Supporting Information

An aminobenzannulation reaction of propargylic ester and isocyanide to access multi-functionalized aryl amine derivatives

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1. General Information

The NMR spectra were recorded on Bruker AC-500 spectrometer (500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR) and JEOL ECX- 400 spectrometer (400 MHz for ^{1}H NMR and 101 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 an X-4 digital melting point apparatus without correction. 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.

2. General procedures

2.1 General procedure for the synthesis of aryl amine 3.

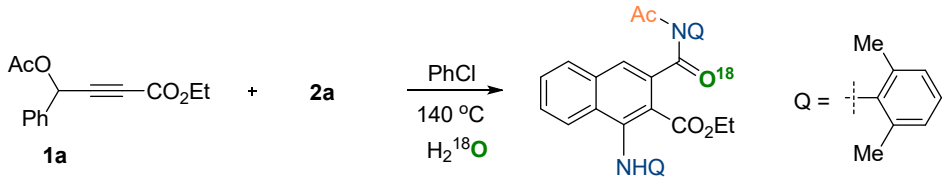
Under air atmosphere, a sealable reaction tube equipped with a magnetic stir bar was charged with propargylic ester **1** (0.5 mmol) and isocyanide **2** (1.5 mmol) in 3.0 mL PhCl at room temperature. The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel placed in an oil bath at 140 °C for 12 hours. After completion of the reaction, the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the desired product.

2.3 General procedure for the synthesis of aniline 5.

Under air atmosphere, a sealable reaction tube equipped with a magnetic stir bar was charged with propargylic ester **4** (0.5 mmol) and isocyanide **2** (1.5 mmol) in 3.0 mL PhCl at room temperature. The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel placed in an oil bath at 140 °C for 2 hours. After completion of the reaction, the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the desired product.

2.4 General procedure for the control experiments.

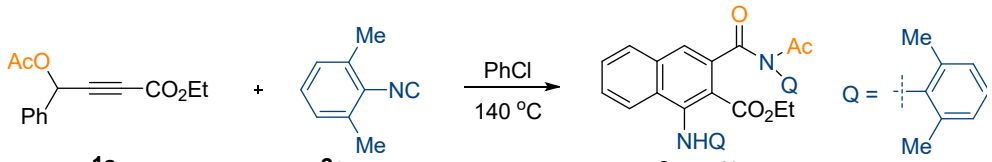
2.4.1 ^{18}O-labeling experiment.



[O^{18}]-**3a**, 0%

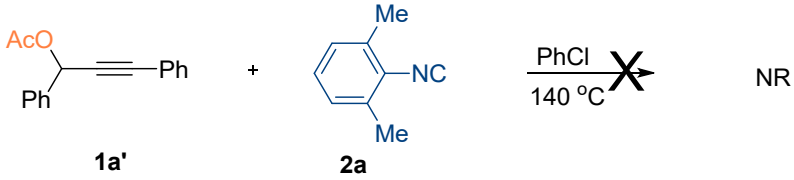
Under air atmosphere, a sealable reaction tube equipped with a magnetic stir bar was charged with propargylic ester **1** (0.5 mmol), isocyanide **2a** (1.5 mmol) and $H_2{}^{18}O$ (3.0 equiv.) in 3.0 mL PhCl at room temperature. The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel placed in an oil bath at 140 °C for 12 hours. After completion of the reaction, the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the solid compound. The analysis of HRMS revealed that no ^{18}O-labeling unit was observed in the isolated compound.

2.4.2 Scale-up synthesis of aryl amine 3a.



Under air atmosphere, a sealable reaction tube equipped with a magnetic stir bar was charged with propargylic ester **1a** (4.0 mmol) and isocyanide **2a** (12.0 mmol) in 8.0 mL PhCl at room temperature. The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel placed in an oil bath at 140 °C for 12 hours. After completion of the reaction, the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the desired product **3a** in 60% yield (1.22 g).

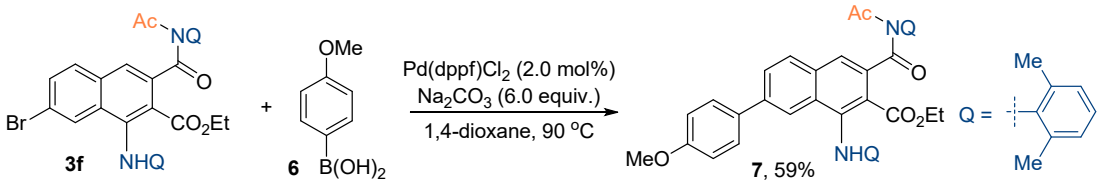
2.4.3 Substituent group effect of alkyne.



Under air atmosphere, a sealable reaction tube equipped with a magnetic stir bar was charged with propargylic ester **1a'** (0.5 mmol) and isocyanide **2a** (1.5 mmol) in 3.0 mL PhCl at room temperature. The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction

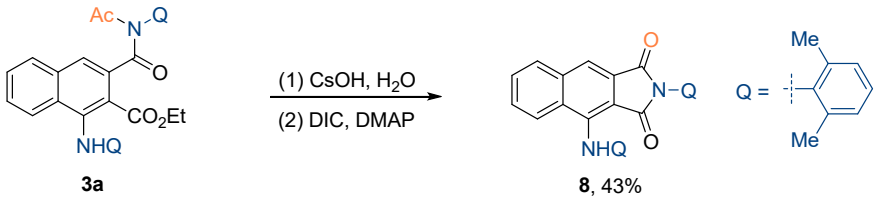
vessel placed in an oil bath at 140 °C for 12 hours. The analysis of TLC showed that no reaction occurred.

2.4.4 Further application of the halo-containing product 3f.



Compound **3f** (176.1 mg, 0.3 mmol) and 4-Methoxyphenylboronic acid **6** (91.2 mg, 0.6 mmol) were dissolved in dioxane-H_2O (6 mL, 4:1). After addition of Pd(dppf)Cl_2 (4.4 mg, 0.006 mmol) and Na_2CO_3 (190.8 mg, 1.8 mmol), the mixture was stirred at 90 °C for 12 hours under a nitrogen atmosphere. After quenching the reaction and extraction with dichloromethane, the organic solvent was removed under vacuum and the residue was purified by column chromatography to afford **7** (108.7 mg, 59% yield) as yellow oil.

2.4.5 The transformation of compound 3a.

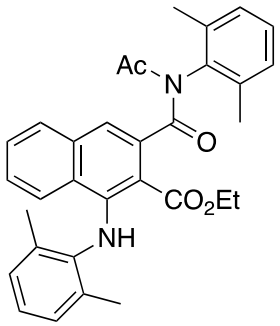


To a stirred solution of **3a** (0.2 mmol, 1.0 equiv) in EtOH (2.0 mL) and H_2O (2.0 mL) was added $CsOH{\cdot}H_2O$ (10.0 mmol, 50.0 equiv.) at room temperature. Then the solution was heated to 80 °C and stirred for 24 h. After being allowed to cool to room temperature, the resulting mixture was acidified to pH = 1 by slow addition of 1N HCI and extracted with $CHCl_3$ (10 × 2.5 mL), the combined organic phases were dried with Na_2SO_4, filtered and concentrated under reduced pressure. The crude carboxylic acid was directly used in the next step without further purification.

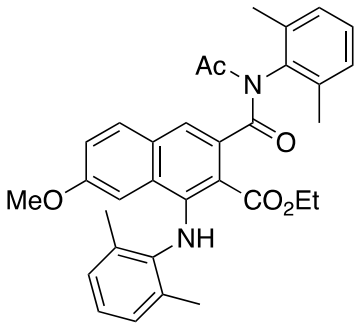
To a stirred solution of the above crude carboxylic acid, *N*-hydroxyphthalimide (0.4 mmol, 2.0 equiv.) and DMAP (0.02 mmol, 0.1 equiv.) in THF (5.0 mL) under argon in the dark was added *N, N'*-disopropylcarbodimide (DIC) (0.44 mmol, 2.2 equiv.) dropwise *via* syringe at room temperature, and the mixture was allowed to stir for 24 h. The resulting mixture was diluted with EtOAc (20 mL) and then washed with 1 N HCI (5.0 mL), saturated $NaHCO_3$ (5.0 mL) and brine (5.0 mL) successively, then dried with Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 15:1) to provide the desired product **8** as yellow oil (36.2 mg, total 43% yield in two steps).

3. Product Characterization

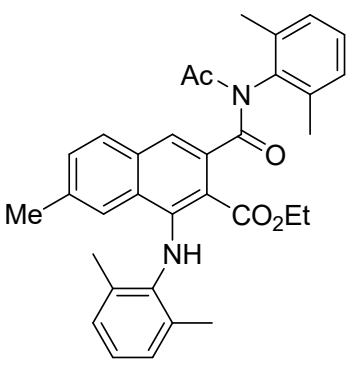
Spectroscopic Data of All Compounds



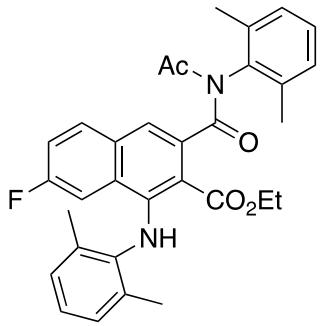
(**3a**) 183 mg, 72% yield, white solid: m. p. 74-76 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.72 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.36 (s, 1H), 7.26 (d, *J* = 4.4 Hz, 1H), 7.21 (d, *J* = 7.3 Hz, 2H), 7.19 – 7.14 (m, 1H), 7.09-7.01 (m, 3H), 4.32 (q, *J* = 7.0 Hz, 2H), 2.42 (s, 6H), 2.10 (d, *J* = 11.7 Hz, 9H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.61, 171.07, 168.20, 147.10, 140.99, 137.16, 136.59, 136.29, 134.63, 133.18, 129.15, 129.09, 129.04, 128.91, 128.64, 126.52, 126.37, 124.99, 124.42, 117.43, 110.01, 61.70, 25.49, 19.27, 18.41, 14.35. HRMS (ESI): Calcd. for $C_{32}H_{32}N_2NaO_4$ $[M+Na]^+$: 531.2254, Found: 531.2250.



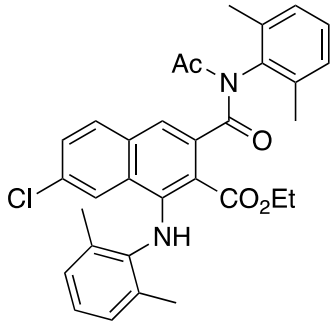
(**3b**) 202 mg, 75% yield, white solid: m. p. 81-82 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.63 (s, 1H), 7.63 (d, *J* = 8.9 Hz, 1H), 7.37 (s, 1H), 7.24 (s, 1H), 7.20 (d, *J* = 7.3 Hz, 2H), 7.13-6.99 (m, 4H), 6.92 (s, 1H), 4.38 (q, *J* = 7.0 Hz, 2H), 3.31 (s, 3H), 2.41 (s, 6H), 2.13 (s, 9H), 1.36 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.87, 171.14, 168.44, 158.07, 145.87, 141.17, 137.37, 136.21, 133.98, 133.58, 130.36, 129.42, 129.09, 129.00, 128.96, 127.90, 125.02, 121.15, 118.23, 111.18, 103.53, 61.76, 54.73, 25.74, 19.26, 18.42, 14.36. HRMS (ESI): Calcd. for $C_{33}H_{34}N_2NaO_5$ $[M+Na]^+$: 561.2360, Found: 561.2357.



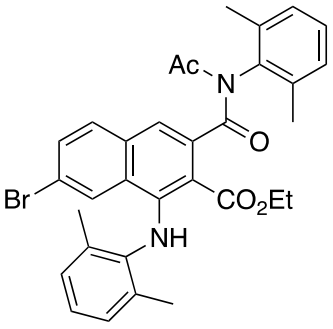
(**3c)** 206 mg, 79% yield, white solid: m. p. 88-89 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.37 (s, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.37 (d, *J* = 9.5 Hz, 2H), 7.32 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.26-7.23 (m, 1H), 7.19 (d, *J* = 7.4 Hz, 2H), 7.05 (q, *J* = 5.3 Hz, 3H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 6H), 2.23 (s, 3H), 2.12 (s, 9H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.80, 171.18, 168.32, 145.83, 140.85, 137.31, 136.45, 136.27, 135.34, 133.08, 132.56, 130.63, 129.10, 129.02, 128.93, 128.82, 126.85, 124.85, 123.71, 117.87, 110.87, 61.61, 25.70, 22.09, 19.22, 18.43, 14.30. HRMS (ESI): Calcd. for $C_{33}H_{35}N_2O_4$ $[M+H]^+$: 523.2591, Found: 523.2582.



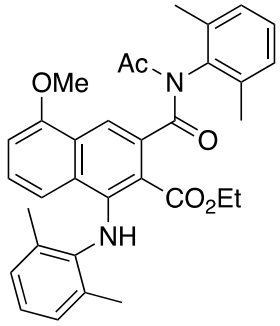
(**3d)** 153 mg, 58% yield, white solid: m. p. 105-106 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.51 (s, 1H), 7.72 (dd, *J* = 8.9, 5.8 Hz, 1H), 7.34 (s, 1H), 7.27 (d, *J* = 6.4 Hz, 1H), 7.25-7.23 (m, 1H), 7.22-7.18 (m, 3H), 7.07 (t, *J* = 3.3 Hz, 3H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 6H), 2.11 (s, 6H), 2.05 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -111.57. ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.57, 170.85, 168.04, 160.71(d, *J* = 246.6 Hz), 146.07(d, *J* = 4.6 Hz)140.35, 137.10, 136.30, 133.14, 131.50, 131.27, 131.20, 131.23(d, *J* = 8.9 Hz), 118.63(d, *J* = 25.0 Hz), 117.20, 111.34, 109.01, 108.82, 61.88, 25.40, 19.25, 18.41, 14.3. HRMS (ESI): Calcd. for $C_{33}H_{32}FN_2O_4$ $[M+H]^+$: 527.2341, Found: 527.2358.



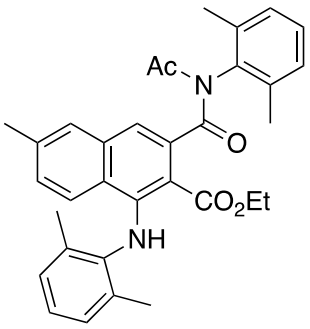
(**3e**) 176 mg, 65% yield, white solid: m. p. 75-76 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.54 (s, 1H), 7.65 (d, J = 8.7 Hz, 1H), 7.54 (d, *J* = 1.9 Hz, 1H), 7.40 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.28 (s, 1H), 7.24 (s, 1H), 7.20 (d, *J* = 7.5 Hz, 2H), 7.10-7.04 (m, 3H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 6H), 2.11 (s, 6H), 2.03 (s, 3H), 1.31 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.49, 170.80, 167.93, 145.91, 140.38, 137.19, 137.03, 136.35, 133.19, 132.99, 132.10, 130.31, 129.34, 129.27, 129.21, 127.10, 125.44, 123.86, 116.72, 61.89, 25.33, 19.24, 18.43, 14.35, 1.16. HRMS (ESI): Calcd. for $C_{32}H_{31}ClN_2NaO_4$ $[M+Na]^+$: 565.1865, Found: 565.1869.



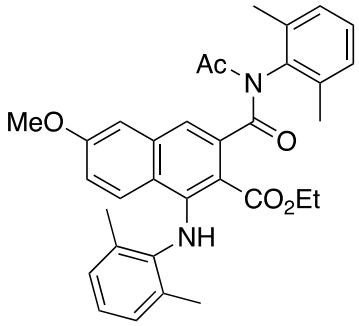
(**3f**) 208 mg, 71% yield, white solid: m. p. 84-85 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.55 (s, 1H), 7.72 (s, 1H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.52 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.25 (d, *J* = 6.0 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 3.4 Hz, 3H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 6H), 2.11 (s, 6H), 2.02 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.46, 170.79, 167.90, 140.37, 137.38, 136.36, 133.24, 131.84, 130.33, 129.27, 129.21, 127.19, 125.49, 120.17, 116.69, 111.07, 61.89, 25.32, 19.22, 18.44, 14.36. HRMS (ESI): Calcd. for $C_{32}H_{31}BrN_2NaO_4$ $[M+Na]^+$: 609.1359, Found: 609.1346.



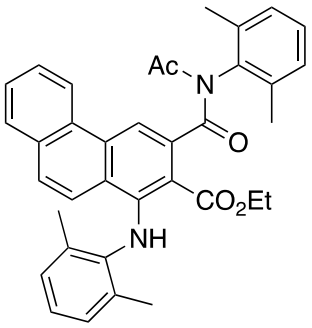
(**3g)** 143 mg, 53% yield, white solid: m. p. 115-116 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.31 (s, 1H), 7.94 (s, 1H), 7.25- 7.22 (m, 1H), 7.21-7.16 (m, 3H), 7.16-7.10 (m, 1H), 7.06-6.98 (m, 3H), 6.83 (d, *J* = 7.5 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 3H), 2.40 (s, 6H), 2.11 (d, *J* = 14.6 Hz, 9H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.87, 171.42, 168.34, 155.85, 145.93, 141.04, 137.41, 136.35, 135.21, 132.92, 129.09, 129.01, 126.87, 126.36, 124.68, 116.32, 112.5, 106.75, 61.71, 55.87, 25.81, 19.31, 18.41, 14.30. HRMS (ESI): Calcd. for $C_{33}H_{34}N_2NaO_5$ $[M+Na]^+$: 561.2360, Found: 561.2368.



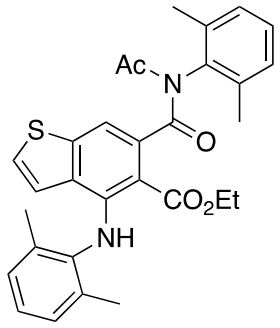
(**3h)**, 122 mg, 47% yield, white solid: m. p. 75-76 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.83 (s, 1H), 7.51 (s, 1H), 7.45 (d, *J* = 8.8 Hz, 1H), 7.30 (s, 1H), 7.25 (d, *J* = 5.7 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.06 (q, *J* = 4.4 Hz, 3H), 6.99 (dd, *J* = 8.8, 1.6 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 9H), 2.11 (d, *J* = 4.3 Hz, 9H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.65, 171.17, 168.29, 147.45, 141.11, 138.83, 137.24, 136.68, 136.28, 134.97, 133.34, 129.12, 129.03, 129.00, 128.49, 128.11, 125.02, 124.57, 124.36, 117.07, 108.96, 61.62, 25.57, 21.48, 19.26, 18.42, 14.39. HRMS (ESI): Calcd. for $C_{33}H_{35}N_2O_4$ $[M+H]^+$: 523.2591, Found: 523.2599.



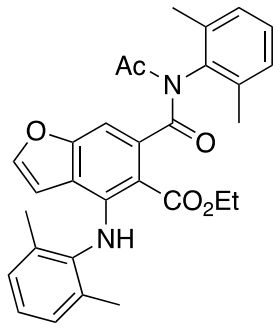
(**3i)** 92 mg, 34% yield, white solid: m. p. 105-106 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.98 (s, 1H), 7.40 (d, *J* = 9.4 Hz, 1H), 7.25 (d, *J* = 6.4 Hz, 1H), 7.20 (d, *J* = 7.9 Hz, 3H), 7.07-7.00 (m, 3H), 6.99 (d, *J* = 2.7 Hz, 1H), 6.74 (dd, *J* = 9.4, 2.7 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 2.42 (s, 6H), 2.08 (d, *J* = 5.2 Hz, 9H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.68, 171.16, 168.25, 159.73, 148.09, 141.22, 137.75, 136.86, 136.34, 133.40, 129.19, 129.09, 126.45, 125.13, 121.10, 118.04, 116.29, 107.59, 107.40, 61.63, 55.46, 25.58, 19.30, 18.50, 14.48. HRMS (ESI): Calcd. for $C_{33}H_{34}N_2NaO_5$ $[M+Na]^+$: 561.2360, Found: 561.2360.



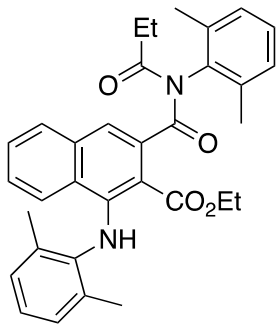
(**3j)** 212 mg, 76% yield, yellow solid: m. p. 170-172 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.50-8.40 (m, 2H), 8.22 (s, 1H), 7.80 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.68-7.59 (m, 2H), 7.52 (d, *J* = 9.4 Hz, 1H), 7.46 (d, *J* = 9.4 Hz, 1H), 7.30-7.26 (m, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.07-6.99 (m, 3H), 4.33 (q, *J* = 7.2 Hz, 2H), 2.49 (s, 6H), 2.13 (s, 3H), 2.09 (s, 6H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.57, 171.32, 168.02, 137.27, 136.36, 132.48, 129.98, 129.28, 129.20, 128.65, 127.88, 127.08, 127.06, 125.01, 124.58, 123.28, 121.75, 113.14, 112.72, 61.92, 25.60, 19.50, 18.54, 14.38. HRMS (ESI): Calcd. for $C_{36}H_{35}N_2O_4$ $[M+H]^+$: 559.2591, Found: 559.2586.



(**3k)** 198 mg, 77% yield, white solid: m. p. 197-198 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.32 (s, 1H), 7.29 (s, 1H), 7.26 (d, *J* = 3.3 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.19-7.11 (m, 3H), 7.02 (d, *J* = 5.7 Hz, 1H), 6.23 (d, *J* = 5.7 Hz, 1H), 4.46 (q, *J* = 7.0 Hz, 2H), 2.42 (s, 6H), 2.18 (s, 6H), 2.04 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.44, 170.88, 168.41, 146.42, 145.00, 137.52, 137.09, 136.28, 129.20, 129.11, 128.66, 128.63, 126.68, 125.13, 122.80, 122.80, 109.62, 106.11, 61.66, 25.27, 18.85, 18.44, 14.48. HRMS (ESI): Calcd. for $C_{30}H_{30}N_2NaO_4S$ $[M+Na]^+$: 537.1818, Found: 537.1819.

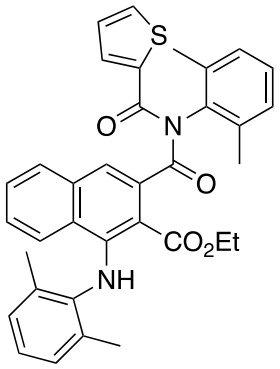


(**3l)** 156 mg, 63% yield, white solid: m. p. 115-116 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.30 (s, 1H), 7.28-7.26 (m, 1H), 7.23-7.18 (m, 4H), 7.15 (d, *J* = 7.4 Hz, 2H), 6.92 (s, 1H), 5.24 (d, *J* = 2.2 Hz, 1H), 4.47 (q, J = 7.1 Hz, 2H), 2.42 (s, 6H), 2.21 (s, 6H), 2.00 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.36, 170.82, 168.23, 157.28, 145.96, 143.71, 139.31, 138.35, 137.49, 137.05, 136.37, 129.25, 129.15, 128.46, 127.37, 115.14, 106.17, 103.61, 99.68, 61.49, 25.14, 18.60, 18.42, 14.55. HRMS (ESI): Calcd. for $C_{30}H_{30}N_2NaO_5$ $[M+Na]^+$: 521.2047, Found: 521.2036.

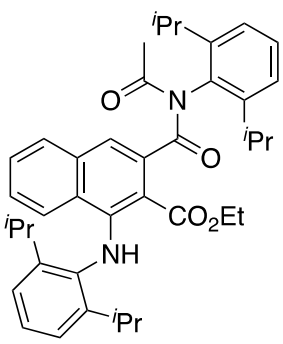


(**3m)** 167 mg, 64% yield, white solid: m. p. 85-86 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.71 (s, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 8.7 Hz, 1H), 7.46 (t, *J* = 7.1 Hz, 1H), 7.32 (s, 1H), 7.24 (s, 1H), 7.20 (d, *J* = 7.5 Hz, 2H), 7.14-7.17 (m, 1H),

7.05 (q, *J* = 5.2 Hz, 3H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 6H), 2.27 (q, *J* = 7.3 Hz, 2H), 2.11 (s, 6H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 176.11, 171.07, 168.30, 147.06, 141.07, 136.94, 136.45, 134.73, 133.23, 129.19, 129.05, 128.90, 128.59, 126.53, 126.28, 124.96, 124.46, 117.34, 110.08, 61.69, 30.64, 19.36, 18.49, 14.38, 9.11. HRMS (ESI): Calcd. for $C_{33}H_{34}N_2NaO_4$ $[M+Na]^+$: 545.2411, Found: 545.2422.

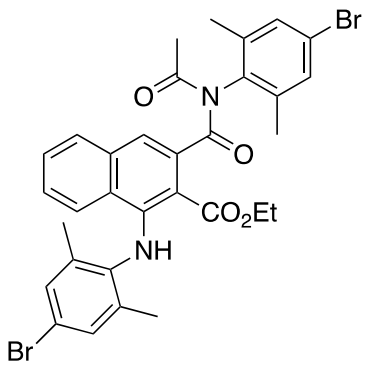


(**3n)** 190 mg, 66% yield, white solid: m. p. 121-120 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.49-7.37 (m, 4H), 7.33-7.27 (m, 1H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.14 (m, 1H), 7.08-6.98 (m, 3H), 6.90-6.85 (m, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 6H), 2.09 (s, 6H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 171.40, 168.62, 164.40, 146.72, 141.06, 137.46, 137.09, 134.71, 134.46, 133.83, 133.18, 129.66, 129.45, 129.13, 129.03, 128.44, 127.44, 126.89, 126.48, 124.85, 124.33, 117.84, 61.74, 19.45, 18.71, 14.32. HRMS (ESI): Calcd. for $C_{35}H_{32}N_2NaO_4S$ $[M+Na]^+$: 599.1975, Found: 599.1921.

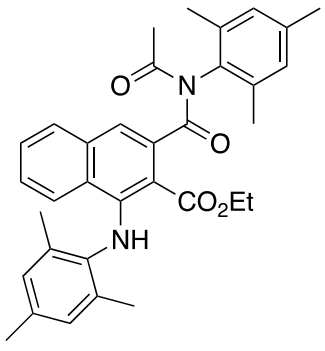


(**3o)** 242 mg, 78% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.46 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 2H), 7.42 – 7.38 (m, 1H), 7.31 (d, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 3H), 7.02 (m, 1H), 4.52 – 4.38 (m, 2H), 3.31 (q, *J* = 6.7 Hz, 2H), 3.19 (s, 2H), 2.16 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.32-1.28 (m, 12H), 1.15 (d, *J* = 6.8 Hz, 6H), 0.92 (d,

J = 6.7 Hz, 6H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 173.14, 171.97, 168.56, 148.95, 145.08, 138.29, 135.38, 134.32, 129.79, 128.99, 128.74, 127.00, 125.94, 125.72, 125.38, 124.57, 124.23, 116.65, 107.07, 61.64, 28.65, 26.03, 24.67, 24.54, 24.03, 22.32, 14.63. HRMS (ESI): Calcd. for $C_{40}H_{48}N_2NaO_4$ $[M+Na]^+$: 643.3506, Found: 643.3503.

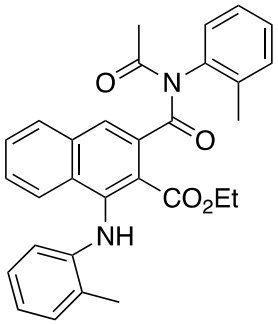


(**3p)** 229 mg, 69% yield, white solid: m. p. 160-161 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.52 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.6 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.35 (d, *J* = 16.0 Hz, 3H), 7.23 (m, 1H), 7.19 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 6H), 2.06 (d, *J* = 10.9 Hz, 9H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.18, 170.83, 168.01, 146.53, 140.16, 138.54, 136.34, 136.30, 135.08, 134.55, 132.08, 131.74, 129.06, 128.94, 126.85, 126.58, 124.25, 122.86, 117.97, 117.66, 110.59, 61.93, 25.53, 19.15, 18.27, 14.37. HRMS (ESI): Calcd. for $C_{32}H_{30}Br_2N_2NaO_4$ $[M+Na]^+$: 687.0465, Found: 687.0455.

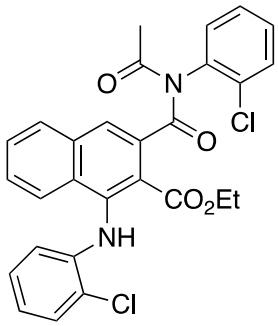


(**3q)** 196 mg, 73% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.80 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.47-7.41 (m, 1H), 7.29 (s, 1H), 7.14 (m, 1H), 7.01 (s, 2H), 6.87 (s, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 6H), 2.33 (s, 3H), 2.29 (s, 3H), 2.06 (d, *J* = 5.4 Hz, 9H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.88, 171.29, 168.35, 147.87, 138.90, 138.49, 135.91, 134.81, 134.72, 134.61, 133.39, 130.00, 129.71, 128.91, 128.63, 126.40, 126.21, 124.62, 117.06, 109.17, 61.69, 25.57, 21.21,

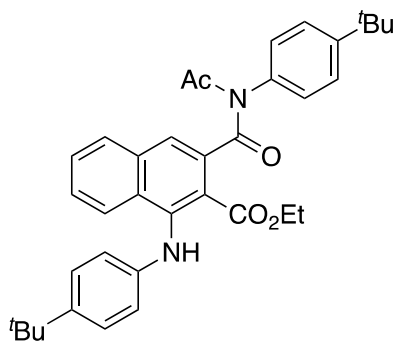
20.96, 19.20, 18.37, 14.42. HRMS (ESI): Calcd. for $C_{34}H_{36}N_2NaO_4$ $[M+Na]^+$: 559.2567, Found: 559.2558.



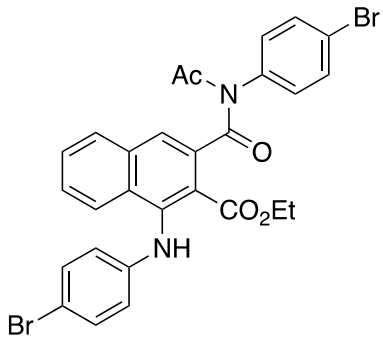
(**3r)** 120 mg, 50% yield, white solid: m. p. 90-91 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.36 (s, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.52-7.48 (m, 1H), 7.43 (s, 1H), 7.33-7.26 (m, 4H), 7.25-7.20 (m, 2H), 6.87 (m, 2H), 6.27 (d, *J* = 8.4 Hz, 1H), 4.41 (m, 2H), 2.49 (s, 3H), 2.40 (s, 3H), 2.32 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.66, 171.56, 167.48, 144.29, 143.93, 136.11, 134.46, 131.44, 130.60, 129.22, 128.84, 128.76, 128.40, 127.38, 126.99, 126.95, 126.88, 126.46, 121.38, 121.17, 117.60, 62.05, 26.32, 18.16, 18.07, 14.21. HRMS (ESI): Calcd. for $C_{30}H_{28}N_2NaO_4$ $[M+Na]^+$: 503.1941, Found: 503.1941.



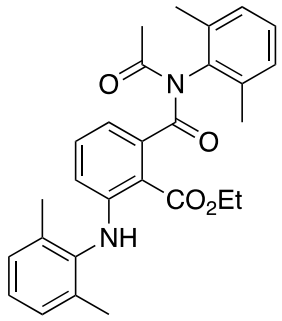
(**3s)** 109 mg, 42% yield, yellow oil.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.90-7.84 (m, 1H), 7.82-7.78 (m, 1H), 7.76 (s, 1H), 7.57-7.52 (m, 1H), 7.50-7.46 (m, 2H), 7.44-7.37 (m, 3H), 7.26-7.23 (m, 1H), 6.93-6.84 (m, 1H), 6.81-6.74 (m, 1H), 6.13 (d, *J* = 8.1 Hz, 1H), 4.42 (dd, *J* = 7.2, 1.5 Hz, 2H), 2.46 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.39, 170.81, 166.89, 142.39, 140.17, 137.04, 134.56, 134.17, 133.02, 130.82, 130.46, 130.29, 129.57, 129.51, 129.11, 128.98, 128.12, 127.87, 127.23, 126.20, 123.29, 121.55, 120.73, 116.21, 62.40, 29.80, 26.19, 14.10. HRMS (ESI): Calcd. for $C_{28}H_{22}Cl_2N_2NaO_4$ $[M+Na]^+$: 543.0849, Found: 543.0843.



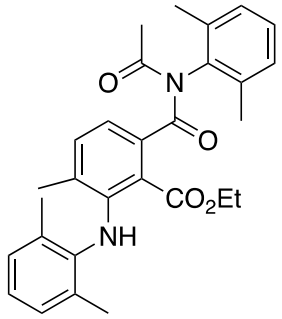
(**3t)** 85 mg, 30% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 (s, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.50 (m, 1H), 7.43 (s, 1H), 7.35-7.29 (m, 3H), 7.15 (dd, *J* = 8.6, 2.0 Hz, 4H), 6.60 (d, *J* = 8.7 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.27 (s, 9H), 1.25 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.28, 172.13, 167.48, 151.48, 144.09, 143.69, 143.21, 136.23, 135.01, 134.42, 128.77, 128.68, 128.33, 128.28, 127.16, 126.85, 126.35, 125.88, 122.52, 117.77, 116.10, 61.96, 34.71, 34.19, 31.51, 31.41, 31.28, 26.82, 14.11. HRMS (ESI): Calcd. for $C_{36}H_{40}N_2NaO_4$ $[M+Na]^+$: 587.2880, Found: 587.2883.



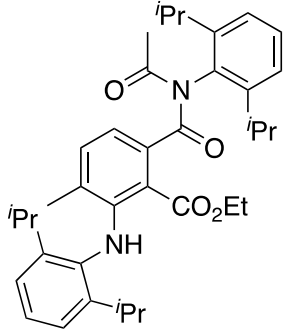
(**3u)** 101 mg, 33% yield, white solid: m. p. 86-87 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.57-7.52 (m, 1H), 7.46 (d, *J* = 3.1 Hz, 2H), 7.44 (s, 1H), 7.42 – 7.36 (m, 1H), 7.28-7.23 (m, 3H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.51 (d, *J* = 8.8 Hz, 2H), 4.40 (q, *J* = 7.2 Hz, 2H), 2.52 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.07, 171.36, 167.21, 144.80, 134.25, 132.67, 132.07, 130.60, 129.22, 128.95, 127.73, 126.68, 123.94, 119.25, 62.29, 26.83, 14.13. HRMS (ESI): Calcd. for $C_{28}H_{22}Br_2N_2NaO_4$ $[M+Na]^+$: 630.9839, Found: 630.9845.



(**5a)** 75 mg, 33% yield, white solid: m. p. 166-167 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.46 (s, 1H), 7.25 (d, *J* = 6.6 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 2H), 7.14 (q, *J* = 3.3 Hz, 4H), 6.66 (dd, *J* = 7.3, 0.9 Hz, 1H), 6.26 (dd, *J* = 8.5, 0.9 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 6H), 2.22 (s, 6H), 1.95 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.19, 171.15, 167.58, 149.17, 142.50, 137.21, 136.98, 136.84, 136.46, 132.90, 129.25, 129.17, 128.70, 126.77, 113.99, 113.82, 109.48, 61.60, 24.99, 18.50, 18.35, 14.53. HRMS (ESI): Calcd. for $C_{28}H_{31}N_2O_4$ $[M+H]^+$: 459.2278, Found: 459.2266.

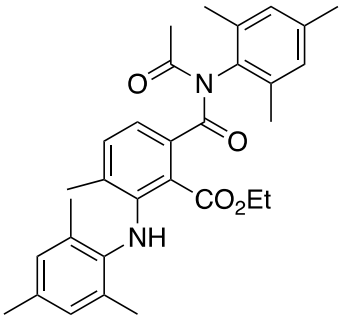


(5b) 99 mg, 42% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.24 – 7.20 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 3H), 6.96 (dd, *J* = 8.3, 6.5 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 6H), 2.13 (s, 6H), 2.04 (s, 3H), 1.85 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.63, 170.86, 168.06, 145.07, 139.74, 137.74, 137.17, 136.25, 133.26, 133.22, 130.30, 129.11, 128.61, 124.42, 118.70, 117.18, 61.71, 25.36, 19.61, 19.32, 18.32, 14.09. HRMS (ESI): Calcd. for $C_{29}H_{33}N_2O_4$ $[M+H]^+$: 473.2435, Found: 473.2431.

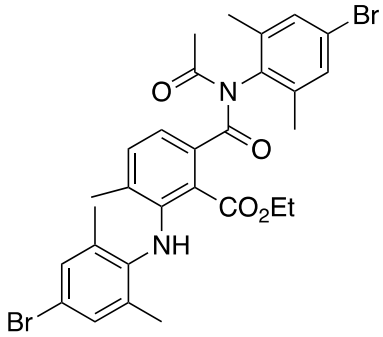


(5c) 198 mg, 68% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 (s, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 2H), 7.24-7.21 (m, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 4.32 (d, *J* =

6.7 Hz, 2H), 3.32-3.13 (m, 4H), 2.14 (s, 3H), 1.71 (s, 3H), 1.34 (d, *J* = 7.1 Hz, 3H), 1.28 (d, *J* = 6.8 Hz, 6H), 1.24 (d, *J* = 6.7 Hz, 6H), 1.16 (t, *J* = 7.5 Hz, 12H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 173.14, 171.66, 168.31, 146.67, 146.41, 145.53, 138.75, 137.18, 134.64, 134.18, 129.69, 128.90, 126.38, 124.45, 123.30, 116.13, 61.72, 28.63, 28.46, 25.88, 24.53, 24.46, 23.89, 22.26, 20.50, 14.34. HRMS (ESI): Calcd. for $C_{37}H_{49}N_2O_4$ $[M+H]^+$: 585.3687, Found: 585.3675.

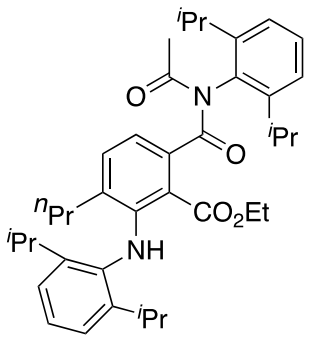


(5d) 120 mg, 48% yield, white solid: m. p. 172-173 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.10 (d, *J* = 7.7 Hz, 1H), 7.03 (s, 1H), 7.01-6.94 (m, 2H), 6.84 (d, *J* = 7.9 Hz, 3H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 2.27 (s, 9H), 2.10 (s, 6H), 2.03 (s, 3H), 1.83 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.86, 171.06, 168.17, 145.65, 138.87, 137.94, 137.12, 135.81, 134.57, 134.11, 133.57, 133.35, 129.91, 129.81, 129.18, 117.91, 116.74, 61.67, 25.39, 21.18, 20.87, 19.69, 19.22, 18.24, 14.09. HRMS (ESI): Calcd. For $C_{31}H_{37}N_2O_4$ $[M+H]^+$: 501.2748, Found: 501.2740.

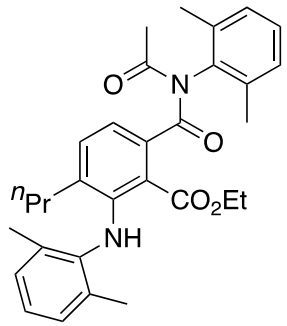


(5e) 113 mg, 36% yield, white solid: m. p. 240-241 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 (s, 2H), 7.14 (d, *J* = 13.1 Hz, 3H), 6.90 – 6.83 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 6H), 2.08 (s, 6H), 2.03 (s, 3H), 1.86 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.17, 170.61, 167.86, 144.65, 138.90, 138.46, 137.54, 136.31, 135.14, 133.45, 132.03, 131.25, 130.66, 122.86, 119.00, 117.60, 117.05, 61.91, 25.38,

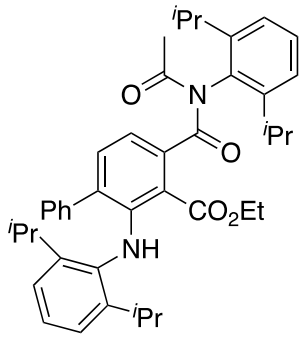
19.68, 19.15, 18.17, 14.10. HRMS (ESI): Calcd. for $C_{29}H_{31}Br_2N_2O_4$ $[M+H]^+$: 631.0625, Found: 631.0610.



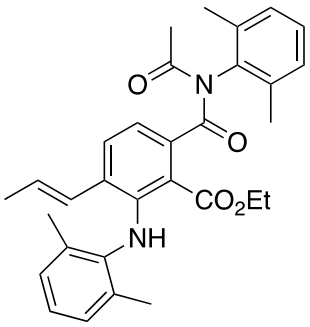
(5f) 232 mg,76% yield, White solid: m. p. 176-177 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45-7.39 (m, 1H), 7.28 (d, *J* = 7.7 Hz, 2H), 7.22 (d, *J* = 4.1 Hz, 1H), 7.21-7.18 (m, 1H), 7.18-7.13 (m, 3H), 6.92 (d, *J* = 7.6 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.29-3.07 (m, 4H), 2.15 (s, 3H), 2.15-2.11 (m, 2H), 1.41-1.34 (m, 2H), 1.27 (dt, *J* = 7.2, 3.8 Hz, 9H), 1.21 (d, *J* = 6.9 Hz, 6H), 1.16 (dd, *J* = 6.9, 3.2 Hz, 12H), 0.71 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 173.31, 171.69, 168.29, 146.36, 145.61, 144.93, 137.84, 137.19, 134.22, 132.61, 129.66, 126.04, 124.42, 123.49, 118.58, 116.89, 61.69, 34.31, 28.71, 28.46, 25.99, 24.47, 24.24, 23.91, 22.68, 22.61, 14.22, 14.15. HRMS (ESI): Calcd. for $C_{39}H_{53}N_2O_4$ $[M+H]^+$: 613.4000, Found: 613.4000.



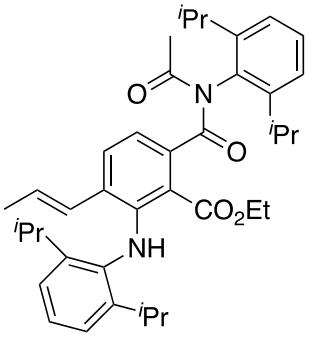
(5g) 67 mg, 27% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.24-7.14 (m, 4H), 7.02 (d, *J* = 7.5 Hz, 2H), 6.95 (dd, *J* = 7.4, 5.3 Hz, 2H), 6.36 (s, 1H), 3.85 (q, *J* = 7.1 Hz, 2H), 2.37-2.33 (m, 2H), 2.29 (s, 6H), 2.13 (s, 6H), 2.04 (s, 3H), 1.53 (m, 2H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.72, 170.93, 168.05, 143.46, 139.61, 136.97, 136.25, 134.80, 132.53, 131.43, 129.11, 129.10, 128.81, 124.09, 120.60, 117.71, 61.56, 34.21, 25.42, 22.21, 19.27, 18.32, 14.13, 13.93. HRMS (ESI): Calcd. for $C_{31}H_{37}N_2O_4$ $[M+H]^+$: 501.2748, Found: 501.2734.



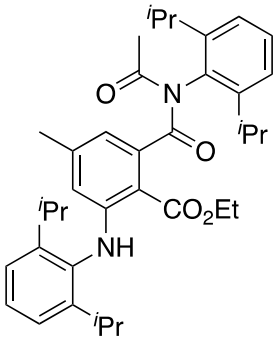
(5h) 148 mg, 46% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.44-7.40 (m, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.25-7.15 (m, 7H), 7.05-6.98 (m, 1H), 6.97-6.91 (m, 3H), 6.78 (s, 1H), 3.86 (d, *J* = 6.9 Hz, 2H), 3.14 (m, 4H), 2.17 (s, 1H), 2.15 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 1H), 1.28 (dd, *J* = 12.9, 6.9 Hz, 10H), 1.20 (d, *J* = 6.8 Hz, 7H), 1.16 (d, *J* = 6.7 Hz, 9H), 1.05 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 173.15, 171.53, 167.64, 145.27, 144.36, 139.37, 138.66, 135.88, 134.07, 133.13, 132.85, 129.75, 128.88, 128.35, 127.51, 126.23, 124.56, 124.48, 123.04, 117.23, 115.42, 61.45, 28.70, 28.64, 28.57, 25.87, 24.58, 24.53, 24.02, 23.84, 23.26, 23.14, 22.31, 14.09. HRMS (ESI): Calcd. For $C_{42}H_{51}N_2O_4$ $[M+H]^+$: 647.3843, Found: 647.3835.



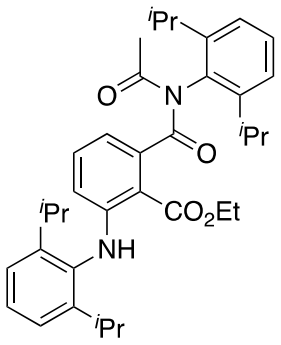
(5i) 82 mg, 33% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.22 (dd, *J* = 12.3, 6.7 Hz, 3H), 7.19-7.11 (m, 3H), 7.01-6.91 (m, 4H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.90 (d, *J* = 14.7 Hz, 1H), 5.84-5.76 (m, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.95 (q, *J* = 7.1 Hz, 1H), 2.32 (s, 8H), 2.13 (d, *J* = 7.2 Hz, 8H), 2.03 (d, *J* = 3.0 Hz, 4H), 1.69 (dd, *J* = 7.0, 1.7 Hz, 1H), 1.51 (dd, *J* = 6.3, 1.3 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.58, 170.79, 167.90, 143.90, 140.04, 138.52, 137.15, 136.30, 133.26, 132.66, 131.20, 130.45, 129.16, 129.14, 128.41, 128.31, 127.81, 127.65, 124.56, 117.01, 116.96, 61.74, 25.32, 19.29, 18.50, 18.34, 14.13. HRMS (ESI): Calcd. for $C_{31}H_{35}N_2O_4$ $[M+H]^+$: 499.2591, Found: 499.2580.



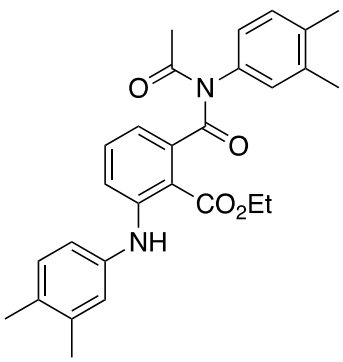
(5j) 119 mg, 39% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.23-7.15 (m, 2H), 7.14-7.03 (m, 3H), 6.77 (d, *J* = 7.7 Hz, 1H), 5.66 (d, *J* = 16.5 Hz, 1H), 5.57 (dq, *J* = 15.3, 6.3 Hz, 1H), 4.34 (d, *J* = 7.0 Hz, 2H), 3.20 (dt, *J* = 13.6, 6.8 Hz, 5H), 2.11 (s, 3H), 1.36 (dd, *J* = 6.3, 1.3 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.27 (d, *J* = 6.9 Hz, 7H), 1.23 (d, *J* = 6.8 Hz, 7H), 1.14 (t, *J* = 7.1 Hz, 14H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 173.08, 171.67, 168.16, 146.50, 145.59, 139.72, 137.47, 134.16, 131.96, 130.01, 129.76, 129.17, 127.09, 126.66, 124.52, 123.22, 115.73, 115.39, 61.77, 28.62, 25.84, 24.63, 24.51, 23.92, 22.02, 18.39, 14.41. HRMS (ESI): Calcd. for $C_{39}H_{51}N_2O_4$ $[M+H]^+$: 611.3843, Found: 611.3832.



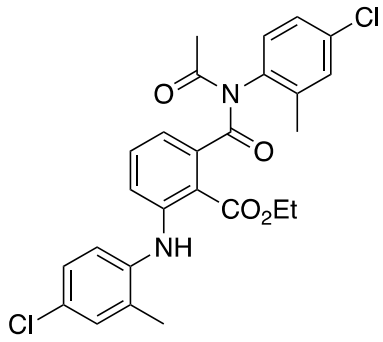
(5k) 96 mg, 33% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.36 – 7.32 (m, 1H), 7.30 (d, *J* = 7.7 Hz, 2H), 7.27 (s, 1H), 7.24 (s, 1H), 6.35 (s, 1H), 6.04 (s, 1H), 4.46 (q, *J* = 7.0 Hz, 2H), 3.33 (s, 2H), 3.12 (p, *J* = 6.7 Hz, 2H), 2.12 (s, 3H), 1.99 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.28 (d, *J* = 6.7 Hz, 12H), 1.15 (dd, *J* = 11.0, 6.9 Hz, 12H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.59, 172.24, 167.37, 150.41, 147.73, 143.74, 134.33, 134.04, 129.89, 127.86, 124.67, 124.10, 113.90, 61.35, 28.50, 28.34, 25.51, 24.86, 23.90, 23.01, 22.02, 14.69. HRMS (ESI): Calcd. for $C_{37}H_{49}N_2O_4$ $[M+H]^+$: 585.3687, Found: 585.3677



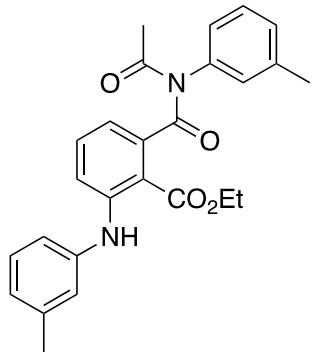
(5l) 213 mg, 82% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.34 (s, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.39-7.31 (m, 3H), 7.28 (d, *J* = 7.7 Hz, 2H), 7.21-7.15 (m, 1H), 6.62 (d, *J* = 7.3 Hz, 1H), 6.29 (dd, *J* = 8.6, 1.0 Hz, 1H), 4.51 (q, *J* = 7.1 Hz, 2H), 3.37 (s, 2H), 3.18 (p, *J* = 6.9 Hz, 2H), 2.01 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.35-1.27 (m, 12H), 1.20 (d, *J* = 6.9 Hz, 6H), 1.18 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.56, 172.01, 167.37, 150.27, 147.73, 134.18, 133.89, 132.89, 129.88, 127.97, 124.63, 124.09, 113.92, 113.08, 109.02, 61.51, 28.42, 28.31, 25.41, 24.81, 23.79, 22.95, 14.57. HRMS (ESI): Calcd. for $C_{36}H_{47}N_2O_4$ $[M+H]^+$: 571.3530, Found: 571.3541.



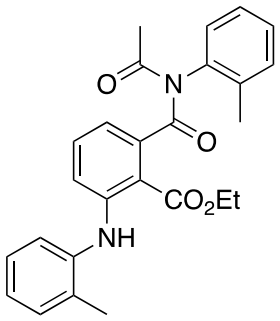
(5m) 73 mg, 32% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.94 (s, 1H), 7.14 (dd, *J* = 8.8, 7.2 Hz, 2H), 7.10-7.05 (m, 2H), 6.97-6.88 (m, 4H), 6.57 (dd, *J* = 7.1, 1.3 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 2.23 (d, *J* = 2.9 Hz, 12H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.04, 172.28, 167.42, 148.23, 140.87, 138.15, 137.92, 137.85, 137.31, 136.37, 132.54, 132.39, 130.63, 130.51, 129.86, 126.11, 124.54, 120.51, 115.73, 115.46, 109.91, 61.51, 26.83, 19.96, 19.61, 19.28, 14.25. HRMS (ESI): Calcd. For $C_{28}H_{30}N_2NaO_4$ $[M+Na]^+$: 481.2098, Found: 481.2100.



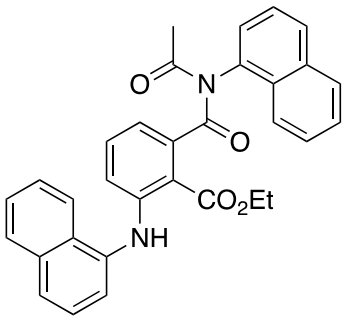
(5n) 77 mg, 31% yield, yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.81 (s, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.25 (d, *J* = 2.2 Hz, 1H), 7.20 (d, *J* = 2.2 Hz, 1H), 7.18-7.16 (m, 2H), 7.15 (s, 1H), 7.13 (s, 1H), 6.80 (dd, *J* = 8.6, 1.1 Hz, 1H), 6.53 (dd, *J* = 7.3, 1.1 Hz, 1H), 4.44 (dd, *J* = 7.2, 0.9 Hz, 2H), 2.30 (s, 3H), 2.28 (s, 3H), 2.21 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.09, 171.43, 167.33, 148.18, 140.99, 138.15, 137.36, 136.46, 134.89, 134.80, 132.83, 131.35, 131.07, 129.99, 127.48, 126.90, 125.43, 115.41, 114.73, 109.88, 61.77, 26.34, 17.97, 17.91, 14.36. HRMS (ESI): Calcd. For $C_{26}H_{24}Cl_2N_2NaO_4$ $[M+Na]^+$: 521.1005, Found: 521.1011.



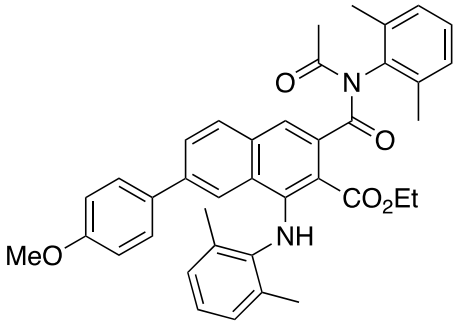
(5o) 58 mg, 27% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.95 (s, 1H), 7.26-7.22 (m, 1H), 7.21-7.18 (m, 1H), 7.16 (d, *J* = 4.2 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.02-6.94 (m, 4H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.60 (t, *J* = 4.2 Hz, 1H), 4.43 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 2.33 (d, *J* = 3.0 Hz, 6H), 1.43 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.95, 167.33, 147.47, 140.64, 140.54, 139.48, 139.43, 138.71, 132.34, 129.63, 129.50, 129.30, 129.24, 125.96, 124.68, 123.08, 119.35, 116.37, 115.97, 110.69, 61.64, 26.88, 21.51, 21.38, 14.23. HRMS (ESI): Calcd. For $C_{26}H_{26}N_2NaO_4$ $[M+Na]^+$: 453.1785, Found: 453.1782.



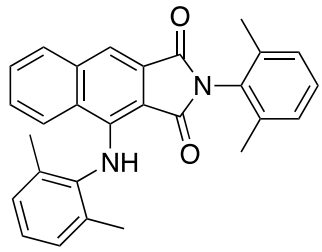
(5p) 65 mg, 30% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.90 (s, 1H), 7.32-7.28 (m, 2H), 7.27 (s, 1H), 7.25 (d, *J* = 1.3 Hz, 2H), 7.22-7.05 (m, 4H), 6.86 (dd, *J* = 8.6, 1.1 Hz, 1H), 6.56 (dd, J = 7.3, 1.0 Hz, 1H), 4.45 (dd, *J* = 7.1, 0.9 Hz, 2H), 2.32 (s, 3H), 2.25 (s, 6H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.26, 171.68, 167.50, 148.43, 141.37, 138.85, 137.91, 136.19, 132.92, 132.63, 131.43, 131.25, 129.22, 128.75, 127.33, 126.81, 124.93, 124.12, 115.31, 114.39, 109.74, 61.58, 26.23, 18.08, 17.94, 14.40. HRMS (ESI): Calcd. For $C_{26}H_{26}N_2NaO_4$ $[M+Na]^+$: 453.1785, Found: 453.1793.



(5q) 85 mg, 35% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.39 (s, 1H), 8.02-7.94 (m, 2H), 7.92 (d, *J* = 5.7 Hz, 1H), 7.90-7.86 (m, 2H), 7.71 (d, *J* = 7.4 Hz, 1H), 7.65-7.59 (m, 1H), 7.58-7.49 (m, 5H), 7.44 (d, *J* = 7.3 Hz, 2H), 6.95 (dd, *J* = 8.6, 7.3 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.55 (d, *J* = 7.2 Hz, 1H), 4.56 (dd, *J* = 7.1, 1.0 Hz, 2H), 2.39 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.90, 172.30, 167.69, 149.12, 140.94, 136.42, 135.46, 134.83, 134.53, 132.53, 130.93, 129.73, 129.68, 128.89, 128.50, 127.60, 127.03, 126.67, 126.48, 126.45, 125.90, 125.67, 125.60, 122.70, 122.08, 121.26, 115.83, 114.90, 109.57, 61.83, 26.39, 14.45. HRMS (ESI): Calcd. For $C_{32}H_{26}N_2NaO_4$ $[M+Na]^+$: 525.1785, Found: 525.1789.



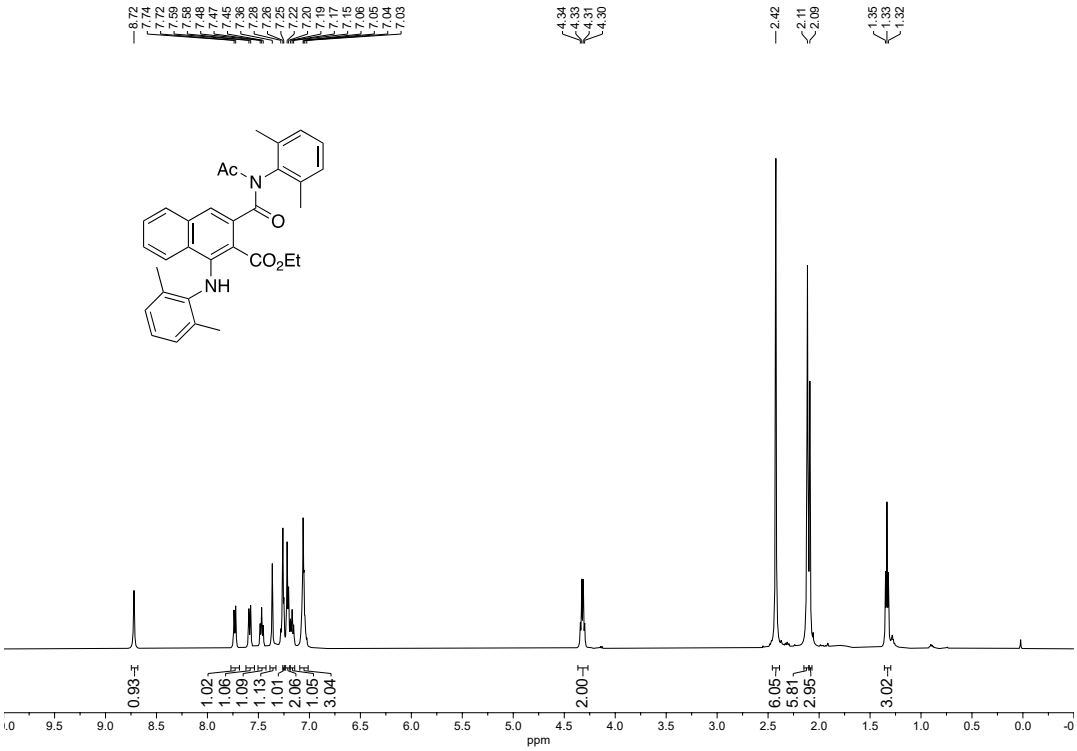
(7) 108.7 mg, 59% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.01 (s, 1H), 7.80-7.67 (m, 3H), 7.36 (s, 1H), 7.28 (d, *J* = 6.0 Hz, 1H), 7.22 (d, *J* = 6.4 Hz, 2H), 7.15 (s, 3H), 7.08 – 7.02 (m, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.40 (q, *J* = 7.0 Hz, 2H), 3.84 (s, 3H), 2.44 (s, 6H), 2.13 (s, 6H), 2.11 (s, 3H), 1.37 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.72, 171.13, 168.29, 159.44, 147.69, 141.39, 138.05, 137.24, 136.38, 136.30, 133.54, 133.38, 132.76, 129.32, 129.24, 129.19, 129.11, 128.27, 127.60, 126.41, 125.17, 122.18, 117.11, 114.26, 109.47, 77.37, 61.78, 55.45, 25.60, 19.32, 18.47, 14.45. HRMS (ESI): Calcd. For $C_{39}H_{38}N_2NaO_5$ $[M+Na]^+$: 637.2673, Found: 637.2679.

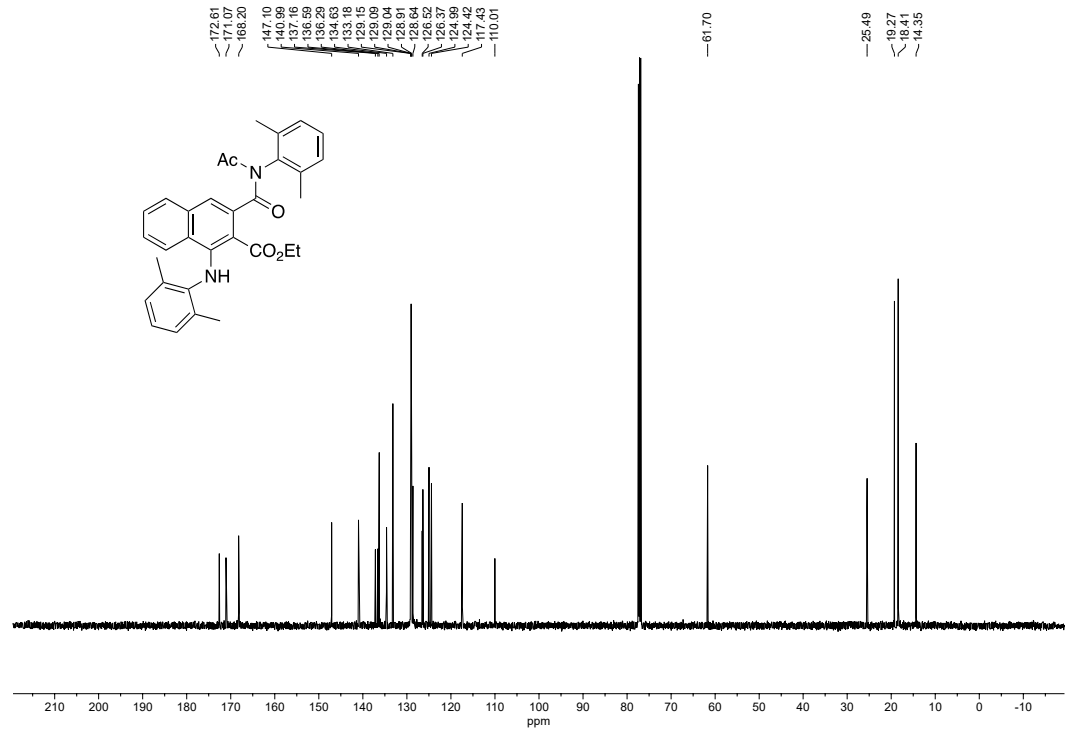


(8) 36.2 mg, 43% yield, yellow soild: m. p. 208-209 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.81 (s, 1H), 7.95 – 7.89 (m, 1H), 7.81 (s, 1H), 7.53 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.46-7.42 (m, 1H), 7.28 (dd, *J* = 8.5, 6.5 Hz, 1H), 7.23-7.18 (m, 4H), 7.16 (dd, *J* = 7.4, 1.5 Hz, 2H), 2.26 (s, 6H), 2.22 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.87, 167.14, 145.95, 138.99, 137.78, 137.06, 136.22, 131.55, 131.31, 130.32, 129.37, 129.30, 129.12, 128.96, 128.55, 128.38, 128.24, 128.15, 127.50, 127.41, 127.28, 125.14, 125.07, 117.40, 115.76, 104.52, 19.06, 18.34. HRMS (ESI): Calcd. For $C_{28}H_{24}N_2NaO_2$ $[M+Na]^+$: 443.1730, Found: 443.1757.

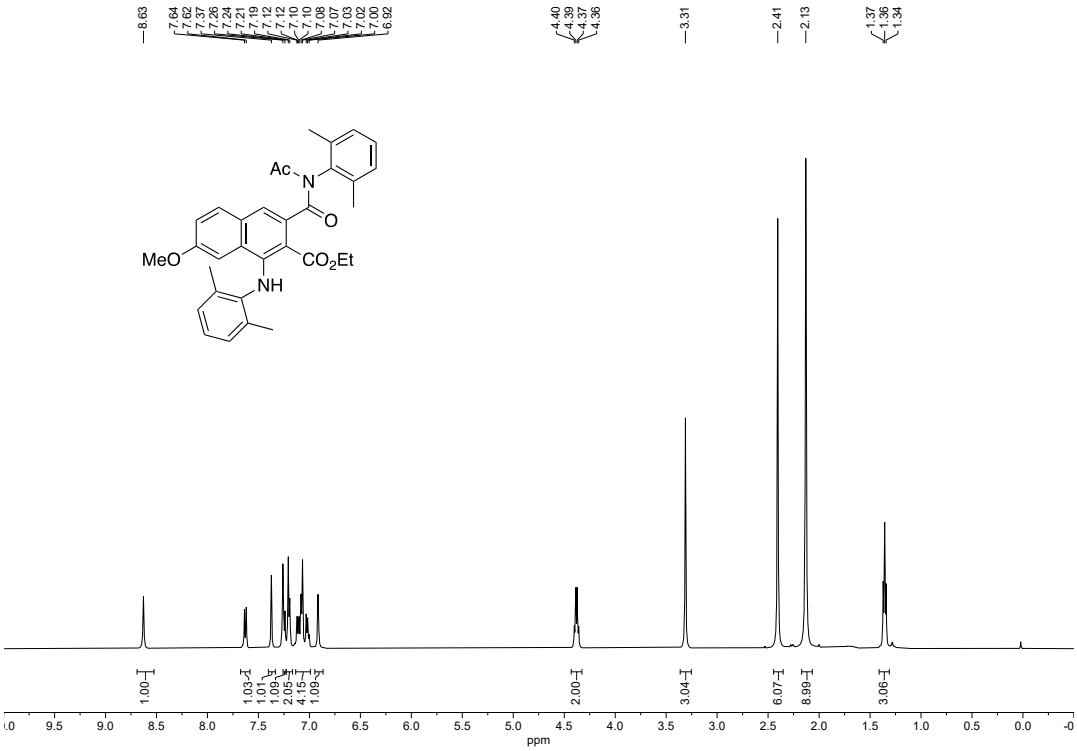
4. ^{1}H NMR and ^{13}C NMR Spectra of All Compounds

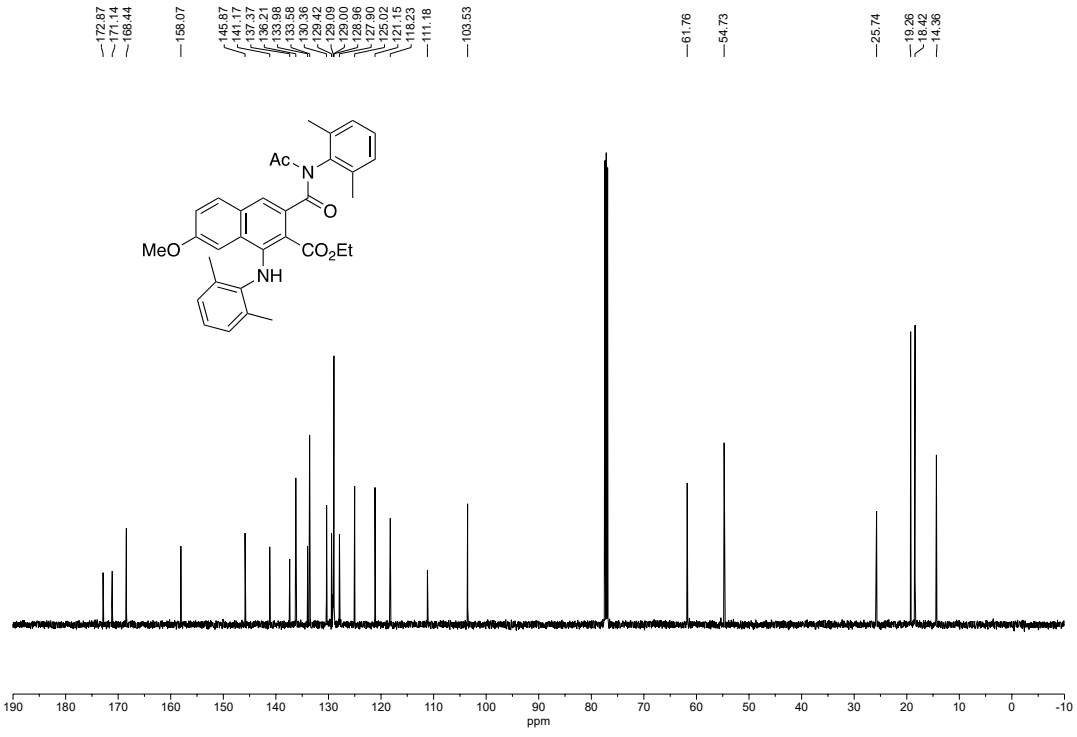
Compound **3a**



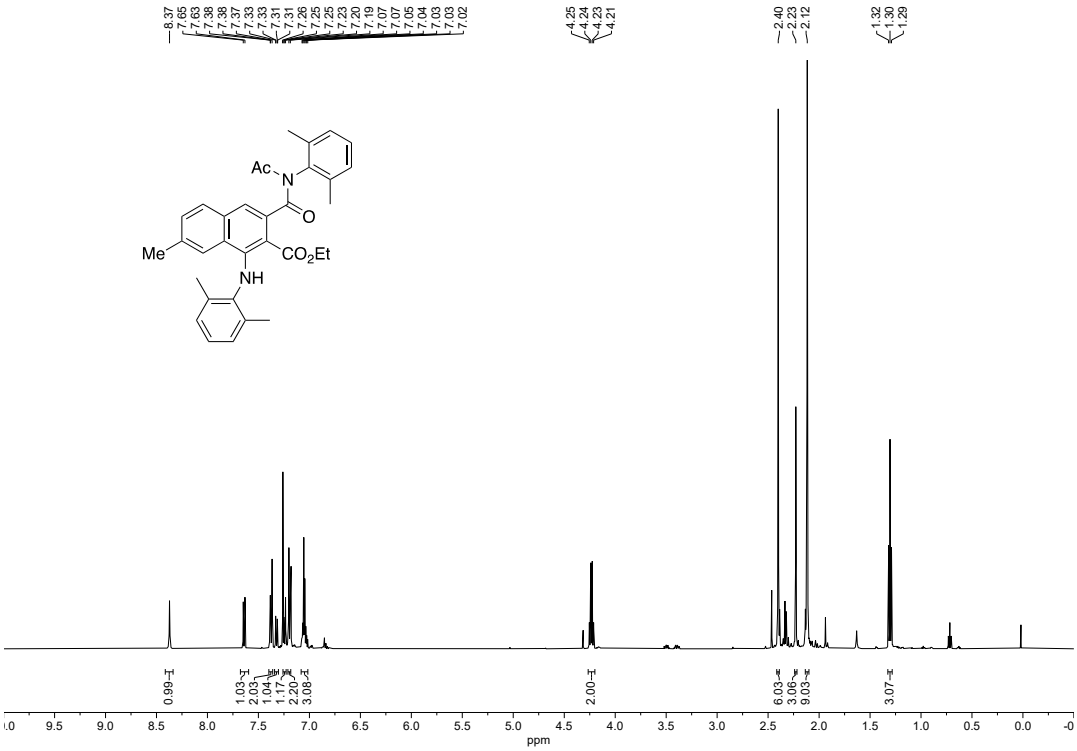


Compound **3b**


8.63
7.64
7.62
7.37
7.26
7.24
7.21
7.19
7.12
7.12
7.10
7.10
7.08
7.07
7.03
7.02
7.00
6.92
4.40
4.39
4.37
4.36
3.31
2.41
2.13
1.37
1.36
1.34
Ac
N
O
MeO
CO2Et
NH
1.00
1.03
1.01
1.09
2.05
4.15
1.09
2.00
3.04
6.07
8.99
3.06
ppm


172.87
171.14
168.44
158.07
145.87
141.17
137.37
136.21
133.98
133.58
130.36
129.42
129.09
129.00
128.96
127.90
125.02
121.15
118.23
111.18
103.53
61.76
54.73
25.74
19.26
18.42
14.36
Ac
N
O
MeO
CO2Et
NH
ppm

Compound **3c**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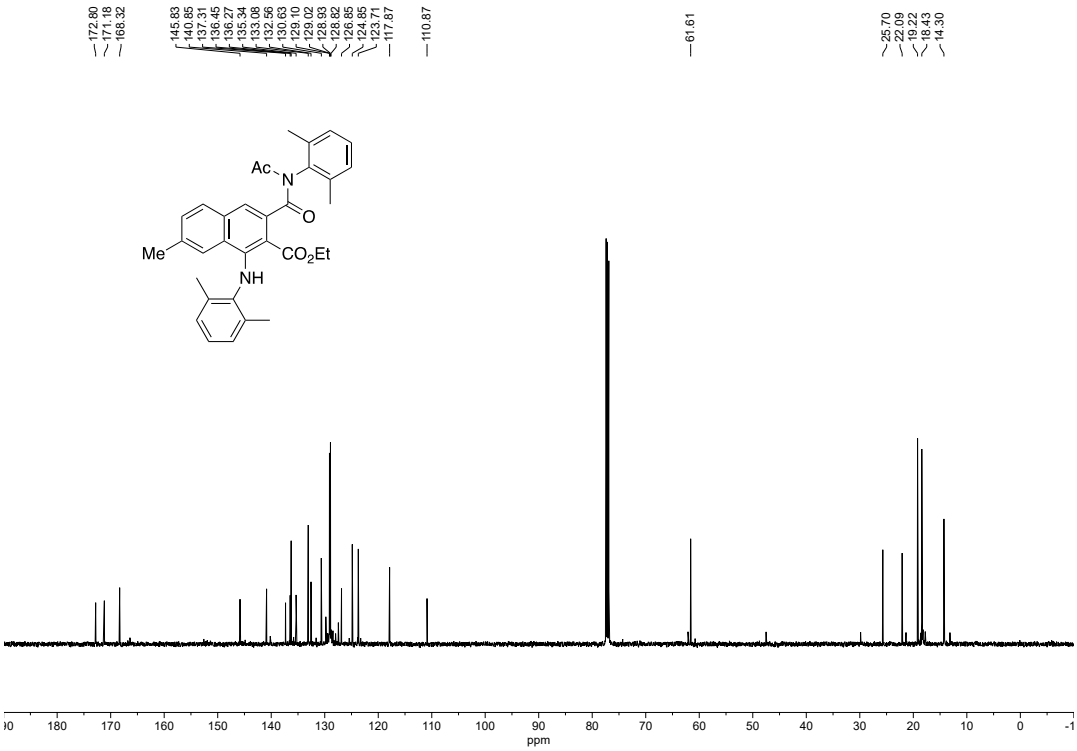
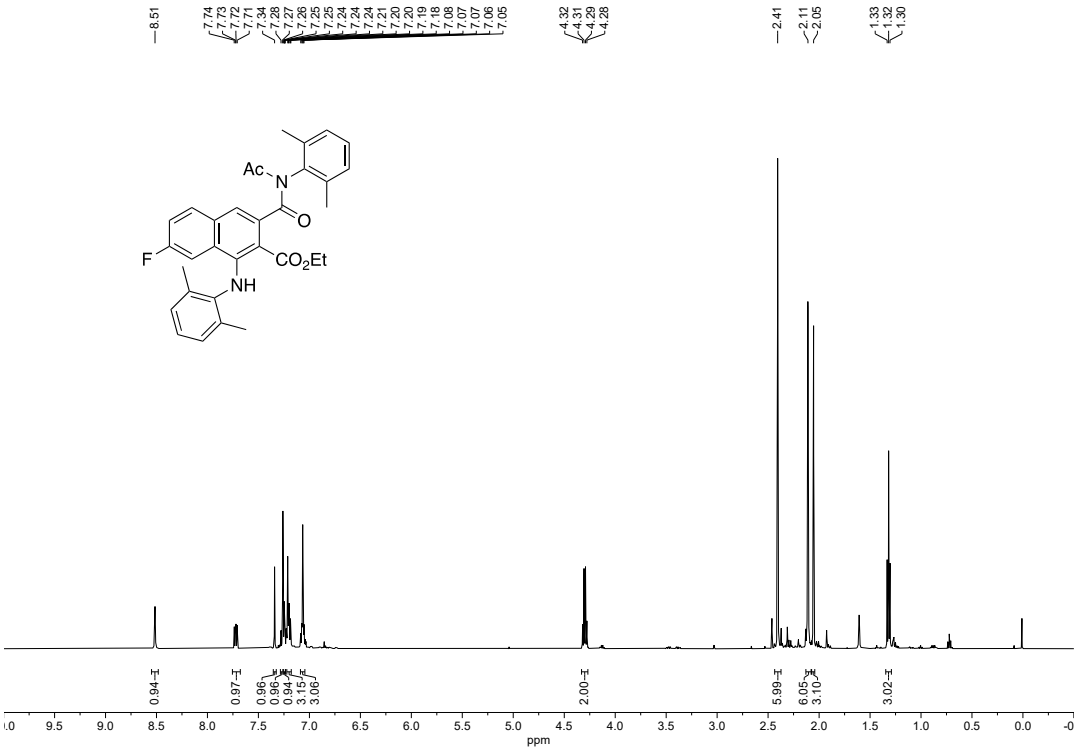
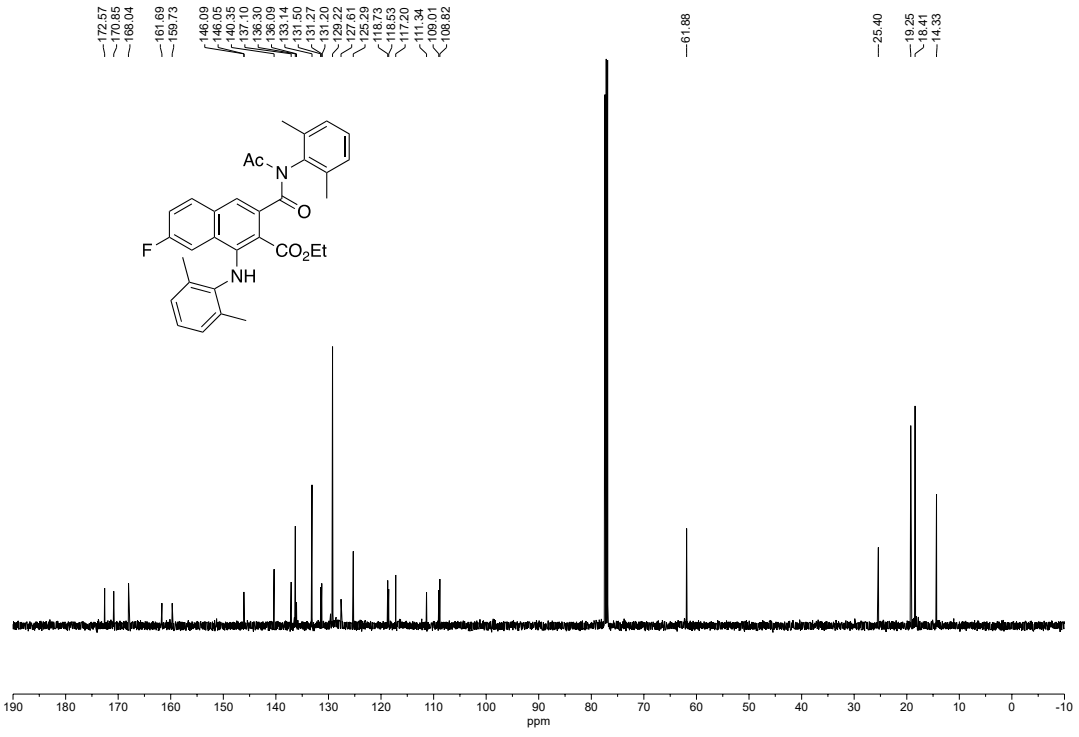
7.65
7.63
7.38
7.38
7.37
7.33
7.33
7.31
7.31
7.26
7.25
7.25
7.23
7.20
7.19
7.07
7.07
7.05
7.04
7.03
7.03
7.02
4.25
4.24
4.23
4.21
2.40
2.23
2.12
1.32
1.30
1.29
Ac
N
O
Me
CO2Et
NH
0.99
1.03
2.03
1.04
1.17
2.20
3.08
2.00
6.03
3.06
9.03
3.07
ppm

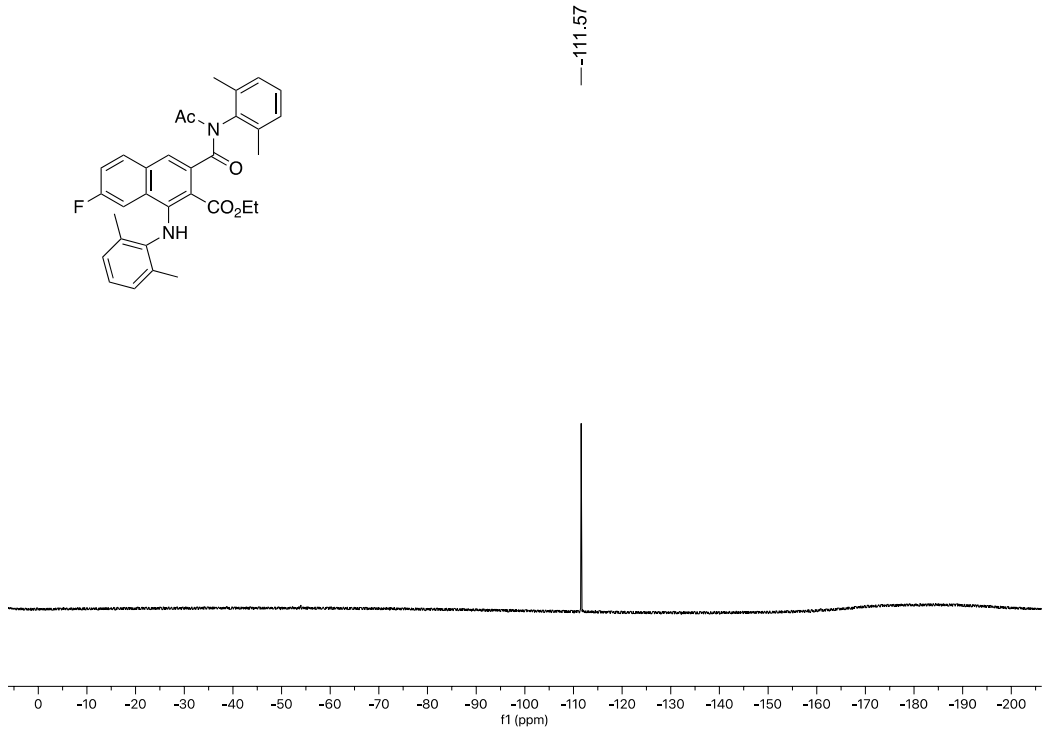

172.80
171.18
168.32
145.83
140.85
137.31
136.45
136.27
135.34
133.08
132.56
130.63
129.10
129.02
128.93
128.82
126.85
124.65
123.71
117.87
110.87
61.61
25.70
22.09
19.22
18.43
14.30
Ac
N
O
Me
CO2Et
NH
ppm

Compound **3d**

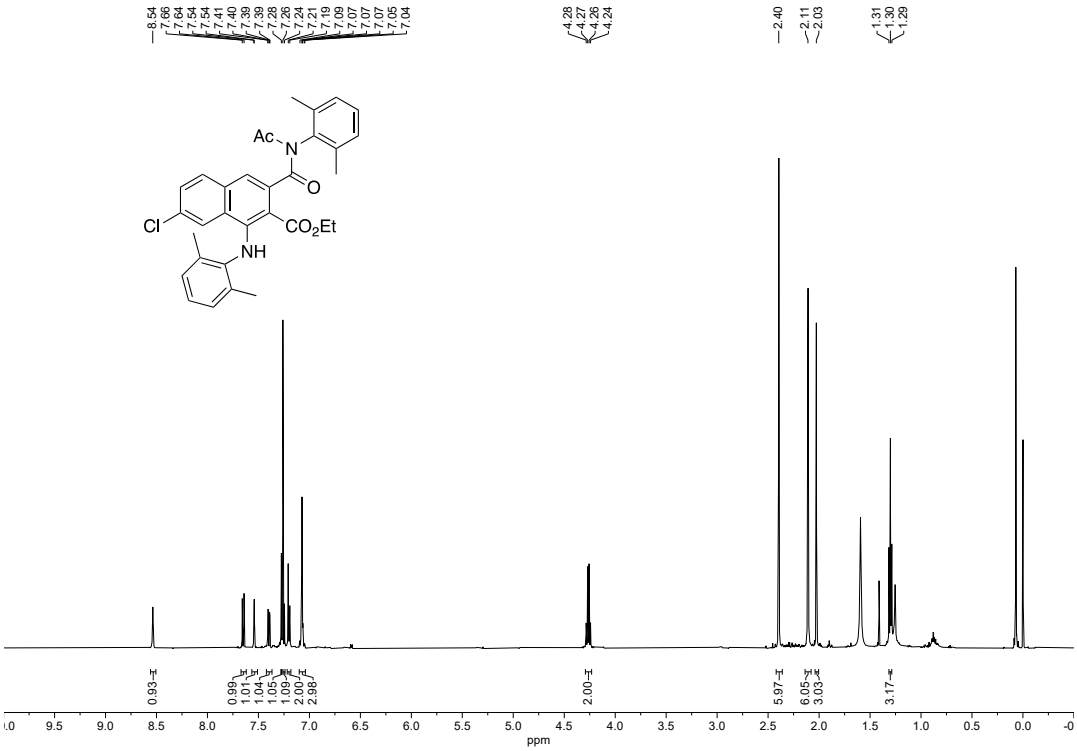

8.51
7.74
7.73
7.72
7.71
7.34
7.28
7.27
7.26
7.25
7.25
7.24
7.24
7.24
7.21
7.20
7.20
7.19
7.18
7.08
7.07
7.07
7.06
7.05
4.32
4.31
4.29
4.28
2.41
2.11
2.05
1.33
1.32
1.30
Ac
N
O
F
CO2Et
NH
0.94
0.97
0.96
0.96
0.94
3.15
3.06
2.00
5.99
6.05
3.10
3.02
ppm

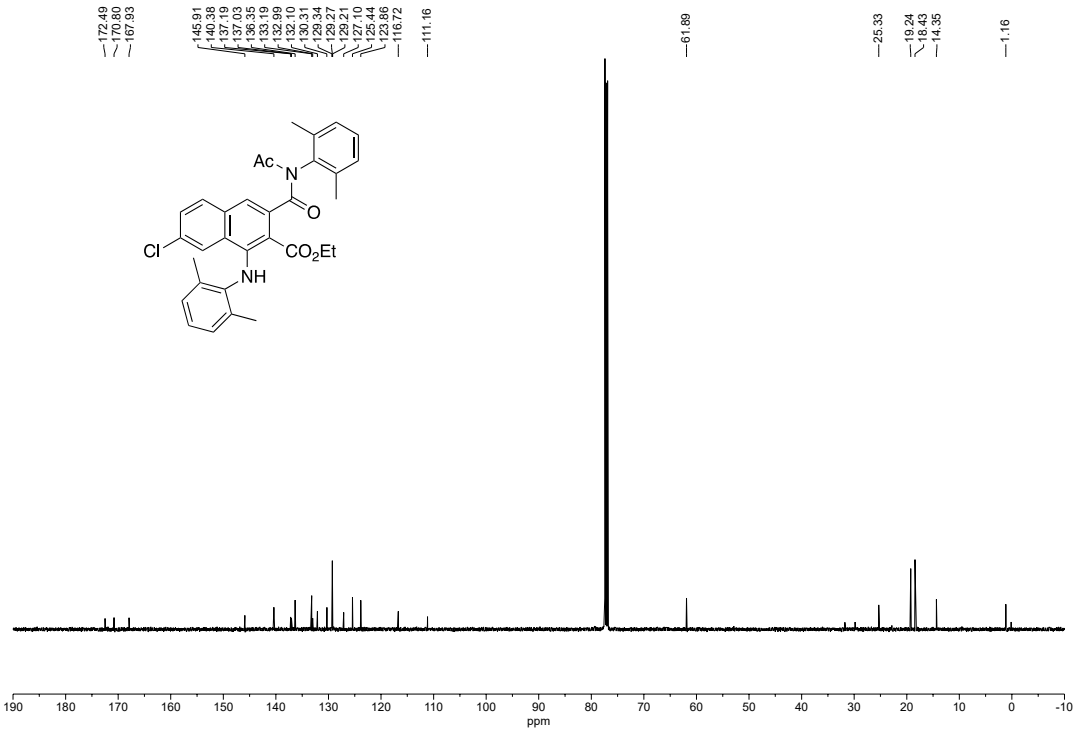

172.57
170.85
168.04
161.69
159.73
146.09
146.05
140.35
137.10
136.30
136.09
133.14
131.50
131.27
131.20
129.22
127.61
125.29
118.73
118.53
117.20
111.34
109.01
108.82
61.68
25.40
19.25
18.41
14.33
Ac
N
O
F
CO2Et
NH
ppm

^{19}F NMR of Compound **3d**

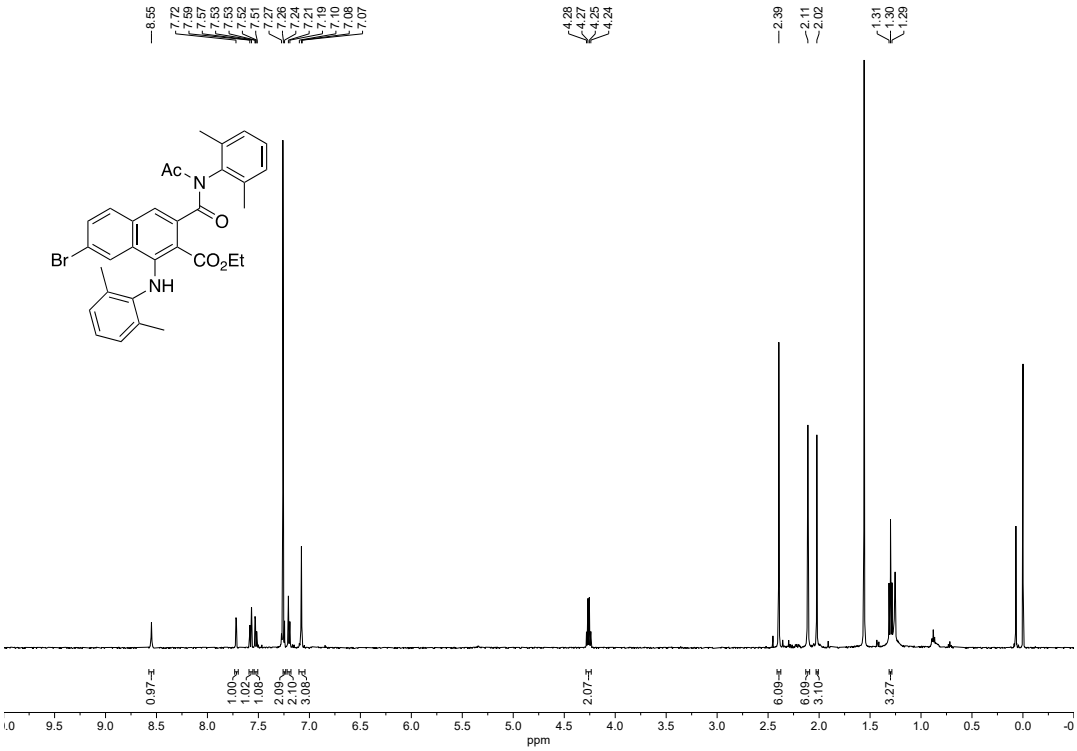


Compound **3e**


8.54
7.66
7.64
7.54
7.54
7.41
7.40
7.39
7.39
7.28
7.26
7.24
7.21
7.19
7.09
7.07
7.07
7.07
7.05
7.04
4.28
4.27
4.26
4.24
2.40
2.11
2.03
1.31
1.30
1.29
Ac
N
O
Cl
CO2Et
NH
0.93
0.99
1.01
1.04
1.05
1.09
2.00
2.98
2.00
5.97
6.05
3.03
3.17
ppm


172.49
170.80
167.93
145.91
140.38
137.19
137.03
136.35
133.19
132.99
132.10
130.31
129.34
129.27
129.21
127.10
125.44
123.86
116.72
111.16
61.69
25.33
19.24
18.43
14.35
1.16
Ac
N
O
Cl
CO2Et
NH
ppm

Compound **3f**


8.55
7.72
7.59
7.57
7.53
7.53
7.52
7.51
7.27
7.26
7.24
7.21
7.19
7.10
7.08
7.07
4.28
4.27
4.25
4.24
2.39
2.11
2.02
1.31
1.30
1.29
Ac
N
O
Br
CO2Et
NH
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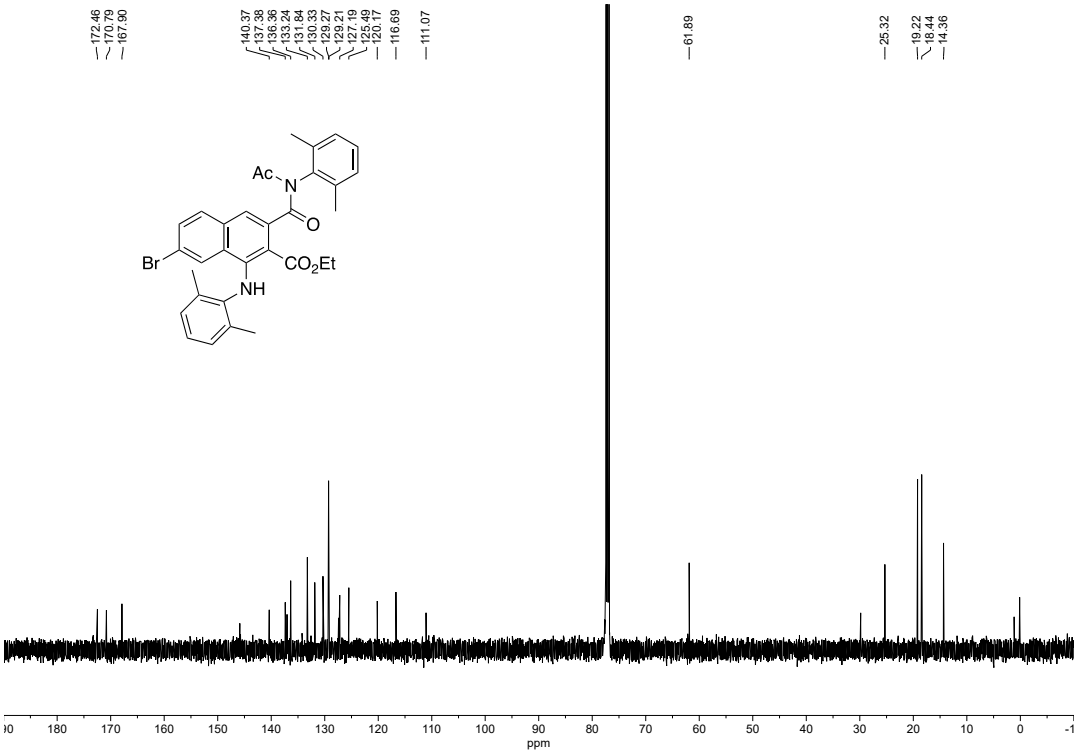
1.00
1.02
1.08
2.09
2.10
3.08
2.07
6.09
6.09
3.10
3.27
ppm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137.38
136.36
133.24
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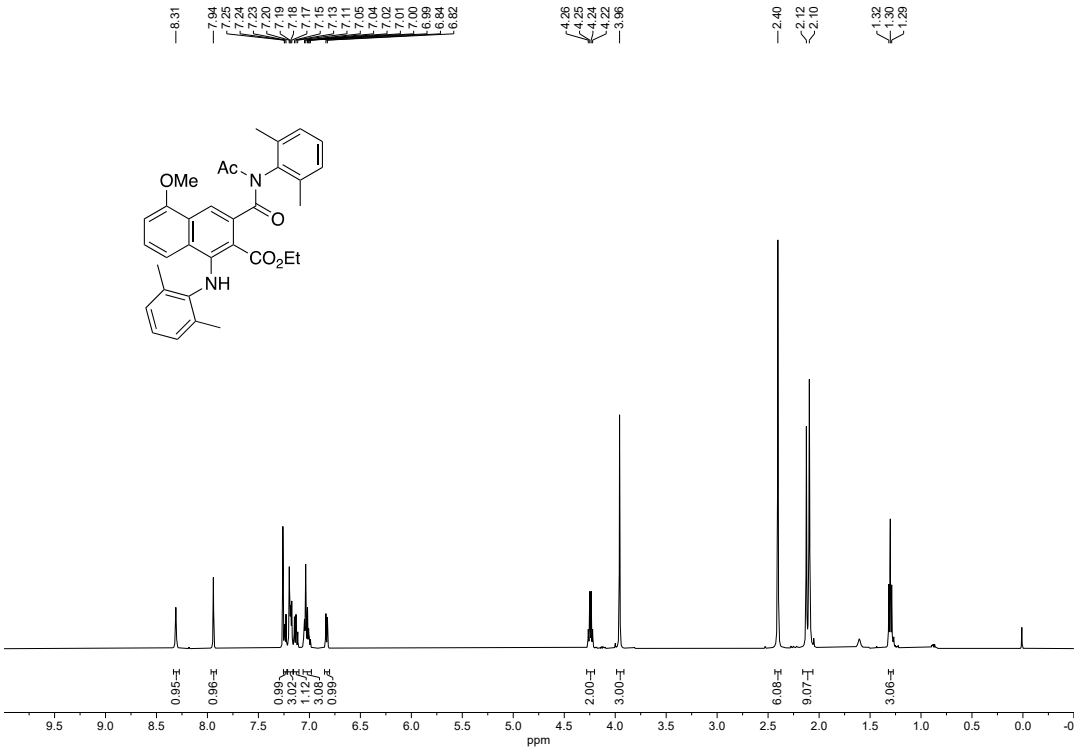
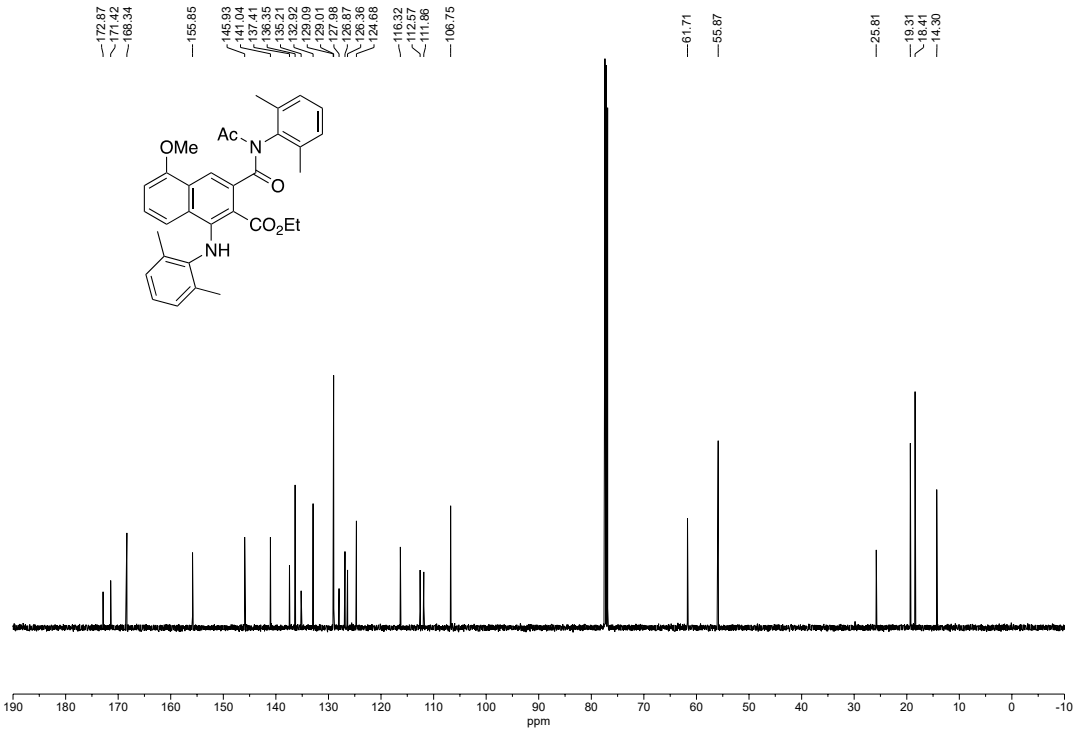
130.33
129.27
129.21
127.19
125.49
120.17
116.69
111.07
61.89
25.32
19.22
18.44
14.36
Ac
N
O
Br
CO2Et
NH
ppm

Compound **3g**


8.31
7.94
7.25
7.24
7.23
7.20
7.19
7.18
7.17
7.15
7.13
7.11
7.05
7.04
7.02
7.01
7.00
6.99
6.84
6.82
4.26
4.25
4.24
4.22
3.96
2.40
2.12
2.10
1.32
1.30
1.29
OMe
Ac
N
O
CO2Et
NH
0.95
0.96
0.99
3.02
1.12
3.08
0.99
2.00
3.00
6.08
9.07
3.06
ppm


172.87
171.42
168.34
155.85
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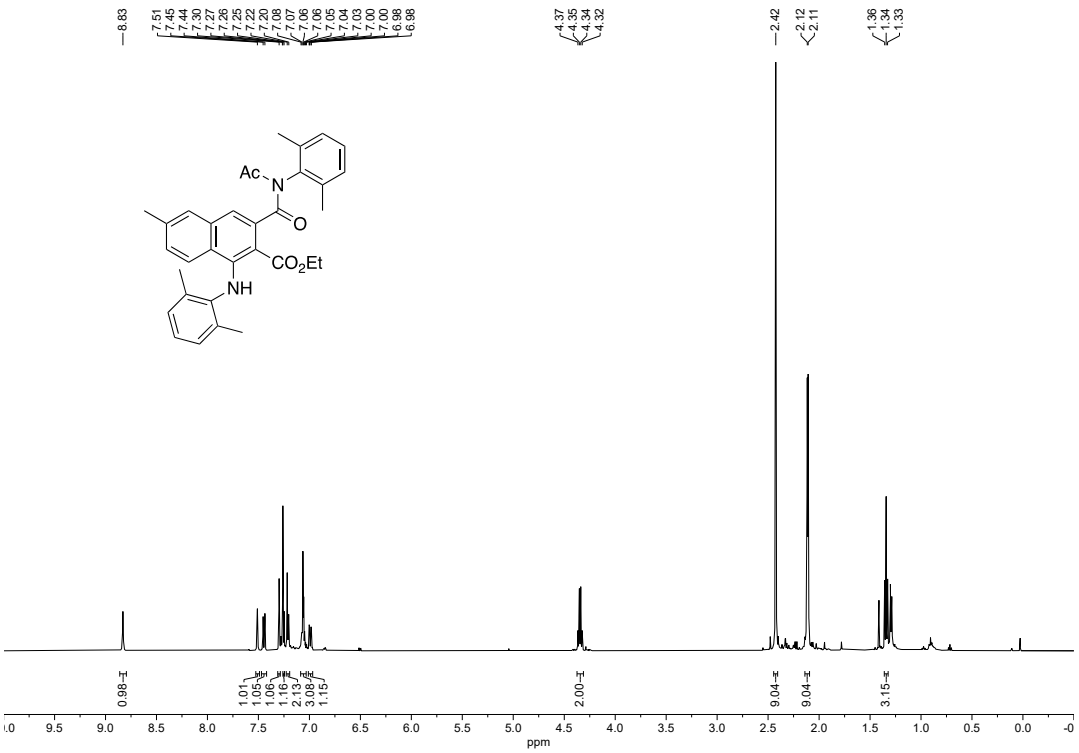
141.04
137.41
136.35
135.21
132.92
129.09
129.01
128.88
127.98
126.87
126.36
124.68
116.32
112.57
111.86
106.75
61.71
55.87
25.81
19.31
18.41
14.30
OMe
Ac
N
O
CO2Et
NH
ppm

Compound **3h**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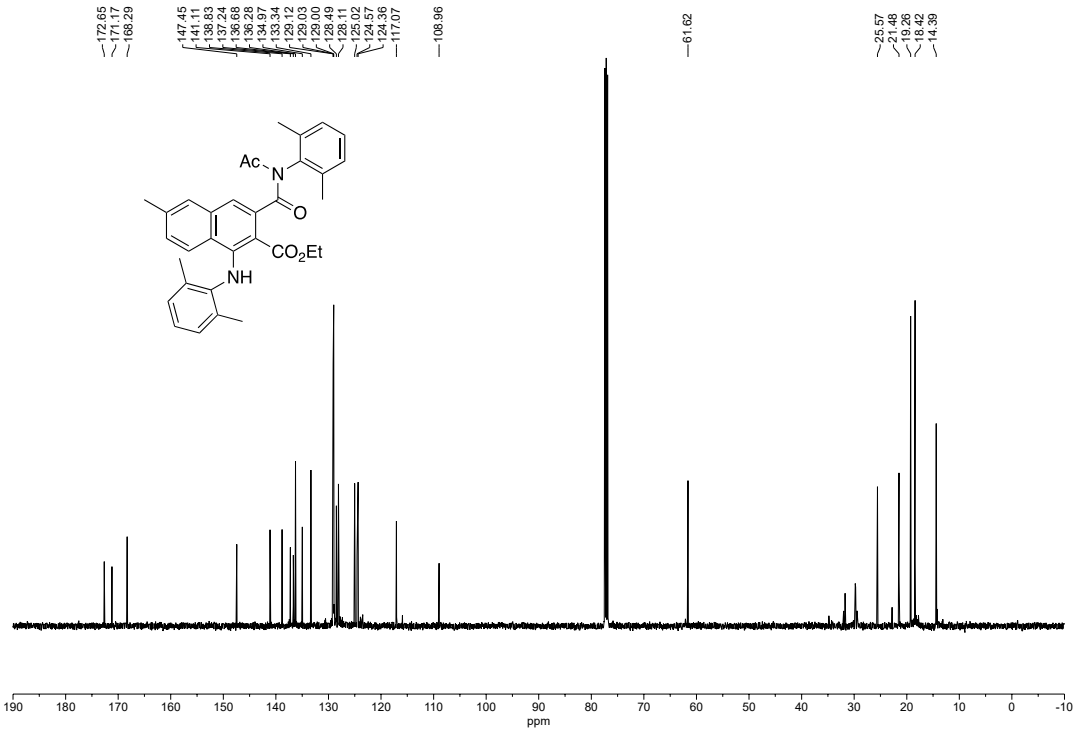
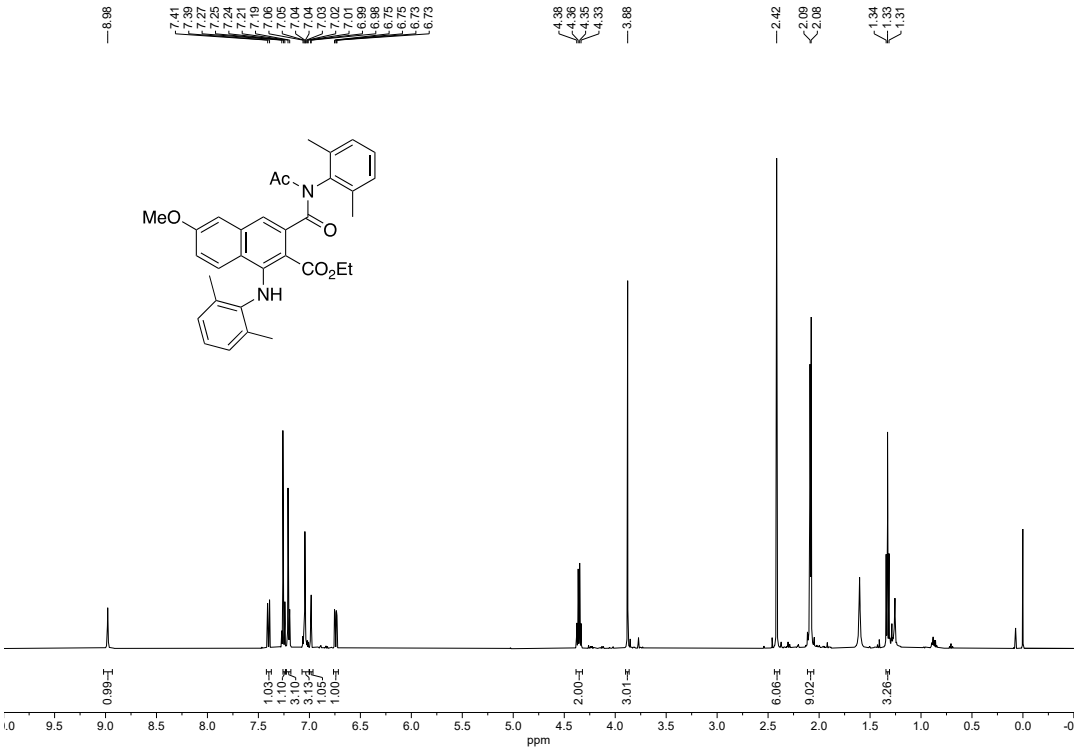
7.27
7.26
7.25
7.22
7.20
7.08
7.07
7.07
7.06
7.05
7.04
7.03
7.00
7.00
6.98
6.98
4.37
4.35
4.34
4.32
2.42
2.12
2.11
1.36
1.34
1.33
Ac
N
O
CO2Et
NH
0.98
1.01
1.05
1.06
1.16
2.13
3.08
1.15
2.00
9.04
9.04
3.15
ppm


172.65
171.17
168.29
147.45
141.11
138.83
137.24
136.68
136.28
134.97
133.34
129.12
129.03
129.00
128.49
128.11
125.02
124.57
124.36
117.07
108.96
61.62
25.57
21.48
19.26
18.42
14.39
Ac
N
O
CO2Et
NH
ppm

Compound **3i**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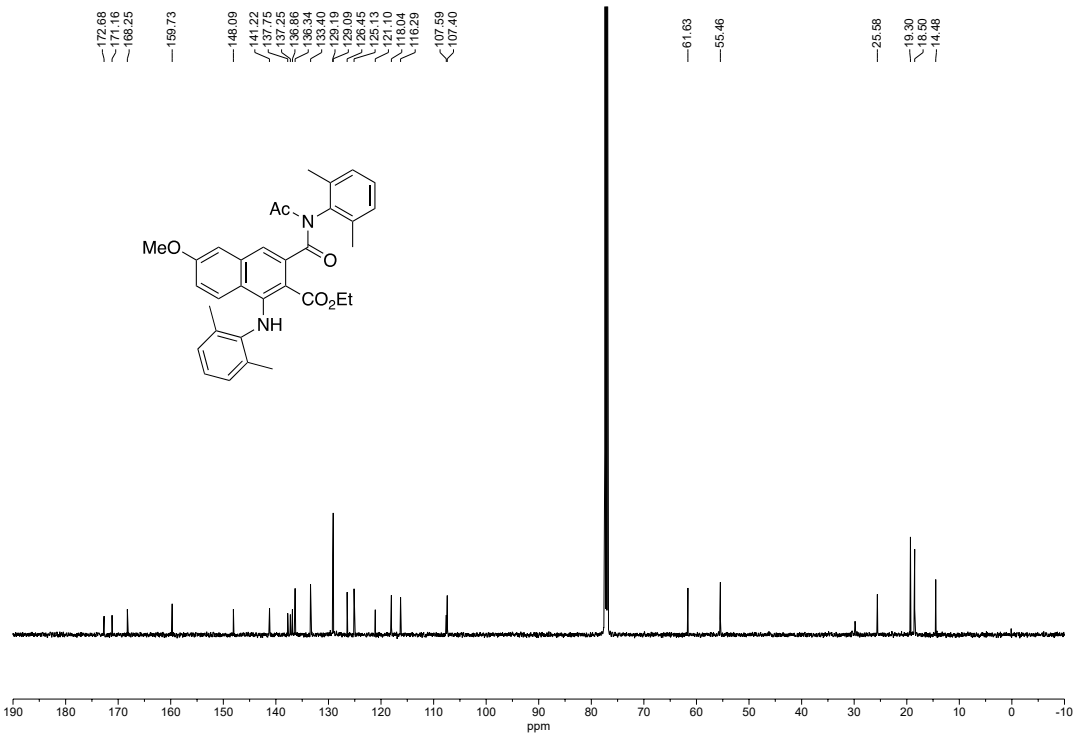
7.27
7.25
7.24
7.21
7.19
7.06
7.05
7.04
7.04
7.03
7.02
7.01
6.99
6.98
6.75
6.73
6.73
4.38
4.36
4.35
4.33
3.88
2.42
2.09
2.08
1.34
1.33
1.31
Ac
N
O
MeO
CO2Et
NH
0.99
1.03
1.10
3.10
3.13
1.05
1.00
2.00
3.01
6.06
9.02
3.26
ppm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141.22
137.75
137.25
136.86
136.34
133.40
129.19
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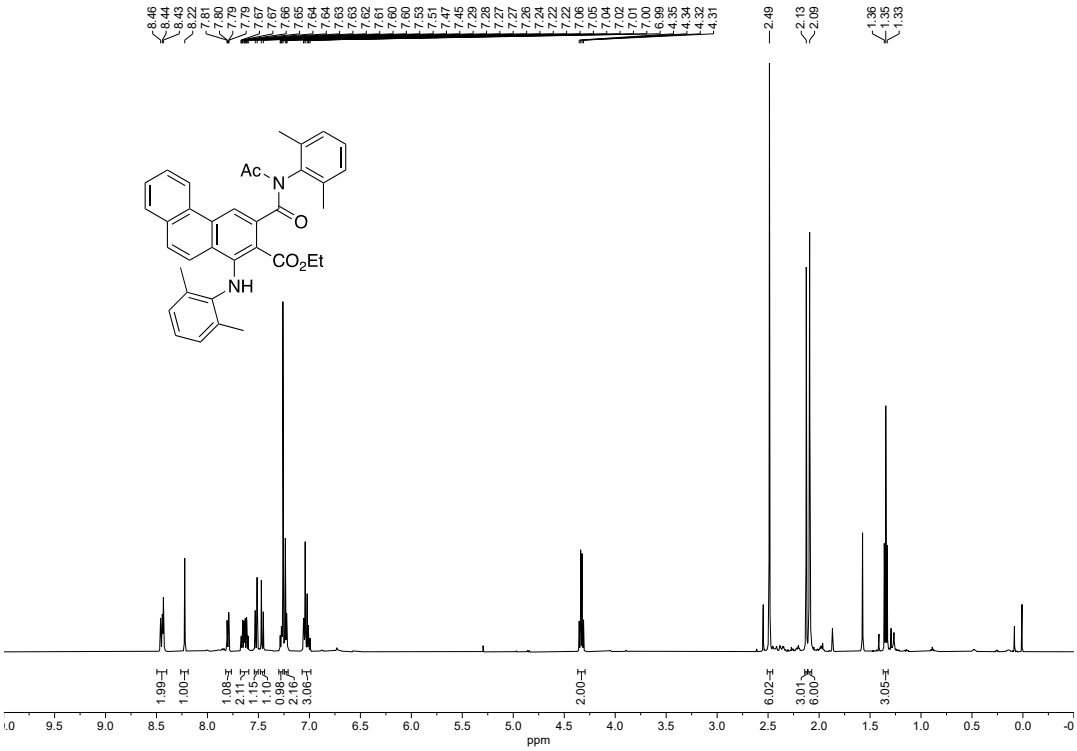
126.45
125.13
121.10
118.04
116.29
107.59
107.40
61.63
55.46
25.58
19.30
18.50
14.48
Ac
N
O
MeO
CO2Et
NH
ppm

Compound **3j**


8.46
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7.79
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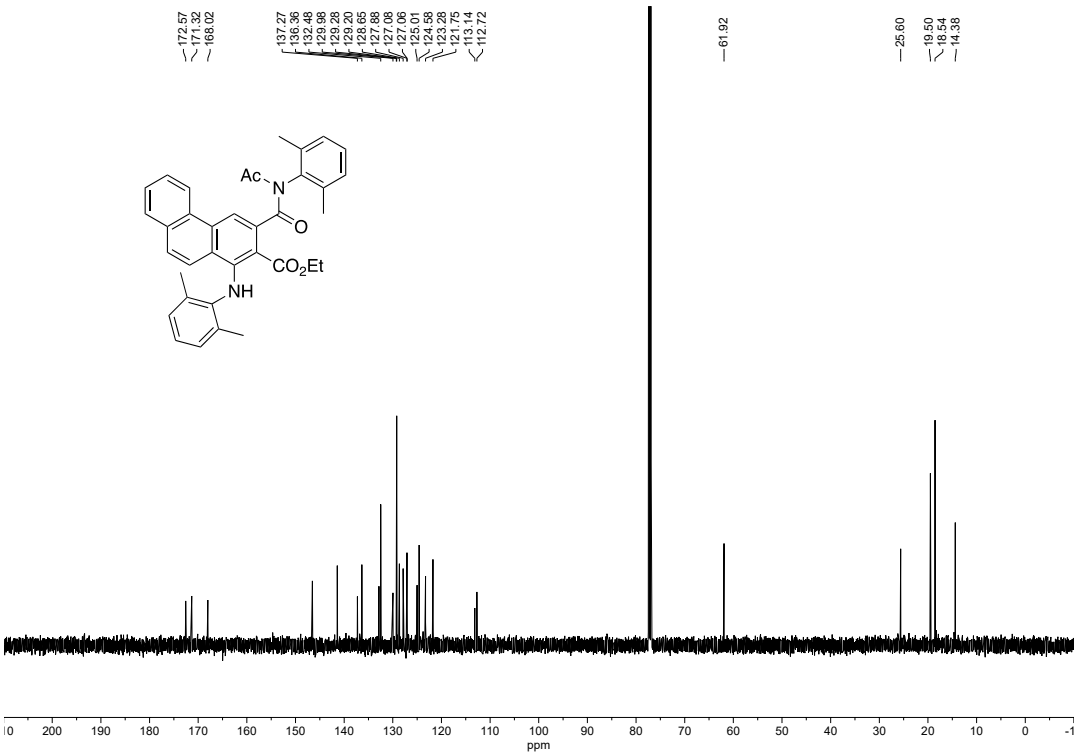
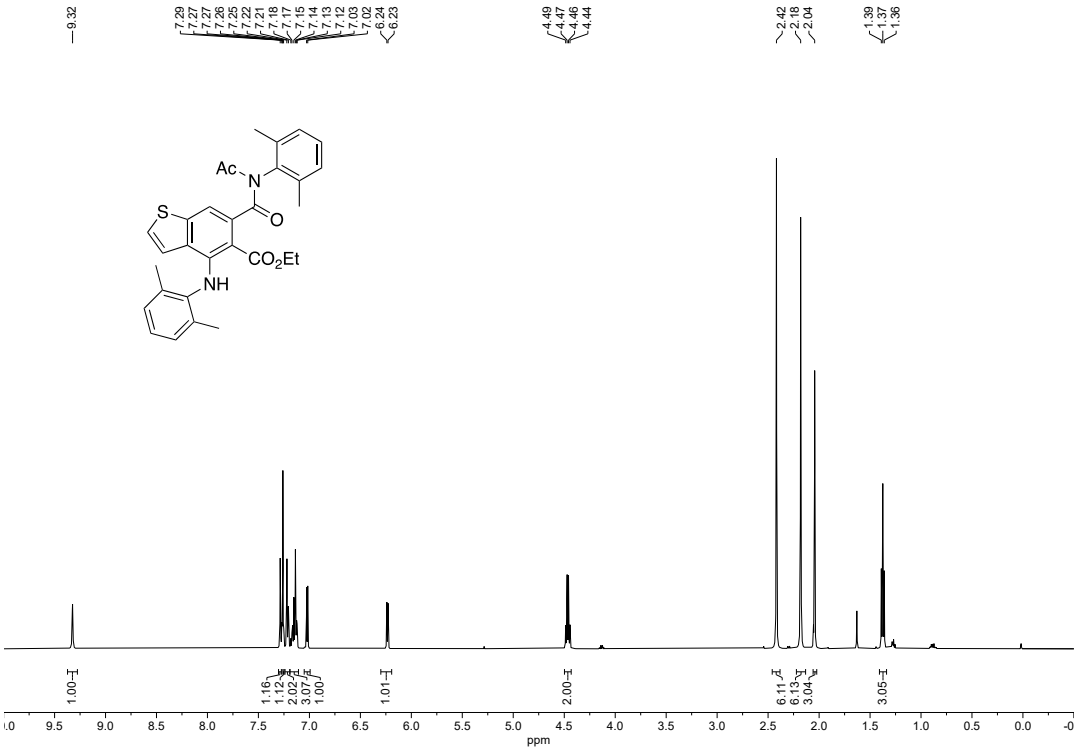
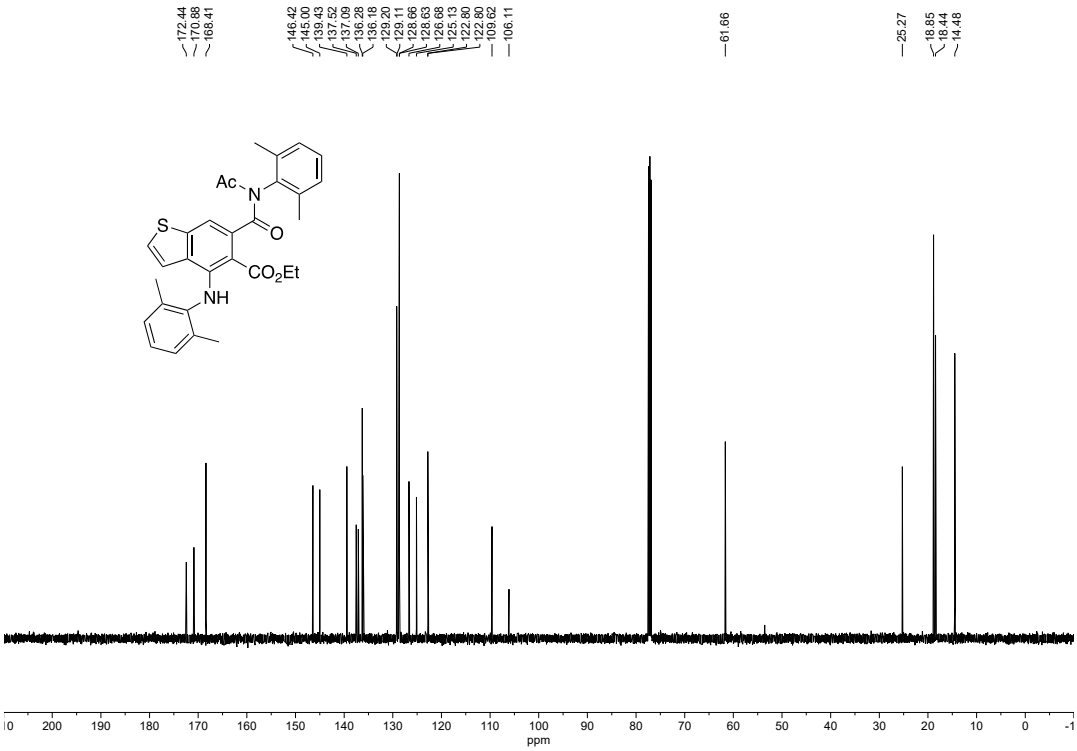
7.67
7.66
7.65
7.64
7.64
7.63
7.63
7.62
7.61
7.60
7.60
7.53
7.51
7.47
7.45
7.28
7.28
7.27
7.27
7.26
7.24
7.22
7.22
7.06
7.05
7.04
7.02
7.01
7.00
6.99
4.35
4.34
4.32
4.31
2.49
2.13
2.09
1.36
1.35
1.33
Ac
N
O
CO2Et
NH
1.99
1.00
1.08
2.11
1.15
1.10
0.99
2.16
3.06
2.00
6.02
3.01
6.00
3.05
ppm


172.57
171.32
168.02
137.27
136.36
132.48
129.98
129.28
129.20
128.65
127.88
127.08
127.06
125.01
124.58
123.28
121.75
113.14
112.72
61.92
25.60
19.50
18.54
14.38
Ac
N
O
CO2Et
NH
ppm

Compound **3k**


9.32
7.29
7.27
7.27
7.26
7.25
7.22
7.21
7.18
7.17
7.15
7.14
7.13
7.12
7.03
7.02
6.24
6.23
4.49
4.47
4.46
4.44
2.42
2.18
2.04
1.39
1.37
1.36
Ac
N
O
S
CO2Et
NH
1.00
1.16
1.12
2.02
3.07
1.00
1.01
2.00
6.11
6.13
3.04
3.05
ppm


172.44
170.88
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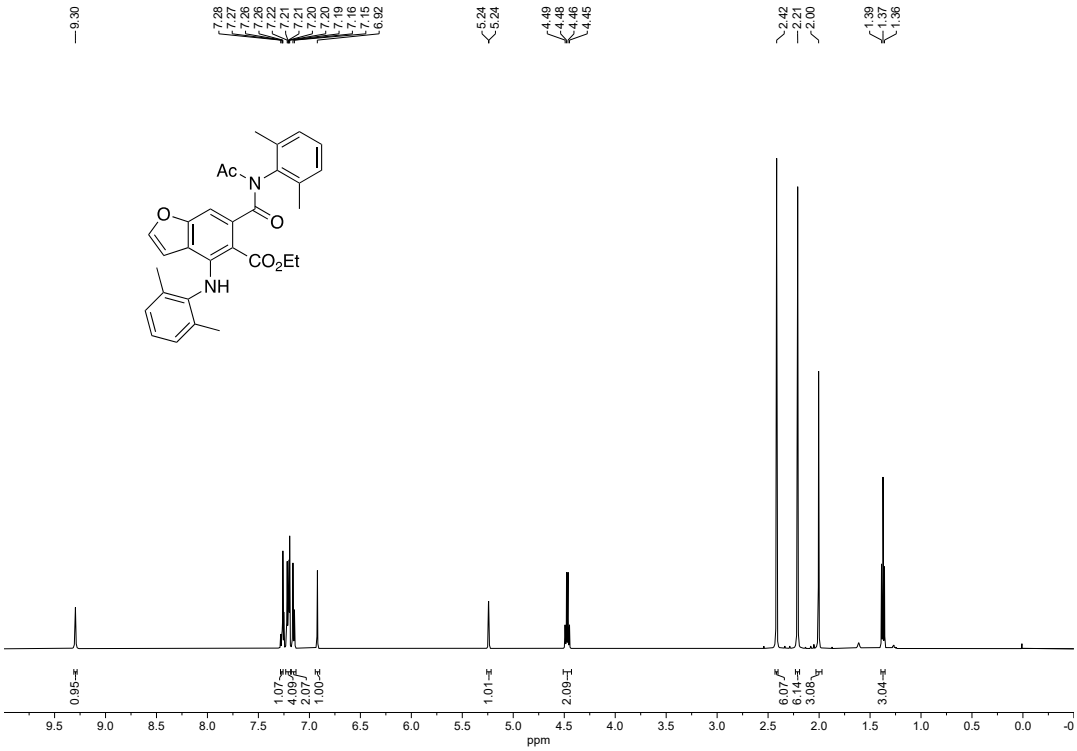
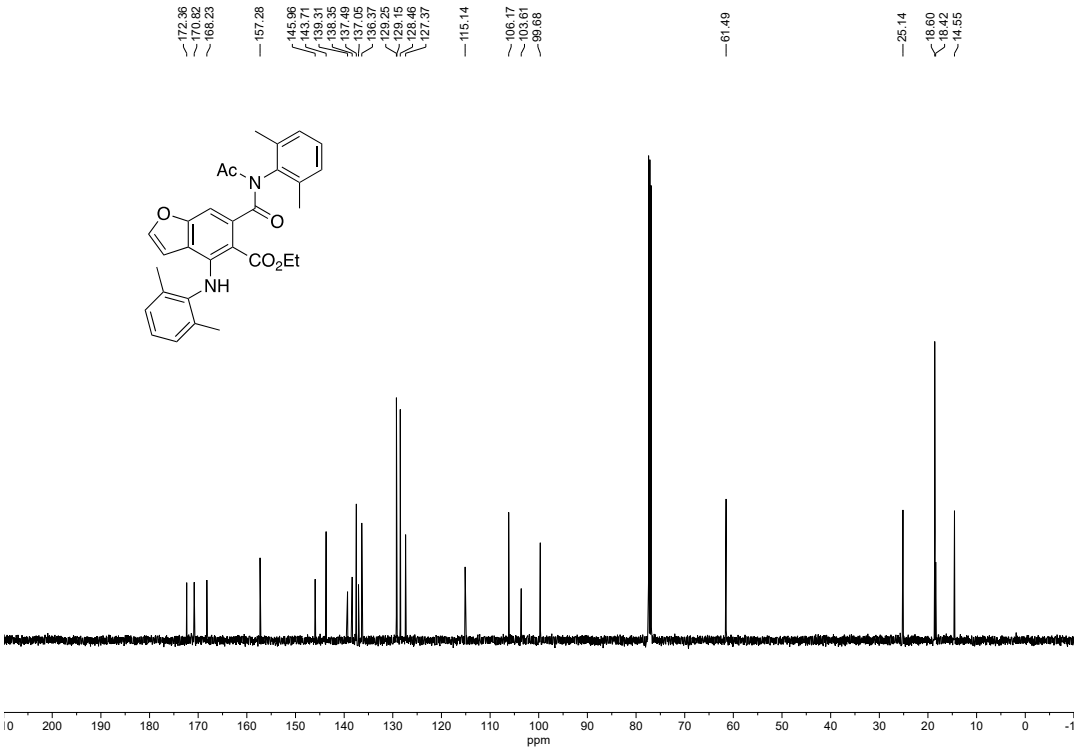
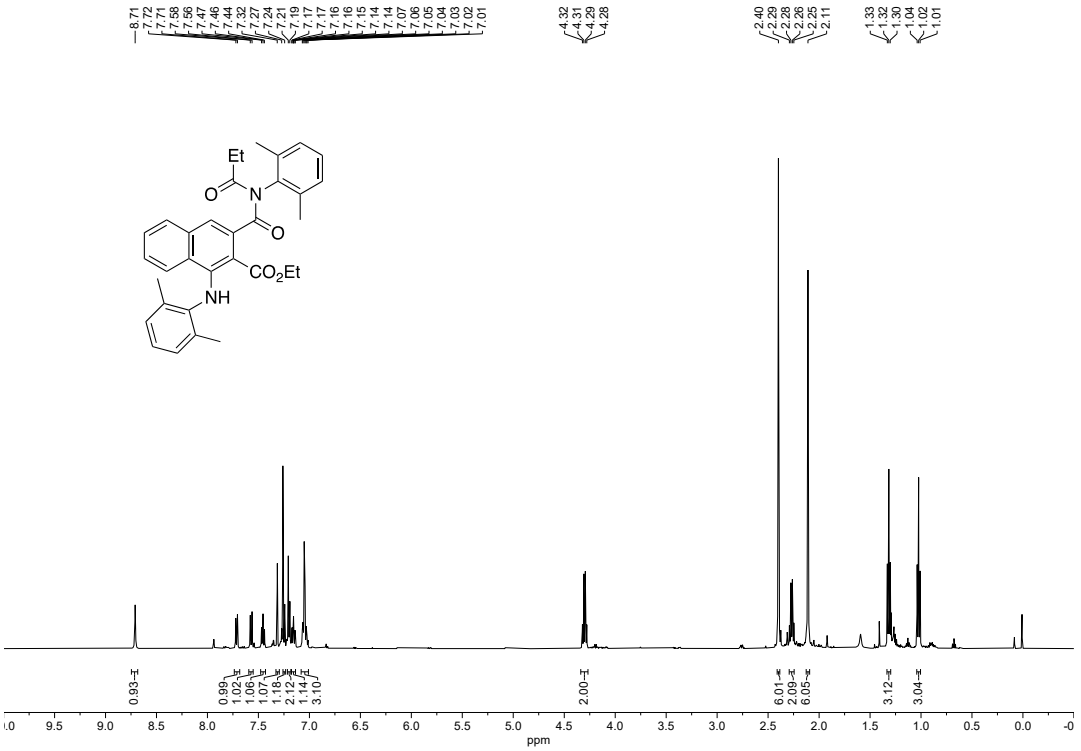
145.00
139.43
137.52
137.09
136.28
136.18
129.20
129.11
128.66
128.63
126.68
125.13
122.80
122.80
109.62
106.11
61.66
25.27
18.85
18.44
14.48
Ac
N
O
S
CO2Et
NH
ppm

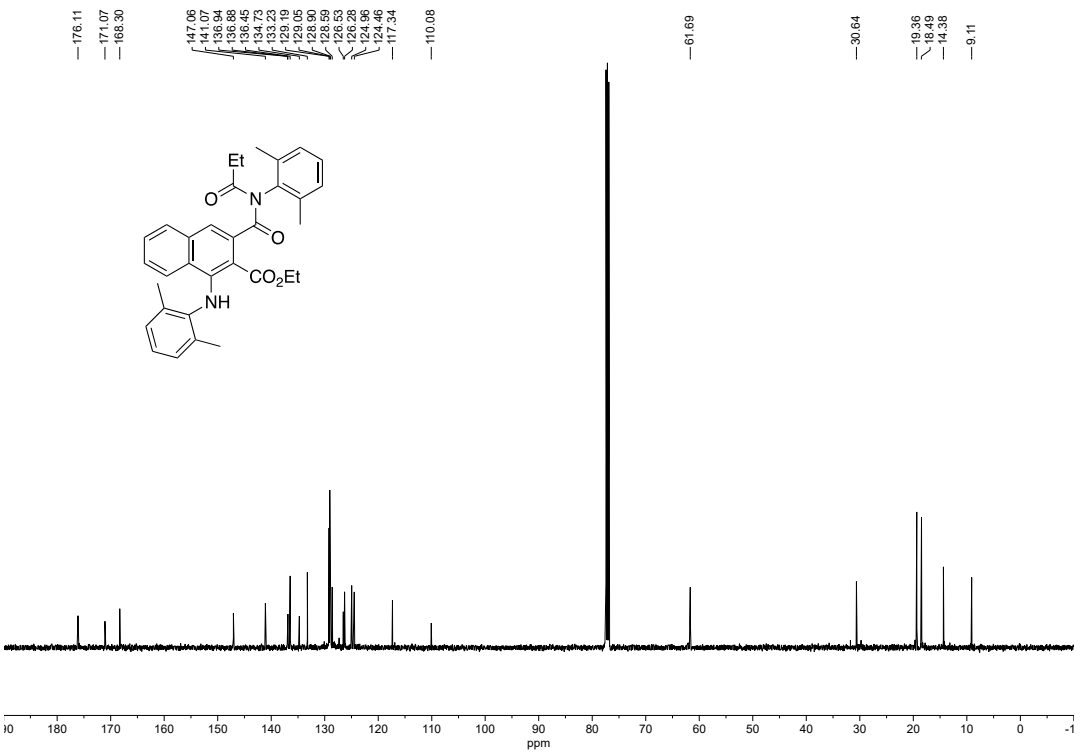
Compound **3l**


9.30
7.28
7.27
7.26
7.26
7.22
7.21
7.21
7.20
7.20
7.19
7.16
7.15
6.92
5.24
5.24
4.49
4.48
4.46
4.45
2.42
2.21
2.00
1.39
1.37
1.36
Ac
N
O
O
CO2Et
NH
0.95
1.07
4.09
2.07
1.00
1.01
2.09
6.07
6.14
3.06
3.04
ppm

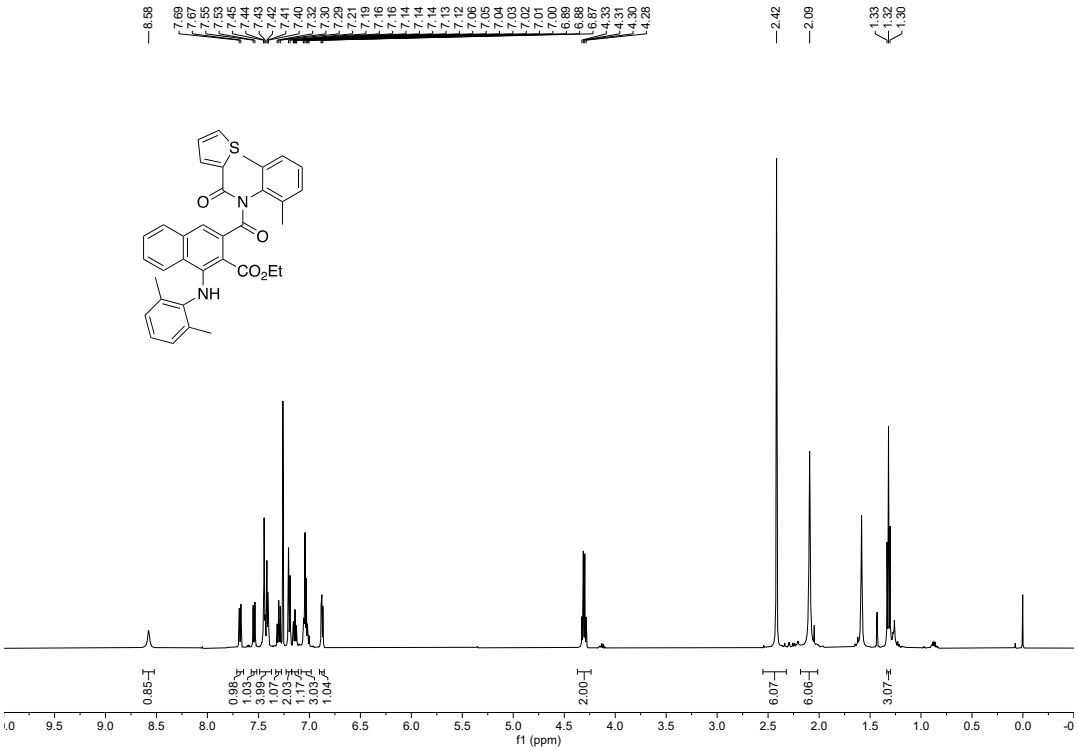

172.36
170.82
168.23
157.28
145.96
143.71
139.31
138.35
137.49
137.05
136.37
129.25
129.15
128.46
127.37
115.14
106.17
103.61
99.68
61.49
25.14
18.60
18.42
14.55
Ac
N
O
O
CO2Et
NH
ppm

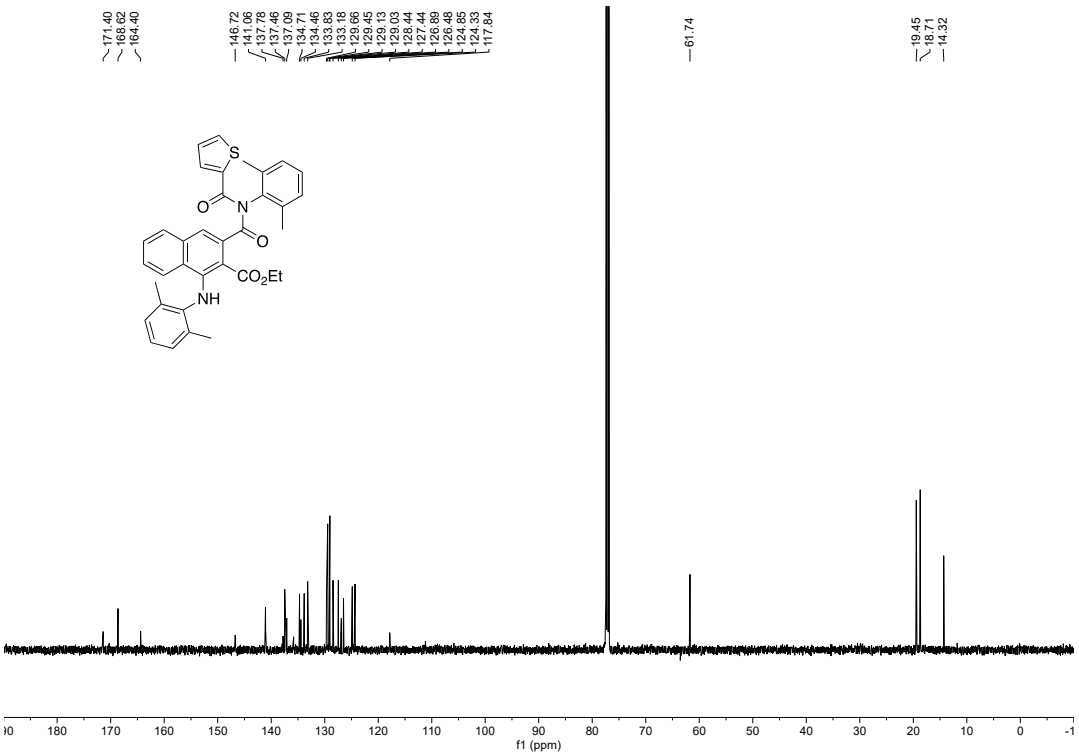
Compound **3m**


8.71
7.72
7.71
7.58
7.56
7.47
7.46
7.44
7.32
7.27
7.24
7.21
7.19
7.17
7.17
7.16
7.16
7.15
7.14
7.14
7.07
7.06
7.05
7.04
7.03
7.02
7.01
4.32
4.31
4.29
4.28
2.40
2.29
2.28
2.26
2.25
2.11
1.33
1.32
1.30
1.04
1.02
1.01
Et
O
N
O
CO2Et
NH
0.93
0.99
1.02
1.06
1.07
1.18
2.12
1.14
3.10
2.00
6.01
2.09
6.05
3.12
3.04
ppm

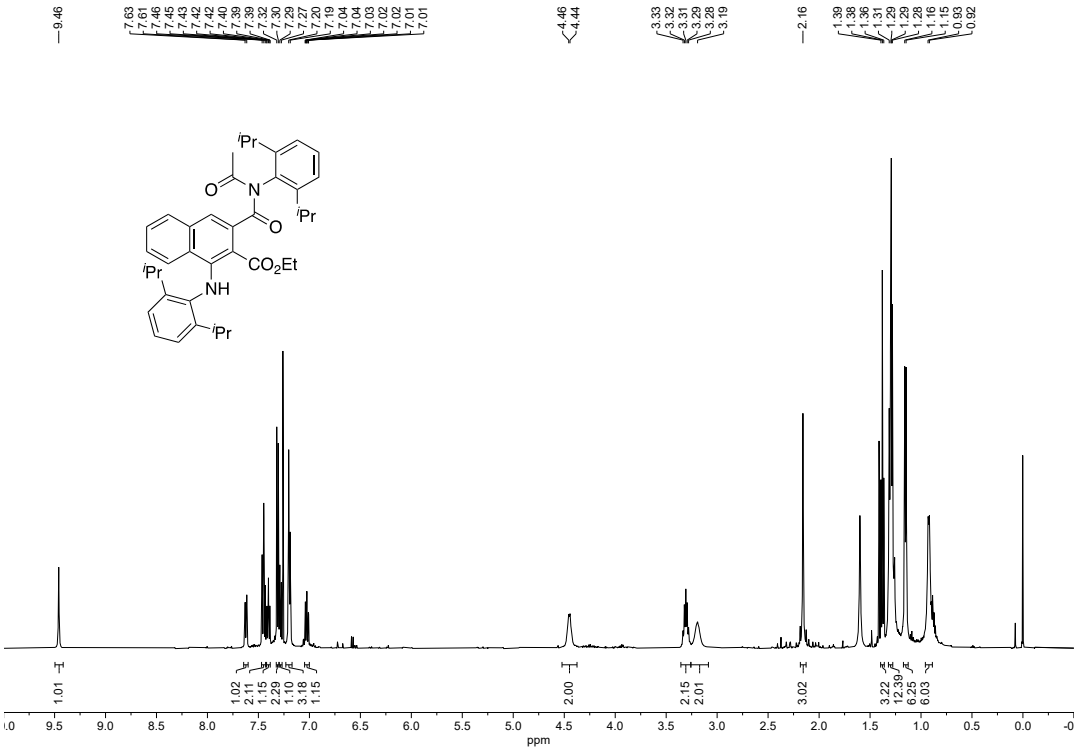

176.11
171.07
168.30
147.06
141.07
136.94
136.88
136.45
134.73
133.23
129.19
129.05
128.90
128.59
126.53
126.28
124.96
124.46
117.34
110.08
61.69
30.64
19.36
18.49
14.38
9.11
Et
O
N
O
CO2Et
NH
ppm

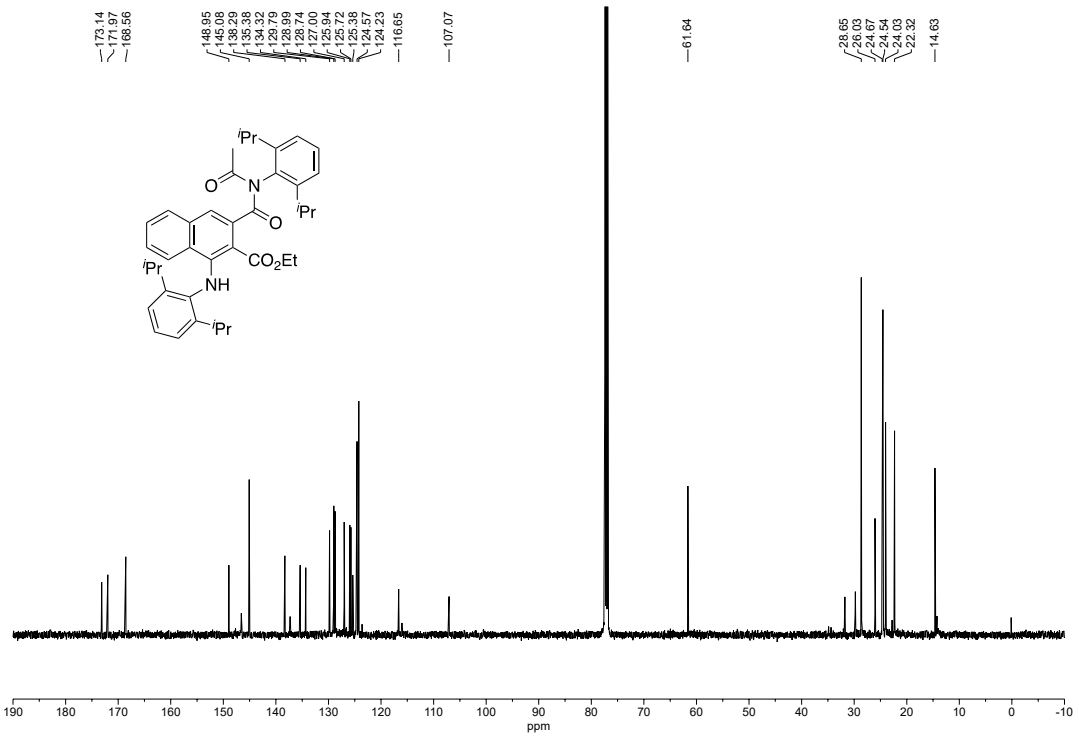
Compound **3n**


8.58
7.69
7.67
7.55
7.53
7.45
7.44
7.43
7.42
7.41
7.40
7.32
7.30
7.29
7.21
7.19
7.16
7.16
7.14
7.14
7.14
7.13
7.12
7.06
7.05
7.04
7.03
7.02
7.01
7.00
6.89
6.88
6.87
4.33
4.31
4.30
4.28
2.42
2.09
1.33
1.32
1.30
S
O
N
O
CO2Et
NH
0.85
0.98
1.03
3.99
1.07
2.03
1.17
3.03
1.04
2.00
6.07
6.06
3.07
f1 (ppm)

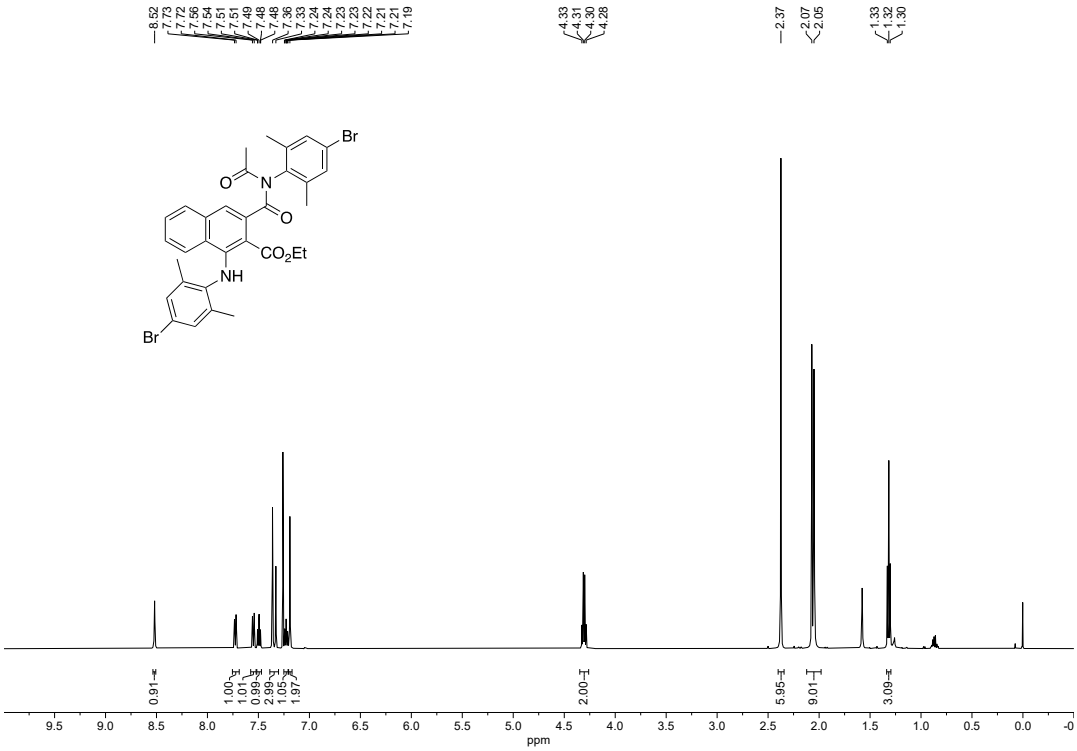

171.40
168.62
164.40
146.72
141.06
137.78
137.46
137.09
134.71
134.46
133.83
133.18
129.66
129.45
129.13
129.03
128.44
127.44
126.89
126.48
124.85
124.33
117.84
61.74
19.45
18.71
14.32
S
O
N
O
CO2Et
NH
f1 (ppm)

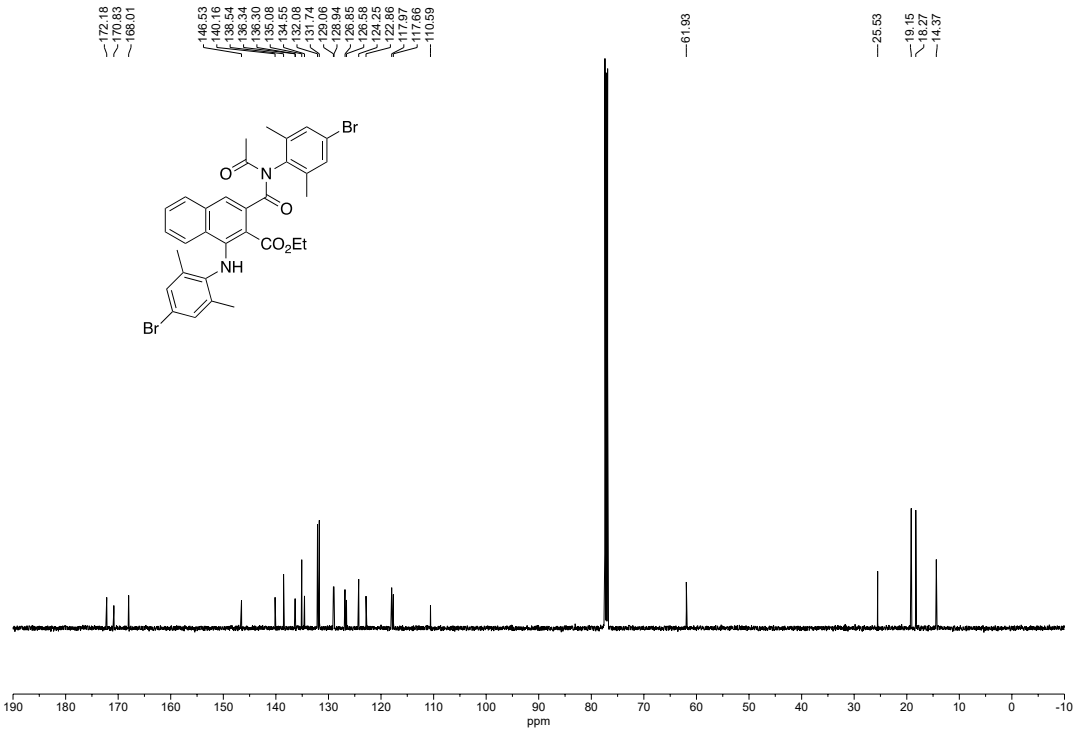
Compound **3o**


9.46
7.63
7.61
7.46
7.45
7.43
7.42
7.42
7.40
7.39
7.39
7.32
7.30
7.29
7.27
7.20
7.19
7.04
7.04
7.03
7.02
7.02
7.01
7.01
4.46
4.44
3.33
3.32
3.31
3.29
3.28
3.19
2.16
1.39
1.38
1.36
1.31
1.29
1.28
1.28
1.16
1.15
0.93
0.92
iPr
O
N
O
iPr
CO2Et
iPr
NH
iPr
1.01
1.02
2.11
1.15
2.29
1.10
3.18
1.15
2.00
2.15
2.01
3.02
3.22
12.39
6.25
6.03
ppm

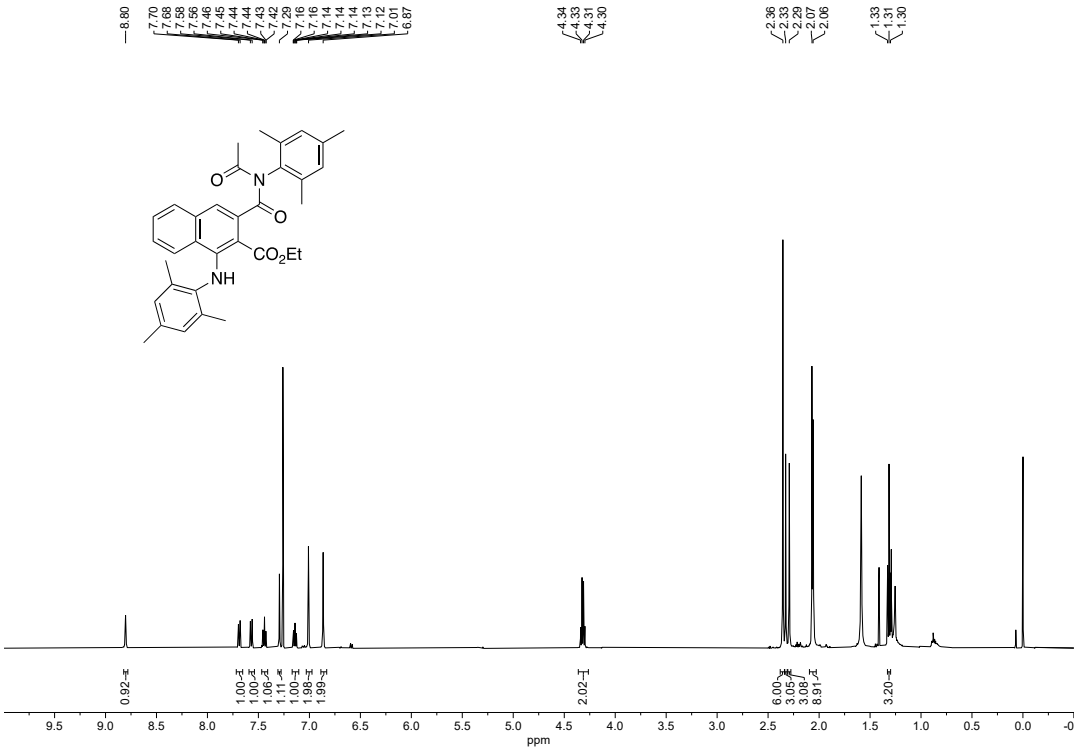

173.14
171.97
168.56
148.95
145.08
138.29
135.38
134.32
129.79
128.99
128.74
127.00
125.94
125.72
125.38
124.57
124.23
116.65
107.07
61.64
28.65
26.03
24.67
24.54
24.03
22.32
14.63
iPr
O
N
O
iPr
CO2Et
iPr
NH
iPr
ppm

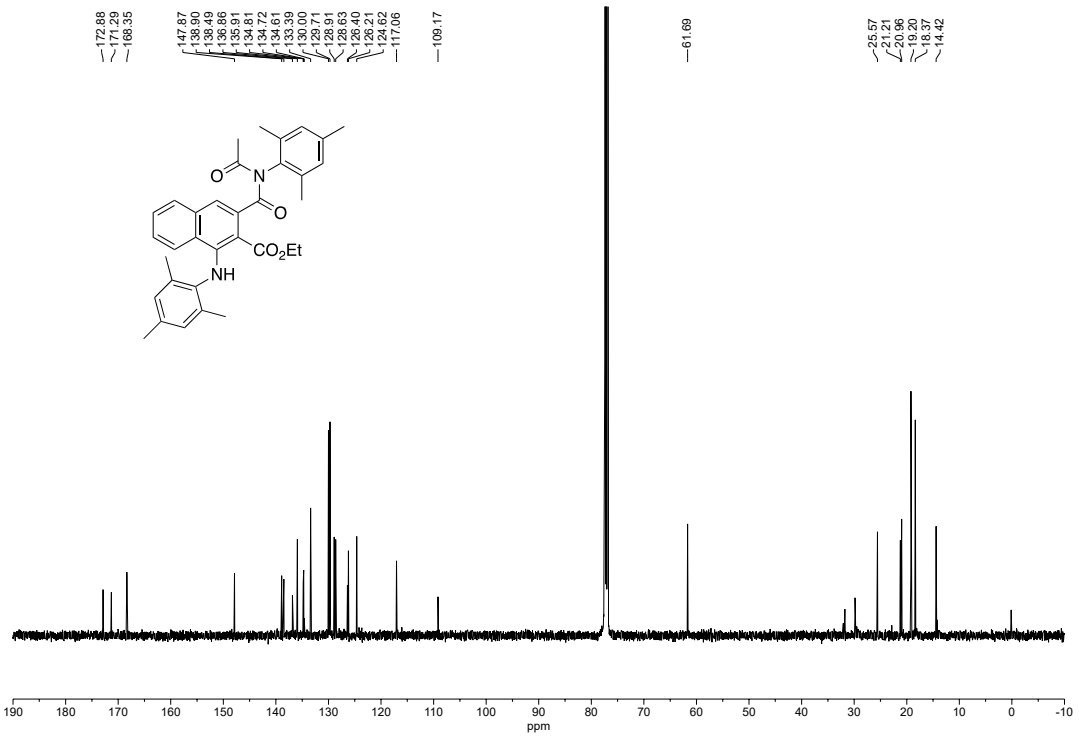
Compound **3p**


8.52
7.73
7.72
7.56
7.54
7.51
7.51
7.49
7.48
7.48
7.36
7.33
7.24
7.24
7.23
7.23
7.22
7.21
7.21
7.19
4.33
4.31
4.30
4.28
2.37
2.07
2.05
1.33
1.32
1.30
Br
O
N
O
CO2Et
NH
Br
0.91
1.00
1.01
0.99
2.99
1.05
1.97
2.00
5.95
9.01
3.09
ppm

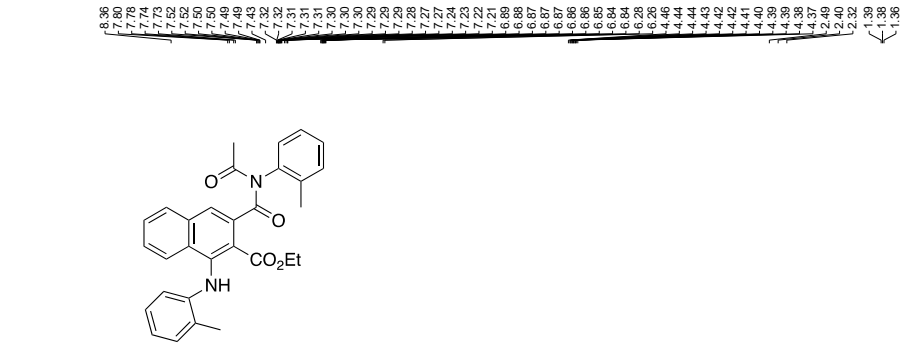

172.18
170.83
168.01
146.53
140.16
138.54
136.34
136.30
135.08
134.55
132.08
131.74
129.06
128.94
126.85
126.58
124.25
122.86
120.27
117.87
117.66
110.59
61.93
25.53
19.15
18.27
14.37
Br
O
N
O
CO2Et
NH
Br
ppm

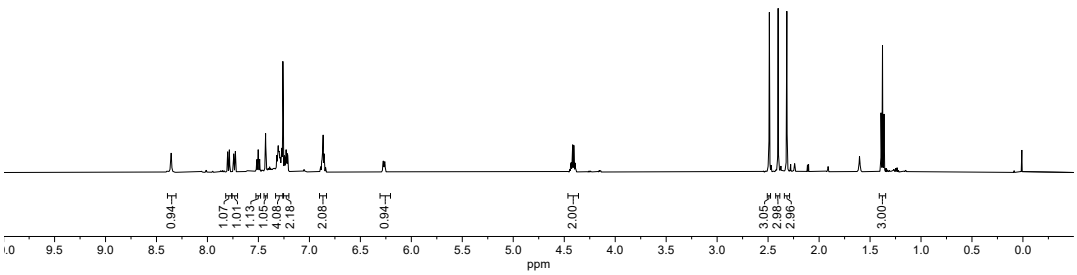
Compound **3q**

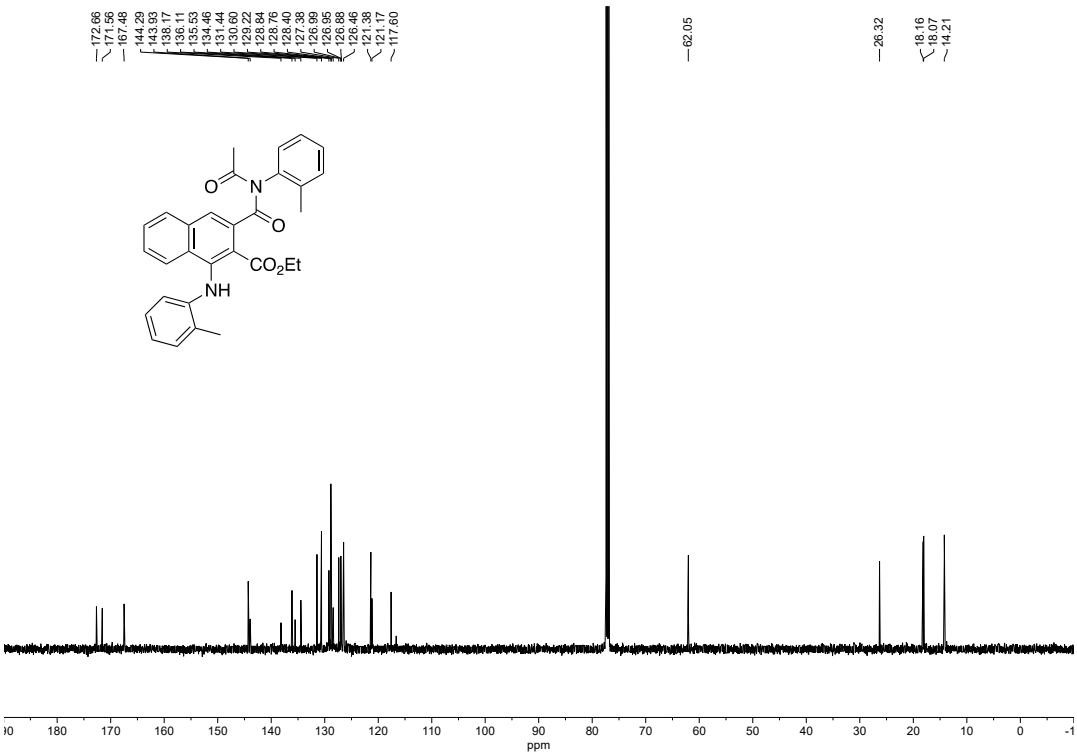

8.80
7.70
7.68
7.58
7.56
7.46
7.45
7.44
7.43
7.42
7.29
7.16
7.16
7.14
7.14
7.14
7.13
7.12
7.01
6.87
4.34
4.33
4.31
4.30
2.36
2.33
2.29
2.07
2.06
1.33
1.31
1.30
O
N
O
CO2Et
NH
0.92
1.00
1.00
1.06
1.11
1.00
1.99
1.99
2.02
6.00
3.05
3.08
8.91
3.20
ppm


172.88
171.29
168.35
147.87
138.90
138.49
136.86
135.91
134.81
134.72
134.61
133.39
130.00
129.71
128.91
128.63
126.40
126.21
124.62
117.06
109.17
61.69
25.57
21.21
20.96
19.20
18.37
14.42
O
N
O
CO2Et
NH
ppm

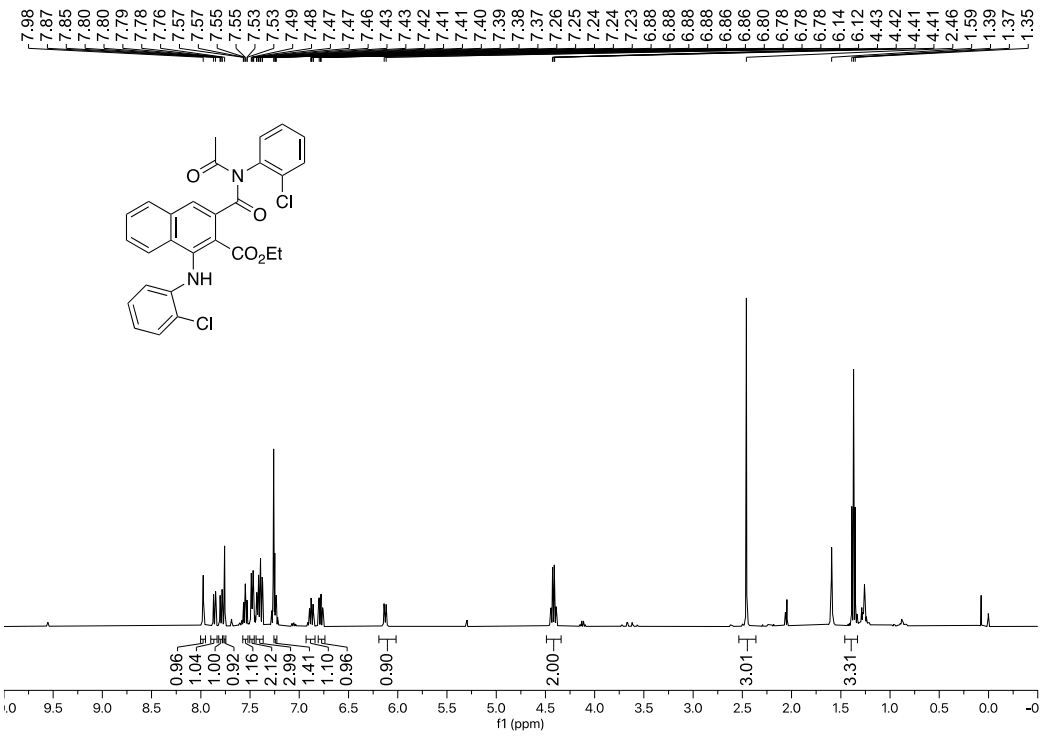
Compound **3r**

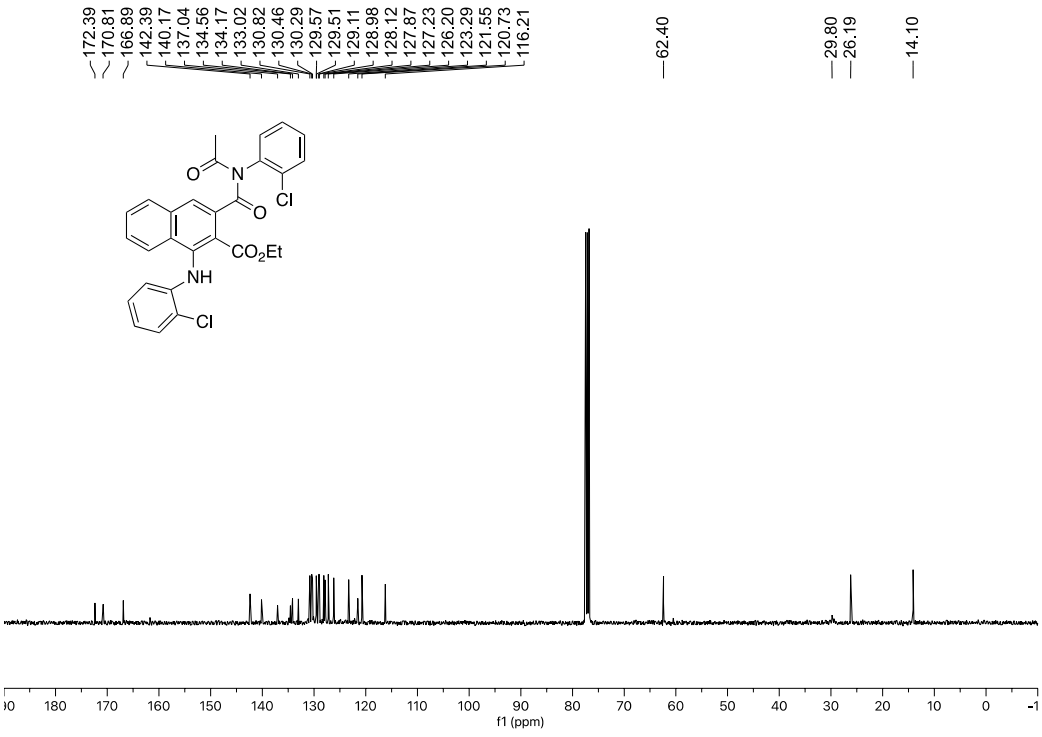




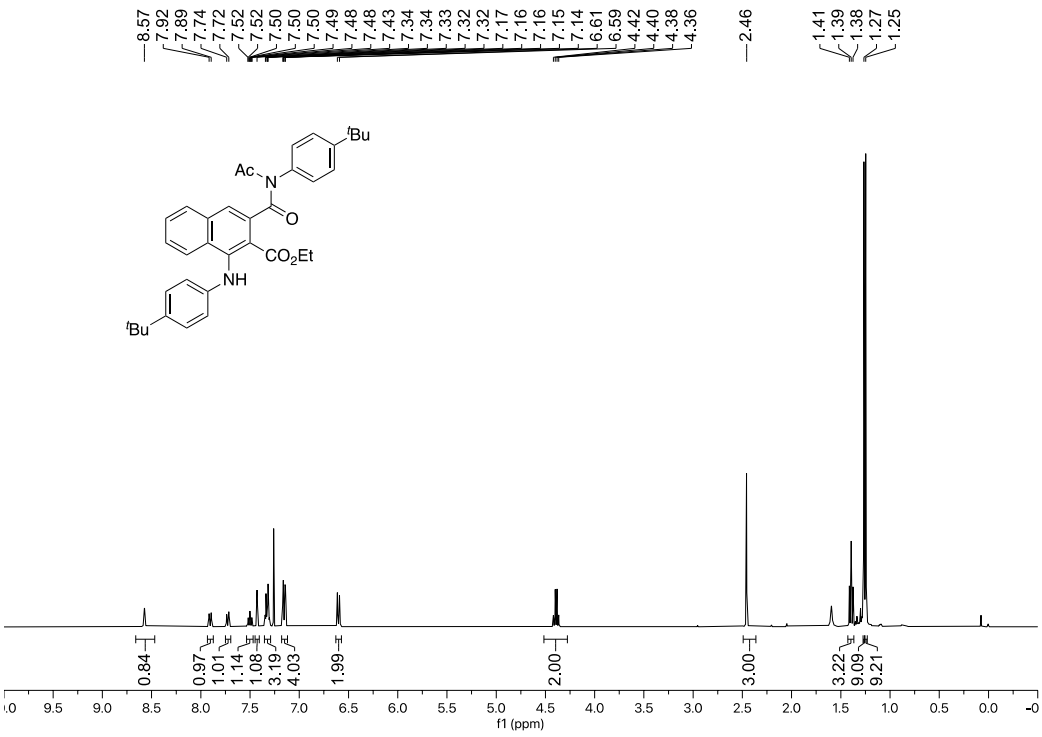


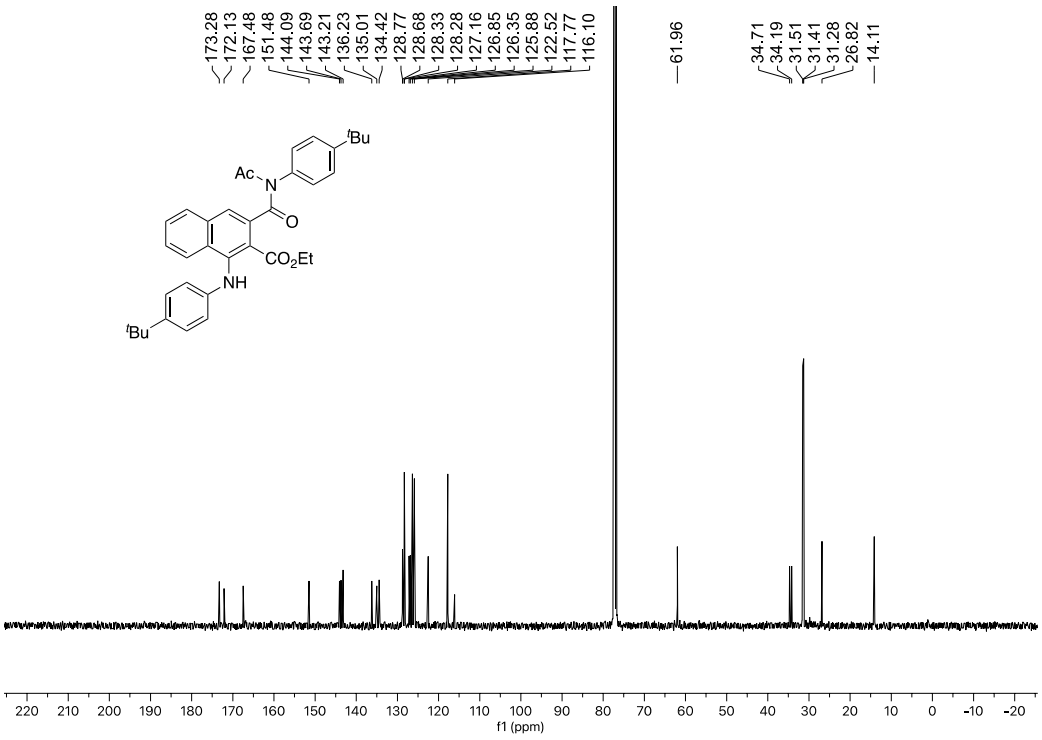
Compound **3s**


7.98 7.87 7.85 7.80 7.80 7.79 7.78 7.76 7.57 7.57 7.55 7.55 7.53 7.53 7.49 7.48 7.47 7.47 7.46 7.43 7.43 7.42 7.41 7.41 7.40 7.39 7.38 7.37 7.26 7.25 7.24 7.24 7.23 6.88 6.88 6.88 6.86 6.86 6.80 6.78 6.78 6.14 6.12 4.43 4.42 4.41 4.41 2.46 1.59 1.39 1.37 1.35
O
N
Cl
O
CO2Et
NH
Cl
0.96 1.04 1.00 0.92 1.16 2.12 2.99 1.41 1.10 0.96 0.90 2.00 3.01 3.31
f1 (ppm)

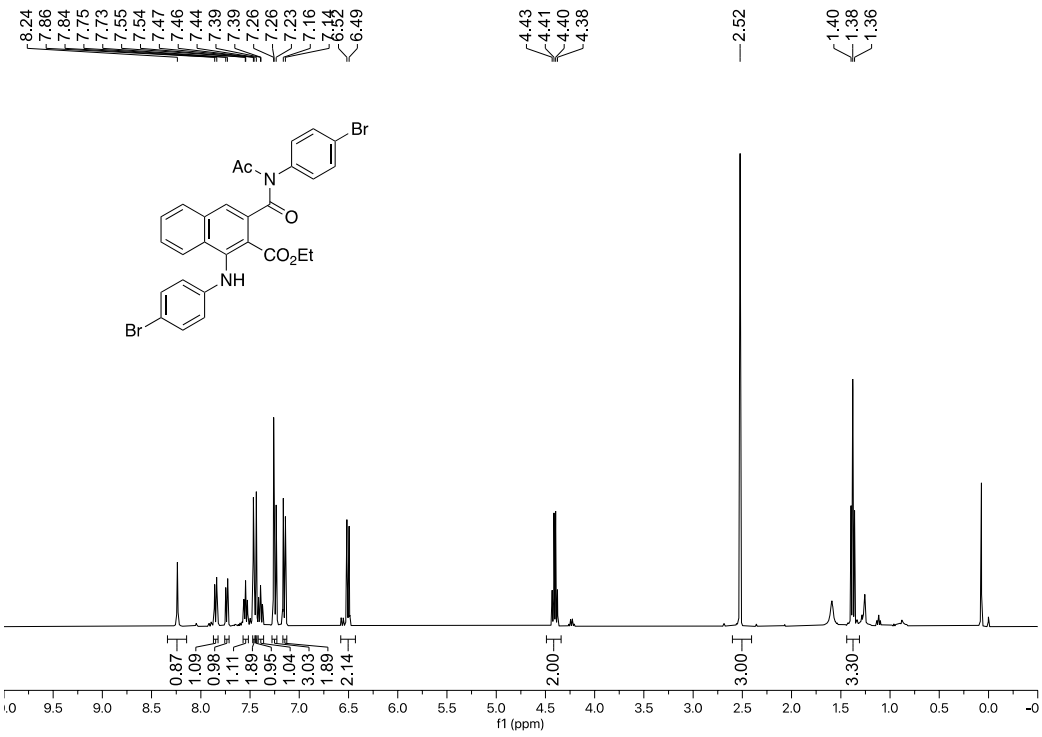

172.39 170.81 166.89 142.39 140.17 137.04 134.56 134.17 133.02 130.82 130.46 130.29 129.57 129.51 129.11 128.98 128.12 127.87 127.23 126.20 123.29 121.55 120.73 116.21
62.40
29.80 26.19
14.10
O
N
Cl
O
CO2Et
NH
Cl
f1 (ppm)

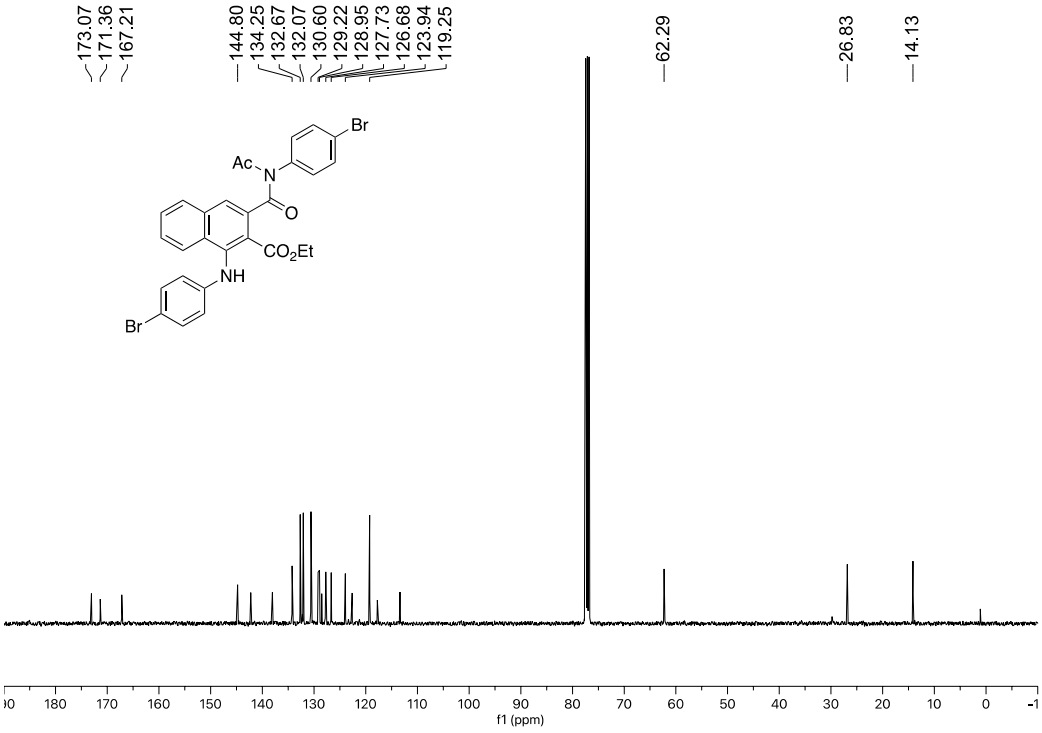
Compound **3t**


8.57
7.92
7.89
7.74
7.72
7.52
7.52
7.50
7.50
7.50
7.49
7.48
7.48
7.43
7.34
7.34
7.33
7.32
7.32
7.17
7.16
7.16
7.15
7.14
6.61
6.59
4.42
4.40
4.38
4.36
2.46
1.41
1.39
1.38
1.27
1.25
tBu
Ac
N
O
CO2Et
NH
tBu
0.84
0.97
1.01
1.14
1.08
3.19
4.03
1.99
2.00
3.00
3.22
9.09
9.21
f1 (ppm)

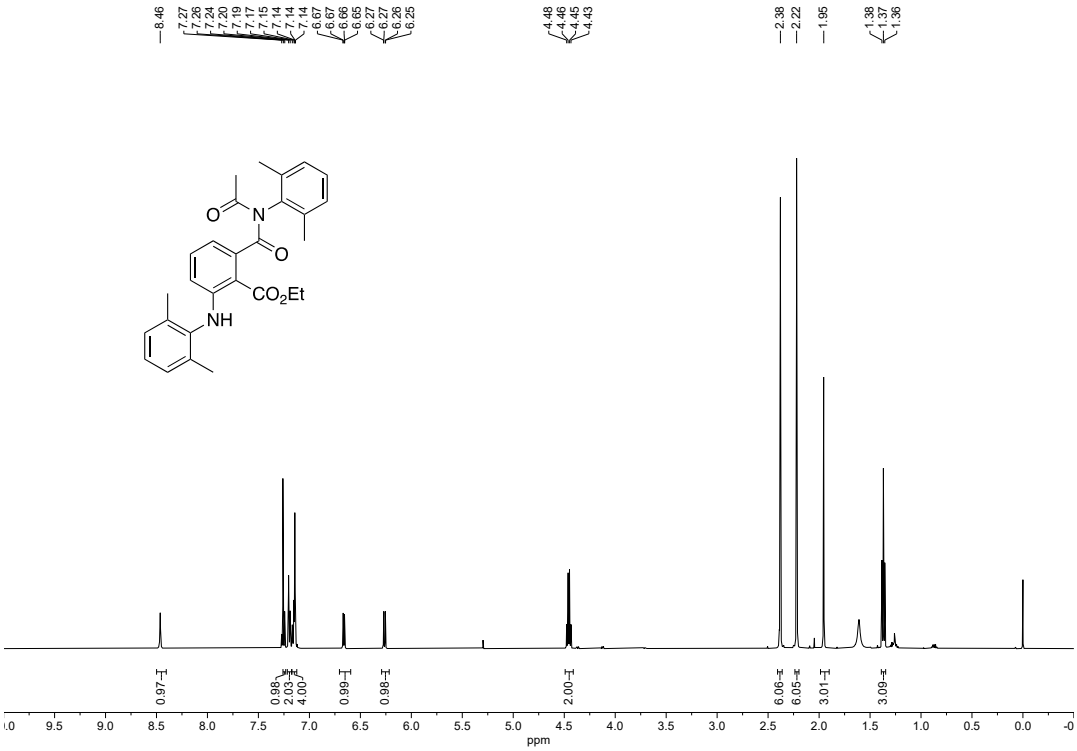

173.28
172.13
167.48
151.48
144.09
143.69
143.21
136.23
135.01
134.42
128.77
128.68
128.33
128.28
127.16
126.85
126.35
125.88
122.52
117.77
116.10
61.96
34.71
34.19
31.51
31.41
31.28
26.82
14.11
tBu
Ac
N
O
CO2Et
NH
tBu
f1 (ppm)

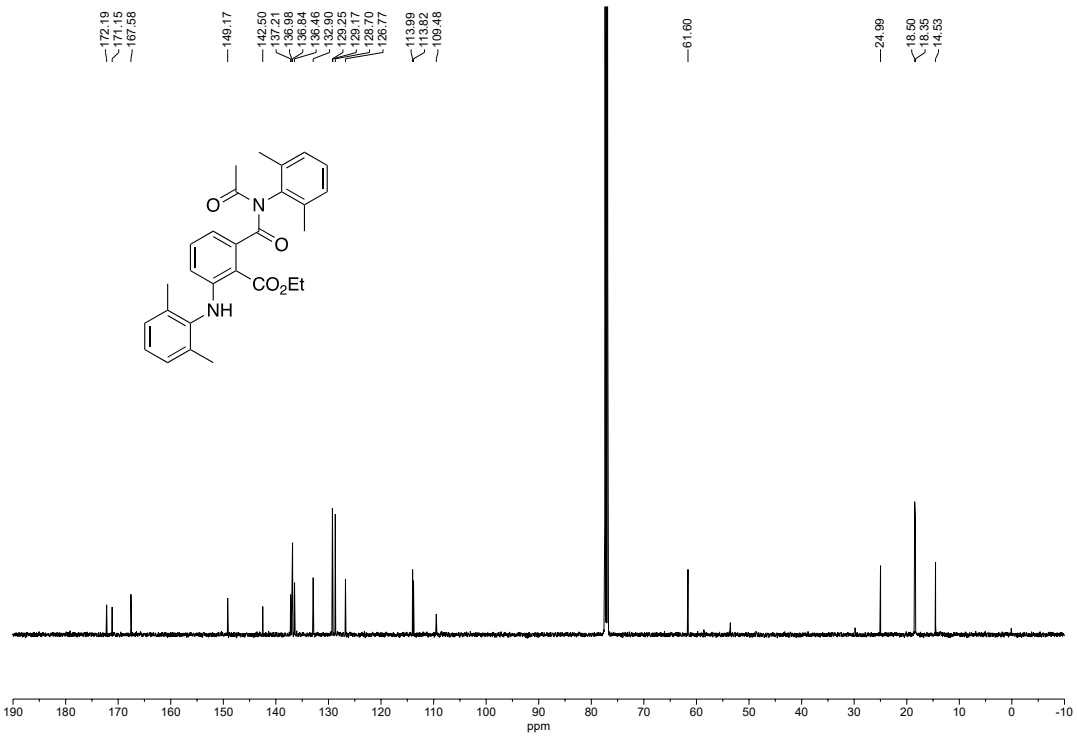
Compound **3u**


8.24
7.86
7.84
7.75
7.73
7.55
7.54
7.47
7.46
7.44
7.39
7.39
7.26
7.26
7.23
7.16
7.14
6.51
6.49
4.43
4.41
4.40
4.38
2.52
1.40
1.38
1.36
Br
Ac
N
O
CO2Et
NH
Br
0.87
1.09
0.98
1.11
1.89
0.95
1.04
3.03
1.89
2.14
2.00
3.00
3.30
f1 (ppm)

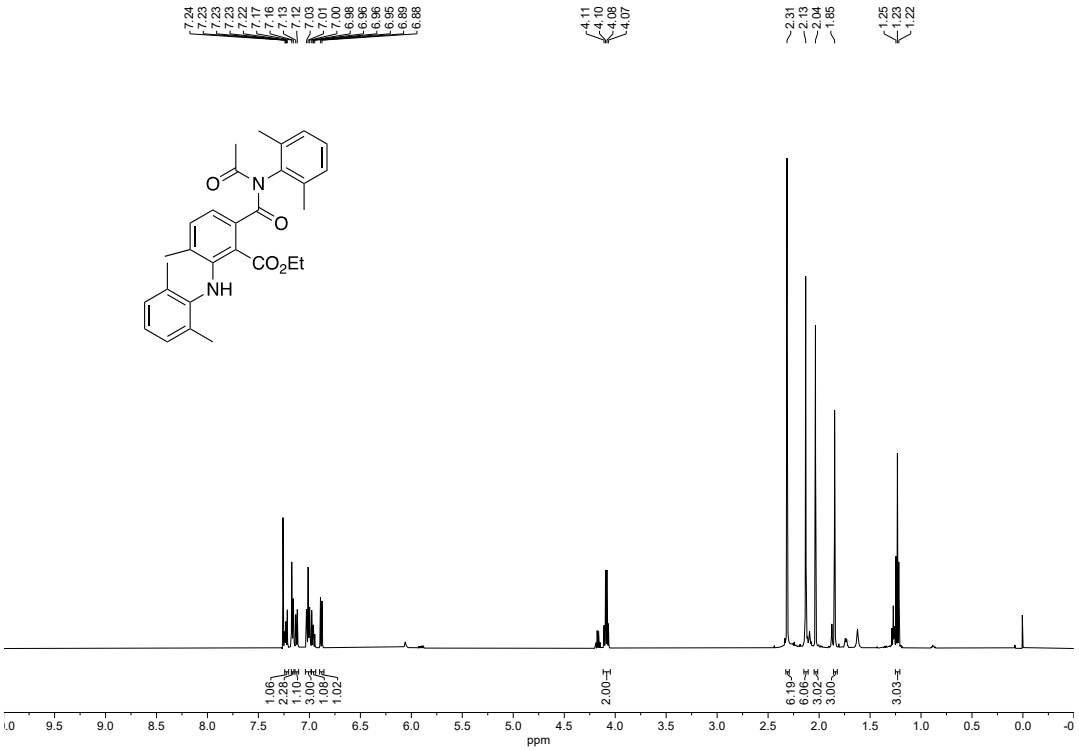

173.07
171.36
167.21
144.80
134.25
132.67
132.07
130.60
129.22
128.95
127.73
126.68
123.94
119.25
62.29
26.83
14.13
Br
Ac
N
O
CO2Et
NH
Br
f1 (ppm)

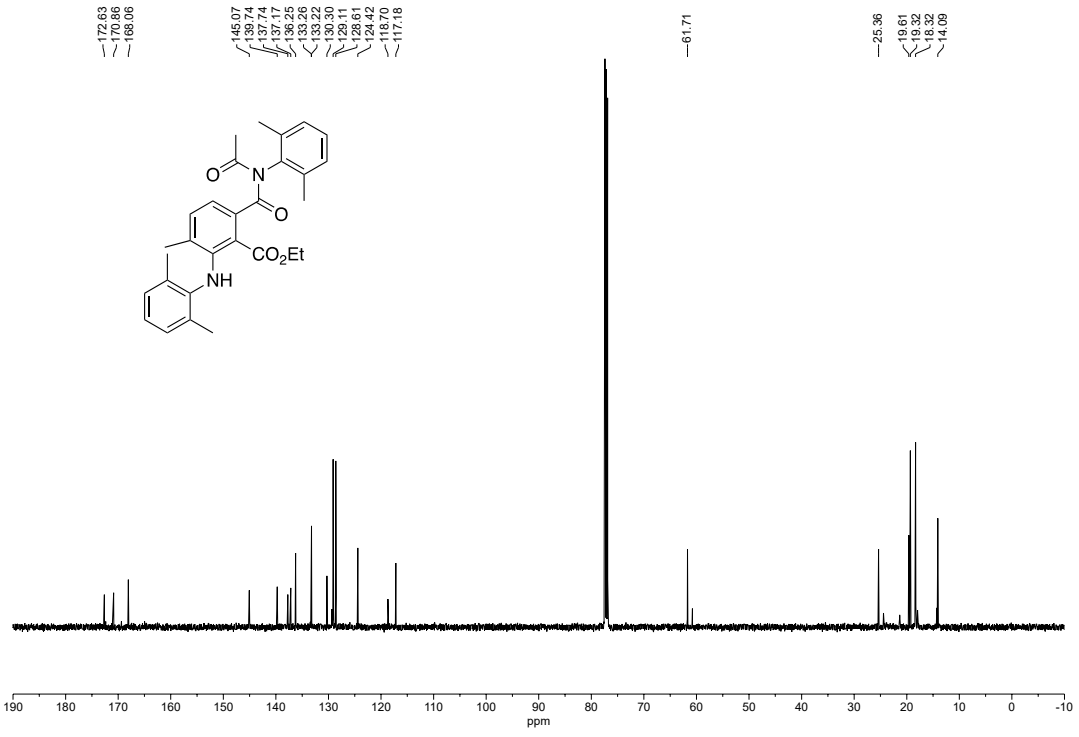
Compound **5a**


8.46
7.27
7.26
7.24
7.20
7.19
7.17
7.15
7.14
7.14
7.14
6.67
6.67
6.66
6.65
6.27
6.27
6.26
6.25
4.48
4.46
4.45
4.43
2.38
2.22
1.95
1.38
1.37
1.36
O
N
O
CO2Et
NH
0.97
0.98
2.03
4.00
0.99
0.98
2.00
6.06
6.05
3.01
3.09
ppm

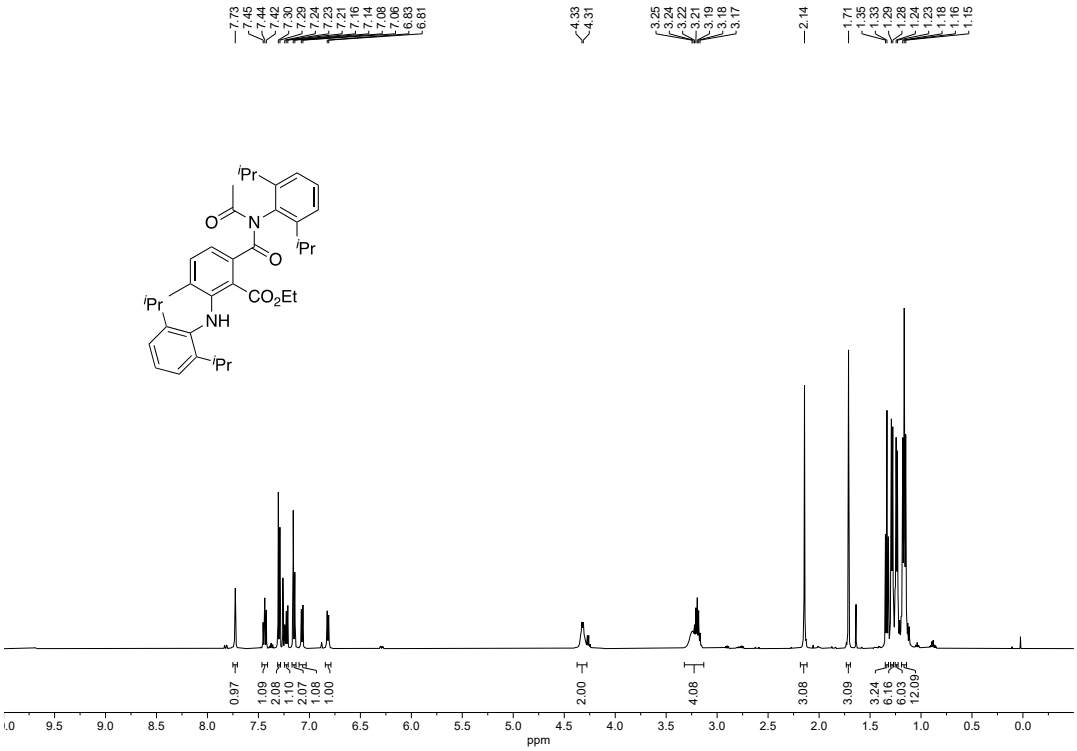

172.19
171.15
167.58
149.17
142.50
137.21
136.98
136.84
136.46
132.90
129.25
129.17
128.70
126.77
113.99
113.82
109.48
61.60
24.99
18.50
18.35
14.53
O
N
O
CO2Et
NH
ppm

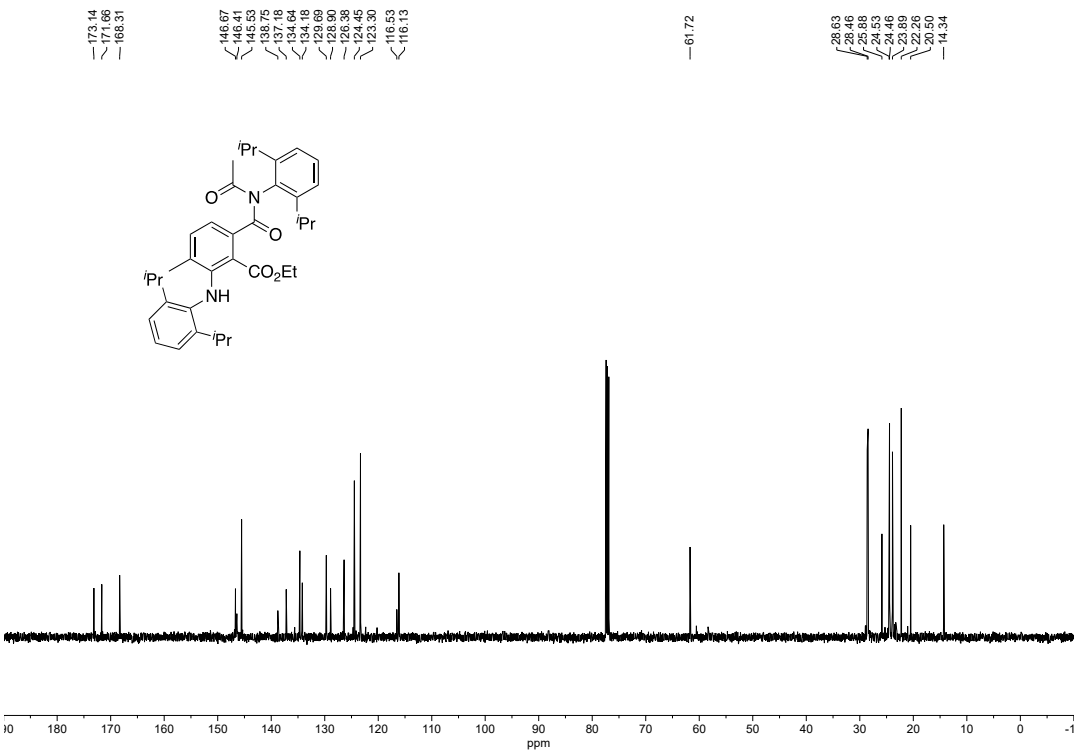
Compound **5b**


7.24
7.23
7.23
7.23
7.22
7.17
7.16
7.13
7.12
7.03
7.01
7.00
6.98
6.96
6.95
6.89
6.88
4.11
4.10
4.08
4.07
2.31
2.13
2.04
1.85
1.25
1.23
1.22
O
N
O
CO2Et
NH
1.06
2.28
1.10
3.00
1.08
1.02
2.00
6.19
6.06
3.02
3.00
3.03
ppm

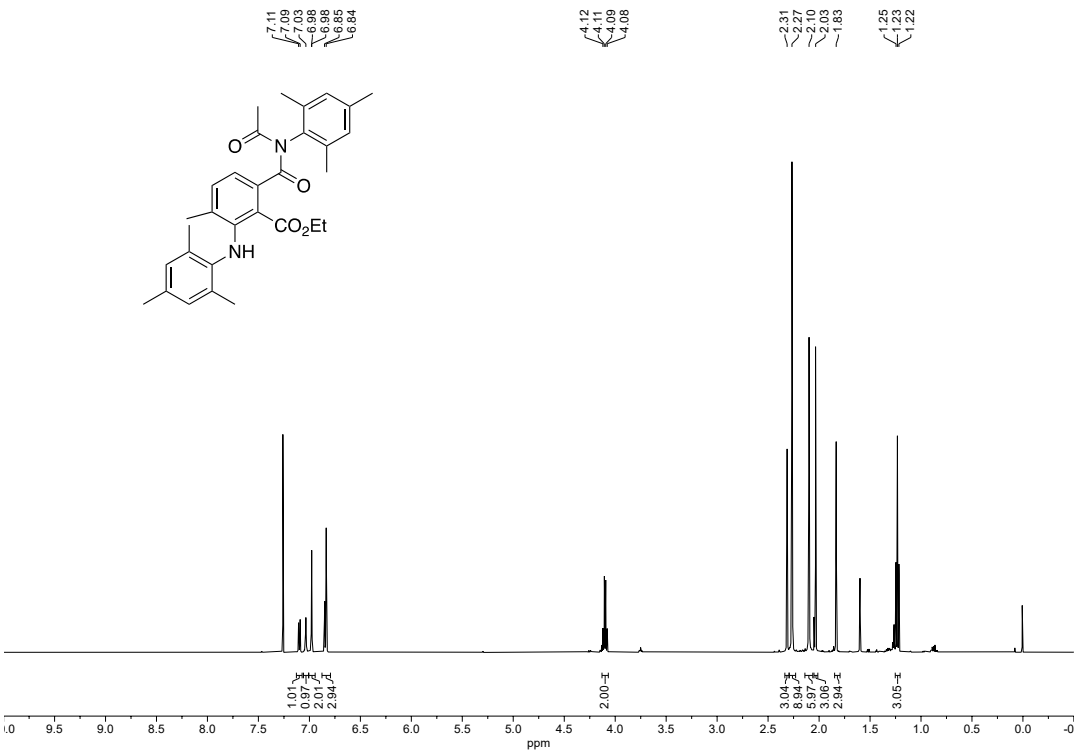

172.63
170.86
168.06
145.07
139.74
137.74
137.17
136.25
133.26
133.22
130.30
129.11
128.61
124.42
118.70
117.18
61.71
25.36
19.61
19.32
18.32
14.09
O
N
O
CO2Et
NH
ppm

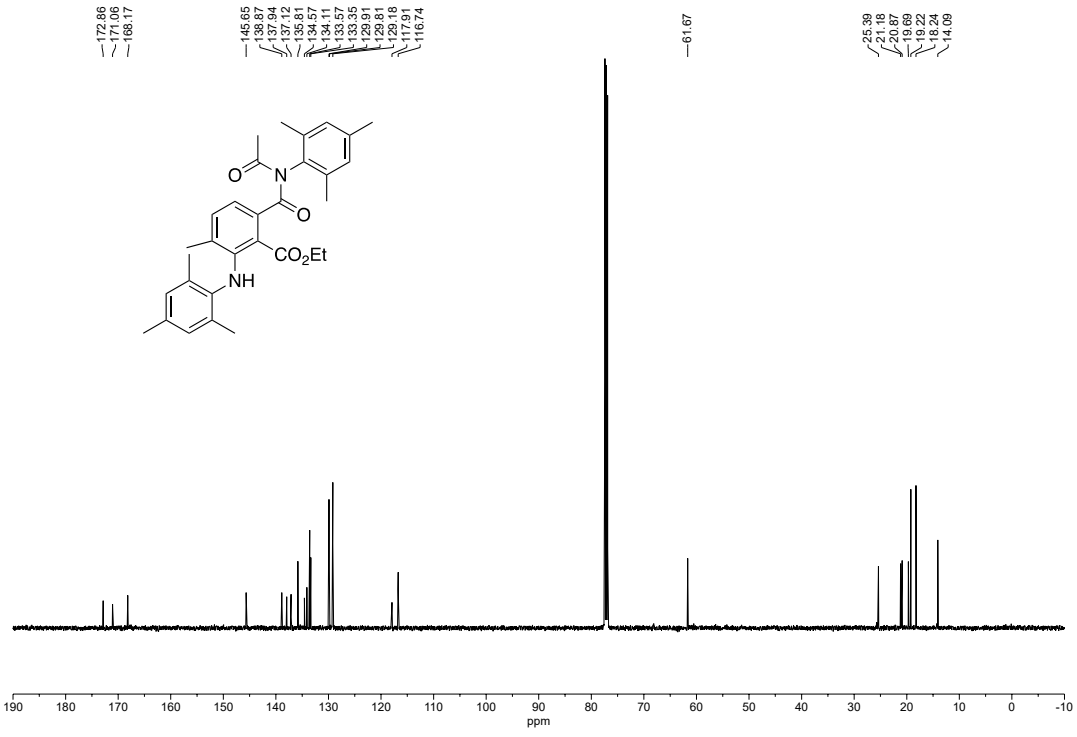
Compound **5c**


7.73
7.45
7.44
7.42
7.30
7.29
7.24
7.23
7.21
7.16
7.14
7.08
7.06
6.83
6.81
4.33
4.31
3.25
3.24
3.22
3.21
3.19
3.18
3.17
2.14
1.71
1.35
1.33
1.29
1.28
1.24
1.23
1.18
1.16
1.15
iPr
O
N
iPr
O
CO2Et
iPr
NH
iPr
0.97
1.09
2.08
1.10
2.07
1.08
1.00
2.00
4.08
3.08
3.09
3.24
6.16
6.03
12.09
ppm

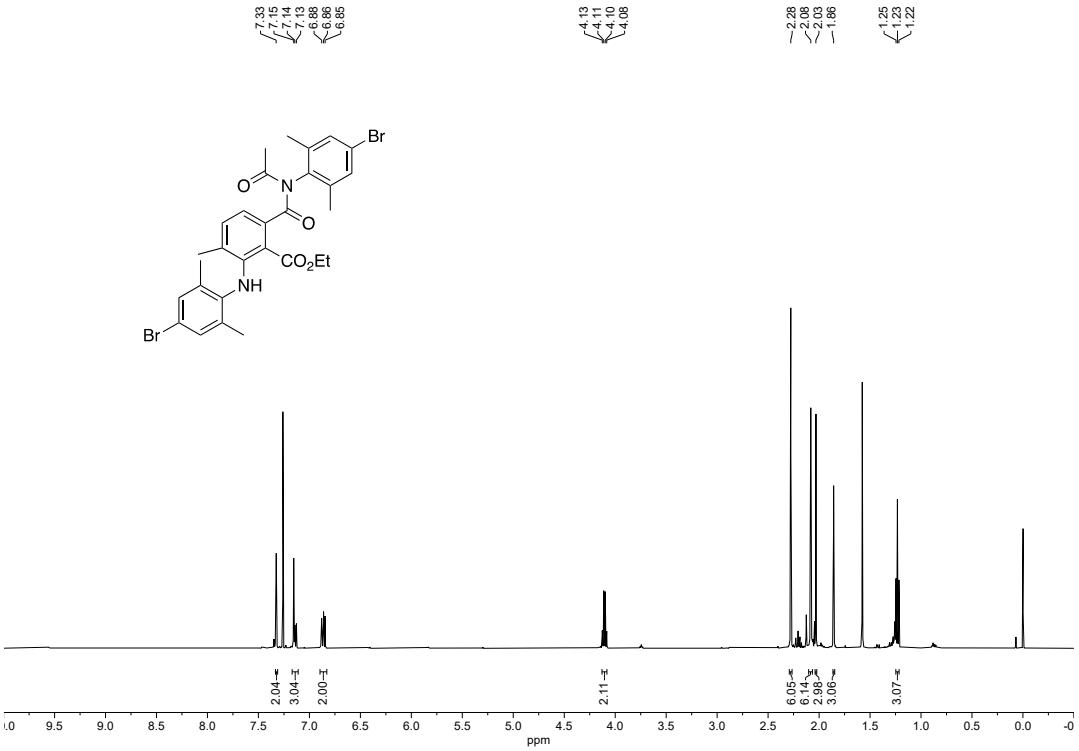

173.14
171.66
168.31
146.67
146.41
145.53
138.75
137.18
134.64
134.18
129.69
128.90
126.38
124.45
123.30
116.53
116.13
61.72
28.63
28.46
25.88
24.53
24.46
23.89
22.26
20.50
14.34
iPr
O
N
iPr
O
CO2Et
iPr
NH
iPr
ppm

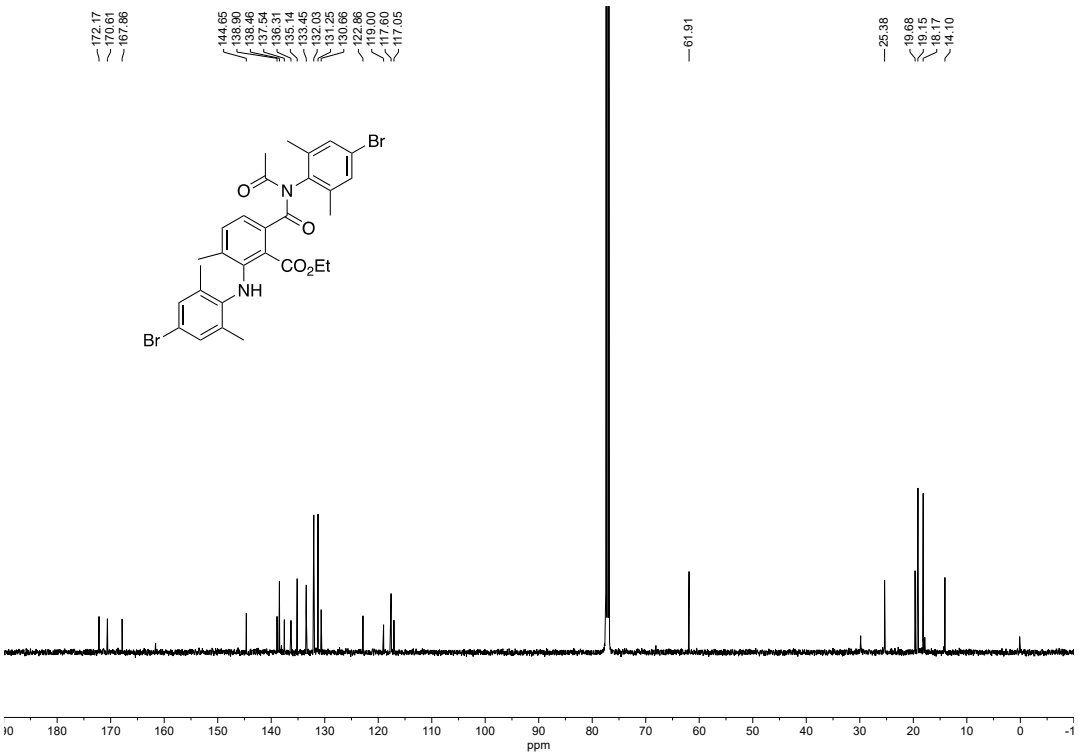
Compound **5d**


7.11
7.09
7.03
6.98
6.98
6.85
6.84
4.12
4.11
4.09
4.08
2.31
2.27
2.10
2.03
1.83
1.25
1.23
1.22
O
N
O
CO2Et
NH
1.01
0.97
2.01
2.94
2.00
3.04
8.94
5.97
3.06
2.94
3.05
ppm

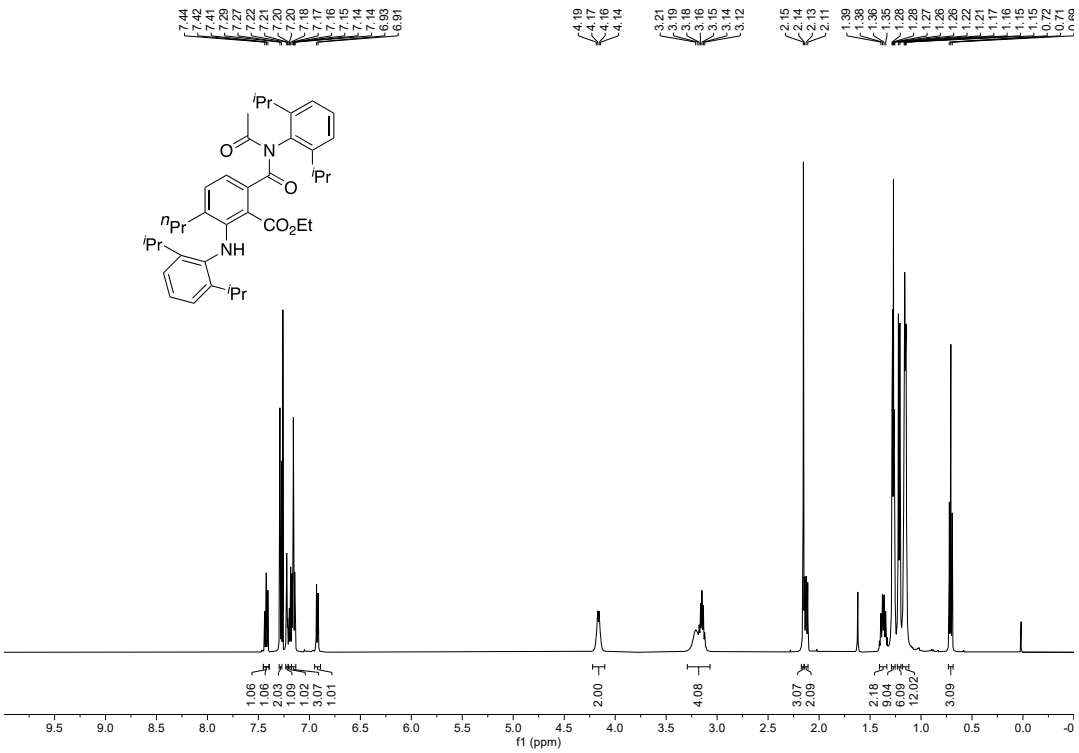

172.86
171.06
168.17
145.65
138.87
137.94
137.12
135.81
134.57
134.11
133.57
133.35
129.91
129.81
129.18
117.91
116.74
61.67
25.39
21.18
20.87
19.69
19.22
18.24
14.09
O
N
O
CO2Et
NH
ppm

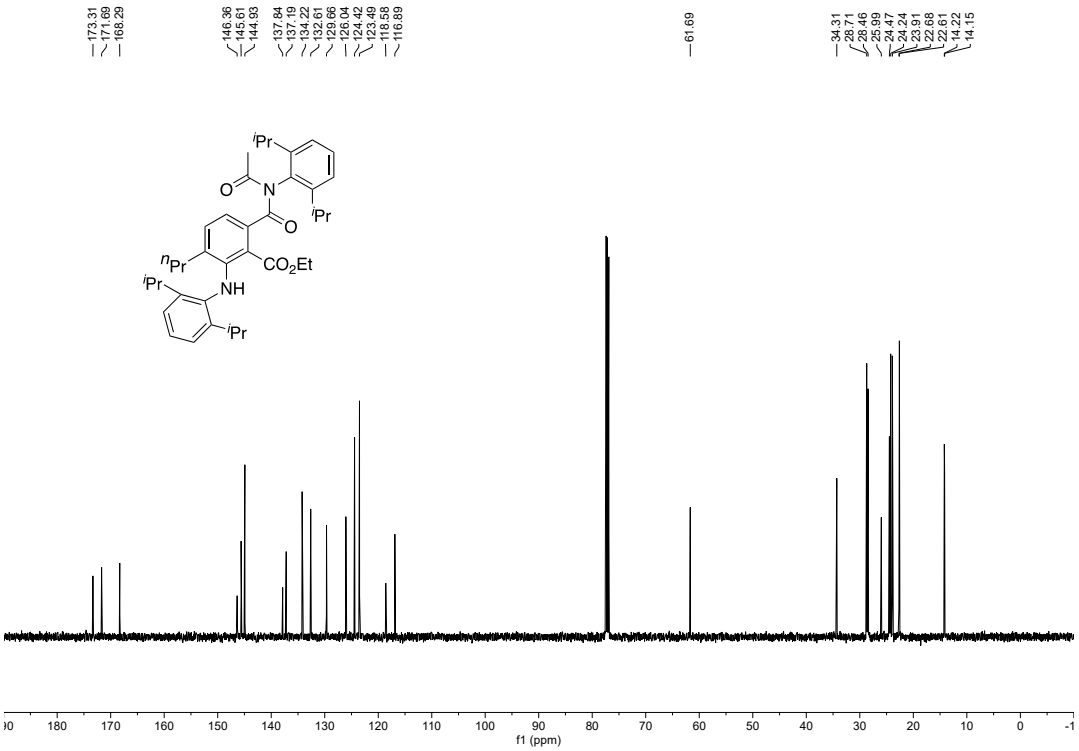
Compound **5e**


7.33
7.15
7.14
7.13
6.88
6.86
6.85
4.13
4.11
4.10
4.08
2.28
2.08
2.03
1.86
1.25
1.23
1.22
Br
O
N
O
CO2Et
NH
Br
2.04
3.04
2.00
2.11
6.05
6.14
2.98
3.06
3.07
ppm

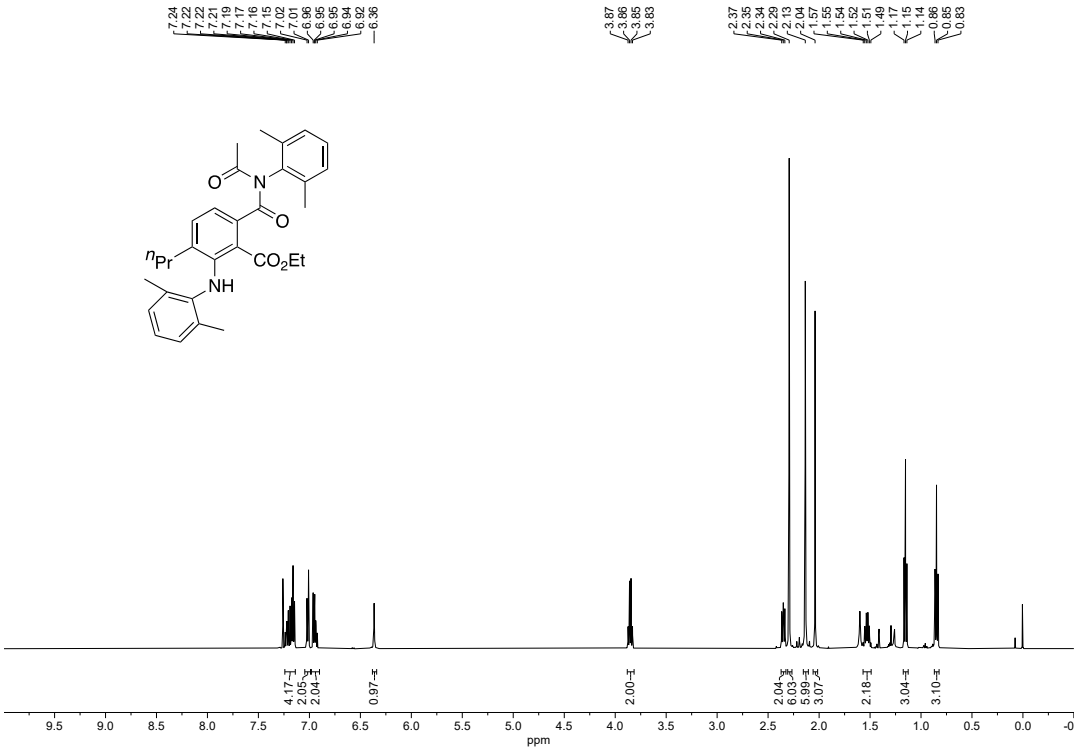

172.17
170.61
167.86
144.65
138.90
138.46
137.54
136.31
135.14
133.45
132.03
131.25
130.66
122.86
119.00
117.60
117.05
61.91
25.38
19.68
19.15
18.17
14.10
Br
O
N
O
CO2Et
NH
Br
ppm

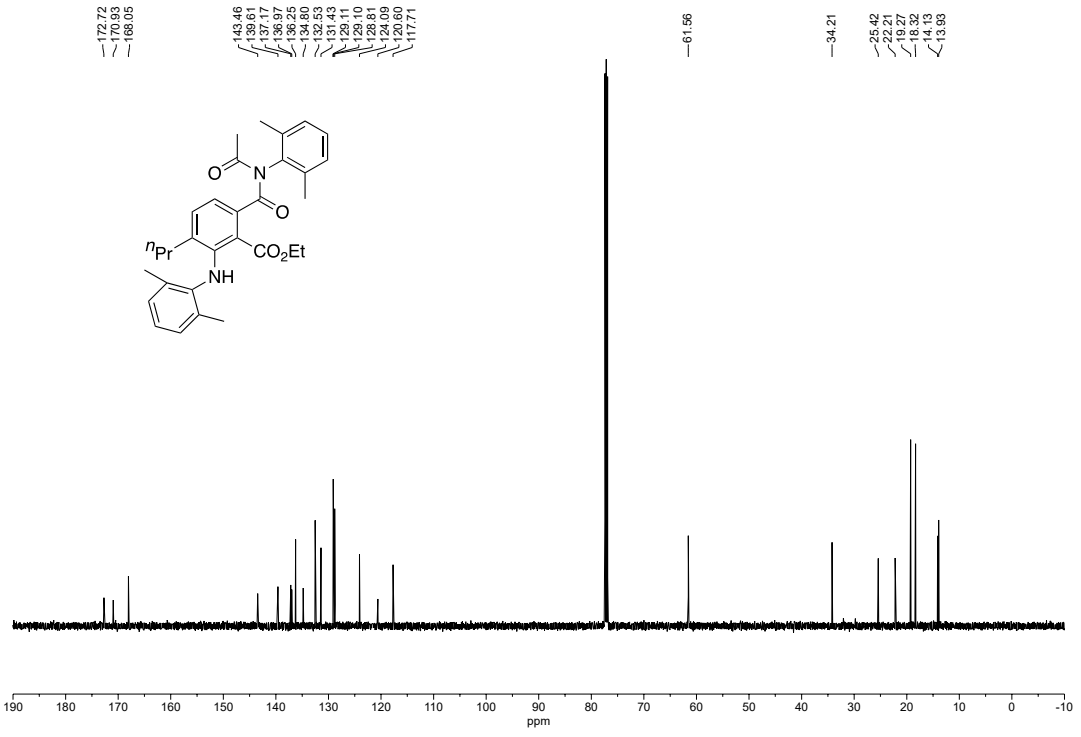
Compound **5f**


7.44
7.42
7.41
7.29
7.27
7.22
7.21
7.20
7.18
7.17
7.16
7.15
7.14
6.93
6.91
4.19
4.17
4.16
4.14
3.21
3.19
3.18
3.16
3.15
3.14
3.12
2.15
2.14
2.13
2.11
1.39
1.38
1.36
1.35
1.28
1.28
1.27
1.26
1.26
1.22
1.21
1.17
1.16
1.15
1.15
0.72
0.71
1.06
1.06
2.03
1.02
3.07
1.01
2.00
4.08
3.07
2.09
2.18
9.04
6.09
12.02
3.09
f1 (ppm)

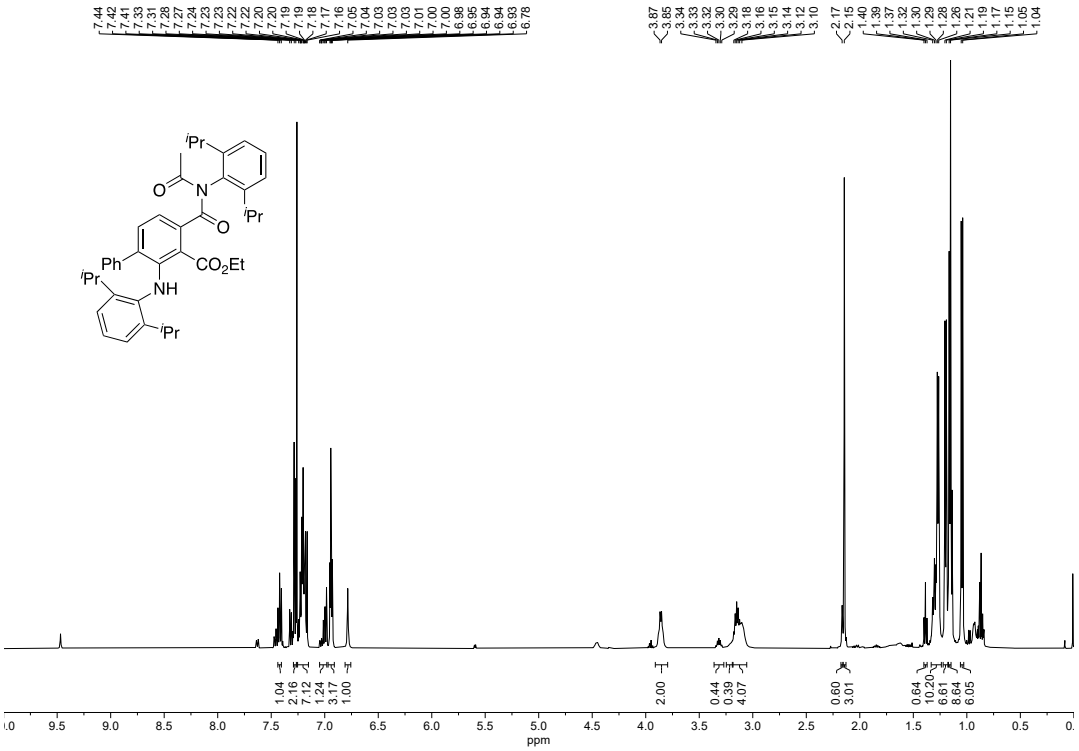

173.31
171.69
168.29
146.36
145.61
144.93
137.84
137.19
134.22
132.61
129.66
126.04
124.42
123.49
118.58
116.89
61.69
34.31
29.71
28.46
25.99
24.47
24.24
23.91
22.68
22.61
14.22
14.15
f1 (ppm)

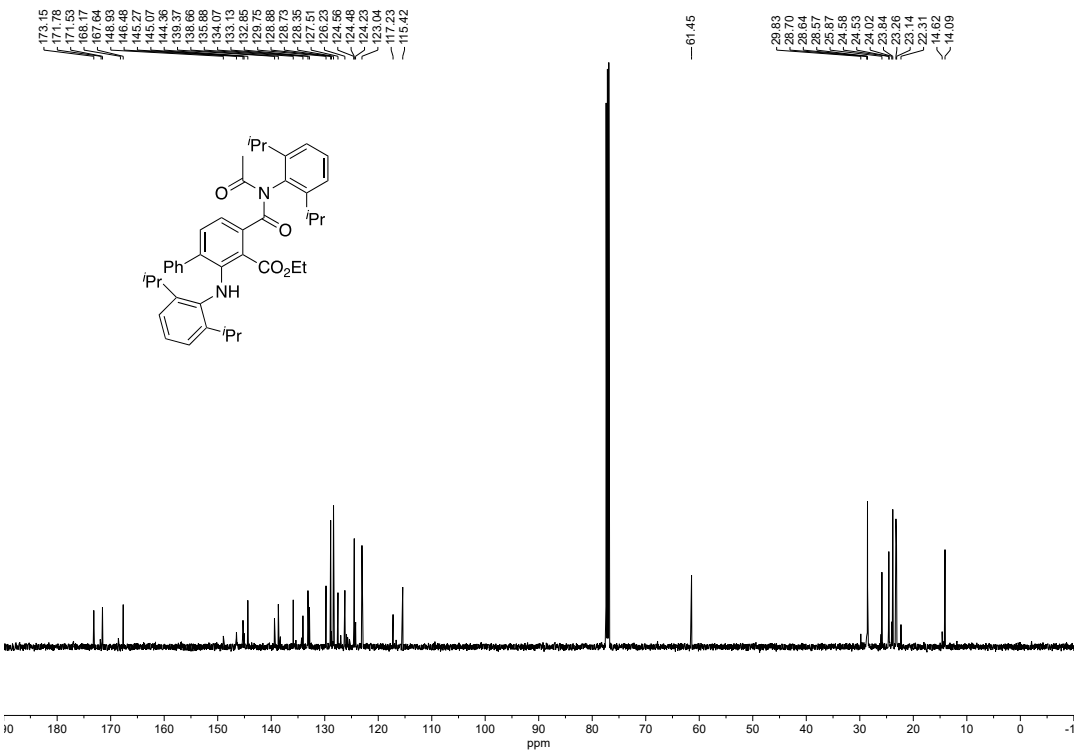
Compound **5g**


7.24
7.22
7.22
7.21
7.19
7.17
7.16
7.15
7.02
7.01
6.96
6.95
6.95
6.94
6.92
6.36
3.87
3.86
3.85
3.83
2.37
2.35
2.34
2.29
2.13
2.04
1.57
1.55
1.54
1.52
1.51
1.49
1.17
1.15
1.14
0.86
0.85
0.83
O
N
O
nPr
CO2Et
NH
4.17
2.05
2.04
0.97
2.00
2.04
6.03
5.99
3.07
2.18
3.04
3.10
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 -0
ppm

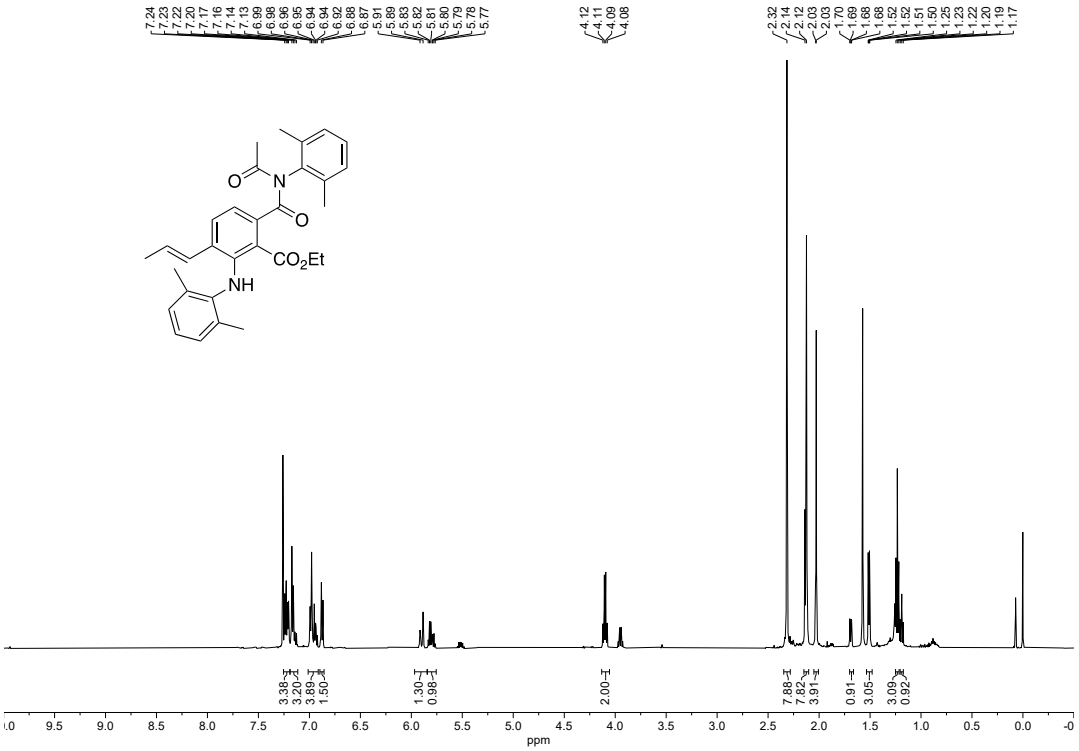

172.72
170.93
168.05
143.46
139.61
137.17
136.97
136.25
134.80
132.53
131.43
129.11
129.10
128.81
124.09
120.60
117.71
61.56
34.21
25.42
22.21
19.27
18.32
14.13
13.93
O
N
O
nPr
CO2Et
NH
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

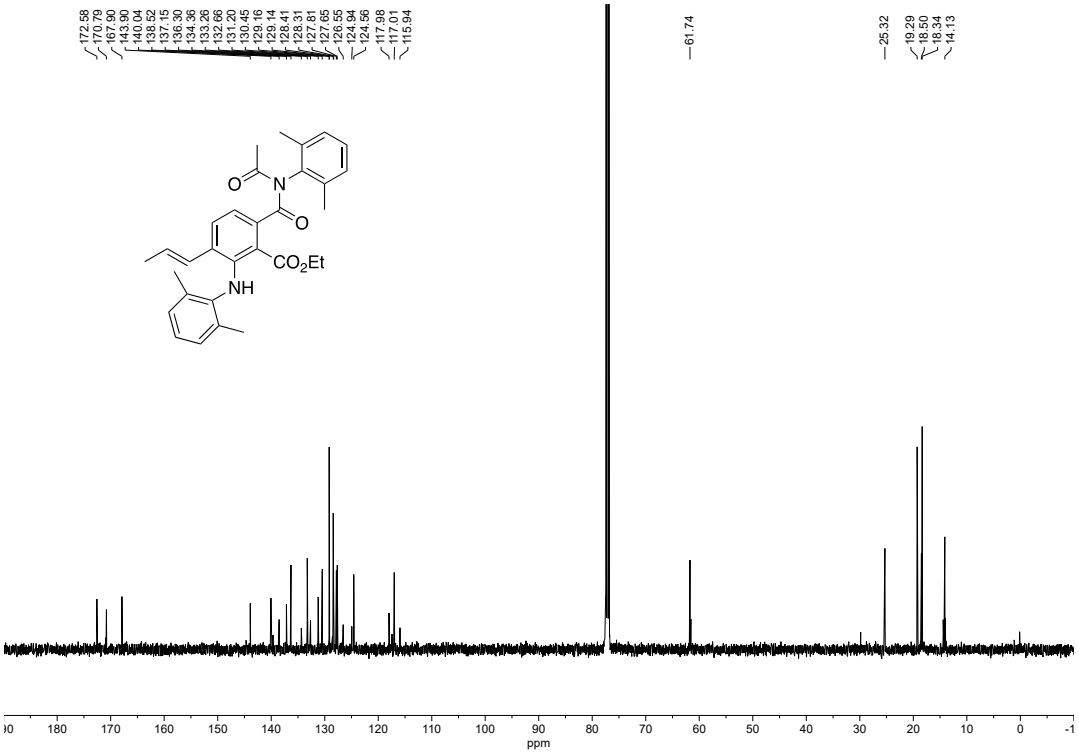
Compound **5h**


7.44
7.42
7.41
7.33
7.31
7.28
7.27
7.24
7.23
7.22
7.22
7.20
7.20
7.19
7.19
7.18
7.17
7.16
7.05
7.04
7.03
7.03
7.03
7.01
7.00
7.00
6.98
6.95
6.94
6.94
6.93
6.78
3.87
3.85
3.34
3.33
3.32
3.30
3.29
3.18
3.16
3.15
3.14
3.12
3.10
2.17
2.15
1.40
1.39
1.37
1.32
1.30
1.29
1.28
1.26
1.21
1.19
1.17
1.15
1.05
1.04
1.04
2.16
7.12
7.24
3.17
1.00
2.00
0.44
0.39
4.07
0.60
3.01
0.64
10.20
6.61
8.64
6.05
ppm

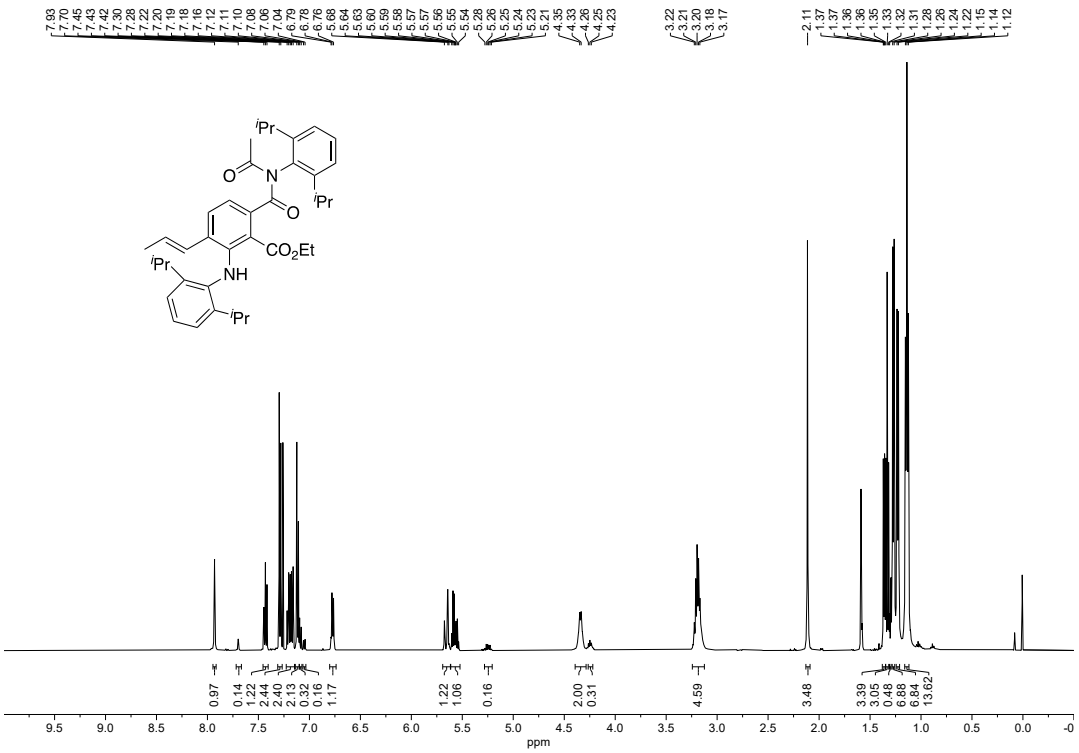

173.15
171.78
171.53
168.17
167.64
148.93
146.48
145.77
145.07
144.36
139.37
138.66
135.88
134.07
133.13
132.85
129.75
128.88
128.73
128.35
127.51
126.23
124.56
124.48
124.23
123.04
117.23
115.42
61.45
29.83
28.70
28.64
28.57
25.87
24.58
24.53
24.02
23.84
23.26
23.14
22.31
14.62
14.09
ppm

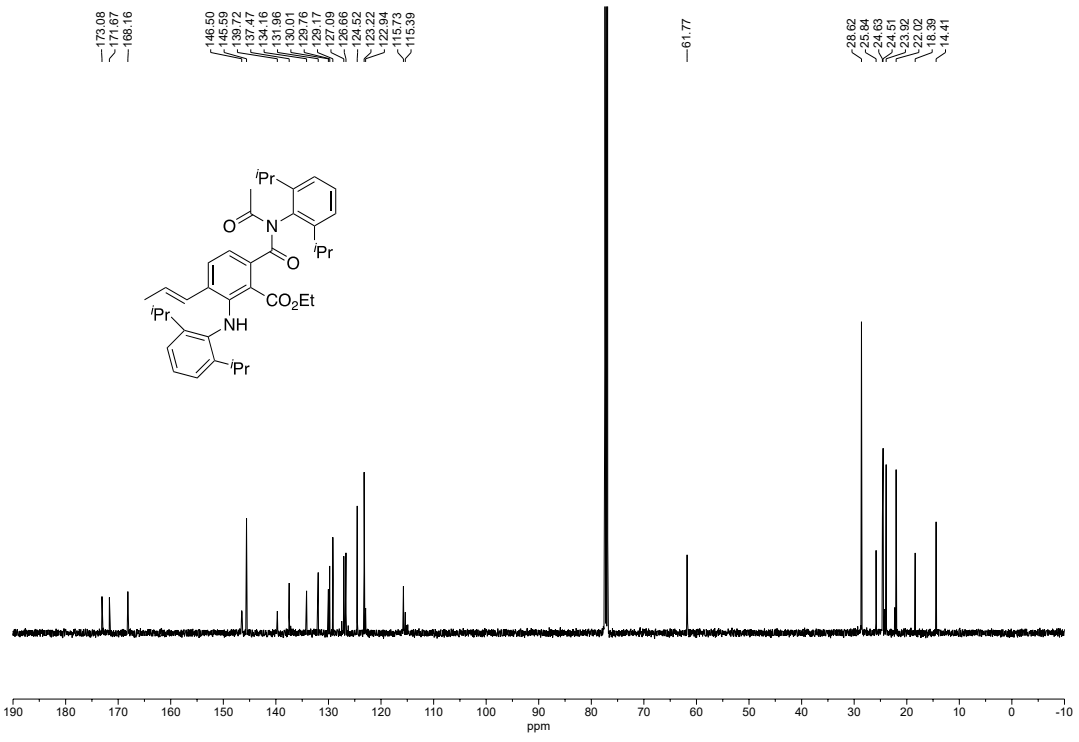
Compound **5i**


7.24
7.23
7.22
7.20
7.17
7.16
7.14
7.13
6.99
6.98
6.96
6.95
6.94
6.94
6.92
6.88
6.87
5.91
5.89
5.83
5.82
5.81
5.80
5.78
5.77
4.12
4.11
4.09
4.08
2.32
2.14
2.12
2.03
2.03
1.70
1.69
1.68
1.68
1.52
1.51
1.50
1.25
1.23
1.22
1.20
1.19
1.17
O
N
O
CO2Et
NH
3.38
3.20
3.89
1.50
1.30
0.96
2.00
7.88
7.82
3.91
0.91
3.05
3.09
0.92
ppm

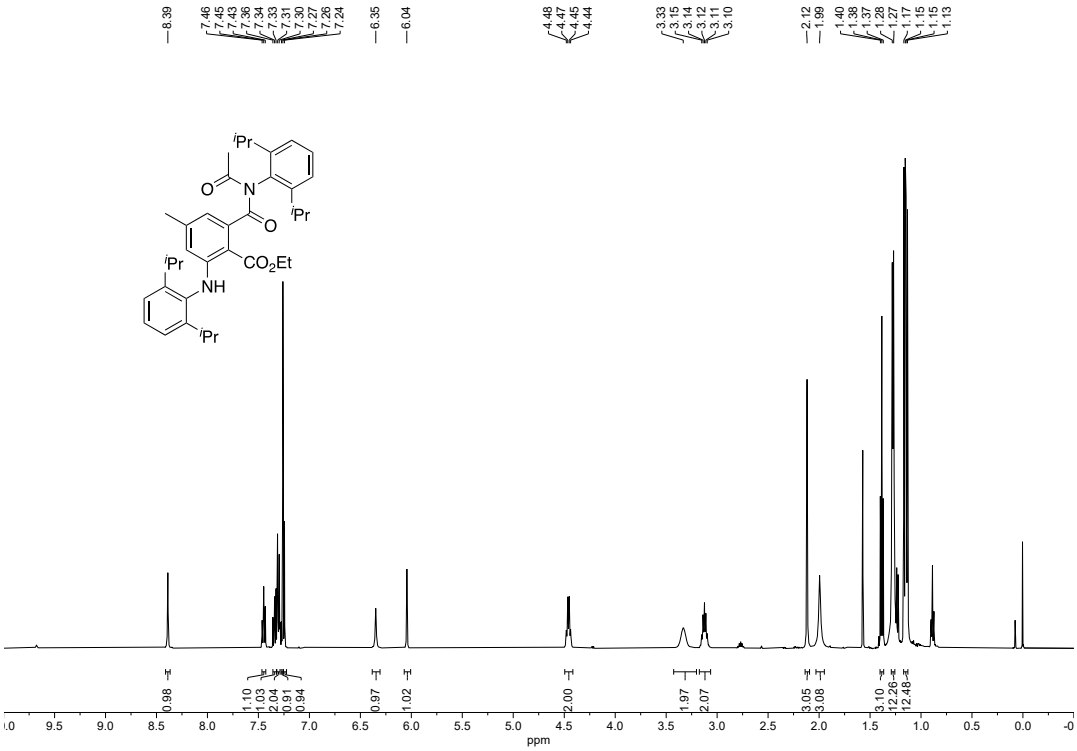

172.58
170.79
167.90
143.90
140.04
138.62
137.15
136.30
134.36
133.26
132.66
131.20
130.45
129.16
129.14
128.41
128.31
127.81
127.65
126.55
124.94
124.56
117.98
117.01
115.94
61.74
25.32
19.29
18.50
18.34
14.13
O
N
O
CO2Et
NH
ppm

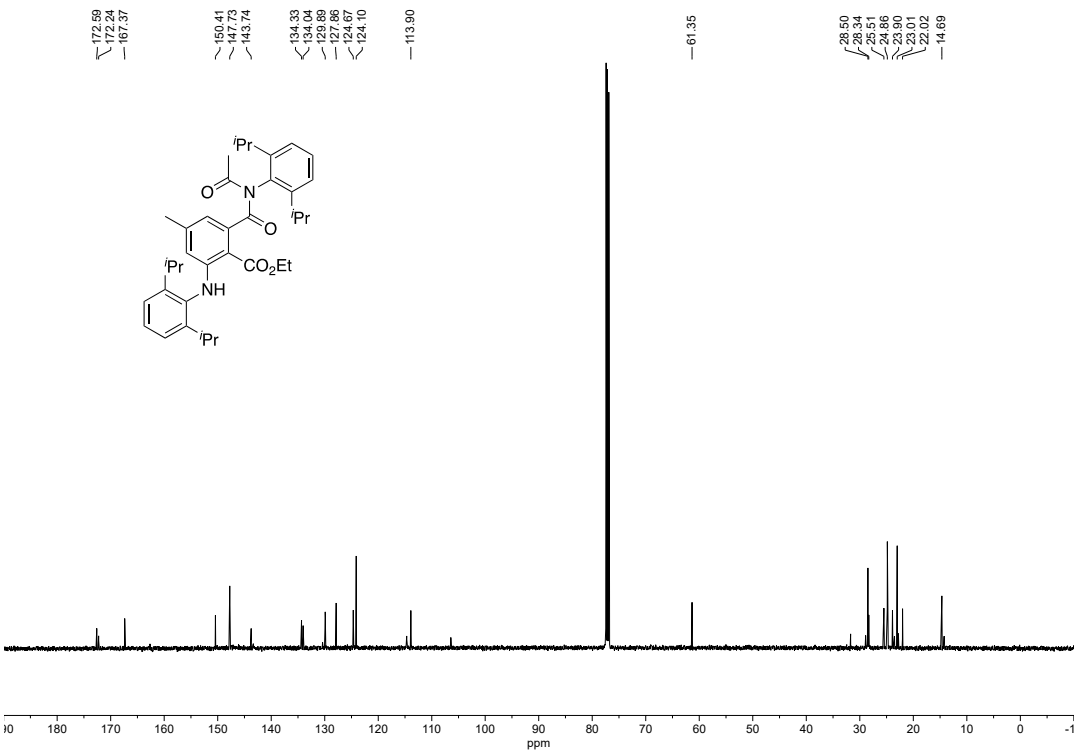
Compound **5j**


7.93 7.70 7.45 7.43 7.42 7.30 7.28 7.22 7.20 7.19 7.18 7.16 7.12 7.11 7.10 7.08 7.06 7.04 6.79 6.78 6.76 5.68 5.64 5.63 5.60 5.59 5.58 5.57 5.57 5.56 5.55 5.54 5.28 5.26 5.25 5.24 5.23 5.21 4.35 4.33 4.26 4.25 4.23 3.22 3.21 3.20 3.18 3.17 2.11 1.37 1.37 1.36 1.36 1.35 1.33 1.32 1.31 1.28 1.26 1.24 1.22 1.15 1.14 1.12
iPr
O
N
iPr
O
CO2Et
iPr
NH
iPr
0.97 0.14 1.22 2.44 2.40 2.13 2.32 0.16 1.17 1.22 1.06 0.16 2.00 0.31 4.59 3.48 3.39 3.05 0.48 6.88 6.84 13.62
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 -0
ppm

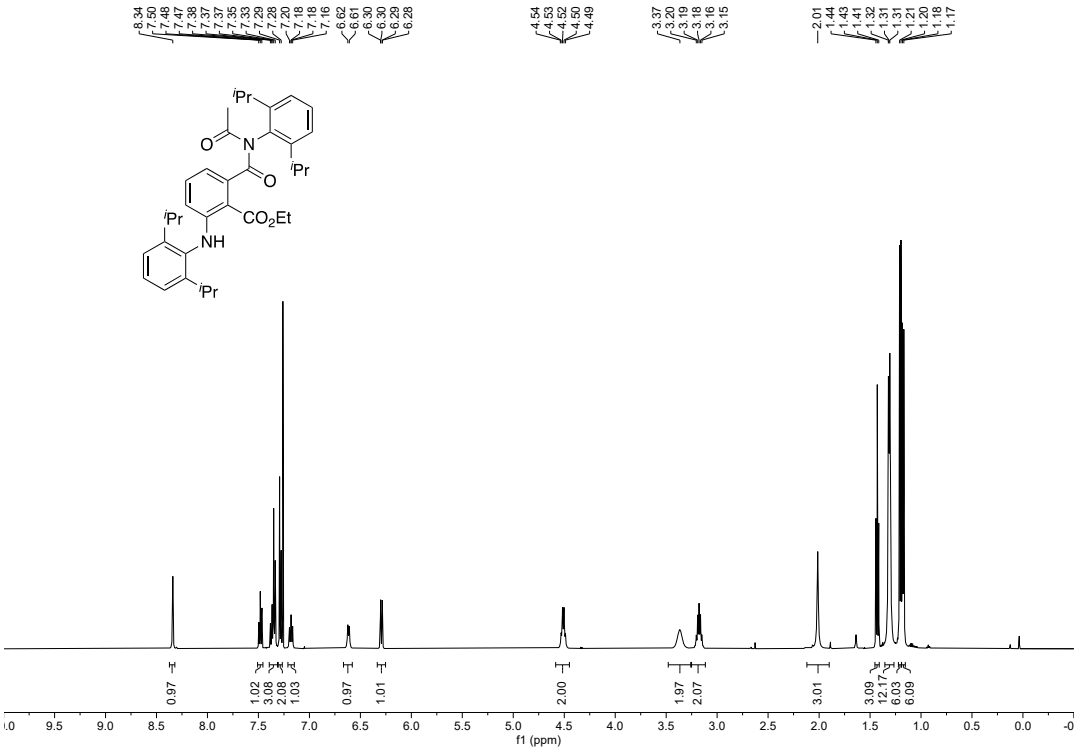

173.08 171.67 168.16 146.50 145.59 139.72 137.47 134.16 131.66 130.01 129.76 128.17 127.09 126.66 124.52 123.22 122.94 115.73 115.39 61.77 28.62 25.94 24.63 24.51 23.92 22.02 18.39 14.41
iPr
O
N
iPr
O
CO2Et
iPr
NH
iPr
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

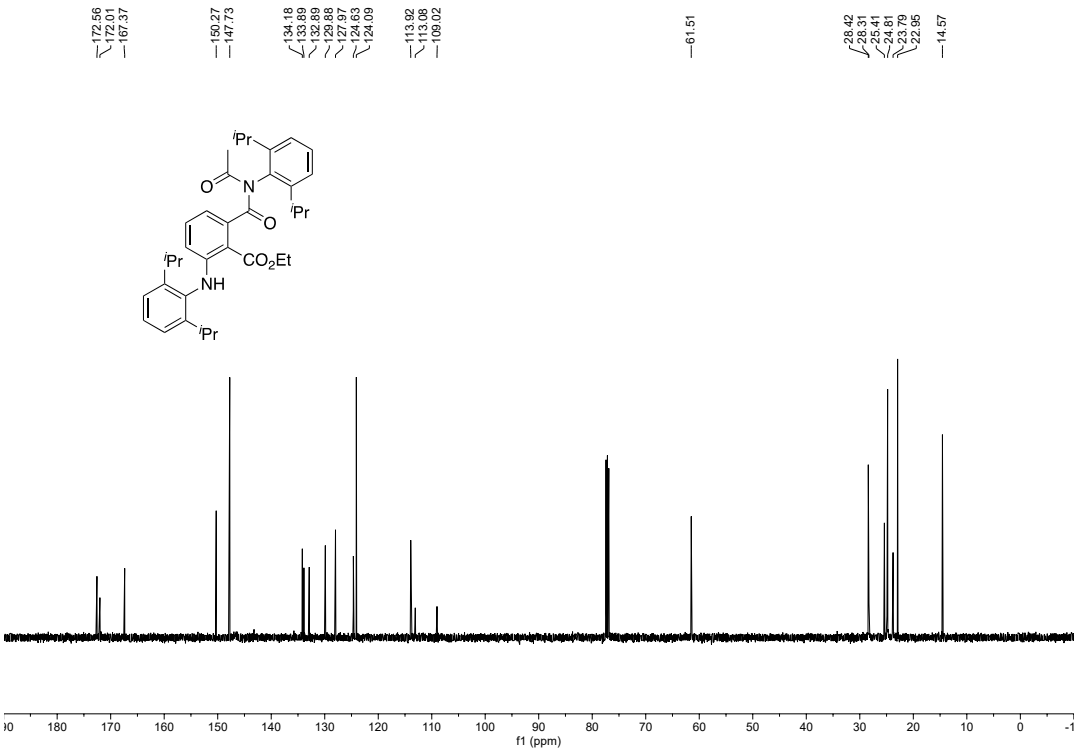
Compound **5k**


8.39
7.46
7.45
7.43
7.36
7.34
7.33
7.31
7.30
7.27
7.26
7.24
6.35
6.04
4.48
4.47
4.45
4.44
3.33
3.15
3.14
3.12
3.11
3.10
2.12
1.99
1.40
1.38
1.37
1.28
1.27
1.17
1.15
1.13
iPr
O
N
O
iPr
iPr
CO2Et
NH
iPr
0.98
1.10
1.03
2.04
0.91
0.94
0.97
1.02
2.00
1.97
2.07
3.05
3.08
3.10
12.28
12.48
ppm

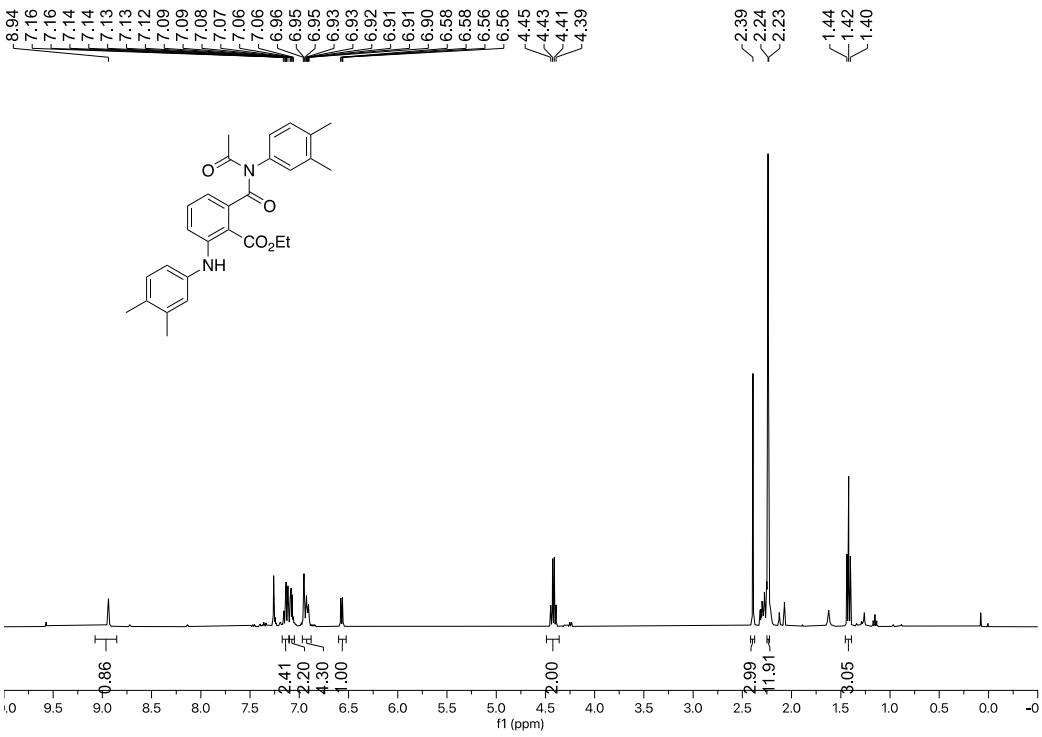

172.59
172.24
167.37
150.41
147.73
143.74
134.33
134.04
129.89
127.86
124.67
124.10
113.90
61.35
28.50
28.34
25.51
24.86
23.90
23.01
22.02
14.69
iPr
O
N
O
iPr
iPr
CO2Et
NH
iPr
ppm

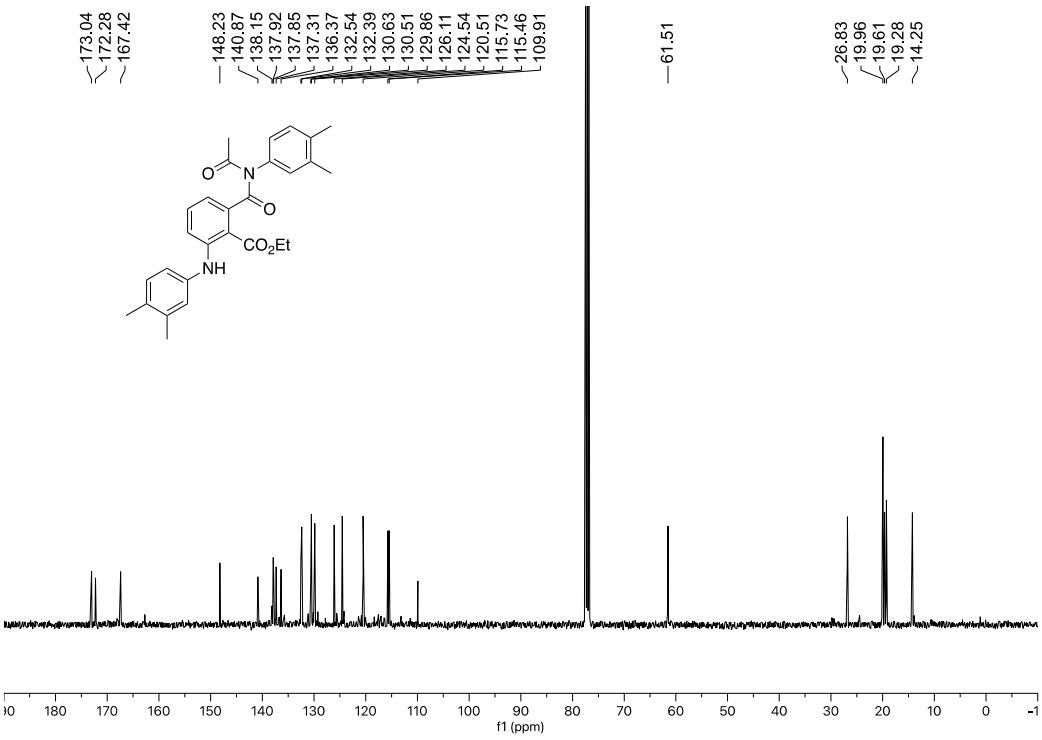
Compound **5l**


8.34
7.50
7.48
7.47
7.39
7.37
7.35
7.33
7.29
7.28
7.20
7.18
7.18
7.16
6.62
6.61
6.30
6.30
6.29
6.28
4.54
4.53
4.52
4.50
4.49
3.37
3.20
3.19
3.18
3.16
3.15
2.01
1.44
1.43
1.41
1.32
1.31
1.31
1.21
1.20
1.18
1.17
iPr
iPr
iPr
iPr
CO2Et
NH
0.97
1.02
3.08
2.08
1.03
0.97
1.01
2.00
1.97
2.07
3.01
3.09
12.17
6.03
6.09
f1 (ppm)

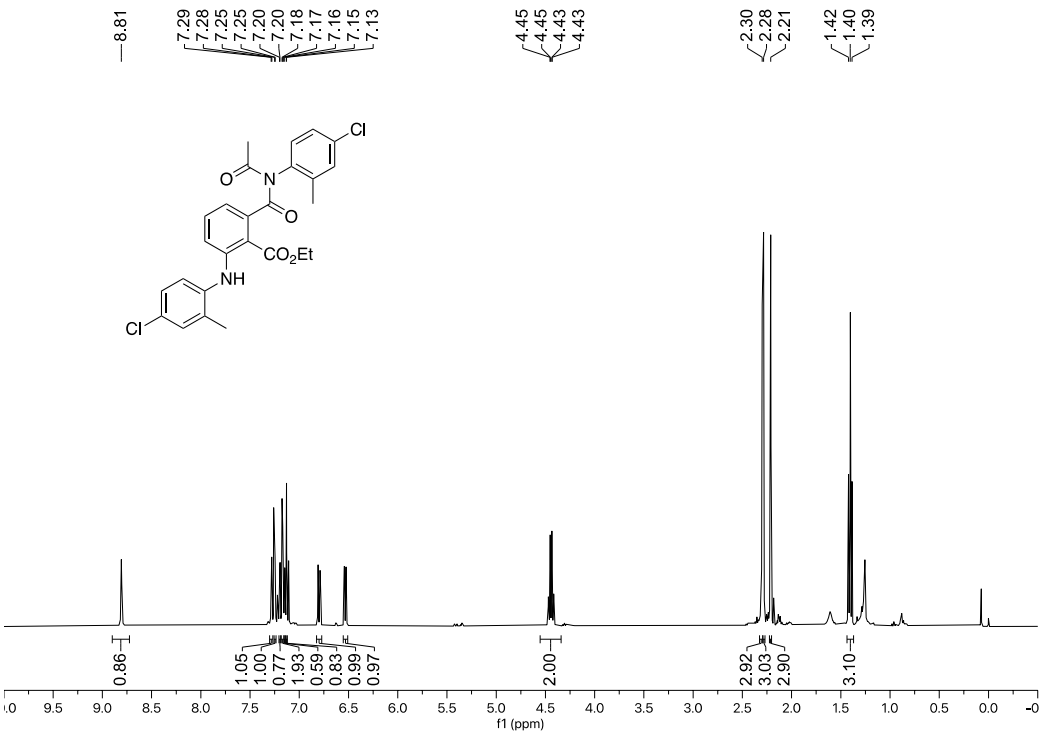

172.56
172.01
167.37
150.27
147.73
134.18
133.89
132.89
129.88
127.97
124.63
124.09
113.92
113.08
109.02
61.51
28.42
28.31
25.41
24.81
23.79
22.95
14.57
iPr
iPr
iPr
iPr
CO2Et
NH
f1 (ppm)

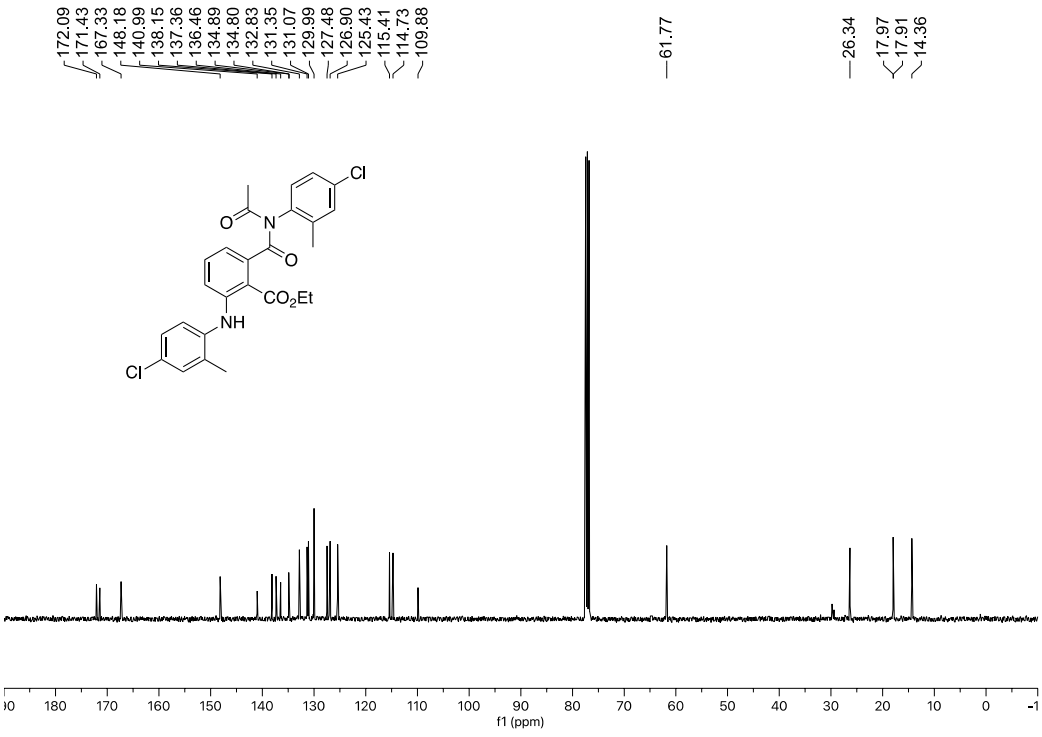
Compound **5m**


8.94
7.16
7.16
7.14
7.14
7.13
7.13
7.12
7.09
7.09
7.08
7.07
7.06
7.06
6.96
6.95
6.95
6.93
6.93
6.92
6.91
6.91
6.90
6.58
6.58
6.56
6.56
4.45
4.43
4.41
4.39
2.39
2.24
2.23
1.44
1.42
1.40
O
N
O
CO2Et
NH
0.86
2.41
2.20
4.30
1.00
2.00
2.99
11.91
3.05
f1 (ppm)

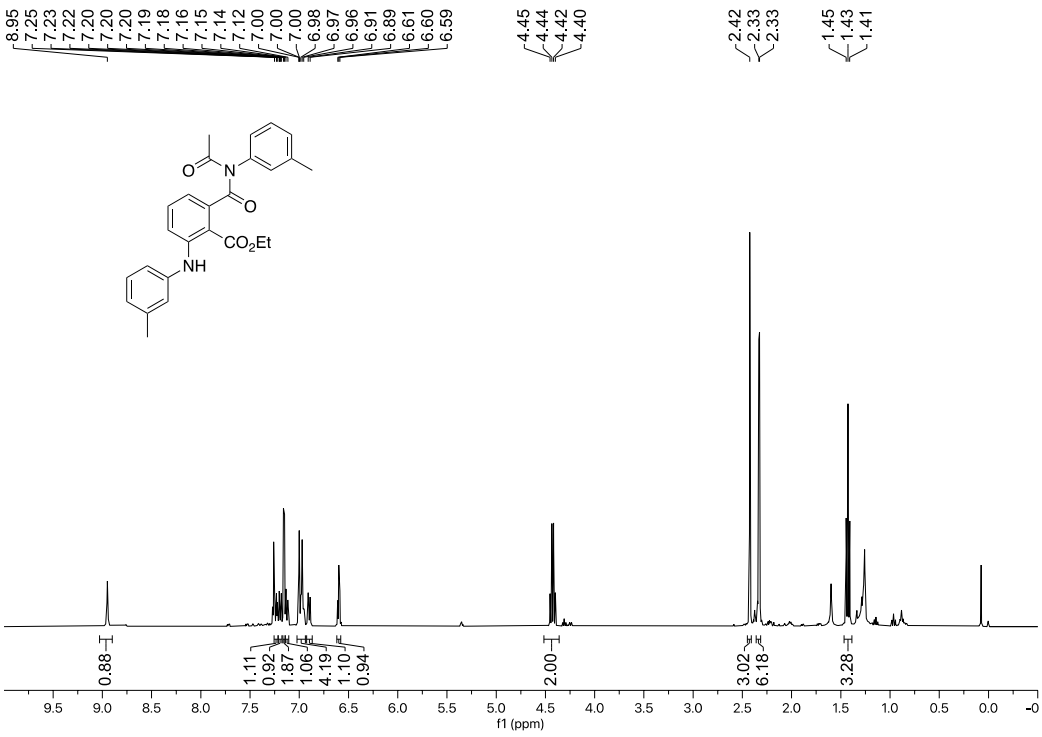

173.04
172.28
167.42
148.23
140.87
138.15
137.92
137.85
137.31
136.37
132.54
132.39
130.63
130.51
129.86
126.11
124.54
120.51
115.73
115.46
109.91
61.51
26.83
19.96
19.61
19.28
14.25
O
N
O
CO2Et
NH
f1 (ppm)

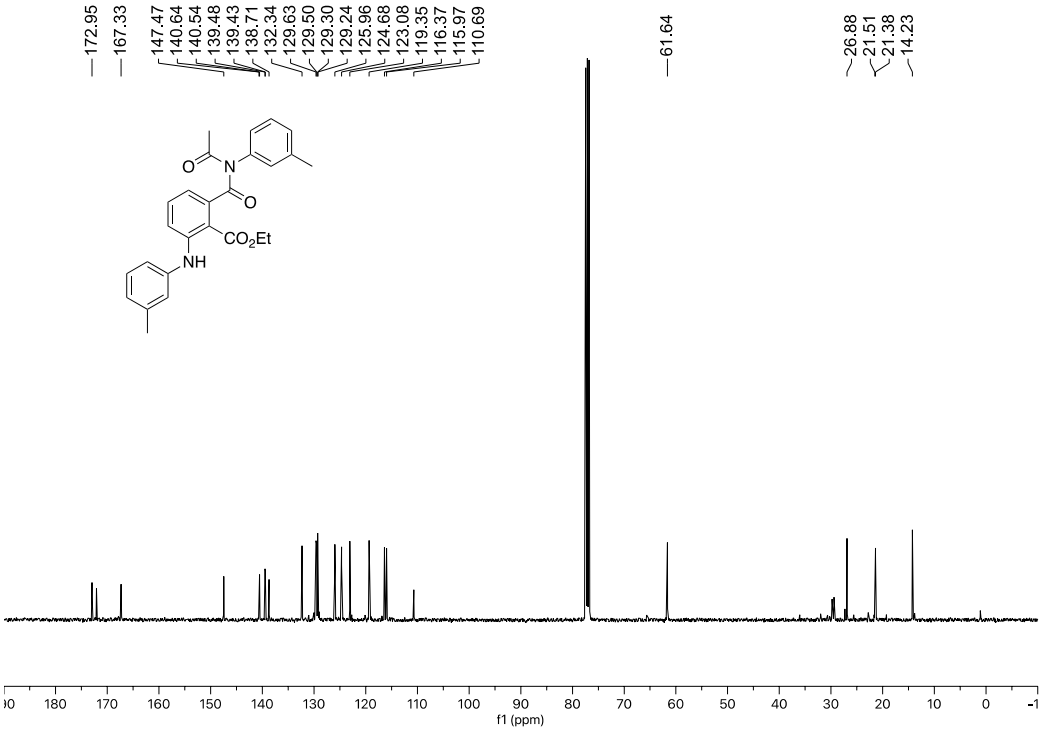
Compound **5n**


8.81
7.29
7.28
7.25
7.25
7.20
7.20
7.18
7.17
7.16
7.15
7.13
4.45
4.45
4.43
4.43
2.30
2.28
2.21
1.42
1.40
1.39
Cl
O
N
O
CO2Et
NH
Cl
0.86
1.05
1.00
0.77
1.93
0.59
0.83
0.99
0.97
2.00
2.92
3.03
2.90
3.10
f1 (ppm)

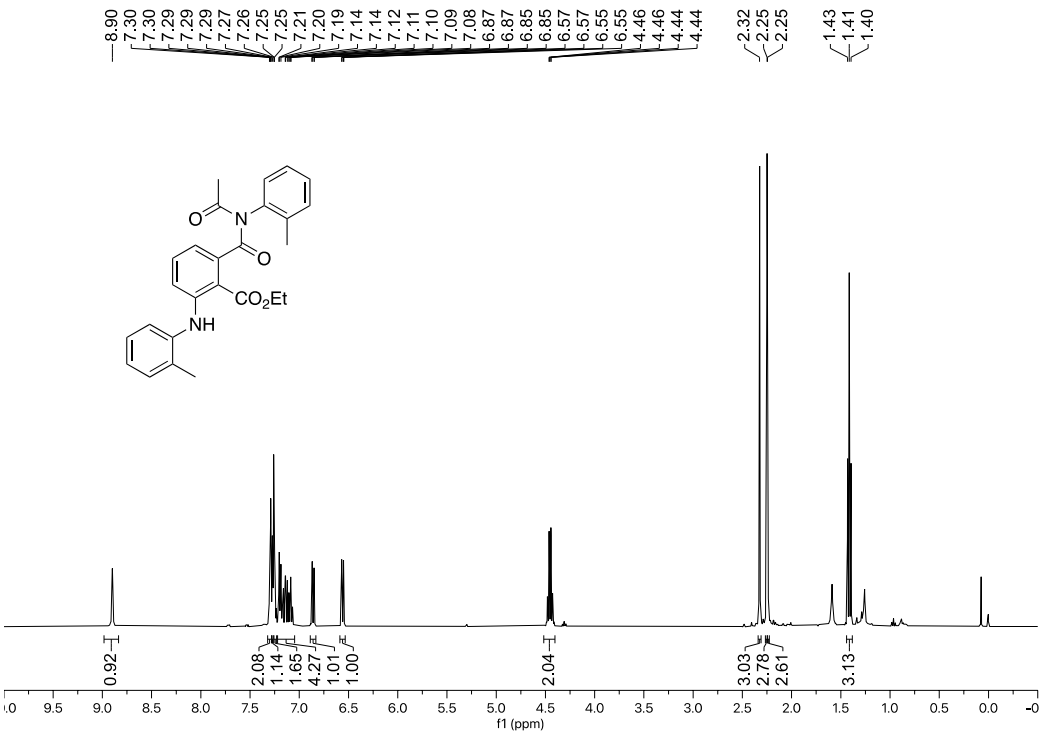

172.09
171.43
167.33
148.18
140.99
138.15
137.36
136.46
134.89
134.80
132.83
131.35
131.07
129.99
127.48
126.90
125.43
115.41
114.73
109.88
61.77
26.34
17.97
17.91
14.36
Cl
O
N
O
CO2Et
NH
Cl
f1 (ppm)

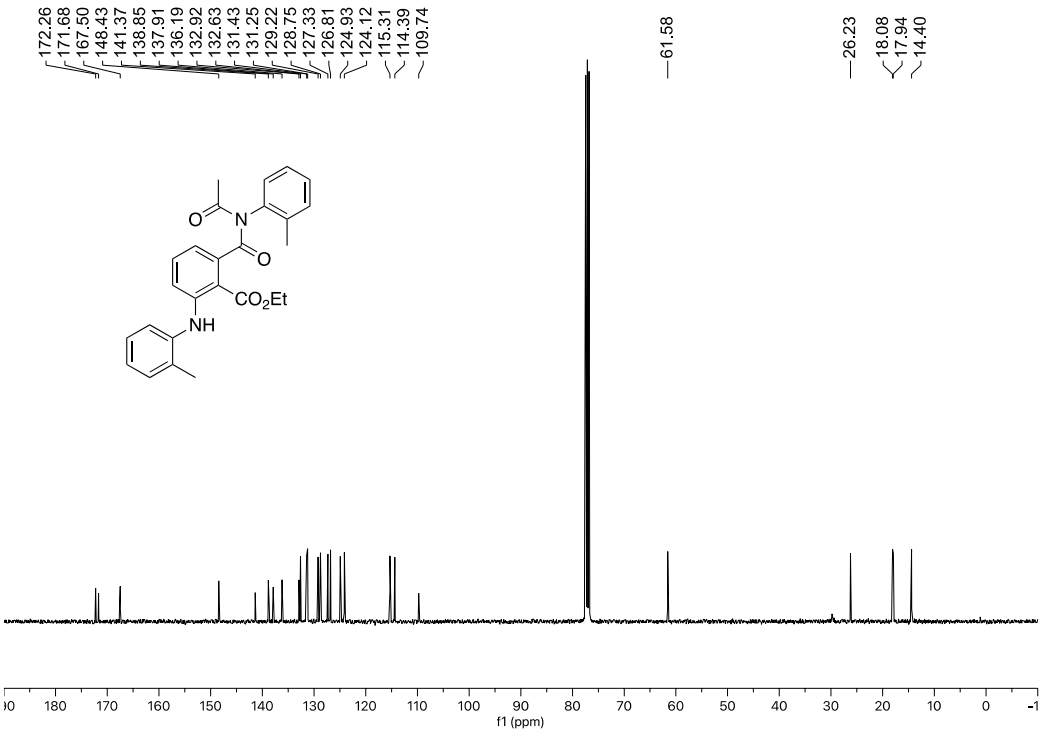
Compound **5o**


8.95
7.25
7.23
7.22
7.20
7.20
7.20
7.19
7.18
7.16
7.15
7.14
7.12
7.00
7.00
7.00
6.98
6.97
6.96
6.91
6.89
6.61
6.60
6.59
4.45
4.44
4.42
4.40
2.42
2.33
2.33
1.45
1.43
1.41
O
N
O
CO2Et
NH
0.88
1.11
0.92
1.87
1.06
4.19
1.10
0.94
2.00
3.02
6.18
3.28
f1 (ppm)

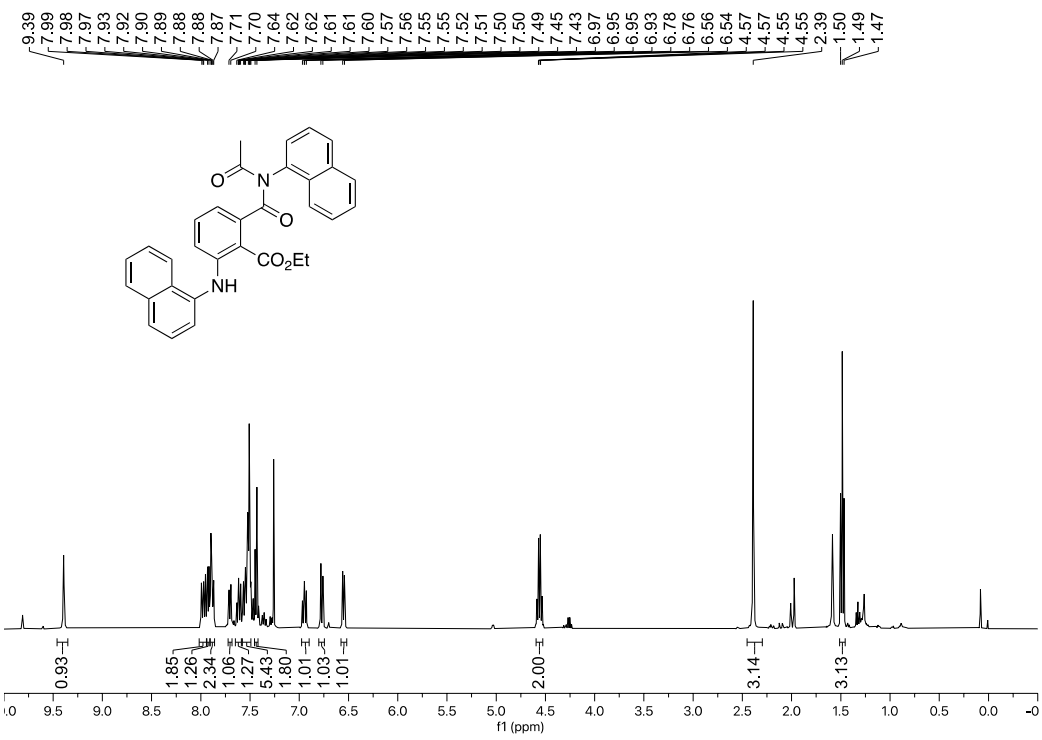

172.95
167.33
147.47
140.64
140.54
139.48
139.43
138.71
132.34
129.63
129.50
129.30
129.24
125.96
124.68
123.08
119.35
116.37
115.97
110.69
61.64
26.88
21.51
21.38
14.23
O
N
O
CO2Et
NH
f1 (ppm)

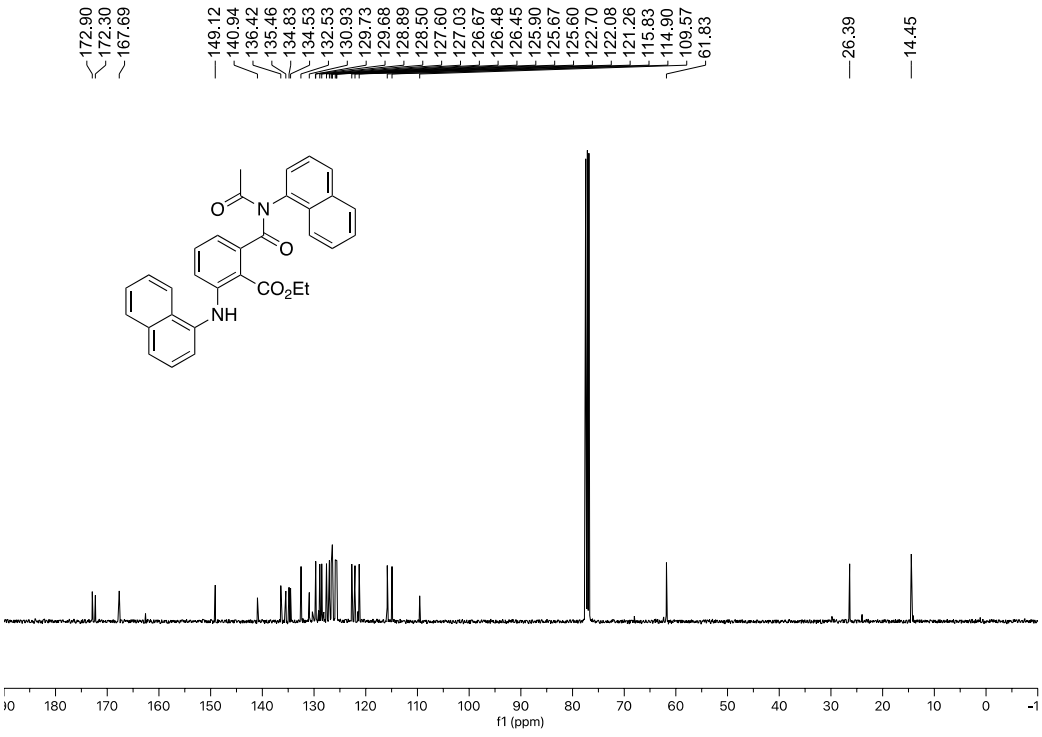
Compound **5p**


8.90
7.30
7.30
7.29
7.29
7.29
7.27
7.26
7.25
7.25
7.21
7.20
7.19
7.14
7.14
7.12
7.11
7.10
7.09
7.08
6.87
6.87
6.85
6.85
6.57
6.57
6.55
6.55
4.46
4.44
4.44
2.32
2.25
2.25
1.43
1.41
1.40
O
N
O
CO2Et
NH
0.92
2.08
1.14
1.65
4.27
1.01
1.00
2.04
3.03
2.78
2.61
3.13
f1 (ppm)

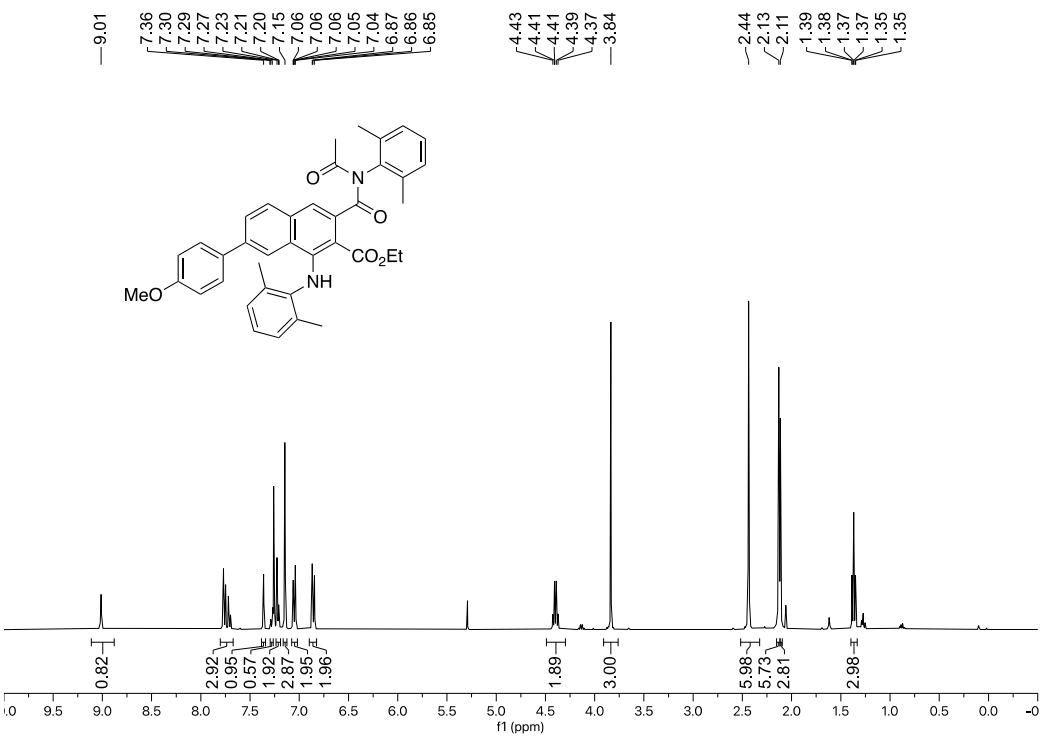

172.26
171.68
167.50
148.43
141.37
138.85
137.91
136.19
132.92
132.63
131.43
131.25
129.22
128.75
127.33
126.81
124.93
124.12
115.31
114.39
109.74
61.58
26.23
18.08
17.94
14.40
O
N
O
CO2Et
NH
f1 (ppm)

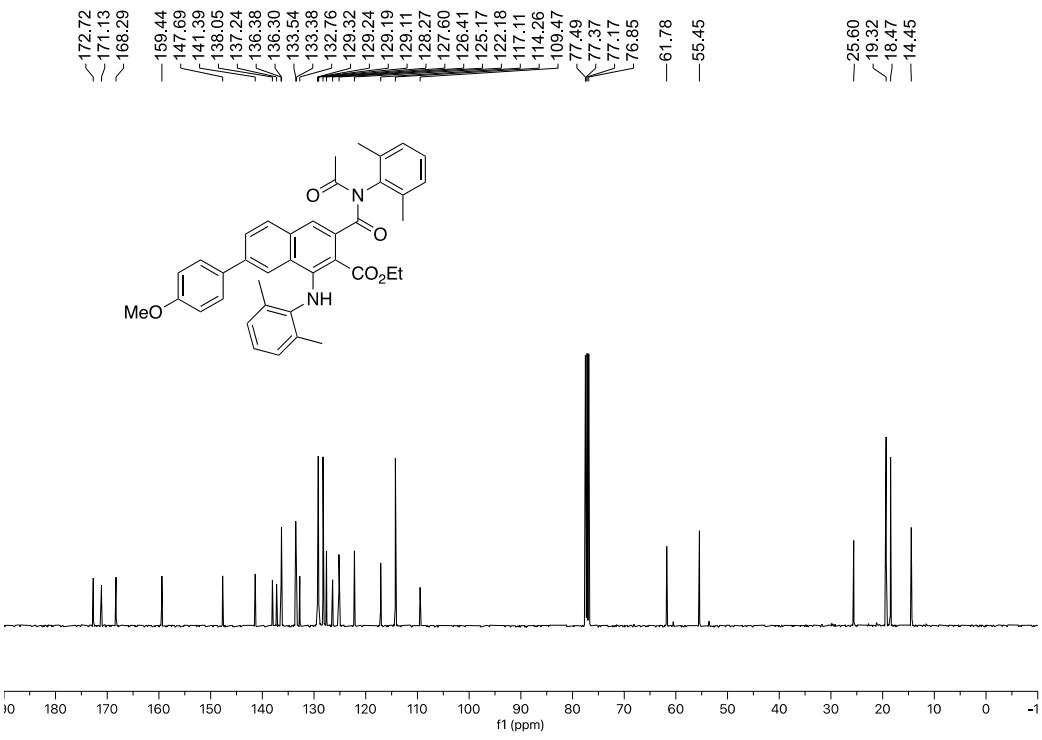
Compound **5q**


9.39
7.99
7.98
7.97
7.93
7.92
7.90
7.89
7.88
7.88
7.87
7.71
7.70
7.64
7.62
7.62
7.61
7.61
7.60
7.57
7.56
7.55
7.55
7.52
7.51
7.50
7.50
7.49
7.45
7.43
6.97
6.95
6.95
6.93
6.78
6.76
6.56
6.54
4.57
4.57
4.55
4.55
2.39
1.50
1.49
1.47
O
N
O
CO2Et
NH
0.93
1.85
1.26
2.34
1.06
1.27
5.43
1.80
1.01
1.03
1.01
2.00
3.14
3.13
f1 (ppm)

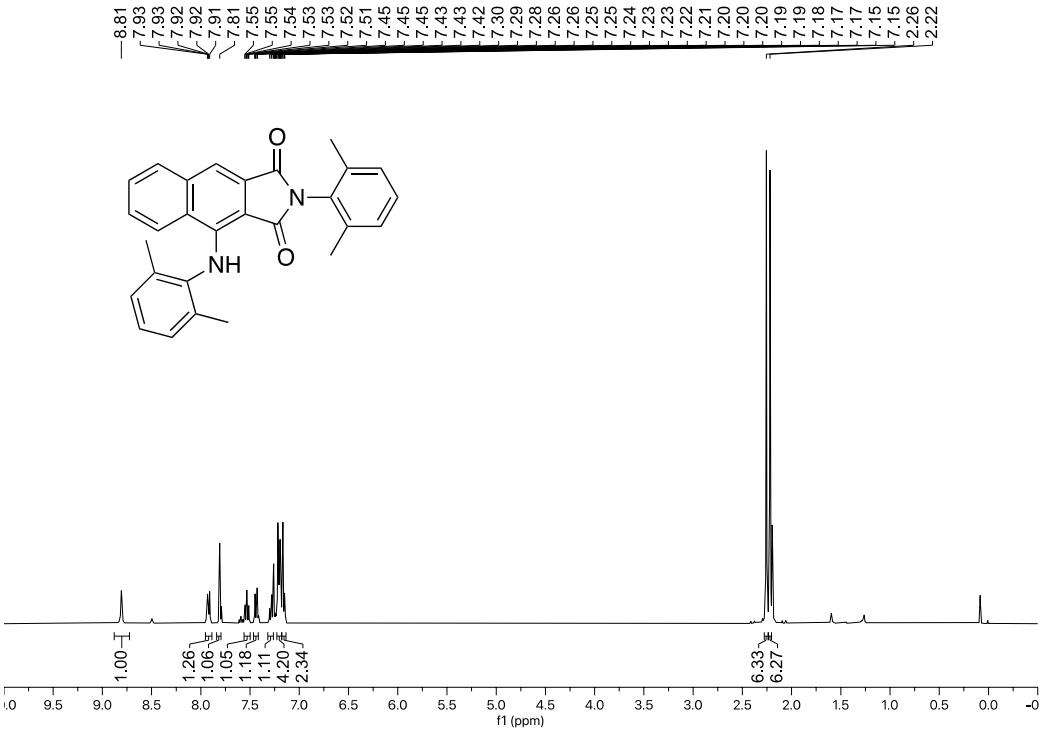

172.90
172.30
167.69
149.12
140.94
136.42
135.46
134.83
134.53
132.53
130.93
129.73
129.68
128.89
128.50
127.60
127.03
126.67
126.48
126.45
125.90
125.67
125.60
122.70
122.08
121.26
115.83
114.90
109.57
61.83
26.39
14.45
O
N
O
CO2Et
NH
f1 (ppm)

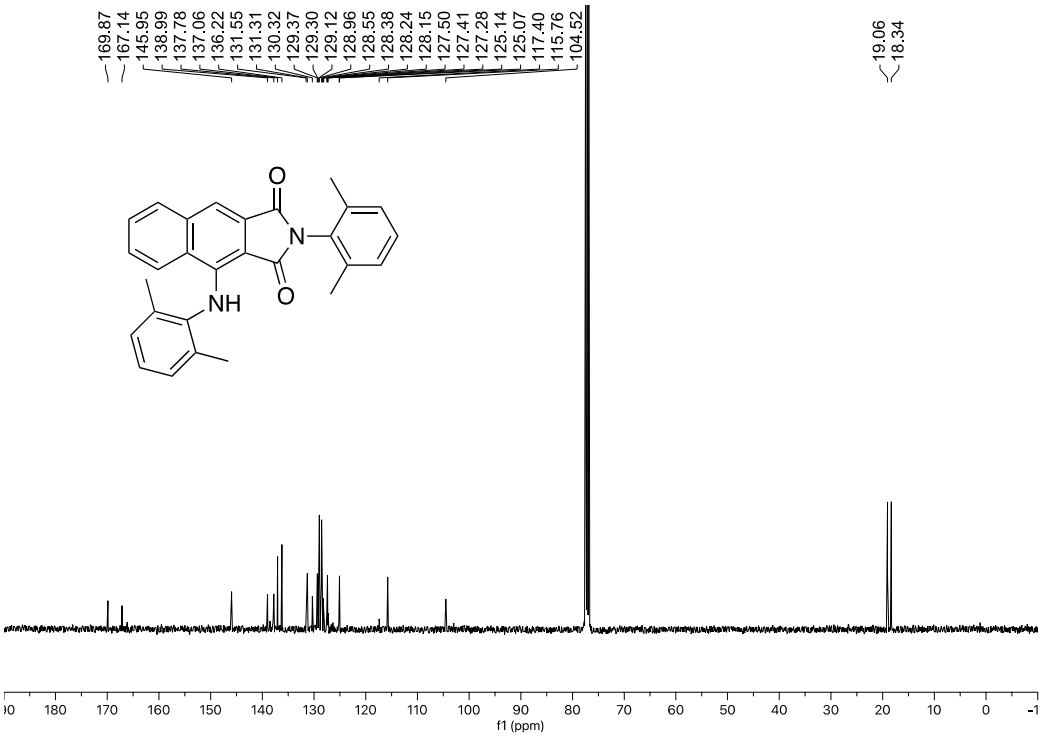
Compound **7**


9.01
7.36
7.30
7.29
7.27
7.23
7.21
7.20
7.15
7.06
7.06
7.06
7.05
7.04
6.87
6.86
6.85
4.43
4.41
4.41
4.39
4.37
3.84
2.44
2.13
2.11
1.39
1.38
1.37
1.37
1.35
1.35
O
N
O
CO2Et
NH
MeO
0.82
2.92
0.95
0.57
1.92
2.87
1.95
1.96
1.89
3.00
5.98
5.73
2.81
2.98
f1 (ppm)


172.72
171.13
168.29
159.44
147.69
141.39
138.05
137.24
136.38
136.30
133.54
133.38
132.76
129.32
129.24
129.19
129.11
128.27
127.60
126.41
125.17
122.18
117.11
114.26
109.47
77.49
77.37
77.17
76.85
61.78
55.45
25.60
19.32
18.47
14.45
O
N
O
CO2Et
NH
MeO
f1 (ppm)

Compound **8**


8.81
7.93
7.93
7.92
7.92
7.91
7.81
7.55
7.55
7.54
7.53
7.53
7.52
7.51
7.45
7.45
7.43
7.43
7.42
7.30
7.29
7.28
7.26
7.26
7.25
7.25
7.24
7.23
7.23
7.22
7.21
7.20
7.20
7.20
7.19
7.19
7.18
7.17
7.17
7.15
7.15
2.26
2.22
O
N
O
NH
1.00
1.26
1.06
1.05
1.18
1.11
4.20
2.34
6.33
6.27
f1 (ppm)


169.87
167.14
145.95
138.99
137.78
137.06
136.22
131.55
131.31
130.32
129.37
129.30
129.12
128.96
128.55
128.38
128.24
128.15
127.50
127.41
127.28
125.14
125.07
117.40
115.76
104.52
19.06
18.34
O
N
O
NH
f1 (ppm)