DABCO-catalyzed unusual [4+2] cycloaddition reaction: non-substituted allenoate acts as a four-carbon synthon and facile synthesis of spirooxindoles

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1. General information:

All reactions were performed under N_2 atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. TLC monitored all reactions with silica gel-coated plates. Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H- and ^{13}C-NMR spectrum was recorded at ambient temperature on Bruker 400 instruments. All spectra were referenced to $CDCl_3$ (^{1}H δ 7.26 ppm and ^{13}C NMR δ 77.00 ppm). HRMS were obtained on Waters Xevo Q-TOF MS with ESI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected. Substrates **1** were synthesized according to the known procedure.[1]

2. Typical procedure for the synthesis of products 3:

Substrate **1** and DABCO (12 mol%) were added to an oven-dried round bottomflask with a magnetic stir bar. The solvent $CH_3OH/CHCl_3$ (2 mL, v/v = 1:1.5) and allenoate **2a** (1 eq.) were then added. The resulting mixture was stirred at 60 ^{o}C for two hours. Then, another batch of DABCO (12 mol%) and allenoate **2a** (1 eq.) was added and stirred for another two hours. A last batch of DABCO and allenoate **2a** were added and stirred for one to three hours more (see Table 2). When the reaction was completed, the solvent was evaporated and the crude residue was purified by column chromatography (ethyl acetate: petroleum ether = 1:2) with silica gel as stationary phase to obtain the product.

1 Y. Liu, Y. Du, A. Yu, D. Qin and X. Meng, *Tetrahedron*, 2015, **71**, 7706-7716.

3. Characterization of the Products

Ethyl-(E)-3-ethoxy-3-(4-methoxy-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)acrylate *(3a):* yield 42 mg (63%, white solid); mp 204-205 ^{o}C; IR (KBr) 3444, 2925, 2358, 2339, 2027, 1714, 1660, 1614 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ .74 (s, 1H), 7.19 (td, *J* = 7.8, 1.2 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.97 (td, *J* = 7.6, 0.8 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 5.51 (d, *J* = 1.2 Hz, 1H), 5.31 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.77 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 3.59-3.71 (m, 2H), 3.39-3.47 (m, 1H), 2.53 (dd, *J* = 17.2, 4.8 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.68, 178.91, 175.44, 170.77, 167.03, 141.61, 128.94, 128.52, 124.11, 122.37, 109.11, 100.62, 92.42, 64.32, 61.26, 59.66, 56.15, 40.75, 29.39, 14.26, 13.04 ppm; ESI-HRMS: calcd. for $C_{21}H_{23}NO_6$+H 386.1604, found 386.1610.

Ethyl-(E)-3-ethoxy-3-(4-methoxy-5'-methyl-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)acrylate *(3b):* yield 37 mg (57%, white solid); mp 209-210 ^{o}C; IR (KBr) 3445, 2940, 2360, 2341, 2026, 1731, 1660, 1614 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.52 (s, 1H), 6.98 (dt, *J* = 8.0, 1.0 Hz 1H), 6.89 (s, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 5.51 (d, *J* = 1.6 Hz, 1H), 5.28 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.77 (s, 1H), 4.08-4.16 (m, 2H), 3.79 (s, 3H), 3.58-3.70 (m, 2H), 3.40-3.48 (m, 1H), 2.52 (dd, *J* = 17.2, 4.8 Hz, 1H), 2.25 (s, 3H), 1.24 (d, *J* = 7.0 Hz, 3H), 1.13 (td, *J* = 7.2, 1.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.87, 178.90, 175.31, 170.86, 167.05, 139.05, 131.70, 128.94, 124.90, 108.75, 100.68, 92.43, 64.29, 61.36, 59.64, 56.14, 40.77, 29.35, 21.14, 14.32, 13.10 ppm; ESI-HRMS: calcd. for $C_{22}H_{25}NO_6$+H 400.1760, found 400.1761.

Ethyl-(E)-3-(4,5'-dimethoxy-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)-3-ethoxyacrylate *(3c):* yield 47 mg (73%, white solid); mp 213-214 ^{o}C; IR (KBr) 3452, 2944, 2361, 2342, 2026, 1704, 1664, 1612 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.60 (s, 1H), 6.65-6.79 (m, 3H), 5.51 (d, *J*= 1.6 Hz, 1H), 5.30 (dd, *J* = 12.4, 4.8 Hz, 1H), 4.78 (s, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 3.71 (s, 3H), 3.59-3.70 (m, 2H), 3.40-3.48 (m, 1H), 2.51 (dd, *J* = 16.8, 4.8 Hz, 1H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.13

(t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ192.66, 178.97, 175.19, 170.75, 167.10, 155.57, 134.88, 130.08, 114.13, 110.60, 109.49, 100.64, 92.51, 64.31, 61.82, 59.65, 56.15, 55.57, 40.71, 29.38, 14.26, 13.11ppm; ESI-HRMS: calcd. for $C_{22}H_{25}NO_7$+H 416.1709, found 416.1703.

Ethyl-(E)-3-ethoxy-3-(5'-fluoro-4-methoxy-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)acrylate ***(3d)****:* yield 56 mg (86%, white solid); mp 211-212 ^{o}C; IR (KBr) 3452, 2940, 2362, 2344, 2026, 1711, 1656, 1609 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 6.90 (td, *J* = 8.8, 2.4 Hz, 1H), 6.84 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.74 (dd, *J* = 8.4, 4.2 Hz, 1H), 5.50 (d, *J* = 1.6 Hz, 1H), 5.29 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.80 (s, 1H), 4.08-4.18 (m, 2H), 3.80 (s, 3H), 3.58-3.71 (m, 2H), 3.41-3.49 (m, 1H), 2.52 (dd, *J* = 17.2, 4.8 Hz, 1H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.13 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.09, 179.14, 175.50, 170.21, 167.02, 158.85 (d, *J*=238.4 Hz), 137.65(d, *J*=2.1Hz), 130.56(d, *J*=8.5 Hz), 114.98 (d, *J*=23.5 Hz), 112.23(d, *J*=25.0 Hz),109.66 (d, *J*=25.0 Hz), 100.47, 92.69, 64.38, 61.92, 59.82, 56.22, 40.61, 29.26, 14.23, 13.05 ppm; ESI-HRMS: calcd. for $C_{21}H_{22}FNO_6$+H 404.1509, found 404.1510.

Ethyl-(E)-3-(5'-chloro-4-methoxy-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)-3-ethoxyacrylate ***(3e)****:* yield 58 mg (90%, white solid); mp 232-233 ^{o}C; IR (KBr) 3442, 2924, 2361, 2342, 2026, 1711, 1656, 1610 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.16 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.07 (d, *J* = 2.0 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 5.50 (d, *J* = 1.6 Hz, 1H), 5.30 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.80 (s, 1H), 4.08-4.20 (m, 2H), 3.80 (s, 3H), 3.58-3.71 (m, 2H), 3.42-3.49 (m, 1H), 2.53 (dd, *J* = 16.8, 4.8 Hz, 1H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.13 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ191.91, 179.16, 175.13, 170.04, 167.01, 140.24, 130.68, 128.60, 127.71, 124.75, 110.07, 100.46, 92.87, 64.38, 61.70, 59.89, 56.24, 40.59, 29.20, 14.28, 13.11ppm; ESI-HRMS: calcd. for $C_{21}H_{22}ClNO_6$+H 420.1214, found 420.1216.

Ethyl-(E)-3-(5'-bromo-4-methoxy-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)-3-ethoxyacrylate ***(3f)****:* yield 48 mg (77%, white solid); mp 232-233 ^{o}C; IR (KBr) 3442, 2923, 2361, 2343, 2026, 1709, 1658, 1609 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.31 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.21 (d, *J* = 1.6 Hz, 1H), 6.69 (d,

J = 8.0 Hz, 1H), 5.50 (s, 1H), 5.30 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.80 (s, 1H), 4.07-4.22 (m, 2H), 3.80 (s, 3H), 3.57-3.72 (m, 2H), 3.42-3.50 (m, 1H), 2.52 (dd, *J* = 17.0, 4.8 Hz, 1H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.13 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ191.95, 179.20, 175.08, 169.98, 167.01, 140.70, 131.48, 130.99, 127.47, 115.00, 110.62, 100.45, 92.87, 64.39, 61.64, 59.92, 56.26, 40.54, 29.13, 14.31, 13.11 ppm; ESI-HRMS: calcd. for $C_{21}H_{22}BrNO_6$+H 464.0709, found 464.0700.

Ethyl-(E)-3-ethoxy-3-(5'-iodo-4-methoxy-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)acrylate ***(3g)****:* yield 42 mg (68%, white solid); mp 239-240 ^{o}C; IR (KBr) 3392, 2952, 2361, 2342, 2026, 1706, 1656, 1608 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.50 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.37 (d, *J* = 1.6 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 5.50 (d, *J* = 1.6 Hz, 1H), 5.30 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.80 (s, 1H), 4.10-4.22 (m, 2H), 3.80 (s, 3H), 3.66-3.72 (m, 1H), 3.61 (ddd, *J* = 17.2,12.0,1.6, Hz, 1H), 3.43-3.50 (m, 1H), 2.51 (dd, *J* = 17.2, 4.8 Hz, 1H), 1.29 (d, *J* = 7.0 Hz, 3H), 1.13 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.88, 179.17, 174.74, 169.98, 167.00, 141.37, 137.41, 133.18, 131.34, 111.12, 100.49, 92.99, 84.82, 64.36, 61.52, 59.97, 56.23, 40.57, 29.15, 14.39, 13.14 ppm; ESI-HRMS: calcd. for $C_{21}H_{22}INO_6$+H 512.0570, found 512.0571.

Ethyl-(E)-3-ethoxy-3-(4-methoxy-2,2'-dioxo-5'-(trifluoromethoxy)spiro[cyclohexane-1,3'-indolin]-3-en-6-yl)acrylate ***(3h)****:* yield 42 mg (67%, white solid); mp 188-189 ^{o}C; IR (KBr) 3397, 2945, 2360, 2341, 2026, 1714, 1657, 1606 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.06 (dt, *J* = 8.4, 1.6 Hz, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 5.50 (d, *J* = 1.2 Hz, 1H), 5.38 (dd, *J* = 12.4, 4.8 Hz, 1H), 4.79 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 3.59-3.72 (m, 2H), 3.41-3.48 (m, 1H), 2.51 (dd, *J* = 17.2, 4.8 Hz, 1H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.13 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.74, 179.21, 175.08, 169.98, 166.97, 144.45, 140.26, 130.36, 121.78, 119.22, 118.46, 109.46, 100.43, 92.88, 64.31, 61.82, 59.80, 56.26, 40.44, 29.21, 14.14, 13.10 ppm; ESI-HRMS: calcd. for $C_{22}H_{22}F_3NO_7$+H 470.1427, found 470.1433.

Ethyl-(E)-3-ethoxy-3-(4-methoxy-5'-nitro-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)acrylate ***(3i)****:* yield 41 mg (64%, white solid); mp 243-244 ^{o}C; IR

(KBr) 3442, 2925, 2361,2343, 2026, 1710, 1657, 1605 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.01 (d, *J* = 2.4 Hz, 1H), 7.87 (s, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 5.52 (d, *J* = 1.2 Hz, 1H), 5.42 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.81 (s, 1H), 4.08-4.17 (m, 2H), 3.83 (s, 3H), 3.57-3.71 (m, 2H), 3.42-3.49 (m, 1H), 2.60 (dd, *J* = 17.2, 4.8 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.03, 179.56, 175.27, 169.37, 166.81, 147.56, 143.40, 129.93, 125.86, 120.39, 108.86, 100.20, 93.26, 64.47, 61.58, 60.14, 56.42, 40.46, 29.16, 14.18, 13.16 ppm; ESI-HRMS: calcd. for $C_{21}H_{22}N_2O_8$+H 431.1454, found 431.1456.

Ethyl-(E)-3-ethoxy-3-(6'-fluoro-4-methoxy-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)acrylate ***(3j)****:* yield 43 mg (66%, white solid); mp 212-213 °C; IR (KBr) 3393, 2946, 2360, 2342, 2025, 1713, 1656, 1609 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.02 (dd, *J* = 8.4, 5.4 Hz, 1H), 6.66 (ddd, *J* = 9.6, 8.4, 2.4 Hz, 1H), 6.56 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.51 (d, *J* = 1.2 Hz, 1H), 5.30 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.79 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 3.57-3.71 (m, 2H), 3.42-3.50 (m, 1H), 2.52 (dd, *J* = 17.2, 4.8 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.32, 179.03, 175.87, 170.49, 167.02, 163.04 (d, *J* = 243.4 Hz), 143.07 (d, *J* = 12.1 Hz), 125.34 (d, *J* = 9.8 Hz), 124.34 (d, *J* = 2.9 Hz), 108.75 (d, *J* = 22.4 Hz), 100.54, 97.89 (d, *J* = 27.2 Hz), 92.62, 64.39, 60.97, 59.72, 56.21, 40.72, 29.36, 14.25, 13.06 ppm; ESI-HRMS: calcd. for $C_{21}H_{22}FNO_6$+H 404.1509, found 404.1510.

Ethyl-(E)-3-(6'-chloro-4-methoxy-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)-3-ethoxyacrylate ***(3k)****:* yield 21 mg (33%, white solid); mp 217-218 °C; IR (KBr) 3441, 2925, 2361, 2343, 2026, 1712, 1662, 1610 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 2.0 Hz, 1H), 5.50 (s, 1H), 5.31 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.80 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 3.59-3.71 (m, 2H), 3.44-3.50 (m, 1H), 2.52 (dd, *J* = 17.2, 4.8 Hz, 1H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.15 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.08, 179.10, 175.46, 170.36, 167.01, 142.79, 134.20, 127.39, 125.19, 122.45, 109.82, 100.47, 92.65, 64.43, 61.05, 59.76, 56.26, 40.58, 29.34, 14.25, 13.11 ppm; ESI-HRMS: calcd. for $C_{21}H_{22}ClNO_6$+H 420.1214, found 420.1213.

Ethyl-(E)-3-(6'-bromo-4-methoxy-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)-3-ethoxyacrylate ***(3l)****:* yield 48 mg (76%, white solid); mp 206-207 ^{o}C; IR (KBr) 3441, 2941, 2360, 2342, 2026, 1712, 1662, 1610; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.98 (s, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 5.50 (s, 1H), 5.30 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.80 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 3.56-3.71 (m, 2H), 3.43-3.52 (m, 1H), 2.52 (dd, *J* = 17.2, 4.8 Hz, 1H), 1.25 (t, *J* = 7.0 Hz,3H), 1.15 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.94, 179.09, 175.26, 170.34, 167.00, 142.93, 127.95, 125.57, 125.37, 122.12, 112.53, 100.45, 92.67, 64.44, 61.10, 59.77, 56.26, 40.51, 29.33, 14.26, 13.13 ppm; ESI-HRMS: calcd. for $C_{21}H_{22}BrNO_6$+H 464.0709, found 464.0711.

Ethyl-(E)-3-ethoxy-3-(7'-fluoro-4-methoxy-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)acrylate ***(3m)***: yield 55 mg (84%, white solid); mp168-169^{o}C; IR (KBr) 3301, 2943, 2360, 2342, 2026, 1727, 1709, 1603 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 6.91-7.00 (m, 2H), 6.88 (dd, *J* = 7.2, 1.2 Hz, 1H), 5.50 (d, *J* = 1.2 Hz, 1H), 5.30 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.79 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 3.67-3.74 (m, 1H), 3.60 (ddd, *J* = 16.8, 12.0,1.6 Hz, 1H), 3.43-3.51 (m, 1H), 2.54 (dd, *J* = 17.2, 4.8 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.85, 179.04, 174.14, 170.43, 166.97, 146.53 (d, *J*= 241.3 Hz), 131.64 (d, *J* = 3.5 Hz), 128.81 (d, *J* = 12.2 Hz), 123.02 (d, *J* = 5.8 Hz), 119.90 (d, *J* = 3.4 Hz), 115.55 (d, *J* = 16.8 Hz), 100.38, 92.59, 64.40, 61.54, 61.52, 59.73, 56.21, 40.80, 29.33, 14.25, 13.04 ppm; ESI-HRMS: calcd. for $C_{21}H_{22}FNO_6$+H 404.1509, found 404.1513.

Ethyl-(E)-3-(7'-chloro-4-methoxy-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)-3-ethoxyacrylate ***(3n)****:* yield 56 mg (86%, white solid); mp 144-145 ^{o}C; IR (KBr) 3440, 2940, 2392, 2349, 2026, 1714, 1661, 1612 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.19 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.98 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 5.50 (d, *J* = 1.6 Hz, 1H), 5.26-5.31 (m, 1H), 4.79 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 3.66-3.73 (m, 1H), 3.56-3.63 (m, 1H), 3.42-3.50 (m, 1H), 2.55 (dd, *J* = 17.2, 4.8 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.75, 179.04, 173.93, 170.39, 166.95,

139.31, 130.26, 128.40, 123.30, 122.48, 114.22, 100.35, 92.54, 64.45, 62.22, 59.74, 56.23, 40.91, 29.35, 14.24, 12.97 ppm; ESI-HRMS: calcd. for $C_{21}H_{22}ClNO_6$+H 420.1214, found 420.1213.

Ethyl-(E)-3-(7'-bromo-4-methoxy-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)-3-ethoxyacrylate *(3o):* yield 55 mg (88%, white solid); mp 204-205 ^{o}C; IR (KBr) 3446, 2942, 2361, 2342, 2026, 1715, 1701, 1649, 1602 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.32 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.02 (dt, *J* = 7.2, 0.8 Hz, 1H), 6.88 (t, *J* = 8.0 Hz,1H), 5.50 (d, *J* = 1.6 Hz, 1H), 5.27 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.79 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 3.67-3.73 (m, 1H), 3.59 (ddd, *J* = 17.2, 12.4,1.6 Hz, 1H), 3.43-3.48 (m, 1H), 2.55 (dd, *J* = 16.8, 4.8 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.67, 179.00, 173.58, 170.40, 166.94, 140.97, 131.14, 130.21, 123.67, 123.12, 102.04, 100.37, 92.62, 64.46, 62.60, 59.73, 56.22, 41.05, 29.41, 14.26, 13.01 ppm; ESI-HRMS: calcd. for$C_{21}H_{22}BrNO_6$+H 464.0709, found 464.0710.

Ethyl-(E)-3-(5',6'-difluoro-4-methoxy-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)-3-ethoxyacrylate *(3p)*： yield 43 mg (66%, white solid); mp 212-213 ^{o}C; IR (KBr) 3395, 2946, 2357, 2329, 2026, 1713, 1657, 1610 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 6.95 (dd, *J* = 9.6, 7.8 Hz, 1H), 6.66 (dd, *J* = 10.0, 6.4 Hz, 1H), 5.50 (s, 1H), 5.29 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.82 (s, 1H), 4.08-4.12 (m, 2H), 3.81 (s, 3H), 3.57-3.72 (m, 2H), 3.44-3.52 (m, 1H), 2.51 (dd, *J* = 17.2, 4.8 Hz, 1H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.15 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.83, 179.26, 175.82, 169.93, 167.01, 150.48 (dd, *J* = 246, 13.8 Hz), 146.58 (dd, *J* = 246, 13.8 Hz), 137.98 (dd, *J* = 10, 2.5 Hz), 124.35 (dd, *J* = 6.6, 3.8 Hz), 113.91(d, *J* = 20.4, Hz), 100.37, 99.38 (d, *J* = 22.7 Hz), 92.85, 64.45, 61.59, 59.89, 56.30, 40.49, 29.17, 14.20, 13.04 ppm; ESI-HRMS: calcd. for $C_{21}H_{21}F_2NO_6$+H 422.1415, found 422.1425.

Ethyl-(E)-3-ethoxy-3-(4-methoxy-1'-methyl-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)acrylate *(3q)*： yield 45 mg (68%, white solid); mp188-189 ^{o}C; IR (KBr) 2935, 2360, 2341, 2026, 1740, 1658, 1608 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 5.50 (d, *J* = 1.2 Hz, 1H), 5.32 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.75 (s, 1H),

4.11 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 3.57-3.69 (m, 2H), 3.30-3.39 (m, 1H), 3.14 (s, 3H), 2.53 (dd, *J* = 16.8, 4.8 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.77, 178.88, 173.23, 170.91, 166.97, 144.46, 128.55, 128.29, 123.79, 122.44, 107.44, 100.60, 92.47, 63.92, 60.83, 59.65, 56.13, 40.72, 29.56, 26.18, 14.27, 13.48 ppm; ESI-HRMS: calcd. for $C_{22}H_{25}NO_6$+H 400.1760, found 400.1768.

Ethyl-(E)-3-(5'-chloro-4-methoxy-1'-methyl-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)-3-ethoxyacrylate *(3r)*：yield 52 mg (82%, white solid); mp 162-163 °C; IR (KBr) 2940, 2361, 2342, 2026, 1727, 1657, 1606 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.09 (d, *J* = 2.0 Hz, 1H), 6.69 (d, *J* = 8.4 Hz, 1H), 5.49 (d, *J* = 1.6 Hz, 1H), 5.30 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.78 (s, 1H), 4.08-4.20 (m, 2H), 3.80 (s, 3H), 3.59-3.67 (m, 2H), 3.35-3.43 (m, 1H), 3.12 (s, 3H), 2.53 (dd, *J* = 17.2, 4.8 Hz, 1H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.07 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.96, 179.09, 172.70, 170.19, 166.93, 143.07, 129.97, 128.55, 127.80, 124.49, 108.27, 100.43, 92.90, 63.98, 61.16, 59.86, 56.19, 40.56, 29.36, 26.28, 14.28, 13.53 ppm; ESI-HRMS: calcd. for $C_{22}H_{24}ClNO_6$+H 434.1371, found 434.1379.

Ethyl-(E)-3-(5'-bromo-4-methoxy-1'-methyl-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)-3-ethoxyacrylate *(3s):* yield 50 mg (80%, white solid); mp186-187 °C; IR (KBr) 2939, 2360, 2342, 2026, 1731, 1647, 1610 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.22 (d, *J* = 2.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.49 (d, *J* = 1.2 Hz, 1H), 5.30 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.78 (s, 1H), 4.09-4.20 (m, 2H), 3.80 (s, 3H), 3.59-3.67 (m, 2H), 3.36-3.43 (m, 1H), 3.12 (s, 3H), 2.53 (dd, *J* = 16.8, 4.8 Hz, 1H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.07 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.94, 179.10, 172.57, 170.13, 166.93, 143.52, 131.44, 130.29, 127.20, 115.10, 108.79, 100.42, 92.91, 63.97, 61.11, 59.89, 56.20, 40.53, 29.31, 26.24, 14.30, 13.54ppm; ESI-HRMS: calcd. for $C_{21}H_{24}BrNO_6$+H 478.0865, found 478.0872.

Ethyl-(E)-3-(1'-benzyl-4-methoxy-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)-3-ethoxyacrylate *(3t):* yield 48 mg (77%, white solid); mp 159-160 °C; IR (KBr)

2943, 2361, 2341, 2026, 1709, 1656, 1610 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23-7.29 (m, 5H), 6.51 (d, *J* = 8.0 Hz, 1H), 5.52 (d, *J* = 1.2 Hz, 1H), 5.36 (dd, *J* = 12.0, 4.8 Hz, 1H), 5.17 (d, *J* = 15.6 Hz, 1H), 4.81 (s, 1H), 4.46 (d, *J* = 15.6 Hz, 1H), 4.10-4.21 (m, 2H), 3.81 (s, 3H), 3.59-3.72 (m, 2H), 3.39-3.46 (m, 1H), 2.55 (dd, *J* = 17.2, 4.8 Hz, 1H), 1.28 (t, *J* = 7.0 Hz, 3H), 1.01 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.89, 179.08, 172.85, 170.10, 166.99, 142.78, 135.20, 131.38, 130.49, 128.80, 127.60, 127.21, 126.99, 115.24, 109.85, 100.43, 93.06, 64.05, 61.20, 59.92, 56.21, 43.61, 40.31, 29.36, 14.32, 13.37 ppm; ESI-HRMS: calcd. for $C_{28}H_{28}BrNO_6$+H 554.1178, found 554.1172.

Ethyl-(E)-3-(1'-benzyl-5'-chloro-4-methoxy-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)-3-ethoxyacrylate ***(3u)****:* yield 55 mg (90%, white solid); mp 84-85 ^oC; IR (KBr) 2938, 2361, 2342, 2025, 1722, 1693, 1655, 1610 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23-7.30 (m, 5H), 7.12 (dd, *J* = 6.4, 2.4 Hz, 2H), 6.56 (d, *J* = 8.8 Hz, 1H), 5.53 (d, *J* = 1.2 Hz, 1H), 5.36 (dd, *J* = 12.0, 4.8 Hz, 1H), 5.18 (d, *J* = 16.0 Hz, 1H), 4.81 (s, 1H), 4.46 (d, *J* = 16.0 Hz, 1H), 4.10-4.20 (m, 2H), 3.81 (s, 3H), 3.59-3.72 (m, 2H), 3.39-3.46 (m, 1H), 2.56 (dd, *J* = 17.2, 4.8 Hz, 1H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.01 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.92, 179.07, 172.98, 170.15, 167.00, 142.31, 135.25, 130.16, 128.80, 128.50, 127.91, 127.60, 127.01, 124.47, 109.34, 100.44, 93.03, 64.06, 61.24, 59.90, 56.21, 43.65, 40.34, 29.40, 14.30, 13.36 ppm; ESI-HRMS: calcd. for $C_{28}H_{28}ClNO_6$+H 510.1683, found 510.1688.

Ethyl-(E)-3-(1'-benzyl-5'-bromo-4-methoxy-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)-3-ethoxyacrylate ***(3v)****:* yield 54 mg (90%, white solid); mp 159-160 ^oC; IR (KBr) 2939,2361, 2342, 1723, 1707, 1651, 1611 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23-7.29 (m, 5H), 6.51 (d, *J* = 8.0 Hz, 1H), 5.52 (d, *J* = 1.2 Hz, 1H), 5.36 (dd, *J* = 12.0, 4.8 Hz, 1H), 5.17 (d, *J* = 15.6 Hz, 1H), 4.81 (s, 1H), 4.46 (d, *J* = 15.6 Hz, 1H), 4.10-4.21 (m, 2H), 3.81 (s, 3H), 3.59-3.72 (m, 2H), 3.39-3.46 (m, 1H), 2.55 (dd, *J* = 17.2, 4.8 Hz, 1H), 1.28 (t, *J* = 7.0 Hz, 3H), 1.01 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.89, 179.08, 172.85, 170.10, 166.99, 142.78, 135.20, 131.38, 130.49, 128.80, 127.60, 127.21, 126.99, 115.24, 109.85, 100.43, 93.06, 64.05, 61.20, 59.92, 56.21, 43.61, 40.31, 29.36, 14.32, 13.37 ppm; ESI-HRMS: calcd. for

$C_{28}H_{28}BrNO_6$+H 554.1178, found 554.1172.

tert-butyl-(E)-6-(1,3-diethoxy-3-oxoprop-1-en-1-yl)-4-methoxy-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-ene-1'-carboxylate *(3w):* yield 38 mg (62%, brown oil); IR (KBr) 2931, 2360, 2341, 2026,1764, 1723, 1704, 1661, 1609 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.29 (td, *J* = 7.2, 1.6 Hz, 1H), 7.12 (td, *J* = 7.2, 0.8 Hz, 1H), 7.08 (dd, *J* = 7.6, 1.6 Hz, 1H), 5.51 (d, *J* = 1.2 Hz, 1H), 5.28 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.77 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 3.52-3.65 (m, 2H), 3.32-3.40 (m, 1H), 2.58 (dd, *J* = 17.2, 4.8 Hz, 1H), 1.60 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.98, 179.05, 170.91, 170.27, 166.87, 149.20, 140.85, 128.41, 127.46, 126.87, 124.35, 123.52, 114.51, 100.39, 92.70, 83.98, 65.09, 64.33, 59.72, 56.16, 41.65, 29.56, 28.00, 14.17, 12.99 ppm; ESI-HRMS: calcd. for $C_{26}H_{31}NO_8$+H 486.2128, found 486.2122.

Ethyl-(E)-3-ethoxy-3-(1'-(ethoxymethyl)-4-methoxy-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)acrylate *(3x):* yield 52 mg (81%, brown oil); IR (KBr) 2937, 2361, 2342, 2026, 1719, 1659, 1611 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (td, *J* = 8.0, 1.2 Hz, 1H), 7.11 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.04 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 5.50 (d, *J* = 1.2 Hz, 1H), 5.34 (dd, *J* = 12.0, 4.8 Hz, 1H), 5.23 (d, *J* = 10.8 Hz, 1H), 4.96 (d, *J* = 10.8 Hz, 1H), 4.77 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 3.41-3.66 (m, 5H), 2.55 (dd, *J* = 17.2, 4.8 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.0 Hz, 3H), 1.01 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ192.56, 178.81, 173.88, 170.53, 166.94, 142.85, 128.61, 127.80, 123.72, 122.89, 108.91, 100.49, 92.53, 69.69, 63.99, 61.01, 59.64, 56.11, 40.56, 29.44, 14.76, 14.22, 13.10 ppm; ESI-HRMS: calcd. for $C_{24}H_{29}NO_7$+H 444.2022, found 444.2029.

Ethyl-(E)-3-(3-bromo-4-methoxy-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)-3-ethoxyacrylate *(4):* yield 16 mg (27%, white solid); mp 239-240 ^oC; IR (KBr) 3446, 2940, 2360, 2342, 2026, 1715, 1701, 1662, 1654, 1623 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.21 (td, *J* =8.0,1.2 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 5.30 (dd, *J* =11.4,5.0 Hz, 1H), 4.82 (s, 1H), 4.10-4.16 (m, 2H), 4.04 (s, 3H), 3.65-3.72 (m, 2H), 3.40-3.45 (m, 1H), 2.89

(dd, *J* = 17.0, 5.0 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO) δ185.25, 175.42, 173.42, 169.79, 166.43, 142.85, 128.68, 128.43, 123.78, 121.27, 109.01, 99.07, 92.69, 79.17, 64.42, 60.91, 59.29, 57.24, 27.02, 14.17, 12.90 ppm; ESI-HRMS: calcd. for $C_{21}H_{22}BrNO_6$+H 466.0691, found 466.0687.

Ethyl-(E)-3-ethoxy-3-((1S,6R)-4-methoxy-3-(benzen-2-yl)-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)acrylate ***(5g-Ph)****:* yield 25 mg (56%, white solid); mp 248-249 ^{o}C; IR (KBr) 3446, 2944, 2360, 2342, 2026, 1703, 1657, 1622, 1606 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.49 – 7.52 (m, 2H), 7.46 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.37-7.41 (m, 3H), 7.29-7.32 (m, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 5.57 (d, *J* = 1.6 Hz, 1H), 5.45 (dd, *J* = 12.0, 4.8Hz, 1H), 4.80 (s, 1H), 4.02-4.10 (m, 2H), 3.84 (s, 3H), 3.66-3.74 (m, 2H), 3.51-3.46 (m, 1H), 2.56 (dd, *J* = 17.2, 4.8 Hz, 1H), 1.15-1.20 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.60, 179.07, 175.38, 170.57, 167.11, 140.84, 135.54, 129.47, 128.55, 127.41, 126.71, 123.20, 109.32, 100.68, 92.67, 64.33, 61.58, 59.68, 56.22, 40.70, 29.24, 14.14, 13.17 ppm; ESI-HRMS: calcd. for $C_{27}H_{27}NO_6$+H 462.1917, found 462.1917.

Ethyl-(E)-3-ethoxy-3-(4-methoxy-3-(naphthalen-2-yl)-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)acrylate ***(5g-Naph)****:* yield 38 mg (77%, white solid); mp 253-254 ^{o}C; IR (KBr) 3446, 2931, 2360, 2342, 2026, 1719, 1700, 1684, 1670, 1653, 1647 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ8.13 (s, 1H), 7.94 (d, *J* = 1.6 Hz, 1H), 7.81-7.85 (m, 3H), 7.65 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.56 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.50 (d, *J* = 1.6 Hz, 1H), 7.44-7.48(m, 2H), 6.92 (d, *J* = 8.0 Hz, 1H), 5.57 (d, *J* = 1.6 Hz, 1H), 5.48 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.79 (s, 1H), 3.97-4.07 (m, 2H), 3.82 (s, 3H), 3.67-3.73 (m, 2H), 3.46-3.51 (m, 1H), 2.56 (dd, *J* = 17.0, 4.8 Hz, 1H), 1.18 (t, *J* = 7.0 Hz, 3H), 1.09 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.89, 179.30, 175.77, 170.50, 167.13, 141.17, 138.18, 135.35, 133.64, 132.31, 129.63, 128.13, 127.98, 127.74, 127.51, 126.12, 125.58, 125.35, 125.04, 123.36, 109.67, 100.76, 92.73, 64.40, 61.74, 59.67, 56.23, 40.78, 29.28, 14.09, 13.12 ppm; ESI-HRMS: calcd. for $C_{31}H_{29}NO_6$+H 512.2073, found 512.2074.

Ethyl-(E)-3-ethoxy-4-((E)-2-oxoindolin-3-ylidene)but-2-enoate ***(1a)****:* yield 374 mg (96%, orange solid); mp 135-136 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.25

(s, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 8.0 Hz, 1H), 6.95 (t, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 5.45 (s, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 1.53 (t, *J* = 7.0 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.42, 166.36, 164.34, 142.95, 130.82, 130.73, 126.96, 121.72, 121.18, 110.33, 98.69, 64.70, 60.25, 14.31, 14.16 ppm; ESI-HRMS: calcd. for $C_{16}H_{17}NO_4$+H 288.1236, found 288.1230.

Ethyl-(E)-3-ethoxy-4-((E)-5-methyl-2-oxoindolin-3-ylidene)but-2-enoate ***(1b)****:* yield 299 mg (80%, orange solid); mp 181-182 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.09 (s, 1H), 7.75 (s, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 5.45 (s, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.30 (s, 3H), 1.56 (t, *J* = 7.0 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.83, 165.91, 164.24, 141.86, 131.55, 131.13, 129.97, 127.66, 124.88, 120.48, 109.71, 98.29, 64.99, 59.66, 20.63, 14.25, 14.07 ppm; ESI-HRMS: calcd. for $C_{17}H_{19}NO_4$+H 302.1392, found 302.1391.

Ethyl-(E)-3-ethoxy-4-((E)-5-methoxy-2-oxoindolin-3-ylidene)but-2-enoate ***(1c)****:* yield 197 mg (55%, brick red solid); mp 181-182 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.21 (s, 1H), 7.46 (d, *J* = 2.4 Hz, 1H), 6.80 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 5.45 (s, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 1.54 (t, *J* = 7.0 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.32, 166.29, 164.25, 155.16, 136.80, 131.17, 127.20, 122.10, 115.62, 114.13, 110.32, 98.86, 64.74, 60.26, 55.98, 14.32, 14.28 ppm; ESI-HRMS: calcd. for $C_{17}H_{19}NO_5$+H 318.1342, found 318.1344.

Ethyl-(E)-3-ethoxy-4-((E)-5-fluoro-2-oxoindolin-3-ylidene)but-2-enoate ***(1d)****:* yield 355 mg (96%, orange solid); mp 188-189 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.35 (s, 1H), 7.67 (dd, *J* = 9.6, 2.8 Hz, 1H), 6.96 (td, *J* = 8.4, 2.8 Hz, 1H), 6.80 (dd, *J* = 8.4, 4.4 Hz, 1H), 5.48 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 1.57 (t, *J* = 7.0 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.18, 166.18, 163.80, 138.92, 132.07 (d, *J* = 9.8 Hz), 131.94 (d, *J* = 2.4 Hz), 128.49 (d, *J* = 12.0 Hz), 128.04, 117.03 (d, *J* = 23.9 Hz), 114.53 (d, *J* = 26.3 Hz),

110.48 (d, *J* = 7.8 Hz), 99.61, 64.91, 60.36, 14.31, 14.16 ppm; ESI-HRMS: calcd. for $C_{16}H_{16}FNO_4$+H 306.1142, found 306.1136.

Ethyl-(E)-4-((E)-5-chloro-2-oxoindolin-3-ylidene)-3-ethoxybut-2-enoate ***(1e)****:* yield 223 mg (63%, orange solid); mp181-182 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.38 (s, 1H), 7.98 (d, *J* = 2.4 Hz, 1H), 7.21 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.49 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 1.60 (t, *J* = 7.0 Hz, 3H), 1.31 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.44, 165.74, 163.47, 142.87, 130.55, 129.84, 126.74, 126.45, 125.28, 121.88, 111.35, 99.51, 65.16, 59.78, 14.18, 14.01 ppm; ESI-HRMS: calcd. for $C_{16}H_{16}ClNO_4$+H 322.0846, found 322.0847.

Ethyl-(E)-4-((E)-5-bromo-2-oxoindolin-3-ylidene)-3-ethoxybut-2-enoate ***(1f)****:* yield 301 mg (93%, orange solid); mp 217-218 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.38 (s, 1H), 8.14 (d, *J* = 2.0 Hz, 1H), 7.35 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.49 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 1.61 (t, *J* = 7.0 Hz, 3H), 1.31 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.33, 165.75, 163.48, 143.25, 133.35, 129.72, 129.48, 126.40, 122.34, 112.94, 111.88, 99.57, 65.20, 59.80, 14.20, 14.11 ppm; ESI-HRMS: calcd. for $C_{16}H_{16}BrNO_4$+H 366.0341, found 366.0340.

Ethyl-(E)-3-ethoxy-4-((E)-5-iodo-2-oxoindolin-3-ylidene)but-2-enoate ***(1g)****:* yield 214 mg (71%, brick red solid); mp 232-233 ^oC; ^1H NMR (400 MHz, DMSO-d_6) δ 10.77 (s, 1H), 8.26 (d, *J* = 1.6 Hz, 1H), 8.16 (s, 1H), 7.59 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.60 (s, 1H), 4.10-4.17 (m, 4H), 1.51 (t, *J* = 7.0 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.17, 165.77, 163.58, 143.68, 139.07, 134.98, 129.55, 126.17, 122.76, 112.38, 99.48, 83.98, 65.23, 59.80, 14.33, 14.22 ppm; ESI-HRMS: calcd. for $C_{16}H_{16}INO_4$+H 414.0202, found 414.0197.

Ethyl-(E)-3-ethoxy-4-((E)-2-oxo-5-(trifluoromethoxy)indolin-3-ylidene)but-2-enoate ***(1h)****:* yield 64 mg (20%, orange solid); mp 156-157 ^oC; ^1H NMR (400 MHz, DMSO-d_6) δ 10.87 (s, 1H), 8.21 (s, 1H), 7.84 (d, *J* = 2.4 Hz, 1H), 7.31 (ddd, *J* = 8.4, 2.4, 1.2 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 5.63 (s, 1H), 4.11-4.18 (m, 4H), 1.42 (t, *J* =

7.0 Hz, 3H), 1.23 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.74, 165.82, 163.42, 143.28, 142.66, 129.86, 126.96, 124.55, 121.58, 121.39, 120.46, 110.94, 99.82, 65.25, 59.89, 14.22, 13.77 ppm; ESI-HRMS: calcd. for $C_{17}H_{16}F_3NO_5$+H 372.1059, found 372.1053.

Ethyl- (E)-3-ethoxy-4-((E)-5-nitro-2-oxoindolin-3-ylidene)but-2-enoate ***(1i)****:* yield 200 mg (58%, yellow solid); mp 263-264 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.39 (s, 1H), 8.78 (d, *J* = 2.4 Hz, 1H), 8.33 (s, 1H), 8.22 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 1H), 5.68 (s, 1H), 4.12-4. 20 (m, 4H), 1.55 (t, *J* = 7.0 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.97, 165.69, 163.04, 149.70, 141.87, 128.76, 127.77, 127.45, 122.48, 120.57, 110.13, 100.57, 65.44, 59.90, 14.15, 13.90 ppm; ESI-HRMS: calcd. for $C_{16}H_{16}N_2O_6$+H 333.1087, found 333.1097.

Ethyl -(E)-3-ethoxy-4-((E)-6-fluoro-2-oxoindolin-3-ylidene)but-2-enoate ***(1j)****:* yield 203 mg (55%, yellow solid); mp 174-175 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.26 (s, 1H), 7.86 (dd, *J* = 9.2, 5.8 Hz, 1H), 6.62-6.67(m, 2H), 5.45 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.10 (q, *J* = 7.0 Hz, 2H), 1.52 (t, *J* = 7.0 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.10, 165.94, 163.96, 146.09 (d, *J* = 12.6 Hz), 129.76 (d, *J* = 1.9 Hz), 128.99 (d, *J* = 10.4 Hz), 124.88 (d, *J* = 3.0Hz),116.94 (d, *J* = 2.8 Hz), 107.86 (d, *J* = 22.3 Hz), 98.48, 98.13 (d, *J* = 26.7 Hz), 65.00, 59.74, 14.26, 13.99 ppm; ESI-HRMS: calcd. for $C_{16}H_{16}FNO_4$+H 306.1142, found 306.1147.

Ethyl- (E)-4-((E)-6-chloro-2-oxoindolin-3-ylidene)-3-ethoxybut-2-enoate ***(1k)****:* yield 63 mg (18%, orange solid); mp 185-186 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.31 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 6.93 (dd, *J* =8.0, 1.6 Hz, 1H), 6.91 (d, *J* = 1.6 Hz, 1H), 5.47 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 1.52 (t, *J* = 6.8 Hz, 3H), 1.31 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.68, 165.83, 163.74, 145.37, 135.29, 129.68, 128.30, 125.91, 121.11, 119.30, 110.01, 98.81, 64.99, 59.72, 14.20, 13.92 ppm; ESI-HRMS: calcd. for $C_{16}H_{16}ClNO_4$+H 322.0846, found 322.0841.

Ethyl-(E)-4-((E)-6-bromo-2-oxoindolin-3-ylidene)-3-ethoxybut-2-enoate ***(1l)****:* yield 230 mg (71%, orange solid); mp178-179 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37

(s, 1H), 8.32 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.10 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.05 (d, *J* = 1.6 Hz, 1H), 5.47 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.10 (q, *J* = 7.0 Hz, 2H), 1.52 (t, *J* = 7.0 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.55, 165.82, 163.75, 145.41, 129.77, 128.49, 126.08, 124.00, 119.63, 112.81, 98.83, 64.99, 59.71, 14.19, 13.90 ppm; ESI-HRMS: calcd. for $C_{16}H_{16}NBrO_4$+H 366.0341, found 366.0336.

Ethyl- (E)-3-ethoxy-4-((E)-7-fluoro-2-oxoindolin-3-ylidene)but-2-enoate ***(1m)****:* yield 273 mg (74%, orange solid); mp 201-202 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.17 (s, 1H), 8.09 (s, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.21 (m, 1H), 6.98 (td, *J* = 8.0, 5.2 Hz, 1H), 5.59 (s, 1H), 4.09-4.18 (m, 4H), 1.40 (t, *J* = 7.0 Hz, 3H), 1.22 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.51, 165.86, 163.70, 146.63 (d, *J* = 240.4 Hz), 131.07 (d, *J* = 12.9 Hz), 130.08 (d, *J* = 4.1 Hz), 127.01, 123.27 (d, *J* = 4.5 Hz),122.96 (d, *J* = 3.2 Hz), 121.83 (d, *J* = 6.0 Hz), 117.72 (d, *J* = 17.2 Hz), 98.81, 65.03, 59.75, 14.19, 13.91 ppm; ESI-HRMS: calcd. for $C_{16}H_{16}FNO_4$+H 306.1142, found 306.1143.

Ethyl-(E)-4-((E)-7-chloro-2-oxoindolin-3-ylidene)-3-ethoxybut-2-enoate ***(1n)****:* yield 248 mg (70%, orange solid); mp 140-141 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.09 (s, 1H), 8.10 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.00 (t, *J* = 8.0 Hz, 1H), 5.59 (s, 1H), 4.11-4.17 (m, 4H), 1.40 (t, *J* = 7.0 Hz, 3H), 1.22 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.53, 165.78, 163.56, 141.39, 130.61, 130.22, 127.14, 125.35, 122.35, 122.20, 114.34, 98.89, 64.98, 59.69, 14.15, 13.85 ppm; ESI-HRMS: calcd. for $C_{16}H_{16}ClNO_4$+H 322.0846, found 322.0846.

Ethyl-(E)-4-((E)-7-bromo-2-oxoindolin-3-ylidene)-3-ethoxybut-2-enoate ***(1o)****:* yield 174 mg (54%, orange solid); mp 179-180 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.94 (s, 1H), 8.08 (s, 1H), 7.83 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.48 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.93 (t, *J* = 8.0 Hz, 1H), 5.59 (s, 1H), 4.10-4.18 (m, 4H), 1.40 (t, *J* = 7.0 Hz, 3H), 1.22 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.51, 165.84, 163.61, 143.05, 133.62, 130.45, 127.22, 125.87, 122.82, 122.24, 102.56, 98.93, 65.05, 59.76, 14.21, 13.91 ppm; ESI-HRMS: calcd. for $C_{16}H_{16}BrNO_4$+H 366.0341, found 366.0343.

Ethyl-(E)-4-((E)-5,6-difluoro-2-oxoindolin-3-ylidene)-3-ethoxybut-2-enoate ***(1p)****:* yield 250 mg (71%, orange solid); mp 180-181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.36 (s, 1H), 7.84 (dd, *J* = 11.2, 8.0 Hz, 1H), 6.73 (dd, *J* = 9.8, 6.6 Hz, 1H), 5.49 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.12 (q, *J* = 7.0 Hz, 2H), 1.57 (t, *J* = 7.2 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.72, 165.69, 163.35, 151.01 (dd, *J* = 248.4, 14.1 Hz), 144.62 (dd, *J* = 235, 13.2 Hz), 141.28 (dd, *J* = 10, 1.9 Hz), 129.29 (t, *J* = 2.7 Hz), 125.68 (d, *J* = 3.5 Hz), 116.38 (dd, *J* = 7.8, 3.8 Hz), 116.07 (d, *J* = 21.5Hz), 99.59, 99.42 (d, *J* = 5.5 Hz), 65.08, 59.73, 14.13, 13.87 ppm; ESI-HRMS: calcd. for $C_{16}H_{15}F_2NO_4$+H 324.1047, found 324.1051.

Ethyl-(E)-3-ethoxy-4-((E)-1-methyl-2-oxoindolin-3-ylidene)but-2-enoate ***(1q)****:* yield 344 mg (92%, orange solid); mp 82-83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.83 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.29 (td, *J* = 7.6, 1.2 Hz, 1H), 6.97 (td, *J* = 7.6, 1.2 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 5.43 (s, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.24 (s, 3H), 1.51 (t, *J* = 7.0 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.21, 166.21, 164.24, 145.29, 130.53, 130.24, 127.03, 126.53, 121.68, 120.69, 107.95, 98.56, 64.64, 60.20, 26.14, 14.31, 14.13 ppm; ESI-HRMS: calcd. for $C_{17}H_{19}NO_4$+H 302.1392, found 302.1398.

Ethyl-(E)-4-((E)-5-chloro-1-methyl-2-oxoindolin-3-ylidene)-3-ethoxybut-2-enoate ***(1r)****:* yield 309 mg (90%, orange solid); mp 141-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.94 (d, *J* = 2.4 Hz, 1H), 7.26 (dd, *J* = 8.4,2.4 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 5.47 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.23 (s, 3H), 1.58 (t, *J* = 7.0 Hz, 3H), 1.31 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.93, 166.06, 163.64, 143.73, 129.98, 129.25, 128.09, 127.14, 127.11, 121.96, 108.73, 99.68, 64.95, 60.35, 26.29, 14.31, 14.19 ppm; ESI-HRMS: calcd. for $C_{17}H_{18}ClNO_4$+H 336.1003, found 336.1003.

Ethyl-(E)-4-((E)-5-bromo-1-methyl-2-oxoindolin-3-ylidene)-3-ethoxybut-2-enoate ***(1s)****:* yield 310 mg (98%, orange solid); mp 131-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.10 (d, *J* = 2.0 Hz, 1H), 7.40 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 5.47 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.10 (q, *J* = 7.0 Hz, 2H), 3.22 (s, 3H), 1.59 (t, *J* = 7.0 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ

167.82, 166.05, 163.62, 144.17, 132.82, 129.85, 129.09, 128.08, 122.38, 114.43, 109.26, 99.75, 64.98, 60.35, 26.26, 14.32, 14.25 ppm; ESI-HRMS: calcd. for $C_{17}H_{18}BrNO_4$+H 380.0497, found 380.0499.

Ethyl- (E)-4-((E)-1-benzyl-2-oxoindolin-3-ylidene)-3-ethoxybut-2-enoate ***(1t)****:* yield 270 mg (85%, orange solid); mp 121-122 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.84 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.26 – 7.31 (m, 5H), 7.17 (td, *J* = 7.6, 1.2 Hz, 1H), 6.94 (td, *J* = 7.6, 1.2 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 5.45 (s, 1H), 4.95 (s, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.11 (q, *J* = 7.0 Hz, 2H), 1.52 (t, *J* = 7.0 Hz, 3H), 1.31 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.33, 166.23, 164.23, 144.40, 135.86, 130.47, 130.08, 128.66, 127.49, 127.31, 126.65, 121.75, 120.83, 109.00, 98.68, 64.68, 60.24, 43.73, 14.33, 14.15 ppm; ESI-HRMS: calcd. for $C_{23}H_{23}NO_4$+H 378.1705, found 378.1703.

Ethyl-(E)-4-((E)-1-benzyl-5-chloro-2-oxoindolin-3-ylidene)-3-ethoxybut-2-enoate ***(1u)****:* yield 218 mg (72%, orange solid); mp 110-111 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.96 (d, *J* = 2.0 Hz, 1H), 7.26 – 7.35 (m, 5H), 7.13 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 5.49 (s, 1H), 4.94 (s, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 1.58 (t, *J* = 7.0 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.04, 166.07, 163.63, 142.79, 135.45, 129.94, 129.10, 128.75, 128.43, 127.66, 127.25, 127.19, 122.13, 109.80, 99.78, 64.98, 60.37, 43.83, 14.32, 14.18 ppm; ESI-HRMS: calcd. for $C_{23}H_{22}ClNO_4$+H 412.1316, found 412.1319.

Ethyl-(E)-4-((E)-1-benzyl-5-bromo-2-oxoindolin-3-ylidene)-3-ethoxybut-2-enoate ***(1v)****:* yield 248 mg (86%, orange solid); mp 129-130 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.12 (d, *J* = 2.0 Hz, 1H), 7.26-7.34 (m, 6H), 6.54 (d, *J* = 8.4 Hz, 1H), 5.49 (s, 1H), 4.94 (s, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 4.12 (q, *J* = 7.0 Hz, 2H), 1.59 (t, *J* = 7.0 Hz,3H), 1.32 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.93, 166.06, 163.61, 143.23, 135.41, 132.78, 129.95, 128.94, 128.76, 128.43, 127.67, 127.24, 122.56, 114.58, 110.31, 99.85, 65.00, 60.39, 43.82, 14.32, 14.24 ppm; ESI-HRMS: calcd. for $C_{23}H_{22}BrNO_4$+H 456.0811, found 456.0811.

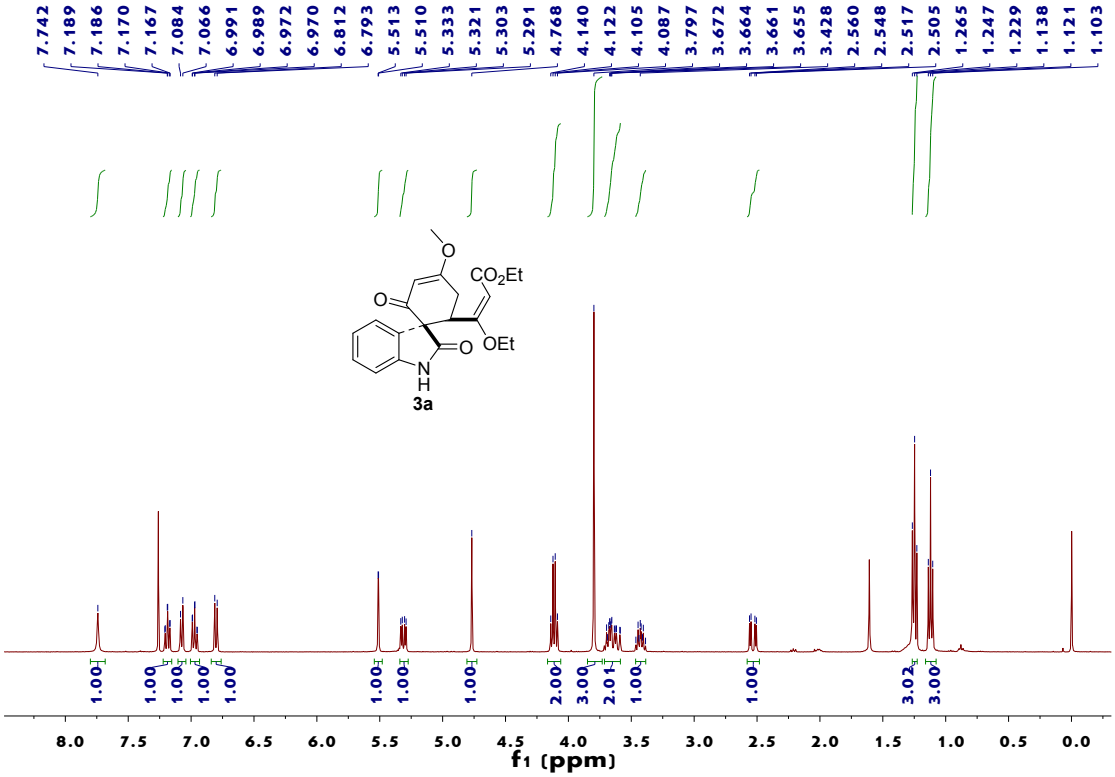
tert-butyl-(E)-3-((E)-2,4-diethoxy-4-oxobut-2-en-1-ylidene)-2-oxoindoline-1-carboxylate ***(1w)****:* yield 260 mg (83%, yellow solid); mp 112-113 ^oC; ^1H NMR (400

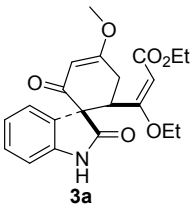
MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.88 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.34 (td, *J* = 8.0, 1.2 Hz, 1H), 7.10 (td, *J* = 8.0, 1.2 Hz, 1H), 5.44 (s, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 1.64 (s, 9H), 1.49 (t, *J* = 7.0 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.18, 166.11, 163.90, 149.24, 141.05, 130.71, 129.01, 128.10, 126.10, 123.63, 121.07, 114.92, 98.83, 84.16, 64.74, 60.25, 28.08, 14.32, 14.09 ppm; ESI-HRMS: calcd. for $C_{21}H_{25}NO_6$+H 388.1760, found 388.1750.

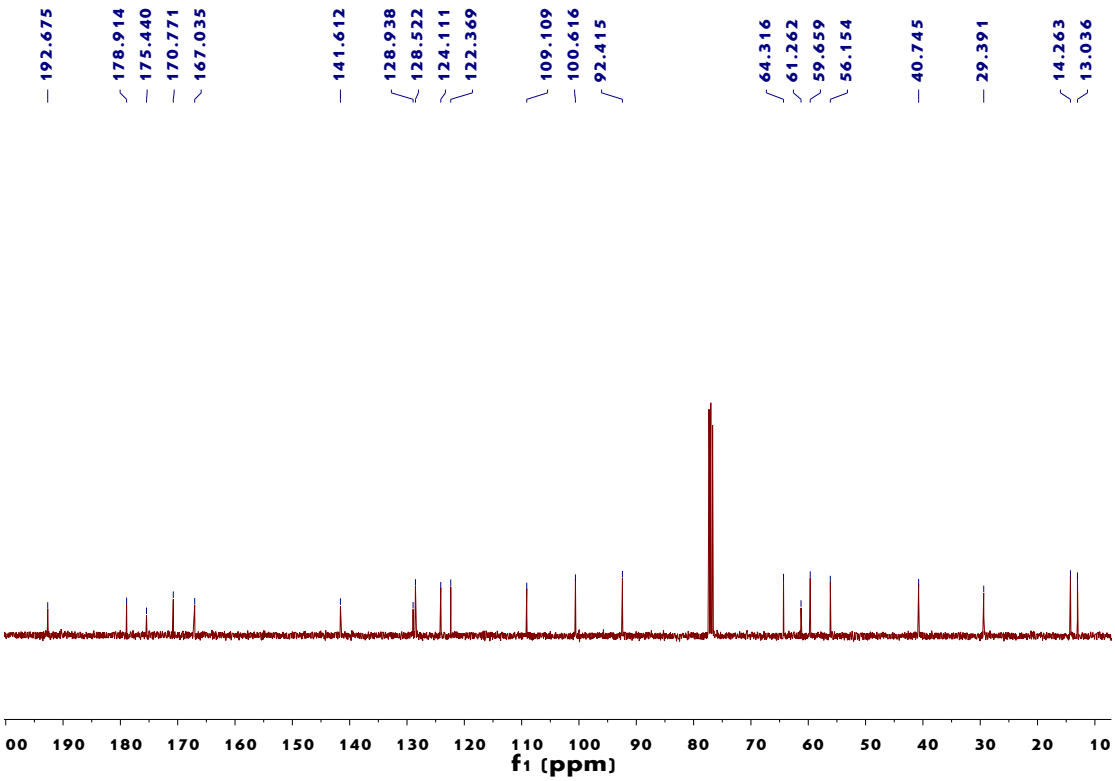
Ethyl-(E)-3-ethoxy-4-((E)-1-(ethoxymethyl)-2-oxoindolin-3-ylidene)but-2-enoate ***(1x)****:* yield 212 mg (63%, orange solid); mp 96-97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.87 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.30 (td, *J* = 7.6, 1.2 Hz, 1H), 6.99 – 7.05 (m, 2H), 5.45 (s, 1H), 5.22 (s, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.55 (q, *J* = 7.2 Hz, 2H), 1.52 (t, *J* = 7.0 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.17 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.59, 166.21, 164.16, 143.80, 130.70, 129.98, 127.52, 126.64, 122.22, 120.66, 109.58, 98.75, 69.82, 64.70, 64.12, 60.24, 14.86, 14.32, 14.15 ppm; ESI-HRMS: calcd. for $C_{19}H_{23}NO_5$+H 346.1654, found 346.1658.

Ethyl-(E)-3-((1S,6R)-4-(benzyloxy)-2,2'-dioxospiro[cyclohexane-1,3'-indolin]-3-en-6-yl)-3-ethoxyacrylate ***(3a-OBn)****:* yield 33 mg (40%, white solid); mp 209-210 °C; IR (KBr) 3447, 2940, 2360, 2342, 2026, 1703, 1664, 1613 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.36-7.43 (m, 5H), 7.20 (td, *J* = 7.6, 1.2 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 5.63 (d, *J* = 1.2 Hz, 1H), 5.36 (dd, *J* = 12.0, 4.8 Hz, 1H), 5.00 (q, *J* = 11.6 Hz, 2H), 4.77 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.64-3.72 (m, 2H), 3.40-3.46 (m, 1H), 2.61 (dd, *J* = 17.2, 4.8 Hz, 1H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.13 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.72, 177.83, 175.24, 170.73, 167.04, 141.52, 134.82, 128.88, 128.67, 128.57, 128.53, 127.96, 124.20, 122.42, 109.07, 101.56, 92.46, 71.02, 64.31, 61.28, 59.68, 40.65, 29.59, 14.27, 13.08 ppm; ESI-HRMS: calcd. for $C_{27}H_{27}NO_6$+H 462.1917, found 462.1921.

4. Copies of ^{1}H NMR and ^{13}C NMR



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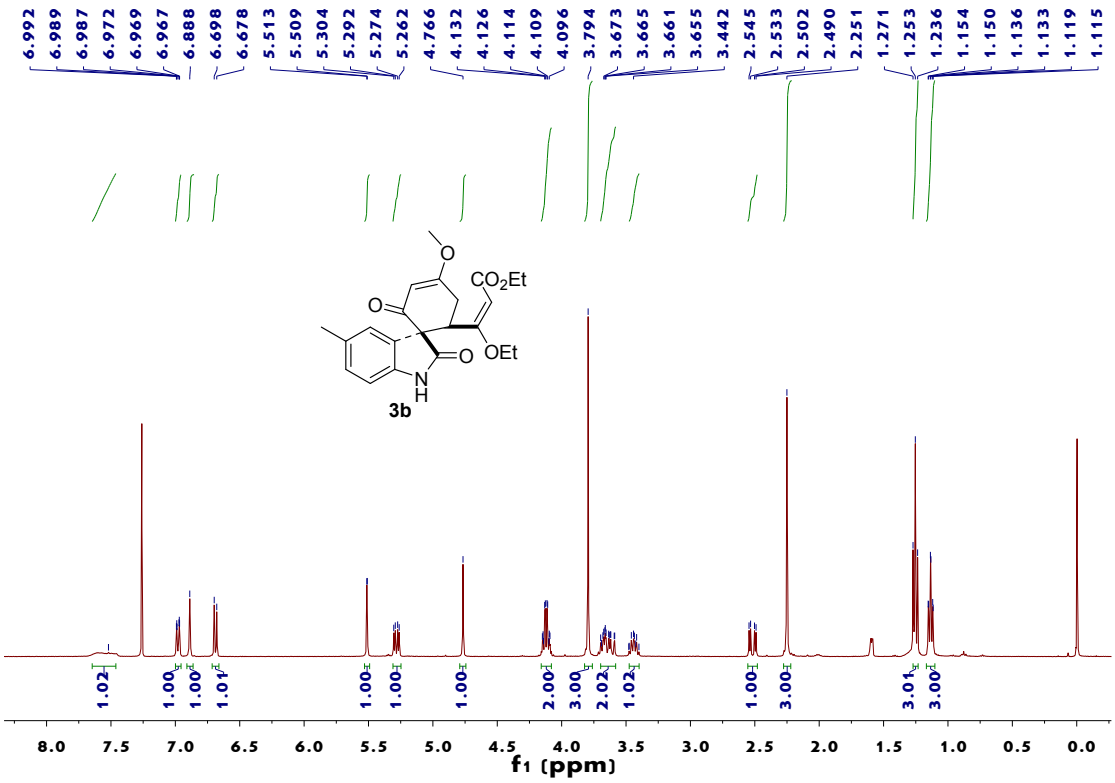
f1 (ppm)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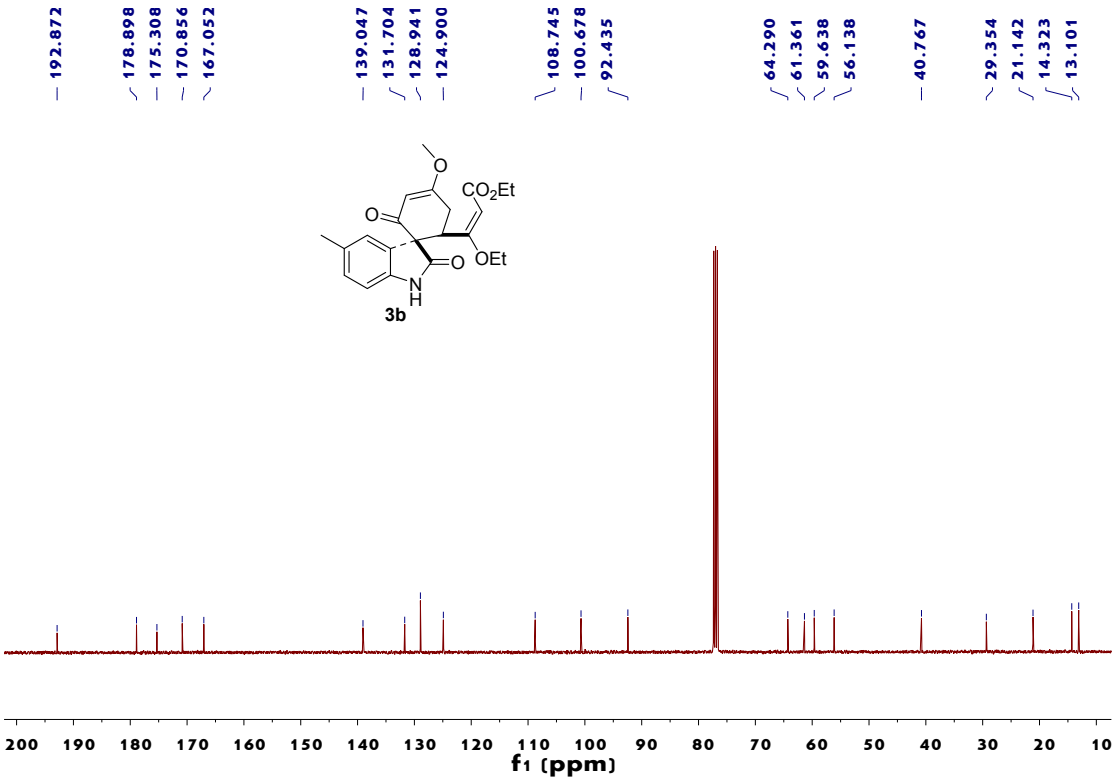
OEt
3b
f1 (ppm)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29.354
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O
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N
H
3b
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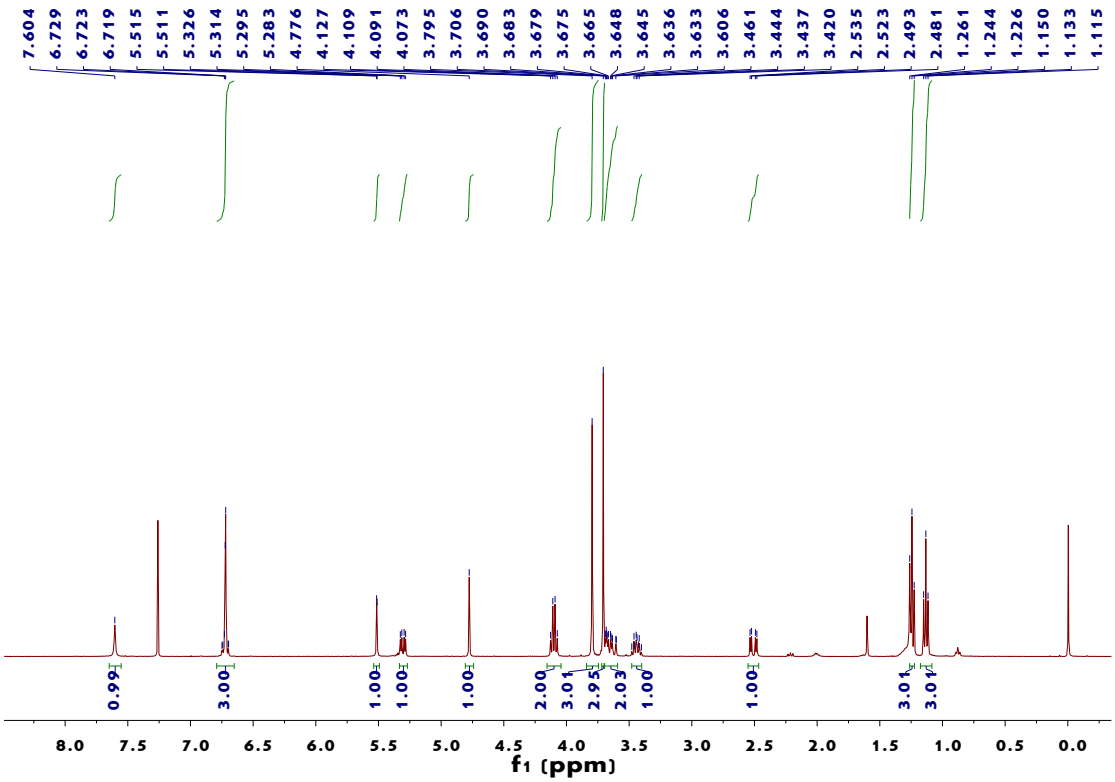
f1 (ppm)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1.00
3.01
3.01
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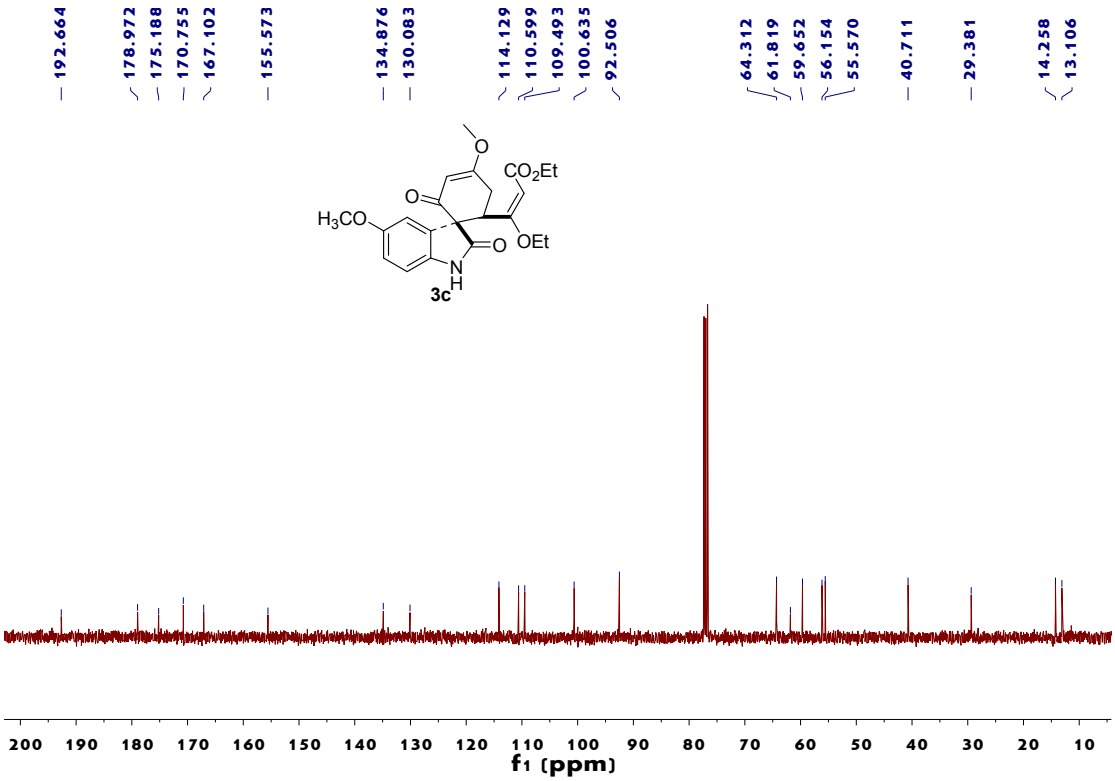
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13.106
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3c
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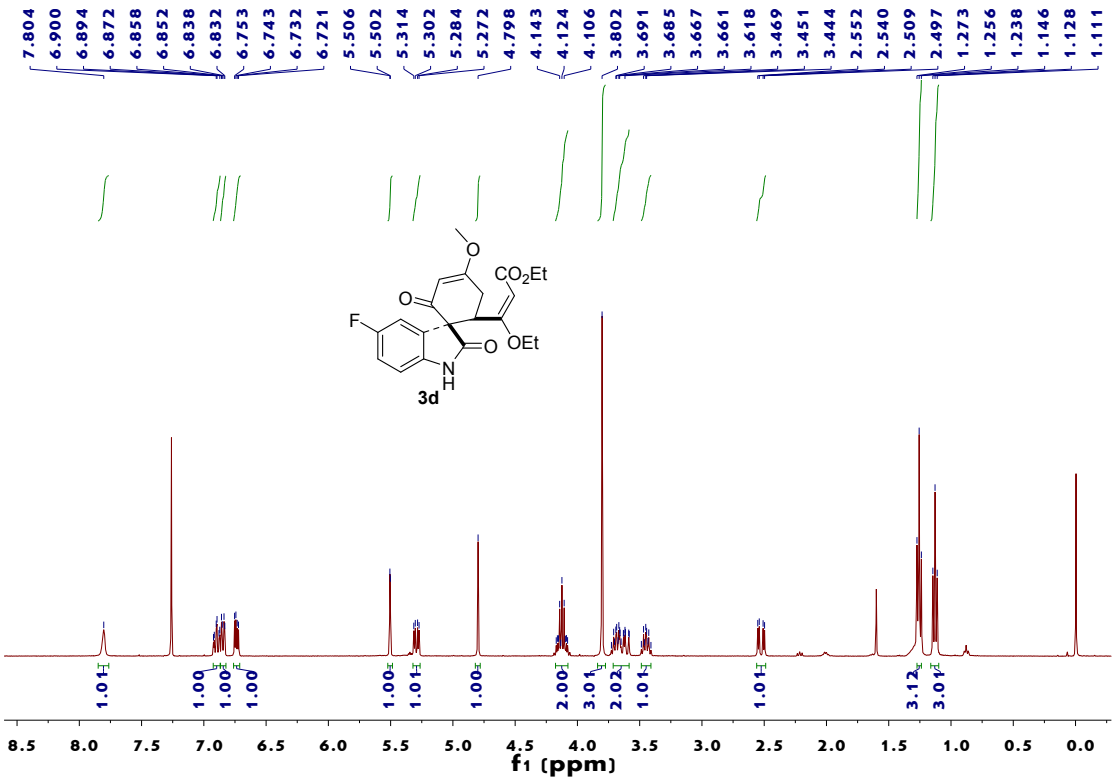
f1 (ppm)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F
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N
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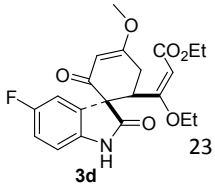
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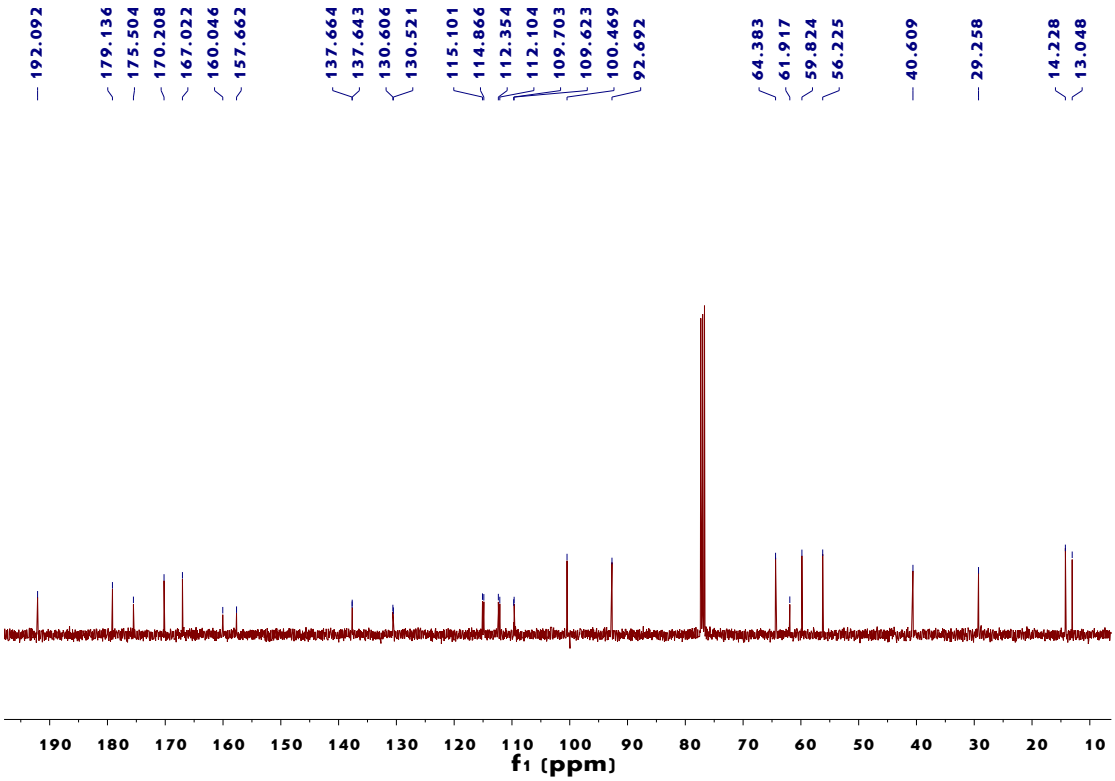
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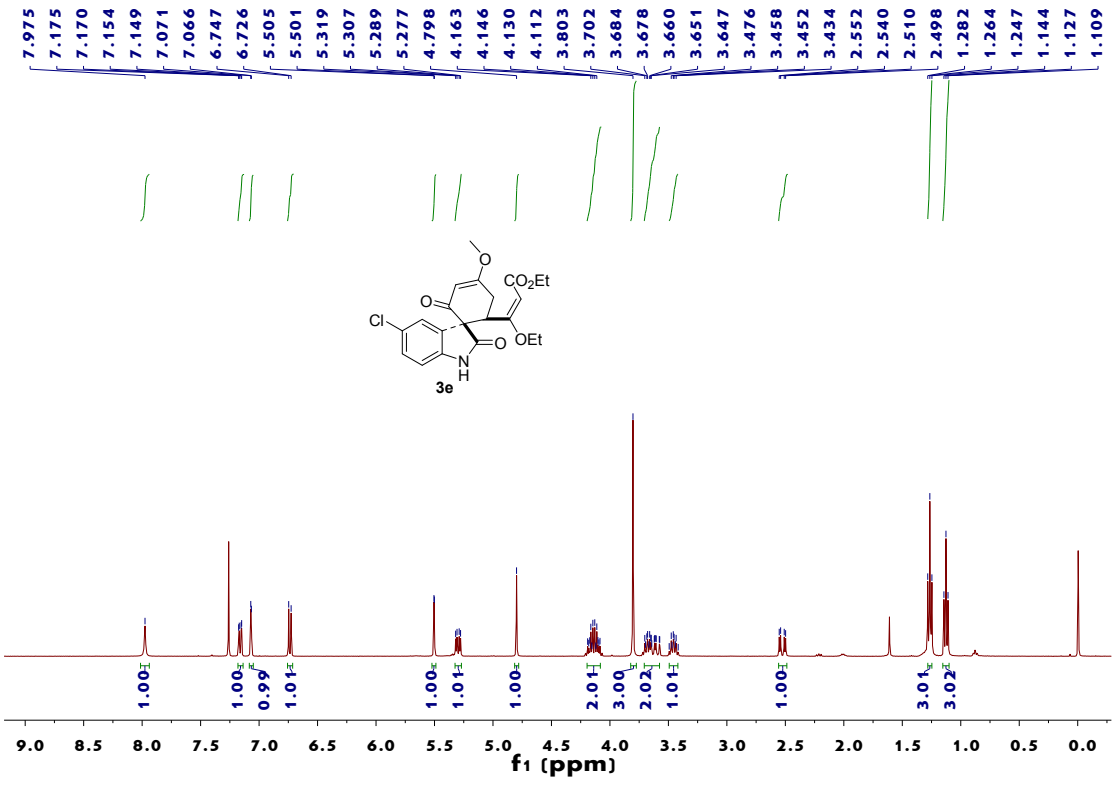
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OEt
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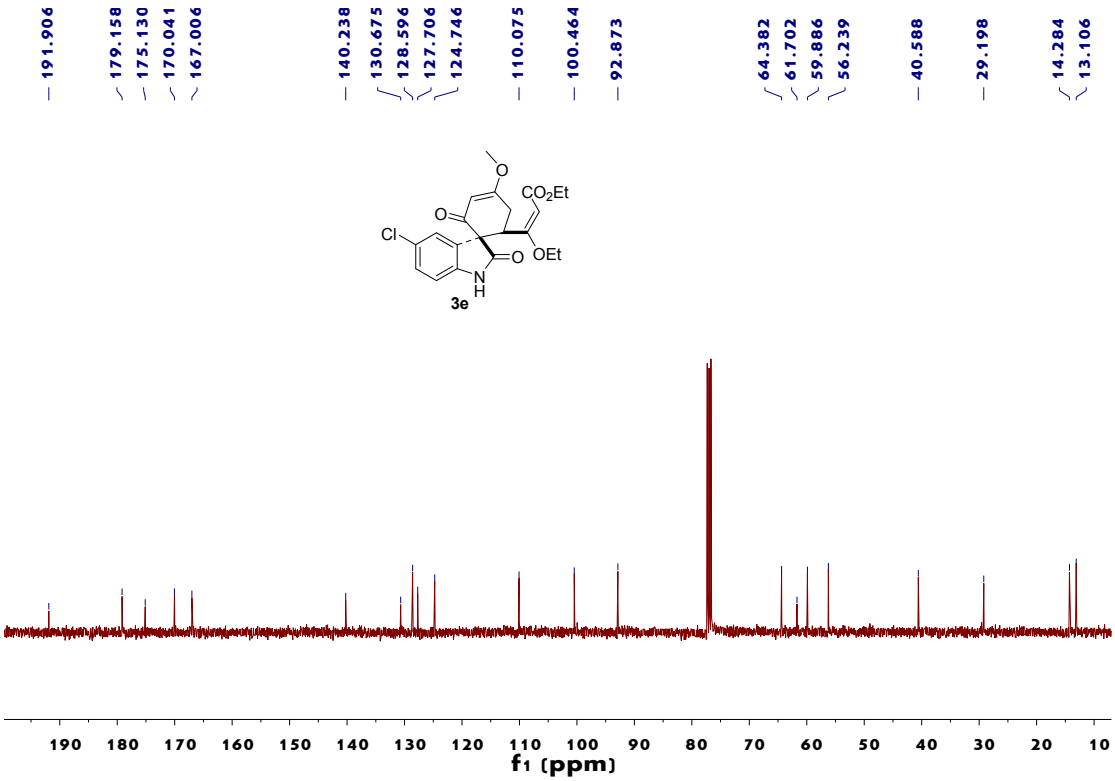
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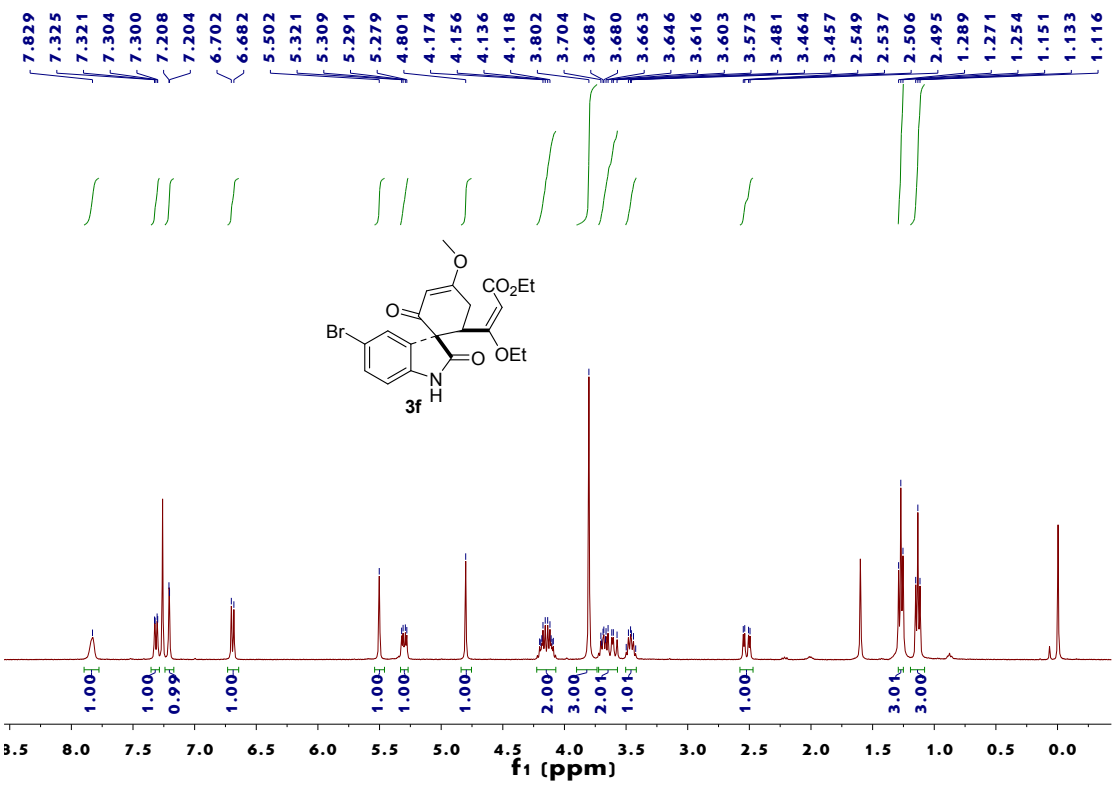
f1 (ppm)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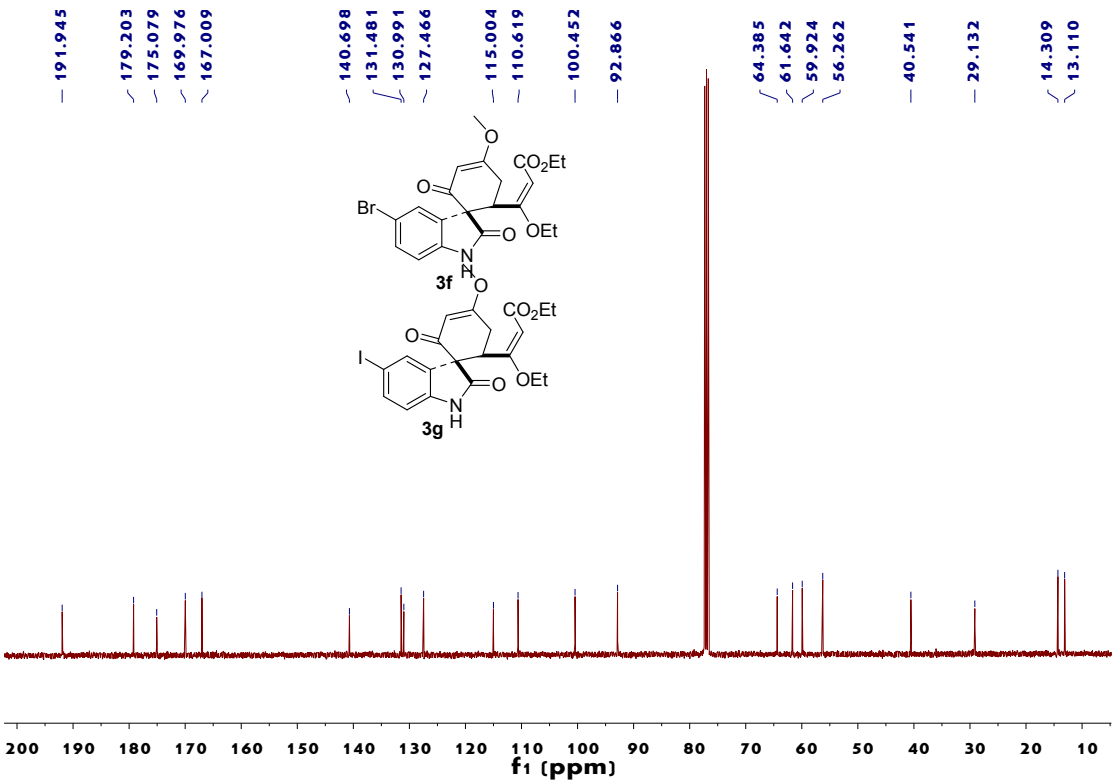
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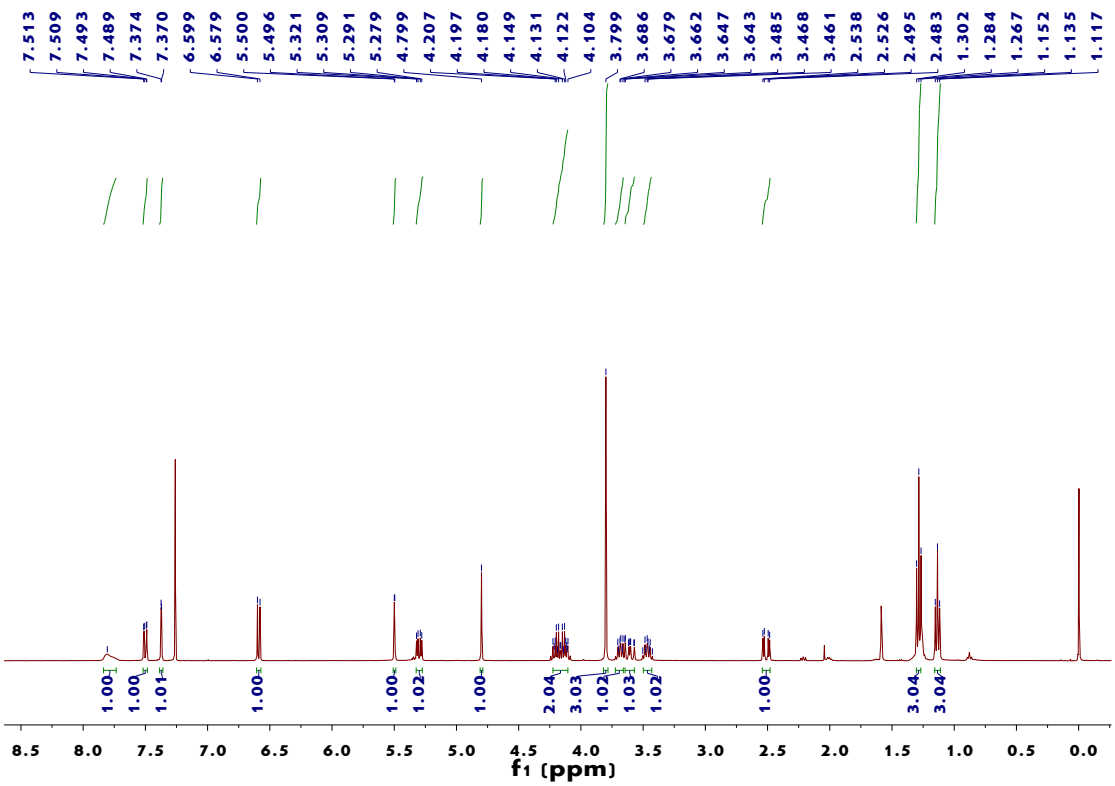
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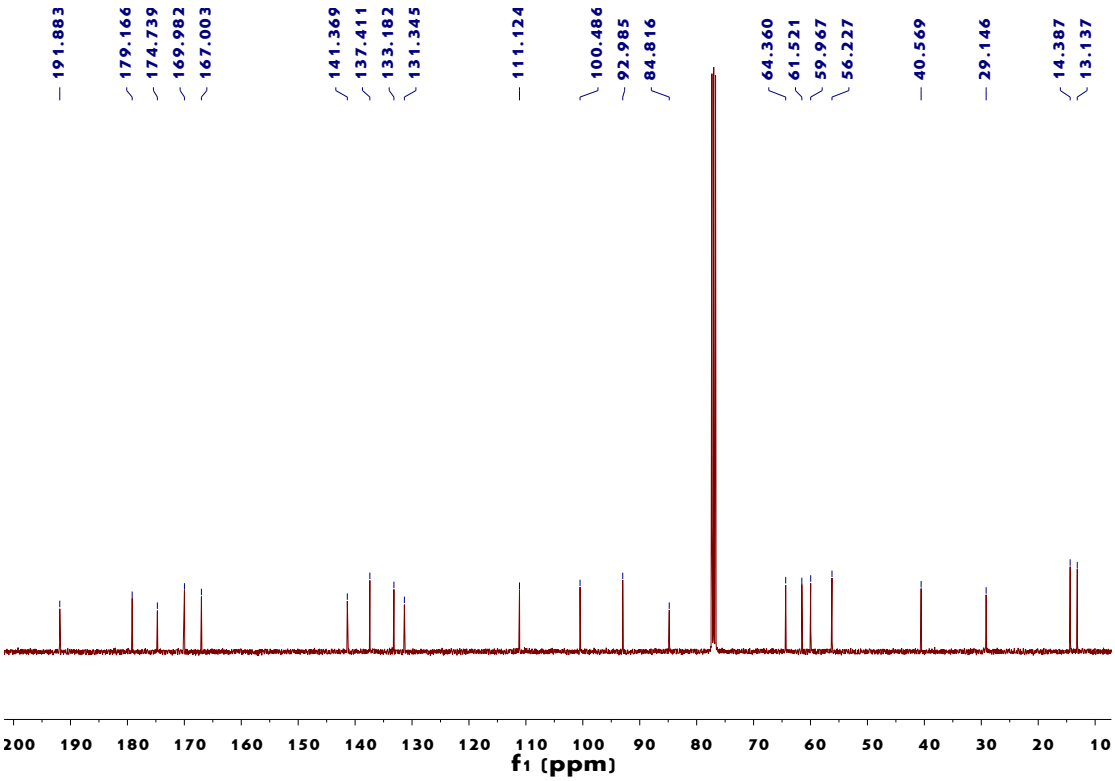
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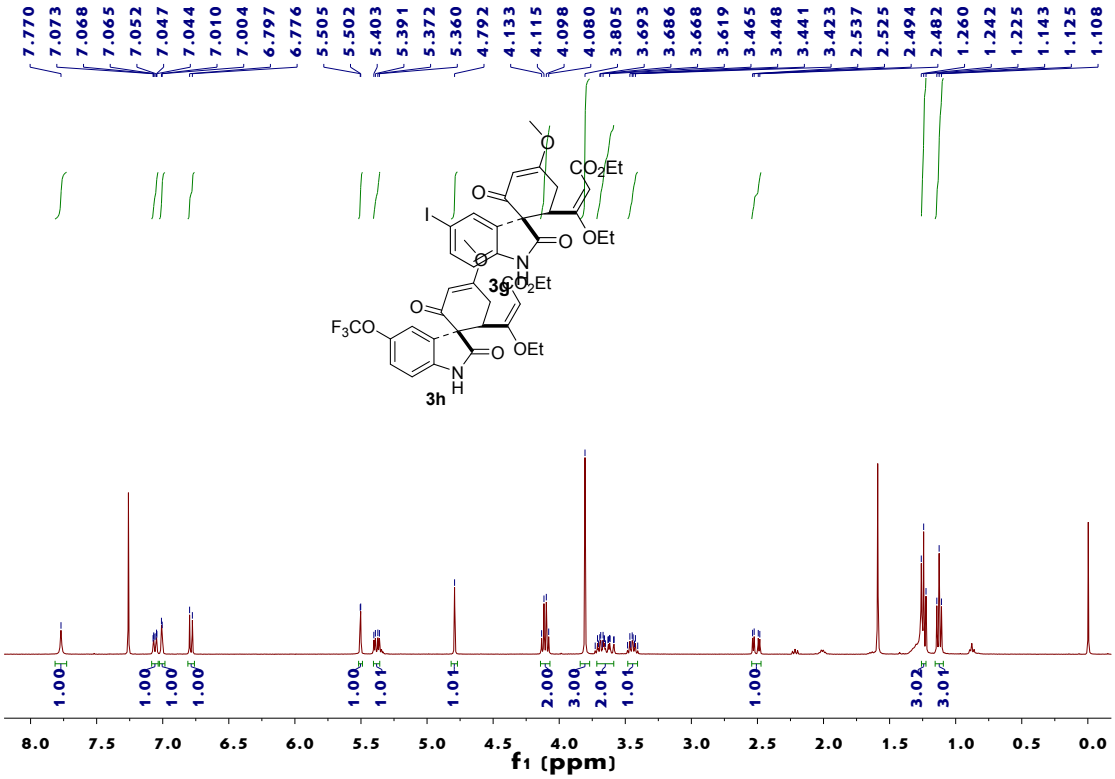
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OEt
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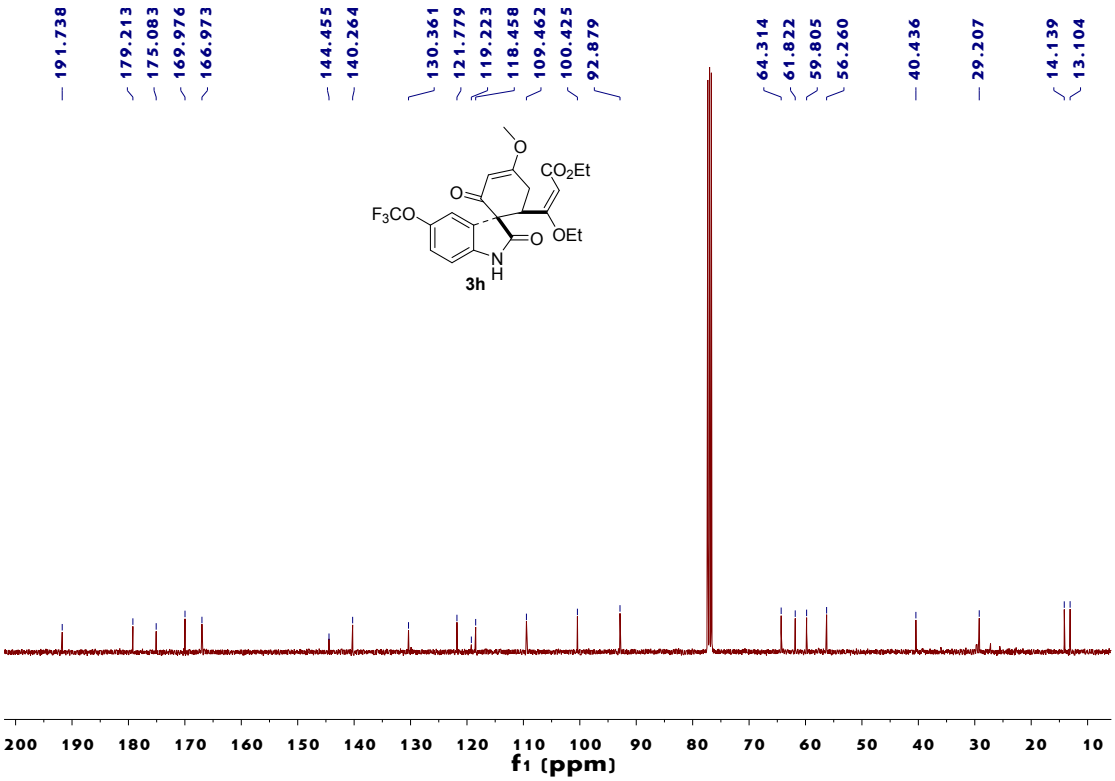
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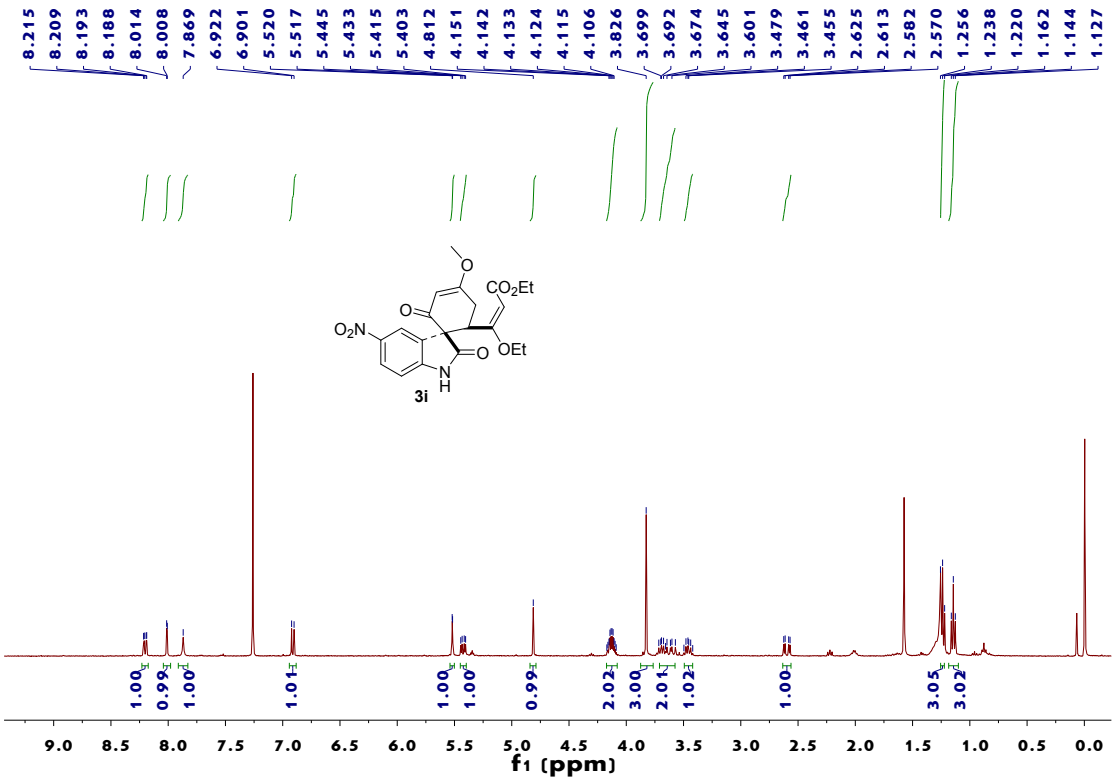
f1 (ppm)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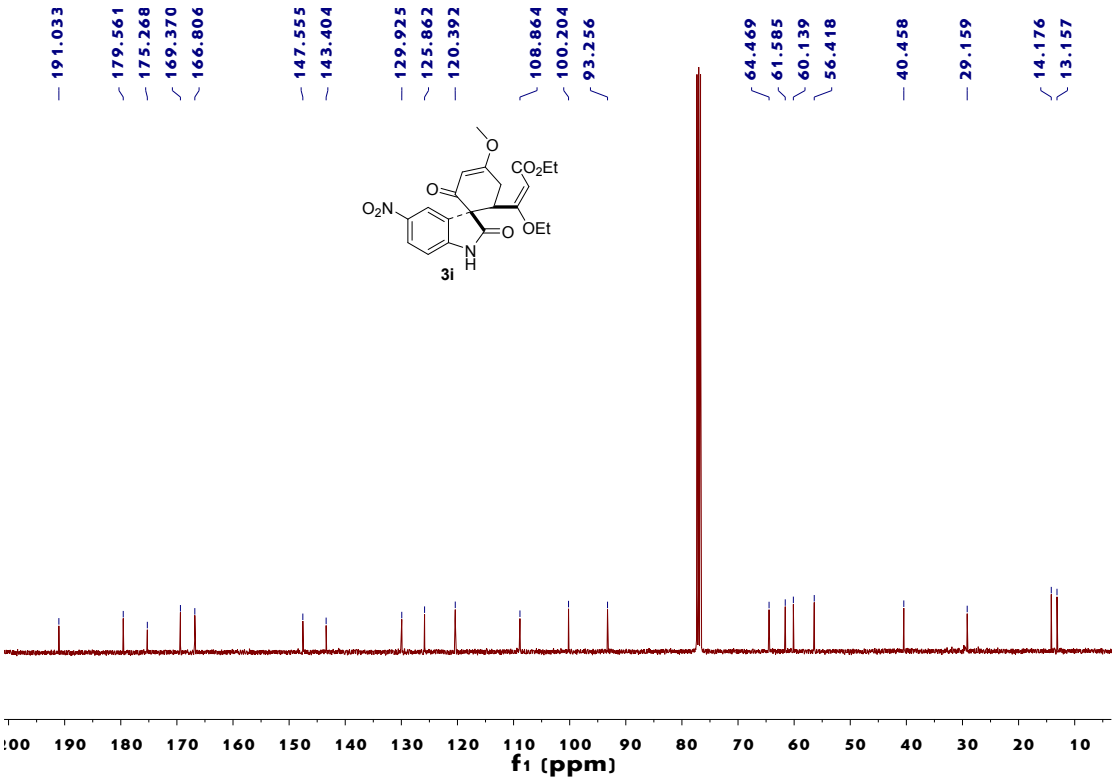
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129.925
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120.392
108.864
100.204
93.256
64.469
61.585
60.139
56.418
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14.176
13.157
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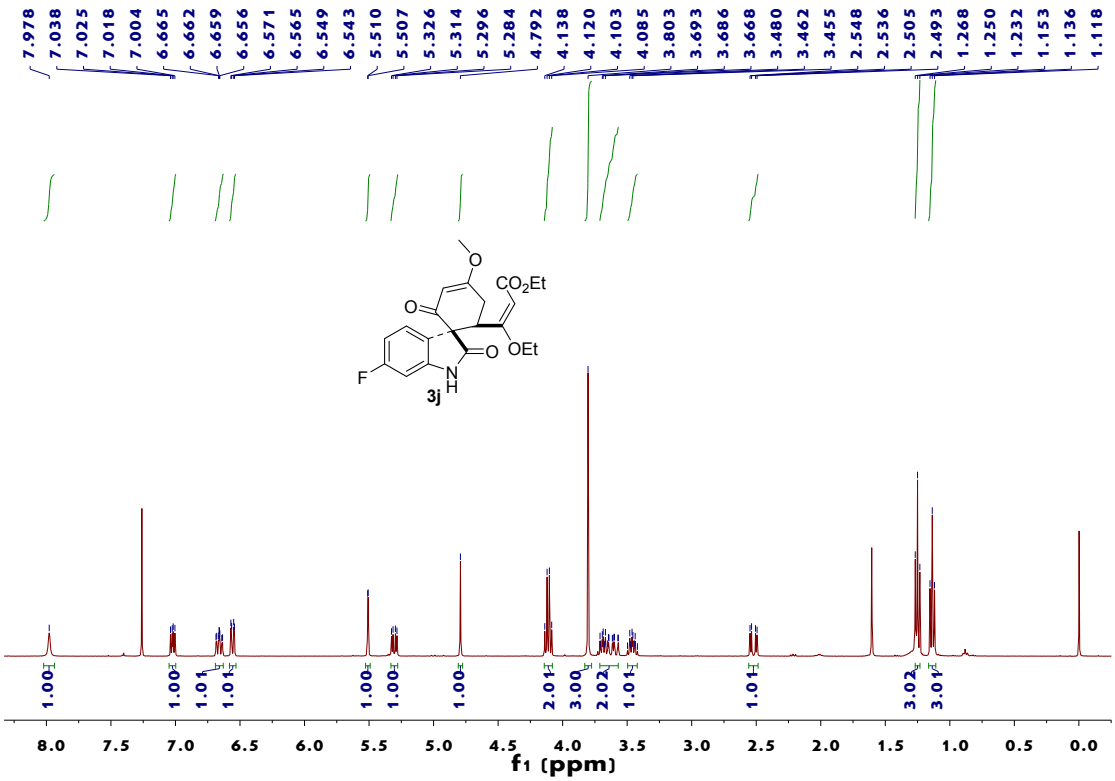
CO2Et
O
O2N
O
OEt
N
H
3i
f1 (ppm)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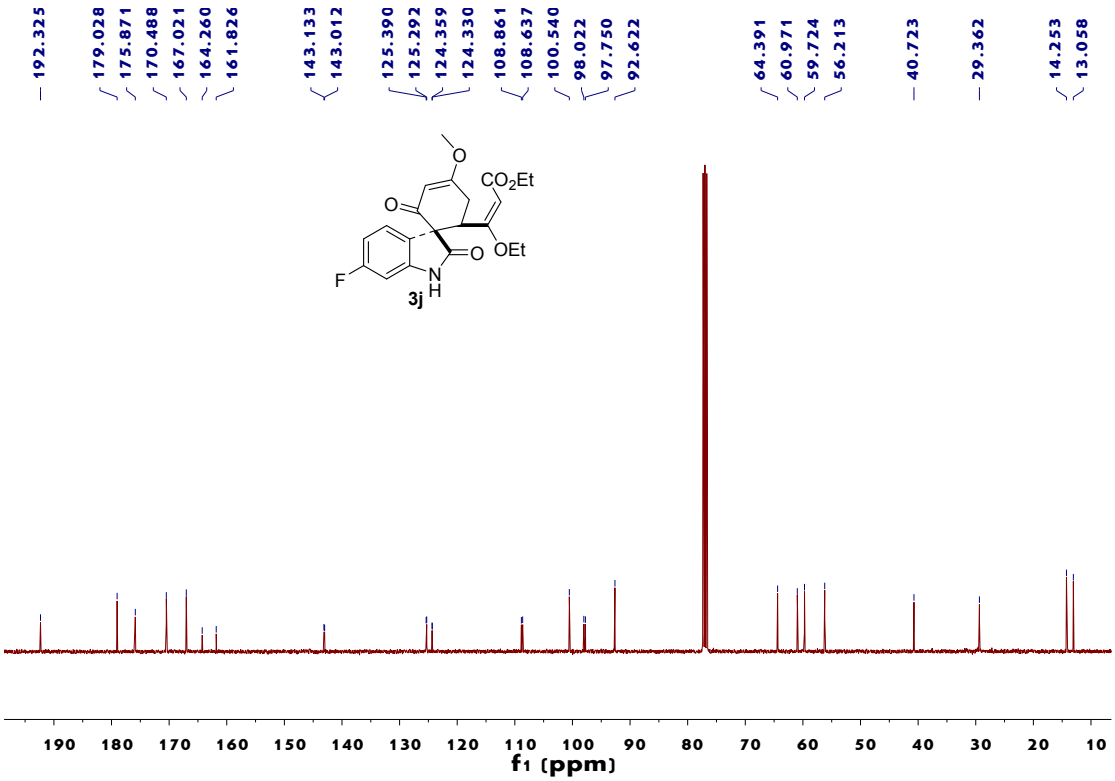
6.543
5.510
5.507
5.326
5.314
5.296
5.284
4.792
4.138
4.120
4.103
4.085
3.803
3.693
3.686
3.668
3.480
3.462
3.455
2.548
2.536
2.505
2.493
1.268
1.250
1.232
1.153
1.136
1.118
O
CO2Et
O
O
OEt
F
N
H
3j
1.00
1.00
1.01
1.01
1.00
1.00
1.00
2.01
3.00
2.02
1.01
1.01
3.02
3.01
f1 (ppm)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124.330
108.861
108.637
100.540
98.022
97.750
92.622
64.391
60.971
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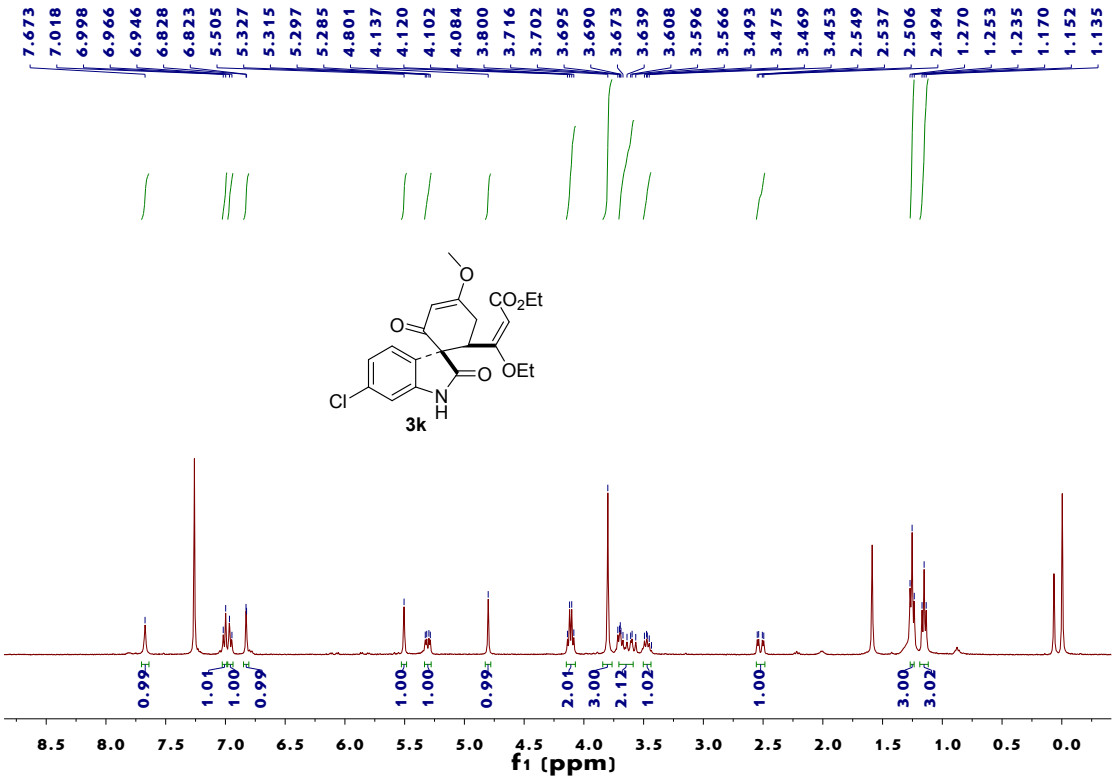
56.213
40.723
29.362
14.253
13.058
CO2Et
OEt
F
3j
f1 (ppm)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4.137
4.120
4.102
4.084
3.800
3.716
3.702
3.695
3.690
3.673
3.639
3.608
3.596
3.566
3.493
3.475
3.469
3.453
2.549
2.537
2.506
2.494
1.270
1.253
1.235
1.170
1.152
1.135
CO2Et
OEt
Cl
3k
0.99
1.01
1.00
0.99
1.00
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0.99
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3.00
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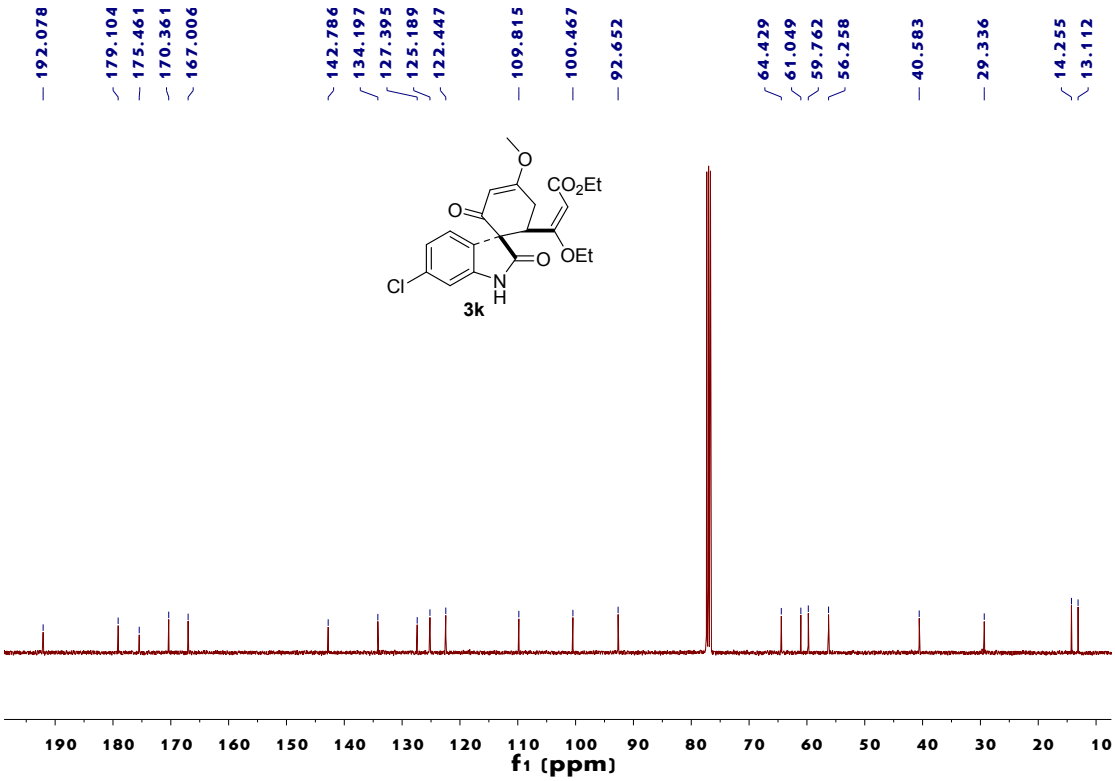
1.00
3.00
3.02
f1 (ppm)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127.395
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92.652
64.429
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56.258
40.583
29.336
14.255
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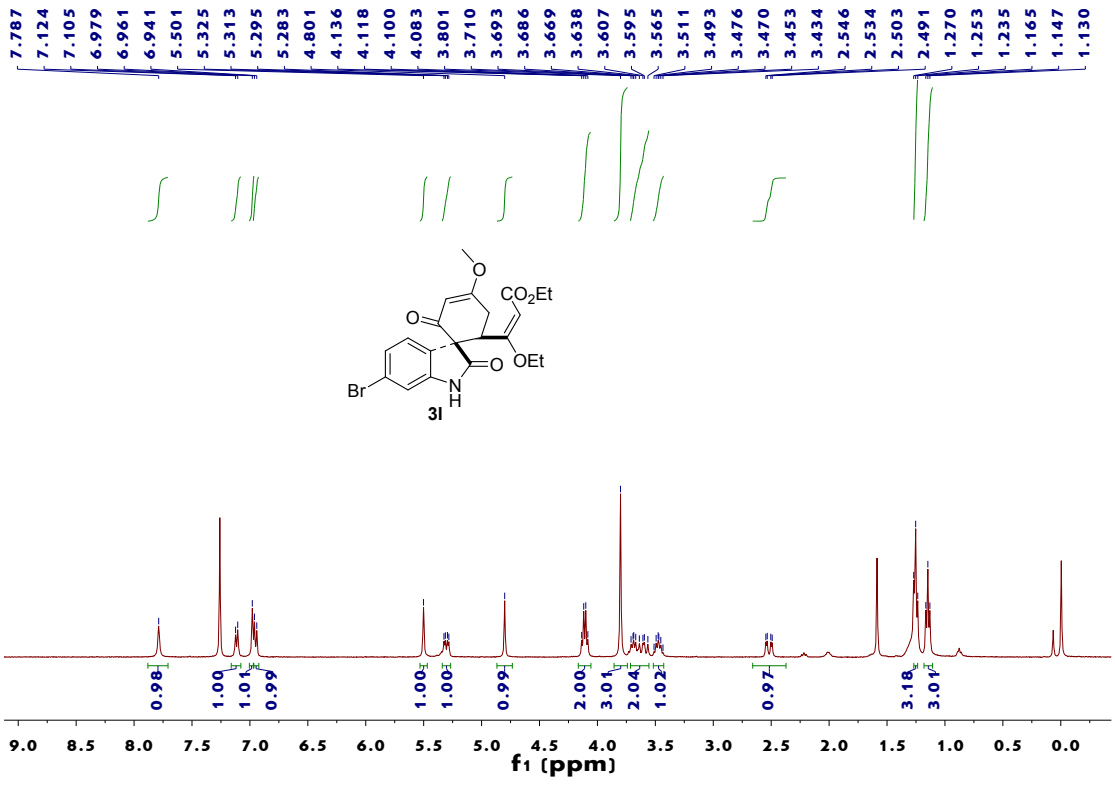
CO2Et
OEt
Cl
3k
f1 (ppm)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5.313
5.295
5.283
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4.118
4.100
4.083
3.801
3.710
3.693
3.686
3.669
3.638
3.607
3.595
3.565
3.511
3.493
3.476
3.470
3.453
3.434
2.546
2.534
2.503
2.491
1.270
1.253
1.235
1.165
1.147
1.130
CO2Et
OEt
Br
3l
0.98
1.00
1.01
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1.00
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0.99
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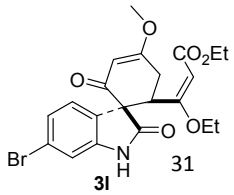
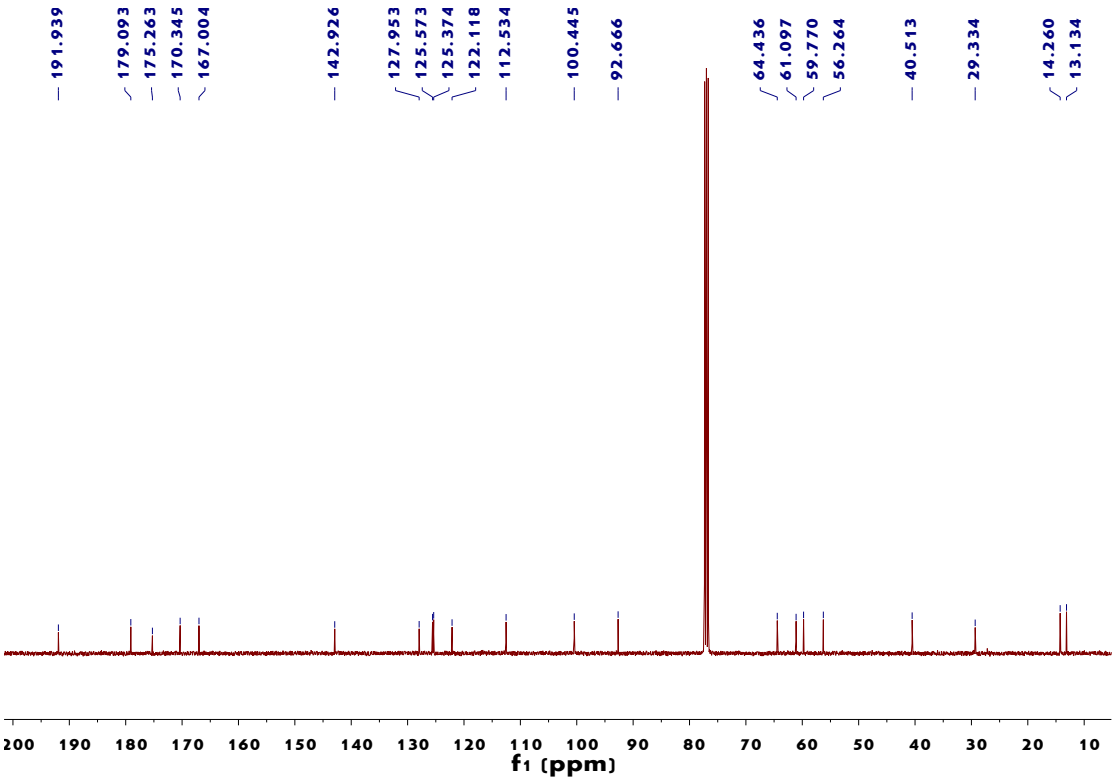
1.02
0.97
3.18
3.01
f1 (ppm)


CO2Et
OEt
Br
3l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59.770
56.264
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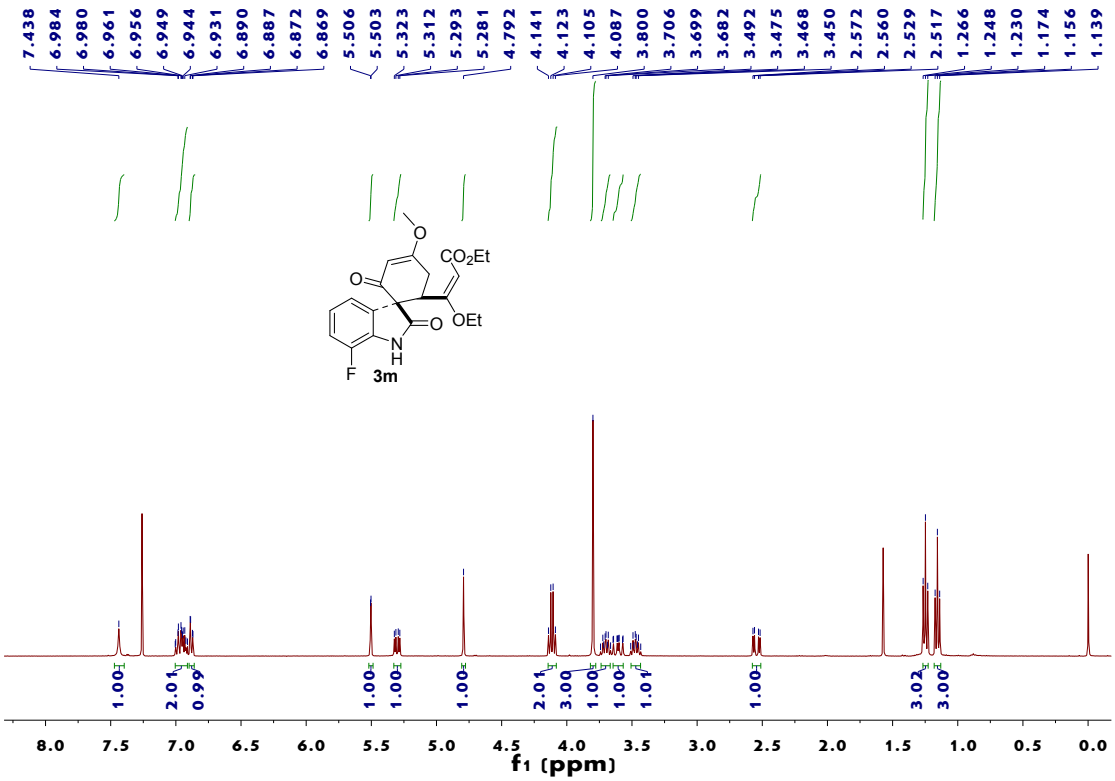
13.134
f1 (ppm)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6.980
6.961
6.956
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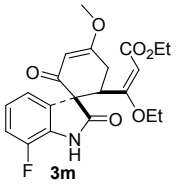
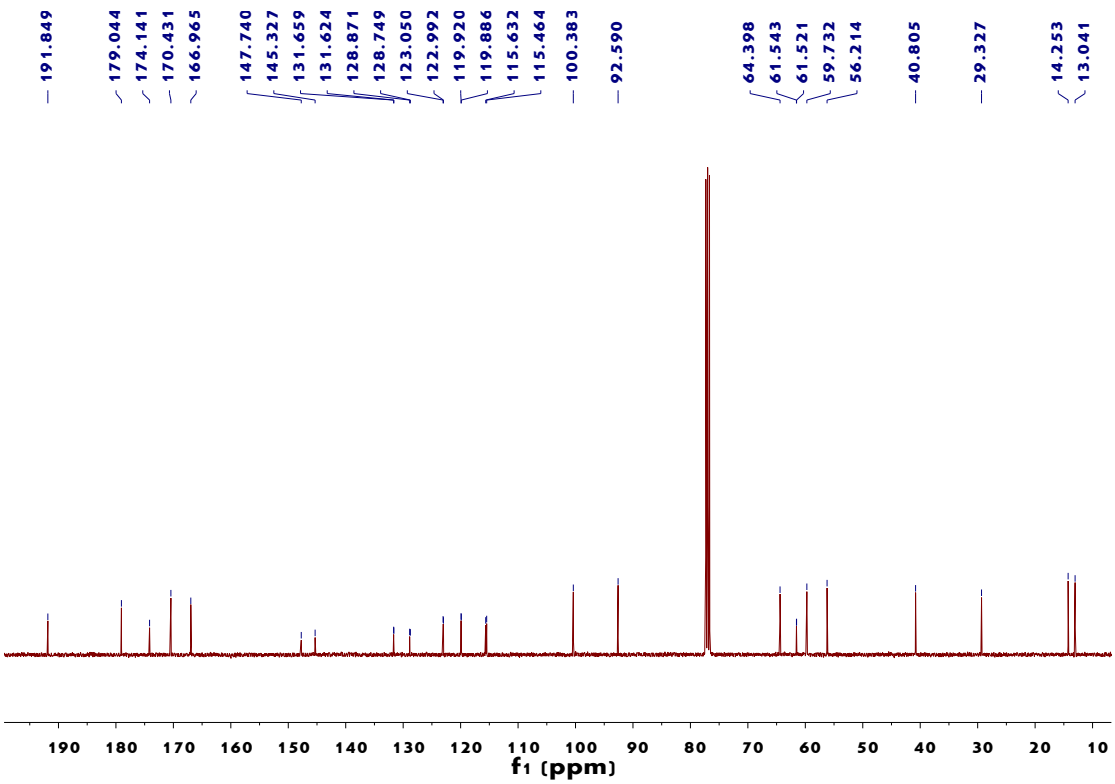
6.944
6.931
6.890
6.887
6.872
6.869
5.506
5.503
5.323
5.312
5.293
5.281
4.792
4.141
4.123
4.105
4.087
3.800
3.706
3.699
3.682
3.492
3.475
3.468
3.450
2.572
2.560
2.529
2.517
1.266
1.248
1.230
1.174
1.156
1.139
CO2Et
OEt
3m
1.00
2.01
0.99
1.00
1.00
1.00
2.01
3.00
1.00
1.00
1.01
1.00
3.02
3.00
f1 (ppm)


CO2Et
OEt
3m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119.920
119.886
115.632
115.464
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29.327
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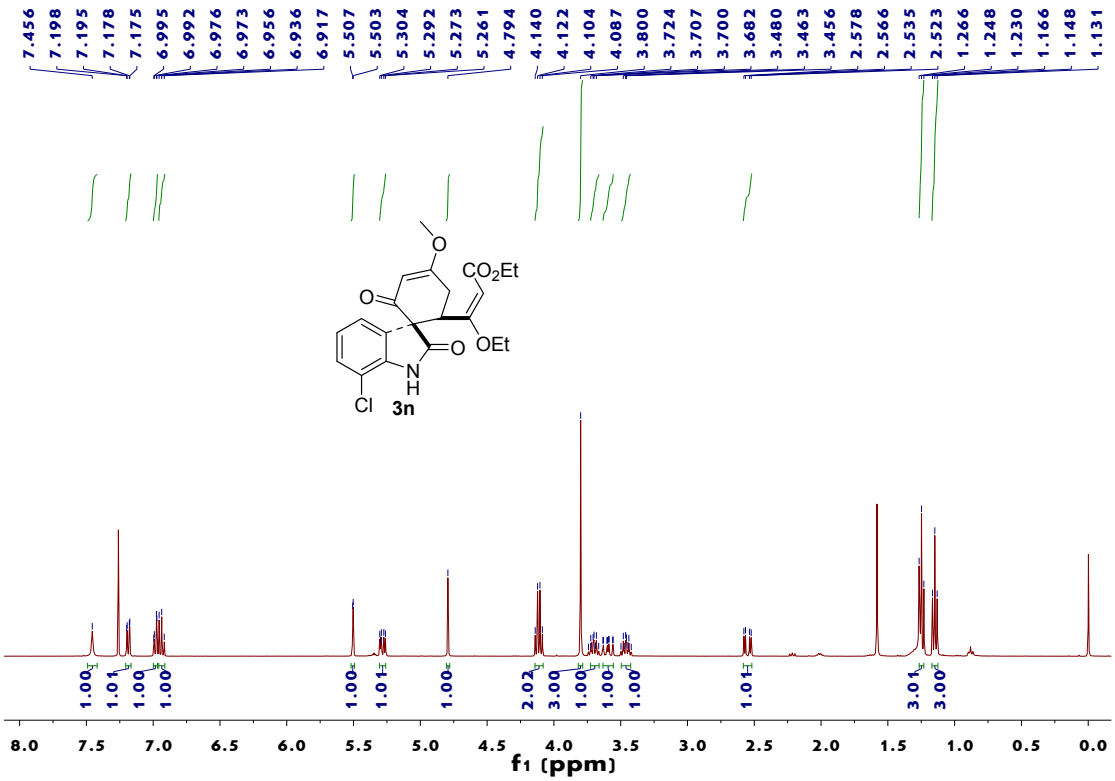
13.041
f1 (ppm)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6.995
6.992
6.976
6.973
6.956
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6.917
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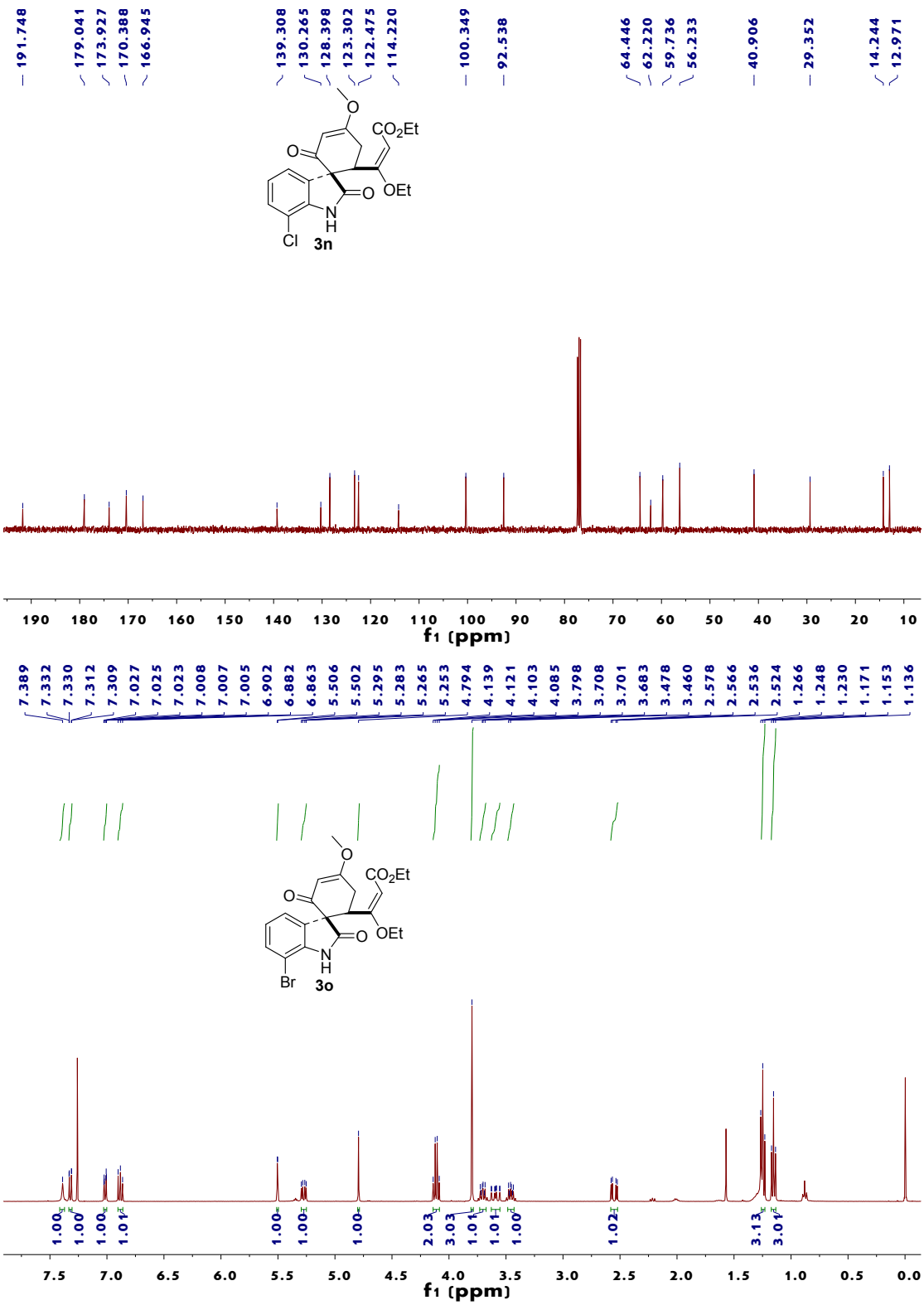
5.503
5.304
5.292
5.273
5.261
4.794
4.140
4.122
4.104
4.087
3.800
3.724
3.707
3.700
3.682
3.480
3.463
3.456
2.578
2.566
2.535
2.523
1.266
1.248
1.230
1.166
1.148
1.131
CO2Et
OEt
Cl
3n
1.00
1.01
1.00
1.00
1.00
1.01
1.00
2.02
3.00
1.00
1.00
1.00
1.01
3.01
3.00
f1 (ppm)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123.302
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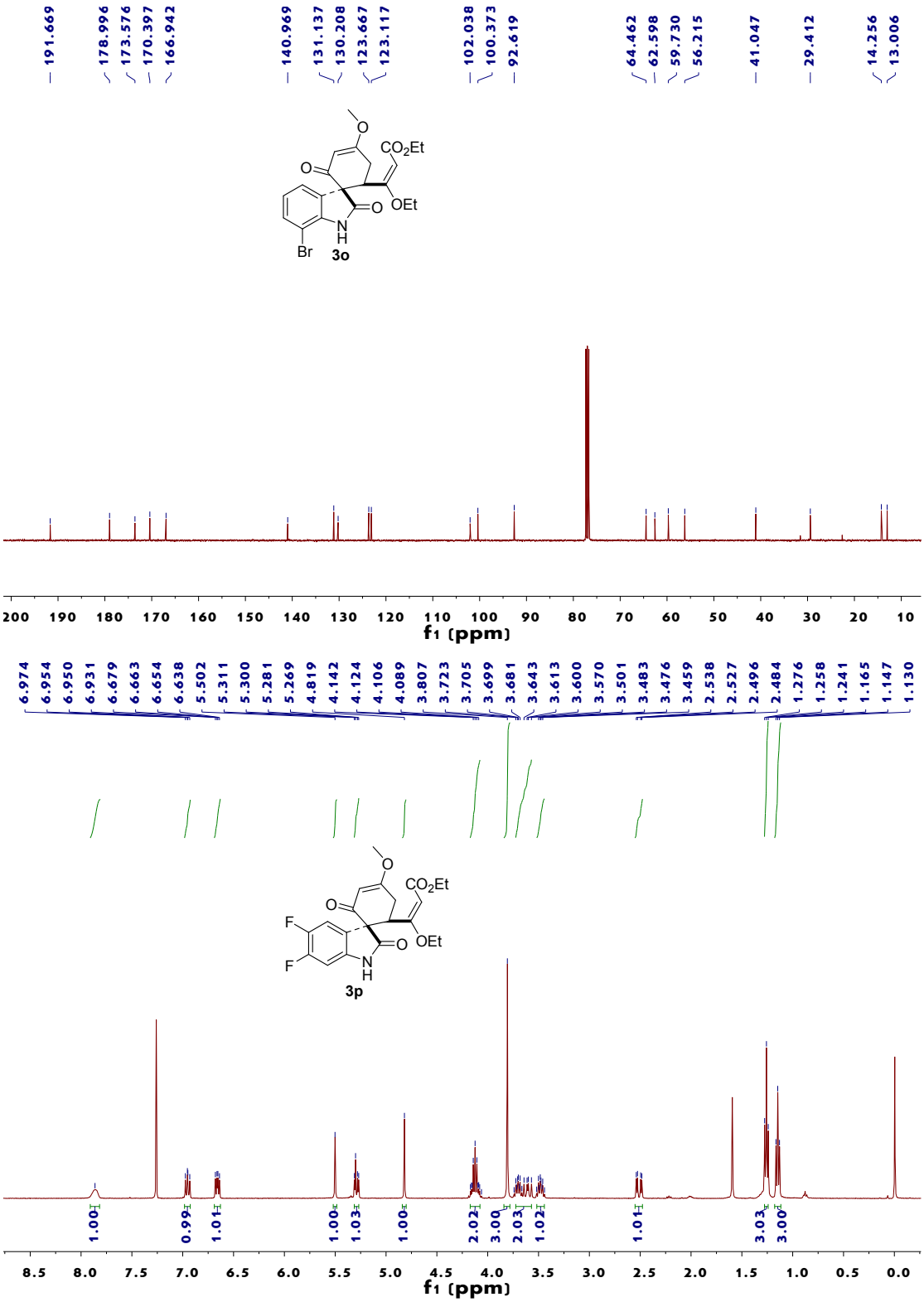
100.349
92.538
64.446
62.220
59.736
56.233
40.906
29.352
14.244
12.971
CO2Et
OEt
Cl
3n
f1 (ppm)
7.389
7.332
7.330
7.312
7.309
7.027
7.025
7.023
7.008
7.007
7.005
6.902
6.882
6.863
5.506
5.502
5.295
5.283
5.265
5.253
4.794
4.139
4.121
4.103
4.085
3.798
3.708
3.701
3.683
3.478
3.460
2.578
2.566
2.536
2.524
1.266
1.248
1.230
1.171
1.153
1.136
CO2Et
OEt
Br
3o
1.00
1.00
1.00
1.01
1.00
1.00
1.00
2.03
3.03
1.01
1.01
1.00
1.02
3.13
3.01
f1 (ppm)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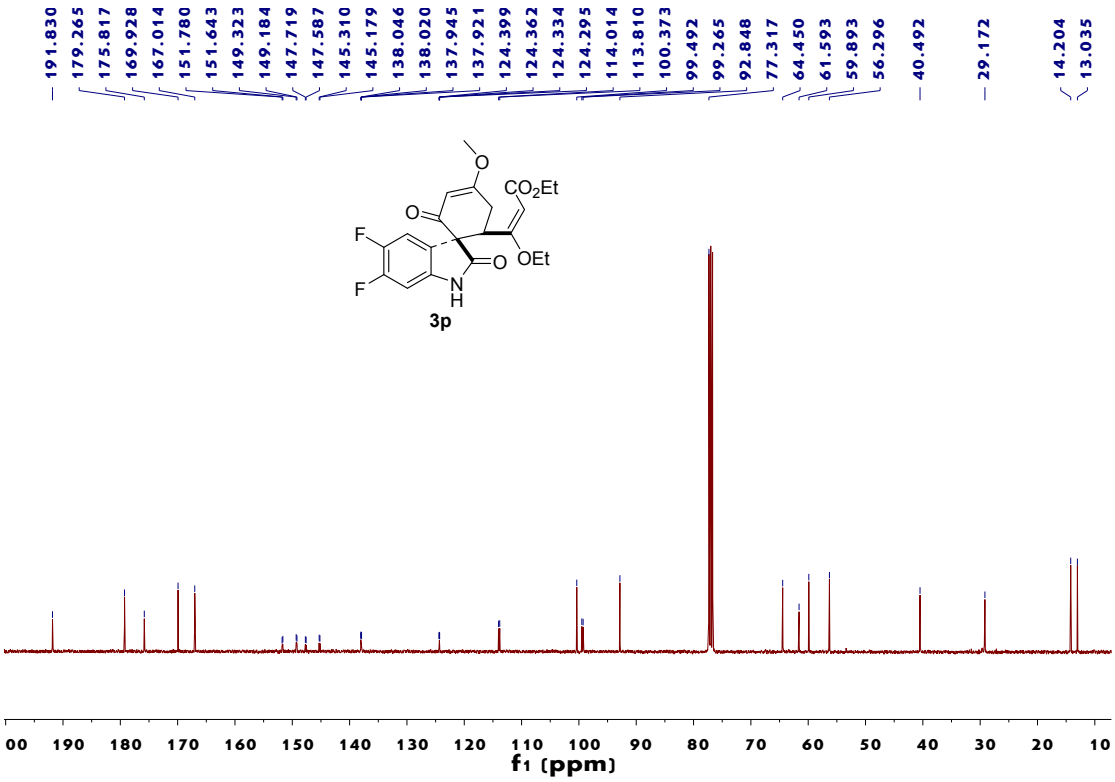
64.462
62.598
59.730
56.215
41.047
29.412
14.256
13.006
CO2Et
OEt
Br
3o
f1 (ppm)
6.974
6.954
6.950
6.931
6.679
6.663
6.654
6.638
5.502
5.311
5.300
5.281
5.269
4.819
4.142
4.124
4.106
4.089
3.807
3.723
3.705
3.699
3.681
3.643
3.613
3.600
3.570
3.501
3.483
3.476
3.459
2.538
2.527
2.496
2.484
1.276
1.258
1.241
1.165
1.147
1.130
CO2Et
OEt
F
F
3p
1.00
0.99
1.01
1.00
1.03
1.00
2.02
3.00
2.03
1.02
1.01
3.03
3.00
f1 (ppm)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124.334
124.295
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99.492
99.265
92.848
77.317
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61.593
59.893
56.296
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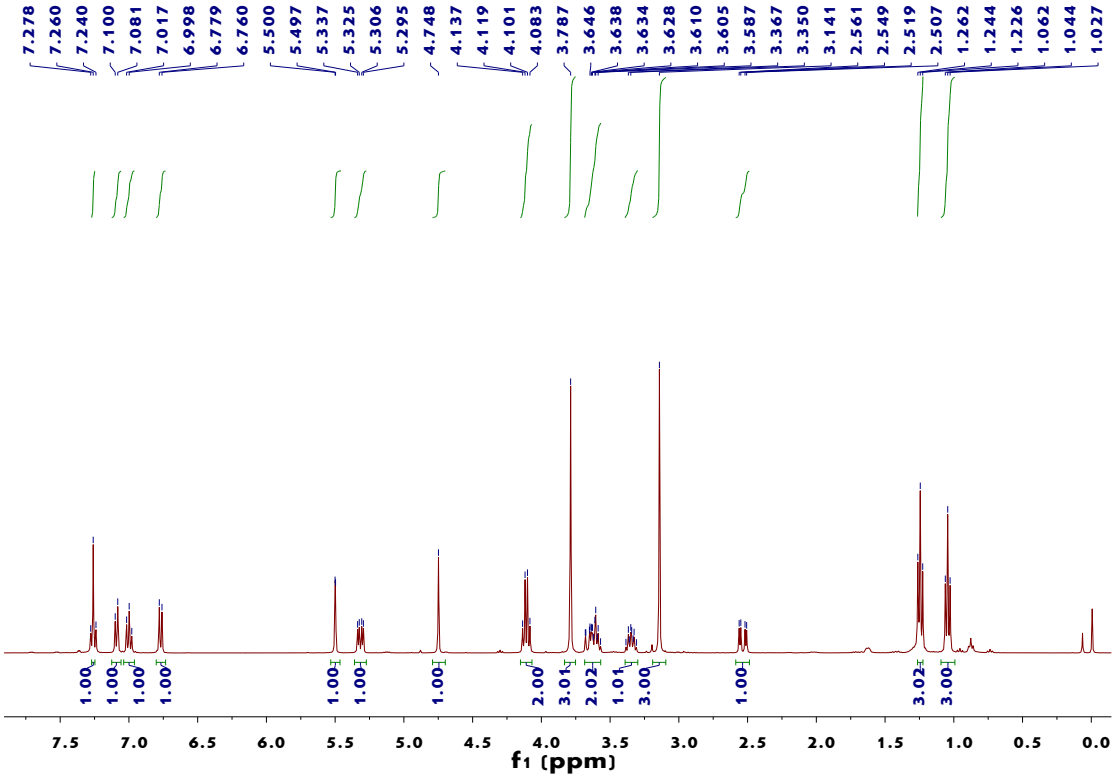
CO2Et
O
F
F
O
OEt
N
H
3p
f1 (ppm)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5.306
5.295
4.748
4.137
4.119
4.101
4.083
3.787
3.646
3.638
3.634
3.628
3.610
3.605
3.587
3.367
3.350
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2.549
2.519
2.507
1.262
1.244
1.226
1.062
1.044
1.027
1.00
1.00
1.00
1.00
1.00
1.00
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2.00
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2.02
1.01
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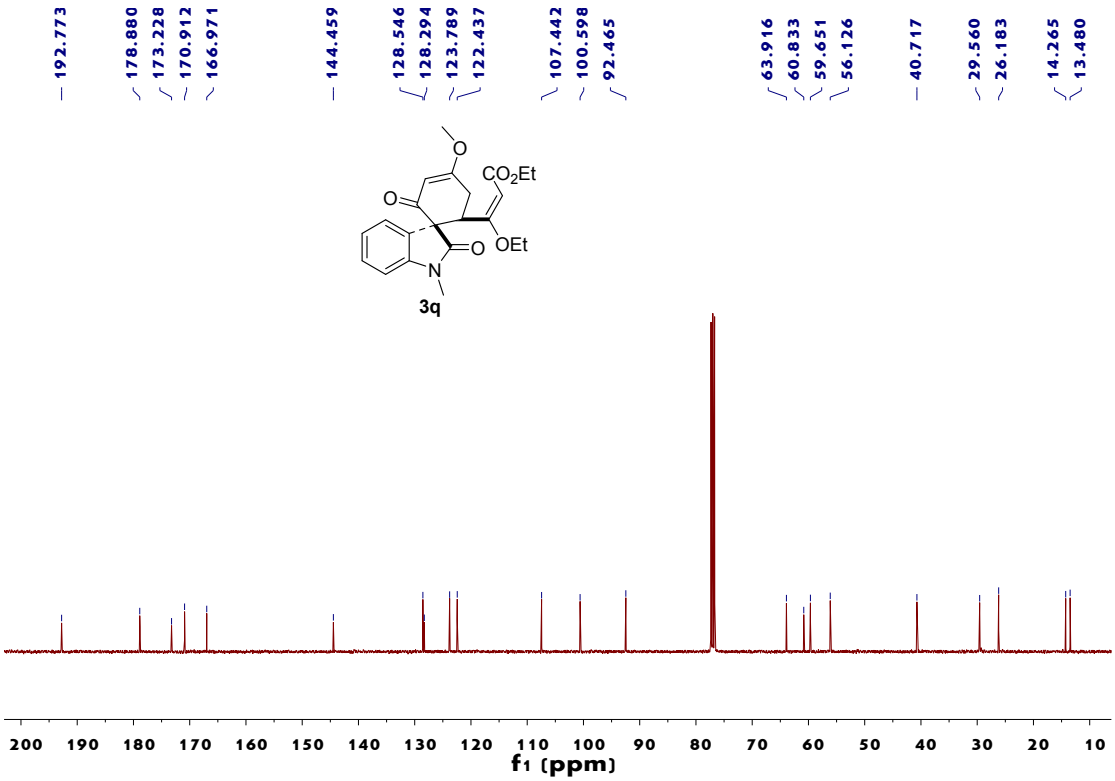
1.00
3.02
3.00
f1 (ppm)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92.465
63.916
60.833
59.651
56.126
40.717
29.560
26.183
14.265
13.480
O
CO2Et
O
O
OEt
N
3q
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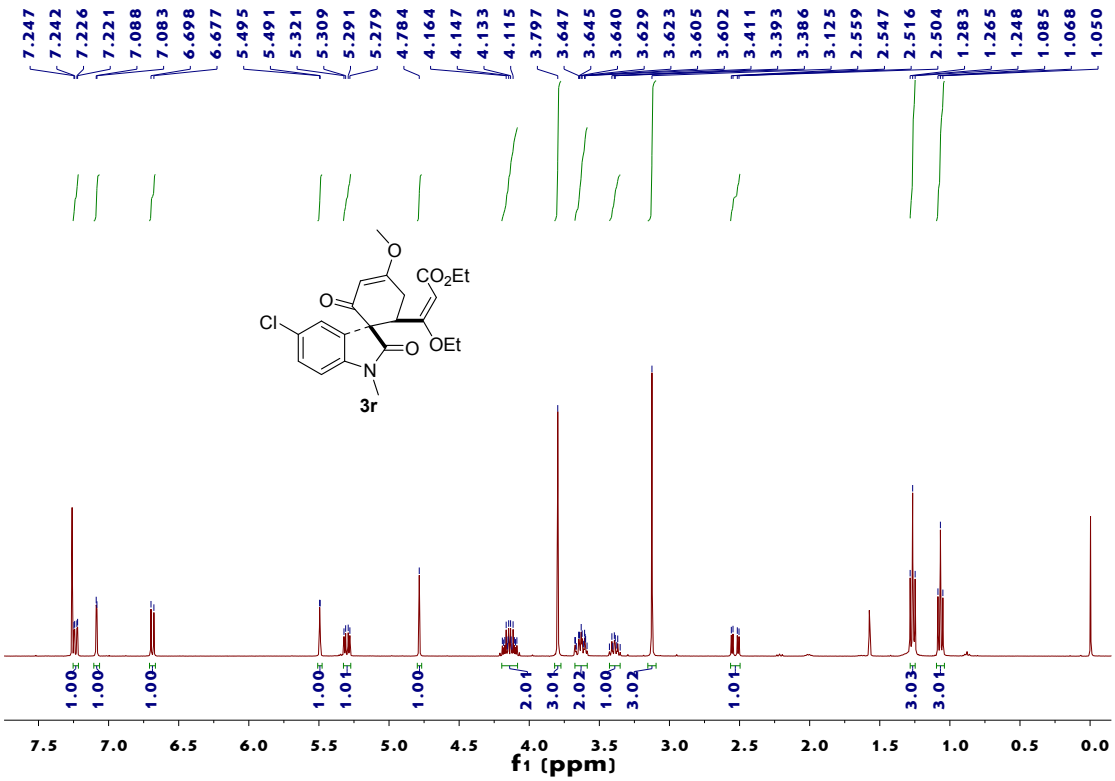
f1 (ppm)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3.645
3.640
3.629
3.623
3.605
3.602
3.411
3.393
3.386
3.125
2.559
2.547
2.516
2.504
1.283
1.265
1.248
1.085
1.068
1.050
O
CO2Et
O
Cl
O
OEt
N
3r
1.00
1.00
1.00
1.00
1.01
1.00
2.01
3.01
2.02
1.00
3.02
1.01
3.03
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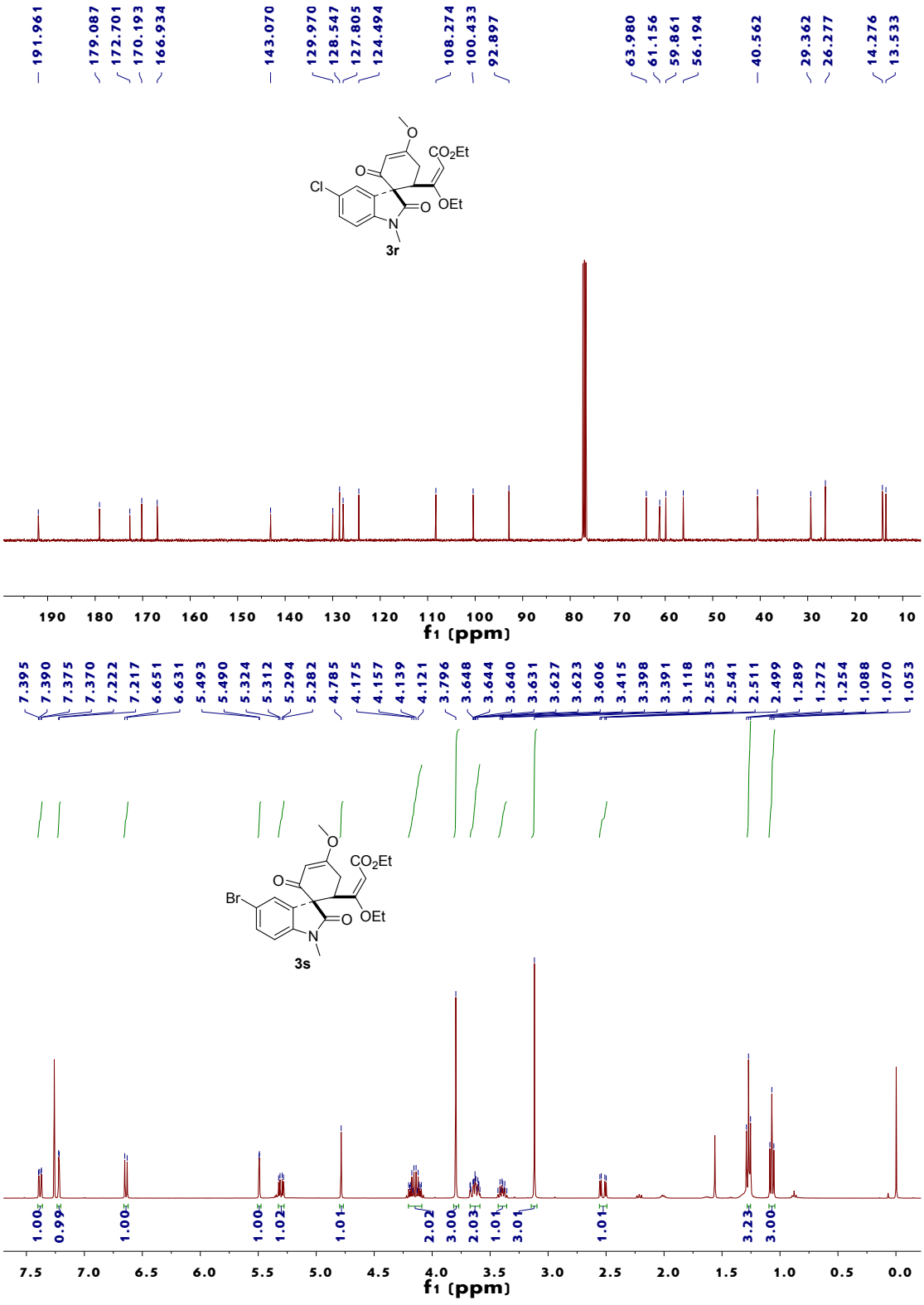
f1 (ppm)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40.562
29.362
26.277
14.276
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O
CO2Et
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Cl
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OEt
N
3r
f1 (ppm)
7.395
7.390
7.375
7.370
7.222
7.217
6.651
6.631
5.493
5.490
5.324
5.312
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5.282
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4.139
4.121
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3.644
3.640
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3.627
3.623
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3.415
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3.391
3.118
2.553
2.541
2.511
2.499
1.289
1.272
1.254
1.088
1.070
1.053
O
CO2Et
O
Br
O
OEt
N
3s
1.00
0.99
1.00
1.00
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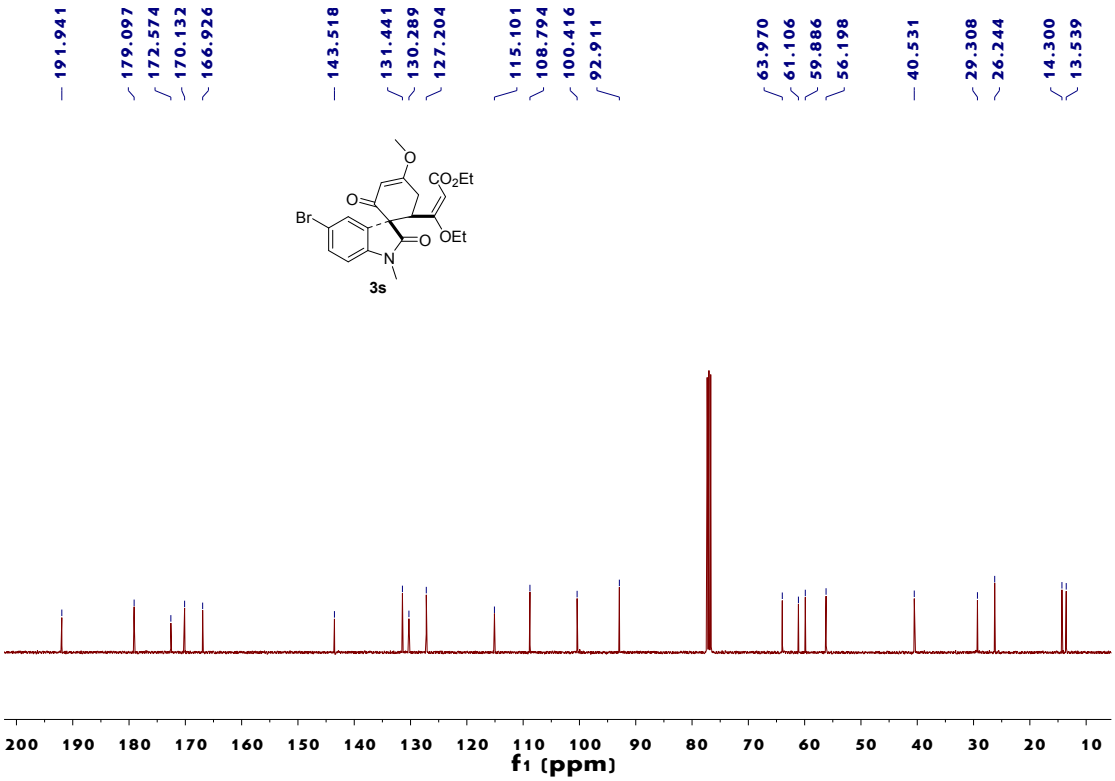
2.02
3.00
2.03
1.01
3.01
1.01
3.23
3.00
f1 (ppm)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63.970
61.106
59.886
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26.244
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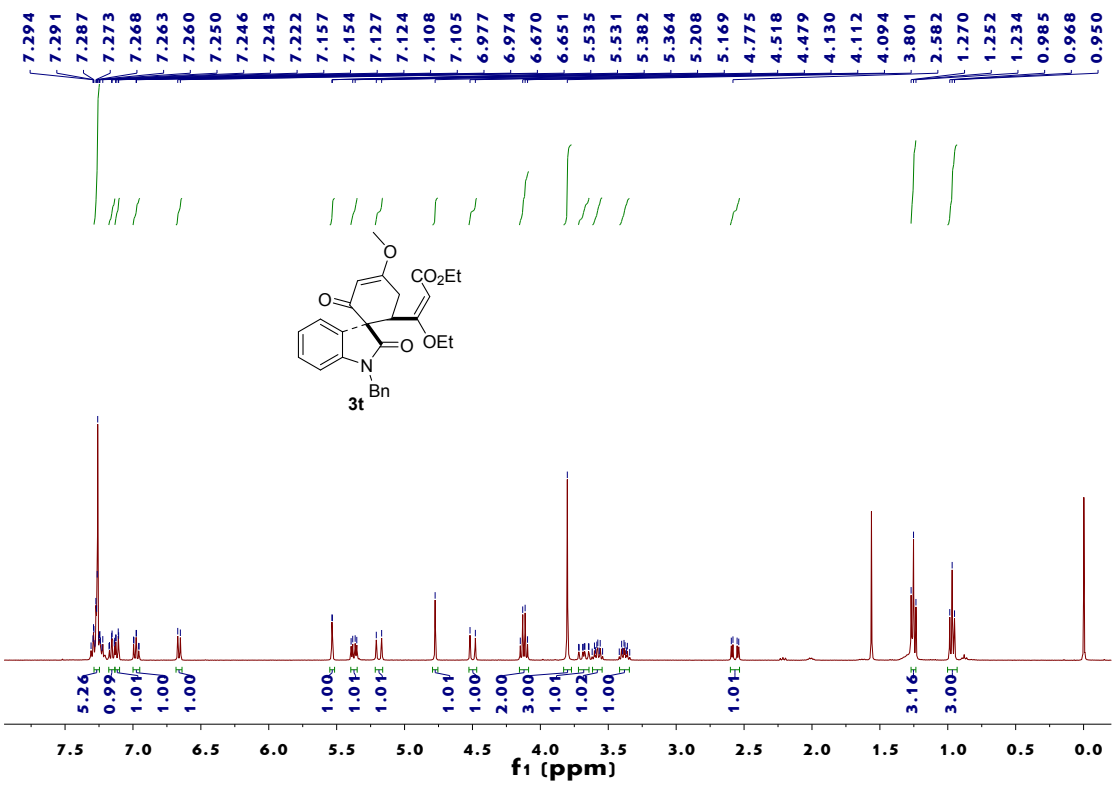
13.539
CO2Et
O
Br
OEt
N
3s
f1 (ppm)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7.243
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7.127
7.124
7.108
7.105
6.977
6.974
6.670
6.651
5.535
5.531
5.382
5.364
5.208
5.169
4.775
4.518
4.479
4.130
4.112
4.094
3.801
2.582
1.270
1.252
1.234
0.985
0.968
0.950
CO2Et
O
OEt
N
Bn
3t
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1.00
1.00
1.00
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2.00
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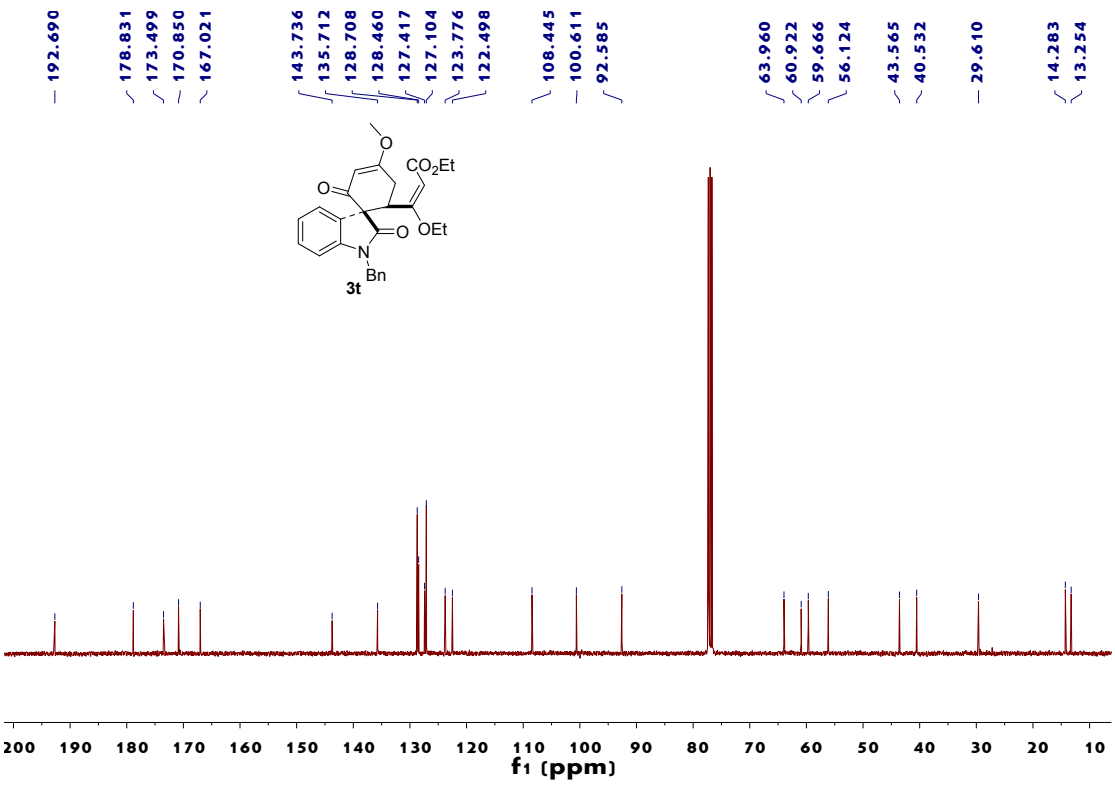
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128.708
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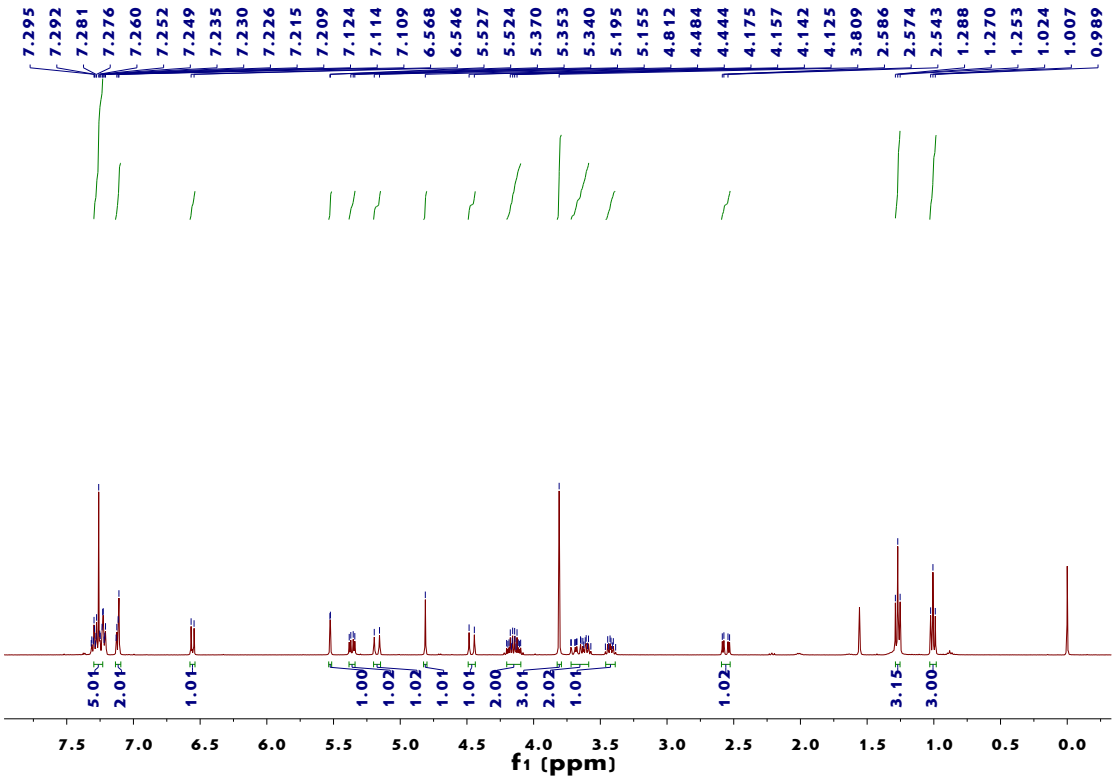
122.498
108.445
100.611
92.585
63.960
60.922
59.666
56.124
43.565
40.532
29.610
14.283
13.254
O
CO2Et
O
O
OEt
N
Bn
3t
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.249
7.235
7.230
7.226
7.215
7.209
7.124
7.114
7.109
6.568
6.546
5.527
5.524
5.370
5.353
5.340
5.195
5.155
4.812
4.484
4.444
4.175
4.157
4.142
4.125
3.809
2.586
2.574
2.543
1.288
1.270
1.253
1.024
1.007
0.989
5.01
2.01
1.01
1.00
1.02
1.02
1.01
1.01
2.00
3.01
2.02
1.01
1.02
3.15
3.00
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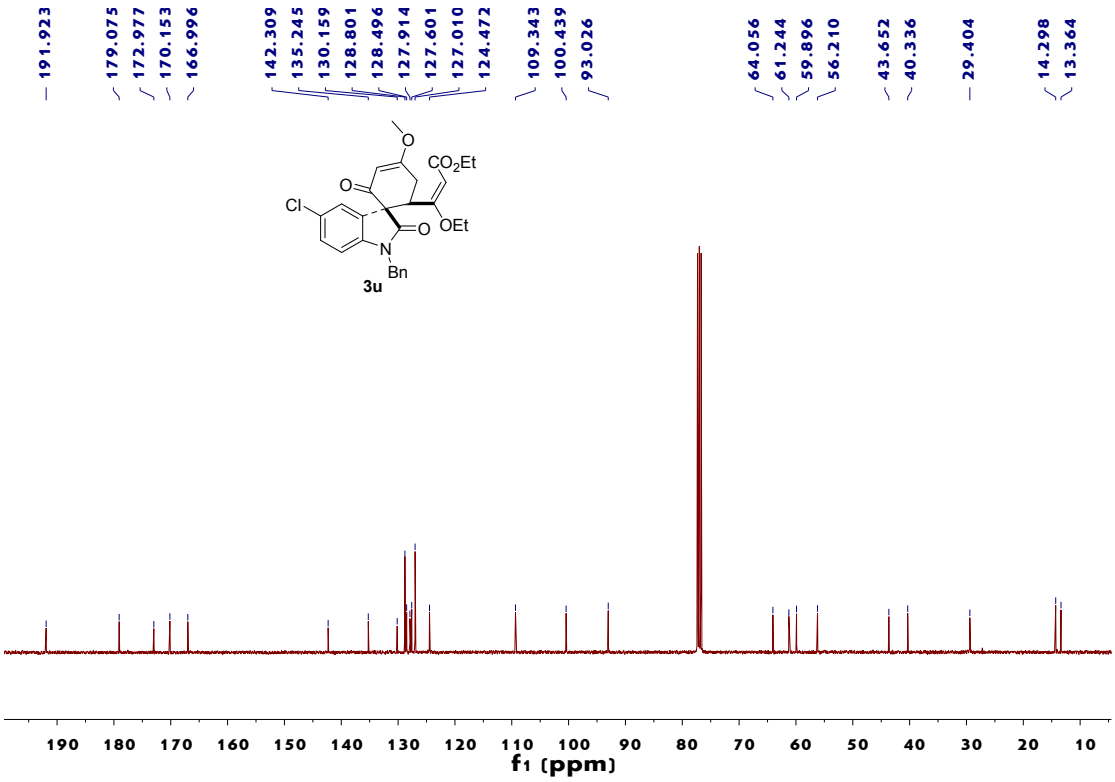
f1 (ppm)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170.153
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135.245
130.159
128.801
128.496
127.914
127.601
127.010
124.472
109.343
100.439
93.026
64.056
61.244
59.896
56.210
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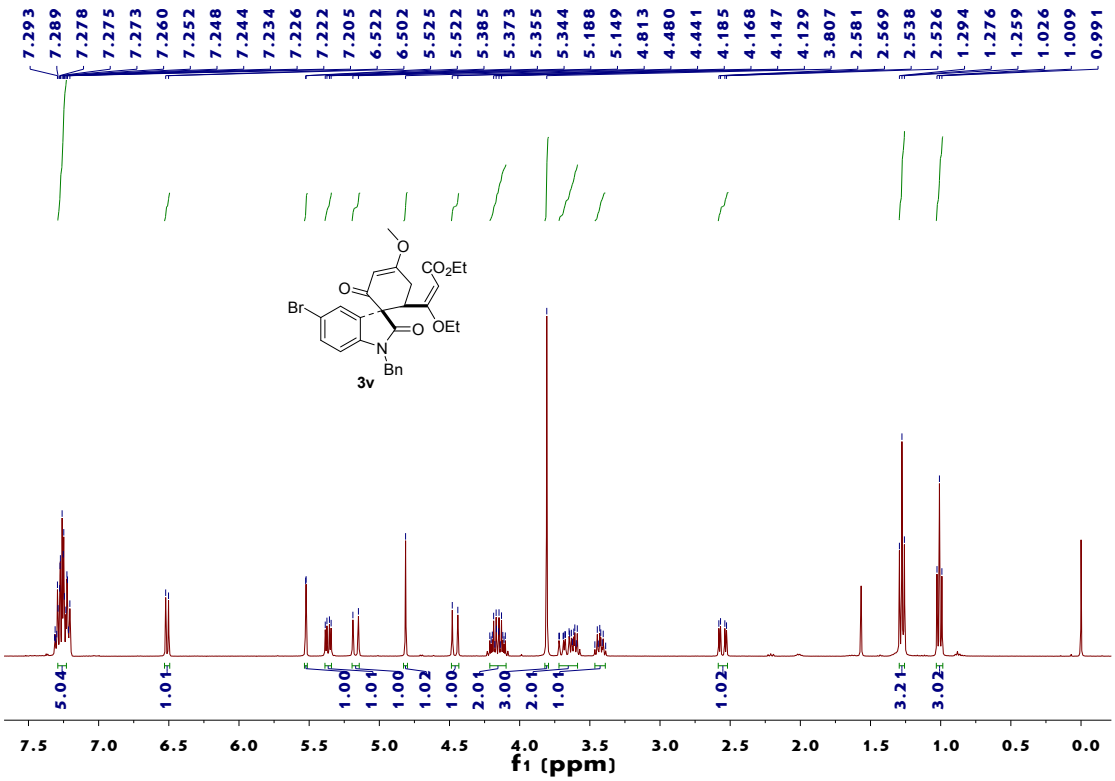
29.404
14.298
13.364
CO2Et
O
Cl
OEt
N
Bn
3u
f1 (ppm)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7.248
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7.222
7.205
6.522
6.502
5.525
5.522
5.385
5.373
5.355
5.344
5.188
5.149
4.813
4.480
4.441
4.185
4.168
4.147
4.129
3.807
2.581
2.569
2.538
2.526
1.294
1.276
1.259
1.026
1.009
0.991
CO2Et
O
Br
OEt
N
Bn
3v
5.04
1.01
1.00
1.01
1.00
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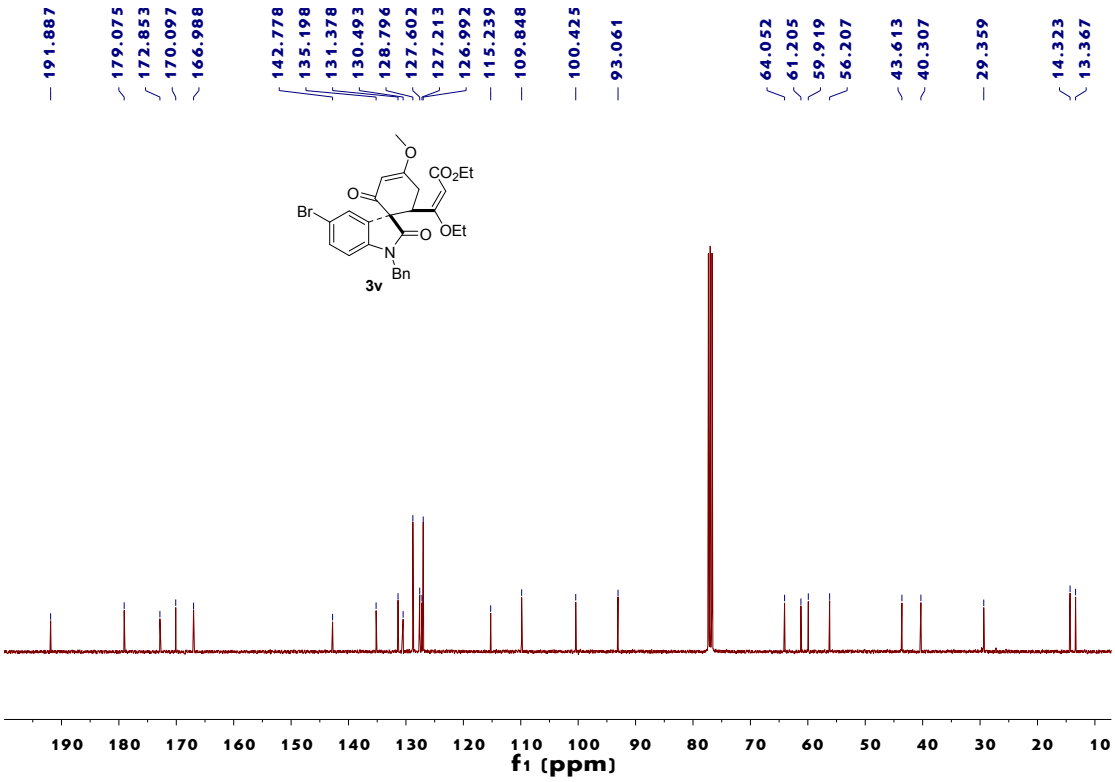
1.00
2.01
3.00
2.01
1.01
1.02
3.21
3.02
f1 (ppm)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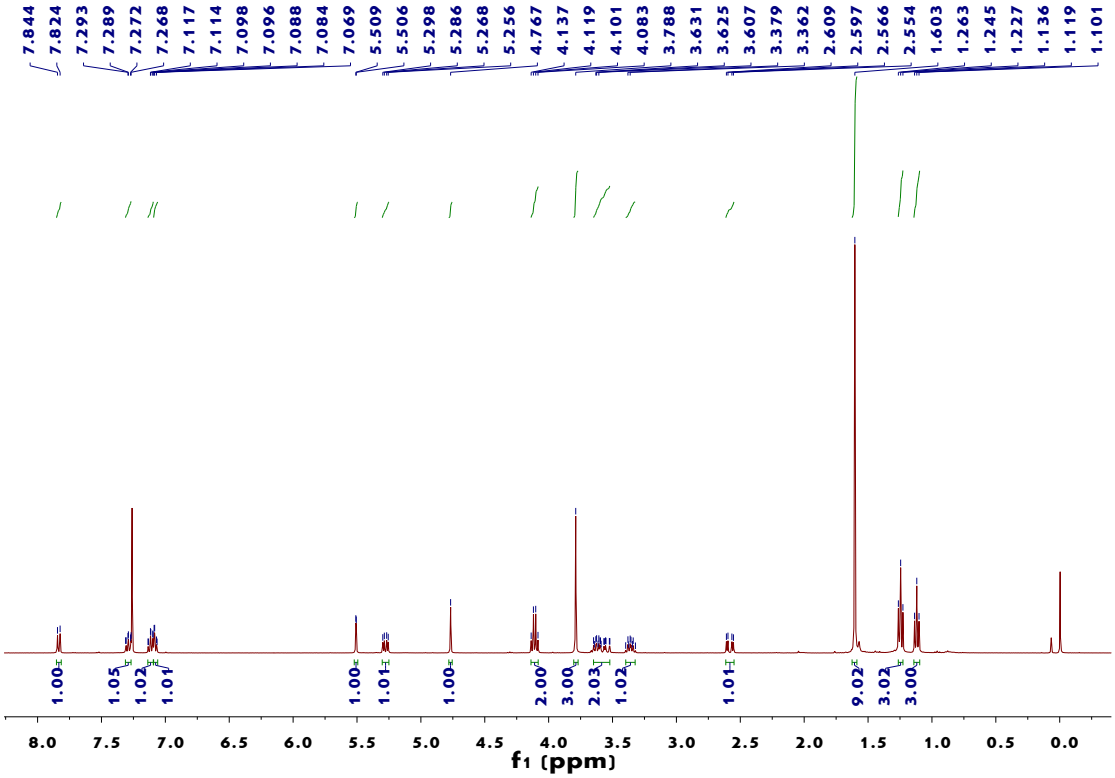
115.239
109.848
100.425
93.061
64.052
61.205
59.919
56.207
43.613
40.307
29.359
14.323
13.367
O
CO2Et
O
Br
O
OEt
N
Bn
3v
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.114
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7.096
7.088
7.084
7.069
5.509
5.506
5.298
5.286
5.268
5.256
4.767
4.137
4.119
4.101
4.083
3.788
3.631
3.625
3.607
3.379
3.362
2.609
2.597
2.566
2.554
1.603
1.263
1.245
1.227
1.136
1.119
1.101
1.00
1.05
1.02
1.01
1.00
1.01
1.00
2.00
3.00
2.03
1.02
1.01
9.02
3.02
3.00
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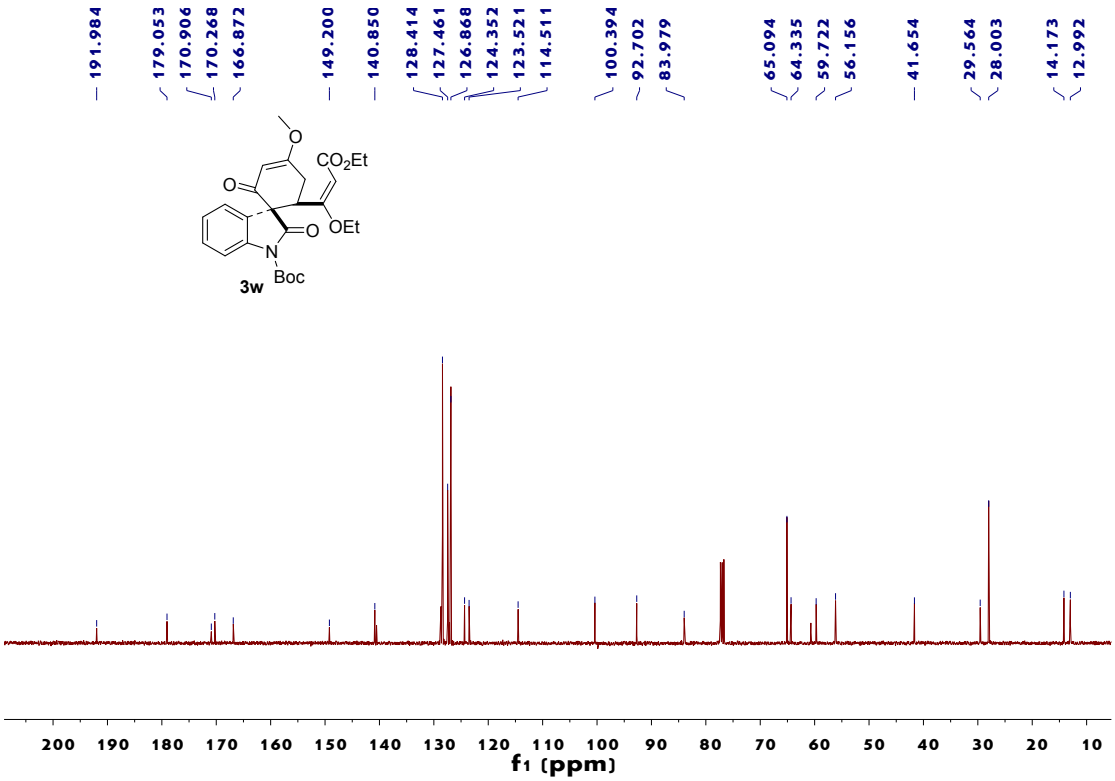
f1 (ppm)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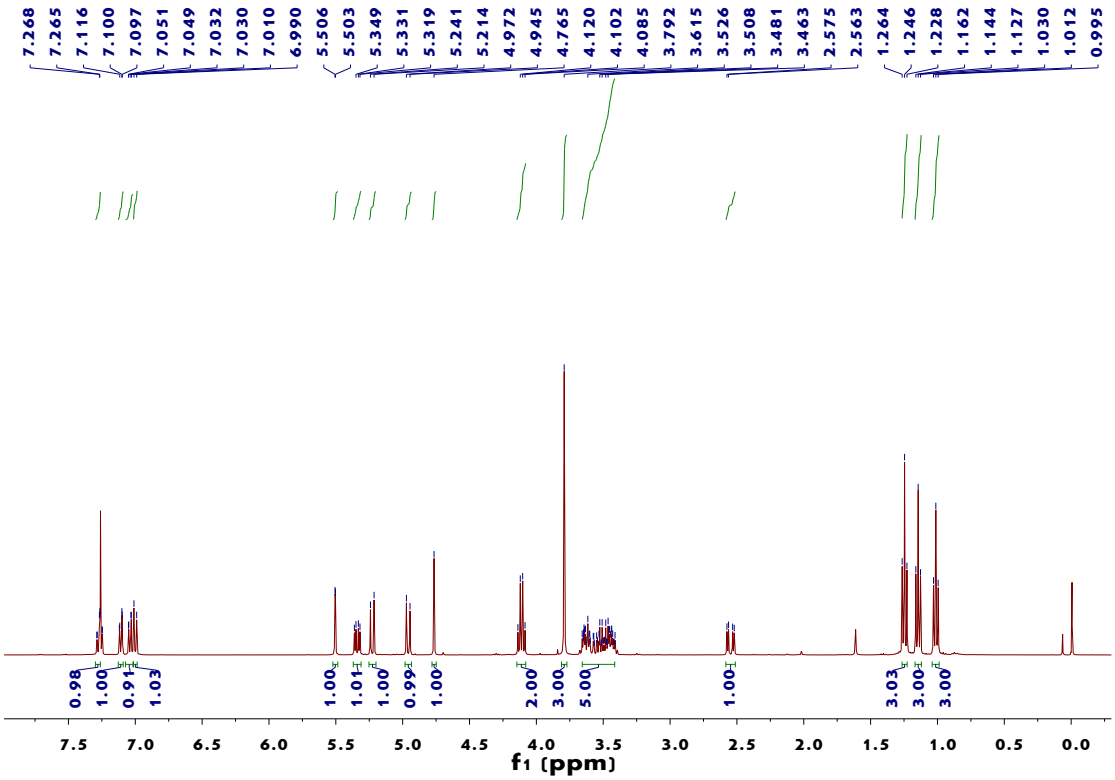
127.461
126.868
124.352
123.521
114.511
100.394
92.702
83.979
65.094
64.335
59.722
56.156
41.654
29.564
28.003
14.173
12.992
O
CO2Et
O
OEt
O
N
Boc
3w
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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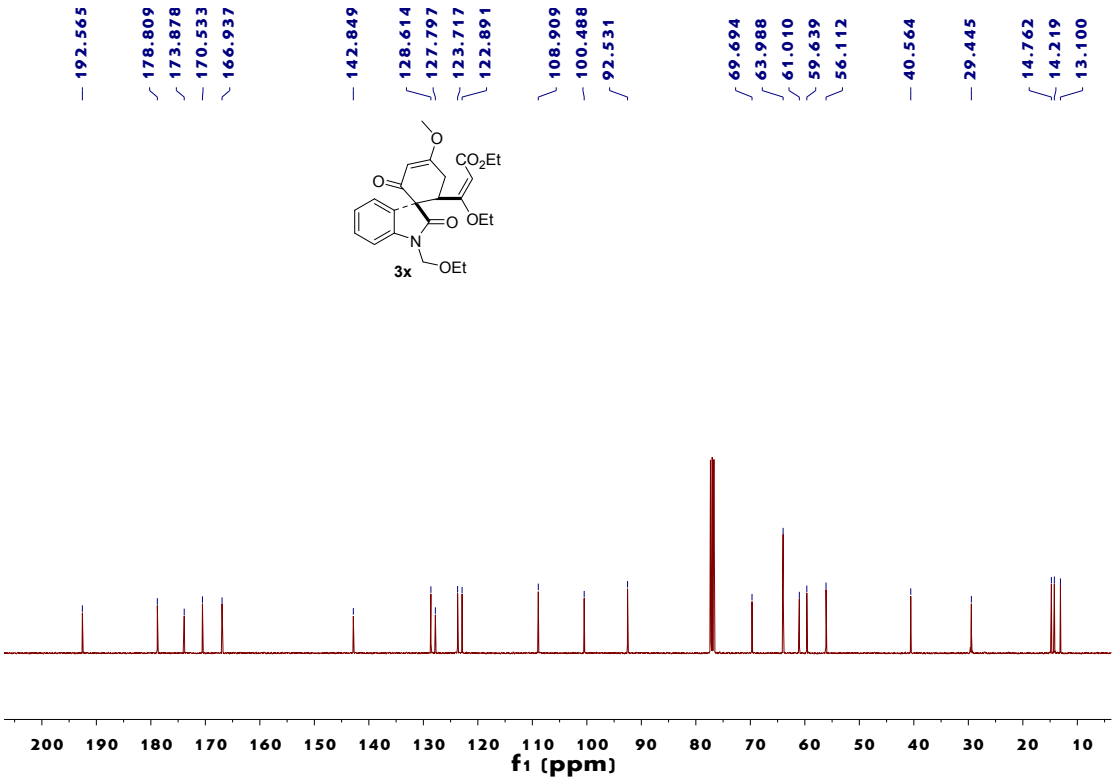
7.051
7.049
7.032
7.030
7.010
6.990
5.506
5.503
5.349
5.331
5.319
5.241
5.214
4.972
4.945
4.765
4.120
4.102
4.085
3.792
3.615
3.526
3.508
3.481
3.463
2.575
2.563
1.264
1.246
1.228
1.162
1.144
1.127
1.030
1.012
0.995
0.98
1.00
0.91
1.03
1.00
1.01
1.00
0.99
1.00
2.00
3.00
5.00
1.00
3.03
3.00
3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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127.797
123.717
122.891
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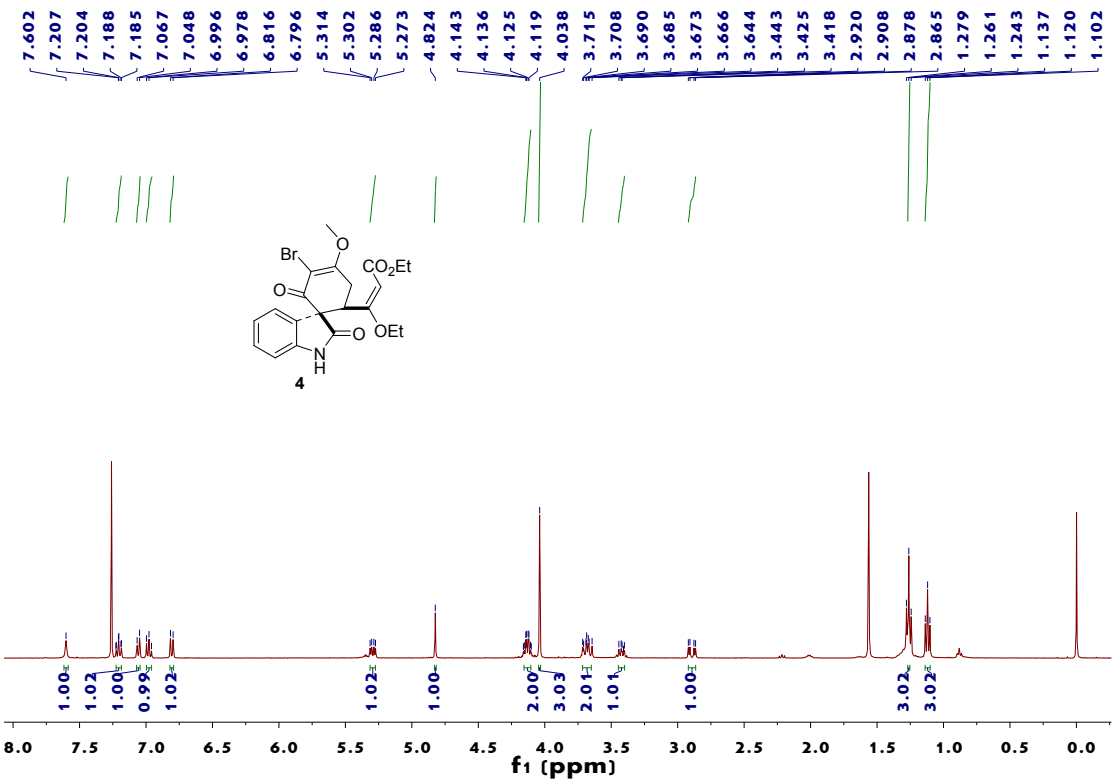
100.488
92.531
69.694
63.988
61.010
59.639
56.112
40.564
29.445
14.762
14.219
13.100
CO2Et
OEt
OEt
3x
f1 (ppm)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7.185
7.067
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6.996
6.978
6.816
6.796
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5.302
5.286
5.273
4.824
4.143
4.136
4.125
4.119
4.038
3.715
3.708
3.690
3.685
3.673
3.666
3.644
3.443
3.425
3.418
2.920
2.908
2.878
2.865
1.279
1.261
1.243
1.137
1.120
1.102
Br
CO2Et
OEt
4
1.00
1.02
1.00
0.99
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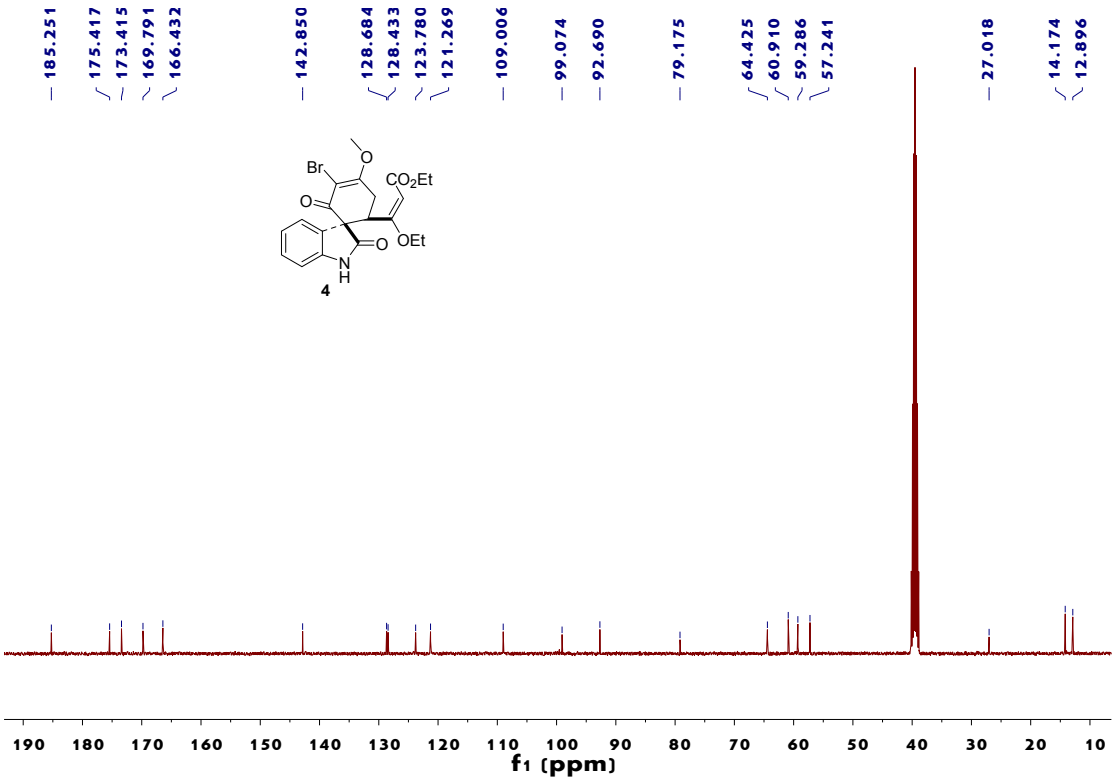
1.02
1.00
2.00
3.03
2.01
1.01
1.00
3.02
3.02
f1 (ppm)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173.415
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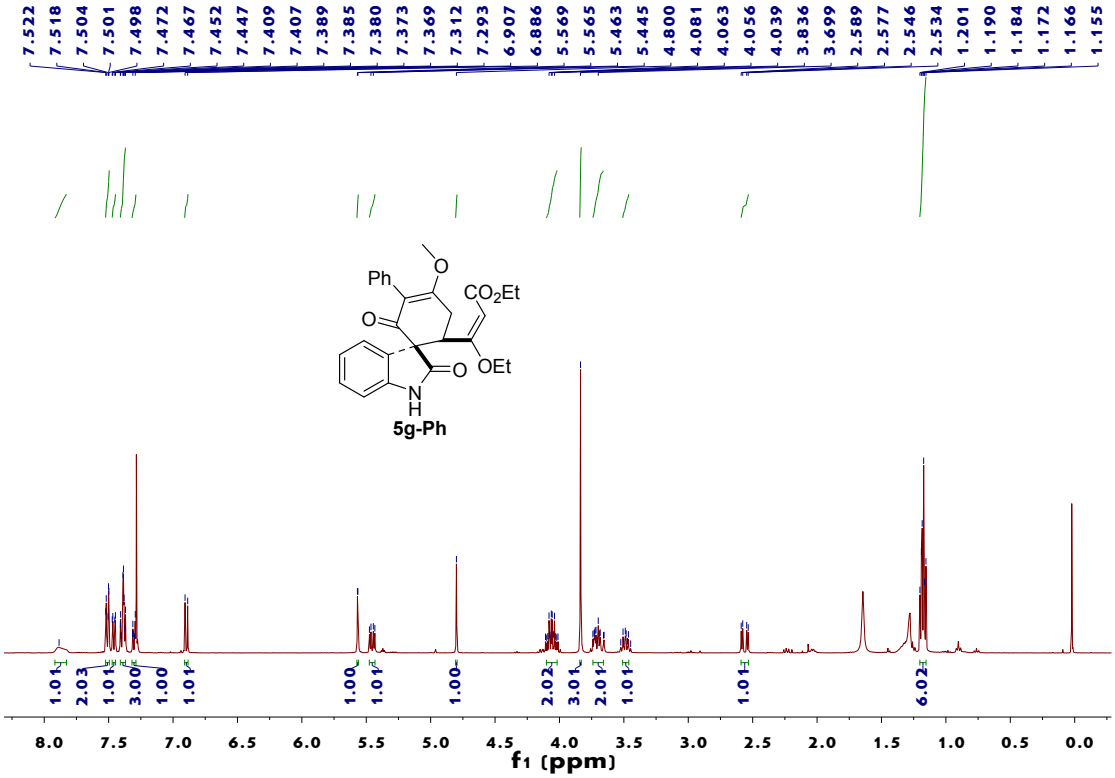
128.433
123.780
121.269
109.006
99.074
92.690
79.175
64.425
60.910
59.286
57.241
27.018
14.174
12.896
Br
O
CO2Et
O
O
OEt
N
H
4
f1 (ppm)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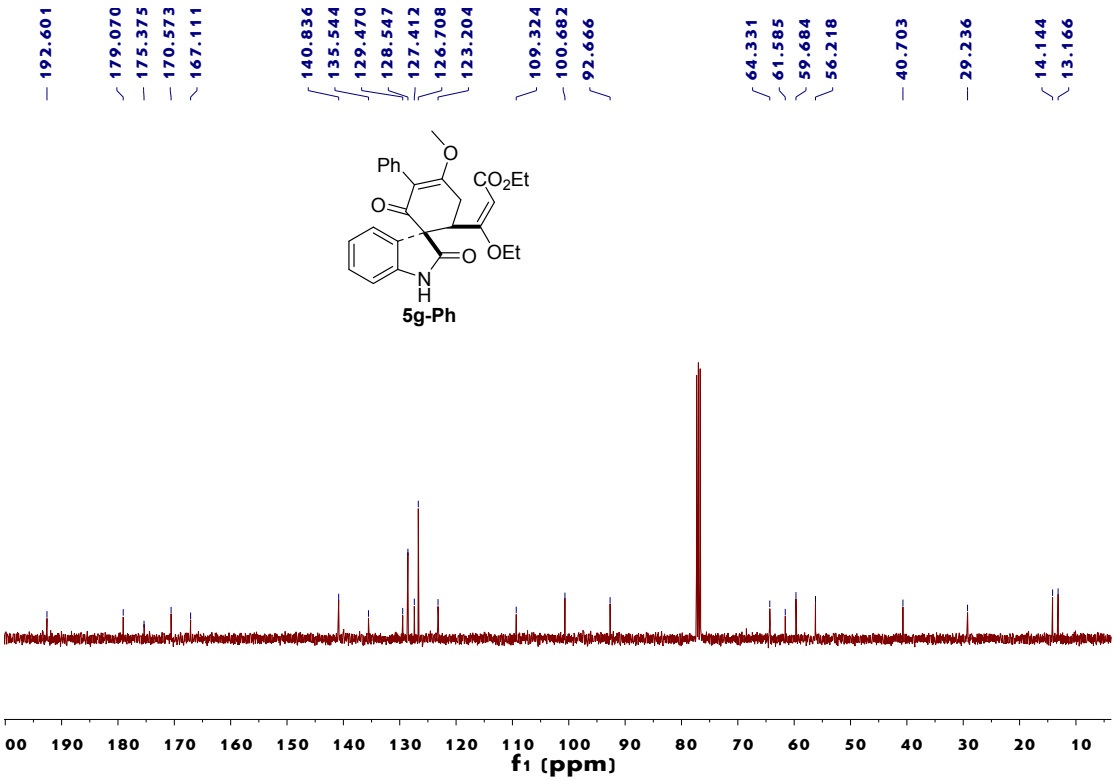
7.498
7.472
7.467
7.452
7.447
7.409
7.407
7.389
7.385
7.380
7.373
7.369
7.312
7.293
6.907
6.886
5.569
5.565
5.463
5.445
4.800
4.081
4.063
4.056
4.039
3.836
3.699
2.589
2.577
2.546
2.534
1.201
1.190
1.184
1.172
1.166
1.155
Ph
O
CO2Et
O
O
OEt
N
H
5g-Ph
1.01
2.03
1.01
3.00
1.00
1.01
1.00
1.01
1.00
2.02
3.01
2.01
1.01
1.01
6.02
f1 (ppm)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175.375
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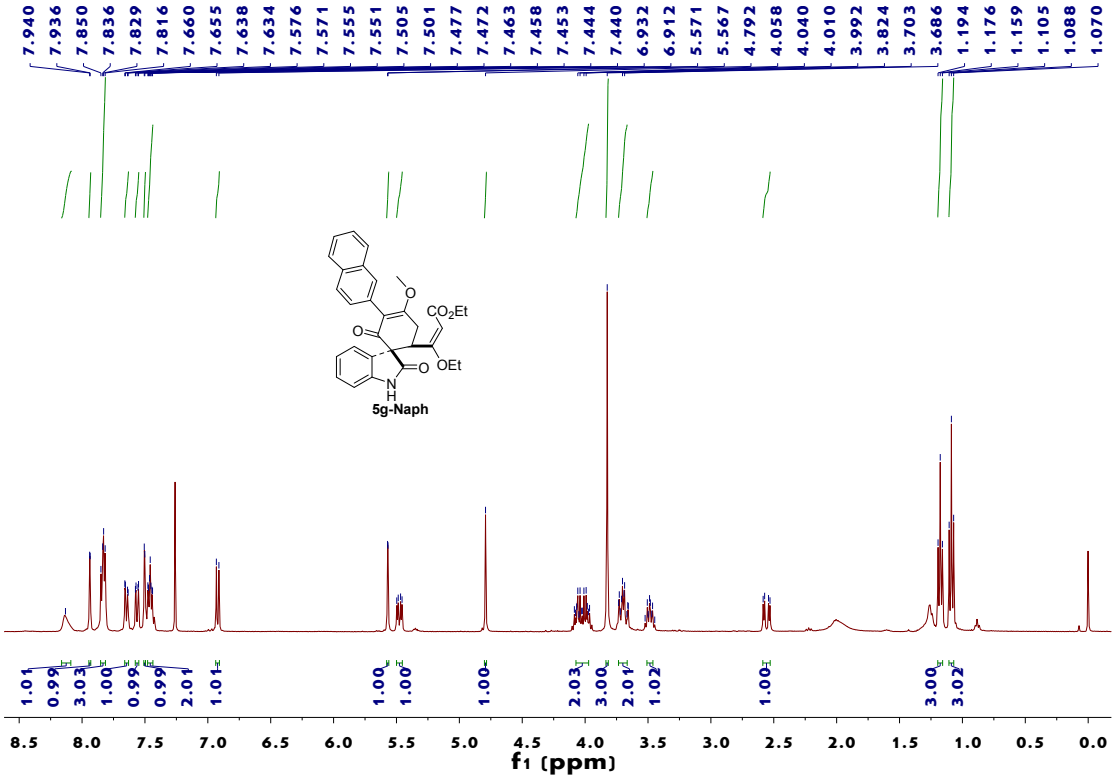
167.111
140.836
135.544
129.470
128.547
127.412
126.708
123.204
109.324
100.682
92.666
64.331
61.585
59.684
56.218
40.703
29.236
14.144
13.166
Ph
O
CO2Et
O
O
OEt
N
H
5g-Ph
f1 (ppm)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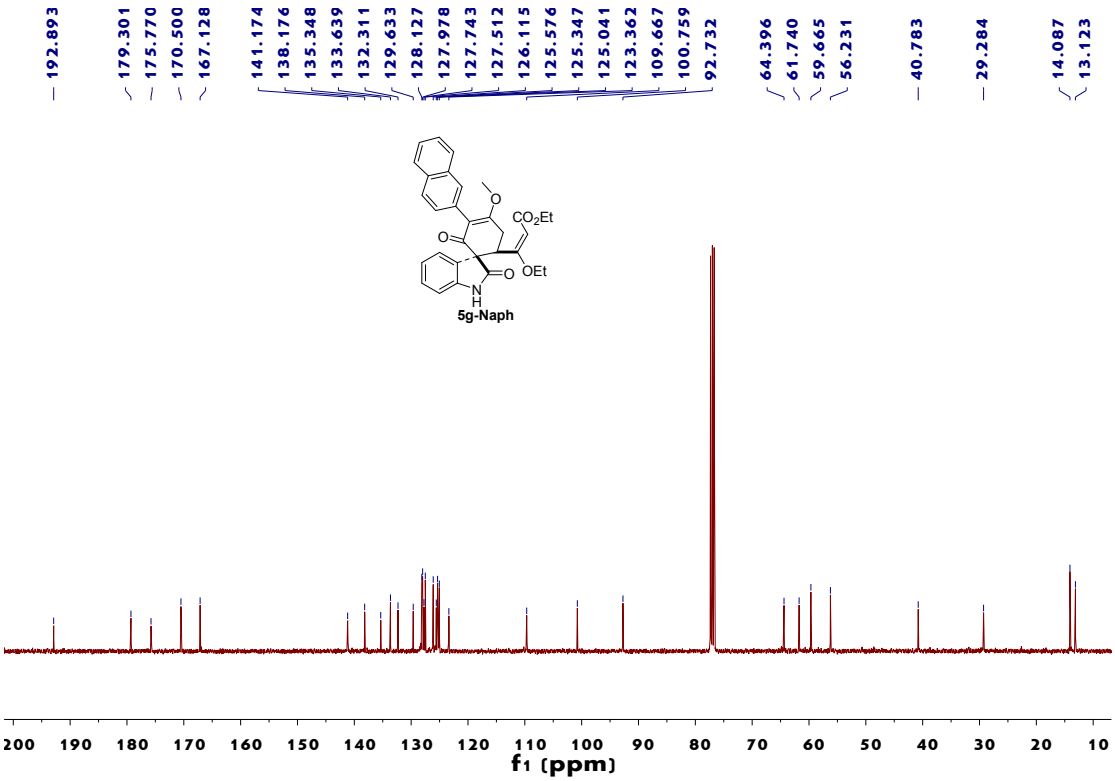
7.836
7.829
7.816
7.660
7.655
7.638
7.634
7.576
7.571
7.555
7.551
7.505
7.501
7.477
7.472
7.463
7.458
7.453
7.444
7.440
6.932
6.912
5.571
5.567
4.792
4.058
4.040
4.010
3.992
3.824
3.703
3.686
1.194
1.176
1.159
1.105
1.088
1.070
CO2Et
O
O
OEt
N
H
5g-Naph
1.01
0.99
3.03
1.00
0.99
0.99
2.01
1.01
1.00
1.00
1.00
2.03
3.00
2.01
1.02
1.00
3.00
3.02
f1 (ppm)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133.639
132.311
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128.127
127.978
127.743
127.512
126.115
125.576
125.347
125.041
123.362
109.667
100.759
92.732
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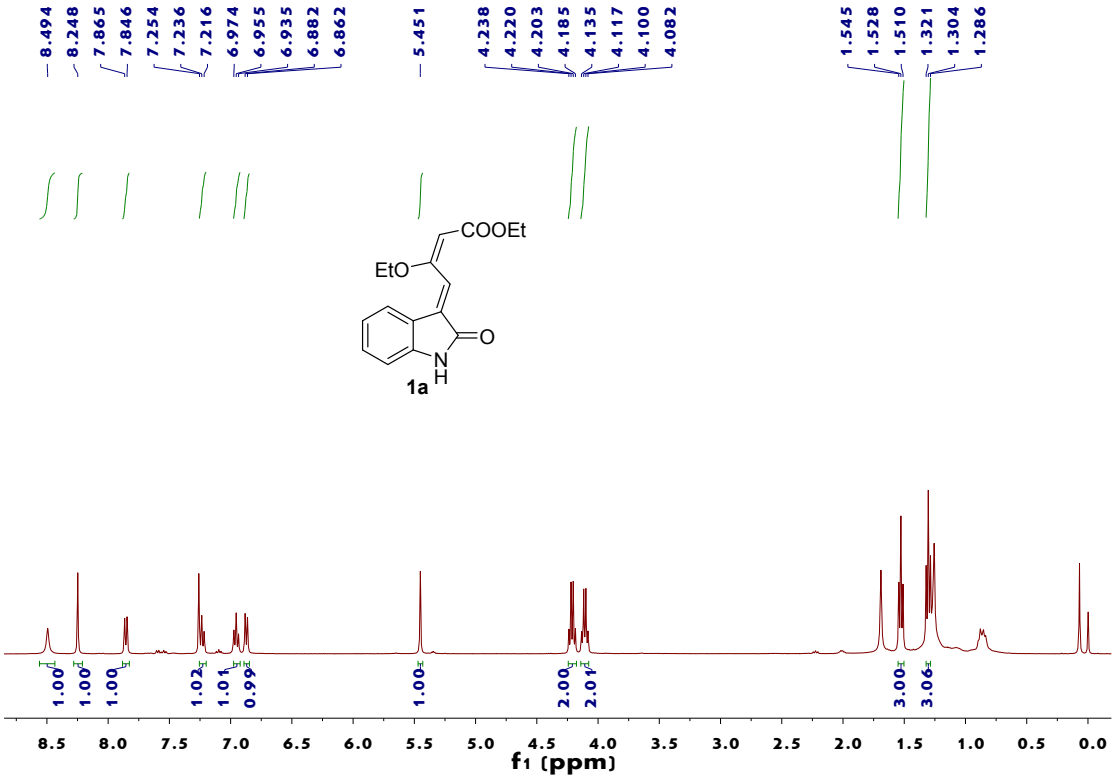
56.231
40.783
29.284
14.087
13.123
CO2Et
OEt
5g-Naph
f1 (ppm)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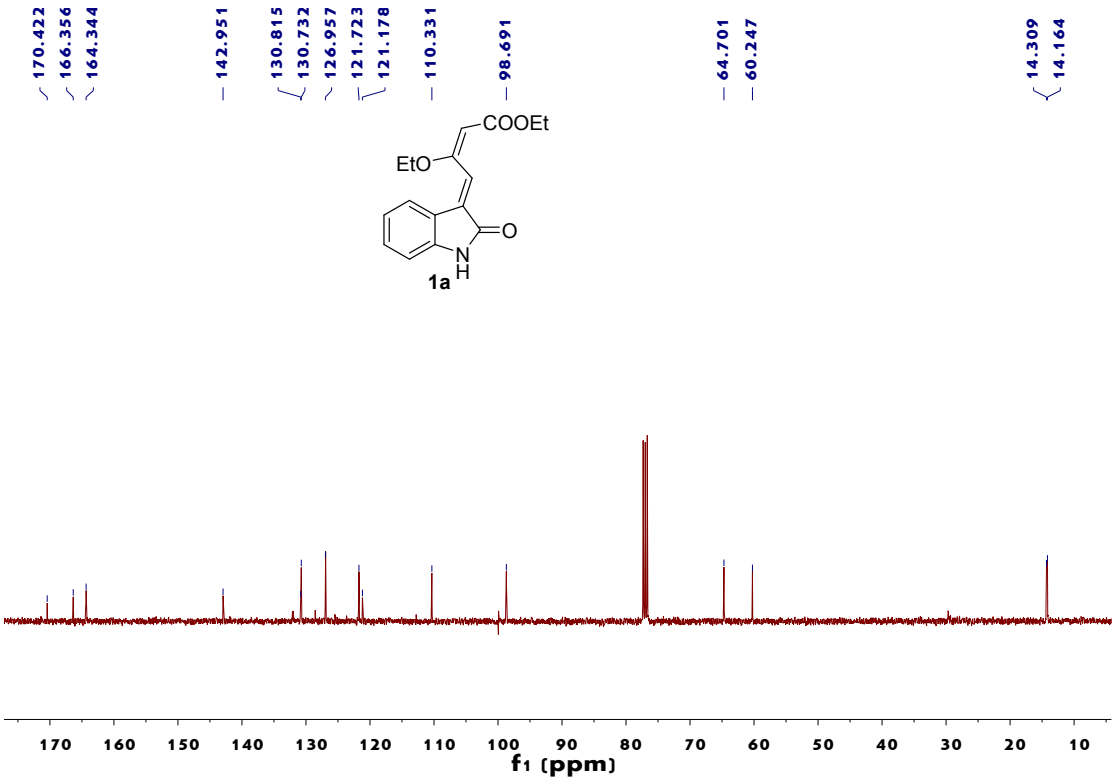
6.882
6.862
5.451
4.238
4.220
4.203
4.185
4.135
4.117
4.100
4.082
1.545
1.528
1.510
1.321
1.304
1.286
COOEt
EtO
1a
1.00
1.00
1.00
1.02
1.01
0.99
1.00
2.00
2.01
3.00
3.06
f1 (ppm)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130.732
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121.723
121.178
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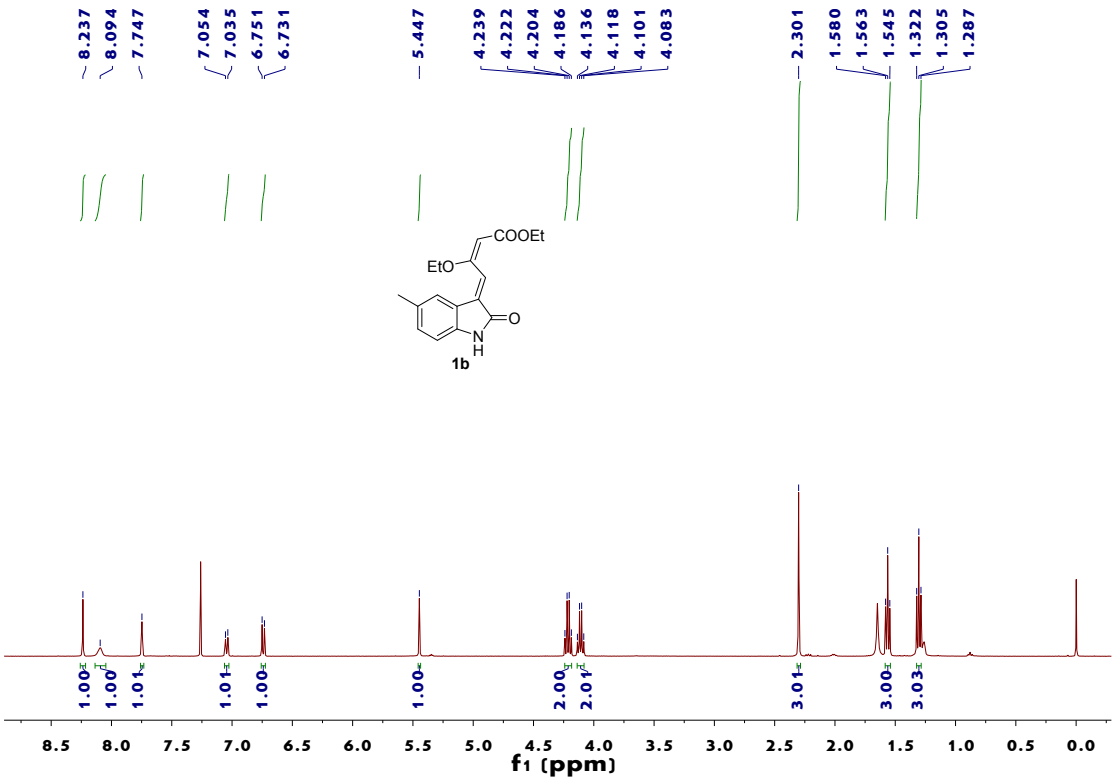
60.247
14.309
14.164
COOEt
EtO
O
N
H
1a
f1 (ppm)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6.731
5.447
4.239
4.222
4.204
4.186
4.136
4.118
4.101
4.083
2.301
1.580
1.563
1.545
1.322
1.305
1.287
COOEt
EtO
O
N
H
1b
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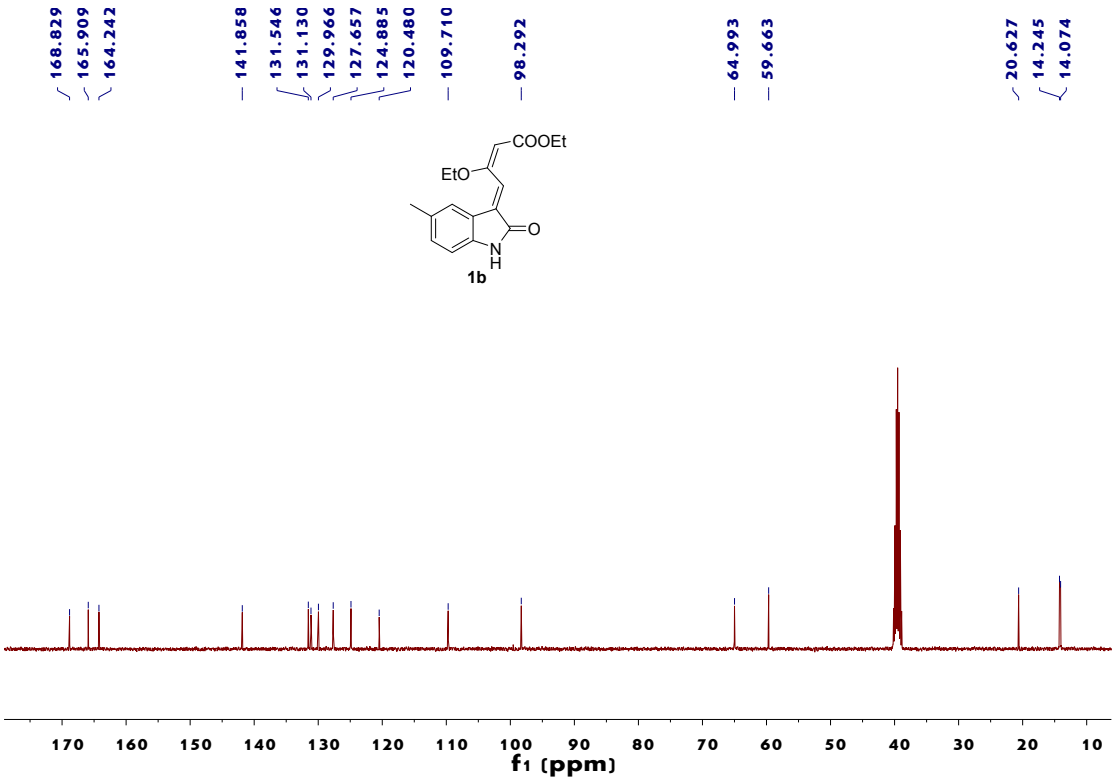
1.00
1.01
1.01
1.00
1.00
2.00
2.01
3.01
3.00
3.03
f1 (ppm)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127.657
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64.993
59.663
20.627
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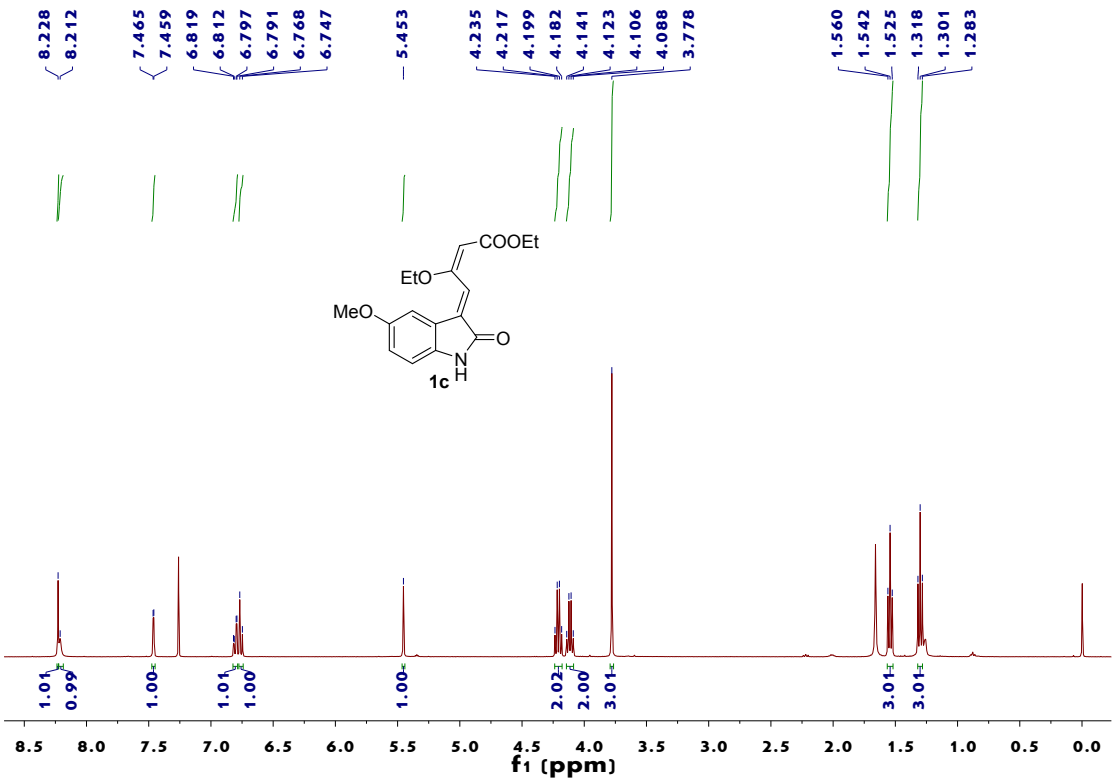
COOEt
EtO
O
N
H
1b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.459
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6.791
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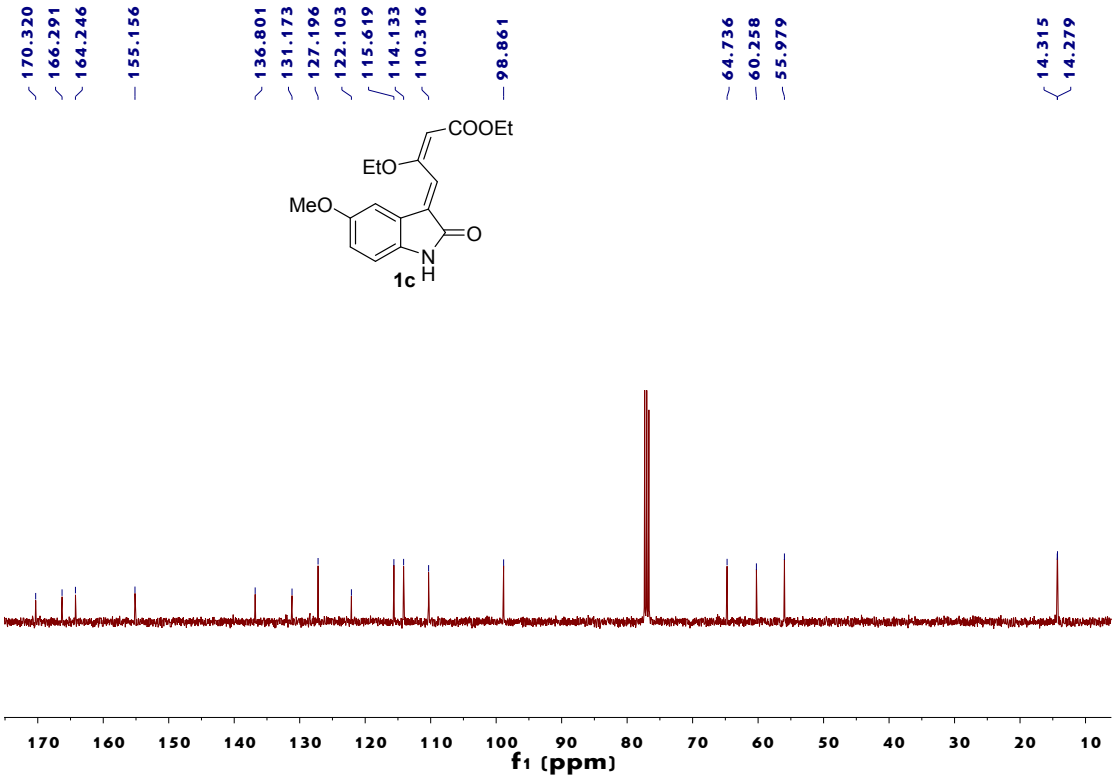
6.747
5.453
4.235
4.217
4.199
4.182
4.141
4.123
4.106
4.088
3.778
1.560
1.542
1.525
1.318
1.301
1.283
COOEt
EtO
MeO
O
N
H
1c
1.01
0.99
1.00
1.01
1.00
1.00
2.02
2.00
3.01
3.01
3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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98.861
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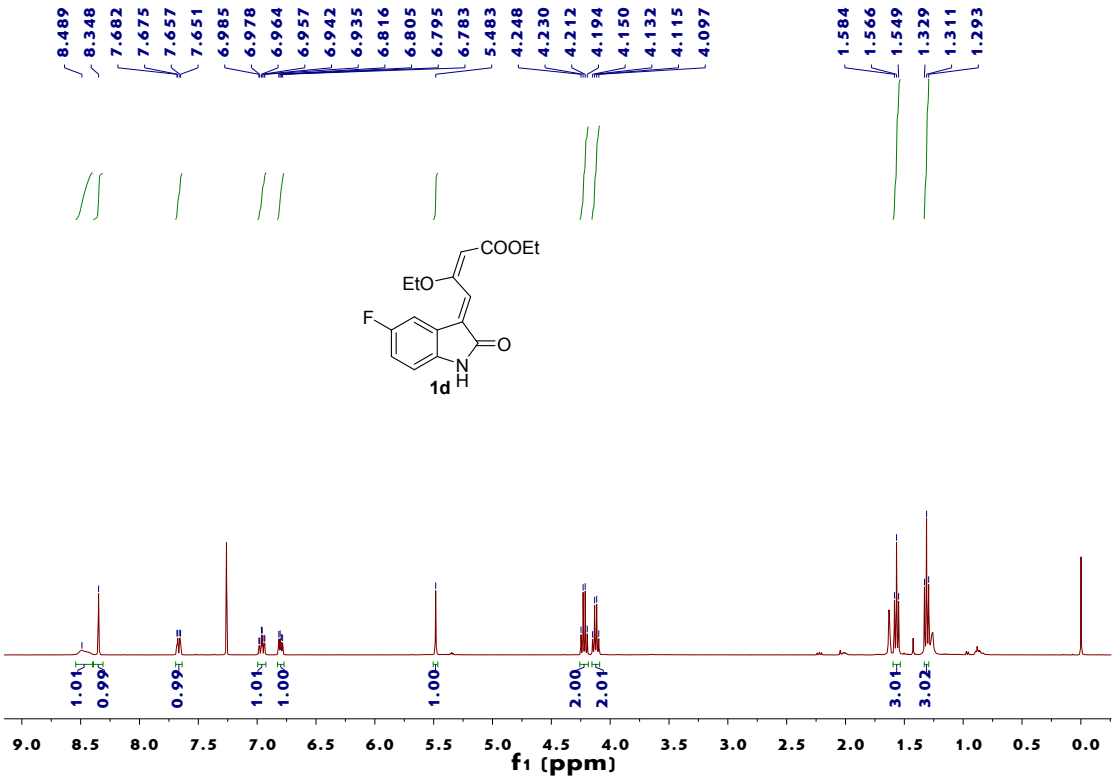
55.979
14.315
14.279
COOEt
EtO
MeO
O
N
H
1c
f1 (ppm)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6.978
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6.957
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6.935
6.816
6.805
6.795
6.783
5.483
4.248
4.230
4.212
4.194
4.150
4.132
4.115
4.097
1.584
1.566
1.549
1.329
1.311
1.293
COOEt
EtO
F
O
N
H
1d
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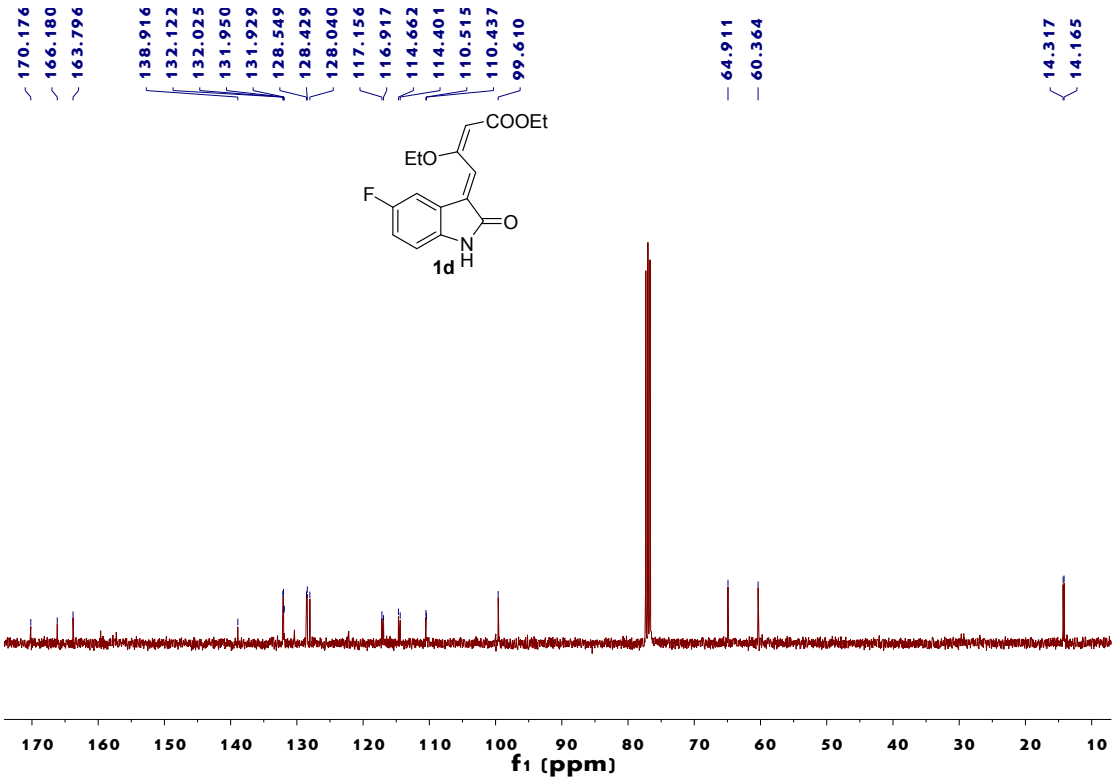
0.99
0.99
1.01
1.00
1.00
2.00
2.01
3.01
3.02
f1 (ppm)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131.950
131.929
128.549
128.429
128.040
117.156
116.917
114.662
114.401
110.515
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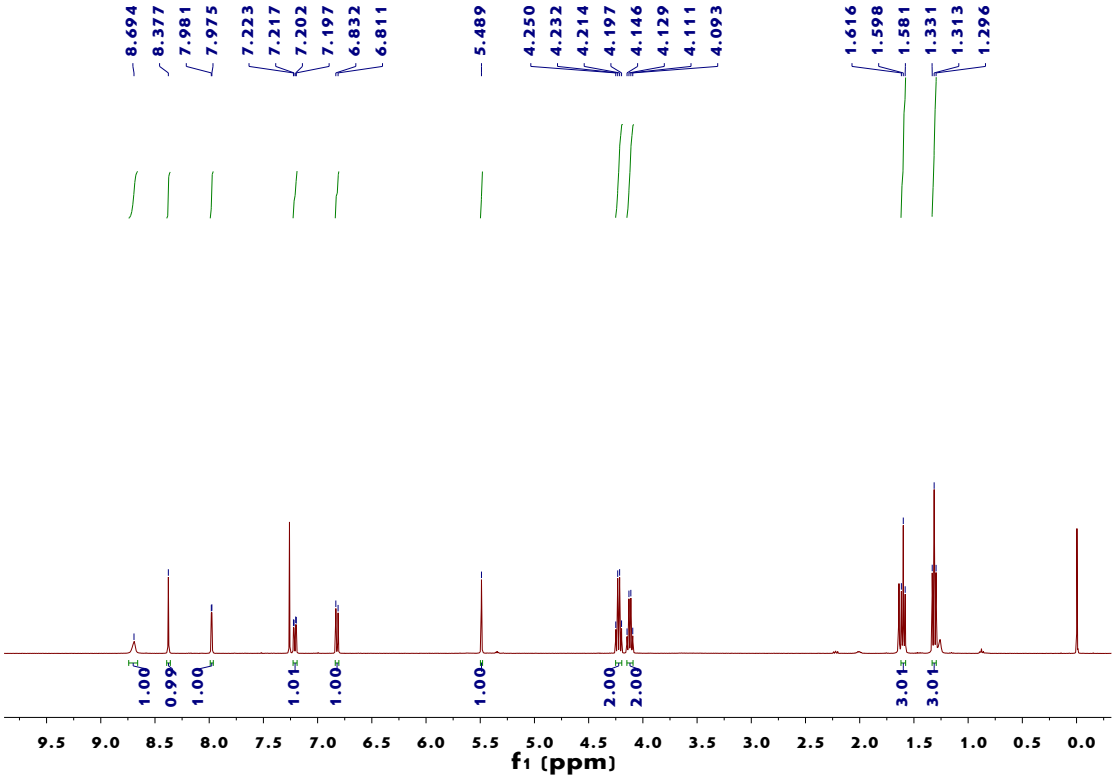
60.364
14.317
14.165
COOEt
EtO
F
O
N
H
1d
f1 (ppm)


8.694
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6.811
5.489
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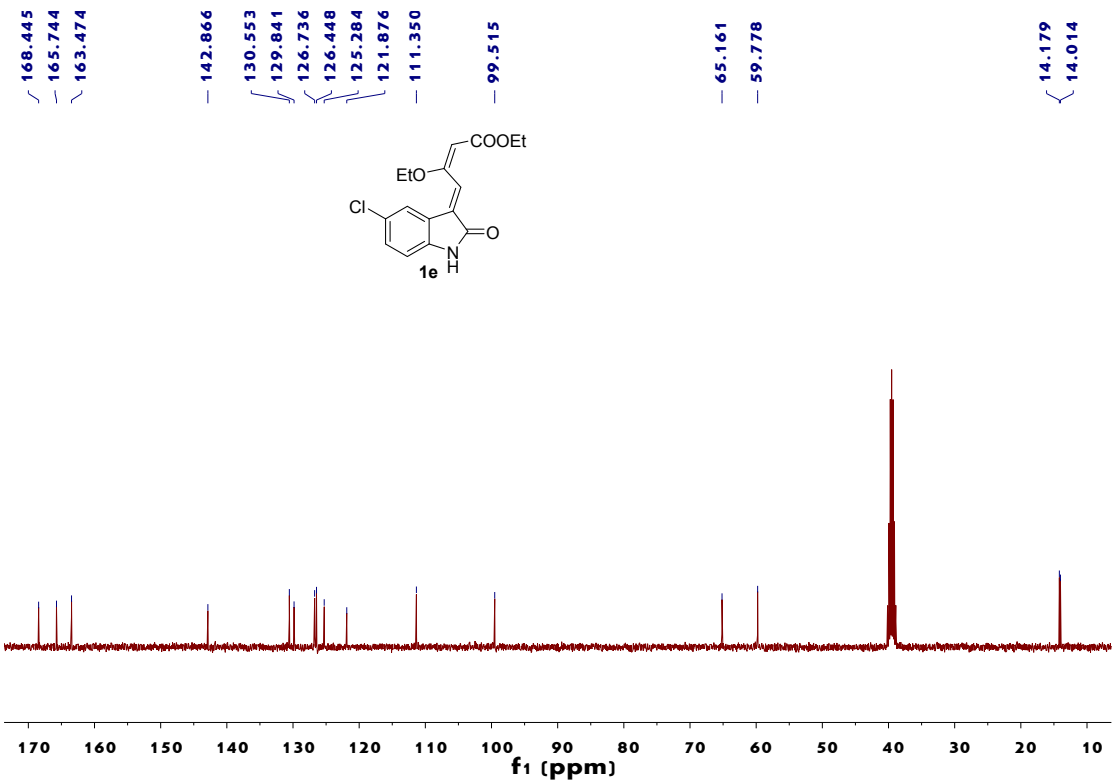
4.232
4.214
4.197
4.146
4.129
4.111
4.093
1.616
1.598
1.581
1.331
1.313
1.296
1.00
0.99
1.00
1.01
1.00
1.00
2.00
2.00
3.01
3.01
f1 (ppm)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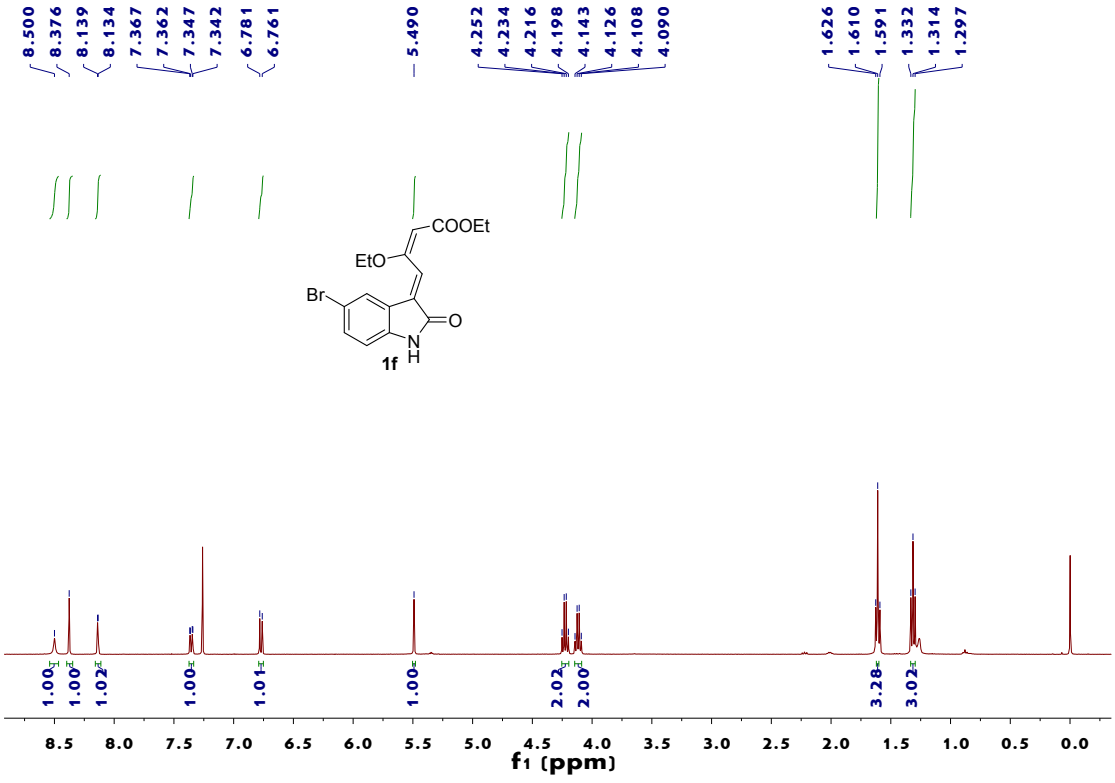
165.744
163.474
142.866
130.553
129.841
126.736
126.448
125.284
121.876
111.350
99.515
65.161
59.778
14.179
14.014
COOEt
EtO
Cl
O
N
H
1e
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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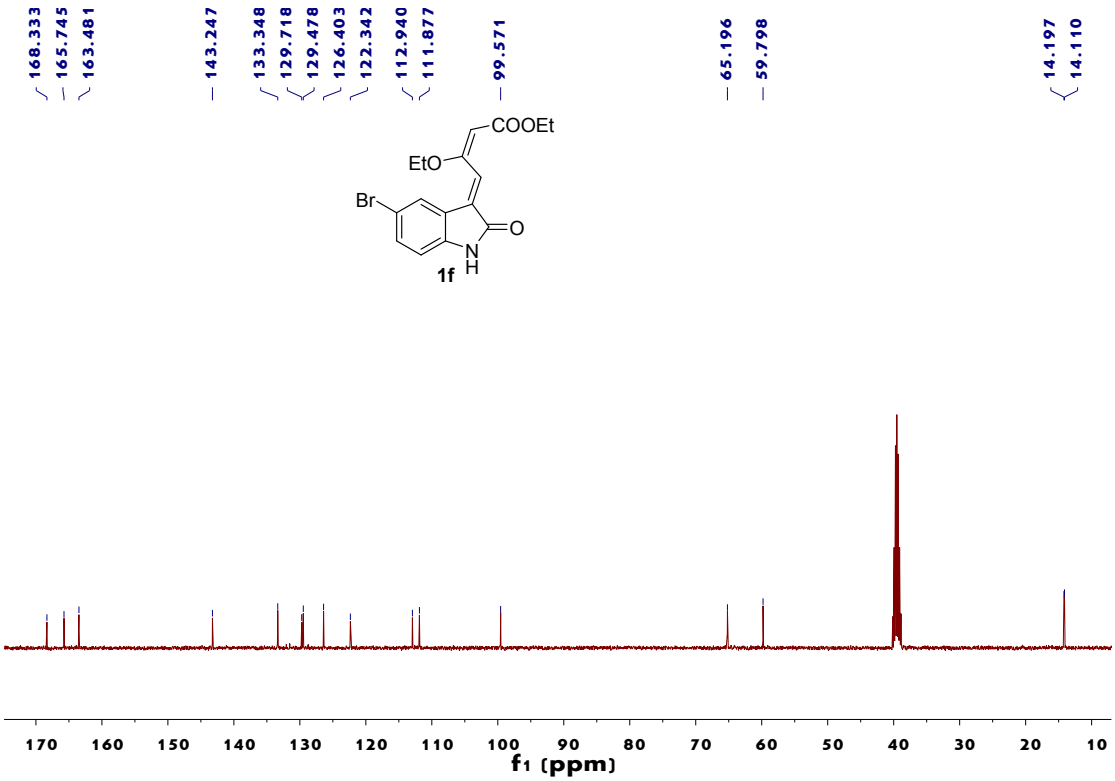
8.139
8.134
7.367
7.362
7.347
7.342
6.781
6.761
5.490
4.252
4.234
4.216
4.198
4.143
4.126
4.108
4.090
1.626
1.610
1.591
1.332
1.314
1.297
COOEt
EtO
Br
O
N
H
1f
1.00
1.00
1.02
1.00
1.01
1.00
2.02
2.00
3.28
3.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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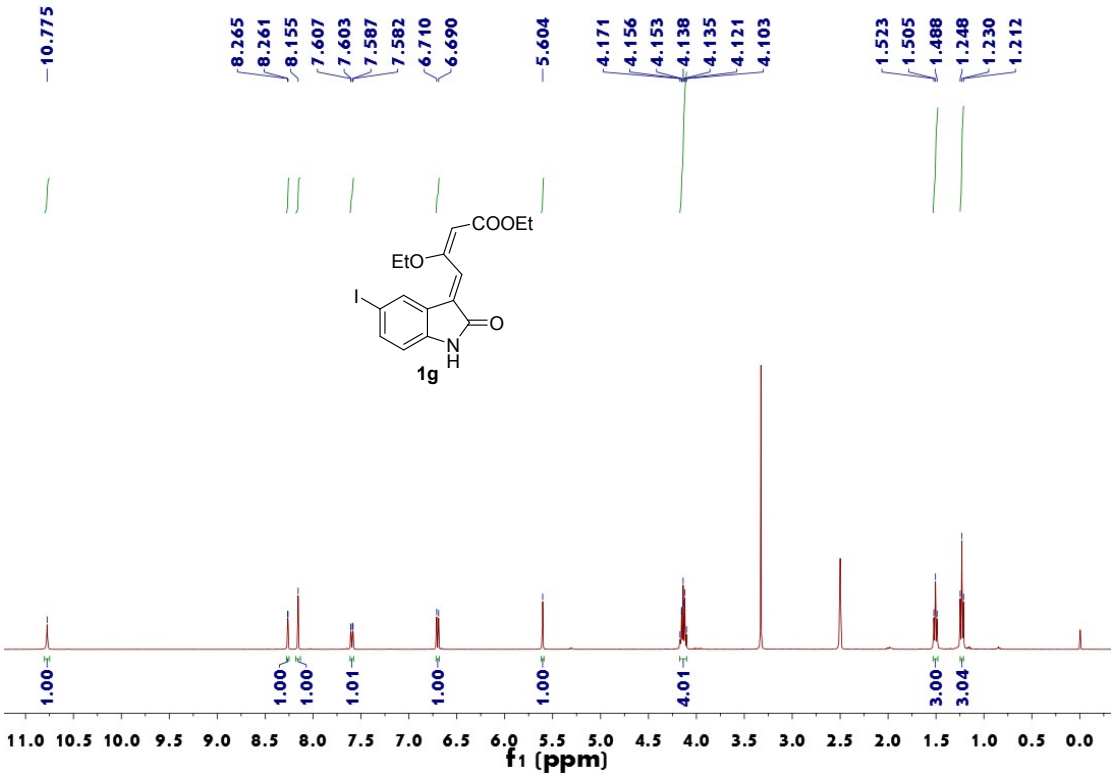
163.481
143.247
133.348
129.718
129.478
126.403
122.342
112.940
111.877
99.571
65.196
59.798
14.197
14.110
COOEt
EtO
Br
O
N
H
1f
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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8.261
8.155
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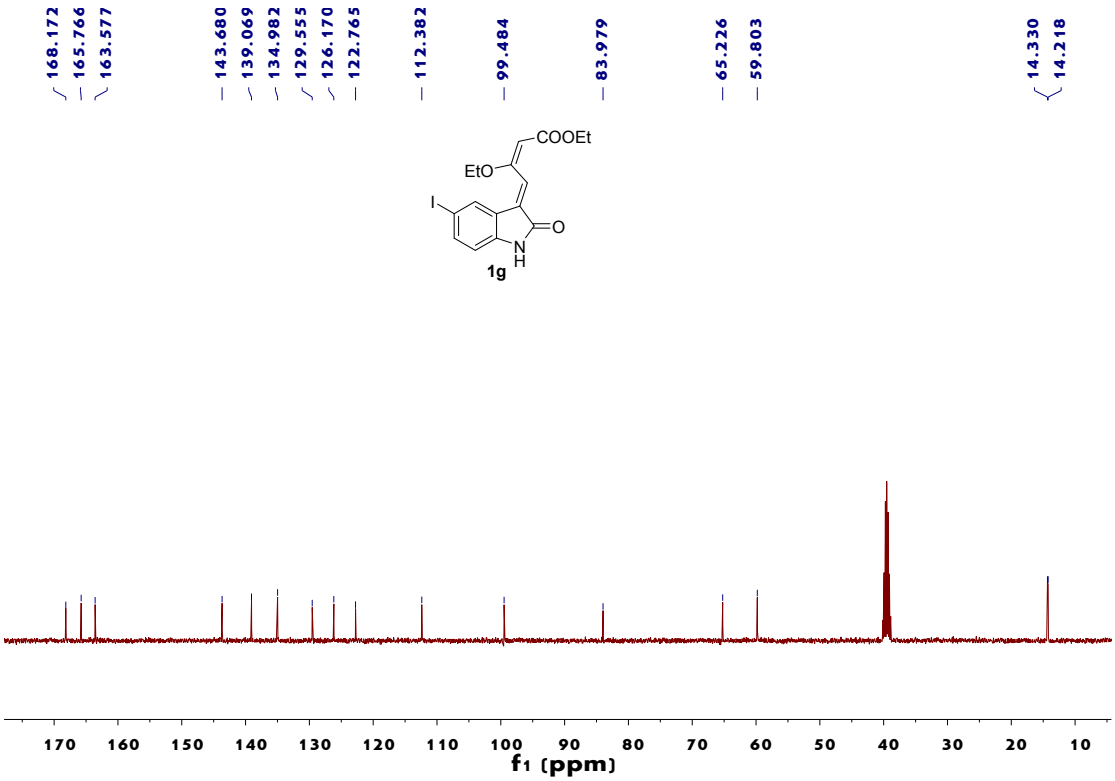
7.603
7.587
7.582
6.710
6.690
5.604
4.171
4.156
4.153
4.138
4.135
4.121
4.103
1.523
1.505
1.488
1.248
1.230
1.212
COOEt
EtO
I
O
N
H
1g
1.00
1.00
1.00
1.01
1.00
1.00
4.01
3.00
3.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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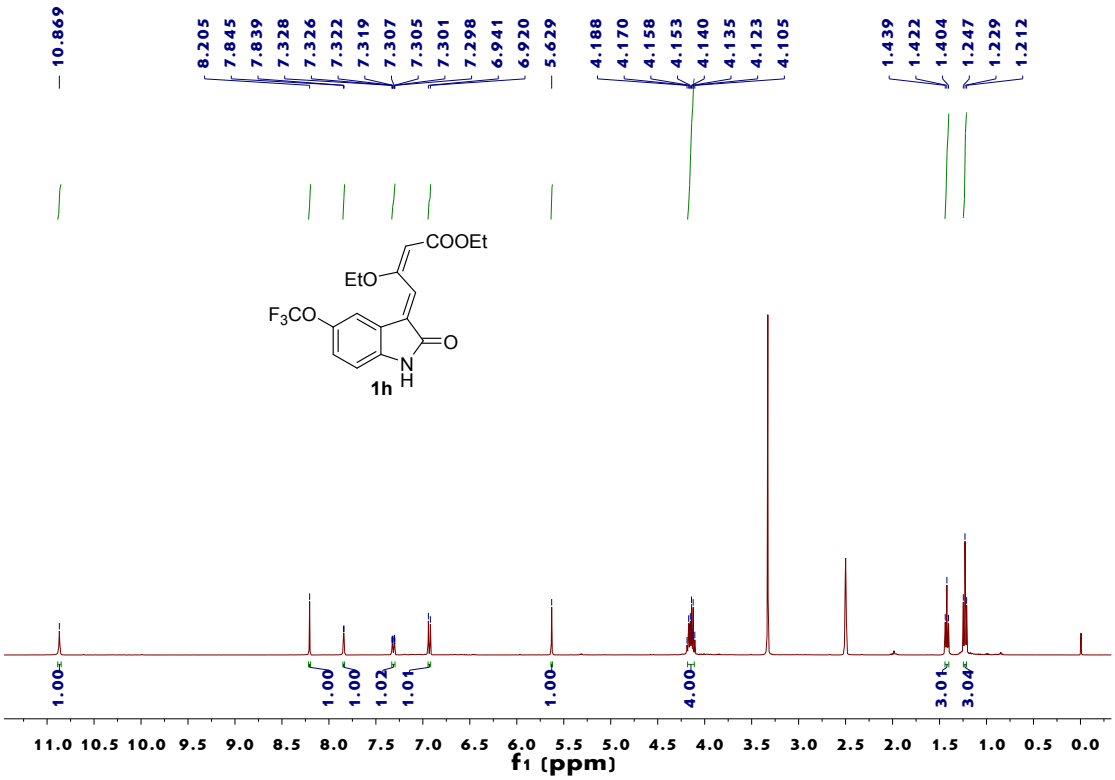
163.577
143.680
139.069
134.982
129.555
126.170
122.765
112.382
99.484
83.979
65.226
59.803
14.330
14.218
COOEt
EtO
I
O
N
H
1g
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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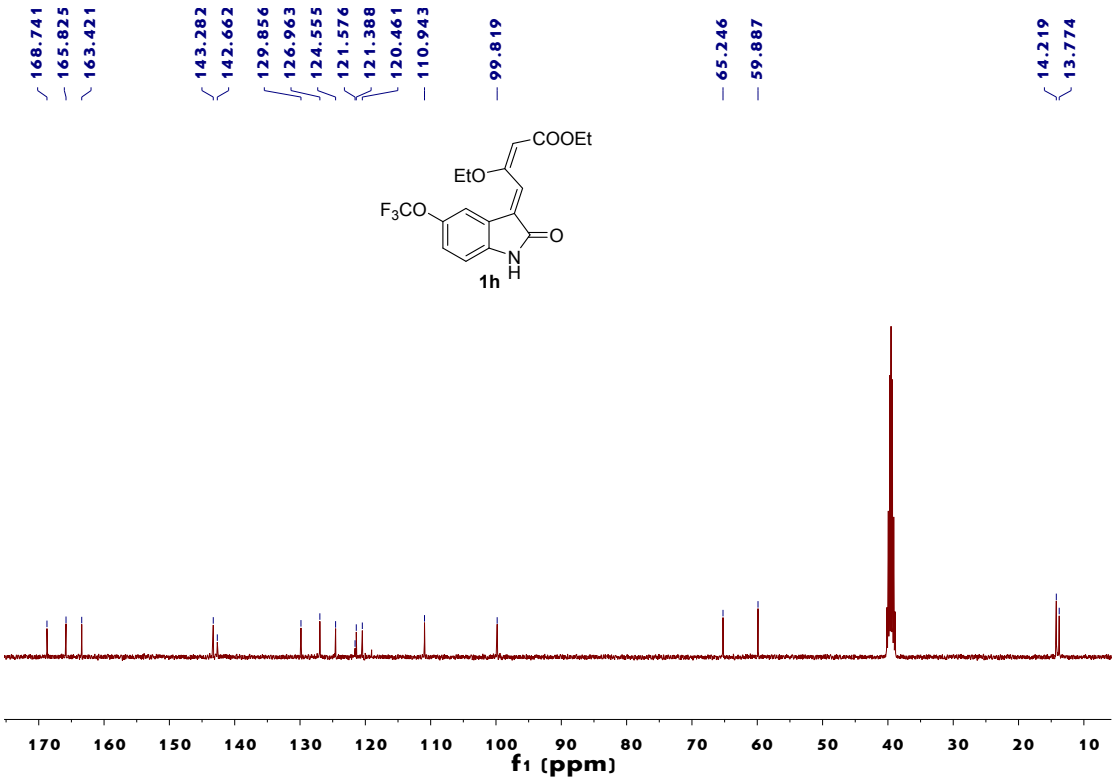
7.845
7.839
7.328
7.326
7.322
7.319
7.307
7.305
7.301
7.298
6.941
6.920
5.629
4.188
4.170
4.158
4.153
4.140
4.135
4.123
4.105
1.439
1.422
1.404
1.247
1.229
1.212
COOEt
EtO
F3CO
O
N
H
1h
1.00
1.00
1.00
1.02
1.01
1.00
4.00
3.01
3.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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163.421
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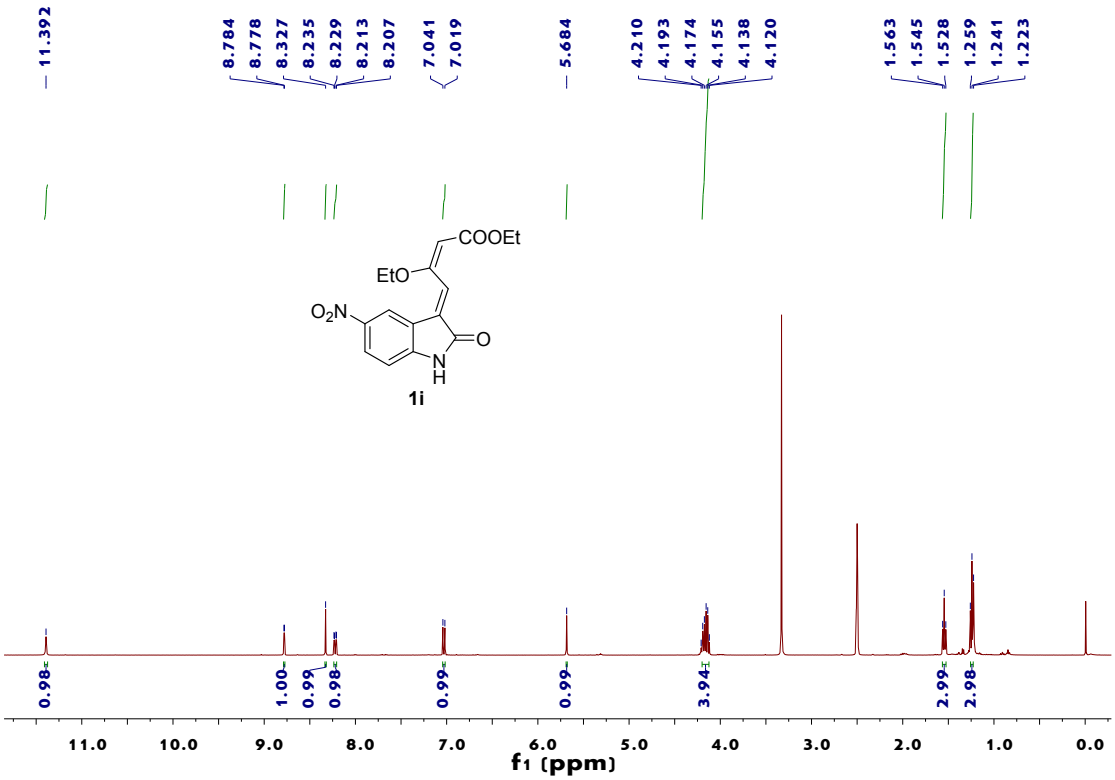
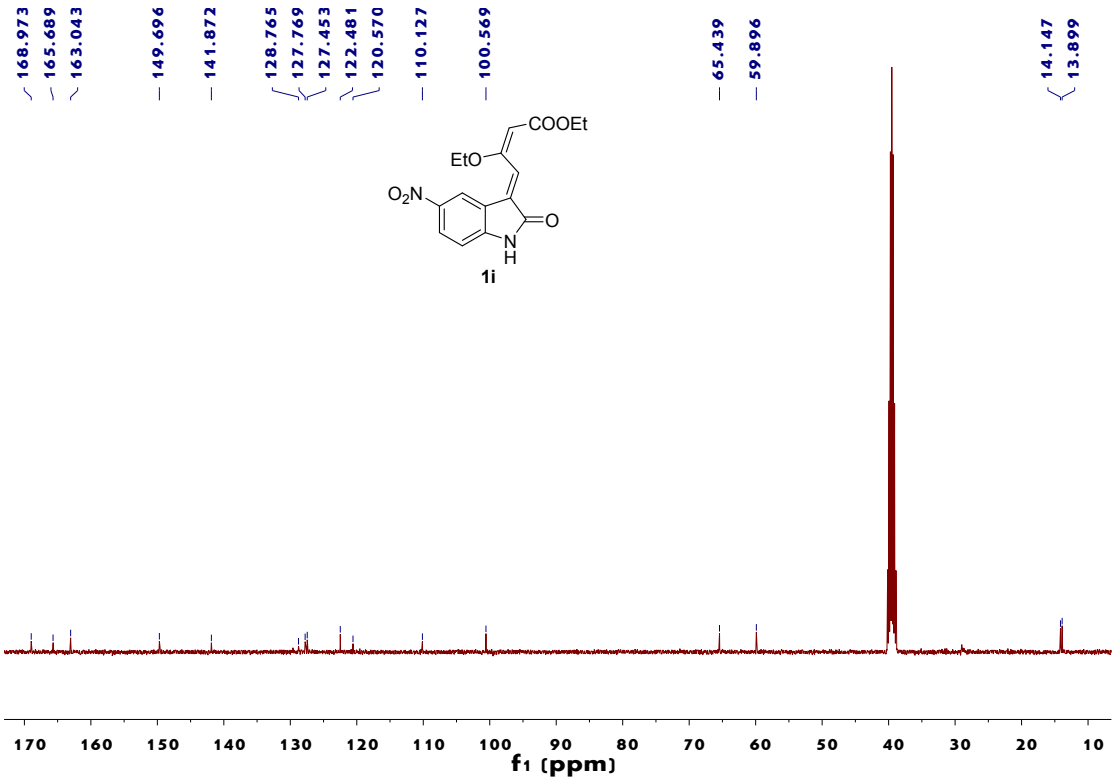
142.662
129.856
126.963
124.555
121.576
121.388
120.461
110.943
99.819
65.246
59.887
14.219
13.774
COOEt
EtO
F3CO
O
N
H
1h
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


11.392
8.784
8.778
8.327
8.235
8.229
8.213
8.207
7.041
7.019
5.684
4.210
4.193
4.174
4.155
4.138
4.120
1.563
1.545
1.528
1.259
1.241
1.223
COOEt
EtO
O2N
O
N
H
1i
0.98
1.00
0.99
0.98
0.99
0.99
3.94
2.99
2.98
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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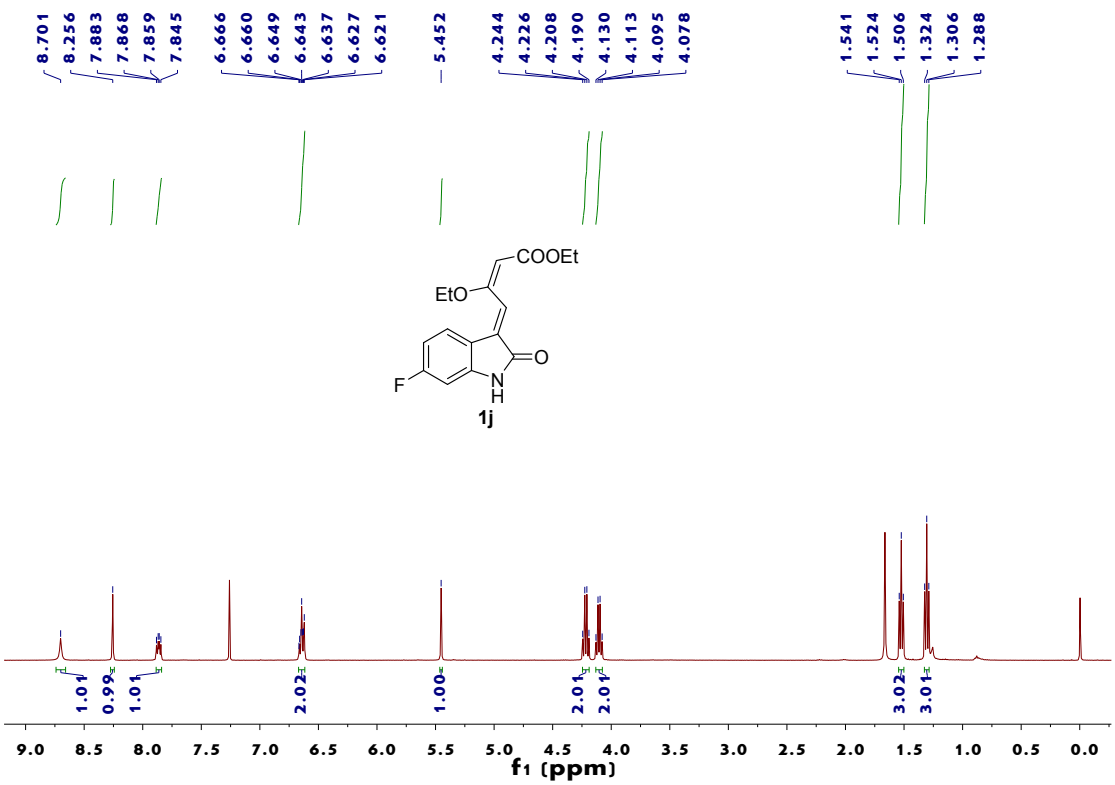
163.043
149.696
141.872
128.765
127.769
127.453
122.481
120.570
110.127
100.569
65.439
59.896
14.147
13.899
COOEt
EtO
O2N
O
N
H
1i
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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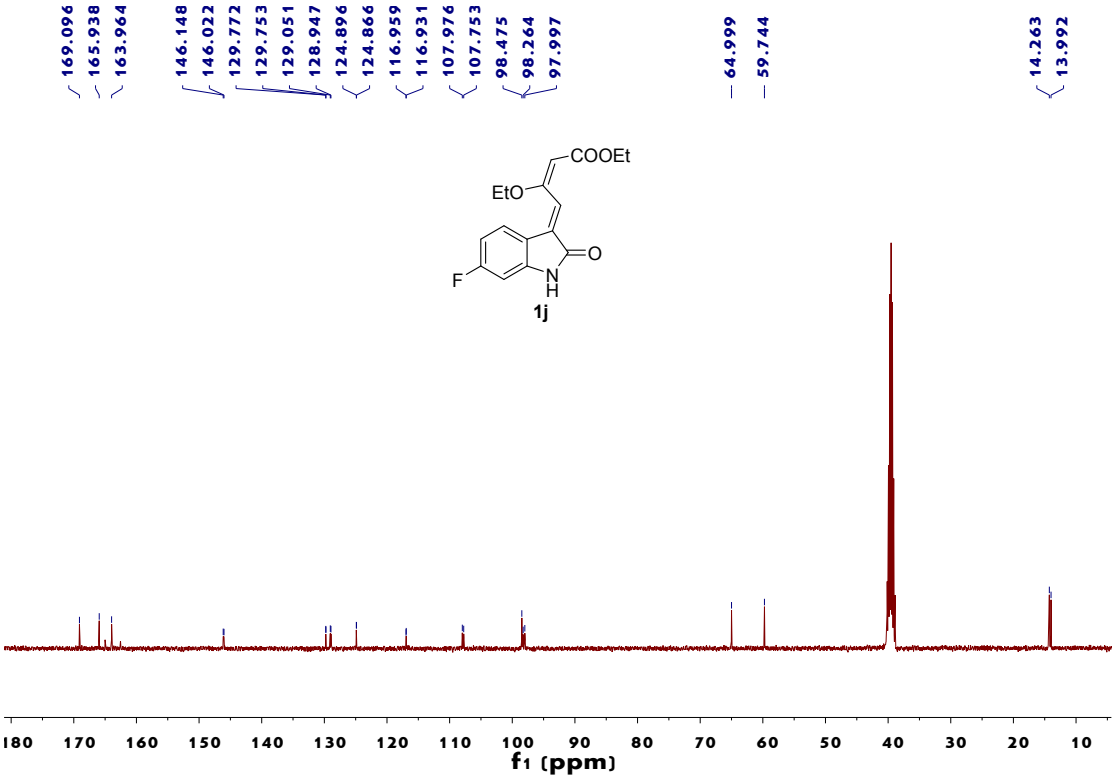
8.256
7.883
7.868
7.859
7.845
6.666
6.660
6.649
6.643
6.637
6.627
6.621
5.452
4.244
4.226
4.208
4.190
4.130
4.113
4.095
4.078
1.541
1.524
1.506
1.324
1.306
1.288
COOEt
EtO
O
F
N
H
1j
1.01
0.99
1.01
2.02
1.00
2.01
2.01
3.02
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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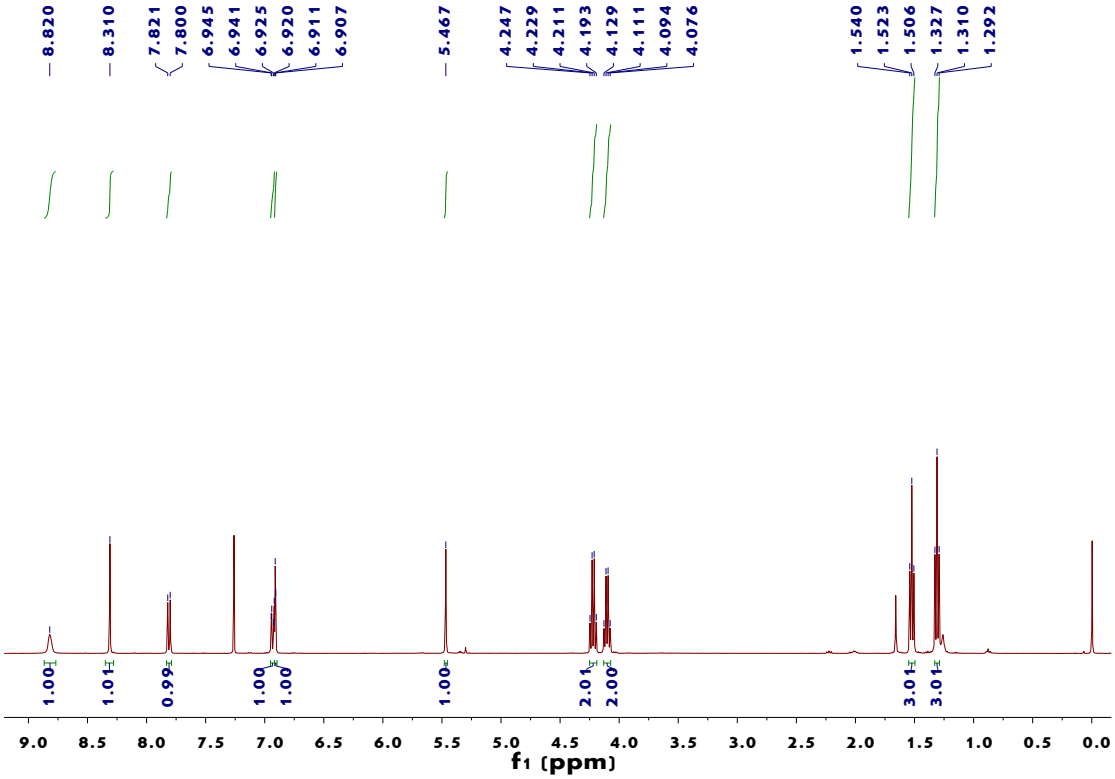
165.938
163.964
146.148
146.022
129.772
129.753
129.051
128.947
124.896
124.866
116.959
116.931
107.976
107.753
98.475
98.264
97.997
64.999
59.744
14.263
13.992
COOEt
EtO
O
F
N
H
1j
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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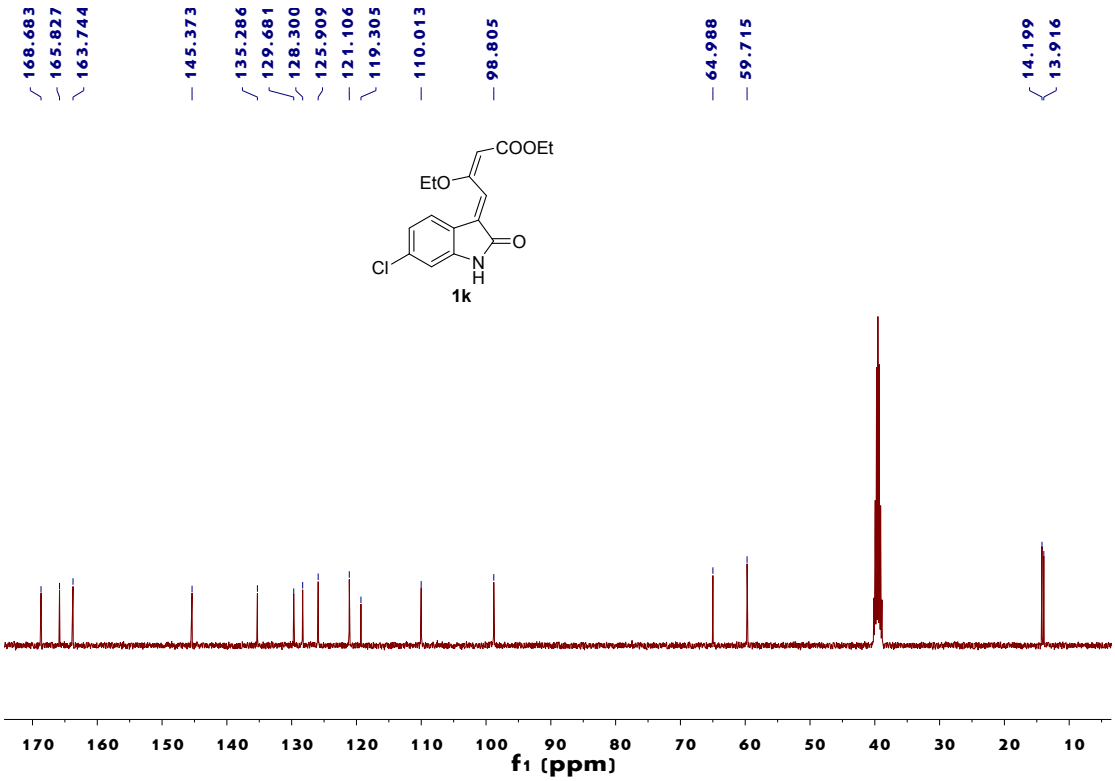
8.310
7.821
7.800
6.945
6.941
6.925
6.920
6.911
6.907
5.467
4.247
4.229
4.211
4.193
4.129
4.111
4.094
4.076
1.540
1.523
1.506
1.327
1.310
1.292
1.00
1.01
0.99
1.00
1.00
1.00
2.01
2.00
3.01
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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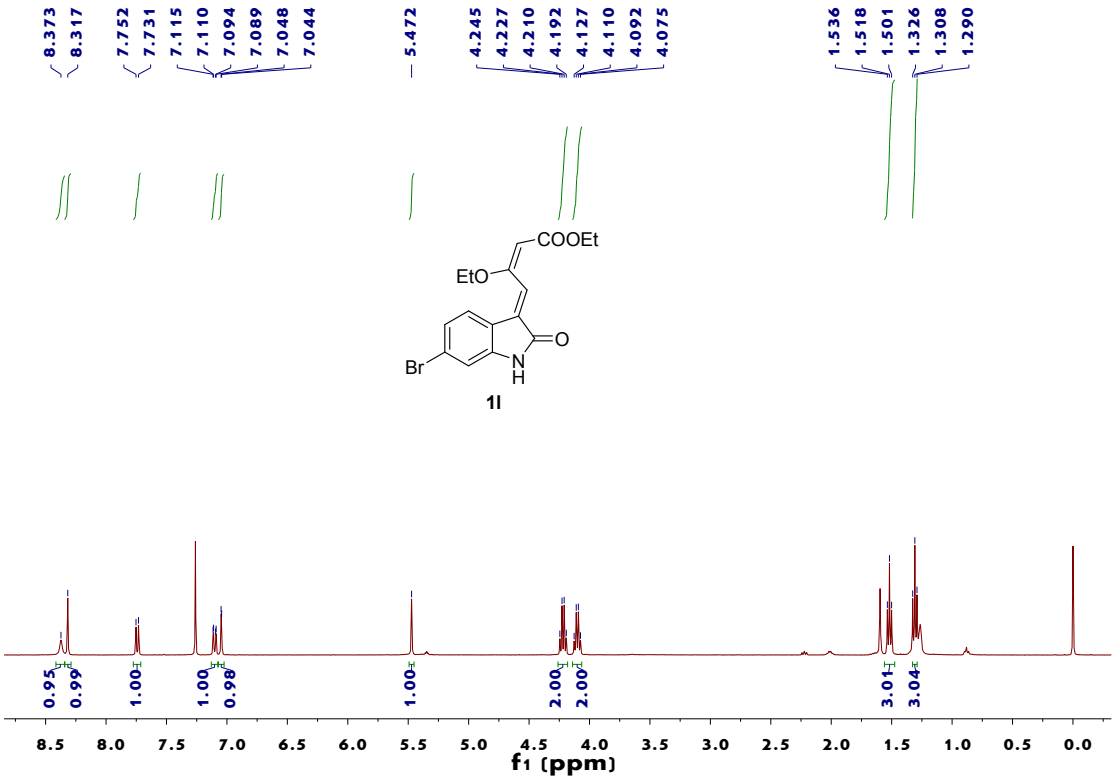
163.744
145.373
135.286
129.681
128.300
125.909
121.106
119.305
110.013
98.805
64.988
59.715
14.199
13.916
COOEt
EtO
O
Cl
N
H
1k
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.731
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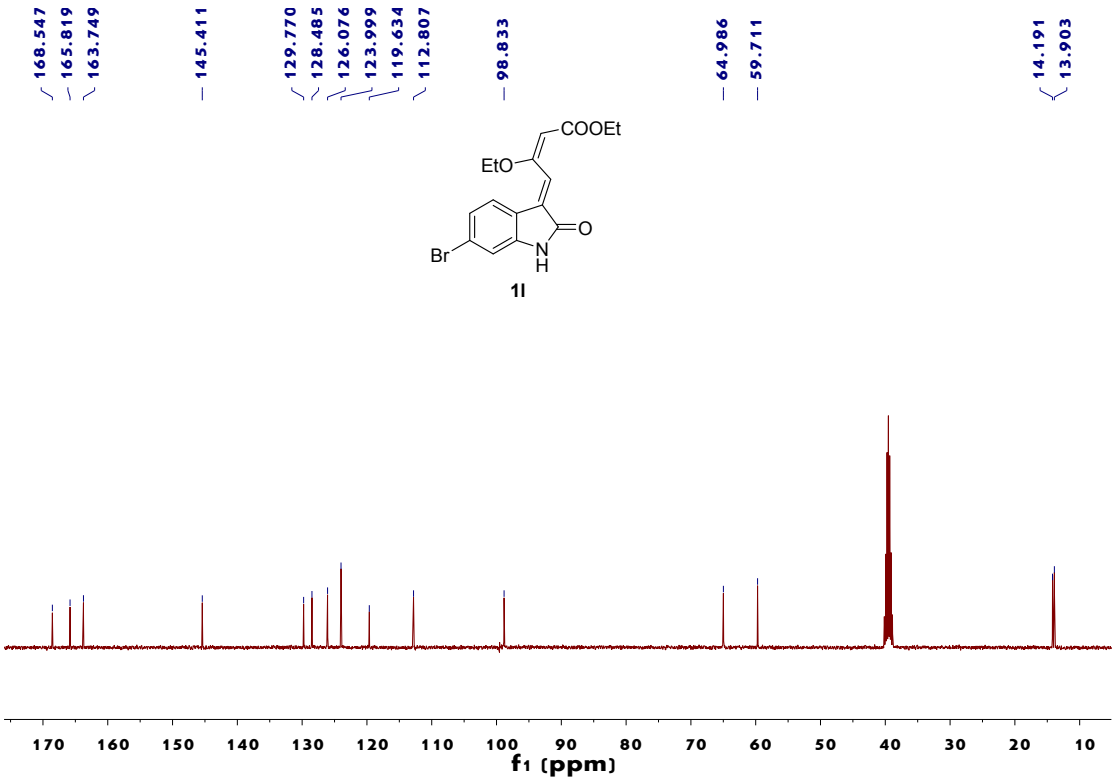
7.110
7.094
7.089
7.048
7.044
5.472
4.245
4.227
4.210
4.192
4.127
4.110
4.092
4.075
1.536
1.518
1.501
1.326
1.308
1.290
COOEt
EtO
O
Br
N
H
1l
0.95
0.99
1.00
1.00
0.98
1.00
2.00
2.00
3.01
3.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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145.411
129.770
128.485
126.076
123.999
119.634
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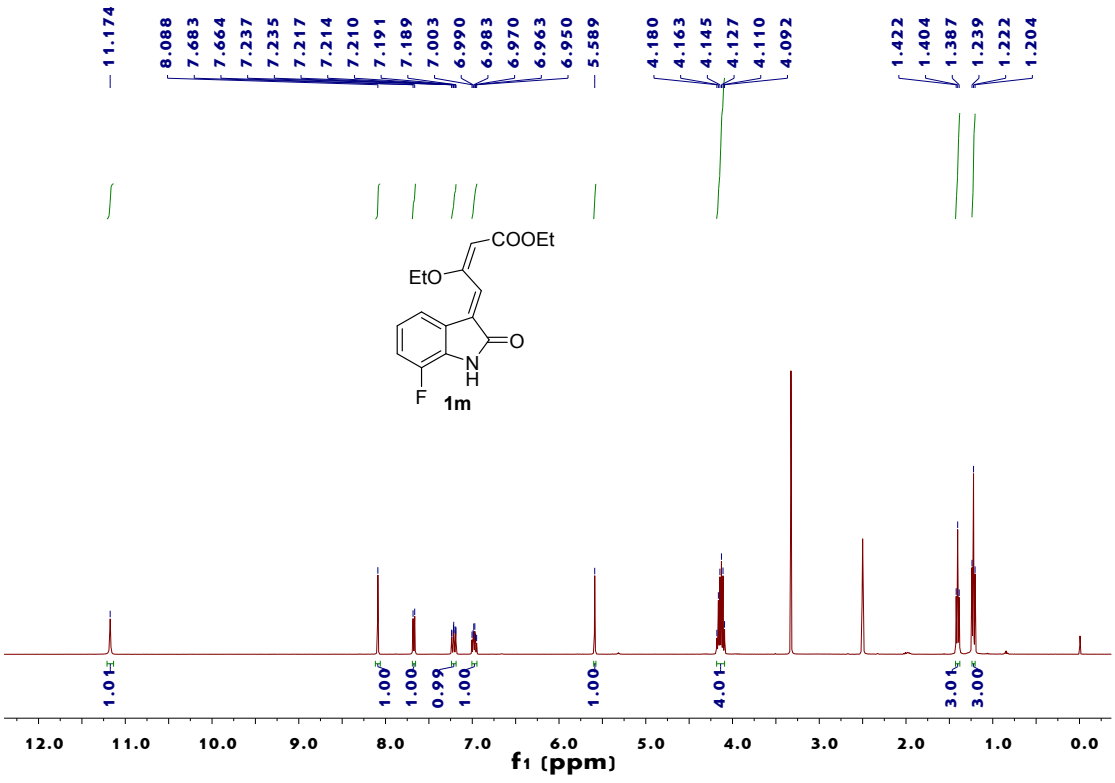
59.711
14.191
13.903
COOEt
EtO
O
N
H
Br
1l
f1 (ppm)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7.664
7.237
7.235
7.217
7.214
7.210
7.191
7.189
7.003
6.990
6.983
6.970
6.963
6.950
5.589
4.180
4.163
4.145
4.127
4.110
4.092
1.422
1.404
1.387
1.239
1.222
1.204
COOEt
EtO
O
N
H
F
1m
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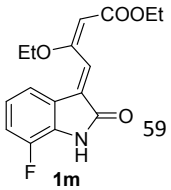
1.00
1.00
0.99
1.00
1.00
4.01
3.01
3.00
f1 (ppm)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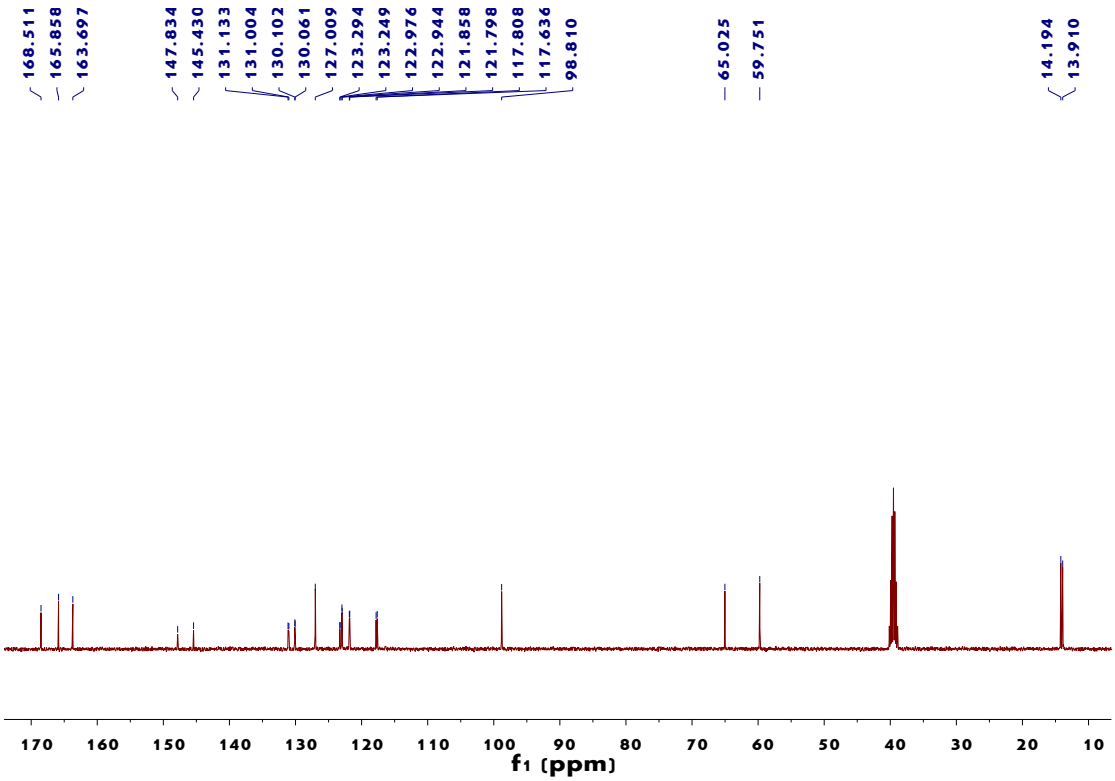
EtO
O
N
H
F
1m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145.430
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131.004
130.102
130.061
127.009
123.294
123.249
122.976
122.944
121.858
121.798
117.808
117.636
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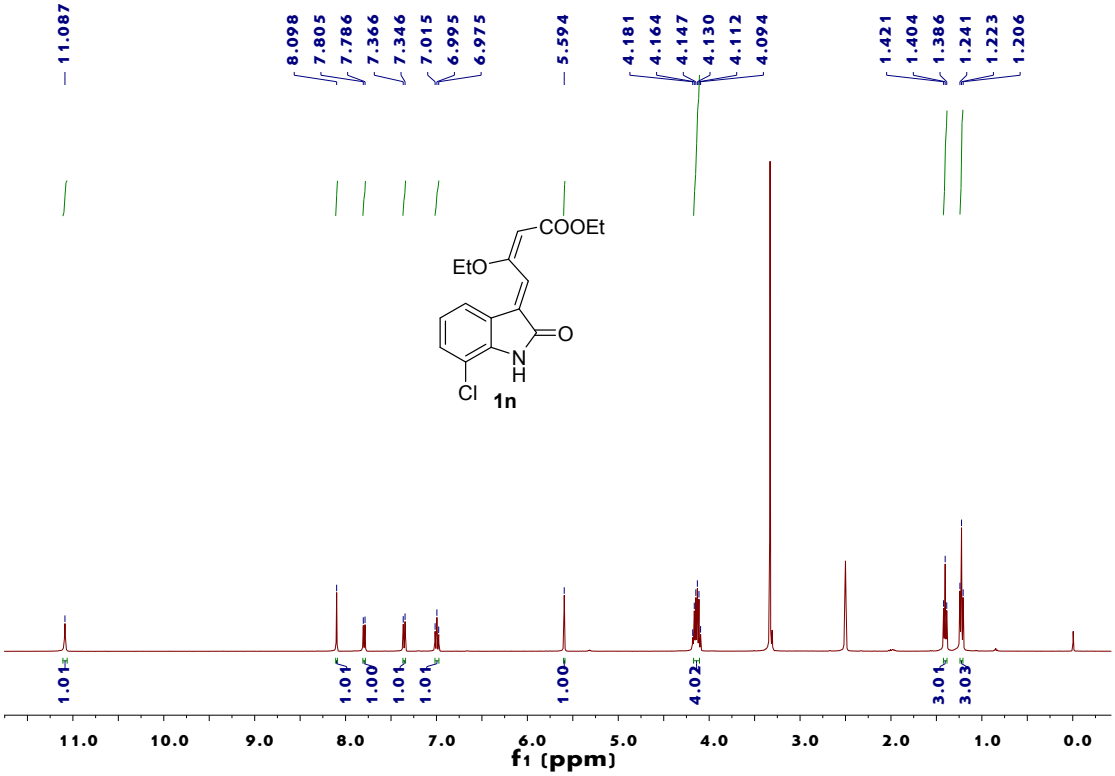
65.025
59.751
14.194
13.910
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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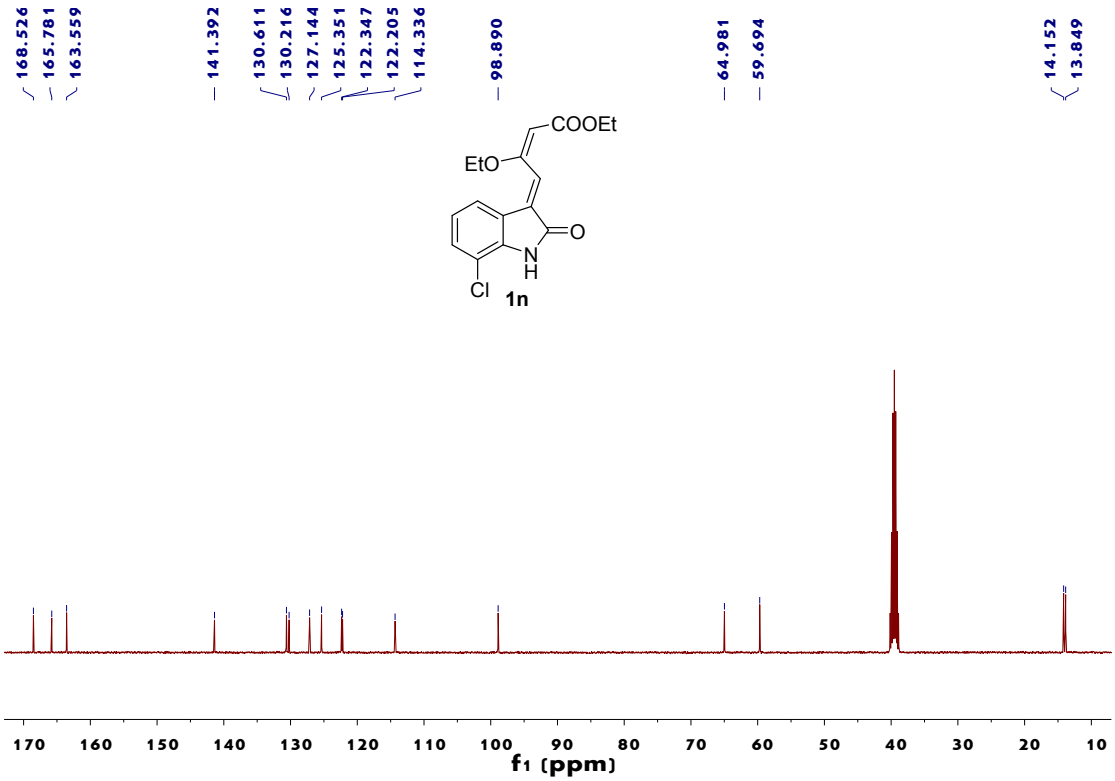
7.346
7.015
6.995
6.975
5.594
4.181
4.164
4.147
4.130
4.112
4.094
1.421
1.404
1.386
1.241
1.223
1.206
COOEt
EtO
O
N
H
Cl
1n
1.01
1.01
1.00
1.01
1.01
1.00
4.02
3.01
3.03
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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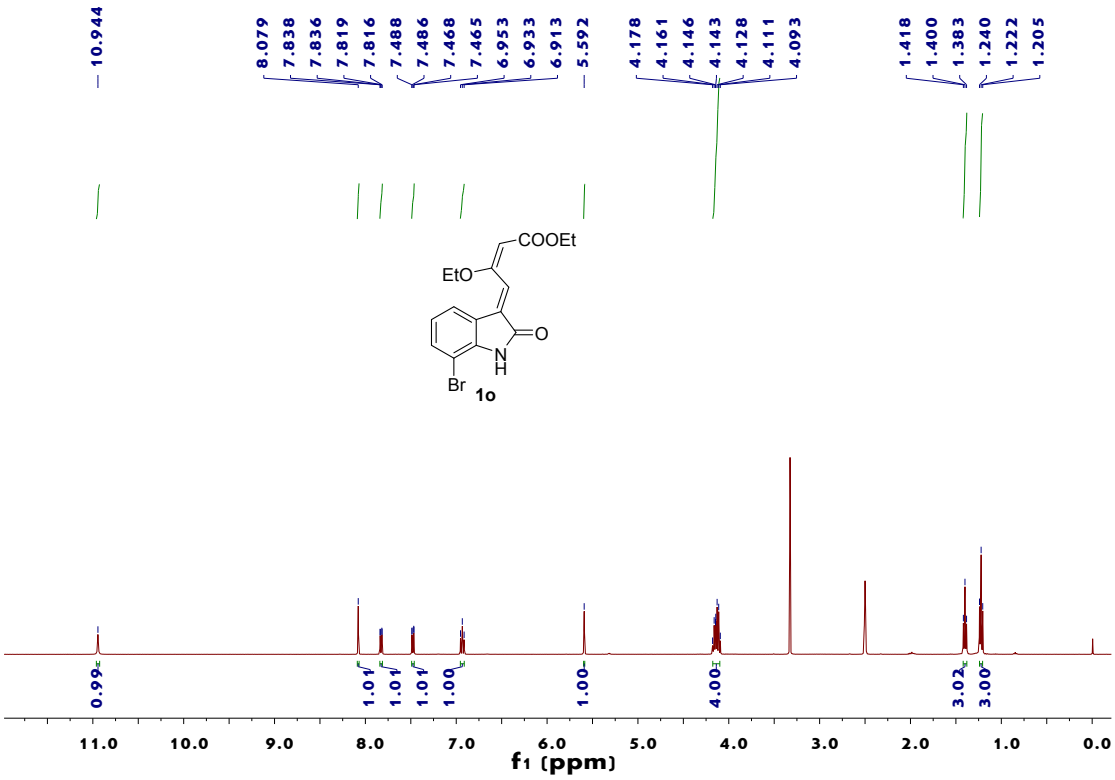
130.216
127.144
125.351
122.347
122.205
114.336
98.890
64.981
59.694
14.152
13.849
COOEt
EtO
O
N
H
Cl
1n
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.816
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7.486
7.468
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6.953
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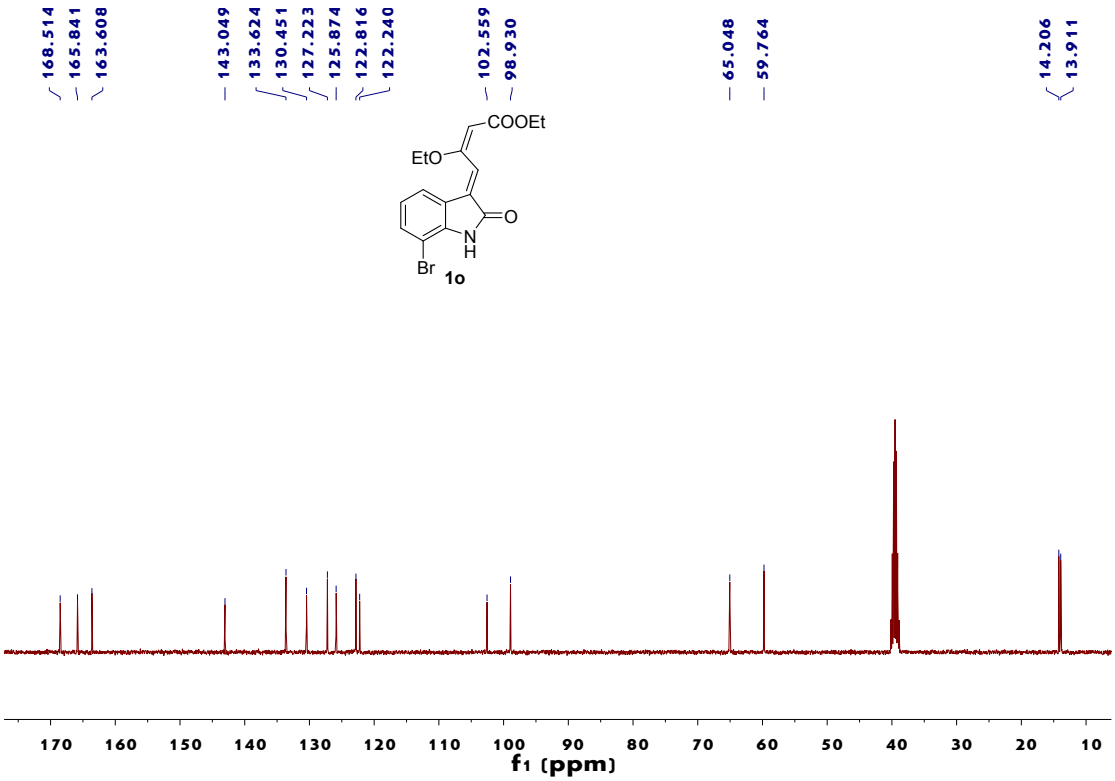
6.913
5.592
4.178
4.161
4.146
4.143
4.128
4.111
4.093
1.418
1.400
1.383
1.240
1.222
1.205
COOEt
EtO
O
N
H
Br
1o
0.99
1.01
1.01
1.01
1.00
1.00
4.00
3.02
3.00
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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130.451
127.223
125.874
122.816
122.240
102.559
98.930
65.048
59.764
14.206
13.911
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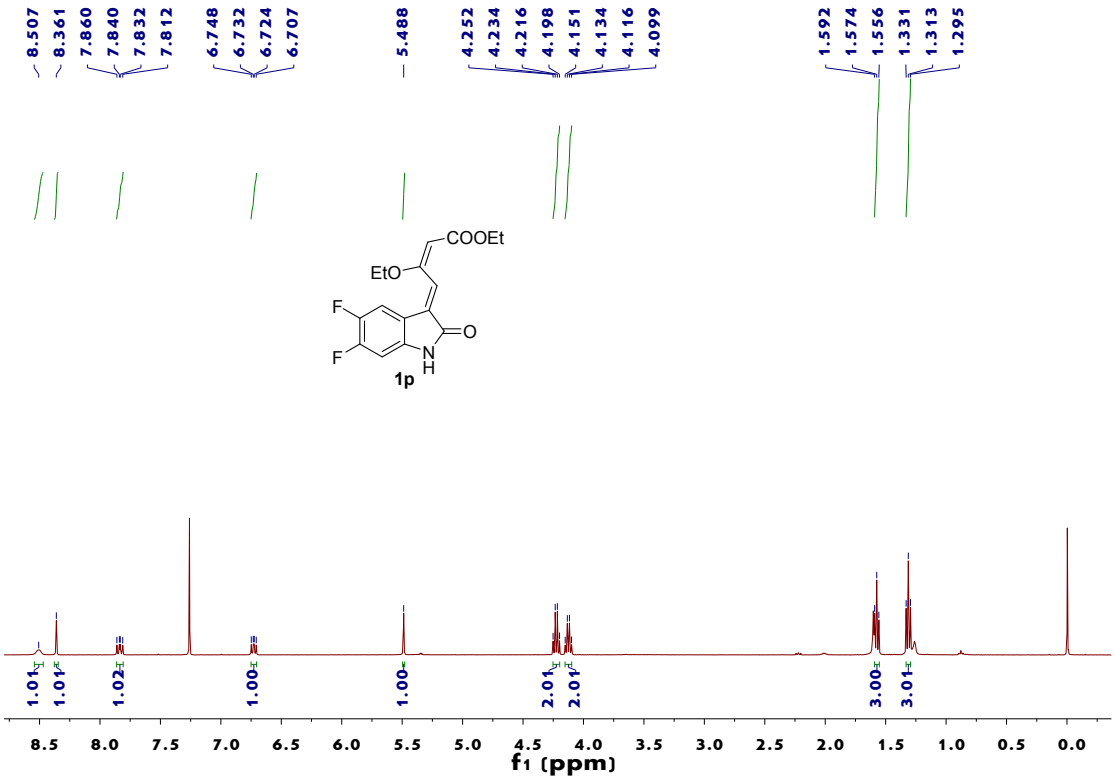
EtO
O
N
H
Br
1o
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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6.732
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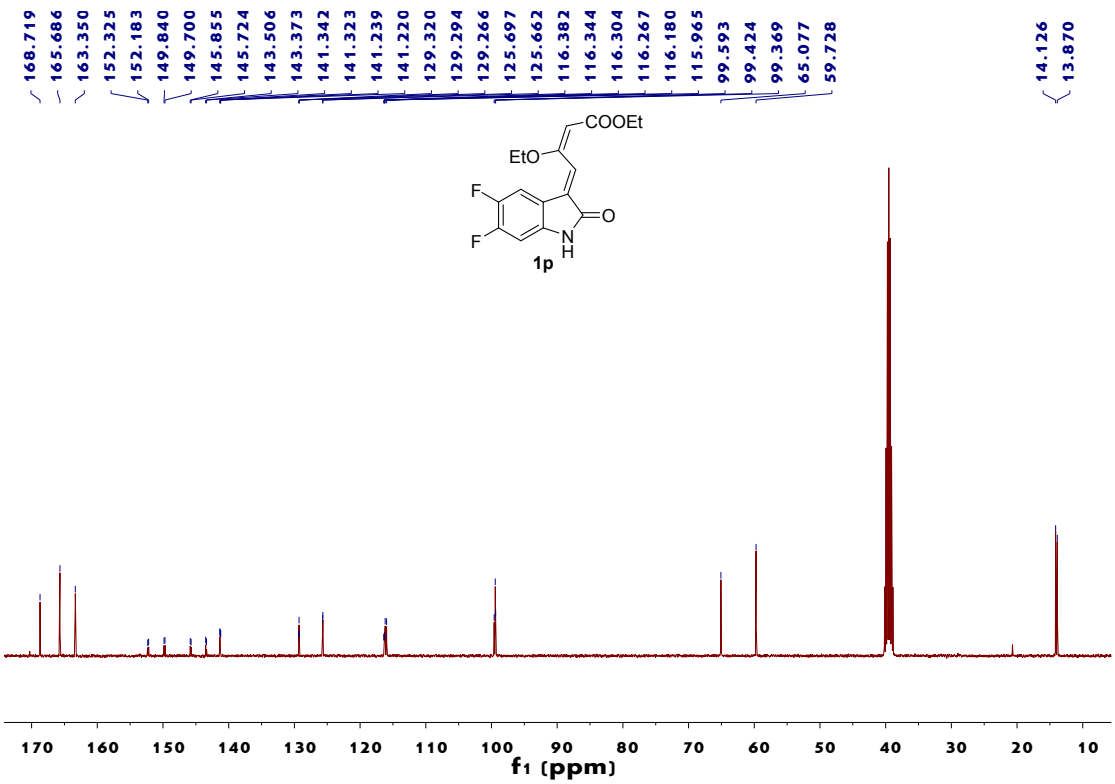
6.707
5.488
4.252
4.234
4.216
4.198
4.151
4.134
4.116
4.099
1.592
1.574
1.556
1.331
1.313
1.295
COOEt
EtO
F
F
O
N
H
1p
1.01
1.01
1.02
1.00
1.00
2.01
2.01
3.00
3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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152.325
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145.855
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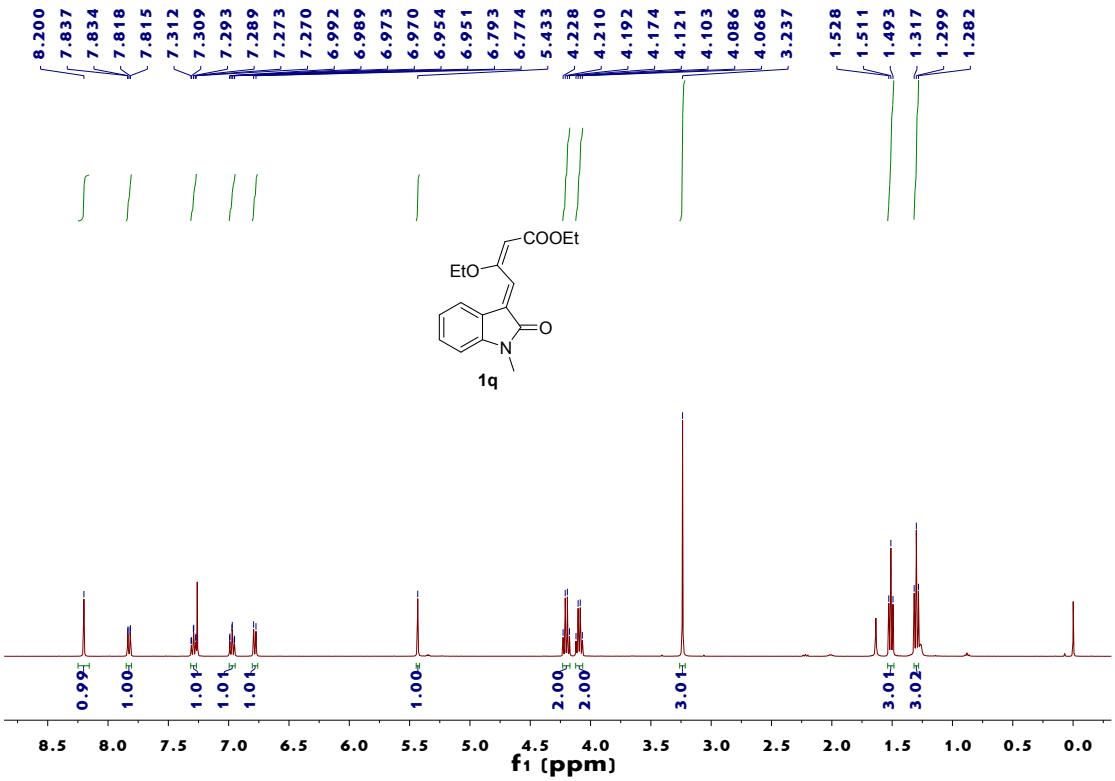
143.373
141.342
141.323
141.239
141.220
129.320
129.294
129.266
125.697
125.662
116.382
116.344
116.304
116.267
116.180
115.965
99.593
99.424
99.369
65.077
59.728
14.126
13.870
COOEt
EtO
F
F
O
N
H
1p
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.293
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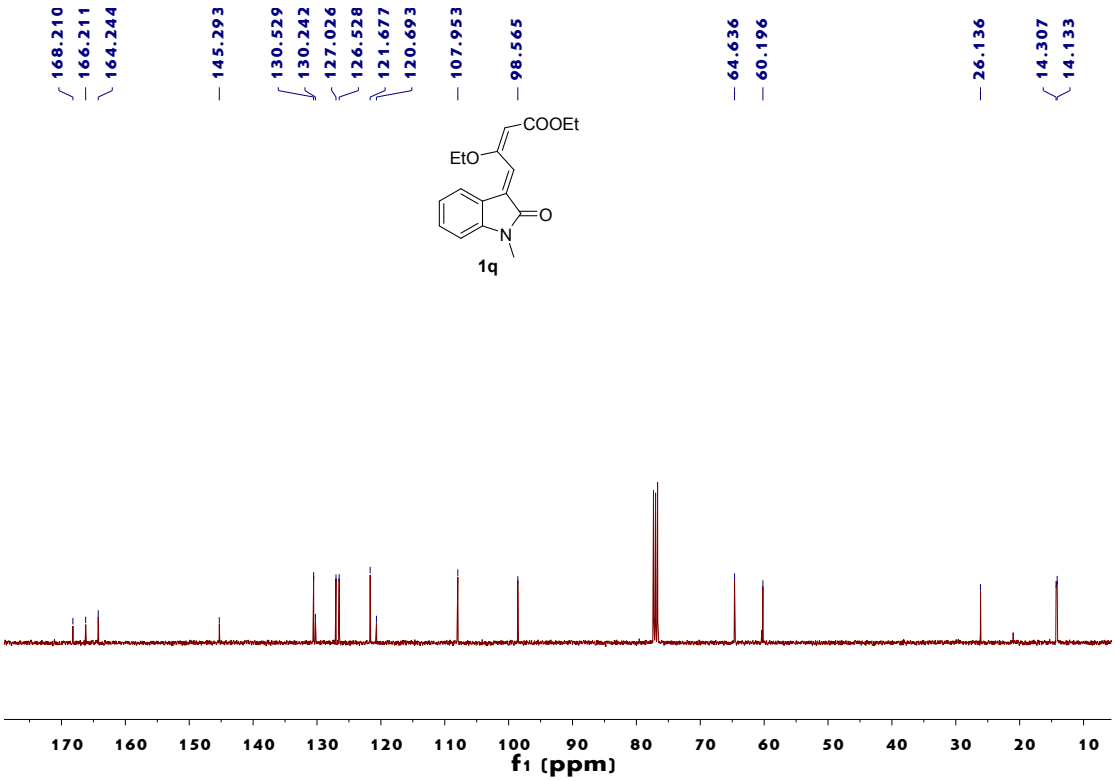
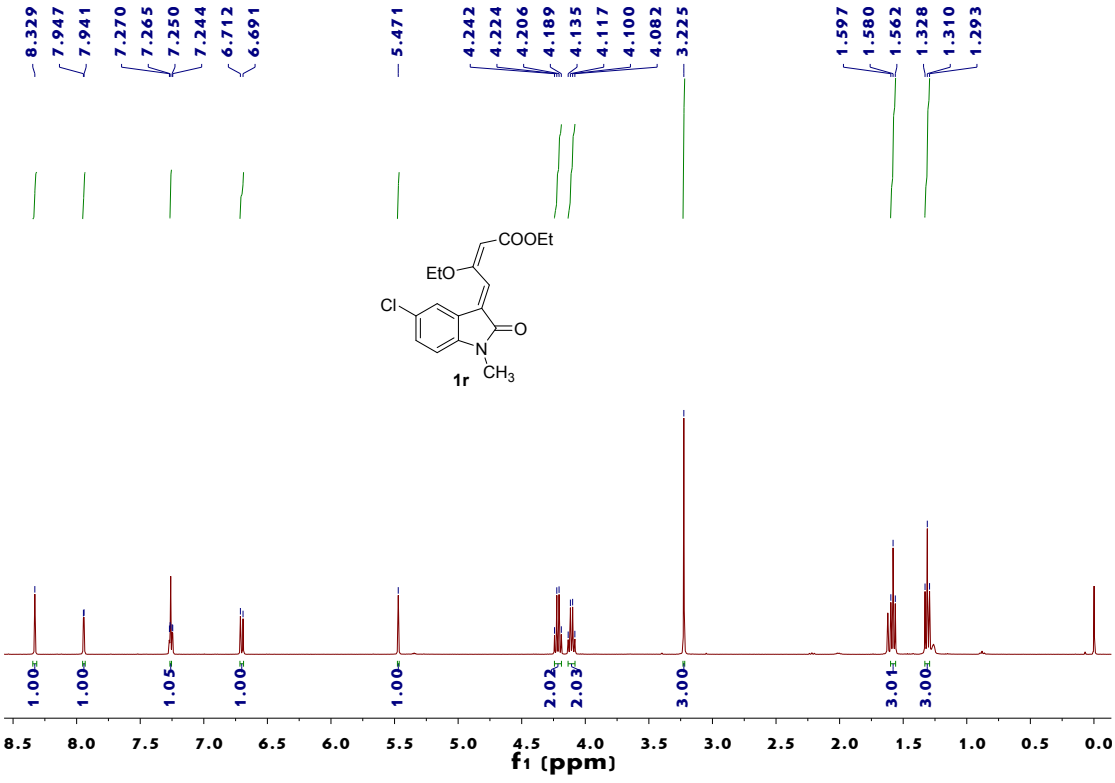
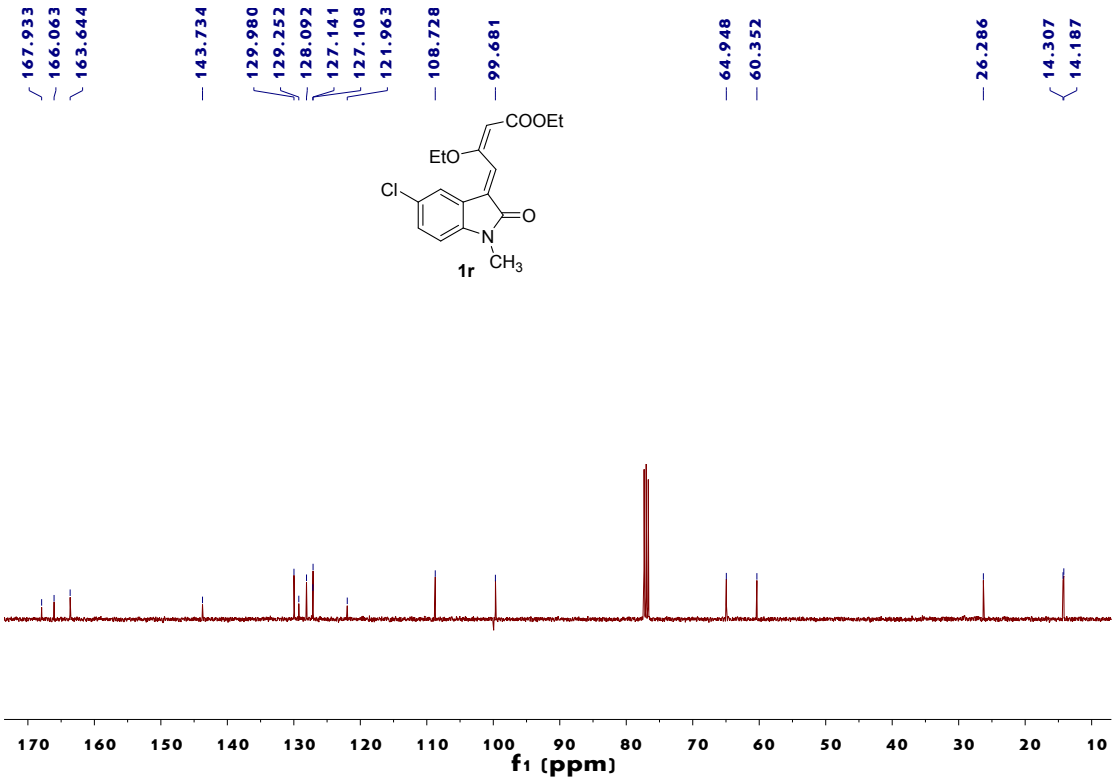
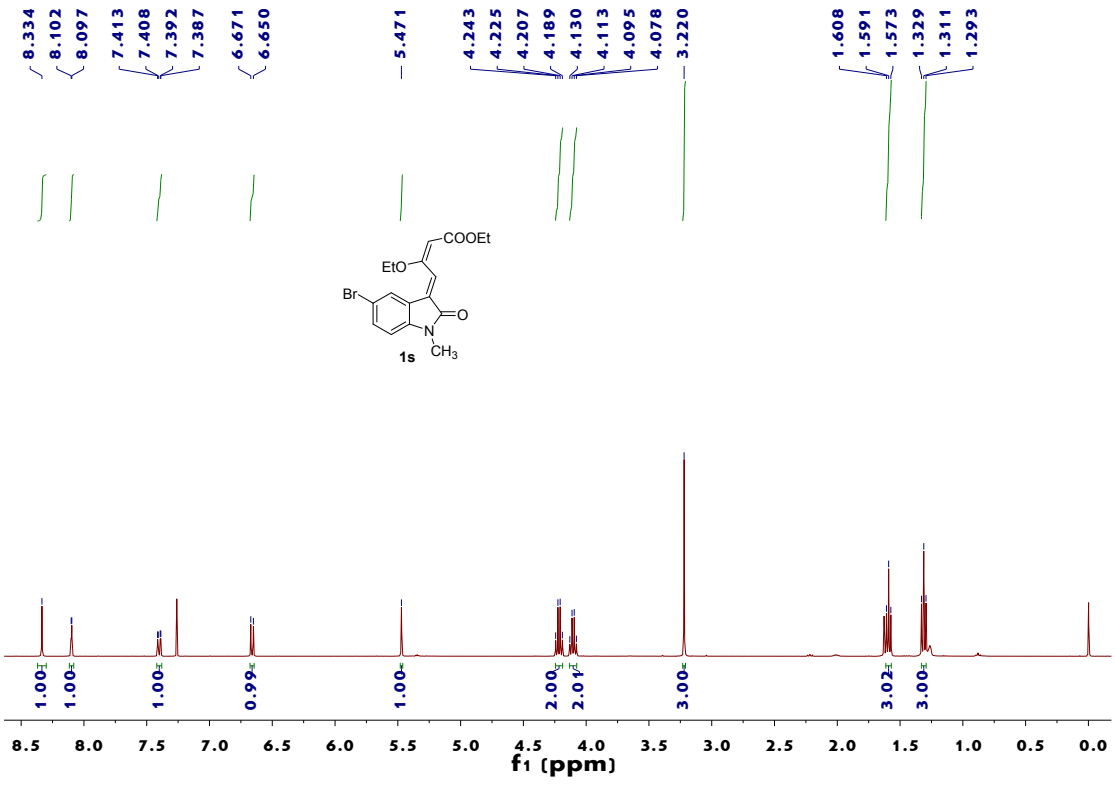
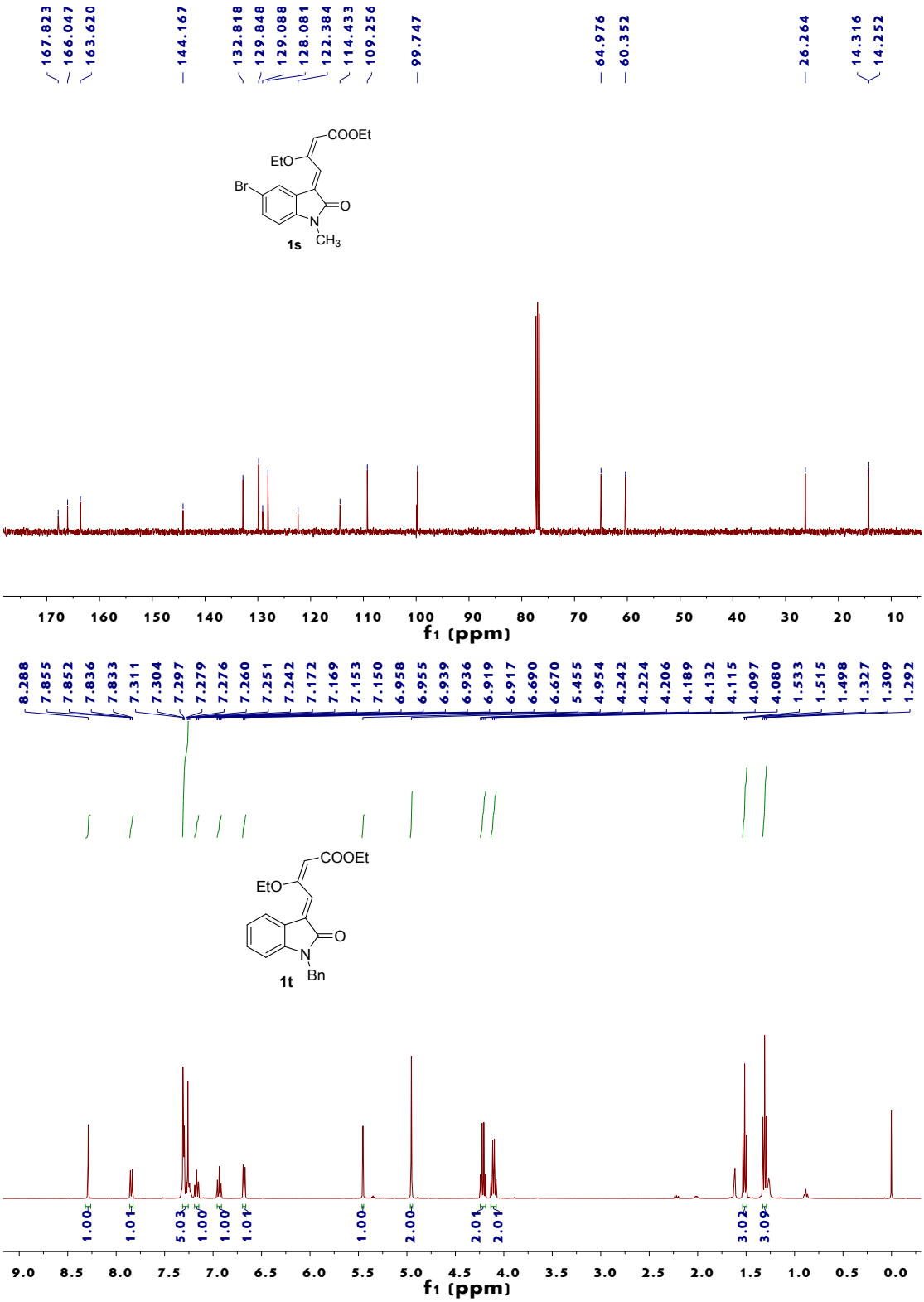
7.270
6.992
6.989
6.973
6.970
6.954
6.951
6.793
6.774
5.433
4.228
4.210
4.192
4.174
4.121
4.103
4.086
4.068
3.237
1.528
1.511
1.493
1.317
1.299
1.282
COOEt
EtO
O
N
1q
0.99
1.00
1.01
1.01
1.01
1.00
2.00
2.00
3.01
3.01
3.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

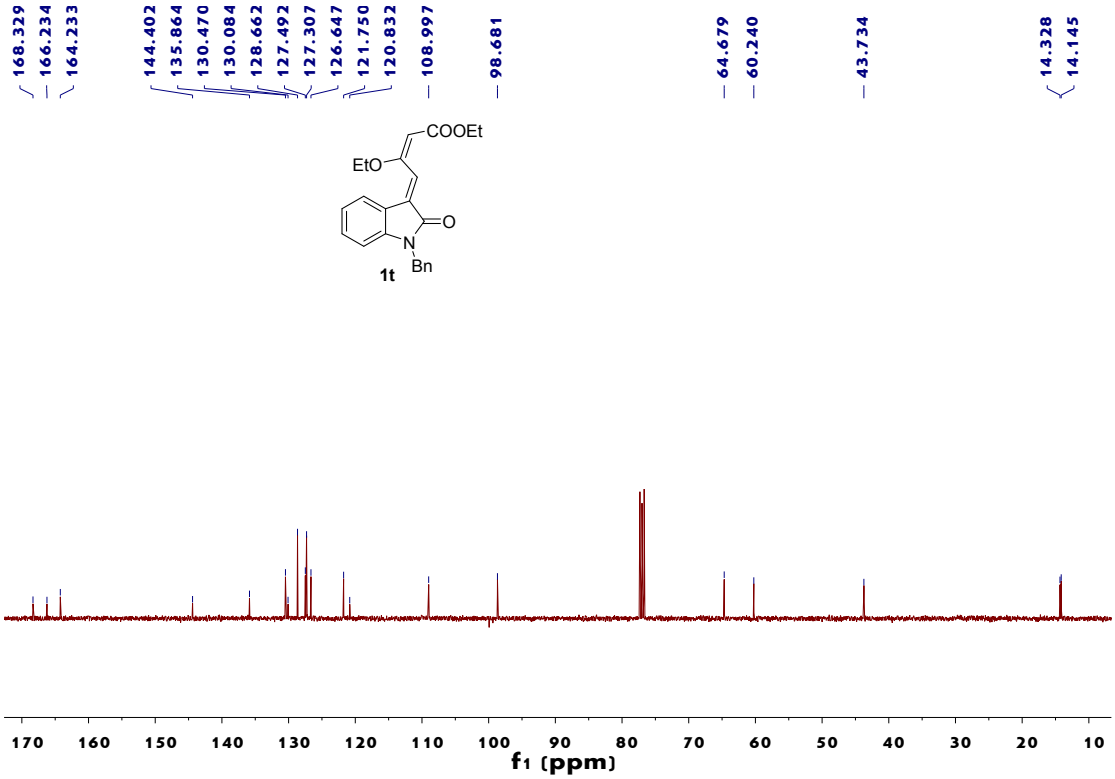

168.210
166.211
164.244
145.293
130.529
130.242
127.026
126.528
121.677
120.693
107.953
98.565
64.636
60.196
26.136
14.307
14.133
COOEt
EtO
O
N
1q
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

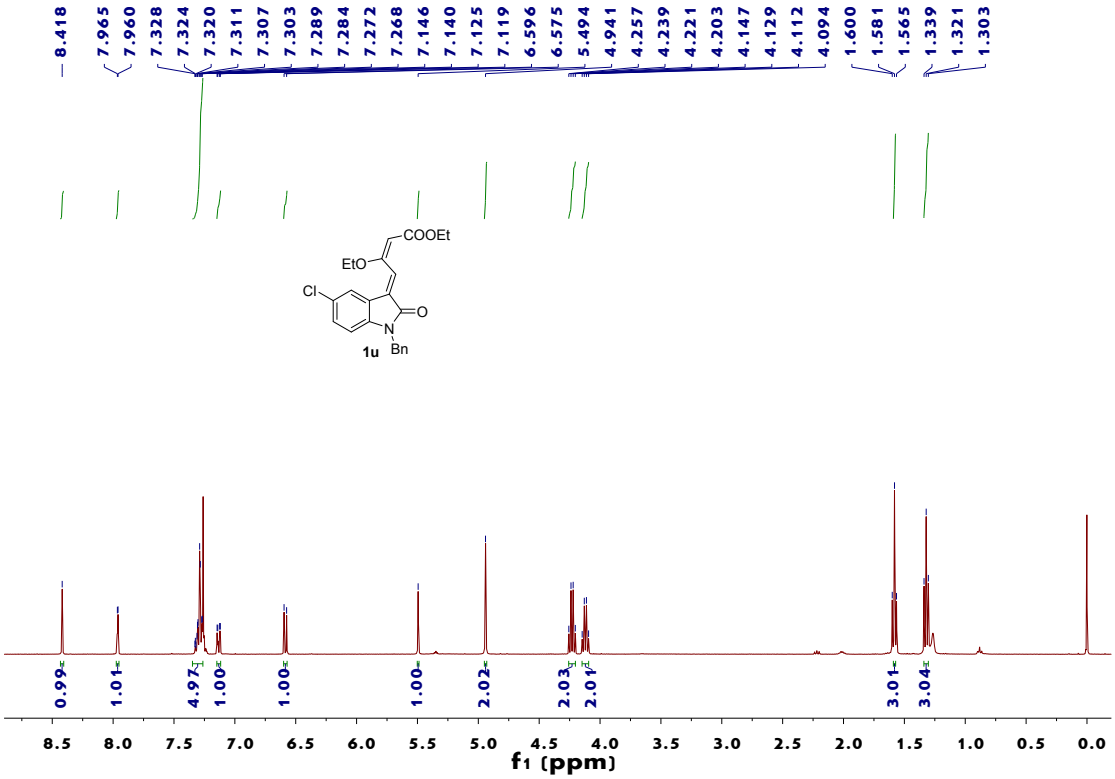

8.329
7.947
7.941
7.270
7.265
7.250
7.244
6.712
6.691
5.471
4.242
4.224
4.206
4.189
4.135
4.117
4.100
4.082
3.225
1.597
1.580
1.562
1.328
1.310
1.293
COOEt
EtO
Cl
O
N
CH3
1r
1.00
1.00
1.05
1.00
1.00
2.02
2.03
3.00
3.01
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

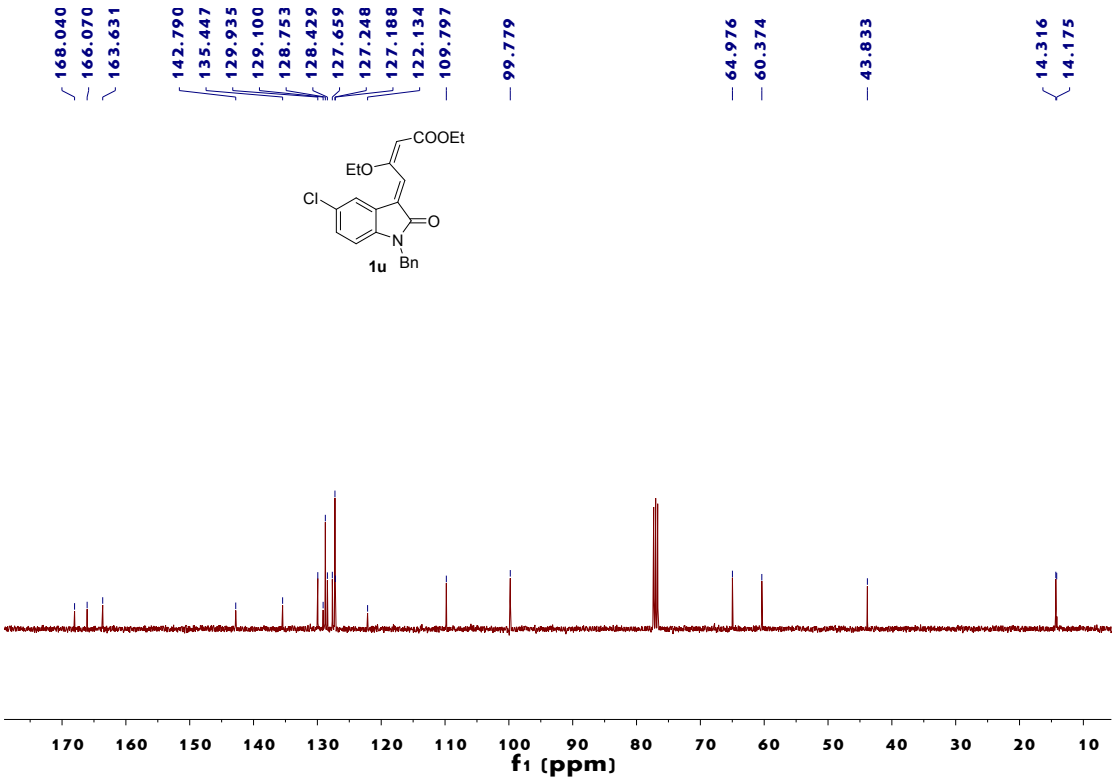

167.933
166.063
163.644
143.734
129.980
129.252
128.092
127.141
127.108
121.963
108.728
99.681
64.948
60.352
26.286
14.307
14.187
COOEt
EtO
Cl
O
N
CH3
1r
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

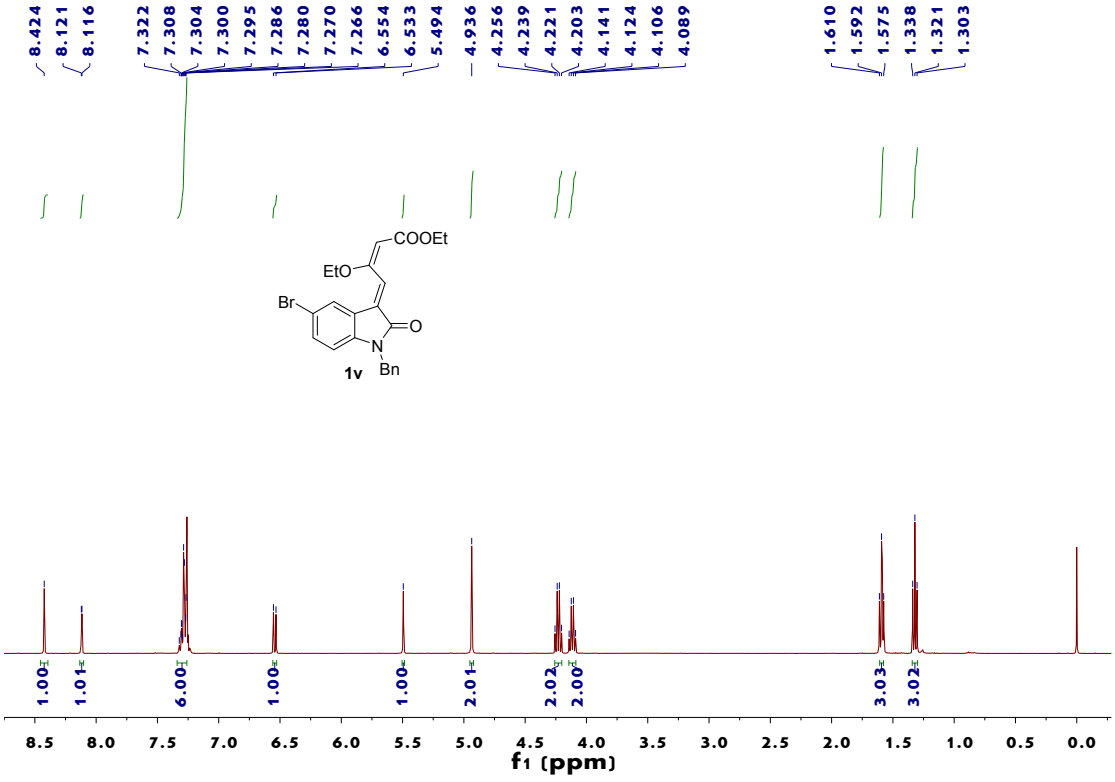

8.334
8.102
8.097
7.413
7.408
7.392
7.387
6.671
6.650
5.471
4.243
4.225
4.207
4.189
4.130
4.113
4.095
4.078
3.220
1.608
1.591
1.573
1.329
1.311
1.293
COOEt
EtO
Br
O
N
CH3
1s
1.00
1.00
1.00
0.99
1.00
2.00
2.01
3.00
3.02
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

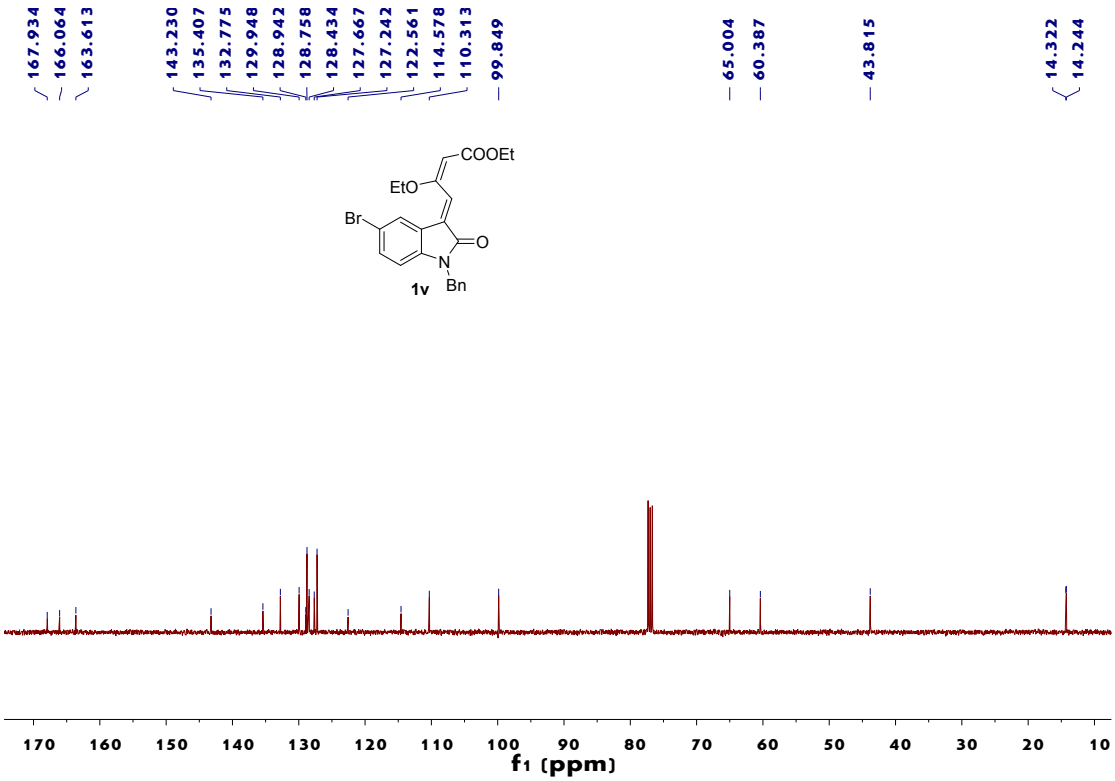

167.823
166.047
163.620
144.167
132.818
129.848
129.088
128.081
122.384
114.433
109.256
99.747
64.976
60.352
26.264
14.316
14.252
COOEt
EtO
Br
O
N
CH3
1s
f1 (ppm)
8.288
7.855
7.852
7.836
7.833
7.311
7.304
7.297
7.279
7.276
7.260
7.251
7.242
7.172
7.169
7.153
7.150
6.958
6.955
6.939
6.936
6.919
6.917
6.690
6.670
5.455
4.954
4.242
4.224
4.206
4.189
4.132
4.115
4.097
4.080
1.533
1.515
1.498
1.327
1.309
1.292
COOEt
EtO
O
N
Bn
1t
1.00
1.01
5.03
1.00
1.00
1.01
1.00
2.00
2.01
2.01
3.02
3.09
f1 (ppm)

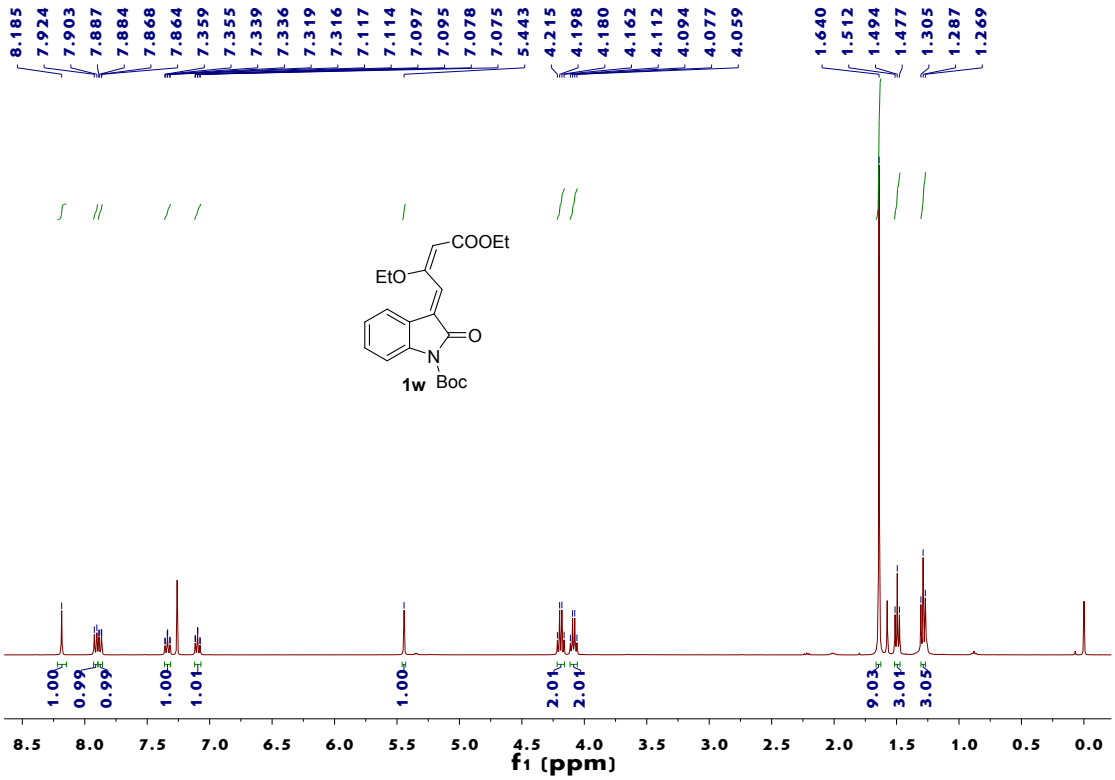

168.329
166.234
164.233
144.402
135.864
130.470
130.084
128.662
127.492
127.307
126.647
121.750
120.832
108.997
98.681
64.679
60.240
43.734
14.328
14.145
COOEt
EtO
O
N
Bn
1t
f1 (ppm)

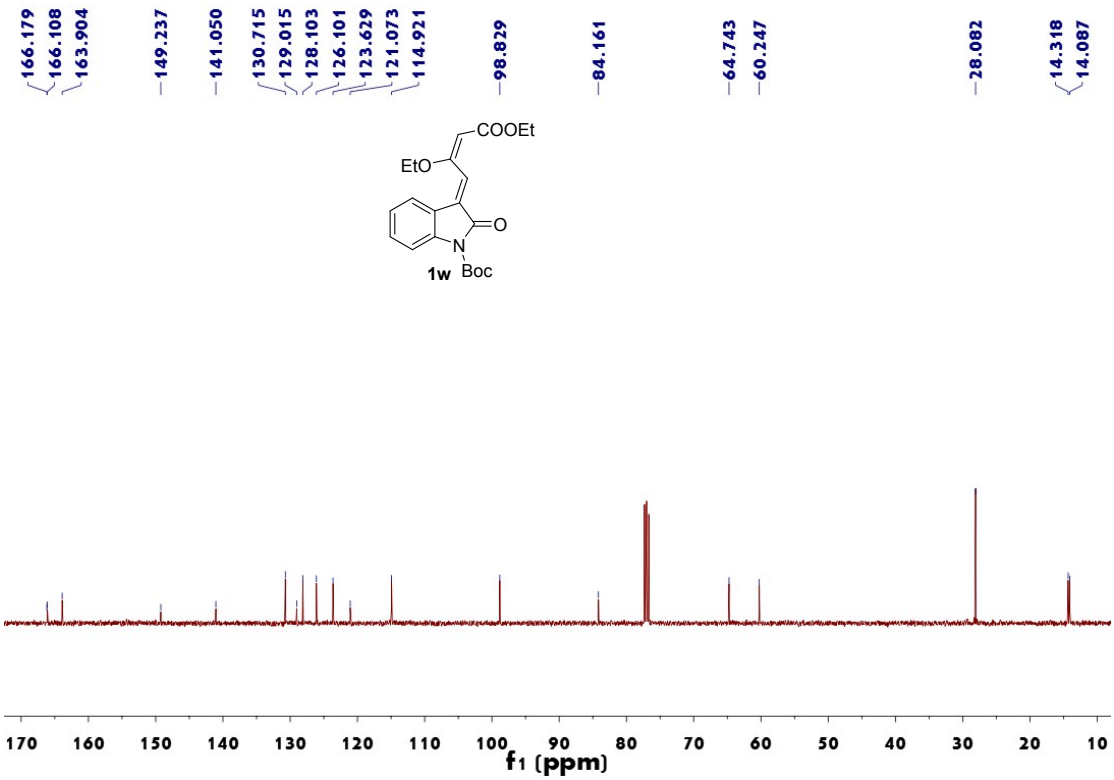

8.418
7.965
7.960
7.328
7.324
7.320
7.311
7.307
7.303
7.289
7.284
7.272
7.268
7.146
7.140
7.125
7.119
6.596
6.575
5.494
4.941
4.257
4.239
4.221
4.203
4.147
4.129
4.112
4.094
1.600
1.581
1.565
1.339
1.321
1.303
COOEt
EtO
Cl
O
N
Bn
1u
0.99
1.01
4.97
1.00
1.00
1.00
2.02
2.03
2.01
3.01
3.04
f1 (ppm)

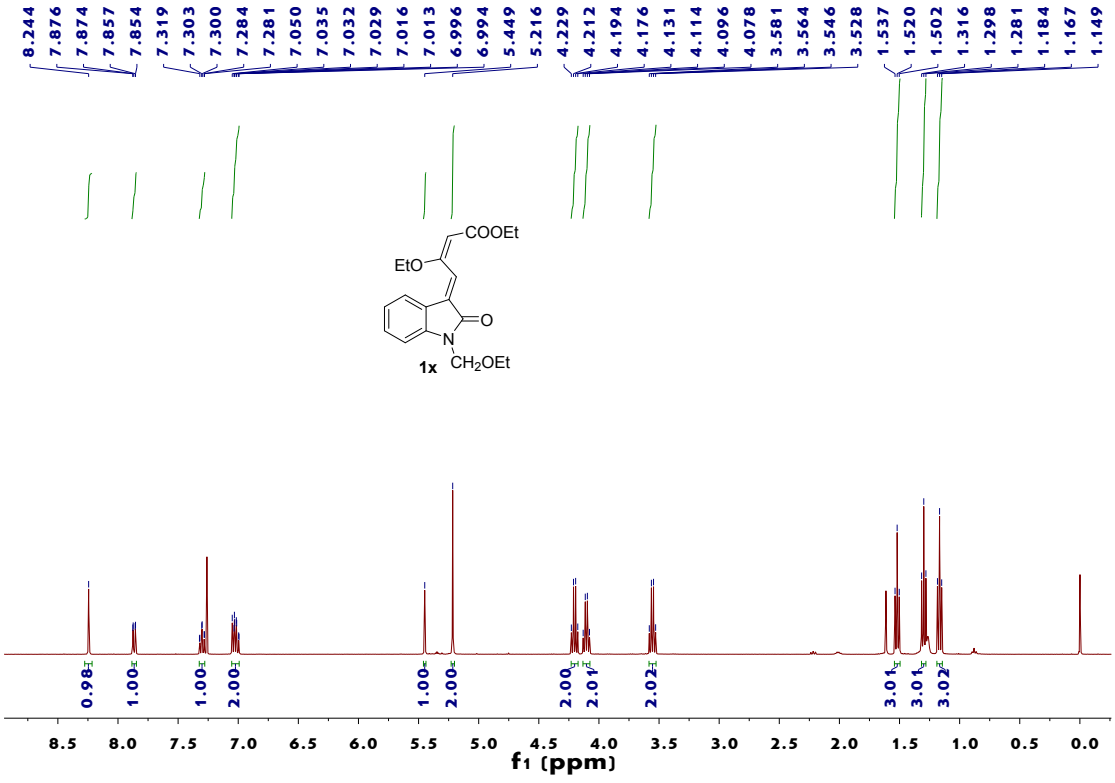

168.040
166.070
163.631
142.790
135.447
129.935
129.100
128.753
128.429
127.659
127.248
127.188
122.134
109.797
99.779
64.976
60.374
43.833
14.316
14.175
COOEt
EtO
Cl
O
N
Bn
1u
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

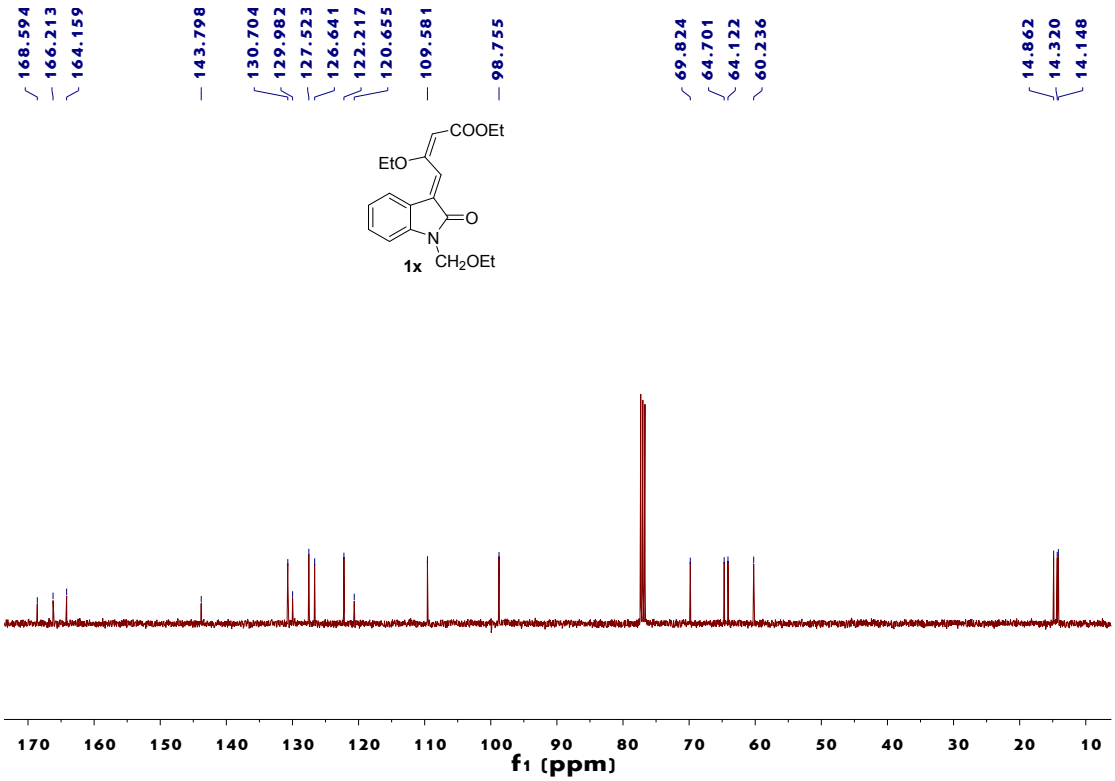

8.424
8.121
8.116
7.322
7.308
7.304
7.300
7.295
7.286
7.280
7.270
7.266
6.554
6.533
5.494
4.936
4.256
4.239
4.221
4.203
4.141
4.124
4.106
4.089
1.610
1.592
1.575
1.338
1.321
1.303
COOEt
EtO
Br
O
N
Bn
1v
1.00
1.01
6.00
1.00
1.00
2.01
2.02
2.00
3.03
3.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

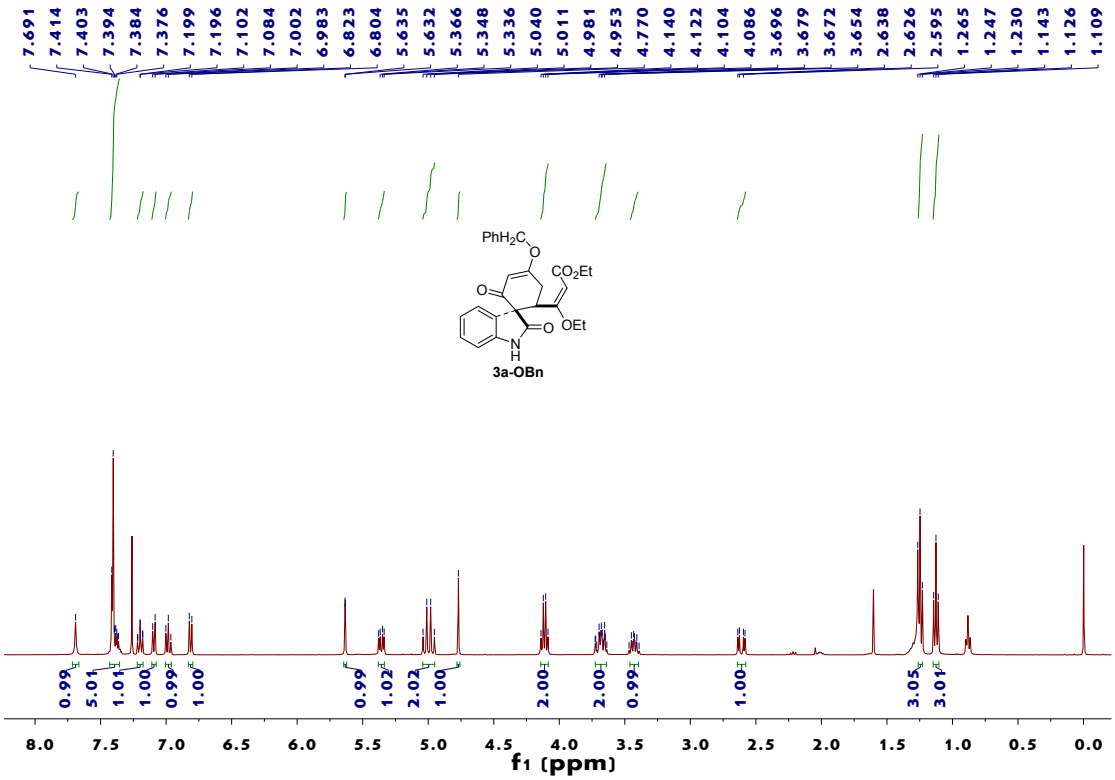

167.934
166.064
163.613
143.230
135.407
132.775
129.948
128.942
128.758
128.434
127.667
127.242
122.561
114.578
110.313
99.849
65.004
60.387
43.815
14.322
14.244
COOEt
EtO
Br
O
N
Bn
1v
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

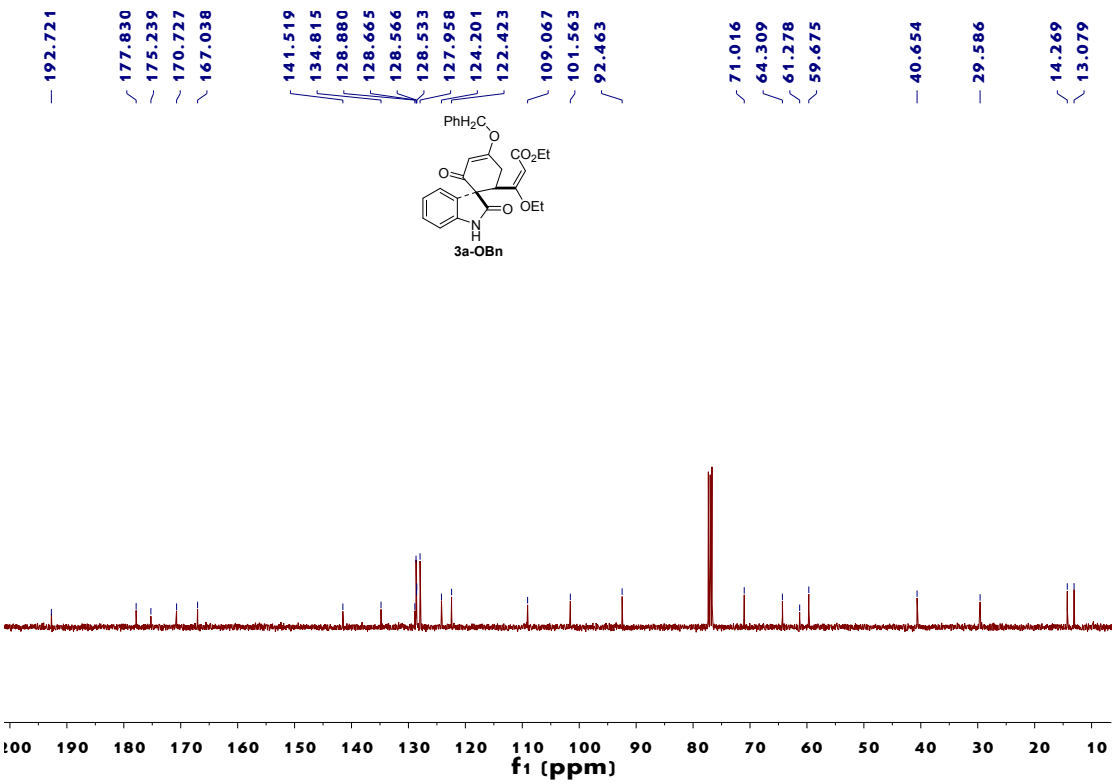

8.185
7.924
7.903
7.887
7.884
7.868
7.864
7.359
7.355
7.339
7.336
7.319
7.316
7.117
7.114
7.097
7.095
7.078
7.075
5.443
4.215
4.198
4.180
4.162
4.112
4.094
4.077
4.059
1.640
1.512
1.494
1.477
1.305
1.287
1.269
COOEt
EtO
O
N
Boc
1w
1.00
0.99
0.99
1.00
1.01
1.00
2.01
2.01
9.03
3.01
3.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.179
166.108
163.904
149.237
141.050
130.715
129.015
128.103
126.101
123.629
121.073
114.921
98.829
84.161
64.743
60.247
28.082
14.318
14.087
COOEt
EtO
O
N
Boc
1w
f1 (ppm)


8.244
7.876
7.874
7.857
7.854
7.319
7.303
7.300
7.284
7.281
7.050
7.035
7.032
7.029
7.016
7.013
6.996
6.994
5.449
5.216
4.229
4.212
4.194
4.176
4.131
4.114
4.096
4.078
3.581
3.564
3.546
3.528
1.537
1.520
1.502
1.316
1.298
1.281
1.184
1.167
1.149
COOEt
EtO
O
N
CH2OEt
1x
0.98
1.00
1.00
2.00
1.00
2.00
2.00
2.01
2.02
3.01
3.01
3.02
f1 (ppm)

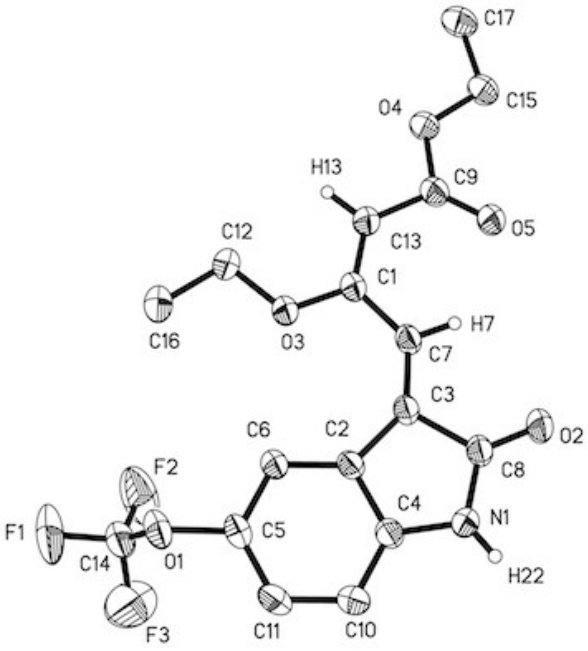

168.594
166.213
164.159
143.798
130.704
129.982
127.523
126.641
122.217
120.655
109.581
98.755
69.824
64.701
64.122
60.236
14.862
14.320
14.148
COOEt
EtO
O
N
CH2OEt
1x
f1 (ppm)


7.691
7.414
7.403
7.394
7.384
7.376
7.199
7.196
7.102
7.084
7.002
6.983
6.823
6.804
5.635
5.632
5.366
5.348
5.336
5.040
5.011
4.981
4.953
4.770
4.140
4.122
4.104
4.086
3.696
3.679
3.672
3.654
2.638
2.626
2.595
1.265
1.247
1.230
1.143
1.126
1.109
PhH2C
O
CO2Et
OEt
N
H
3a-OBn
f1 (ppm)

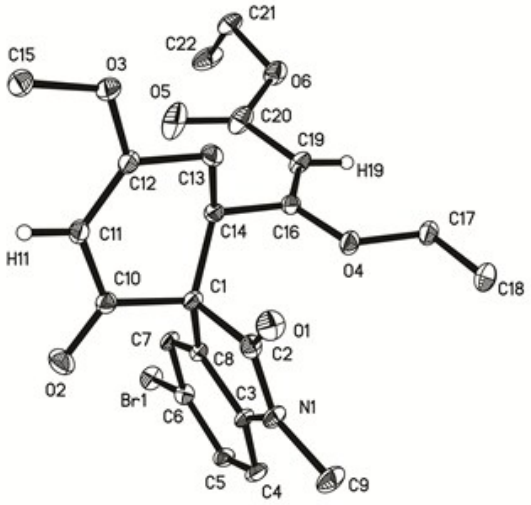


5 X-ray structure of **1h** and **3s**

1h



3s


C21
C22
C15
O3
O6
O5
C20
C19
H19
C12
C13
C17
C11
C14
C16
H11
O4
C10
C1
C18
O1
C7
C8
C2
O2
Br1
C3
N1
C6
C5
C4
C9