Electronic Supplementary Material (ESI) for ChemComm.

Domino Reaction of 2-Isocyanophenyloxyacrylate and Aryne to Synthesize Arenes with Vicinal Olefin and Benzoxazole

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Supporting Information

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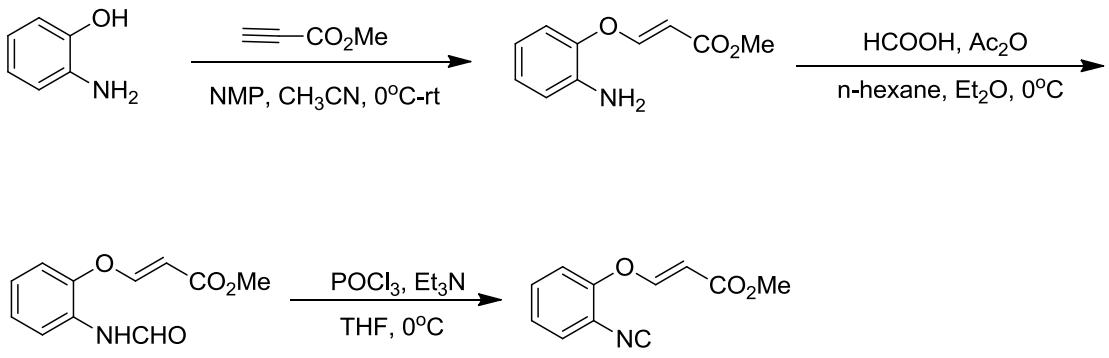
1 General Information

The NMR spectra were recorded on Bruker AC – 500 spectrometer (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR) with $CDCl_3$ as the solvent and TMS as internal reference. ^{1}H NMR spectral data were reported as follows: chemical shift (δ, ppm), multiplicity, integration, and coupling constant (Hz). ^{13}C NMR spectral data were reported in terms of the chemical shift. The following abbreviations were used to indicate multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. Low-resolution mass spectra were obtained on a Shimadzu LCMS-2010EV spectrometer in ESI mode and reported as m/z. High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument. Melting points were obtained on a X-4 digital melting point apparatus without correction. Chemical yields referred to pure isolated product. Purification of products was accomplished by column chromatography packed with silica gel. Unless otherwise stated, all reagents were commercially purchased and used without further purification. Aryne precursors 1 were prepared following published procedures.[1, 2]

2 Representative procedure for the preparation of substrates 1

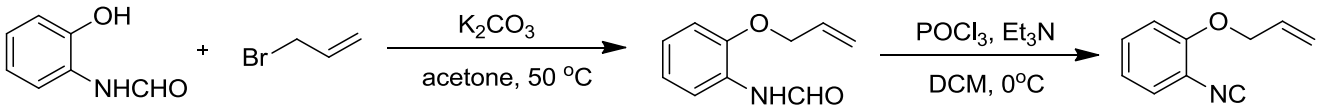


Setp 1: In a 100 mL round-bottom flask, a mixture of 2-aminophenol (20 mmol, 1 equiv) propiolate (24 mmol, 1.2 equiv) was dissolved in acetonitrile (60 mL) and was cooled to 0 ℃. Then N-methylmorpholine (1.2 mmol, 0.06 equiv) was added into the reaction mixture. The reaction mixture was allowed to warmed to room temperature and stirred for 12 h. After the solvent was removed, the crude product was purified by column chromatography to afford (*E*)-methyl 3-(2-aminophenoxy)acrylate (3.32 g, 86%) as a yellow liquid.[3]

Step 2: Acetyl formyl anhydride (prepared by stirring 2.0 equiv of acetic anhydride and 2.0 equiv of formic acid for 2 h at 55 ℃) was added dropwise to a solution of (*E*)-methyl 3-(2-aminophenoxy) acrylate (3.32 g, 17.2 mmol, 1.0 equiv) in Et_2O at 0 ℃ , and the mixture was stirred for 0.5h at 0 ℃, and then filtered to give (*E*)-methyl 3-(2-formamidophenoxy)acrylate (3.42 g, 90%) as a white solid.

Step 3: A solution of (*E*)-methyl 3-(2-formamidophenoxy)acrylate (3.42 g, 15.48 mmol, 1.0 equiv) and NEt_3 (69.66 mmol, 4.5 equiv) in THF (100 mL) was cooled at 0 ^oC, then $POCl_3$ (23.22 mmol, 1.5 equiv) was added dropwise. After the reaction was completed, a saturated Na_2CO_3 aqueous solution was added at 0 ℃ and the mixture was extracted with EA (3 ×100 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to column chromatography on neutral Al_2O_3 to give (*E*)-methyl 3-(2-isocyanophenoxy)acrylate (**1a**, 2.60 g, 83%) as a white solid.[4,5]

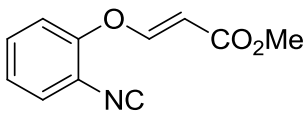
Representative procedure for the preparation of 1-(allyloxy)-2-isocyanobenzene



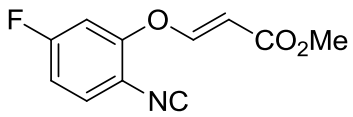
To a solution of phenols N-(2-hydroxyphenyl)formamide (10 mmol, 1.0 equiv) and potassium carbonate (20 mmol, 2.0 equiv) in acetone (30 ml) was added allyl bromide (24 mmol, 1.2 equiv). The resulting mixture was then stirred at 50 ^oC for 12 hours. After filtration through celite and washed with ethyl acetate, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel to afford the product N-(2-(allyloxy)phenyl)-formamide (1.51g, 85%) as yellow oil.[6,7]

A solution of N-(2-(allyloxy)phenyl)formamide (1.51 g, 8.5 mmol, 1.0 equiv) and NEt_3 (38.25 mmol, 4.5 equiv) in DCM (50 mL) was cooled at 0 ℃, then $POCl_3$ (12.75 mmol, 1.5 equiv) was added dropwise. After the reaction was completed, a saturated Na_2CO_3 aqueous solution was added at 0 ℃ and the mixture was extracted with EA (3 ×50 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to column chromatography on neutral Al_2O_3 to give 1-(allyloxy)-2-isocyanobenzene (0.95 g, 70%) as a yellow liquid.

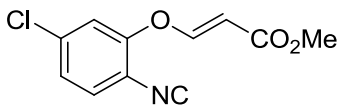
Analytical Data of Substrate 1



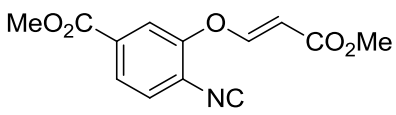
(**1a**): 2.60 g, 64% yield, white solid: m.p. 62-63°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.75 (d, *J* = 12.0 Hz, 1H), 7.45-7.41 (m, 2H), 7.22 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.17-7.15 (m, 1H), 5.63 (d, *J* = 12.0 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 170.0, 167.0, 157.5, 150.8, 130.9, 128.4, 125.6, 118.8, 118.4, 103.9, 51.65. HRMS (ESI): calcd. for $C_{11}H_{10}NO_3$ $[M+H]^+$ 204.0661, Found: 204.0670.



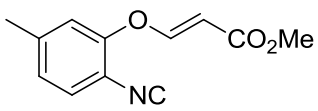
(**1b**): 0.91g, 41% yield, white solid: m.p. 117-118°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.70 (d, *J* = 12.0 Hz, 1H), 7.45-7.42 (m, 1H), 6.95-6.90 (m, *2*H), 5.72 (d, *J* = 12.0 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 170.1, 166.6, 162.7 (d, $^{1}J_{C\text{-}F}$ = 252.5 Hz), 156.3, 151.9 (d, $^{3}J_{C\text{-}F}$ = 10.0 Hz), 129.5 (d, $^{3}J_{C\text{-}F}$ = 10.0 Hz), 114.6, 112.6 (d, $^{2}J_{C\text{-}F}$ = 47.5 Hz), 106.5 (d, $^{2}J_{C\text{-}F}$ = 52.5 Hz), 105.2, 51.8. HRMS (ESI): calcd. for $C_{22}H_{17}F_2N_2O_6$ $[2M+H]^+$ 443.1055, Found: 443.1050.



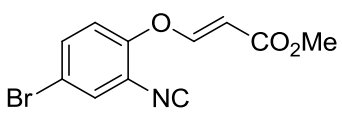
(**1c**): 1.19 g, 50% yield, white solid: m.p. 92-93°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.70 (d, *J* = 12.0 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.20-7.17 (m, *2*H), 5.71 (d, *J* = 12.0 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 171.3, 166.6, 156.4, 151.2, 136.5, 129.0, 125.7, 119.0, 116.8, 105.1, 51.8. HRMS (ESI): calcd. for $C_{22}H_{17}Cl_2N_2O_6$ $[2M+H]^+$ 475.0464, Found: 475.0450.



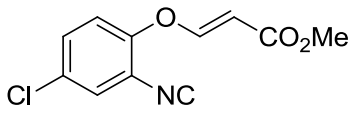
(**1d**): 1.28 g, 49% yield, white solid: m.p. 95-96°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.88 (d, *J* = 8.0 Hz, 1H), 7.82 (s, 1H), 7.77 (d, *J* = 12.5 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 5.72 (d, *J* = 12.0 Hz, 1H), 3.94 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 172.8, 166.7, 164.8, 156.5, 150.7, 132.6, 128.4, 126.4, 121.4, 119.1, 105.0, 53.0, 51.8. HRMS (ESI): calcd. for $C_{13}H_{12}NO_5$ $[M+H]^+$ 262.0715, Found: 262.0712.



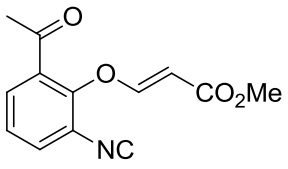
(**1e**): 1.22 g, 56% yield, white solid: m.p. 75-76°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.73 (d, *J* = 12.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.95 (s, 1H), 3.74 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 169.1, 167.1, 157.7, 150.5, 142.0, 127.9, 126.2, 119.3, 103.6, 51.6, 21.6. HRMS (ESI): calcd. for $C_{12}H_{12}NO_3$ $[M+H]^+$ 218.0817, Found: 218.0825.



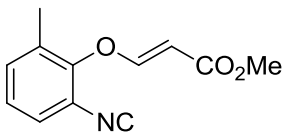
(**1f**): 1.52 g, 54% yield, red solid: m.p. 89-90°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.69 (d, *J* = 12.0 Hz, 1H), 7.58 (d, *J* = 2.0 Hz, 1H), 7.54 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.05 (d, *J* = 9.0 Hz, 1H), 5.66 (d, *J* = 12.0 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 171.8, 166.7, 156.8, 150.0, 134.0, 131.1, 120.0, 119.3, 117.6, 104.6, 51.8. HRMS (ESI): calcd. for $C_{11}H_9BrNO_3$ $[M+H]^+$ 281.9766, Found: 281.9760.



(**1g**): 1.23g, 52% yield, white solid: m.p. 86-87°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.70 (d, *J* = 12.0 Hz, 1H), 7.43 (d, *J* = 2.5 Hz, 1H), 7.40 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 1H), 5.65 (d, *J* = 12.0 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 171.8, 166.7, 157.0, 149.5, 131.0, 130.7 128.2, 119.8, 119.0, 104.5, 51.7. HRMS (ESI): calcd. for $C_{11}H_9ClNO_3$ $[M+H]^+$ 238.0271, Found: 238.0280.

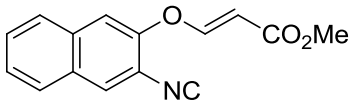


(**1h**): 1.44 g, 59% yield, yellow solid: m.p. 76-78°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.84 (d, *J* = 7.5 Hz, 1H), 7.70 (d, *J* = 12.5 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.40-7.37 (m, 1H), 5.28 (d, *J* = 12.5 Hz, 1H), 3.71 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 195.8, 172.1, 166.4, 159.2, 148.8, 133.2, 131.8, 131.4, 127.1, 121.1, 102.5, 51.7, 30.8. HRMS (ESI): calcd. for $C_{26}H_{23}N_2O_8$ $[2M+H]^+$ 491.1454, Found: 491.1449.

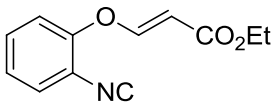


(**1i**): 0.87g, 40% yield, yellow solid: m.p. 50-51°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.73 (d, *J* = 12.5 Hz, 1H), 7.29 (d, *J* = 7.0 Hz, 2H), 7.18 (t, *J* = 7.5 Hz,

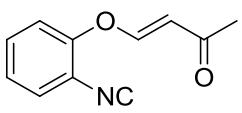
1H), 5.11 (d, *J* = 12.5 Hz, 1H), 3.70 (s, 3H), 2.24 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 169.8, 167.0, 159.4, 147.9, 132.6, 132.5, 126.6, 125.8, 120.2, 100.5, 51.5, 16.0. HRMS (ESI): calcd. for $C_{24}H_{23}N_2O_6$ $[2M+H]^+$ 435.1556, Found: 435.1552.



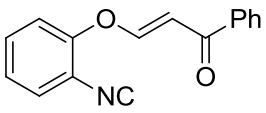
(**1j**): 1.57g, 62% yield, white solid: m.p. 90-91°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.93 (s, 1H), 7.87 (d, *J* = 12.5 Hz, 1H), 7.80 (t, *J* = 8.5 Hz, 1H), 7.59 (t, *J* = 7.0 Hz, 1H), 7.54 (t, *J* = 7.0 Hz, 1H), 7.50 (s, 1H), 5.74 (d, *J* = 12.0 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 169.8, 167.1, 157.6, 147.5, 133.3, 129.8, 128.9, 128.2, 127.9, 127.5, 127.1, 117.3, 115.0, 104.3, 51.7. HRMS (ESI): calcd. for $C_{15}H_{12}NO_3$ $[M+H]^+$ 254.0817, Found: 254.0813.



(**1k**): 1.32 g, 61% yield, yellow solid: m.p. 59-60°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.74 (d, *J* = 12.0 Hz, 1H), 7.44-7.41 (m, 1H), 7.21 (td, *J* = 7.5, 1.0 Hz, 1H), 7.17 (dd, *J* = 9.0, 1.0 Hz, 1H), 5.61 (d, *J* = 12.0 Hz, 1H), 4.20 (q, *J* = 7.5 Hz, 2H), 1.28 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 169.9, 166.6, 157.4, 150.8, 130.9, 128.4, 125.6, 118.9, 118.4, 104.2, 60.5, 14.4. HRMS (ESI): calcd. for $C_{24}H_{23}N_2O_6$ $[2M+H]^+$ 435.1556, Found: 435.1552.

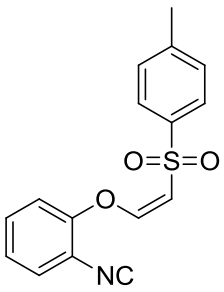


(**1l**): 1.03 g, 55% yield, brown solid: m.p. 66-67°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.68 (d, *J* = 12.0 Hz, 1H), 7.45-7.41 (m, 2H), 7.23 (td, *J* = 8.0, 1.5 Hz, 1H), 7.16 (dd, *J* = 8.5 Hz, 1.0 Hz, 1H), 5.94 (d, *J* = 12.5 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 196.9, 170.0, 157.2, 150.6, 130.9, 128.4, 125.8, 119.0, 118.5, 112.9, 28.8. HRMS (ESI): calcd. for $C_{22}H_{19}N_2O_4$ $[2M+H]^+$ 375.1345, Found: 375.1337.

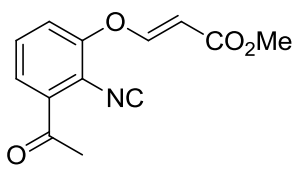


(**1m**): 0.50 g, 20% yield, yellow solid: m.p. 65-66°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.95-7.90 (m, 3H), 7.58 (tt, *J* = 7.0, 1.5 Hz, 1H), 7.50-7.44 (m, 4H), 7.25-7.21 (m, 2H), 6.87 (d, *J* = 11.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 190.0, 170.0,

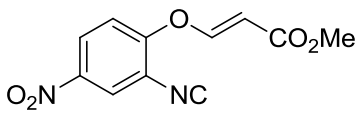
158.0, 151.2, 138.0, 133.1, 131.0, 128.8, 128.4, 128.3, 125.5, 118.2, 108.7. HRMS (ESI): calcd. For $C_{16}H_{12}NO_2$ $[M+H]^+$ 250.0868, Found: 250.0875.



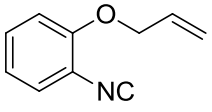
(**1n**): 0.30 g, 10% yield, brown solid: m.p. 72-73°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.02 (d, *J* = 8.5 Hz, 1H), 7.43-7.39 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.21 (td, *J* = 7.5, 1.0 Hz, 1H), 7.08 (dd, *J* = 8.5, 1.0 Hz , 1H), 6.76 (d, *J* = 6.5 Hz, 1H), 6.02 (d, *J* = 6.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 170.7, 151.3, 149.3, 144.7, 138.9, 131.0, 130.0, 128.6, 128.0, 125.8, 118.1, 115.6, 21.8. HRMS (ESI): calcd. For $C_{16}H_{14}NO_3S$ $[M+H]^+$ 300.0694, Found: 300.0688.



(**1o**): 0.93 g, 38% yield, white solid: m.p. 118-119°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.74 (d, *J* = 12.0 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 5.68 (d, *J* = 12.0 Hz, 1H), 3.74 (s, 3H), 2.71 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 196.3, 176.4, 166.8, 157.0, 151.9, 137.3, 130.4, 125.4, 121.6, 116.0, 104.6, 51.8, 29.9. HRMS (ESI): calcd. for $C_{13}H_{12}NO_4$ $[M+H]^+$ 246.0766, Found: 246.0762.



(**1p**): 0.92 g, 37% yield, yellow solid: m.p. 145-147°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.34 (m, 1H), 7.78 (d, *J* = 12.0 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 5.93 (d, *J* = 12.5 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 173.5, 168.2, 155.2, 154.4, 143.7, 126.3, 124.2, 117.1, 107.6, 52.0. HRMS (ESI): calcd. for $C_{11}H_9N_2O_5$ $[M+H]^+$ 249.0511, Found: 249.0517.



(**1q**): 0.95 g, 60% yield, yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.35-7.26 (m, 2H), 6.95-6.91 (m, 2H), 6.09-6.02 (m, 1H), 5.49 (dq, *J* = 17.0, 1.5 Hz, 1H), 5.33 (dq, *J* = 10.5, 1.5 Hz, 1H), 4.64 (dt, *J* = 5.0, 1.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) =

167.6, 154.1, 132.2, 130.4, 127.8, 120.8, 118.2, 116.7, 113.3, 69.6. HRMS (ESI): calcd. for $C_{10}H_{10}NO$ $[M+H]^+$ 160.0762, Found: 160.0766.

3 General procedure

3.1 General Procedure for the Formation of Product **3** or **4.**

To a Schlenk tube containing isocyanide **1** (0.5 mmol), CsF (2.0 mol) in was added CH_3CN (5.0 mL) and the reaction mixture was stirred for 5 minutes at room temperature, followed by the addition of benzyne precusor **2** (0.75 mmol) at the same temperature. The Schlenk tube was then placed in a preheated (80^{o}C) oil bath. The progress of the reaction was monitored by TLC. After completion of the reaction, CH_3CN was evaporated on a rotary evaporator. The crude products obtained were purified by flash silica gel column chromatography using a gradient of ethyl acetate:petroleum ether to afford the corresponding products **3 or 4**.

3.2 General Procedure for the Formation of Product **6**

Into a flame-dried 25 mL Schlenk tube were added **3** (0.2 mmol, 1.0 equiv) , $[Cp^*RhCl_2]_2$ (3 mg, 2.5 mol %), NaOAc (16 mg,1equiv), and $Cu(OAc)_2$ (64 mg, 2.0 equiv) under nitrogen flow, the tube was sealed with rubber, evacuated, and refilled with nitrogen three times, and then DCE (2 mL) and alkenes were added via syringe. The tube was sealed with a glass stopper, evacuated, and refilled with nitrogen three times and heated at 90 ℃ for the duration of the reaction. After being cooled to room temperature, the reaction mixture was quenched with 10 mL of saturated ammonium chloride solution and extracted with ethyl acetate (3 × 10 mL), the organic phase was combined, washed with brine (2 × 10 mL), dried under anhydrous $MgSO_4$, and concentrated under reduced pressure, and the residue mixture was purified by flash column chromatography.[8,9]

3.3 Genor the Formation of Product **8**

Under N_2 atmosphereral Procedure fe, $AlMe_3$ (0.3 mL, 1M in hexane) was added to the solution of **3a** (55.8 mg, 0.2 mmol) and 4-methoxyaniline (73.8 mg, 0.6 mmol) in toluene (2 mL). The resulting

solution was heated under reflux for 24 h. After completion of the reaction, a saturated NH_4Cl aqueous solution was added, and the mixture was extracted with EA (3 × 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (eluant: petroleum ether/ethyl acetate = 1:1) to give the desired product **10** (56mg, 70%) as a white solid.

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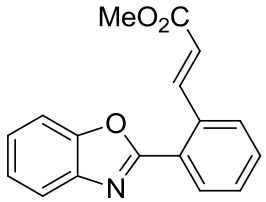
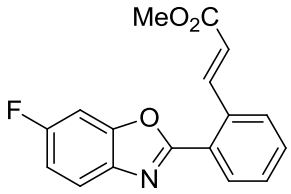
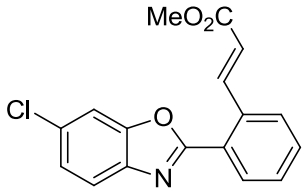
4 Characterization Data



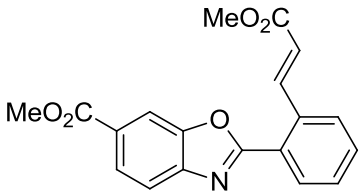
(**3a**): 99 mg, 71% yield, white solid: m.p. 90-91°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.83 (d, *J* = 16.0 Hz, 1H), 8.21-8.20 (m, 1H), 7.86-7.84 (m, 1H), 7.75-7.73 (m, 1H), 7.62-7.60 (m, 1H), 7.54-7.52 (m, 2H), 7.40-7.36 (m, 2H), 6.48 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.3, 161.9, 150.6, 143.9, 142.2, 135.1, 131.3, 130.4, 129.9, 128.1, 126.6, 125.6, 124.8, 120.9, 120.8, 110.7, 51.92. HRMS (ESI): calcd. for $C_{17}H_{14}NO_3$ $[M+H]^+$ 280.0974, Found: 280.0960.



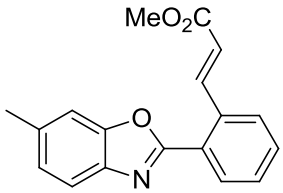
(**3b**): 98 mg, 66% yield, white solid: m.p. 95-97°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.80 (d, *J* = 16.0 Hz, 1H), 8.19-8.15 (m, 1H), 7.78-7.76 (m, 1H), 7.74-7.72 (m, 1H), 7.56-7.51(m, 2H), 7.33 (dd, *J* = 8.0, 2.5 Hz, 1H), 7.15-7.11 (m, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.3, 162.5 (d, $^{4}J_{C-F}$ = 3.8 Hz), 161.0 (d, $^{1}J_{C-F}$ = 243.8 Hz), 150.6 (d, $^{3}J_{C-F}$ = 15.0 Hz), 143.8, 138.5 (d, $^{5}J_{C-F}$ = 1.3 Hz), 135.0, 131.4, 130.1 (d, $^{2}J_{C-F}$ = 28.8 Hz), 128.1, 126.2, 121.1 (d, $^{3}J_{C-F}$ = 11.3 Hz), 121.0, 112.9 (d, $^{4}J_{C-F}$ = 5.0 Hz), 98.8 (d, $^{2}J_{C-F}$ = 27.5 Hz), 51.96. HRMS (ESI): calcd. for $C_{17}H_{13}FNO_3$ $[M+H]^+$ 298.0879, Found: 298.0874.



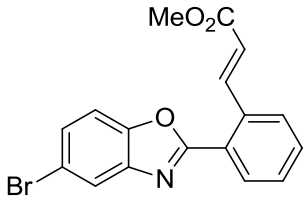
(**3c**): 100 mg, 64% yield, white solid: m.p. 112-113°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.80 (d, *J* = 16.0 Hz, 1H), 8.19-8.17 (m, 1H), 7.78-7.76 (m, 1H), 7.75-7.72 (m, 2H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.57-7.51 (m, 2H), 7.35 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.15-7.11 (m, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.2, 162.5, 150.8, 143.7, 141.0, 135.2, 131.6, 131.3, 130.3, 130.0, 128.2, 126.00, 125.5, 121.2, 121.1, 111.4, 52.0. HRMS (ESI): calcd. for $C_{17}H_{13}ClNO_3$ $[M+H]^+$ 314.0584, Found: 314.0573.



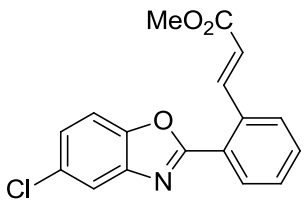
(**3d**): 135 mg, 80% yield, white solid: m.p. 148-149°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.82 (d, *J* = 16.0 Hz, 1H), 8.28 (d, *J* = 1.0 Hz, 1H), 8.24-8.22 (m, 1H), 8.10 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.2, 166.7, 164.4, 150.2, 146.0, 143.7, 135.5, 131.9, 130.6, 130.0, 128.3, 127.6, 126.5, 125.8, 121.2, 120.3, 112.5, 52.5, 52.0. HRMS (ESI): calcd. for $C_{19}H_{16}NO_5$ $[M+H]^+$ 338.1028, Found: 338.1023.



(**3e**): 69 mg, 47% yield, white solid: m.p. 115-117°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.82 (d, *J* = 16.0 Hz, 1H), 8.19-8.16 (m, 1H), 7.73-7.69 (m, 2H), 7.53-7.49 (m, 2H), 7.40 (s, 1H), 7.18 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.3, 161.4, 150.9, 144.0, 140.0, 136.1, 134.9, 131.1, 130.2, 129.9, 128.00, 126.7, 126.0, 120.7, 120.0, 110.9, 51.9, 21.9. HRMS (ESI): calcd. for $C_{18}H_{16}NO_3$ $[M+H]^+$ 294.1130, Found: 294.1126.

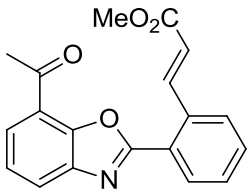


(**3f**): 120 mg, 67% yield, white solid: m.p. 118-120°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.78 (d, *J* = 16.0 Hz, 1H), 8.20-8.18 (m, 1H), 7.99-7.98 (m, 1H), 7.74 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.58-7.52 (m, 2H), 7.51-7.47 (m, 2H), 6.47 (d, *J* = 16.0 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.2, 163.1, 149.6, 143.8, 143.7, 135.3, 131.7, 130.4, 130.0, 128.7, 128.2, 126.0, 123.7, 121.1, 117.5, 112.00, 52.0. HRMS (ESI): calcd. for $C_{17}H_{13}BrNO_3$ $[M+H]^+$ 358.0079, Found: 358.0072.

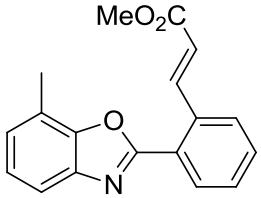


(**3g**): 108 mg, 69% yield, white solid: m.p. 122-124°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.79 (d, *J* = 16.0 Hz, 1H), 8.20-8.18 (m, 1H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.74 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.58-7.51 (m, 3H), 7.36 (dd, *J* = 9.0, 2.0 Hz, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$):

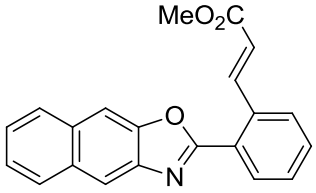
δ (ppm) = 167.2, 163.3, 149.2, 143.7, 143.3, 135.3, 131.7, 130.4, 130.3, 130.0, 128.2, 126.0, 126.0, 121.2, 120.7, 111.5, 52.0. HRMS (ESI): calcd. for $C_{17}H_{13}ClNO_3$ $[M+H]^+$ 314.0584, Found: 314.0573.



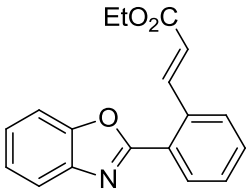
(**3h**): 136 mg, 85% yield, white solid: m.p. 138-140°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.77 (d, *J* = 16.0 Hz, 1H), 8.27-8.26 (m, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.98 (dd, *J* = 7.5, 0.5 Hz, 1H), 7.75-7.73 (m, 1H), 7.59-7.54 (m, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 6.48 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H), 2.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 194.7, 167.0, 162.5, 149.3, 143.5, 143.3, 135.1, 131.8, 130.6, 130.1, 128.3, 126.1, 125.7, 125.7, 124.8, 121.9, 121.3, 51.92, 30.54. HRMS (ESI): calcd. for $C_{19}H_{16}NO_4$ $[M+H]^+$ 322.1079, Found: 322.1007.



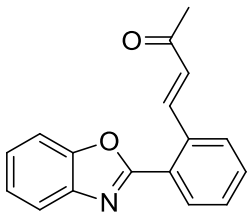
(**3i**): 76 mg, 52% yield, white solid: m.p. 95-96°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.83 (d, *J* = 16.0 Hz, 1H), 8.27-8.25 (m, 1H), 7.74-7.72 (m, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.55-7.53 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 7.0 Hz, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.3, 161.8, 150.0, 144.0, 141.6, 135.0, 131.3, 130.4, 129.9, 128.1, 126.7, 126.6, 124.8, 121.4, 120.9, 118.0, 51.9, 15.3. HRMS (ESI): calcd. for $C_{18}H_{16}NO_3$ $[M+H]^+$ 294.1130, Found: 294.1121.



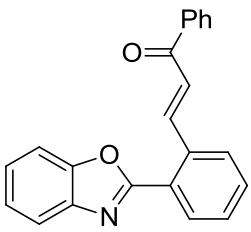
(**3j**): 118 mg, 72% yield, white solid: m.p. 171-172°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.93 (d, *J* = 16.0 Hz, 1H), 8.29-8.27 (m, 1H), 8.00 (d, *J* = 7.5 Hz, 1H), 7.94 (d, *J* = 7.5 Hz, 1H), 7.75-7.73 (m, 1H), 7.57-7.52 (m, 2H), 7.51-7.46 (m, 2H), 6.49 (d, *J* = 16.0 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.3, 163.8, 149.3, 143.9, 142.0, 135.6, 132.0, 131.7, 131.6, 130.6, 129.9, 128.7, 128.2, 128.0, 126.2, 125.7, 124.8, 121.0, 118.2, 106.5, 51.9. HRMS (ESI): calcd. for $C_{21}H_{16}NO_3$ $[M+H]^+$ 330.1130, Found: 330.1127 .



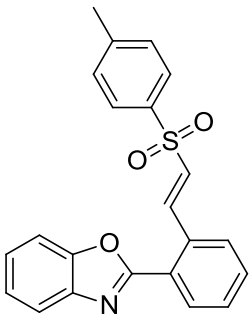
(**3k**): 98 mg, 67% yield, yellow viscous liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.84 (d, *J* = 16.0 Hz, 1H), 8.23-8.20 (m, 1H), 7.86-7.83 (m, 1H), 7.77-7.74 (m, 1H), 7.63-7.60 (m, 1H), 7.57-7.52 (m, 2H), 7.41-7.36 (m, 2H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.30 (q, *J* = 7.0 Hz, 2H), 1.36 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 166.9, 162.0, 150.7, 143.6, 142.2, 135.2, 131.3, 130.4, 129.9, 128.1, 126.6, 125.6, 124.8, 121.4, 120.8, 110.8, 60.7, 14.5. HRMS (ESI): calcd. for $C_{18}H_{16}NO_3$ $[M+H]^+$ 294.1130, Found: 294.1123.



(3l): 95 mg, 72% yield, white solid: m.p. 103-105^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.83 (d, *J* = 16.0 Hz, 1H), 8.25-8.22 (m, 1H), 7.83-7.80 (m, 1H), 7.77-7.73 (m, 1H), 7.63-7.59 (m, 1H), 7.56-7.53 (m, 2H), 7.42-7.37 (m, 2H), 6.67 (d, *J* = 16.0 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 199.3, 161.9, 150.5, 143.2, 142.2, 135.2, 131.4, 130.4, 130.3, 130.1, 128.0, 126.4, 125.8, 124.9, 120.6, 110.7, 27.0. HRMS (ESI): calcd. for $C_{17}H_{14}NO_2$ $[M+H]^+$ 264.1025, Found: 264.1018.

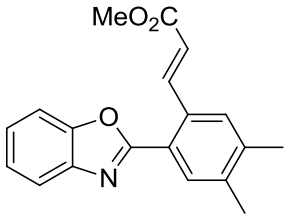


(3m): 102 mg, 63% yield, yellow solid: m.p. 86-87^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.85 (d, *J* = 15.5 Hz, 1H), 8.26-8.24 (m, 1H), 8.12-8.09 (m, 2H), 7.87-7.83 (m, 2H), 7.62-7.57 (m, 4H), 7.54-7.51 (m, 2H), 7.42-7.38 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 191.9, 162.0, 150.7, 144.4, 142.3, 138.2, 135.8, 132.8, 131.4, 130.4, 130.1, 129.1, 128.7, 128.2, 126.9, 126.1, 125.7, 124.8, 120.7, 110.8. HRMS (ESI): calcd. for $C_{22}H_{16}NO_2$ $[M+H]^+$ 326.1181, Found: 326.1175.

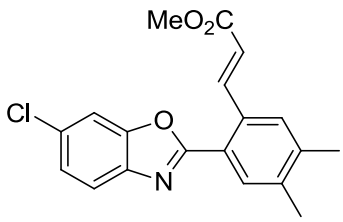


(3n): 154 mg, 82% yield, white solid: m.p. 134-135^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.11 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.82 (d, *J* = 11.5 Hz, 1H), 7.71-7.68 (m, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.55-7.47 (m, 3H), 7.39-7.33 (m, 4H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 11.5 Hz, 1H), ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 161.5, 150.2, 144.0, 142.6, 142.0, 137.7, 133.1, 132.1, 131.9, 130.6, 139.3, 129.1, 128.7,

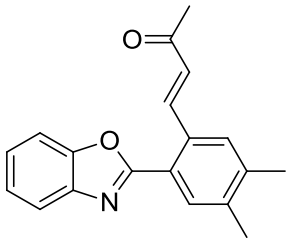
127.6, 125.5, 124.7, 124.5, 120.4, 110.5. HRMS (ESI): calcd. for $C_{22}H_{18}NO_3S$ $[M+H]^+$ 376.1007, Found: 376.1010.



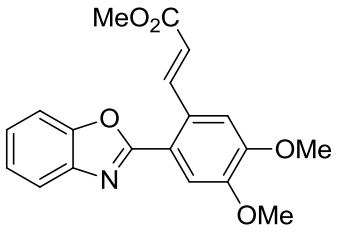
(**4a**): 114 mg, 74% yield, white solid: m.p. 176-178°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.80 (d, *J* = 16.0 Hz, 1H), 7.96 (s, 1H), 7.84-7.80 (m, 1H), 7.60-7.57 (m, 1H), 7.49 (s, 1H), 7.37-7.34 (m, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 2.35 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.5, 162.3, 150.5, 143.8, 142.2, 140.5, 139.2, 132.4, 131.3, 129.0, 125.3, 124.6, 124.0, 120.5, 119.7, 110.6, 51.8, 20.0, 19.7. HRMS (ESI): calcd. for $C_{19}H_{18}NO_3$ $[M+H]^+$ 308.1287, Found:308.1285.



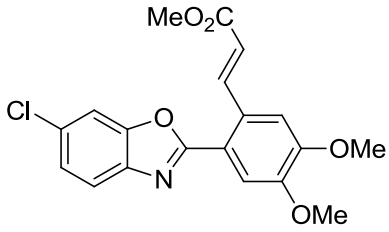
(**4b**): 119 mg, 70% yield, white solid: m.p. 157-159°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.76 (d, *J* = 16.0 Hz, 1H), 7.90 (s, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.56 (d, *J* = 1.5 Hz, 1H), 7.47 (s, 1H), 7.32 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H), 2.33 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.4, 162.9, 150.6, 143.6, 141.0, 140.9, 139.2, 132.5, 131.2, 130.9, 129.1, 125.3, 123.4, 120.9, 119.9, 111.2, 51.8, 20.0, 19.7. HRMS (ESI): calcd. for $C_{19}H_{17}ClNO_3$ $[M+H]^+$ 342.0897, Found: 342.0891.



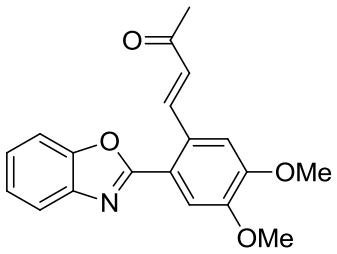
(**4c**): 82 mg, 56 % yield, white solid: m.p. 102-104°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.79 (d, *J* = 16.0 Hz, 1H), 7.97 (s, 1H), 7.80-7.76 (m, 1H), 7.59-7.55 (m, 1H), 7.49 (s, 1H), 7.38-7.34 (m, 2H), 6.63 (d, *J* = 16.0 Hz, 1H), 2.47 (s, 3H), 2.35 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 199.4, 162.2, 150.3, 143.2, 142.1, 140.7, 139.4, 132.5, 131.2, 129.4, 129.0, 125.4, 124.7, 123.9, 120.3, 110.6, 26.8, 20.0, 19.8. HRMS (ESI): calcd. for $C_{19}H_{18}NO_2$ $[M+H]^+$ 292.1338, Found: 292.1334.



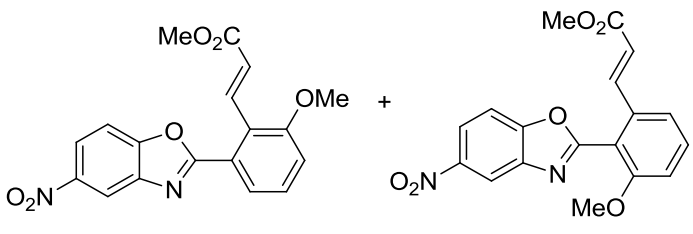
(**4d**): 122 mg, 72% yield, white solid: m.p. 155-156^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.85 (d, *J* = 16.0 Hz, 1H), 7.84-7.81 (m, 1H), 7.68 (s, 1H), 7.62-7.58 (m, 1H), 7.39-7.35 (m, 2H), 7.18 (s, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.03 (s, 3H), 3.99 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.4, 161.9, 151.2, 150.5, 150.4, 143.4, 142.1, 128.4, 125.3, 124.7, 120.4, 119.8, 119.1, 112.2, 110.6, 109.6, 56.3, 56.1, 51.8. HRMS (ESI): calcd. for $C_{19}H_{18}NO_5$ $[M+H]^+$ 340.1185, Found: 340.1179 .



(**4e**): 132 mg, 71% yield, white solid: m.p. 200-201^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.82 (d, *J* = 16.0 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.63 (s, 1H), 7.60 (d, *J* = 2.0 Hz, 1H), 7.34 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.17 (s, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 4.02 (s, 3H), 3.99 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.4, 162.6, 151.6, 150.7, 150.5, 143.4, 141.0, 130.9, 128.7, 125.5, 120.9, 119.4, 119.3, 112.2, 111.3, 109.8, 56.4, 56.2, 52.0. HRMS (ESI): calcd. for $C_{19}H_{17}ClNO_5$ $[M+H]^+$ 374.0795, Found: 374.0795.

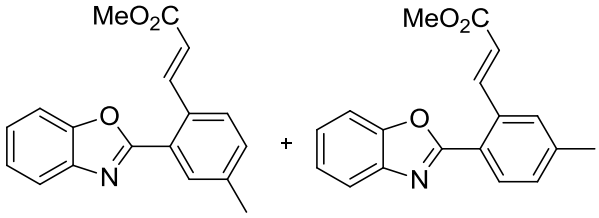


(**4f**): 118 mg, 73% yield, white solid: m.p. 134-136^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.87 (d, *J* = 16.0 Hz, 1H), 7.81-7.78 (m, 1H), 7.70 (s, 1H), 7.62-7.58 (m, 1H), 7.40-7.36 (m, 2H), 7.20 (s, 1H), 6.62 (d, *J* = 16.0 Hz, 1H), 4.04 (s, 3H), 3.99 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 199.4, 161.9, 151.4, 150.6, 150.3, 143.0, 142.1, 129.0, 128.6, 125.5, 124.8, 120.3, 119.7, 112.7, 110.6, 109.5, 56.4, 56.2, 26.7. HRMS (ESI): calcd. for $C_{19}H_{18}NO_4$ $[M+H]^+$ 324.1236, Found: 324.1228.

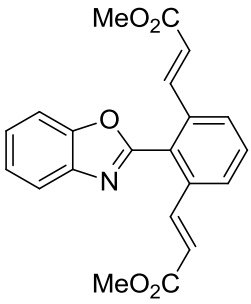


(**4g+4g'**): 135 mg, 76% yield, white solid: m.p. 153-155^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.70 (d, *J* = 2.0 Hz, 1H), 8.39 (d, *J* = 16.0 Hz, 1H), 8.33 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.72 (dd, *J* =

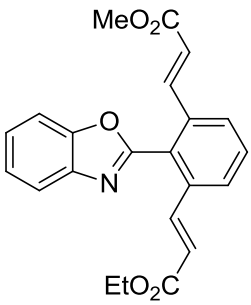
8.0, 2.0 Hz, 1H), 7.68 (d, *J* = 9.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 1H), 6.75 (d, *J* = 16.0 Hz, 1H), 3.96 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 168.1, 165.3, 159.3, 154.1, 145.5, 142.4, 138.5, 130.4, 127.5, 124.5, 123.9, 123.1, 121.6, 117.0, 114.7, 111.0, 56.1, 51.9. HRMS (ESI): calcd. for $C_{18}H_{15}N_2O_6$ $[M+H]^+$ 355.0930, Found: 355.0921.



(**4h+4h'**): 94 mg, 64% yield, white solid: m.p. 130-132°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.81 (t, *J* = 16.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 0.26H), 8.03 (s, 0.79 H), 7.85-7.84 (m, 1H), 7.65 (d, *J* = 8.0 Hz, 0.88H), 7.62-7.59 (m, 1H), 7.54 (s, 0.25H), 7.39-7.34 (m, 3H), 6.49-6.44 (m, 1H), 3.84 (s, 0.91H), 3.83 (s, 2H), 2.47 (s, 2H), 2.46 (s, 0.89 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.5, 167.4, 162.2, 150.7, 150.6, 144.0, 143.7, 142.3, 142.2, 141.8, 140.4, 134.9, 132.26, 132.25, 130.9, 130.9, 130.4, 128.7, 128.0, 126.5, 125.6, 125.4, 124.8, 124.7, 123.9, 120.7, 120.7, 120.6, 120.0, 110.8, 110.7, 51.9, 21.4. HRMS (ESI): calcd. for $C_{18}H_{16}NO_3$ $[M+H]^+$ 294.1130, Found: 294.1125 .

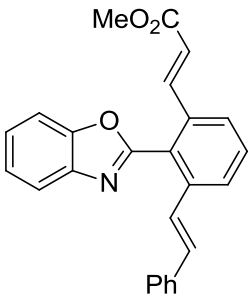


(**6a**): 44 mg, 61% yield, white solid: m.p. 126-128°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.90-7.88 (m, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 16.0 Hz, 2H), 7.65-7.62 (m, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.46-7.42 (m, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 3.73 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 166.7, 159.8, 151.2, 141.9, 141.5, 136.5, 131.2, 128.4, 128.1, 126.1, 125.1, 121.7, 121.0, 111.1, 52.0. HRMS (ESI): calcd. For $C_{21}H_{18}NO_5$ $[M+H]^+$ 364.1185, Found: 364.1180.

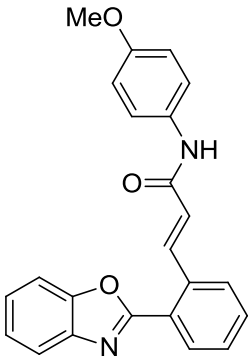


(**6b**): 49 mg, 65% yield, viscous liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.90-7.87 (m, 1H), 7.78 (dd, *J* = 7.5, 2.5 Hz, 1H), 7.73 (d, *J* = 16.0, 8.0 Hz, 1H), 7.64-7.62 (m, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.46-7.42 (m, 2H), 6.42 (dd, *J* = 15.5, 3.5 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 3.73 (s, 1H), 1.25 (t, *J* = 7.5 Hz, 3H). ^{13}C

NMR (125 MHz, $CDCl_3$): δ (ppm) = 166.7, 166.3, 159.8, 151.1, 141.9, 141.6, 141.5, 136.6, 136.4, 131.2, 128.4, 128.1, 126.1, 125.1, 122.1, 121.7, 121.0, 111.1, 60.8, 52.0, 14.3. HRMS (ESI): calcd. For $C_{22}H_{20}NO_5$ $[M+H]^+$ 378.1341, Found: 378.1335.



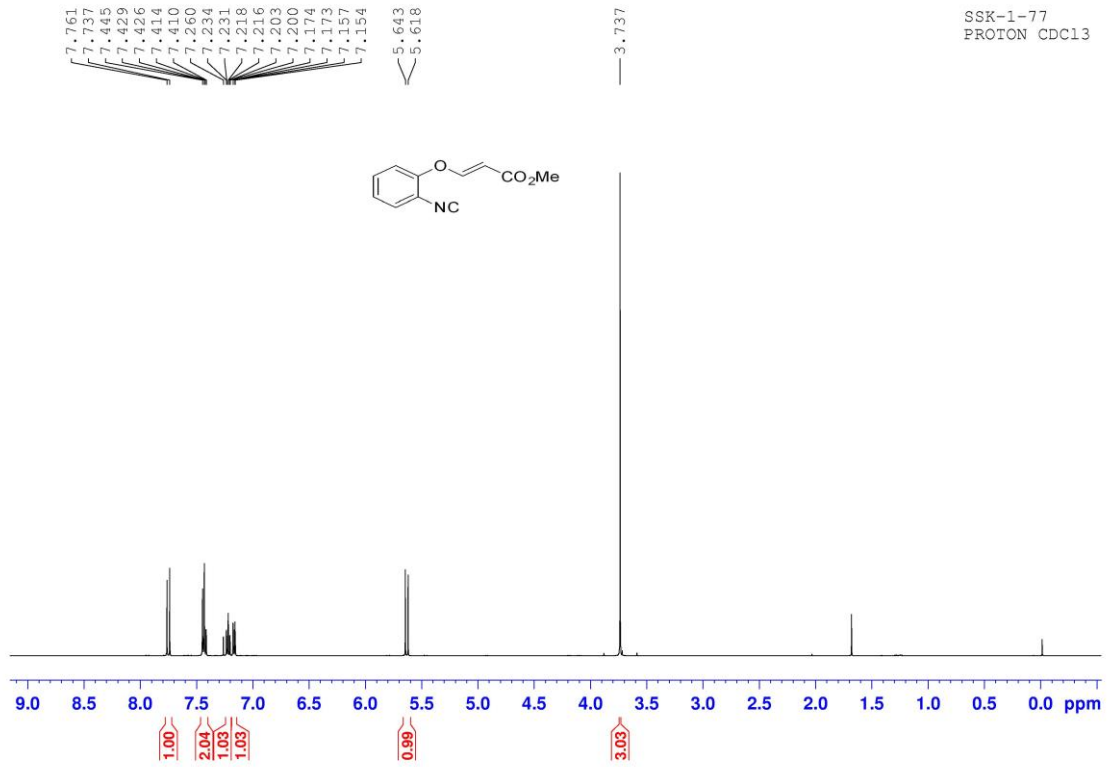
(**6c**): 34 mg, 45% yield, viscous liquid. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.92-7.89 (m, 1H), 7.86 (d, *J* = 7.0 Hz, 1H), 7.71-7.67 (m, 2H), 7.50-7.62 (m, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.46-7.43 (m, 2H), 7.36-7.34 (m, 2H), 7.28 (t, *J* = 7.0 Hz, 1H), 7.23 (tt, *J* = 6.5, 1.5 Hz, 1H), 7.10 (d, *J* = 1.5 Hz, 1H), 6.42 (d, *J* = 15.5 Hz, 1H), 3.73 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 166.9, 160.9, 151.1, 142.3, 141.6, 139.4, 136.9, 136.1, 132.6, 131.1, 128.8, 128.3, 127.5, 127.0, 126.9, 126.0, 125.8, 125.6, 124.9, 121.1, 120.9, 111.1, 51.9. HRMS (ESI): calcd. For $C_{25}H_{20}NO_3$ $[M+H]^+$ 382.1443, Found: 382.1437.

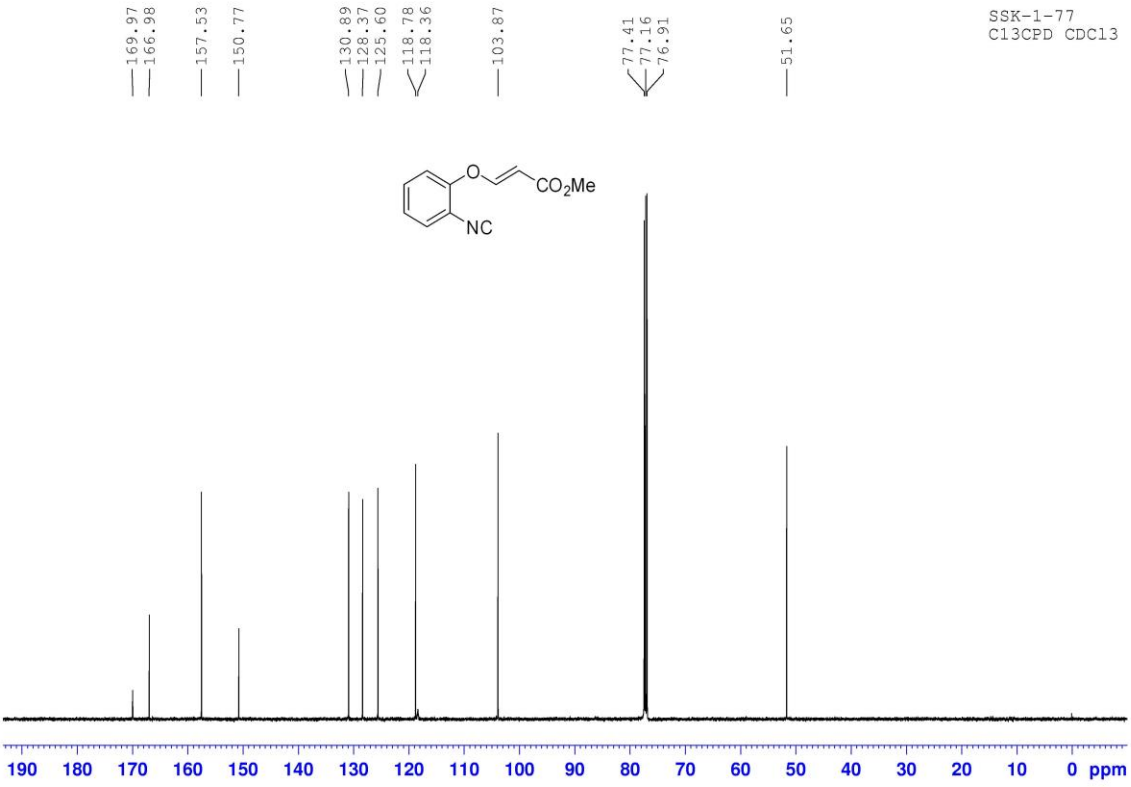


(**8**): 56 mg, 76% yield, white solid: m.p. 257-258°C. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) = 10.2 (s, 1H), 8.57 (d, *J* = 15.5 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.90-7.88 (m, 2H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.71 (t, *J* = 7.0 Hz, 1H), 7.66-7.63 (m, 3H), 7.50-7.44 (m, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 15.5 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 162.9, 161.5, 155.4, 149.9, 141.5, 138.0, 135.1, 132.4, 131.8, 130.3, 129.7, 127.6, 125.9, 125.53, 125.47, 125.0, 120.7, 120.1, 114.0, 111.0, 55.2. HRMS (ESI): calcd. For $C_{23}H_{19}N_2O_3$ $[M+H]^+$ 371.1396, Found: 371.1399.

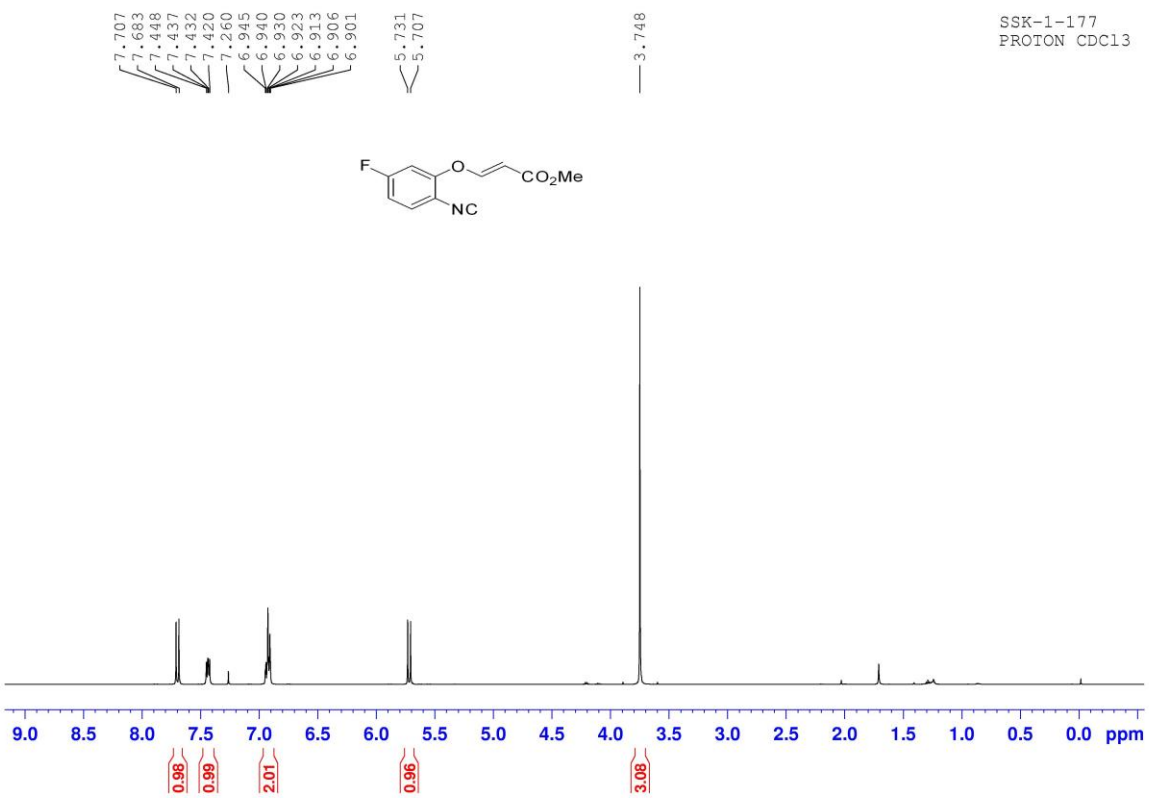
5 ^{1}H NMR and ^{13}C NMR Spectra of All Compounds

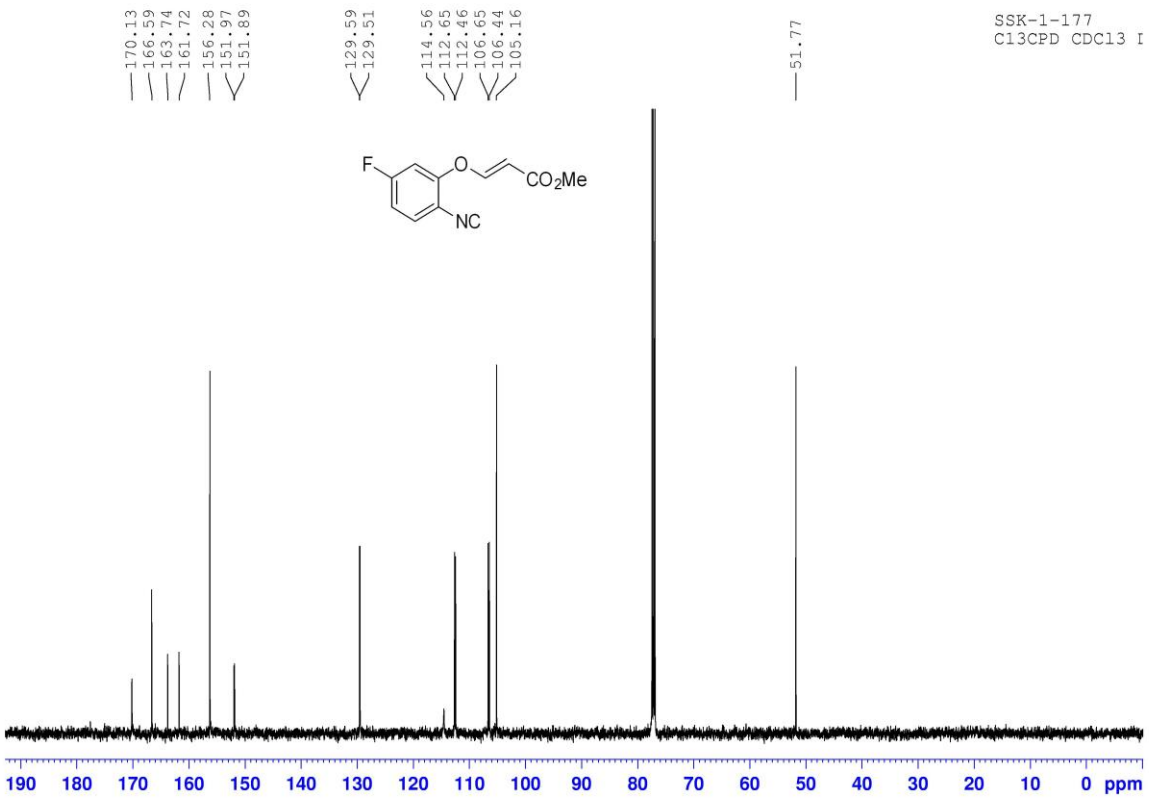
Compound **1a**



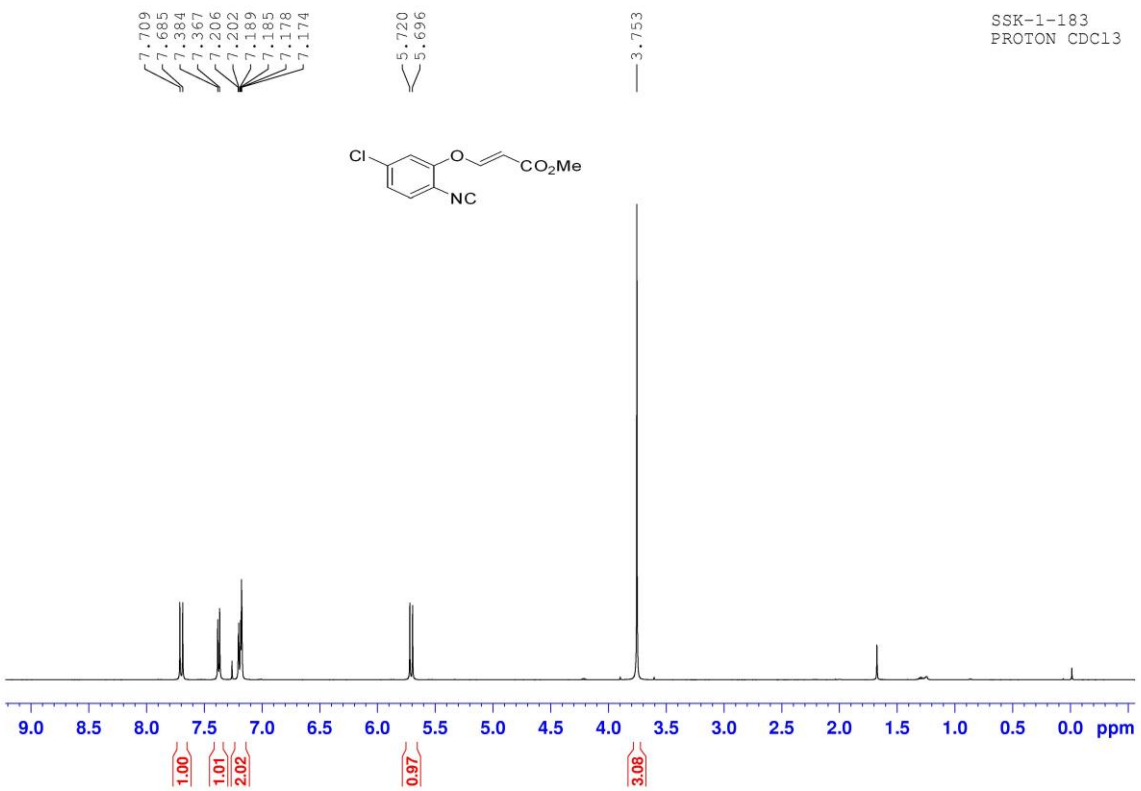


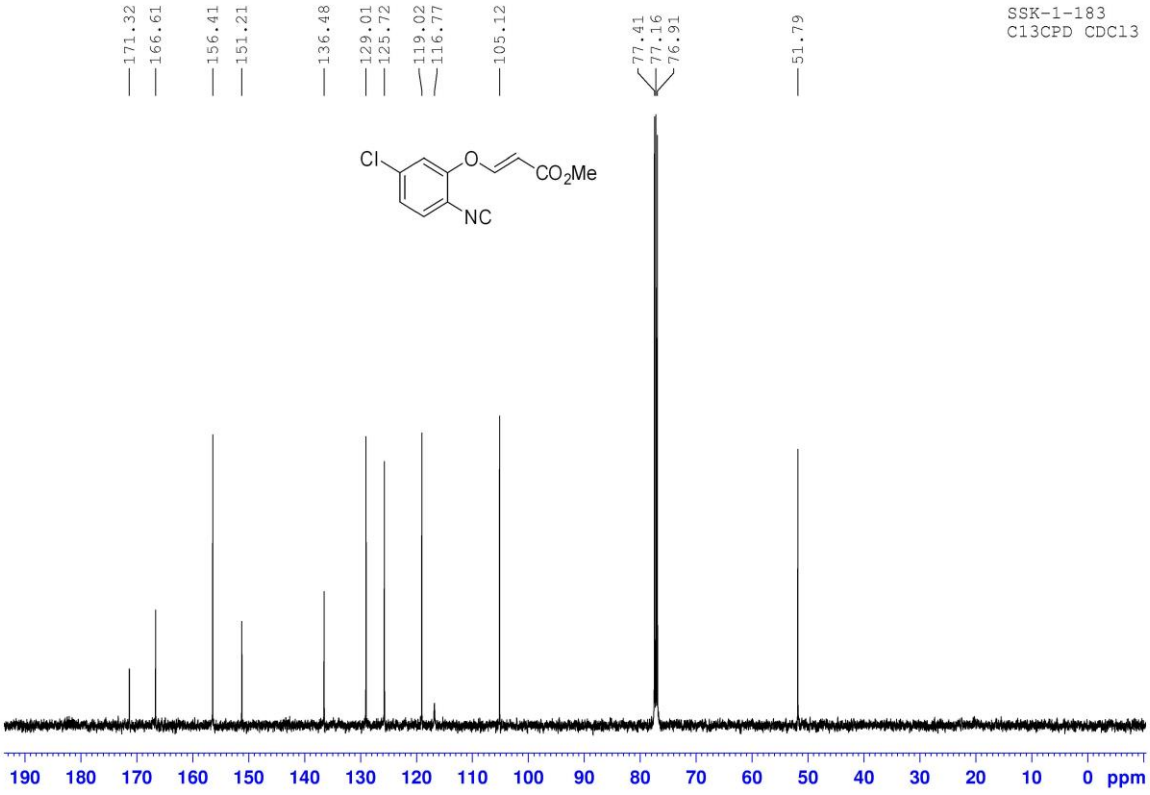
Compound **1b**


7.707
7.683
7.448
7.437
7.432
7.420
7.260
6.945
6.940
6.930
6.923
6.913
6.906
6.901
5.731
5.707
3.748
SSK-1-177
PROTON CDCl3
F
O
CO2Me
NC
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.98
0.99
2.01
0.96
3.08

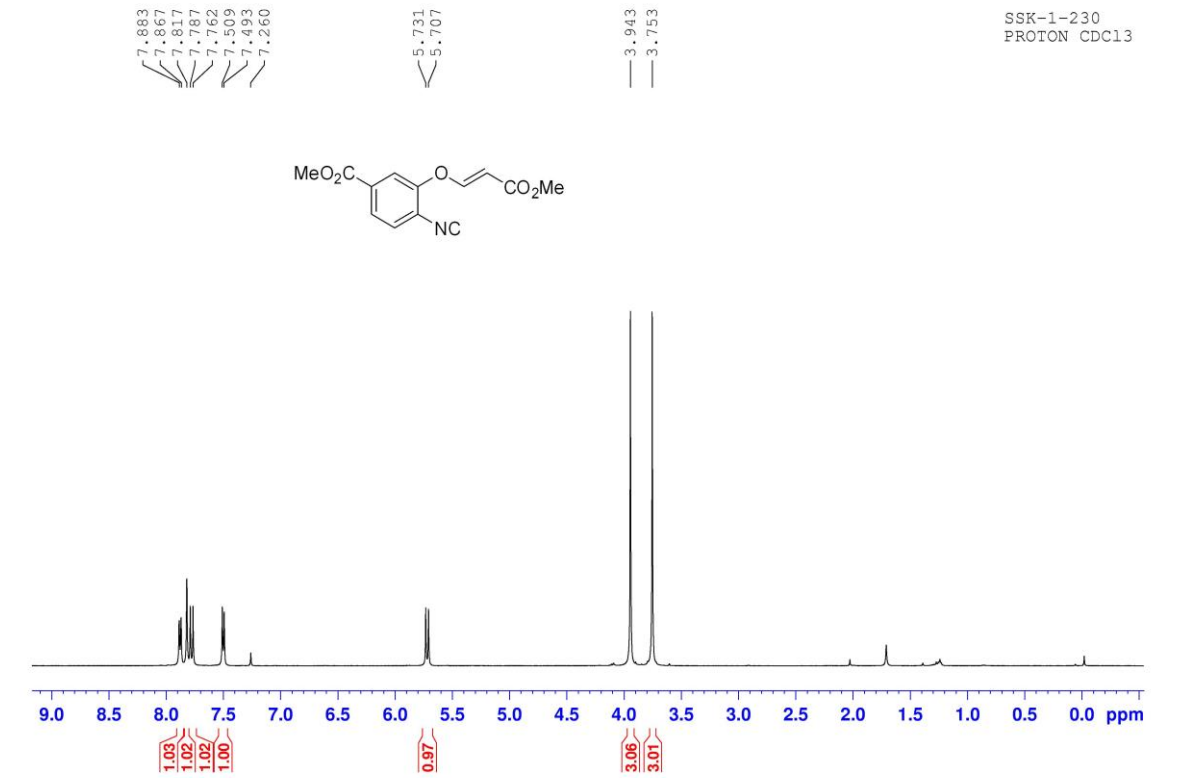

170.13
166.59
163.74
161.72
156.28
151.97
151.89
129.59
129.51
114.56
112.65
112.46
106.65
106.44
105.16
51.77
SSK-1-177
C13CPD CDCl3 I
F
O
CO2Me
NC
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

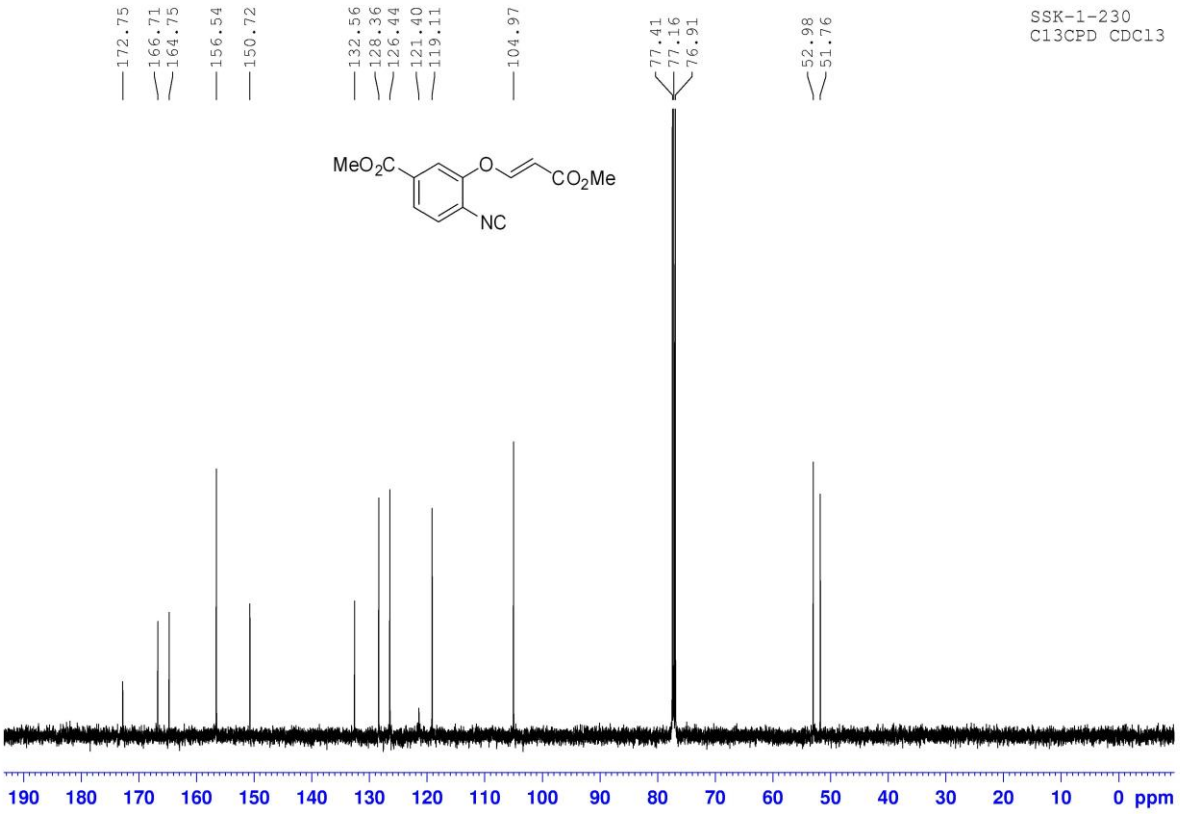
Compound **1c**


7.709
7.685
7.384
7.367
7.206
7.202
7.189
7.185
7.178
7.174
5.720
5.696
3.753
SSK-1-183
PROTON CDC13
Cl
O
CO2Me
NC
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.01
2.02
0.97
3.08

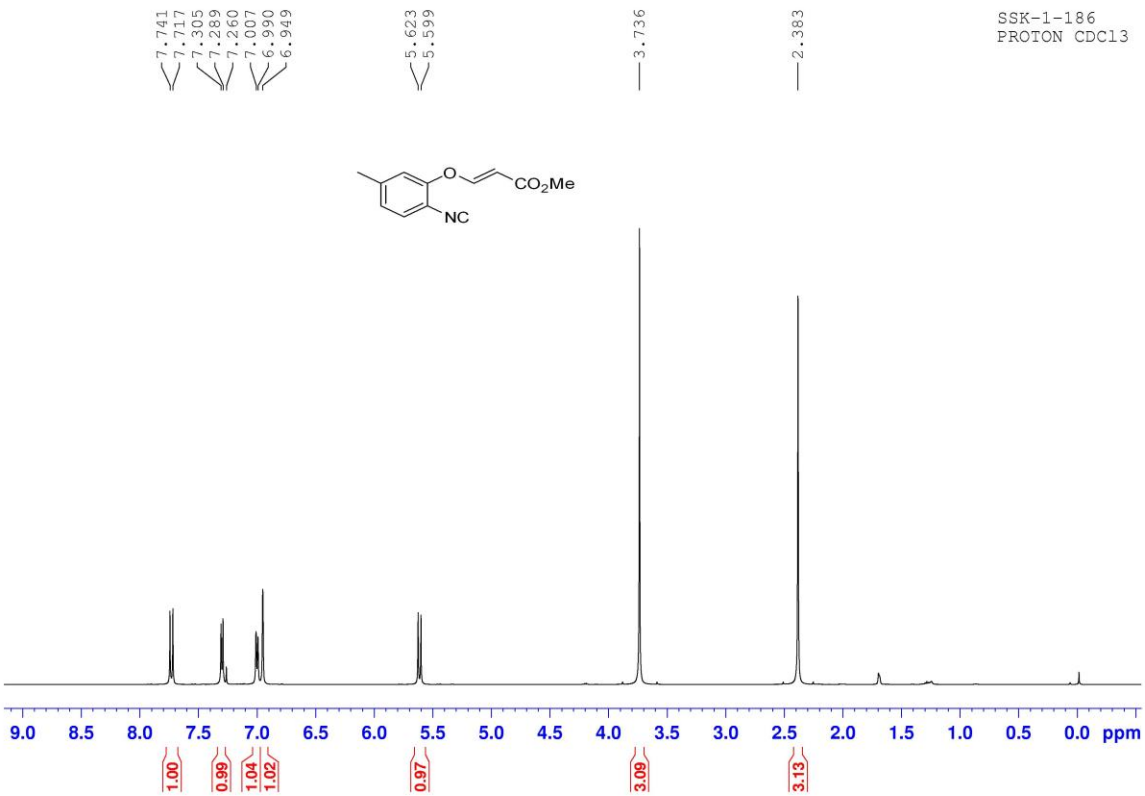

171.32
166.61
156.41
151.21
136.48
129.01
125.72
119.02
116.77
105.12
77.41
77.16
76.91
51.79
SSK-1-183
C13CPD CDC13
Cl
O
CO2Me
NC
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

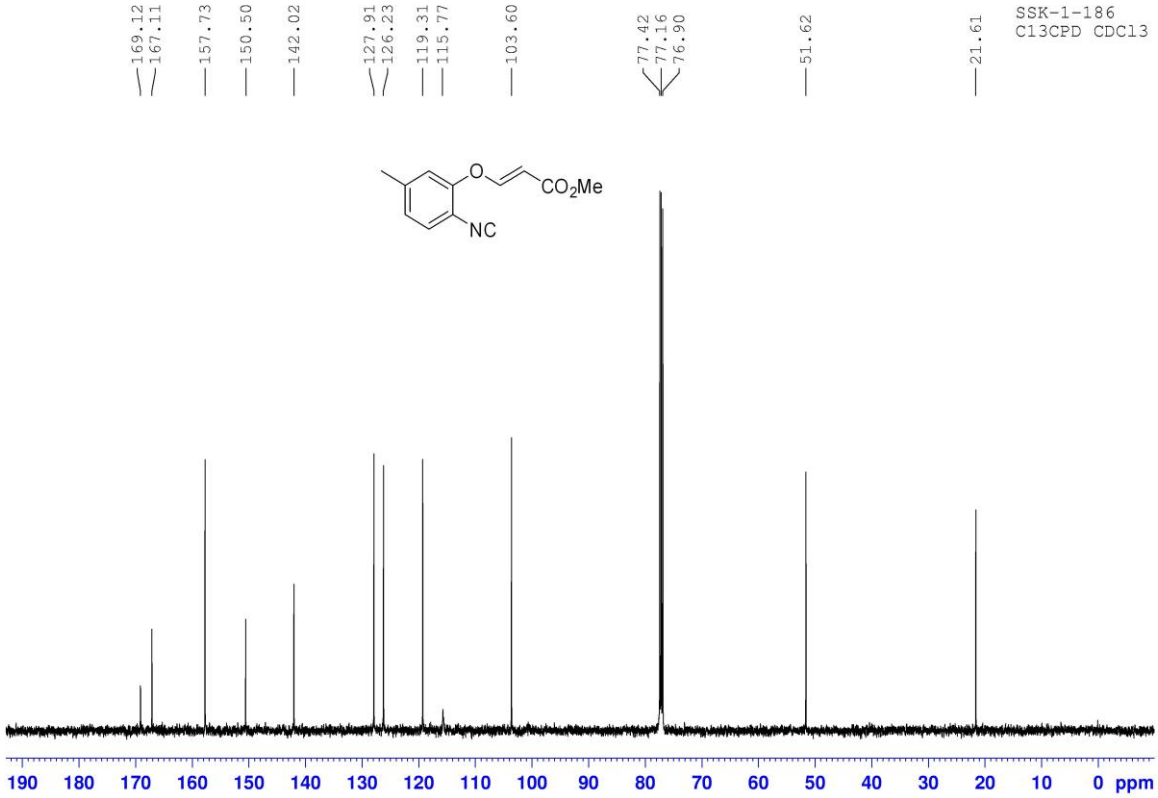
Compound **1d**


7.883
7.867
7.817
7.787
7.762
7.509
7.493
7.260
5.731
5.707
3.943
3.753
SSK-1-230
PROTON CDCl3
MeO2C
O
CO2Me
NC
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.03
1.02
1.02
1.00
0.97
3.06
3.01

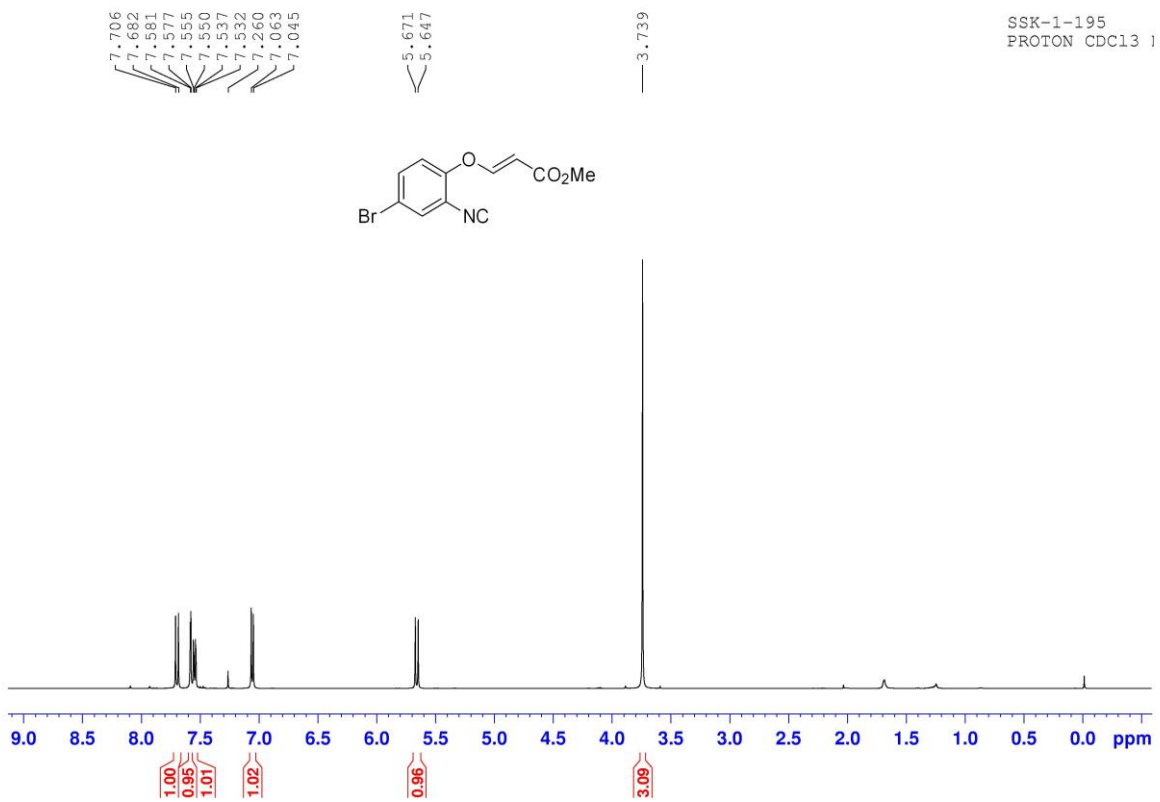

172.75
166.71
164.75
156.54
150.72
132.56
128.36
126.44
121.40
119.11
104.97
77.41
77.16
76.91
52.98
51.76
SSK-1-230
C13CPD CDCl3
MeO2C
O
CO2Me
NC
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

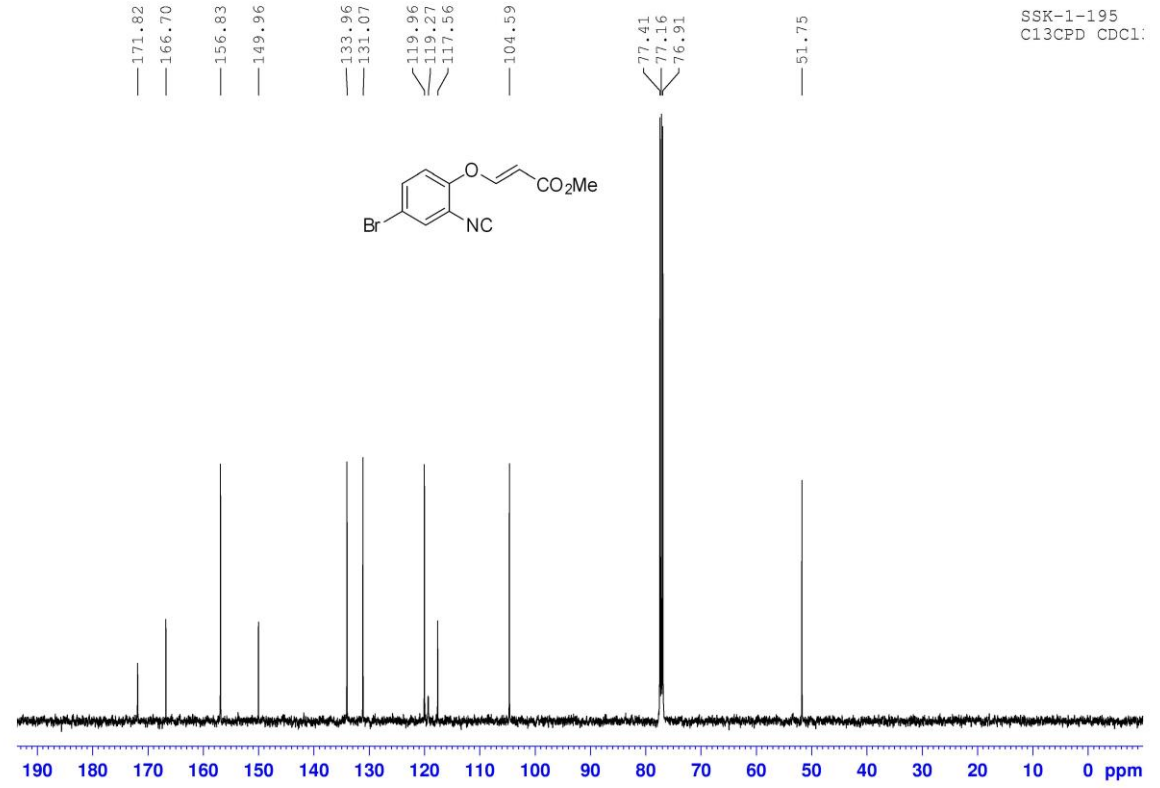
Compound **1e**


7.741
7.717
7.305
7.289
7.260
7.007
6.990
6.949
5.623
5.599
3.736
2.383
SSK-1-186
PROTON CDCl3
O
CO2Me
NC
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
0.99
1.04
1.02
0.97
3.09
3.13

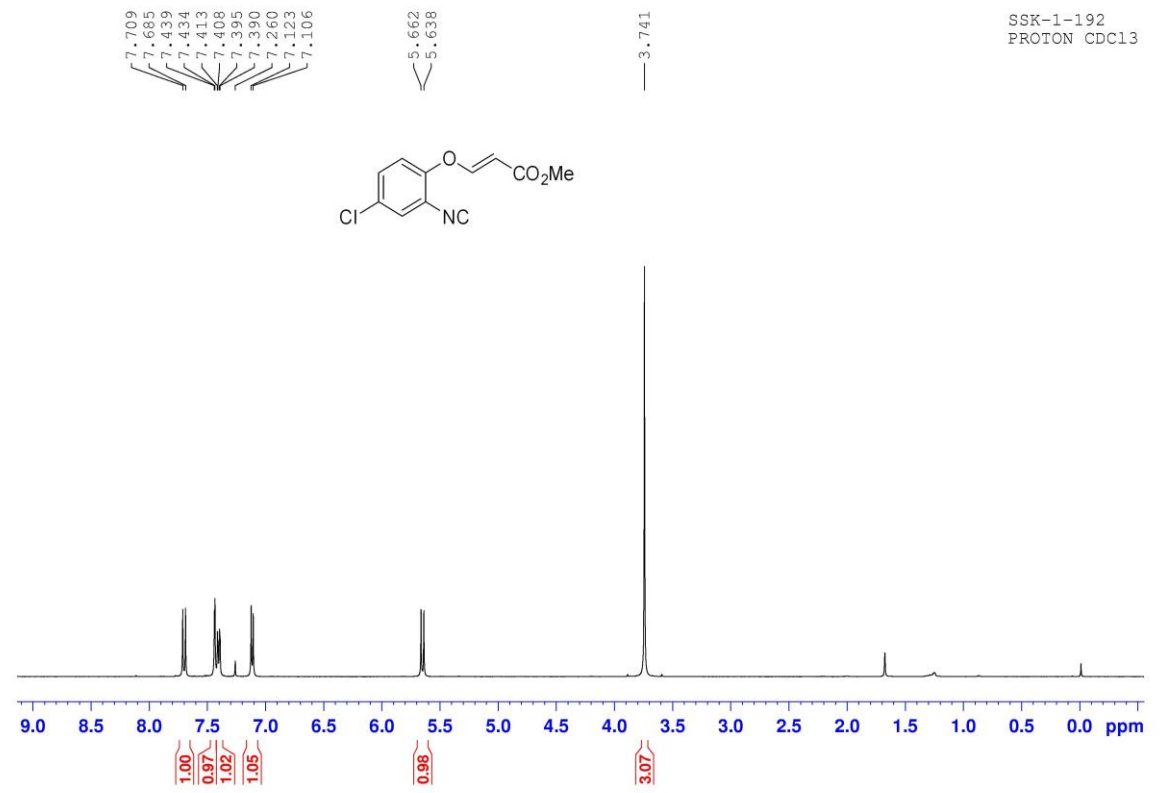

169.12
167.11
157.73
150.50
142.02
127.91
126.23
119.31
115.77
103.60
77.42
77.16
76.90
51.62
21.61
SSK-1-186
C13CPD CDCl3
O
CO2Me
NC
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

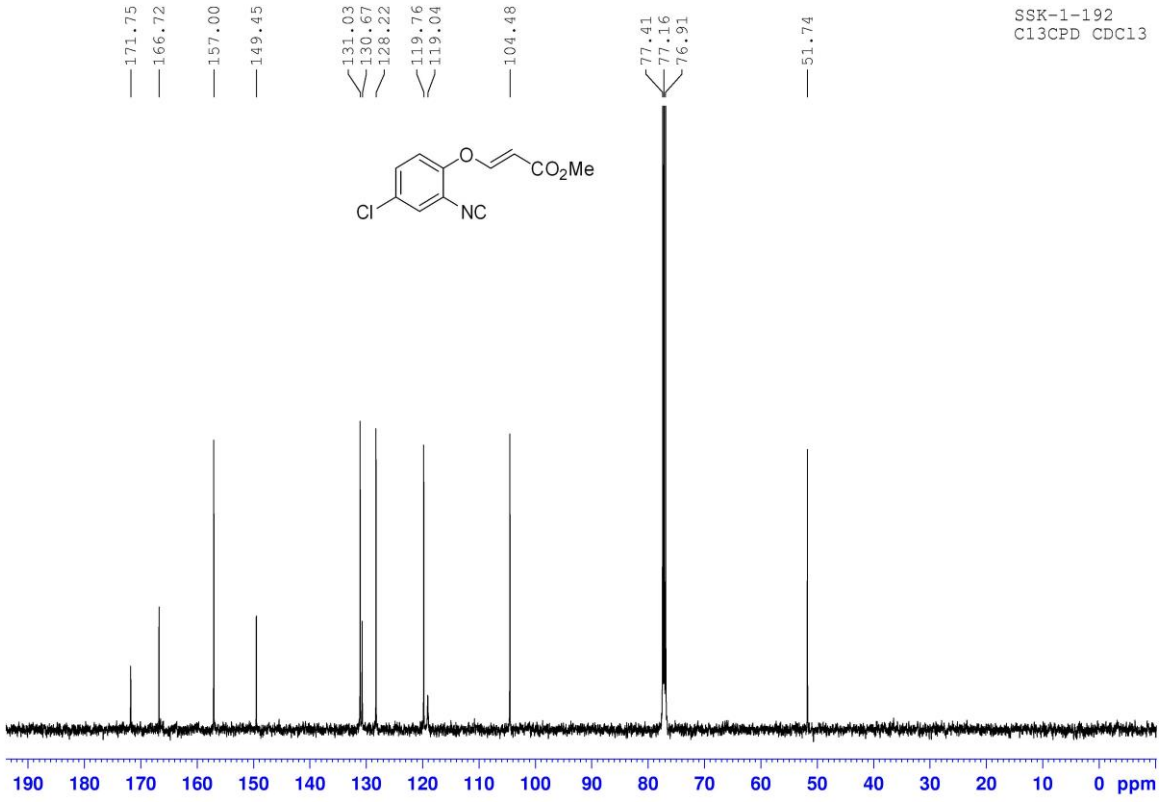
Compound **1f**


7.706
7.682
7.581
7.577
7.555
7.550
7.537
7.532
7.260
7.063
7.045
5.671
5.647
3.739
SSK-1-195
PROTON CDCl3
O
CO2Me
Br
NC
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
0.95
1.01
1.02
0.96
3.09

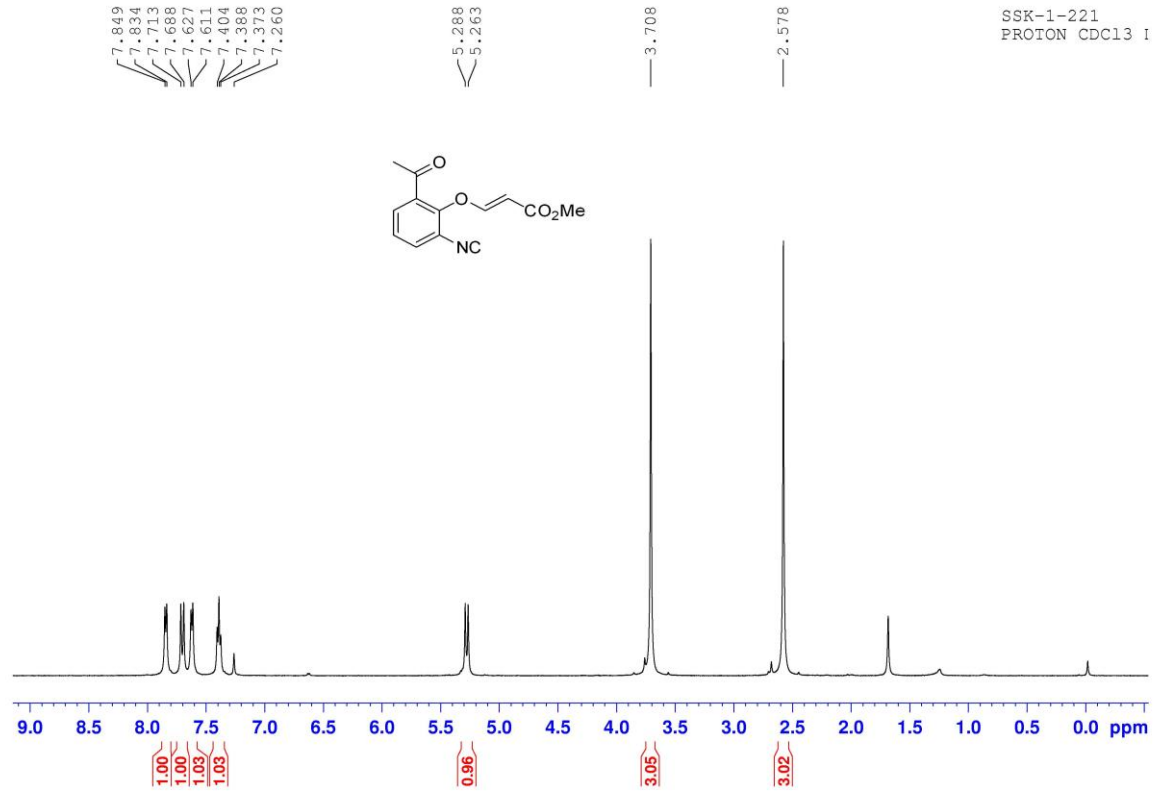

171.82
166.70
156.83
149.96
133.96
131.07
119.96
119.27
117.56
104.59
77.41
77.16
76.91
51.75
SSK-1-195
C13CPD CDCl3
O
CO2Me
Br
NC
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

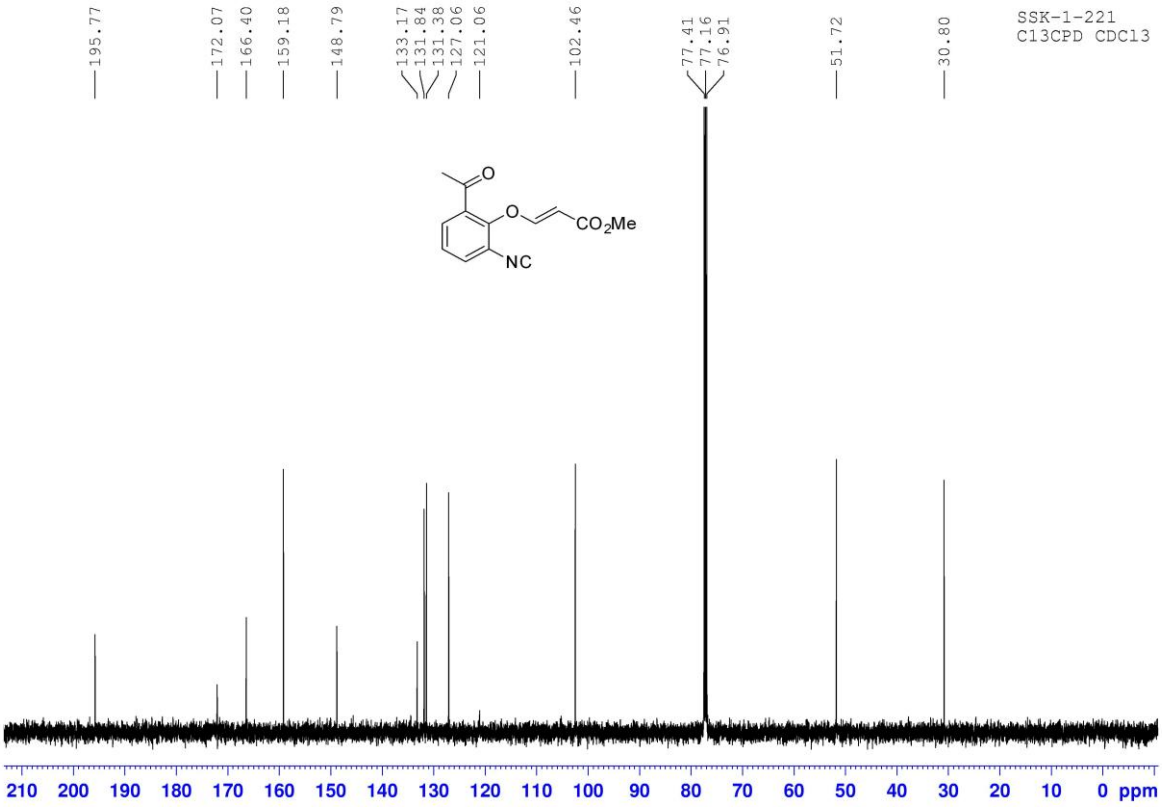
Compound 1**g**


7.709
7.685
7.439
7.434
7.413
7.408
7.395
7.390
7.260
7.123
7.106
5.662
5.638
3.741
SSK-1-192
PROTON CDCl3
O
CO2Me
Cl
NC
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
0.97
1.02
1.05
0.98
3.07

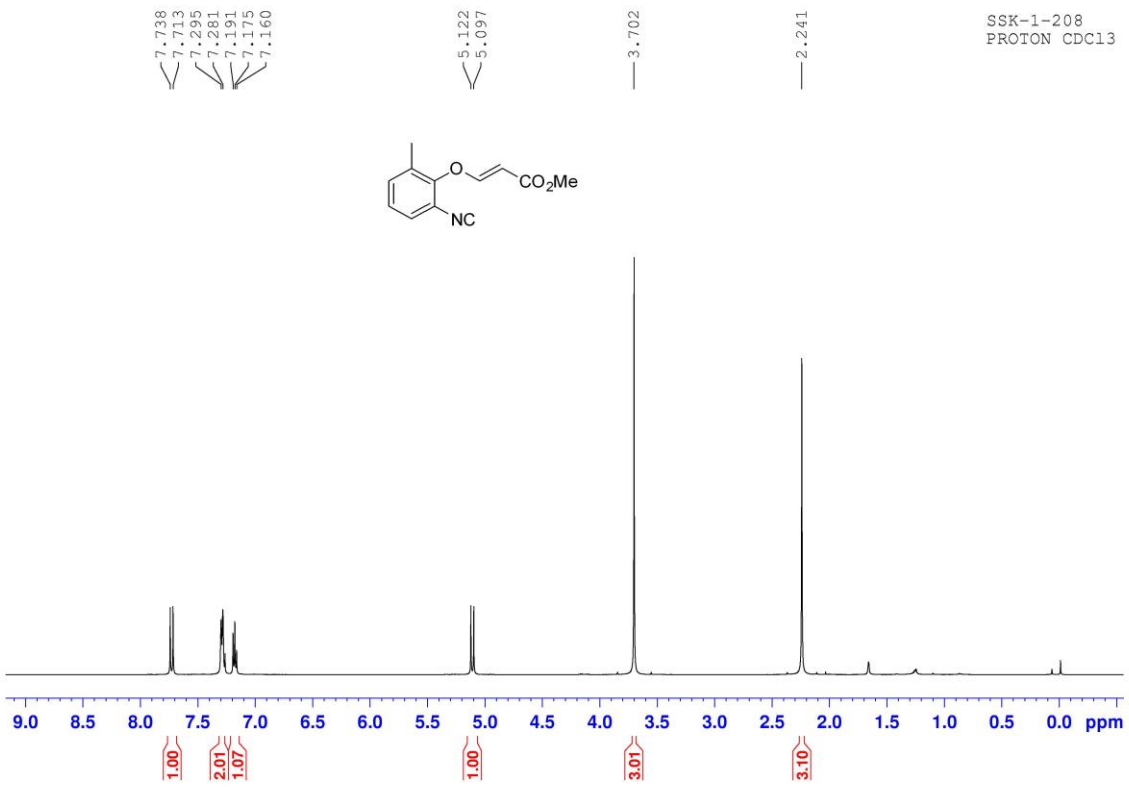

171.75
166.72
157.00
149.45
131.03
130.67
128.22
119.76
119.04
104.48
77.41
77.16
76.91
51.74
SSK-1-192
C13CPD CDCl3
O
CO2Me
Cl
NC
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

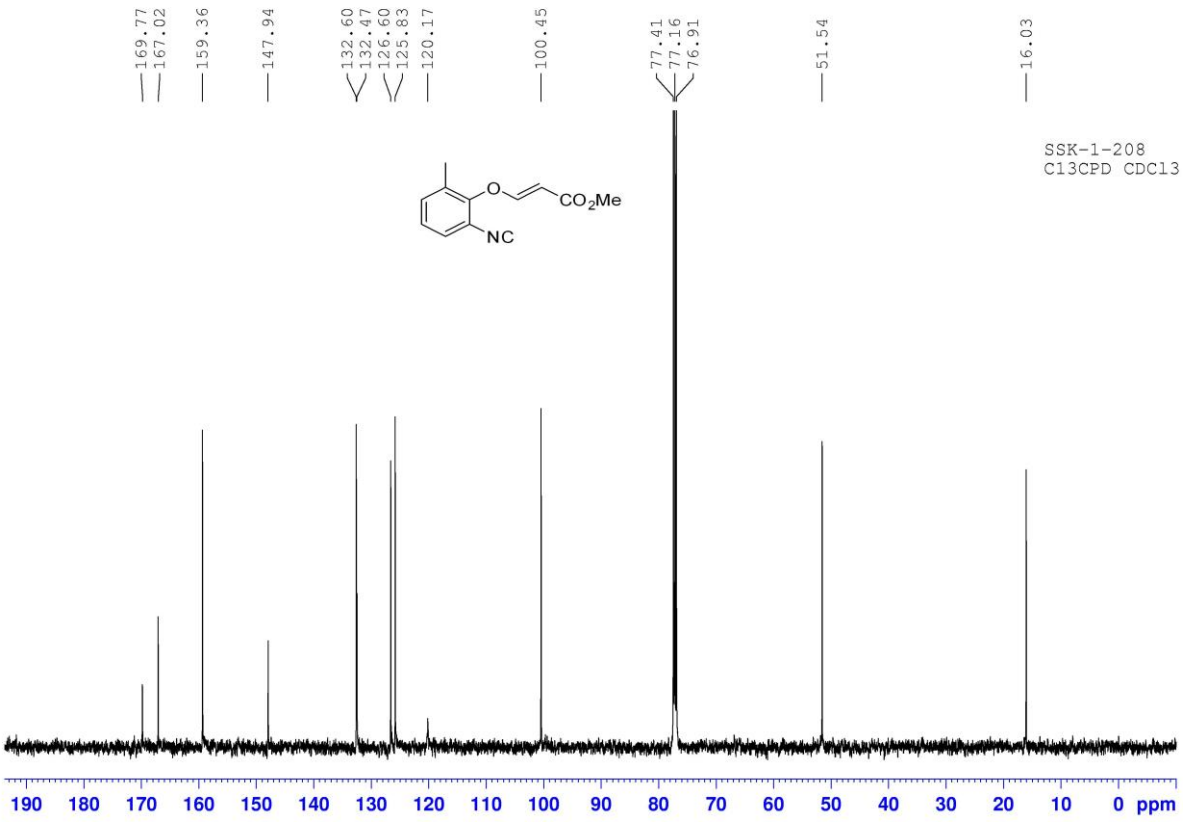
Compound **1h**


7.849
7.834
7.713
7.688
7.627
7.611
7.404
7.388
7.373
7.260
5.288
5.263
3.708
2.578
SSK-1-221
PROTON CDCl3 I
O
O
CO2Me
NC
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.00
1.03
1.03
0.96
3.05
3.02

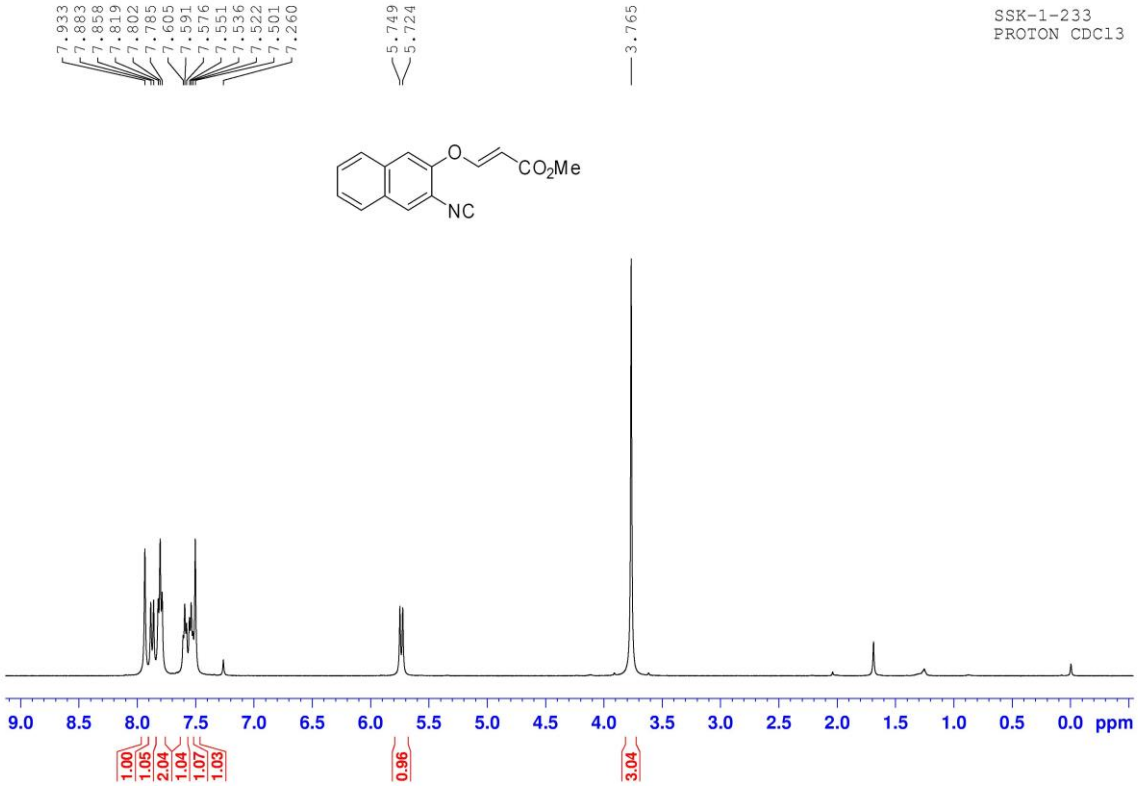

195.77
172.07
166.40
159.18
148.79
133.17
131.84
131.38
127.06
121.06
102.46
77.41
77.16
76.91
51.72
30.80
SSK-1-221
C13CPD CDCl3
O
O
CO2Me
NC
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

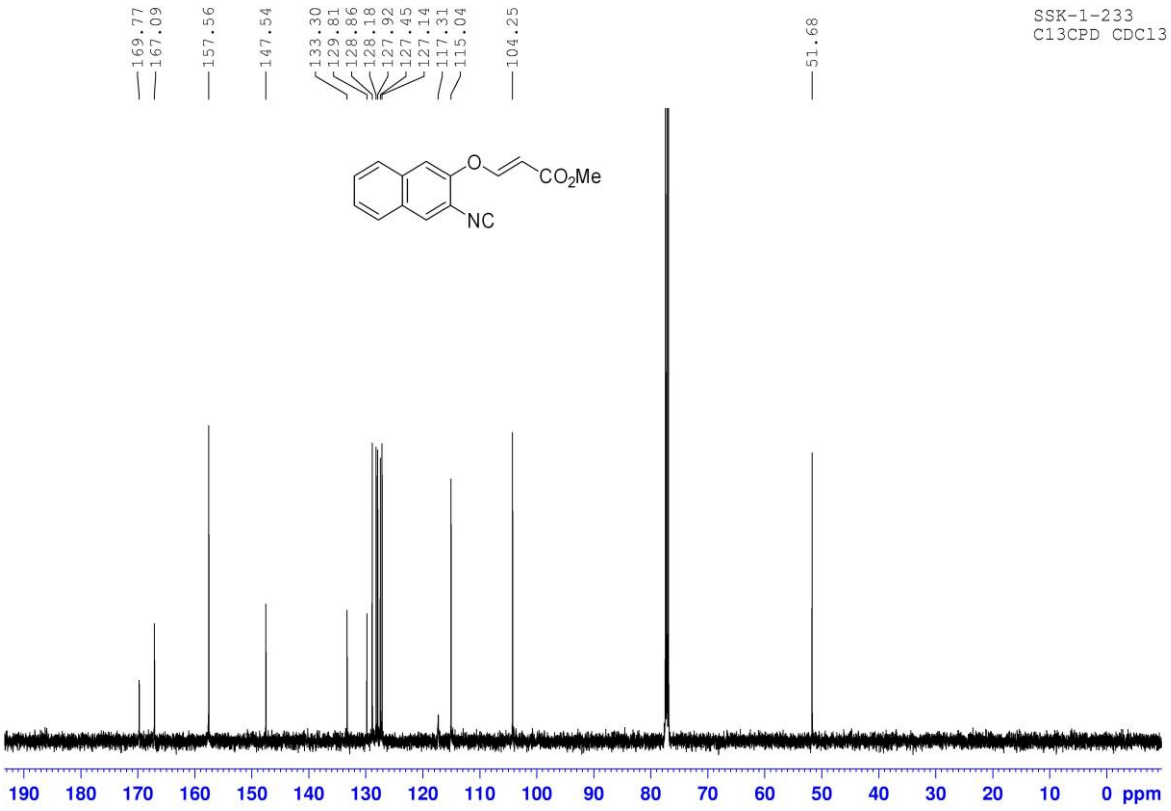
Compound **1i**


7.738
7.713
7.295
7.281
7.191
7.175
7.160
5.122
5.097
3.702
2.241
SSK-1-208
PROTON CDCl3
CO2Me
NC
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
2.01
1.07
1.00
3.01
3.10

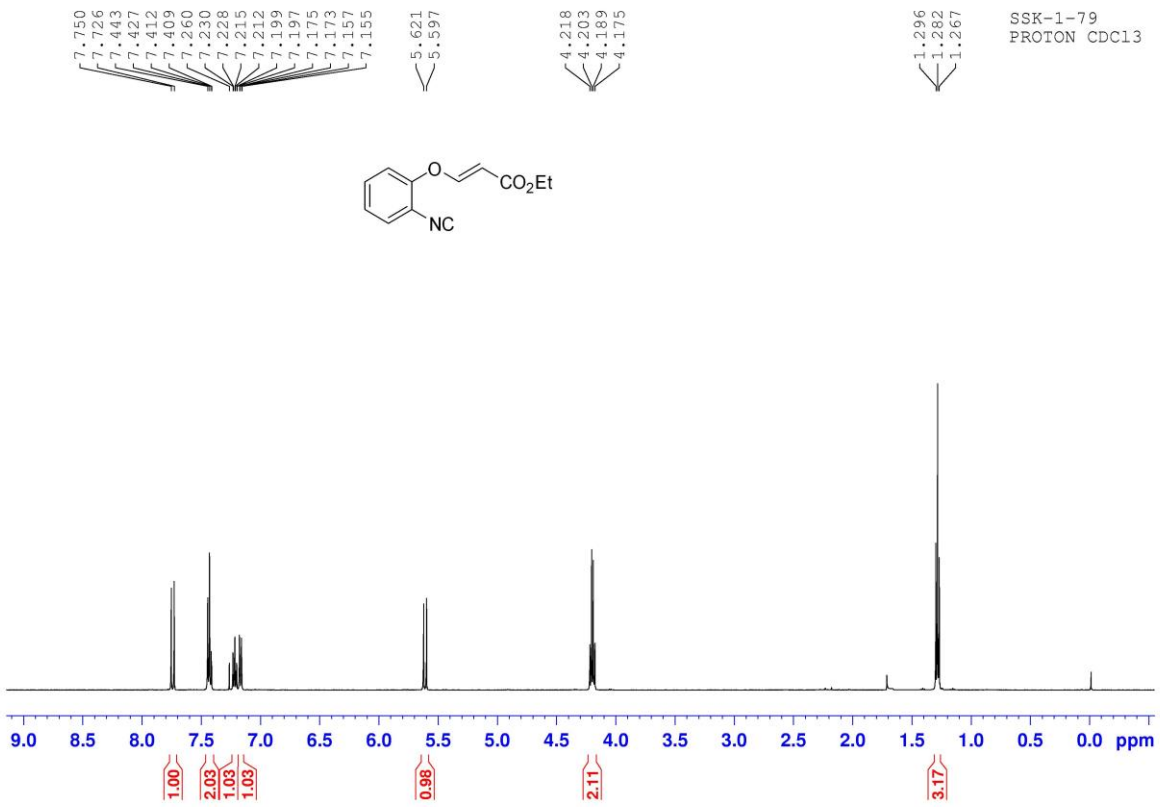

169.77
167.02
159.36
147.94
132.60
132.47
126.60
125.83
120.17
100.45
77.41
77.16
76.91
51.54
16.03
SSK-1-208
C13CPD CDCl3
CO2Me
NC
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

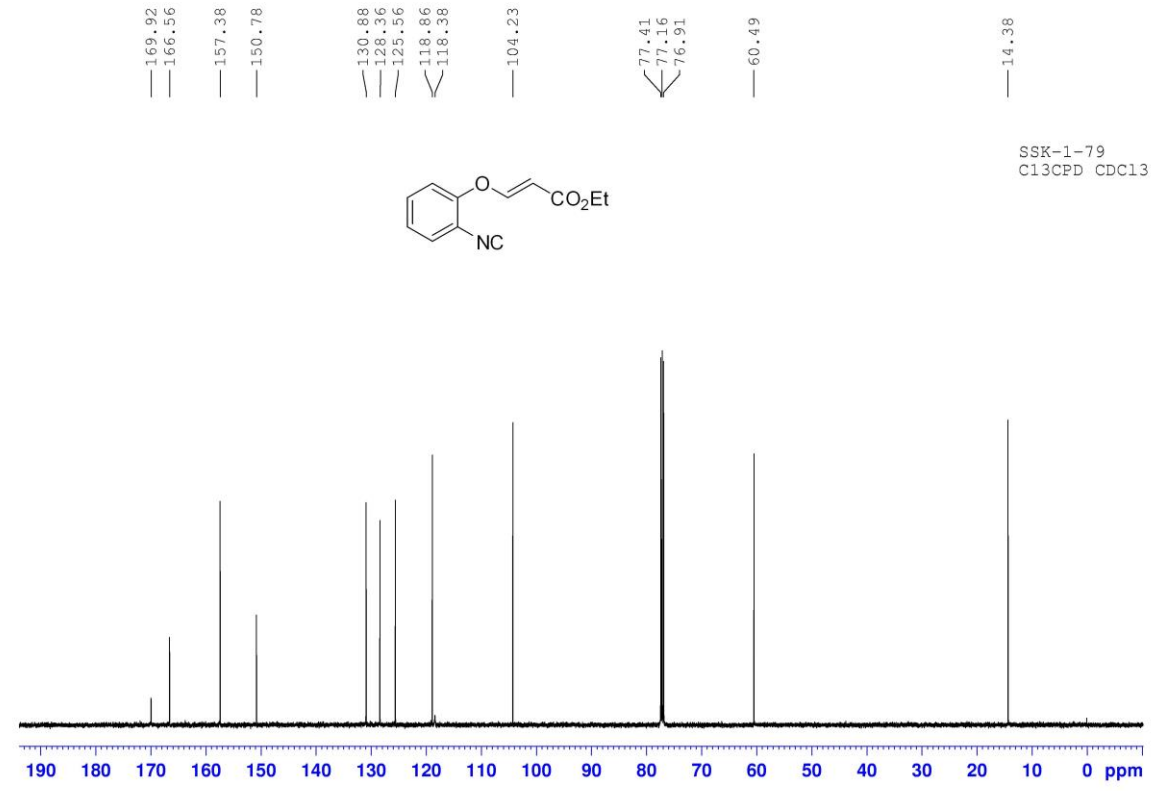
Compound **1j**


7.933
7.883
7.858
7.819
7.802
7.785
7.605
7.591
7.576
7.551
7.536
7.522
7.501
7.260
5.749
5.724
3.765
SSK-1-233
PROTON CDCl3
O
CO2Me
NC
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.05
2.04
1.04
1.07
1.03
0.96
3.04

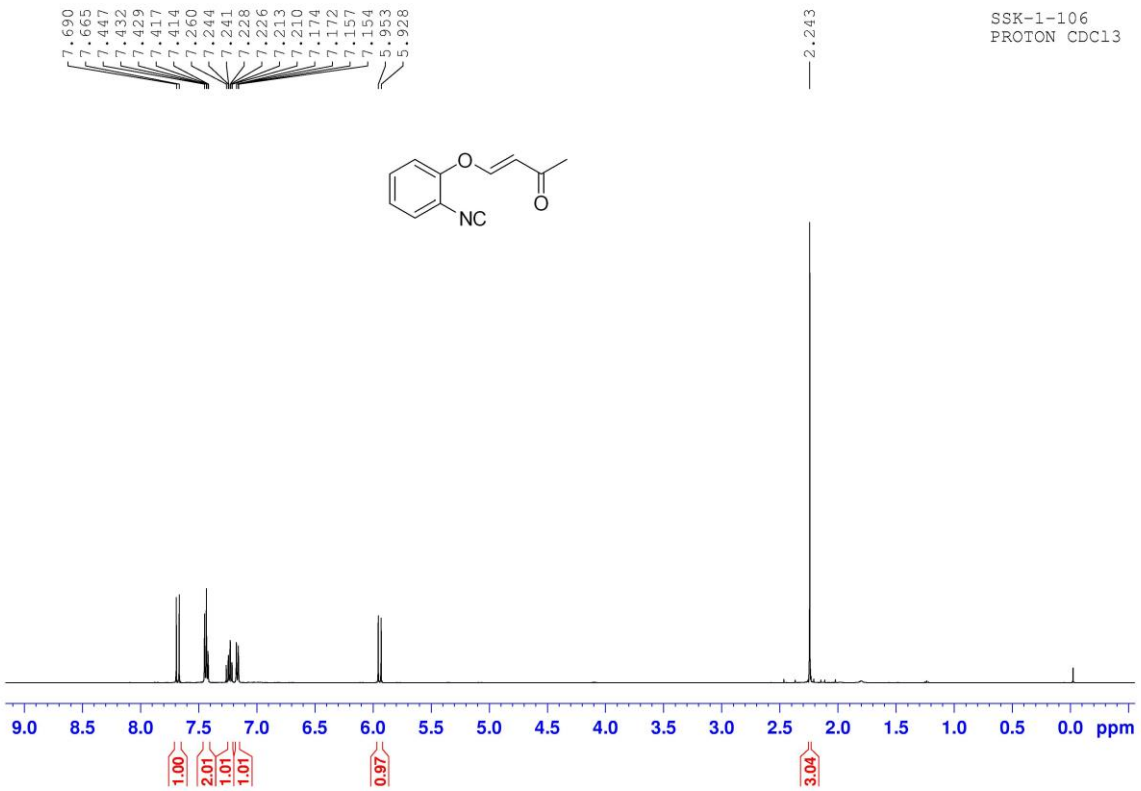

169.77
167.09
157.56
147.54
133.30
129.81
128.86
128.18
127.92
127.45
127.14
117.31
115.04
104.25
51.68
SSK-1-233
C13CPD CDCl3
O
CO2Me
NC
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

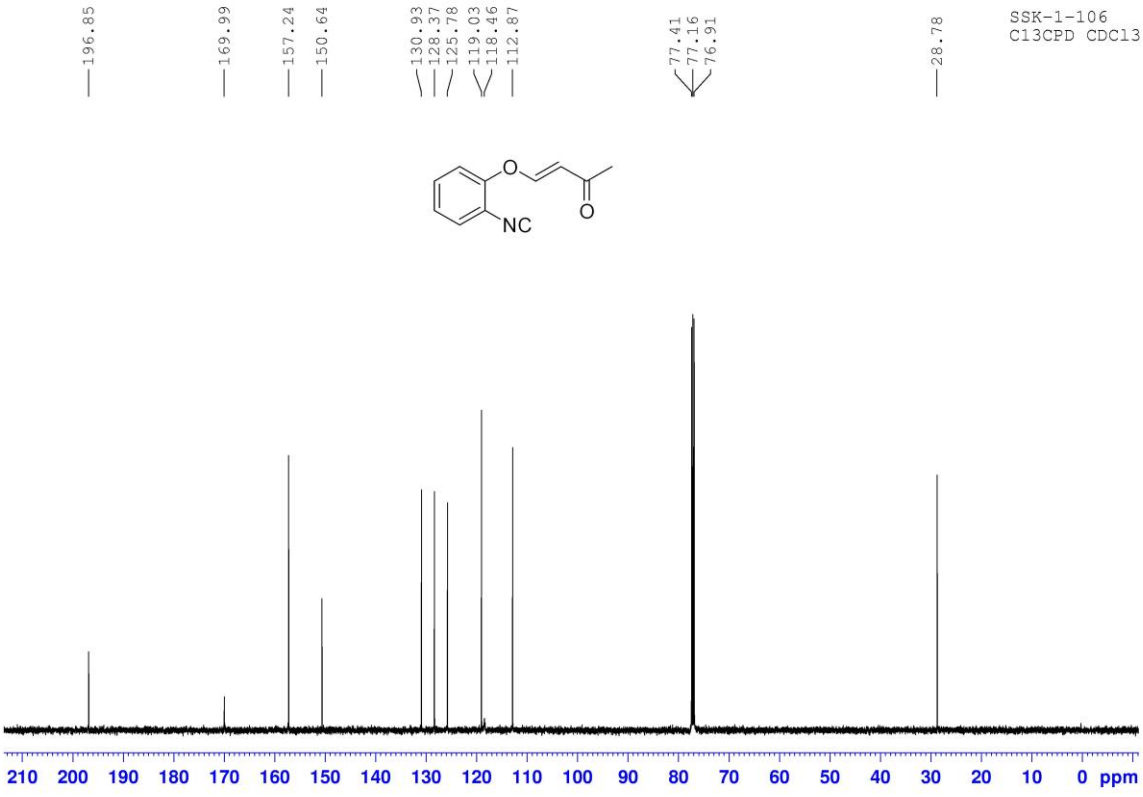
Compound **1k**


7.750
7.726
7.443
7.427
7.412
7.409
7.260
7.230
7.228
7.215
7.212
7.199
7.197
7.175
7.173
7.157
7.155
5.621
5.597
4.218
4.203
4.189
4.175
1.296
1.282
1.267
SSK-1-79
PROTON CDCl3
O
CO2Et
NC
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
2.03
1.03
1.03
0.98
2.11
3.17

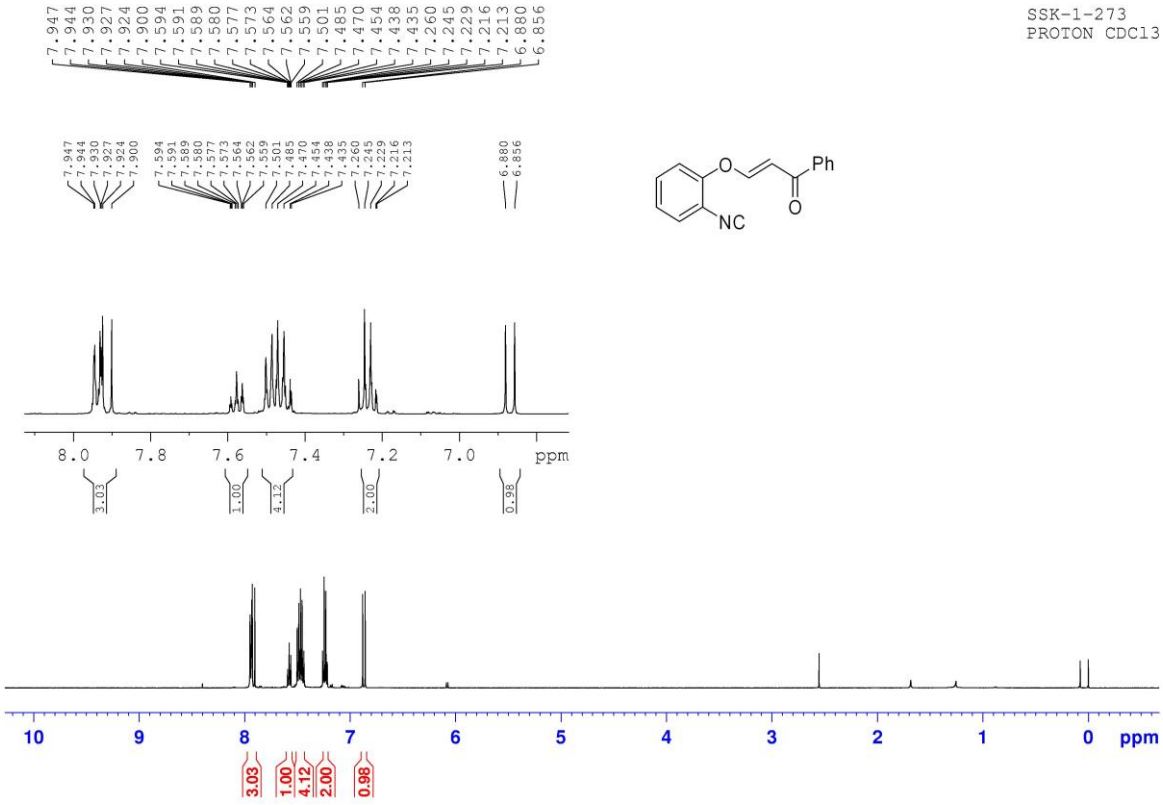

169.92
166.56
157.38
150.78
130.88
128.36
125.56
118.86
118.38
104.23
77.41
77.16
76.91
60.49
14.38
SSK-1-79
C13CPD CDCl3
O
CO2Et
NC
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

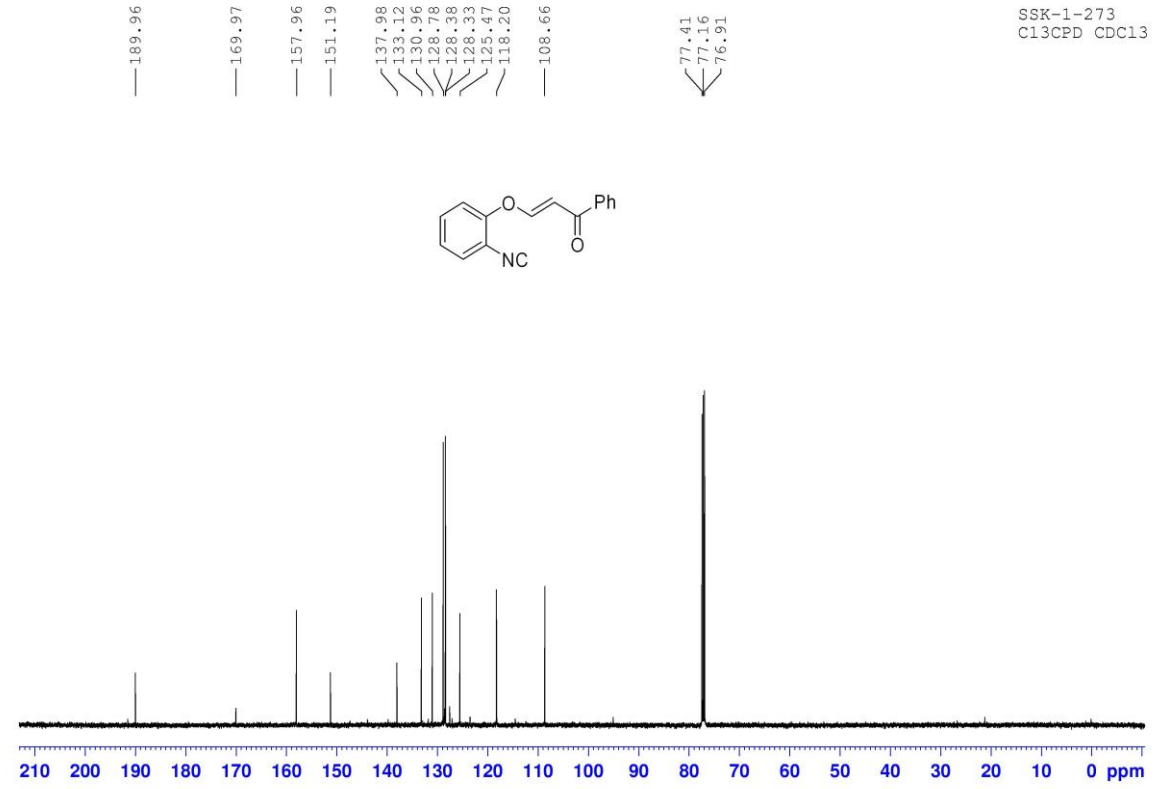
Compound **1l**


7.690
7.665
7.447
7.432
7.429
7.417
7.414
7.260
7.244
7.241
7.228
7.226
7.213
7.210
7.174
7.172
7.157
7.154
5.953
5.928
2.243
SSK-1-106
PROTON CDCl3
O
O
NC
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
2.01
1.01
1.01
0.97
3.04

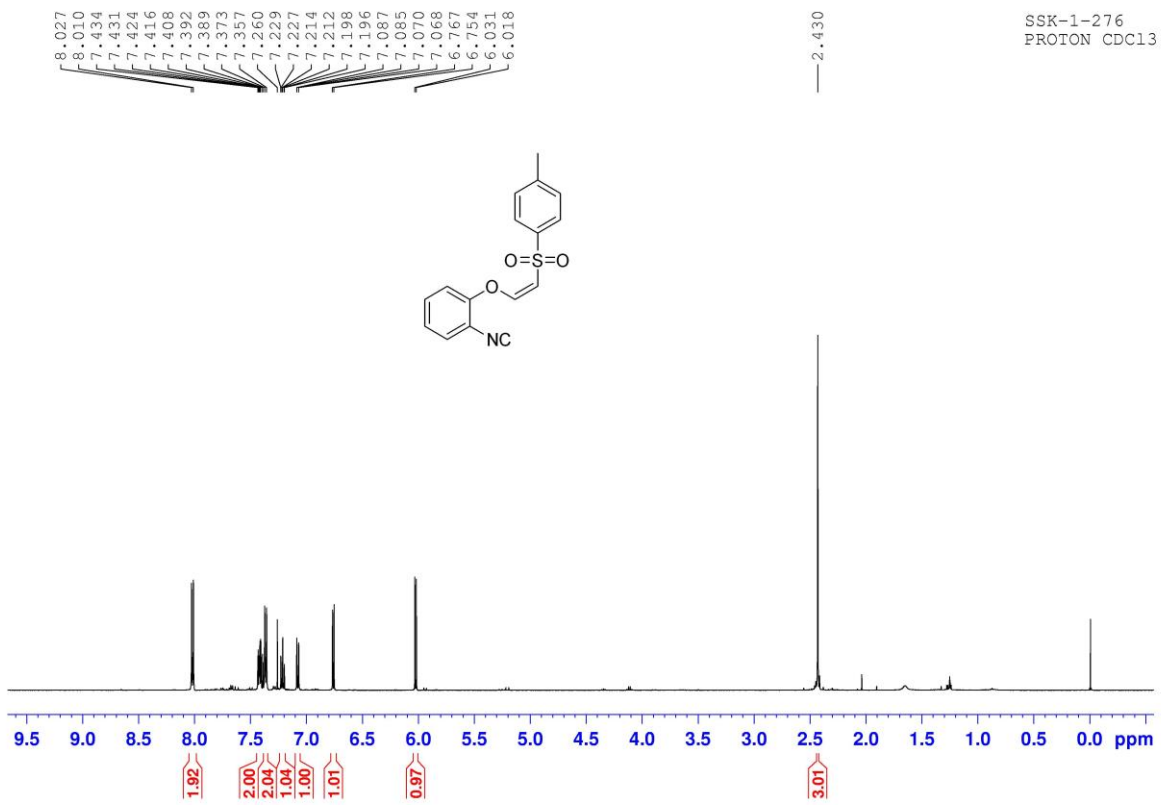

196.85
169.99
157.24
150.64
130.93
128.37
125.78
119.03
118.46
112.87
77.41
77.16
76.91
28.78
SSK-1-106
C13CPD CDCl3
O
O
NC
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

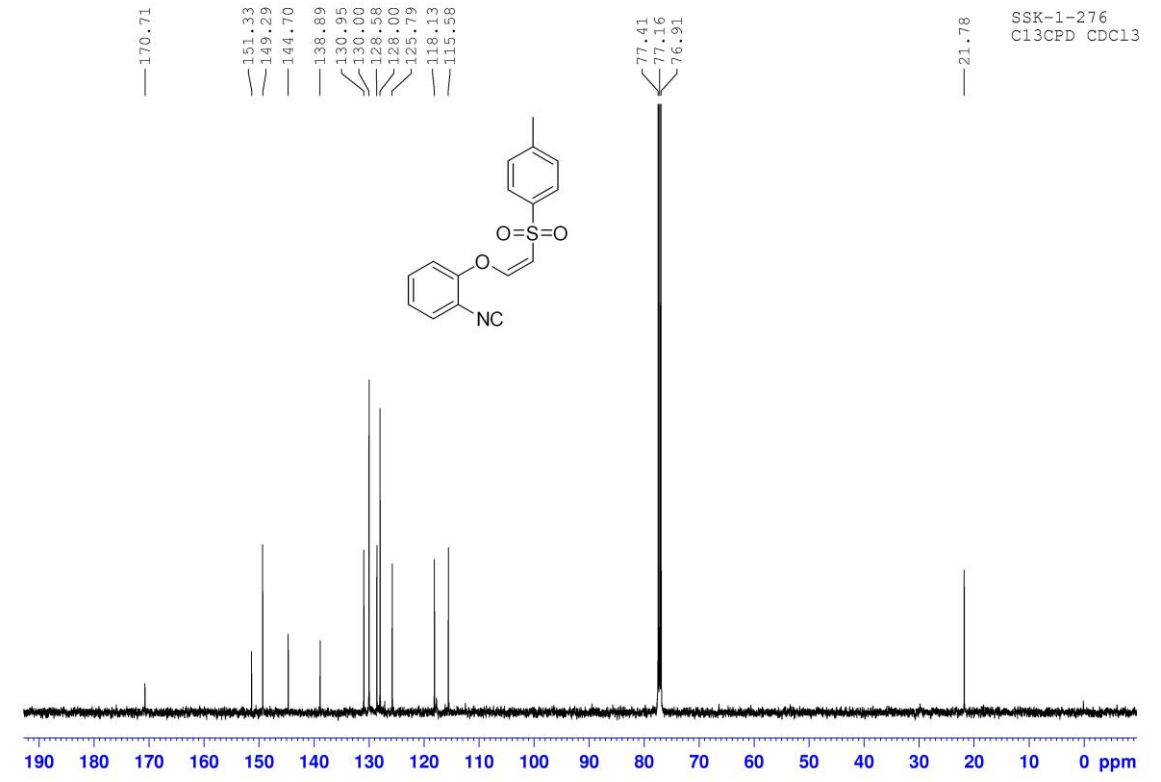
Compound **1m**


SSK-1-273
PROTON CDCl3
7.947
7.944
7.930
7.927
7.924
7.900
7.594
7.591
7.589
7.580
7.577
7.573
7.564
7.562
7.559
7.501
7.485
7.470
7.454
7.438
7.435
7.260
7.245
7.229
7.216
7.213
6.880
6.856
O
Ph
O
NC
8.0
7.8
7.6
7.4
7.2
7.0
ppm
3.03
1.00
4.12
2.00
0.98
10
9
8
7
6
5
4
3
2
1
0
ppm

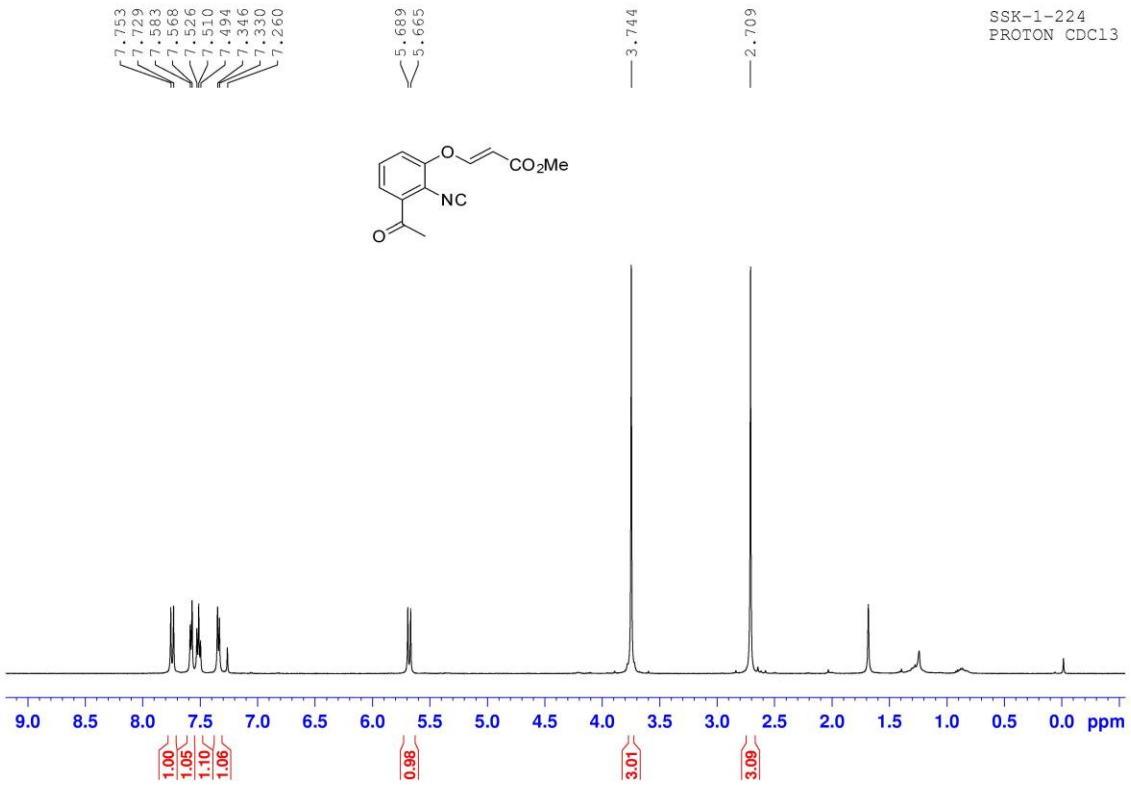

SSK-1-273
C13CPD CDCl3
189.96
169.97
157.96
151.19
137.98
133.12
130.96
128.78
128.38
128.33
125.47
118.20
108.66
77.41
77.16
76.91
O
Ph
O
NC
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

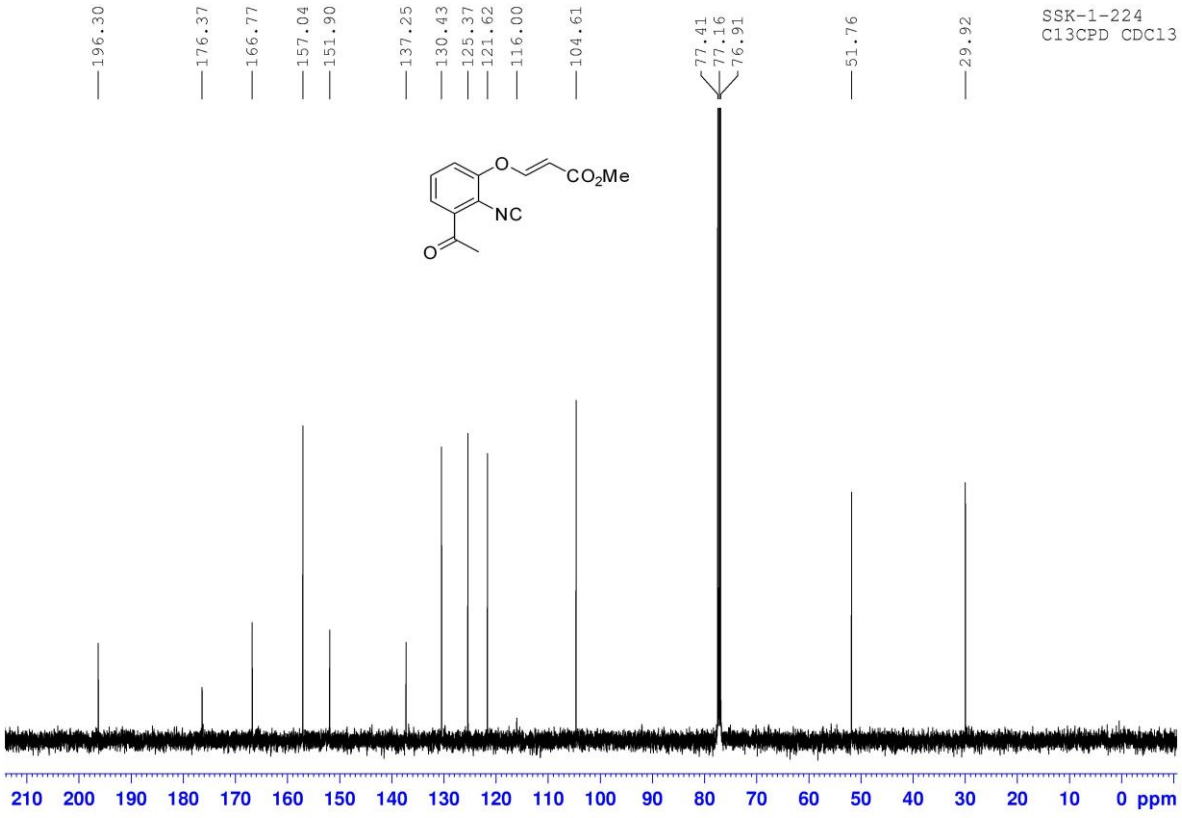
Compound **1n**


8.027
8.010
7.434
7.431
7.424
7.416
7.408
7.392
7.389
7.373
7.357
7.260
7.229
7.227
7.214
7.212
7.198
7.196
7.087
7.085
7.070
7.068
6.767
6.754
6.031
6.018
2.430
SSK-1-276
PROTON CDCl3
O=S=O
O
NC
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.92
2.00
2.04
1.04
1.00
1.01
0.97
3.01

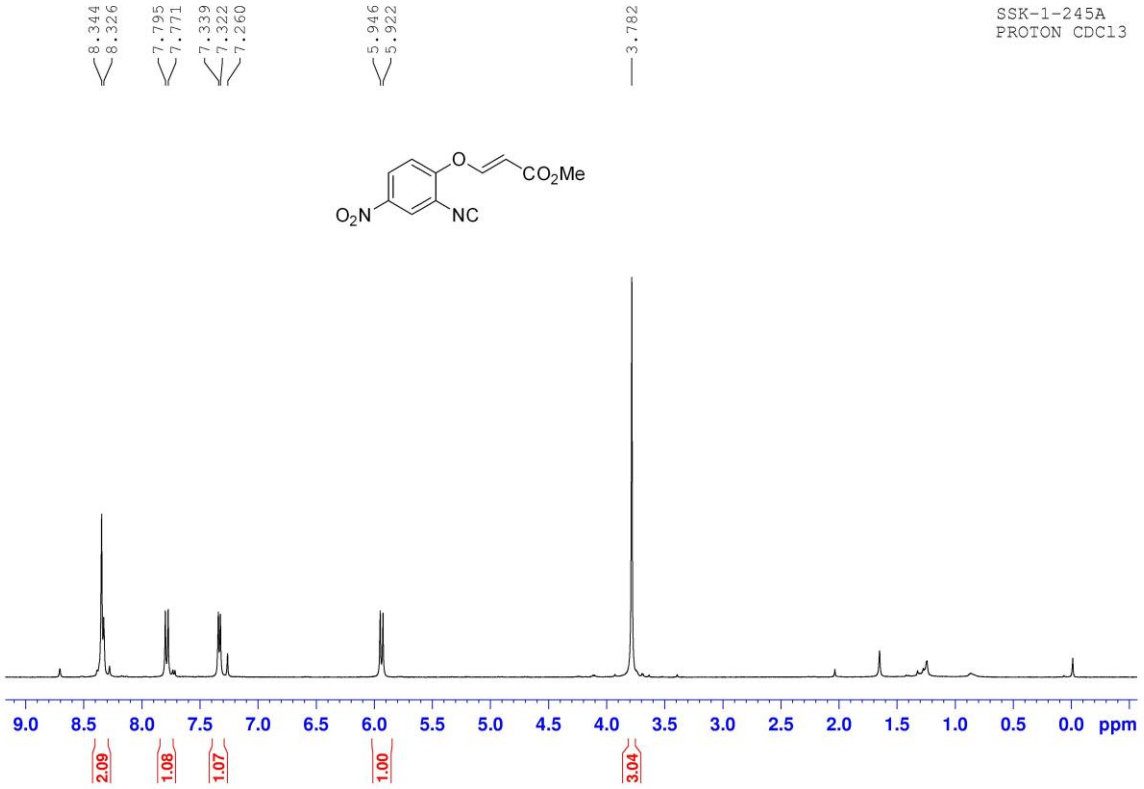

170.71
151.33
149.29
144.70
138.89
130.95
130.00
128.58
128.00
125.79
118.13
115.58
77.41
77.16
76.91
21.78
SSK-1-276
C13CPD CDCl3
O=S=O
O
NC
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

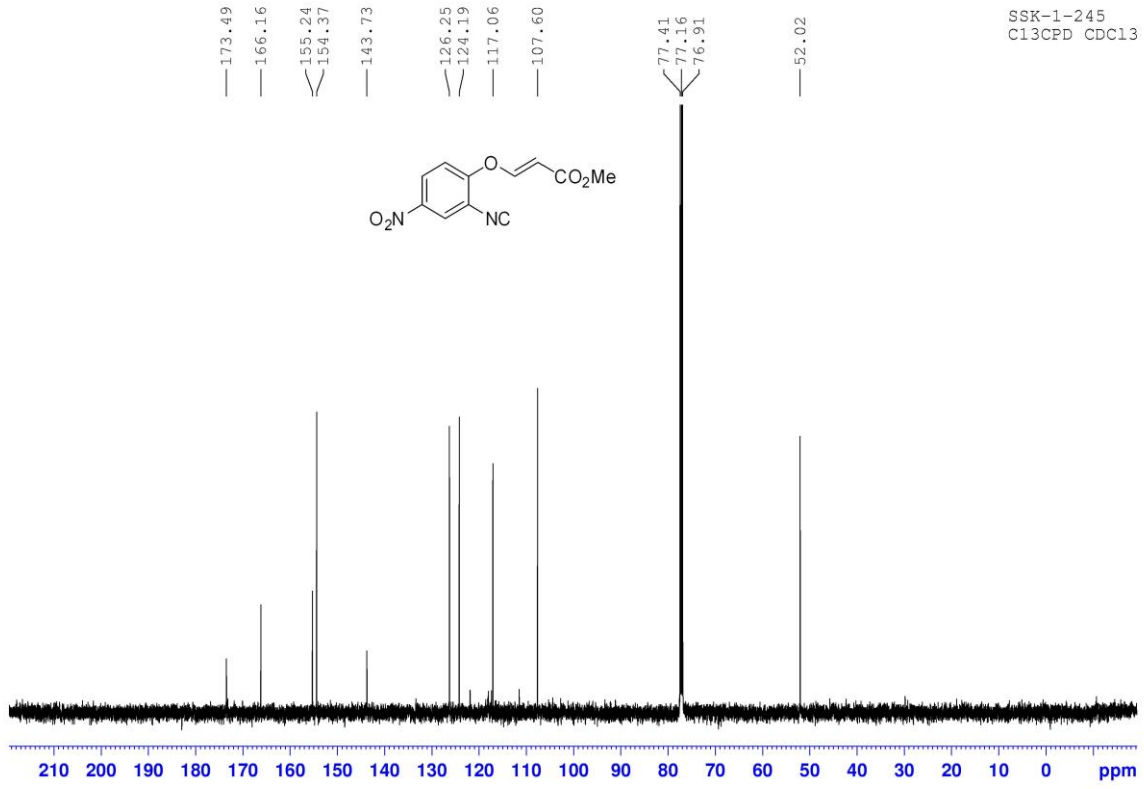
Compound **1o**


7.753
7.729
7.583
7.568
7.526
7.510
7.494
7.346
7.330
7.260
5.689
5.665
3.744
2.709
SSK-1-224
PROTON CDCl3
CO2Me
NC
O
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.05
1.10
1.06
0.98
3.01
3.09

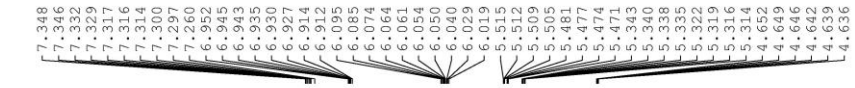

196.30
176.37
166.77
157.04
151.90
137.25
130.43
125.37
121.62
116.00
104.61
77.41
77.16
76.91
51.76
29.92
SSK-1-224
C13CPD CDCl3
CO2Me
NC
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Compound **1p**

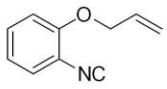

8.344
8.326
7.795
7.771
7.339
7.322
7.260
5.946
5.922
3.782
SSK-1-245A
PROTON CDCl3
O
CO2Me
O2N
NC
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.09
1.08
1.07
1.00
3.04

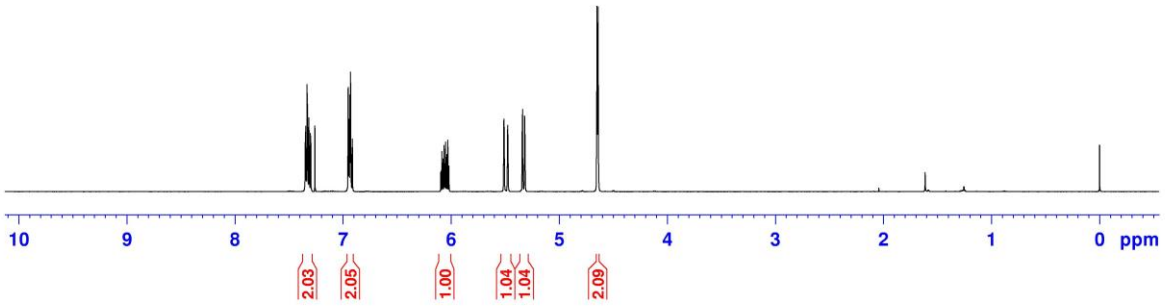

173.49
166.16
155.24
154.37
143.73
126.25
124.19
117.06
107.60
77.41
77.16
76.91
52.02
SSK-1-245
C13CPD CDCl3
O
CO2Me
O2N
NC
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

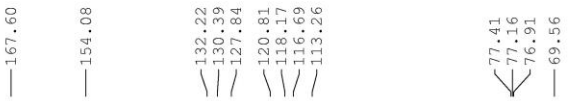
Compound **1q**



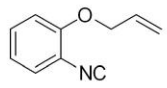
SSK-1-302-2
PROTON CDCl3

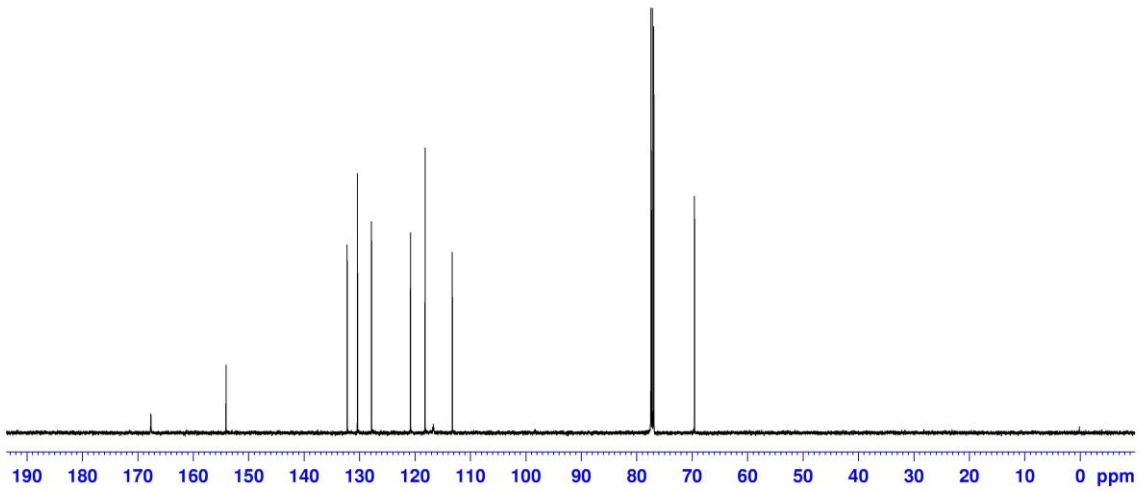




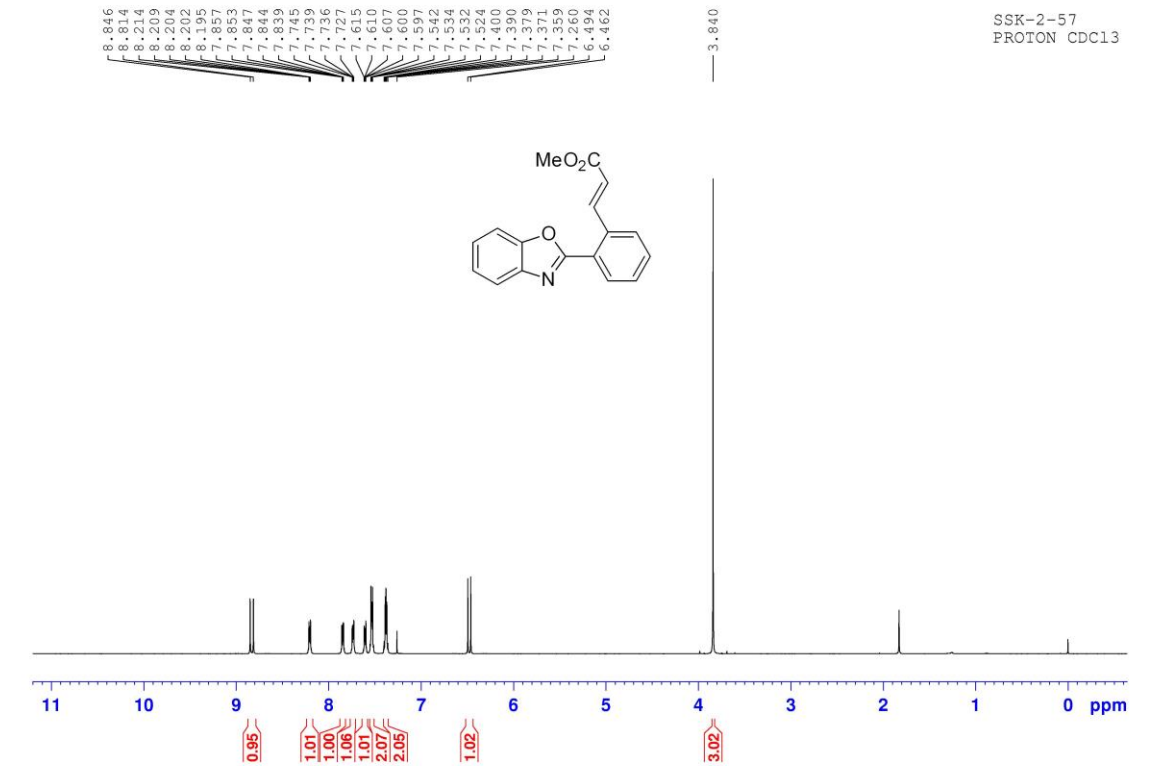


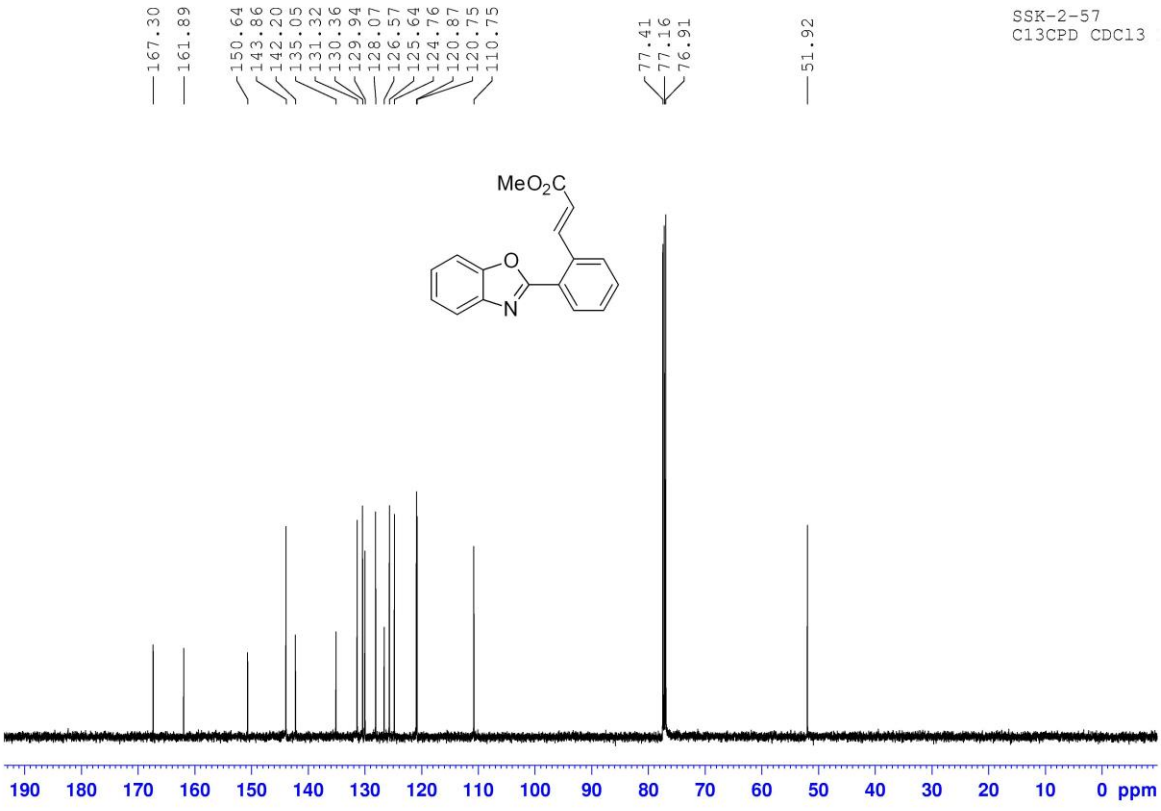
SSK-1-302-2
C13CPD CDCl3



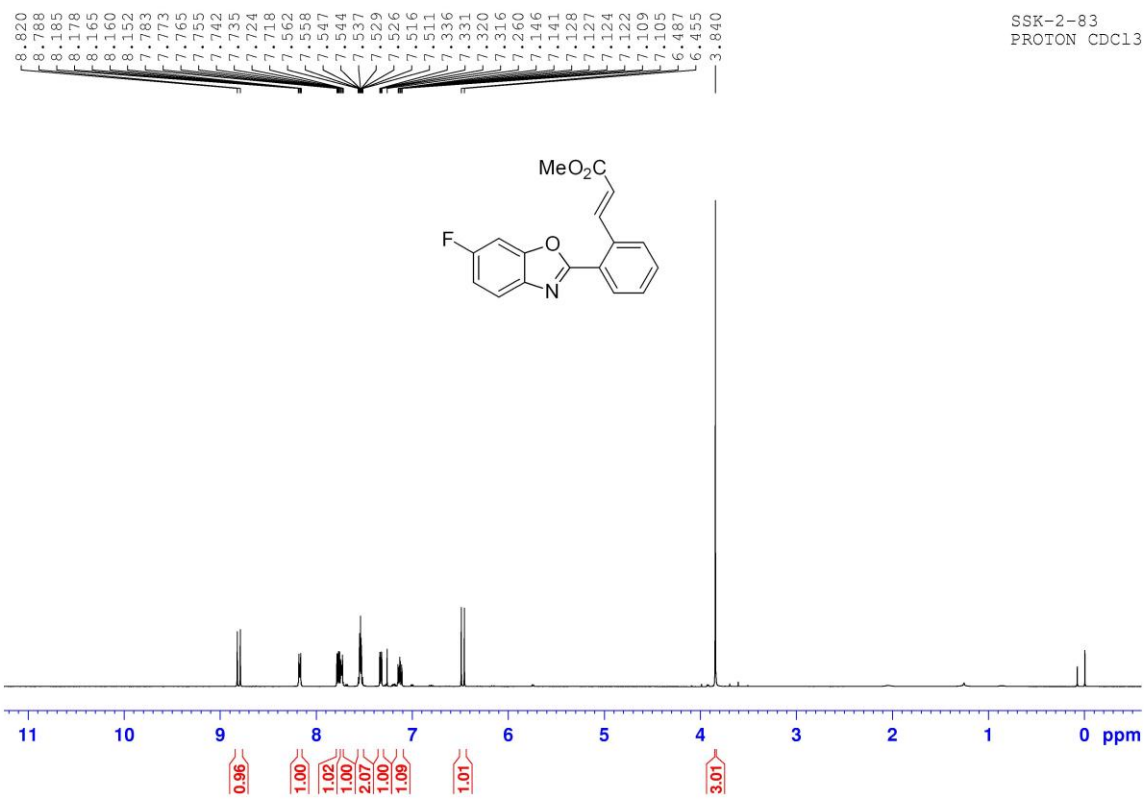


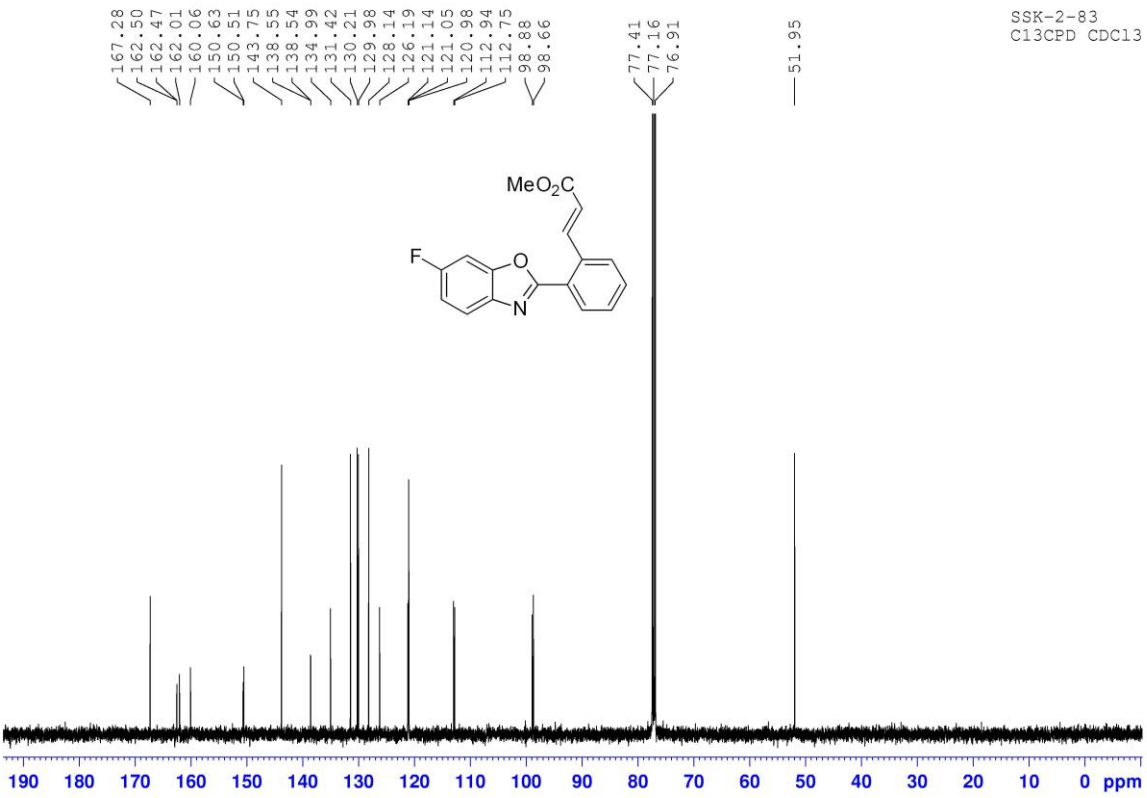
Compound **3a**


8.846
8.814
8.214
8.209
8.204
8.202
8.195
7.857
7.853
7.847
7.844
7.839
7.745
7.739
7.736
7.727
7.615
7.610
7.607
7.600
7.597
7.542
7.534
7.532
7.524
7.400
7.390
7.379
7.371
7.359
7.260
6.494
6.462
3.840
SSK-2-57
PROTON CDC13
MeO2C
O
N
11
10
9
8
7
6
5
4
3
2
1
0 ppm
0.95
1.01
1.00
1.06
1.01
2.07
2.05
1.02
3.02

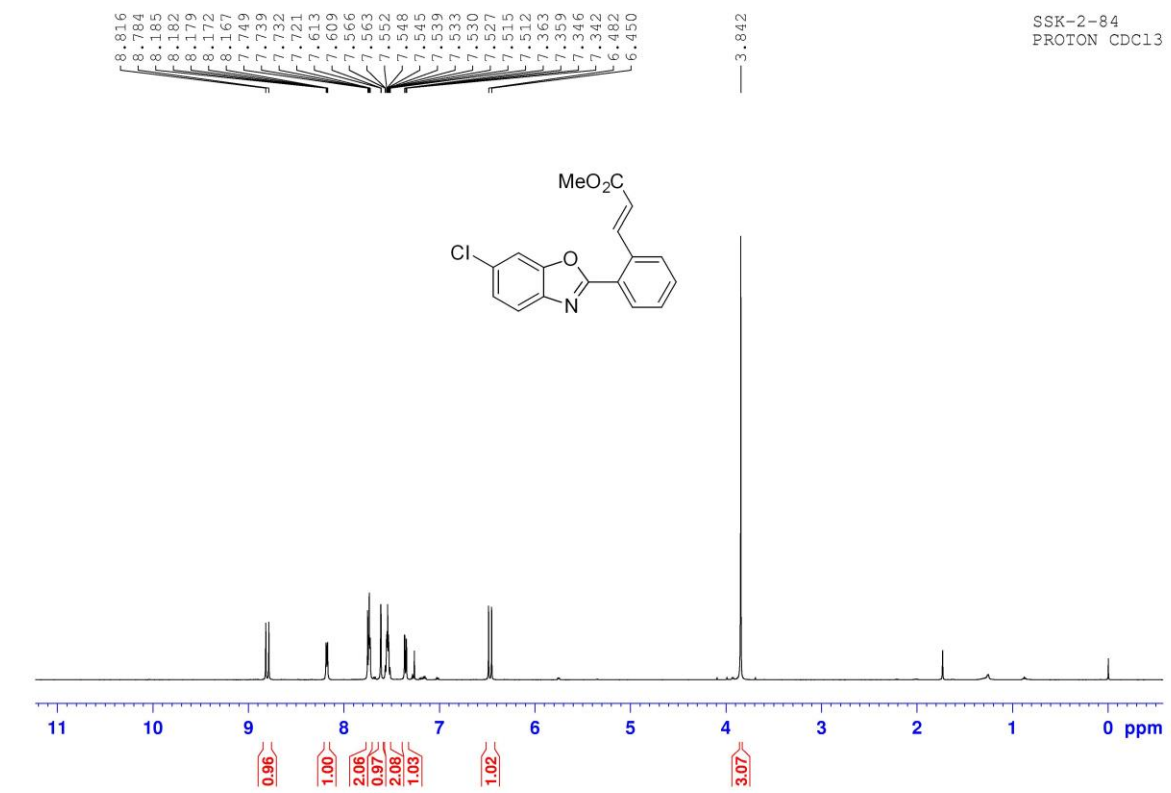

167.30
161.89
150.64
143.86
142.20
135.05
131.32
130.36
129.94
128.07
126.57
125.64
124.76
120.87
120.75
110.75
77.41
77.16
76.91
51.92
SSK-2-57
C13CPD CDC13
MeO2C
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

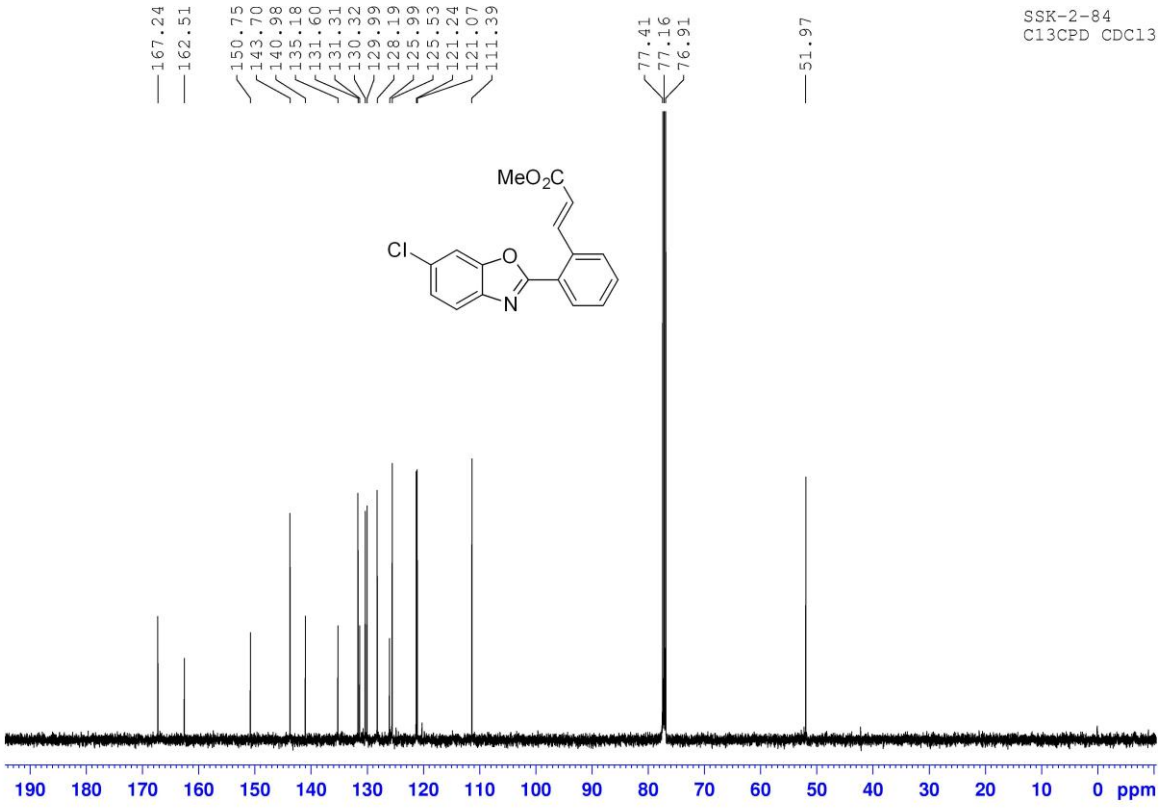
Compound **3b**


8.820
8.788
8.185
8.178
8.165
8.160
8.152
7.783
7.773
7.765
7.755
7.742
7.735
7.724
7.718
7.562
7.558
7.547
7.544
7.537
7.529
7.526
7.516
7.511
7.336
7.331
7.320
7.316
7.260
7.146
7.141
7.128
7.127
7.124
7.122
7.109
7.105
6.487
6.455
3.840
SSK-2-83
PROTON CDCl3
MeO2C
F
O
N
11
10
9
8
7
6
5
4
3
2
1
0 ppm
0.96
1.00
1.02
1.00
2.07
1.00
1.09
1.01
3.01

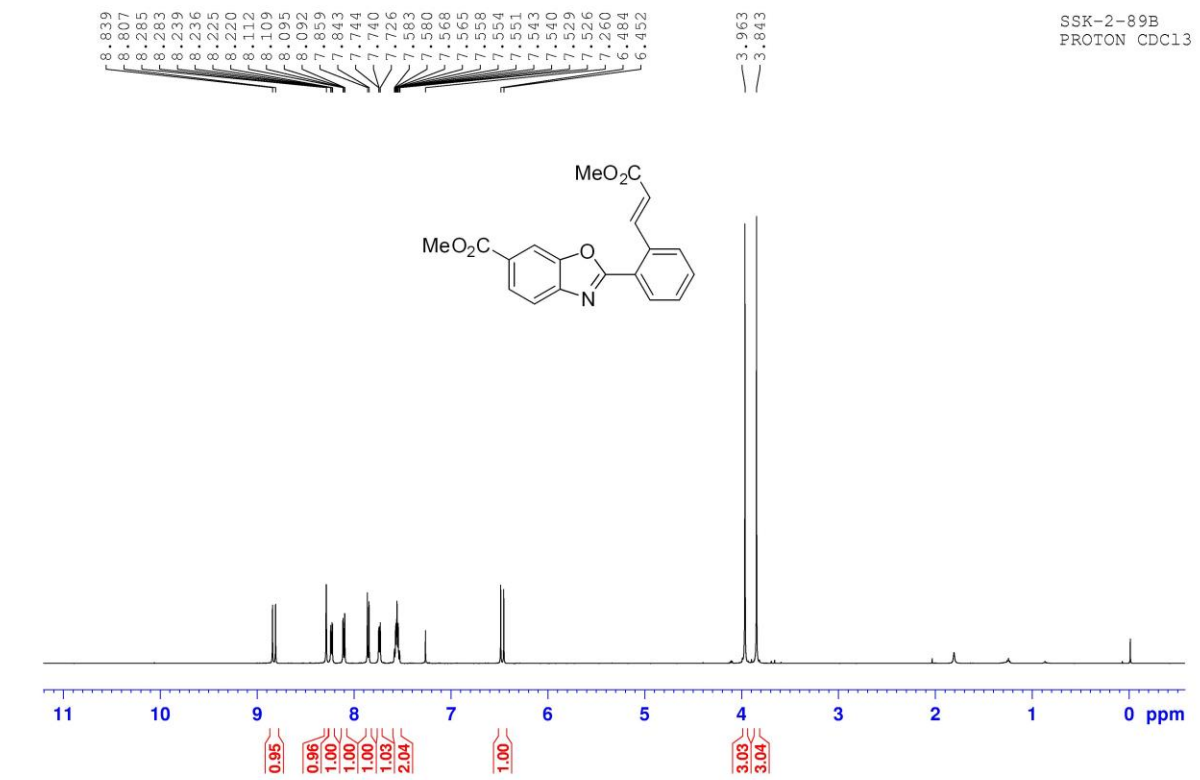

167.28
162.50
162.47
162.01
160.06
150.63
150.51
143.75
138.55
138.54
134.99
131.42
130.21
129.98
128.14
126.19
121.14
121.05
120.98
112.94
112.75
98.88
98.66
77.41
77.16
76.91
51.95
SSK-2-83
C13CPD CDCl3
MeO2C
F
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

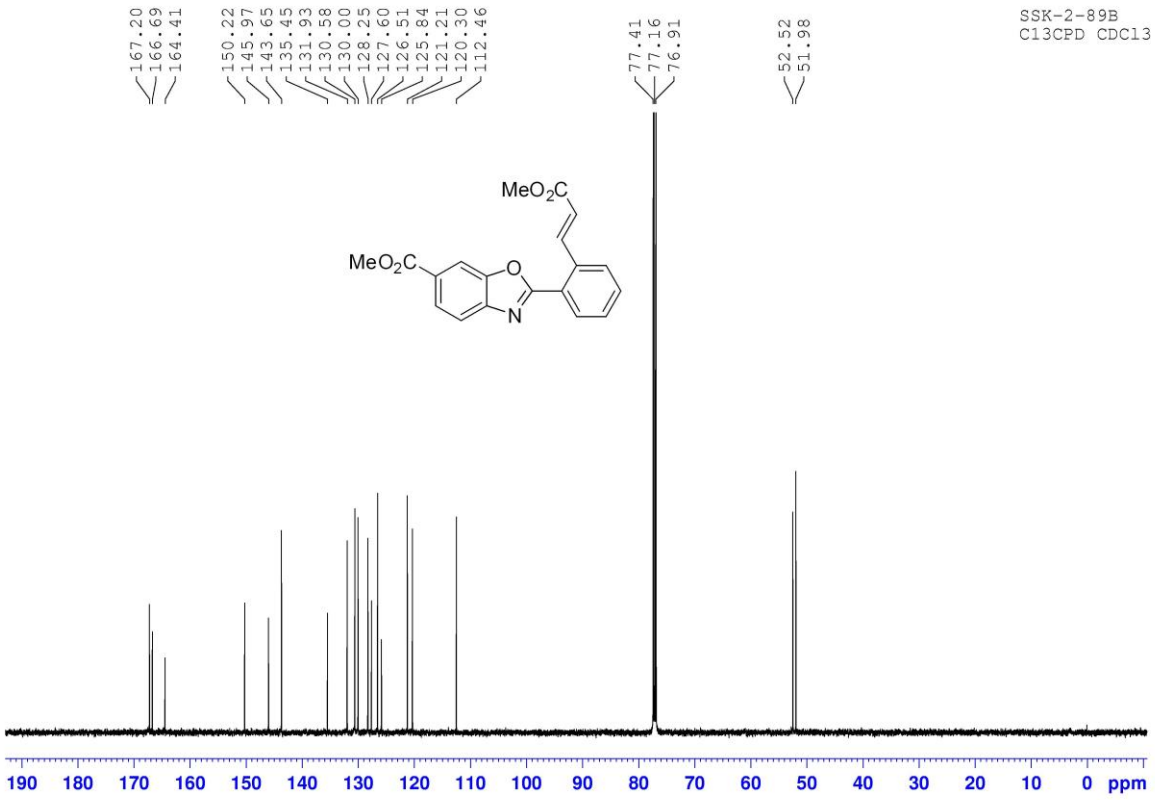
Compound **3c**


8.816
8.784
8.185
8.182
8.179
8.172
8.167
7.749
7.739
7.732
7.721
7.613
7.609
7.566
7.563
7.552
7.548
7.545
7.539
7.533
7.530
7.527
7.515
7.512
7.363
7.359
7.346
7.342
6.482
6.450
3.842
SSK-2-84
PROTON CDCl3
MeO2C
Cl
O
N
11
10
9
8
7
6
5
4
3
2
1
0 ppm
0.96
1.00
2.06
0.97
2.08
1.03
1.02
3.07

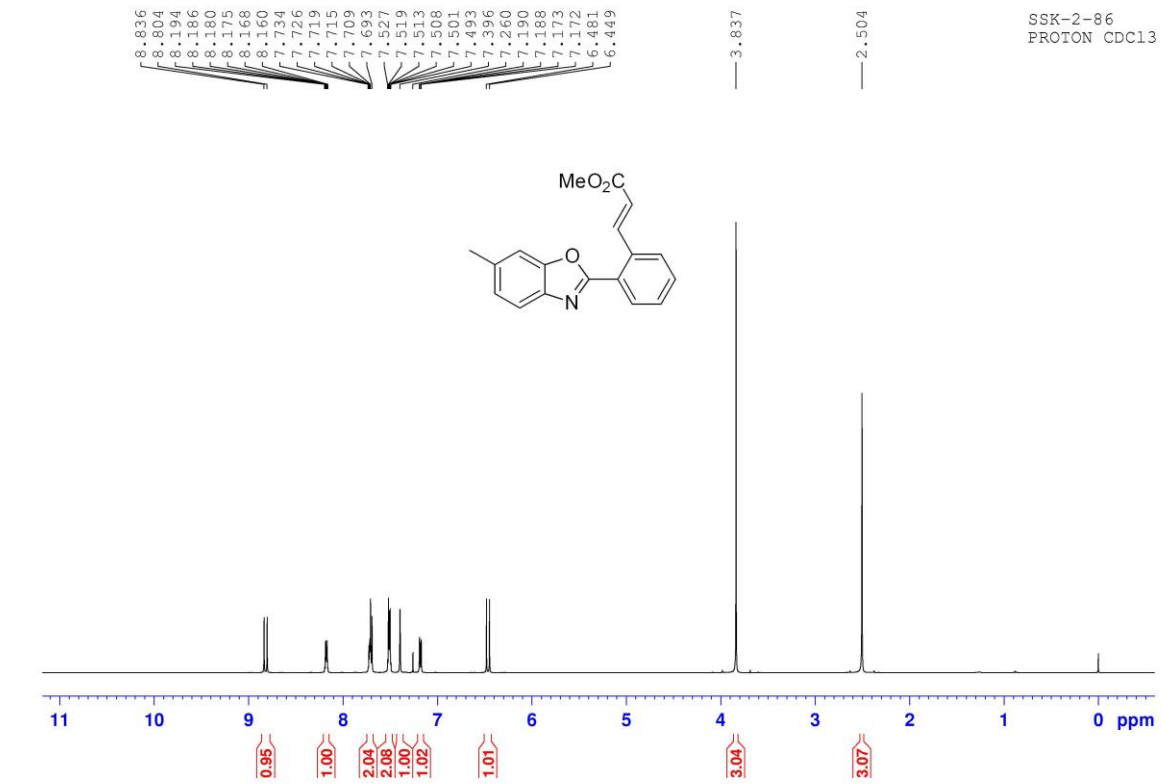

167.24
162.51
150.75
143.70
140.98
135.18
131.60
131.31
130.32
129.99
128.19
125.99
125.53
121.24
121.07
111.39
77.41
77.16
76.91
51.97
SSK-2-84
C13CPD CDCl3
MeO2C
Cl
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

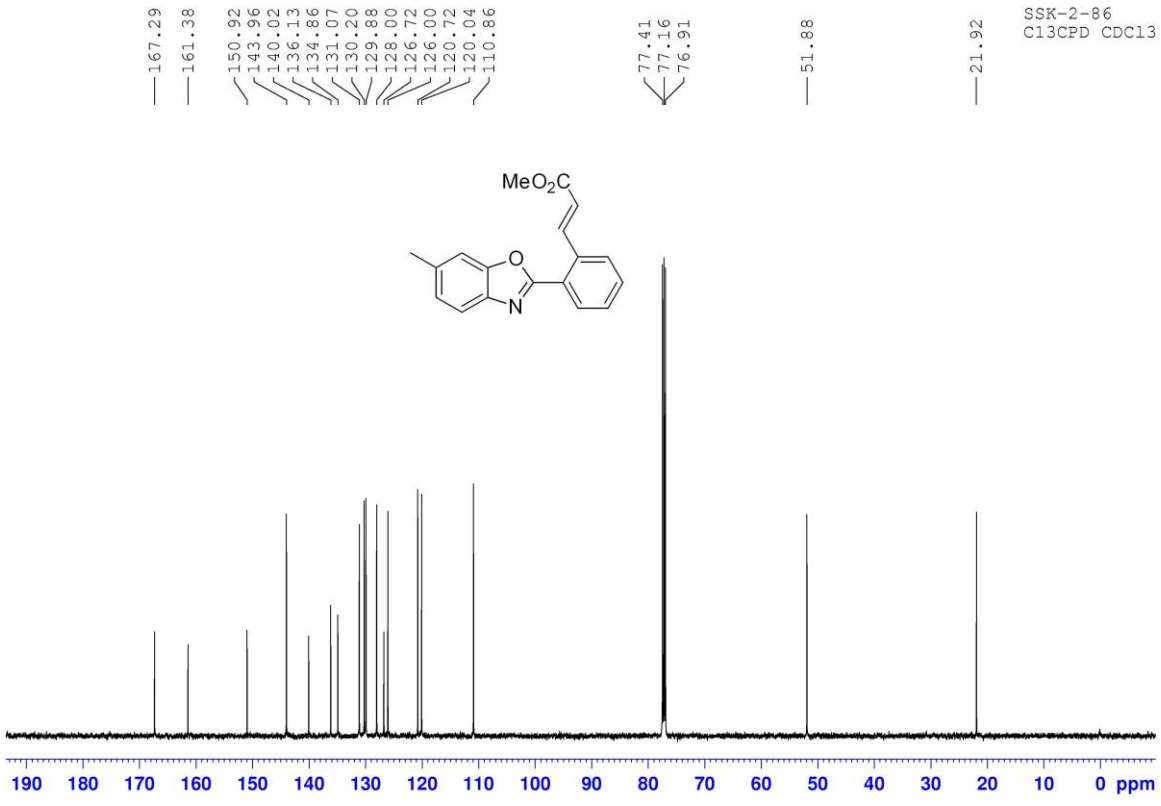
Compound **3d**


8.839
8.807
8.285
8.283
8.239
8.236
8.225
8.220
8.112
8.109
8.095
8.092
7.859
7.843
7.744
7.740
7.726
7.583
7.580
7.568
7.565
7.558
7.554
7.551
7.543
7.540
7.529
7.526
7.260
6.484
6.452
3.963
3.843
SSK-2-89B
PROTON CDCl3
MeO2C
MeO2C
O
N
11
10
9
8
7
6
5
4
3
2
1
0 ppm
0.95
0.96
1.00
1.00
1.00
1.03
2.04
1.00
3.03
3.04

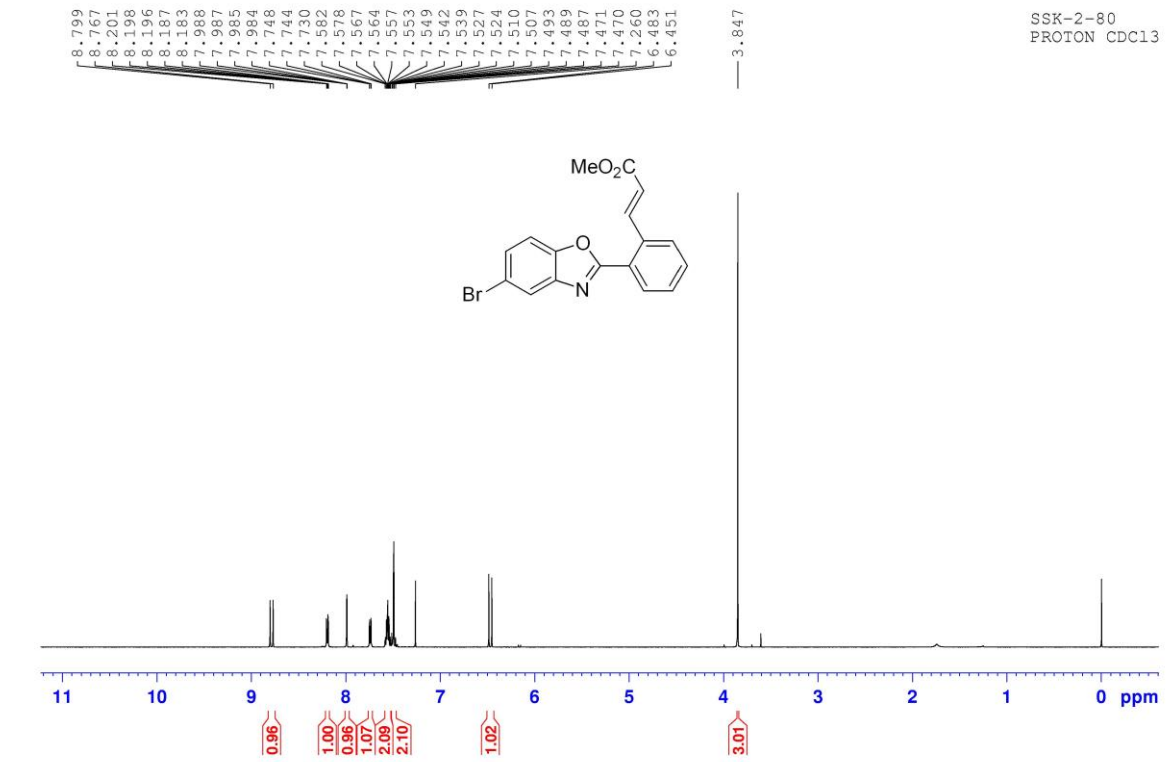

167.20
166.69
164.41
150.22
145.97
143.65
135.45
131.93
130.58
130.00
128.25
127.60
126.51
125.84
121.21
120.30
112.46
77.41
77.16
76.91
52.52
51.98
SSK-2-89B
C13CPD CDCl3
MeO2C
MeO2C
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

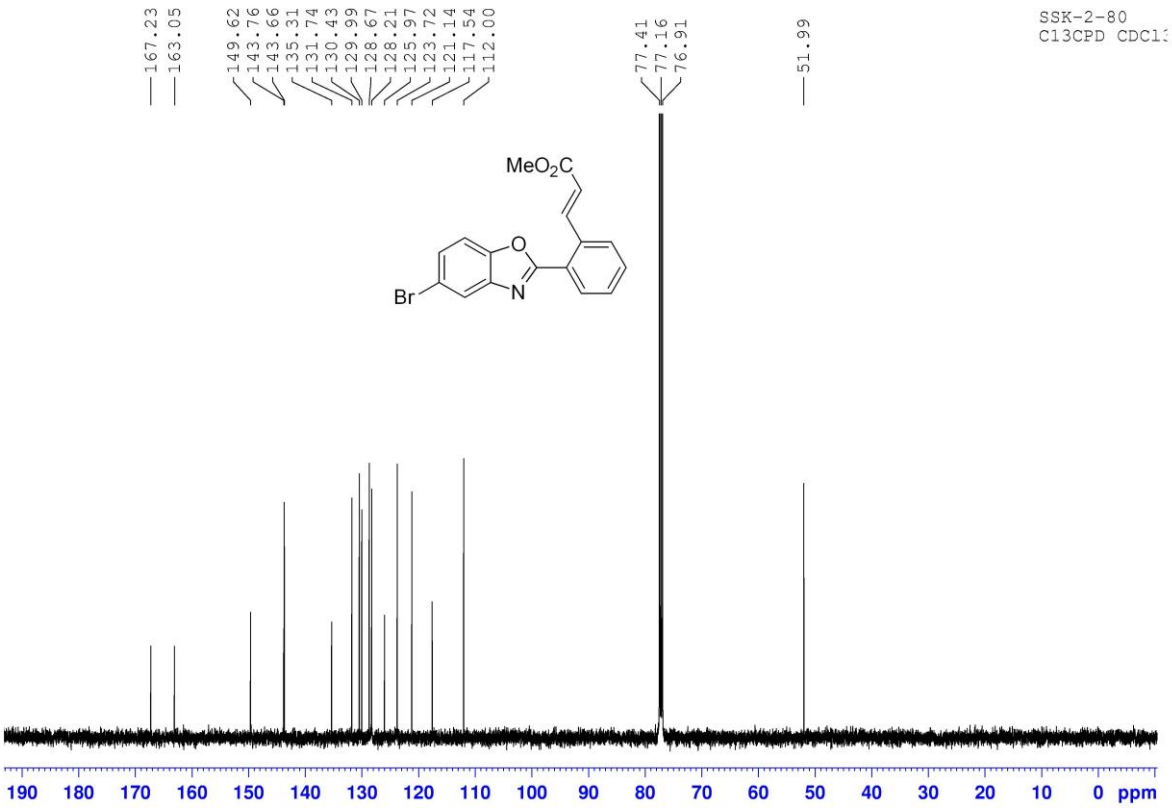
Compound **3e**


8.836
8.804
8.194
8.186
8.180
8.175
8.168
8.160
7.734
7.726
7.719
7.715
7.709
7.693
7.527
7.519
7.513
7.508
7.501
7.493
7.396
7.260
7.190
7.188
7.173
7.172
6.481
6.449
3.837
2.504
SSK-2-86
PROTON CDCl3
MeO2C
O
N
11
10
9
8
7
6
5
4
3
2
1
0 ppm
0.95
1.00
2.04
2.08
1.00
1.02
1.01
3.04
3.07

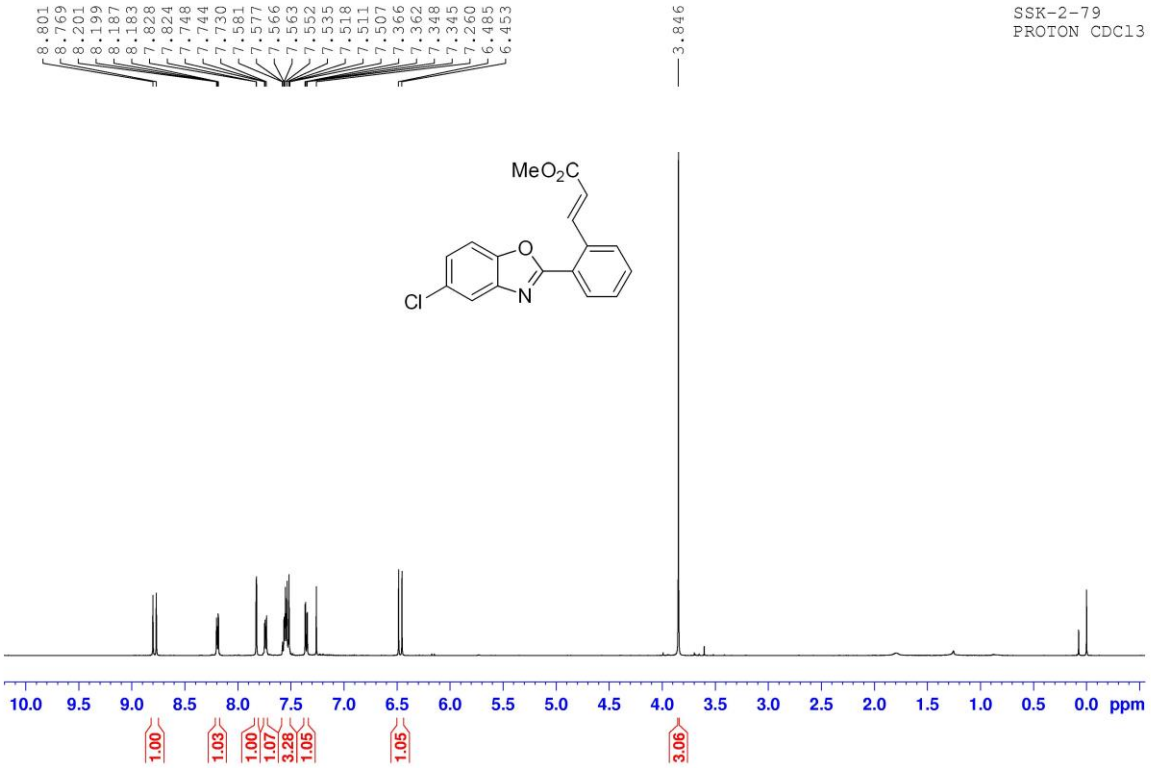

167.29
161.38
150.92
143.96
140.02
136.13
134.86
131.07
130.20
129.88
128.00
126.72
126.00
120.72
120.04
110.86
77.41
77.16
76.91
51.88
21.92
SSK-2-86
C13CPD CDCl3
MeO2C
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

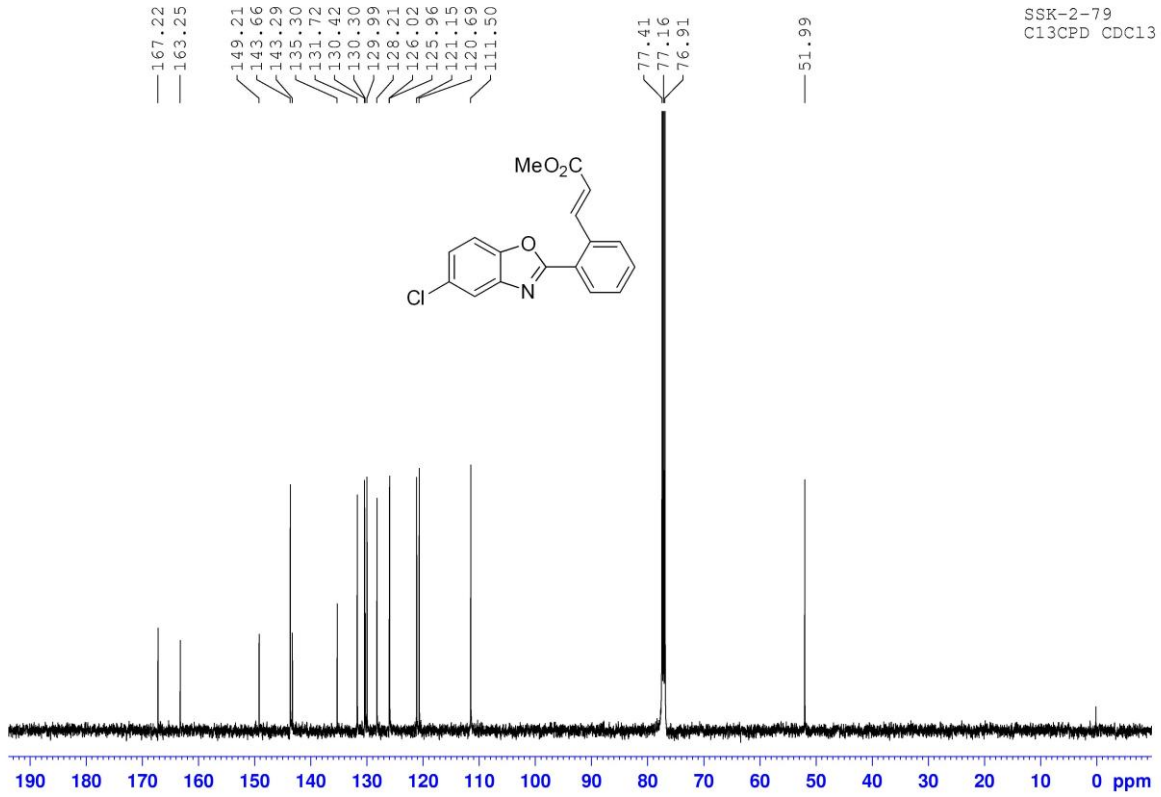
Compound **3f**


8.799
8.767
8.201
8.198
8.196
8.187
8.183
7.988
7.987
7.985
7.984
7.748
7.744
7.730
7.582
7.578
7.567
7.564
7.557
7.553
7.549
7.542
7.539
7.527
7.524
7.510
7.507
7.493
7.489
7.487
7.471
7.470
7.260
6.483
6.451
3.847
SSK-2-80
PROTON CDCl3
MeO2C
O
N
Br
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.96
1.00
0.96
1.07
2.09
2.10
1.02
3.01

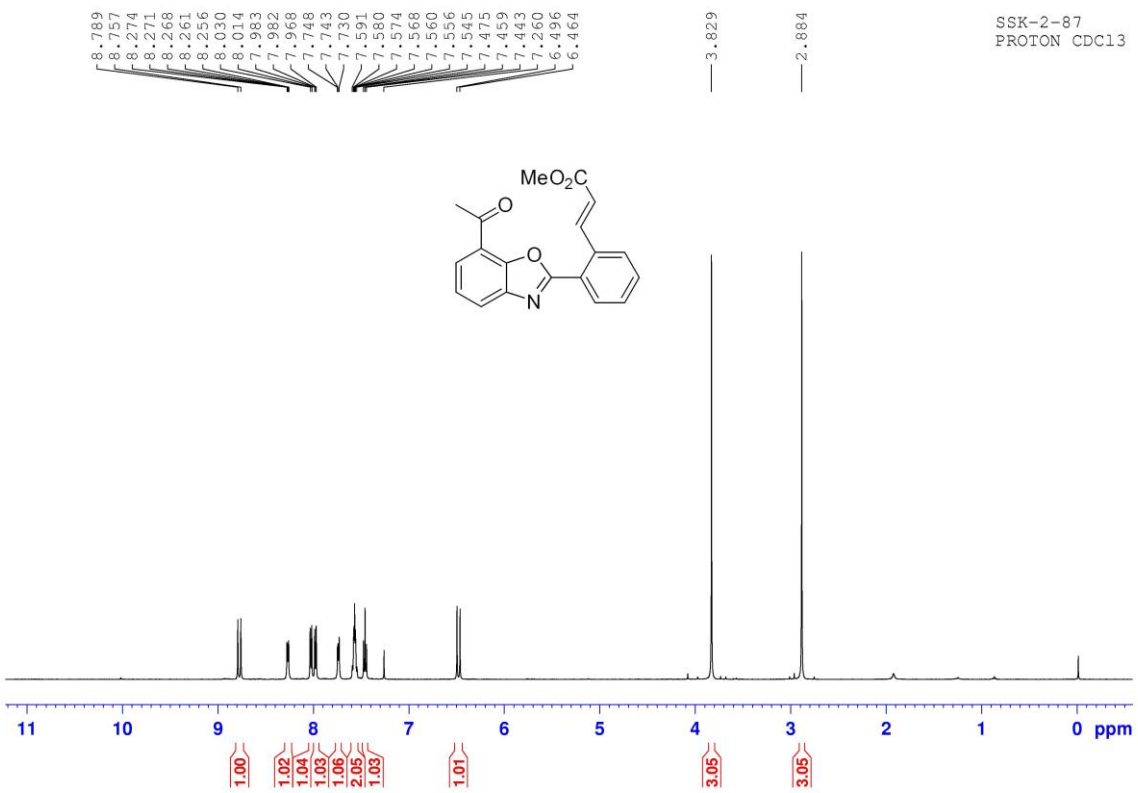

167.23
163.05
149.62
143.76
143.66
135.31
131.74
130.43
129.99
128.67
128.21
125.97
123.72
121.14
117.54
112.00
77.41
77.16
76.91
51.99
SSK-2-80
C13CPD CDCl3
MeO2C
O
N
Br
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

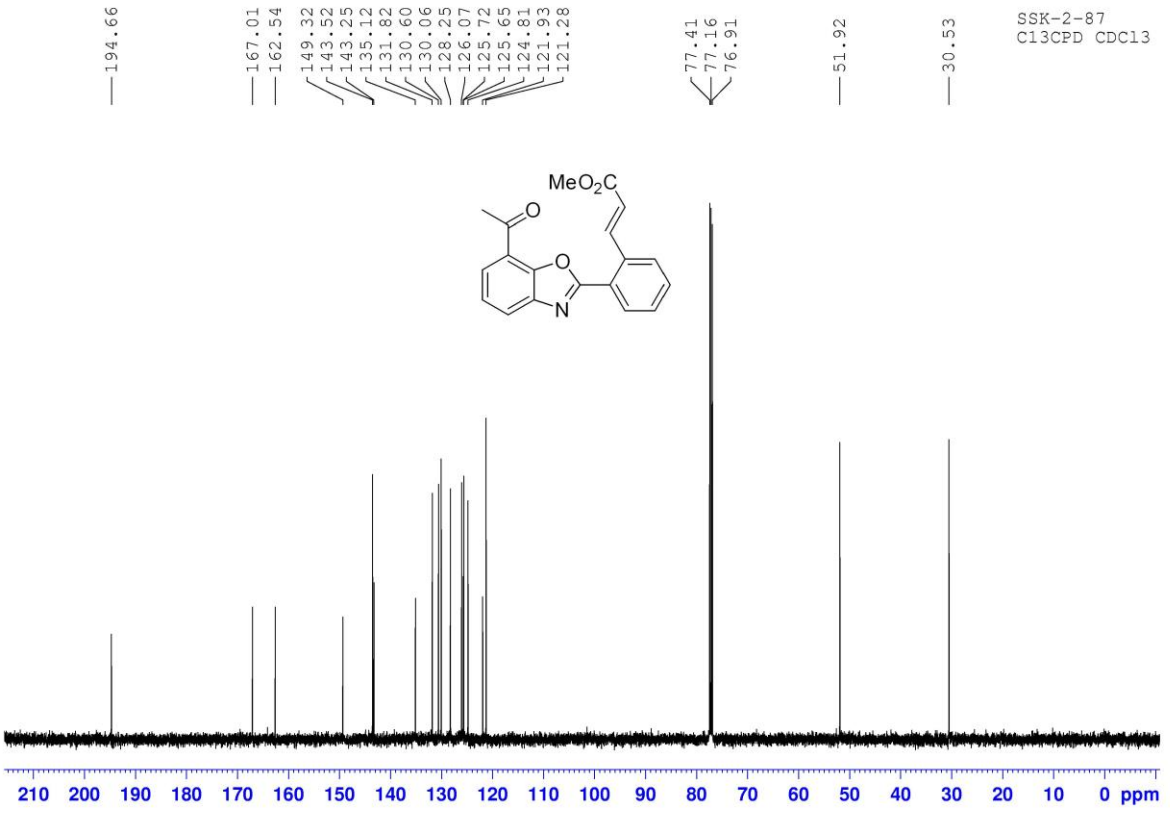
Compound **3g**


8.801
8.769
8.201
8.199
8.187
8.183
7.828
7.824
7.748
7.744
7.730
7.581
7.577
7.566
7.563
7.552
7.535
7.518
7.511
7.507
7.366
7.362
7.348
7.345
7.260
6.485
6.453
3.846
SSK-2-79
PROTON CDCl3
MeO2C
O
N
Cl
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.03
1.00
1.07
3.28
1.05
1.05
3.06

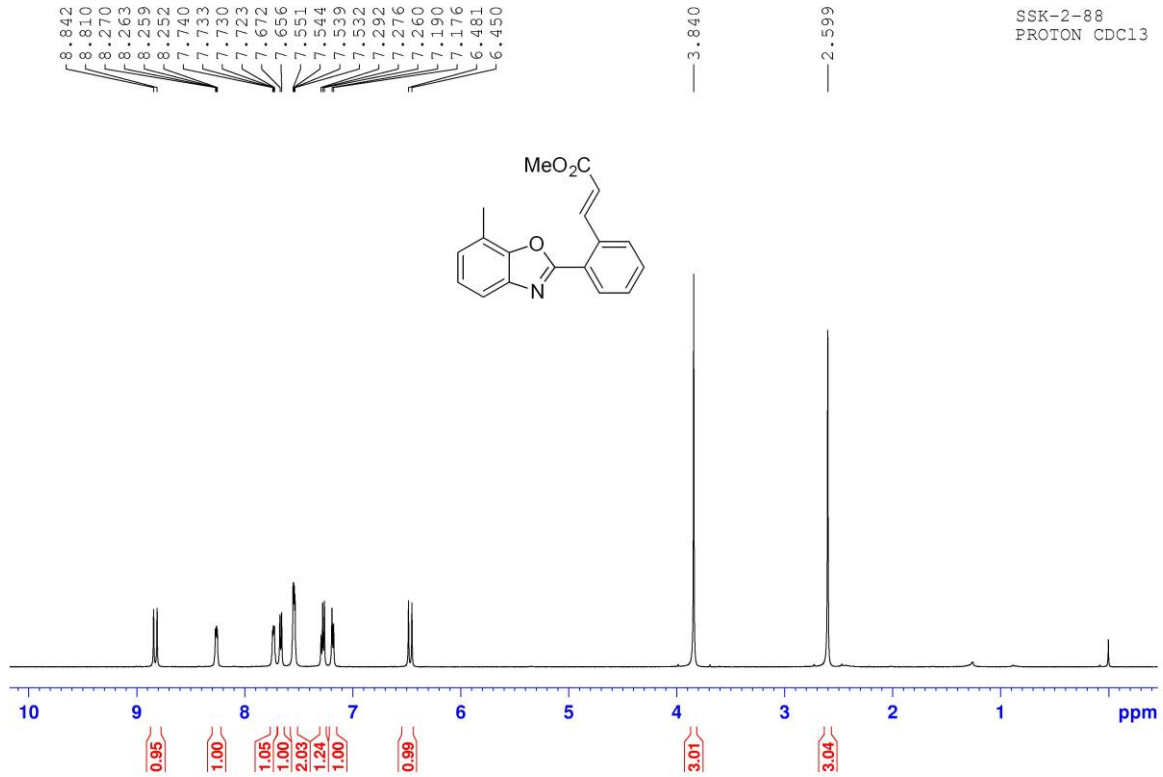

167.22
163.25
149.21
143.66
143.29
135.30
131.72
130.42
130.30
129.99
128.21
126.02
125.96
121.15
120.69
111.50
77.41
77.16
76.91
51.99
SSK-2-79
C13CPD CDCl3
MeO2C
O
N
Cl
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

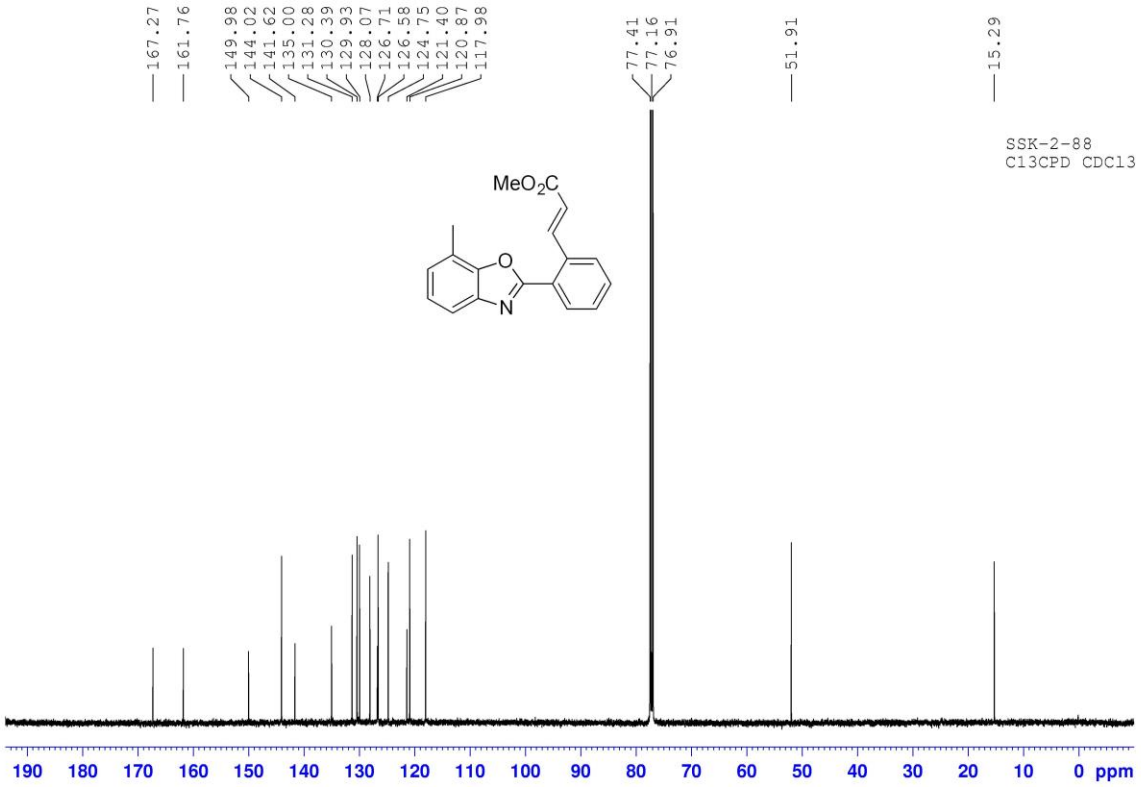
Compound **3h**


8.789
8.757
8.274
8.271
8.268
8.261
8.256
8.030
8.014
7.983
7.982
7.968
7.748
7.743
7.730
7.591
7.580
7.574
7.568
7.560
7.556
7.545
7.475
7.459
7.443
7.260
6.496
6.464
3.829
2.884
SSK-2-87
PROTON CDCl3
MeO2C
O
O
N
11
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.02
1.04
1.03
1.06
2.05
1.03
1.01
3.05
3.05

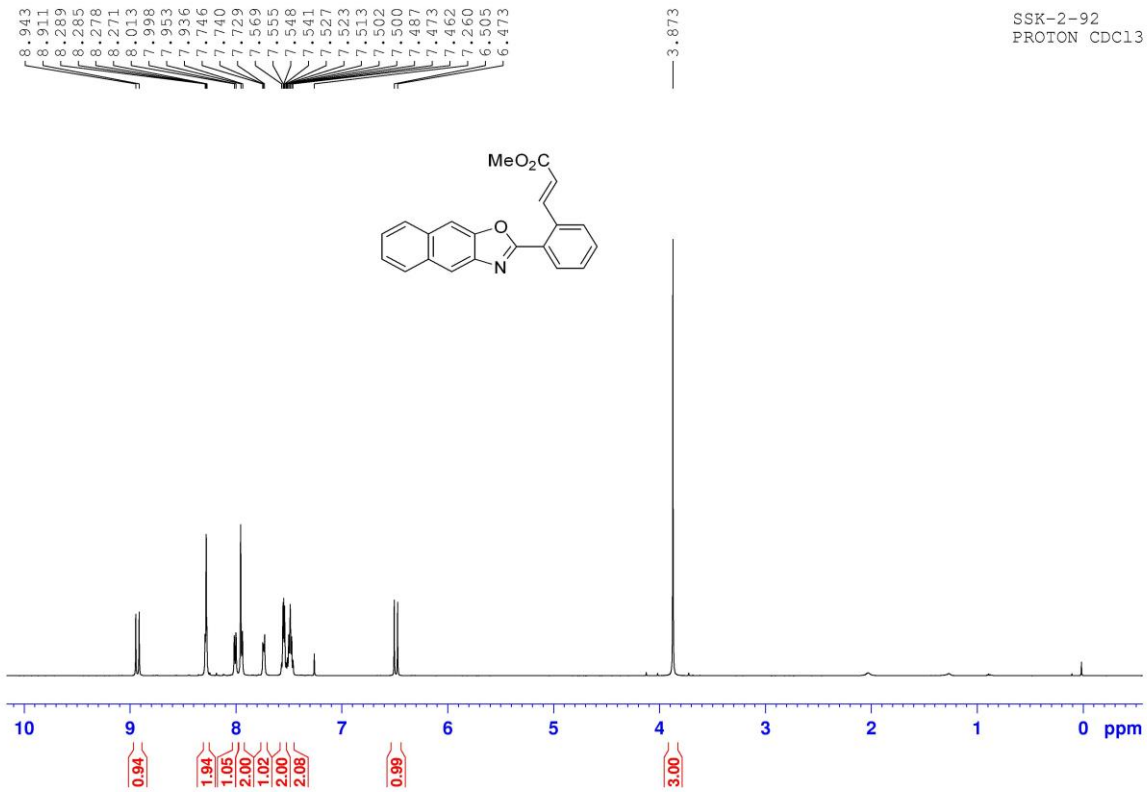

194.66
167.01
162.54
149.32
143.52
143.25
135.12
131.82
130.60
130.06
128.25
126.07
125.72
125.65
124.81
121.93
121.28
77.41
77.16
76.91
51.92
30.53
SSK-2-87
C13CPD CDCl3
MeO2C
O
O
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

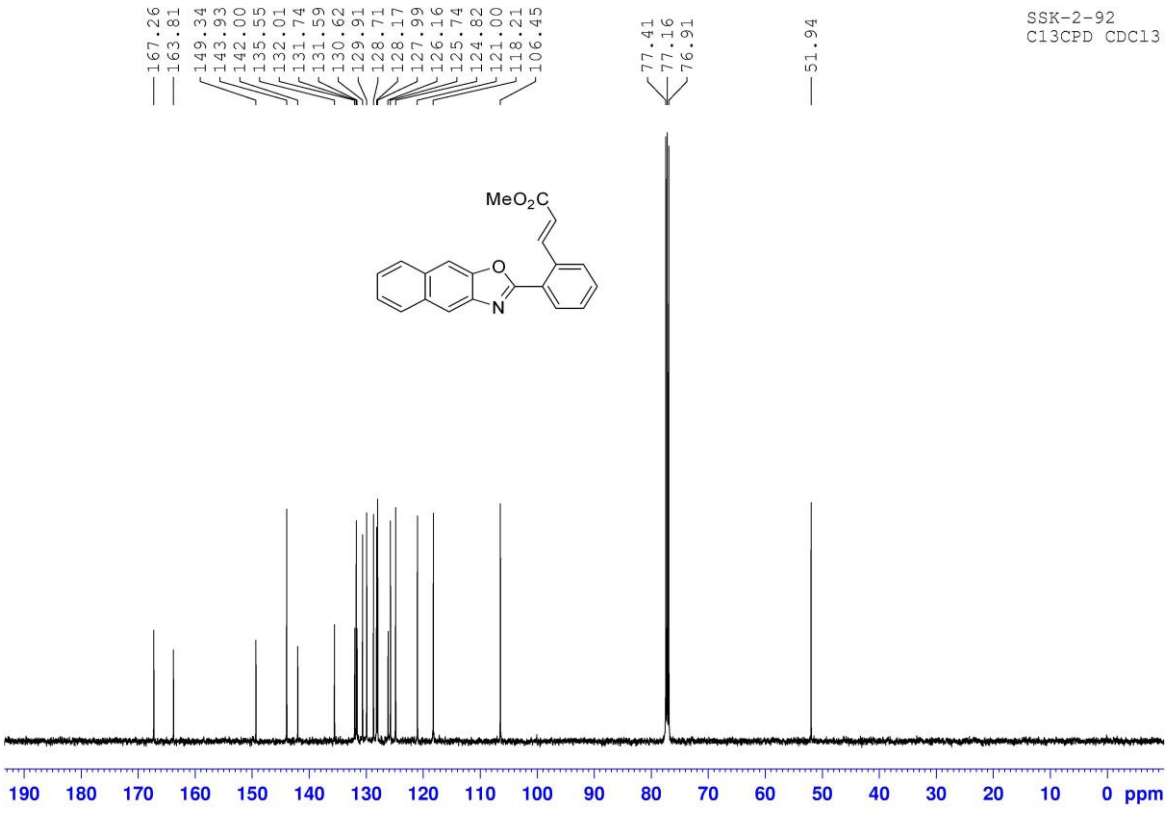
Compound **3i**


8.842
8.810
8.270
8.263
8.259
8.252
7.740
7.733
7.730
7.723
7.672
7.656
7.551
7.544
7.539
7.532
7.292
7.276
7.260
7.190
7.176
6.481
6.450
3.840
2.599
SSK-2-88
PROTON CDCl3
MeO2C
O
N
10
9
8
7
6
5
4
3
2
1
ppm
0.95
1.00
1.05
1.00
2.03
1.24
1.00
0.99
3.01
3.04

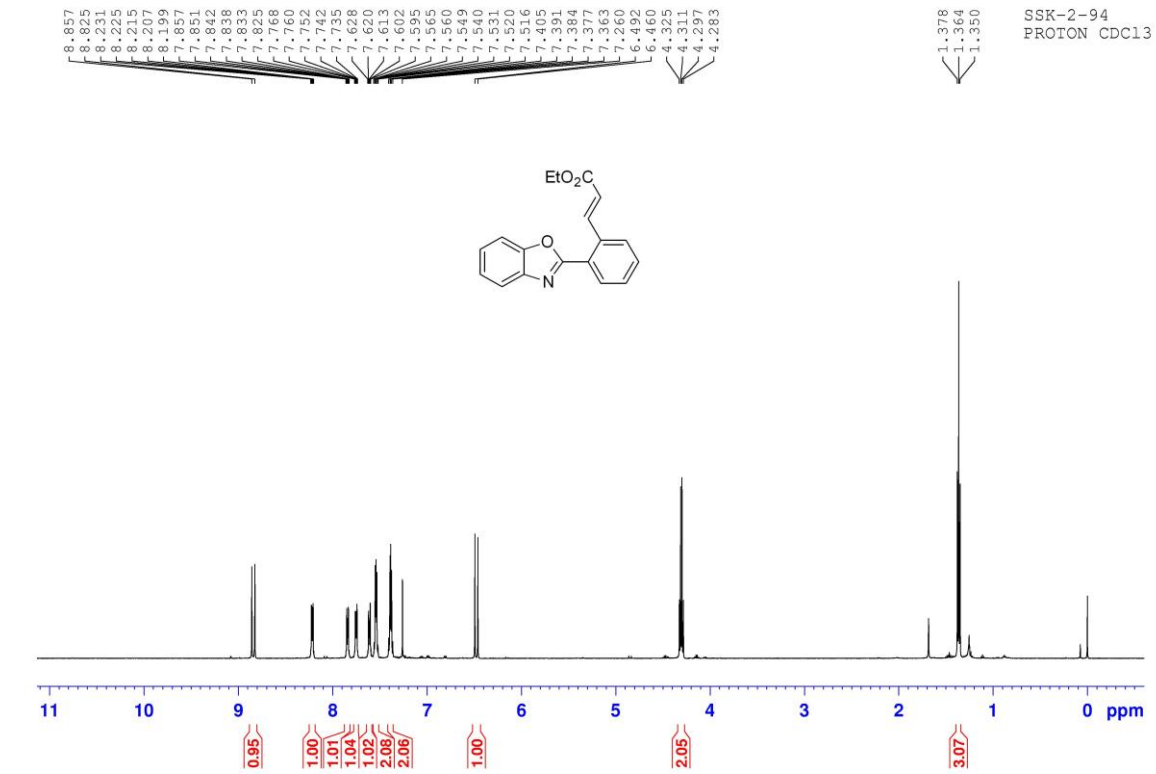

167.27
161.76
149.98
144.02
141.62
135.00
131.28
130.39
129.93
128.07
126.71
126.58
124.75
121.40
120.87
117.98
77.41
77.16
76.91
51.91
15.29
SSK-2-88
C13CPD CDCl3
MeO2C
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

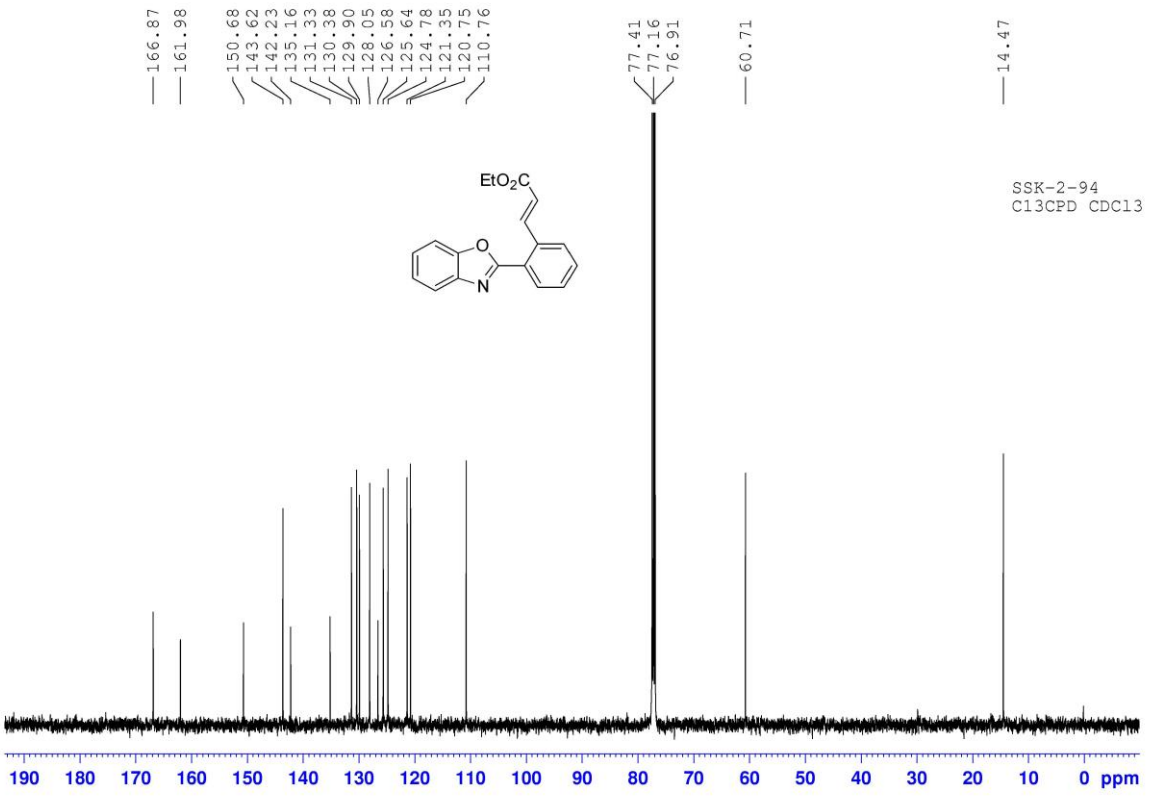
Compound **3j**


8.943
8.911
8.289
8.285
8.278
8.271
8.013
7.998
7.953
7.936
7.746
7.740
7.729
7.569
7.555
7.548
7.541
7.527
7.523
7.513
7.502
7.500
7.487
7.473
7.462
7.260
6.505
6.473
3.873
SSK-2-92
PROTON CDCl3
MeO2C
O
N
10
9
8
7
6
5
4
3
2
1
0 ppm
0.94
1.94
1.05
2.00
1.02
2.00
2.08
0.99
3.00

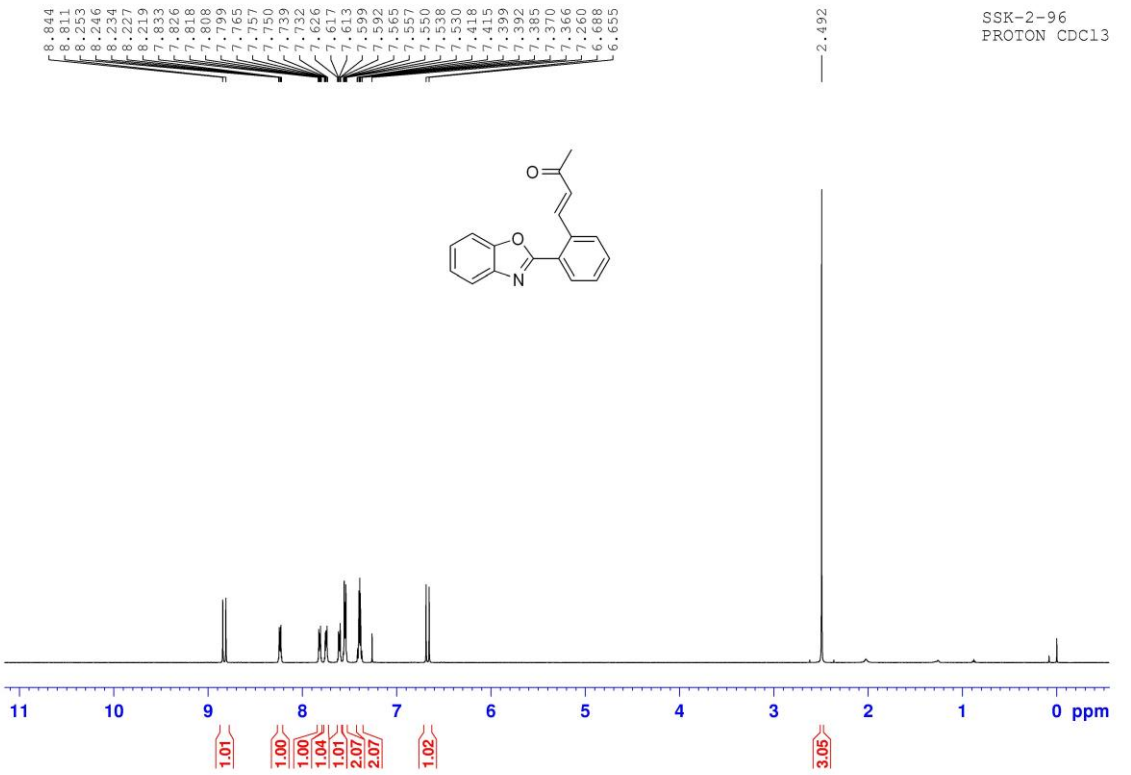

167.26
163.81
149.34
143.93
142.00
135.55
132.01
131.74
131.59
130.62
129.91
128.71
128.17
127.99
126.16
125.74
124.82
121.00
118.21
106.45
77.41
77.16
76.91
51.94
SSK-2-92
C13CPD CDCl3
MeO2C
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

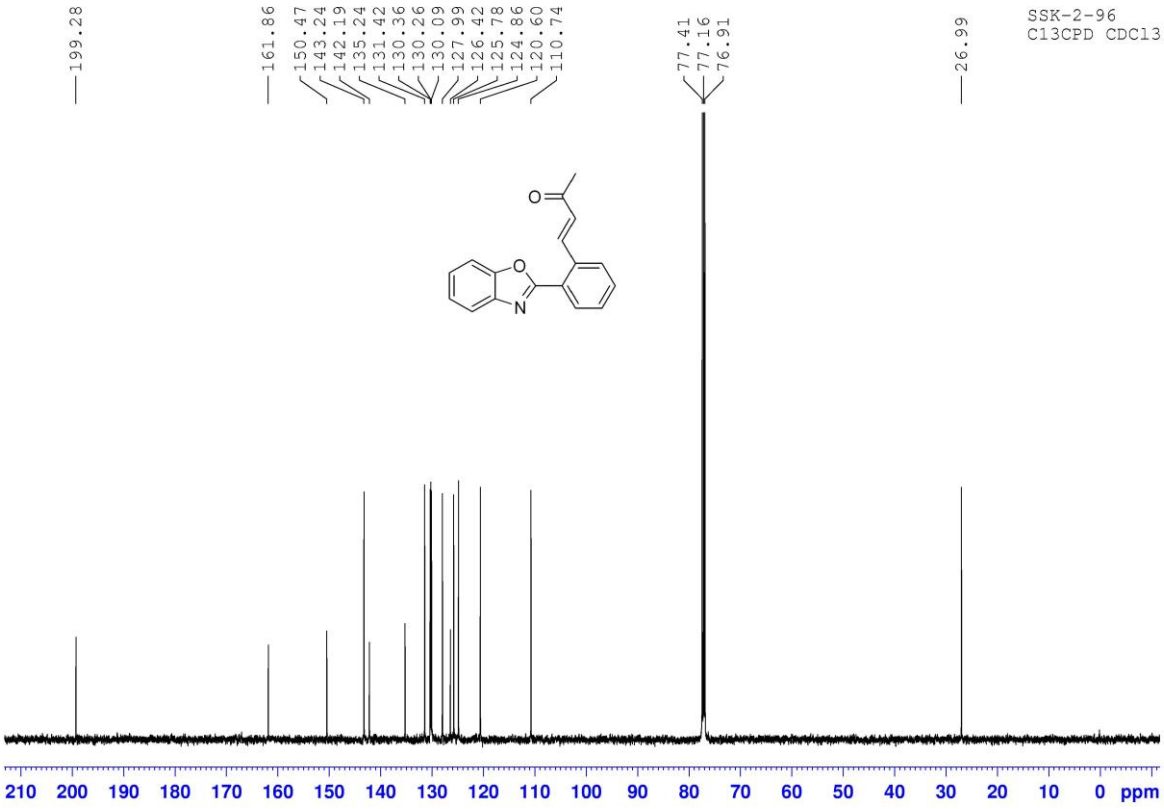
Compound **3k**


8.857
8.825
8.231
8.225
8.215
8.207
8.199
7.857
7.851
7.842
7.838
7.833
7.825
7.768
7.760
7.752
7.742
7.735
7.628
7.620
7.613
7.602
7.595
7.565
7.560
7.549
7.540
7.531
7.520
7.516
7.405
7.391
7.384
7.377
7.363
7.260
6.492
6.460
4.325
4.311
4.297
4.283
1.378
1.364
1.350
SSK-2-94
PROTON CDCl3
EtO2C
O
N
11
10
9
8
7
6
5
4
3
2
1
0 ppm
0.95
1.00
1.01
1.04
1.02
2.08
2.06
1.00
2.05
3.07

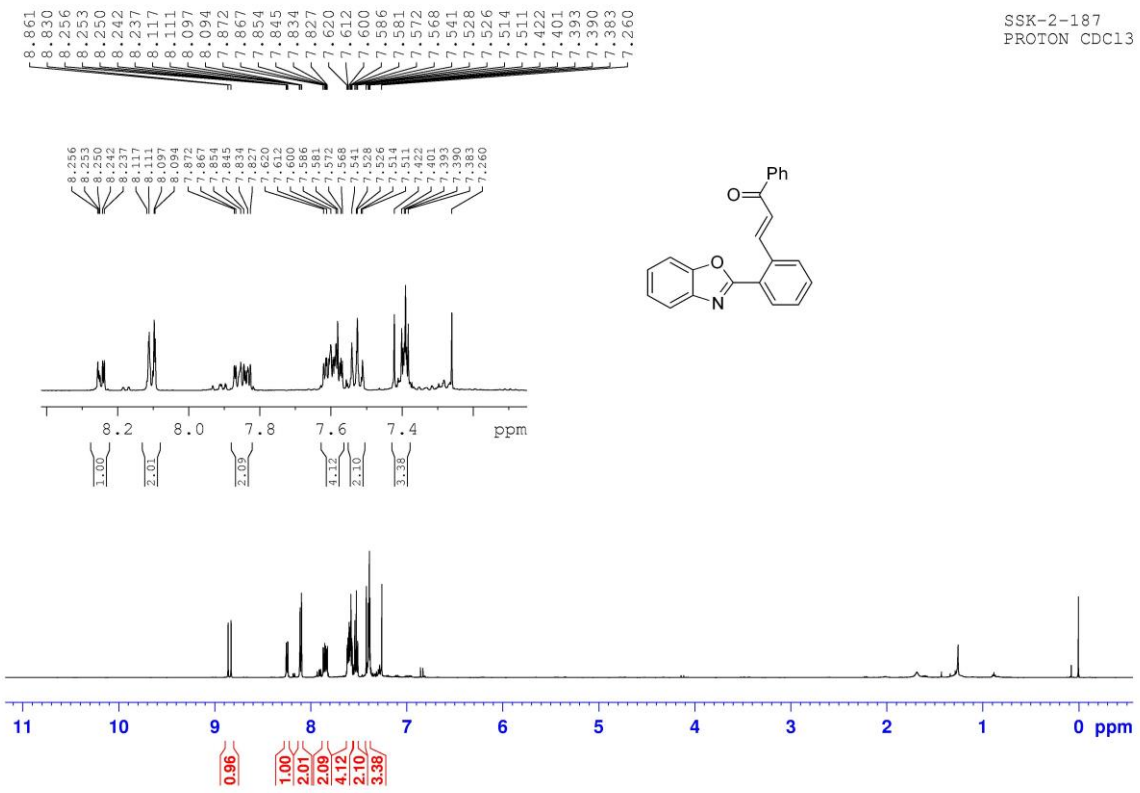

166.87
161.98
150.68
143.62
142.23
135.16
131.33
130.38
129.90
128.05
126.58
125.64
124.78
121.35
120.75
110.76
77.41
77.16
76.91
60.71
14.47
EtO2C
O
N
SSK-2-94
C13CPD CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

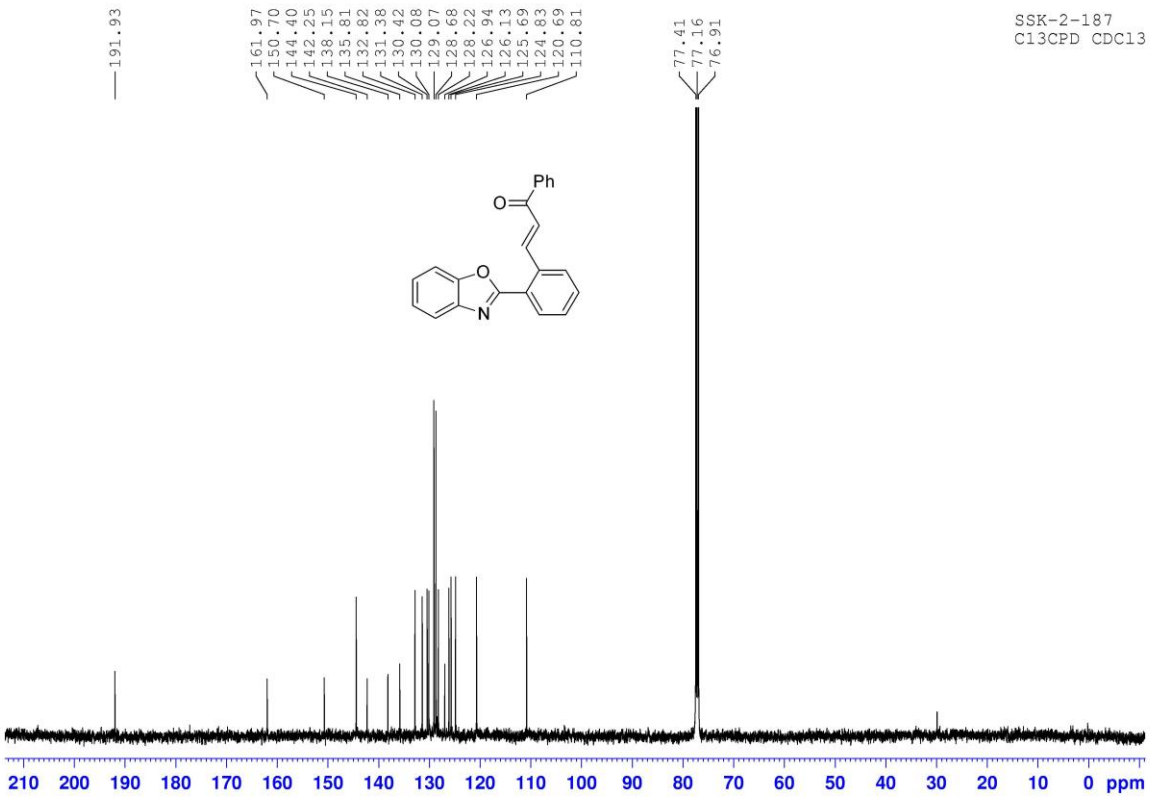
Compound **3l**


8.844
8.811
8.253
8.246
8.234
8.227
8.219
7.833
7.826
7.818
7.808
7.799
7.765
7.757
7.750
7.739
7.732
7.626
7.617
7.613
7.599
7.592
7.565
7.557
7.550
7.538
7.530
7.418
7.415
7.399
7.392
7.385
7.370
7.366
7.260
6.688
6.655
2.492
SSK-2-96
PROTON CDCl3
O
O
N
11
10
9
8
7
6
5
4
3
2
1
0 ppm
1.01
1.00
1.00
1.04
1.01
2.07
2.07
1.02
3.05

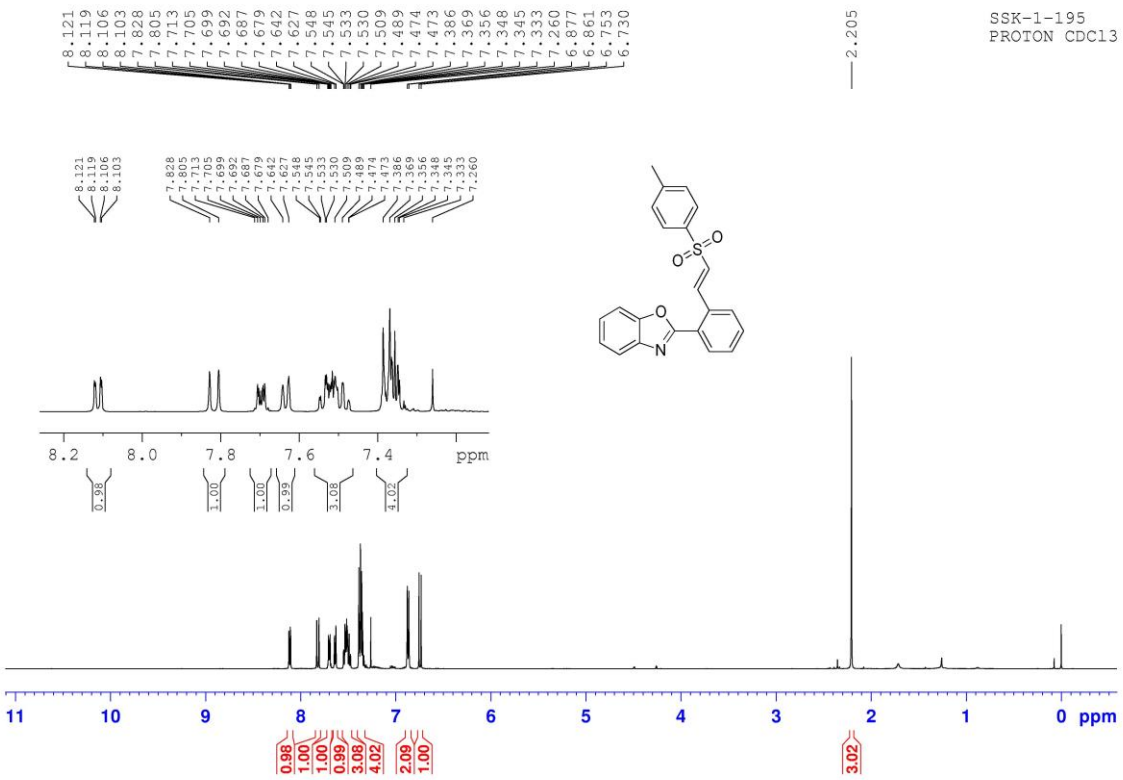

199.28
161.86
150.47
143.24
142.19
135.24
131.42
130.36
130.26
130.09
127.99
126.42
125.78
124.86
120.60
110.74
77.41
77.16
76.91
26.99
SSK-2-96
C13CPD CDCl3
O
O
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

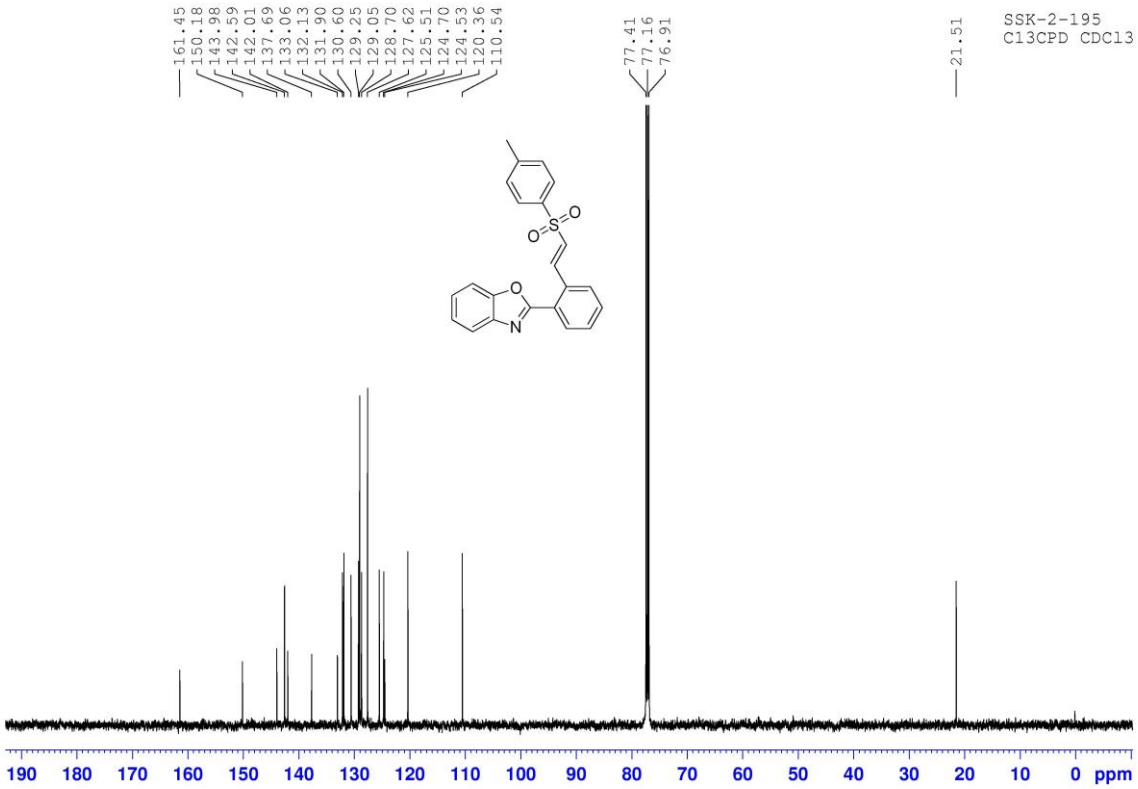
Compound **3m**


SSK-2-187
PROTON CDCl3
8.861
8.830
8.256
8.253
8.250
8.242
8.237
8.117
8.111
8.097
8.094
8.872
7.867
7.854
7.845
7.834
7.827
7.620
7.612
7.600
7.586
7.581
7.572
7.568
7.541
7.528
7.526
7.514
7.511
7.422
7.401
7.393
7.390
7.383
7.260
Ph
O
O
N
8.2
8.0
7.8
7.6
7.4
ppm
1.00
2.01
2.09
4.12
2.10
3.38
11
10
9
8
7
6
5
4
3
2
1
0 ppm
0.96
1.00
2.01
2.09
4.12
2.10
3.38

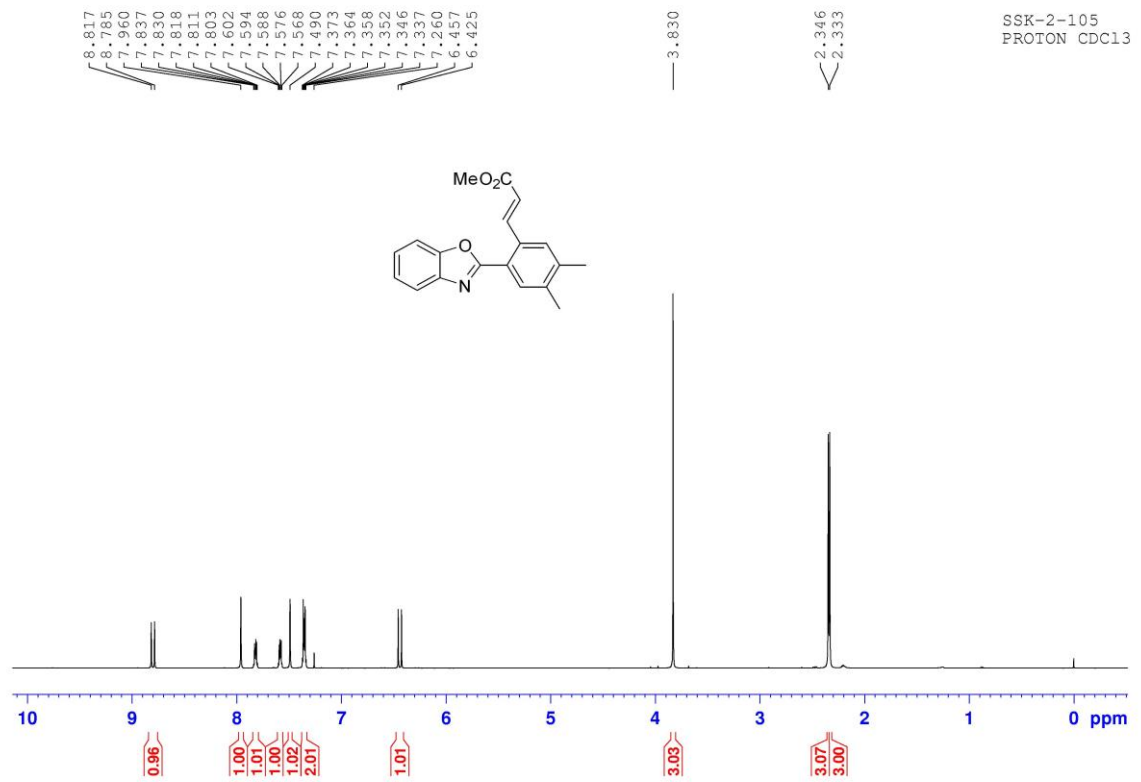

SSK-2-187
C13CPD CDCl3
191.93
161.97
150.70
144.40
142.25
138.15
135.81
132.82
131.38
130.42
130.08
129.07
128.68
128.22
126.94
126.13
125.69
124.83
120.69
110.81
77.41
77.16
76.91
Ph
O
O
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

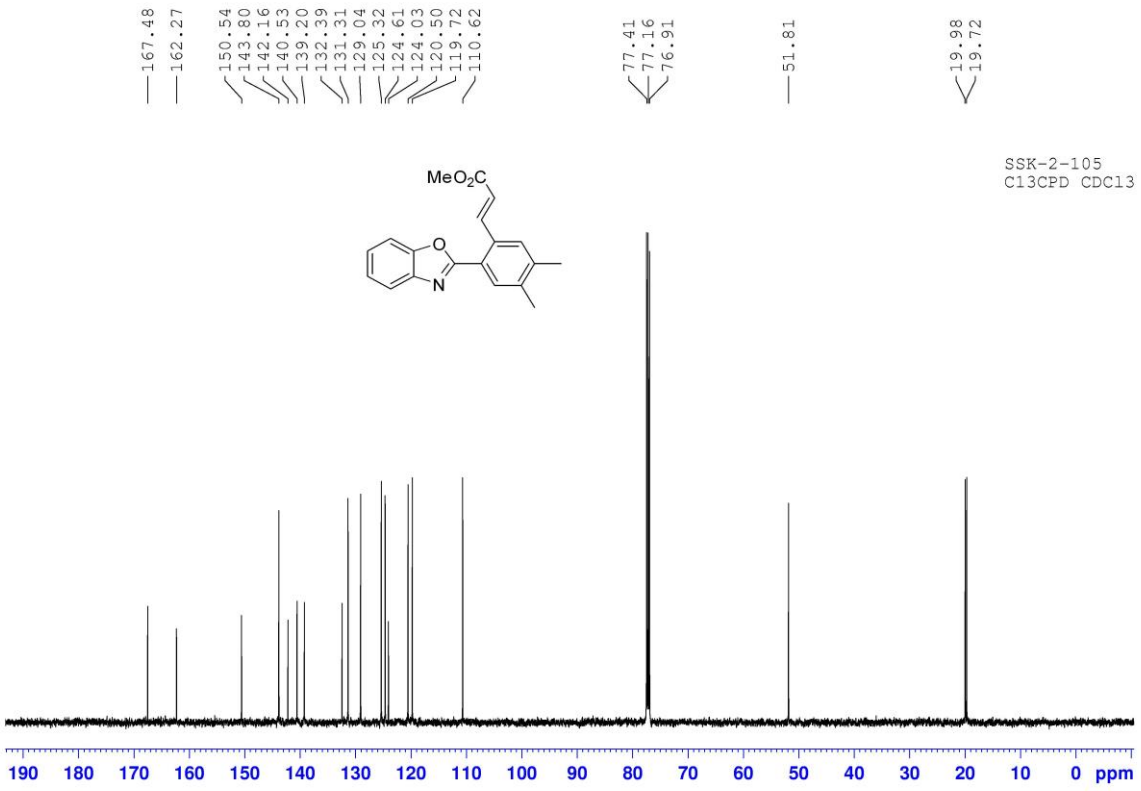
Compound **3n**


SSK-1-195
PROTON CDCl3
8.121
8.119
8.106
8.103
7.828
7.805
7.713
7.705
7.699
7.692
7.687
7.679
7.642
7.627
7.548
7.545
7.533
7.530
7.509
7.489
7.474
7.473
7.386
7.369
7.356
7.348
7.345
7.333
7.260
6.877
6.861
6.753
6.730
2.205
8.2
8.0
7.8
7.6
7.4
ppm
0.98
1.00
1.00
0.99
3.08
4.02
2.09
1.00
3.02
11
10
9
8
7
6
5
4
3
2
1
0 ppm

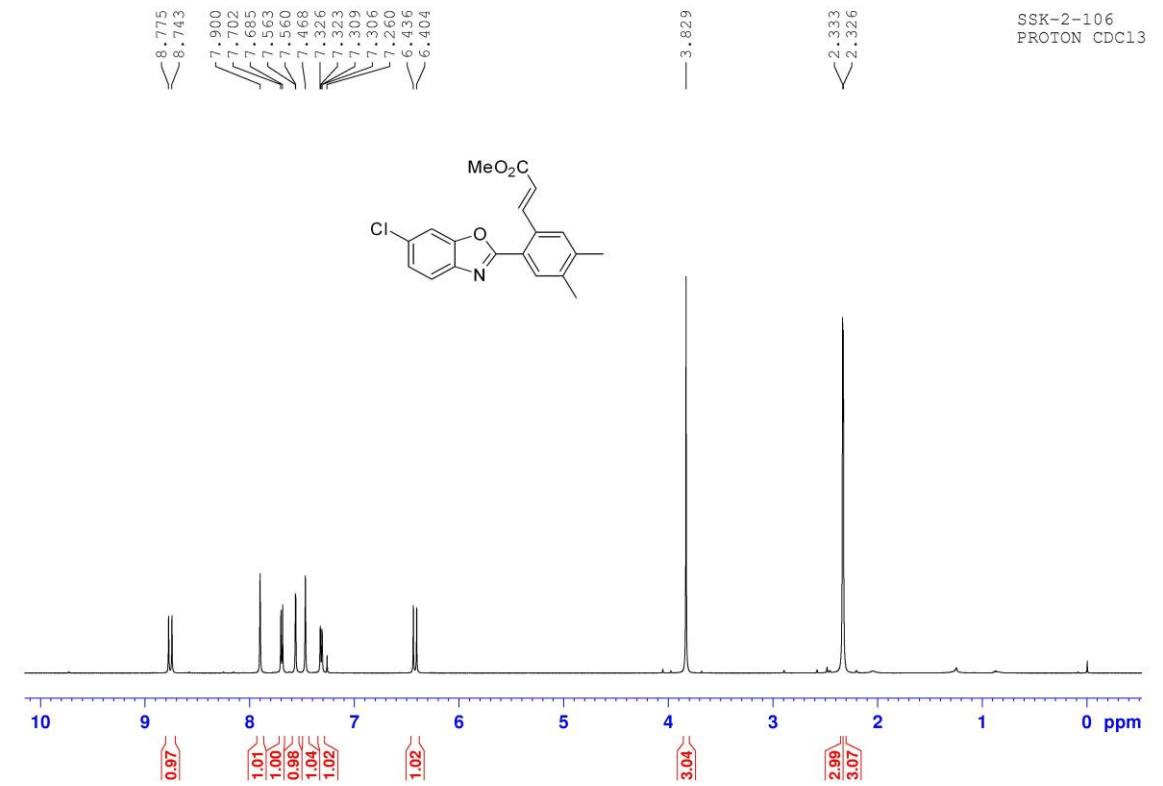

SSK-2-195
C13CPD CDCl3
161.45
150.18
143.98
142.59
142.01
137.69
133.06
132.13
131.90
130.60
129.25
129.05
128.70
127.62
125.51
124.70
124.53
120.36
110.54
77.41
77.16
76.91
21.51
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

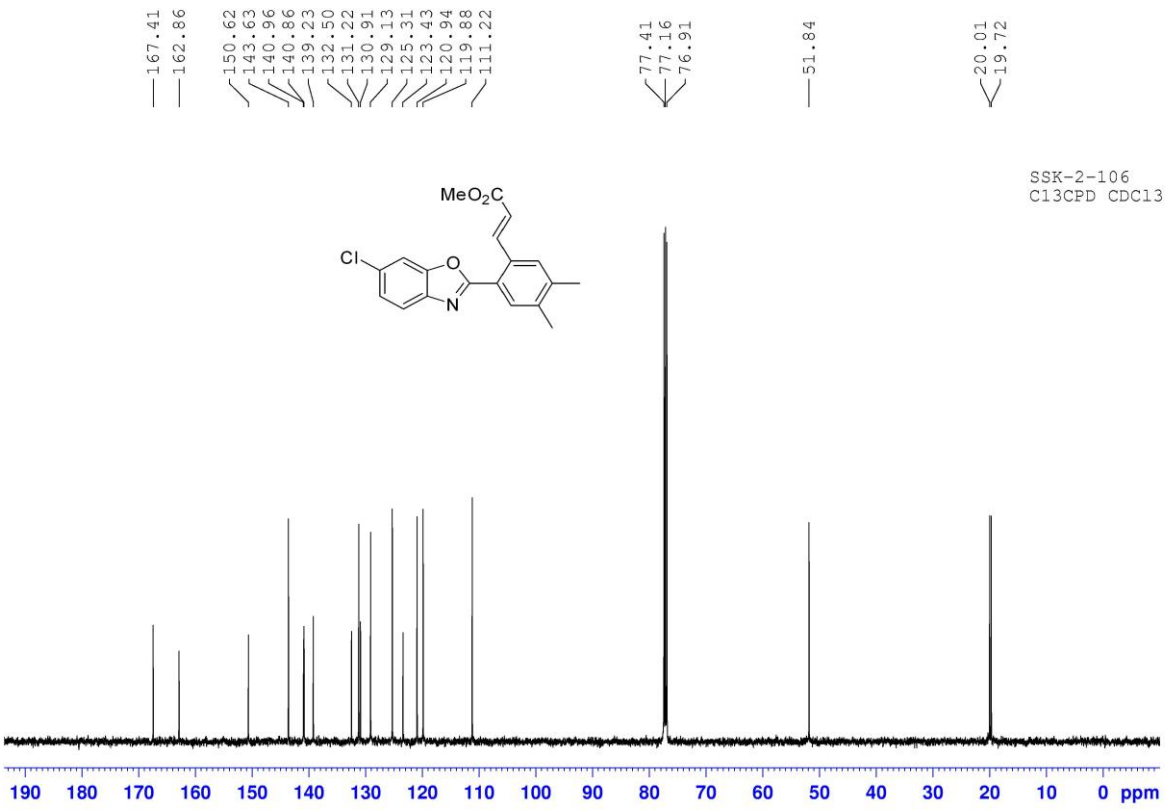
Compound **4a**


8.817
8.785
7.960
7.837
7.830
7.818
7.811
7.803
7.602
7.594
7.588
7.576
7.568
7.490
7.373
7.364
7.358
7.352
7.346
7.337
7.260
6.457
6.425
3.830
2.346
2.333
SSK-2-105
PROTON CDCl3
MeO2C
O
N
10
9
8
7
6
5
4
3
2
1
0 ppm
0.96
1.00
1.01
1.00
1.02
2.01
1.01
3.03
3.07
3.00

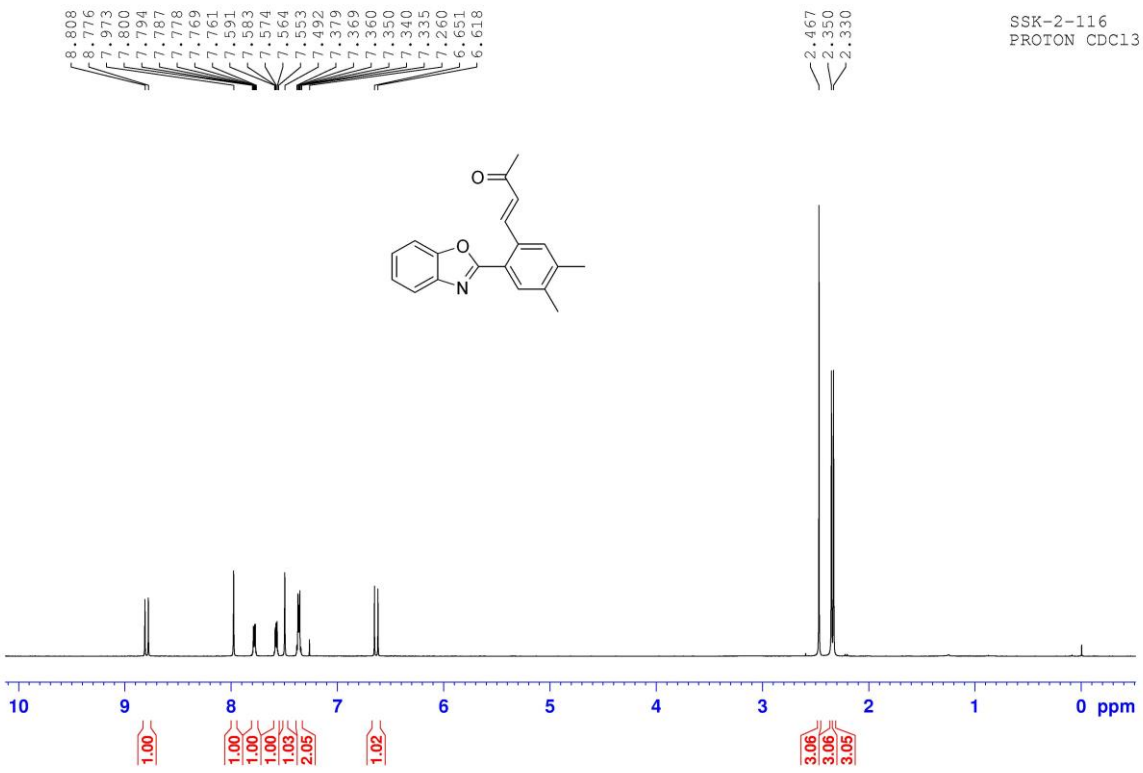

167.48
162.27
150.54
143.80
142.16
140.53
139.20
132.39
131.31
129.04
125.32
124.61
124.03
120.50
119.72
110.62
77.41
77.16
76.91
51.81
19.98
19.72
SSK-2-105
C13CPD CDCl3
MeO2C
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

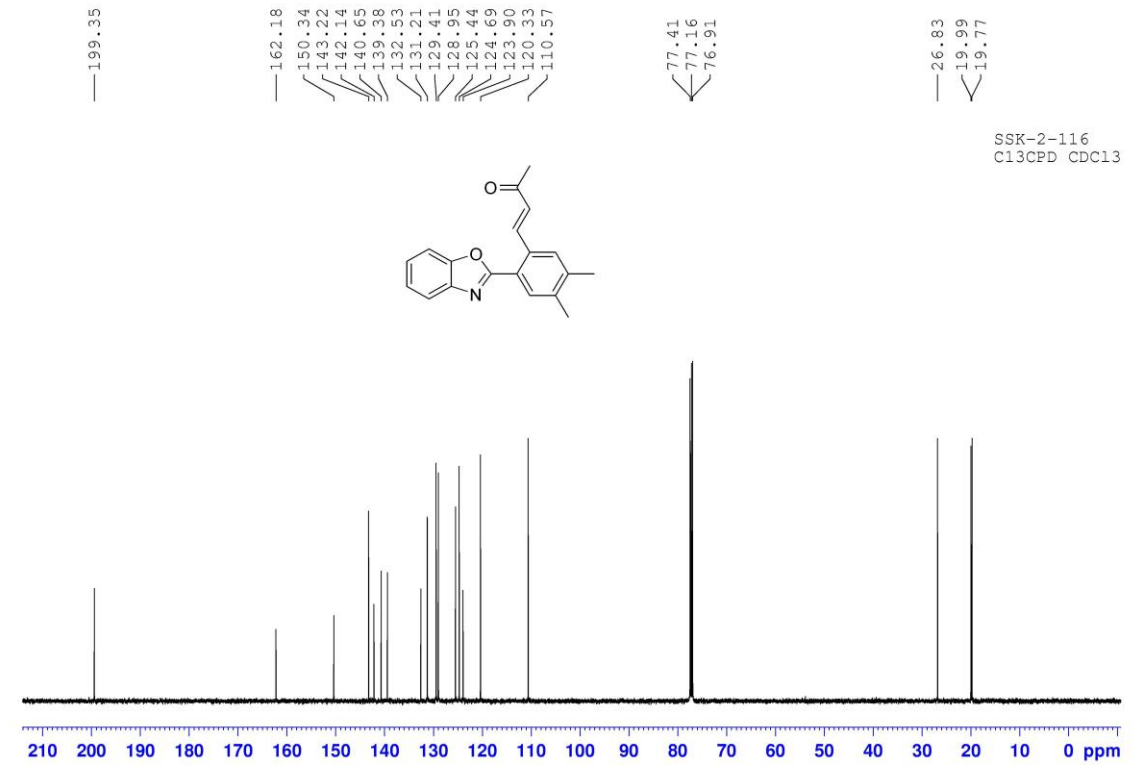
Compound **4b**


8.775
8.743
7.900
7.702
7.685
7.563
7.560
7.468
7.326
7.323
7.309
7.306
7.260
6.436
6.404
3.829
2.333
2.326
SSK-2-106
PROTON CDCl3
MeO2C
Cl
O
N
10
9
8
7
6
5
4
3
2
1
0 ppm
0.97
1.01
1.00
0.98
1.04
1.02
1.02
3.04
2.99
3.07

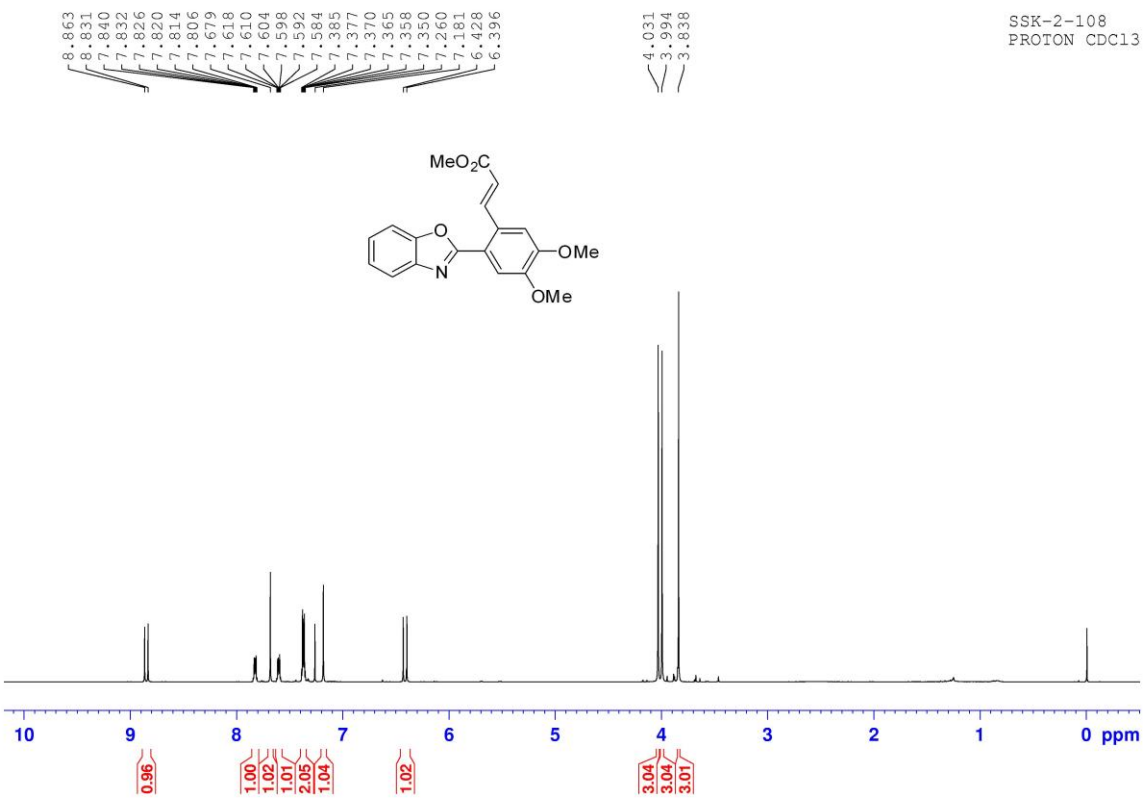

167.41
162.86
150.62
143.63
140.96
140.86
139.23
132.50
131.22
130.91
129.13
125.31
123.43
120.94
119.88
111.22
77.41
77.16
76.91
51.84
20.01
19.72
SSK-2-106
C13CPD CDCl3
MeO2C
Cl
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

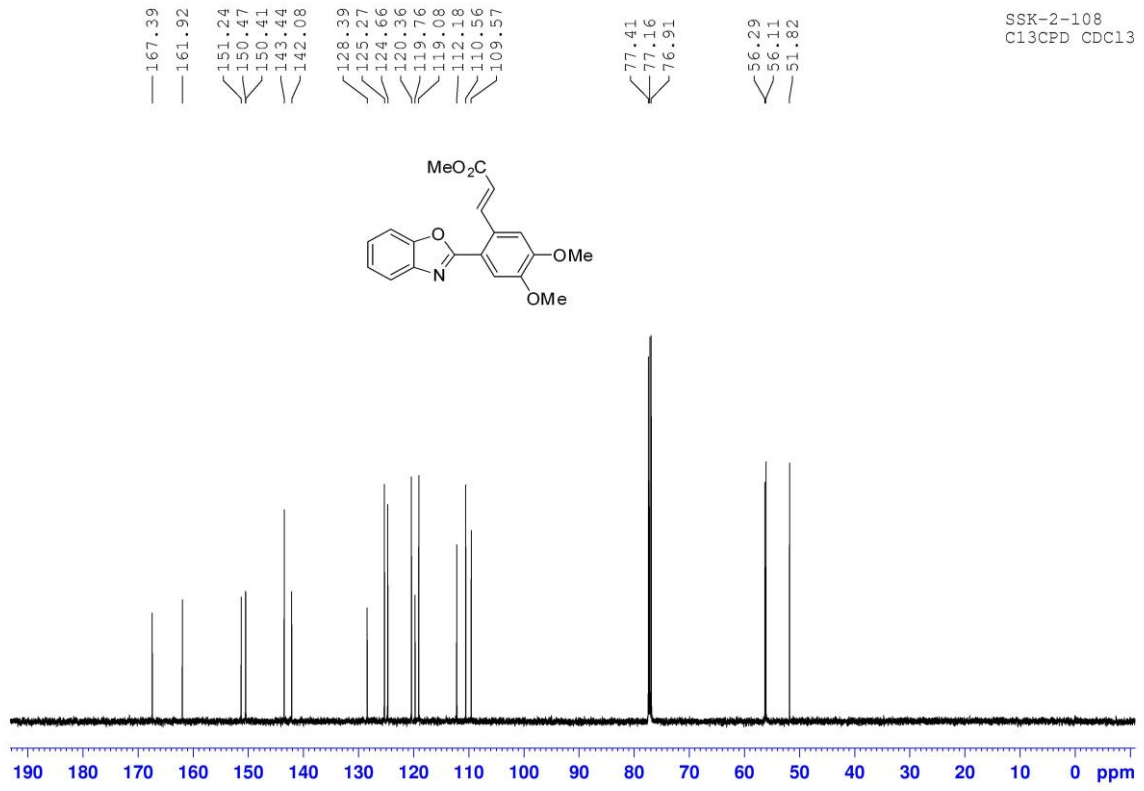
Compound **4c**


8.808
8.776
7.973
7.800
7.794
7.787
7.778
7.769
7.761
7.591
7.583
7.574
7.564
7.553
7.492
7.379
7.369
7.360
7.350
7.340
7.335
7.260
6.651
6.618
2.467
2.350
2.330
SSK-2-116
PROTON CDCl3
O
O
N
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.00
1.00
1.00
1.03
2.05
1.02
3.06
3.06
3.05

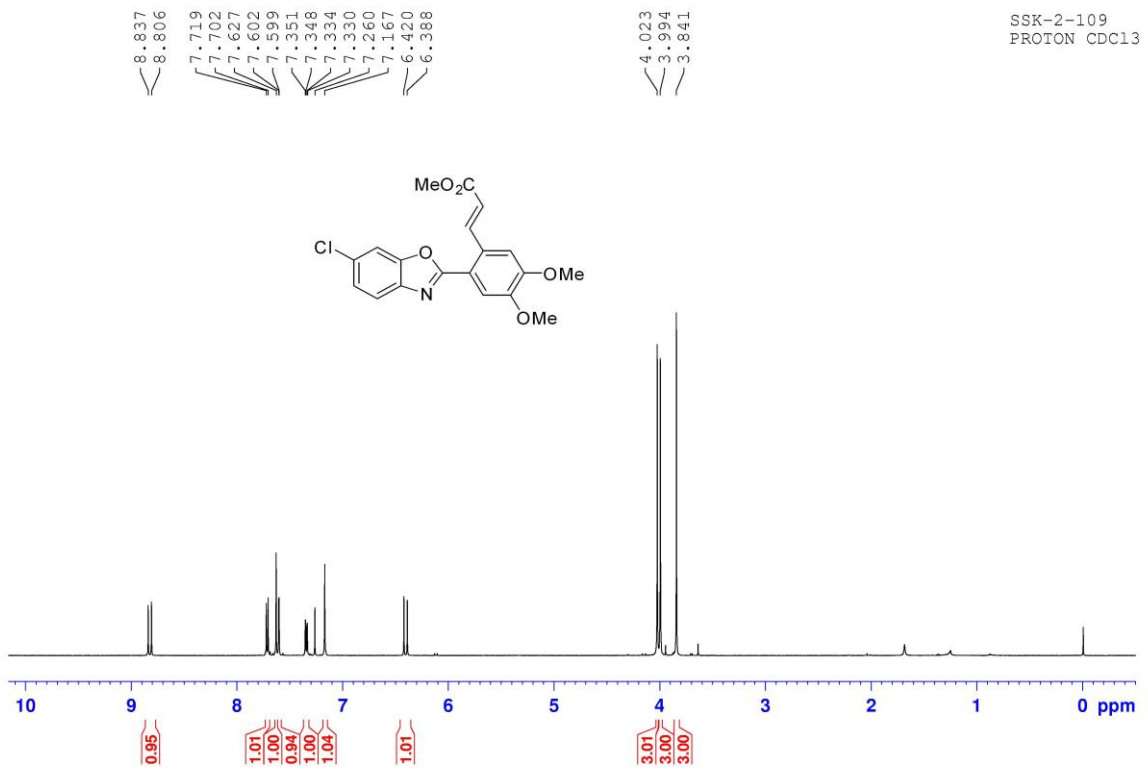

199.35
162.18
150.34
143.22
142.14
140.65
139.38
132.53
131.21
129.41
128.95
125.44
124.69
123.90
120.33
110.57
77.41
77.16
76.91
26.83
19.99
19.77
SSK-2-116
C13CPD CDCl3
O
O
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

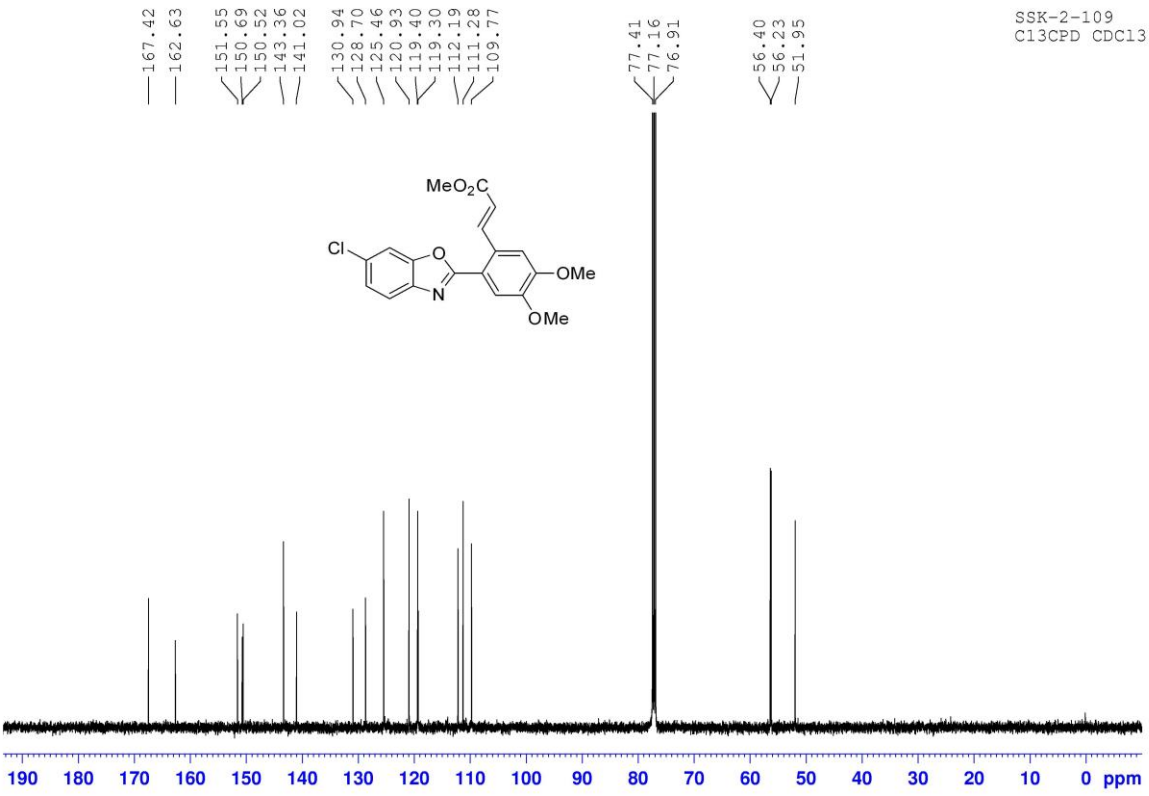
Compound **4d**


8.863
8.831
7.840
7.832
7.826
7.820
7.814
7.806
7.679
7.618
7.610
7.604
7.598
7.592
7.584
7.385
7.377
7.370
7.365
7.358
7.350
7.260
7.181
6.428
6.396
4.031
3.994
3.838
SSK-2-108
PROTON CDC13
MeO2C
OMe
OMe
10 9 8 7 6 5 4 3 2 1 0 ppm
0.96
1.00
1.02
1.01
2.05
1.04
1.02
3.04
3.04
3.01

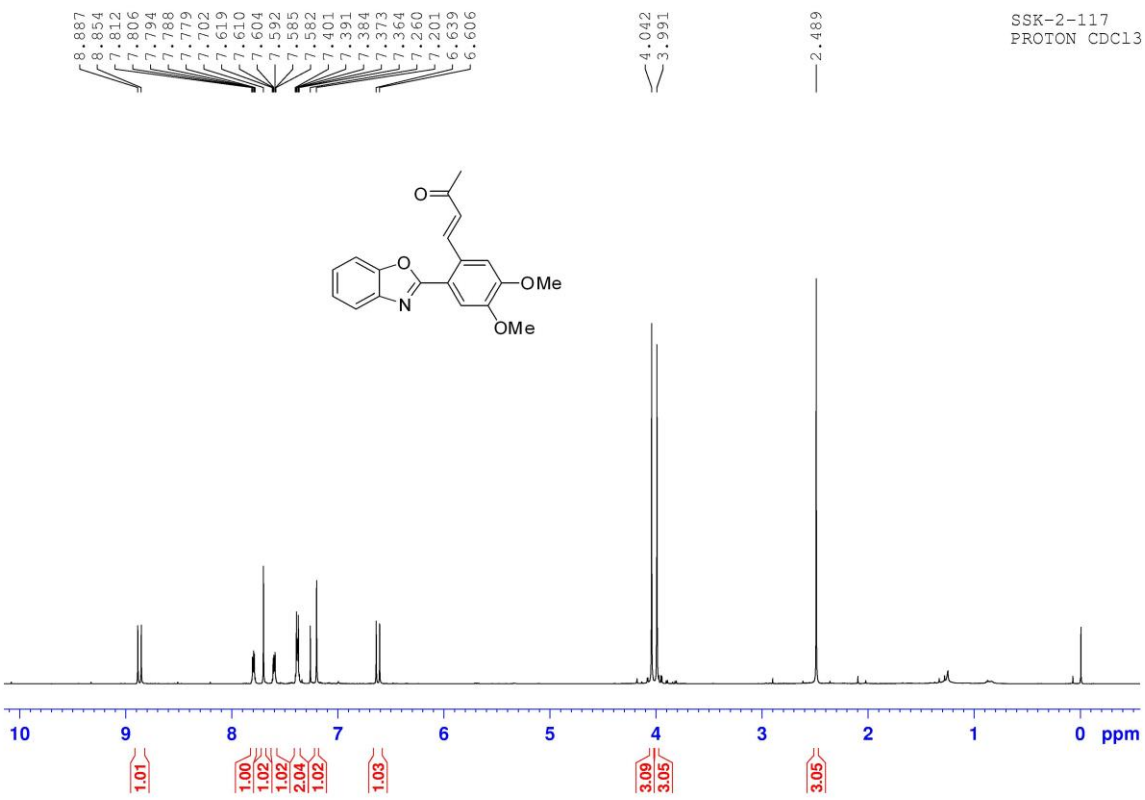

167.39
161.92
151.24
150.47
150.41
143.44
142.08
128.39
125.27
124.66
120.36
119.76
119.08
112.18
110.56
109.57
77.41
77.16
76.91
56.29
56.11
51.82
SSK-2-108
C13CPD CDC13
MeO2C
OMe
OMe
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

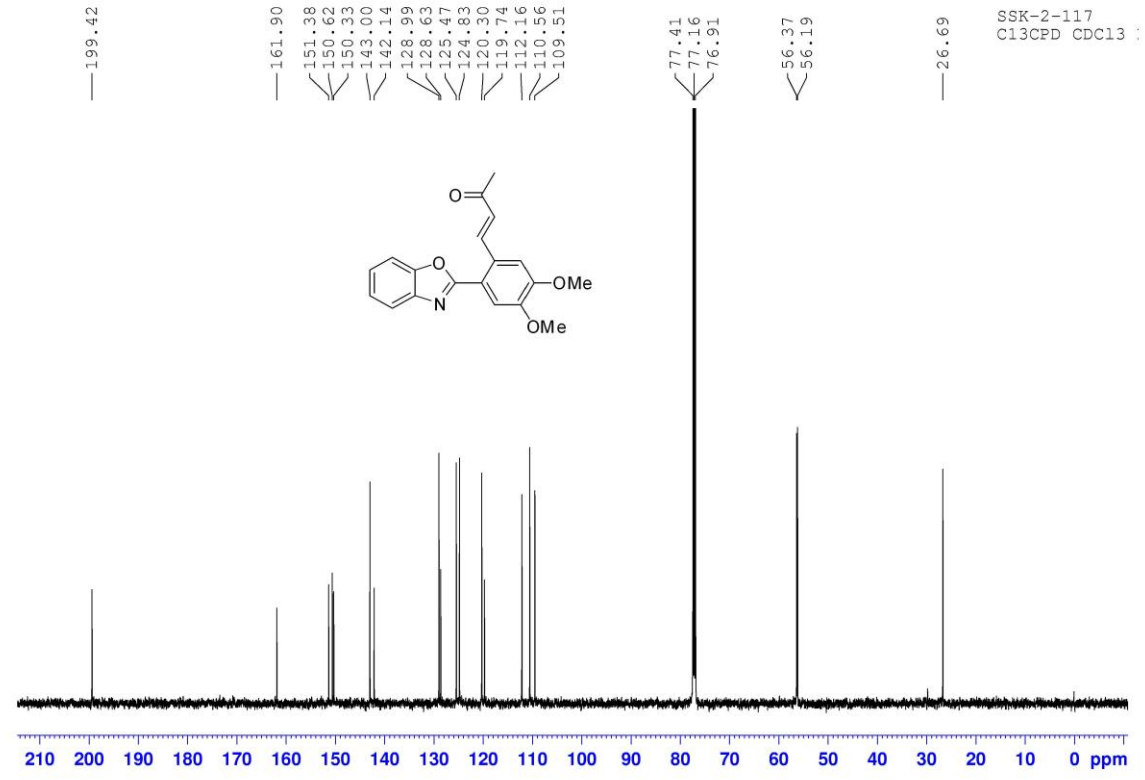
Compound **4e**


8.837
8.806
7.719
7.702
7.627
7.602
7.599
7.351
7.348
7.334
7.330
7.260
7.167
6.420
6.388
4.023
3.994
3.841
SSK-2-109
PROTON CDCl3
MeO2C
Cl
O
N
OMe
OMe
10
9
8
7
6
5
4
3
2
1
0 ppm
0.95
1.01
1.00
0.94
1.00
1.04
1.01
3.01
3.00
3.00

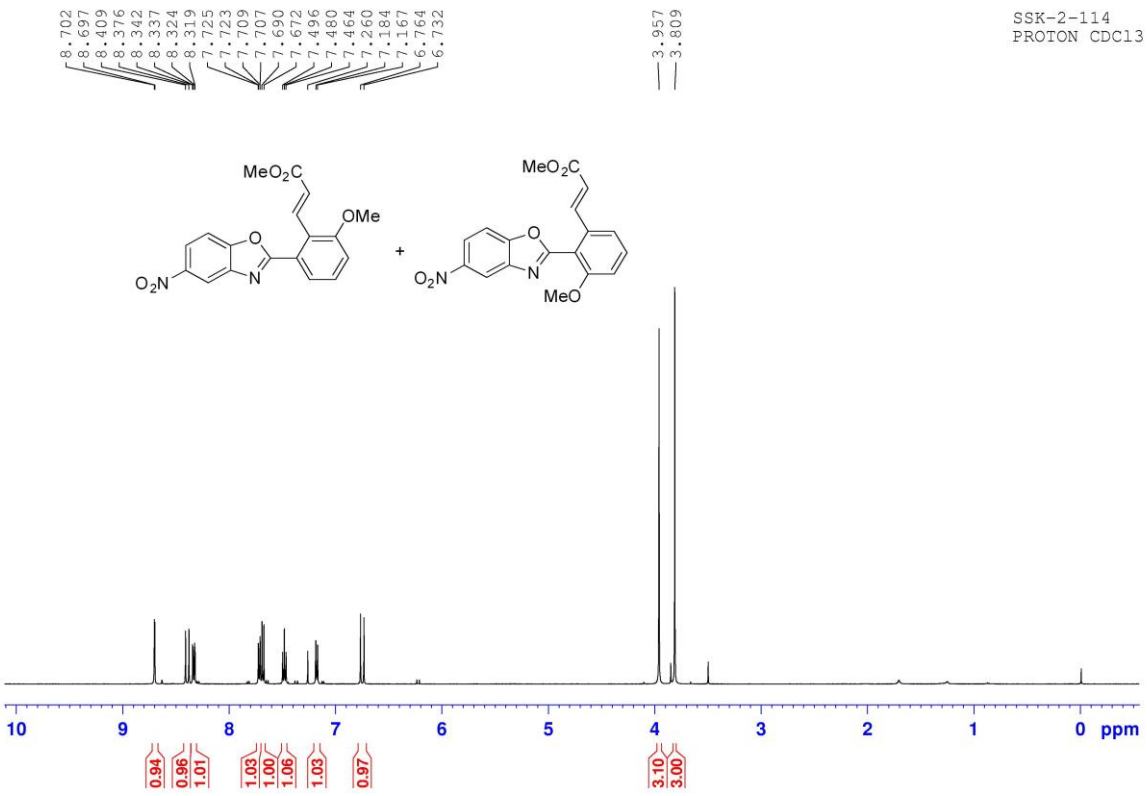

167.42
162.63
151.55
150.69
150.52
143.36
141.02
130.94
128.70
125.46
120.93
119.40
119.30
112.19
111.28
109.77
77.41
77.16
76.91
56.40
56.23
51.95
SSK-2-109
C13CPD CDCl3
MeO2C
Cl
O
N
OMe
OMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

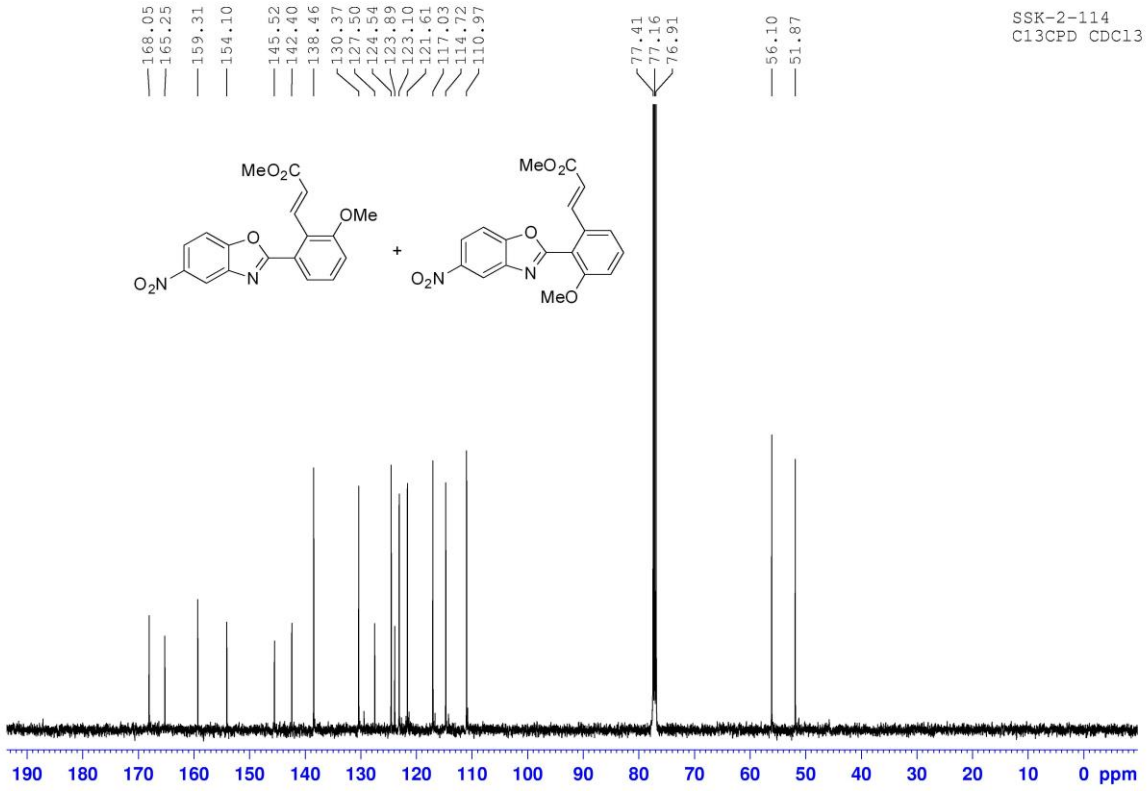
Compound **4f**


8.887
8.854
7.812
7.806
7.794
7.788
7.779
7.702
7.619
7.610
7.604
7.592
7.585
7.582
7.401
7.391
7.384
7.373
7.364
7.260
7.201
6.639
6.606
4.042
3.991
2.489
SSK-2-117
PROTON CDCl3
O
O
N
OMe
OMe
10
9
8
7
6
5
4
3
2
1
0 ppm
1.01
1.00
1.02
1.02
2.04
1.02
1.03
3.09
3.05
3.05

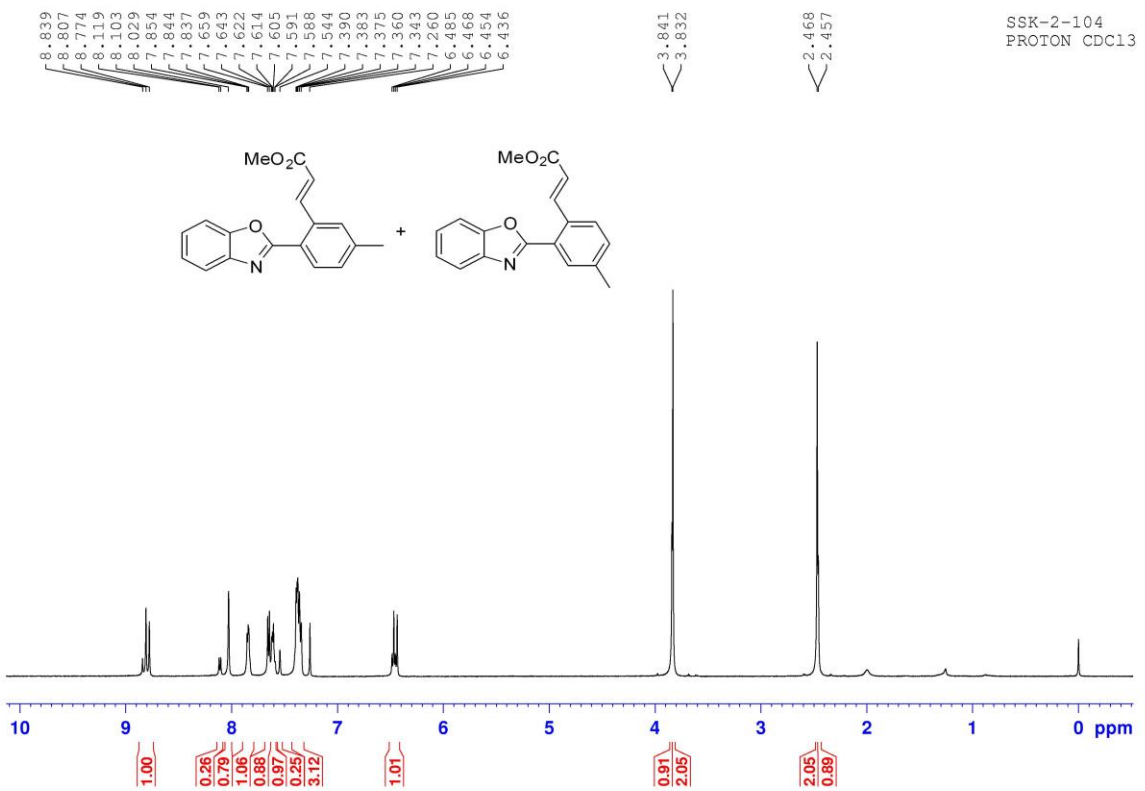

199.42
161.90
151.38
150.62
150.33
143.00
142.14
128.99
128.63
125.47
124.83
120.30
119.74
112.16
110.56
109.51
77.41
77.16
76.91
56.37
56.19
26.69
SSK-2-117
C13CPD CDCl3
O
O
N
OMe
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

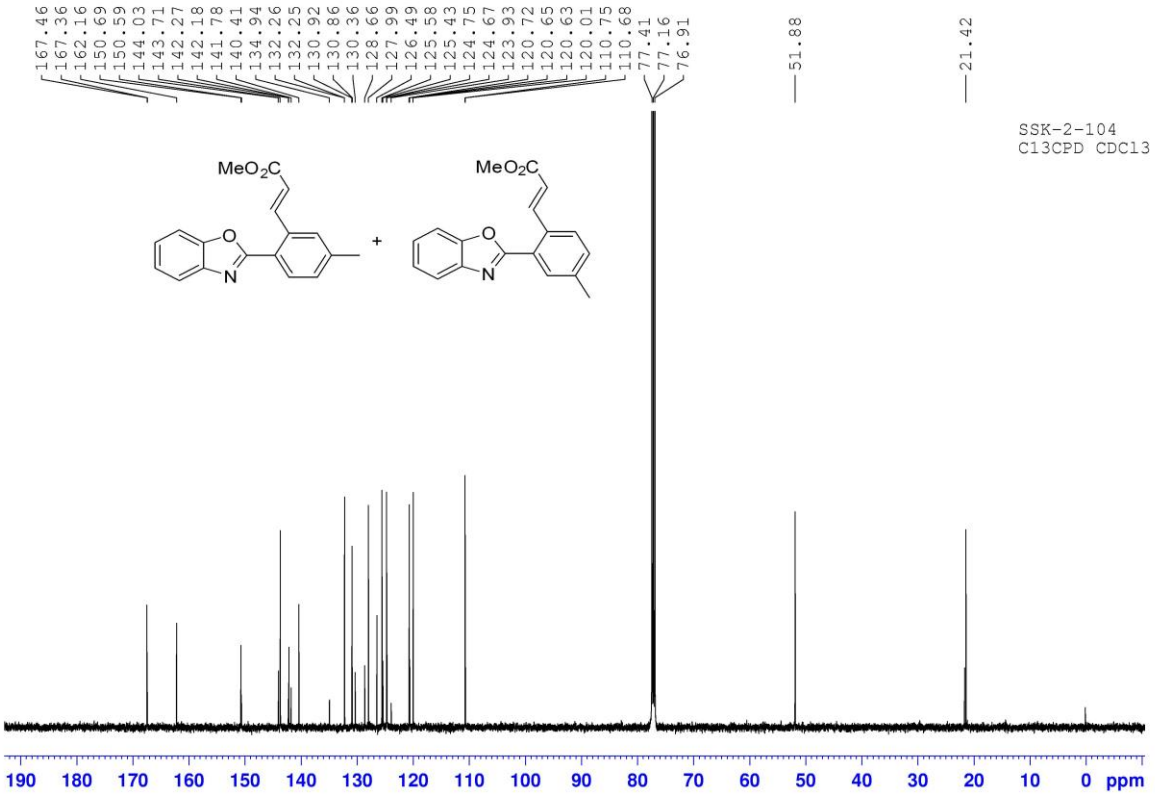
Compound **4g+4g'**



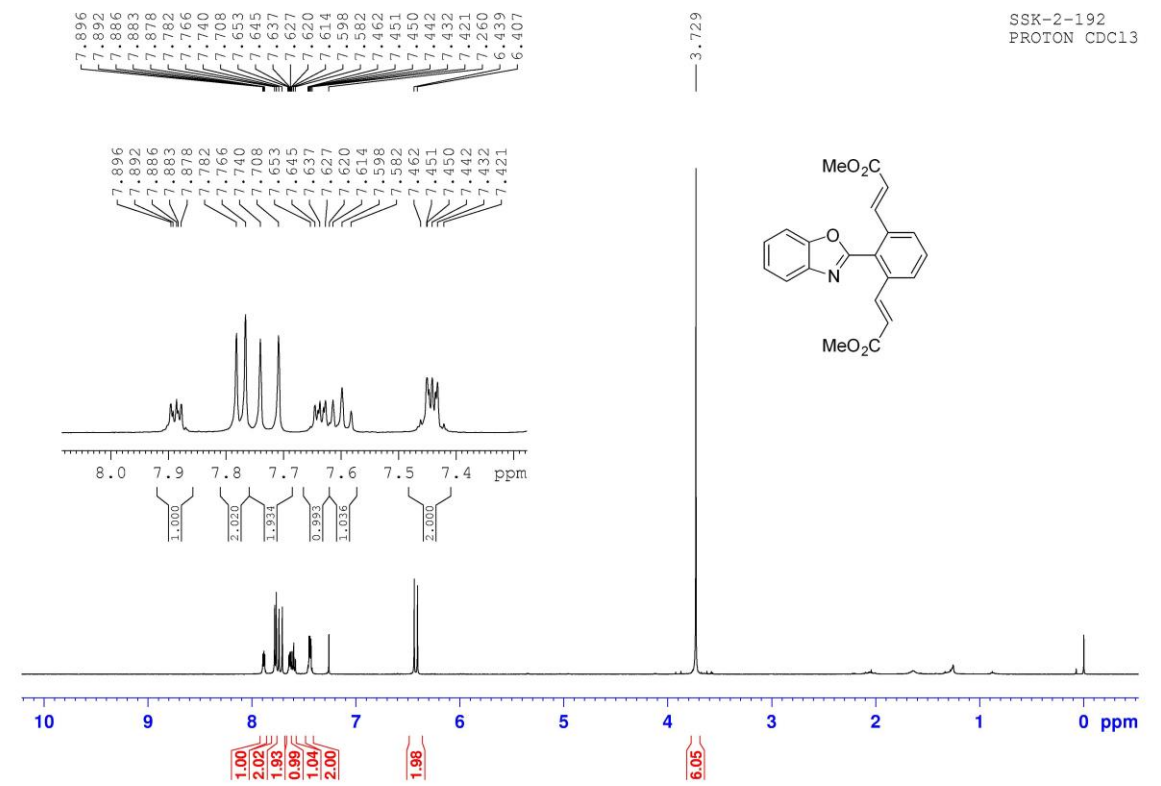


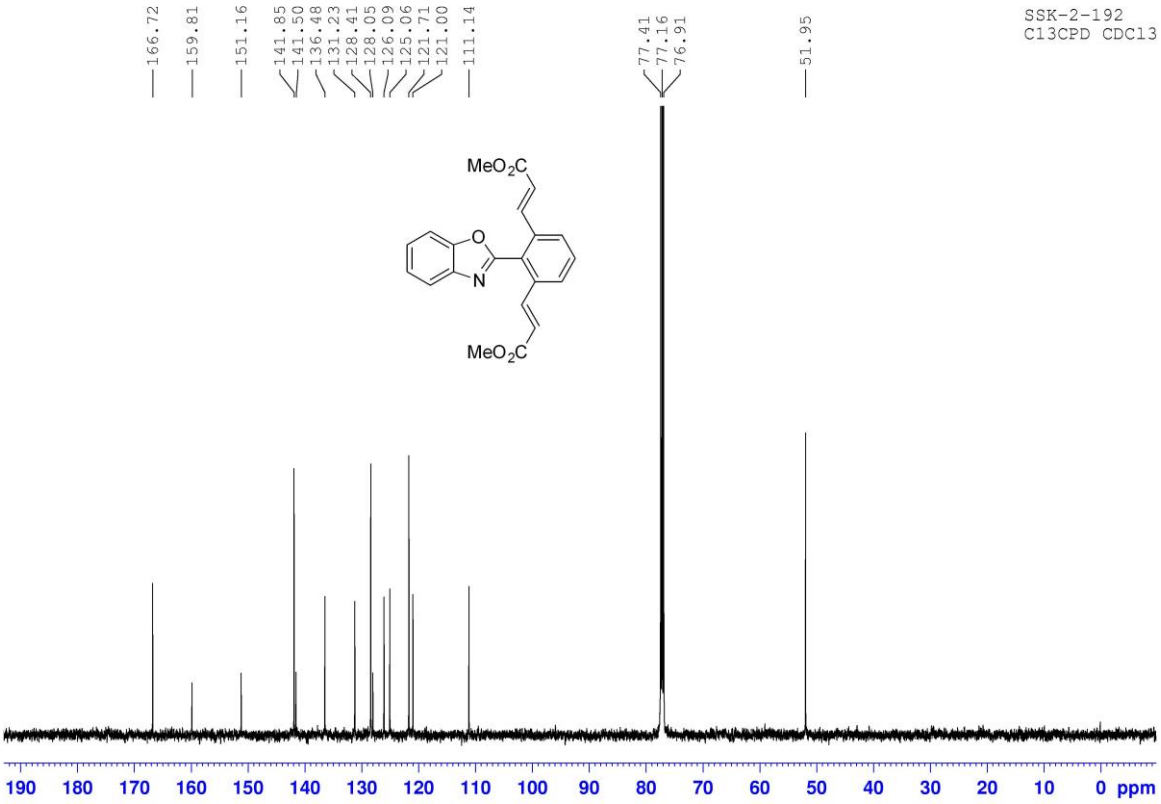
Compound **4h+4h'**



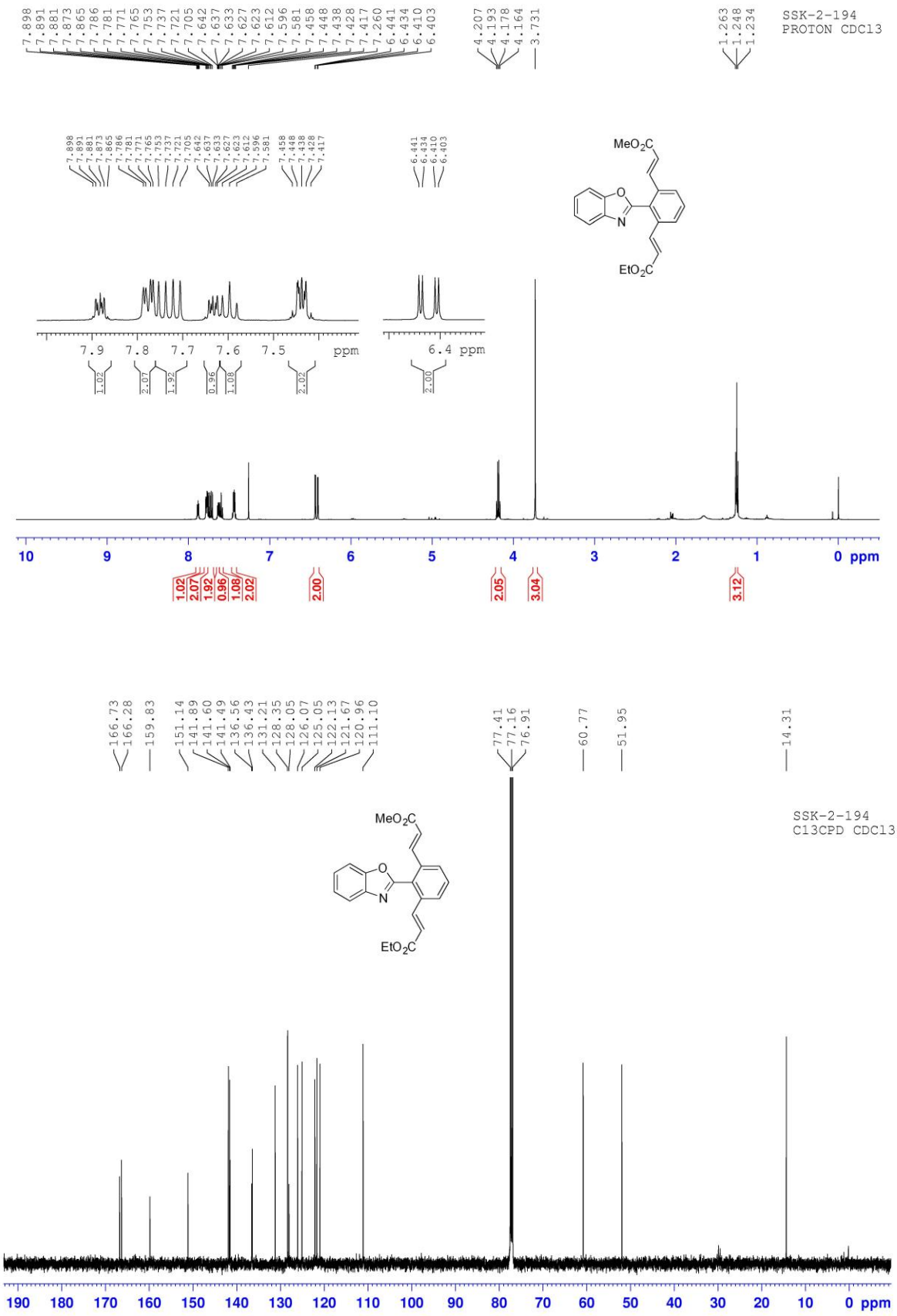


Compound **6a**

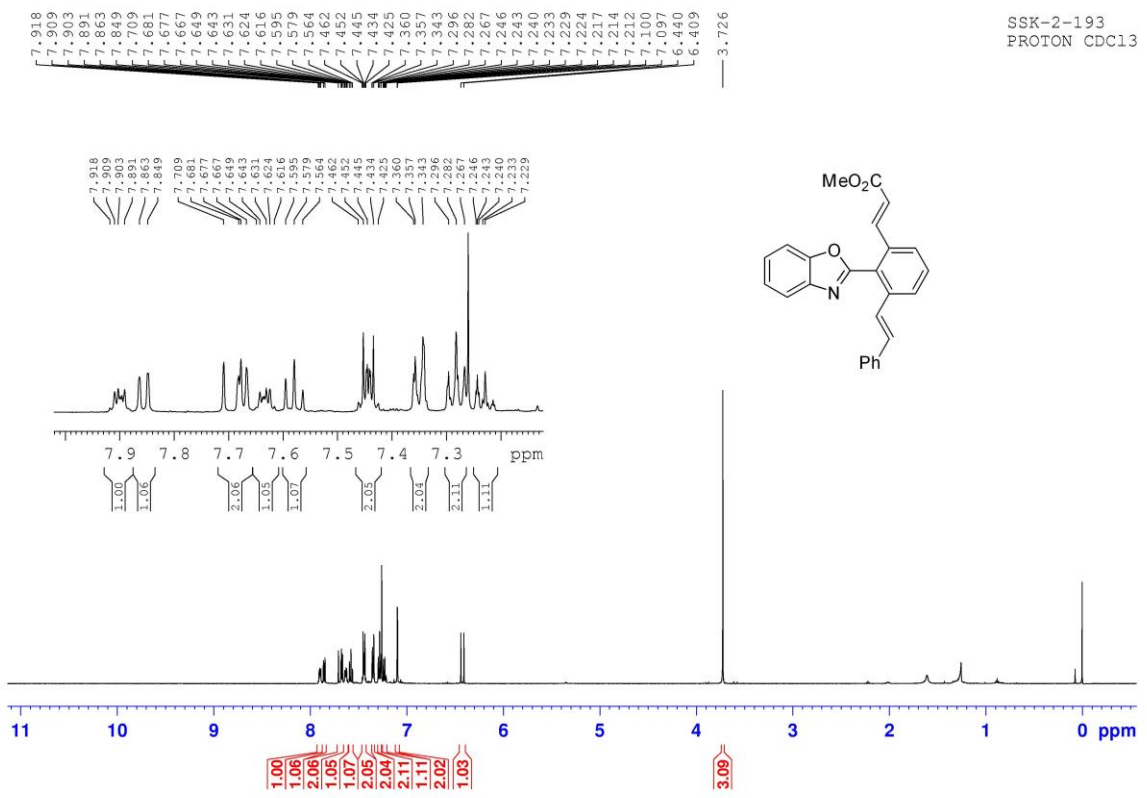

SSK-2-192
PROTON CDCl3
7.896
7.892
7.886
7.883
7.878
7.782
7.766
7.740
7.708
7.653
7.645
7.637
7.627
7.620
7.614
7.598
7.582
7.462
7.451
7.450
7.442
7.432
7.421
7.260
6.439
6.407
3.729
MeO2C
MeO2C
8.0 7.9 7.8 7.7 7.6 7.5 7.4 ppm
1.000
2.020
1.934
0.993
1.036
2.000
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
2.02
1.93
0.99
1.04
2.00
1.98
6.05

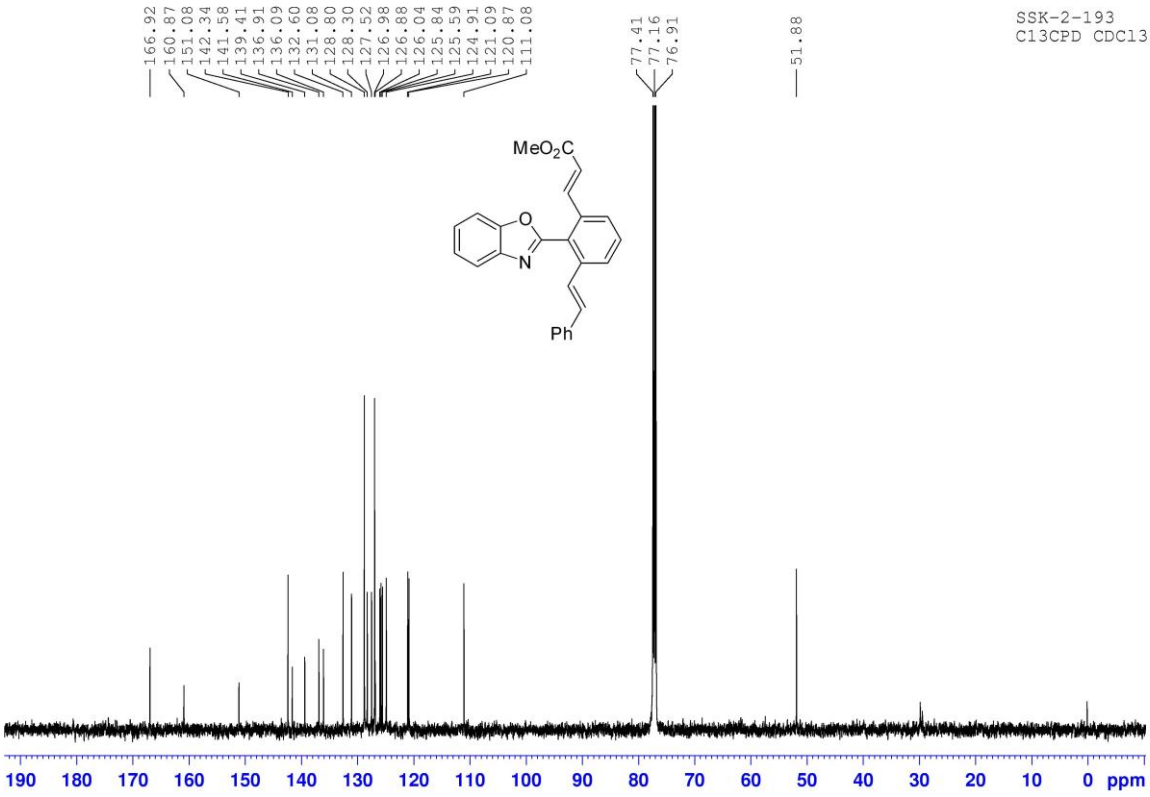

SSK-2-192
C13CPD CDCl3
166.72
159.81
151.16
141.85
141.50
136.48
131.23
128.41
128.05
126.09
125.06
121.71
121.00
111.14
77.41
77.16
76.91
51.95
MeO2C
MeO2C
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Compound **6b**

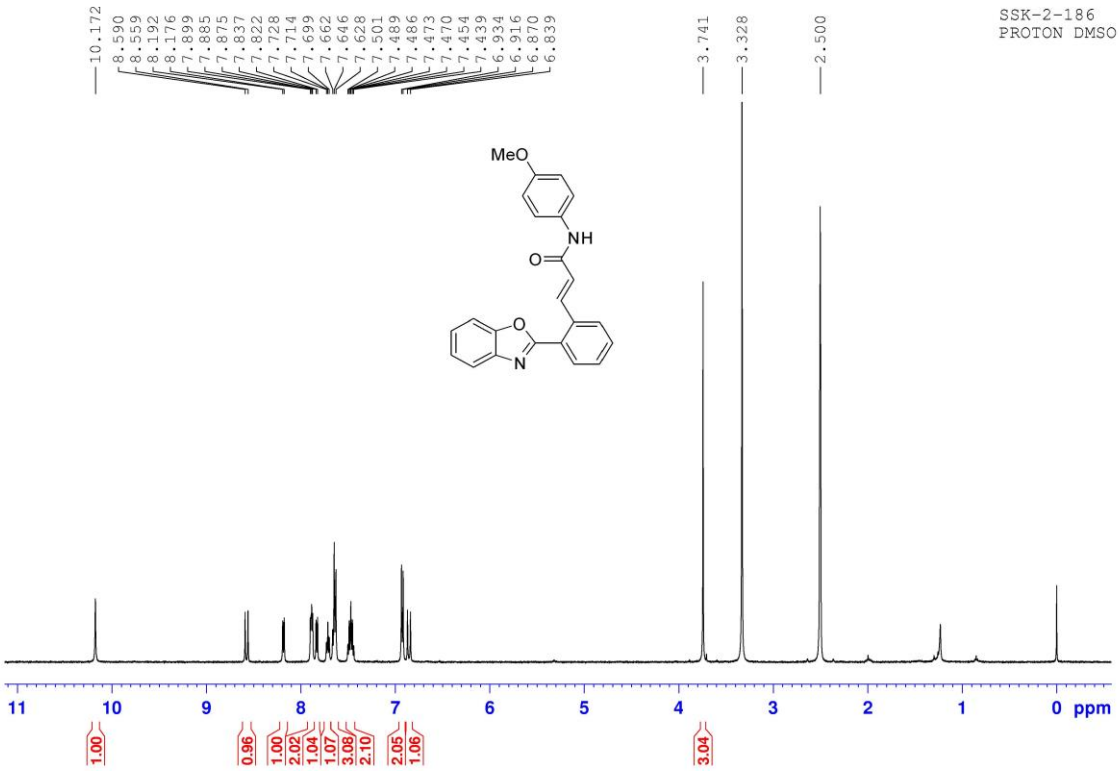


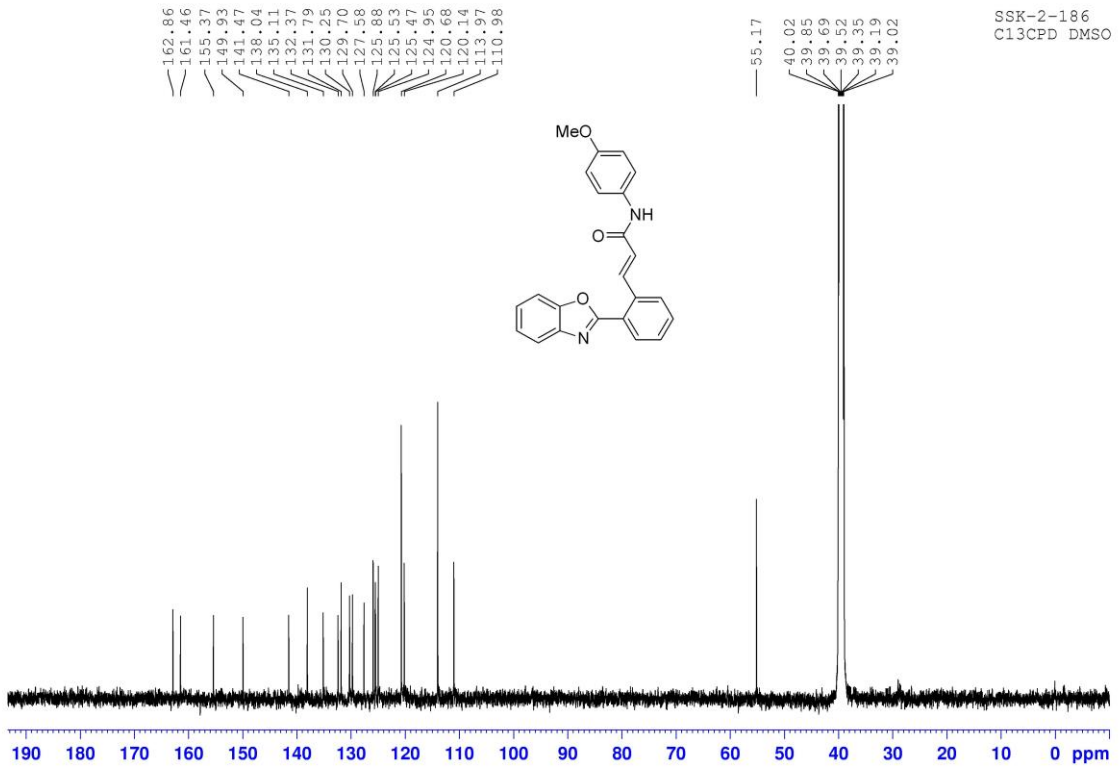
Compound **6c**


SSK-2-193
PROTON CDCl3
MeO2C
Ph
ppm


SSK-2-193
C13CPD CDCl3
MeO2C
Ph
ppm

Compound **8**


SSK-2-186
PROTON DMSO
10.172
8.590
8.559
8.192
8.176
7.899
7.885
7.875
7.837
7.822
7.728
7.714
7.699
7.662
7.646
7.628
7.501
7.489
7.486
7.473
7.470
7.454
7.439
6.934
6.916
6.870
6.839
3.741
3.328
2.500
MeO
NH
O
O
N
11
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
0.96
1.00
2.02
1.04
1.07
3.08
2.10
2.05
1.06
3.04


SSK-2-186
C13CPD DMSO
162.86
161.46
155.37
149.93
141.47
138.04
135.11
132.37
131.79
130.25
129.70
127.58
125.88
125.53
125.47
124.95
120.68
120.14
113.97
110.98
55.17
40.02
39.85
39.69
39.52
39.35
39.19
39.02
MeO
NH
O
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm