

Supporting Information

Reductive Annulations of Arylidene Malonates With Unsaturated Electrophiles Using Photoredox/Lewis Acid Cooperative Catalysis

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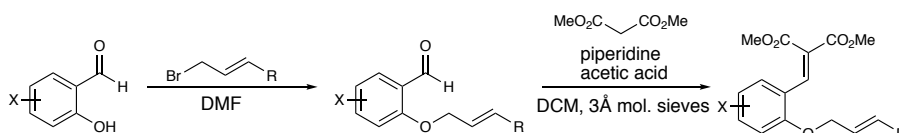
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General Information

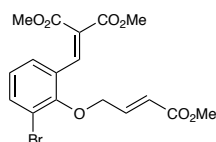
All reactions were carried out under an argon or nitrogen atmosphere in flame-dried glassware with magnetic stirring. Solvents used in reactions were purified by passage through a bed of activated alumina. Unless stated otherwise, reagents were purified prior to use following the guidelines of Perrin and Armarego.¹ Purification of reaction products was carried out by flash chromatography on Biotage Isolera 4 systems with Ultra-grade silica cartridges. Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light. Infrared spectra were recorded on a Bruker Tensor 37 FT-IR spectrometer. ¹H NMR spectra were recorded on an AVANCE III 500 MHz spectrometer with direct cryoprobe (500 MHz) and Bruker Avance III 600 MHz (151 MHz) system. Spectra are reported in ppm using solvent as an internal standard (CDCl₃ at 7.26 ppm). Peak multiplicities are reported as (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad; coupling constant(s) in Hz; integration.) Proton-decoupled ¹³C NMR spectra were recorded on an AVANCE III 500 MHz with direct cryoprobe (125 MHz) spectrometer and Bruker Avance III 600 MHz (151 MHz) system. These are reported in ppm using solvent as an internal standard (CDCl₃ at 77.16 ppm). Low-resolution mass spectra were obtained on WATERS Acquity-H UPLC-MS with a single quad detector (ESI) Varian1200 Quadrupole Mass Spectrometer. High-resolution mass spectra were obtained using an Agilent 6120A LC-time of flight mass spectrometer. Gas chromatography experiments were run on Agilent 7890A/5975C GC/MS System. Enantioselectivity measurements were made on an Agilent 1290 Infinity SFC, using a Chiralpak ID-3 column. Blue light was generated by 3 40 W Kessil H150 LED lights.

Iridium and Ruthenium photocatalysts were obtained from Strem Chemical and Sigma-Aldrich respectively and used as received. Photocatalysts 3DPAFIPN and CZIPN were synthesized according to Molander et al.²

Preparation of Salicylaldehyde Derived Arylidene Malonates

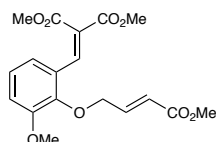


To an oven-dried scintillation vial under nitrogen was added NaH (60 wt %, 1.2 equiv) and DMF (0.5 M), and the mixture was cooled to 0 °C. A solution of salicylaldehyde (1 equiv) dissolved in DMF (1.0 M) was slowly added, and upon addition completion, the mixture was allowed to stir at 0 °C for 30 minutes. A solution of allyl bromide electrophile (1.2 equiv) dissolved in DMF (1.0 M) was slowly added, and then reaction mixture was allowed to stir overnight as it warmed to room temperature. Upon reaction completion, sat. aq. NH₄Cl was added, and the aqueous layer was



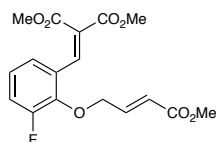
Prepared according to the general procedure with 71% overall yield over two steps.

Analytical Data: ^1H NMR (500 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.62 – 7.56 (m, 1H), 7.27 (d, J = 7.7 Hz, 1H), 7.08 – 6.96 (m, 2H), 6.25 (d, J = 15.4 Hz, 1H), 4.60 – 4.54 (m, 2H), 3.83 (s, 3H), 3.75 (d, J = 5.3 Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.42, 166.15, 163.94, 154.32, 141.62, 138.08, 135.50, 129.40, 128.36, 128.23, 125.94, 122.37, 117.98, 77.27, 77.22, 77.02, 76.76, 72.66, 52.83, 52.66, 51.73. LRMS (ESI): Mass calcd for $\text{C}_{17}\text{H}_{17}\text{BrO}_7$ $[\text{M}+\text{H}]^+$: 413.0; found 413.1 HRMS (ESI): Mass calcd for $\text{C}_{17}\text{H}_{17}\text{BrO}_7$ $[\text{M}+\text{H}]^+$: 413.0158; found 413.0160 FTIR (neat): 2984, 2784, 2345, 1676, 1659, 1628, 1552, 1481, 1280, 1248, 1214, 1166, 1129, 1044, 1008, 961, 884, 708



Prepared according to the general procedure with 67% overall yield over two steps.

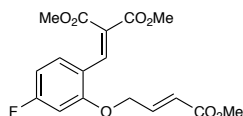
Analytical Data: ^1H NMR (500 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 7.29 – 7.20 (m, 2H), 7.19 – 7.09 (m, 2H), 6.41 (dd, J = 15.8, 2.2 Hz, 1H), 4.86 (dd, J = 4.9, 1.9 Hz, 2H), 4.10 – 4.02 (m, 6H), 3.98 – 3.93 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 194.33, 166.75, 166.57, 164.33, 152.57, 146.51, 143.04, 138.59, 138.43, 127.73, 126.95, 124.58, 121.66, 120.23, 114.56, 109.82, 100.99, 77.36, 77.10, 76.85, 72.00, 55.89, 55.82, 52.63, 52.52, 51.62. LRMS (ESI): Mass calcd for $\text{C}_{18}\text{H}_{20}\text{O}_8$ $[\text{M}+\text{H}]^+$: 365.1; found 365.2 HRMS (ESI): Mass calcd for $\text{C}_{18}\text{H}_{20}\text{O}_8$ $[\text{M}+\text{H}]^+$: 365.1158; found 365.1160 FTIR (neat): 2984, 2444, 2241, 1683, 1641, 1625, 1511, 1467, 1276, 1253, 1210, 1167, 1163, 1102, 1016, 961, 878, 701



Prepared according to the general procedure with 73% overall yield over two steps.

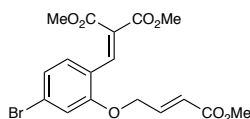
Analytical Data: ^1H NMR (500 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.31 – 7.22 (m, 2H), 7.22 – 7.11 (m, 2H), 6.33 (dt, J = 15.7, 1.9 Hz, 1H), 4.90 (dd, J = 4.8, 1.8 Hz, 2H), 3.98 (s, 2H), 3.89 (d, J = 6.2 Hz, 5H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.37, 166.29, 164.09, 155.97, 154.00, 144.79, 144.70, 142.00, 137.42, 137.39, 128.51, 128.49, 127.74, 124.22, 124.15, 124.12, 124.09, 122.19, 119.05, 118.89, 77.34, 77.08, 76.83, 72.53, 72.49, 52.74, 52.58, 51.69. LRMS (ESI): Mass calcd for

C₁₇H₁₇FO₇ [M+H]⁺: 353.1; found 353.1 HRMS (ESI): Mass calcd for C₁₇H₁₇FO₇ [M+H]⁺: 353.0959; found 353.0961 FTIR (neat): 2999, 2398, 2107, 1706, 1657, 1605, 1586, 1379, 1303, 1259, 1195, 1187, 1133, 1089, 997, 967, 883, 707



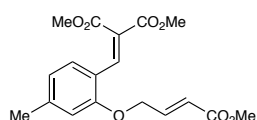
Prepared according to the general procedure with 61% overall yield over two steps.

Analytical Data: ¹H NMR (500 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.24 (dd, *J* = 8.6, 6.6 Hz, 1H), 6.94 (dt, *J* = 15.8, 4.2 Hz, 1H), 6.56 (td, *J* = 8.3, 2.1 Hz, 1H), 6.47 (dd, *J* = 10.4, 2.3 Hz, 1H), 6.07 – 6.00 (m, 1H), 4.64 (dd, *J* = 4.0, 2.0 Hz, 2H), 3.74 (t, *J* = 1.1 Hz, 3H), 3.70 – 3.63 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 166.96, 166.08, 165.92, 164.47, 163.91, 157.83, 157.75, 141.10, 137.26, 130.43, 130.35, 125.57, 122.31, 118.71, 118.68, 108.41, 108.24, 100.58, 100.37, 77.36, 77.11, 76.85, 67.23, 52.60, 52.53, 51.77. LRMS (ESI): Mass calcd for C₁₇H₁₇FO₇ [M+H]⁺: 353.1; found 353.1 HRMS (ESI): Mass calcd for C₁₇H₁₇FO₇ [M+H]⁺: 353.0959; found 353.0960 FTIR (neat): 2993, 2942, 1766, 1690, 1655, 1616, 1562, 1445, 1298, 1249, 1191, 1186, 1151, 1042, 1000, 961, 922, 807

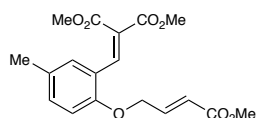


Prepared according to the general procedure with 75% overall yield over two steps.

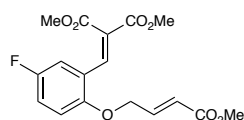
Analytical Data: ¹H NMR (500 MHz, Chloroform-*d*) δ 8.26 (s, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.35 – 7.26 (m, 1H), 7.24 (d, *J* = 1.8 Hz, 1H), 6.39 (dt, *J* = 15.8, 2.0 Hz, 1H), 5.00 (dd, *J* = 4.2, 2.1 Hz, 2H), 4.10 (s, 3H), 4.02 (d, *J* = 7.2 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 165.75, 165.11, 163.33, 155.70, 140.08, 136.32, 128.98, 125.39, 124.70, 123.60, 121.29, 120.63, 114.67, 76.32, 76.26, 76.06, 75.81, 66.24, 51.68, 51.60, 50.80. LRMS (ESI): Mass calcd for C₁₇H₁₇BrO₇ [M+H]⁺: 413.0; found 413.1 HRMS (ESI): Mass calcd for C₁₇H₁₇BrO₇ [M+H]⁺: 413.0158; found 413.0156 FTIR (neat): 2969, 2582, 1919, 1688, 1652, 1615, 1491, 1320, 1271, 1256, 1215, 1165, 1129, 1077, 1001, 933, 891, 813



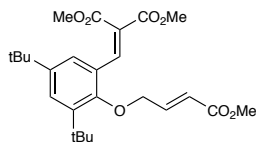
¹H NMR (500 MHz, Chloroform-*d*) δ = 8.14 (s, 1H), 7.25 (d, J =7.9, 1H), 7.09 (dt, J =15.8, 4.1, 1H), 6.77 (d, J =7.9, 1H), 6.66 (s, 1H), 6.17 (dt, J =15.8, 2.0, 1H), 4.75 (dd, J =4.1, 2.0, 2H), 3.85 (s, 2H), 3.78 (d, J =16.8, 5H), 2.34 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 167.33, 166.33, 164.73, 156.46, 143.16, 142.08, 138.31, 128.84, 124.67, 122.21, 121.85, 119.68, 112.90, 112.66, 77.37, 77.11, 76.86, 66.89, 52.51, 52.47, 51.72, 21.91. LRMS (ESI): Mass calcd for C₁₈H₂₀O₇ [M+H]⁺: 349.1; found 349.1 HRMS (ESI): Mass calcd for C₁₈H₂₀O₇ [M+H]⁺: 349.1209; found 349.1208 FTIR (neat): 3000, 2616, 2232, 1664, 1633, 1611, 1552, 1442, 1275, 1227, 1212, 1165, 1126, 1022, 1012, 925, 905, 803



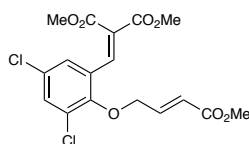
¹H NMR (500 MHz, Chloroform-*d*) δ = 8.22 (s, 1H), 7.26 – 7.21 (m, 2H), 7.17 (dt, J =15.8, 4.1, 1H), 6.84 (d, J =8.9, 1H), 6.25 (dt, J =15.8, 2.1, 1H), 4.82 (dd, J =4.2, 2.0, 2H), 3.95 (s, 3H), 3.87 (d, J =18.6, 5H), 2.35 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 167.33, 166.33, 164.73, 156.46, 143.16, 142.08, 138.31, 128.84, 124.67, 122.21, 121.85, 119.68, 112.90, 112.66, 77.37, 77.11, 76.86, 66.89, 52.51, 52.47, 51.72, 21.91. LRMS (ESI): Mass calcd for C₁₈H₂₀O₇ [M+H]⁺: 349.1; found 349.1 HRMS (ESI): Mass calcd for C₁₈H₂₀O₇ [M+H]⁺: 349.1209; found 349.1210 FTIR (neat): 2967, 2772, 1975, 1678, 1650, 1612, 1571, 1435, 1283, 1231, 1192, 1188, 1143, 1070, 992, 943, 897, 792



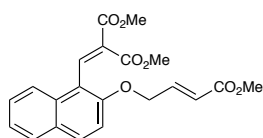
¹H NMR (500 MHz, Chloroform-*d*) δ = 8.22 (s, 1H), 7.23 (dt, J =26.7, 4.3, 2H), 7.00 – 6.92 (m, 1H), 6.31 (dt, J =15.9, 2.3, 1H), 4.93 – 4.87 (m, 2H), 4.00 (dd, J =21.7, 2.7, 5H), 3.93 (s, 2H), 3.92 (d, J =5.6, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 166.53, 166.21, 164.25, 157.85, 155.94, 152.66, 141.70, 137.02, 126.99, 123.76, 123.69, 122.13, 118.31, 118.13, 115.56, 115.36, 113.40, 113.34, 77.32, 77.06, 76.81, 67.67, 52.73, 52.66, 51.78. LRMS (ESI): Mass calcd for C₁₇H₁₇FO₇ [M+H]⁺: 353.1; found 353.1 HRMS (ESI): Mass calcd for C₁₇H₁₇FO₇ [M+H]⁺: 353.0959; found 353.0961 FTIR (neat): 2992, 2745, 2037, 1696, 1634, 1608, 1500, 1439, 1278, 1224, 1205, 1175, 1162, 1027, 998, 962, 920, 815



¹H NMR (500 MHz, Chloroform-*d*) δ = 7.78 (s, 1H), 7.24 (d, *J*=2.5, 1H), 7.06 (d, *J*=2.3, 1H), 6.89 (dt, *J*=15.7, 3.9, 1H), 6.15 (dd, *J*=15.7, 2.2, 1H), 4.34 (dd, *J*=3.9, 2.2, 2H), 3.69 – 3.54 (m, 9H), 1.12 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 166.77, 166.64, 164.34, 154.88, 146.45, 142.81, 142.21, 141.06, 126.98, 126.85, 126.28, 124.38, 121.20, 77.28, 77.23, 77.03, 76.77, 73.55, 52.62, 52.58, 51.69, 35.26, 34.65, 31.38, 30.74. LRMS (ESI): Mass calcd for C₂₅H₃₄O₇ [M+H]⁺: 447.2; found 447.1 HRMS (ESI): Mass calcd for C₂₅H₃₄O₇ [M+H]⁺: 447.2305; found 447.2307 FTIR (neat): 2978, 2578, 2191, 1689, 1632, 1606, 1592, 1310, 1291, 1267, 1207, 1185, 1138, 1066, 1002, 967, 851, 786

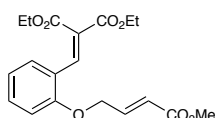


¹H NMR (500 MHz, Chloroform-*d*) δ = 7.65 (s, 1H), 7.24 (d, *J*=2.4, 1H), 7.03 (d, *J*=2.4, 1H), 6.83 (dt, *J*=15.8, 4.7, 1H), 6.03 (dt, *J*=15.7, 1.9, 1H), 4.40 (dd, *J*=4.8, 1.8, 2H), 3.67 (d, *J*=1.0, 3H), 3.59 (dd, *J*=16.2, 1.1, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 166.20, 165.61, 163.61, 151.93, 141.19, 136.47, 131.80, 130.27, 130.21, 129.38, 129.36, 127.27, 122.60, 77.34, 77.29, 77.09, 76.83, 72.72, 52.90, 52.71, 51.71. LRMS (ESI): Mass calcd for C₁₇H₁₆Cl₂O₇ [M+H]⁺: 403.1; found 403.1 HRMS (ESI): Mass calcd for C₁₇H₁₆Cl₂O₇ [M+H]⁺: 403.0273; found 403.0271 FTIR (neat): 2967, 2537, 1842, 1708, 1654, 1614, 1538, 1391, 1306, 1262, 1206, 1188, 1131, 1120, 993, 935, 902, 748



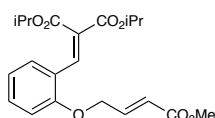
Prepared according to the general procedure with 78% overall yield over two steps.

Analytical Data: ¹H NMR (500 MHz, Chloroform-*d*) δ = 8.37 (s, 1H), 7.95 – 7.85 (m, 2H), 7.63 – 7.55 (m, 1H), 7.52 – 7.44 (m, 1H), 7.26 – 7.12 (m, 1H), 6.22 (dt, *J*=15.8, 2.1, 1H), 4.92 (dd, *J*=4.3, 2.0, 1H), 4.01 (s, 2H), 3.83 (s, 2H), 3.58 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 166.33, 165.64, 164.90, 152.96, 142.37, 140.50, 131.94, 131.64, 129.86, 129.01, 128.42, 127.48, 124.49, 123.77, 122.12, 117.40, 113.85, 77.32, 77.07, 76.82, 68.00, 52.69, 52.00, 51.74. LRMS (ESI): Mass calcd for C₂₁H₂₀O₇ [M+H]⁺: 385.1; found 385.1 HRMS (ESI): Mass calcd for C₂₁H₂₀O₇ [M+H]⁺: 385.1209; found 385.1210 FTIR (neat): 2996, 2543, 2196, 1677, 1641, 1622, 1543, 1441, 1306, 1266, 1192, 1163, 1148, 1046, 990, 930, 831, 792



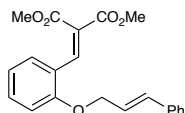
Prepared according to the general procedure with 85% overall yield over two steps.

Analytical Data: ^1H NMR (500 MHz, Chloroform-*d*) δ = 7.96 (s, 1H), 7.25 (dd, J =7.9, 1.6, 1H), 7.19 – 7.12 (m, 1H), 6.91 (dt, J =15.8, 3.9, 1H), 6.77 (t, J =7.5, 1H), 6.68 (d, J =8.3, 1H), 6.01 (dt, J =15.8, 2.1, 1H), 4.57 (dd, J =4.1, 2.1, 2H), 4.12 (dq, J =14.1, 7.1, 4H), 3.56 (s, 3H), 1.18 (t, J =7.1, 3H), 1.07 (t, J =7.1, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.45, 166.14, 164.05, 156.24, 142.03, 137.33, 131.92, 129.02, 126.55, 122.49, 121.58, 121.11, 111.96, 77.54, 77.28, 77.03, 66.72, 61.43, 61.39, 51.53, 14.01, 13.79. LRMS (ESI): Mass calcd for $\text{C}_{19}\text{H}_{22}\text{O}_7$ $[\text{M}+\text{H}]^+$: 363.1; found 363.2 HRMS (ESI): Mass calcd for $\text{C}_{19}\text{H}_{22}\text{O}_7$ $[\text{M}+\text{H}]^+$: 363.1365; found 363.1363 FTIR (neat): 2991, 2700, 2301, 1699, 1655, 1602, 1512, 1400, 1296, 1250, 1200, 1181, 1131, 1043, 1002, 965, 840, 802



Prepared according to the general procedure with 75% overall yield over two steps.

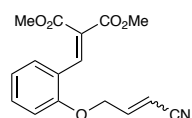
Analytical Data: ^1H NMR (500 MHz, Chloroform-*d*) δ = 7.86 (s, 1H), 7.23 (dd, J =7.8, 1.5, 1H), 7.15 – 7.04 (m, 1H), 6.86 (dt, J =15.8, 3.9, 1H), 6.71 (t, J =7.6, 1H), 6.61 (d, J =8.3, 1H), 5.97 (dd, J =15.8, 2.0, 1H), 5.02 – 4.88 (m, 2H), 4.53 (dd, J =4.1, 2.1, 2H), 3.56 – 3.42 (m, 4H), 1.10 (d, J =6.3, 5H), 1.02 (d, J =6.1, 5H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.34, 166.17, 166.08, 163.70, 156.28, 142.05, 136.62, 131.75, 129.20, 128.24, 127.42, 127.03, 122.77, 121.71, 121.14, 111.89, 77.34, 77.09, 76.84, 69.11, 69.06, 66.78, 51.66, 46.19, 42.25, 21.74, 21.49. LRMS (ESI): Mass calcd for $\text{C}_{21}\text{H}_{26}\text{O}_7$ $[\text{M}+\text{H}]^+$: 390.2; found 390.2 HRMS (ESI): Mass calcd for $\text{C}_{21}\text{H}_{26}\text{O}_7$ $[\text{M}+\text{H}]^+$: 390.1679; found 390.1680 FTIR (neat): 2998, 2486, 1967, 1703, 1639, 1614, 1546, 1385, 1280, 1237, 1203, 1179, 1124, 1030, 994, 930, 846, 705



Prepared according to the general procedure with 82% overall yield over two steps.

Analytical Data: ^1H NMR (500 MHz, Chloroform-*d*) δ = 8.14 (s, 1H), 7.35 – 7.20 (m, 5H), 7.21 – 7.13 (m, 1H), 6.89 – 6.81 (m, 2H), 6.63 (dt, J =16.0, 1.6, 1H), 6.31 (dt, J =16.0, 5.7, 1H), 4.65 (dd, J =5.8, 1.6, 2H), 3.74 (s, 2H), 3.70 (s, 2H), 3.65 (s, 2H), 3.30 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.23, 166.92, 164.73, 157.21, 139.00, 136.27, 133.14, 132.16, 129.01, 128.64, 128.02, 126.63, S-8

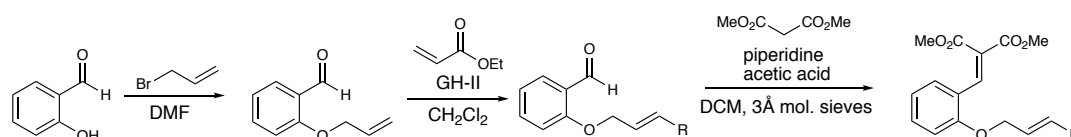
125.48, 123.92, 122.58, 120.85, 112.48, 77.48, 77.23, 76.97, 69.33, 69.21, 54.48, 52.54, 52.51, 52.47, 41.09. LRMS (ESI): Mass calcd for $C_{21}H_{20}O_5[M+H]^+$: 353.1; found 353.2 HRMS (ESI): Mass calcd for $C_{21}H_{20}O_5[M+H]^+$: 353.1311; found 353.1310 FTIR (neat): 2990, 2600, 2211, 1666, 1636, 1606, 1515, 1453, 1293, 1251, 1220, 1172, 1143, 1103, 993, 956, 831, 741



Prepared according to the general procedure with 55% overall yield over two steps. Isolated as an inseparable 1:1 mixture of Z/E isomers (4-bromobut-2-enenitrile used for SN2 reaction was an inseparable 1:1 mixture of Z/E isomers)

Analytical Data: 1H NMR (500 MHz, Chloroform-*d*) δ = 7.96 (d, $J=2.7$, 1H), 7.56 – 7.46 (m, 1H), 7.32 – 7.19 (m, 2H), 7.22 – 7.11 (m, 1H), 6.90 – 6.81 (m, 1H), 6.84 – 6.67 (m, 2H), 5.63 (dt, $J=16.4$, 2.3, 1H), 5.51 – 5.44 (m, 1H), 5.17 (s, 1H), 4.88 – 4.76 (m, 1H), 4.62 (dd, $J=3.7$, 2.3, 1H), 3.75 – 3.59 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.00, 166.88, 164.62, 164.45, 156.03, 155.79, 149.17, 148.77, 147.88, 138.76, 138.22, 134.48, 132.16, 132.08, 129.56, 129.40, 129.28, 126.39, 126.10, 124.90, 122.81, 121.95, 121.74, 116.85, 116.63, 114.70, 112.06, 111.96, 101.78, 101.24, 77.27, 77.22, 77.02, 76.77, 66.78, 66.46, 52.75, 52.65, 52.57, 52.51, 41.14. LRMS (ESI): Mass calcd for $C_{16}H_{15}NO_5$ [M+H] $^+$: 302.1; found 302.2 HRMS (ESI): Mass calcd for $C_{16}H_{15}NO_5$ [M+H] $^+$: 302.0950; found 302.0951 FTIR (neat): 2975, 2818, 2044, 1670, 1638, 1625, 1592, 1373, 1297, 1270, 1197, 1181, 1135, 1114, 1019, 924, 886, 745

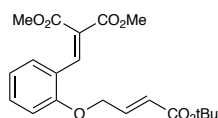
Preparation of Salicylaldehyde Derived Arylidene Malonates Requiring Metathesis Reactions



To an oven-dried scintillation vial under nitrogen was added NaH (60 wt %, 1.2 equiv) and DMF (0.5 M), and the mixture was cooled to 0 °C. A solution of salicylaldehyde (1 equiv) dissolved in DMF (1.0 M) was slowly added, and upon addition completion, the mixture stirred at 0 °C for 30 minutes. A solution of allyl bromide electrophile (1.2 equiv) dissolved in DMF (1.0 M) was slowly added and then reaction was allowed to stir overnight as it warmed to room temperature. Upon reaction completion, sat. aq. NH_4Cl was added, and the aqueous layer was extracted 3x with EtOAc. The combined organic layers were washed with H_2O and sat. aq. NaCl, passed through a Biotage Isololute phase separator, and concentrated to dryness under reduced pressure on a rotary evaporator to obtain the crude SN2 product, which was directly used in the next reaction without purification.

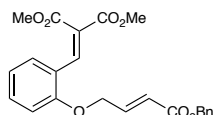
A flame dried round bottom flask was charged with alkene starting material (1.0 equiv) in CH₂Cl₂ (0.5 M), ethyl acrylate (5.0 equiv) and flushed with Ar. Grubbs-Hoveyda second generation catalyst (2.5 mol %) was added in one portion and the reaction was stirred at room temperature under an atmosphere of Ar. The homogeneous solution was allowed to stir for 6 hours. Once the reaction was complete, the reaction was concentrated to dryness under reduced pressure on a rotary evaporator. The crude product was directly used in the next reaction without purification

To a scintillation vial was added the crude aldehyde from the previous step (1 equiv). Malonate or ketoester was added (1.1 equiv), along with 250 wt % activated 4 Å molecular sieves (powder). A magnetic stir bar and CH₂Cl₂ (2.0 M) were added, followed by acetic acid (0.1 equiv) and piperidine (0.1 equiv). The mixture was stirred overnight. Silica was added, and the reaction concentrated under reduced pressure. The resulting mixture was loaded onto a column of silica and purified via flash column chromatography (10-20% EtOAc/hexanes) to yield the desired product.



Prepared according to the general procedure with 65% overall yield over three steps.

Analytical Data: ¹H NMR (500 MHz, Chloroform-*d*) δ = 8.05 (s, 1H), 7.28 – 7.15 (m, 3H), 6.90 – 6.80 (m, 2H), 6.77 – 6.71 (m, 1H), 5.95 (dt, *J*=15.7, 2.0, 1H), 4.63 (dd, *J*=4.3, 2.0, 2H), 3.75 (s, 2H), 3.66 (d, *J*=18.0, 5H), 1.39 (s, 7H). ¹³C NMR (126 MHz, CDCl₃) δ 167.10, 166.92, 165.17, 164.60, 156.53, 140.46, 138.56, 133.52, 132.09, 130.24, 129.03, 128.69, 128.45, 128.15, 125.76, 124.26, 122.58, 121.25, 112.12, 80.80, 77.33, 77.07, 76.82, 67.11, 60.39, 52.57, 52.54, 52.50, 41.11, 28.09. LRMS (ESI): Mass calcd for C₂₀H₂₄O₇[M+H]⁺: 377.2; found 377.2 HRMS (ESI): Mass calcd for C₂₀H₂₄O₇[M+H]⁺: 377.1522; found 377.1520 FTIR (neat): 2982, 2944, 1952, 1669, 1647, 1607, 1595, 1384, 1276, 1244, 1197, 1180, 1138, 1066, 992, 950, 893, 688

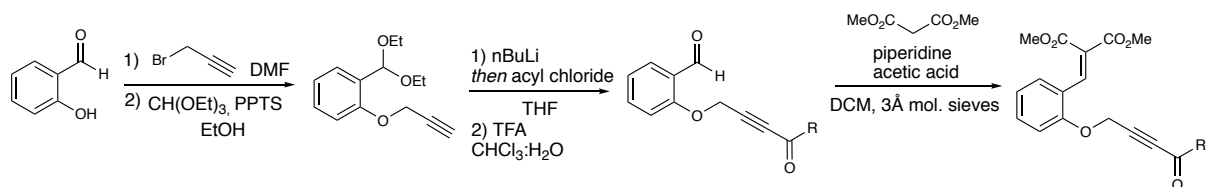


Prepared according to the general procedure with 52% overall yield over three steps.

Analytical Data: ¹H NMR (500 MHz, Chloroform-*d*) δ = 8.01 (s, 1H), 7.28 – 7.15 (m, 7H), 6.98 (dt, *J*=15.7, 4.1, 1H), 6.81 (t, *J*=7.6, 1H), 6.70 (d, *J*=8.1, 1H), 6.07 (dt, *J*=15.8, 2.0, 1H), 5.07 (s, 2H), 4.63 (dd, *J*=4.2, 2.1, 2H), 3.66 (d, *J*=23.6, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 167.06, 165.66, 164.57, 156.38, 142.33, 138.48, 135.77, 132.07, 129.10, 128.59, 128.31, 125.89, 122.66, 122.10, 121.39, 112.10, 77.30, 77.24, 77.04, 76.79, 67.01, 66.50, 52.58, 52.52. LRMS (ESI): Mass calcd for

$C_{23}H_{22}O_7[M+H]^+$: 411.1; found 411.1 HRMS (ESI): Mass calcd for $C_{23}H_{22}O_7[M+H]^+$: 411.1365; found 411.1367 FTIR (neat): 2964, 2533, 2087, 1691, 1640, 1607, 1571, 1384, 1297, 1230, 1192, 1186, 1123, 1027, 992, 987, 882, 765

Preparation of Salicylaldehyde Derived Alkyne Electrophiles

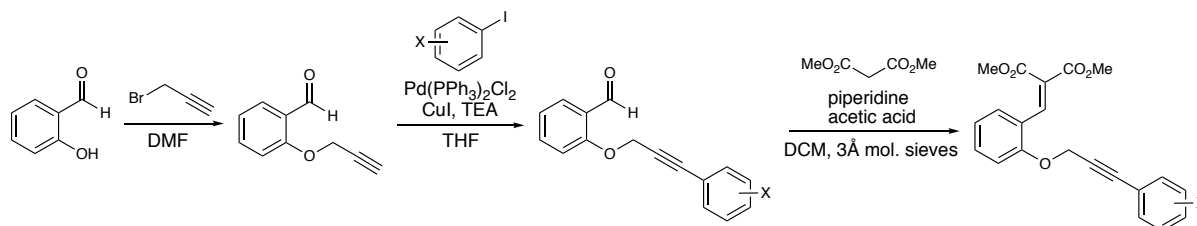


To an oven-dried scintillation vial under nitrogen was added NaH (60 wt %, 1.2 equiv) and DMF (0.5 M), and the mixture was cooled to 0 °C. A solution of salicylaldehyde (1 equiv) dissolved in DMF (1.0 M) was slowly added, and upon addition completion, the mixture stirred at 0 °C for 30 minutes. A solution of propargyl bromide (1.2 equiv) dissolved in DMF (1.0 M) was slowly added and then reaction was allowed to stir overnight as it warmed to room temperature. Upon reaction completion, sat. aq. NH_4Cl was added, and the aqueous layer was extracted 3x with EtOAc. The combined organic layers were washed with H_2O and sat. aq. $NaCl$, passed through a Biotage Isololute phase separator, and concentrated to dryness under reduced pressure on a rotary evaporator to obtain the crude S_N2 product, which was directly used in the next reaction without purification.

In an oven dried round-bottom flask, salicylaldehyde propargyl ether (1 equiv) was dissolved in dry ethanol (0.2 M) under N_2 atmosphere. Triethyl orthoformate (1.7 equiv) and PPTS (1 mol %) were added, and the resulting solution was refluxed for 3 h. Upon reaction completion, the reaction mixture was quenched with few drops of Et_3N and concentrated to dryness under reduced pressure on a rotary evaporator. The oil was diluted in EtOAc (50 mL), washed with 10 % $NaHCO_3$ (2×20 mL), followed by saturated $NaCl$ (2×10 mL) and then dried over Na_2SO_4 . The combined organic layers were concentrated to dryness under reduced pressure on a rotary evaporator. The crude product was directly used in the next reaction without purification.

In an oven dried round-bottom flask, the acetal-protected salicylaldehyde (1.0 equiv) was dissolved in dry THF (0.2 M). The solution was stirred at 78 °C, and *n*-BuLi (1.1 equiv, 2.5 M in hexanes) was slowly added to the flask over 10 min, and the reaction was stirred for another 30 min. At the same temperature, acyl chloride (1.7 equiv) dissolved in THF (0.2 M) was slowly added to the reaction mixture and stirred for an additional 2 h. Upon reaction completion, the reaction mixture was allowed to warm to room temperature and quenched with sat. aq. NH_4Cl (20 mL). Then the reaction mixture was diluted with EtOAc (50 mL), washed with water (3×50 mL), followed by saturated $NaCl$ (2×10 mL), and then dried over Na_2SO_4 . The combined organic layers were concentrated to

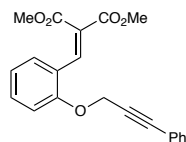
Preparation of Salicylaldehyde Derived Alkyne-Aryl Arylidene Malonates



To an oven dried scintillation vial under nitrogen was added NaH (60 wt %, 1.2 equiv) and DMF (0.5 M), and the mixture was cooled to 0 °C. A solution of salicylaldehyde (1 equiv) dissolved in DMF (1.0 M) was slowly added, and upon addition completion, the mixture stirred at 0 °C for 30 minutes. A solution of propargyl bromide (1.2 equiv) dissolved in DMF (1.0 M) was slowly added and then reaction was allowed to stir overnight as it warmed to room temperature. Upon reaction completion, sat. aq. NH_4Cl was added, and the aqueous layer was extracted 3x with EtOAc. Upon reaction completion, sat. aq. NH_4Cl was added, and the aqueous layer was extracted 3x with EtOAc. The combined organic layers were washed with H_2O and sat. aq. NaCl , passed through a Biotage Isolute phase separator, and concentrated to dryness under reduced pressure on a rotary evaporator to obtain the crude SN2 product, which was directly used in the next reaction without purification.

To a scintillation vial was added the crude 2-prop-2-ynoxy-benzaldehyde derivatives (1.0 equiv) with substituted iodobenzene (1.2 equiv), $\text{Pd(PPh}_3)_2\text{Cl}_2$ (2 mol %), CuI (4 mol %) and triethylamine (1.5 equiv) in dry THF (0.2 M). The reaction was stirred for 18 hours until reaction completion NH_4Cl was added, and the aqueous layer was extracted 3x with EtOAc. The combined organic layers were washed with H_2O and sat. aq. NaCl , passed through a Biotage Isolute phase separator, and concentrated to dryness under reduced pressure on a rotary evaporator to obtain the crude product, which was directly used in the next reaction without purification.

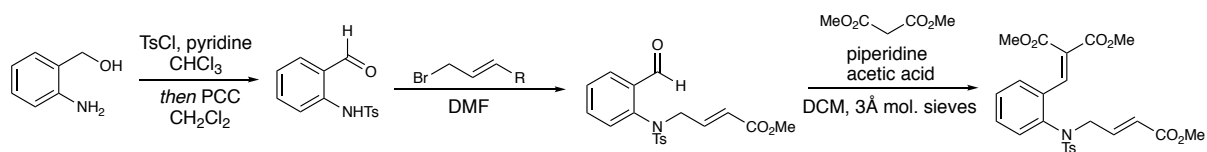
To a scintillation vial was added the crude aldehyde from the previous step (1 equiv). Malonate or ketoester was added (1.1 equiv) as well as 250 wt % activated 4 Å molecular sieves (powder). A magnetic stirbar and CH_2Cl_2 (2.0 M) were added, followed by acetic acid (0.1 equiv) and piperidine (0.1 equiv). The mixture was stirred overnight. Silica was added and the reaction concentrated under reduced pressure. The resulting mixture was loaded onto a column of silica and purified via flash column chromatography (10-20% EtOAc/hexanes) to yield the desired product.



Prepared according to the general procedure with 70% overall yield over three steps.

Analytical Data: ^1H NMR (500 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.39 – 7.26 (m, 4H), 7.29 – 7.17 (m, 3H), 7.08 (dd, $J = 8.4, 1.0$ Hz, 1H), 6.90 (td, $J = 7.6, 1.0$ Hz, 1H), 4.90 (s, 2H), 3.77 (s, 3H), 3.70 (d, $J = 19.1$ Hz, 6H), 3.32 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.17, 166.93, 164.71, 156.31, 138.94, 131.97, 131.79, 131.55, 129.17, 128.80, 128.32, 125.69, 122.89, 122.07, 121.40, 112.84, 87.74, 83.38, 77.31, 77.27, 77.06, 76.81, 57.10, 52.57, 52.56, 52.50, 41.13. LRMS (ESI): Mass calcd for $\text{C}_{21}\text{H}_{18}\text{O}_5[\text{M}+\text{H}]^+$: 351.1; found 351.1 HRMS (ESI): Mass calcd for $\text{C}_{21}\text{H}_{18}\text{O}_5[\text{M}+\text{H}]^+$: 351.1154; found 351.1153 FTIR (neat): 2972, 2382, 2316, 1708, 1637, 1599, 1489, 1355, 1277, 1234, 1212, 1182, 1134, 1060, 1008, 976, 900, 798

Preparation of Tetrahydroquinoline-Precursor Arylidene Malonate

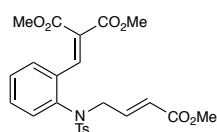


To a dry and N_2 -flushed round bottom flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of 2-aminobenzyl alcohol (1.0 equiv) in CHCl_3 (0.2 M). TsCl (1.1 equiv) and pyridine (5 mol %) were added, and the reaction mixture was stirred for 12 h at room temperature. Once the reaction was complete, the reaction was concentrated to dryness under reduced pressure on a rotary evaporator. Without purification, the crude product was dissolved in CH_2Cl_2 (0.5 M) and PCC (1.2 equiv) was added. The reaction mixture was stirred for 4 h at room temperature and then filtered through celite followed by washing with CH_2Cl_2 . The combined organic layers were concentrated to dryness under reduced pressure on a rotary evaporator. The crude product was directly used in the next reaction without purification.

To an oven dried scintillation vial under nitrogen was added NaH (60 wt %, 1.2 equiv) and DMF (0.5 M), and the mixture was cooled to 0°C . A solution of N-tosyl-aldehyde (1 equiv) dissolved in DMF (1.0 M) was slowly added, and upon addition completion, the mixture stirred at 0°C for 30 minutes. A solution of allyl bromide (1.2 equiv) dissolved in DMF (1.0 M) was slowly added and then reaction was allowed to stir overnight as it warmed to room temperature. Upon reaction completion, sat. aq. NH_4Cl was added, and the aqueous layer was extracted 3x with EtOAc. The combined organic layers were washed with H_2O and saturated NaCl followed by passage through a Biotage Isololute phase separator and concentration concentrated to dryness under reduced pressure on a rotary S-14

evaporator to obtain the crude SN2 product, which was directly used in the next reaction without purification.

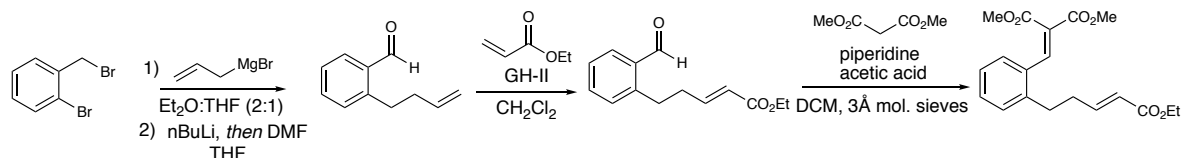
To a scintillation vial was added the crude aldehyde from the previous step (1 equiv). Malonate or ketoester was added (1.1 equiv), as well as 250 wt % activated 4 Å molecular sieves (powder). A magnetic stirbar and mL of CH₂Cl₂ (2.0 M) were added, followed by acetic acid (0.1 equiv) and piperidine (0.1 equiv). The mixture was stirred overnight. Silica was added and the reaction concentrated under reduced pressure. The resulting mixture was loaded onto a column of silica and purified via flash column chromatography (10-20% EtOAc/hexanes) to yield the desired product.



Prepared according to the general procedure with 62% overall yield over four steps.

Analytical Data: ¹H NMR (500 MHz, Chloroform-*d*) δ = 7.64 (s, 1H), 7.57 – 7.48 (m, 2H), 7.32 – 7.20 (m, 4H), 7.02 – 6.93 (m, 1H), 6.72 (dt, *J*=15.7, 6.6, 1H), 5.73 (dt, *J*=15.7, 1.5, 1H), 5.24 (s, 1H), 4.20 (dd, *J*=6.6, 1.4, 2H), 3.78 (s, 3H), 3.69 (s, 1H), 3.61 (d, *J*=3.8, 5H), 2.38 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 166.20, 165.81, 163.72, 147.09, 144.24, 141.33, 140.13, 138.13, 135.79, 134.37, 130.89, 130.51, 129.83, 129.10, 129.00, 128.30, 127.76, 124.60, 119.73, 77.29, 77.04, 76.78, 61.84, 53.44, 52.90, 52.67, 52.52, 51.65, 51.61, 21.62. LRMS (ESI): Mass calcd for C₂₄H₂₅NO₈S [M+H]⁺: 487.1; found 487.2 HRMS (ESI): Mass calcd for C₂₄H₂₅NO₈S [M+H]⁺: 487.1309; found 487.1311 FTIR (neat): 2977, 2957, 2293, 1671, 1644, 1602, 1488, 1342, 1295, 1265, 1195, 1172, 1143, 1067, 1012, 956, 845, 764

Preparation of Tetrahydronaphthalene-Precursor Arylidene Malonate



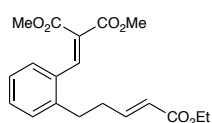
To a round-bottom flask flushed with N₂ was charged Mg turnings (5.0 equiv) and anhydrous ether (0.5 M). A tip of iodine and a drop of 1,2-dibromoethane were successively added. After leaving the mixture at 0 °C for 30 min, a solution of allyl bromide (2.0 equiv) in dry ether (0.5 M) was added dropwise to the mixture to prepare a solution of a Grignard reagent. To a solution of 2-bromobenzyl bromide (1.0 equiv) in anhydrous THF (0.5 M) was added dropwise the prepared solution of a Grignard reagent at rt, and the reaction mixture was stirred at rt overnight. The following day, 25 mL of H₂O was added to the mixture, which was then extracted with ether (15 mL × 3). The S-15

combined ethereal solution was washed with H₂O (15 mL × 3) and dried over anhydrous MgSO₄. The reaction was concentrated to dryness under reduced pressure on a rotary evaporator. The crude product was directly used in the next reaction without purification.

Under N₂, to a solution of 1-bromo or iodo aryl compound (1.0 equiv) in anhydrous diethyl ether (0.25 M) at -78 °C was slowly added *n*-BuLi (1.1 equiv, 2.5 M in hexanes). The reaction was stirred at the same temperature for 40 min, and DMF (3.0 equiv) was added dropwise. The reaction was allowed to warm to room temperature over 1 h before it was quenched with saturated aqueous NH₄Cl. The reaction mixture was diluted with diethyl ether (30 mL), washed with saturated NH₄Cl (10 mL) and saturated NaCl (10 mL), dried over Na₂SO₄, and concentrated to dryness under reduced pressure on a rotary evaporator. The crude product was directly used in the next reaction without purification.

A flame dried round bottom flask was charged with alkene starting material (1.0 equiv) in CH₂Cl₂ (0.5 M), ethyl acrylate (5.0 equiv) and flushed with Ar. Grubbs-Hoveyeda second generation catalyst (2.5 mol %) was added in one portion and the reaction was stirred at room temperature under an atmosphere of Ar. The homogeneous solution was stirred for 6 hours. Once the reaction was complete, the reaction was concentrated to dryness under reduced pressure on a rotary evaporator. The crude product was directly used in the next reaction without purification.

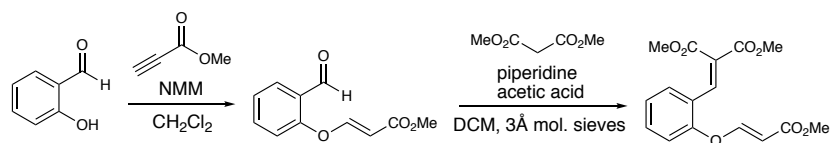
To a scintillation vial was added the crude aldehyde from the previous step (1 equiv). Malonate or ketoester was added (1.1 equiv), as well as 250 wt % activated 4 Å molecular sieves (powder). A magnetic stirbar and CH₂Cl₂ (2.0 M) were added, followed by acetic acid (0.1 equiv) and piperidine (0.1 equiv). The mixture was stirred overnight. Silica was added and the reaction concentrated under reduced pressure. The resulting mixture was loaded onto a column of silica and purified via flash column chromatography (10-20% EtOAc/hexanes) to yield the desired product.



Prepared according to the general procedure with 58% overall yield over four steps. Isolated as a ~2:1 mixture of E/Z isomers

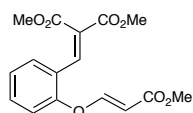
Analytical Data: ¹H NMR (500 MHz, Chloroform-*d*) δ = 7.99 (s, 1H), 7.33 – 7.24 (m, 2H), 7.23 – 7.13 (m, 2H), 6.93 (dt, *J*=15.7, 6.9, 1H), 5.79 (dt, *J*=15.7, 1.6, 1H), 4.15 (q, *J*=7.1, 2H), 3.85 (s, 3H), 3.70 (d, *J*=31.0, 5H), 3.38 (s, 1H), 2.82 (dd, *J*=8.8, 6.8, 2H), 2.49 – 2.40 (m, 2H), 1.26 (t, *J*=7.1, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 166.52, 166.42, 164.20, 147.16, 142.22, 140.18, 132.35, 130.26, 129.58, 128.09, 126.71, 122.31, 77.27, 77.02, 76.76, 60.24, 52.74, 52.49, 41.14, 33.23, 32.23, 14.26. LRMS (ESI): Mass calcd for C₁₉H₂₂O₆[M+H]⁺: 347.1; found 347.1 HRMS (ESI): Mass calcd for C₁₉H₂₂O₆[M+H]⁺: 347.1416; found 347.1418 FTIR (neat): 2997, 2710, 2244, 1663, 1637, 1613, 1562, 1374, 1283, 1254, 1206, 1181, 1146, 1104, 1021, 939, 865, 728

Preparation of Dihydrobenzofuran-Precursor Arylidene Malonate



A solution of alcohol (1.0 equiv), methyl propiolate (1.1 equiv), and N-methylmorpholine (5 mol %) in CH₂Cl₂ (0.4 M) was stirred at room temperature for 4 h. The solution was then washed with water and saturated aqueous NaCl and dried over anhydrous sodium sulfate. The combined organic layers were concentrated to dryness under reduced pressure on a rotary evaporator. The crude product was directly used in the next reaction without purification.

To a scintillation vial was added the crude aldehyde from the previous step (1 equiv). Malonate or ketoester was added (1.1 equiv) along with 250 wt % activated 4 Å molecular sieves (powder). A magnetic stir bar and CH₂Cl₂ (2.0 M) were added, followed by acetic acid (0.1 equiv) and piperidine (0.1 equiv). The mixture was stirred overnight. Silica was added and the crude reaction mixture was concentrated under reduced pressure. The resulting mixture was loaded onto a column of silica and purified via flash column chromatography (10-20% EtOAc/hexanes) to yield the desired product.

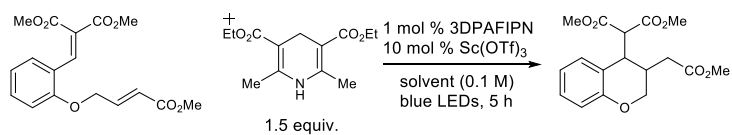


Prepared according to the general procedure with 85% overall yield over two steps.

Analytical Data: ¹H NMR (500 MHz, Chloroform-*d*) δ = 8.07 (s, 1H), 7.90 (d, *J*=12.3, 1H), 7.62 – 7.50 (m, 2H), 7.37 – 7.29 (m, 1H), 7.23 (dd, *J*=8.1, 1.1, 1H), 5.71 (d, *J*=12.2, 1H), 4.00 (s, 3H), 3.90 (d, *J*=24.6, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 167.14, 166.44, 164.16, 158.28, 153.89, 152.07, 137.19, 132.14, 129.38, 127.68, 125.26, 124.52, 118.03, 103.19, 83.24, 77.33, 77.08, 76.82, 52.75, 52.60, 51.42, 50.44. LRMS (ESI): Mass calcd for C₁₆H₁₆O₇[M+H]⁺: 321.1; found 321.1 HRMS (ESI): Mass calcd for C₁₆H₁₆O₇[M+H]⁺: 321.0896; found 321.0899 FTIR (neat): 2994, 2495, 2353, 1669, 1633, 1605, 1531, 1484, 1281, 1226, 1208, 1168, 1122, 1094, 994, 983, 868, 743

Selected Optimization Data:

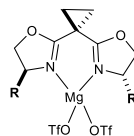
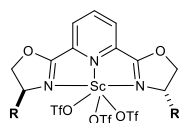
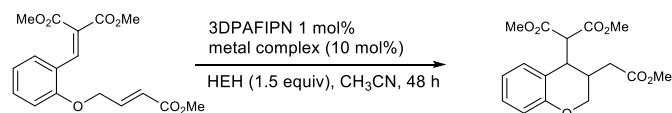
Table 1. Effect of Solvent



Entry:	Conditions:	GC Yield:
1	CH ₃ CN	84
2	DMF	38
3	MeOH	<5
4	DMSO	45
5	DMPU	38
6	CH ₂ Cl ₂	<5
7	THF	<5

[a] Yield determined by GC with bibenzyl as internal standard.

Table 2. Chiral Ligand Screen



entry	R	yield*	dr	er	entry	R	yield	dr	er
1	Ph	53	1.5:1	50:50	5	Inda	52	3:1	50:50
2	Inda	51	2:1	50:50	6	<i>t</i> Bu	56	2.5:1	50:50
3	<i>i</i> Pr	50	2.5:1	50:50					
4	Bn	10	1.5:1	50:50					

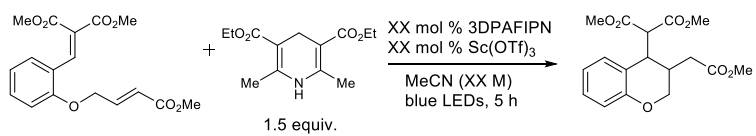
*all reactions showed incomplete conversion

[a] Yield determined by GC with bibenzyl as internal standard.

[b] dr determined by ¹H NMR

[c] er determined by SFC on a chiral stationary phase

Table 3. Effect of Concentration and Catalyst Loading

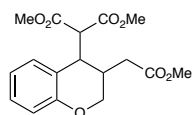


Entry:	Conditions:	GC Yield:
1	10% Sc(OTf) ₃ , 0.5% 3DPAFIPN, 0.2 M	62
2	5% Sc(OTf) ₃ , 0.5% 3DPAFIPN, 0.2 M	51
3	5% Sc(OTf) ₃ , 1% 3DPAFIPN, 0.2 M	65
4	10% Sc(OTf) ₃ , 1% 3DPAFIPN, 0.2 M	81
5	10% Sc(OTf) ₃ , 0.5% 3DPAFIPN, 0.1 M	65
6	5% Sc(OTf) ₃ , 0.5% 3DPAFIPN, 0.1 M	55
7	10% Sc(OTf) ₃ , 0.5% 3DPAFIPN, 0.05 M	42
8	5% Sc(OTf) ₃ , 1% 3DPAFIPN, 0.05 M	41

[a] Yield determined by GC with bibenzyl as internal standard.

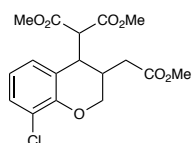
General Procedure for Reductive Cyclization

To a 2 dram vial was added arylidene malonate (1.0 equiv). The reaction vessel was equipped with a cap and stir bar and was then taken into a glovebox. 3DPAFIPN (1 mol %) and Sc(OTf)₃ (10 mol %) were added to the vial, which was then removed from the glovebox. The vial was then charged with a solution of HEH (1.5 equiv) and sparged CH₃CN (0.1 M). The mixture was stirred until homogenous. The vial was then placed between 3 Kessil blue LED lights and irradiated for 5 hours (with a small fan placed for cooling). Conversion of the malonate was monitored by UPLC/MS. Upon complete conversion, the reaction was concentrated under reduced pressure onto silica gel. This silica was loaded onto a column of silica gel and isolated via flash column chromatography (2-20% ethyl acetate/hexanes) to yield the product as a mixture of diastereomers.



Prepared according to the general procedure in 86% yield in a 1.2:1 ratio of diastereomers

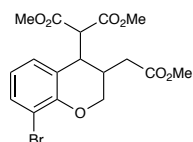
¹H NMR (500 MHz, Chloroform-*d*) δ = 7.11 (qd, J =8.1, 1.7, 1H), 7.04 – 6.93 (m, 1H), 6.93 – 6.74 (m, 2H), 4.27 – 4.15 (m, 1H), 3.95 – 3.83 (m, 1H), 3.77 (d, J =3.8, 3H), 3.74 – 3.53 (m, 6H), 3.46 – 3.35 (m, 2H), 2.69 (dddd, J =13.1, 9.0, 6.2, 3.6, 1H), 2.44 (dq, J =13.6, 7.1, 1H), 2.41 – 2.26 (m, 2H), 2.28 – 2.13 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 172.29, 171.72, 168.93, 168.52, 168.22, 167.96, 153.52, 130.64, 128.98, 128.87, 128.81, 121.17, 120.50, 120.08, 118.86, 116.95, 116.50, 77.28, 77.23, 77.03, 76.77, 66.49, 64.20, 58.82, 54.07, 53.03, 52.85, 52.61, 52.49, 51.94, 51.78, 38.82, 37.50, 35.36, 32.08, 32.06, 31.54. LRMS (ESI): Mass calcd for C₁₇H₂₀O₇[M+H]⁺: 337.1; found 337.1 HRMS (ESI): Mass calcd for C₁₇H₂₀O₇[M+H]⁺: 337.1209; found 337.1211 FTIR (neat): 3090, 2816, 2624, 1887, 1670, 1642, 1628, 1495, 1335, 1304, 1247, 1220, 1168, 1138, 1103, 998, 987, 860, 709



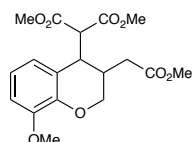
Prepared according to the general procedure in 61% yield in a 1.2:1 ratio of diastereomers

¹H NMR (500 MHz, Chloroform-*d*) δ = 7.22 (td, J =9.1, 8.5, 1.6, 1H), 6.93 (dd, J =7.8, 1.5, 1H), 6.73 (q, J =7.6, 1H), 4.40 – 4.31 (m, 1H), 4.26 (dd, J =12.4, 2.1, 1H), 3.96 – 3.89 (m, 1H), 3.78 (s, 1H), 3.77 (s, 2H), 3.68 (s, 1H), 3.67 (s, 2H), 3.67 – 3.54 (m, 1H), 3.55 (s, 2H), 3.44 (d, J =16.6, 2H), 2.48 – 2.23 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 172.00, 171.37, 168.78, 168.25, 167.99, 167.73, 149.50, 149.26, 129.69, 129.49, 129.15, 127.63, 123.05, 121.63, 121.36, 120.66, 120.56, 120.14, 77.28, 77.23, 77.02, 76.77, 67.01, 65.18, 58.59, 53.85, 53.12, 52.96, 52.64, 52.57, 52.03, 51.86, 38.81, 37.44, 35.27,

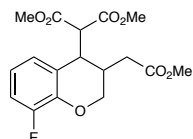
32.10, 31.99, 31.28. LRMS (ESI): Mass calcd for $C_{17}H_{19}ClO_7$ $[M+H]^+$: 371.1; found 371.1 HRMS (ESI): Mass calcd for $C_{17}H_{19}ClO_7$ $[M+H]^+$: 371.0819; found 371.0821
FTIR (neat): 3090, 2877, 2475, 1734, 1664, 1658, 1622, 1499, 1473, 1304, 1254, 1211, 1176, 1128, 1076, 1016, 985, 849, 825



Prepared according to the general procedure in 70% yield in a 1.2:1 ratio of diastereomers
 1H NMR (500 MHz, Chloroform-*d*) δ = 7.38 (ddd, $J=9.7, 7.8, 1.6$, 1H), 6.97 (dd, $J=7.8, 1.5$, 1H), 6.67 (q, $J=7.7$, 1H), 4.39 – 4.30 (m, 1H), 4.26 (dd, $J=12.0, 2.2$, 1H), 4.20 – 4.05 (m, 1H), 3.92 (dd, $J=8.0, 4.1$, 1H), 3.77 (s, 2H), 3.67 (s, 1H), 3.66 (s, 2H), 3.64 – 3.51 (m, 1H), 3.55 (s, 2H), 3.48 – 3.32 (m, 2H), 2.77 – 2.66 (m, 1H), 2.48 – 2.32 (m, 2H), 2.31 – 2.14 (m, 1H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.99, 171.35, 168.78, 168.23, 167.98, 167.72, 150.11, 132.79, 132.59, 129.93, 128.43, 123.04, 121.18, 120.73, 120.67, 110.87, 110.55, 77.29, 77.24, 77.03, 76.78, 67.10, 65.35, 58.60, 53.83, 53.11, 52.96, 52.62, 52.56, 52.03, 51.86, 38.95, 37.54, 35.28, 32.12, 32.07, 31.34, 14.21. LRMS (ESI): Mass calcd for $C_{17}H_{19}BrO_7$ $[M+H]^+$: 415.1; found 415.2 HRMS (ESI): Mass calcd for $C_{17}H_{19}BrO_7$ $[M+H]^+$: 415.0314; found 415.0316 FTIR (neat): 3090, 2964, 2557, 2069, 1708, 1647, 1606, 1550, 1354, 1292, 1229, 1189, 1168, 1122, 1048, 1016, 978, 900, 778

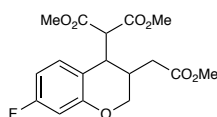


Prepared according to the general procedure in 62% yield in a 1.2:1 ratio of diastereomers
 1H NMR (500 MHz, Chloroform-*d*) δ = 6.87 – 6.73 (m, 1H), 6.77 – 6.65 (m, 1H), 6.61 (dd, $J=6.5, 2.9$, 1H), 4.37 – 4.19 (m, 1H), 4.21 – 4.06 (m, 1H), 3.96 – 3.80 (m, 3H), 3.76 (s, 2H), 3.84 – 3.67 (m, 2H), 3.65 (s, 2H), 3.70 – 3.59 (m, 1H), 3.56 (s, 2H), 3.62 – 3.46 (m, 1H), 3.48 – 3.32 (m, 2H), 2.80 – 2.55 (m, 1H), 2.47 (dt, $J=15.9, 7.9$, 1H), 2.40 – 2.27 (m, 1H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.23, 168.20, 167.92, 148.14, 142.94, 122.27, 120.71, 119.97, 119.62, 119.52, 117.61, 110.41, 110.35, 77.28, 77.23, 77.02, 76.77, 66.85, 64.63, 58.89, 58.85, 55.98, 55.87, 55.81, 54.16, 53.04, 52.95, 52.86, 52.64, 52.50, 51.92, 51.75, 50.89, 39.14, 38.64, 37.37, 35.23, 31.95, 31.87, 31.30. LRMS (ESI): Mass calcd for $C_{18}H_{22}O_8$ $[M+H]^+$: 367.1; found 367.1 HRMS (ESI): Mass calcd for $C_{18}H_{22}O_8$ $[M+H]^+$: 367.1315; found 367.1317 FTIR (neat): 3028, 2893, 2704, 2196, 1693, 1631, 1600, 1531, 1428, 1273, 1269, 1218, 1165, 1128, 1091, 995, 938, 896, 696



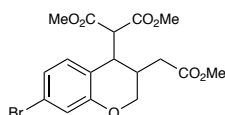
Prepared according to the general procedure in 74% yield in a 1.5:1 ratio of diastereomers

^1H NMR (500 MHz, Chloroform-*d*) δ = 7.00 – 6.88 (m, 1H), 6.84 – 6.66 (m, 2H), 4.35 – 4.27 (m, 1H), 4.25 – 4.10 (m, 1H), 3.78 (s, 1H), 3.77 (s, 2H), 3.67 (s, 2H), 3.72 – 3.60 (m, 2H), 3.59 (t, $J=7.4$, 1H), 3.56 (s, 2H), 3.51 – 3.42 (m, 2H), 2.50 – 2.27 (m, 3H) ^{13}C NMR (126 MHz, CDCl_3) δ 172.03, 171.45, 168.74, 168.31, 168.01, 167.74, 152.30, 150.35, 142.05, 141.96, 125.57, 125.54, 123.96, 123.93, 123.77, 121.40, 119.85, 119.80, 119.44, 119.38, 115.38, 115.23, 115.11, 77.27, 77.02, 76.77, 66.71, 64.64, 58.59, 53.90, 53.11, 52.95, 52.68, 52.56, 52.01, 51.85, 38.34, 38.32, 37.11, 35.25, 31.96, 31.91, 31.31. LRMS (ESI): Mass calcd for $\text{C}_{17}\text{H}_{19}\text{FO}_7$ $[\text{M}+\text{H}]^+$: 355.1; found 355.1 HRMS (ESI): Mass calcd for $\text{C}_{17}\text{H}_{19}\text{FO}_7$ $[\text{M}+\text{H}]^+$: 355.1115; found 355.1110 FTIR (neat): 3093, 2766, 2601, 1918, 1667, 1639, 1599, 1489, 1346, 1278, 1238, 1215, 1183, 1151, 1082, 1016, 983, 854, 747



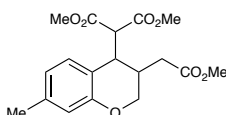
Prepared according to the general procedure in 68% yield in a 1.5:1 ratio of diastereomers

^1H NMR (500 MHz, Chloroform-*d*) δ = 6.93 (ddd, $J=41.9$, 8.3, 6.5, 1H), 6.57 – 6.46 (m, 2H), 4.25 – 4.15 (m, 2H), 4.12 – 4.02 (m, 1H), 3.87 (dd, $J=7.9$, 4.2, 1H), 3.77 (d, $J=3.4$, 1H), 3.77 (s, 2H), 3.77 – 3.64 (m, 4H), 3.62 – 3.51 (m, 3H), 3.44 (d, $J=1.0$, 1H), 3.39 (d, $J=10.3$, 1H), 2.74 – 2.63 (m, 1H), 2.45 – 2.24 (m, 2H) ^{13}C NMR (126 MHz, CDCl_3) δ 172.12, 171.50, 168.87, 168.39, 168.12, 167.83, 163.81, 161.86, 154.65, 154.55, 131.79, 131.71, 130.10, 114.69, 114.67, 108.01, 107.83, 107.32, 107.15, 104.09, 103.90, 103.51, 77.27, 77.02, 76.77, 66.34, 64.37, 58.69, 53.90, 53.06, 52.91, 52.63, 52.56, 52.00, 51.84, 38.29, 36.91, 35.26, 32.16, 32.13, 31.36. LRMS (ESI): Mass calcd for $\text{C}_{17}\text{H}_{19}\text{FO}_7$ $[\text{M}+\text{H}]^+$: 355.1; found 355.1 HRMS (ESI): Mass calcd for $\text{C}_{17}\text{H}_{19}\text{FO}_7$ $[\text{M}+\text{H}]^+$: 355.1115; found 355.1114 FTIR (neat): 3052, 2886, 2485, 2252, 1708, 1656, 1626, 1544, 1331, 1286, 1255, 1208, 1186, 1121, 1109, 994, 952, 839, 719



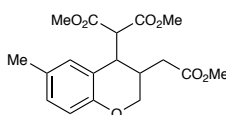
Prepared according to the general procedure in 84% yield in a 1.2:1 ratio of diastereomers

^1H NMR (500 MHz, Chloroform-*d*) δ = 7.02 – 6.94 (m, 1H), 6.97 – 6.84 (m, 2H), 4.16 (d, J =2.1, 1H), 4.07 (td, J =11.8, 11.1, 8.2, 1H), 3.77 (s, 2H), 3.76 (d, J =7.1, 1H), 3.72 – 3.52 (m, 7H), 3.46 (s, 1H), 3.37 (d, J =10.1, 1H), 2.45 – 2.23 (m, 3H) ^{13}C NMR (126 MHz, CDCl_3) δ 172.05, 171.48, 168.31, 168.02, 167.73, 154.32, 141.64, 132.43, 131.90, 130.23, 123.68, 123.14, 122.03, 121.55, 120.10, 119.65, 117.99, 114.80, 77.28, 77.22, 77.02, 76.77, 66.60, 66.52, 64.44, 58.49, 53.72, 52.95, 52.63, 51.85, 38.38, 37.06, 35.28, 32.04, 31.95, 31.26, 29.94. LRMS (ESI): Mass calcd for $\text{C}_{17}\text{H}_{19}\text{BrO}_7$ $[\text{M}+\text{H}]^+$: 415.1; found 415.2 HRMS (ESI): Mass calcd for $\text{C}_{17}\text{H}_{19}\text{BrO}_7$ $[\text{M}+\text{H}]^+$: 415.0314; found 415.0318 FTIR (neat): 3100, 2967, 2561, 2235, 1686, 1650, 1625, 1567, 1371, 1303, 1258, 1217, 1185, 1124, 1120, 1013, 933, 900, 802



Prepared according to the general procedure in 88% yield in a 1.2:1 ratio of diastereomers

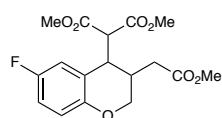
^1H NMR (500 MHz, Chloroform-*d*) δ = 6.91 – 6.70 (m, 1H), 6.67 – 6.56 (m, 2H), 4.23 – 4.03 (m, 2H), 3.91 – 3.80 (m, 1H), 3.76 (d, J =2.9, 2H), 3.74 – 3.52 (m, 5H), 3.48 (s, 1H), 3.36 (d, J =10.3, 1H), 2.48 – 2.34 (m, 1H), 2.37 – 2.22 (m, 2H), 2.25 – 2.13 (m, 3H) ^{13}C NMR (126 MHz, CDCl_3) δ 172.35, 171.83, 168.27, 168.00, 153.28, 139.05, 138.83, 130.37, 128.46, 121.57, 121.43, 121.08, 118.11, 117.28, 116.86, 115.79, 77.29, 77.23, 77.03, 76.78, 66.57, 64.12, 58.88, 54.13, 52.99, 52.82, 52.64, 52.50, 51.91, 51.75, 38.60, 37.32, 35.32, 32.15, 31.94, 31.59, 21.05. LRMS (ESI): Mass calcd for $\text{C}_{18}\text{H}_{22}\text{O}_7$ $[\text{M}+\text{H}]^+$: 351.1; found 351.1 HRMS (ESI): Mass calcd for $\text{C}_{18}\text{H}_{22}\text{O}_7$ $[\text{M}+\text{H}]^+$: 351.1366; found 351.1365 FTIR (neat): 3093, 2893, 2538, 1936, 1699, 1631, 1625, 1522, 1451, 1290, 1247, 1200, 1182, 1121, 1059, 997, 945, 895, 756



Prepared according to the general procedure in 91% yield in a 1.2:1 ratio of diastereomers

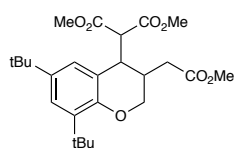
^1H NMR (500 MHz, Chloroform-*d*) δ = 6.91 (td, J =8.2, 2.1, 1H), 6.80 – 6.71 (m, 1H), 6.74 – 6.60 (m, 1H), 4.23 – 4.01 (m, 2H), 3.91 – 3.79 (m, 1H), 3.81 – 3.69 (m, 3H), 3.72 – 3.63 (m, 3H), 3.66 – 3.55 (m, 1H), 3.51 (d, J =56.4, 3H), 3.35 (d, J =10.2, 1H), 2.44 (dd, J =18.0, 10.2, 1H), 2.38 – 2.26 (m, 2H), 2.28 – 2.14 (m, 1H), 2.19 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 172.35, 171.75, 168.97, 168.55, S-23

168.29, 167.99, 151.49, 151.26, 130.77, 129.67, 129.62, 129.42, 129.16, 129.12, 120.82, 118.50, 116.65, 116.20, 77.28, 77.23, 77.03, 76.77, 66.39, 64.13, 58.86, 54.13, 53.00, 52.82, 52.52, 52.37, 51.92, 51.76, 38.86, 37.53, 35.38, 32.20, 32.08, 31.63, 20.50, 20.48. LRMS (ESI): Mass calcd for C₁₈H₂₂O₇ [M+H]⁺: 351.1; found 351.1 HRMS (ESI): Mass calcd for C₁₈H₂₂O₇ [M+H]⁺: 351.1366; found 351.1367 FTIR (neat): 3042, 2854, 2608, 2018, 1689, 1636, 1628, 1580, 1467, 1299, 1238, 1219, 1179, 1120, 1086, 1012, 951, 856, 759



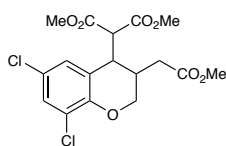
Prepared according to the general procedure in 92% yield in a 1.3:1 ratio of diastereomers

¹H NMR (500 MHz, Chloroform-*d*) δ = 6.93 – 6.76 (m, 1H), 6.80 – 6.70 (m, 1H), 6.68 (ddd, *J*=30.4, 8.4, 3.1, 1H), 4.23 – 4.02 (m, 2H), 3.77 (s, 2H), 3.91 – 3.73 (m, 1H), 3.75 – 3.65 (m, 2H), 3.67 (s, 2H), 3.61 (s, 2H), 3.52 (s, 1H), 3.38 (d, *J*=10.0, 1H), 2.48 – 2.25 (m, 3H) ¹³C NMR (126 MHz, CDCl₃) δ 172.12, 171.61, 168.68, 168.01, 167.73, 157.56, 155.66, 149.58, 119.92, 118.00, 117.93, 117.36, 116.47, 116.08, 115.89, 115.49, 115.01, 114.83, 77.28, 77.02, 76.77, 66.59, 64.37, 58.64, 53.82, 53.11, 52.94, 52.65, 51.84, 38.76, 37.50, 35.33, 31.88, 31.33. LRMS (ESI): Mass calcd for C₁₇H₁₉FO₇ [M+H]⁺: 355.1; found 355.1 HRMS (ESI): Mass calcd for C₁₇H₁₉FO₇ [M+H]⁺: 355.1115; found 355.1117 FTIR (neat): 3081, 2939, 2530, 2298, 1666, 1635, 1620, 1564, 1423, 1303, 1223, 1194, 1188, 1158, 1089, 1007, 928, 901, 775



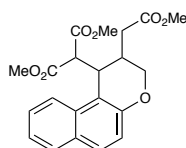
Prepared according to the general procedure in 91% yield in a 1.1:1 ratio of diastereomers

¹H NMR (500 MHz, Chloroform-*d*) δ = 7.14 (d, *J*=2.5, 1H), 6.85 (d, *J*=2.4, 1H), 4.22 – 4.14 (m, 1H), 4.09 (dt, *J*=11.5, 1.9, 1H), 3.95 – 3.83 (m, 1H), 3.86 – 3.73 (m, 1H), 3.76 (s, 2H), 3.76 – 3.65 (m, 2H), 3.66 (s, 2H), 3.55 (s, 2H), 3.46 (s, 1H), 3.44 – 3.33 (m, 1H), 2.45 – 2.28 (m, 2H), 1.33 (d, *J*=24.0, 1H), 1.32 (s, 8H), 1.30 – 1.18 (m, 2H), 1.22 (s, 7H). ¹³C NMR (126 MHz, CDCl₃) δ 172.52, 168.30, 168.27, 150.17, 141.90, 136.79, 125.14, 123.17, 118.83, 77.28, 77.23, 77.03, 76.77, 66.26, 64.22, 59.09, 52.77, 52.48, 51.72, 39.85, 35.83, 34.95, 34.93, 34.22, 31.73, 31.62, 31.58, 31.55, 29.68. LRMS (ESI): Mass calcd for C₂₅H₃₆O₇ [M+H]⁺: 449.2; found 449.2 HRMS (ESI): Mass calcd for C₂₅H₃₆O₇ [M+H]⁺: 449.2461; found 449.2462 FTIR (neat): 3039, 2804, 2587, 1770, 1690, 1630, 1615, 1569, 1413, 1305, 1243, 1216, 1168, 1134, 1084, 1002, 956, 852, 759



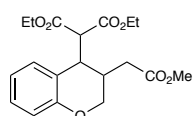
Prepared according to the general procedure in 90% yield in a 1.2:1 ratio of diastereomers

^1H NMR (500 MHz, Chloroform-*d*) δ = 7.26 – 7.19 (m, 1H), 6.97 – 6.93 (m, 1H), 4.34 (dt, $J=12.1$, 1.7, 1H), 4.26 – 4.04 (m, 2H), 3.77 (s, 3H), 3.67 (s, 3H), 3.61 (s, 3H), 3.68 – 3.46 (m, 2H), 3.47 – 3.38 (m, 1H), 2.45 – 2.13 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 171.79, 167.76, 167.45, 148.14, 129.38, 129.15, 128.78, 127.49, 124.93, 122.51, 121.76, 77.27, 77.22, 77.02, 76.77, 67.02, 65.36, 58.40, 53.65, 53.21, 53.05, 52.77, 52.71, 52.10, 51.93, 38.68, 37.30, 35.21, 32.04, 31.84, 31.07. LRMS (ESI): Mass calcd for $\text{C}_{17}\text{H}_{18}\text{Cl}_2\text{O}_7$ $[\text{M}+\text{H}]^+$: 405.1; found 405.1 HRMS (ESI): Mass calcd for $\text{C}_{17}\text{H}_{18}\text{Cl}_2\text{O}_7$ $[\text{M}+\text{H}]^+$: 405.0430; found 405.0428 FTIR (neat): 3097, 2839, 2540, 2264, 1682, 1658, 1622, 1496, 1398, 1304, 1254, 1218, 1165, 1128, 1033, 1001, 941, 887, 799



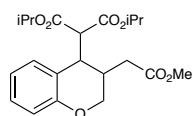
Prepared according to the general procedure in 82% yield in a 1.5:1 ratio of diastereomers

^1H NMR (500 MHz, Chloroform-*d*) δ = 7.83 (d, $J=8.5$, 1H), 7.78 – 7.57 (m, 2H), 7.44 (dddd, $J=8.4$, 6.6, 5.2, 1.3, 1H), 7.33 – 7.24 (m, 1H), 7.00 (dd, $J=8.9$, 3.0, 1H), 4.38 – 4.28 (m, 1H), 4.29 – 4.06 (m, 2H), 3.81 (s, 1H), 3.81 – 3.55 (m, 6H), 3.03 (s, 2H), 2.78 (s, 1H), 2.58 – 2.38 (m, 2H), 2.33 (dd, $J=16.5$, 5.8, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 172.37, 171.23, 169.71, 168.72, 168.29, 168.09, 151.46, 132.99, 132.28, 129.42, 129.23, 128.83, 128.55, 128.05, 126.44, 126.31, 123.31, 123.26, 122.89, 121.91, 118.65, 118.42, 110.56, 77.30, 77.25, 77.05, 76.79, 64.76, 64.15, 57.80, 53.99, 53.04, 52.78, 52.14, 52.06, 51.86, 51.78, 35.86, 34.60, 33.08, 32.90, 32.73, 32.01, 14.22. LRMS (ESI): Mass calcd for $\text{C}_{21}\text{H}_{22}\text{O}_7$ $[\text{M}+\text{H}]^+$: 387.1; found 387.1 HRMS (ESI): Mass calcd for $\text{C}_{21}\text{H}_{22}\text{O}_7$ $[\text{M}+\text{H}]^+$: 387.1366; found 387.1364 FTIR (neat): 3006, 2943, 2689, 2235, 1669, 1657, 1608, 1515, 1340, 1305, 1264, 1199, 1166, 1140, 1046, 1000, 987, 832, 747



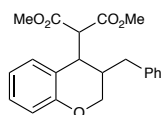
Prepared according to the general procedure in 86% yield in a 1.2:1 ratio of diastereomers

^1H NMR (500 MHz, Chloroform-*d*) δ = 7.20 – 6.89 (m, 2H), 6.90 – 6.73 (m, 2H), 4.35 – 4.07 (m, 5H), 4.09 – 3.96 (m, 1H), 3.98 – 3.88 (m, 1H), 3.77 – 3.62 (m, 3H), 3.62 – 3.50 (m, 1H), 3.45 – 3.33 (m, 1H), 2.52 – 2.26 (m, 2H), 1.35 – 1.12 (m, 4H), 1.04 (dt, $J=30.5, 7.1$, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 172.33, 171.77, 167.89, 167.64, 153.55, 130.85, 129.10, 128.85, 128.70, 120.42, 120.02, 119.11, 116.83, 116.40, 77.28, 77.23, 77.02, 76.77, 66.50, 64.24, 62.05, 61.85, 61.73, 61.58, 59.08, 54.32, 51.90, 51.76, 38.68, 37.29, 35.40, 32.09, 32.07, 31.63, 14.06, 13.82, 13.65. LRMS (ESI): Mass calcd for $\text{C}_{19}\text{H}_{24}\text{O}_7$ $[\text{M}+\text{H}]^+$: 365.1; found 365.2 HRMS (ESI): Mass calcd for $\text{C}_{19}\text{H}_{24}\text{O}_7$ $[\text{M}+\text{H}]^+$: 365.1522; found 365.1525 FTIR (neat): 3033, 2854, 2391, 1822, 1663, 1650, 1626, 1544, 1486, 1300, 1252, 1210, 1184, 1151, 1039, 1008, 935, 904, 742



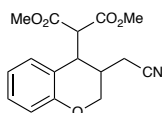
Prepared according to the general procedure in 82% yield in a 1.2:1 ratio of diastereomers

^1H NMR (500 MHz, Chloroform-*d*) δ = 7.15 – 6.99 (m, 2H), 6.76 (q, $J=8.4, 7.6$, 2H), 5.14 – 5.06 (m, 1H), 5.09 – 4.94 (m, 1H), 4.89 (hept, $J=6.3$, 1H), 4.78 (dq, $J=12.5, 6.4$, 1H), 4.25 – 4.09 (m, 2H), 3.79 – 3.66 (m, 1H), 3.66 (s, 1H), 3.66 (s, 2H), 3.55 – 3.45 (m, 1H), 3.40 (d, $J=9.7$, 1H), 2.48 – 2.38 (m, 1H), 2.42 – 2.17 (m, 2H), 1.28 – 1.19 (m, 5H), 1.22 – 1.10 (m, 3H), 1.08 (d, $J=6.3$, 1H), 0.98 (s, 1H), 0.99 – 0.88 (m, 2H), 0.87 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 172.37, 171.86, 167.75, 167.44, 167.24, 153.85, 153.56, 131.06, 129.23, 128.74, 128.58, 120.40, 120.01, 119.34, 116.75, 116.40, 77.28, 77.02, 76.77, 69.71, 69.64, 69.44, 69.42, 69.27, 66.65, 64.29, 59.41, 54.64, 51.86, 51.73, 38.43, 37.04, 35.45, 32.04, 31.99, 31.69, 21.73, 21.54, 21.51, 21.40, 21.17. LRMS (ESI): Mass calcd for $\text{C}_{21}\text{H}_{28}\text{O}_7$ $[\text{M}+\text{H}]^+$: 393.2; found 393.2 HRMS (ESI): Mass calcd for $\text{C}_{21}\text{H}_{28}\text{O}_7$ $[\text{M}+\text{H}]^+$: 393.1835; found 393.1837 FTIR (neat): 3072, 2984, 2652, 1843, 1671, 1653, 1601, 1501, 1474, 1283, 1270, 1199, 1180, 1161, 1049, 1007, 971, 884, 740



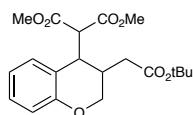
Prepared according to the general procedure in 85% yield in a 1.1:1 ratio of diastereomers

^1H NMR (500 MHz, Chloroform-*d*) δ = 7.32 – 7.19 (m, 5H), 7.15 (ddd, J =8.5, 7.3, 1.7, 1H), 7.06 (dd, J =7.7, 1.6, 1H), 6.96 – 6.86 (m, 2H), 4.60 (d, J =10.3, 1H), 4.21 (d, J =9.2, 1H), 4.09 (dd, J =11.8, 1.5, 1H), 3.79 (dd, J =11.7, 2.4, 1H), 3.47 (dddd, J =10.5, 9.1, 2.4, 1.5, 1H), 3.40 (s, 3H), 3.22 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 169.59, 168.65, 156.02, 137.23, 131.52, 128.39, 128.27, 127.90, 127.40, 121.22, 120.63, 118.00, 77.27, 77.22, 77.02, 76.76, 65.01, 64.28, 52.10, 51.91, 42.45, 36.13, 34.40, 14.13. LRMS (ESI): Mass calcd for $\text{C}_{21}\text{H}_{22}\text{O}_5$ $[\text{M}+\text{H}]^+$: 355.1; found 355.1 HRMS (ESI): Mass calcd for $\text{C}_{21}\text{H}_{22}\text{O}_5$ $[\text{M}+\text{H}]^+$: 355.1311; found 355.1310 FTIR (neat): 3067, 2980, 2871, 1654, 1651, 1605, 1555, 1504, 1421, 1281, 1270, 1190, 1180, 1161, 1079, 1021, 925, 880, 742



Prepared according to the general procedure in 81% yield in a 1.2:1 ratio of diastereomers

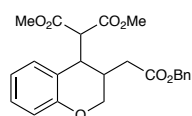
^1H NMR (500 MHz, Chloroform-*d*) δ = 7.51 – 7.34 (m, 1H), 7.31 – 7.20 (m, 1H), 7.18 – 7.02 (m, 2H), 4.53 – 4.46 (m, 1H), 4.42 (dd, J =12.2, 2.3, 1H), 4.00 (s, 3H), 3.97 – 3.85 (m, 2H), 3.85 (s, 3H), 3.70 (dd, J =9.8, 1.7, 1H), 2.66 (d, J =7.9, 2H), 2.61 – 2.51 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.92, 167.76, 153.07, 144.50, 130.52, 129.42, 121.13, 117.82, 117.58, 117.28, 115.18, 77.30, 77.05, 76.79, 63.18, 58.40, 53.00, 52.69, 52.61, 38.10, 32.46, 29.79, 19.60, 12.81. LRMS (ESI): Mass calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 304.1; found 304.1 HRMS (ESI): Mass calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 304.1107; found 304.1105 FTIR (neat): 3037, 2910, 2591, 1791, 1694, 1653, 1623, 1585, 1365, 1283, 1227, 1197, 1176, 1162, 1063, 999, 924, 885, 773



Prepared according to the general procedure in 77% yield in a 1.5:1 ratio of diastereomers

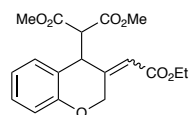
^1H NMR (500 MHz, Chloroform-*d*) δ = 7.11 (qd, J =7.9, 1.7, 1H), 6.99 (dd, J =8.0, 1.8, 1H), 6.95 – 6.86 (m, 1H), 6.81 – 6.74 (m, 2H), 4.25 – 4.12 (m, 2H), 4.07 (dd, J =11.1, 9.4, 1H), 3.93 – 3.87 (m, 1H), 3.77 (d, J =6.2, 3H), 3.64 – 3.55 (m, 1H), 3.55 (s, 2H), 3.42 (s, 1H), 2.71 – 2.61 (m, 1H), 2.39 – 2.15 (m, 2H), 2.07 (dd, J =15.9, 9.2, 1H), 1.43 (d, J =3.6, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 171.10, 170.46, 168.99, 168.58, 168.26, 167.98, 153.81, 153.55, 130.61, 129.03, 128.90, 128.75, 121.35, S-27

120.37, 119.96, 119.14, 116.89, 116.45, 81.16, 80.86, 77.27, 77.02, 76.76, 66.39, 64.35, 58.80, 53.99, 52.98, 52.82, 52.53, 52.46, 38.90, 37.52, 36.76, 33.73, 32.29, 31.56, 28.10, 28.06. LRMS (ESI): Mass calcd for C₂₀H₂₆O₇ [M+H]⁺: 379.1; found 379.2, HRMS (ESI): Mass calcd for C₂₀H₂₆O₇ [M+H]⁺: 379.1679; found 379.1681 FTIR (neat): 3057, 2972, 2548, 1877, 1676, 1643, 1616, 1541, 1374, 1297, 1252, 1211, 1177, 1126, 1068, 1009, 955, 867, 782



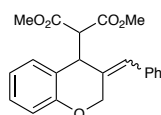
Prepared according to the general procedure in 88% yield in a 1.2:1 ratio of diastereomers

¹H NMR (500 MHz, Chloroform-*d*) δ = 7.39 – 7.25 (m, 5H), 7.11 (qd, *J*=7.1, 6.2, 1.6, 1H), 6.98 (dd, *J*=8.2, 1.7, 1H), 6.78 (dt, *J*=8.1, 5.6, 2H), 5.16 – 5.05 (m, 2H), 4.26 – 4.15 (m, 2H), 4.09 (dd, *J*=11.2, 8.9, 1H), 3.93 (dd, *J*=8.2, 4.1, 1H), 3.75 (s, 2H), 3.71 (s, 1H), 3.66 – 3.55 (m, 1H), 3.56 (s, 2H), 3.43 (d, *J*=11.2, 2H), 2.71 (tq, *J*=8.9, 4.2, 1H), 2.49 (dd, *J*=18.0, 10.1, 1H), 2.44 – 2.31 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 171.68, 171.13, 168.20, 167.95, 153.51, 135.71, 130.64, 128.99, 128.83, 128.80, 128.62, 128.56, 128.40, 128.37, 128.28, 128.25, 121.18, 120.50, 120.08, 118.85, 116.95, 116.50, 77.27, 77.22, 77.02, 76.76, 66.76, 66.54, 66.50, 64.21, 58.80, 54.05, 53.00, 52.84, 52.61, 52.49, 38.85, 37.51, 35.58, 32.28, 32.06, 31.52. LRMS (ESI): Mass calcd for C₂₃H₂₄O₇ [M+H]⁺: 413.2; found 413.2 HRMS (ESI): Mass calcd for C₂₃H₂₄O₇ [M+H]⁺: 413.1522; found 413.1525 FTIR (neat): 3004, 2936, 2750, 1987, 1683, 1629, 1627, 1524, 1394, 1279, 1254, 1194, 1186, 1153, 1110, 998, 945, 849, 698



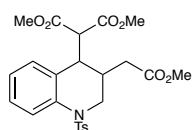
Prepared according to the general procedure in 81% yield in a 1:1 ratio of *Z/E* isomers

¹H NMR (500 MHz, Chloroform-*d*) δ = 7.30 (dd, *J*=7.7, 1.7, 1H), 7.28 (s, 2H), 7.21 – 7.10 (m, 1H), 6.99 – 6.82 (m, 1H), 5.89 (p, *J*=0.9, 1H), 5.62 (d, *J*=8.4, 1H), 5.01 (dd, *J*=14.3, 1.9, 1H), 4.53 (dt, *J*=14.4, 1.2, 1H), 4.26 – 4.12 (m, 2H), 3.86 (d, *J*=8.5, 1H), 3.71 (s, 2H), 3.68 (s, 1H), 3.59 (s, 2H), 1.55 (s, 1H), 1.31 (t, *J*=7.1, 3H), 1.26 (t, *J*=9.8, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 167.77, 167.59, 165.12, 154.26, 151.22, 130.12, 129.06, 122.63, 121.66, 117.52, 117.02, 77.27, 77.22, 77.02, 76.76, 69.30, 60.52, 57.24, 52.68, 52.47, 52.39, 37.80, 28.64, 14.20. LRMS (ESI): Mass calcd for C₁₈H₂₀O₇ [M+H]⁺: 349.1; found 349.1 HRMS (ESI): Mass calcd for C₁₈H₂₀O₇ [M+H]⁺: 349.1209; found 349.1210 FTIR (neat): 3095, 2750, 2389, 1840, 1691, 1658, 1619, 1525, 1471, 1276, 1264, 1204, 1163, 1129, 1099, 1019, 946, 862, 727



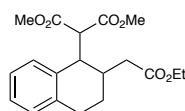
Prepared according to the general procedure in 86% yield in a 1:1 ratio of *Z/E* isomers

^1H NMR (500 MHz, Chloroform-*d*) δ = 7.45 – 7.16 (m, 5H), 7.13 (s, 1H), 7.19 – 7.03 (m, 1H), 7.03 (d, $J=8.2$, 1H), 7.00 – 6.77 (m, 2H), 5.12 – 4.94 (m, 1H), 4.93 (s, 1H), 4.59 (dd, $J=12.9$, 1.5, 1H), 4.25 (d, $J=10.8$, 1H), 3.97 – 3.85 (m, 1H), 3.80 – 3.71 (m, 1H), 3.68 (s, 1H), 3.65 (s, 2H), 3.61 (d, $J=13.1$, 1H), 3.51 (s, 1H), 3.24 (d, $J=7.7$, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 169.61, 167.45, 155.83, 154.06, 135.54, 133.18, 132.08, 132.01, 131.78, 131.07, 129.45, 129.26, 129.03, 128.97, 128.71, 128.65, 128.63, 128.56, 128.53, 128.40, 128.28, 128.16, 127.55, 127.45, 126.63, 126.53, 122.30, 121.32, 121.22, 120.64, 117.19, 117.05, 112.45, 112.03, 87.15, 84.00, 77.27, 77.02, 76.76, 70.38, 65.22, 57.49, 57.41, 56.70, 52.67, 52.54, 52.41, 51.42, 45.58, 37.90, 30.29. LRMS (ESI): Mass calcd for $\text{C}_{21}\text{H}_{20}\text{O}_5$ $[\text{M}+\text{H}]^+$: 353.1; found 353.1 HRMS (ESI): Mass calcd for $\text{C}_{21}\text{H}_{20}\text{O}_5$ $[\text{M}+\text{H}]^+$: 353.1311; found 353.1312 FTIR (neat): 3080, 2843, 2561, 1773, 1672, 1655, 1618, 1552, 1486, 1295, 1268, 1215, 1187, 1134, 1062, 1017, 987, 855, 766



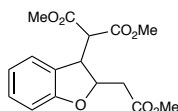
Prepared according to the general procedure in 85% yield in a 1.3:1 ratio of diastereomers

^1H NMR (500 MHz, Chloroform-*d*) δ = 7.84 (ddd, $J=13.3$, 8.4, 1.1, 1H), 7.71 – 7.59 (m, 2H), 7.37 – 7.19 (m, 3H), 7.07 (dd, $J=7.7$, 1.8, 1H), 7.06 – 6.92 (m, 1H), 3.89 – 3.79 (m, 1H), 3.77 (d, $J=2.6$, 4H), 3.77 – 3.67 (m, 1H), 3.69 (s, 1H), 3.67 (s, 2H), 3.64 – 3.43 (m, 1H), 3.44 (s, 2H), 3.35 (s, 1H), 2.78 (d, $J=11.0$, 1H), 2.62 (dp, $J=10.0$, 3.8, 3.2, 1H), 2.42 (d, $J=2.1$, 3H), 2.18 (d, $J=7.1$, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 171.79, 167.70, 167.60, 144.08, 136.21, 135.49, 130.71, 129.80, 129.76, 128.53, 128.20, 128.12, 127.18, 127.11, 126.43, 124.08, 122.91, 122.34, 77.29, 77.03, 76.78, 56.24, 52.98, 52.85, 52.35, 52.24, 52.04, 51.96, 51.82, 47.99, 47.00, 41.79, 37.39, 34.52, 34.16, 32.78, 21.57. LRMS (ESI): Mass calcd for $\text{C}_{24}\text{H}_{27}\text{NO}_8\text{S}$ $[\text{M}+\text{H}]^+$: 490.2; found 490.2 HRMS (ESI): Mass calcd for $\text{C}_{24}\text{H}_{27}\text{NO}_8\text{S}$ $[\text{M}+\text{H}]^+$: 490.1457; found 490.1455 FTIR (neat): 3029, 2819, 2633, 2317, 1706, 1632, 1604, 1546, 1331, 1304, 1247, 1192, 1168, 1141, 1072, 1008, 957, 886, 713



Prepared according to the general procedure in 82% yield in a 1.2:1 ratio of diastereomers

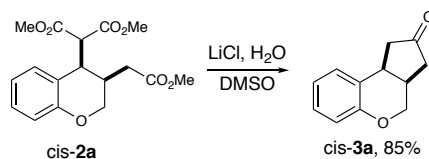
^1H NMR (500 MHz, Chloroform-*d*) δ = 7.31 – 7.19 (m, 4H), 7.12 (dt, $J=15.7$, 6.8, 1H), 4.34 – 4.19 (m, 2H), 3.80 (s, 6H), 3.85 – 3.72 (m, 1H), 3.35 (d, $J=7.7$, 2H), 2.95 – 2.85 (m, 2H), 2.60 (dtd, $J=8.1$, 6.7, 1.6, 2H), 1.43 – 1.31 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 169.23, 166.52, 147.76, 138.99, 135.40, 129.92, 129.59, 129.50, 129.38, 129.30, 127.21, 127.16, 126.55, 122.00, 77.28, 77.23, 77.03, 76.78, 60.38, 60.25, 52.71, 52.63, 52.57, 38.06, 35.69, 33.37, 31.25, 30.89, 30.73, 29.71, 28.46, 14.28. LRMS (ESI): Mass calcd for $\text{C}_{19}\text{H}_{24}\text{O}_6$ $[\text{M}+\text{H}]^+$: 349.1; found 349.1 HRMS (ESI): Mass calcd for $\text{C}_{19}\text{H}_{24}\text{O}_6$ $[\text{M}+\text{H}]^+$: 349.1573; found 349.1573 FTIR (neat): 3090, 2759, 2533, 2099, 1660, 1630, 1623, 1531, 1475, 1302, 1259, 1209, 1178, 1133, 1075, 1000, 968, 904, 804



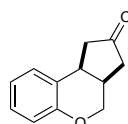
Prepared according to the general procedure in 72% yield in a 1.1:1 ratio of diastereomers

^1H NMR (500 MHz, Chloroform-*d*) δ = 7.24 – 7.00 (m, 2H), 6.86 – 6.76 (m, 2H), 5.07 – 5.00 (m, 1H), 3.86 – 3.79 (m, 1H), 3.82 – 3.72 (m, 1H), 3.75 – 3.64 (m, 8H), 3.67 – 3.56 (m, 1H), 2.85 – 2.67 (m, 2H) ^{13}C NMR (126 MHz, CDCl_3) δ 170.68, 168.08, 168.02, 158.81, 129.62, 125.35, 125.08, 120.83, 110.43, 82.41, 77.27, 77.02, 76.76, 56.01, 52.86, 52.65, 51.91, 46.42, 40.28. LRMS (ESI): Mass calcd for $\text{C}_{16}\text{H}_{18}\text{O}_7$ $[\text{M}+\text{H}]^+$: 323.1; found 323.1 HRMS (ESI): Mass calcd for $\text{C}_{16}\text{H}_{18}\text{O}_7$ $[\text{M}+\text{H}]^+$: 323.1053; found 323.1051 FTIR (neat): 3016, 2953, 2588, 1766, 1667, 1633, 1628, 1580, 1446, 1306, 1250, 1212, 1178, 1138, 1107, 991, 990, 906, 798

Procedure for Krapcho Decarboxylation and Dieckmann Condensation



To a 0.5-2 mL Biotage microwave vial outfitted with a magnetic stir bar was added 2a (1 equiv) and LiCl (4.1 equiv). Water (3 equiv) was then added, followed by DMSO (0.5 M). The vial was then sealed and heated in an oil bath at 140 °C for 18 hours. Upon observation of complete conversion, the vial was removed from oil bath and allowed to cool to room temperature. The solution was diluted with water (15 mL) and extracted with EtOAc (3 x 10 mL). The organic extracts were then pooled and washed with water (4 x 15 mL) and saturated brine solution (4 x 15 mL). The organic extracts were then concentrated under reduced pressure onto silica gel and loaded onto a column of silica gel. 3a was then isolated via flash chromatography (5-40% ethyl acetate/hexanes) as a thick, clear oil (85%).



^1H NMR (500 MHz, Chloroform-*d*) δ = 7.17 – 7.07 (m, 2H), 7.00 – 6.89 (m, 1H), 6.86 (d, J =8.2, 1H), 4.21 – 4.11 (m, 1H), 3.95 (dd, J =11.2, 7.5, 1H), 3.61 (dt, J =8.7, 6.7, 1H), 2.86 – 2.75 (m, 2H), 2.56 – 2.42 (m, 2H), 2.25 (ddd, J =19.1, 6.4, 1.5, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 217.18, 153.87, 129.97, 127.93, 121.45, 117.30, 77.28, 77.03, 76.77, 65.58, 45.81, 39.53, 34.68, 34.62, 33.89, 22.66. LRMS (ESI): Mass calcd for $\text{C}_{12}\text{H}_{21}\text{O}_2$ $[\text{M}+\text{H}]^+$: 189.1; found 189.1 HRMS (ESI): Mass calcd for $\text{C}_{12}\text{H}_{21}\text{O}_2$ $[\text{M}+\text{H}]^+$: 189.0837; found 189.0835 FTIR (neat): 3095, 1720, 1472, 1325, 1241, 1170, 1111, 1032, 968, 904, 804

Stern-Volmer Fluorescence Quenching Experiments

Stern-Volmer fluorescence quenching experiments were run with freshly prepared solutions of 2.0×10^{-6} M 3DPAFIPN in acetonitrile at room temperature under an inert Ar atmosphere. The solutions were irradiated at 425 nm and fluorescence was measured at 523 nm. Control experiments show that, at the concentrations employed in these studies, neither arylidene malonates nor $\text{Sc}(\text{OTf})_3$ measurably quench the excited state of 3DPAFIPN (Figure 3). The data summarized in the tables is the fluorescence intensity measured three times for each sample. The data shown in the graphs is the average of three experiments.

Stern-Volmer Fluorescence Quenching: Figure 6 Table Data and Individual Graphs

Vial	1	2	3	Average	I0/I	[1a] mol/L	var 1a, No Sc(Otf)3
0	514	513	513	513.3	1.0	0	
1	510	508	508	508.7	1.0	0.02	
2	509	519	520	516.0	1.0	0.04	
3	508	507	510	508.3	1.0	0.06	
4	507	508	505	506.7	1.0	0.08	
5	517	514	517	516.0	1.0	0.1	

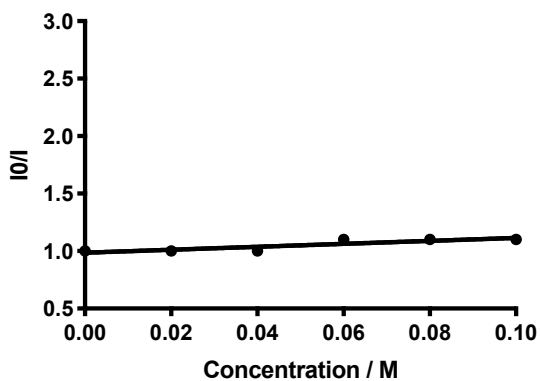
Vial	1	2	3	Average	I0/I	[1a] mol/L	var 1a, 0.1 M Sc(Otf)3
0	510	511	514	511.7	1.0	0	
1	420	418	418	418.7	1.2	0.02	
2	330	348	348	342.0	1.5	0.04	
3	291	292	292	291.7	1.8	0.06	
4	251	253	253	252.3	2.0	0.08	
5	221	218	218	219.0	2.3	0.1	

Vial	1	2	3	Average	I0/I	[HEH] mol/L	var HEH, No Sc(Otf)3, No 1a
0	510	511	511	510.7	1.0	0	
1	410	405	404	406.3	1.3	0.02	
2	312	316	308	312.0	1.6	0.04	
3	252	246	257	251.7	2.0	0.06	
4	208	221	215	214.7	2.4	0.08	
5	172	173	170	171.7	3.0	0.1	

Vial	1	2	3	Average	I0/I	[HEH] mol/L	var HEH, No Sc(Otf)3, 0.1 M 1a
0	515	502	508	507.3	1.0	0	
1	409	402	407	404.3	1.3	0.02	
2	300	308	309	304.3	1.7	0.04	
3	252	251	252	246.7	2.1	0.06	
4	212	209	211	211.3	2.4	0.08	
5	168	180	174	176.3	2.9	0.1	

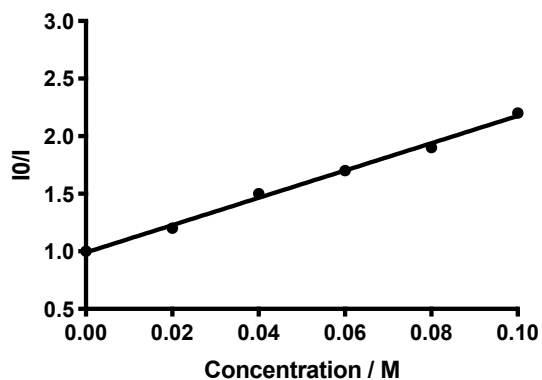
Vial	1	2	3	Average	I0/I	[HEH] mol/L	var HEH, 0.1 M 1a, 0.1 M Sc(Otf)3
0	512	514	513	507.3	1.0	0	
1	418	406	412	404.7	1.3	0.02	
2	308	298	295	304.7	1.7	0.04	
3	248	255	252	249.0	2.0	0.06	
4	205	205	190	210.3	2.4	0.08	
5	169	173	175	172.0	2.9	0.1	

AM (no Sc(OTf)₃)



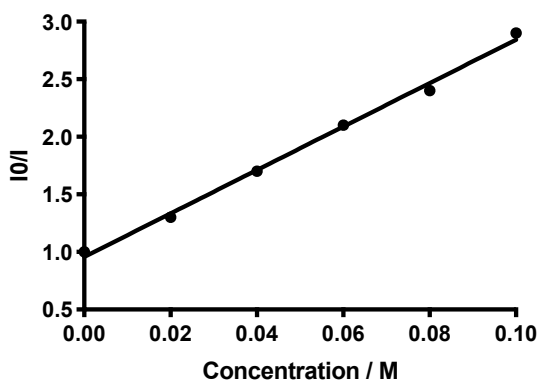
	AM (no Sc(OTf) ₃)
Equation	Y = 1.286*X + 0.9857
	AM (no Sc(OTf) ₃)
R squared	0.7714

Sc(OTf)₃ (0.1 M AM)



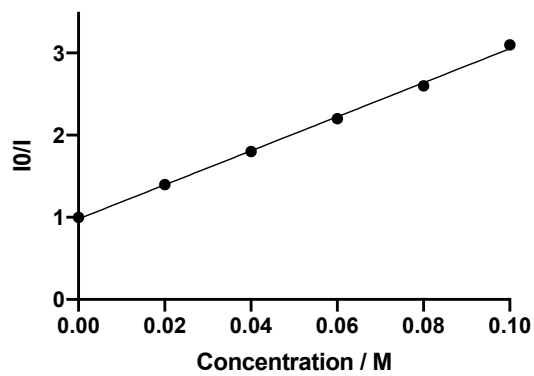
	Sc(OTf) ₃ (0.1 M AM)
Equation	Y = 11.86*X + 0.9905
	Sc(OTf) ₃ (0.1 M AM)
R square	0.9958

HEH, no AM, Sc(OTf)₃



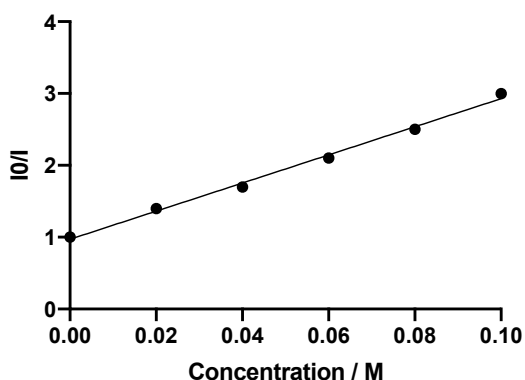
	HEH
Equation	Y = 18.86*X + 0.9571
	HEH
R square	0.9957

HEH, 0.1 M AM/Sc(OTf)₃



	HEH (0.1 M AM/Sc(OTf) ₃)
Equation	Y = 20.71*X + 0.9810
	HEH (0.1 M AM/Sc(OTf) ₃)
R square	0.9984

HEH, 0.1 M AM



	HEH (0.1 M AM)
Equation	Y = 19.57*X + 0.9714
	HEH (0.1 M AM)
R square	0.9949

Stern-Volmer Fluorescence Quenching: Varying 1a and Sc(Otf)₃

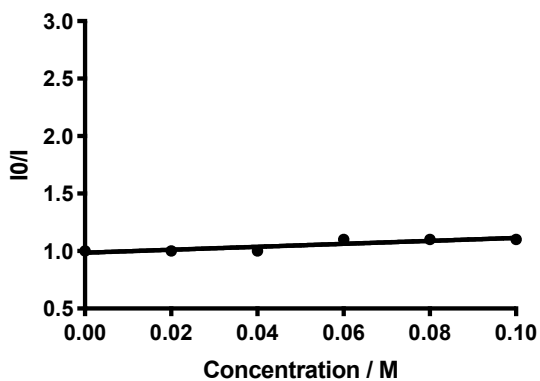
Vial	1	2	3	Average	I ₀ /I	[1a] mol/L	var 1a, No Sc(Otf) ₃
0	514	513	513	513.3	1.0	0	
1	510	508	508	508.7	1.0	0.02	
2	509	519	520	516.0	1.0	0.04	
3	508	507	510	508.3	1.0	0.06	
4	507	508	505	506.7	1.0	0.08	
5	517	514	517	516.0	1.0	0.1	

Vial	1	2	3	Average	I ₀ /I	[Sc(Otf) ₃] mol/L	var Sc(Otf) ₃ , no 1a
0	513	514	512	513.0	1.0	0	
1	512	511	511	511.3	1.0	0.02	
2	513	511	511	511.7	1.0	0.04	
3	511	515	513	513.0	1.0	0.06	
4	513	511	514	512.7	1.0	0.08	
5	512	510	515	512.3	1.0	0.1	

Vial	1	2	3	Average	I ₀ /I	[1a] mol/L	var 1a, 0.1 M Sc(Otf) ₃
0	510	511	514	511.7	1.0	0	
1	420	418	418	418.7	1.2	0.02	
2	330	348	348	342.0	1.5	0.04	
3	291	292	292	291.7	1.8	0.06	
4	251	253	253	252.3	2.0	0.08	
5	221	218	218	219.0	2.3	0.1	

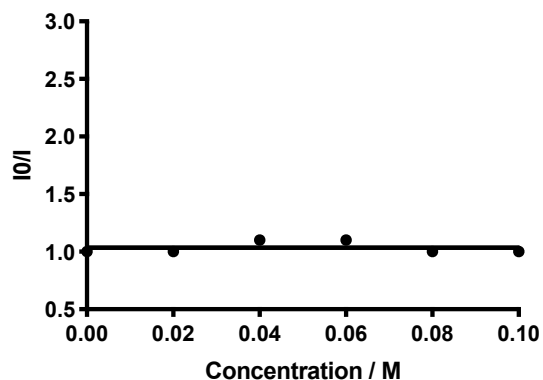
Vial	1	2	3	Average	I ₀ /I	[Sc(Otf) ₃] mol/L	var Sc(Otf) ₃ , 0.1 M 1a
0	510	511	511	510.7	1.0	0	
1	423	425	422	423.3	1.2	0.02	
2	343	345	347	345.0	1.5	0.04	
3	304	301	303	302.7	1.7	0.06	
4	266	268	270	268.0	1.9	0.08	
5	231	227	234	230.7	2.2	0.1	

AM (no Sc(OTf)₃)



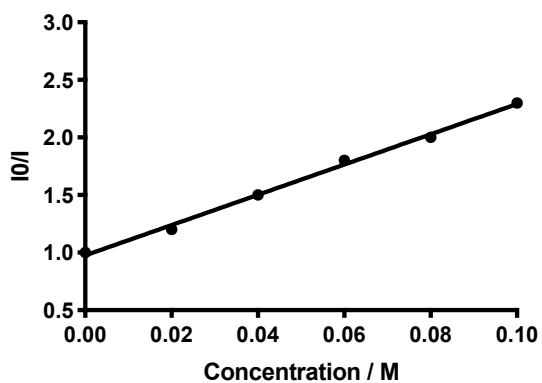
	AM (no Sc(OTf) ₃)
Equation	Y = 1.286*X + 0.9857
	AM (no Sc(OTf) ₃)
R squared	0.7714

Sc(OTf)₃ (no AM)



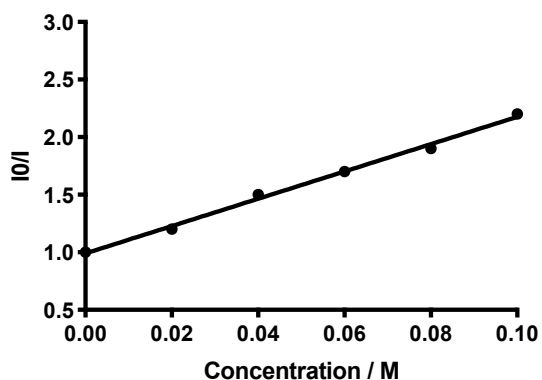
	Sc(OTf) ₃ (no AM)
Equation	Y = -3.098e-017*X + 1.033
	Sc(OTf) ₃ (no AM)
R square	5.038e-034

AM (0.1 M Sc(OTf)₃)



	AM (0.1 M Sc(OTf) ₃)
Equation	Y = 13.14*X + 0.9762
	AM (0.1 M Sc(OTf) ₃)
R square	0.9965

Sc(OTf)₃ (0.1 M AM)



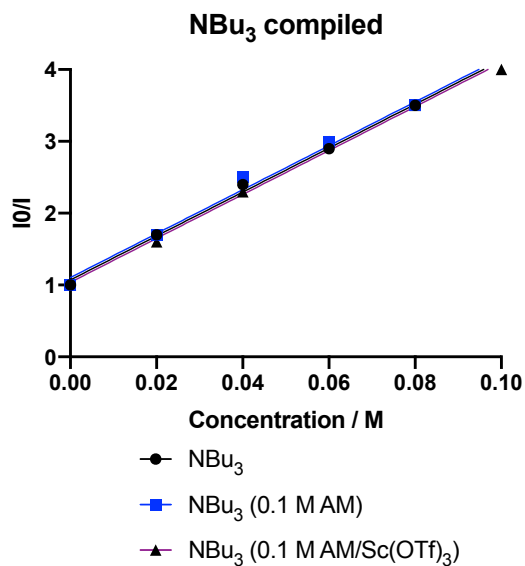
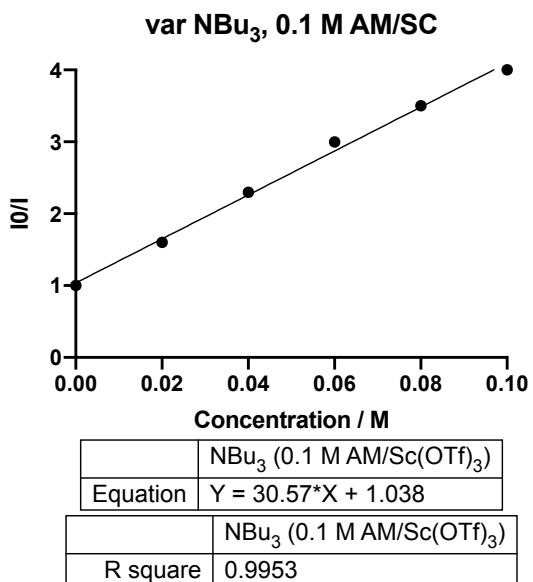
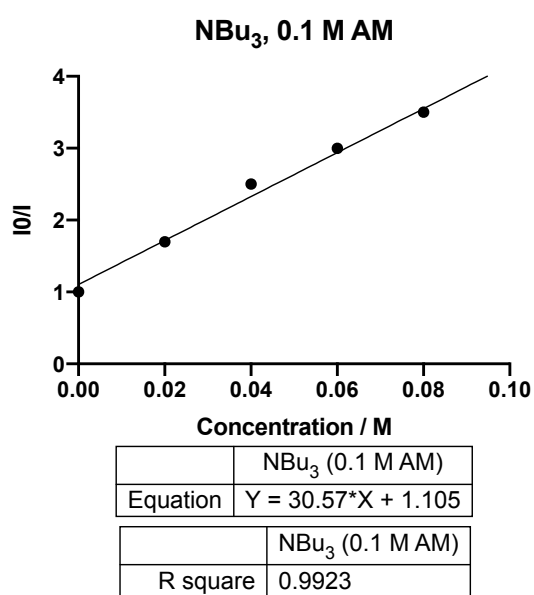
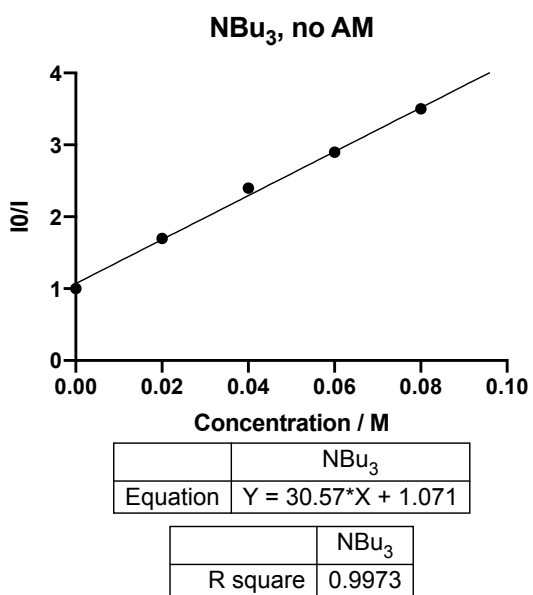
	Sc(OTf) ₃ (0.1 M AM)
Equation	Y = 11.86*X + 0.9905
	Sc(OTf) ₃ (0.1 M AM)
R square	0.9958

Stern-Volmer Fluorescence Quenching: NBU₃ Quenching with and without 1a and Sc(OTf)₃

Vial	1	2	3	Average	I0/I	[nBu ₃] mol/L	var NBU ₃ , 0.1 M 1a, No Sc(OTf) ₃
0	504	508	497	503.0	1.0	0	
1	305	303	307	305.0	1.6	0.02	
2	211	206	210	209.0	2.4	0.04	
3	166	180	172	172.7	2.9	0.06	
4	149	152	149	150.0	3.4	0.08	
5	130	121	124	125.0	4.0	0.1	

Vial	1	2	3	Average	I0/I	[nBu ₃] mol/L	var NBU ₃ , No 1a, No Sc(OTf) ₃
0	498	507	505	503.3	1.0	0	
1	314	317	313	314.7	1.6	0.02	
2	217	207	208	210.7	2.4	0.04	
3	175	168	171	171.3	2.9	0.06	
4	146	142	147	145.0	3.5	0.08	
5	135	122	124	127.0	4.0	0.1	

Vial	1	2	3	Average	I0/I	[nBu ₃] mol/L	var NBU ₃ , 0.1 M Sc(OTf) ₃ , 0.1 M 1a
0	510	501	502	504.3	1.0	0	
1	308	312	305	308.3	1.6	0.02	
2	220	220	212	217.3	2.3	0.04	
3	178	171	161	170.0	3.0	0.06	
4	140	145	143	142.7	3.5	0.08	
5	134	117	119	123.3	4.1	0.1	



Stern-Volmer Fluorescence Quenching: HEH Quenching with and without 1a and varying conc. of Sc(Otf)₃

Vial	1	2	3	Average	I0/I	[HEH] mol/L	var HEH, No Sc(Otf) ₃ , No 1a
0	510	511	511	510.7	1.0	0	
1	410	405	404	406.3	1.3	0.02	
2	312	316	308	312.0	1.6	0.04	
3	252	246	257	251.7	2.0	0.06	
4	208	221	215	214.7	2.4	0.08	
5	172	173	170	171.7	3.0	0.1	

Vial	1	2	3	Average	I0/I	[HEH] mol/L	var HEH, No Sc(Otf) ₃ , 0.1 M 1a
0	515	502	508	507.3	1.0	0	
1	409	402	407	404.3	1.3	0.02	
2	300	308	309	304.3	1.7	0.04	
3	252	251	252	246.7	2.1	0.06	
4	212	209	211	211.3	2.4	0.08	
5	168	180	174	176.3	2.9	0.1	

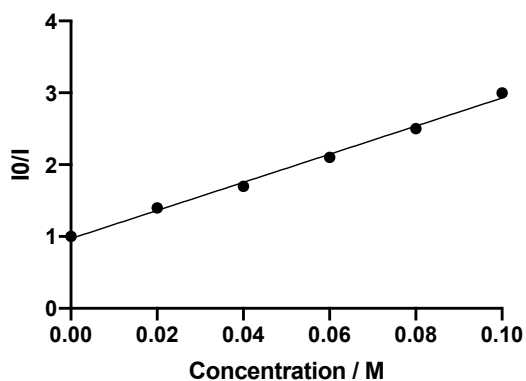
Vial	1	2	3	Average	I0/I	[HEH] mol/L	var HEH, 0.1 M 1a, 10 mol % Sc(Otf) ₃
0	519	514	520	517.7	1.0	0	
1	418	419	410	415.7	1.2	0.02	
2	293	295	292	293.3	1.8	0.04	
3	242	246	246	244.7	2.1	0.06	
4	192	190	191	191.0	2.7	0.08	
5	174	173	174	173.7	3.0	0.1	

Vial	1	2	3	Average	I0/I	[HEH] mol/L	var HEH, 0.1 M 1a, 25 mol % Sc(Otf) ₃
0	517	519	517	517.7	1.0	0	
1	414	402	417	411.0	1.3	0.02	
2	292	294	299	295.0	1.8	0.04	
3	244	249	243	245.3	2.1	0.06	
4	201	205	192	199.3	2.6	0.08	
5	169	170	166	168.3	3.1	0.1	

Vial	1	2	3	Average	I0/I	[HEH] mol/L	var HEH, 0.1 M 1a,, 50 mol % Sc(Otf) ₃
0	512	517	520	516.3	1.0	0	
1	408	418	405	410.3	1.3	0.02	
2	306	290	292	296.0	1.7	0.04	
3	255	240	248	247.7	2.1	0.06	
4	191	204	196	197.0	2.6	0.08	
5	168	171	170	169.7	3.0	0.1	

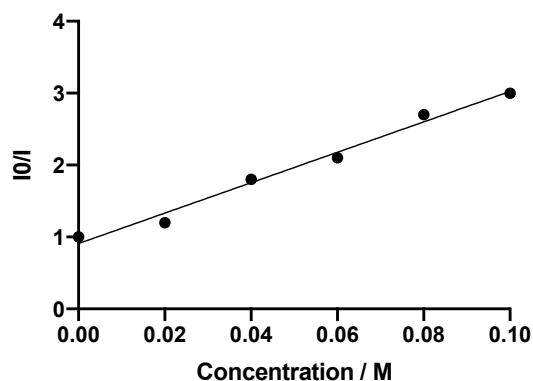
Vial	1	2	3	Average	I0/I	[HEH] mol/L	var HEH, 0.1 M 1a, 0.1 M Sc(Otf) ₃
0	512	514	513	507.3	1.0	0	
1	418	406	412	404.7	1.3	0.02	
2	308	298	295	304.7	1.7	0.04	
3	248	255	252	249.0	2.0	0.06	
4	205	205	190	210.3	2.4	0.08	
5	169	173	175	172.0	2.9	0.1	

HEH, 0.1 M AM, No Sc(OTf)₃



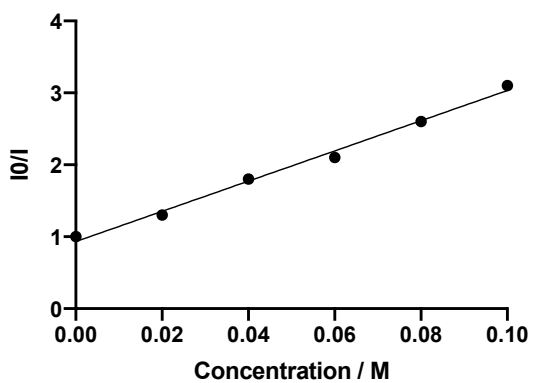
	HEH (0.1 M AM)
Equation	$Y = 19.57 * X + 0.9714$
	HEH (0.1 M AM)
R square	0.9949

var HEH, 0.1 M AM, 10 mol % Sc(OTf)₃



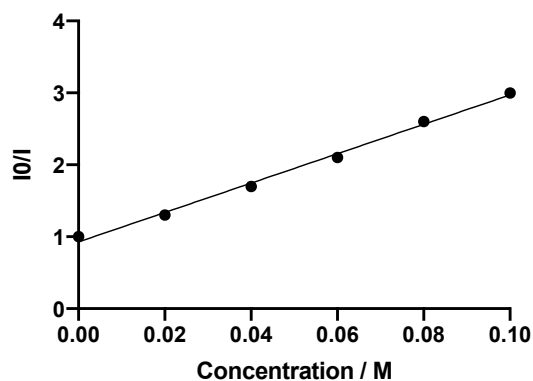
	HEH (0.1 M AM, 10 mol % Sc(OTf) ₃)
Equation	$Y = 21.14 * X + 0.9095$
	HEH (0.1 M AM, 10 mol % Sc(OTf) ₃)
R square	0.9861

var HEH, 0.1 M AM, 25 mol % Sc(OTf)₃

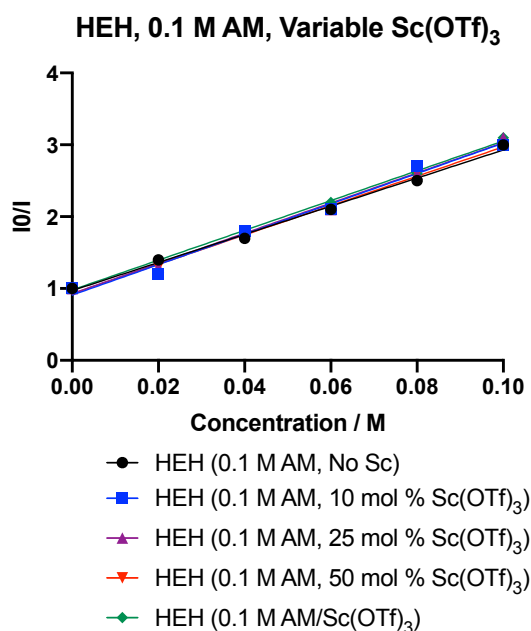
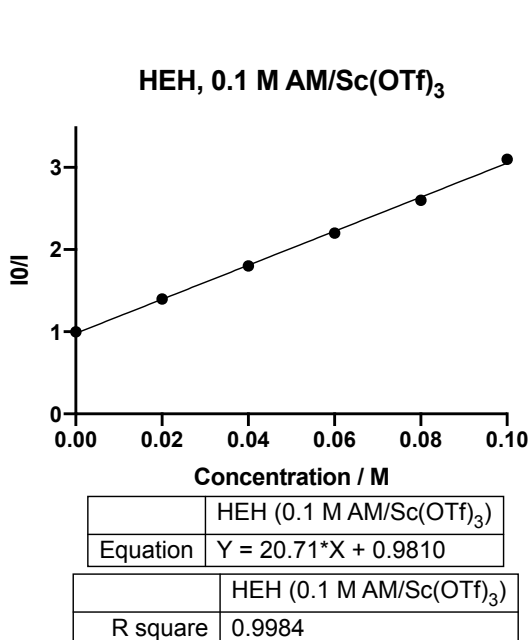


	HEH (0.1 M AM, 25 mol % Sc(OTf) ₃)
Equation	$Y = 21.00 * X + 0.9333$
	HEH (0.1 M AM, 25 mol % Sc(OTf) ₃)
R square	0.9931

var HEH, 0.1 M AM, 50 mol % Sc(OTf)₃



	HEH (0.1 M AM, 50 mol % Sc(OTf) ₃)
Equation	$Y = 20.43 * X + 0.9286$
	HEH (0.1 M AM, 50 mol % Sc(OTf) ₃)
R square	0.9953



Procedure for Determination of Quantum Yield

The photon flux of the fluorimeter was determined using a ferrioxalate Hatchard – Parker actinometer as described by Yoon et al.³ Based on the average of three experiments, the photon flux at 420 nm (10 nm slit width) was determined to be 5.27712E-09 einsteins s⁻¹. UV/Vis absorbance spectra of 3DPAFIPN in MeCN (0.1 M) indicated that essentially all light was absorbed at 420 nm ($f = 0.99148$). A screw-top quartz cuvette with Teflon septa was charged with **1a** (0.2 mmol, 1 equiv), 3DPAFIPN (1 mol %), scandium triflate (10 mol %), HEH (1.5 equiv), and a small Teflon coated magnetic stirbar in a glovebox. The cuvette was sealed and removed from glovebox. The cuvette was then capped with a PTFE stopper, and 2 mL sparged MeCN added. The solution was stirred until homogenous. The sample was placed in the fluorimeter and irradiated ($\lambda = 420$ nm, slit width= 10.0 nm) for 5400 s (3 hours). ¹H NMR based on a trimethoxybenzene standard determined the yield of product formed was 30%. The average quantum yield of the two experiments was determined to be 1.0.

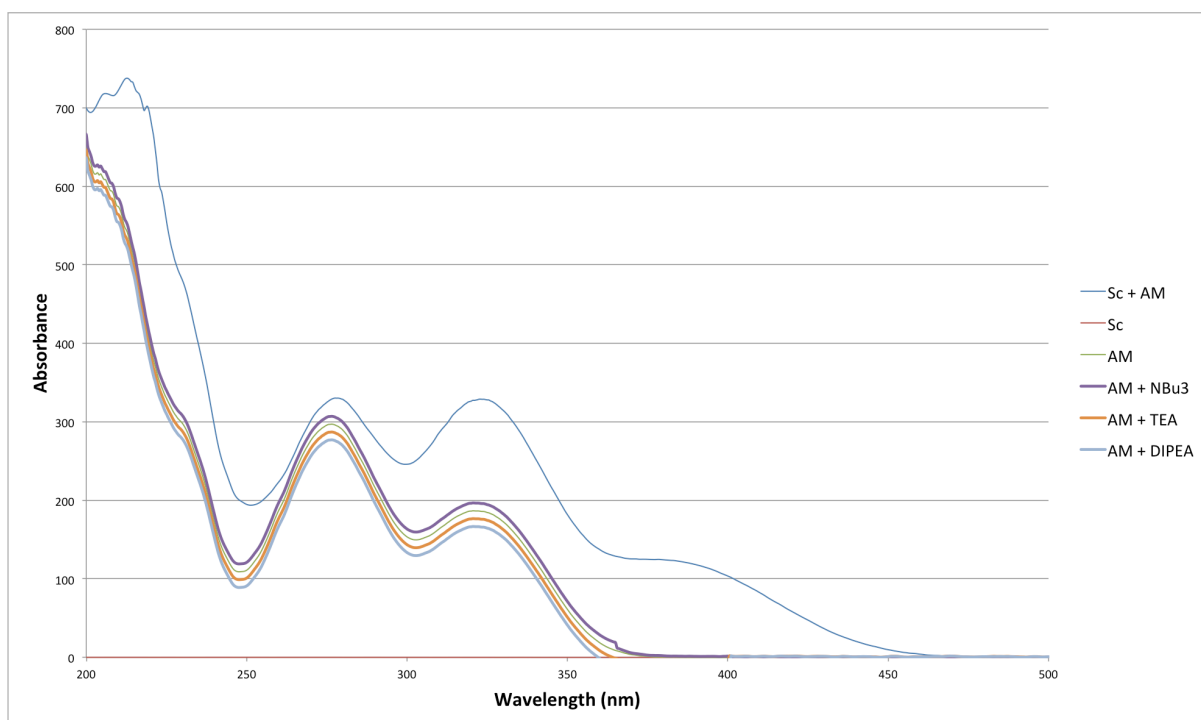
Procedure for Light/Dark Experiment

To verify the necessity of light to maintain the conversion of **1a** to **2a**, a “light/dark” experiment was performed. A J-Young NMR tube was charged with **1a** (0.2 mmol, 1 equiv), 3DPAFIPN (1 mol %), scandium triflate (10 mol %), and HEH (1.5 equiv) in a glovebox. Upon removal from the glovebox, the reaction mixture was irradiated with 456 nm Kessil blue LEDs for periods of 1 hour, followed by 2 hours of no irradiation (3 cycles of 3 hours, 9 hours total). Notably, the reaction progressed steadily during periods of irradiation, while no conversion was observed

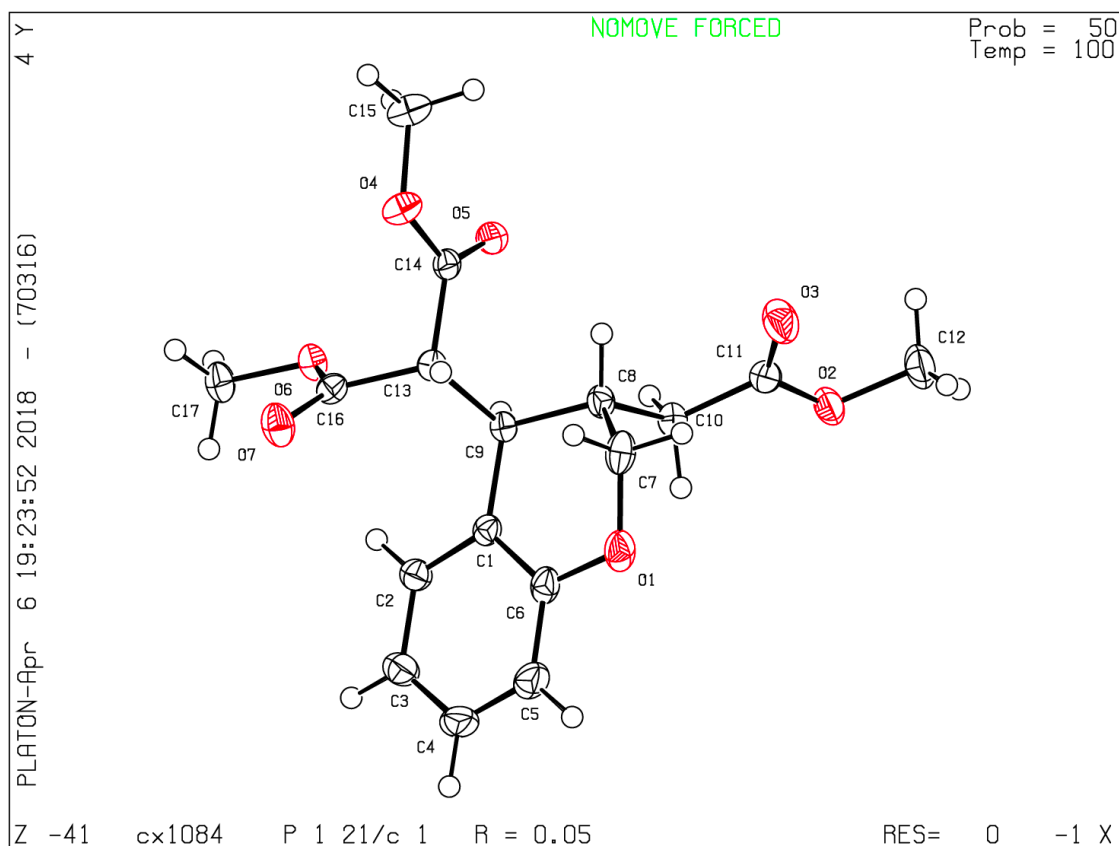
during periods without irradiation. This is indicative that propagation is likely not a operational mechanistic process over the course of the reaction.

Procedure for UV-Vis Experiments

A 1 dram vial equipped with a rubber septum and a stir bar was charged with **1a** (0.1 mmol, 1 equiv), scandium triflate (0 or 100 mol %), and tertiary amine (0 or 150 mol %) in a glovebox. Upon removal from the glovebox, the reaction mixture was stirred for 2 hours, followed by measurement of the UV-Vis spectra using a Thermo Fisher Nanodrop One Spectrophotometer.

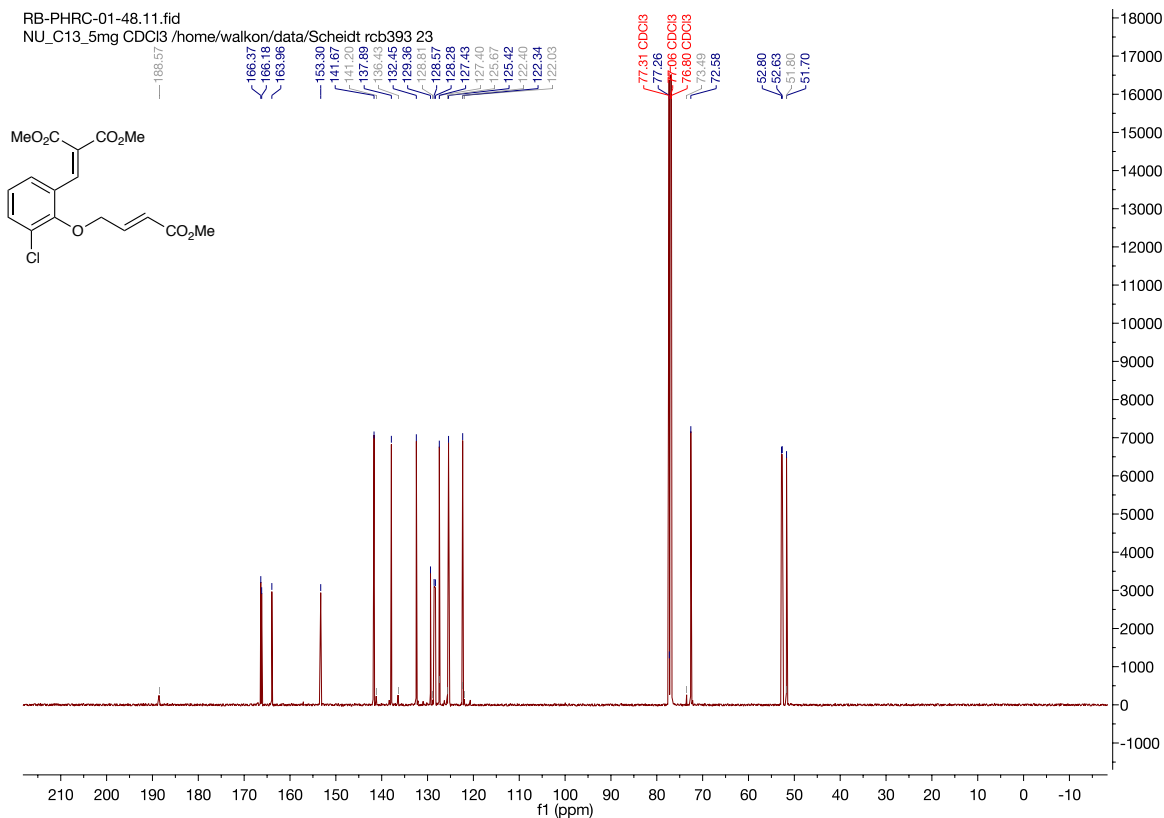
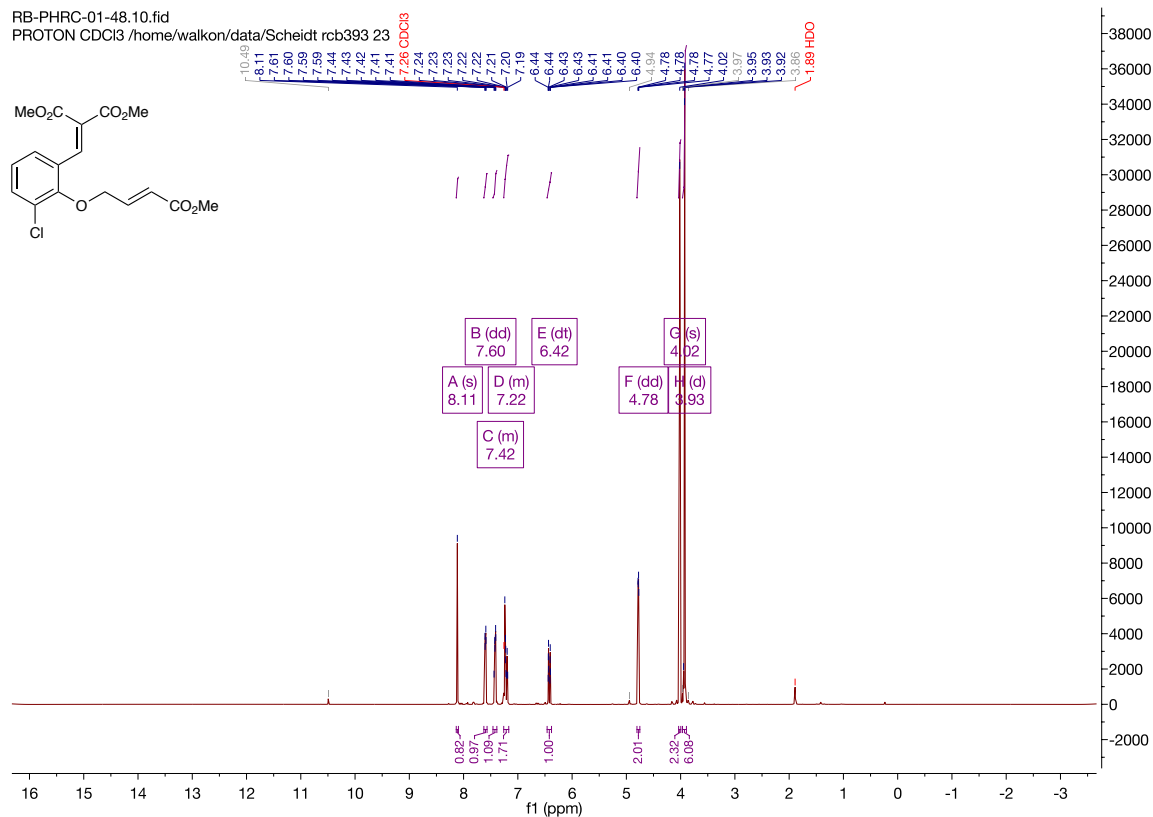


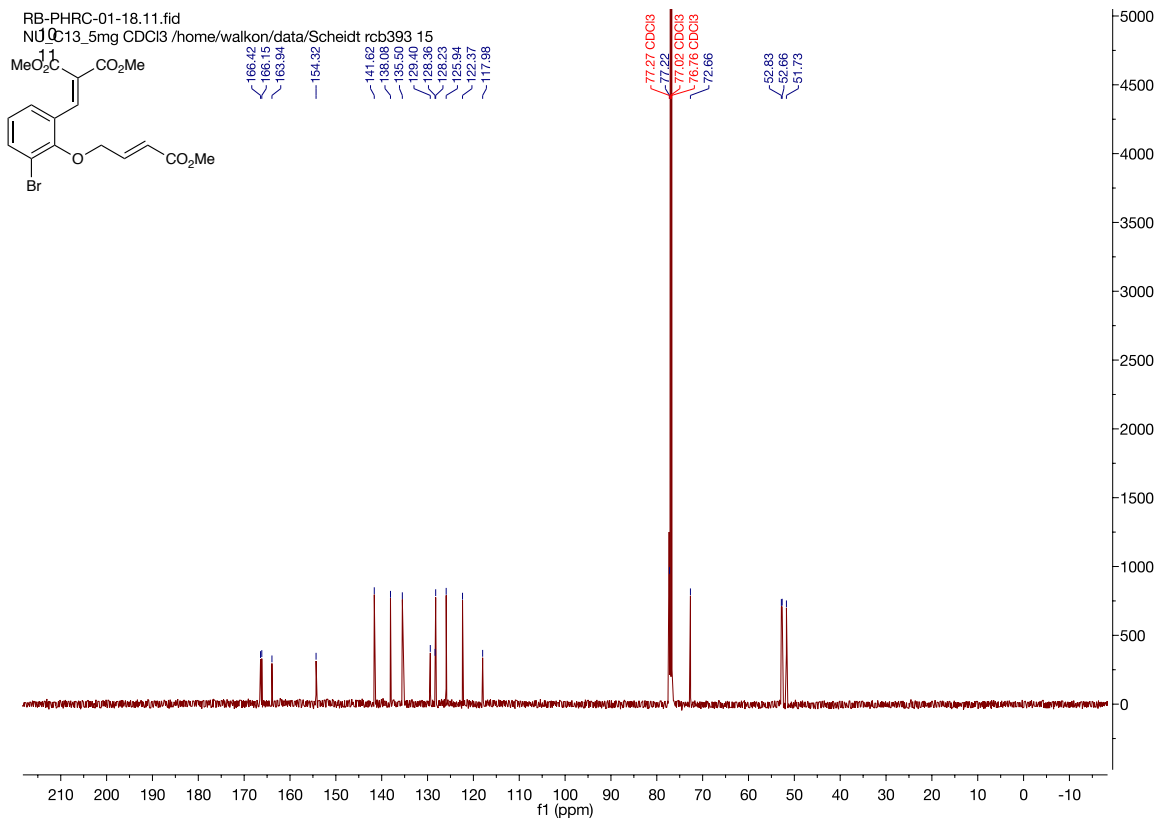
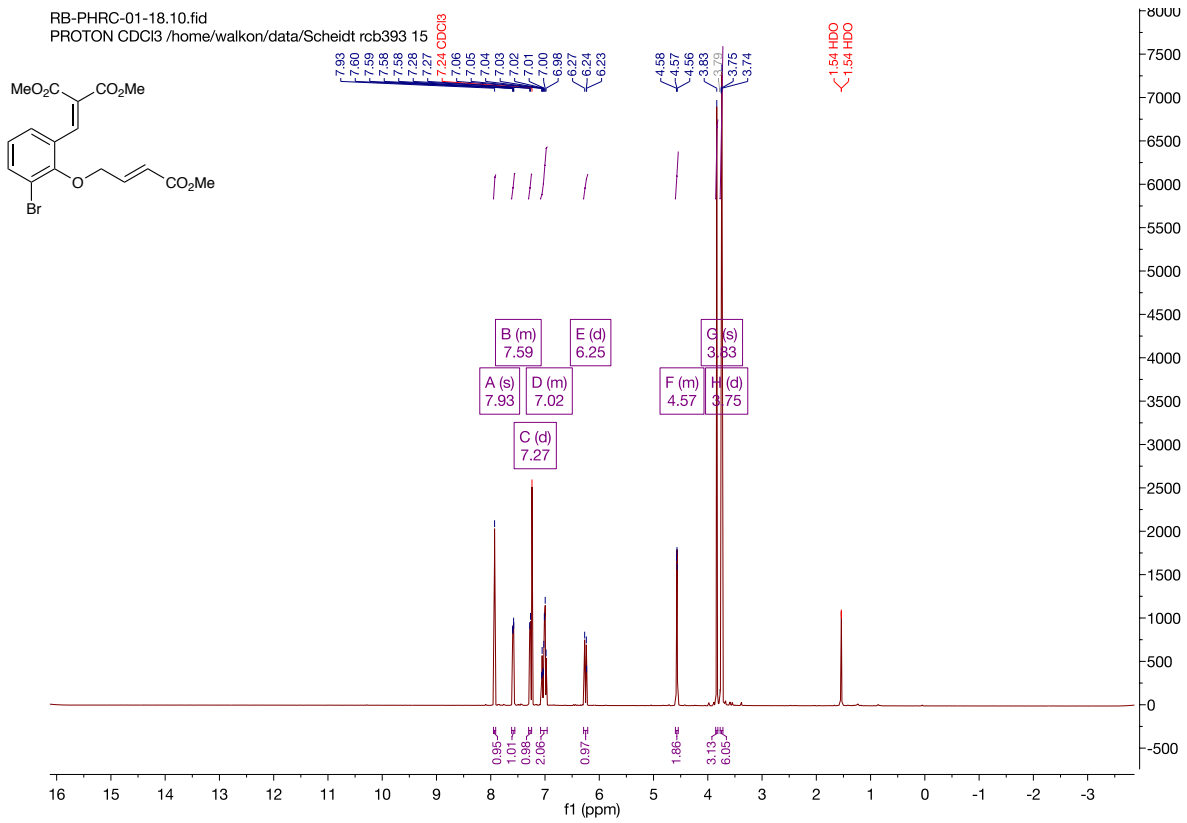
ORTEPS of Crystallographic Structure



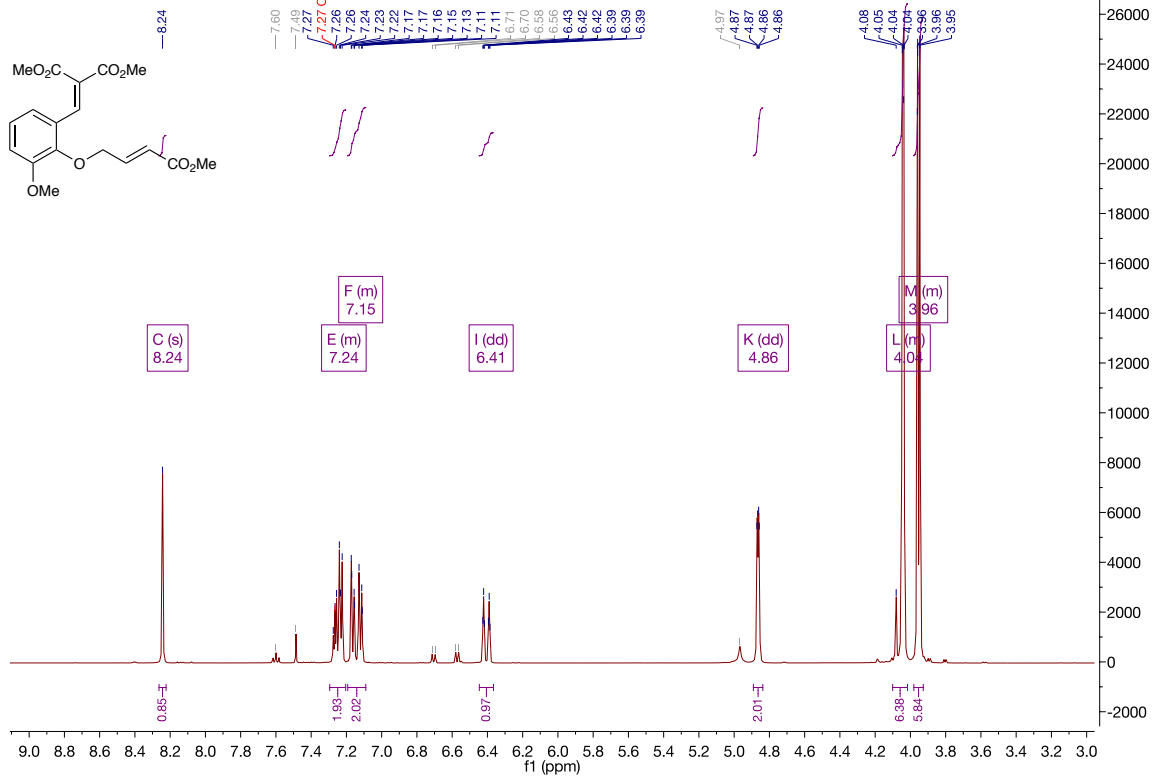
A single crystal of *trans*-2a was grown by evaporative diffusion in dichloromethane with hexanes as the anti-solvent at room temperature. This crystal structure was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1835356. Further information can be found in the CIF file.

NMR Spectra for Cyclization Starting Materials

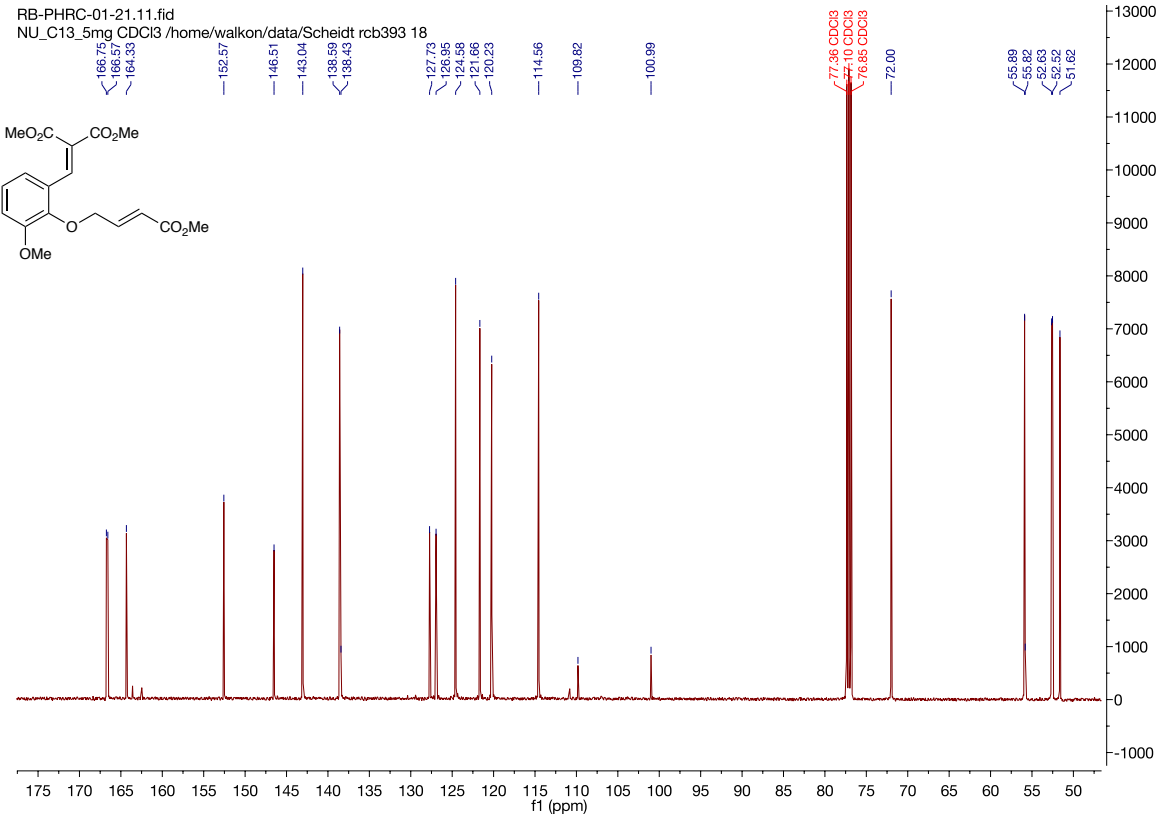




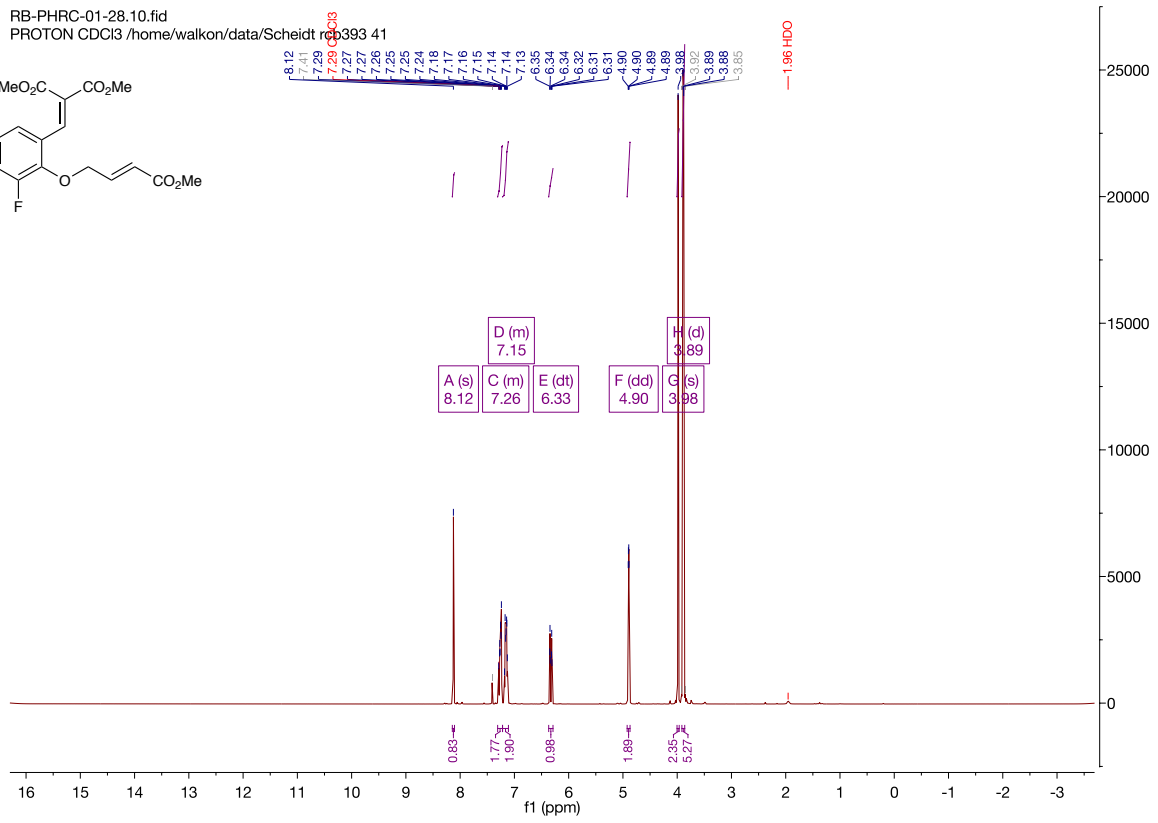
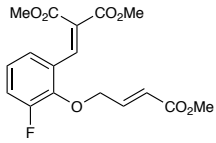
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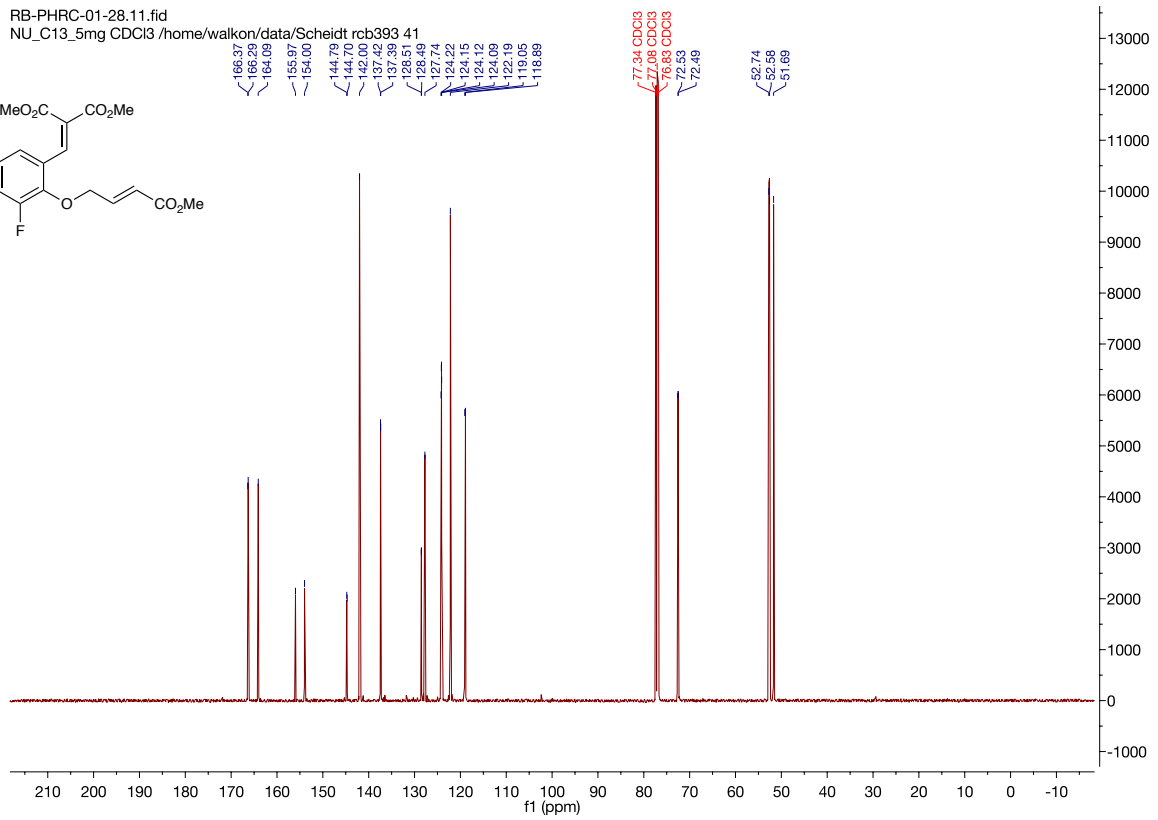
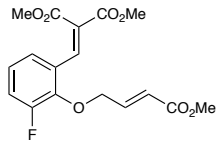
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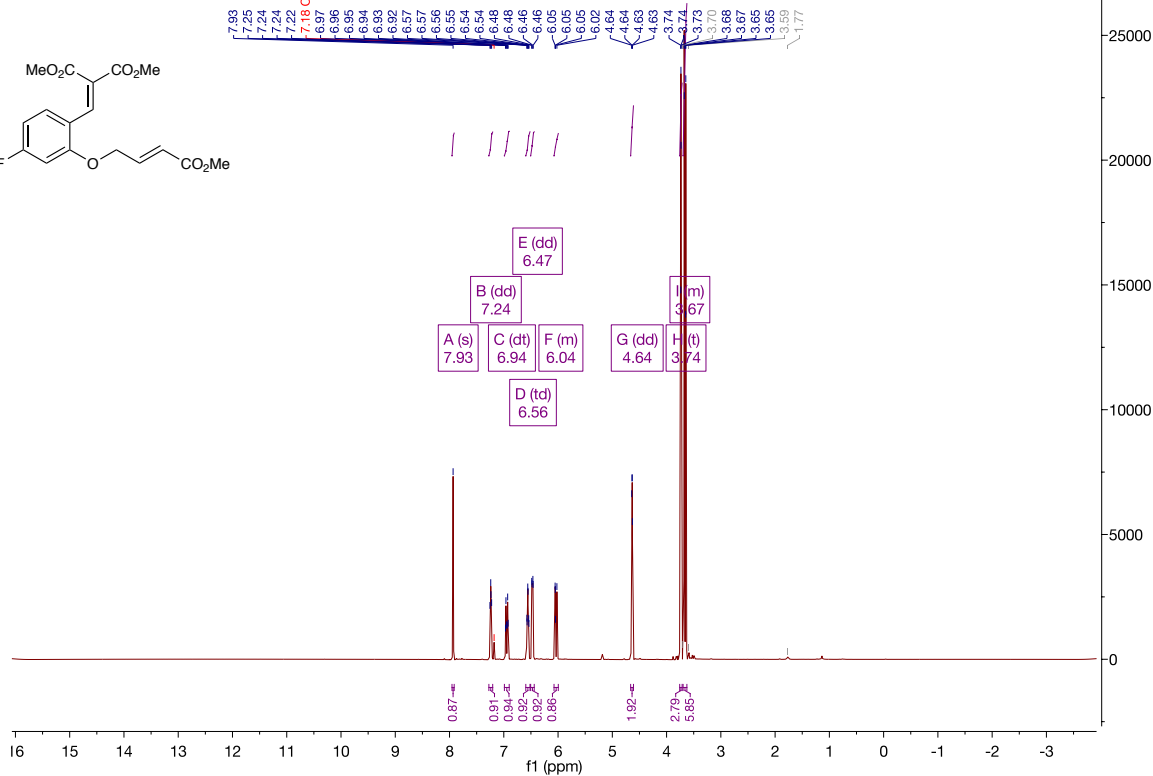
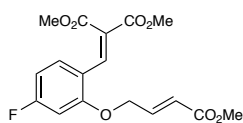
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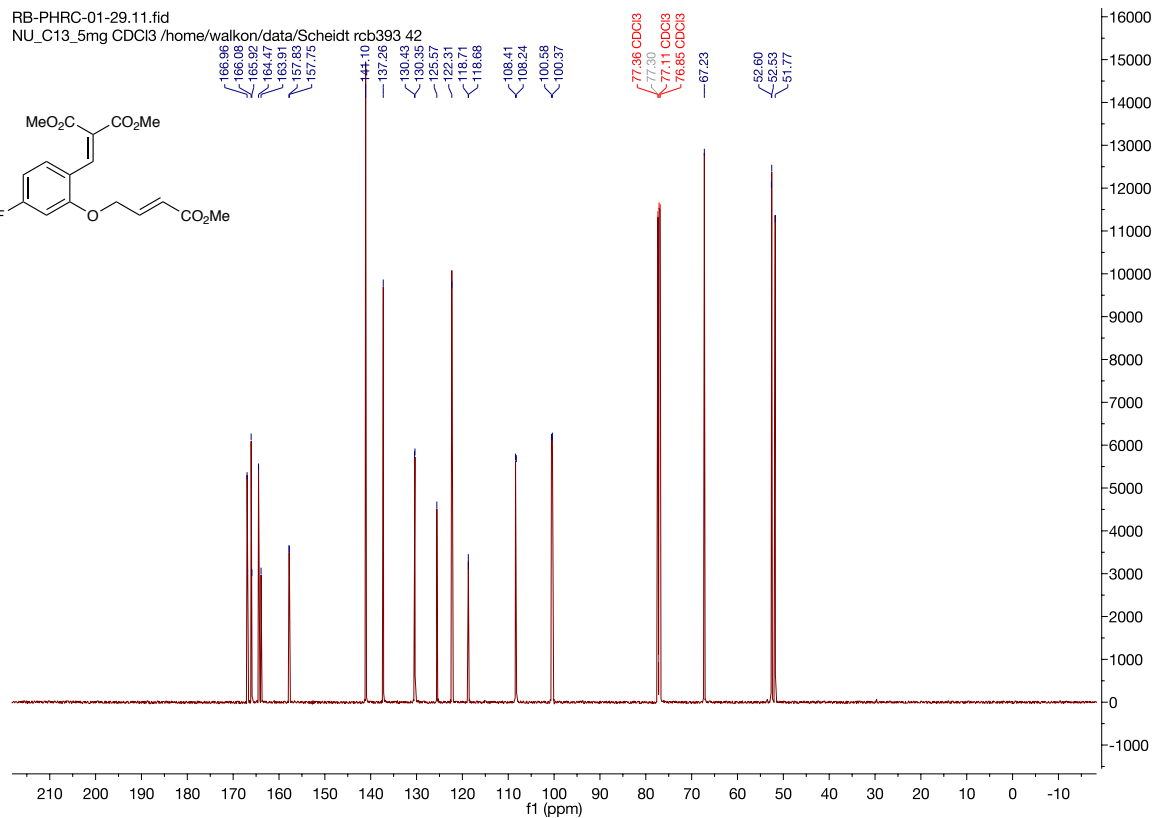
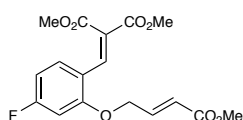
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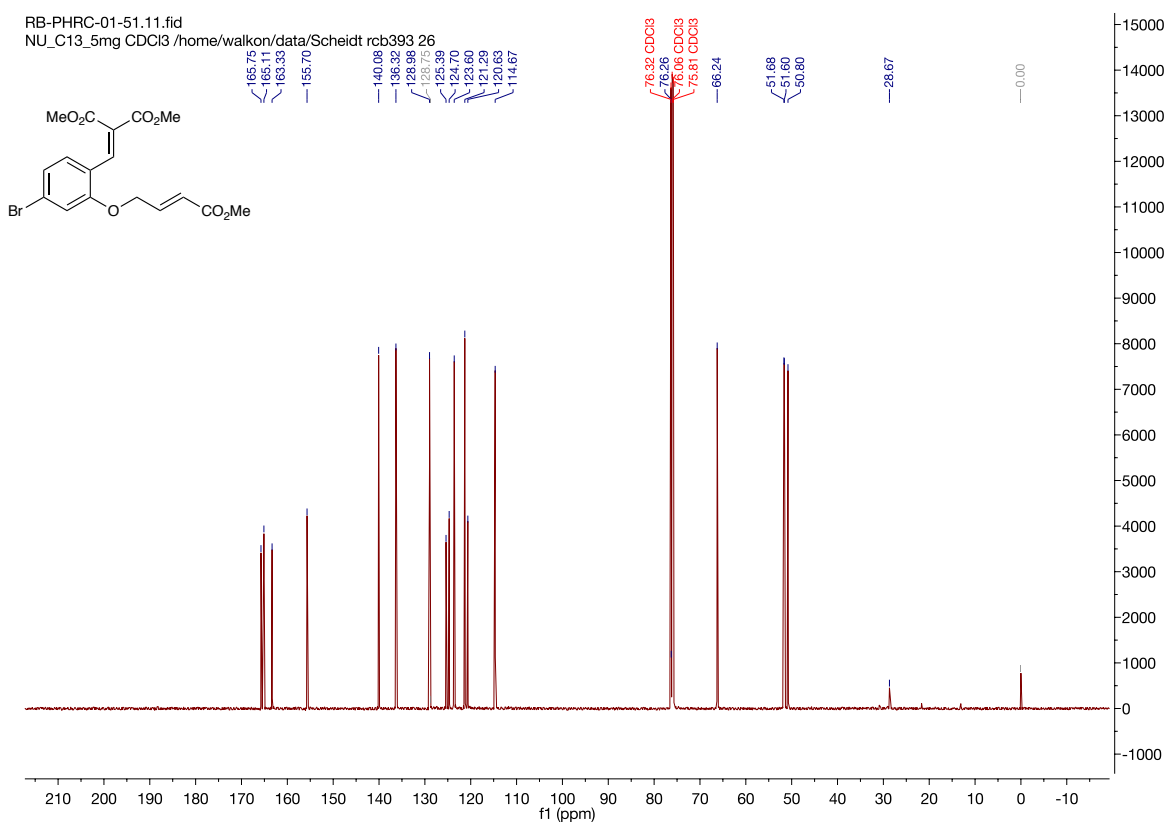
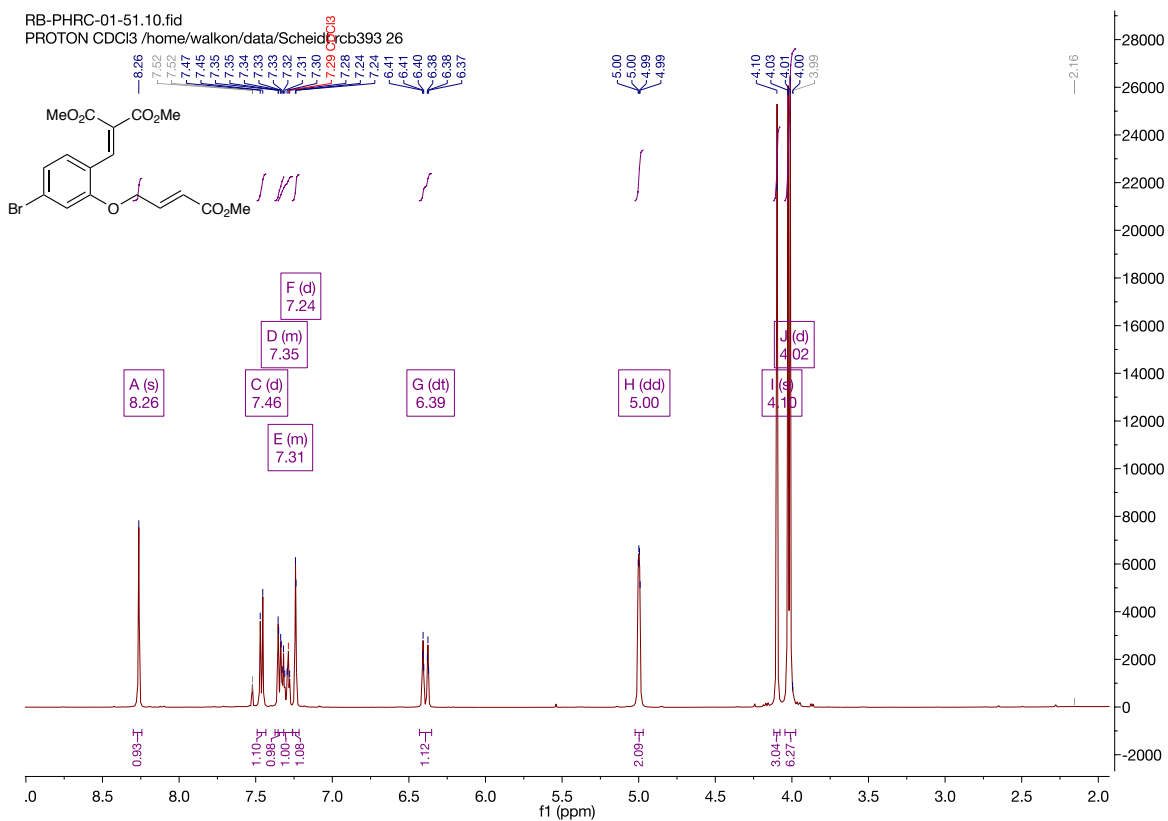


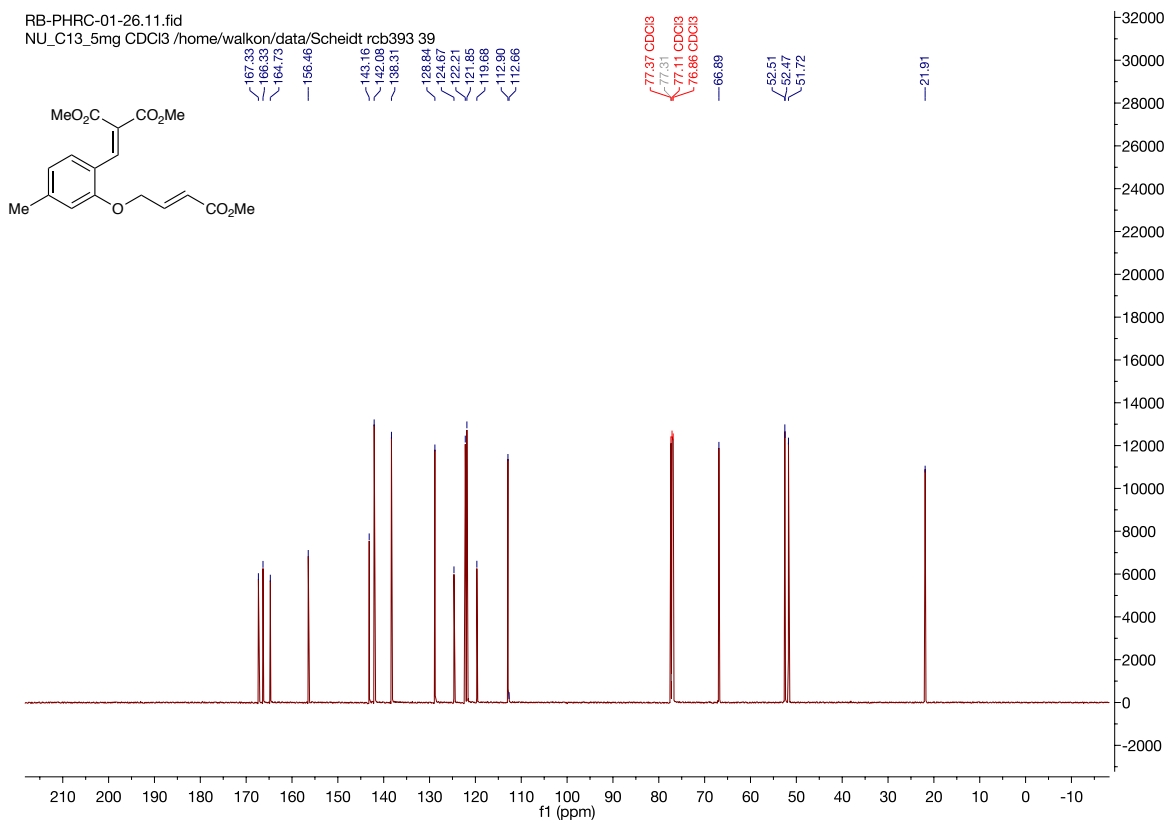
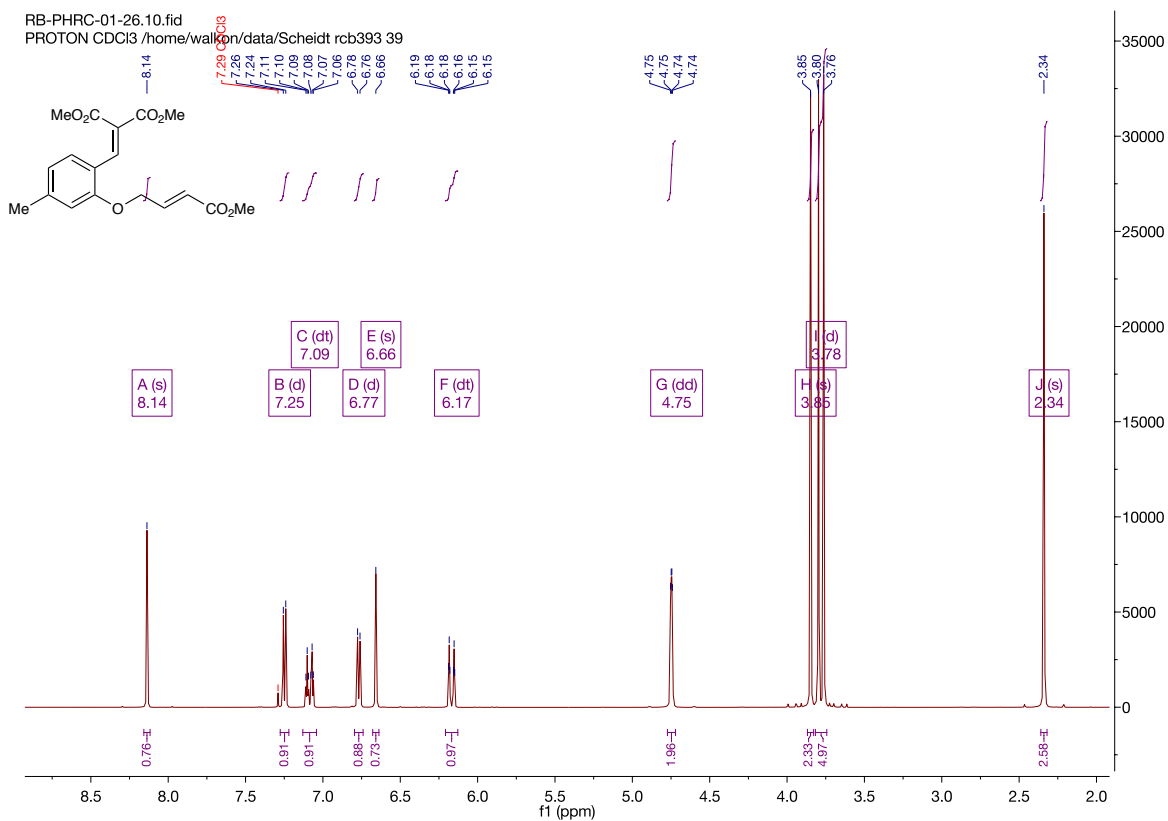
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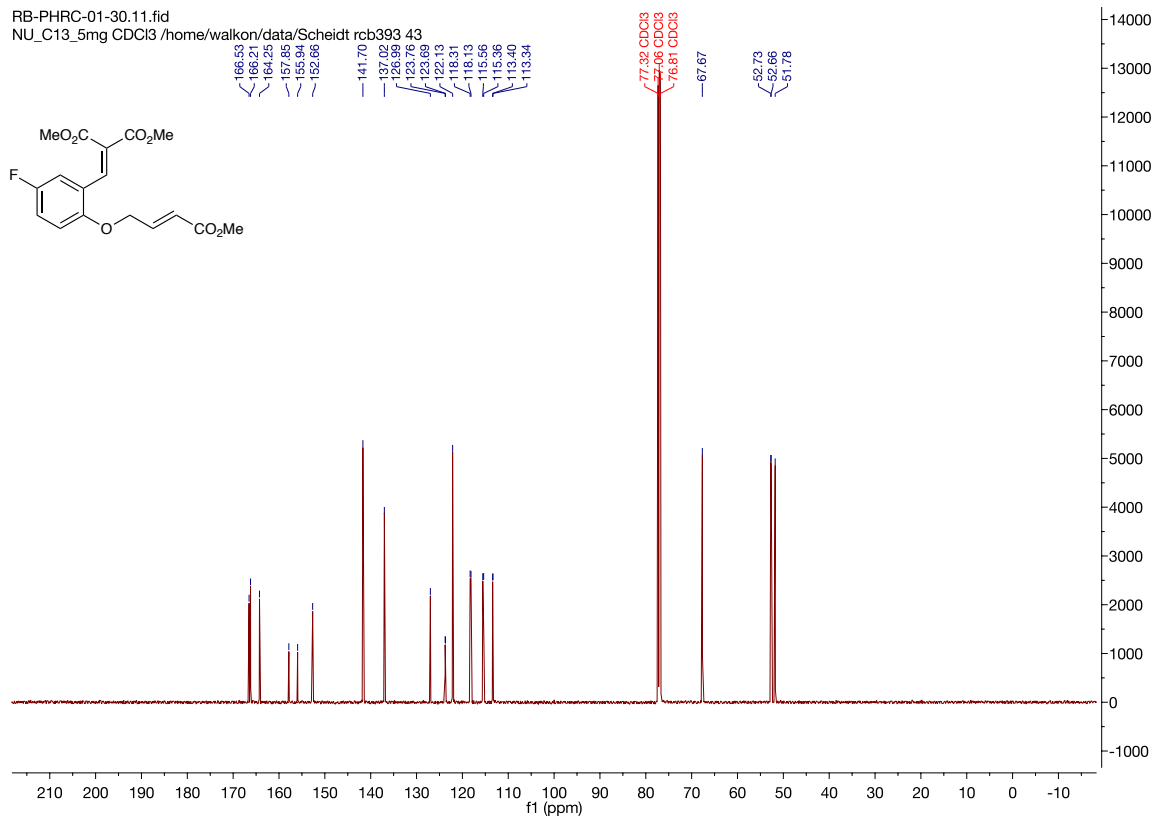
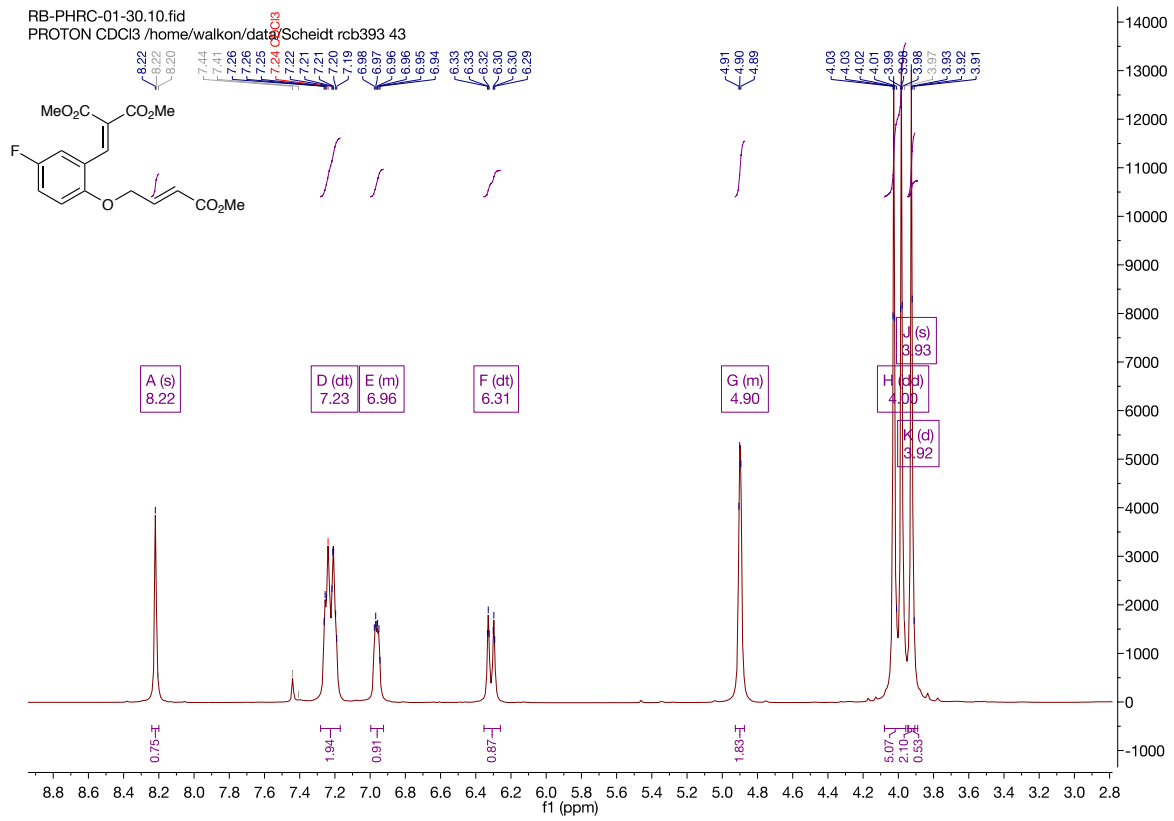


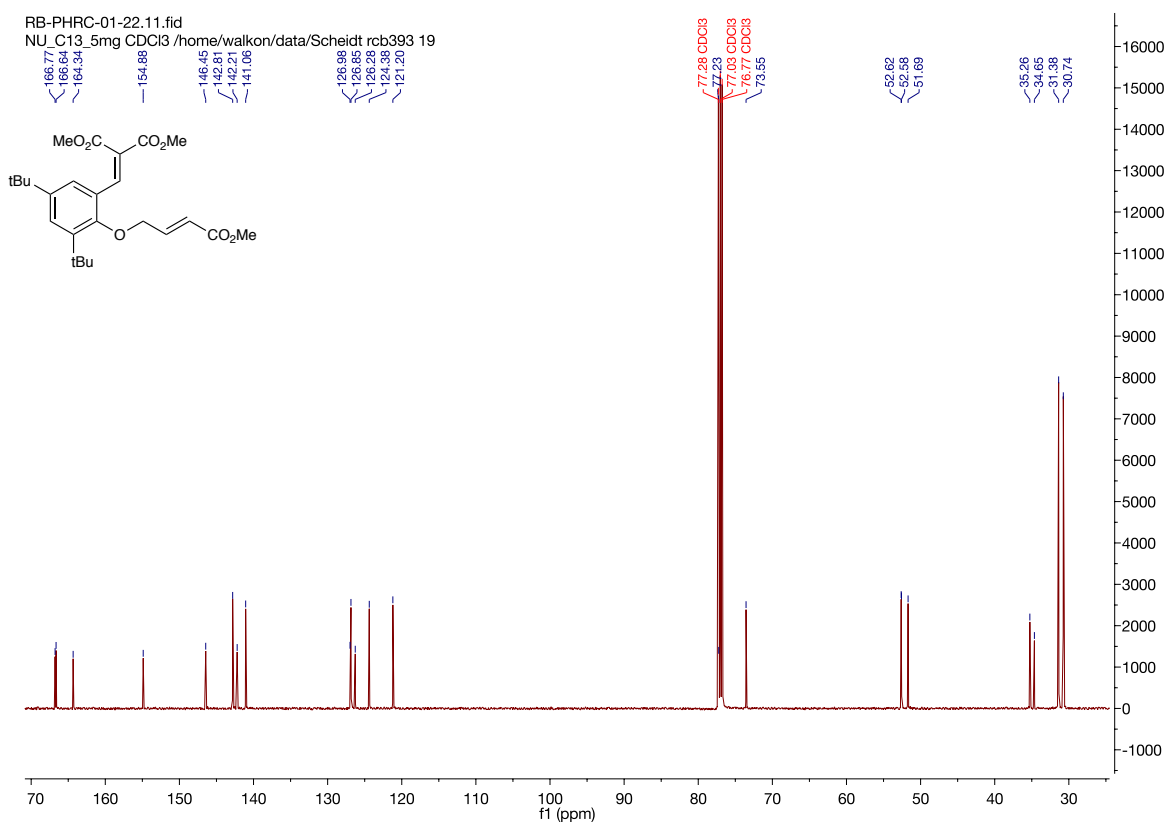
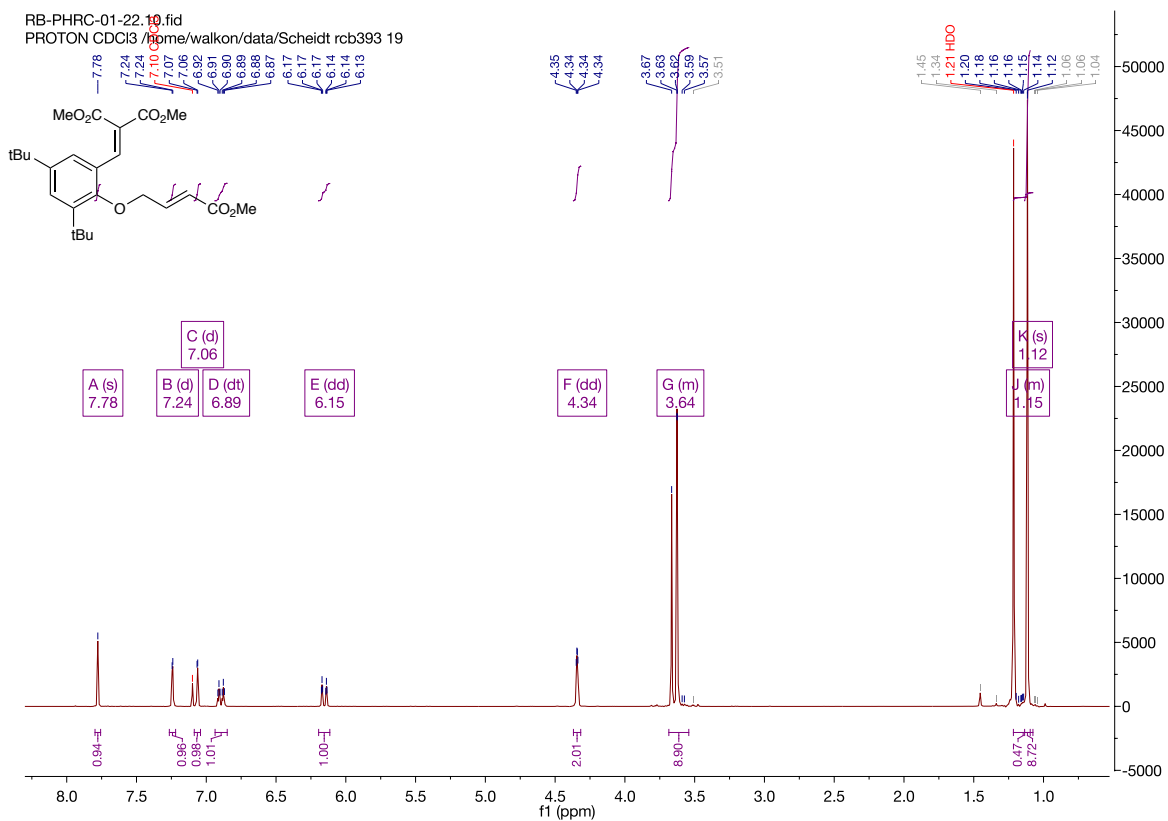
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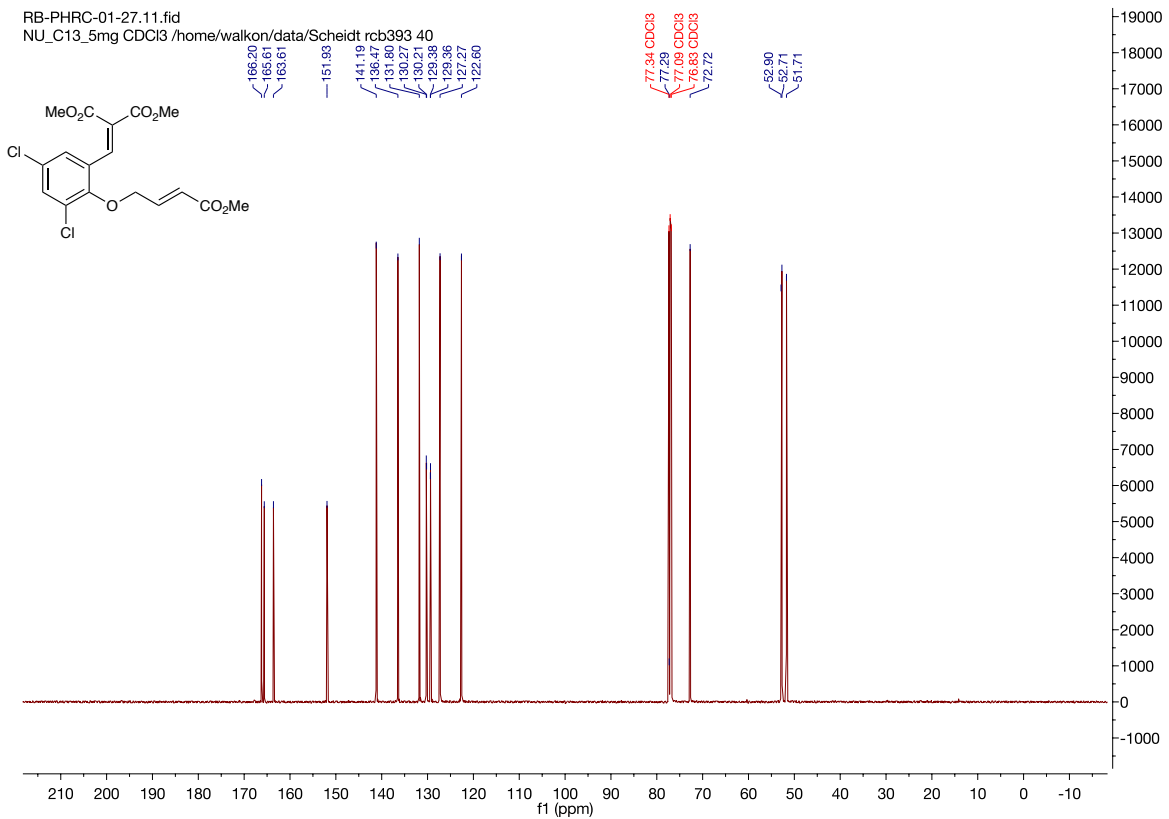
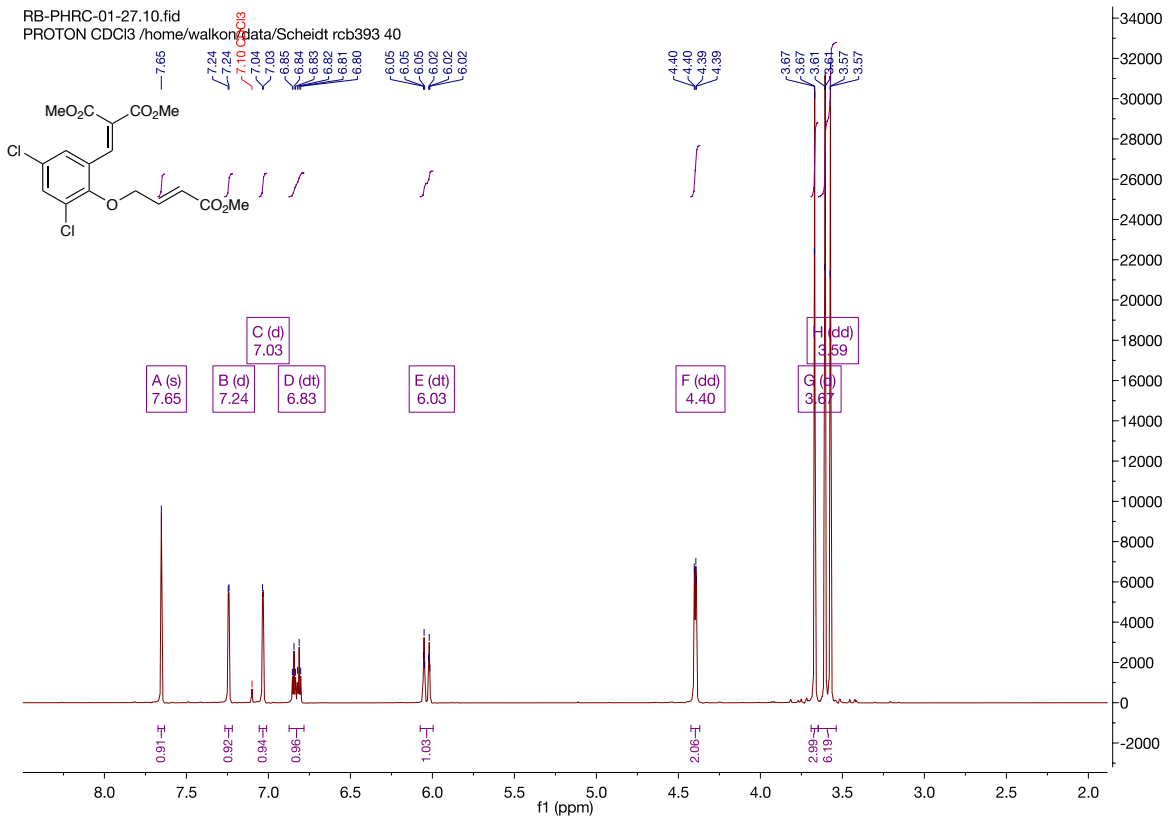


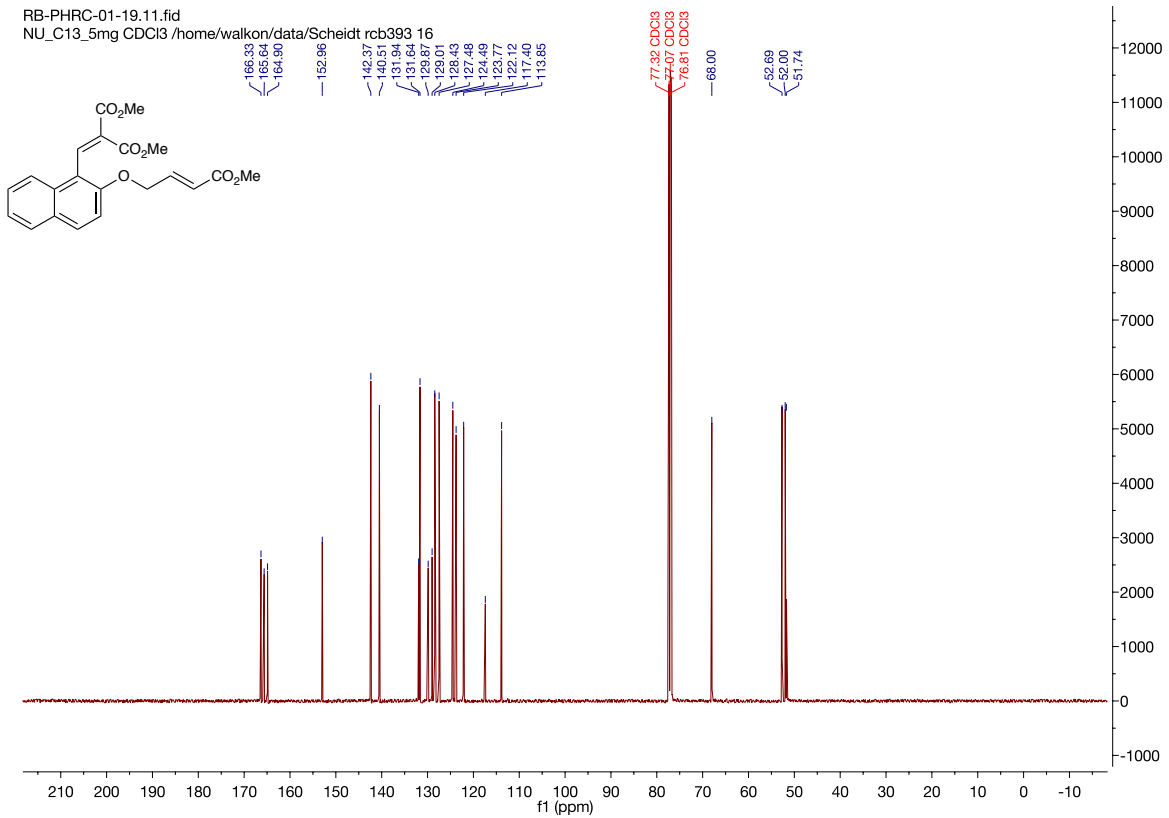
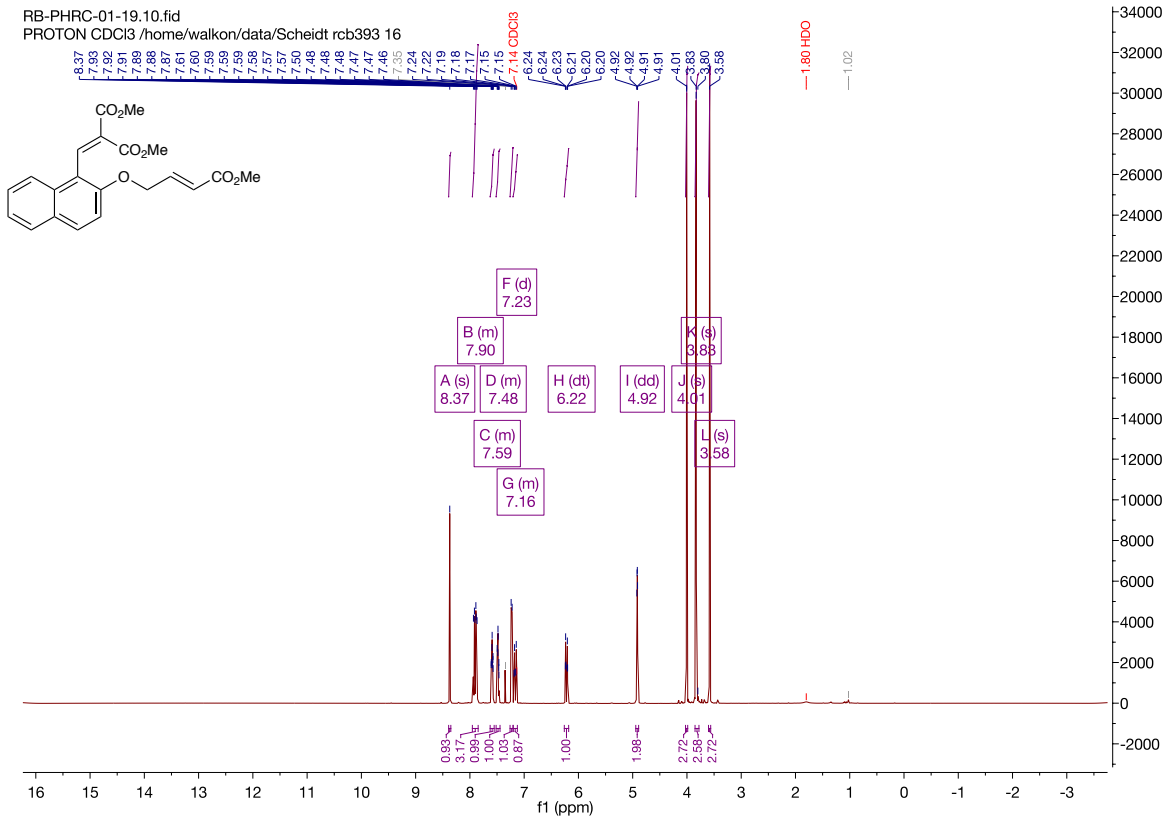


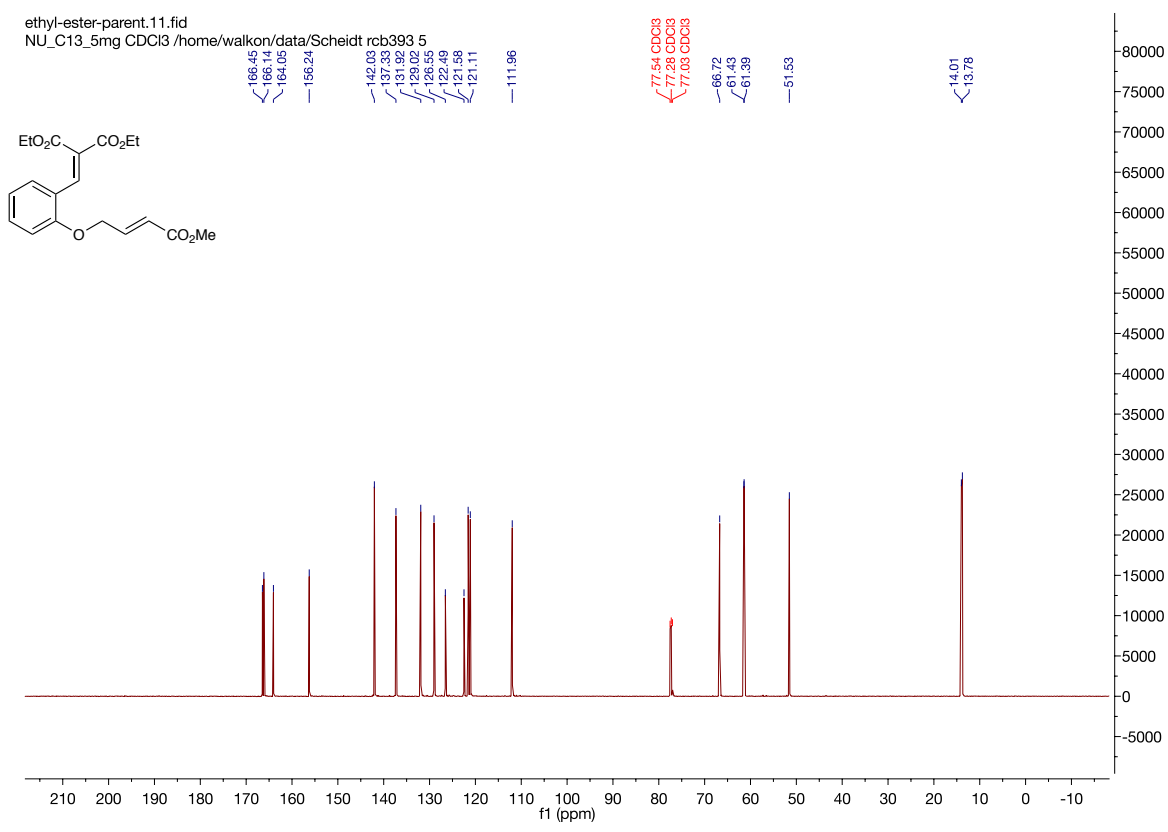
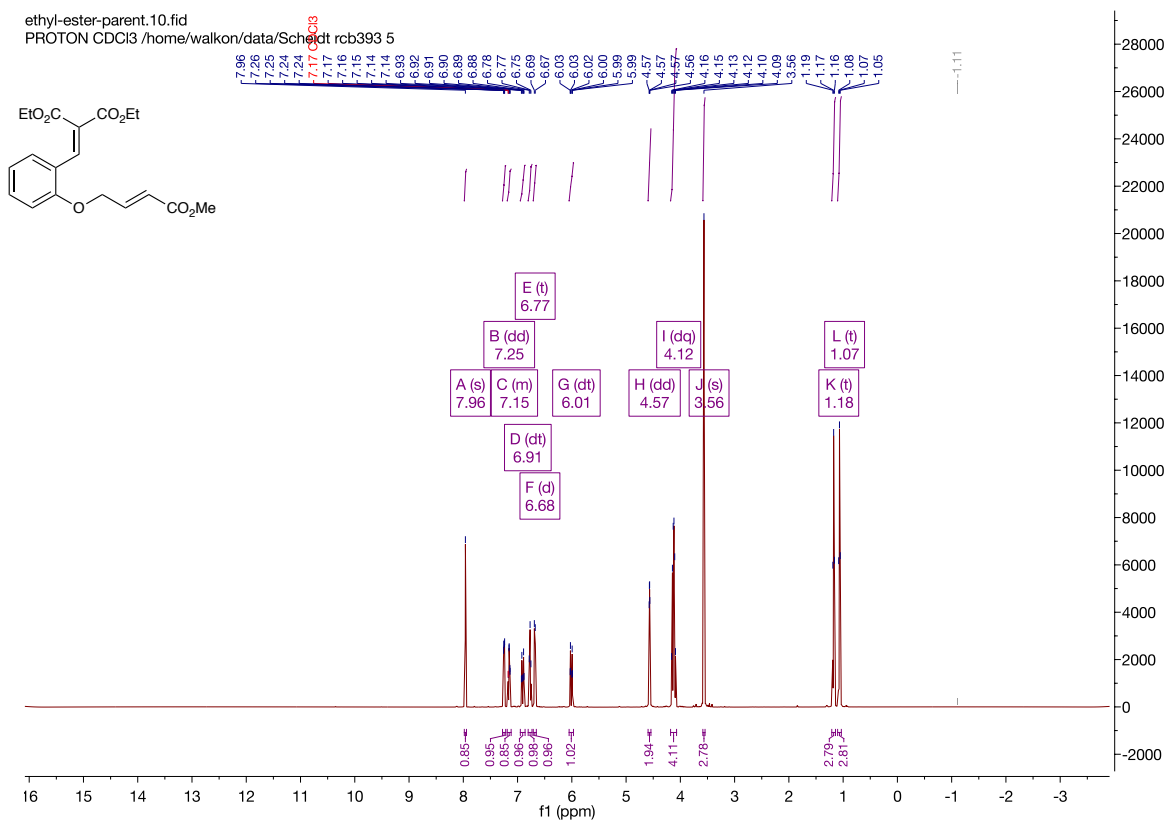


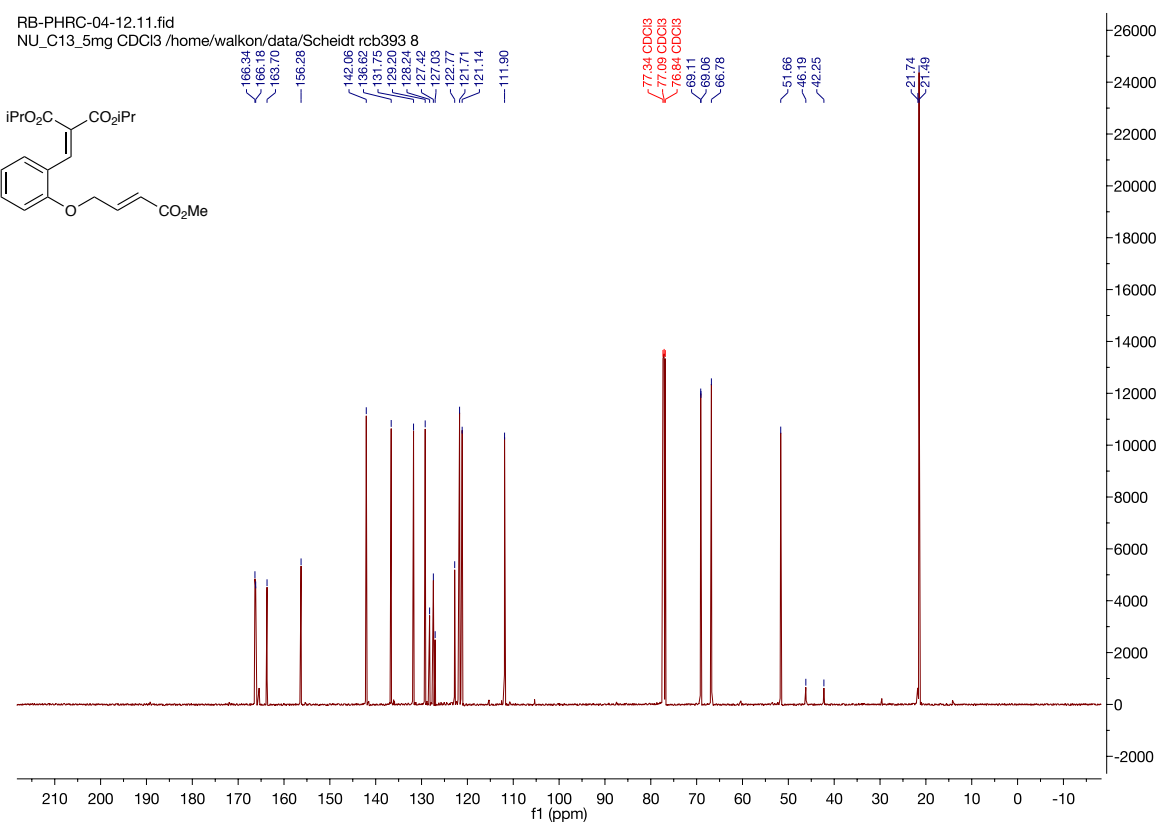
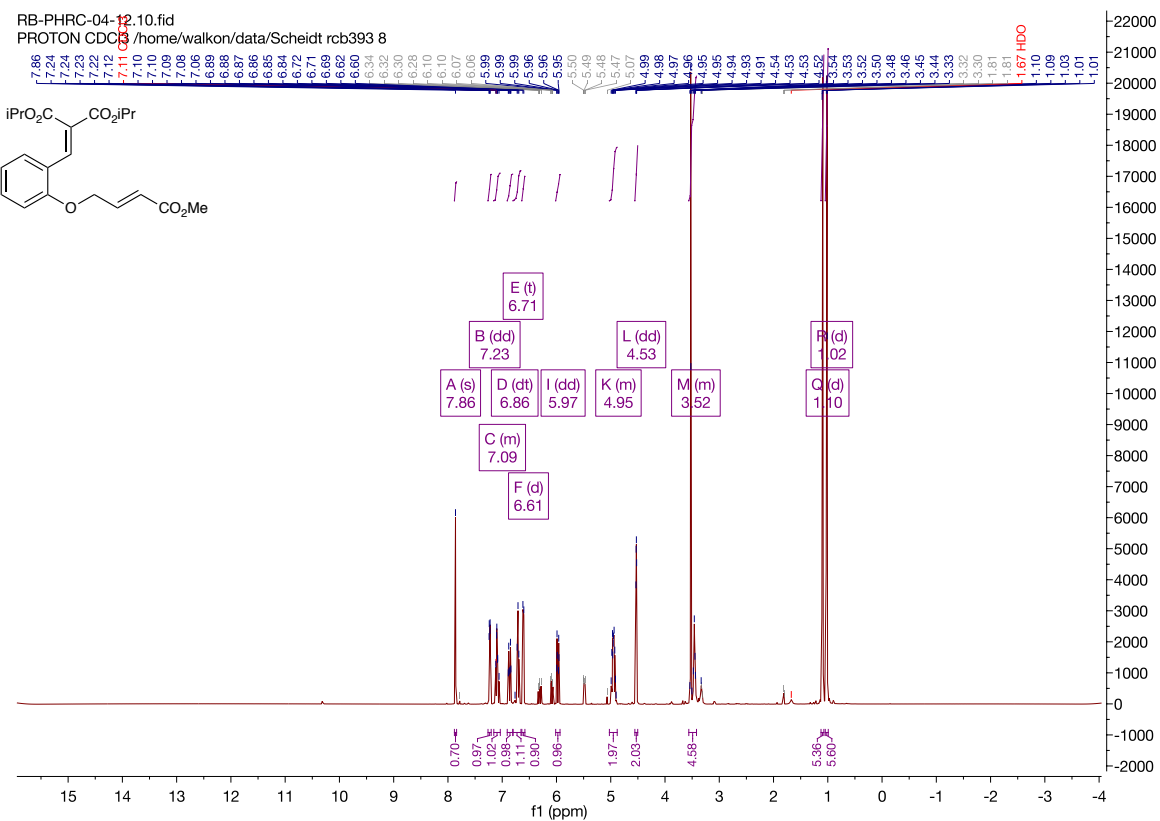


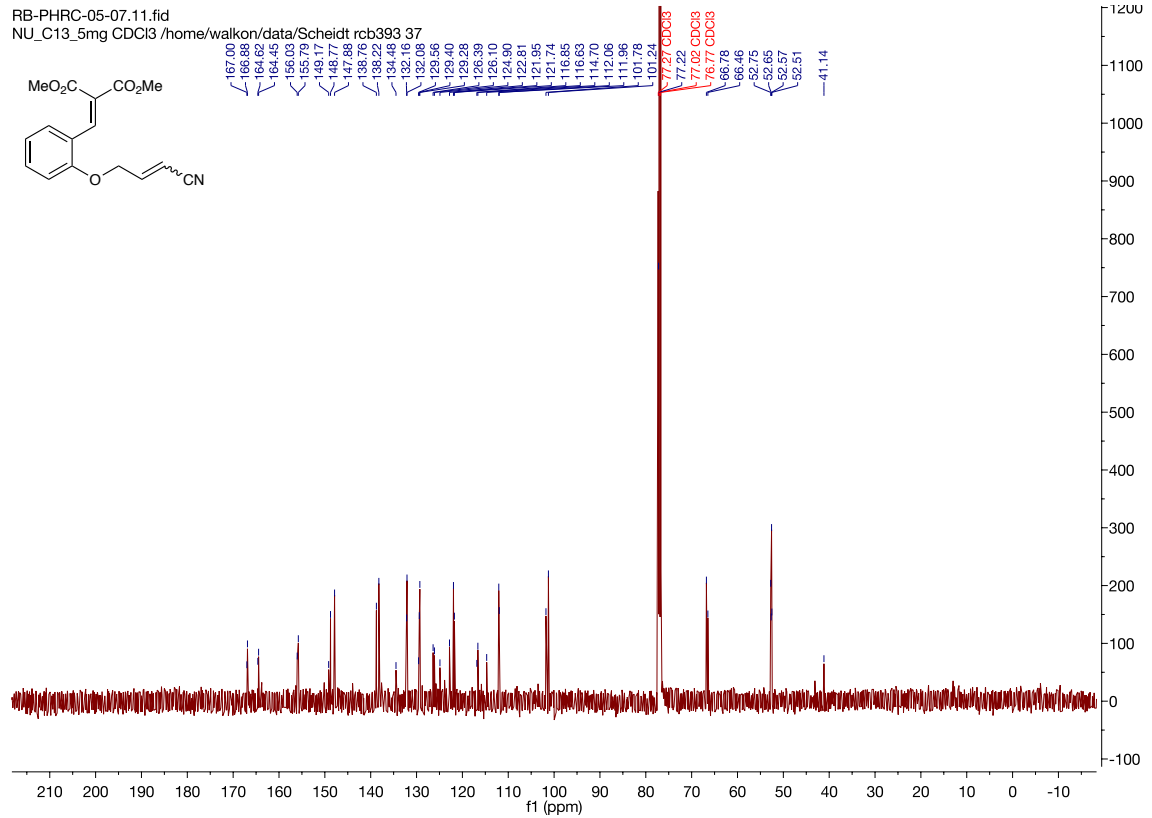
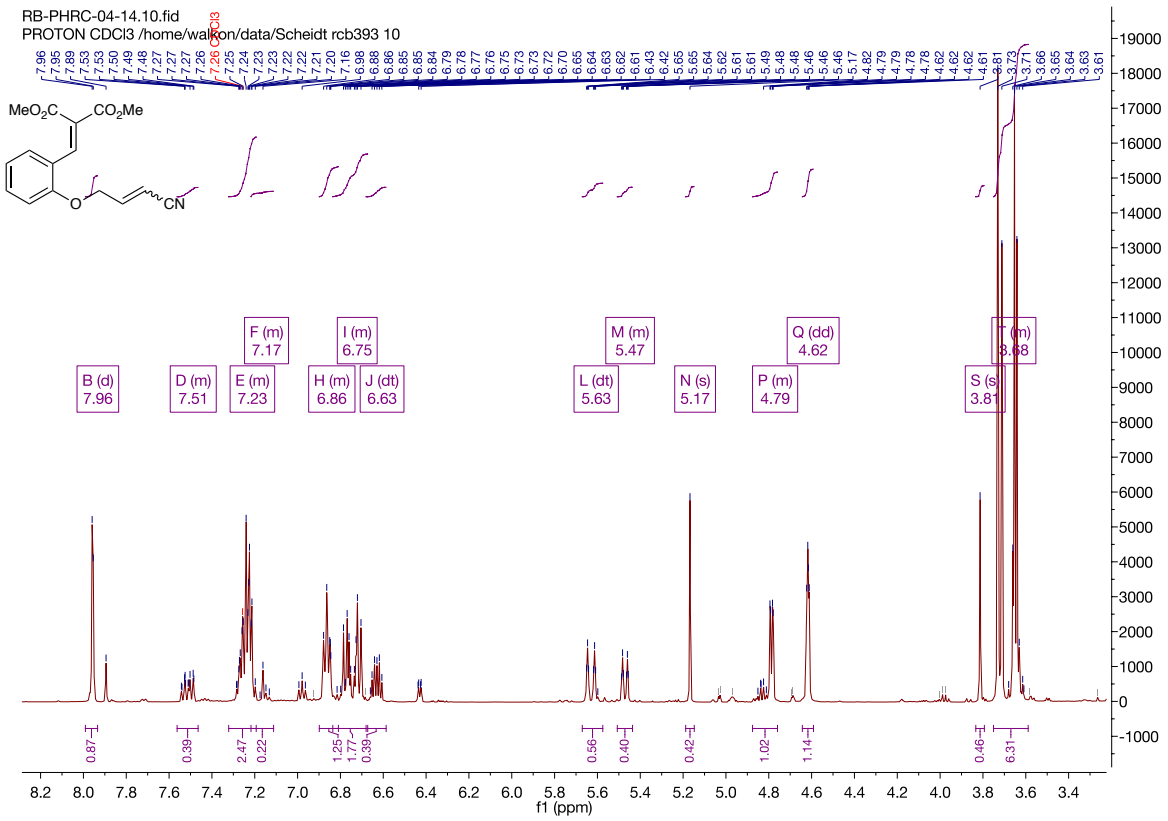


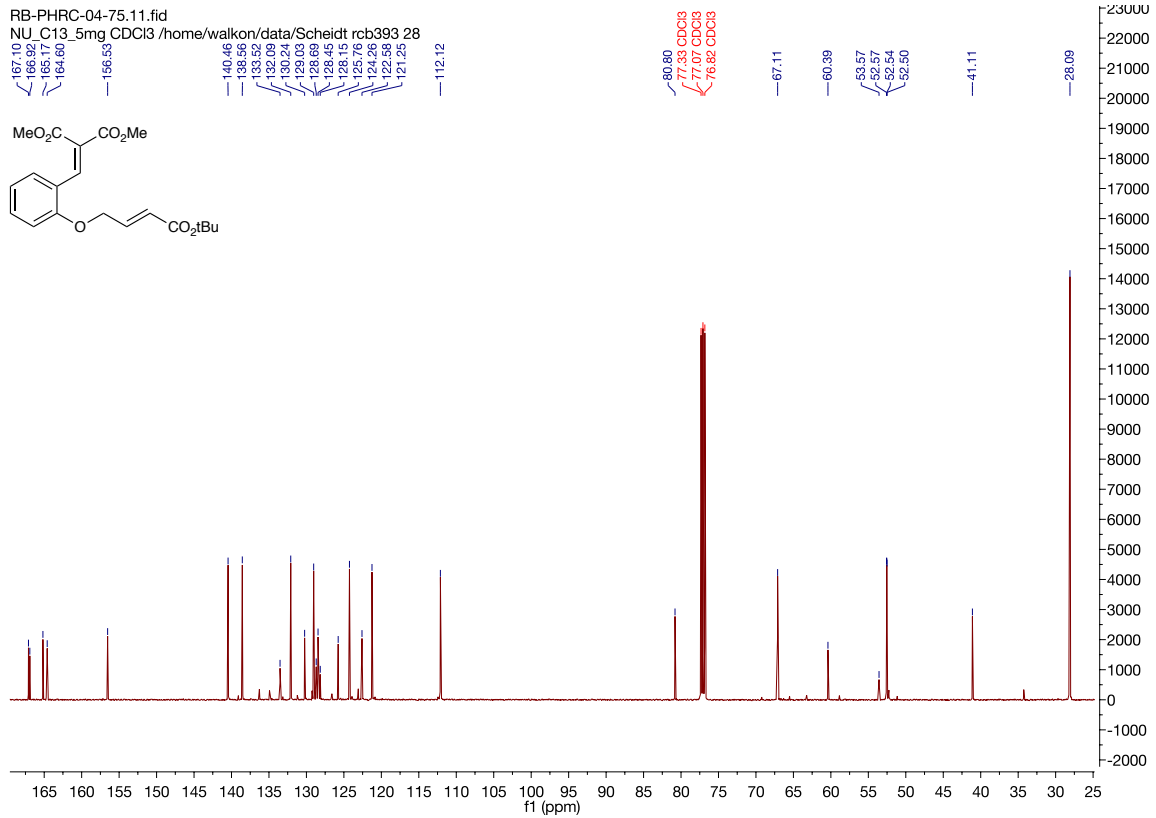
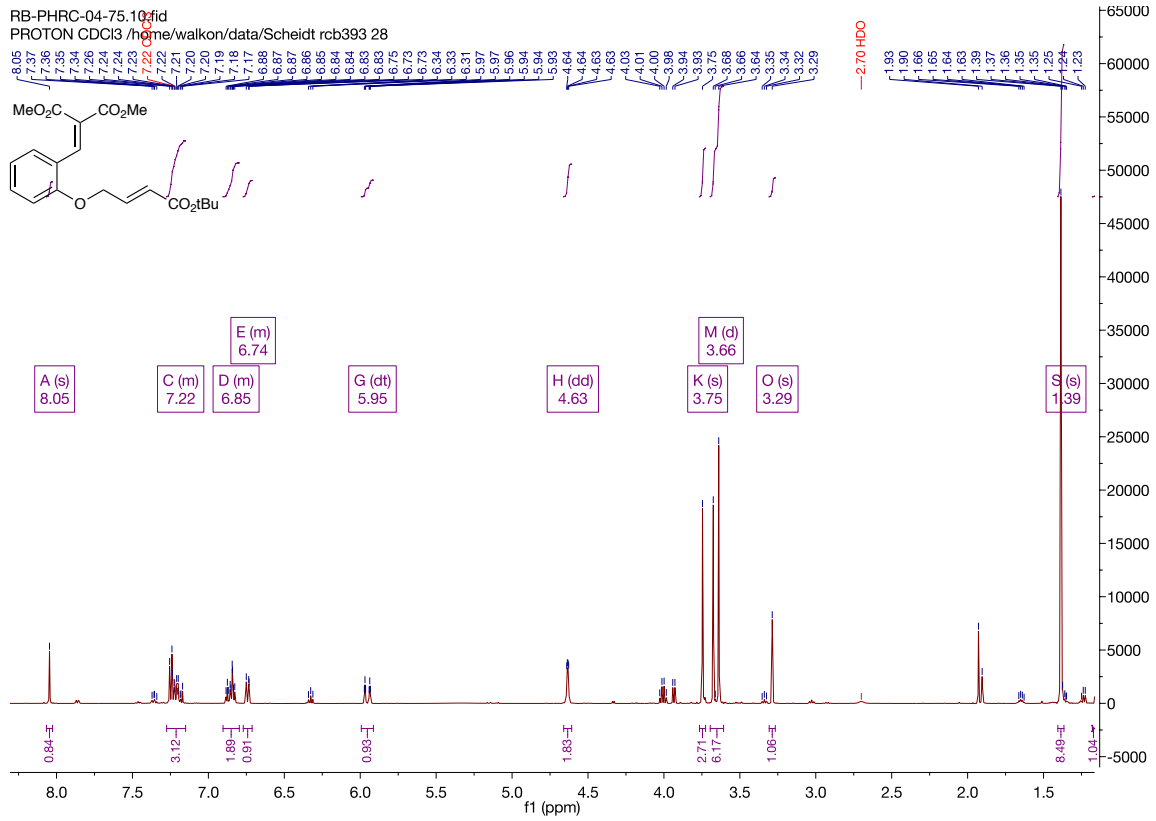




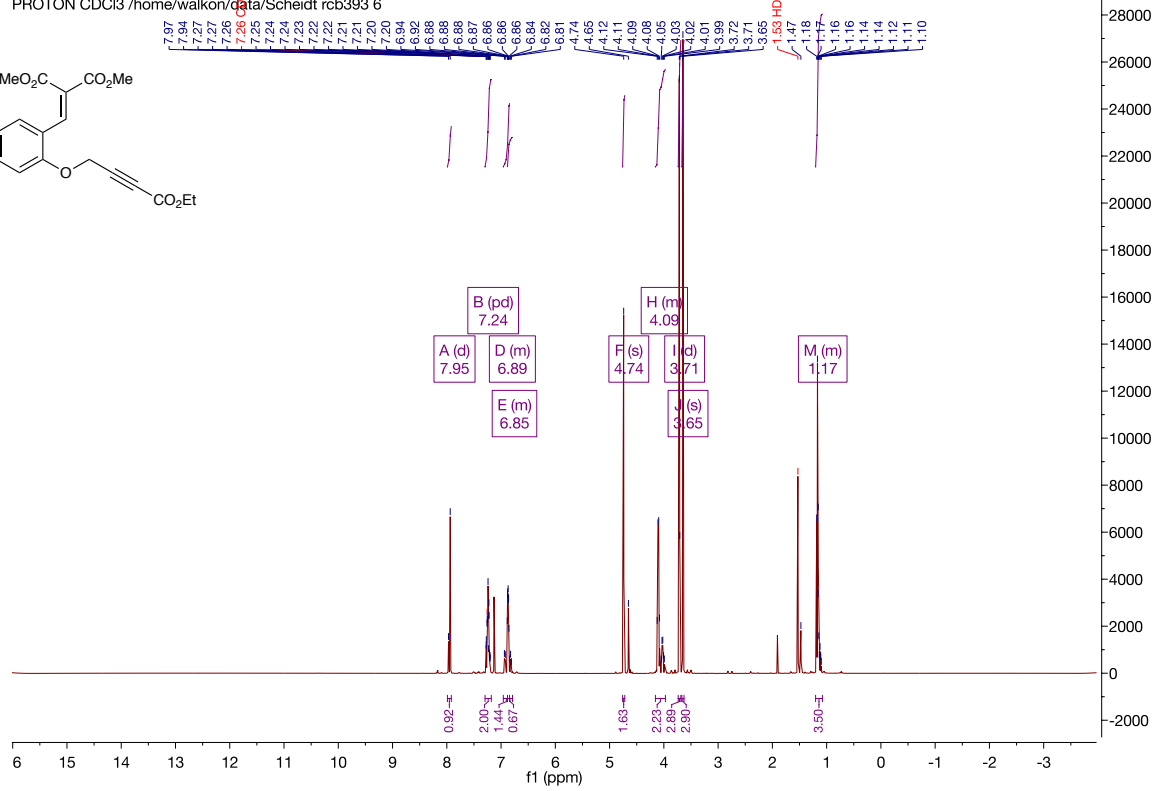
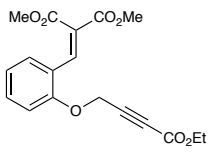




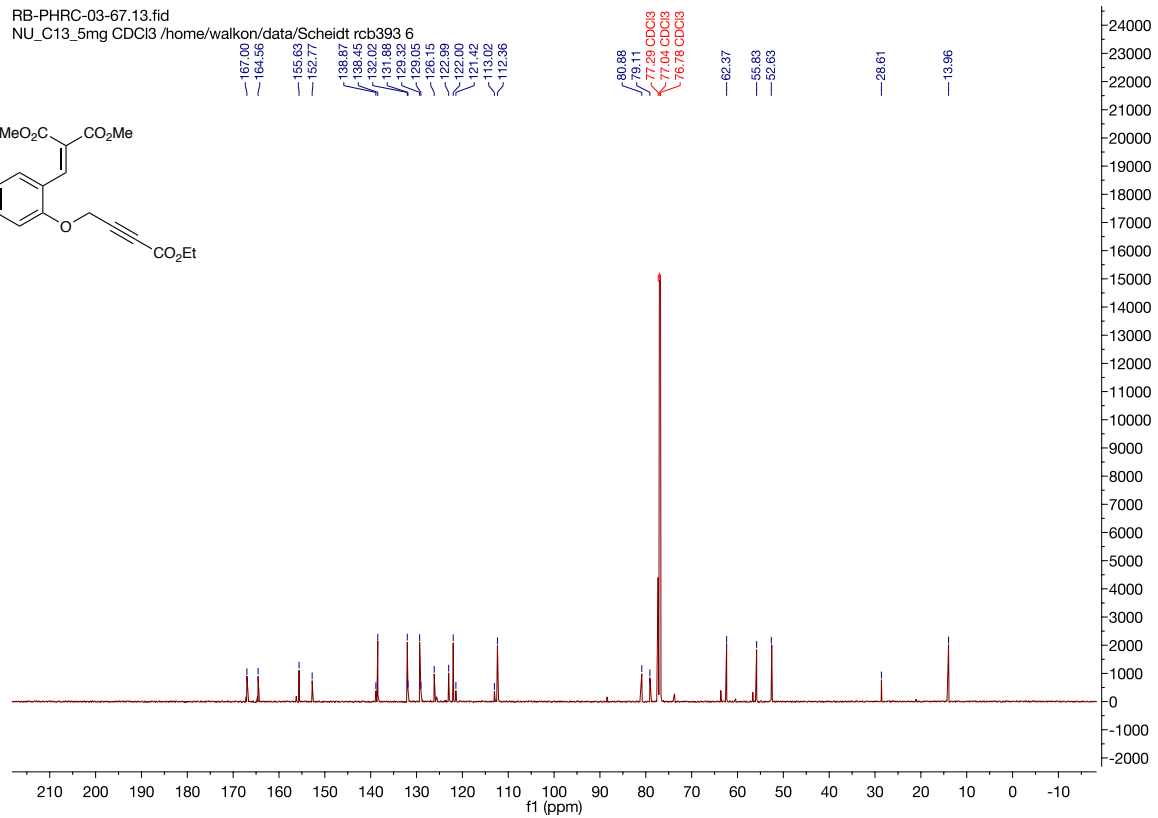
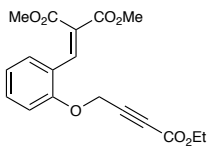


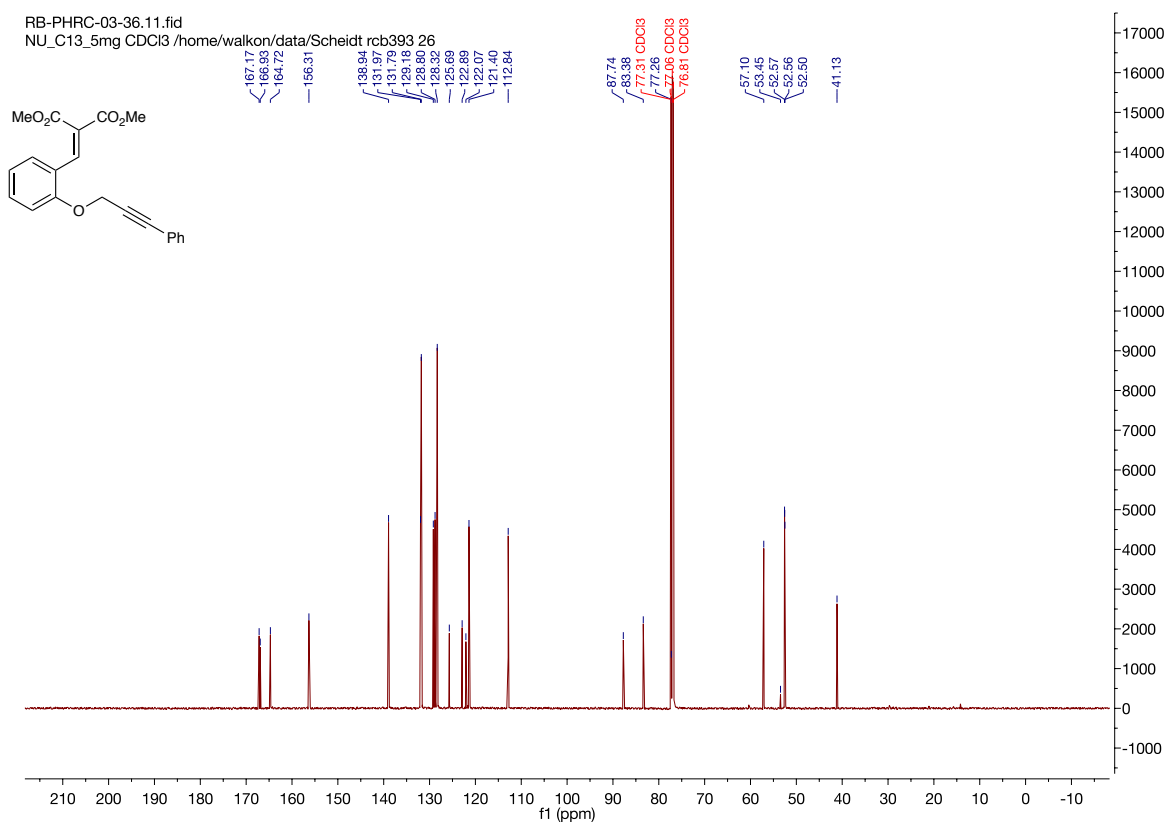
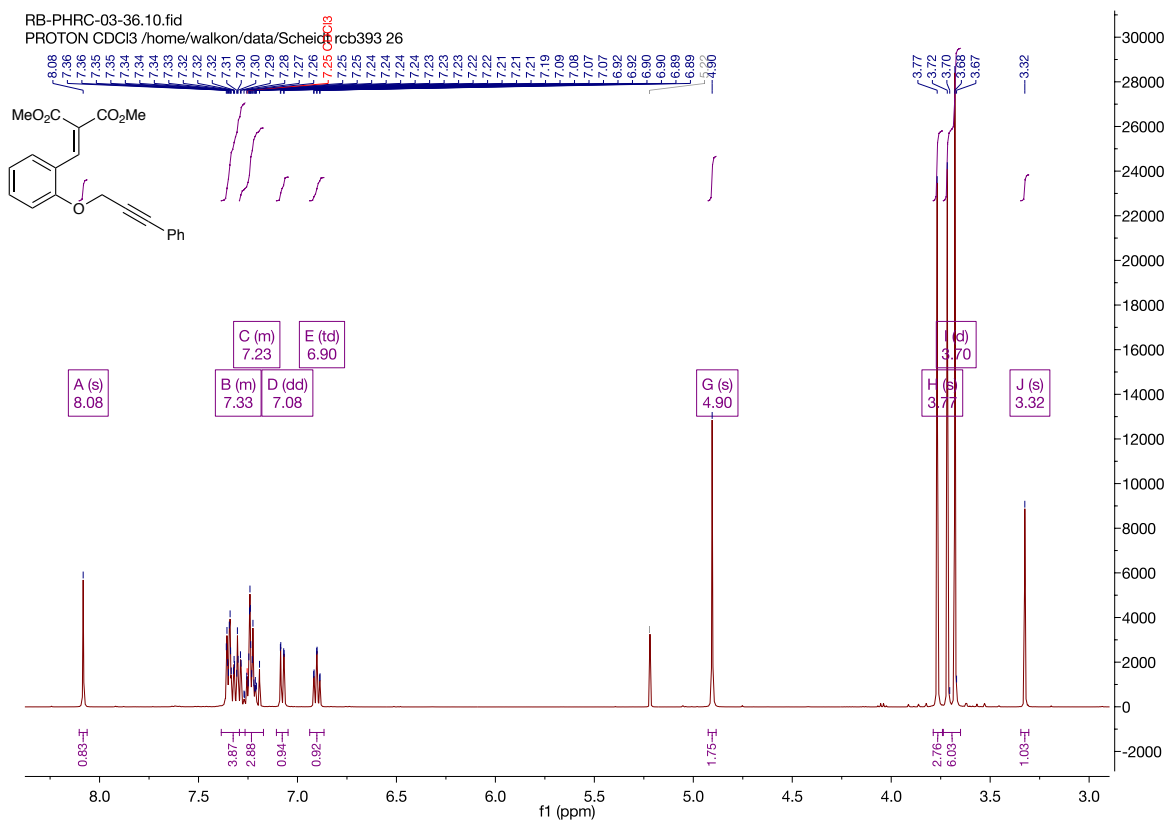


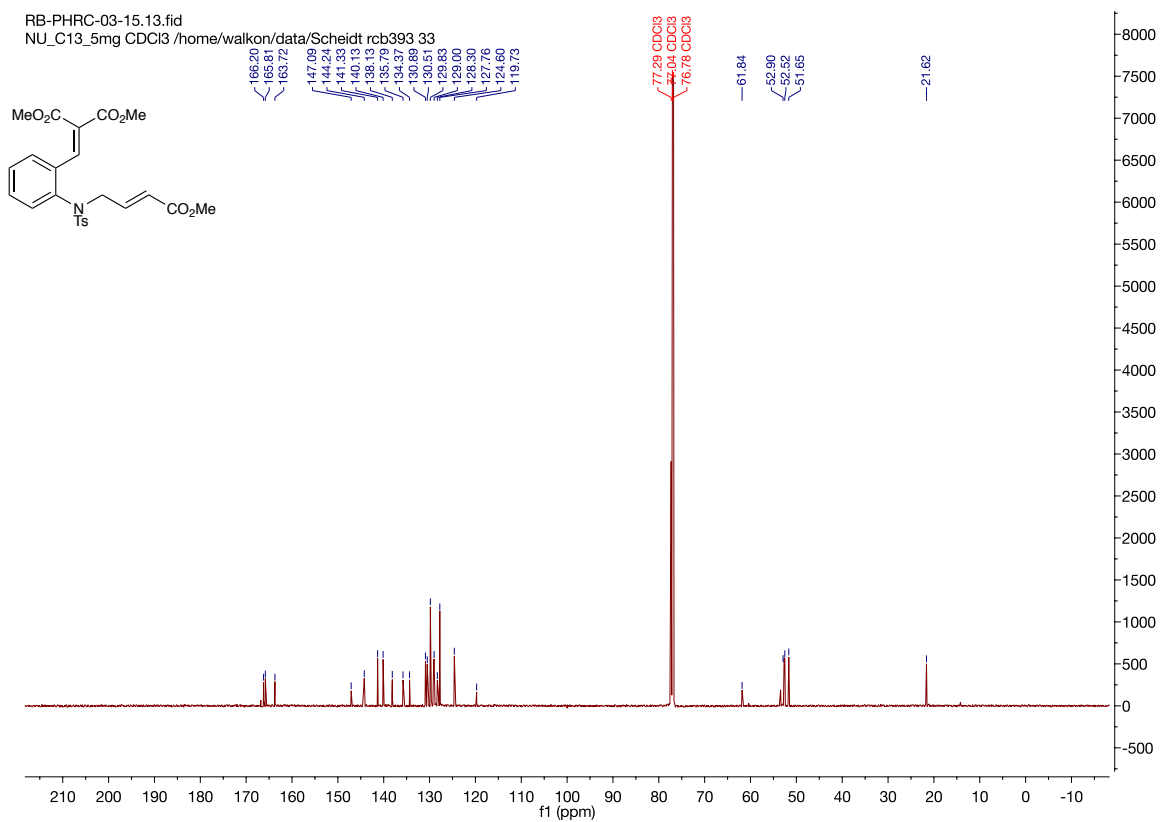
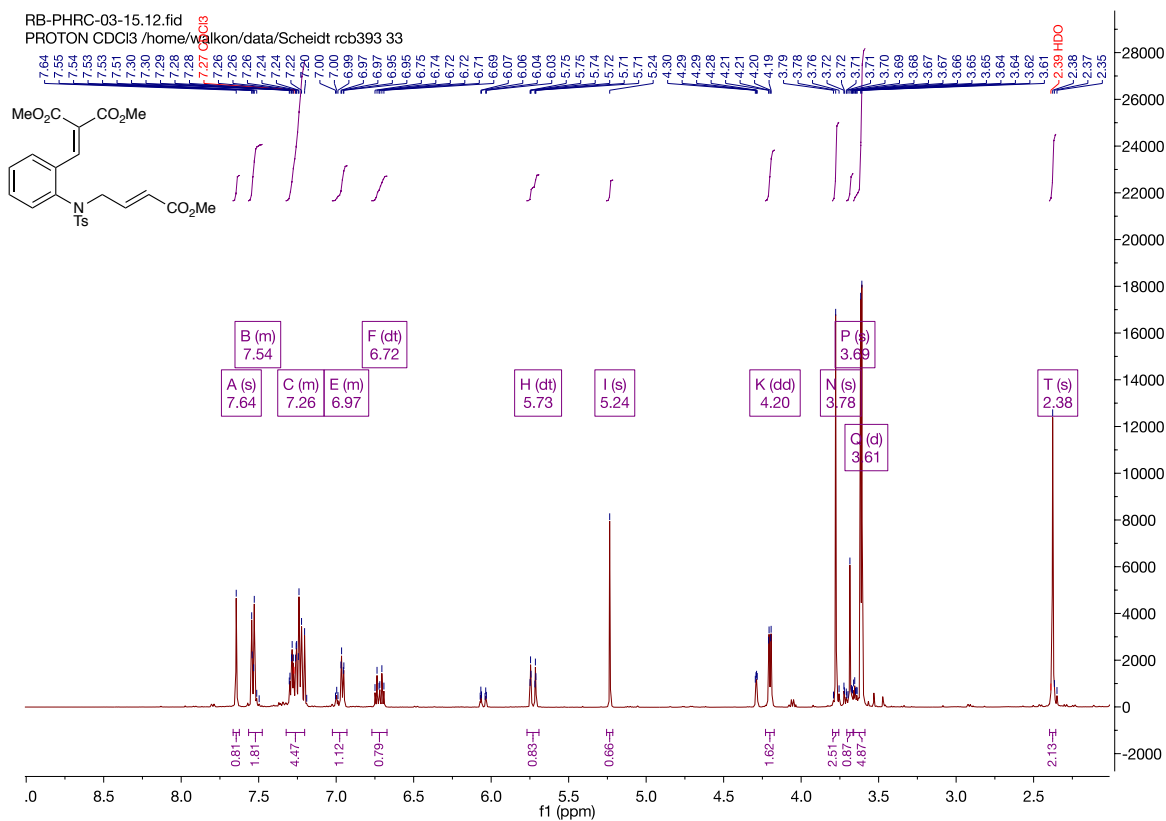
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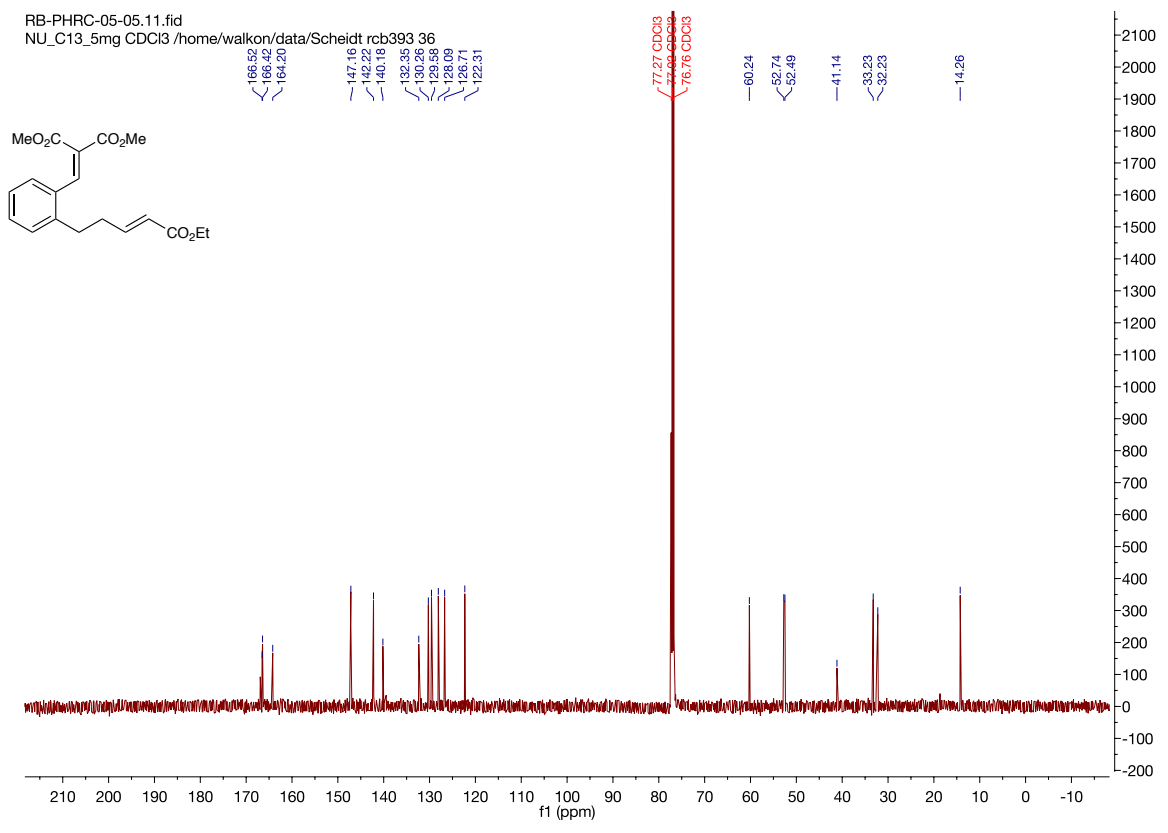
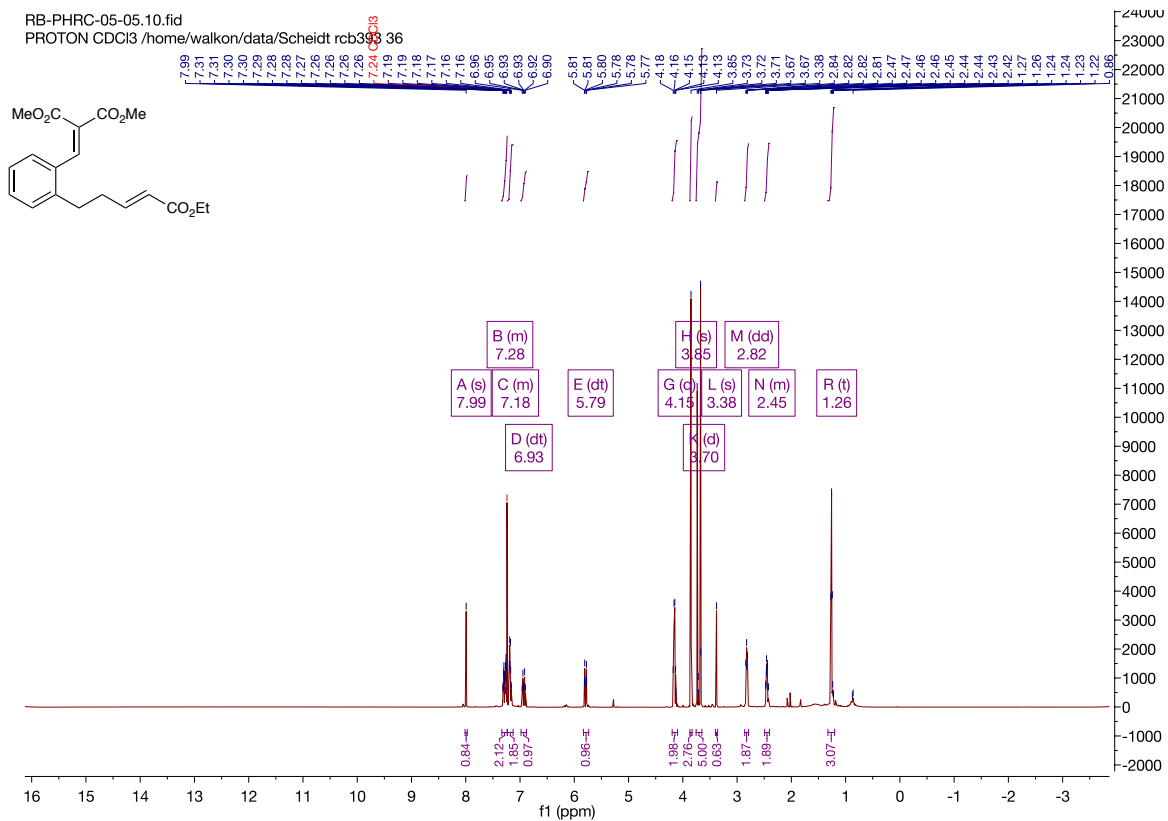


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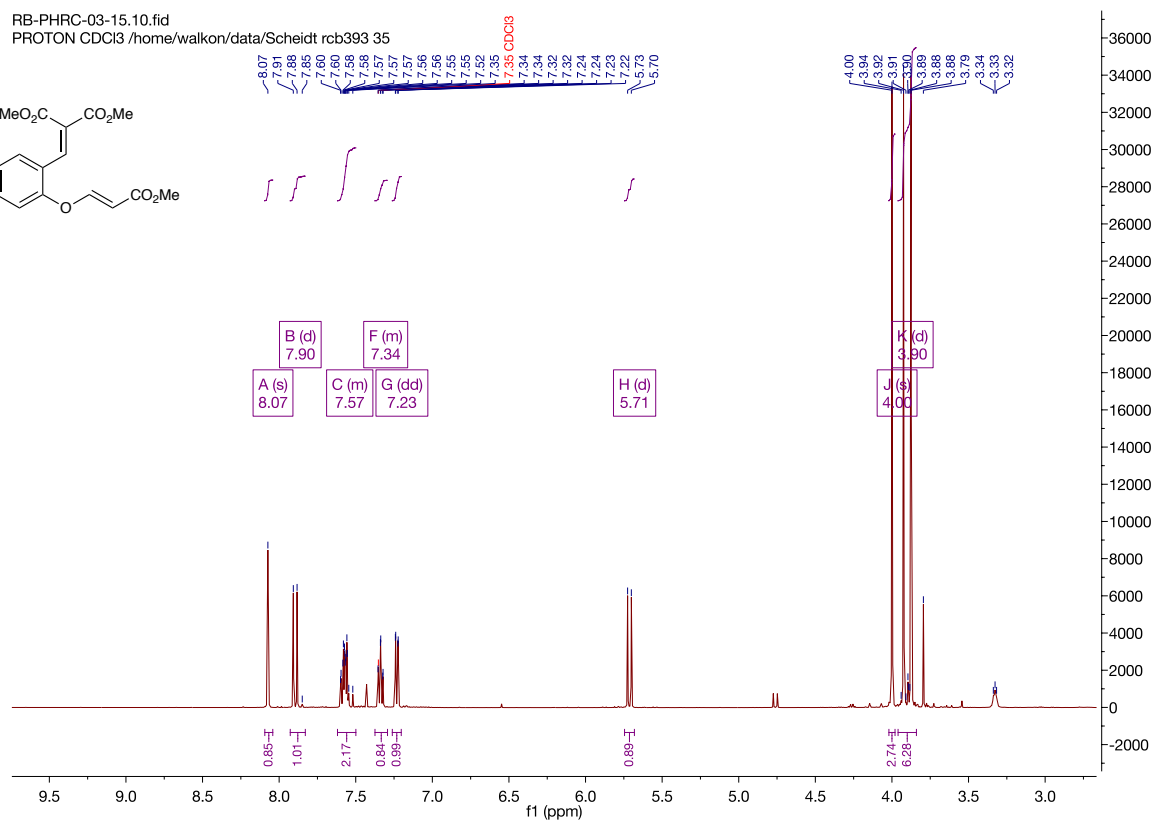
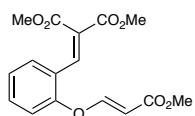




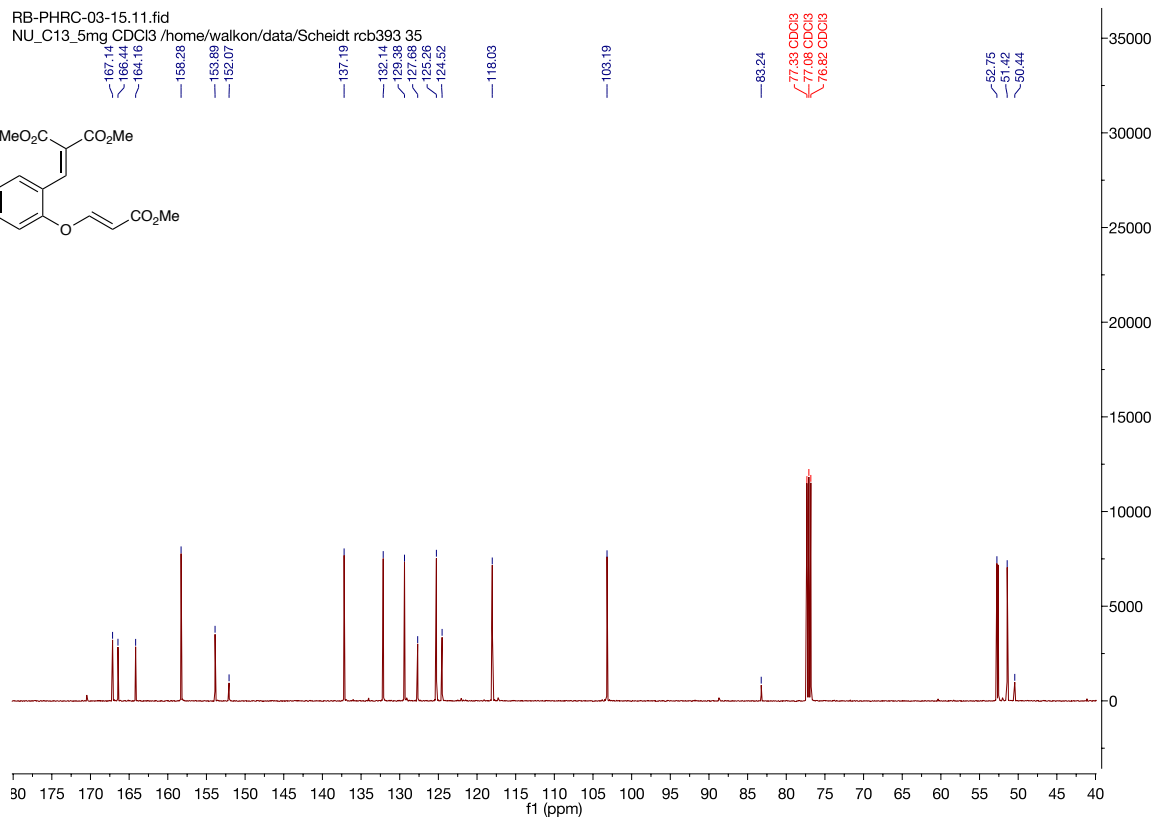
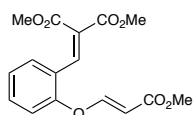


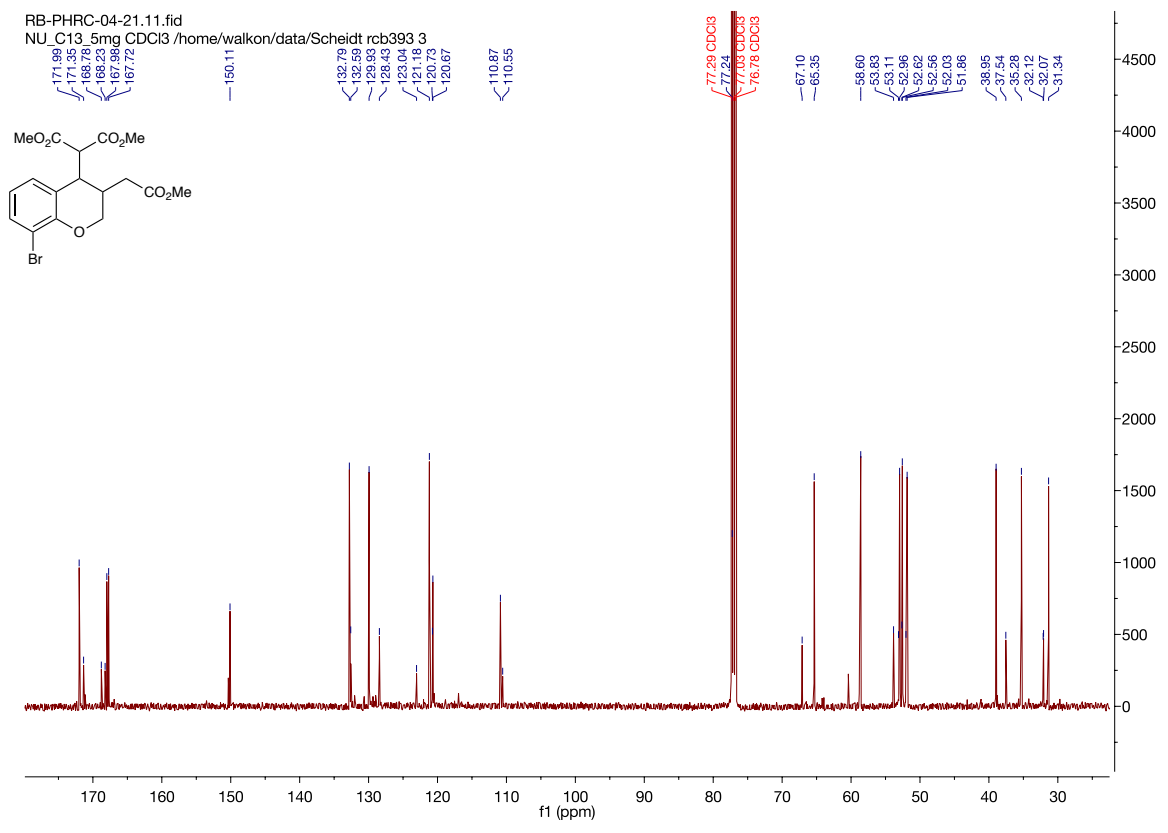
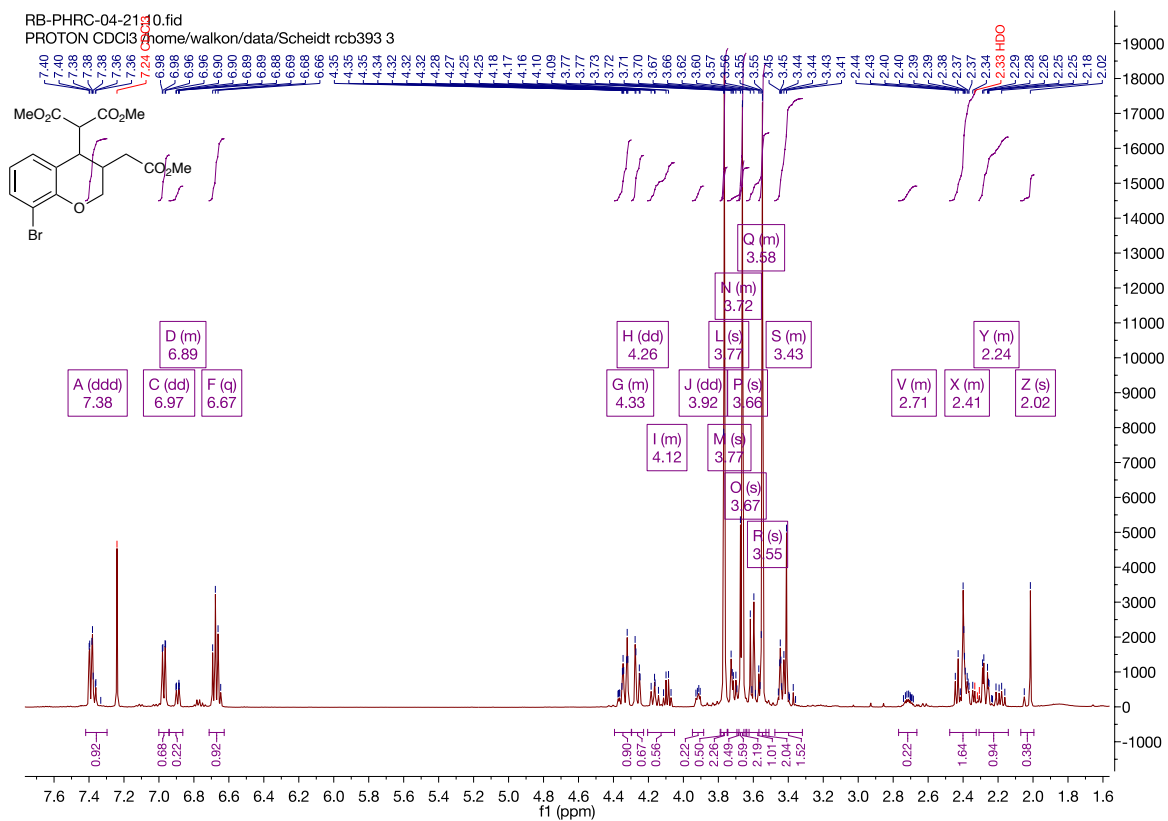


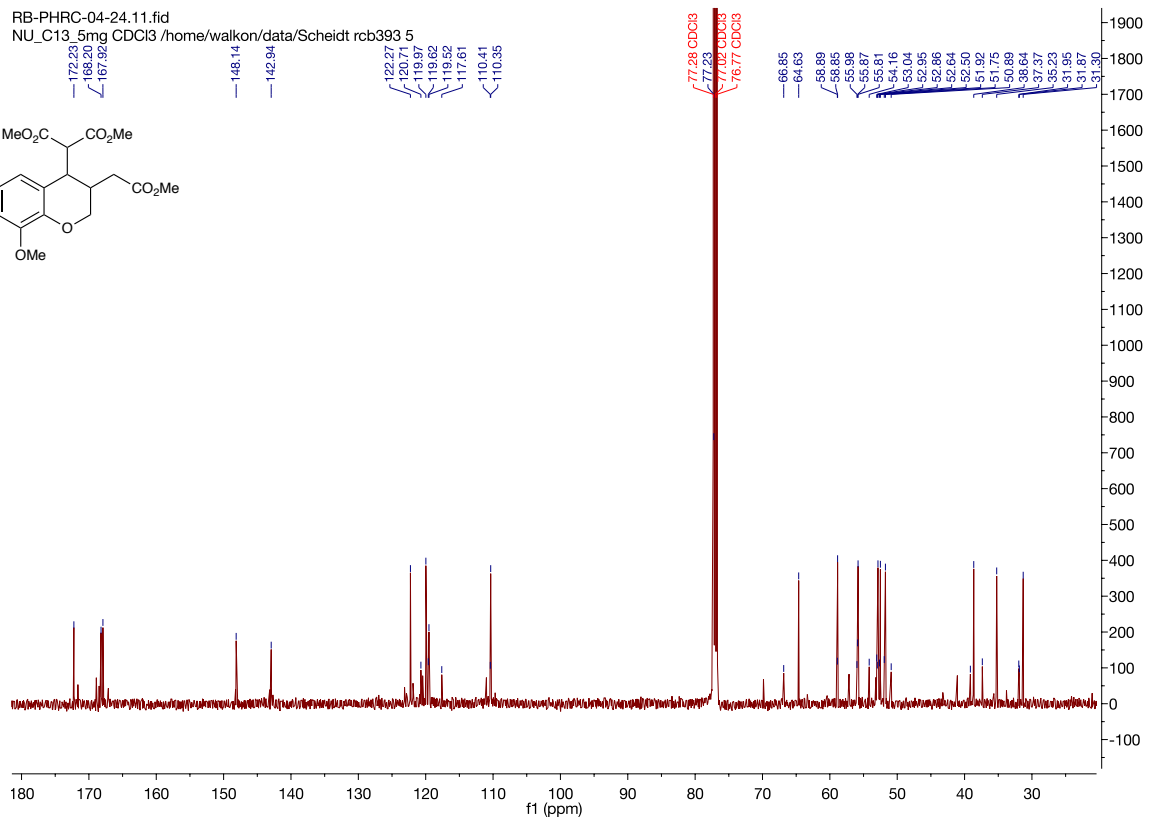
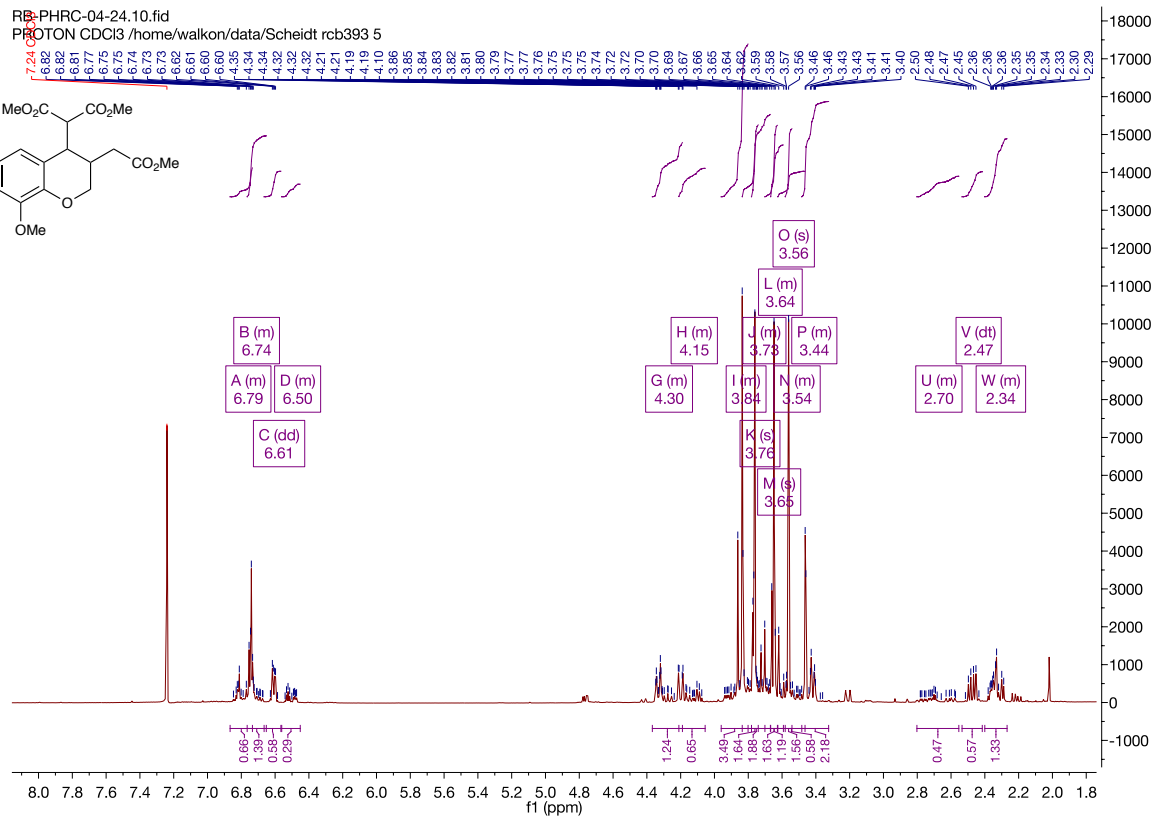
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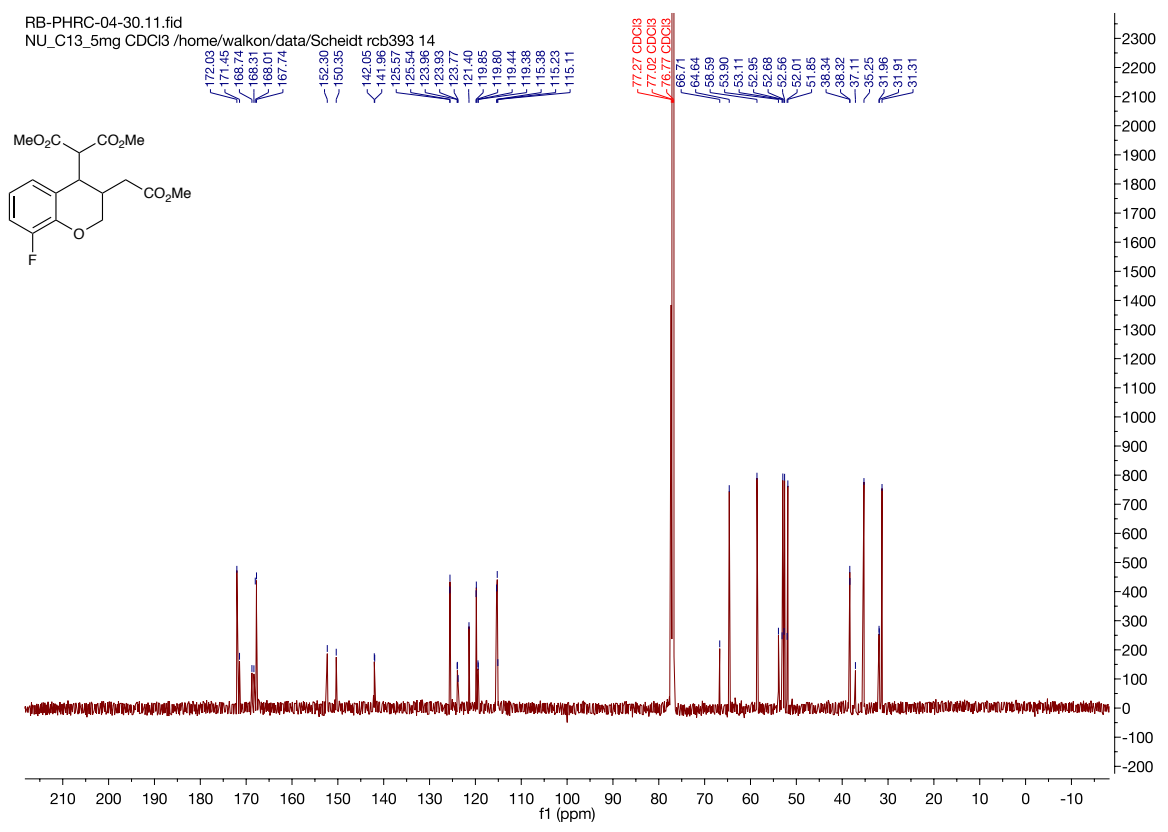
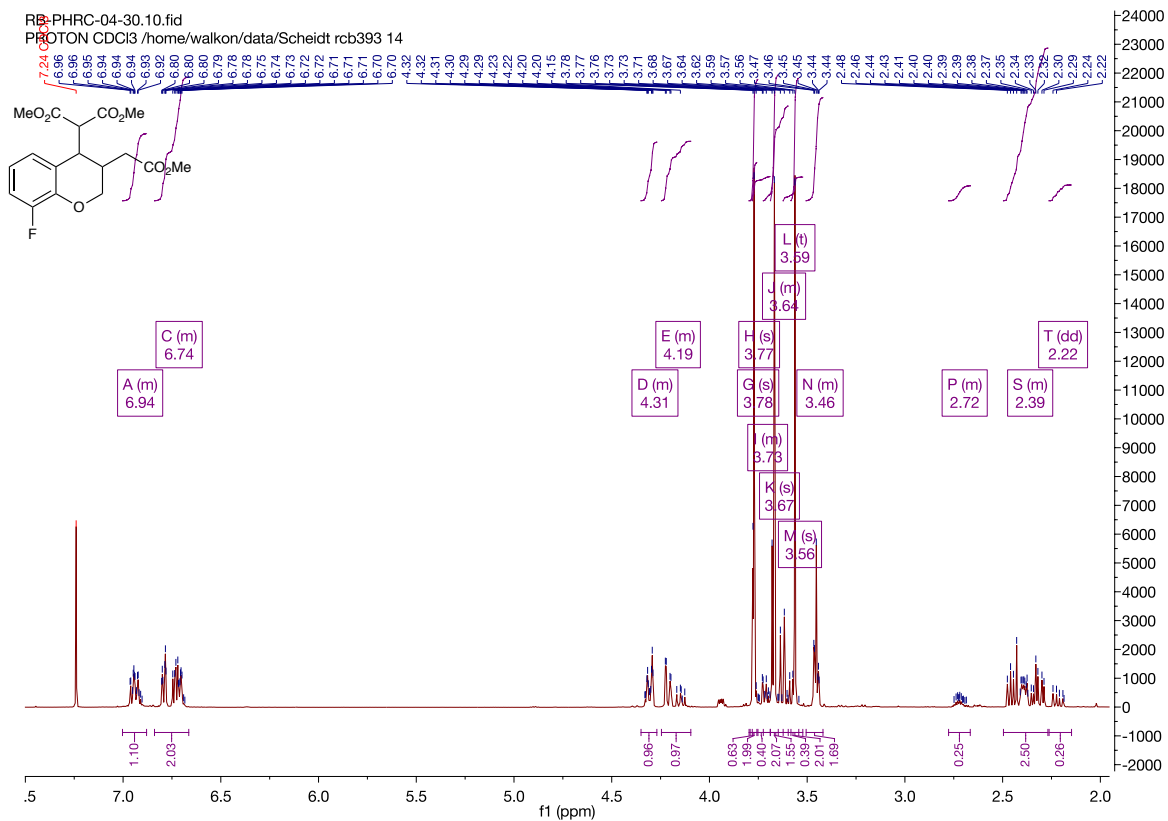


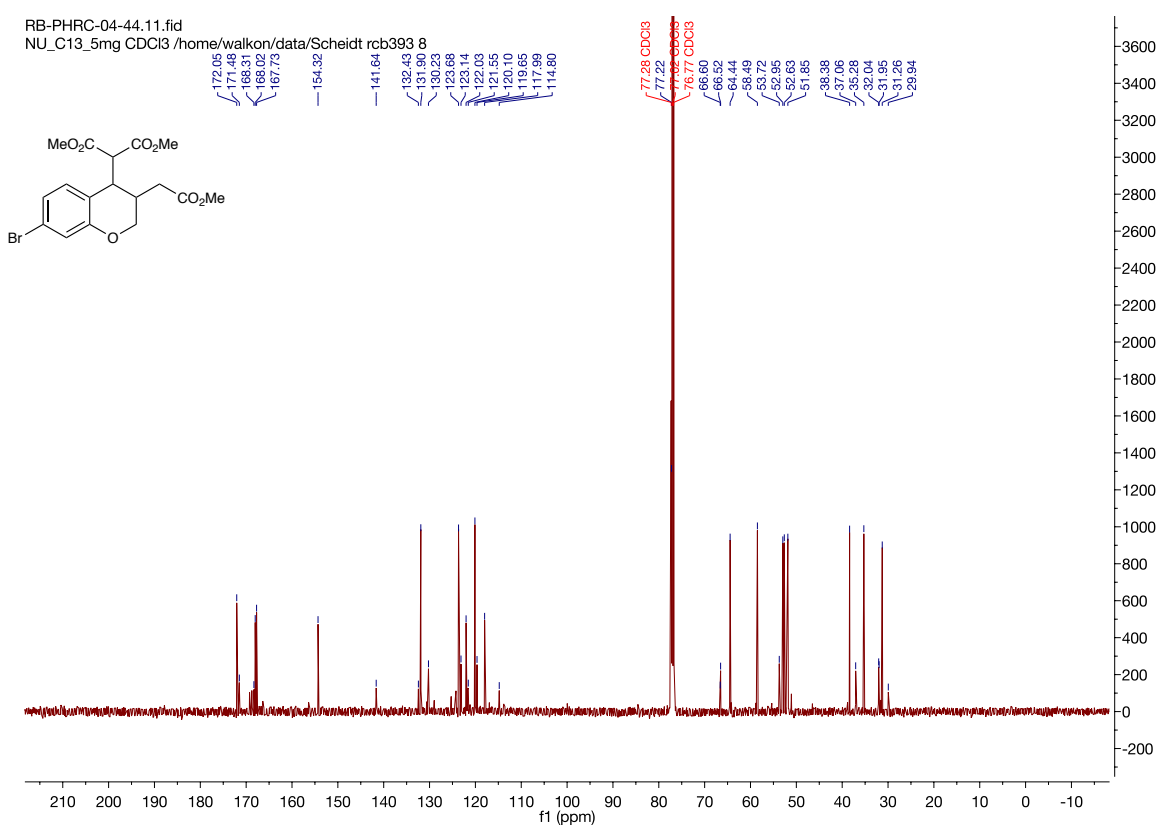
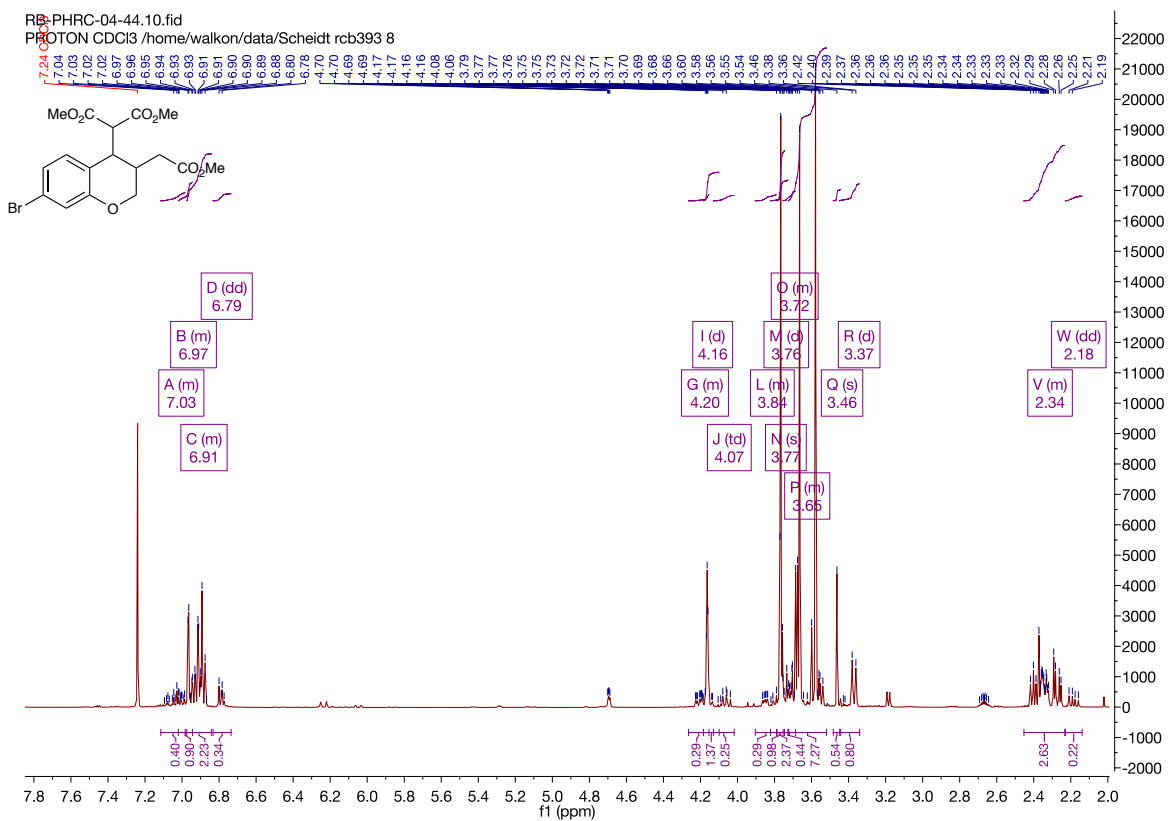
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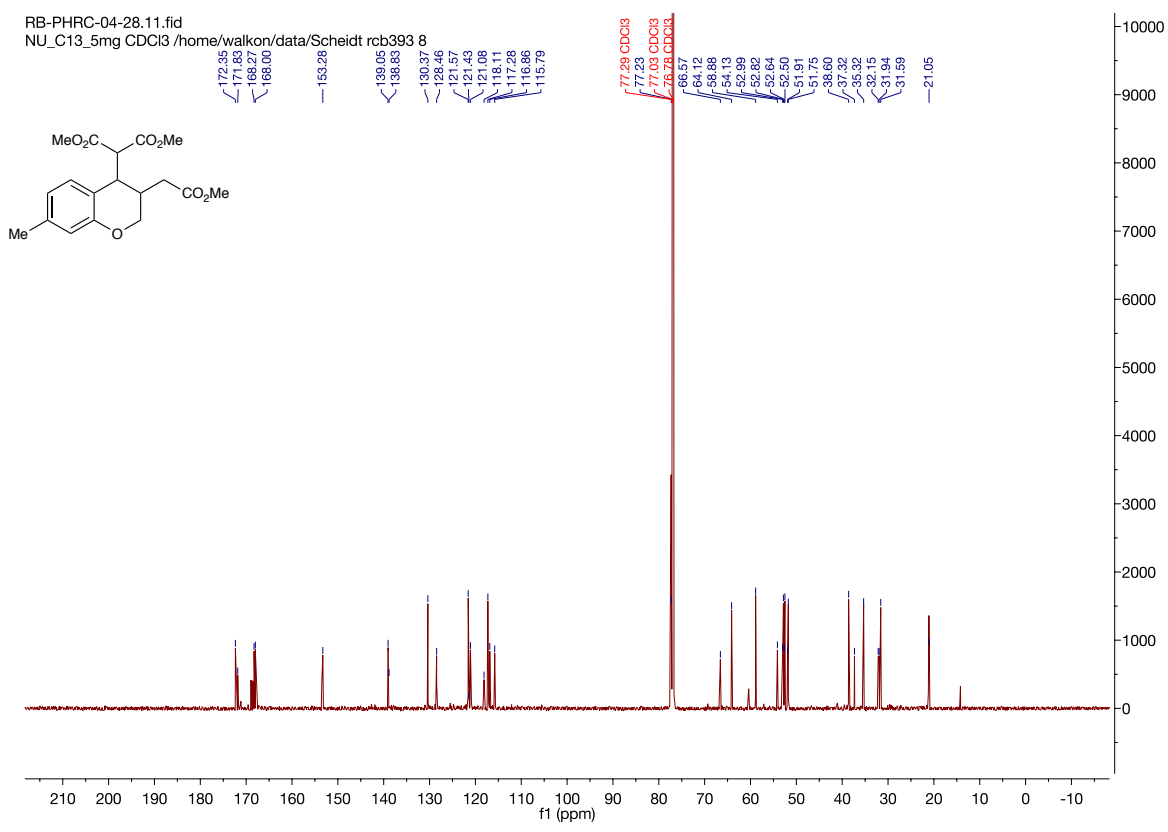
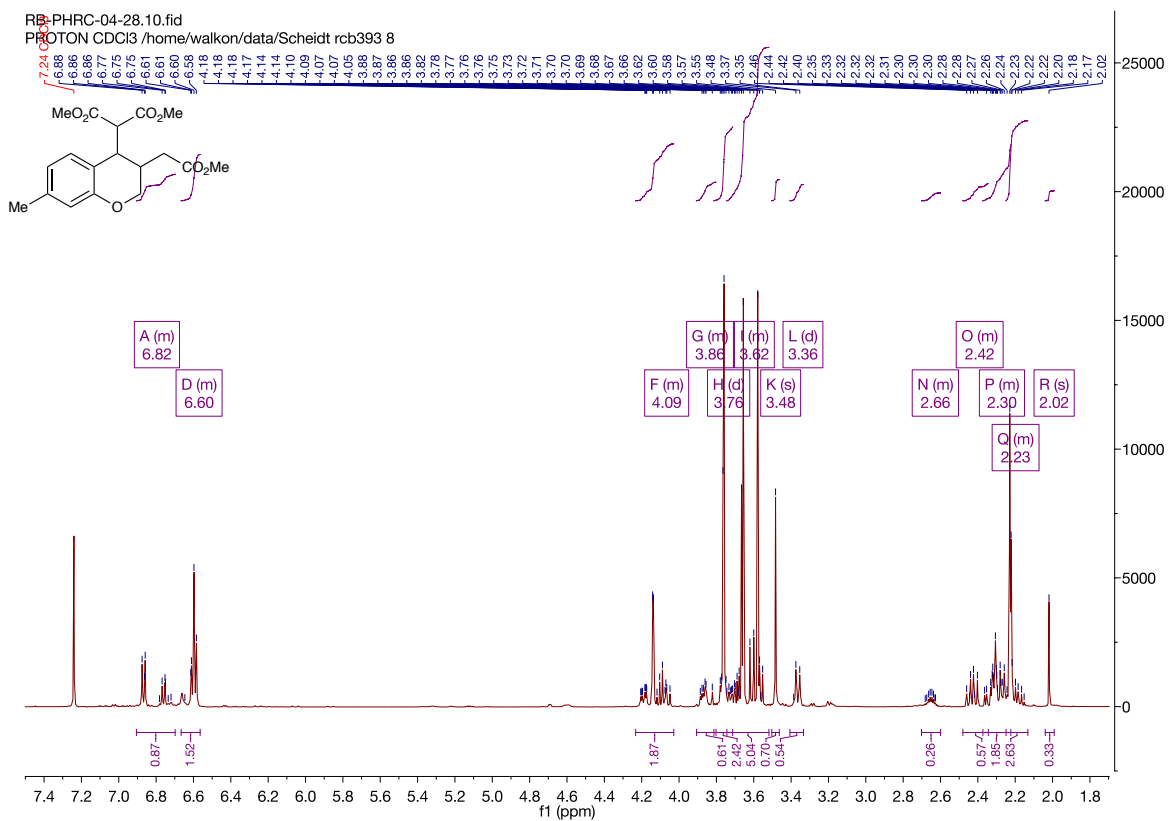


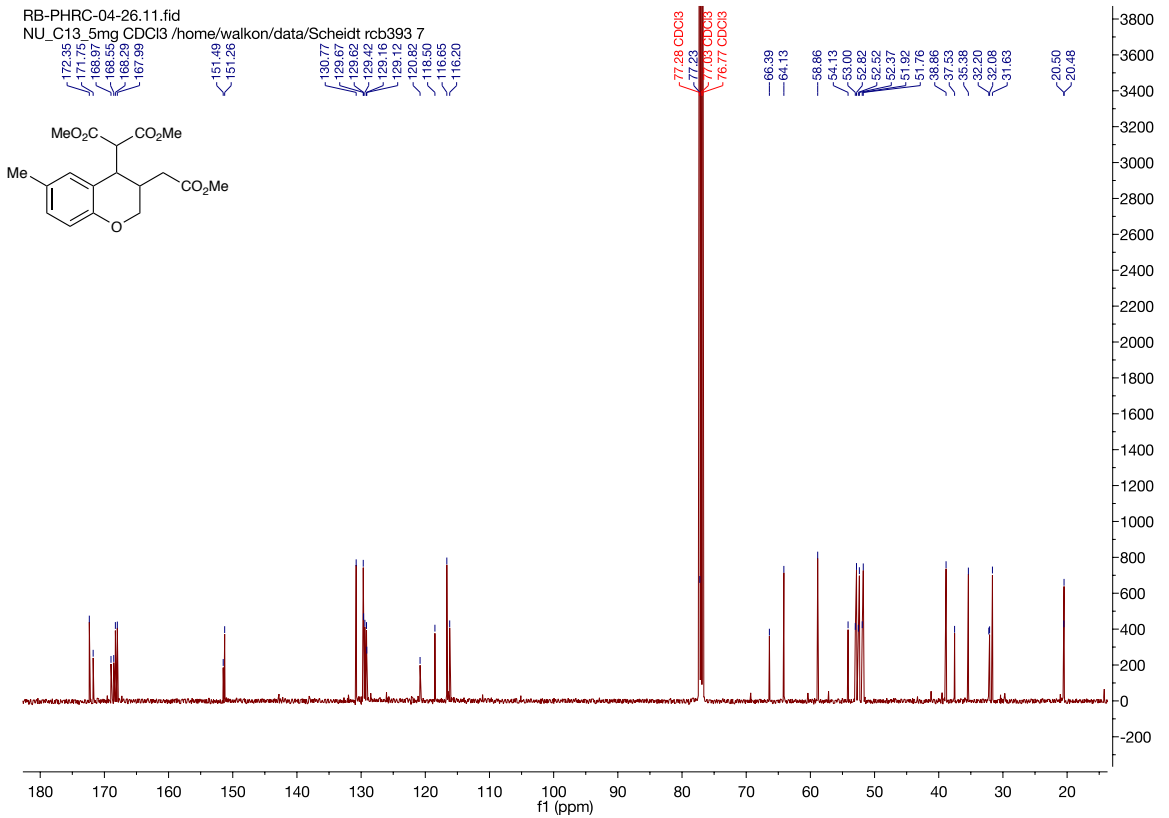
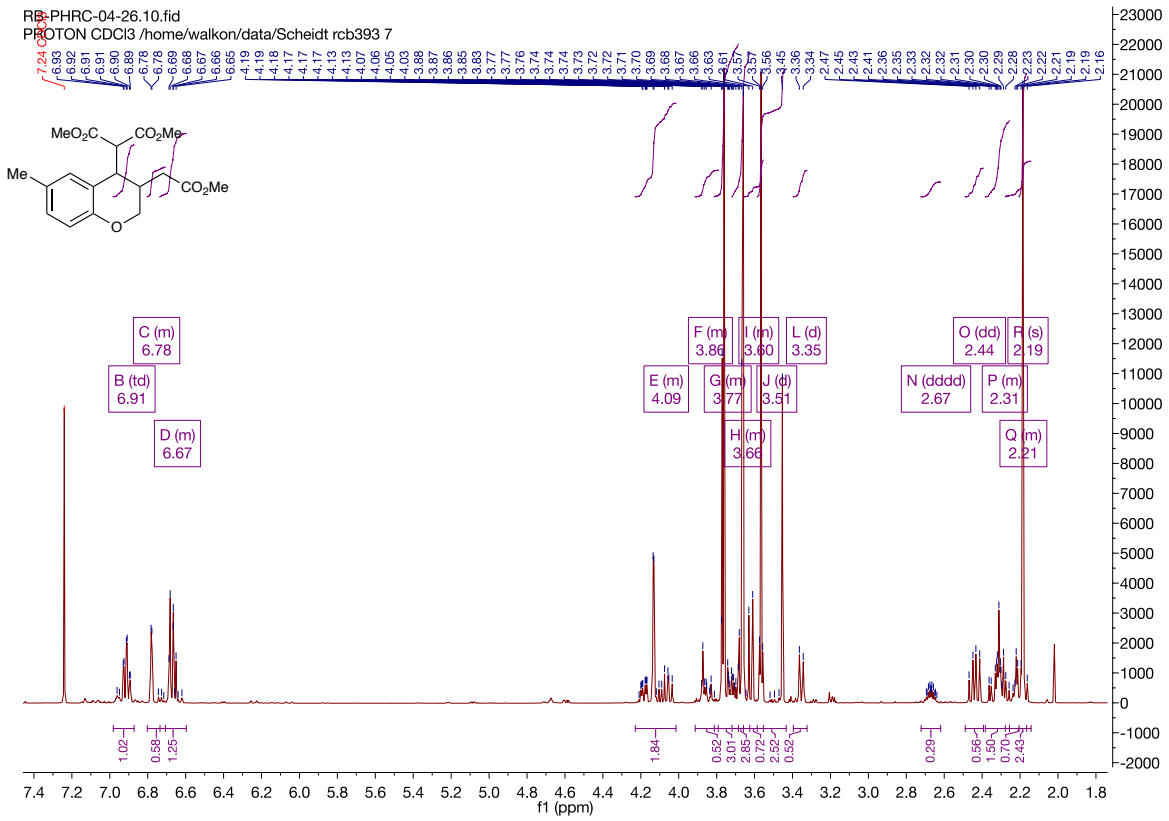


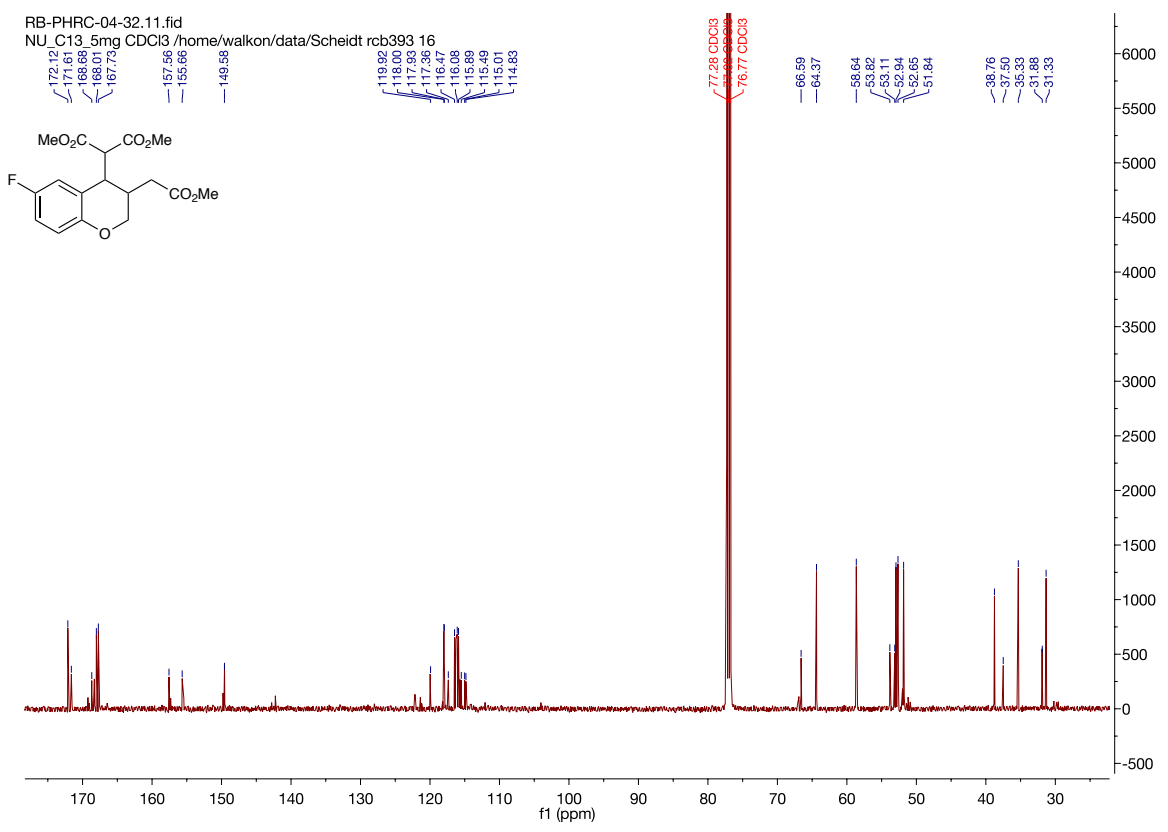
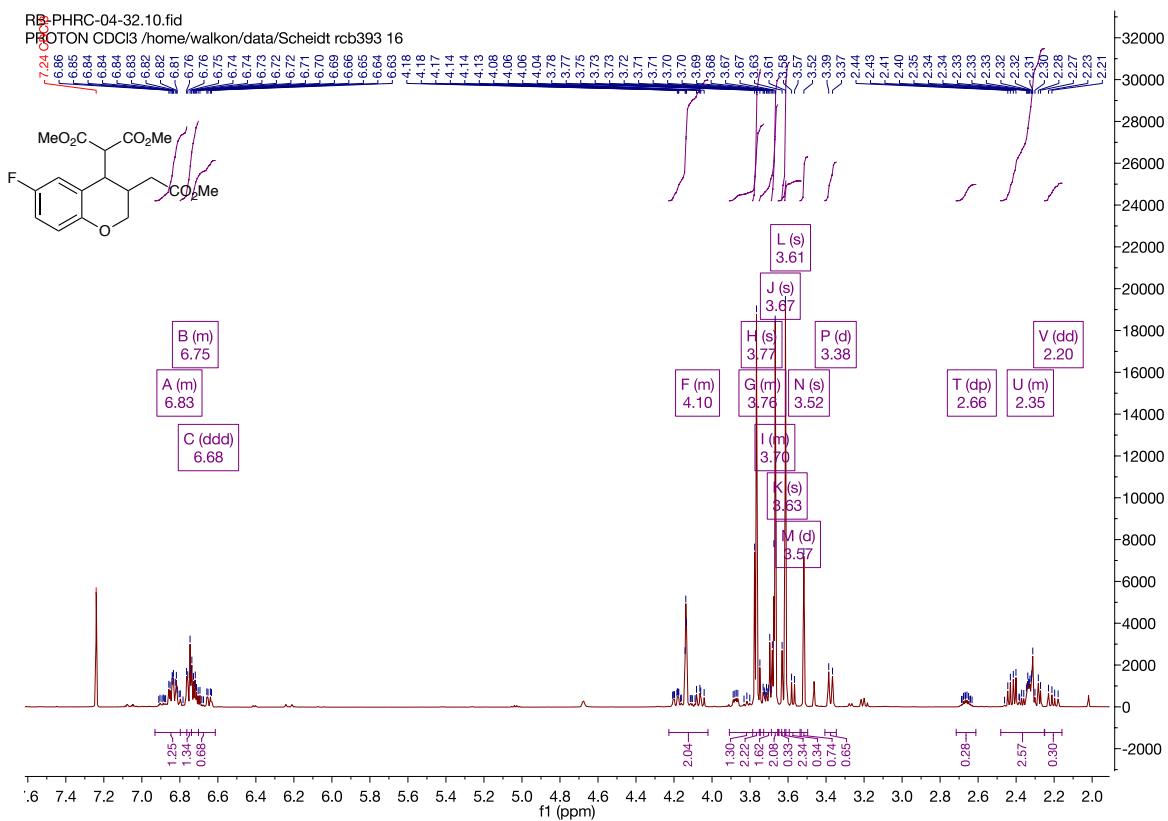


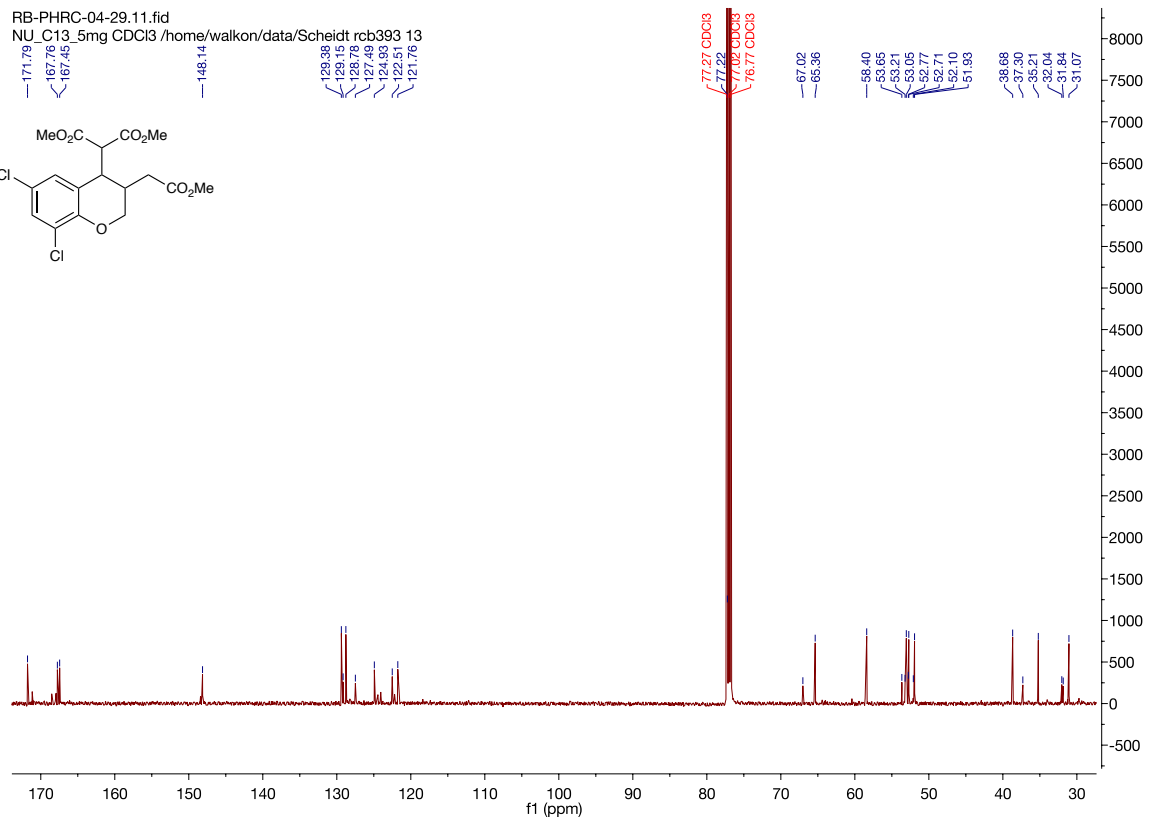
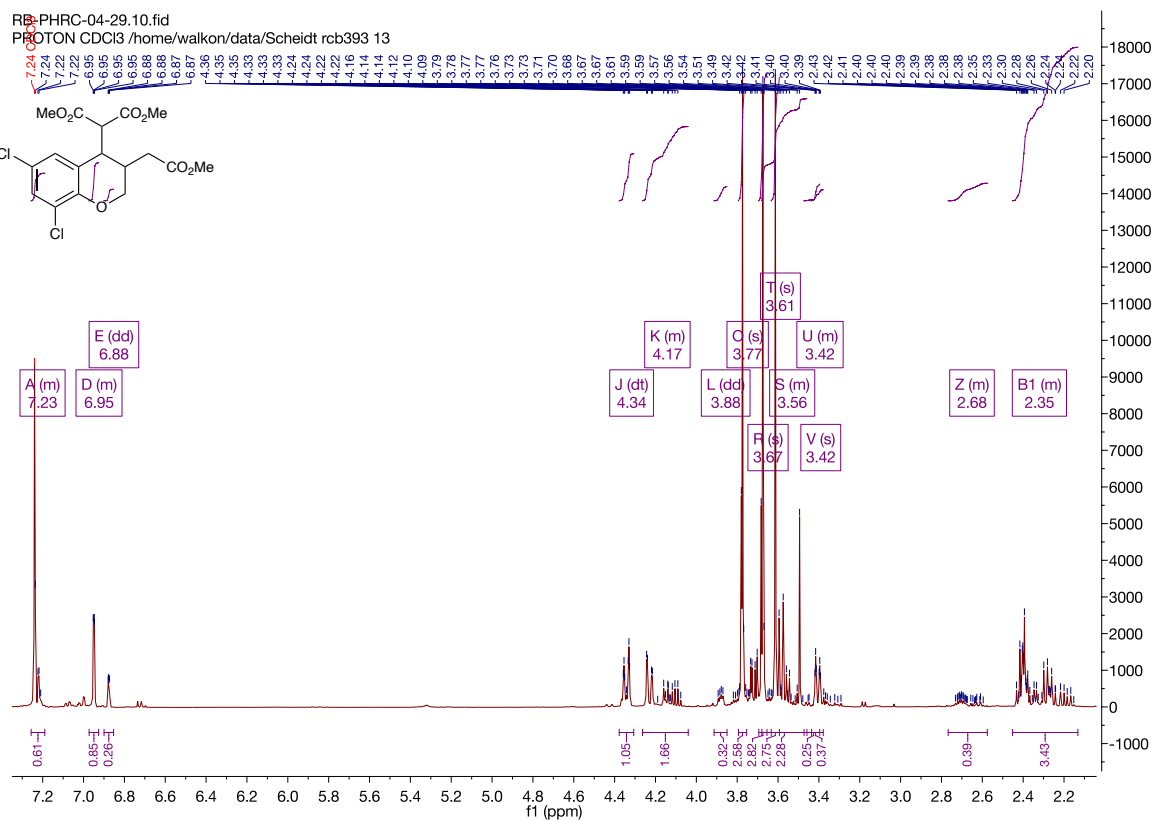


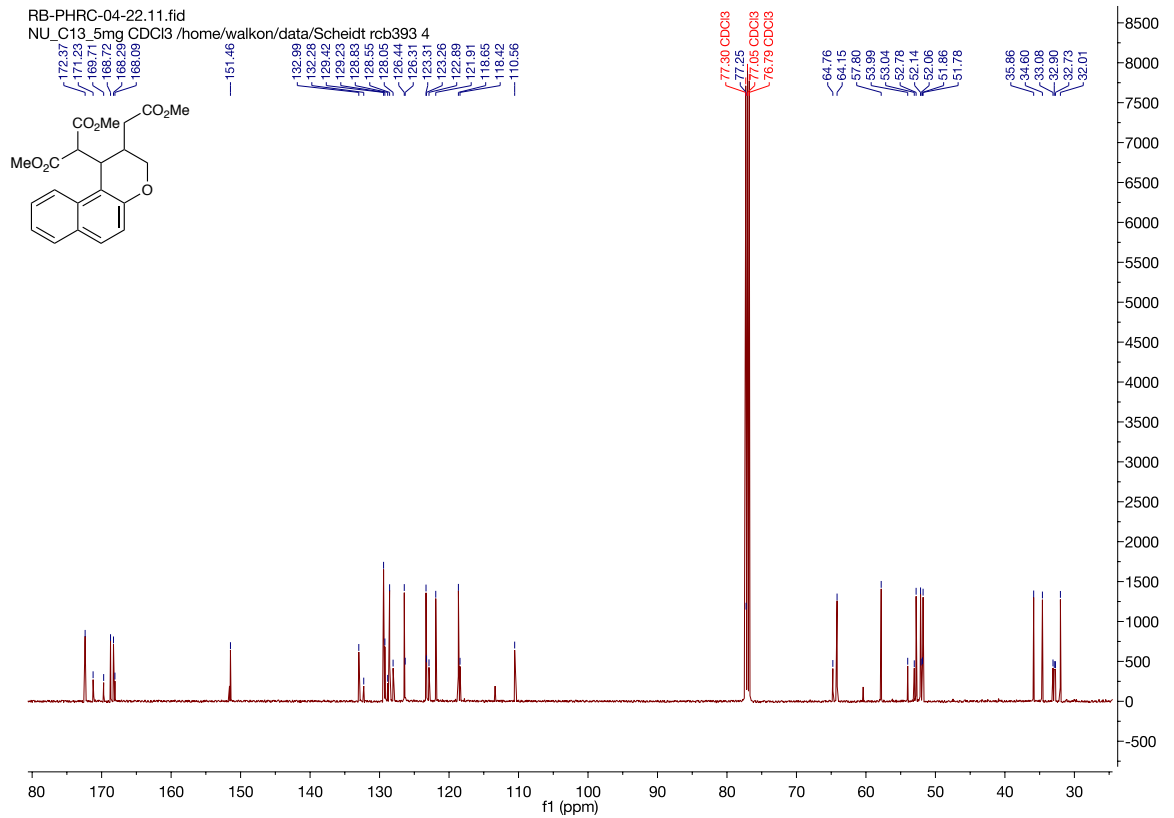
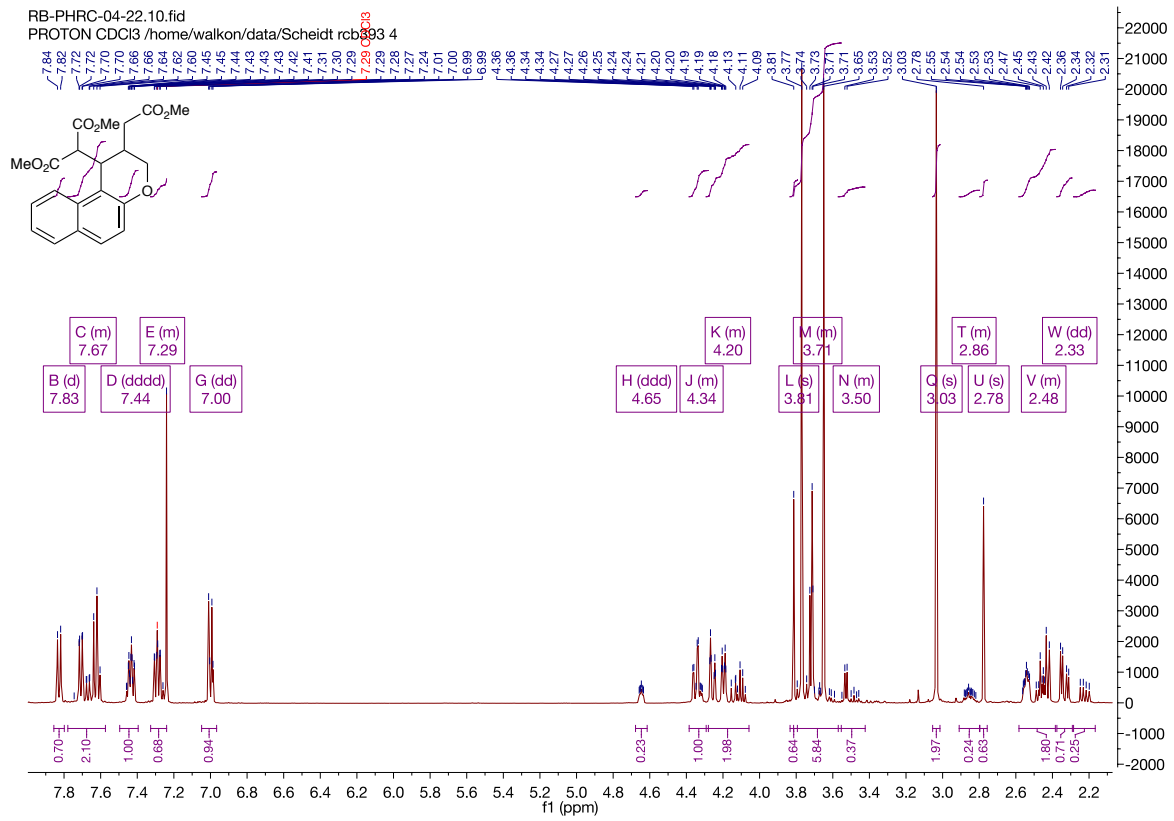


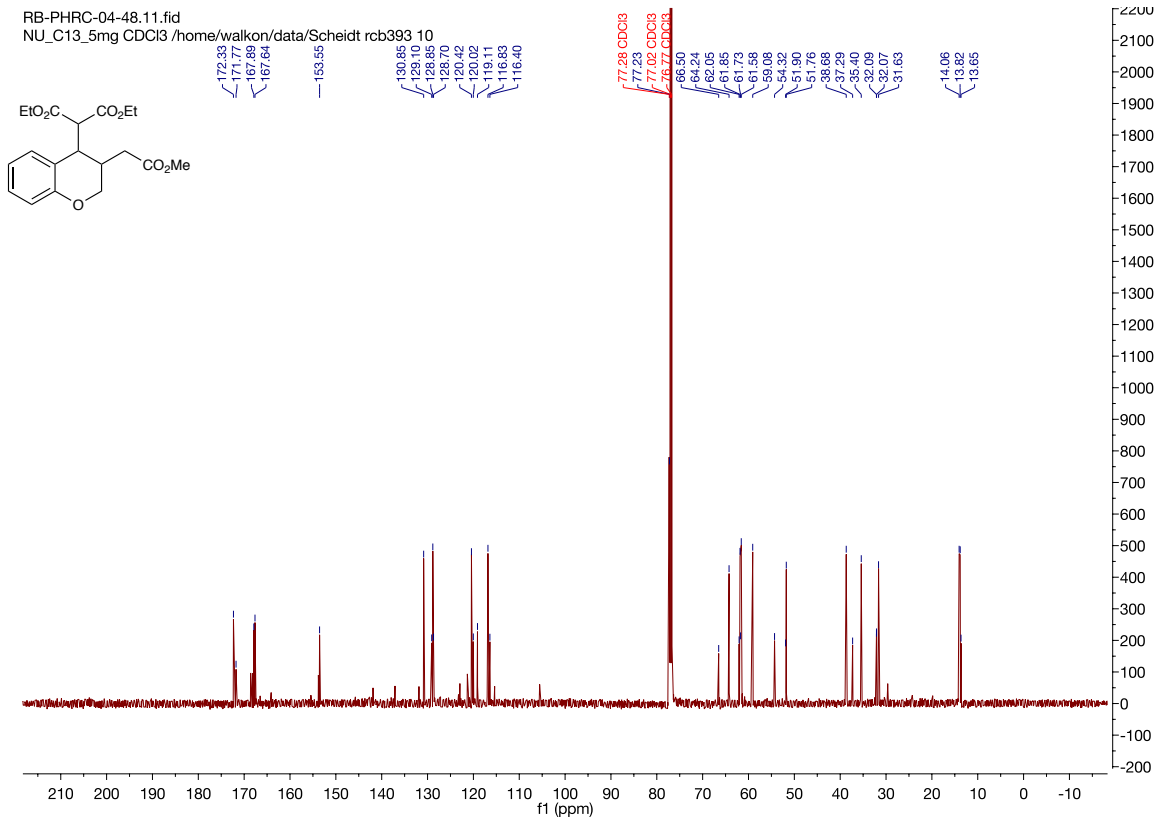
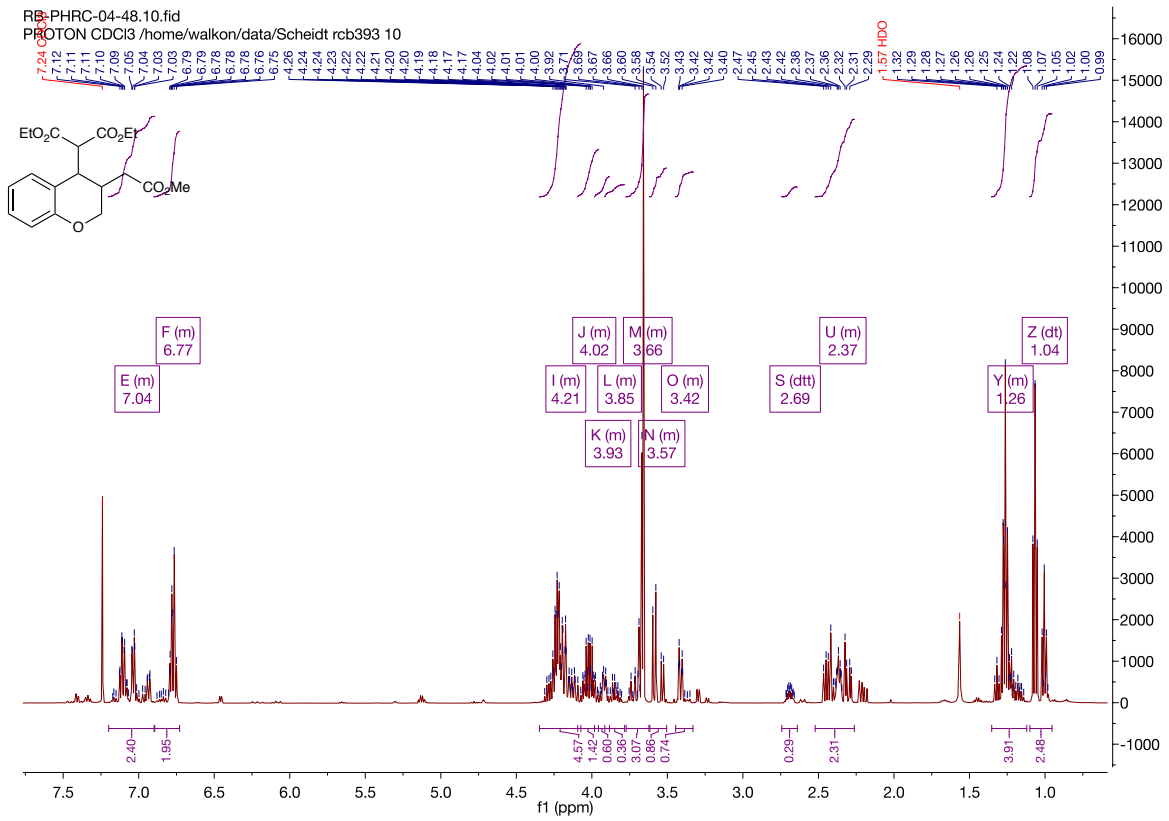


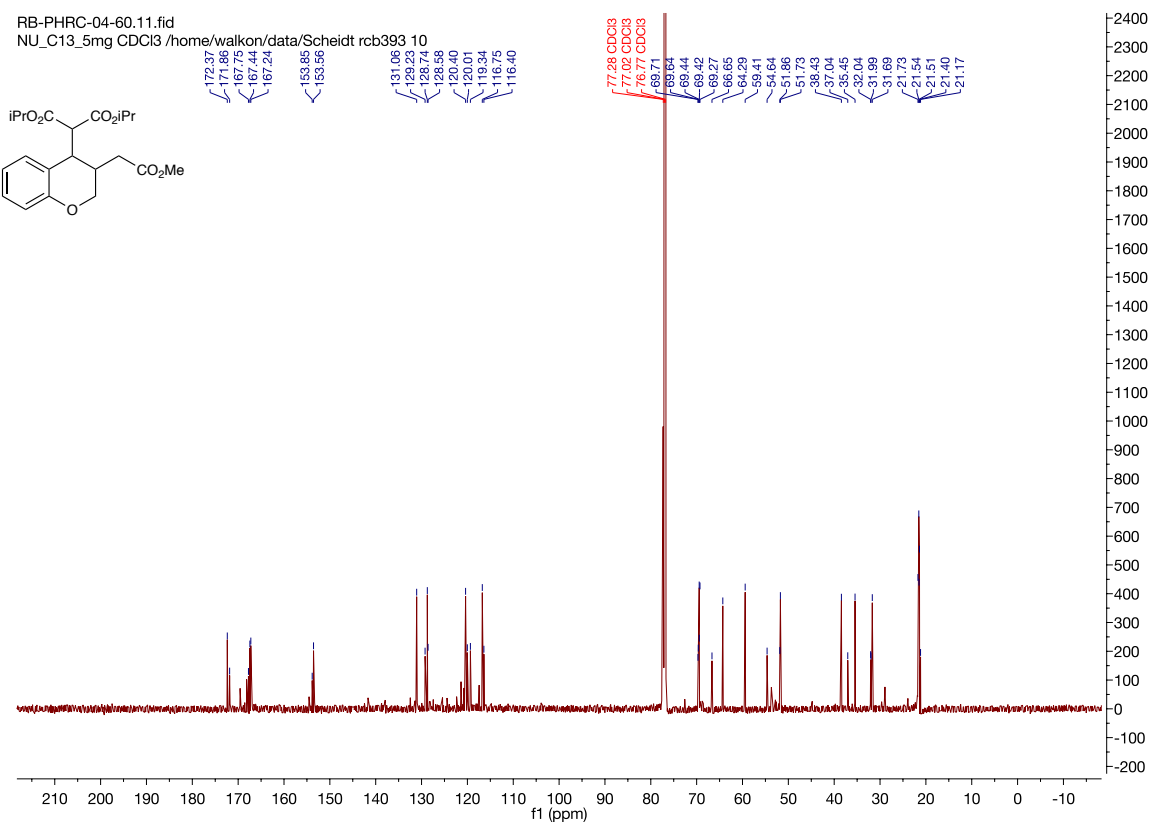
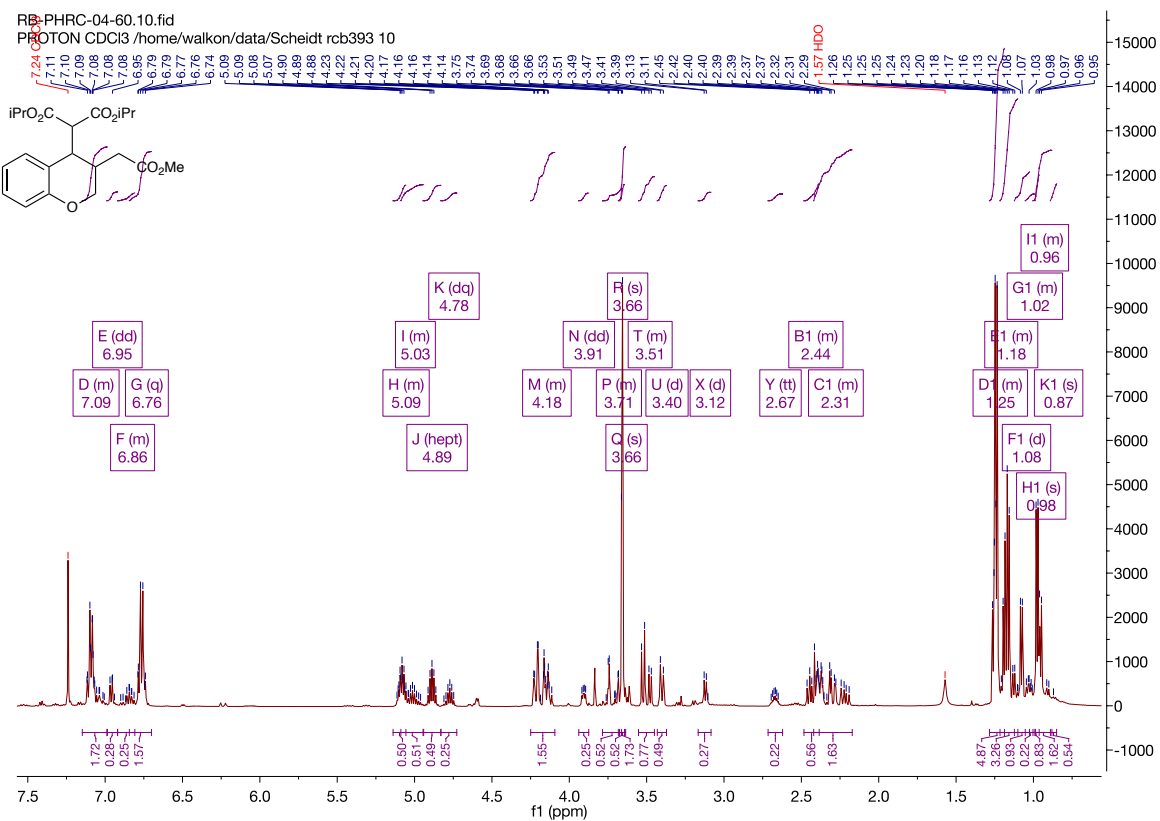


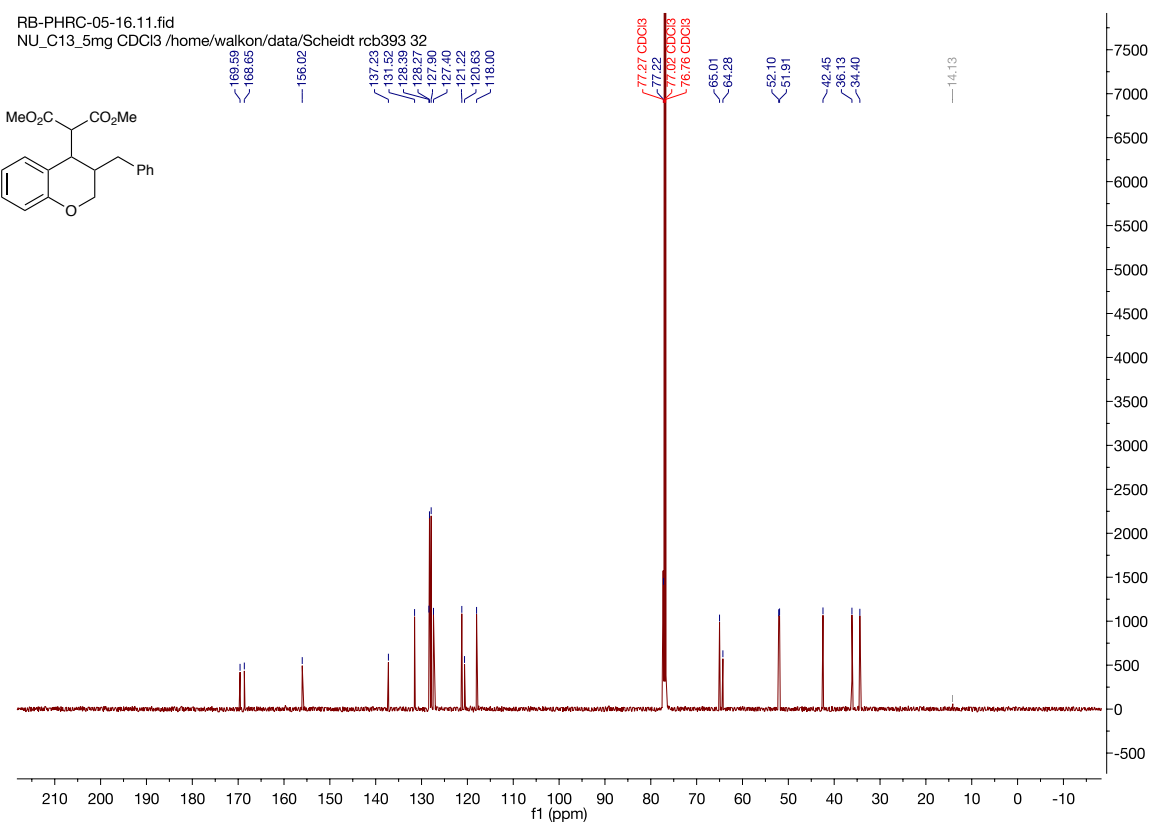
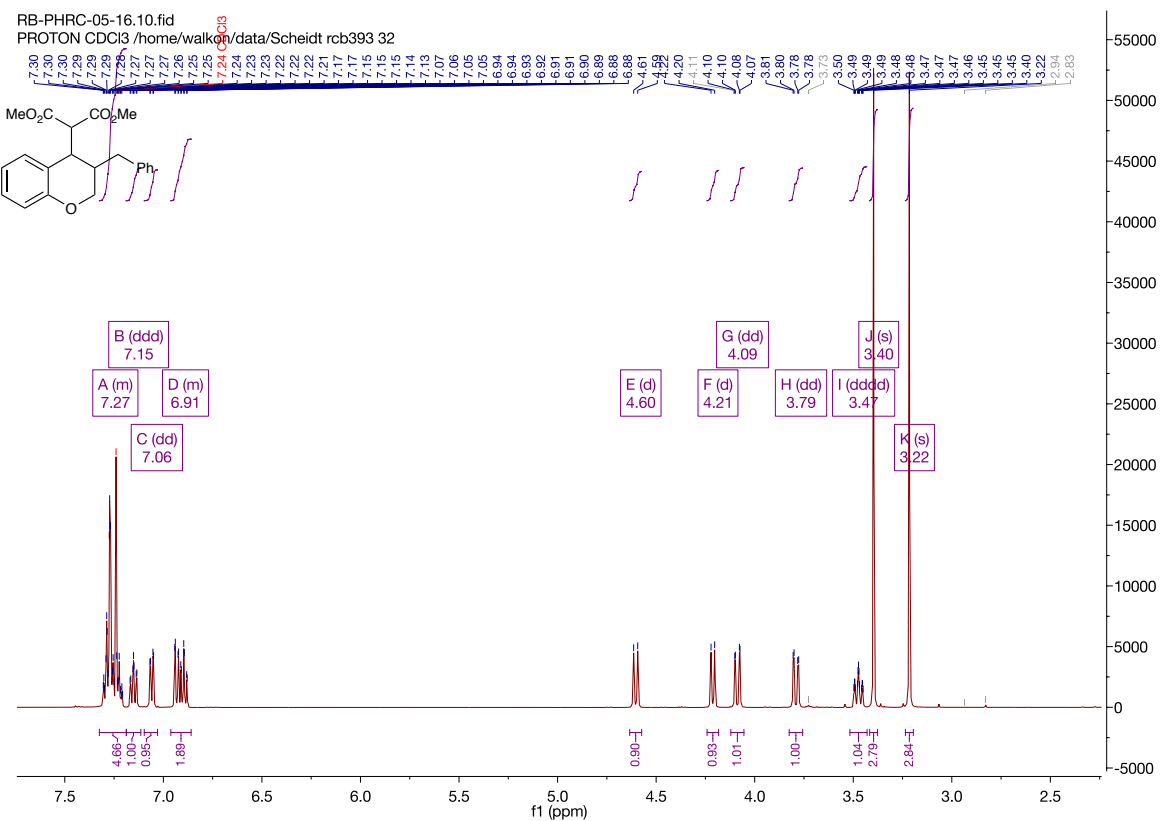


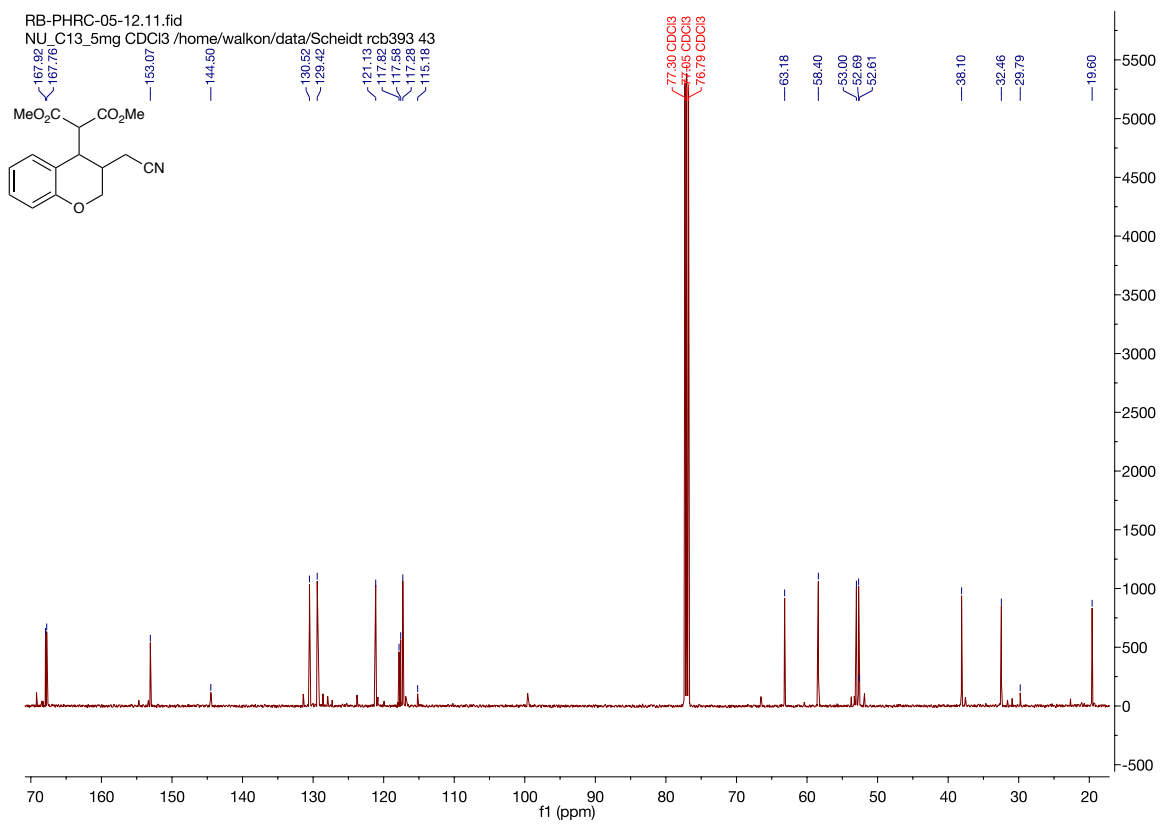
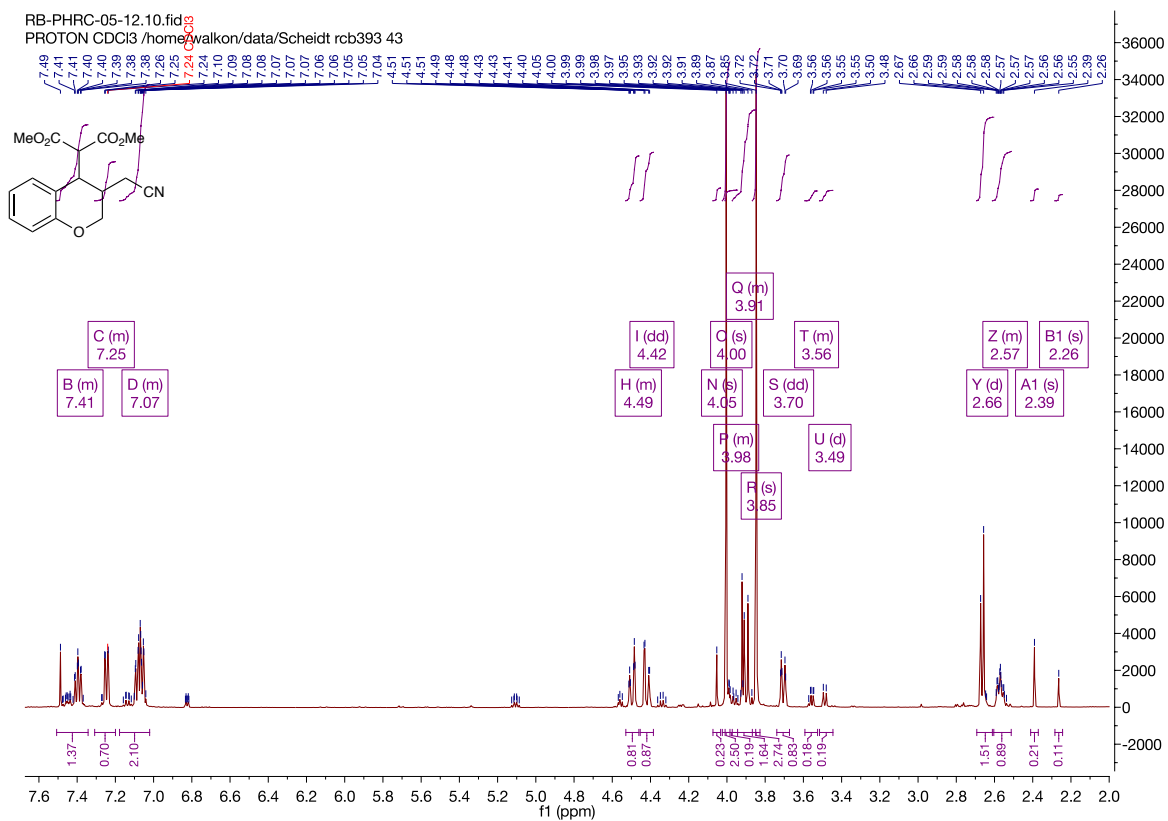


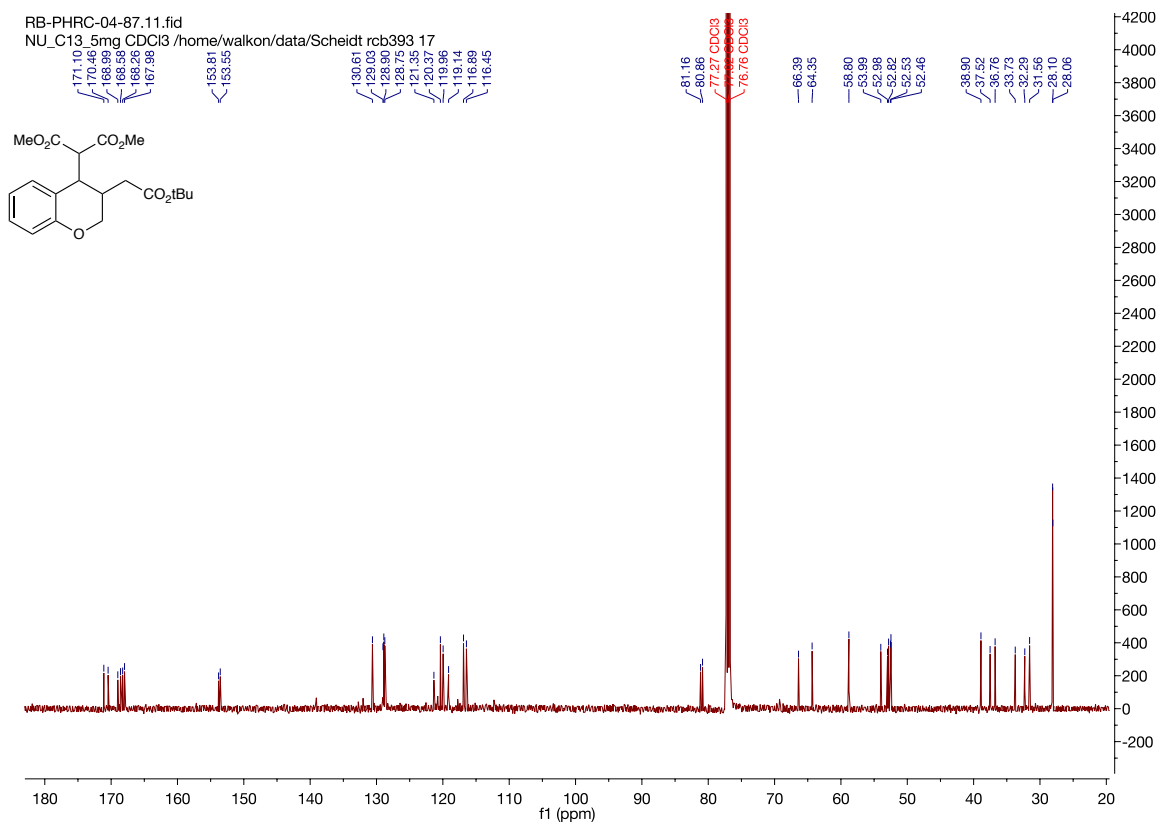
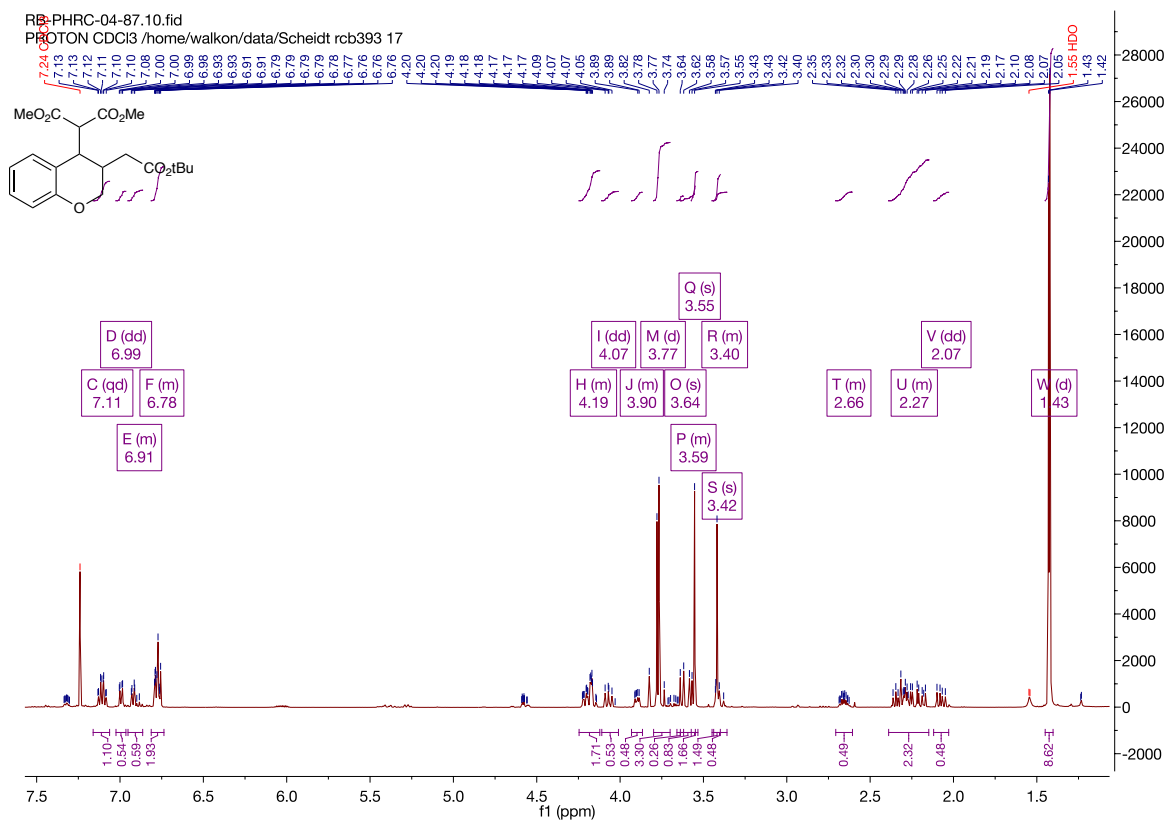


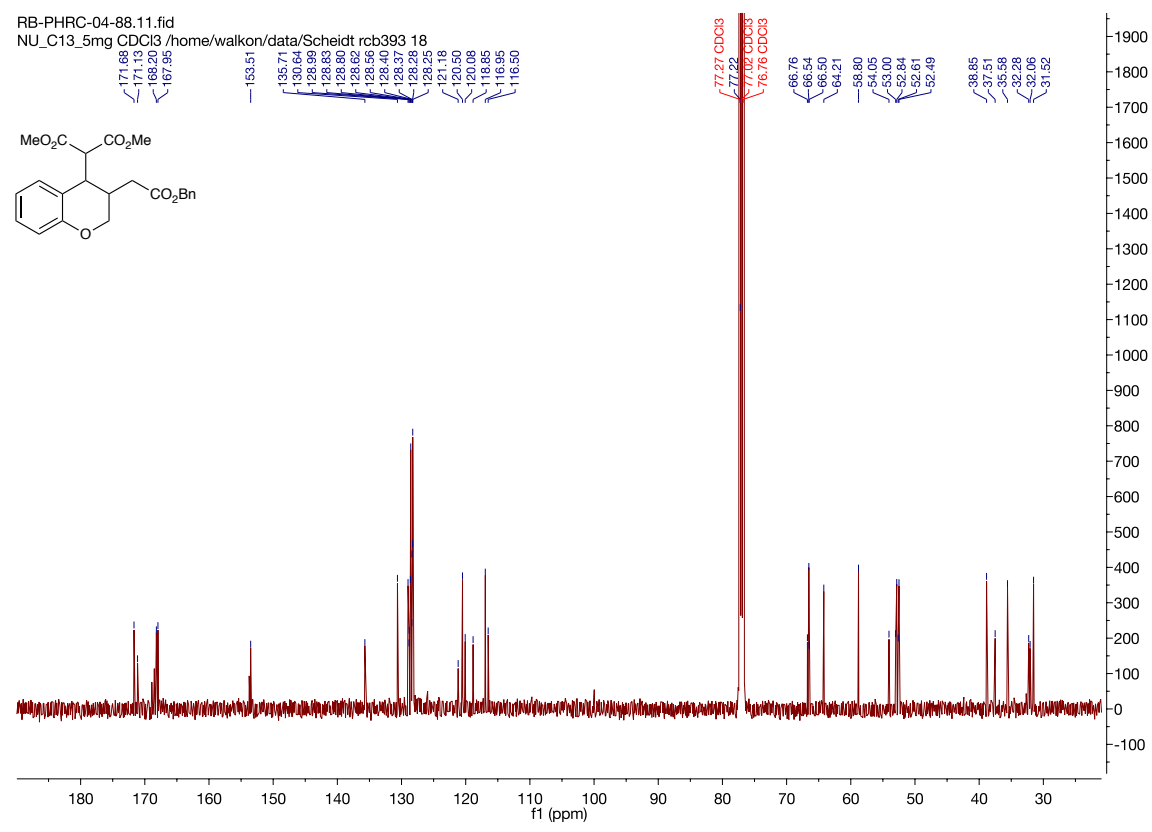
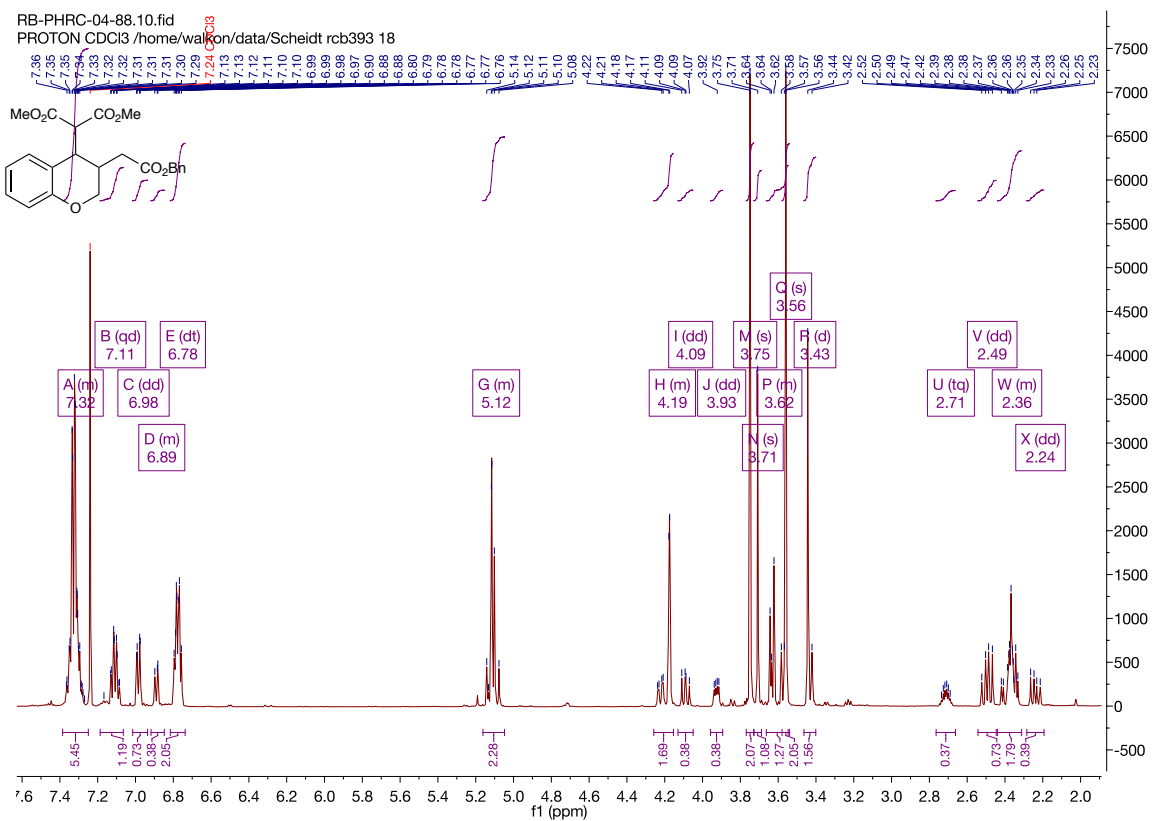


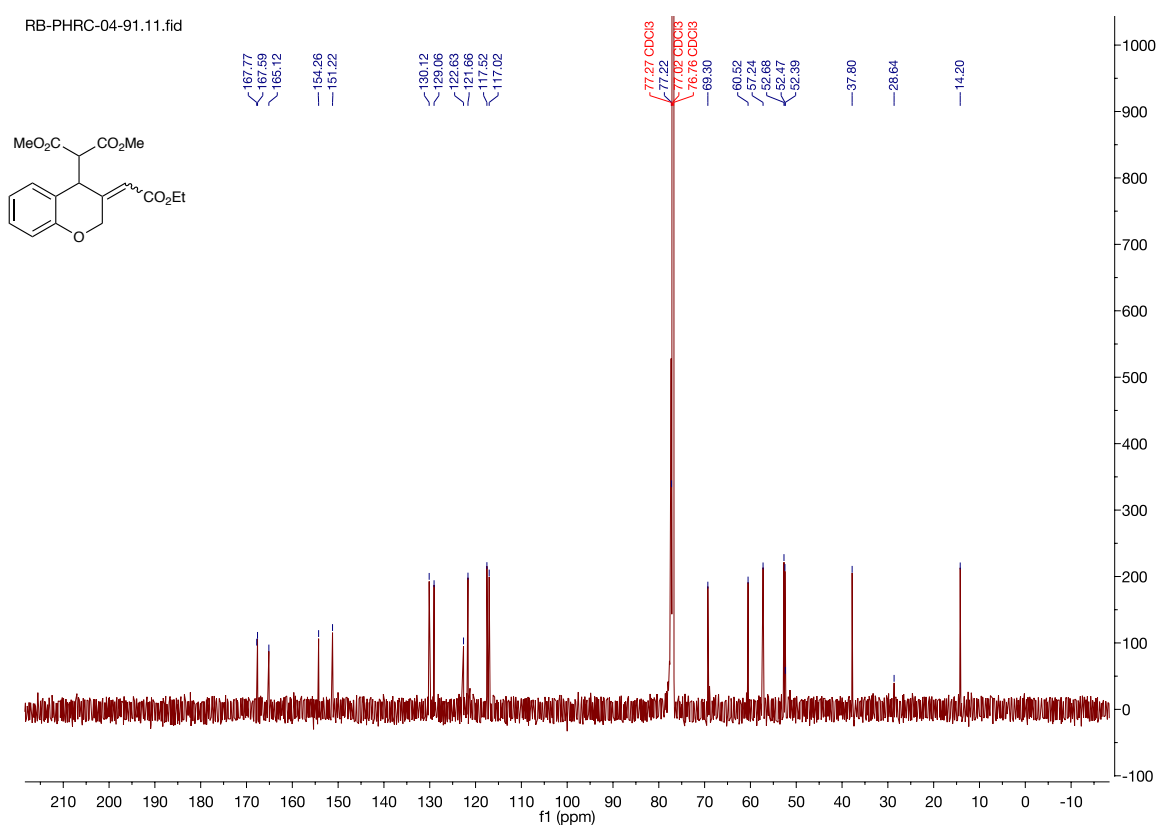
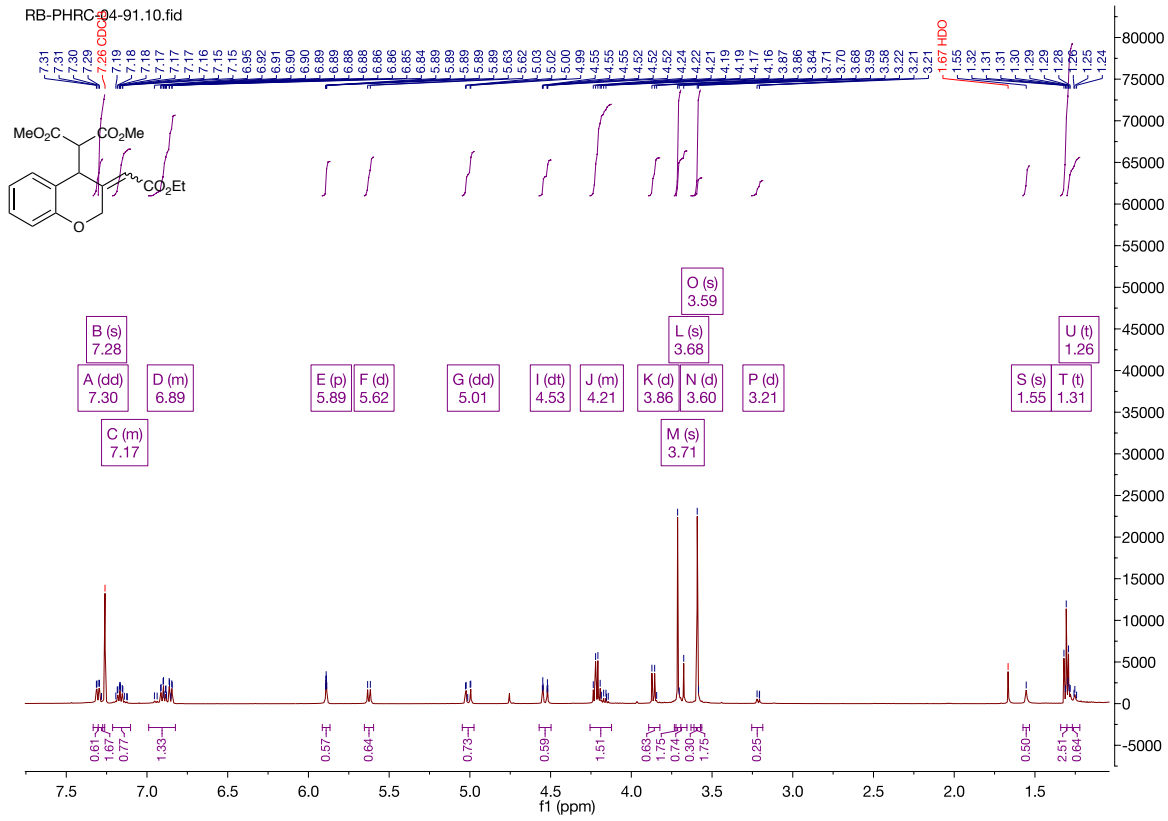


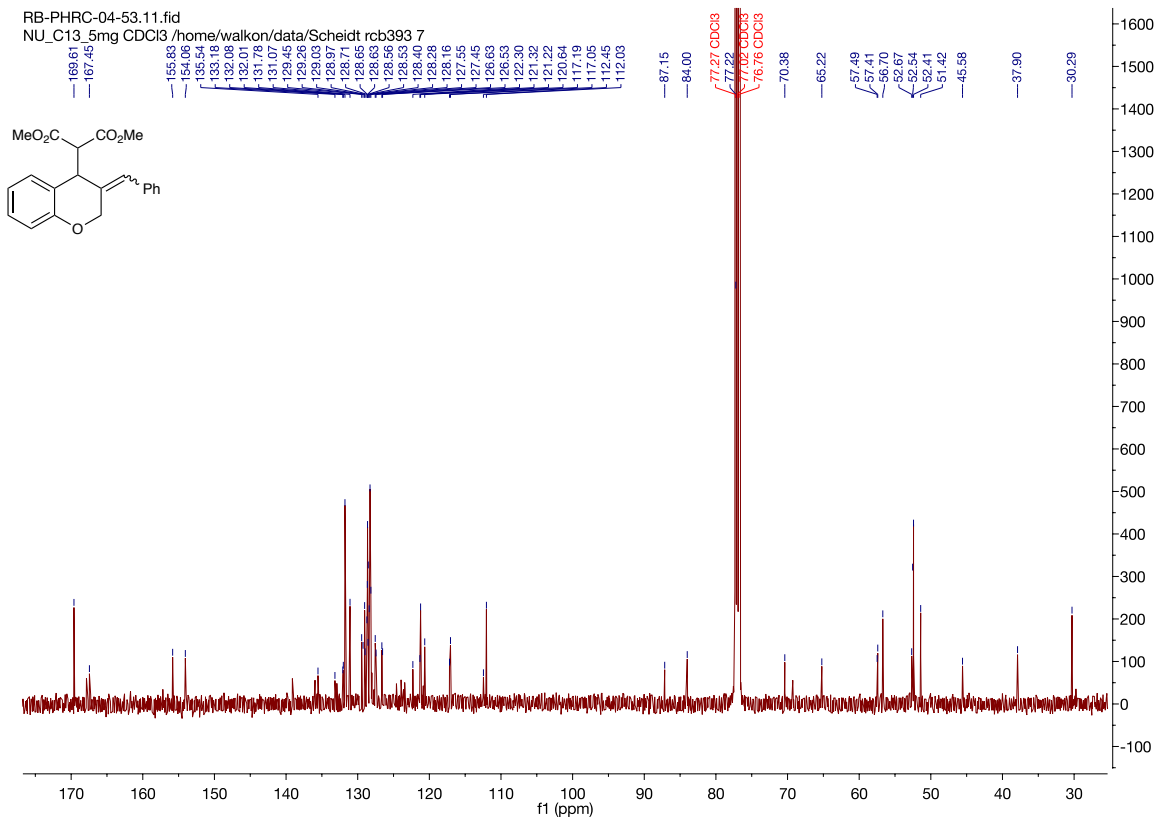
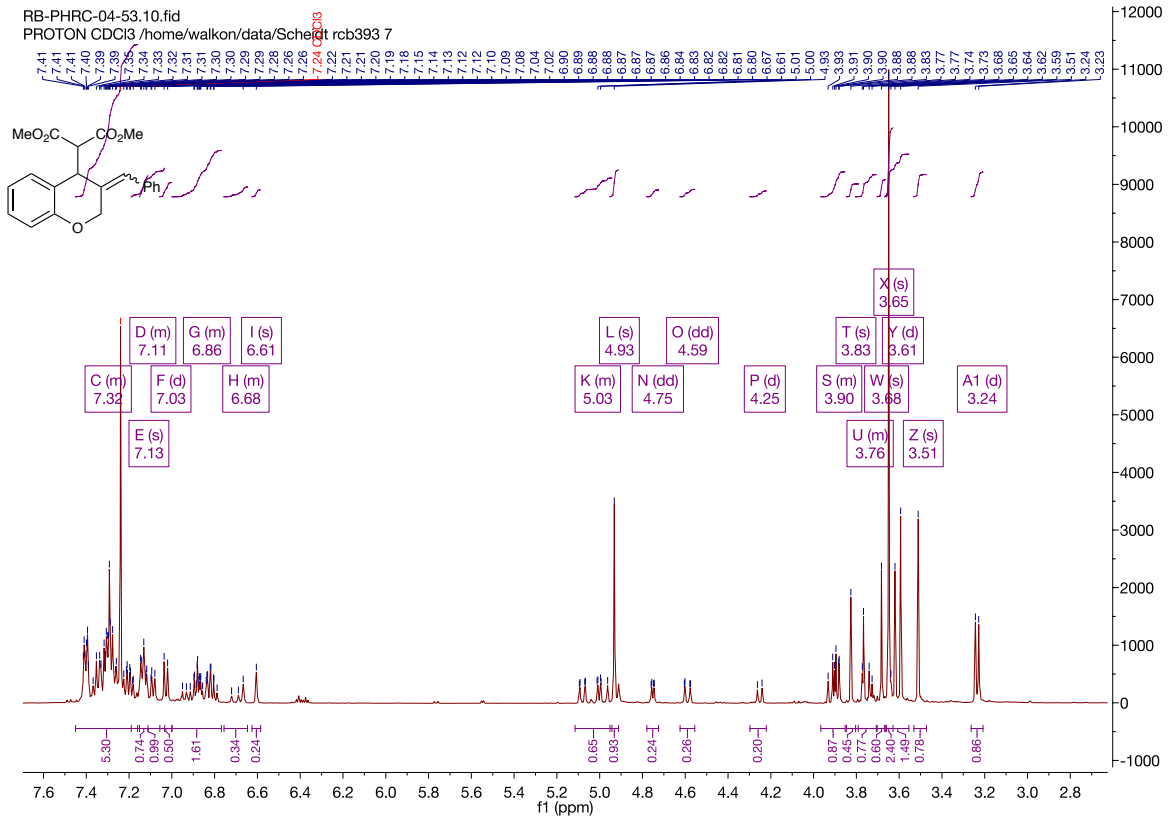


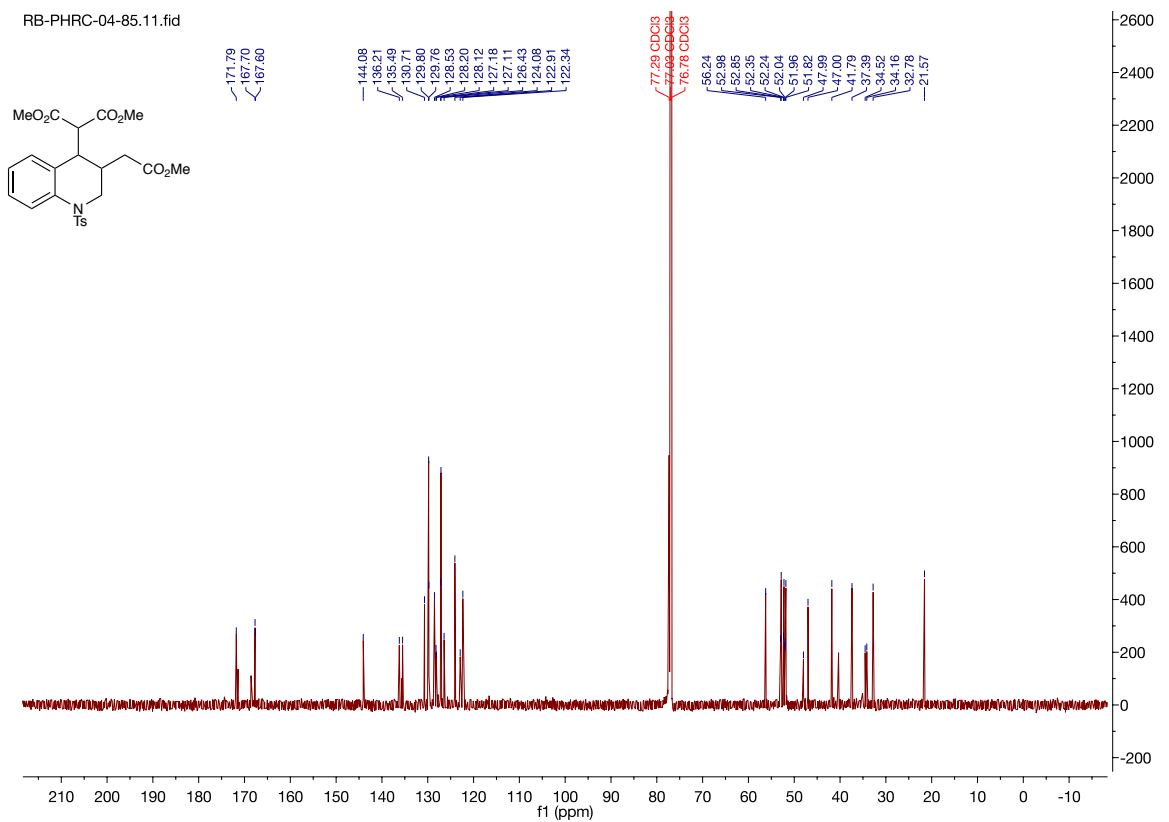
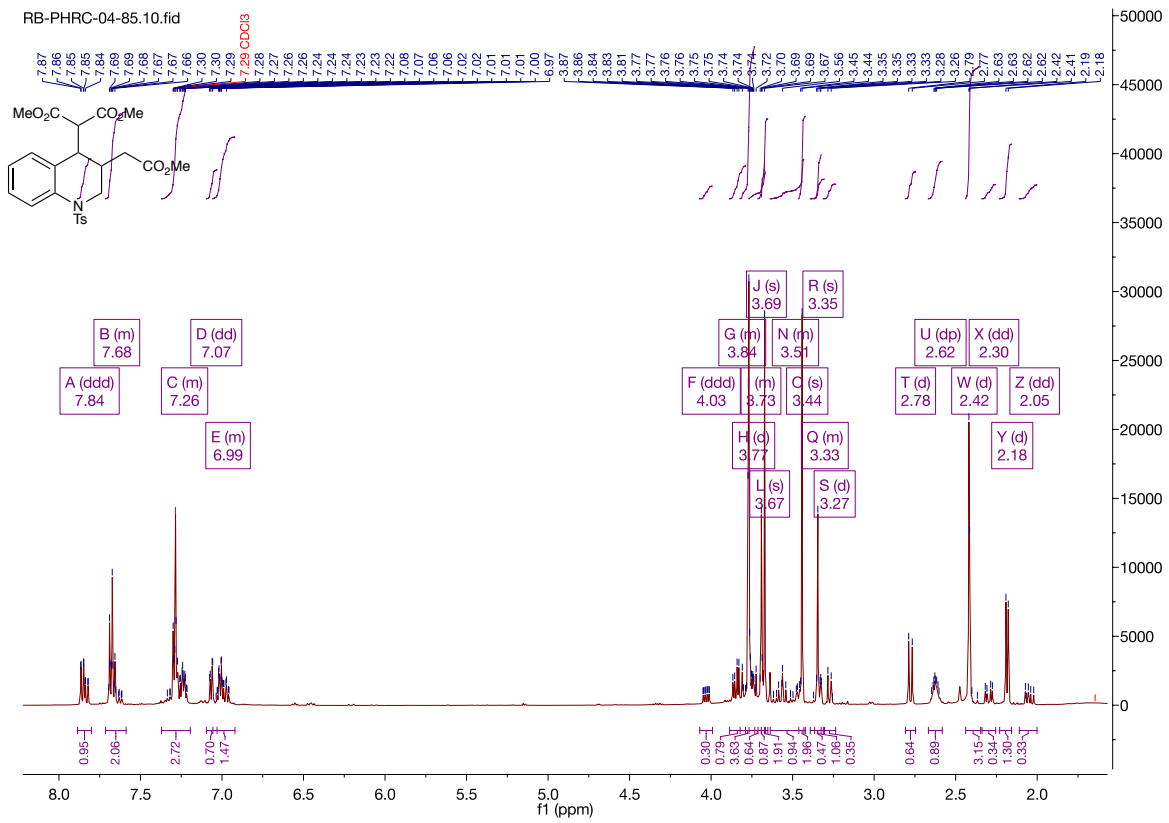


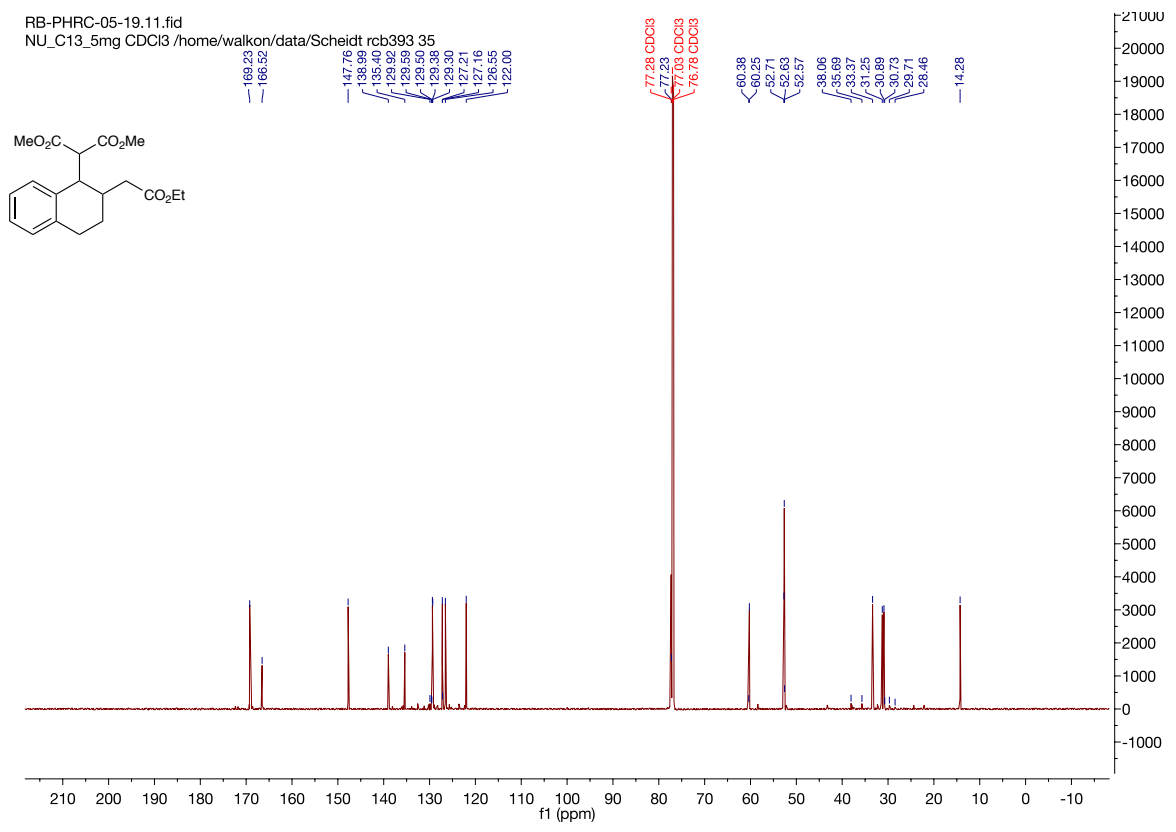
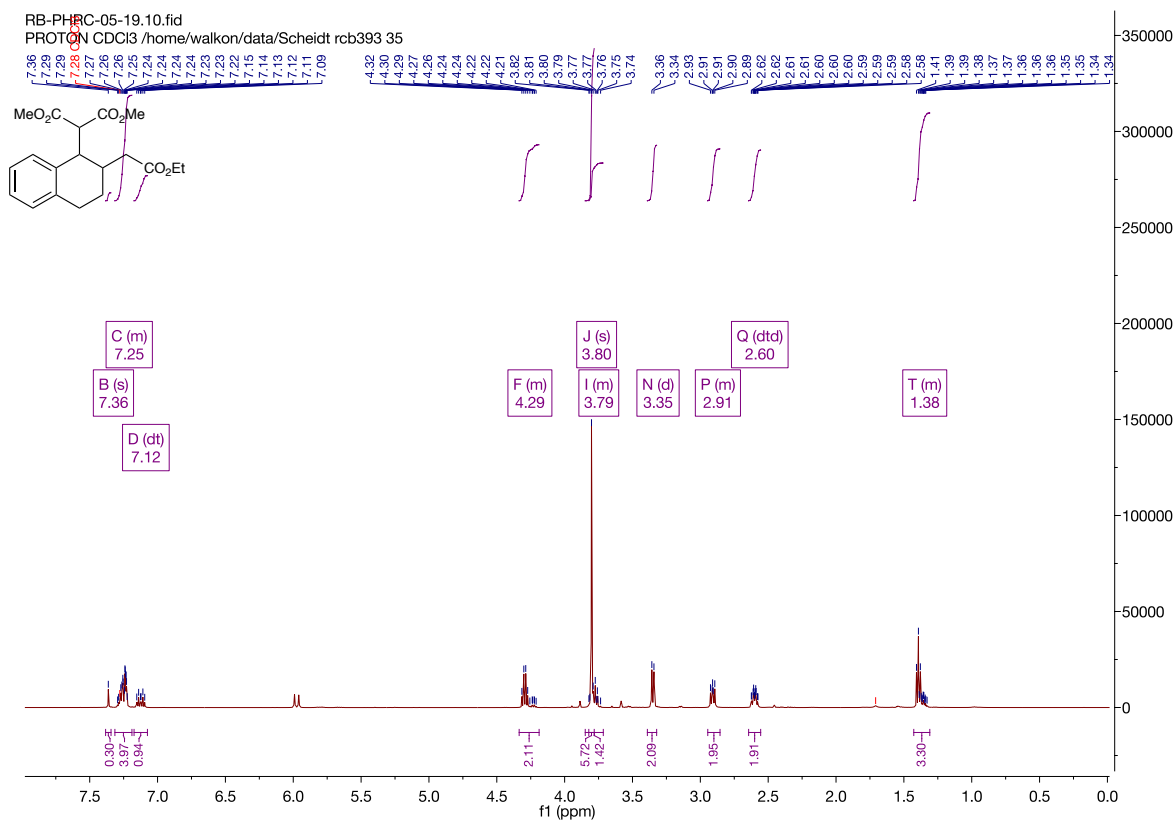


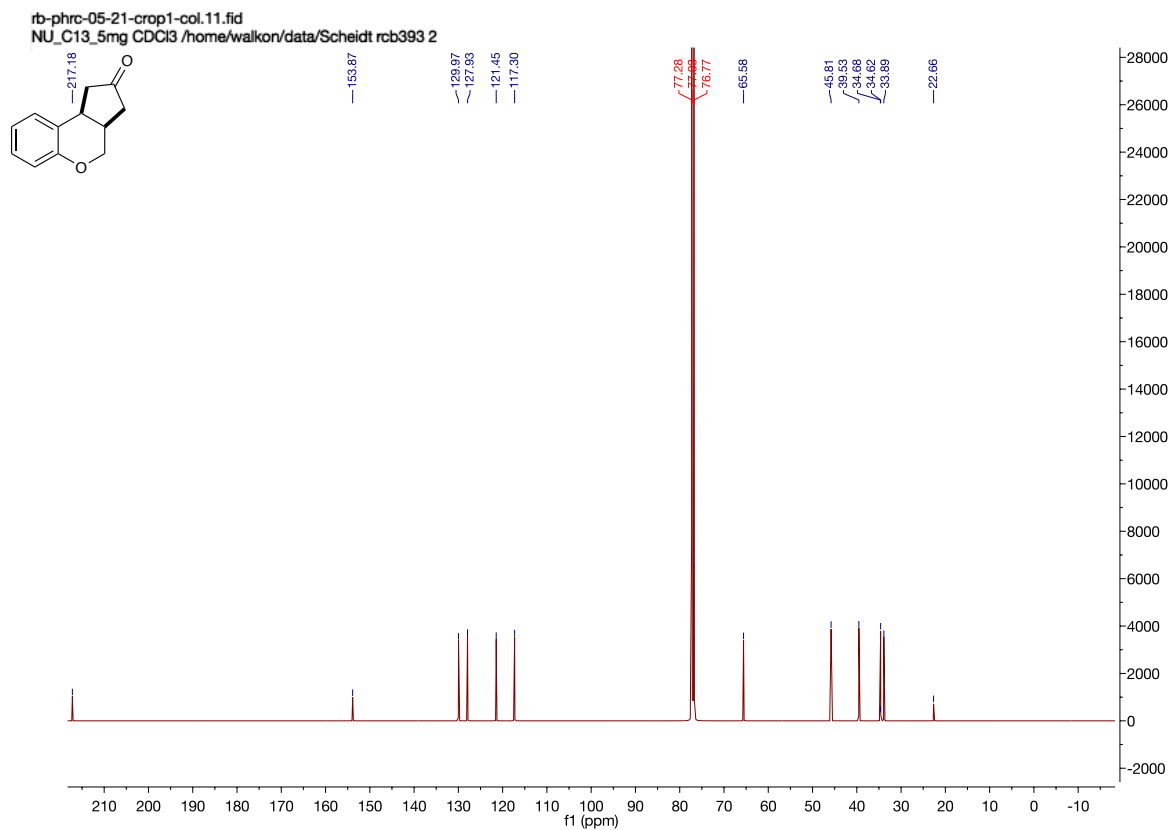
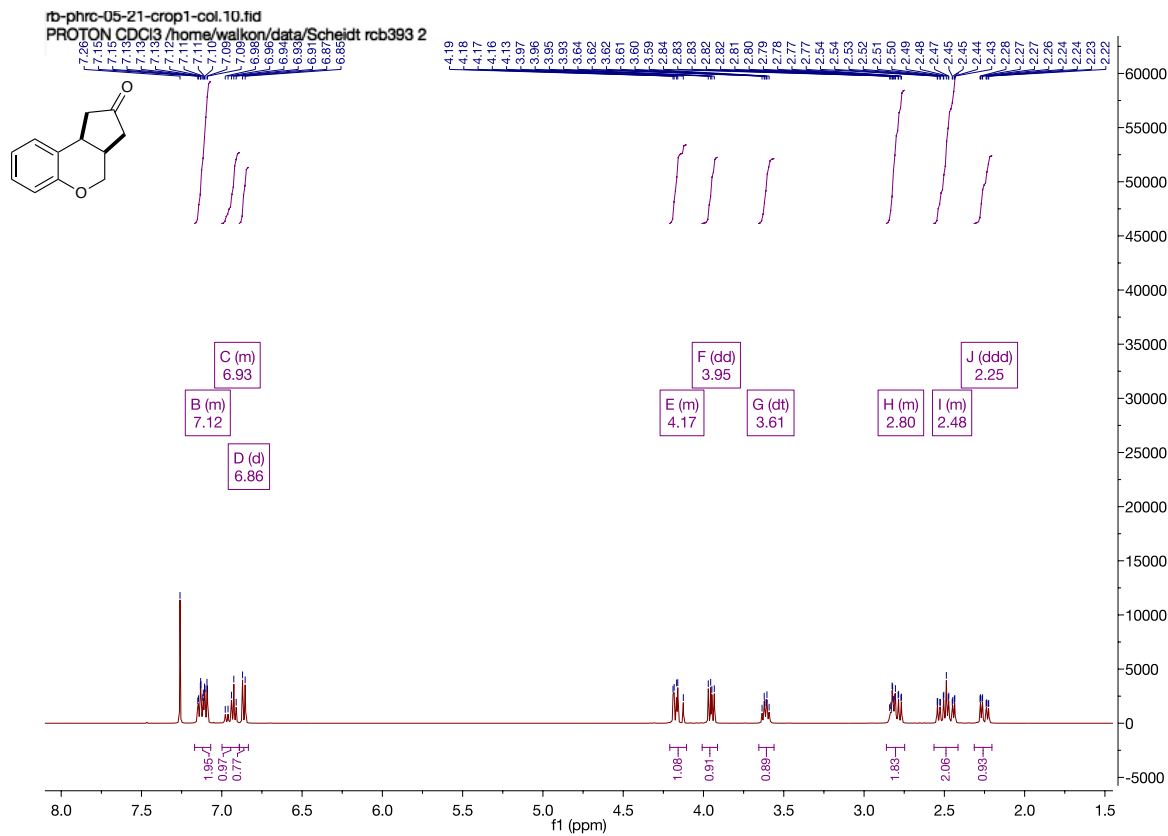












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