Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

For

A Metal-Free Strategy for the Cross-Dehydrogenative Coupling of the 1, 3-Dicarbonyl Compounds with 2-Methoxyethanol

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(1) General Information

^{1}H, ^{13}C, and DEPT NMR spectra were recorded on a 400 MHz Varian Unity Plus or Varian Mercury plus spectrometer. The chemical shift (δ) values are reported in parts per million (ppm), and the coupling constants (J) are given in Hz. The spectra were recorded using $CDCl_3$ as a solvent. ^{1} H NMR chemical shifts are referenced to tetramethylsilane (TMS) (0 ppm). ^{13}C NMR was referenced to $CDCl_3$ (77.0 ppm) or DMSO-d_6 (39.51 ppm). The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublet; ddd, doublet of doublet; dt, doublet of triplets; td, triplet of doublet; m, multiplet. Mass spectra and high-resolution mass spectra (HRMS) were measured using the ESI (FT-MS solariX) at National Sun Yat-Sen University, Kaohsiung, Taiwan. Melting points were determined on an EZ-Melt (Automated melting point apparatus). All products reported showed ^{1}H NMR spectra in agreement with the assigned structures. Reaction progress and product mixtures were routinely monitored by TLC using Merck TLC aluminum sheets (silica gel 60 F254). Column chromatography was carried out with 230–400 mesh silica gel 60 (Merck) and a mixture of hexane/ethyl acetate or hexane as eluent. Preparative TLC was run on Merck TLC aluminum sheets (silica gel 60 F254).

(2) Mechanistic studies:

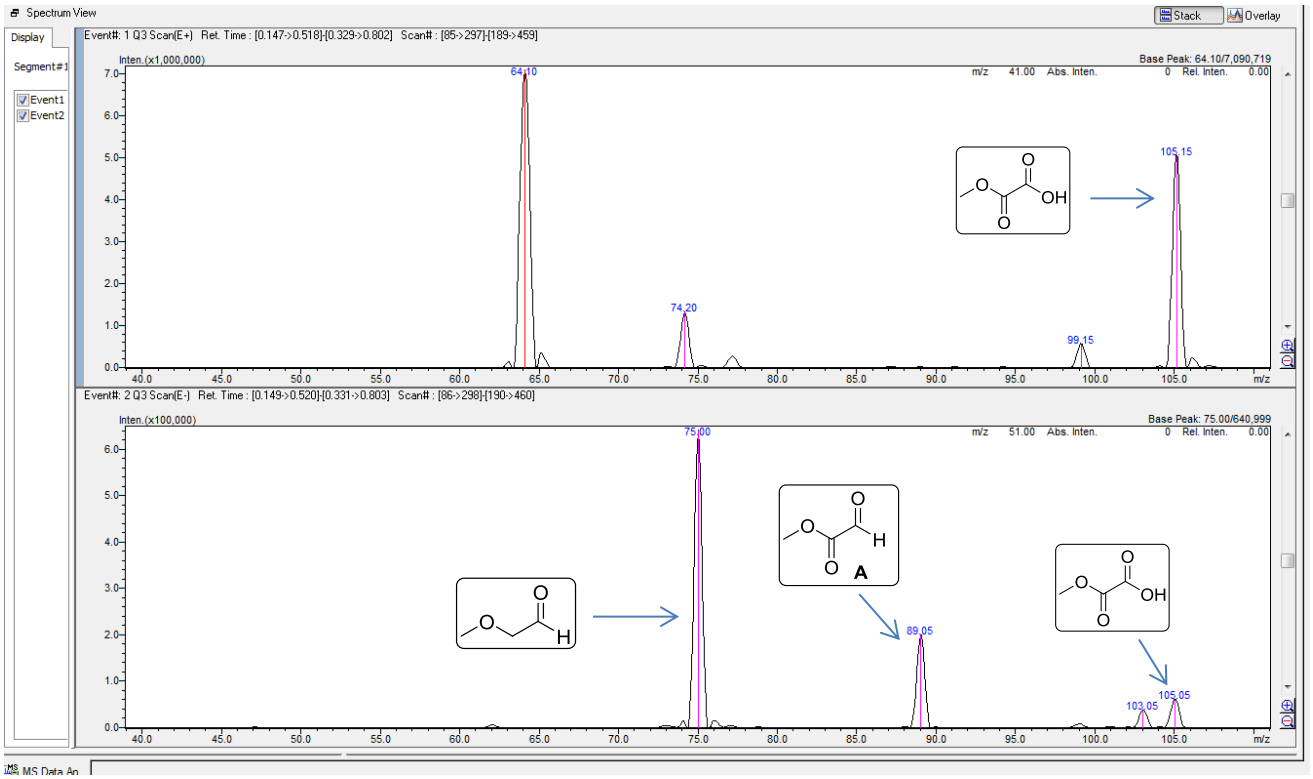


Fig S_1: LC-MS observed fragments of 2-methoxyacetaldehyde, methyl 2-oxoacetate, 2-methoxy-2-oxoacetic acid from 2-Methoxyethanol.

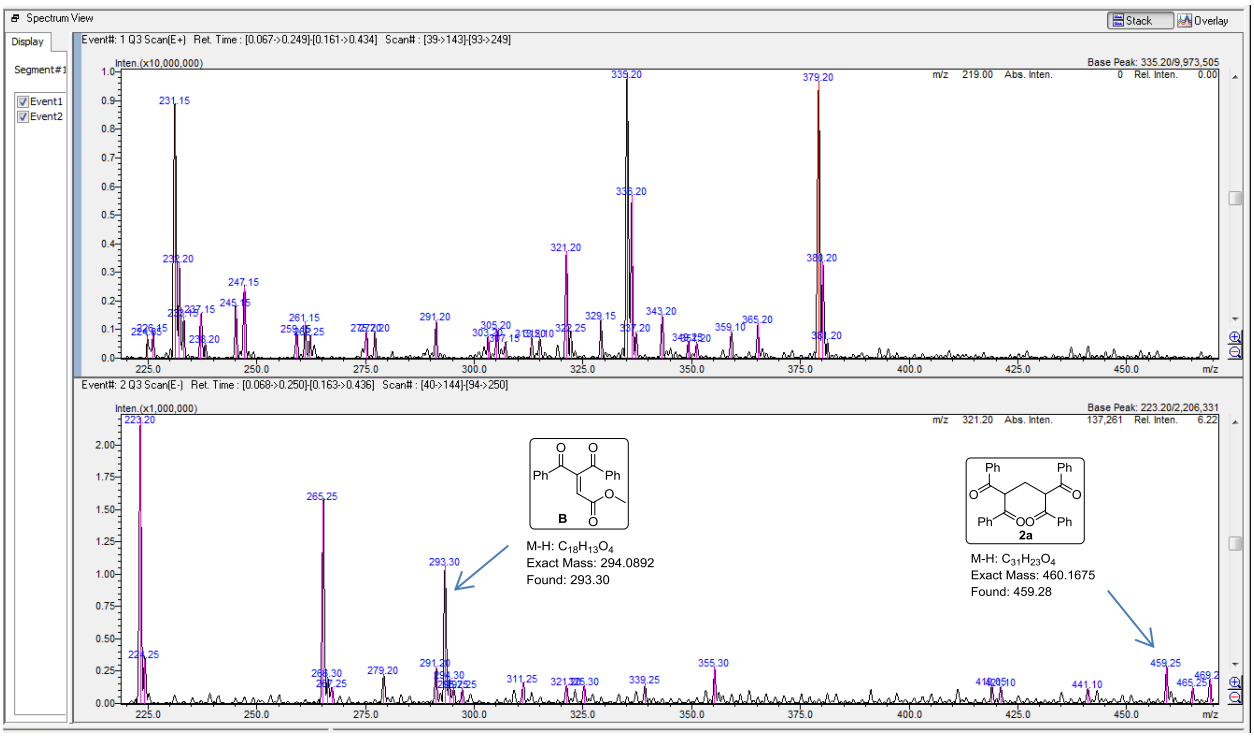
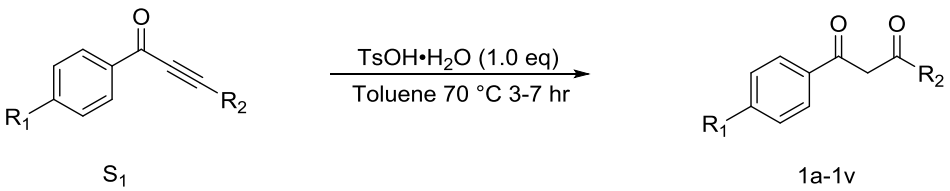


Fig S_2: LC-MS observed fragments of intermediate (C) and product 2a.

(3) Experimental Procedures

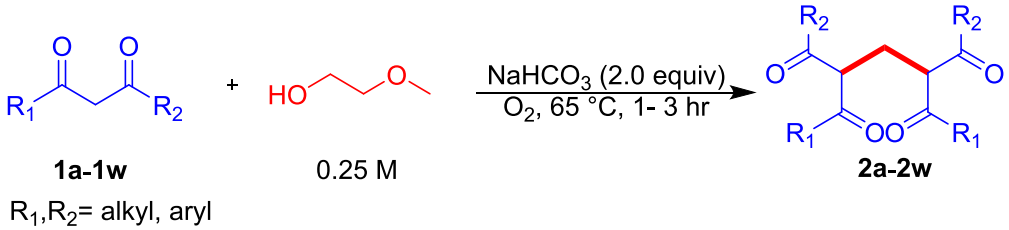
(i) Preparation of 1, 3-dicarbonyl derivatives (S_2)



S_1 1a-1v

An oven-dried sealed tube was charged alkynones[1] S_1 (0.5 mmol), Toluene (3 ml), and TsOH. H_2O (1.0 equiv) and allowed to stir at 70 °C until the completion of the reaction (3-7 h) by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10.0 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate, and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting (Hexane/EtOAc = 99/1) to afford pure 1-3, dicarbonyl compounds **1a-1v** in 60-80% yields.

(ii) General Experimental Procedure for the Synthesis methylene-bridged *bis*-1, 3-Dicarbonyl compounds with 2-methoxyethanol as "CH_2" Source

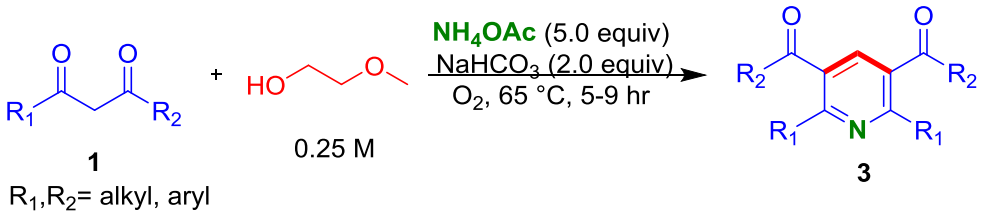


1a-1w 0.25 M **2a-2w**

R_1,R_2= alkyl, aryl

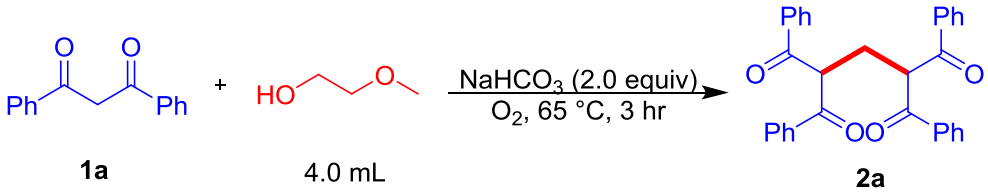
To an oven-dried sealed tube was charged with 1, 3-dicarbonyl compounds **1a-1w** (0.2 mmol), 2-methoxyethanol (0.25 M), and $NaHCO_3$ (2.0 equiv), and allowed to stir at 65 °C under O_2 until the completion of the reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10.0 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate. The combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford pure methylene-bridged *bis*-1, 3-Dicarbonyl compounds **2a-2w** in 51 - 94% yields.

(iii) General Experimental Procedure for the Synthesis of tetra-substituted pyridine with 2-methoxyethanol as "CH_2" Source and NH_4OAc as "N" source



To an oven-dried sealed tube was charged with 1,3-dicarbonyl compounds **1a, 1b, 1d, 1o, 1p, 1q, 1r, 1t, 1w** (0.20 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv), and NH_4OAc (5.0 equiv) allowed to stir at 65 °C until the completion of the reaction (5-9 h) by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 5.0 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate, and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude product was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford pure tetra-substituted pyridine derivatives **3a, 3b, 3d, 3o, 3p, 3q, 3r, 3t, 3w** in 45-83% yields.

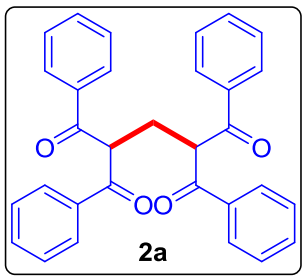
(iv) General Experimental Procedure for the Gram Scale Synthesis of 2,4-dibenzoyl-1,5-diphenylpentane-1,5-dione with 2-Methoxyethanol as "CH_2" Source.



To an oven-dried sealed tube was charged with 1, 3-dicarbonyl compound **1a** (4.46 mmol), 2-methoxyethanol (5.0 mL), and $NaHCO_3$ (2.0 equiv), and allowed to stir at 65 °C under O_2 until the completion of the reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 25 mL of water. The water layer was extracted with (3X20 mL) of ethyl acetate. The combined ethyl acetate layer was given brine wash (1X20 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford pure 2, 4-dibenzoyl-1, 5-diphenylpentane-1, 5-dione **2a** in 62% yields.

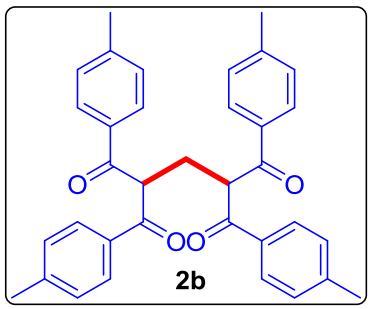
(4) Spectral Characterization

2,4-dibenzoyl-1,5-diphenylpentane-1,5-dione (**2a**)[2]: Following the general procedure, a 15 mL reaction tube



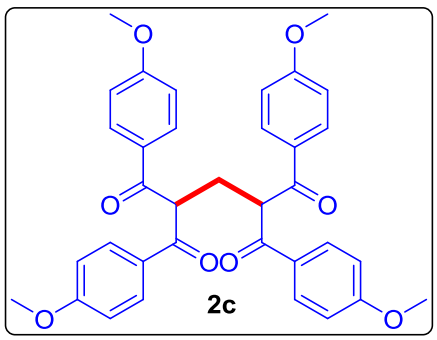
was charged with 1,3-diphenylpropane-1, 3-dione (**1a**) (45 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding 2,4-dibenzoyl-1,5-diphenylpentane-1,5-dione (**2b**) as a yellow solid (43 mg, yield = 94 %); Mp. 169-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.12 (m, 8H), 7.59 (t, *J* = 7.6 Hz, 4H), 7.49 (t, *J* = 8.0 Hz, 8H), 5.74 (t, *J* = 7.2 Hz, 2H), 2.76 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.57, 135.40, 133.87, 129.02, 128.91, 128.80, 128.70, 53.97, 28.91.

2,4-*bis*(4-methylbenzoyl)-1,5-di-*p*-tolylpentane-1,5-dione (**2b**)[2]: Following the general procedure, a 15 mL



reaction tube was charged with 1,3-di-*p*-tolylpropane-1,3-dione (**1b**) (50 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding 2,4-*bis*(4-methylbenzoyl)-1,5-di-*p*-tolylpentane-1,5-dione (**2b**) as a white solid (46 mg, yield = 90%); Mp. 195-196.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33-8.00 (m, 8H), 7.27-7.24 (m, 8H), 5.66 (t, *J* = 6.8 Hz, 2H), 2.70 (t, *J* = 6.8 Hz, 2H), 2.38 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.32, 144.69, 133.10, 129.64, 128.92, 53.89, 29.07, 21.68.

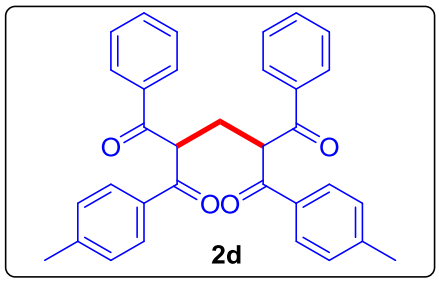
2,4-*bis*(4-methoxybenzoyl)-1,5-*bis*(4-methoxyphenyl)pentane-1,5-dione (**2c**): Following the general



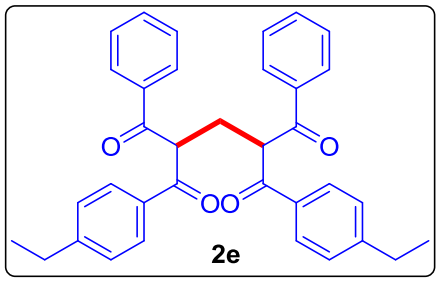
procedure, a 15 mL reaction tube was charged with 1,3-*bis*(4-methoxyphenyl)propane-1,3-dione (**1c**) (57 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of

water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding 2,4-*bis*(4-methoxybenzoyl)-1,5-*bis*(4-methoxyphenyl)pentane-1,5-dione (**2c**) as a white solid (52 mg, yield =89%); Mp. 170.1-172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.10 (m, 8H), 6.96-6.92 (m, 8H), 5.61 (t, *J* = 6.8 Hz, 2H), 3.85 (s, 12H), 2.70 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.32, 163.95, 131.15, 128.61, 114.13, 55.49, 53.68, 29.28. HRMS (ESI) Calc'd for $C_{35}H_{32}O_8Na$ [M + Na]$^{+}$: 603.1995; found: 603.1994.

(2*R*,4*S*)-2,4-dibenzoyl-1,5-di-*p*-tolylpentane-1,5-dione (**2d**)[2]: Following the general procedure, a 15 mL reaction tube was charged with 1-phenyl-3-(*p*-tolyl)propane-1,3-dione (**1d**) (48 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding (2*R*,4*S*)-2,4-dibenzoyl-1,5-di-*p*-tolylpentane-1,5-dione (**2d**) as a yellow liquid (41 mg, yield = 83%); The ratio of the two diastereomers is 8:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-7.97 (m, 8H), 7.58-7.44 (m, 6H), 7.28-7.25 (m, 4H), 5.70 (t, *J* = 6.8 Hz, 2H), 2.73 (t, *J* = 7.2 Hz, 2H), 2.39 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.66, 196.64, 196.18, 196.16, 144.83, 135.53, 135.50, 133.73, 132.98, 132.95, 129.69, 128.94, 128.83, 128.76, 128.74, 53.92, 28.98, 21.67.

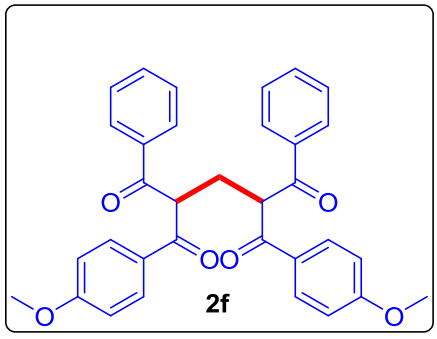


(2*R*,4*S*)-2,4-dibenzoyl-1,5-*bis*(4-ethylphenyl)pentane-1,5-dione (**2e**): Following the general procedure, a 15 mL reaction tube was charged with 1-(4-ethylphenyl)-3-phenylpropane-1,3-dione (**1e**) (50 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding (2*R*,4*S*)-2,4-dibenzoyl-1,5-di-*p*-tolylpentane-1,5-dione (**2e**) as a yellow liquid (42 mg, yield = 81%); The ratio of the two diastereomers is 6:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (ddd, *J* = 6.8, 3.6, 2.4 Hz, 4H), 8.07-8.04 (m, 5H), 7.59-7.55 (m, 2H), 7.49-

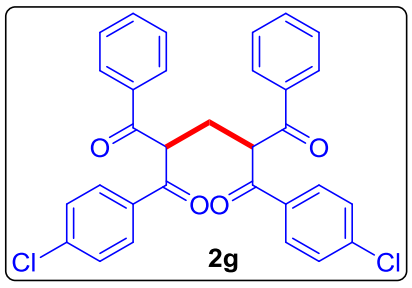


7.45 (m, 5H), 7.31-7.27 (m, 5H), 5.71 (t, *J* = 7.2 Hz, 2H), 2.75-2.66 (m, 8H), 1.24 (td, *J* = 7.6, 1.2 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.70, 196.20, 150.95, 135.54, 135.52, 133.74, 133.48, 133.17, 133.14, 129.07, 129.06, 128.96, 128.85, 128.79, 128.68, 128.53, 128.42, 128.22, 128.09, 54.94, 53.94, 35.94, 29.00, 28.96, 23.73, 15.04. HRMS (ESI) Calc'd for $C_{35}H_{32}O_4Na$ $[M + Na]^+$: 539.2198; found: 539.2200.

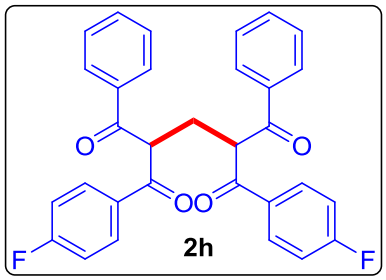
2,4-*bis*(4-methoxybenzoyl)-1,5-*bis*(4-methoxyphenyl)pentane-1,5-dione (**2f**)[2]: Following the general procedure, a 15 mL reaction tube was charged with 1,3-*bis*(4-methoxyphenyl)propane-1,3-dione (**1f**) (51 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding 2,4-*bis*(4-methoxybenzoyl)-1,5-*bis*(4-methoxyphenyl)pentane-1,5-dione (**2f**) as a yellow solid (41 mg, yield = 78%); Mp. 151-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21-8.19 (m, 2H), 8.14 - 8.07 (m, 6H), 7.56 (ddd, *J* = 7.2, 3.2, 2.0 Hz, 2H), 7.46 (dt, *J* = 12.8, 8.0 Hz, 4H), 6.99-6.93 (m, 4H), 5.67 (t, *J* = 6.8 Hz, 2H), 3.87 (s, *J* = 8.8 Hz, 6H), 2.73 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.77, 195.16, 195.09, 164.14, 164.07, 135.73, 135.57, 133.72, 133.65, 131.38, 131.22, 128.96, 128.91, 128.77, 128.63, 128.50, 128.32, 114.25, 114.20, 55.54, 55.52, 53.87, 53.84, 29.14.



(2*R*,4*S*)-2,4-dibenzoyl-1,5-*bis*(4-chlorophenyl)pentane-1,5-dione (**2g**)[3]: Following the general procedure, a 15 mL reaction tube was charged with 1-(4-chlorophenyl)-3-phenylpropane-1,3-dione (**1g**) (52 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding (2*R*,4*S*)-2,4-dibenzoyl-1,5-*bis*(4-chlorophenyl)pentane-1,5-dione (**2g**) as a white solid (40 mg, yield = 76%); Mp. 134.8-135.6°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.05 (m, 8H), 7.61 (t, *J* = 7.6 Hz, 2H), 7.52-7.45 (m, 8H), 5.64 (t, *J* = 7.2 Hz, 2H), 2.72 (tt, *J* = 14.0, 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.28, 195.43, 140.54, 135.25, 134.07, 133.72, 130.25, 130.18, 129.43, 129.40, 129.12, 129.09, 128.79, 128.73, 53.97, 28.78.

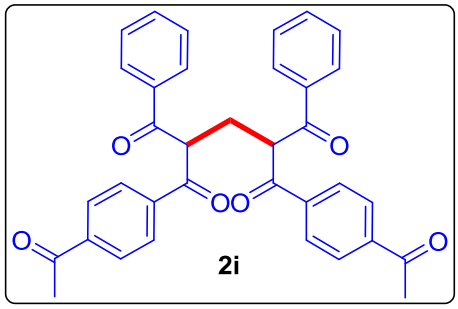


(2*R*, 4*S*)-2,4-dibenzoyl-1,5-*bis*(4-fluorophenyl)pentane-1,5-dione (**2h**)[4]: Following the general procedure, a



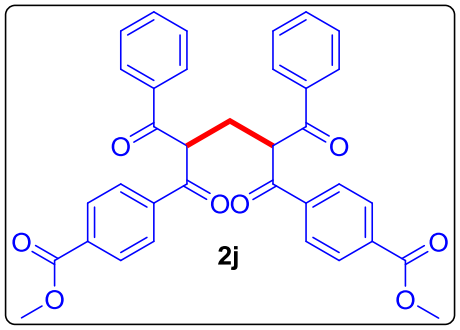
15 mL reaction tube was charged with 1-(4-fluorophenyl)-3-phenylpropane-1, 3-dione (**1h**) (48 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding (2*R*,4*S*)-2,4-dibenzoyl-1,5-*bis*(4-fluorophenyl)pentane-1,5-dione (**2h**) as a white solid (38 mg, yield = 76%); Mp. 171.5-172.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 - 8.06 (m, 8H), 7.62-7.56 (m, 2H), 7.51 - 7.45 (m, 4H), 7.20-7.13 (m, 4H), 5.66 (t, *J* = 7.2 Hz, 2H), 2.79-2.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.37, 195.03, 167.51, 167.46, 164.96 (d, J_F = 254 Hz), 164.91, 135.38, 135.28 (d, J_F = 10 Hz), 134.02, 133.98, 131.83, 131.80, 131.72, 131.62, 131.60, 131.51, 129.09, 129.05, 128.78, 128.68, 116.38 (d, J_F = 21.8 Hz), 116.34, 116.16, 116.12, 53.95, 28.86.

(2*R*,4*S*)-2,4-*bis*(4-acetylbenzoyl)-1,5-diphenylpentane-1,5-dione (**2i**): Following the general procedure, a 15

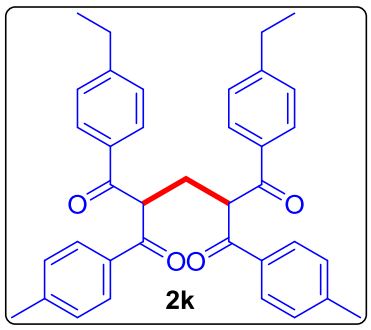


mL reaction tube was charged with 1-(4-acetylphenyl)-3-phenylpropane-1, 3-dione (**1i**) (53 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding (2*R*,4*S*)-2,4-*bis*(4-acetylbenzoyl)-1,5-diphenylpentane-1,5-dione (**2i**) as a white solid (45 mg, yield = 82%); Mp. 136.1-137.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 8.4, 6.4 Hz, 4H), 8.15-8.10 (m, 4H), 8.06 - 8.03 (m, 4H), 7.64-7.60 (m, 2H), 7.53 -7.49 (m, 4H), 5.73 (dd, *J* = 8.8, 6.8 Hz, 2H), 2.76 (t, *J* = 6.8 Hz, 2H), 2.63 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.24, 196.24, 196.10, 140.68, 138.53, 135.12, 134.19, 129.16, 128.96, 128.84, 54.24, 28.69, 26.91. HRMS (ESI) Calc’ d for $C_{35}H_{28}O_6Na$ $[M + Na]^+$: 567.1784; found: 567.1780

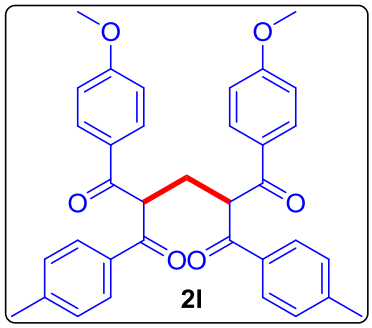
Dimethyl 4, 4'-((2*R*, 4*S*)-2, 4-dibenzoylpentanedioyl) dibenzoate (**2j**): Following the general procedure, a 15 mL reaction tube was charged with methyl 4-(3-oxo-3-phenylpropanoyl) benzoate (**1j**) (56 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding dimethyl 4,4'-((2*R*,4*S*)-2,4-dibenzoylpentanedioyl)dibenzoate (**2j**) as a yellow solid (49 mg, yield = 85%); Mp. 152-153.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 - 8.10 (m, 12H), 7.62 (t, *J* = 6.8 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 4H), 5.72 (t, *J* = 6.8 Hz, 2H), 3.93 (s, 6H), 2.76 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.23, 196.12, 165.95, 138.63, 135.12, 134.51, 134.15, 130.18, 129.14, 128.85, 128.80, 128.67, 128.62, 54.22, 52.51, 28.70. HRMS (ESI) Calc'd for $C_{35}H_{28}O_8Na$ $[M + Na]^+$: 599.1682; found: 599.1680.



(2*R*,4*S*)-2,4-*bis*(4-ethylbenzoyl)-1,5-di-*p*-tolylpentane-1,5-dione (**2k**): Following the general procedure, a 15 mL reaction tube was charged with 1-(4-ethylphenyl)-3-(*p*-tolyl)propane-1,3-dione (**1k**) (53 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding (2*R*,4*S*)-2,4-*bis*(4-ethylbenzoyl)-1,5-di-*p*-tolylpentane-1,5-dione (**2k**) as a white solid (43 mg, yield = 79%); Mp. 166-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (td, *J* = 8.4, 2.8 Hz, 8H), 7.29-7.25 (m, 9H), 5.67 (t, *J* = 6.8 Hz, 2H), 2.72-2.67 (m, 6H), 2.39 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.36, 196.33, 196.31, 150.80, 144.70, 133.27, 133.10, 129.65, 129.03, 128.94, 128.47, 53.90, 29.08, 28.96, 21.69, 15.05. HRMS (ESI) Calc'd for $C_{37}H_{36}O_4Na$ $[M + Na]^+$: 567.2511; found: 567.2511.

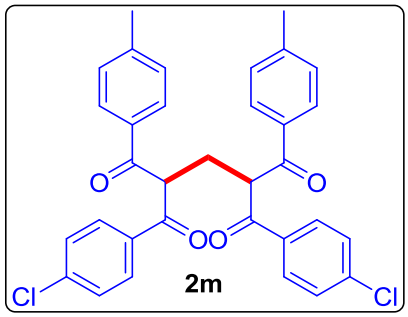


(2*R*, 4*S*)-2,4-*bis*(4-methoxybenzoyl)-1,5-di-*p*-tolylpentane-1,5-dione (**2l**)[2]: Following the general procedure, a



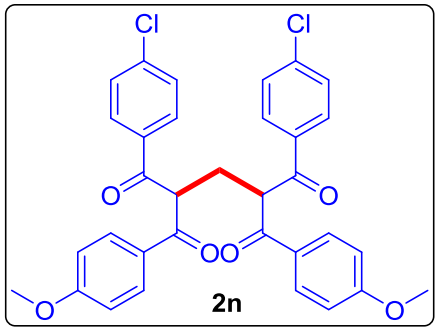
15 mL reaction tube was charged with 1-(4-methoxyphenyl)-3-(*p*-tolyl)propane-1,3-dione (**1l**) (54 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding (2*R*,4*S*)-2,4-*bis*(4-methoxybenzoyl)-1,5-di-*p*-tolylpentane-1,5-dione (**2l**) as a white solid (41 mg, yield = 74%); Mp. 87.9-88.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18- 8.16 (m, 2H), 8.12-8.10 (m, 2H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.27-7.22 (m, 5H), 6.98-6.92 (m, 4H), 5.63 (t, *J* = 7.2 Hz, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 2.70 (t, *J* = 7.2 Hz, 2H), 2.38 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.41, 195.28, 195.24, 164.04, 163.98, 144.66, 144.60, 133.28, 133.14, 131.32, 131.19, 129.64, 129.60, 128.91, 128.79, 128.60, 128.45, 114.18, 114.15, 109.98, 55.51, 53.80, 29.19, 21.69, 21.66.

(2*R*, 4*S*)-2,4-*bis*(4-chlorobenzoyl)-1,5-di-*p*-tolylpentane-1,5-dione (**2m**) : Following the general procedure, a

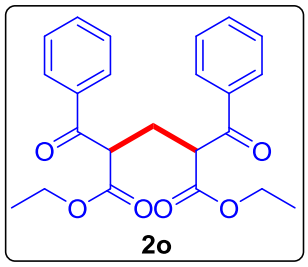


15 mL reaction tube was charged with 1-(4-chlorophenyl)-3-(*p*-tolyl)propane-1,3-dione (**1m**) (55 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding (2*R*,4*S*)-2,4-*bis*(4-chlorobenzoyl)-1,5-di-*p*-tolylpentane-1,5-dione (**2m**) as a white solid (46 mg, yield = 83%); Mp. 165-166.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 - 8.04 (m, 4H), 7.99 (dd, *J* = 8.4, 6.4 Hz, 4H), 7.4 -7.43 (m, 4H), 7.28 (dd, *J* = 8.0, 3.2 Hz, 4H), 5.60 (dd, *J* = 6.8, 6.0 Hz, 2H), 2.72-2.65 (m, 2H), 2.40 (d, *J* = 1.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.91, 195.88, 195.55, 145.12, 145.10, 140.43, 133.81, 133.79, 132.83, 132.81, 130.20, 130.16, 129.79, 129.77, 129.35, 129.33, 128.91, 128.88, 53.90, 28.85, 21.71. HRMS (ESI) Calc’ d for C_{33} H_{26} O_4 Na Cl [M + Na]$^+$: 579.1106; found: 579.1107.

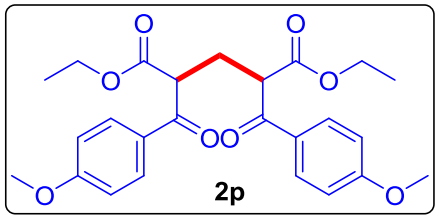
(2*R*,4*S*)-2,4-*bis*(4-chlorobenzoyl)-1,5-*bis*(4-methoxyphenyl)pentane-1,5-dione (**2n**): Following the general procedure, a 15 mL reaction tube was charged with 1-(4-chlorophenyl)-3-(4-methoxyphenyl)propane-1,3-dione (**1n**) (58 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding (2*R*,4*S*)-2,4-*bis*(4-chlorobenzoyl)-1,5-*bis*(4-methoxyphenyl)pentane-1,5-dione (**2n**) as a yellow solid (47 mg, yield = 80%); Mp. 158-159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.02 (m, 8H), 7.45 (dd, *J* = 8.8, 6.8 Hz, 4H), 6.97 (dd, *J* = 8.8, 7.6 Hz, 4H), 5.58 (td, *J* = 6.8, 2.0 Hz, 2H), 3.87 (s, 6H), 2.72-2.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.62, 194.81, 194.74, 164.25, 164.21, 140.33, 140.29, 133.96, 133.86, 131.28, 131.19, 130.12, 130.05, 129.30, 129.28, 128.27, 128.14, 114.30, 114.28, 55.55, 53.84, 53.80, 28.98. HRMS (ESI) Calc'd for $C_{33}H_{26}O_6NaCl_2$ $[M + Na]^+$: 611.3902; found: 611.3900.



diethyl (2*R*,4*S*)-2,4-dibenzoylpentanedioate (**2o**)[2]: Following the general procedure, a 15 mL reaction tube was charged with ethyl 3-oxo-3-phenylpropanoate (**1o**) (38 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding diethyl (2*R*,4*S*)-2,4-dibenzoylpentanedioate (**2o**) as a yellow solid (36 mg, yield = 90%); Mp. 88.1-89 °C; The ratio of the two diastereomers is 9:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dt, *J* = 8.4, 2.0 Hz, 4H), 7.60-7.56 (m, 2H), 7.52-7.45 (m, 5H), 4.63 (dd, *J* = 7.4, 7.2 Hz, 2H), 4.26-4.18 (m, 4H), 2.56 (dd, *J* = 7.6, 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.13, 169.65, 135.37, 133.77, 128.88, 128.77, 61.64, 51.55, 51.29, 28.17, 13.98.

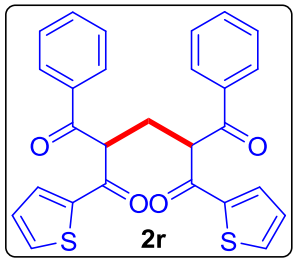


Diethyl (2*R*, 4*S*)-2, 4-*bis* (4-methoxybenzoyl) pentanedioate (**2p**)[3]: Following the general procedure, a 15 mL reaction tube was charged with ethyl 3-(4-methoxyphenyl)-3-oxopropanoate (**1p**) (44 mg, 0.2 mmol), 2-methoxyethanol (0.25 M),



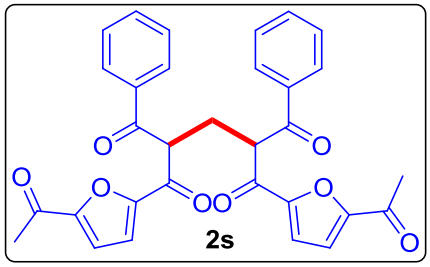
$NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding diethyl (2*R*,4*S*)-2,4-*bis*(4-methoxybenzoyl)pentanedioate (**2p**) as a yellow solid (35 mg, yield = 76%); Mp. 89-90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 - 8.02 (m, 4H), 6.96 - 6.92 (m, 4H), 4.56 (t, *J* = 7.2 Hz, 2H), 4.22 (dd, *J* = 6.8, 6.0 Hz, 4H), 3.88 (s, 6H), 2.52 (t, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.70, 169.94, 164.02, 131.36, 131.26, 128.35, 113.95, 61.51, 55.49, 51.34, 28.57, 14.02.

(2*R*,4*S*)-2,4-dibenzoyl-1,5-di(thiophen-2-yl)pentane-1,5-dione (**2r**)[5]: Following the general procedure, a 15 mL reaction tube was charged with 1-phenyl-3-(thiophen-2-yl)propane-1,3-dione (**1r**) (46 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding (2*R*,4*S*)-2,4-dibenzoyl-1,5-di(thiophen-2-yl)pentane-1,5-dione (**2r**) as a white solid (38 mg, yield = 81%); Mp. 165.5-166.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 - 8.09 (m, 4H), 8.07 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.01 (dd, *J* = 4.0, 1.2 Hz, 1H), 7.68 (ddd, *J* = 6.0, 5.2, 1.2 Hz, 2H), 7.59 (ddd, *J* = 9.2, 7.6, 1.2 Hz, 2H), 7.49 (q, *J* = 8.0 Hz, 4H), 7.15 (ddd, *J* = 8.8, 5.2, 4.0 Hz, 2H), 5.54 (t, *J* = 6.8 Hz, 2H), 2.80 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.89, 195.88, 189.00, 188.98, 142.85, 135.44, 135.42, 135.20, 133.93, 133.66, 133.63, 129.02, 128.78, 128.74, 128.67, 55.12, 55.10, 29.39.



2r

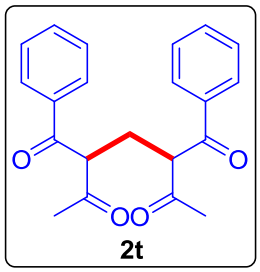
(2*R*, 4*S*)-2,4-*bis* (5-acetylfuran-2-carbonyl)-1,5-diphenylpentane-1,5-dione (**2s**): Following the general procedure, a 15 mL reaction tube was charged with 1-(5-acetylfuran-2-yl)-3-phenylpropane-1,3-dione (**1s**) (51 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting



2s

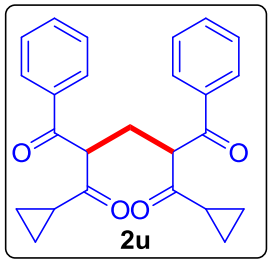
from (Hex/EA = 9/1) to afford the corresponding (2*R*,4*S*)-2,4-*bis*(5-acetylfuran-2-carbonyl)-1,5-diphenylpentane-1,5-dione (**2s**) as a yellow solid (29 mg, yield = 56%); Mp. 76-77 °C; The ratio of the two diastereomers is 1.5:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 7.2 Hz, 2H), 8.13 (d, *J* = 7.2 Hz, 1H), 7.67 - 7.45 (m, 8H), 7.31 (d, *J* = 4.0 Hz, 1H), 7.17 (dd, *J* = 16.0, 4.0 Hz, 2H), 5.57 (t, *J* = 6.4 Hz, 1H), 5.49 (t, *J* = 7.2 Hz, 1H), 2.78-2.67 (m, 2H), 2.27 (s, 2H), 2.11 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.08, 195.59, 187.49, 187.31, 185.60, 185.00, 154.24, 153.97, 152.01, 151.64, 135.47, 134.97, 134.36, 134.20, 129.18, 129.16, 129.10, 128.82, 119.04, 118.28, 116.73, 116.66, 54.28, 54.15, 27.51, 27.02, 25.99, 25.74. HRMS (ESI) Calc'd for $C_{31}H_{24}O_8Na$ $[M + Na]^+$: 547.1369; found: 547.1367.

(3*R*, 5*S*)-3,5-dibenzoylheptane-2,6-dione (**2t**)[2]: Following the general procedure, a 15 mL reaction tube was



charged with 1-phenylbutane-1, 3-dione (**1t**) (32 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding (3*R*,5*S*)-3,5-dibenzoylheptane-2,6-dione (**2t**) as a yellow liquid (29 mg, yield = 86%); The ratio of the two diastereomers is 1.1:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (ddd, *J* = 8.4, 7.2, 5.2 Hz, 4H), 7.63 - 7.59 (m, 2H), 7.54 - 7.47 (m, 4H), 4.72 (t, *J* = 6.8 Hz, 1H), 4.64 (t, *J* = 7.2 Hz, 1H), 2.60-2.45 (m, 2H), 2.19 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.92, 203.36, 196.60, 196.37, 135.90, 135.58, 134.03, 129.01, 128.95, 128.89, 128.79, 59.33, 59.15, 29.40, 29.09, 27.38, 27.01.

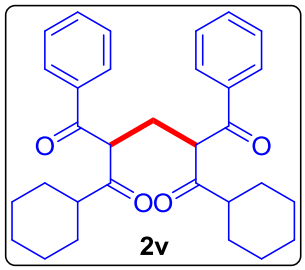
(2*R*,4*S*)-2,4-dibenzoyl-1,5-dicyclopropylpentane-1,5-dione (**2u**): Following the general procedure, a 15 mL



reaction tube was charged with 1-cyclopropyl-3-phenylpropane-1, 3-dione (**1u**) (38 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding (2*R*,4*S*)-2,4-dibenzoyl-1,5-dicyclopropylpentane-1,5-dione (**2u**) as a yellow liquid (35 mg, yield = 89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.04 (m, 2H), 8.02-8.00 (m, 2H), 7.62-7.55 (m, 2H), 7.51-7.49 (m, 2H), 7.47-7.45 (m, 2H), 4.77 (dt, *J* = 4.8, 6.8 Hz, 2H), 2.70-2.62 (m, 2H), 2.04-1.99 (m, 2H), 1.13-1.04 (m, 3H), 1.99-1.80 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.00, 196.21, 136.25, 136.06, 133.81, 133.78, 128.89, 128.85, 128.78, 128.76, 59.82, 59.68,

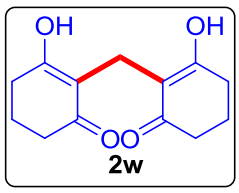
27.13, 27.02, 20.53, 20.30, 12.34, 12.30, 12.03, 11.99. HRMS (ESI) Calc'd for C_{25} H_{24} O_4 Na $[M + Na]^+$: 411.1572; found: 411.1575.

(2*R*, 4*S*)-2,4-dibenzoyl-1,5-dicyclohexylpentane-1,5-dione (**2v**): Following the general procedure, a 15 mL



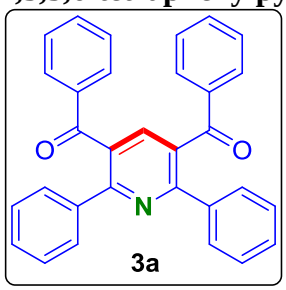
reaction tube was charged with 1-cyclohexyl-3-phenylpropane-1, 3-dione (**1v**) (46 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding (2*R*,4*S*)-2,4-dibenzoyl-1,5-dicyclohexylpentane-1,5-dione (**2v**) as a yellow liquid (43 mg, yield = 92%); The ratio of the two diastereomers is 1:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 - 8.19 (m, 2H), 8.05 - 8.02 (m, 2H), 7.64-7.59 (m, 2H), 7.55 - 7.50 (m, 4H), 4.94 (dd, *J* = 8.0, 6.4 Hz, 1H), 4.82 (t, *J* = 7.2 Hz, 1H), 2.50 - 2.30 (m, 4H), 1.83 - 1.60 (m, 10H), 1.50 - 1.28 (m, 3H), 1.20 - 1.15 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.92, 203.36, 196.60, 196.37, 135.90, 135.58, 134.03, 129.01, 128.95, 128.89, 128.79, 59.33, 59.15, 29.40, 29.09, 27.38, 27.01. HRMS (ESI) Calc'd for C_{31} H_{36} O_4 Na $[M + Na]^+$: 495.2511; found: 495.2510.

2,2'-methylene-*bis*-(3-hydroxycyclohex-2-en-1-one) (**2w**)[6]: Following the general procedure, a 15 mL



reaction tube was charged with cyclohexane-1, 3-dione (**1w**) (22 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10.0 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate, and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 2,2'-methylene-*bis*-(3-hydroxycyclohex-2-en-1-one) (**2w**) as a white solid (12 mg, yield = 51%); Mp. 130.1-131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.14 (s, 2H), 2.48 (dd, *J* = 17.6, 9.2 Hz, 4H), 2.38 - 2.31 (m, 4H), 1.93 (ddd, *J* = 14.0, 9.2, 4.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.99, 114.66, 32.28, 20.29, 16.46.

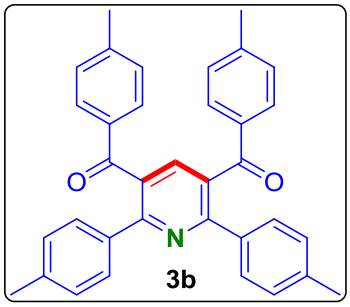
2,3,5,6-tetraphenylpyridine (**3a**)[8]: Following the general procedure, a 15 mL reaction tube was charged with 1,



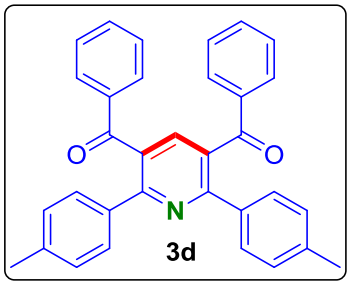
3-diphenylpropane-1,3-dione (**1a**) (45 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv), NH4OAC (5.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled

to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate, and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding 2, 3, 5, 6-tetraphenylpyridine (**3a**) as a white solid (32 mg, yield = 72%); Mp. 197-198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.74 - 7.72 (m, 4H), 7.70 - 7.66 (m, 4H), 7.47 - 7.43 (m, 2H), 7.33 – 7.27 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.60, 158.00, 138.79, 138.55, 136.35, 133.51, 131.85, 129.88, 129.52, 129.40, 128.45, 128.37.

(2,6-di-p-tolylpyridine-3,5-diyl)*bis*(p-tolylmethanone) (**3b**)[8]: Following the general procedure, a 15 mL reaction tube was charged with 1,3-di-*p*-tolylpropane-1,3-dione (**1b**) (50 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv), NH_4OAc (5.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate, and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding (2,6-di-*p*-tolylpyridine-3,5-diyl)*bis*(*p*-tolylmethanone) (**3b**) as a yellow solid (30 mg, yield = 60%); Mp. 184-185.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.64 (dd, *J* = 18.0, 7.2 Hz, 8H), 7.12 (dd, *J* = 18.0, 6.8 Hz, 8H), 2.35 (s, 6H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.39, 157.51, 144.53, 139.39, 138.30, 135.80, 133.94, 131.47, 130.23, 129.42, 129.24, 129.11, 21.70, 21.28.

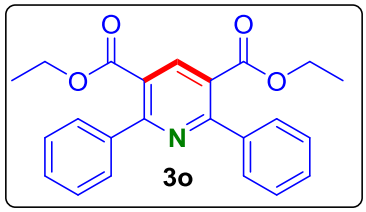


(2,6-di-p-tolylpyridine-3,5-diyl)*bis*(phenylmethanone) (**3d**)[9]: Following the general procedure, a 15 mL reaction tube was charged with 1-phenyl-3-(*p*-tolyl)propane-1,3-dione (**1d**) (48 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv), NH_4OAc (5.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate, and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding (2,6-di-*p*-tolylpyridine-3,5-diyl)*bis*(phenylmethanone) (**3d**) as a red solid (33 mg, yield = 70%); Mp. 202.1-203 °C; The ratio of the two diastereomers is 2:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.76 - 7.57 (m, 8H), 7.35 - 7.26 (m, 6H), 7.14-7.07 (m, 4H), 2.34 (s, 4H), 2.28 (s, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.77, 196.22, 157.81, 157.73, 157.64, 144.61, 144.58, 139.51, 138.63, 138.55, 138.38,

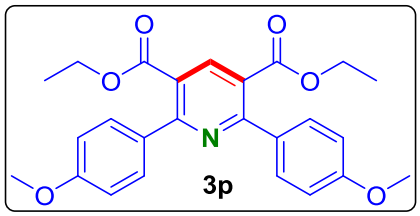


136.42, 135.76, 133.89, 133.48, 132.06, 131.80, 131.56, 130.14, 129.98, 129.48, 129.31, 129.23, 129.14, 128.48, 128.36, 21.69, 21.26.

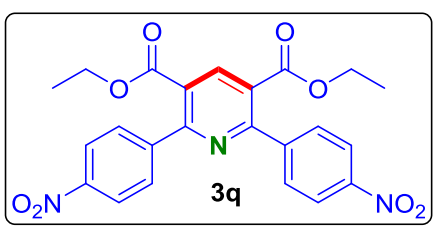
Diethyl 2, 6-diphenylpyridine-3, 5-dicarboxylate (3o)[8]: Following the general procedure, a 15 mL reaction tube was charged with ethyl 3-oxo-3-phenylpropanoate (**1o**) (38 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv), NH_4OAc (5.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of the reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate, and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding diethyl 2,6-diphenylpyridine-3,5-dicarboxylate (**3o**) as a yellow liquid (31 mg, yield = 83%); Mp. 52-53 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.64-7.61 (m, 4H), 6.44-7.42 (m, 4H), 4.21 (q, *J* = 7.2 Hz, 4H), 1.10 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.41, 159.75, 140.28, 139.38, 129.17, 128.94, 128.08, 124.83, 61.68, 13.70.



Diethyl 2,6-*bis*(4-methoxyphenyl)pyridine-3,5-dicarboxylate (3p)[10]: Following the general procedure, a 15 mL reaction tube was charged with ethyl 3-(4-methoxyphenyl)-3-oxopropanoate (**1p**) (44 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv), NH_4OAc (5.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate, and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding diethyl 2,6-*bis*(4-methoxyphenyl)pyridine-3,5-dicarboxylate (**3p**) as a white solid (34 mg, yield = 79%); Mp. 100-101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.62 (d, *J* = 8.8 Hz, 4H), 6.96 (d, *J* = 8.8 Hz, 4H), 4.24 (q, *J* = 7.2 Hz, 4H), 3.89 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.79, 160.67, 158.93, 140.47, 131.78, 130.56, 123.47, 113.52, 61.57, 55.33, 13.87.

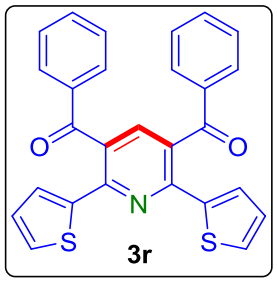


Diethyl 2, 6-*bis*(4-nitrophenyl)pyridine-3,5-dicarboxylate (3q)[11]: Following the general procedure, a 15 mL reaction tube was charged with ethyl 3-(4-nitrophenyl)-3-oxopropanoate (**1q**) (47 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv), NH_4OAc (5.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was



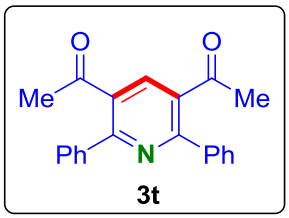
cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate, and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding diethyl 2,6-*bis*(4-nitrophenyl)pyridine-3,5-dicarboxylate (**3q**) as a yellow solid (34 mg, yield = 73%); Mp. 195.5-196.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.32 (d, *J* = 8.8 Hz, 4H), 7.77 (d, *J* = 8.8 Hz, 4H), 4.27 (q, *J* = 7.2 Hz, 4H), 1.19 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.76, 158.24, 148.30, 145.02, 141.29, 129.98, 125.96, 123.34, 62.31, 13.82.

(2,6-di(thiophen-2-yl)pyridine-3,5-diyl)*bis*(phenylmethanone) (3r): Following the general procedure, a 15 mL reaction tube was charged 1-phenyl-3-(thiophen-2-yl)propane-1,3-dione (**1r**) (46 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv), NH_4OAc (5.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate, and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding (2,6-di(thiophen-2-yl)pyridine-3,5-diyl)*bis*(phenylmethanone) (3r) as a yellow solid (34 mg, yield = 76%); Mp. 202.1-202.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.76 (dd, *J* = 7.6, 4.4 Hz, 4H), 7.64 - 7.62 (m, 2H), 7.36 - 7.32 (m, 8H), 6.97 - 6.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.43, 157.56, 143.58, 138.50, 138.10, 135.58, 135.52, 131.75, 129.52, 129.42, 128.51, 128.25. HRMS (ESI) Calc'd for $C_{27}H_{18}NO_2S_2$ $[M + H]^+$: 452.0779; found: 452.0780.



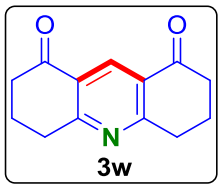
3r

(2,6-dimethylpyridine-3,5-diyl)*bis*(phenylmethanone) (3t)[12]: Following the general procedure, a 15 mL reaction tube was charged with 1-phenylbutane-1, 3-dione (**1t**) (32 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv), NH_4OAc (5.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of the reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate, and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding (2,6-dimethylpyridine-3,5-diyl)*bis*(phenylmethanone) (**3t**) as a yellow liquid (20 mg, yield = 63%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (m, 4H), 7.61 (dd, *J* = 7.6, 4.0 Hz, 3H), 7.48 (t, *J* = 8.0 Hz, 4H), 2.62 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.06, 158.01, 136.77, 136.64, 133.82, 130.63, 129.96, 128.77, 23.39.

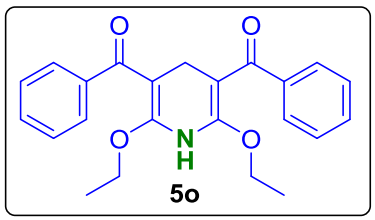


3t

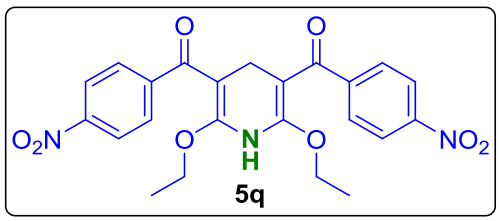
3,4,6,7-tetrahydroacridine-1,8 (2*H*, 5*H*)-dione (3w)[13]: Following the general procedure, a 15 mL reaction tube was charged with ethyl 3-(4-nitrophenyl)-3-oxopropanoate (**1w**) (22 mg, 0.2 mmol), 2-methoxyethanol (0.25 M), $NaHCO_3$ (2.0 equiv), NH_4OAc (5.0 equiv) and allowed to stir at 65 °C under O_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate, and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 9/1) to afford the corresponding diethyl 3,4,6,7-tetrahydroacridine-1,8(2*H*,5*H*)-dione (**3w**) as a brown solid (10 mg, yield = 45 %); Mp. 159.5-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 3.19 (t, *J* = 6.0 Hz, 4H), 2.72 (t, *J* = 6.0 Hz, 4H), 2.25 - 2.18 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.50, 167.08, 134.88, 127.37, 38.39, 32.77, 21.39.



diethyl 2,6-diphenyl-1,4-dihydropyridine-3,5-dicarboxylate (5o)[14]: Following the general procedure, a 15 mL reaction tube was charged with diethyl (2*R*, 4*S*)-2, 4-dibenzoylpentanedioate (**2o**) (79 mg, 0.2 mmol Ethanol (2 mL), NH_4OAc (5.0 equiv) and allowed to stir at 100 °C under N_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate, and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding diethyl 2,6-diphenyl-1,4-dihydropyridine-3,5-dicarboxylate (**5o**) as a yellow solid (52 mg, yield = 69%); Mp 53.2-54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.35 (m, 6H), 7.32 - 7.30 (m, 4H), 5.46 (s, 1H), 3.95 (q, *J* = 7.2 Hz, 4H), 3.62 (s, 2H), 0.95 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.16, 146.52, 136.85, 128.96, 128.29, 127.82, 100.15, 59.68, 25.83, 13.80.

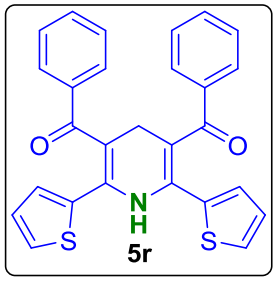


(2,6-diethoxy-1,4-dihydropyridine-3,5-diyl)*bis*((4-nitrophenyl)methanone) (5q)[14]: Following the general procedure, a 15 mL reaction tube was charged with diethyl 2,6-*bis* (4-nitrophenyl)pyridine-3,5-dicarboxylate (**2q**) (97 mg, 0.2 mmol), Ethanol (2 mL), NH_4OAc (5.0 equiv) and allowed to stir at 100 °C under N_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate, and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA



= 8/2) to afford the corresponding (2,6-diethoxy-1,4-dihydropyridine-3,5-diyl) *bis* ((4-nitrophenyl)methanone) (**5q**) as a yellow solid (58 mg, yield = 62%); Mp. 177.5-179 °C; The ratio of the two diastereomers is 7:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 4H), 7.50 (d, *J* = 8.6 Hz, 4H), 5.57 (s, 1H), 3.97 (q, *J* = 7.2 Hz, 4H), 3.62 (s, 2H), 1.00 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.20, 147.94, 144.06, 142.84, 129.97, 129.21, 123.61, 123.31, 102.10, 60.27, 25.61, 13.88.

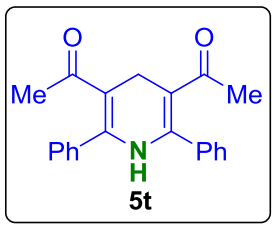
(2,6-di(thiophen-2-yl)-1,4-dihydropyridine-3,5-diyl)*bis*(phenylmethanone) (**5r**): Following the general



5r

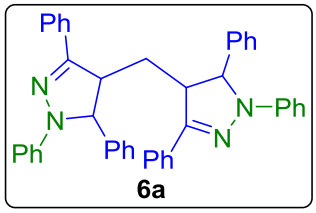
procedure, a 15 mL reaction tube was charged with (2*R*,4*S*)-2,4-dibenzoyl-1,5-di(thiophen-2-yl)pentane-1,5-dione (**2r**) (94 mg, 0.2 mmol), Ethanol (2 mL), NH_4OAc (5.0 equiv) and allowed to stir at 100 °C under N_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate, and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding (2,6-di(thiophen-2-yl)-1,4-dihydropyridine-3,5-diyl)*bis*(phenylmethanone) (**5r**) as a yellow solid (66 mg, yield = 73%); Mp. 113.5-114.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 7.65 -7.61(m, 6H), 7.50 - 7.46 (m, 8H), 7.09 (dd, *J* = 4.8, 3.6 Hz, 2H), 6.01 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.78, 162.57, 147.07, 137.31, 130.73, 130.60, 129.01, 128.21, 127.76, 127.15, 126.28, 91.60. HRMS (ESI) Calc'd for $C_{27}H_{19}NO_2S_2$ $[M + H]^+$: 453.0563; found: 453.0560.

(2,6-dimethyl-1,4-dihydropyridine-3,5-diyl)*bis*(phenylmethanone) (**5t**)[12]: Following the general procedure, a



5t

15 mL reaction tube was charged with (3*R*,5*S*)-3,5-dibenzoylheptane-2,6-dione (**2t**) (67 mg, 0.2 mmol), Ethanol (2 mL), NH_4OAc (5.0 equiv) and allowed to stir at 100 °C under N_2 until the completion of the reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate, and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding (2,6-dimethyl-1,4-dihydropyridine-3,5-diyl)*bis*(phenylmethanone) (**5t**) as a yellow solid (39 mg, yield = 62%); Mp. 142.1-143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (s, 1H), 7.87 (dd, *J* = 7.6, 1.2 Hz, 4H), 7.45 - 7.37 (m, 6H), 5.73 (s, 2H), 2.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.38, 163.02, 140.12, 130.74, 128.14, 127.02, 92.22, 22.83.



6a

***bis*(1,3,5-triphenyl-4,5-dihydro-1*H*-pyrazol-4-yl) methane** (**6a**)[14]: Following the general procedure, a 15 mL reaction tube was charged with 2,4-dibenzoyl-1,5-

diphenylpentane-1,5-dione (**2a**) (92 mg, 0.2 mmol), CH_3COOH (0.1 ml), EtOH (3 mL) and allowed to stir at 90 °C under N_2 until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate, and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding *bis* (1,3,5-triphenyl-4,5-dihydro-1*H*-pyrazol-4-yl)methane (**6a**) as a brown solid (96 mg, yield = 79%); Mp. 206-207.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 - 7.45 (m, 4H), 7.39 - 7.31 (m, 6H), 7.28 - 7.10 (m, 12H), 6.98 (d, *J* = 6.4 Hz, 4H), 6.88 (d, *J* = 6.8 Hz, 4H), 4.18 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.38, 141.33, 139.85, 133.38, 130.17, 130.11, 128.42, 128.39, 127.88, 127.84, 127.36, 126.71, 124.95, 116.40, 20.43.

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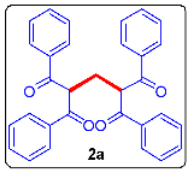

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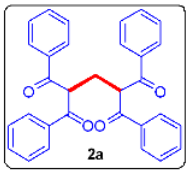

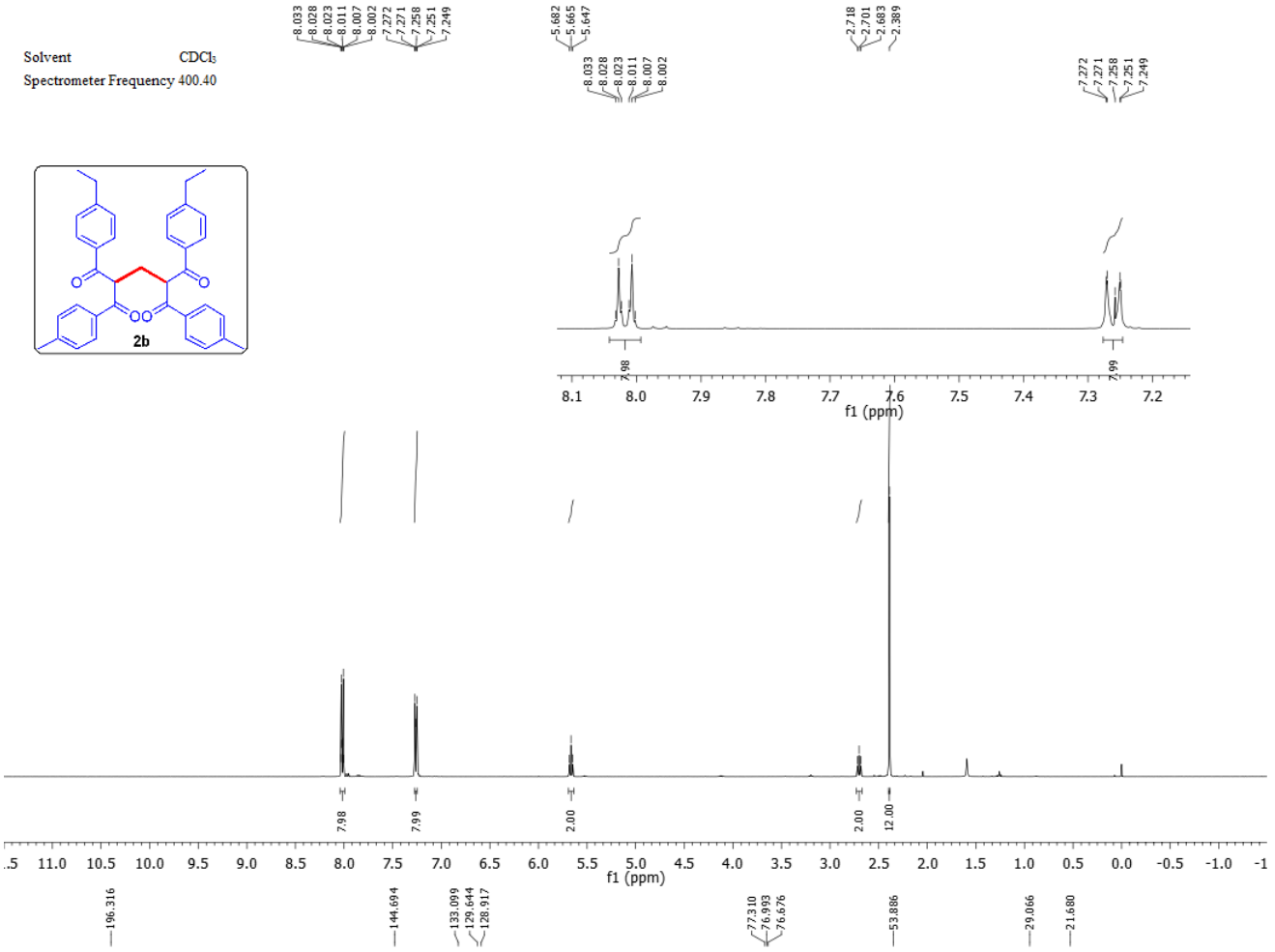
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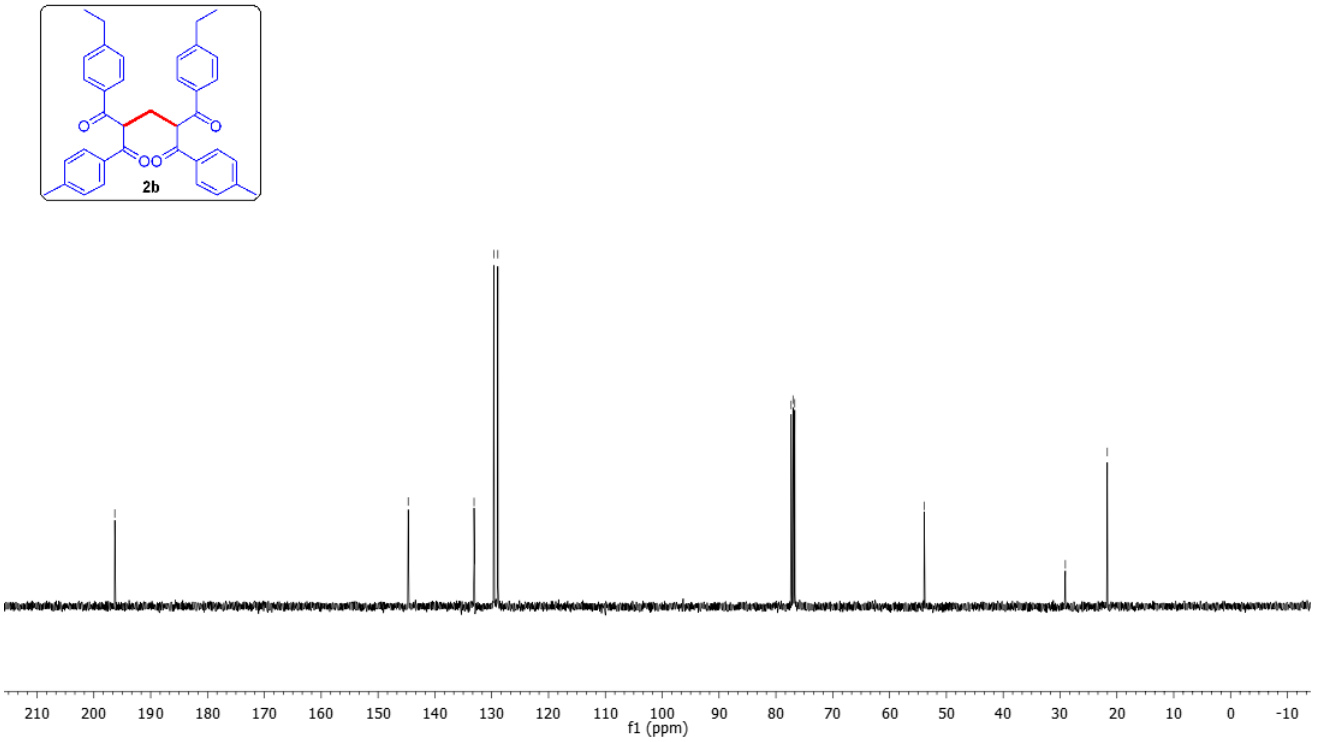
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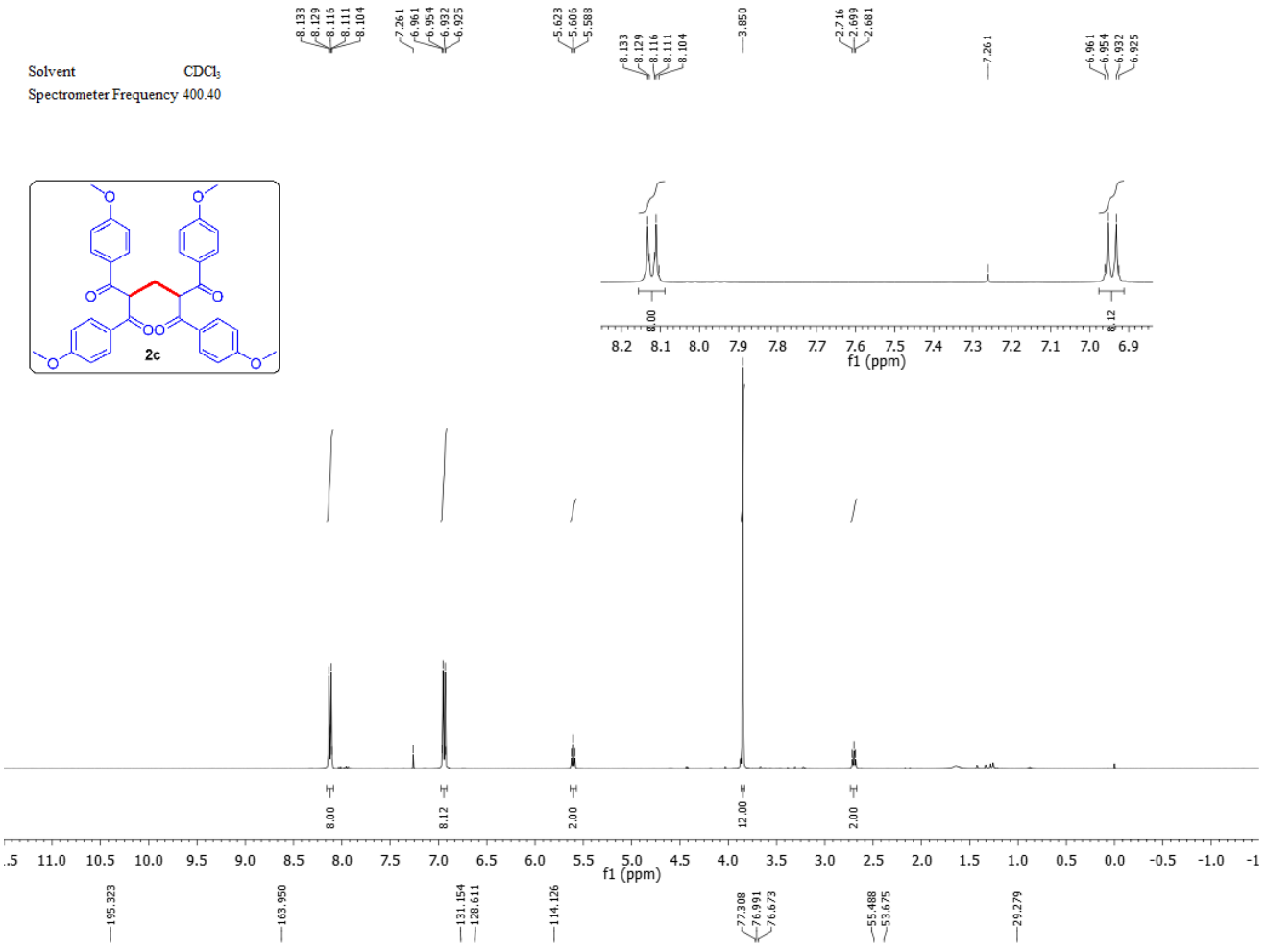
f1 (ppm)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3.850
2.716
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Solvent CDCl3
Spectrometer Frequency 400.40
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8.12
f1 (ppm)
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Solvent CDCl3
Spectrometer Frequency 100.69
2c
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 400.40

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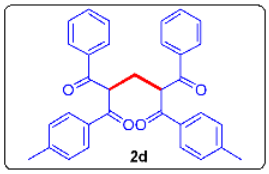

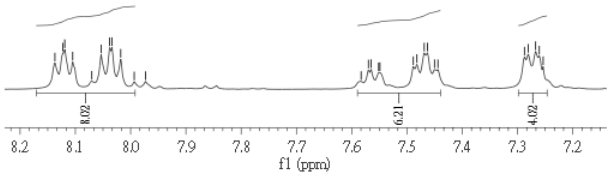

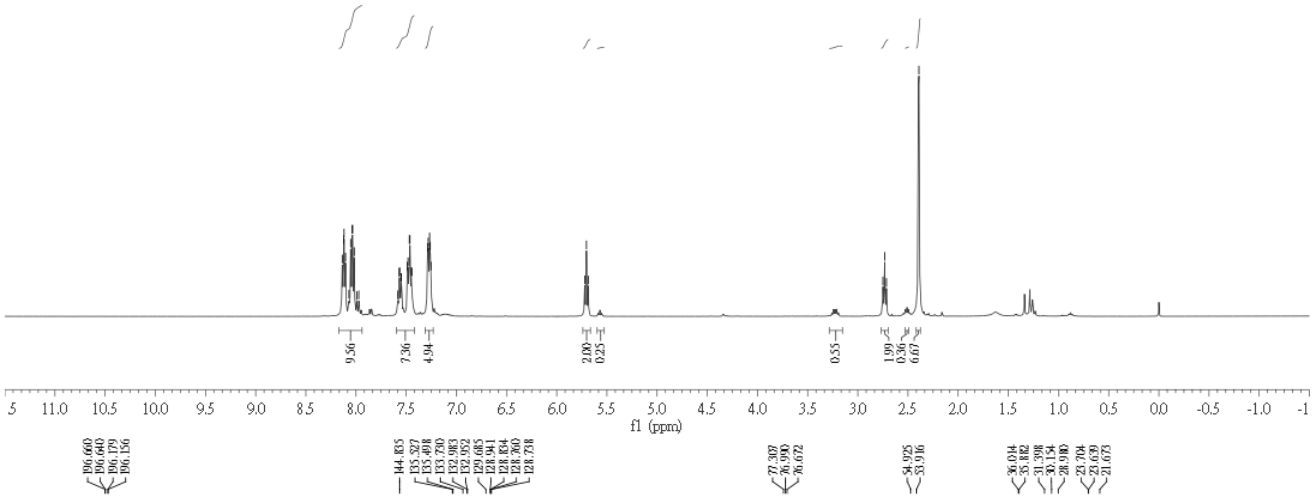

Solvent $CDCl_3$

Spectrometer Frequency 100.69

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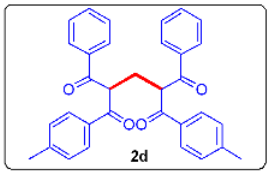

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Spectrometer Frequency 400.40
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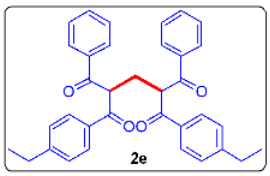

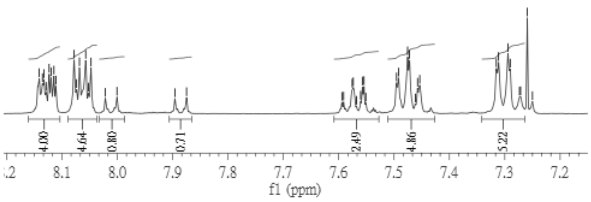

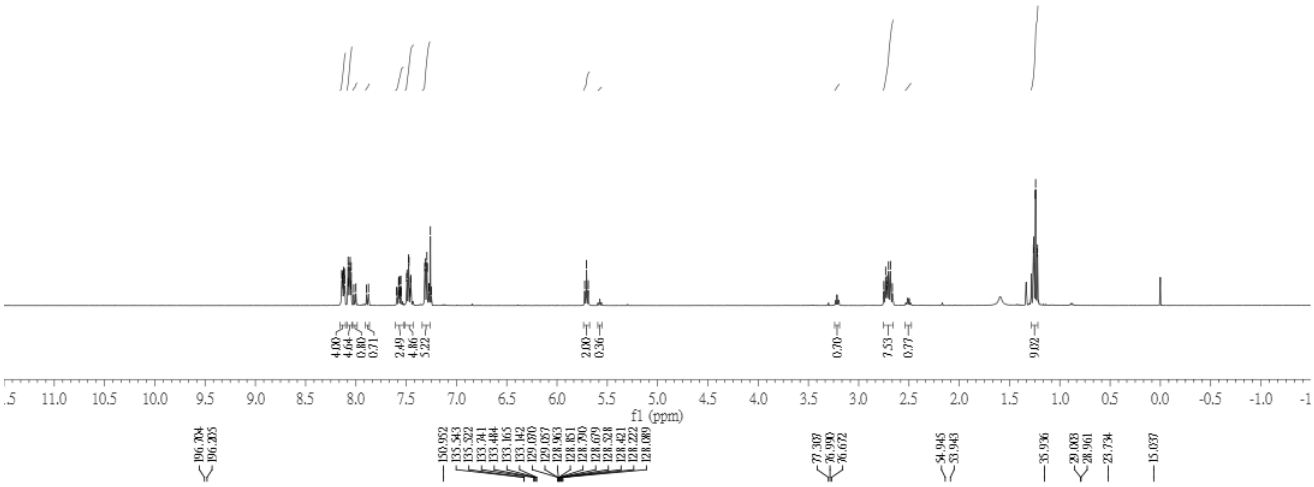

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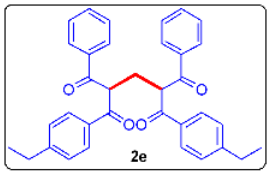

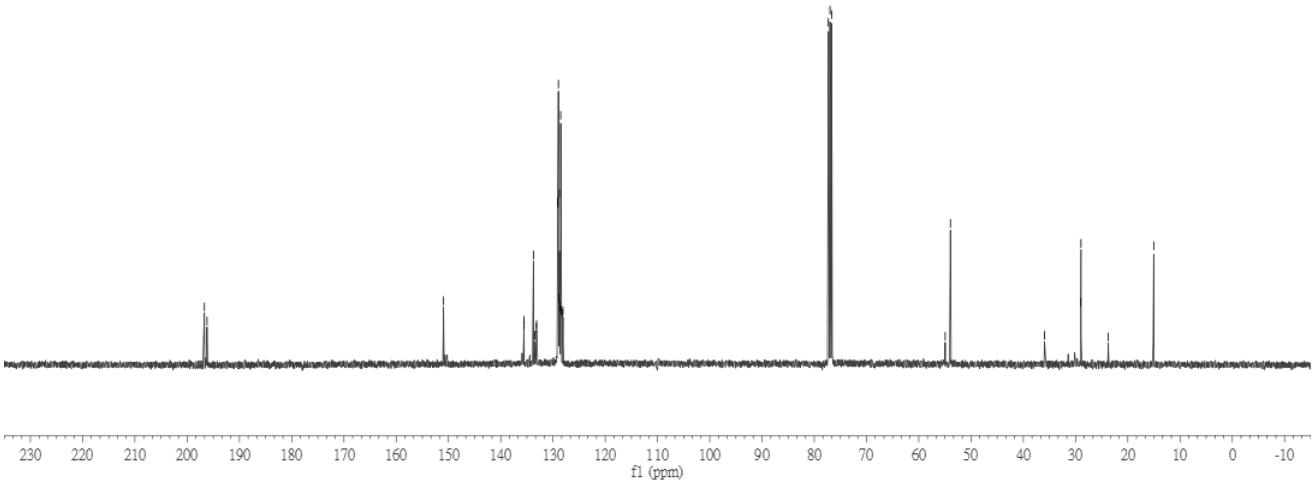

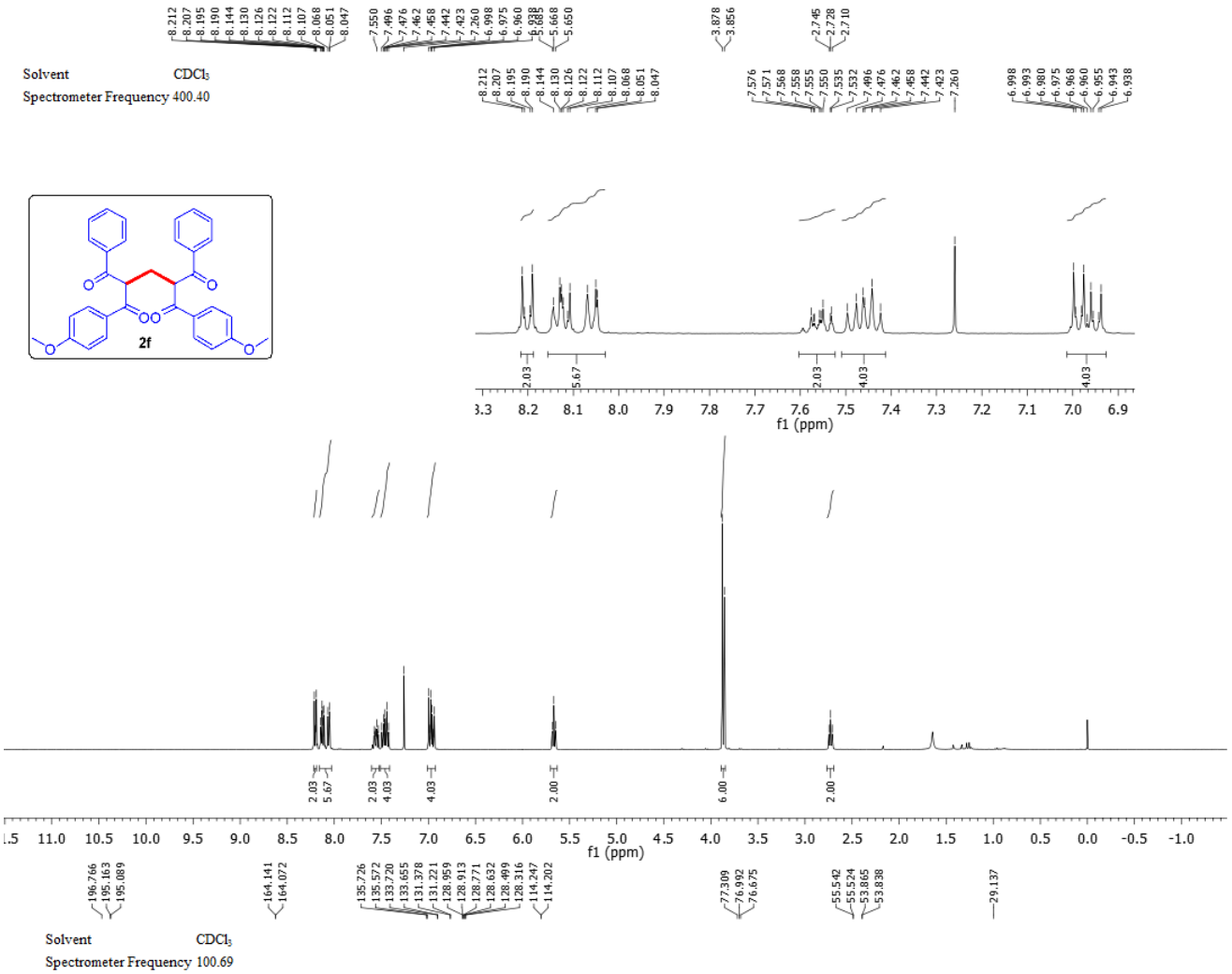
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2f
f1 (ppm)

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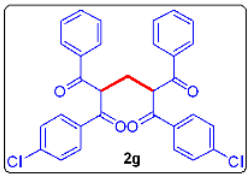

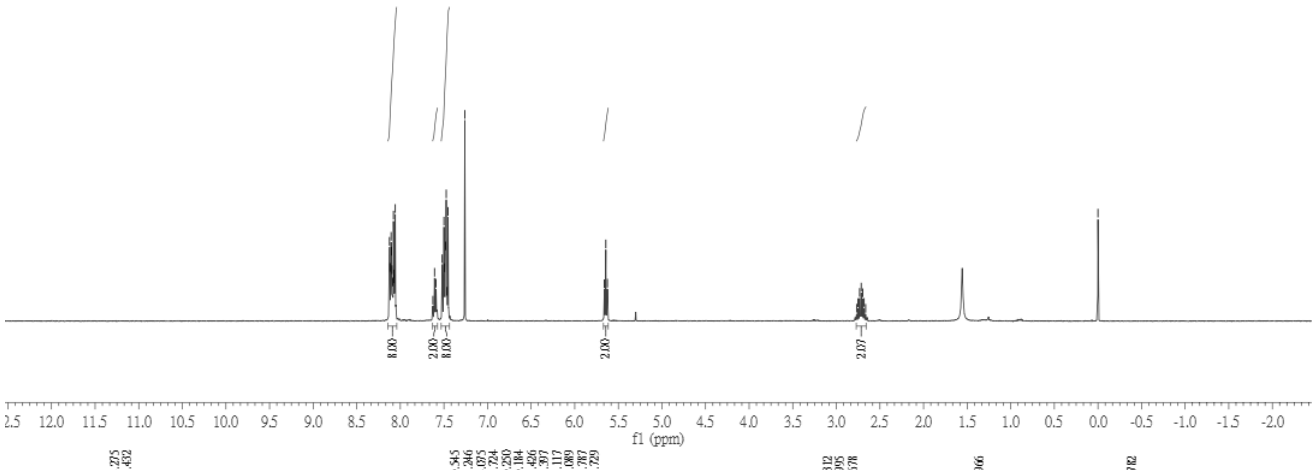

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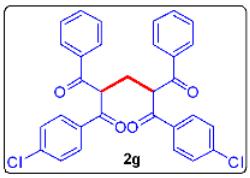

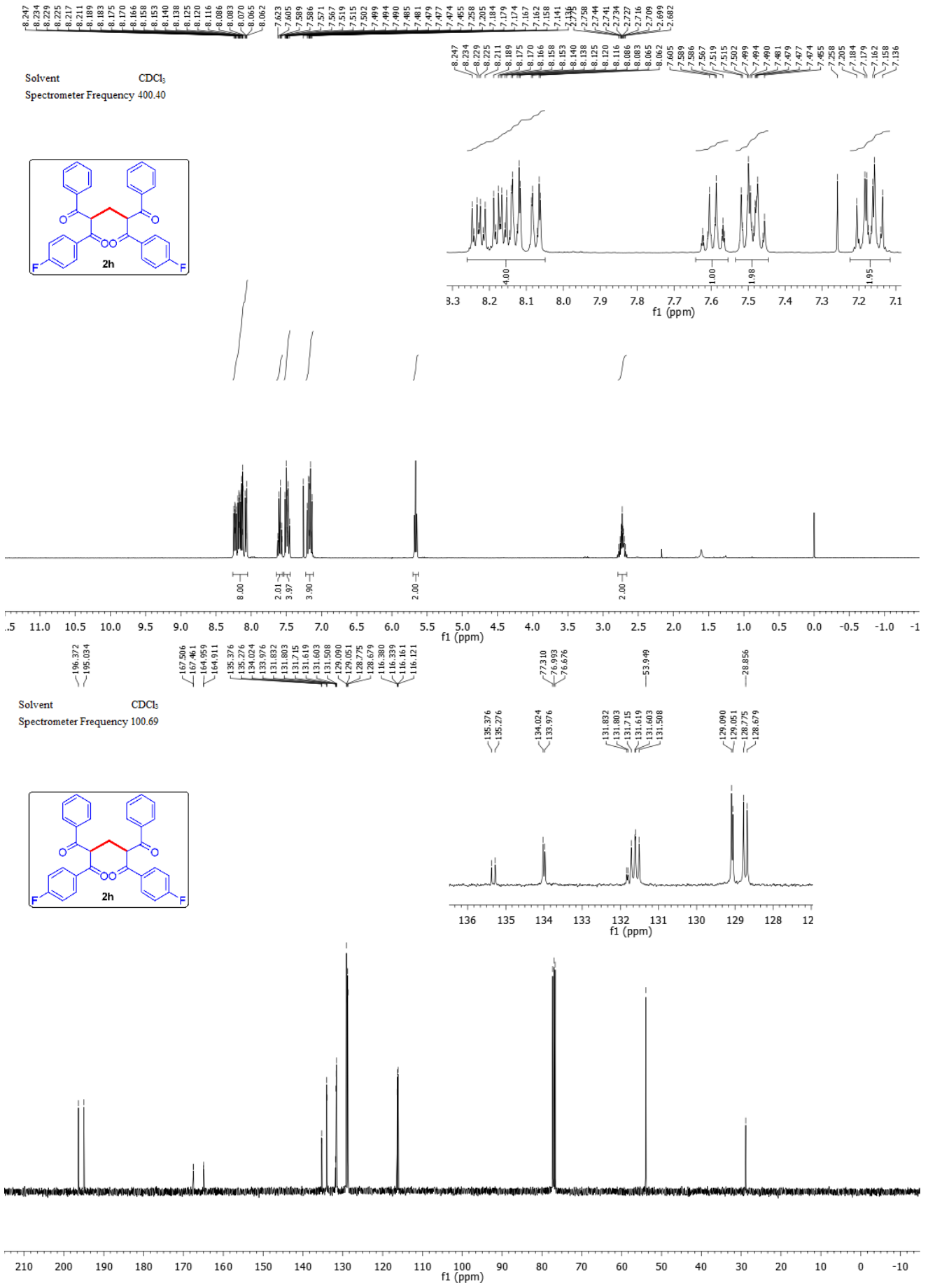
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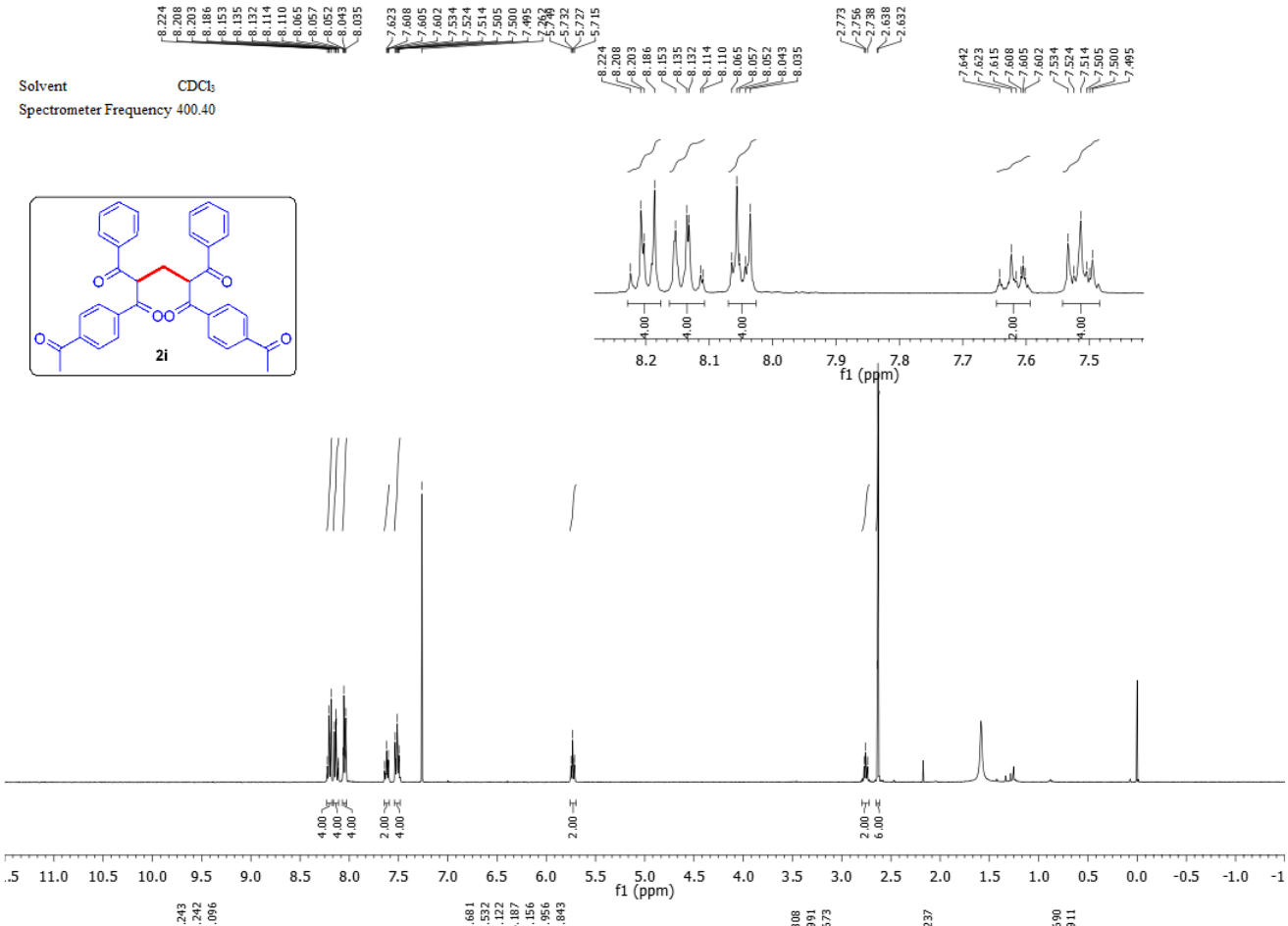
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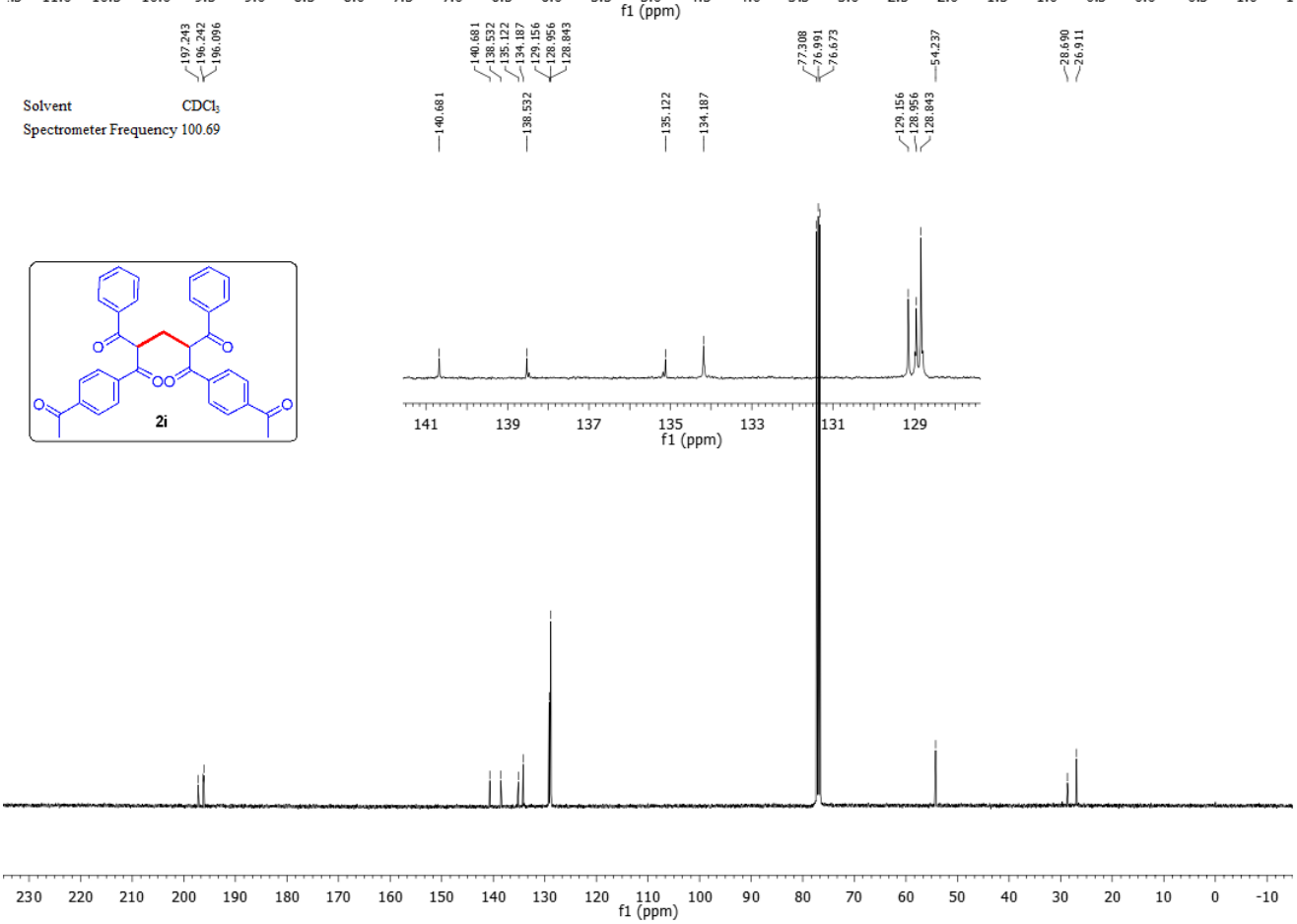
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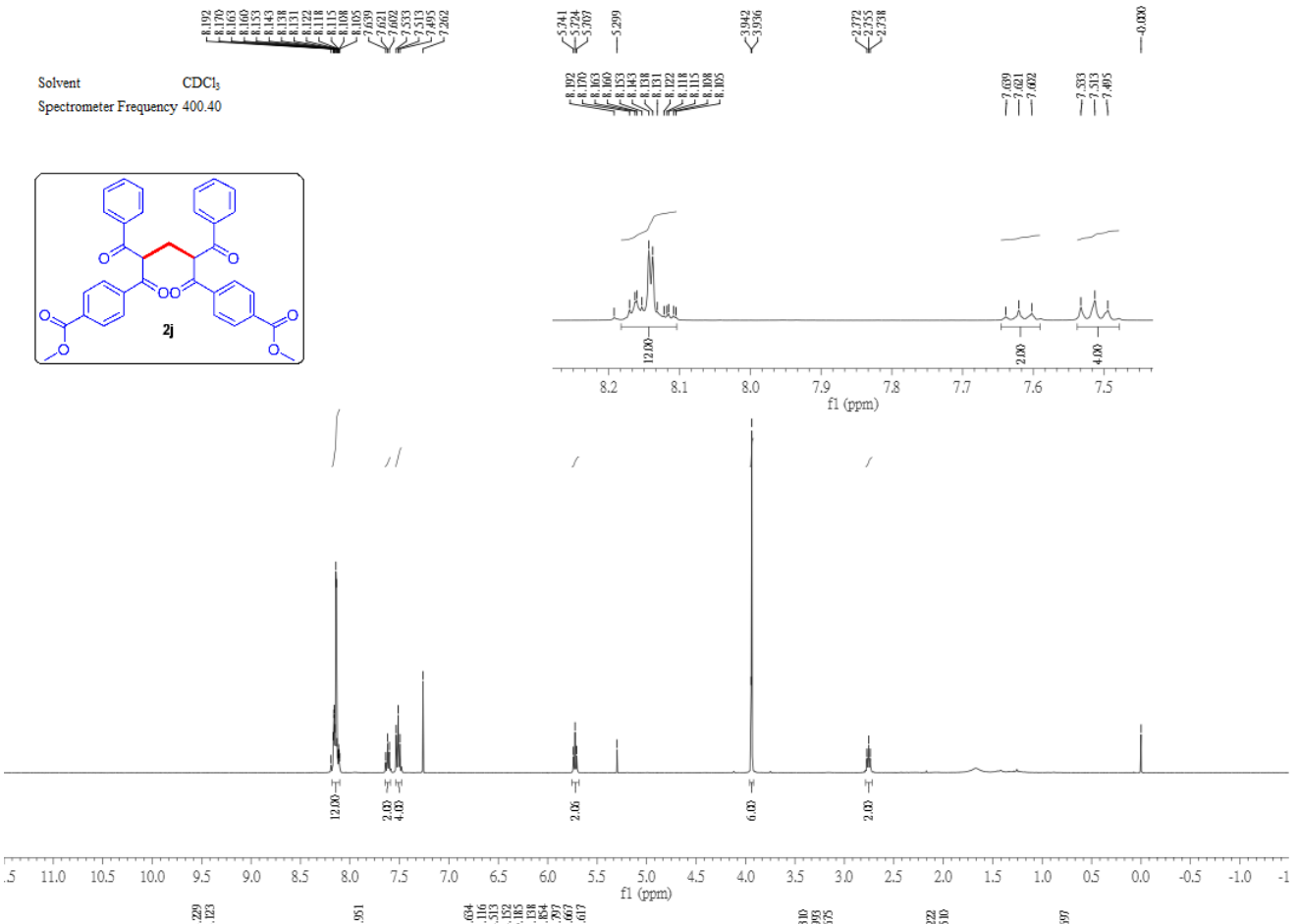
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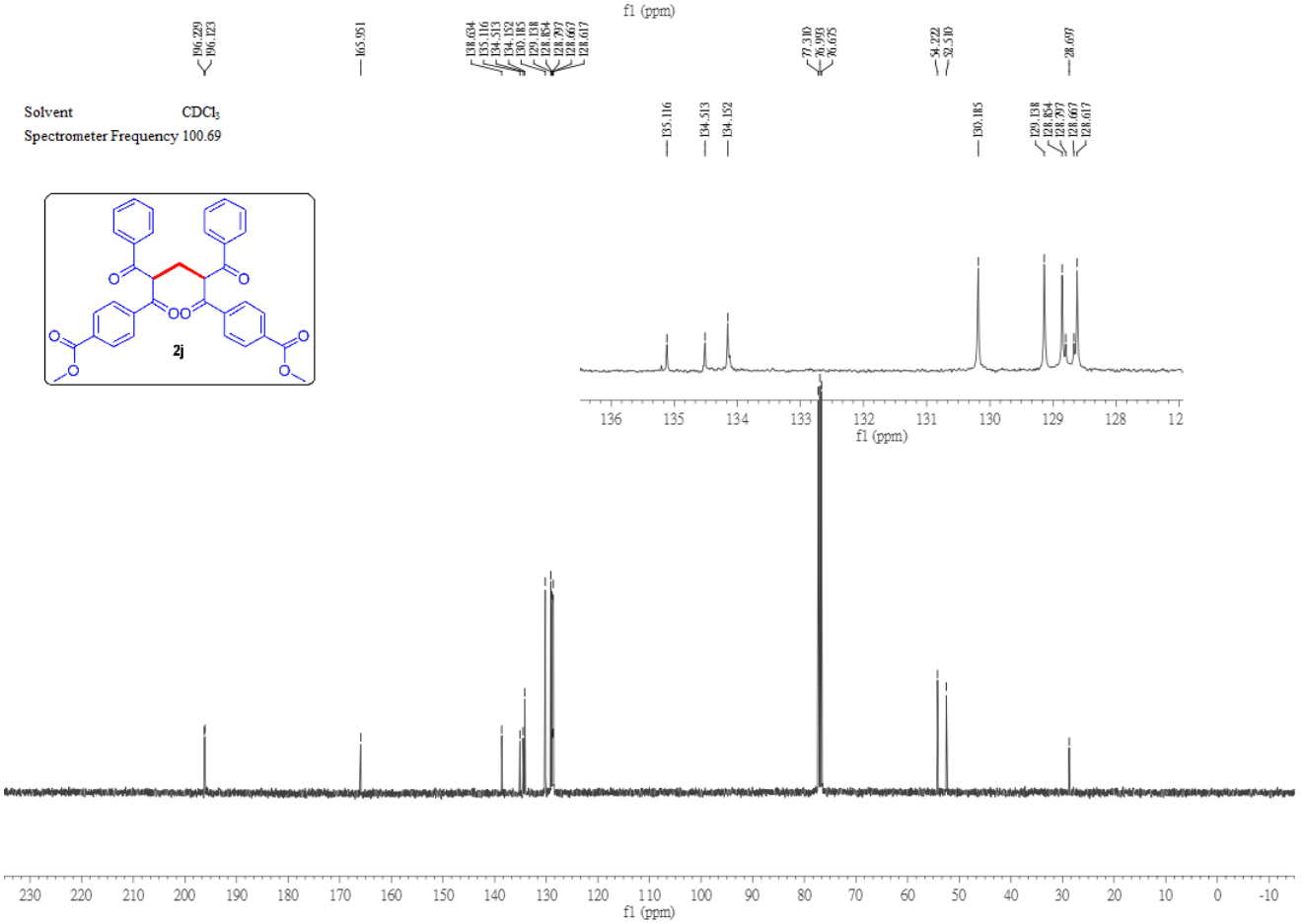
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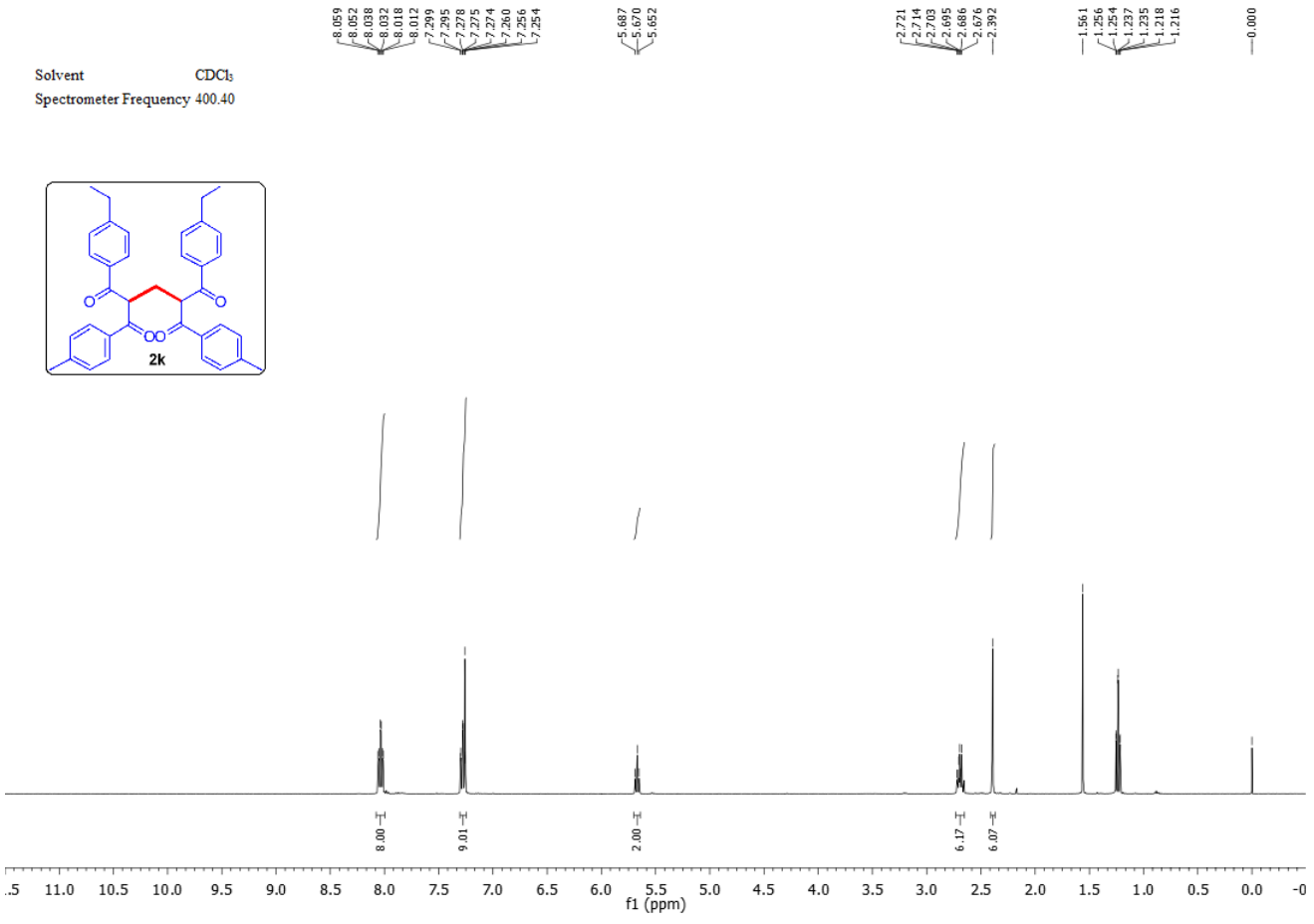
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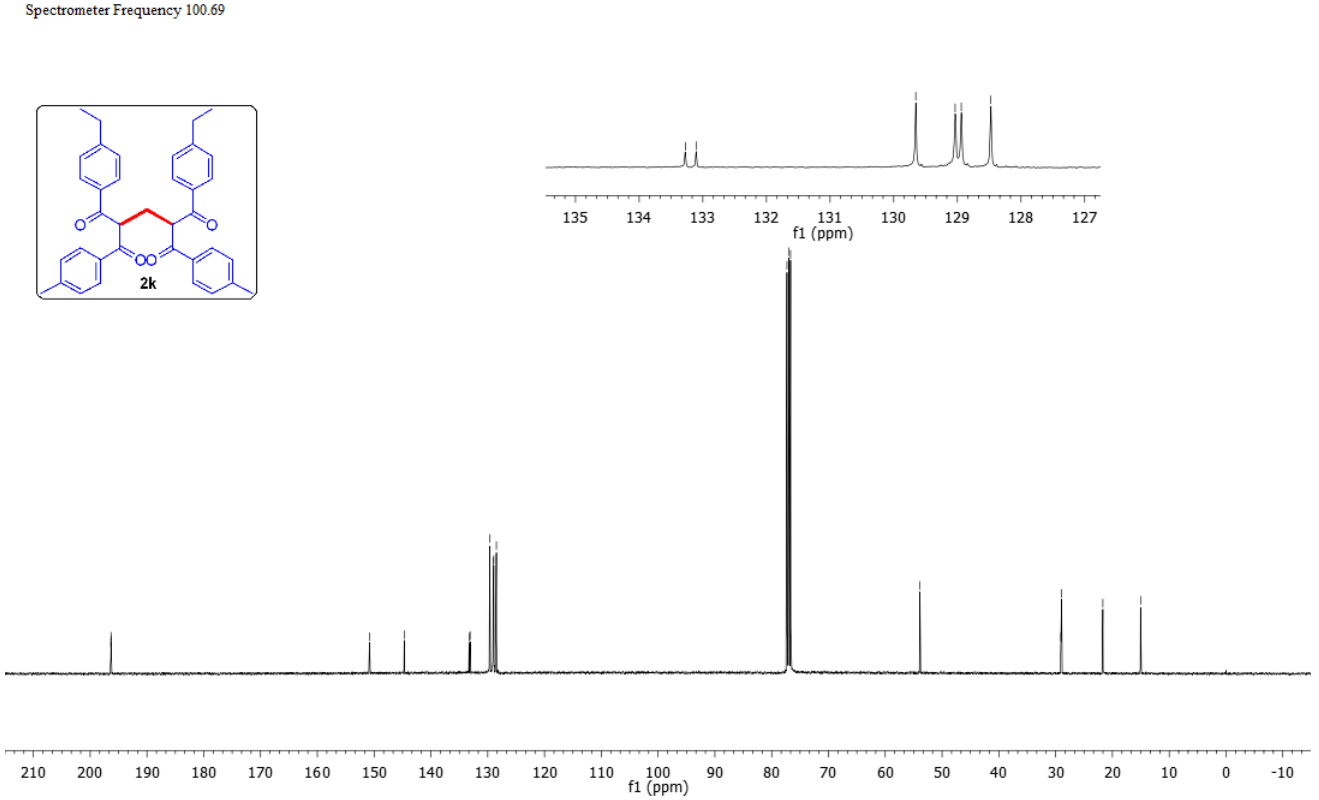
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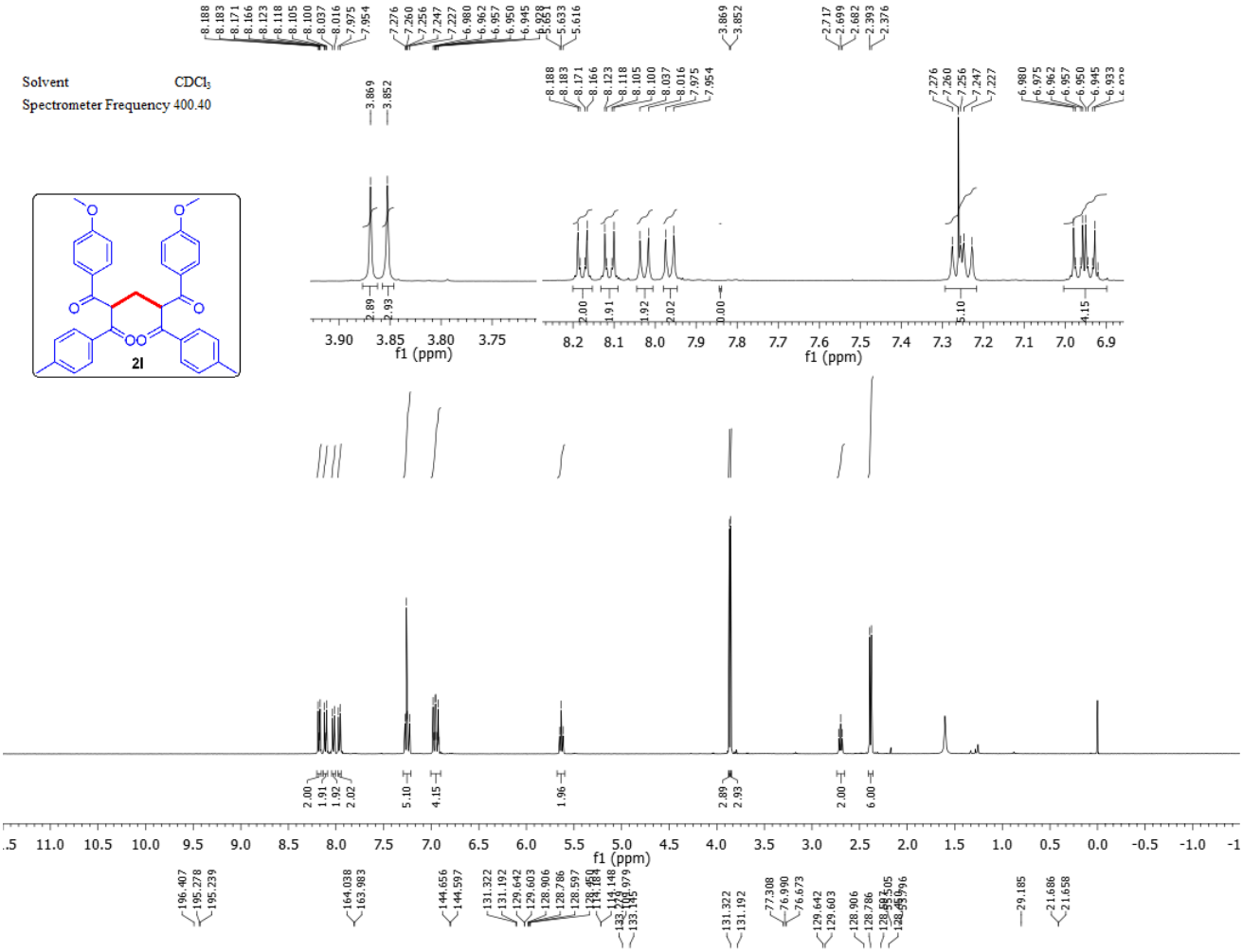
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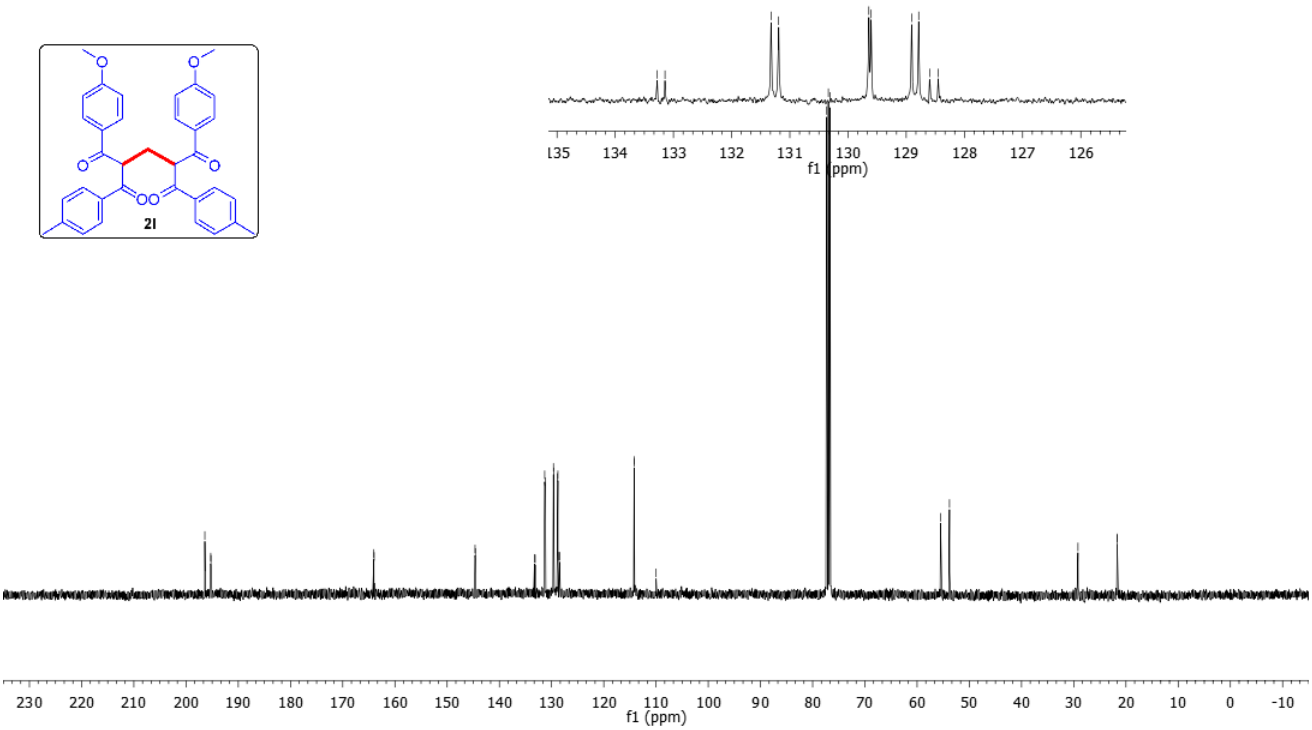
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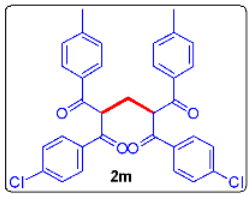
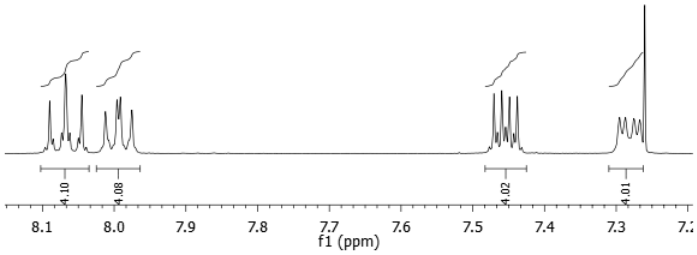
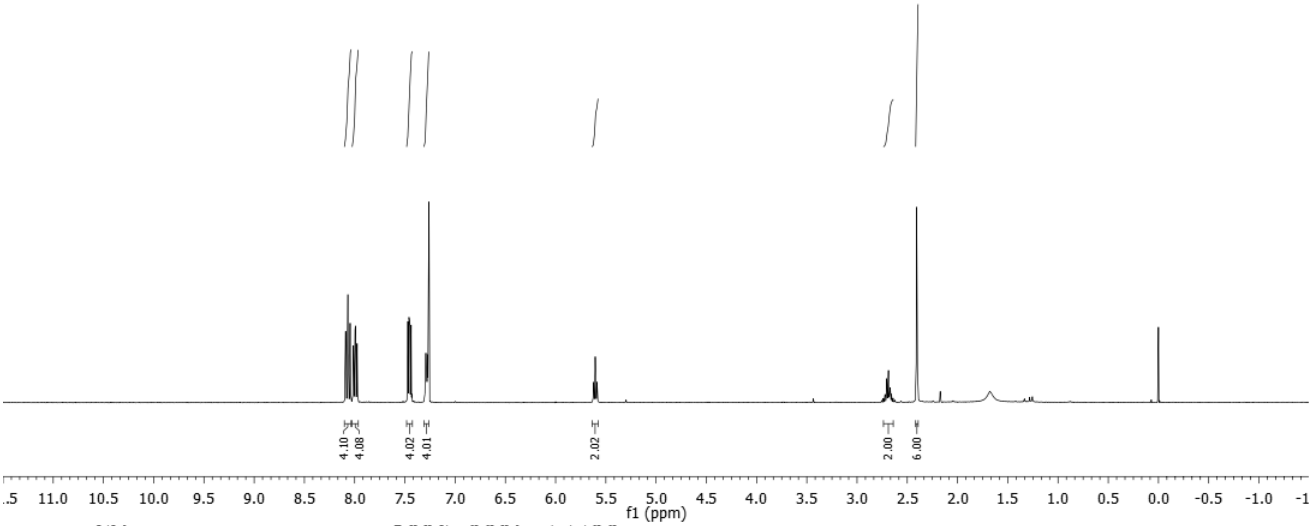
Solvent $CDCl_3$

Spectrometer Frequency 400.40

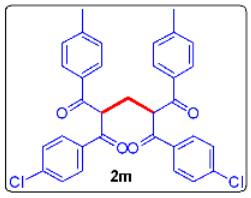


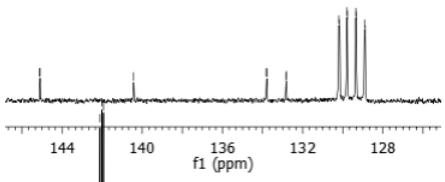




Solvent $CDCl_3$

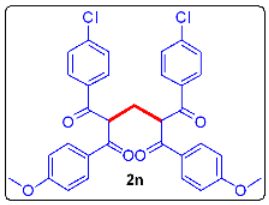
Spectrometer Frequency 100.69

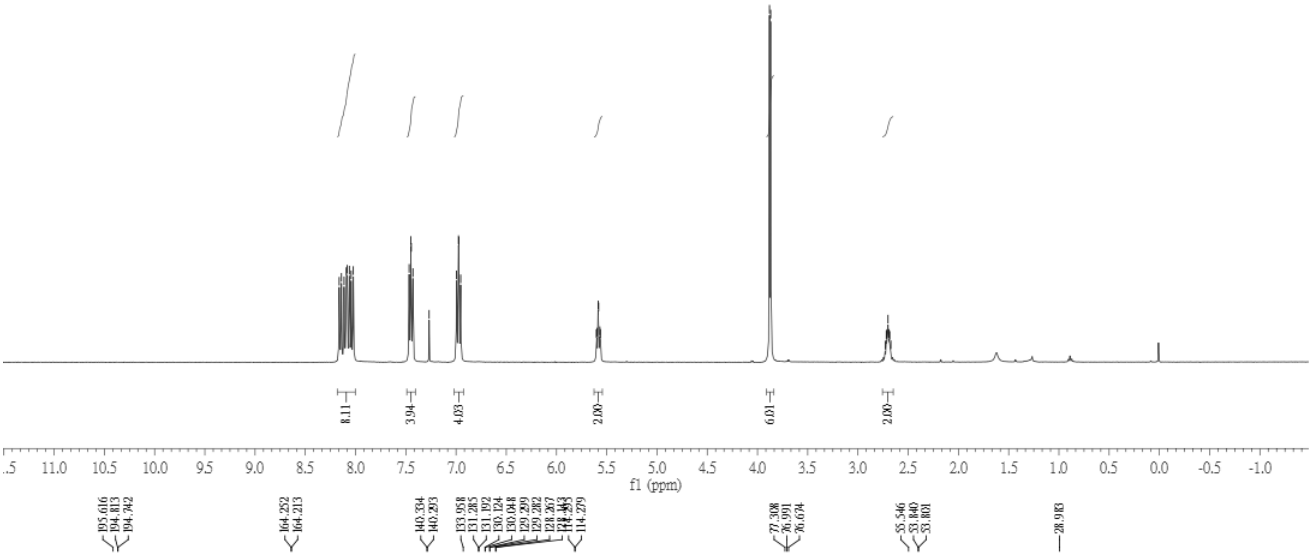




Solvent $CDCl_3$

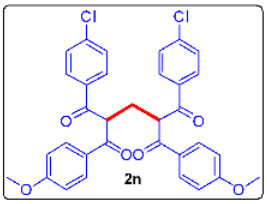
Spectrometer Frequency 400.40

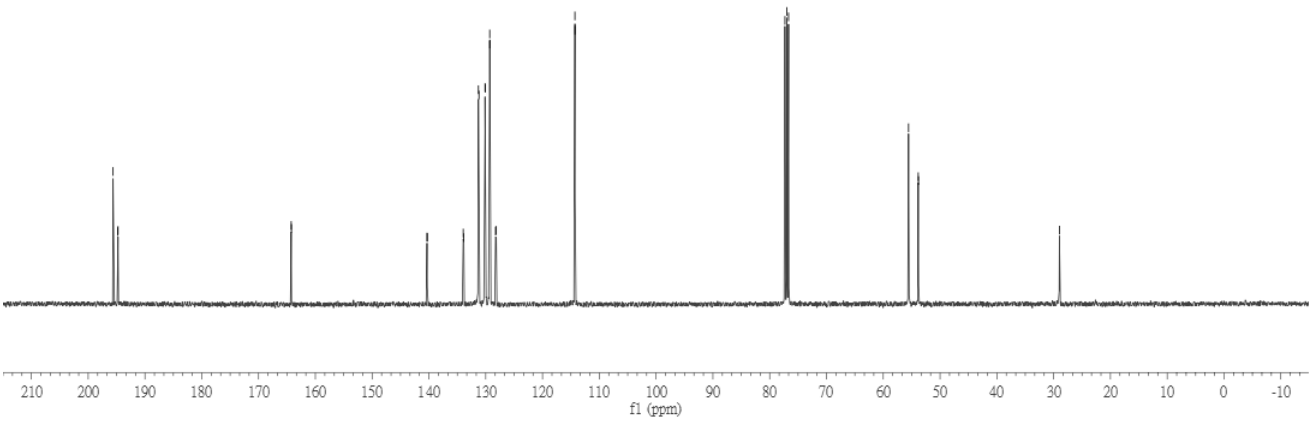




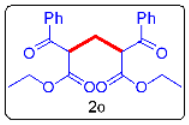
Solvent $CDCl_3$

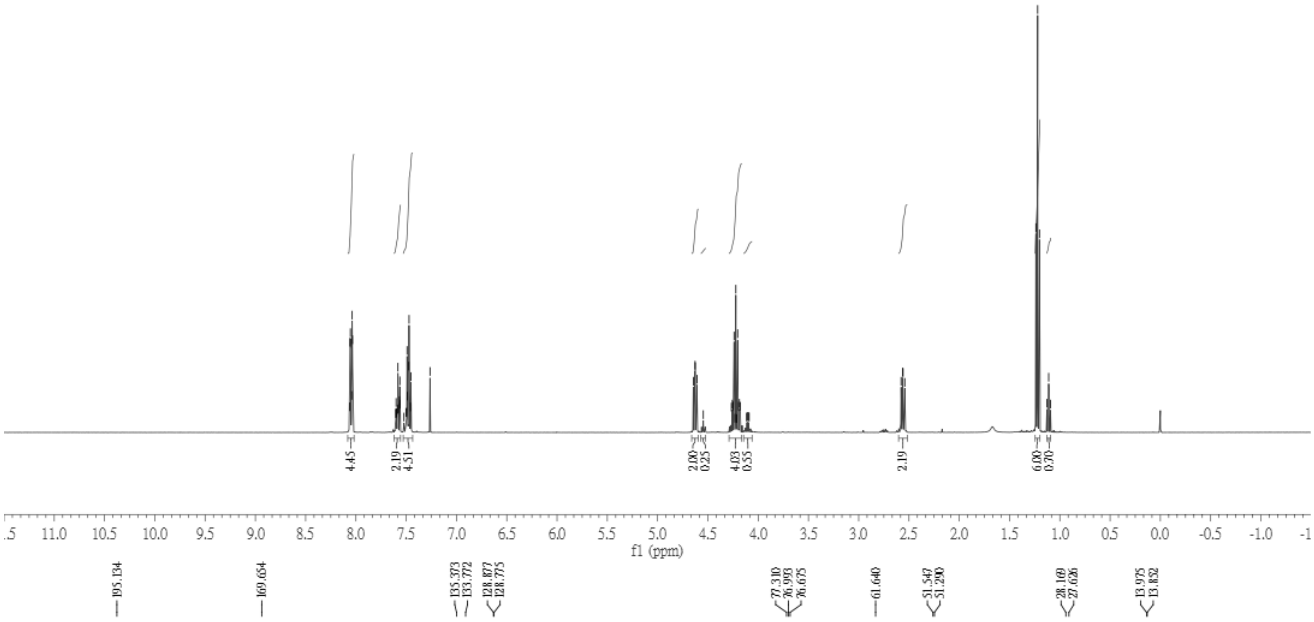
Spectrometer Frequency 100.69



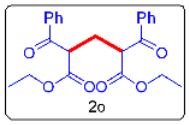


Solvent $CDCl_3$
Spectrometer Frequency 400.40
Nucleus ^1H



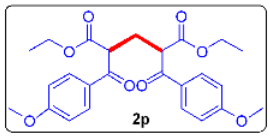


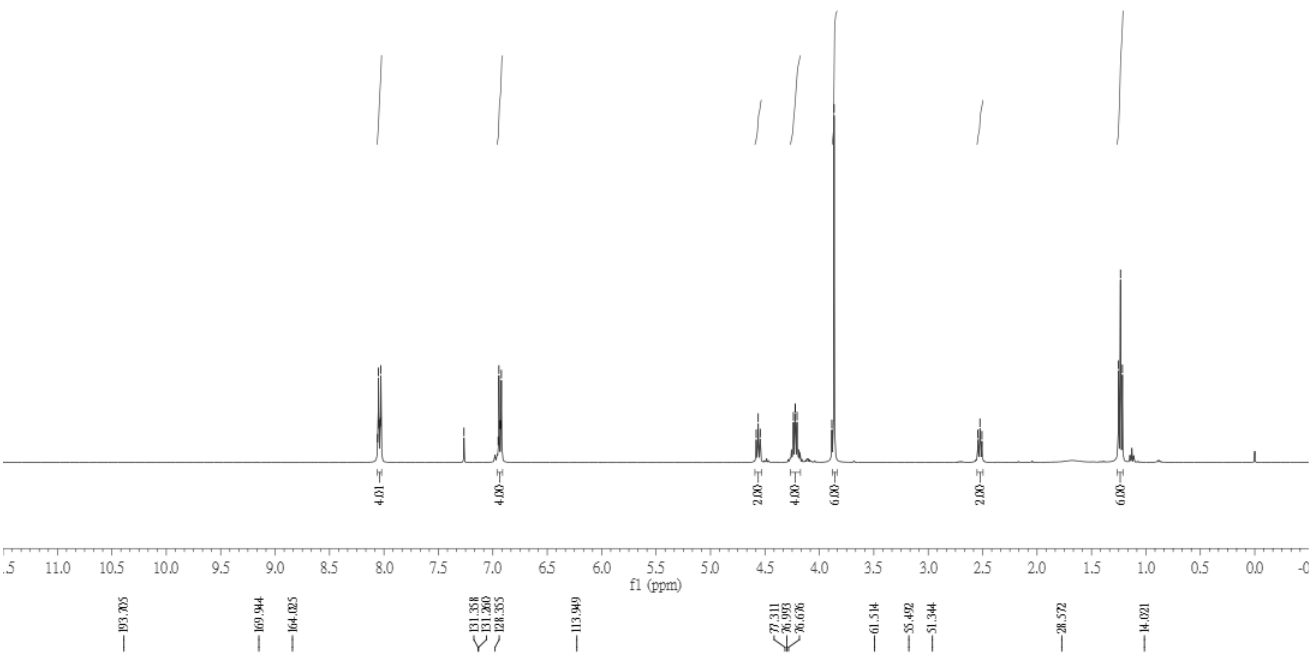
Solvent $CDCl_3$
Spectrometer Frequency 100.69
Nucleus ^{13}C



Solvent $CDCl_3$

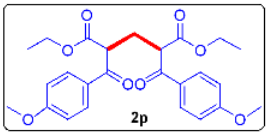
Spectrometer Frequency 400.40

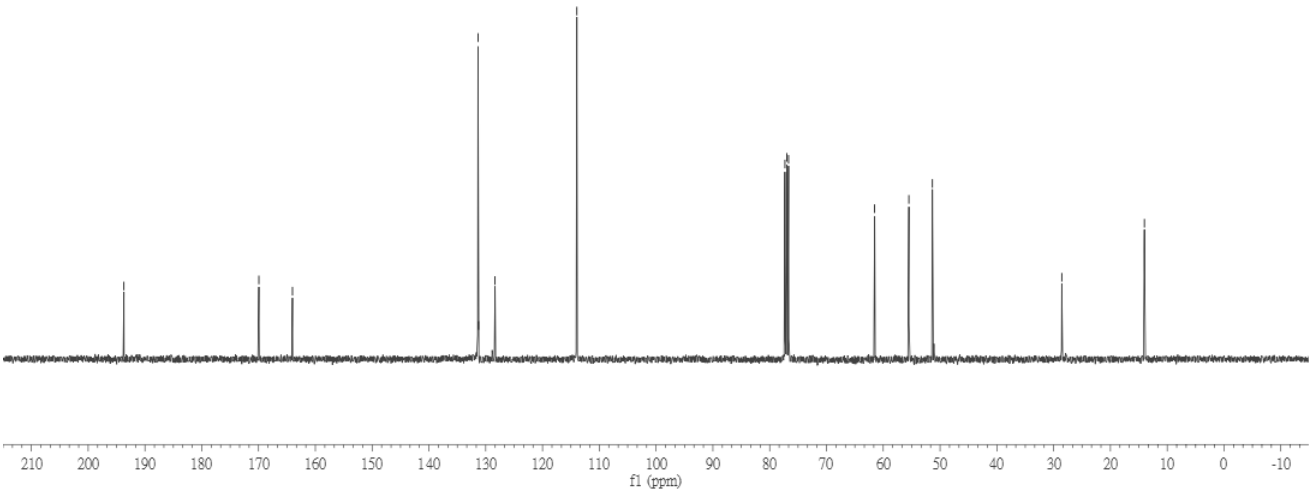


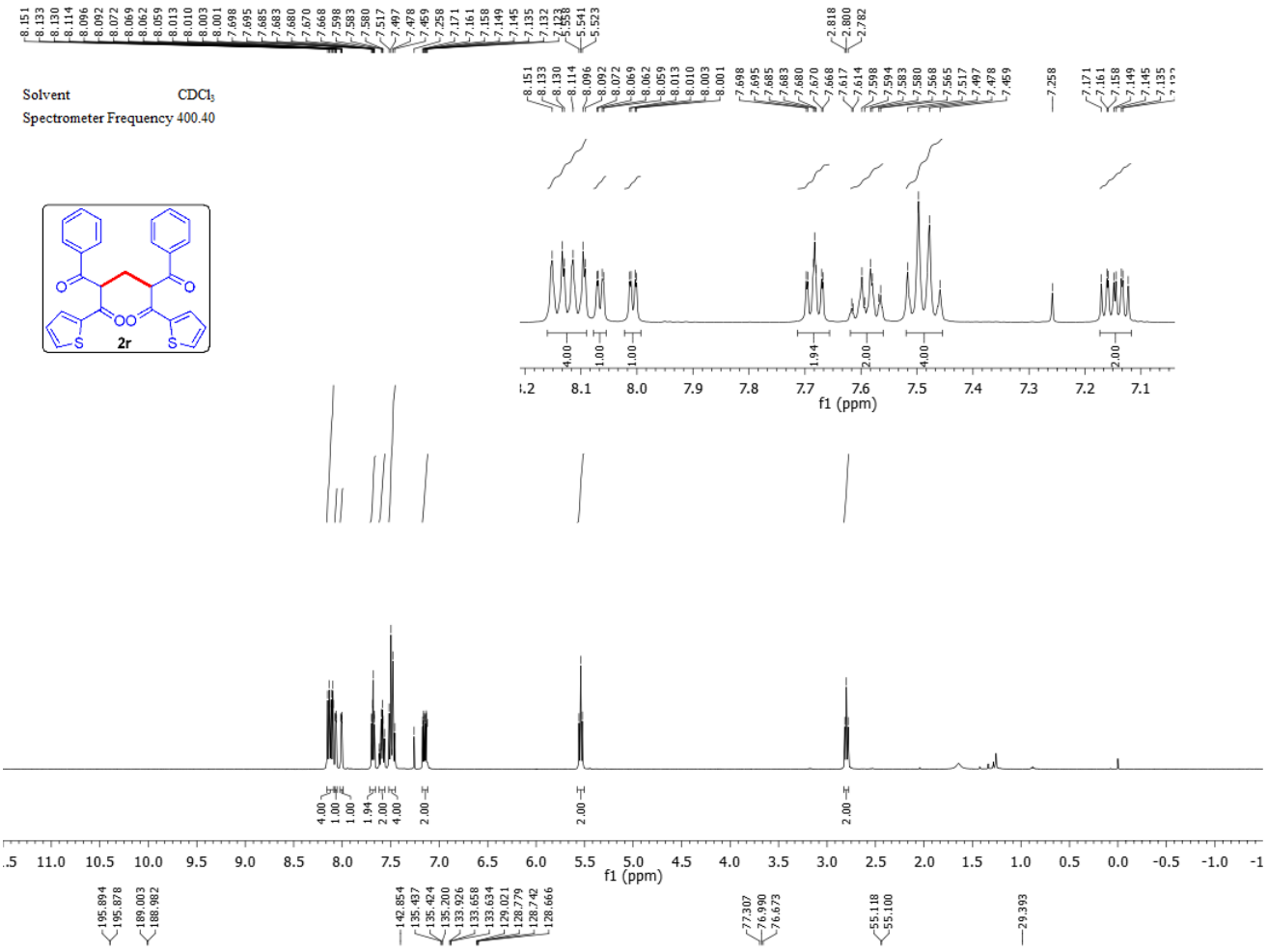


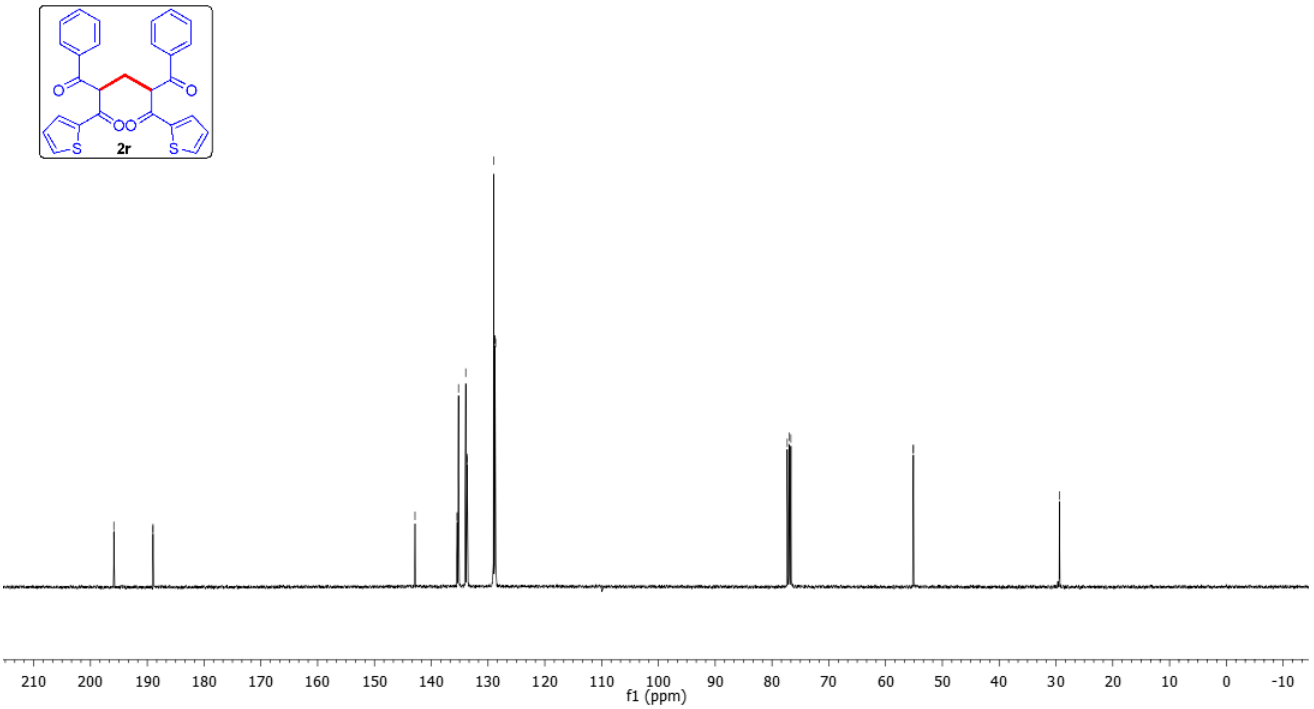
Solvent $CDCl_3$

Spectrometer Frequency 100.69

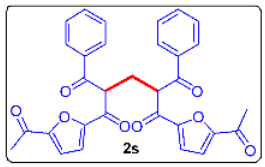


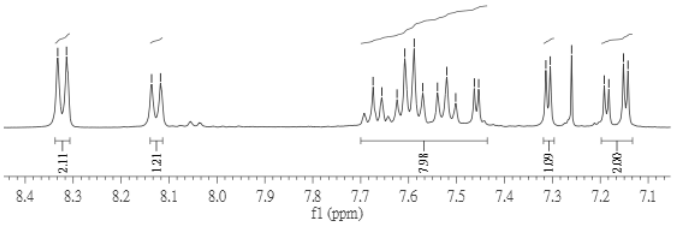


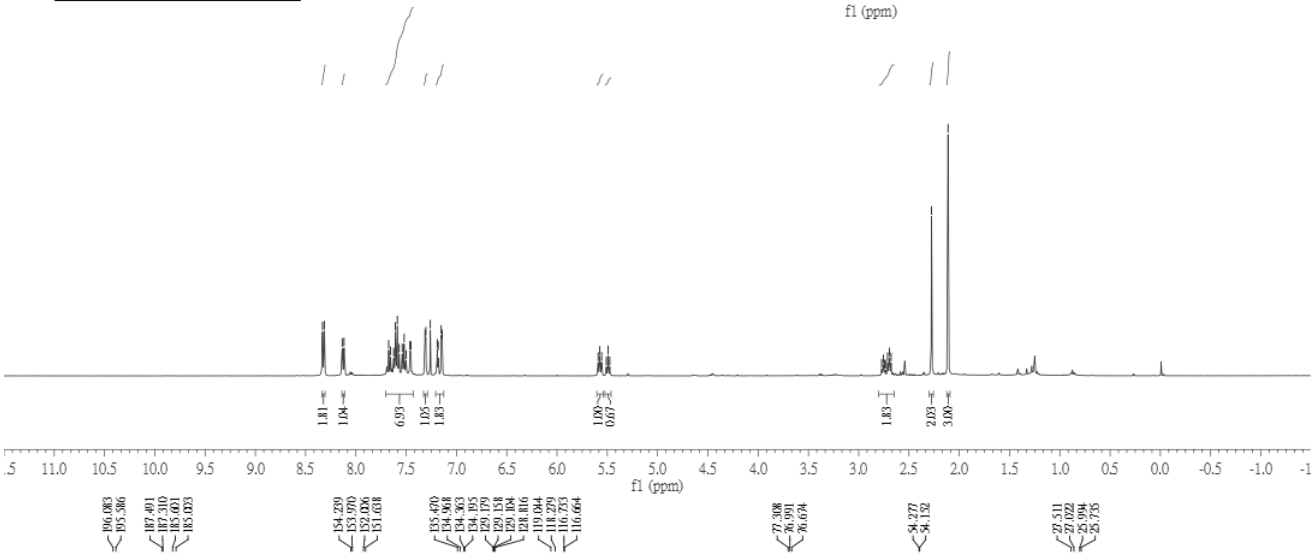

Solvent CDCl3
Spectrometer Frequency 400.40
2r
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 100.69
2r
f1 (ppm)

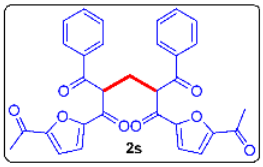
Solvent $CDCl_3$
Spectrometer Frequency 400.40
Nucleus ^1H

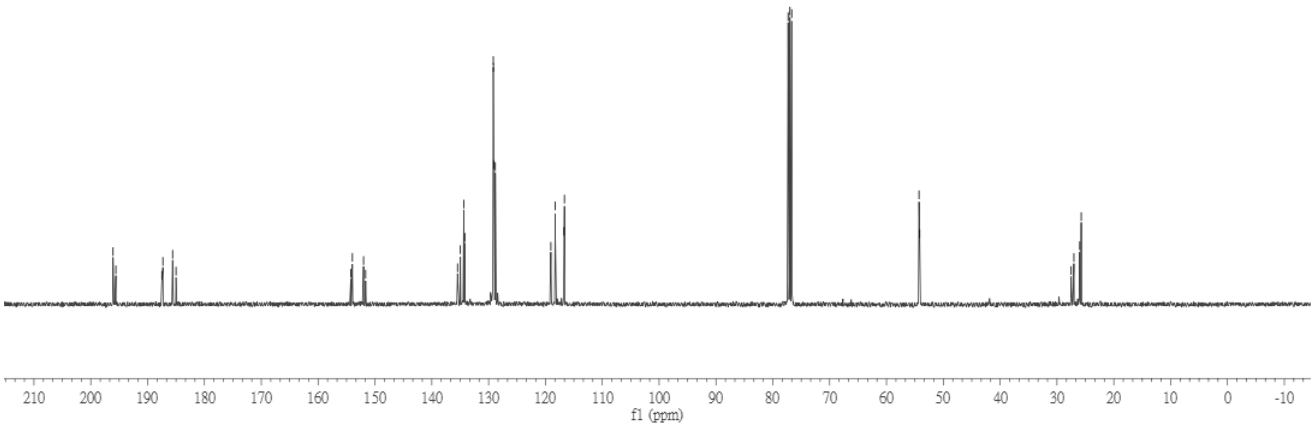


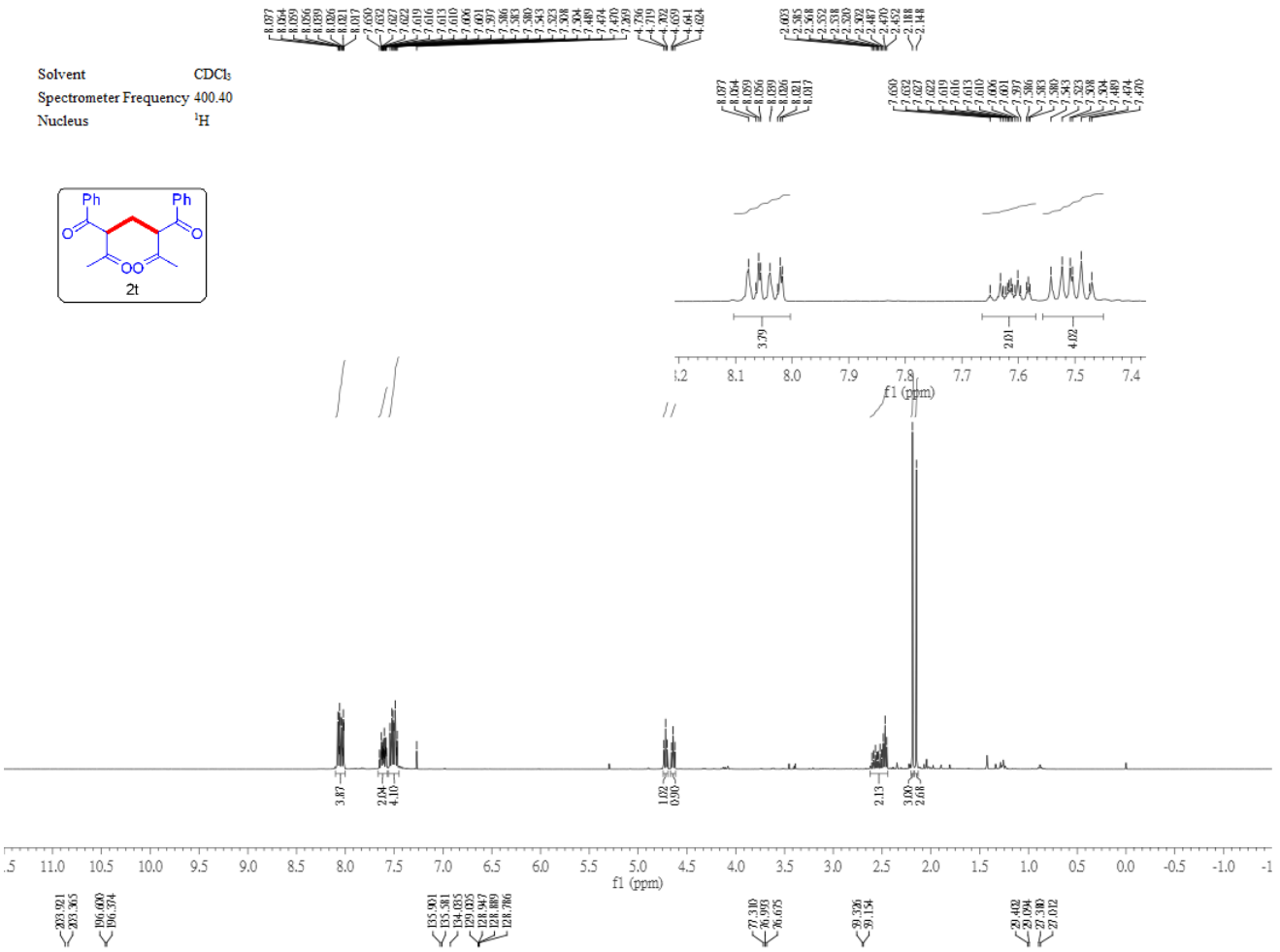


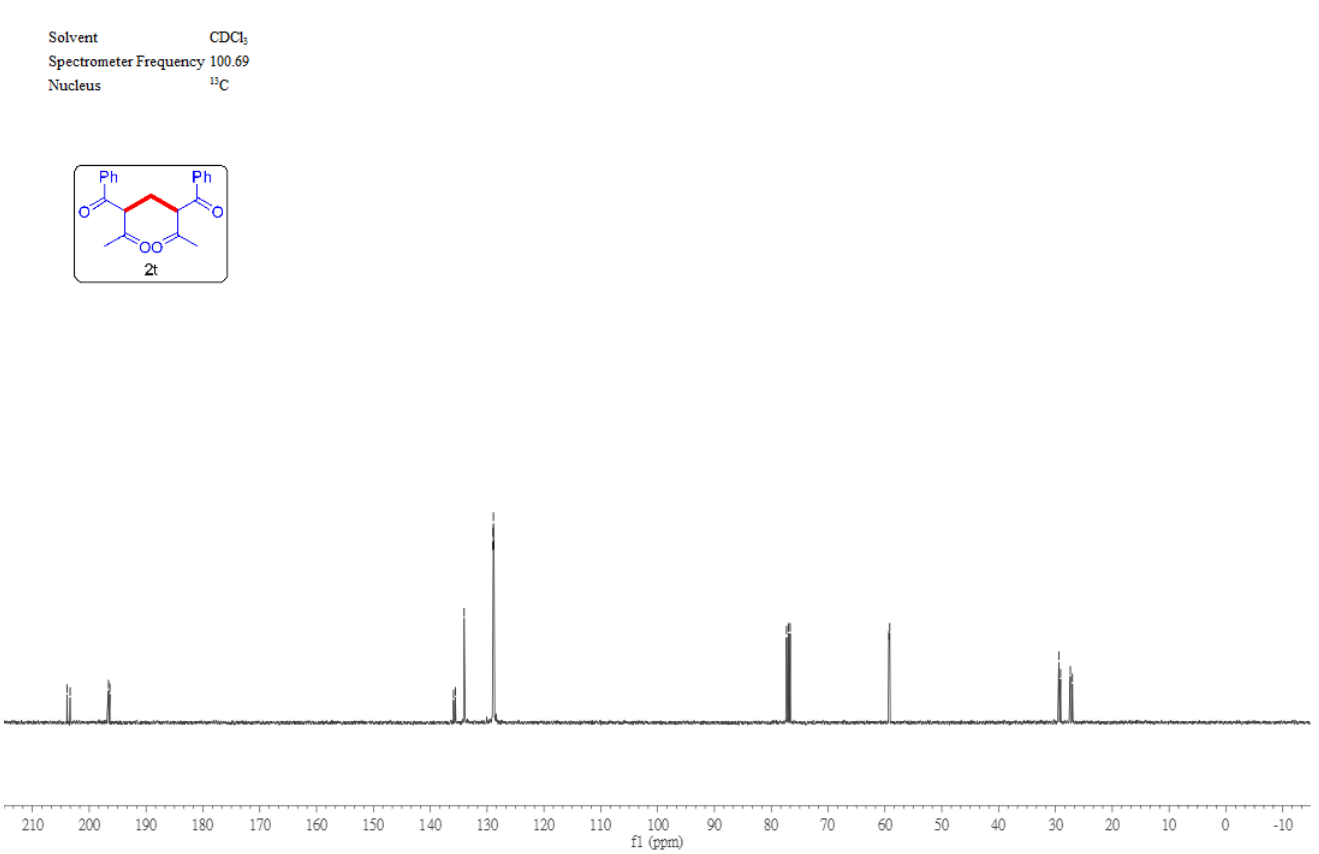


Solvent $CDCl_3$
Spectrometer Frequency 100.69
Nucleus ^{13}C

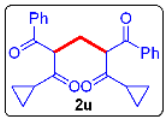


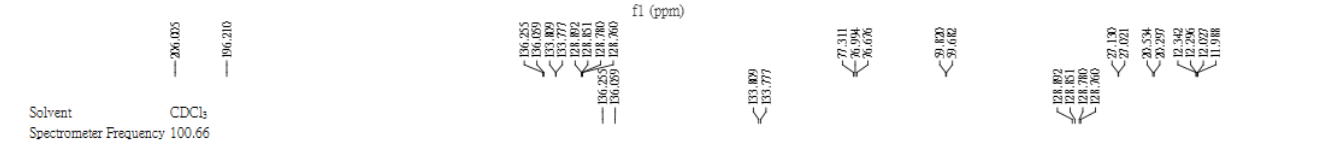



Solvent CDCl3
Spectrometer Frequency 400.40
Nucleus 1H
Ph
Ph
O
O
O
O
2t
f1 (ppm)

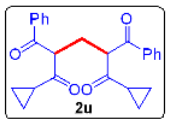

Solvent CDCl3
Spectrometer Frequency 100.69
Nucleus 13C
Ph
Ph
O
O
O
O
2t
f1 (ppm)

Solvent $CDCl_3$
Spectrometer Frequency 600



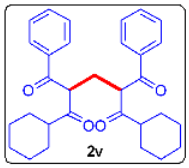


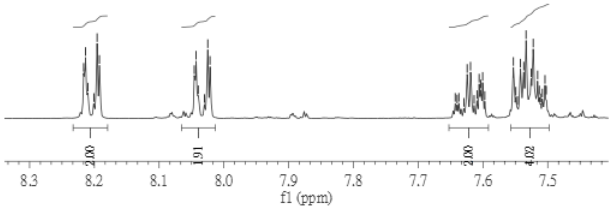
Solvent $CDCl_3$
Spectrometer Frequency 100.66

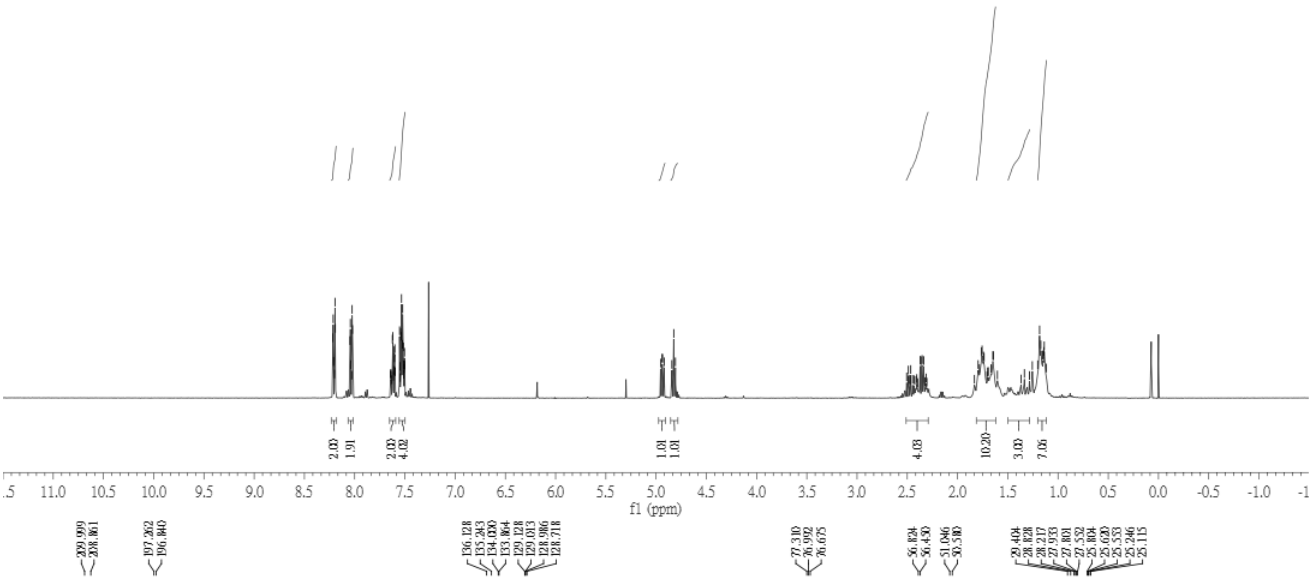


Solvent $CDCl_3$

Spectrometer Frequency 400.40

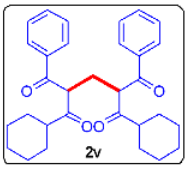


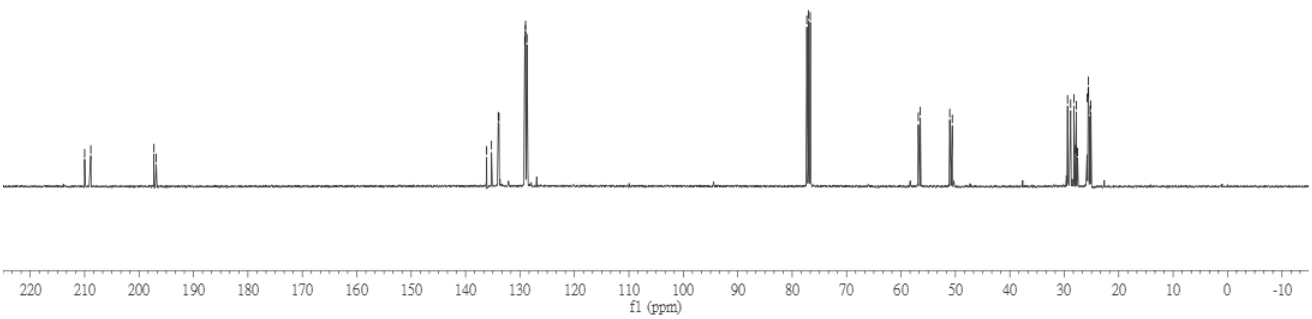




Solvent $CDCl_3$

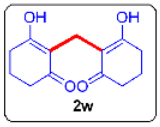
Spectrometer Frequency 100.69





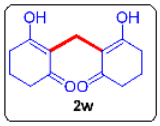
Solvent $CDCl_3$

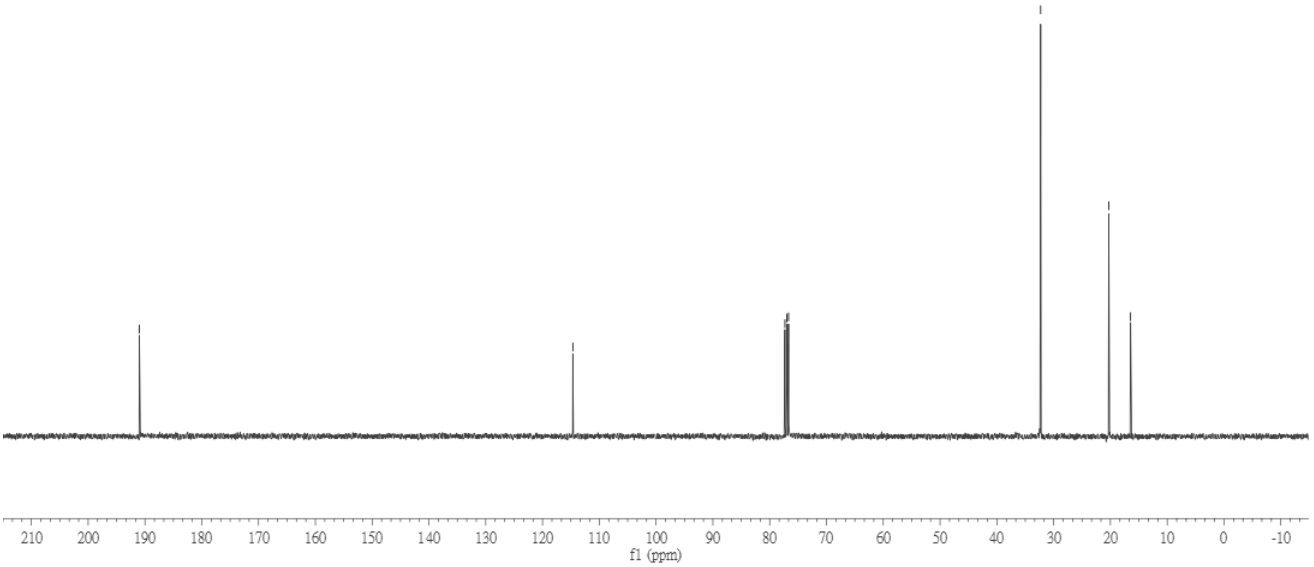
Spectrometer Frequency 400.40



Solvent $CDCl_3$

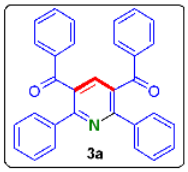
Spectrometer Frequency 100.69

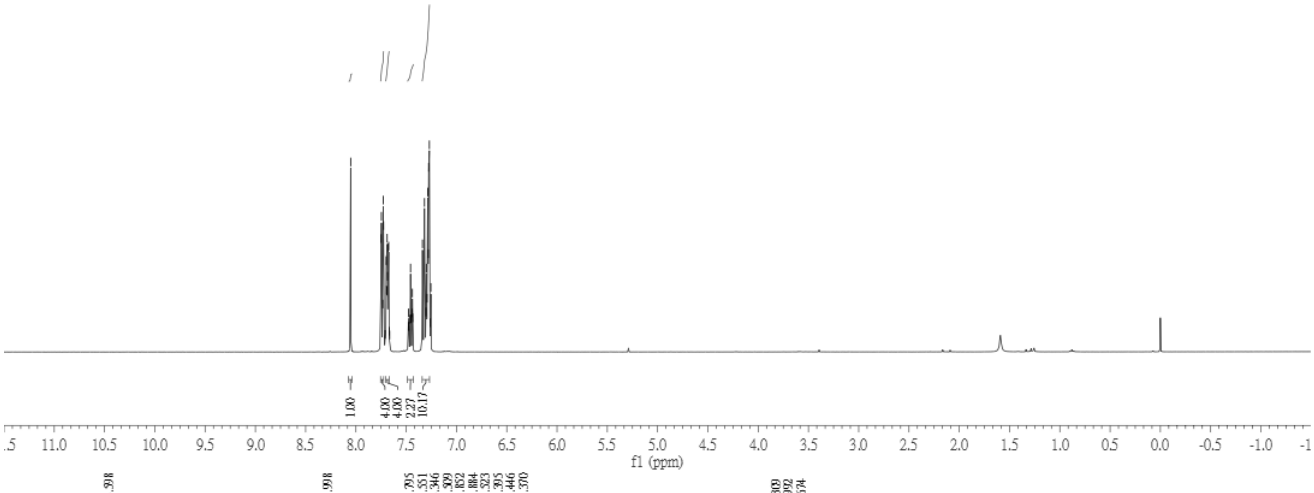




Solvent $CDCl_3$

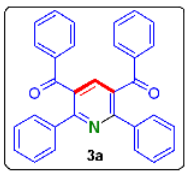
Spectrometer Frequency 400.40

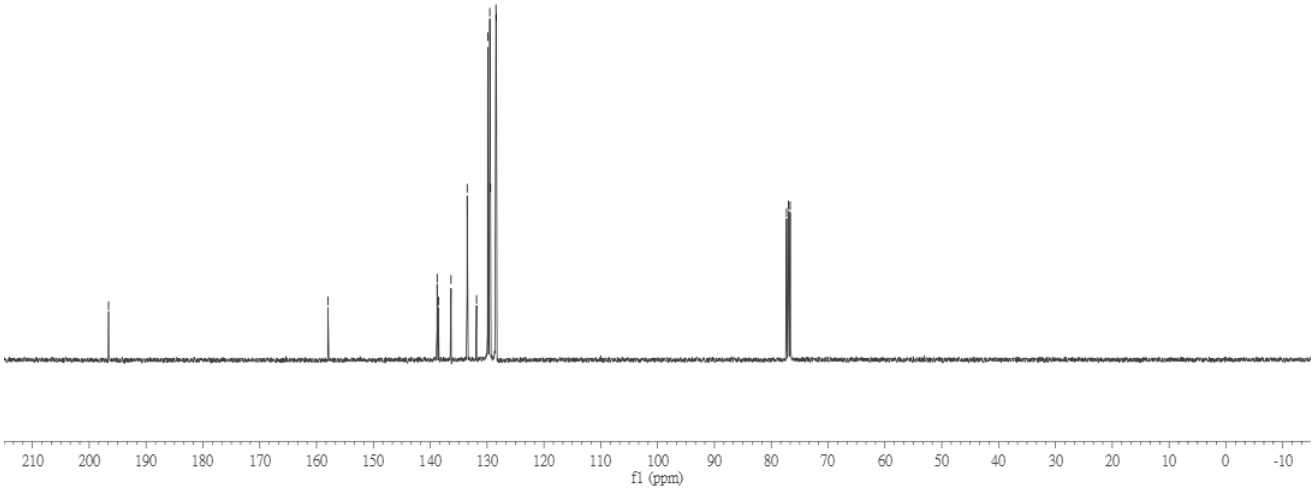




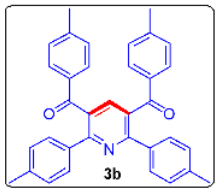
Solvent $CDCl_3$

Spectrometer Frequency 100.69

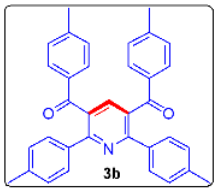




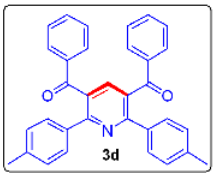
Solvent CDCl3
Spectrometer Frequency 400.40

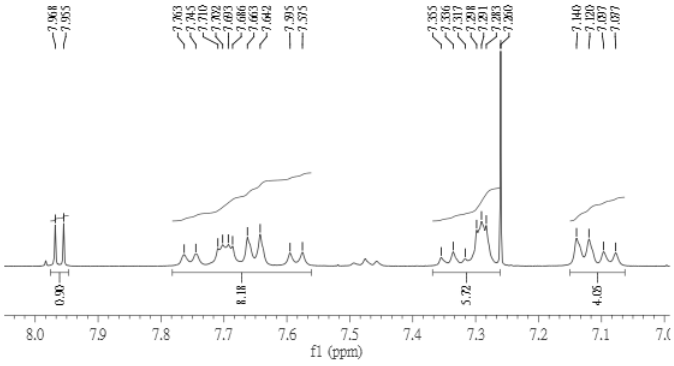


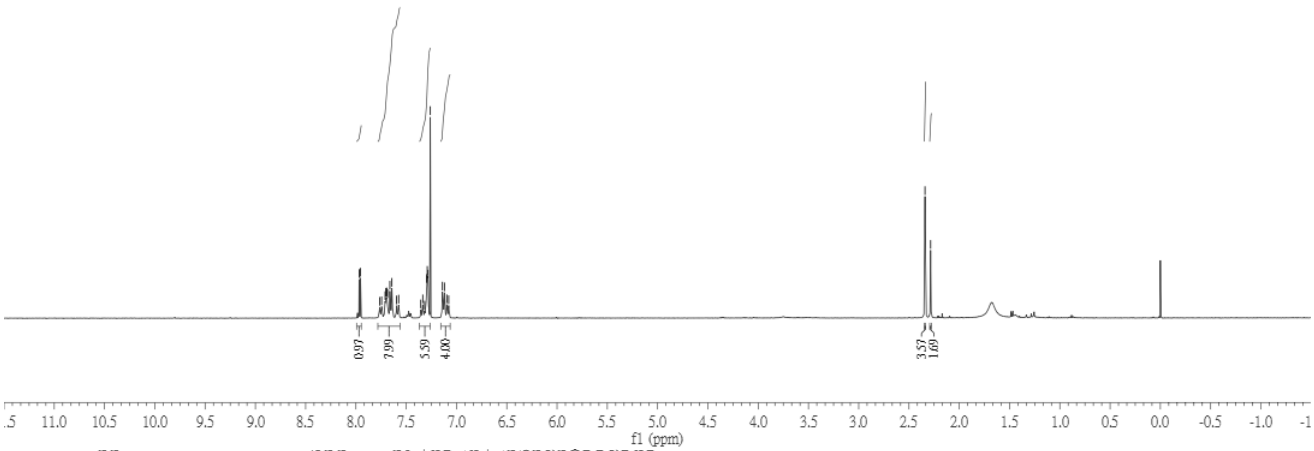
Solvent CDCl3
Spectrometer Frequency 100.69



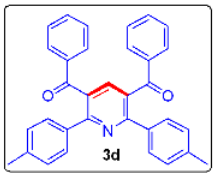
Solvent $CDCl_3$
Spectrometer Frequency 400.40
Nucleus ^1H

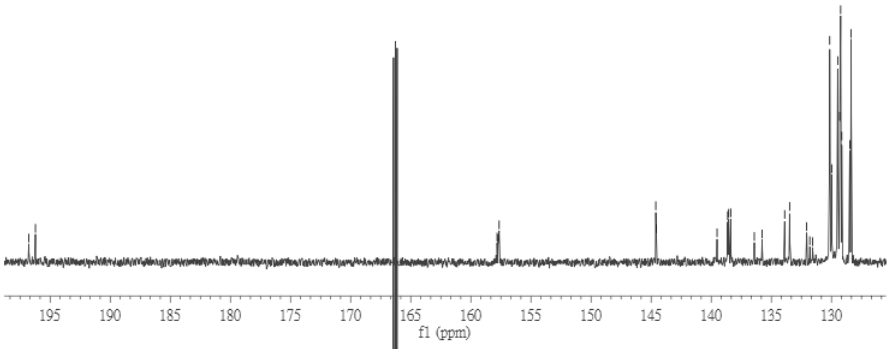


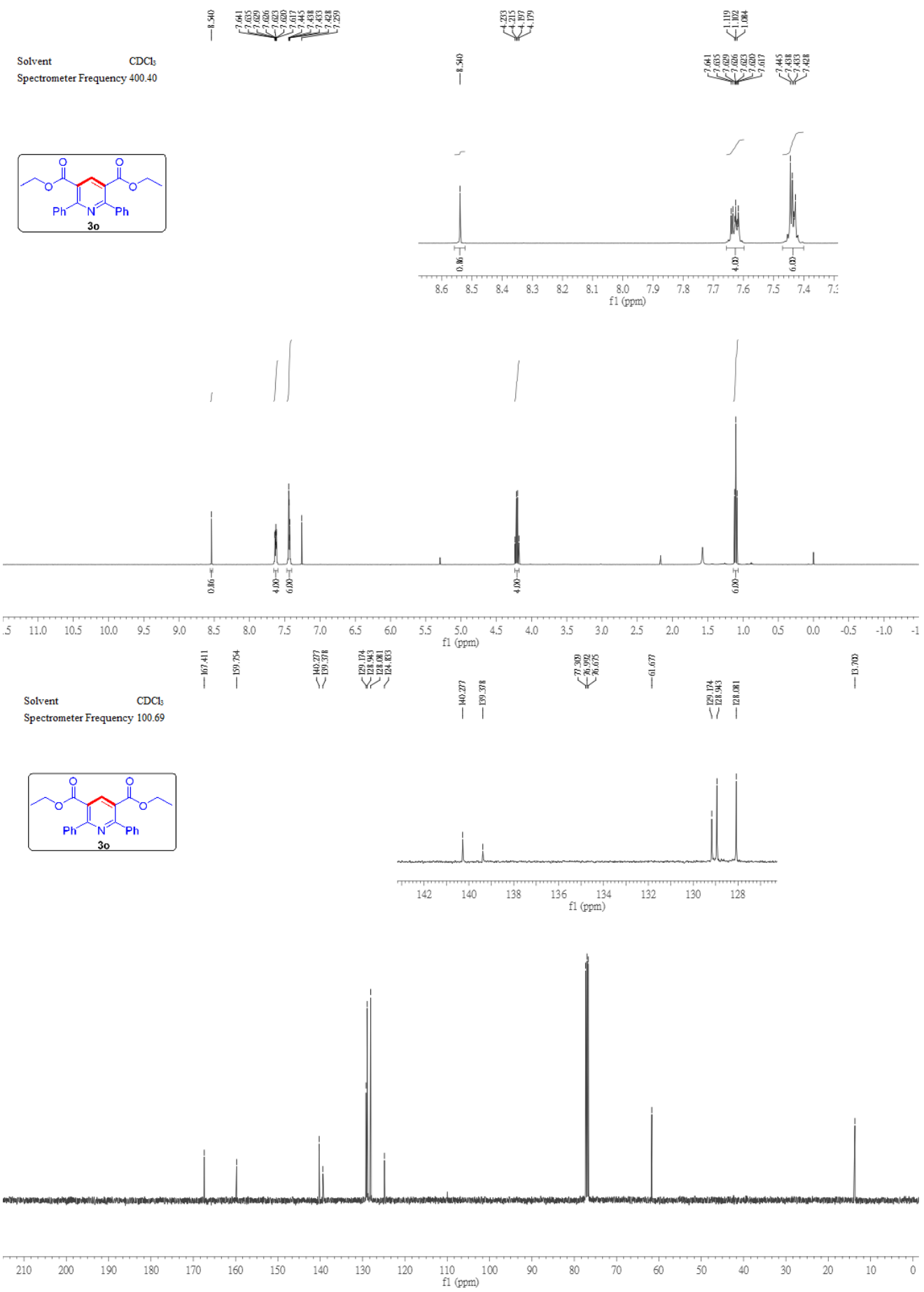


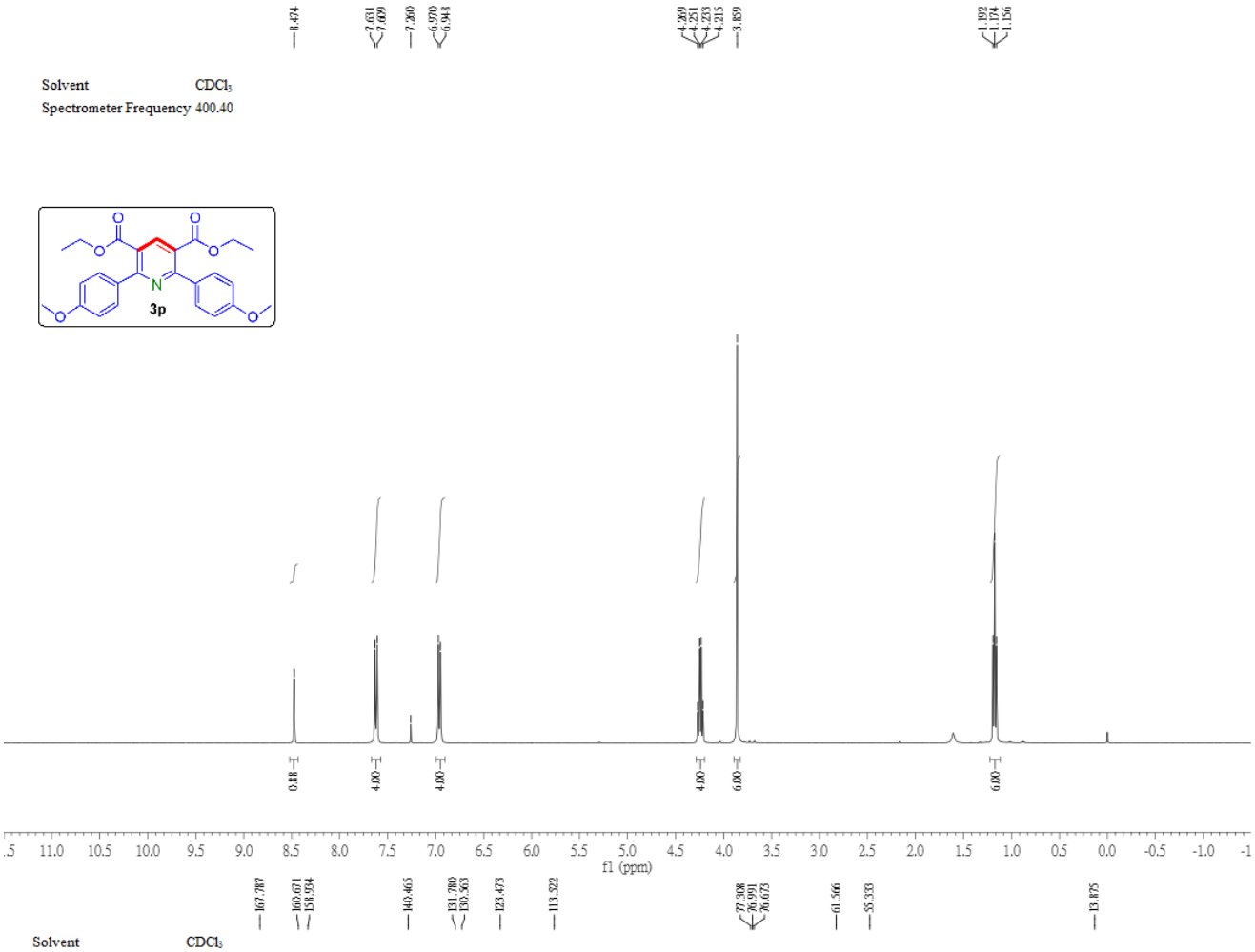


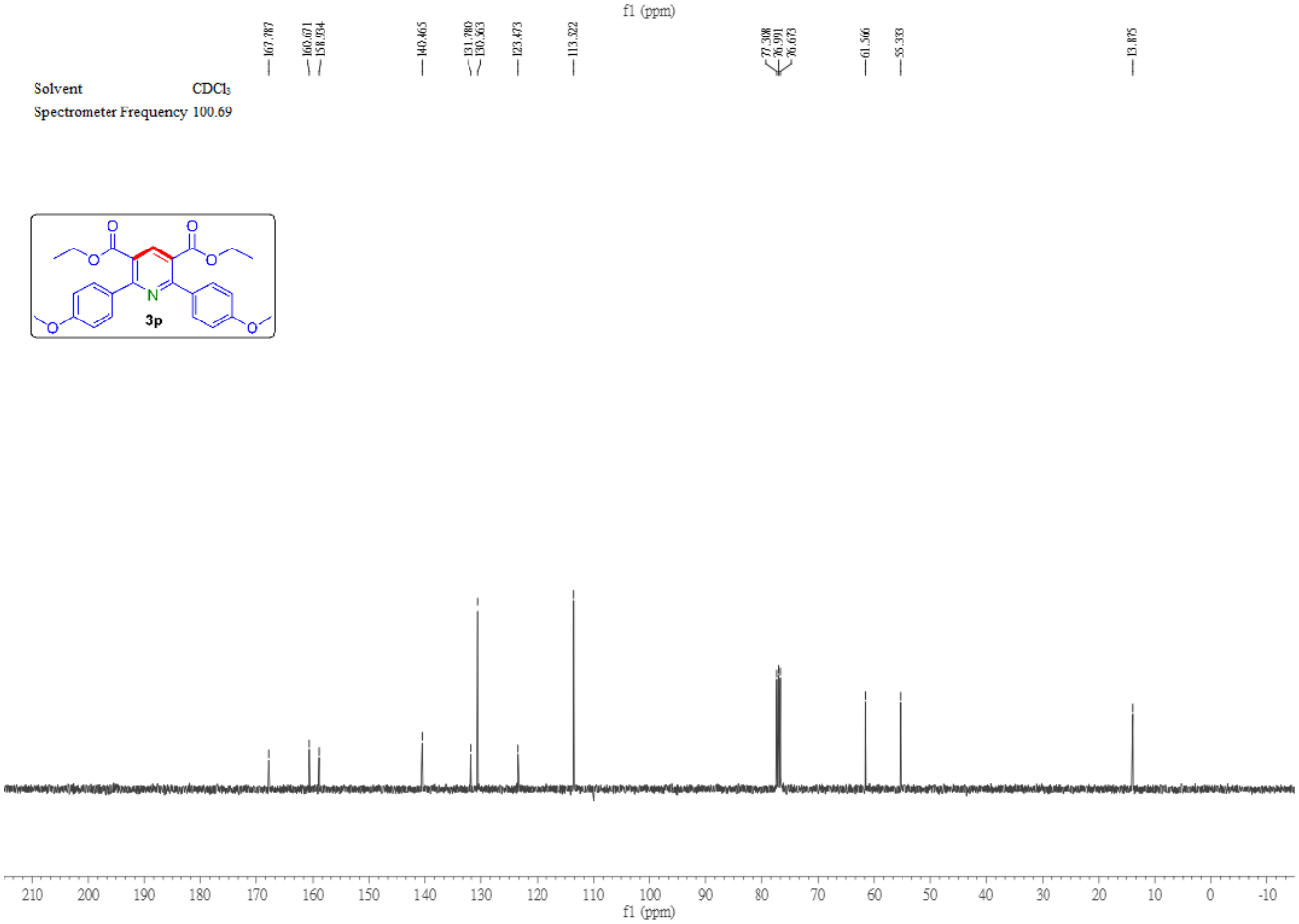
Solvent $CDCl_3$
Spectrometer Frequency 100.69
Nucleus ^{13}C

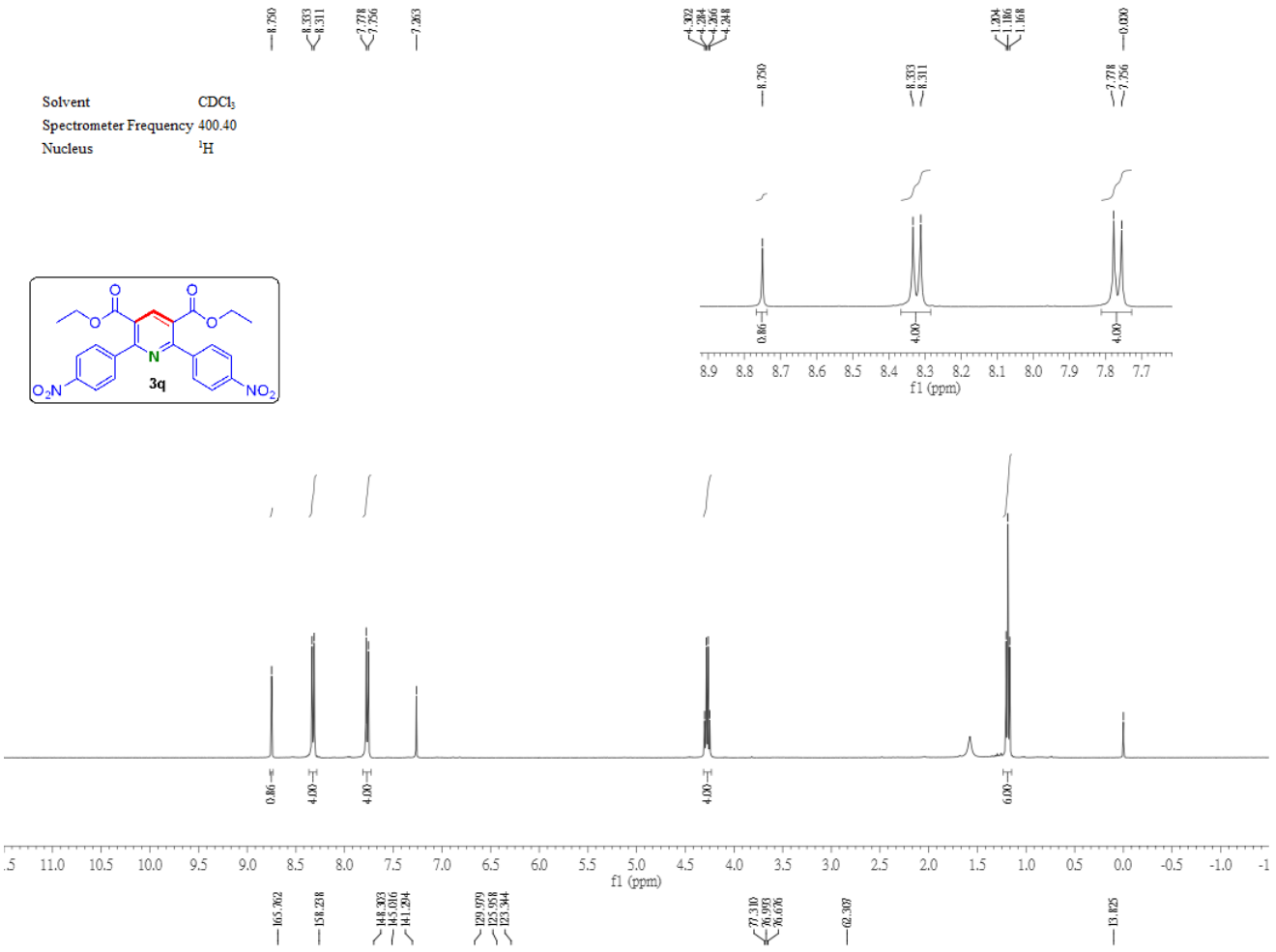


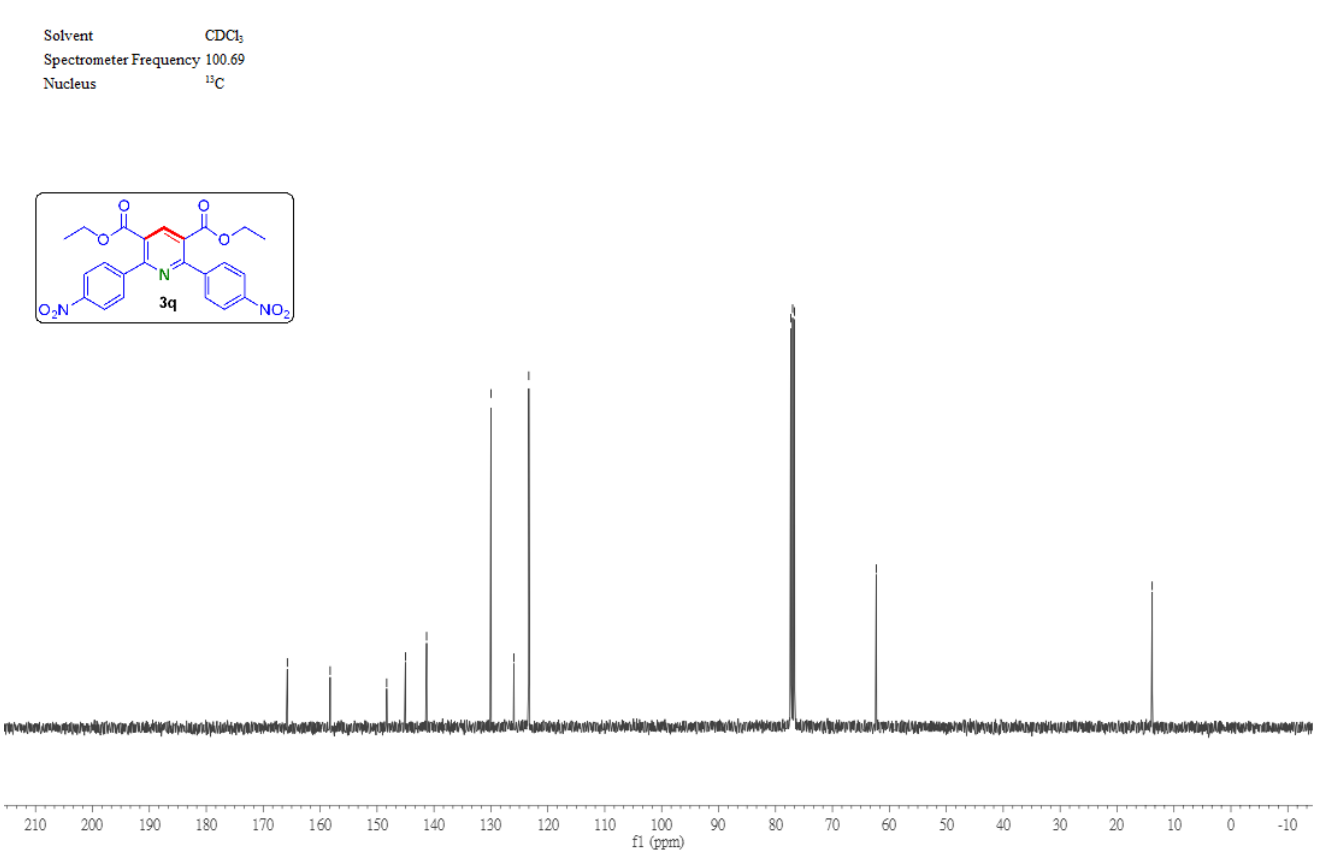


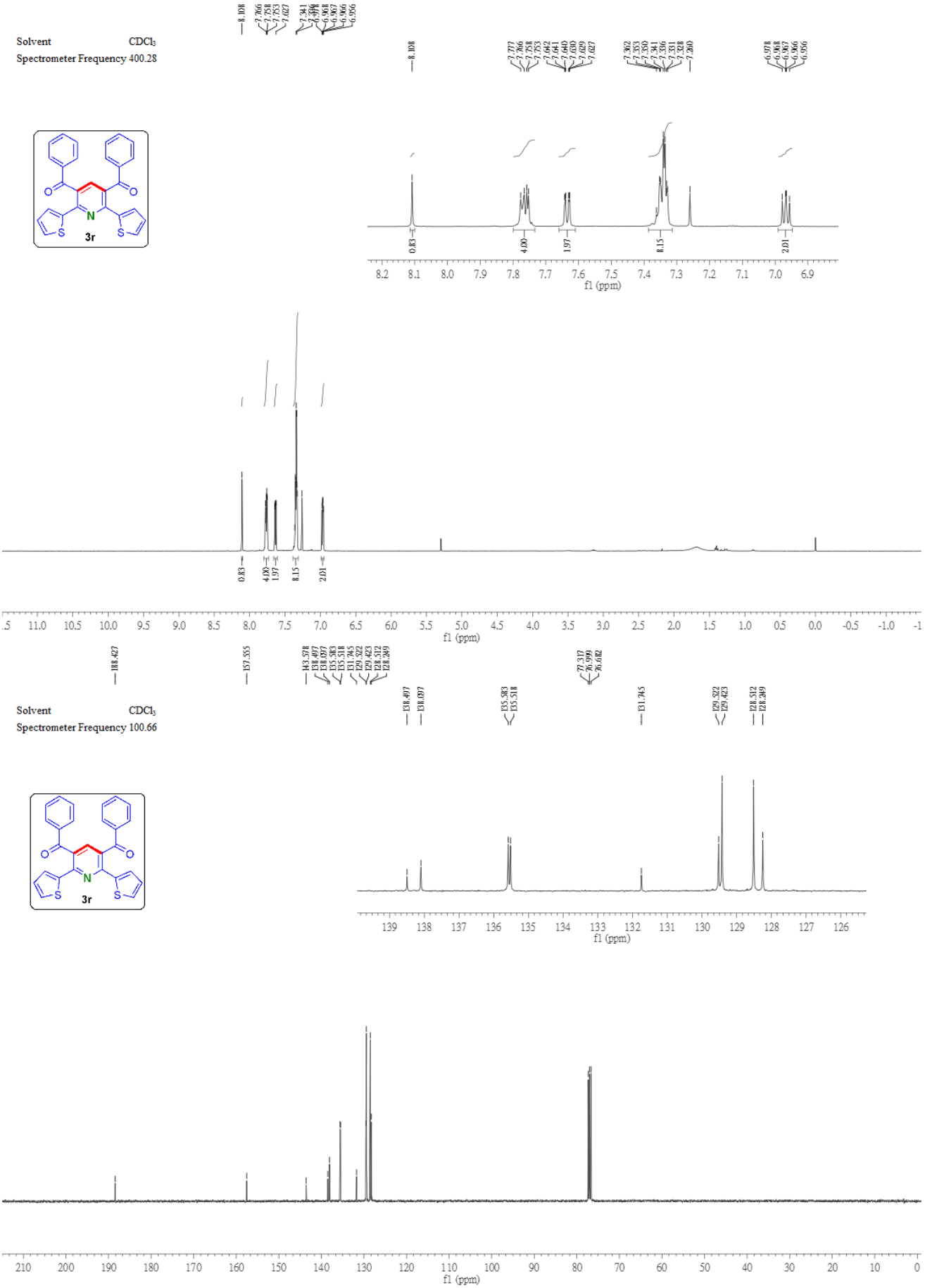

Solvent CDCl3
Spectrometer Frequency 400.40
3o
f1 (ppm)
Solvent CDCl3
Spectrometer Frequency 100.69
3o
f1 (ppm)
f1 (ppm)


8.494
7.631
7.609
7.360
6.970
6.948
4.369
4.251
4.233
4.215
3.859
1.192
1.174
1.156
Solvent CDCl3
Spectrometer Frequency 400.40
3p
0.88
4.00
4.00
4.00
6.00
6.00
f1 (ppm)

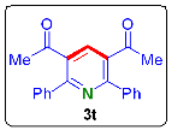

167.787
160.671
158.934
140.465
131.780
130.363
123.473
113.522
77.308
76.991
76.673
61.566
55.333
13.875
Solvent CDCl3
Spectrometer Frequency 100.69
3p
f1 (ppm)


8.750
8.333
8.311
7.778
7.756
7.263
4.302
4.284
4.266
4.248
1.204
1.186
1.168
0.000
Solvent CDCl3
Spectrometer Frequency 400.40
Nucleus 1H
3q
0.86
4.00
4.00
4.00
6.00
f1 (ppm)

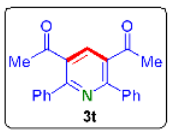

165.762
158.238
148.393
145.096
141.294
129.979
125.958
123.344
77.310
76.993
76.676
62.307
13.825
Solvent CDCl3
Spectrometer Frequency 100.69
Nucleus 13C
3q
f1 (ppm)

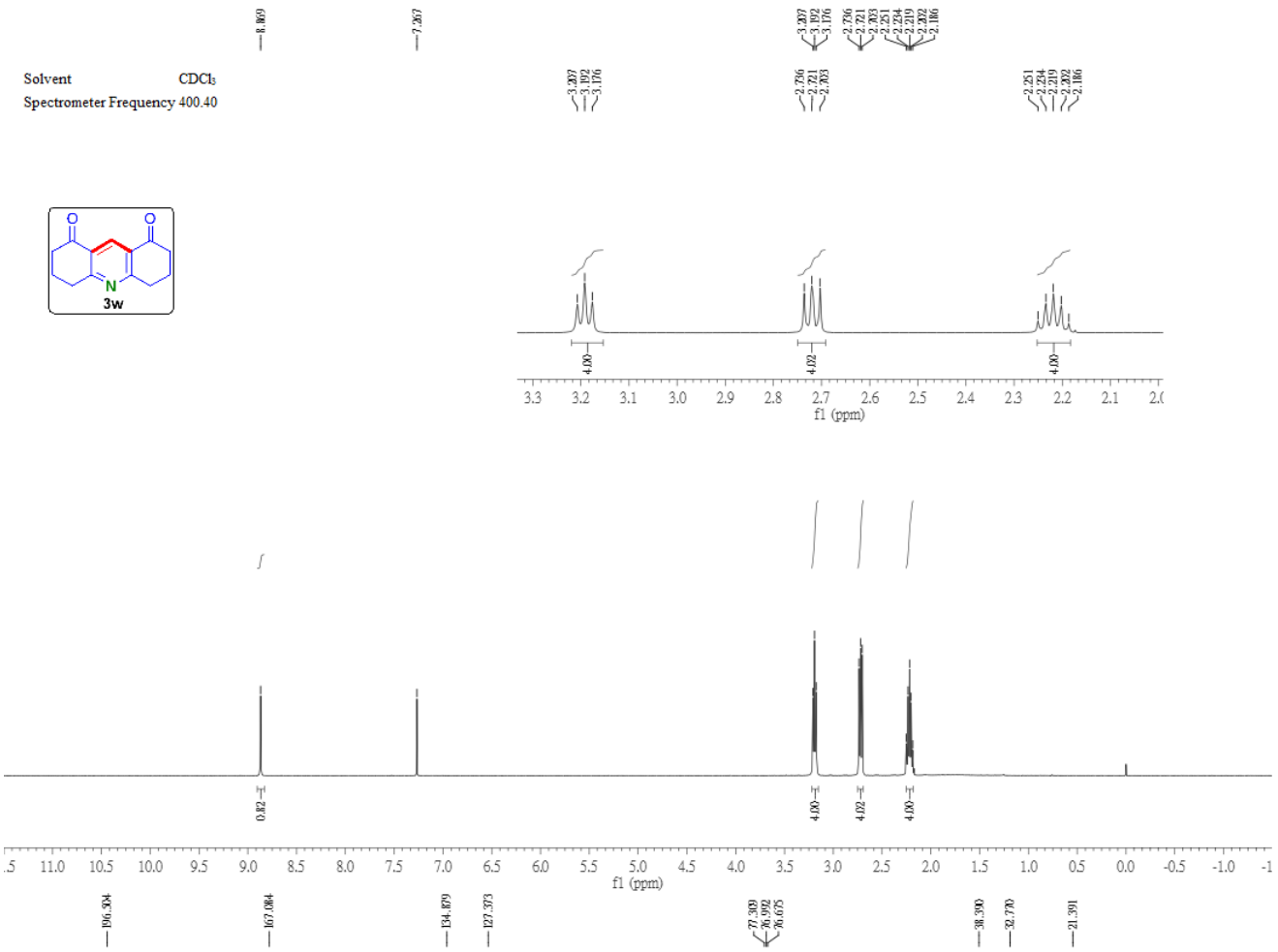

Solvent CDCl3
Spectrometer Frequency 400.28
3r
f1 (ppm)
Solvent CDCl3
Spectrometer Frequency 100.66
3r
f1 (ppm)

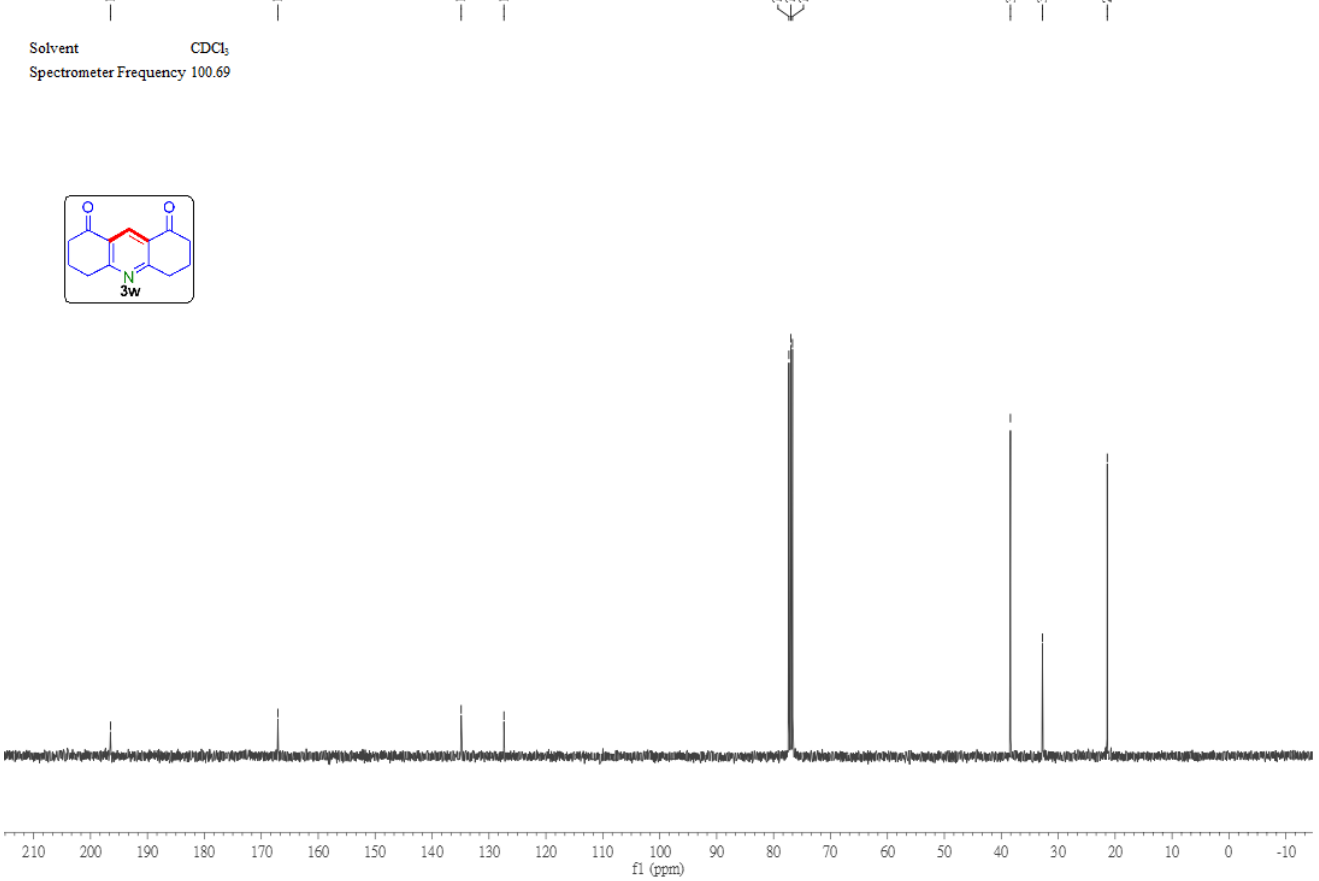
Solvent $CDCl_3$
Spectrometer Frequency 400.28
Nucleus ^1H

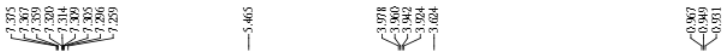


Solvent $CDCl_3$
Spectrometer Frequency 100.66
Nucleus ^{13}C

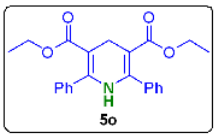


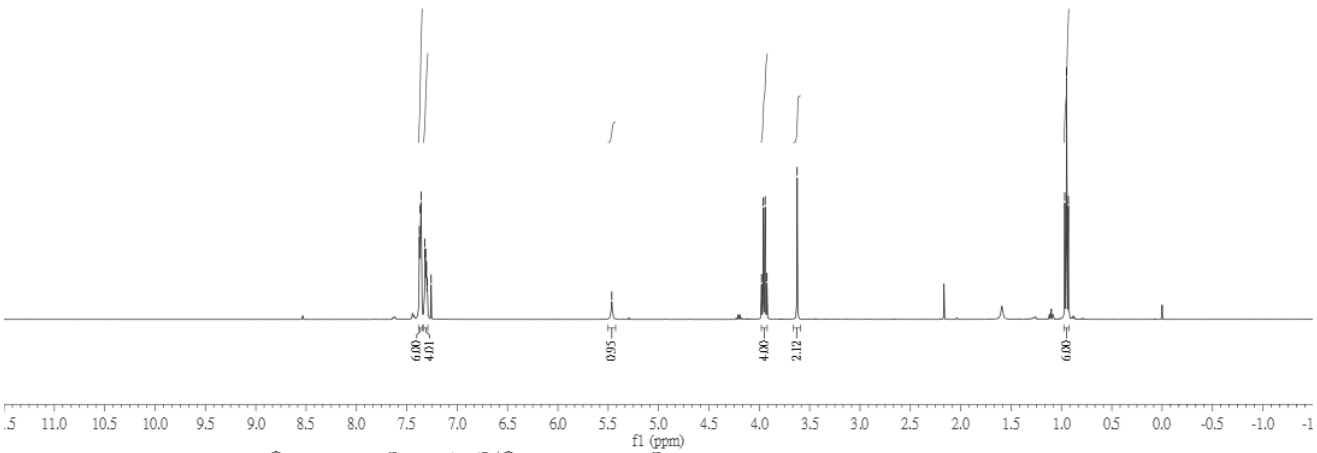

8.869
7.267
3.207
3.192
3.176
2.736
2.721
2.703
2.251
2.234
2.219
2.202
2.186
Solvent CDCl3
Spectrometer Frequency 400.40
3w
4.00
4.02
4.00
f1 (ppm)
0.82
4.00
4.02
4.00
f1 (ppm)

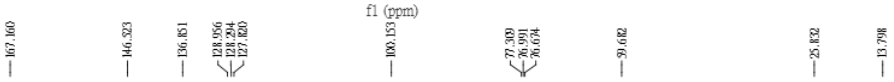

196.504
167.084
134.879
127.373
77.309
76.992
76.675
38.390
32.770
21.391
Solvent CDCl3
Spectrometer Frequency 100.69
3w
f1 (ppm)



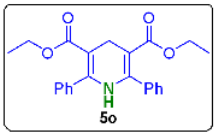
Solvent $CDCl_3$
Spectrometer Frequency 400.40
Nucleus ^1H

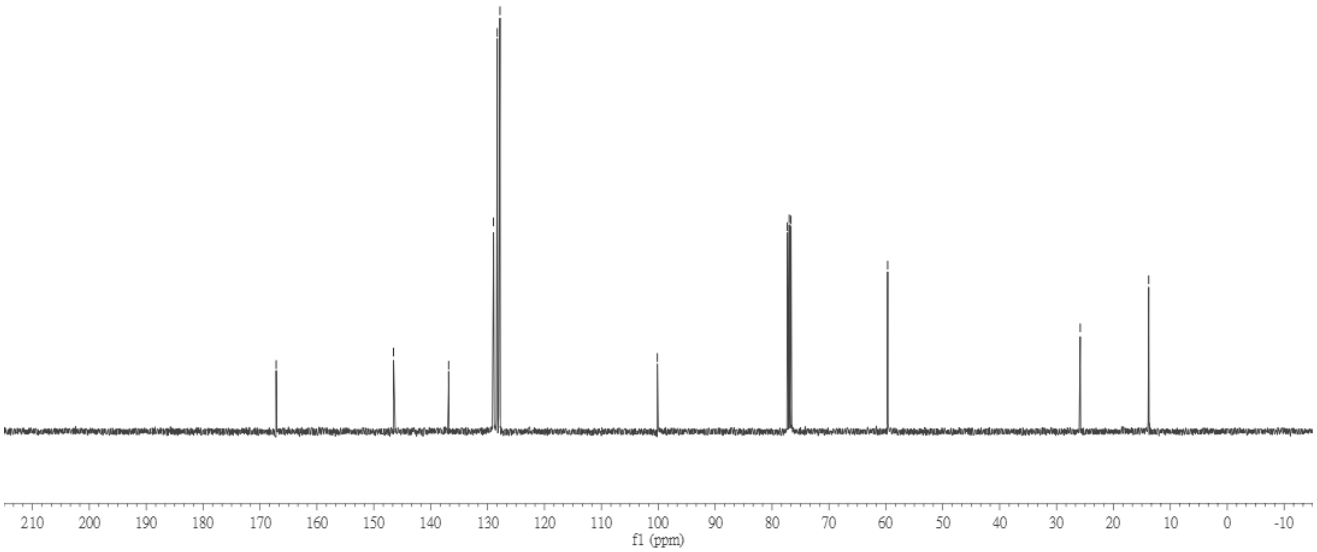




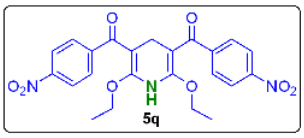


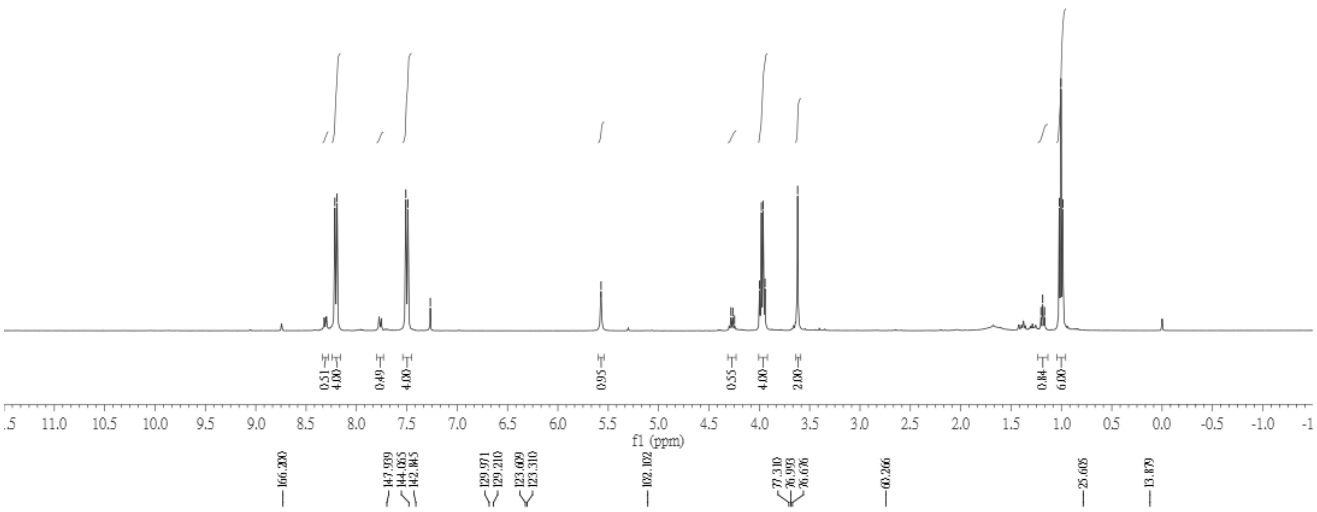
Solvent $CDCl_3$
Spectrometer Frequency 100.69
Nucleus ^{13}C



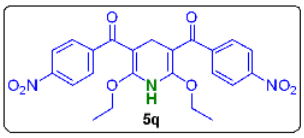


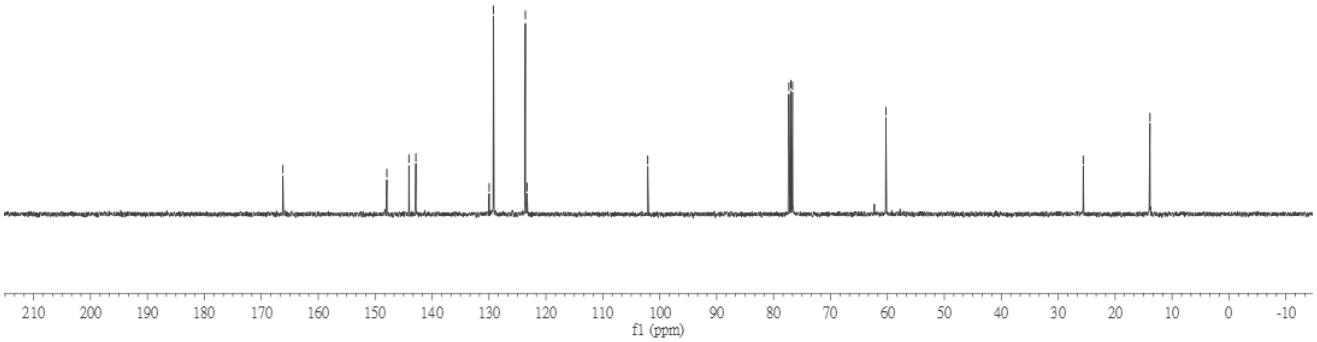
Solvent $CDCl_3$
Spectrometer Frequency 400.40
Nucleus ^1H

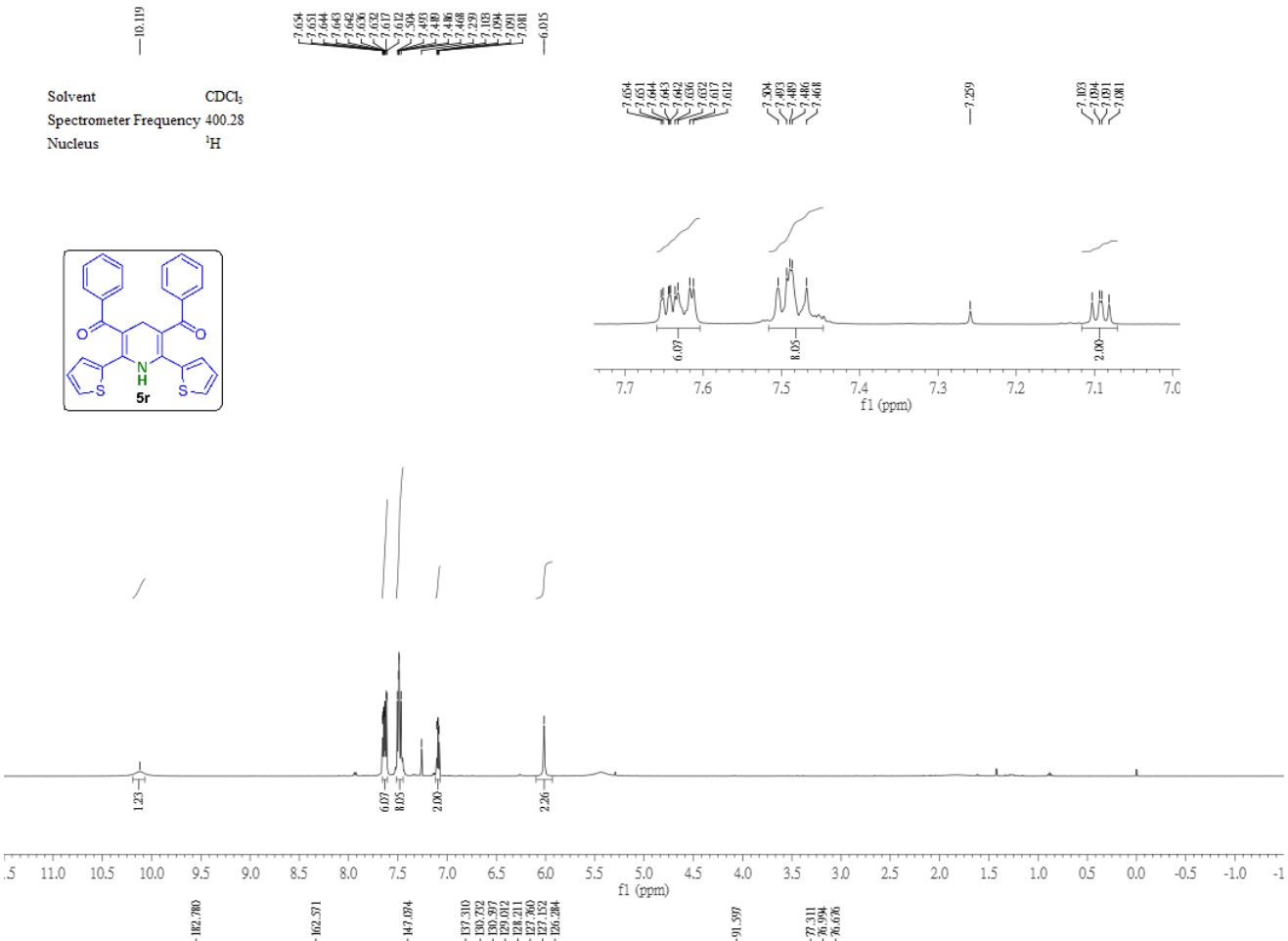


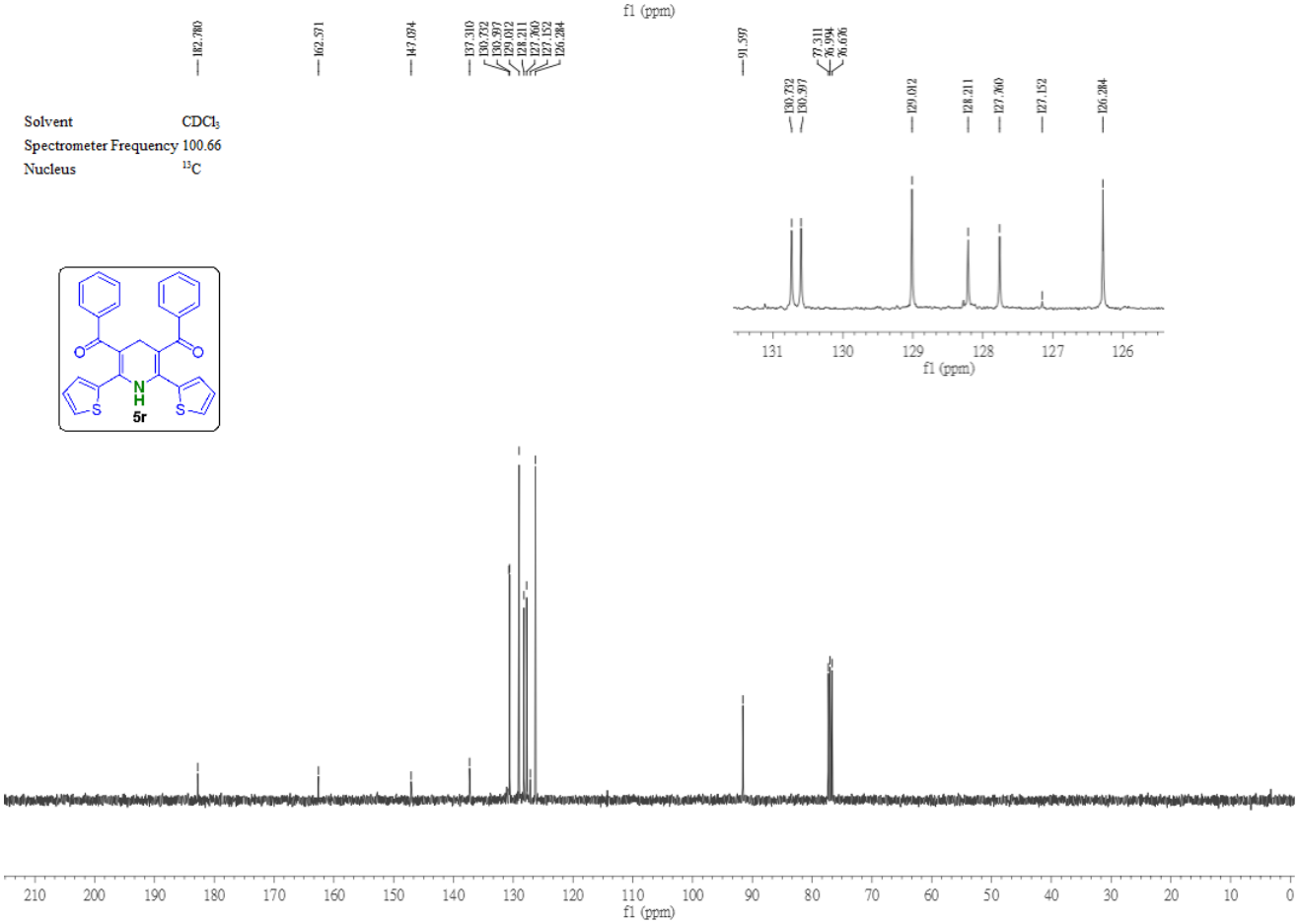


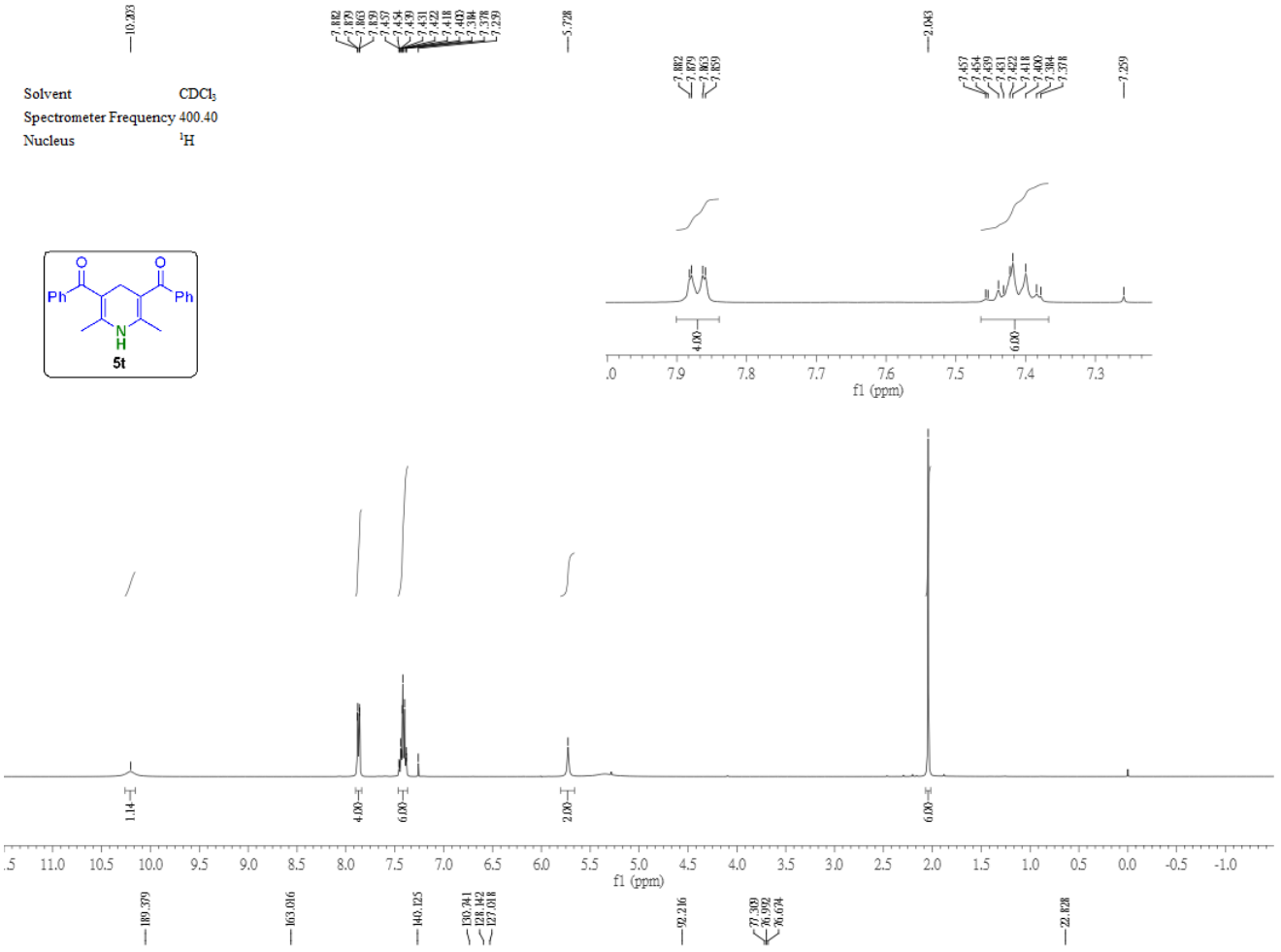
Solvent $CDCl_3$
Spectrometer Frequency 100.69
Nucleus ^{13}C

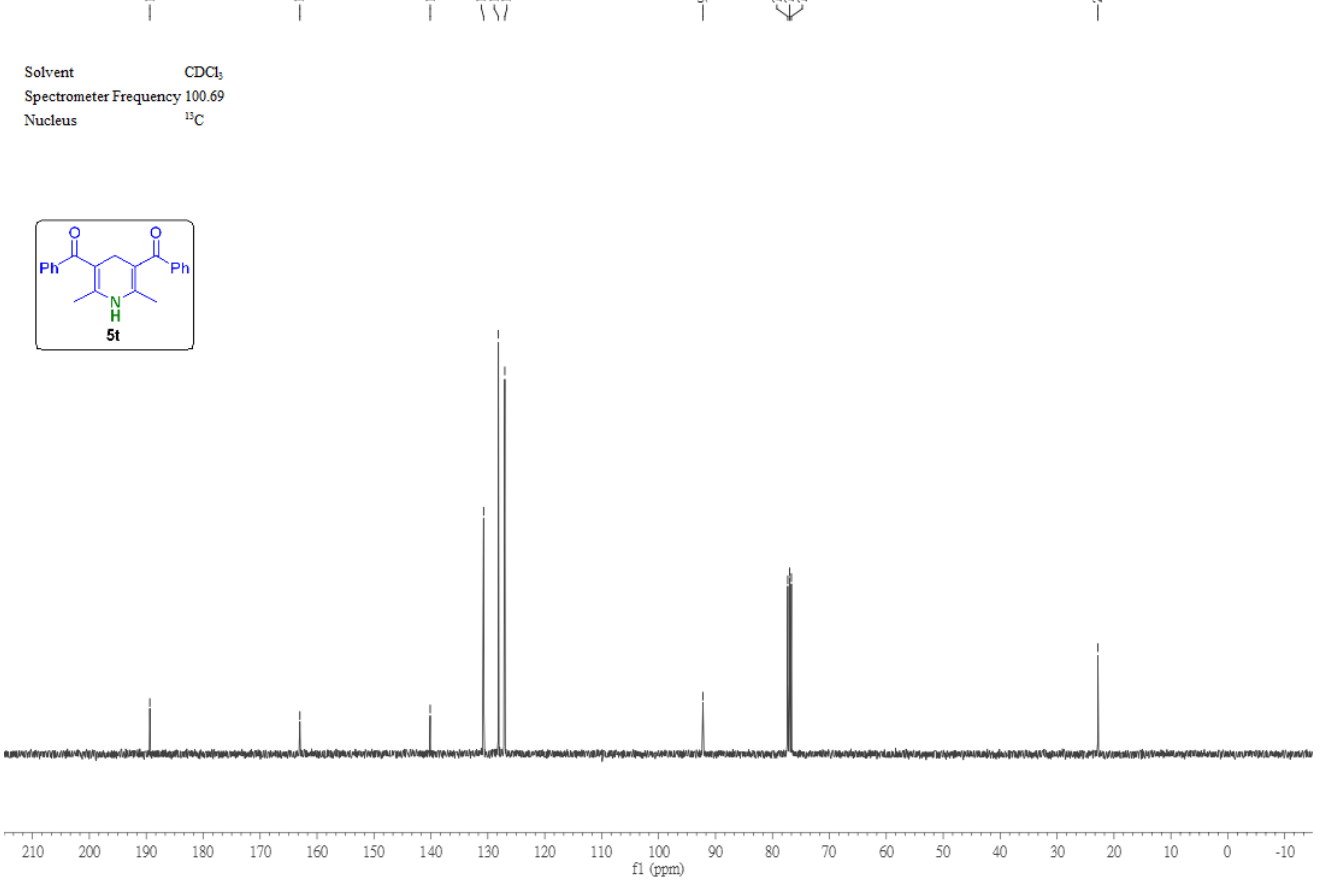


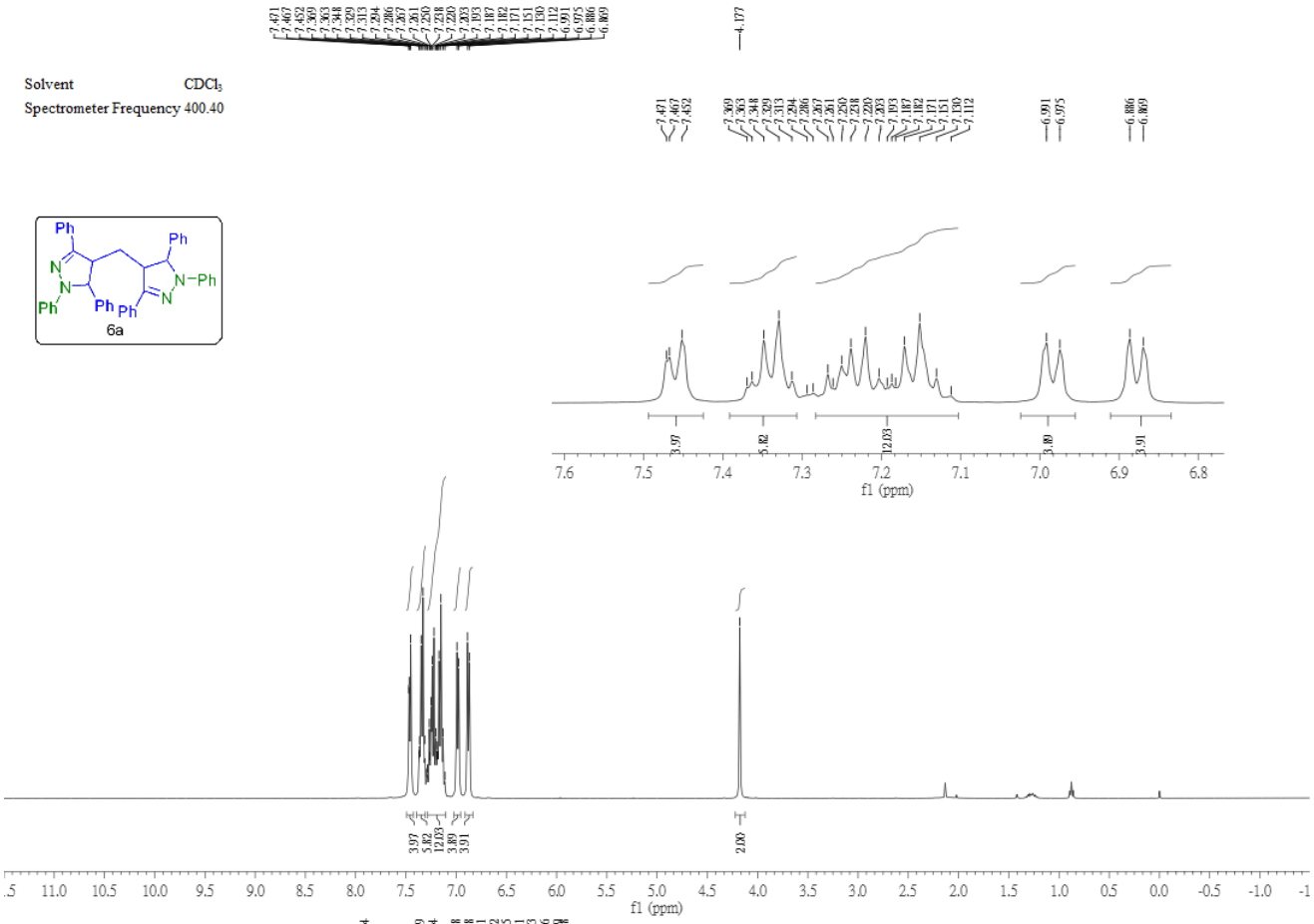


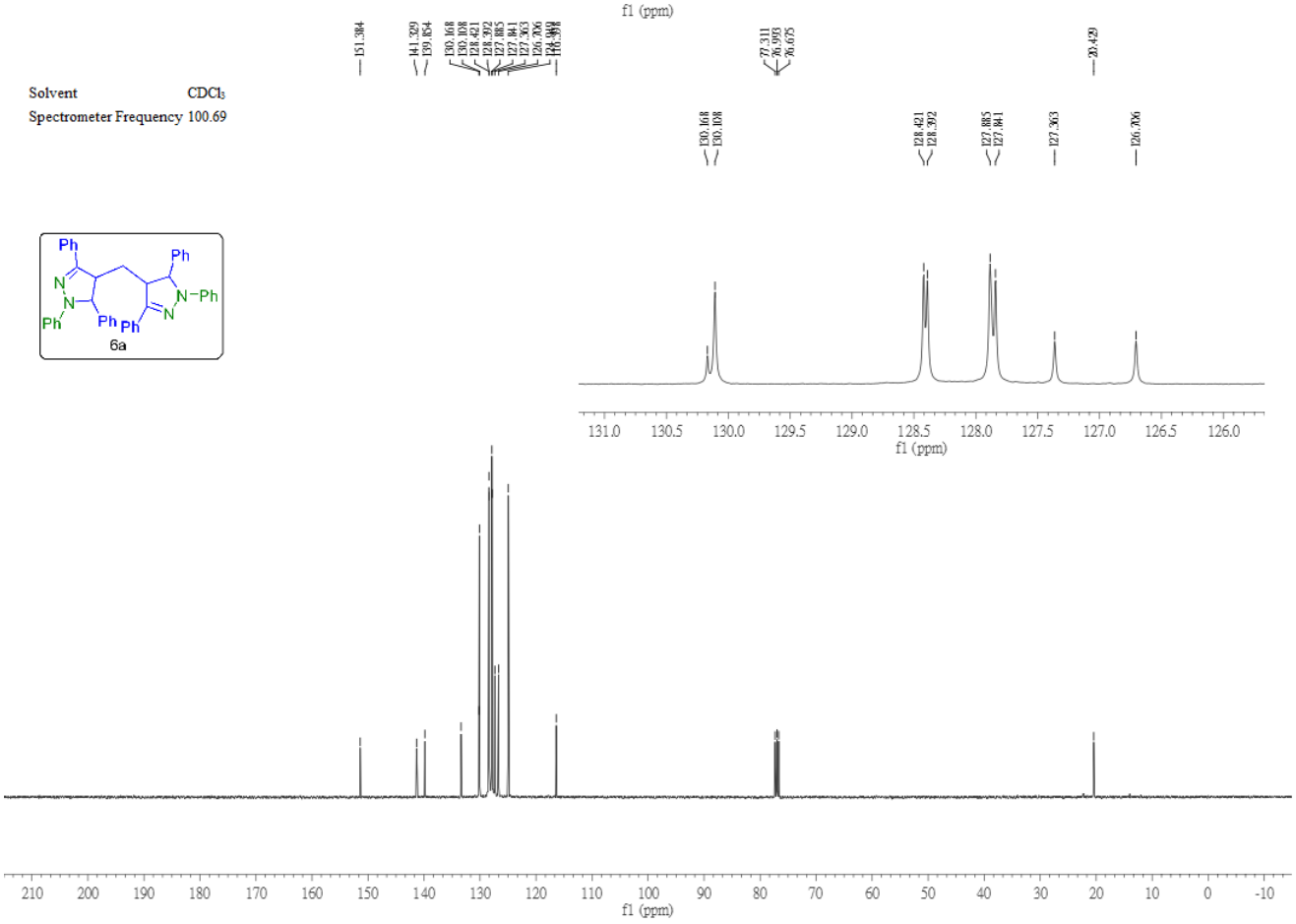

10.119
7.654
7.651
7.644
7.643
7.642
7.636
7.632
7.617
7.612
7.504
7.495
7.489
7.486
7.468
7.239
7.103
7.094
7.091
7.081
6.035
Solvent CDCl3
Spectrometer Frequency 400.28
Nucleus 1H
5r
6.07
8.05
2.00
f1 (ppm)
1.23
2.26


182.780
162.571
147.034
137.310
130.732
130.597
129.012
128.211
127.760
127.152
126.284
91.597
77.311
76.994
76.676
Solvent CDCl3
Spectrometer Frequency 100.66
Nucleus 13C
5r
f1 (ppm)


10.203
7.882
7.879
7.863
7.859
7.457
7.454
7.439
7.431
7.422
7.418
7.400
7.384
7.378
7.239
5.728
2.043
7.259
Solvent CDCl3
Spectrometer Frequency 400.40
Nucleus 1H
Ph
Ph
N
H
5t
4.00
6.00
f1 (ppm)
1.14
4.00
6.00
2.00
6.00
f1 (ppm)


189.379
163.016
140.125
130.941
128.142
127.018
92.216
77.309
76.992
76.674
22.828
Solvent CDCl3
Spectrometer Frequency 100.69
Nucleus 13C
Ph
Ph
N
H
5t
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 400.40
6a
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 100.69
6a
f1 (ppm)

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) I

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: I

Bond precision: C-C = 0.0065 A Wavelength=0.71073

Cell: a=7.8605(5) b=11.7131(10) c=13.7225(7)
alpha=90 beta=94.580(5) gamma=90
Temperature: 143 K

	Calculated	Reported
Volume	1259.41(15)	1259.41(15)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C31 H22 F2 O4	C31 H22 F2 O4
Sum formula	C31 H22 F2 O4	C31 H22 F2 O4
Mr	496.49	496.48
Dx,g cm-3	1.309	1.309
Z	2	2
Mu (mm-1)	0.096	0.096
F000	516.0	516.0
F000'	516.30	
h,k,lmax	9,13,16	9,13,16
Nref	4435[2338]	4297
Tmin,Tmax		0.726,1.000
Tmin'		

Correction method= # Reported T Limits: Tmin=0.726 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.84/0.97 Theta(max)= 24.997

R(reflections)= 0.0534(3603) wR2(reflections)= 0.1473(4297)

S = 1.011 Npar= 336

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
DIFMX02_ALERT_1_C  The maximum difference density is > 0.1*ZMAX*0.75
           The relevant atom site should be identified.
STRVA01_ALERT_4_C           Flack parameter is too small
           From the CIF: _refine_ls_abs_structure_Flack   -0.700
           From the CIF: _refine_ls_abs_structure_Flack_su    1.400
PLAT053_ALERT_1_C Minimum Crystal Dimension Missing (or Error) ...     Please Check
PLAT054_ALERT_1_C Medium  Crystal Dimension Missing (or Error) ...     Please Check
PLAT089_ALERT_3_C Poor Data / Parameter Ratio (Zmax < 18) ........       6.90 Note
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....       3.56 Report
PLAT097_ALERT_2_C Large Reported Max.  (Positive) Residual Density       0.85 eA-3
PLAT230_ALERT_2_C Hirshfeld Test Diff for    F2       --C22      .        5.2 s.u.
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............     0.0065 Ang.
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.595         21 Report
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         37 Report
PLAT032_ALERT_4_G Std. Uncertainty on Flack Parameter Value High .      1.400 Report
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large       0.10 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          1 Report
PLAT791_ALERT_4_G Model has Chirality at C2          (Sohnke SpGr)          S Verify
PLAT791_ALERT_4_G Model has Chirality at C17         (Sohnke SpGr)          R Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............        955 Note
PLAT870_ALERT_4_G ALERTS Related to Twinning Effects Suppressed ..          ! Info
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        55% Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          1 Note
PLAT916_ALERT_2_G Hooft y and Flack x Parameter Values Differ by .       0.30 Check
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...         34 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
  10 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  12 ALERT level G = General information/check it is not something unexpected

   3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   7 ALERT type 2 Indicator that the structure model may be wrong or deficient
   6 ALERT type 3 Indicator that the structure quality may be low
   6 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

checkCIF publication errors

Alert level A

```
PUBL004_ALERT_1_A  The contact author's name and address are missing,
           _publ_contact_author_name and _publ_contact_author_address.
PUBL005_ALERT_1_A  _publ_contact_author_email, _publ_contact_author_fax and
           _publ_contact_author_phone are all missing.
           At least one of these should be present.
PUBL006_ALERT_1_A  _publ_requested_journal is missing
           e.g. 'Acta Crystallographica Section C'
PUBL008_ALERT_1_A  _publ_section_title is missing. Title of paper.
PUBL009_ALERT_1_A  _publ_author_name is missing. List of author(s) name(s).
PUBL010_ALERT_1_A  _publ_author_address is missing. Author(s) address(es).
```

```
PUBL012_ALERT_1_A  _publ_section_abstract is missing.
            Abstract of paper in English.
```

```
   7 ALERT level A = Data missing that is essential or data in wrong format
   0 ALERT level G = General alerts. Data that may be required is missing
```

Publication of your CIF

You should attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the nature of your study may justify the reported deviations from journal submission requirements and the more serious of these should be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. *checkCIF* was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

If level A alerts remain, which you believe to be justified deviations, and you intend to submit this CIF for publication in a journal, you should additionally insert an explanation in your CIF using the Validation Reply Form (VRF) below. This will allow your explanation to be considered as part of the review process.

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

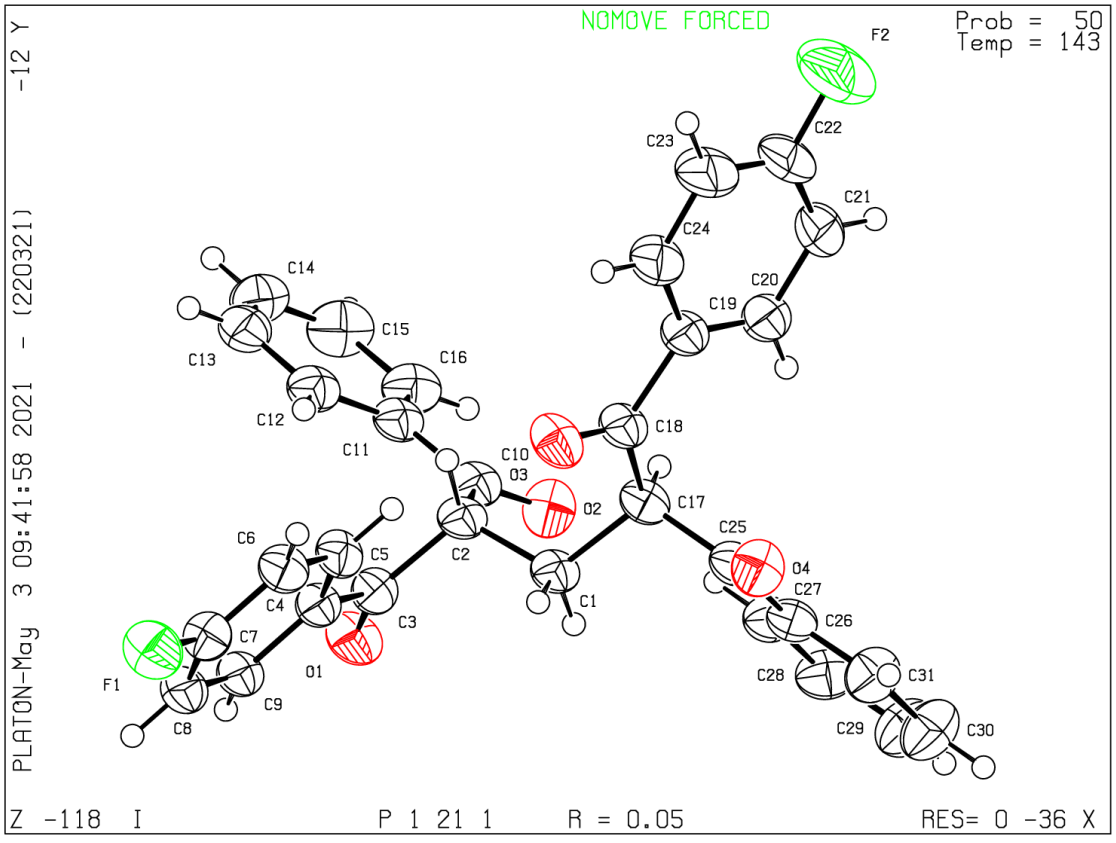
```
# start Validation Reply Form
_vrf_PUBL004_GLOBAL
;
PROBLEM: The contact author’s name and address are missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;
_vrf_PUBL009_GLOBAL
;
PROBLEM: _publ_author_name is missing. List of author(s) name(s).
RESPONSE: ...
;
```

```
_vrf_PUBL010_GLOBAL
;
PROBLEM: _publ_author_address is missing. Author(s) address(es).
RESPONSE: ...
;
_vrf_PUBL012_GLOBAL
;
PROBLEM: _publ_section_abstract is missing.
RESPONSE: ...
;
# end Validation Reply Form
```

If you wish to submit your CIF for publication in Acta Crystallographica Section C or E, you should upload your CIF via the web. If you wish to submit your CIF for publication in IUCrData you should upload your CIF via the web. If your CIF is to form part of a submission to another IUCr journal, you will be asked, either during electronic submission or by the Co-editor handling your paper, to upload your CIF via our web site.

PLATON version of 22/03/2021; check.def file version of 19/03/2021

Datablock I - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) I

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: I

Bond precision: C-C = 0.0016 A Wavelength=0.71073

Cell: a=5.9854(1) b=20.6879(4) c=18.0213(3)
alpha=90 beta=95.780(2) gamma=90
Temperature: 113 K

	Calculated	Reported
Volume	2220.15(7)	2220.15(7)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C31 H21 N O2	C31 H21 N O2
Sum formula	C31 H21 N O2	C31 H21 N O2
Mr	439.49	439.49
Dx,g cm-3	1.315	1.315
Z	4	4
Mu (mm-1)	0.082	0.082
F000	920.0	920.0
F000'	920.39	
h,k,lmax	7,26,23	7,26,22
Nref	4878	4684
Tmin,Tmax	0.976,0.976	0.808,1.000
Tmin'	0.976	

Correction method= # Reported T Limits: Tmin=0.808 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.960 Theta(max)= 27.035

R(reflections)= 0.0358(4037) wR2(reflections)= 0.0935(4684)

S = 1.067 Npar= 307

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level G

PLAT910_ALERT_3_G	Missing # of FCF Reflection(s) Below Theta(Min).	1 Note
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L= 0.600	191 Note
PLAT933_ALERT_2_G	Number of OMIT Records in Embedded .res File ...	3 Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	21 Info

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0 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
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2 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

checkCIF publication errors

Alert level A

PUBL004_ALERT_1_A The contact author's name and address are missing,
_publ_contact_author_name and _publ_contact_author_address.
PUBL005_ALERT_1_A _publ_contact_author_email, _publ_contact_author_fax and
_publ_contact_author_phone are all missing.
At least one of these should be present.
PUBL006_ALERT_1_A _publ_requested_journal is missing
e.g. 'Acta Crystallographica Section C'
PUBL008_ALERT_1_A _publ_section_title is missing. Title of paper.
PUBL009_ALERT_1_A _publ_author_name is missing. List of author(s) name(s).
PUBL010_ALERT_1_A _publ_author_address is missing. Author(s) address(es).
PUBL012_ALERT_1_A _publ_section_abstract is missing.
Abstract of paper in English.

7 **ALERT level A** = Data missing that is essential or data in wrong format
0 **ALERT level G** = General alerts. Data that may be required is missing

Publication of your CIF

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```
# start Validation Reply Form
_vrf_PUBL004_GLOBAL
;
PROBLEM: The contact author’s name and address are missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;
_vrf_PUBL009_GLOBAL
;
PROBLEM: _publ_author_name is missing. List of author(s) name(s).
RESPONSE: ...
;
_vrf_PUBL010_GLOBAL
;
PROBLEM: _publ_author_address is missing. Author(s) address(es).
RESPONSE: ...
;
_vrf_PUBL012_GLOBAL
;
```

```
PROBLEM: _publ_section_abstract is missing.
RESPONSE: ...
;
# end Validation Reply Form
```

If you wish to submit your CIF for publication in Acta Crystallographica Section C or E, you should upload your CIF via the web. If you wish to submit your CIF for publication in IUCrData you should upload your CIF via the web. If your CIF is to form part of a submission to another IUCr journal, you will be asked, either during electronic submission or by the Co-editor handling your paper, to upload your CIF via our web site.

PLATON version of 22/03/2021; check.def file version of 19/03/2021

Datablock I - ellipsoid plot