

Electronic Supplementary Information

Enantioselective Michael addition of malonates to β,γ -unsaturated α -ketoesters catalysed by Cu(II) complexes bearing binaphthyl-proline hybrid ligands

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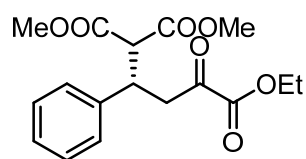
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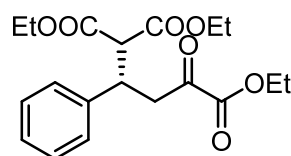
1. Experimental Data of Enantioselective Michael Addition Reactions

1,1-dimethyl 4-ethyl (2*S*)-4-oxo-2-phenylbutane-1,1,4-tricarboxylate (3a)



Yellow oil (93% yield, 92% ee); $[\alpha]_D^{20} = +14.2$ ($c = 0.80$, CH_2Cl_2); HPLC analysis Daicel Chiralcel AS-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (major) = 11.60 min, t (minor) = 12.91 min; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.17 (m, 5H), 4.18 (q, $J = 7.1$ Hz, 2H), 3.97 (td, $J = 9.2, 5.0$ Hz, 1H), 3.69 (m, 4H), 3.47 – 3.20 (m, 5H), 1.24 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 191.7, 168.4, 167.8, 160.5, 139.8, 128.6, 128.1, 127.5, 62.5, 57.0, 52.8, 52.4, 43.1, 40.0, 13.9. **HRMS (ESI)**: exact mass calcd for $\text{C}_{17}\text{H}_{20}\text{NaO}_7^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 359.1101, found m/z 359.1096.

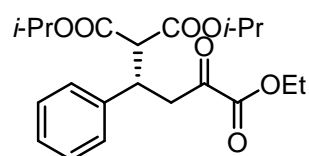
1,1-diethyl 4-ethyl (2*S*)-4-oxo-2-phenylbutane-1,1,4-tricarboxylate (3b)



Yellow oil (88% yield, 86% ee); $[\alpha]_D^{20} = +9.90$ ($c = 1.00$, CH_2Cl_2); HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (minor) = 9.00 min, t (major) = 10.82 min; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.18 (m, 5H), 4.31 – 4.14 (m, 4H), 4.03 (m, 1H), 3.93 (m, 2H), 3.73 (dd, $J = 10.2, 1.5$ Hz, 1H), 3.49 – 3.22 (m, 2H), 1.28 (m, 6H), 0.99 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 191.7, 168.1, 167.4, 160.5, 139.9, 128.5, 128.2, 127.4, 62.5, 61.8, 61.4, 57.3, 43.4, 40.0, 14.0, 13.9, 13.7.

Note: The absolute configuration of product 3b could be determined as (*S*)-configuration after comparing the sign of specific optical rotation with reference result (Org. Chem. Front., 2019,6, 2907-2915). This is also in agreement with the structure model in which Re-attack occurred during the reaction.¹

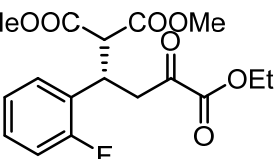
1,1-diisopropyl 4-ethyl (2*S*)-4-oxo-2-phenylbutane-1,1,4-tricarboxylate (3c)



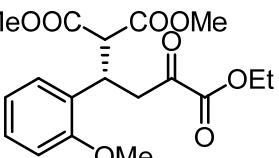
Yellow oil (89% yield, 90% ee); $[\alpha]_D^{20} = +16.2$ ($c = 0.90$, CH_2Cl_2); HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (minor) = 9.11 min, t (major) = 13.11 min; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.09 (m, 5H), 5.05 (m,

1H), 4.76 (pd, $J = 6.3, 1.6$ Hz, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 4.09 – 3.88 (m, 1H), 3.68 (dd, $J = 10.4, 1.6$ Hz, 1H), 3.51 – 3.09 (m, 2H), 1.30 (td, $J = 7.1, 1.6$ Hz, 3H), 1.24 (td, $J = 6.2, 1.6$ Hz, 6H), 1.03 (dd, $J = 6.3, 1.6$ Hz, 3H), 0.95 (dd, $J = 6.3, 1.6$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform- d) δ 191.7, 167.7, 166.9, 160.5, 139.9, 128.5, 128.4, 127.3, 69.4, 68.9, 62.4, 57.5, 43.7, 39.9, 21.6, 21.5, 21.3, 21.2, 13.9. **HRMS (ESI)**: exact mass calcd for $\text{C}_{21}\text{H}_{28}\text{NaO}_7^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 415.1727, found m/z 415.1723.

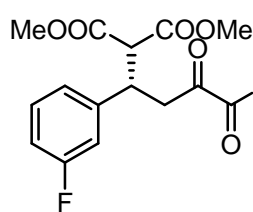
1,1-dimethyl 4-ethyl (2*S*)-2-(2-fluorophenyl)-4-oxobutane-1,1,4-tricarboxylate (3d)


 Yellow oil (85% yield, 82% ee); $[\alpha]_{\text{D}}^{20} = +10.72$ ($c = 0.80, \text{CH}_2\text{Cl}_2$);
 HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (major) = 8.84 min, t (minor) = 11.35 min; ^1H NMR (400 MHz, Chloroform- d) δ 7.32 – 7.16 (m, 2H), 7.12 – 6.82 (m, 2H), 4.36 – 4.10 (m, 3H), 3.95 (d, $J = 10.2$ Hz, 1H), 3.83 – 3.64 (m, 3H), 3.58 – 3.23 (m, 5H), 1.40 – 1.24 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform- d) δ 191.5, 168.3, 167.8, 162.2, 160.4, 159.7, 130.8, 130.7, 129.4, 129.3, 126.4, 126.3, 124.2, 124.2, 116.0, 115.7, 62.6, 55.1, 55.1, 52.8, 52.5, 41.8, 41.8, 35.6, 13.9. **HRMS (ESI)**: exact mass calcd for $\text{C}_{17}\text{H}_{19}\text{FNaO}_7^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 377.1007, found m/z 377.1003.

1,1-dimethyl 4-ethyl (*S*)-2-(2-methoxyphenyl)-4-oxobutane-1,1,4-tricarboxylate (3e)

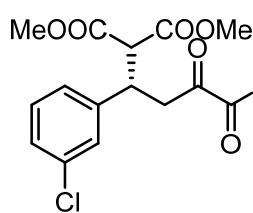

 Yellow oil (84% yield, 86% ee); $[\alpha]_{\text{D}}^{20} = +17.42$ ($c = 0.70, \text{CH}_2\text{Cl}_2$);
 HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (major) = 9.09 min, t (minor) = 11.68 min; ^1H NMR (400 MHz, Chloroform- d) δ 7.23 – 7.13 (m, 2H), 6.90 – 6.76 (m, 2H), 4.30 – 4.21 (m, 2H), 4.20 – 4.09 (m, 2H), 3.84 (s, 3H), 3.72 (s, 3H), 3.54 – 3.47 (m, 1H), 3.46 (s, 3H), 3.37 – 3.27 (m, 1H), 1.31 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform- d) δ 192.2, 168.9, 168.3, 160.6, 157.3, 130.5, 128.7, 127.0, 120.5, 110.9, 62.3, 55.2, 54.4, 52.6, 52.3, 41.3, 37.3, 13.9. **HRMS (ESI)**: exact mass calcd for $\text{C}_{18}\text{H}_{22}\text{NaO}_8^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 389.1207, found m/z 389.1210.

1,1-dimethyl 4-ethyl (*S*)-2-(3-fluorophenyl)-4-oxobutane-1,1,4-tricarboxylate (3f)



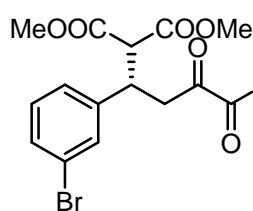
Yellow oil (87% yield, 86% ee); $[\alpha]_{\text{D}}^{20} = +4.88$ ($c = 1.00$, CH_2Cl_2); HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (major) = 8.84 min, t (minor) = 11.35 min; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.20 – 7.14 (m, 1H), 6.97 (d, $J = 7.7$ Hz, 1H), 6.93 – 6.78 (m, 2H), 4.20 (q, $J = 7.1$ Hz, 2H), 3.97 (td, $J = 9.2, 5.0$ Hz, 1H), 3.74 – 3.60 (m, 4H), 3.46 (s, 3H), 3.30 (m, 2H), 1.26 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 191.3, 168.2, 167.6, 163.9, 161.5, 160.4, 142.4, 142.3, 130.2, 130.1, 123.8, 123.8, 115.2, 115.0, 114.6, 114.4, 62.6, 56.7, 52.8, 52.6, 42.9, 39.6, 13.9. **HRMS (ESI)**: exact mass calcd for $\text{C}_{17}\text{H}_{19}\text{FNaO}_7^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 377.1007, found m/z 377.1005.

1,1-dimethyl 4-ethyl (*S*)-2-(3-chlorophenyl)-4-oxobutane-1,1,4-tricarboxylate (3g)



Yellow oil (90% yield, 91% ee); $[\alpha]_{\text{D}}^{20} = +20.84$ ($c = 1.60$, CH_2Cl_2); HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (major) = 8.37 min, t (minor) = 10.75 min; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.26 – 7.12 (m, 4H), 4.27 (m, 2H), 4.01 (m, 1H), 3.79 – 3.69 (m, 4H), 3.54 (s, 3H), 3.45 – 3.29 (m, 2H), 1.33 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 191.3, 168.2, 167.6, 160.3, 141.9, 134.4, 129.9, 128.2, 127.7, 126.4, 62.7, 56.6, 52.9, 52.6, 42.8, 39.5, 13.9. **HRMS (ESI)**: exact mass calcd for $\text{C}_{17}\text{H}_{19}\text{ClNaO}_7^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 393.0712, found m/z 393.0709.

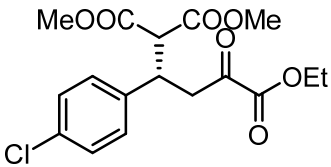
1,1-dimethyl 4-ethyl (*S*)-2-(3-bromophenyl)-4-oxobutane-1,1,4-tricarboxylate (3h)



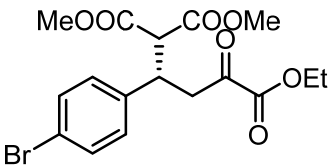
Yellow oil (94% yield, 92% ee); $[\alpha]_{\text{D}}^{20} = +9.46$ ($c = 1.00$, CH_2Cl_2); HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (major) = 8.91 min, t (minor) = 11.64 min; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.40 (t, $J = 1.8$ Hz, 1H), 7.35 (m, 1H), 7.22 – 7.13 (m, 2H), 4.28 (td, $J = 7.2, 1.1$ Hz, 2H), 4.00 (m, 1H), 3.76 – 3.71 (m, 4H), 3.54 (s, 3H), 3.44 – 3.30 (m, 2H), 1.33 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 191.3, 168.2, 167.6, 160.4, 142.2, 131.2, 130.7, 130.2, 126.9, 122.6, 62.7, 56.7, 52.9,

52.6, 42.8, 39.5, 13.9. **HRMS (ESI)**: exact mass calcd for $C_{17}H_{19}BrNaO_7^+$ ($M+Na$)⁺ requires m/z 437.0206, found m/z 437.0204.

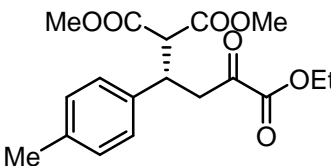
1,1-dimethyl 4-ethyl (*S*)-2-(4-chlorophenyl)-4-oxobutane-1,1,4-tricarboxylate (3i)

 Yellow oil (95% yield, 90% ee); $[\alpha]_D^{20} = +15.49$ ($c = 1.00$, CH_2Cl_2); HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $T = 25^\circ C$, UV = 210 nm; t (minor) = 11.59 min, t (major) = 12.52 min; 1H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.03 (m, 4H), 4.40 – 4.16 (m, 2H), 4.02 (m, 1H), 3.85 – 3.62 (m, 4H), 3.52 (s, 3H), 3.44 – 3.27 (m, 2H), 1.32 (t, $J = 7.2$ Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 191.4, 168.2, 167.6, 160.4, 138.3, 133.3, 129.5, 128.8, 62.6, 56.7, 52.9, 52.6, 43.0, 39.3, 13.9. **HRMS (ESI)**: exact mass calcd for $C_{17}H_{19}ClNaO_7^+$ ($M+Na$)⁺ requires m/z 393.0712, found m/z 393.0706.

1,1-dimethyl 4-ethyl (*S*)-2-(4-bromophenyl)-4-oxobutane-1,1,4-tricarboxylate (3j)

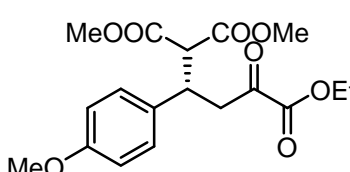
 Yellow oil (92% yield, 90% ee); $[\alpha]_D^{20} = +14.63$ ($c = 1.00$, CH_2Cl_2); HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $T = 25^\circ C$, UV = 210 nm; t (minor) = 12.66 min, t (major) = 13.77 min; 1H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.37 (m, 2H), 7.17 – 7.10 (m, 2H), 4.26 (m, 2H), 4.00 (m, 1H), 3.76 – 3.70 (m, 4H), 3.52 (s, 3H), 3.44 – 3.27 (m, 2H), 1.32 (t, $J = 7.2$ Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 191.4, 168.2, 167.6, 160.4, 138.8, 131.8, 129.9, 121.5, 62.7, 56.6, 52.9, 52.6, 42.9, 39.4, 13.9. **HRMS (ESI)**: exact mass calcd for $C_{17}H_{19}BrNaO_7^+$ ($M+Na$)⁺ requires m/z 437.0206, found m/z 437.0202.

1,1-dimethyl 4-ethyl (*S*)-2-(4-methylphenyl)-4-oxobutane-1,1,4-tricarboxylate (3k)

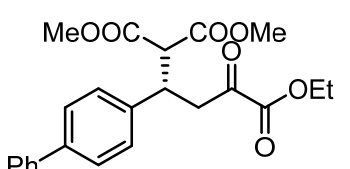
 Yellow oil (90% yield, 91% ee); $[\alpha]_D^{20} = +33.63$ ($c = 1.00$, CH_2Cl_2); HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, $T = 25^\circ C$, UV = 210 nm; t (major) = 15.87 min, t (minor) = 17.03 min; 1H NMR (400 MHz, Chloroform-*d*) δ 7.12 (d, $J = 8.2$ Hz, 2H), 7.07 (d, $J = 8.0$ Hz, 2H), 4.24 (m, 2H), 4.00 (td, $J = 9.2, 5.0$ Hz, 1H), 3.75 (d, $J = 13.1$ Hz, 4H), 3.43

– 3.26 (m, 2H), 2.28 (s, 3H), 1.31 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform- d) δ 191.8, 168.5, 167.9, 160.5, 137.1, 136.7, 129.3, 127.9, 62.5, 57.1, 52.7, 52.5, 43.2, 39.6, 21.0, 13.9. **HRMS (ESI)**: exact mass calcd for $\text{C}_{18}\text{H}_{22}\text{NaO}_7^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 373.1258, found m/z 373.1253.

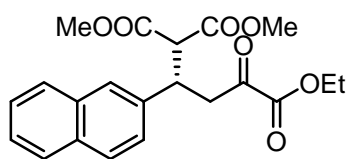
1,1-dimethyl 4-ethyl (*S*)-2-(4-methoxyphenyl)-4-oxobutane-1,1,4-tricarboxylate (3l)

 Yellow oil (87% yield, 90% ee); $[\alpha]_{\text{D}}^{20} = +9.92$ ($c = 0.80$, CH_2Cl_2); HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (minor) = 14.08 min, t (major) = 16.04 min; ^1H NMR (400 MHz, Chloroform- d) δ 7.16 (d, $J = 8.2$ Hz, 2H), 6.80 (d, $J = 8.3$ Hz, 2H), 4.25 (q, $J = 7.1$ Hz, 2H), 3.99 (td, $J = 9.4, 4.9$ Hz, 1H), 3.82 – 3.66 (m, 7H), 3.51 (s, 3H), 3.43 – 3.25 (m, 2H), 1.31 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform- d) δ 191.8, 168.5, 167.9, 160.5, 158.8, 131.6, 129.1, 114.0, 62.5, 57.2, 55.2, 52.7, 52.5, 43.3, 39.3, 13.9. **HRMS (ESI)**: exact mass calcd for $\text{C}_{18}\text{H}_{22}\text{NaO}_8^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 389.1207, found m/z 389.1202.

1,1-dimethyl 4-ethyl (*S*)-2-(biphenyl-4-yl)-4-oxobutane-1,1,4-tricarboxylate (3m)

 Yellow oil (84% yield, 89% ee); $[\alpha]_{\text{D}}^{20} = +12.4$ ($c = 0.70$, CH_2Cl_2); HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (minor) = 15.32 min, t (major) = 19.43 min; ^1H NMR (400 MHz, Chloroform- d) δ 7.57 – 7.48 (m, 4H), 7.41 (dd, $J = 8.5, 6.8$ Hz, 2H), 7.37 – 7.27 (m, 3H), 4.25 (m, 2H), 4.09 (td, $J = 9.3, 5.0$ Hz, 1H), 3.82 (d, $J = 9.8$ Hz, 1H), 3.75 (s, 3H), 3.57 – 3.43 (m, 4H), 3.35 (dd, $J = 18.1, 5.0$ Hz, 1H), 1.31 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform- d) δ 191.7, 168.4, 167.9, 160.5, 140.5, 140.3, 138.8, 128.8, 128.5, 127.4, 127.3, 127.0, 62.6, 56.9, 52.8, 52.5, 43.1, 39.6, 13.9. **HRMS (ESI)**: exact mass calcd for $\text{C}_{23}\text{H}_{24}\text{NaO}_7^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 435.1414, found m/z 435.1411.

1,1-dimethyl 4-ethyl (*S*)-2-(2-naphthalenyl)-4-oxobutane-1,1,4-tricarboxylate (**3n**)

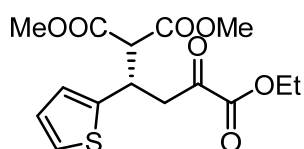


Yellow oil (93% yield, 90% ee); $[\alpha]_{\text{D}}^{20} = +11.8$ ($c = 1.00$, CH_2Cl_2);

HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (major) =

14.95 min, t (minor) = 16.87 min; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.78 (dd, $J = 8.2, 3.4$ Hz, 3H), 7.70 (d, $J = 2.0$ Hz, 1H), 7.50 – 7.41 (m, 2H), 7.38 (dd, $J = 8.6, 1.9$ Hz, 1H), 4.21 (m, 3H), 3.90 (d, $J = 10.1$ Hz, 1H), 3.75 (s, 3H), 3.54 (dd, $J = 18.0, 8.8$ Hz, 1H), 3.49 – 3.31 (m, 4H), 1.26 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 191.7, 168.5, 167.8, 160.5, 137.3, 133.3, 132.7, 128.4, 127.9, 127.6, 127.1, 126.2, 126.0, 125.9, 62.5, 57.0, 52.8, 52.5, 43.1, 40.1, 13.9. **HRMS (ESI)**: exact mass calcd for $\text{C}_{21}\text{H}_{22}\text{NaO}_7^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 409.1258, found m/z 409.1255.

1,1-dimethyl 4-ethyl (*S*)-2-(2-thiophenyl)-4-oxobutane-1,1,4-tricarboxylate (**3o**)

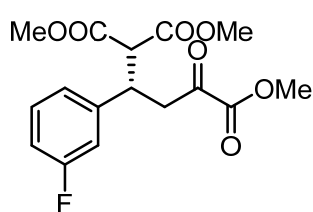


Yellow oil (96% yield, 92% ee); $[\alpha]_{\text{D}}^{20} = +18.86$ ($c = 1.60$, CH_2Cl_2);

HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (major) = 9.78

min, t (minor) = 11.48 min; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.15 (dd, $J = 5.1, 1.3$ Hz, 1H), 6.92 (dd, $J = 3.6, 1.4$ Hz, 1H), 6.88 (dd, $J = 5.0, 3.5$ Hz, 1H), 4.37 (td, $J = 8.7, 4.8$ Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 3.81 (d, $J = 8.9$ Hz, 1H), 3.74 (d, $J = 1.4$ Hz, 3H), 3.61 (d, $J = 1.4$ Hz, 3H), 3.53 – 3.34 (m, 2H), 1.34 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 191.3, 168.1, 167.7, 160.4, 142.7, 126.7, 126.0, 124.6, 62.6, 57.4, 52.8, 52.7, 43.8, 35.2, 13.9. **HRMS (ESI)**: exact mass calcd for $\text{C}_{15}\text{H}_{18}\text{NaO}_7\text{S}^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 365.0665, found m/z 365.0663.

Trimethyl (*S*)-2-(3-fluorophenyl)-4-oxobutane-1,1,4-tricarboxylate (**3aa**)²



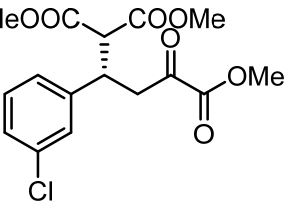
Yellow oil (92% yield, 83% ee); $[\alpha]_{\text{D}}^{20} = +4.88$ ($c = 1.00$, CH_2Cl_2);

HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (major) = 9.86 min, t (minor) = 13.25 min; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ

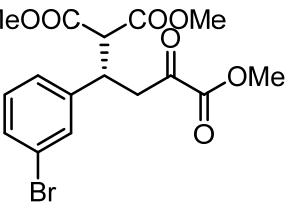
7.27 – 7.22 (m, 1H), 7.04 (m, 1H), 7.00 – 6.88 (m, 2H), 4.04 (td, $J = 9.1, 5.2$ Hz, 1H), 3.82 (s, 3H), 3.75 (d, $J = 8.7$ Hz, 4H), 3.53 (s, 3H), 3.46 – 3.31 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*)

δ 190.9, 168.2, 167.6, 164.0, 161.5, 160.8, 142.4, 142.3, 130.2, 130.1, 123.8, 123.7, 115.2, 115.0, 114.6, 114.4, 56.7, 53.1, 52.8, 52.6, 43.0, 39.5.

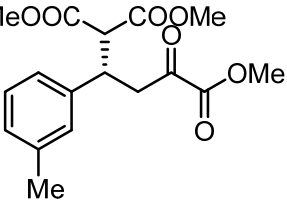
Trimethyl (*S*)-2-(3-chlorophenyl)-4-oxobutane-1,1,4-tricarboxylate (3ab)²

 Yellow oil (92% yield, 90% ee); $[\alpha]_{\text{D}}^{20} = +8.96$ ($c = 0.80$, CH_2Cl_2); HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (major) = 9.71 min, t (minor) = 12.94 min; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.13 (m, 4H), 4.01 (m, 1H), 3.83 (s, 3H), 3.74 (d, $J = 5.6$ Hz, 4H), 3.54 (s, 3H), 3.46 – 3.30 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 190.9, 168.2, 167.6, 160.7, 141.9, 134.4, 129.9, 128.2, 127.8, 126.4, 56.6, 53.1, 52.9, 52.6, 42.9, 39.5.

Trimethyl (*S*)-2-(3-bromophenyl)-4-oxobutane-1,1,4-tricarboxylate (3ac)³

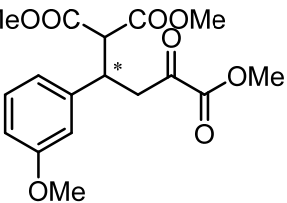
 Yellow oil (90% yield, 91% ee); $[\alpha]_{\text{D}}^{20} = +14.4$ ($c = 1.20$, CH_2Cl_2); HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (major) = 9.58 min, t (minor) = 11.99 min; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.32 (m, 2H), 7.23 – 7.11 (m, 2H), 4.06 – 3.95 (m, 1H), 3.83 (s, 3H), 3.73 (d, $J = 6.6$ Hz, 4H), 3.54 (s, 3H), 3.46 – 3.30 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 190.9, 168.2, 167.6, 160.7, 142.2, 131.1, 130.7, 130.2, 126.9, 122.6, 56.6, 53.1, 52.9, 52.6, 42.9, 39.4.

Trimethyl (*S*)-2-(3-methylphenyl)-4-oxobutane-1,1,4-tricarboxylate (3ad)⁴

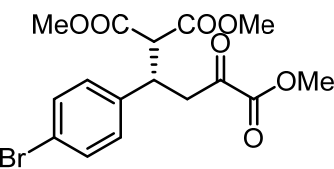
 Yellow oil (93% yield, 90% ee); $[\alpha]_{\text{D}}^{20} = +16.82$ ($c = 0.50$, CH_2Cl_2); HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (major) = 10.01 min, t (minor) = 12.19 min; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.19 – 7.13 (t, $J = 7.5$ Hz, 1H), 7.11 – 6.96 (dd, $J = 9.6, 4.5$ Hz, 3H), 4.04 – 3.97 (td, $J = 9.0, 5.3$ Hz, 1H), 3.85 – 3.79 (s, 3H), 3.75 – 3.71 (d, $J = 4.8$ Hz, 3H), 3.56 – 3.48 (s, 3H), 3.45 – 3.29 (m, 2H), 2.38 – 2.18 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 191.2, 168.5, 167.8, 160.8, 139.7,

138.2, 128.7, 128.4, 128.2, 124.8, 57.0, 53.0, 52.7, 52.4, 43.1, 39.8, 21.4.

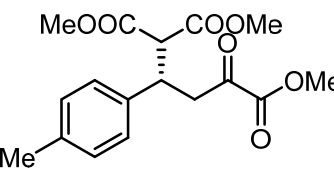
Trimethyl (*S*)-2-(3-methoxyphenyl)-4-oxobutane-1,1,4-tricarboxylate (3ae)

 Yellow oil (86% yield, 86% ee); $[\alpha]_{\text{D}}^{20} = +30.51$ ($c = 1.20$, CH_2Cl_2); HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (major) = 13.36 min, t (minor) = 18.05 min; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.17 – 7.05 (t, $J = 7.9$ Hz, 1H), 6.85 – 6.58 (m, 3H), 4.01 – 3.88 (td, $J = 9.0, 5.1$ Hz, 1H), 3.79 – 3.72 (s, 3H), 3.72 – 3.69 (s, 3H), 3.67 – 3.61 (s, 3H), 3.53 – 3.40 (s, 3H), 3.40 – 3.21 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 191.2, 168.4, 167.8, 160.8, 159.6, 141.3, 129.6, 120.1, 113.9, 112.8, 56.9, 55.2, 53.0, 52.8, 52.5, 43.1, 39.9. HRMS (ESI): exact mass calcd for $\text{C}_{17}\text{H}_{20}\text{NaO}_8^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 375.1050, found m/z 375.1055.

Trimethyl (*S*)-2-(4-bromophenyl)-4-oxobutane-1,1,4-tricarboxylate (3af)⁴

 Yellow oil (95% yield, 91% ee); $[\alpha]_{\text{D}}^{20} = +16.94$ ($c = 1.00$, CH_2Cl_2); HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (minor) = 14.31 min, t (major) = 15.69 min; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.27 (m, 2H), 7.11 – 7.02 (m, 2H), 3.93 (m, $J = 9.9, 8.7, 5.0$ Hz, 1H), 3.74 (s, 3H), 3.70 – 3.62 (m, 4H), 3.45 (s, 3H), 3.37 – 3.21 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 189.9, 167.2, 166.6, 159.7, 137.8, 130.7, 128.8, 120.4, 55.6, 52.1, 51.8, 51.6, 42.0, 38.3.

Trimethyl (*S*)-2-(4-methylphenyl)-4-oxobutane-1,1,4-tricarboxylate (3ag)³

 Yellow oil (94% yield, 90% ee); $[\alpha]_{\text{D}}^{20} = +5.08$ ($c = 0.50$, CH_2Cl_2); HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (major) = 20.39 min, t (minor) = 22.15 min; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.15 – 7.10 (m, 2H), 7.07 (d, $J = 8.0$ Hz, 2H), 4.01 (m, $J = 9.9, 8.6, 5.1$ Hz, 1H), 3.80 (s, 3H), 3.74 (d, $J = 11.9$ Hz, 4H), 3.51 (s, 3H), 3.44 – 3.28 (m, 2H), 2.28 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 191.3, 168.5,

167.9, 160.9, 137.1, 136.6, 129.3, 127.8, 57.1, 53.0, 52.8, 52.5, 43.3, 39.5, 21.1.

Trimethyl (*S*)-2-(4-methoxyphenyl)-4-oxobutane-1,1,4-tricarboxylate (3ah)²

Yellow oil (87% yield, 82% ee); $[\alpha]_{\text{D}}^{20} = +9.92$ ($c = 0.80$, CH_2Cl_2);
HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH
= 80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (minor)
= 17.61 min, t (major) = 19.74 min; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.12 (m, 2H),
6.84 – 6.76 (m, 2H), 4.00 (m, $J = 10.0, 8.7, 5.0$ Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.75 – 3.68 (m,
4H), 3.51 (s, 3H), 3.43 – 3.27 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 191.4, 168.5,
167.9, 160.9, 158.8, 131.6, 129.1, 114.0, 57.2, 55.2, 53.0, 52.8, 52.5, 43.4, 39.2, 29.7.

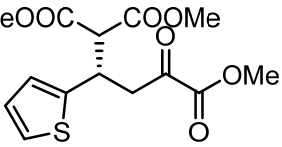
Trimethyl (*S*)-2-(biphenyl-4-yl)-4-oxobutane-1,1,4-tricarboxylate (3ai)⁴

Yellow oil (88% yield, 86% ee); $[\alpha]_{\text{D}}^{20} = +16.06$ ($c = 0.40$, CH_2Cl_2);
HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH =
80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (minor) =
17.90 min; t (major) = 24.13 min; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.48 (m, 4H), 7.42
(dd, $J = 8.4, 6.7$ Hz, 2H), 7.33 (t, $J = 7.8$ Hz, 3H), 4.09 (td, $J = 9.1, 5.0$ Hz, 1H), 3.82 (d, $J = 7.1$ Hz,
4H), 3.75 (s, 3H), 3.57 – 3.33 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 191.3, 168.5,
167.9, 160.8, 140.5, 140.3, 138.8, 128.8, 128.5, 127.4, 127.3, 127.0, 56.9, 53.1, 52.9, 52.6, 43.2, 39.6.

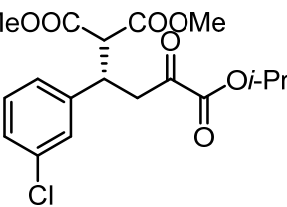
Trimethyl (*S*)-2-(2-naphthalenyl)-4-oxobutane-1,1,4-tricarboxylate (3aj)²

Yellow oil (89% yield, 91% ee); $[\alpha]_{\text{D}}^{20} = +12.12$ ($c = 1.00$, CH_2Cl_2);
HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH =
80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (major) =
17.12 min; t (minor) = 19.15 min; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.75 (m, 3H), 7.70
(d, $J = 1.9$ Hz, 1H), 7.48 – 7.42 (m, 2H), 7.38 (dd, $J = 8.5, 1.9$ Hz, 1H), 4.26 – 4.18 (m, 1H), 3.89 (d,
 $J = 9.7$ Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.54 (dd, $J = 18.1, 8.7$ Hz, 1H), 3.48 – 3.37 (m, 4H).
 $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 191.2, 168.5, 167.8, 160.9, 137.3, 133.3, 132.7, 128.4,
127.9, 127.6, 127.1, 126.2, 126.0, 125.9, 57.0, 53.0, 52.8, 52.5, 43.2, 40.0.

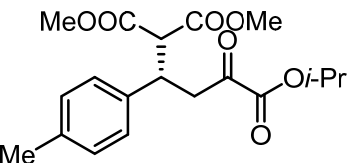
Trimethyl (*S*)-2-(2-thiophenyl)-4-oxobutane-1,1,4-tricarboxylate (**3ak**)²

 Yellow oil (96% yield, 92% ee); $[\alpha]_{\text{D}}^{20} = +9.44$ ($c = 0.50$, CH_2Cl_2);
HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (major) = 11.44 min; t (minor) = 13.63 min; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.15 (dd, $J = 5.1, 1.3$ Hz, 1H), 6.93 – 6.86 (m, 2H), 4.37 (td, $J = 8.6, 4.9$ Hz, 1H), 3.86 – 3.79 (m, 4H), 3.74 (s, 3H), 3.61 (s, 3H), 3.54 – 3.36 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 190.9, 168.1, 167.7, 160.8, 142.6, 126.8, 126.0, 124.6, 57.4, 53.1, 52.8, 52.7, 43.9, 35.2.

1,1-dimethyl 4-isopropyl (*S*)-2-(3-chlorophenyl)-4-oxobutane-1,1,4-tricarboxylate (**3al**)

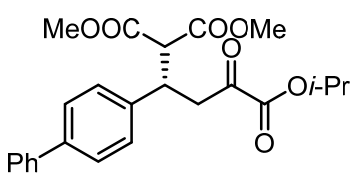
 Yellow oil (93% yield, 90% ee); $[\alpha]_{\text{D}}^{20} = +16.90$ ($c = 0.90$, CH_2Cl_2);
HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (major) = 10.21 min; t (minor) = 12.41 min; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.25 (t, $J = 2.0$ Hz, 1H), 7.23 – 7.17 (m, 2H), 7.15 (dt, $J = 6.8, 2.0$ Hz, 1H), 5.08 (p, $J = 6.3$ Hz, 1H), 4.01 (m, 1H), 3.80 – 3.68 (m, 4H), 3.53 (s, 3H), 3.44 – 3.27 (m, 2H), 1.31 (dd, $J = 6.3, 5.4$ Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 191.7, 168.2, 167.6, 159.9, 141.9, 134.4, 129.9, 128.3, 127.7, 126.4, 71.0, 56.7, 52.9, 52.6, 42.8, 39.6, 21.5, 21.5. **HRMS (ESI)**: exact mass calcd for $\text{C}_{18}\text{H}_{21}\text{ClNaO}_7^+$ ($\text{M}+\text{Na}$)⁺ requires m/z 407.0868, found m/z 407.0863.

1,1-dimethyl 4-isopropyl (*S*)-2-(4-methylphenyl)-4-oxobutane-1,1,4-tricarboxylate (**3am**)

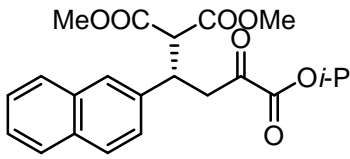
 Yellow oil (93% yield, 90% ee); $[\alpha]_{\text{D}}^{20} = +29.8$ ($c = 1.60$, CH_2Cl_2);
HPLC analysis Daicel Chiralcel IB column, *n*-hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (major) = 7.91 min; t (minor) = 8.81 min; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.12 (d, $J = 8.1$ Hz, 2H), 7.07 (d, $J = 7.9$ Hz, 2H), 5.05 (p, $J = 6.2$ Hz, 1H), 4.05 – 3.95 (m, 1H), 3.79 – 3.68 (m, 4H), 3.50 (d, $J = 1.1$ Hz, 3H), 3.42 – 3.24 (m, 2H), 2.28 (s, 3H), 1.30 – 1.26 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 192.1, 168.5, 167.9, 160.1, 137.1, 136.7, 129.3, 127.9, 70.8, 57.1, 52.8, 52.5, 43.2,

39.7, 21.5, 21.5, 21.1. **HRMS (ESI)**: exact mass calcd for $C_{19}H_{24}NaO_7^+$ ($M+Na$) $^+$ requires m/z 387.1414, found m/z 387.1410.

1,1-dimethyl 4-isopropyl (*S*)-2-(biphenyl-4-yl)-4-oxobutane-1,1,4-tricarboxylate (3an)

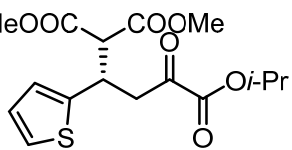
 Yellow oil (90% yield, 86% ee); $[\alpha]_D^{20} = +18.98$ ($c = 1.00$, CH_2Cl_2);
HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, $T = 25^\circ C$, UV = 210 nm; t (minor) = 12.14 min; t (major) = 20.89 min; 1H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.49 (m, 4H), 7.44 – 7.39 (m, 2H), 7.36 – 7.30 (m, 3H), 5.06 (p, $J = 6.3$ Hz, 1H), 4.12 – 4.05 (m, 1H), 3.82 (d, $J = 9.9$ Hz, 1H), 3.75 (s, 3H), 3.52 (s, 3H), 3.46 (dd, $J = 18.0, 8.9$ Hz, 1H), 3.33 (dd, $J = 18.0, 4.9$ Hz, 1H), 1.29 (dd, $J = 8.7, 6.3$ Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 192.0, 168.4, 167.9, 160.1, 140.5, 140.2, 138.8, 128.8, 128.5, 127.4, 127.3, 127.0, 70.9, 57.0, 52.9, 52.6, 43.1, 39.7, 21.6, 21.5. **HRMS (ESI)**: exact mass calcd for $C_{24}H_{26}NaO_7^+$ ($M+Na$) $^+$ requires m/z 449.1571, found m/z 449.1566.

1,1-dimethyl 4-isopropyl (*S*)-2-(2-naphthalenyl)-4-oxobutane-1,1,4-tricarboxylate (3ao)

 Yellow oil (85% yield, 87% ee); $[\alpha]_D^{20} = +6.51$ ($c = 0.90$, CH_2Cl_2);
HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, $T = 25^\circ C$, UV = 210 nm; t (major) = 17.97 min; t (minor) = 19.54 min; 1H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.74 (m, 3H), 7.71 (d, $J = 1.8$ Hz, 1H), 7.50 – 7.41 (m, 2H), 7.39 (dd, $J = 8.5, 1.8$ Hz, 1H), 5.02 (p, $J = 6.3$ Hz, 1H), 4.22 (td, $J = 9.4, 4.8$ Hz, 1H), 3.90 (d, $J = 10.0$ Hz, 1H), 3.75 (s, 3H), 3.52 (dd, $J = 18.0, 9.0$ Hz, 1H), 3.45 (s, 3H), 3.37 (dd, $J = 18.0, 4.8$ Hz, 1H), 1.26 (d, $J = 5.8$ Hz, 3H), 1.22 (d, $J = 6.2$ Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 192.0, 168.5, 167.8, 160.1, 137.3, 133.3, 132.7, 128.4, 127.9, 127.6, 127.2, 126.2, 126.0, 125.9, 70.8, 57.0, 52.9, 52.5, 43.1, 40.2, 21.5, 21.5. **HRMS (ESI)**: exact mass calcd for $C_{22}H_{24}NaO_7^+$ ($M+Na$) $^+$ requires m/z 423.1414, found m/z 423.1411.

1,1-dimethyl 4-isopropyl (*S*)-2-(2-thiophenyl)-4-oxobutane-1,1,4-tricarboxylate (3ap)

MeOOC

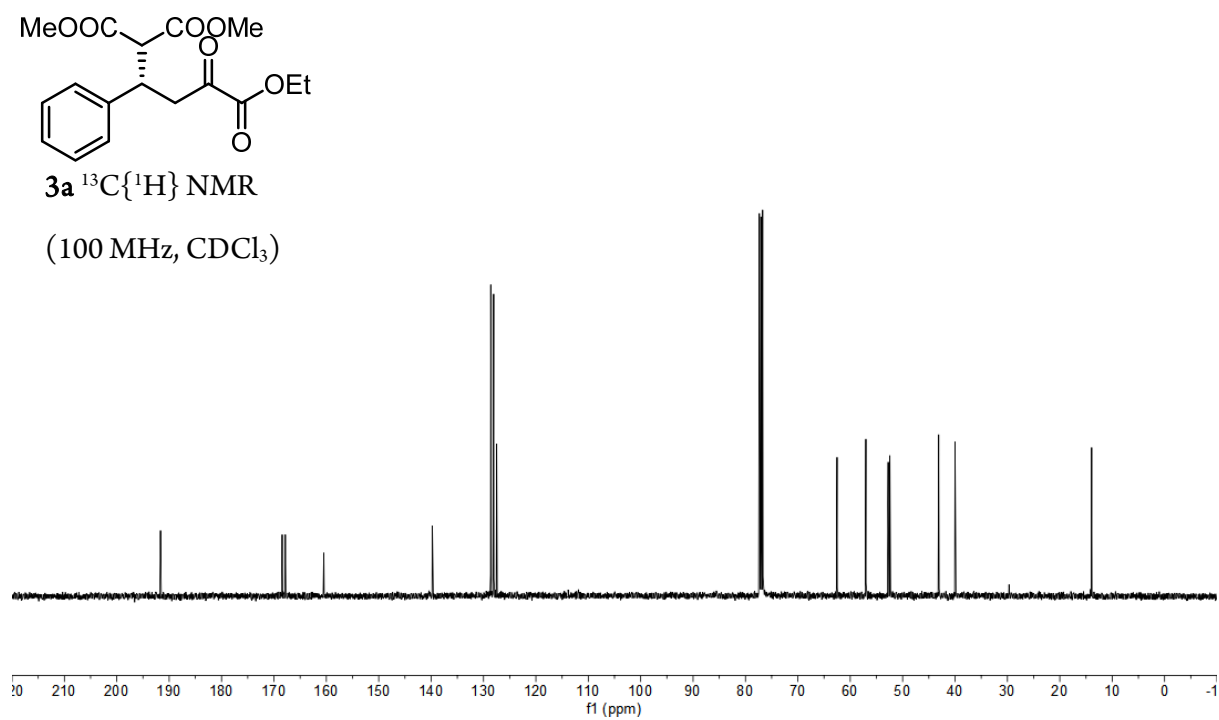
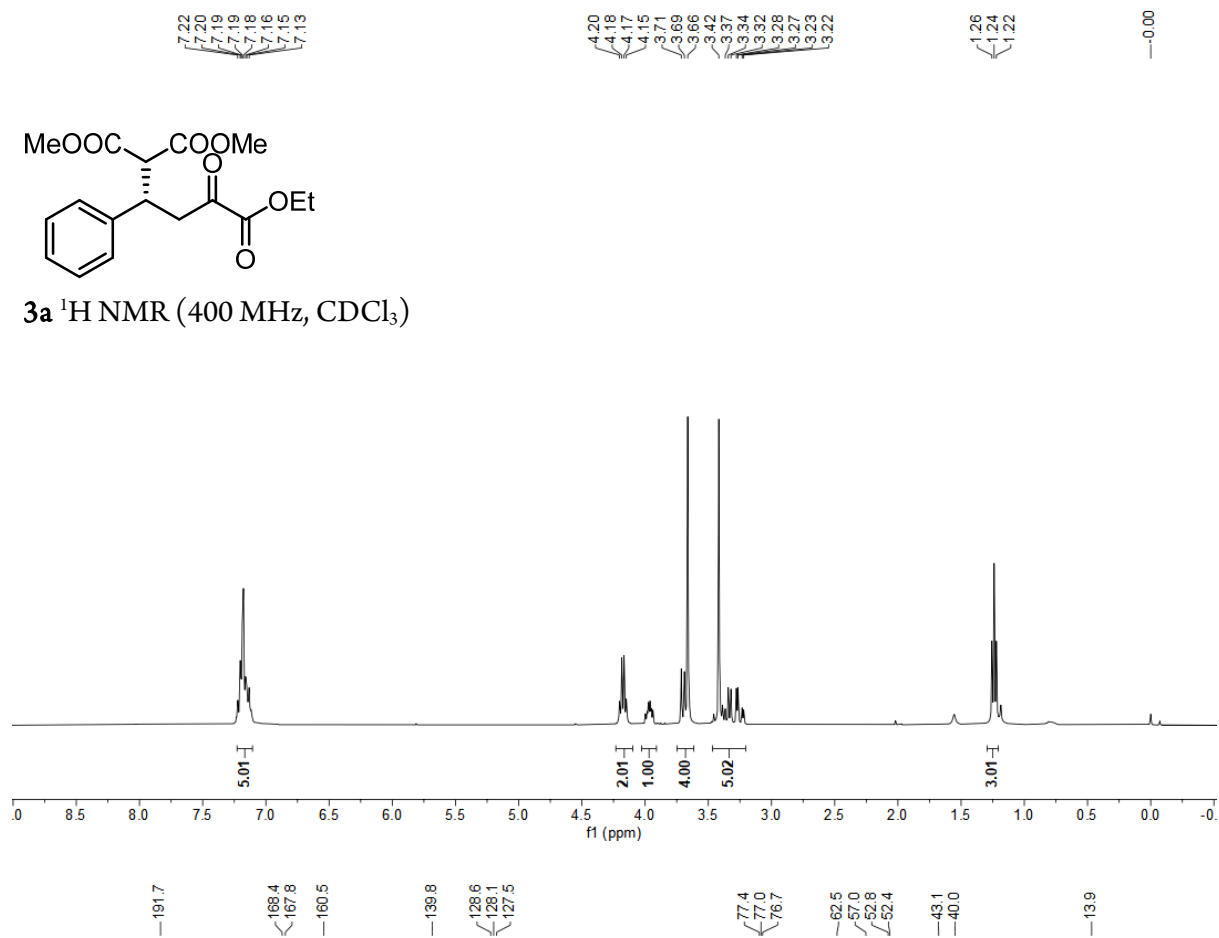


Yellow oil (93% yield, 90% ee); $[\alpha]_{\text{D}}^{20} = +8.11$ ($c = 0.90$, CH_2Cl_2);

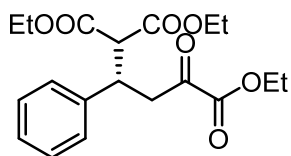
HPLC analysis Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, $T = 25^\circ\text{C}$, UV = 210 nm; t (major) =

12.00 min; t (minor) = 14.31 min; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.15 (dd, $J = 5.1, 1.3$ Hz, 1H), 6.96 – 6.85 (m, 2H), 5.09 (p, $J = 6.3$ Hz, 1H), 4.37 (td, $J = 8.8, 4.8$ Hz, 1H), 3.81 (d, $J = 9.0$ Hz, 1H), 3.74 (s, 3H), 3.60 (s, 3H), 3.52 – 3.31 (m, 2H), 1.31 (dd, $J = 6.3, 3.3$ Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 191.7, 168.1, 167.7, 160.0, 142.7, 126.8, 126.0, 124.6, 70.9, 57.4, 52.8, 52.7, 43.8, 35.3, 21.5. **HRMS (ESI)**: exact mass calcd for $\text{C}_{16}\text{H}_{20}\text{NaO}_7\text{S}^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 379.0822, found m/z 379.0817.

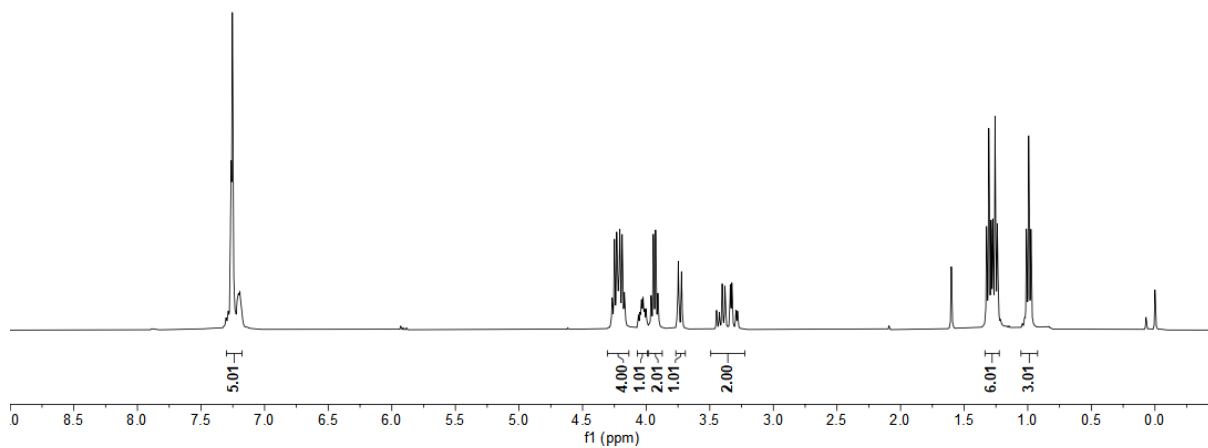
2. NMR Spectra of the Products



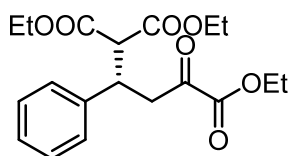
7.29
7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.20
7.19
7.18
4.27
4.25
4.23
4.22
4.21
4.19
4.17
4.15
4.04
4.02
4.01
4.01
4.00
4.00
3.96
3.96
3.94
3.94
3.93
3.92
3.91
3.90
3.75
3.74
3.72
3.72
3.45
3.44
3.43
3.40
3.40
3.38
3.38
3.34
3.34
3.33
3.32
3.29
3.29
3.28
1.33
1.32
1.31
1.30
1.29
1.28
1.27
1.26
1.25
1.24
1.24
1.01
1.01
0.99
0.98
0.97
0.00



3b ^1H NMR (400 MHz, CDCl_3)

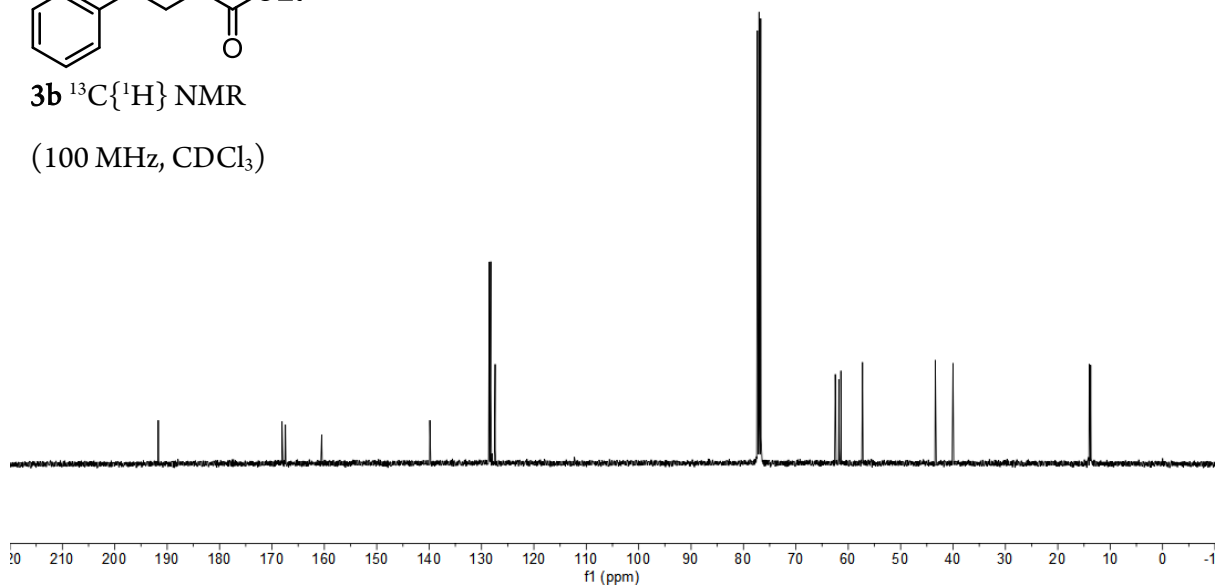


191.7
168.1
167.4
160.5
139.9
128.5
128.2
127.4
77.3
77.0
76.7
62.5
61.8
61.4
57.3
43.4
40.0
14.0
13.9
13.7

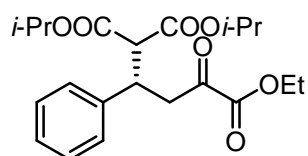


3b $^{13}\text{C}\{^1\text{H}\}$ NMR

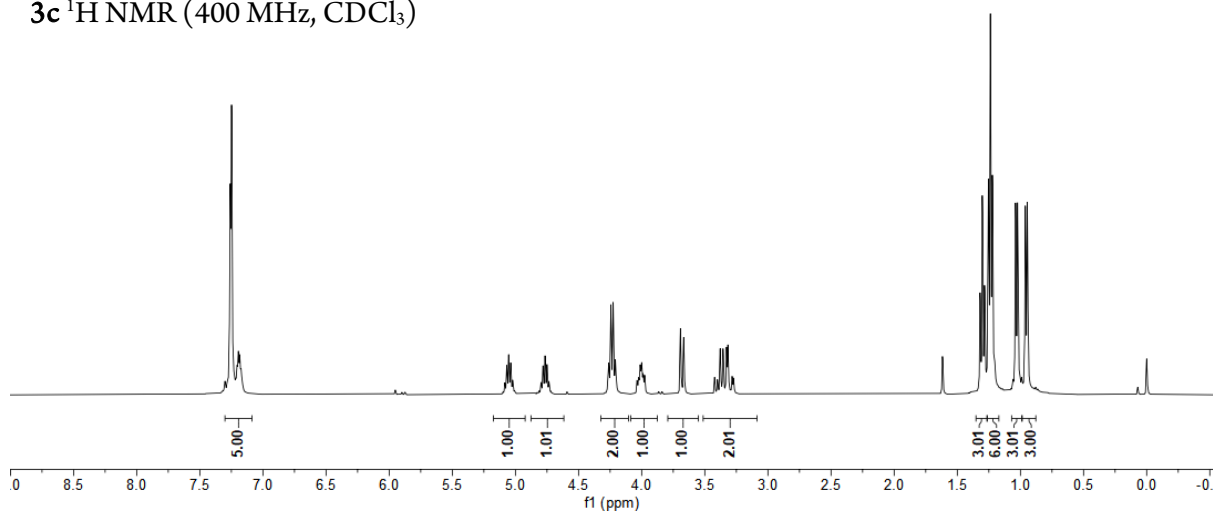
(100 MHz, CDCl_3)



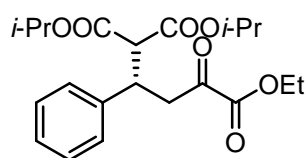
7.27
7.26
7.26
7.25
7.25
7.22
7.21
7.19
7.18
7.17
5.07
5.05
5.05
5.04
5.03
4.78
4.78
4.77
4.76
4.75
4.75
4.26
4.24
4.24
4.23
4.21
4.02
4.01
4.00
3.99
3.99
3.98
3.97
3.69
3.69
3.67
3.66
3.42
3.38
3.37
3.36
3.35
3.33
3.33
3.32
3.31
3.29
3.28
3.27
1.32
1.32
1.30
1.30
1.29
1.28
1.25
1.25
1.24
1.23
1.22
1.22
1.04
1.04
1.02
1.02
0.96
0.96
0.94
0.94
0.00
0.00



3c ^1H NMR (400 MHz, CDCl_3)

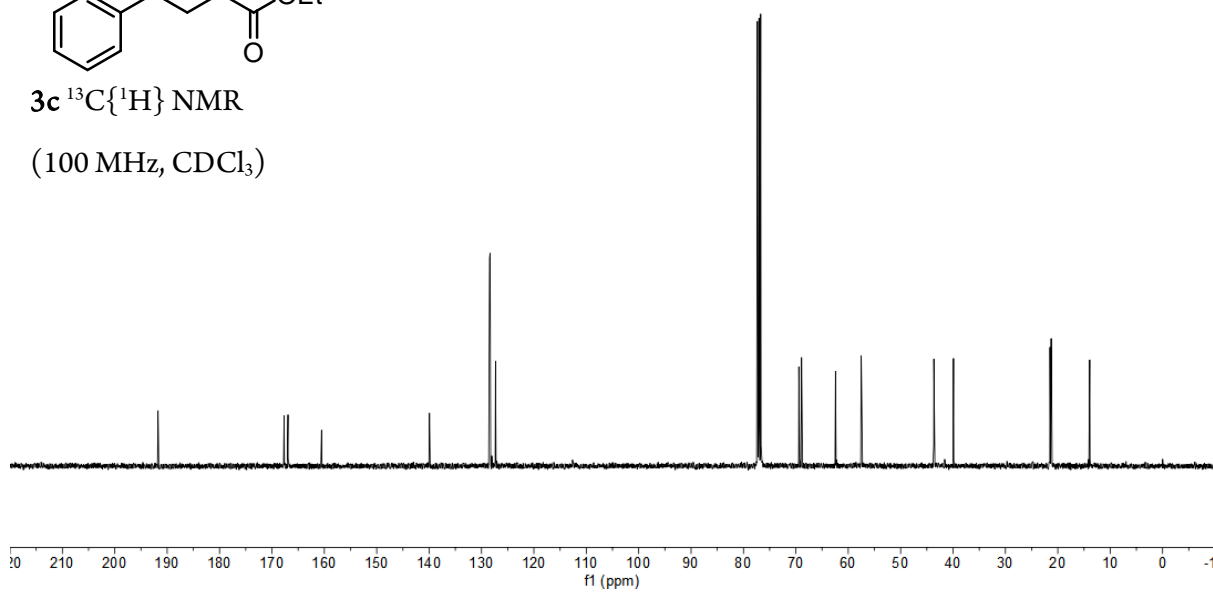


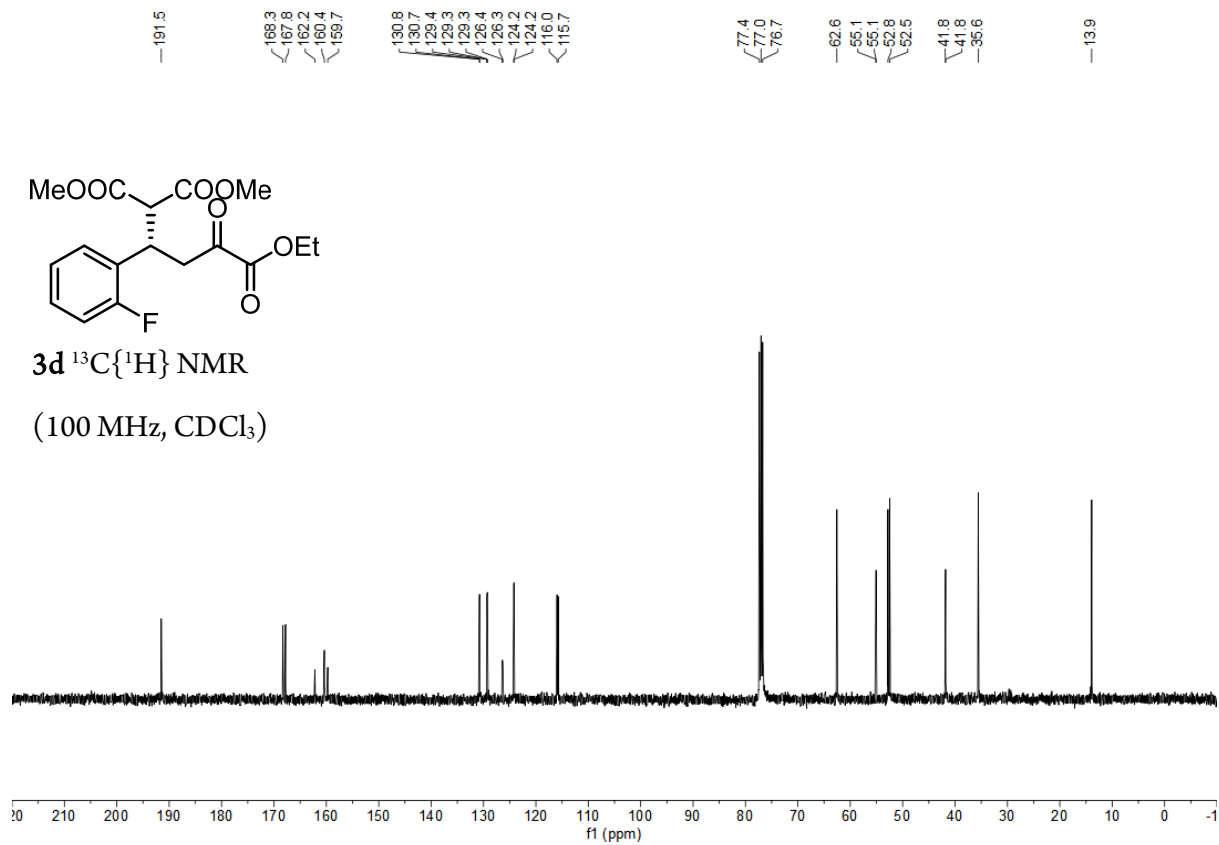
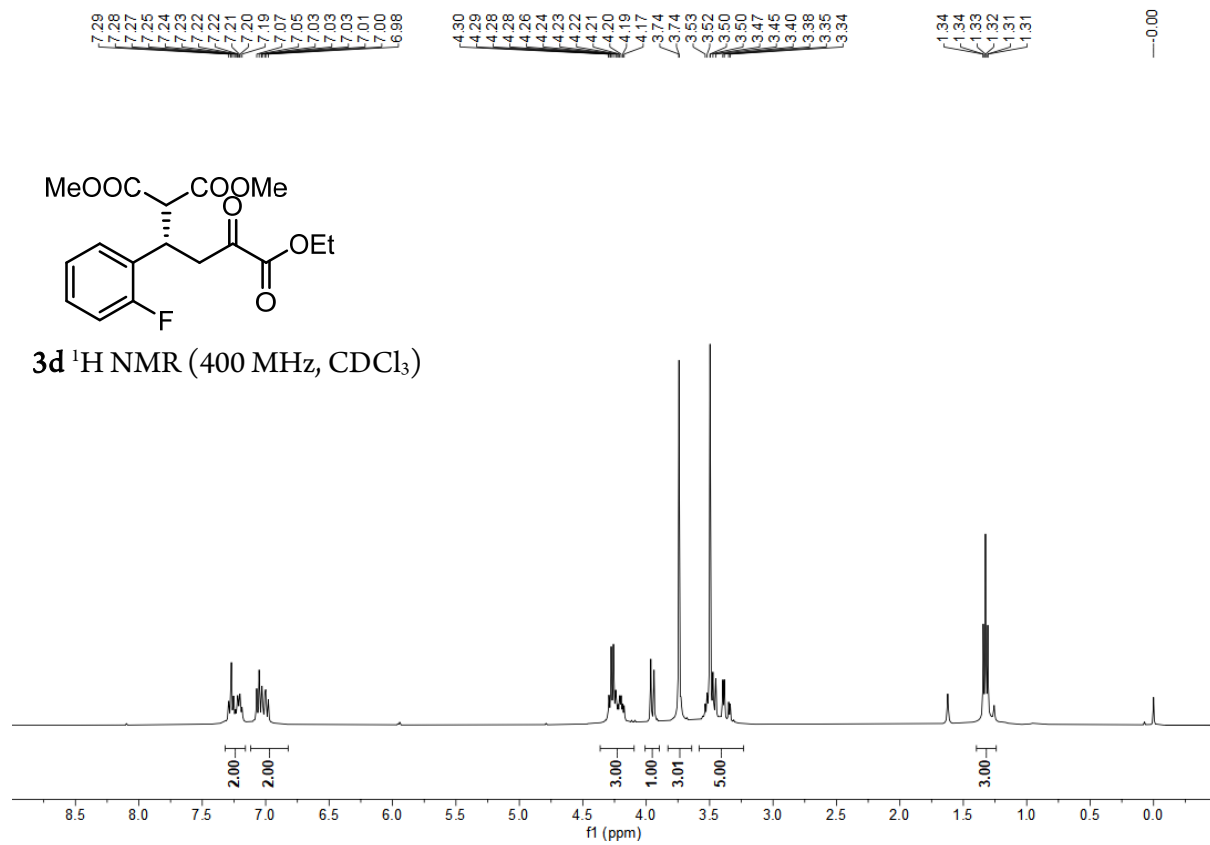
191.7
167.7
166.9
160.5
139.9
128.5
128.4
128.4
127.3
77.3
77.0
76.7
69.4
68.9
62.4
57.5
43.7
39.9
21.6
21.5
21.3
21.2
13.9

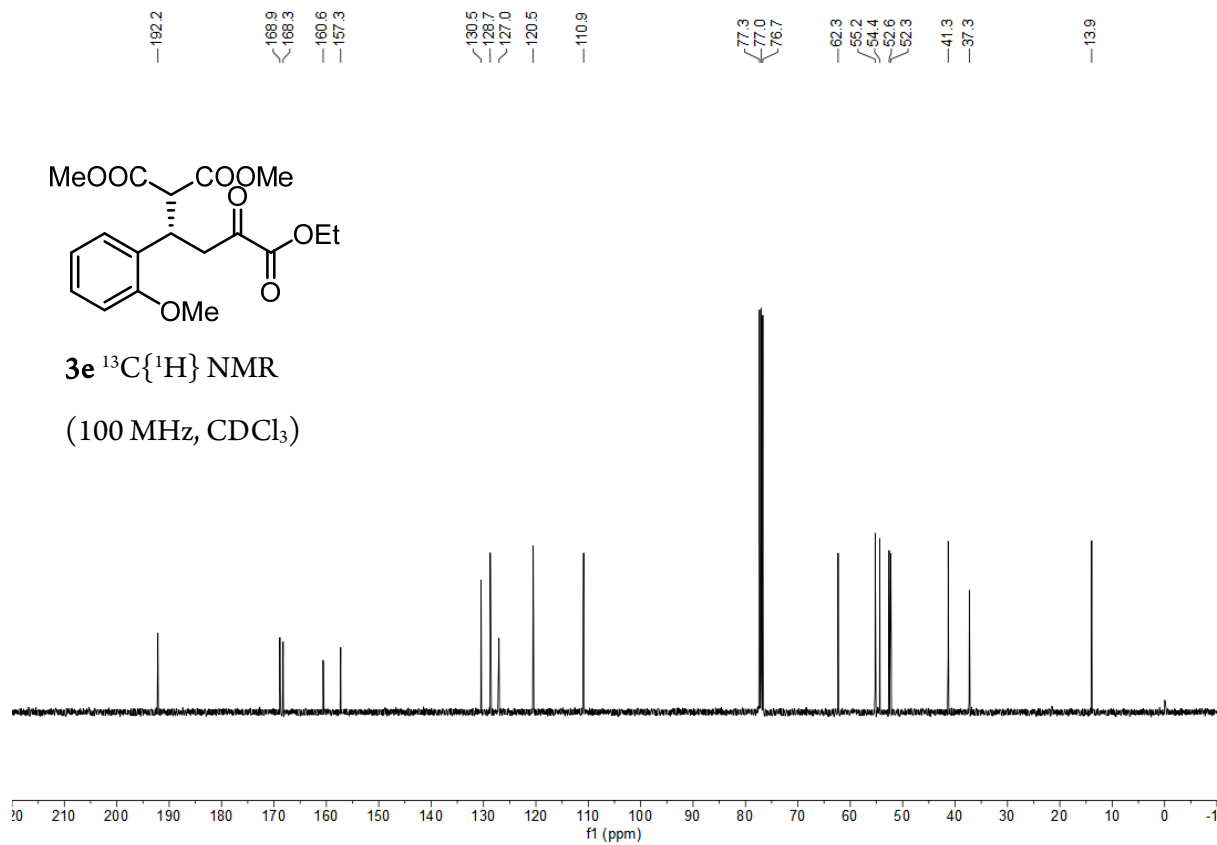
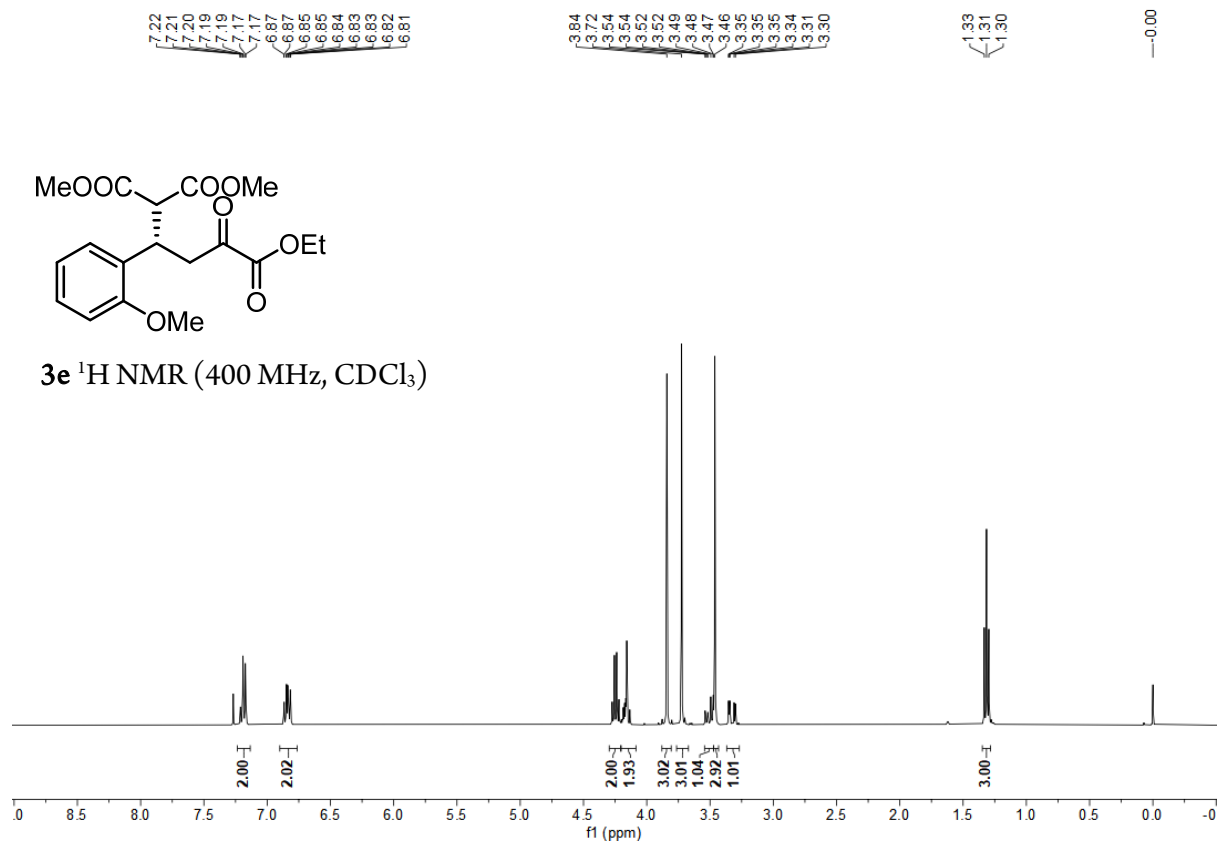


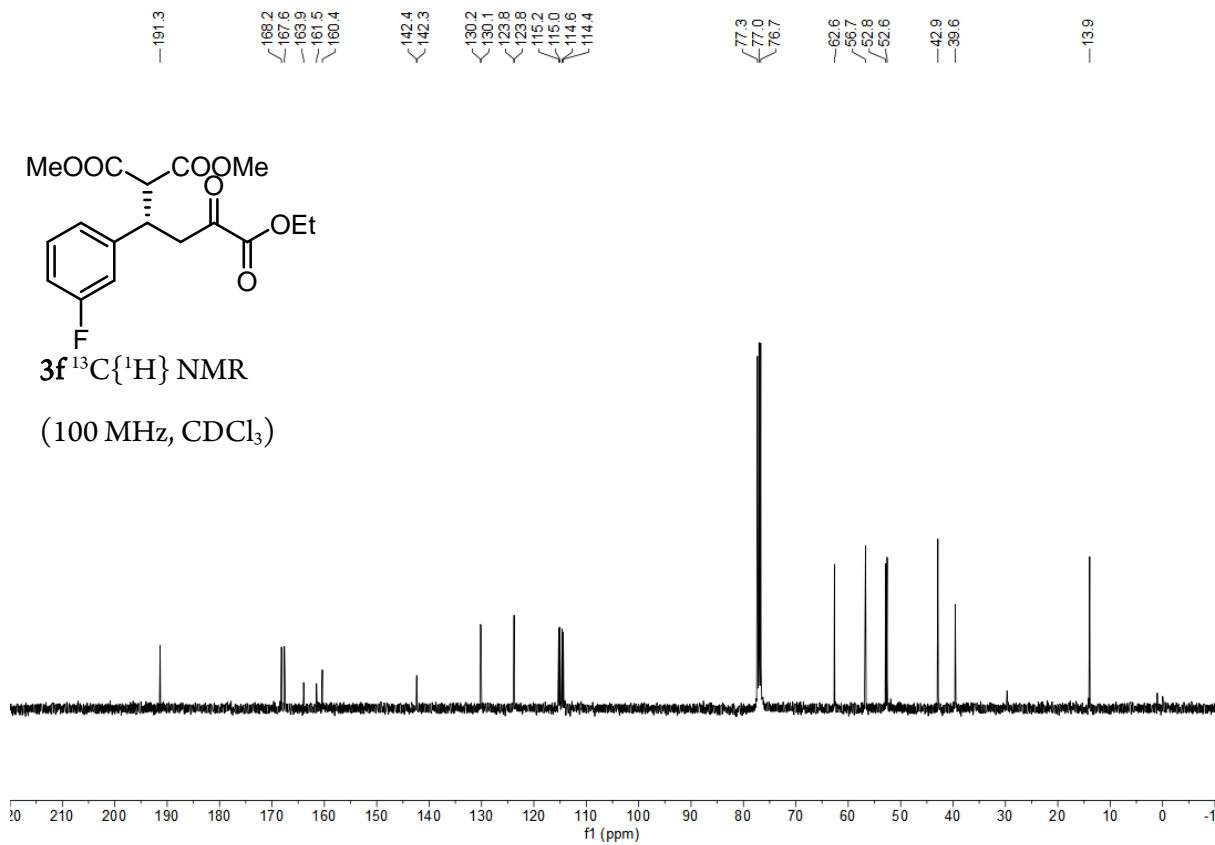
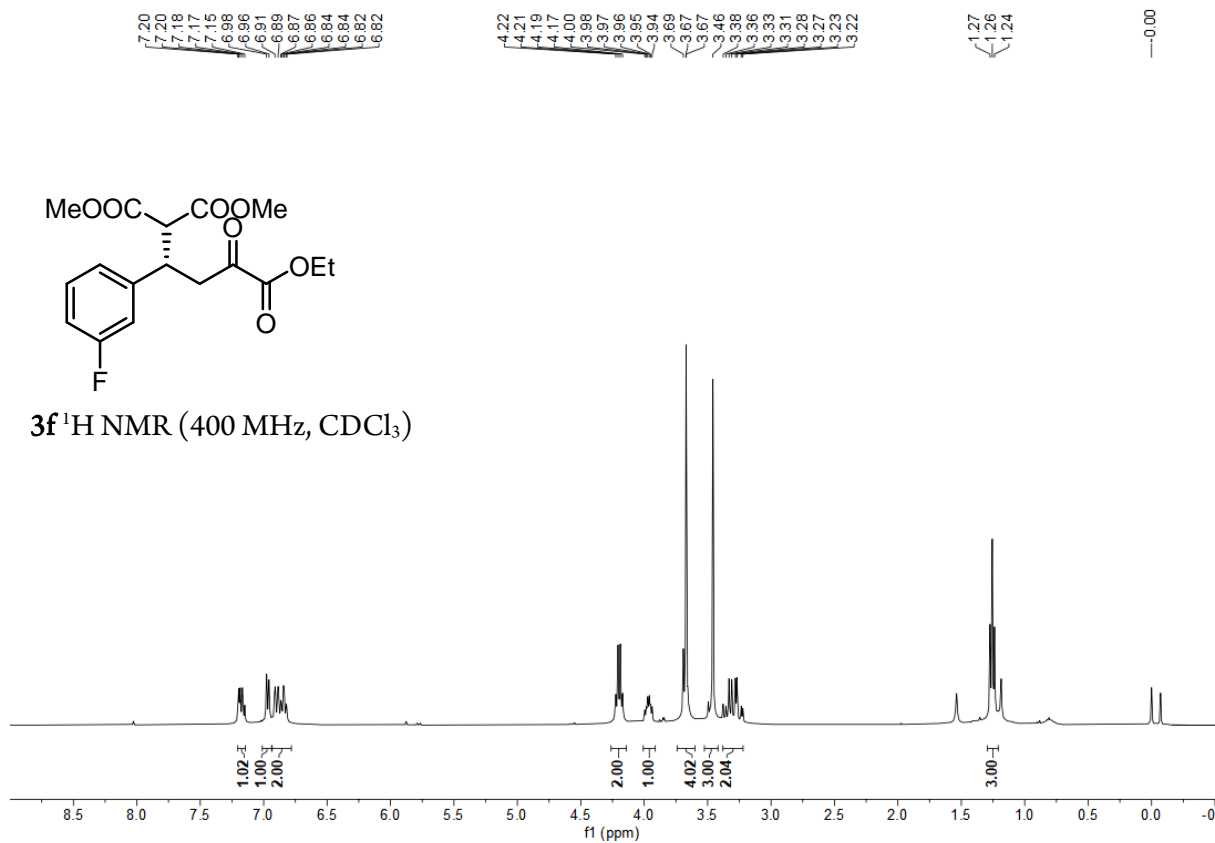
3c $^{13}\text{C}\{^1\text{H}\}$ NMR

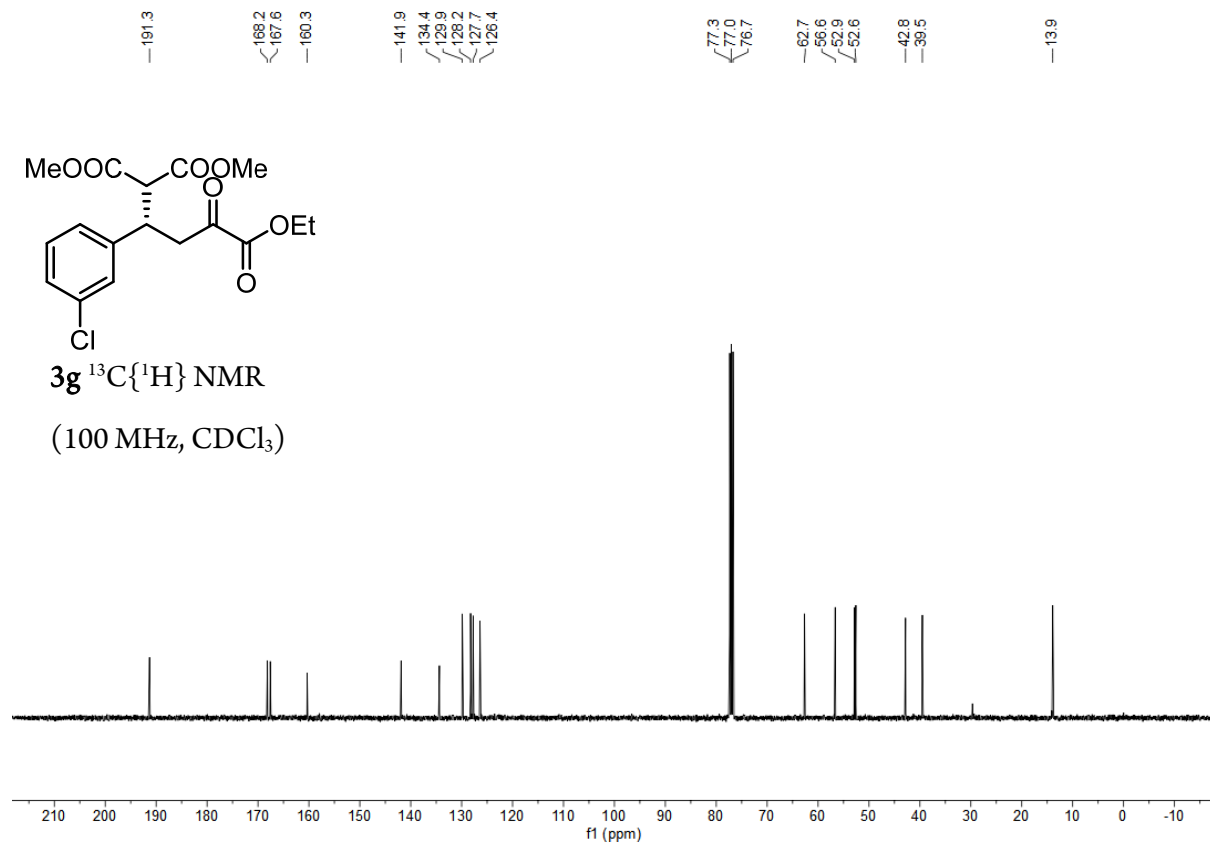
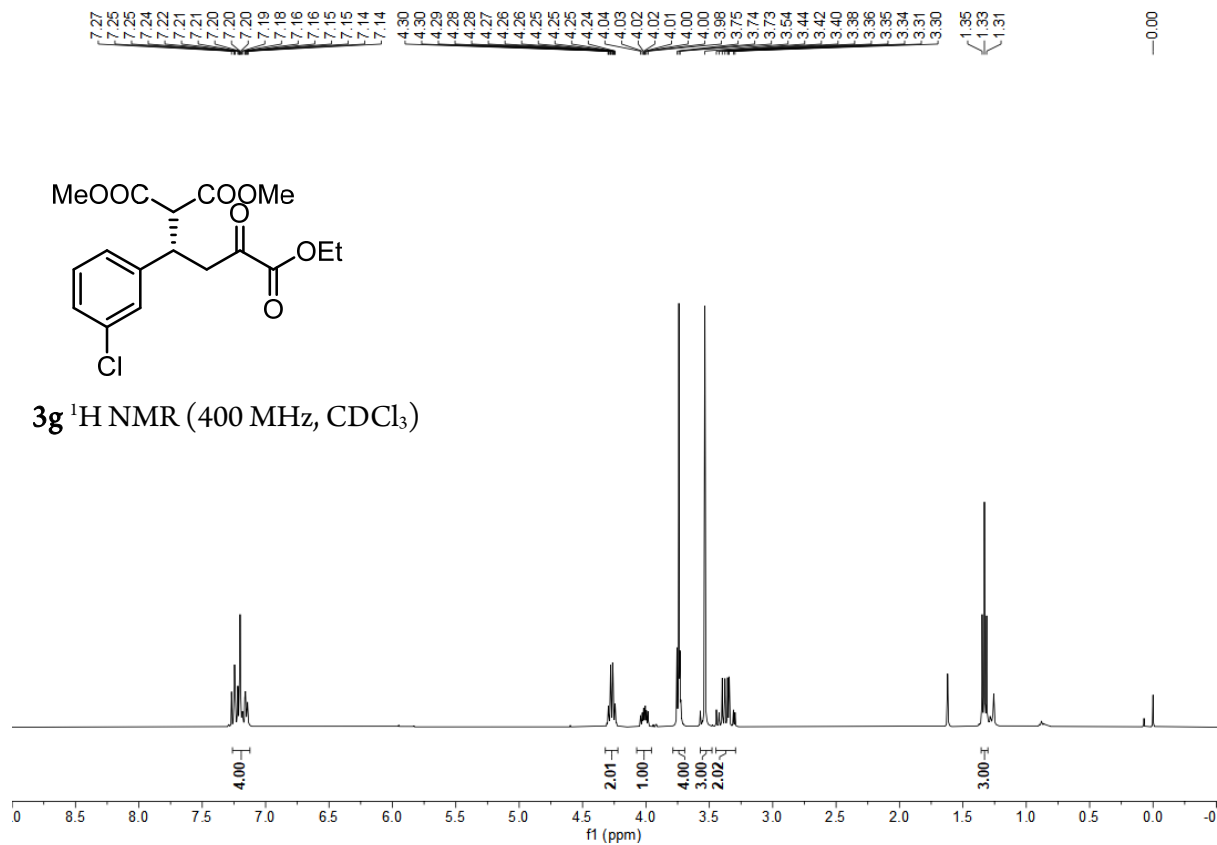
(100 MHz, CDCl_3)

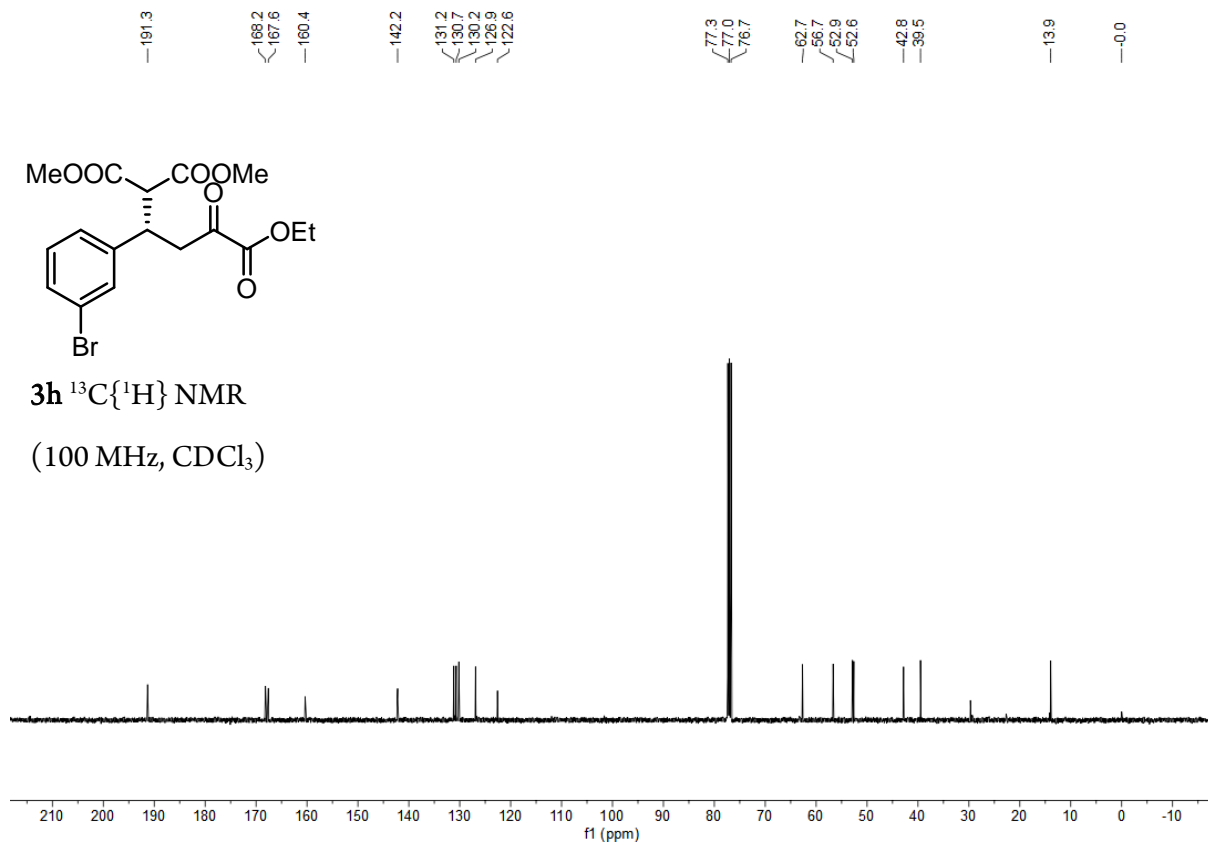
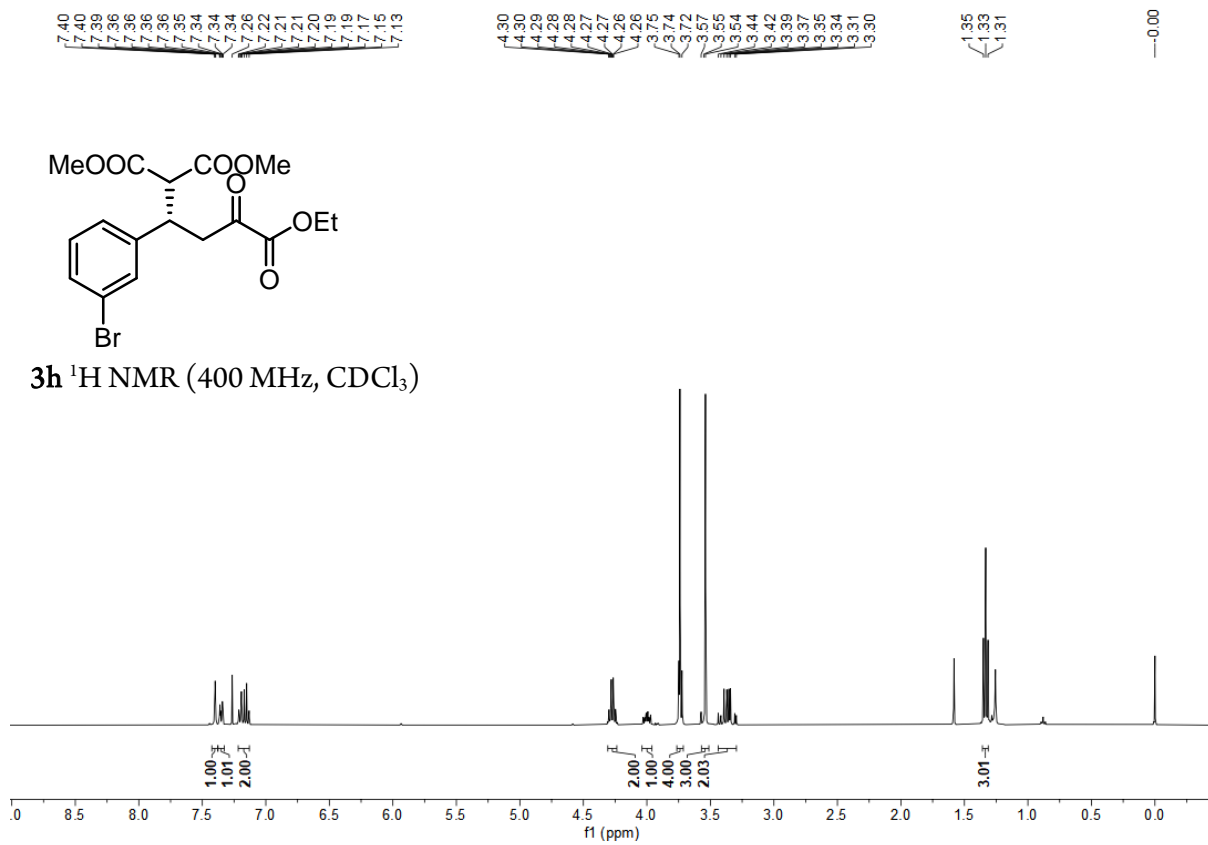


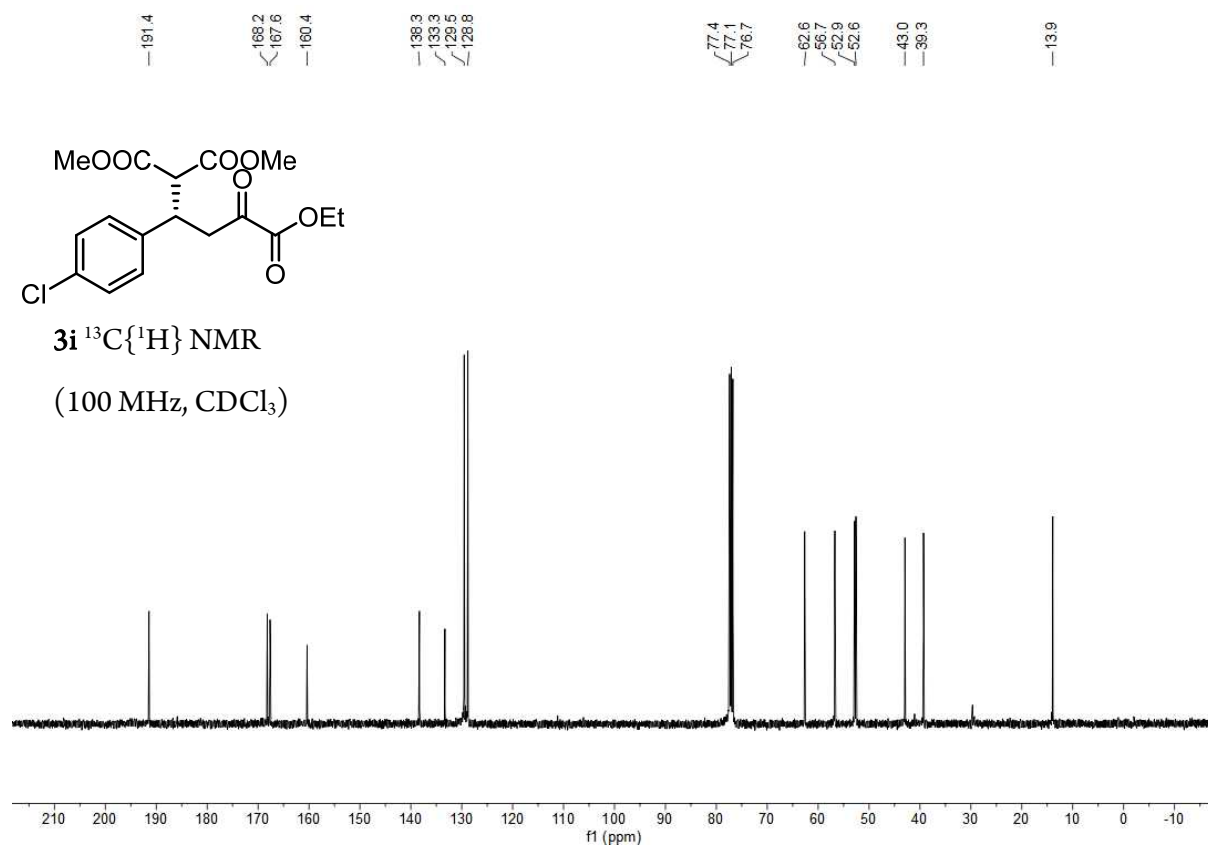
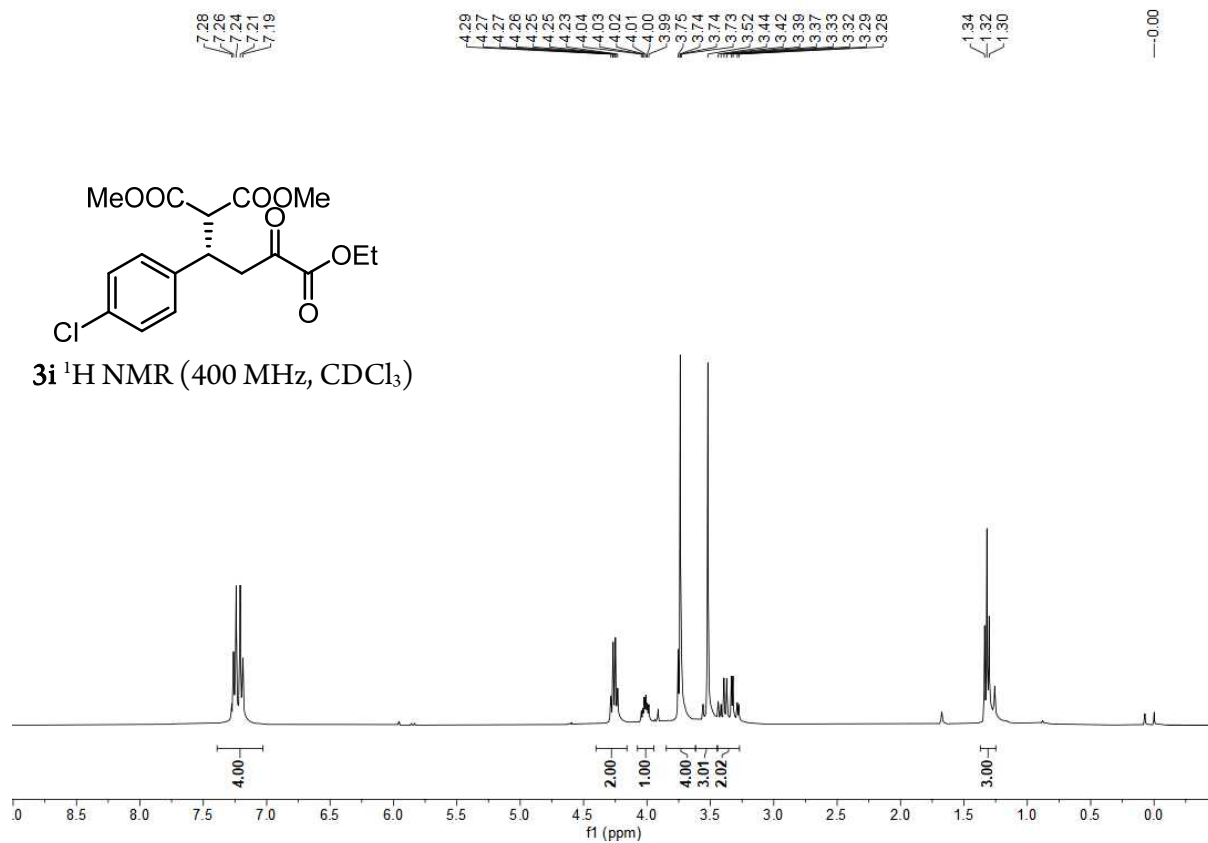


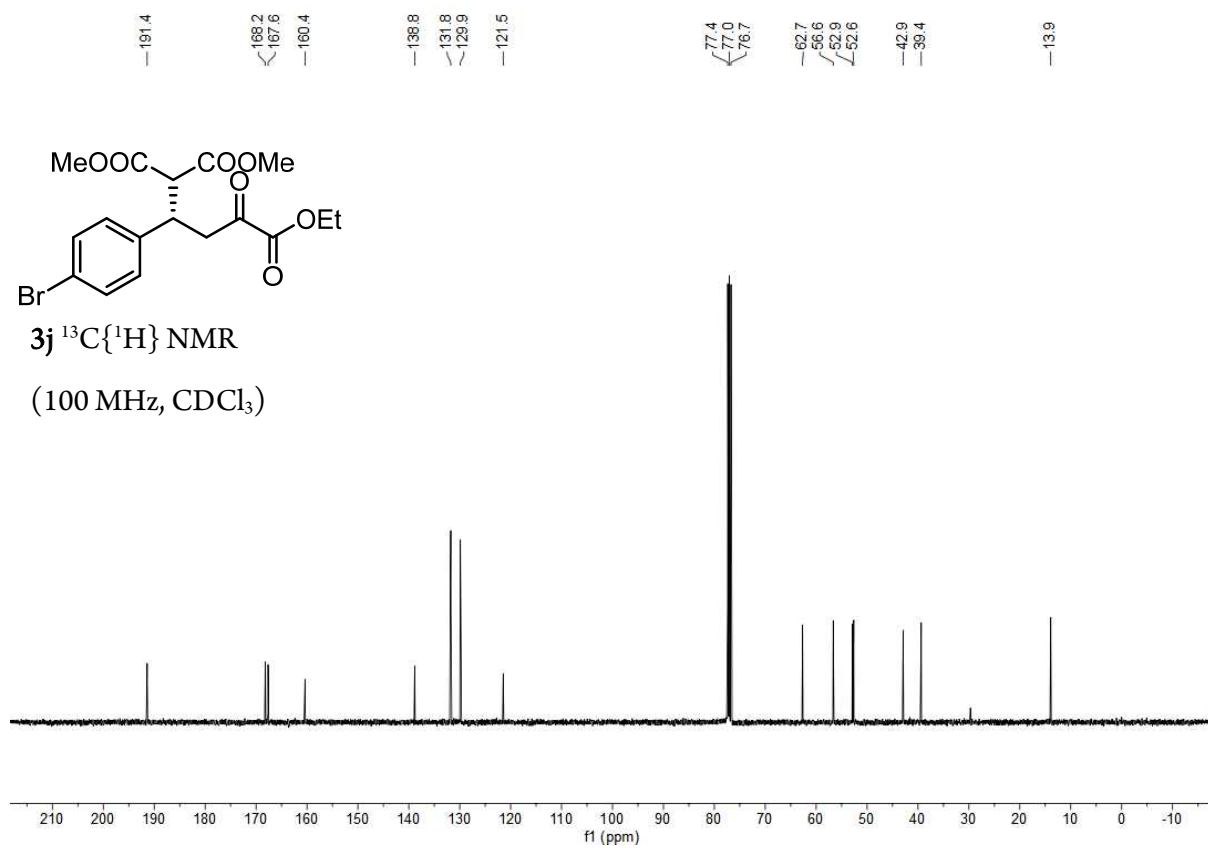
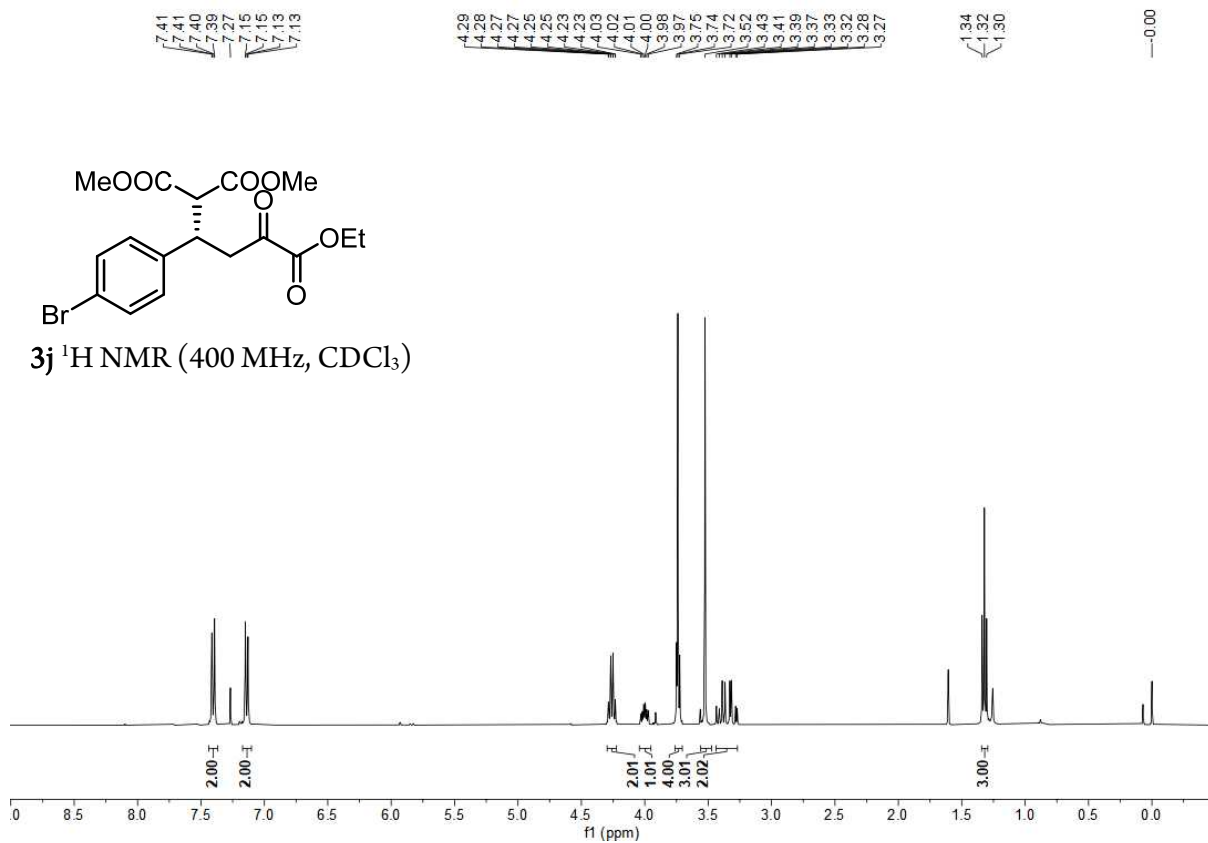


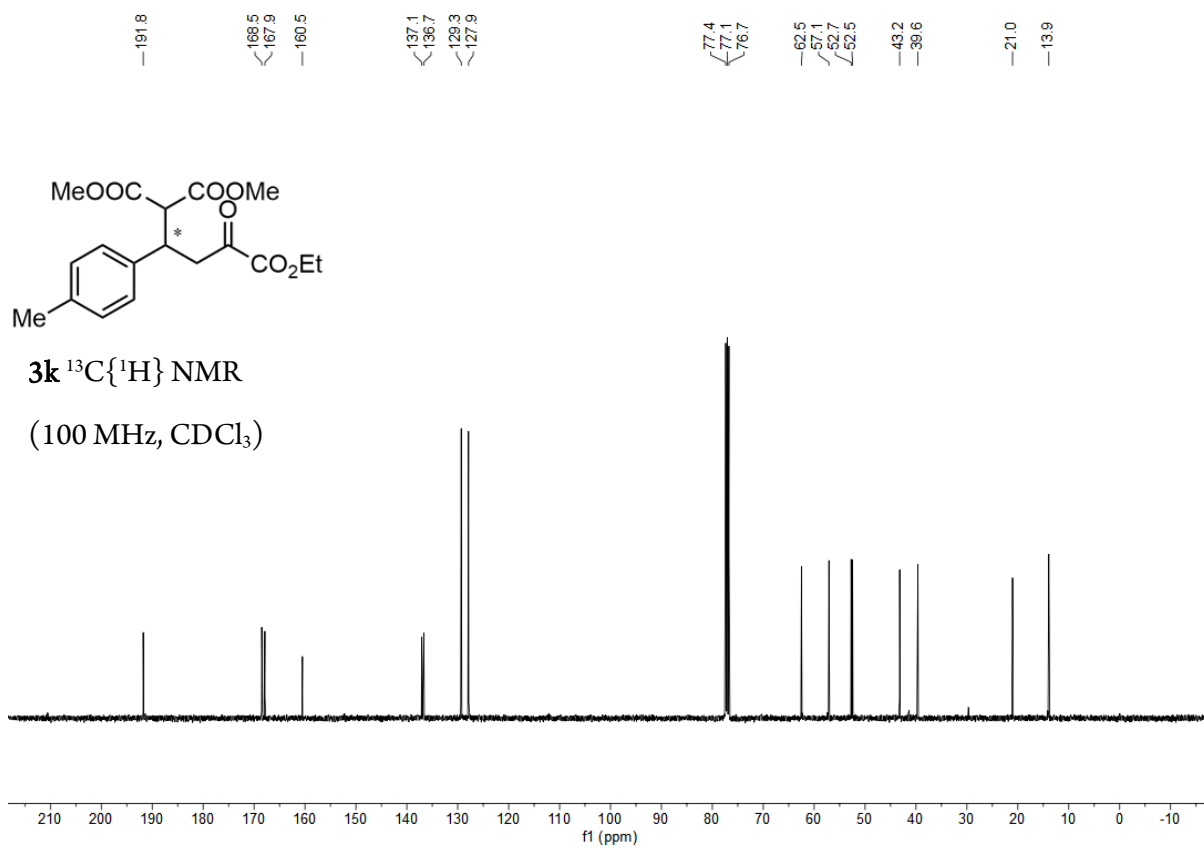
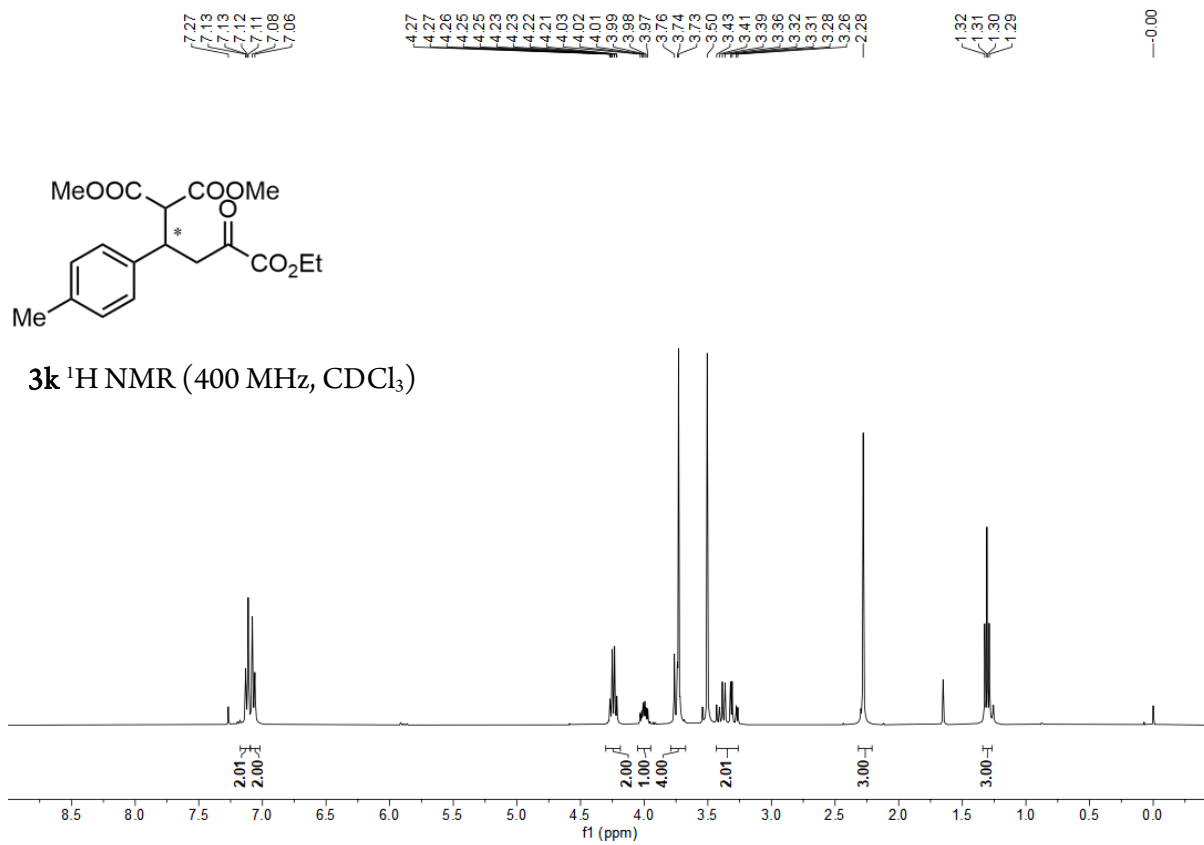


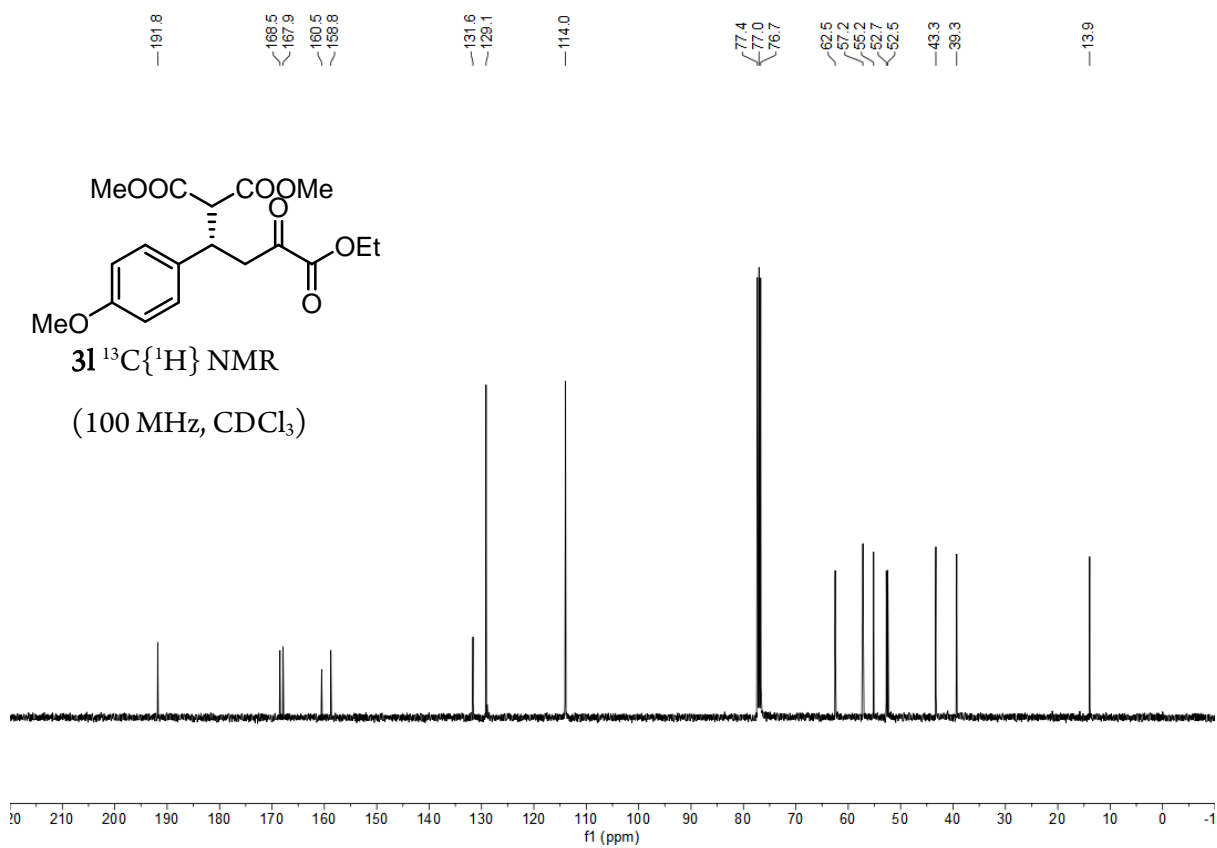
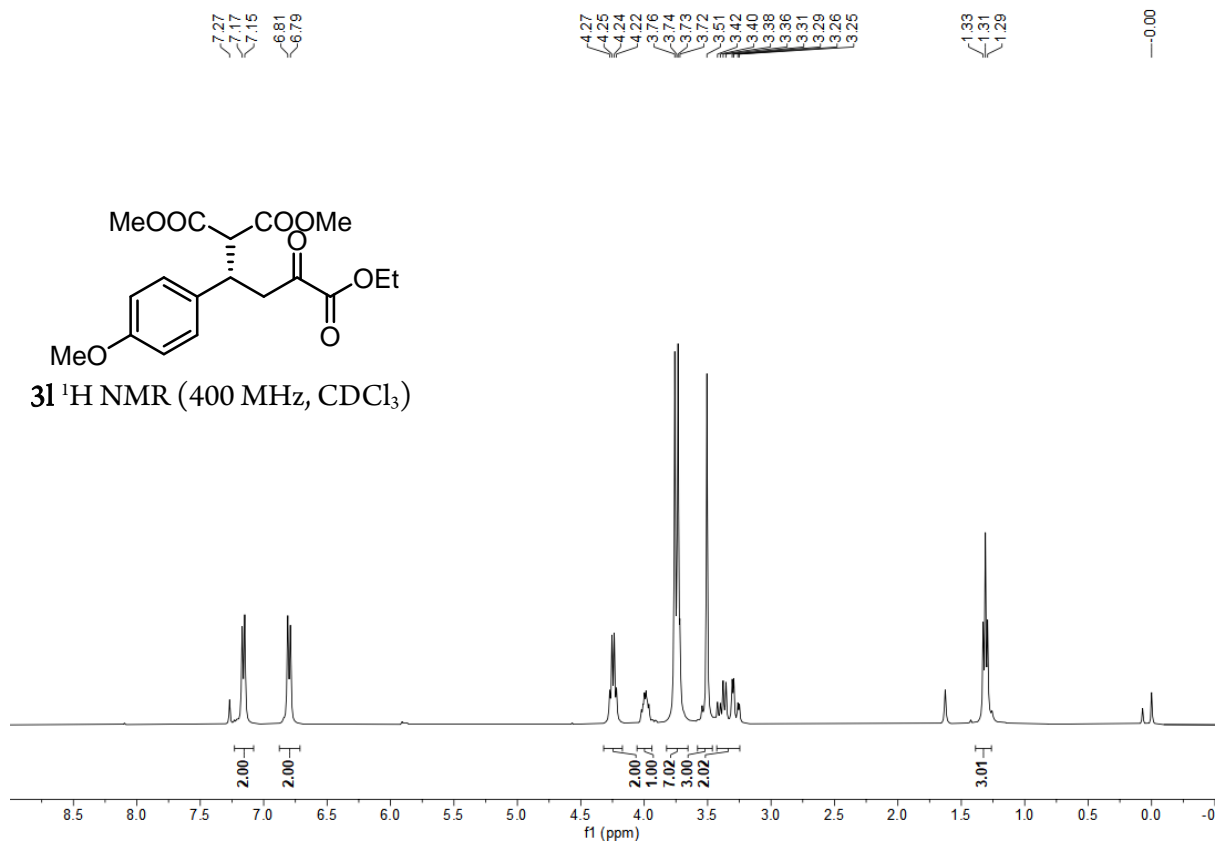


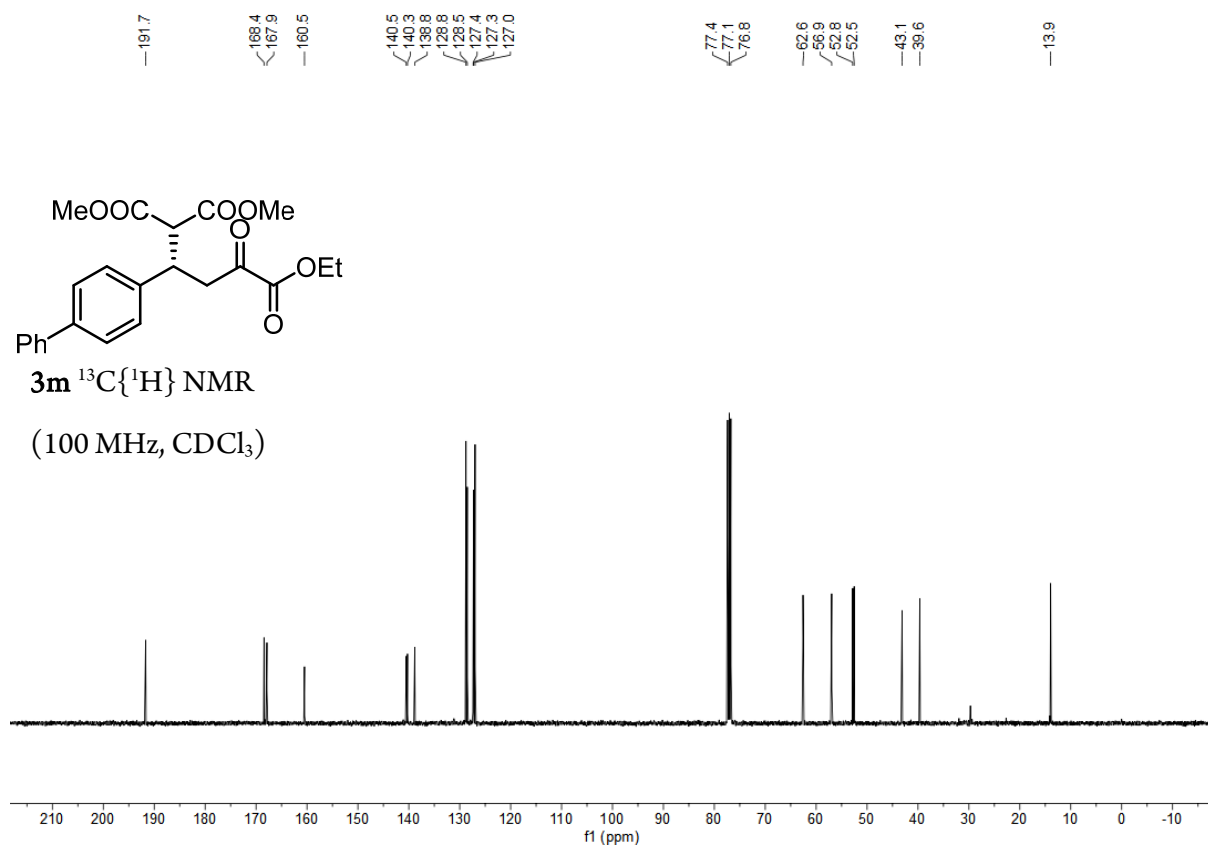
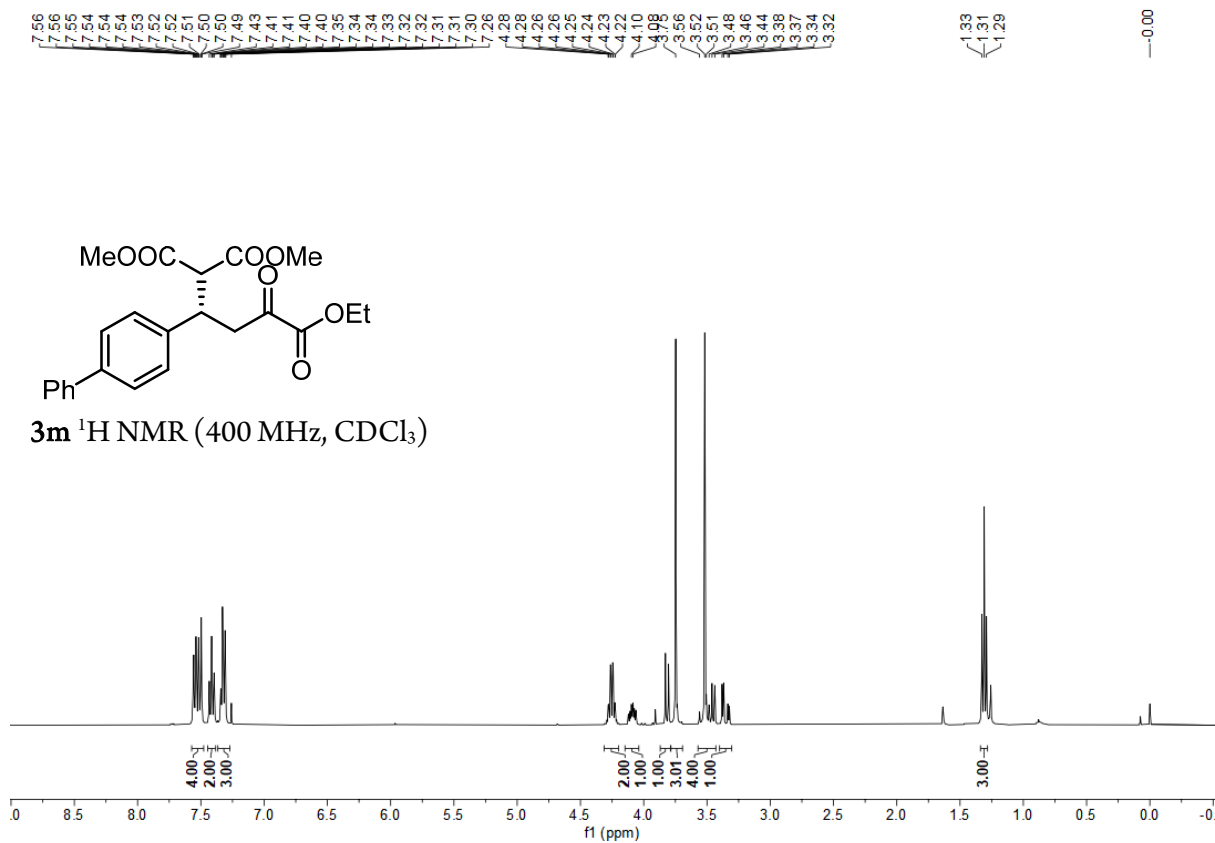


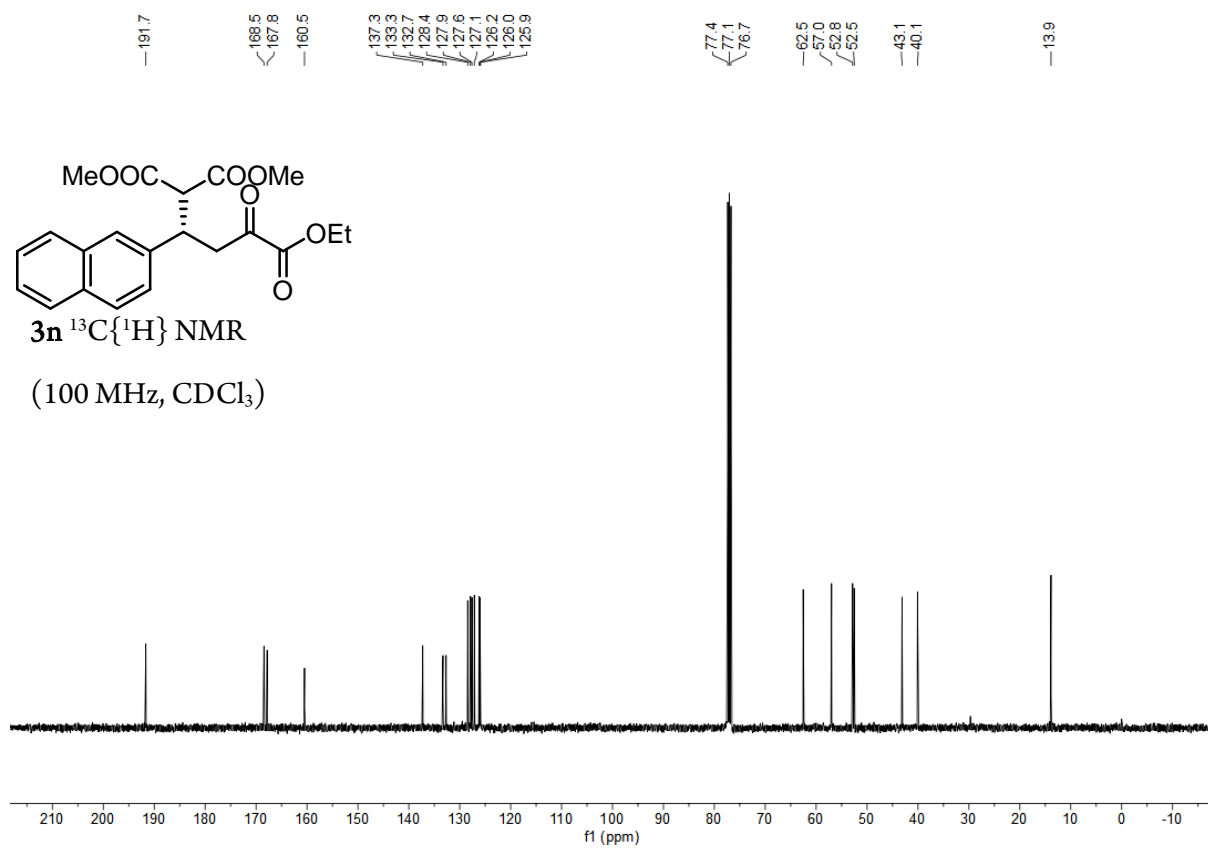
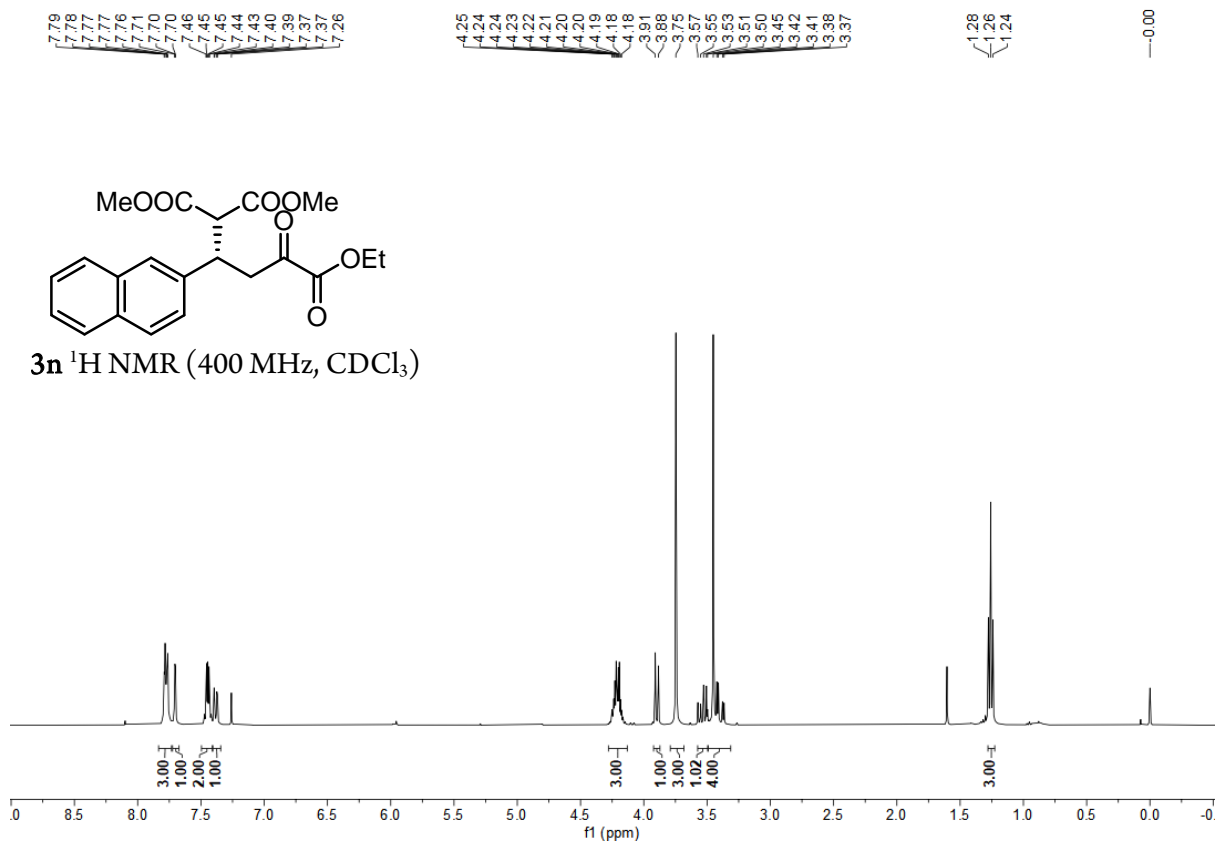


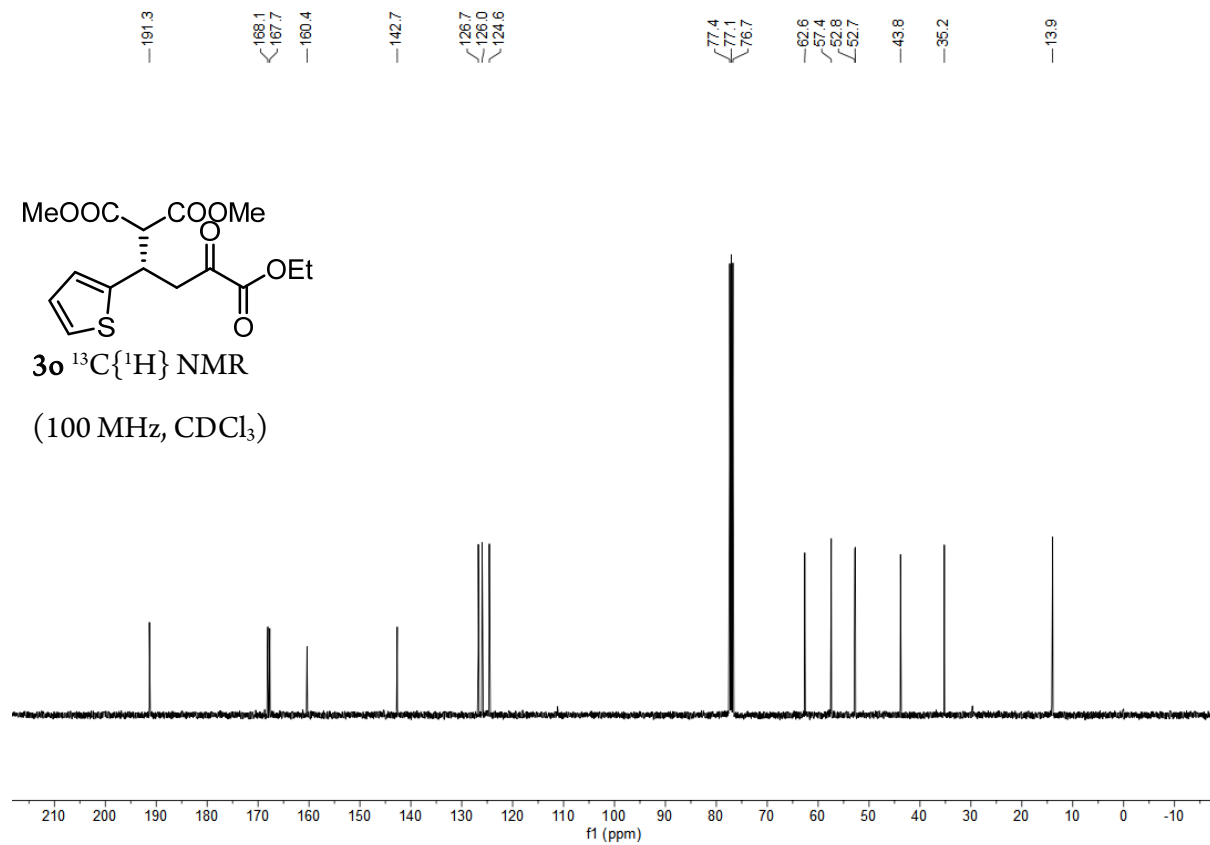
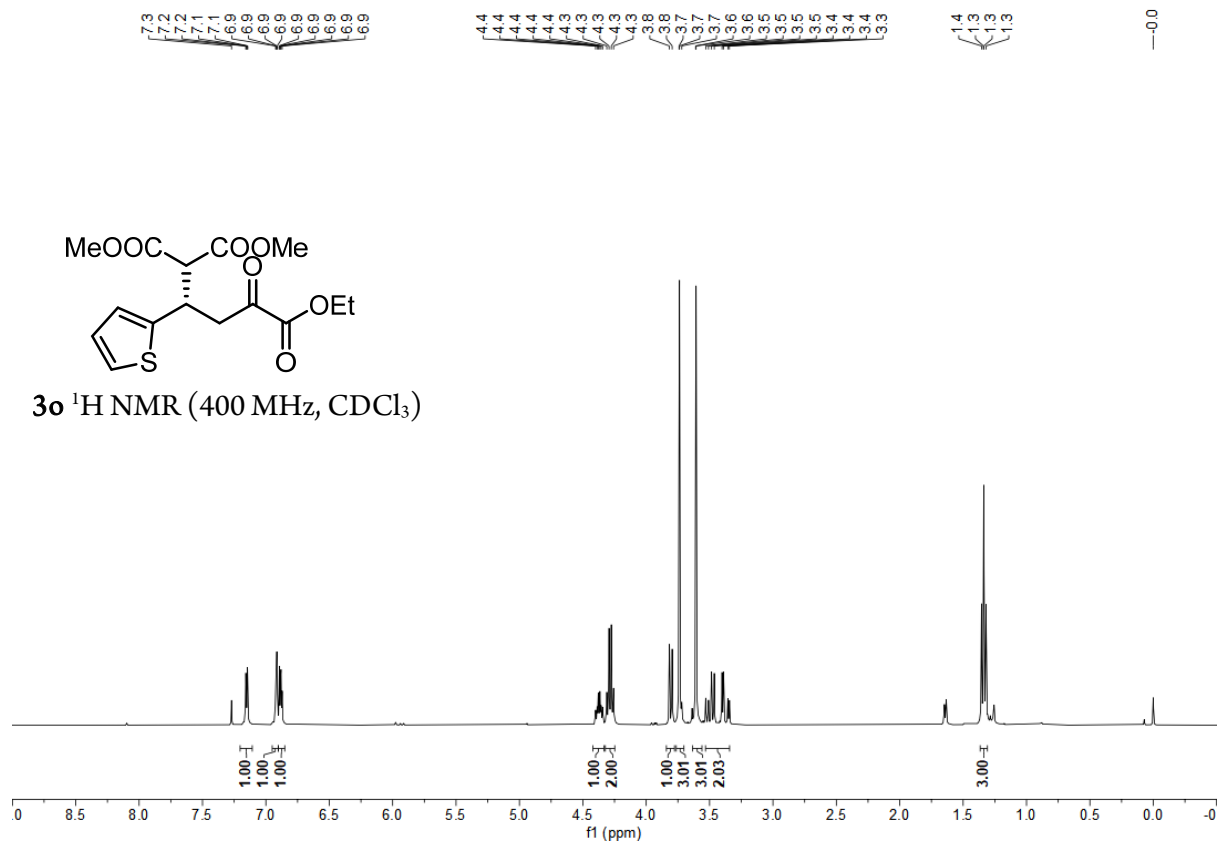


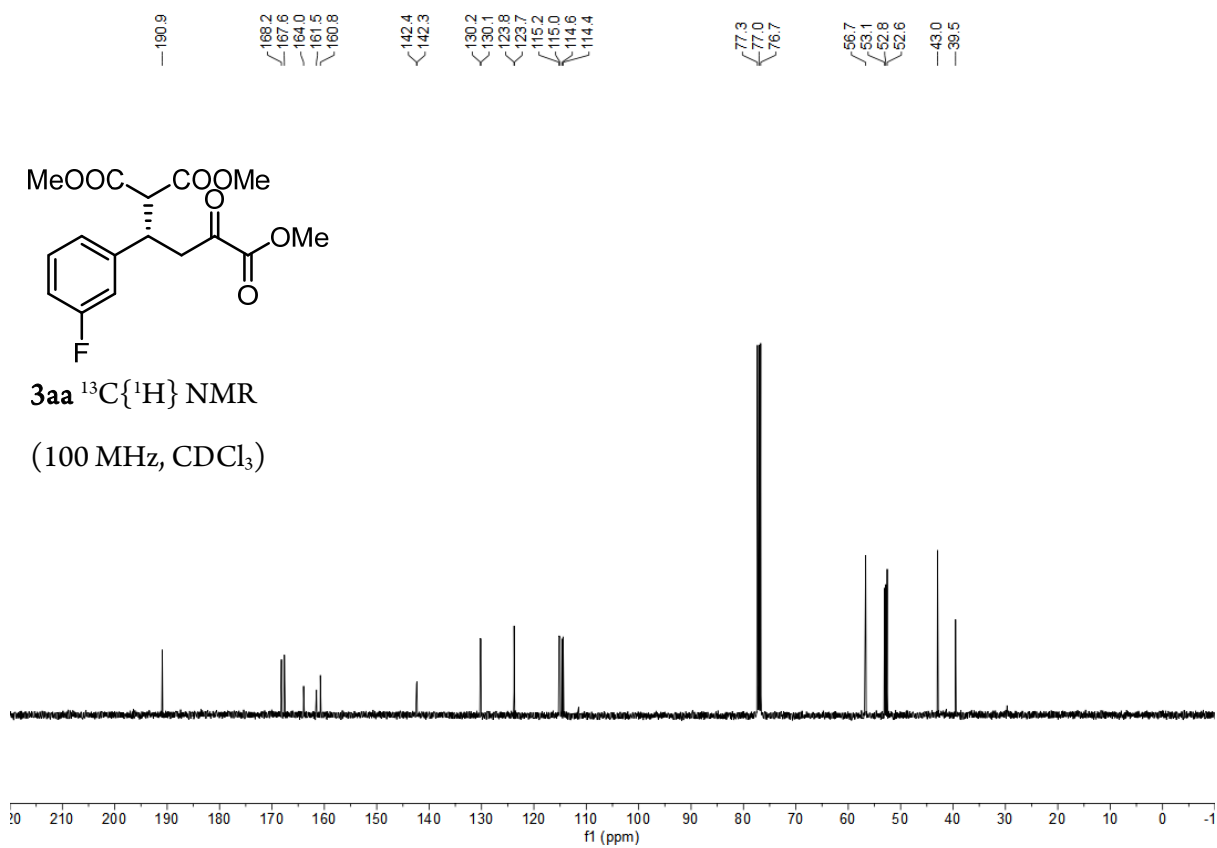
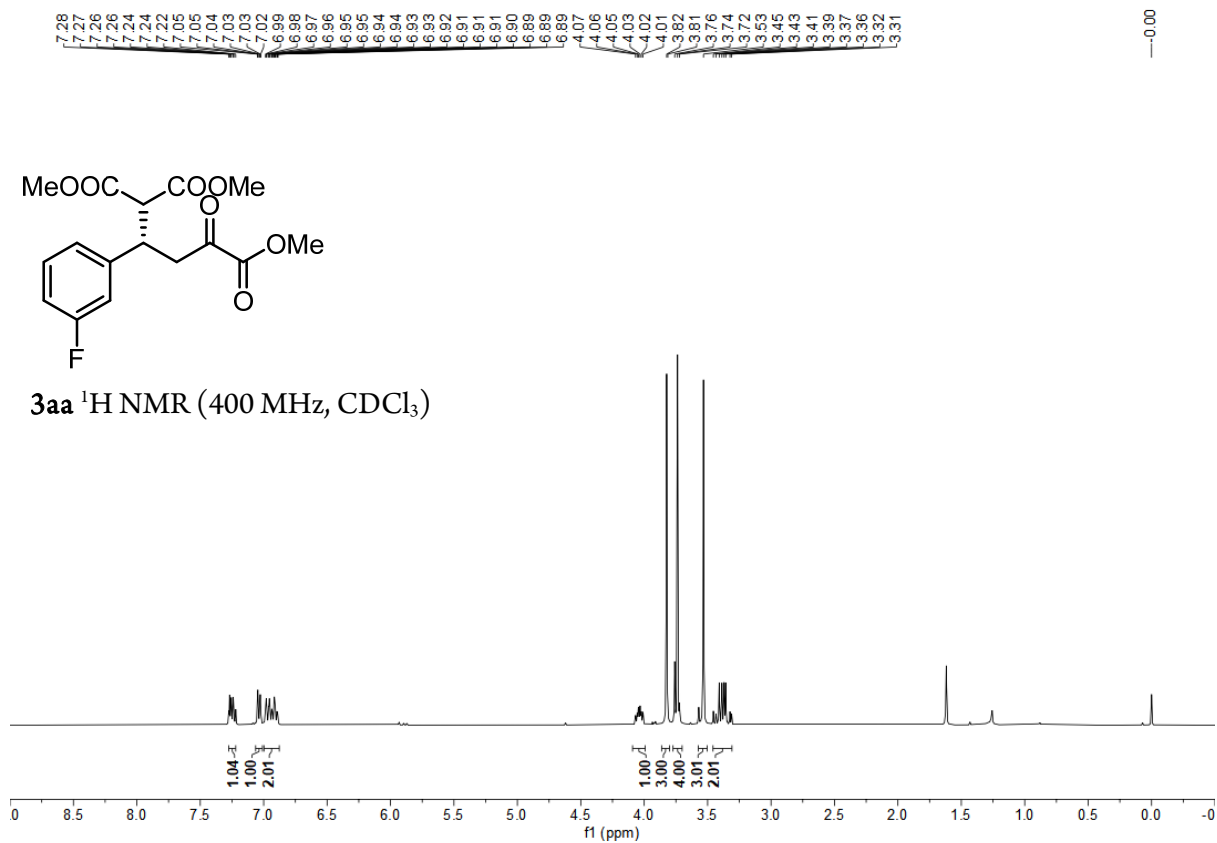


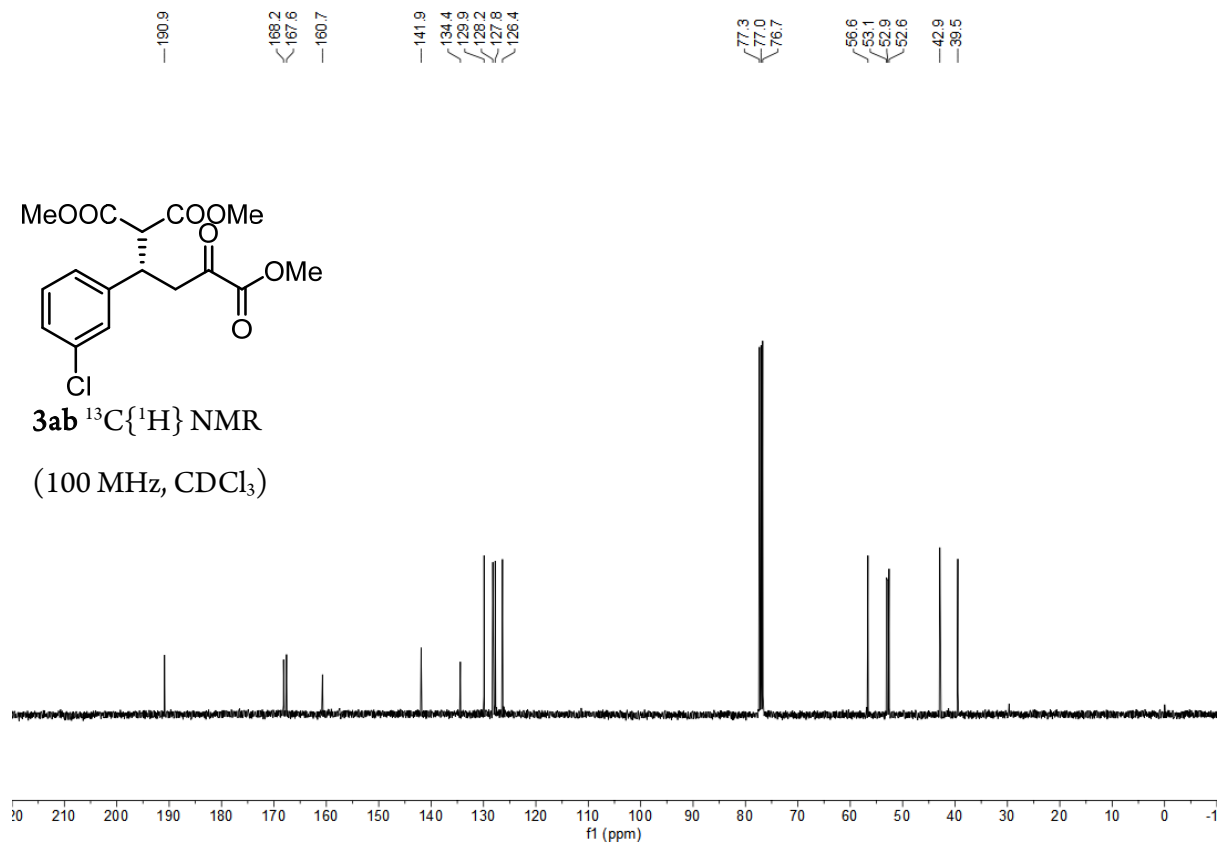
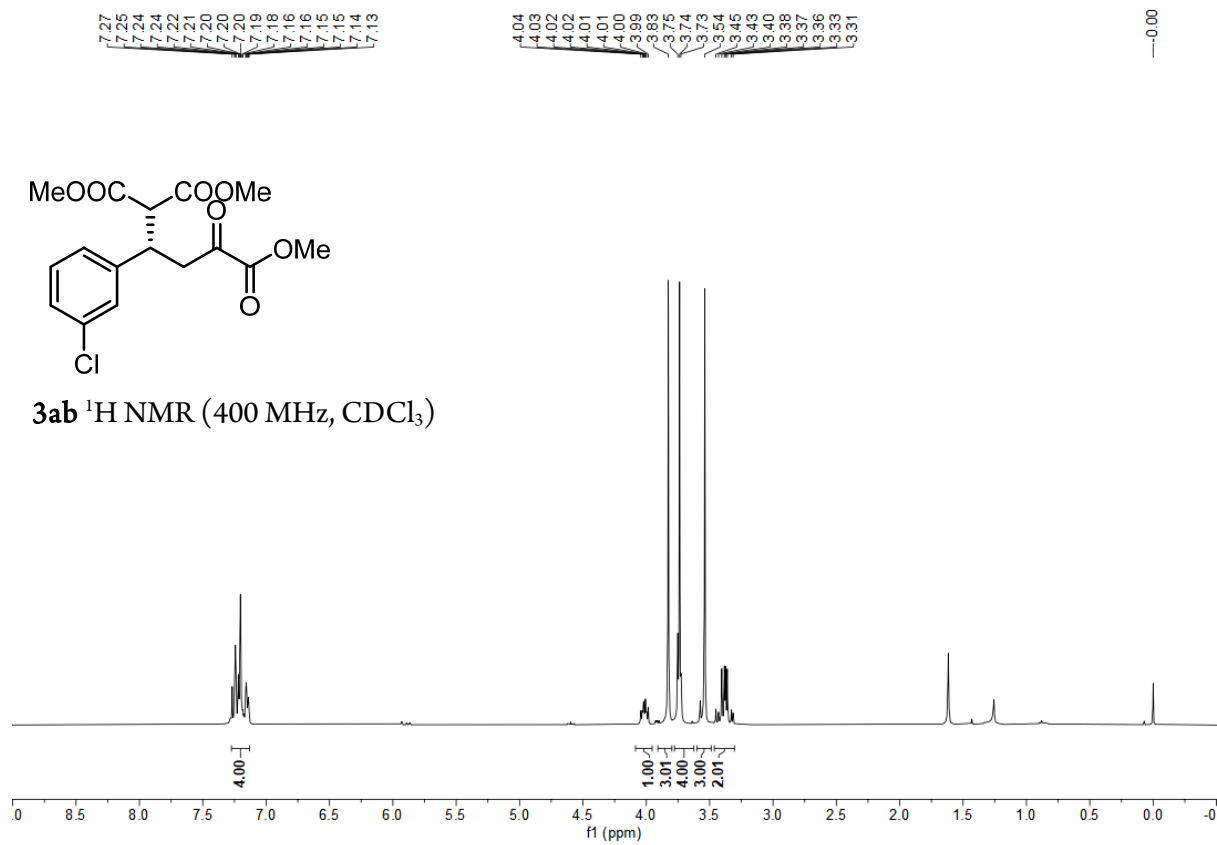


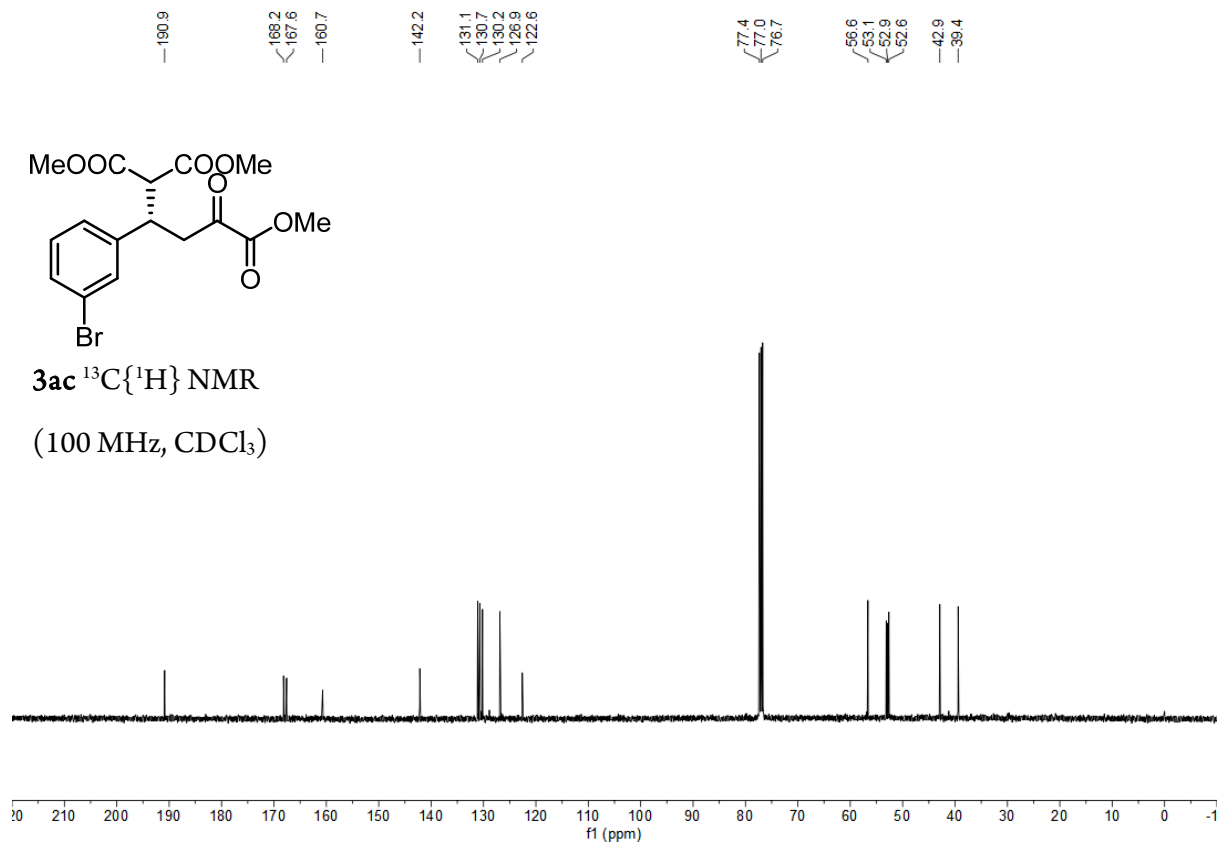
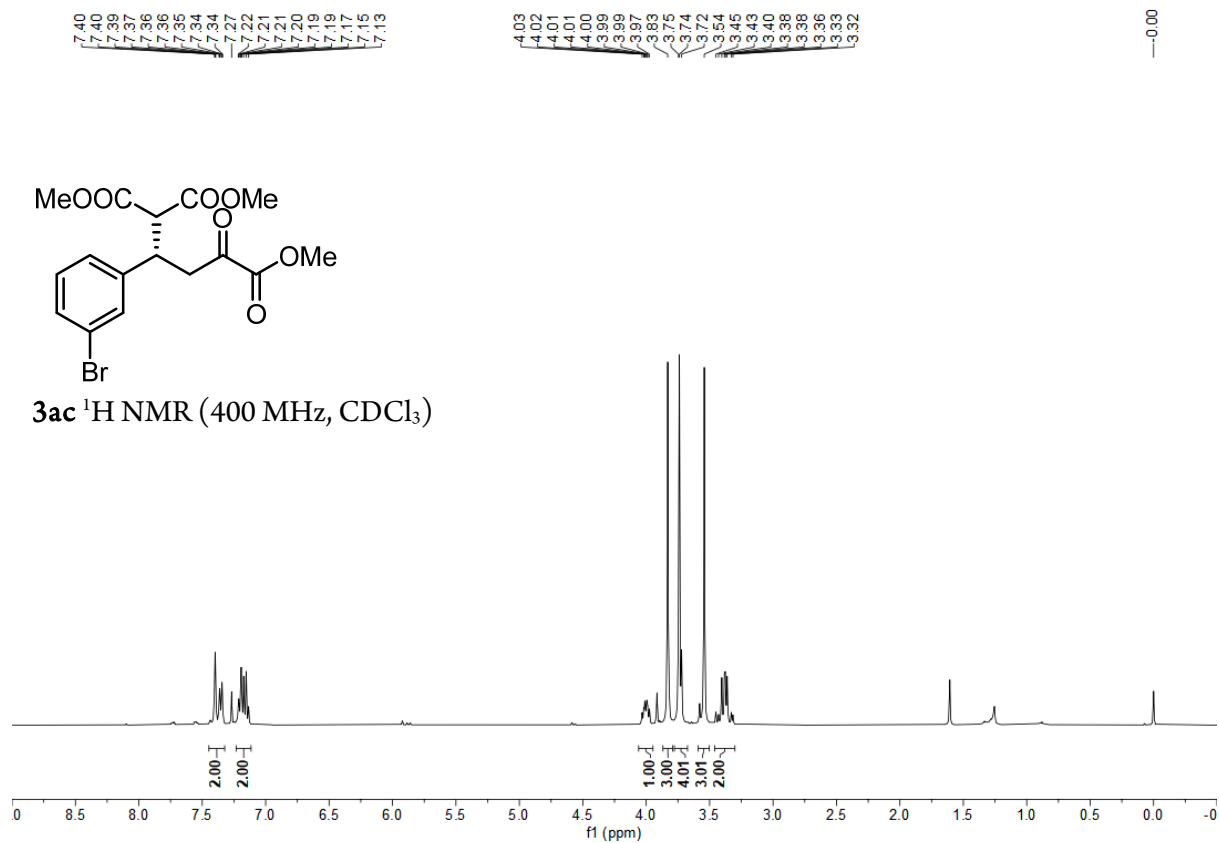


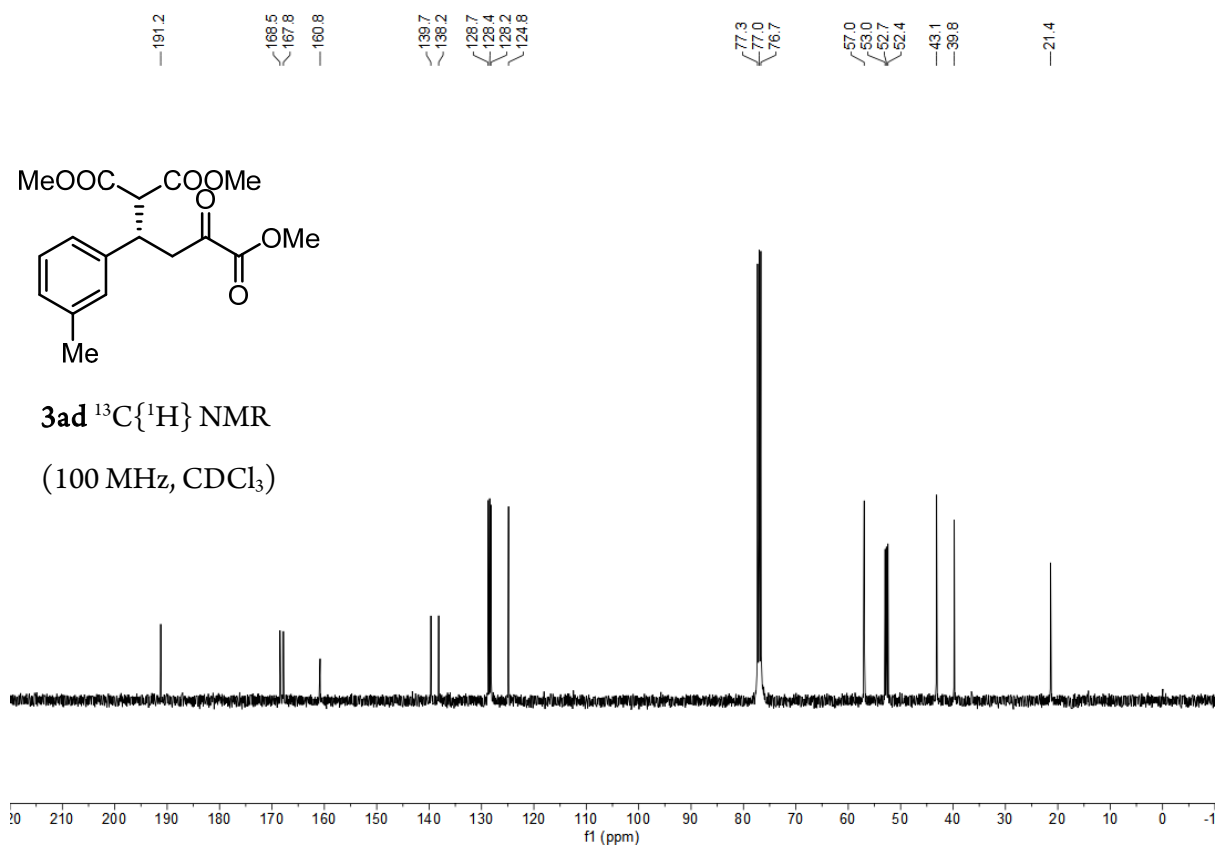
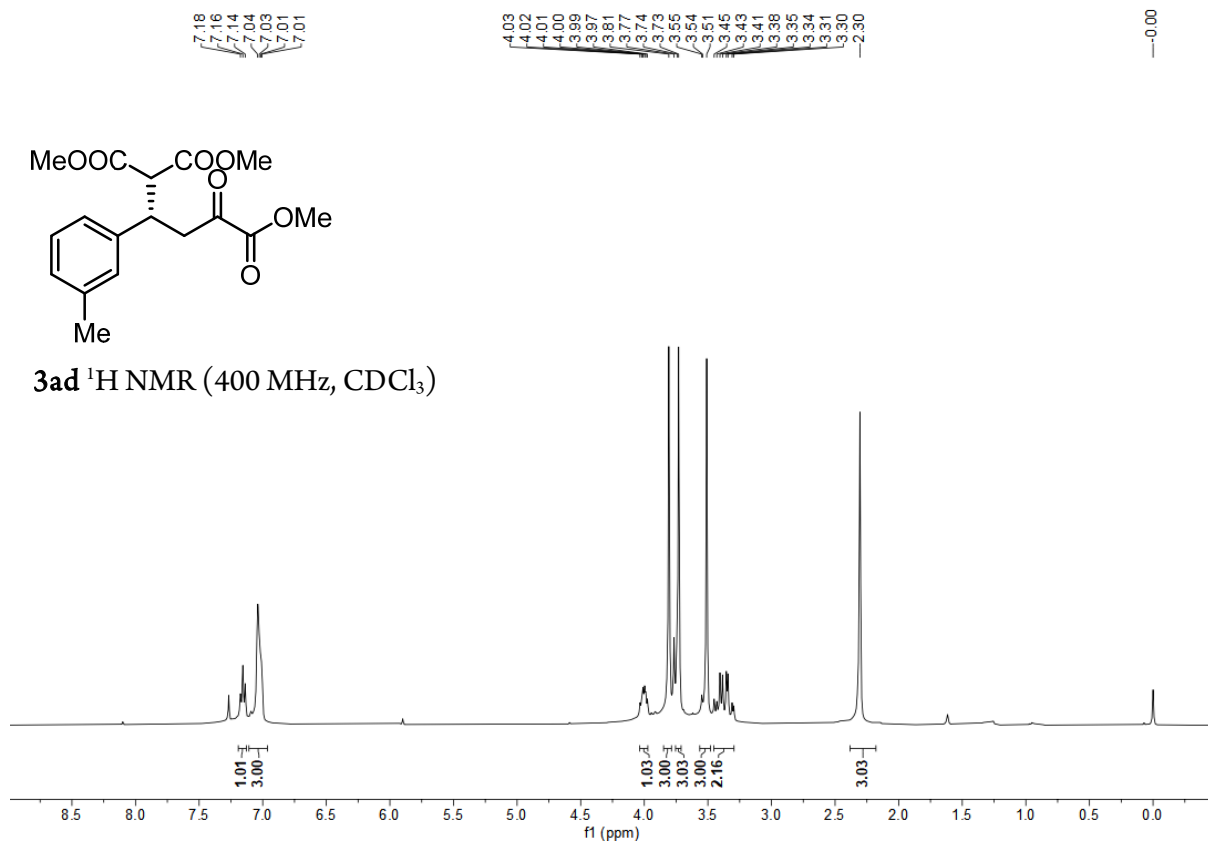


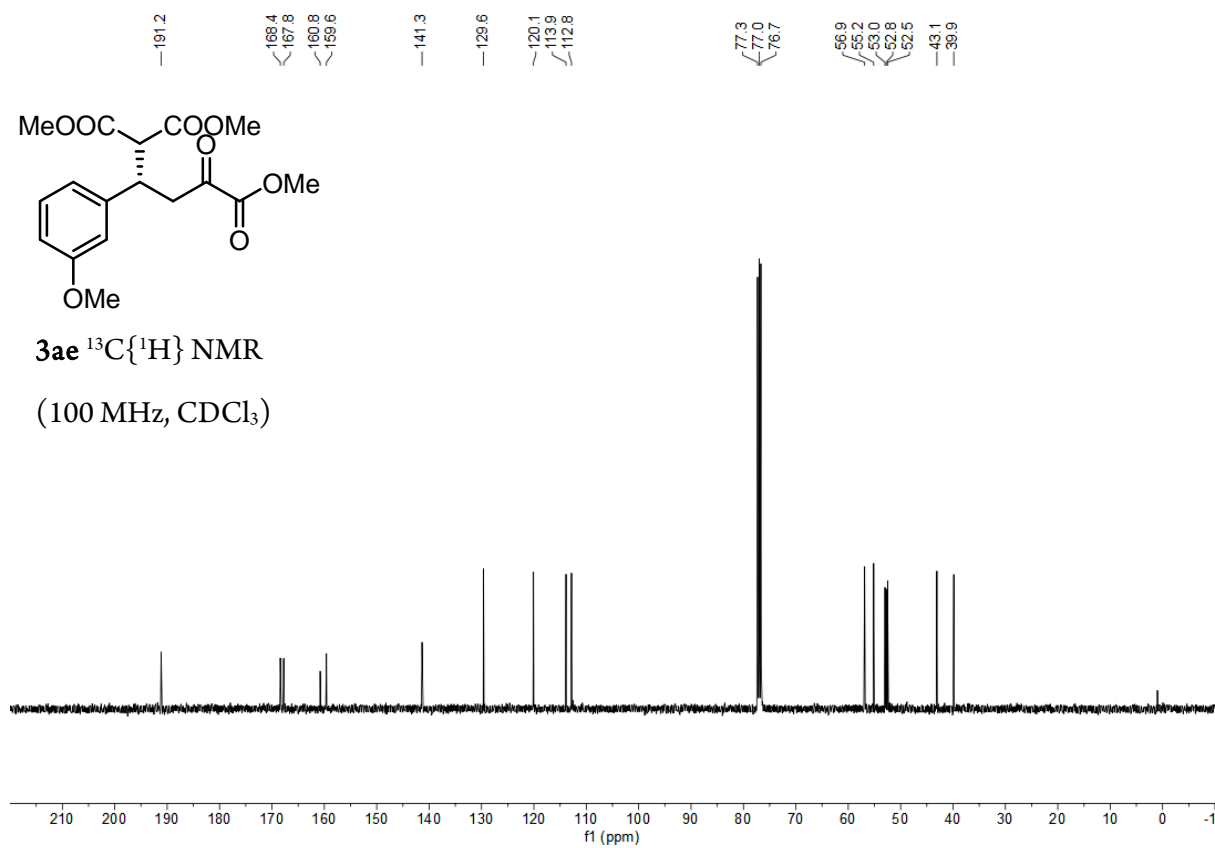
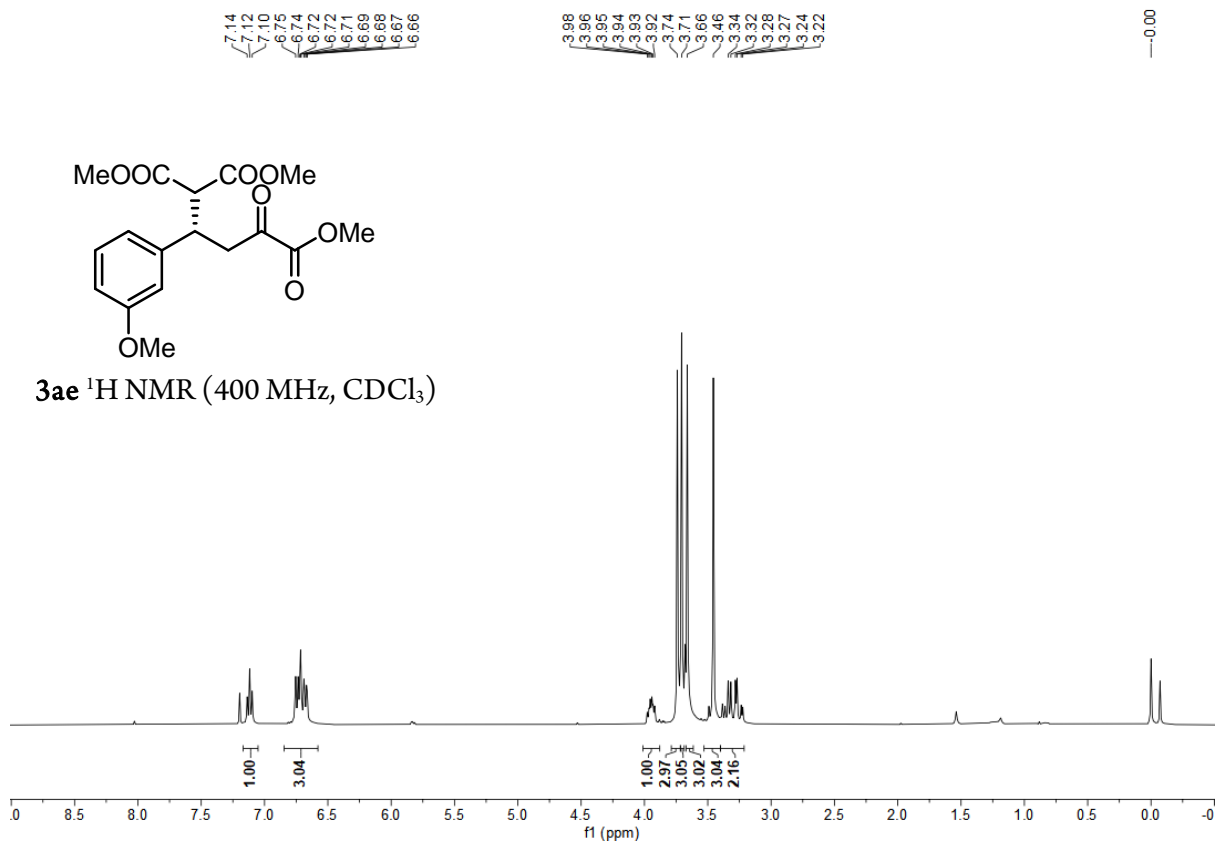


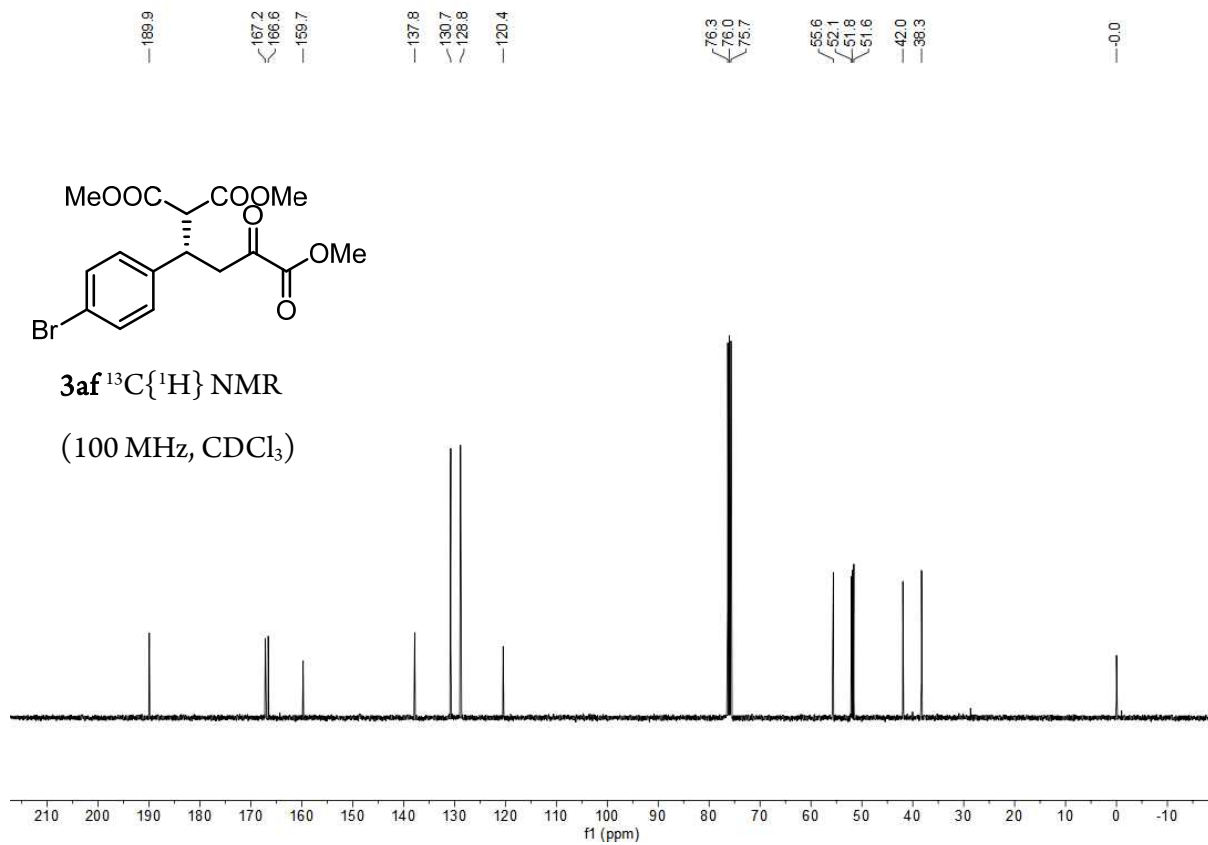
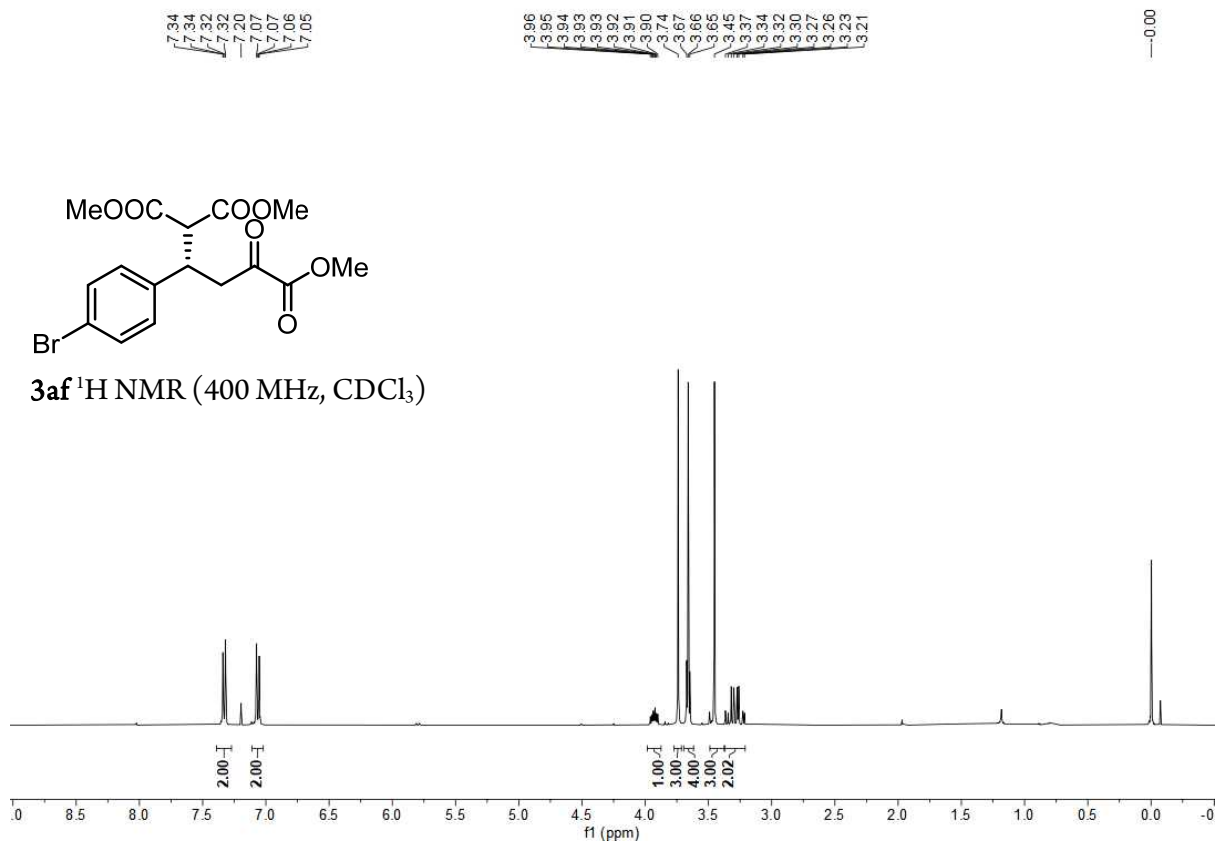


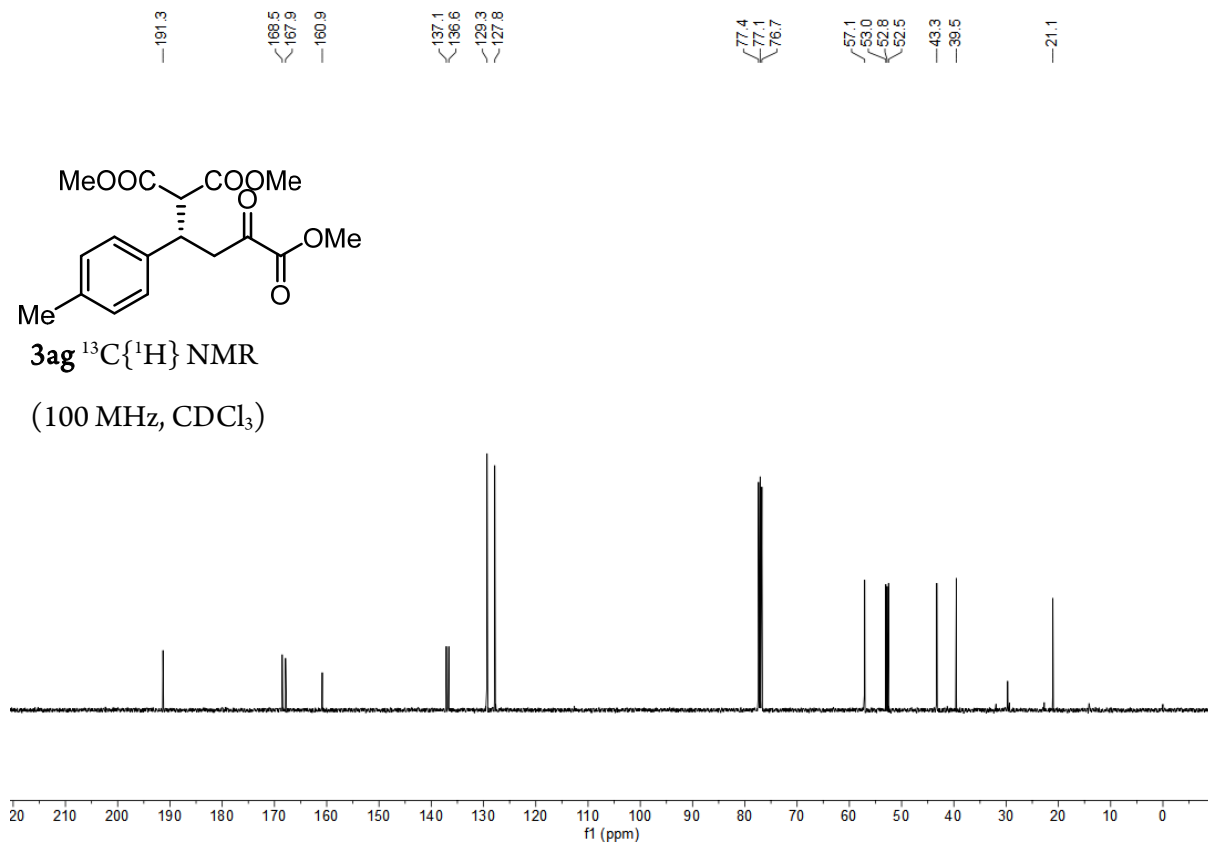
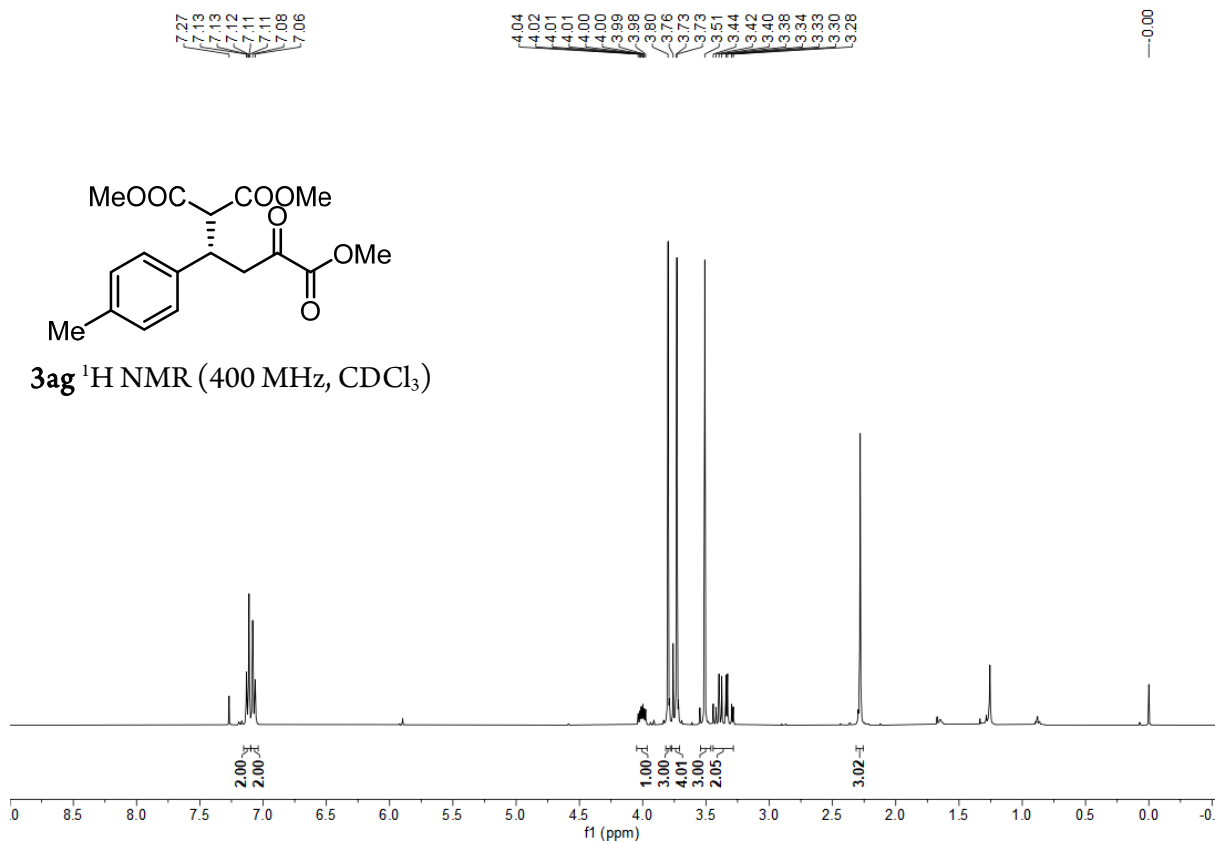


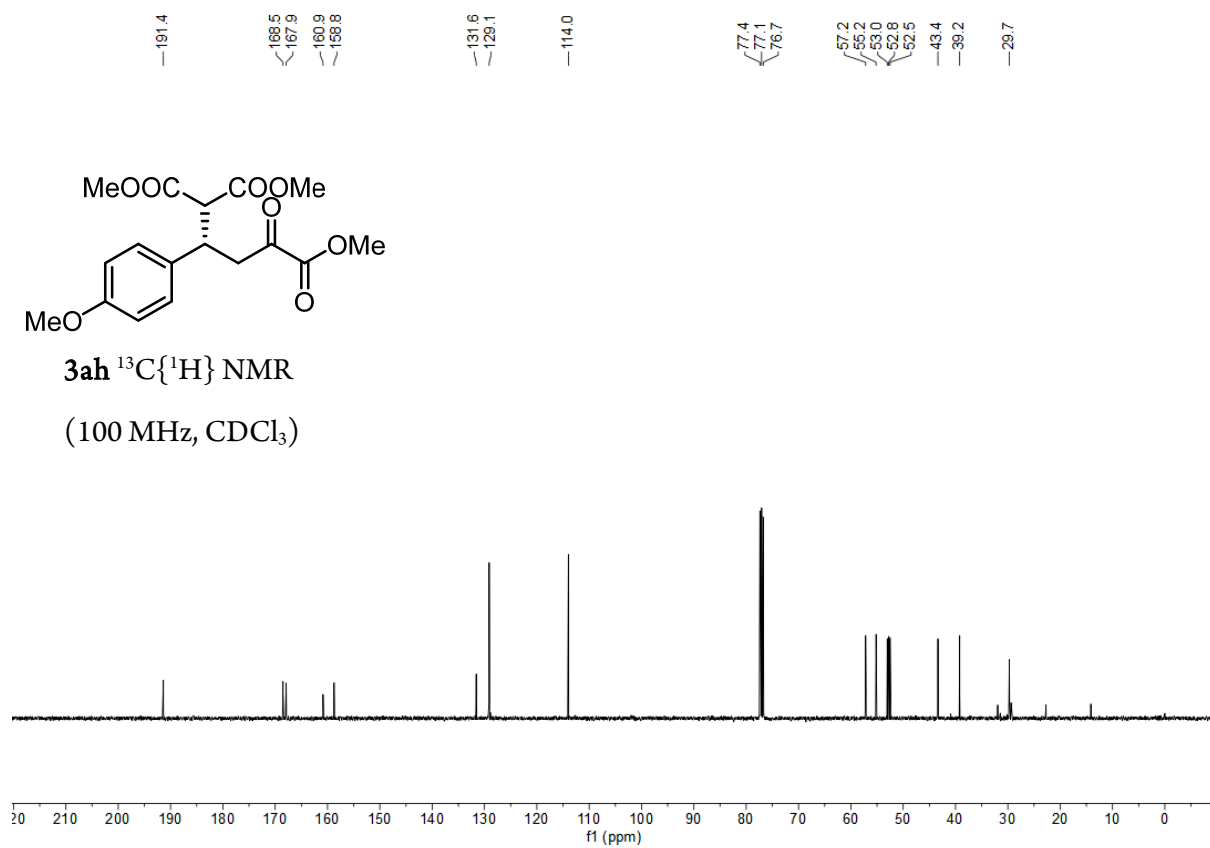
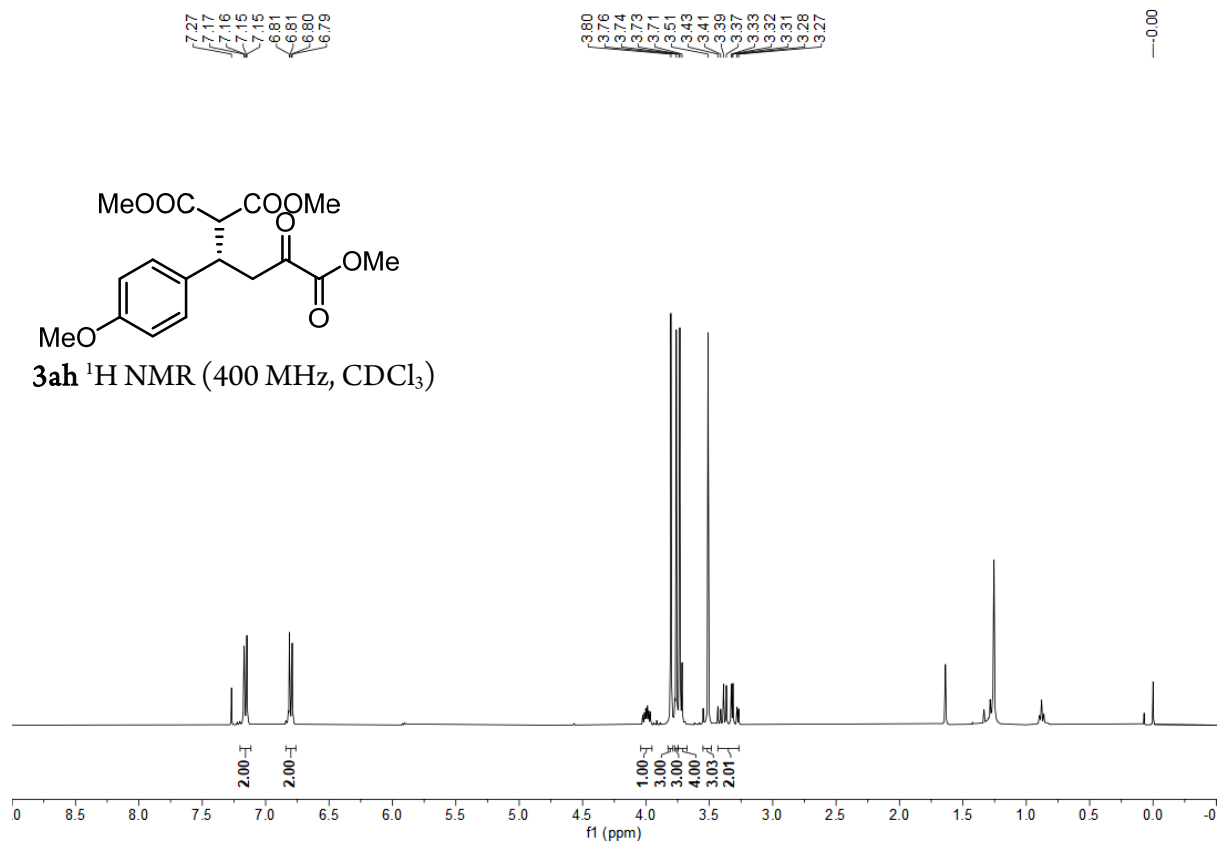


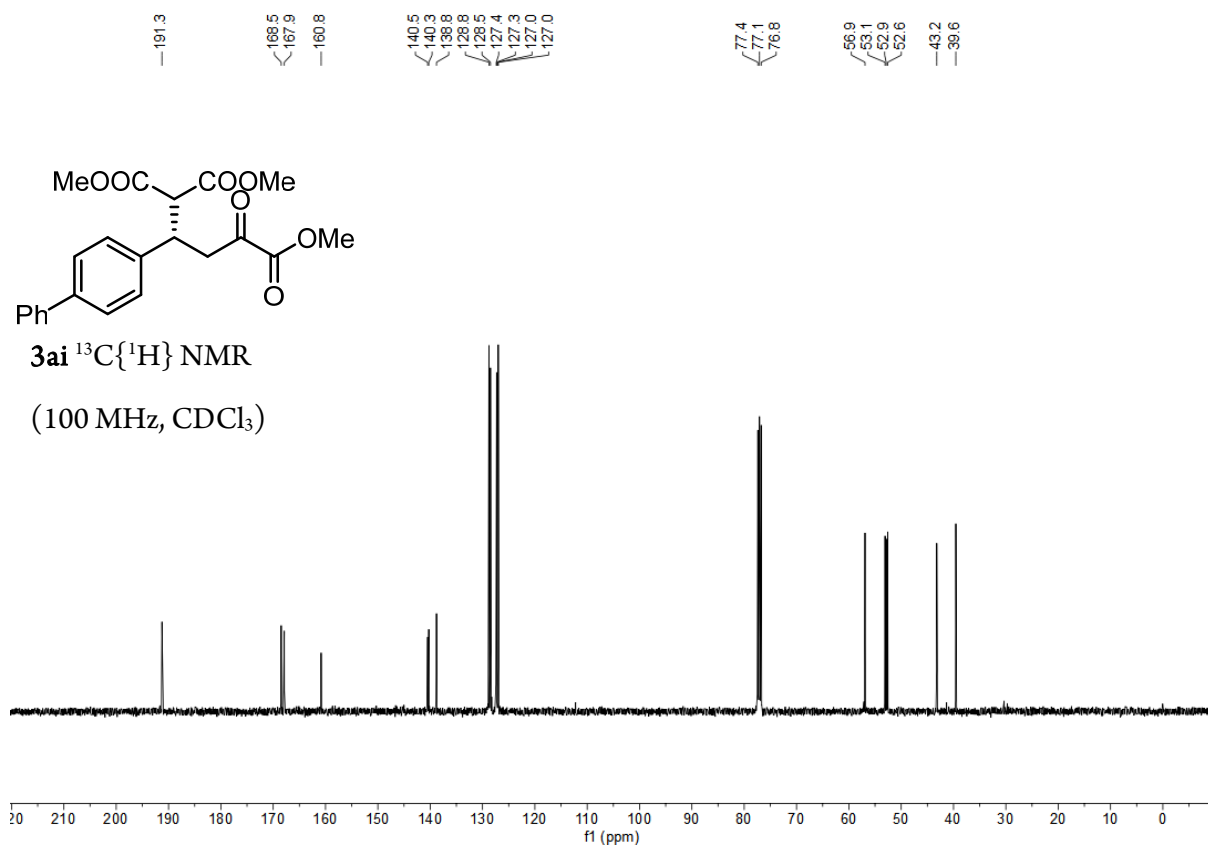
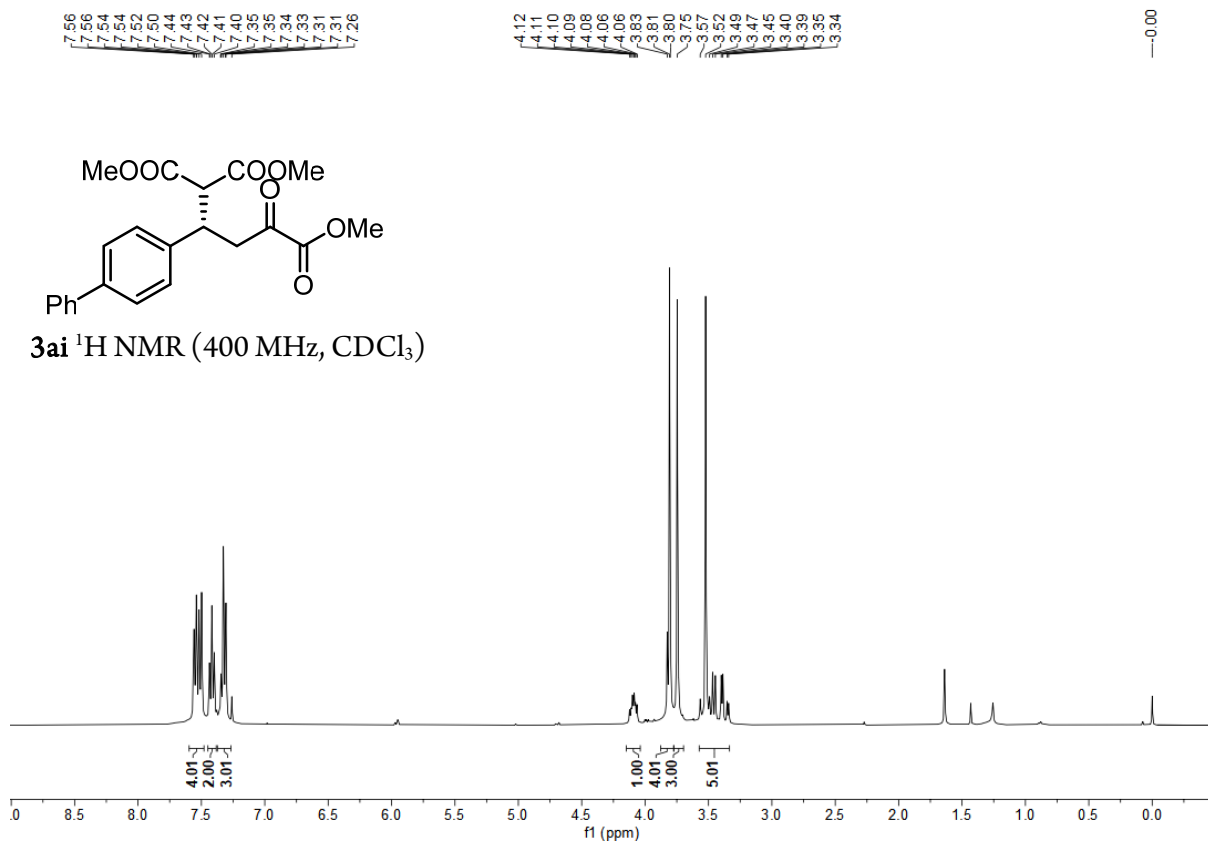


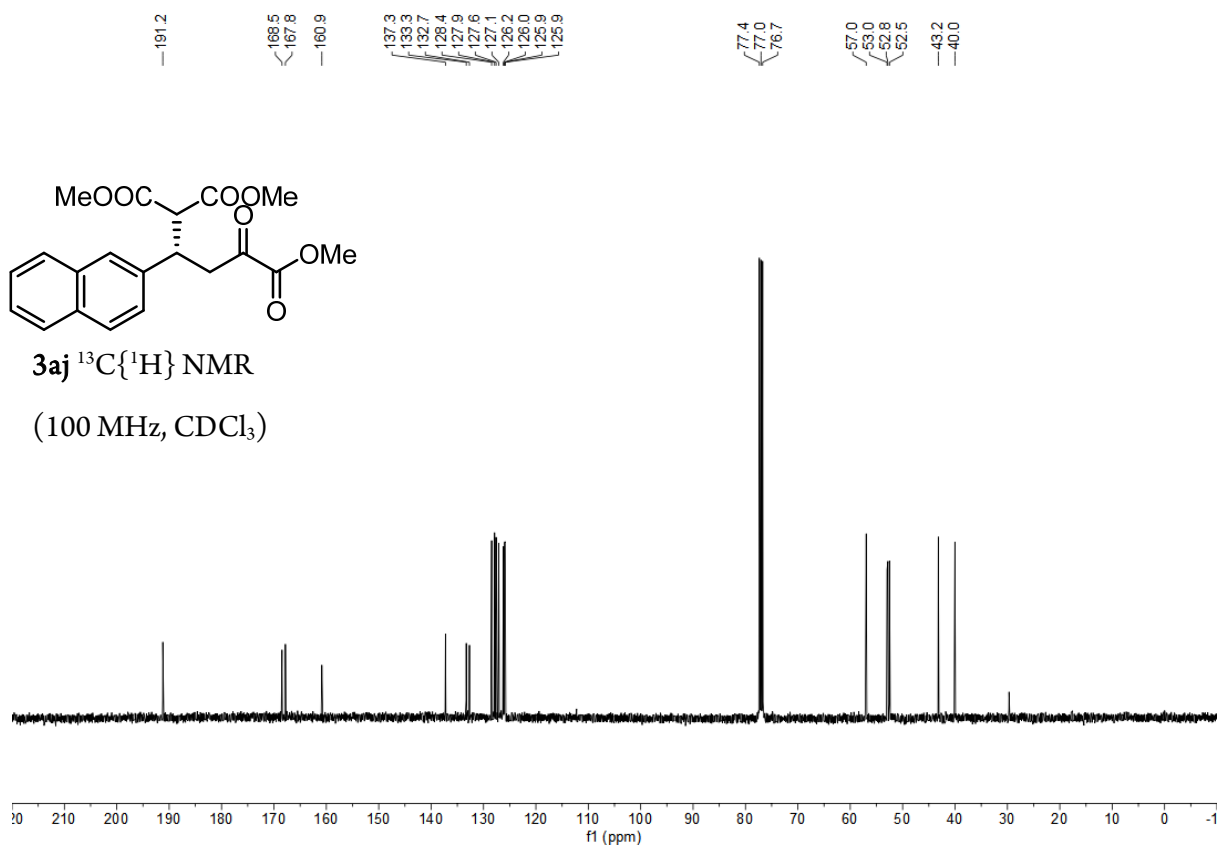
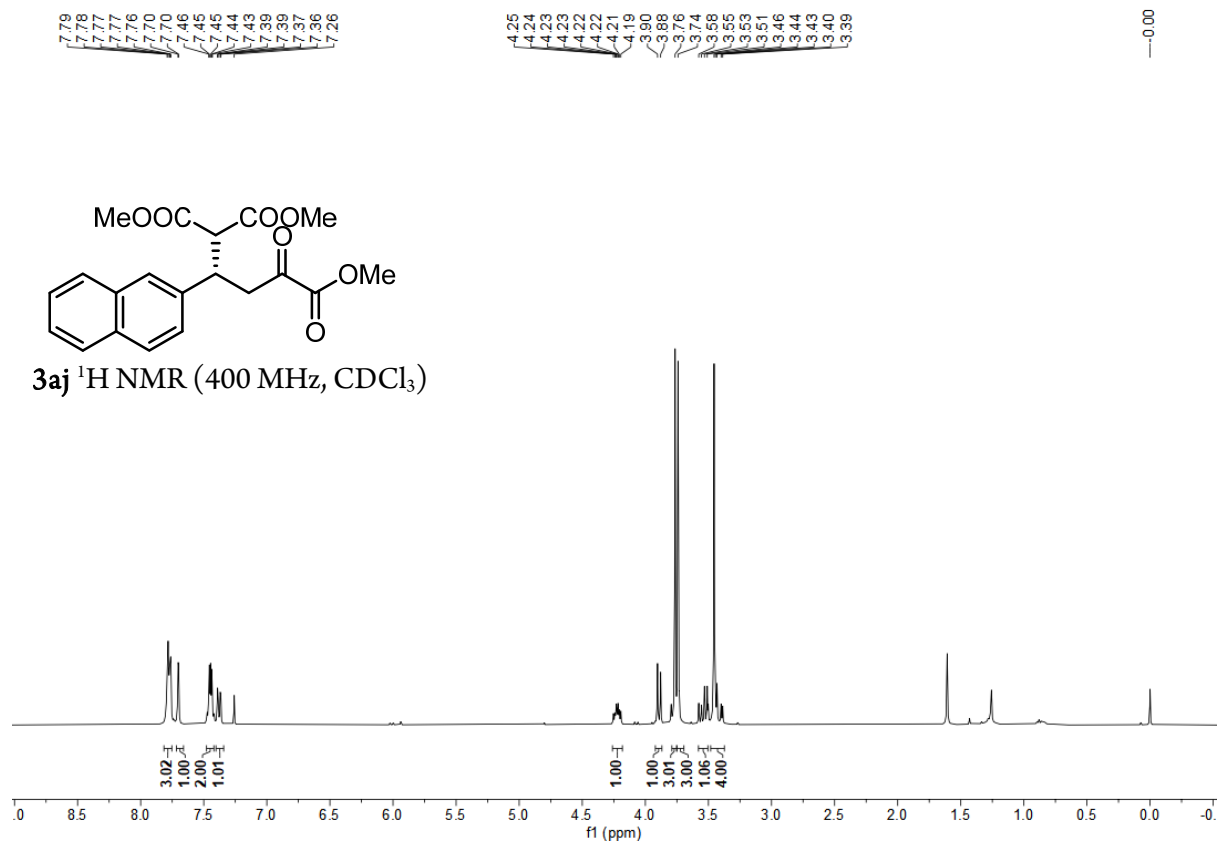


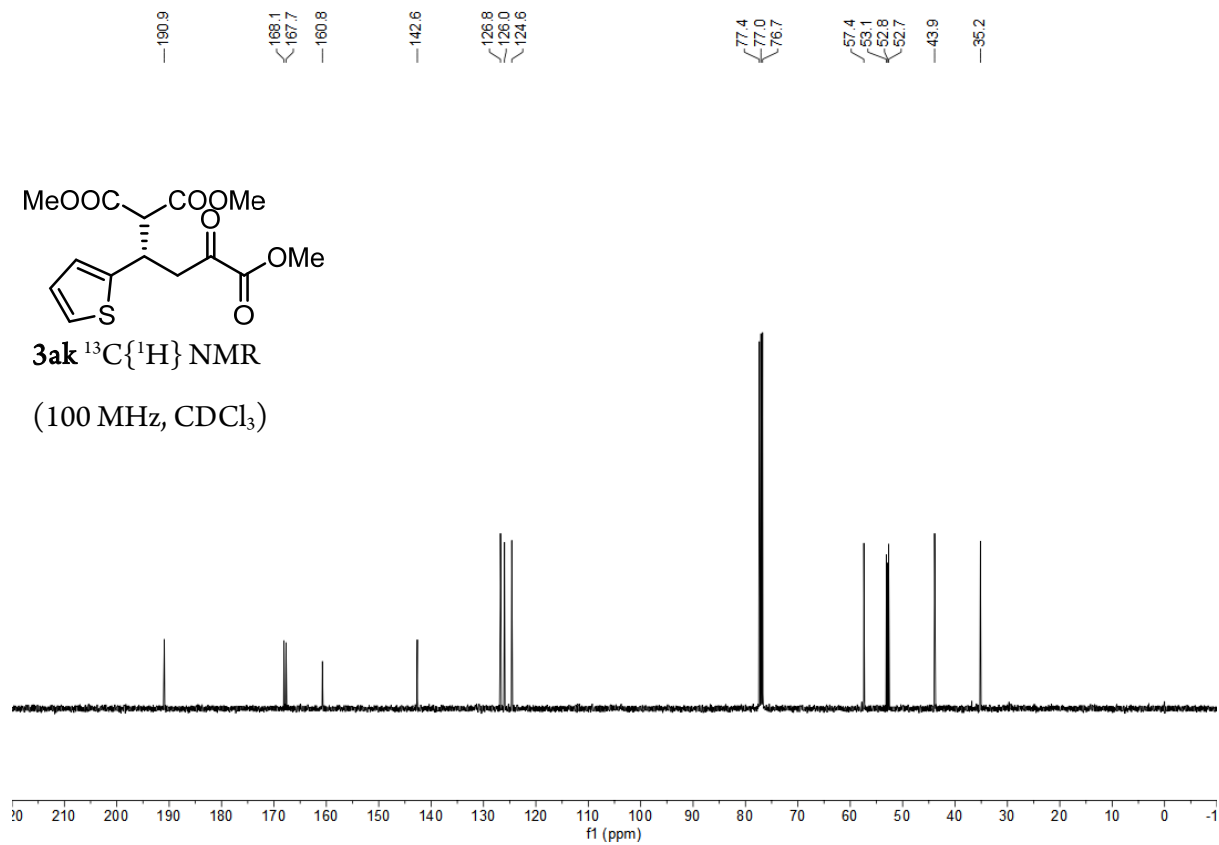
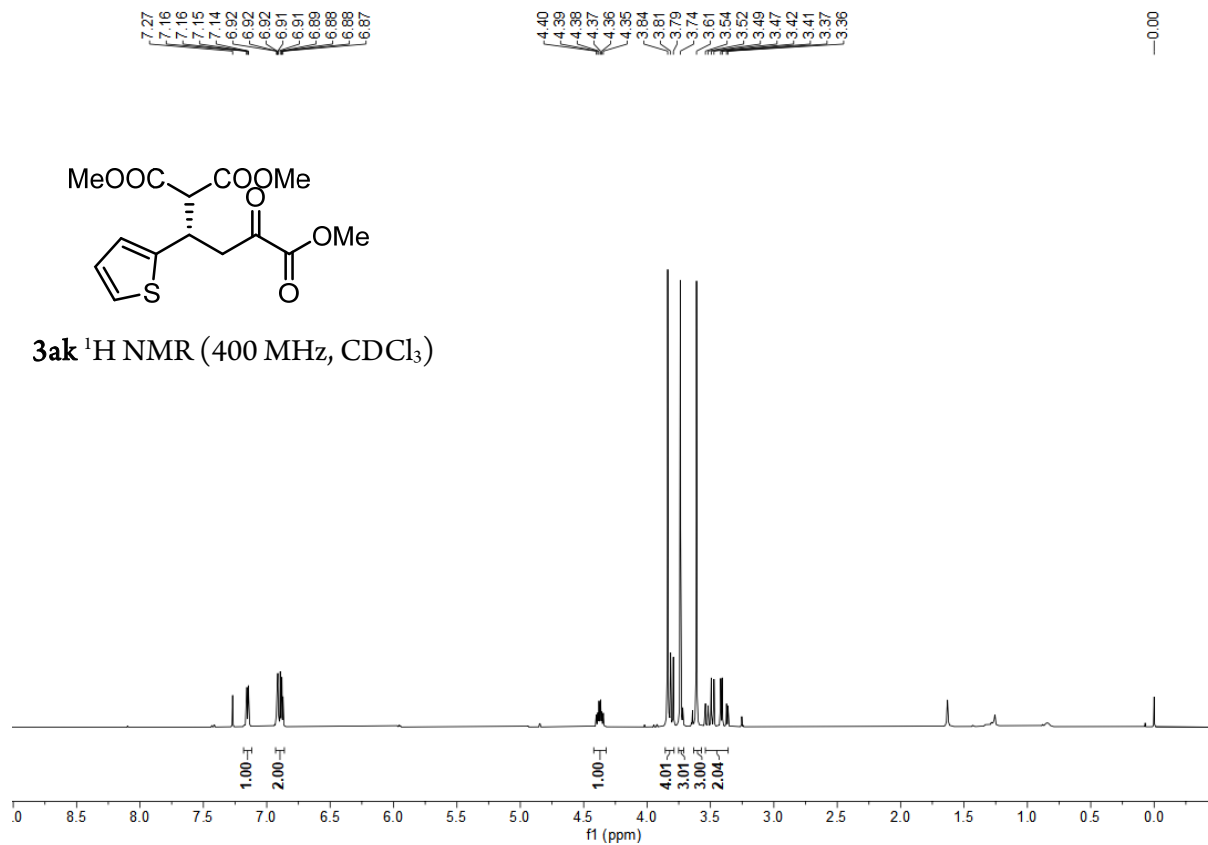


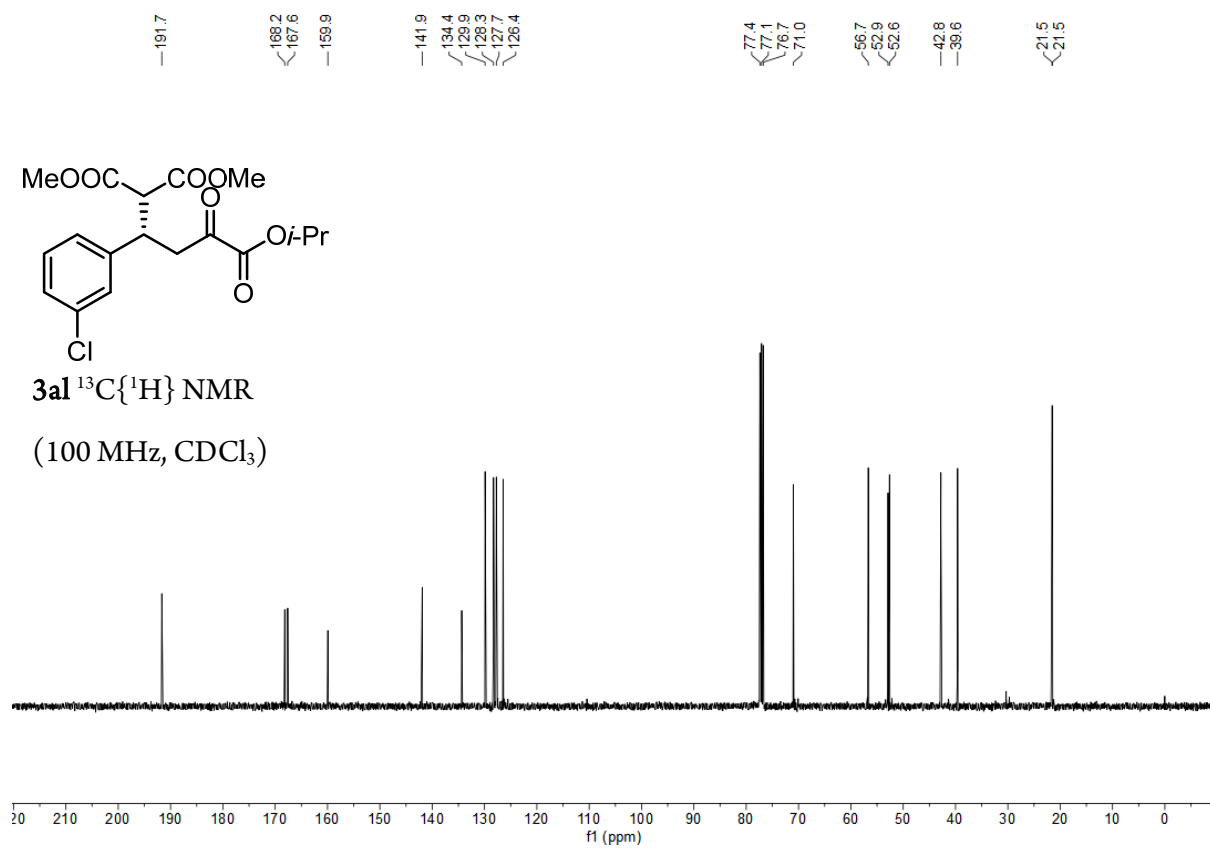
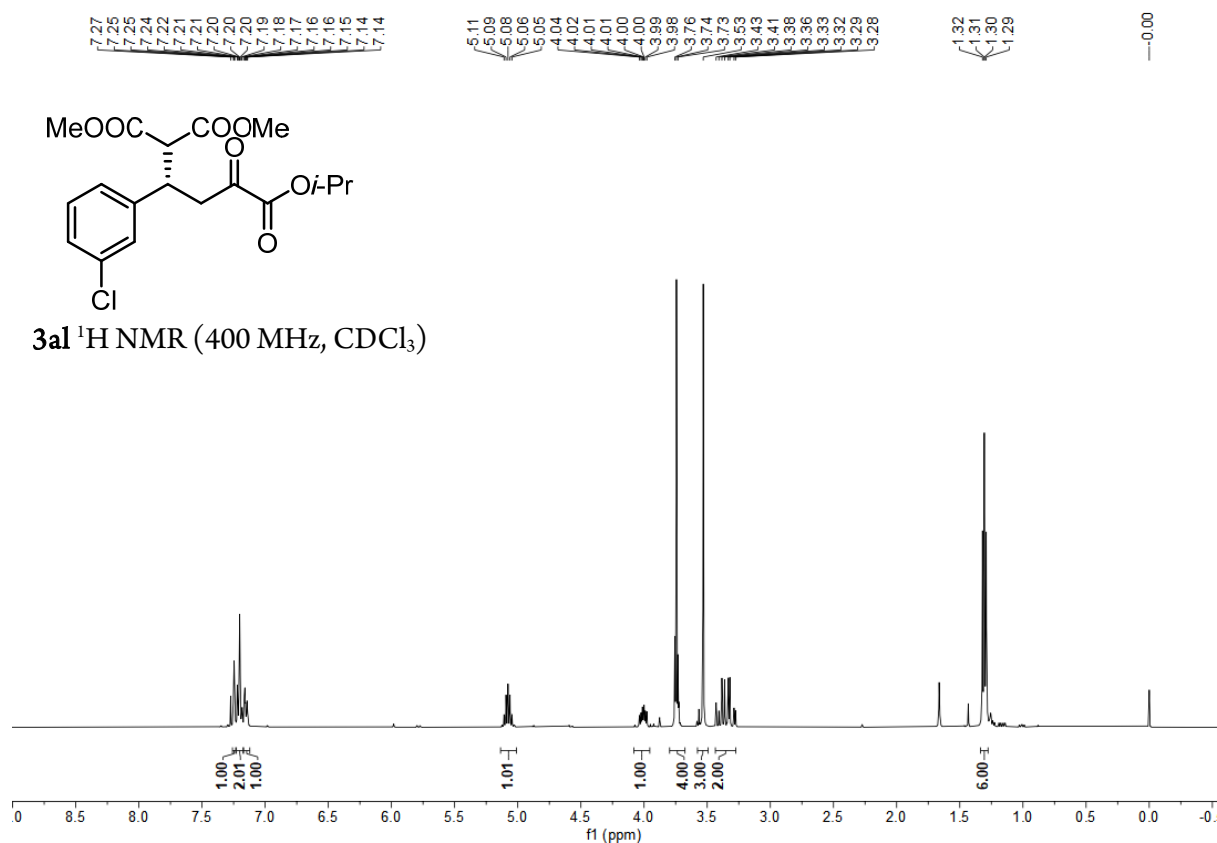


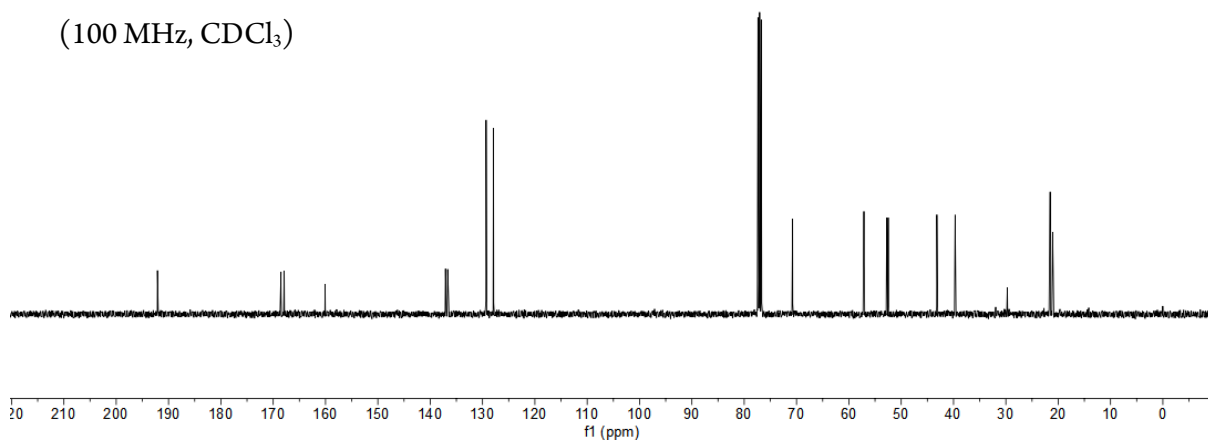
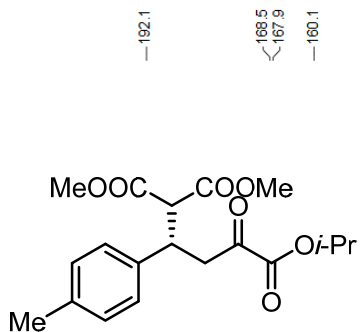
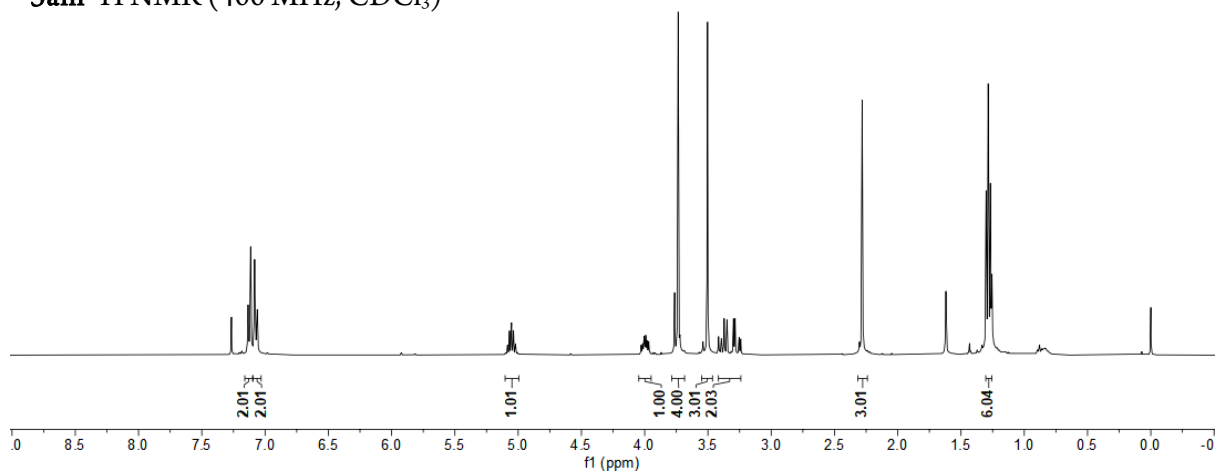
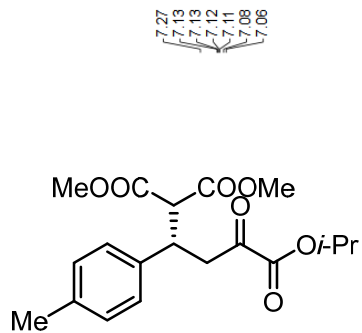


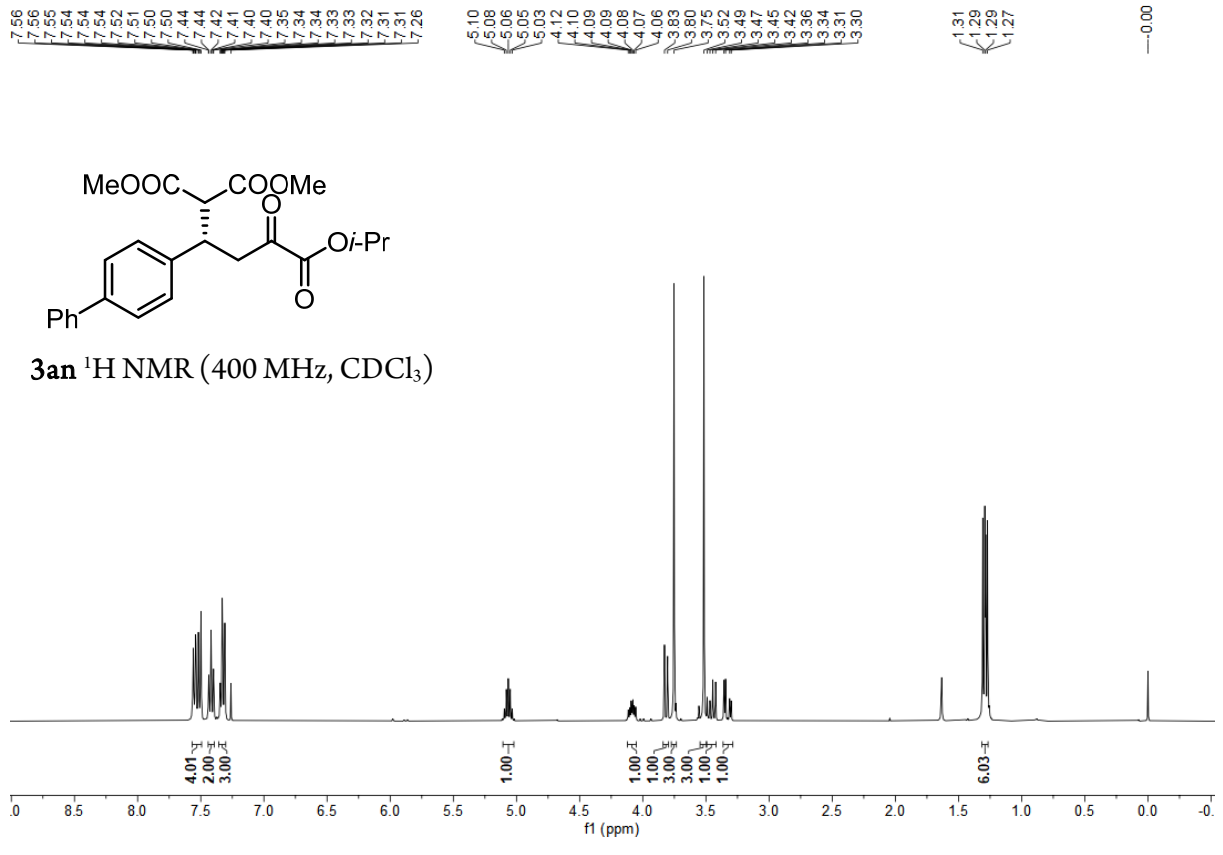


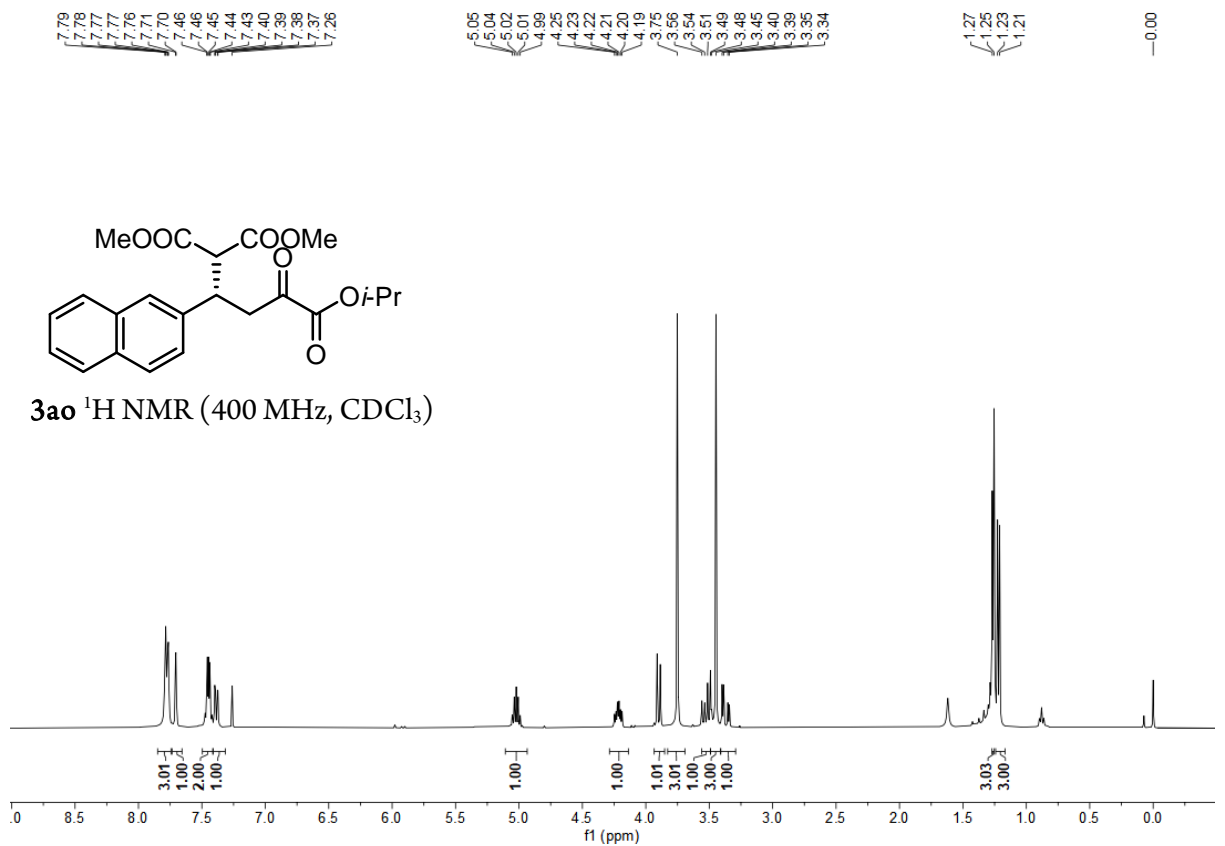
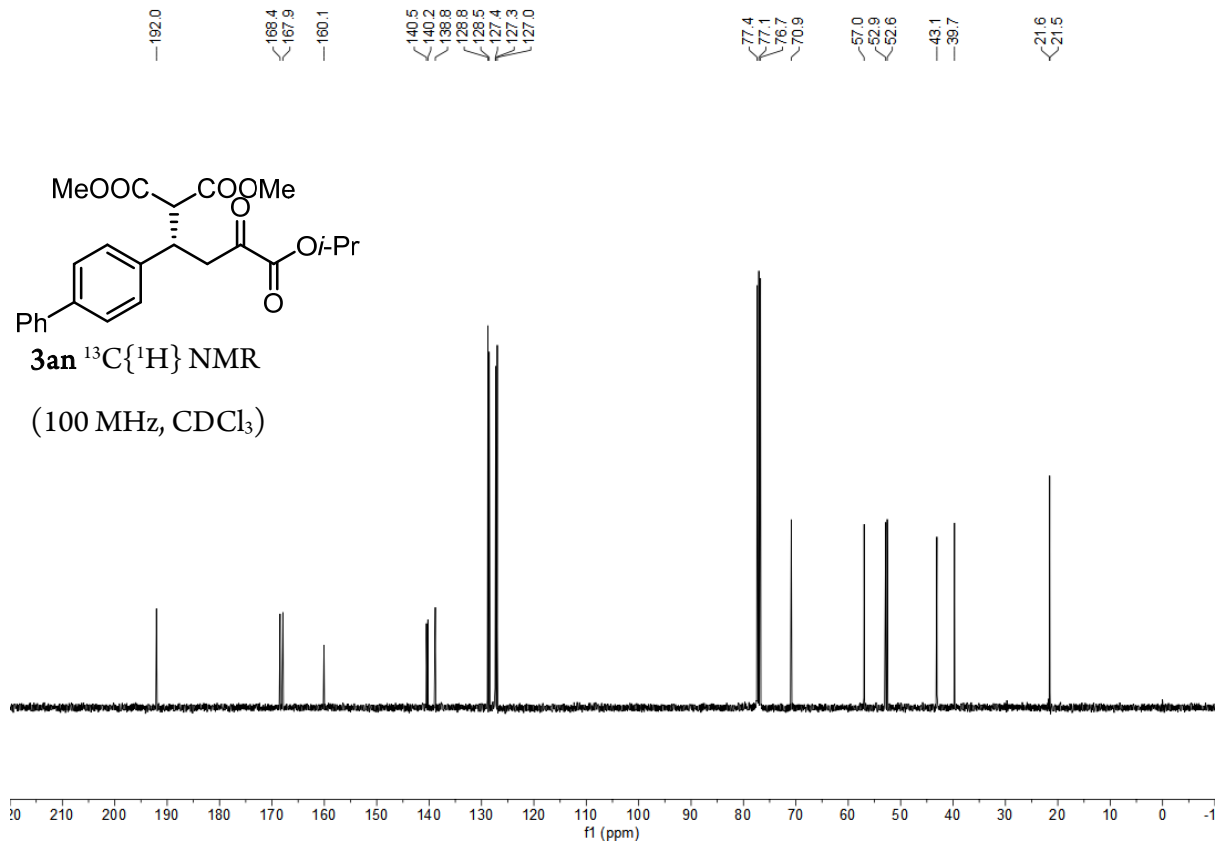


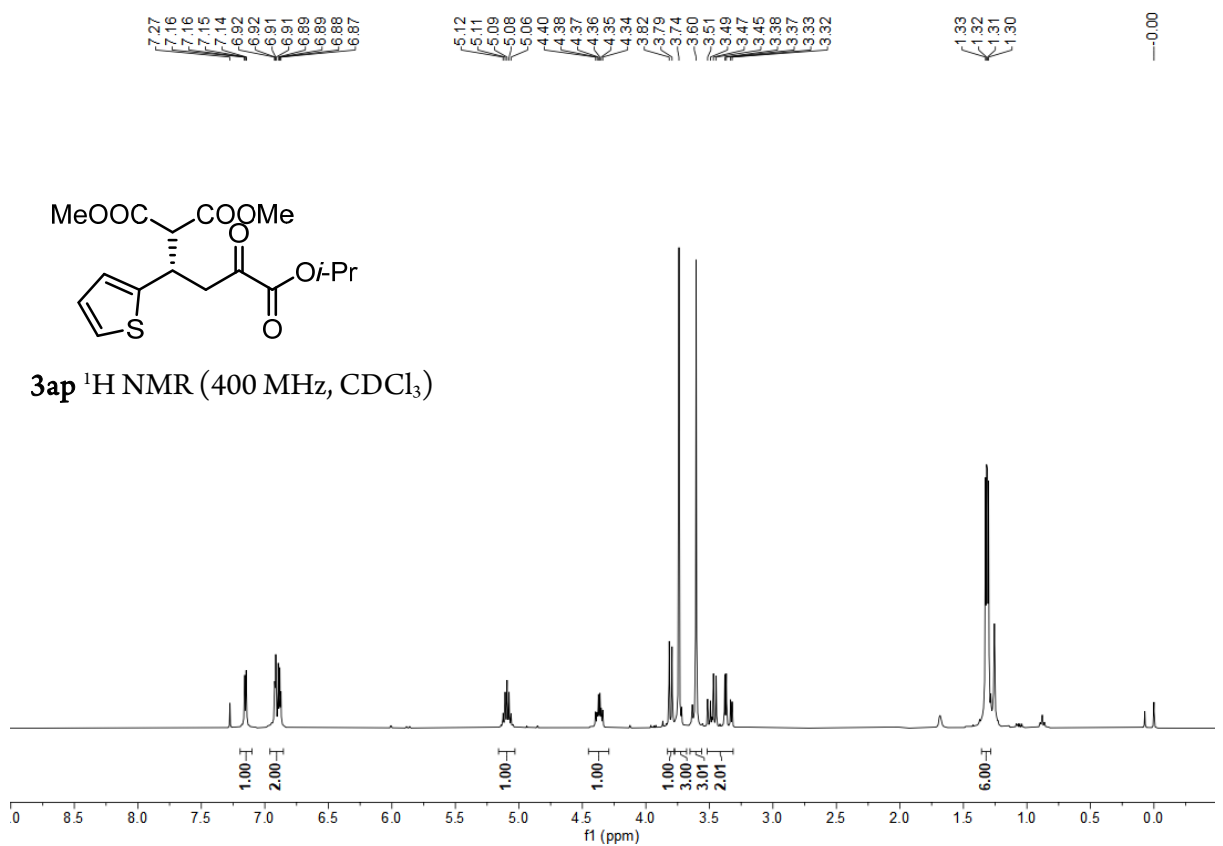
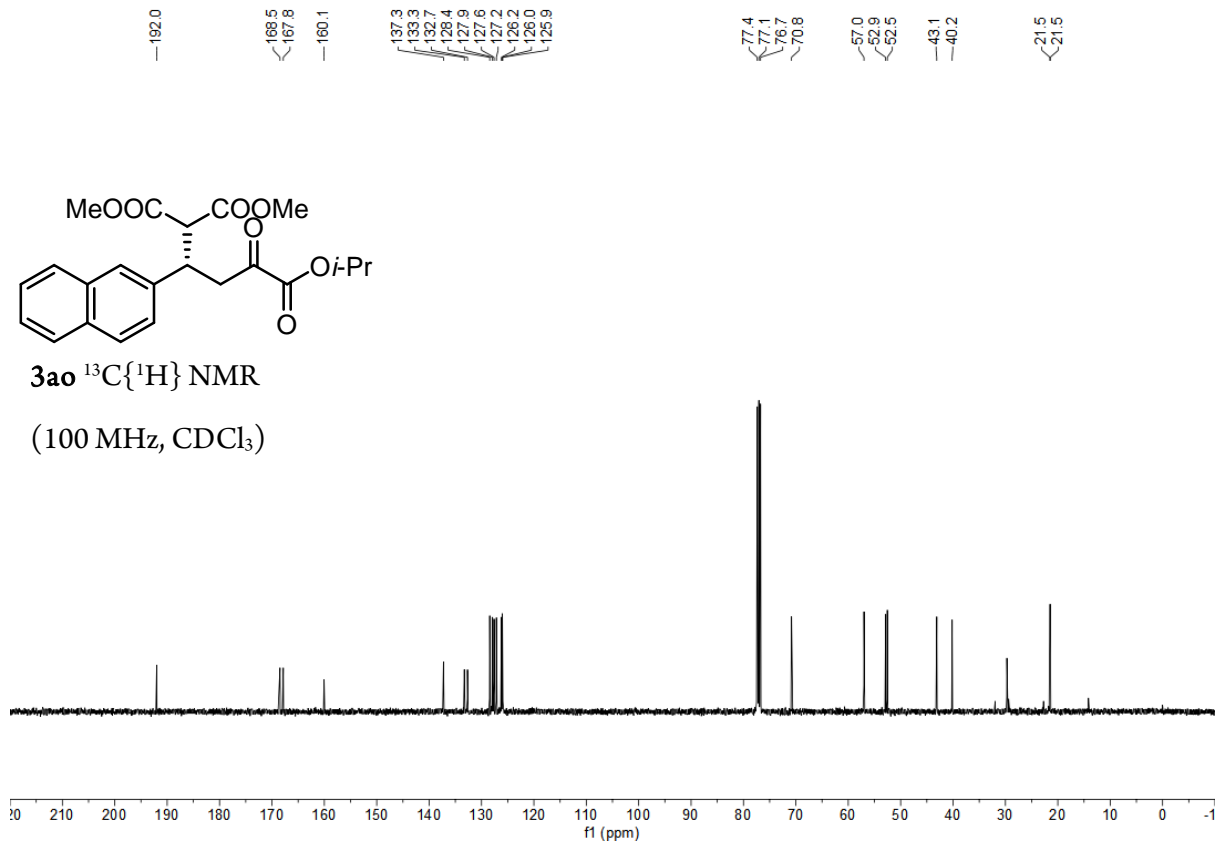




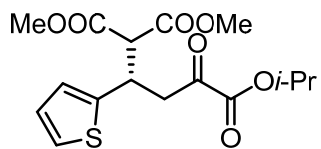






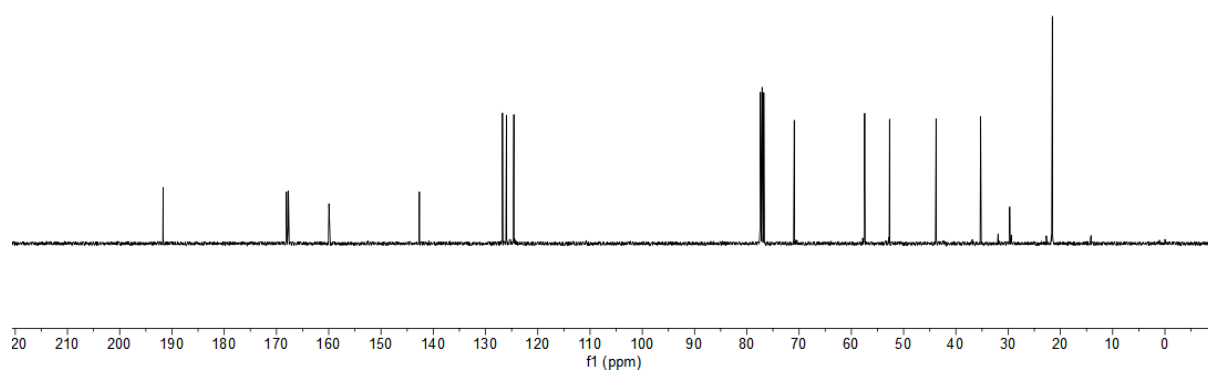


191.7
168.1
167.7
160.0
142.7
126.8
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77.4
77.1
76.8
70.9
57.4
52.8
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35.3
21.5

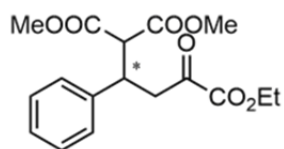


3ap $^{13}\text{C}\{^1\text{H}\}$ NMR

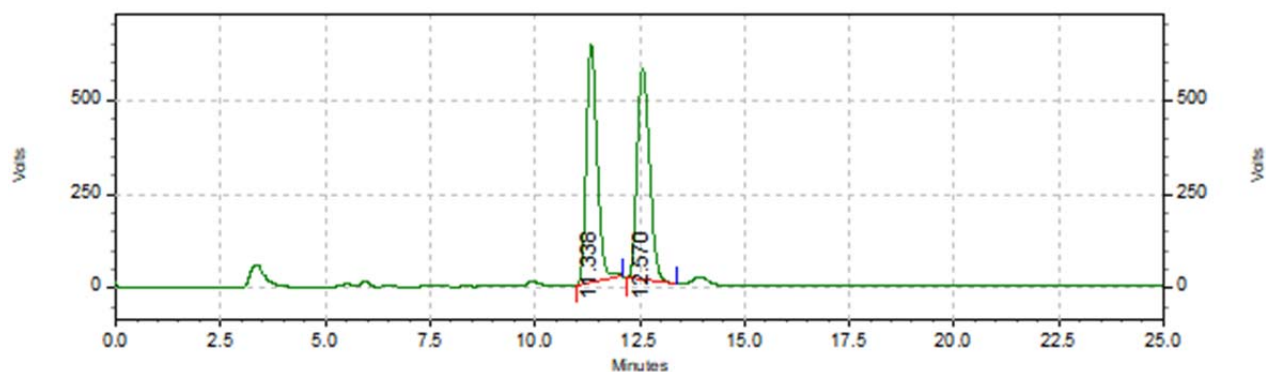
(100 MHz, CDCl_3)



3. HPLC Charts of the Products



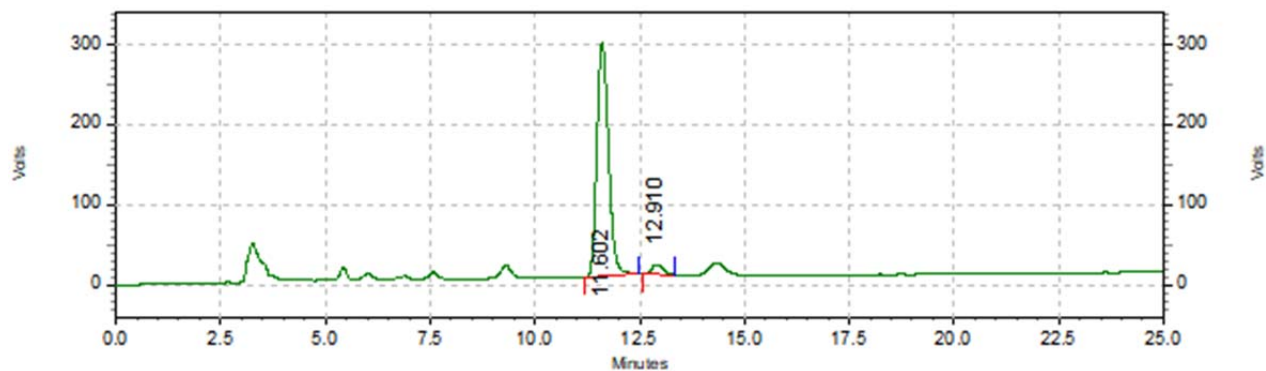
racemic sample:



Results:

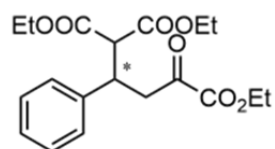
Time	Area	Area%	Height	Height%
11.338	11502820	49.884	634118	52.980
12.570	11556180	50.116	562783	47.020
Totals	23059000	100.000	1196901	100.000

asymmetric sample:

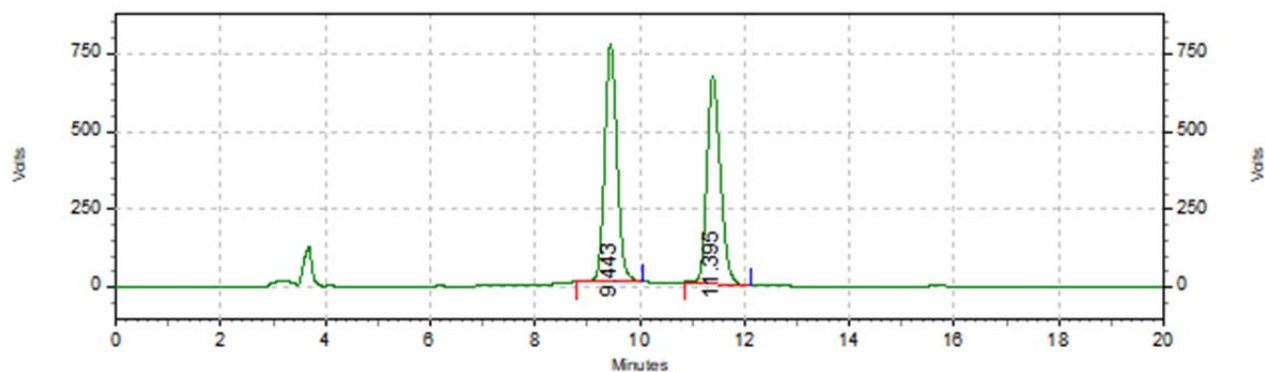


Results:

Time	Area	Area%	Height	Height%
11.602	5600099	96.009	292929	95.954
12.910	232775	3.991	12352	4.046
Totals	5832874	100.000	305281	100.000



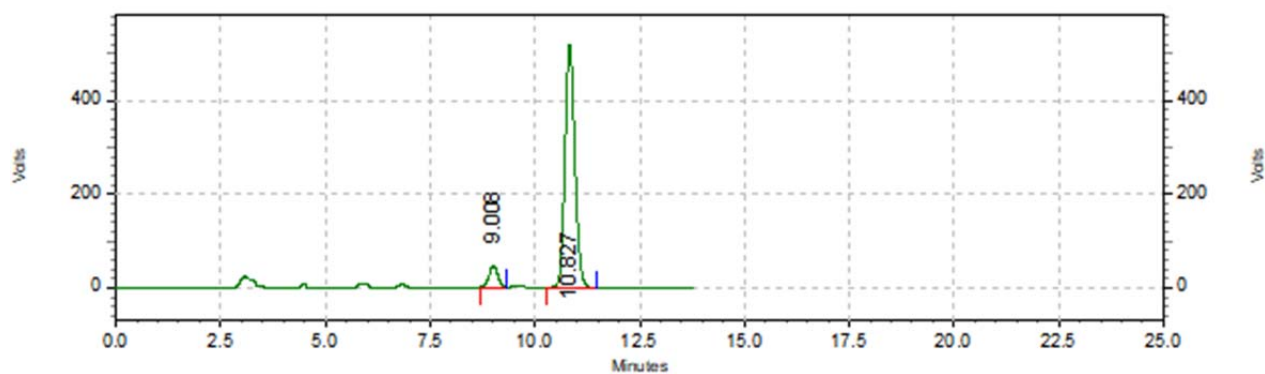
racemic sample:



Results:

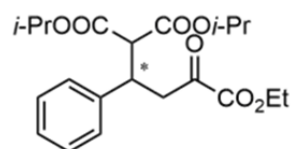
Time	Area	Area%	Height	Height%
9.443	12461780	51.218	765253	53.497
11.395	11869148	48.782	665199	46.503
Totals	24330928	100.000	1430452	100.000

asymmetric sample:

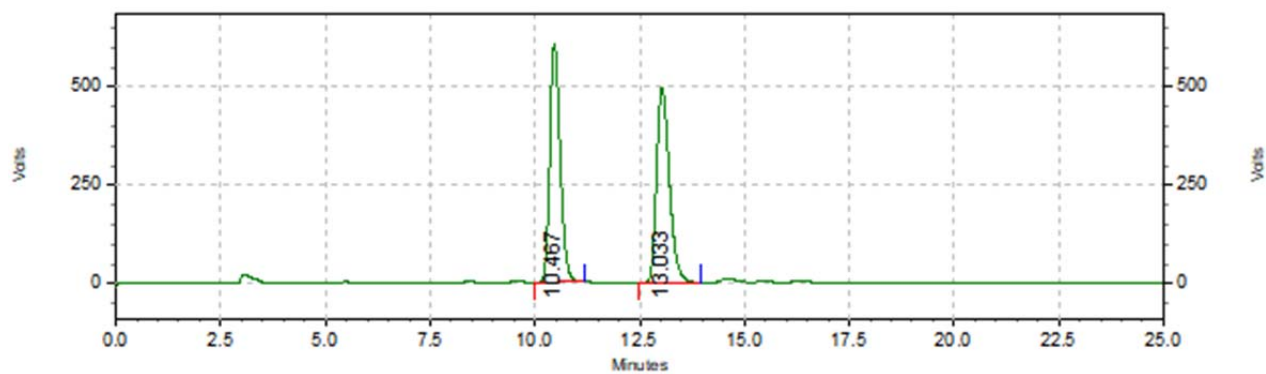


Results:

Time	Area	Area%	Height	Height%
9.008	636041	6.958	45236	8.024
10.827	8504647	93.042	518543	91.976
Totals	9140688	100.000	563779	100.000



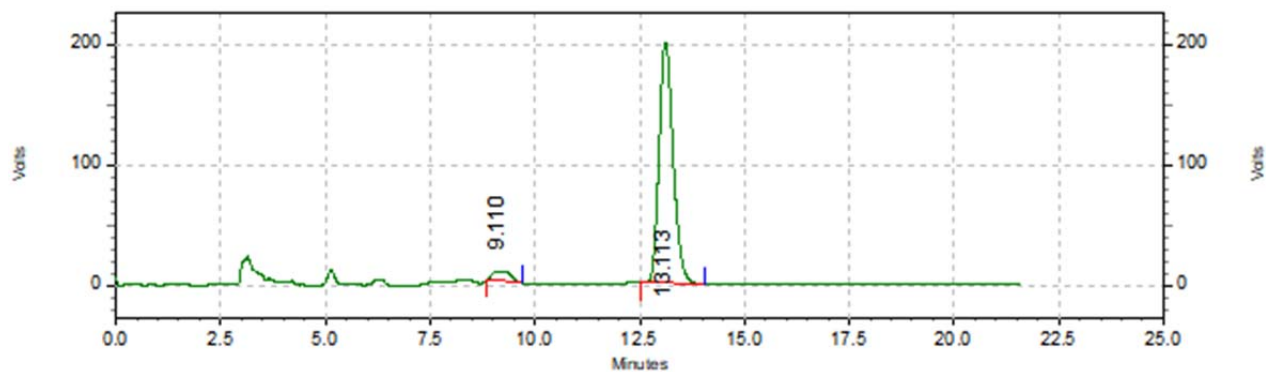
racemic sample:



Results:

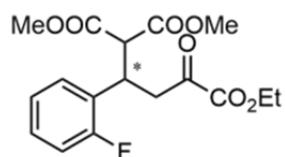
Time	Area	Area%	Height	Height%
10.467	10440191	49.947	605618	55.029
13.033	10462323	50.053	494917	44.971
Totals	20902514	100.000	1100535	100.000

asymmetric sample:

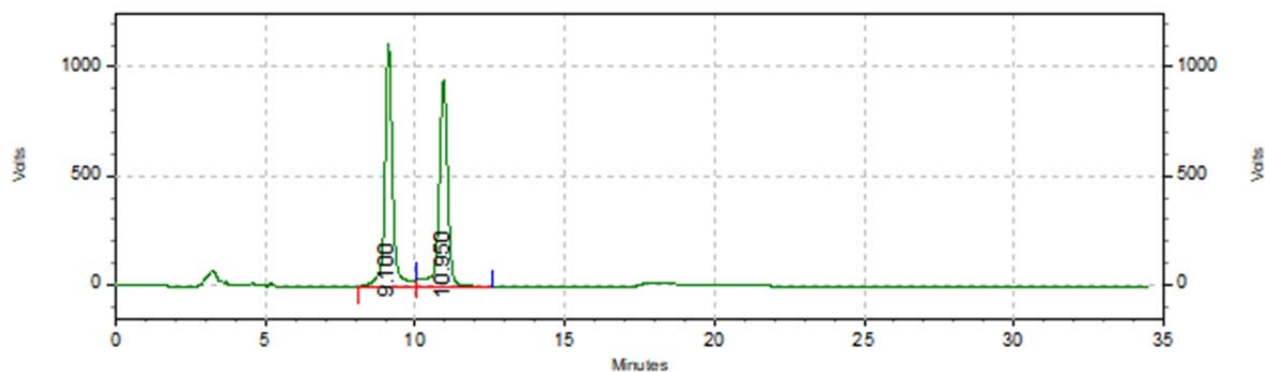


Results:

Time	Area	Area%	Height	Height%
9.110	246754	4.998	8199	3.929
13.113	4690089	95.002	200481	96.071
Totals	4936843	100.000	208680	100.000



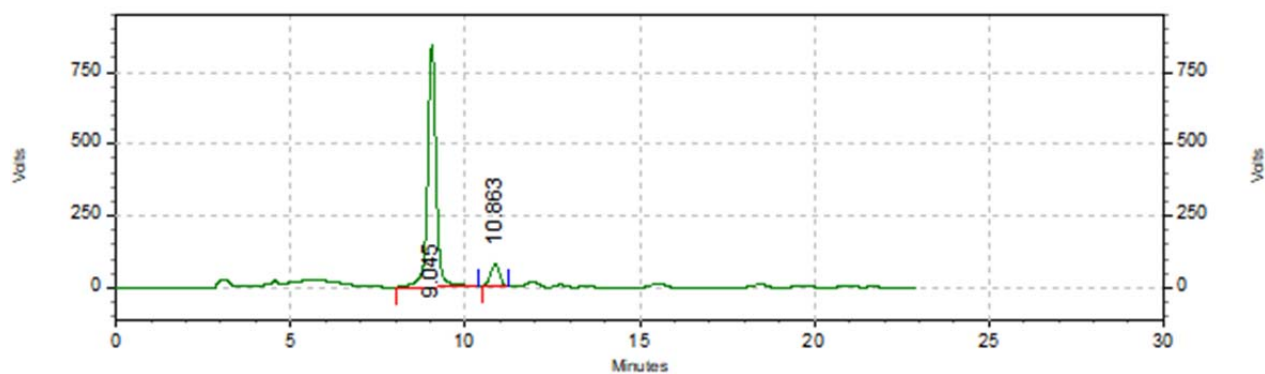
racemic sample:



Results:

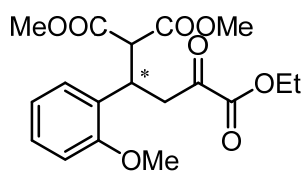
Time	Area	Area%	Height	Height%
9.100	19871533	50.674	1115302	54.061
10.950	19343297	49.326	947748	45.939
Totals	39214830	100.000	2063050	100.000

asymmetric sample:

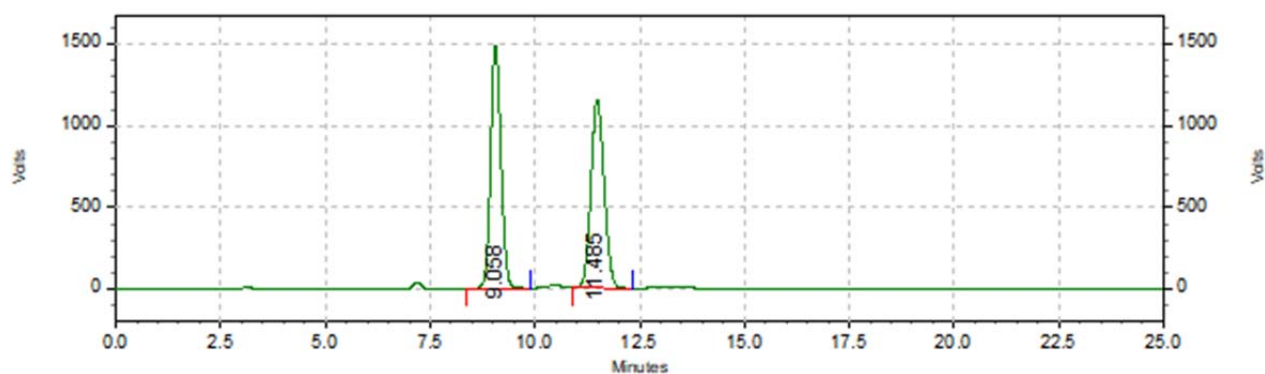


Results:

Time	Area	Area%	Height	Height%
9.045	14069328	91.038	841674	91.692
10.863	1384972	8.962	76264	8.308
Totals	15454300	100.000	917938	100.000



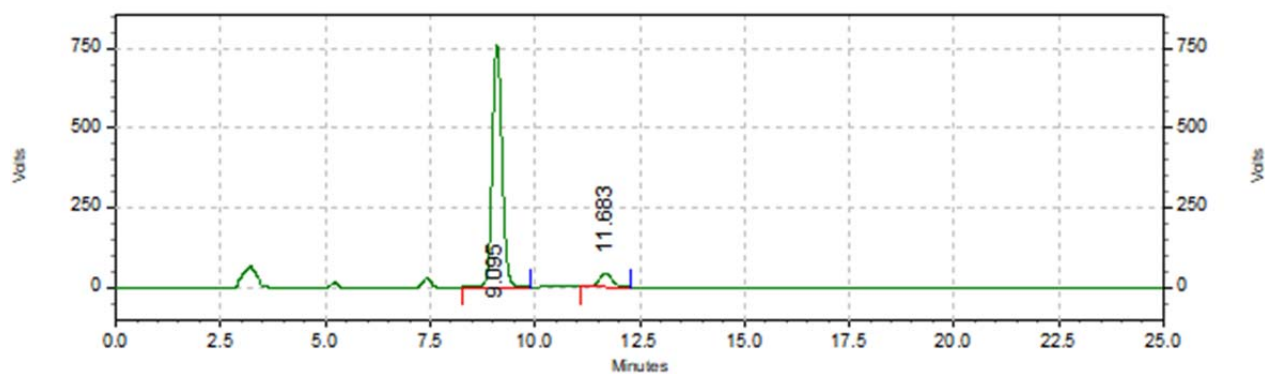
racemic sample:



Results:

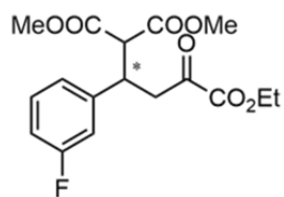
Time	Area	Area%	Height	Height%
9.058	25682381	50.482	1482910	56.304
11.485	25192064	49.518	1150855	43.696
Totals	50874445	100.000	2633765	100.000

asymmetric sample:

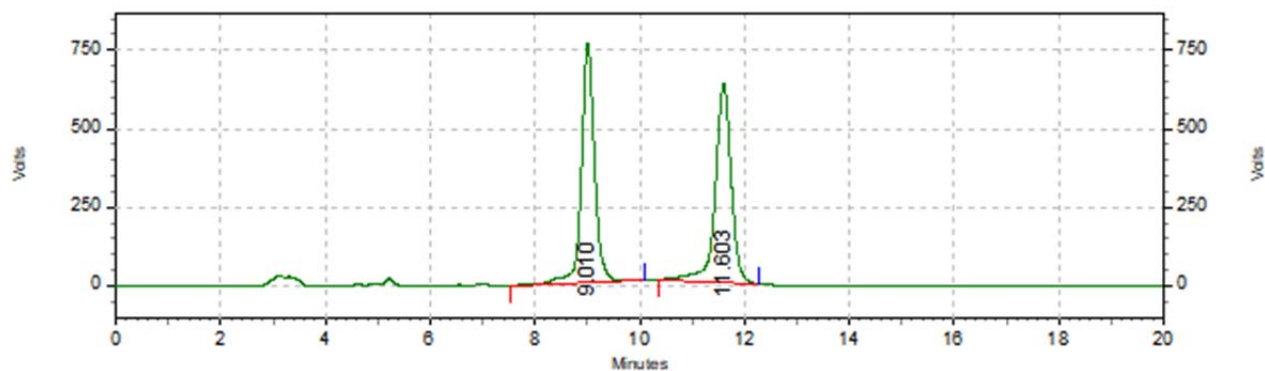


Results:

Time	Area	Area%	Height	Height%
9.095	12172161	93.114	756929	94.627
11.683	900138	6.886	42977	5.373
Totals	13072299	100.000	799906	100.000



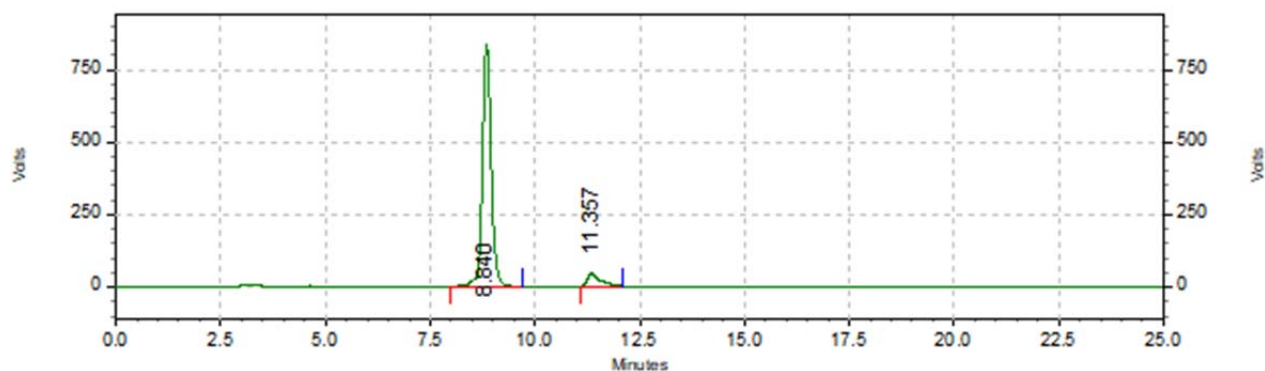
racemic sample:



Results:

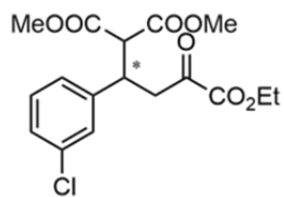
Time	Area	Area%	Height	Height%
9.010	13240711	49.643	761344	54.665
11.603	13431347	50.357	631391	45.335
Totals	26672058	100.000	1392735	100.000

asymmetric sample:

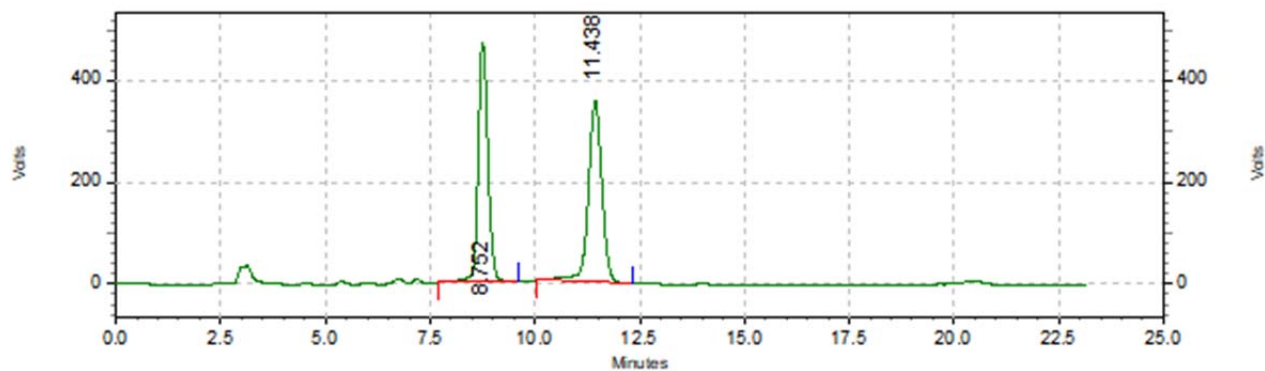


Results:

Time	Area	Area%	Height	Height%
8.840	12020711	92.715	834668	95.067
11.357	944495	7.285	43313	4.933
Totals	12965206	100.000	877981	100.000



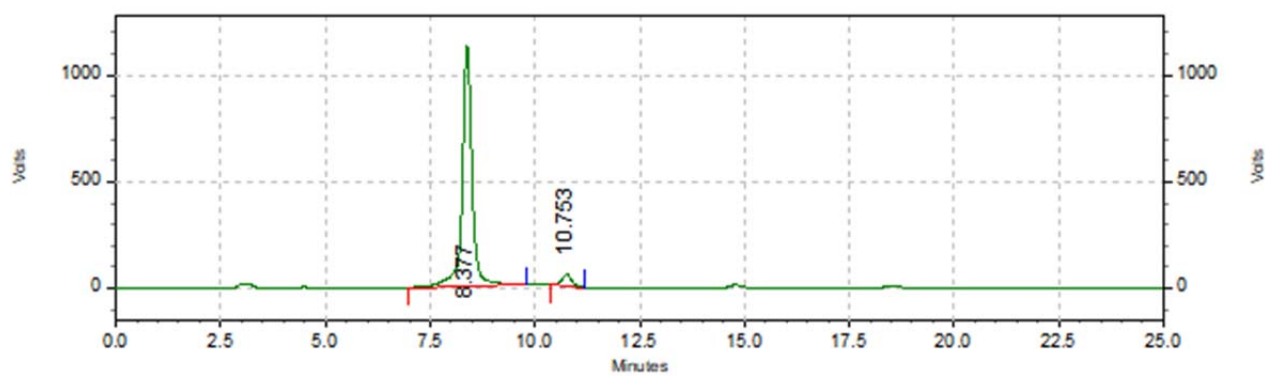
racemic sample:



Results:

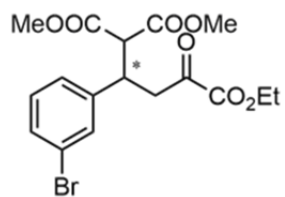
Time	Area	Area%	Height	Height%
8.752	7568497	48.131	470996	56.871
11.438	8156431	51.869	357183	43.129
Totals	15724928	100.000	828179	100.000

asymmetric sample:

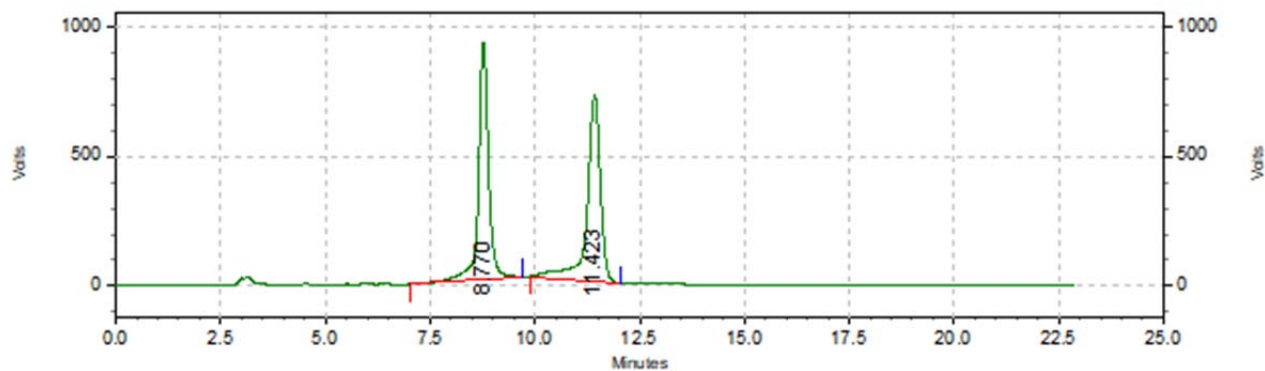


Results:

Time	Area	Area%	Height	Height%
8.377	18807653	95.450	1130786	95.484
10.753	896475	4.550	53482	4.516
Totals	19704128	100.000	1184268	100.000



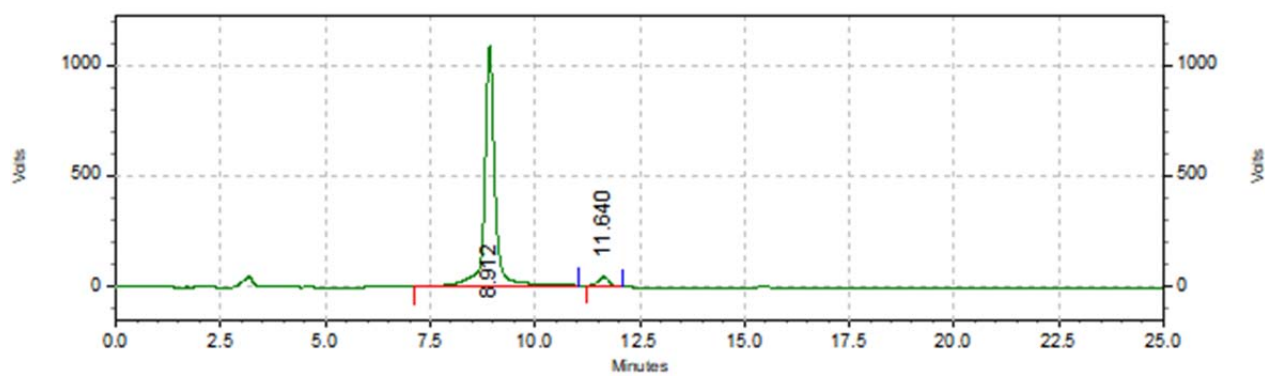
racemic sample:



Results:

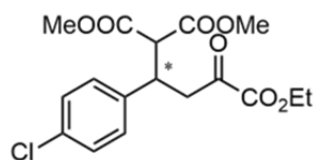
Time	Area	Area%	Height	Height%
8.770	15280966	48.654	916455	55.874
11.423	16126217	51.346	723763	44.126
Totals	31407183	100.000	1640218	100.000

asymmetric sample:

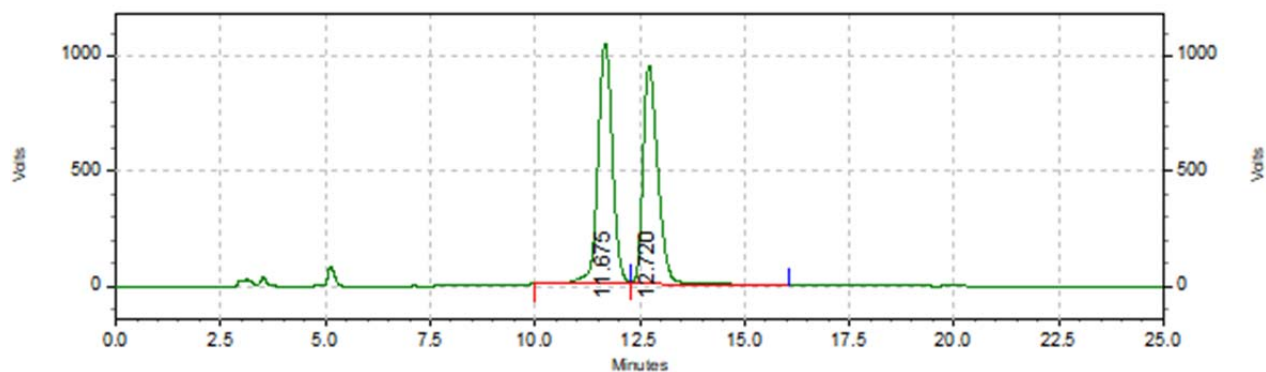


Results:

Time	Area	Area%	Height	Height%
8.912	18888454	96.174	1086958	96.353
11.640	751424	3.826	41146	3.647
Totals	19639878	100.000	1128104	100.000



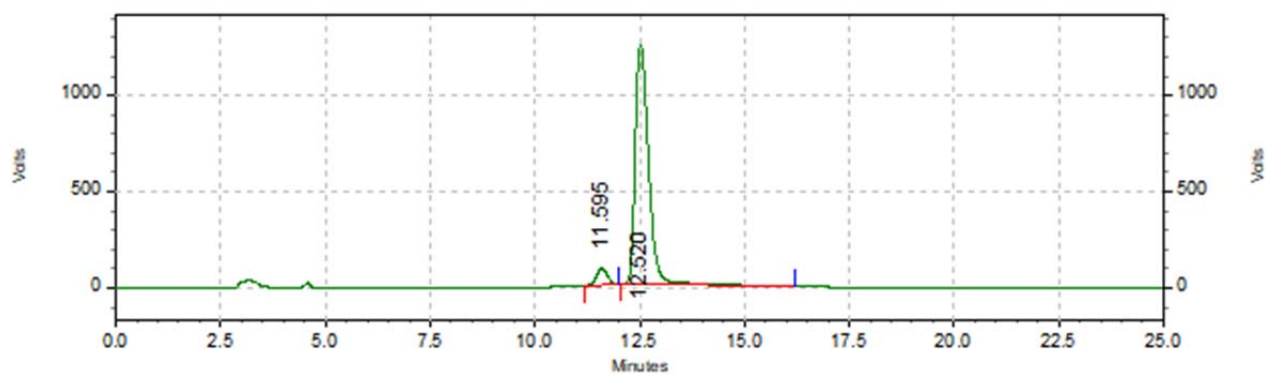
racemic sample:



Results:

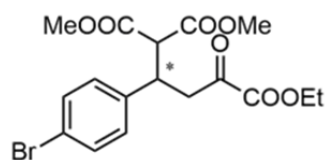
Time	Area	Area%	Height	Height%
11.675	25366757	51.732	1045963	52.362
12.720	23668468	48.268	951615	47.638
Totals	49035225	100.000	1997578	100.000

asymmetric sample:

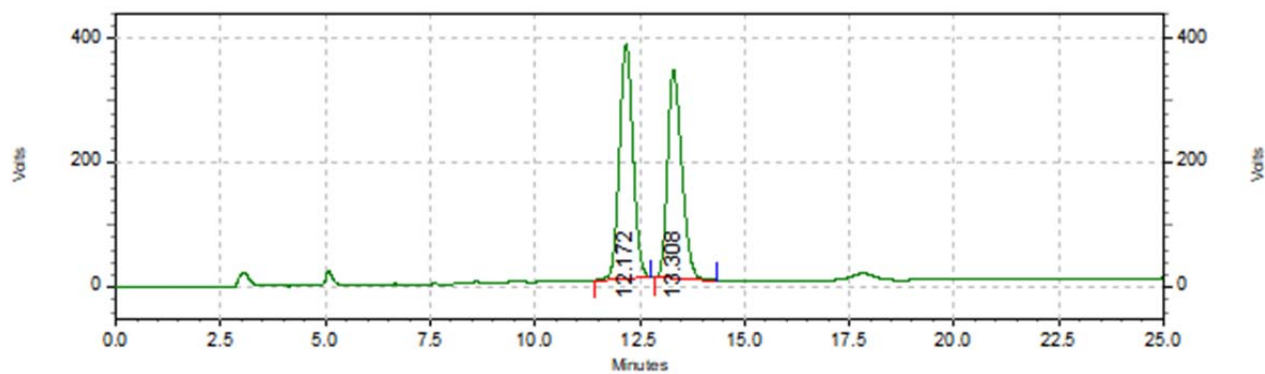


Results:

Time	Area	Area%	Height	Height%
11.595	1544381	5.244	85258	6.407
12.520	27907473	94.756	1245531	93.593
Totals	29451854	100.000	1330789	100.000



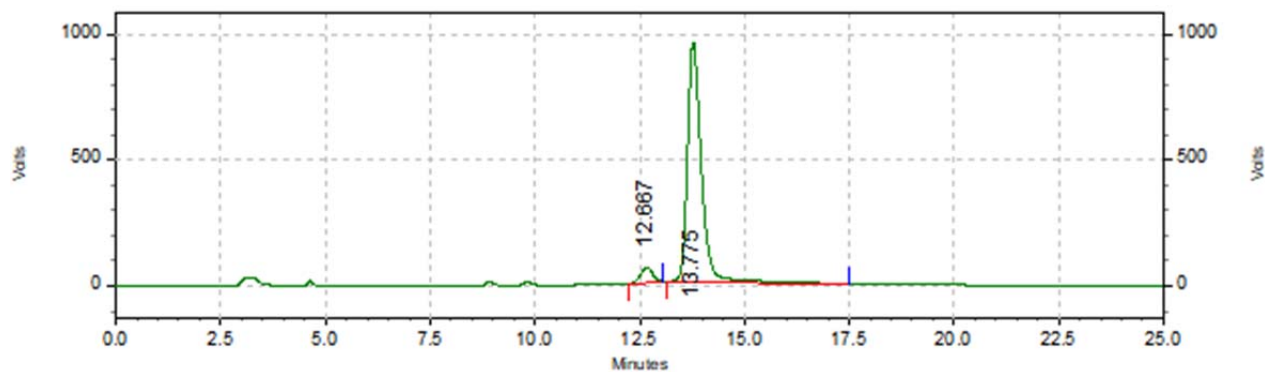
racemic sample:



Results:

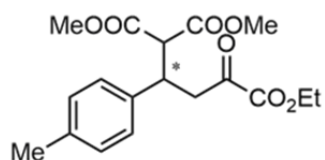
Time	Area	Area%	Height	Height%
12.172	8444736	51.549	377900	53.001
13.308	7937332	48.451	335111	46.999
Totals	16382068	100.000	713011	100.000

asymmetric sample:

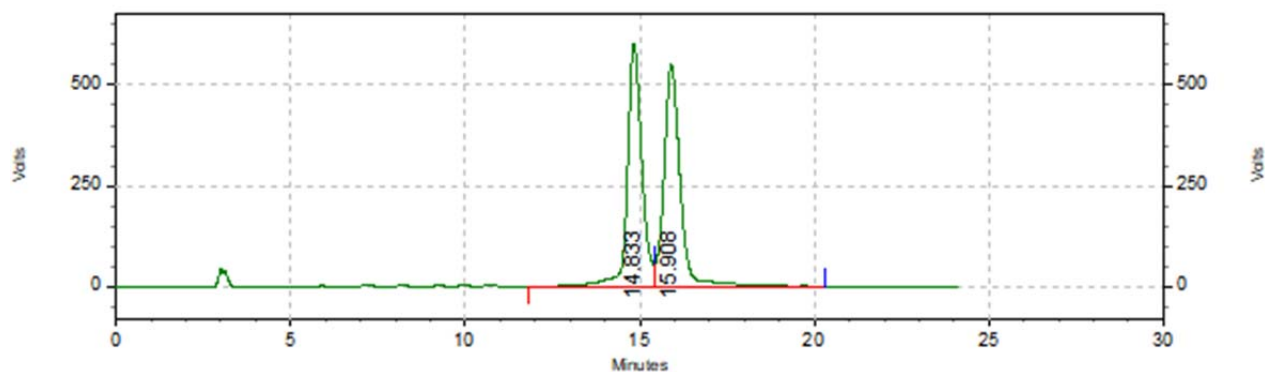


Results:

Time	Area	Area%	Height	Height%
12.667	1161263	4.977	60822	6.018
13.775	22169401	95.023	949925	93.982
Totals	23330664	100.000	1010747	100.000



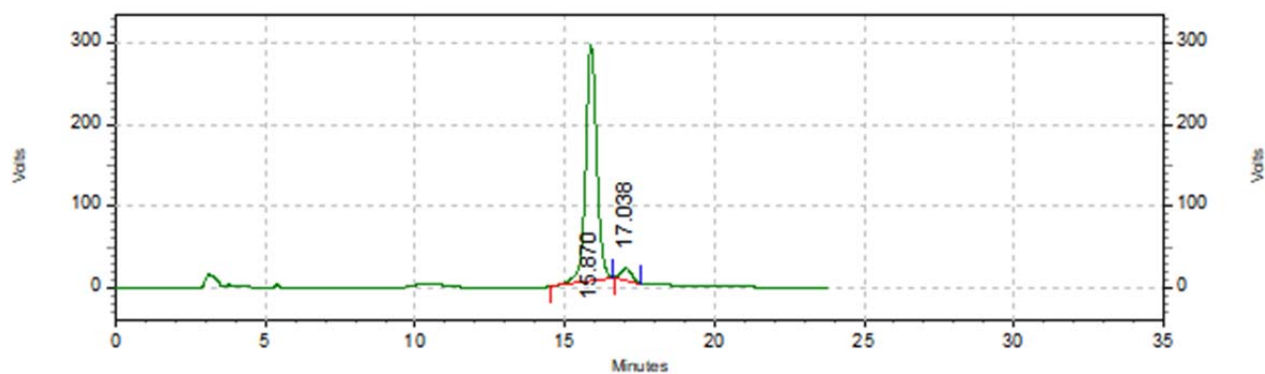
racemic sample:



Results:

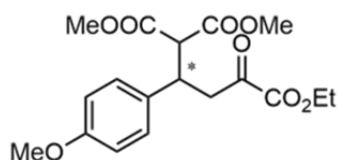
Time	Area	Area%	Height	Height%
14.833	17040630	49.210	599424	52.255
15.908	17587777	50.790	547687	47.745
Totals	34628407	100.000	1147111	100.000

asymmetric sample:

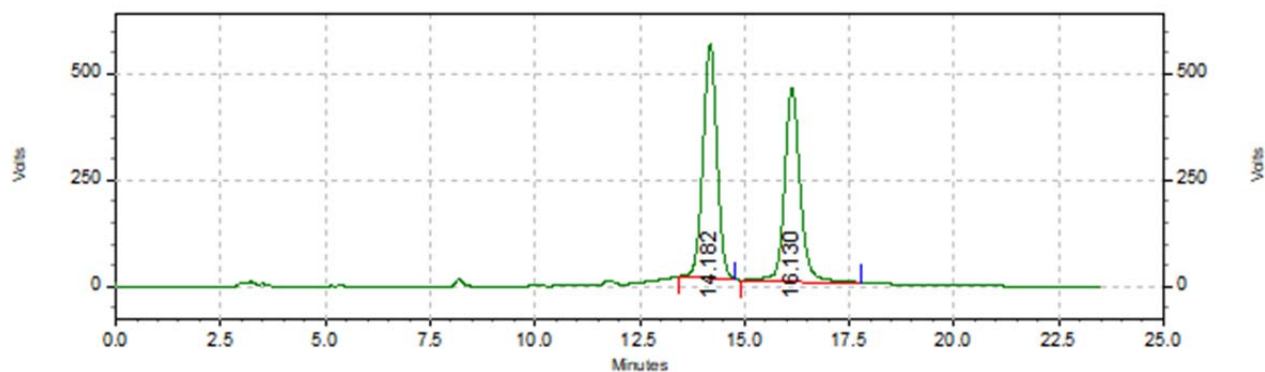


Results:

Time	Area	Area%	Height	Height%
15.870	7407112	95.556	289459	95.375
17.038	344482	4.444	14038	4.625
Totals	7751594	100.000	303497	100.000



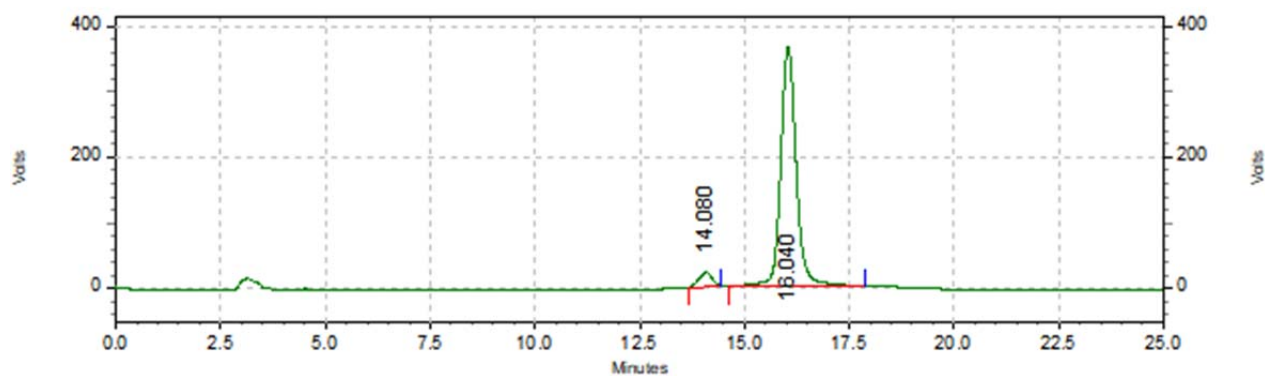
racemic sample:



Results:

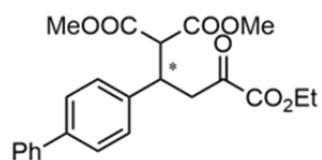
Time	Area	Area%	Height	Height%
14.182	12800035	52.373	550829	54.830
16.130	11640064	47.627	453781	45.170
Totals	24440099	100.000	1004610	100.000

asymmetric sample:

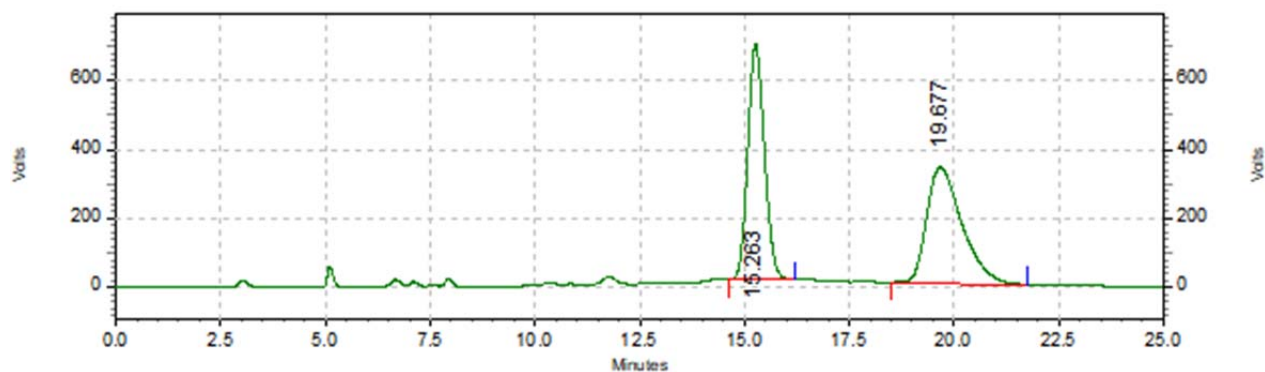


Results:

Time	Area	Area%	Height	Height%
14.080	484216	4.871	21942	5.663
16.040	9457193	95.129	365492	94.337
Totals	9941409	100.000	387434	100.000



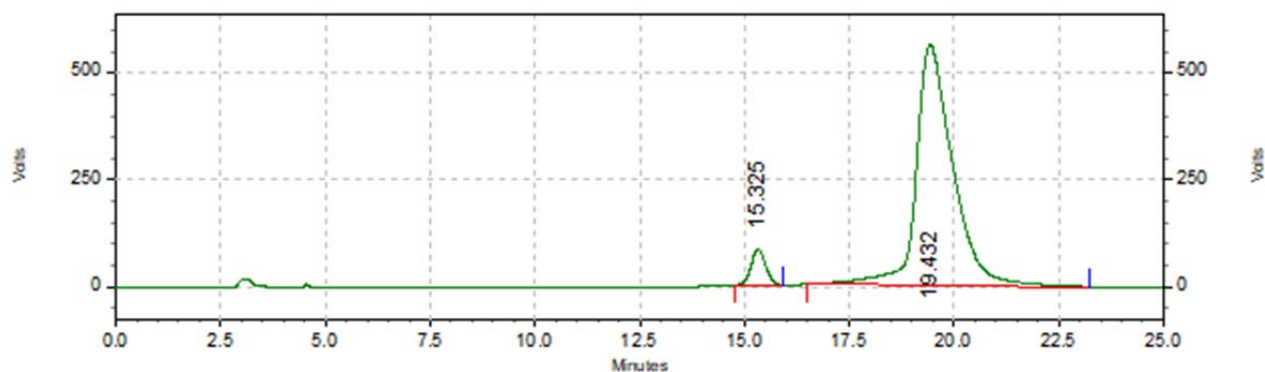
racemic sample:



Results:

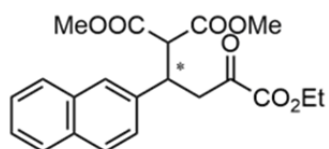
Time	Area	Area%	Height	Height%
15.263	18880977	49.064	684555	67.026
19.677	19601275	50.936	336766	32.974
Totals	38482252	100.000	1021321	100.000

asymmetric sample:

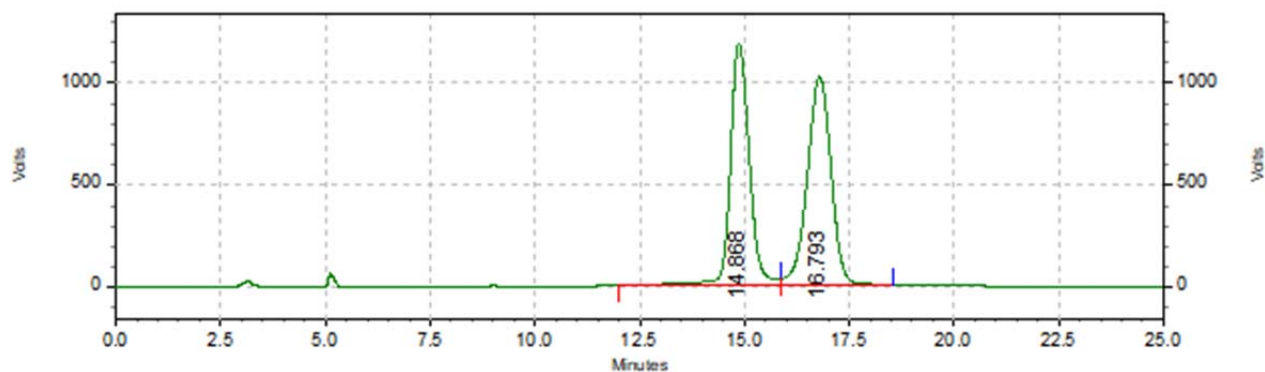


Results:

Time	Area	Area%	Height	Height%
15.325	2033784	5.598	84255	13.008
19.432	34294483	94.402	563468	86.992
Totals	36328267	100.000	647723	100.000



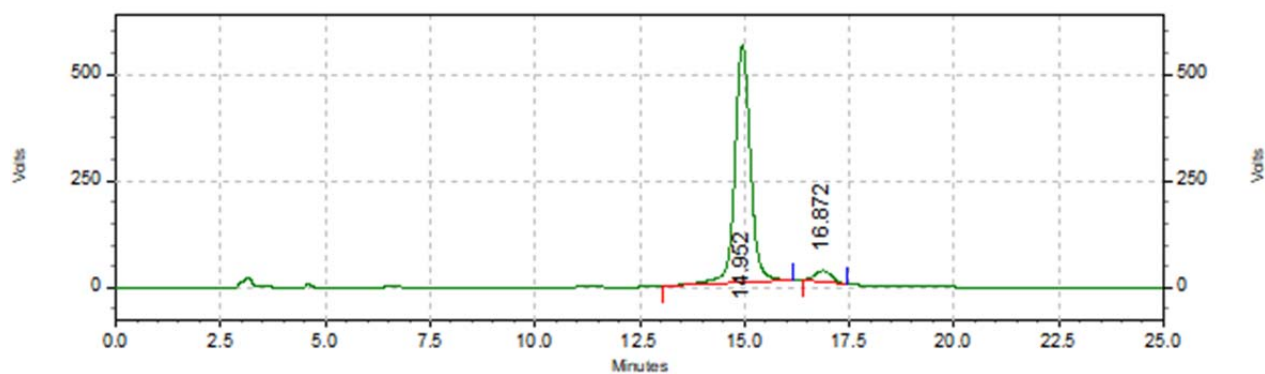
racemic sample:



Results:

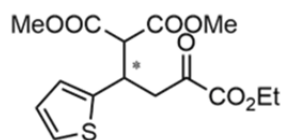
Time	Area	Area%	Height	Height%
14.868	36902993	47.841	1179318	53.720
16.793	40234329	52.159	1015990	46.280
Totals	77137322	100.000	2195308	100.000

asymmetric sample:

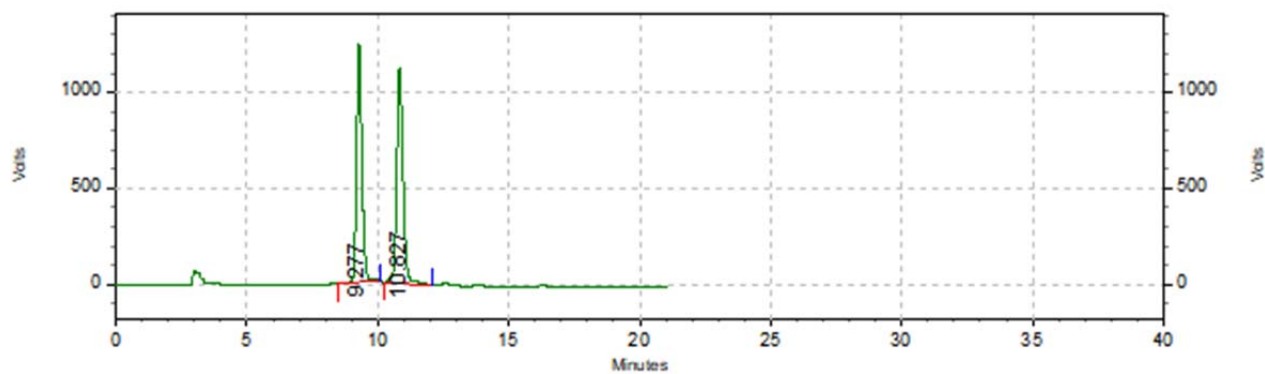


Results:

Time	Area	Area%	Height	Height%
14.952	14405237	95.044	558242	95.518
16.872	751194	4.956	26196	4.482
Totals	15156431	100.000	584438	100.000



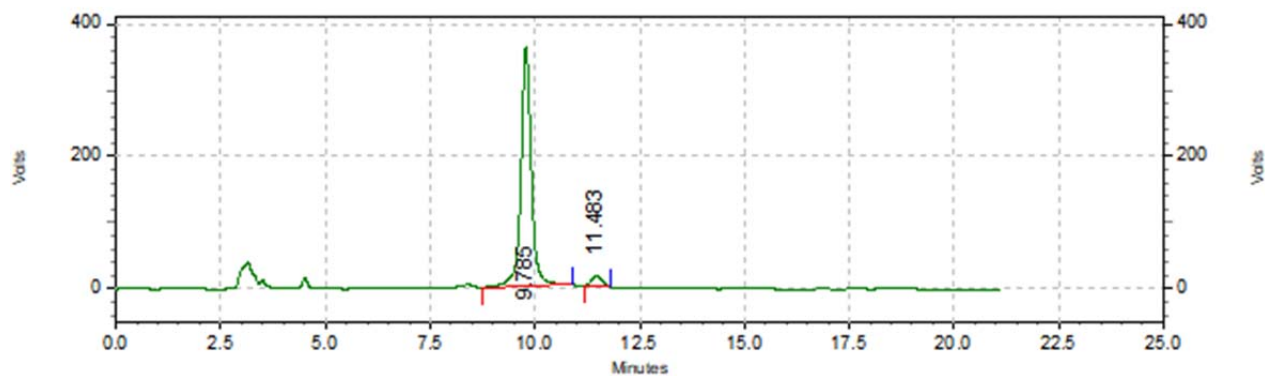
racemic sample:



Results:

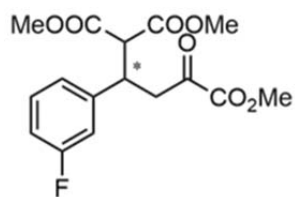
Time	Area	Area%	Height	Height%
9.277	18132299	48.908	1245217	52.568
10.827	18941946	51.092	1123540	47.432
Totals	37074245	100.000	2368757	100.000

asymmetric sample:

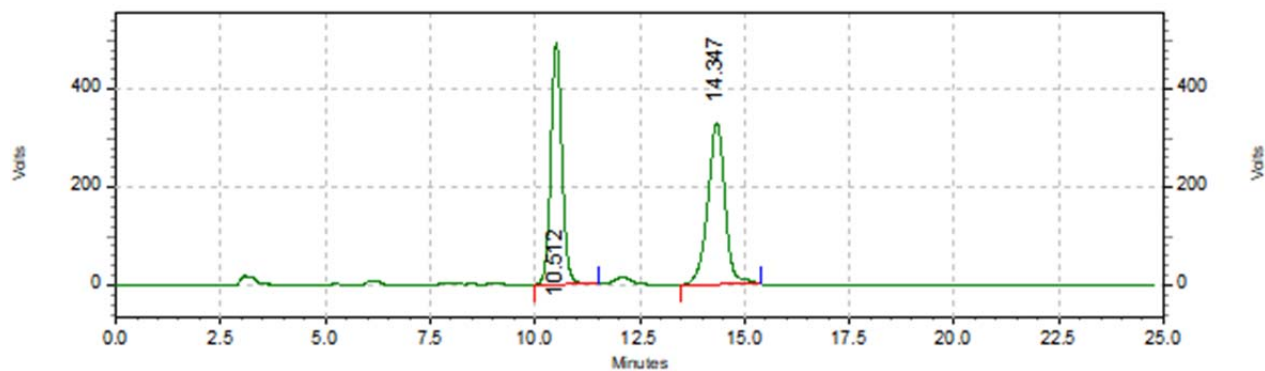


Results:

Time	Area	Area%	Height	Height%
9.785	6265096	96.045	361764	95.933
11.483	258000	3.955	15336	4.067
Totals	6523096	100.000	377100	100.000



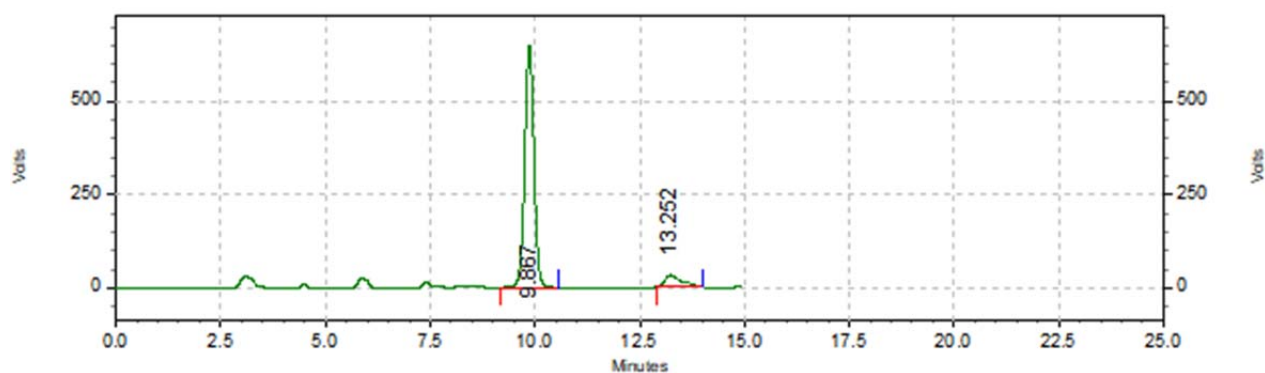
racemic sample:



Results:

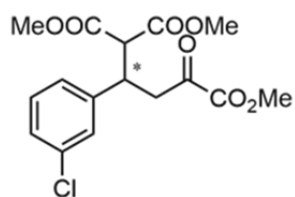
Time	Area	Area%	Height	Height%
10.512	9041120	48.980	492451	59.918
14.347	9417609	51.020	329425	40.082
Totals	18458729	100.000	821876	100.000

asymmetric sample:

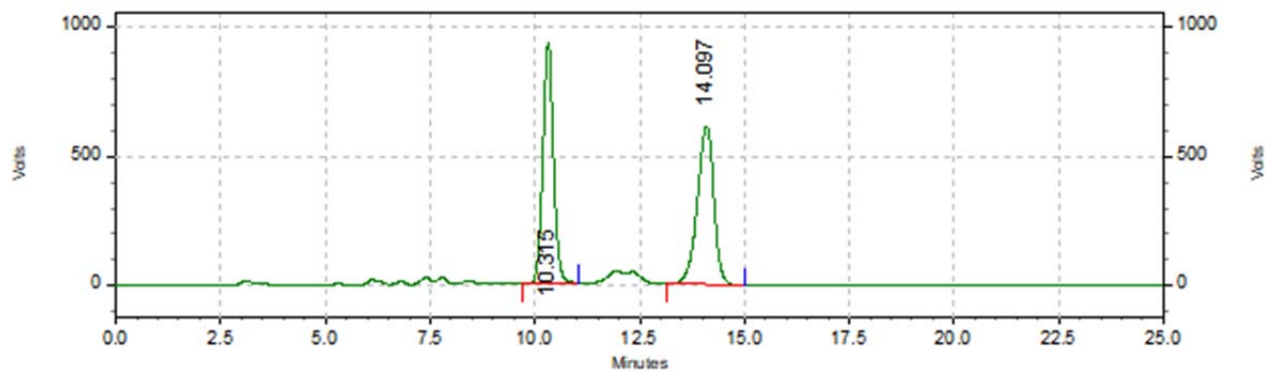


Results:

Time	Area	Area%	Height	Height%
9.867	9885948	91.659	647276	95.396
13.252	899595	8.341	31242	4.604
Totals	10785543	100.000	678518	100.000



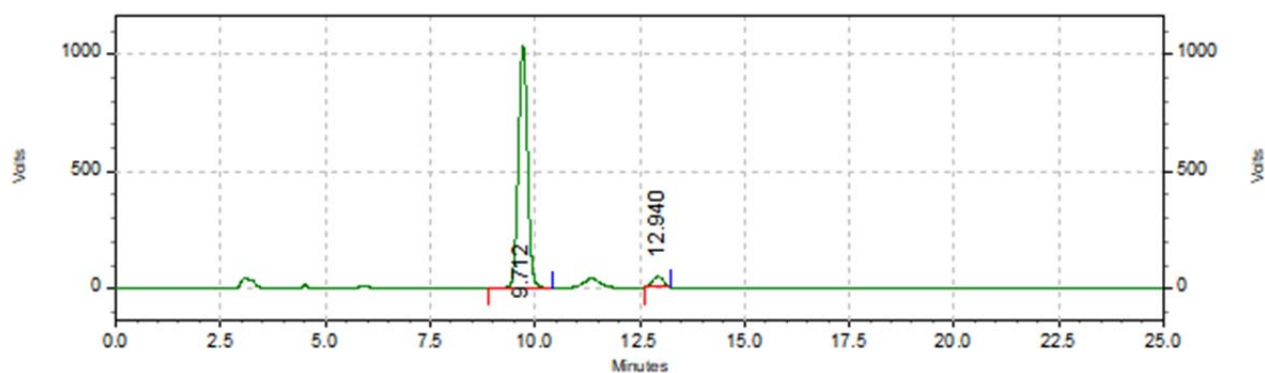
racemic sample:



Results:

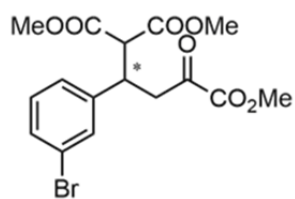
Time	Area	Area%	Height	Height%
10.315	16548124	49.495	932061	60.272
14.097	16885511	50.505	614361	39.728
Totals	33433635	100.000	1546422	100.000

asymmetric sample:

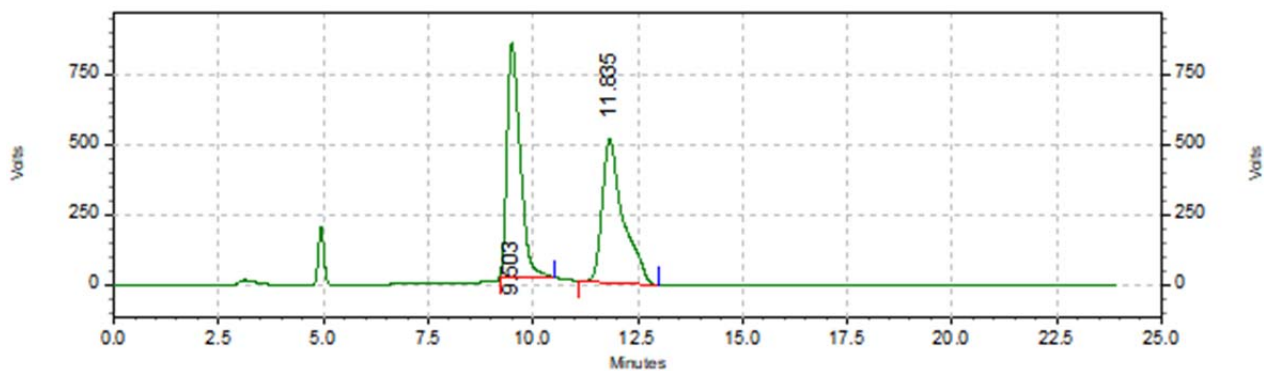


Results:

Time	Area	Area%	Height	Height%
9.712	15538267	95.041	1034189	95.899
12.940	810764	4.959	44223	4.101
Totals	16349031	100.000	1078412	100.000



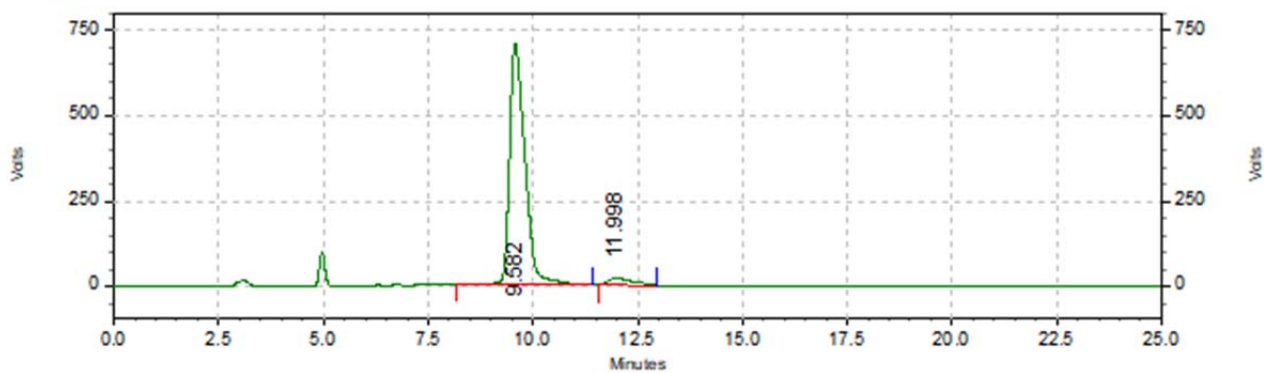
racemic sample:



Results:

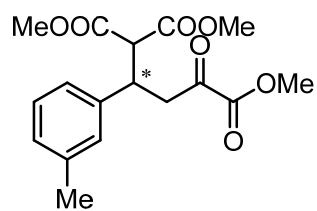
Time	Area	Area%	Height	Height%
9.503	18127258	50.707	835255	62.052
11.835	17621795	49.293	510794	37.948
Totals	35749053	100.000	1346049	100.000

asymmetric sample:

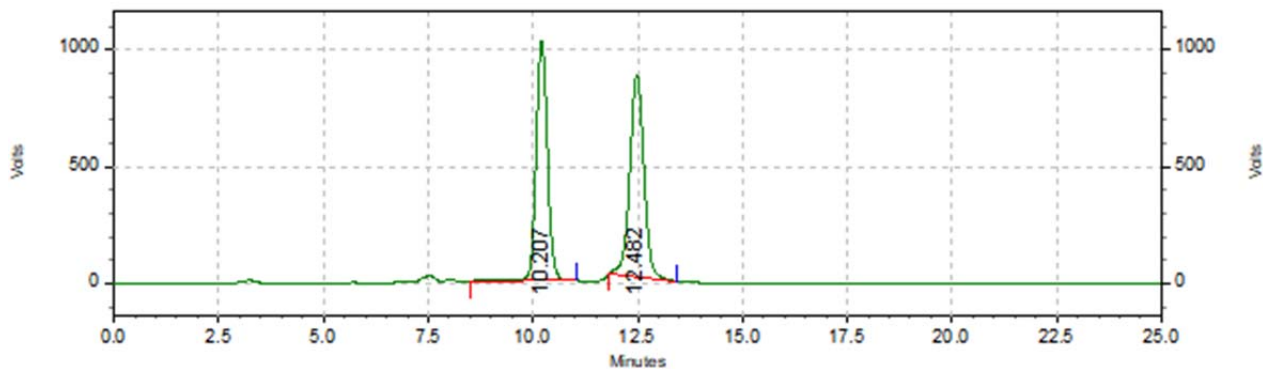


Results:

Time	Area	Area%	Height	Height%
9.582	17986554	95.611	706215	97.330
11.998	825660	4.389	19376	2.670
Totals	18812214	100.000	725591	100.000



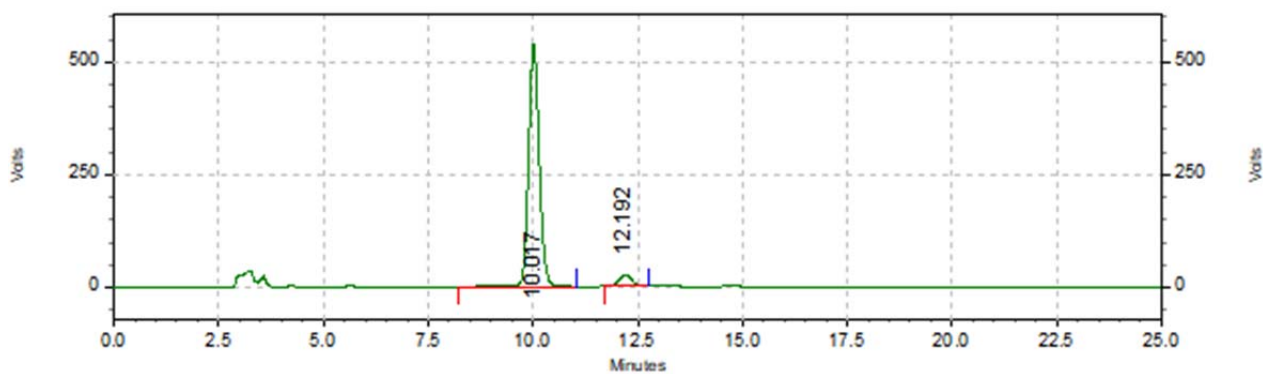
racemic sample:



Results:

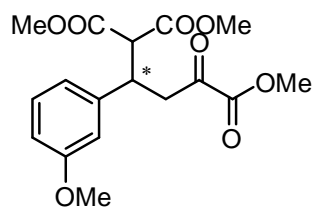
Time	Area	Area%	Height	Height%
10.207	19427856	49.161	1025504	54.386
12.482	20090936	50.839	860100	45.614
Totals	39518792	100.000	1885604	100.000

asymmetric sample:

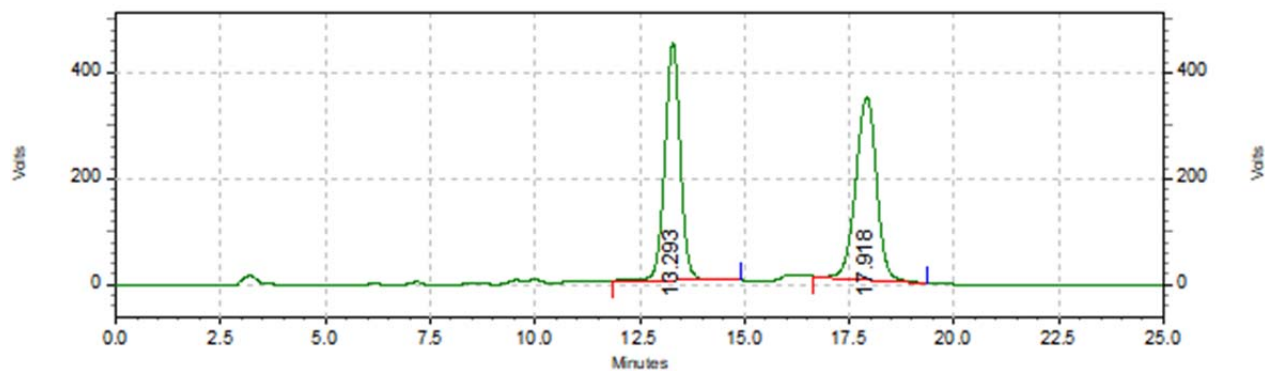


Results:

Time	Area	Area%	Height	Height%
10.017	9484257	95.165	536996	95.746
12.192	481851	4.835	23860	4.254
Totals	9966108	100.000	560856	100.000



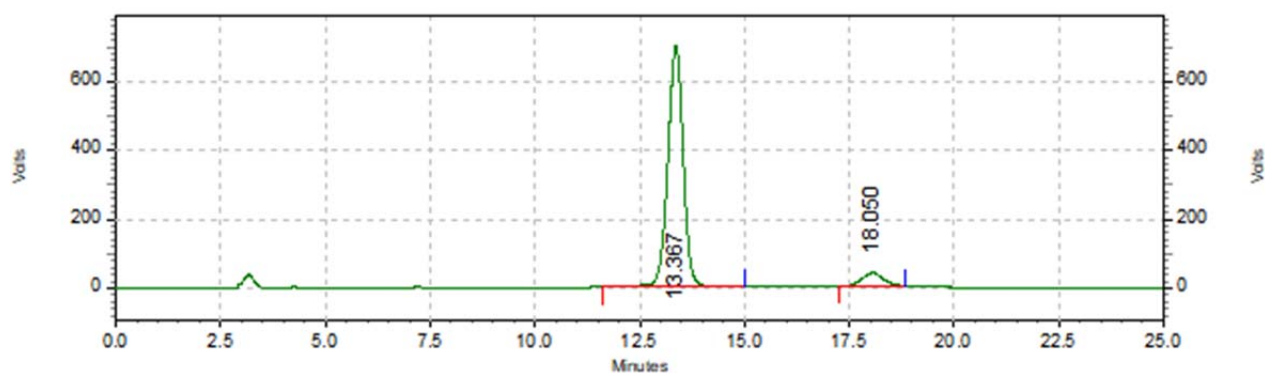
racemic sample:



Results:

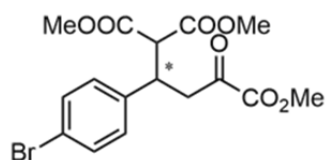
Time	Area	Area%	Height	Height%
13.293	11495684	49.230	448139	56.631
17.918	11855466	50.770	343197	43.369
Totals	23351150	100.000	791336	100.000

asymmetric sample:

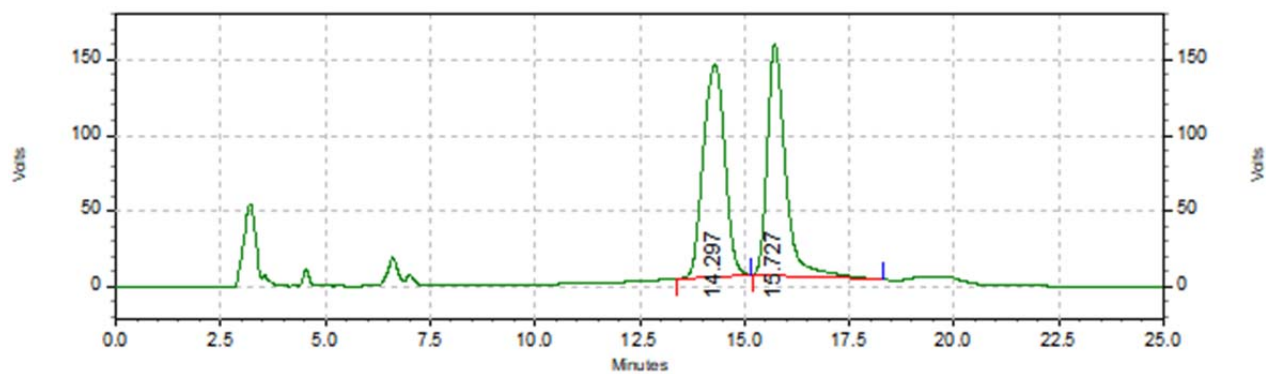


Results:

Time	Area	Area%	Height	Height%
13.367	17880424	92.939	699643	94.773
18.050	1358511	7.061	38591	5.227
Totals	19238935	100.000	738234	100.000



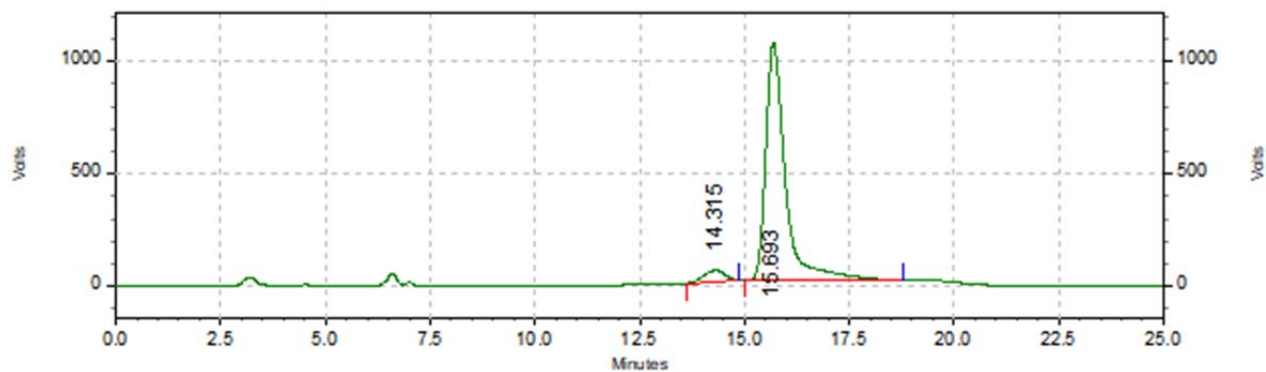
racemic sample:



Results:

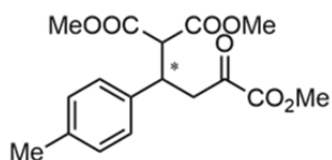
Time	Area	Area%	Height	Height%
14.297	5000768	51.901	140274	47.771
15.727	4634425	48.099	153364	52.229
Totals	9635193	100.000	293638	100.000

asymmetric sample:

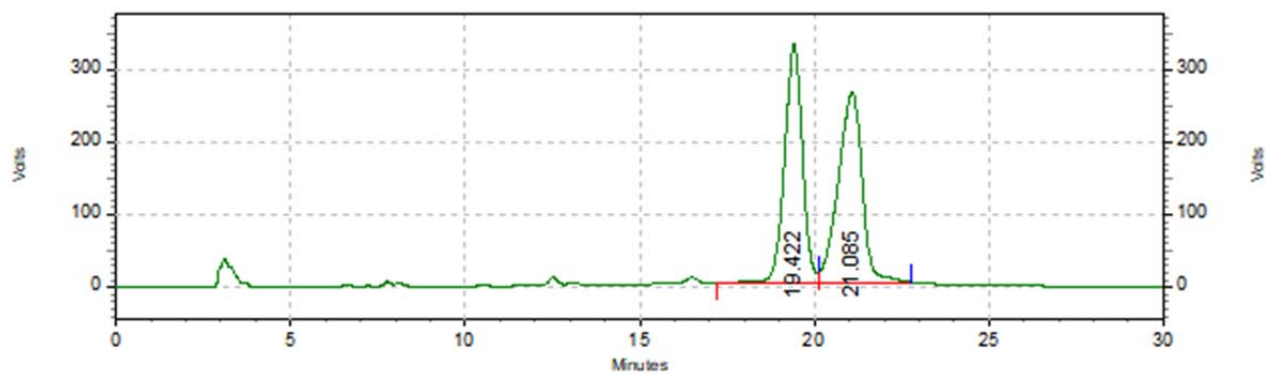


Results:

Time	Area	Area%	Height	Height%
14.315	1657281	4.576	48661	4.409
15.693	34559385	95.424	1054913	95.591
Totals	36216666	100.000	1103574	100.000



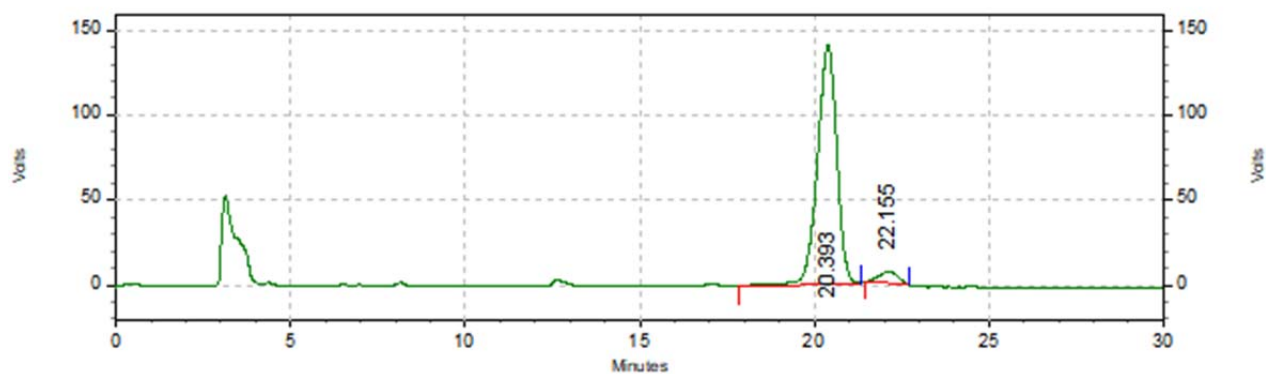
racemic sample:



Results:

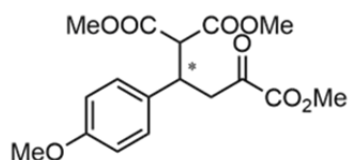
Time	Area	Area%	Height	Height%
19.422	11637076	48.429	328745	55.706
21.085	12392189	51.571	261401	44.294
Totals	24029265	100.000	590146	100.000

asymmetric sample:

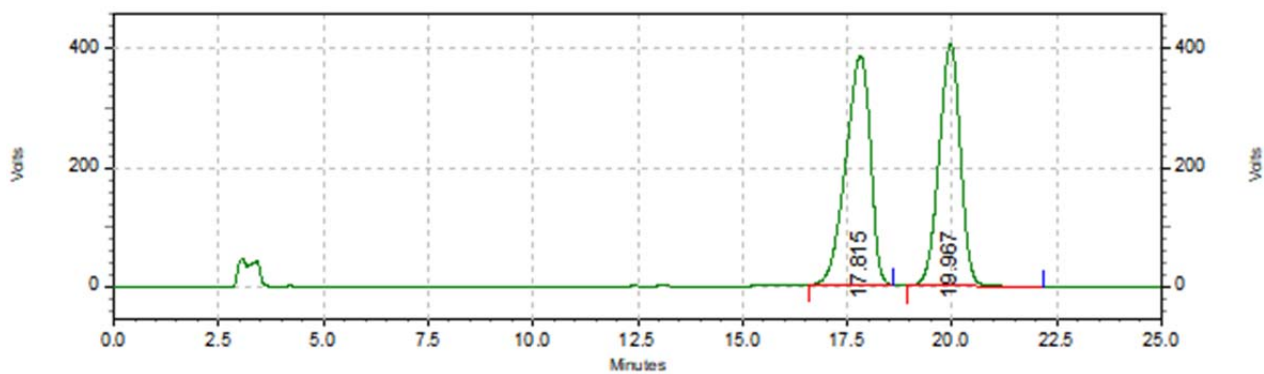


Results:

Time	Area	Area%	Height	Height%
20.393	5424702	95.052	140868	95.180
22.155	282395	4.948	7134	4.820
Totals	5707097	100.000	148002	100.000



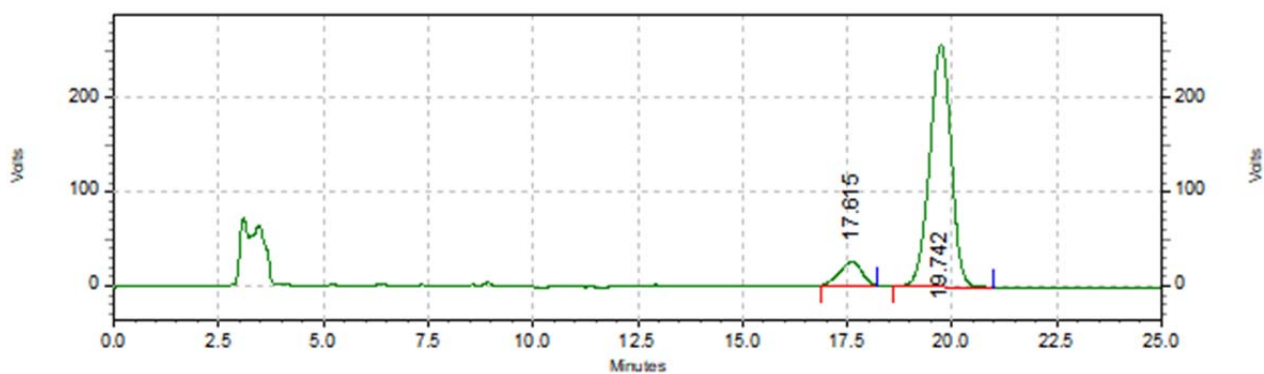
racemic sample:



Results:

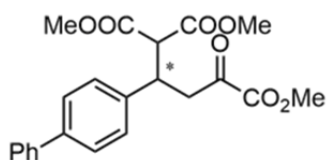
Time	Area	Area%	Height	Height%
17.815	15689155	52.254	384469	48.603
19.967	14335623	47.746	406565	51.397
Totals	30024778	100.000	791034	100.000

asymmetric sample:

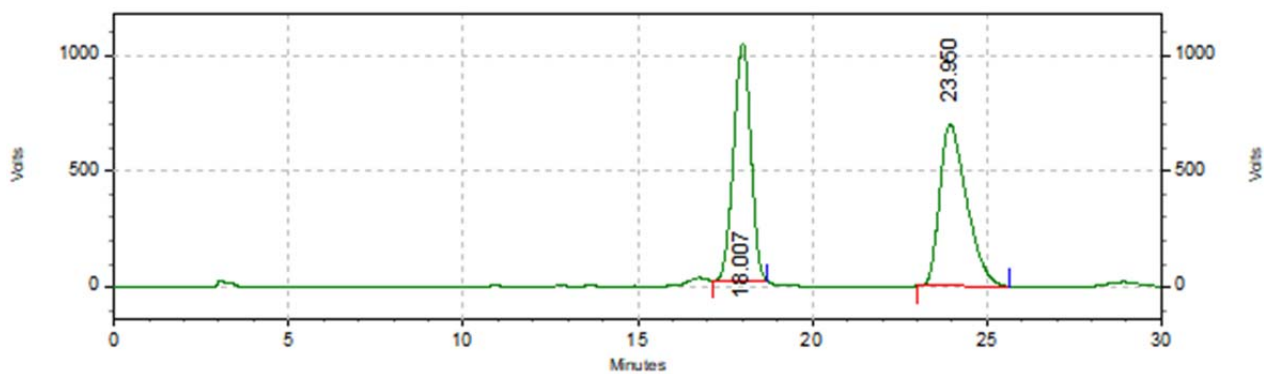


Results:

Time	Area	Area%	Height	Height%
17.615	924145	9.261	25373	8.980
19.742	9055278	90.739	257163	91.020
Totals	9979423	100.000	282536	100.000



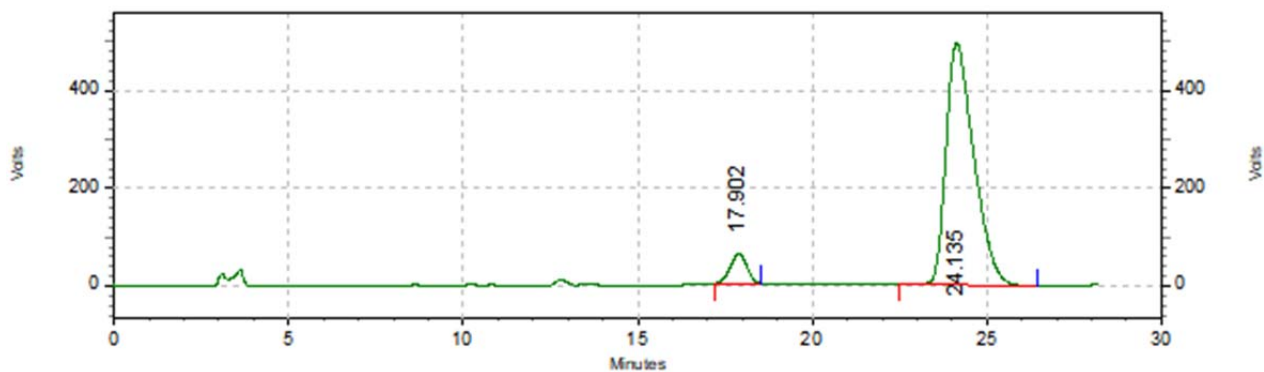
racemic sample:



Results:

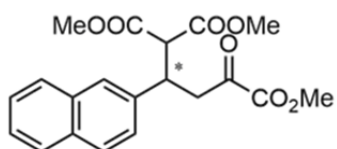
Time	Area	Area%	Height	Height%
18.007	35066083	48.337	1023655	59.409
23.950	37478830	51.663	699419	40.591
Totals	72544913	100.000	1723074	100.000

asymmetric sample:

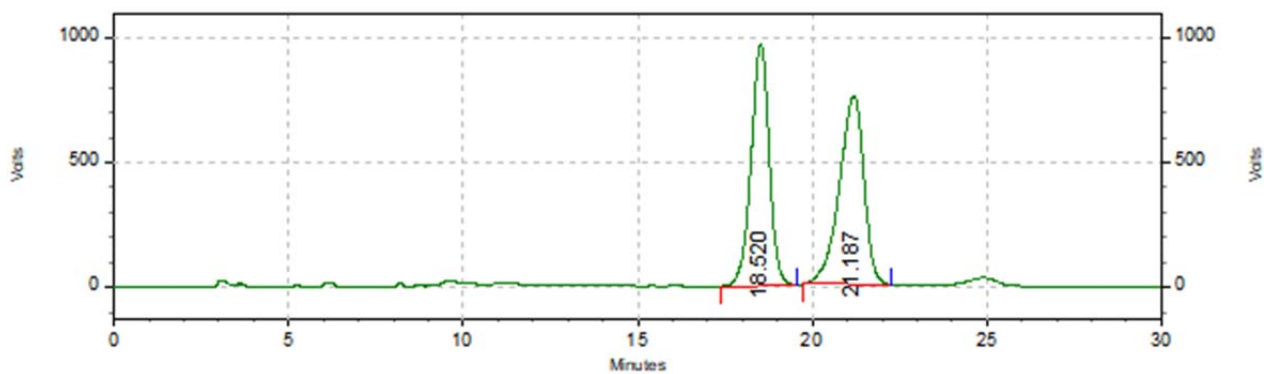


Results:

Time	Area	Area%	Height	Height%
17.902	2028301	6.928	61708	11.102
24.135	27248086	93.072	494123	88.898
Totals	29276387	100.000	555831	100.000



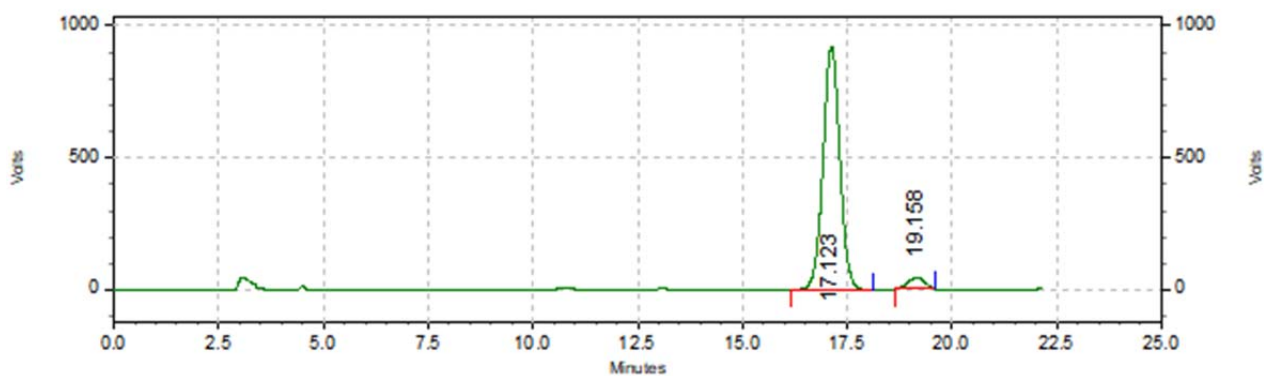
racemic sample:



Results:

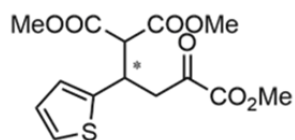
Time	Area	Area%	Height	Height%
18.520	34738241	48.443	967785	56.228
21.187	36971675	51.557	753395	43.772
Totals	71709916	100.000	1721180	100.000

asymmetric sample:

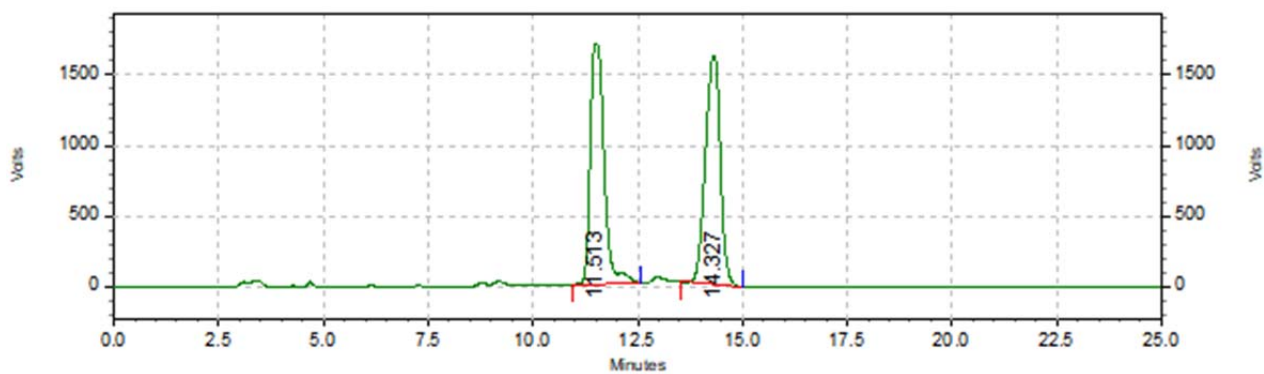


Results:

Time	Area	Area%	Height	Height%
17.123	25594536	95.579	918618	95.543
19.158	1183958	4.421	42855	4.457
Totals	26778494	100.000	961473	100.000



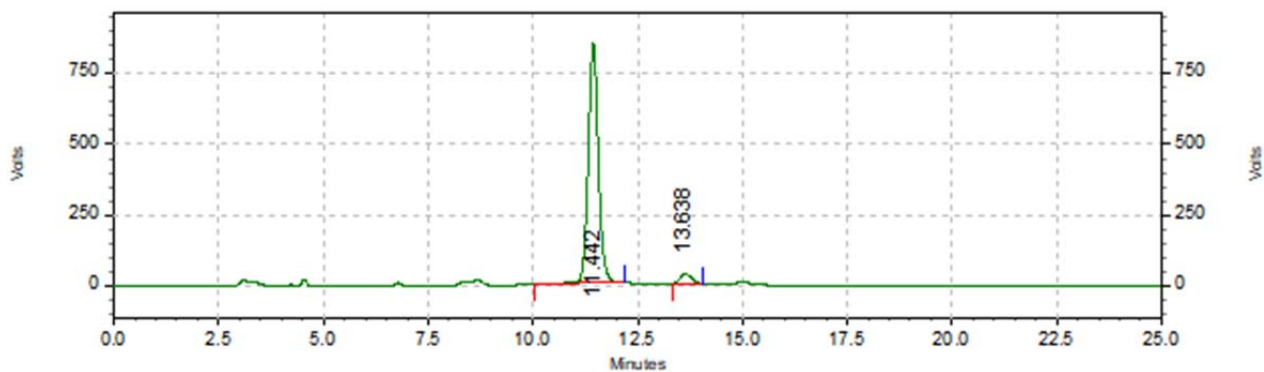
racemic sample:



Results:

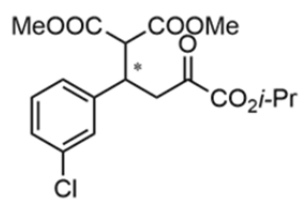
Time	Area	Area%	Height	Height%
11.513	38905375	49.274	1693287	51.190
14.327	40051947	50.726	1614544	48.810
Totals	78957322	100.000	3307831	100.000

asymmetric sample:

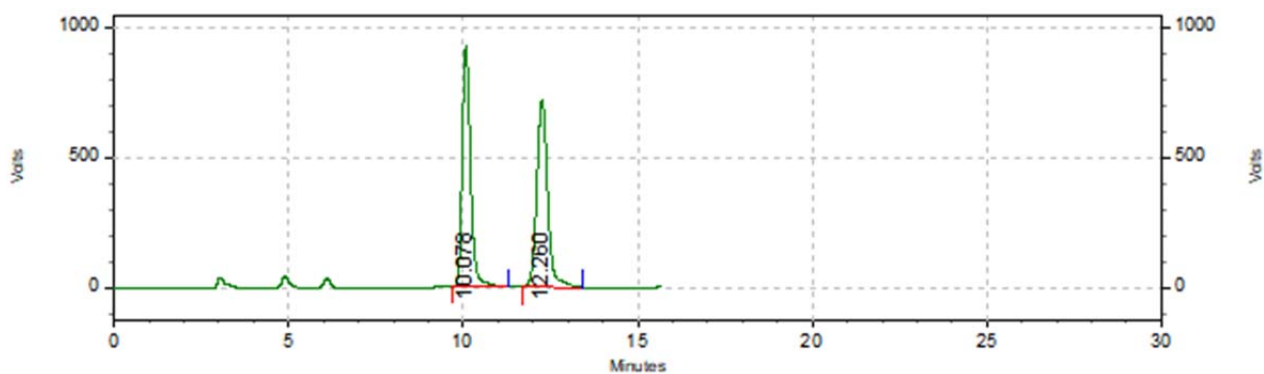


Results:

Time	Area	Area%	Height	Height%
11.442	14422695	95.919	846410	96.189
13.638	613627	4.081	33539	3.811
Totals	15036322	100.000	879949	100.000



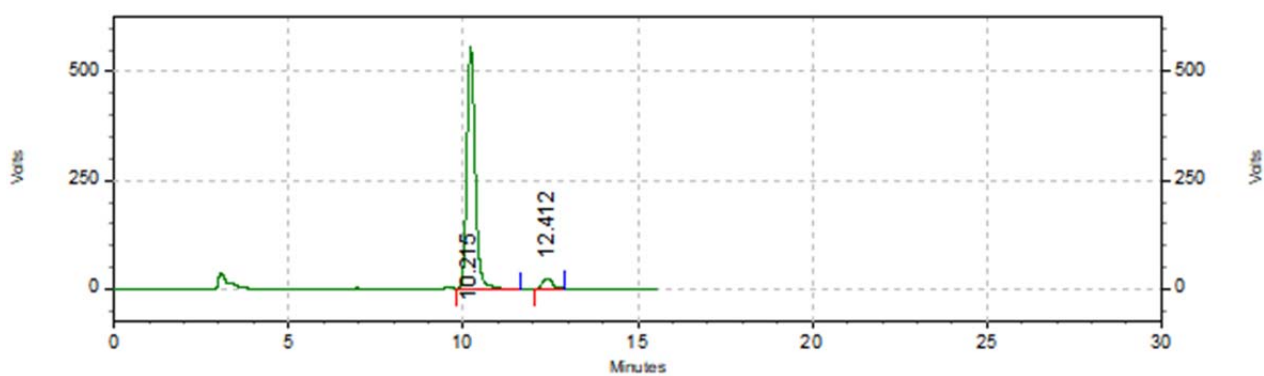
racemic sample:



Results:

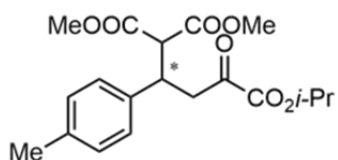
Time	Area	Area%	Height	Height%
10.078	15287242	49.614	924956	56.272
12.260	15525319	50.386	718762	43.728
Totals	30812561	100.000	1643718	100.000

asymmetric sample:

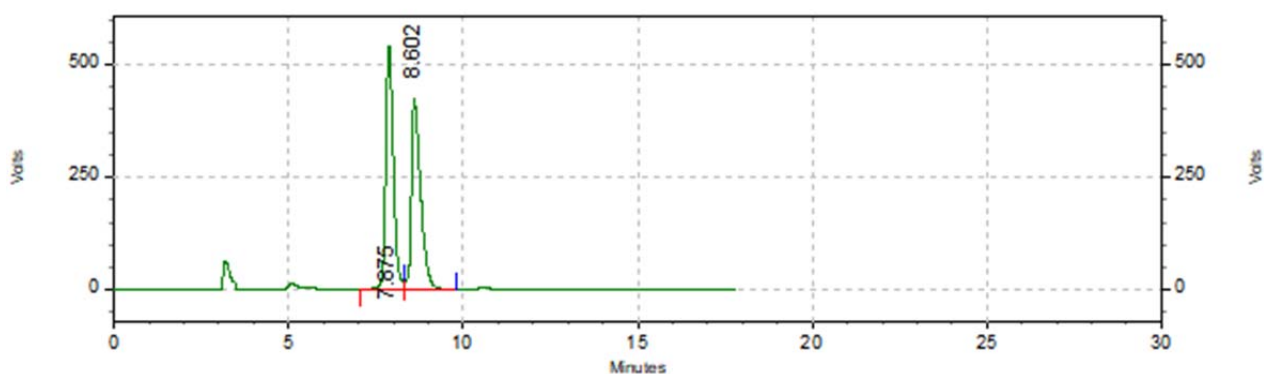


Results:

Time	Area	Area%	Height	Height%
10.215	9080860	95.080	556084	95.886
12.412	469857	4.920	23857	4.114
Totals	9550717	100.000	579941	100.000



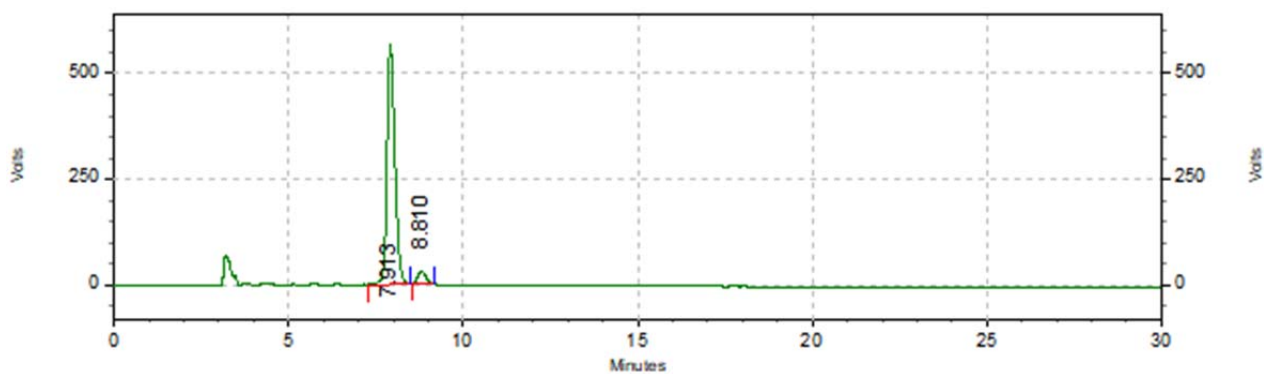
racemic sample:



Results:

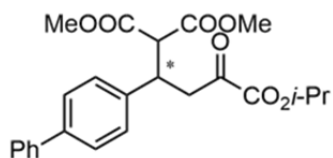
Time	Area	Area%	Height	Height%
7.875	8127496	50.989	539094	56.167
8.602	7812285	49.011	420704	43.833
Totals	15939781	100.000	959798	100.000

asymmetric sample:

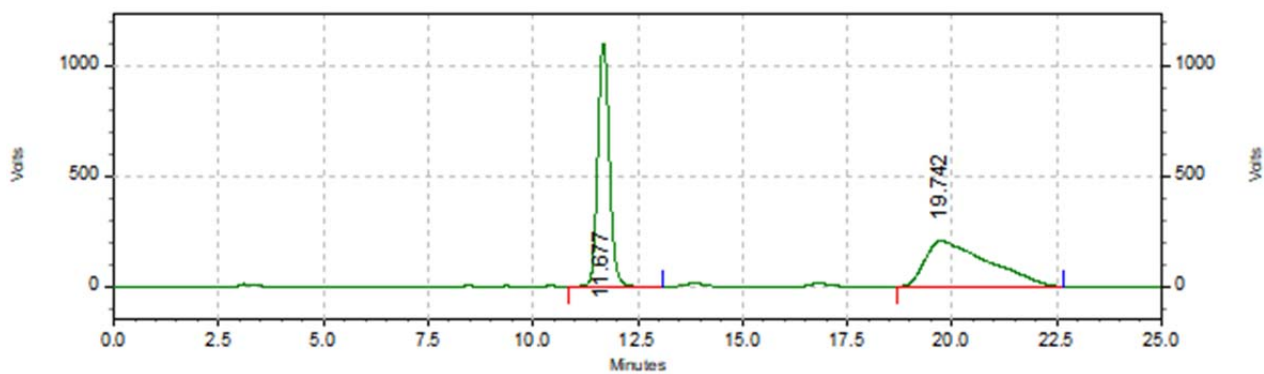


Results:

Time	Area	Area%	Height	Height%
7.913	8899405	94.944	565678	95.125
8.810	473919	5.056	28991	4.875
Totals	9373324	100.000	594669	100.000



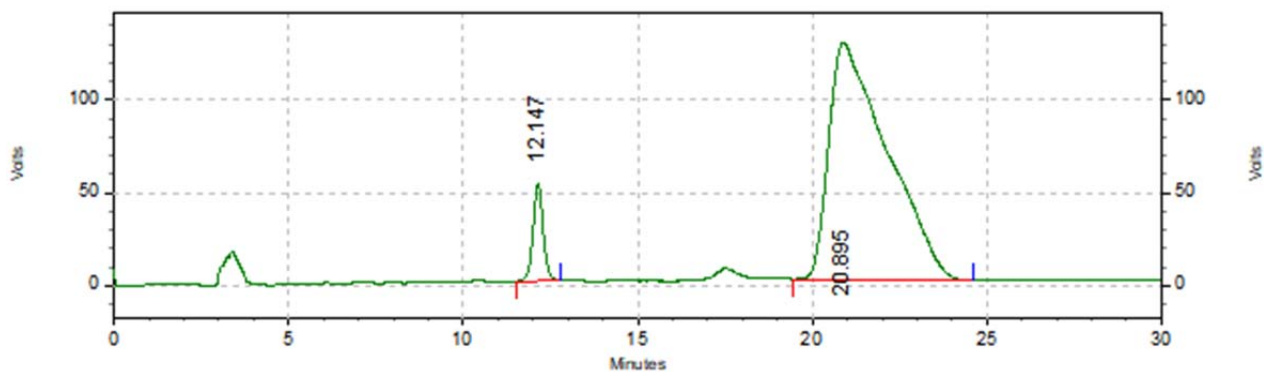
racemic sample:



Results:

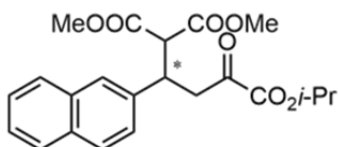
Time	Area	Area%	Height	Height%
11.677	21274289	49.228	1100503	84.042
19.742	21941734	50.772	208967	15.958
Totals	43216023	100.000	1309470	100.000

asymmetric sample:

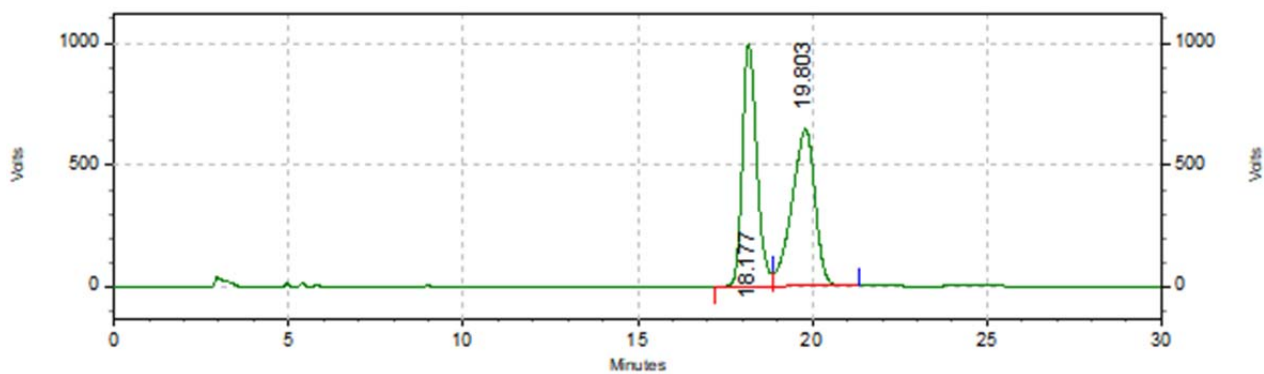


Results:

Time	Area	Area%	Height	Height%
12.147	1068888	6.747	52755	29.303
20.895	14772526	93.253	127277	70.697
Totals	15841414	100.000	180032	100.000



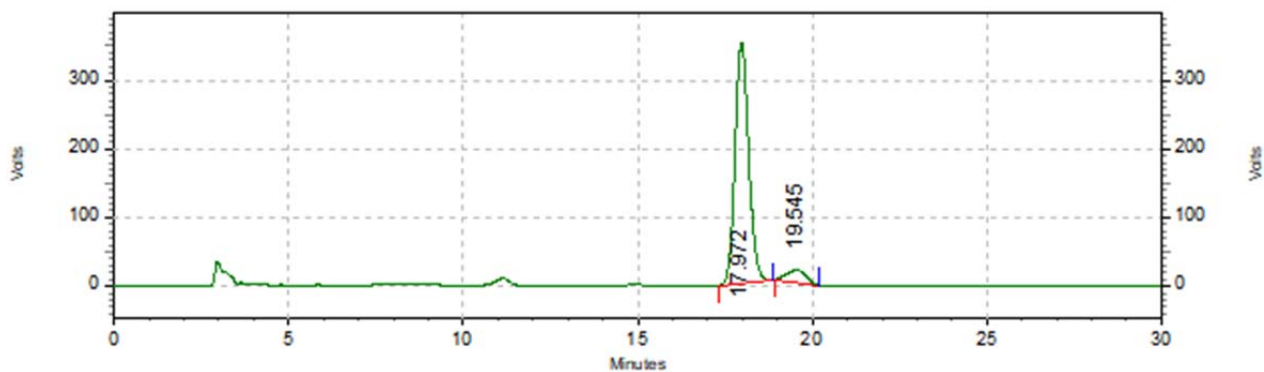
racemic sample:



Results:

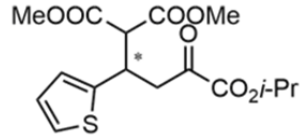
Time	Area	Area%	Height	Height%
18.177	28287009	49.052	991087	60.755
19.803	29380797	50.948	640202	39.245
Totals	57667806	100.000	1631289	100.000

asymmetric sample:

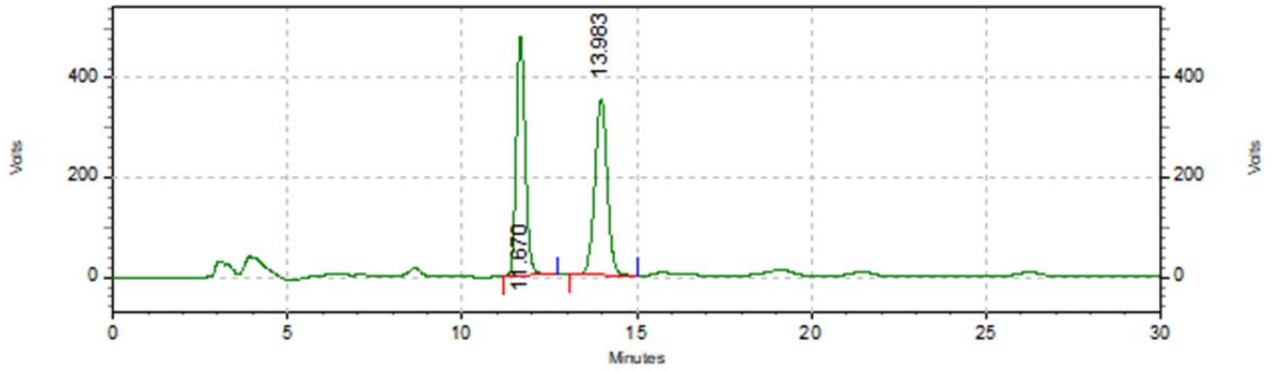


Results:

Time	Area	Area%	Height	Height%
17.972	9483962	93.683	350232	95.251
19.545	639456	6.317	17460	4.749
Totals	10123418	100.000	367692	100.000



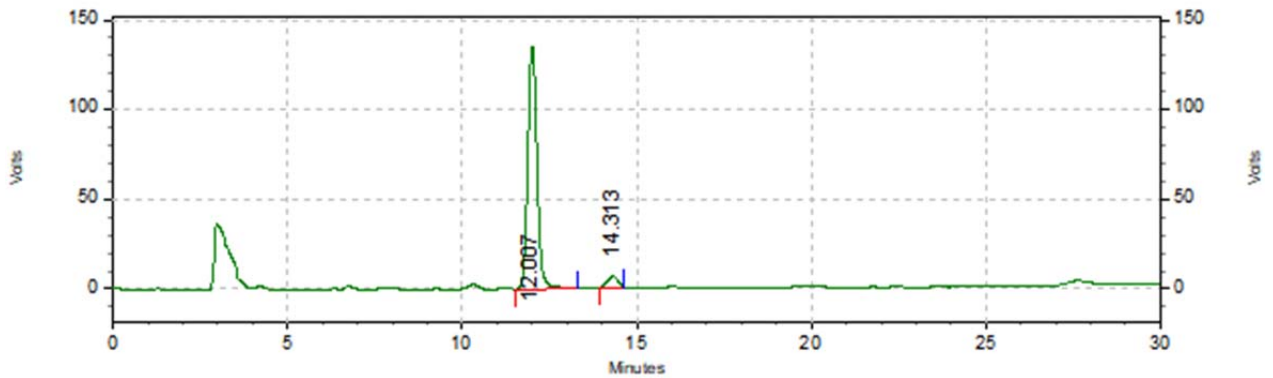
racemic sample:



Results:

Time	Area	Area%	Height	Height%
11.670	8644920	49.997	481380	57.688
13.983	8646091	50.003	353070	42.312
Totals	17291011	100.000	834450	100.000

asymmetric sample:



Results:

Time	Area	Area%	Height	Height%
12.007	2482705	95.162	135212	95.842
14.313	126217	4.838	5866	4.158
Totals	2608922	100.000	141078	100.000

4. References

- (1) Espinosa, M.; Blay, G.; Cardona, L.; Merino, P.; Pedro, J. R. *Organic Chemistry Frontiers* **2019**, *6*, 2907.
- (2) Cele, Z. E. D.; Sosibo, S. C.; Andersson, P. G.; Kruger, H. G.; Maguire, G. E. M.; Govender, T. *Tetrahedron: Asymmetry* **2013**, *24*, 191.
- (3) Konda, S.; Zhao, J. C. G. *Tetrahedron Lett.* **2014**, *55*, 5216.
- (4) Zhou, L.; Lin, L.; Wang, W.; Ji, J.; Liu, X.; Feng, X. *Chem Commun (Camb)* **2010**, *46*, 3601.