Supporting Information

"Tandem cyclization of vinyl radicals: A sustainable approach to Indolines utilizing visible-light photoredox catalysis"

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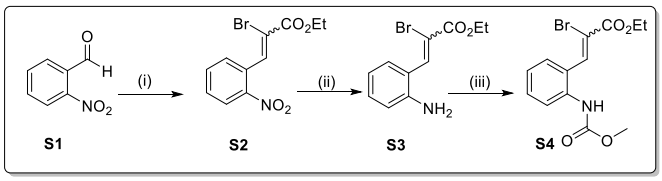
1. General information:

Unless otherwise stated, all commercial chemicals were used as received without further purification. All photochemical and non photochemical reactions were performed using common dry, inert atmosphere techniques. The blue light irradiation was done using blue light emitting diodes (700 mA, λ_{max} = 455 nm) produced by Oslon SSL. All the reactions were monitored by TLC and visualized by a dual short/long wavelength UV lamp. Analytical thin layer chromatography was performed on Merck TLC aluminium sheets silica gels 60 F 254. Purifications by column chromatography were performed on silica gel (0.063-0.200 mm). UV-visible spectra were measured on Varian Cary 50 spectrophotometer. Melting points were recorded on Stanford Research Systems OptiMelt MPA 100 automated melting point system. All products were characterized by appropriate techniques such as ^{1}H-NMR, ^{19}F-NMR, ^{13}C-NMR, FT-IR and HRMS analysis. FT-IR (Cary 630) spectroscopy was carried out on a spectrometer,

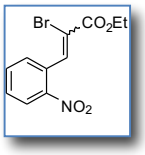
equipped with a diamond single reflection ATR-System. NMR spectra were recorded on Bruker Avance 300 spectrometer. Chemical shifts for ^{1}H-NMR were reported as δ, parts per million, relative to the signal of $CHCl_3$ at 7.26 ppm. Chemical shifts for ^{13}C-NMR were reported as δ, parts per million, relative to the signal of $CHCl_3$ at 77.2 ppm and TMS as an internal standard. Coupling constants (*J*) are given in Hertz (Hz). The following notations indicate the multiplicity of the signals: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, and m = multiplet. Mass spectra were recorded at the Central Analytical Laboratory at the Department of Chemistry of the University of Regensburg on Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS.

2. Synthesis of starting material precursor:[1]



Reagents and conditions: (i) KO^{t}Bu (1.5 equiv), triethyl-α-bromophosphonoacetate (1.5 equiv), THF, 0 °C - rt, 3 h, 94% (**S2**); (ii) Fe-powder (3.5 equiv), EtOH/HCl, reflux, 3 h, 83% (**S3**); (iii) Methyl chloroformate (1.5 equiv), $^{i}Pr_2Et$ (3.0 equiv), CH_2Cl_2, 0 °C - rt, 12 h, 87% (**S4**).

Ethyl 2-bromo-3-(2-nitrophenyl)acrylate (S2):

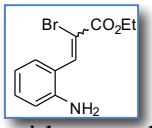


Potassium *tert*-butoxide (22.28 g, 198.5 mmol, 1.50 equiv) was slowly added to triethyl-α-bromophosphonoacetate (60.30 g, 198.5 mmol, 1.50 equiv) in anhydrous THF (250 mL) under positive nitrogen atmosphere at 0 ^{o}C. The resulting mixture allowed to stir for 1 h, followed by slow addition of 2-nitrobenzaldehyde **S1** (20.00 g, 132.3 mmol, 1.00 equiv) to the reaction mixture, resulting mixture stirred further for 2 h at 0 ^{o}C under inert atmosphere. The progress of the reaction was monitored by TLC analysis (staining with 2, 4-DNP / $KMnO_4$); after complete consumption of the starting material, reaction was quenched by adding saturated ammonium chloride solution (100 mL), and extracted with ethyl acetate (3 x 150 mL). Combined organic phases were washed with brine (100 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 4:1, R_f = 0.49) afforded **2a** as a yellow solid (37.33 g, 94% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.46 (s, 1H), 8.19 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.75 – 7.68 (m, 1H), 7.65 – 7.54 (m, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 162.3, 146.9, 139.2, 133.7, 131.2, 130.9, 129.9, 124.8, 117.3, 63.1, 14.1.

The obtained data is in accordance with literature data.[1]

Ethyl 3-(2-aminophenyl)-2-bromoacrylate (S3):

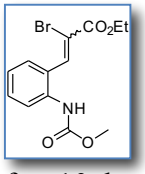


Ethyl 2-bromo-3-(2-nitrophenyl)acrylate **S2** (35.00 g, 116.62 mmol, 1.00 equiv) was dissolved under reflux in EtOH (150 mL) in a three-necked-flask, which equipped with a cooling condensor and a dropping funnel. Then Fe-powder (22.80 g, 408.1 mmol, 3.5 equiv) and 37% aq. HCl (90 mL) were added by a dropping funnel over 2 h under reflux, and the resulting mixture was refluxed for an additional hour. The mixture was concentrated on a rotary evaporator. Saturated $NaHCO_3$ (200 mL) was then added to adjust the pH of the aqueous layer to 8, and then aqueous layer was extracted with CH_2Cl_2 (3 × 150 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.60) afforded **S3** as a pale yellow solid (26.00 g, 83% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.73 – 7.57 (m, 1H), 7.23 – 7.16 (m, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 6.73 (dd, *J* = 8.1, 0.6 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.70 (bs, 1H), 1.38 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 162.2, 143.9, 136.4, 129.9, 128.3, 118.8, 117.2, 115.0, 114.6, 61.8, 13.2.

The obtained data is in accordance with literature data.[1]

Ethyl 2-bromo-3-(2-((methoxycarbonyl)amino)phenyl)acrylate (S4):



To a solution of **S4** (25.00 g, 92.93 mmol, 1.0 equiv) in CH_2Cl_2 (150 mL) was added ^{i}Pr$_2$Et (36.03 g, 278.81 mmol, 3 equiv) followed by methylchloroformate (13.17 g, 139.39 mmol, 1.5 equiv) a 0 °C. The mixture was then stirred at room temperature for 10 h, subsequently diluted with EtOAc (100 mL) and saturated NH_4Cl (100 mL). This mixture was additionally extracted with EtOAc (2 × 100 mL). And the combined organic phases were washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 4:1, R_f = 0.60) afforded a pale yellow solid **S4** (26.50 g, 87% yield).

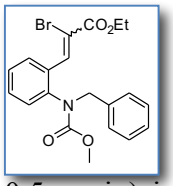
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H,), 7.39 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.16 (dt, *J* = 7.6, 0.9 Hz, 1H,), 7.01 (d, *J* = 8.0 Hz, 1H), 6.23 (s, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.15 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H,); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 162.6, 154.1, 137.5, 135.5, 130.3, 129.0, 125.7, 123.9, 121.9, 118.4, 63.1, 52.6, 14.2.

The obtained data is in accordance with literature data.[1]

3. General procedure (GP-1) for *N*-benzylation:

$ArCH_2Br$ (1.5 mmol, 1.5 equiv) was added to a solution of **S4** (0.328 g, 1.0 mmol, 1.0 equiv), K_2CO_3 (0.415 g, 3.0 mmol, 3.0 equiv) and tetrabutylammonium bromide (0.161 g, 0.5 mmol, 0.5 equiv) in MeCN (60 mL). The mixture was stirred at room temperature for a further 48 h. Then reaction mixture was diluted with EtOAc (50 mL), washed with brine solution (50 mL), and extracted with EtOAc (3 × 50 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1) afforded **7**.

Ethyl 3-(2-(benzyl(methoxycarbonyl)amino)phenyl)-2-bromoacrylate (7a):

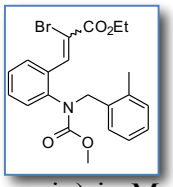


Following **GP-1**, **7a** was prepared from **S4** (5 g, 15.23 mmol, 1.00 equiv), benzyl bromide or (bromomethyl)benzene (3.90 g, 22.85 mmol, 1.5 equiv), K_2CO_3 (6.30 g, 45.69 mmol, 3.00 equiv), and tetrabutylammonium bromide (2.45 g, 7.61 mmol, 0.5 equiv) in MeCN (150 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.43) afforded **7a** as a pale yellow oil (5.90 g, Z:E = 99:01, 93% yield).

^{1}H NMR (300 MHz, $CDCl_3$, Z-isomer): δ 7.79 (d, *J* = 5.4 Hz, 1H), 7.70 (s, 1H), 7.40 – 7.29 (m, 2H), 7.27 – 7.21 (m, 3H), 7.20 (s, 2H), 7.09 – 7.02 (m, 1H), 4.75 (s, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.63 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$, Z-isomer):** δ 162.68, 155.98, 140.41, 138.29, 136.85, 133.18, 130.41, 129.94, 129.08, 128.50, 128.27, 127.82, 127.23, 116.34, 62.80, 54.59, 53.25, 14.21.

The obtained data is in accordance with literature data.[1]

Ethyl 2-bromo-3-(2-((methoxycarbonyl)(2-methylbenzyl)amino)phenyl)acrylate (7b):

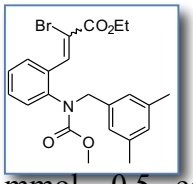


Following **GP-1**, **7b** was prepared from **S4** (5.00 g, 15.23 mmol, 1.00 equiv), 2-Methylbenzyl bromide (4.23 g, 22.85 mmol, 1.5 equiv), K_2CO_3 (6.30 g, 45.69 mmol, 3.00 equiv), and tetrabutylammonium bromide (2.45 g, 7.61 mmol, 0.5 equiv) in MeCN (150 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.51) afforded **7b** as a pale yellow solid (6.19 g, Z:E = 89:11, 94% yield); Mp 64-66 ^{o}C (decomposed).

^{1}H NMR (300 MHz, $CDCl_3$, Z-isomer): δ 7.76 (d, *J* = 6.5 Hz, 1H), 7.68 (s, 1H), 7.38 – 7.26 (m, 2H), 7.15 – 6.97 (m, 5H), 5.05 – 4.70 (m, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.63 (s, 3H), 2.14 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$, Z-isomer):** δ 162.66, 155.82, 140.24, 138.09, 136.78, 134.57, 133.48, 130.46, 130.40, 129.84, 128.25, 127.99, 127.26, 125.99, 116.16, 62.77, 53.27, 51.60, 19.19, 14.24; **IR (neat, cm^{-1}):** 2981, 2951, 1700, 1598, 1569, 1480, 1453,

1438, 1373, 1289, 1265, 1185, 1126, 1101, 1035, 1011, 977, 910, 893, 866, 781, 756, 736, 663; **HRMS (ESI):** exact m/z calculated for $C_{21}H_{23}BrNO_4$ $(M+H)^+$: 432.0805; Found: 432.081 $(M+H)^+$.

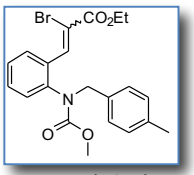
Ethyl 2-bromo-3-(2-((3,5-dimethylbenzyl)(methoxycarbonyl)amino)phenyl)acrylate (7c):



Following **GP-1**, **7c** was prepared from **S4** (0.328 g, 1.0 mmol, 1.00 equiv), 1-(bromomethyl)-3,5-dimethylbenzene (0.298 g, 1.5 mmol, 1.5 equiv), K_2CO_3 (0.415 g, 3.0 mmol, 3.00 equiv), and tetrabutylammonium bromide (0.161 g, 0.5 mmol, 0.5 equiv) in MeCN (60 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.46) afforded **7c** as a pale yellow syrup (0.405 g, Z:E = 82:18, 91% yield).

^{1}H NMR (300 MHz, $CDCl_3$, Z-isomer): δ 7.78 (s, 2H), 7.33 (m, 2H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.85 (s, 1H), 6.78 (s, 2H), 4.79 – 4.62 (m, 2H), 4.29 (q, *J* = 7.1, 2H), 3.62 (s, 3H), 2.22 (s, 6H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$, Z-isomer):** δ 171.09, 162.64, 155.94, 140.62, 138.29, 137.93, 136.72, 133.18, 130.39, 129.87, 129.43, 128.28, 127.14, 126.79, 115.88, 62.73, 54.54, 53.17, 21.24, 14.18; **IR (neat, cm^{-1}):** 2984, 2953, 1700, 1599, 1485, 1443, 1376, 1288, 1249, 1215, 1136, 1106, 1021, 991, 849, 761, 715; **HRMS (ESI):** exact m/z calculated for $C_{22}H_{25}BrNO_4$ $(M+H)^+$: 446.0961; Found: 446.0968 $(M+H)^+$.

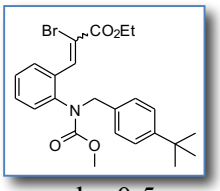
Ethyl 2-bromo-3-(2-((methoxycarbonyl)(4-methylbenzyl)amino)phenyl)acrylate (7d):



Following **GP-1**, **7d** was prepared from **S4** (0.328 g, 1.0 mmol, 1.00 equiv), 1-(bromomethyl)-4-methylbenzene (0.278 g, 1.5 mmol, 1.5 equiv), K_2CO_3 (0.415 g, 3.0 mmol, 3.00 equiv), and tetrabutylammonium bromide (0.161 g, 0.5 mmol, 0.5 equiv) in MeCN (60 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.40) afforded **7d** as a colourless viscous oil (0.396 g, Z:E = 99:01, 92% yield).

^{1}H NMR (300 MHz, $CDCl_3$, Z-isomer): δ 7.77 (d, *J* = 10.5 Hz, 1H), 7.69 (s, 1H), 7.41 – 7.29 (m, 2H), 7.04 (s, 4H), 4.72 (m, 2H), 4.29 (q, *J* = 7.1, 2H), 3.62 (s, 3H), 2.29 (s, 3H), 1.36 (t, *J* = 7.1, 3H); **^{13}C NMR (75 MHz, $CDCl_3$, Z-isomer):** δ 162.66, 155.93, 140.46, 138.29, 137.46, 133.80, 133.23, 130.42, 129.90, 129.17, 129.04, 128.31, 127.18, 116.18, 62.75, 54.31, 53.20, 21.17, 14.20; **IR (neat, cm^{-1}):** 2983, 2953, 1702, 1617, 1598, 1514, 1482, 1443, 1376, 1317, 1292, 1234, 1215, 1188, 1134, 1102, 1036, 990, 902, 844, 711, 761, 660; **HRMS (ESI):** exact m/z calculated for $C_{21}H_{23}BrNO_4$ $(M+H)^+$: 432.0805; Found: 432.0811 $(M+H)^+$.

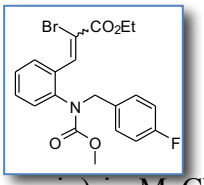
Ethyl 2-bromo-3-(2-((4-(tert-butyl)benzyl)(methoxycarbonyl)amino)phenyl)acrylate (7e):



Following **GP-1**, **7e** was prepared from **S4** (0.328 g, 1.0 mmol, 1.00 equiv), 1-(bromomethyl)-4-(tert-butyl)benzene (0.340 g, 1.5 mmol, 1.5 equiv), K_2CO_3 (0.415 g, 3.0 mmol, 3.00 equiv), and tetrabutylammonium bromide (0.161 g, 0.5 mmol, 0.5 equiv) in MeCN (60 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.43) afforded **7e** as a colourless viscous oil (0.427 g, Z:E = 99:01, 90% yield).

^{1}H NMR (300 MHz, $CDCl_3$, Z-isomer): δ 7.86 – 7.75 (m, 2H), 7.42 – 7.32 (m, 2H), 7.31 – 7.22 (m, 3H), 7.14 (m, 2H), 4.72 (s, 2H), 4.30 (q, *J* = 7.1Hz, 2H), 3.63 (s, 3H), 1.37 (t, *J* = 7.1Hz, 3H), 1.28 (s, 9H); **^{13}C NMR (75 MHz, $CDCl_3$, Z-isomer):** δ 162.65, 155.93, 150.62, 140.63, 138.24, 133.75, 133.16, 130.43, 129.88, 128.75, 128.34, 127.18, 126.90, 125.33, 116.16, 62.75, 54.28, 53.20, 34.50, 31.32, 14.23; **IR (neat, cm^{-1}):** 2956, 2906, 2868, 1704, 1617, 1598, 1481, 1444, 1377, 1318, 1293, 1232, 1189, 1135, 1104, 1038, 983, 904, 850, 760, 671, 657; **HRMS (ESI):** exact m/z calculated for $C_{24}H_{29}BrNO_4$ $(M+H)^+$: 474.1274; Found: 474.1282 $(M+H)^+$.

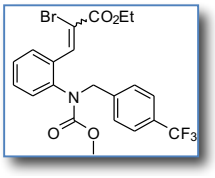
Ethyl 2-bromo-3-(2-((4-fluorobenzyl)(methoxycarbonyl)amino)phenyl)acrylate (7f):



Following **GP-1**, **7f** was prepared from **S4** (0.328 g, 1.0 mmol, 1.00 equiv), 1-(bromomethyl)-4-fluorobenzene (0.284 g, 1.5 mmol, 1.5 equiv), K_2CO_3 (0.415 g, 3.0 mmol, 3.00 equiv), and tetrabutylammonium bromide (0.161 g, 0.5 mmol, 0.5 equiv) in MeCN (60 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.52) afforde **7f** as a colourless viscous oil (0.384 g, Z:E = 99:01, 88% yield).

^{1}H NMR (300 MHz, $CDCl_3$, Z-isomer): δ 7.77 (d, *J* = 6.0 Hz, 1H), 7.67 (s, 1H), 7.38 – 7.27 (m, 2H), 7.20 – 7.08 (m, 2H), 7.05 – 6.99 (m, 1H), 6.94 – 6.85 (m, 2H), 4.83 – 4.57 (m, 1H), 4.26 (q, *J* = 7.1Hz, 2H), 3.59 (s, 3H), 1.32 (t, *J* = 7.1Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$, Z-isomer):** δ 163.98, 162.58, 160.71, 155.92, 140.25, 138.13, 134.16, 133.14, 132.77 (d, *J* = 3.2 Hz), 130.87 (d, *J* = 8.1 Hz), 130.48, 130.01, 128.33, 62.81, 53.81, 53.24, 14.14; **^{19}F NMR (282 MHz, $CDCl_3$, Z-isomer:** δ -114.76, **E-isomer:** δ -115.25); **IR (neat, cm^{-1}):** 2983, 2954, 1702, 1602, 1509, 1482, 1445, 1376, 1215, 1189, 1157, 1135, 1095, 1035, 1016, 983, 902, 839, 756, 656; **HRMS (ESI):** exact m/z calculated for $C_{20}H_{20}BrFNO_4$ $(M+H)^+$: 436.0554; Found: 436.0562 $(M+H)^+$.

Ethyl 2-bromo-3-(2-((methoxycarbonyl)(4-(trifluoromethyl)benzyl)amino)phenyl)acrylate (7g):

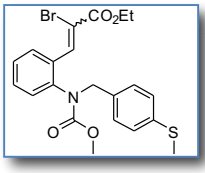


Following **GP-1**, **7g** was prepared from **S4** (0.328 g, 1.0 mmol, 1.00 equiv), 1-(bromomethyl)-4-(trifluoromethyl)benzene (0.359 g, 1.5 mmol, 1.5

equiv), K_2CO_3 (0.415 g, 3.0 mmol, 3.00 equiv), and tetrabutylammonium bromide (0.161 g, 0.5 mmol, 0.5 equiv) in MeCN (60 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.33) afforded **7g** as a pale yellow viscous oil (0.418 g, Z:E 95:05, 86% yield).

^{1}H NMR (300 MHz, $CDCl_3$, Z-isomer): δ 7.81 – 7.72 (m, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.27 (m, 4H), 7.05 (d, *J* = 6.6 Hz, 1H), 4.77 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.62 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$, Z-isomer):** δ 162.48, 155.98, 140.91, 140.24, 137.97, 133.03, 130.55, 130.11, 129.71, 129.32, 128.19, 127.48, 125.43 (q, *J* = 3.7 Hz), 124.05 (q, *J* = 272.07 Hz), 122.25, 116.61, 62.84, 54.15, 53.35, 14.06; **^{19}F NMR (282 MHz, $CDCl_3$, Z-isomer):** δ -63.03; **IR (neat, cm^{-1}):** 2956, 1704, 1619, 1598, 1483, 1446, 1421, 1378, 1322, 1301, 1253, 1236, 1190, 1161, 1111, 1064, 1037, 1018, 985, 906, 852, 820, 760, 660; **HRMS (ESI):** exact m/z calculated for $C_{21}H_{20}BrF_3NO_4$ $(M+H)^+$: 486.0522; Found: 486.0528 $(M+H)^+$.

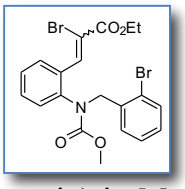
Ethyl 2-bromo-3-(2-((methoxycarbonyl)(4-(methylthio)benzyl)amino)phenyl)acrylate (7h):



Following **GP-1**, **7h** was prepared from **S4** (0.328 g, 1.0 mmol, 1.00 equiv), (4-(bromomethyl)phenyl)(methyl)sulfane (0.326 g, 1.5 mmol, 1.5 equiv), K_2CO_3 (0.415 g, 3.0 mmol, 3.00 equiv), and tetrabutylammonium bromide (0.161 g, 0.5 mmol, 0.5 equiv) in MeCN (60 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.49) afforded **7h** as a pale yellow viscous oil (0.441 g, Z:E = 91:09, 95% yield).

^{1}H NMR (300 MHz, $CDCl_3$, Z-isomer): δ 7.79 (d, *J* = 5.9 Hz, 1H), 7.71 (s, 1H), 7.41 – 7.28 (m, 2H), 7.18 – 6.99 (m, 5H), 4.81 – 4.59 (m, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.61 (s, 3H), 2.43 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$, Z-isomer):** δ 162.60, 155.94, 140.38, 138.21, 138.09, 133.56, 133.14, 130.46, 129.98, 129.62, 128.35, 127.60, 127.28, 126.76, 126.40, 116.34, 62.83, 54.13, 53.24, 14.20; **IR (neat, cm^{-1}):** 2982, 2952, 2922, 1701, 1618, 1597, 1570, 1482, 1442, 1376, 1234, 1215, 1188, 1135, 1092, 1035, 1016, 983, 840, 804, 759, 656; **HRMS (ESI):** exact m/z calculated for $C_{21}H_{23}BrNO_4S$ $(M+H)^+$: 464.0526; Found: 464.0536 $(M+H)^+$.

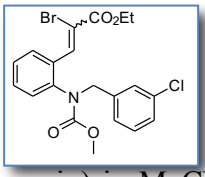
Ethyl 2-bromo-3-(2-((2-bromobenzyl)(methoxycarbonyl)amino)phenyl)acrylate (7i):



Following **GP-1**, **7i** was prepared from **S4** (0.328 g, 1.0 mmol, 1.00 equiv), 1-bromo-2-(bromomethyl)benzene (0.375 g, 1.5 mmol, 1.5 equiv), K_2CO_3 (0.415 g, 3.0 mmol, 3.00 equiv), and tetrabutylammonium bromide (0.161 g, 0.5 mmol, 0.5 equiv) in MeCN (60 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.31) afforded **7i** as a pale yellow solid (0.462 g, Z:E = 99:01, 93% yield). Mp 58-60 ^{o}C (decomposed).

^{1}H NMR (300 MHz, $CDCl_3$, Z-isomer): δ 7.90 (d, *J* = 10.5 Hz, 1H), 7.88 – 7.75 (m, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.24 (t, *J* = 7.1 Hz, 1H), 7.19 – 7.07 (m, 2H), 4.99 (s, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$, Z-isomer):** δ 162.73, 155.92, 140.09, 138.07, 136.03, 133.17, 132.93, 131.27, 130.41, 129.89, 129.37, 128.20, 127.55, 127.32, 124.19, 116.30, 62.83, 53.68, 53.40, 14.25; **IR (neat, cm^{-1}):** 2976, 2952, 1707, 1614, 1596, 1569, 1440, 1378, 1297, 1250, 1213, 1189, 1140, 1105, 1026, 983, 896, 875, 782, 752, 653; **HRMS (ESI):** exact m/z calculated for $C_{20}H_{20}Br_2NO_4$ $(M+H)^+$: 495.9754; Found: 495.9756 $(M+H)^+$.

Ethyl 2-bromo-3-(2-((3-chlorobenzyl)(methoxycarbonyl)amino)phenyl)acrylate (7j):

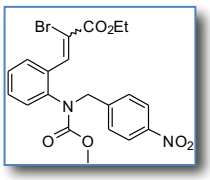


Following **GP-1**, **7j** was prepared from **S4** (0.328 g, 1.0 mmol, 1.00 equiv), 1-(bromomethyl)-3-chlorobenzene (0.308 g, 1.5 mmol, 1.5 equiv), K_2CO_3 (0.415 g, 3.0 mmol, 3.00 equiv), and tetrabutylammonium bromide (0.161 g, 0.5 mmol, 0.5 equiv) in MeCN (60 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.36) afforded **7j** as a pale yellow oil (0.402 g, Z:E = 99:01, 89% yield).

^{1}H NMR (300 MHz, $CDCl_3$, Z-isomer): δ 7.73 (d, *J* = 6.7 Hz, 1H), 7.69 (s, 1H), 7.36 – 7.23 (m, 2H), 7.20 – 7.05 (m, 3H), 6.99 (m, 2H), 4.65 (m, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.56 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 1H); **^{13}C NMR (75 MHz, $CDCl_3$, , Z-isomer):** δ 162.50, 155.90, 140.21, 138.88, 137.95, 134.27, 133.05, 130.55, 130.03, 129.79, 129.04, 128.21, 128.04, 127.43, 127.19, 116.46, 62.86, 54.07, 53.32, 14.19.

The obtained data is in accordance with literature data.[1]

Ethyl 2-bromo-3-(2-((methoxycarbonyl)(4-nitrobenzyl)amino)phenyl)acrylate (7k):



Following **GP-1**, **7k** was prepared from **S4** (0.209 g, 0.5 mmol, 1.00 equiv), 1-(bromomethyl)-4-nitrobenzene (0.324 g, 1.5 mmol, 1.5 equiv), K_2CO_3 (0.415 g, 3.0 mmol, 3.00 equiv), and tetrabutylammonium bromide (0.161 g, 0.5 mmol, 0.5 equiv) in MeCN (60 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.32) afforded **7k** as a pale yellow oil (0.407 g, Z:E = 99:01, 88% yield).

^{1}H NMR (300 MHz, $CDCl_3$, Z-isomer): δ 8.07 (d, *J* = 8.7 Hz, 2H), 7.74 (d, *J* = 7.4 Hz, 2H), 7.42 – 7.28 (m, 4H), 7.05 (d, *J* = 6.8 Hz, 1H), 4.79 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.62 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$, Z-isomer):** δ 162.45, 155.99, 147.45,

144.24, 140.04, 137.89, 132.94, 130.66, 130.21, 129.82, 128.21, 127.68, 123.74, 116.65, 62.98, 53.93, 53.51, 14.12.

The obtained data is in accordance with literature data.[1]

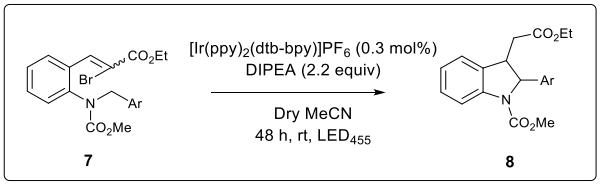
4. Reduction potentials:

Redox potentials of the α-bromocinnamates were measured by cyclic voltammetry in acetonitrile (MeCN) containing tetrabutylammonium tetrafluoroborate (0.1 M) as a supporting electrolyte. All values are given vs. Saturated Calomel Electrode (SCE). The scan rate was 50 mV S^{-1}.

α-Bromocinnamates	**Reduction potential (V)**
7a	-1.50
7b	-1.48
7c	-1.47
7d	-1.51
7e	-1.52
7f	-1.51
7g	-1.50
7h	-1.48
7i	-1.45
7j	-1.50
7k	-1.19

Table S1: Reduction potentials of the α-bromocinnamate ethyl esters vs SCE

5. General procedure (GP-2) for photocatalysis:



An oven dried 10 mL schlenk flask was charged with **7** (0.50 mmol, 1.00 equiv) and $[Ir(ppy)_2(dtb\text{-}bpy)]PF_6$ (1.37 mg, 0.003 equiv, 0.3 mol %) in anhydrous MeCN (2.0 mL). Then, anhydrous DIPEA (0.191 mL, 1.1 mmol, 2.2 equiv) was added and the resulting suspension was deoxygenated by three freeze-pump-thaw cycles. The resulting reaction mixture was irradiated with blue light emitting diode (LED, λ_{max} = 455 nm) at room temperature for 48 h. After

completion of reaction mixture, the crude mixture was filtered and washed with ethyl acetate. The crude residue was concentrated *in vacuo*. Purification of the crude product by column chromatography on silica gel by using hexanes and ethyl acetate afforded the pure product **8**.

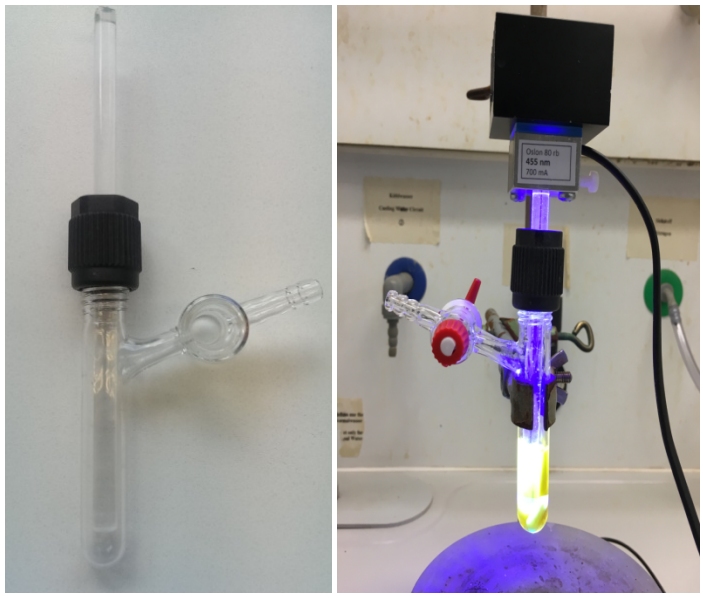
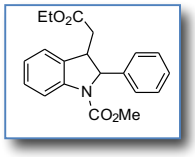


Figure 1: Experimental set-up for photochemical reaction

Methyl 3-(2-ethoxy-2-oxoethyl)-2-phenylindoline-1-carboxylate (8a):



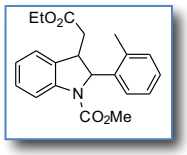
Following **GP-2**, **8a** was prepared from **7a** (1.254 g, 3.0 mmol, 1.00 equiv), $[Ir(ppy)_2(dtb\text{-}bpy)]PF_6$ (8.22 mg, 0.003 equiv, 0.3 mol %) and DIPEA (1.146 mL, 1.1 mmol, 2.2 equiv) in MeCN (10 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.46) afforded **8a** as a white solid (0.773 g, cis / trans = 78:22, 75% yield).

^{1}H NMR (300 MHz, $CDCl_3$, cis isomer): δ 7.87 (s, 1H), 7.37 – 7.09 (m, 4H), 7.05 – 6.85 (m, 4H), 5.58 (d, *J* = 9.6 Hz, 1H), 4.23 (td, *J* = 10.0, 4.9 Hz, 1H), 4.09 – 3.99 (dq, *J* = 7.2 Hz, 2H), 3.63 (s, 3H), 2.70 – 2.49 (m, 1H), 1.97 (dd, *J* = 17.4, 10.2 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H);

^{1}H NMR (300 MHz, $CDCl_3$, trans isomer): δ 7.29 – 7.07 (m, 5H), 7.03 – 6.92 (m, 4H), 5.17 (s, 1H), 4.23 (ddd, *J* = 12.1, 8.5, 3.5 Hz, 1H), 4.19 – 4.10 (m, 1H), 4.04 (dq, *J* = 7.1 Hz, 2H), 2.56 (d, *J* = 4.9 Hz, 1H), 1.97 (dd, *J* = 17.4, 10.2 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$, cis isomer):** δ 172.23, 153.51, 138.26, 128.63, 128.39, 127.92, 127.46, 126.93, 125.29, 123.42, 123.11, 114.56, 66.40, 60.67, 52.65, 41.18, 34.20, 14.16; **^{13}C NMR (75 MHz, $CDCl_3$, trans isomer):** δ 171.53, 147.41, 141.00, 128.34, 138.21, 130.62, 128.53, 128.34, 128.12, 127.46, 127.00, 125.29, 115.02, 60.84, 52.71, 41.00, 33.97, 14.24.

The obtained data is in accordance with literature data.[1]

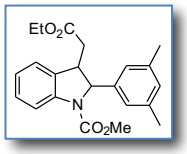
Methyl 3-(2-ethoxy-2-oxoethyl)-2-(o-tolyl)indoline-1-carboxylate (8b):



Following **GP-2**, **8b** was prepared from **7b** (1.296 g, 3.0 mmol, 1.00 equiv), $[Ir(ppy)_2(dtb\text{-}bpy)]PF_6$ (8.22 mg, 0.003 equiv, 0.3 mol %) and DIPEA (1.146 mL, 1.1 mmol, 2.2 equiv) in MeCN (10 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.48) afforded **8b** as a white solid (0.879 g, cis / trans = 55:45, 83% yield); Mp 51-53 ^oC (decomposed).

^{1}H NMR (300 MHz, $CDCl_3$, cis isomer): δ 7.86 (bs, 1H), 7.35 – 7.23 (m, 3H), 7.01 (dt, *J* = 11.9, 5.8 Hz, 4H), 5.89 (d, *J* = 10.1 Hz, 1H), 4.37 (dt, *J* = 17.3, 8.6 Hz, 1H),, 4.01 (q, *J* = 7.1 Hz, 2H), 3.66 (s, 3H), 3.53 (td, *J* = 7.0, 1.9 Hz, 1H), 2.74 (qd, *J* = 15.4, 7.1 Hz, 1H), 2.45 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); **^{1}H NMR (300 MHz, $CDCl_3$, trans isomer):** δ 7.20 – 7.06 (m, 7H), 6.89 (dd, *J* = 14.8, 7.6 Hz, 2H), 5.41 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 3H), 2.54 (dd, *J* = 17.1, 5.9 Hz, 1H), 2.46 (s, 3H), 2.25 – 2.12 (m, 1H), 1.31 – 1.25 (m, 1H), 1.20 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$, cis isomer):** δ 172.09, 153.48, 140.59, 136.84, 132.74, 130.63, 128.28, 127.75, 126.50, 126.23, 125.05, 124.21, 123.08, 114.61, 61.39, 60.60, 52.63, 41.57, 35.10, 19.49, 14.09; **^{13}C NMR (75 MHz, $CDCl_3$, trans isomer):** δ 171.26, 153.61, 142.95, 135.81, 134.44, 130.49, 128.69, 127.35, 125.97, 125.90, 123.68, 123.26, 122.86, 114.90, 65.06, 61.39, 52.72, 46.01, 40.42, 19.37, 14.16; **IR (neat, cm^{-1}):** 2955, 1705, 1599, 1483, 1461, 1440, 1376, 1346, 1329, 1308, 1274, 1248, 1156, 1138, 1054, 1020, 746; **HRMS (ESI):** exact m/z calculated for $C_{21}H_{24}NO_4$ $(M+H)^+$: 354.17; Found: 354.1708 $(M+H)^+$.

Methyl 2-(3,5-dimethylphenyl)-3-(2-ethoxy-2-oxoethyl)indoline-1-carboxylate (8c):

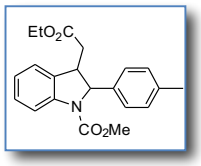


Following **GP-2**, **8c** was prepared from **7c** (0.223 g, 0.5 mmol, 1.00 equiv), $[Ir(ppy)_2(dtb\text{-}bpy)]PF_6$ (1.37 mg, 0.003 equiv, 0.3 mol %) and DIPEA (0.191 mL, 1.1 mmol, 2.2 equiv) in MeCN (1.5 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.53) afforded **8c** as a pale yellow solid (0.141 g, cis / trans = 71:29, 77% yield); Mp 69-71 ^oC (decomposed).

^{1}H NMR (300 MHz, $CDCl_3$, cis isomer): δ 7.84 (bs, 1H), 7.35 – 7.22 (m, 2H), 7.08 – 6.96 (m, 2H), 6.87 (dd, *J* = 25.7, 9.0 Hz, 2H), 5.56 (d, *J* = 10.0 Hz, 1H), 4.19 (ddd, *J* = 9.5, 4.7, 1.5 Hz, 1H), 4.11 (qd, *J* = 7.2, 1.9 Hz, 2H), 3.69 (s, 3H), 2.71 – 2.62 (m, 1H), 2.19 (s, 6H), 2.09 – 1.97 (m, 1H), 1.25 – 1.19 (t, *J* = 7.2 Hz, 3H); **^{1}H NMR (300 MHz, $CDCl_3$, trans isomer):** δ 7.51 – 7.39 (m, 1H), 7.14 (d, *J* = 7.4 Hz, 2H), 6.60 (s, 4H), 5.18 (d, *J* = 1.9 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 3H), 3.55 (dd, *J* = 10.5, 4.0 Hz, 1H), 2.58 (d, *J* = 4.9 Hz, 1H), 2.27 (d, *J* = 6.8 Hz, 1H), 2.24 (s, 6H), 1.29 – 1.23 (m, 3H); **^{13}C NMR (75 MHz, $CDCl_3$, cis isomer):** δ 172.35, 153.58, 142.44, 138.10, 137.76, 129.63, 129.20, 128.55, 128.27, 124.55, 123.45, 123.26, 123.03,

114.56, 66.32, 60.63, 52.63, 41.26, 34.25, 21.35, 14.23; **^{13}C NMR (75 MHz, $CDCl_3$, trans isomer):** δ 171.42, 153.84, 143.04, 138.44, 138.20, 132.13, 131.23, 130.90, 128.16, 124.81, 124.43, 122.93, 122.74, 115.03, 68.07, 61.21, 60.38, 40.99, 29.74, 21.39, 18.90; **IR (neat, cm^{-1}):** 2956, 2920, 1709, 1601, 1484, 1461, 1384, 1338, 1308, 1264, 1248, 1174, 1138, 1057, 1022, 850, 766, 750, 718, 679; **HRMS (ESI):** exact m/z calculated for $C_{22}H_{26}NO_4$ $(M+H)^+$: 368.1856; Found: 368.1864 $(M+H)^+$.

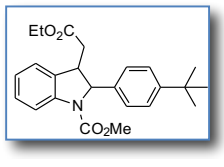
Methyl 3-(2-ethoxy-2-oxoethyl)-2-(p-tolyl)indoline-1-carboxylate (8d):



Following **GP-2**, **8d** was prepared from **7d** (0.216 g, 0.5 mmol, 1.00 equiv), $[Ir(ppy)_2(dtb\text{-}bpy)]PF_6$ (1.37 mg, 0.003 equiv, 0.3 mol %) and DIPEA (0.191 mL, 1.1 mmol, 2.2 equiv) in MeCN (1.5 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.33) afforded **8d** as a white solid (0.141 g, cis / trans = 92:08, 80% yield); Mp 93-95 °C (decomposed).

^{1}H NMR (300 MHz, $CDCl_3$, cis isomer, major): δ 7.82 (bs, 1H), 7.30 – 7.19 (m, 1H), 7.01 – 6.91 (m, 4H), 6.83 (d, *J* = 8.0 Hz, 2H), 5.55 (d, *J* = 9.6 Hz, 1H), 4.19 (ddd, *J* = 14.3, 9.5, 6.1 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.63 (s, 3H), 2.59 (dt, *J* = 17.4, 4.1 Hz, 1H), 2.24 (s, 3H), 2.00 (dd, *J* = 17.4, 10.1 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$, cis isomer, major):** δ 172.28, 153.54, 137.52, 135.19, 129.29, 129.07, 128.28, 126.82, 123.40, 123.04, 114.56, 66.23, 60.66, 52.65, 41.01, 34.19, 21.17, 14.17; **IR (neat, cm^{-1}):** 2955, 2929, 1706, 1598, 1513, 1482, 1460, 1377, 1339, 1304, 1269, 1250, 1167, 1155, 1136, 1111, 1053, 1021, 999, 809, 766, 743; **HRMS (ESI):** exact m/z calculated for $C_{21}H_{24}NO_4$ $(M+H)^+$: 354.17; Found: 354.1709 $(M+H)^+$.

Methyl 2-(4-(tert-butyl)phenyl)-3-(2-ethoxy-2-oxoethyl)indoline-1-carboxylate (8e):

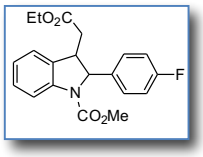


Following **GP-2**, **8e** was prepared from **7e** (0.236 g, 0.5 mmol, 1.00 equiv), $[Ir(ppy)_2(dtb\text{-}bpy)]PF_6$ (1.37 mg, 0.003 equiv, 0.3 mol %) and DIPEA (0.191 mL, 1.1 mmol, 2.2 equiv) in MeCN (1.5 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.84) afforded **8e** as a pale yellow solid (0.166 g, cis / trans = 73:27, 84% yield); Mp 43-45 °C (decomposed).

^{1}H NMR (300 MHz, $CDCl_3$, cis isomer): δ 7.78 (bs, 1H), 7.30 – 7.12 (m, 3H), 7.03 – 6.91 (m, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 5.56 (d, *J* = 9.5 Hz, 1H), 4.27 – 4.12 (m, 1H), 4.12 – 3.98 (m, 2H), 3.64 (s, 3H), 2.74 – 2.48 (m, 1H), 2.01 (dd, *J* = 17.4, 10.0 Hz, 1H), 1.21 (s, 9H), 1.15 (t, *J* = 7.1 Hz, 3H); **^{1}H NMR (300 MHz, $CDCl_3$, trans isomer):** δ 7.16 (d, *J* = 8.4 Hz, 3H), 7.08 (dd, *J* = 7.4, 5.1 Hz, 3H), 6.98 – 6.92 (m, 2H), 5.16 (s, 1H), 4.27 – 4.12 (m, 1H), 4.12 – 3.98 (m, 2H), 3.64 (s, 3H), 3.54 – 3.44 (m, 1H), 2.74 – 2.48 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.22 (s, *J* = 1.1

Hz, 9H); **^{13}C NMR (75 MHz, $CDCl_3$, cis isomer):** δ 172.33, 153.56, 150.63, 135.01, 128.25, 126.60, 125.49, 125.19, 123.37, 123.27, 123.03, 114.60, 66.19, 60.58, 52.64, 41.16, 34.47, 31.30, 29.73, 14.17; **^{13}C NMR (75 MHz, $CDCl_3$, trans isomer):** δ 171.56, 153.87, 150.17, 139.12, 132.19, 128.55, 126.25, 125.31, 125.27, 124.94, 123.27, 115.09, 67.92, 60.81, 52.73, 41.93, 34.15, 31.37, 29.73, 14.25; **IR (neat, cm^{-1}):** 2958, 2868, 1708, 1600, 1512, 1483, 1440, 1380, 1267, 1159, 1138, 1055, 1019, 927, 832, 812, 764, 747; **HRMS (ESI):** exact m/z calculated for $C_{24}H_{30}NO_4$ $(M+H)^+$: 396.2169; Found: 396.2179 $(M+H)^+$.

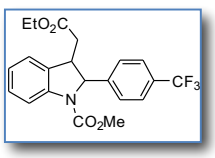
Methyl 3-(2-ethoxy-2-oxoethyl)-2-(4-fluorophenyl)indoline-1-carboxylate (8f):



Following **GP-2**, **8f** was prepared from **7f** (0.218 g, 0.5 mmol, 1.00 equiv), $[Ir(ppy)_2(dtb\text{-}bpy)]PF_6$ (1.37 mg, 0.003 equiv, 0.3 mol %) and DIPEA (0.191 mL, 1.1 mmol, 2.2 equiv) in MeCN (1.5 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.49) afforded **8f** as a white solid (0.128 g, cis / trans = 73:27, 72% yield); Mp 46-48 °C (decomposed).

^{1}H NMR (300 MHz, $CDCl_3$, cis isomer): δ 7.82 (bs, 1H), 7.25 (ddd, *J* = 6.2, 3.3, 1.2 Hz, 1H), 7.05 – 6.81 (m, 5H), 5.59 (d, *J* = 9.6 Hz, 1H), 4.26 – 4.19 (m, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 3H), 2.69 – 2.62 (m, 1H), 1.96 (dd, *J* = 17.5, 10.5 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H); **^{1}H NMR (300 MHz, $CDCl_3$, trans isomer):** δ 7.56 (s, 1H), 7.28 – 7.23 (m, 1H), 7.13 (dd, *J* = 13.6, 6.6 Hz, 1H), 7.05 – 6.81 (m, 5H), 5.15 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 1H), 3.64 (s, 3H), 3.46 (t, *J* = 7.3 Hz, 1H), 2.61 (d, *J* = 4.7 Hz, 1H), 1.24 (m, 1H), 1.22 (t, *J* = 7.1 Hz, 3H); **^{19}F NMR (282 MHz, $CDCl_3$):** δ -114.71 (**cis**), -115.70 (**trans**); **^{13}C NMR (75 MHz, $CDCl_3$, cis isomer):** δ 172.11, 163.97, 160.71, 153.42, 134.15 (d, *J* = 3.63 Hz), 128.66 (d, *J* = 8.4 Hz), 128.45, 123.47, 123.23, 115.44, 115.16, 114.63, 65.73, 60.75, 52.70, 41.04, 34.11, 29.71, 14.16; **^{13}C NMR (75 MHz, $CDCl_3$, trans isomer):** δ 171.63, 163.97, 160.71, 153.42, 134.15 (d, *J* = 3.63 Hz), 131.65, 128.66 (d, *J* = 8.4 Hz), 127.03, 124.85, 115.60, 115.32, 115.08, 61.67, 60.88, 50.20, 40.90, 35.71, 29.67, 14.24; **IR (neat, cm^{-1}):** 2956, 2930, 2855, 1705, 1602, 1509, 1483, 1441, 1378, 1309, 1269, 1220, 1176, 1158, 1096, 1054, 1019, 824, 748; **HRMS (ESI):** exact m/z calculated for $C_{20}H_{21}FNO_4$ $(M+H)^+$: 358.1449; Found: 358.1458 $(M+H)^+$.

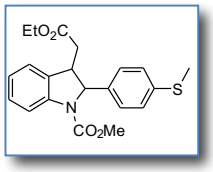
Methyl 3-(2-ethoxy-2-oxoethyl)-2-(4-(trifluoromethyl)phenyl)indoline-1-carboxylate (8g):



Following **GP-2**, **8g** was prepared from **7g** (0.243 g, 0.5 mmol, 1.00 equiv), $[Ir(ppy)_2(dtb\text{-}bpy)]PF_6$ (1.37 mg, 0.003 equiv, 0.3 mol %) and DIPEA (0.191 mL, 1.1 mmol, 2.2 equiv) in MeCN (1.5 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.37) afforded **8g** as a white solid (0.142 g, cis / trans = 77:23, 70% yield); Mp 49-51 °C (decomposed).

^{1}H NMR (300 MHz, $CDCl_3$, cis isomer): δ 7.83 (bs, 1H), 7.46 (dd, *J* = 14.2, 8.1 Hz, 1H), 7.34 – 7.22 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.06 – 6.95 (m, 2H), 5.66 (d, *J* = 9.7 Hz, 1H), 4.27 (td, *J* = 10.2, 4.7 Hz, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 3H), 2.69 – 2.58 (m, 1H), 2.00 – 1.85 (m, 1H), 1.15 (t, *J* = 7.1, Hz, 3H); **^{1}H NMR (300 MHz, $CDCl_3$, trans isomer):** δ 7.59 (s, 1H), 7.57 – 7.47 (m, 1H), 7.39 – 7.22 (m, 2H), 7.16 (d, *J* = 4.7 Hz, 2H), 7.02 – 6.96 (m, 2H), 5.24 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 1H), 3.64 (s, 3H), 3.52 – 3.41 (m, 1H), 2.61 (d, *J* = 4.8 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 1H); **^{19}F NMR (282 MHz, $CDCl_3$):** δ -63.01 (**trans**), -63.09 (**cis**); **^{13}C NMR (75 MHz, $CDCl_3$, cis isomer):** δ 171.97, 153.33, 142.35, 130.34, 129.91, 128.61, 127.44, 125.38 (q, *J* = 3.8 Hz), 123.85 (q, *J* = 273.42 Hz), 123.63, 123.50, 123.40, 114.67, 65.91, 60.83, 52.81, 41.00, 34.17, 29.72, 14.07; **IR (neat, cm^{-1}):** 2957, 2930, 2855, 1709, 1619, 1600, 1484, 1442, 1379, 1322, 1274, 1255, 1163, 1110, 1064, 1017, 839, 818, 748,664; **HRMS (ESI):** exact m/z calculated for $C_{21}H_{21}F_3NO_4$ $(M+H)^+$: 408.1417; Found: 408.1428 $(M+H)^+$.

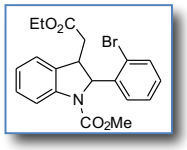
Methyl 3-(2-ethoxy-2-oxoethyl)-2-(4-(trifluoromethyl)phenyl)indoline-1-carboxylate (8h):



Following **GP-2**, **8h** was prepared from **7h** (0.232 g, 0.5 mmol, 1.00 equiv), $[Ir(ppy)_2(dtb\text{-}bpy)]PF_6$ (1.37 mg, 0.003 equiv, 0.3 mol %) and DIPEA (0.191 mL, 1.1 mmol, 2.2 equiv) in MeCN (1.5 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.53) afforded **8h** as a white solid (0.171 g, cis / trans = 75:25, 89% yield); Mp 65-67 °C (decomposed).

^{1}H NMR (300 MHz, $CDCl_3$, cis isomer): δ 7.81 (bs, 1H), 7.17 – 7.08 (m, 2H), 7.07 – 6.96 (m, 3H), 6.87 (d, *J* = 8.3 Hz, 2H), 5.55 (d, *J* = 9.6 Hz, 1H), 4.26 – 4.17 (m, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 3H), 2.67 – 2.59 (m, 1H), 2.39 (s, 3H), 2.01 (dd, *J* = 17.5, 10.2 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H); **^{1}H NMR (300 MHz, $CDCl_3$, trans isomer):** δ 7.28 – 7.18 (m, 1H), 7.17 – 7.07 (m, 3H), 7.07 – 6.92 (m, 4H), 5.13 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 3H), 3.45 (dd, *J* = 16.9, 10.2 Hz, 1H), 2.57 (d, *J* = 4.9 Hz, 1H), 2.42 (s, 3H), 1.26 (dd, *J* = 9.4, 4.9 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 2H); **^{13}C NMR (75 MHz, $CDCl_3$, cis isomer):** δ 172.20, 153.46, 138.05, 135.03, 128.37, 127.46, 126.83, 126.25, 125.88, 123.43, 123.14, 114.58, 66.05, 60.73, 52.70, 41.08, 34.13, 15.58, 14.18; **^{13}C NMR (75 MHz, $CDCl_3$, trans isomer):** δ 171.45, 150.95, 137.36, 134.35, 128.59, 127.40, 126.77, 126.36, 126.30, 123.37, 122.73, 115.06, 66.52, 60.86, 52.77, 40.95, 29.71, 15.85, 14.25; **IR (neat, cm^{-1}):** 2975, 2955, 2922, 1707, 1599, 1483, 1459, 1438, 1378, 1349, 1309, 1270, 1246, 1181, 1157, 1136, 1090, 1053, 1018, 968, 928, 839, 806, 745, 680; **HRMS (ESI):** exact m/z calculated for $C_{21}H_{24}NO_4S$ $(M+H)^+$: 386.1421; Found: 386.1424 $(M+H)^+$.

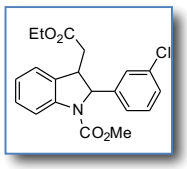
Methyl 2-(2-bromophenyl)-3-(2-ethoxy-2-oxoethyl)indoline-1-carboxylate (8i):



Following **GP-2**, **8i** was prepared from **7i** (0.249 g, 0.5 mmol, 1.00 equiv), $[Ir(ppy)_2(dtb\text{-}bpy)]PF_6$ (1.37 mg, 0.003 equiv, 0.3 mol %) and DIPEA (0.191 mL, 1.1 mmol, 2.2 equiv) in MeCN (1.5 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.30) afforded **8i** as a pale yellow syrup (0.167 g, cis / trans = 79:21, 80% yield).

^{1}H NMR (300 MHz, $CDCl_3$, cis isomer): δ 7.83 (bs, 1H), 7.28 – 7.12 (m, 4H), 7.03 – 6.91 (m, 3H), 5.59 (d, *J* = 9.7 Hz, 1H), 4.33 – 4.19 (m, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.63 (s, 3H), 2.63 – 2.53 (m, 1H), 1.97 (dd, *J* = 17.5, 10.2 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H); **^{1}H NMR (300 MHz, $CDCl_3$, trans isomer):** δ 7.47 (m, 1H), 7.28 – 7.12 (m, 4H), 7.03 – 6.91 (m, 3H), 4.70 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 1H), 3.63 (s, 3H), 3.54 – 3.45 (m, 1H), 2.66 – 2.61 (m, 1H), 1.27 – 1.22 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$, cis isomer):** δ 172.23, 153.51, 138.25, 128.63, 128.38, 127.92, 127.45, 126.93, 125.29, 123.98, 123.42, 123.11, 114.56, 66.40, 60.67, 52.65, 41.00, 34.20, 14.16; **^{13}C NMR (75 MHz, $CDCl_3$, trans isomer):** δ 171.58, 152.96, 138.14, 131.98, 130.39, 128.87, 128.08, 128.04, 127.33, 124.53, 123.97, 123.34, 115.05, 66.44, 60.83, 52.77, 41.00, 29.70, 14.24; **IR (neat, cm^{-1}):** 2958, 2922, 2851, 1708, 1596, 1575, 1482, 1439, 1378, 1334, 1307, 1269, 1252, 1176, 1136, 1080, 1053, 1021, 933, 793, 766, 749, 757; **HRMS (ESI):** exact m/z calculated for $C_{20}H_{21}BrNO_4$ $(M+H)^+$: 418.0621; Found: 418.0624 $(M+H)^+$.

Methyl 2-(3-chlorophenyl)-3-(2-ethoxy-2-oxoethyl)indoline-1-carboxylate (8j):



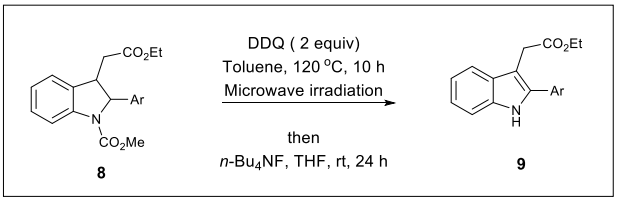
Following **GP-2**, **8j** was prepared from **7j** (0.226 g, 0.5 mmol, 1.00 equiv), $[Ir(ppy)_2(dtb\text{-}bpy)]PF_6$ (1.37 mg, 0.003 equiv, 0.3 mol %) and DIPEA (0.191 mL, 1.1 mmol, 2.2 equiv) in MeCN (1.5 mL). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.33) afforded **8j** as a white solid (0.147 g, cis / trans = 75:25, 79% yield).

^{1}H NMR (300 MHz, $CDCl_3$, cis isomer): δ 7.83 (s, 1H), 7.29 – 7.18 (m, 2H), 7.20 – 7.14 (m, 1H), 7.10 (dd, *J* = 10.1, 5.4 Hz, 1H), 7.02 – 6.95 (m, 2H), 6.83 (d, *J* = 7.4 Hz, 1H), 5.56 (d, *J* = 9.6 Hz, 1H), 4.30 – 4.21 (m, 1H), 4.11 – 4.03 (q, *J* = 7.1 Hz, 2H), 3.65 (s, 3H), 2.66 (dd, *J* = 9.1, 3.3 Hz, 1H), 1.94 (dd, *J* = 17.5, 10.6 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H); **^{1}H NMR (300 MHz, $CDCl_3$, trans isomer):** δ 7.75 (s, 1H), 7.30 – 7.17 (m, 3H), 7.14 – 7.04 (m, 2H), 7.04 – 6.92 (m, 2H), 5.15 (s, 1H), 4.21 – 4.12 (q, *J* = 7.1 Hz, 2H), 3.65 (s, 3H), 3.48 (t, *J* = 7.3 Hz, 1H), 2.63 (dd, *J* = 9.0, 2.7 Hz, 1H), 1.25 (dd, *J* = 7.1, 5.4 Hz, 1H), 1.25 – 1.21 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$, cis isomer):** δ 172.13, 153.36, 140.43, 134.25, 129.99, 129.79, 128.54,

128.16, 127.68, 127.26, 125.56, 124.94, 123.32, 114.65, 65.92, 60.91, 52.80, 41.08, 34.16, 14.17.

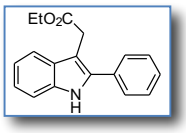
The obtained data is in accordance with literature data.[1]

6. General procedure (GP-3) for aromatization and deprotection of indolines:



A solution of indoline **8** (2 mmol, 1.0 equiv) and DDQ (4 mmol, 2.0 equiv) in toluene (15 mL) was placed in a sealed vessel in a microwave and irradiated at 120 °C for 10 h. After completion of the reaction, the solvent was removed and the residue was washed with saturated $NaHCO_3$ (15 mL) solution, and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was dissolved in THF (20 mL) and treated with Bu_4NF (10 mmol, 5 equiv) for 24 h at room temperature. After complete conversion of the starting material, the reaction mixture was concentrated *in vacuo*. Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc) afforded **9** as a pure compound.

Ethyl 2-(2-phenyl-1*H*-indol-3-yl)acetate (9a):

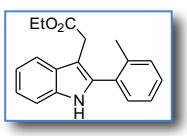


Following **GP-3**, **9a** was prepared from **8a** (0.678 g, 2.0 mmol, 1.00 equiv). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.35) afforded **8a** as a pale yellow oil (0.335 g, 60% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (bs, 1H), 7.72 – 7.64 (m, 3H), 7.53 – 7.44 (m, 2H), 7.44 – 7.34 (m, 2H), 7.27 – 7.12 (m, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 172.29, 136.19, 135.75, 132.43, 129.07, 128.97, 128.28, 128.08, 122.57, 120.05, 119.38, 110.88, 105.76, 60.91, 31.21, 14.26.

The obtained data is in accordance with literature data.[2]

Ethyl 2-(2-(o-tolyl)-1*H*-indol-3-yl)acetate (9b):



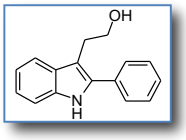
Following **GP-3**, **9b** was prepared from **8b** (0.706 g, 2.0 mmol, 1.00 equiv). Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.36) afforded **9b** as a pale yellow oil (0.369 g, 63% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (bs, 1H), 7.69 (dd, *J* = 11.5, 4.3 Hz, 1H), 7.46 – 7.15 (m, 7H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 2H), 2.27 (s, 3H), 1.25 – 1.18 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 172.12, 137.91, 136.04, 135.61, 131.81, 131.22, 130.36, 128.88, 128.17, 125.72, 122.14, 119.82, 119.20, 110.87, 106.53, 60.71, 31.01, 20.07, 14.23; **IR (neat, cm^{-1}):** 3355; 2978, 2925, 1717, 1486, 1456, 1367, 1306, 1265, 1238, 1175, 1155, 1110, 1026, 943, 740, 693; **HRMS (ESI):** exact m/z calculated for $C_{19}H_{20}NO_4$ $(M+H)^+$: 293.1410 Found: 293.1417 $(M+H)^+$.

7. Reduction of indole esters with $LiAlH_4$:

2-(2-phenyl-1*H*-indol-3-yl)ethan-1-ol (10):



To a stirred suspension of $LiAlH_4$ (0.040 g, 1.04 mmol) in dry THF (4 mL) was added **9a** (0.200 g, 0.716 mmol) slowly at 0 °C. The resulting solution was stirred at room temperature for 10 h. The reaction mixture was quenched by using wet Na_2SO_4 and diluted with EtOAc (20 mL), filtered through pad of celite and concentrated under reduced pressure to give crude alcohol **10**. Purification of the crude product by column chromatography (silica gel, hexanes–EtOAc, 9:1, R_f = 0.13) afforded **10** as a pale yellow solid (0.206 g, 84% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (bs, 1H), 7.68 – 7.56 (m, 3H), 7.51 – 7.41 (m, 2H), 7.41 – 7.32 (m, 2H), 7.17 (m, 2H), 3.95 (t, *J* = 6.7 Hz, 2H), 3.16 (t, *J* = 6.7 Hz, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 135.92, 132.87, 129.18, 128.95, 128.18, 127.90, 122.49, 119.84, 119.16, 110.96, 108.86, 63.01, 28.06.

The obtained data is in accordance with literature data.[3]

8. References:

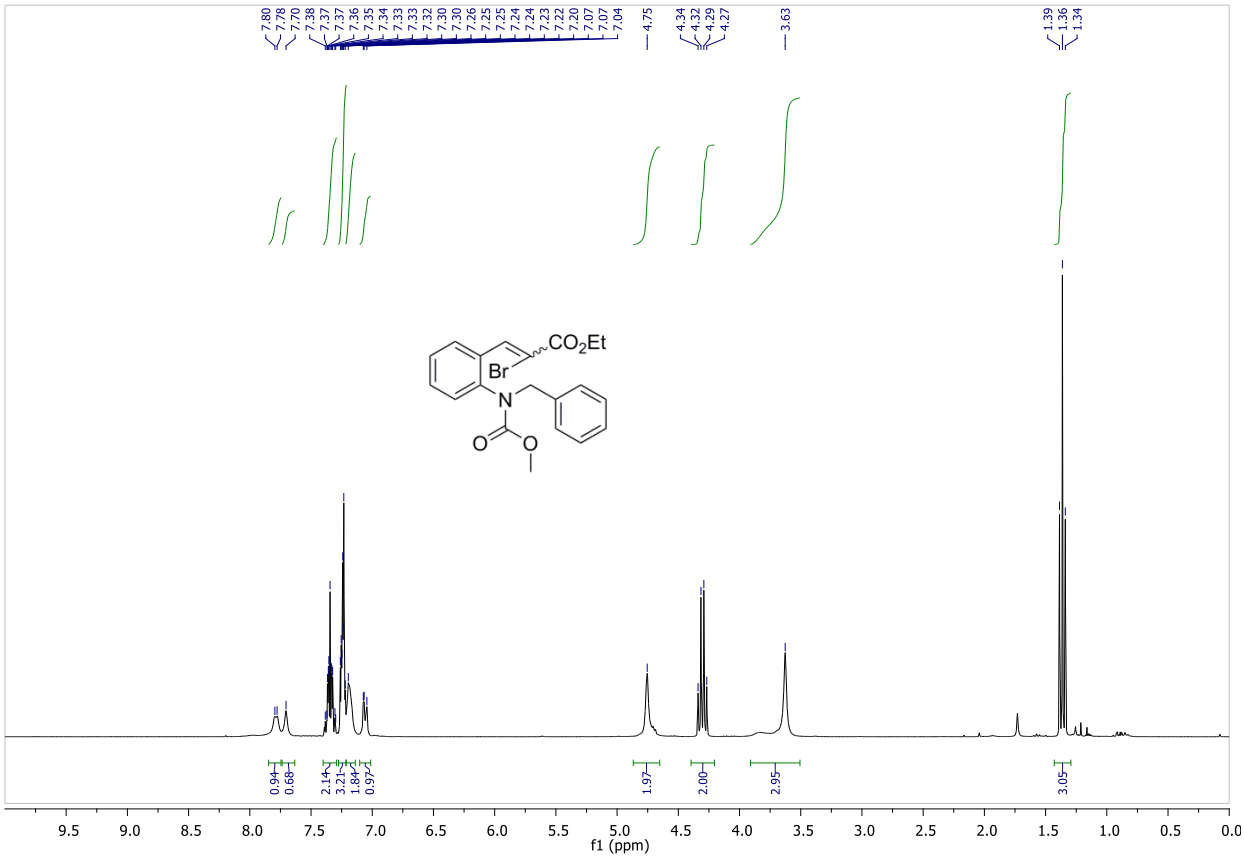
1. I. Prediger, T. Weiss and O. Reiser, *Synthesis* 2008, **14**, 2191–2198.

2. X. Wang, D. V. Gribkov and D. Sames, *J. Org. Chem.* 2007, **72**, 1476-1479.

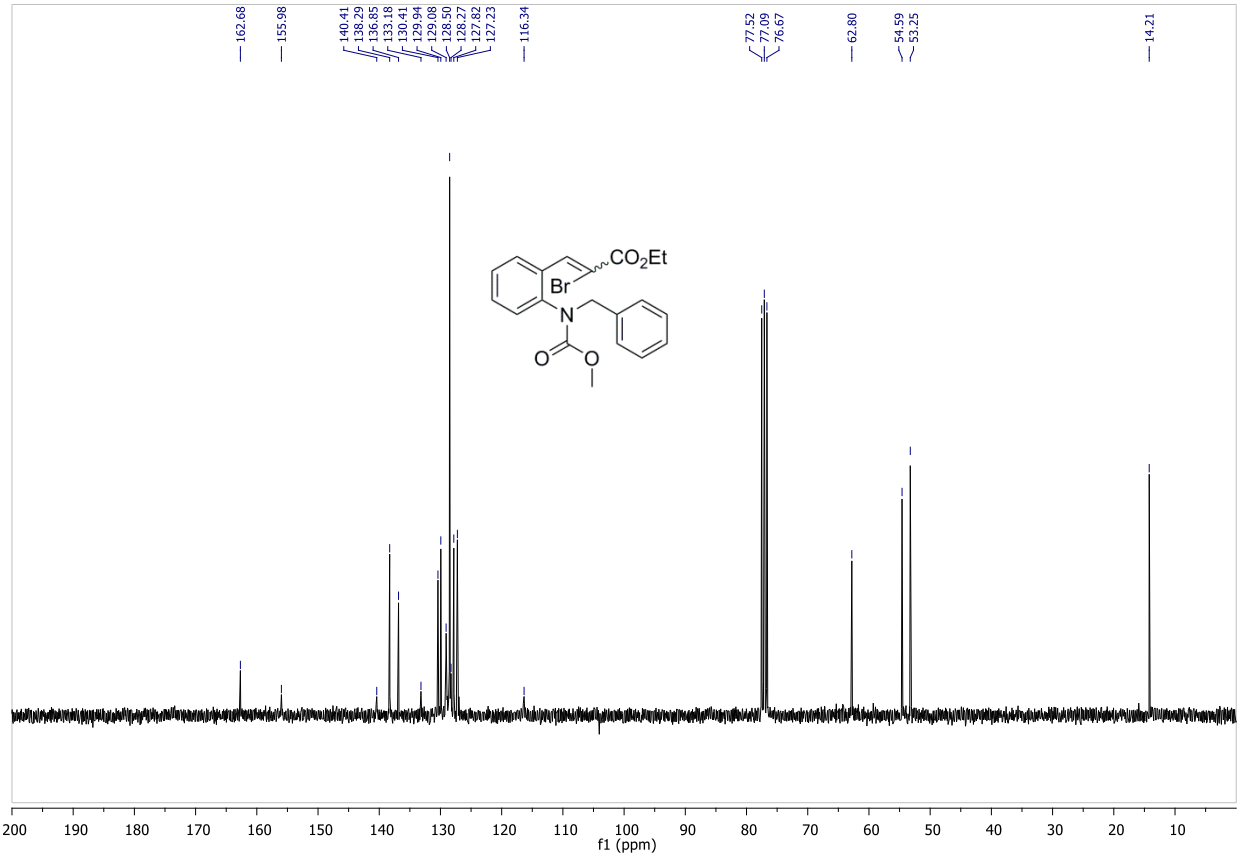
3. C. Liu, W. Zhang, L.-X. Dai and S.-L. You, *Org. Lett.* 2012, **14**, 4525-4527.

9. NMR spectra:

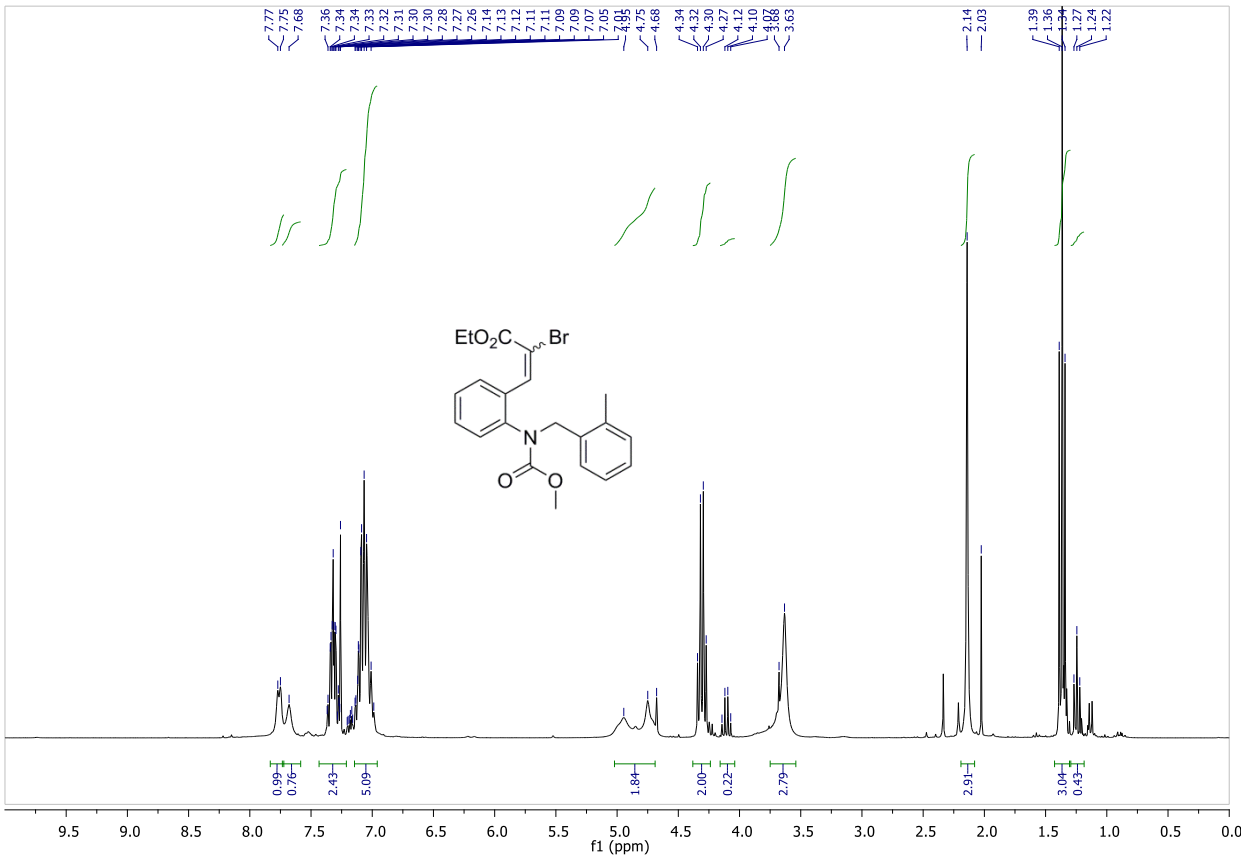
^{1}H-NMR: **7a**



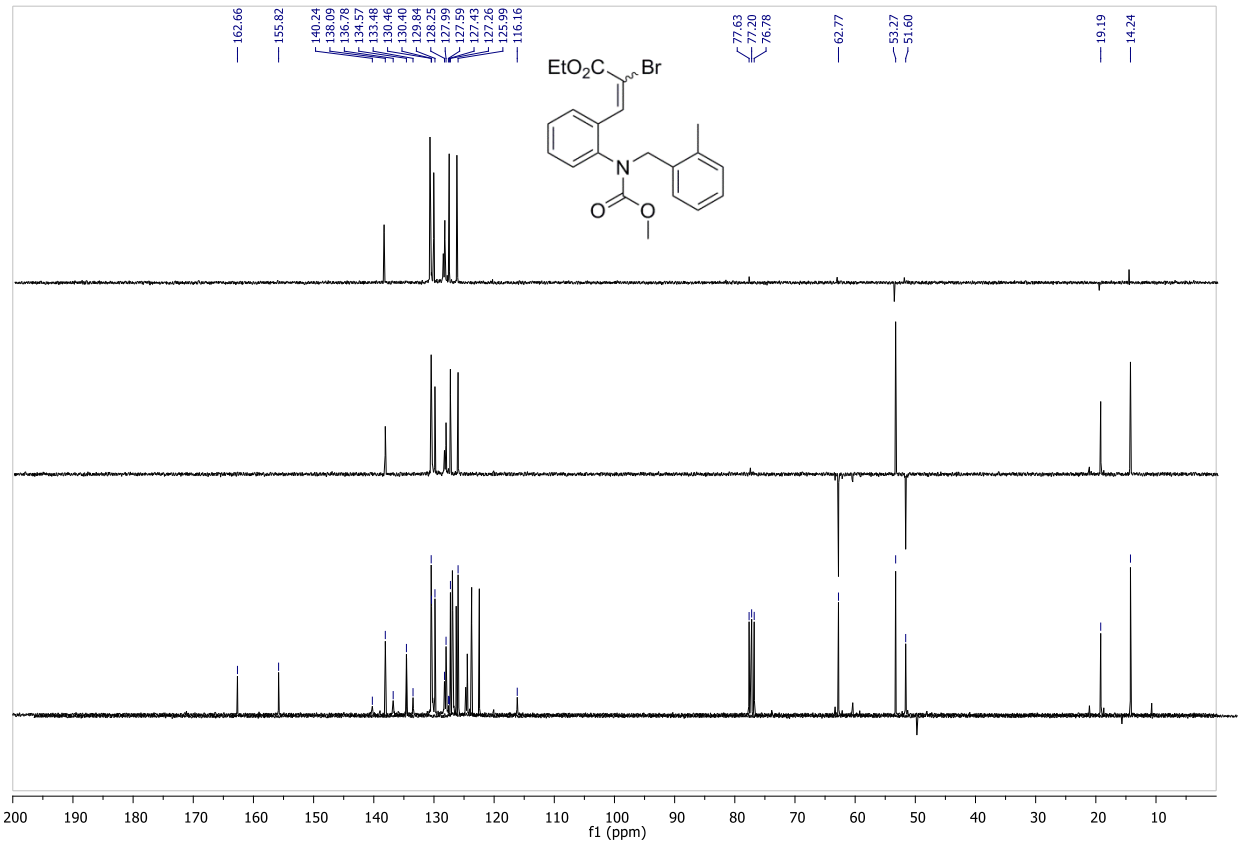
^{13}C-NMR: **7a**



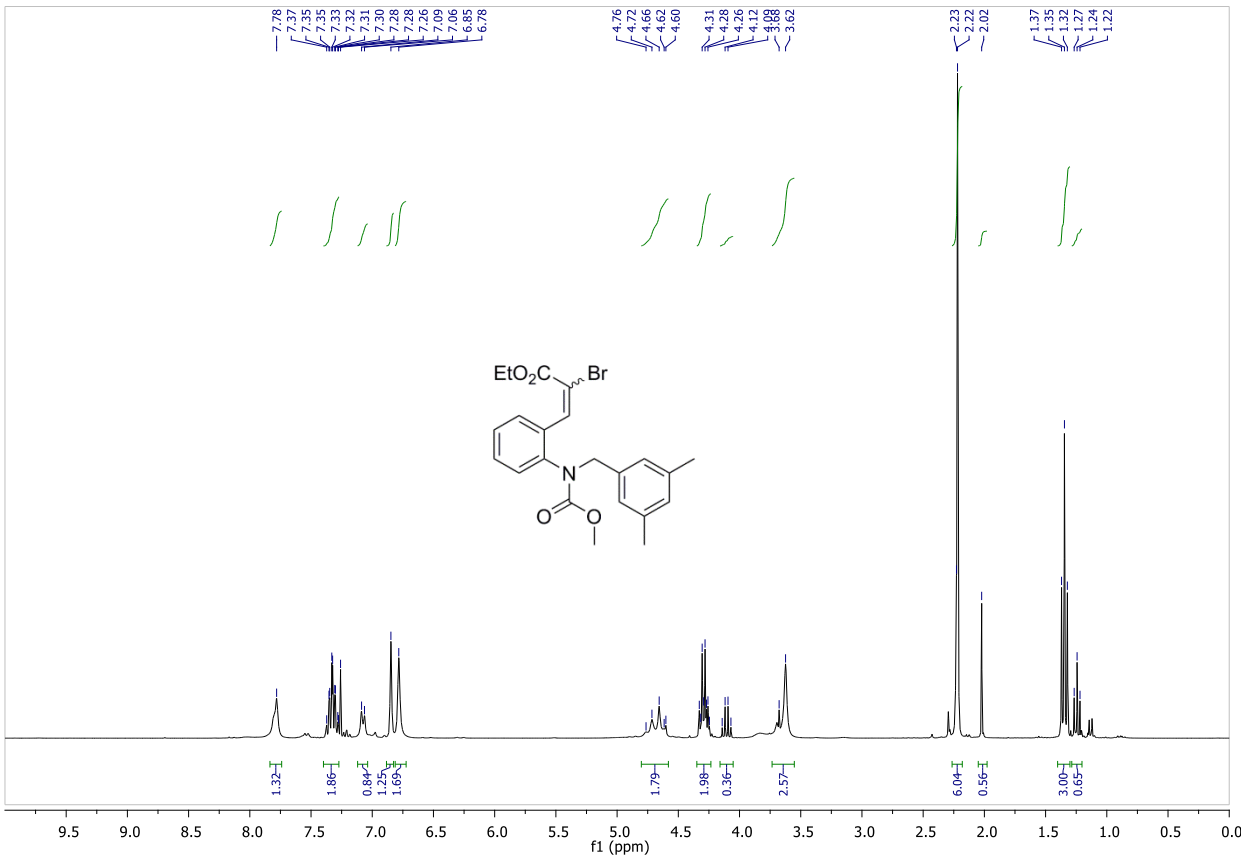
^{1}H-NMR: **7b**



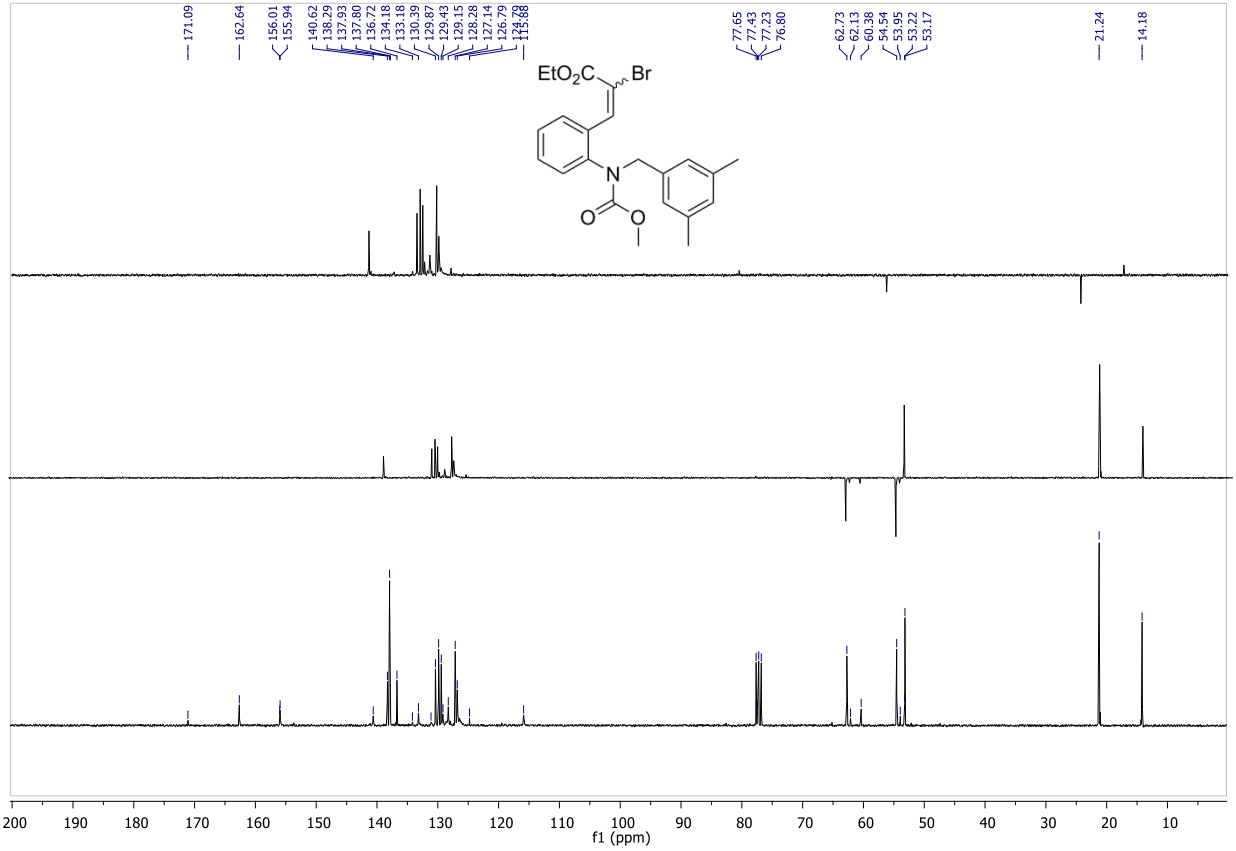
^{13}C-NMR: **7b**



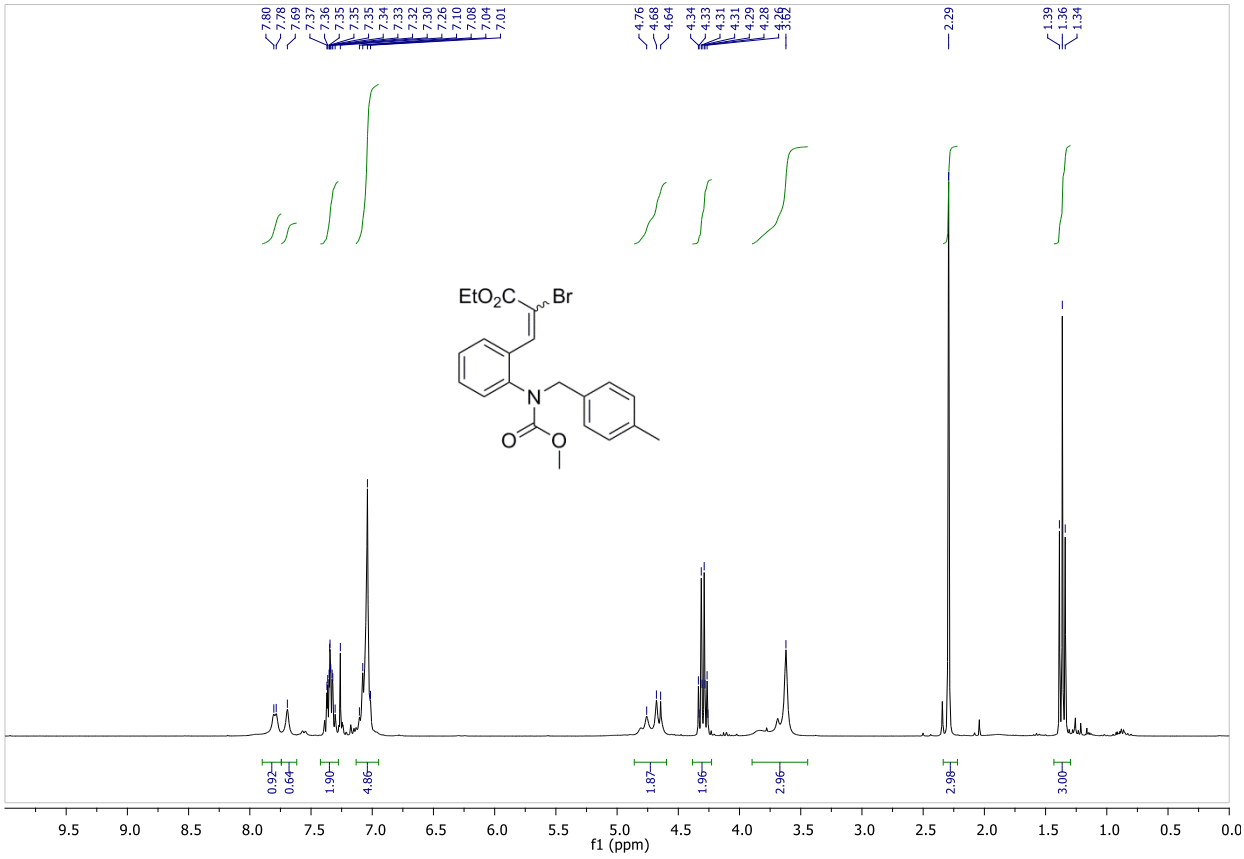
^{1}H-NMR: **7c**



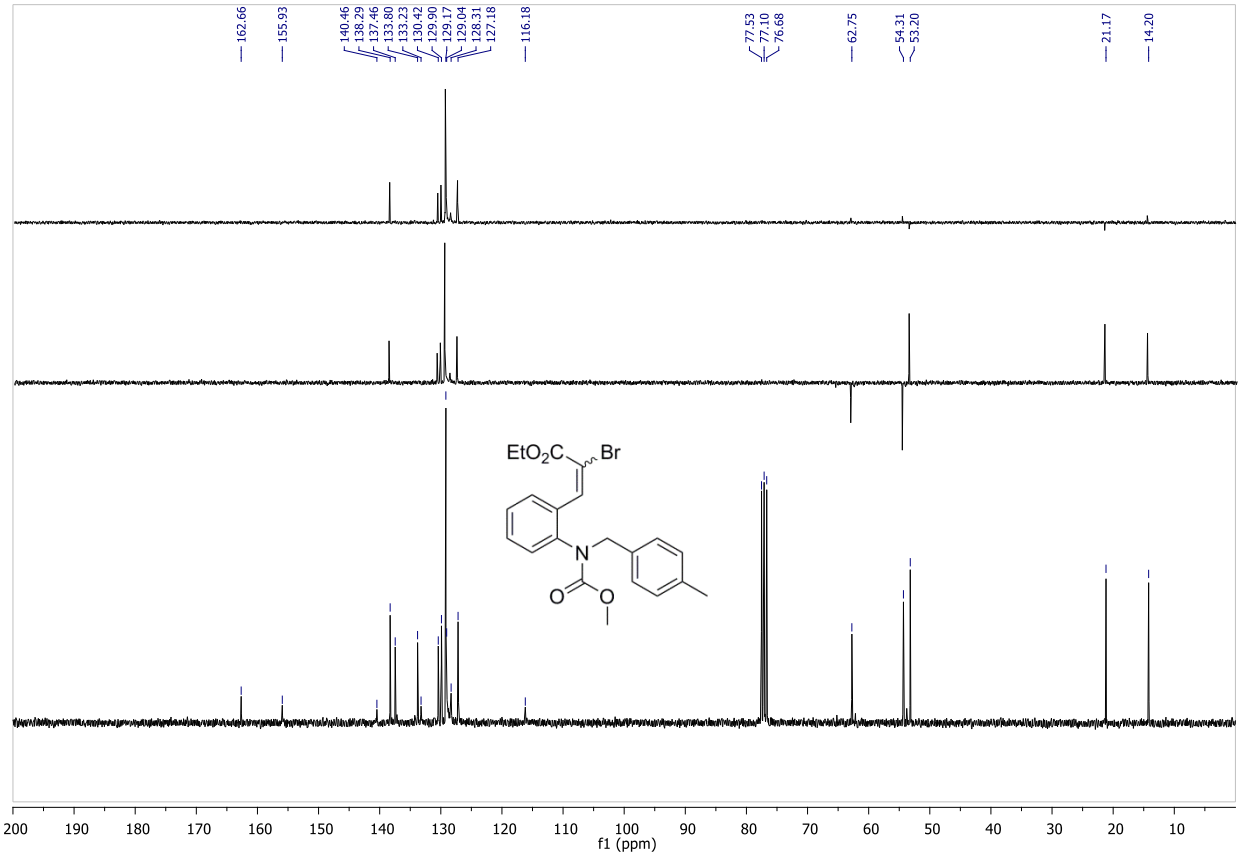
^{13}C-NMR: **7c**



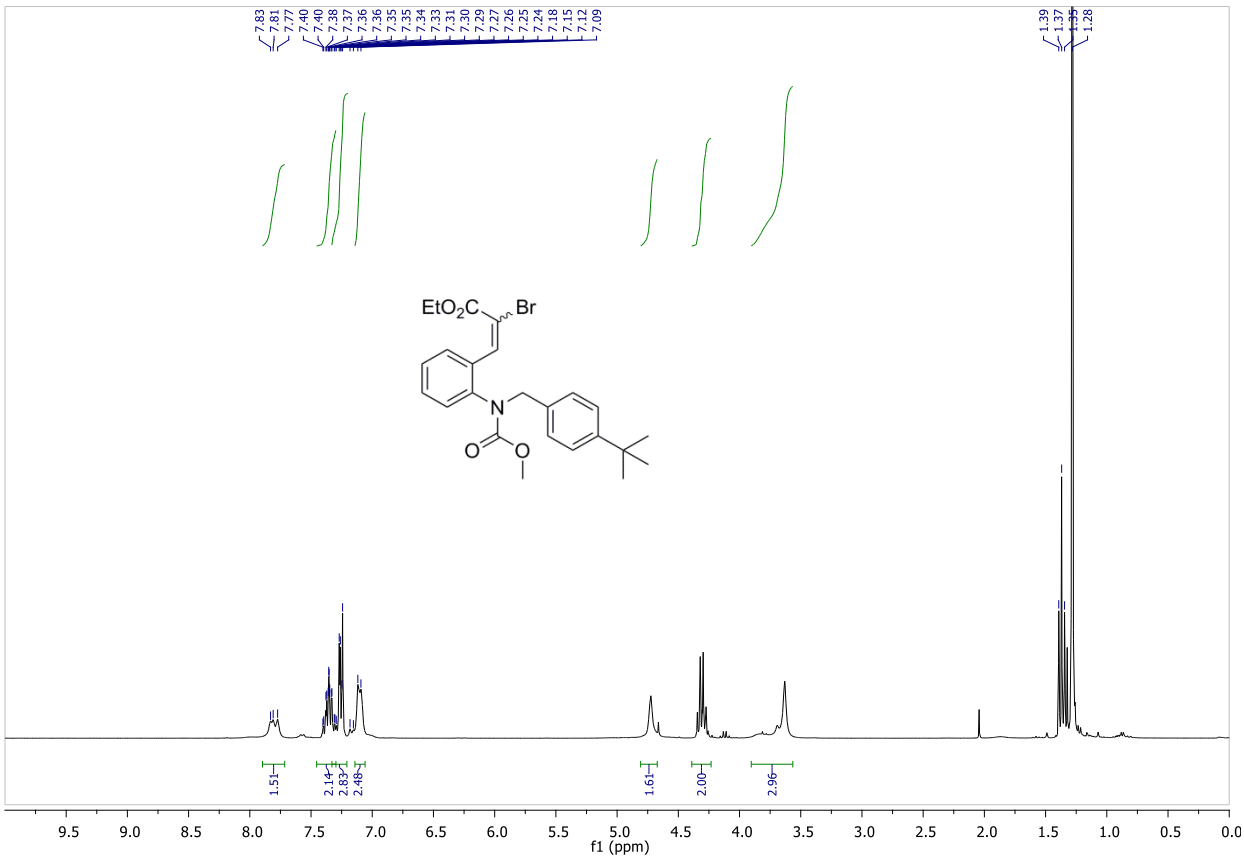
^{1}H-NMR: **7d**



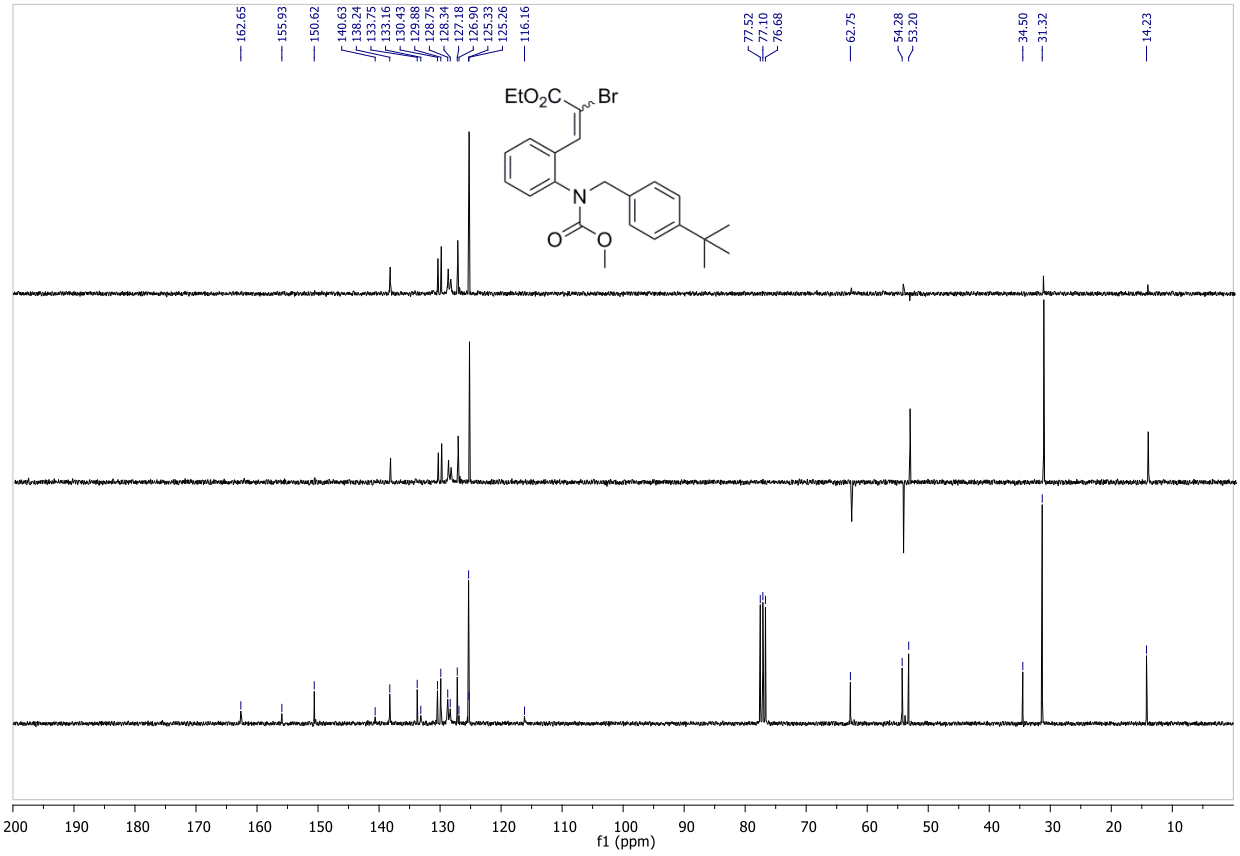
^{13}C-NMR: **7d**



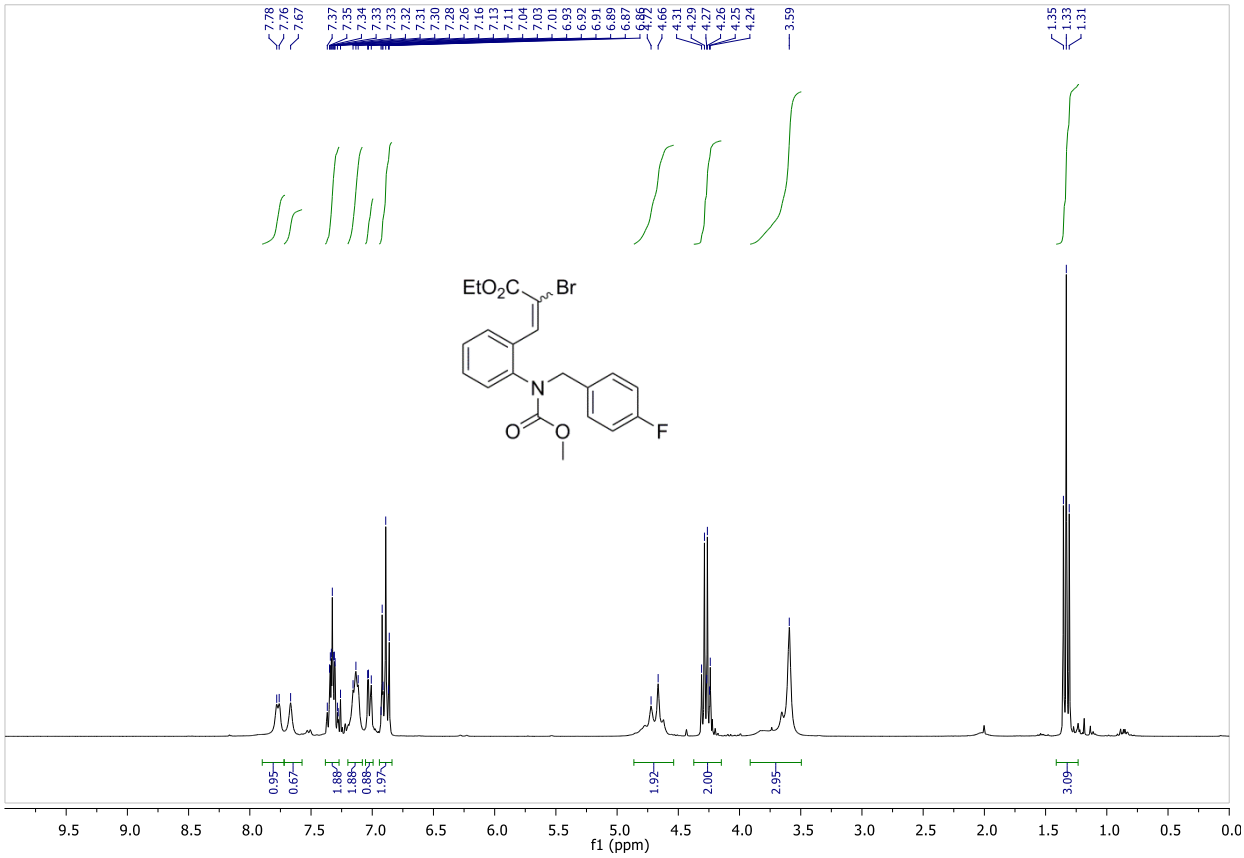
^{1}H-NMR: **7e**



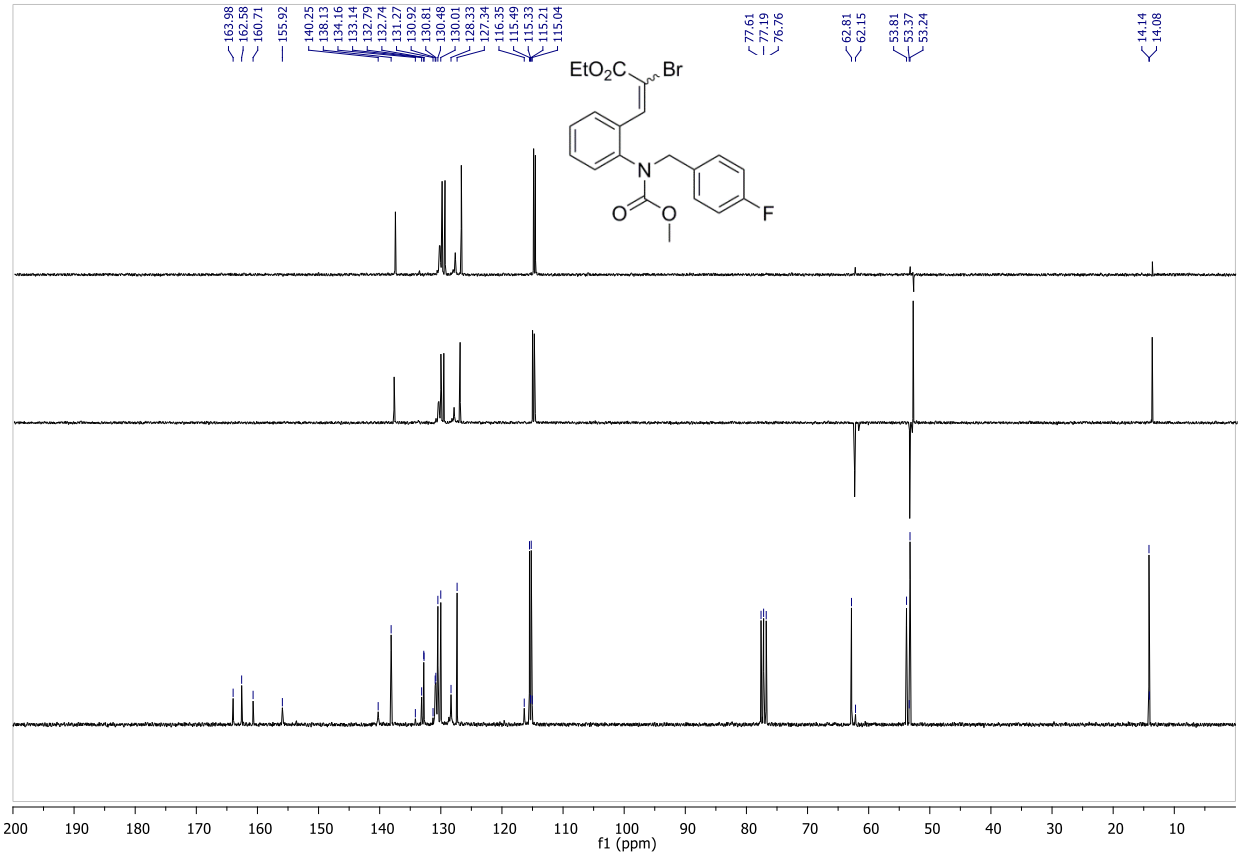
^{13}C-NMR: **7e**



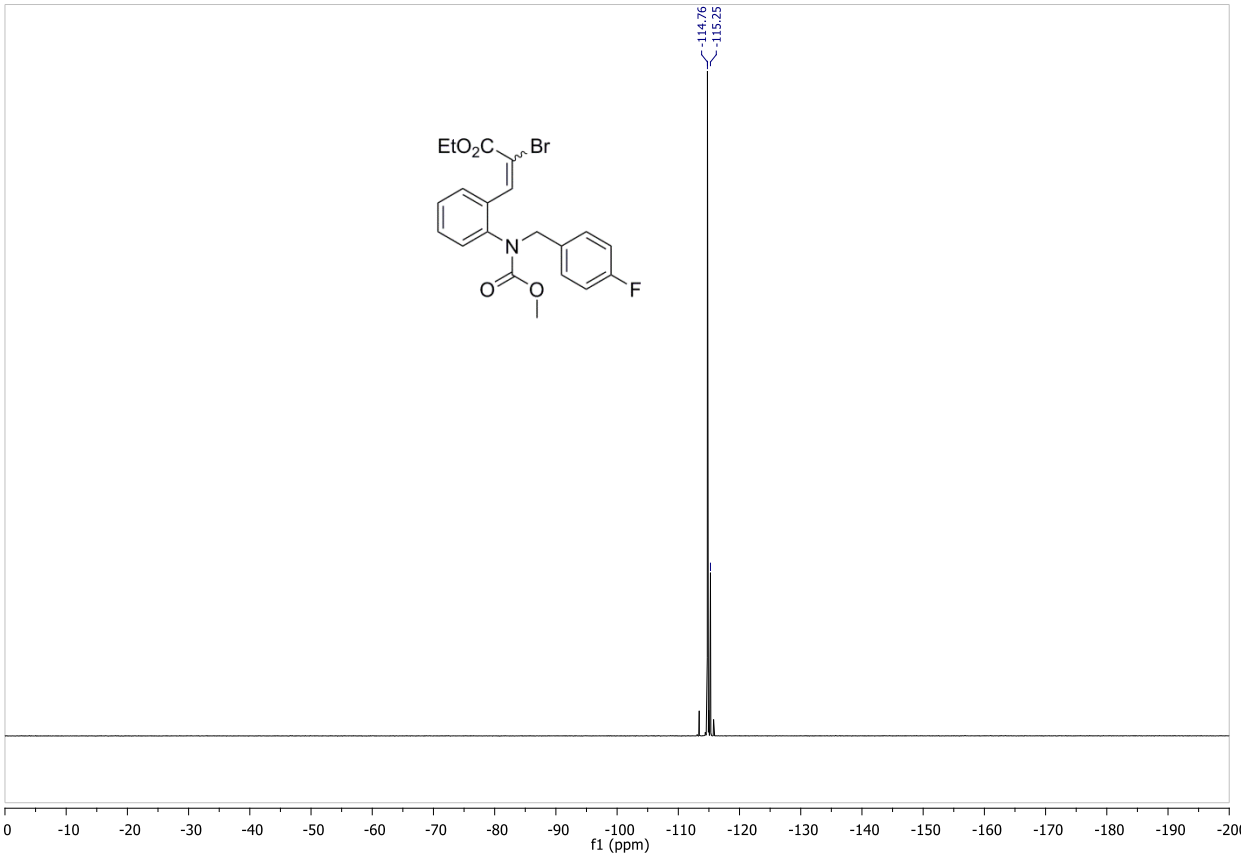
^{1}H-NMR: **7f**



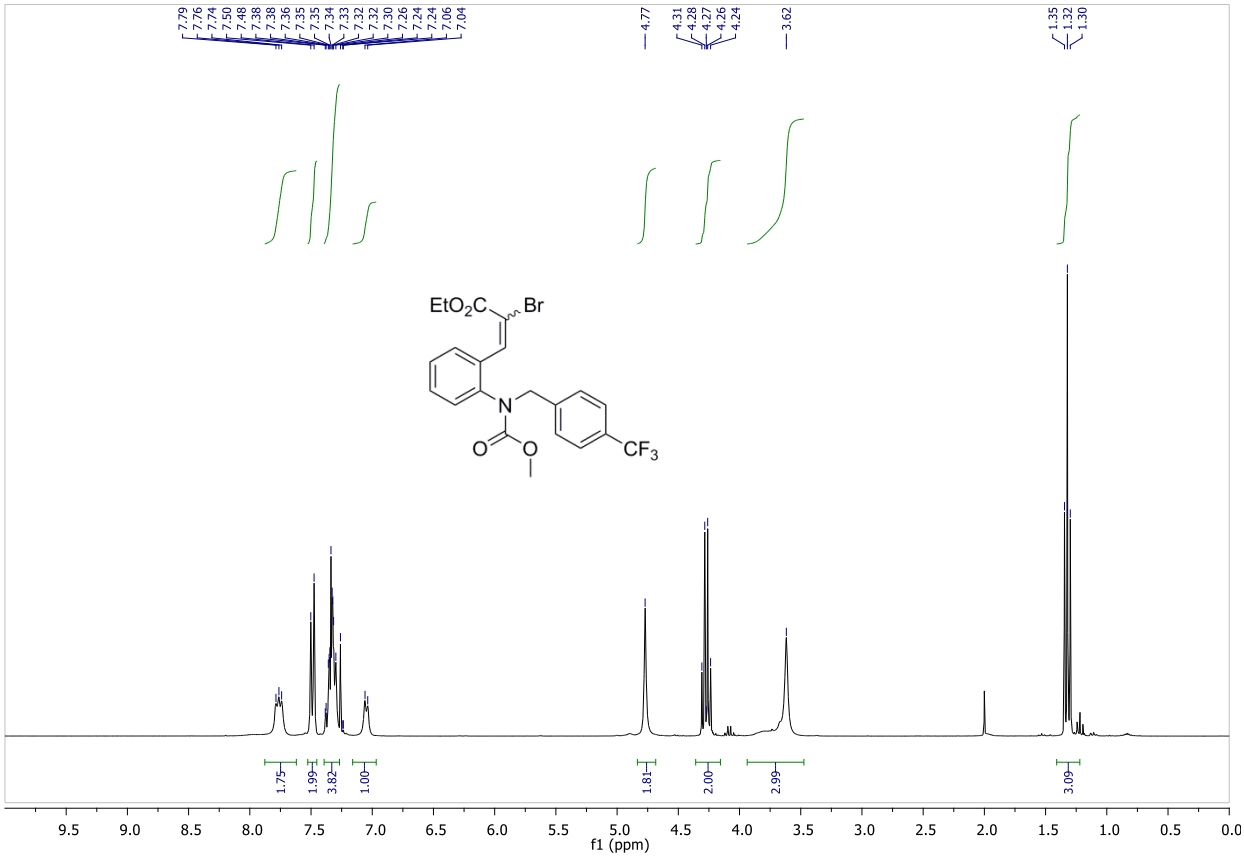
^{13}C-NMR: **7f**



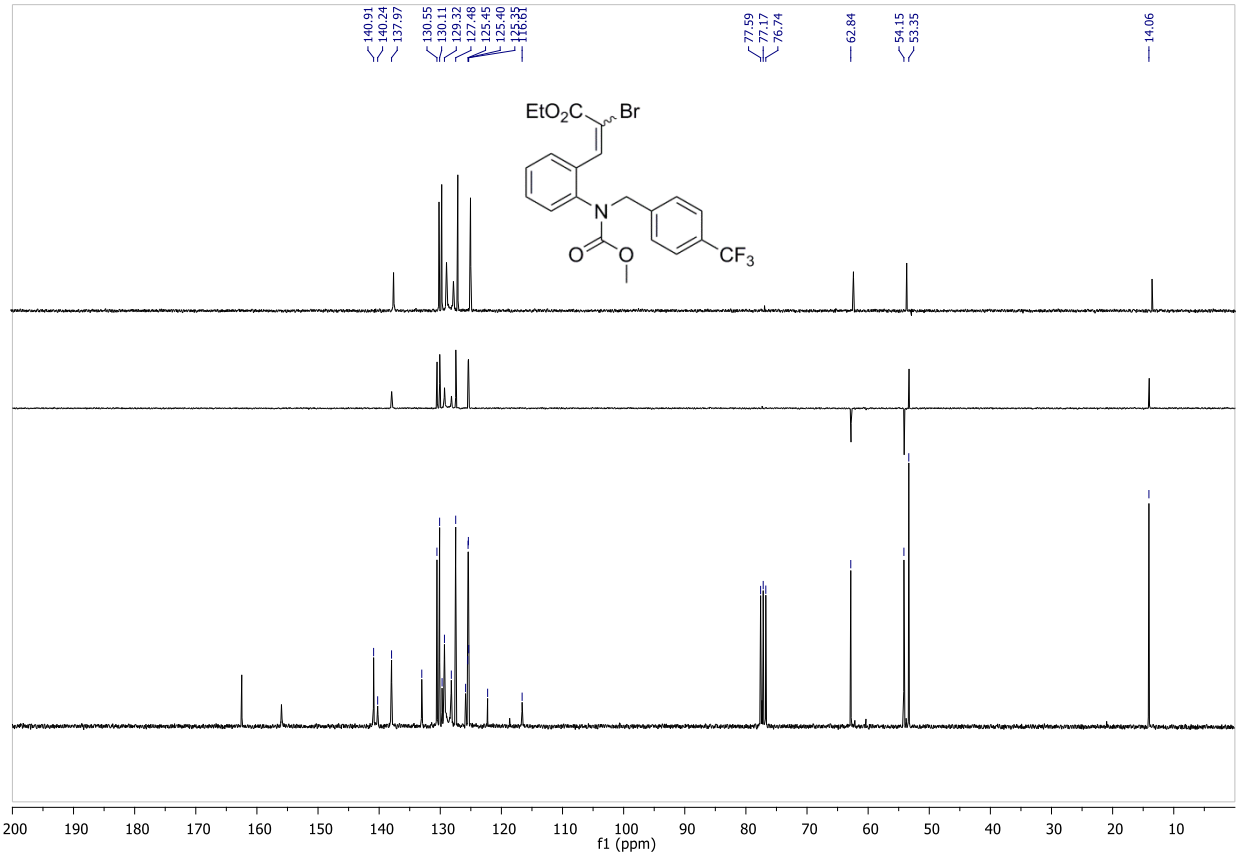
^{19}F-NMR: **7f**


-114.76
-115.25
EtO2C
Br
N
O
O
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

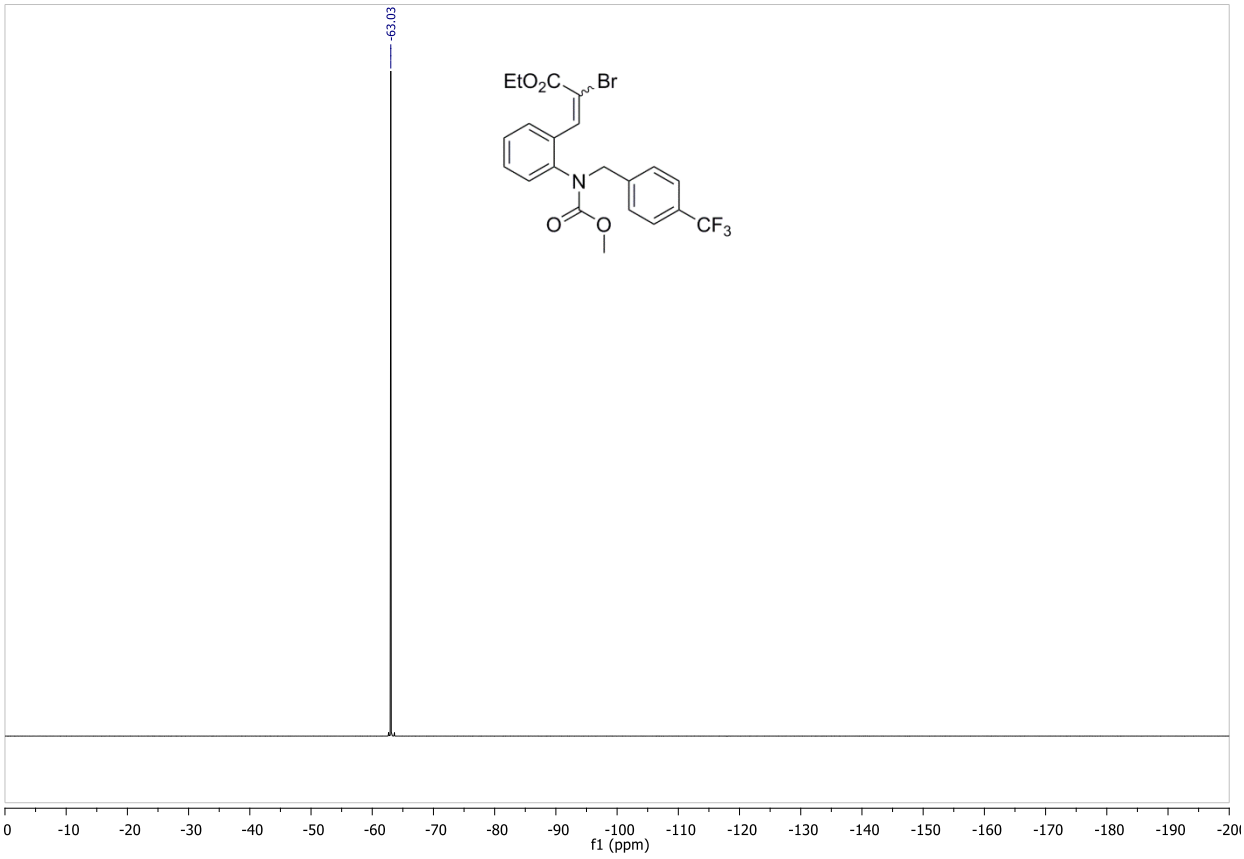
^{1}H-NMR: **7g**



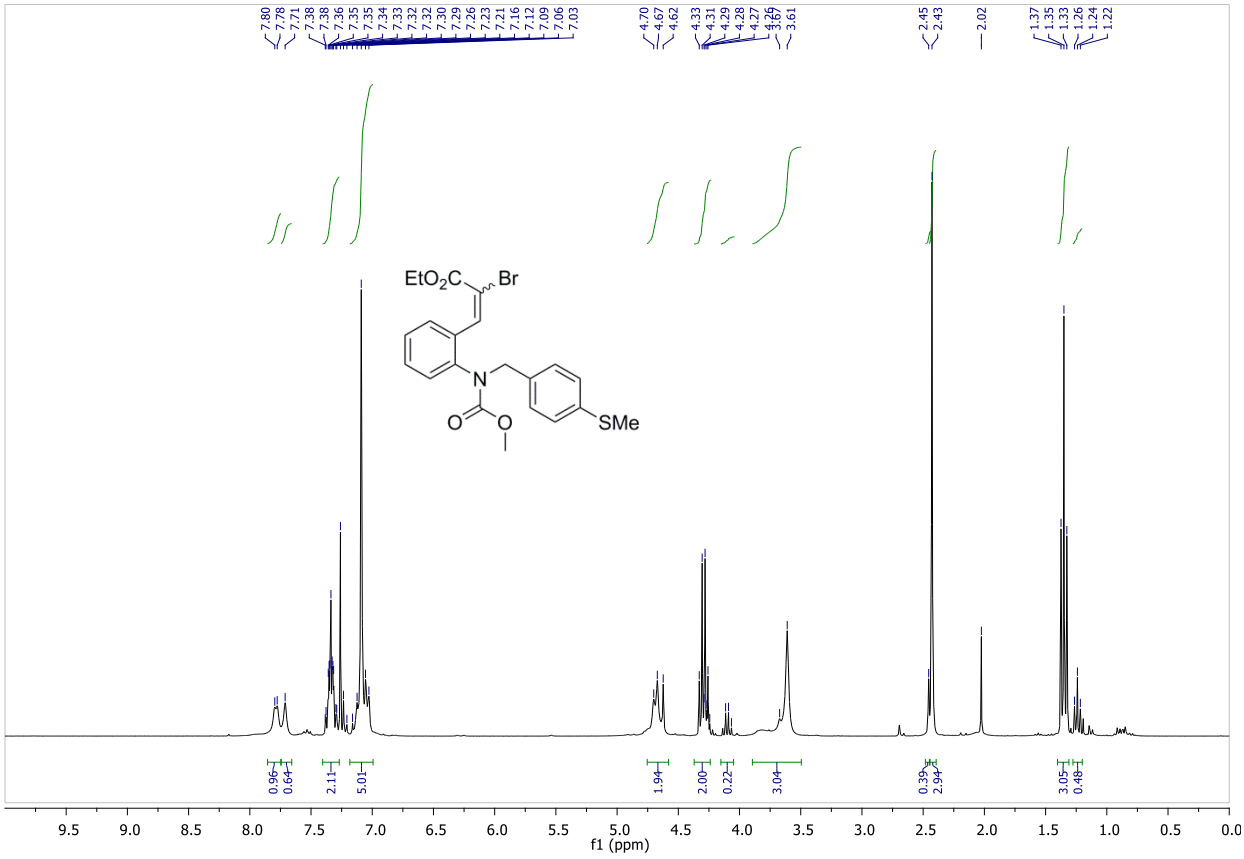
^{13}C-NMR: **7g**



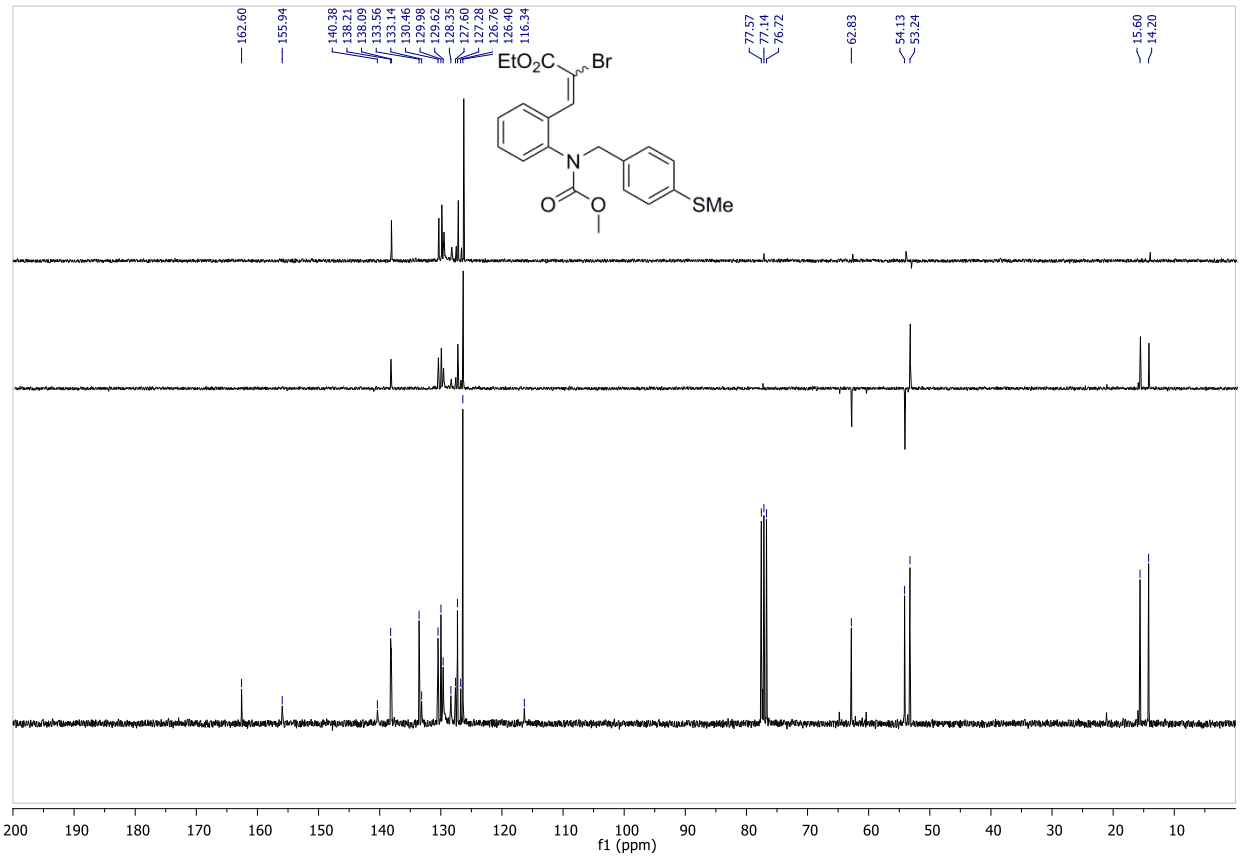
^{19}F-NMR: **7g**


-63.03
EtO2C
Br
N
O
O
CF3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

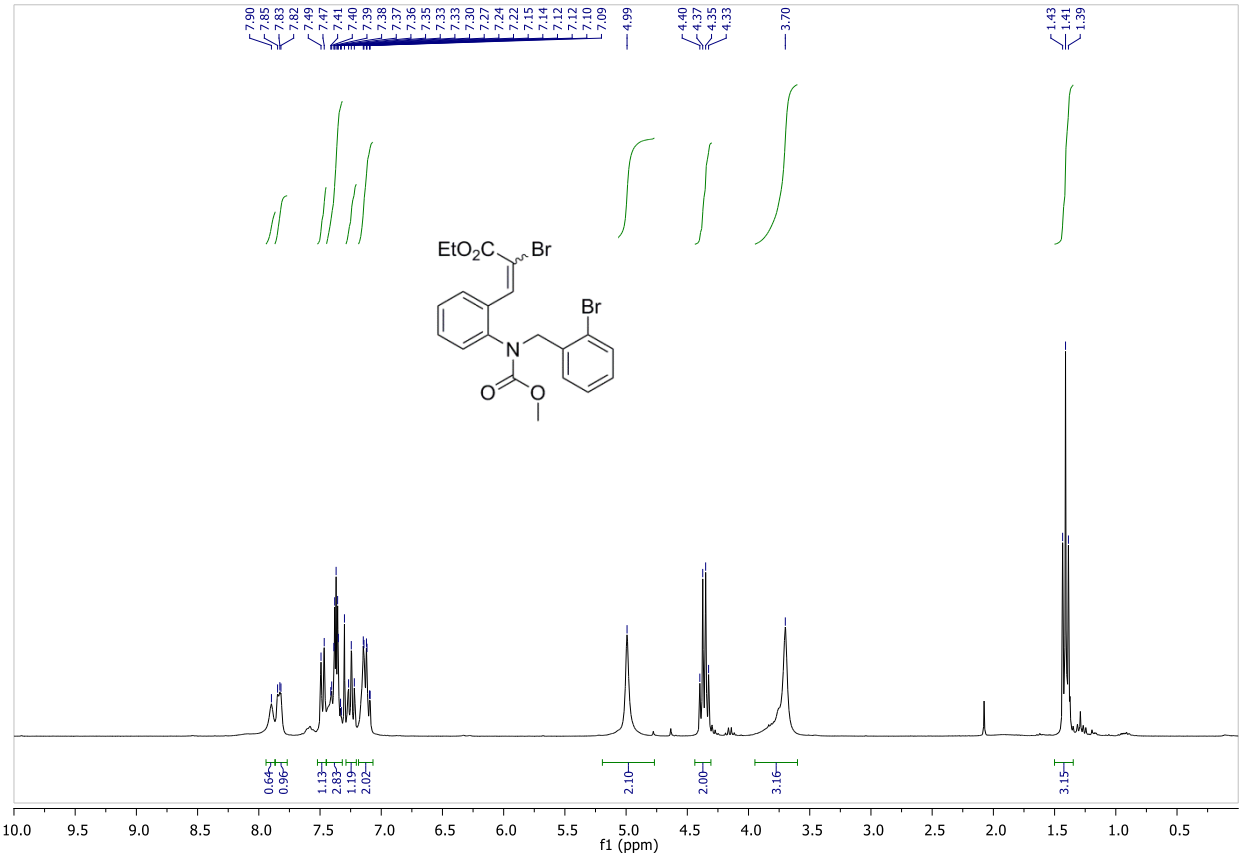
^{1}H-NMR: **7h**



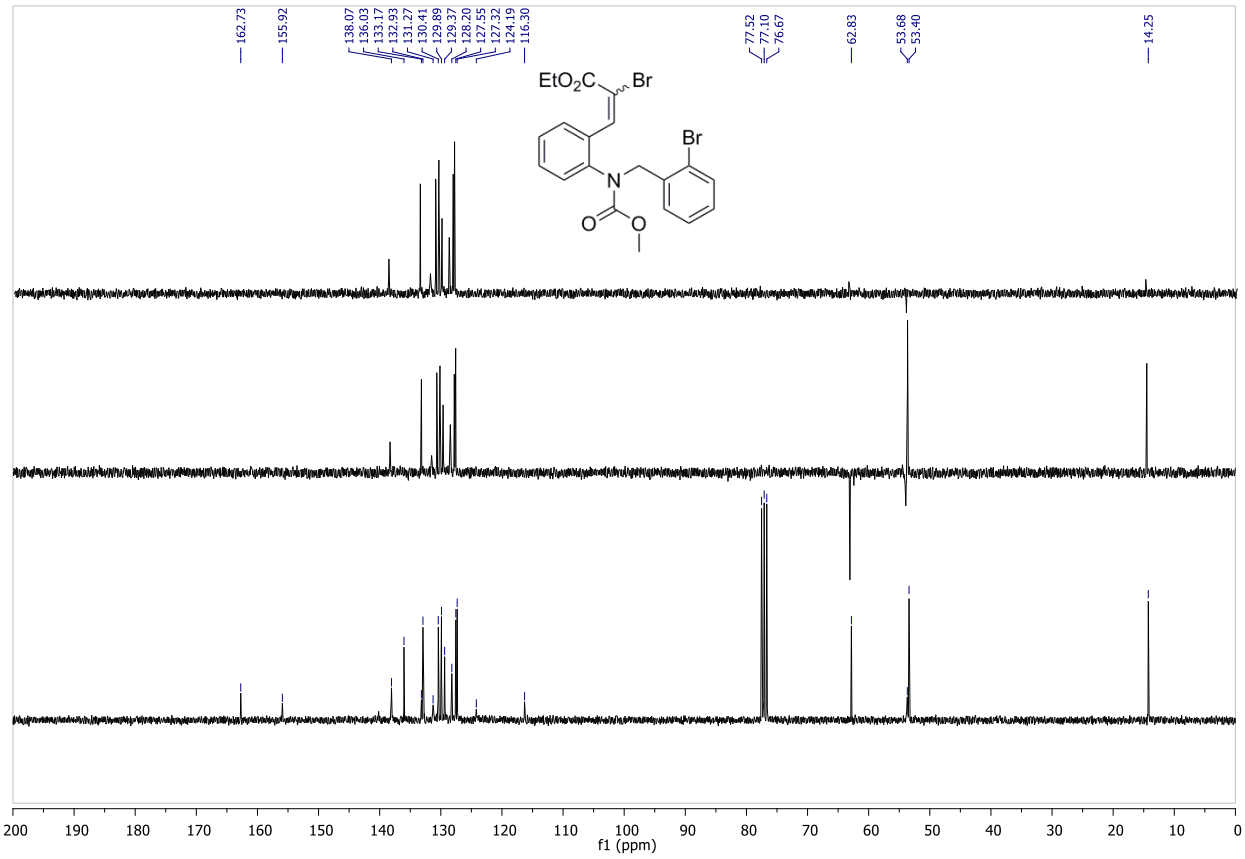
^{13}C-NMR: **7h**



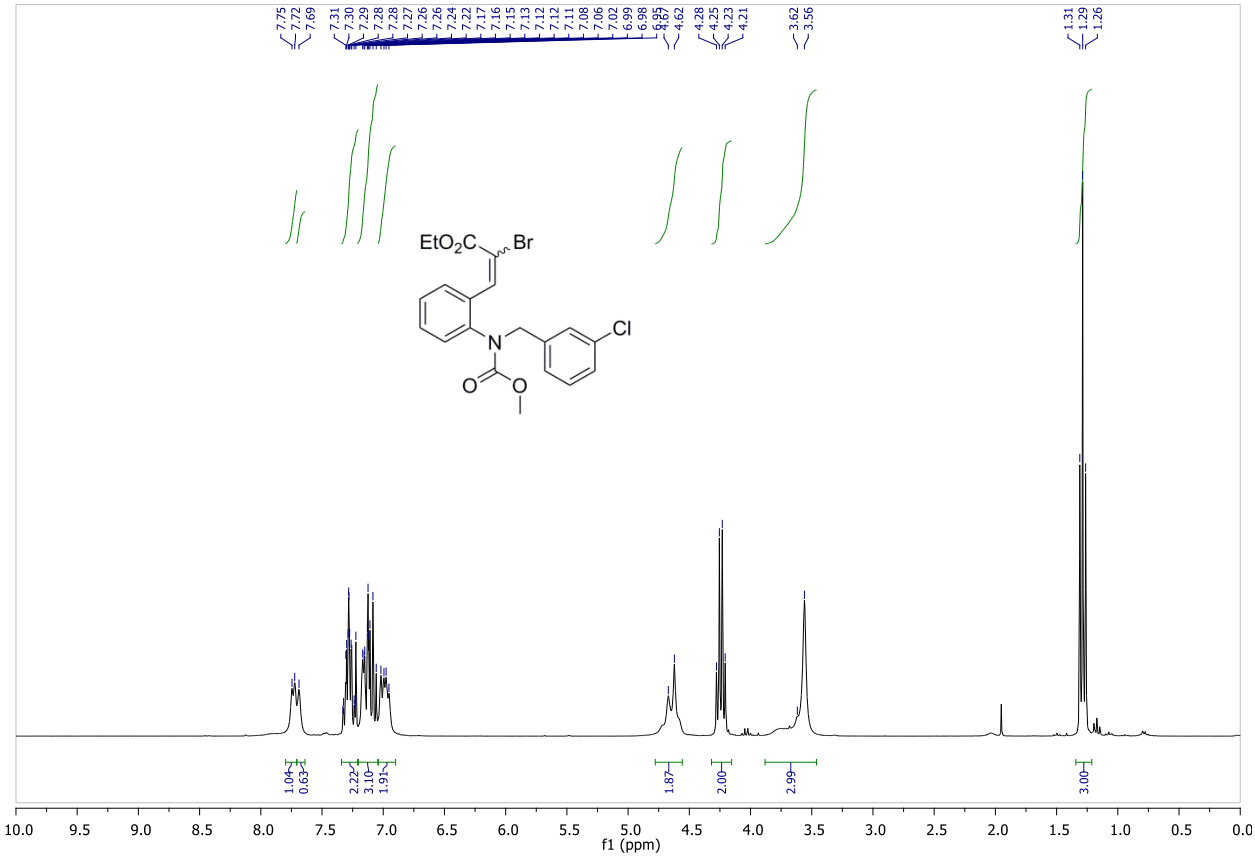
^{1}H-NMR: **7i**



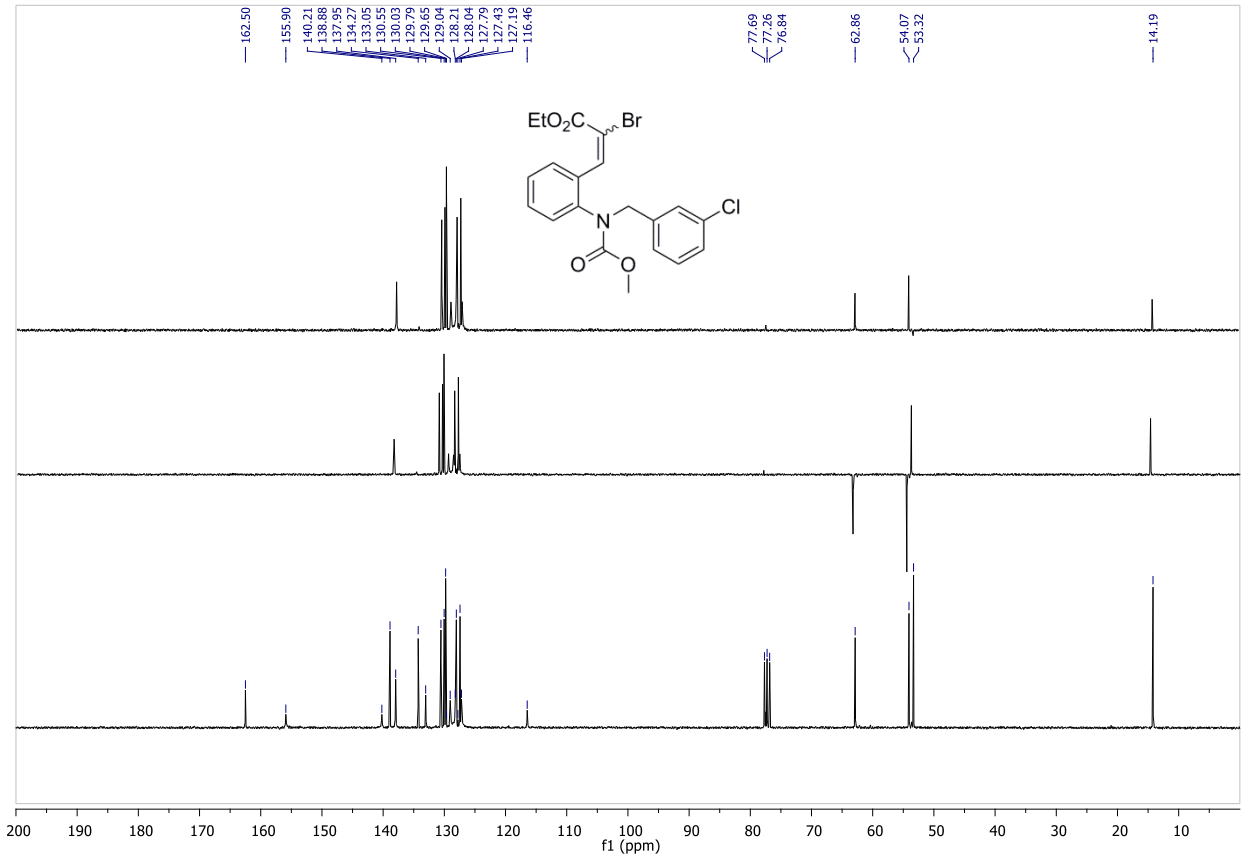
^{13}C-NMR: **7i**



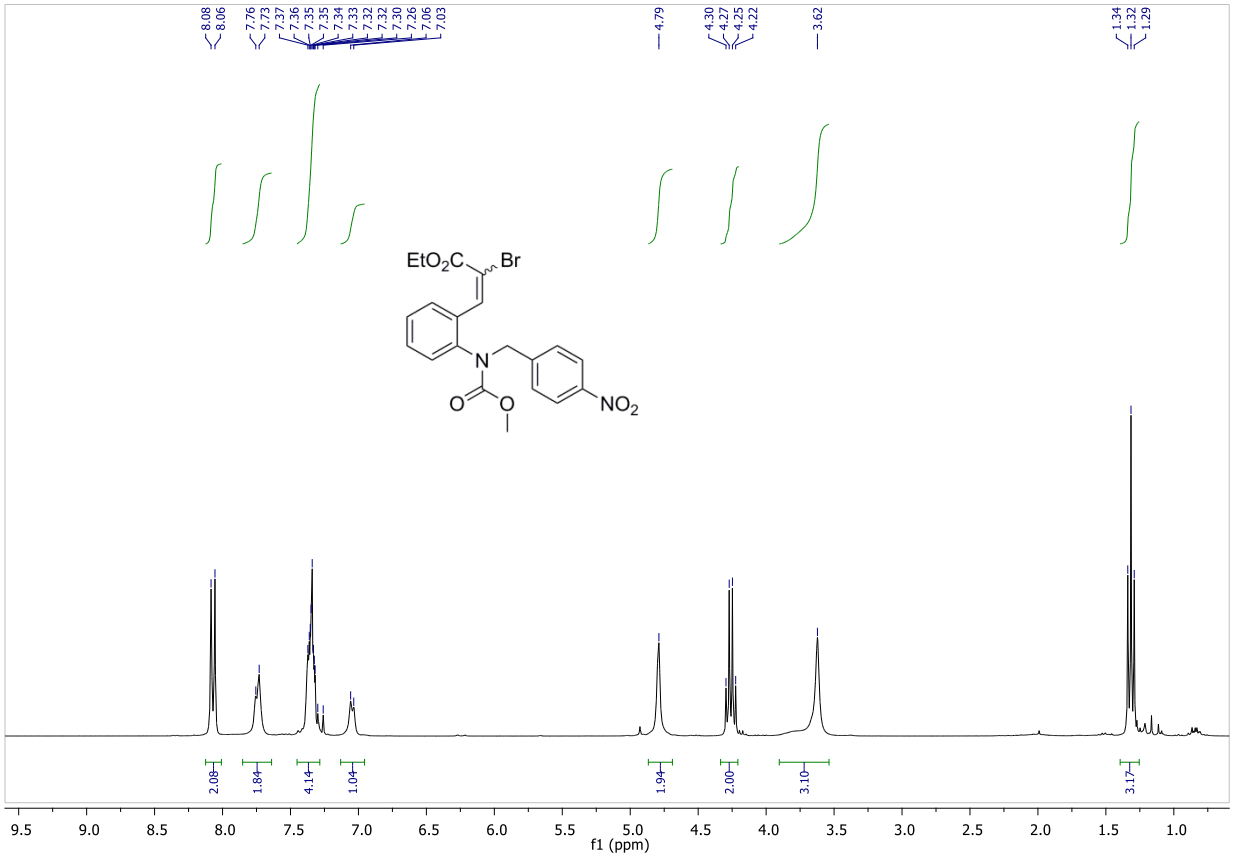
^{1}H-NMR: **7j**



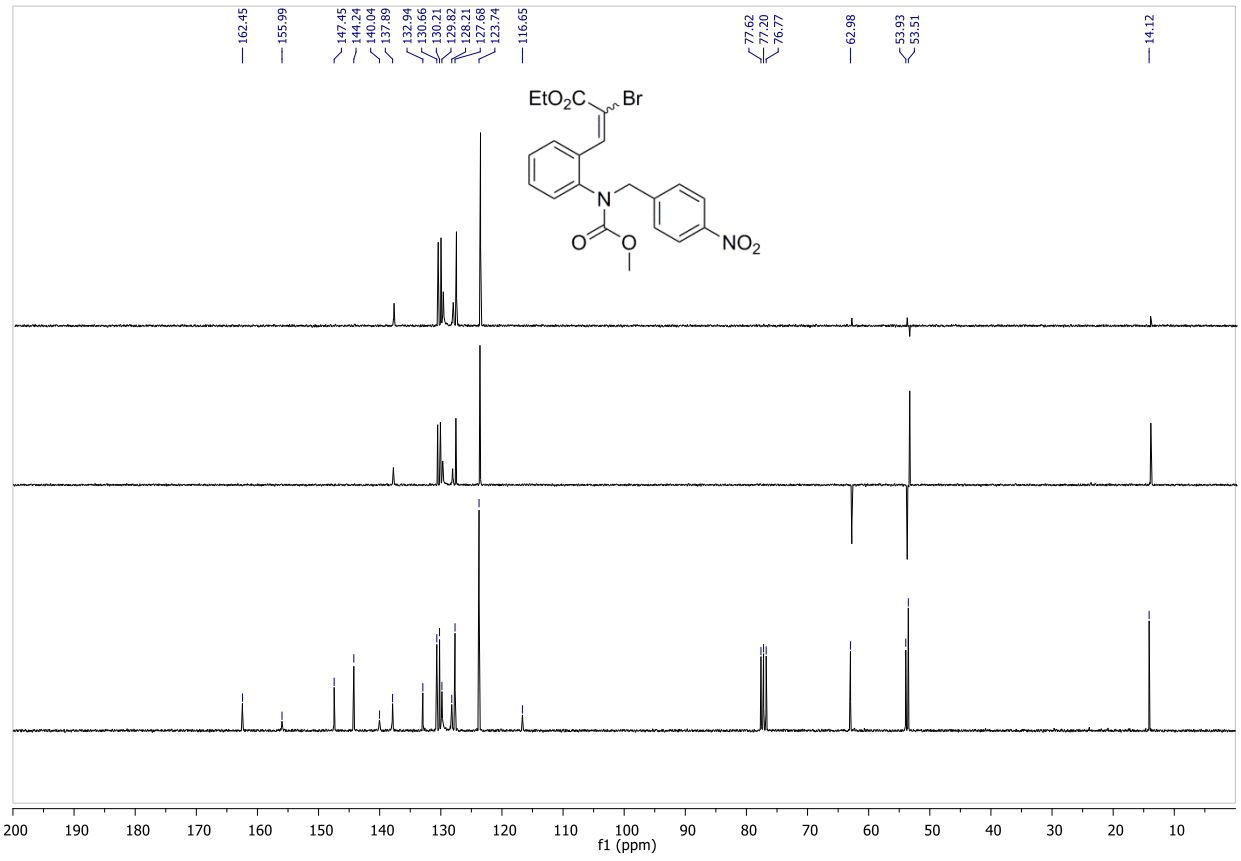
^{13}C-NMR: **7j**



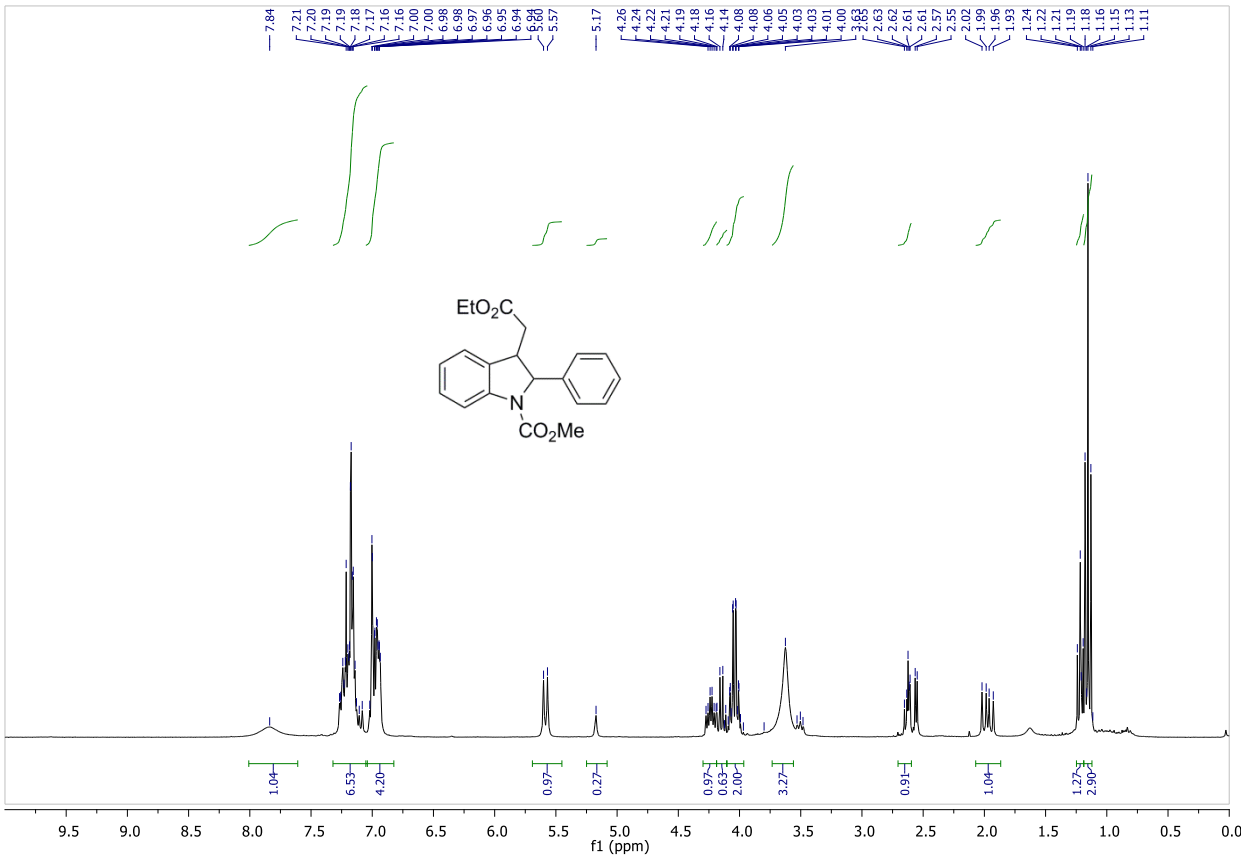
^{1}H-NMR: **7k**



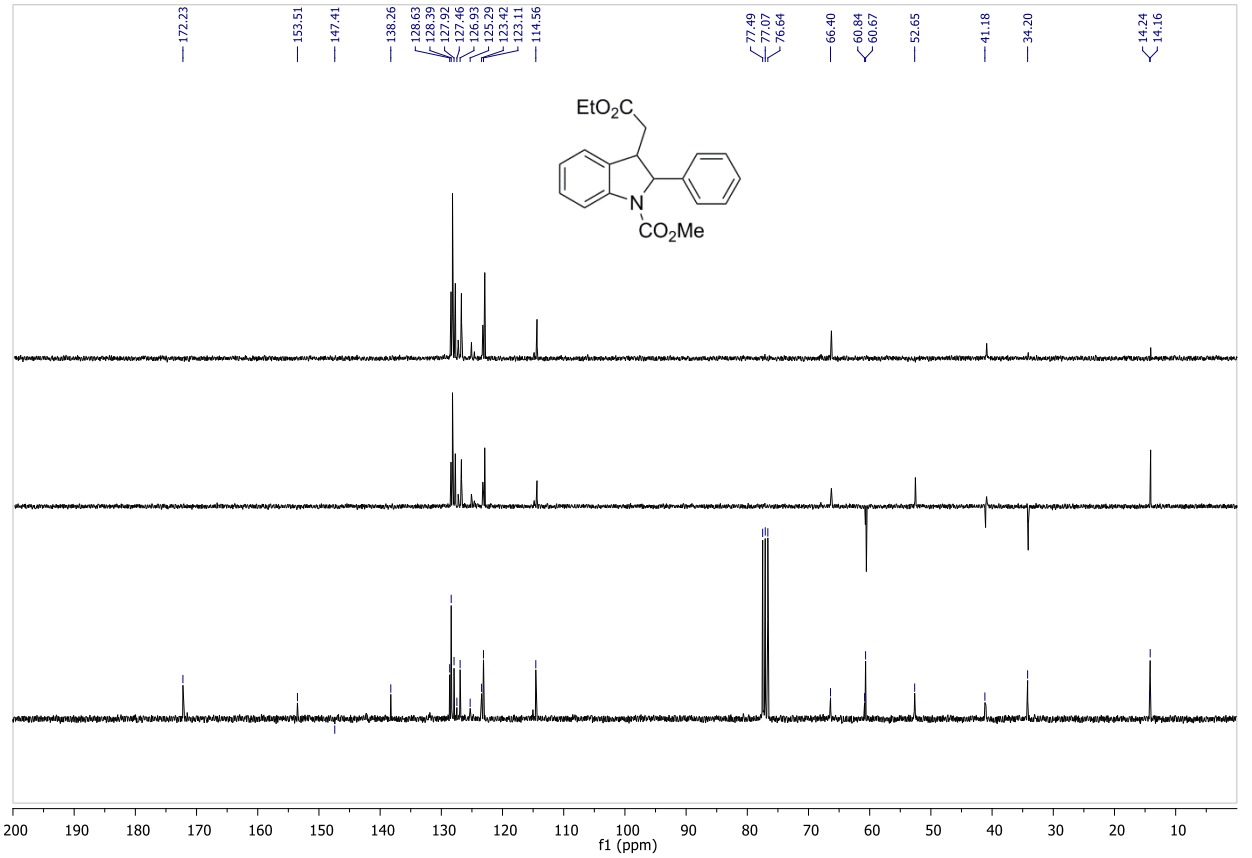
^{13}C-NMR: **7k**



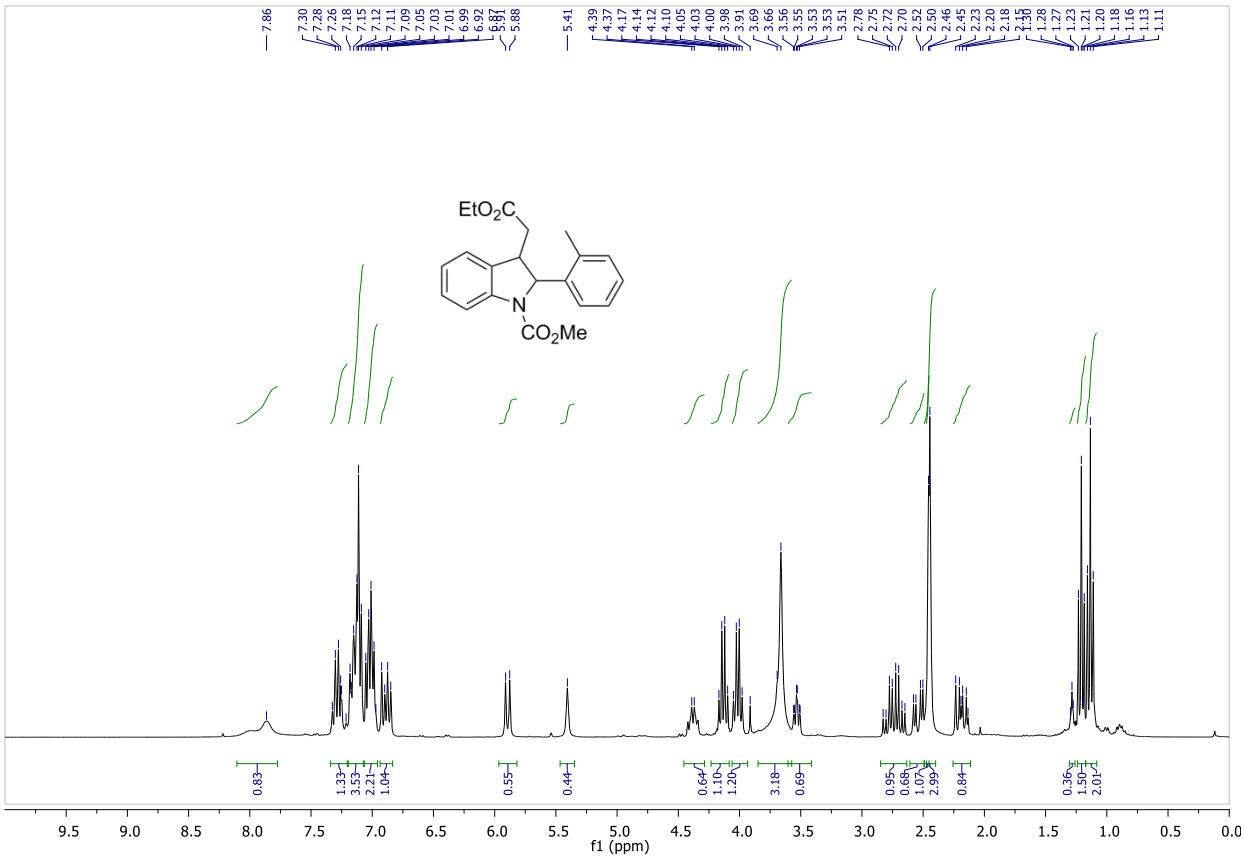
^{1}H-NMR: **8a**



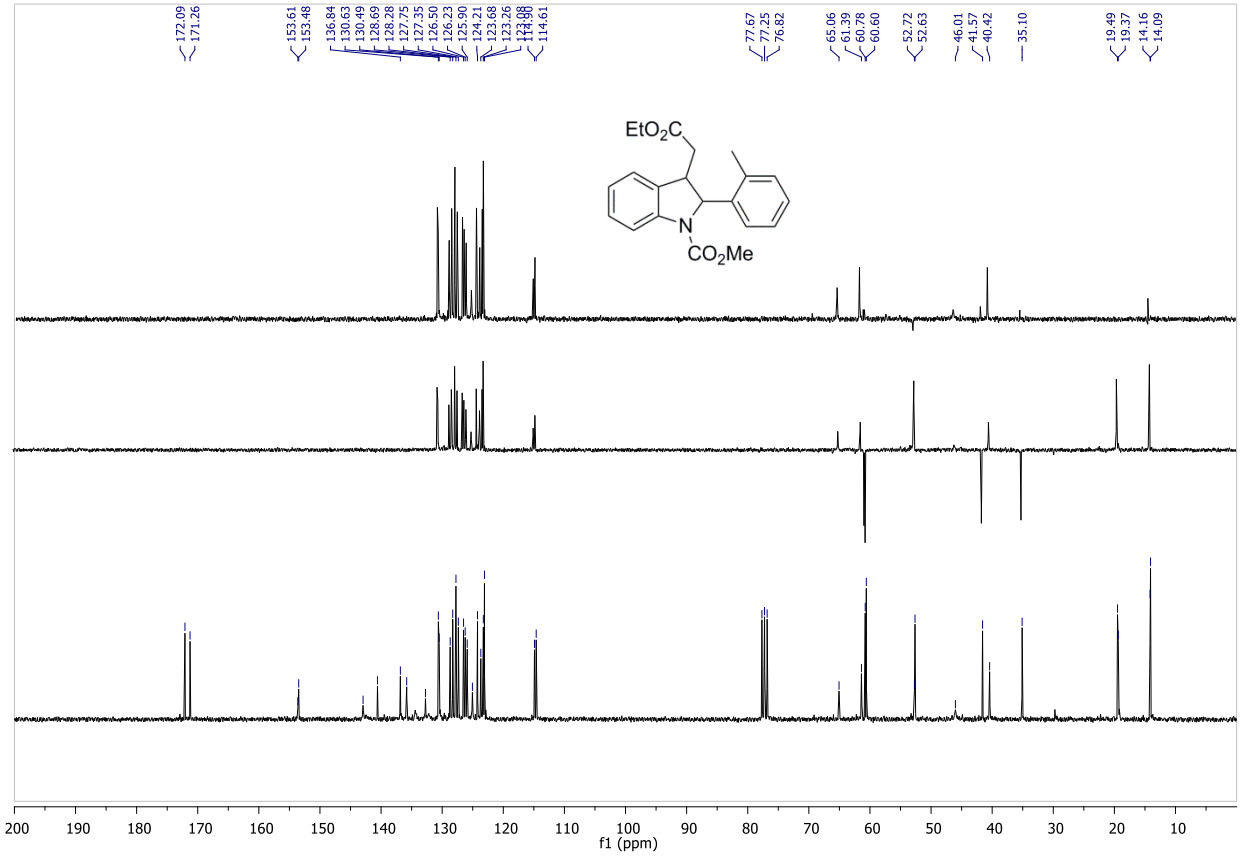
^{13}C-NMR: **8a**



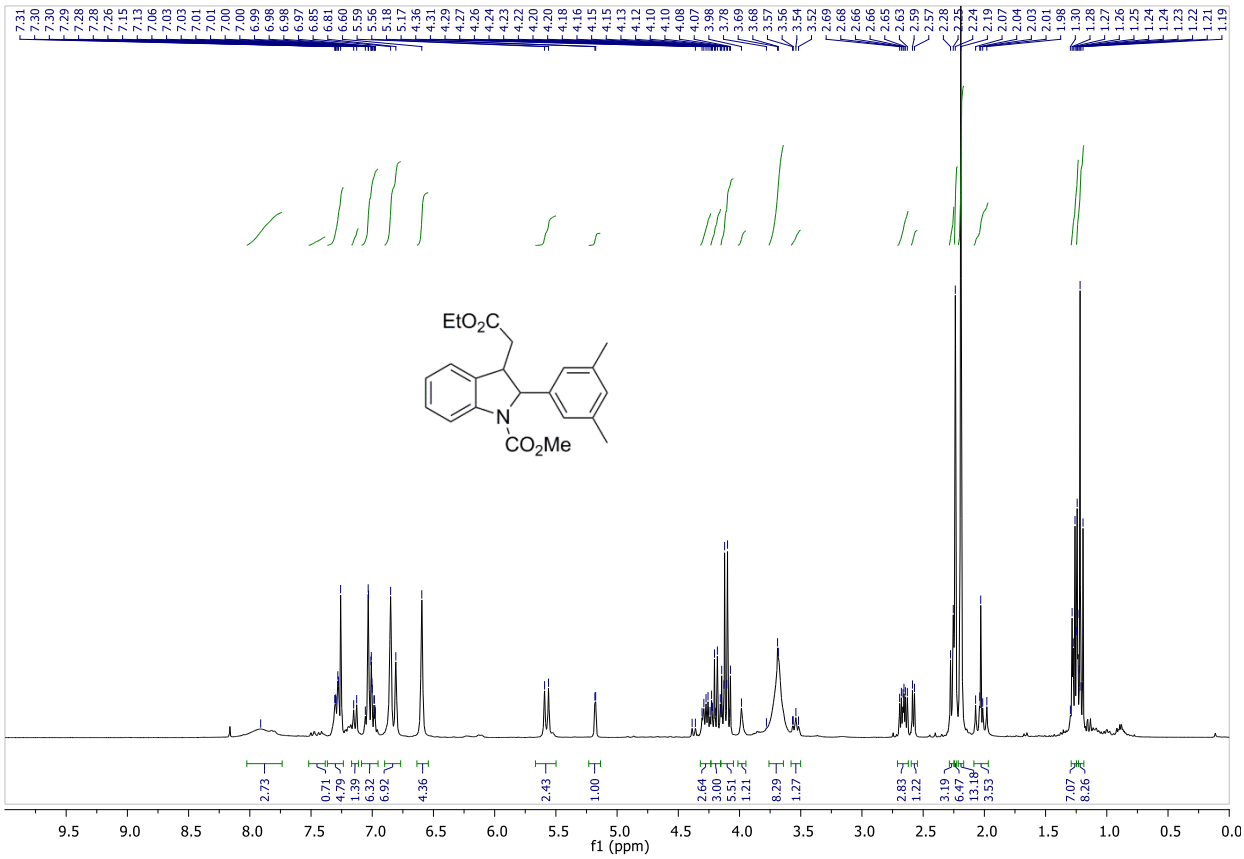
^{1}H-NMR: **8b**



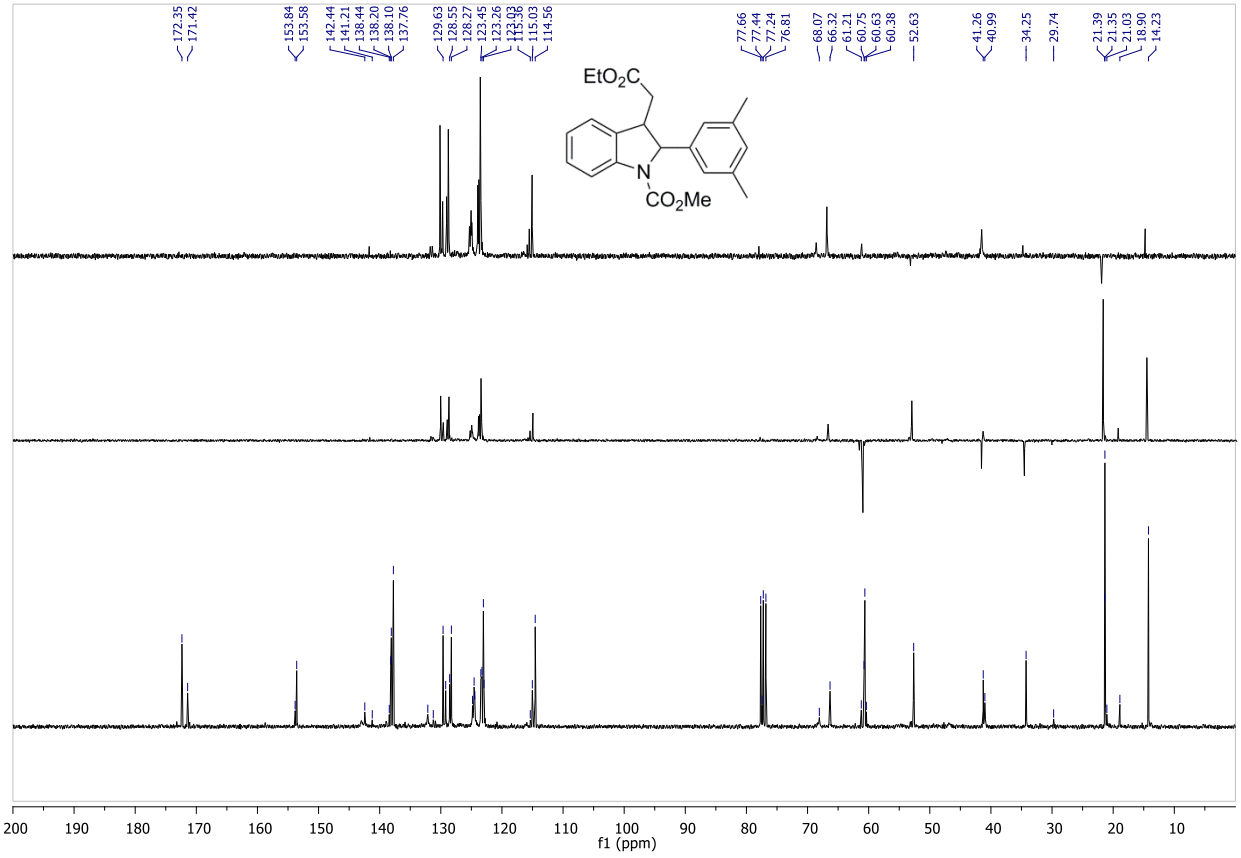
^{13}C-NMR: **8b**



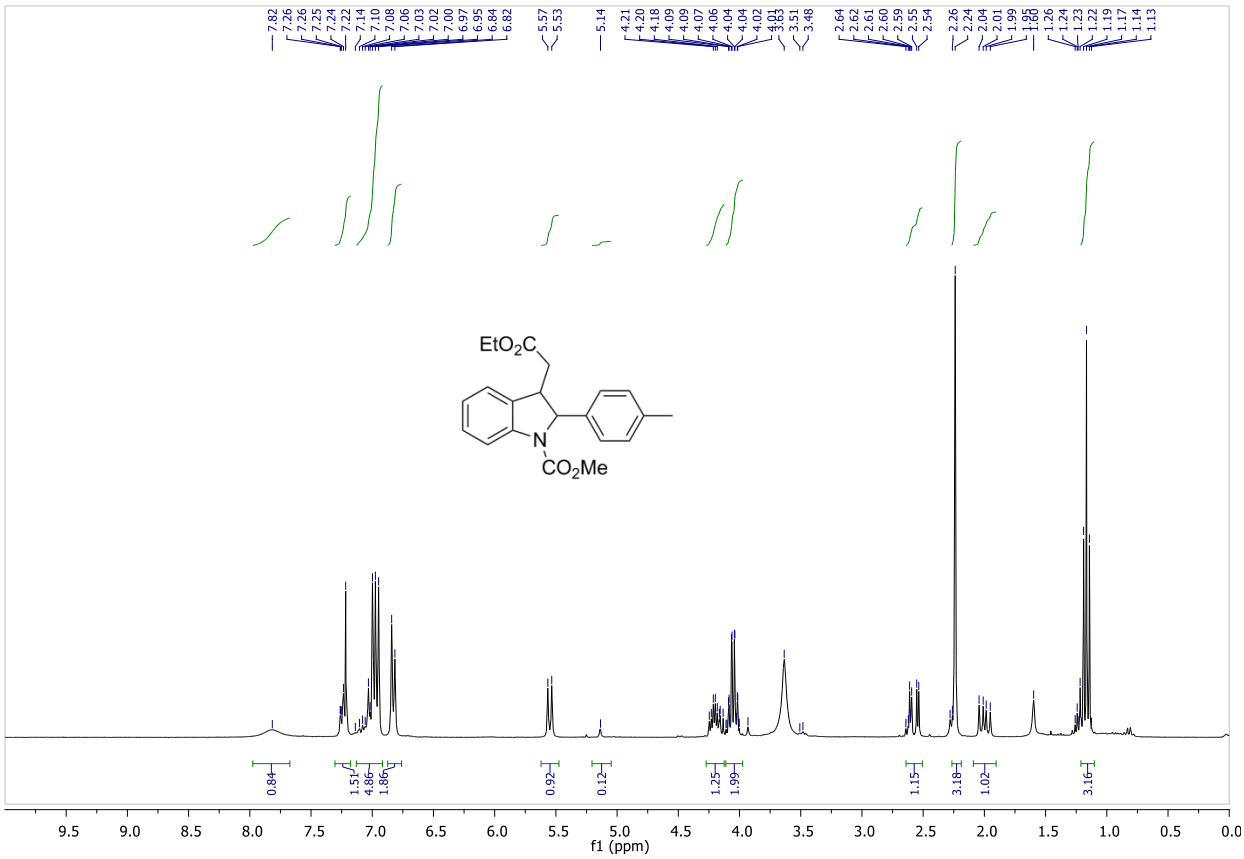
^{1}H-NMR: **8c**



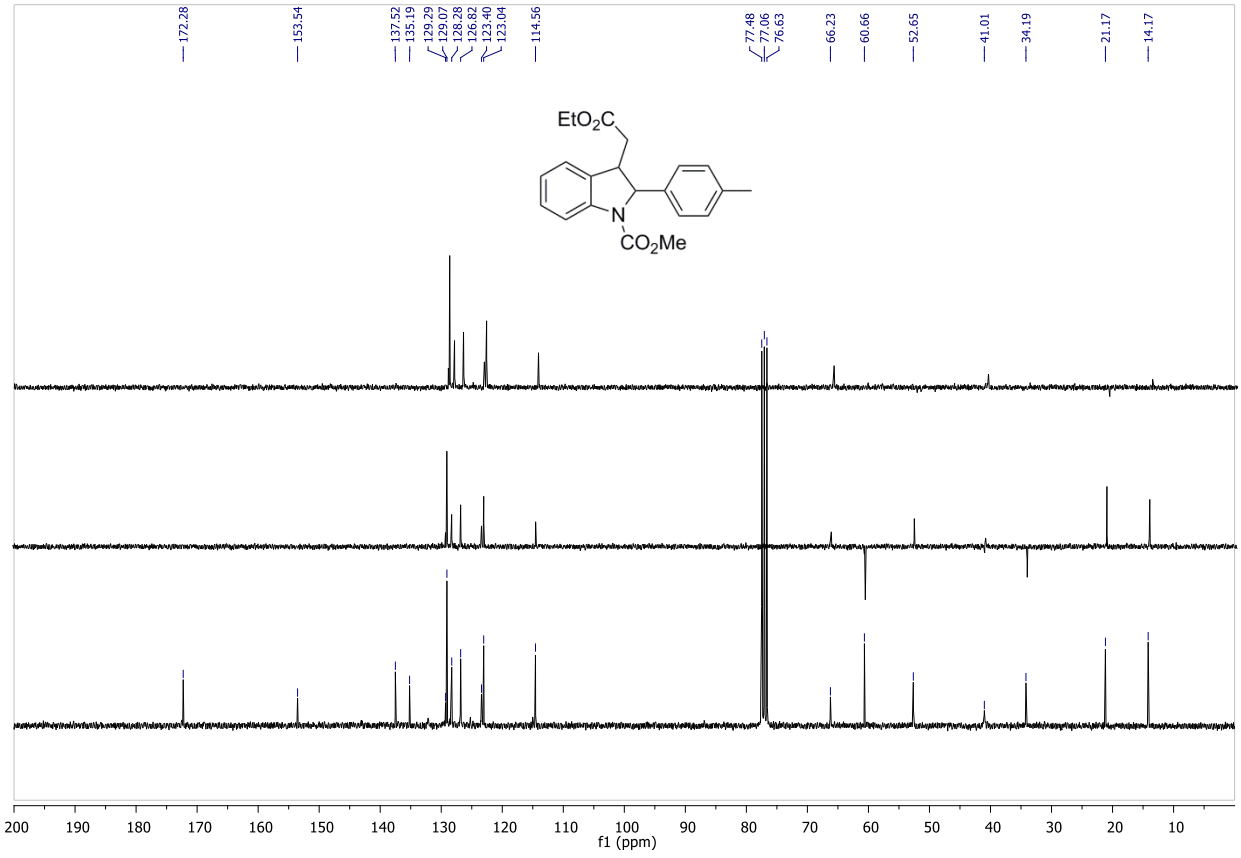
^{13}C-NMR: **8c**



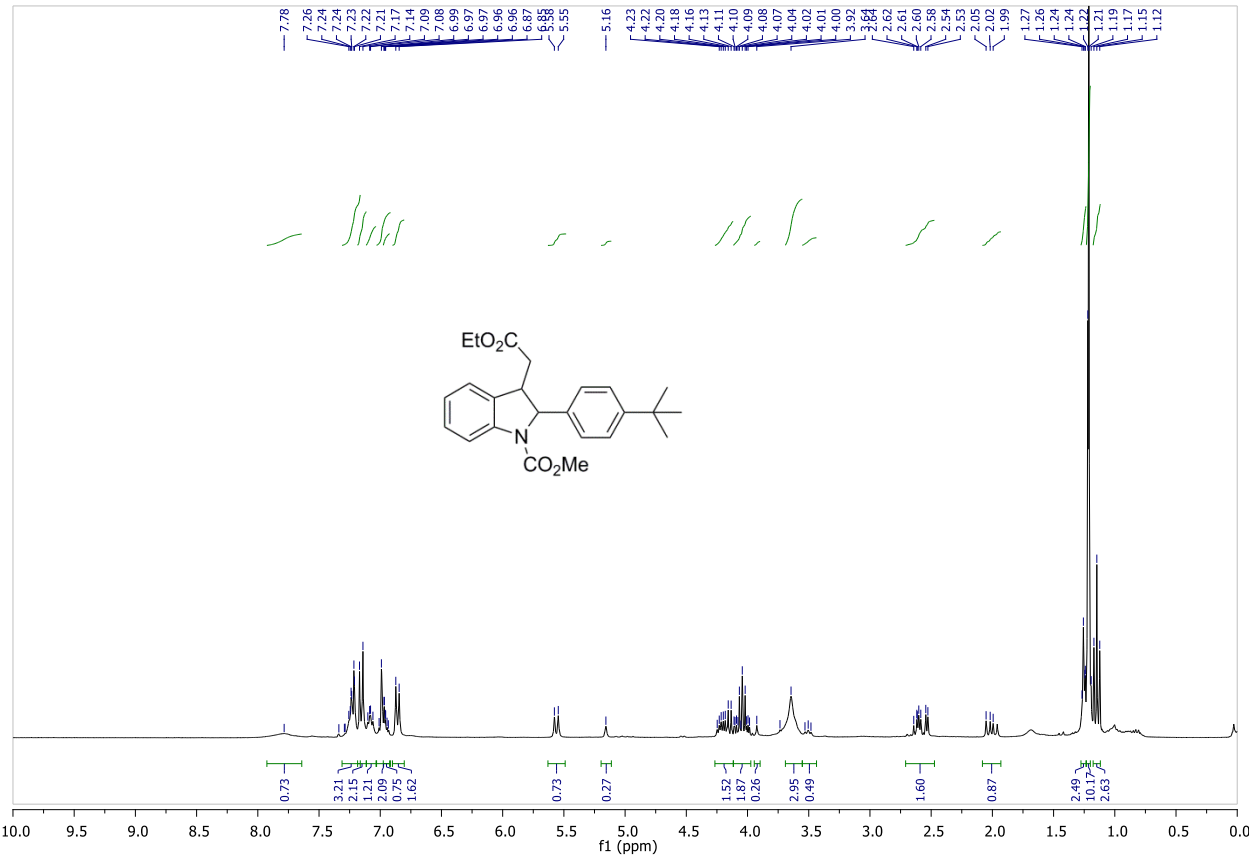
^{1}H-NMR: **8d**



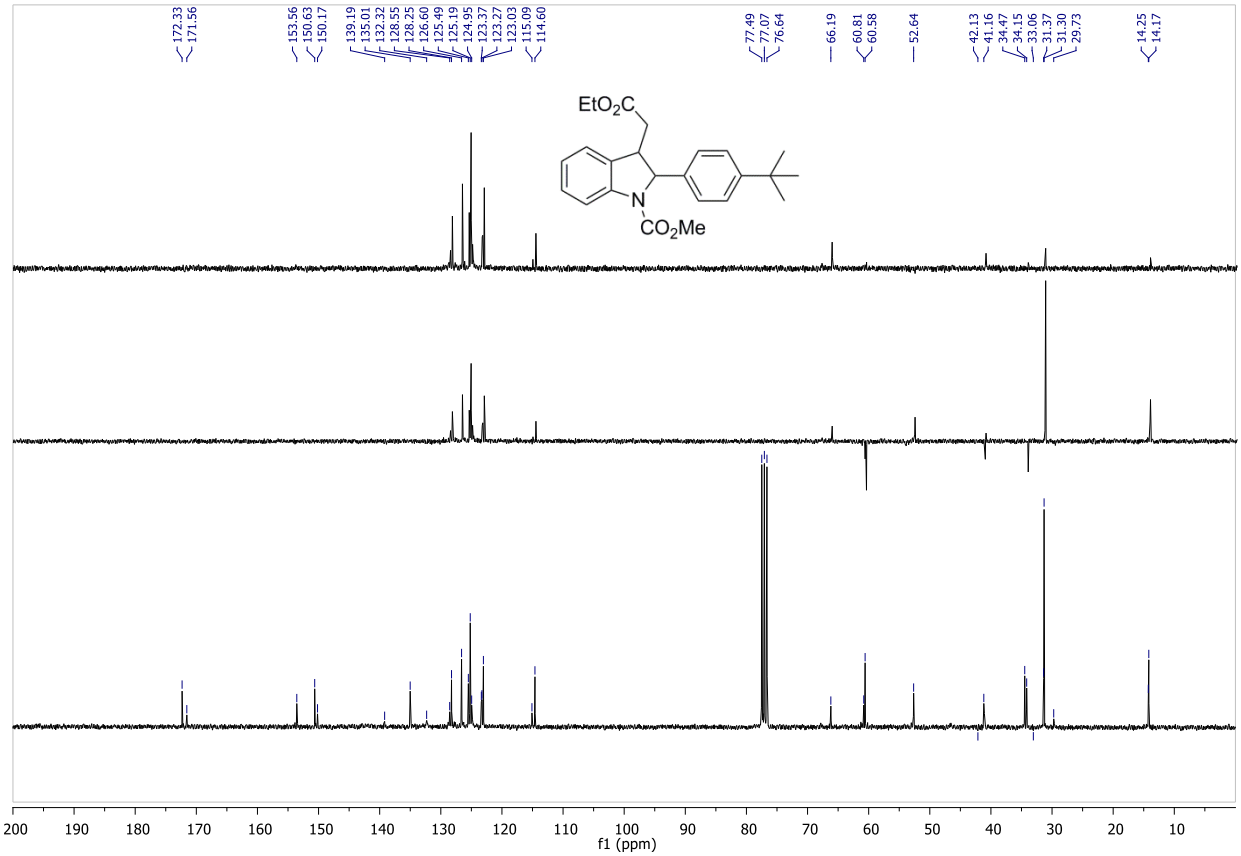
^{13}C-NMR: **8d**



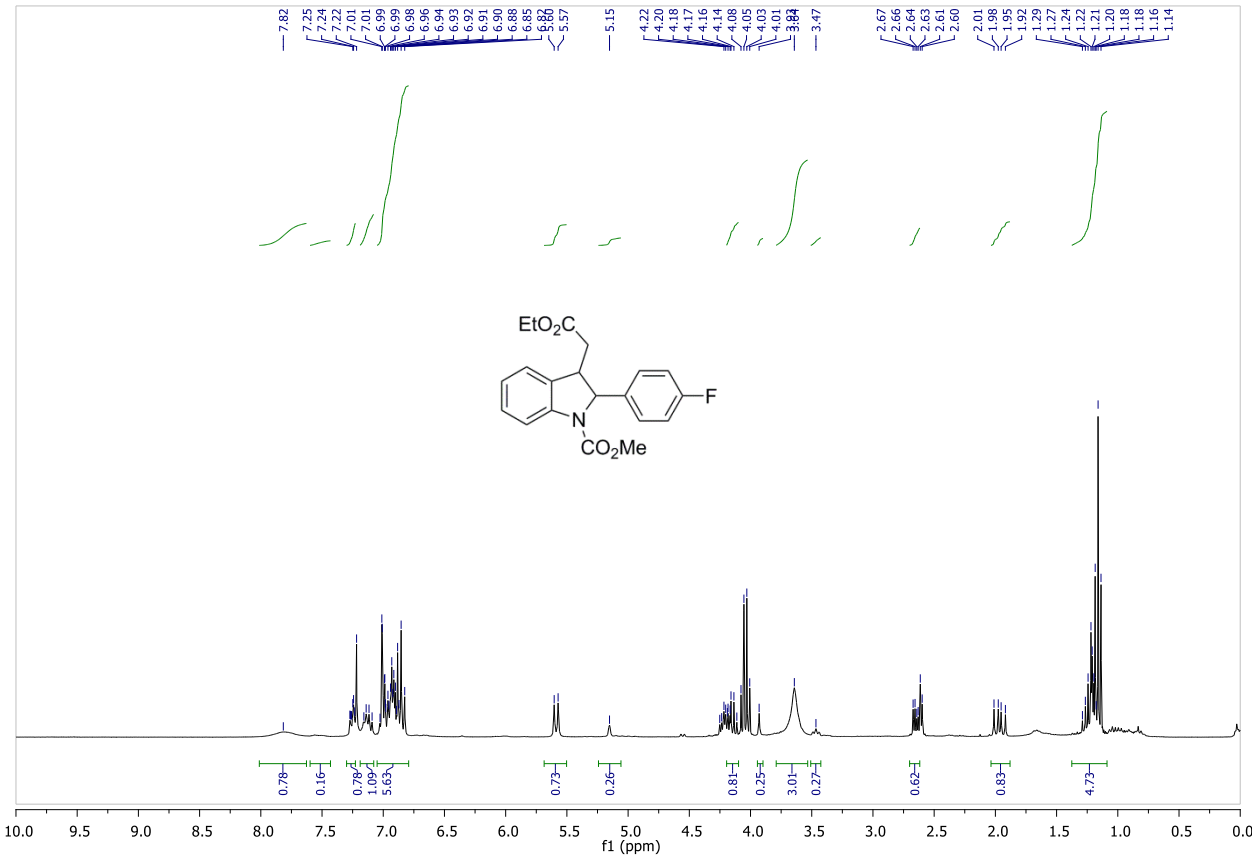
^{1}H-NMR: **8e**



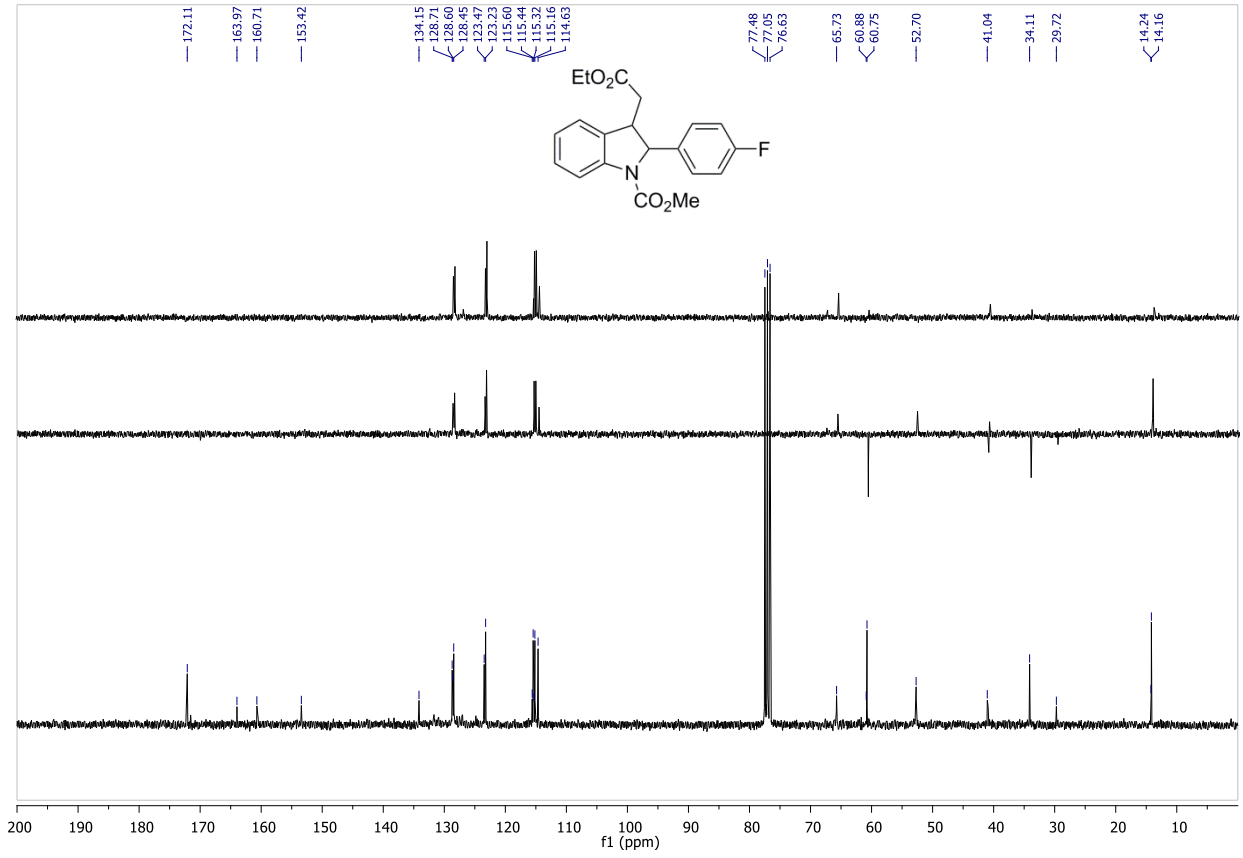
^{13}C-NMR: **8e**



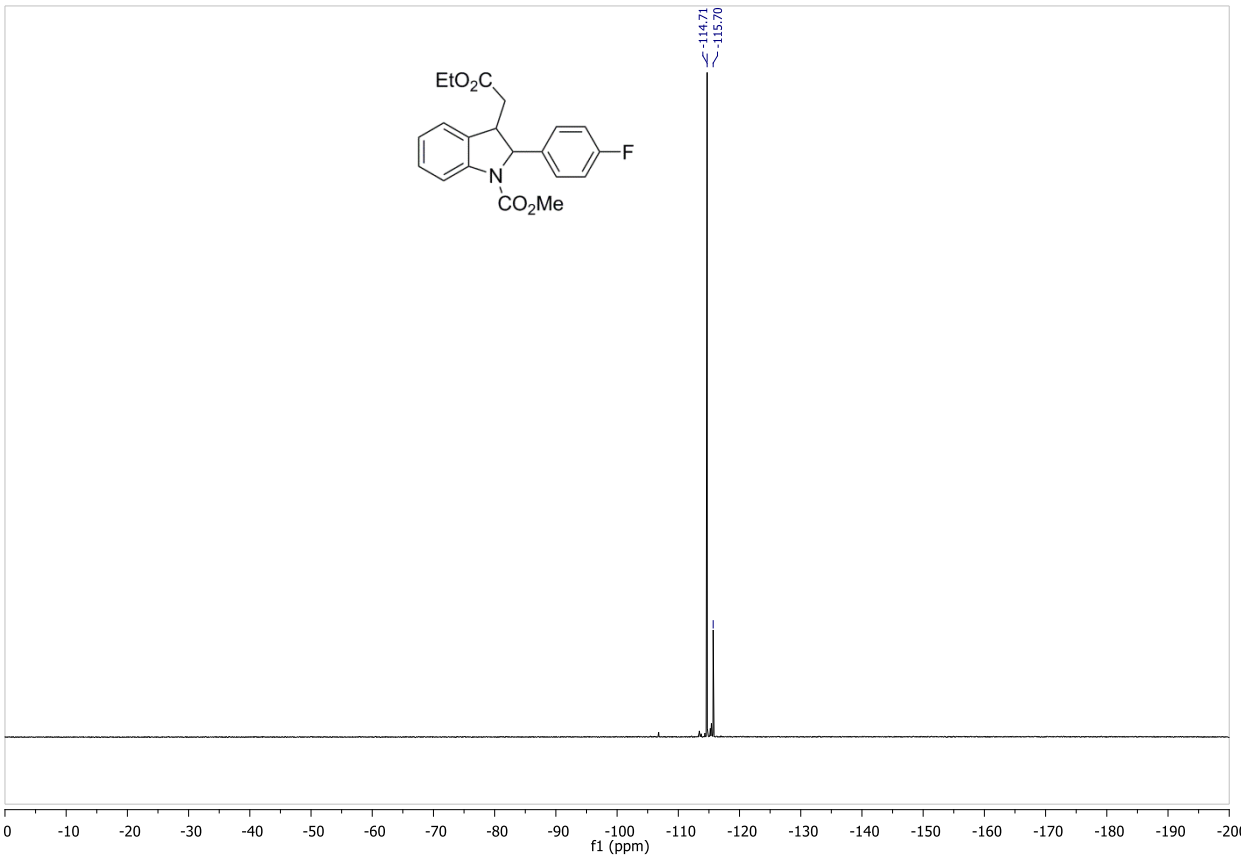
^{1}H-NMR: **8f**



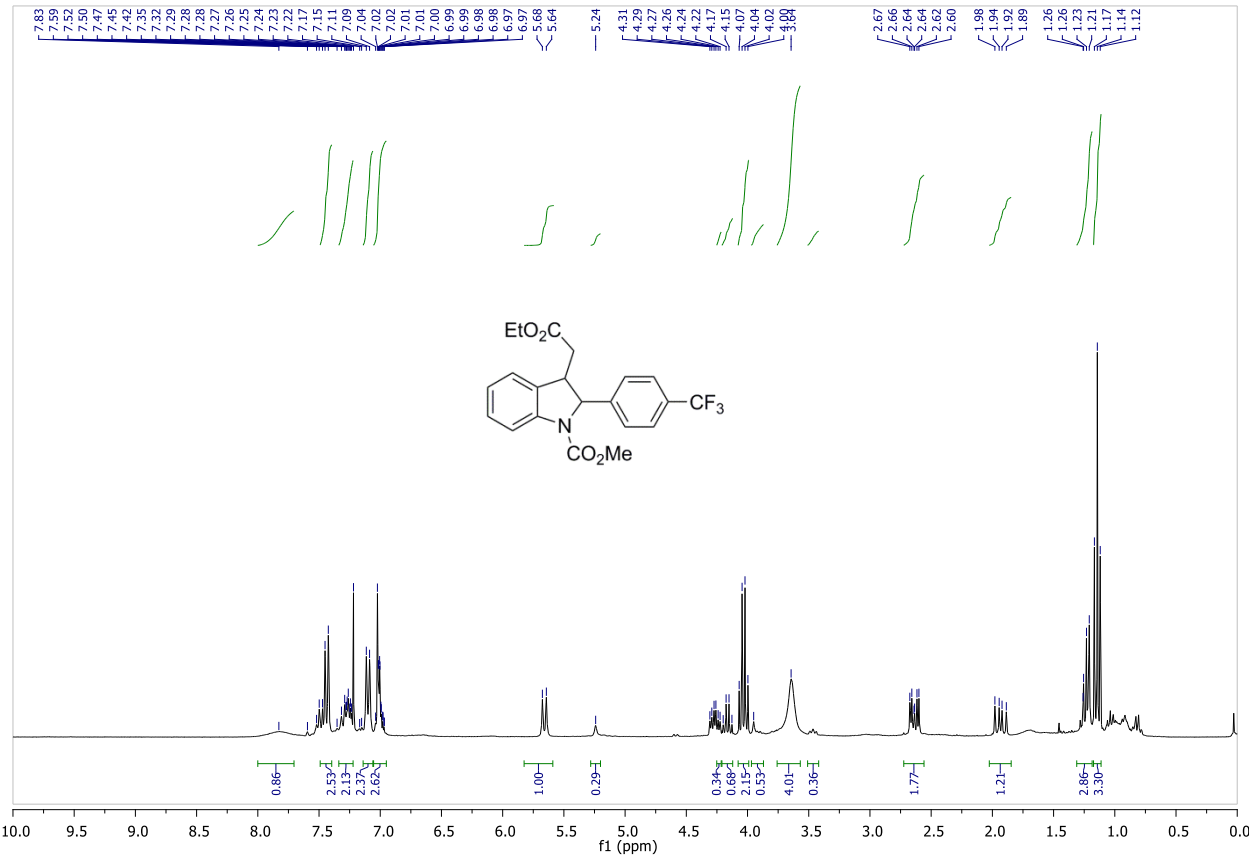
^{13}C-NMR: **8f**



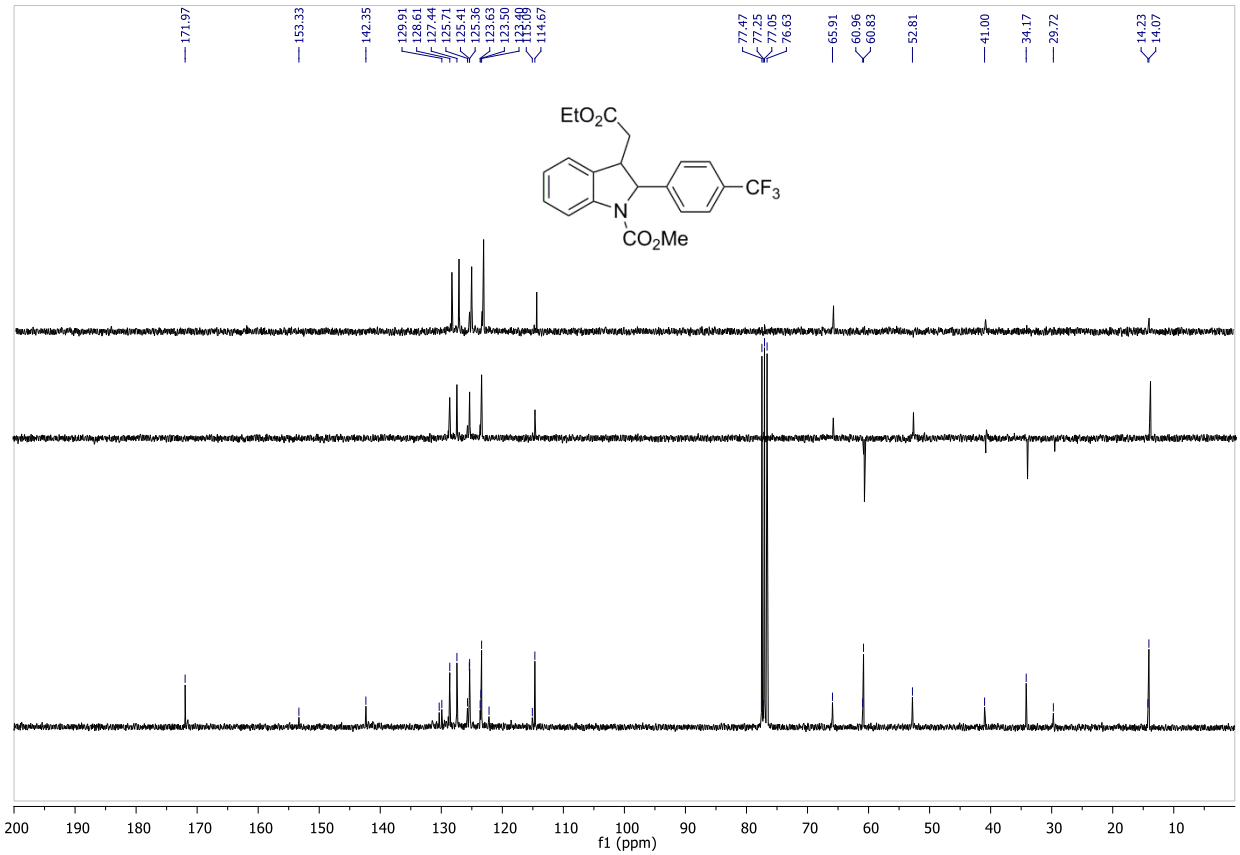
^{19}F-NMR: **8f**


-114.71
-115.70
EtO2C
F
N
CO2Me
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

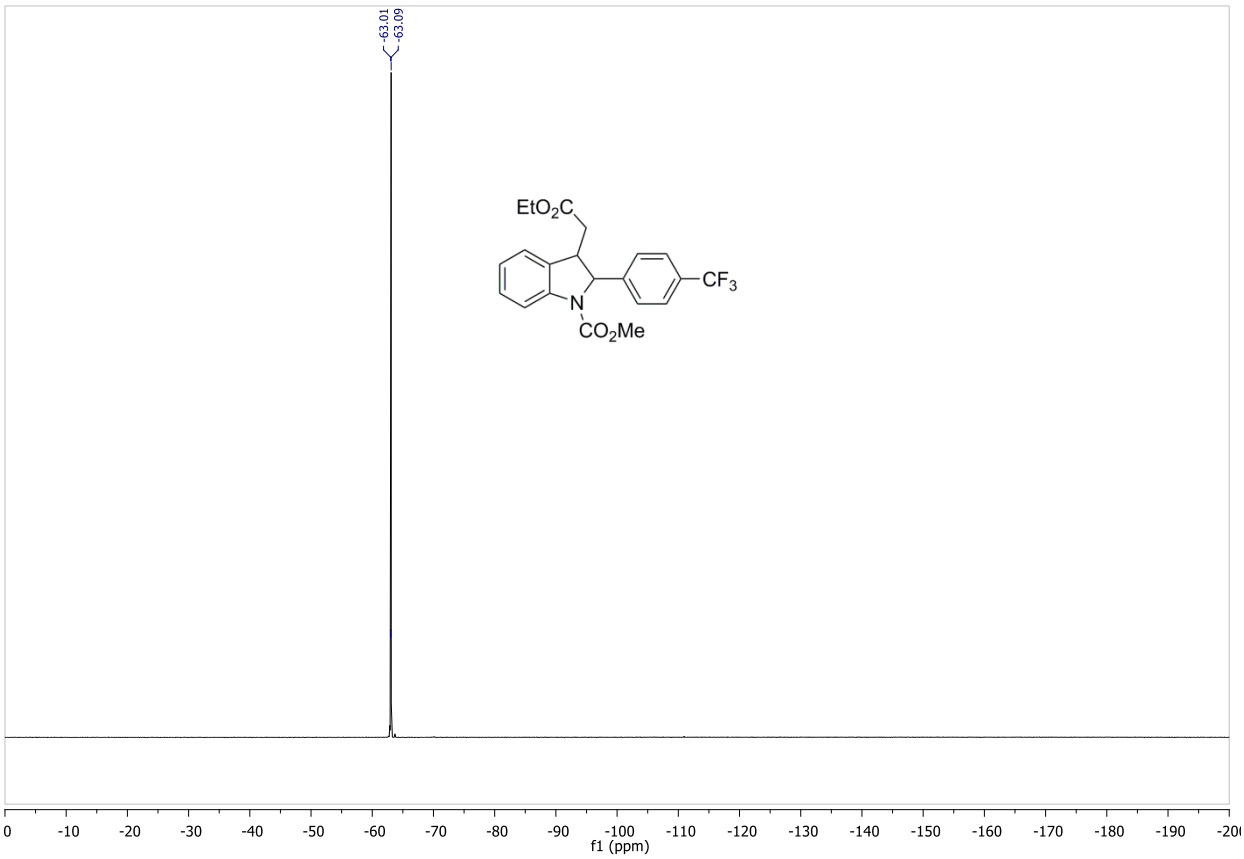
^{1}H-NMR: **8g**



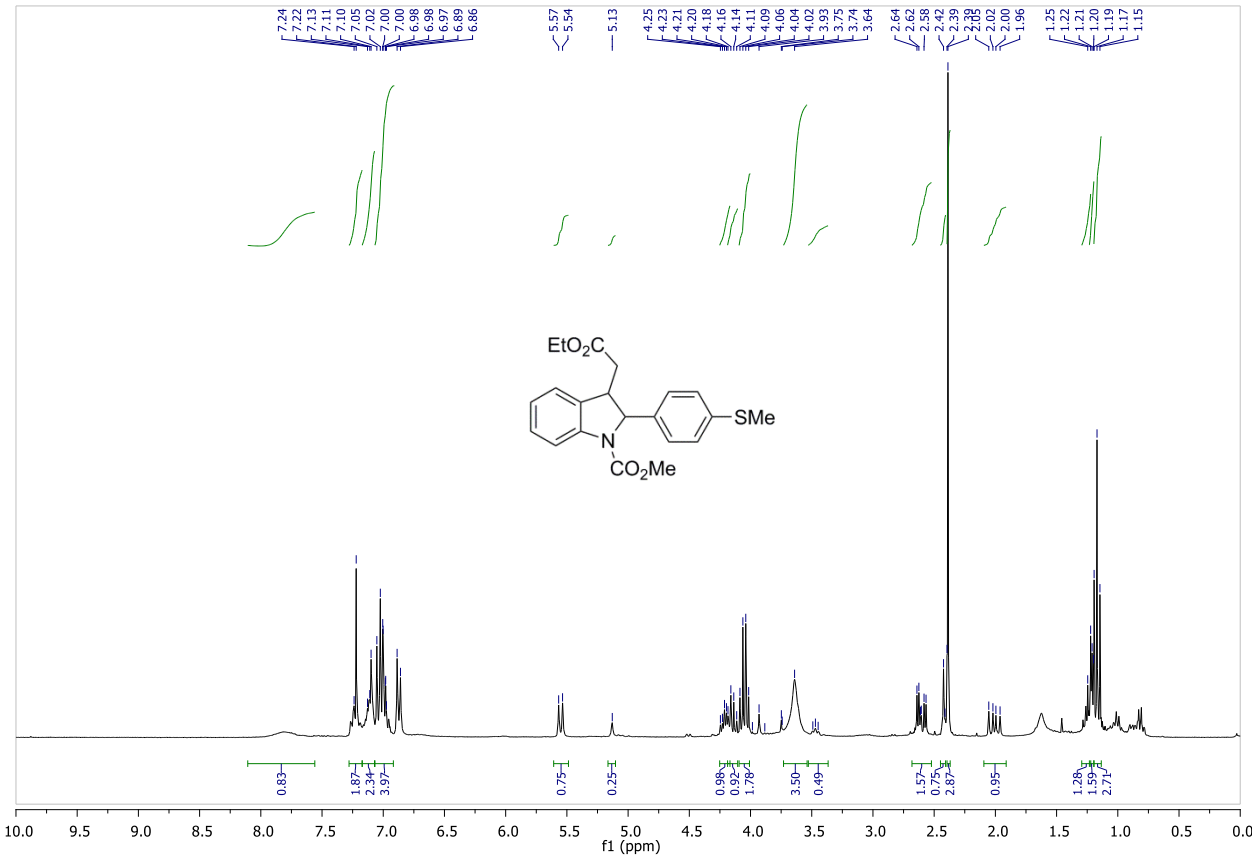
^{13}C-NMR: **8g**



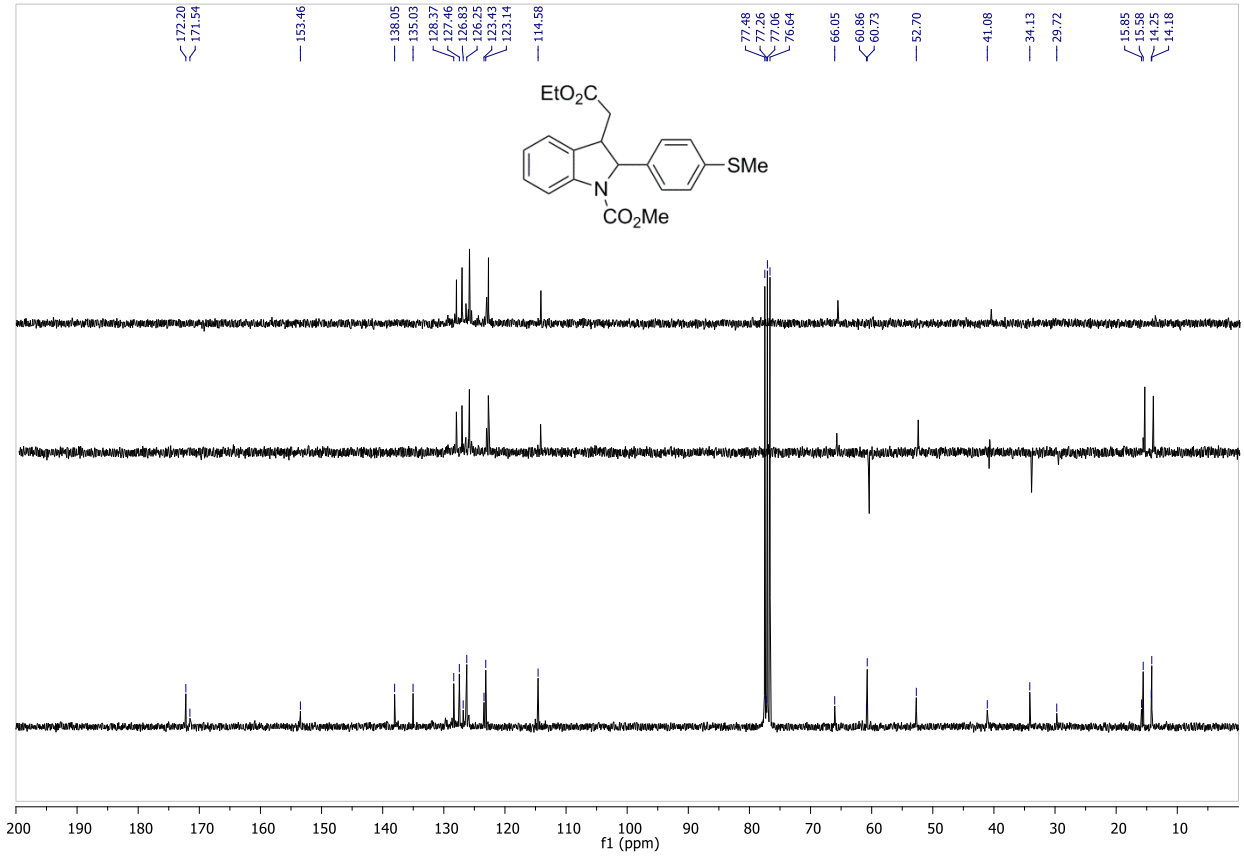
^{19}F-NMR: **8g**


-63.01
-63.09
EtO2C
CF3
N
CO2Me
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

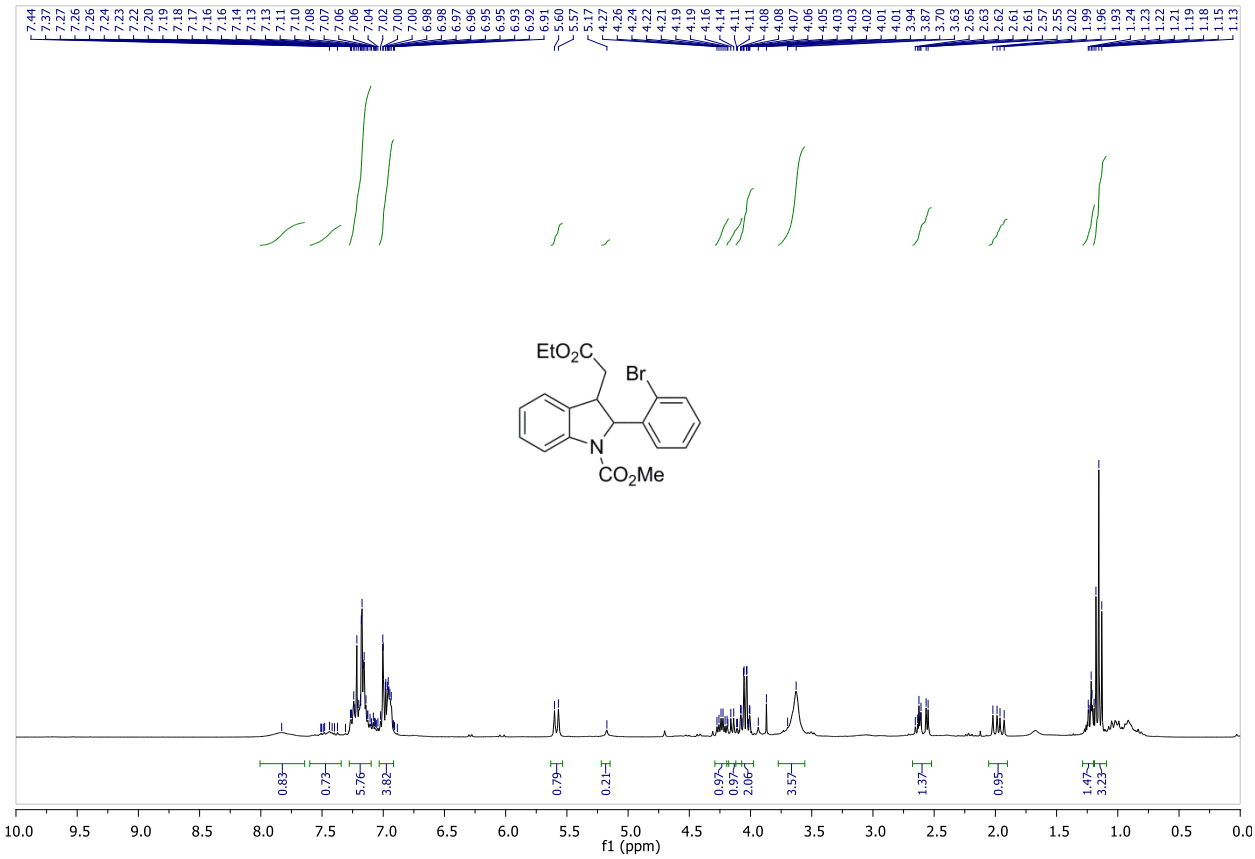
^{1}H-NMR: **8h**



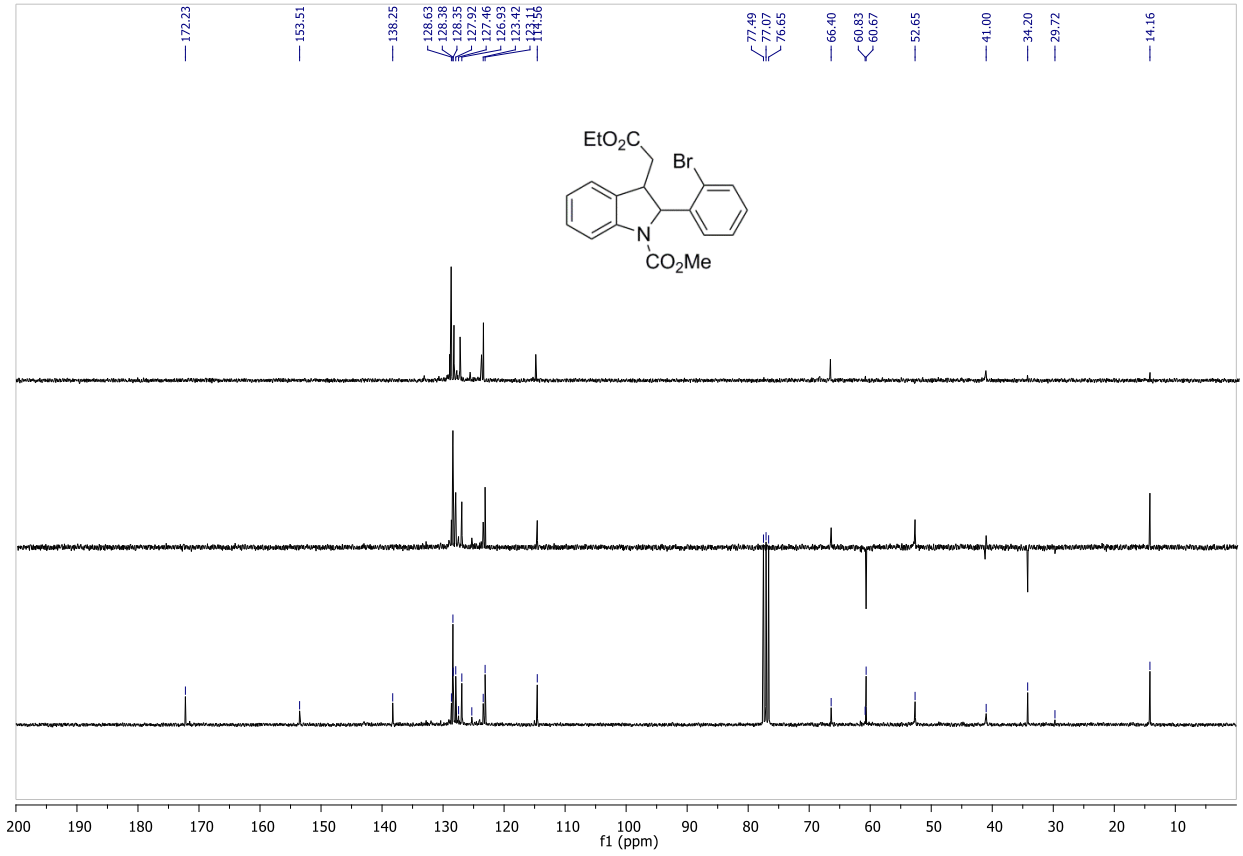
^{1}H-NMR: **8h**



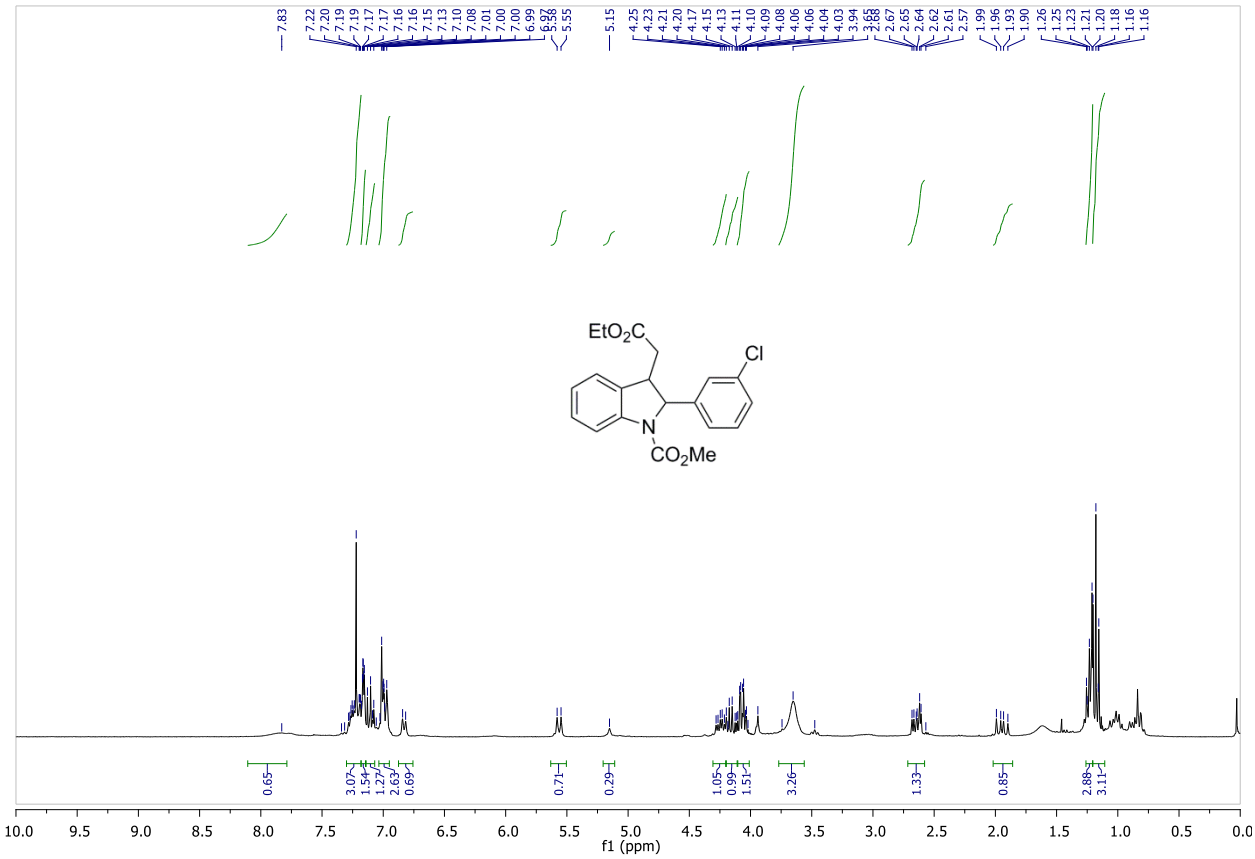
^{1}H-NMR: **8i**



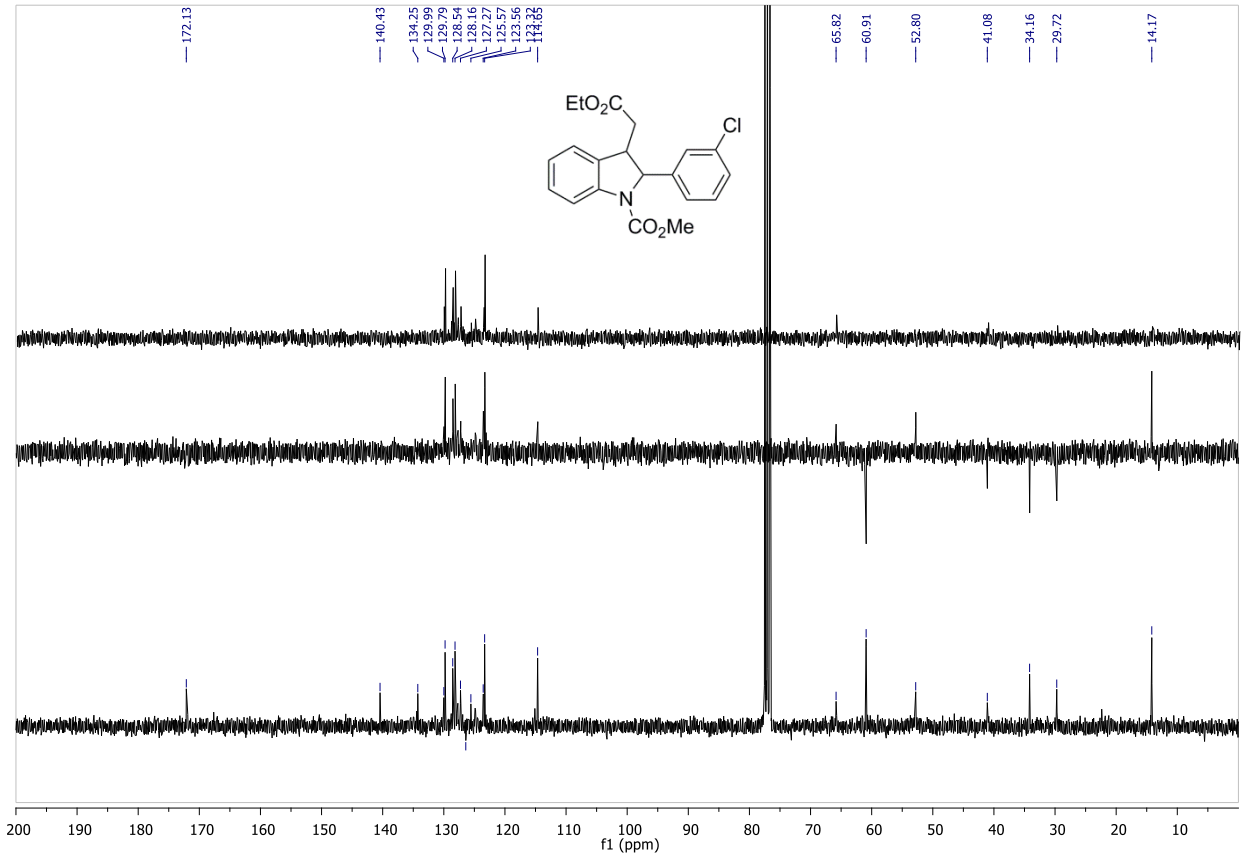
^{13}C-NMR: **8i**



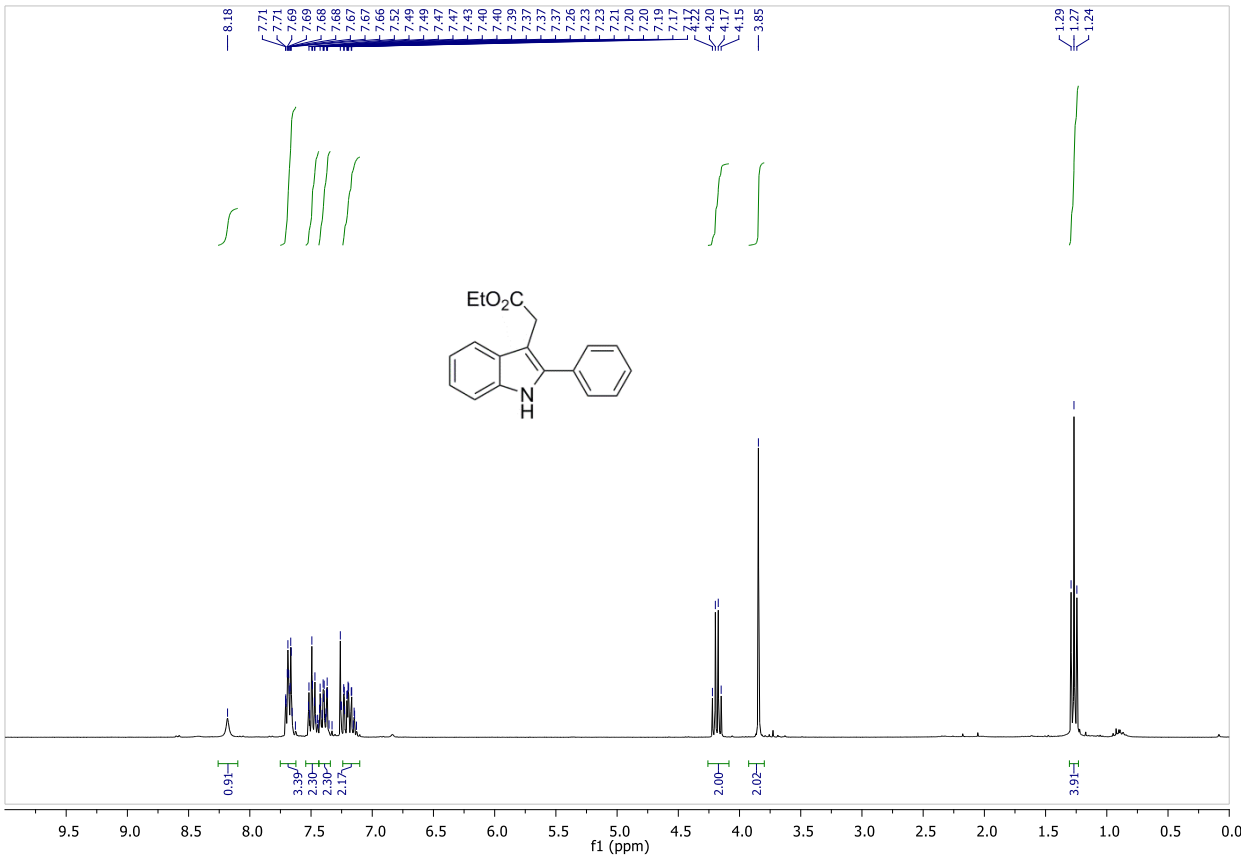
^{1}H-NMR: **8j**



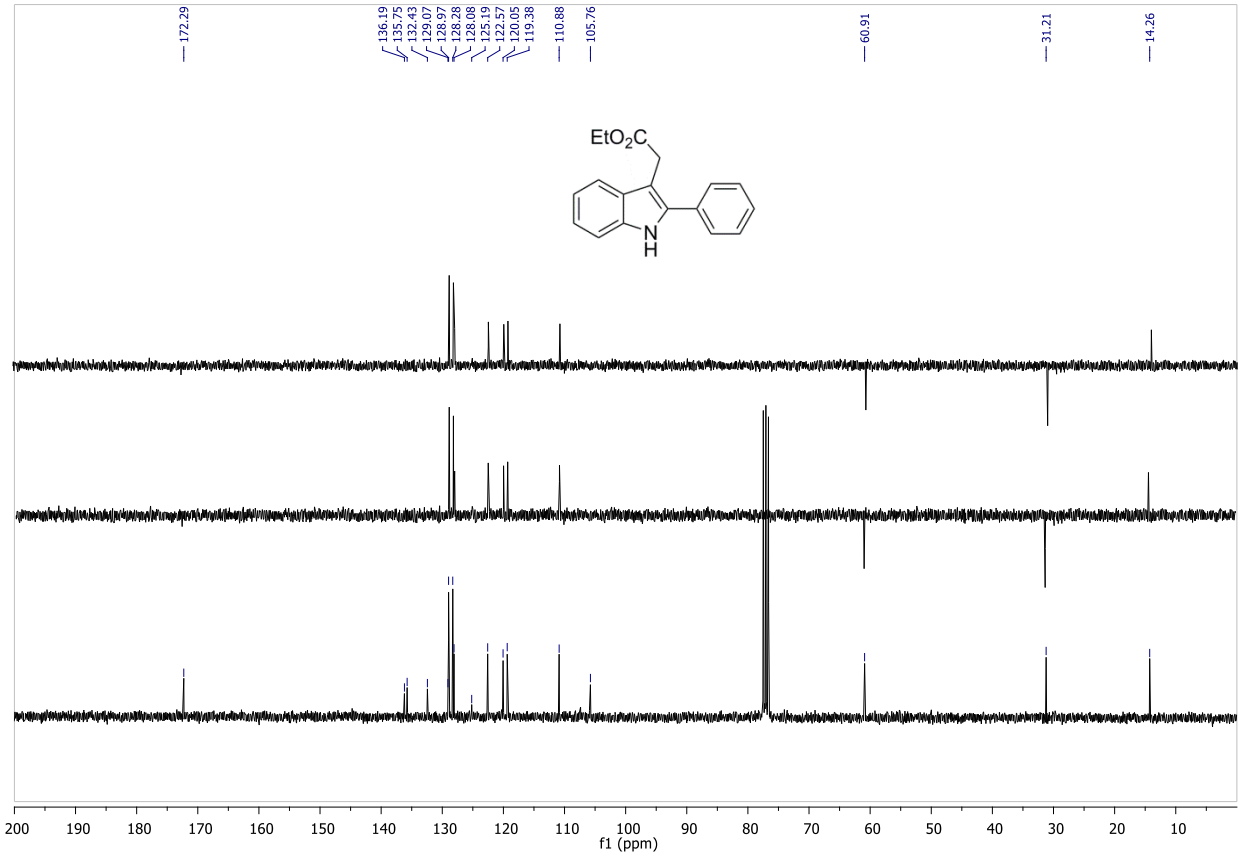
^{13}C-NMR: **8j**



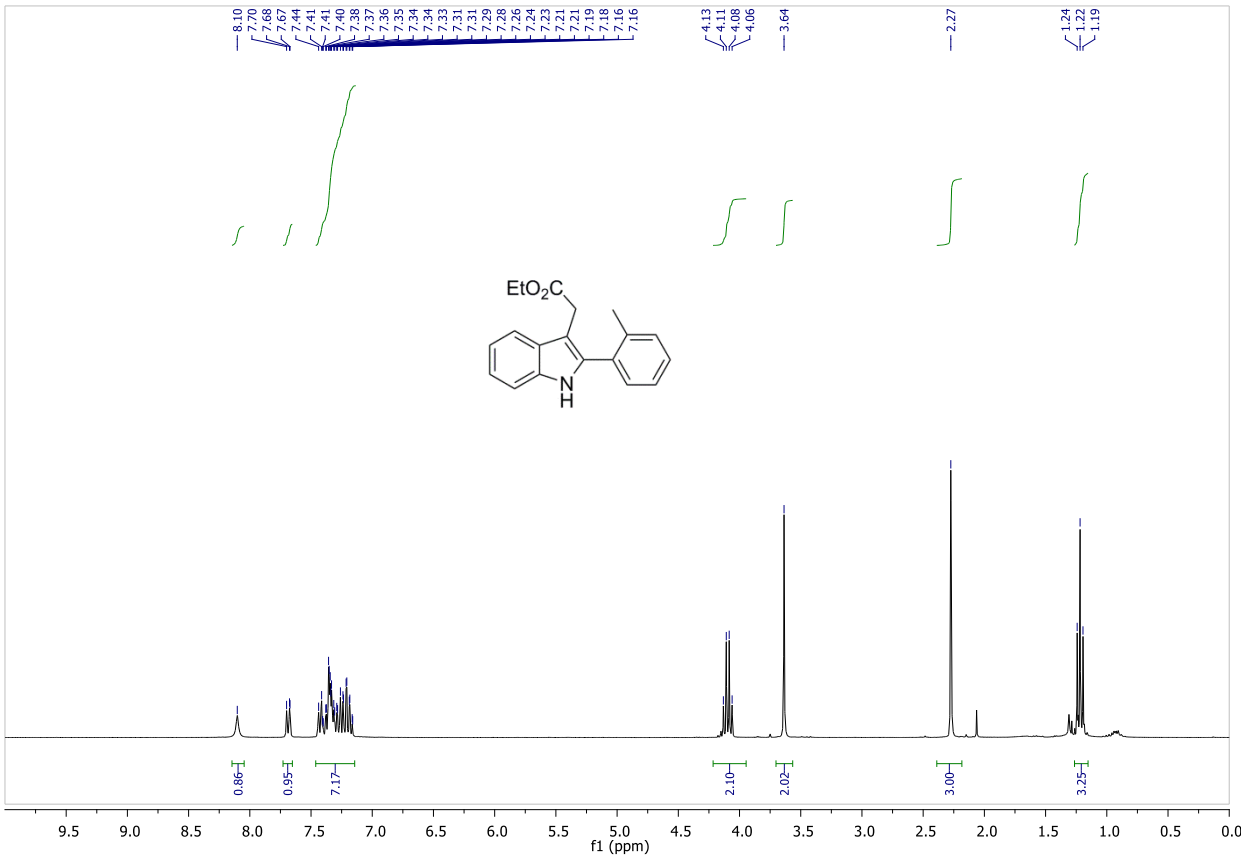
^{1}H-NMR: **9a**



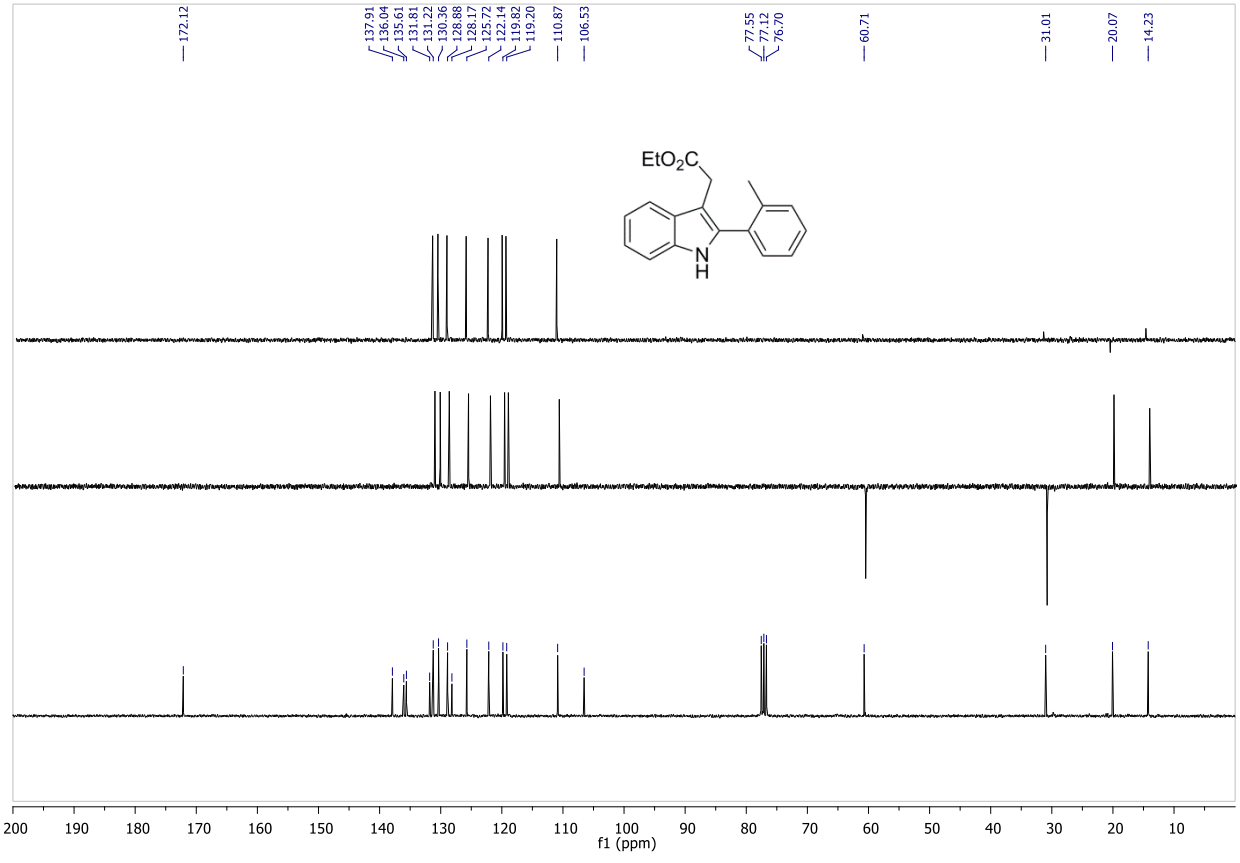
^{13}C-NMR: **9a**



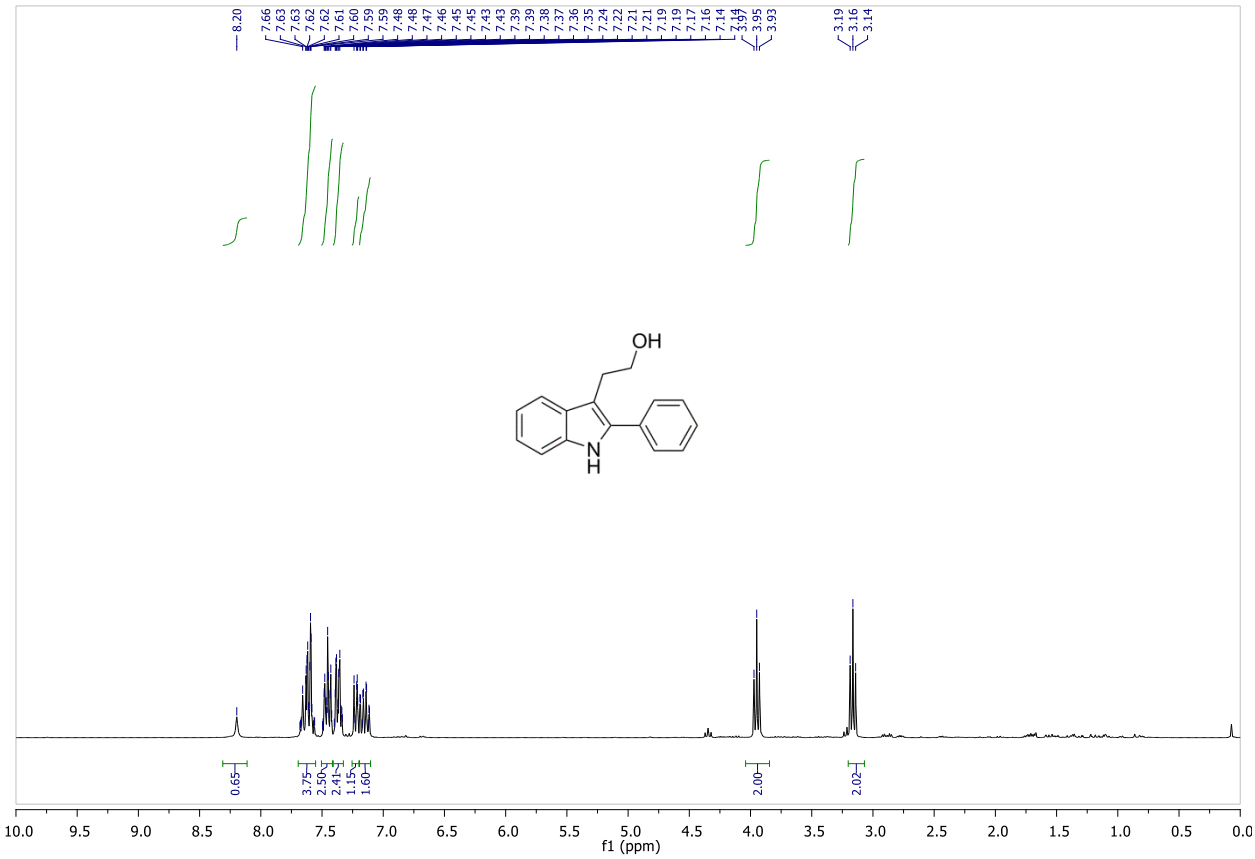
^{1}H-NMR: **9b**



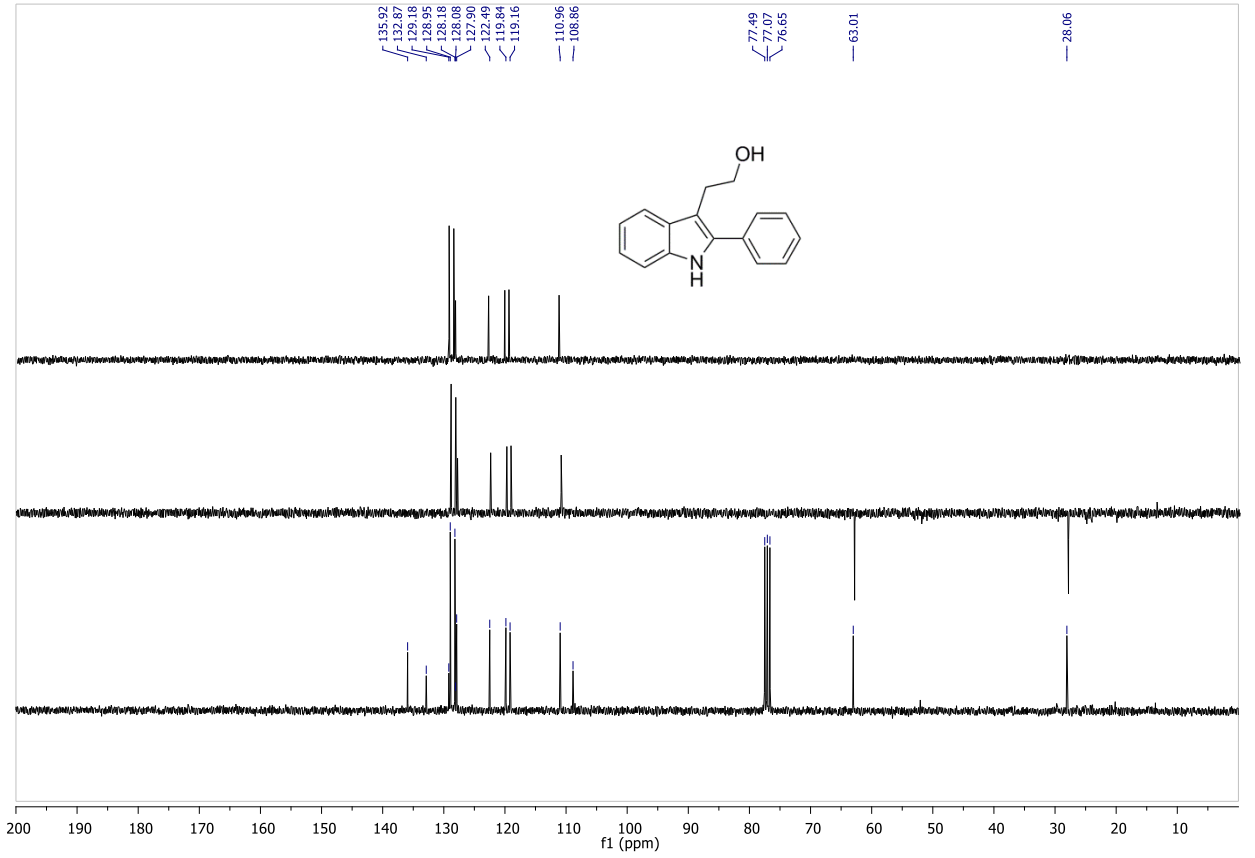
^{13}C-NMR: **9b**



^{1}H-NMR: **10**



^{13}C-NMR: **10**



10. Crystal data: 8b

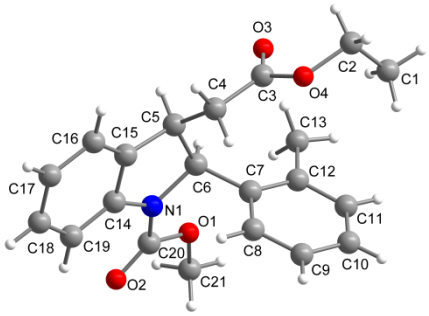


Figure 2: Single-crystal X-ray crystallographic analysis of **8b.**

Crystal data. $C_{21}H_{23}NO_4$, M_r = 353.40, monoclinic, $P2_1/c$ (No. 14), a = 10.2857(2) Å, b = 22.5658(4) Å, c = 7.71479(14) Å, β = 97.8249(18)°, α = γ = 90°, V = 1773.97(6) Å^3, T = 123.01(10) K, Z = 4, Z' = 1, μ(CuK_α) = 0.742, 15306 reflections measured, 3706 unique (R_{int} = 0.0331) which were used in all calculations. The final wR_2 was 0.1167 (all data) and R_1 was 0.0422 (I > 2(I)).

Compound	**8b**
Formula	$C_{21}H_{23}NO_4$
$D_{calc.}$/ g cm^{-3}	1.323
μ/mm^{-1}	0.742
Formula weight	353.40
Colour	clear colourless
Shape	irregular
Size/mm^3	0.30×0.14×0.10
T/K	123.01(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.2857(2)
b/Å	22.5658(4)
c/Å	7.71479(14)
α/°	90
β/°	97.8249(18)
γ/°	90
V/Å^3	1773.97(6)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	CuK_α
Θ_{min}/°	3.918
Θ_{max}/°	76.327
Measured refl.	15306
Independent refl.	3706
Reflections used	3222
R_{int}	0.0331
Parameters	248
Restraints	0
Largest peak	0.602
Deepest hole	-0.278
GooF	1.034
wR_2 (all data)	0.1167
wR_2	0.1101
R_1 (all data)	0.0487
R_1	0.0422

Table S2: Fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for **8b**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	**x**	**y**	**z**	U_{eq}
O(4)	2038.1(10)	7329.3(4)	2472.2(14)	28.1(2)
O(2)	3276.6(11)	5048.7(5)	408.5(13)	30.5(2)
O(3)	3679.0(11)	7940.0(5)	3639.7(15)	31.4(3)
O(1)	3913.0(19)	4509.9(10)	2840.1(19)	26.5(6)
N(1)	4081.2(11)	6984.5(5)	2883.9(15)	23.0(2)
C(7)	2808.4(13)	6117.5(6)	3630.0(18)	21.6(3)
C(15)	5459.3(14)	6982.9(6)	3221.3(17)	22.6(3)
C(8)	3399.3(14)	6099.6(6)	5368.2(18)	24.2(3)
C(20)	3306.9(14)	7462.3(6)	3057.8(18)	23.6(3)
C(12)	1541.8(14)	5884.5(6)	3188.7(18)	23.8(3)
C(6)	3556.6(13)	6395.2(6)	2268.5(17)	21.6(3)
C(3)	3937.9(14)	4993.7(6)	1817.9(19)	25.5(3)

Atom	x	y	z	U_{eq}
C(14)	5935.6(14)	6445.4(6)	2675.8(17)	23.0(3)
C(4)	4973.4(14)	5419.5(6)	2623.4(18)	23.7(3)
C(9)	2782.3(15)	5836.9(6)	6660.8(18)	26.0(3)
C(5)	4817.7(13)	6048.8(6)	1898.4(17)	22.1(3)
C(16)	6301.2(15)	7422.4(7)	3978.6(19)	27.0(3)
C(11)	927.3(15)	5629.4(6)	4515(2)	27.7(3)
C(19)	7273.3(14)	6339.0(7)	2864.5(19)	28.6(3)
C(10)	1541.4(15)	5596.9(6)	6226.4(19)	28.6(3)
C(13)	812.5(15)	5911.0(7)	1353(2)	30.6(3)
C(17)	7646.0(15)	7308.0(7)	4152(2)	32.1(3)
C(18)	8134.5(15)	6777.9(7)	3601(2)	33.2(3)
C(21)	1125.6(16)	7803.7(7)	2589(3)	37.9(4)
C(2)	3024.9(17)	4030.4(7)	2189(2)	36.3(4)
C(1)	1657.3(18)	4166.4(8)	2492(2)	41.2(4)
O(1A)	3390(20)	4726(7)	3131(15)	31(4)

Table S3: Anisotropic displacement parameters (×10^4) **8b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(4)	24.6(5)	20.4(5)	38.9(6)	-0.4(4)	2.8(4)	4.1(4)
O(2)	39.4(6)	28.6(5)	23.3(5)	2.3(4)	3.7(4)	-1.1(4)
O(3)	34.0(6)	21.1(5)	38.3(6)	-4.5(4)	2.0(5)	1.7(4)
O(1)	29.6(9)	20.6(9)	28.6(6)	4.7(5)	0.9(6)	-0.7(7)
N(1)	22.9(6)	18.7(5)	27.8(6)	0.4(4)	4.3(4)	-0.2(4)
C(7)	23.7(6)	16.9(6)	24.6(6)	0.6(5)	5.1(5)	3.0(5)
C(15)	24.3(7)	23.3(6)	20.6(6)	3.3(5)	4.5(5)	-0.1(5)
C(8)	25.6(7)	21.5(6)	25.4(7)	-0.6(5)	3.3(5)	1.6(5)
C(20)	27.0(7)	20.8(6)	23.3(6)	1.9(5)	4.4(5)	1.9(5)
C(12)	24.5(7)	20.7(6)	25.9(7)	0.0(5)	2.7(5)	0.9(5)
C(6)	23.4(6)	18.2(6)	23.0(6)	0.5(5)	2.6(5)	0.8(5)
C(3)	31.2(7)	22.4(7)	23.7(6)	0.3(5)	7.0(5)	1.5(5)
C(14)	24.6(7)	23.3(6)	21.6(6)	2.3(5)	4.7(5)	-0.6(5)
C(4)	26.7(7)	21.3(6)	23.6(6)	0.6(5)	5.1(5)	2.5(5)
C(9)	33.9(8)	22.4(6)	21.7(6)	0.5(5)	3.7(5)	4.1(5)
C(5)	24.1(7)	21.5(6)	21.3(6)	1.3(5)	5.1(5)	1.1(5)
C(16)	30.3(7)	24.5(7)	26.4(7)	-0.5(5)	4.2(6)	-2.9(5)
C(11)	27.3(7)	24.5(7)	32.2(7)	0.0(5)	7.2(6)	-2.6(5)
C(19)	26.4(7)	29.1(7)	31.0(7)	2.4(6)	6.6(6)	2.3(6)
C(10)	36.6(8)	23.5(7)	27.9(7)	2.7(5)	12.4(6)	-1.0(6)
C(13)	26.0(7)	35.5(8)	29.0(7)	2.3(6)	-0.4(6)	-3.0(6)
C(17)	28.1(8)	33.6(8)	33.6(8)	0.3(6)	0.5(6)	-7.9(6)
C(18)	22.7(7)	39.2(8)	37.2(8)	4.7(7)	3.0(6)	-1.0(6)
C(21)	27.4(8)	26.7(7)	58.9(10)	-3.8(7)	3.3(7)	7.4(6)
C(2)	41.1(9)	29.7(8)	37.8(8)	1.0(6)	4.1(7)	0.1(7)
C(1)	40.9(9)	43.3(10)	39.4(9)	6.2(7)	4.9(7)	-0.9(7)
O(1A)	41(9)	17(6)	34(6)	-11(4)	5(5)	10(6)

Table S4: Bond lengths in Å for **8b**.

Atom	Atom	Length/Å
O(4)	C(20)	1.3554(18)
O(4)	C(21)	1.4346(17)
O(2)	C(3)	1.2080(18)
O(3)	C(20)	1.2096(18)
O(1)	C(3)	1.349(2)
O(1)	C(2)	1.460(2)
N(1)	C(15)	1.4059(18)
N(1)	C(20)	1.3579(18)
N(1)	C(6)	1.4883(16)
C(7)	C(8)	1.3954(19)
C(7)	C(12)	1.4032(19)
C(7)	C(6)	1.5194(18)
C(15)	C(14)	1.394(2)
C(15)	C(16)	1.392(2)
C(8)	C(9)	1.386(2)
C(12)	C(11)	1.398(2)

Atom	Atom	Length/Å
C(12)	C(13)	1.5106(19)
C(6)	C(5)	1.5735(18)
C(3)	C(4)	1.5045(19)
C(3)	O(1A)	1.368(14)
C(14)	C(5)	1.5150(19)
C(14)	C(19)	1.385(2)
C(4)	C(5)	1.5267(18)

Atom	Atom	Length/Å
C(9)	C(10)	1.385(2)
C(16)	C(17)	1.395(2)
C(11)	C(10)	1.386(2)
C(19)	C(18)	1.397(2)
C(17)	C(18)	1.386(2)
C(2)	C(1)	1.489(2)
C(2)	O(1A)	1.748(14)

Table S5: Bond angles in ° for **8b**.

Atom	Atom	Atom	Angle/°
C(20)	O(4)	C(21)	114.98(12)
C(3)	O(1)	C(2)	117.35(12)
C(15)	N(1)	C(6)	111.68(11)
C(20)	N(1)	C(15)	125.02(12)
C(20)	N(1)	C(6)	123.29(12)
C(8)	C(7)	C(12)	119.39(13)
C(8)	C(7)	C(6)	118.75(12)
C(12)	C(7)	C(6)	121.86(12)
C(14)	C(15)	N(1)	109.46(12)
C(16)	C(15)	N(1)	129.04(13)
C(16)	C(15)	C(14)	121.49(13)
C(9)	C(8)	C(7)	121.44(13)
O(4)	C(20)	N(1)	110.02(12)
O(3)	C(20)	O(4)	124.24(13)
O(3)	C(20)	N(1)	125.74(14)
C(7)	C(12)	C(13)	122.60(13)
C(11)	C(12)	C(7)	118.31(13)
C(11)	C(12)	C(13)	119.08(13)
N(1)	C(6)	C(7)	110.11(11)
N(1)	C(6)	C(5)	103.28(10)
C(7)	C(6)	C(5)	115.35(11)
O(2)	C(3)	O(1)	123.80(14)

Atom	Atom	Atom	Angle/°
O(2)	C(3)	C(4)	125.90(13)
O(2)	C(3)	O(1A)	118.2(6)
O(1)	C(3)	C(4)	110.13(12)
O(1A)	C(3)	C(4)	108.6(5)
C(15)	C(14)	C(5)	110.75(12)
C(19)	C(14)	C(15)	120.27(13)
C(19)	C(14)	C(5)	128.98(13)
C(3)	C(4)	C(5)	114.19(11)
C(10)	C(9)	C(8)	119.36(13)
C(14)	C(5)	C(6)	103.57(10)
C(14)	C(5)	C(4)	111.62(11)
C(4)	C(5)	C(6)	116.33(11)
C(15)	C(16)	C(17)	117.41(14)
C(10)	C(11)	C(12)	121.76(14)
C(14)	C(19)	C(18)	119.07(14)
C(9)	C(10)	C(11)	119.68(13)
C(18)	C(17)	C(16)	121.74(14)
C(17)	C(18)	C(19)	120.01(14)
O(1)	C(2)	C(1)	110.70(17)
C(1)	C(2)	O(1A)	84.3(8)
C(3)	O(1A)	C(2)	100.1(10)

Table S6: Torsion angles in ° for **8b**.

Atom	Atom	Atom	Atom	Angle/°
O(2)	C(3)	C(4)	C(5)	22.3(2)
O(2)	C(3)	O(1A)	C(2)	60.6(13)
O(1)	C(3)	C(4)	C(5)	-162.43(16)
N(1)	C(15)	C(14)	C(5)	0.37(15)
N(1)	C(15)	C(14)	C(19)	179.68(12)
N(1)	C(15)	C(16)	C(17)	-179.52(13)
N(1)	C(6)	C(5)	C(14)	10.34(13)
N(1)	C(6)	C(5)	C(4)	133.18(12)
C(7)	C(8)	C(9)	C(10)	-1.3(2)
C(7)	C(12)	C(11)	C(10)	-0.7(2)
C(7)	C(6)	C(5)	C(14)	-109.84(12)
C(7)	C(6)	C(5)	C(4)	13.01(16)
C(15)	N(1)	C(20)	O(4)	174.21(12)
C(15)	N(1)	C(20)	O(3)	-5.5(2)
C(15)	N(1)	C(6)	C(7)	112.70(12)
C(15)	N(1)	C(6)	C(5)	-11.00(14)
C(15)	C(14)	C(5)	C(6)	-6.97(14)
C(15)	C(14)	C(5)	C(4)	-

Atom	Atom	Atom	Atom	Angle/°
				132.88(12)
C(15)	C(14)	C(19)	C(18)	-0.3(2)
C(15)	C(16)	C(17)	C(18)	-0.2(2)
C(8)	C(7)	C(12)	C(11)	-1.4(2)
C(8)	C(7)	C(12)	C(13)	177.27(13)
C(8)	C(7)	C(6)	N(1)	-49.23(16)
C(8)	C(7)	C(6)	C(5)	67.14(16)
C(8)	C(9)	C(10)	C(11)	-0.9(2)
C(20)	N(1)	C(15)	C(14)	-
				171.75(13)
C(20)	N(1)	C(15)	C(16)	8.5(2)
C(20)	N(1)	C(6)	C(7)	-68.43(16)
C(20)	N(1)	C(6)	C(5)	167.87(12)
C(12)	C(7)	C(8)	C(9)	2.4(2)
C(12)	C(7)	C(6)	N(1)	130.23(13)
C(12)	C(7)	C(6)	C(5)	-
				113.41(14)
C(12)	C(11)	C(10)	C(9)	1.9(2)
C(6)	N(1)	C(15)	C(14)	7.09(15)
C(6)	N(1)	C(15)	C(16)	-
				172.61(13)
C(6)	N(1)	C(20)	O(4)	-4.51(18)
C(6)	N(1)	C(20)	O(3)	175.78(13)
C(6)	C(7)	C(8)	C(9)	-
				178.12(12)
C(6)	C(7)	C(12)	C(11)	179.16(12)
C(6)	C(7)	C(12)	C(13)	-2.2(2)
C(3)	O(1)	C(2)	C(1)	-80.0(2)
C(3)	C(4)	C(5)	C(6)	65.10(15)
C(3)	C(4)	C(5)	C(14)	-
				176.36(11)
C(14)	C(15)	C(16)	C(17)	0.8(2)
C(14)	C(19)	C(18)	C(17)	0.9(2)
C(4)	C(3)	O(1A)	C(2)	-147.6(5)
C(5)	C(14)	C(19)	C(18)	178.91(13)
C(16)	C(15)	C(14)	C(5)	-
				179.90(12)
C(16)	C(15)	C(14)	C(19)	-0.6(2)
C(16)	C(17)	C(18)	C(19)	-0.6(2)
C(19)	C(14)	C(5)	C(6)	173.80(14)
C(19)	C(14)	C(5)	C(4)	47.89(19)
C(13)	C(12)	C(11)	C(10)	-
				179.43(13)
C(21)	O(4)	C(20)	O(3)	-0.1(2)
C(21)	O(4)	C(20)	N(1)	-
				179.86(13)
C(2)	O(1)	C(3)	O(2)	-0.3(3)
C(2)	O(1)	C(3)	C(4)	-
				175.73(18)
C(1)	C(2)	O(1A)	C(3)	-123.4(10)
O(1A)	C(3)	C(4)	C(5)	-126.8(10)

Table S7: Hydrogen fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **8b**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H(8)	4225	6268	5666	29
H(6)	2964	6444	1171	26
H(4A)	5827	5270	2436	28
H(4B)	4952	5433	3876	28
H(9)	3198	5822	7809	31
H(5)	4819	6032	629	27
H(16)	5980	7779	4354	32
H(11)	84	5478	4241	33
H(19)	7594	5980	2506	34
H(10)	1122	5415	7079	34
H(13A)	673	6317	1009	46
H(13B)	-19	5715	1321	46
H(13C)	1320	5717	564	46
H(17)	8230	7595	4651	39
H(18)	9036	6715	3721	40
H(21A)	1303	8119	1819	57
H(21B)	1216	7948	3769	57
H(21C)	248	7661	2256	57
H(2AA)	3311	3664	2781	44
H(2AB)	3050	3976	947	44
H(2BC)	3147	4002	967	44
H(2BD)	3426	3700	2866	44
H(1A)	1647	4257	3706	62
H(1B)	1107	3829	2174	62
H(1C)	1336	4501	1791	62