Supporting information

Efficient Access to Chiral Dihydrobenzoxazinones via Rh-Catalyzed Hydrogenation

Ziyi Chen,[a] Xuguang Yin,[a] Xiu-Qin Dong,*[a] and Xumu Zhang[a,b]

[a] Key Laboratory of Biomedical Polymers, Engineering Research Centre of Organosilicon Compounds & Materials, Ministry of Education, College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei, 430072, P. R. China.

[b] Department of Chemistry and Shenzhen Grubbs Institute, Southern University of Science and Technology, Shenzhen, Guangdong, 518055, P. R. China.

E-mail address: xiuqindong@whu.edu.cn.

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I. General remark

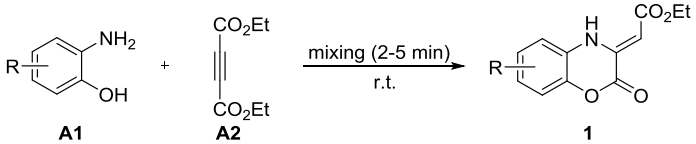
Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification. Anhydrous solvents were purchased from J&K and transferred by syringe. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker ADVANCE III (400 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts are reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the $CDCl_3$ at 7.26 ppm (for ^{1}H NMR) or 77.00 ppm (for ^{13}C NMR). Data are reported as: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in hertz (Hz) and signal area integration in natural numbers. ^{13}C NMR analyses were run with decoupling. Enantiomeric excess values were determined by Daicel chiral column on an Agilent 1260 Series HPLC instrument. Optical rotations [α]D were measured on a PERKIN ELMER polarimeter 343 instrucment. Column Chromatography was performed with silica gel Merck 60 (300-400 mesh).

Substrate **1** were synthesized from the corresponding substituted aminophenol according to method A.[1] The corresponding substituted aminophenol of **1g** and **1h** were prepared according to method B.[2]

The absolute configuration of product **2d** is (*R*), which was determined by X-ray analysis.[3] The absolute configurations of other hydrogenation products were assigned by analogy.

II. General procedure for the synthesis of substrates

General procedure of method A



A1 A2 1

To a beaker with pre-weighted solid aminophenol (**A1**, 5 mmol), a dropwise of stoichiometric diethyl acetylenedicarboxylate (**A2**, 5 mmol) was added slowly and

stirred with the help of a spatula for 2-5 minutes. The liquid disappeared and a relatively exothermic phenomenon occurred, and then were purified by flash chromatography on silica gel. They were further purified through recrystalization in CH_2Cl_2 and petroleum ether to give the substrate **1** (**1l** was prepared with dimethyl acetylenedicarboxylate).

General procedure of method B

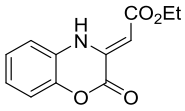
Step 1

To a stirred suspension of substituted phenol (**S1**, 10 mmol) in acetonitrile (30 mL), solid sodium nitrite (1.5 equiv.) and potassium hydrogen sulfate (2.0 equiv.) was then added. Later maintained the reaction temperature at 50 °C for 4-6 h and the crude product was analyzed by GC-MS. The reaction was vacuumed to evaporate acetonitrile and then extracted with H_2O (30 mL) and ethanol acetate (30 mL×2). The organic layer was dried over Na_2SO_4, concentrated and purified by flash chromatography on silica gel to give the product for step 2.

Step 2

To a suspension of corresponding *O*-nitrophenol (**S2**) in dichloromethane, Pd/C powder (5 %) was added. In the atmosphere of H_2 at 5 atm and being stirred for 6 h, **S2** was hydrogenated to generate corresponding substituted aminophenol (**S3**). Then **S3** was used for the synthesis of **1g** and **1h** according to method A.

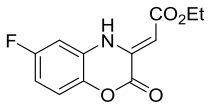
Ethyl (*Z*)-2-(2-oxo-2H-benzo[b][1,4]oxazin-3(4H)-ylidene)acetate **1a**



Yellow solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 10.68 (s, 1H), 7.15-7.11 (m, 2H), 7.02 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.96 (dd, *J* = 8.3, 1.4 Hz, 1H), 5.92 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ =

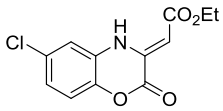
169.87, 155.92, 139.93, 137.98, 125.61, 124.17, 122.66, 116.96, 114.76, 91.10, 60.34, 14.23.

Ethyl (*Z*)-2-(6-fluoro-2-oxo-2H-benzo[b][1,4]oxazin-3(4H)-ylidene)acetate **1b**



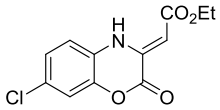
Yellow solid; m. p. 110-112 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 10.70 (s, 1H), 7.10 (dd, *J* = 8.5, 4.9 Hz, 1H), 6.74-6.68 (m, 2H), 5.97 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 169.74, 159.71 (d, *J* = 243.0 Hz), 155.58, 137.31, 136.11 (d, *J* = 3.0 Hz), 125.06 (d, *J* = 12.0 Hz), 118.13 (d, *J* = 9.0 Hz), 109.24 (d, *J* = 24.0 Hz), 101.91 (d, *J* = 28.0 Hz), 92.49, 60.59, 14.21. ESI-HRMS Calculated for $C_{12}H_{11}FNO_4^+$ ([M+H]$^+$): 252.0667; Found: 252.0665.

Ethyl (*Z*)-2-(6-chloro-2-oxo-2H-benzo[b][1,4]oxazin-3(4H)-ylidene)acetate **1c**



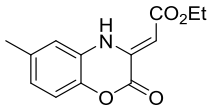
Yellow solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 10.69 (s, 1H), 7.08 (d, *J* = 9.2 Hz, 1H), 6.98-6.96 (m, 2H), 5.97 (s, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 1.33 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 169.67, 155.44, 138.48, 137.25, 130.82, 125.13, 122.49, 118.08, 114.64, 92.64, 60.61, 14.22.

Ethyl (*Z*)-2-(7-chloro-2-oxo-2H-benzo[b][1,4]oxazin-3(4H)-ylidene)acetate **1d**



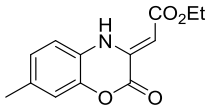
Yellow solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 10.69 (s, 1H), 7.15 (d, *J* = 1.9 Hz, 1H), 7.10 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 5.93 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 169.78, 155.28, 140.13, 137.31, 127.41, 125.71, 123.02, 117.30, 115.48, 92.03, 60.53, 14.22.

Ethyl (*Z*)-2-(6-methyl-2-oxo-2H-benzo[b][1,4]oxazin-3(4H)-ylidene)acetate **1e**



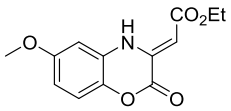
Yellow solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 10.61 (s, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.81- 6.78 (m, 1H), 6.75-6.74 (m, 1H), 5.89 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 169.88, 156.09, 138.05, 137.93, 135.65, 123.73, 123.34, 116.60, 115.00, 90.81, 60.27, 20.91, 14.24.

Ethyl (*Z*)-2-(7-methyl-2-oxo-2H-benzo[b][1,4]oxazin-3(4H)-ylidene)acetate **1f**



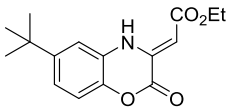
Yellow solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 10.63 (s, 1H), 6.93-6.91 (m, 2H), 6.84-6.82 (m, 1H), 5.87 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 169.97, 156.10, 139.76, 138.04, 132.93, 126.22, 121.65, 117.19, 114.46, 90.26, 60.23, 20.77, 14.25.

Ethyl (*Z*)-2-(6-methoxy-2-oxo-2H-benzo[b][1,4]oxazin-3(4H)-ylidene)acetate **1g**



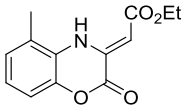
Yellow solid; m.p. 135-136 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 10.69 (s, 1H), 7.06 (d, *J* = 9.0 Hz, 1H), 6.55 (dd, *J* = 9.0, 2.8 Hz, 1H), 6.48 (d, *J* = 2.8 Hz, 1H), 5.93 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 169.97, 157.21, 156.06, 137.99, 134.13, 124.67, 117.68, 108.40, 99.73, 91.28, 60.40, 55.72, 14.25. ESI-HRMS Calculated for $C_{13}H_{13}NNaO_5^+$ ([M+Na]$^+$): 286.0686; Found: 286.0684.

Ethyl (*Z*)-2-(6-(tert-butyl)-2-oxo-2H-benzo[b][1,4]oxazin-3(4H)-ylidene)acetate **1h**



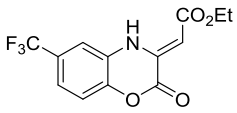
Yellow solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 10.71 (s, 1H), 7.08-7.03 (m, 2H), 6.97 (d, *J* = 2.1 Hz, 1H), 5.91 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 170.08, 156.22, 149.27, 138.28, 137.85, 123.50, 119.92, 116.42, 111.91, 90.66, 60.33, 34.62, 31.27, 14.28.

Ethyl (*Z*)-2-(5-methyl-2-oxo-2H-benzo[b][1,4]oxazin-3(4H)-ylidene)acetate **1i**



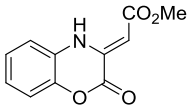
Yellow solid; m. p. 142-143 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 10.85 (s, 1H), 7.02-6.99 (m, 2H), 6.92 (t, *J* = 7.8 Hz, 1H), 5.94 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 170.22, 156.04, 140.02, 138.10, 126.72, 123.13, 122.74, 122.17, 114.73, 91.02, 60.37, 16.16, 14.30. ESI-HRMS Calculated for $C_{13}H_{14}NO_4^+$ ([M+H]$^+$): 248.0917; Found: 248.0918.

Ethyl (*Z*)-2-(2-oxo-6-(trifluoromethyl)-2H-benzo[b][1,4]oxazin-3(4H)-ylidene)acetate **1j**



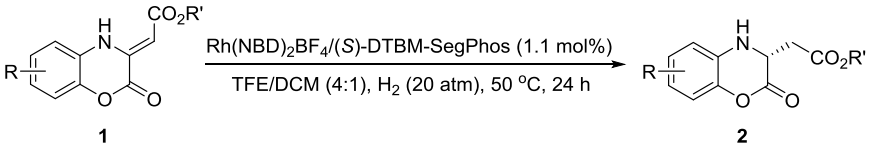
Green solid; m.p. 120-121 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 10.80 (s, 1H), 7.29-7.22 (m, 3H), 5.99 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 169.59, 155.18, 141.91 (d, *J* = 1.0 Hz), 137.14, 128.16 (q, *J* = 3.3 Hz), 124.67 (d, *J* = 2.0 Hz), 119.54 (d, *J* = 3.0 Hz), 117.58, 112.12 (d, *J* = 4.0 Hz), 112.05 (d, *J* = 4.0 Hz), 93.16, 60.72, 14.19.

Methyl (*Z*)-2-(2-oxo-2H-benzo[b][1,4]oxazin-3(4H)-ylidene)acetate **1k**



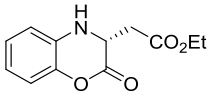
Yellow solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 10.67 (s, 1H), 7.16-7.12 (m, 2H), 7.04-6.96 (m, 2H), 5.93 (s, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 170.26, 155.91, 139.95, 138.10, 125.68, 124.10, 122.80, 117.02, 114.81, 90.65, 51.49.

III. General procedure of asymmetric hydrogenation of substrates



A mixture of $Rh(NBD)_2BF_4$ (0.003 mmol, 1.1 mg) with (*S*)-DTBM-SegPhos (0.0033 mmol, 3.9 mg) resolved in anhydrous trifluoroethanol (TFE, 1 mL) was accomplished in a Ar-filled glovebox. The mixed solution was then stirred at room temperature for 40 min in the glovebox. An aliquot of the catalyst solution (0.3 mL, 0.001 mmol) was transferred by syringe into the vials charged with different substrates **1** (0.1 mmol for each) in anhydrous TFE (0.5 mL) together with anhydrous CH_2Cl_2 (0.2 mL). The vials were subsequently transferred into an autoclave into which hydrogen gas was charged. The reaction was then stirred under H_2 (20 atm) at 50 °C for 24 h. After completed, the hydrogen gas was released slowly and carefully. The solution was concentrated and passed through a short column of silica gel (eluant: EA) to remove the metal complex. And it was purified by flash chromatography on silica gel. The ee values of all compounds were determined by HPLC on a chiral stationary phase.

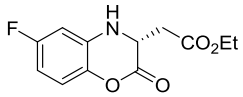
(*R*)-Ethyl 2-(2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)acetate **2a**



Brown solid; m.p. 66-68 °C; 96% conv., 21.9 mg, 93% yield, 97% ee; $[\alpha]_D^{20}$ = +3.14 (c = 0.7, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 16.5 min (major), 17.8 min (minor). ^{1}H NMR (400 MHz, Chloroform-*d*)

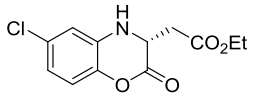
δ = 7.04-6.99 (m, 2H), 6.88-6.84 (m, 1H), 6.81-6.78 (m, 1H), 4.76 (s, 1H), 4.29 (dt, *J* = 10.3, 2.7 Hz, 1H), 4.24-4.19 (m, 2H), 3.18 (dd, *J* = 17.5, 2.9 Hz, 1H), 2.82 (dd, *J* = 17.5, 10.3 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 171.26, 165.61, 140.94, 132.32, 125.16, 120.56, 116.87, 115.39, 61.39, 51.40, 35.58, 14.11. ESI-HRMS Calculated for $C_{12}H_{14}NO_4^+$ ($[M+H]^+$): 236.0917; Found: 236.0918.

(*R*)-ethyl 2-(6-fluoro-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)acetate **2b**



Brown solid; m.p. 116-118 °C; 92% conv., 23.2 mg, 92% yield, 97% ee; $[\alpha]_D^{20}$ = +2.5 (c = 0.8, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 97:3; flow rate = 0.5 mL/min; UV detection at 210 nm; t_R = 52.9 min (minor), 54.9 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.96 (dd, *J* = 8.7, 5.0 Hz, 1H), 6.54-6.50 (m, 2H), 4.87 (s, 1H), 4.30-4.19 (m, 3H), 3.17 (dd, *J* = 17.6, 2.8 Hz, 1H), 2.81 (dd, *J* = 17.6, 10.4 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 171.14, 165.07, 159.68 (d, *J* = 241.0 Hz), 136.86 (d, *J* = 2.0 Hz), 133.28 (d, *J* = 11.0 Hz), 117.70 (d, *J* = 10.0 Hz), 106.66 (d, *J* = 24.0 Hz), 102.33 (d, *J* = 27.0 Hz), 61.48, 50.93, 35.57, 14.06. ESI-HRMS Calculated for $C_{13}H_{17}FNO_5^+$ ($[M+CH_3OH+H]^+$): 286.1085; Found: 286.1083.

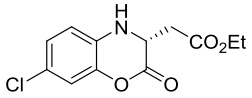
(*R*)-Ethyl 2-(6-chloro-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)acetate **2c**



White solid; m.p. 104-108 °C; >99% conv., 22.9 mg, 85% yield, >99% ee; $[\alpha]_D^{20}$ = +44.2 (c = 0.6, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 97:3; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 31.5 min (minor), 36.2 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.95-6.92 (m, 1H), 6.83-6.79 (m, 2H), 4.85 (s, 1H), 4.30-4.19 (m, 3H), 3.16 (dd, *J* = 17.7, 2.8 Hz, 1H), 2.81 (dd, *J* = 17.6, 10.5 Hz, 1H), 1.29 (t, *J* = 7.1

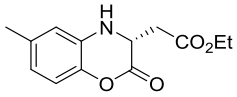
Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 171.09, 164.88, 139.33, 133.18, 130.16, 120.24, 117.85, 115.16, 61.53, 51.01, 35.55, 14.09. ESI-HRMS Calculated for $C_{13}H_{17}ClNO_5^+$ ([M+CH_3OH+H]$^+$): 302.0790; Found: 302.0789.

(*R*)-Ethyl 2-(7-chloro-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)acetate **2d**



Yellow solid; m.p. 108-110 °C; >99% conv., 23.9 mg, 89% yield, >99% ee; $[\alpha]_D^{20}$ = +61.8 (c = 0.6, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 27.4 min (major), 37.4 min (minor). ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.03 (d, *J* = 2.2 Hz, 1H), 6.98 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 4.81 (s, 1H), 4.28-4.18 (m, 3H), 3.17 (dd, *J* = 17.6, 2.8 Hz, 1H), 2.81 (dd, *J* = 17.6, 10.3 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 171.16, 164.84, 141.04, 131.03, 125.07, 125.00, 117.14, 116.08, 61.50, 51.19, 35.47, 14.09. ESI-HRMS Calculated for $C_{13}H_{17}ClNO_5^+$ ([M+CH_3OH+H]$^+$): 302.0790; Found: 302.0789.

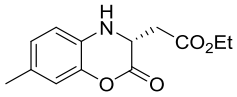
(*R*)-Ethyl 2-(6-methyl-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)acetate **2e**



White solid; m.p. 68-70 °C; >99% conv., 22.9 mg, 92% yield, 97% ee; $[\alpha]_D^{20}$ = +41.2 (c = 0.8, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 35.7 min (major), 39.6 min (minor). ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.90 (d, *J* = 8.1 Hz, 1H), 6.66-6.60 (m, 2H), 4.68 (s, 1H), 4.27-4.18 (m, 3H), 3.15 (dd, *J* = 17.5, 2.8 Hz, 1H), 2.80 (dd, *J* = 17.5, 10.4 Hz, 1H), 2.27 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 171.24, 165.78, 138.90, 135.00, 131.95, 121.08, 116.49, 115.81, 61.33, 51.40, 35.51, 20.90, 14.08. ESI-HRMS

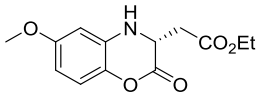
Calculated for $C_{13}H_{15}NNaO_4^+$ ([M+Na]$^+$): 272.0893; Found: 272.0892.

(*R*)-Ethyl 2-(7-methyl-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)acetate **2f**



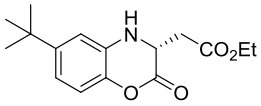
White solid; m.p. 49-50 ^oC; >99% conv., 22.2 mg, 89% yield, 99% ee; $[\alpha]_D^{20}$ = -1.7 (c = 0.5, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 16.2 min (major), 19.9 min (minor). ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.84-6.80 (m, 2H), 6.69 (d, *J* = 7.9 Hz, 1H), 4.63 (s, 1H), 4.25-4.18 (m, 3H), 3.16 (dd, *J* = 17.5, 2.9 Hz, 1H), 2.81 (dd, *J* = 17.5, 10.3 Hz, 1H), 2.28 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 171.26, 165.88, 140.89, 130.52, 129.75, 125.59, 117.19, 115.27, 61.32, 51.55, 35.44, 20.57, 14.08. ESI-HRMS Calculated for $C_{13}H_{16}NO_4^+$ ([M+H]$^+$): 250.1074; Found: 250.1082.

(*R*)-Ethyl 2-(6-methoxy-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)acetate **2g**



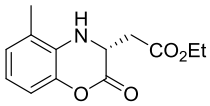
White solid; m.p. 72-74 ^oC; >99% conv., 22.6 mg, 85% yield, 98% ee; $[\alpha]_D^{20}$ = +11.4 (c = 0.07, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 46.0 min (minor), 58.5 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.93 (d, *J* = 8.8 Hz, 1H), 6.40-6.33 (m, 2H), 4.76 (s, 1H), 4.27-4.20 (m, 3H), 3.75 (s, 3H), 3.16 (dd, *J* = 17.5, 2.7 Hz, 1H), 2.80 (dd, *J* = 17.6, 10.4 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 171.32, 165.64, 156.96, 135.11, 133.00, 117.39, 105.45, 100.92, 61.40, 55.57, 51.26, 35.53, 14.10. ESI-HRMS Calculated for $C_{14}H_{20}NO_6^+$ ([M+CH_3OH+H]$^+$): 298.1285; Found: 298.1322.

(*R*)-Ethyl 2-(6-(tert-butyl)-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)acetate **2h**



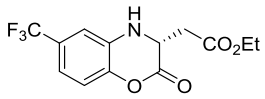
White solid; m.p. 79-81 ºC; >99% conv., 25.0 mg, 86% yield, 92% ee; $[\alpha]_D^{20}$ = +11.4 (c = 0.5, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 17.1 min (major), 19.6 min (minor). ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.95 (d, *J* = 8.5 Hz, 1H), 6.87 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.81 (d, *J* = 2.2 Hz, 1H), 4.73 (s, 1H), 4.28-4.19 (m, 3H), 3.20 (dd, *J* = 17.5, 2.8 Hz, 1H), 2.82 (dd, *J* = 17.6, 10.4 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 171.47, 165.92, 148.58, 138.85, 131.72, 117.68, 116.27, 112.58, 61.41, 51.50, 35.69, 34.50, 31.38, 14.16. ESI-HRMS Calculated for $C_{16}H_{21}NNaO_4^+$ ($[M+Na]^+$): 314.1363; Found: 314.1381.

(*R*)-Ethyl 2-(5-methyl-2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)acetate **2i**



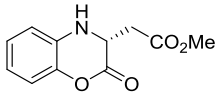
White solid; m.p. 74-76 ºC; 92% conv., 21.9 mg, 88% yield, 97% ee; $[\alpha]_D^{20}$ = +55.0 (c = 0.6, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, hexane: isopropanol = 97:3; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 15.6 min (major), 17.1 min (minor). ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.91-6.89 (m, 2H), 6.77 (t, *J* = 7.8 Hz, 1H), 4.83 (s, 1H), 4.26-4.21 (m, 3H), 3.17 (dd, *J* = 17.5, 2.8 Hz, 1H), 2.83 (dd, *J* = 17.5, 10.5 Hz, 1H), 2.21 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 171.41, 165.71, 140.85, 130.70, 126.35, 123.73, 119.88, 114.68, 61.39, 51.35, 35.37, 16.40, 14.12. ESI-HRMS Calculated for $C_{13}H_{16}NO_4^+$ ($[M+H]^+$): 250.1074; Found: 250.1073.

(*R*)-Ethyl 2-(2-oxo-6-(trifluoromethyl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl) acetate **2j**



White solid; m.p. 149-151 °C; 81% conv., 24.2 mg, 80% yield, 88% ee; $[\alpha]_D^{20}$ = -2.1 (c = 0.9, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 16.5 min (major), 18.3 min (minor). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14–7.09 (m, 2H), 7.06-7.05 (m, 1H), 5.00 (s, 1H), 4.35-4.32 (m, 1H), 4.27-4.19 (m, 2H), 3.19 (dd, *J* = 17.5, 2.8 Hz, 1H), 2.84 (dd, *J* = 17.6, 10.3 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 171.05, 164.56, 142.76, 132.52, 127.58 (d, *J* = 33.0 Hz), 117.46 (d, *J* = 4.0 Hz), 117.23, 112.38 (d, *J* = 3.0 Hz), 61.61, 51.07, 35.64, 14.09. ESI-HRMS Calculated for $C_{14}H_{17}F_3NO_5^+$ ($[M+CH_3OH+H]^+$): 336.1053; Found: 336.1051.

(*R*)-Methyl 2-(2-oxo-3,4-dihydro-2H-benzo[b][1,4]oxazin-3-yl)acetate **2k**



Brown solid; m.p. 122-124 °C; 92% conv., 19.2 mg, 87% yield, 99% ee; $[\alpha]_D^{20}$ = +4.0 (c = 0.3, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection at 210 nm; t_R = 32.7 min (minor), 41.0 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.04-6.99 (m, 2H), 6.88-6.79 (m, 2H), 4.29 (dd, *J* = 10.3, 2.8 Hz, 1H), 3.76 (s, 3H), 3.20 (dd, *J* = 17.6, 2.8 Hz, 1H), 2.84 (dd, *J* = 17.6, 10.3 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 171.72, 165.58, 140.91, 132.26, 125.18, 120.60, 116.87, 115.41, 52.31, 51.34, 35.34. ESI-HRMS Calculated for $C_{12}H_{16}NO_5^+$ ($[M+CH_3OH+H]^+$): 254.1023; Found: 254.1020.

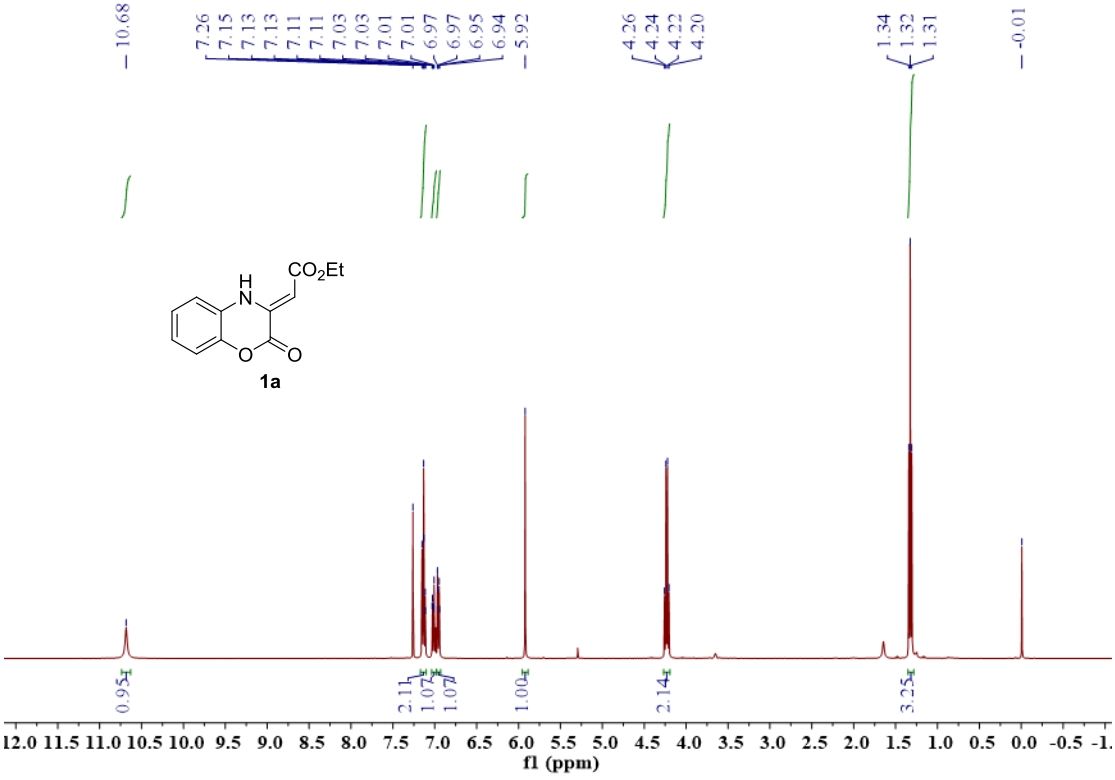
IV. Reference

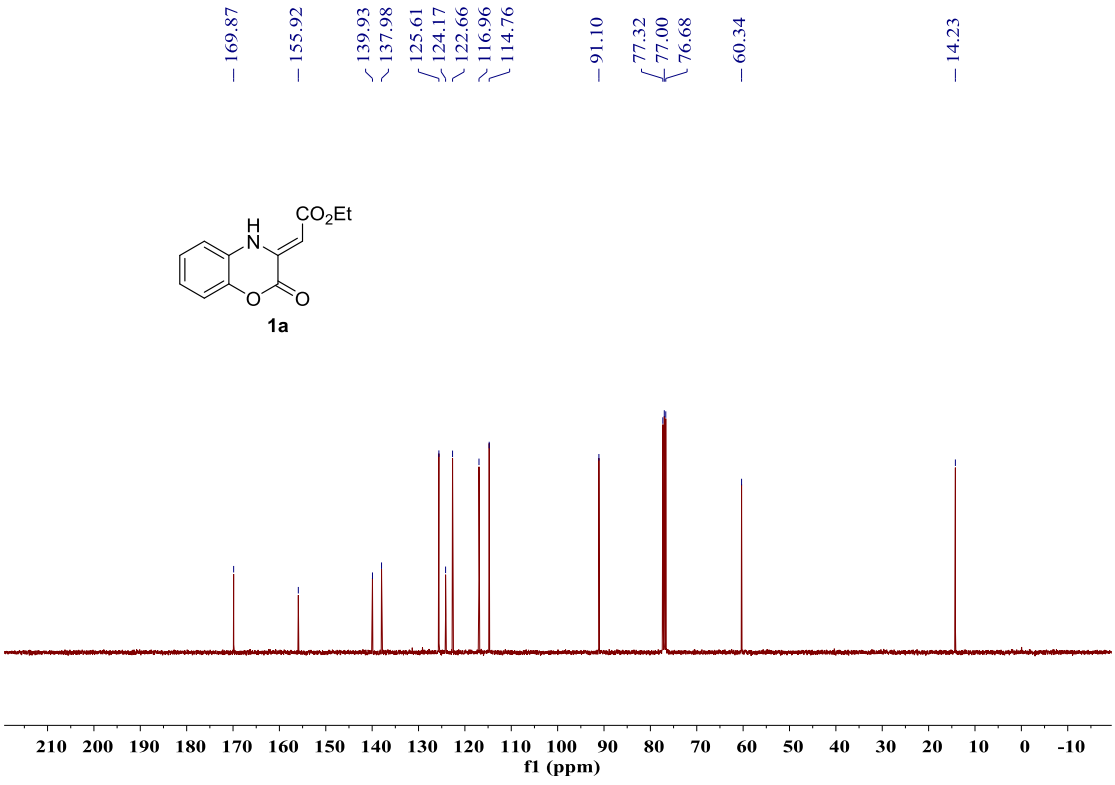
[1] G. Choudhary, R. K. Peddinti, *Green Chem.* **2011**, *13*, 3290.

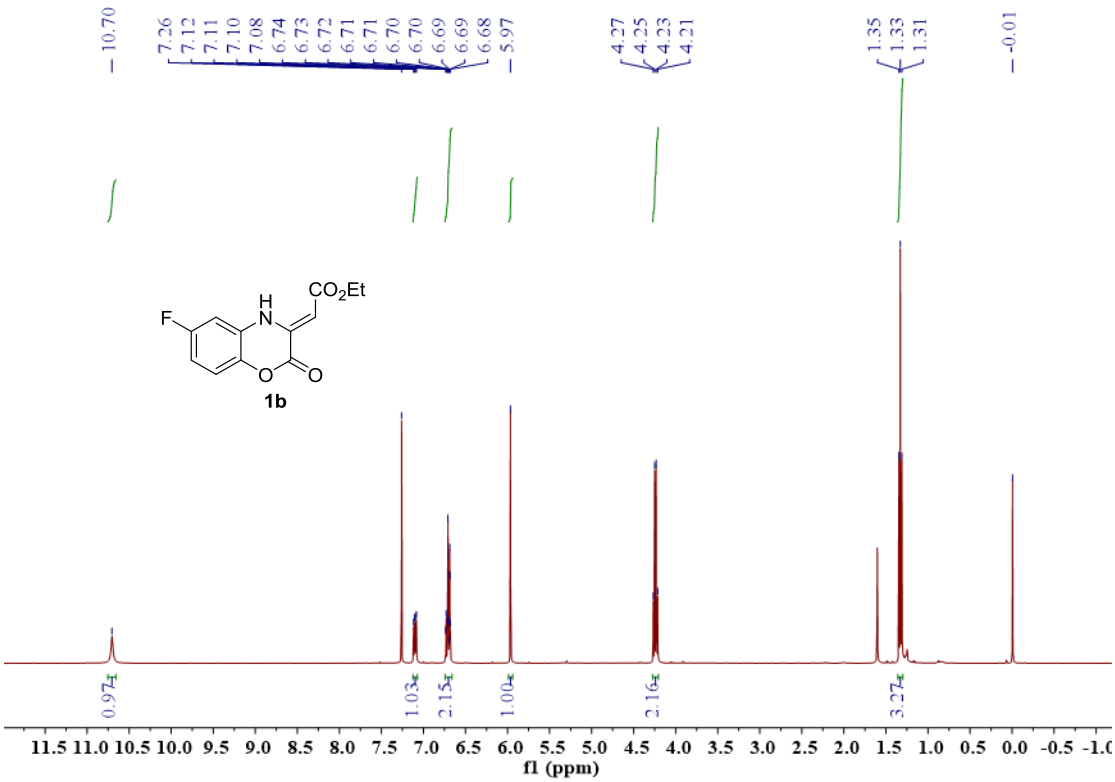
[2] M. M. Heravi, H. A. Oskooie and B. Baghernejad, *J. Chin. Chem. Soc.* **2007**, *54*, 767.

[3] The X-ray crystal data of compound **2d** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1905706. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK [Fax: +44 (1223)336033 or Email: deposit@ccdc.cam.ac.uk].

V. NMR spectra



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6.70
6.69
6.69
6.68
5.97
4.27
4.25
4.23
4.21
1.35
1.33
1.31
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CO2Et
H
N
F
O
O
1b
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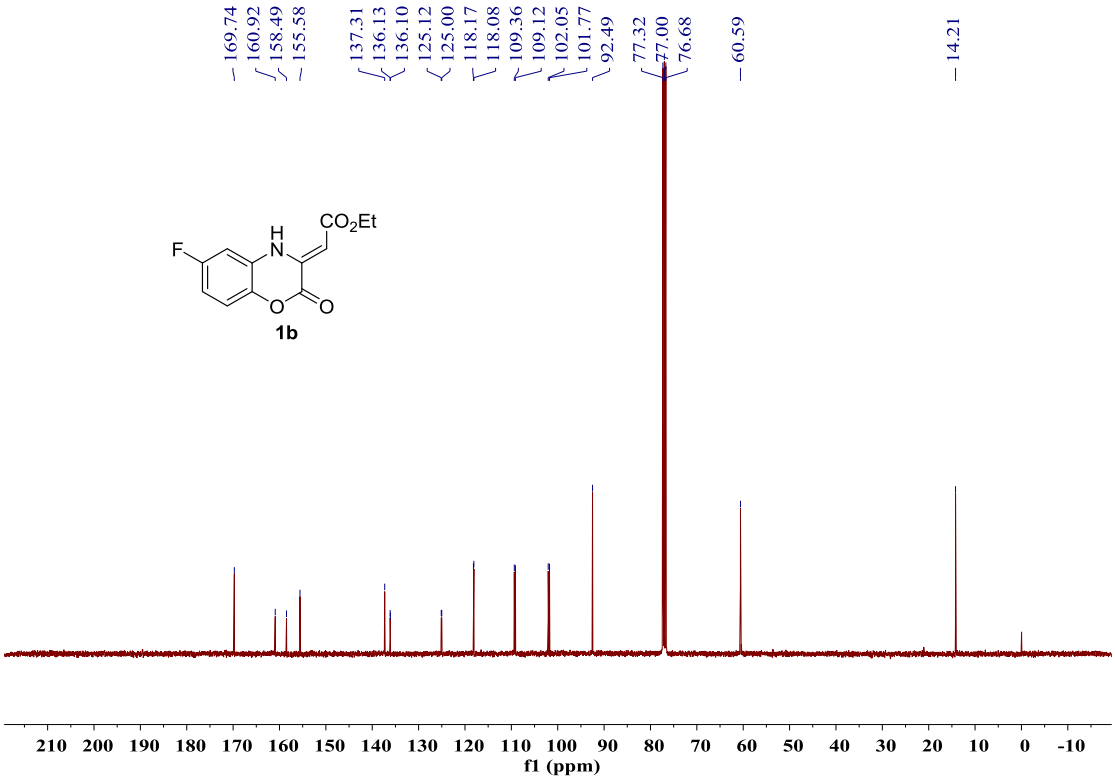
1.03
2.15
1.00
2.16
3.27
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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109.12
102.05
101.77
92.49
77.32
77.00
76.68
60.59
14.21
CO2Et
H
N
F
O
O
1b
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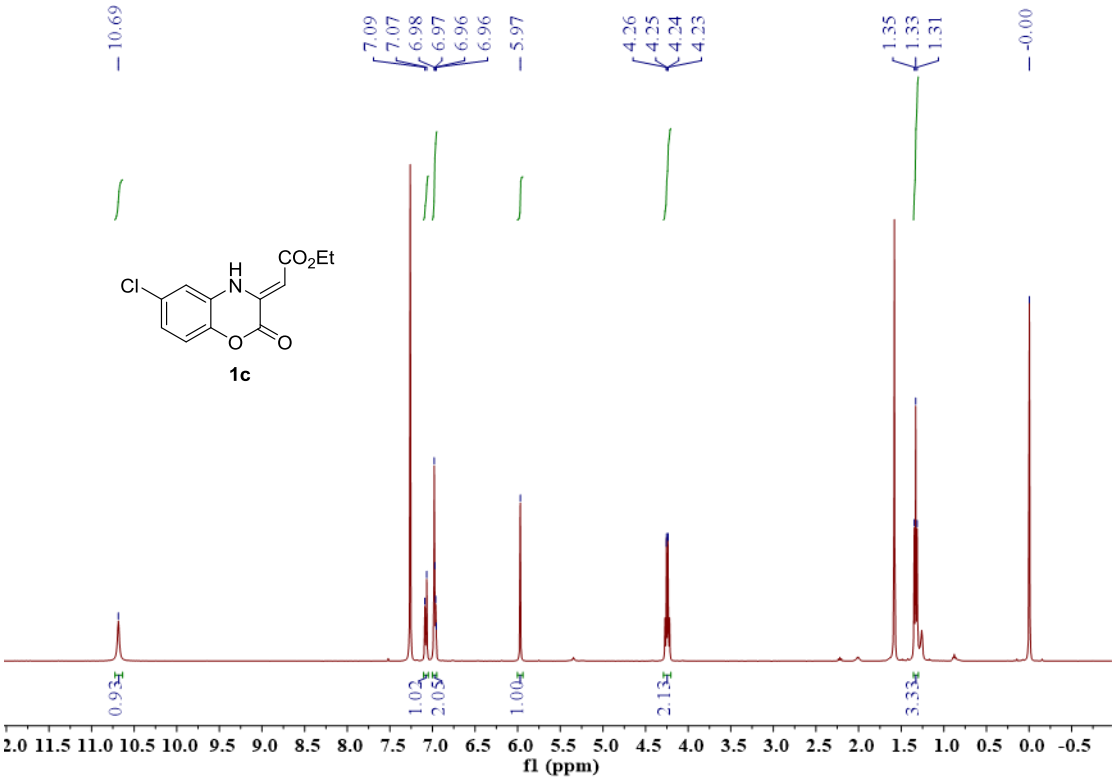
f1 (ppm)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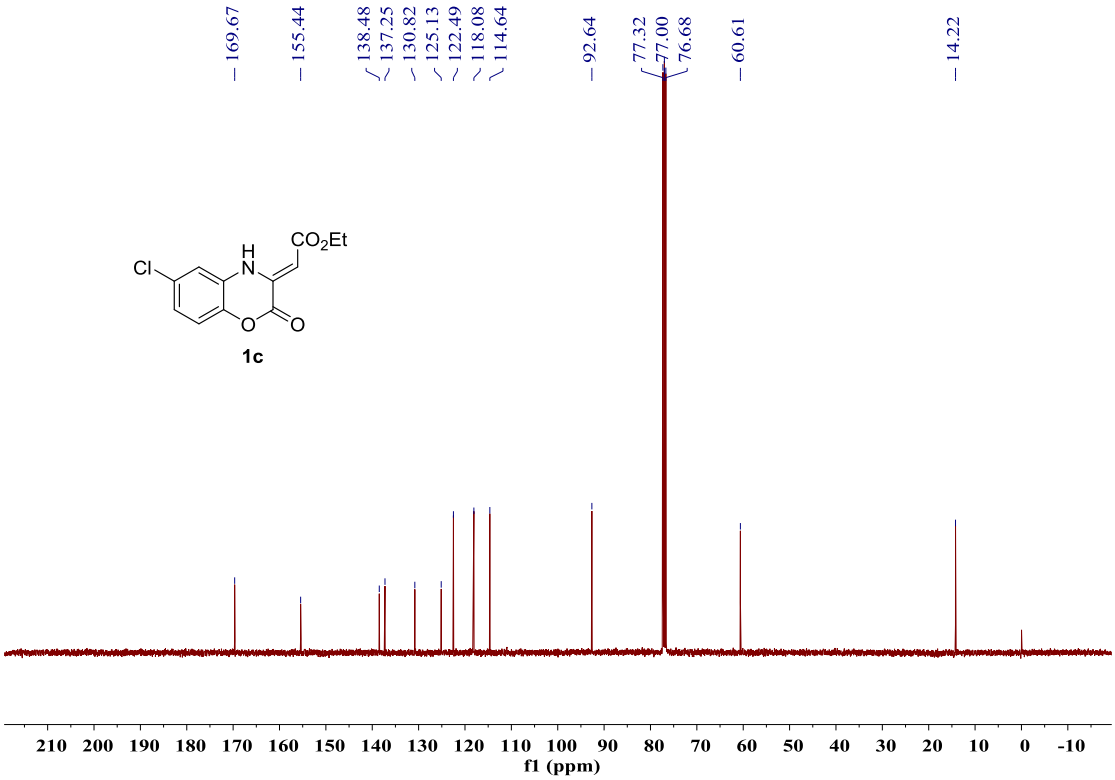
f1 (ppm)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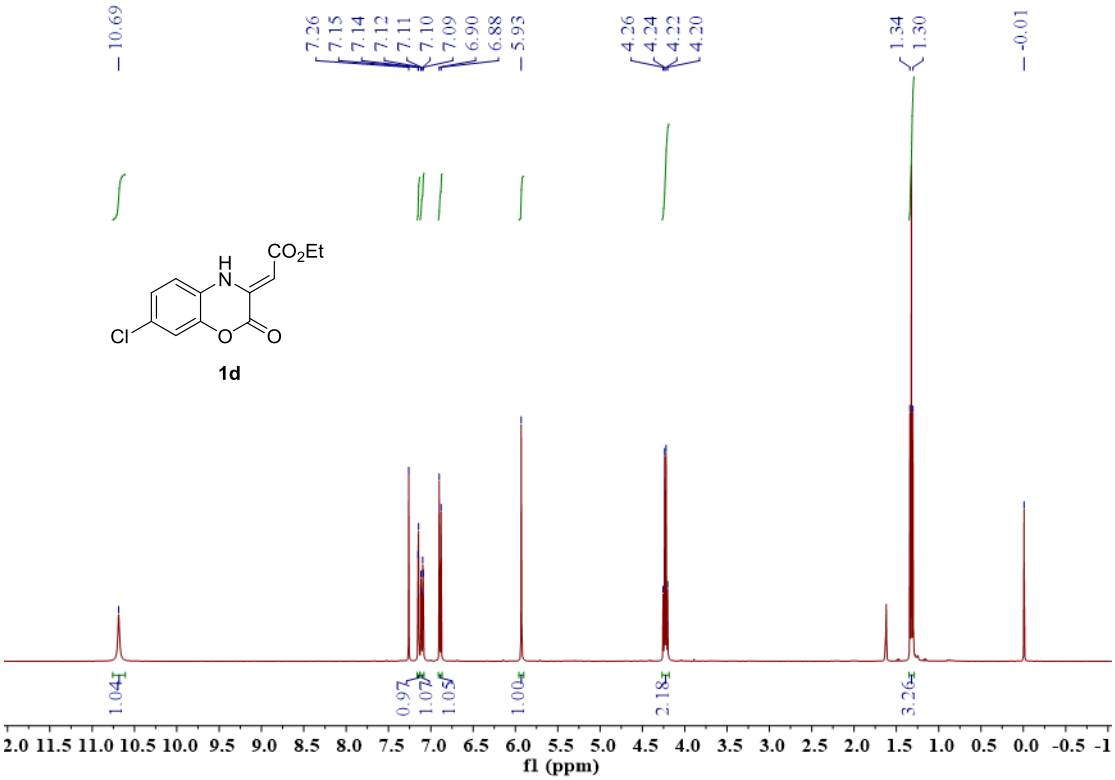
Cl
H
N
O
O
1c
f1 (ppm)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4.22
4.20
1.34
1.30
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CO2Et
H
N
Cl
O
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1.07
1.05
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2.0 11.5 11.0 10.5 10.0 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 -0.5 -1
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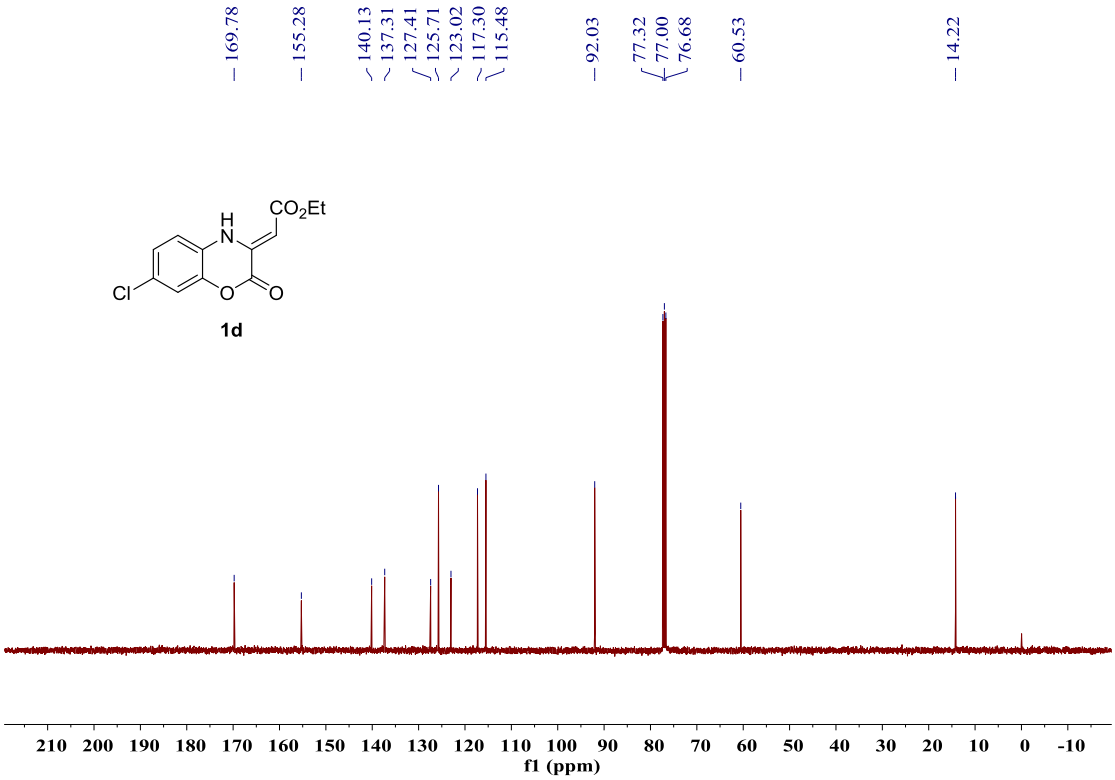
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60.53
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N
Cl
O
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1d
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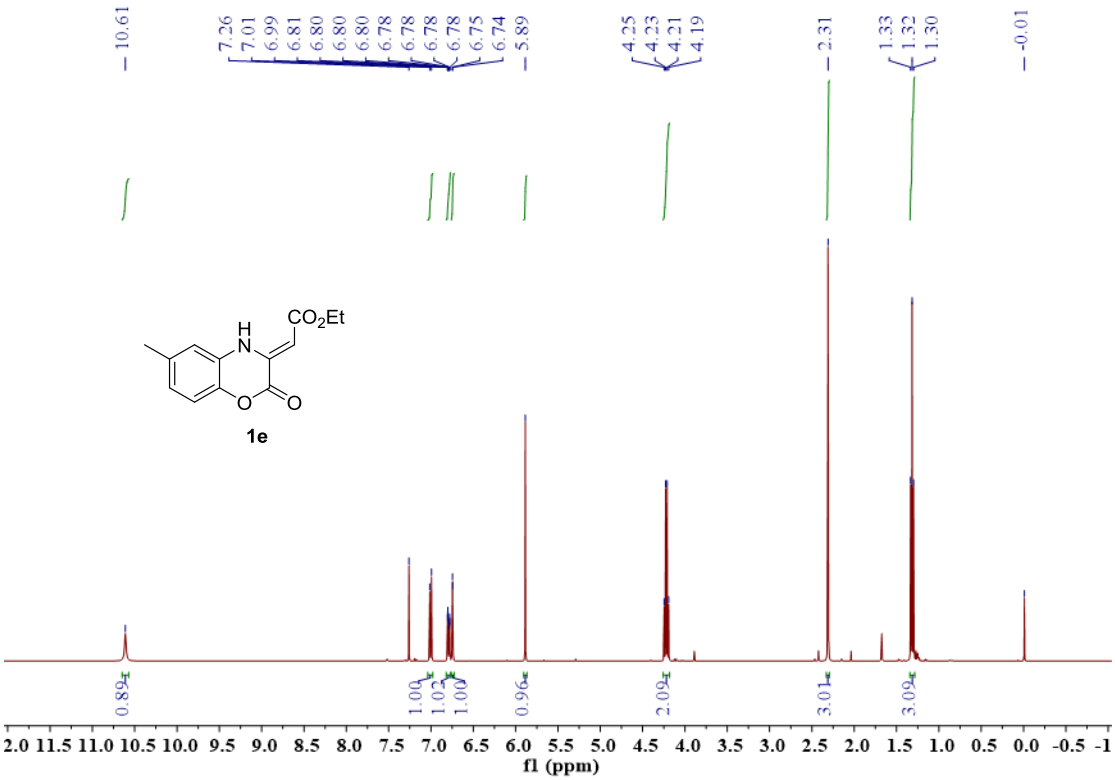
f1 (ppm)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6.75
6.74
5.89
4.25
4.23
4.21
4.19
2.31
1.33
1.32
1.30
-0.01
CO2Et
H
N
O
O
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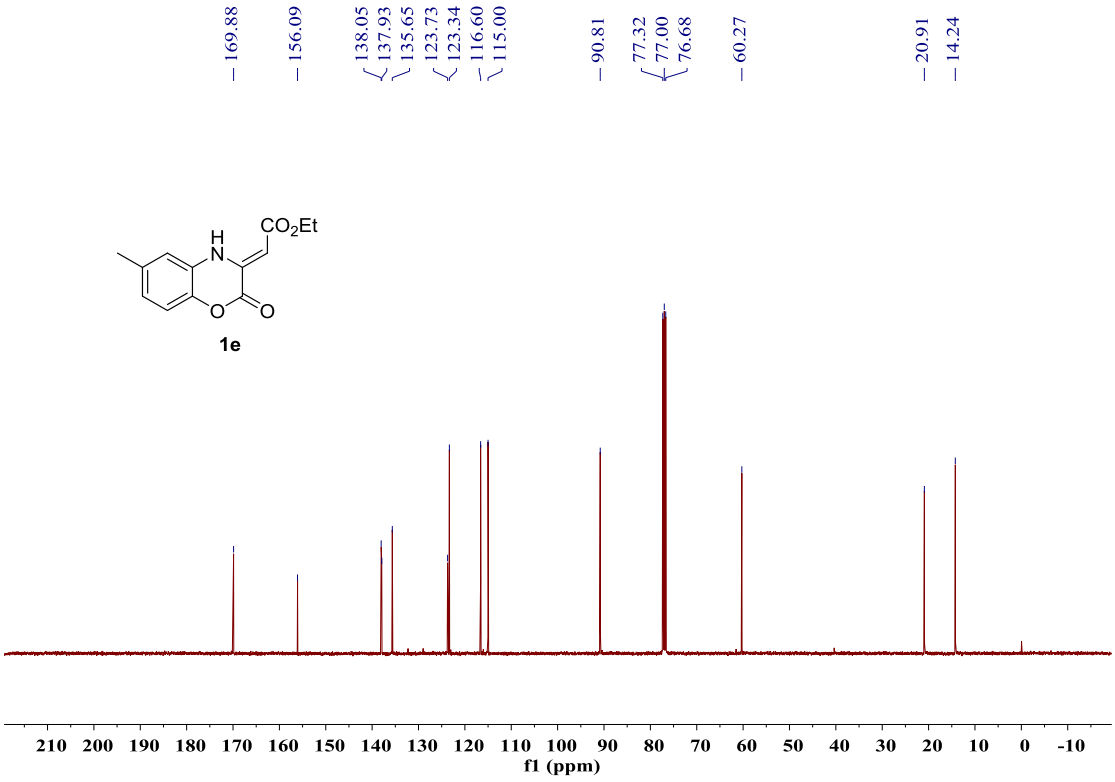
0.89
1.00
1.02
1.00
0.96
2.09
3.01
3.09
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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76.68
60.27
20.91
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H
N
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O
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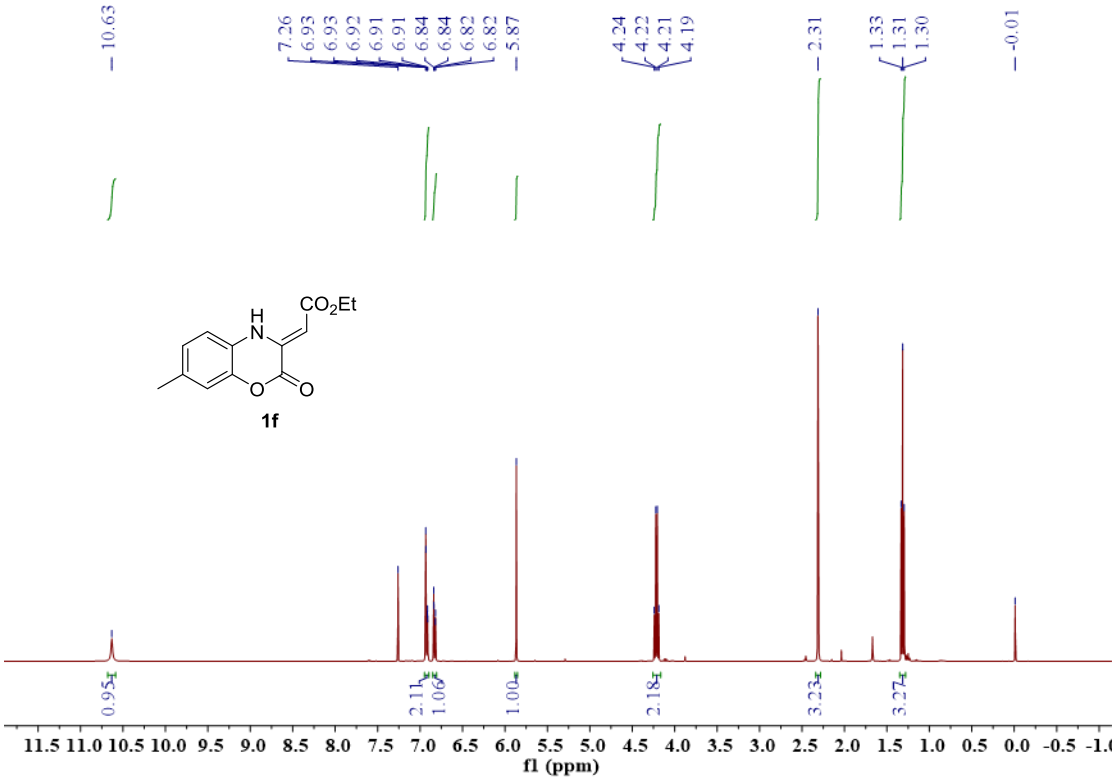
f1 (ppm)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4.22
4.21
4.19
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1.31
1.30
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CO2Et
H
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O
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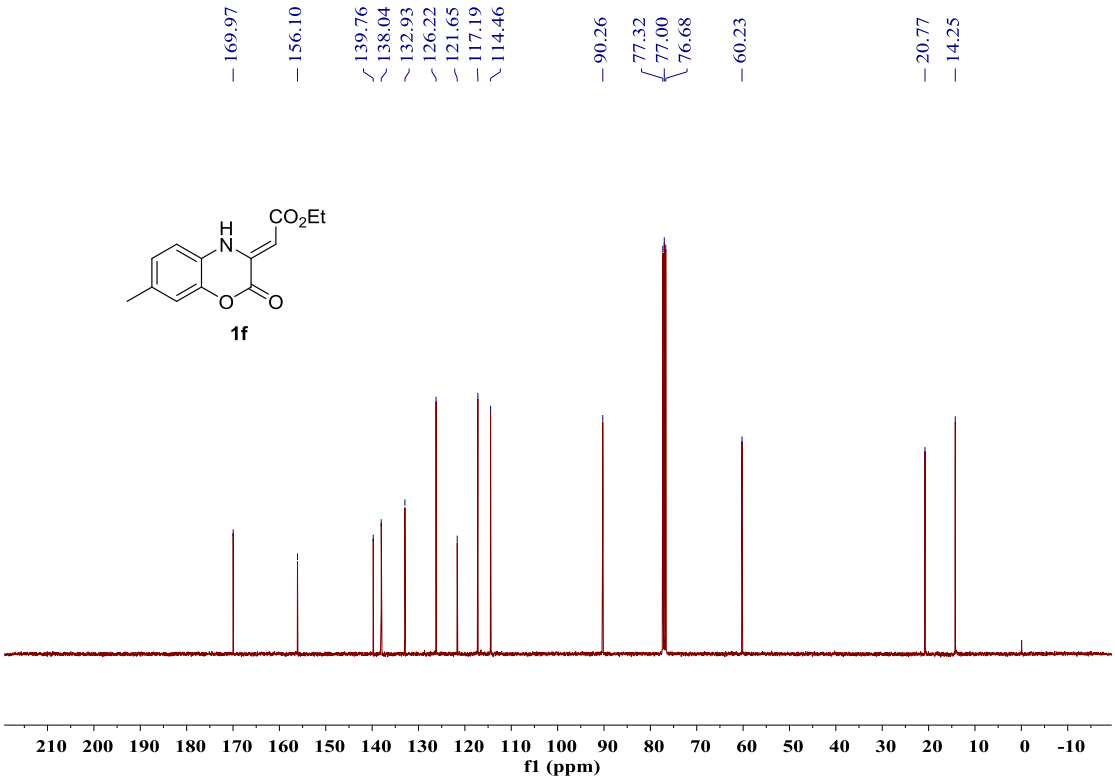
2.11
1.06
1.00
2.18
3.23
3.27
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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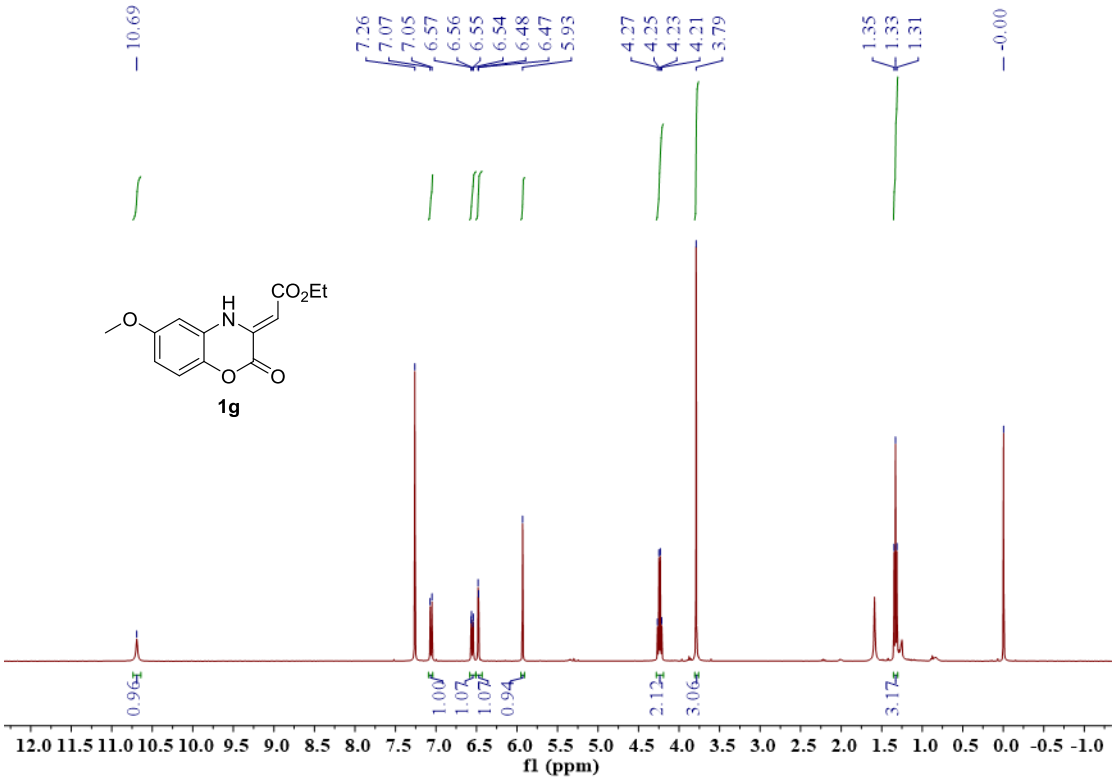
f1 (ppm)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1.33
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CO2Et
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N
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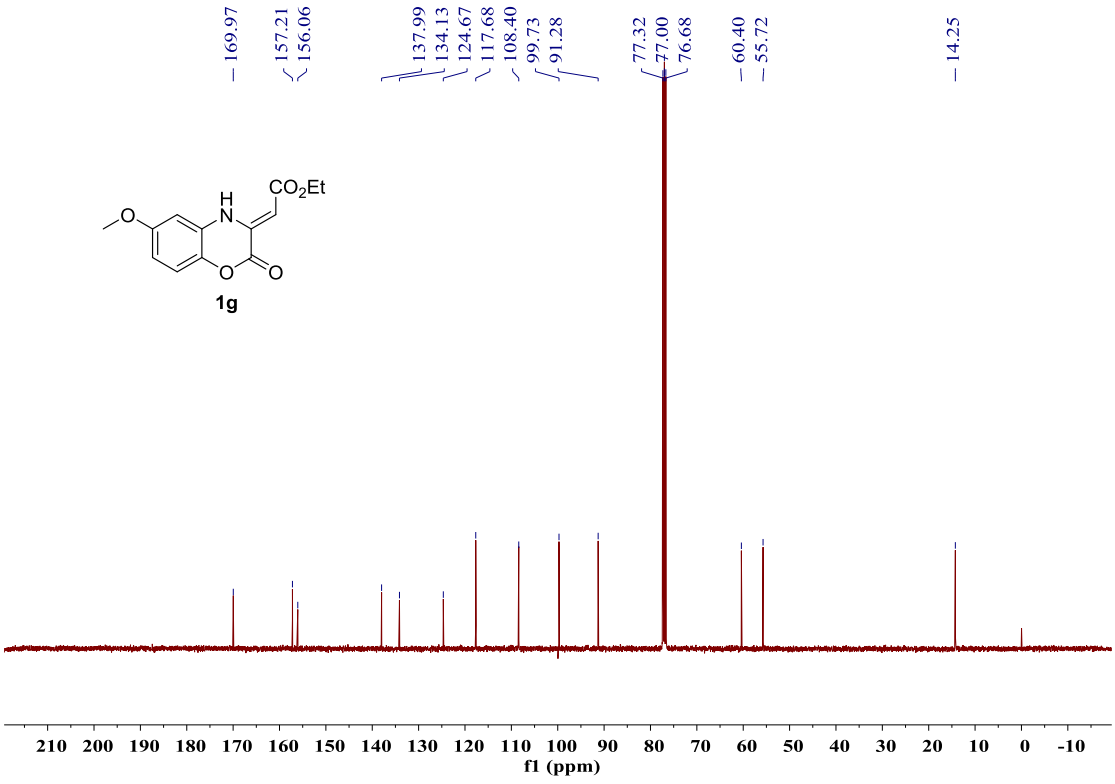
1g
0.96
1.00
1.02
1.07
0.94
2.12
3.06
3.17
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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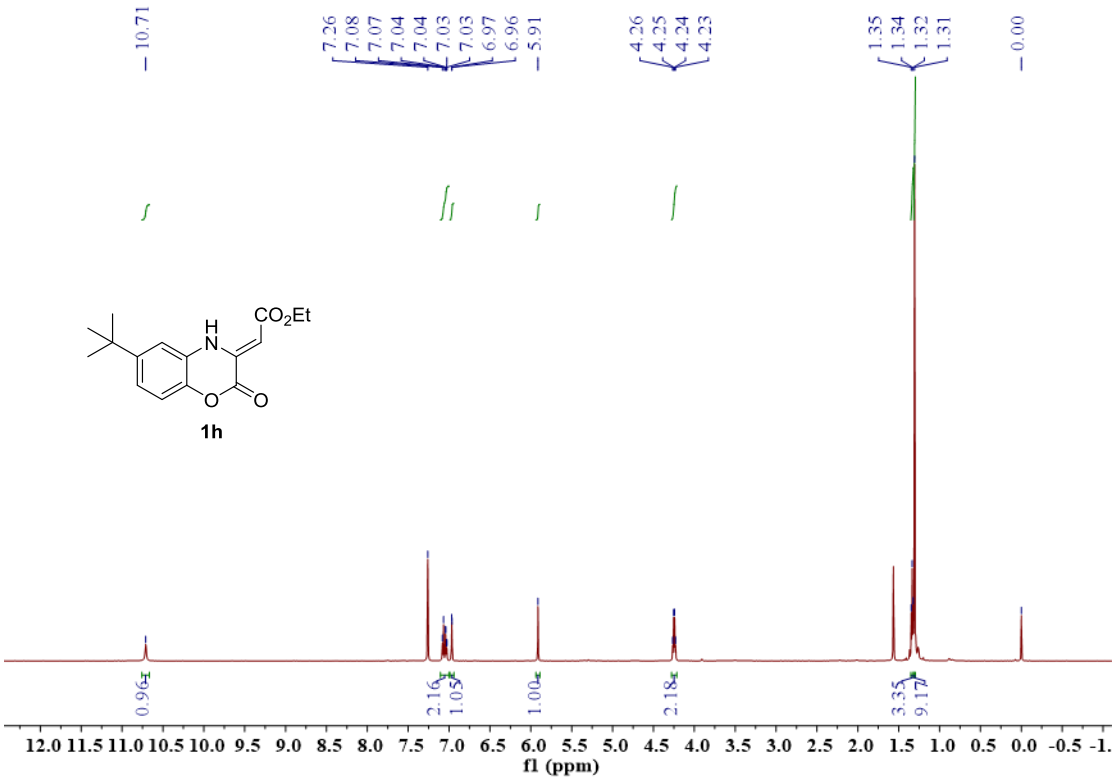
157.21
156.06
137.99
134.13
124.67
117.68
108.40
99.73
91.28
77.32
77.00
76.68
60.40
55.72
14.25
CO2Et
H
N
O
O
O
1g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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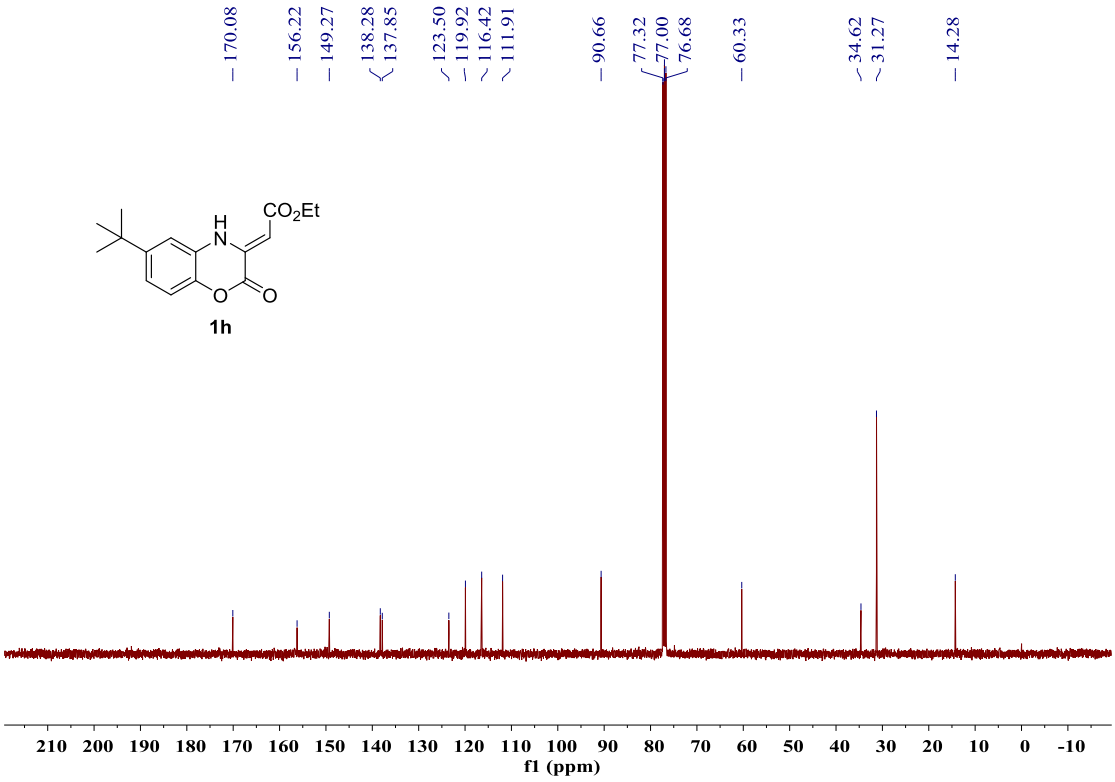
7.26
7.08
7.07
7.04
7.04
7.03
7.03
6.97
6.96
5.91
4.26
4.25
4.24
4.23
1.35
1.34
1.32
1.31
0.00
CO2Et
H
N
O
O
1h
0.96
2.16
1.05
1.00
2.18
3.35
9.17
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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138.28
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123.50
119.92
116.42
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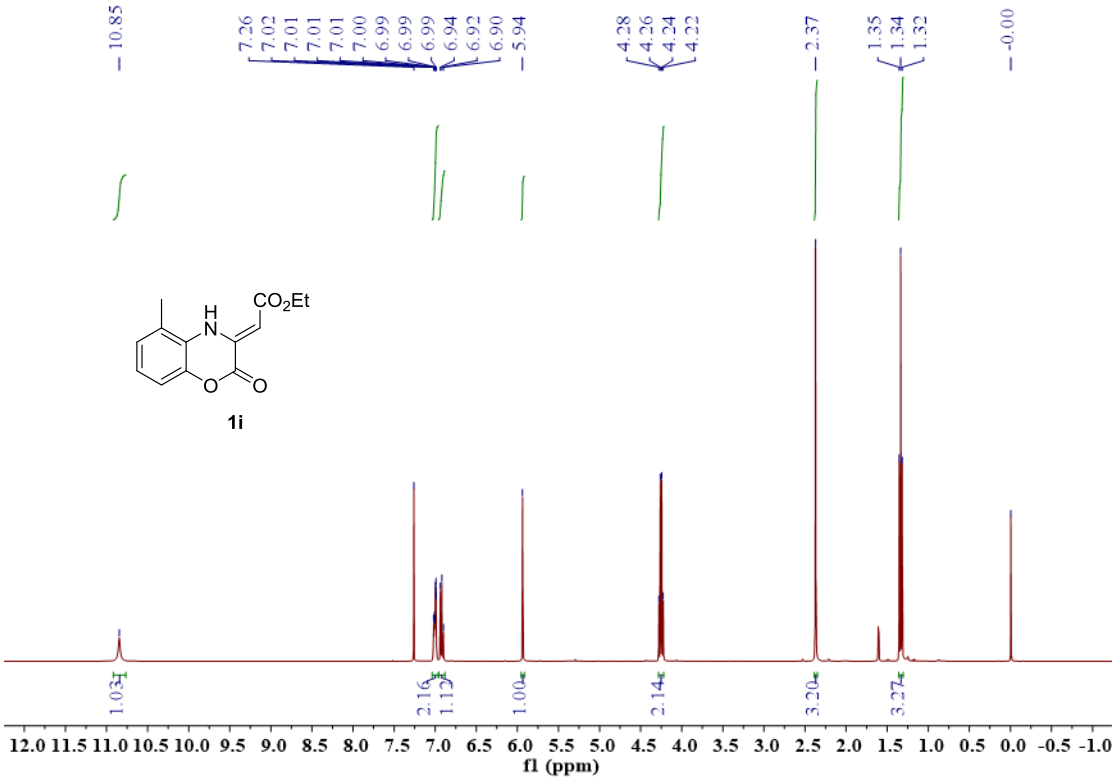
90.66
77.32
77.00
76.68
60.33
34.62
31.27
14.28
CO2Et
H
N
O
O
1h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.02
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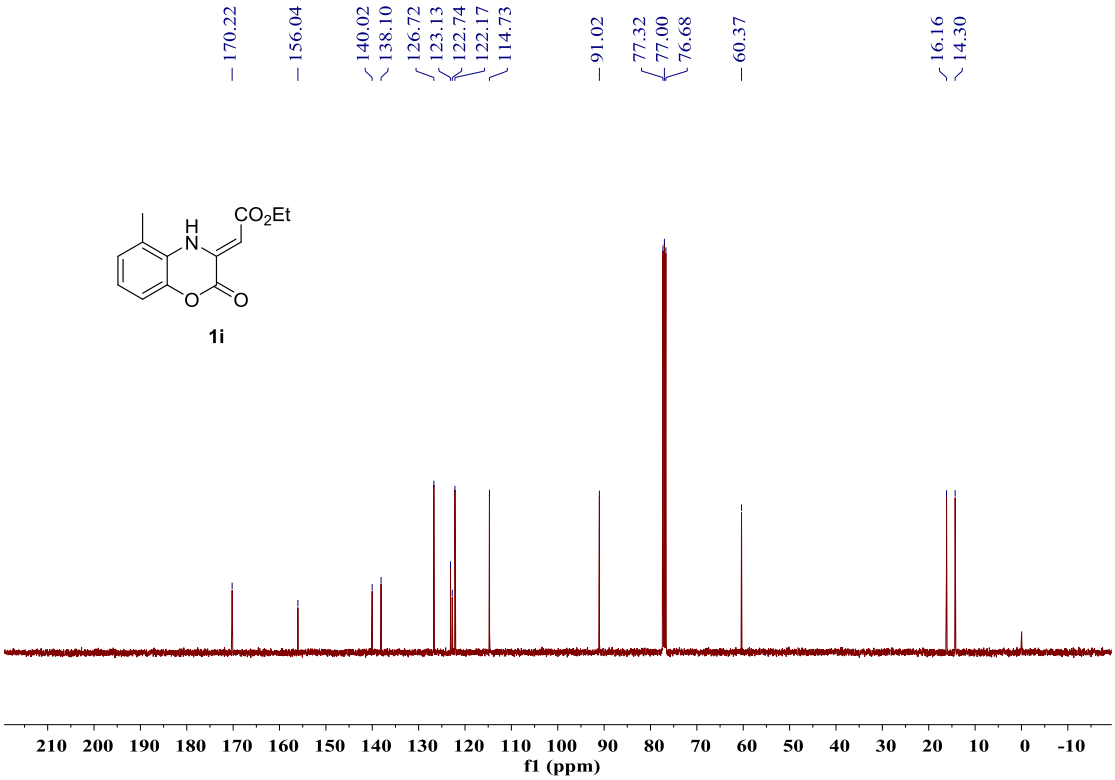
7.01
7.01
7.00
6.99
6.99
6.99
6.94
6.92
6.90
5.94
4.28
4.26
4.24
4.22
2.37
1.35
1.34
1.32
-0.00
CO2Et
H
N
O
O
1i
1.03
2.16
1.13
1.00
2.14
3.20
3.27
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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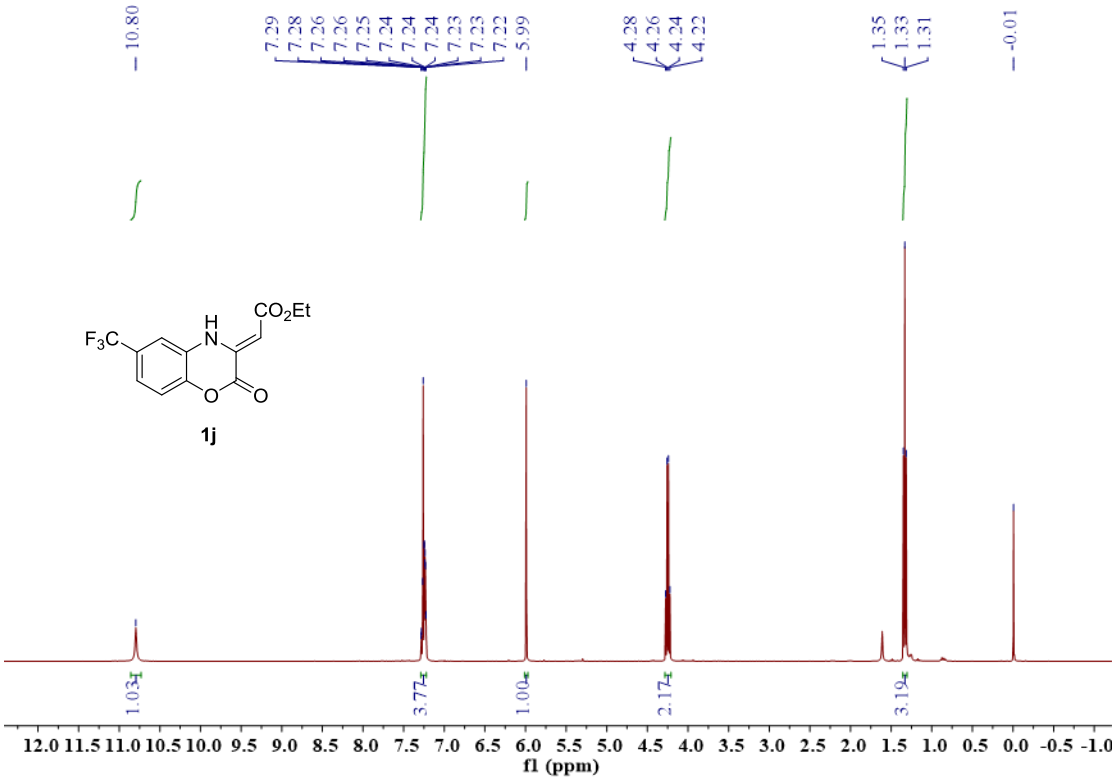
156.04
140.02
138.10
126.72
123.13
122.74
122.17
114.73
91.02
77.32
77.00
76.68
60.37
16.16
14.30
CO2Et
H
N
O
O
1i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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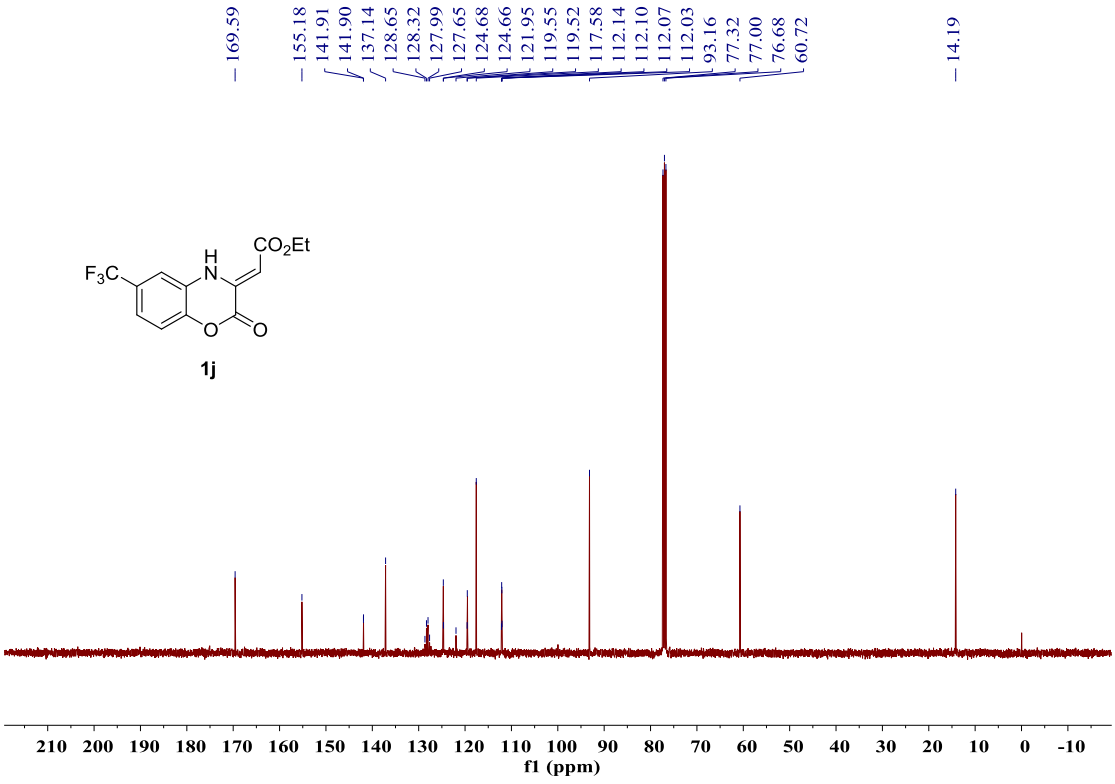
7.29
7.28
7.26
7.26
7.25
7.24
7.24
7.24
7.23
7.23
7.22
5.99
4.28
4.26
4.24
4.22
1.35
1.33
1.31
-0.01
CO2Et
F3C
H
N
O
O
1j
1.03
3.77
1.00
2.17
3.19
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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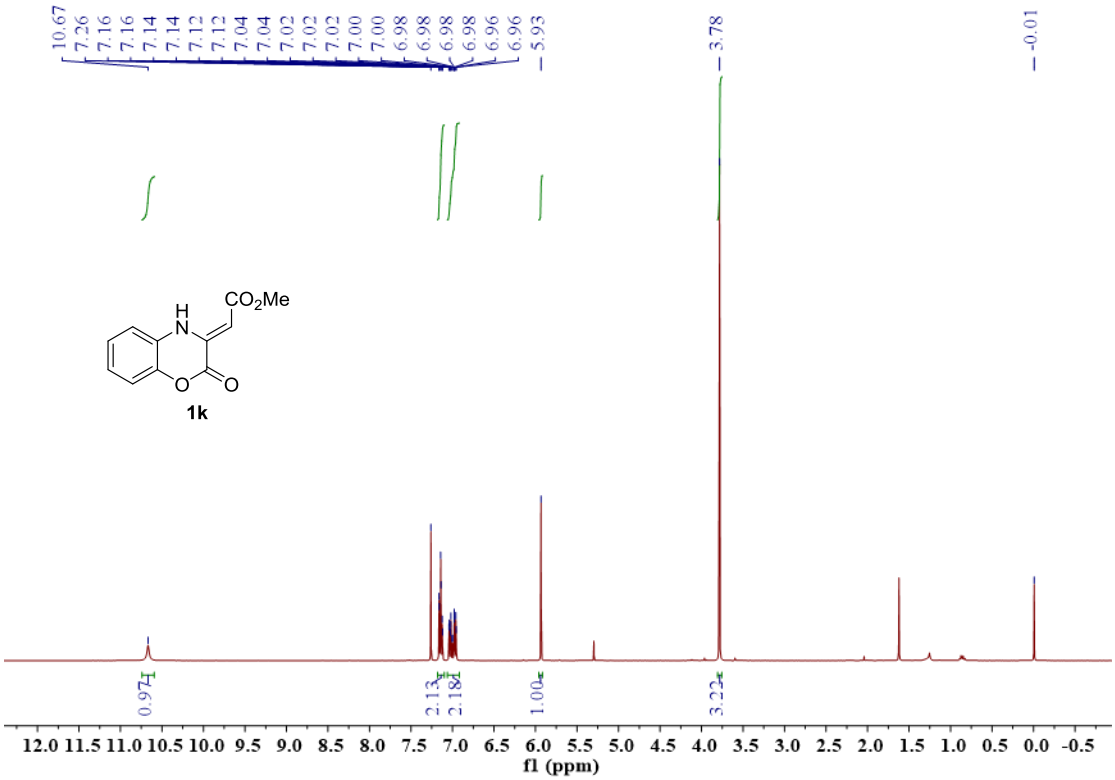
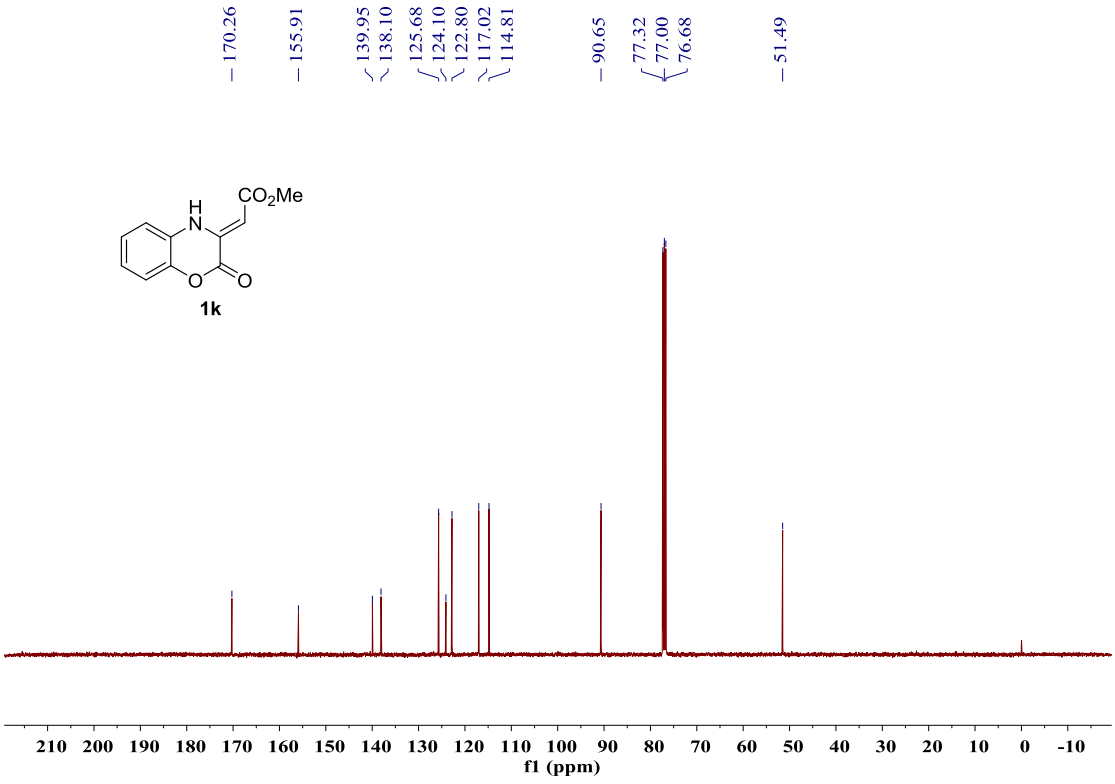
128.65
128.32
127.99
127.65
124.68
124.66
121.95
119.55
119.52
117.58
112.14
112.10
112.07
112.03
93.16
77.32
77.00
76.68
60.72
14.19
CO2Et
F3C
H
N
O
O
1j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


10.67
7.26
7.16
7.16
7.14
7.14
7.12
7.12
7.04
7.04
7.02
7.02
7.02
7.00
7.00
6.98
6.98
6.98
6.96
6.96
5.93
3.78
-0.01
CO2Me
H
N
O
O
1k
0.97
2.13
2.18
1.00
3.22
12.0 11.5 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 -0.5
f1 (ppm)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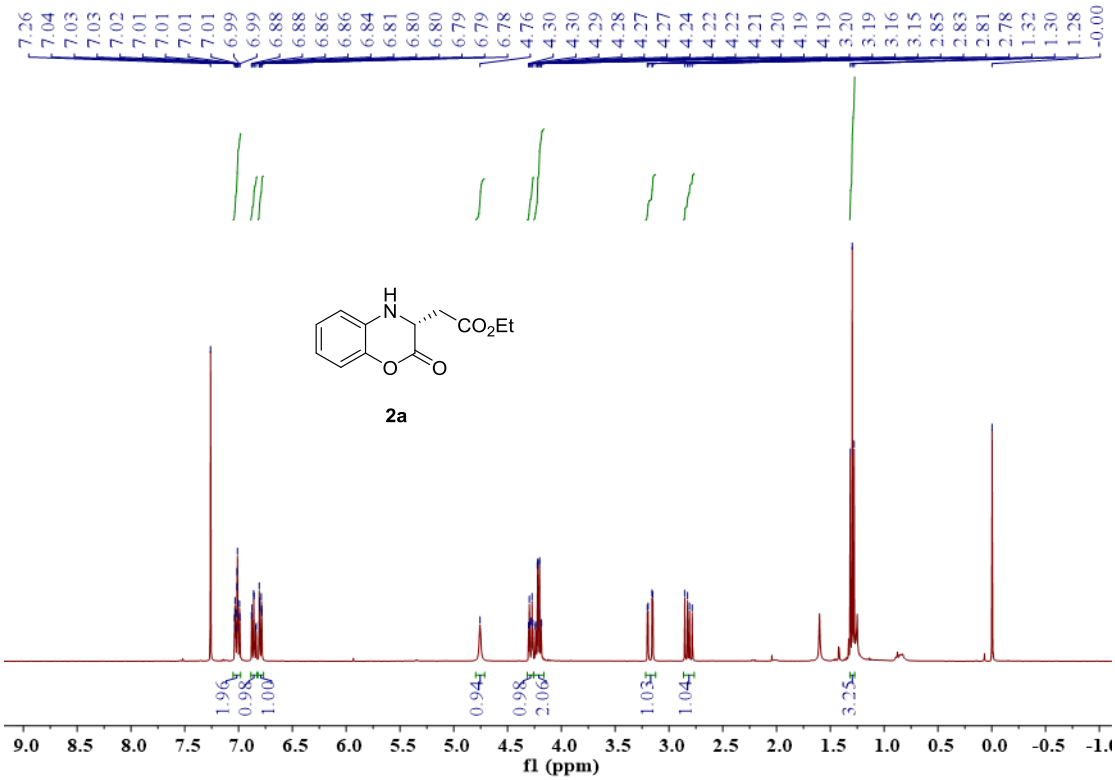
155.91
139.95
138.10
125.68
124.10
122.80
117.02
114.81
90.65
77.32
77.00
76.68
51.49
CO2Me
H
N
O
O
1k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.04
7.03
7.03
7.02
7.01
7.01
7.01
7.01
6.99
6.99
6.88
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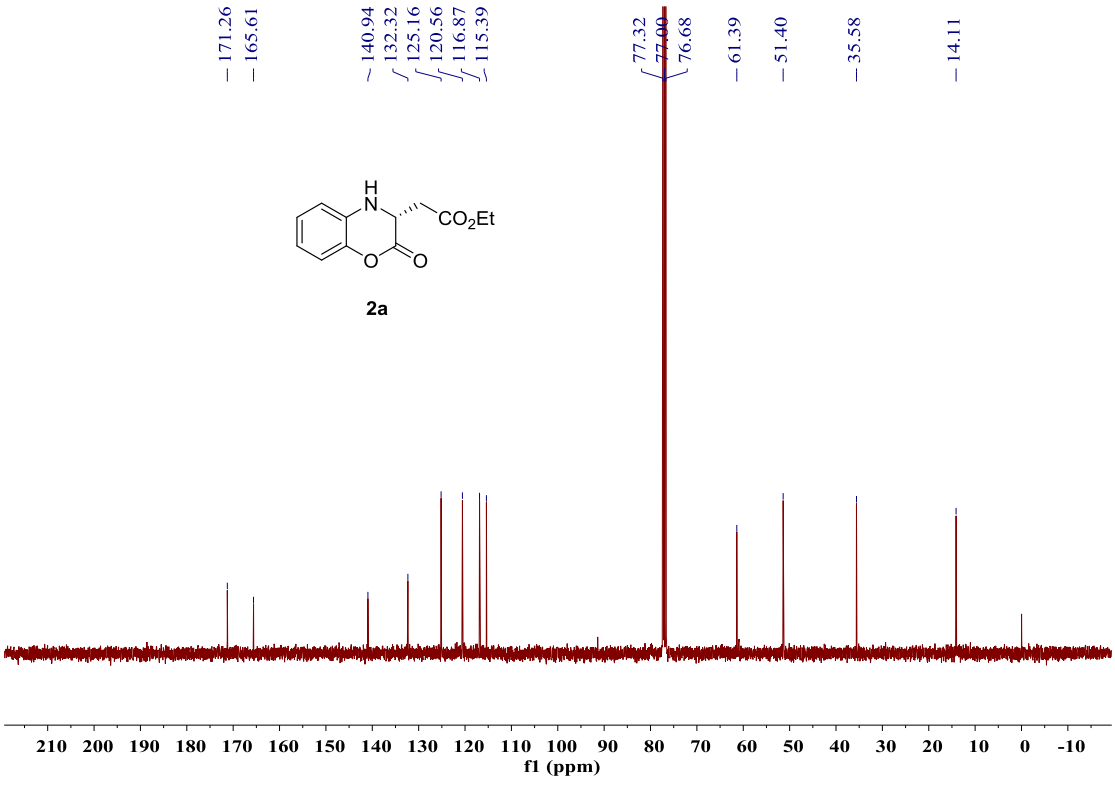
6.86
6.86
6.84
6.81
6.80
6.80
6.79
6.79
6.78
4.76
4.30
4.30
4.29
4.28
4.27
4.27
4.24
4.22
4.22
4.21
4.20
4.19
4.19
3.20
3.19
3.16
3.15
2.85
2.83
2.81
2.78
1.32
1.30
1.28
-0.00
H
N
CO2Et
O
O
1.96
0.98
1.00
0.94
0.98
2.06
1.03
1.04
3.25
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

2a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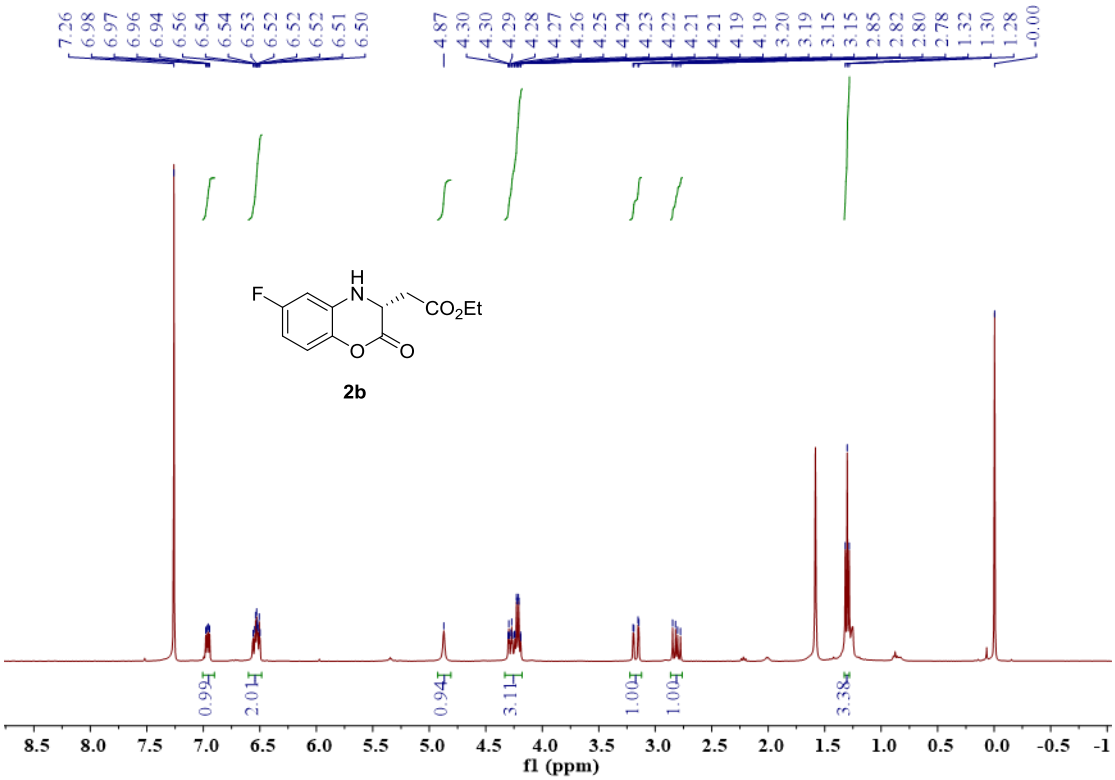
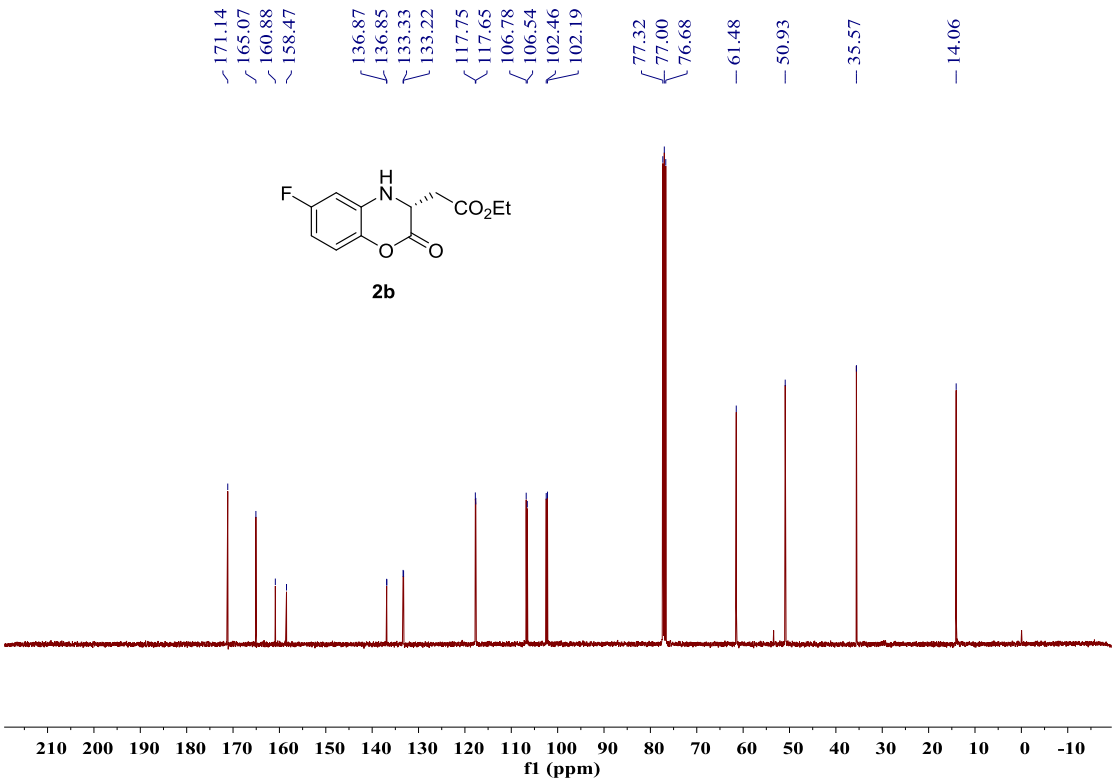
165.61
140.94
132.32
125.16
120.56
116.87
115.39
77.32
77.00
76.68
61.39
51.40
35.58
14.11
H
N
CO2Et
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2a


7.26
6.98
6.97
6.96
6.94
6.56
6.54
6.54
6.53
6.52
6.52
6.52
6.51
6.50
4.87
4.30
4.30
4.29
4.28
4.27
4.26
4.25
4.24
4.23
4.22
4.21
4.21
4.19
4.19
3.20
3.19
3.15
3.15
2.85
2.82
2.80
2.78
1.32
1.30
1.28
0.00
F
H
N
O
O
CO2Et
2b
0.99
2.01
0.94
3.11
1.00
1.00
3.38
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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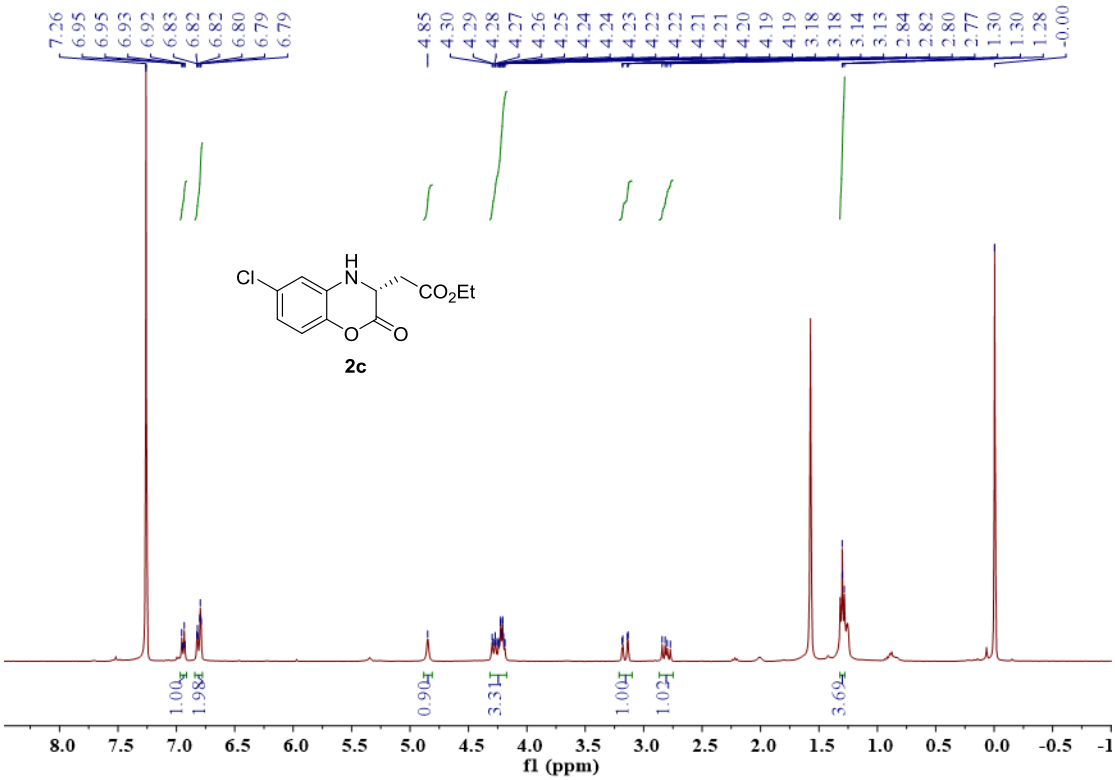
165.07
160.88
158.47
136.87
136.85
133.33
133.22
117.75
117.65
106.78
106.54
102.46
102.19
77.32
77.00
76.68
61.48
50.93
35.57
14.06
F
H
N
O
O
CO2Et
2b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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6.95
6.95
6.93
6.92
6.83
6.82
6.82
6.80
6.79
6.79
4.85
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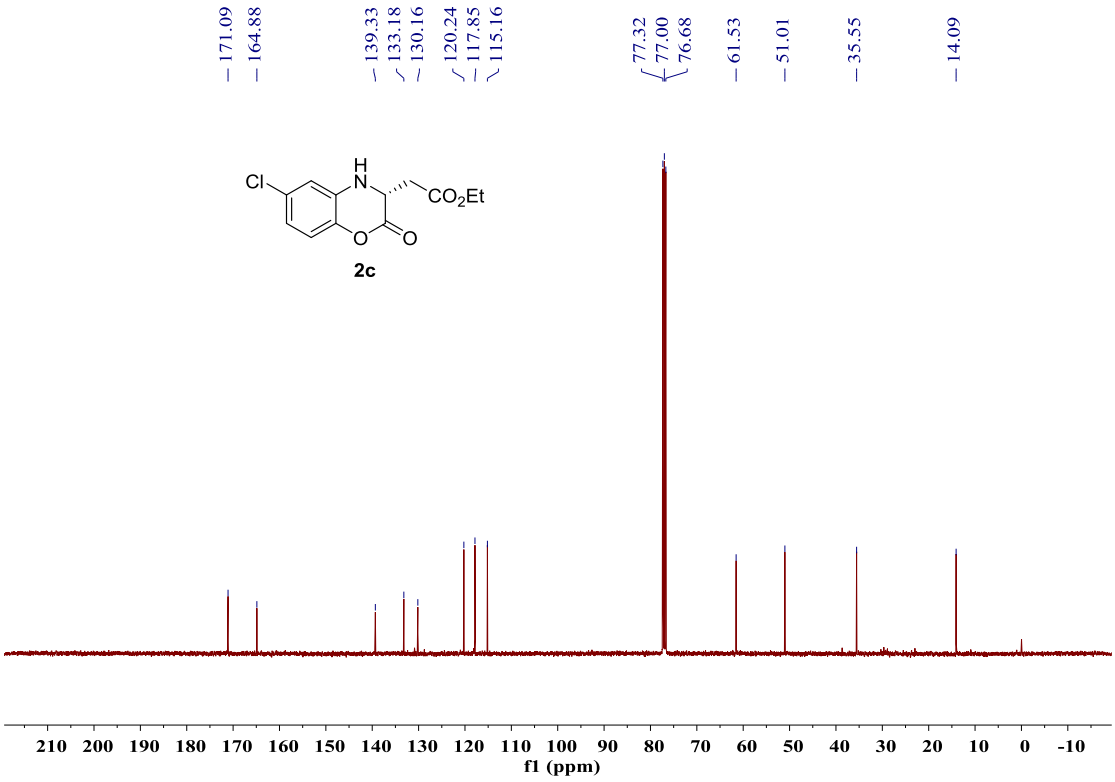
4.29
4.28
4.27
4.26
4.25
4.24
4.24
4.23
4.22
4.22
4.21
4.21
4.20
4.19
4.19
3.18
3.18
3.14
3.13
2.84
2.82
2.80
2.77
1.30
1.30
1.28
0.00
Cl
H
N
CO2Et
O
O
2c
1.00
1.98
0.90
3.31
1.00
1.02
3.69
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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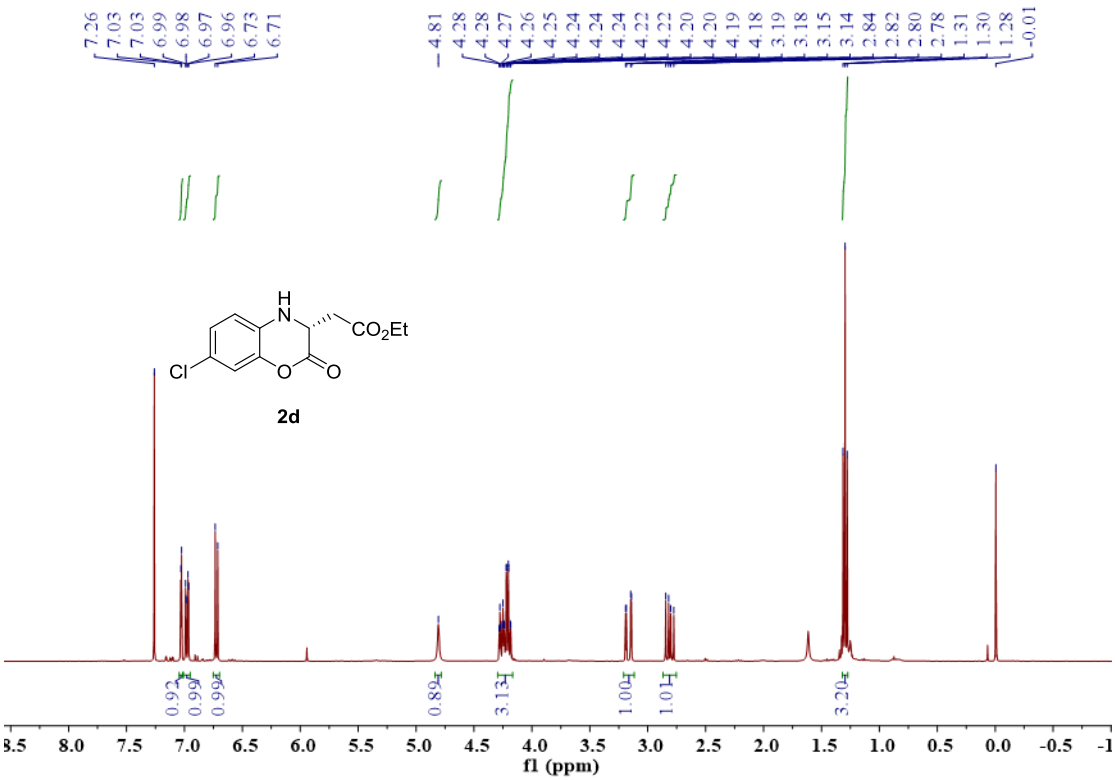
139.33
133.18
130.16
120.24
117.85
115.16
77.32
77.00
76.68
61.53
51.01
35.55
14.09
Cl
H
N
CO2Et
O
O
2c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.03
7.03
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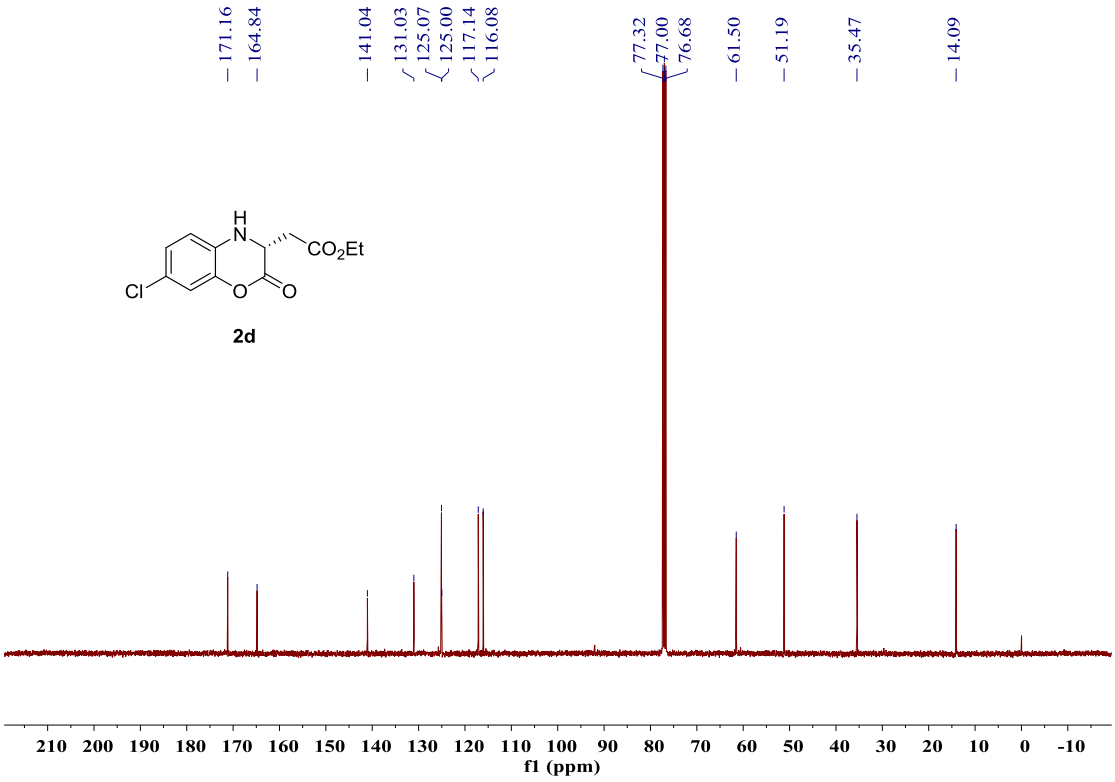
6.97
6.96
6.73
6.71
4.81
4.28
4.28
4.27
4.26
4.25
4.24
4.24
4.24
4.22
4.22
4.20
4.20
4.19
4.18
3.19
3.18
3.15
3.14
2.84
2.82
2.80
2.78
1.31
1.30
1.28
-0.01
H
N
CO2Et
Cl
O
O
2d
0.92
0.99
0.99
0.89
3.13
1.00
1.01
3.20
f1 (ppm)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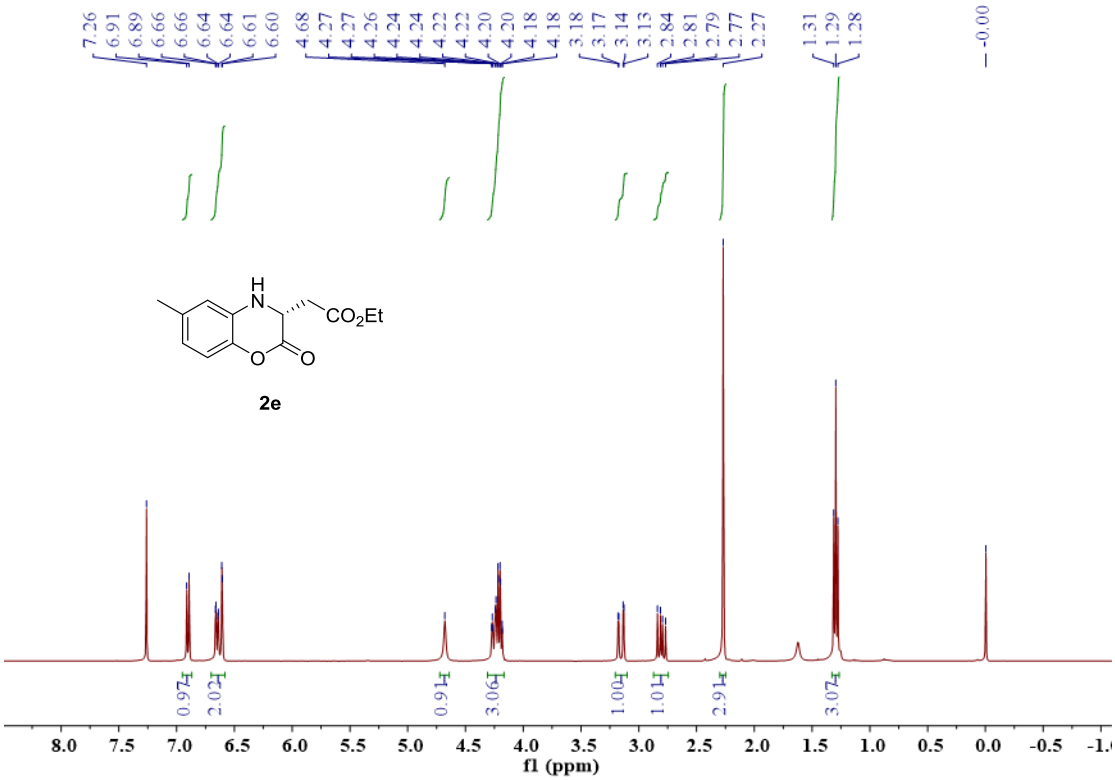
125.00
117.14
116.08
77.32
77.00
76.68
61.50
51.19
35.47
14.09
H
N
CO2Et
Cl
O
O
2d
f1 (ppm)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6.66
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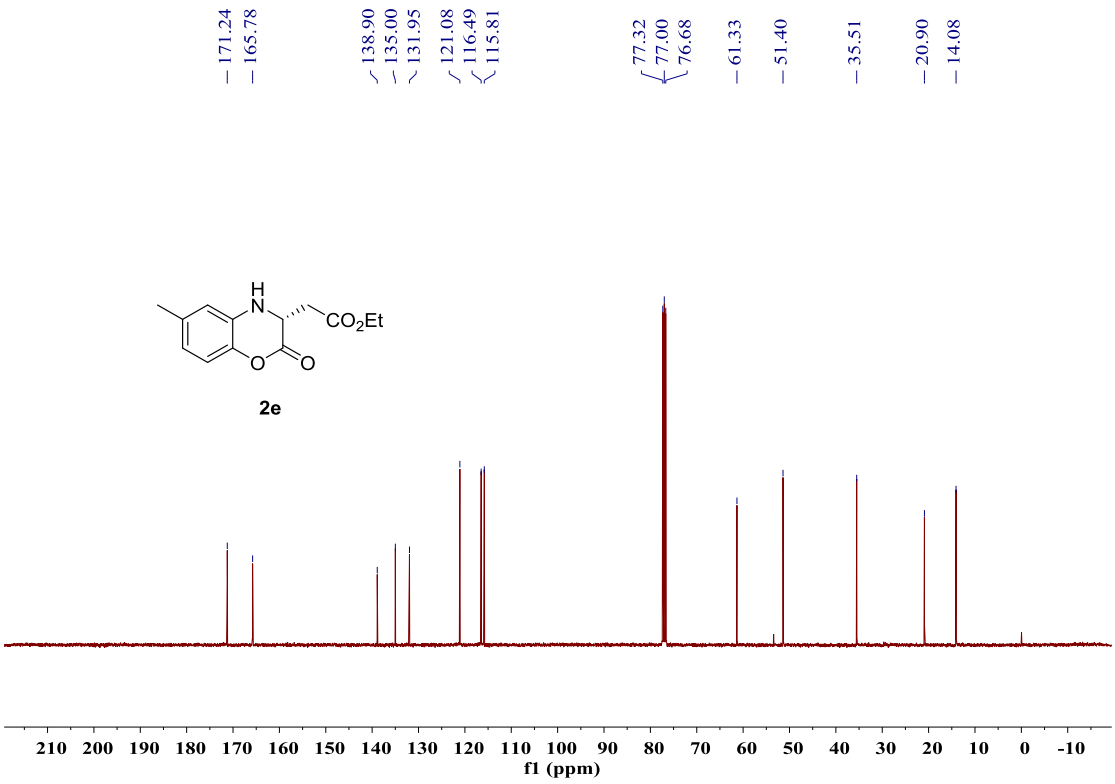
6.64
6.64
6.61
6.60
4.68
4.27
4.27
4.26
4.24
4.24
4.22
4.22
4.20
4.20
4.18
4.18
3.18
3.17
3.14
3.13
2.84
2.81
2.79
2.77
2.27
1.31
1.29
1.28
-0.00
H
N
CO2Et
O
O
0.97
2.02
0.91
3.06
1.00
1.01
2.91
3.07
f1 (ppm)

2e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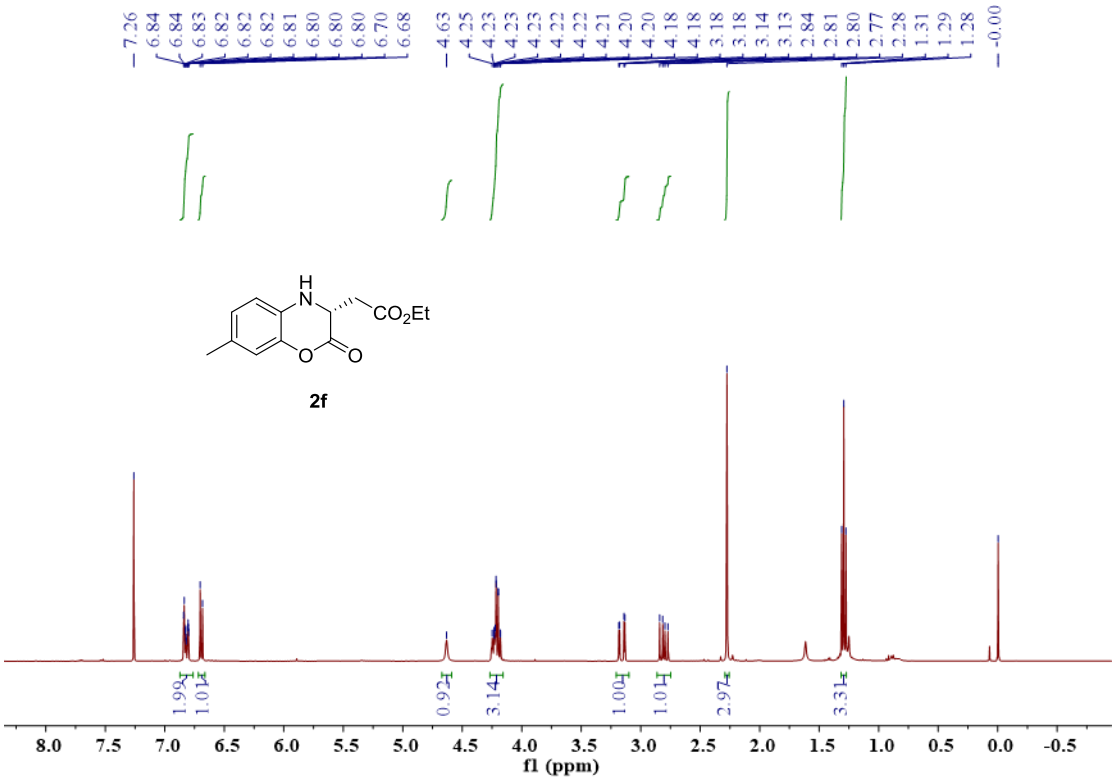
121.08
116.49
115.81
77.32
77.00
76.68
61.33
51.40
35.51
20.90
14.08
H
N
CO2Et
O
O
f1 (ppm)

2e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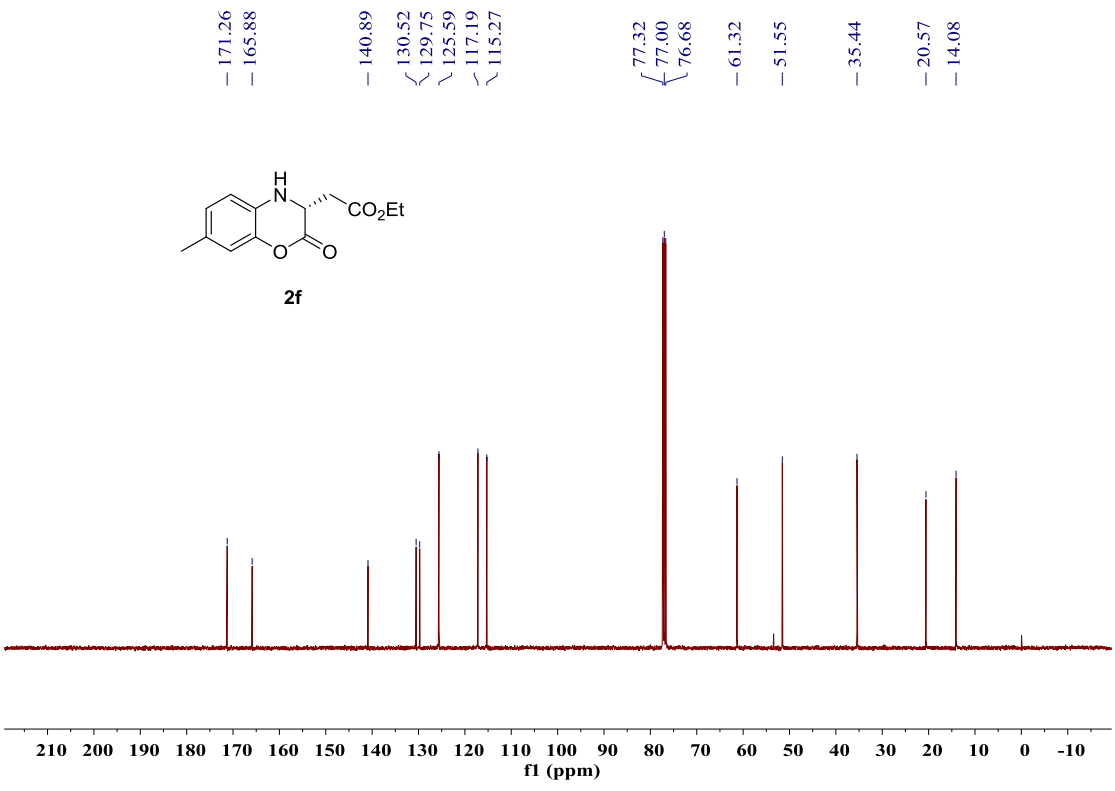
6.84
6.83
6.82
6.82
6.82
6.81
6.80
6.80
6.80
6.70
6.68
4.63
4.25
4.23
4.23
4.23
4.22
4.22
4.21
4.20
4.20
4.18
4.18
3.18
3.18
3.14
3.13
2.84
2.81
2.80
2.77
2.28
1.31
1.29
1.28
-0.00
H
N
CO2Et
O
O
1.99
1.01
0.92
3.14
1.00
1.01
2.97
3.31
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

2f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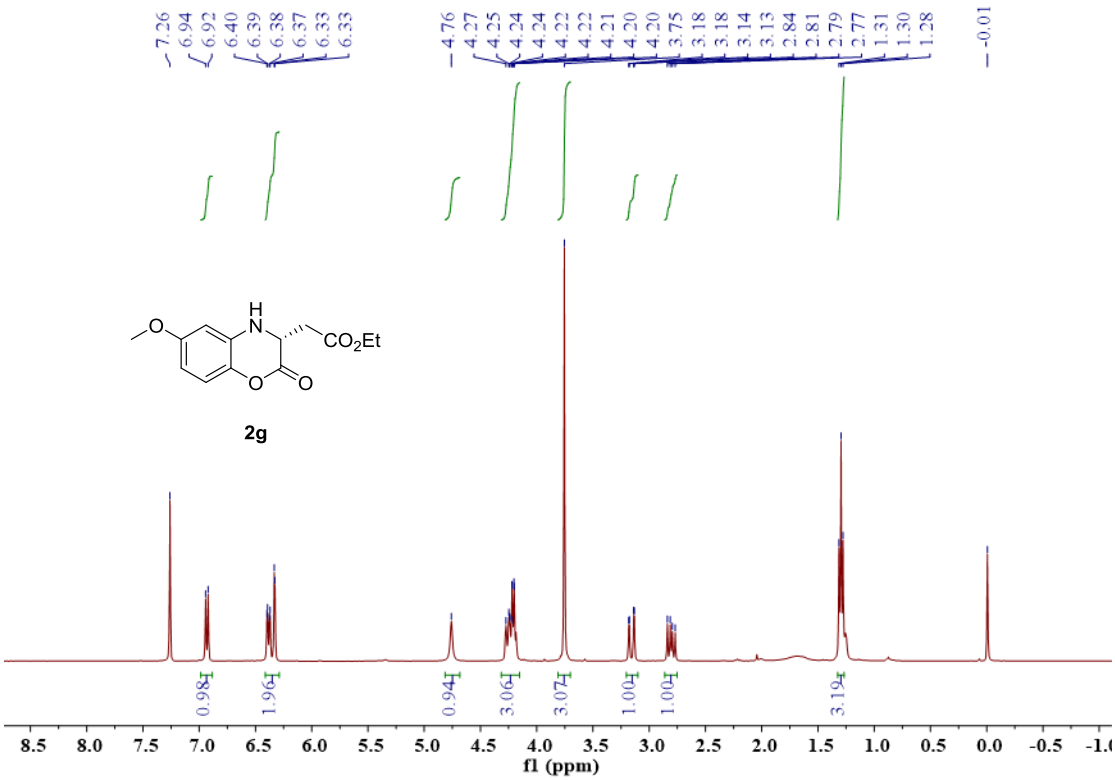
117.19
115.27
77.32
77.00
76.68
61.32
51.55
35.44
20.57
14.08
H
N
CO2Et
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2f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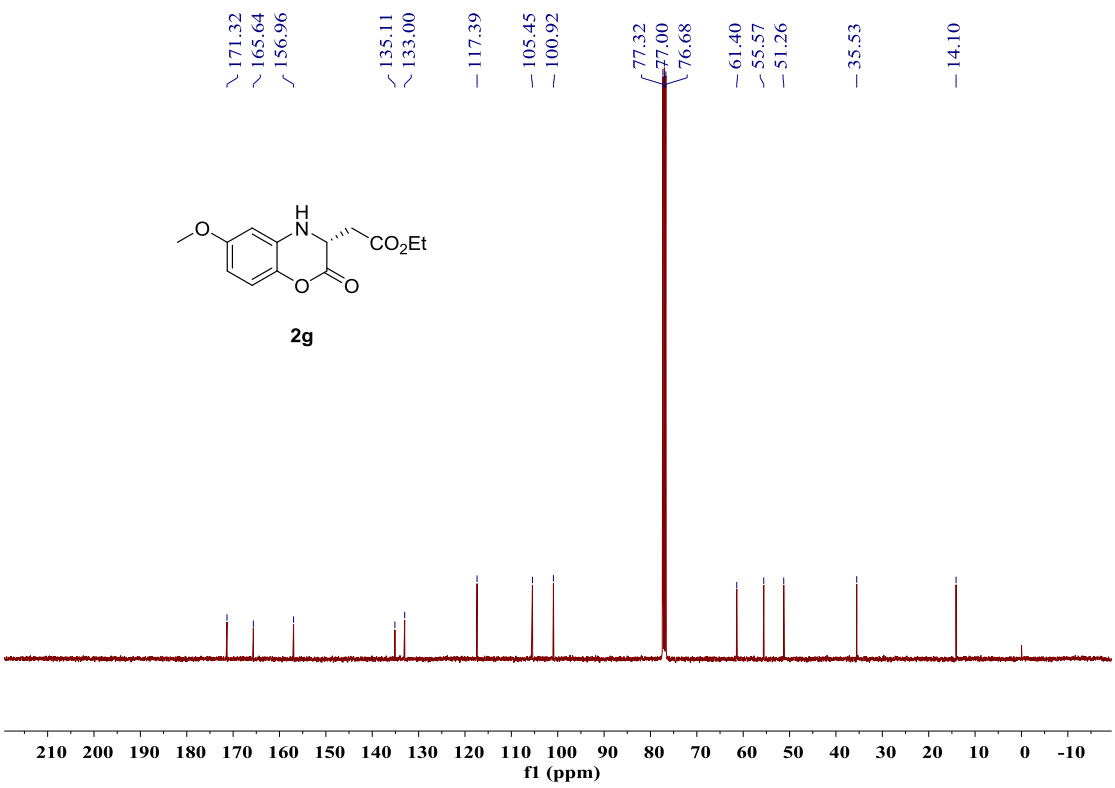
6.92
6.40
6.39
6.38
6.37
6.33
6.33
4.76
4.27
4.25
4.24
4.24
4.22
4.22
4.21
4.20
4.20
3.75
3.18
3.18
3.14
3.13
2.84
2.81
2.79
2.77
1.31
1.30
1.28
-0.01
H
N
O
O
O
CO2Et
0.98
1.96
0.94
3.06
3.07
1.00
1.00
3.19
f1 (ppm)

2g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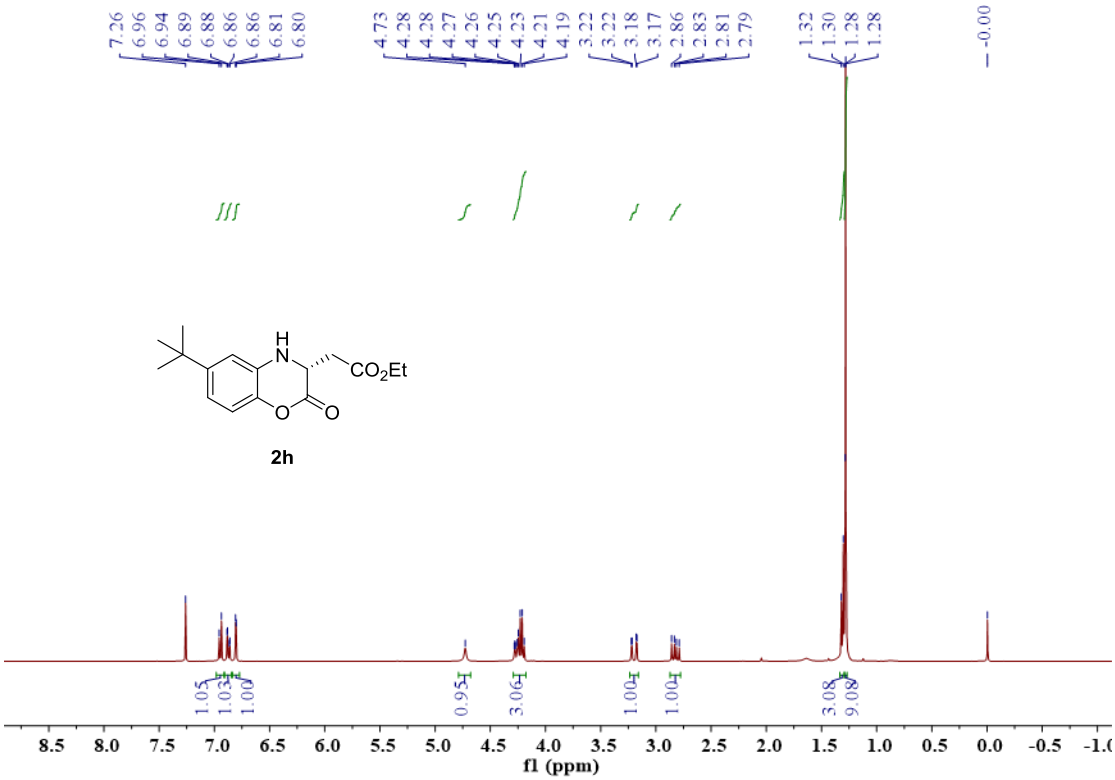
156.96
135.11
133.00
117.39
105.45
100.92
77.32
77.00
76.68
61.40
55.57
51.26
35.53
14.10
H
N
O
O
O
CO2Et
f1 (ppm)

2g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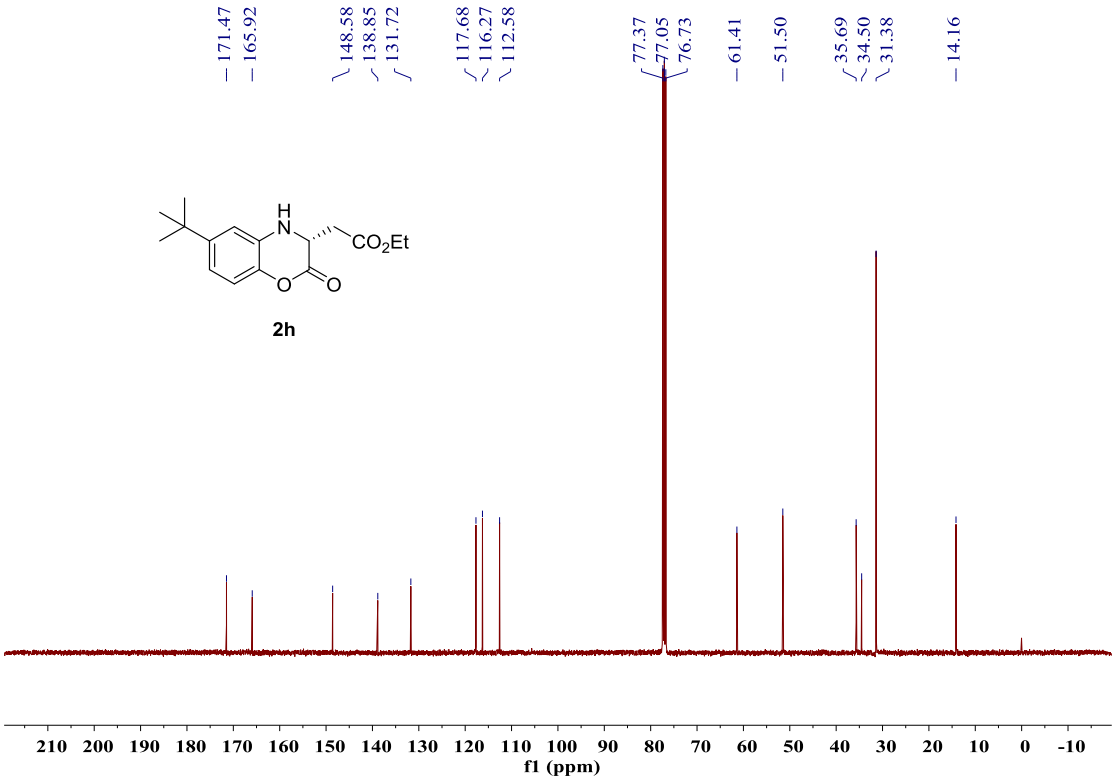
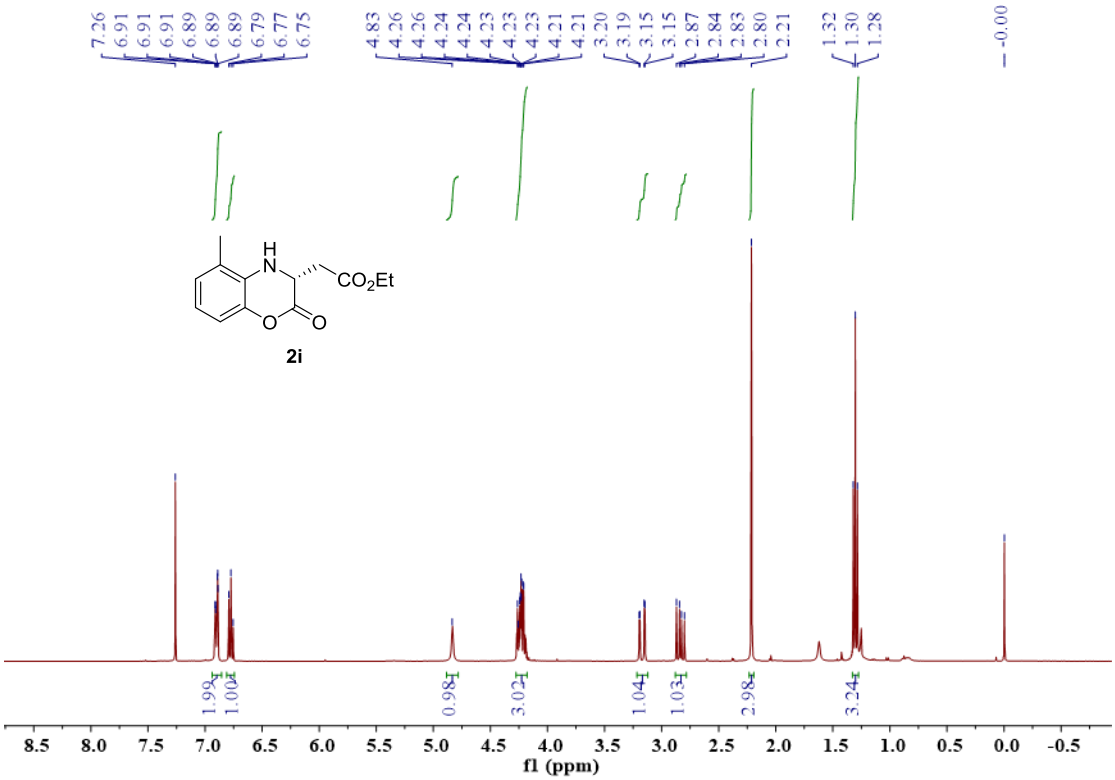
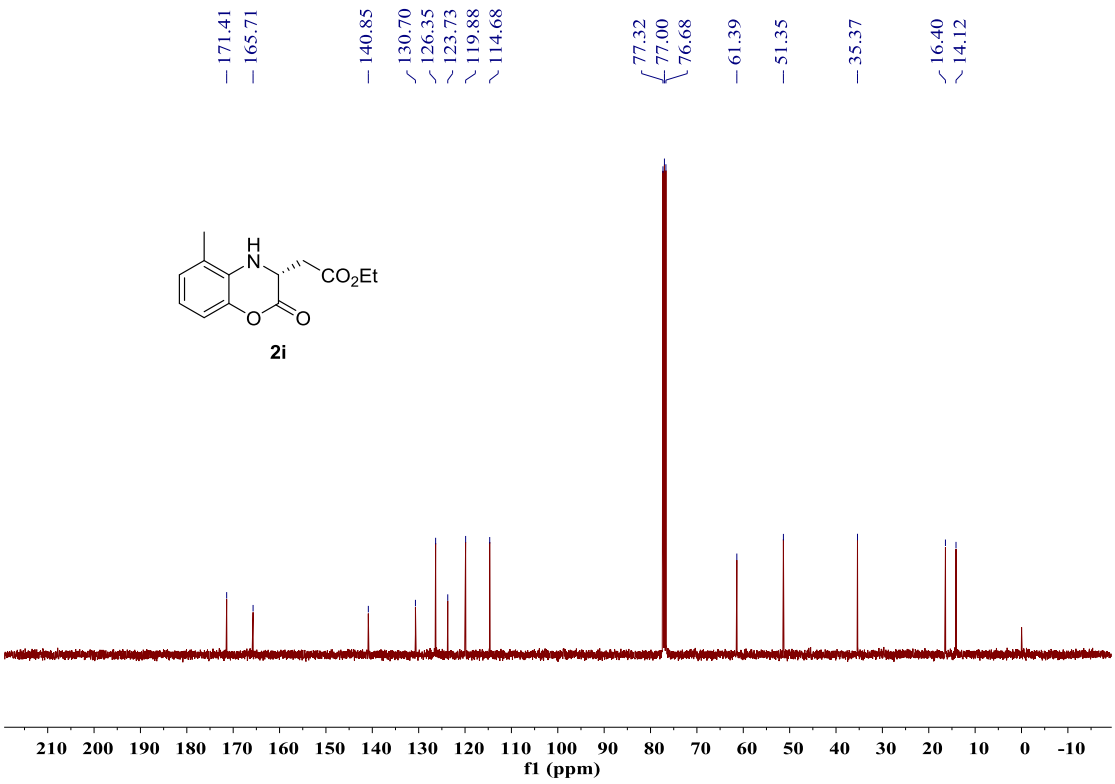
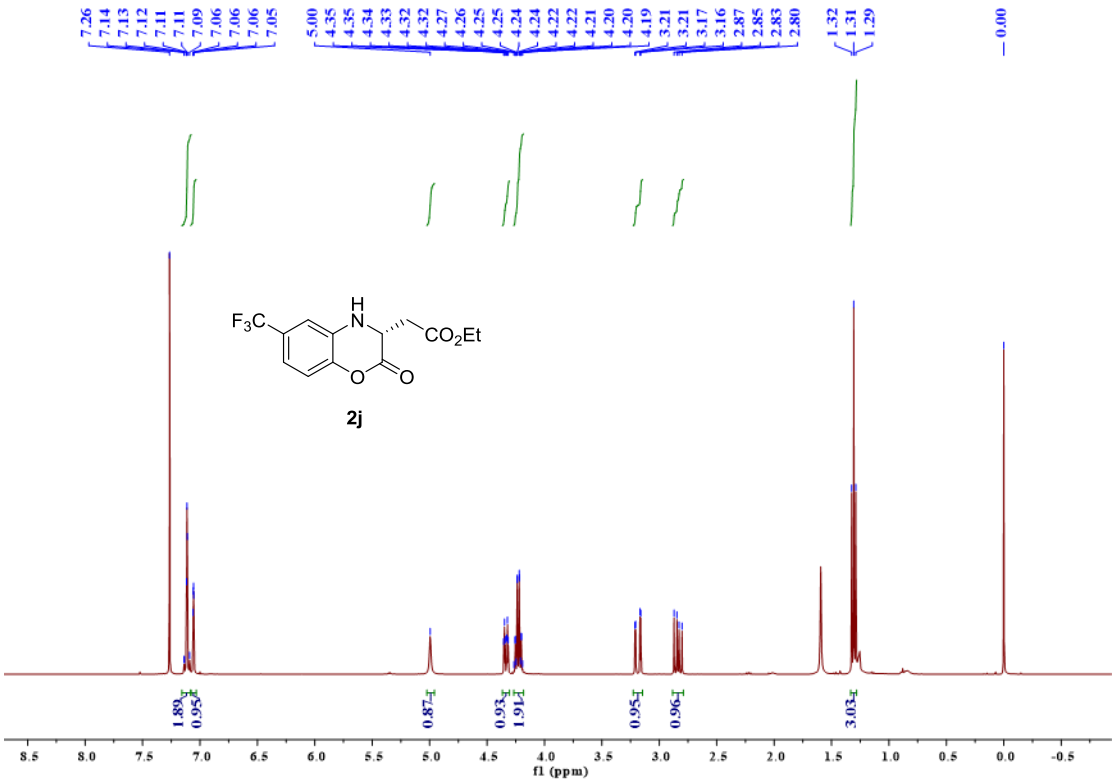
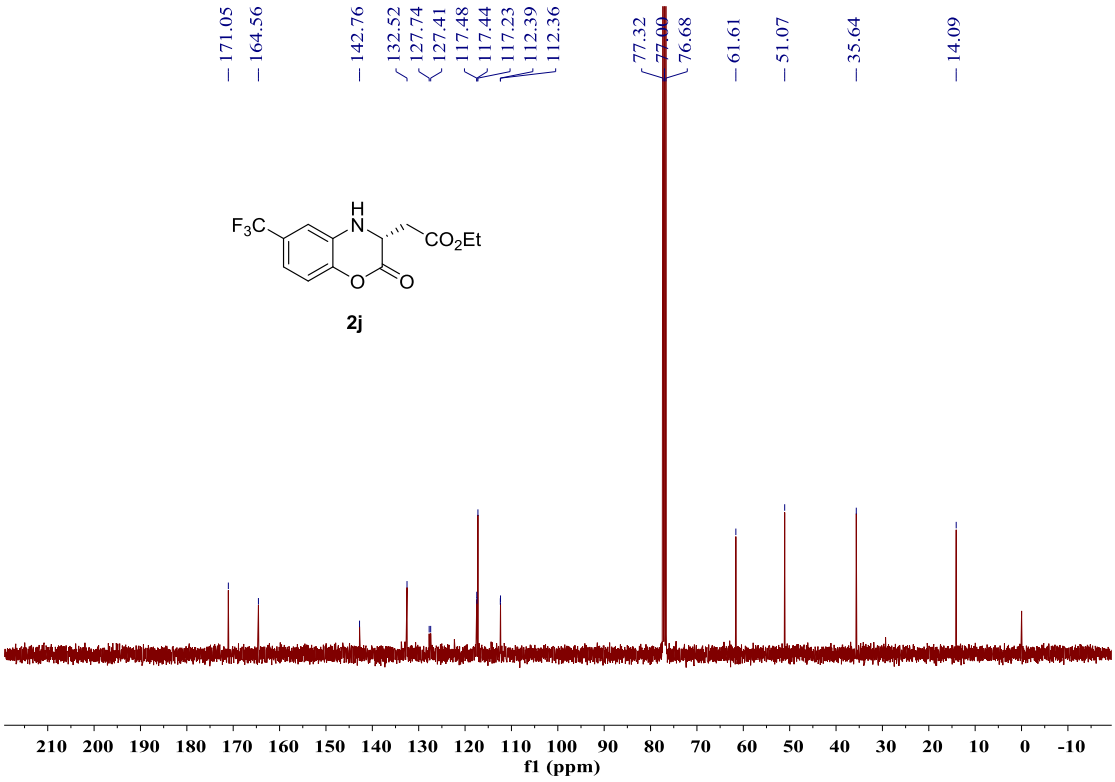
6.94
6.89
6.88
6.86
6.86
6.81
6.80
4.73
4.28
4.28
4.27
4.26
4.25
4.23
4.21
4.19
3.22
3.22
3.18
3.17
2.86
2.83
2.81
2.79
1.32
1.30
1.28
1.28
-0.00
H
N
CO2Et
O
O
2h
1.05
1.03
1.00
0.95
3.06
1.00
1.00
3.08
9.08
f1 (ppm)

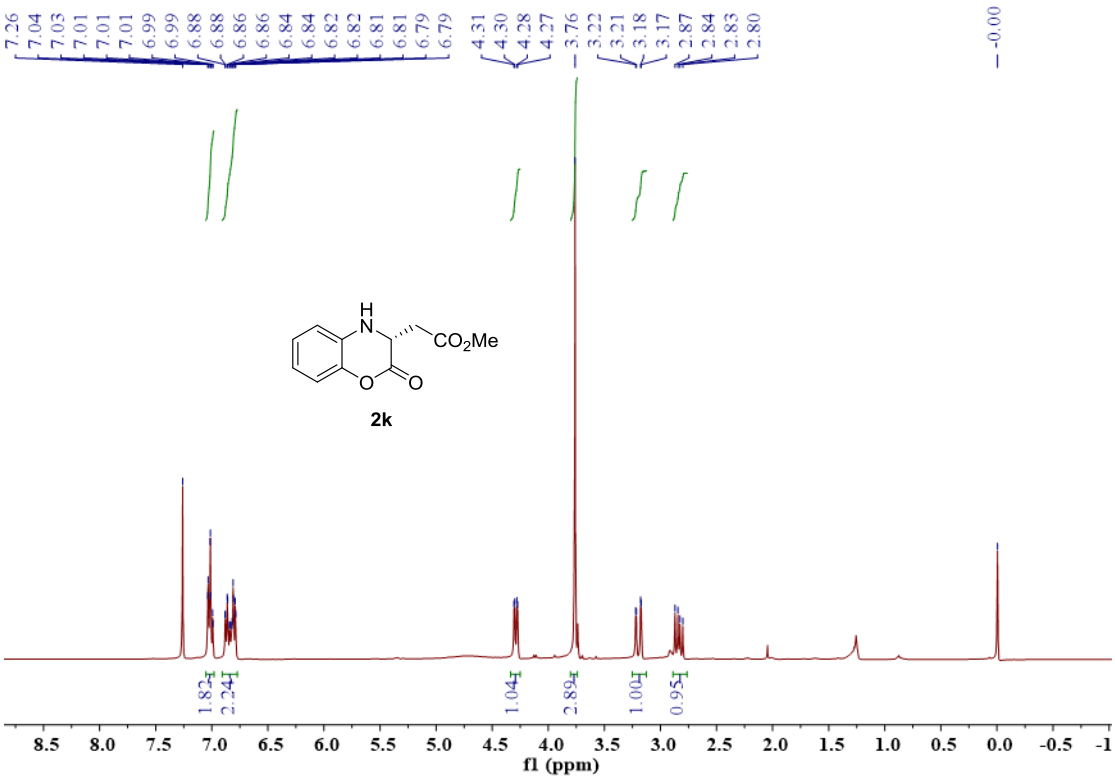

171.47
165.92
148.58
138.85
131.72
117.68
116.27
112.58
77.37
77.05
76.73
61.41
51.50
35.69
34.50
31.38
14.16
H
N
CO2Et
O
O
2h
f1 (ppm)


7.26
6.91
6.91
6.91
6.89
6.89
6.89
6.79
6.77
6.75
4.83
4.26
4.26
4.24
4.24
4.23
4.23
4.23
4.21
4.21
3.20
3.19
3.15
3.15
2.87
2.84
2.83
2.80
2.21
1.32
1.30
1.28
-0.00
H
N
CO2Et
O
O
2i
1.99
1.00
0.98
3.02
1.04
1.03
2.98
3.24
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


171.41
165.71
140.85
130.70
126.35
123.73
119.88
114.68
77.32
77.00
76.68
61.39
51.35
35.37
16.40
14.12
H
N
CO2Et
O
O
2i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

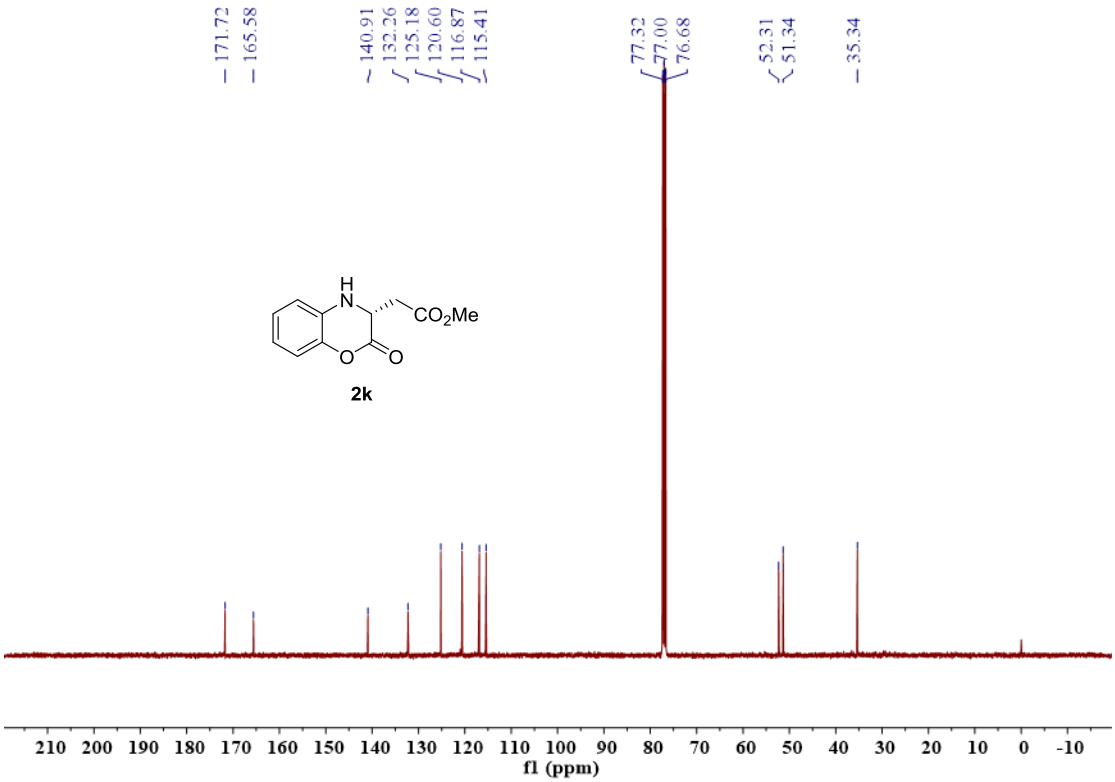

7.26
7.14
7.13
7.12
7.11
7.11
7.09
7.06
7.06
7.06
7.05
5.00
4.35
4.35
4.34
4.33
4.32
4.32
4.27
4.26
4.25
4.25
4.24
4.24
4.22
4.22
4.21
4.20
4.20
4.19
3.21
3.21
3.17
3.16
2.87
2.85
2.83
2.80
1.32
1.31
1.29
0.00
F3C
N
H
CO2Et
O
O
2j
1.89
0.95
0.87
0.93
1.91
0.95
0.96
3.03
f1 (ppm)


171.05
164.56
142.76
132.52
127.74
127.41
117.48
117.44
117.23
112.39
112.36
77.32
77.00
76.68
61.61
51.07
35.64
14.09
F3C
N
H
CO2Et
O
O
2j
f1 (ppm)


7.26
7.04
7.03
7.01
7.01
7.01
6.99
6.99
6.88
6.88
6.86
6.86
6.84
6.84
6.82
6.82
6.81
6.81
6.79
6.79
4.31
4.30
4.28
4.27
3.76
3.22
3.21
3.18
3.17
2.87
2.84
2.83
2.80
-0.00
1.82
2.24
1.04
2.89
1.00
0.95
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

H
N
CO2Me
O
O

2k


171.72
165.58
140.91
132.26
125.18
120.60
116.87
115.41
77.32
77.00
76.68
52.31
51.34
35.34
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

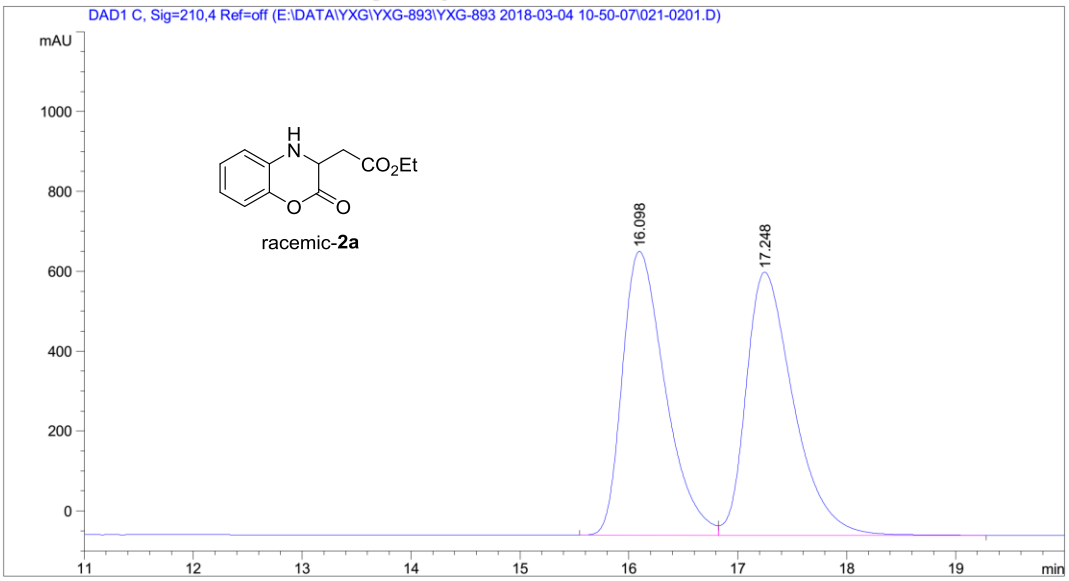
H
N
CO2Me
O
O

2k

VI. HPLC spectra

Data File E:\DATA\YXG\YXG-893\YXG-893 2018-03-04 10-50-07\021-0201.D
Sample Name: CZY-RACE

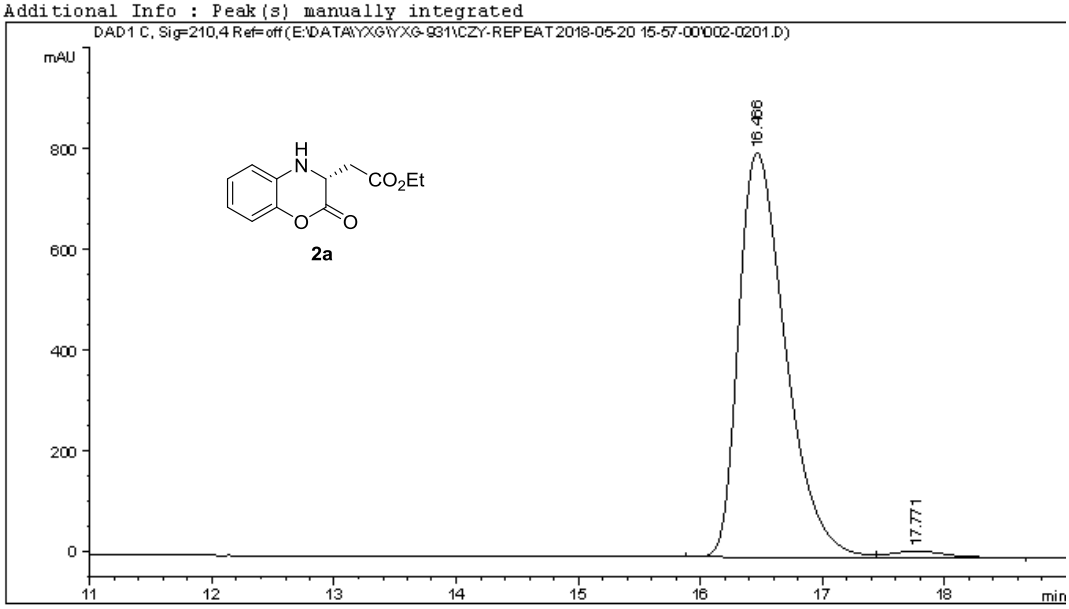
```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   2
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 21
    Injection Date  : 3/4/2018 11:04:24 AM               Inj :   1
                                                   Inj Volume : 3.000 µl
    Acq. Method     : E:\DATA\YXG\YXG-893\YXG-893 2018-03-04 10-50-07\DAD-OD(1-2)-95-5-1ML-3UL-
                      210NM-40MIN.M
    Last changed    : 3/4/2018 10:50:08 AM by SYSTEM
    Analysis Method : E:\DATA\YXG\YXG-893\YXG-893 2018-03-04 10-50-07\DAD-OD(1-2)-95-5-1ML-3UL-
                      210NM-40MIN.M (Sequence Method)
    Last changed    : 11/27/2018 9:33:33 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  16.098 BV    0.4189 1.94251e4   710.70105  49.4433
       2  17.248 VB    0.4558 1.98626e4   658.70929  50.5567

    Totals :                  3.92877e4  1369.41034
```

Data File E:\DATA\YXG\YXG-931\CZY-REPEAT 2018-05-20 15-57-00\002-0201.D
Sample Name: CZY-0519-96

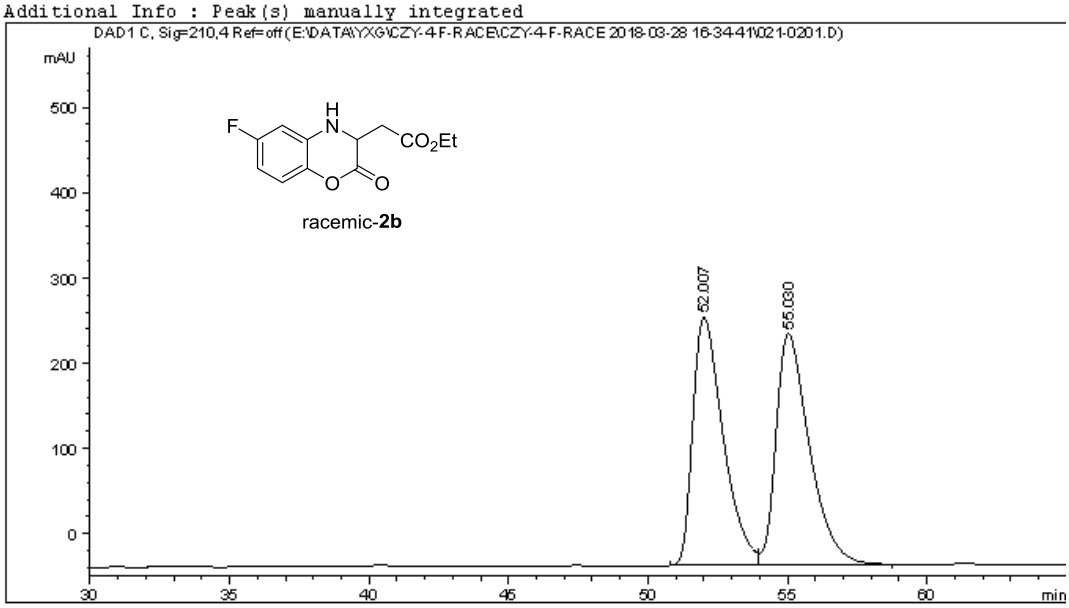
```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 2
    Injection Date  : 5/20/2018 4:10:00 PM                Inj :   1
                                                     Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\YXG\YXG-931\CZY-REPEAT 2018-05-20 15-57-00\DAD-0D(1-2)-95-5-1ML-
                      2UL-ALL-25MIN.M
    Last changed    : 5/20/2018 3:57:00 PM by SYSTEM
    Analysis Method : E:\DATA\YXG\YXG-931\CZY-REPEAT 2018-05-20 15-57-00\DAD-0D(1-2)-95-5-1ML-
                      2UL-ALL-25MIN.M (Sequence Method)
    Last changed    : 11/27/2018 5:51:52 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  16.466 BV    0.4091 2.14374e4   804.00061  98.2343
       2  17.771 VB    0.3616  385.32266   13.23580   1.7657

    Totals :                  2.18227e4   817.23641

    ======================================================================
                            *** End of Report ***
```

Data File E:\DATA\YXG\CZY-4-F-RACE\CZY-4-F-RACE 2018-03-28 16-34-41\021-0201.D
Sample Name: CZY-4-F-RACE

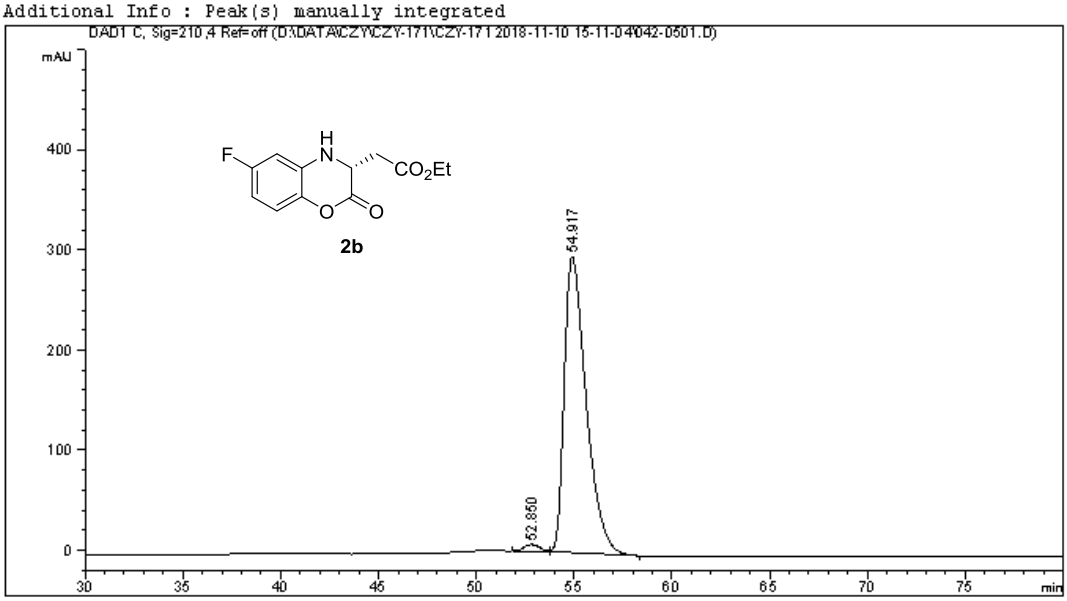
```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 21
    Injection Date  : 3/28/2018 4:47:56 PM                 Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\YXG\CZY-4-F-RACE\CZY-4-F-RACE 2018-03-28 16-34-41\DAD-OD(1-2)-97
                      -3-0.5ML-5UL-210NM-70MIN.M
    Last changed    : 3/28/2018 5:54:42 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\YXG\CZY-4-F-RACE\CZY-4-F-RACE 2018-03-28 16-34-41\DAD-OD(1-2)-97
                      -3-0.5ML-5UL-210NM-70MIN.M (Sequence Method)
    Last changed    : 11/27/2018 9:27:11 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  52.007 BV    1.0872 2.20450e4   291.20303  49.3849
       2  55.030 VB    1.1280 2.25942e4   271.20145  50.6151

    Totals :                  4.46392e4   562.40448

    ======================================================================
```

Data File D:\DATA\CZY\CZY-171\CZY-171 2018-11-10 15-11-04\042-0501.D
Sample Name: CZY-171-2-4-F

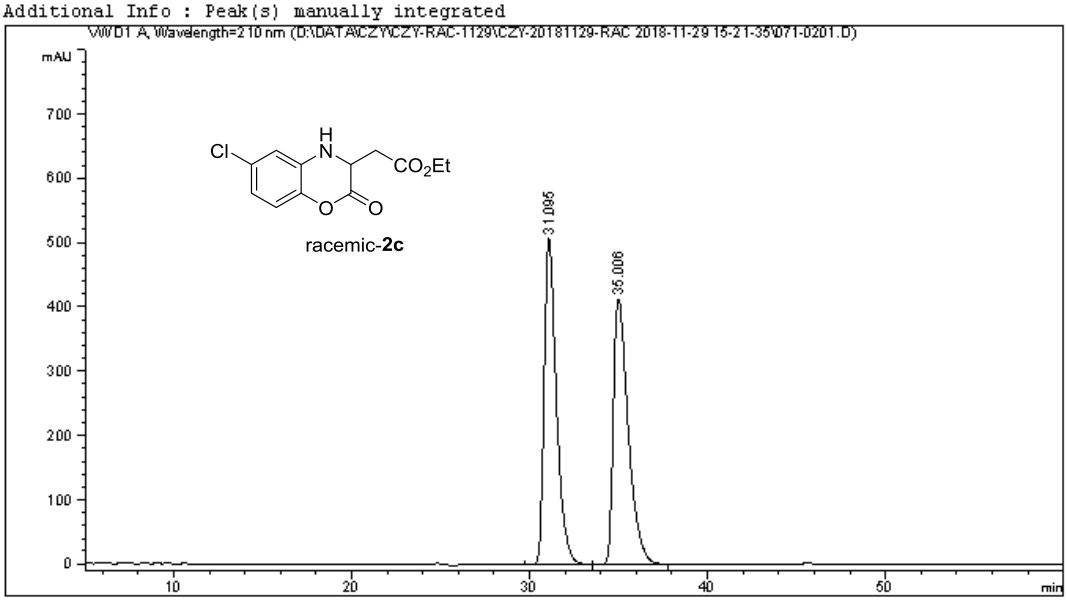
```
    ======================================================================
    Acq. Operator   :                                Seq. Line :   5
    Acq. Instrument : Instrument 2                    Location : Vial 42
    Injection Date  : 11/10/2018 4:27:51 PM               Inj :   1
                                                    Inj Volume : 3.000 µl
    Acq. Method     : D:\DATA\CZY\CZY-171\CZY-171 2018-11-10 15-11-04\DAD-0D(1-2)-97-3-0.5ML-3UL-
                      ALL-80MIN.M
    Last changed    : 5/26/2018 2:44:22 PM
    Analysis Method : D:\METHOD\LGY\DAD-0J(1-6)-95-5--1ML-5UL-ALL-60MIN.M
    Last changed    : 11/27/2018 8:45:36 PM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  52.850 BB    0.6623  354.51184    6.34039   1.5275
       2  54.917 BB    1.1156 2.28540e4   295.08643  98.4725

    Totals :                  2.32085e4   301.42681
```

Data File D:\DATA\CZY\CZY-RAC-1129\CZY-20181129-RAC 2018-11-29 15-21-35\071-0201.D
Sample Name: CZY-4-CL-RAC

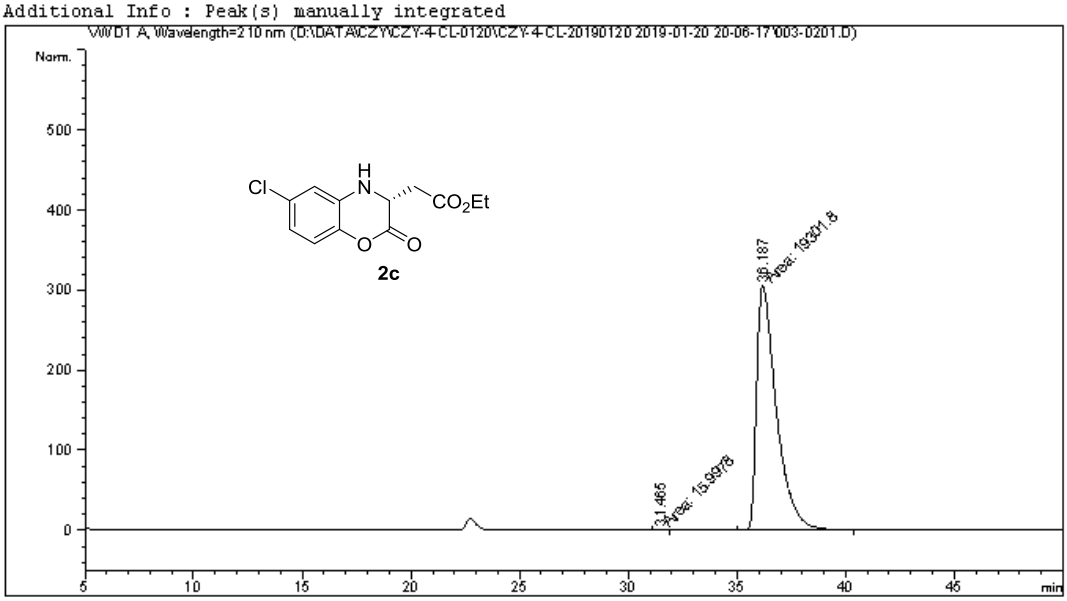
```
=====================================================================
Acq. Operator   :                              Seq. Line :   2
Acq. Instrument : Instrument 1                  Location : Vial 71
Injection Date  : 11/29/2018 3:33:18 PM              Inj :   1
                                               Inj Volume : 3.000 µl
Acq. Method     : D:\DATA\CZY\CZY-RAC-1129\CZY-20181129-RAC 2018-11-29 15-21-35\VWD-AD(1-2)-
                  97-3-1ML-3UL-210NM-70MIN.M
Last changed    : 7/18/2018 9:36:56 AM
Analysis Method : D:\METHOD\GUAN YUQING\DAD-0J(1-6)-96-4-0.8ML-5UL-ALL-110MIN.M
Last changed    : 1/11/2019 9:51:37 AM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  31.095 BB    0.7159 2.41259e4   507.21054  50.0592
   2  35.006 BB    0.8897 2.40688e4   413.12375  49.9408

Totals :                 4.81947e4   920.33429
```

Data File D:\DATA\CZY\CZY-4-CL-0120\CZY-4-CL-20190120 2019-01-20 20-06-17\003-0201.D
Sample Name: CZY-4-CL

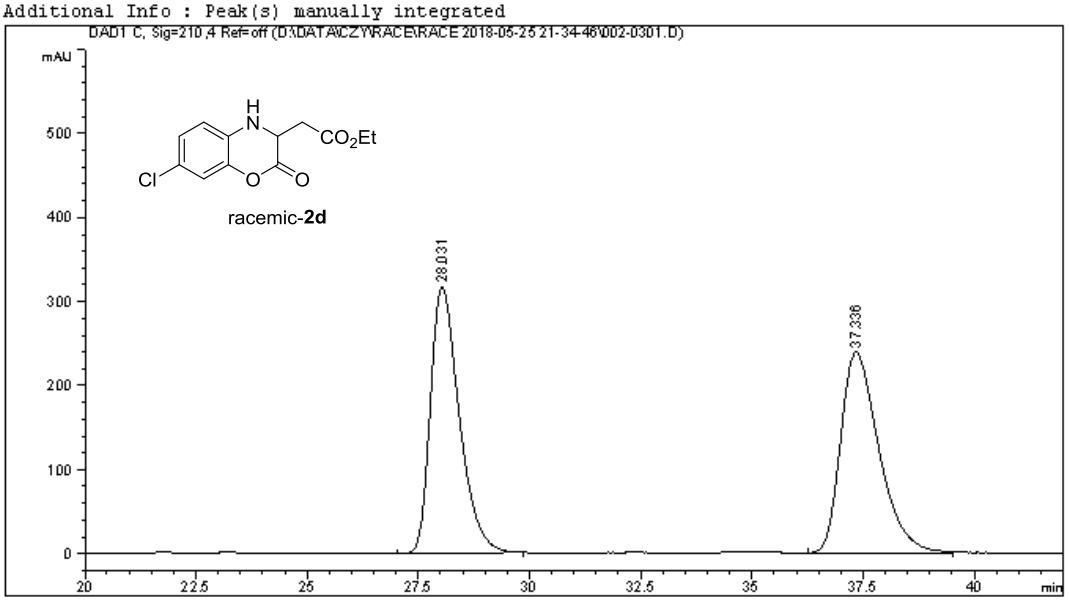
```
    ======================================================================
    Acq. Operator   :                                 Seq. Line :   2
    Acq. Instrument : Instrument 1                     Location : Vial 3
    Injection Date  : 1/20/2019 8:17:59 PM                  Inj :   1
                                                    Inj Volume : 3.000 µl
    Acq. Method     : D:\DATA\CZY\CZY-4-CL-0120\CZY-4-CL-20190120 2019-01-20 20-06-17\VWD-AD(1-2)
                      -97-3-1ML-3UL-210NM-50MIN.M
    Last changed    : 1/20/2019 8:07:26 PM
    Analysis Method : D:\METHOD\CZY\VWD-AD(1-2)-97-3-1ML-3UL-210NM-50MIN.M
    Last changed    : 1/20/2019 9:54:55 PM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  31.465 MM    0.5711   15.99777 4.66839e-1   0.0828
       2  36.187 MM    1.0552 1.93018e4   304.88022  99.9172

    Totals :                  1.93178e4   305.34706
```

Data File D:\DATA\CZY\RACE\RACE 2018-05-25 21-34-46\002-0301.D
Sample Name: CZY-RACE-5-CL-2

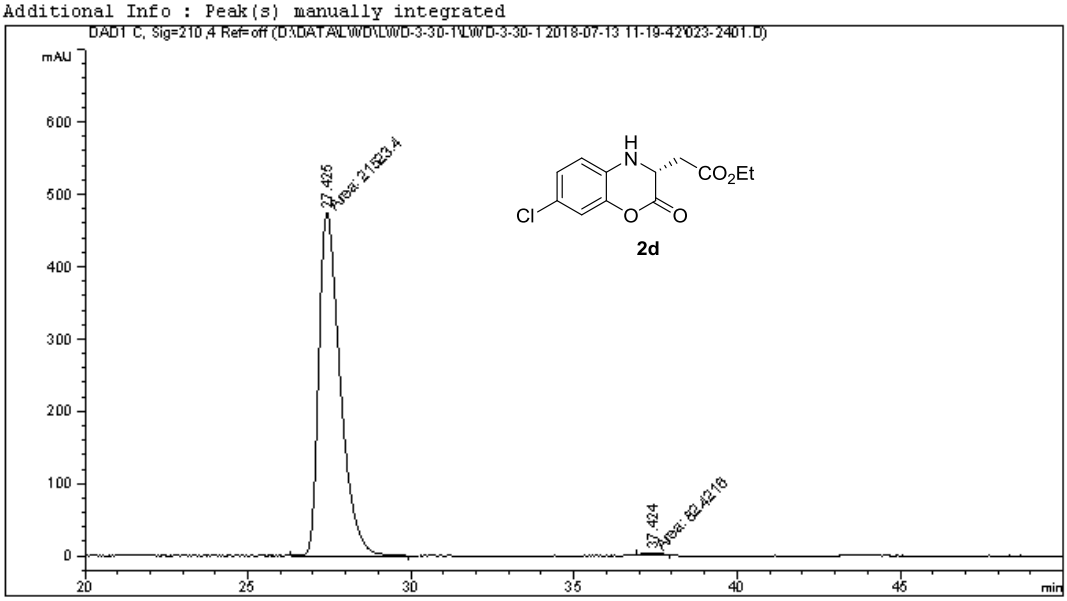
```
    ======================================================================
    Acq. Operator   :                                 Seq. Line :   3
    Acq. Instrument : Instrument 2                     Location : Vial 2
    Injection Date  : 5/25/2018 10:47:42 PM                 Inj :   1
                                                    Inj Volume : 3.000 µl
    Acq. Method     : D:\DATA\CZY\RACE\RACE 2018-05-25 21-34-46\DAD-0D(1-2)-98-2-1ML-3UL-ALL-
                      60MIN.M
    Last changed    : 5/25/2018 9:31:05 PM
    Analysis Method : D:\METHOD\LGY\DAD-0J(1-6)-95-5--1ML-5UL-ALL-60MIN.M
    Last changed    : 11/27/2018 8:59:44 PM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  28.031 BB    0.6538 1.42180e4   316.70486  49.9217
       2  37.336 BV    0.8621 1.42626e4   239.02939  50.0783

    Totals :                  2.84807e4   555.73425
```

Data File D:\DATA\LWD\LWD-3-30-1\LWD-3-30-1 2018-07-13 11-19-42\023-2401.D
Sample Name: CZY-0323-5-Cl

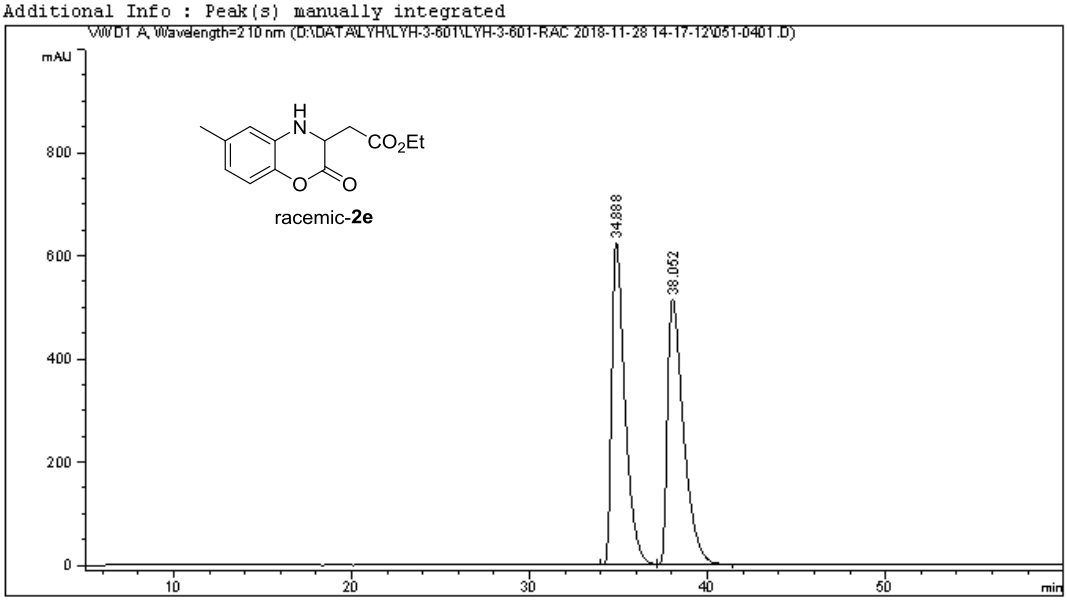
```
======================================================================
Acq. Operator   :                                Seq. Line :  24
Acq. Instrument : Instrument 2                    Location : Vial 23
Injection Date  : 7/14/2018 3:12:20 AM                 Inj :  1
                                                 Inj Volume : 3.000 µl
Acq. Method     : D:\DATA\LWD\LWD-3-30-1\LWD-3-30-1 2018-07-13 11-19-42\DAD-0D(1-2)-98-2-1ML-
                  3UL-ALL-50MIN.M
Last changed    : 7/13/2018 5:55:47 PM
Analysis Method : D:\METHOD\LGY\DAD-0J(1-6)-95-5--1ML-5UL-ALL-60MIN.M
Last changed    : 11/27/2018 8:50:25 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
======================================================================
                          Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  27.425 MM    0.7560 2.15234e4   474.49420  99.6185
   2  37.424 MM    0.5157   82.42159    2.66377   0.3815

Totals :                  2.16058e4   477.15797
```

Data File D:\DATA\LYH\LYH-3-601\LYH-3-601-RAC 2018-11-28 14-17-12\051-0401.D
Sample Name: CZY-4ME-RAC

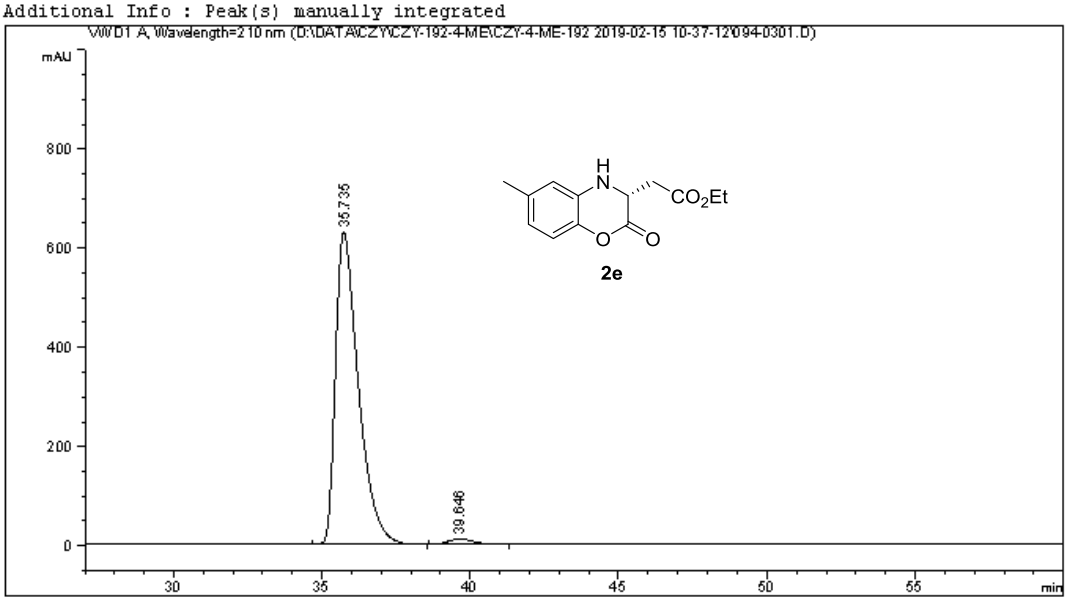
```
    ======================================================================
    Acq. Operator   :                              Seq. Line :   4
    Acq. Instrument : Instrument 1                  Location : Vial 51
    Injection Date  : 11/28/2018 4:25:38 PM              Inj :   1
                                                  Inj Volume : 3.000 µl
    Acq. Method     : D:\DATA\LYH\LYH-3-601\LYH-3-601-RAC 2018-11-28 14-17-12\VWD-AD(1-2)-98-2-
                      1ML-3UL-210NM-60MIN.M
    Last changed    : 7/13/2018 6:06:01 PM
    Analysis Method : D:\METHOD\GUAN YUQING\DAD-0J(1-6)-96-4-0.8ML-5UL-ALL-110MIN.M
    Last changed    : 1/11/2019 9:53:53 AM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  34.888 BB    0.7773 3.2222le4   623.11316  49.9983
       2  38.052 BB    0.9515 3.22244e4   513.21271  50.0017

    Totals :                  6.44465e4  1136.32587
```

Data File D:\DATA\CZY\CZY-192-4-ME\CZY-4-ME-192 2019-02-15 10-37-12\094-0301.D
Sample Name: CZY-192-4-ME-EE

```
    ======================================================================
    Acq. Operator   :                                Seq. Line :   3
    Acq. Instrument : Instrument 1                    Location : Vial 94
    Injection Date  : 2/15/2019 11:00:40 AM               Inj :   1
                                                    Inj Volume : 3.000 µl
    Acq. Method     : D:\DATA\CZY\CZY-192-4-ME\CZY-4-ME-192 2019-02-15 10-37-12\VWD-AD(1-2)-98-2-
                      1ML-3UL-210NM-60MIN.M
    Last changed    : 7/13/2018 6:06:01 PM
    Analysis Method : D:\METHOD\LYH\VWD-AD(1-2)-95-5-1ML-1UL-210NM-35MIN.M
    Last changed    : 2/15/2019 12:22:23 PM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

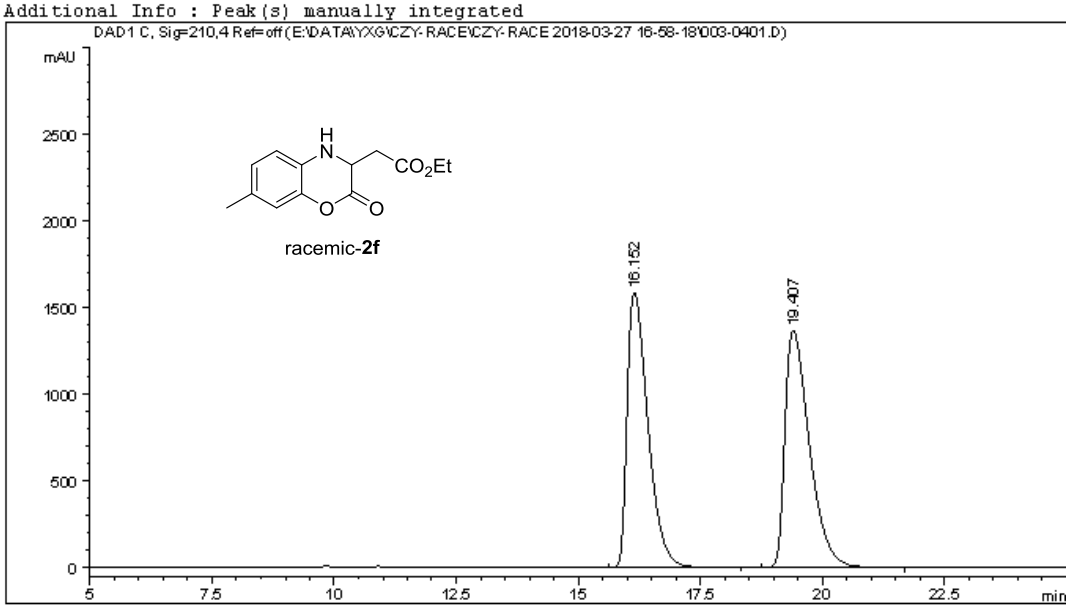


2e

```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  35.735 BB    0.8089 3.36277e4   628.85211  98.2220
       2  39.646 BB    0.8528  608.71466   10.68295   1.7780

    Totals :                  3.42364e4   639.53506
```

Data File E:\DATA\YXG\CZY-RACE\CZY-RACE 2018-03-27 16-58-18\003-0401.D
Sample Name: CZY-0326-64-1-5-ME-RACE

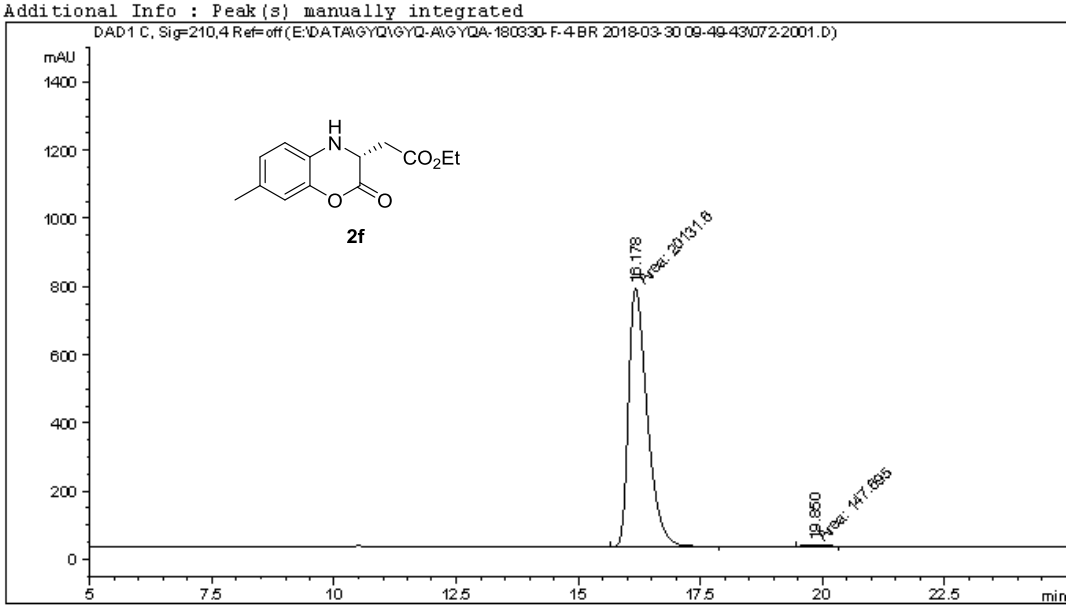
```
    ================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   4
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 3
    Injection Date  : 3/27/2018 6:27:20 PM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\YXG\CZY-RACE\CZY-RACE 2018-03-27 16-58-18\DAD-OD(1-2)-95-5-1ML-
                      5UL-ALL-35MIN.M
    Last changed    : 3/27/2018 4:58:18 PM by SYSTEM
    Analysis Method : E:\DATA\YXG\CZY-RACE\CZY-RACE 2018-03-27 16-58-18\DAD-OD(1-2)-95-5-1ML-
                      5UL-ALL-35MIN.M (Sequence Method)
    Last changed    : 11/27/2018 9:20:07 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ================================================================
                           Area Percent Report
    ================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  16.152 BB    0.4422 4.67470e4  1584.50586  49.4646
       2  19.407 BB    0.5071 4.77590e4  1368.72595  50.5354

    Totals :                  9.45060e4  2953.23181


    ================================================================
                           *** End of Report ***
```

Data File E:\DATA\GYQ\GYQ-A\GYQA-180330-F-4-BR 2018-03-30 09-49-43\072-2001.D
Sample Name: CZY-5-ME(2)

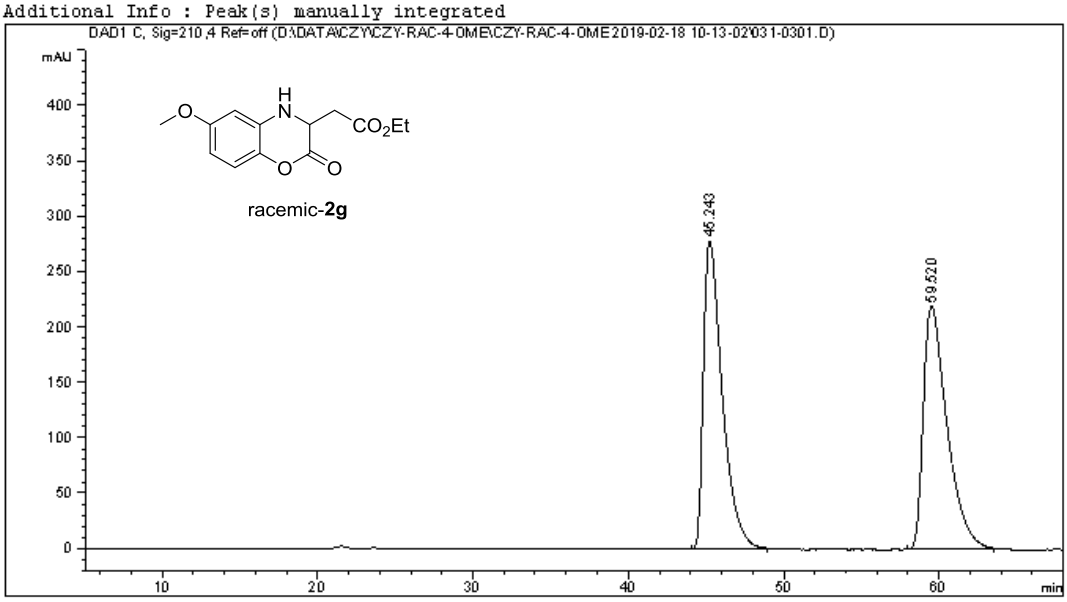
```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  20
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 72
    Injection Date  : 3/30/2018 10:59:26 PM                 Inj :  1
                                                    Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\GYQ\GYQ-A\GYQA-180330-F-4-BR 2018-03-30 09-49-43\DAD-0D(1-2)-95-
                      5-1ML-2UL-ALL-25MIN.M
    Last changed    : 3/30/2018 8:40:16 PM by SYSTEM
    Analysis Method : E:\DATA\GYQ\GYQ-A\GYQA-180330-F-4-BR 2018-03-30 09-49-43\DAD-0D(1-2)-95-
                      5-1ML-2UL-ALL-25MIN.M (Sequence Method)
    Last changed    : 11/27/2018 9:11:50 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|-------|
       1  16.178 MM    0.4429 2.01316e4   757.55823  99.2717
       2  19.850 MM    0.4481  147.69542    5.49341   0.7283

    Totals :                  2.02793e4   763.05163

    ======================================================================
                              *** End of Report ***
```

Data File D:\DATA\CZY\CZY-RAC-4-OME\CZY-RAC-4-OME 2019-02-18 10-13-02\031-0301.D
Sample Name: CZY-RAC-4-OME

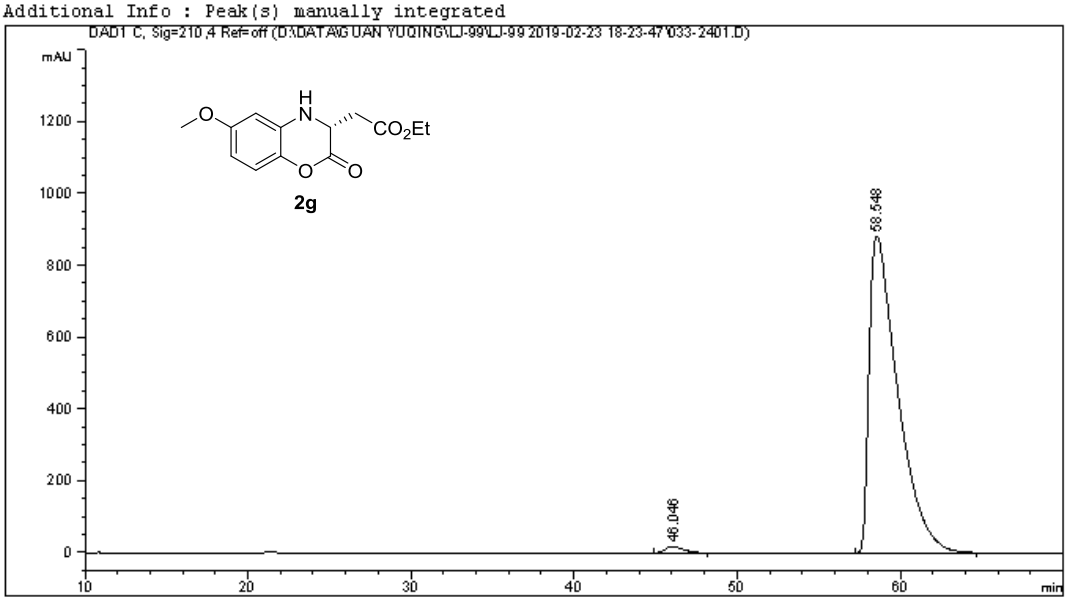
```
    ======================================================================
    Acq. Operator   :                              Seq. Line :   3
    Acq. Instrument : Instrument 2                  Location : Vial 31
    Injection Date  : 2/18/2019 10:37:04 AM              Inj :   1
                                                  Inj Volume : 3.000 µl
    Acq. Method     : D:\DATA\CZY\CZY-RAC-4-OME\CZY-RAC-4-OME 2019-02-18 10-13-02\DAD-OD(1-2)-98-
                      2-1ML-3UL-ALL-60MIN.M
    Last changed    : 2/18/2019 11:45:02 AM
                      (modified after loading)
    Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\DAD-OD(1-2)-90-10-0.5ML-5UL-ALL-20MIN.M
    Last changed    : 2/18/2019 11:49:50 AM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  45.243 BB    1.1955 2.33584e4   277.65860  50.1970
       2  59.520 BB    1.2971 2.31751e4   218.91783  49.8030

    Totals :                  4.65335e4   496.57643
```

Data File D:\DATA\GUAN YUQING\LJ-99\LJ-99 2019-02-23 18-23-47\033-2401.D
Sample Name: czy-4-ome-2

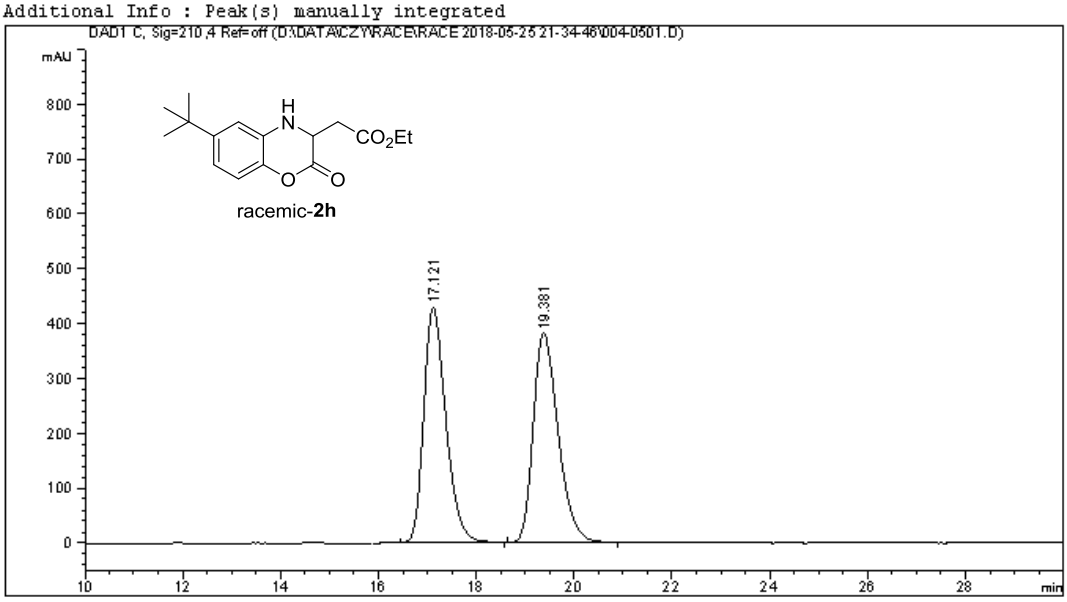
```
    ======================================================================
    Acq. Operator   :                                 Seq. Line :  24
    Acq. Instrument : Instrument 2                     Location : Vial 33
    Injection Date  : 2/24/2019 2:28:25 AM                  Inj :  1
                                                    Inj Volume : 3.000 µl
    Acq. Method     : D:\DATA\GUAN YUQING\LJ-99\LJ-99 2019-02-23 18-23-47\DAD-0D(1-2)-98-2-1ML-
                      3UL-ALL-70MIN.M
    Last changed    : 2/18/2019 12:23:56 PM
    Analysis Method : D:\METHOD\LG\DAD-0D(1-2)-98-2-0.5ML-3UL-ALL-20MIN.M
    Last changed    : 2/24/2019 9:09:43 AM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                           Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  46.046 BB    0.9034 1335.68518   17.44245   1.2259
       2  58.548 BB    1.4376 1.07622e5   882.00824  98.7741

    Totals :                  1.08958e5   899.45069
```

Data File D:\DATA\CZY\RACE\RACE 2018-05-25 21-34-46\004-0501.D
Sample Name: CZY-RACE-4-tBU

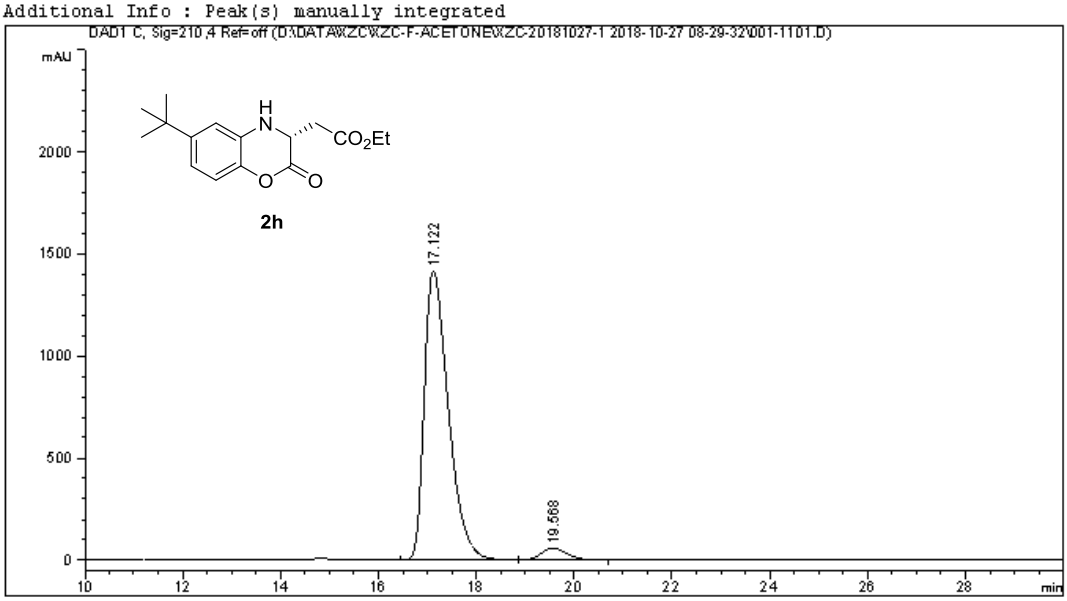
```
==================================================================
Acq. Operator   :                              Seq. Line :   5
Acq. Instrument : Instrument 2                  Location : Vial 4
Injection Date  : 5/26/2018 12:49:37 AM              Inj :   1
                                               Inj Volume : 3.000 µl
Acq. Method     : D:\DATA\CZY\RACE\RACE 2018-05-25 21-34-46\DAD-0D(1-2)-98-2-1ML-3UL-ALL-
                  60MIN.M
Last changed    : 5/25/2018 9:31:05 PM
Analysis Method : D:\METHOD\LGY\DAD-0J(1-6)-95-5--1ML-5UL-ALL-60MIN.M
Last changed    : 11/27/2018 8:56:14 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.121 BB    0.4748 1.34788e4   428.66589  49.9595
   2  19.381 BB    0.5394 1.35006e4   381.00394  50.0405

Totals :                  2.69794e4   809.66983
```

Data File D:\DATA\XZC\XZC-F-ACETONE\XZC-20181027-1 2018-10-27 08-29-32\001-1101.D
Sample Name: CZY-158-4-tBU-CHIRAL

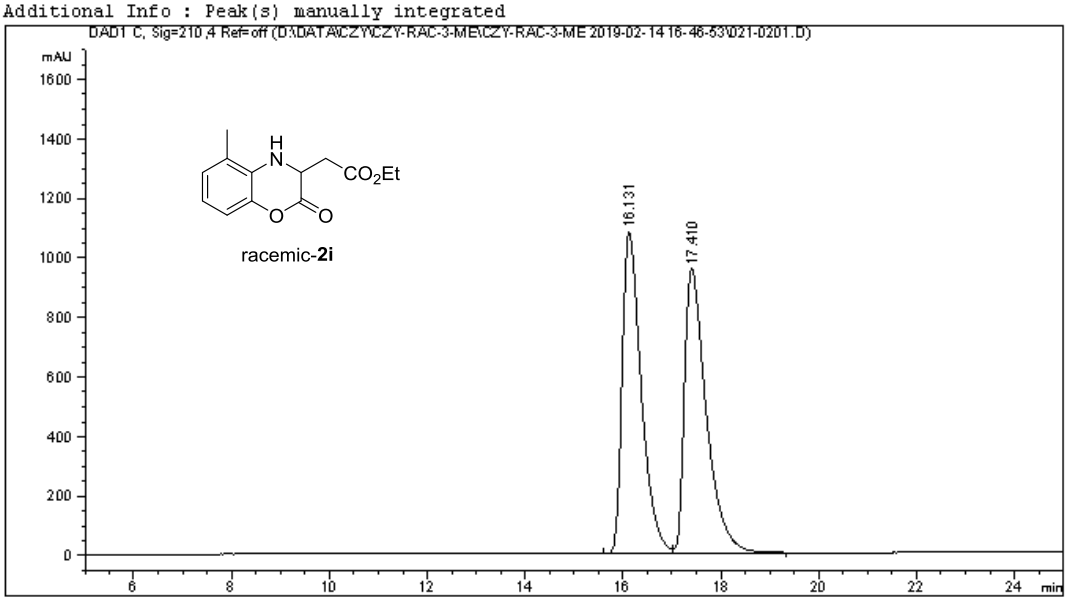
```
    ======================================================================
    Acq. Operator   :                               Seq. Line :  11
    Acq. Instrument : Instrument 2                   Location : Vial 1
    Injection Date  : 10/27/2018 2:32:03 PM               Inj :   1
                                                   Inj Volume : 3.000 µl
    Acq. Method     : D:\DATA\XZC\XZC-F-ACETONE\XZC-20181027-1 2018-10-27 08-29-32\DAD-0D(1-2)-98
                      -2-1ML-3UL-ALL-30MIN.M
    Last changed    : 7/24/2018 9:34:37 PM
    Analysis Method : D:\METHOD\LGY\DAD-0J(1-6)-95-5--1ML-5UL-ALL-60MIN.M
    Last changed    : 11/27/2018 8:54:20 PM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  17.122 BB    0.5230 4.84296e4  1416.08008  95.9435
       2  19.568 BB    0.5409 2047.61719   57.29540   4.0565

    Totals :                  5.04772e4  1473.37548
```

Data File D:\DATA\CZY\CZY-RAC-3-ME\CZY-RAC-3-ME 2019-02-14 16-46-53\021-0201.D
Sample Name: CZY-3-ME-RAC

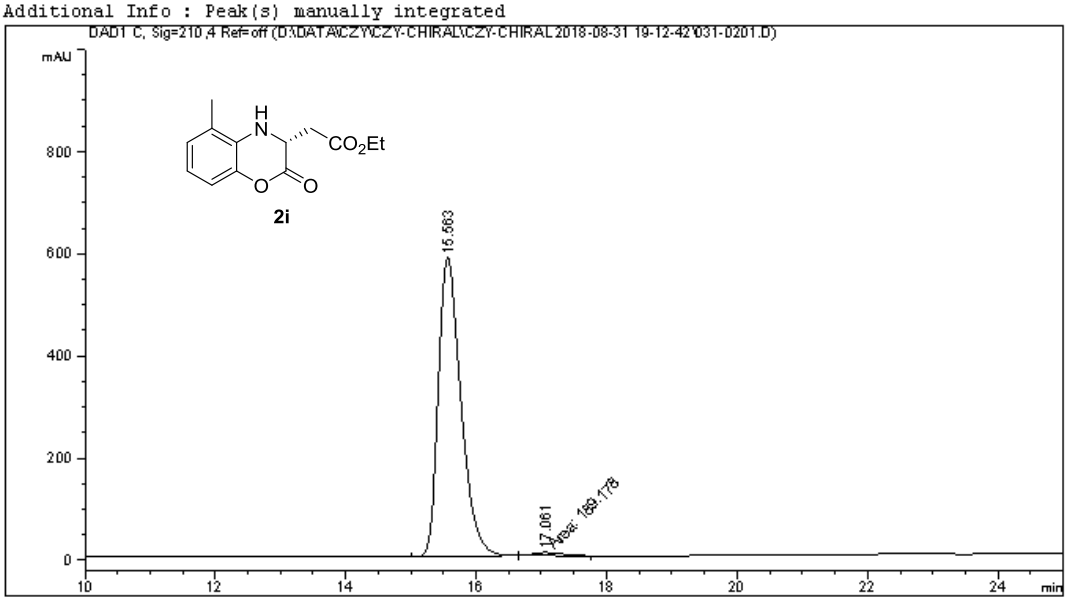
```
    ======================================================================
    Acq. Operator   :                                Seq. Line :   2
    Acq. Instrument : Instrument 2                    Location : Vial 21
    Injection Date  : 2/14/2019 4:59:01 PM                 Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : D:\DATA\CZY\CZY-RAC-3-ME\CZY-RAC-3-ME 2019-02-14 16-46-53\DAD-0D(1-2)-97-3-
                      1ML-5UL-ALL-25MIN.M
    Last changed    : 8/31/2018 7:15:51 PM
    Analysis Method : D:\METHOD\GUAN YUQING\DAD-0J(1-6)-90-10-0.8ML-5UL-ALL-115MIN.M
    Last changed    : 2/14/2019 5:24:49 PM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  16.131 BV    0.4079 2.92339e4  1079.65430  49.7162
       2  17.410 VB    0.4630 2.95676e4   955.59766  50.2838

    Totals :                  5.88015e4  2035.25195
```

Data File D:\DATA\CZY\CZY-CHIRAL\CZY-CHIRAL 2018-08-31 19-12-42\031-0201.D
Sample Name: CZY-3-ME-EE

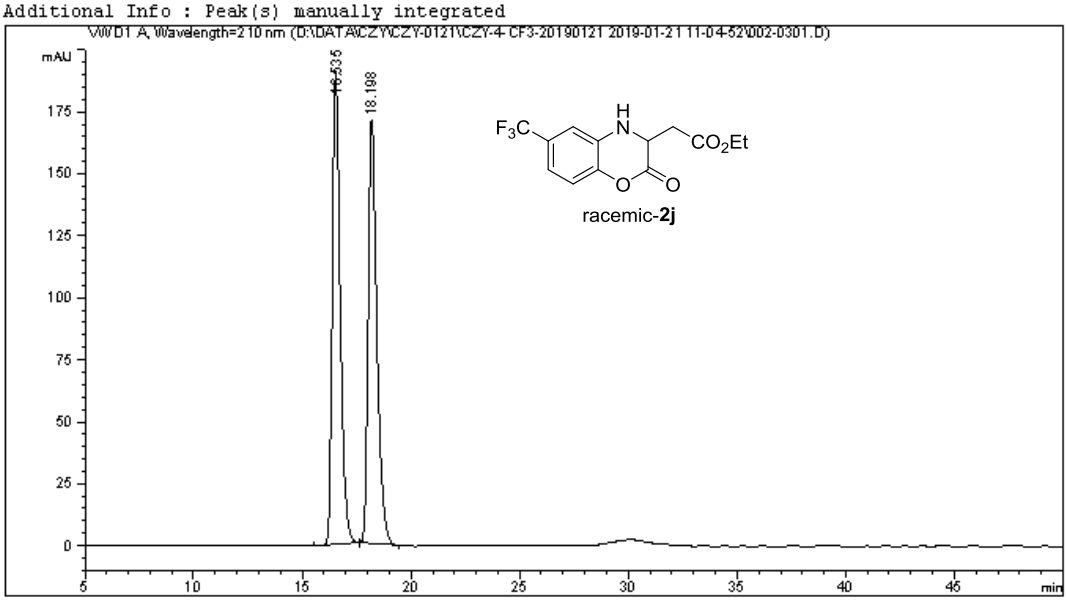
```
    ======================================================================
    Acq. Operator   :                                Seq. Line :   2
    Acq. Instrument : Instrument 2                    Location : Vial 31
    Injection Date  : 8/31/2018 7:24:56 PM                 Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : D:\DATA\CZY\CZY-CHIRAL\CZY-CHIRAL 2018-08-31 19-12-42\DAD-OD(1-2)-97-3-1ML-
                      5UL-ALL-25MIN.M
    Last changed    : 8/31/2018 7:15:51 PM
    Analysis Method : D:\METHOD\LGY\DAD-OJ(1-6)-95-5--1ML-5UL-ALL-60MIN.M
    Last changed    : 11/27/2018 8:39:56 PM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  15.563 BB    0.3680 1.4016le4   583.99731  98.6683
       2  17.061 MM    0.5015  189.17816    6.28679   1.3317

    Totals :                  1.42053e4   590.28411
```

Data File D:\DATA\CZY\CZY-0121\CZY-4-CF3-20190121 2019-01-21 11-04-52\002-0301.D
Sample Name: CZY-4-CF3-RAC

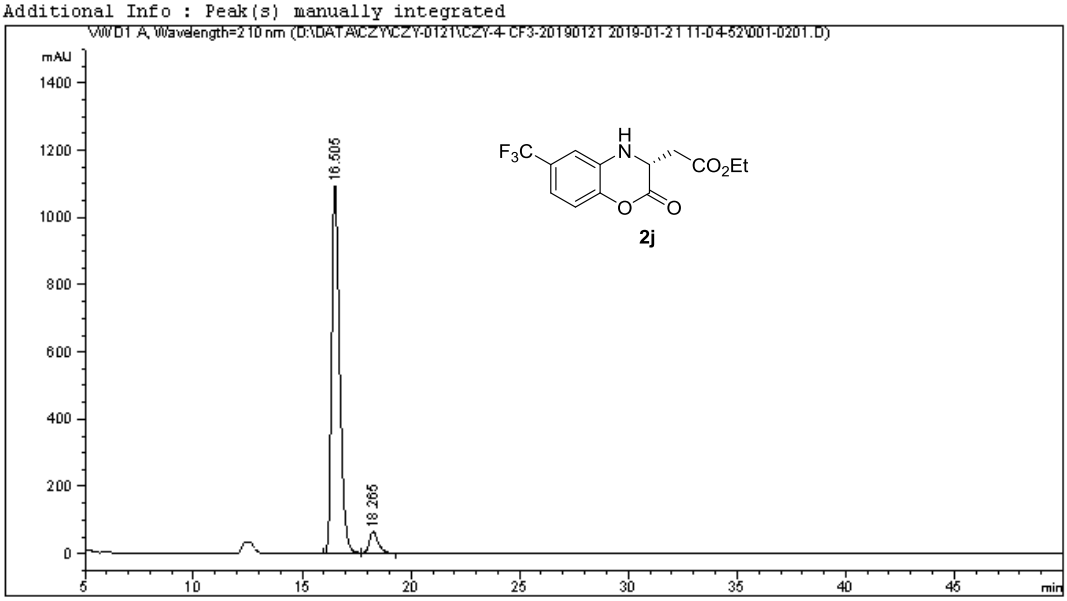
```
    ======================================================================
    Acq. Operator   :                                Seq. Line :   3
    Acq. Instrument : Instrument 1                    Location : Vial 2
    Injection Date  : 1/21/2019 12:07:22 PM               Inj :   1
                                                    Inj Volume : 3.000 µl
    Acq. Method     : D:\DATA\CZY\CZY-0121\CZY-4-CF3-20190121 2019-01-21 11-04-52\VWD-AD(1-2)-95-
                      5-1ML-3UL-210NM-50MIN.M
    Last changed    : 1/14/2019 8:17:05 PM
    Analysis Method : D:\METHOD\CZY\VWD-AD(1-2)-95-5-1ML-3UL-210NM-30MIN.M
    Last changed    : 1/21/2019 3:07:59 PM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  16.535 BB    0.3809 4810.63037  190.93573  50.0541
       2  18.198 BB    0.4247 4800.22412  170.88565  49.9459

    Totals :                  9610.85449  361.82138
```

Data File D:\DATA\CZY\CZY-0121\CZY-4-CF3-20190121 2019-01-21 11-04-52\001-0201.D
Sample Name: CZY-4-CF3-EE

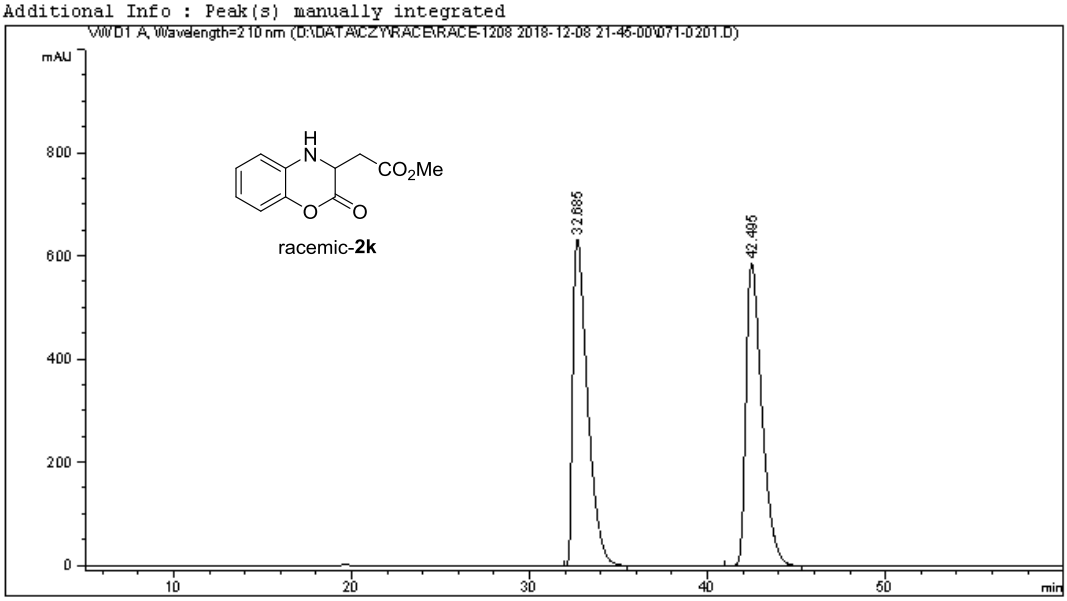
```
    ======================================================================
    Acq. Operator   :                              Seq. Line :   2
    Acq. Instrument : Instrument 1                  Location : Vial 1
    Injection Date  : 1/21/2019 11:16:35 AM              Inj :   1
                                                  Inj Volume : 3.000 µl
    Acq. Method     : D:\DATA\CZY\CZY-0121\CZY-4-CF3-20190121 2019-01-21 11-04-52\VWD-AD(1-2)-95-
                      5-1ML-3UL-210NM-50MIN.M
    Last changed    : 1/14/2019 8:17:05 PM
    Analysis Method : D:\METHOD\CZY\VWD-AD(1-2)-95-5-1ML-3UL-210NM-30MIN.M
    Last changed    : 1/21/2019 3:11:17 PM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  16.505 BB    0.3884 2.77626e4  1092.70007  94.0868
       2  18.265 BB    0.4195 1744.82361   62.92595   5.9132

    Totals :                  2.95074e4  1155.62603
```

Data File D:\DATA\CZY\RACE\RACE-1208 2018-12-08 21-45-00\071-0201.D
Sample Name: CZY-RAC-STA-Methl

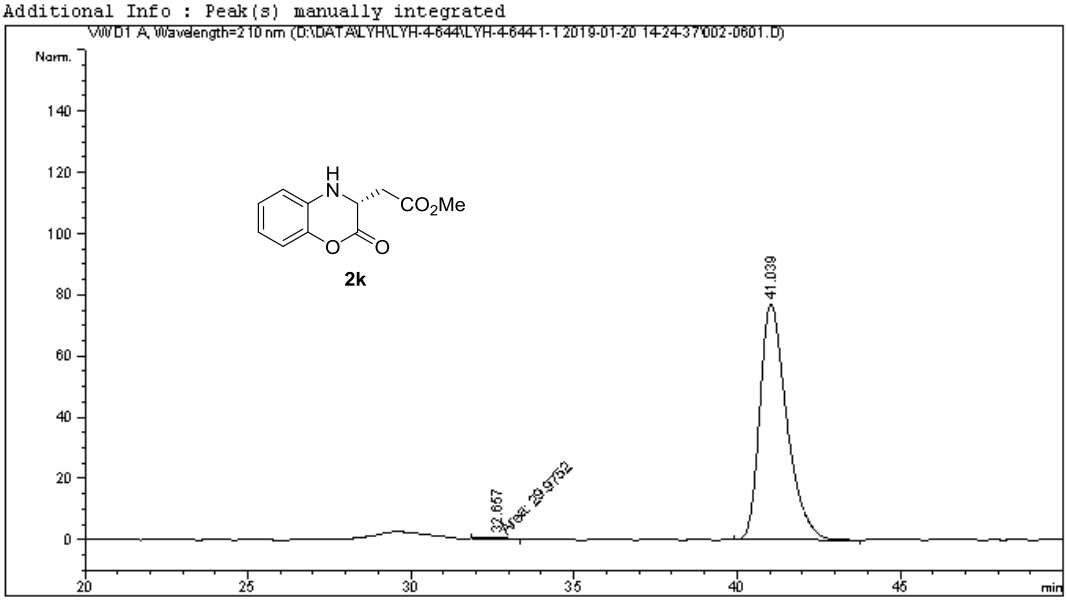
```
    ======================================================================
    Acq. Operator   :                                Seq. Line :   2
    Acq. Instrument : Instrument 1                    Location : Vial 71
    Injection Date  : 12/8/2018 9:56:44 PM                 Inj :   1
                                                   Inj Volume : 3.000 µl
    Acq. Method     : D:\DATA\CZY\RACE\RACE-1208 2018-12-08 21-45-00\VWD-AD(1-2)-95-5-1ML-3UL-
                      210NM-60MIN.M
    Last changed    : 11/29/2018 6:18:21 PM
    Analysis Method : D:\METHOD\GUAN YUQING\DAD-0J(1-6)-96-4-0.8ML-5UL-ALL-110MIN.M
    Last changed    : 1/11/2019 9:56:05 AM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  32.685 BB    0.8630 3.63563e4   634.00806  49.9491
       2  42.495 BB    0.9519 3.64305e4   586.29413  50.0509

    Totals :                  7.27868e4  1220.30219
```

Data File D:\DATA\LYH\LYH-4-644\LYH-4-644-1-1 2019-01-20 14-24-37\002-0601.D
Sample Name: CZY-STA-ME

```
    ======================================================================
    Acq. Operator   :                                Seq. Line :   6
    Acq. Instrument : Instrument 1                    Location : Vial 2
    Injection Date  : 1/20/2019 4:34:34 PM                 Inj :   1
                                                   Inj Volume : 3.000 µl
    Acq. Method     : D:\DATA\LYH\LYH-4-644\LYH-4-644-1-1 2019-01-20 14-24-37\VWD-AD(1-2)-95-5-
                      1ML-3UL-210NM-50MIN.M
    Last changed    : 1/14/2019 8:17:05 PM
    Analysis Method : D:\METHOD\LYH\VWD-AD(1-2)-95-5-1ML-1UL-210NM-35MIN.M
    Last changed    : 1/20/2019 7:55:21 PM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  32.657 MM    0.7496   29.97522 6.66454e-1   0.6736
       2  41.039 BB    0.8773 4420.34717   76.94138  99.3264

    Totals :                  4450.32239   77.60783
```