Supporting Information

A Convenient Proline Catalysed Paal-Knorr Synthesis of Highly Substituted Pyrrole: Construction of Pyrrolo[2,1-a]isoquinoline scaffold

Pooja Sivaganesan,[a] Chibisree Elanchezhian,[a] Diksha Bansal,[a] Jit Sarkar,[b,c] and Saikat Chaudhuri*[a,b]

[a]Organic and Bio-Organic Chemistry laboratory, CSIR-CLRI, Chennai-600020, India

[b]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India

[c]Polymer Science and Technology Unit, Advanced Material Laboratory, CSIR-CLRI, Chennai-600020, India

e-mail: schaudhuri@clri.res.in

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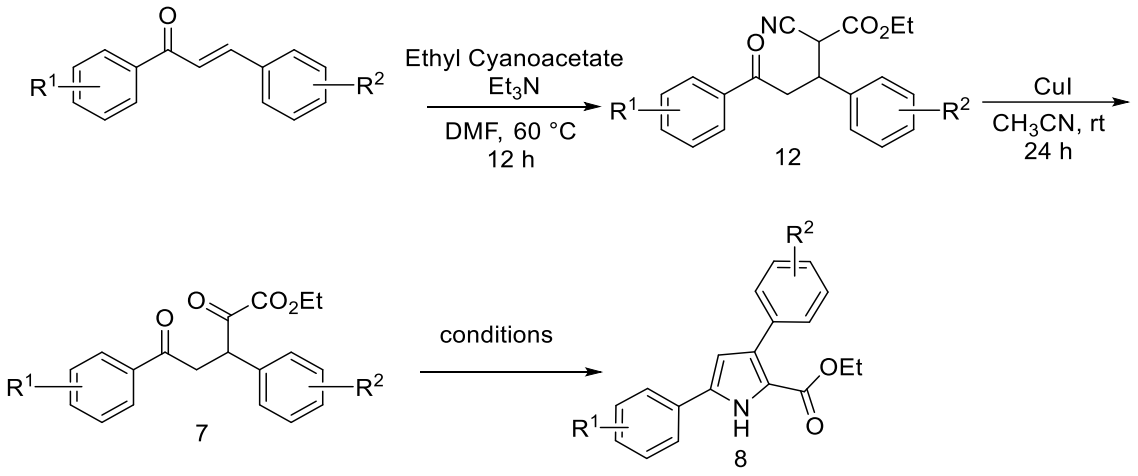
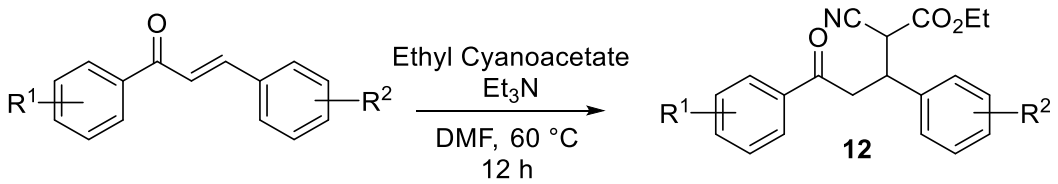
Materials and Methods

Unless otherwise stated, reactions were performed in oven-dried glassware fitted with rubber septa under a nitrogen atmosphere and were stirred with Teflon-coated magnetic stirring bars. Liquid reagents and solvents were transferred *via* syringe using standard Schlenk techniques. Thin layer chromatography was performed using Merck Silicagel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation. Silicagel (particle size 100-200 mesh) was used for flash chromatography. ^{1}H and ^{13}C NMR spectra were recorded 400 MHz spectrometers with ^{13}C operating frequencies of 100 MHz respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal (δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR). Data for ^{1}H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, and number of hydrogen). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). High-resolution mass spectrometry (HRMS) data were recorded on MicrOTOF-Q-II mass spectrometer using methanol as solvent. High resolution mass spectra and NMR data were obtained from the at the CATERS department CSIR-Central Leather Research Institute.

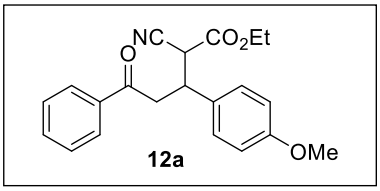
General Scheme for the Synthesis of Pyrrole



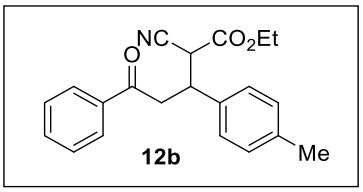
General experimental approach for the Construction of Ethyl 2-cyano-5-oxo-3,5-diphenylpentanoate derivative:



In a round bottom flask chalcone (4.0 mmol; 1.0 equivalence) and ethyl cyano acetate (6.0 mmol; 1.5 equivalence) was solvated in 5 mL of DMF. The procedure began by adding triethylamine (16.0 mmol; 4.0 equivalents) into solution. The whole reaction setup was placed in a stirrer containing heated oil and made to stay at 65 ºC while heating continued for 16 hours end point being the full consumption of chalcone. The termination of reaction, that was validated with the aid of TLC showing absolute starting material consumption. The organic layer after separation was separated using a separation funnel and subsequently extracted with aid of water, dried over anhydrous sodium sulphate, and purified using vacuum pump. The products were then purified via chromatography using column using a mixture of Hexane and EtOAc to obtain the inseparable diastereomer **12**.

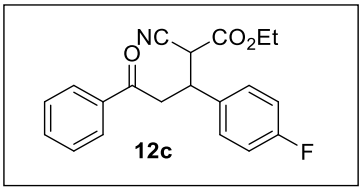


ethyl 2-cyano-3,5-bis(4-methoxyphenyl)-5-oxopentanoate (12a): 1.24g (88% yield). The product was obtained as orange gel, dr = 1:1.6 (observed from the unpurified mixture) $R_{f=}$ 0.42 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) data of inseparable diastereomeric mixture spectrum of **4a**, δ: 7.97-7.72 (m, 2H for major dr + 2H for minor dr), 7.59-7.54 (m, 1H for major dr + 1H for minor dr), 7.48-7.42 (m, 2H for major dr + 2H for minor dr), 7.34-7.27 (m, 2H for major dr + 2H for minor dr), 6.87-6.83 (m, 2H for major dr + 2H for minor dr), 4.32 (d, *J* = 5.4 Hz, 1H for major dr), 4.19-4.07 (m, 3H for major dr + 3H for minor dr), 3.88 (d, *J* = 5.4 Hz, 1H for minor dr), 3.77 (s, 3H for major dr), 3.75 (s, 3H for major dr), 3.71-3.63 (m, 1H for major dr + 2H for minor dr), 3.53-3.47 (m, 1H for major dr), 1.20 (t, *J* = 7.3 Hz, 3H for minor dr), 1.14 (t, *J* = 7.3 Hz, 3H for major dr); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ: 197.3, 196.8, 165.32, 165.1, 159.4, 159.2, 136.5, 136.3, 133.7, 133.5, 131.1, 130.4, 129.2, 128.8, 128.8, 128.7, 128.1, 115.9, 115.8, 114.3, 114.2, 62.9, 62.6, 55.2, 44.3, 43.6, 41.8, 40.7, 40.2, 39.4, 13.9, 13.8.



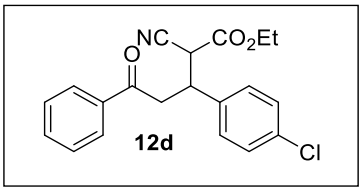
ethyl 2-cyano-5-oxo-5-phenyl-3-(p-tolyl)pentanoate (12b): 1.21g (90% yield). The product was obtained as light Green coloured gel, dr = 1:1.5 (observed from the unpurified mixture) $R_{f=}$ 0.48 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) data of inseparable diastereomeric mixture mixture spectrum of **4b**, δ: 7.98-7.93 (m, 2H for major dr + 2H for minor dr), 7.61-7.55 (m, 1H for major dr + 1H for minor dr), 7.49-7.46 (m, 2H for major dr + 2H for minor dr), 7.31-7.24 (m, 2H for major dr + 2H for minor dr), 7.16-7.12 (m, 2H for major dr + 2H for minor dr) 4.34 (d, *J* = 4.9 Hz, 1H for major dr), 4.21-4.07 (m, 3H for major dr + 3H for minor dr), 3.89 (d, *J* = 5.4 Hz, 1H for minor dr), 3.73-3.65 (m, 1H for major dr + 2H for minor dr), 3.54-3.48 (m, 1H for major dr), 2.32-2.31 (m, 3H for major dr + 3H for minor dr) 1.21 (t, *J* = 6.8 Hz, 3H for minor dr), 1.14 (t, *J* = 7.4 Hz, 3H for major dr); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ: 197.3, 196.7 165.2, 165.1, 137.9, 137.8, 136.5, 136.3, 136.2, 135.3 (2C), 133.7, 133.5, 129.6, 129.5, 128.8, 128.7,

128.1, 127.9, 127.5, 115.8, 115.7, 63.0, 62.6, 44.3, 43.4, 41.7, 40.8, 40.4, 40.0, 21.09, 21.06, 13.86(2C).



12c

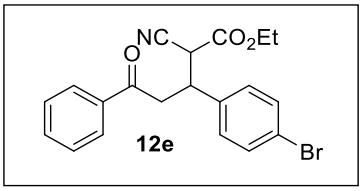
ethyl 2-cyano-3-(4-fluorophenyl)-5-oxo-5-phenylpentanoate (12c): 1.25g (92% yield). The product was obtained as yellow gel, dr = 1:1.6 (observed from the unpurified mixture) R_f = 0.45 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) data of inseparable diastereomeric mixture mixture spectrum of **4c**, δ: 7.98-7.72 (m, 2H for major dr + 2H for minor dr), 7.61-7.56 (m, 1H for major dr + 1H for minor dr), 7.49-7.34 (m, 4H for major dr + 4H for minor dr), 7.05-7.00 (m, 2H for major dr + 2H for minor dr), 4.33 (d, *J* = 5.9 Hz, 1H for major dr), 4.20-4.07 (m, 3H for major dr + 3H for minor dr), 3.89 (d, *J* = 5.9 Hz, 1H for minor dr), 3.71-3.64 (m, 1H for major dr + 2H for minor dr), 3.54-3.48 (m, 1H for major dr), 1.21 (t, *J* = 7.3 Hz, 3H for minor dr), 1.13 (t, *J* = 7.3 Hz, 3H for major dr); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ: 196.9, 196.4, 164.9, 164.8, 161.7, 161.3, 136.2, 134.97, 134.17, 134.3, 133.8, 133.6, 129.9, 129.8, 129.5, 129.4, 128.8, 128.8, 128.6, 128.5, 128.4, 128.1, 127.9, 127.9, 127.8, 116.0, 115.9, 115.8, 115.7, 115.6, 115.5, 63.1, 62.8, 44.07, 43.4, 41.7, 40.6, 40.1, 39.4, 13.9 (2C).



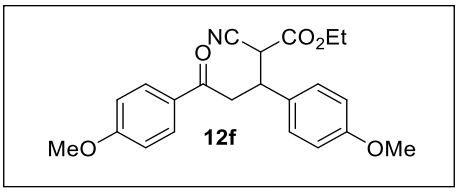
12d

ethyl 3-(4-chlorophenyl)-2-cyano-5-oxo-5-phenylpentanoate (12d): 1.29g (91% yield). The product was obtained as light yellow gel, dr = 1:1.6 (observed from the unpurified mixture) R_f = 0.44 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) data of inseparable diastereomeric mixture mixture spectrum of **4d**, δ: 7.97-7.92 (m, 2H for major dr + 2H for minor dr), 7.62-7.57 (m, 1H for major dr + 1H for minor dr), 7.50-7.45 (m, 2H for major dr + 2H for minor dr), 7.38-7.31 (m, 4H for major dr + 4H for minor dr), 4.33 (d, *J* = 5.5 Hz, 1H for major dr), 4.22-4.09 (m, 3H for major dr + 3H for minor dr), 3.88 (d, *J* = 5.5 Hz, 1H for minor dr), 3.71-3.64 (m, 1H for major dr + 2H for minor dr), 3.54-3.48 (m, 1H for major dr), 1.22 (t, *J*=7.2 Hz, 3H for minor dr), 1.15 (t, *J*=7.2 Hz, 3H for major dr); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ: 196.8, 196.3, 164.8, 164.7,

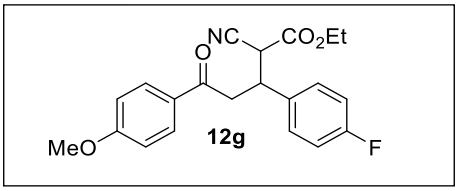
137.7, 136.8, 136.3, 136.1, 134.2, 133.8, 133.7, 129.5, 129.1, 129.1, 129.0, 128.9, 128.8, 128.0, 115.5, 115.4, 77.4, 77.2, 77.0, 76.8, 63.1, 62.9, 43.9, 43.2, 41.5, 40.5, 40.2, 39.5, 13.9 (2C).



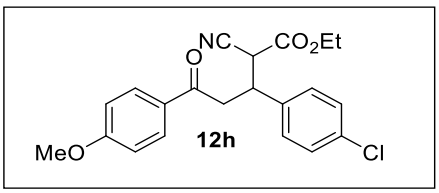
ethyl 3-(4-bromophenyl)-2-cyano-5-oxo-5-phenylpentanoate (12e): 1.46g (91% yield). The product was obtained as yellow gel, dr = 1:1.6 (observed from the unpurified mixture) $R_{f=}$ 0.50 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) data of inseparable diastereomeric mixture mixture spectrum of **4e**, δ: 7.96-7.92 (m, 2H for major dr + 2H for minor dr), 7.61-7.55 (m, 1H for major dr + 1H for minor dr), 7.49-7.44 (m, 4H for major dr + 4H for minor dr), 7.31-7.25 (m, 2H for major dr + 2H for minor dr), 4.33 (d, *J*=6.1 Hz, 1H for major dr), 4.20-4.08 (m, 3H for major dr + 3H for minor dr), 3.89 (d, *J*=6.1 Hz, 1H for minor dr), 3.70-3.63 (m, 1H for major dr + 2H for minor dr), 3.54-3.48 (m, 1H for major dr), 1.21 (t, *J*=7.1 Hz, 3H for minor dr), 1.14 (t, *J*=7.1 Hz, 3H for major dr); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ: 196.8, 196.3, 164.9, 164.8, 138.2, 137.4, 136.2, 136.1, 133.9, 133.7, 132.1, 132.0, 129.9, 129.5, 128.9, 128.8, 128.1, 122.3, 122.1, 115.6, 115.5, 63.2, 62.9, 43.8, 43.1, 41.4, 40.4, 40.2, 39.5, 14.0, 13.9.



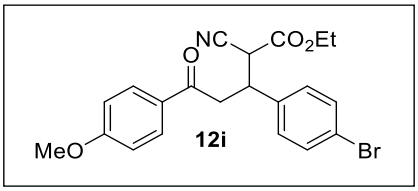
ethyl 2-cyano-3,5-bis(4-methoxyphenyl)-5-oxopentanoate (12f): 1.33g (87% yield). The product was obtained as colourless gel, dr = 1:1.7(observed from the unpurified mixture) $R_{f=}$ 0.38 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$), data of inseparable diastereomeric mixture mixture spectrum of **4f**, δ: 7.95-7.91 (m, 5H), 7.34-7.31 (m, 3H), 7.29-7.27 (m, 2H), 6.94-6.90 (m, 5H), 6.87-6.82 (m, 5H), 4.31 (d, *J* = 5.40 Hz, 2H), 4.16-3.88 (m, 9H), 3.84-3.83 (m, 8H), 3.76-3.74 (m, 8H), 3.65-3.57 (m, 3H), 3.46-3.41 (m, 2H), 1.19 (t, *J* = 7.37 Hz, 3H), 1.13 (t, *J* =7.37 Hz,5H); **^{13}C-NMR (100 MHz, $CDCl_3$)** δ: 195.7, 195.2, 165.25, 162.16, 163.9, 163.8, 159.3, 159.2, 131.3, 130.5, 130.41, 130.40, 129.5, 129.4, 129.2, 128.8, 116.0, 115.8, 114.2, 114.1, 113.9, 113.8, 62.9, 62.6, 55.53, 55.51, 55.2 (2C), 44.3, 43.7, 41.3, 40.3, 40.2, 39.5, 13.89, 13.87.



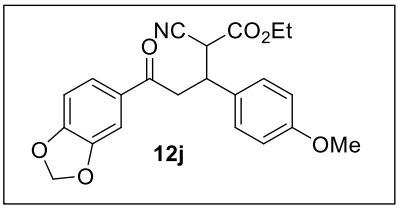
ethyl 2-cyano-3-(4-fluorophenyl)-5-(4-methoxyphenyl)-5-oxopentanoate (12g): 1.34g (92% yield). The product was obtained as yellow coloured gel, dr = 1:1.8 (observed from the unpurified mixture) R_f = 0.46 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) data of inseparable diastereomeric mixture mixture spectrum of **4g**, δ: 7.93-7.88 (m, 2H for major dr + 2H for minor dr), 7.40-7.31 (m, 2H for major dr + 2H for minor dr), 7.02-6.96 (m, 2H for major dr + 2H for minor dr), 6.92-6.88 (m, 2H for major dr + 2H for minor dr), 4.33 (d, *J* = 5.4 Hz, 1H for major dr), 4.17-4.04 (m, 3H for major dr + 3H for minor dr), 3.89 (d, *J*=5.4 Hz, 1H for minor dr), 3.83-3.82 (m, 3H for major dr + 3H for minor dr), 3.63-3.57 (m, 1H for major dr + 2H for minor dr), 3.46-3.40 (m, 1H for major dr) 1.17 (t, *J* = 6.8 Hz, 3H for minor dr), 1.11 (t, *J* = 6.8 Hz, 3H for major dr); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ: 195.3, 194.9, 165.0, 164.9, 164.0, 163.9, 163.7, 163.5, 161.2, 161.0, 135.13, 135.10, 134.4, 134.3, 130.40, 130.37, 129.9, 129.8, 129.5, 129.43, 129.42, 129.3, 115.9, 115.98, 115.74, 115.68, 115.62, 115.57, 113.94113.88, 63.0, 62.7, 55.52, 55.50, 44.0, 43.4, 41.2, 40.3, 40.2, 39.5, 14.1, 14.0.



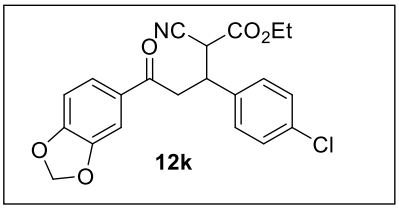
ethyl 3-(4-chlorophenyl)-2-cyano-5-(4-methoxyphenyl)-5-oxopentanoate (12h): 1.40g (91% yield). The product was obtained as brown gel, dr = 1:1.7 (observed from the unpurified mixture) R_f = 0.42 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) data of inseparable diastereomeric mixture mixture spectrum of **4h**, δ: 7.95-7.90 (m, 2H for major dr + 2H for minor dr), 7.37-7.29 (m, 4H for major dr + 4H for minor dr), 6.94-6.91 (m, 2H for major dr + 2H for minor dr), 4.34 (d, *J* = 4.9 Hz, 1H for major dr), 4.20-4.07 (m, 3H for major dr + 3H for minor dr), 3.86 (s, 3H for major dr), 3.85 (s, 3H for major dr), 3.68-3.58(m, 1H for major dr + 2H for minor dr), 3.46-3.41 (m, 1H for major dr) 1.21 (t, *J* = 7.4 Hz, 3H for minor dr), 1.14 (t, *J* = 7.4 Hz, 3H for major dr); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ: 195.2, 194.7, 164.9, 164.8, 164.1, 163.0, 137.8, 137.0, 134.1, 133.0, 130.42, 130.40, 129.5, 129.3, 129.2, 129.15, 129.12, 129.0, 115.6, 115.5, 113.98, 113.91, 63.1, 62.8, 55.6, 55.5, 43.9, 43.0, 41.0, 40.3, 39.9, 39.5, 14.1, 13.9.



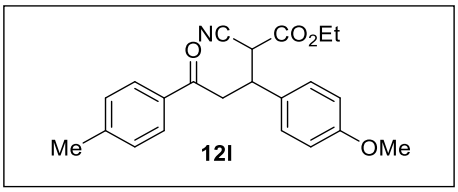
ethyl 3-(4-bromophenyl)-2-cyano-5-(4-methoxyphenyl)-5-oxopentanoate (12i): 1.54g (90% yield). The product was obtained as yellow liquid jelly, dr = 1:1.8 (observed from the unpurified mixture) R_f = 0.46 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) data of inseparable diastereomeric mixture mixture spectrum of **4i**, δ: 7.95-7.90 (m, 2H for major dr + 2H for minor dr), 7.48-7.44 (m, 2H for major dr + 2H for minor dr), 7.31-7.27 (m, 2H for major dr + 2H for minor dr), 6.97-6.91 (m, 2H for major dr + 2H for minor dr), 4.34 (d, *J* = 6.1 Hz, 1H for major dr), 4.19-4.08 (m, 3H for major dr + 3H for minor dr), 3.89-3.86 (m, 3H for major dr + 3H for major dr), 3.85-3.58(m, 1H for major dr + 2H for minor dr), 3.47-3.41 (m, 1H for major dr) 1.21 (t, *J*=7.3 Hz, 3H for minor dr), 1.15 (t, *J* = 7.3 Hz, 3H for major dr); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ: 195.2, 194.7, 164.9, 164.8, 164.1, 163.9, 138.4, 137.5, 132.1, 131.9, 130.4, 130.39, 129.9, 129.5, 129.3, 129.2, 122.2, 122.0, 115.6, 115.5, 113.98, 113.91, 63.1, 62.8, 55.57, 55.57, 43.9, 43.1, 40.9, 40.4, 39.9, 39.6, 13.88(2C).



ethyl 5-(benzo[d][1,3]dioxol-5-yl)-2-cyano-3-(4-methoxyphenyl)-5-oxopentanoate (12j): 1.41g (88% yield). The product was obtained as colourless gel, dr = 1:1.8 (observed from the unpurified mixture) R_f= 0.48 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) data of inseparable diastereomeric mixture mixture spectrum of **4j**, δ: 7.59-7.55 (m, 3H), 7.42-7.38 (m, 3H), 7.32-7.25 (m, 5H), 6.87-6.85 (m, 6H), 6.84-6.83 (m, 2H), 6.05-6.04 (m, 3H), 6.03 (d, *J* = 1.47 Hz, 2H), 4.30 (d, *J* = 5.44 Hertz, 2H), 4.20-4.16 (m, 2H), 4.12-4.10 (m, 5H), 4.09-4.06 (m, 3H), 3.78 (s, 5H), 3.77 (s, 3H), 3.60-3.53 (m, 3H), 3.43-3.37 (m, 2H), 1.21 (t, *J* = 7.19 Hz, 3H), 1.14 (t, *J* = 7.19 Hz, 6H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ: 195.2, 194.2, 165.2, 165.1, 159.4, 159.2, 152.3, 152.1, 148.4, 148.3, 131.2, 130.4, 129.2, 128.8, 124.6, 124.5, 115.8, 115.7, 114.3, 114.2, 108.0, 107.9, 107.8, 107.77, 102.0, 101.9, 62.9, 62.6, 60.4, 55.2, 44.3, 43.6, 41.5, 40.4, 40.3, 39.6, 14.2, 13.9.

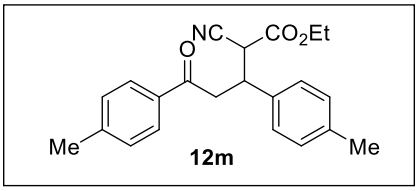


ethyl 5-(benzo[d][1,3]dioxol-5-yl)-3-(4-chlorophenyl)-2-cyano-5-oxopentanoate (12k): 1.31g (82% yield). The product was obtained as colourless gel, dr = 1:1.5 (observed from the unpurified mixture) $R_{f=}$ 0.48 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) data of inseparable diastereomeric mixture mixture spectrum of **4j**, δ: δ: 7.58-7.54 (m, 1H for major dr + 1H for minor dr, 7.41-7.27 (m, 5H for major dr + 5H for minor dr), 6.86-6.83 (m, 1H for major dr + 1H for minor dr), 6.04 (s, 2H for major dr), 6.03 (s, 2H for minor dr), 4.21-4.08 (m, 3H for major dr + 3H for minor dr), 4.31 (d, 1H for major dr, *J* = 5.41 Hz), multiplet), 3.88 (d, 1H, *J* = 5.3 Hz), 3.62-3.55 (m, 1H for major dr + 2H for minor dr), 3.43-3.39 (m, 1H for minor dr), 1.22 (t, 3H for minor dr, *J* = 7.34 Hz), 1.14 (t, *J* = 7.34 Hz, 3H for major dr); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ: 194.7, 194.3, 164.92, 164.78, 152.4, 152.2, 148.4, 148.3, 137.7, 136.9, 134.1, 133.9, 131.1, 131.0, 129.5, 129.1, 129.0, 128.6, 124.6, 124.5, 115.54, 115.50, 108.04, 108.0, 107.8, 107.7, 102.1, 102.0, 63.1, 62.8, 43.9, 43.2, 41.2, 40.3, 40.1, 39.6, 13.8 (2C).



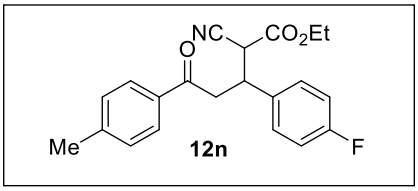
ethyl 2-cyano-3-(4-methoxyphenyl)-5-oxo-5-(p-tolyl)pentanoate (12l): 1.3g (89% yield). The product was obtained as light yellow coloured gel, yield: 84%. dr = 1:1.5 (observed from the unpurified mixture) $R_{f=}$ 0.52 (20% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) data of inseparable diastereomeric mixture mixture spectrum of **4k**, δ: 7.87-7.83(m, 2H for major dr + 2H for minor dr), 7.34-7.32 (m, 1H for major dr + 2H for minor dr), 7.29-7.26 (m, 2H for major dr + 1H for minor dr), 7.25-7.24 (m, 1H for major dr + 1H for minor dr), 6.87-6.83 (m, 2H for major dr + 1H for minor dr), 4.32 (d, *J* = 5.40 Hz, 1H for major dr,), 4.16-4.07 (m, 3H for major dr + 3H for minor dr), 3.88 (d, *J* = 5.23 Hz, 1H for minor dr), 3.78 (s, 3H for major dr), 3.77 (s, 3H for minor dr), 3.68-3.60 (m, 1H for major dr + 2H for minor dr), 3.46 (dd, *J* = 17.76, 5.06 Hz, 1H for major dr,), 2.41 (s, 3H for major dr), 2.40 (s, 3H for minor dr), 1.14 (t, *J* = 7.15 Hz, 3H for

minor dr), 1.21 (t, J = 7.15 Hz, 3H for major dr); **^{13}C-NMR (100 MHz, CDCl$_3$)** δ: 196.9, 196.3, 165.2,165.1, 159.4, 159.2, 144.7, 144.4, 134.0, 133.9, 131.2, 130.4, 129.5, 129.4, 129.2, 128.8, 128.2 (2C), 115.9, 115.8, 114.3, 114.2, 62.9, 55.2 (2C), 44.4, 43.6, 41.6, 40.5, 40.2, 39.5, 21.70, 21.67, 13.90, 13.88.



12m

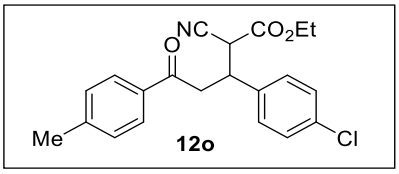
ethyl 2-cyano-5-oxo-3,5-di-p-tolylpentanoate (12m): 1.24g (89% yield). The product was obtained as light brown gel, dr = 1:1.6 (observed from the unpurified mixture) R_f = 0.50 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, CDCl$_3$) data of inseparable diastereomeric mixture mixture spectrum of **4l**, δ: 7.87-7.83(m, 2H for major dr + 2H for minor dr), 7.30-7.23 (m, 4H for major dr + 4H for minor dr), 7.14-7.11 (m, 2H for major dr + 2H for minor dr), 4.34 (d, J = 5.5 Hz, 1H for major dr,), 4.19-4.06 (m, 3H for major dr + 3H for minor dr), 3.89 (d, J = 5.5 Hz, 1H for minor dr), 3.70-3.62 (m, 1H for major dr + 2H for minor dr), 3.50-3.44 (m, 1H for major dr,), 2.40-2.39 (m, 3H for major dr + 3H for minor dr), 2.31-2.29 (m, 3H for major dr + 3H for minor dr), 1.20 (t, J = 7.2 Hz, 3H for minor dr), 1.21 (t, J = 7.2 Hz, 3H for major dr); **^{13}C-NMR (100 MHz, CDCl$_3$)** δ: 196.8, 196.3, 165.2, 165.1, 144.6, 144.4, 137.9, 137.7, 136.3, 135.4, 134.0, 133.4, 129.6, 129.5, 129.5, 129.4, 128.2, 127.9, 127.6, 115.9, 115.8, 62.9, 62.6, 44.3, 43.5, 41.5, 40.5, 40.4, 39.8, 21.7, 21.6, 21.10, 21.0, 14.0, 13.9.



12n

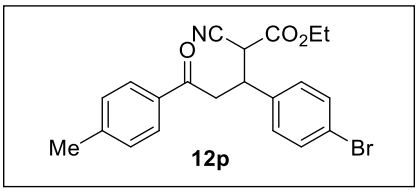
ethyl 2-cyano-3-(4-fluorophenyl)-5-oxo-5-(p-tolyl)pentanoate (12n): 1.3g (92% yield). The product was obtained as yellow gel, dr = 1:1.7 (observed from the unpurified mixture) R_f = 0.48 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, CDCl$_3$) data of inseparable diastereomeric mixture mixture spectrum of **4m**, δ: 7.87-7.83(m, 2H for major dr + 2H for minor dr), 7.42-7.24 (m, 2H for major dr + 2H for minor dr), 7.28-7.24 (m, 2H for major dr + 2H for minor dr), 7.05-6.09 (m, 2H for major dr + 2H for minor dr), 4.33 (d, J = 5.5 Hz, 1H for major dr,), 4.18-4.07 (m,

3H for major dr + 3H for minor dr), 3.90 (d, J = 5.5 Hz, 1H for minor dr), 3.68-3.61 (m, 1H for major dr + 2H for minor dr), 3.51-3.47 (m, 1H for major dr,), 2.41-2.40 (m, 3H for major dr + 3H for minor dr), 1.20 (t, J = 6.8 Hz, 3H for minor dr), 1.13 (t, J = 6.8 Hz, 3H for major dr); **^{13}C-NMR (100 MHz, $CDCl_3$)** δ: 196.5, 196.0, 165.0, 164.9, 163.7, 163.5, 161.2, 161.0, 144.8, 144.6, 133.7, 129.9, 129.8, 129.5, 129.4, 128.2, 115.9, 115.8, 115.7, 115.69, 115.61, 11.57, 63.0, 62.9, 44.0, 43.4, 41.5, 40.4, 40.2, 39.4, 21.7, 21.7, 13.9, 13.8.



12o

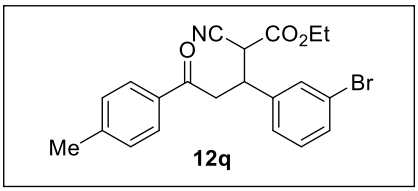
ethyl 3-(4-chlorophenyl)-2-cyano-5-oxo-5-(p-tolyl)pentanoate (12o): 1.35g (91% yield). The product was obtained as dark yellow gel, dr = 1:1.7 (observed from the unpurified mixture) R_f = 0.50 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) data of inseparable diastereomeric mixture mixture spectrum of **4n**, δ: 7.87-7.82 (m, 2H for major dr + 2H for minor dr), 7.37-7.24 (m, 6H for major dr + 6H for minor dr), 4.33 (d, J = 5.2 Hz, 1H for major dr,), 4.21-4.08 (m, 3H for major dr + 3H for minor dr), 3.88 (d, J = 5.2 Hz, 1H for minor dr), 3.67-3.61 (m, 1H for major dr + 2H for minor dr), 3.50-3.44 (m, 1H for major dr,), 2.41-2.40 (m, 3H for major dr + 3H for minor dr), 1.21 (t, J = 7.2 Hz, 3H for minor dr), 1.14 (t, J = 7.4 Hz, 3H for major dr); **^{13}C-NMR (100 MHz, $CDCl_3$)** δ: 196.4, 195.9, 164.9, 164.8, 144.9, 144.6, 137.7, 136.9, 134.1, 133.9, 133.8, 133.7, 129.54, 129.51, 129.4, 129.2, 129.1, 129.0, 128.1, 115.7, 115.5, 63.1, 62.8, 43.9, 43.1, 41.3, 40.2, 39.5, 22.7, 21.7, 21.6, 14.1, 13.9.



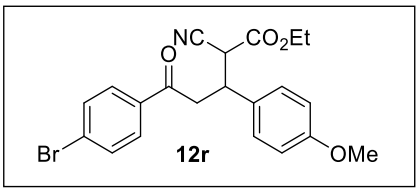
12p

ethyl 3-(4-bromophenyl)-2-cyano-5-oxo-5-(p-tolyl)pentanoate (12p): 1.49g (90% yield). The product was obtained as dark yellow gel, dr = 1:1.7 (observed from the unpurified mixture) R_f = 0.50 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) data of inseparable diastereomeric mixture mixture spectrum of **4p**, δ: 7.75-7.71(m, 2H for major dr + 2H for minor dr), 7.35-7.31 (m, 2H for major dr + 2H for minor dr), 7.21-7.12 (m, 4H for major dr + 4H for minor dr), 4.23 (d, J = 5.4 Hz, 1H for major dr,), 4.08-3.96 (m, 3H for major dr + 3H for minor dr), 3.80 (d, J =

5.4 Hz, 1H for minor dr), 3.56-3.49 (m, 1H for major dr + 2H for minor dr), 3.40-3.34 (m, 1H for major dr,), 2.28-2.27 (m, 3H for major dr + 3H for minor dr), 1.08 (t, *J* = 7.3 Hz, 3H for minor dr), 1.02 (t, *J* = 7.3 Hz, 3H for major dr); **^{13}C-NMR (100 MHz, CDCl$_3$)** δ: 196.4, 195.9, 164.9, 164.8, 144.8, 144.6, 138.4, 137.6, 133.8, 133.7, 132.0, 131.9, 129.9, 129.6, 129.5, 129.4, 128.2, 122.2, 122.0, 115.6, 115.5, 63.1, 62.8, 43.8, 43.2, 41.3, 40.3, 40.2, 39.6, 21.71, 21.70, 13.9 (2C).

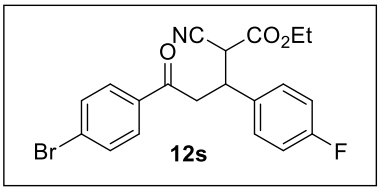


ethyl 3-(3-bromophenyl)-2-cyano-5-oxo-5-(p-tolyl)pentanoate (12q): 1.5g (90% yield). The product was obtained as yellow gel, dr = 1:1.5 (observed from the unpurified mixture) R_f = 0.42 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, CDCl$_3$) data of inseparable diastereomeric mixture mixture spectrum of **4o**, δ: 7.80-7.76 (m, 2H for major dr + 2H for minor dr), 7.46-7.42 (m, 2H for major dr + 2H for minor dr), 7.37-7.30 (m, 2H for major dr + 2H for minor dr), 7.24-6.11 (m, 4H for major dr + 4H for minor dr), 4.27 (d, *J* = 5.1 Hz, 1H for major dr,), 4.14-4.02 (m, 3H for major dr + 3H for minor dr), 3.82 (d, *J* = 5.1 Hz, 1H for minor dr), 3.62-3.54 (m, 1H for major dr + 2H for minor dr), 3.43-3.37 (m, 1H for major dr), 2.34-2.33 (m, 3H for major dr + 3H for minor dr), 1.14 (t, *J* = 7.2 Hz, 3H for minor dr), 1.07 (t, *J* = 7.2 Hz, 3H for major dr); **^{13}C-NMR (100 MHz, CDCl$_3$)** δ: 196.3, 195.8, 164.9, 164.7, 144.9, 144.6, 141.6, 140.7, 133.8, 133.6, 131.42, 131.40, 131.3, 130.9, 130.5, 130.4, 129.5, 129.4, 128.2, 126.6, 126.5, 122.9, 122.8, 115.5, 115.3, 63.2, 62.9, 43.8, 43.1, 41.2, 40.4, 40.2, 39.7, 21.74, 21.71, 13.9 (2C).



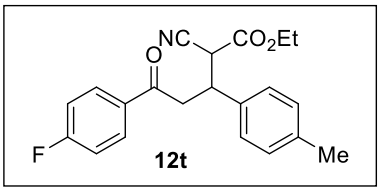
ethyl 5-(4-bromophenyl)-2-cyano-3-(4-methoxyphenyl)-5-oxopentanoate (12r): 1.5g (88% yield). The product was obtained as light yellow gel, dr = 1:1.5 (observed from the unpurified mixture) Rf= 0.53 (20% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, CDCl$_3$) data of inseparable diastereomeric mixture mixture spectrum of **4q**, δ: 7.83-7.78 (m, 2H for major dr + 2H for minor dr), 7.62-7.58 (m, 2H for major dr + 2H for minor dr), 7.32-7.25 (m, 2H for major dr + 2H for

minor dr), 6.87-6.83 (m, 2H for major dr + 2H for minor dr), 4.27 (d, *J* = 5.6 Hz, 1H for major dr), 4.20-4.07 (m, 3H for major dr + 3H for minor dr), 3.86 (d, *J* = 5.6 Hertz 1H for minor dr), 3.78 (s, 3H for major dr), 3.76 (s, 3H for minor dr), 3.62-6.57 (m, 1H for major dr + 2H for minor dr), 3.49-3.43 (m, 1H for major dr), 1.21 (t, *J* = 7.25 Hz 3H for minor dr,), 1.13 (t, *J* = 7.2 Hertz 3H for major dr) ; **^{13}C-NMR (100 MHz, CDCl$_3$)** δ: 196.3, 195.8, 165.1, 165.0, 159.4, 159.3, 135.2, 135.0, 132.1, 132.0, 130.9, 130.1, 129.58, 129.57, 129.4, 129.1, 129.0, 128.7, 115.8, 115.7, 114.3, 114.2, 63.0, 62.7, 55.3 (2C), 44.3, 43.5, 41.8, 40.7, 40.1, 39.1, 14.1, 13.9.



12s

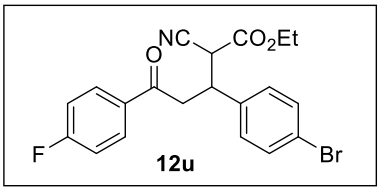
ethyl 5-(4-bromophenyl)-2-cyano-3-(4-fluorophenyl)-5-oxopentanoate (12s): 1.5g (91% yield). The product was obtained as yellow gel, dr = 1:1.2 (observed from the unpurified mixture) R_f = 0.4 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, CDCl$_3$) data of inseparable diastereomeric mixture mixture spectrum of **4r**, δ: 7.83-7.78 (m, 2H for major dr + 2H for minor dr), 7.63-7.57 (m, 2H for major dr + 2H for minor dr), 7.40-7.32 (m, 2H for major dr + 2H for minor dr), 7.05-7.00 (m, 2H for major dr + 2H for minor dr), 4.30 (d, *J* = 5.3 Hz, 1H for major dr,), 4.21-4.07 (m, 3H for major dr + 3H for minor dr), 3.87 (d, *J* = 5.3 Hz, 1H for minor dr), 3.67-3.54 (m, 1H for major dr + 2H for minor dr), 3.50-3.44 (m, 1H for major dr,), 1.22 (t, *J* = 7.2 Hz, 3H for minor dr), 1.13 (t, *J* = 7.2 Hz, 3H for major dr); **^{13}C-NMR (100 MHz, CDCl$_3$)** δ: 195.9, 195.4, 164.9, 164.7, 163.8, 161.3, 135.0, 134.9, 134.81, 137.80, 133.96, 133.93, 132.2, 132.1, 129.8, 129.5, 129.51, 129.50, 129.4, 129.3, 129.2, 128.9, 116.0, 115.9, 115.8 115.7, 115.5, 115.4, 63.1, 62.8, 43.9, 43.3, 41.6, 40.6, 40.0, 39.3, 13.9, 13.8.



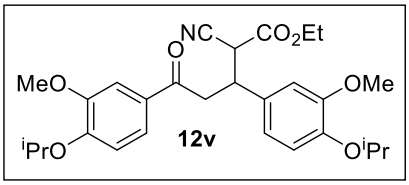
12t

ethyl 2-cyano-5-(4-fluorophenyl)-5-oxo-3-(p-tolyl)pentanoate (12t): 1.25g (85% yield). The product was obtained as light yellow coloured gel, dr = 1:1.5 (observed from the unpurified mixture) R_f = 0.52 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, CDCl$_3$) data of inseparable diastereomeric mixture mixture spectrum of **4t**, δ: 8.01-7.95(m, 2H for major dr + 2H for minor

dr), 7.29-7.23 (m, 2H for major dr + 2H for minor dr), 7.16-7.10 (m, 4H for major dr + 4H for minor dr), 4.32 (d, *J* = 4.9 Hz, 1H for major dr,), 4.19-4.07 (m, 3H for major dr + 3H for minor dr), 3.88 (d, *J* = 4.9 Hz, 1H for minor dr), 3.69-3.61 (m, 1H for major dr + 2H for minor dr), 3.50-3.45 (m, 1H for major dr,), 2.32-2.31 (m, 3H for major dr + 3H for minor dr), 1.22 (t, *J* = 7.2 Hz, 3H for minor dr), 1.13 (t, *J* = 7.3 Hz, 3H for major dr); **^{13}C-NMR (100 MHz, CDCl$_3$)** δ: 195.6, 195.1, 167.4, 165.2, 165.0, 164.8, 138.0, 137.9, 136.1, 135.2, 132.93, 132.90, 132.8, 132.7, 130.8, 130.7, 129.72, 129.70, 129.5, 127.9, 127.5, 127.0, 116.1, 116.0, 115.8, 115.74, 115.70, 63.0, 62.7, 44.2, 43.4, 41.7, 40.5, 40.4, 39.8, 21.1, 21.0, 13.9, 13.8.



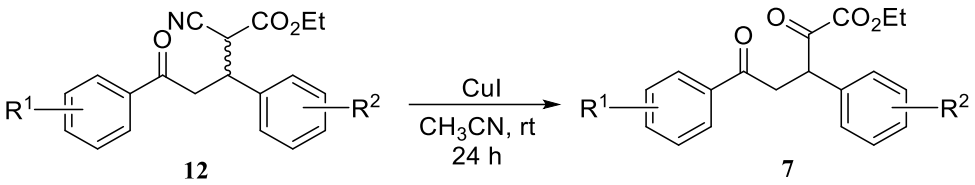
ethyl 3-(4-bromophenyl)-2-cyano-5-(4-fluorophenyl)-5-oxopentanoate (12u): 1.5g (90% yield). The product was obtained as yellow coloured gel, dr = 1:1.5 (observed from the unpurified mixture) R_f = 0.48 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, CDCl$_3$) data of inseparable diastereomeric mixture mixture spectrum of **4s**, δ: 8.01-7.95(m, 2H for major dr + 2H for minor dr), 7.49-7.46 (m, 2H for major dr + 2H for minor dr), 7.31-7.24 (m, 2H for major dr + 2H for minor dr), 7.17-7.11 (m, 2H for major dr + 2H for minor dr), 4.31 (d, *J* = 5.6 Hz, 1H for major dr,), 4.22-4.09 (m, 3H for major dr + 3H for minor dr), 3.88 (d, *J* = 5.6 Hz, 1H for minor dr), 3.67-3.60 (m, 1H for major dr + 2H for minor dr), 3.50-3.45 (m, 1H for major dr,), 1.23 (t, *J* = 6.9 Hz, 3H for minor dr), 1.15 (t, *J* = 6.9 Hz, 3H for major dr); **^{13}C-NMR (100 MHz, CDCl$_3$)** δ: 195.1, 194.7, 164.9, 164.7, 138.1, 137.2, 132.1, 132.0, 130.84, 130.81, 130.75, 130.72, 129.8, 129.4, 122.4, 116.1, 116.0, 115.9, 115.8, 115.4, 63.2, 62.9, 43.8, 43.0, 41.4, 40.3, 40.2, 39.5, 14.1, 13.9.



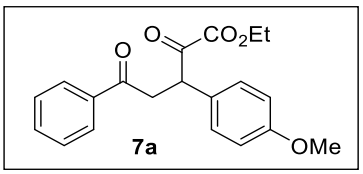
ethyl 2-cyano-3,5-bis(4-isopropoxy-3-methoxyphenyl)-5-oxopentanoate (12v): 1.77g (89% yield). The product was obtained as yellow coloured gel, dr = 1:1.7 (observed from the unpurified mixture) R_f = 0.46 (20% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, CDCl$_3$) data of inseparable diastereomeric mixture mixture spectrum of **4s**, δ: 7.59-7.56 (m, 1H for major dr + 1H for minor

dr), 7.49-7.45 (m, 1H for major dr + 1H for minor dr), 6.93-6.79 (m, 4H for major dr + 4H for minor dr), 4.67-4.62 (m, 1H for major dr + 1H for minor dr), 4.50-4.44 (m, 1H for major dr + 1H for minor dr), 4.32 (d, J = 5.3Hz, 1H for major dr), 4.17-4.15 (m, 1H for major dr), 4.10-4.03 (m, 2H for major dr + 3H for minor dr), 3.89-3.82 (m, 6H for major dr + 6H for minor dr), 3.61-3.56 (m, 3H for minor dr), 3.47-3.42 (m, 1H for major dr), 1.40-1.37 (m, 6H for major dr + 6H for minor dr), 1.34-1.31 (m, 6H for major dr + 6H for minor dr), 1.19 (t, J = 7.1 Hz, 3H for minor dr), 1.11 (t, J = 7.1 Hz, 3H for major dr); **^{13}C-NMR (100 MHz, $CDCl_3$)** δ: 195.8, 195.3, 165.2, 165.1, 152.4, 152.2, 150.4, 150.2, 150.0, 149.9, 147.1, 147.0, 132.1, 131.2, 129.4, 129.2, 122.8, 122.7, 120.2, 119.6, 115.99, 115.93, 115.6, 115.5, 112.8(2C), 112.0, 111.8, 110.8, 110.7, 71.32, 71.30, 71.26 (2C), 62.9, 62.7, 56.08, 56.05, 56.03 (2C), 44.4, 43.5, 41.3, 40.8, 40.14, 40.10, 22.06 (2C), 21.9, 21.8, 13.9 (2C).

General experimental approach for the Construction of Ethyl 2,5-dioxo-3,5-diphenylpentanoate derivative (7):

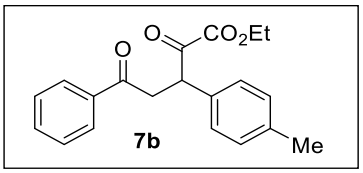


The diastereomeric mixture of compound **12** (3.0 mmol, 1 equivalent) and CuI (420 milligrams, 2.2 mmol) in 6mL of acetonitrile solvent was made to stir at normal temperature for over a day in a dry RB under an open flask medium. The reaction's completion was determined by TLC analysis. A celite pad was employed to filter the mixture. The organic compound is extracted from crude mixture by using dichloro methane. Water was used for removal of inorganic stuff from organic layer. $MgSO_4$. Is used to dry out the organic layer. The organic layer had been concentrated underneath vacuum. Flask column chromatography is used to purify the product using 100-200 mesh silica gel yielding substituted 1,4 – dicarbonyl compound **7**.

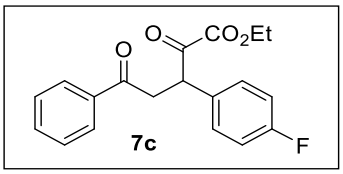


ethyl 3-(4-methoxyphenyl)-2,5-dioxo-5-phenylpentanoate (7a): 868mg (83% yield). The product was obtained as yellow sticky jelly, R_f = 0.56 (15% EtOAc in n-hexane). **^{1}H-NMR** (400

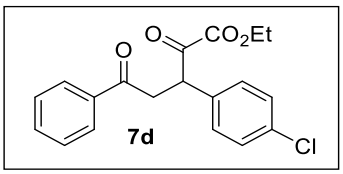
MHz, $CDCl_3$) δ: 7.96-7.94 (m, 2H), 7.58-7.54 (m, 1H), 7.46-7.43 (m, 2H), 7.28-7.24 (m, 2H), 6.90-6.87 (m, 2H), 5.10 (dd, *J* = 10.69, 4.1 Hz, 1H), 4.31-4.23 (m, 2H), 4.03-3.95 (m, 1H), 3.78 (s, 3H), 3.39 (dd, *J* = 18.3, 3.8 Hz, 1H), 1.30 (t, *J* = 7.5 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 197.5, 192.2, 160.5, 159.4, 136.0, 133.5, 130.1, 128.7, 128.2, 127.0, 114.6, 62.5, 55.7, 47.6, 43.0, 13.9.



ethyl 2,5-dioxo-5-phenyl-3-(p-tolyl)pentanoate (7b): 837mg (82% yield). The product was obtained as sticky yellow coloured jelly, R_f = 0.47 (10% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 7.96-7.94 (m, 2H), 7.58-7.54 (m, 1H), 7.47-7.43 (m, 2H), 7.24-7.22 (m, 2H), 7.17-7.15 (m, 2H), 5.12 (dd, *J* = 10.58, 3.7 Hz, 1H), 4.35-4.23 (m, 2H), 4.05-3.98 (m, 1H), 3.40 (dd, *J* = 18.2, 3.8 Hz, 1H), 2.33 (s, 3H), 1.31 (t, *J* = 7.3 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 197.5, 192.2, 160.4, 137.8, 136.0, 133.5, 132.2, 129.9, 128.8, 128.7, 128.2, 62.5, 48.0, 43.1, 21.1, 14.0.

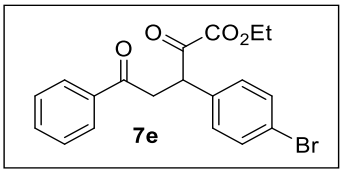


ethyl 3-(4-fluorophenyl)-2,5-dioxo-5-phenylpentanoate (7c): 838mg (85% yield). The product was obtained as dark yellow sticky jelly, R_f = 0.45 (10% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 7.96-7.94 (m, 2H), 7.60-7.56 (m, 1H), 7.48-7.44 (m, 2H), 7.35-7.31 (m, 2H), 7.06-7.02 (m, 2H), 5.14 (dd, *J* = 10.6, 4.0 Hz, 1H), 4.32-4.28 (m, 2H), 4.03-3.96 (m, 1H), 3.43 (dd, *J* = 18.07, 3.8 Hz, 1H), 1.32 (t, *J* = 7.3 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 197.3, 192.1, 163.7, 161.2, 160.3, 135.8, 133.6, 131.1, 131.0, 130.6, 130.5, 128.7, 128.2, 116.2, 116.0, 62.6, 47.5, 43.2, 13.9.

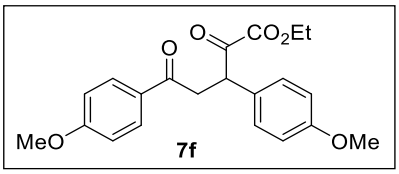


ethyl 3-(4-chlorophenyl)-2,5-dioxo-5-phenylpentanoate (7d): 867mg (84% yield). The product was obtained as yellow sticky jelly, R_f = 0.46 (10% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz,

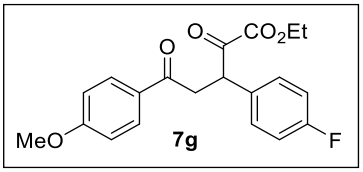
$CDCl_3$) δ: 7.95-7.93 (m, 2H), 7.59-7.55 (m, 1H), 7.48-7.44 (m, 2H), 7.47-7.43 (m, 2H), 7.33-7.28 (m, 4H), 5.13 (dd, *J* = 10.4, 3.9 Hz, 1H), 4.34-4.25 (m, 2H), 4.03-3.96 (m, 1H), 3.99 (dd, *J* = 18.4, 3.2 Hz, 1H), 1.32 (t, *J* = 7.5 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 197.1, 191.9, 160.3, 135.8, 134.0, 133.9, 133.7, 130.2, 129.3, 128.7, 128.2, 62.7, 47.7, 43.1, 13.9.



ethyl 3-(4-bromophenyl)-2,5-dioxo-5-phenylpentanoate (7e): 980mg (84% yield). The product was obtained as orange sticky jelly, R_f = 0.50 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 8.00-7.93 (m, 2H), 7.60-7.56 (m, 1H), 7.50-7.43 (m, 4H), 7.25-7.23 (m, 2H), 5.12 (dd, *J* = 10.6, 4.2 Hz, 1H), 4.34-4.25 (m, 2H), 4.03-3.96 (m, 1H), 3.43 (dd, *J* = 18.3, 3.9 Hz, 1H), 1.32 (t, *J* = 7.7 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 197.1, 191.8, 160.2, 135.7, 134.4, 133.7, 132.3, 130.7, 128.7, 128.2, 122.2, 62.7, 47.8, 43.1, 13.9.

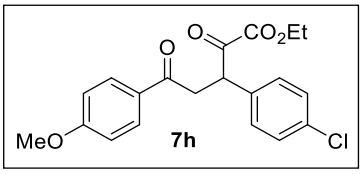


ethyl 3,5-bis(4-methoxyphenyl)-2,5-dioxopentanoate (7f): 900mg (81% yield). The product was obtained as light yellow sticky jelly, R_f = 0.52 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 7.94-7.92 (m, 2H), 7.27 (d, *J* = 2.52 Hz, 1H), 7.26 (d, *J* = 2.52 Hz, 1H), 6.93-6.86 (m, 1H), 5.08 (dd, *J* = 10.52, 3.94 Hz, 1H), 4.28 (q, *J* = 7.25 Hertz, 2H), 3.98-3.91 (m, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 3.37 (dd, *J* = 17.94, 4.10 Hz, 1H), 1.31 (t, *J* = 7.26 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 196.0, 192.3, 163.8, 160.6, 159.3, 130.5, 130.0, 129.1, 127.2, 114.5, 113.8, 62.5, 55.5, 55.3, 47.5, 42.9, 14.0.

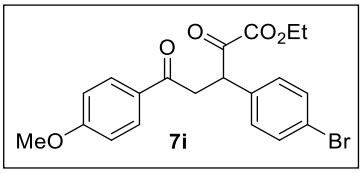


ethyl 3-(4-fluorophenyl)-5-(4-methoxyphenyl)-2,5-dioxopentanoate (7g): 983mg (85% yield). The product was obtained as dark orange sticky jelly, R_f = 0.44 (10% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 7.92-7.90 (m, 2H), 7.34-7.30 (m, 2H), 7.04-7.00 (m, 2H), 6.91-6.89

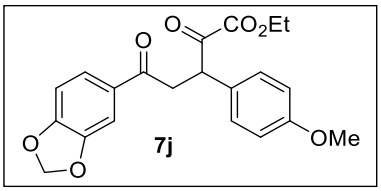
(m, 2H), 5.11 (dd, J = 10.5, 3.8 Hz, 1H), 4.32-4.24 (m, 2H), 3.97-3.90 (m, 1H), 3.84 (s, 3H), 3.39 (dd, J = 17.8, 4.0 Hz, 1H), 1.30 (t, J = 6.23 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 195.7, 192.2, 163.9, 163.6, 161.2, 160.4, 131.3, 131.2, 130.6, 130.51, 130.50, 128.9, 116.1, 115.9, 113.8, 62.6, 55.5, 47.5, 43.1, 13.9.



ethyl 3-(4-chlorophenyl)-5-(4-methoxyphenyl)-2,5-dioxopentanoate (7h): 933 mg (83% yield). The product was obtained as yellow jelly, yield: 80%. R_f = 0.49 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 7.92-7.90 (m, 2H), 7.33-7.28 (m, 4H), 6.92-6.90 (m, 2H), 5.10 (dd, J = 10.6, 4.0 Hz 1H), 4.37-4.25 (m, 2H), 3.97-3.90 (m, 1H), 3.85 (s, 3H), 3.39 (dd, J = 18.0, 3.9 Hz, 1H), 1.32 (t , J = 7.1 Hz, 3H), **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 195.6, 190.0, 163.9, 160.3, 134.1, 134.0, 130.5, 130.2, 129.3, 128.8, 113.9, 62.6, 55.5, 47.7, 43.1, 13.9.;

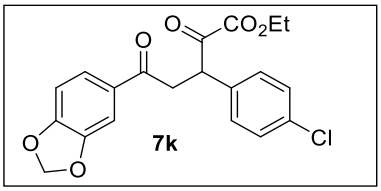


ethyl 3-(4-bromophenyl)-5-(4-methoxyphenyl)-2,5-dioxopentanoate (7i): 1.05g (84% yield). The product was obtained as dark yellow sticky liquid, R_f = 0.56 (10% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 7.92-7.89 (m, 2H), 7.47-7.45 (m, 2H), 7.24-7.22 (m, 2H), 6.92-6.90 (m, 2H), 5.09 (dd, J = 10.8, 3.9 Hz, 1H), 4.34-4.25 (m, 2H), 3.97-3.90 (m, 1H), 3.85 (s, 3H), 3.39 (dd, J = 18.1, 4.0 Hz, 1H), 1.32 (t, J = 7.0 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 195.6, 191.9, 163.9, 160.3, 134.6, 132.2, 130.7, 130.6, 128.8, 122.1, 113.9, 62.8, 55.5, 47.7, 43.1, 13.9.

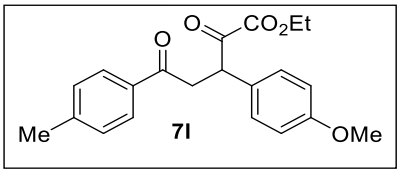


ethyl 5-(benzo[d][1,3]dioxol-5-yl)-3-(4-methoxyphenyl)-2,5-dioxopentanoate (7j): 922mg (80% yield). The product was obtained as pale yellow sticky jelly, R_f = 0.54 (20% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 7.56 (d, J = 8.20 Hertz, 1H), 7.40 (s, 1H), 7.26-7.23 (m,

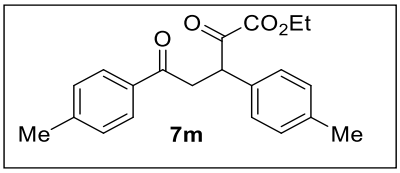
2H), 6.88-6.82 (m, 2H), 6.03 (s, 2H), 5.07 (dd, J = 10.36, 3.67 Hz, 1H), 4.29 (q, *J* = 7.25 Hz, 2H), 3.95-3.87 (m, 1H), 3.80 (s, 3H), 3.32 (dd, *J* = 14.19, 3.82 Hz, 1H), 1.31 (t, *J* = 7.16 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 195.6, 192.3, 160.5, 159.3, 152.1, 148.2, 130.6, 130.0, 127.0, 124.6, 114.5, 107.9, 107,8, 101.9, 62.5, 55.5, 55.3, 47.5, 42.9, 14.0.



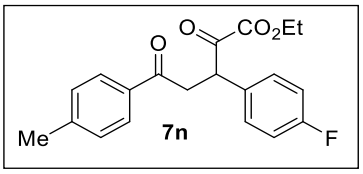
ethyl 5-(benzo[d][1,3]dioxol-5-yl)-3-(4-chlorophenyl)-2,5-dioxopentanoate (7k): 921mg (79% yield). The product was obtained as pale-yellow sticky jelly, R_f = 0.52 (10% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: : 7.55 (dd, *J* = 8.26, 1.63 Hz, 1H), 7.39 (d, *J* = 1.63 Hz, 1H), 7.33-7.27 (m, 4H), 6.83 (d, *J* = 8.20 Hz, 1H), 6.04 (s, 2H), 5.10 (dd, *J* = 10.56, 3.92 Hz, 1H), 4.34-4.25 (m, 2H), 3.95-3.88 (m, 1H), 3.35 (dd, *J* = 18.0, 4.0 Hz, 1H), 1.32 (t, *J* = 7.16 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 195.2, 191.9, 160.3, 152.2, 148.3, 134.0, 133.9, 130.6, 130.2, 129.3, 124.7, 108.0, 107.9, 102.0, 62.7, 47.4, 43.0, 13.9.



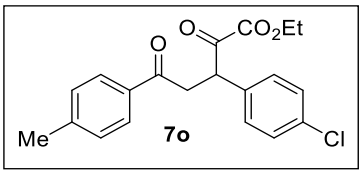
ethyl 3-(4-methoxyphenyl)-2,5-dioxo-5-(p-tolyl)pentanoate (7l): 872mg (82% yield). The product was obtained as bright yellow sticky liquid, R_f= 0.44 (5% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 7.85-7.83 (m, 2H), 7.26-7.25 (m, 2H), 7.24-7.23 (m, 2H), 6.88-6.66 (m, 2H), 5.08 (dd, *J* = 10.55, 3.94 Hz, 1H), 4.35-4.23 (m, 2H), 4.00-3.91 (m, 1H), 3.79 (s, 3H), 3.38 (dd, *J* = 18.12, 3.96 Hz, 1H), 2.40 (s, 3H), 1.13 (t, *J* = 7.13 Hz, 3H).; **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 197.2, 192.2, 160.5, 159.3, 144.4, 133.6, 130.1, 129.3, 128.3, 127.1, 114.6, 62.5, 55.3, 47.6, 43.0, 21.7, 14.0.



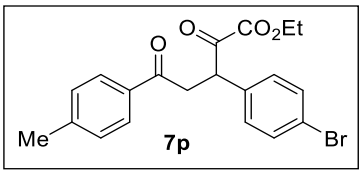
ethyl 2,5-dioxo-3,5-di-p-tolylpentanoate (7m): 911mg (83% yield). The product was obtained as yellow brown solid. R_f = 0.48 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ:7.86-7.84(m, 2H), 7.25-7.23(m, 2H), 7.16-7.14(m, 2H),5.11(dd, *J*=10.8,3.6Hz, 1H), 4.32-4.23(m, 2H),4.03-3.95(m, 1H), 3.39(dd, *J*=18.3,3.3Hz, 1H), 2.40(s, 3H), 2.33(s, 3H), 1.31(t, *J*=7.3Hz, 3H).; **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 197.1, 192.3, 160.5, 144.4, 137.8, 133.5, 132.3, 129.8, 129.3, 128.8, 128.3, 62.5, 48.0, 43.1, 21.7, 21.1, 13.9



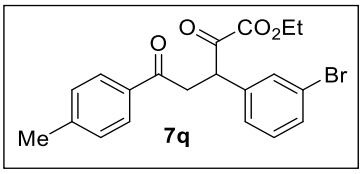
ethyl 3-(4-fluorophenyl)-2,5-dioxo-5-(p-tolyl)pentanoate (7n): 863mg (84% yield). The product was obtained as yellow sticky jelly, R_f = 0.56 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 7.85-7.83 (m, 2H), 7.34-7.31 (m, 2H), 7.25-7.23 (m, 2H), 7.05-7.01 (m, 2H), 5.12 (dd, *J* = 10.6, 4.0 Hz, 1H), 4.33-4.24 (m, 2H), 4.00-3.93 (m, 1H), 3.41 (dd, *J* = 18.02, 4.0 Hz, 1H), 2.39 (s, 3H), 1.31 (t, *J* = 7.16 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 196.9, 192.1, 163.6, 161.2, 160.5, 144.7, 133..3, 131.2, 131.1, 130.6, 130.5, 129.4, 128.3, 116.2, 115.9, 62.6, 47.5, 43.2, 21.7, 13.9.



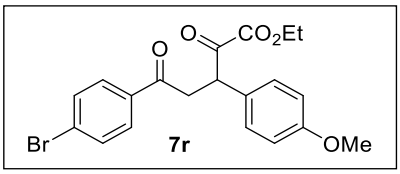
ethyl 3-(4-chlorophenyl)-2,5-dioxo-5-(p-tolyl)pentanoate (7o): 894mg (83% yield). The product was obtained as orange sticky jelly, R_f = 0.48 (10% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 7.85-7.83 (m, 2H), 7.33-7.28 (m, 4H), 7.26-7.23 (m, 2H), 5.12 (dd, *J* = 10.9, 3.8 Hz, 1H), 4.34-4.25 (m, 2H), 4.00-3.93 (m, 1H), 3.41 (dd, *J* = 17.9, 4.2 Hz, 1H), 2.40 (s, 3H), 1.31 (t, *J* = 7.3 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 196.7, 191.9, 160.3, 144.6, 134.0, 133.9, 133.3, 130.2, 129.4, 129.3, 128.3, 62.7, 47.7, 43.2, 21.7, 13.9.



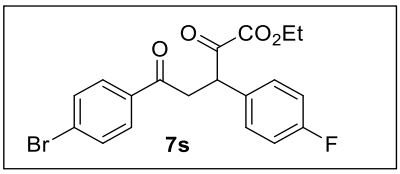
ethyl 3-(4-bromophenyl)-2,5-dioxo-5-(p-tolyl)pentanoate (7p): 1g (83mg). The product was obtained as brown sticky jelly, R_f = 0.50 (10% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 7.83-7.81 (m, 2H), 7.46-7.44 (m, 2H), 7.24-7.22 (m, 4H), 5.09 (dd, *J* = 10.7, 3.9 Hz, 1H), 4.32-4.23 (m, 2H), 3.99-3.92 (m, 1H), 3.40 (dd, *J* = 18.1, 4.8 Hz, 1H), 2.28 (s, 3H), 1.31 (t, *J* = 7.6 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 196.7, 191.8, 160.3, 144.6, 134.6, 133.3, 132.2, 130.6, 129.4, 128.3, 122.1, 62.7, 47.7, 43.1, 21.7, 13.9.



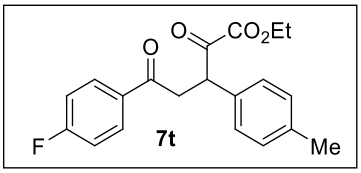
ethyl 3-(3-bromophenyl)-2,5-dioxo-5-(p-tolyl)pentanoate (7q): 1g (83% yield). The product was obtained as dark yellow sticky jelly, R_f = 0.52 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 7.85-7.83 (m, 2H), 7.52-7.51 (m, 1H), 7.42-7.41 (m, 1H), 7.31-7.29 (m, 1H), 7.26-7.20 (m, 3H), 5.10 (dd, *J* = 10.9, 3.6 Hz, 1H), 4.36-4.27 (m, 2H), 4.02-3.95 (m, 1H), 3.42 (dd, *J* = 18.1, 4.3 Hz, 1H), 2.40 (s, 3H), 1.34 (t, *J* = 6.5 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 196.7, 191.8, 160.2, 144.6, 137.8, 133.2, 131.8, 131.1, 130.6, 129.4, 128.3, 127.6, 123.1, 62.7, 47.9, 43.3, 21.7, 13.9.



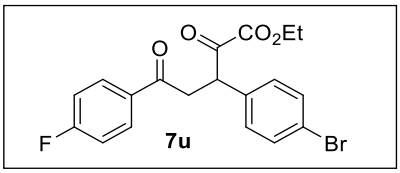
ethyl 5-(4-bromophenyl)-3-(4-methoxyphenyl)-2,5-dioxopentanoate (7r): 1g (81% yield)**.** The product was obtained as liquid, R*f*= 0.50 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 7.82-7.80 (m, 2H), 7.61-7.58 (m, 2H), 7.25-7.23 (m, 2H), 6.89-6.87 (m, 2H), 5.08 (dd, *J* = 10.4, 4.0 Hz, 1H), 4.32-4.23 (m, 2H), 3.98-3.90 (m, 1H), 3.79 (s, 3H), 3.33 (dd, *J* = 18.2, 4.0 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$) δ:** 196.5, 192.0, 160.4, 159.4, 134.8, 132.0, 130.0, 129.7, 128.7, 126.7, 114.6, 62.5, 55.3, 47.6, 42.8,13.9.



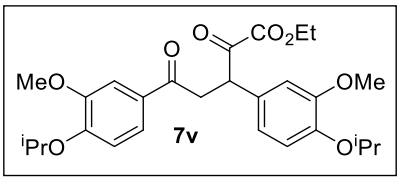
ethyl 5-(4-bromophenyl)-3-(4-fluorophenyl)-2,5-dioxopentanoate (7s): 1.1g (84% yield). The product was obtained as dark yellow sticky jelly, R_f = 0.50 (10% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 7.82-7.79 (m, 2H), 7.62-7.59 (m, 2H), 7.33-7.29 (m, 2H), 7.07-7.02 (m, 2H), 5.13 (dd, *J* = 10.4, 3.9 Hz, 1H), 4.34-4.24 (m, 2H), 3.98-3.91 (m, 1H), 3.37 (dd, *J* = 8.2, 4.2 Hz, 1H), 1.31 (t, *J* = 7.06 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 196.2, 191.1, 160.2, 134.6, 132.0, 130.6, 130.5, 129.7, 128.9, 116.3, 116.1, 62.7, 47.5, 42.9, 13.9.



ethyl 5-(4-fluorophenyl)-2,5-dioxo-3-(p-tolyl)pentanoate (7t): 834 mg (81% yield). The product was obtained as dark yellow sticky liquid R_f = 0.46 (10% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 7.99-7.96 (m, 2H), 7.23-7.21 (m, 2H), 7.16-7.09 (m, 4H), 5.11 (dd, *J* = 3.7, 10.5 Hz, 1H), 4.33-4.20 (m, 2H), 4.01-3.94 (m, 1H), 3.35 (dd, *J* = 18.7, 3.8 Hz, 1H), 2.32 (s, 3H)1.30 (t, *J* = 7.1 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 195.9, 192.2, 167.2, 164.7, 160.4, 137.9, 132.49, 132.46, 132.6, 130.9, 130.8, 129.9, 128.8, 115.9, 115.7, 62.5, 48.1, 42.9, 21.1, 13.9.

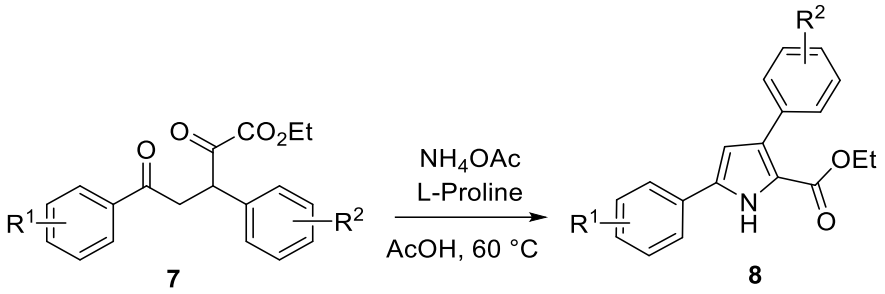


ethyl 3-(4-bromophenyl)-5-(4-fluorophenyl)-2,5-dioxopentanoate (7u): 1.0g (83% yield). The product was obtained as dark yellow sticky liquid R_f = 0.48 (10% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 7.98-7.94 (m, 2H), 7.48-7.46 (m, 2H), 7.23-7.21 (m, 2H), 7.14-7.09 (m, 2H), 5.10 (dd, *J* = 10.6, 4.2 Hz, 1H), 4.33-4.24 (m, 2H), 3.99-3.92 (m, 1H), 3.38 (dd, *J* = 17.8, 4.3 Hz, 1H), 1.31 (t, *J* = 7.5 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 195.5, 191.8, 167.3, 164.8, 160.2, 134.3, 132.3, 132.24, 132.21, 130.9, 130.8, 130.5, 122.2, 116.0, 115.8, 62.7, 47.8, 42.9, 13.9.

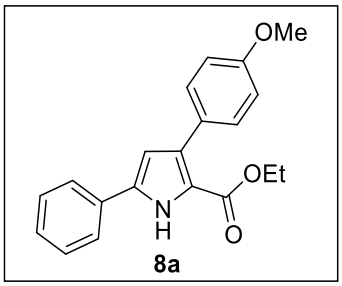


ethyl 3,5-bis(3-isopropoxy-4-methoxyphenyl)-2,5-dioxopentanoate (7v): 1.19g (82% yield). The product was obtained as light sponge type solid, R_f = 0.50 (30% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 7.57-7.54 (m, 1H), 7.48-7.47 (m, 1H), 6.87-6.84 (m, 4H), 5.06 (dd, *J* = 3.5, 10.9 Hz, 1H), 4.68-4.62 (m, 1H), 4.51-4.46 (m, 1H), 4.33-4.25 (m, 2H), 3.96-3.91 (m, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.41(dd, *J* = 3.9, 18.2 Hz, 1H), 1.41-1.34 (m, 12H),1.32 (t, *J* = 7.3 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 196.2, 192.3, 160.6, 152.2, 150.6, 149.9, 147.1, 128.8, 127.7, 122.9, 121.2, 115.6, 112.7, 112.5, 110.7, 71.34, 71.24, 62.5, 56.0, 47.9, 43.0, 26.9, 22.0, 21.9, 21.8, 14.0.

General experimental approach for the Construction of Ethyl 3,5-diaryl-1H-pyrrole-2-carboxylates (8):

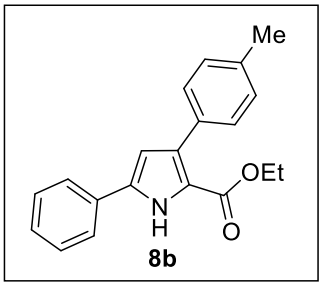


An over dried round-bottom flask was charged with compound **7** (1 mmol, 1.0 equivalent) and Ammonium acetate (1 mmol, 1.0 equivalent) in AcOH solution (3 mL). The mixture was dissolved at the room temperature. To this stirring solution, L-Proline (10.0 mol%) was added. The whole reaction mixture was stirred in a preheated bath maintaining temperature at 60 ℃ under nitrogen atmosphere for 1.2 h. Upon completion of the reaction (monitored using TLC), the reaction mixture was cooled to 25 ℃, and the pH of the solution was balanced to (neutral state) 7-8 by gradually putting on $NaHCO_3$. The water layer underwent extraction with Ethylacetate and the organic layer was separated, washed with brine and dried over anhydrous Na_2SO_4. The crude material was directly purified through column chromatography using *n*-hexane/EtOAc as eluents to afford the desired product pyrrole (**8)** as coloured solid.



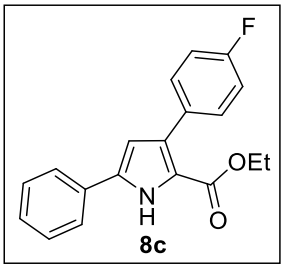
8a

ethyl 3-(4-methoxyphenyl)-5-phenyl-1H-pyrrole-2-carboxylate (8a): 231mg (90% yield). The product was obtained as light pink solid, R_f = 0.4 (5% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.42 (brs, 1H), 7.62-7.61 (m, 2H), 7.58-7.54 (m, 2H), 7.47-7.41 (m, 3H), 7.35-7.30 (m, 1H), 6.96-6.91 (m, 2H), 6.61 (d, *J* = 3.2 Hz, 1H), 4.29 (q, *J* = 7.1Hz, 2H), 3.86 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 161.3, 158.9, 135.4, 133.3, 131.1, 130.7, 129.1, 127.9, 127.5, 124.8, 118.3, 113.2, 109.8, 60.4, 55.3, 14.3. **HRMS** (ES) m/z 322.1445 $[M + H]^+$; calculated for $[C_{20}H_{18}NO_3 + H]^+$: 322.1450



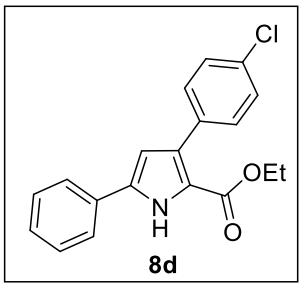
8b

ethyl 5-phenyl-3-(p-tolyl)-1H-pyrrole-2-carboxylate (8b): 219mg (90% yield). The product was obtained as white solid, R_f = 0.49 (10% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.74 (brs, 1H), 7.63-7.61 (m, 2H), 7.53-7.51 (m, 2H), 7.45-7.41 (m, 2H), 7.35-7.31 (m, 1H), 7.22-7.20 (m, 2H), 6.63 (d, *J* = 3.1 Hz, 1H), 4.29 (q, *J* = 7.7Hz, 2H), 2.41 (s, 3H), 1.28 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 161.3, 136.8, 135.4, 133.5, 132.1, 131.2, 129.4, 129.1, 128.4, 127.9, 124.8, 118.5, 109.9, 60.4, 21.3, 14.3. **HRMS** (ES) m/z 306.1497 $[M + H]^+$; calculated for $[C_{20}H_{18}NO_2 + H]^+$: 306.1501



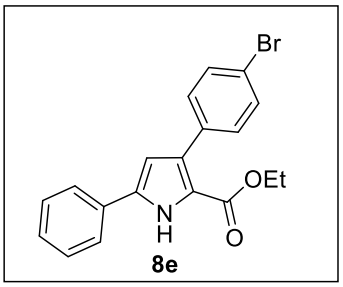
8c

ethyl 3-(4-fluorophenyl)-5-phenyl-1H-pyrrole-2-carboxylate (8c): 225mg (91% yield). The product was obtained as red solid, R_f = 0.50 (2% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.58 (brs, 1H), 7.63-7.61 (m, 2H), 7.58-7.55 (m, 2H), 7.45-7.41 (m, 2H), 7.35-7.33 (m, 1H), 7.10-7.06 (m, 2H), 6.60 (d, *J* = 3.06 Hz, 1H), 4.27 (q, *J* = 6.95 Hz, 2H), 1.29 (t, *J* = 7.37 Hz, 3H) **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 161.4, 161.3, 161.0, 135.6, 132.5, 131.21, 131.20, 131.1, 130.0, 129.1, 128.6, 128.1, 128.0, 124.9, 118.6, 114.6, 114.4, 109.9, 60.5, 14.2. **HRMS** (ES) m/z 310.1244 $[M + H]^+$; calculated for $[C_{19}H_{15}FNO_2 + H]^+$: 310.1250.



8d

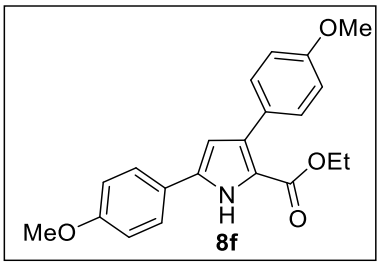
ethyl 3-(4-fluorophenyl)-5-phenyl-1H-pyrrole-2-carboxylate (8d): 237mg (91% yield). The product was obtained as dark pink solid, R_f = 0.48 (10% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.45 (brs, 1H), 7.61-7.59 (m, 2H), 7.54-7.52 (m, 2H), 7.43-7.41 (m, 2H), 7.36-7.33 (m, 3H), 6.59 (d, *J* = 3.2 Hz, 1H), 4.28 (q, *J* = 7.3 Hz, 2H), 1.27 (t, *J* = 6.95 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 161.1, 135.6, 133.6, 133.0, 132.2, 130.89, 130.86, 129.1, 128.0, 127.9, 124.8, 118.6, 109.8, 60.6, 14.3. **HRMS** (ES) m/z 326.0947 $[M + H]^+$; calculated for $[C_{19}H_{15}ClNO_2 + H]^+$: 326.0954.



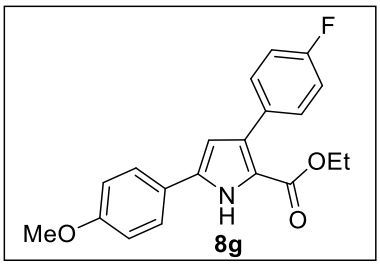
8e

ethyl 3-(4-bromophenyl)-5-phenyl-1H-pyrrole-2-carboxylate (8e): 267mg (90% yield). The product was obtained as pink solid, R_f = 0.46 (5% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.48 (brs, 1H), 7.62-7.59 (m, 2H), 7.52-7.50 (m, 2H), 7.49-7.32 (m, 1H), 7.36-7.32 (m, 1H), 6.60 (d, *J* = 2.92 Hz, 1H), 4.28 (q, *J* = 7.85 Hz, 2H), 1.27 (t, *J* = 7.57 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 161.1, 135.6, 134.0, 132.2, 131.2, 130.9, 130.8, 129.1, 128.1, 121.2, 118.6,

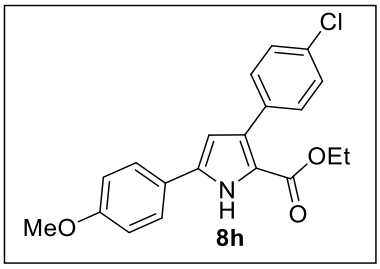
109.7, 60.6, 14.3. **HRMS** (ES) m/z 370.0443 $[M + H]^+$; calculated for $[C_{19}H_{15}BrNO_2 + H]^+$: 370.0450.



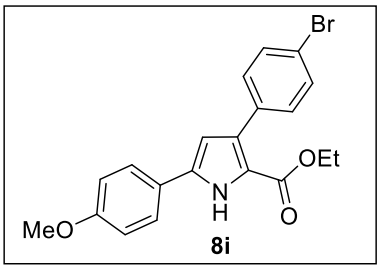
ethyl 3,5-bis(4-methoxyphenyl)-1H-pyrrole-2-carboxylate (8f): 241mg (86% yield). The product was obtained as blue solid, R_f = 0.52 (5% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.27 (brs, 1H), 7.56-7.52 (m, 4H), 6.97-6.92 (m, 4H), 6.50 (d, *J* = 3.11 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 3.85 (m, 6H), 1.28 (t, *J* = 7.01 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 161.3, 159.5, 158.8, 135.5, 133.4, 130.7, 127.6, 126.2, 124.0, 117.7, 114.5, 113.1, 108.9, 60.3, 55.4, 55.3, 14.4. **HRMS** (ES) m/z 352.1551 $[M + H]^+$; calculated for $[C_{21}H_{20}NO_4 + H]^+$: 352.1555.



ethyl 3-(4-fluorophenyl)-5-(4-methoxyphenyl)-1H-pyrrole-2-carboxylate (8g): 230mg (85% yield). The product was obtained as violet solid, R_f = 0.50 (10% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.42 (brs, 1H), 7.57-7.52 (m, 4H), 7.09-7.04 (m, 2H), 6.97-6.94 (m, 2H), 6.47 (d, *J* = 3.15 Hz, 1H), 4.26 (q, *J* = 6.35 Hz, 2H), 3.84 (s, 3H), 1.25 (t, *J* = 7.26 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 161.2, 159.6, 135.7, 132.6, 131.2, 126.2, 123.8, 117.9, 114.6, 114.5, 114.4, 113.8, 109.0, 60.4, 55.4, 14.3. **HRMS** (ES) m/z 340.1349 $[M + H]^+$; calculated for $[C_{20}H_{17}FNO_3 + H]^+$: 340.1355.

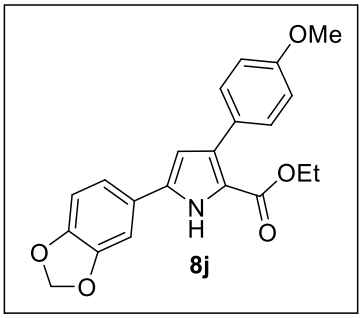


ethyl 3-(4-chlorophenyl)-5-(4-methoxyphenyl)-1H-pyrrole-2-carboxylate (8h): 248mg (87% yield). The product was obtained as Dark violet solid, R_f = 0.48 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.34 (brs, 1H), 7.54-7.51 (m, 4H), 7.36-7.34 (m, 2H), 6.97-6.95 (m, 2H), 6.49(d, *J* = 3.1 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 161.1, 159.6, 135.7, 133.7, 132.9, 132.3, 130.8, 127.8, 126.2, 123.7, 118.0, 114.5, 108.9, 60.4, 55.4, 14.3. **HRMS** (ES) m/z 356.1053 $[M + H]^+$; calculated for $[C_{20}H_{17}ClNO_3 + H]^+$: 356.1059.



8i

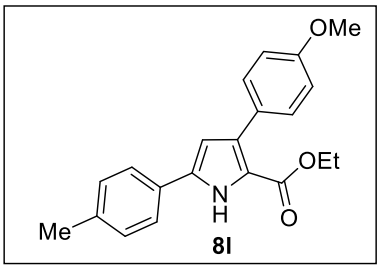
ethyl 3-(4-bromophenyl)-5-(4-methoxyphenyl)-1H-pyrrole-2-carboxylate (8i): 286mg (86% yield). The product was obtained as dark pink solid, R_f = 0.49 (10% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.33 (brs, 1H), 7.53-7.50 (m, 2H), 7.49-7.45 (m, 4H), 6.97-6.95 (m, 2H), 6.49 (d, *J* = 3.05 Hz, 1H), 4.27 (q, *J* = 7.16 Hz, 2H), 3.85 (s, 3H), 1.27 (t, *J* = 7.05 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 161.1, 159.6, 135.7, 134.1, 132.2, 131.2, 130.8, 126.2, 123.7, 121.1, 118.0, 114.5, 108.9, 60.5, 55.4, 14.3. **HRMS** (ES) m/z 400.0548 $[M + H]^+$; calculated for $[C_{20}H_{17}BrNO_2 + H]^+$: 400.0568.



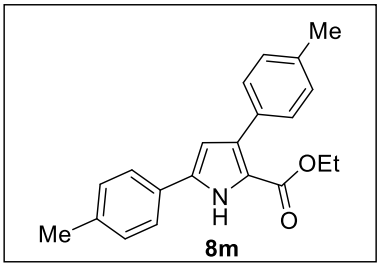
8j

ethyl 5-(benzo[d][1,3]dioxol-5-yl)-3-(3-bromophenyl)-1H-pyrrole-2-carboxylate (8j): 240mg (82% yield). The product was obtained as dark blue solid, R_f = 0.49 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.27 (brs, 1H), 7.54-7.52 (m, 2H), 7.09-7.07 (m, 2H), 6.93-6.91 (m, 2H), 6.87-6.85 (m, 1H), 6.47 (d, *J* = 3.0 Hz, 1H), 6.0 (s, 2H), 4.28 (q, *J* = 7.1Hz, 2H), 3.87 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 161.3, 158.9, 148.3, 147.5, 135.4, 133.3,

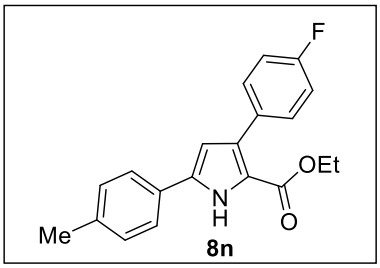
130.6, 127.5, 125.5, 118.6, 117.8, 113.1, 113.1, 109.3, 108.9, 105.6, 101.4, 60.3, 55.3, 14.3. **HRMS** (ES) m/z 366.1342 $[M + H]^+$; calculated for $[C_{21}H_{18}NO_5 + H]^+$: 366.1347.



ethyl 3-(4-methoxyphenyl)-5-(p-tolyl)-1H-pyrrole-2-carboxylate (8l): 236mg (88% yield). The product was obtained as light pink-white solid, R_f = 0.46 (5% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.40 (brs, 1H), 7.56-7.52 (m, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.94-6.90 (m, 2H), 6.55 (d, *J* = 2.9 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 2.37 (s, 3H), 1.27 (t, *J* = 6.8 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 161.3, 158.8, 137.9, 135.6, 133.3, 130.7, 129.7, 128.4, 127.6, 124.7, 117.9, 113.1, 109.4, 60.3, 55.3, 21.3, 14.3. **HRMS** (ES) m/z 336.1600 $[M + H]^+$; calculated for $[C_{21}H_{20}NO_3 + H]^+$: 336.1600.

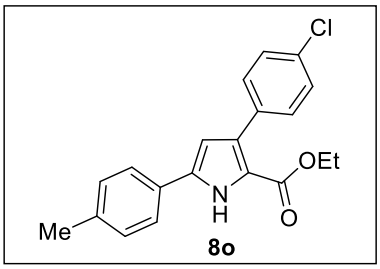


ethyl 3,5-di-p-tolyl-1H-pyrrole-2-carboxylate (8m): 222mg (87% yield). The product was obtained as dark pink solid, R_f = 0.49 (5% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.38 (brs, 1H), 7.52-7.49 (m, 4H), 7.25-7.20 (m, 4H), 6.58 (d, *J* = 3.1 Hz, 1H), 4.29 (q, *J* = 7.0 Hz, 2H), 2.40-2.39 (m, 6H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 161.3, 137.8, 136.7, 135.6, 133.6, 132.0, 129.7, 129.4, 128.41, 128.40, 124.7, 118.1, 109.5, 60.3, 21.3, 14.3. **HRMS** (ES) m/z 320.1651 $[M + H]^+$; calculated for $[C_{21}H_{20}NO_2 + H]^+$: 320.1657.



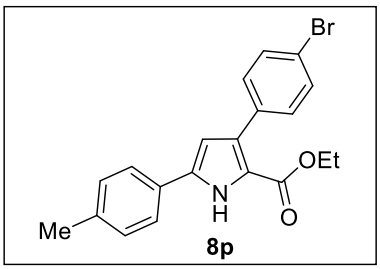
8n

ethyl 3-(4-fluorophenyl)-5-(p-tolyl)-1H-pyrrole-2-carboxylate (8n): 230mg (89% yield). The product was obtained as bright pink solid, R_f = 0.50 (5% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.38 (brs, 1H), 7.57-7.53 (m, 2H), 7.50-7.48 (m, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.08-7.04 (m, 2H), 6.54 (d, *J* = 3.0 Hz, 1H), 4.27 (q, *J* = 7.4 Hz, 2H), 2.38 (s, 3H), 1.26 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 163.4, 161.2, 160.9, 138.0, 135.7, 132.5, 131.19, 131.11, 129.8, 128.2, 124.7, 118.2, 114.6, 114.4, 109.4, 60.4, 21.3, 14.3. **HRMS** (ES) m/z 324.1402 $[M + H]^+$; calculated for $[C_{20}H_{17}FNO_2 + H]^+$: 324.1406.



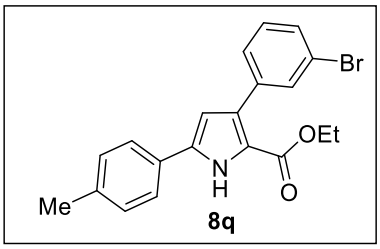
8o

ethyl 3-(4-chlorophenyl)-5-(*p*-tolyl)-1H-pyrrole-2-carboxylate (8o): 236mg (87% yield). The product was obtained as violet solid, R_f = 0.52 (5% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.55 (brs, 1H), 7.55-7.50 (m, 4H), 7.37-7.34 (m, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 6.56 (d, *J* = 3.0 Hz, 1H) 4.28 (q, *J* = 7.0 Hz, 2H), 2.39 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 161.2, 138.1, 135.9, 133.7, 132.9, 132.2, 130.9, 129.8, 128.2, 127.8, 124.8, 118.3, 109.4, 60.5, 21.3, 14.3. **HRMS** (ES) m/z 340.1109 $[M + H]^+$; calculated for $[C_{20}H_{17}ClNO_2 + H]^+$: 340.1111.

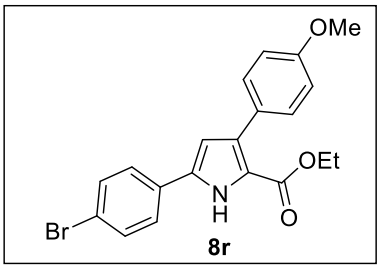


8p

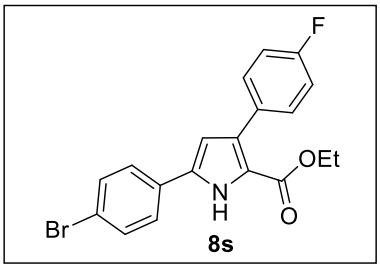
ethyl 3-(4-bromophenyl)-5-(p-tolyl)-1H-pyrrole-2-carboxylate (8p): 270mg (88% yield). The product was obtained as white solid, R_f = 0.42 (10% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.33 (brs, 1H), 7.51-7.46 (m, 6H), 7.25-7.23 (m, 2H), 6.55 (d, *J* = 3.0 Hz, 1H), 4.28 (q, *J* = 7.09 Hz, 2H), 2.39 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 161.0, 138.1, 135.7, 134.1, 132.2, 131.2, 130.8, 129.8, 128.0, 124.7, 121.2, 118.2, 109.3, 60.5, 21.3, 14.3. **HRMS** (ES) m/z 384.0600 $[M + H]^+$; calculated for $[C_{20}H_{17}BrNO_2 + H]^+$: 384.0606.



ethyl 3-(3-bromophenyl)-5-(p-tolyl)-1H-pyrrole-2-carboxylate (8q): 270mg (88% yield). The product was obtained as pale pink solid, R_f = 0.44 (5% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.65 (brs, 1H), 7.76-7.55 (m, 1H), 7.50 (d, *J* = 8.0 Hz, 3H), 7.45-7.43 (m, 1H), 7.25-7.21 (m, 3H), 6.56 (d, *J* = 3.0 Hz, 1H), 4.26 (q, *J* = 7.4 Hz, 2H), 2.37 (s, 3H), 1.26 (t, *J* = 6.8 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 161.4, 138.1, 137.4, 136.0, 132.7, 131.6, 129.9, 129.8, 129.18, 129.17, 128.10, 124.8, 121.6, 118.5, 109.4, 60.6, 21.3, 14.2. **HRMS** (ES) m/z 384.0602 $[M + H]^+$; calculated for $[C_{20}H_{17}BrNO_2 + H]^+$: 384.0606.

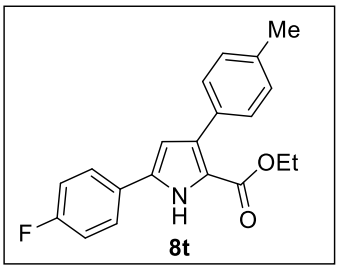


ethyl 5-(4-bromophenyl)-3-(4-methoxyphenyl)-1H-pyrrole-2-carboxylate (8r): 301mg (94% yield). The product was obtained as light orange solid, R_f = 0.46 (10% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.52 (brs, 1H), 7.54-7.51 (m, 4H), 7.49-7.45 (m, 2H), 6.94-6.92 (m, 2H), 6.58 (d, *J* = 3.2 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 161.3, 158.9, 134.3, 133.3, 132.2, 130.7, 130.1, 127.3, 126.3, 121.7, 118.8, 113.2, 110.1, 60.5, 55.3, 14.3. **HRMS** (ES) m/z 400.0554 $[M + H]^+$; calculated for $[C_{20}H_{17}NO_3 + H]^+$: 400.0555.



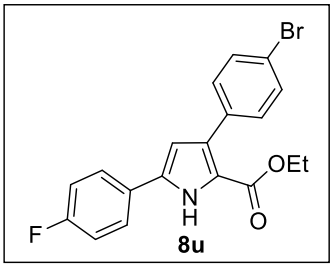
8s

ethyl 5-(4-bromophenyl)-3-(4-fluorophenyl)-1H-pyrrole-2-carboxylate (8s): 300mg (94% yield). The product was obtained as orange solid, R_f = 0.50 (5% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.59 (brs, 1H), 7.55-7.51 (m, 4H), 7.48-7.46 (m, 2H), 7.09-7.05 (m, 3H), 6.57 (d, *J* = 3.1 Hz, 1H), 4.26 (q, *J* = 7.1Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ:163.4, 161.2, 161.0, 134.4, 132.5, 132.2, 131.2, 131.1, 130.94, 130.90, 129.9, 126.3, 121.9, 119.0, 114.7, 114.5, 110.2, 60.6, 14.2. **HRMS** (ES) m/z 388.0352 $[M + H]^+$; calculated for $[C_{19}H_{14}BrFNO_2 + H]^+$: 388.0355.



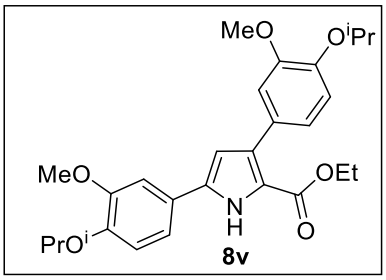
8t

ethyl 5-(4-fluorophenyl)-3-(*p*-tolyl)-1H-pyrrole-2-carboxylate (8t): 245mg (95% yield). The product was obtained as white solid, R_f = 0.50 (20% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.58 (brs, 1H), 7.60-7.57 (m, 2H), 7.50-7.48 (m, 2H), 7.22-7.20 (m, 2H), 7.14-7.10 (m, 2H), 6.55 1 (d, *J* = 3.08 Hz, 1H), 4.28 (q, *J* = 7.3Hz, 2H), 2.40 (s, 3H), 1.27 (t, *J* = 7.28 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 163.7, 161.4, 161.2, 136.9, 134.6, 133.6, 132.0, 129.4, 128.4, 127.6, 127.5, 126.7, 126.6, 118.6, 116.2, 115.9, 109.8, 60.5, 21.3, 14.3.



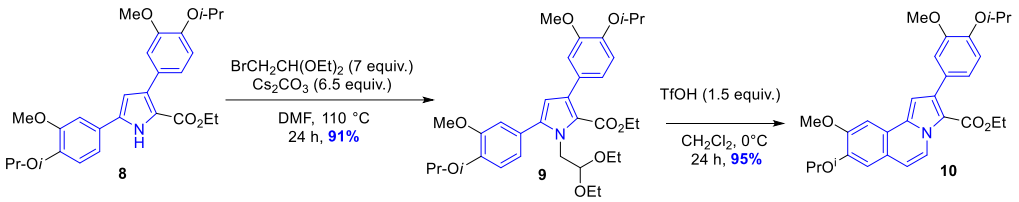
8u

ethyl 3-(4-bromophenyl)-5-(4-fluorophenyl)-1H-pyrrole-2-carboxylate (8u): 295mg (95% yield). The product was obtained as dark blue solid, R_f = 0.52 (5% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.40 (brs, 1H), 7.58-7.55 (m, 2H), 7.52-7.44 (m, 4H), 7.15-7.11 (m, 2H), 6.52 (d, *J* = 3.0 Hz, 1H), 4.28 (q, *J* = 6.4 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 163.8, 161.3, 161.0, 134.7, 133.9, 132.2, 131.2, 130.8, 127.2, 126.9, 126.6, 121.3, 118.6, 116.3, 109.6, 60.6, 14.3.

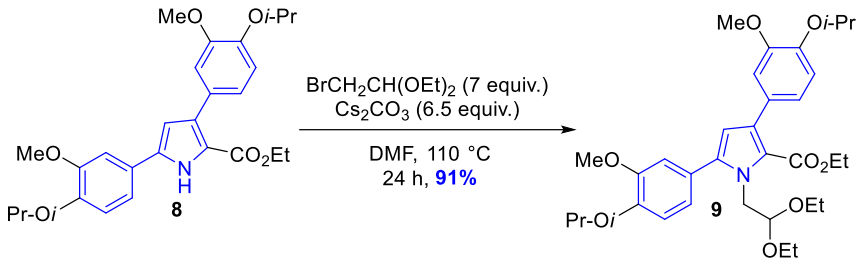


ethyl 3,5-bis(4-isopropoxy-3-methoxyphenyl)-1H-pyrrole-2-carboxylate (8v): 348 mg (93% yield). The product was obtained as yellow solid, R_f = 0.50 (30% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.33 (brs, 1H), 7.19-7.18 (m, 1H), 7.14-7.09 (m, 3H), 6.95-6.90 (m, 2H), 6.52 (d, *J* = 3.1 Hz, 1H), 4.60-4.54 (m, 2H), 4.27 (q, *J* = 7.18 Hz, 2H), 3.92 (s, 3H), 3.89 (s, 3H), 1.40-1.38 (m, 12H), 1.26 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 161.4, 150.7, 149.5, 147.5, 146.6, 135.7, 133.5, 128.3, 124.5, 121.9, 117.8, 117.4, 115.8, 115.1, 113.8, 109.2, 109.1, 71.5, 71.4, 60.3, 56.2, 56.1, 22.2, 22.1, 14.0. **HRMS** (ES) m/z 468.2389 $[M + H]^+$; calculated for $[C_{27}H_{32}NO_6 + H]^+$: 468.2393.

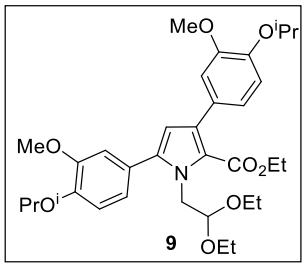
Synthetic Scheme for the construction of Pyrrolo[2,1-a]isoquinoline(10 and 11):



Synthetic Procedure for *N*-Alkylated pyrrole (8):



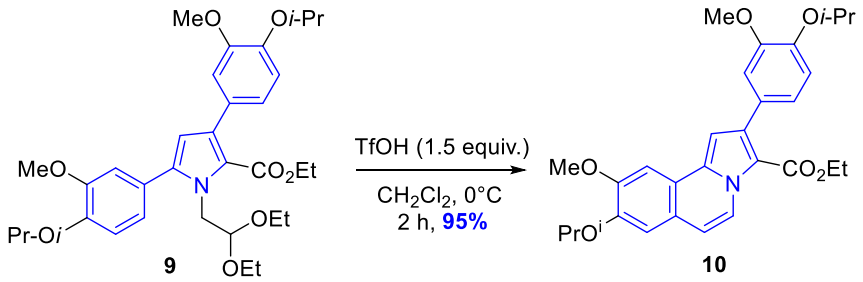
In an oven-dried round bottom flask, compound **6v** (300 mg, 0.64 mmol, 1 equiv.) was taken in dry DMF. In this solution, Bromoacetaldehyde diethyl acetal (885 mg, 4.49 mmol, 7.0 equiv.) and cesium carbonate (1.3 g, 4.17 mmol, 6.5 equiv.) were added subsequently at the room temperature. The whole reaction mixture was kept at preheated oil bath maintaining the temperature 110 ℃, for 24 hrs. The TLC of crude reaction mixture indicated the complete conversion of the starting material. Then the product was set for separation using a separatory funnel using EtOAc and the organic layer was subsequently extracted with the help of water, dried over anhydrous sodium sulphate, and purified using vacuum pump. The product was then purified via column chromatography using a mixture of EtOAc and Hexane to obtain the *N*-alkylated product **8**.



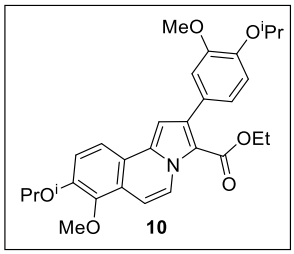
Ethyl 1-(2,2-diethoxyethyl)-3,5-bis(4-isopropoxy-3-methoxyphenyl)-1H-pyrrole-2-carboxylate (9): 340 mg (91% yield). The product was obtained as yellow jelly compound, R_f =

0.50 (20% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 7.12-7.11 (m, 1H), 7.04-7.01 (m, 1H), 6.97-6.87(m, 5H), 4.68-4.65(q, *J* = 7.1 Hz, 2H), 3.87-3.86 (m, 6H), 3.58-3.54 (m, 2H), 3.36-3.32 (m, 2H), 1.39 (t, *J* = 5.9 Hz, 12H), 1.12-1.07 (m, 9H); **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 162.3, 149.9, 149.5, 147.3, 146.2, 141.2, 133.9, 130.1, 125.1, 122.6, 121.9, 119.2, 115.3, 115.1, 113.9, 113.8, 111.9, 102.6, 71.5, 71.3, 63.6, 59.9, 56.1, 56.0, 48.8, 22.2, 22.1, 15.25, 15.20, 14.0. **HRMS** (ES) m/z 584.3526 $[M + H]^+$; calculated for $[C_{33}H_{45}NO_8 + H]^+$: 584.3230.

Synthetic Procedure for Pyrrole fused isoquinoline scaffold (10):



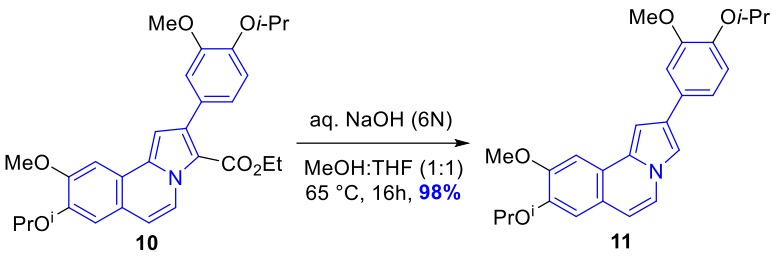
Under nitrogen atmosphere, compound **9** (310mg, 0.53 mmol, 1equiv.) was taken into an oven dried round-bottom flask and dissolved in DCM. To this, a solution of TfOH in DCM (120mg, 0.80 mmol, 1.5 equiv.) was added, while stirring at 0 °C. The reaction mixture was maintained from 0 °C to room temperature for 2 hrs. Upon completion (judged by checking TLC), the reaction was quenched with sodium bicarbonate solution, and the product was extracted into the organic layer using a separatory funnel. The organic layer was then purified by column chromatography using a mixture of EtOAc and Hexane to obtain compound **10**.



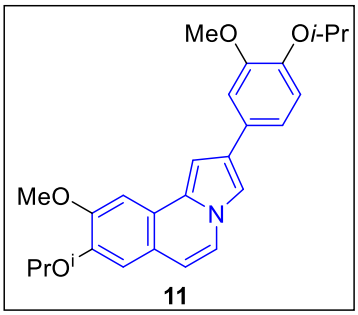
ethyl 8-isopropoxy-2-(4-isopropoxy-3-methoxyphenyl)-7-methoxypyrrolo[2,1-a]isoquinoline-3-carboxylate (10): 247mg (95% yield). The product was obtained as yellow liquid, R_f = 0.54 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.25-9.23 (m, 1H), 7.4 (s, 1H), 7.08-7.03 (m, 3H), 6.93(t, *J* = 8.3Hz, 2H), 6.86-6.85 (m, 1H), 4.73-4.67(m, 1H), 4.61-4.55 (m, 1H), 4.22(q, *J* = 7.4 Hz, 2H), 4.00 (s, 3H), 3.89 (s, 3H), 1.47-1.45(m, 6H), 1.42-1.40 (m, 6H), 1.12 (t, *J* = 6.8 Hz, 3H), **^{13}C-NMR (**100 MHz, $CDCl_3$**)** δ: 162.1, 150.9, 149.9, 148.3, 146.5, 136.9,

134.1, 130.1, 123.9, 122.9, 122.3, 118.9, 115.3, 114.3, 112.2, 111.9, 110.6, 104.9, 102.3, 71.6, 71.3, 59.7, 56.1, 56.0, 22.1, 21.9, 14.0. **HRMS** (ES) m/z 492.2388 $[M + H]^+$; calculated for $[C_{29}H_{33}NO_6 + H]^+$: 492.2393.

Synthetic Procedure for the hydrolysis of Ester group to Acid (11):



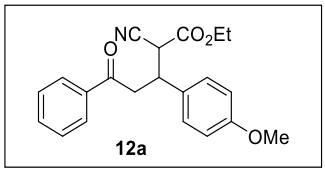
In an oven-dried round bottom flask, compound **10** (100 mg, 0.20 mmol,1 equiv.) was taken in 1:1 mixture of MeOH and THF (total 3mL). To this solution 0.4mL of 6N NaOH solution was added subsequently at the room temperature. The whole reaction mixture was kept at preheated oil bath maintaining the temperature 65 ℃, for 16 hrs. The TLC of crude reaction mixture indicated the complete conversion of the starting material. The work up process was carried out using the 3N HCl (pH maintaining over 2-3) and then the product was set for separation using a separatory funnel using EtOAc and the organic layer was subsequently extracted with the help of water, dried over anhydrous sodium sulphate, and purified using vacuum pump to yield the compound **11** in 98% yield.

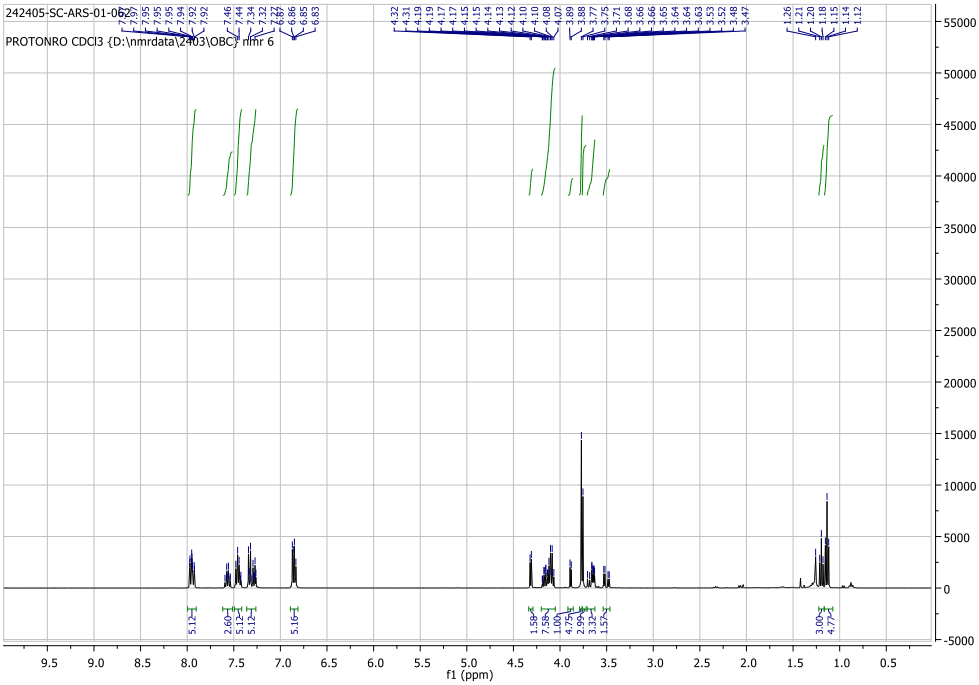


8-isopropoxy-2-(4-isopropoxy-3-methoxyphenyl)-9-methoxypyrrolo[2,1-a]isoquinoline (11): 82 mg (98% yield). The product was obtained as dark brown liquid, R_f = 0.52 (15% EtOAc in n-hexane). **^{1}H-NMR** (400 MHz, DMSO-d_6) δ: 7.93 (d, J = 7.3 Hz, 1H), 7.81-7.80 (m, 1H), 7.61 (s, 1H), 7.32-7.31 (m, 2H), 7.23-7.20 (m, 2H), 6.96-6.94 (m, 2H), 6.77 (d, J = 6.8 Hz, 1H), 4.67-4.61 (m, 1H), 4.55-4.49 (m, 1H), 3.93-3.86 (m, 6H), 1.31 (d, J = 5.9 Hz, 6H), 1.26 (d, J = 5.9 Hz, 6H);

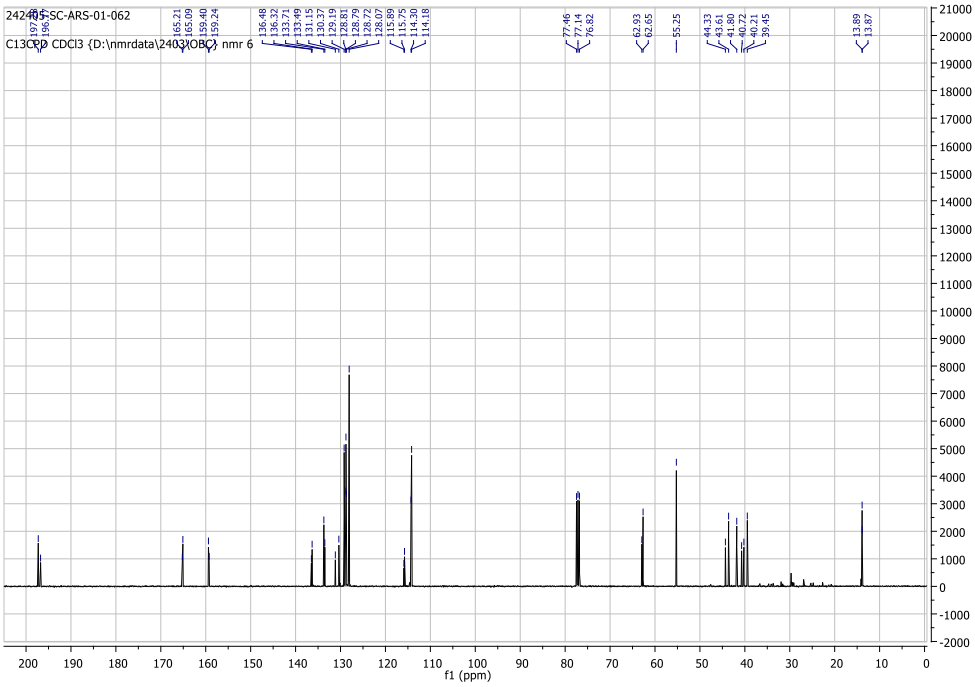
^{13}C-NMR (100 MHz, DMSO-d_6**)** δ: 150.9, 150.8, 146.4, 145.8, 130.3, 129.0, 127.2, 123.5, 121.0, 120.3, 118.0, 116.8, 112.2, 111.4, 110.5, 110.3, 104.6, 96.7, 70.9, 70.7, 56.2, 56.0, 22.5, 22.4.

Spectral Graphics





^{1}H-NMR (400 MHz, $CDCl_3$)



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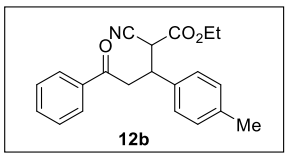
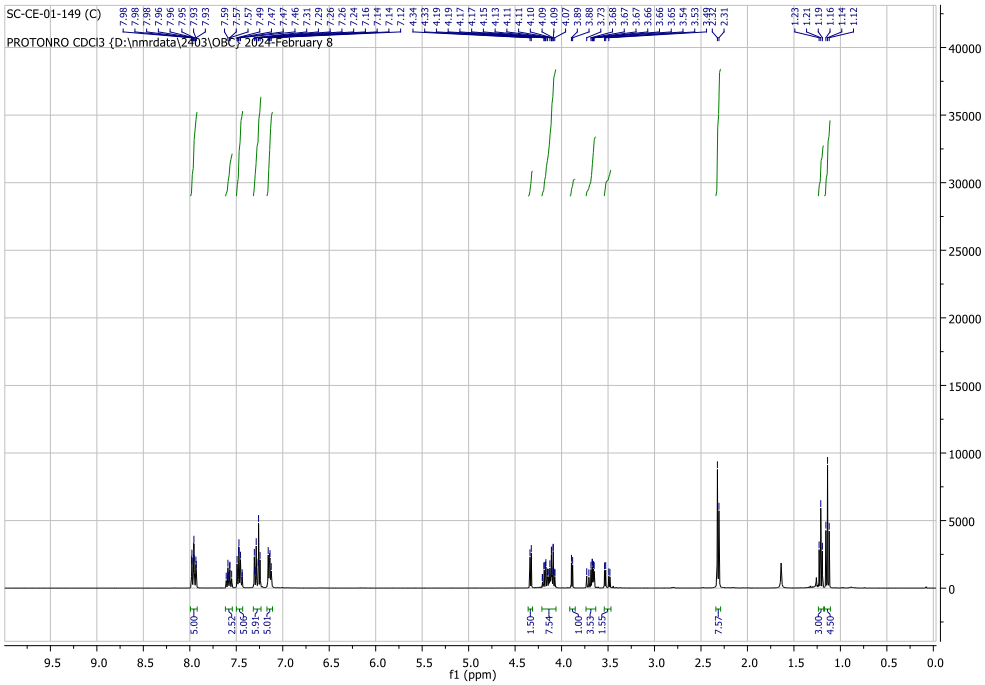


12b



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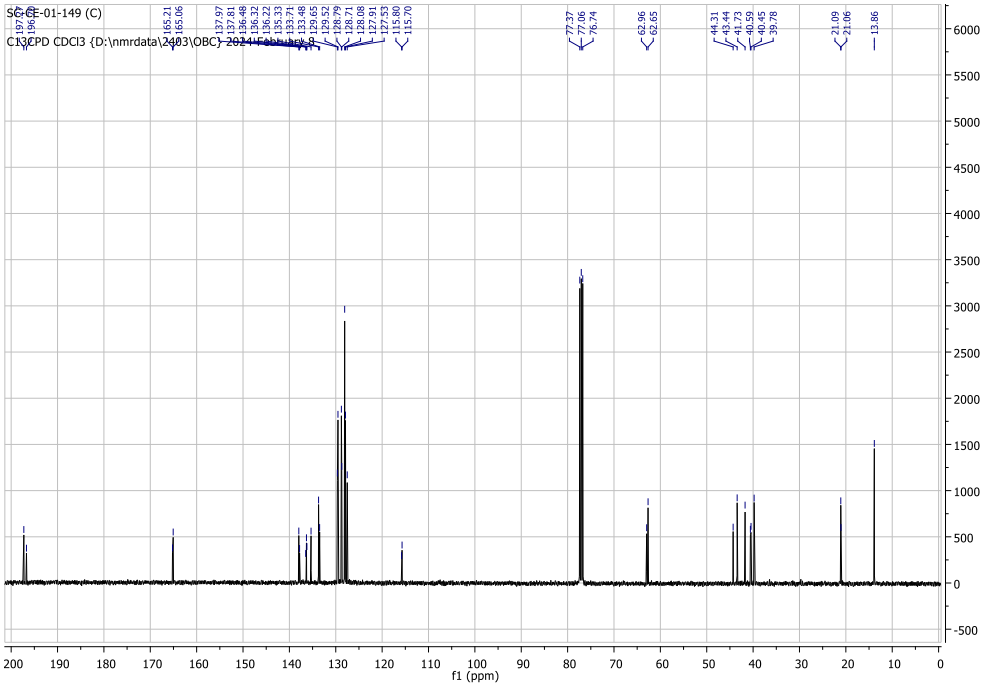

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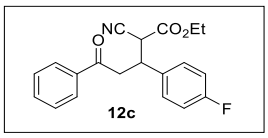

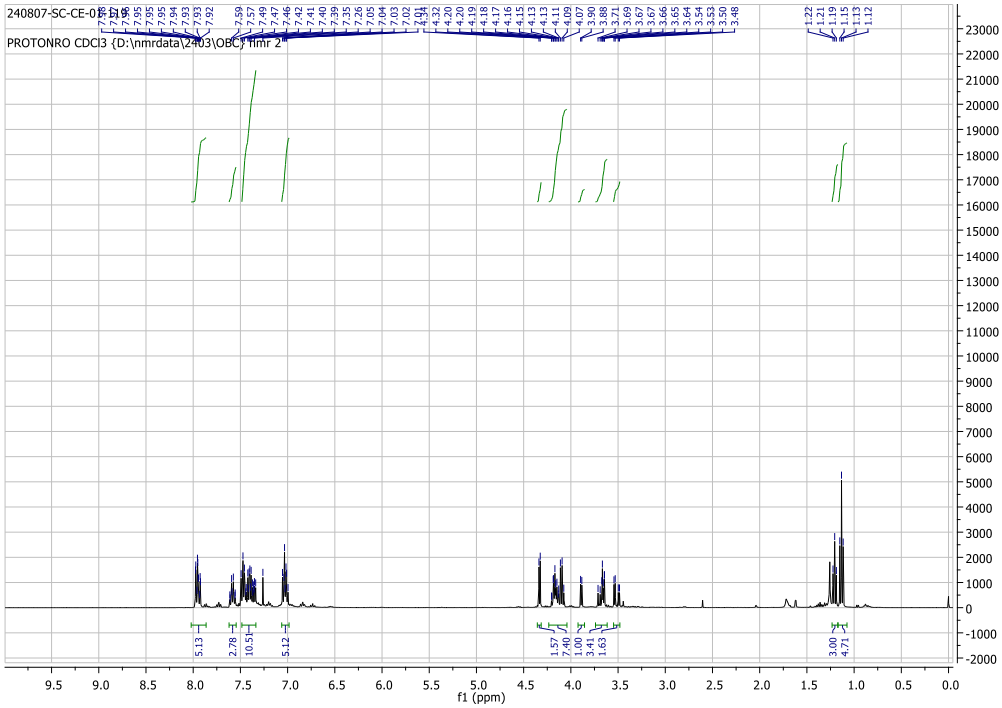

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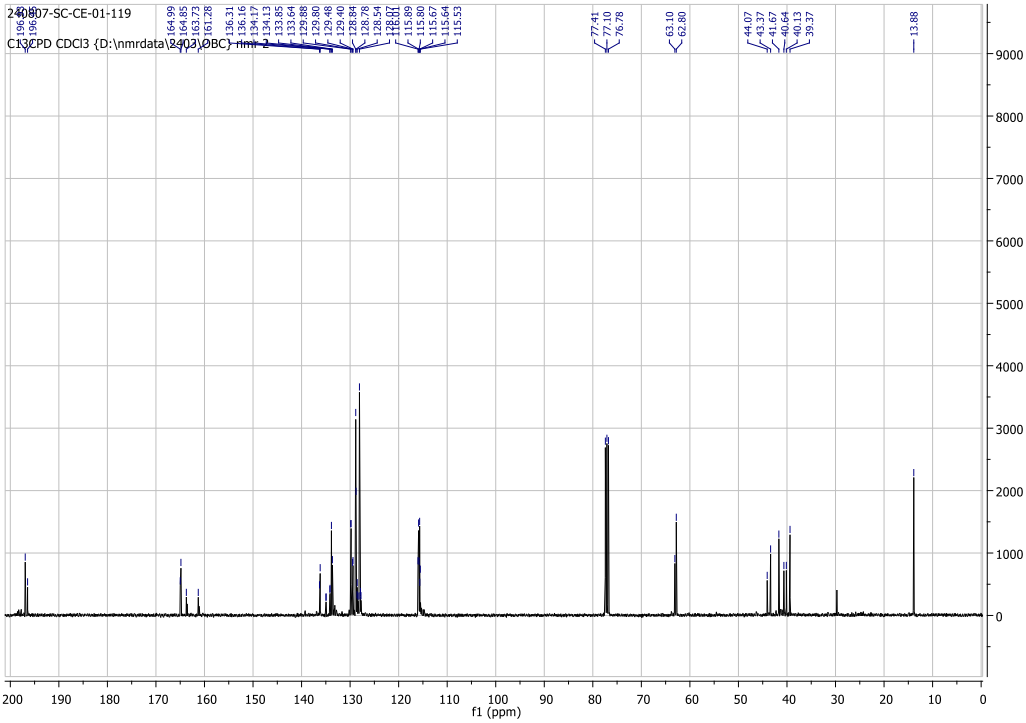

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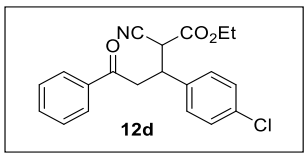

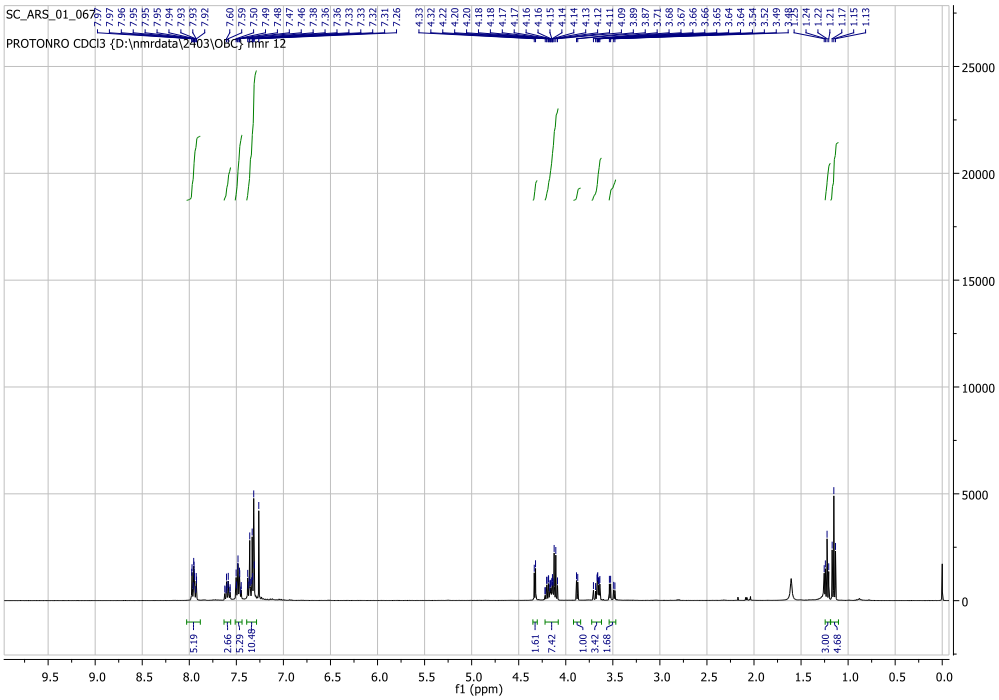

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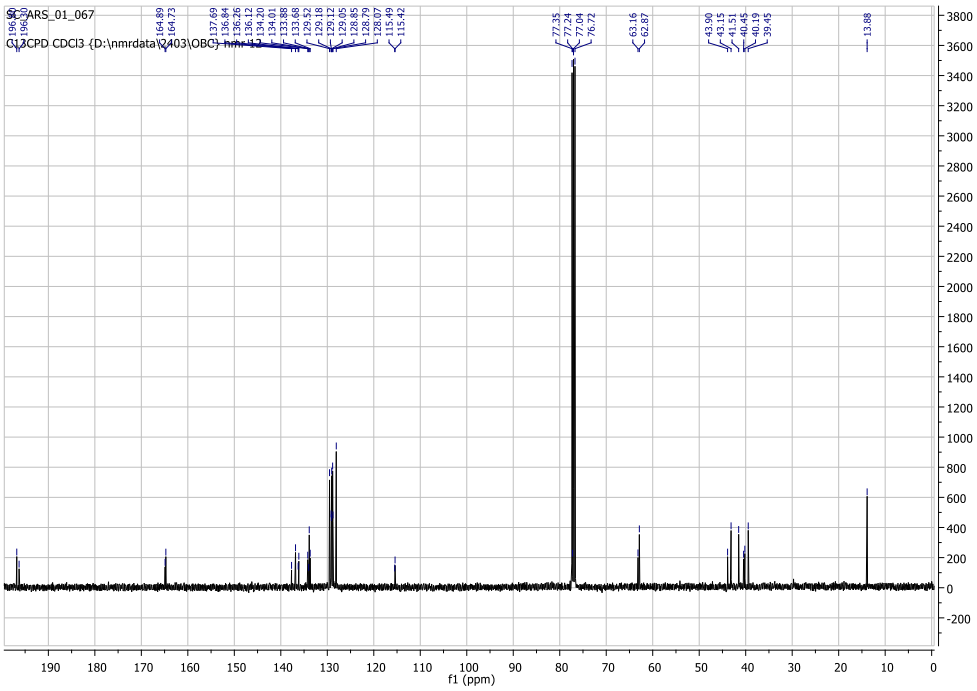

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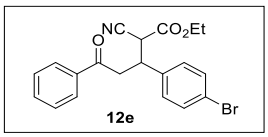

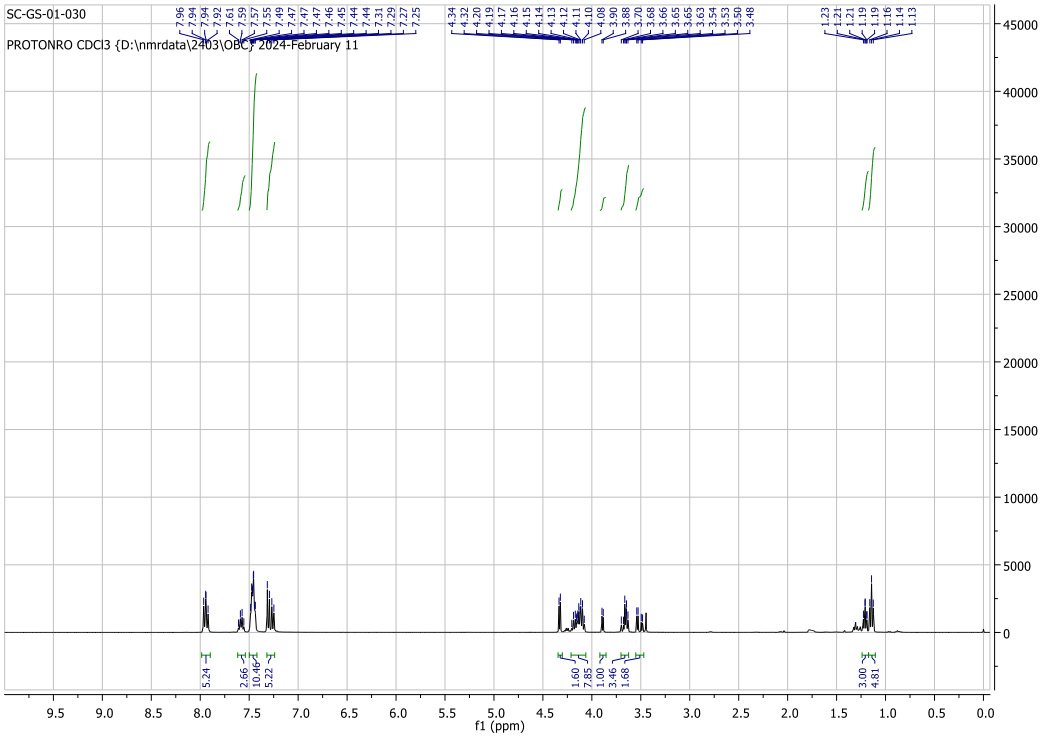

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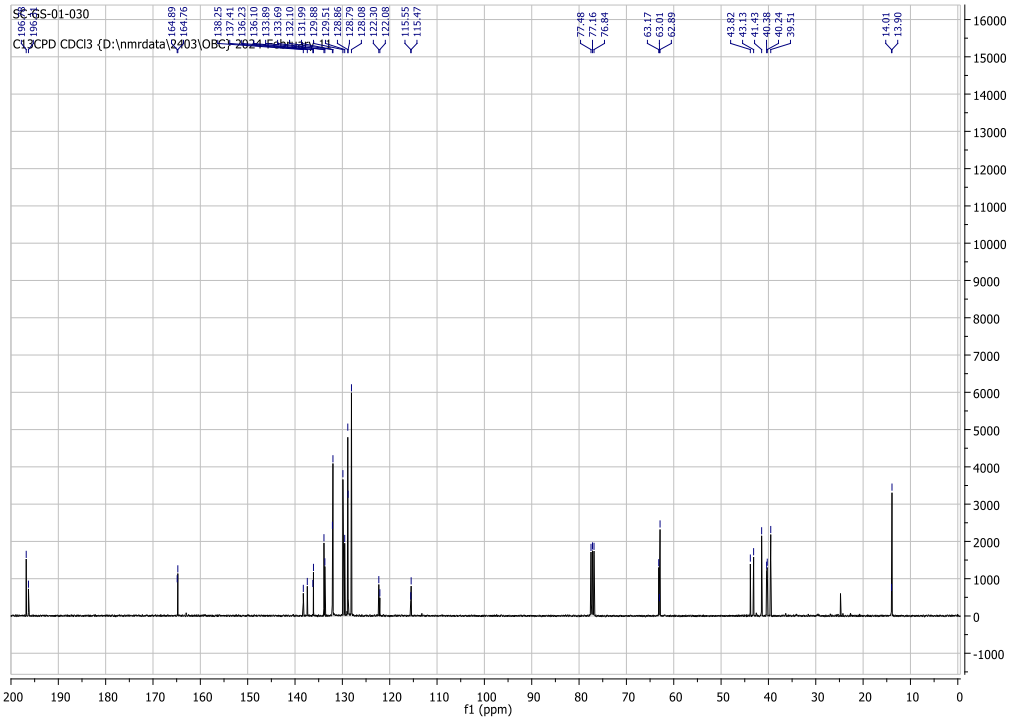

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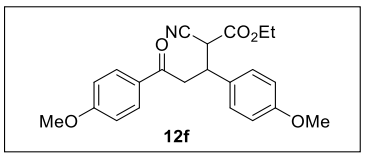

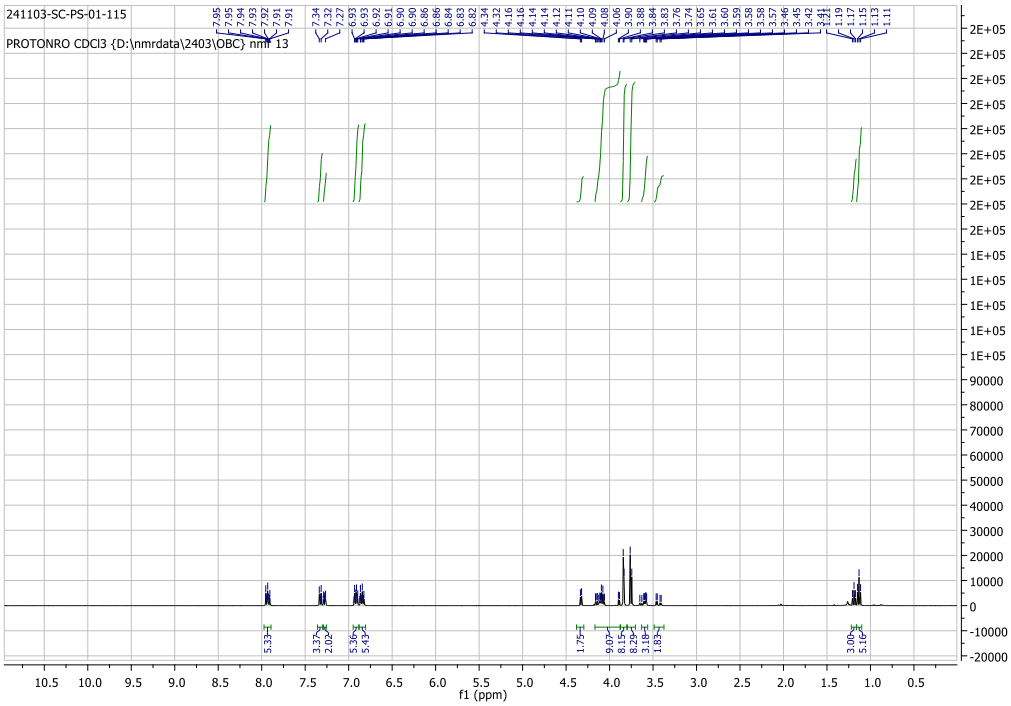

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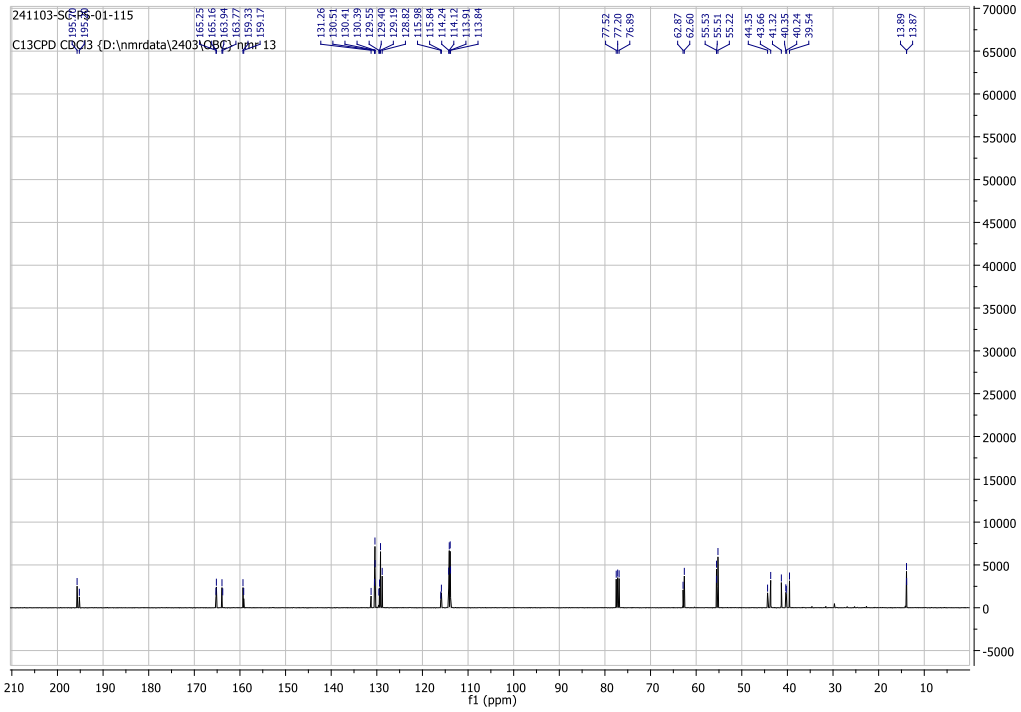

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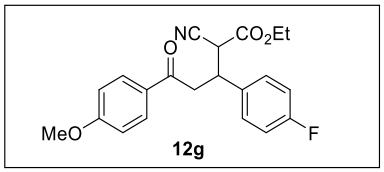

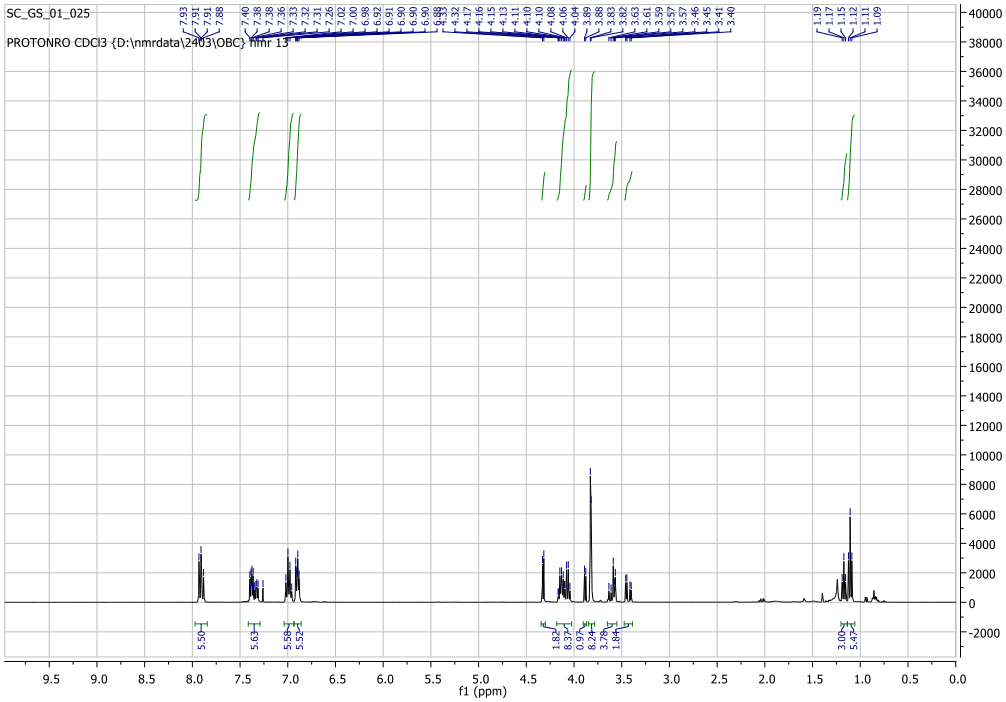

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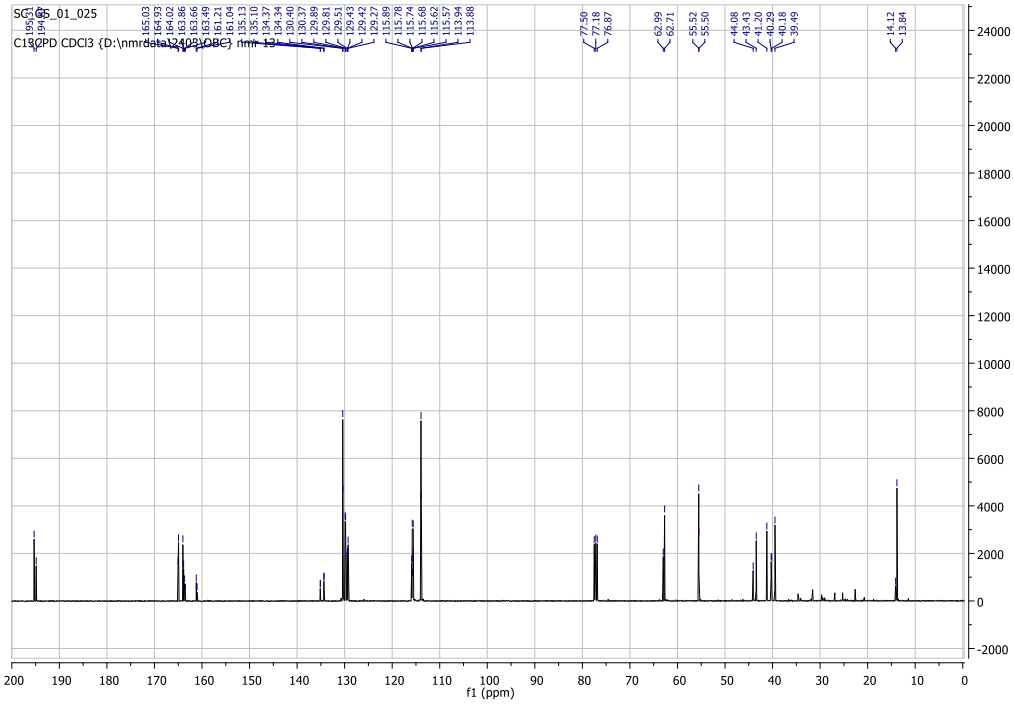

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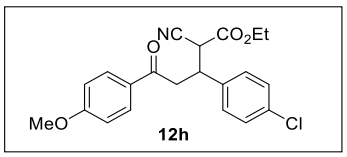

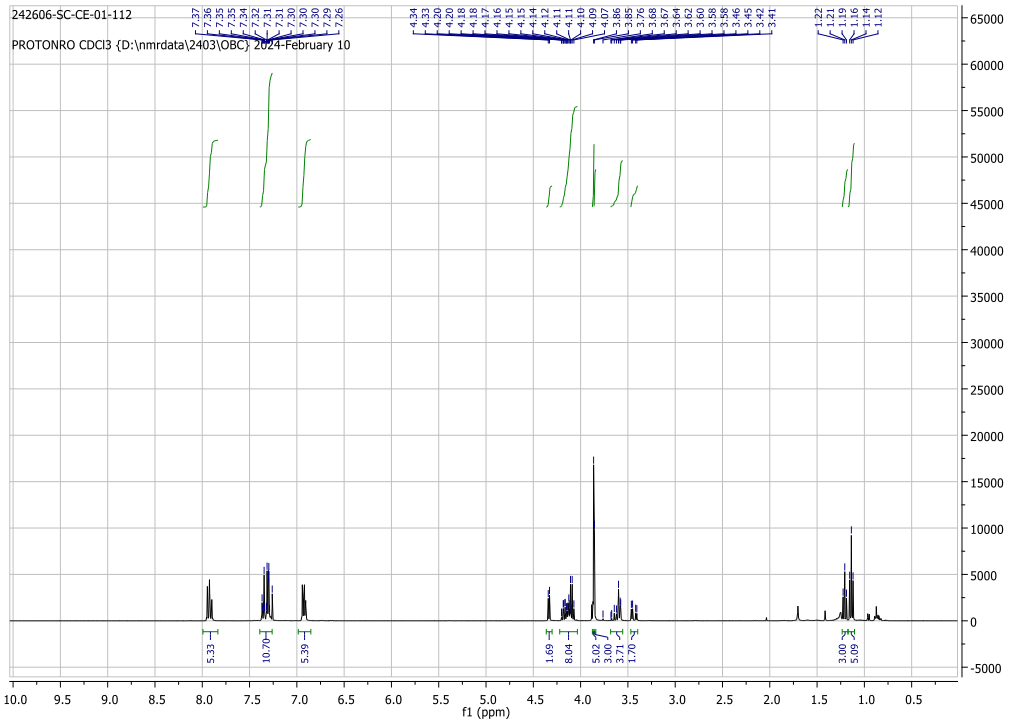

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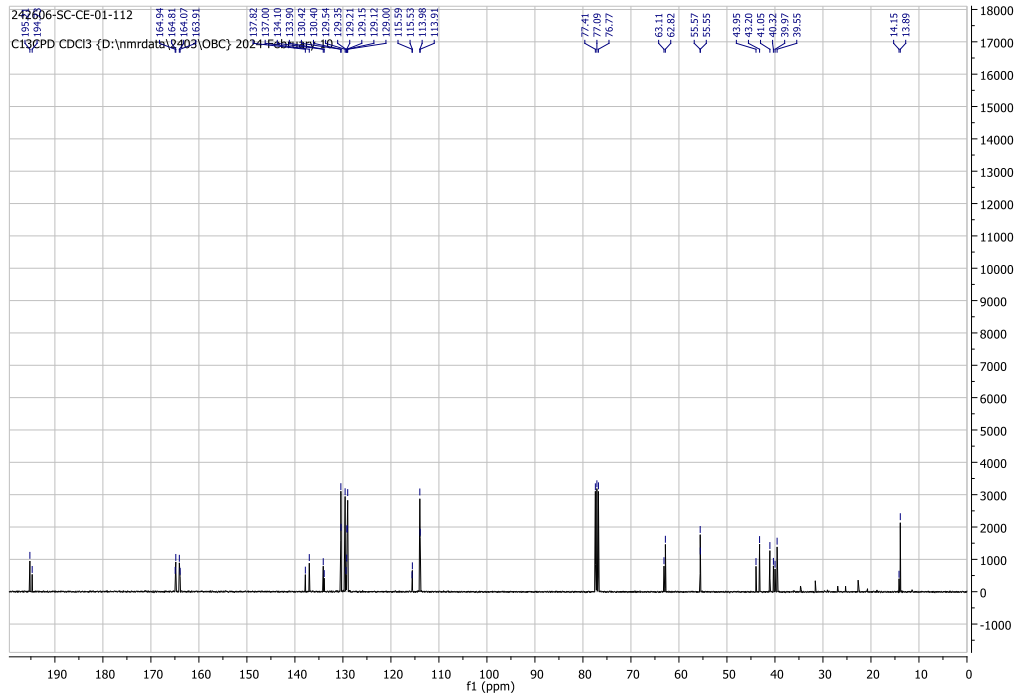

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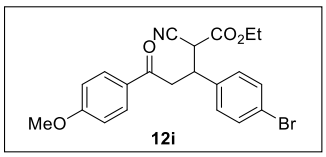

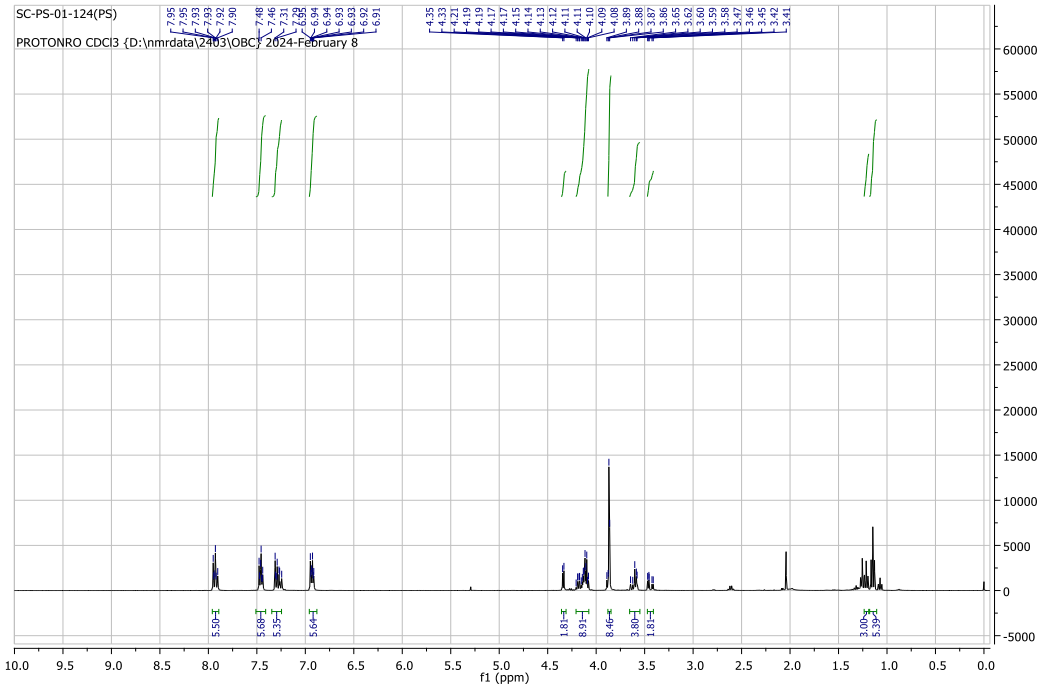

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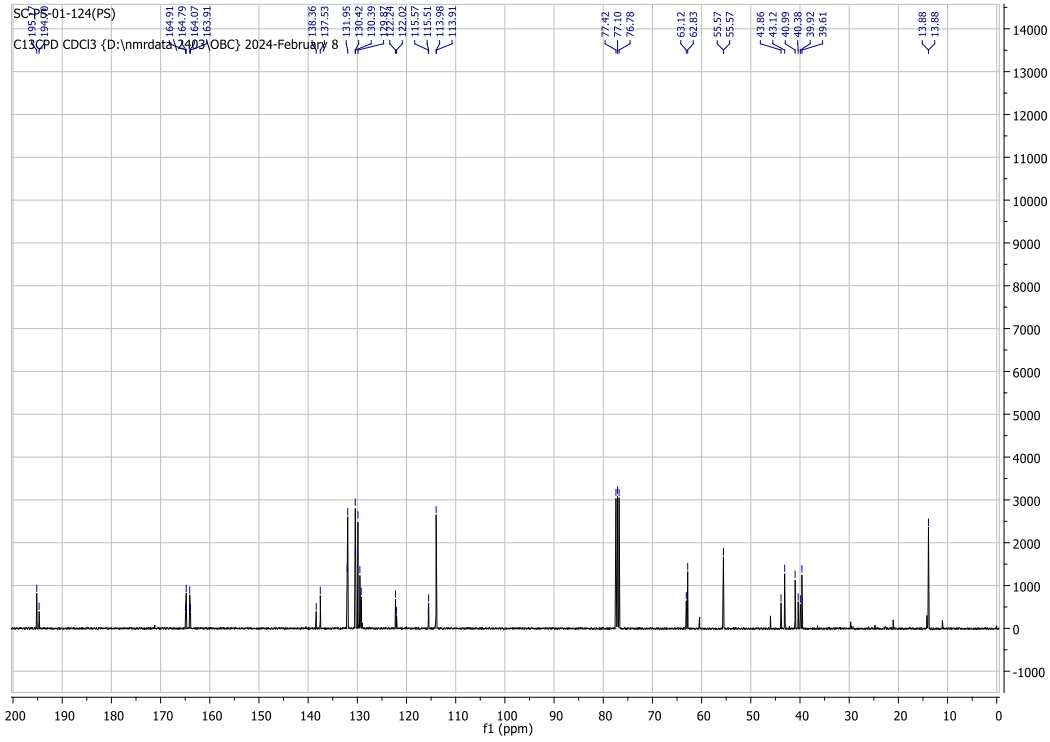

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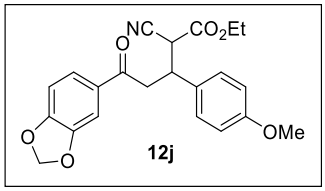

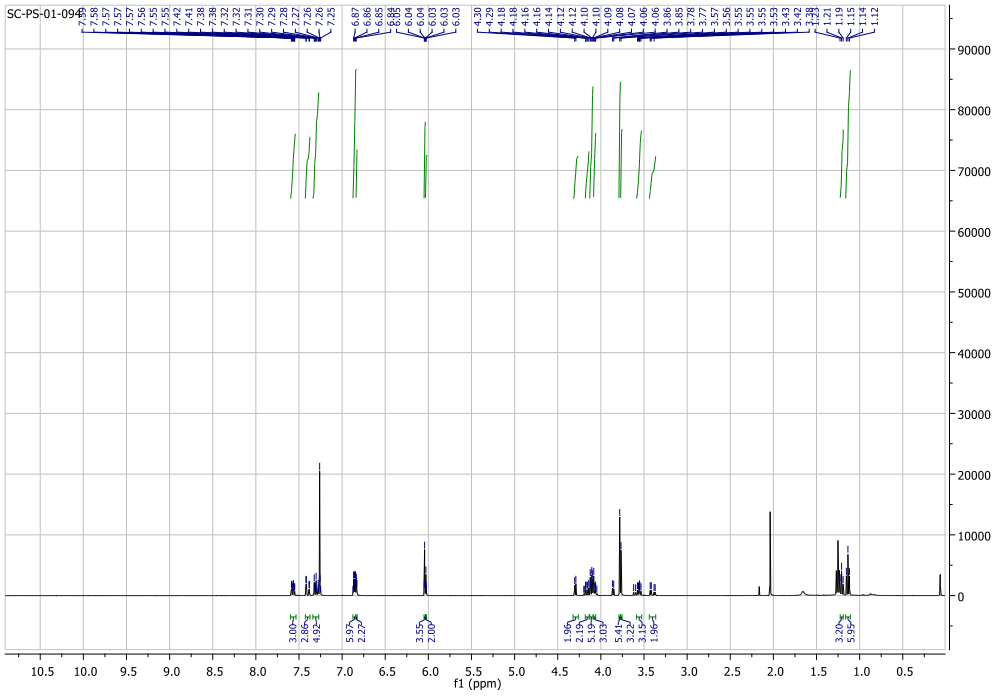

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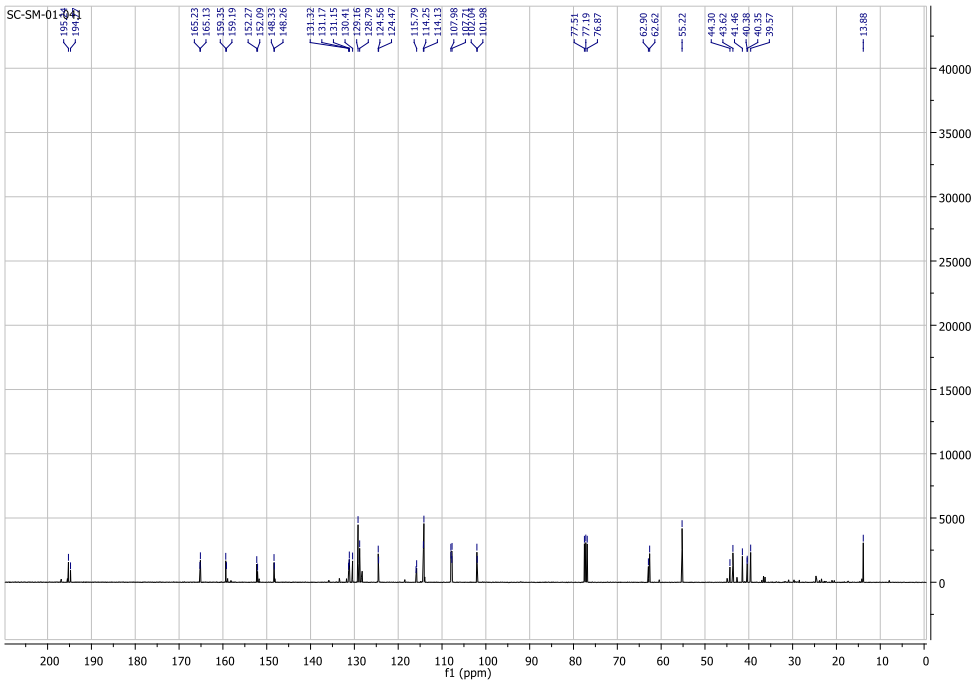

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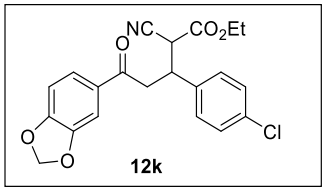

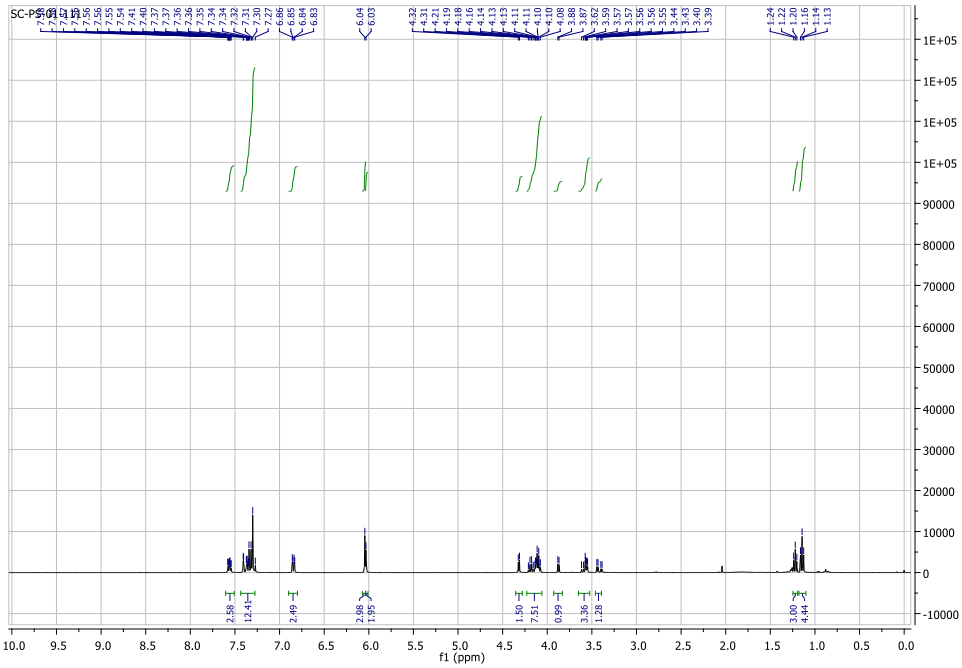

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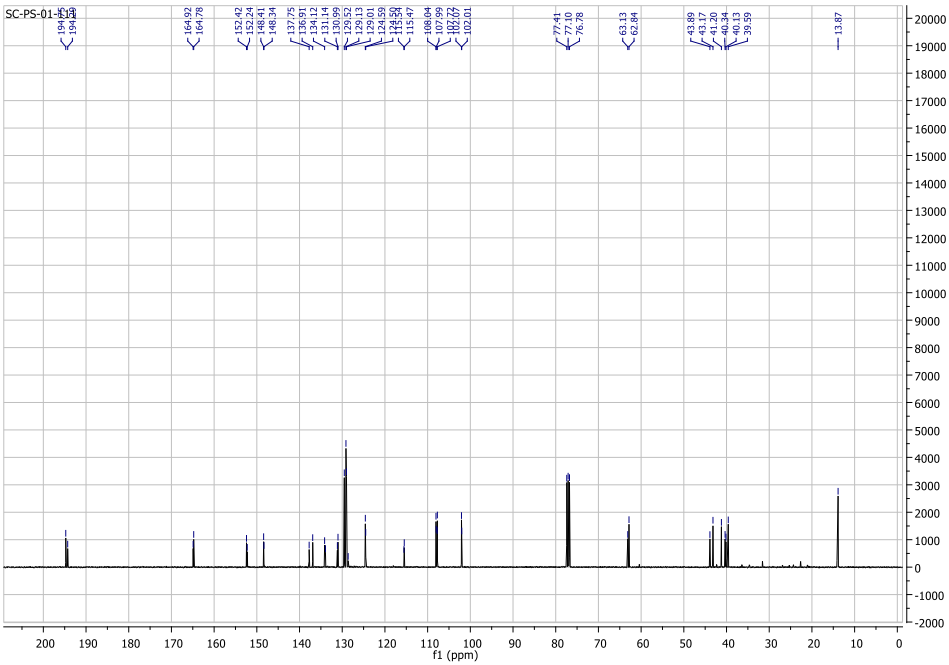

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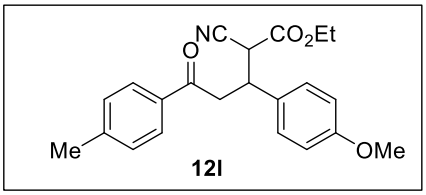

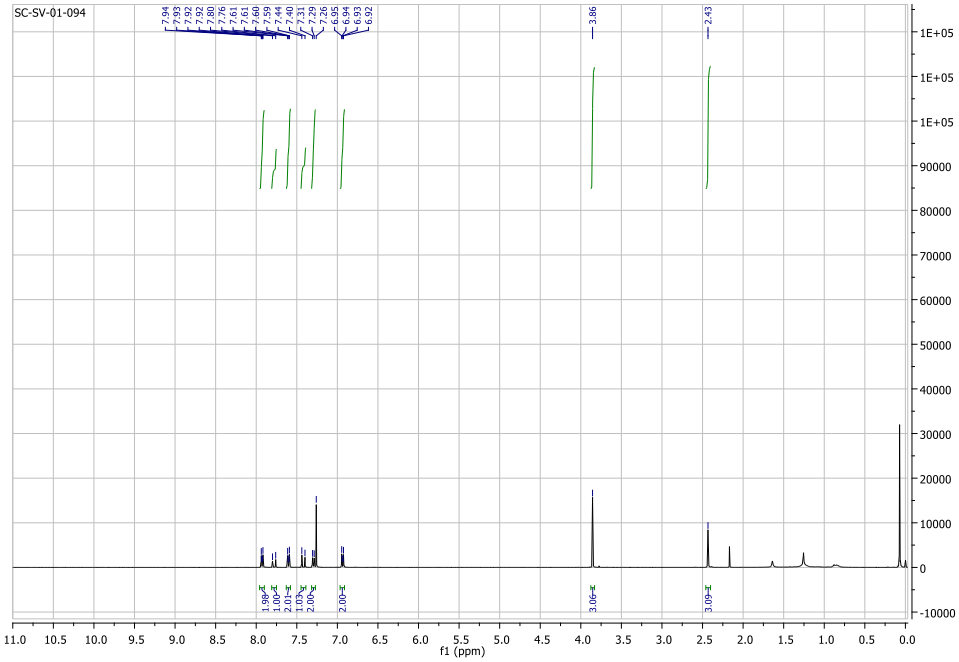

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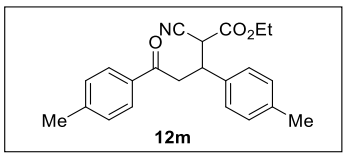
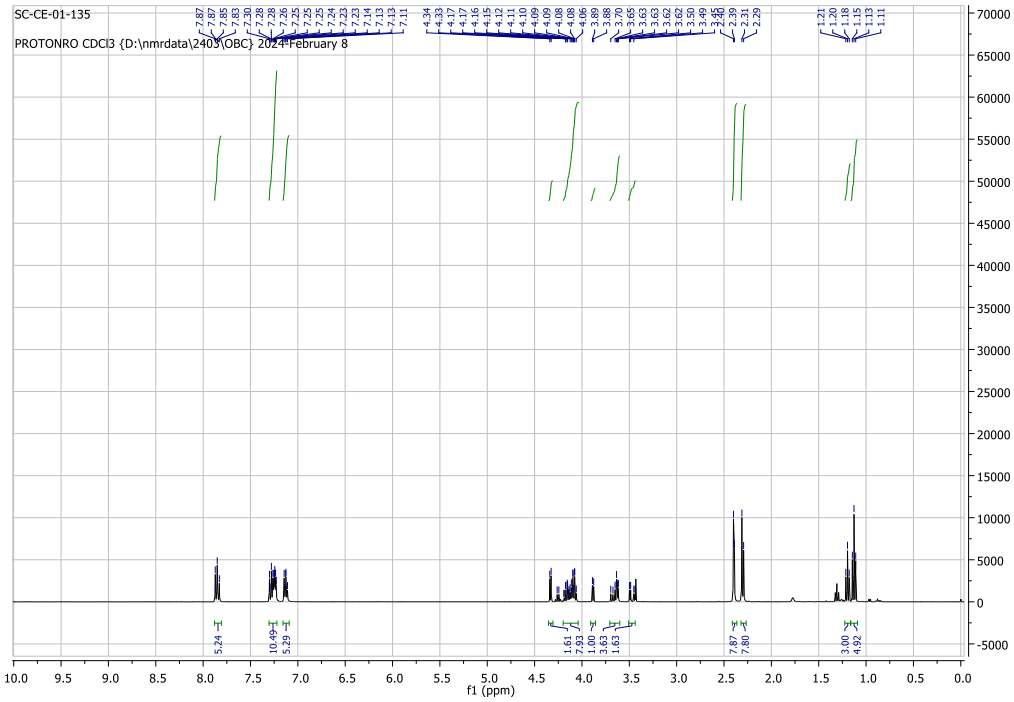


12m



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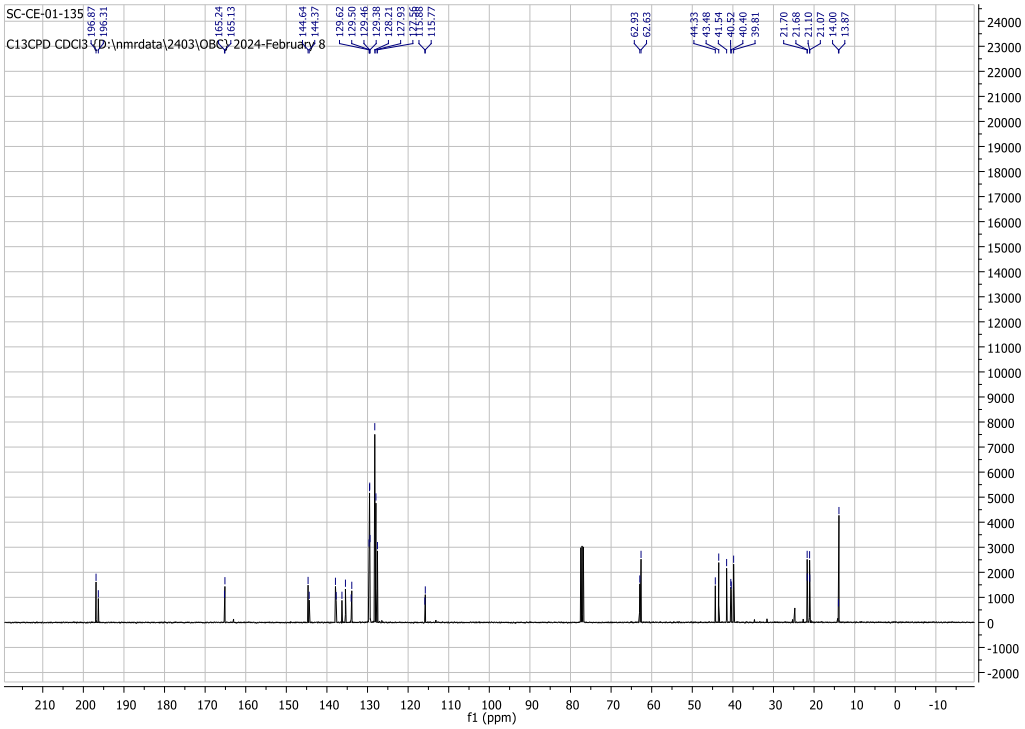

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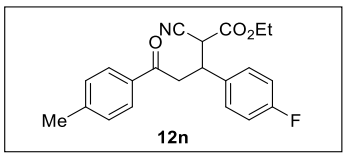

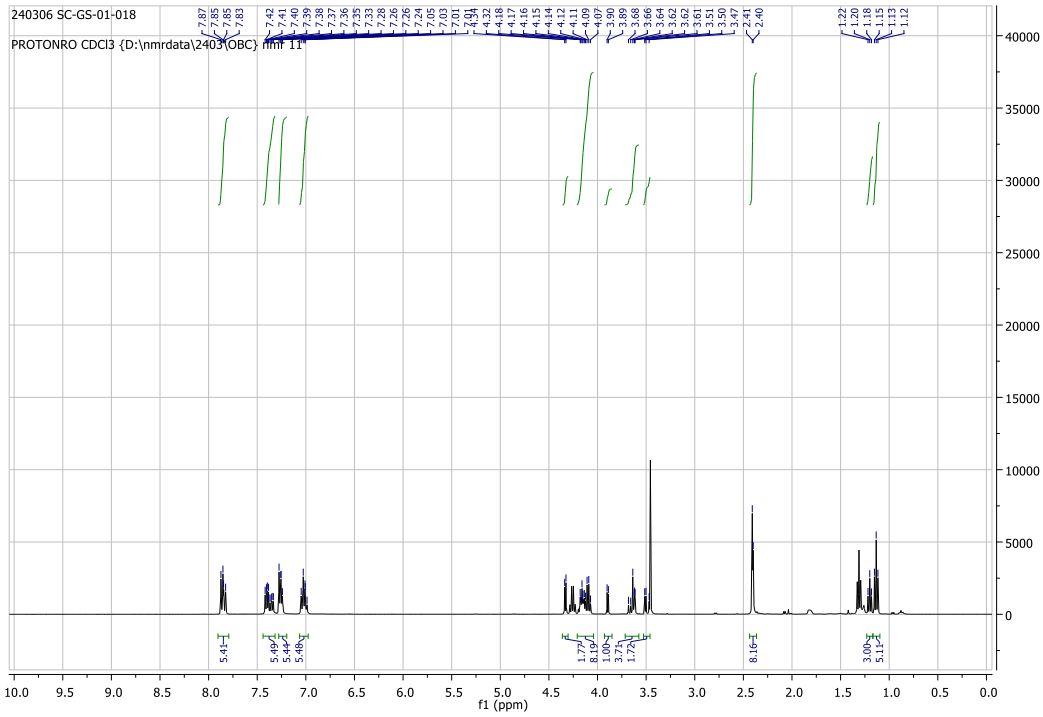

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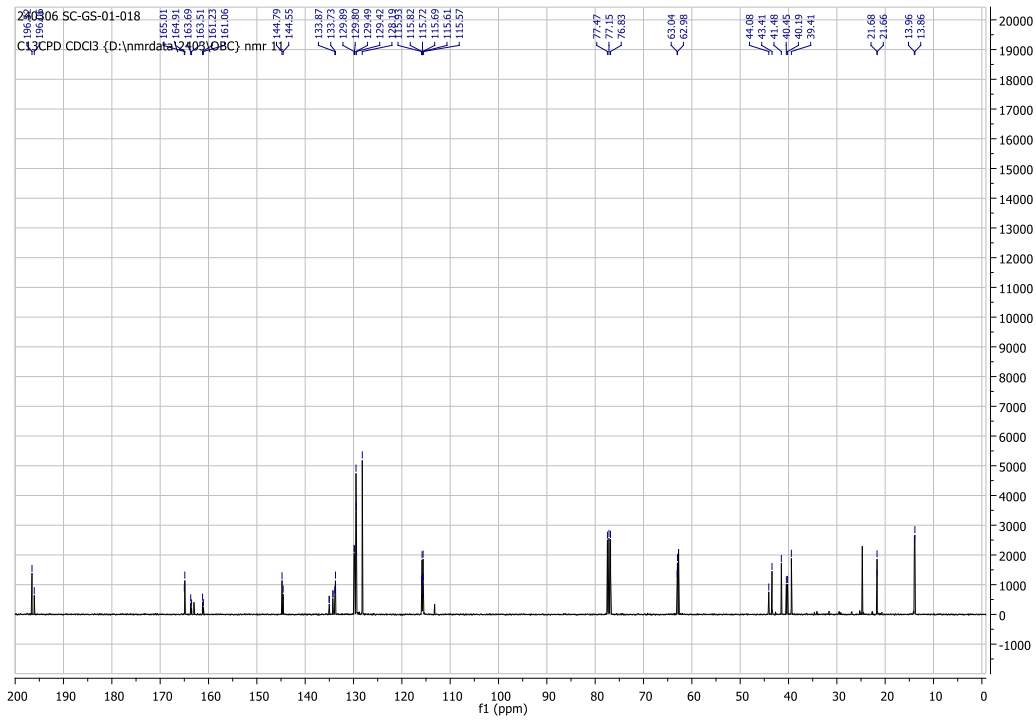

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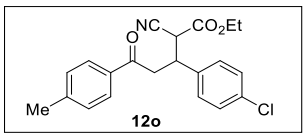

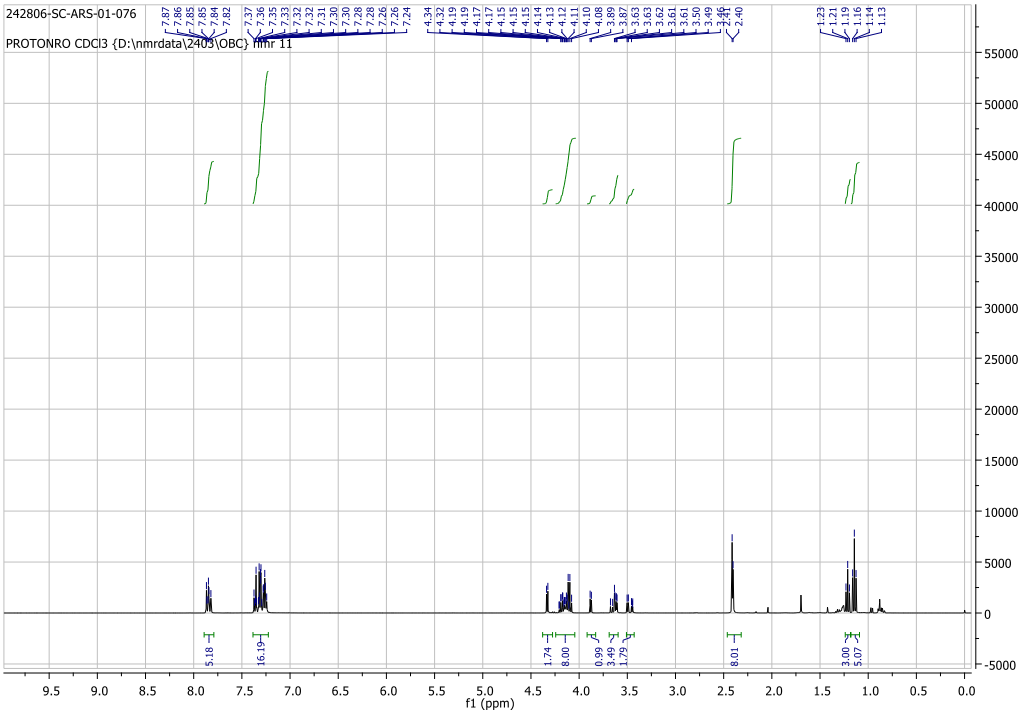

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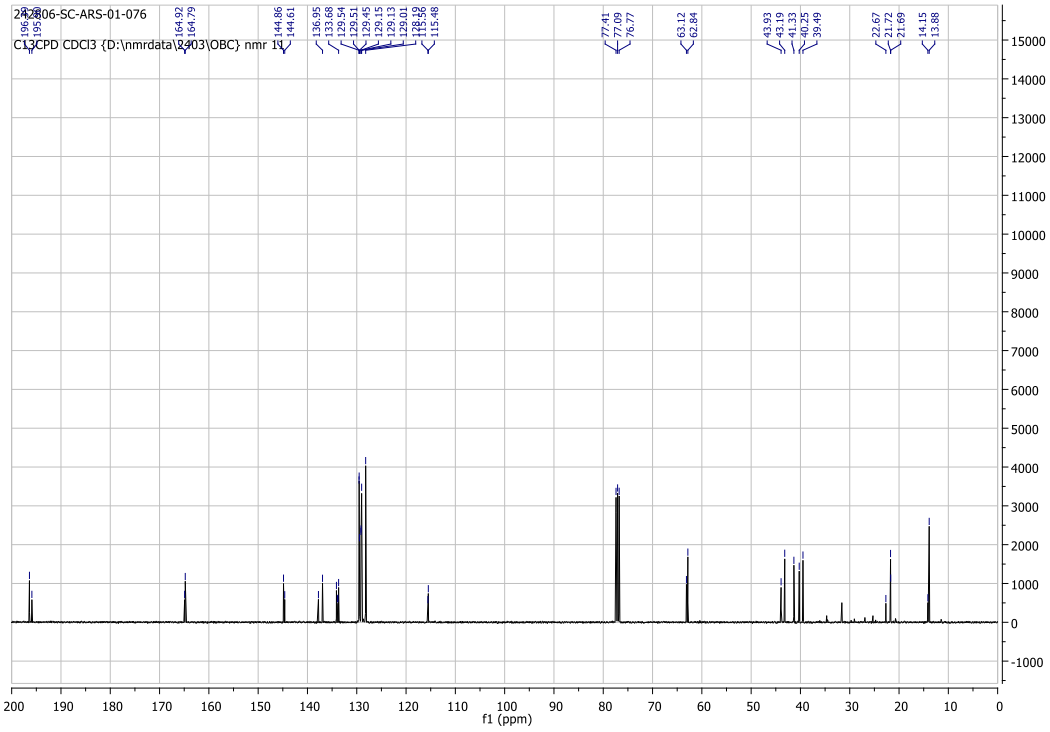

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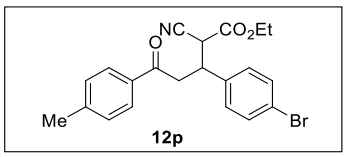

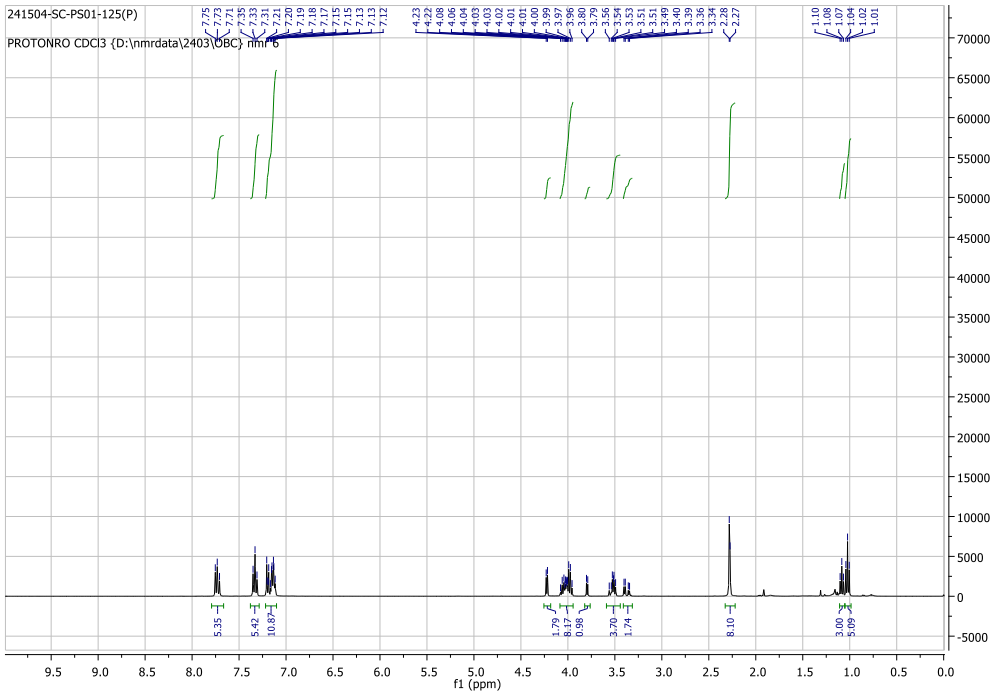

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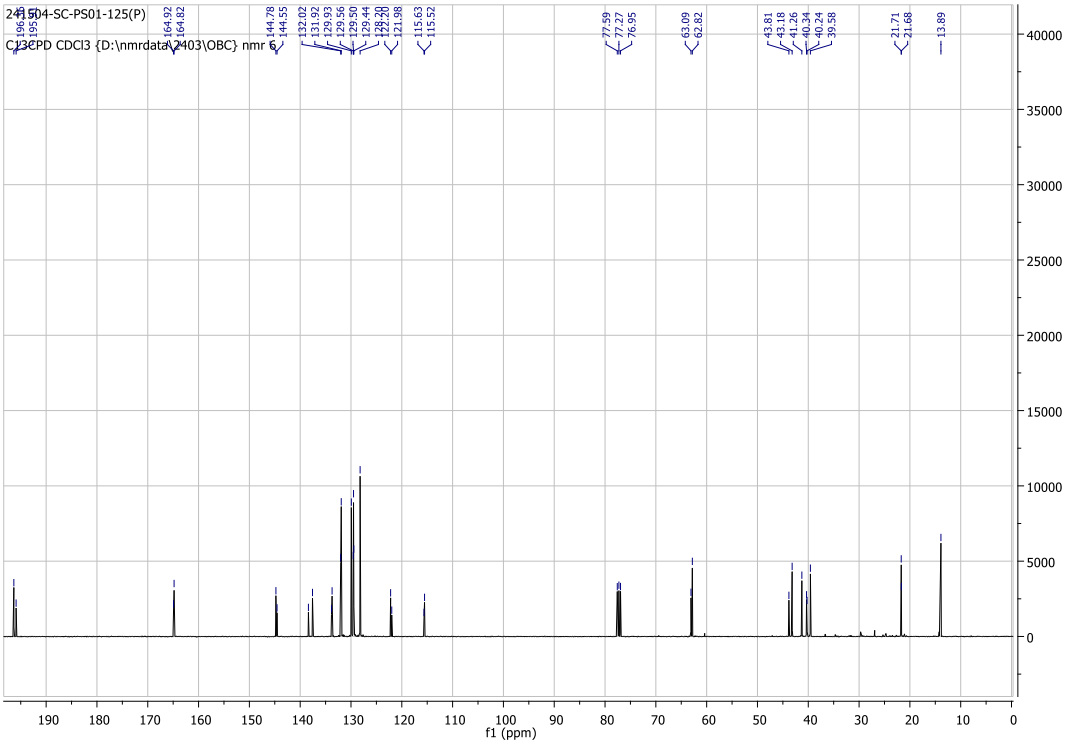

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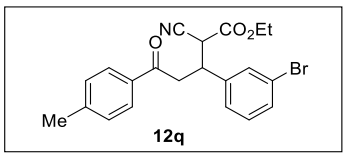
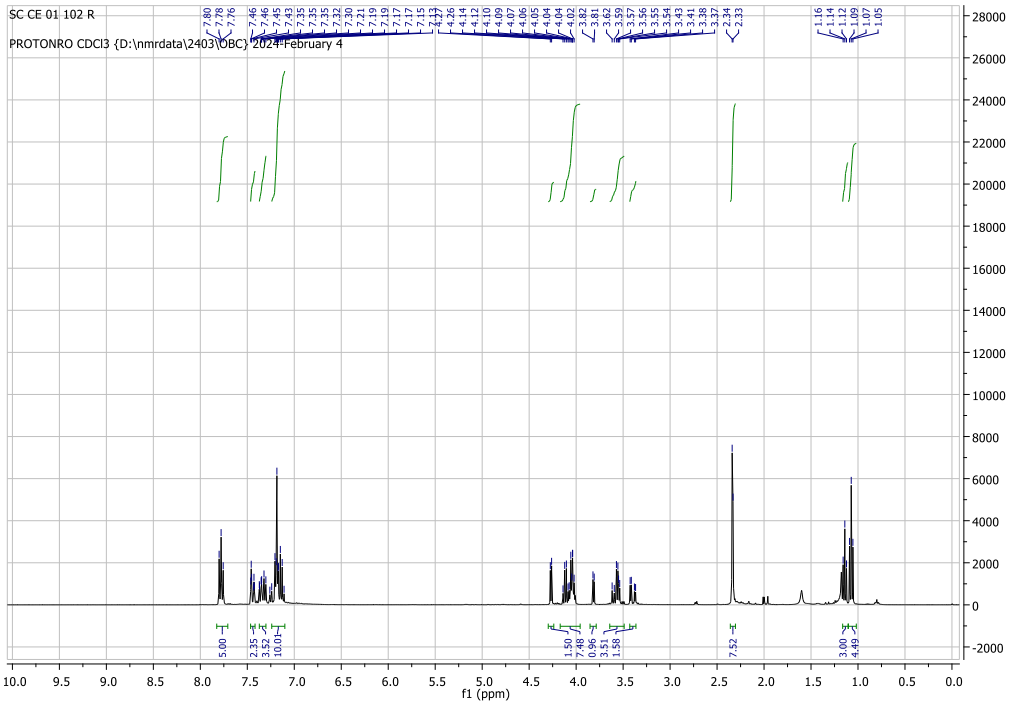


12q



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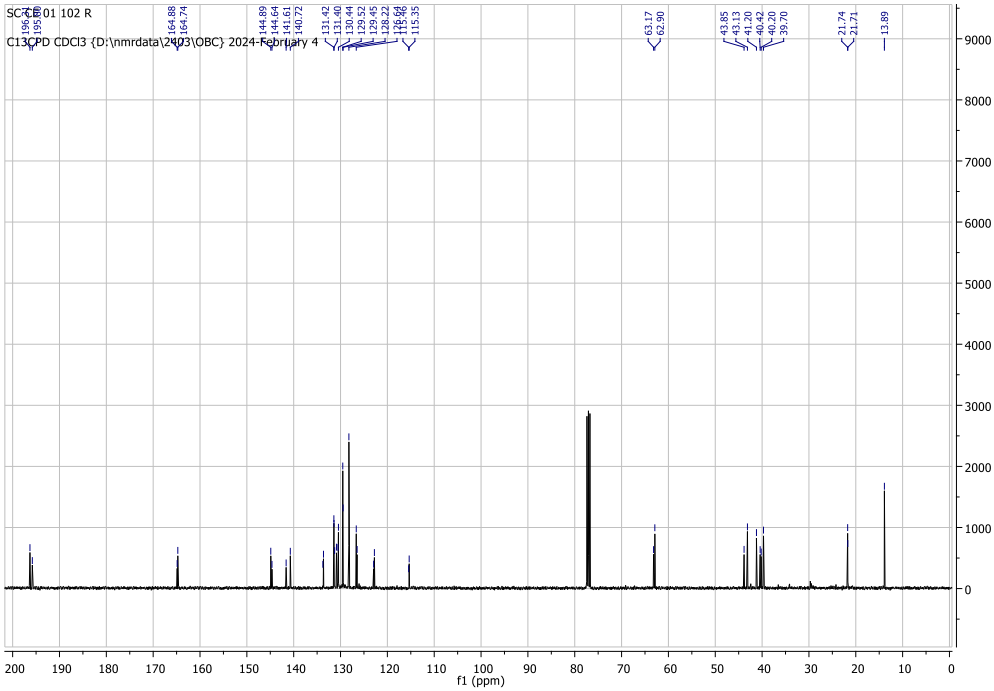

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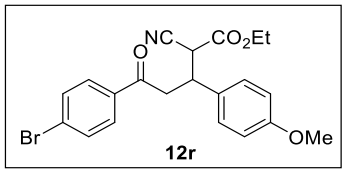

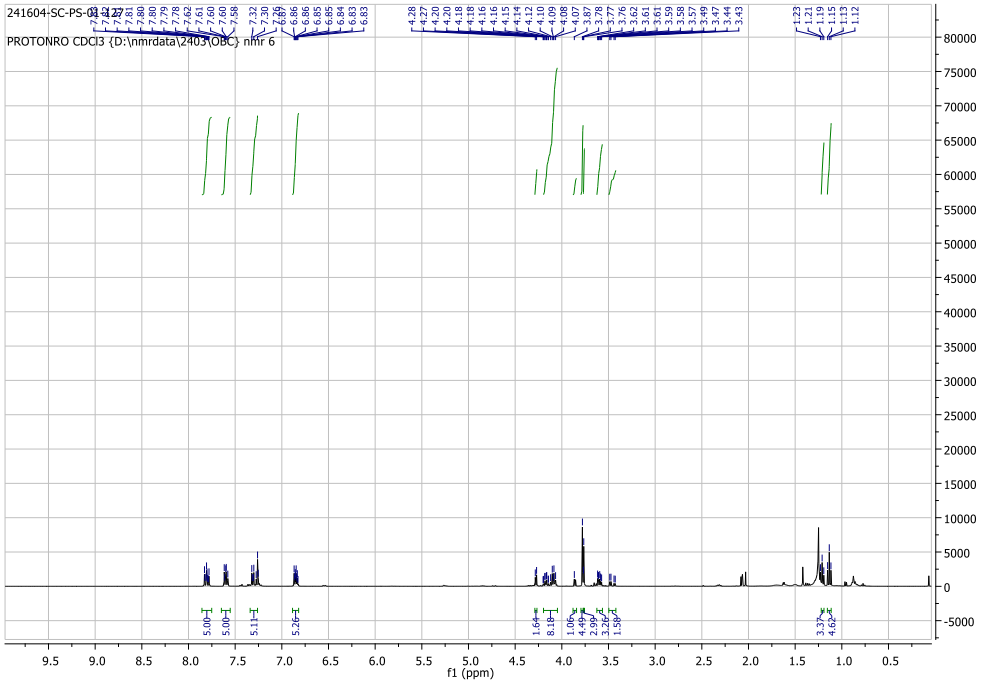

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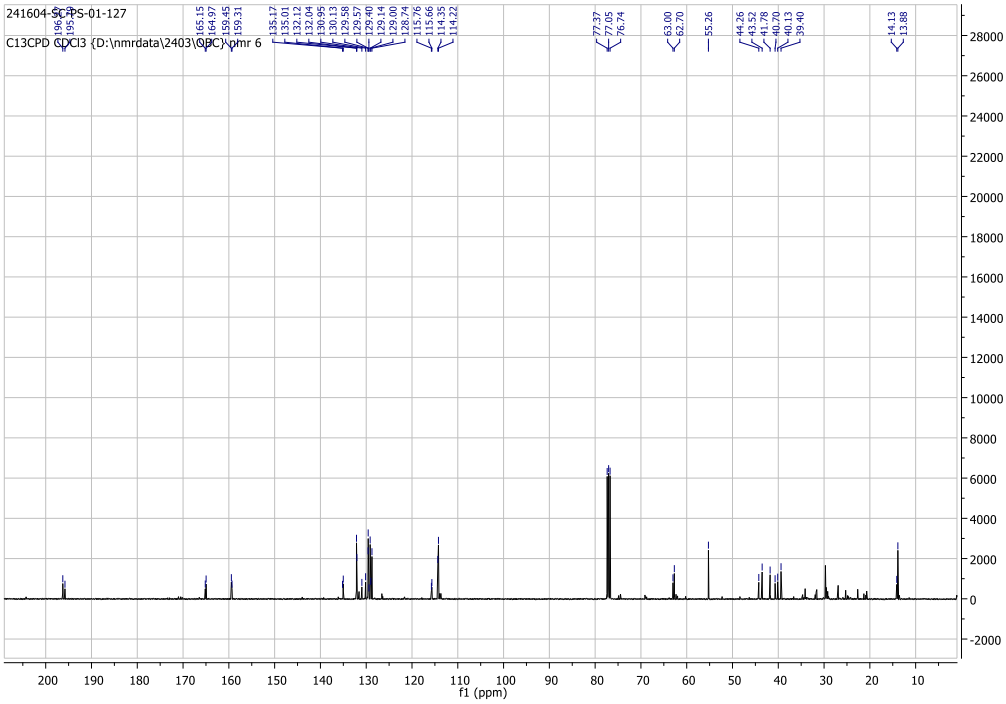
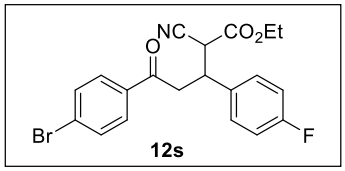
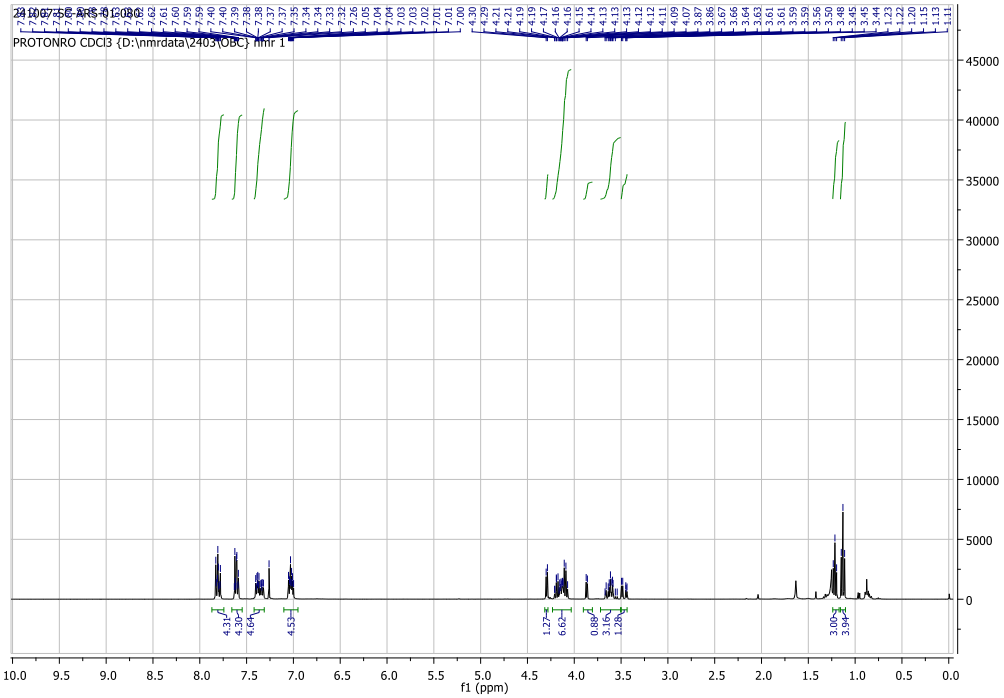
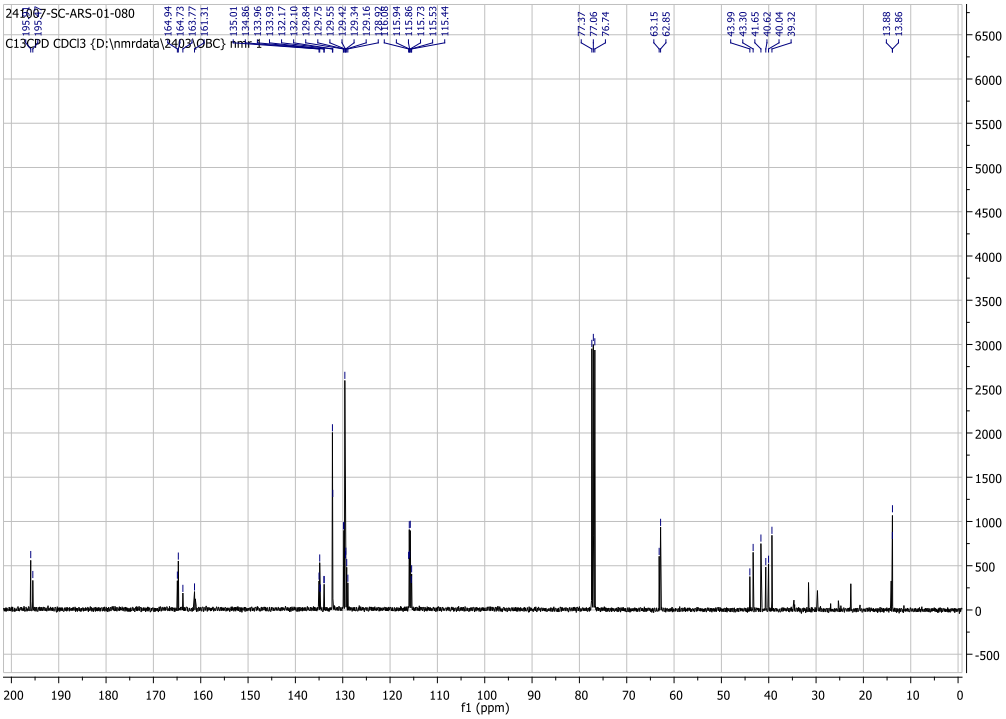


^{13}C-NMR (100 MHz, $CDCl_3$)





^{1}H-NMR (400 MHz, $CDCl_3$)



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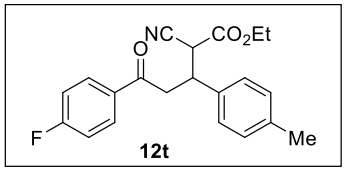

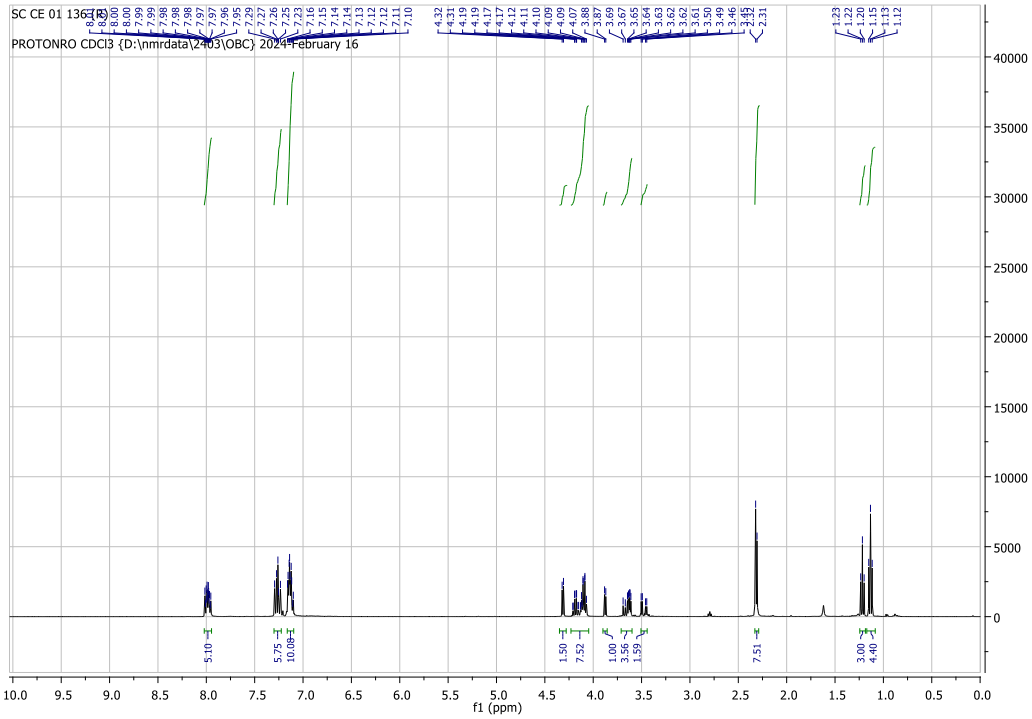

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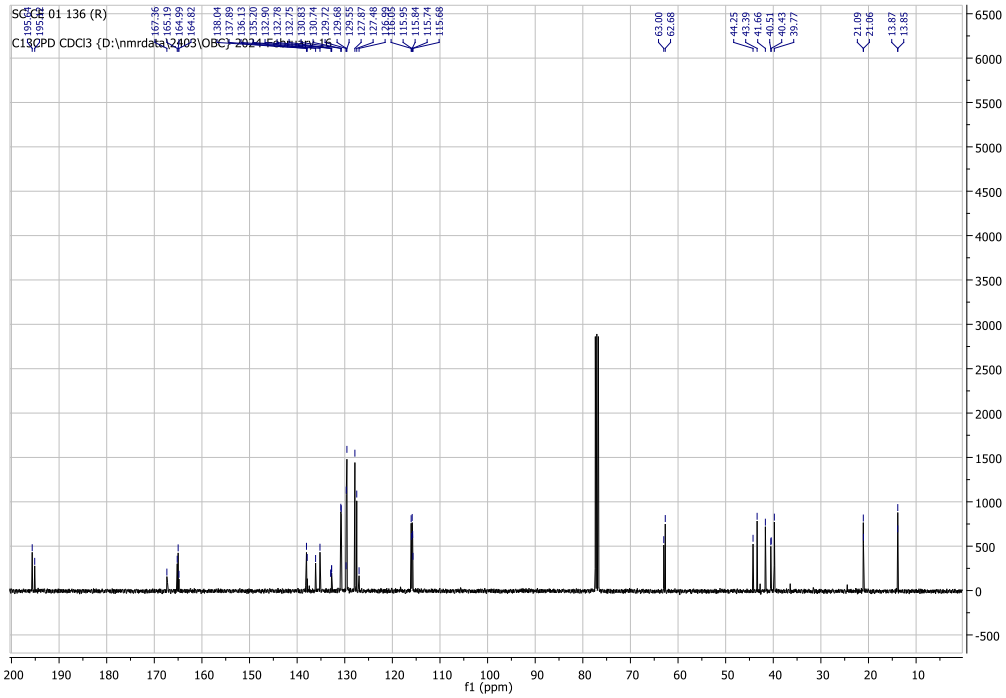

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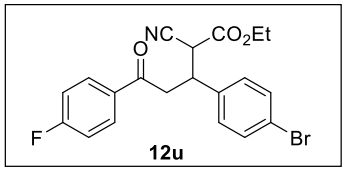

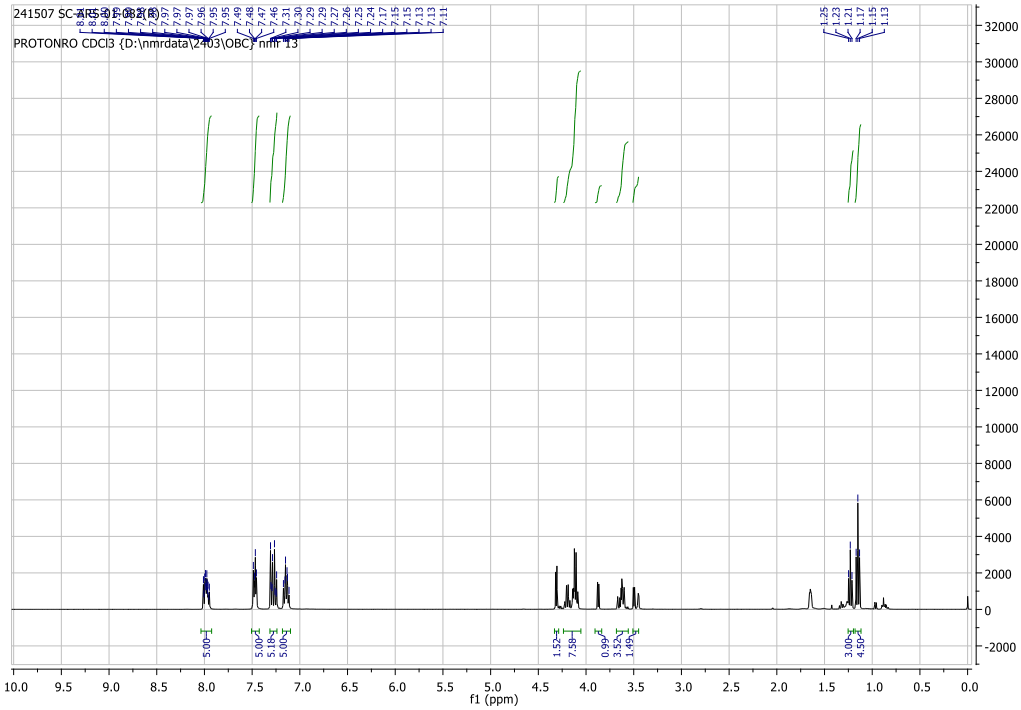

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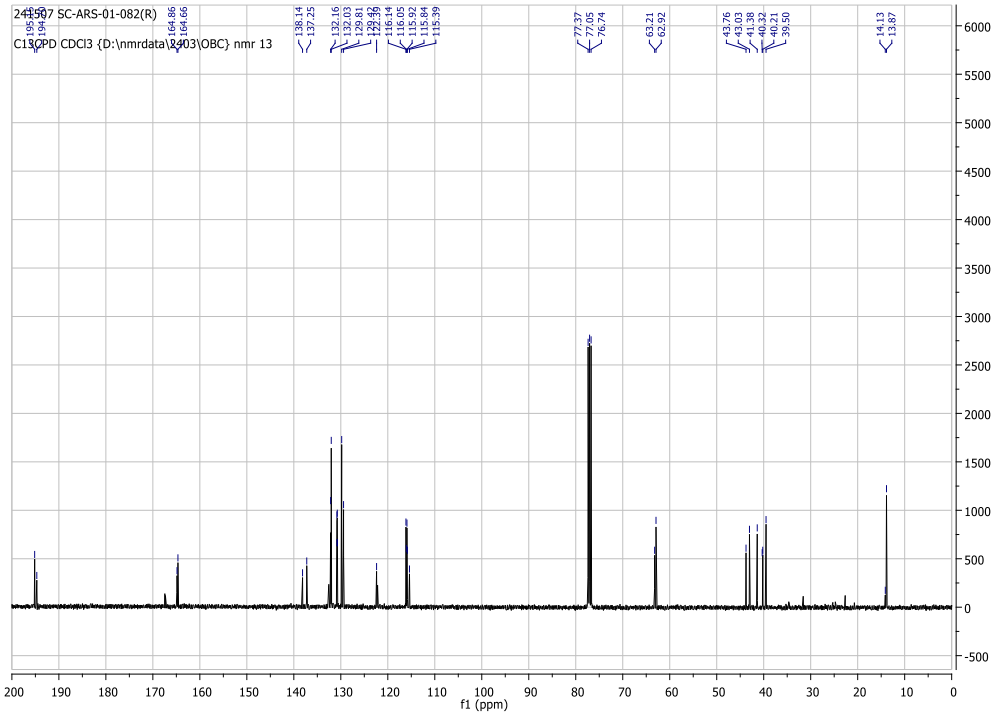

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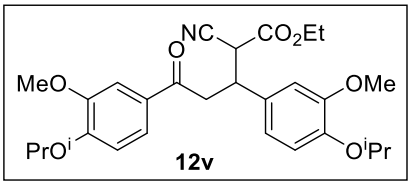

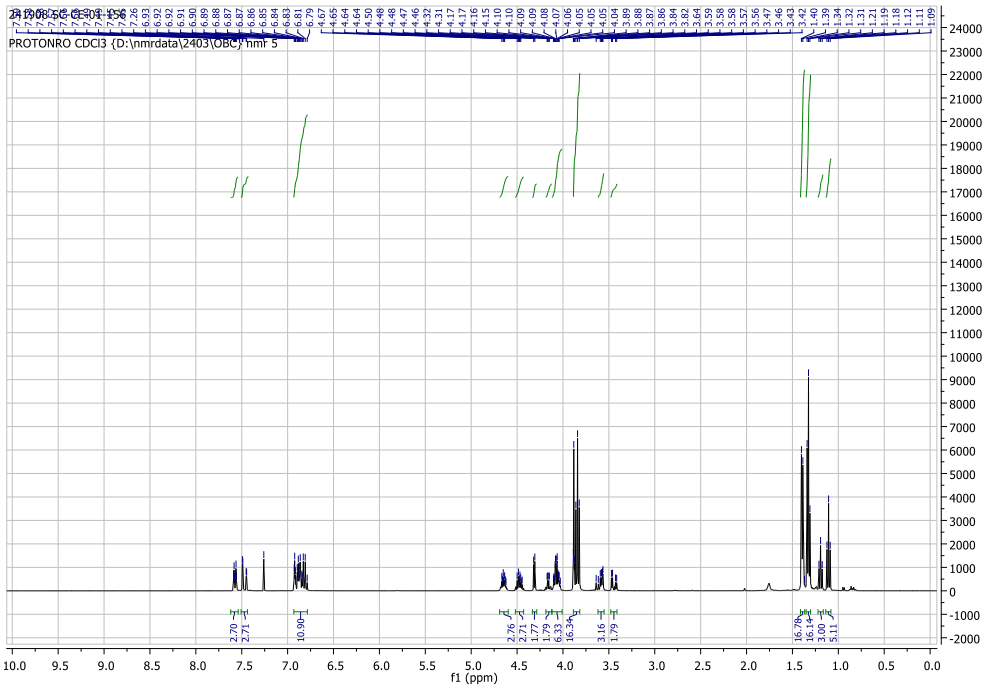

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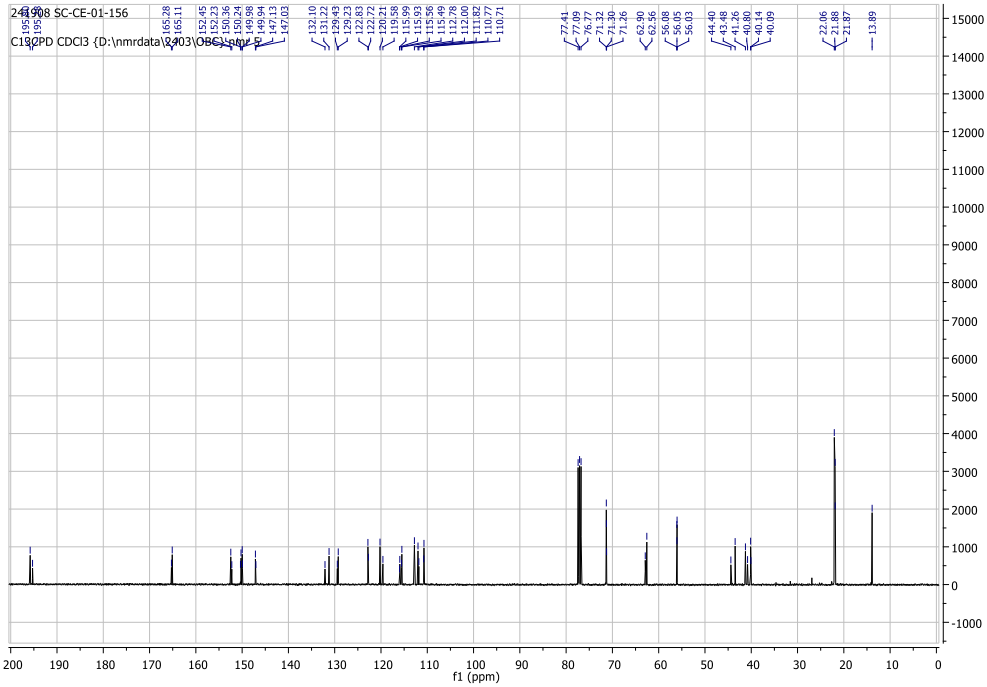

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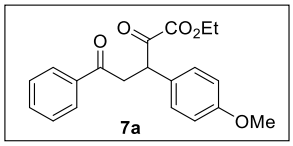

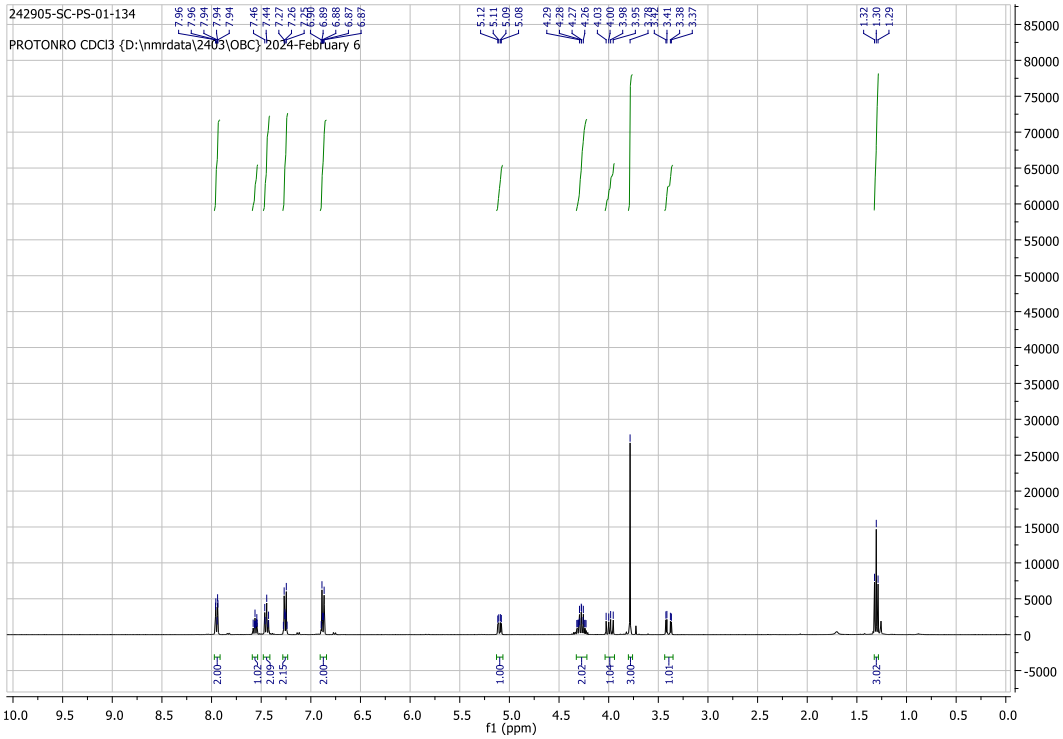

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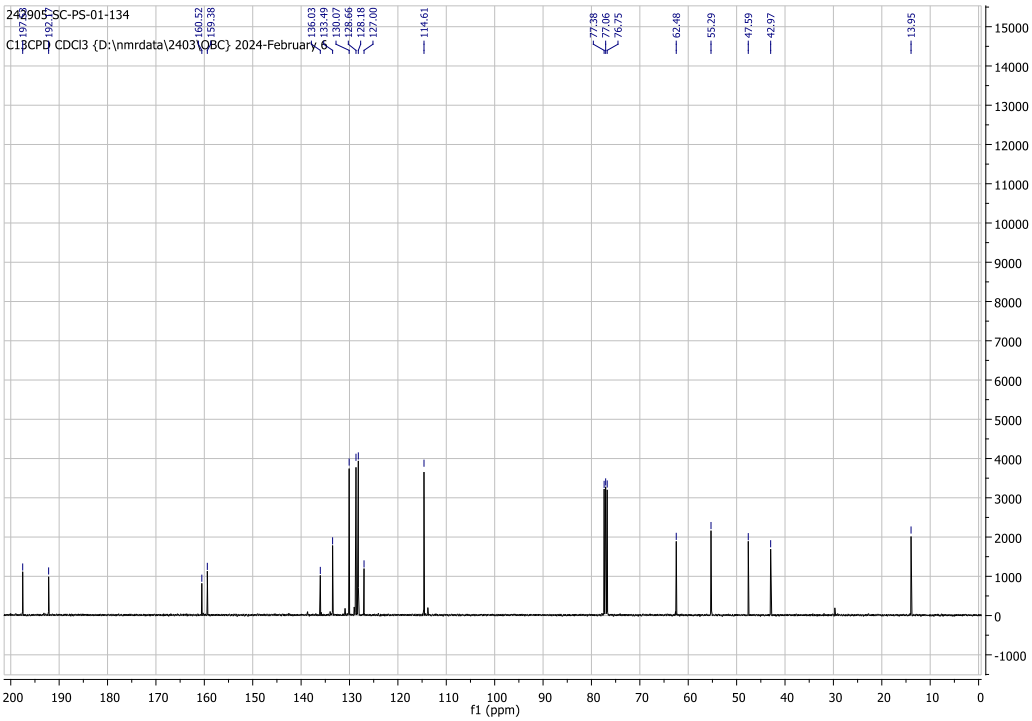

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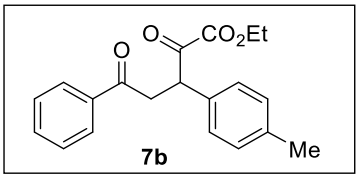

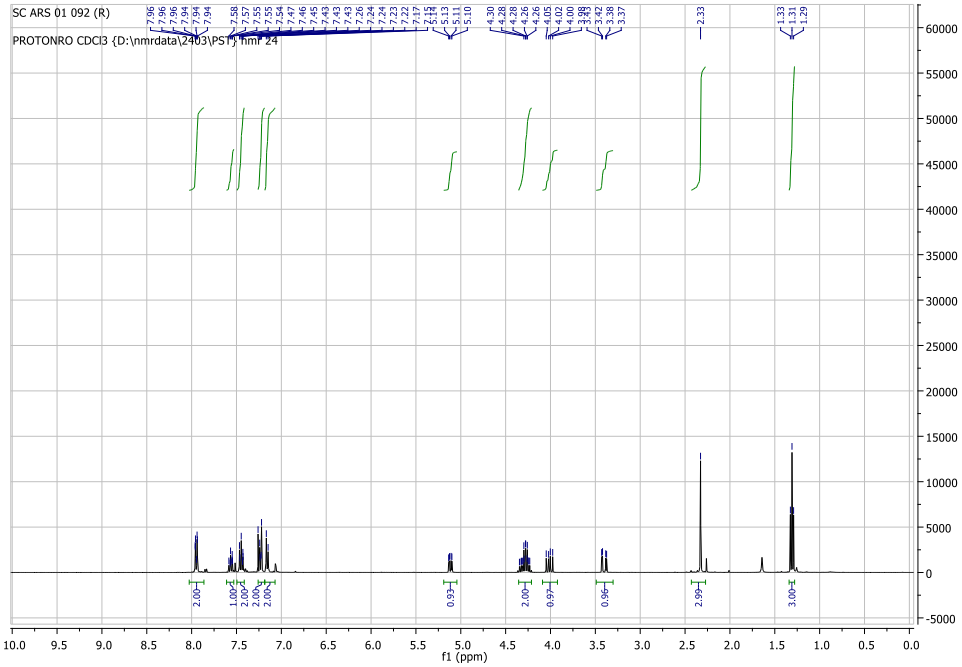

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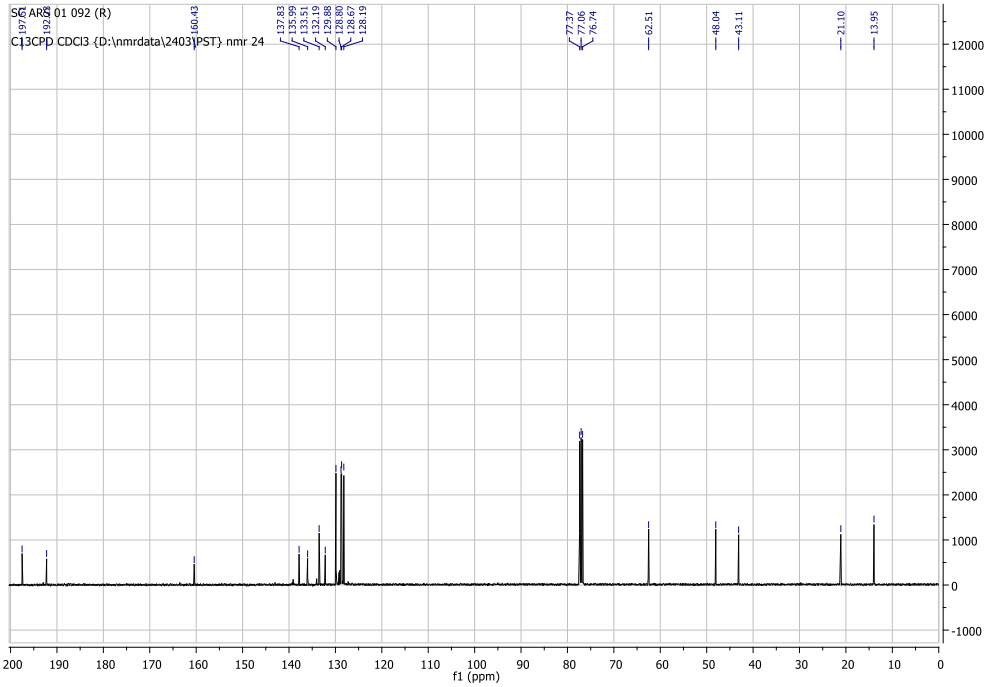

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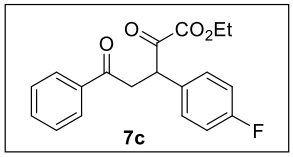

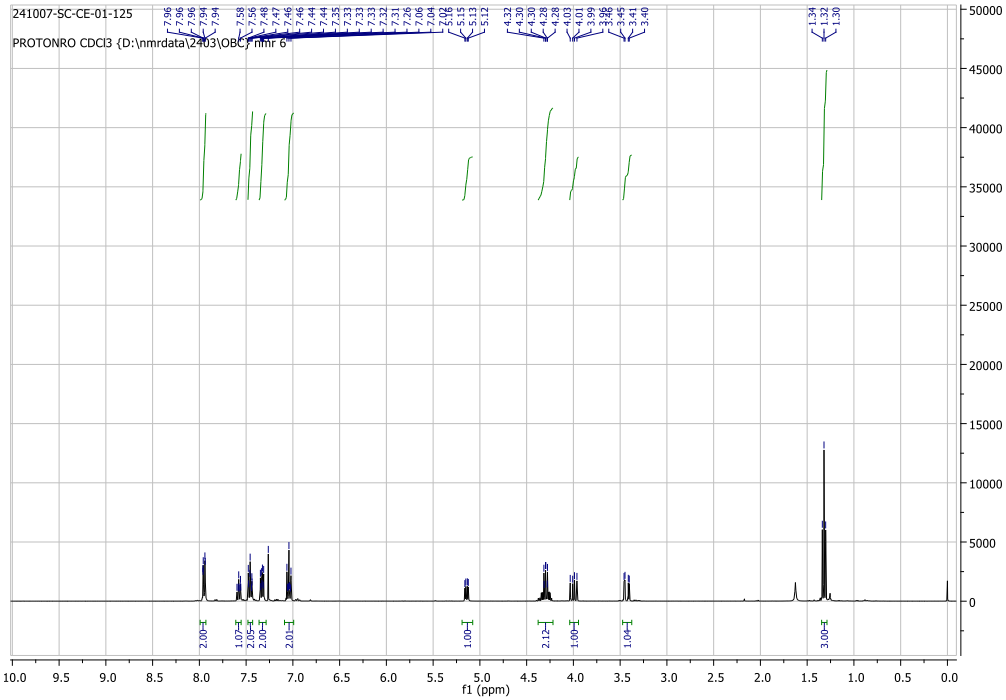

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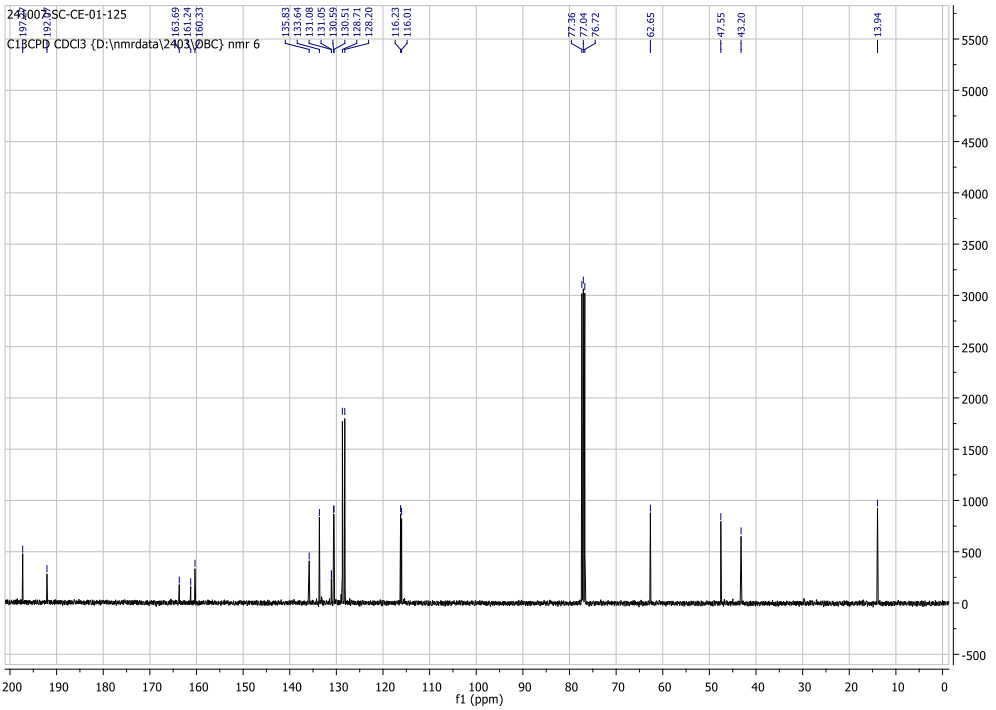

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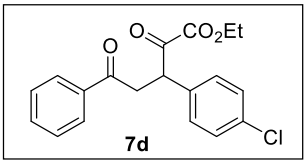

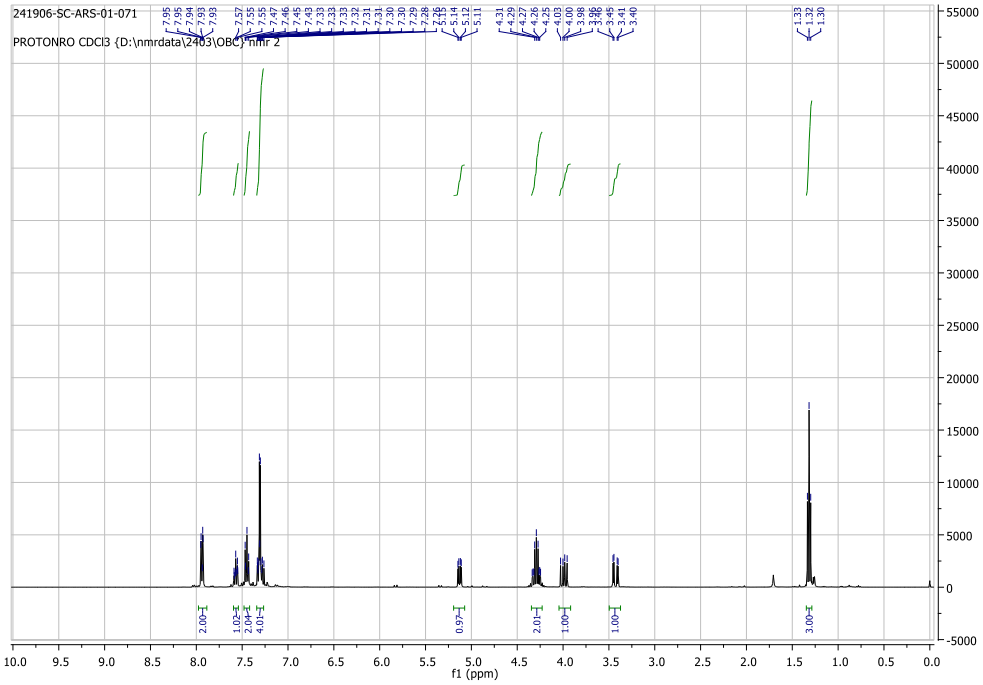

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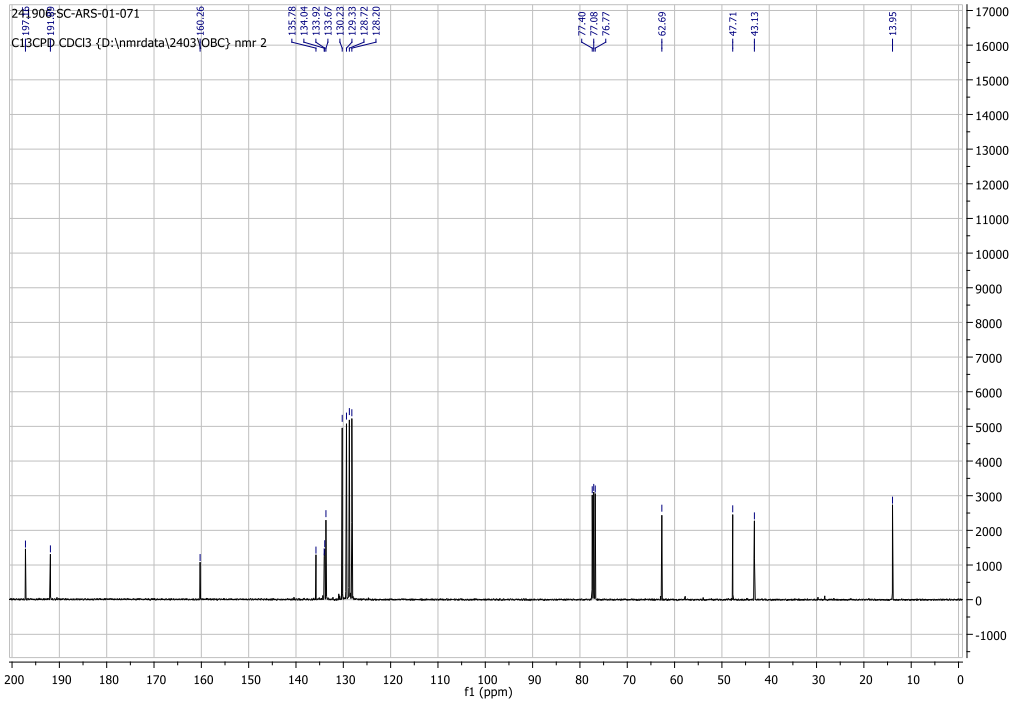

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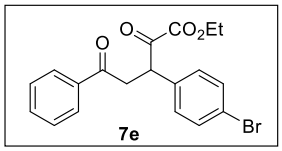

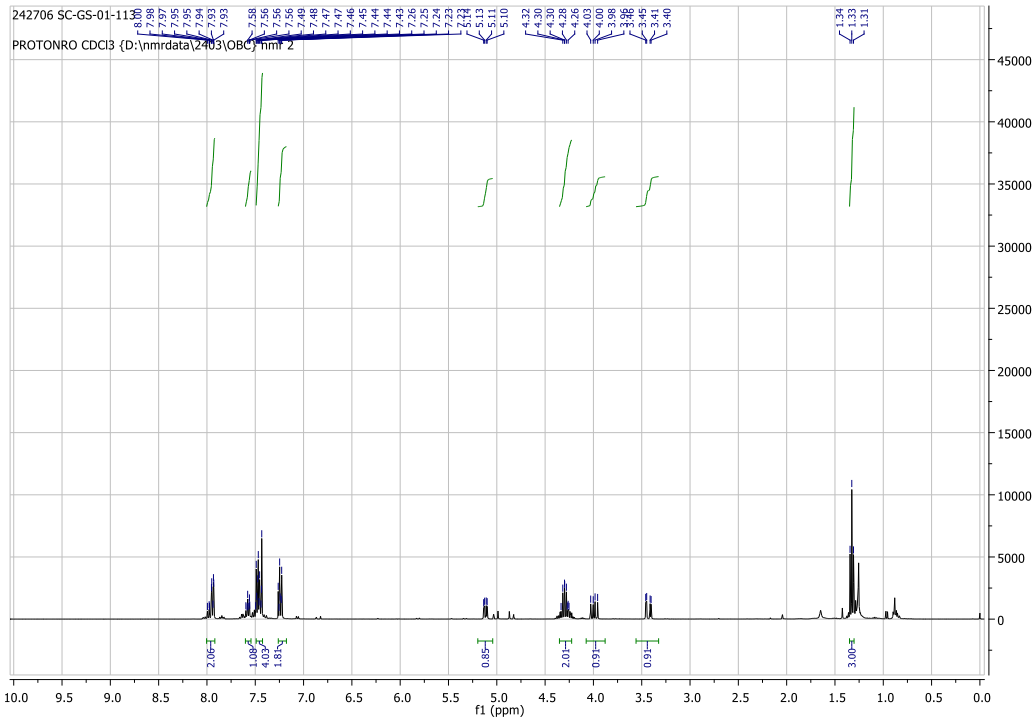

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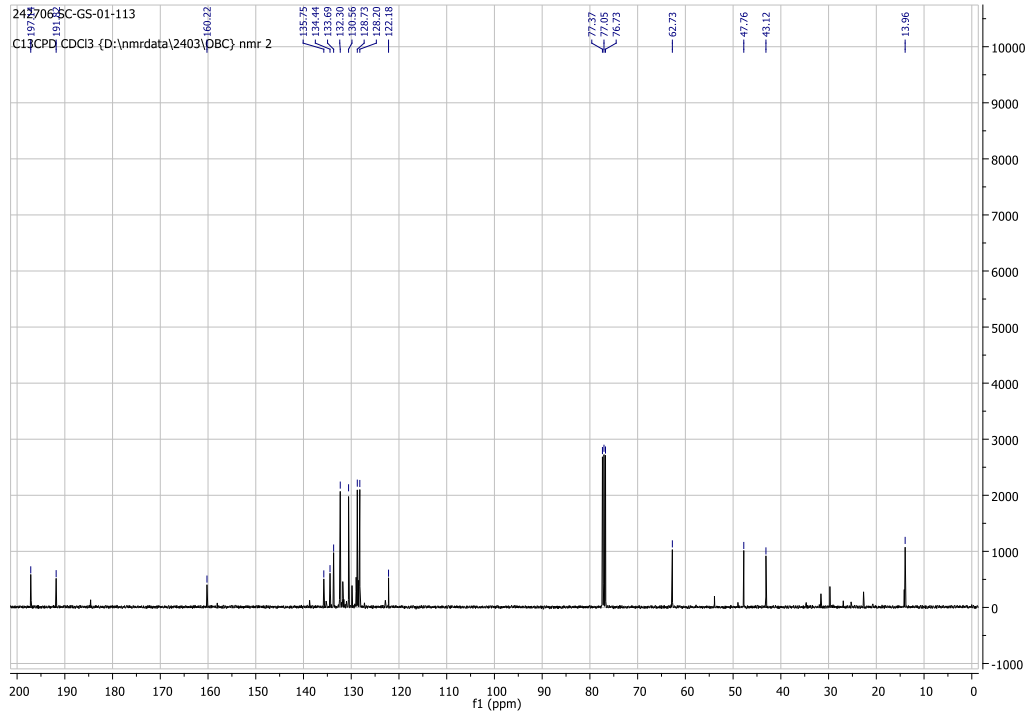

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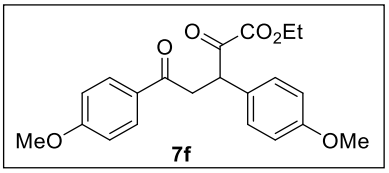

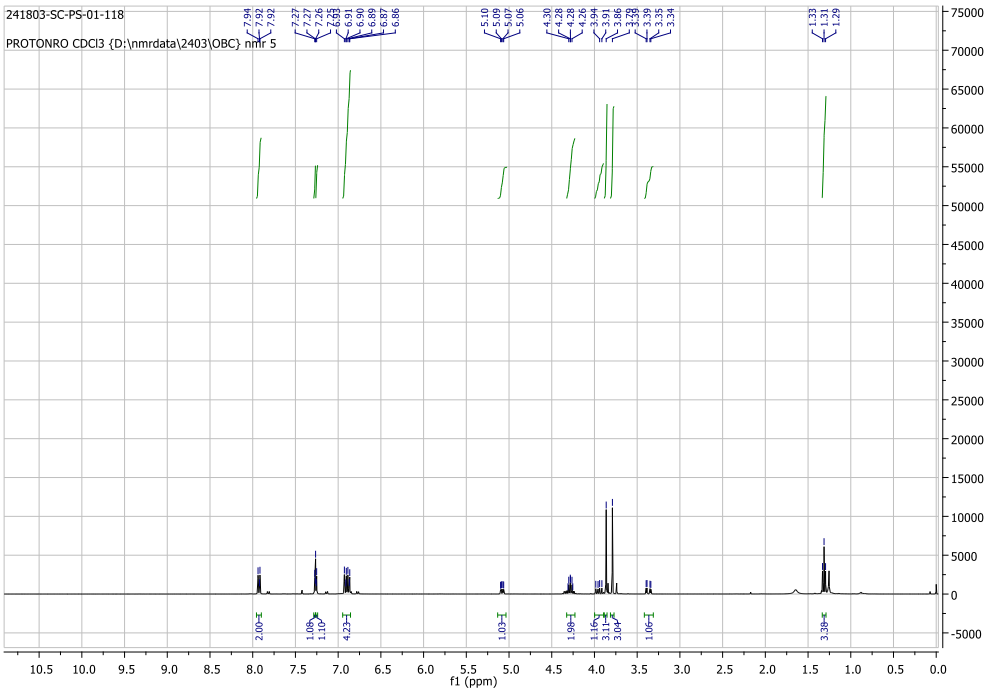

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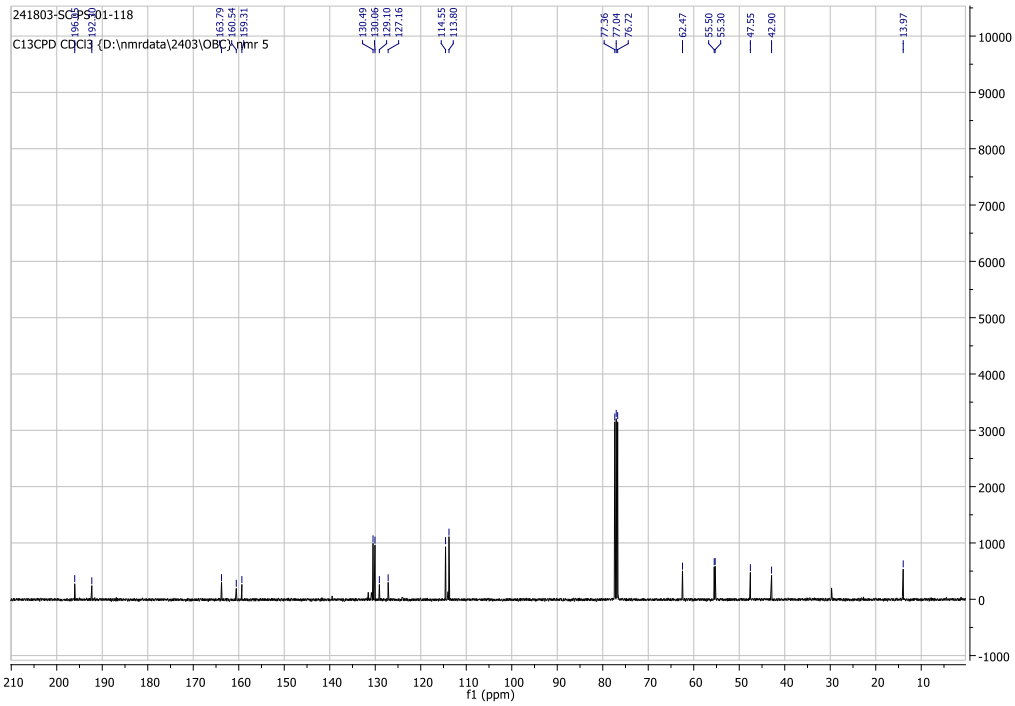

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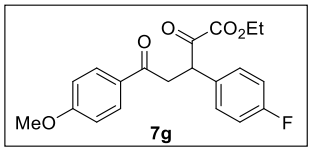

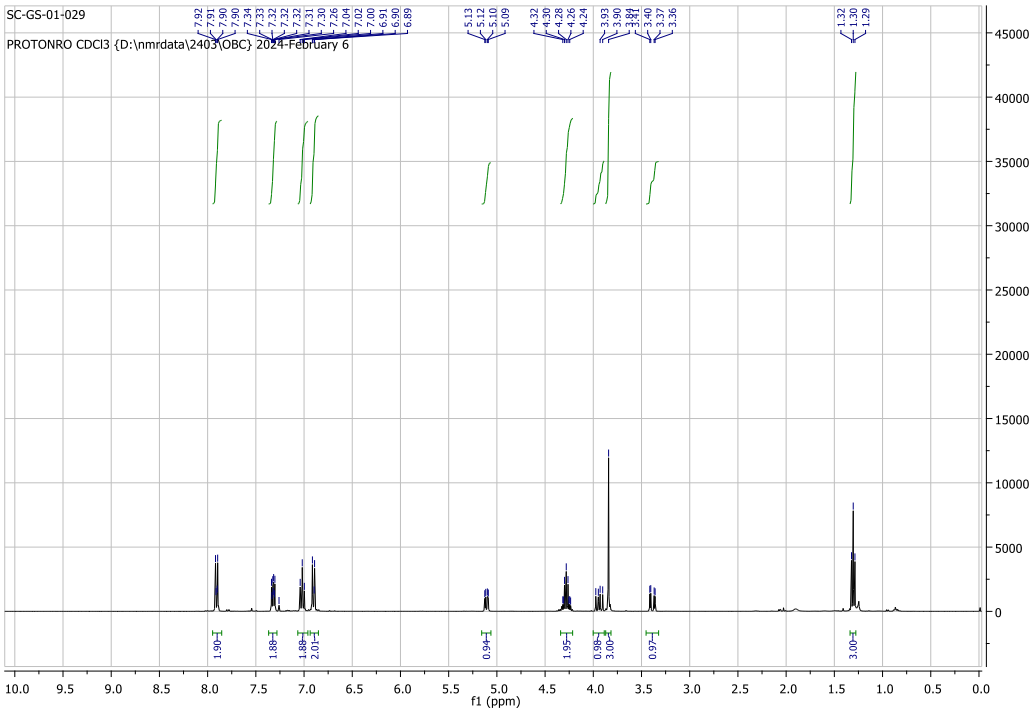

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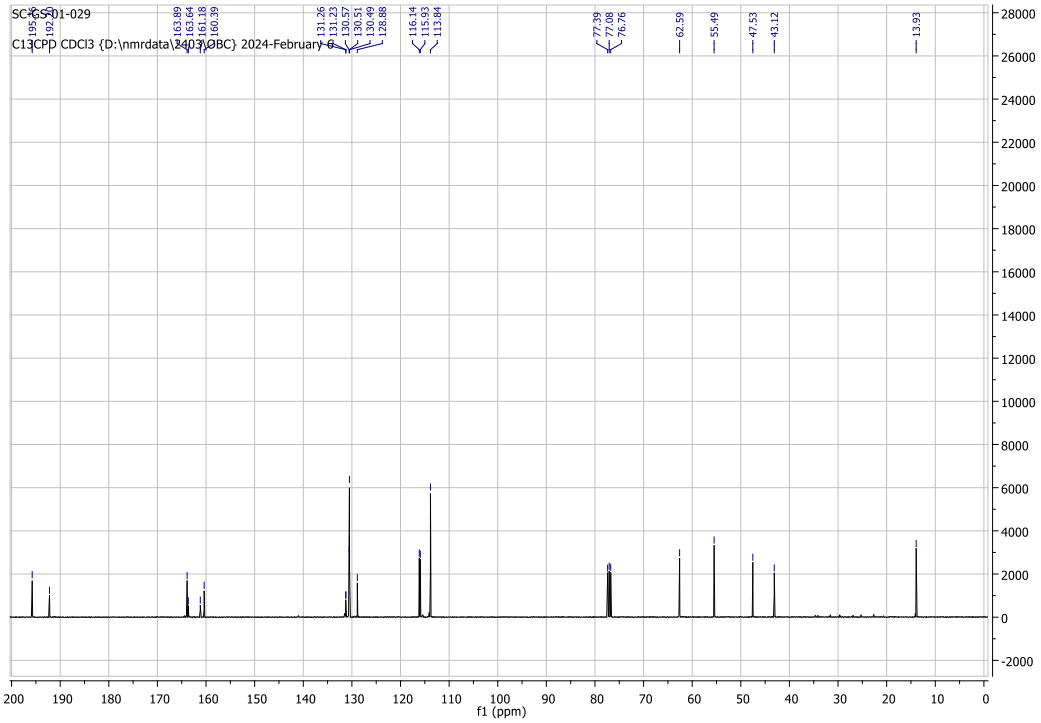

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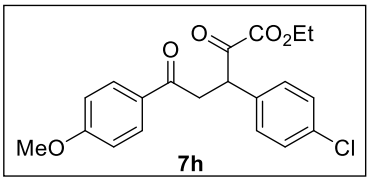
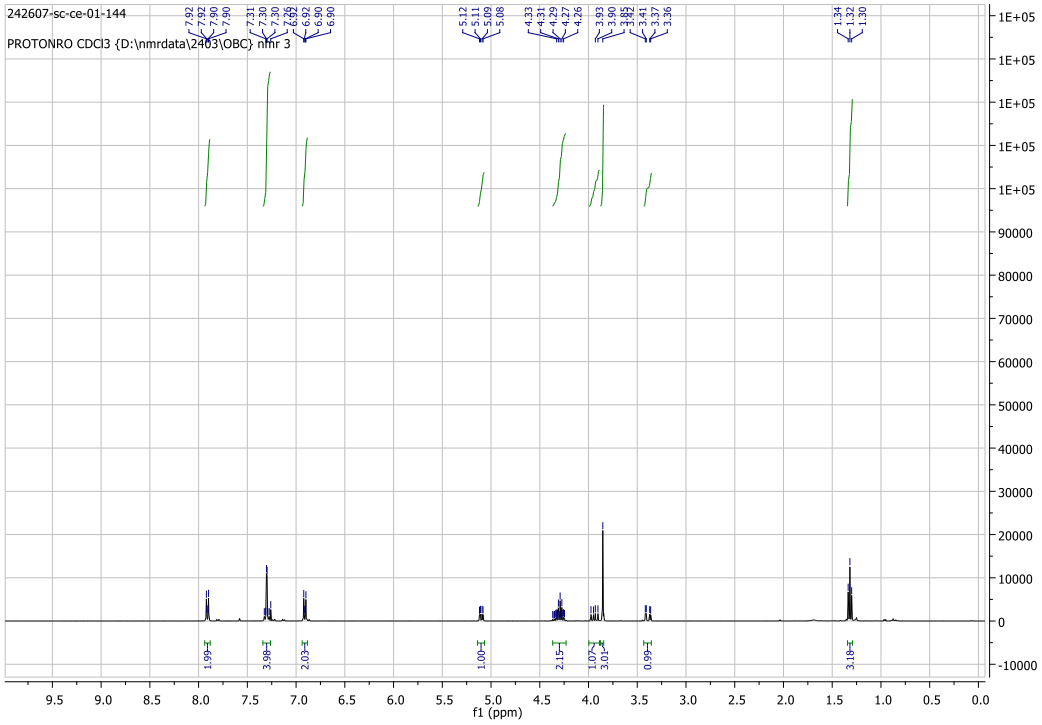
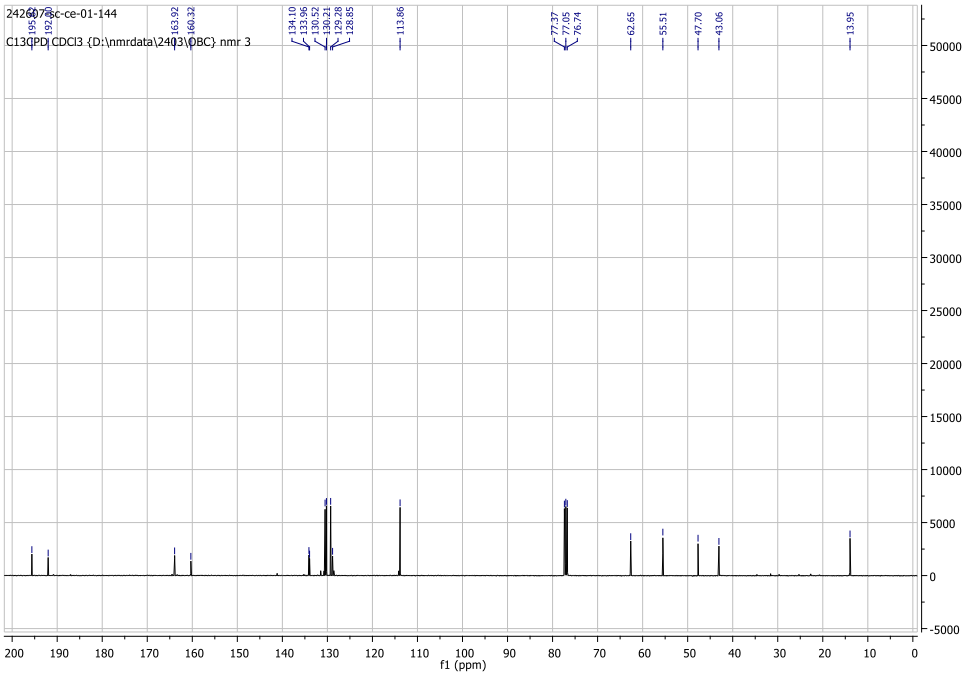




^{1}H-NMR (400 MHz, $CDCl_3$)



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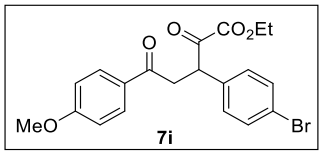
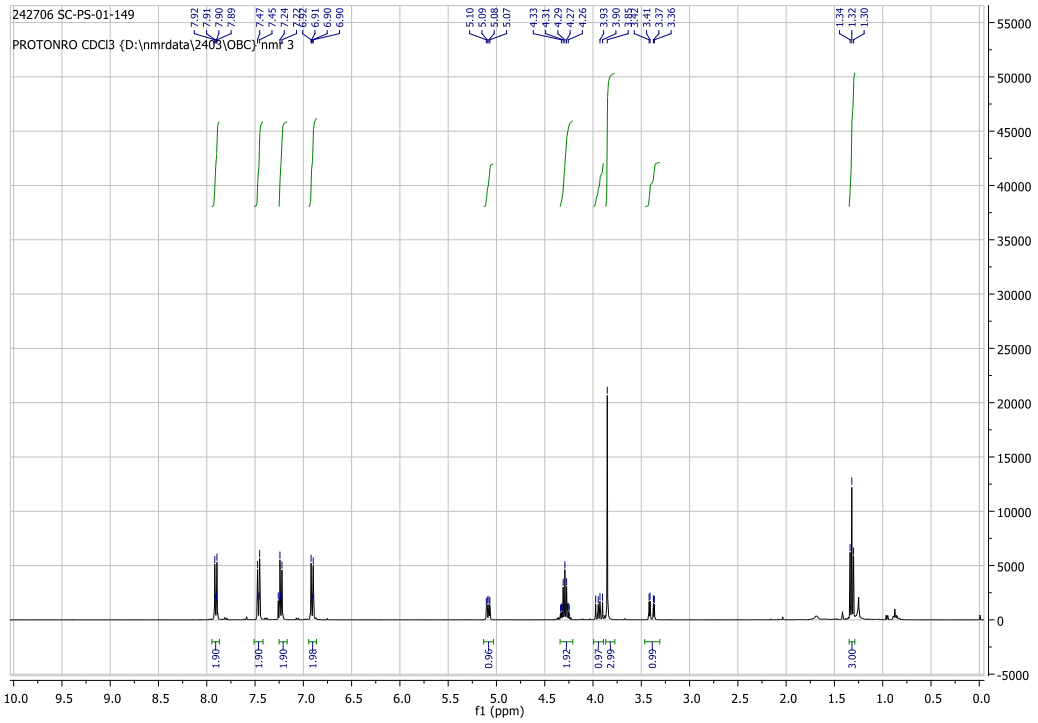
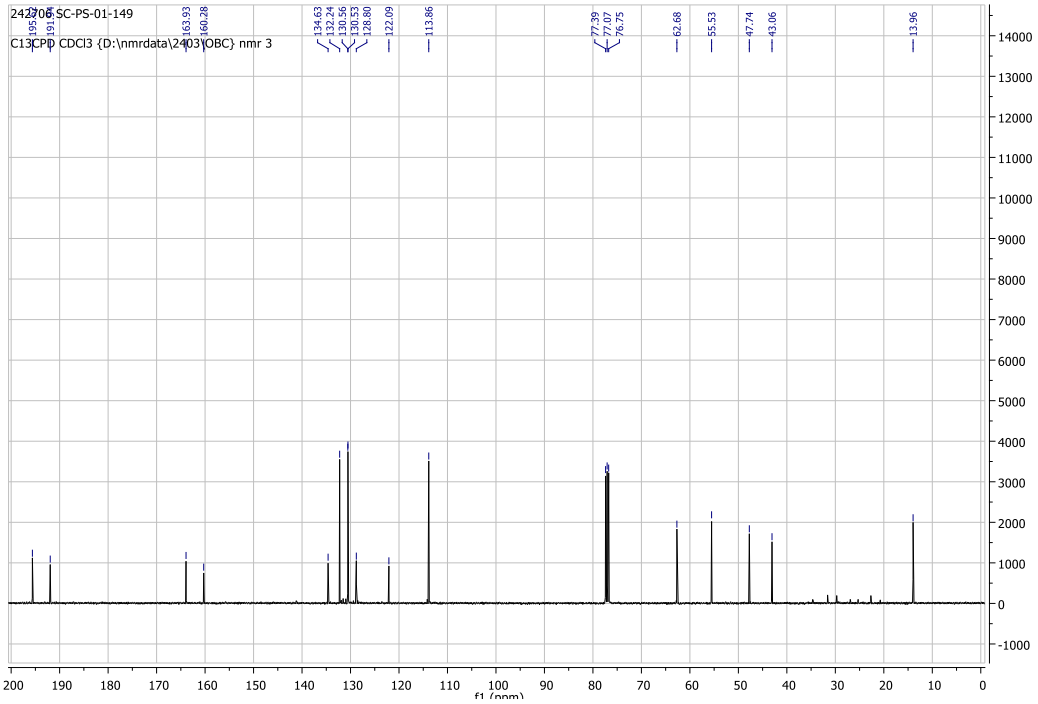




^{1}H-NMR (400 MHz, $CDCl_3$)



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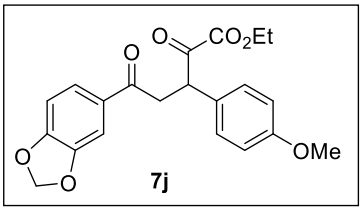
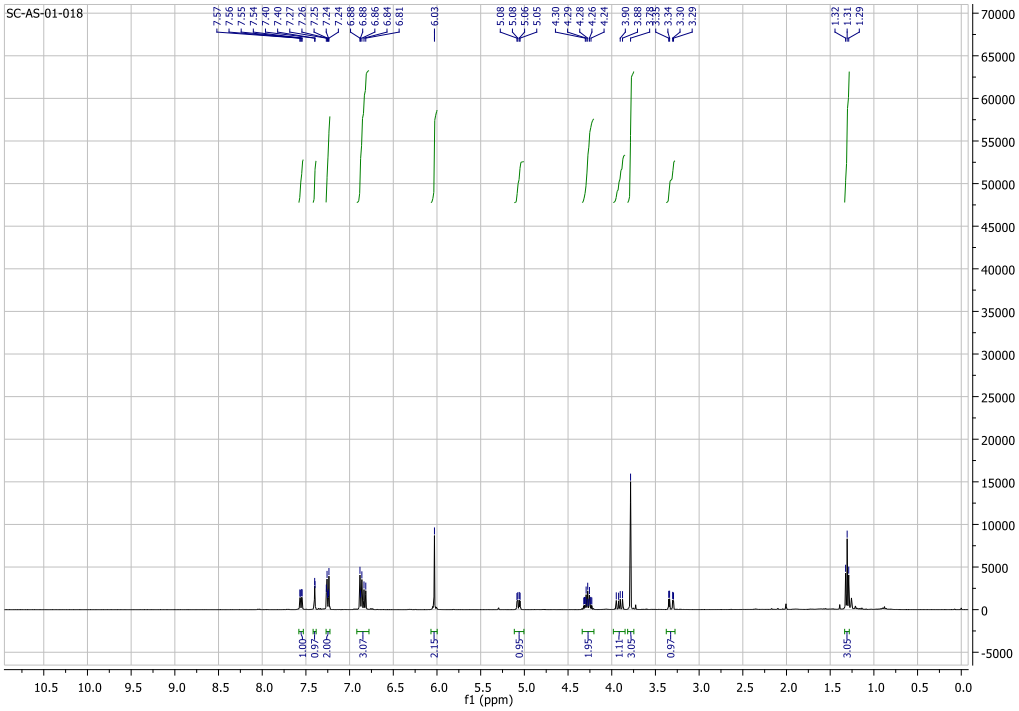
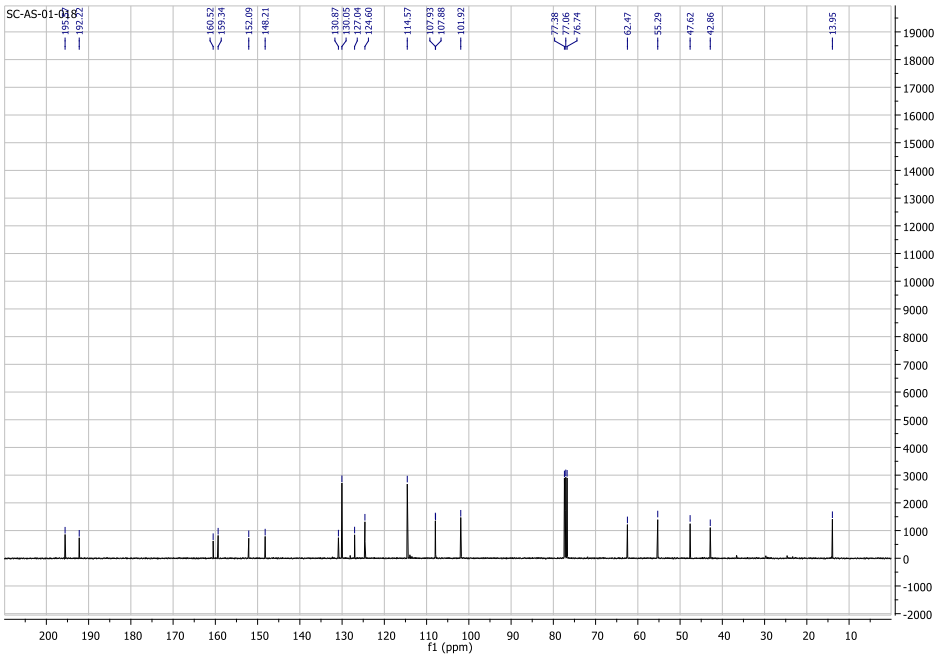




^{1}H-NMR (400 MHz, $CDCl_3$)



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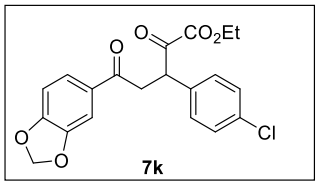

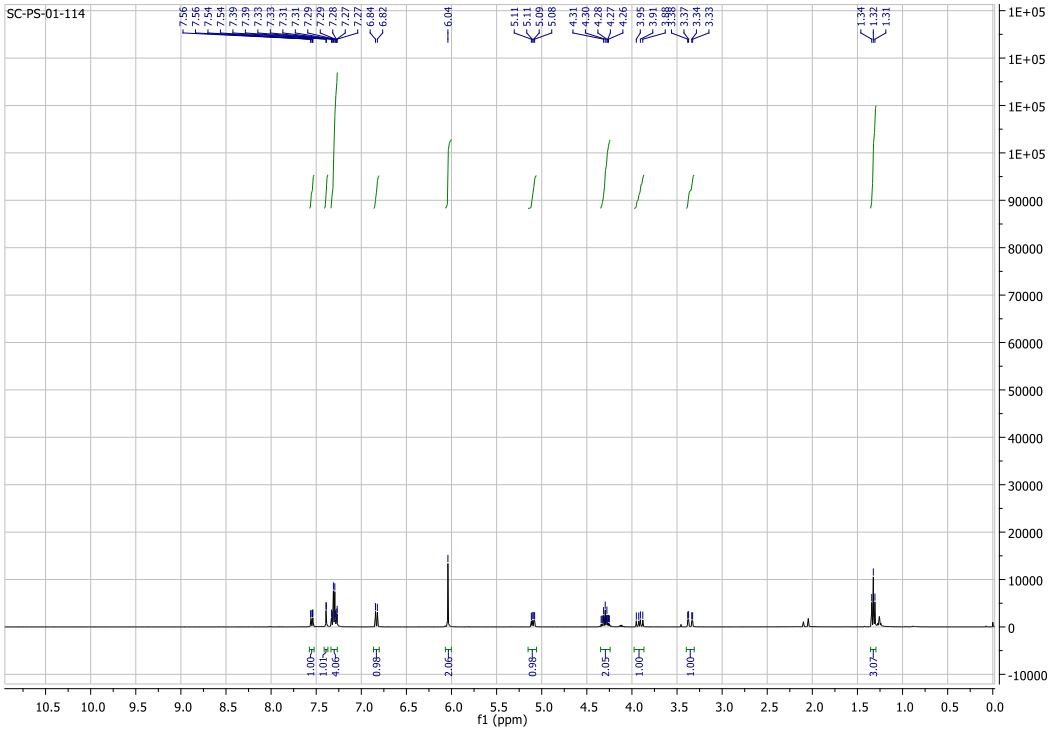

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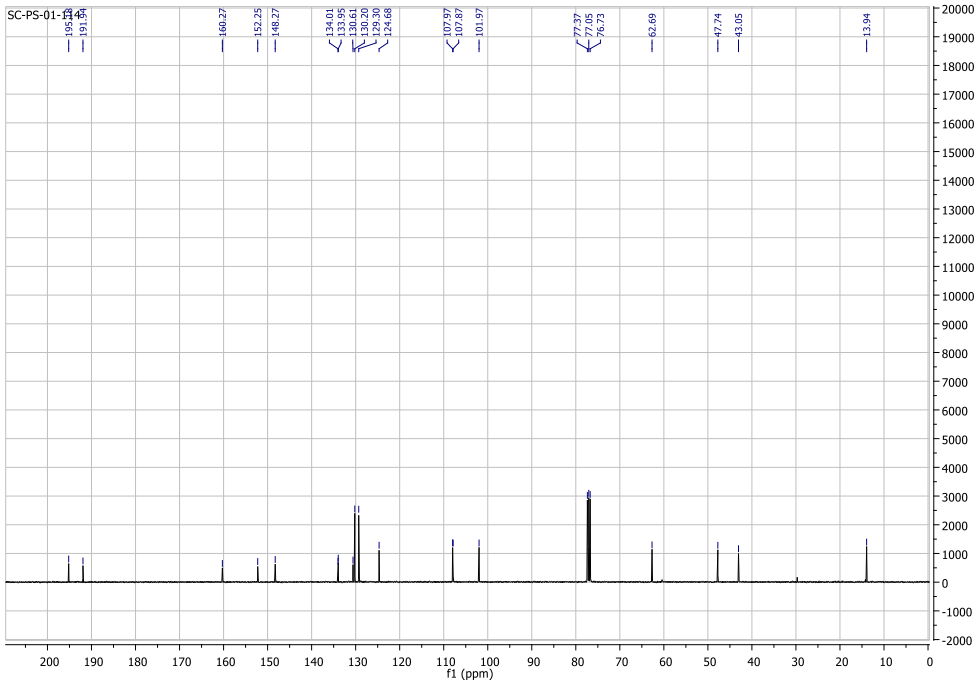

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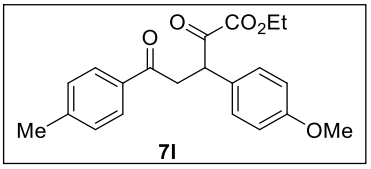

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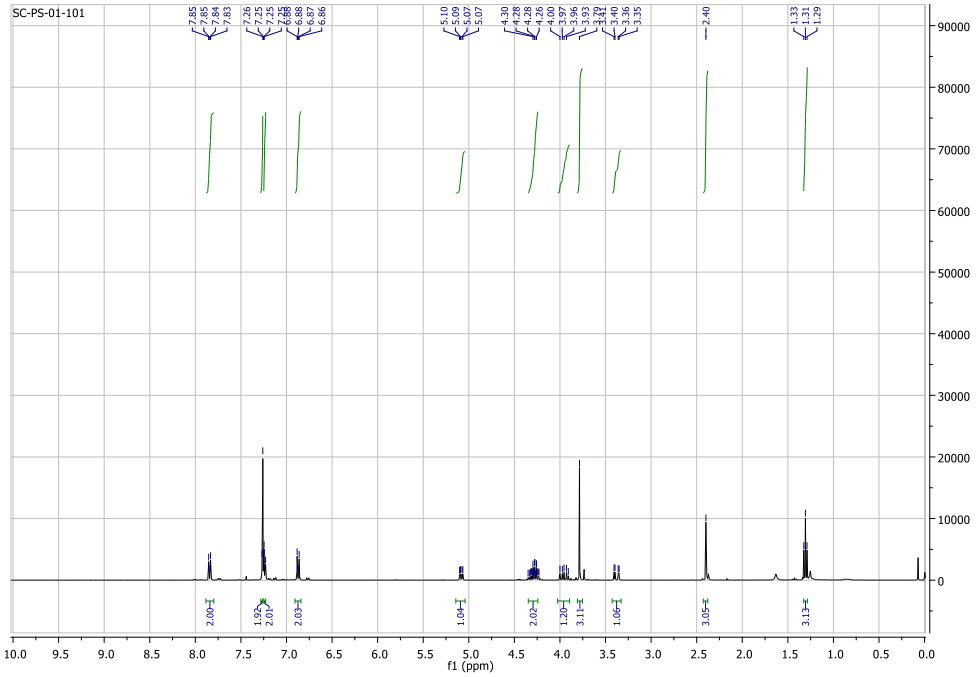

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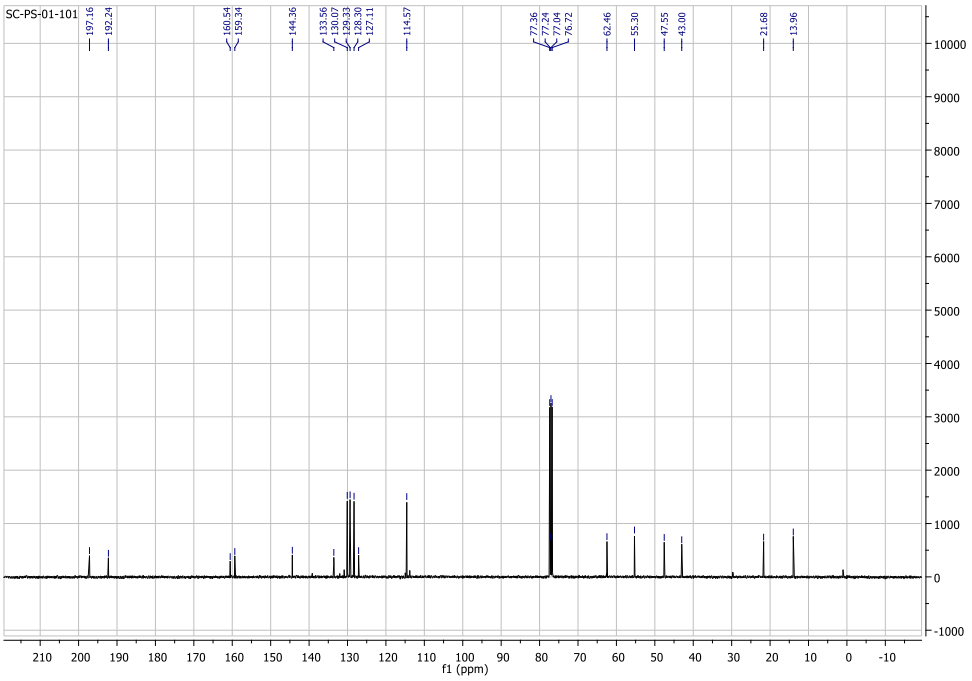

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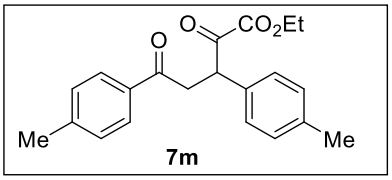

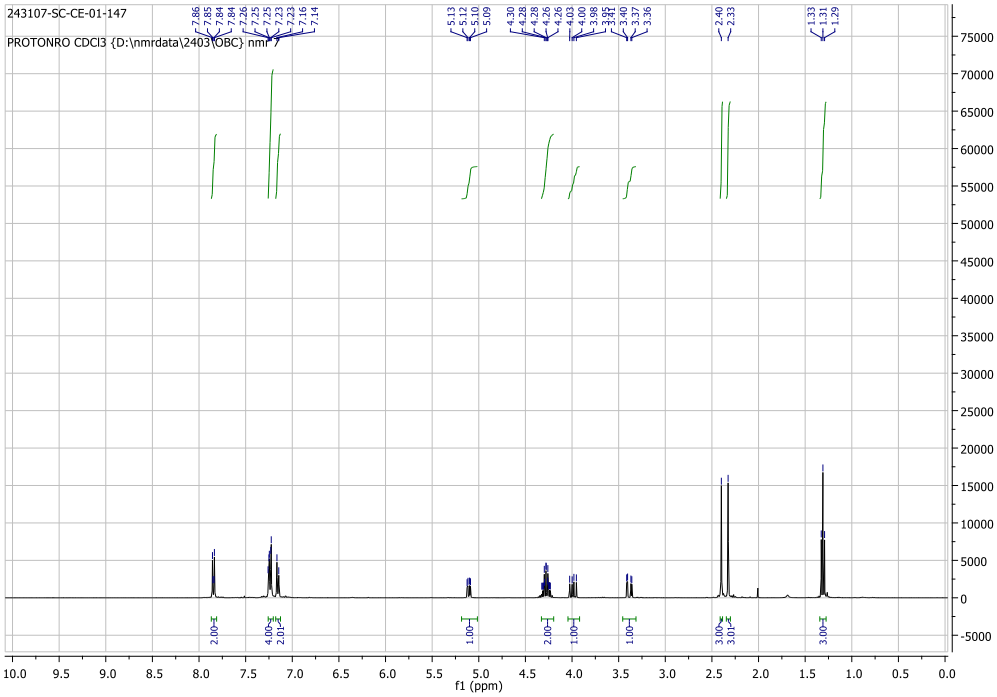

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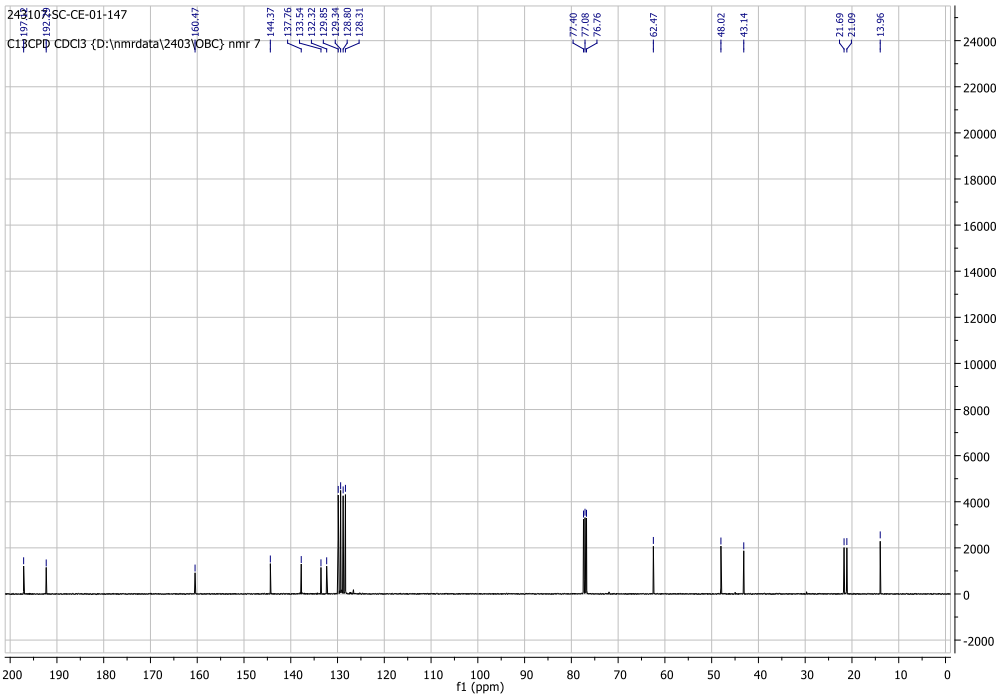

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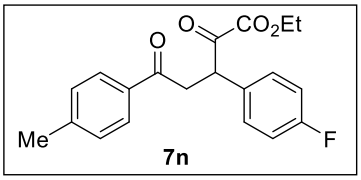

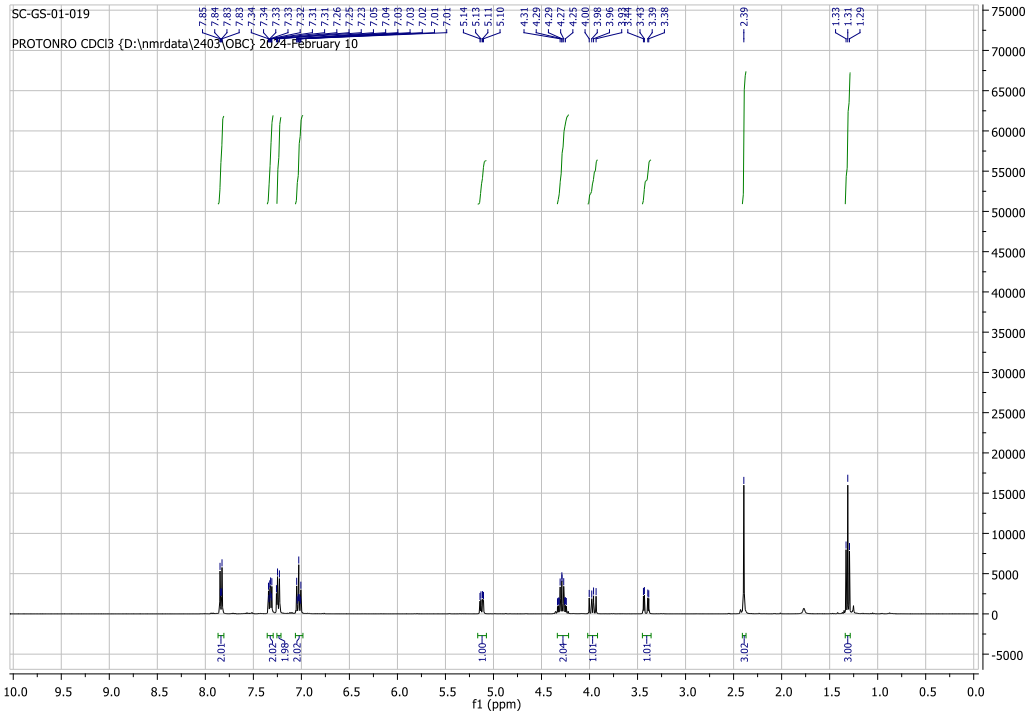

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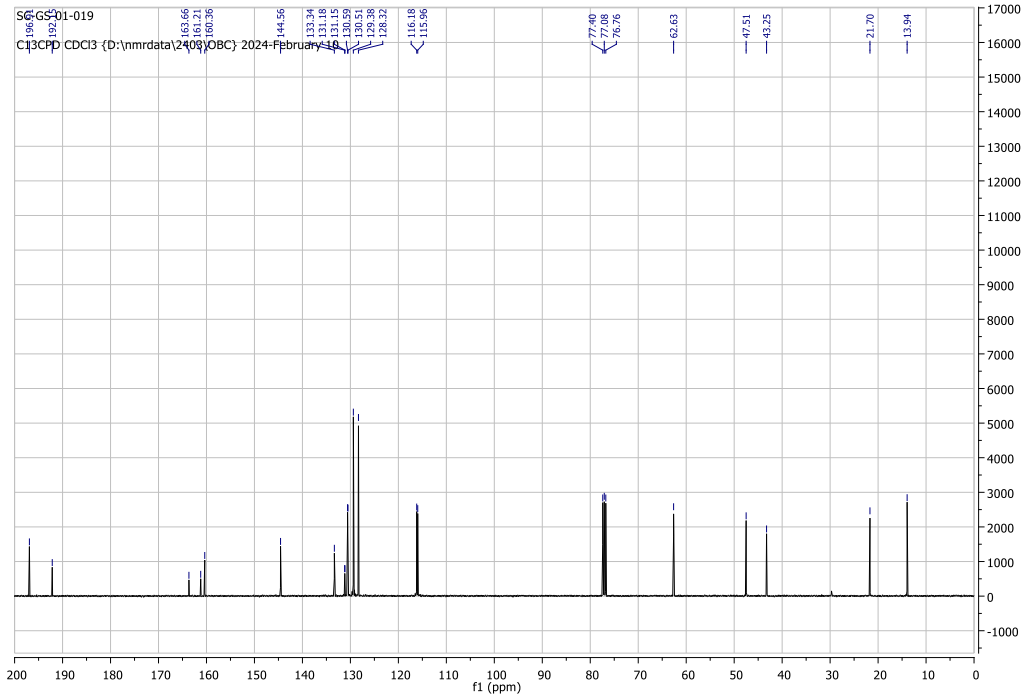

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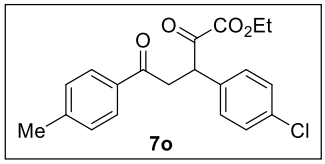

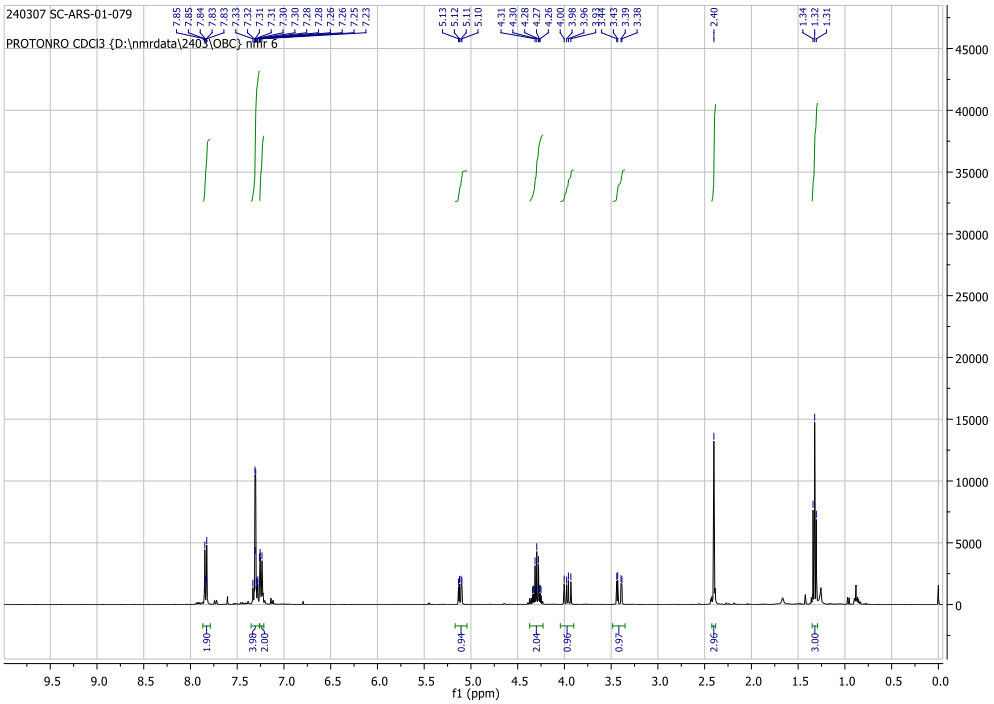

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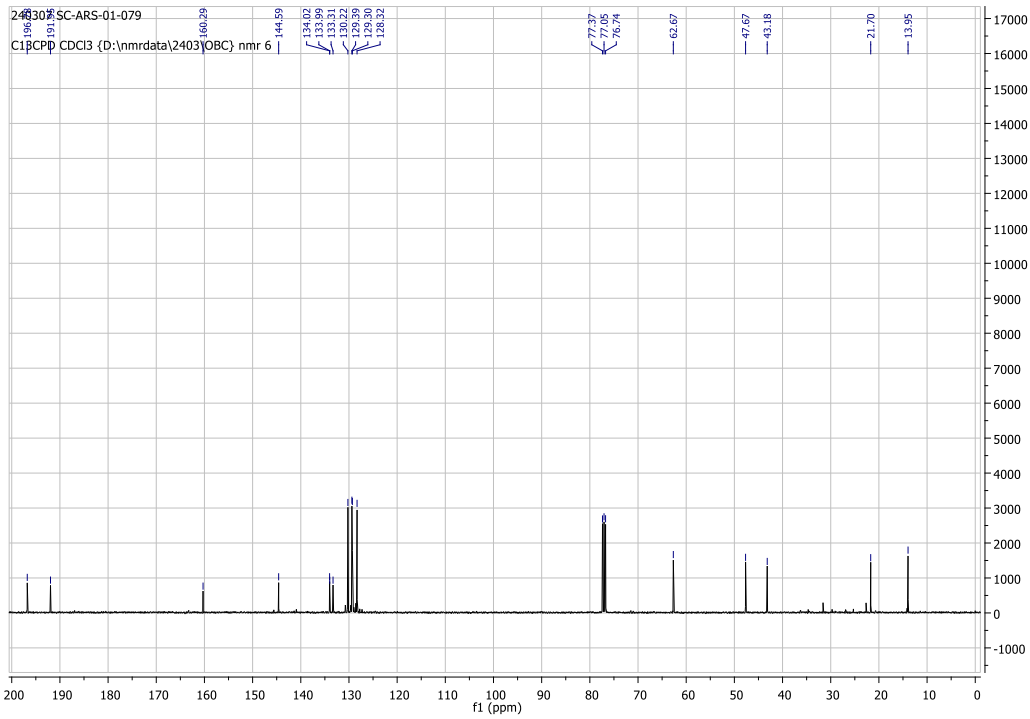
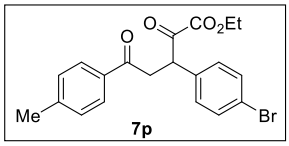


^{13}C-NMR (100 MHz, $CDCl_3$)



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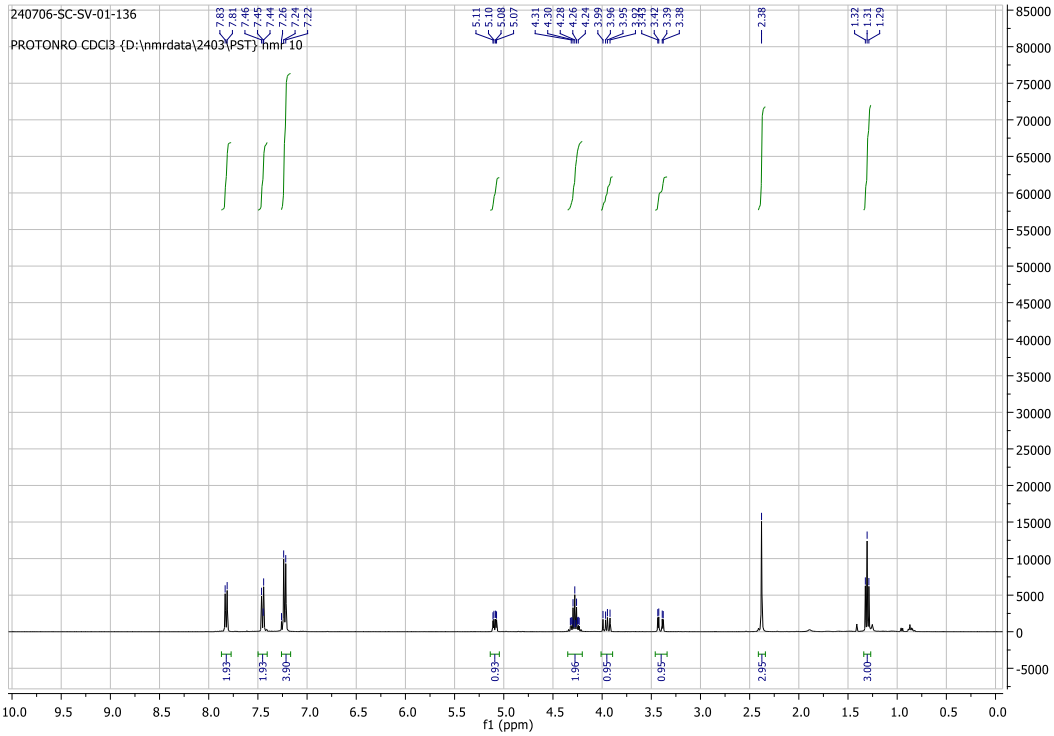
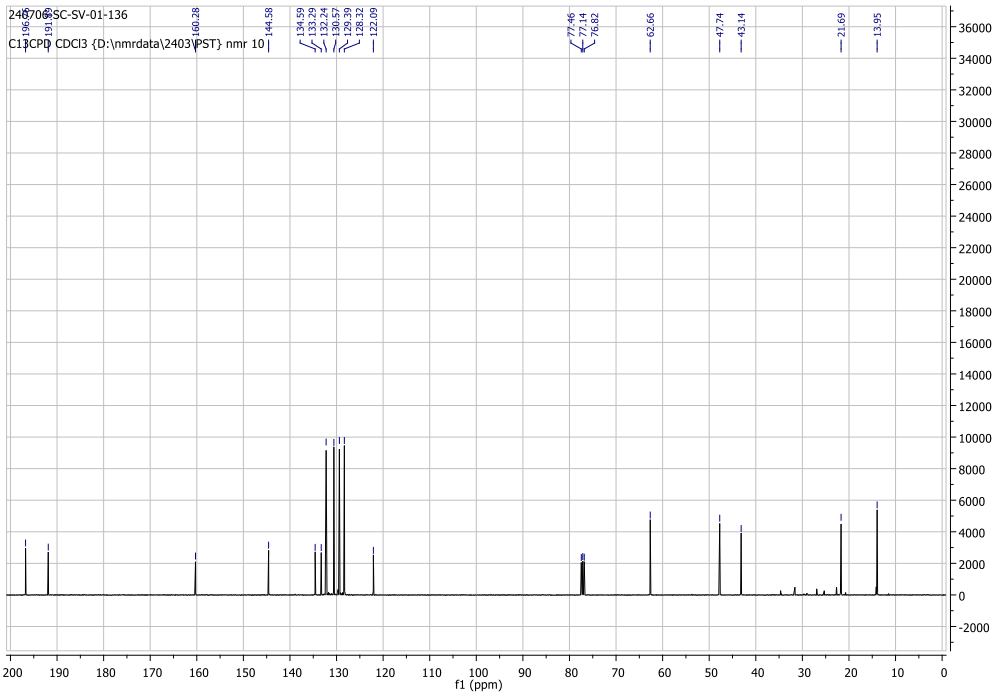
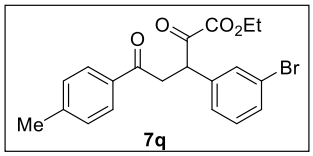
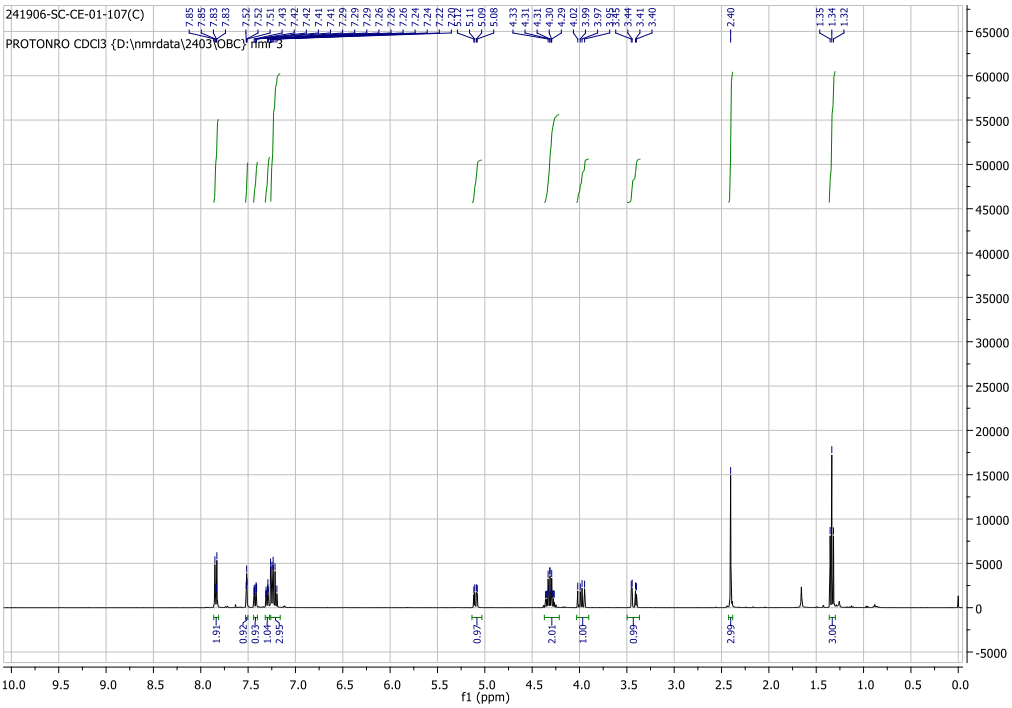


^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (100 MHz, $CDCl_3$)





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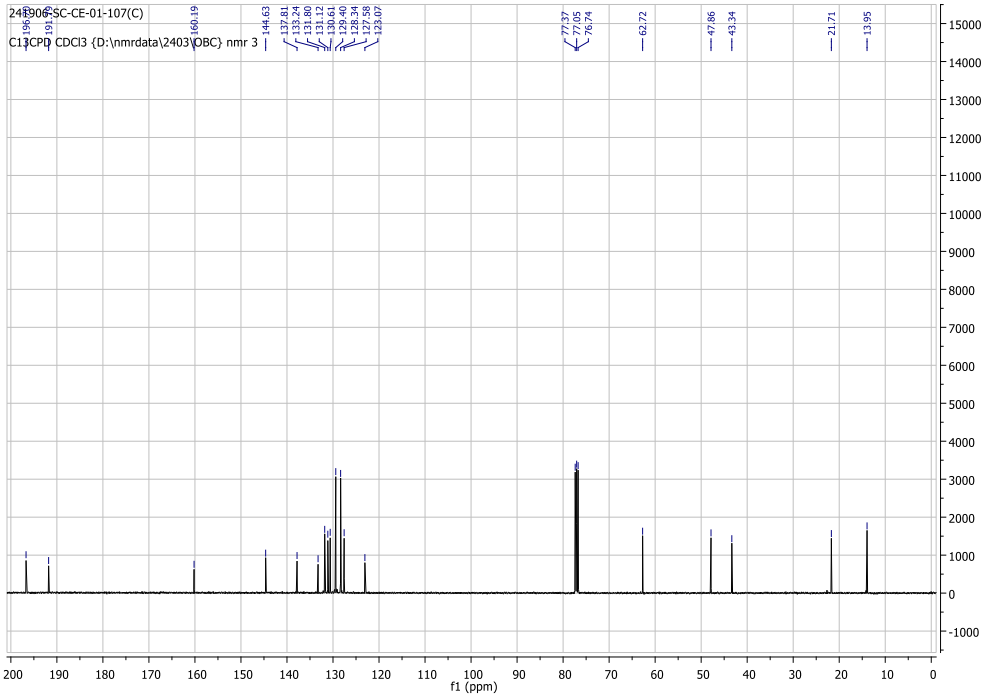
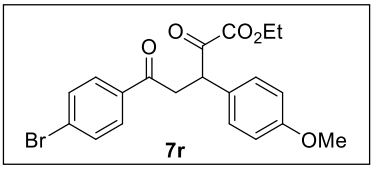
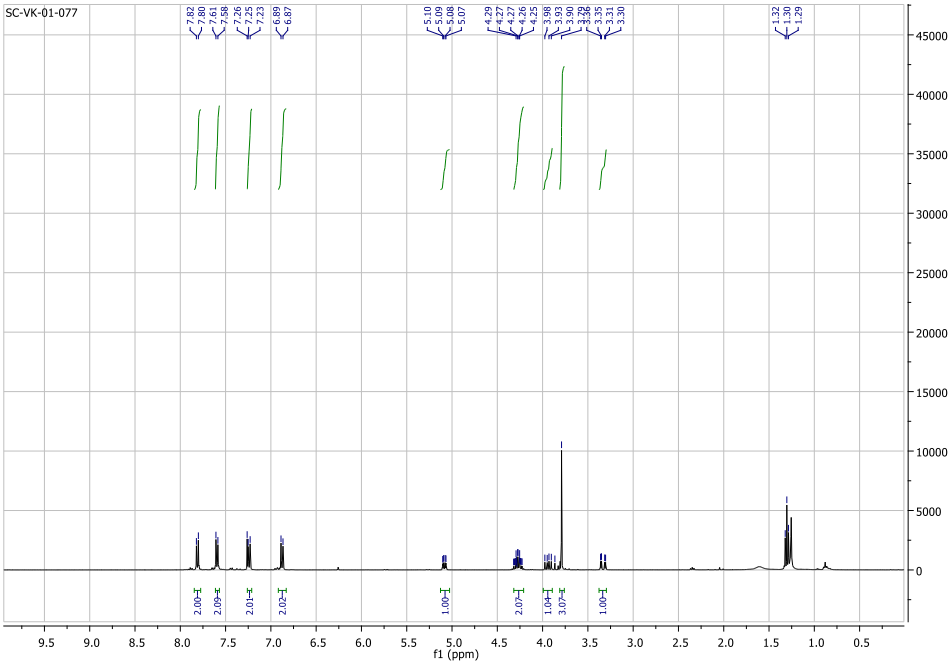


^{13}C-NMR (100 MHz, $CDCl_3$)





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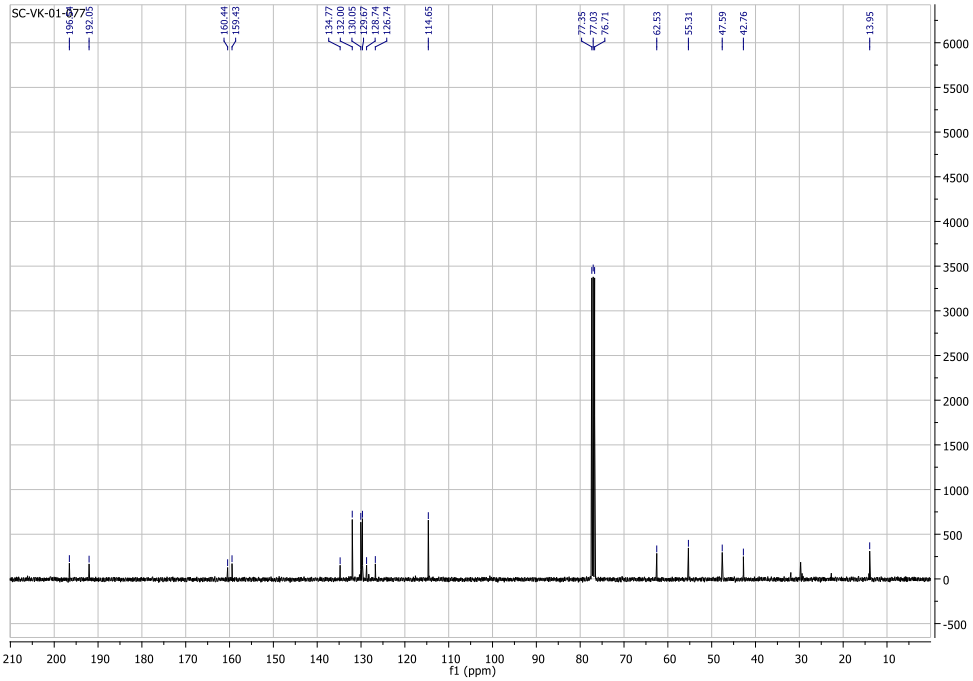

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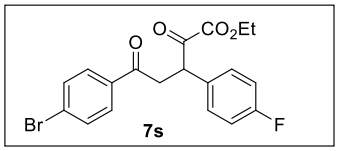

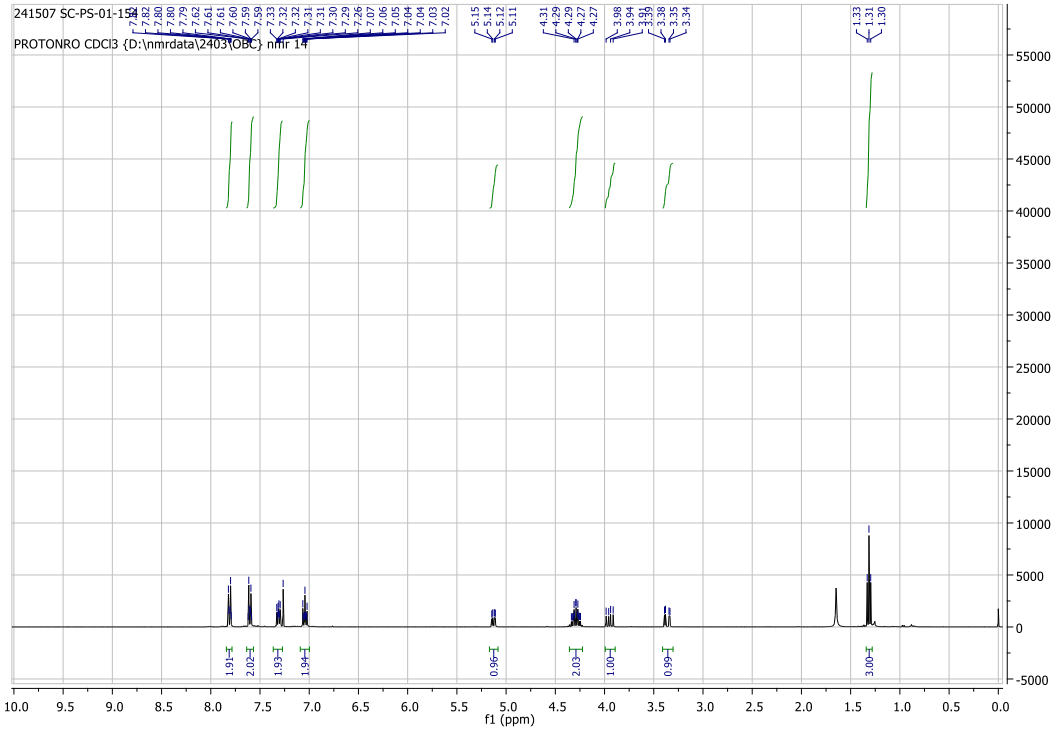

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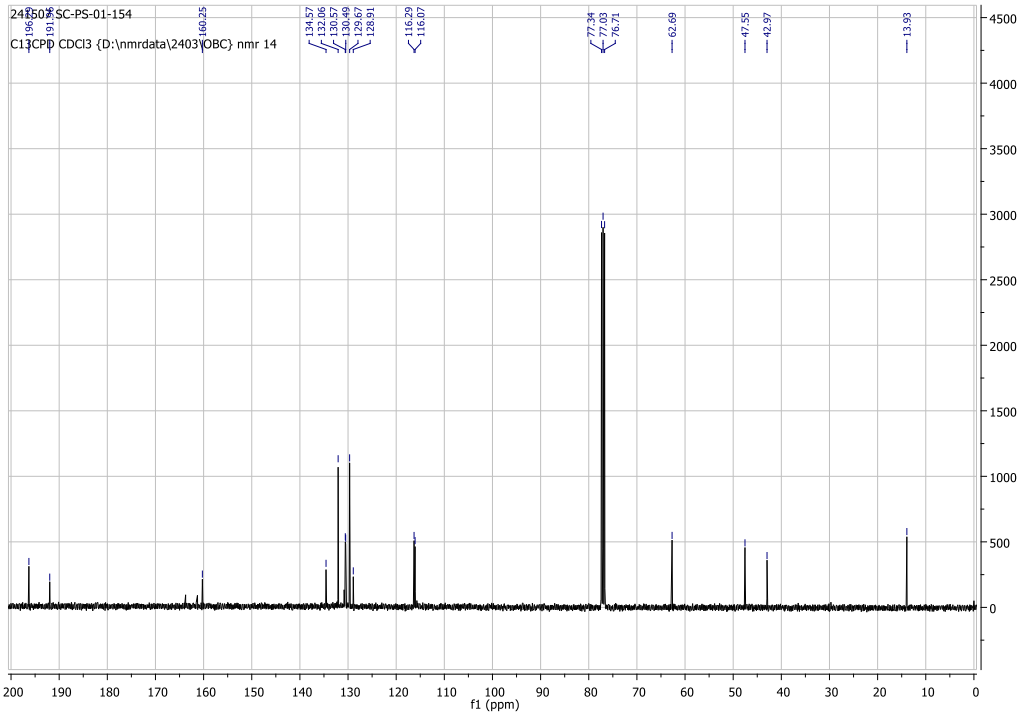

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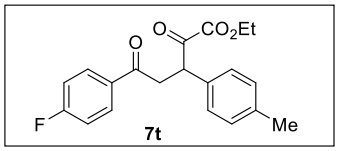

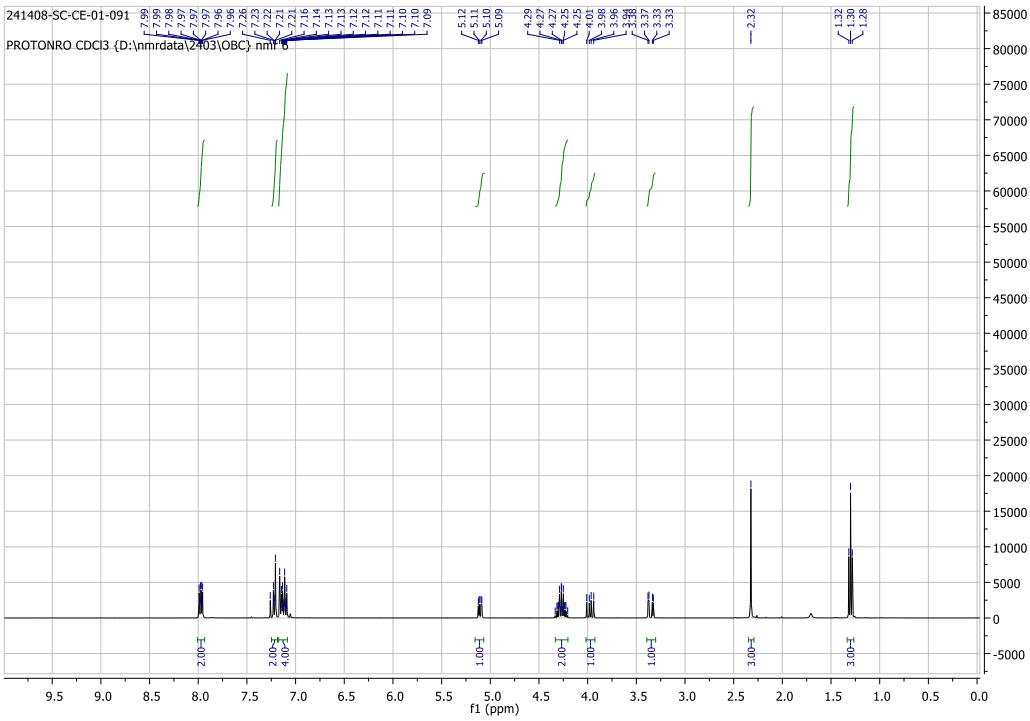

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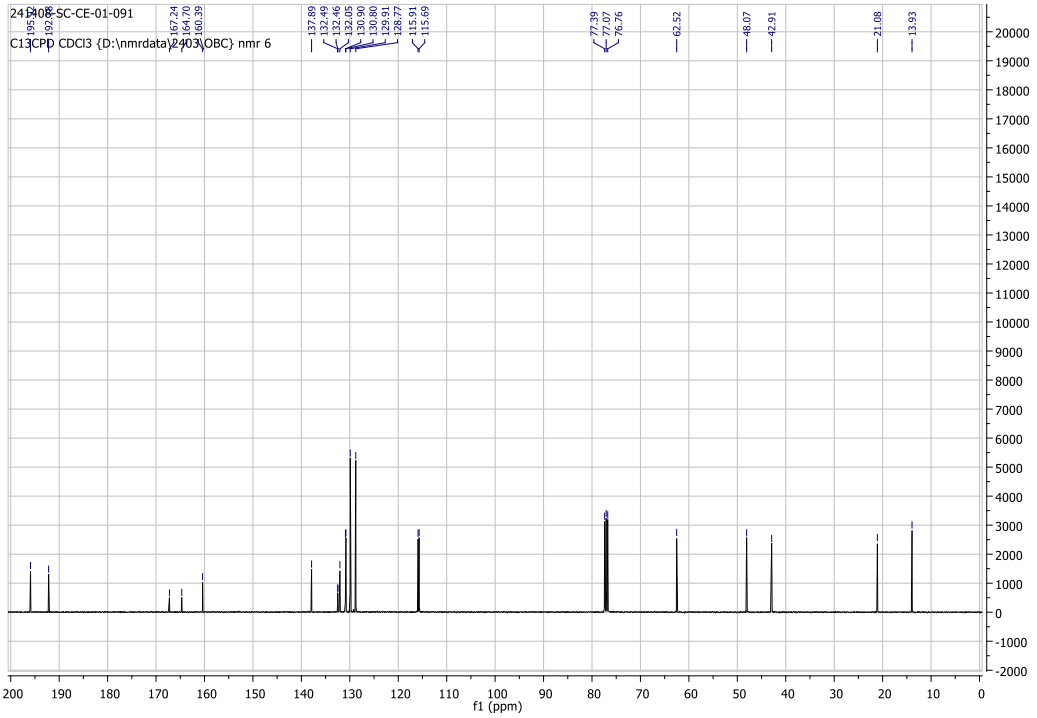

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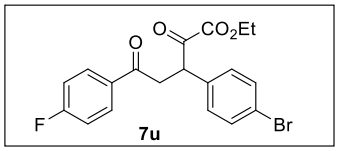

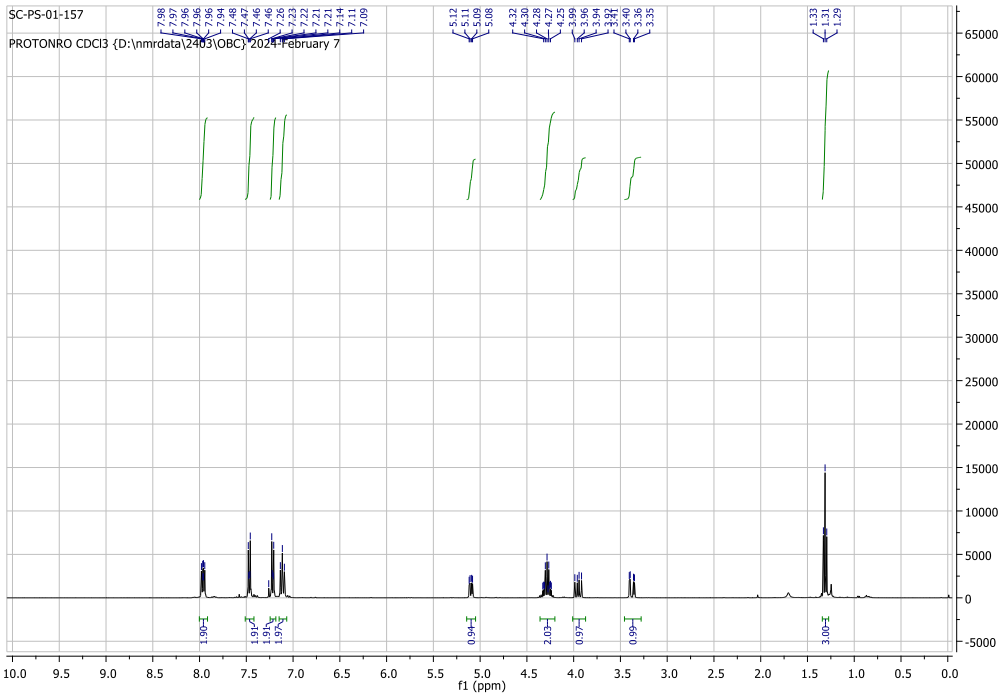

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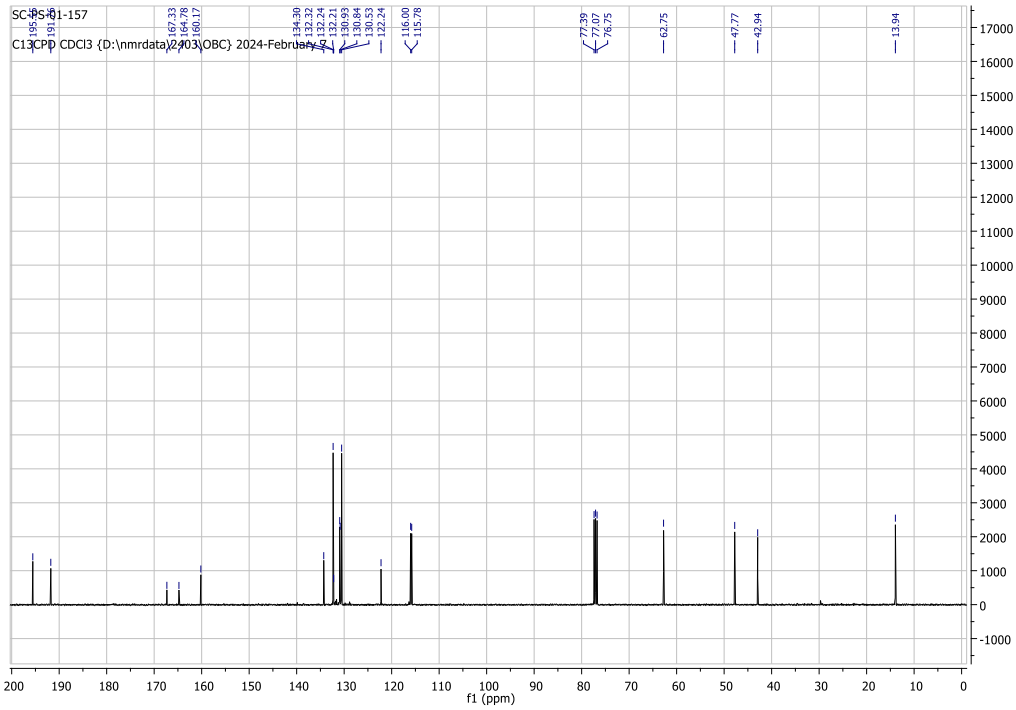

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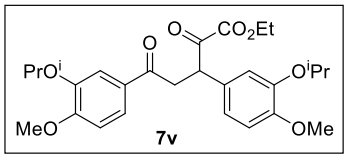

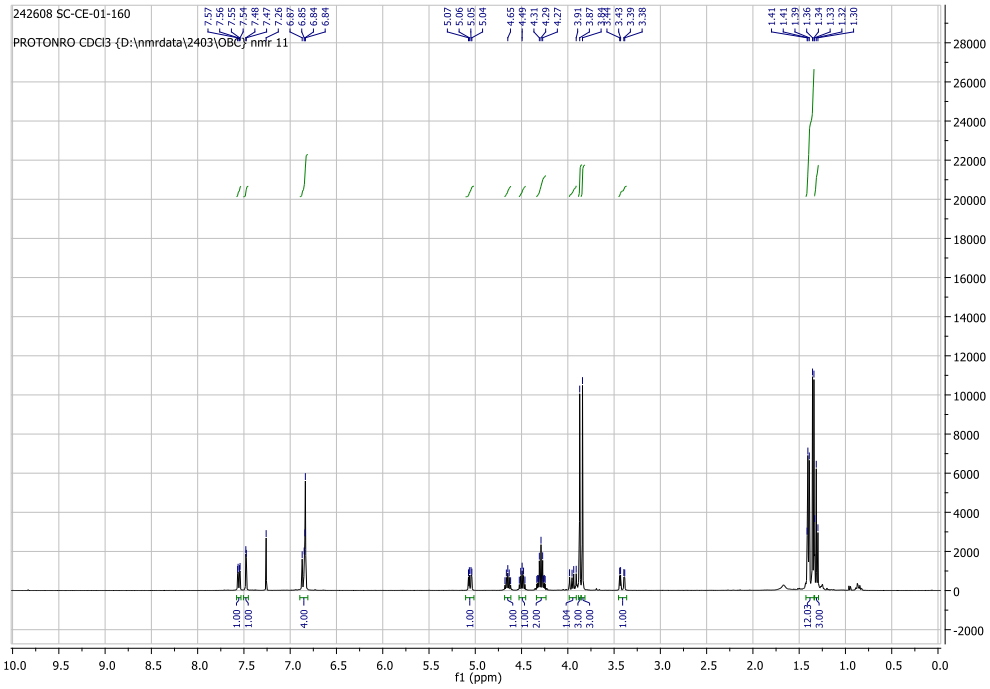

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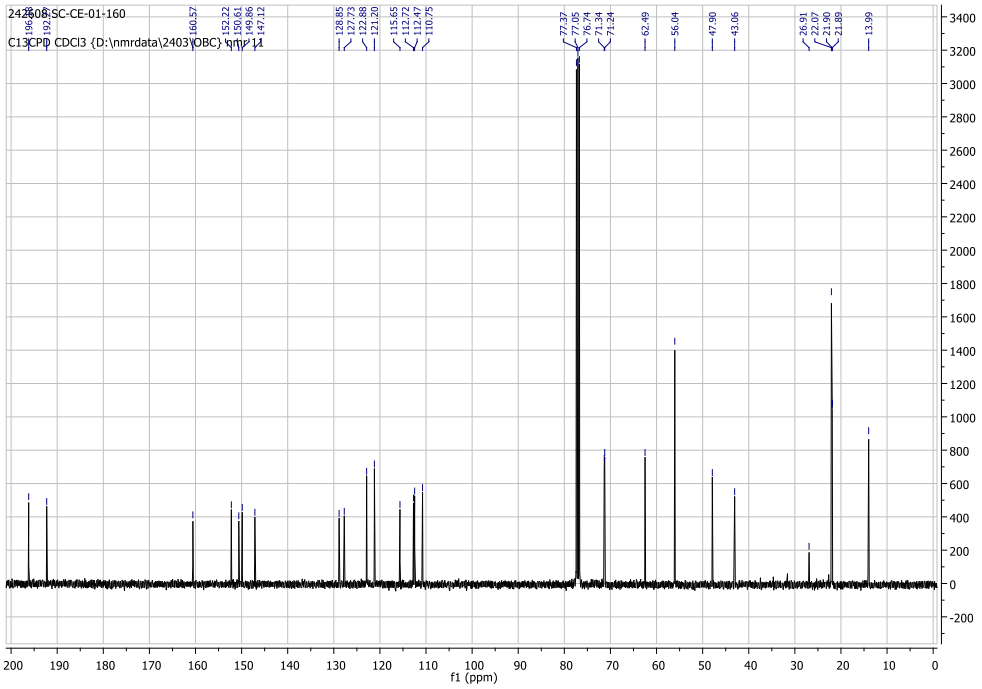

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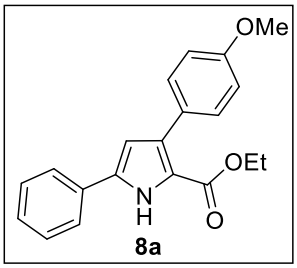

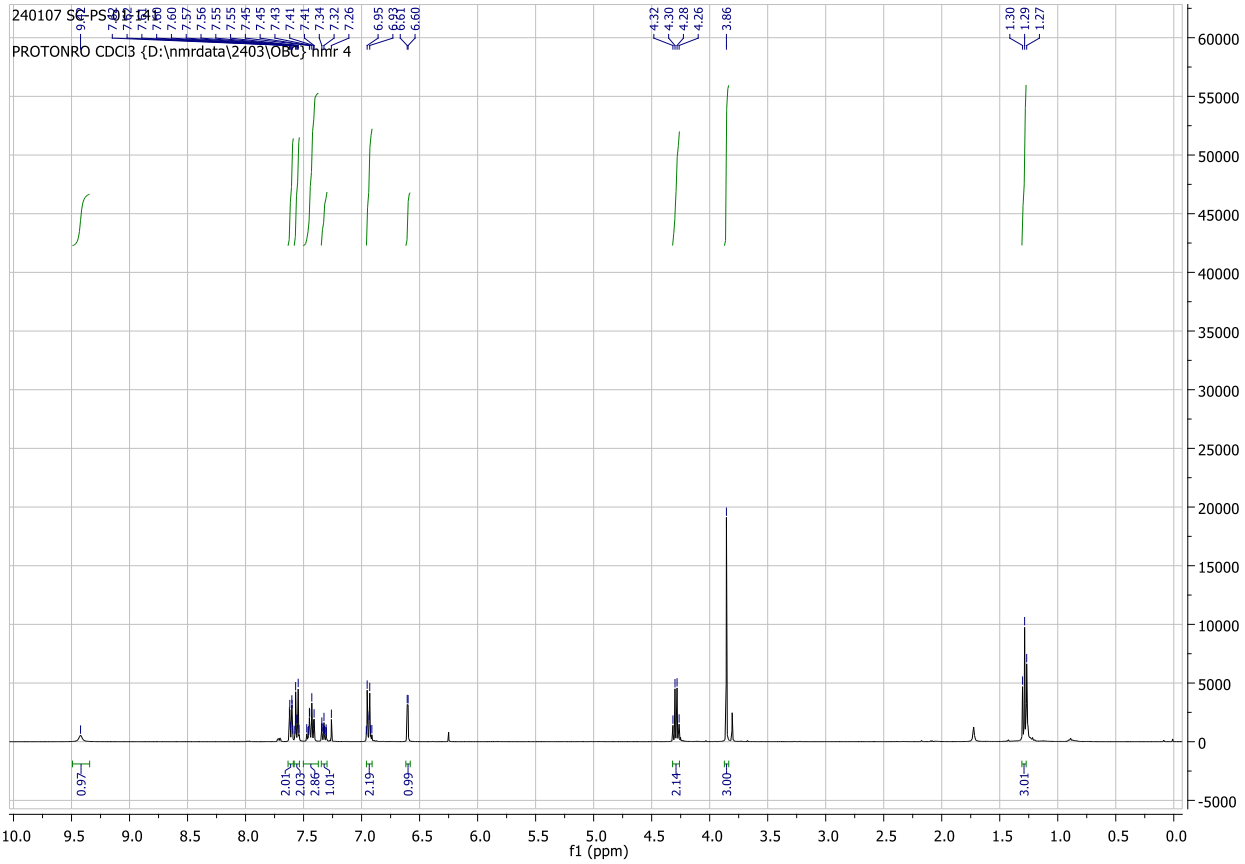

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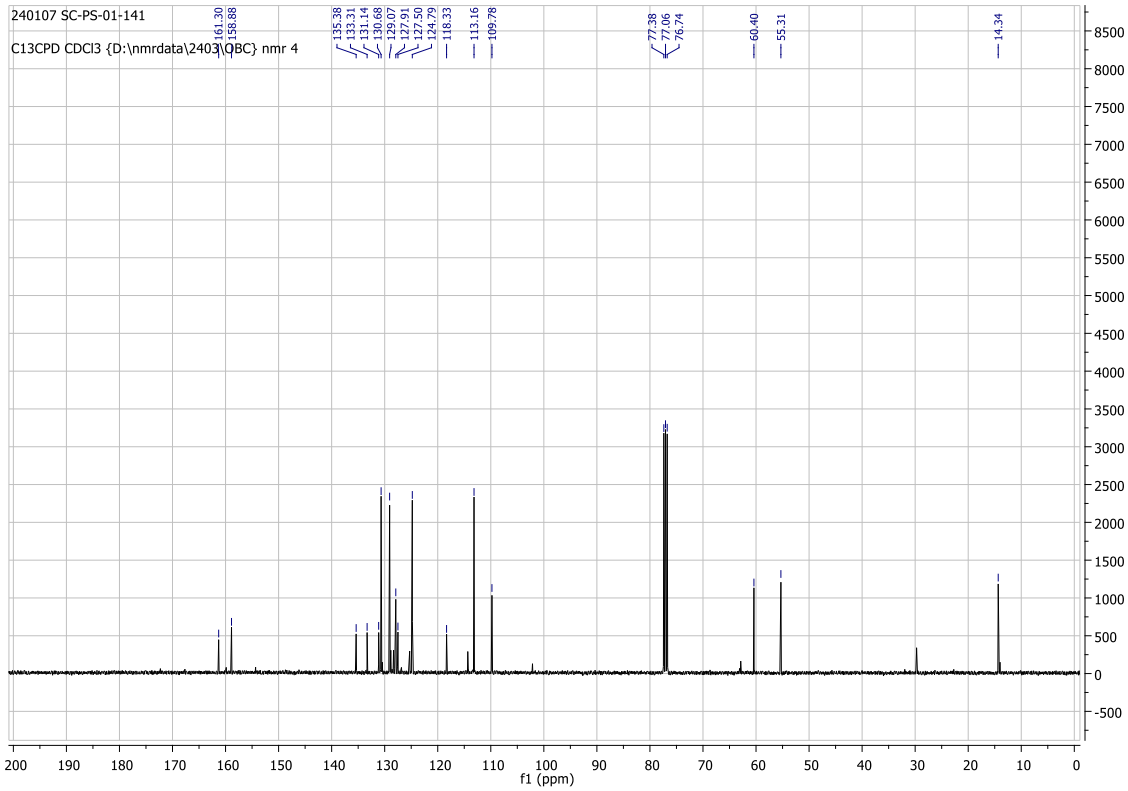
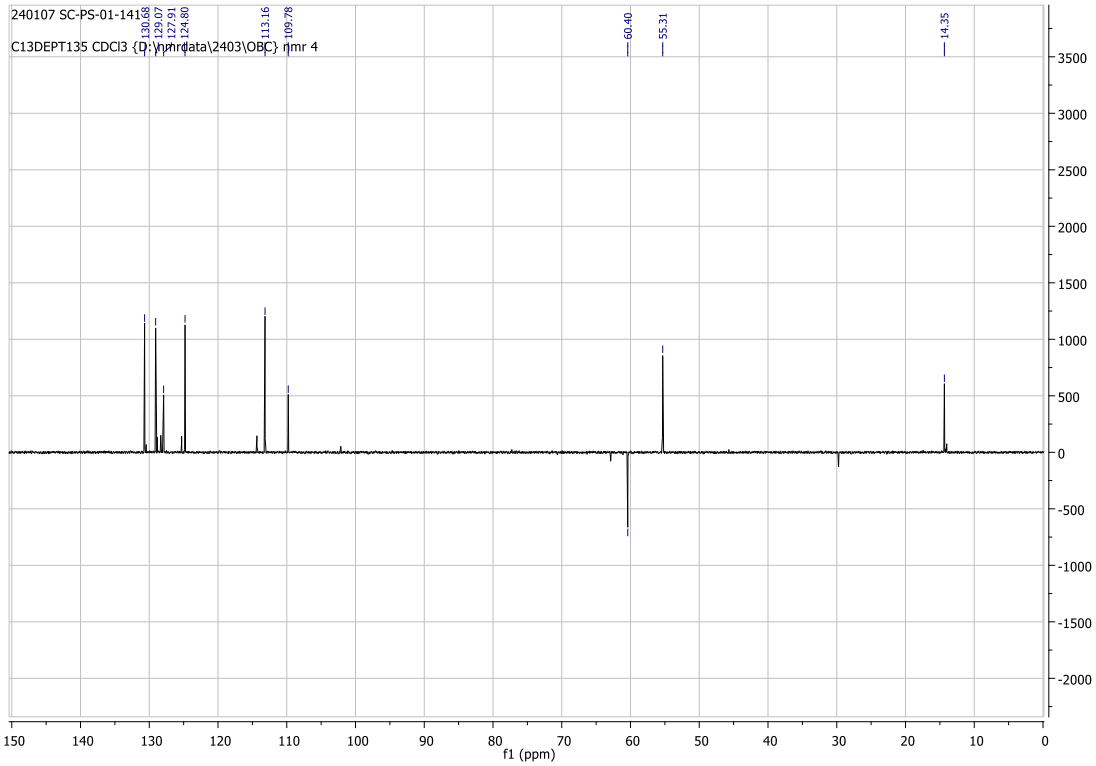
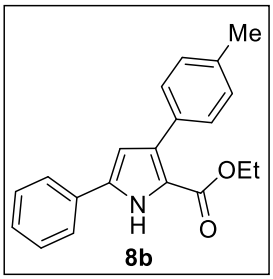
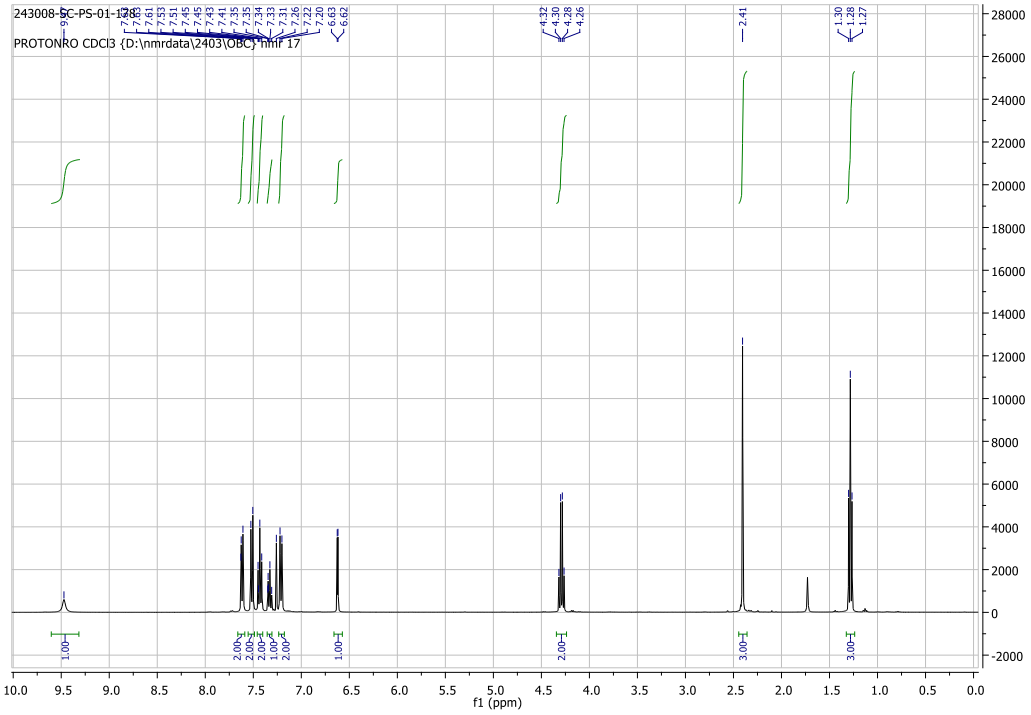


^{13}C-NMR (100 MHz, $CDCl_3$) of **8a**

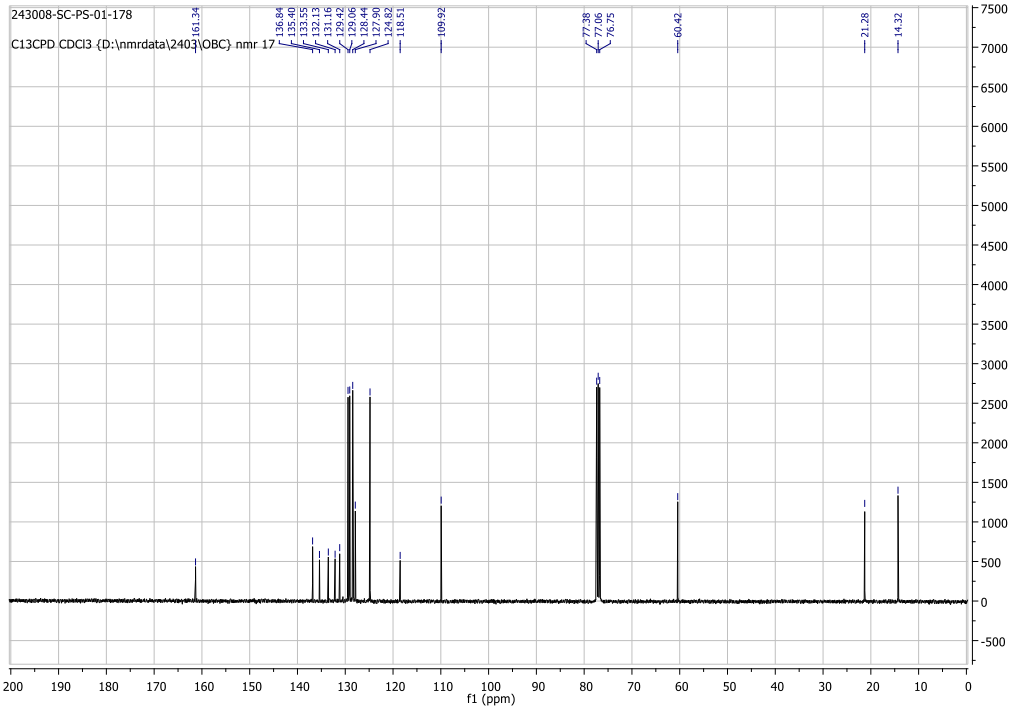


DEPT – 135 of **8a**

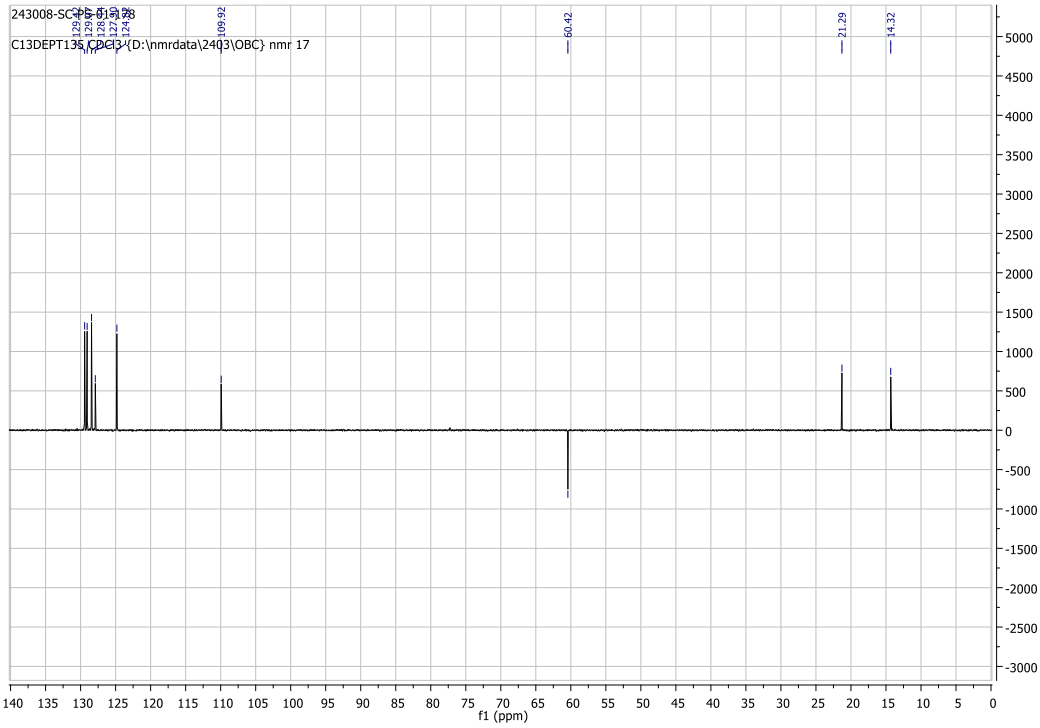




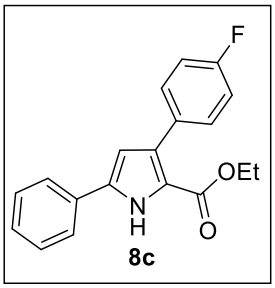
^{1}H-NMR (400 MHz, $CDCl_3$) of **8b**

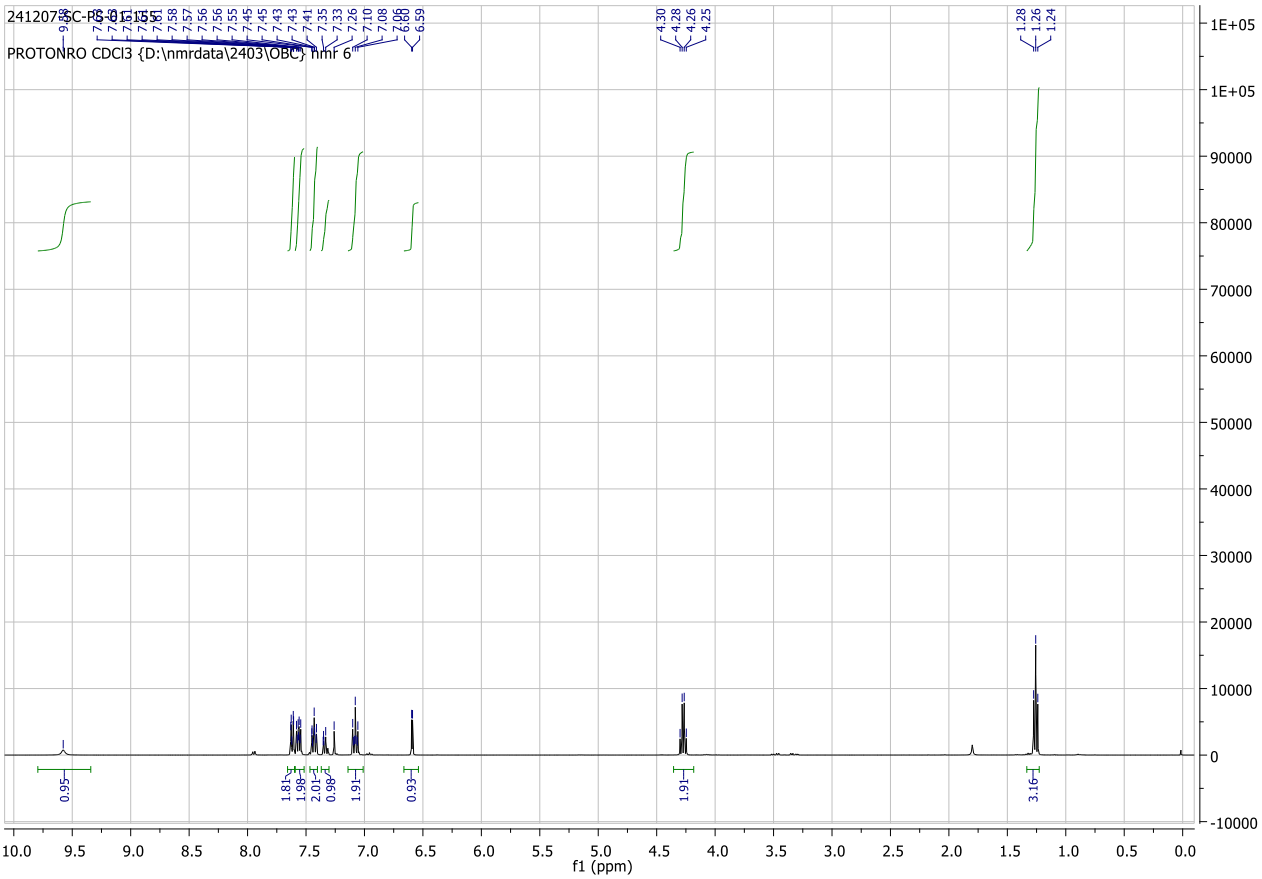


^{13}C-NMR (100 MHz, $CDCl_3$) of **8b**

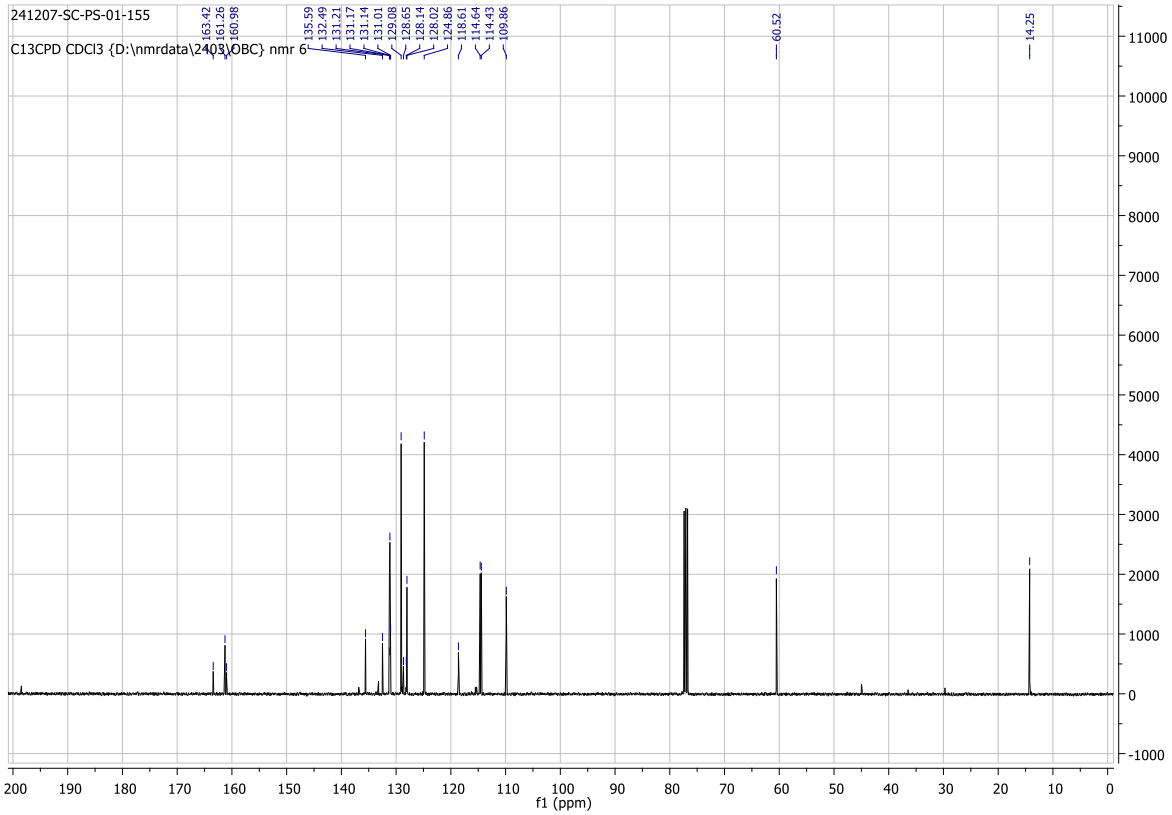


DEPT – 135 of **8b**

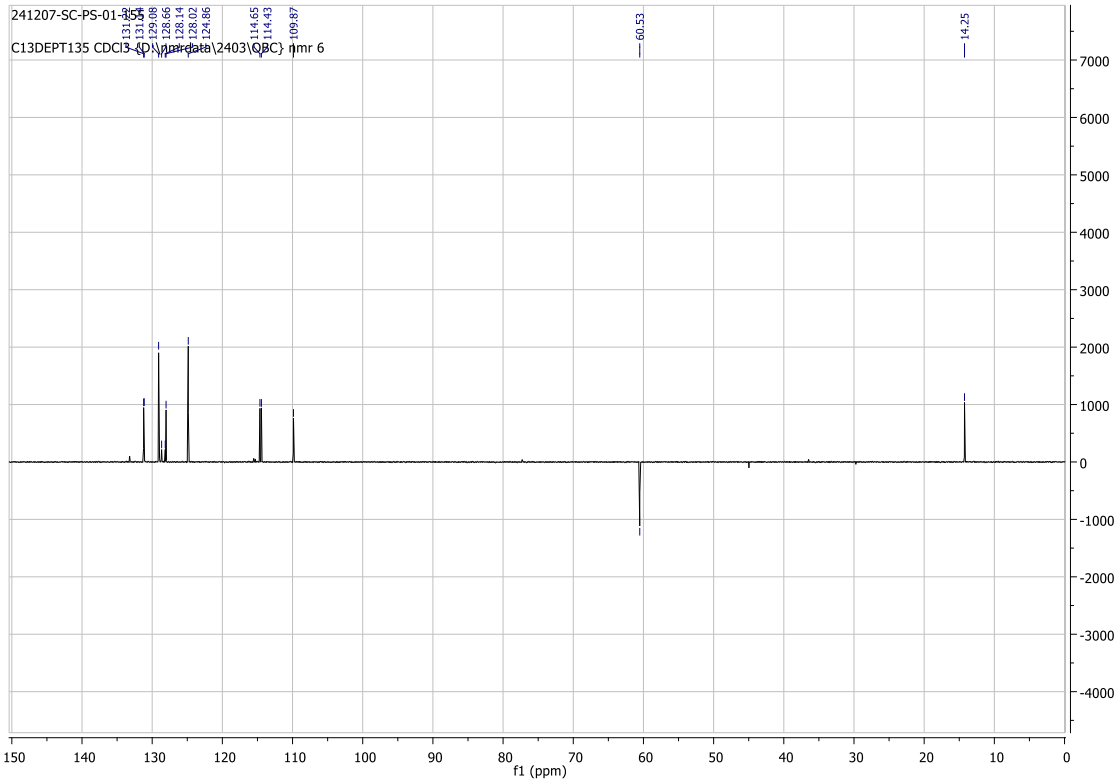




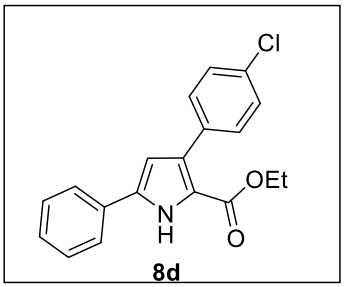
^{1}H-NMR (400 MHz, $CDCl_3$) of **8c**

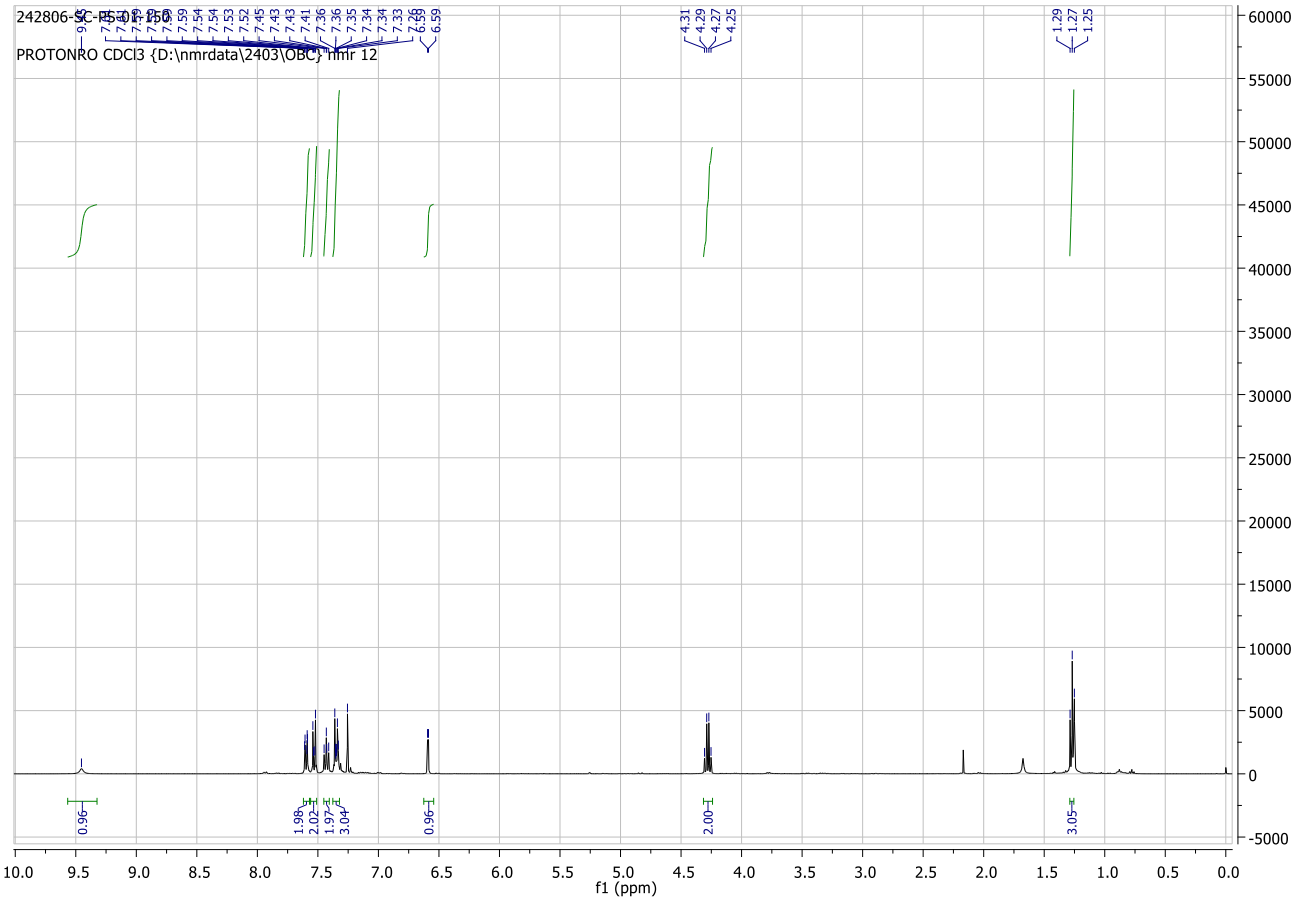


^{13}C-NMR (100 MHz, $CDCl_3$) of **8c**

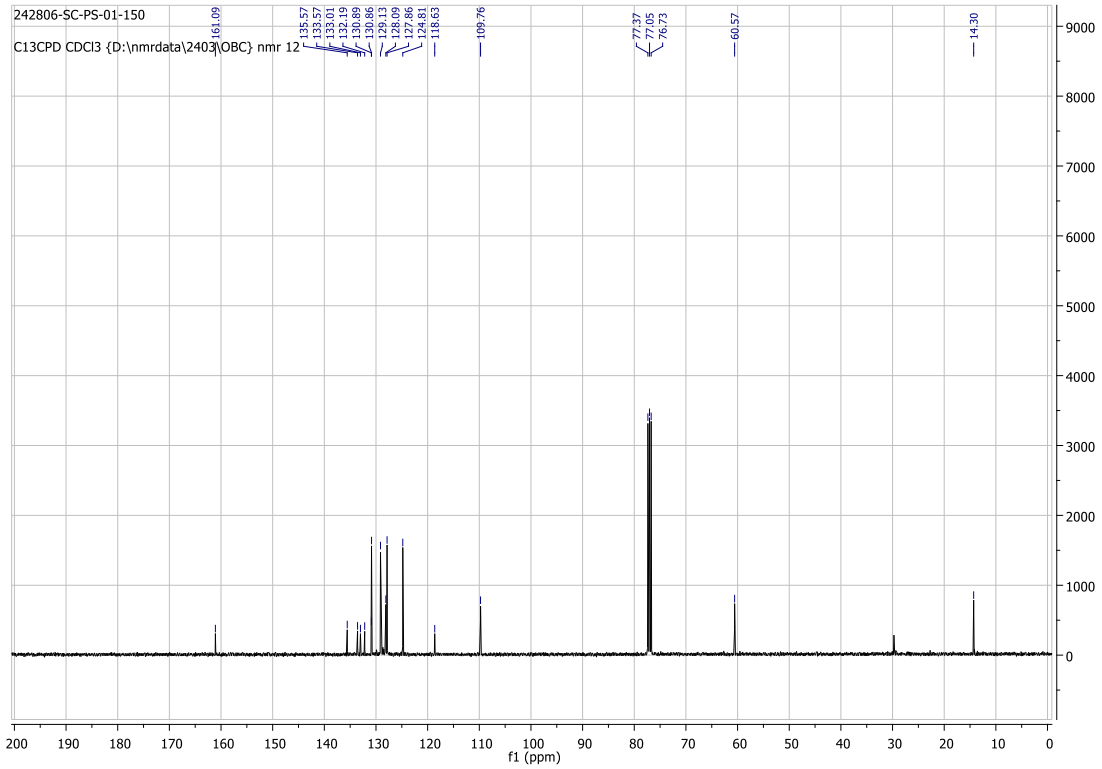


DEPT – 135 of **8c**

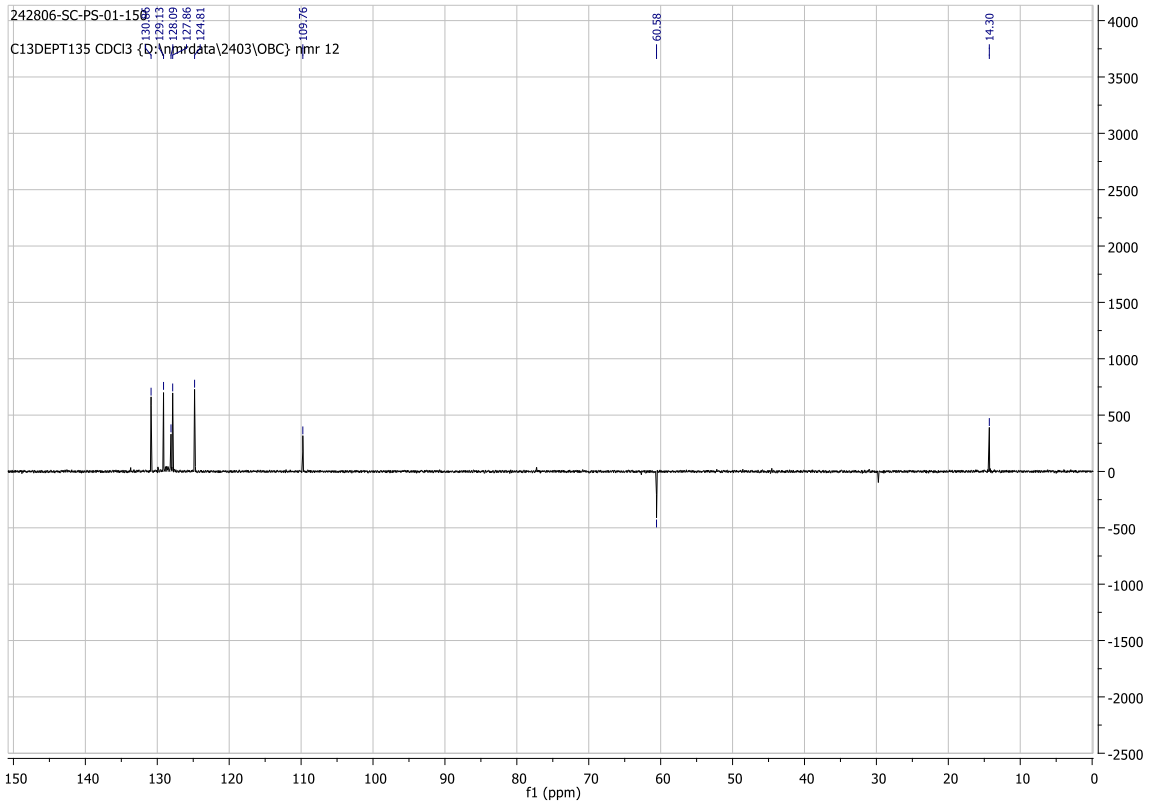




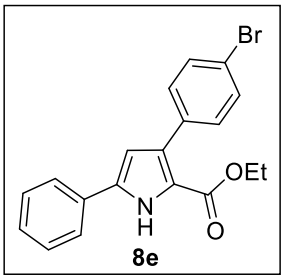
^{1}H-NMR (400 MHz, $CDCl_3$) of **8d**

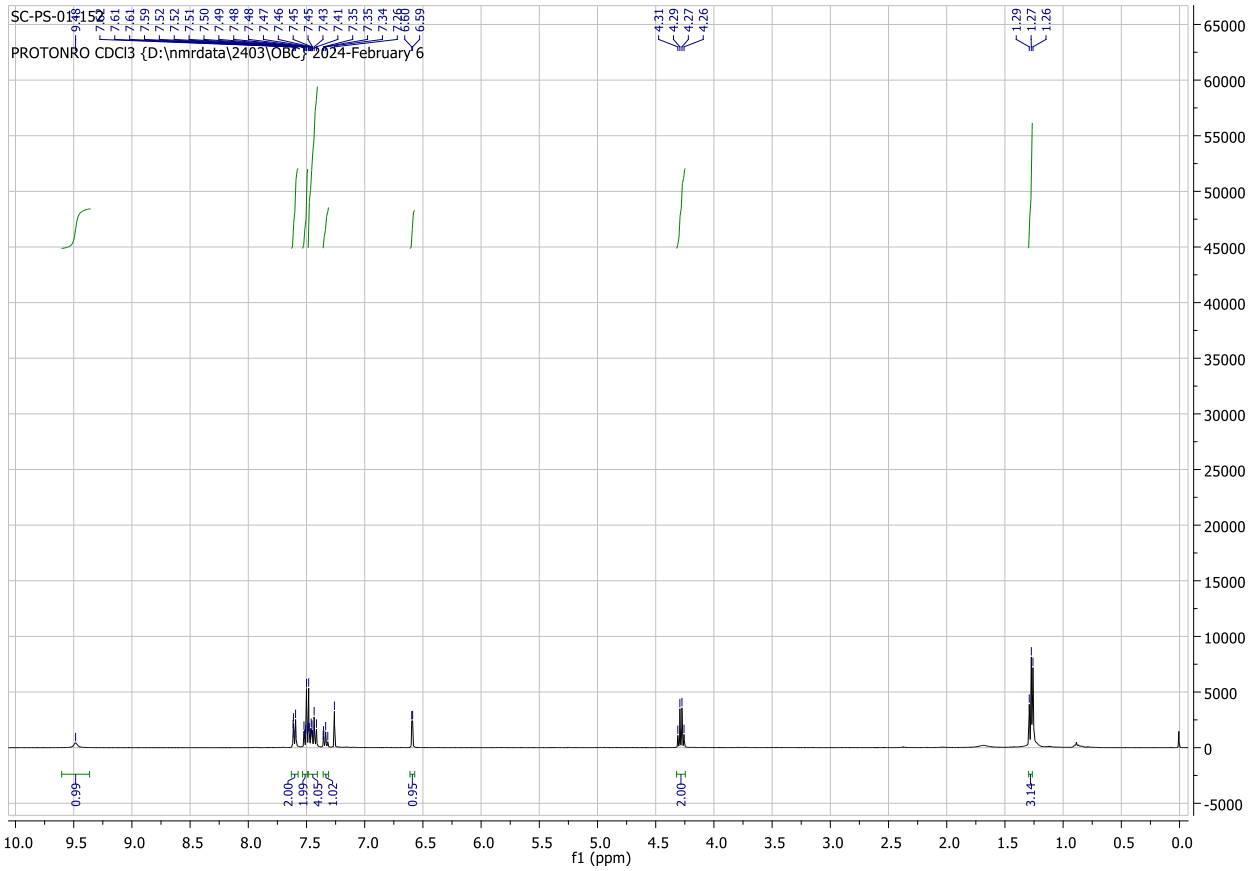


^{13}C-NMR (100 MHz, $CDCl_3$) of **8d**

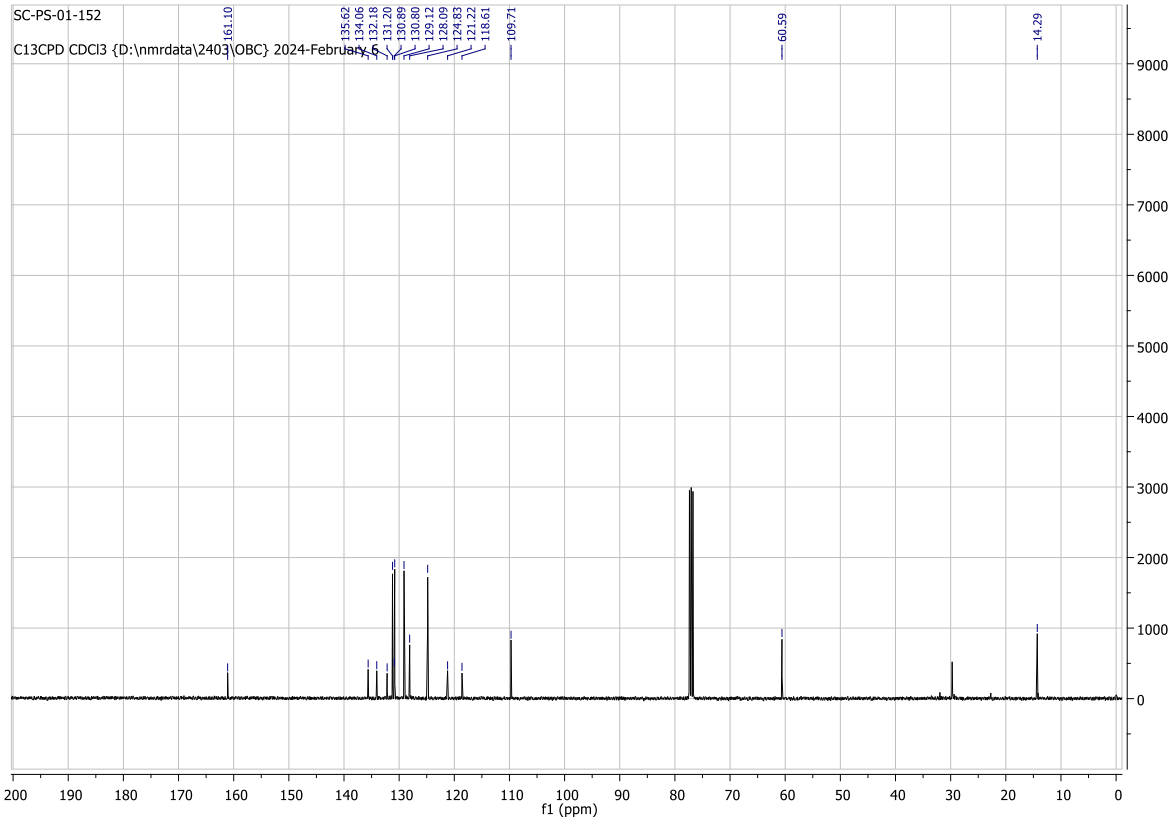


DEPT – 135 of **8d**

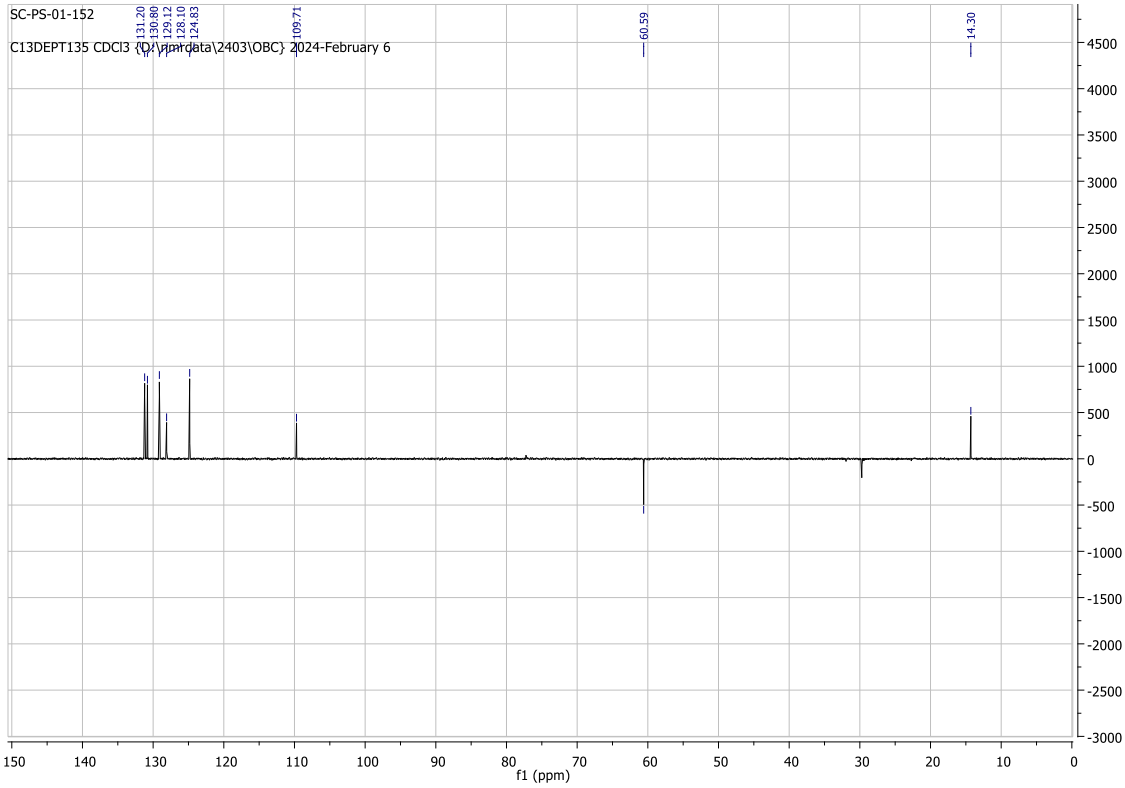




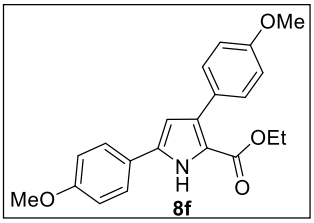
^{1}H-NMR (400 MHz, $CDCl_3$) of **8e**

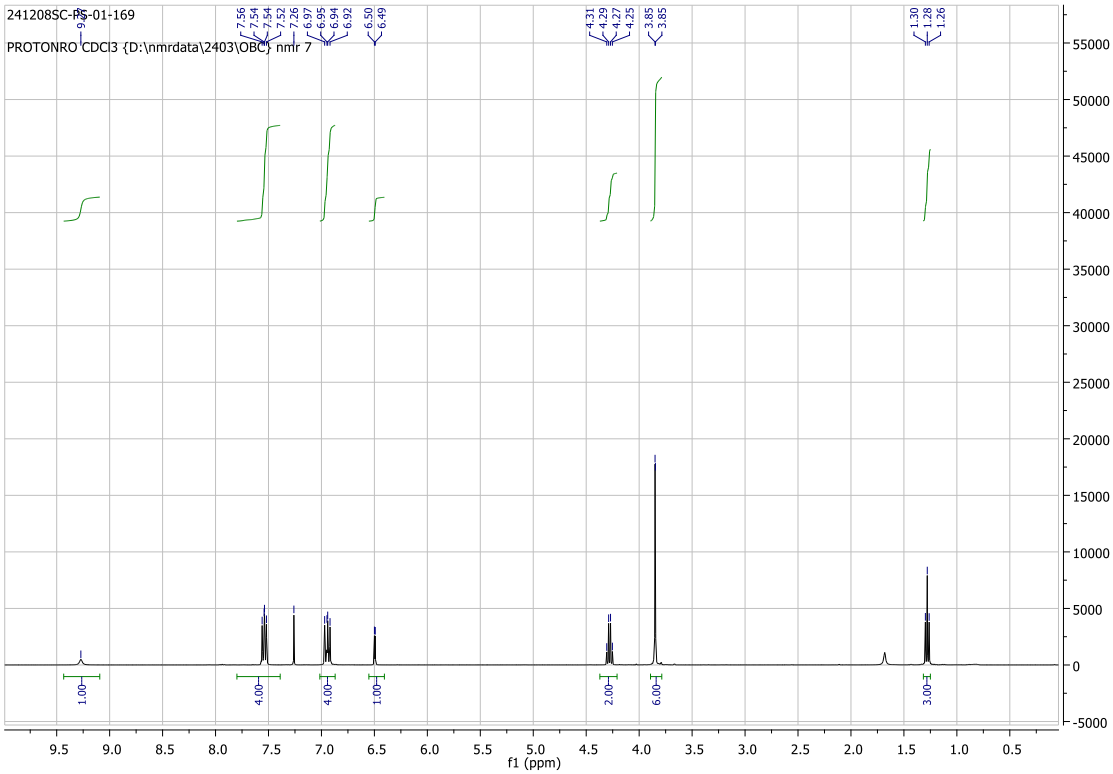


^{13}C-NMR (100 MHz, $CDCl_3$) of **8e**

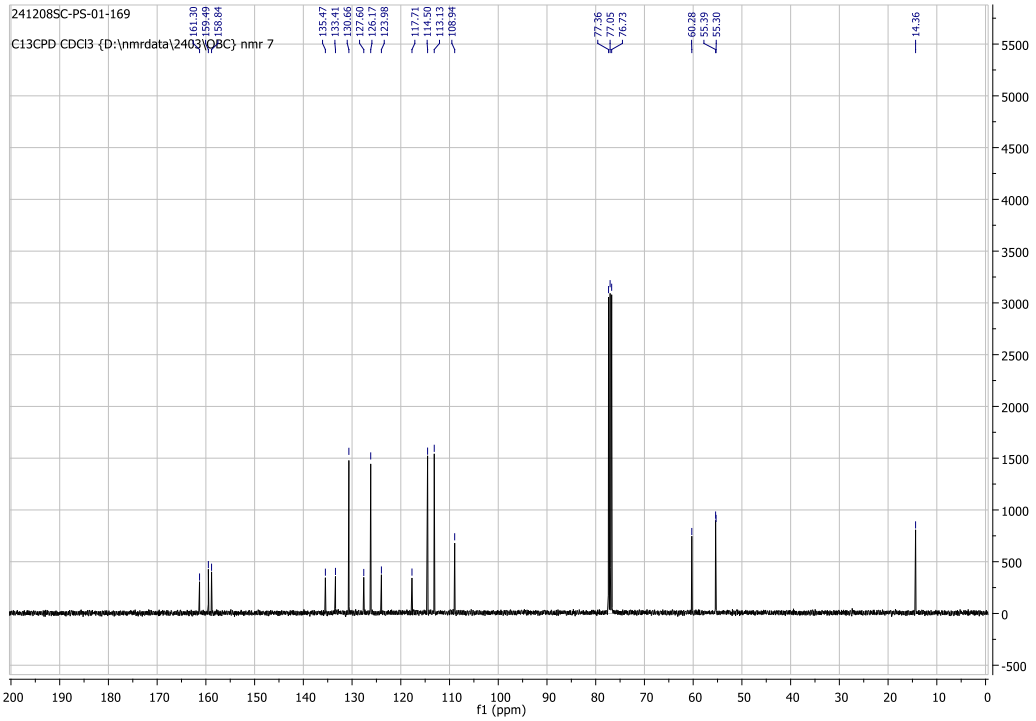


DEPT – 135 of **8e**

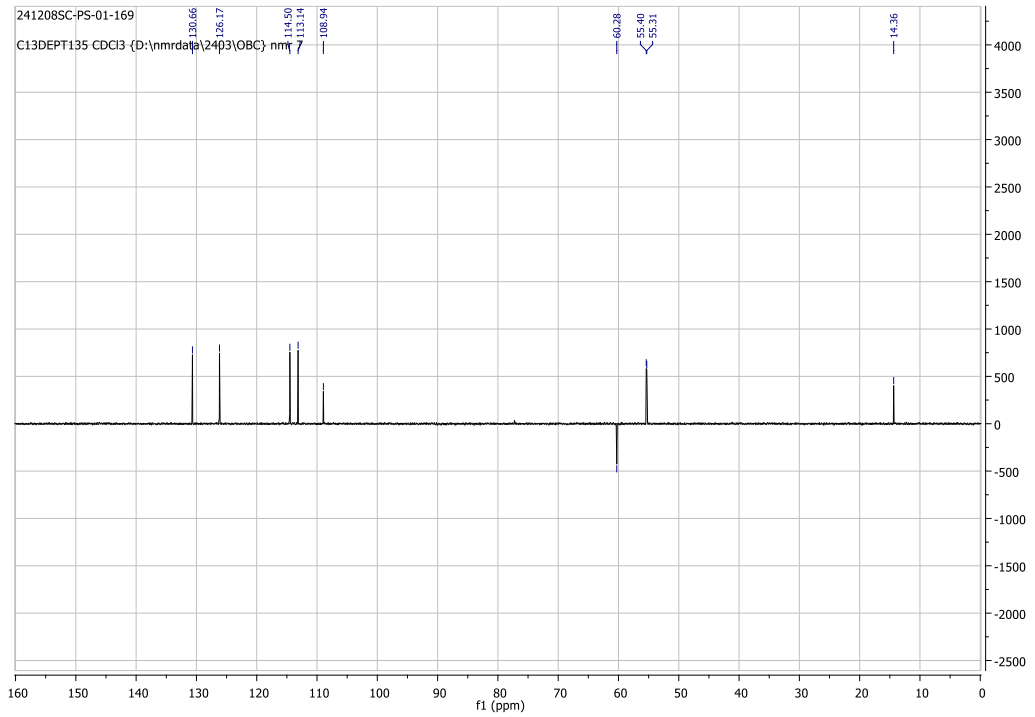




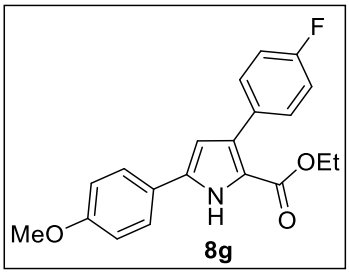
^{1}H-NMR (400 MHz, $CDCl_3$) of **8f**

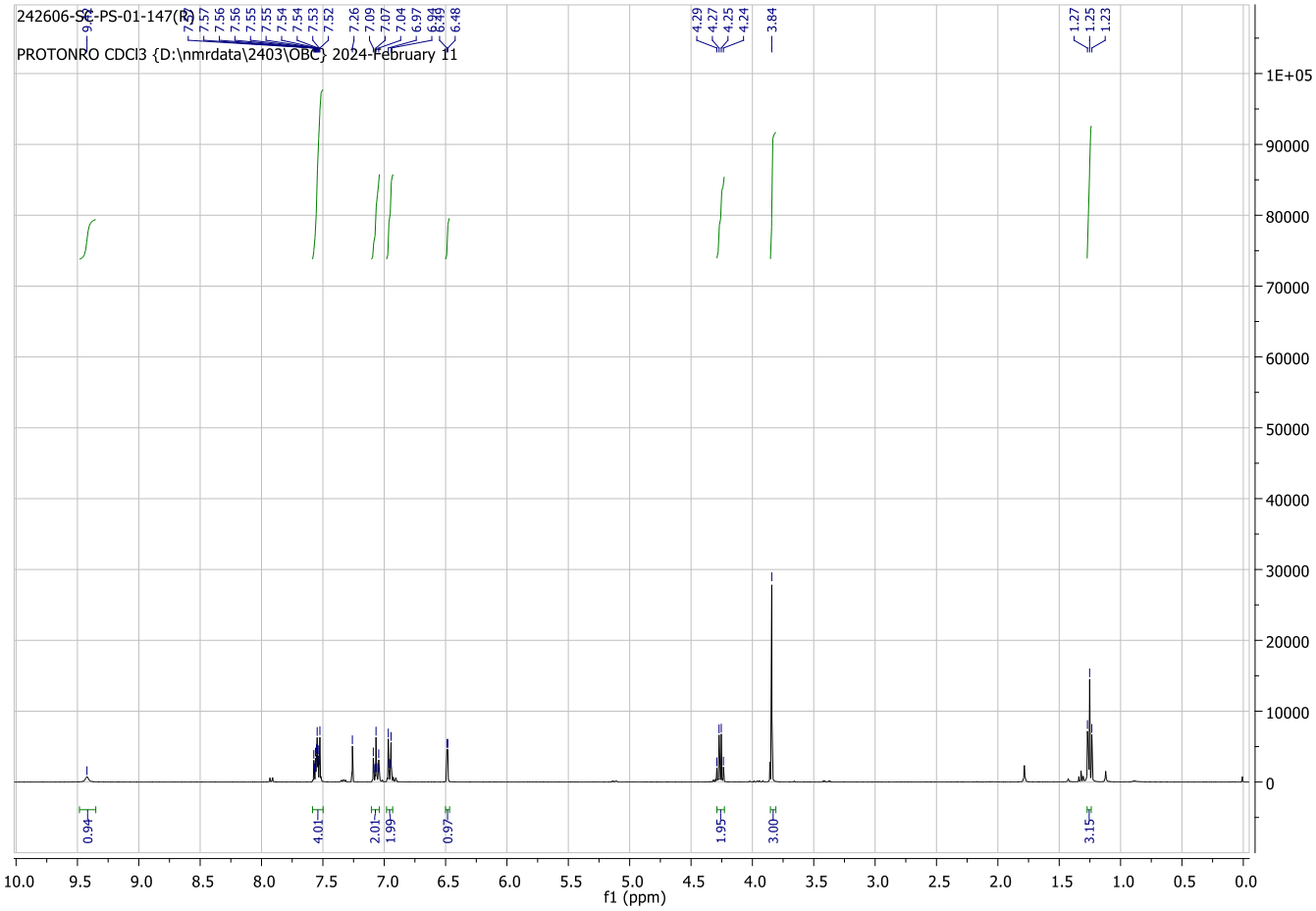


^{13}C-NMR (100 MHz, $CDCl_3$) of **8f**

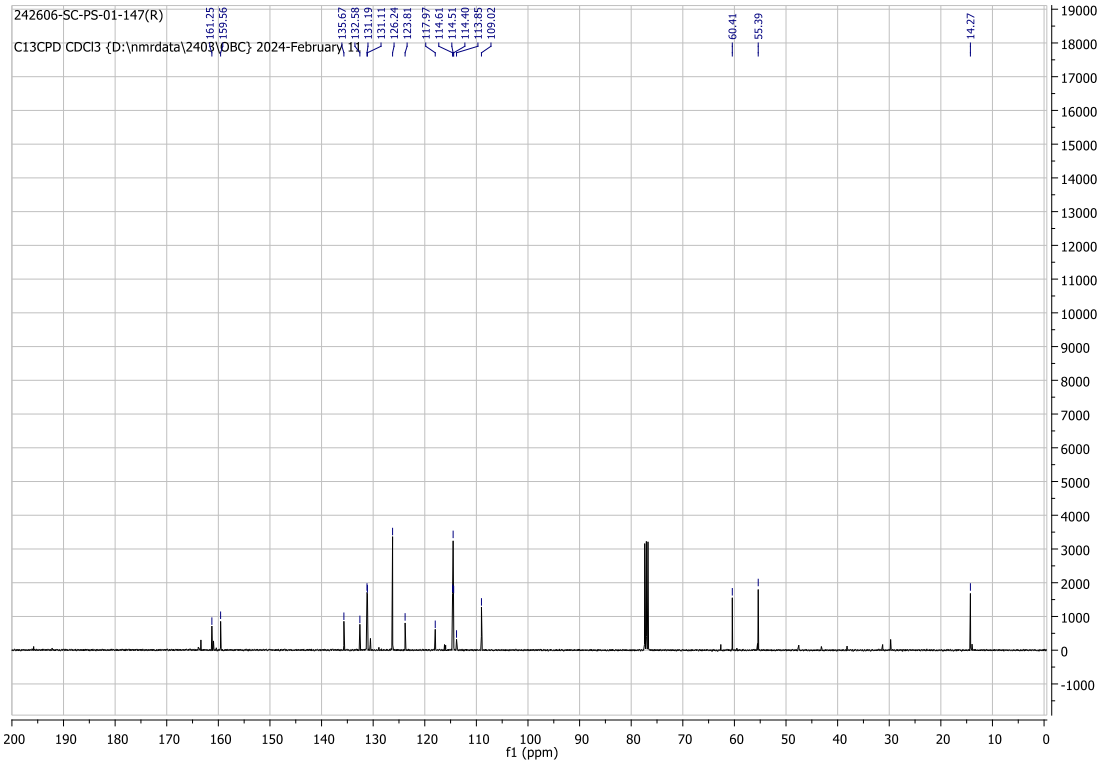


DEPT – 135 of **8f**

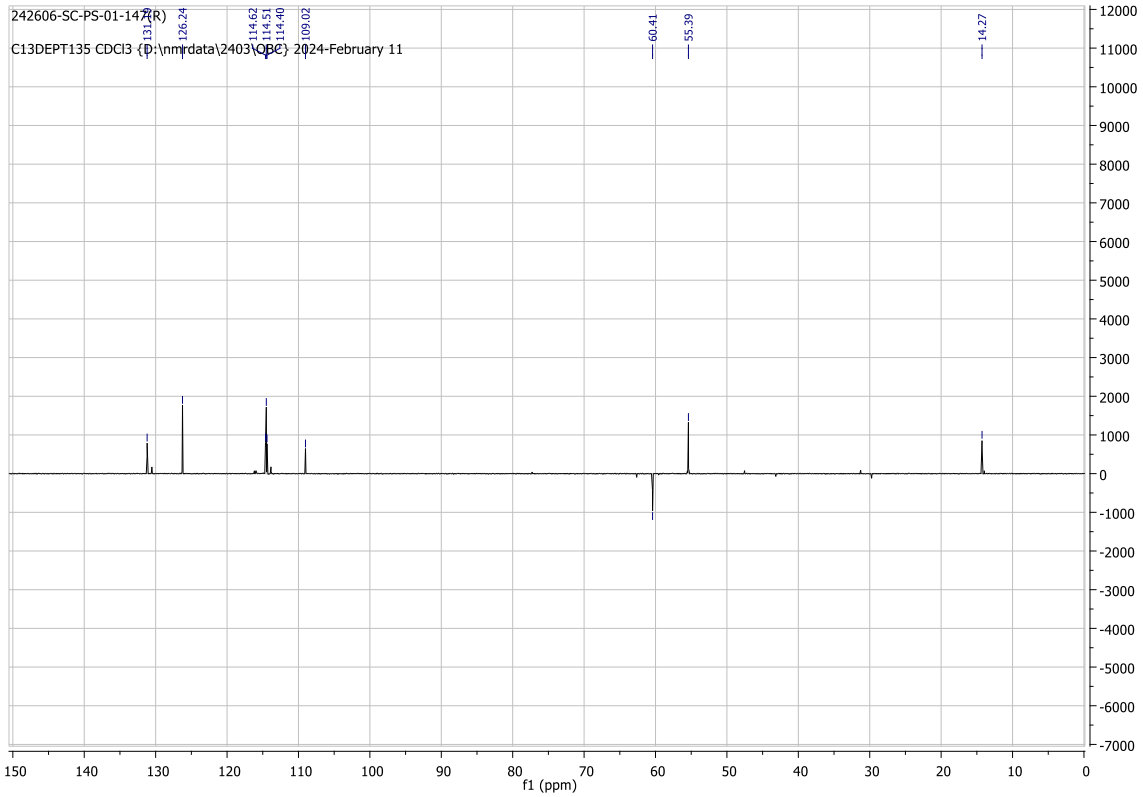




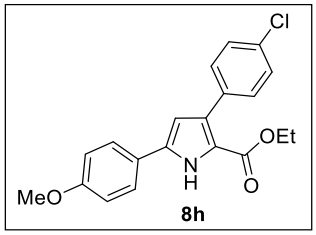
^{1}H-NMR (400 MHz, $CDCl_3$) of **8g**

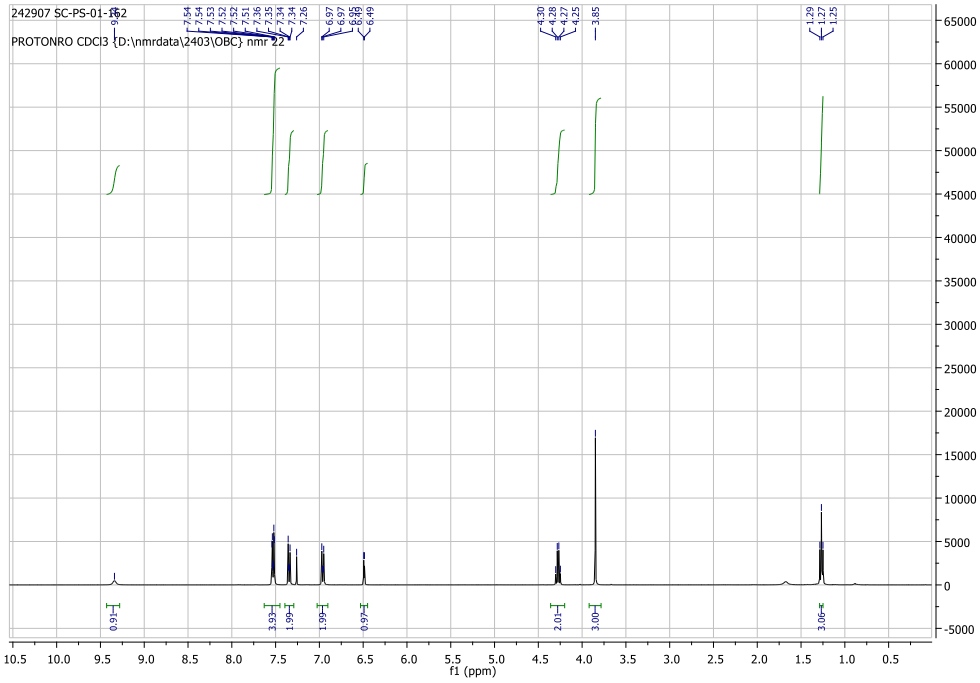


^{13}C-NMR (100 MHz, $CDCl_3$) of **8g**

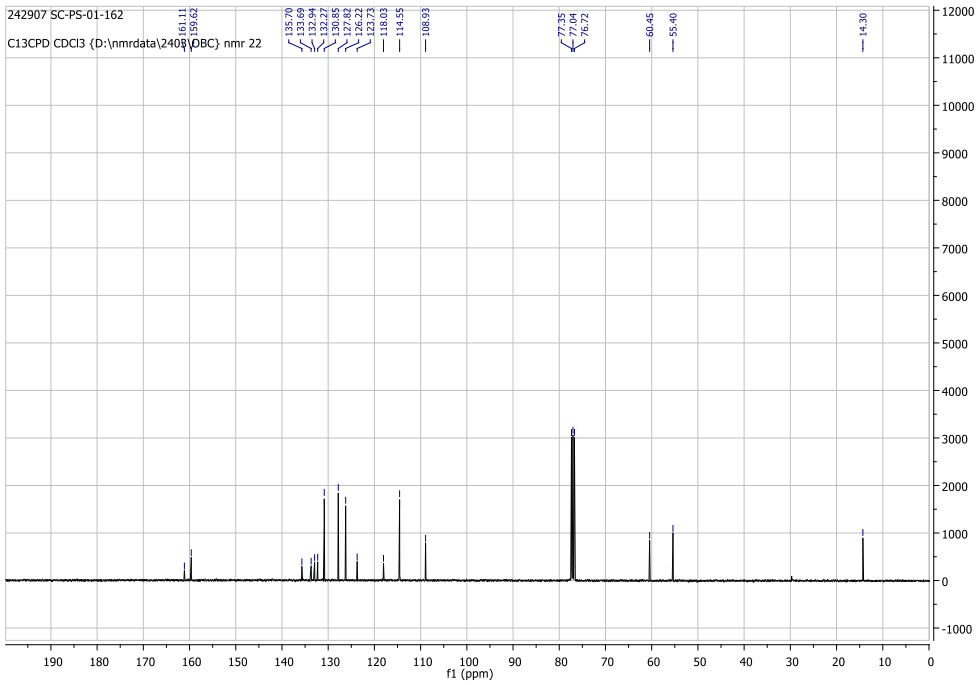


DEPT – 135 of **8g**

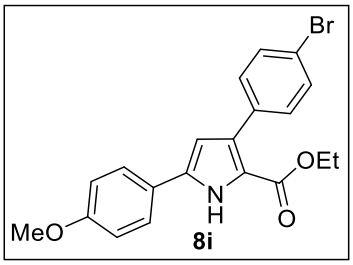


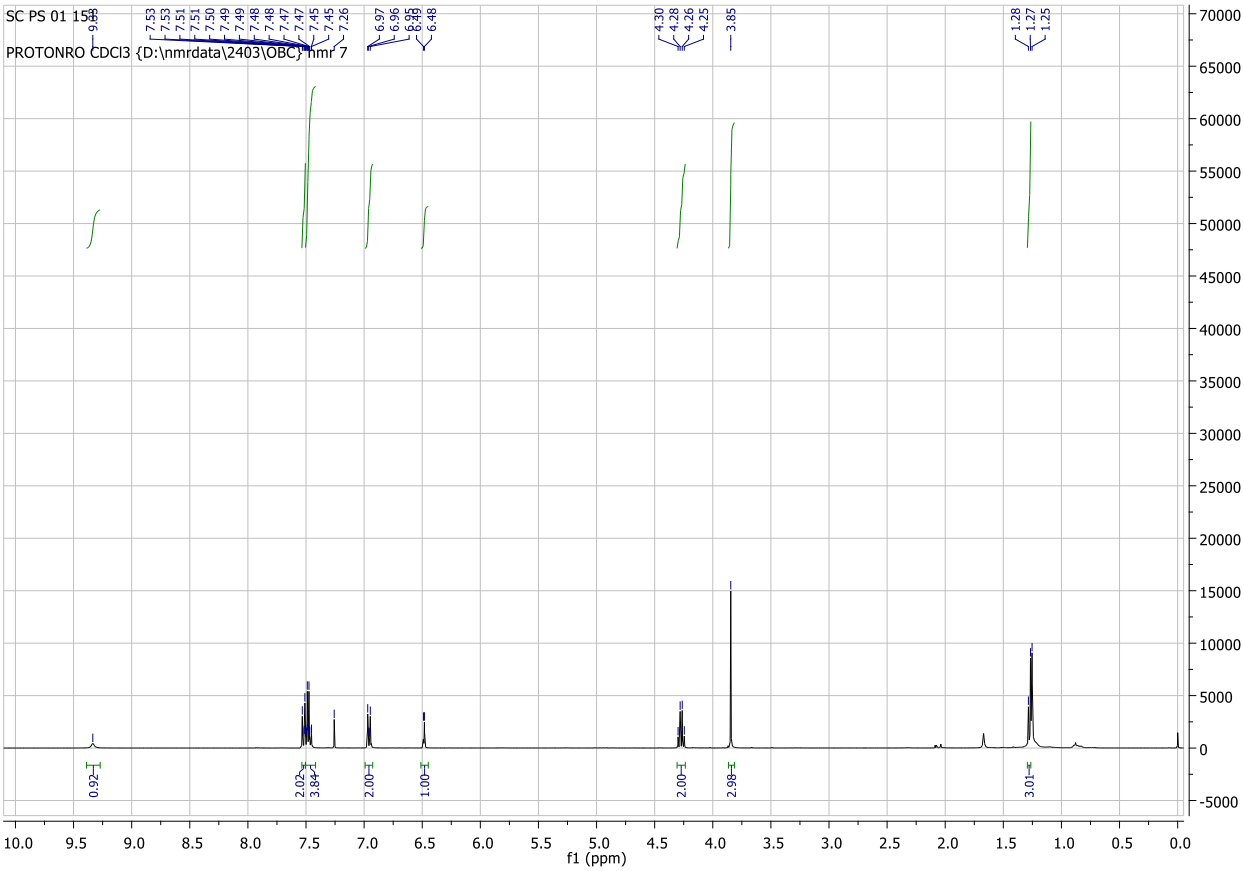


^{1}H-NMR (400 MHz, $CDCl_3$) of **8h**

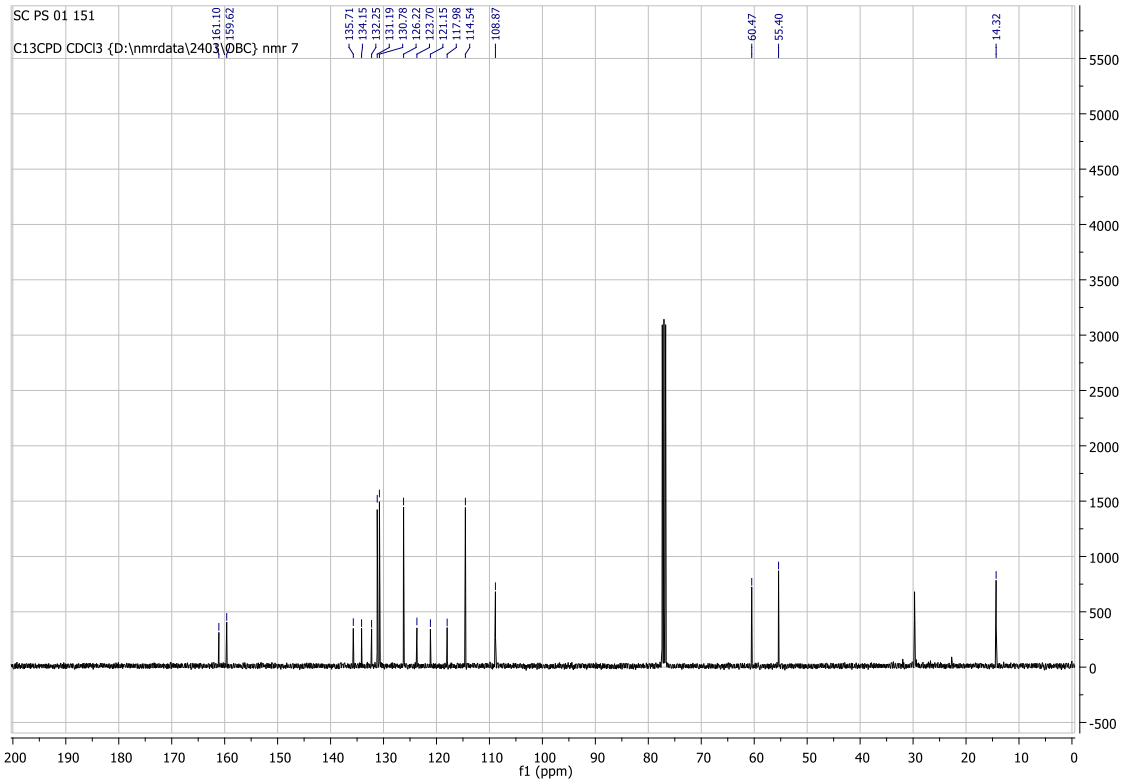


^{13}C-NMR (100 MHz, $CDCl_3$) of **8h**

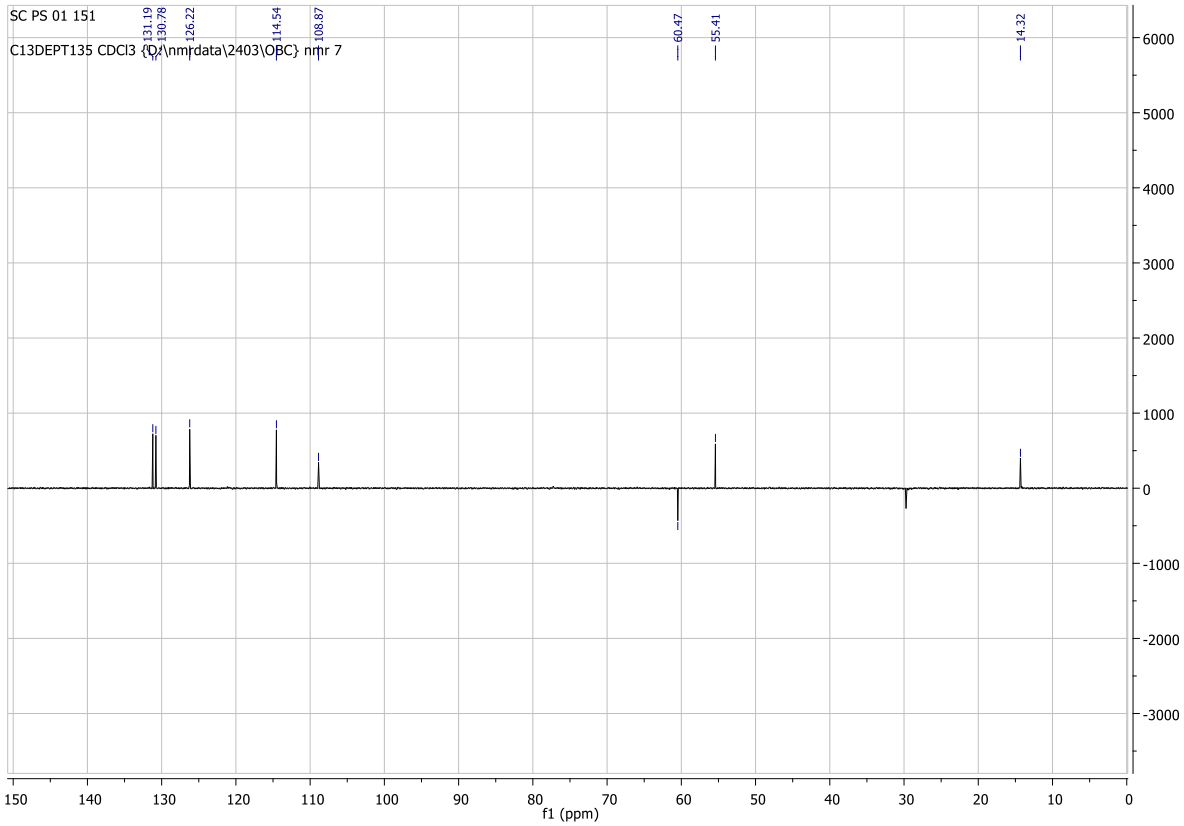




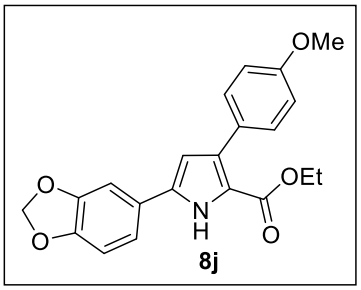
^{1}H-NMR (400 MHz, $CDCl_3$) of **8i**

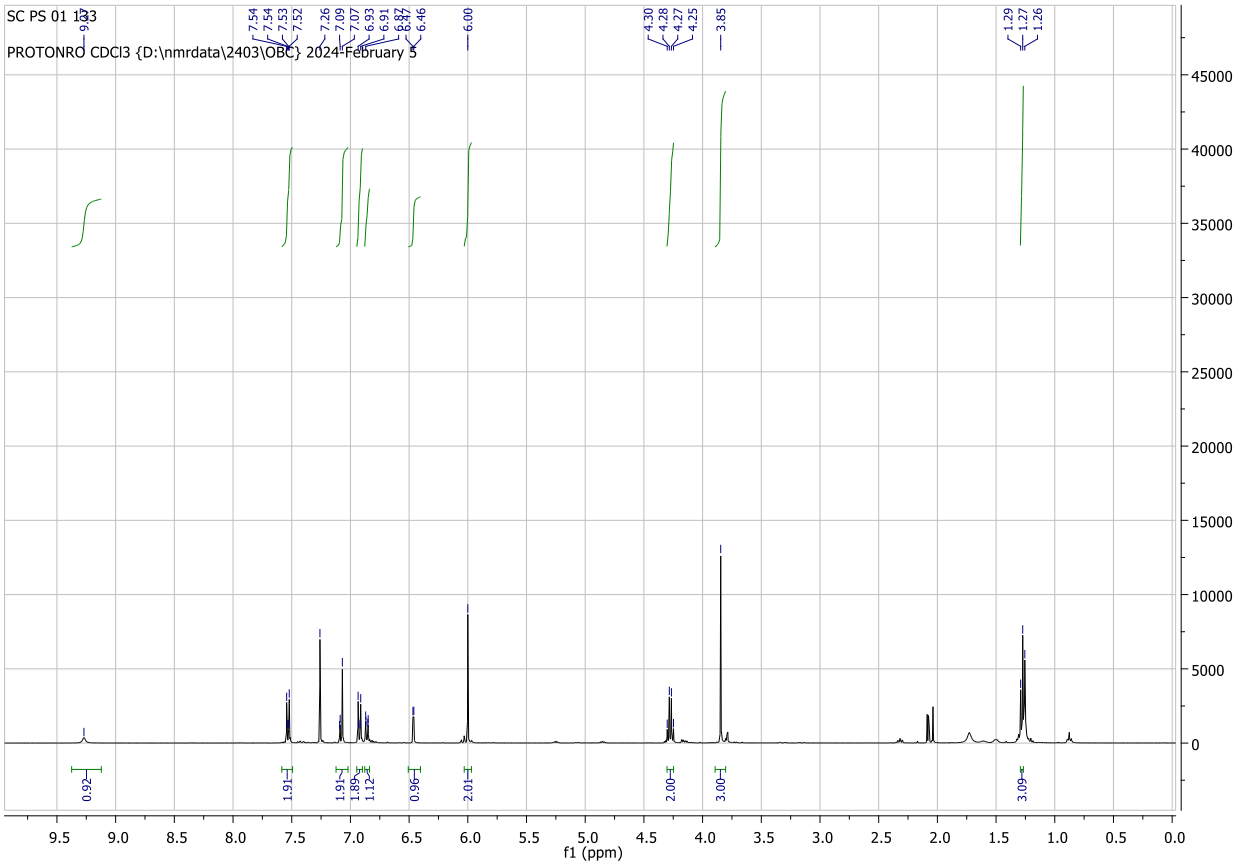


^{13}C-NMR (100 MHz, $CDCl_3$) of **8i**

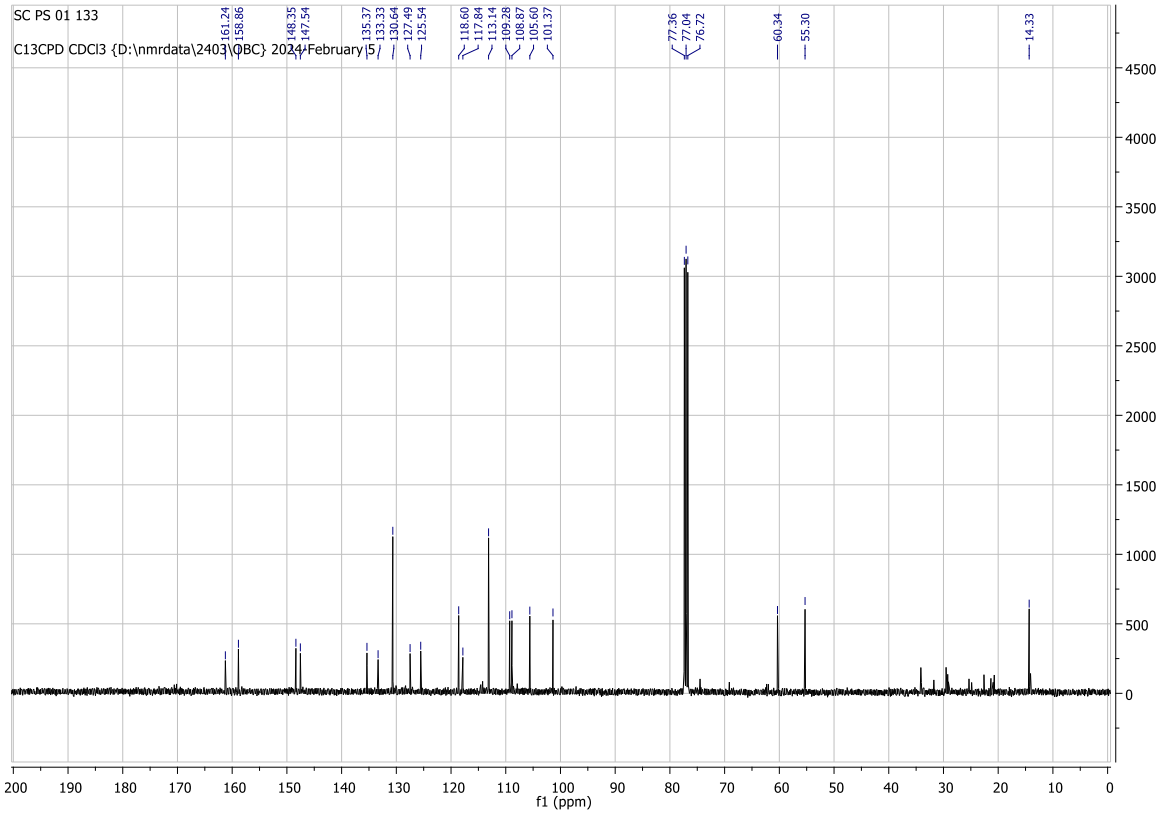


DEPT – 135 of **8i**

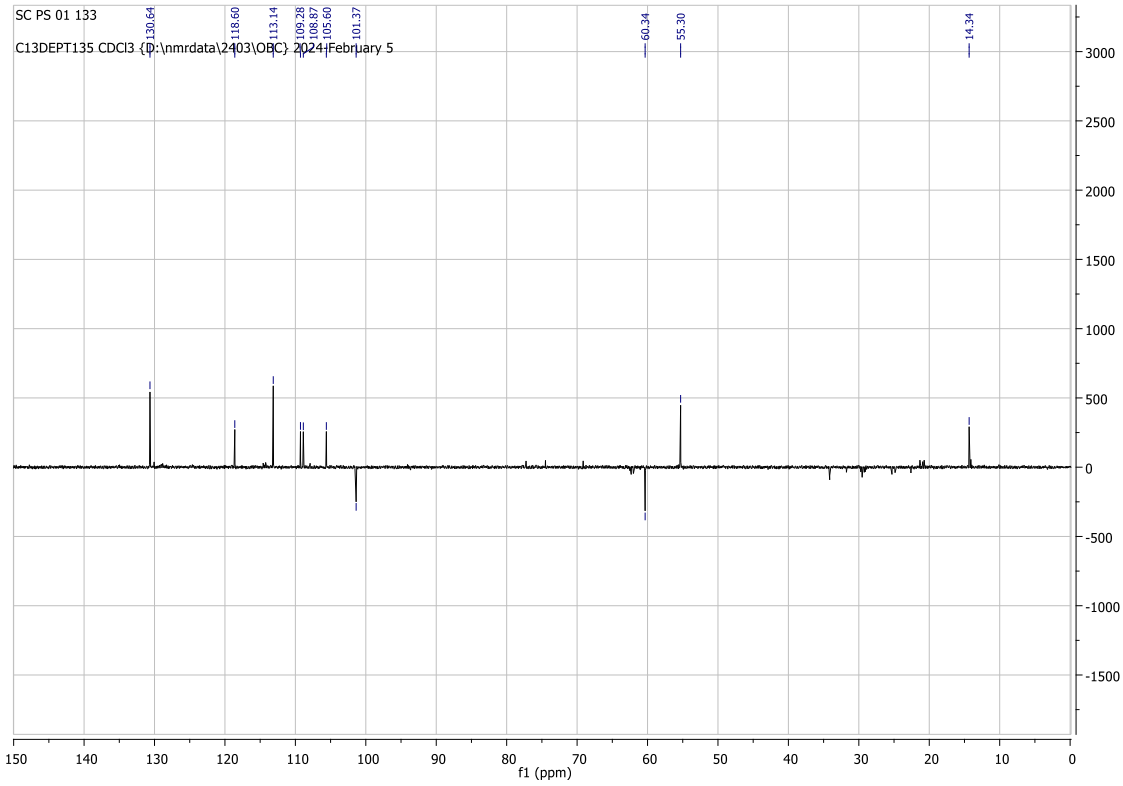




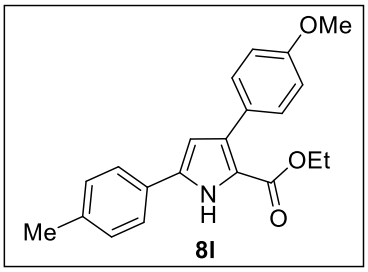
^{1}H-NMR (400 MHz, $CDCl_3$) of **8j**

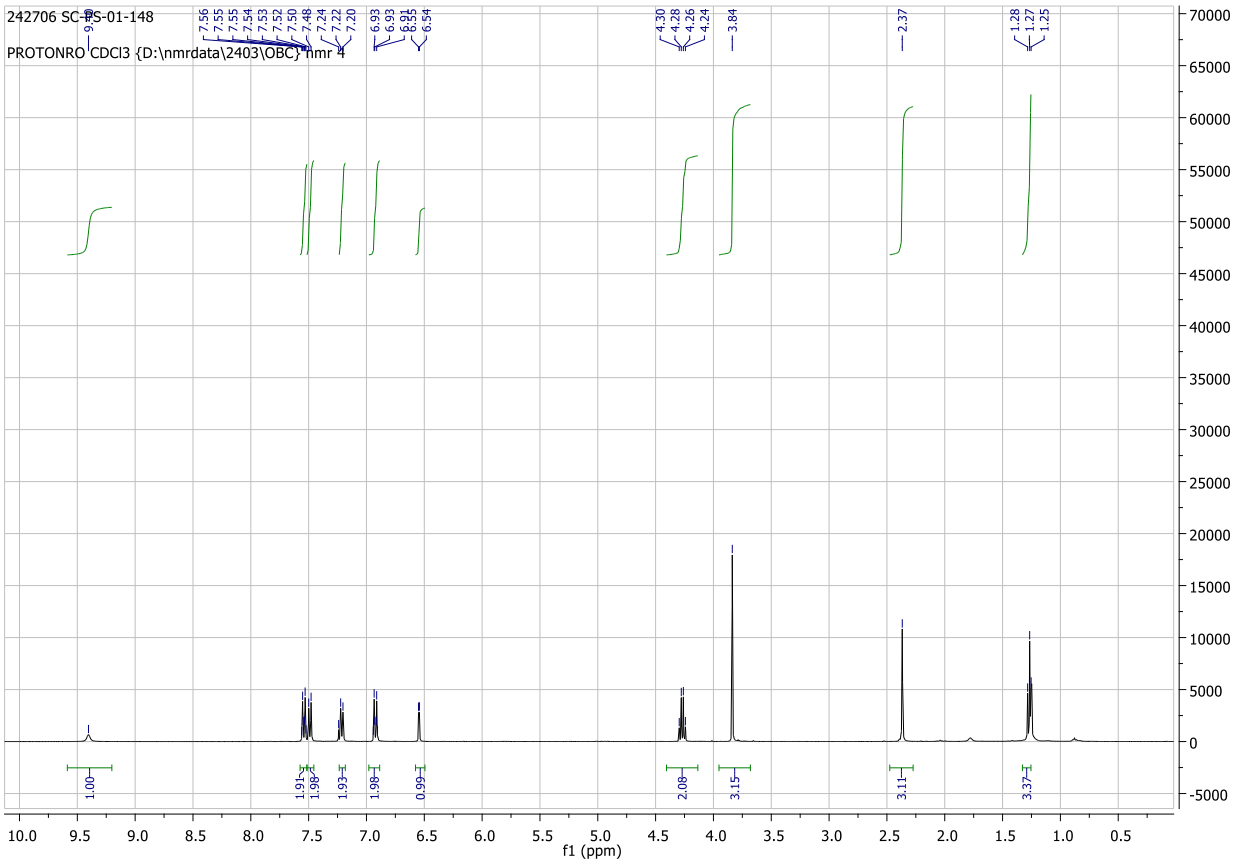


^{13}C-NMR (100 MHz, $CDCl_3$) of **8j**

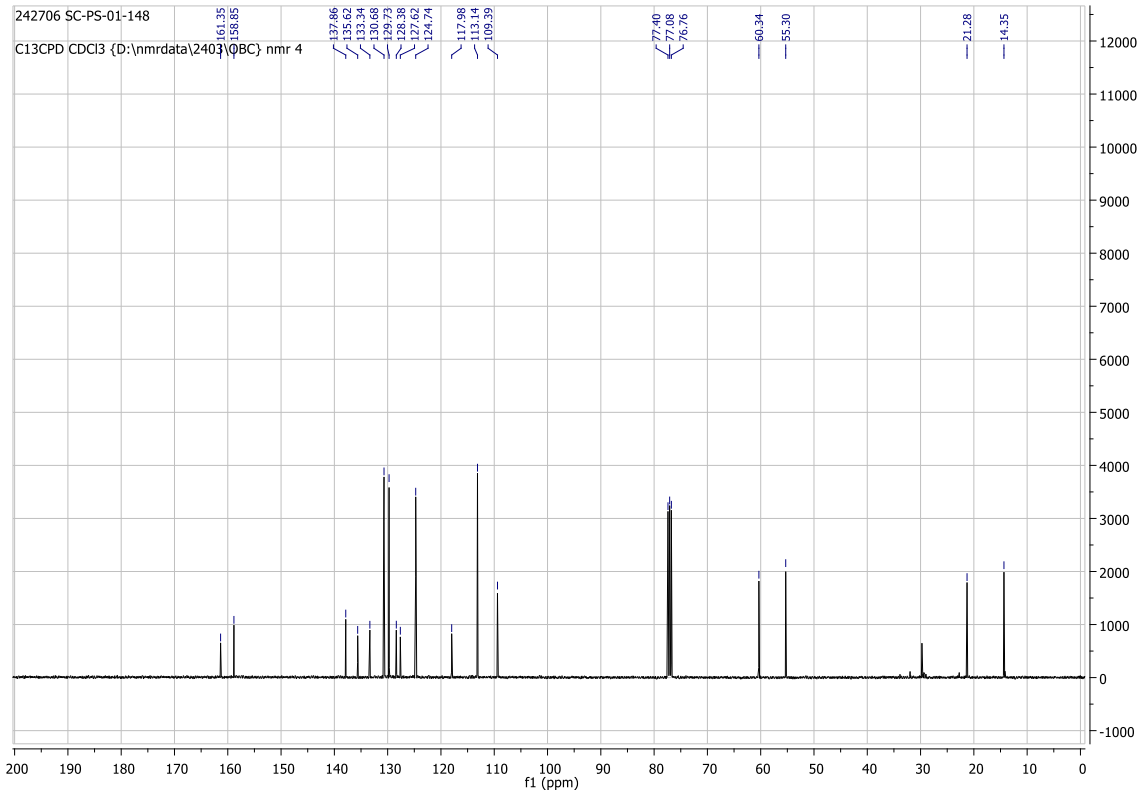


DEPT – 135 of **8i**

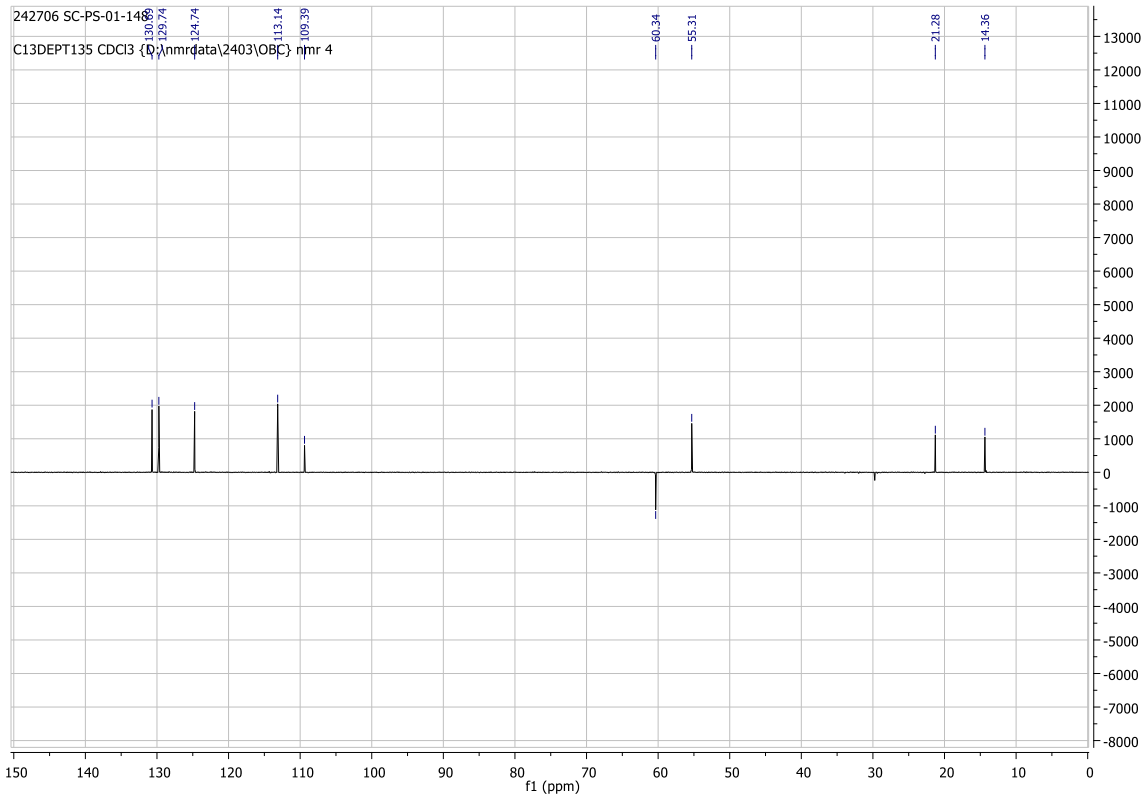




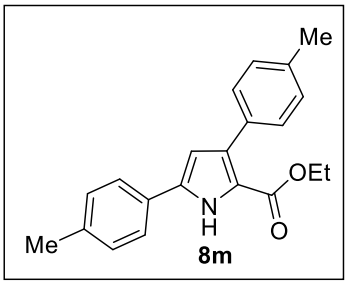
^{1}H-NMR (400 MHz, $CDCl_3$) of **8l**

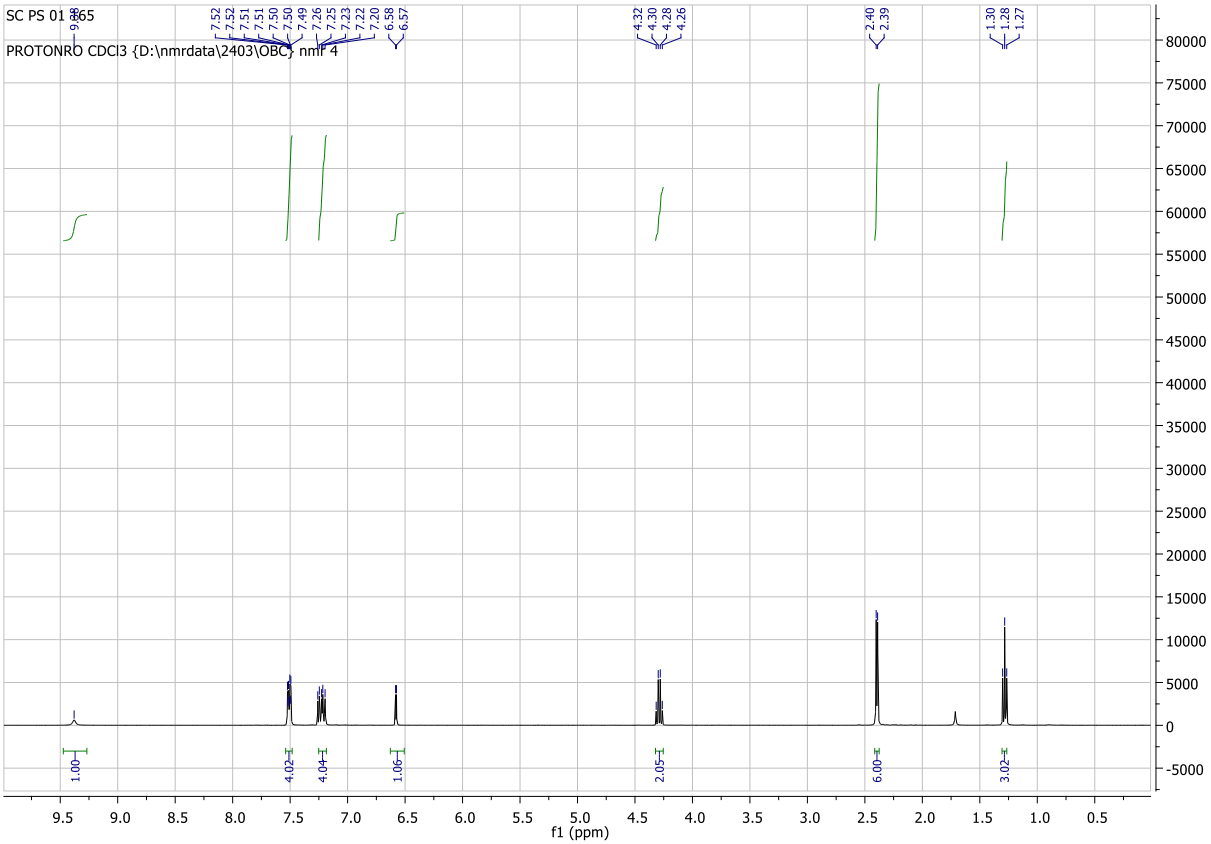


^{13}C-NMR (100 MHz, $CDCl_3$) of **8l**

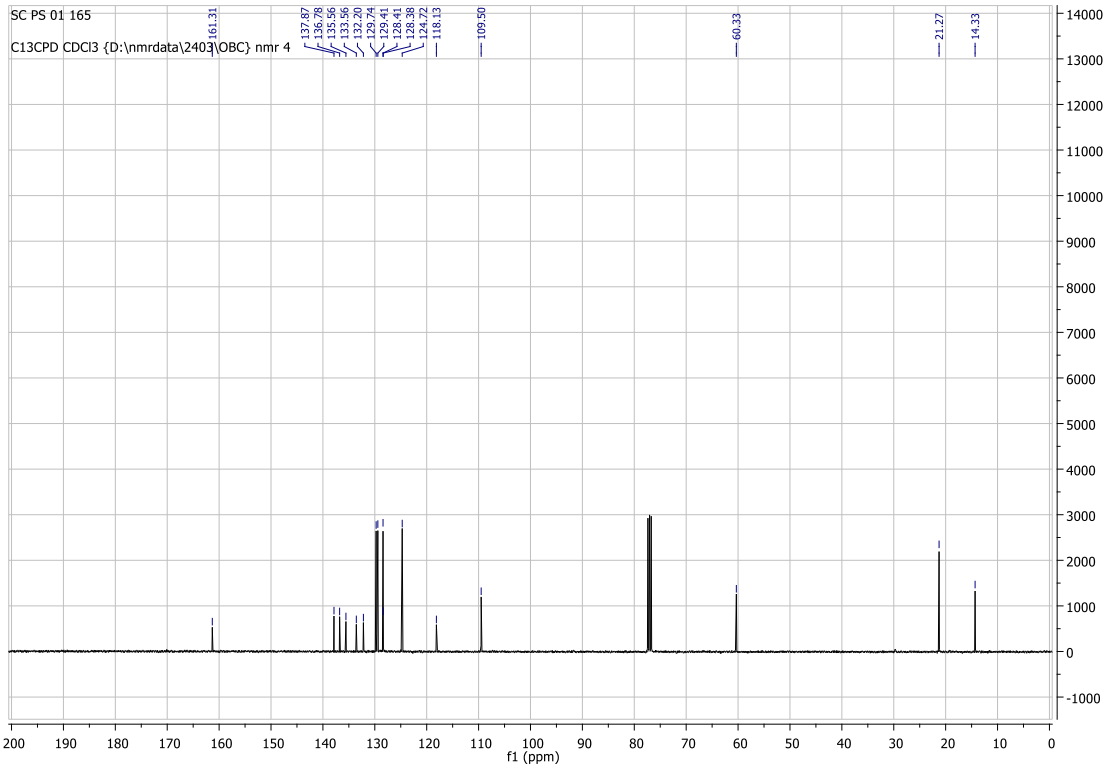


DEPT – 135 of **8l**

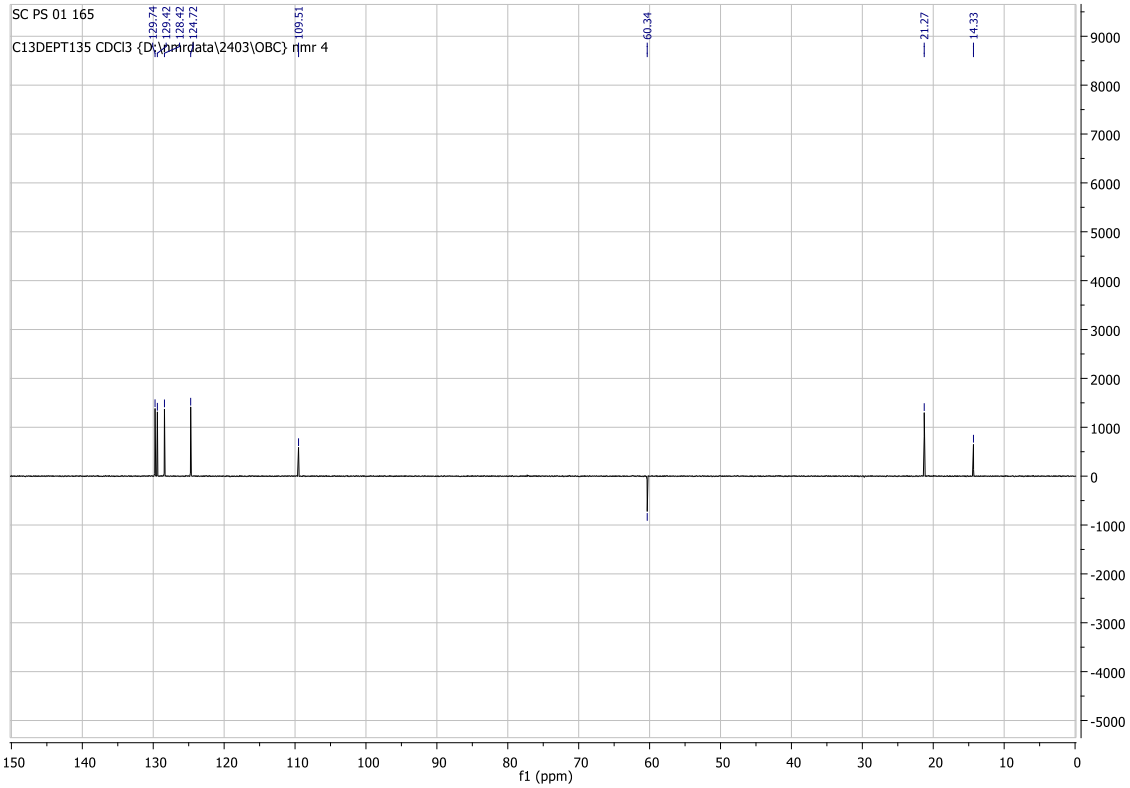




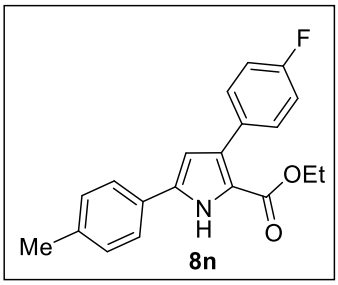
^{1}H-NMR (400 MHz, $CDCl_3$) of **8m**

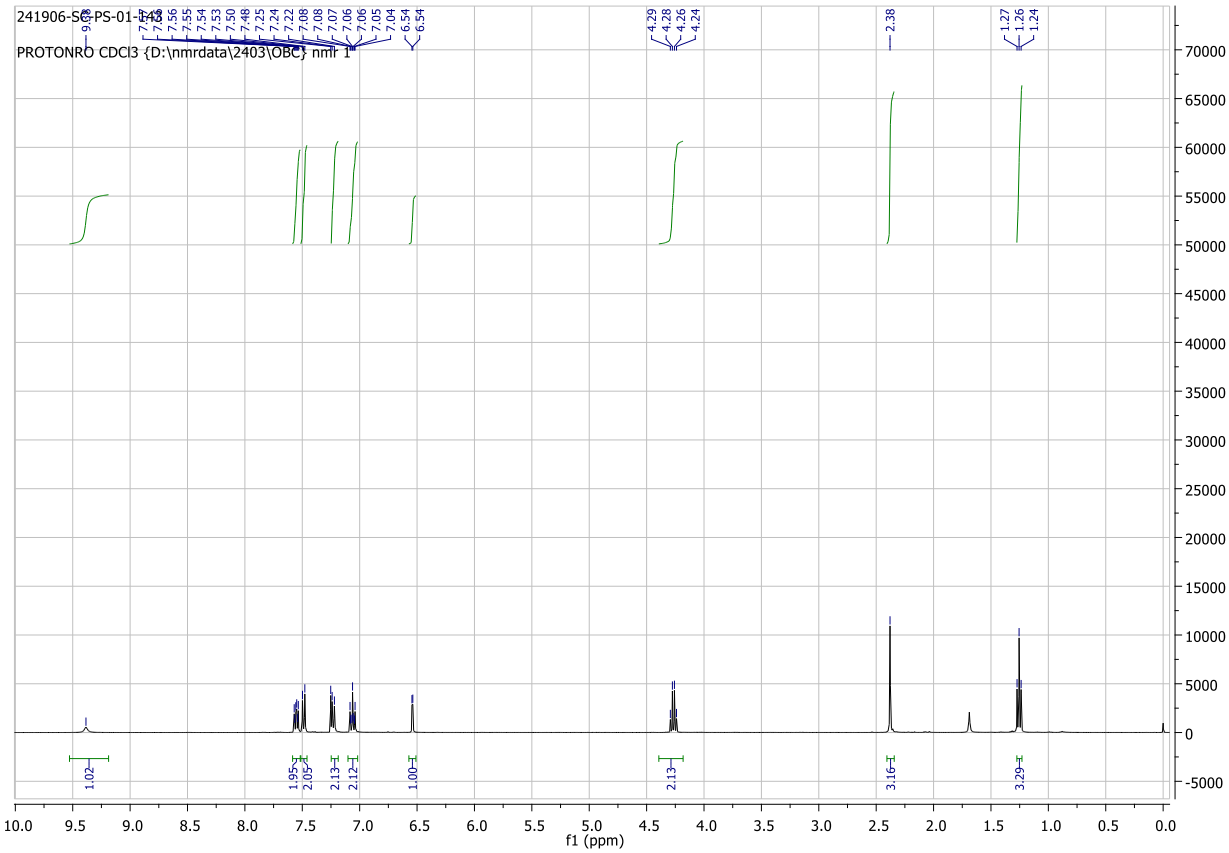


^{13}C-NMR (100 MHz, $CDCl_3$) of **8m**



DEPT – 135 of **8m**





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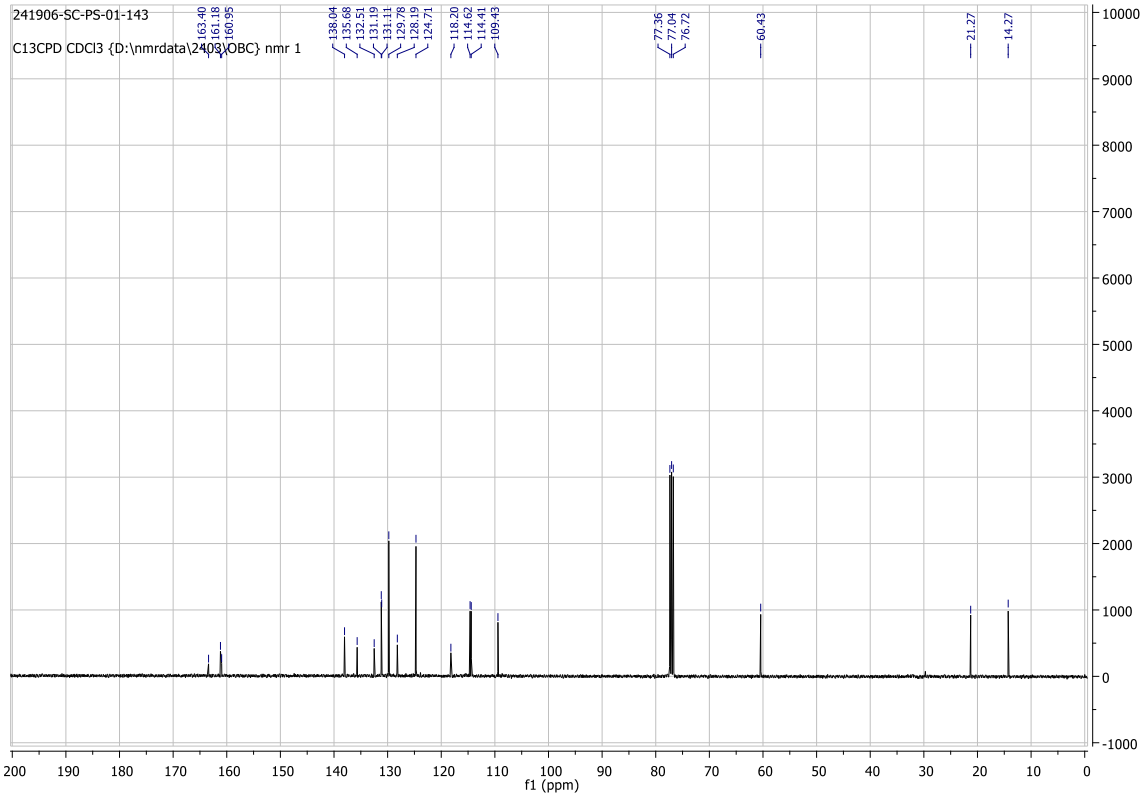
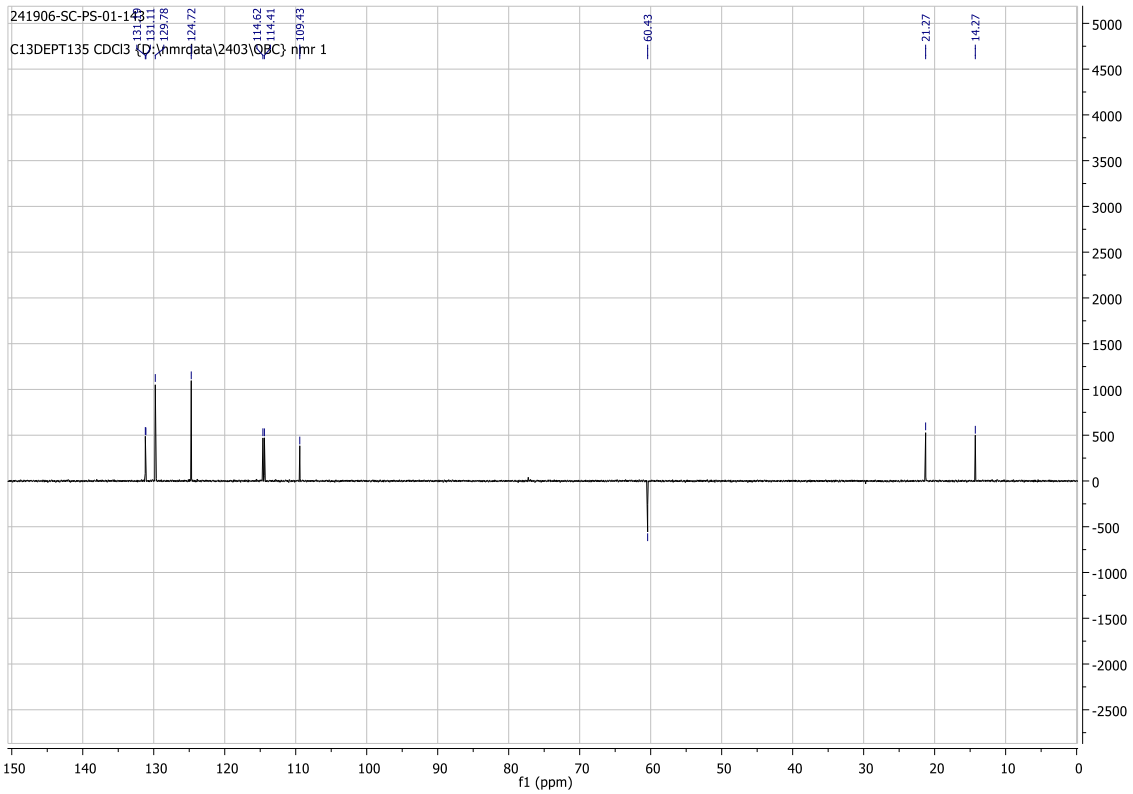
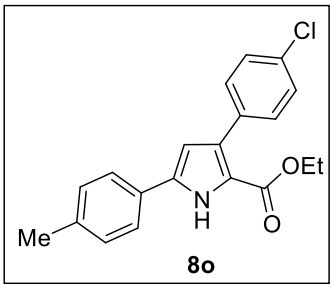
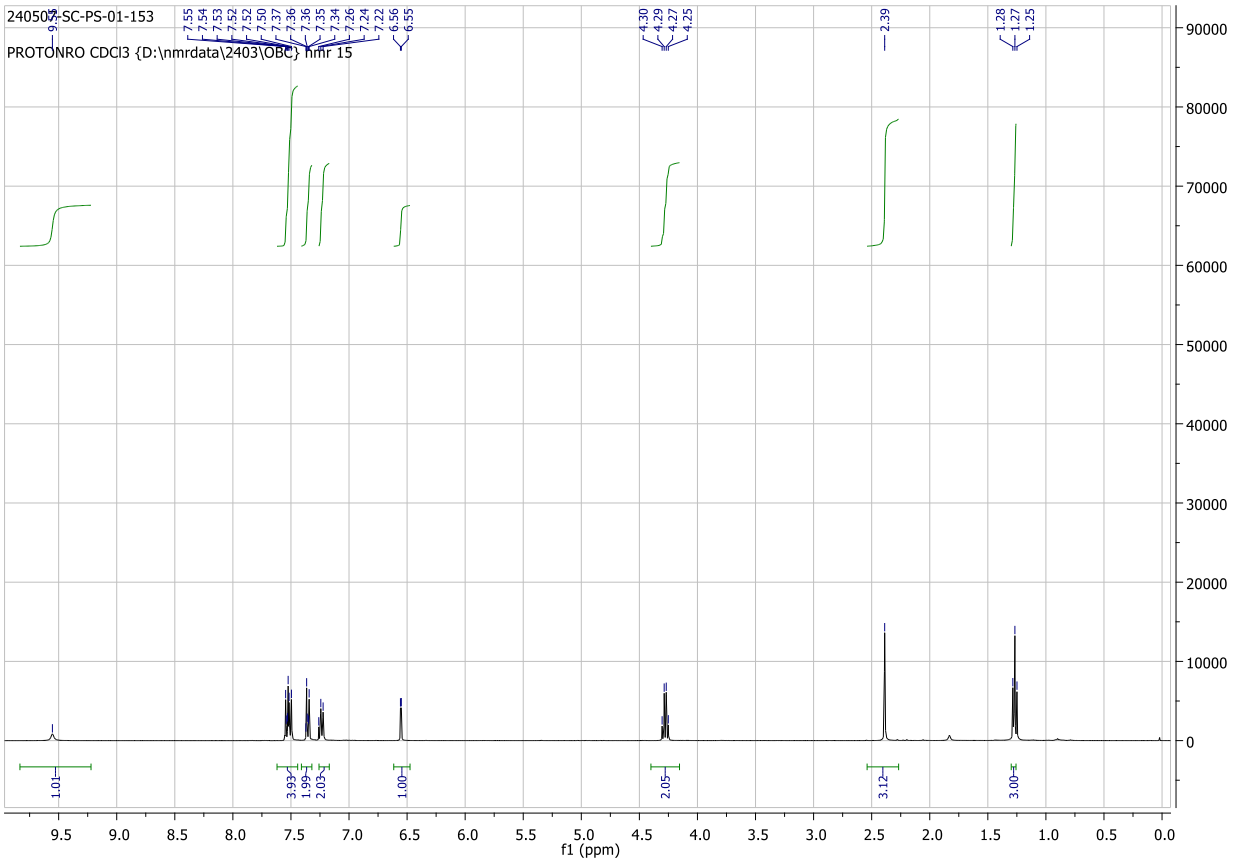


^{13}C-NMR (100 MHz, $CDCl_3$) of **8n**

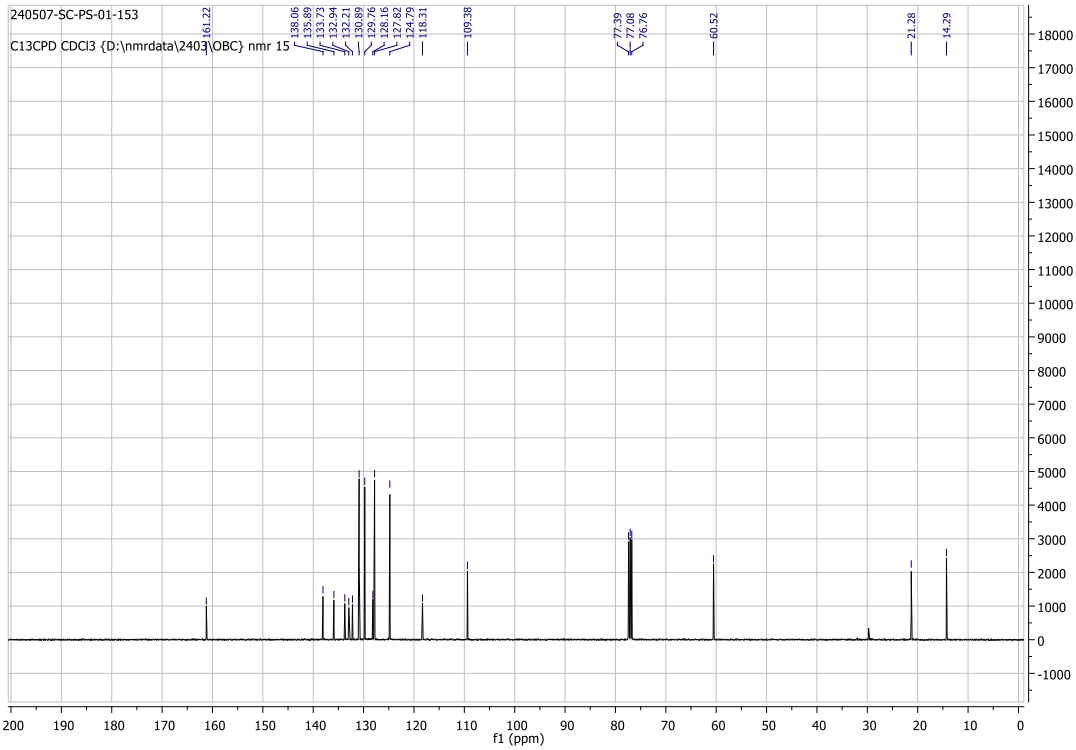


DEPT – 135 of **8n**

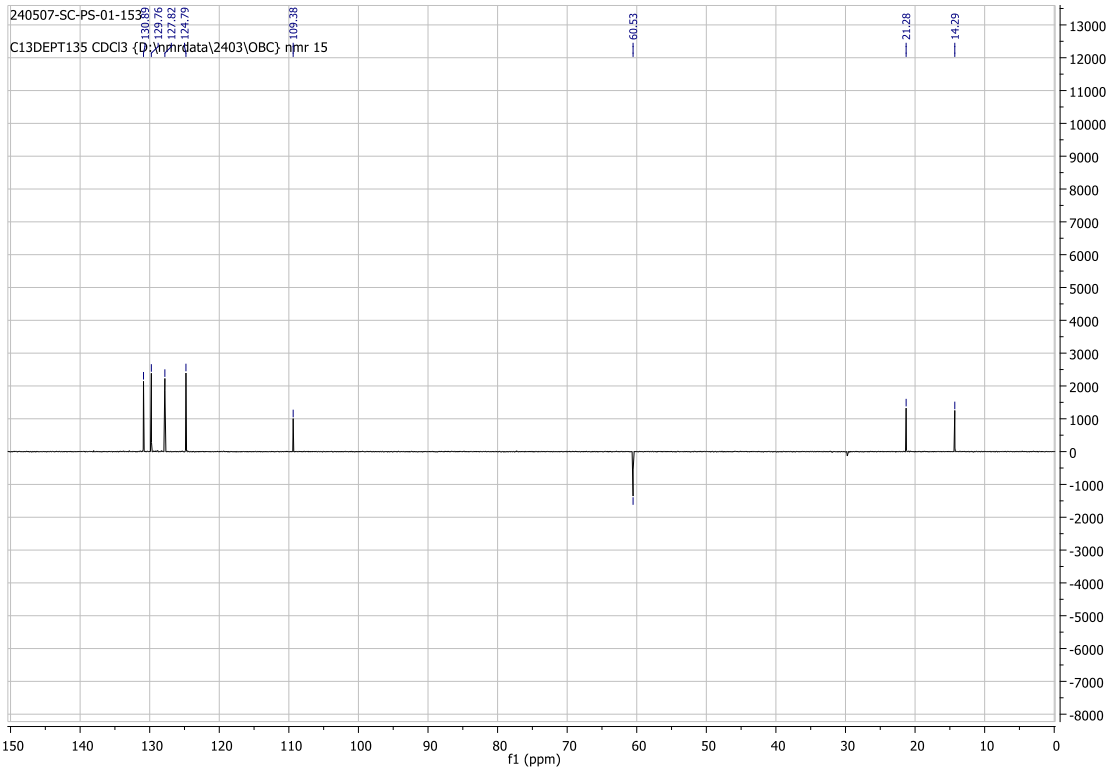




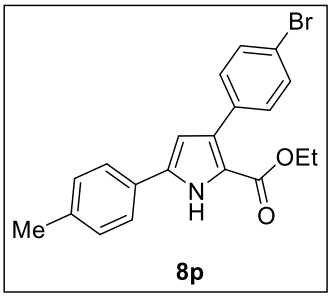
^{1}H-NMR (400 MHz, $CDCl_3$) of **8o**

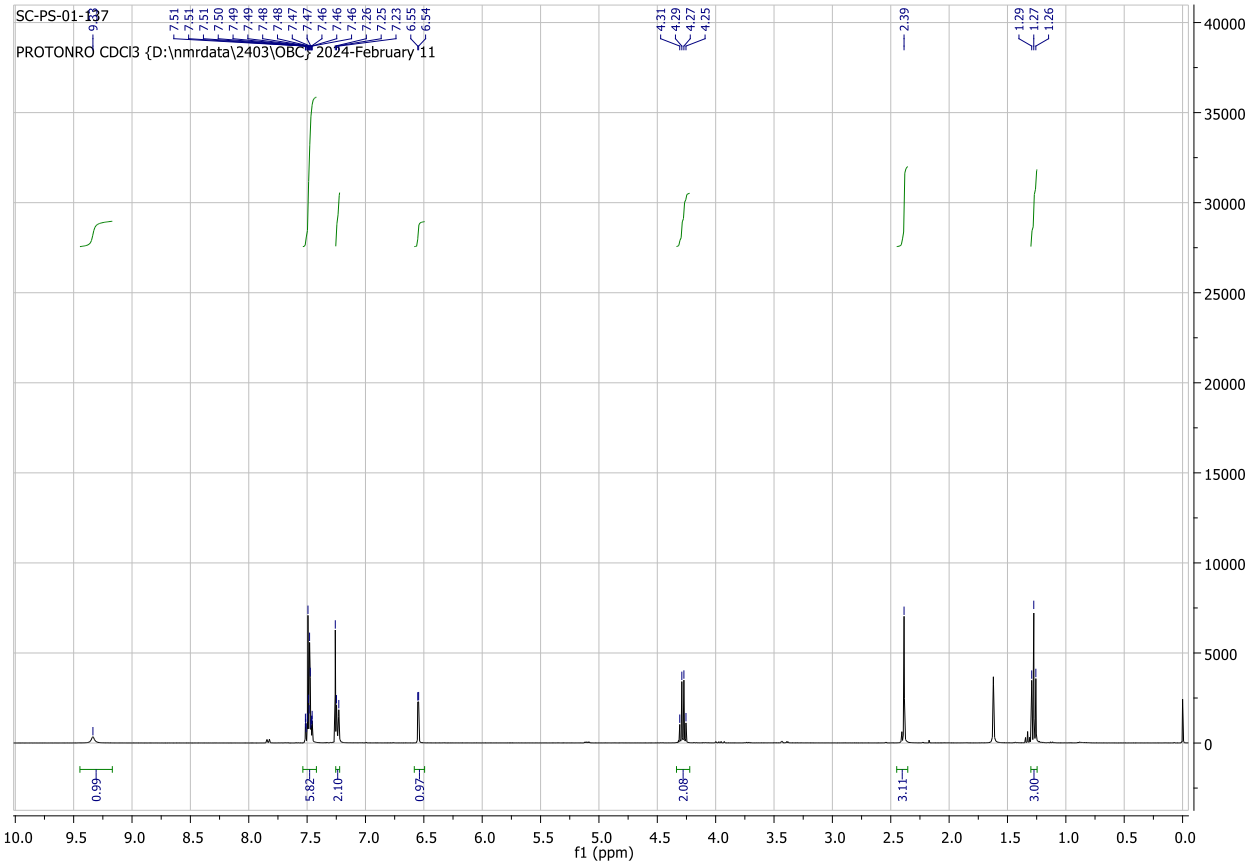


^{13}C-NMR (100 MHz, $CDCl_3$) of **8o**

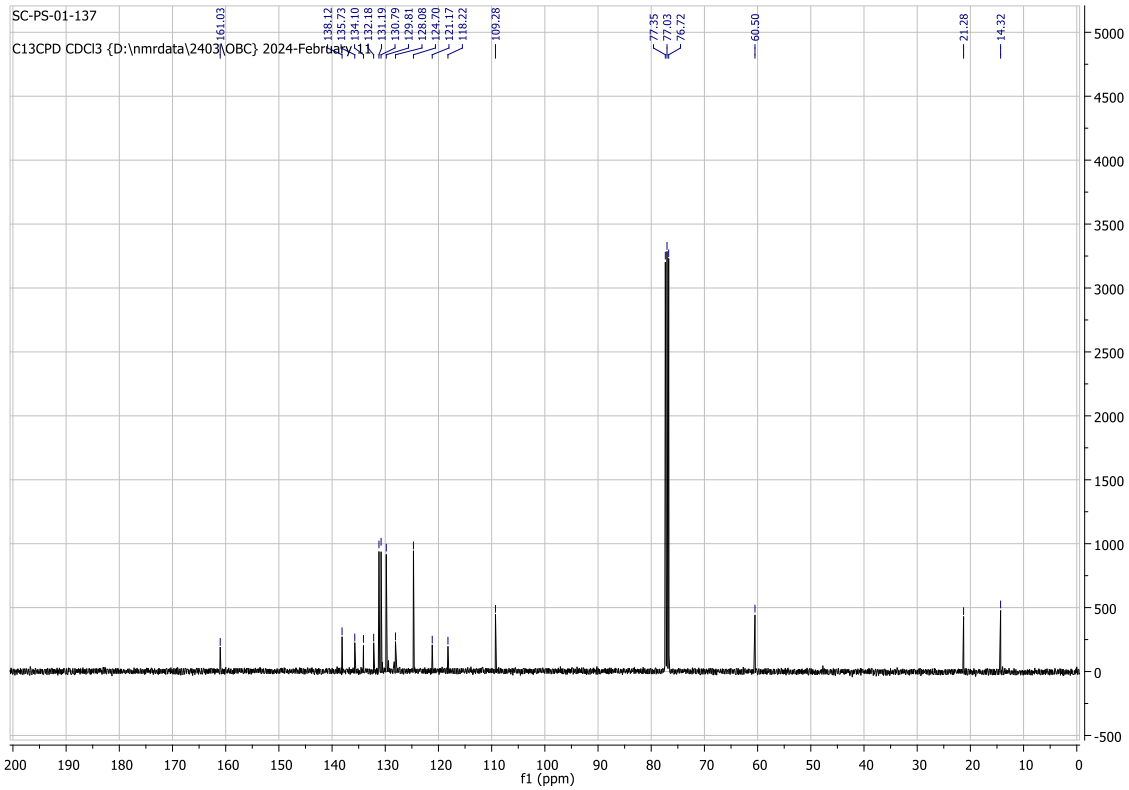


DEPT – 135 of **8o**

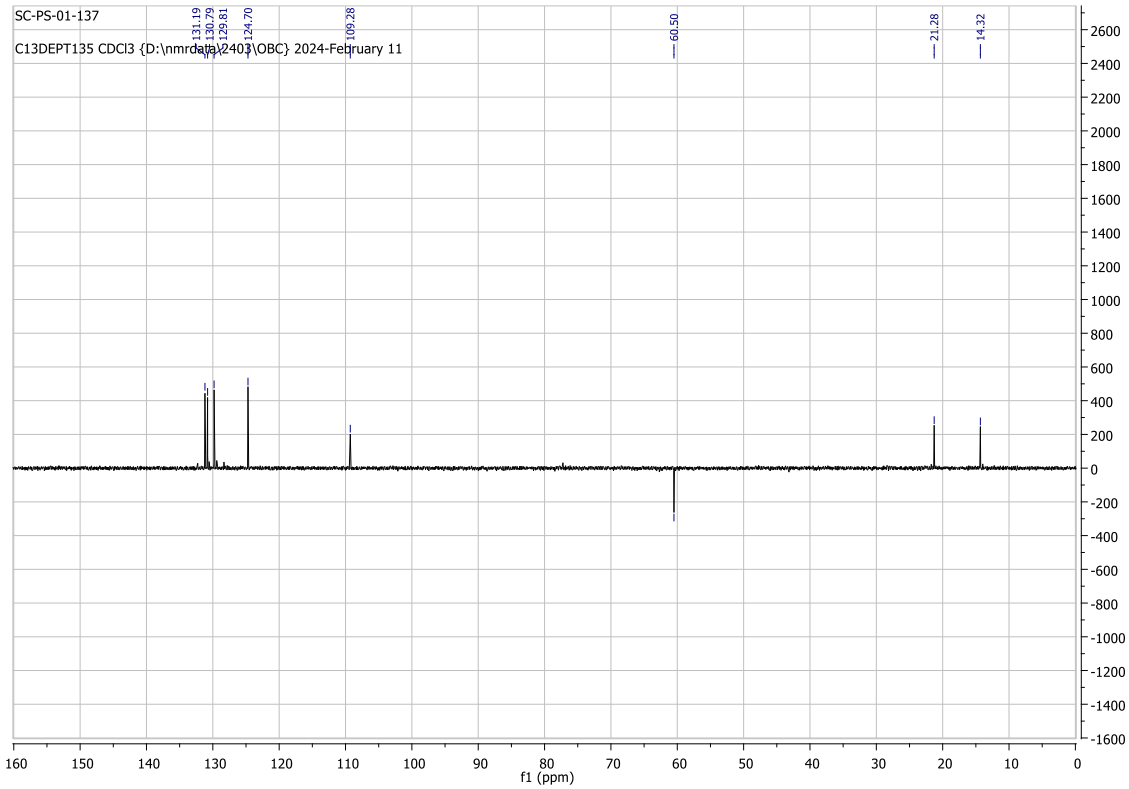




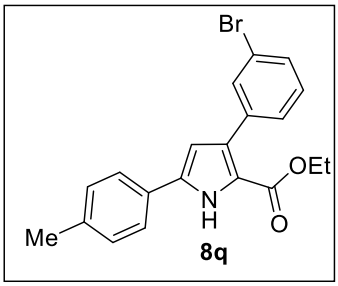
^{1}H-NMR (400 MHz, $CDCl_3$) of **8p**

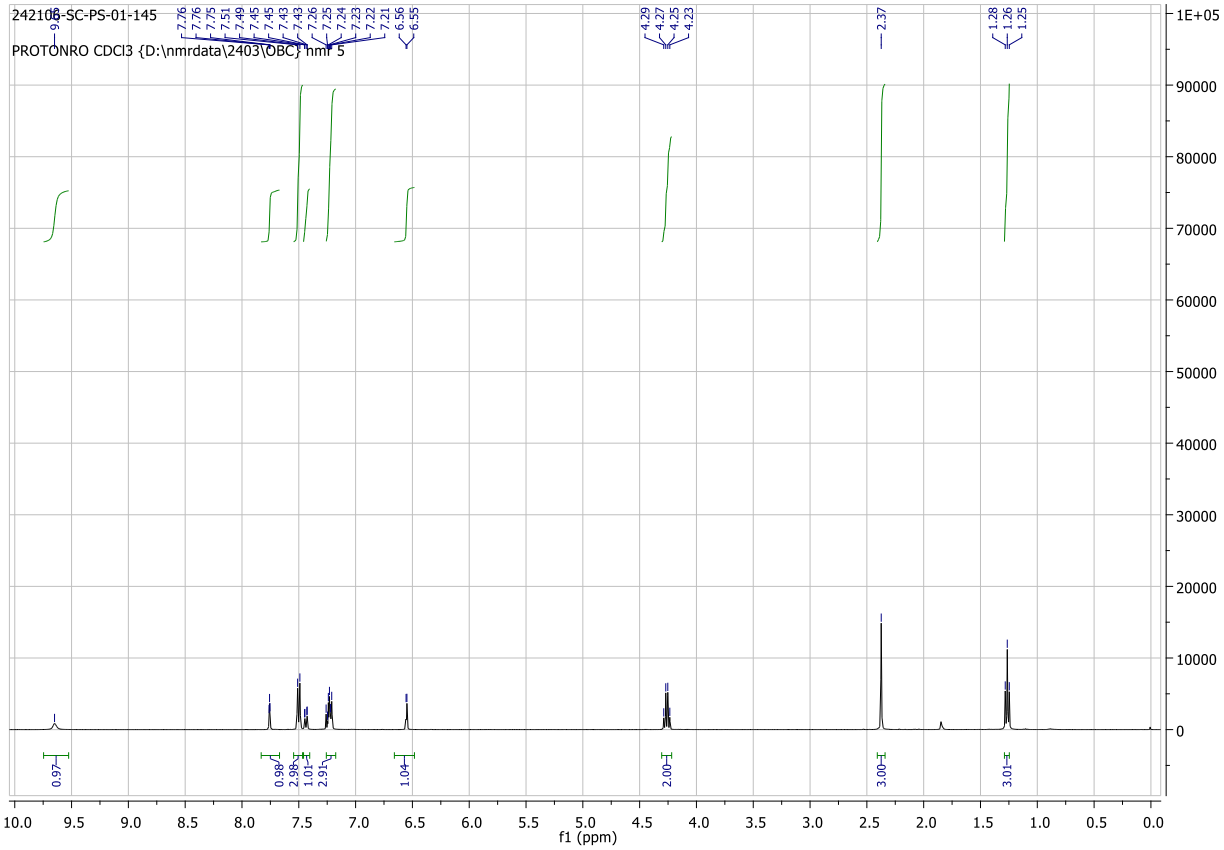


^{13}C-NMR (100 MHz, $CDCl_3$) of **8p**

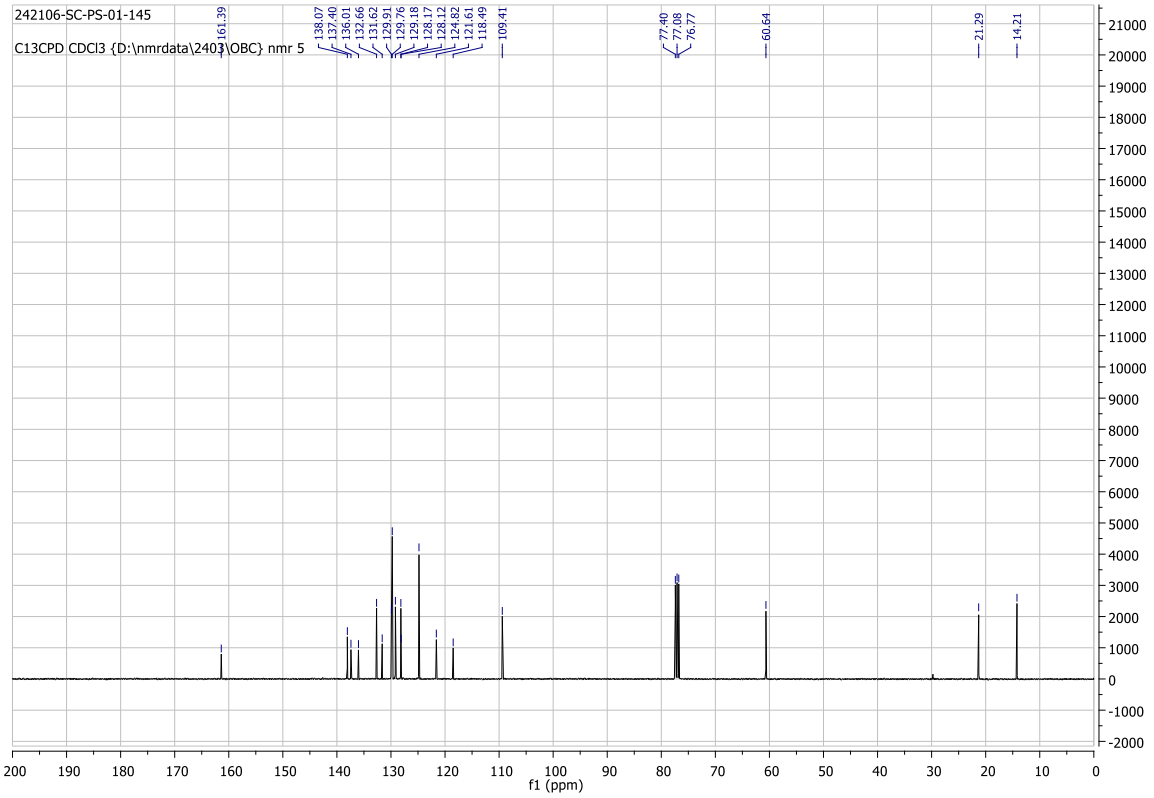


DEPT – 135 of **8p**

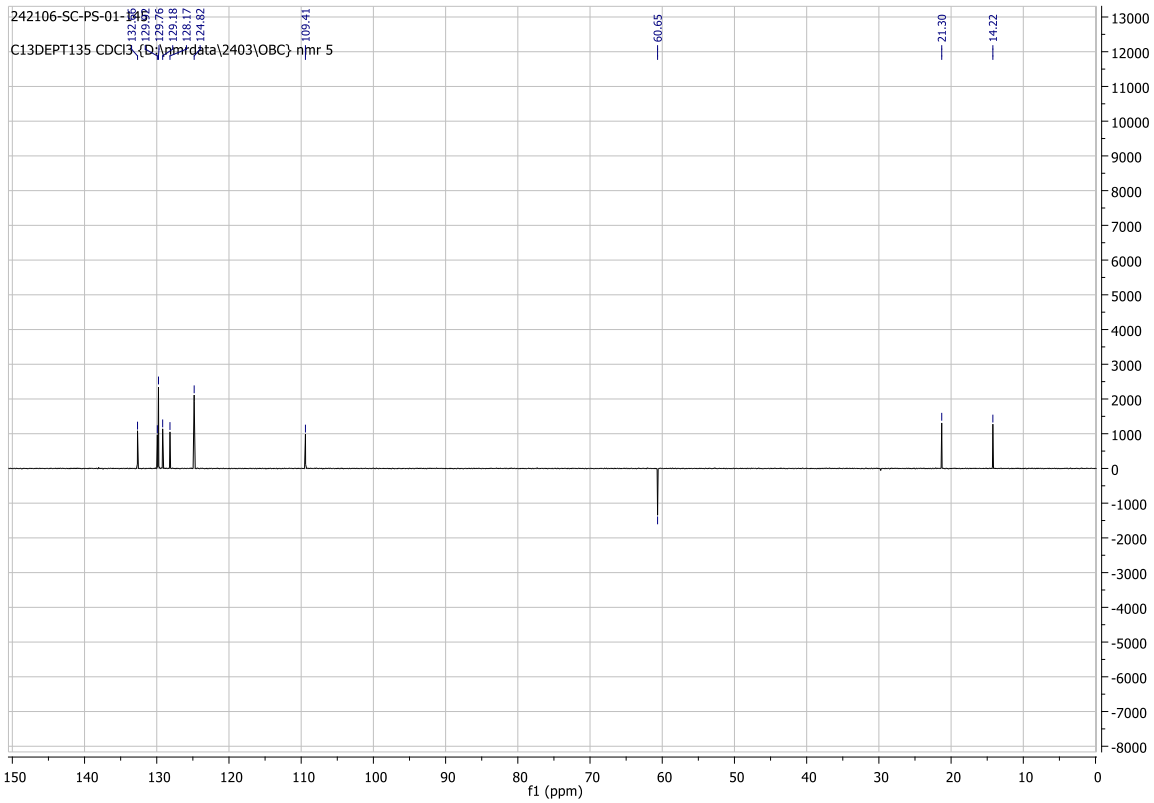




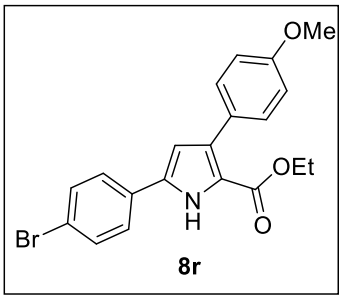
^{1}H-NMR (400 MHz, $CDCl_3$) of **8q**

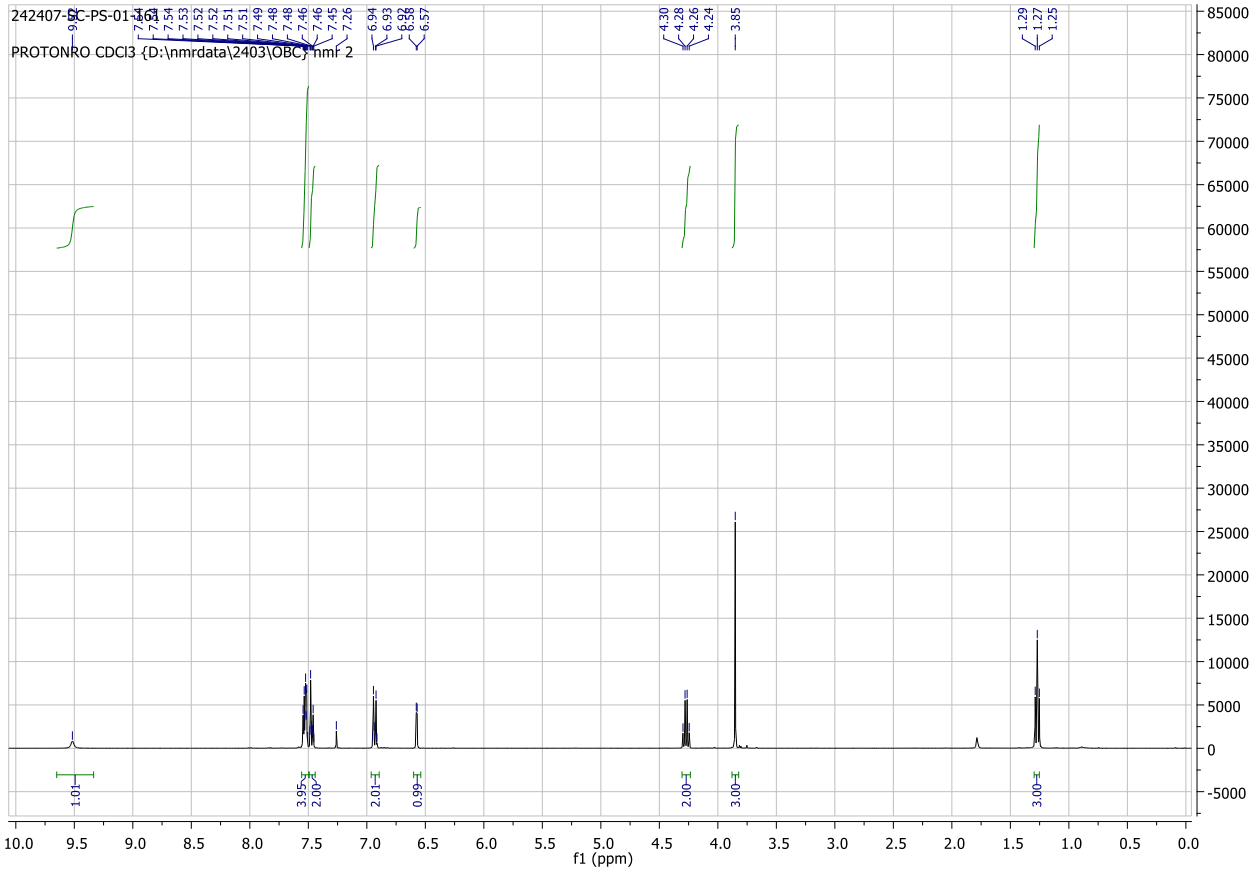


^{13}C-NMR (100 MHz, $CDCl_3$) of **8q**

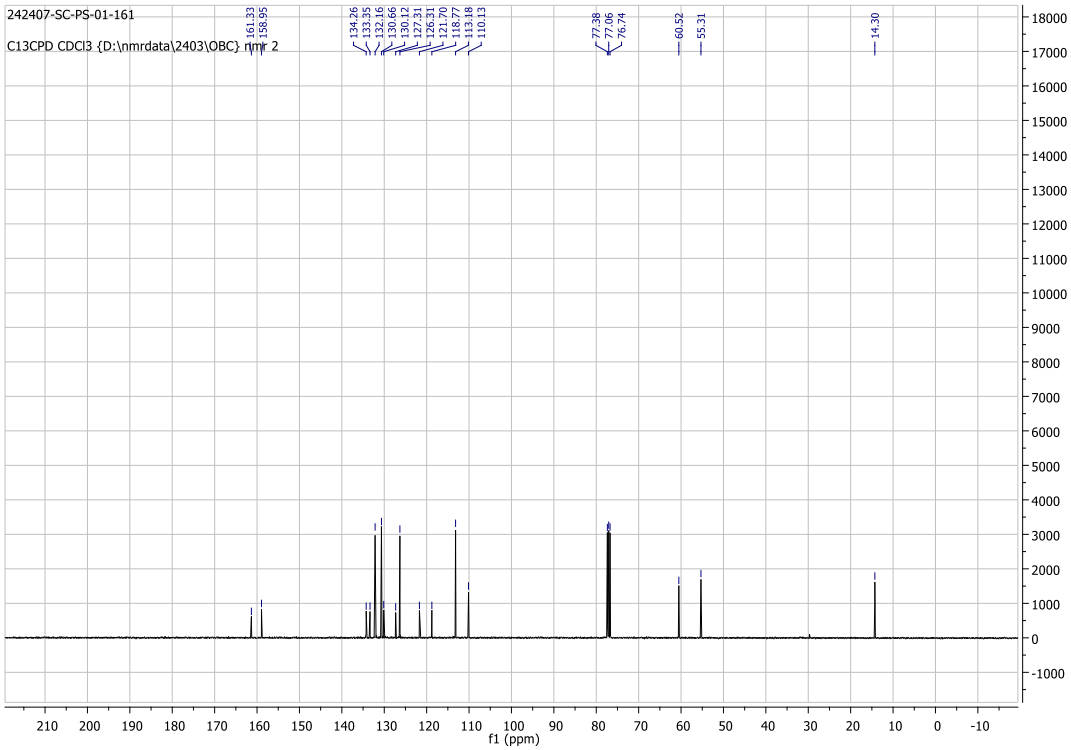


DEPT – 135 of **8q**

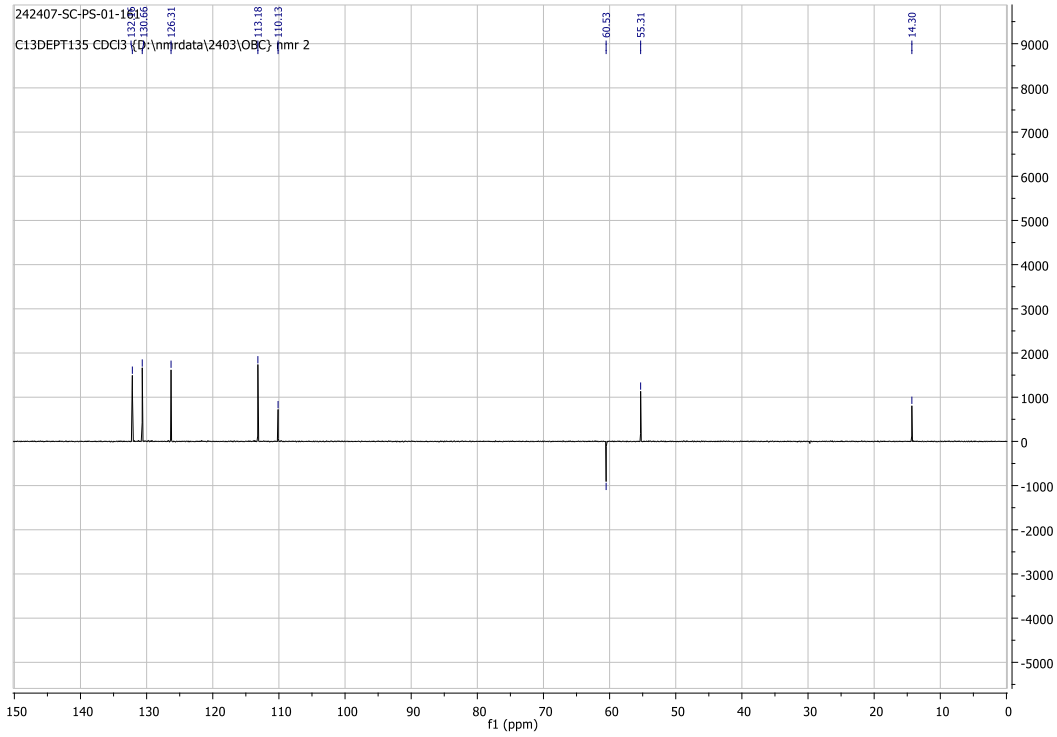




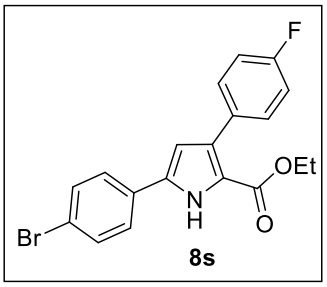
^{1}H-NMR (400 MHz, $CDCl_3$) of **8r**

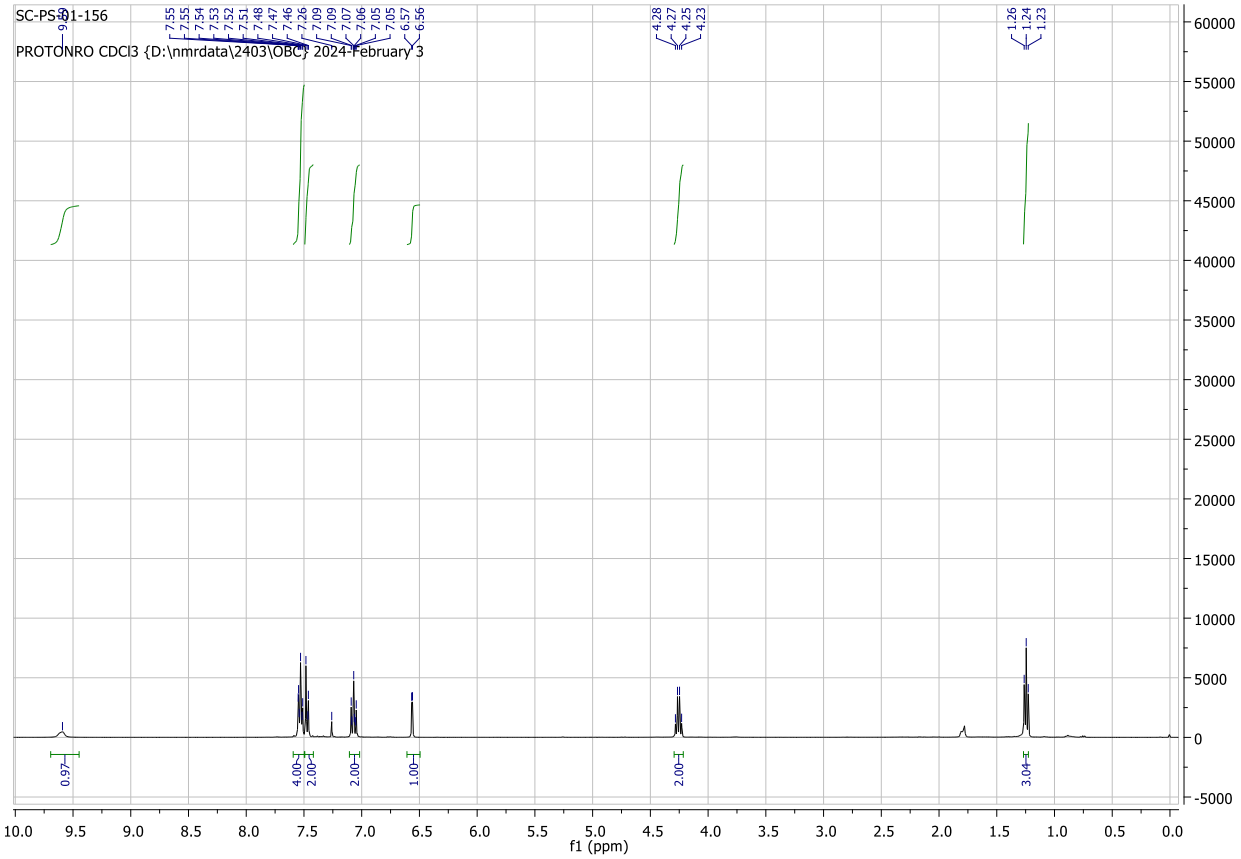


^{13}C-NMR (100 MHz, $CDCl_3$) of **8r**

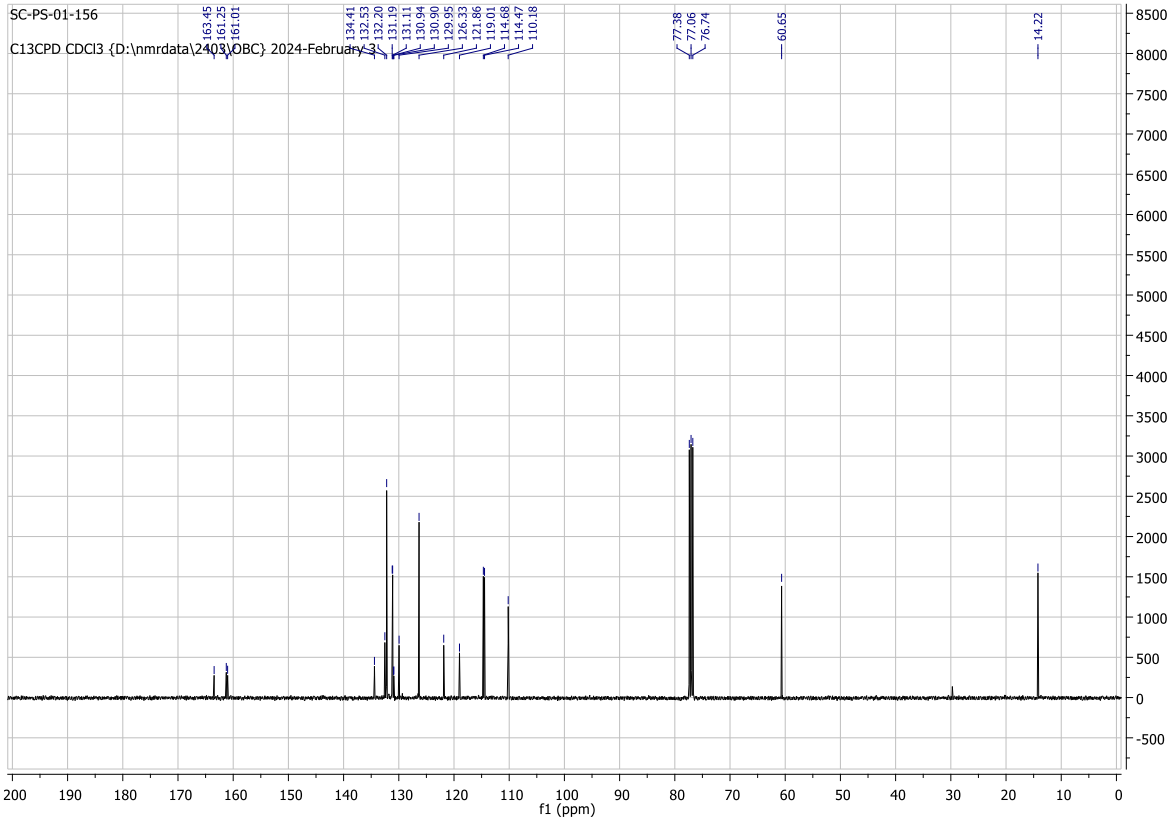


DEPT – 135 of **8r**





^{1}H-NMR (400 MHz, $CDCl_3$) of **8s**



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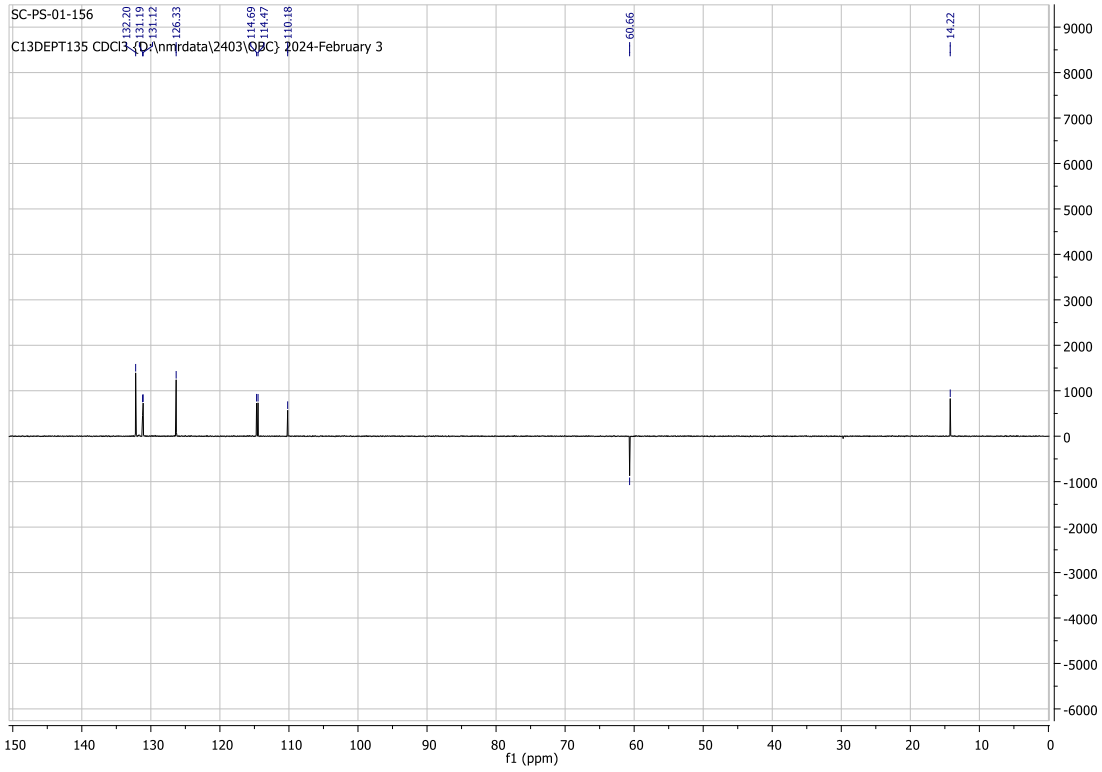
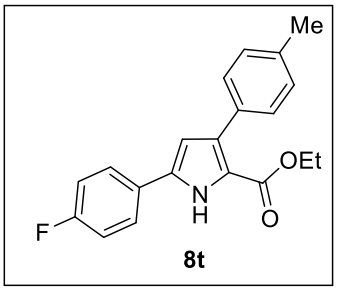
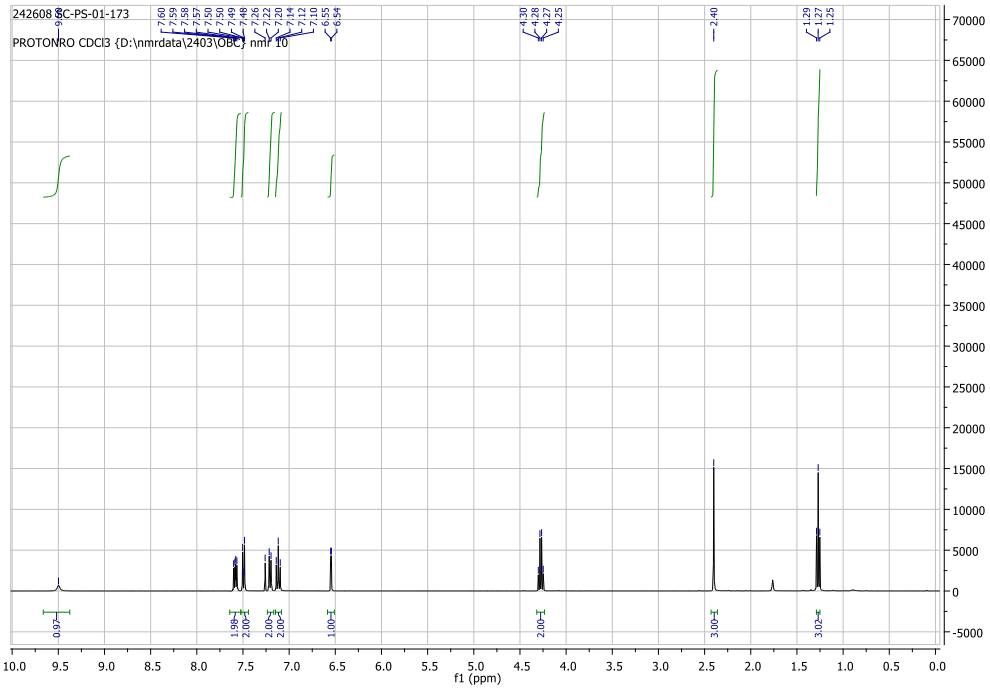
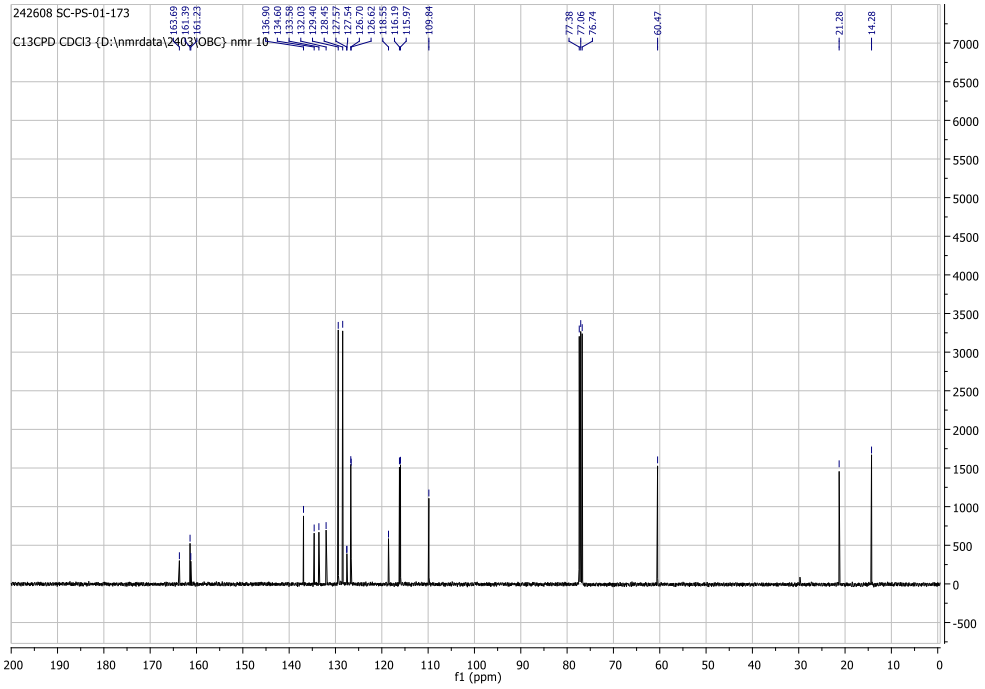


DEPT – 135 of **8s**

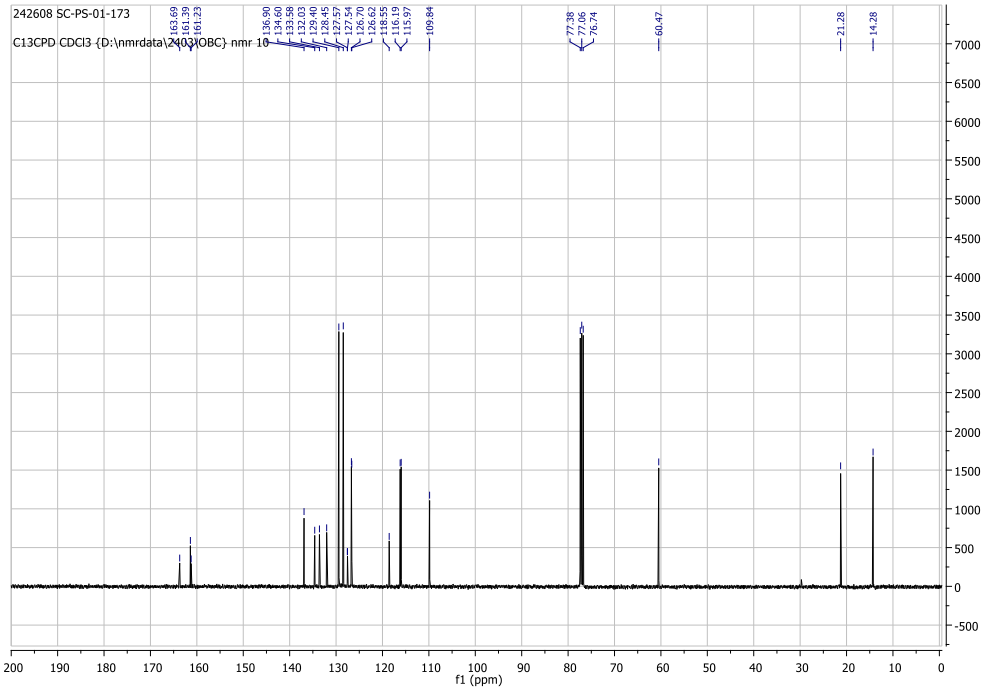




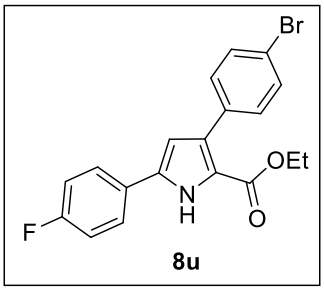
^{1}H-NMR (400 MHz, $CDCl_3$) of **8t**

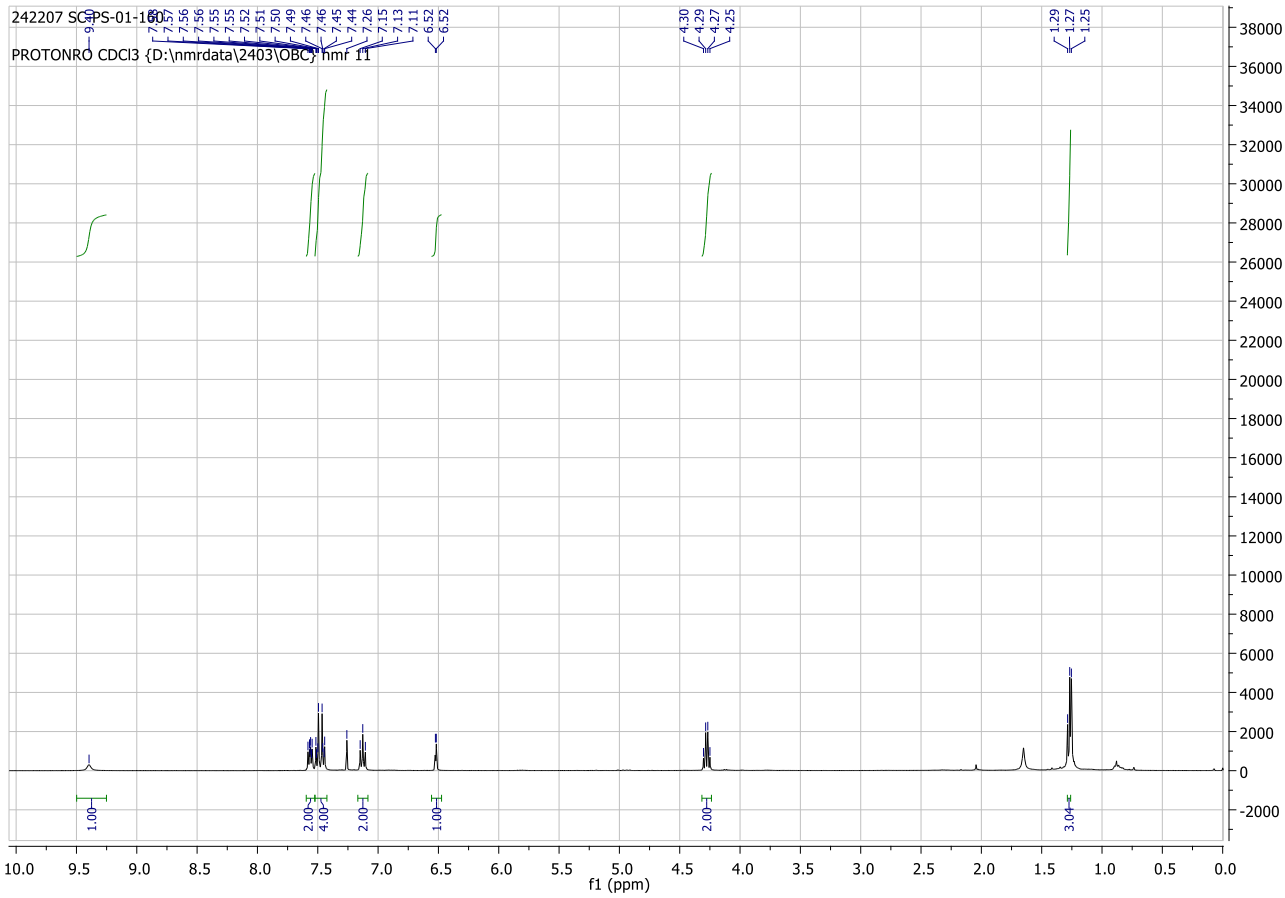


^{13}C-NMR (100 MHz, $CDCl_3$) of **8t**

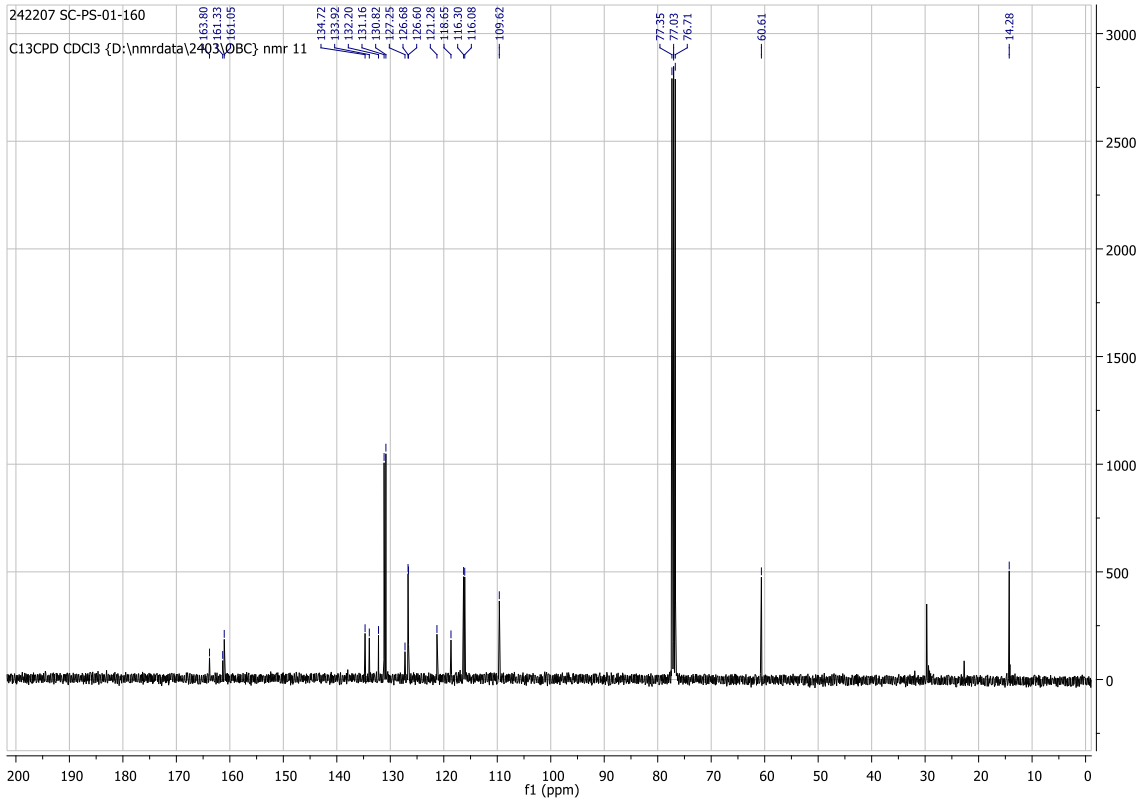


DEPT – 135 of **8t**

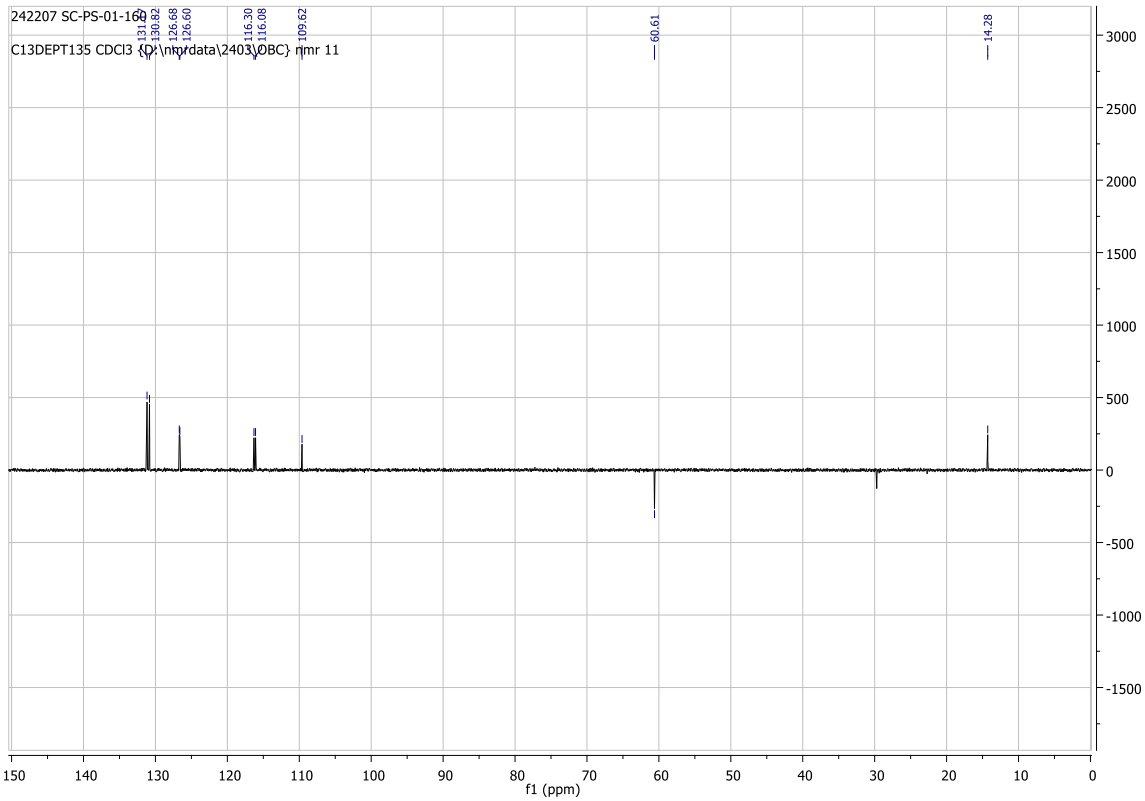




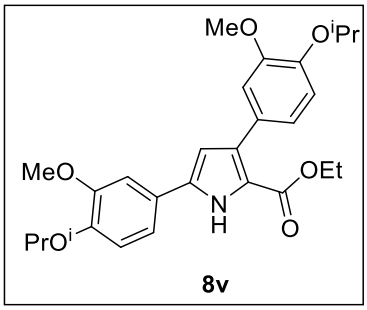
^{1}H-NMR (400 MHz, $CDCl_3$) of **8u**

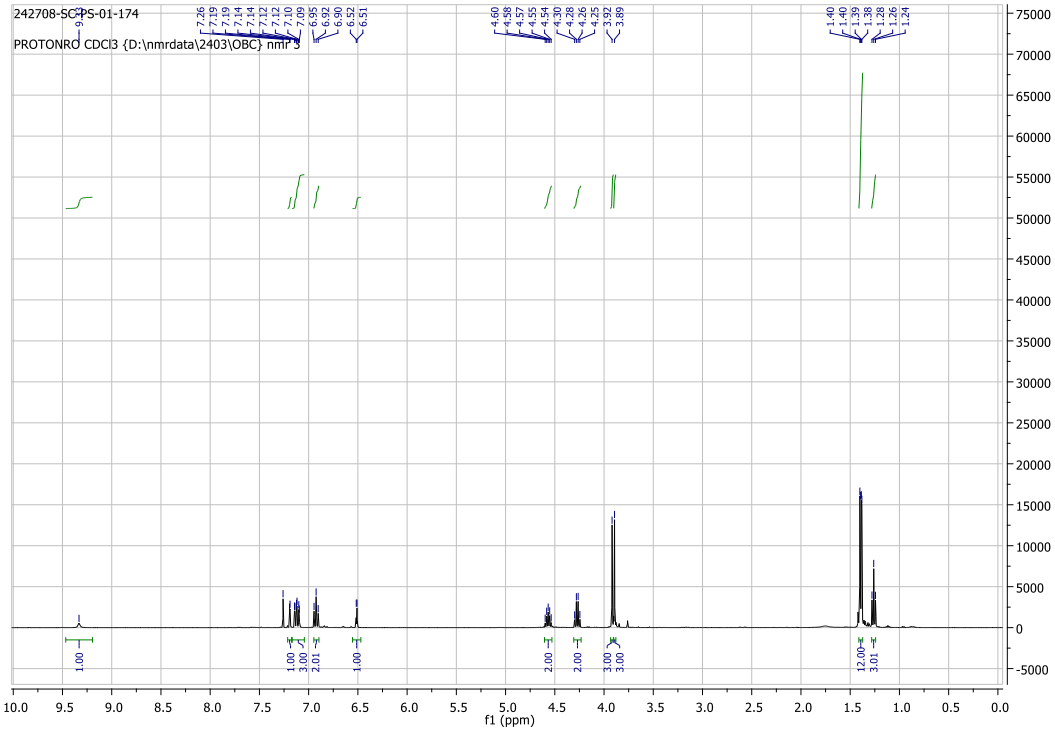


^{13}C-NMR (100 MHz, $CDCl_3$) of **8u**

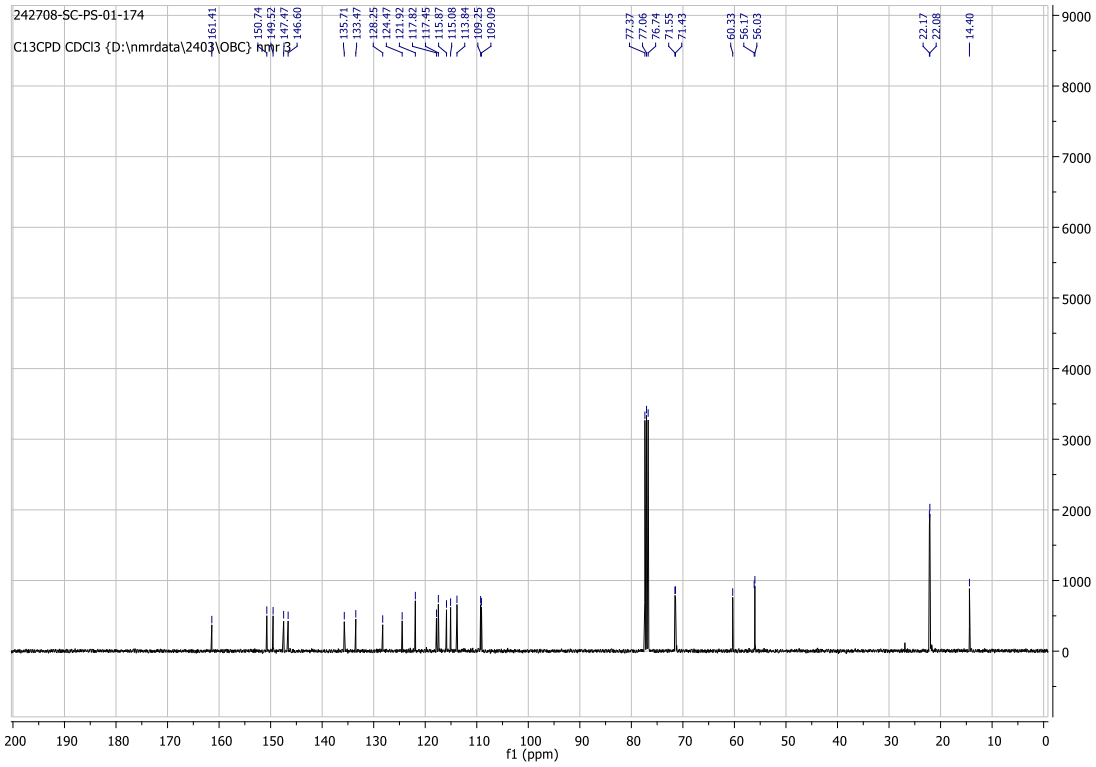


DEPT – 135 of **8u**

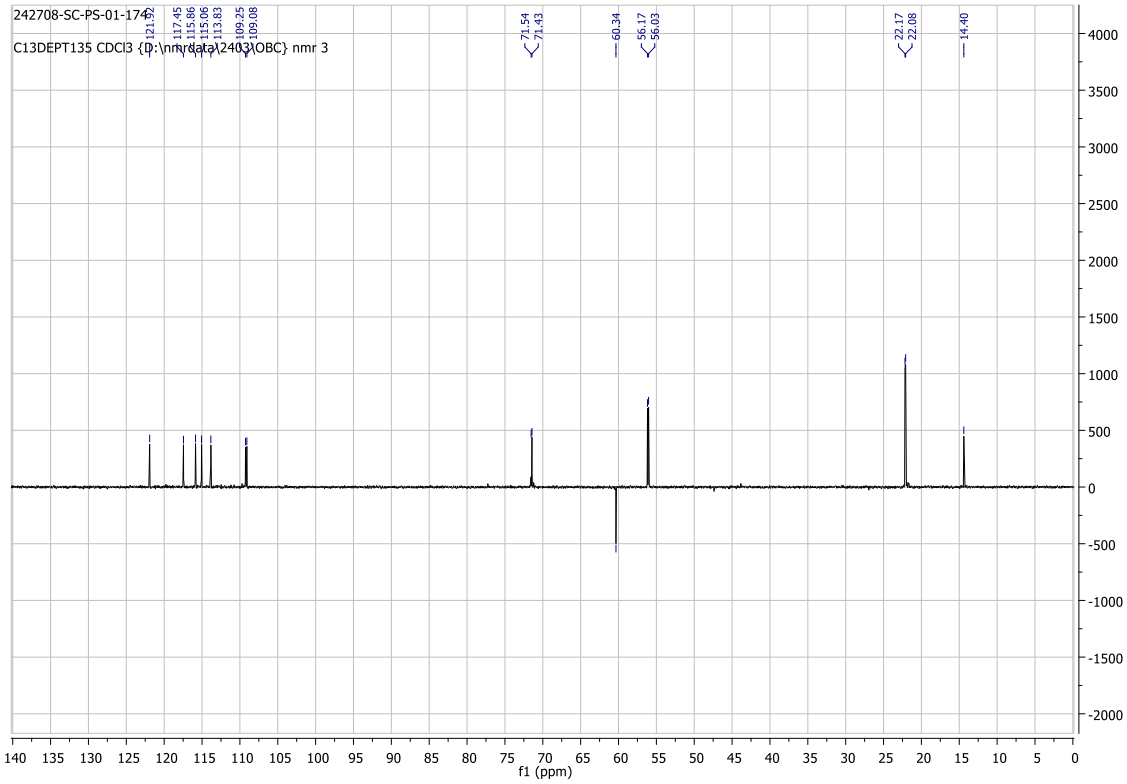




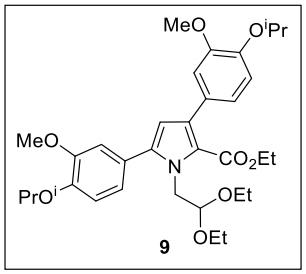
^{1}H-NMR (400 MHz, $CDCl_3$) of **8v**

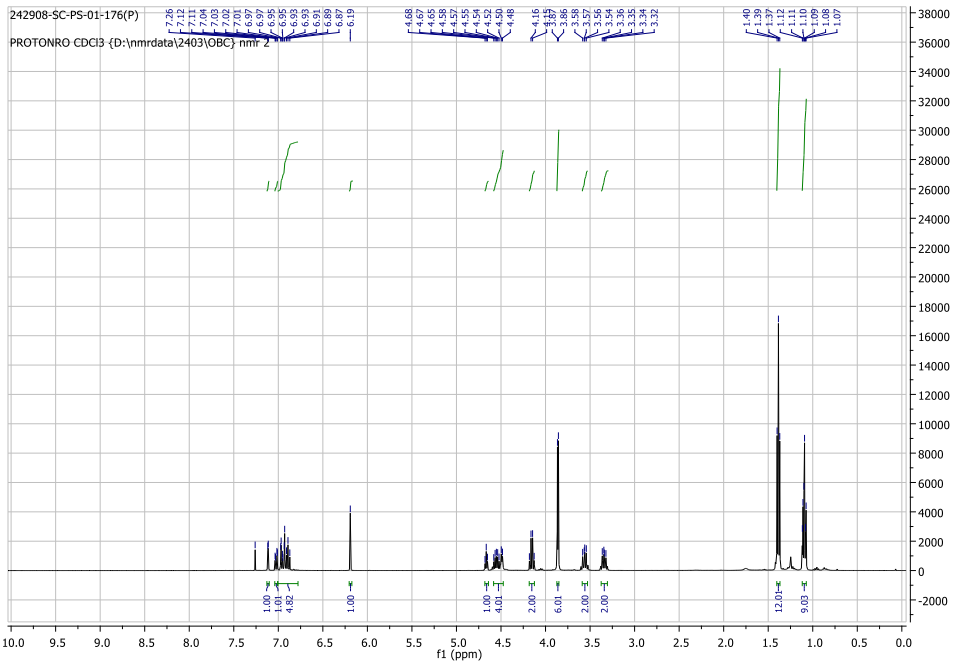


^{13}C-NMR (100 MHz, $CDCl_3$) of **8v**

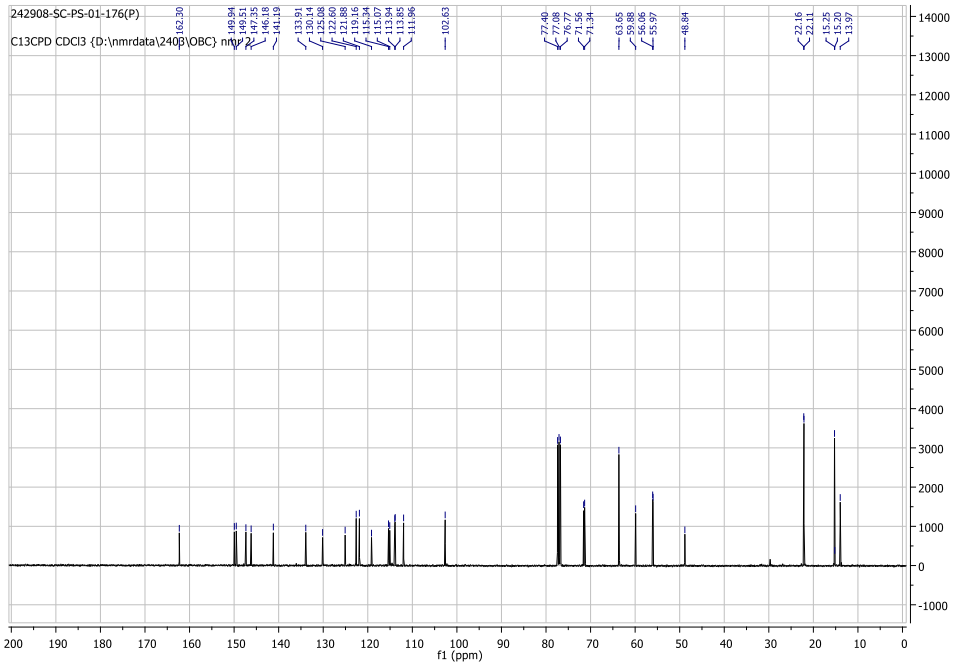


DEPT – 135 of **8v**

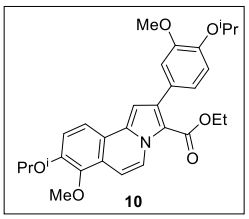


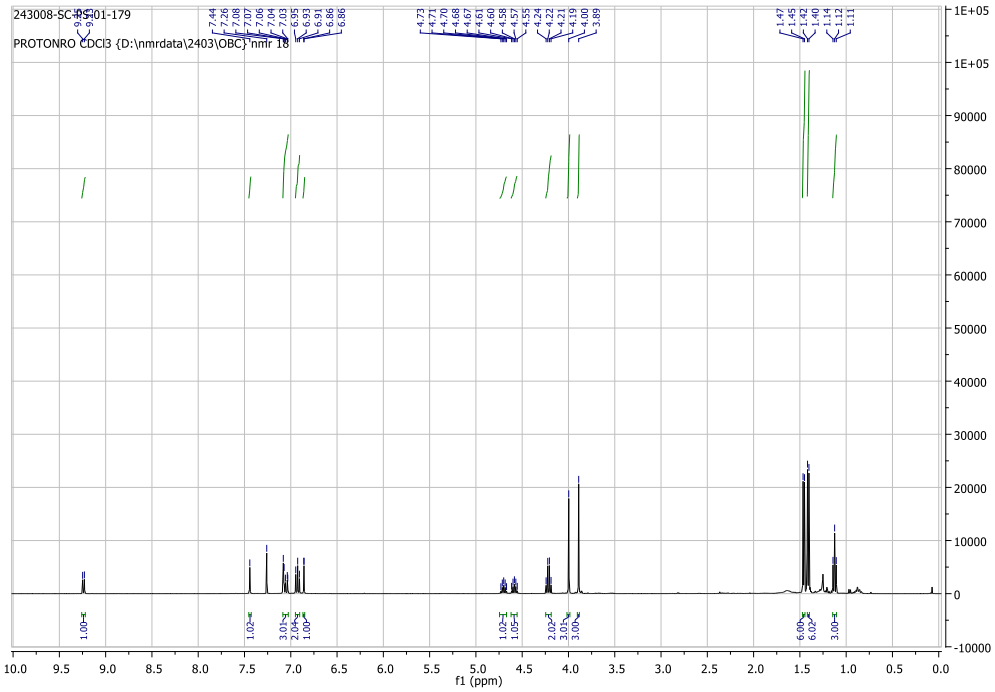


^{1}H-NMR (400 MHz, $CDCl_3$) of **9**

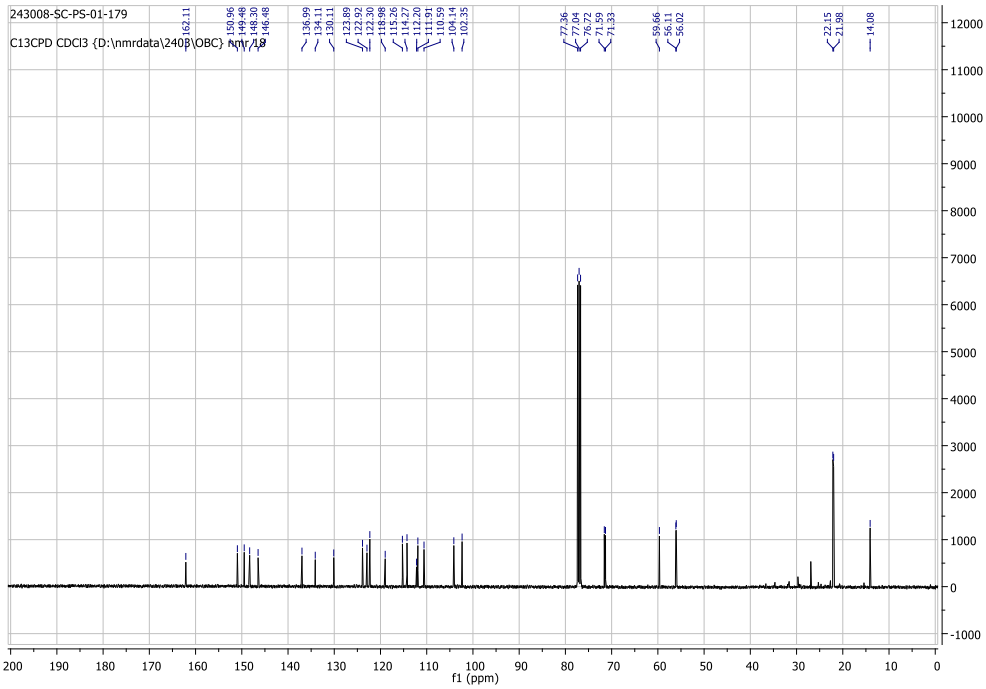


^{13}C-NMR (100 MHz, $CDCl_3$) of **9**

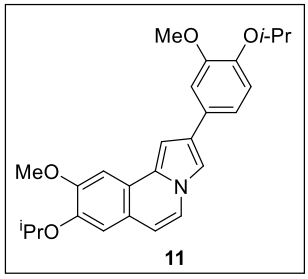


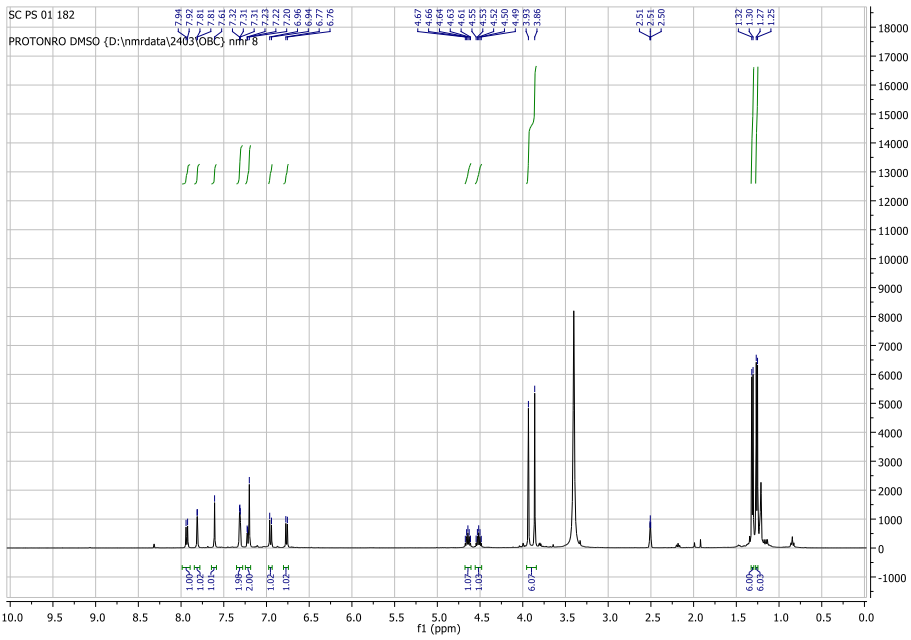


^{1}H-NMR (400 MHz, $CDCl_3$) of **10**

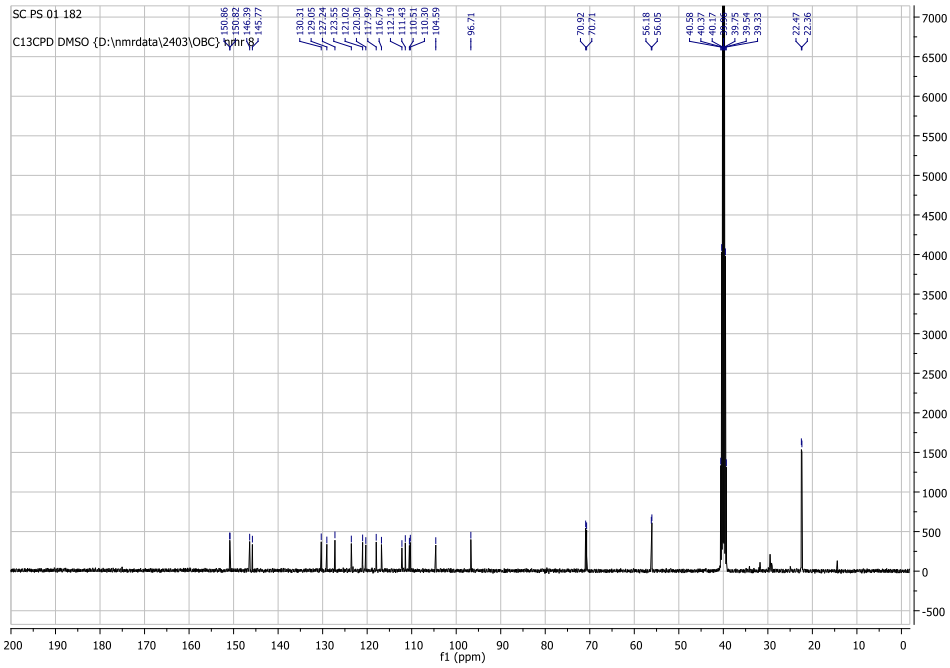


^{13}C-NMR (100 MHz, $CDCl_3$) of **10**





^{1}H-NMR (400 MHz, DMSO-d_6) of **11**



^{13}C-NMR (100 MHz, DMSO-d_6) of **11**