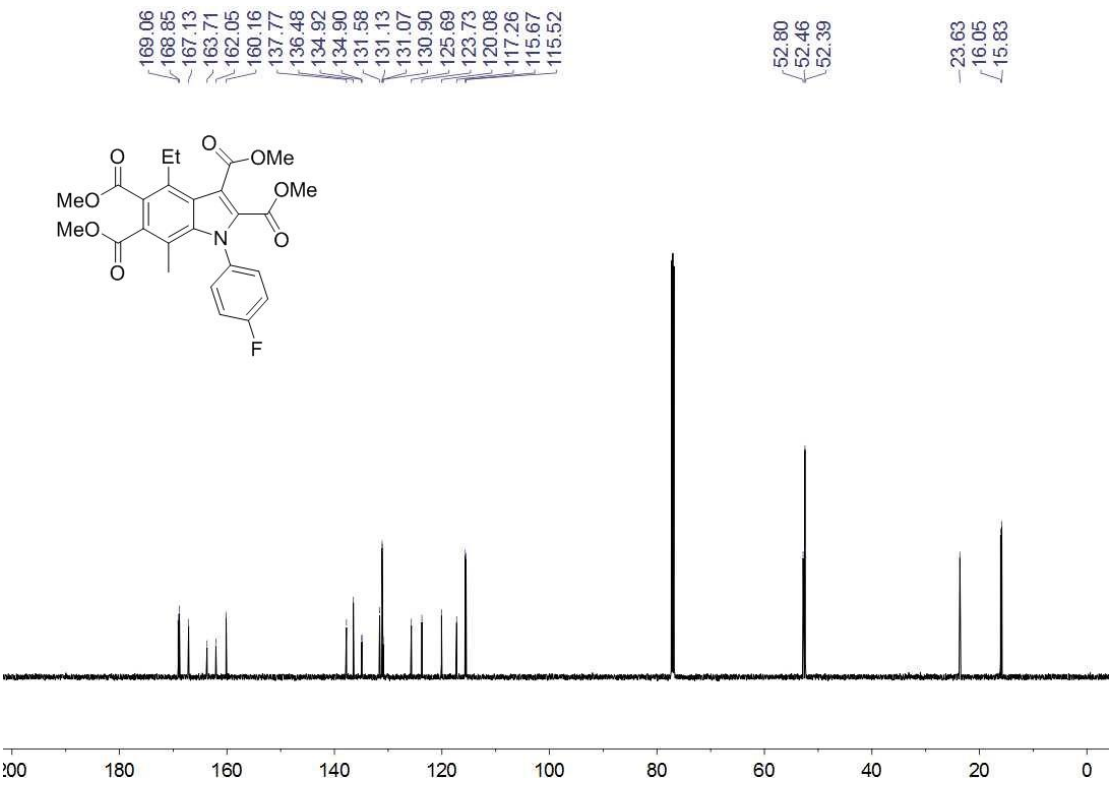


Figure 6. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3ea.**


7.35
7.34
7.34
7.33
7.27
7.17
7.15
7.14
3.97
3.87
3.83
3.71
3.01
3.00
2.99
2.97
1.82
1.27
1.26
1.24
Et
OMe
OMe
MeO
MeO
O
N
F
2.00
2.00
3.02
3.03
3.00
3.02
2.01
3.00
3.18
7
6
5
4
3
2
1
0


169.06
168.85
167.13
163.71
162.05
160.16
137.77
136.48
134.92
134.90
131.58
131.13
131.07
130.90
125.69
123.73
120.08
117.26
115.67
115.52
52.80
52.46
52.39
23.63
16.05
15.83
Et
OMe
OMe
MeO
MeO
O
N
F
200
180
160
140
120
100
80
60
40
20
0

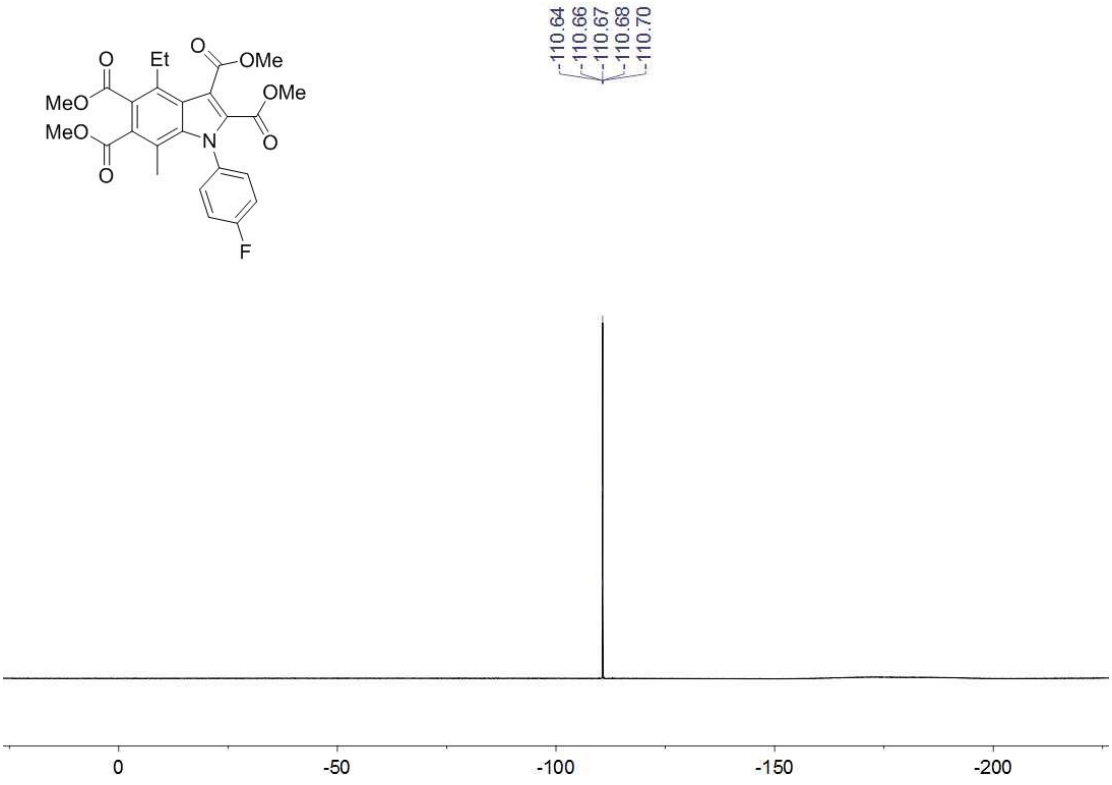
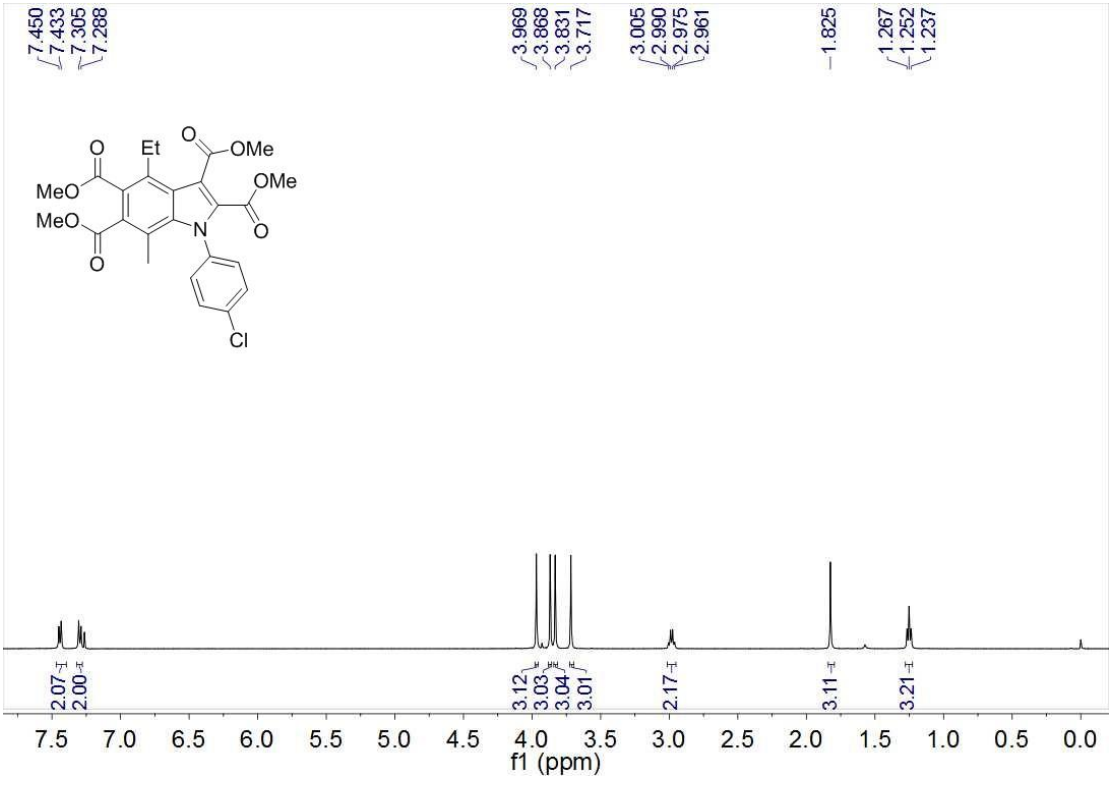


Figure 7. ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR spectra of compound **3fa**



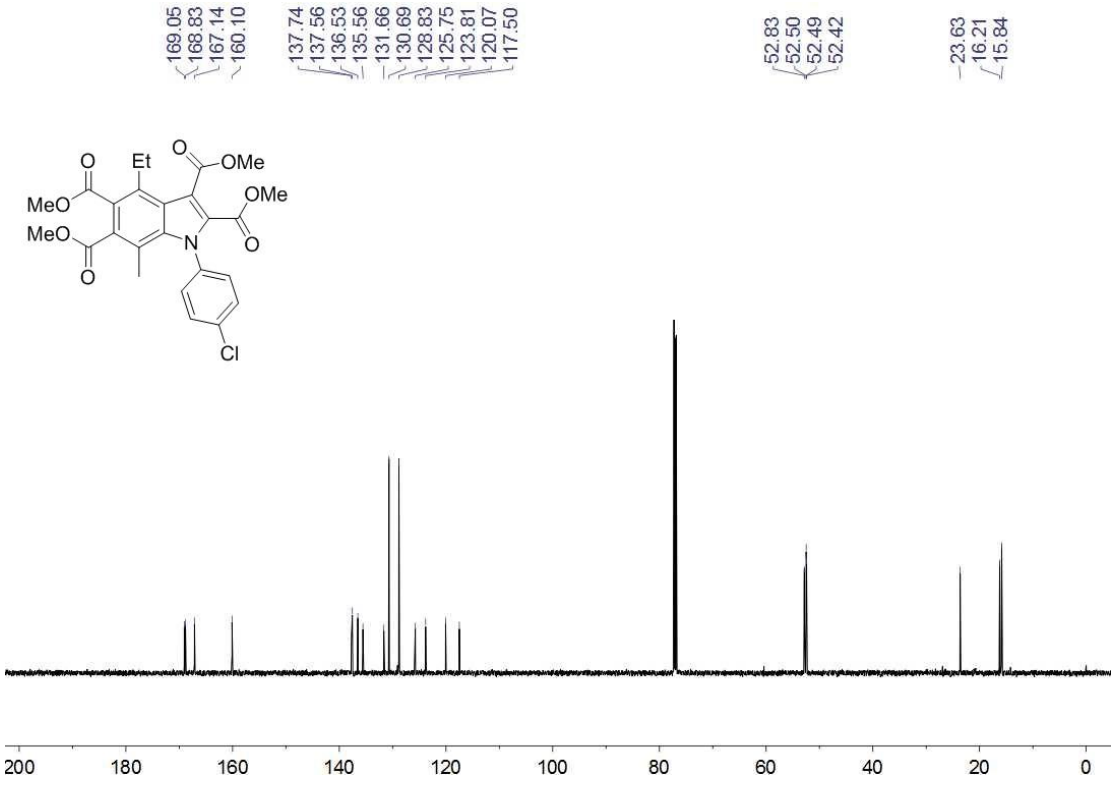
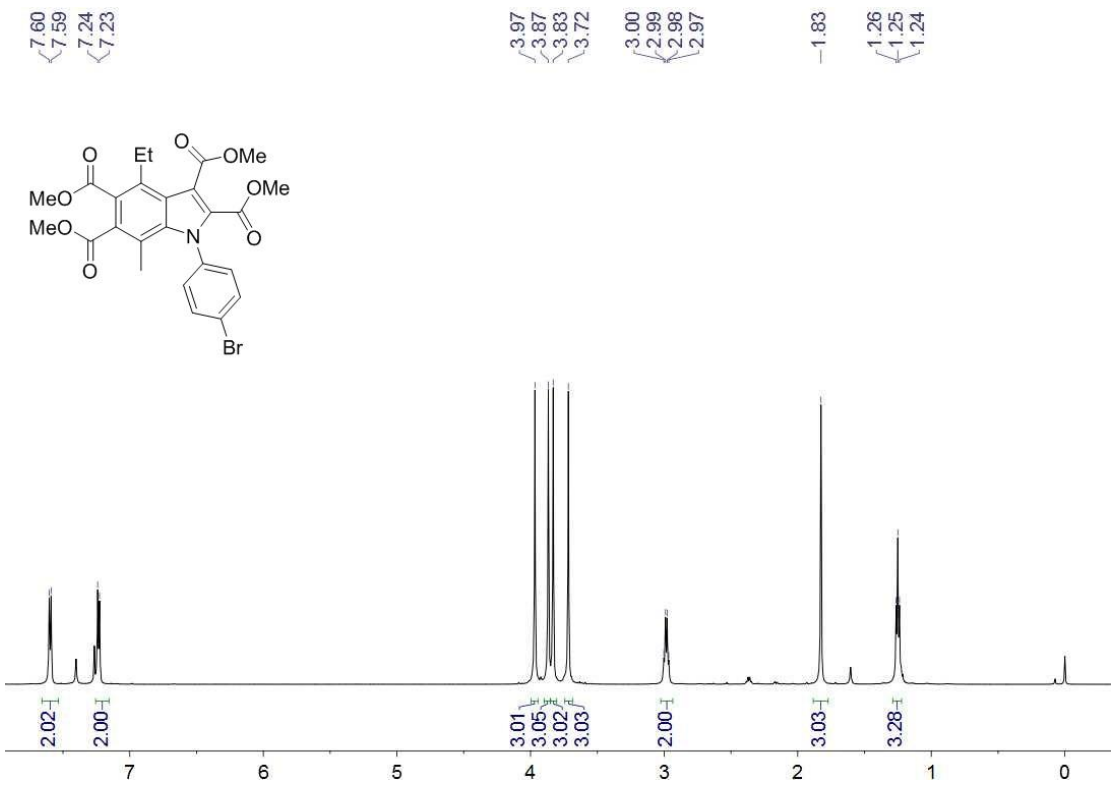


Figure 8. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3ga.**



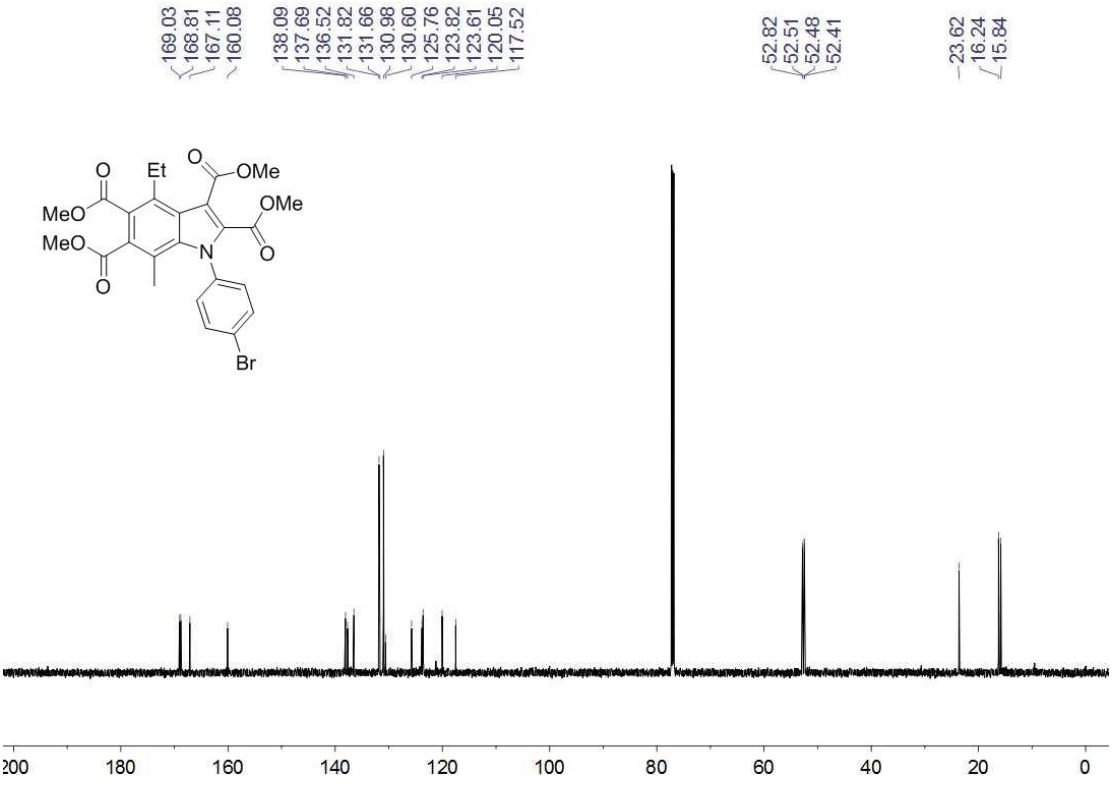
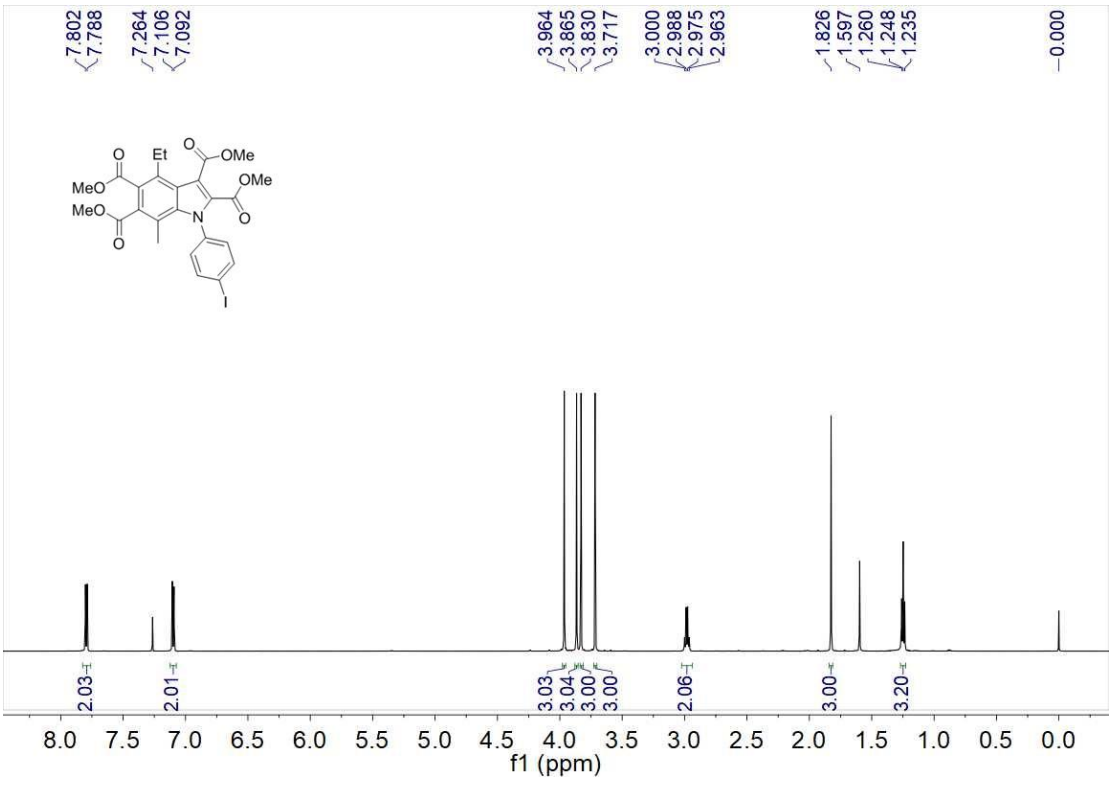


Figure 9. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3ha.**



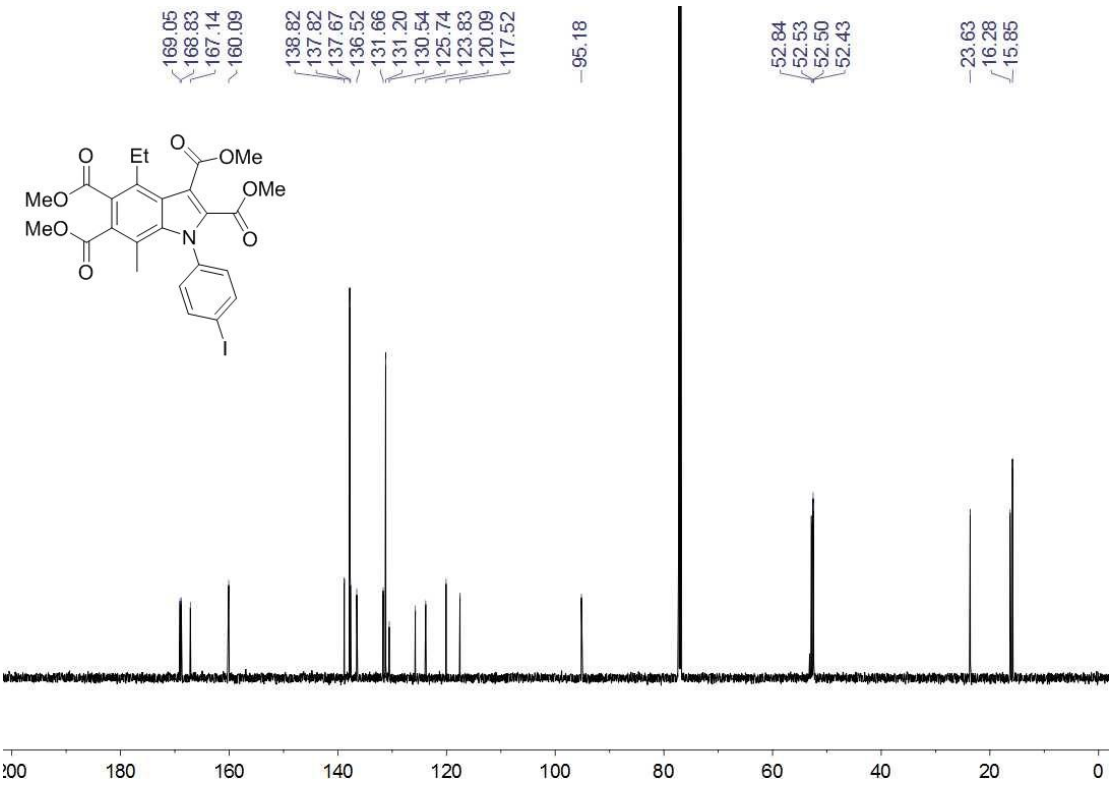
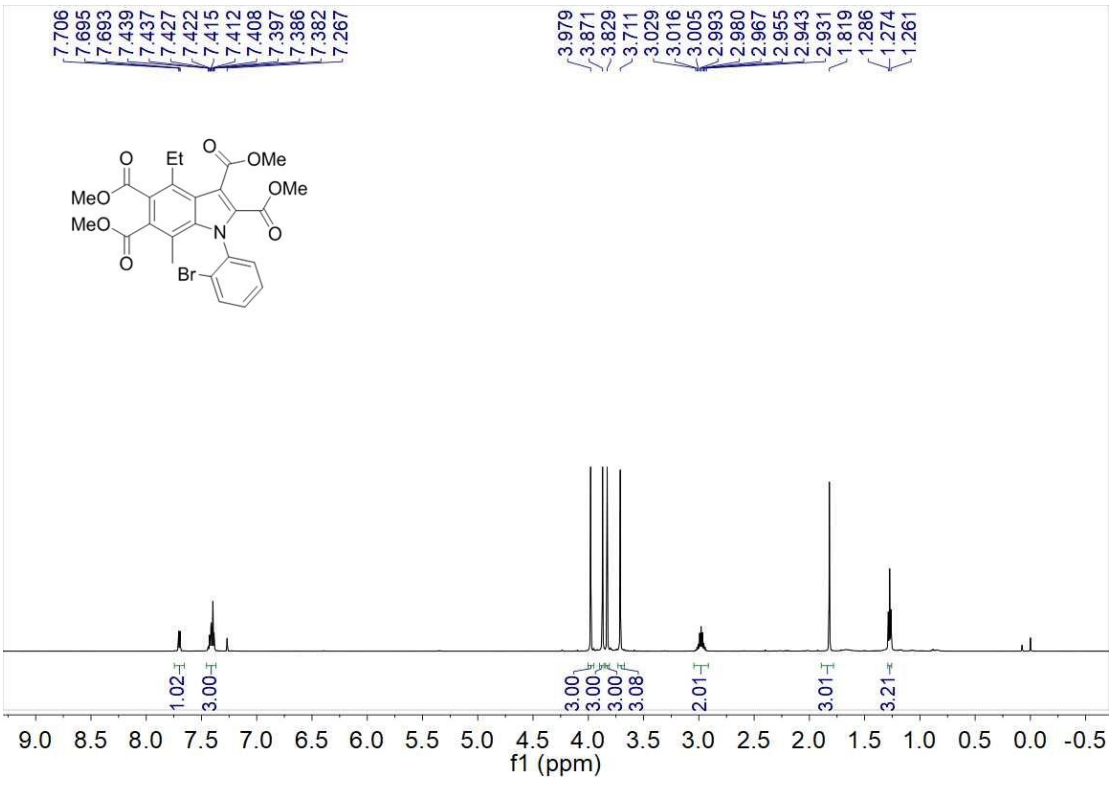


Figure 10. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3ia.**



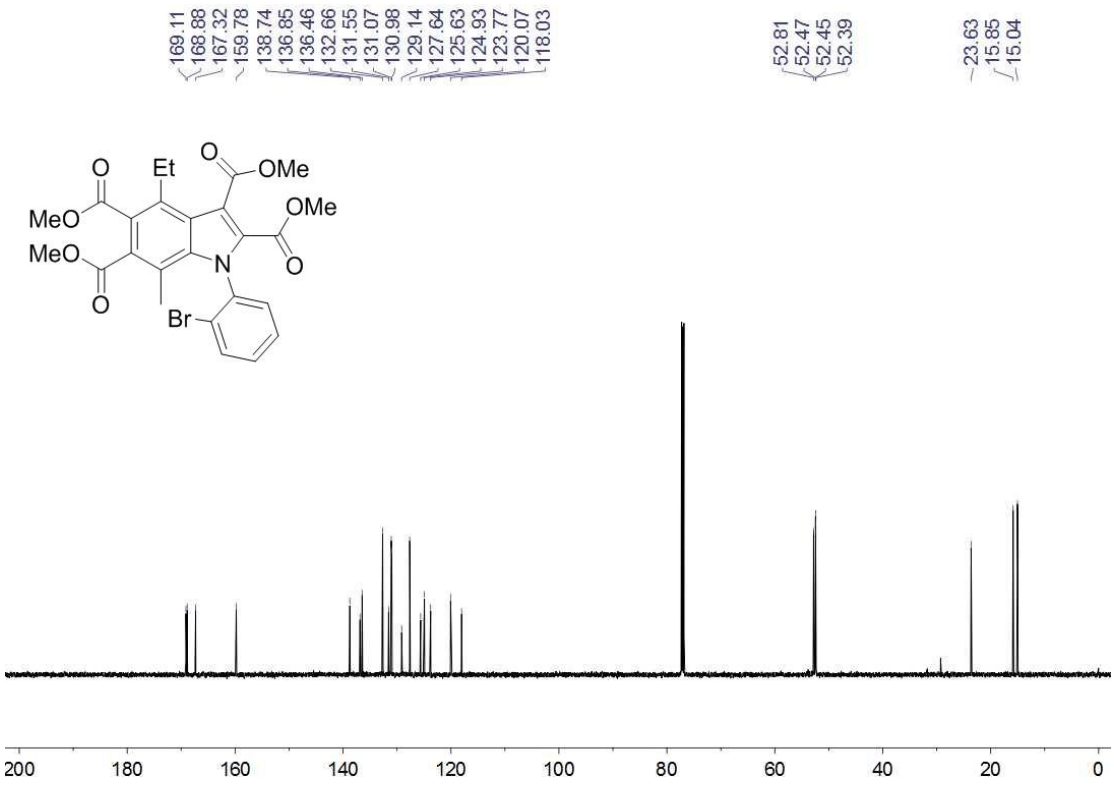
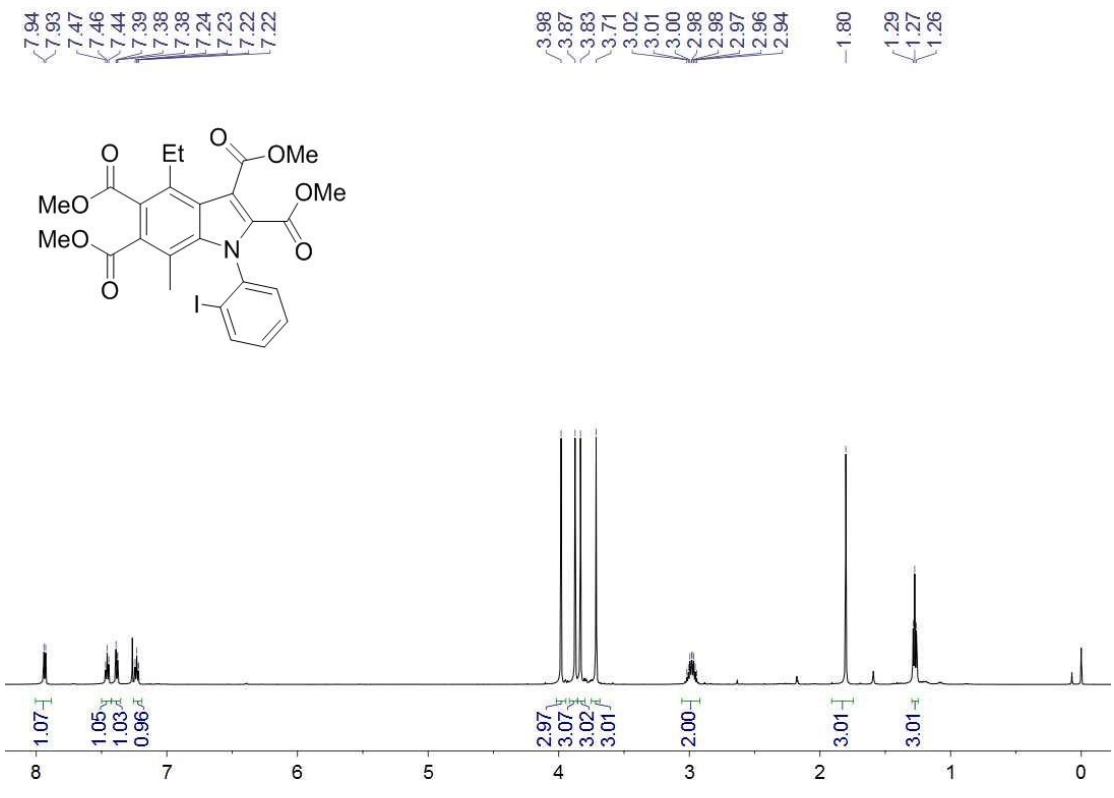


Figure 11. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3ja.**



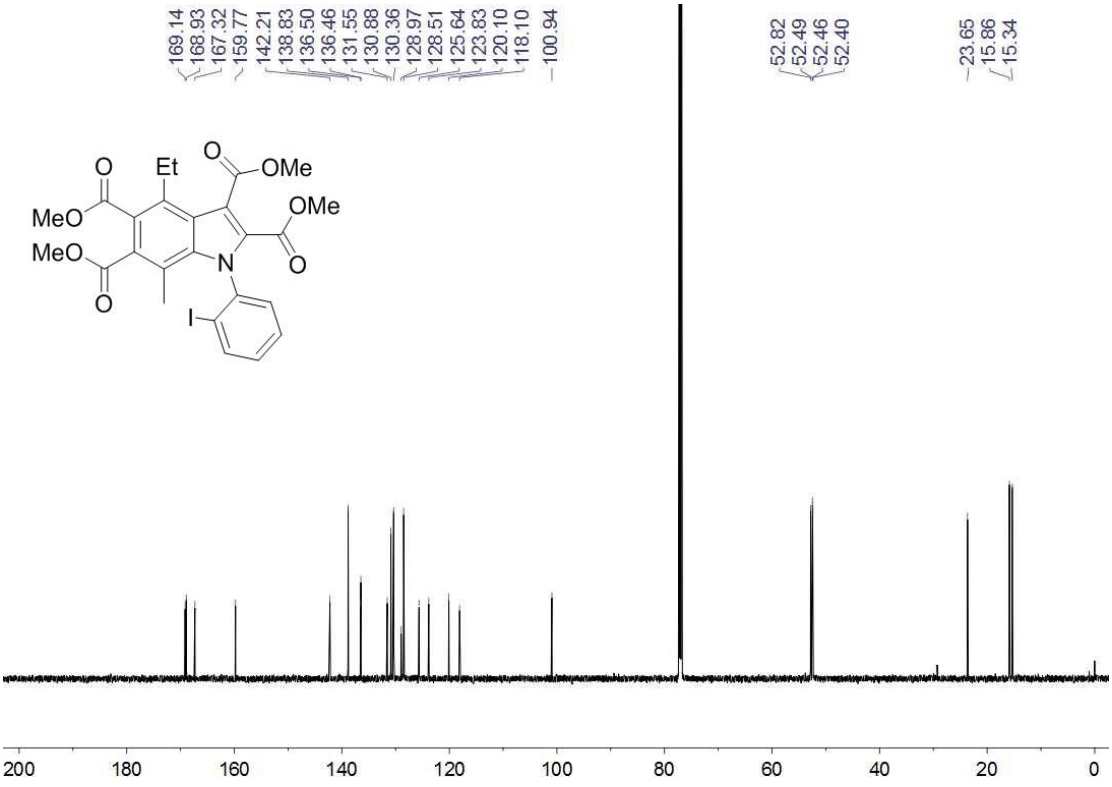
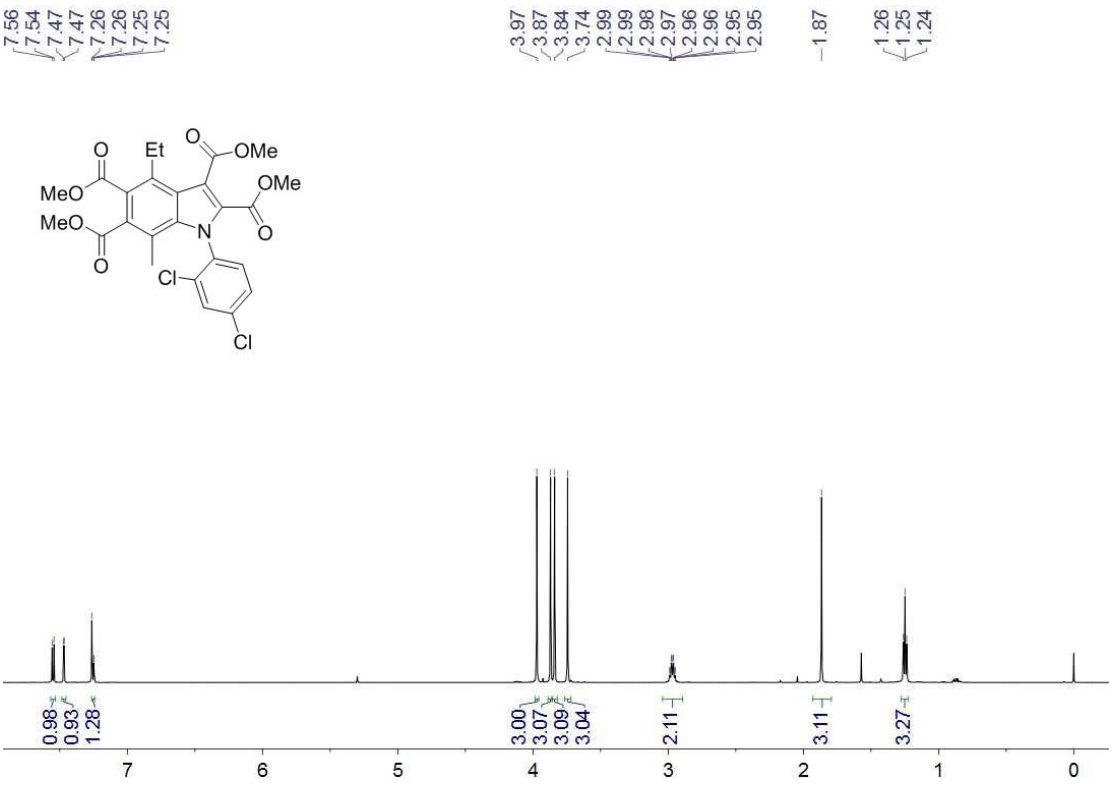


Figure 12. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3ka.**



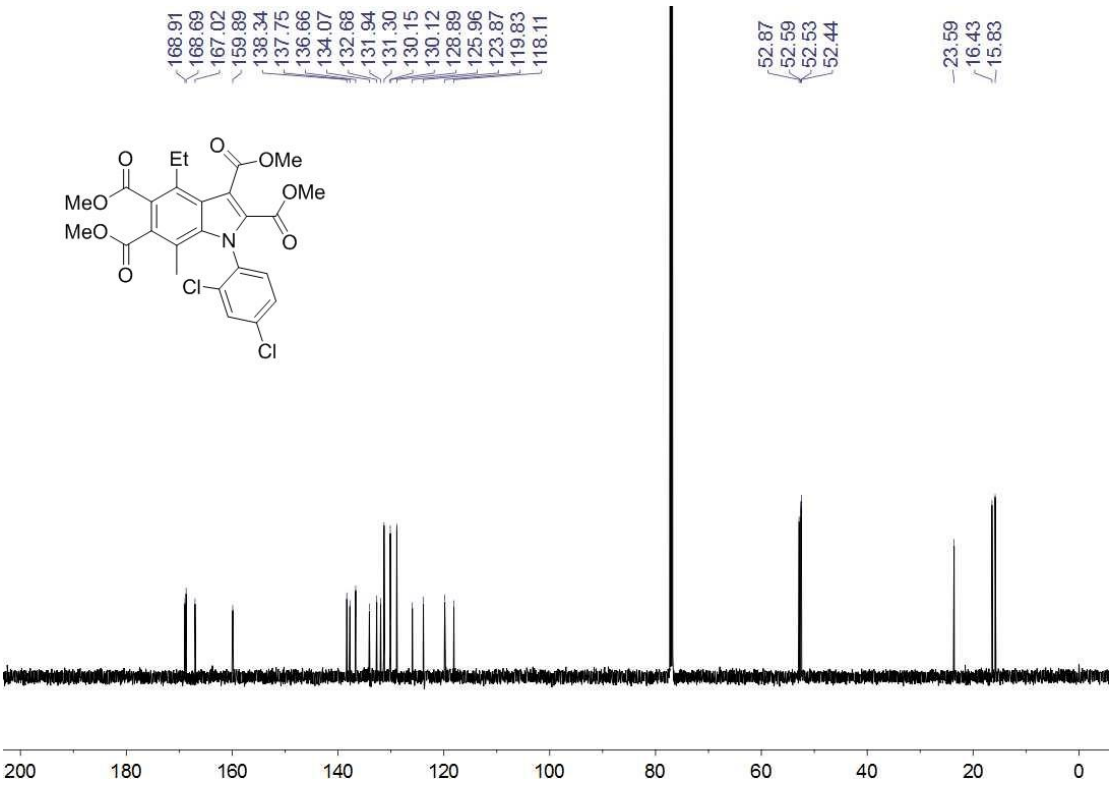
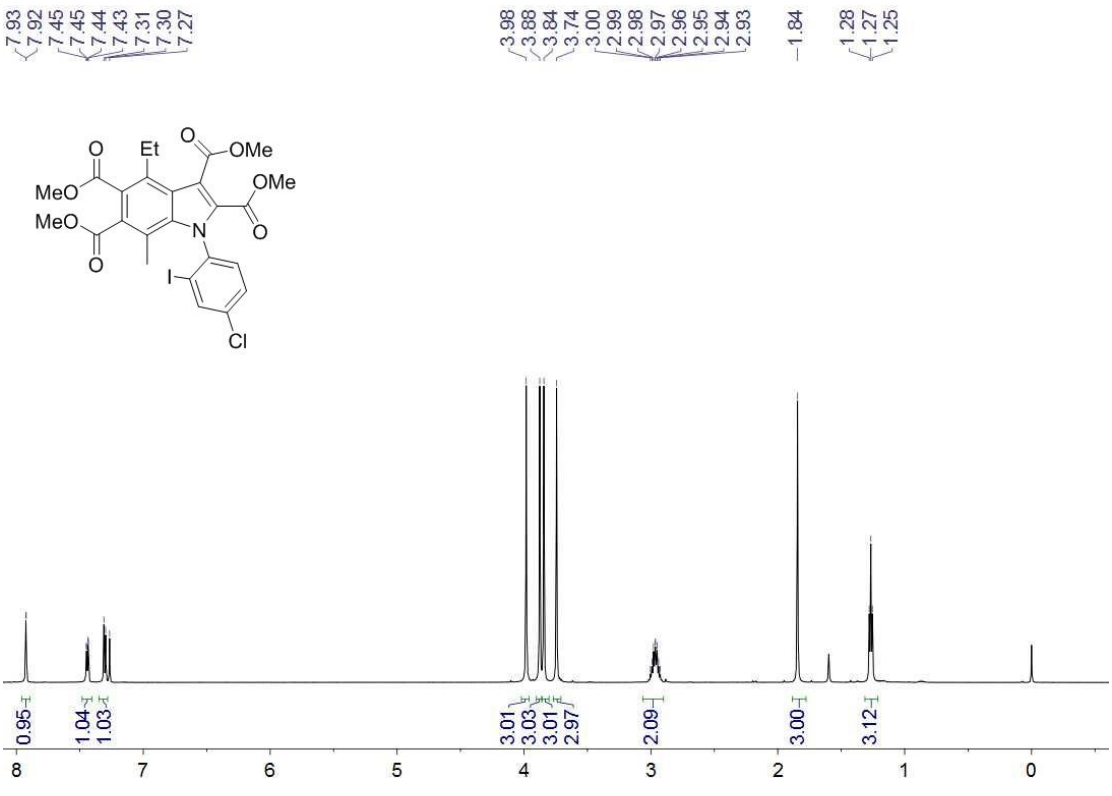


Figure 13. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3la.**



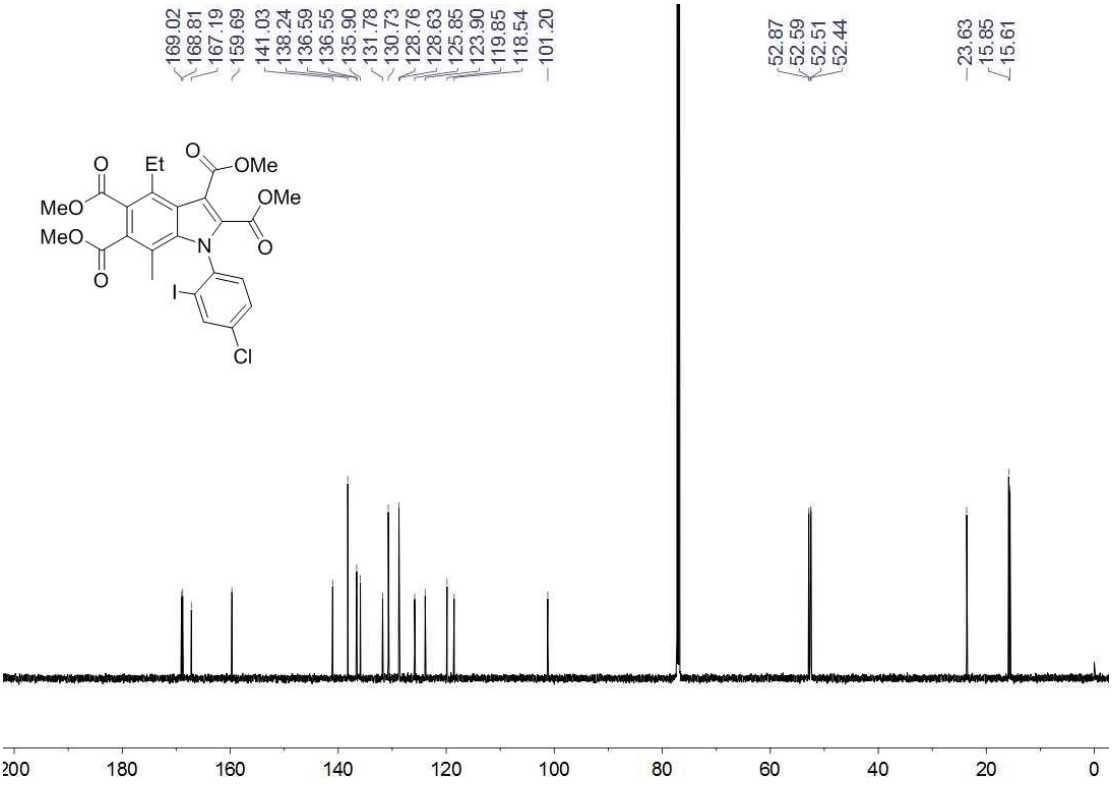
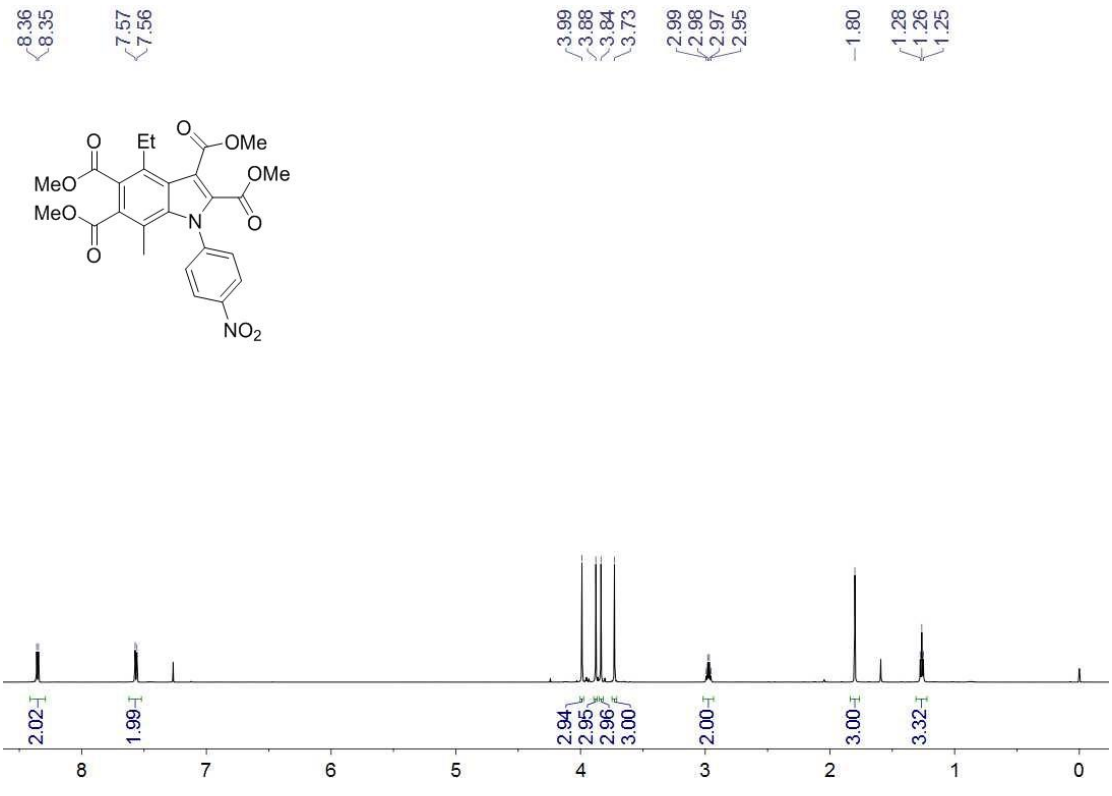


Figure 14. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3ma.**



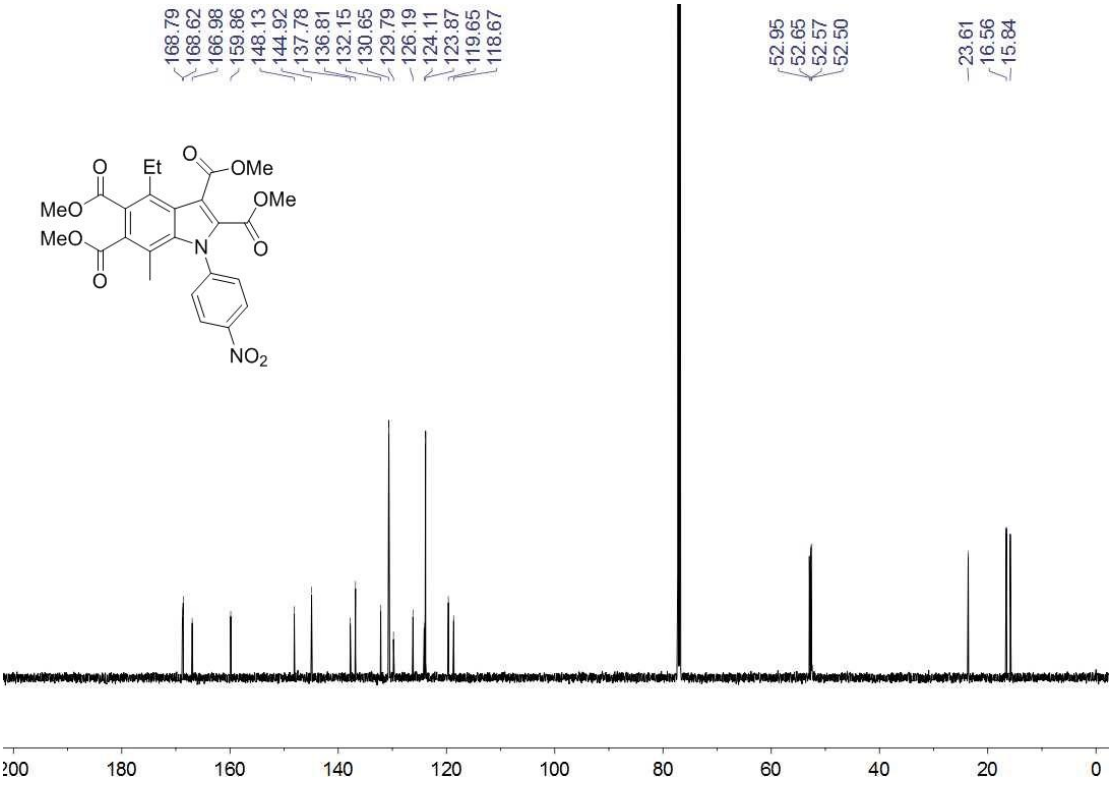
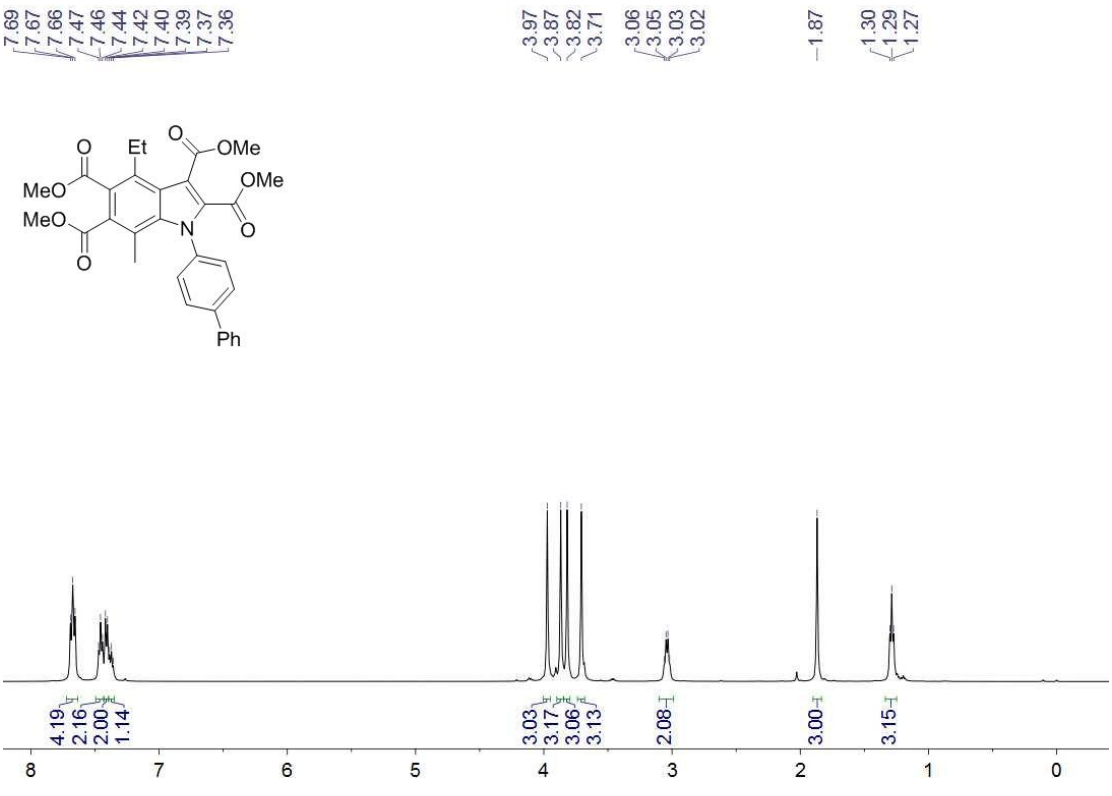


Figure 15. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3na.**



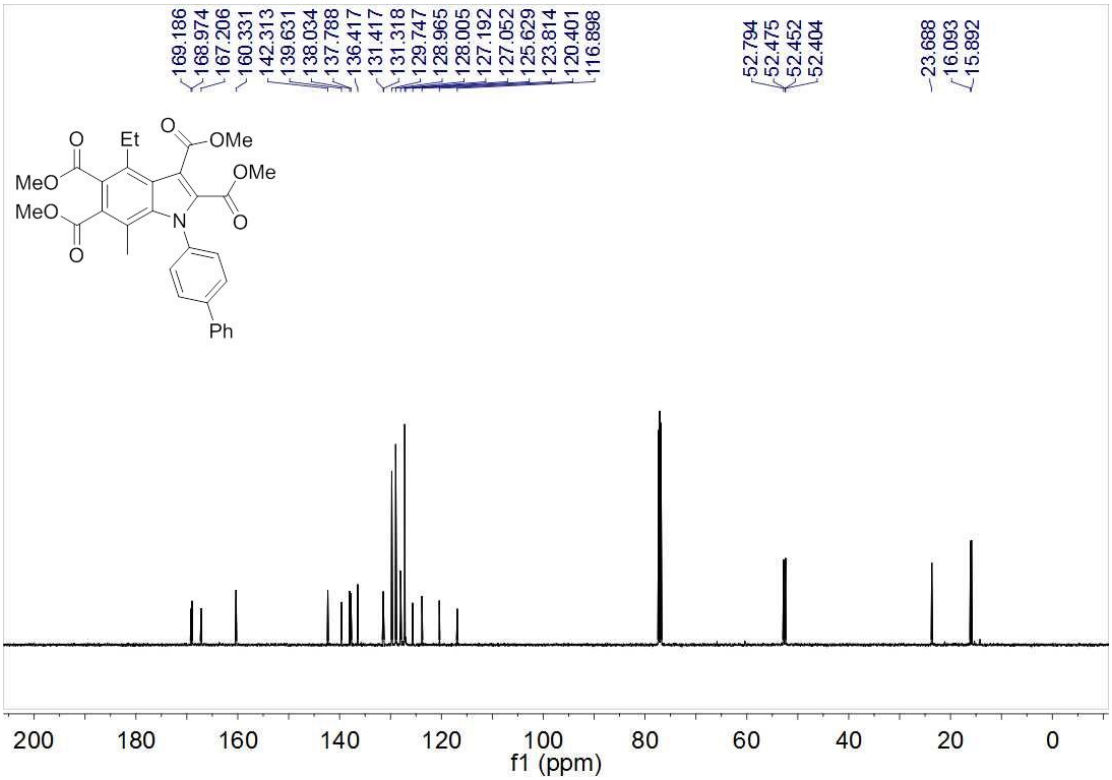
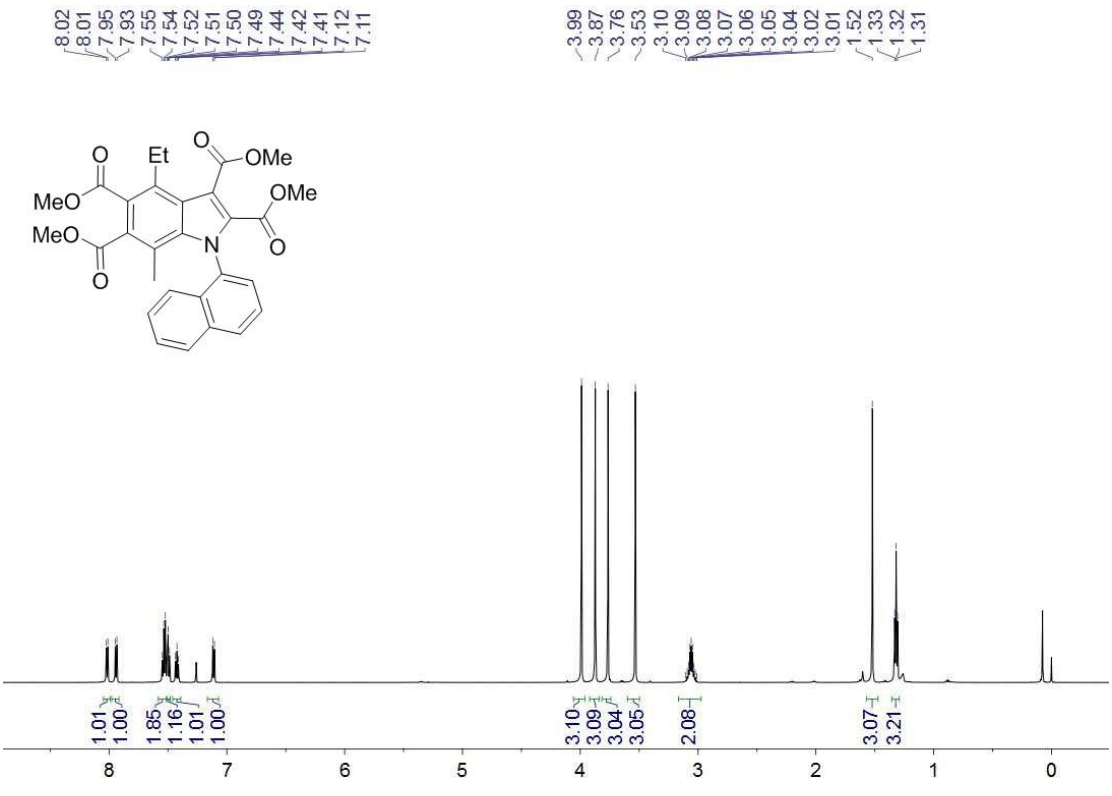


Figure 16. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3oa.**



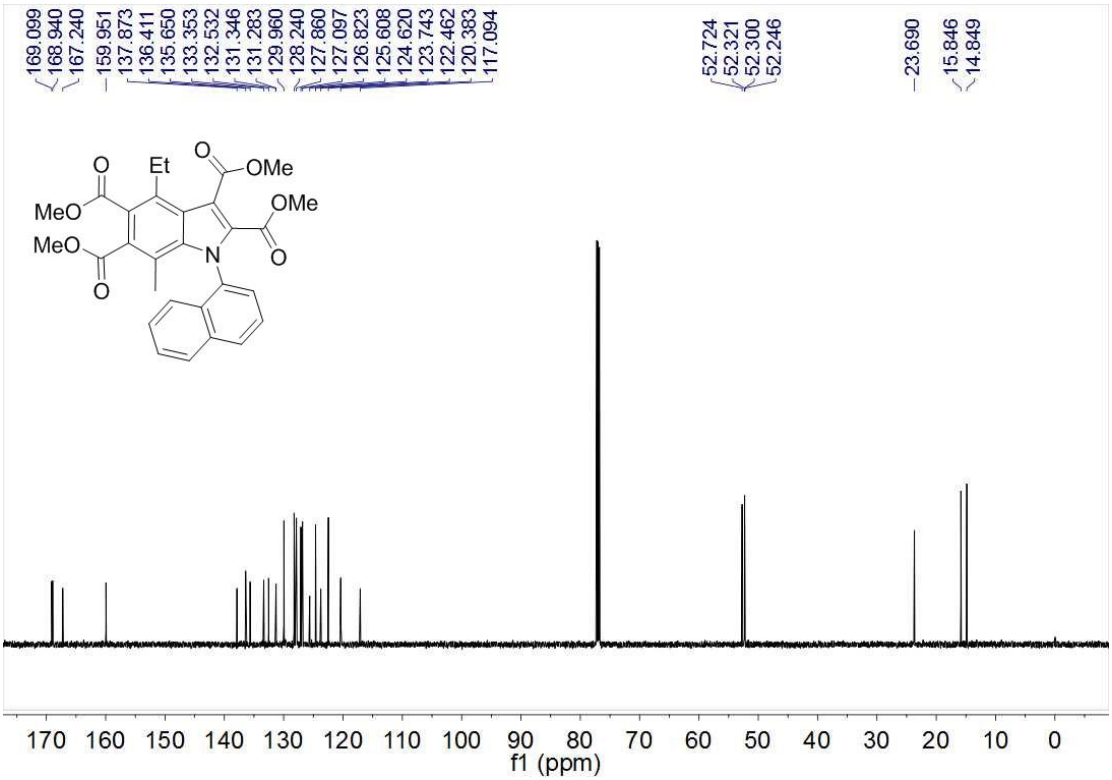
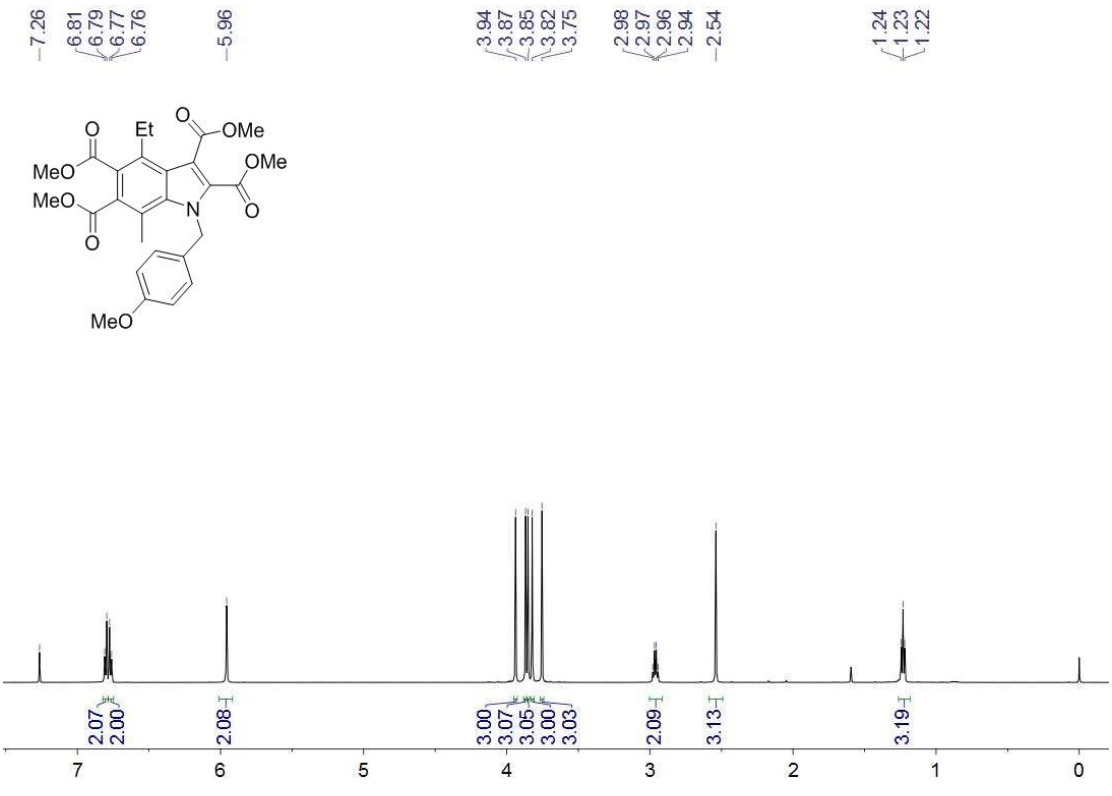


Figure 17. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3pa.**



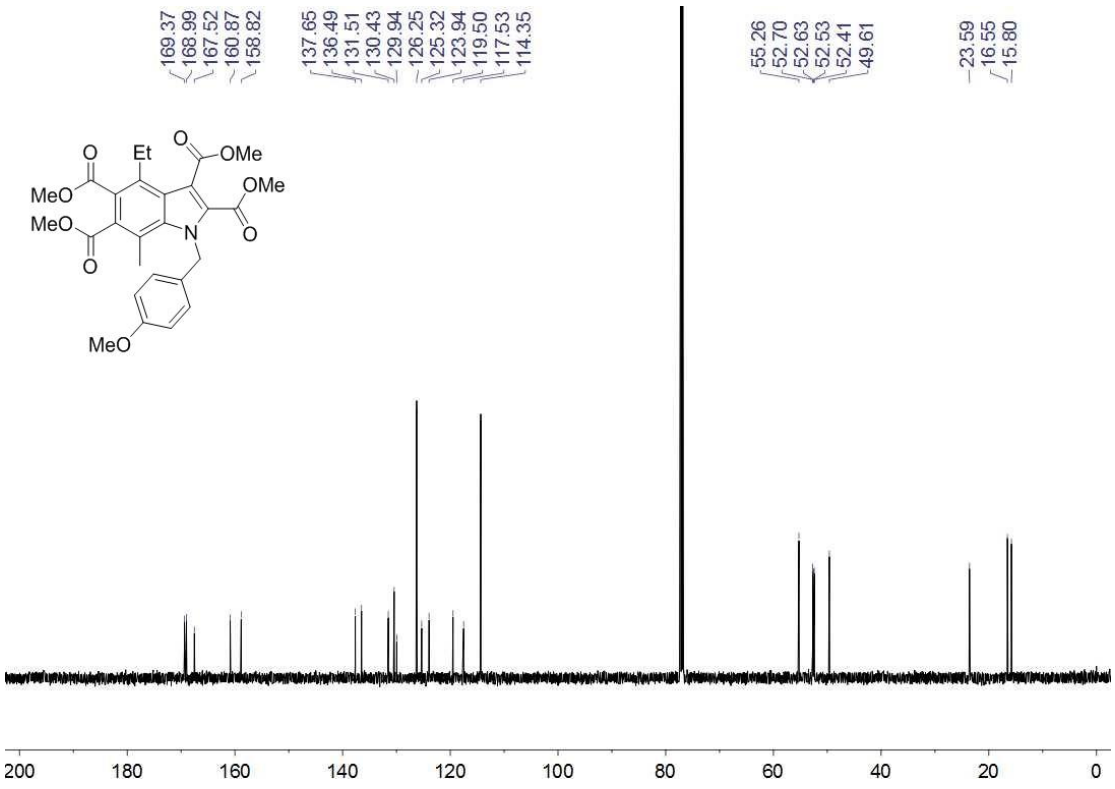
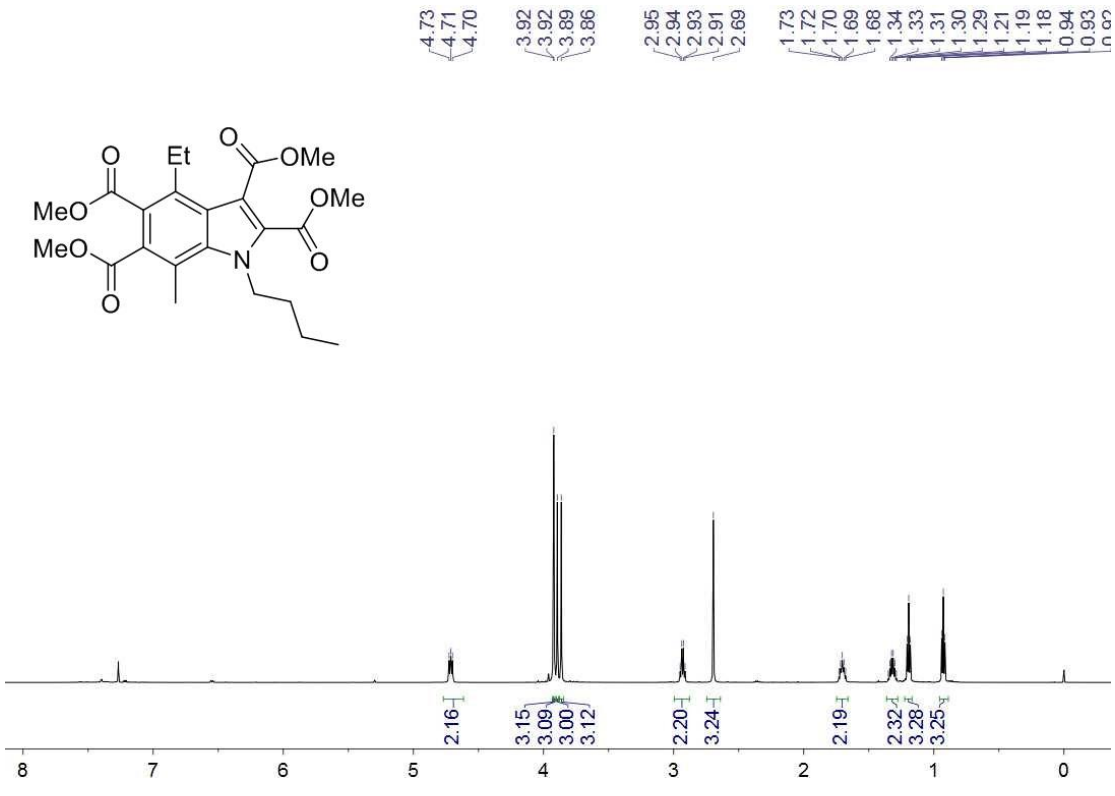


Figure 18. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3qa.**



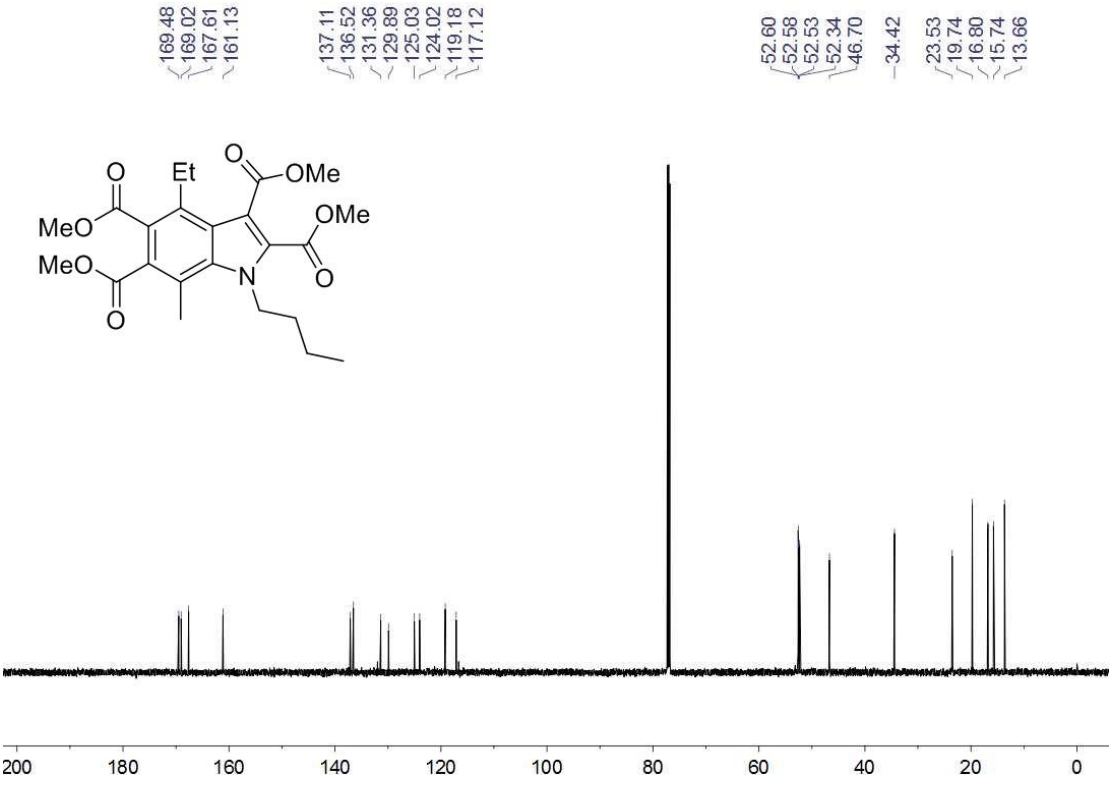
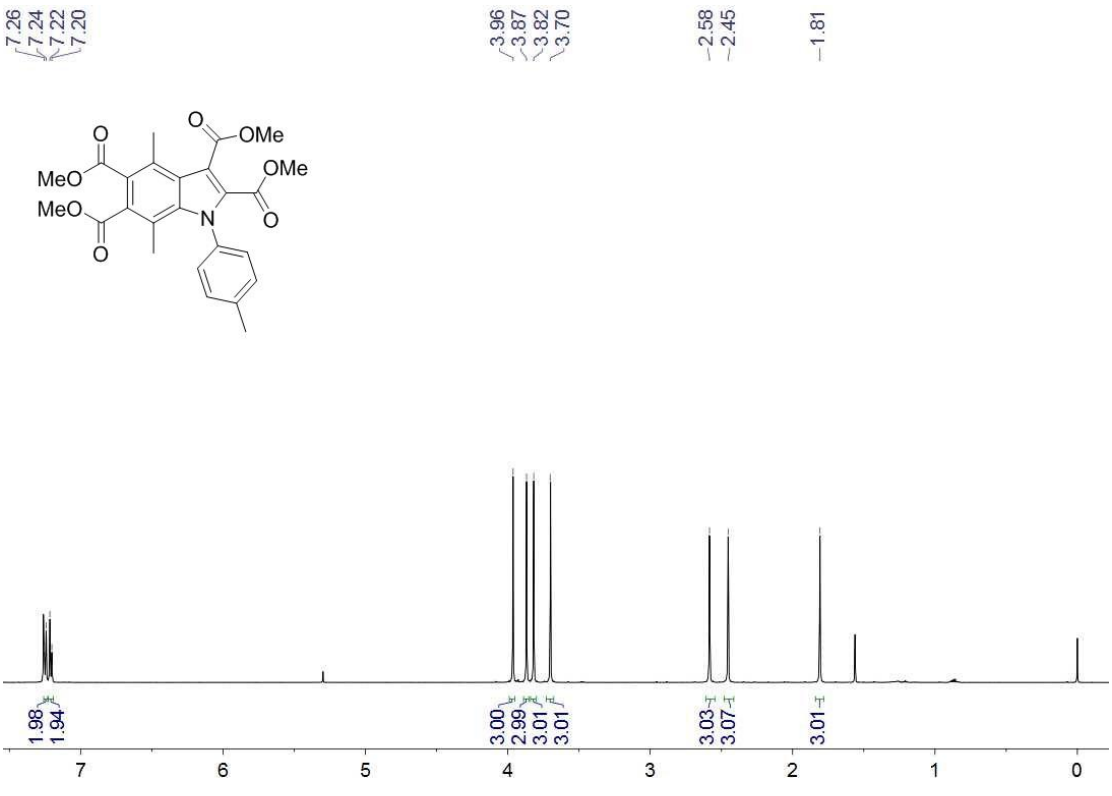


Figure 19. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3ra.**



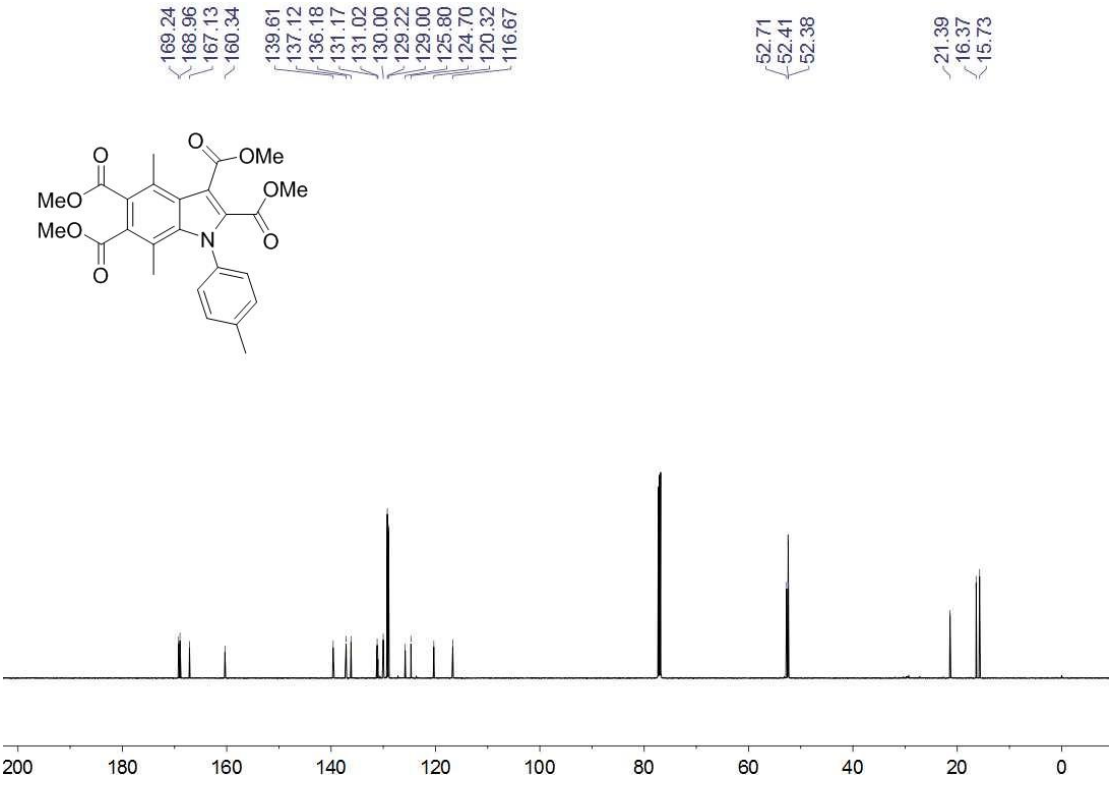
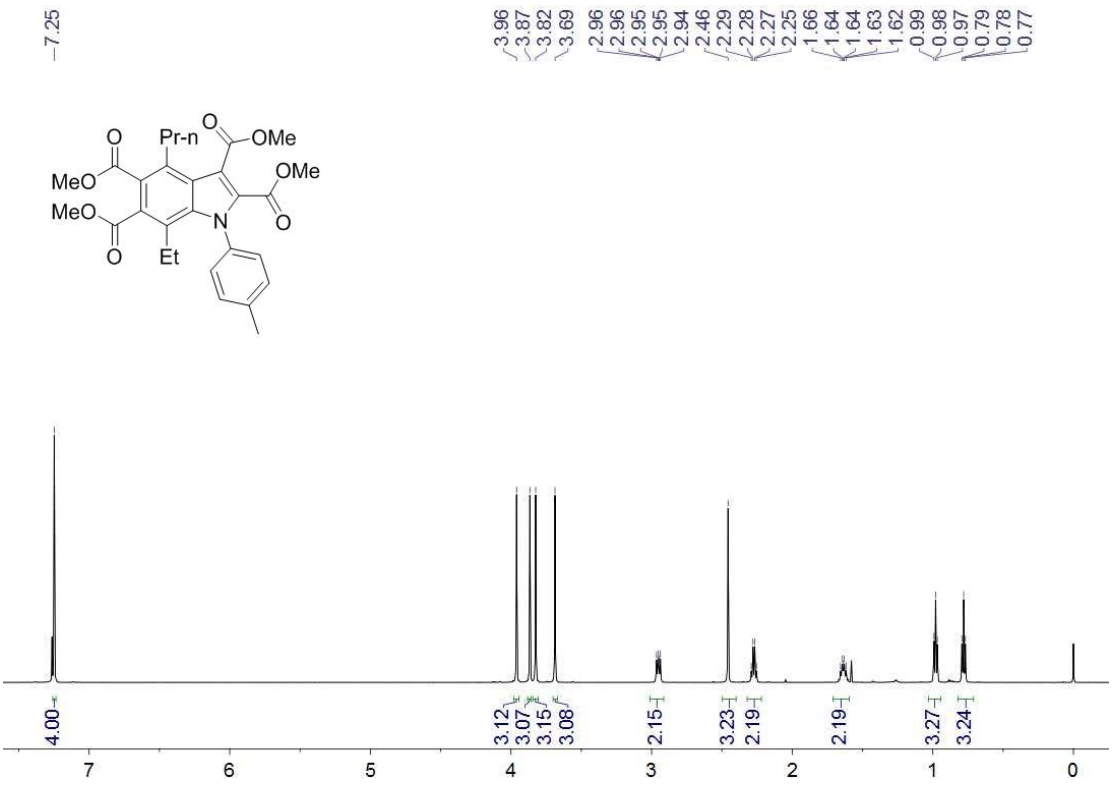


Figure 20. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3sa.**



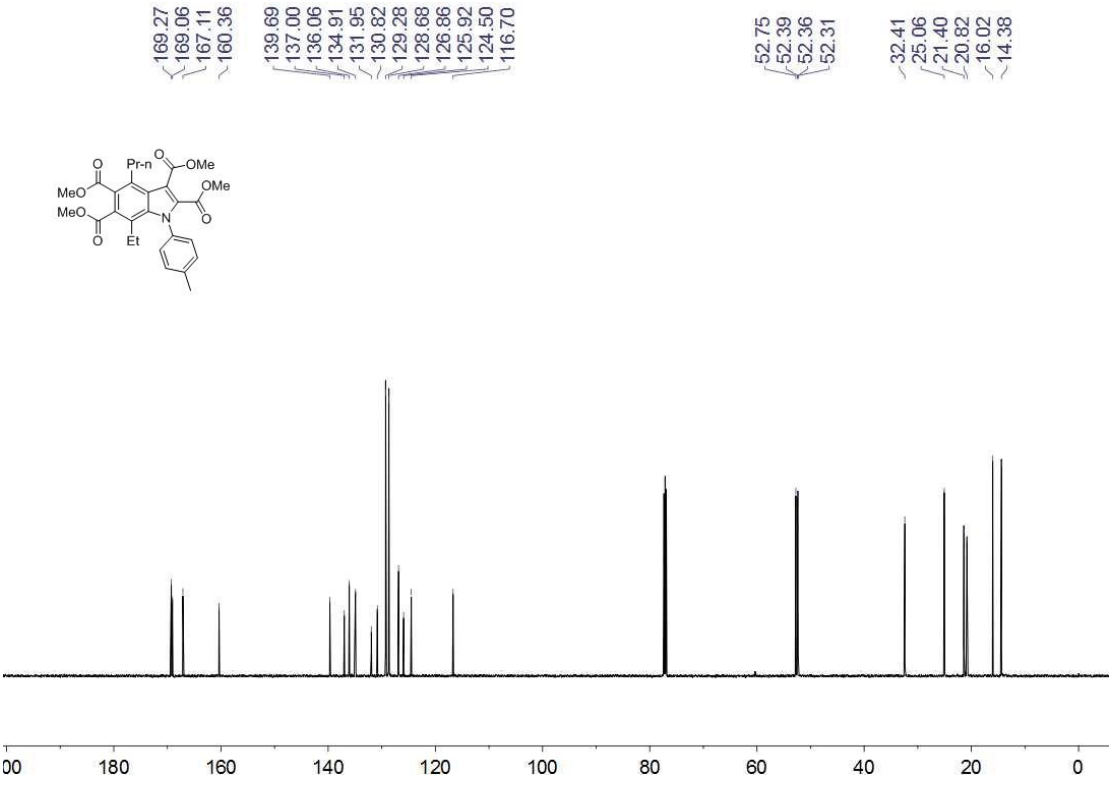
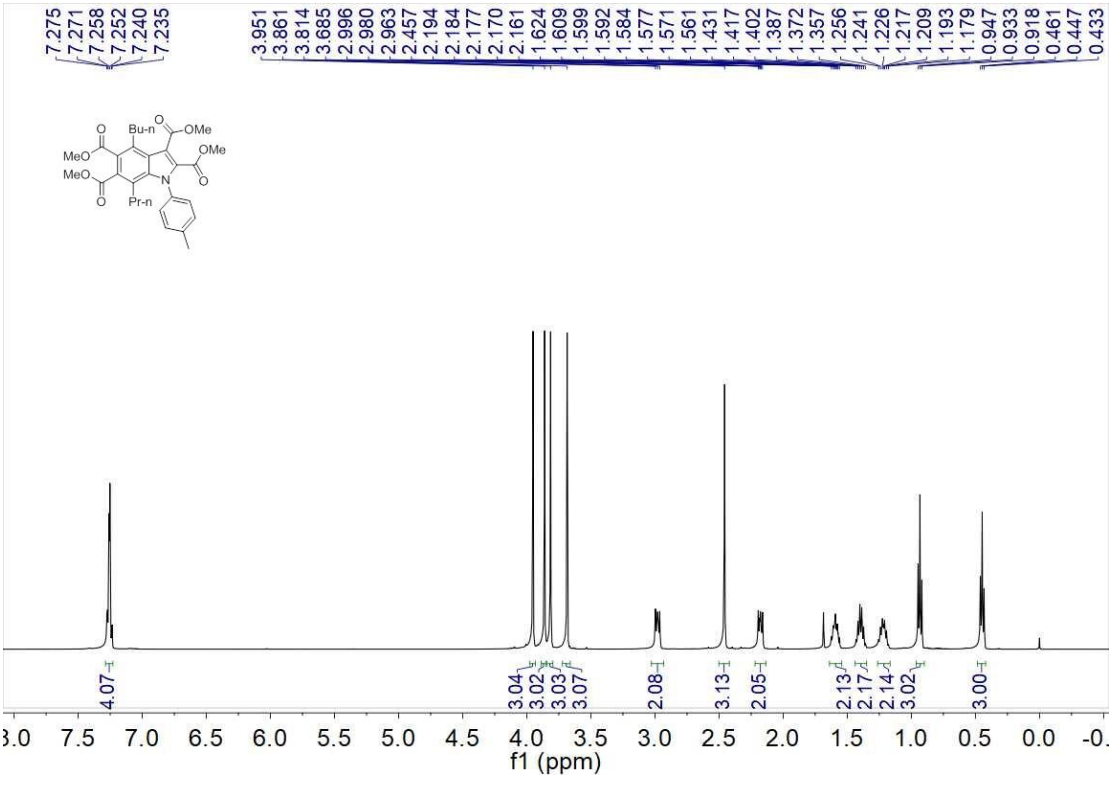


Figure 21. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3ta.**



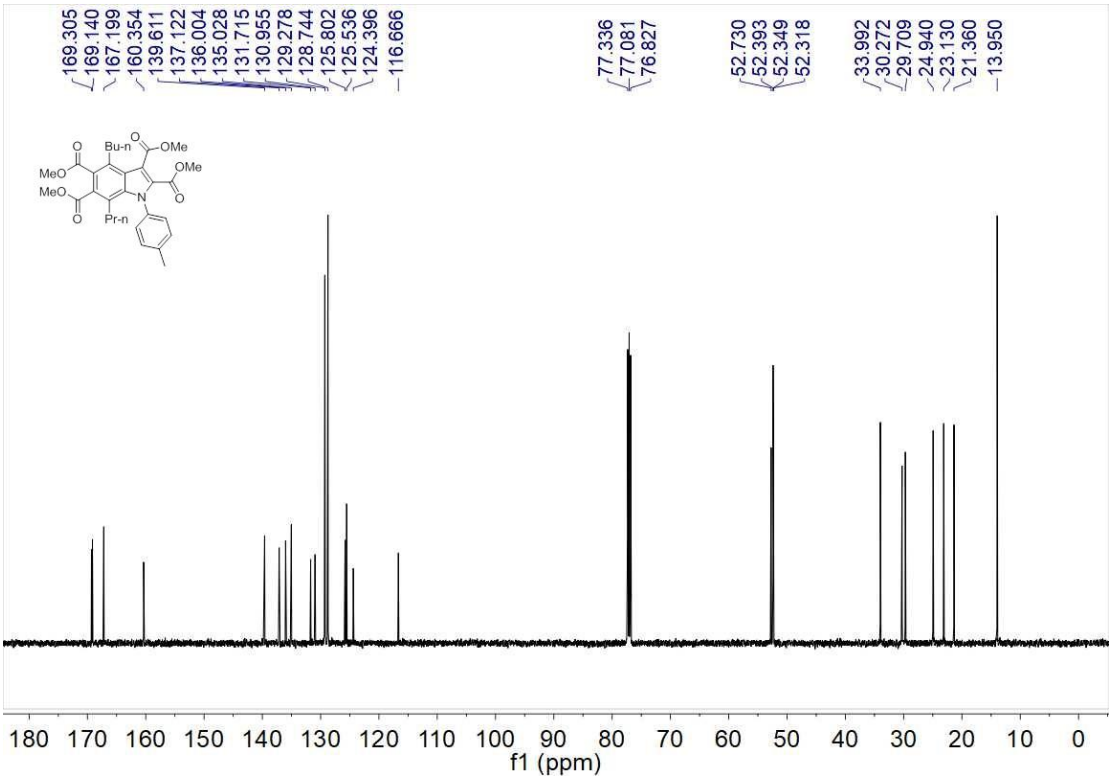
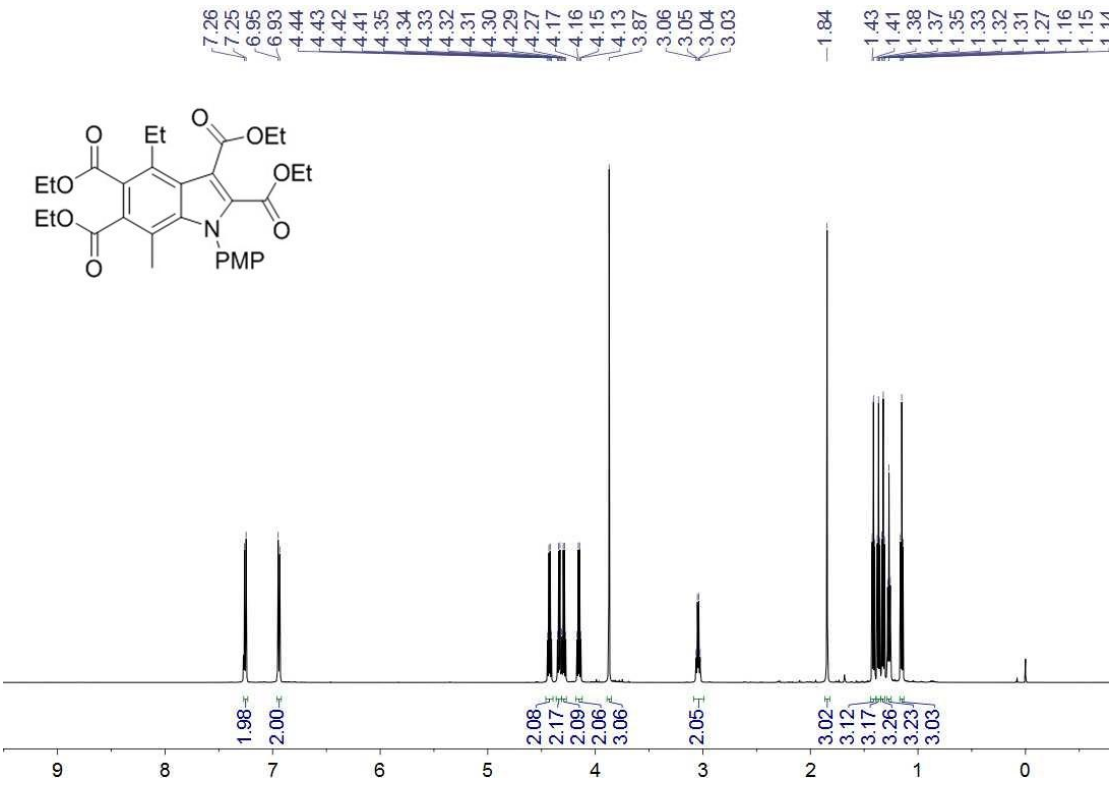


Figure 22. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3ua.**



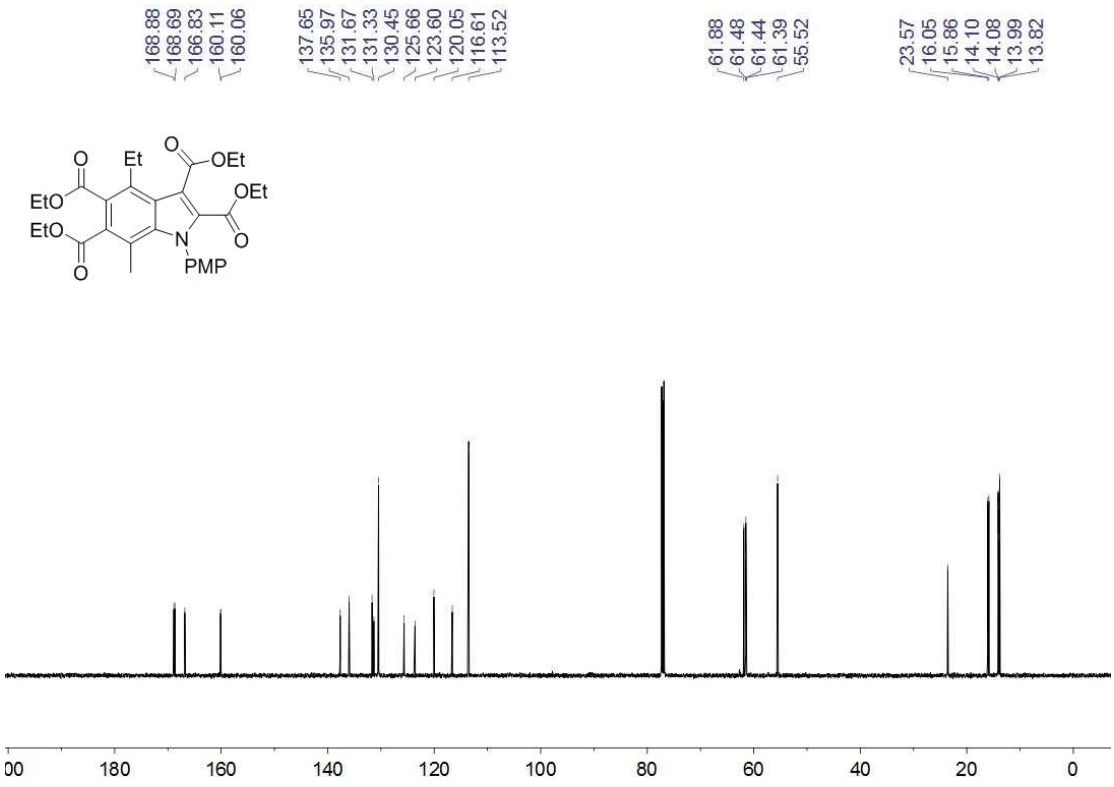
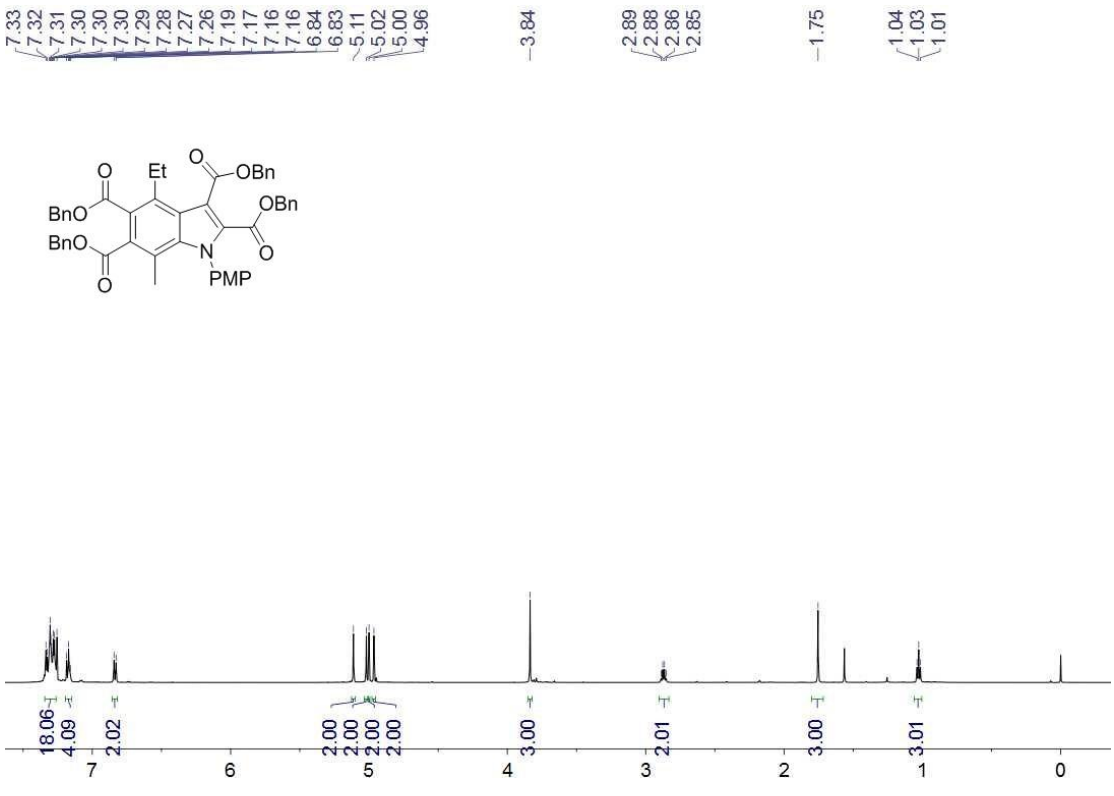


Figure 23. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3ab.**



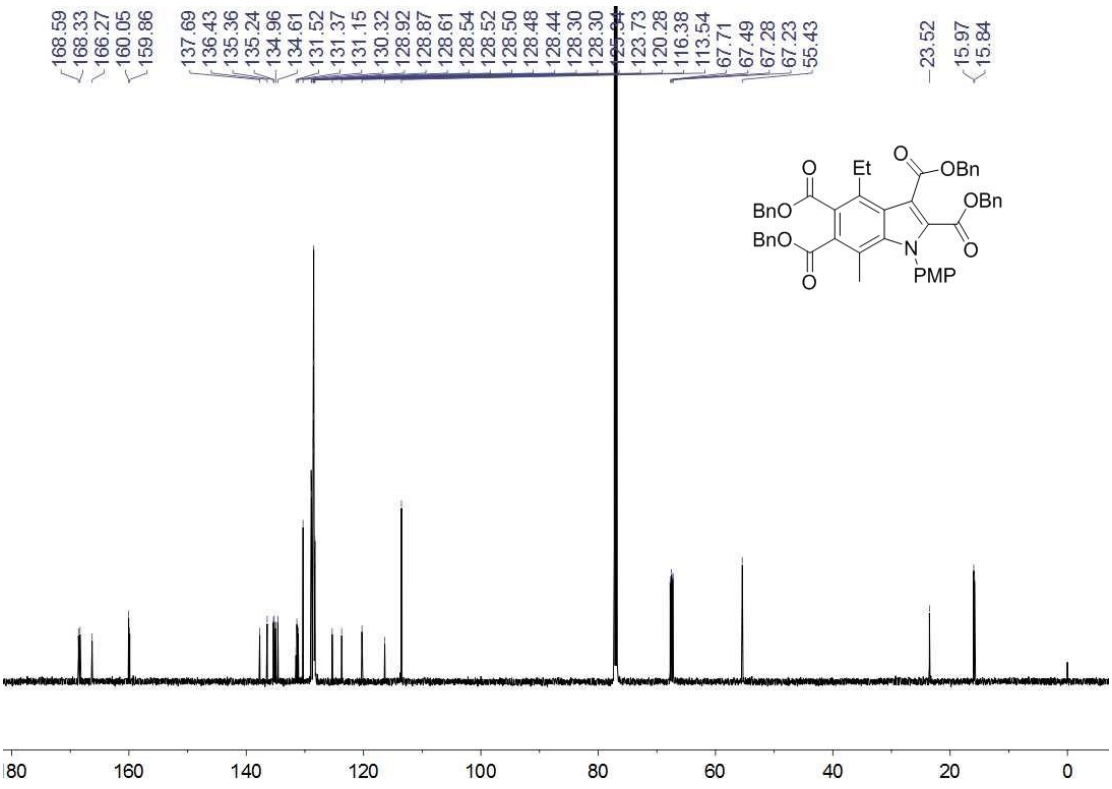
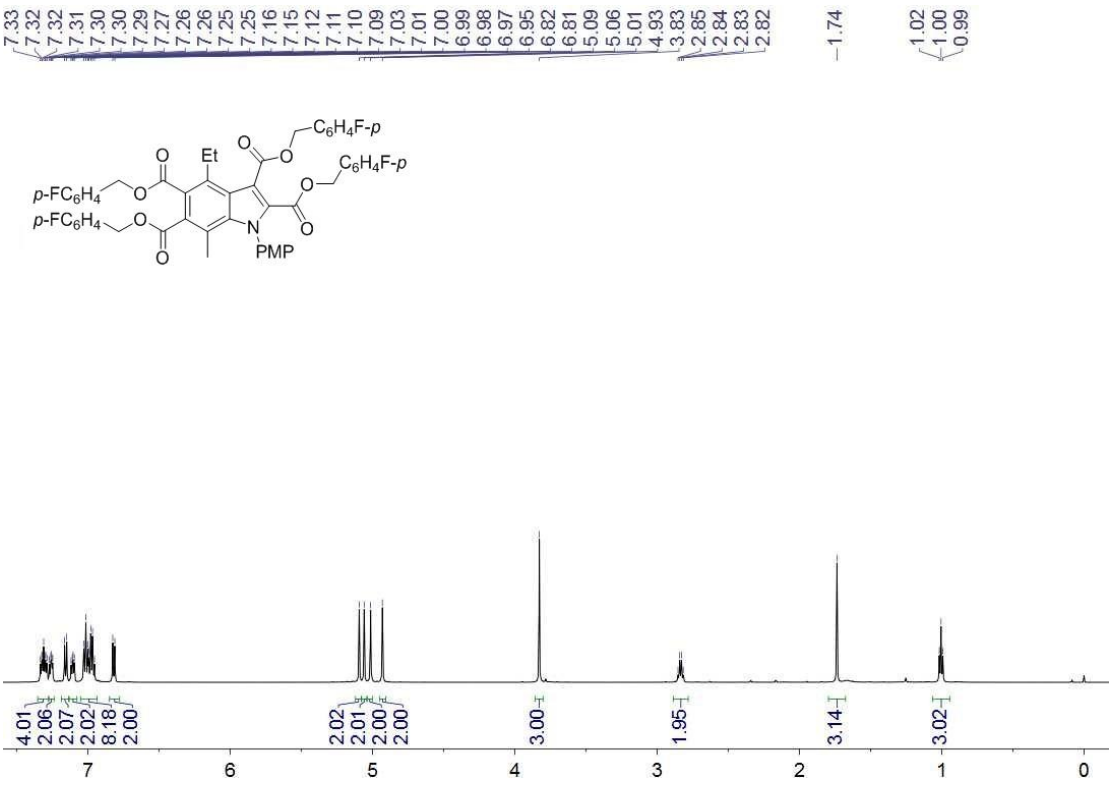


Figure 24. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3ac.**



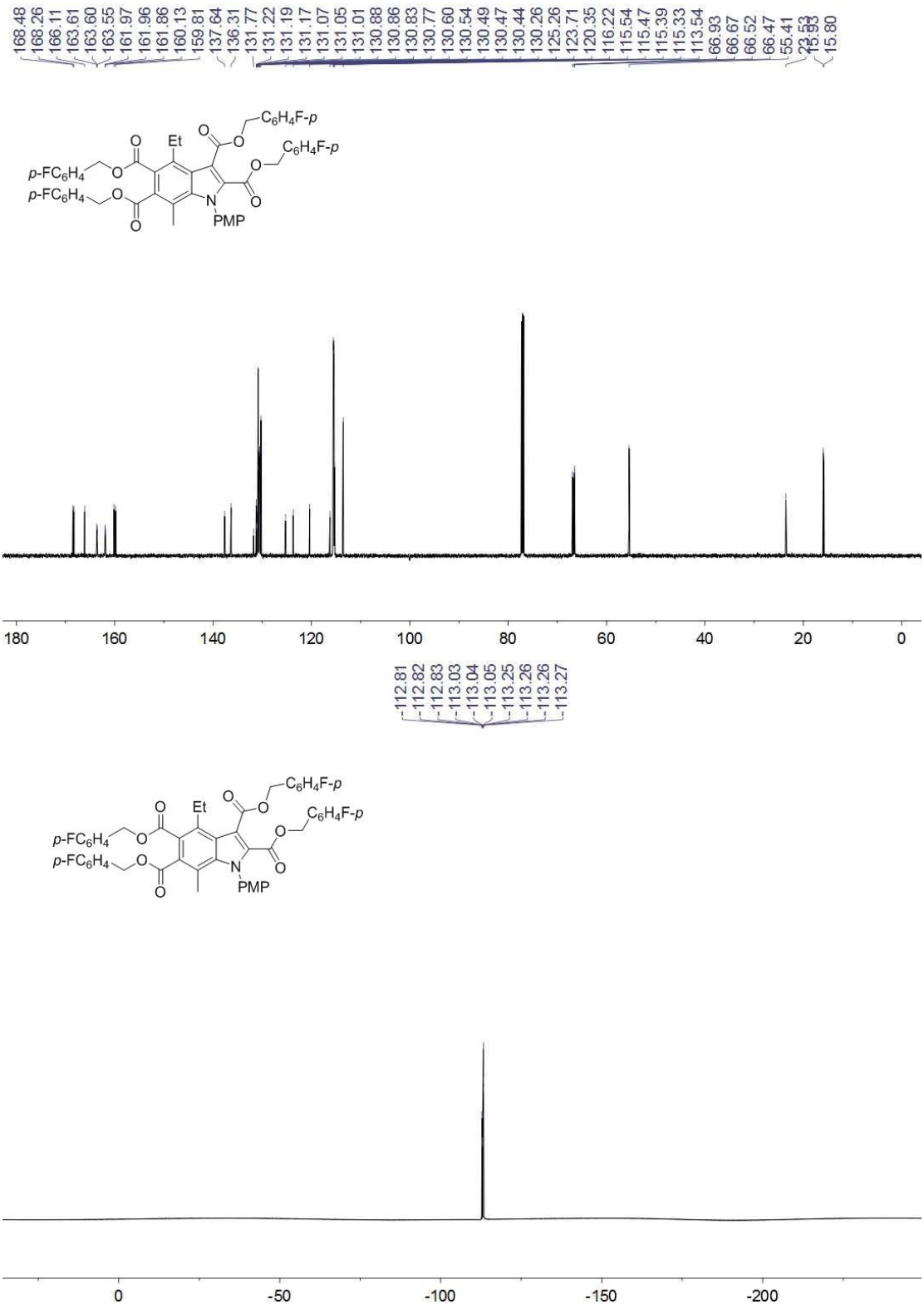


Figure 25. ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR spectra of compound **3ad.**

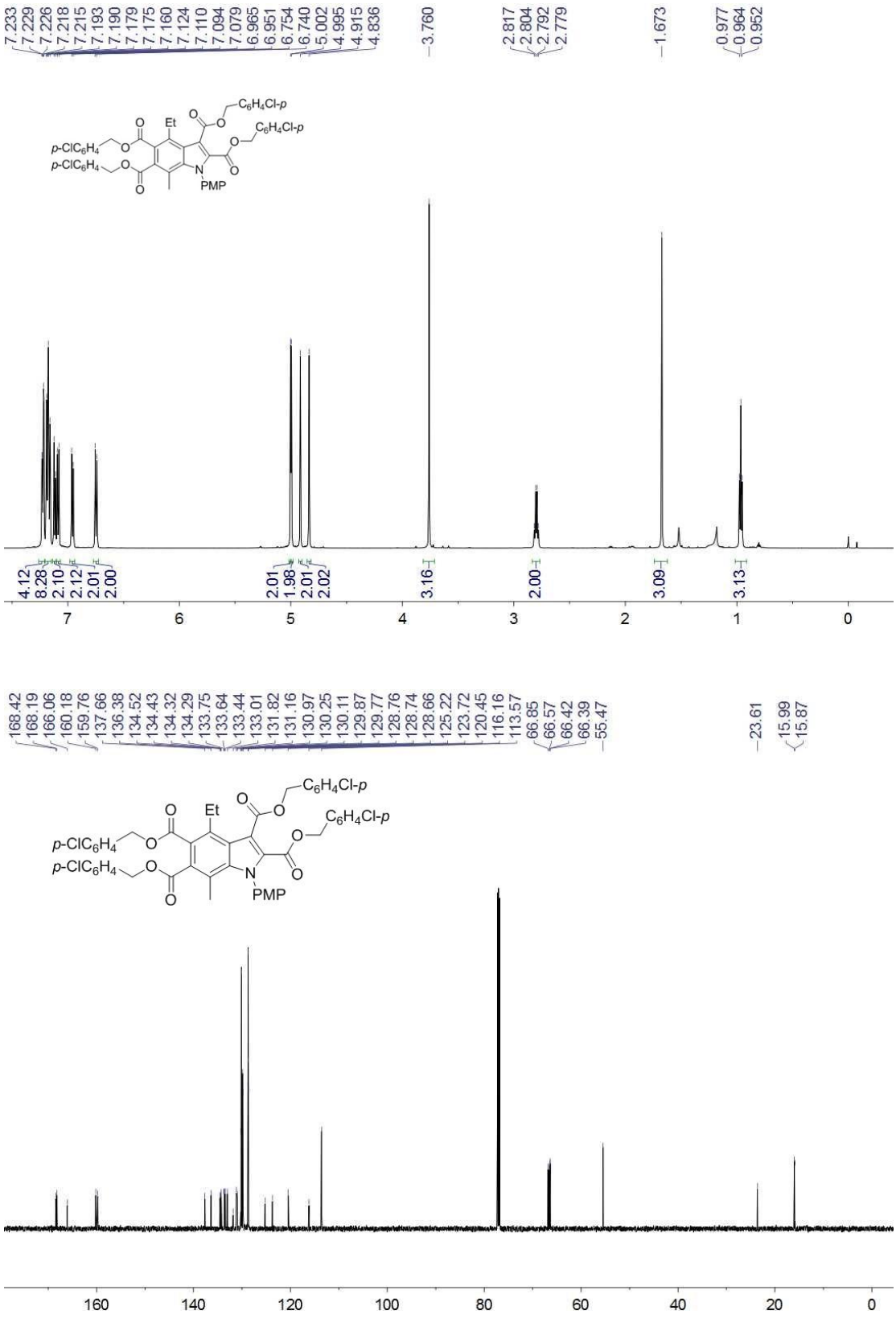


Figure 26. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3ae.**

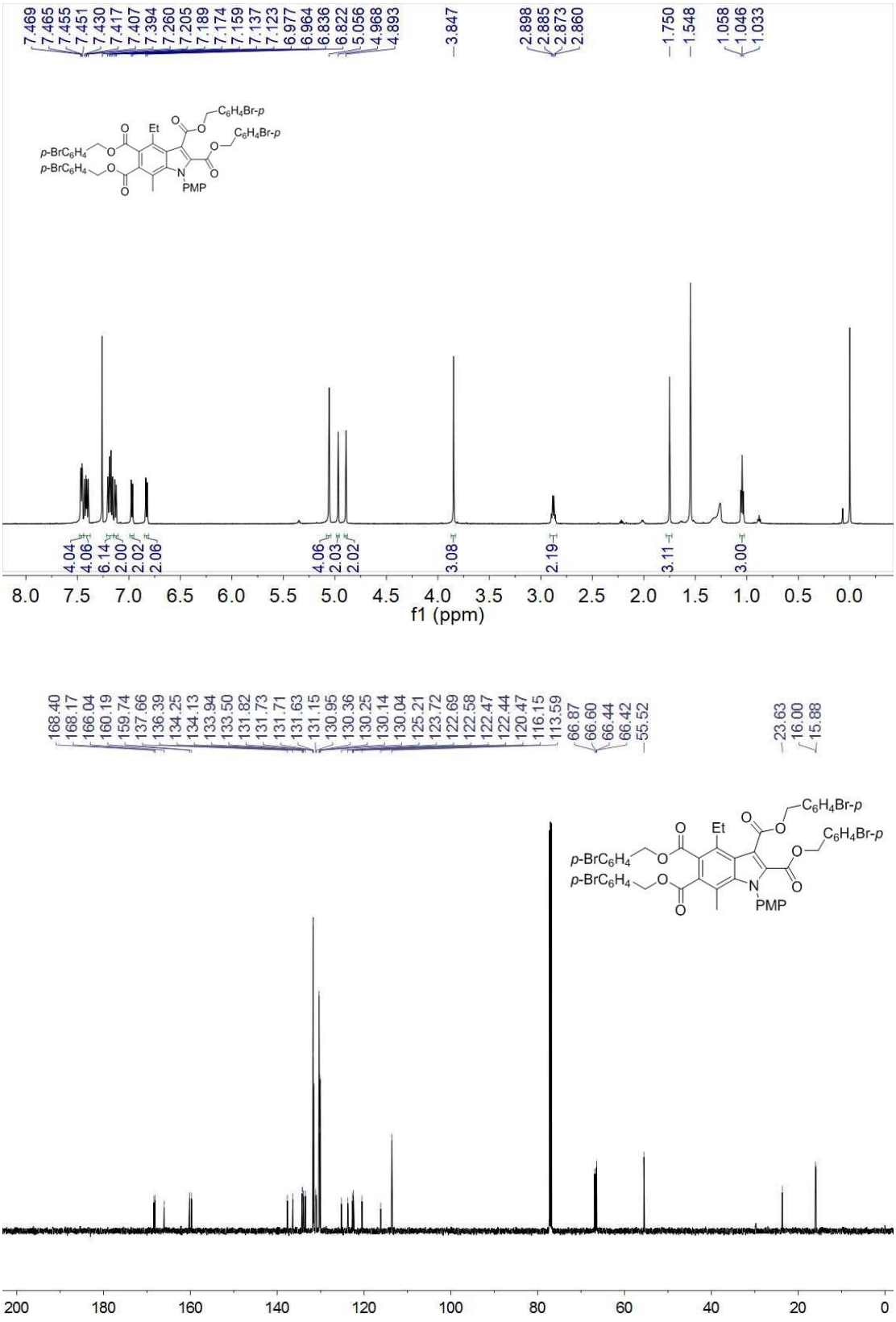


Figure 27. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3af.**

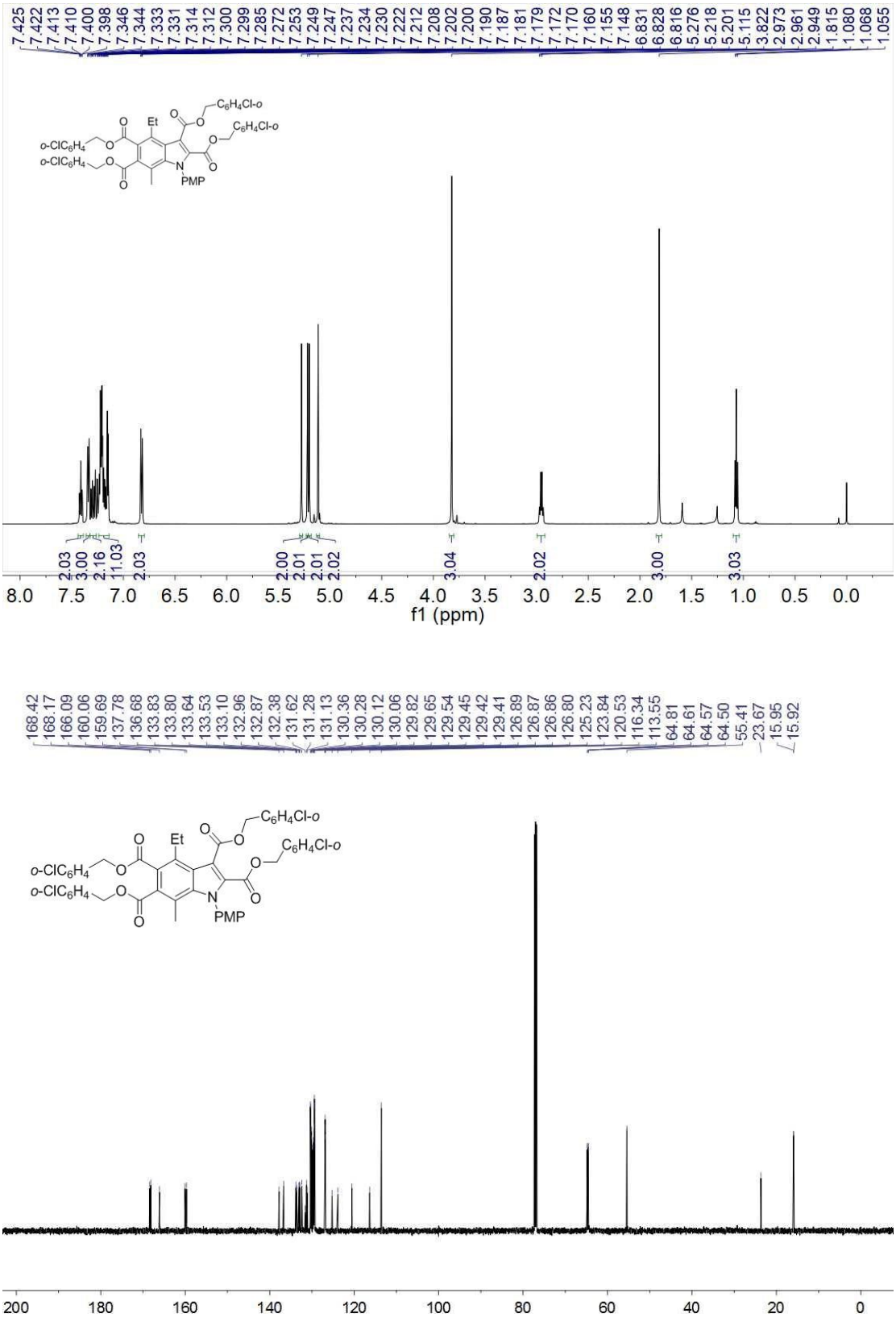


Figure 28. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3ag.**

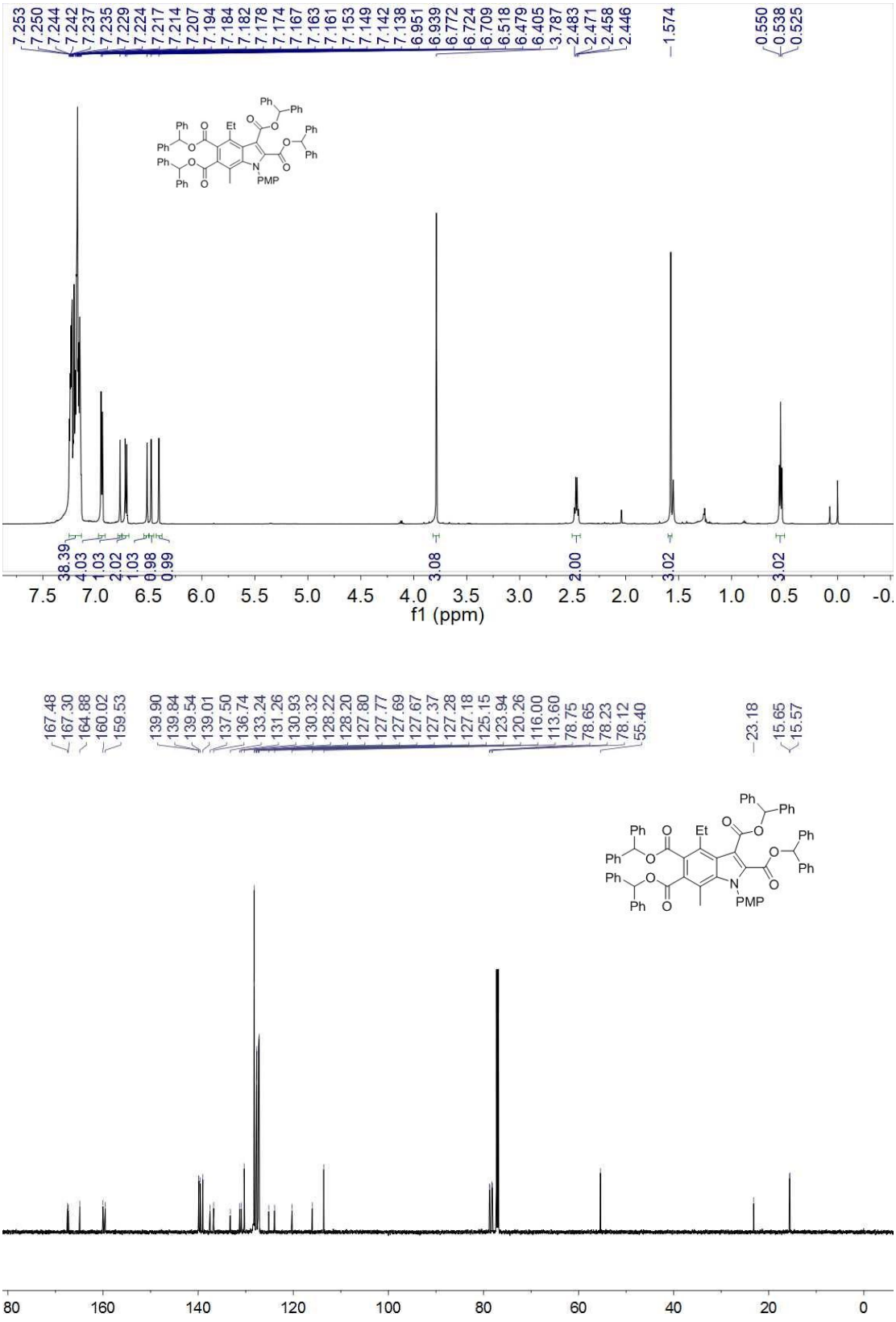


Figure 29. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3ah.**

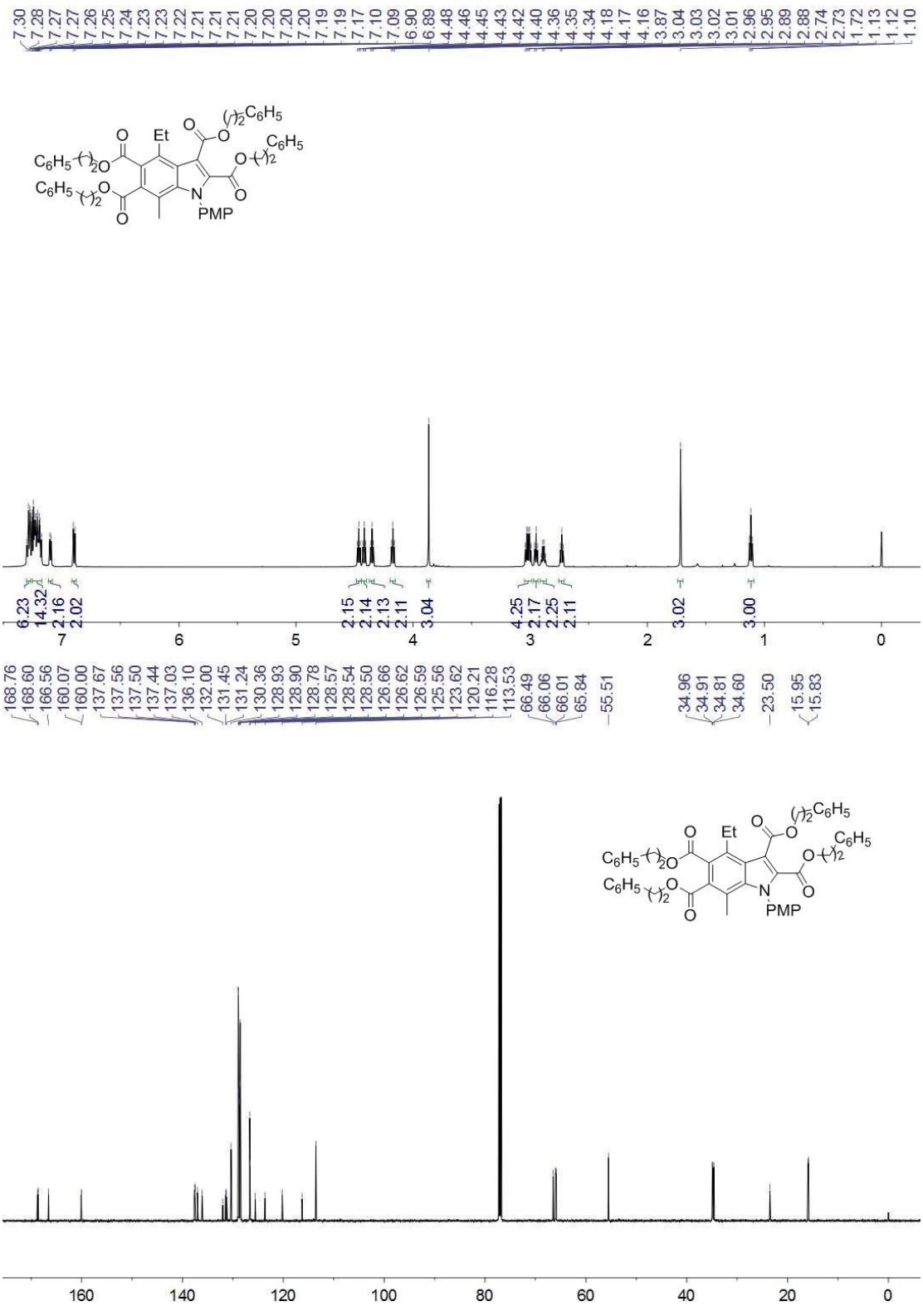


Figure 30. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3ai.**

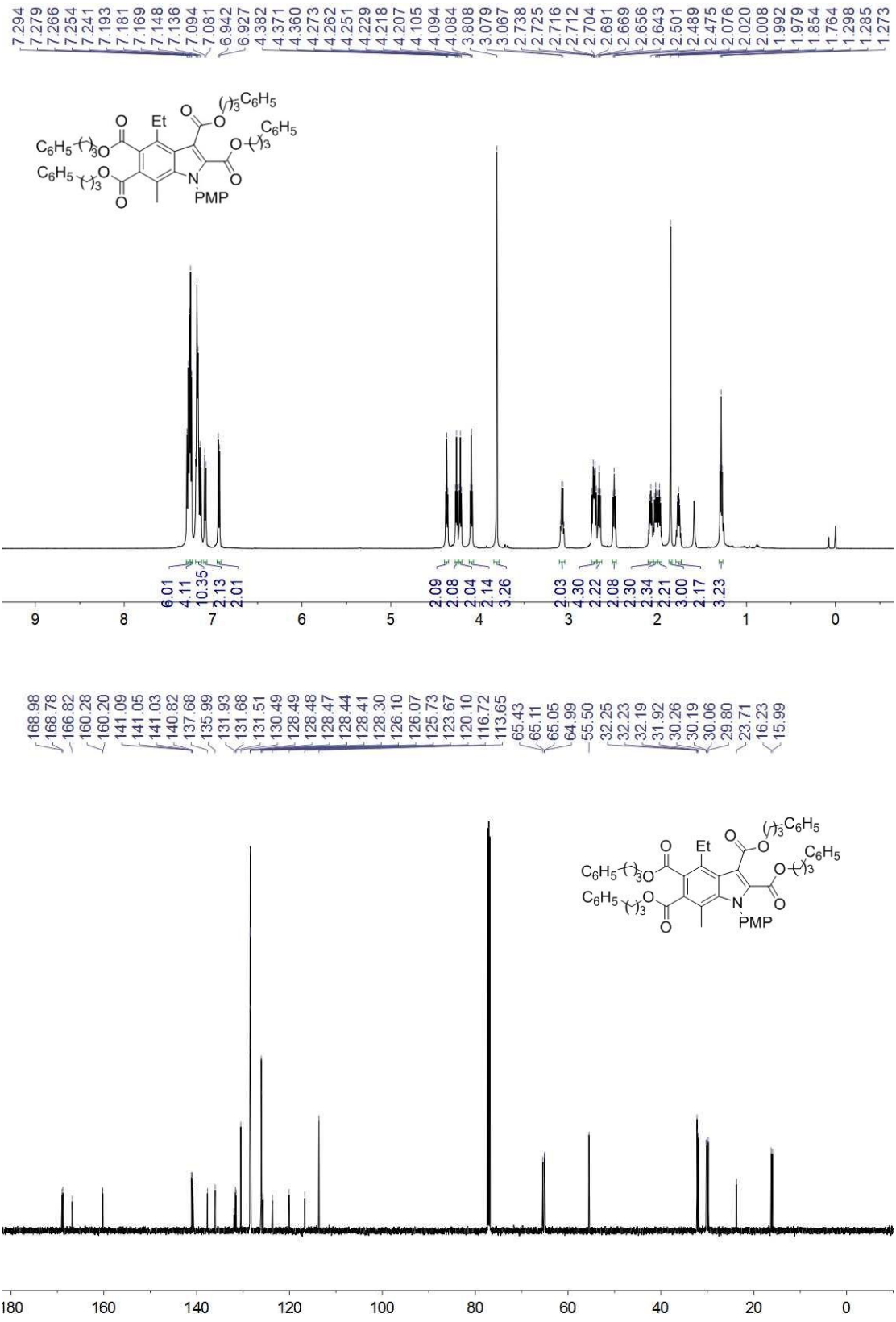


Figure 31. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3aj.**

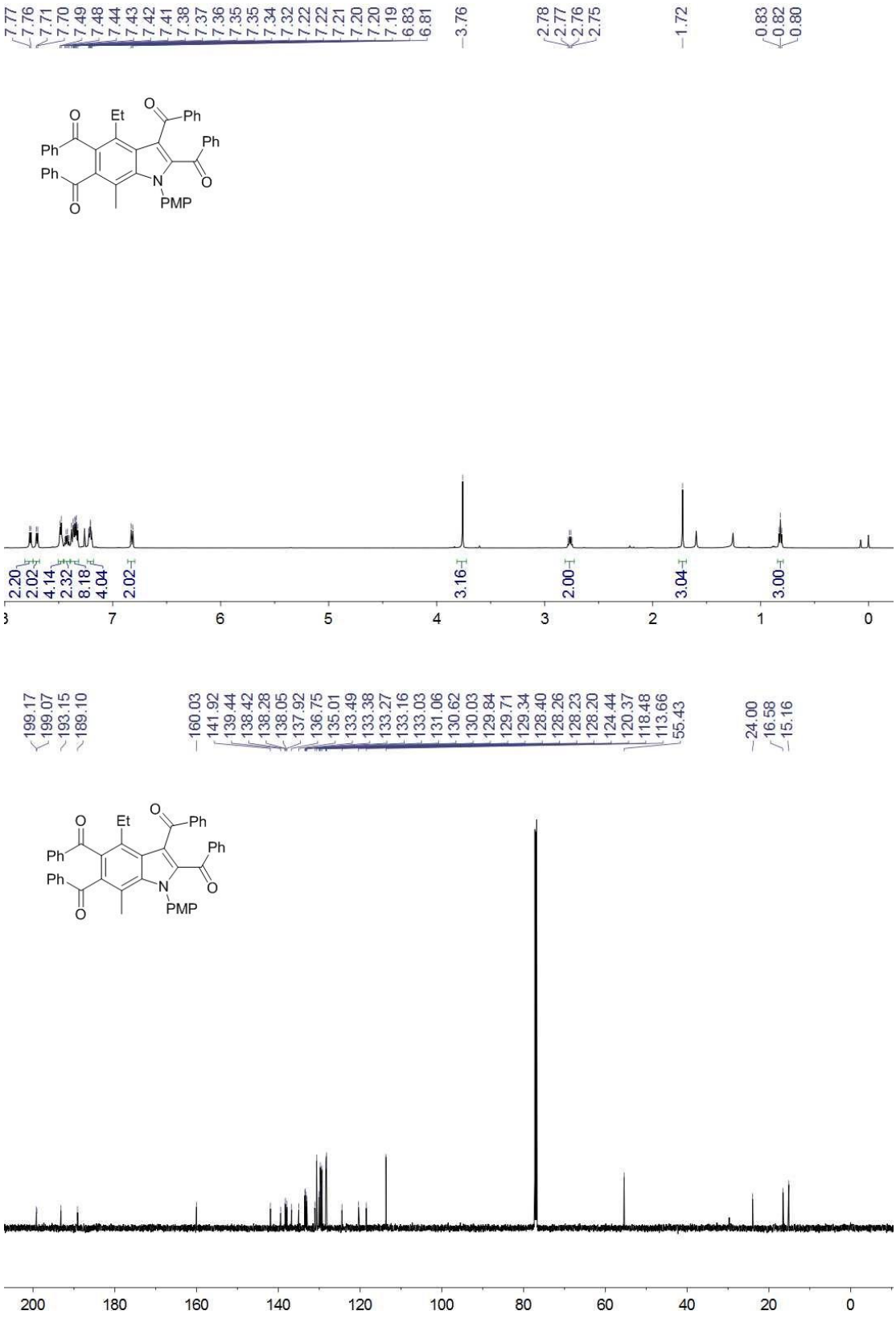


Figure 32. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3ak.**