Supplementary Information

Substitution Controlled Aryne Insertion: Synthesis of Diarylmethane/chromones

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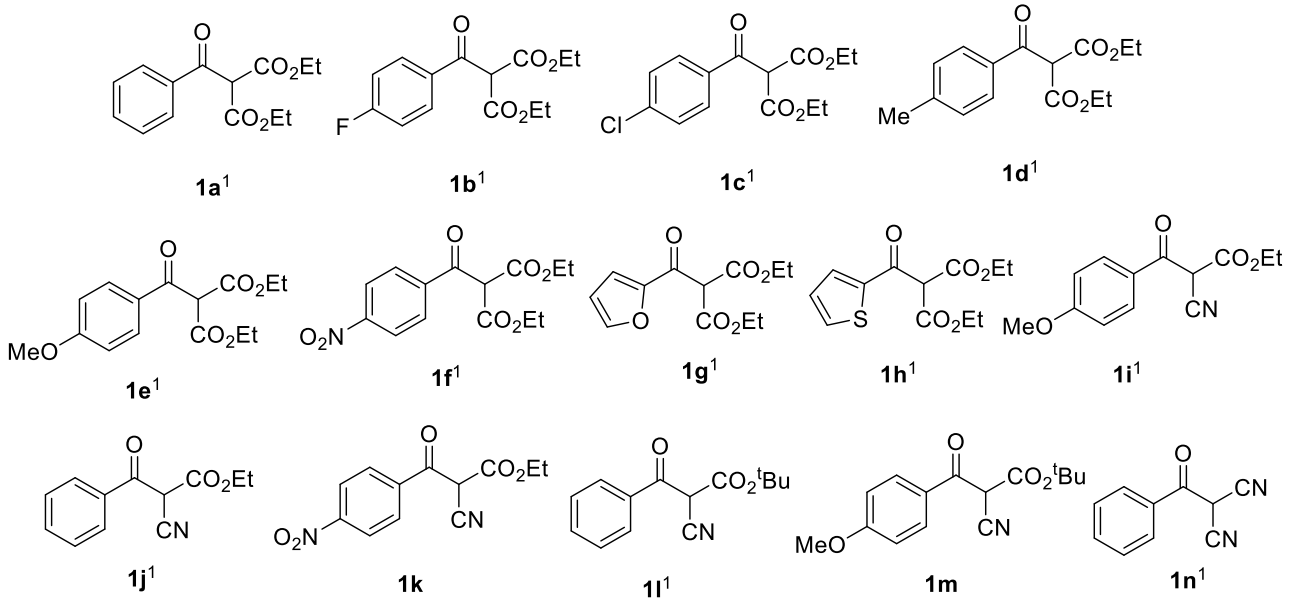
I. General details

General information: Unless otherwise noted, all reagents were used as received from commercial suppliers. All nonaqueous reactions were performed under an atmosphere of nitrogen using oven-dried glassware. All solvents were dried before use, following the standard procedures. Reactions were monitored using thin-layer chromatography (SiO_2). TLC plates were visualized with UV light (254 nm), iodine treatment or using *p*-anisaldehyde stain. Column chromatography was carried out using silica gel (100-200 mesh) packed in glass columns. NMR spectra were recorded at 400, 500 MHz (H) and at 101, 126 MHz (C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (H: δ = 7.26 and C: δ = 77.16 ppm) as internal standard, and coupling constants (*J*) are given in Hz. High-resolution mass spectrometry (HRMS) was obtained by electrospray ionization (ESI) using a Q-TOF mass spectrometer.

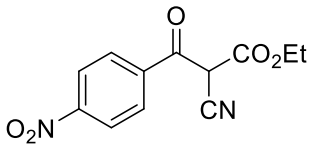
II. Experimental procedures and analytical data

A. General procedure for diethyl 2-benzoylmalonate[1]

Diethyl malonate or alkyl cyano acetate (10 mmol) was added to a solution of magnesium chloride (10 mmol) in dry acetonitrile (40 mL) at 0 °C under nitrogen. Then, triethylamine (20 mmol) was added slowly after 15 min. After 30 min of stirring at 0 °C, corresponding acid chloride (10 mmol) was added and stirring was continued for an hour at same temperature followed by room temperature for overnight. After completion of reaction, the mixture was quenched with 5N HCl (20 mL). The resulting solution was extracted with ethyl acetate (2 x 30 mL) and the combined organic layers were washed with brine (30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (EtOAc/hexanes) to afford the target compound **1a-n**.

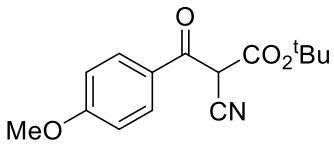


Ethyl 2-cyano-3-(4-nitrophenyl)-3-oxopropanoate (1k)



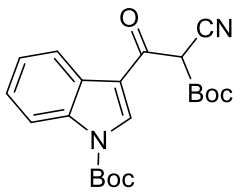
Prepared according to general procedure A using 4-nitrobenzoyl chloride (2.00 g, 10.77 mmol, 1.0 equiv.) and ethyl cyanoacetate (1.15 mL, 10.77 mmol, 1.0 equiv.). Cream colour solid (2.50 g, 89% yield); R_f = 0.6 (30% EtOAc/hexanes); mp = 150−152 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.32 (bs, 1H), 8.36 (d, *J* = 9.0 Hz, 2H), 8.17 (d, *J* = 9.0 Hz, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.2, 170.7, 150.2, 137.0, 129.9, 123.9, 114.9, 81.2, 63.6, 14.1; HRMS (ESI) calcd for $C_{12}H_{11}N_2O_5$ $[M+H]^+$: 263.0662; found 263.0671.

***tert*-Butyl 2-cyano-3-(4-methoxyphenyl)-3-oxopropanoate (1m)**



Prepared according to general procedure A using 4-methoxy benzoyl chloride (1.50 g, 8.82 mmol, 1.0 equiv.) and *tert*-butyl cyanoacetate (1.27 mL, 8.82 mmol, 1.0 equiv.). Light yellow solid (2.06 g, 85% yield); R_f = 0.5 (15% EtOAc/hexanes); mp = 70−72 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.46 (s, 1H), 8.03 (d, *J* = 9.1 Hz, 2H), 6.97 (d, *J* = 9.1 Hz, 2H), 3.87 (s, 3H), 1.59 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.0, 171.4, 163.5, 130.8, 124.0, 116.9, 114.0, 85.0, 78.2, 55.5, 28.1; HRMS (ESI) calcd for $C_{15}H_{18}NO_4Na$ $[M+H]^+$: 276.1230; found 276.1229.

B. Procedure for the syntheses of *tert*-butyl 3-(3-(tert-butoxy)-2-cyano-3-oxopropanoyl)-1*H*-indole-1-carboxylate (1o):



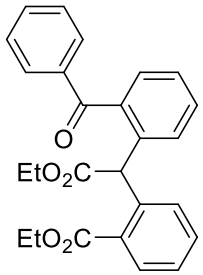
To a suspension of 3-(1*H*-indol-3-yl)-3-oxopropanenitrile[2] (200 mg, 1.08 mmol, 1.0 equiv.) in anhydrous THF (10 mL) was added Boc anhydride (569 mg, 2.60 mmol, 2.4 equiv.) and catalytic DMAP (13 mg, 0.11 mmol, 0.1 equiv.) at 0 ºC and stirred at room temperature for 16 h. Then, the reaction mixture was concentrated under vacuum, diluted with H_2O (30 mL) and extracted with EtOAc (2 x 30 mL). The combined organic phase was washed with brine (30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (EtOAc/hexanes) to afford the target compound

1n as a white solid (259 mg, 62%). R_f = 0.5 (20% EtOAc/hexanes); mp = 158−160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.72 (s, 1H), 8.89 (s, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 8.15 (dd, *J* = 7.3, 0.8 Hz, 1H), 7.45 – 7.32 (m, 2H), 1.69 (s, 9H), 1.61 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 171.5, 148.5, 135.2, 133.8, 132.7, 127.3, 125.7, 124.3, 122.6, 117.3, 115.3, 112.8, 85.7, 85.0, 28.2, 28.0; HRMS (ESI) calcd for $C_{21}H_{25}N_2O_5$ $[M+H]^+$: 385.1758; found 385.1732.

C. General procedure for the syntheses of diarylmethane (3) and chromone (4):

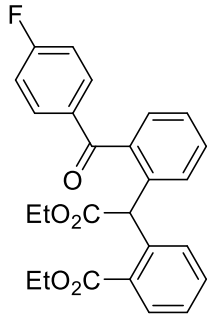
A screw-cap vial equipped with magnetic stir bar was charged with diethyl 2-benzoylmalonate **1** (0.38 mmol, 1.0 equiv.), aryne precursor **2** (0.91 mmol, 2.4 equiv.) (0.76 mmol, 2.0 equiv. for chromones), CsF (1.51 mmol, 4.0 equiv.) in dry THF (4 mL) under nitrogen atmosphere. The reaction mixture was stirred at 60 ºC for 16 h. Then the reaction was cooled to room temperature, diluted with H_2O (20 mL) and extracted with EtOAc (2 x 15 mL). The combined organic phase was washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexanes) to afford diarylmethane **3** or chromone **4**.

Ethyl 2-(1-(2-benzoylphenyl)-2-ethoxy-2-oxoethyl)benzoate (3a)



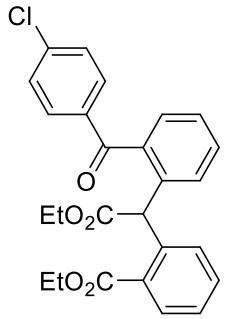
Prepared according to general procedure C using diethyl 2-benzoylmalonate **1a** (100 mg, 0.38 mmol, 1.0 equiv.) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (270 mg, 0.91 mmol, 2.4 equiv.). Light yellow liquid (113 mg, 72% yield); R_f = 0.4 (20% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.66 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.48 – 7.42 (m, 1H), 7.41 – 7.29 (m, 5H), 7.28 – 7.19 (m, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 6.22 (s, 1H), 4.19 – 4.04 (m, 4H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 172.8, 166.8, 139.4, 138.7, 138.2, 137.7, 132.7, 131.9, 130.9, 130.6, 130.4, 130.4, 130.1, 129.8, 129.7, 128.1, 127.1, 126.4, 61.2, 61.0, 51.2, 14.1; HRMS (ESI) calcd for $C_{26}H_{24}O_5Na$ $[M+Na]^+$: 439.1516; found 439.1518.

Ethyl 2-(2-ethoxy-1-(2-(4-fluorobenzoyl)phenyl)-2-oxoethyl)benzoate (3b)



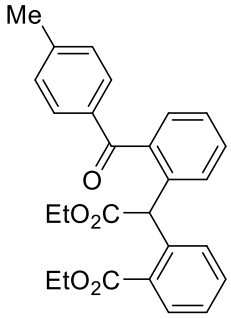
Prepared according to general procedure C using diethyl 2-(4-fluorobenzoyl)malonate **1b** (200 mg, 0.71 mmol, 1.0 equiv.) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (506 mg, 1.70 mmol, 2.4 equiv.). White solid (200 mg, 65% yield); R_f = 0.6 (20% EtOAc/hexanes); mp = 91−93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.79 – 7.72 (m, 2H), 7.48 – 7.40 (m, 2H), 7.38 – 7.27 (m, 3H), 7.24 – 7.16 (m, 2H), 7.09 – 7.01 (m, 2H), 6.26 (s, 1H), 4.25 – 4.09 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.4, 172.8, 166.8, 165.6 (d, J_{C-F} = 256 Hz), 139.4, 138.6, 138.2, 134.0, 133.0 (d, J_{C-F} = 10 Hz), 131.9, 130.9, 130.6, 130.4, 130.1, 129.8, 129.4, 127.2, 126.4, 115.2 (d, J_{C-F} = 21 Hz), 61.2, 61.0, 51.2, 14.1; HRMS (ESI) calcd for $C_{26}H_{24}FO_5$ $[M+H]^+$: 435.1602; found 435.1603.

Ethyl 2-(1-(2-(4-chlorobenzoyl)phenyl)-2-ethoxy-2-oxoethyl)benzoate (3c)



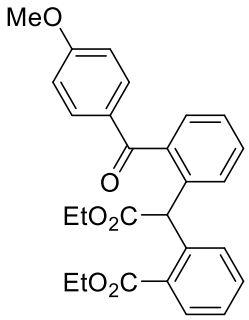
Prepared according to general procedure C using diethyl 2-(4-chlorobenzoyl)malonate **1c** (200 mg, 0.67 mmol, 1.0 equiv.) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (479 mg, 1.61 mmol, 2.4 equiv.). Light yellow liquid (176 mg, 58% yield); R_f = 0.5 (15% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.71 – 7.63 (m, 2H), 7.47 – 7.41 (m, 2H), 7.38 – 7.25 (m, 5H), 7.24 – 7.16 (m, 2H), 6.28 (s, 1H), 4.24 – 4.11 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 172.7, 166.7, 139.4, 139.3, 138.4, 138.3, 136.1, 132.0, 131.7, 131.0, 130.8, 130.4, 130.1, 129.9, 129.5, 128.4, 127.2, 126.4, 61.3, 61.0, 51.2, 14.1; HRMS (ESI) calcd for $C_{26}H_{24}ClO_5$ $[M+H]^+$: 451.1307; found 451.1326.

Ethyl 2-(2-ethoxy-1-(2-(4-methylbenzoyl)phenyl)-2-oxoethyl)benzoate (3d)



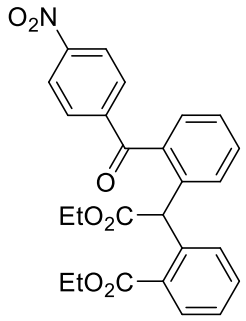
Prepared according to general procedure C using diethyl 2-(4-methylbenzoyl)malonate **1d** (200 mg, 0.72 mmol, 1.0 equiv.) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (514 mg, 1.72 mmol, 2.4 equiv.). Light yellow liquid (185 mg, 60% yield); R_f = 0.6 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.66 – 7.58 (m, 2H), 7.47 – 7.27 (m, 5H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 3H), 6.26 (s, 1H), 4.21 – 4.12 (m, 4H), 2.40 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 172.8, 166.8, 143.7, 139.4, 139.1, 138.0, 135.1, 131.9, 130.9, 130.5, 130.4, 130.3, 130.1, 129.7, 129.6, 128.8, 127.0, 126.4, 61.2, 60.9, 51.3, 21.7, 14.1; HRMS (ESI) calcd for $C_{27}H_{27}O_5$ $[M+H]^+$: 431.1853; found 431.1864.

Ethyl 2-(2-ethoxy-1-(2-(4-methoxybenzoyl)phenyl)-2-oxoethyl)benzoate (3e)



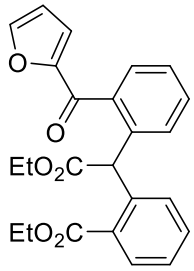
Prepared according to general procedure C using diethyl 2-(4-methoxybenzoyl)malonate **1e** (200 mg, 0.68 mmol, 1.0 equiv.) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (486 mg, 1.63 mmol, 2.4 equiv.). White solid (225 mg, 74% yield); R_f = 0.3 (30% EtOAc/hexanes); mp = 93−95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.74 – 7.65 (m, 2H), 7.47 – 7.27 (m, 5H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.17 (dd, *J* = 7.8, 1.0 Hz, 1H), 6.89 – 6.77 (m, 2H), 6.22 (s, 1H), 4.25 – 4.11 (m, 4H), 3.85 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 172.8, 166.9, 163.5, 139.4, 139.4, 137.7, 132.7, 131.8, 130.8, 130.5, 130.4, 130.2, 130.1, 129.6, 129.2, 127.0, 126.4, 113.5, 61.2, 61.0, 55.5, 51.2, 14.1; HRMS (ESI) calcd for $C_{27}H_{27}O_6$ $[M+H]^+$: 447.1802; found 447.1807.

Ethyl 2-(2-ethoxy-1-(2-(4-nitrobenzoyl)phenyl)-2-oxoethyl)benzoate (3f)



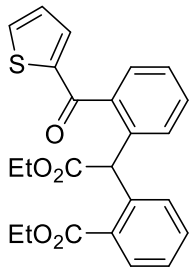
Prepared according to general procedure C using diethyl 2-(4-nitrobenzoyl)malonate **1f** (200 mg, 0.64 mmol, 1.0 equiv.) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (463 mg, 1.55 mmol, 2.4 equiv.). Colourless liquid (176 mg, 59% yield); R_f = 0.4 (30% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.19 (m, 2H), 7.98 – 7.84 (m, 3H), 7.53 – 7.42 (m, 2H), 7.39 – 7.31 (m, 3H), 7.28 – 7.23 (m, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 6.35 (s, 1H), 4.25 – 4.14 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 172.7, 166.5, 150.0, 142.9, 139.4, 139.0, 137.4, 132.1, 131.4, 131.2, 130.3, 130.2, 129.9, 129.8, 127.4, 126.4, 123.3, 61.4, 61.0, 51.2, 14.1; HRMS (ESI) calcd for $C_{26}H_{24}NO_7$ $[M+H]^+$: 462.1547; found 462.1550.

Ethyl 2-(2-ethoxy-1-(2-(furan-2-carbonyl)phenyl)-2-oxoethyl)benzoate (3g)



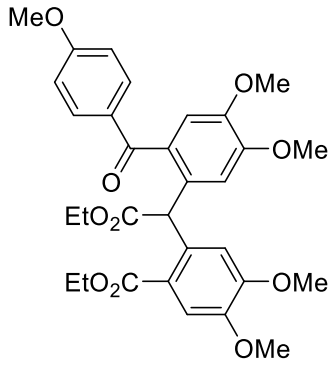
Prepared according to general procedure C using diethyl 2-(furan-2-carbonyl)malonate **1g** (300 mg, 1.18 mmol, 1.0 equiv.) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (844 mg, 2.83 mmol, 2.4 equiv.). Light orange solid (273 mg, 57% yield); R_f = 0.4 (20% EtOAc/hexanes); mp = 90−92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.48 – 7.33 (m, 3H), 7.32 – 7.27 (m, 1H), 7.23 – 7.13 (m, 2H), 6.98 (d, *J* = 3.5 Hz, 1H), 6.52 – 6.49 (m, 1H), 6.33 (s, 1H), 4.25 – 4.15 (m, 4H), 1.26 – 1.18 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.1, 172.8, 166.9, 152.5, 147.4, 139.4, 138.2, 137.6, 131.8, 130.9, 130.9, 130.3, 130.2, 129.9, 129.2, 127.1, 126.6, 121.3, 112.2, 61.2, 61.0, 51.1, 14.1; HRMS (ESI) calcd for $C_{24}H_{23}O_6$ $[M+H]^+$: 407.1489; found 407.1493.

Ethyl 2-(2-ethoxy-2-oxo-1-(2-(thiophene-2-carbonyl)phenyl)ethyl)benzoate (3h)



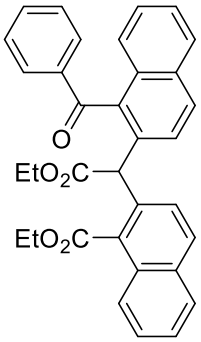
Prepared according to general procedure C using compound diethyl 2-(thiophene-2-carbonyl)malonate **1h** (200 mg, 0.74 mmol, 1.0 equiv.) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (529 mg, 1.78 mmol, 2.4 equiv.). White solid (213 mg, 68% yield); R_f = 0.5 (20% EtOAc/hexanes); mp = 61−63 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 4.6 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.42 – 7.35 (m, 3H), 7.29 – 7.23 (m, 2H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.06 – 7.02 (m, 1H), 6.32 (s, 1H), 4.26 – 4.12 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.5, 172.7, 167.0, 144.5, 139.3, 138.7, 137.8, 135.7, 134.7, 131.8, 130.8, 130.6, 130.5, 130.3, 129.8, 129.0, 127.8, 127.1, 126.5, 61.2, 61.0, 51.1, 14.1, 14.1; HRMS (ESI) calcd for $C_{24}H_{23}O_5S$ $[M+H]^+$: 423.1261; found 423.1269.

Ethyl 2-(1-(4,5-dimethoxy-2-(4-methoxybenzoyl)phenyl)-2-ethoxy-2-oxoethyl)-4,5-dimethoxybenzoate (3i)



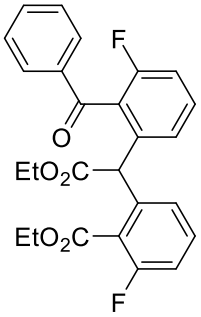
Prepared according to general procedure C using diethyl 2-(4-methoxybenzoyl)malonate **1e** (120 mg, 0.41 mmol, 1.0 equiv.) and 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2b** (350 mg, 0.98 mmol, 2.4 equiv.). Light brown liquid (139 mg, 60% yield); R_f = 0.2 (30% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 2H), 7.46 (s, 1H), 6.92 (s, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.79 (s, 1H), 6.71 (s, 1H), 6.20 (s, 1H), 4.21 – 4.11 (m, 4H), 3.89 (s, 3H), 3.87 (s, 3H), 3.82 (s, 6H), 3.77 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.8, 173.3, 166.4, 163.4, 151.6, 150.3, 147.2, 146.9, 134.0, 132.6, 131.8, 131.3, 130.8, 129.7, 122.1, 114.2, 113.6, 113.4, 113.0, 112.9, 112.5, 61.1, 60.8, 56.1, 56.0, 55.9, 55.5, 50.7, 14.2; HRMS (ESI) calcd for $C_{31}H_{35}O_{10}$ $[M+H]^+$: 567.2225; found 567.2237.

Ethyl 2-(1-(1-benzoylnaphthalen-2-yl)-2-ethoxy-2-oxoethyl)-1-naphthoate (3j)



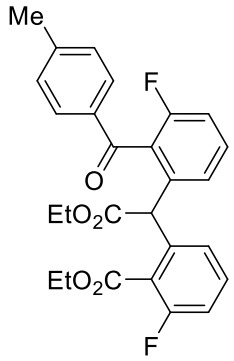
Prepared according to general procedure C using diethyl 2-benzoylmalonate **1a** (100 mg, 0.38 mmol, 1.0 equiv.) and 1-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate **2c** (316 mg, 0.91 mmol, 2.4 equiv.). White solid (117 mg, 60% yield); R_f = 0.3 (20% EtOAc/hexanes); mp = 170−172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.6 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.77 (bs, 5H), 7.55 (bs, 2H), 7.49 – 7.34 (m, 8H), 5.57 (s, 1H), 4.31 – 4.27 (m, 2H), 4.05 (bs, 2H), 1.10 (bs, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 171.7, 168.1, 137.5, 133.6, 132.8, 132.4, 132.3, 131.2, 130.8, 130.1, 130.0, 129.5, 128.3, 128.1, 127.9, 127.1, 127.0, 126.5, 126.4, 126.1, 125.7, 125.3, 61.6, 61.5, 51.8, 14.0; HRMS (ESI) calcd for $C_{34}H_{29}O_5$ $[M+H]^+$: 517.2010; found 517.2027.

Ethyl 2-(1-(2-benzoyl-3-fluorophenyl)-2-ethoxy-2-oxoethyl)-6-fluorobenzoate (3k)



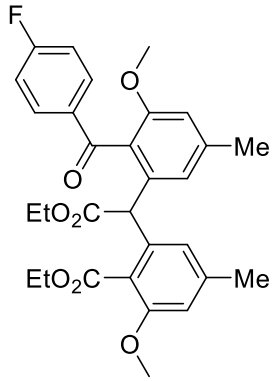
Prepared according to general procedure C using diethyl 2-benzoylmalonate **1a** (150 mg, 0.57 mmol, 1.0 equiv.) and 3-fluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2d** (358 mg, 1.14 mmol, 2.0 equiv.). Light yellow liquid (21 mg, 8% yield); R_f = 0.4 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.41 – 7.37 (m, 2H), 7.33 – 7.28 (m, 1H), 7.13 – 7.05 (m, 2H), 7.01 – 6.93 (m, 2H), 5.50 (s, 1H), 4.26 – 4.17 (m, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 171.2, 164.5, 160.2 (d, J_{C-F} = 254 Hz), 159.6 (d, J_{C-F} = 249 Hz), 138.4, 137.8, 136.9, 133.8, 131.4 (d, J_{C-F} = 9 Hz), 131.2 (d, J_{C-F} = 9 Hz), 129.6, 128.4, 127.5 (d, J_{C-F} = 18 Hz), 125.5, 125.1, 121.9 (d, J_{C-F} = 16 Hz), 115.4 (d, J_{C-F} = 22 Hz), 115.0 (d, J_{C-F} = 22 Hz), 61.8, 61.7, 50.5, 13.9; HRMS (ESI) calcd for $C_{26}H_{23}F_2O_5$ $[M+H]^+$: 453.1508; found 453.1522.

Ethyl 2-(2-ethoxy-1-(3-fluoro-2-(4-methylbenzoyl)phenyl)-2-oxoethyl)-6-fluorobenzoate (3l)



Prepared according to general procedure C using diethyl 2-(4-methylbenzoyl)malonate **1d** (100 mg, 0.36 mmol, 1.0 equiv.) and 3-fluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2d** (227 mg, 0.72 mmol, 2.0 equiv.). Light cream solid (10 mg, 6% yield); R_f = 0.2 (15% EtOAc/hexanes); mp = 127−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.45 – 7.40 (m, 1H), 7.34 – 7.28 (m, 1H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.14 – 7.04 (m, 2H), 7.01 – 6.91 (m, 2H), 5.49 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.1, 171.2, 164.5, 160.2 (d, J_{C-F} = 254 Hz), 159.5 (d, J_{C-F} = 248 Hz), 144.9, 138.2, 137.9, 134.5, 131.4 (d, J_{C-F} = 9 Hz), 131.0 (d, J_{C-F} = 8 Hz), 129.8, 129.1, 127.8 (d, J_{C-F} = 18 Hz), 125.5, 125.0, 121.8 (d, J_{C-F} = 17 Hz), 115.2 (d, J_{C-F} = 22 Hz), 115.0 (d, J_{C-F} = 21 Hz), 61.8, 61.6, 50.5, 21.8, 13.9; HRMS (ESI) calcd for $C_{27}H_{25}F_2O_5$ $[M+H]^+$: 467.1665; found 467.1684.

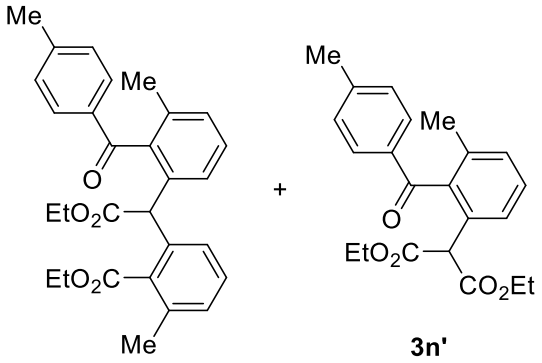
Ethyl 2-(2-ethoxy-1-(2-(4-fluorobenzoyl)-3-methoxy-5-methylphenyl)-2-oxoethyl)-6-methoxy-4-methylbenzoate (3m)



Prepared according to general procedure C using diethyl 2-(4-fluorobenzoyl)malonate **1b** (80 mg, 0.28 mmol, 1.0 equiv.) and 2-methoxy-4-methyl-6-(trimethylsilyl)phenyl trifluoromethane sulfonate **2e** (193 mg, 0.57 mmol, 2.0 equiv.). Yellow liquid (11 mg, 7% yield); R_f = 0.4 (30% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 2H), 7.00 – 6.92 (m, 2H), 6.71 (s, 2H), 6.58 (s, 1H), 6.53 (s, 1H), 5.10 (s, 1H), 4.22 – 4.07 (m, 2H), 4.04 (m, *J* = 7.1, 2.2 Hz, 2H),

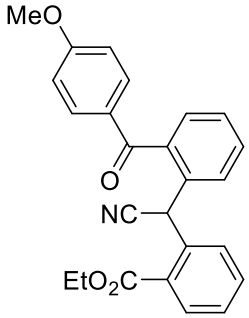
3.71 (s, 3H), 3.63 (s, 3H), 2.37 (s, 3H), 2.26 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2, 171.8, 167.2, 166.8, 165.6 (d, J_{C-F} = 252 Hz), 156.9, 156.7, 140.7, 140.6, 136.6, 135.6, 134.0, 132.2 (d, J_{C-F} = 9 Hz), 126.0, 122.4, 122.1, 121.4, 114.9 (d, J_{C-F} = 21 Hz), 111.3, 111.0, 61.3, 61.1, 55.9, 55.7, 50.6, 22.1, 22.0, 13.9, 13.9; HRMS (ESI) calcd for $C_{30}H_{31}FO_7$ $[M+Na]^+$: 545.1946; found 545.1945.

Ethyl 2-(2-ethoxy-1-(3-methyl-2-(4-methylbenzoyl)phenyl)-2-oxoethyl)-6-methyl benzoate (3n) and Diethyl 2-(2-methyl-6-(4-methylbenzoyl)phenyl)malonate (3n′)



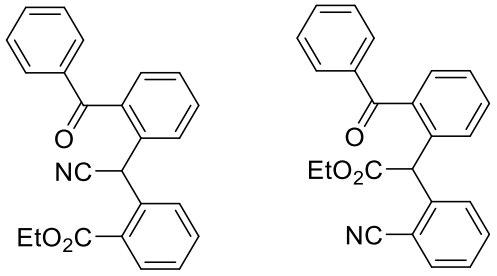
Prepared according to general procedure C using 2-(4-methylbenzoyl)malonate **1d** (100 mg, 0.35 mmol, 1.0 equiv.), 3-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2f** (268 mg, 0.86 mmol, 2.4 equiv.) and obtained **3n′** as a major product along with compound **3n** (~10%). Colorless liquid (79 mg, 61% yield); R_f = 0.4 (20% EtOAc/hexanes); For major compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.7 Hz, 2H), 7.44 (d, J = 7.8 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.25 – 7.21 (m, 3H), 4.16 – 4.06 (m, 4H), 1.14 (t, J = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 167.9, 145.1, 140.2, 134.7, 134.6, 133.2, 130.0, 129.9, 129.8, 129.5, 129.2, 129.1, 128.3, 128.1, 127.9, 126.9, 116.0, 61.8, 54.5, 21.8, 19.7, 13.9; HRMS (ESI) calcd for $C_{22}H_{25}O_5$ $[M+H]^+$: 369.1696; found 369.1690.

Ethyl 2-(cyano(2-(4-methoxybenzoyl)phenyl)methyl)benzoate (3o)



Prepared according to general procedure C using ethyl 2-cyano-3-(4-methoxyphenyl)-3-oxopropanoate **1i** (200 mg, 0.81 mmol, 1.0 equiv.) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (579 mg, 1.94 mmol, 2.4 equiv.). Light yellow solid (239 mg, 74% yield); R_f = 0.4 (15% EtOAc/hexanes); mp = 105−107 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.63 – 7.59 (m, 3H), 7.54 – 7.52 (m, 1H), 7.46 – 7.34 (m, 4H), 7.28 – 7.23 (m, 1H), 6.85 – 6.81 (m, 3H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 166.1, 163.7, 138.1, 136.6, 135.2, 132.6, 132.4, 131.2, 130.7, 130.4, 129.9, 129.8, 129.4, 129.3, 128.2, 127.4, 119.7, 113.4, 61.4, 55.5, 36.6, 14.1; HRMS (ESI) calcd for $C_{25}H_{22}NO_4$ $[M+H]^+$: 400.1543; found 400.1545.

Ethyl 2-((2-benzoylphenyl)(cyano)methyl)benzoate (3p) & Ethyl 2-(2-benzoylphenyl)-2-(2-cyanophenyl)acetate (3p′)



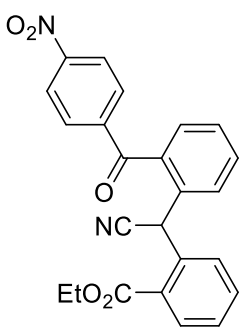
3p **3p'**

Prepared according to general procedure C using ethyl 2-cyano-3-oxo-3-phenylpropanoate **1j** (50 mg, 0.23 mmol, 1.0 equiv.) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (164 mg, 0.55 mmol, 2.4 equiv.).

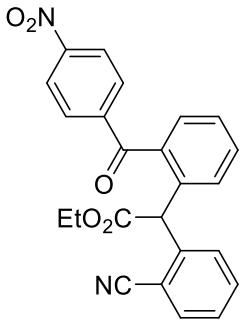
Data for compound 3p: Light yellow liquid (39 mg, 46% yield); R_f = 0.4 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 1H), 7.65 – 7.57 (m, 3H), 7.56 – 7.50 (m, 2H), 7.47 – 7.44 (m, 2H), 7.41 – 7.34 (m, 4H), 7.31 – 7.27 (m, 1H), 6.90 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 166.0, 137.5, 137.1, 136.6, 135.7, 133.1, 132.5, 131.3, 131.2, 130.4, 130.4, 130.2, 129.4, 129.2, 128.2, 128.1, 127.4, 119.7, 61.3, 36.6, 14.1; HRMS (ESI) calcd for $C_{24}H_{20}NO_3$ $[M+H]^+$: 370.1438; found 370.1440.

Data for compound 3p′: Light yellow liquid (20 mg, 24% yield); R_f = 0.3 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.63 – 7.51 (m, 3H), 7.51 – 7.40 (m, 4H), 7.39 – 7.32 (m, 3H), 7.20 (d, *J* = 7.8 Hz, 1H), 5.79 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 171.2, 142.0, 138.4, 137.5, 136.6, 133.4, 133.1, 132.7, 131.0, 130.5, 130.3, 130.0, 129.6, 128.3, 127.8, 127.0, 117.2, 113.6, 61.8, 52.6, 14.1; HRMS (ESI) calcd for $C_{24}H_{20}NO_3$ $[M+H]^+$: 370.1438; found 370.1451.

Ethyl 2-(cyano(2-(4-nitrobenzoyl)phenyl)methyl)benzoate (3q) & Ethyl 2-(2-cyanophenyl)-2-(2-(4-nitrobenzoyl)phenyl)acetate (3q′)



3q



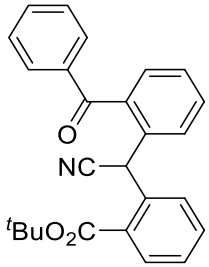
3q'

Prepared according to general procedure C using ethyl 2-cyano-3-(4-nitrophenyl)-3-oxopropanoate **1k** (200 mg, 0.76 mmol, 1.0 equiv.) and 2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** (546 mg, 1.83 mmol, 2.4 equiv.).

Data for compound 3q: White solid (199 mg, 63% yield); R_f = 0.5 (30% EtOAc/hexanes); mp = 180−182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.23 (m, 2H), 7.94 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.87 – 7.82 (m, 2H), 7.64 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.48 (d, *J* = 6.7 Hz, 1H), 7.43 – 7.34 (m, 3H), 6.87 (s, 1H), 4.26 – 4.11 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.4, 165.8, 150.1, 142.3, 136.7, 136.5, 136.4, 132.8, 132.2, 131.6, 131.2, 130.4, 129.7, 128.7, 128.5, 127.5, 123.4, 119.5, 61.4, 36.7, 14.1; HRMS (ESI) calcd for $C_{24}H_{19}N_2O_5$ $[M+H]^+$: 415.1288; found 415.1291.

Data for compound 3q′: Off white solid (28 mg, 9% yield); R_f = 0.4 (30% EtOAc/hexanes); mp = 127−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.7 Hz, 2H), 7.97 (d, *J* = 8.7 Hz, 2H), 7.66 – 7.59 (m, 2H), 7.55 – 7.47 (m, 1H), 7.44 – 7.38 (m, 4H), 7.14 (d, *J* = 7.8 Hz, 1H), 5.83 (s, 1H), 4.48 – 3.87 (m, 2H), 1.28 – 1.25 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0, 171.1, 150.2, 142.6, 141.9, 137.4, 137.0, 133.5, 132.9, 132.0, 131.3, 130.6, 130.4, 129.4, 128.0, 127.2, 123.5, 117.2, 113.6, 62.0, 52.5, 14.1; HRMS (ESI) calcd for $C_{24}H_{19}N_2O_5$ $[M+H]^+$: 415.1288; found 415.1279.

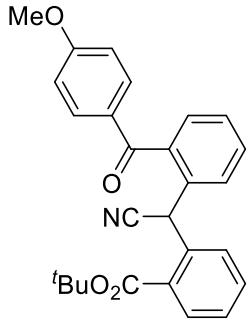
***tert*-Butyl 2-((2-benzoylphenyl)(cyano)methyl)benzoate (3r)**



Prepared according to general procedure C using 1-(*tert*-butyl) 3-ethyl 2-benzoylmalonate **1l** (200 mg, 0.81 mmol, 1.0 equiv.) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (583 mg, 1.95 mmol, 2.4 equiv.). White solid (204 mg, 63% yield); R_f = 0.6 (20% EtOAc/hexanes); mp =

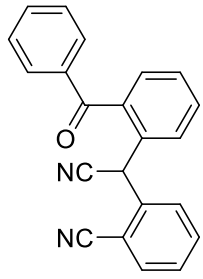
120−122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.73 (m, 1H), 7.66 – 7.60 (m, 3H), 7.56 – 7.48 (m, 2H), 7.41 – 7.31 (m, 6H), 7.25 – 7.20 (m, 1H), 6.79 (s, 1H), 1.50 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 165.4, 137.7, 136.9, 136.1, 135.8, 133.1, 132.0, 131.4, 131.2, 131.0, 130.6, 130.3, 130.2, 129.4, 129.0, 128.1, 127.3, 119.8, 82.2, 36.7, 28.1; HRMS (ESI) calcd for $C_{26}H_{24}NO_3$ $[M+H]^+$: 398.1751; found 398.1744.

***tert*-Butyl 2-(cyano(2-(4-methoxybenzoyl)phenyl)methyl)benzoate (3s)**



Prepared according to general procedure C using 1-(*tert*-butyl) 3-ethyl 2-(4-methoxybenzoyl)malonate **1m** (200 mg, 0.73 mmol, 1.0 equiv.) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (520 mg, 1.75 mmol, 2.4 equiv.). Light yellow liquid (174 mg, 56% yield); R_f = 0.4 (15% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.60 – 7.56 (m, 2H), 7.55 – 7.51 (m, 1H), 7.43 – 7.29 (m, 4H), 7.23 – 7.16 (m, 1H), 6.83 – 6.78 (m, 2H), 6.74 (s, 1H), 3.85 (s, 3H), 1.52 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 165.4, 163.6, 138.2, 136.01, 135.3, 132.7, 131.9, 131.3, 131.0, 130.6, 130.4, 129.6, 129.3, 128.0, 127.3, 119.8, 113.5, 113.3, 82.3, 55.5, 36.7, 28.1; HRMS (ESI) calcd for $C_{27}H_{26}NO_4$ $[M+H]^+$: 428.1856; found 428.1859.

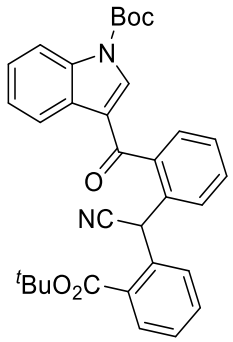
2-((2-benzoylphenyl)(cyano)methyl)benzonitrile (3t)



Prepared according to general procedure C using 2-benzoylmalononitrile **1n** (100 mg, 0.59 mmol, 1.0 equiv.) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (423 mg, 1.42 mmol, 2.4 equiv.). Pale yellow liquid (99 mg, 52% yield); R_f = 0.2 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 2H), 7.63 – 7.55 (m, 6H), 7.50 – 7.43 (m, 3H), 7.38 – 7.35 (m, 2H), 6.18 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 138.6, 137.2, 136.9, 135.2, 133.8, 133.4,

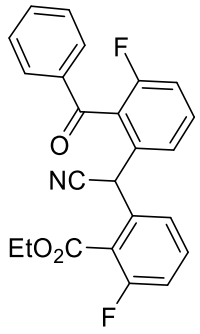
133.2, 131.8, 131.2, 130.3, 129.9, 129.7, 129.2, 128.9, 128.3, 128.2, 125.3, 117.8, 116.3, 112.7, 38.1; HRMS (ESI) calcd for $C_{22}H_{15}N_2O$ $[M+H]^+$: 323.1178; found 323.1174.

tert-Butyl 3-(2-((2-(_tert_-butoxycarbonyl)phenyl)(cyano)methyl)benzoyl)-1_H_-indole-1-carboxylate (3u)

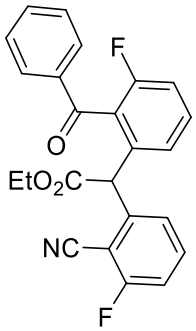


Prepared according to general procedure C using **1o** (100 mg, 0.26 mmol, 1.0 equiv.) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (186 mg, 0.62 mmol, 2.4 equiv.). White solid (90 mg, 65% yield); R_f = 0.4 (20% EtOAc/hexanes); mp = 88−90 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 7.2, 1.3 Hz, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.60 (s, 1H), 7.57 – 7.52 (m, 2H), 7.44 – 7.41 (m, 1H), 7.40 – 7.33 (m, 4H), 7.18 – 7.14 (m, 1H), 6.83 (s, 1H), 1.67 (s, 9H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 165.3, 149.0, 139.1, 136.2, 135.3, 135.0, 135.0, 131.8, 131.3, 131.0, 130.8, 130.4, 129.3, 129.2, 127.8, 127.7, 127.6, 125.6, 124.4, 122.9, 120.0, 119.8, 114.8, 85.5, 82.2, 36.6, 28.1, 28.0; HRMS (ESI) calcd for $C_{33}H_{33}N_2O_5$ $[M+H]^+$: 537.2384; found 537.2378.

Ethyl 2-((2-benzoyl-3-fluorophenyl)(cyano)methyl)-6-fluorobenzoate (3v) and Ethyl 2-(2-benzoyl-3-fluorophenyl)-2-(2-cyano-3-fluorophenyl)acetate (3v′)



3v



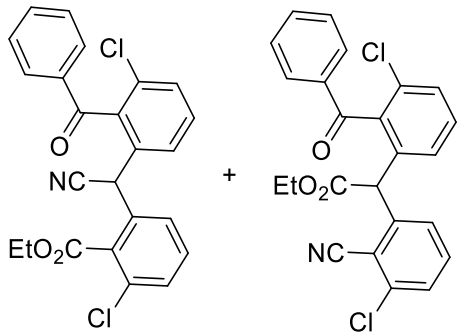
3v'

Prepared according to general procedure C using 2-cyano-3-oxo-3-phenylpropanoate **1j** (100 mg, 0.46 mmol, 1.0 equiv.) and 3-fluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2d** (349 mg, 1.10 mmol, 2.4 equiv.) and obtained trace amount of isomer in major compound **3v**.

Data for compound 3v: Pale yellow liquid (78 mg, 42% yield); R_f = 0.2 (20% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.43 (m, 2H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.19 – 7.14 (m, 1H), 7.11 (t, *J* = 8.2 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.81 – 6.76 (m, 1H), 5.94 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.0, 163.8, 160.4 (d, J_{C-F} = 252 Hz), 159.7 (d, J_{C-F} = 248 Hz), 136.3, 135.4, 134.9, 134.1, 132.2 (d, J_{C-F} = 10 Hz), 131.8 (d, J_{C-F} = 9 Hz), 129.4, 128.3, 126.7 (d, J_{C-F} = 18 Hz), 126.0, 125.2, 121.2 (d, J_{C-F} = 10 Hz), 117.9, 116.6 (d, J_{C-F} = 22 Hz), 116.3 (d, J_{C-F} = 22 Hz), 62.2, 36.6, 14.0; HRMS (ESI) calcd for $C_{24}H_{18}NO_3F_2$ $[M+H]^+$: 406.1249; found 406.1239.

Data for compound 3v′: Pale yellow liquid (57 mg, 30% yield); R_f = 0.3 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.62 – 7.59 (m, 1H), 7.50 – 7.37 (m, 5H), 7.33 – 7.30 (m, 1H), 7.22 – 7.15 (m, 1H), 7.13 – 7.06 (m, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 4.27 – 4.19 (m, 1H), 4.14 – 4.06 (m, 1H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.7, 166.4, 162.8 (d, J_{C-F} = 248 Hz), 160.2 (d, J_{C-F} = 250 Hz), 138.1, 137.7, 136.2 (d, J_{C-F} = 8 Hz), 133.7, 131.8 (d, J_{C-F} = 10 Hz), 130.7 (d, J_{C-F} = 8 Hz), 129.4, 128.5, 126.5 (d, J_{C-F} = 10 Hz),, 124.2, 117.3, 117.2 (d, J_{C-F} = 23 Hz), 116.6 (d, J_{C-F} = 22 Hz), 116.0 (d, J_{C-F} = 24 Hz), 64.0, 56.7, 13.7; HRMS (ESI) calcd for $C_{24}H_{18}NO_3F_2$ $[M+H]^+$: 406.1249; found 406.1259.

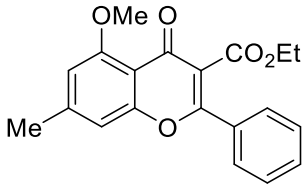
Ethyl 2-((2-benzoyl-3-chlorophenyl)(cyano)methyl)-6-chlorobenzoate (3w) and ethyl 2-(2-benzoyl-3-chlorophenyl)-2-(3-chloro-2-cyanophenyl)acetate (3w′)



3t:3t' (1:0.9)

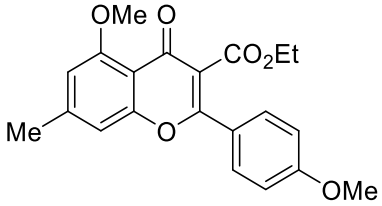
Prepared according to general procedure C using ethyl 2-cyano-3-oxo-3-phenylpropanoate **1j** (100 mg, 0.46 mmol, 1.0 equiv.), 2-chloro-6-(trimethylsilyl)phenyl trifluoromethanesulfonate **2g** (306 mg, 0.92 mmol, 2.0 equiv.). Colorless liquid (131 mg, 65% yield as an inseparable mixture of **3t** and **3t′**); R_f = 0.4 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.3 Hz, 3H), 7.73 – 7.58 (m, 5H), 7.57 – 7.44 (m, 10H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.14 (bs, 3H), 5.53 (s, 1H), 4.80 (s, 1H), 4.30 – 4.24 (m, 2H), 4.14 – 4.07 (m, 1H), 4.04 – 3.96 (m, 1H), 1.30 – 1.26 (m, 3H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.5, 194.3, 165.1, 164.0, 138.2, 138.0, 136.2, 135.5, 134.6, 134.1, 133.7, 133.2, 132.7, 132.6, 132.2, 132.1, 131.3, 130.7, 130.7, 130.2, 130.0, 129.8, 129.7, 129.0, 128.4, 127.9, 127.7, 117.3, 115.0, 63.6, 62.3, 40.3, 37.5, 13.8, 13.7; HRMS (ESI) calcd for $C_{24}H_{18}Cl_2NO_3$ $[M+H]^+$: 438.0658; found 438.0657.

Ethyl 5-methoxy-7-methyl-4-oxo-2-phenyl-4*H*-chromene-3-carboxylate (4a)



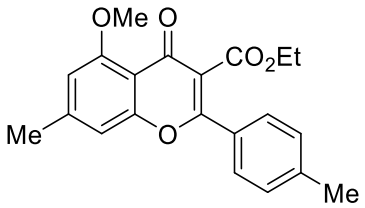
Prepared according to general procedure C using diethyl 2-benzoylmalonate **1a** (120 mg, 0.45 mmol, 1.0 equiv.), 2-methoxy-4-methyl-6-(trimethylsilyl)phenyl trifluoromethane sulfonate **2e** (310 mg, 0.91 mmol, 2.0 equiv.). Pale yellow liquid (69 mg, 45% yield); R_f = 0.1 (30% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.63 (m, 2H), 7.57 – 7.37 (m, 3H), 6.88 (d, *J* = 0.5 Hz, 1H), 6.64 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 3H), 2.45 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 165.3, 160.1, 159.8, 157.8, 145.9, 131.7, 131.3, 128.7, 127.9, 119.7, 111.6, 110.0, 108.2, 61.8, 56.4, 22.4, 14.0; HRMS (ESI) calcd for $C_{20}H_{19}O_5$ $[M+H]^+$: 339.1227; found 339.1229.

Ethyl 5-methoxy-2-(4-methoxyphenyl)-7-methyl-4-oxo-4*H*-chromene-3-carboxylate (4b)



Prepared according to general procedure C using diethyl 2-(4-methoxybenzoyl)malonate **1e** (120 mg, 0.41 mmol, 1.0 equiv.), 2-methoxy-4-methyl-6-(trimethylsilyl)phenyl trifluoromethane sulfonate **2e** (279 mg, 0.82 mmol, 2.0 equiv.). Cream color solid (75 mg, 50% yield); R_f = 0.1 (30% EtOAc/hexanes); mp = 73−75 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 2H), 7.01 – 6.94 (m, 2H), 6.87 (s, 1H), 6.62 (s, 1H), 4.33 – 4.28 (m, 2H), 3.96 (s, 3H), 3.87 (s, 3H), 2.44 (s, 3H), 1.34 – 1.21 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 165.8, 162.0, 159.8, 159.7, 157.8, 145.7, 129.7, 123.9, 118.7, 114.1, 111.5, 110.0, 108.0, 61.8, 56.4, 55.5, 22.4, 14.1; HRMS (ESI) calcd for $C_{21}H_{21}O_6$ $[M+H]^+$: 369.1333; found 369.1331.

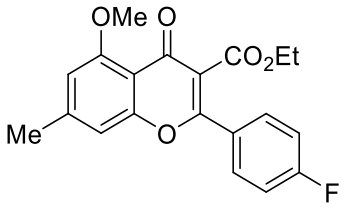
Ethyl 5-methoxy-7-methyl-4-oxo-2-(*p*-tolyl)-4*H*-chromene-3-carboxylate (4c)



Prepared according to general procedure C using diethyl 2-(4-methylbenzoyl)malonate **1d** (80 mg, 0.29 mmol, 1.0 equiv.), 2-methoxy-4-methyl-6-(trimethylsilyl)phenyl trifluoromethanesulfonate

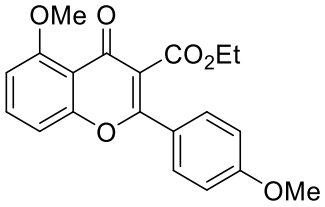
2e (195 mg, 0.57 mmol, 2.0 equiv.). Light yellow solid (56 mg, 55% yield); R_f = 0.1 (30% EtOAc/hexanes); mp = 144−146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 0.4 Hz, 1H), 6.63 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 3H), 2.45 (s, 3H), 2.42 (s, 3H), 1.27 – 1.24 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 165.6, 160.2, 159.8, 157.8, 145.8, 141.9, 129.4, 128.8, 127.9, 119.3, 111.6, 110.0, 108.1, 61.8, 56.4, 22.4, 21.6, 14.0; HRMS (ESI) calcd for $C_{21}H_{21}O_5$ $[M+H]^+$: 353.1384; found 353.1381.

Ethyl 2-(4-fluorophenyl)-5-methoxy-7-methyl-4-oxo-4*H*-chromene-3-carboxylate (4d)



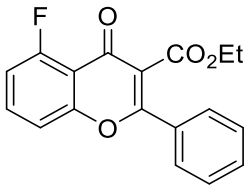
Prepared according to general procedure C using diethyl 2-(4-fluorobenzoyl)malonate **1b** (80 mg, 0.28 mmol, 1.0 equiv.), 2-methoxy-4-methyl-6-(trimethylsilyl)phenyl trifluoromethane sulfonate **2e** (193 mg, 0.57 mmol, 2.0 equiv.). Light yellow liquid (54 mg, 53% yield); R_f = 0.1 (30% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 2H), 7.21 – 7.13 (m, 2H), 6.88 (dd, *J* = 1.3, 0.7 Hz, 1H), 6.64 (d, *J* = 0.7 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 3H), 2.45 (s, 3H), 1.27 – 1.24 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 165.3, 164.4 (d, J_{C-F} = 254 Hz), 159.8, 159.0, 157.8, 146.1, 132.8 (d, J_{C-F} = 9 Hz), 130.3 (d, J_{C-F} = 9 Hz), 127.9, 119.6, 116.0 (d, J_{C-F} = 22 Hz), 115.6, 111.5, 110.0, 108.2, 61.9, 56.4, 22.4, 14.0; HRMS (ESI) calcd for $C_{20}H_{18}FO_5$ $[M+H]^+$: 357.1133; found 357.1132.

Ethyl 5-methoxy-2-(4-methoxyphenyl)-4-oxo-4*H*-chromene-3-carboxylate (4e)



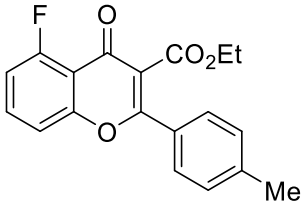
Prepared according to general procedure C using diethyl 2-(4-methoxybenzoyl)malonate **1e** (200 mg, 0.68 mmol, 1.0 equiv.), 2-methoxy-6-(trimethylsilyl)phenyl trifluoromethanesulfonate **2h** (446 mg, 1.36 mmol, 2.0 equiv.). Cream color solid (125 mg, 52% yield); R_f = 0.1 (30% EtOAc/hexanes); mp = 128−130 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 2H), 7.57 (t, *J* = 8.4 Hz, 1H), 7.06 (dd, *J* = 8.4, 0.7 Hz, 1H), 7.02 – 6.95 (m, 2H), 6.82 (d, *J* = 8.1 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 3H), 3.88 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 165.6, 162.1, 160.1, 157.8, 134.2, 129.7, 123.8, 118.8, 114.2, 113.7, 109.9, 106.7, 61.8, 56.5, 55.5, 14.0; HRMS (ESI) calcd for $C_{20}H_{19}O_6$ $[M+H]^+$: 355.1176; found 355.1175.

Ethyl 5-fluoro-4-oxo-2-phenyl-4*H*-chromene-3-carboxylate (4f)



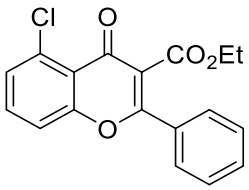
Prepared according to general procedure C using diethyl 2-benzoylmalonate **1a** (150 mg, 0.57 mmol, 1.0 equiv.), 3-fluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2d** (358 mg, 1.14 mmol, 2.0 equiv.), Light yellow liquid (101 mg, 57% yield); R_f = 0.2 (20% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.74 (m, 2H), 7.67 – 7.62 (m, 1H), 7.59 – 7.54 (m, 1H), 7.54 – 7.48 (m, 2H), 7.34 – 7.32 (m, 1H), 7.11 – 7.07 (m, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3, 164.6, 162.1, 160.8 (d, J_{C-F} = 265 Hz), 156.8, 134.3 (d, J_{C-F} = 10 Hz), 131.8, 131.4, 128.8, 128.1, 119.4, 114.0 (d, J_{C-F} = 4 Hz), 113.6 (d, J_{C-F} = 10 Hz), 112.6 (d, J_{C-F} = 20 Hz), 62.1, 13.9; HRMS (ESI) calcd for $C_{18}H_{14}FO_4$ $[M+H]^+$: 313.0871; found 313.0871.

Ethyl 5-fluoro-4-oxo-2-(*p*-tolyl)-4*H*-chromene-3-carboxylate (4g)



Prepared according to general procedure C using diethyl 2-(4-methylbenzoyl)malonate **1d** (100 mg, 0.36 mmol, 1.0 equiv.) and 3-fluoro-2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2d** (227 mg, 0.72 mmol, 2.0 equiv.). Light yellow liquid (63 mg, 54% yield); R_f = 0.2 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 3H), 7.34 – 7.29 (m, 3H), 7.11 – 7.06 (m, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 1.30 – 1.20 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 164.9, 162.1, 160.6 (d, J_{C-F} = 264 Hz), 156.8, 142.5, 134.2 (d, J_{C-F} = 12 Hz), 130.9, 129.6, 128.5, 128.0, 114.0, 112.5 (d, J_{C-F} = 20 Hz), 62.0, 21.6, 14.0; HRMS (ESI) calcd for $C_{19}H_{16}FO_4$ $[M+H]^+$: 327.1027; found 327.1024.

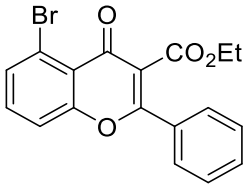
Ethyl 5-chloro-4-oxo-2-phenyl-4*H*-chromene-3-carboxylate (4h)



Prepared according to general procedure C using diethyl 2-benzoylmalonate **1a** (100 mg, 0.38 mmol, 1.0 equiv.), 2-chloro-6-(trimethylsilyl)phenyl trifluoromethanesulfonate **2g** (251 mg, 0.76

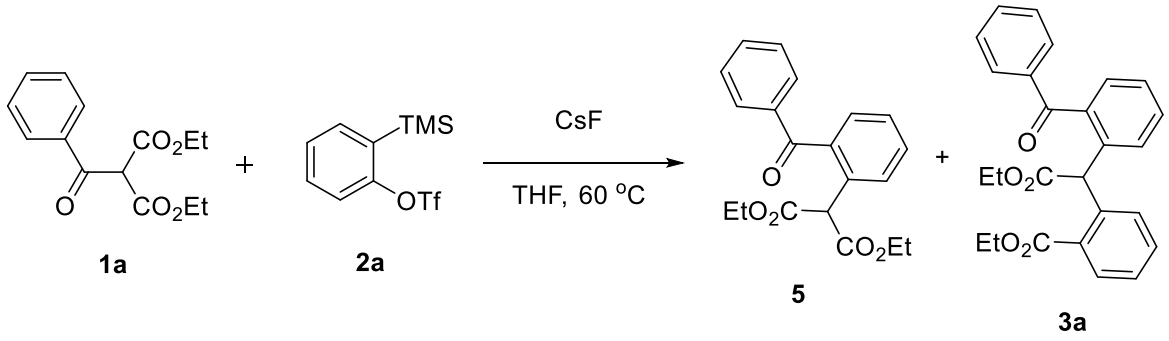
mmol, 2.0 equiv.). Colourless liquid (85 mg, 68% yield); R_f = 0.3 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.74 (m, 2H), 7.59 – 7.48 (m, 4H), 7.46 – 7.40 (m, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 164.8, 161.2, 157.4, 134.1, 133.4, 131.8, 131.3, 128.8, 128.6, 128.0, 120.2, 119.6, 117.3, 62.1, 13.9; HRMS (ESI) calcd for $C_{18}H_{14}ClO_4$ $[M+H]^+$: 329.0575; found 329.0571.

Ethyl 5-bromo-4-oxo-2-phenyl-4*H*-chromene-3-carboxylate (4i)



Prepared according to general procedure C using diethyl 2-benzoylmalonate **1a** (100 mg, 0.38 mmol, 1.0 equiv.), 3-bromo-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2i** (285 mg, 0.76 mmol, 2.0 equiv.), Pale yellow liquid (92 mg, 65% yield); R_f = 0.4 (20% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.74 (m, 2H), 7.68 (dd, *J* = 6.2, 2.8 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.53 – 7.47 (m, 4H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 164.8, 161.2, 157.3, 133.8, 132.4, 131.8, 131.3, 128.9, 128.0, 120.9, 119.2, 118.0, 62.1, 13.9; HRMS (ESI) calcd for $C_{18}H_{14}BrO_4$ $[M+H]^+$: 373.0070; found 373.0065.

Control Experiment:



A screw-cap vial equipped with magnetic stir bar was charged with diethyl 2-benzoylmalonate **1a** (50 mg, 0.19 mmol, 1.0 equiv.), aryne precursor **2a** (67 mg, 0.22 mmol, 1.2 equiv.), CsF (57 mg, 0.38 mmol, 2.0 equiv.) in dry THF (2 mL) under nitrogen atmosphere. The reaction mixture was stirred at 60 ºC for 16 h. Then the reaction was cooled to room temperature, diluted with H_2O (10 mL) and extracted with EtOAc (2 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The LCMS showed the 3.5:1 ratio of inseparable mixture of product **5** and **3a**.

III. X-ray crystallographic data

Compounds **3q** & **4b** were dissolved in a mixture of chloroform-methanol solvents and crystallized in a 5 mL glass vial at room temperature. Appropriate single crystal was selected under microscope and mounted with Paratone Oil on a Cryoloop. X-ray data was collected at room temperature on Bruker D8 QUEST Photon-III-C7diffractometer using monochromatic MoKα radiation (λ = 0.71073Å). Integration and scaling of intensity data were performed by using SAINT.[3] Structure solution and refinements were performed by SHELXT 2018/2[4] and later followed by full-matrix least-square (LS) method embedded in SHELXL-2018/3.[4] Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined isotropically and accordingly generated at the calculated positions considering as riding models.

Crystal Data 3q. Crystal size: 0.32 × 0.15 × 0.12 mm^3, Refined formula: $C_{24}H_{18}N_2O_5$, Formula weight (Mr): 414.40, Crystal system: Triclinic, Space group: *P*-1, Z' = 1, Z = 2, 6140 unique reflections merged from recorded 23684 ones (2.5° < θ < 30.5°) were used for structural analysis (R_{int} = 0.073). Lattice parameters, R-factor on $F^2 > 2\sigma(F^2)$, weighted R-factor, and Goodness-of-fit parameter are follows: a = 8.1443(5) Å, b = 9.6794(6) Å, c = 13.0717(8) Å, α = 81.178(2) β = 89.732(3) γ = 83.318(2), V = 1011.27(11) $Å^3$, R = 0.0558, wR_2 = 0.1751, S = 1.00. Calculated density is 1.361 $g \cdot cm^{-3}$. Linear absorption coefficient (μ) is 0.097 mm^{-1}. Residual electron density (max/min) is 0.18/−0.17 $eÅ^{-3}$. CCDC number 2195956.

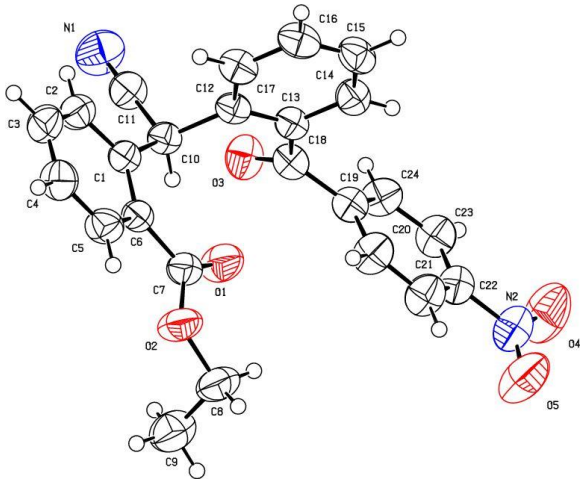


Figure 1: A view of compound **3q**, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.

Crystal Data 4b. Crystal size: 0.28 × 0.11 × 0.10 mm^3, Refined formula: $C_{21}H_{20}O_6$, Formula weight (Mr): 368.37, Crystal system: Monoclinic, Space group: *C*2/c, Z' = 1, Z = 8, 5565 unique reflections merged from recorded 32086 ones (2.5° < θ < 30.6°) were used for structural analysis (R_{int} = 0.046). Lattice parameters, R-factor on $F^2 > 2\sigma(F^2)$, weighted R-factor, and Goodness-of-fit parameter are follows: a = 24.577(3) Å, b = 8.2885(10) Å, c = 18.262(3) Å, α = 90 β = 101.819(7) γ = 90, V = 3641.2(9) $Å^3$, R = 0.0536, wR_2 = 0.2097, S = 1.00. Calculated density is 1.344 $g \cdot cm^{-}$

^{3}. Linear absorption coefficient (μ) is 0.099 mm^{-1}. Residual electron density (max/min) is 0.26/−0.24 $eÅ^{-3}$. CCDC number 2195957.

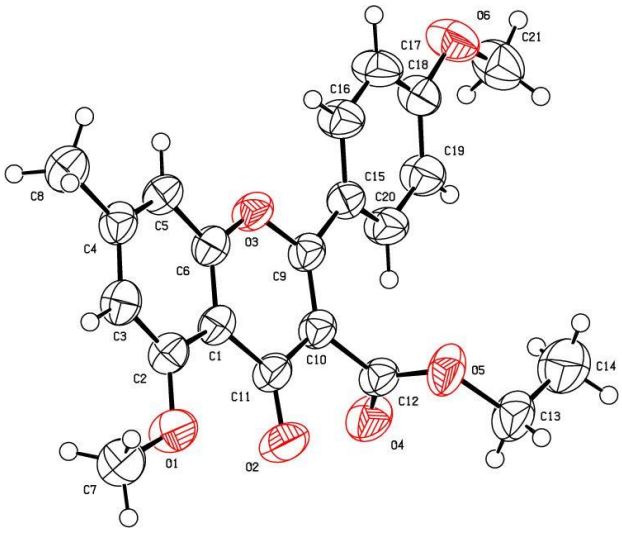


Figure 2: A view of compound **4b**, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.

References:

1. (a) M. T. Jensen, M. Juhl, D. U. Nielsen, M. F. Jacobsen, A. T. Lindhardt and T. Skrydstrup, *J. Org. Chem.* 2016, **81**, 1358; (b) W. Lu, Y. Li, C. Wang, D. Xue, J.-G. Chena and J. Xiao, *Org. Biomol. Chem.* 2014, **12**, 5243; (c) S. S. More, T. K. Mohan, Y. S. Kumar, U. K. S. Kumar and N. B. Patel, *Beilstein J. Org. Chem.* 2011**, 7**, 831; (d) J.-C. Jung, E. B. Watkins and M. A. Avery, *Heterocycles*, 2005, **65**, 77; (e) R. R. Poondra, P. M. Fischer and N. J. Turner, *J. Org. Chem.* 2004, **69**, 6920; (f) J.-C. Jung, E. B. Watkins and M. A. Avery, *Tetrahedron* 2002, **58**, 3639; (g) B. C. Kraybill, L. L. Elkin, J. D. Blethrow, D. O. Morgan and K. M. Shokat, *J. Am. Chem. Soc.*, 2002, **124**, 12118; (h) M. W. Rathke and P. J. Cowan, *J. Org. Chem.* 1985, **50**, 2622.

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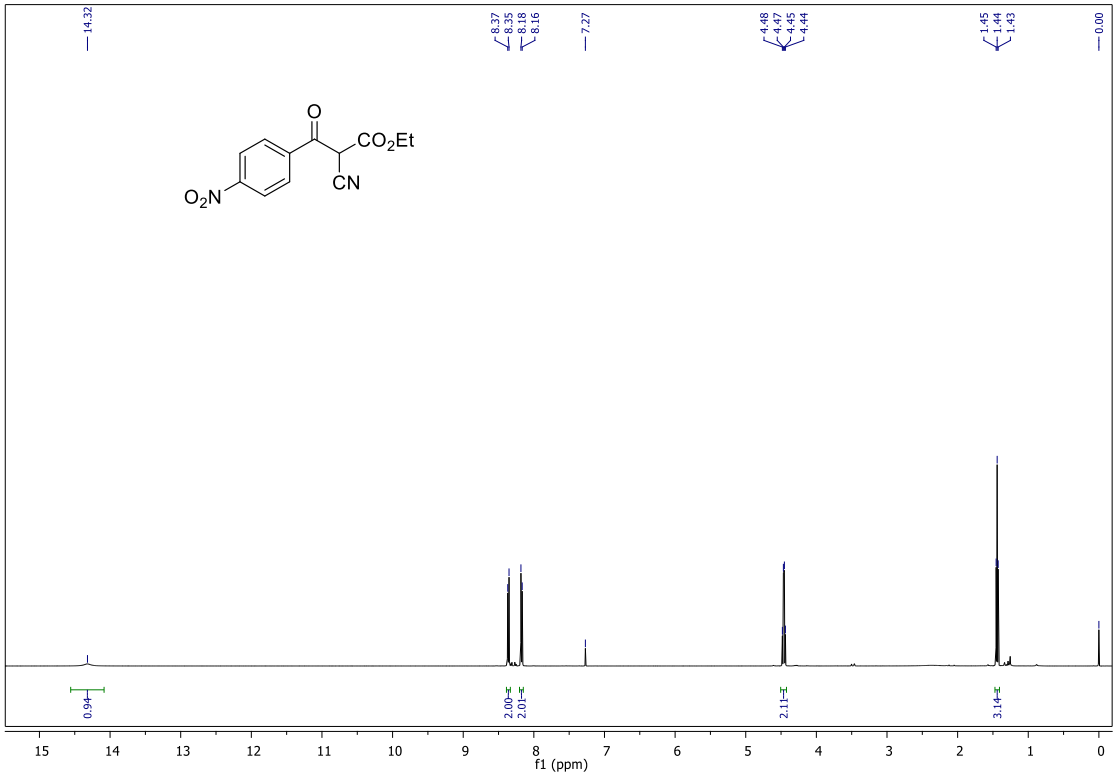
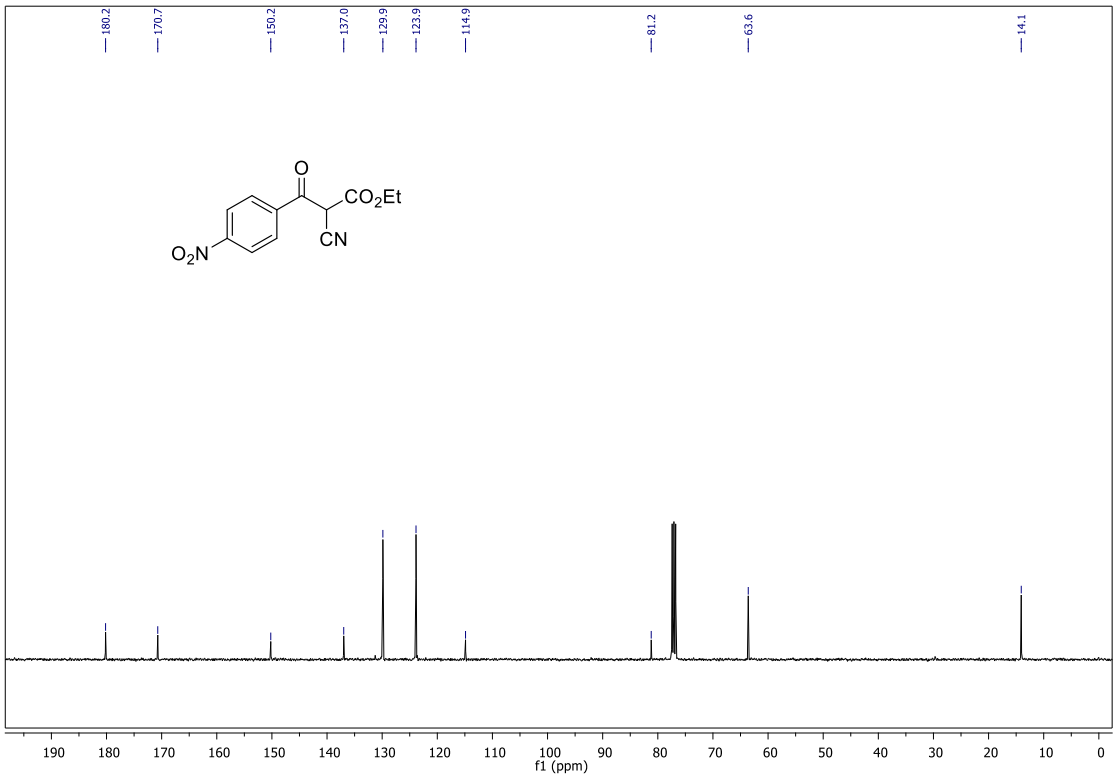
3. SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray System Inc., Madison, Wisconsin, USA, 2001.

4. G. M. Sheldrick, *Acta Cryst*. 2015, **C71**, 3.

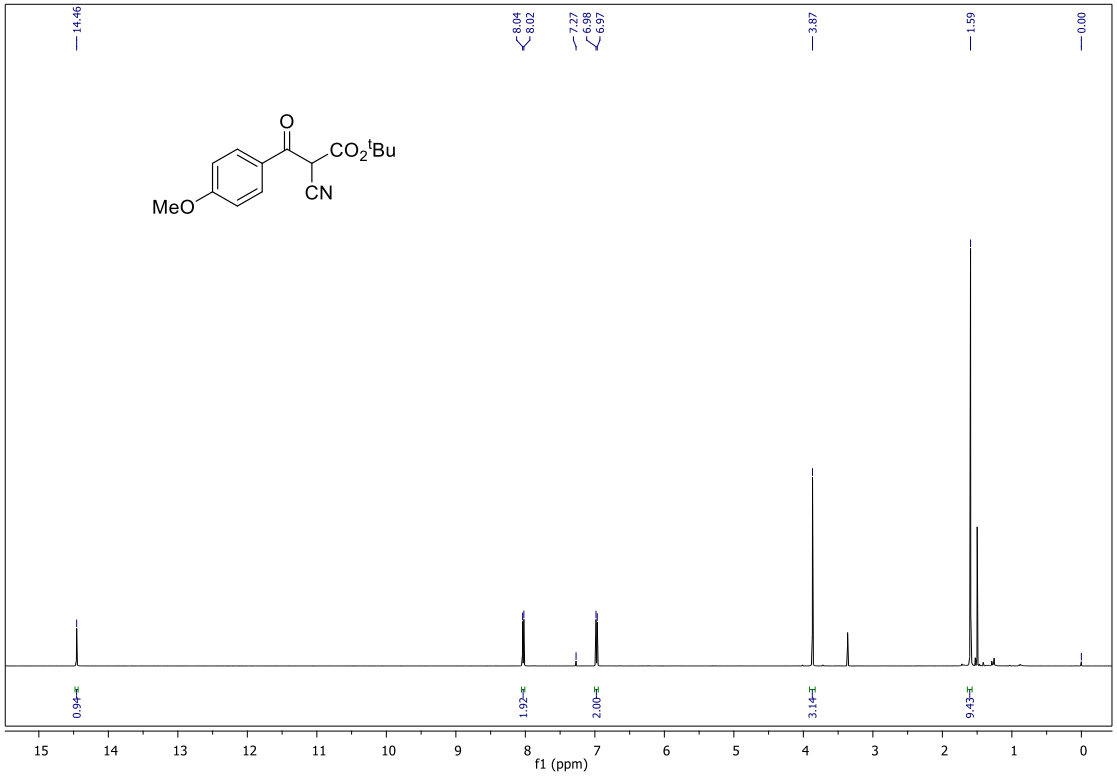
Copies of spectra



^{1}H NMR of compound **1k** in $CDCl_3$ (500 MHz)



^{13}C NMR of compound **1k** in $CDCl_3$ (101 MHz)



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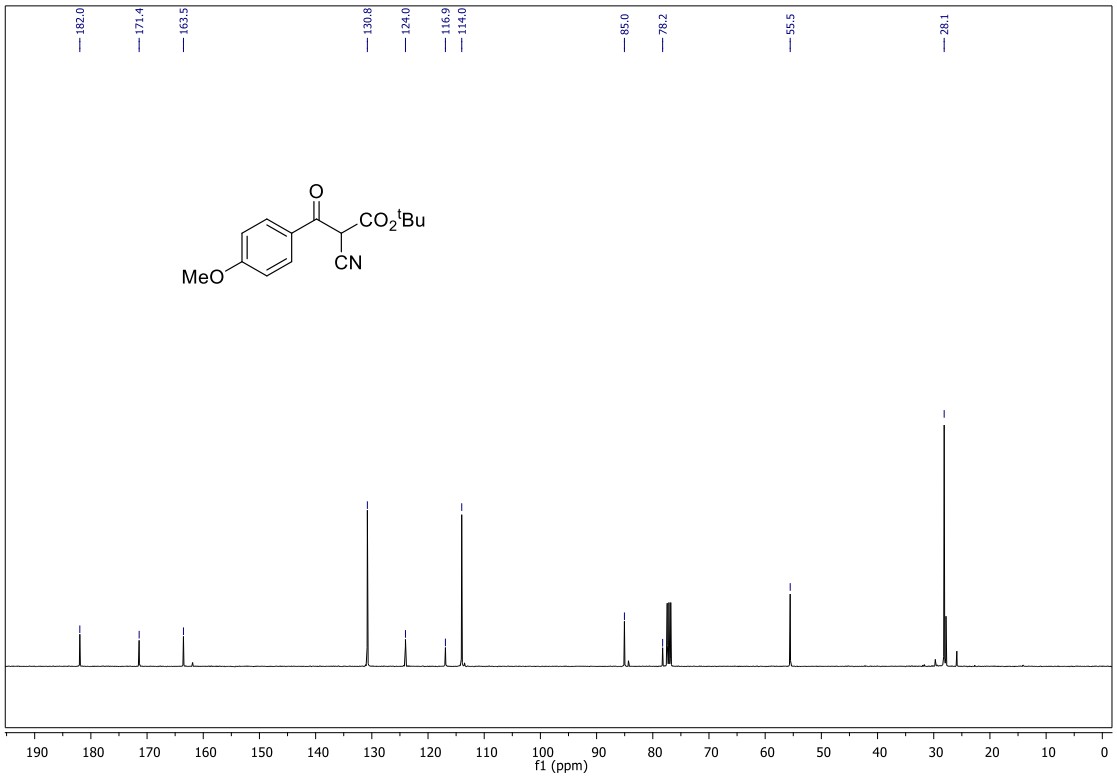

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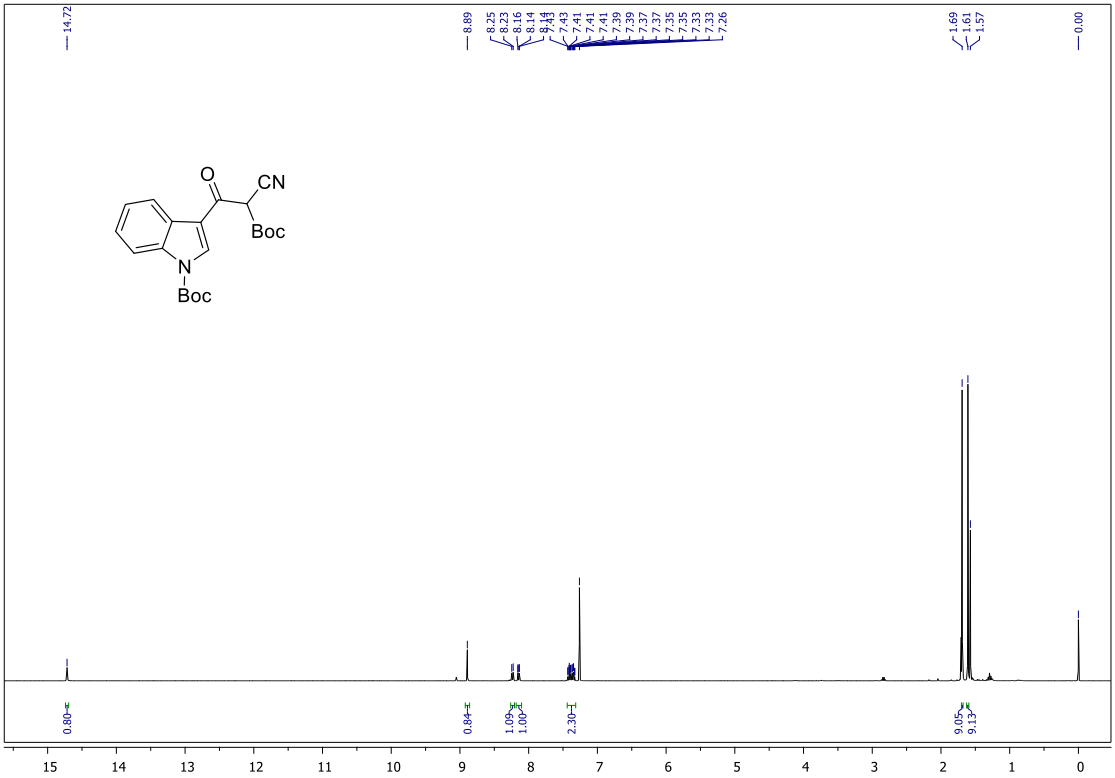
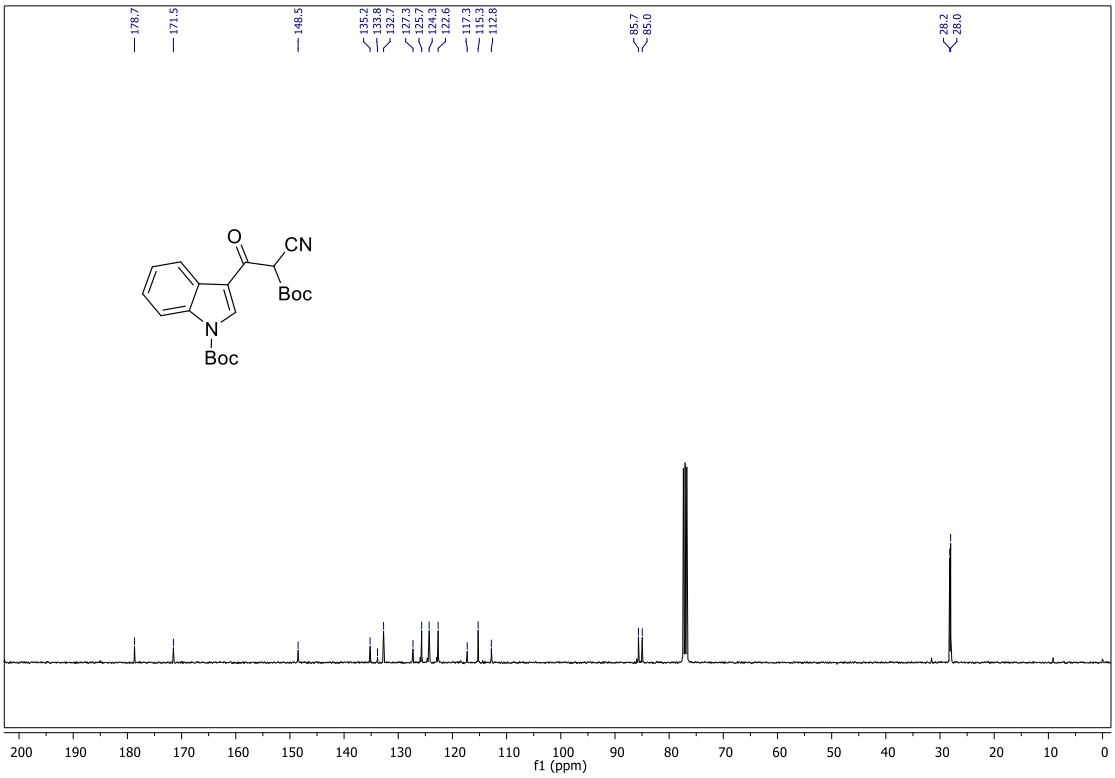


^{1}H NMR of compound **1o** in $CDCl_3$ (400 MHz)



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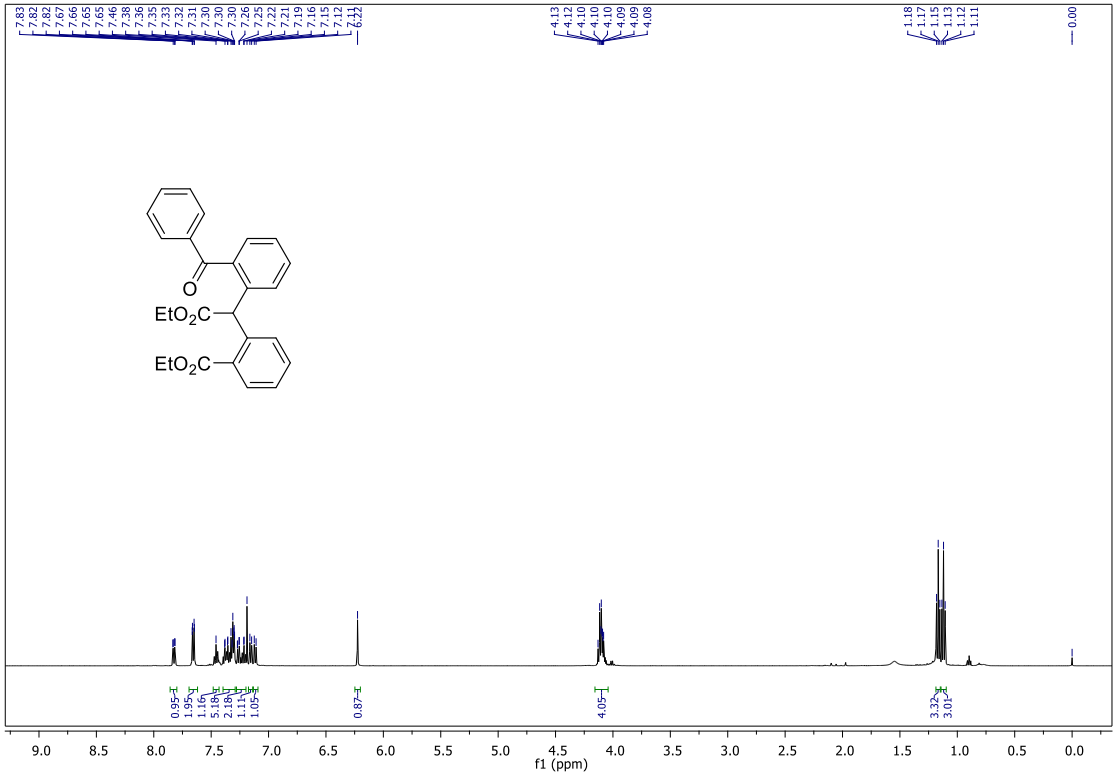
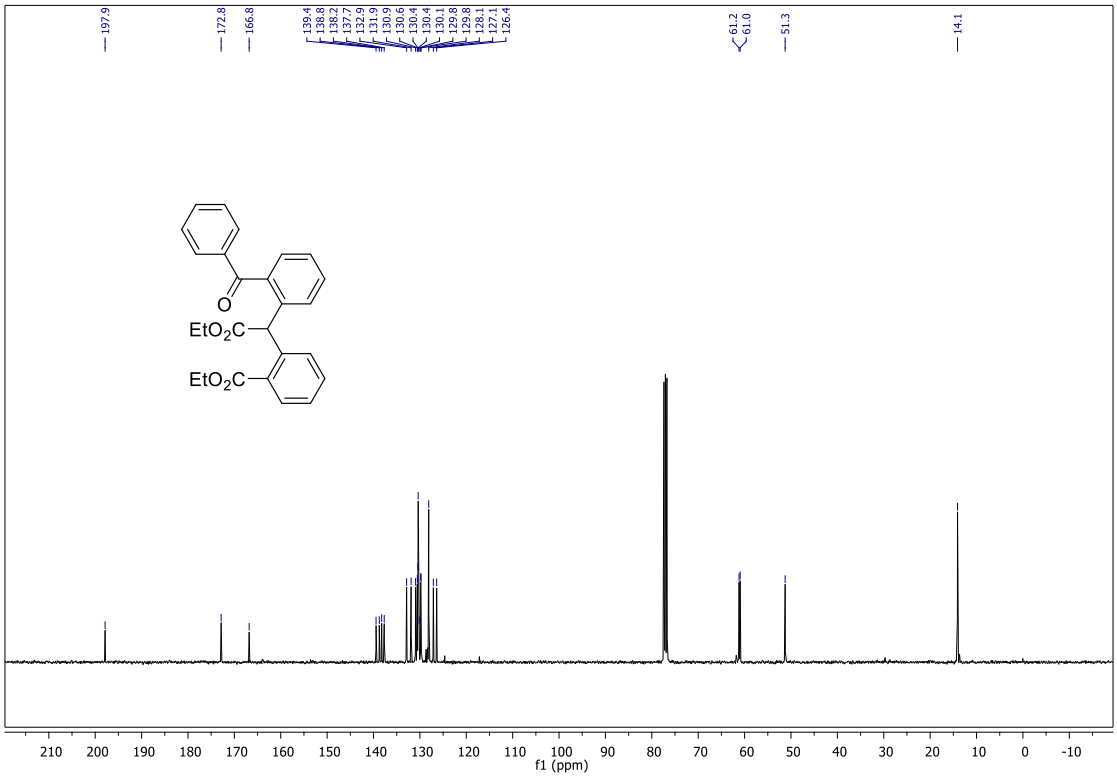
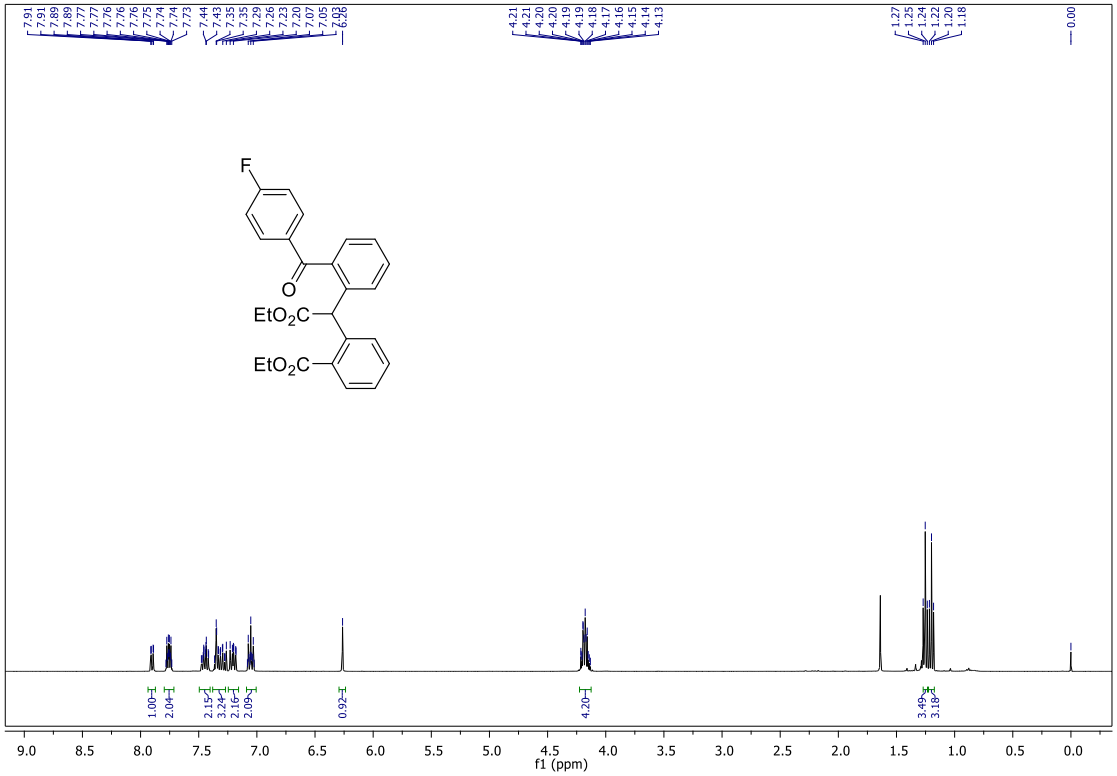


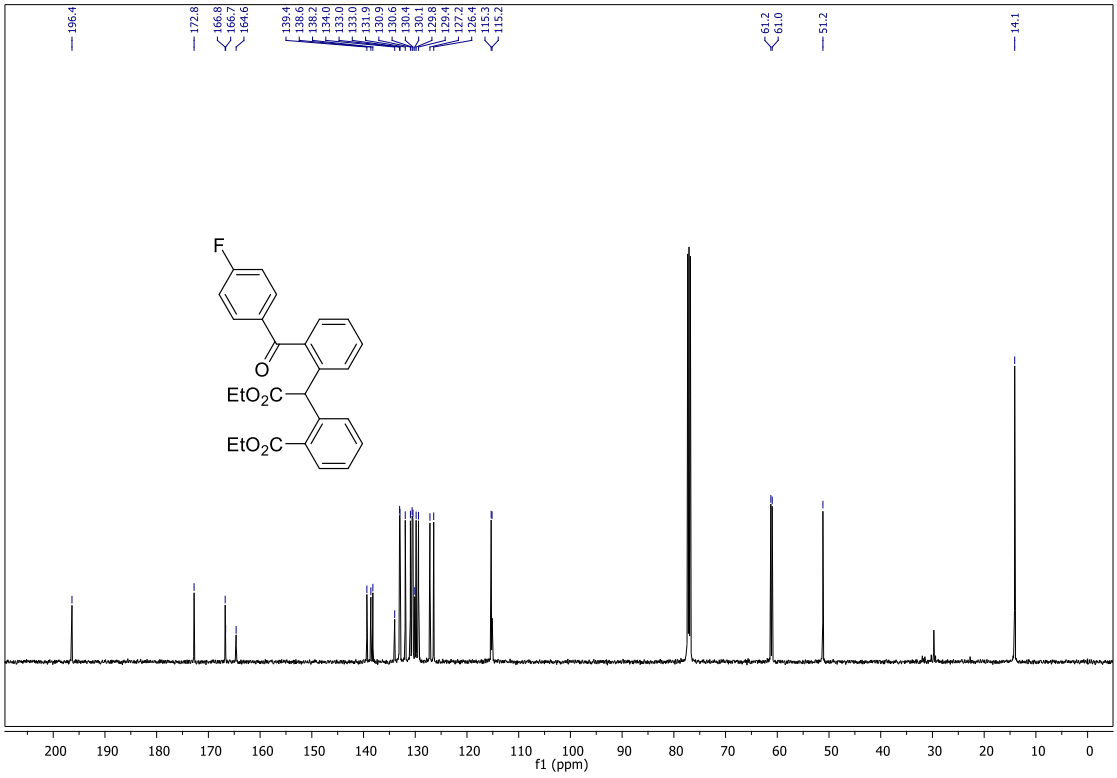
^{1}H NMR of compound **3a** in $CDCl_3$ (500 MHz)



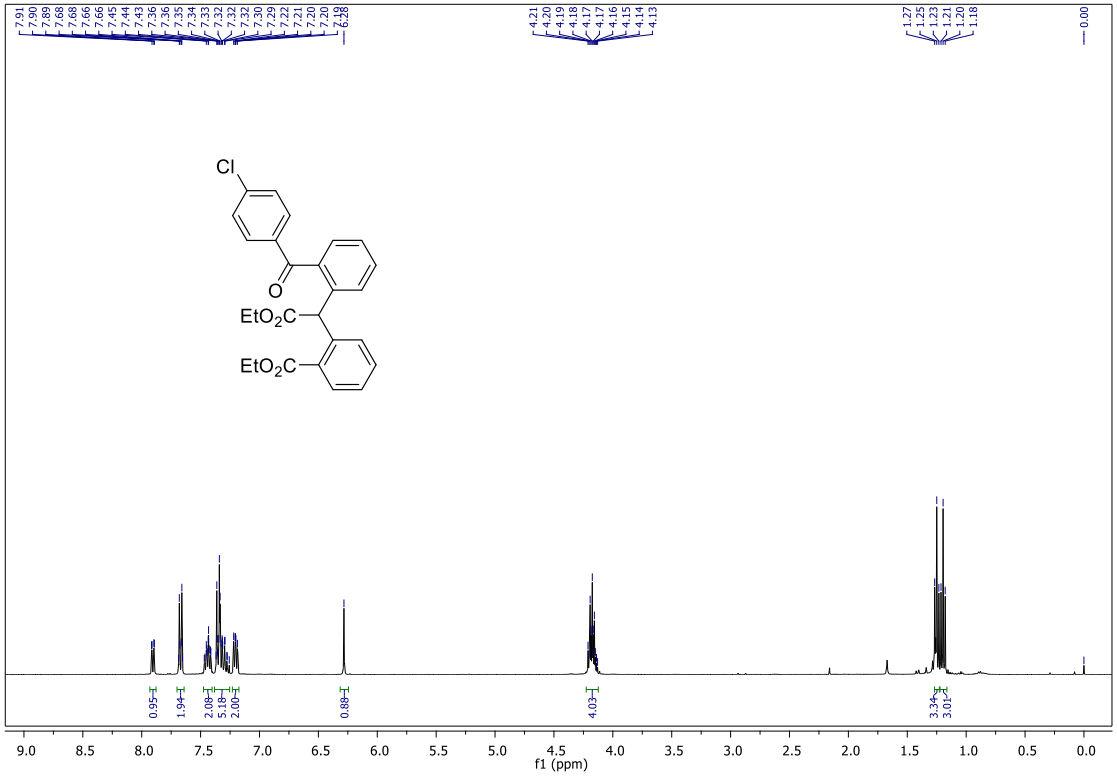
^{13}C NMR of compound **3a** in $CDCl_3$ (101 MHz)



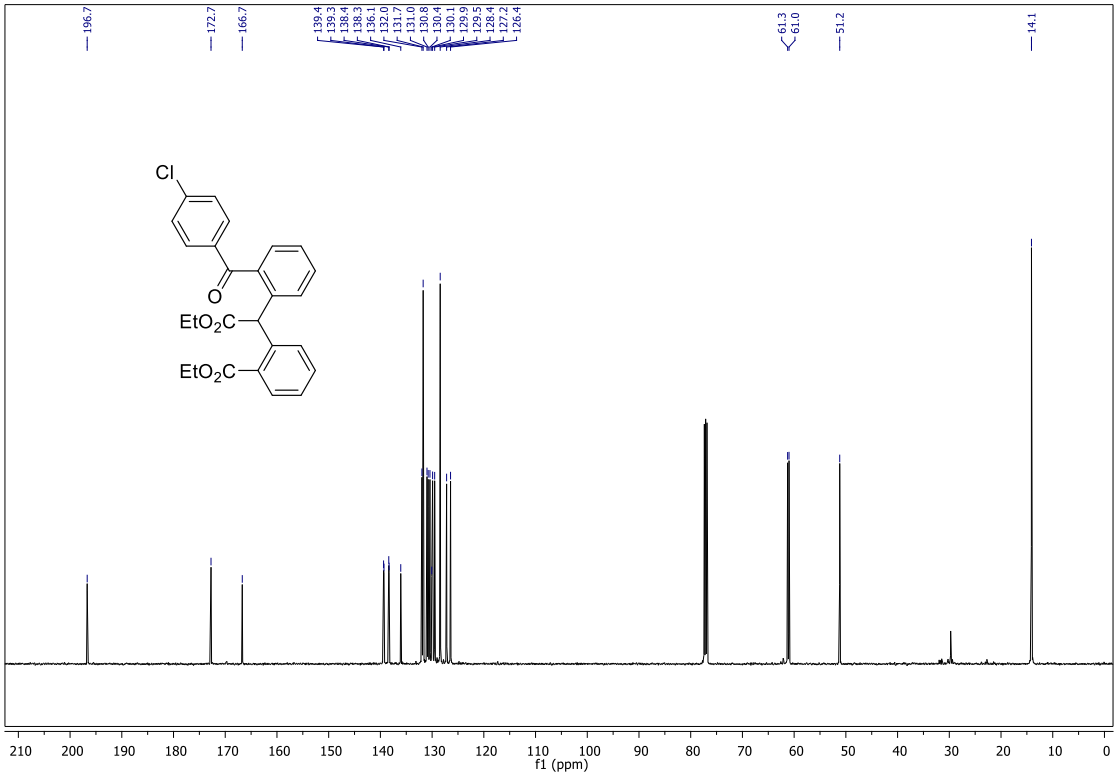
^{1}H NMR of compound **3b** in $CDCl_3$ (400 MHz)



^{13}C NMR of compound **3b** in $CDCl_3$ (126 MHz)



^{1}H NMR of compound **3c** in $CDCl_3$ (400 MHz)



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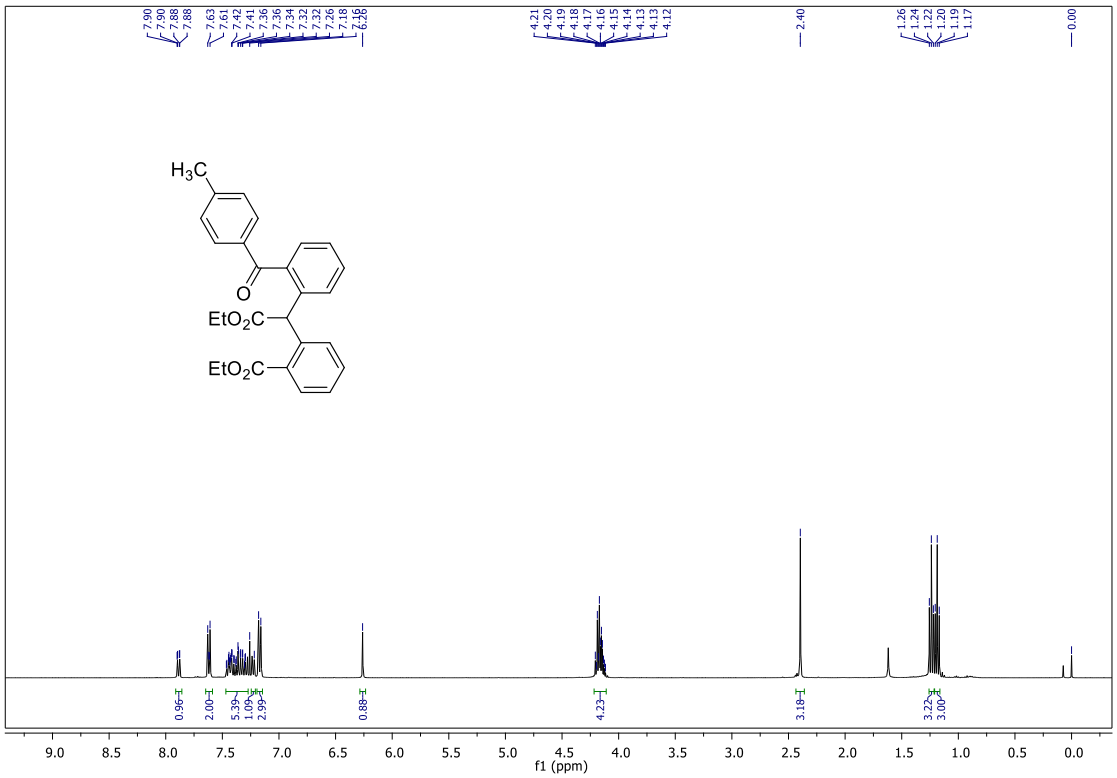
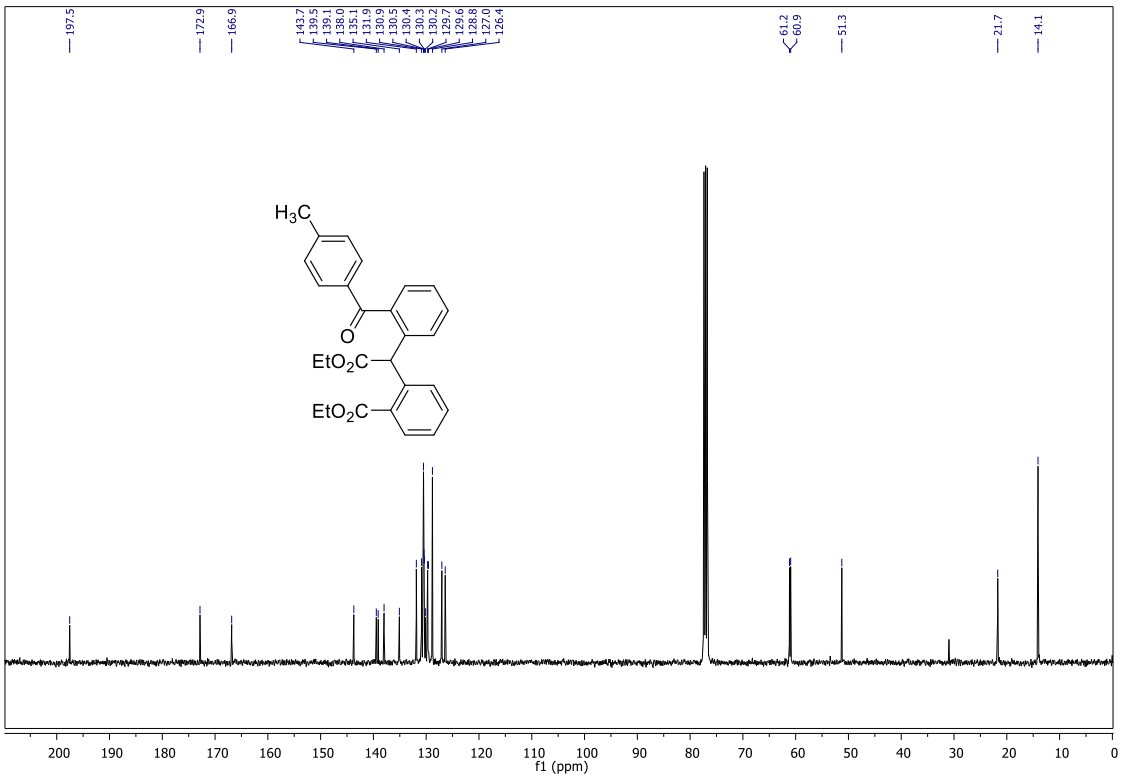


^{1}H NMR of compound **3d** in $CDCl_3$ (400 MHz)



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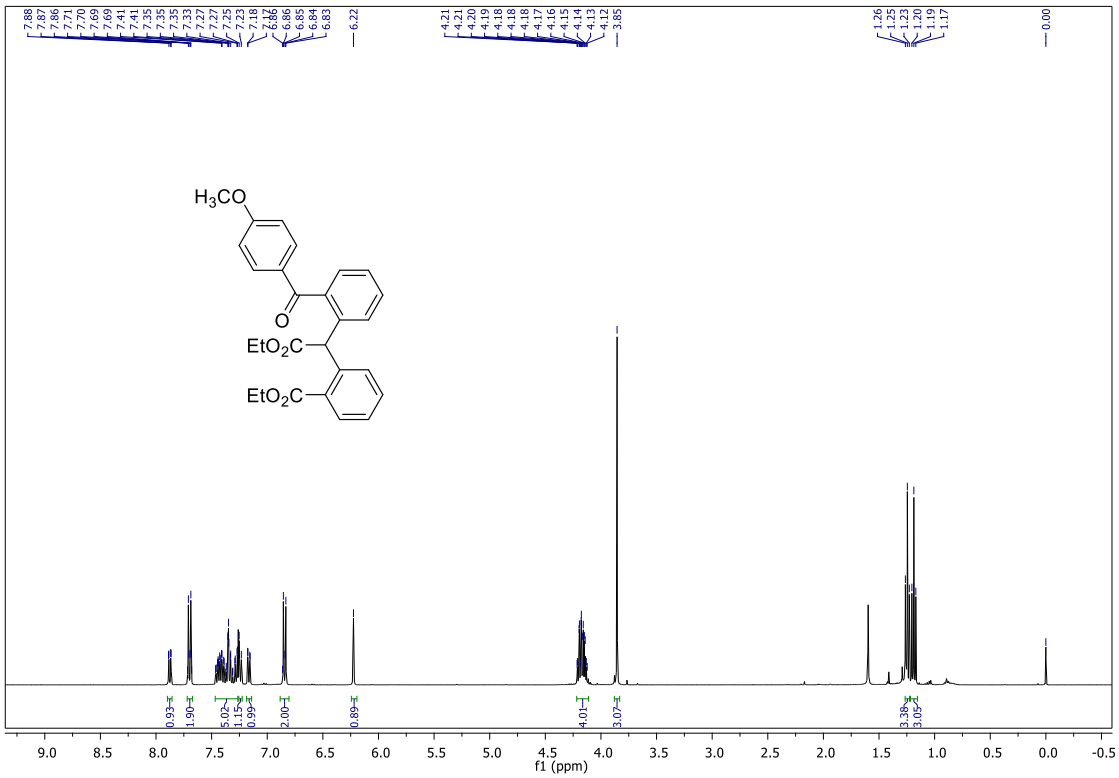
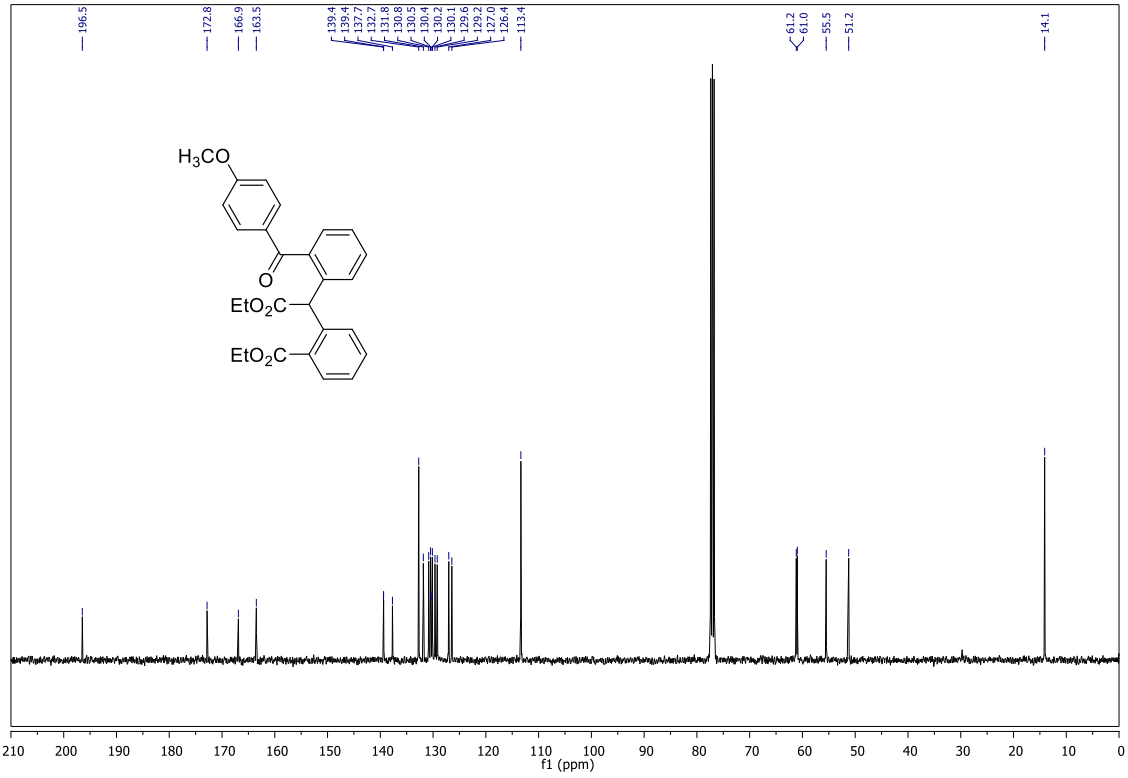
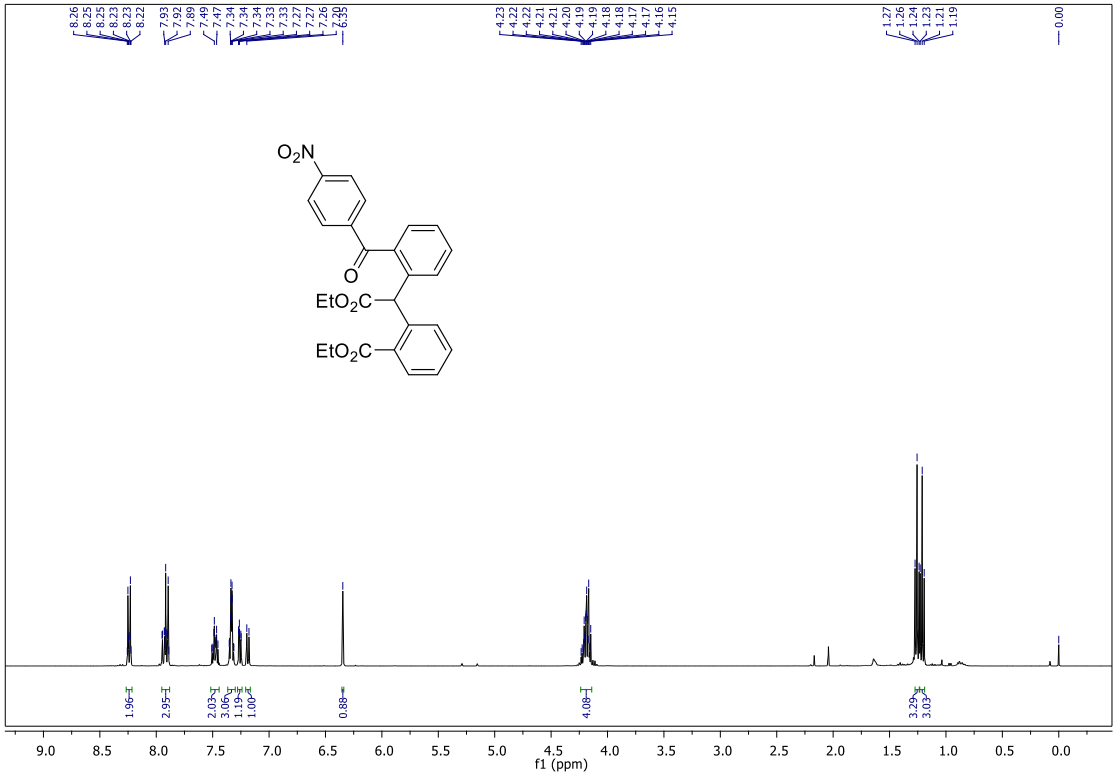


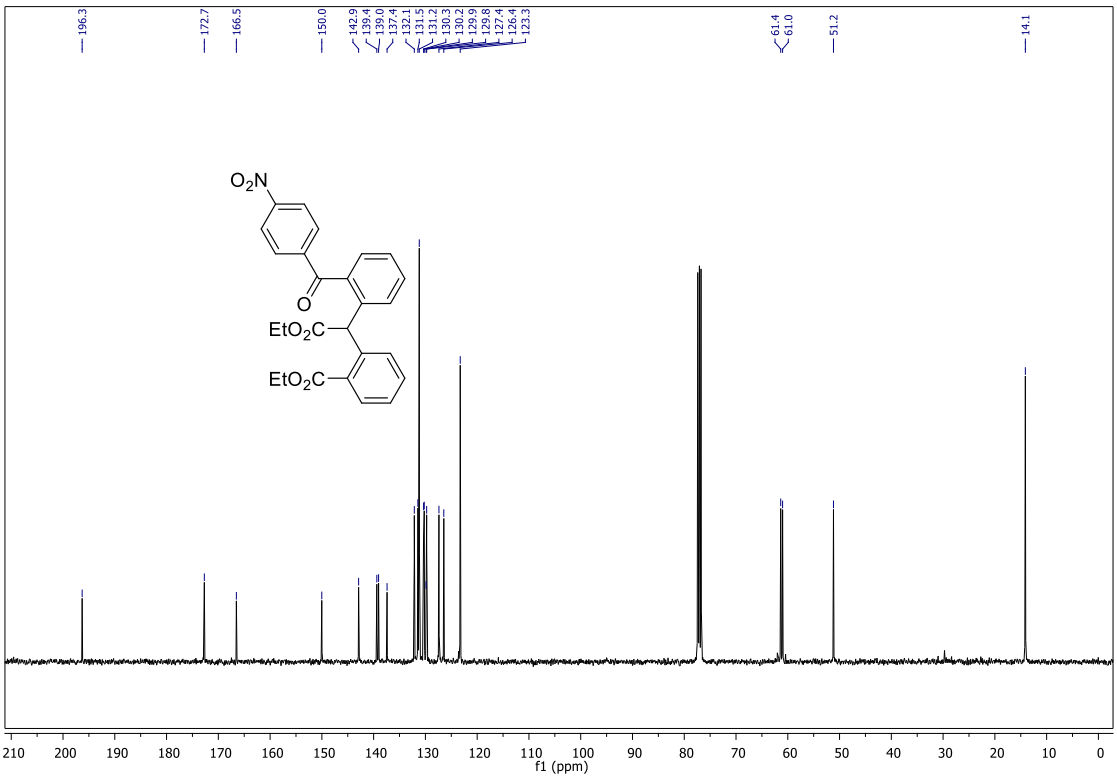
^{1}H NMR of compound **3e** in $CDCl_3$ (400 MHz)



^{13}C NMR of compound **3e** in $CDCl_3$ (101 MHz)



^{1}H NMR of compound **3f** in $CDCl_3$ (400 MHz)



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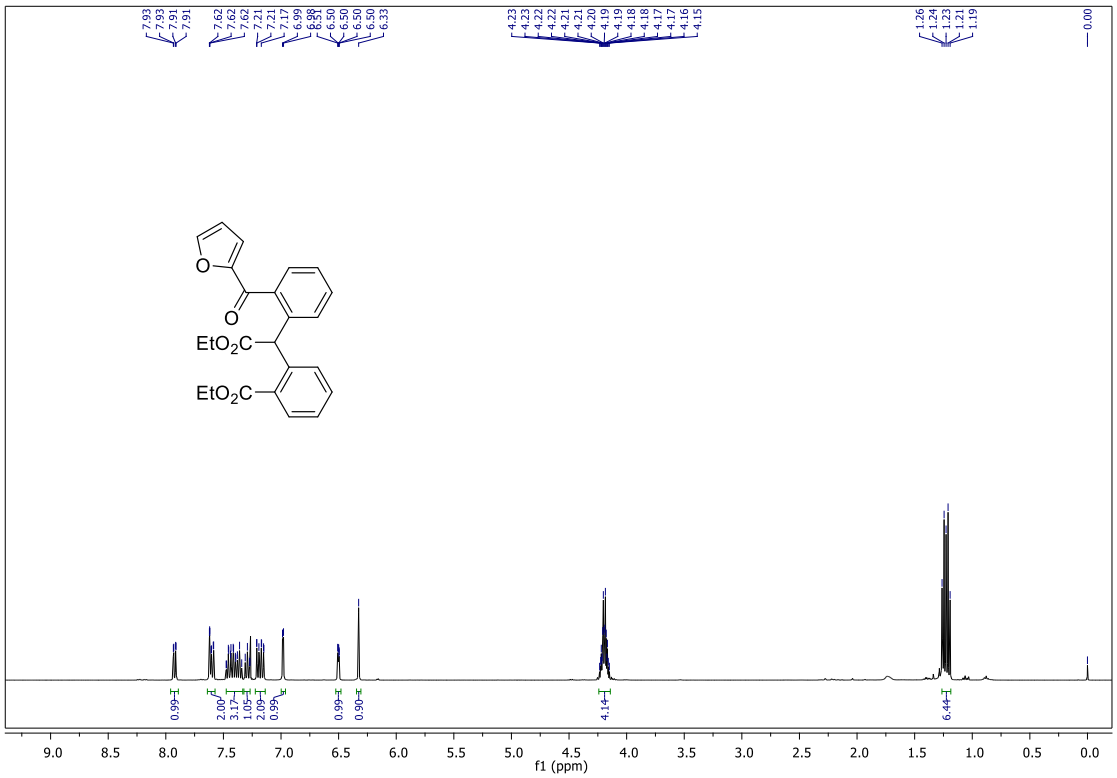
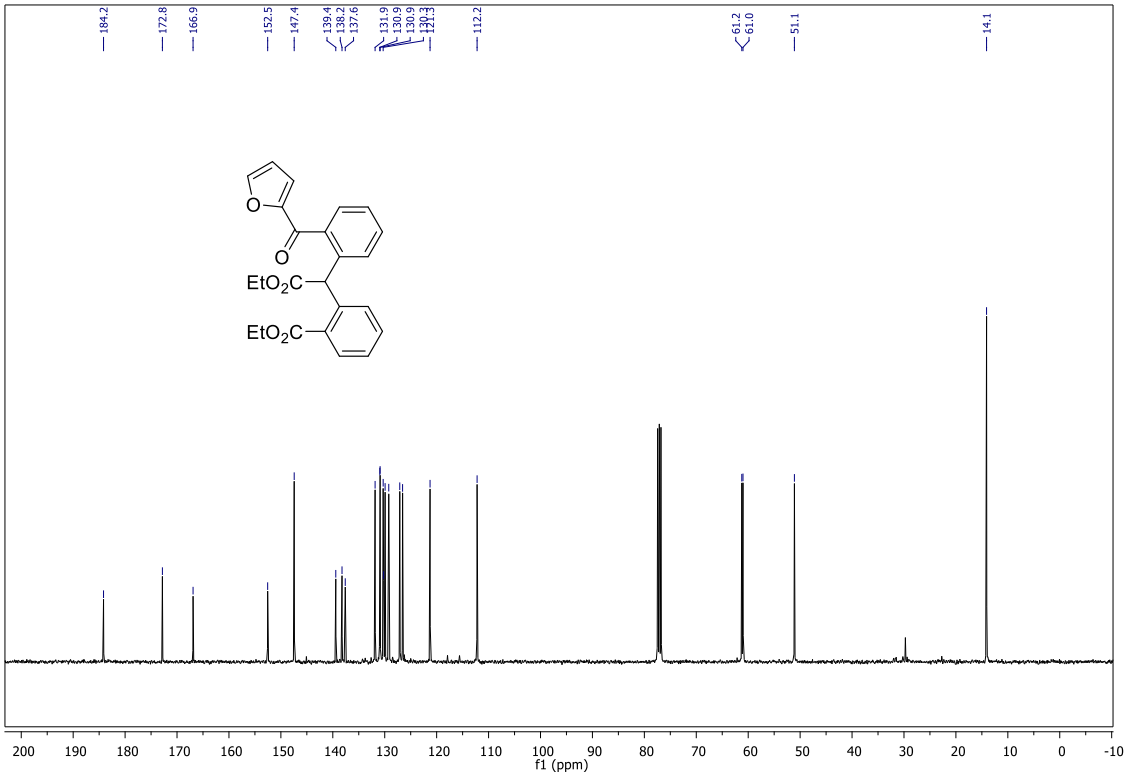
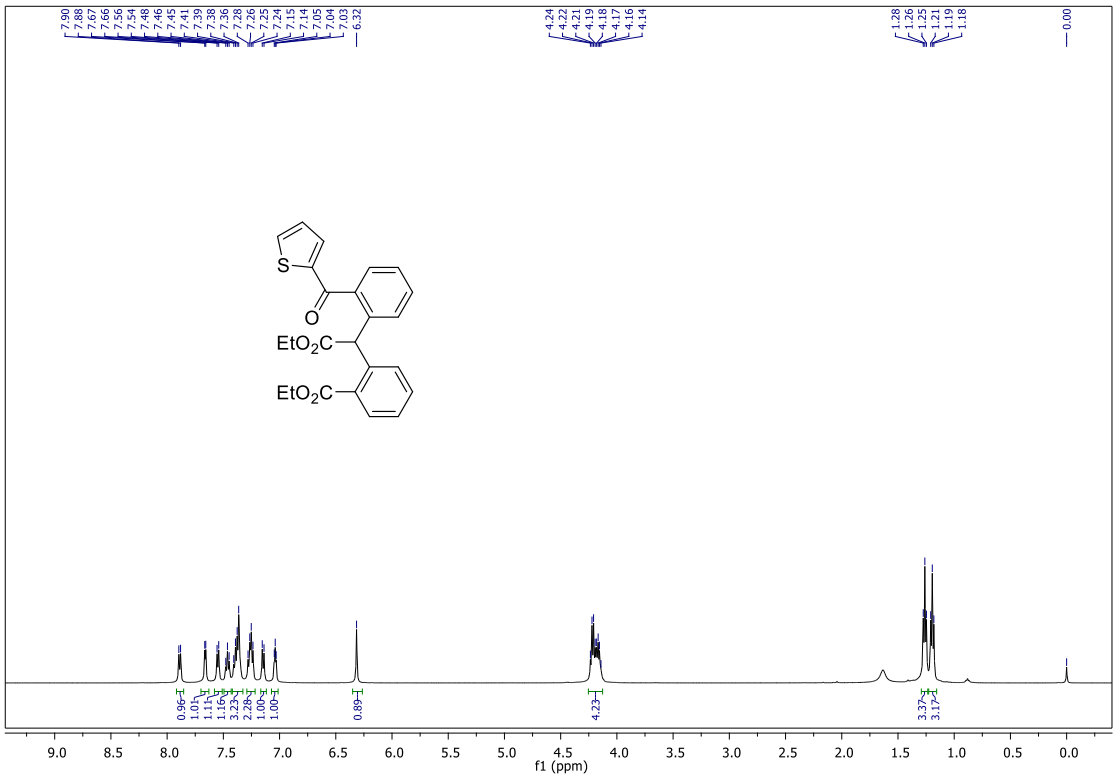


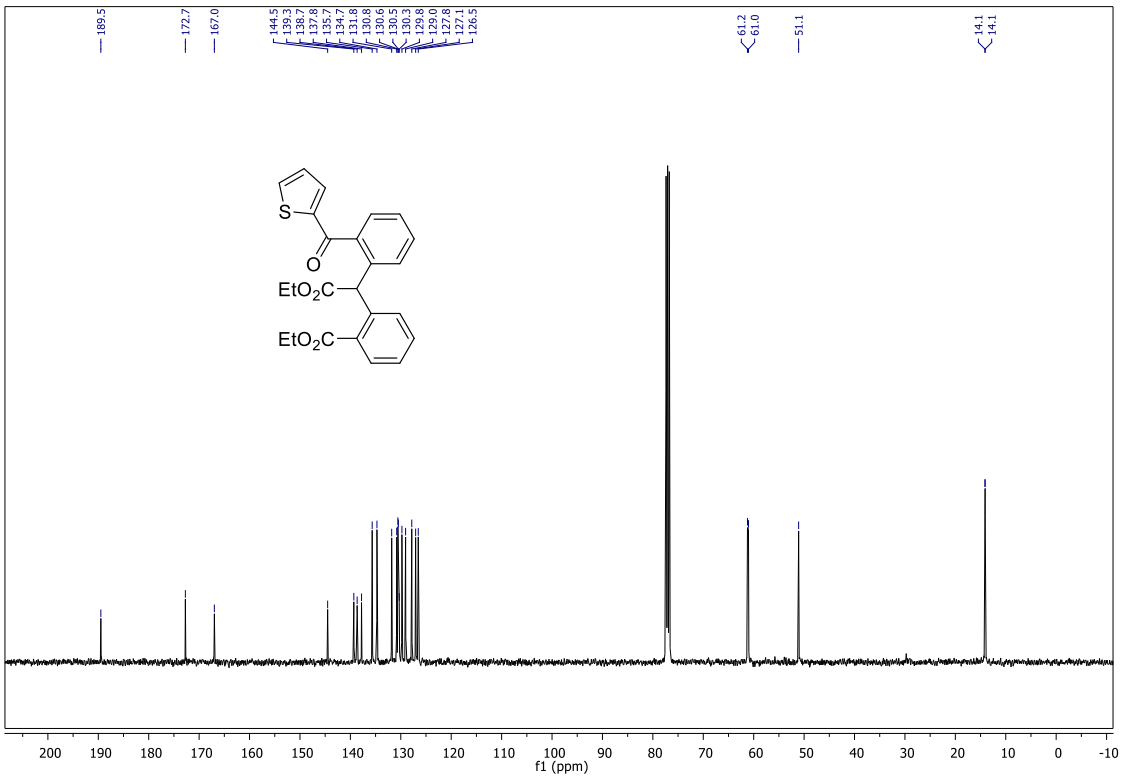
^{1}H NMR of compound **3g** in $CDCl_3$ (400 MHz)



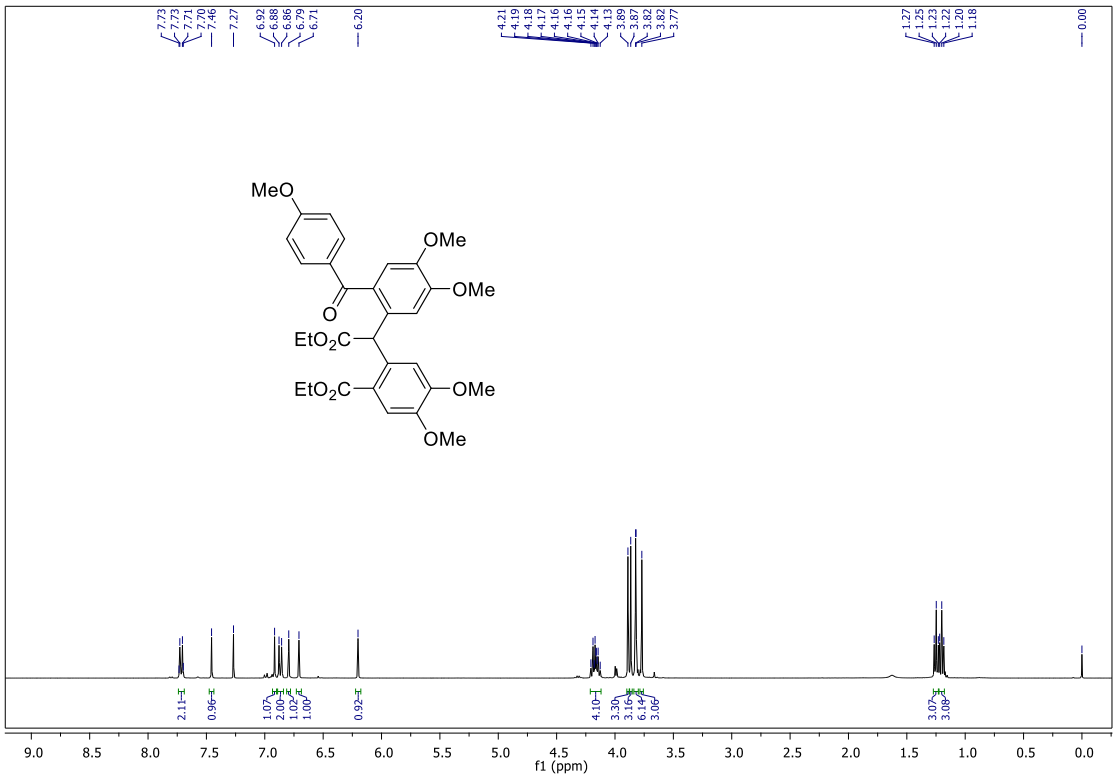
^{13}C NMR of compound **3g** in $CDCl_3$ (101 MHz)



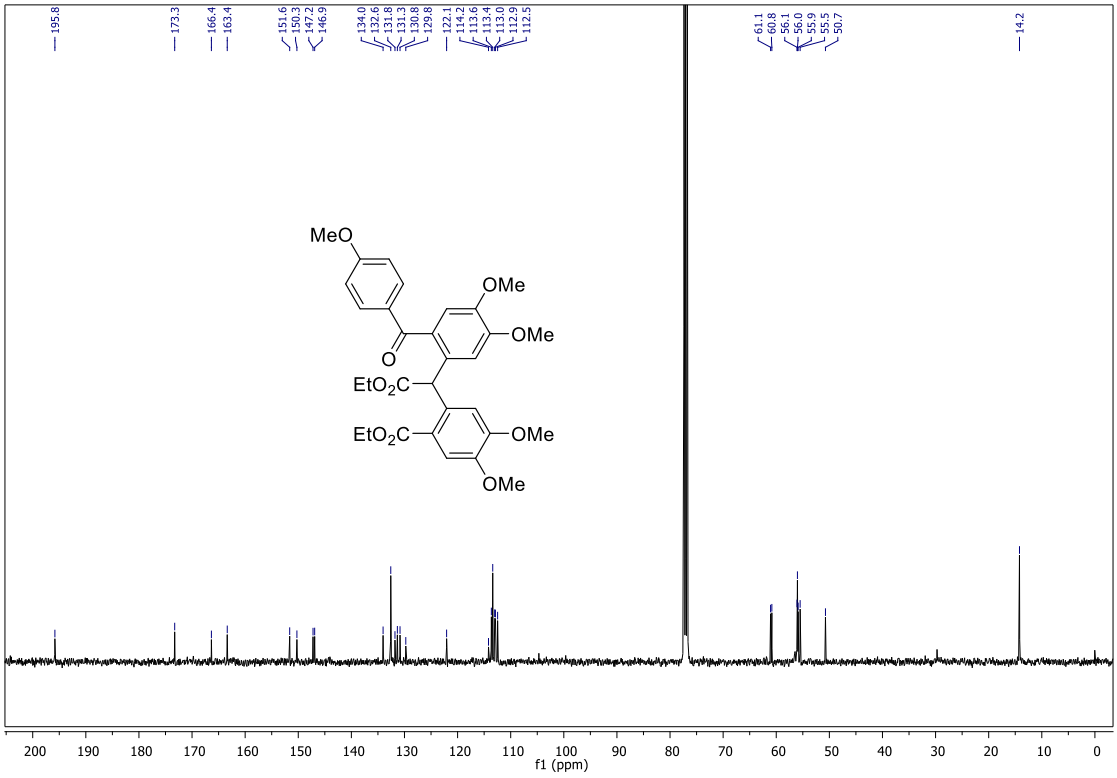
^{1}H NMR of compound **3h** in $CDCl_3$ (500 MHz)



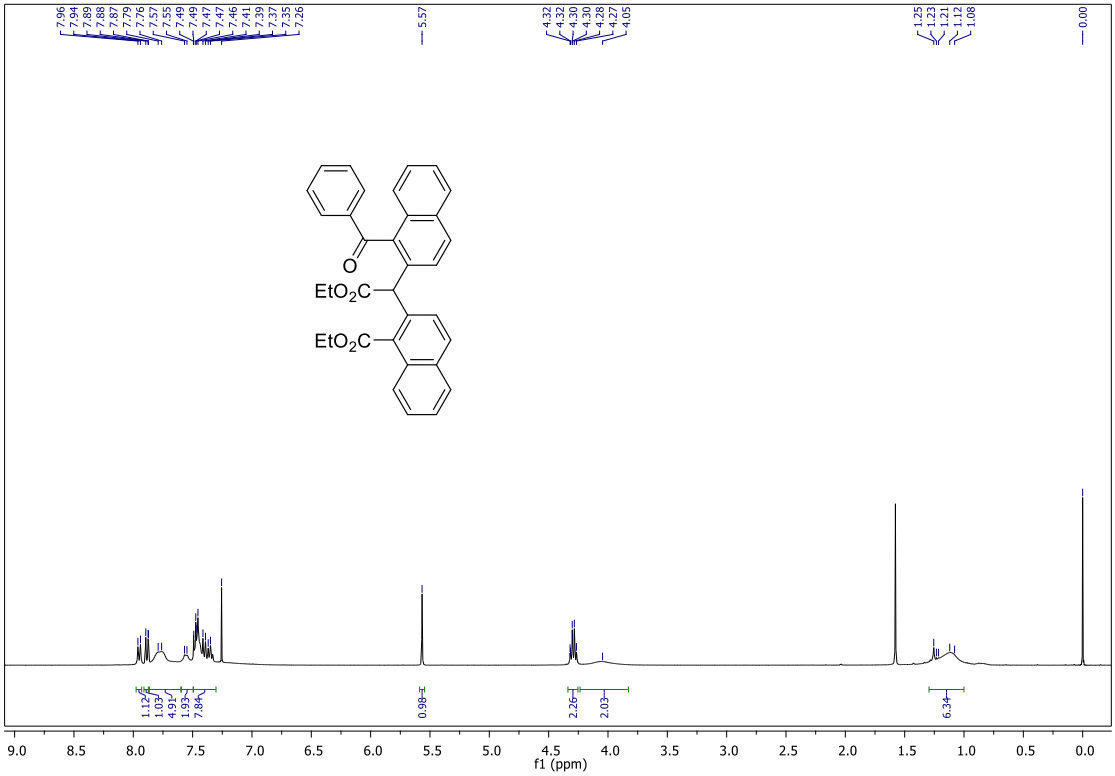
^{13}C NMR of compound **3h** in $CDCl_3$ (101 MHz)



^{1}H NMR of compound **3i** in $CDCl_3$ (400 MHz)



^{13}C NMR of compound **3i** in $CDCl_3$ (101 MHz)



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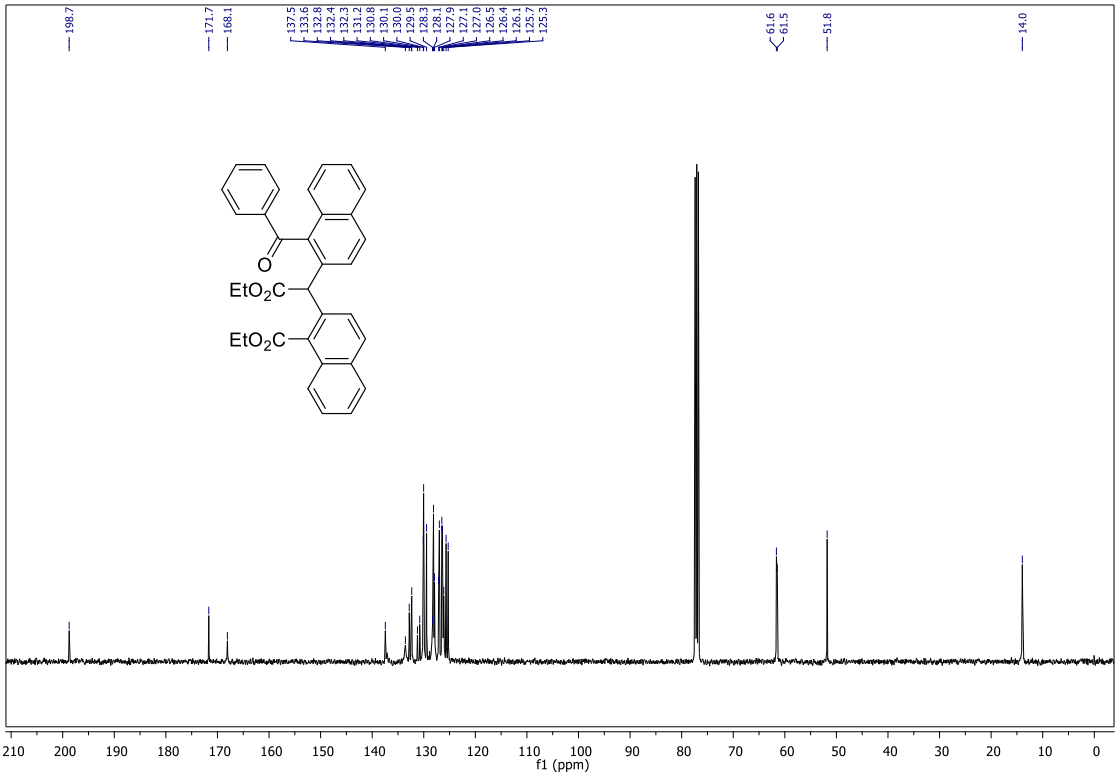

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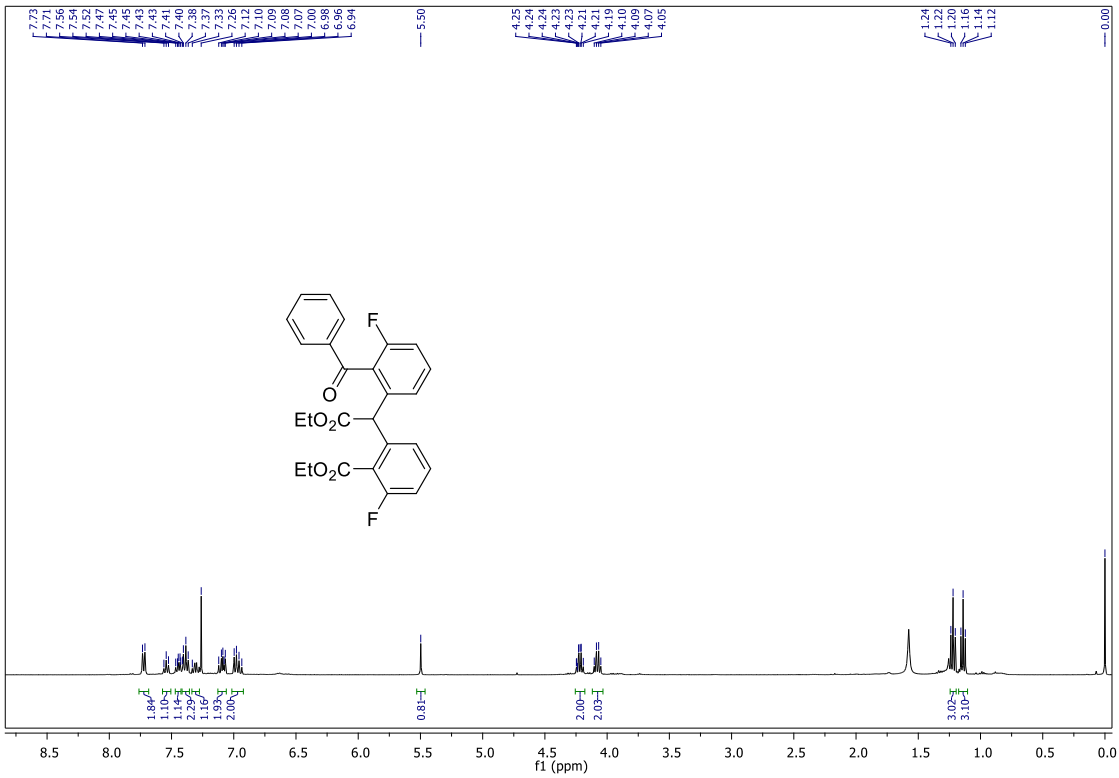

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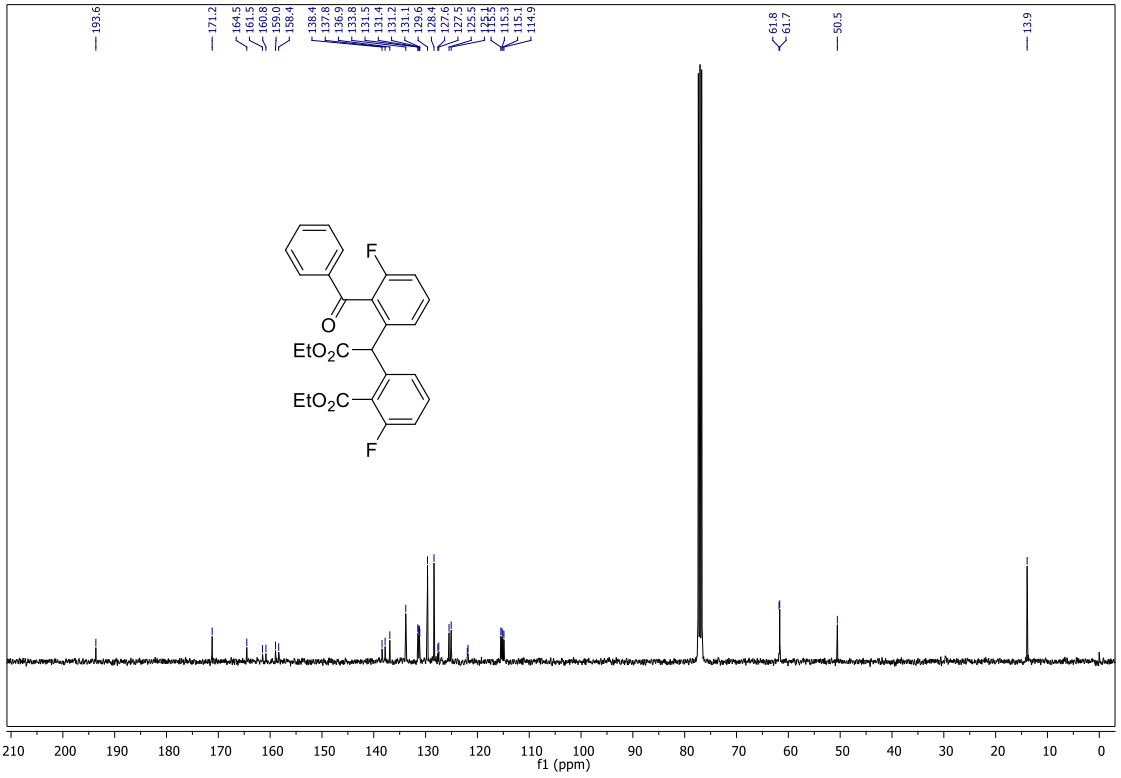

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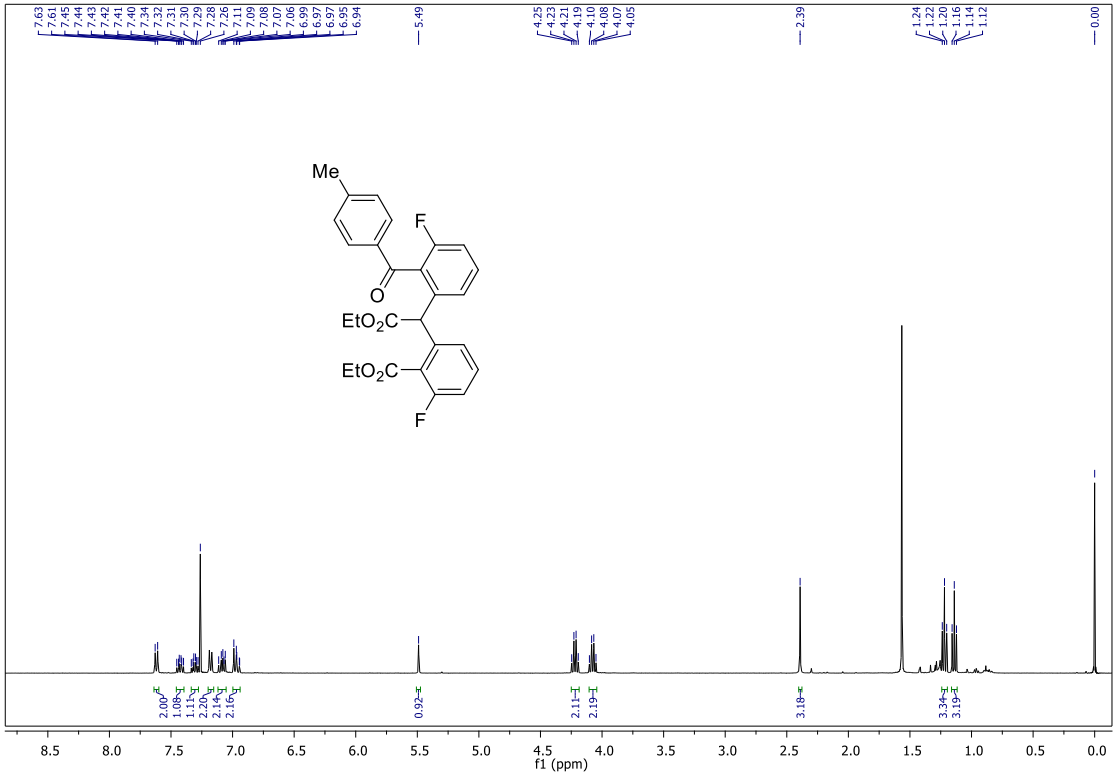
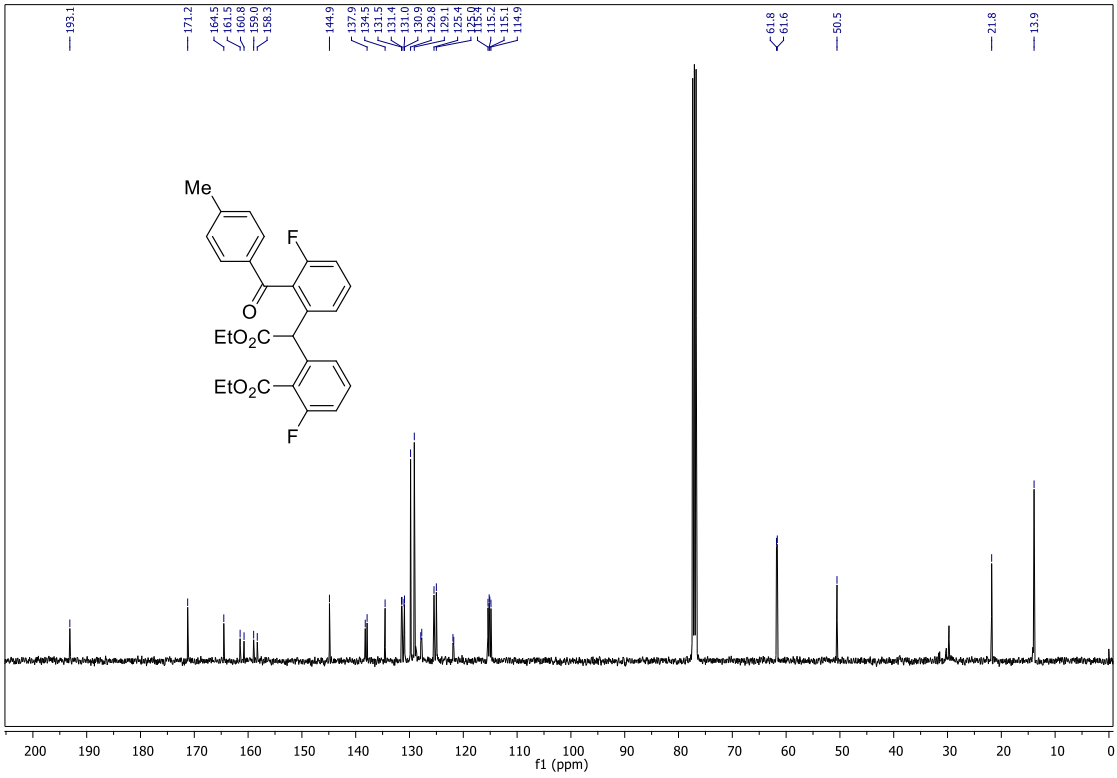


^{1}H NMR of compound **3l** in $CDCl_3$ (400 MHz)



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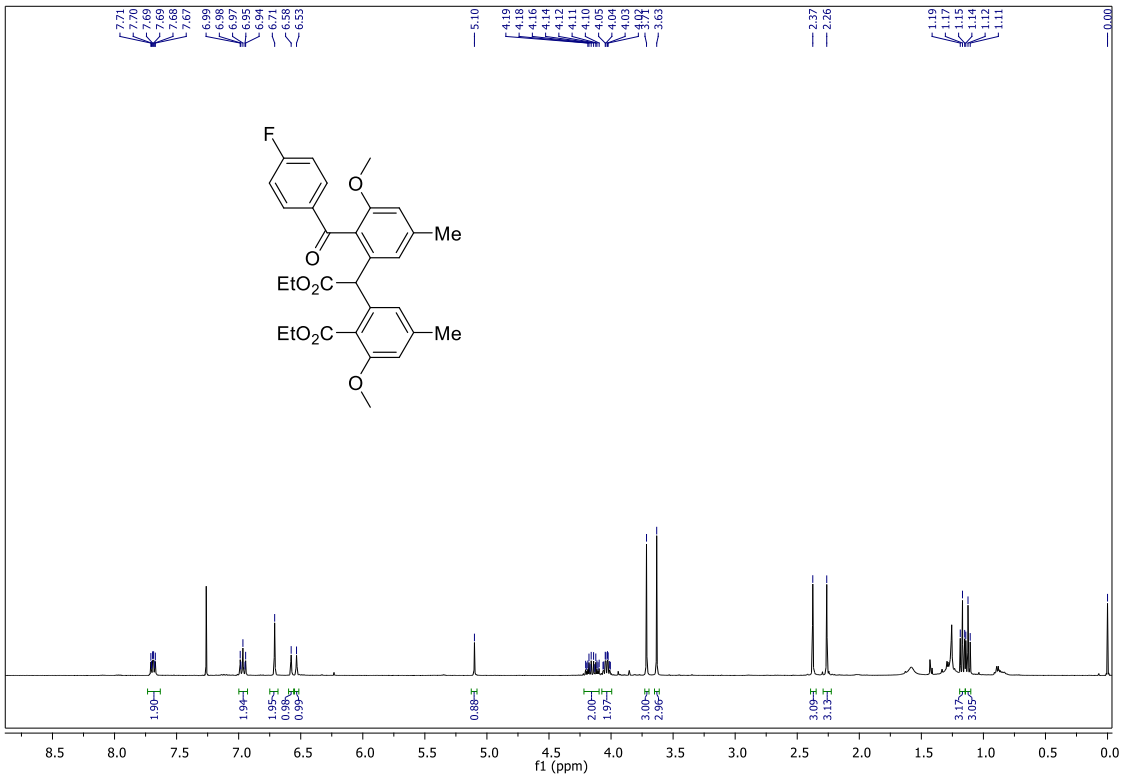

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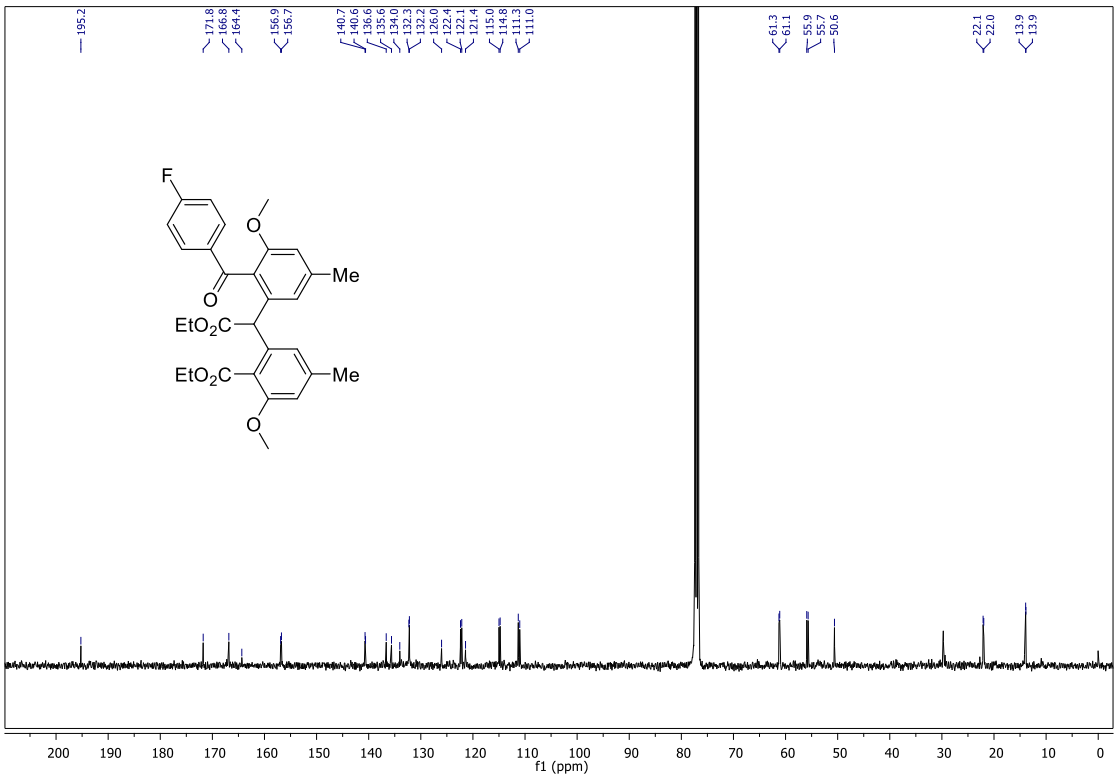

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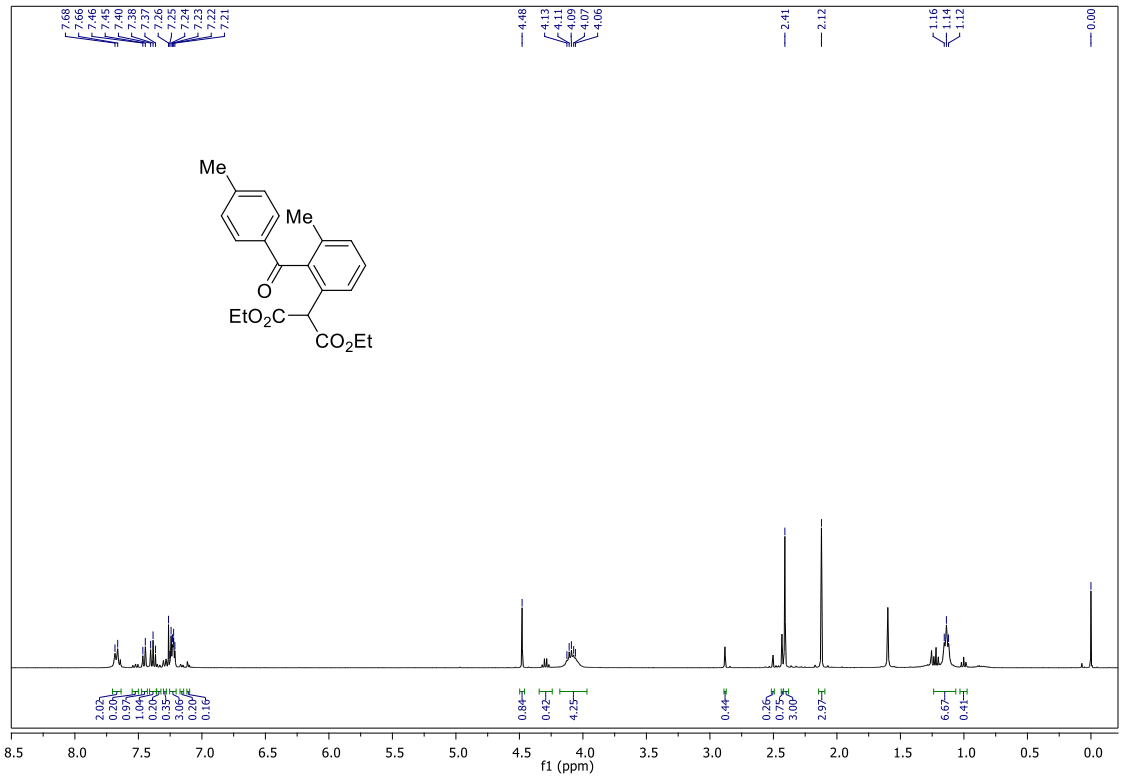
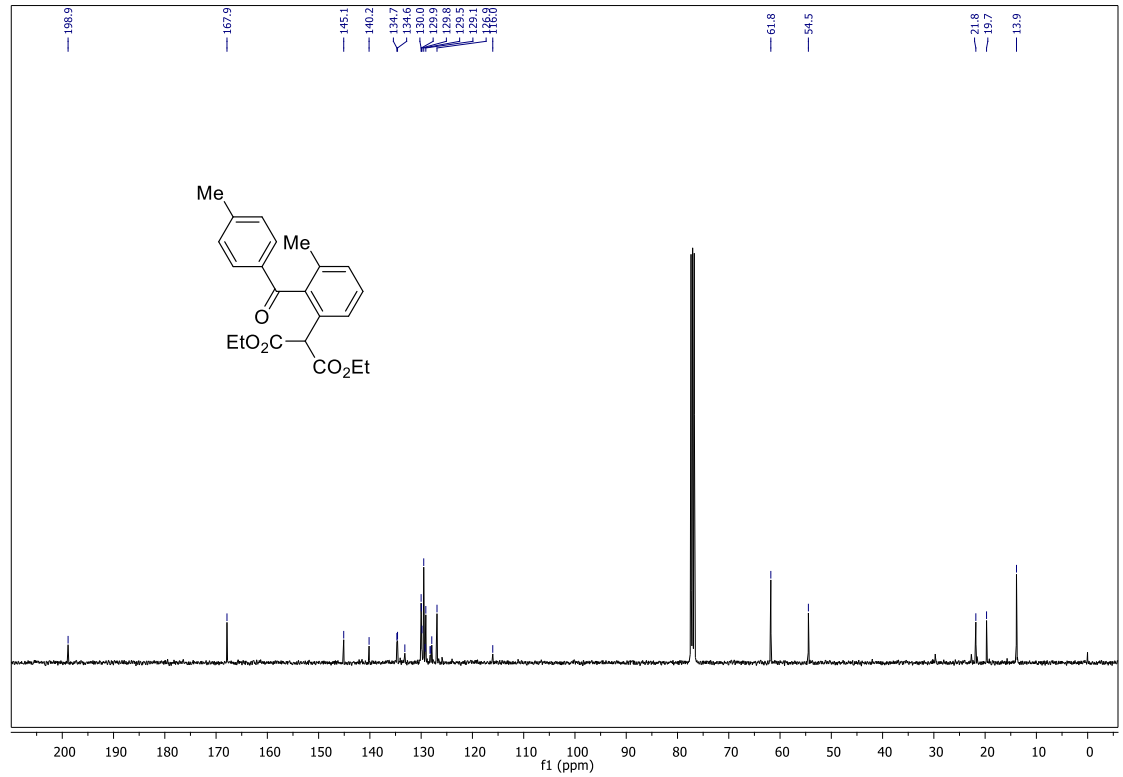


^{1}H NMR of compound **3n′** in $CDCl_3$ (400 MHz)



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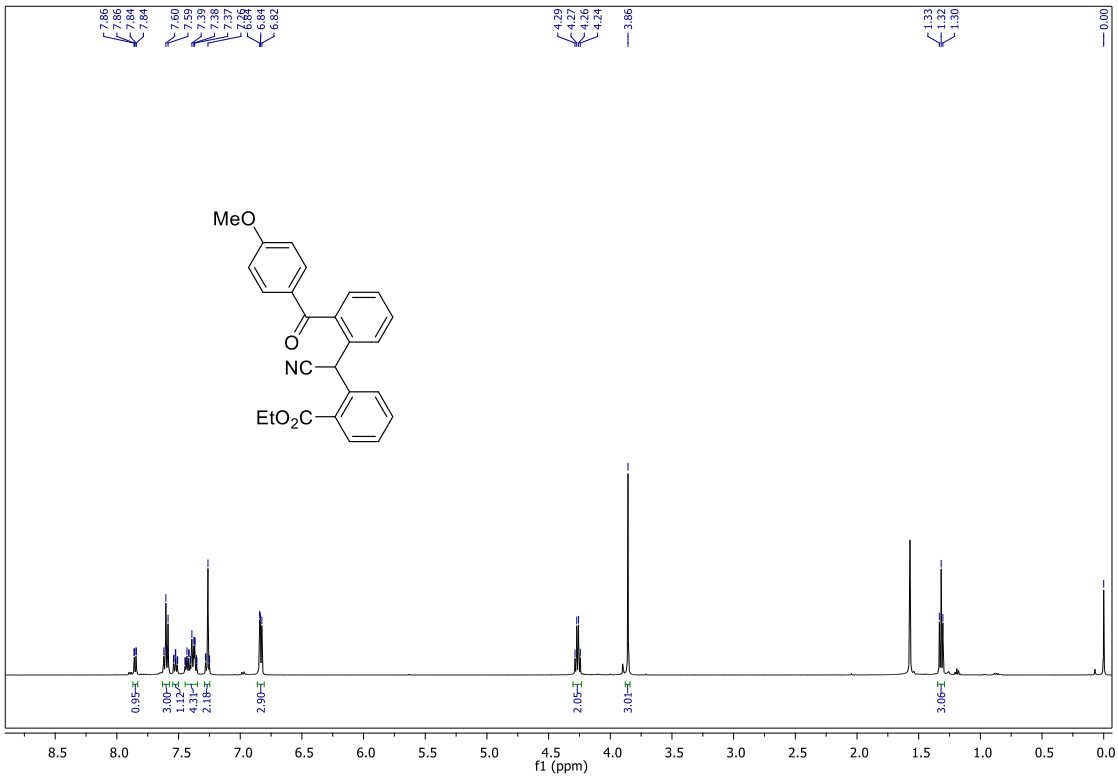

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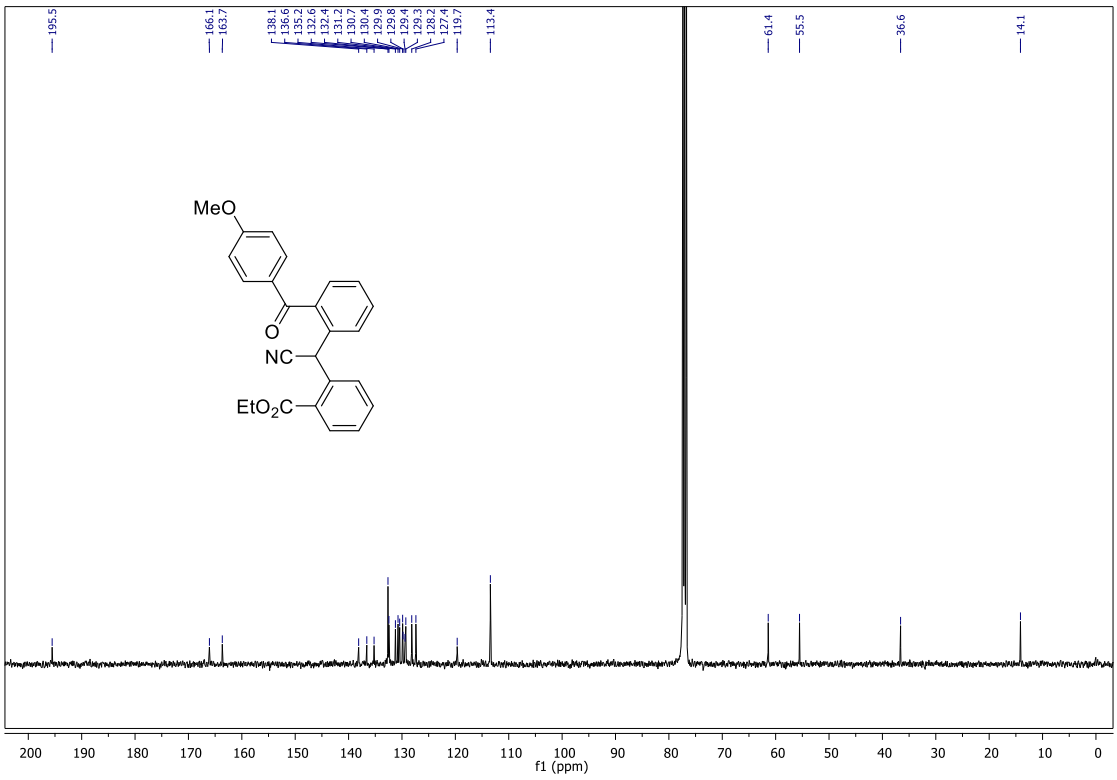

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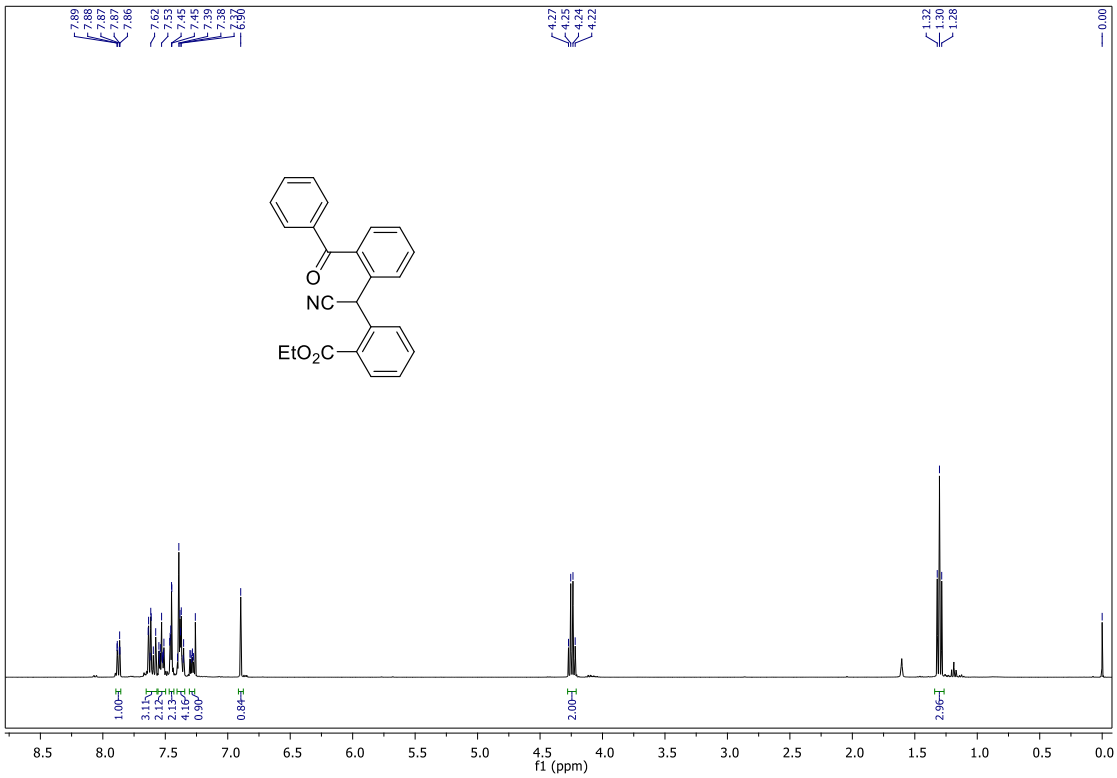
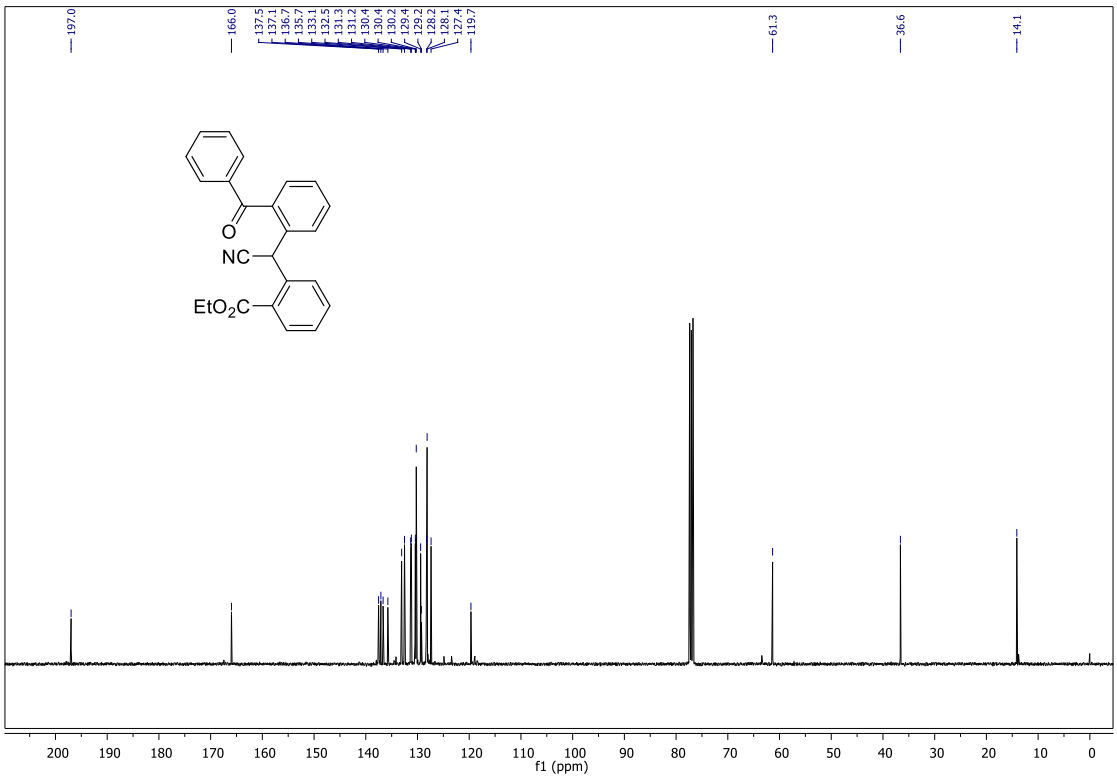
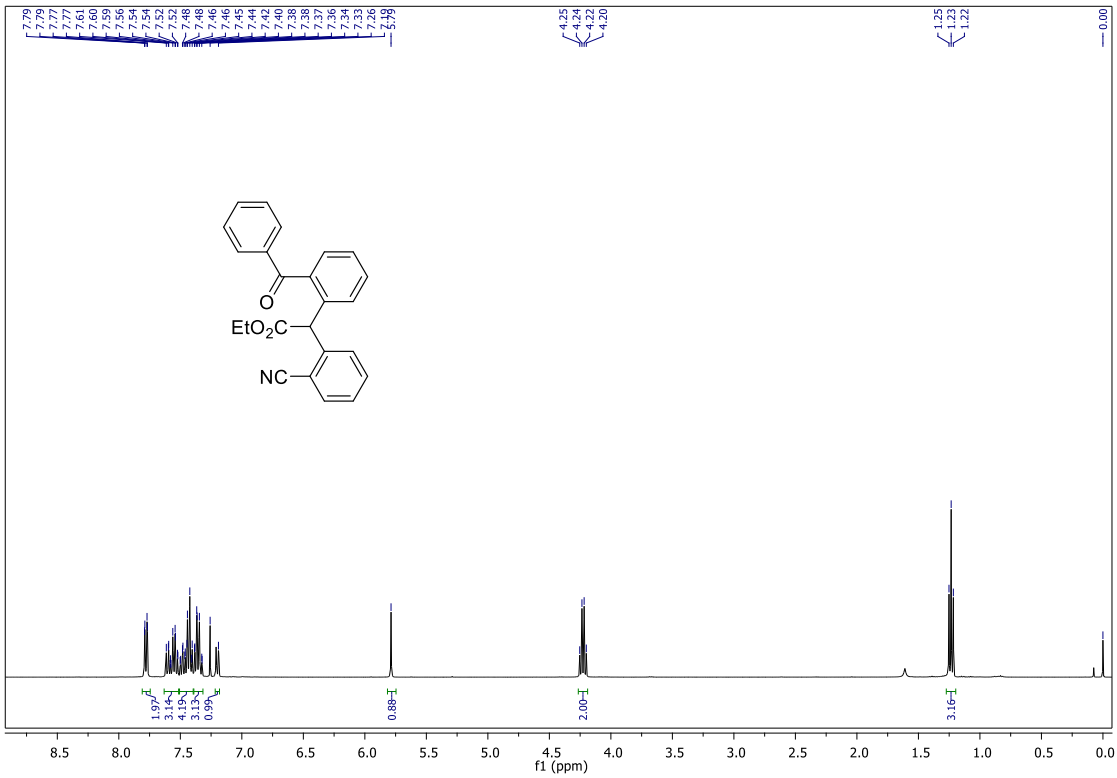


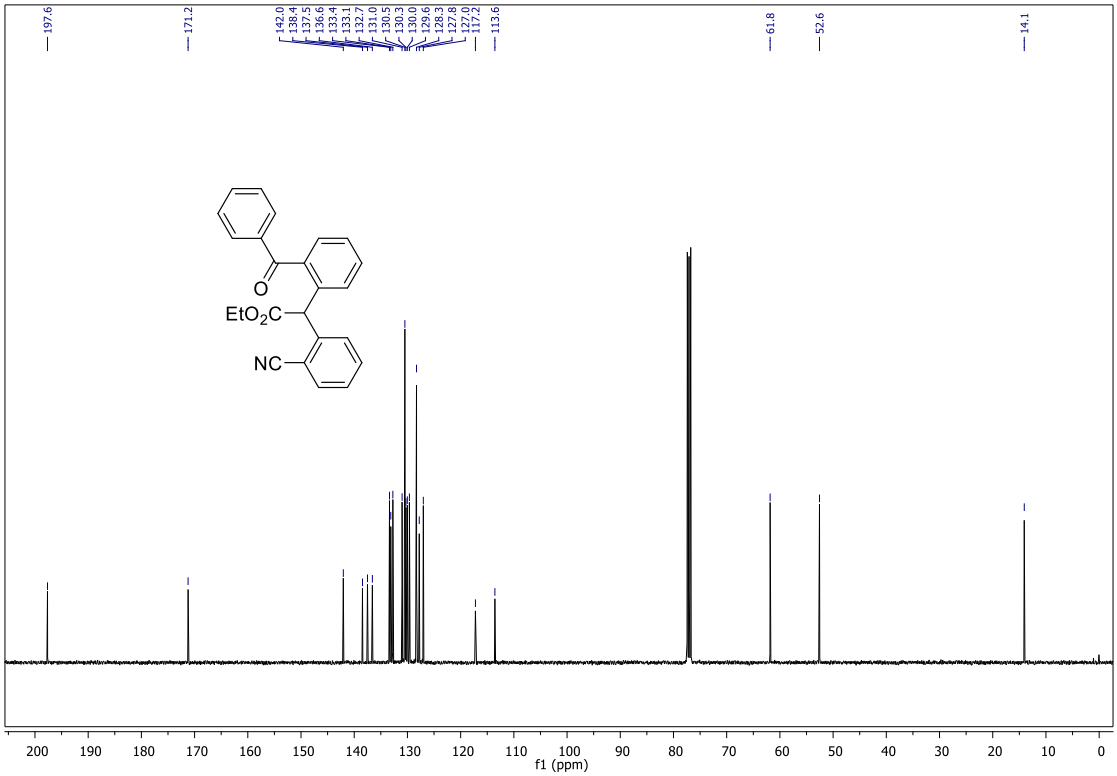
^{1}H NMR of compound **3p** in $CDCl_3$ (400 MHz)



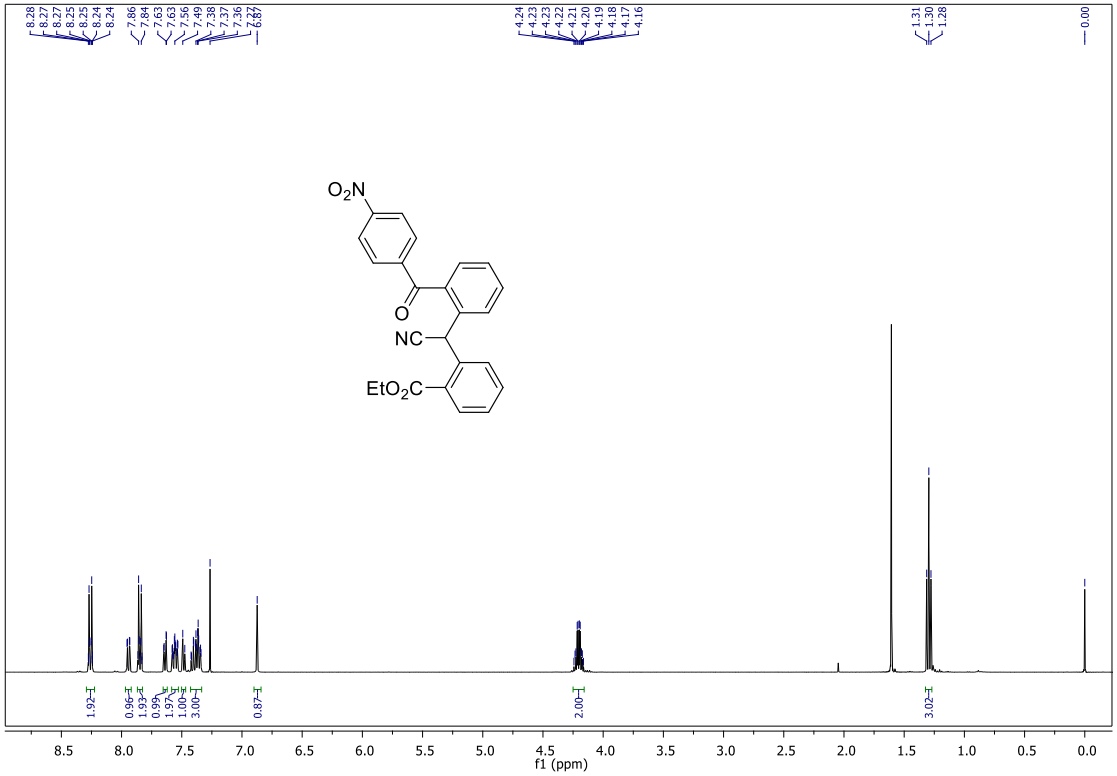
^{13}C NMR of compound **3p** in $CDCl_3$ (101 MHz)



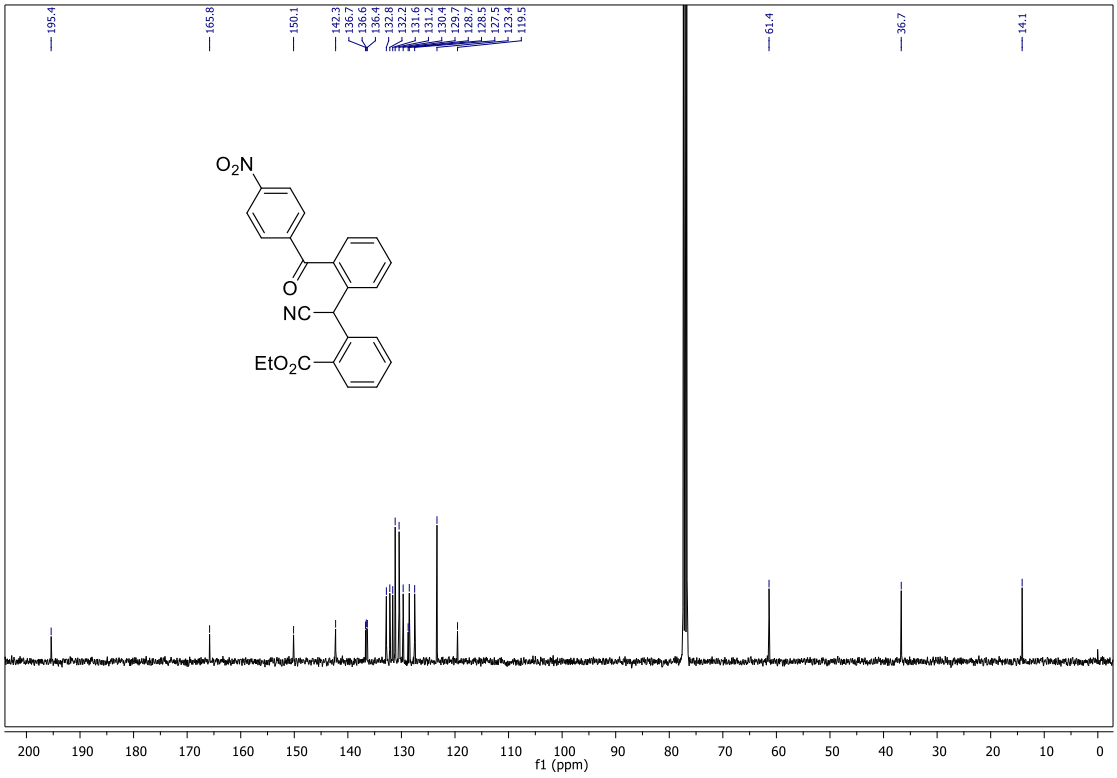
^{1}H NMR of compound **3p′** in $CDCl_3$ (400 MHz)



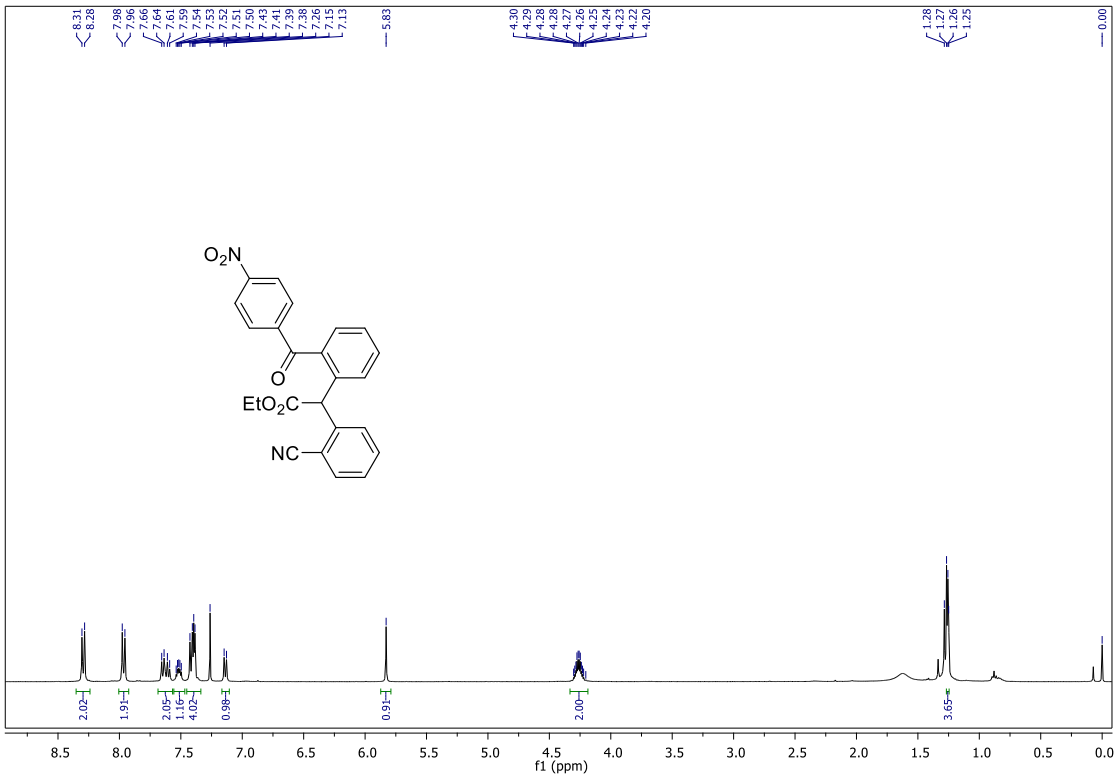
^{13}C NMR of compound **3p′** in $CDCl_3$ (101 MHz)



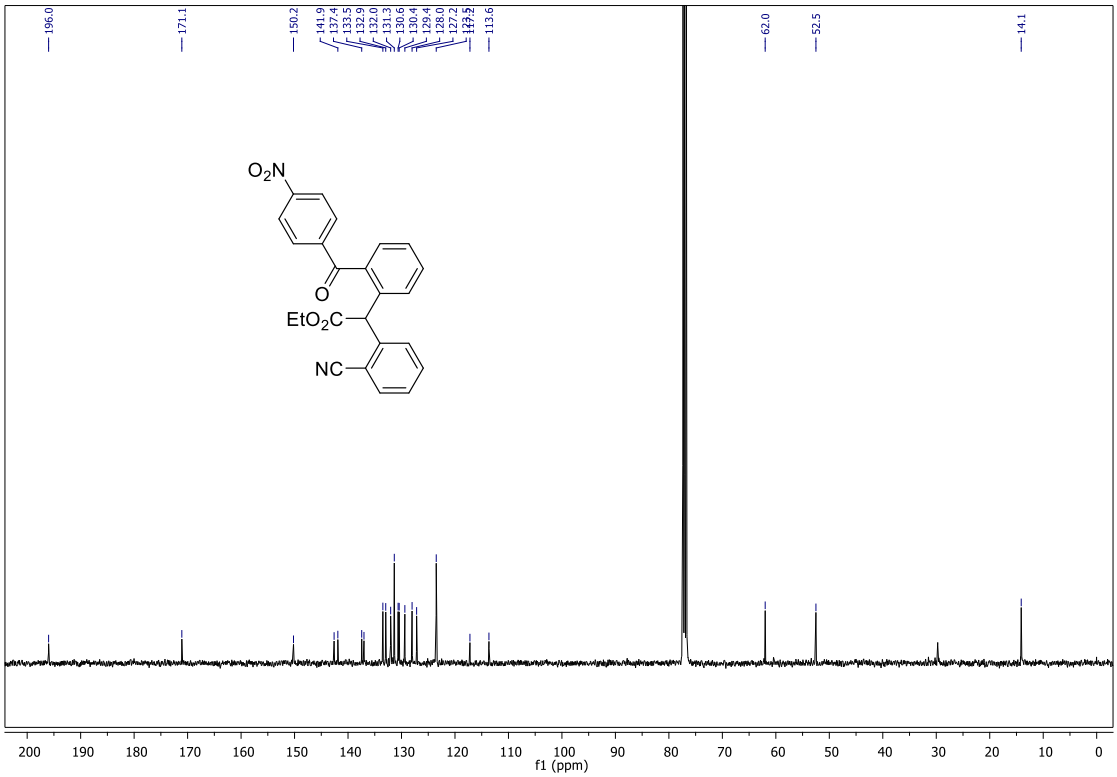
^{1}H NMR of compound **3q** in $CDCl_3$ (400 MHz)



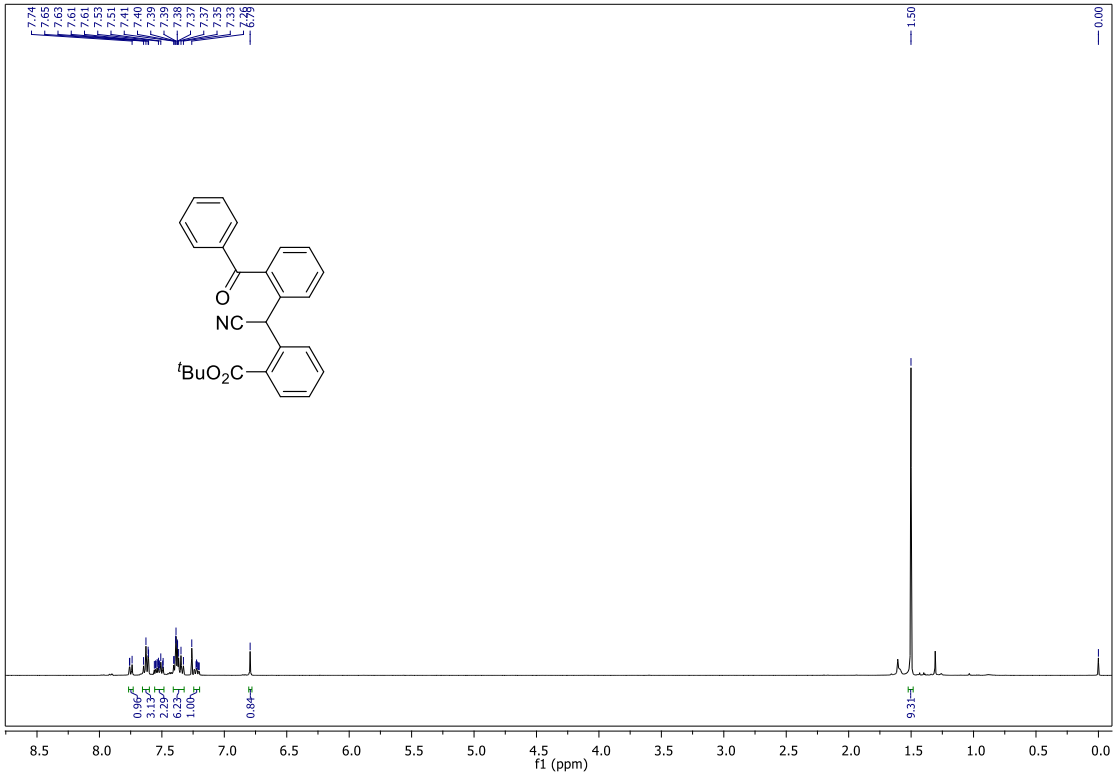
^{13}C NMR of compound **3q** in $CDCl_3$ (101 MHz)



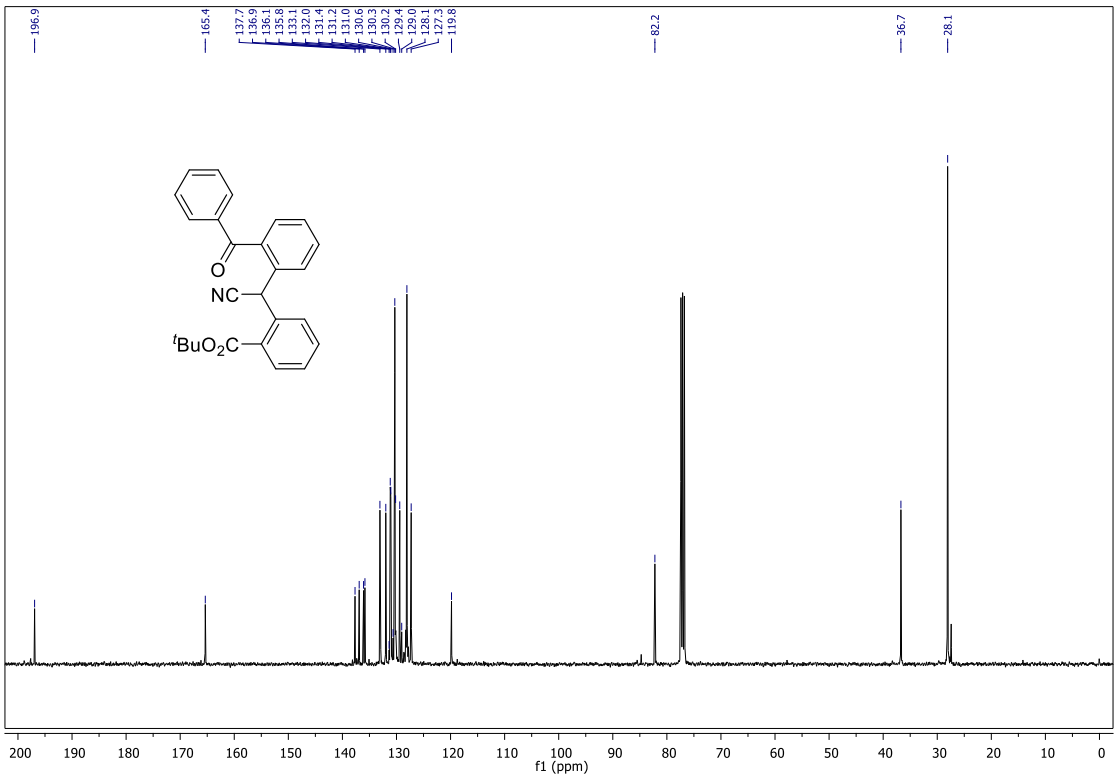
^{1}H NMR of compound **3q′** in $CDCl_3$ (400 MHz)



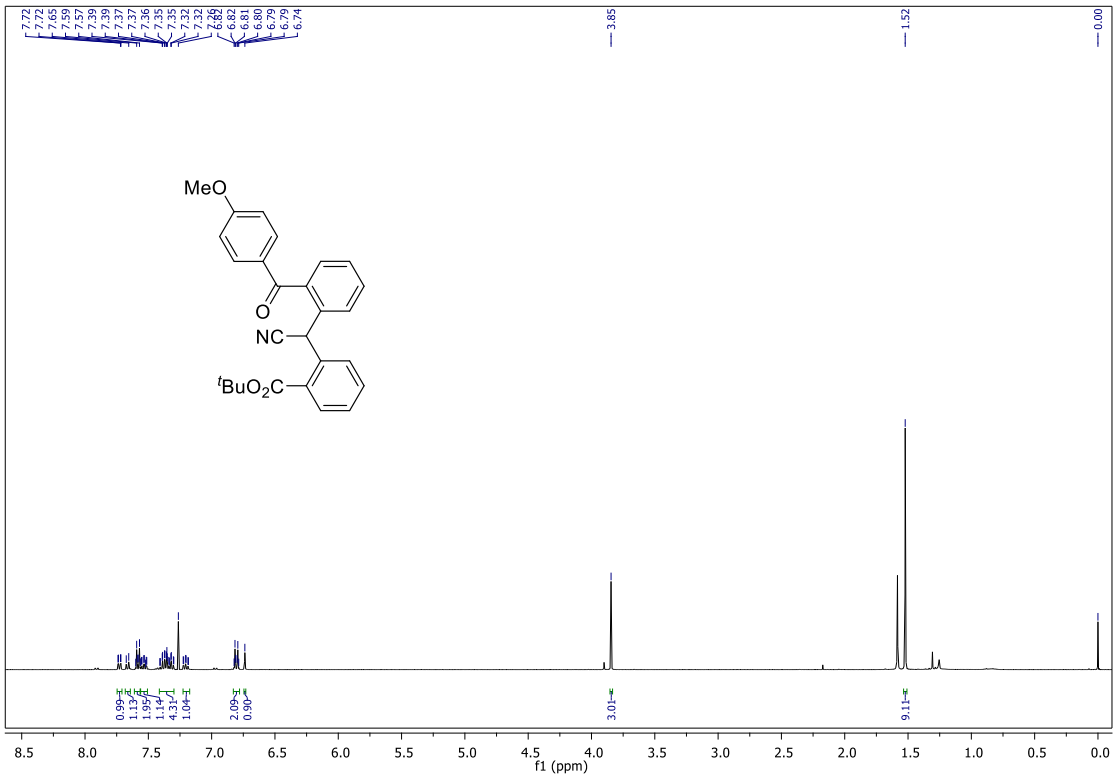
^{13}C NMR of compound **3q′** in $CDCl_3$ (101 MHz)



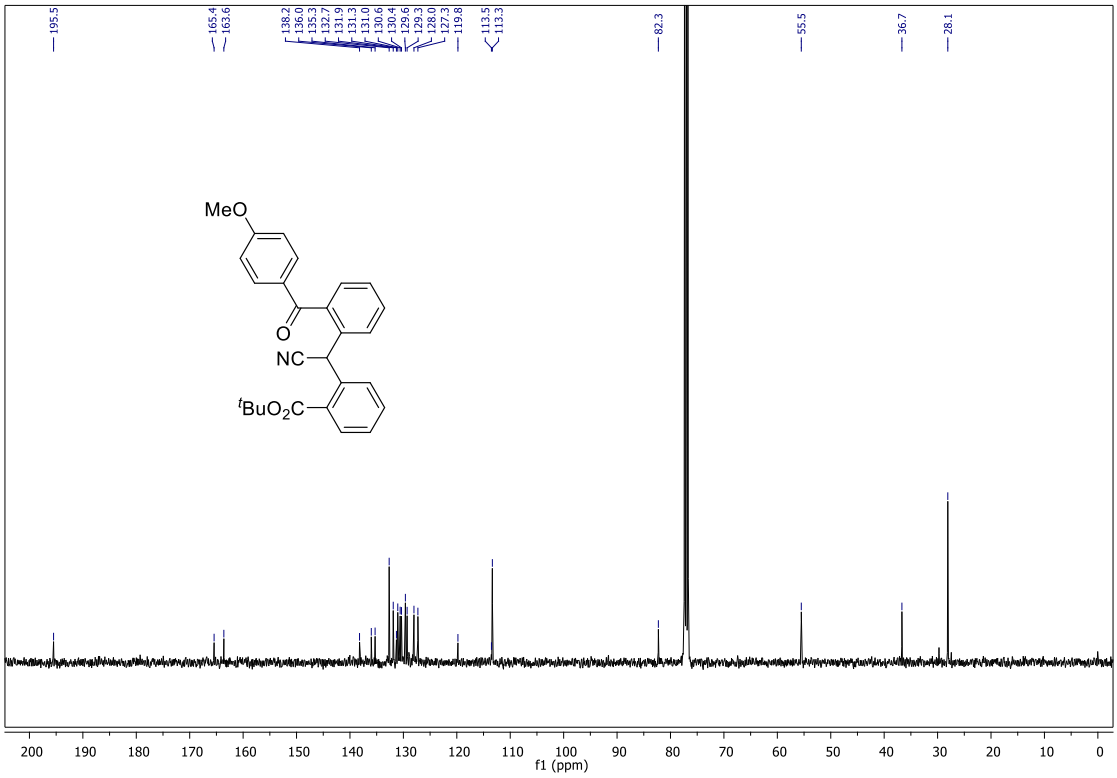
^{1}H NMR of compound **3r** in $CDCl_3$ (400 MHz)



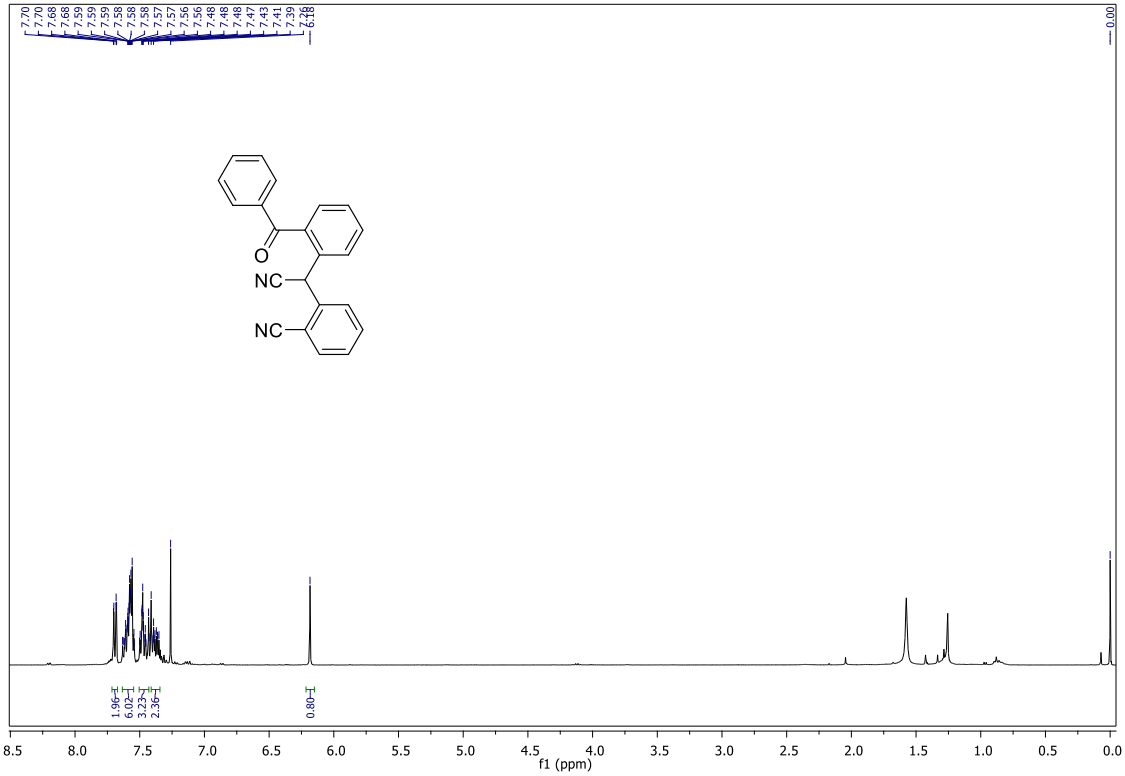
^{13}C NMR of compound **3r** in $CDCl_3$ (101 MHz)



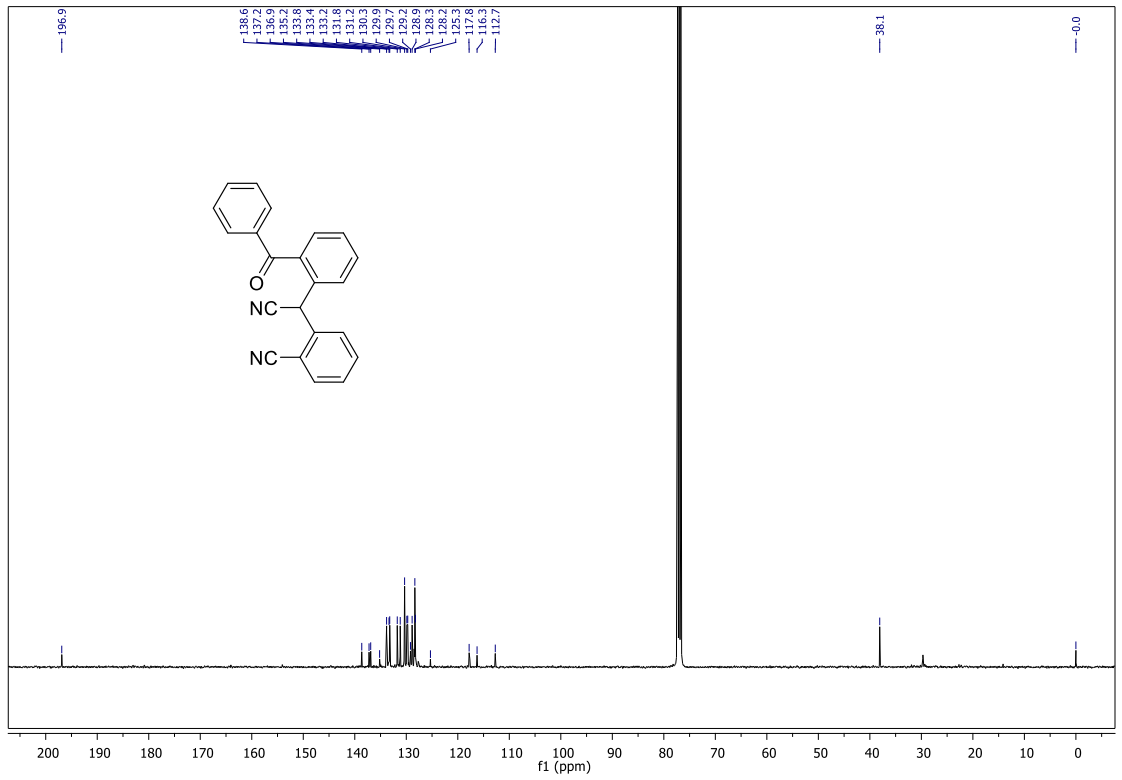
^{1}H NMR of compound **3s** in $CDCl_3$ (400 MHz)



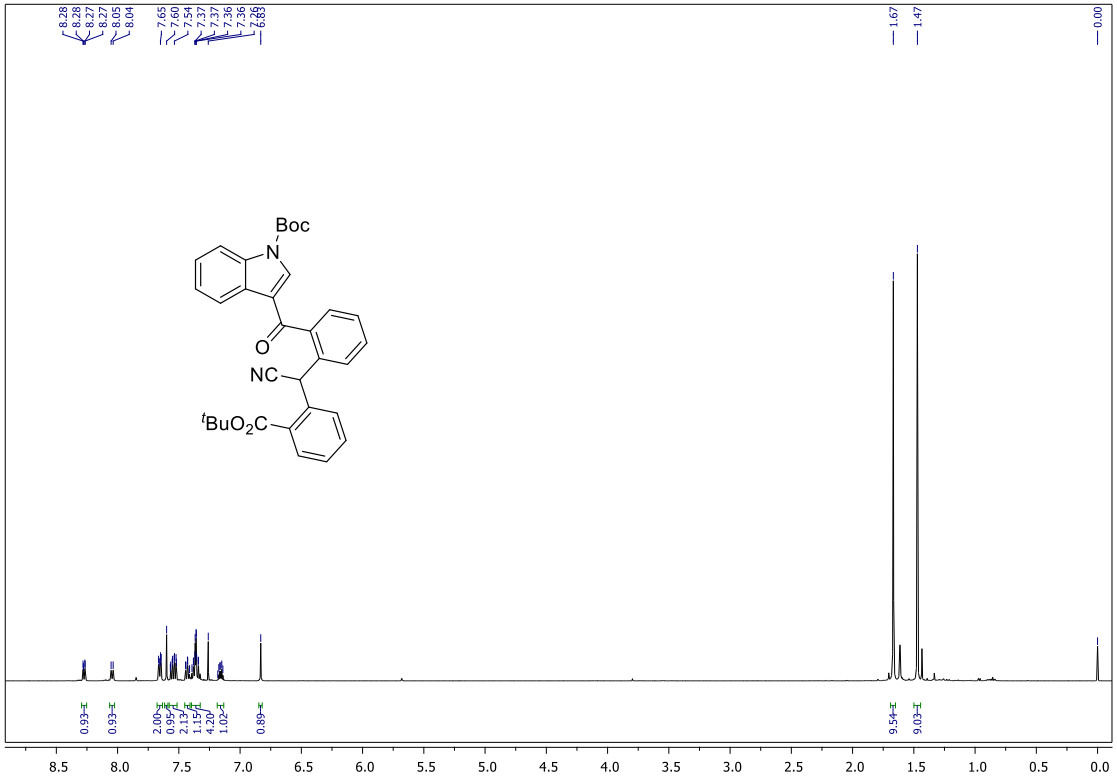
^{13}C NMR of compound **3s** in $CDCl_3$ (101 MHz)



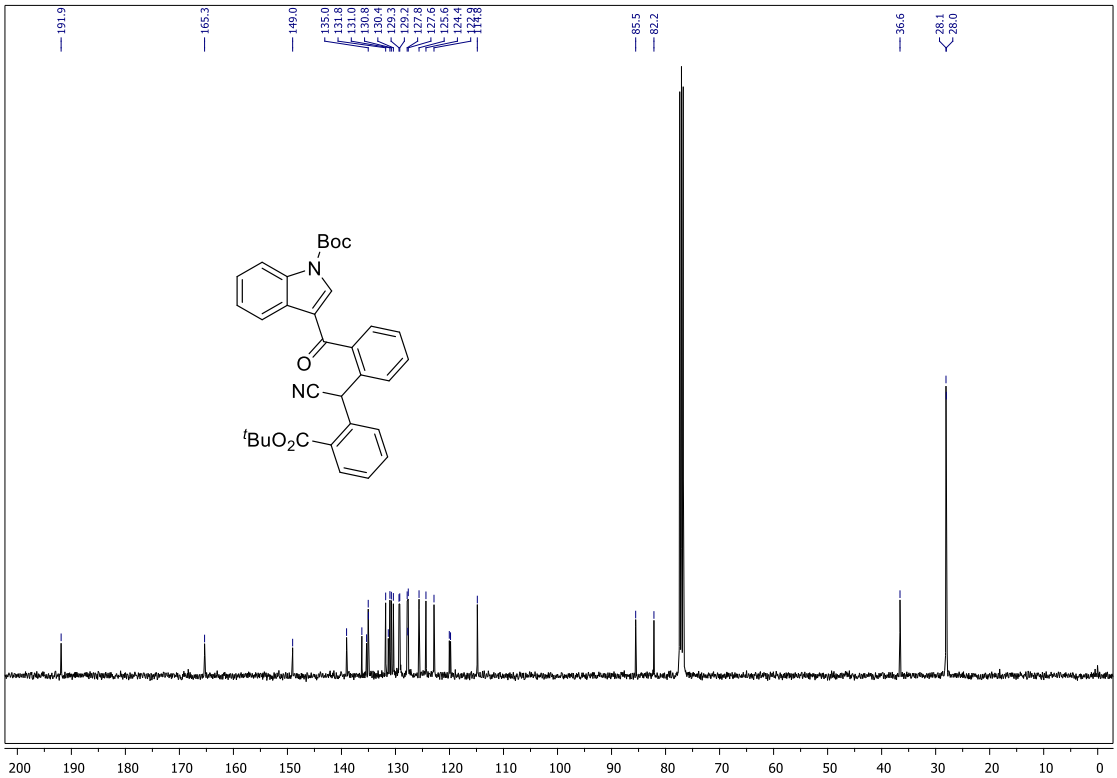
^{1}H NMR of compound **3t** in $CDCl_3$ (400 MHz)



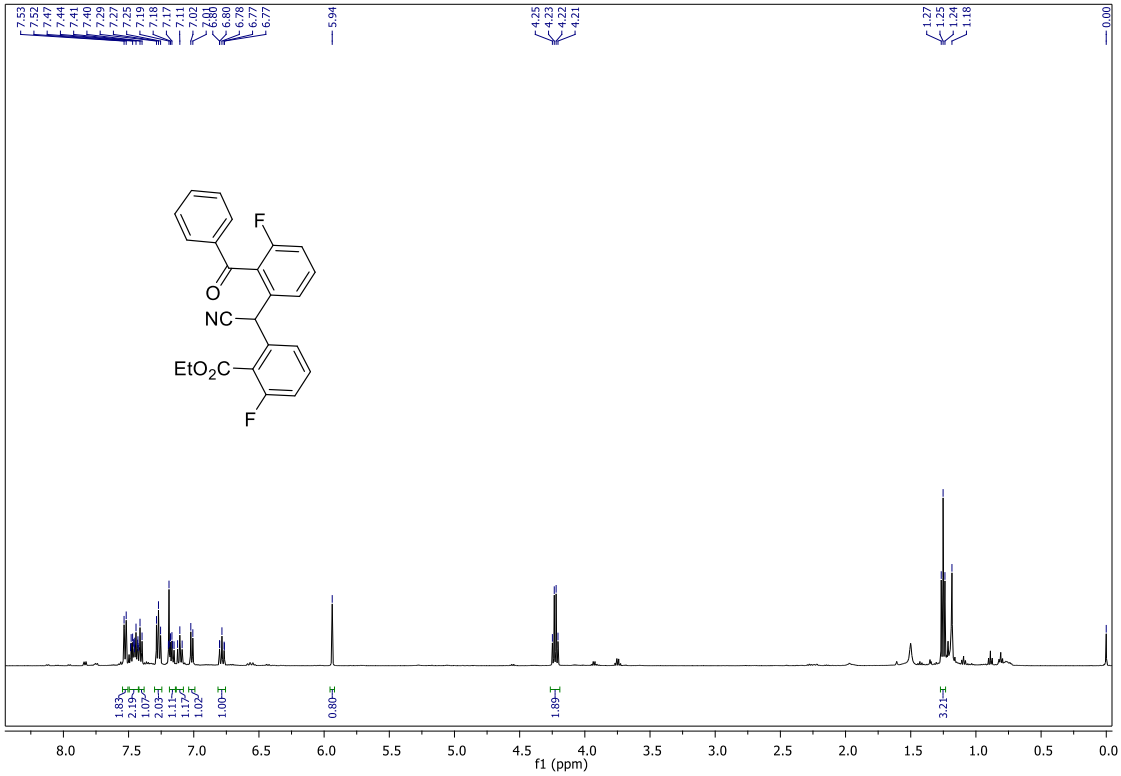
^{13}C NMR of compound **3t** in $CDCl_3$ (101 MHz)



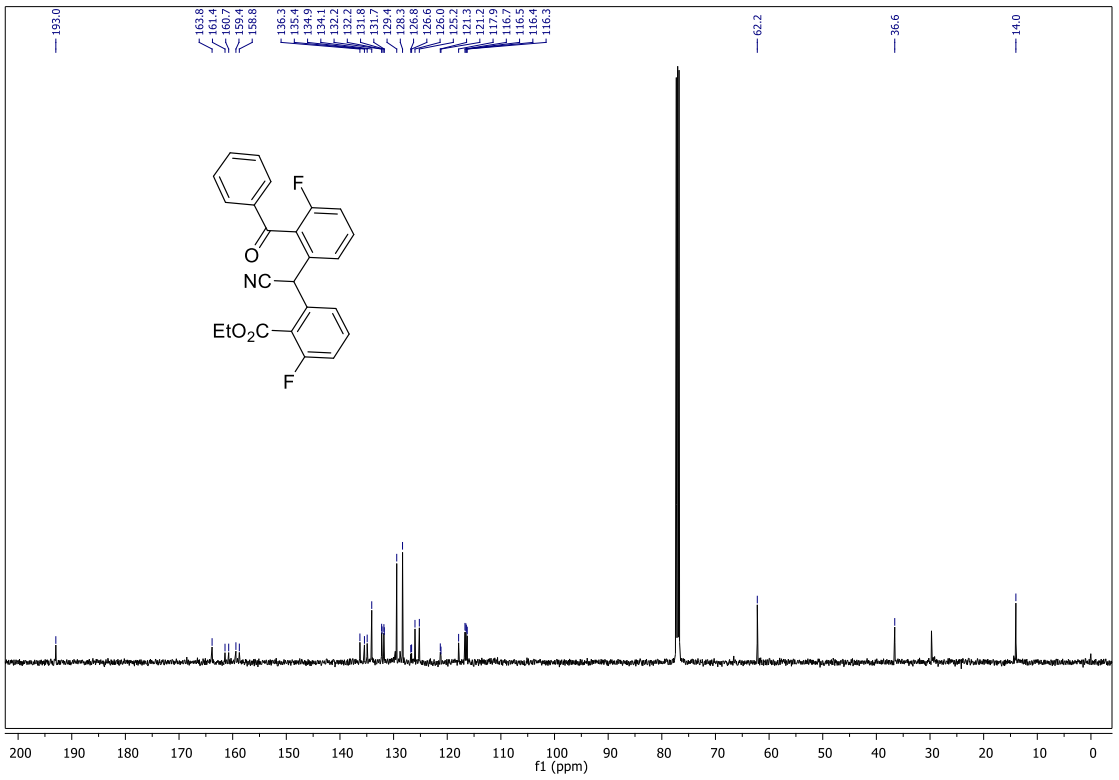
^{1}H NMR of compound **3u** in $CDCl_3$ (500 MHz)



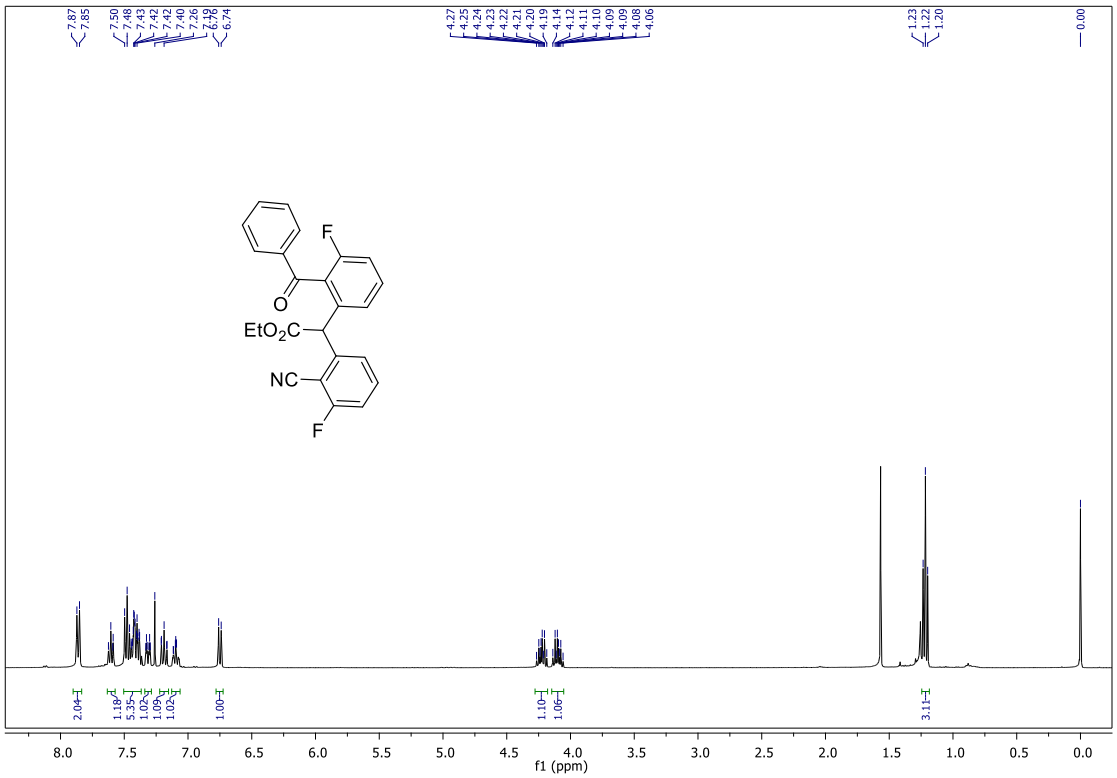
^{13}C NMR of compound **3u** in $CDCl_3$ (101 MHz)



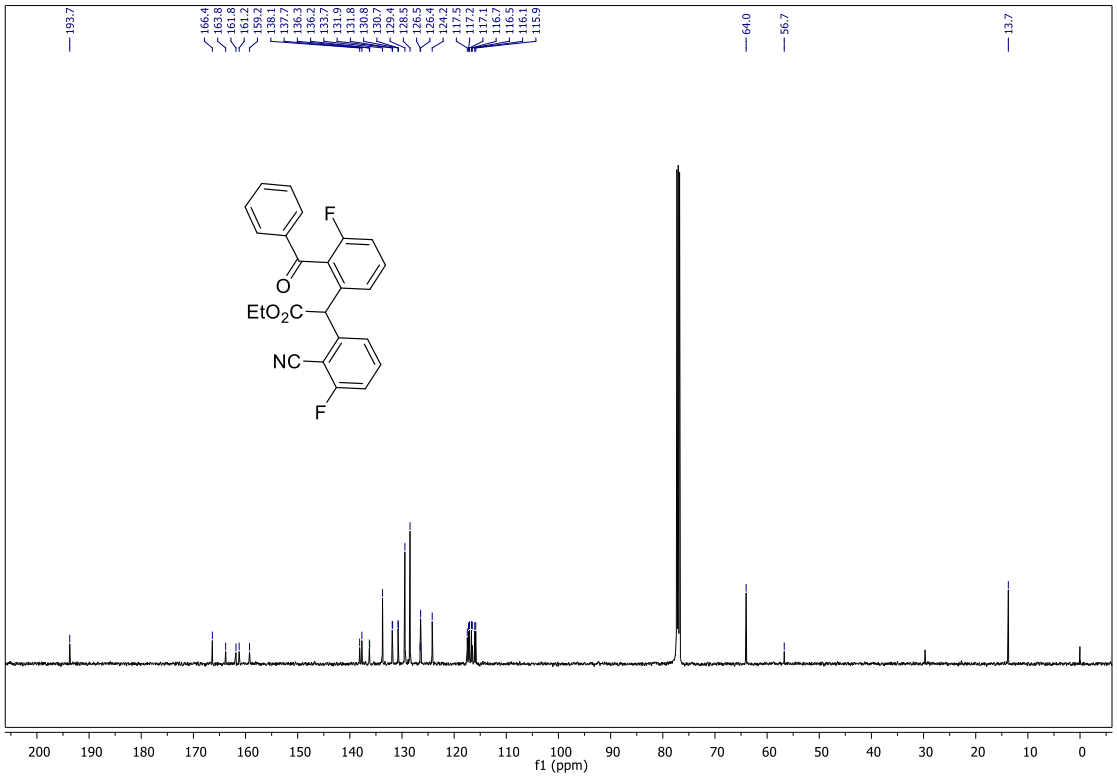
^{1}H NMR of compound **3v** in $CDCl_3$ (500 MHz)



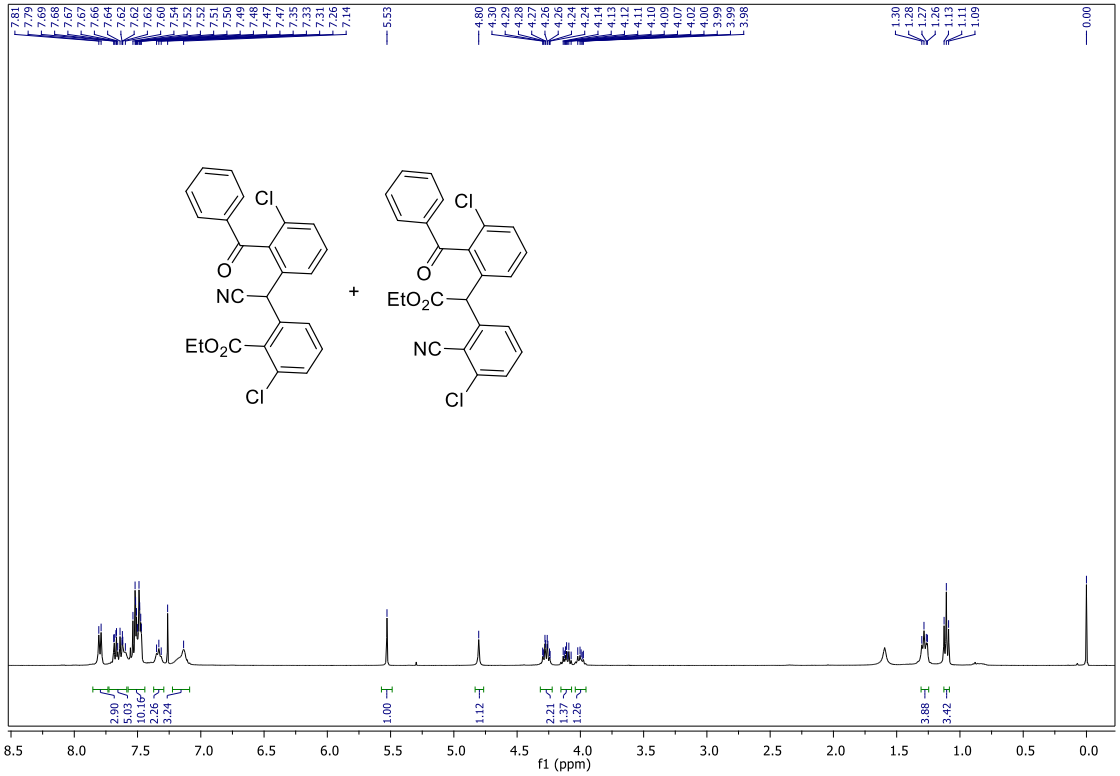
^{13}C NMR of compound **3v** in $CDCl_3$ (126 MHz)



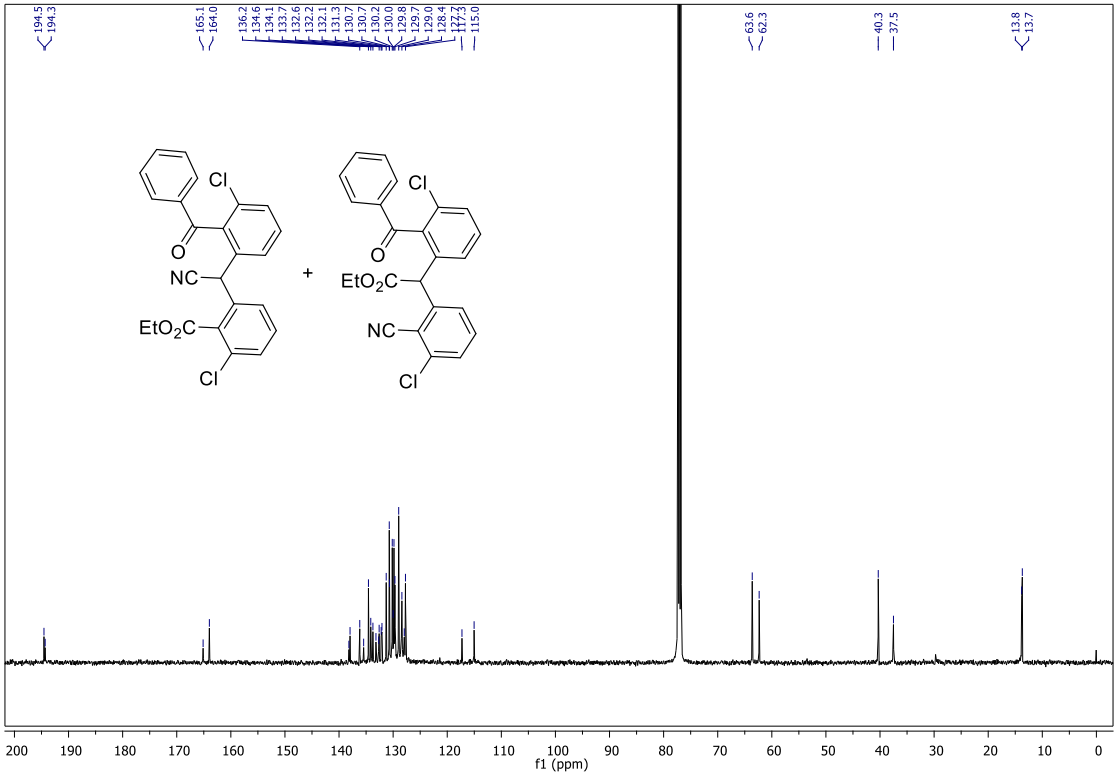
^{1}H NMR of compound **3v′** in $CDCl_3$ (400 MHz)



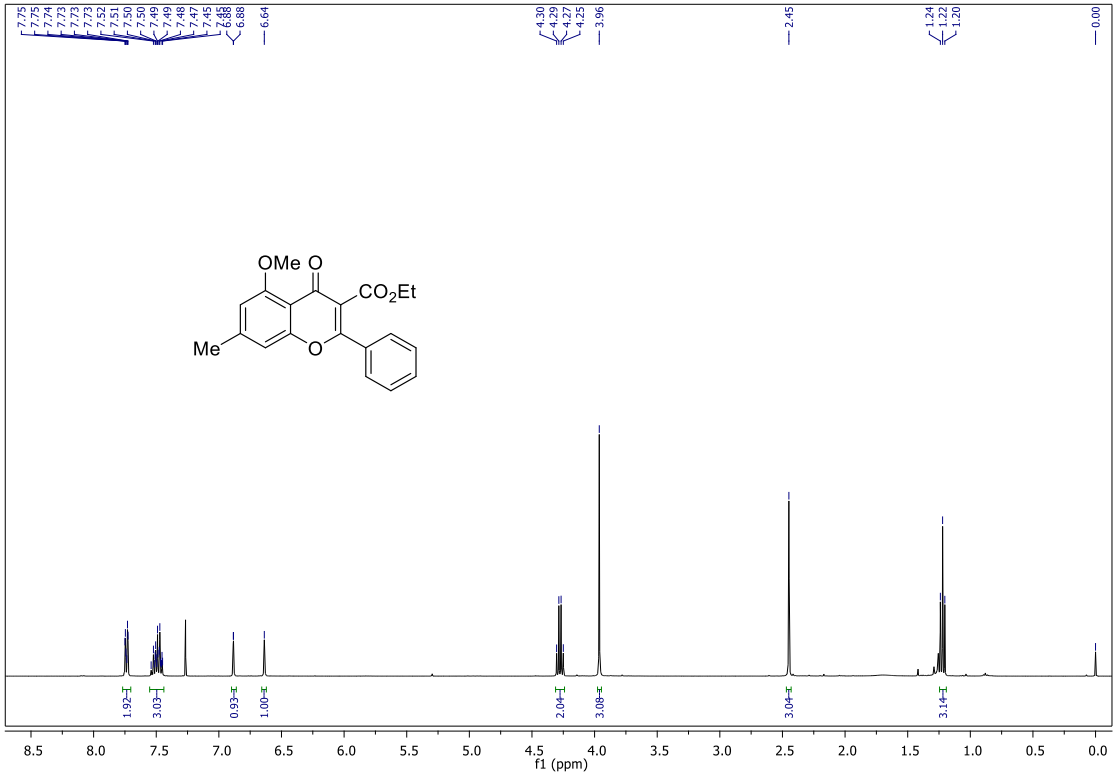
^{13}C NMR of compound **3v′** in $CDCl_3$ (126 MHz)



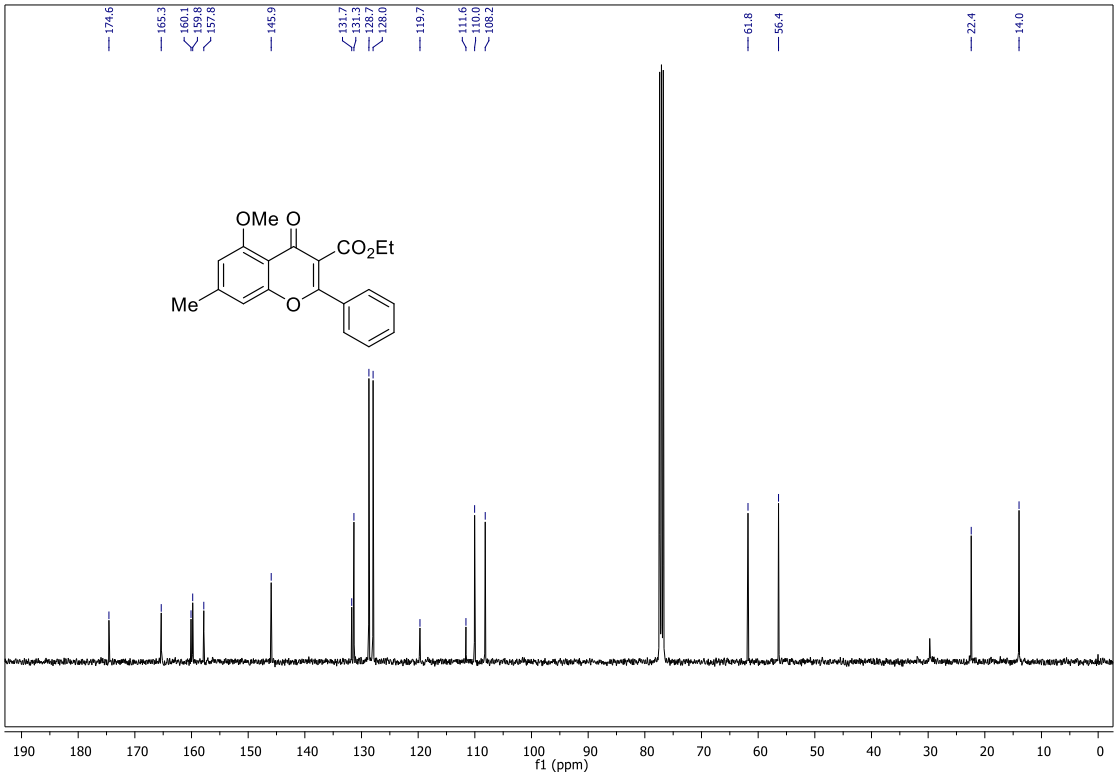
^{1}H NMR of compound **3w** & **3w′** in $CDCl_3$ (400 MHz)



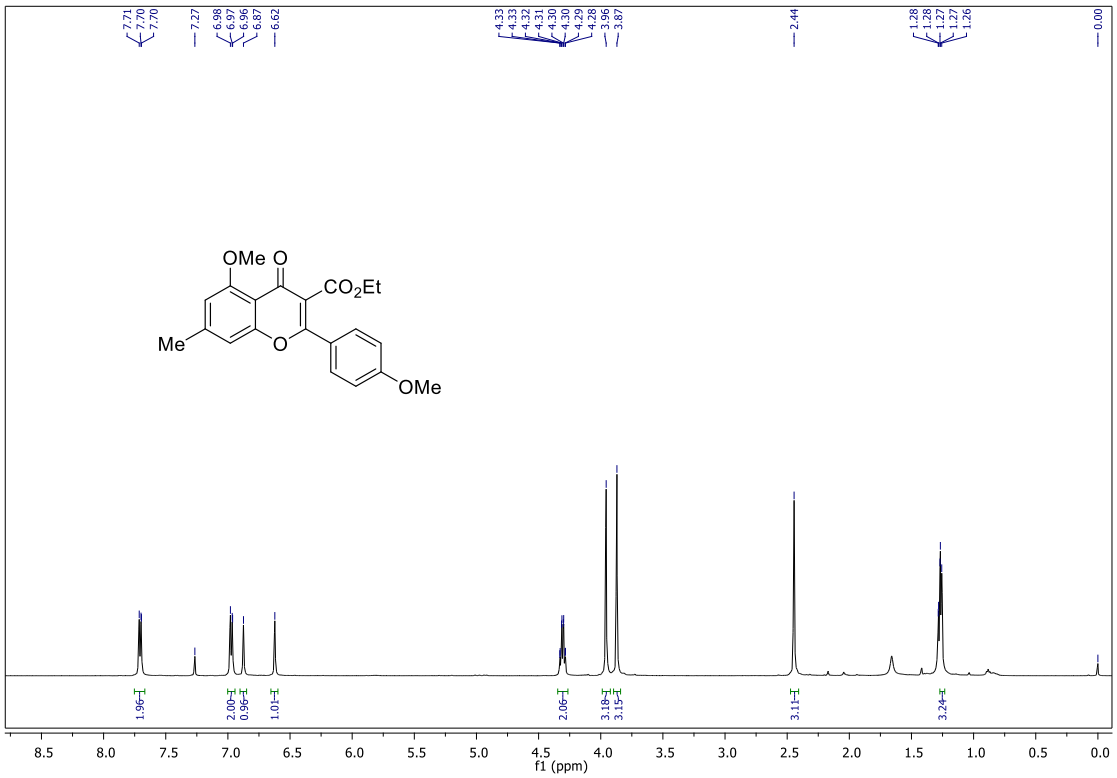
^{13}C NMR of compound **3w** & **3w′** in $CDCl_3$ (126 MHz)



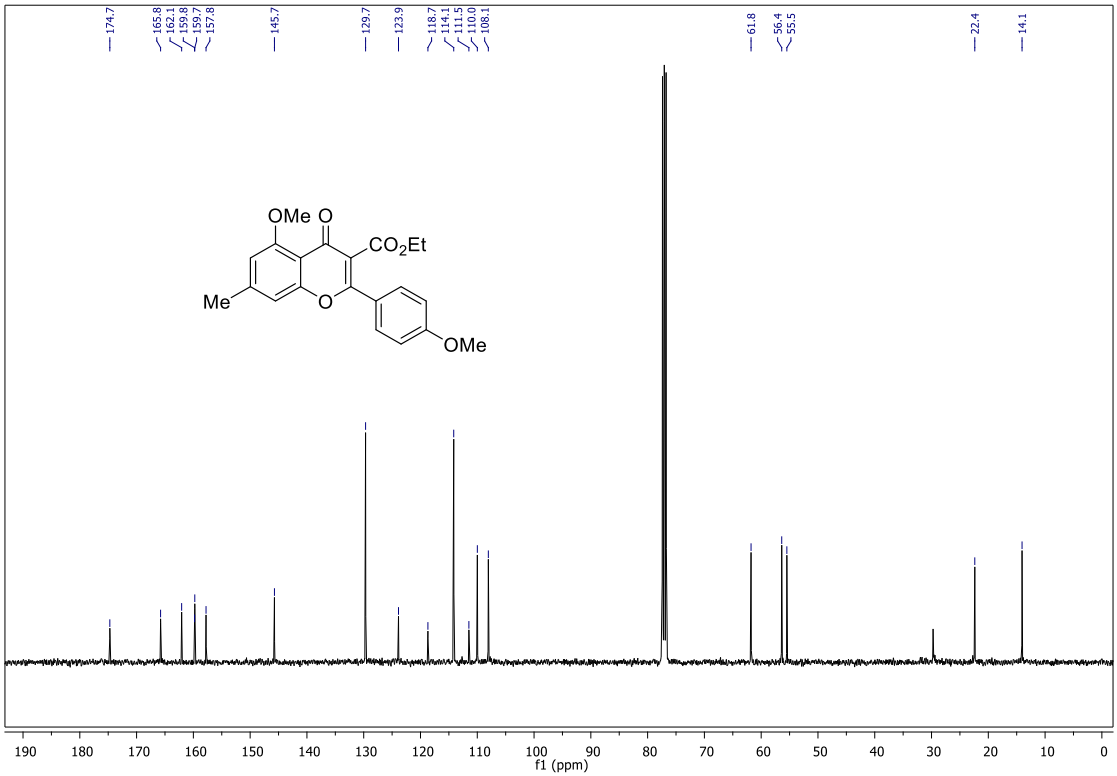
^{1}H NMR of compound **4a** in $CDCl_3$ (400 MHz)



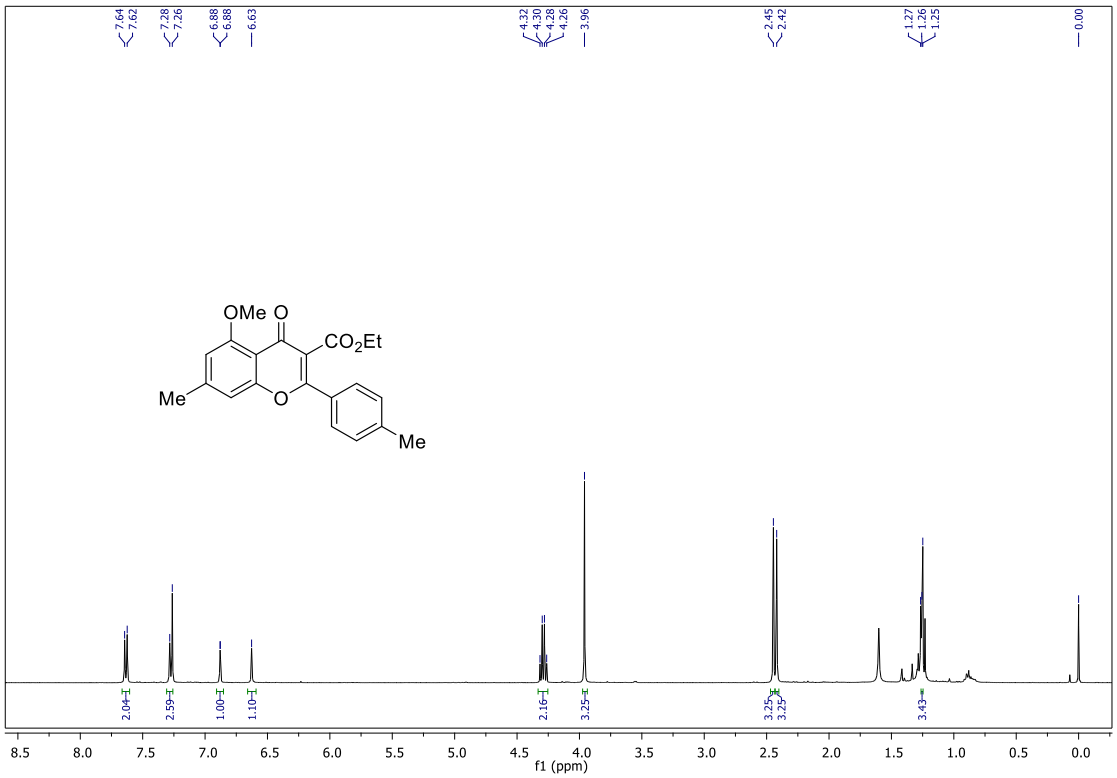
^{13}C NMR of compound **4a** in $CDCl_3$ (101 MHz)



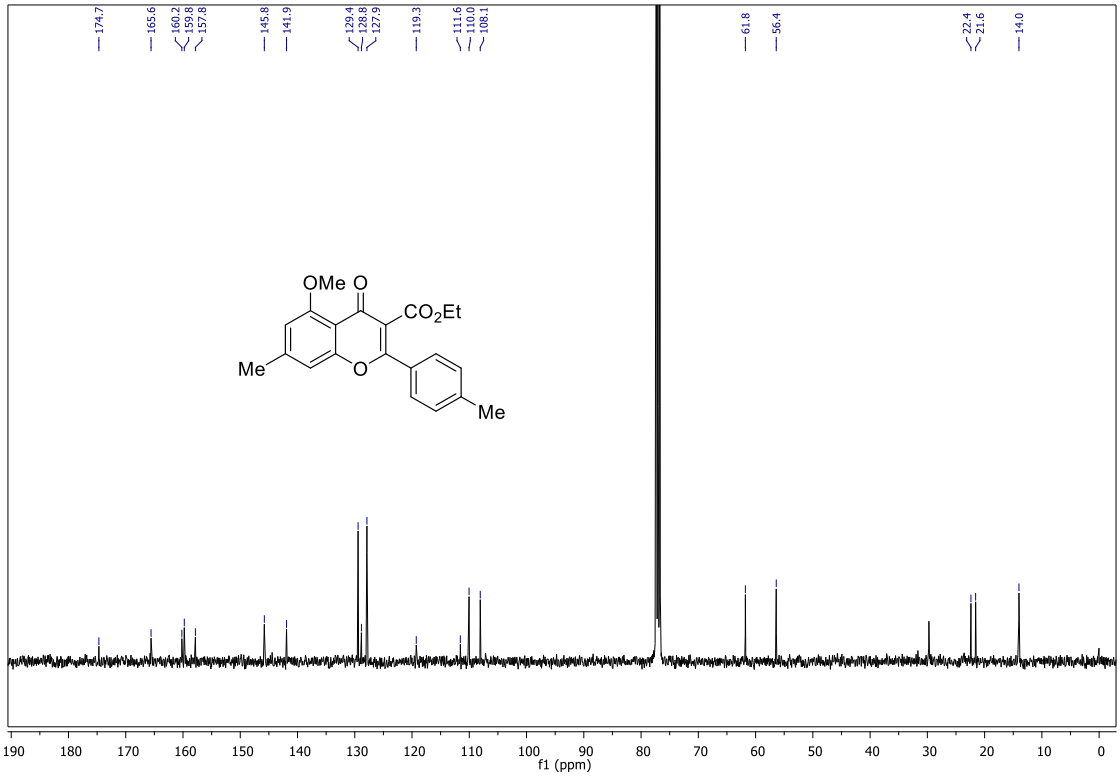
^{1}H NMR of compound **4b** in $CDCl_3$ (500 MHz)



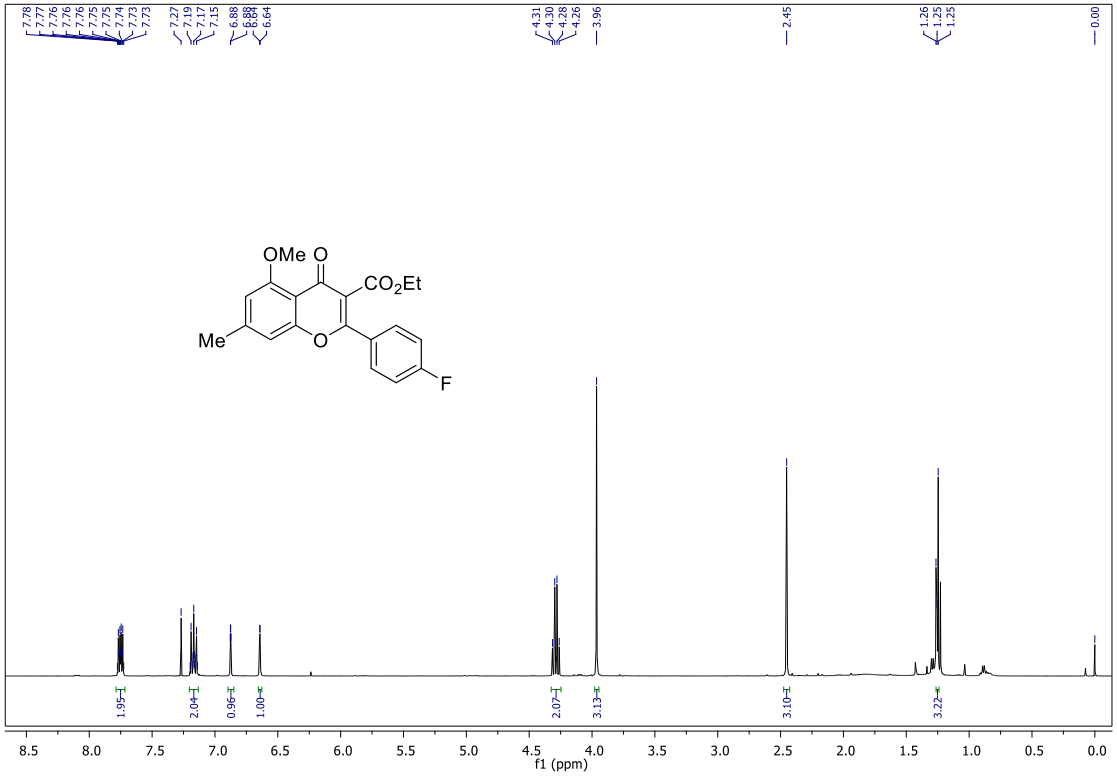
^{13}C NMR of compound **4b** in $CDCl_3$ (101 MHz)



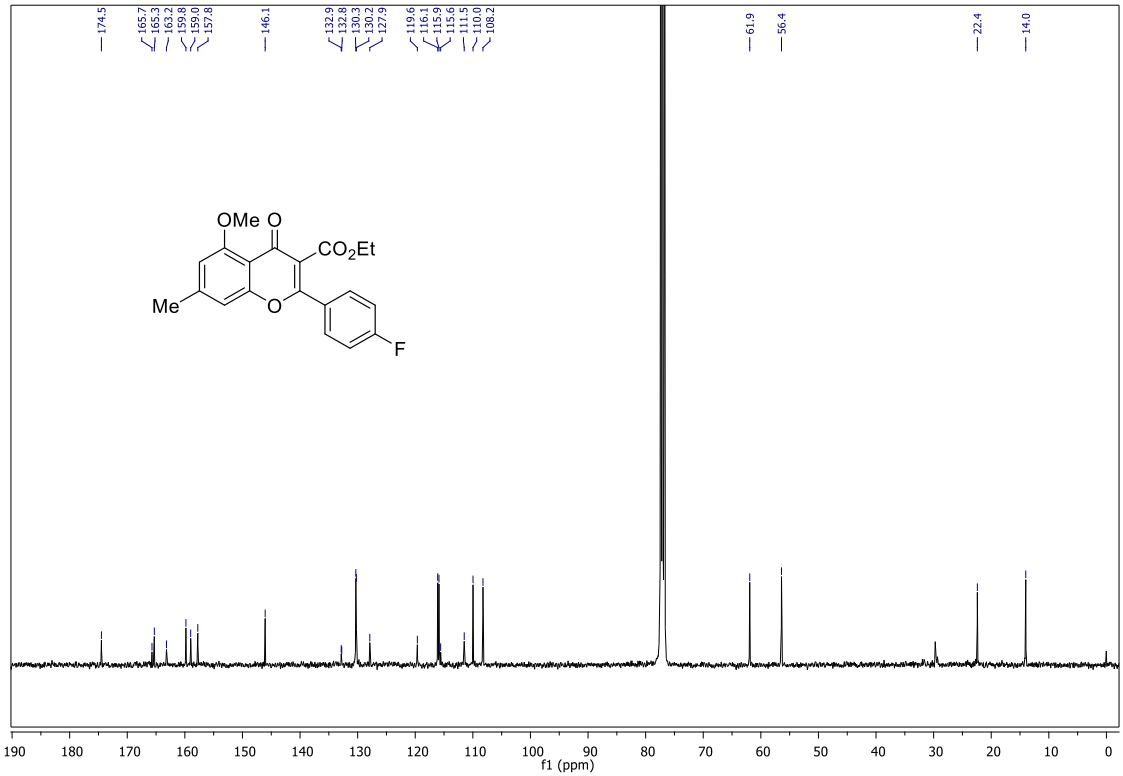
^{1}H NMR of compound **4c** in $CDCl_3$ (400 MHz)



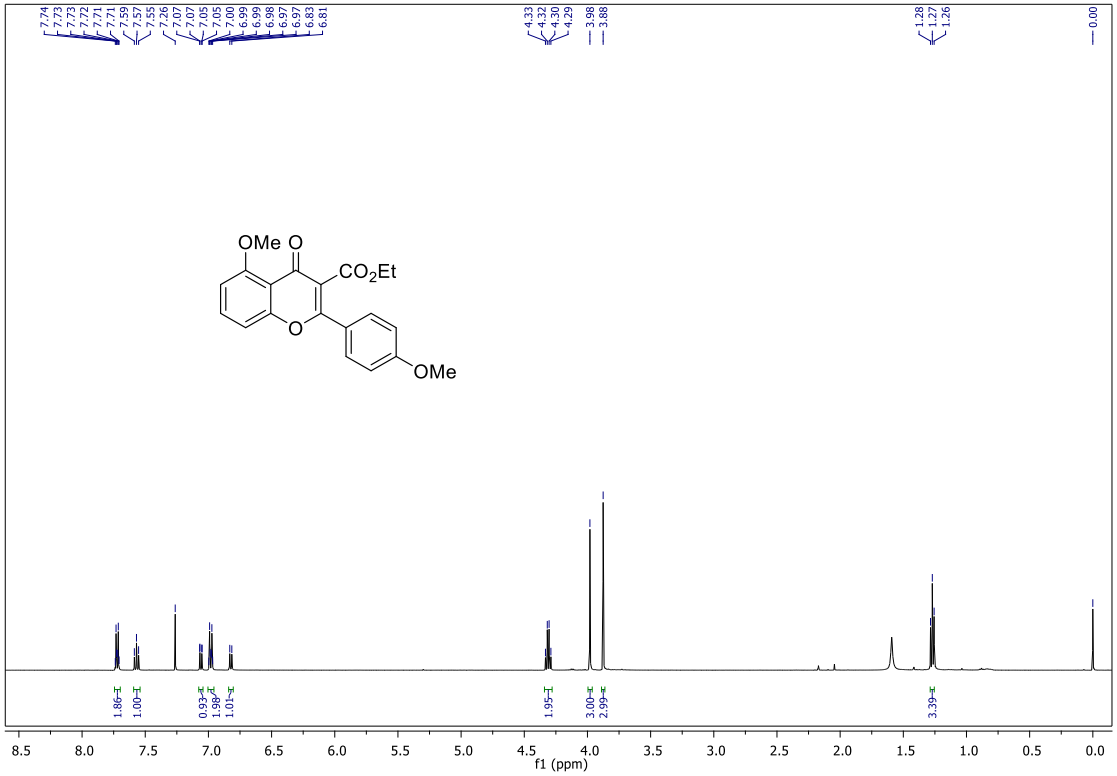
^{13}C NMR of compound **4c** in $CDCl_3$ (101 MHz)



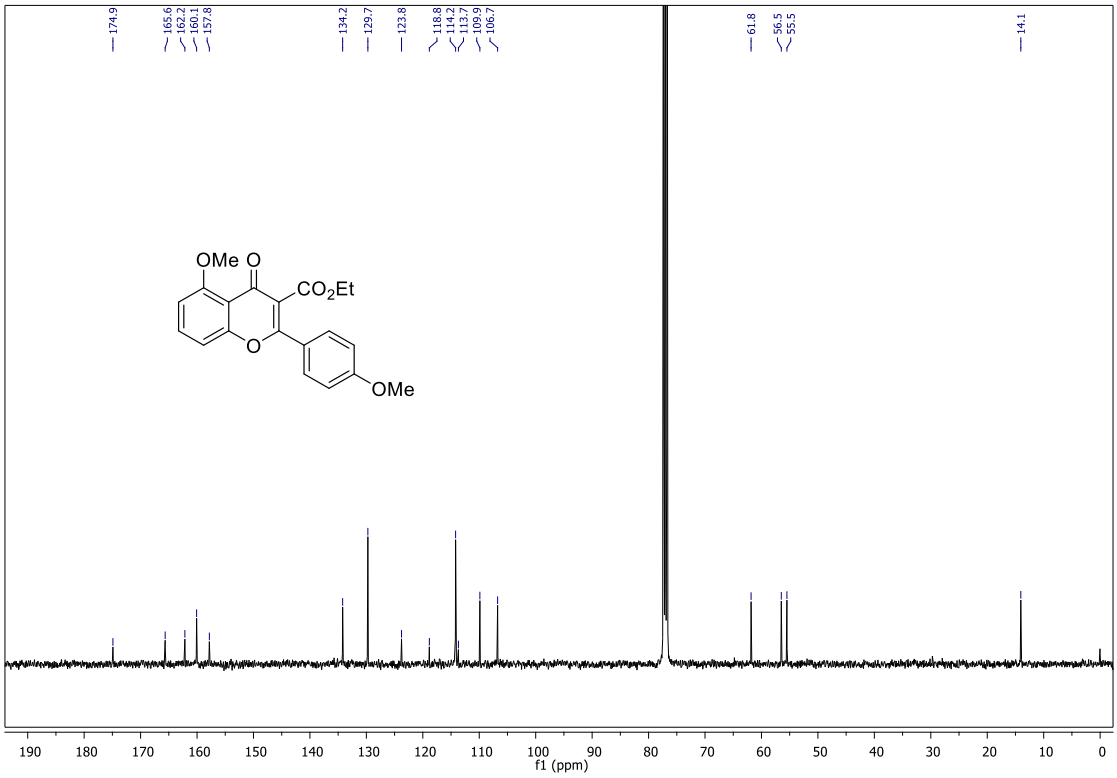
^{1}H NMR of compound **4d** in $CDCl_3$ (400 MHz)



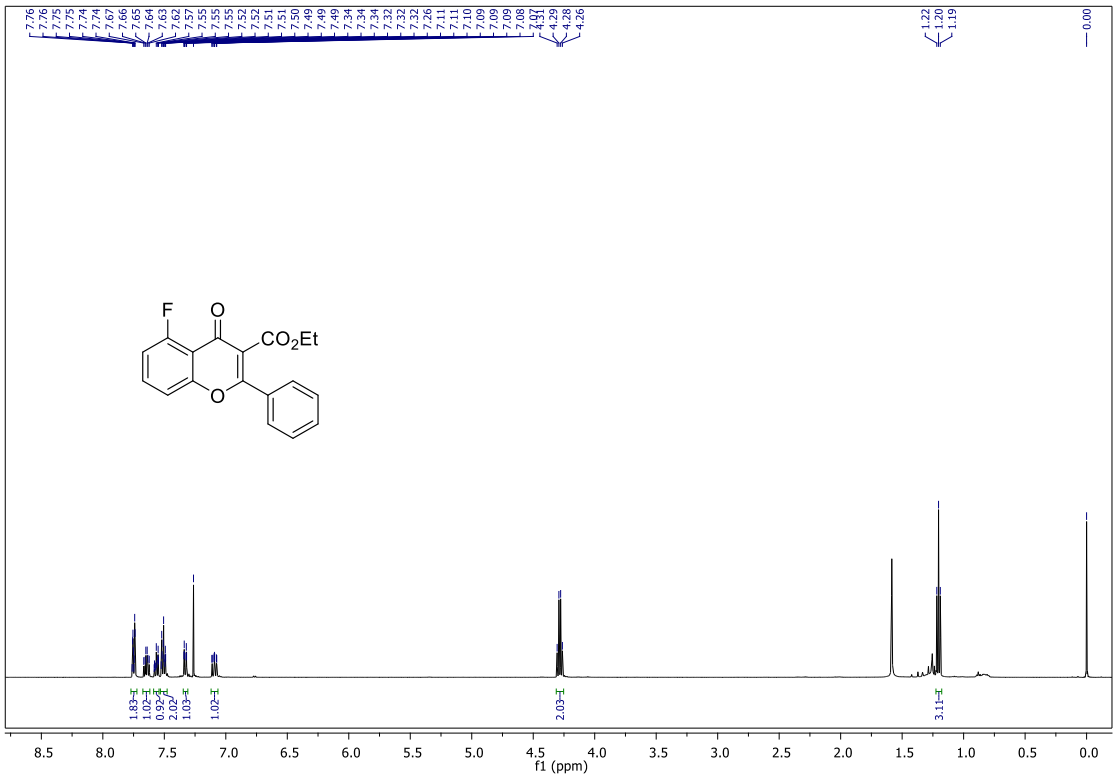
^{13}C NMR of compound **4d** in $CDCl_3$ (101 MHz)



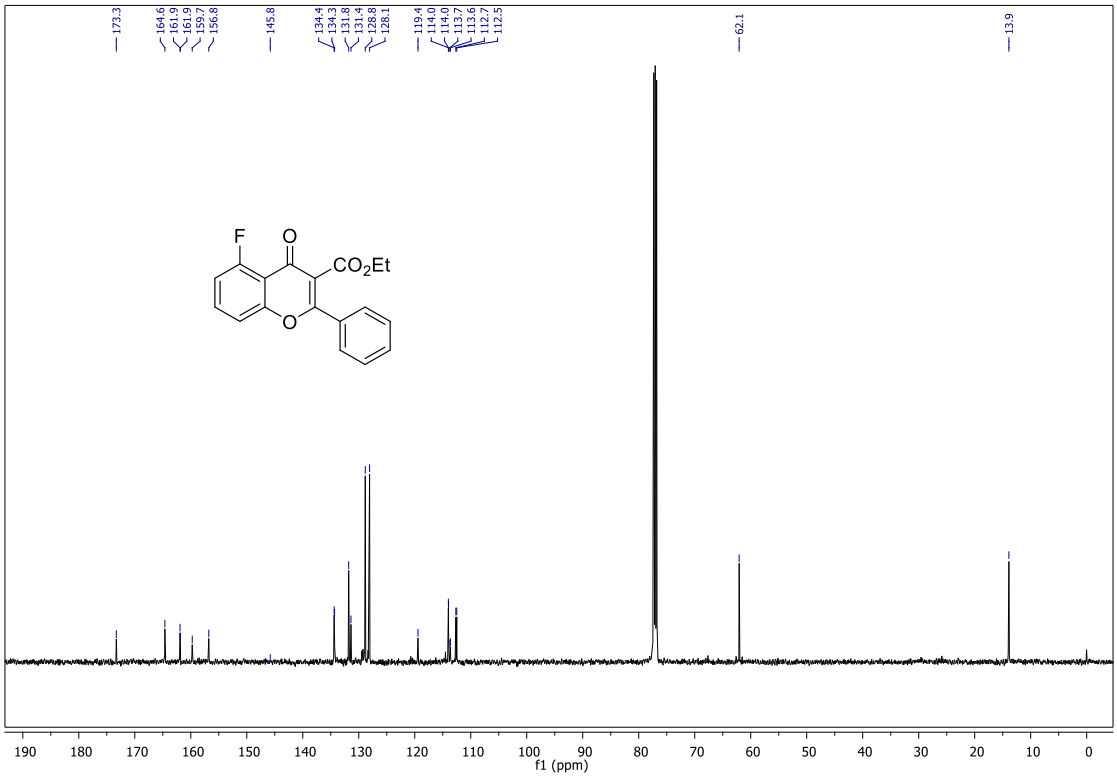
^{1}H NMR of compound **4e** in $CDCl_3$ (500 MHz)



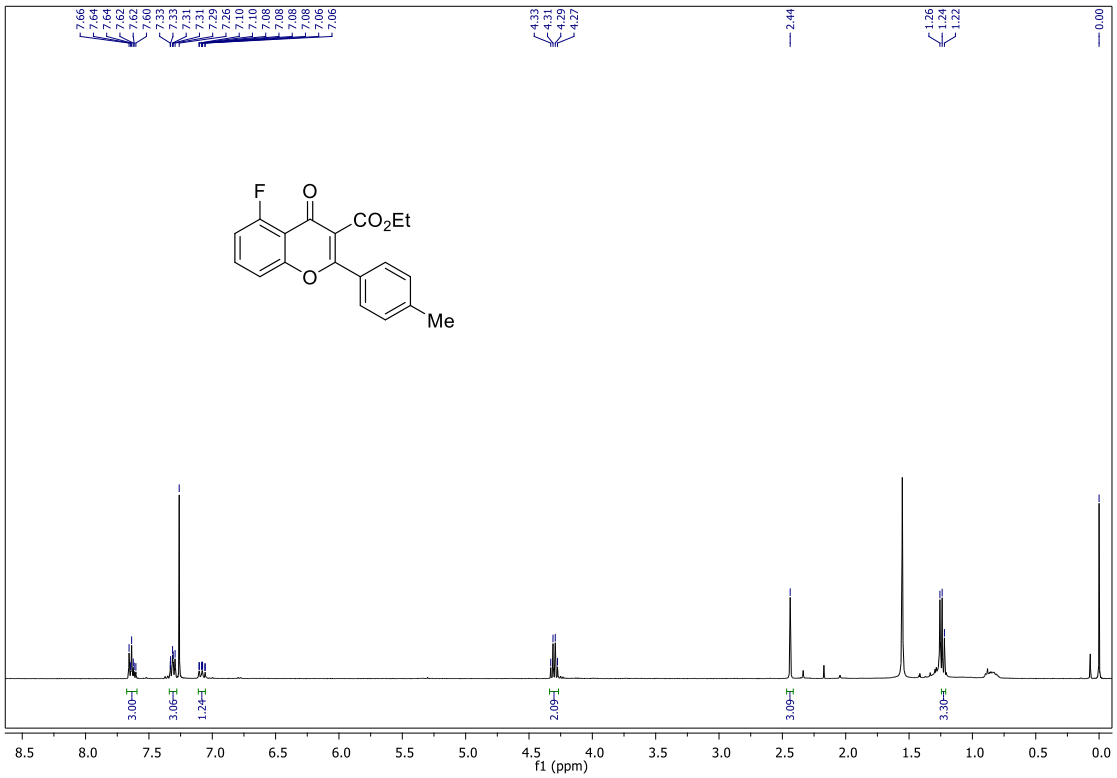
^{13}C NMR of compound **4e** in $CDCl_3$ (101 MHz)



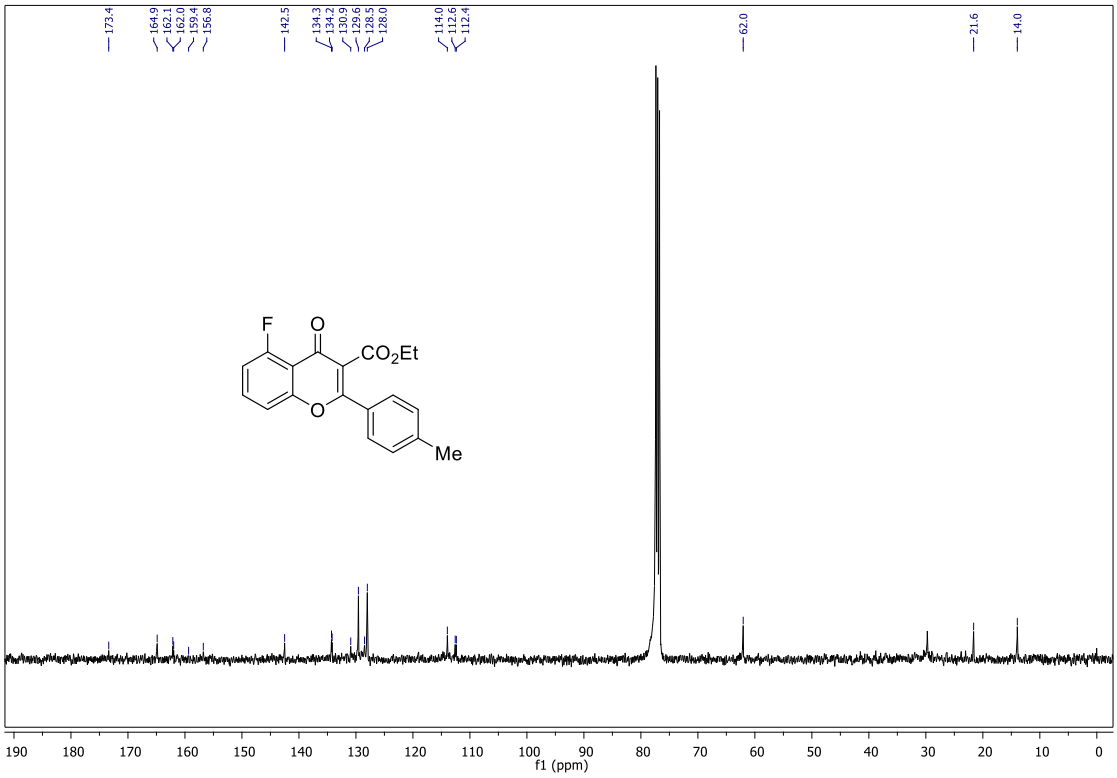
^{1}H NMR of compound **4f** in $CDCl_3$ (500 MHz)



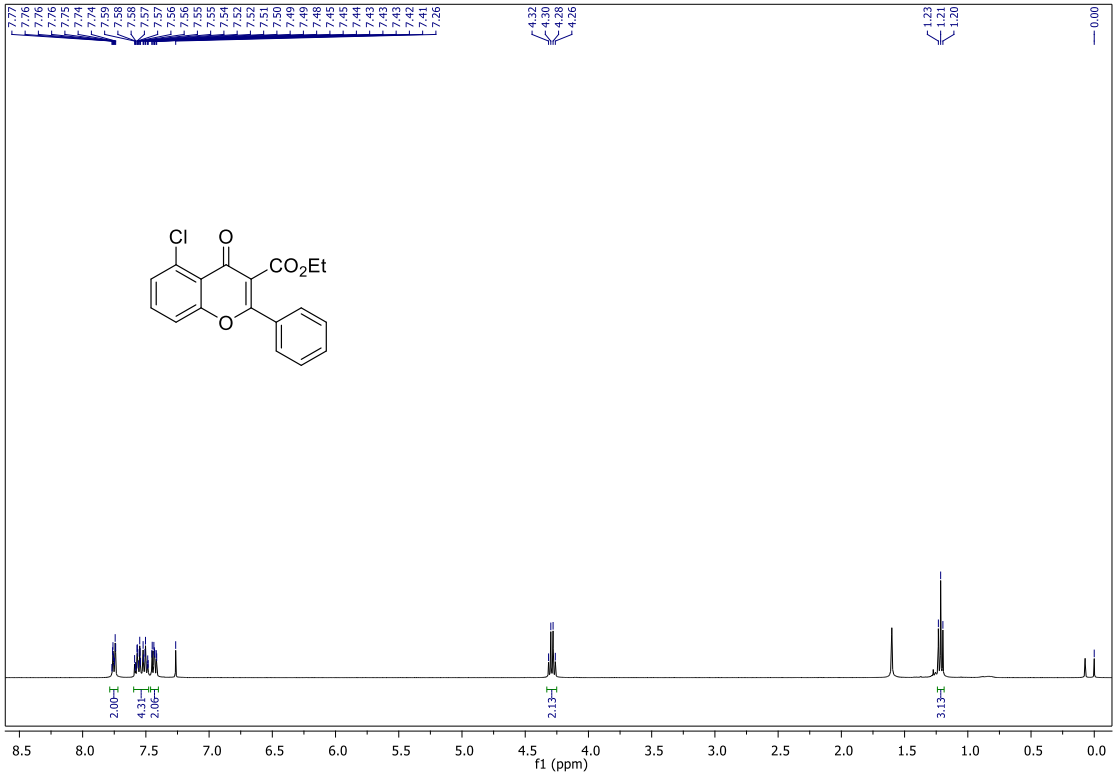
^{13}C NMR of compound **4f** in $CDCl_3$ (126 MHz)



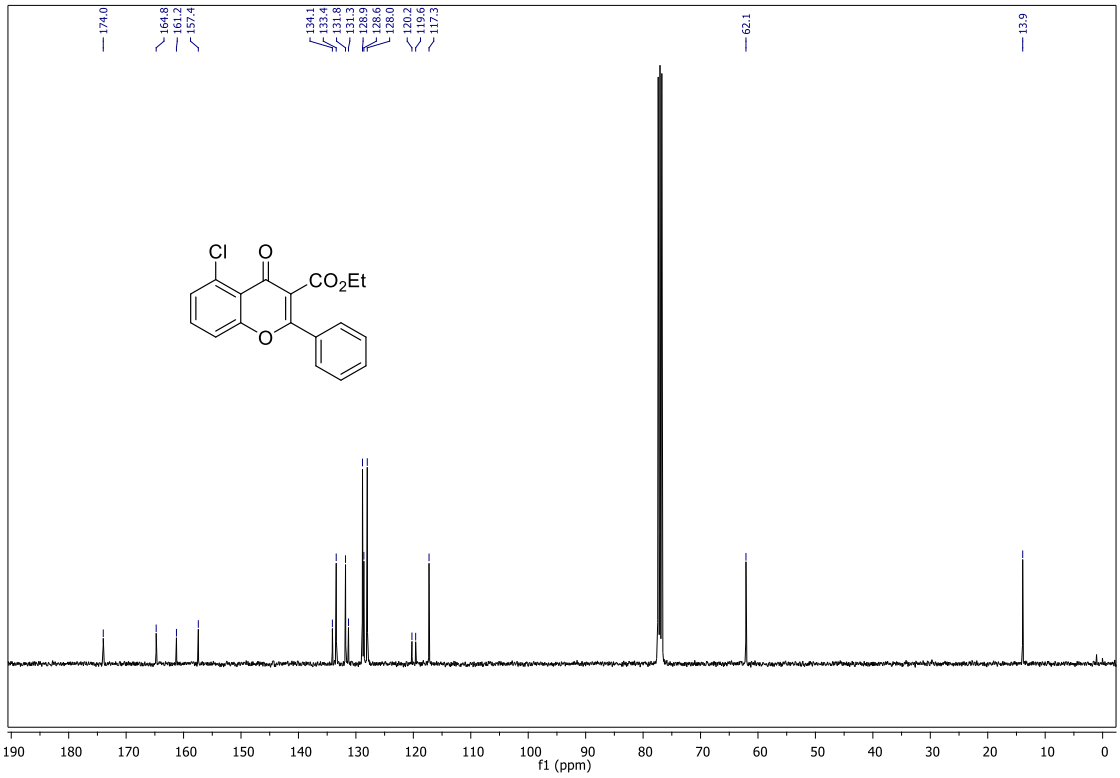
^{1}H NMR of compound **4g** in $CDCl_3$ (400 MHz)



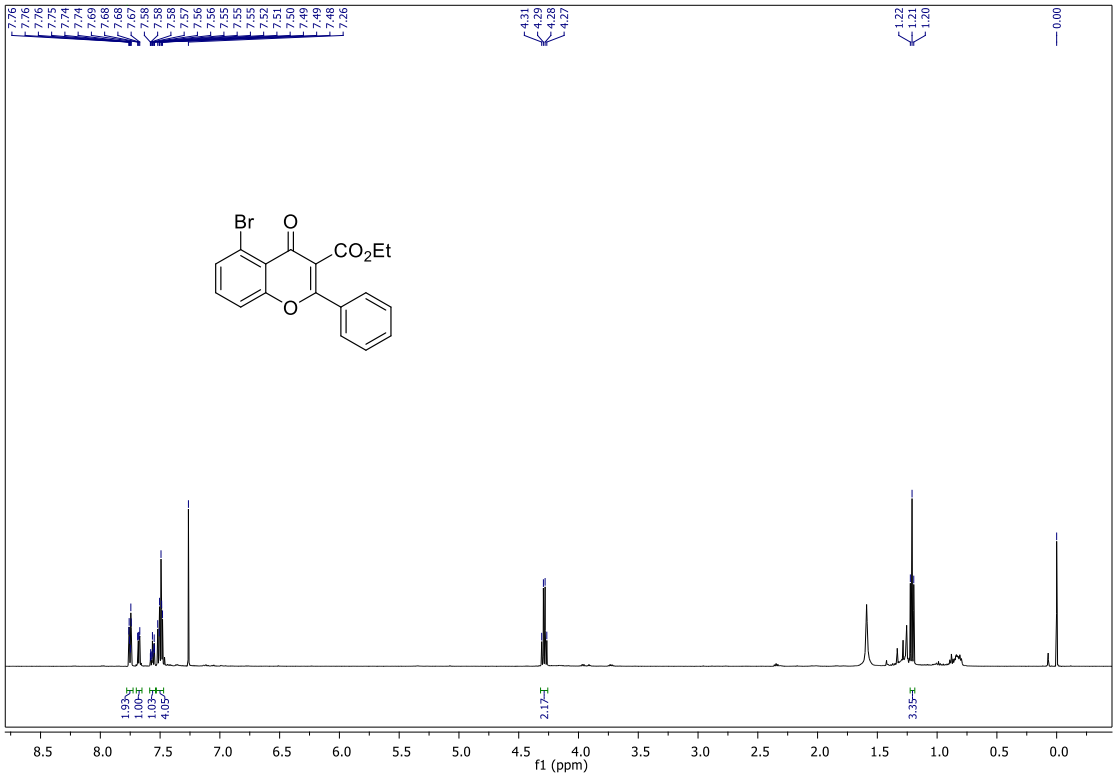
^{13}C NMR of compound **4g** in $CDCl_3$ (101 MHz)



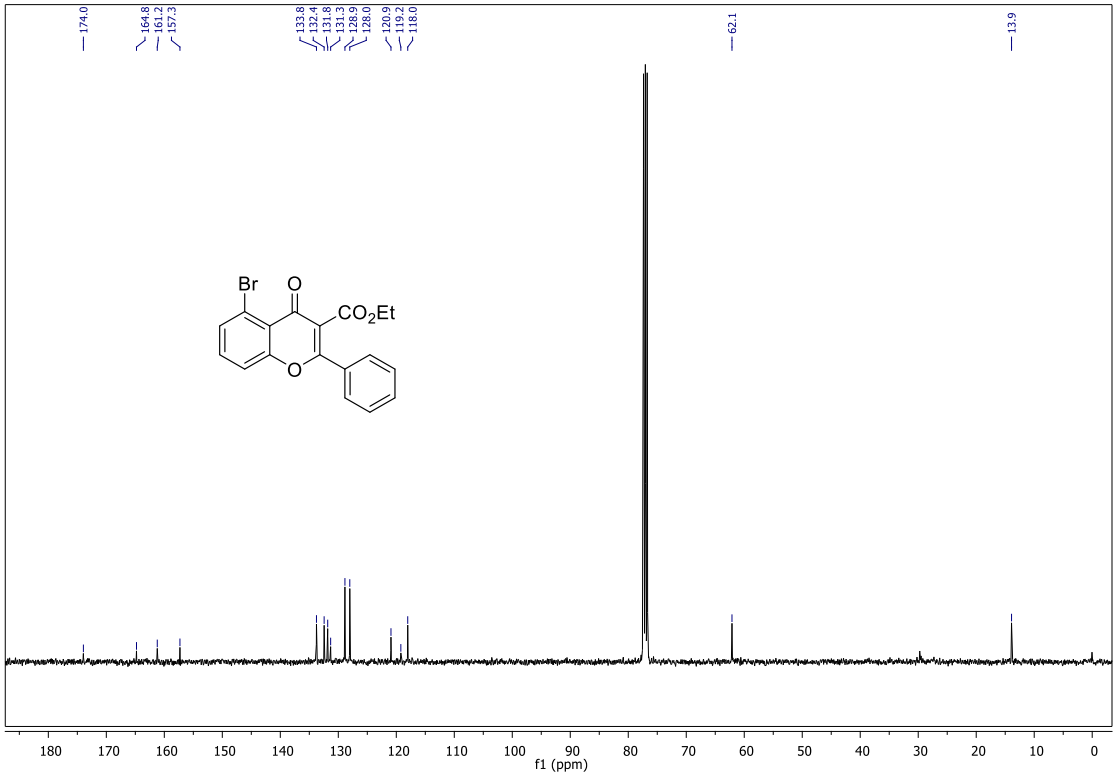
^{1}H NMR of compound **4h** in $CDCl_3$ (400 MHz)



^{13}C NMR of compound **4h** in $CDCl_3$ (101 MHz)



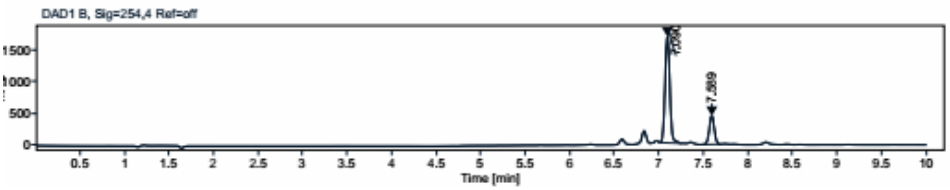
^{1}H NMR of compound **4i** in $CDCl_3$ (500 MHz)



^{13}C NMR of compound **4i** in $CDCl_3$ (101 MHz)

LCMS of control experiment

Data file	:	C:\Users\Public\Documents\ChemStation\1\Data\LCMS-20221205 2022-12-19 17-09-49\SCS-SR_340.D			
Acq. method	:	NSJ-LCMS-ESI-METHOD-100-1000-ACN90%.M			
Sample name	:	SCS-SR_340	**Instrument**	:	LCMS
Injection	:	1 of 1	**Injection volume**	:	10.000
Injection date	:	12/19/2022 6:13:14 PM	**Location**	:	P2-B1
Last changed	:	2023-01-13 17:06:09+05:30	**Flow rate**	:	0.5 mL per min
Column	:	Luna 5 µm C-18(2) 100	**Mobile phase**	:	A-0.1% FA in Water, B- 0.1% FA in ACN
Gradient	:	Time(min)/% B- 0.01/10, 1/10, 4/90, 8/90, 8.01/10, 10/10			



Signal: DAD1 B, Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
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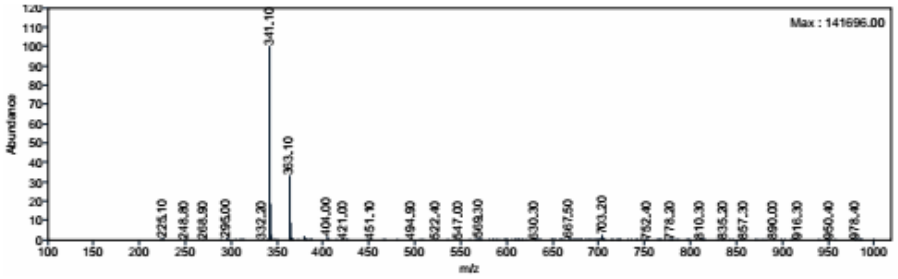
7.589	BB	0.0612	1752.6896	452.7064	21.9651	
		Sum	7979.4191			

Signal: MSD1 TIC, MS File, MM-ES, Pos, Scan, Frag: 70

RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.143	BB	0.0701	765289.8125	196298.3125	19.9637	
7.664	BB	0.1098	3068118.2500	465124.7188	80.0363	
		Sum	3833408.0625			

Signal MSD1 TIC, MS File, MM-ES, Pos, Scan, Frag: 70

Peak RT 7.143



Peak RT 7.664