ELECTRONIC SUPPORTING INFORMATION FOR

Chiral Cobalt(III) tris(1,2-Diamine) Catalysts that Incorporate Nitrogenous Base Containing Anions for the Bifunctional Activation of Nucleophiles and Electrophiles in Enantioselective Addition Reactions

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General Information

All operations were carried out under air atmospheres. NMR spectra were recorded on standard FT spectrometers at ambient probe temperatures (500 MHz) or 298 K (400 MHz). Chemical shifts (δ/ppm) were generally referenced to solvent signals: ^{1}H, residual $CHCl_3$ (7.26), acetone-d_5, (2.05), or CHD_2CN (1.94); ^{13}C, $CDCl_3$ (77.16) or acetone-d_6 (29.84). IR spectra were recorded on a Shimadzu IRAffinity-1 spectrometer (Pike MIRacle ATR system, diamond/ZnSe crystal). Capillary thermolyses were monitored with an Optimelt MPA 100 instrument. Microanalyses were conducted by Atlantic Microlab. HPLC analyses were carried out with a Shimadzu instrument package (pump/autosampler/detector LC-20AD/SIL-20A/SPD-M20A).

The di-*t*-butyl azodicarboxylate (98%, Aldrich) was recrystallized from heptane (warm until dissolved) and petroleum ether (30-60 ˚C; added cold and sample kept at room temperature until precipitation). The (*E*)-cinnamaldehyde, 4-formylbenzoic acid methyl ester, nicotinic acid, 2-methoxynicotinic acid, 6-aminonicotinic acid, 6-chloronicotinic acid, 6-methylnicotinic acid, isonicotinic acid, picolinic acid, 3-(dimethylamino)benzoic acid, 2-pyridinesulfonic acid, ammonium acetate, *N*,*N*-dimethylaniline, dimethyl malonate, diethyl malonate, di-*t*-butyl malonate, Ph_2SiMe_2, *trans*-β-nitrostyrene, and routine chemicals not specifically noted were used as received from common commercial sources.

Syntheses of nitroolefin substrates

Nitroolefins **6a-d** and **6h-k** were used from a previous work, in which they were prepared by Henry reactions with nitromethane.[s1] Nitroolefins **6f**,**n** were available commercially, and **6e**,**l**, **m** were synthesized by literature procedures.[s2]

***trans-p*-(methoxycarbonyl)-β-nitrostyrene (6g).**[s3] A round-bottom flask was charged with 4-formylbenzoic acid methyl ester (0.250 g, 1.52 mmol, 1.0 equiv), nitromethane (1.5 mL), and ammonium acetate (0.035 g, 0.457 mmol, 30 mol%). The mixture was refluxed (2 h) and allowed to cool. The thick slurry was transferred to a sintered glass frit, and the solvent was pulled through by vacuum. The residue was triturated with a minimal amount of methanol, and

the solid transferred to a vial and dried by oil pump vacuum (rt, 14 h) to give **6g** as a yellow-green solid (0.124 g, 0.598 mmol, 39%), mp 178.4-181.8 ˚C (open capillary). IR (powder film, cm^{-1}): 3103, 3051, 2959, 1710, 1635, 1517, 1497, 1281, 1105, 960, 770.

NMR ($CDCl_3$, δ/ppm): ^1H (400 MHz) 8.11 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 8.02 (d, $^3J_{HH}$ = 13.7 Hz, 1H), 7.62 (d, $^3J_{HH}$ = 13.7 Hz, 1H), 7.62 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 3.95 (s, 3H); $^{13}C\{^1H\}$ (100 MHz) 166.1, 138.8, 137.7, 134.3, 133.2, 130.6, 129.1, 52.7 (8 × s).

(1*E*,3*E*)-1-phenyl-4-nitro-1,3-butadiene (**6o**). A round-bottom flask was charged with (*E*)-cinnamaldehyde (0.25 mL, 2.0 mmol, 1.0 equiv), nitromethane (1.5 mL), and ammonium acetate (0.046 g, 0.595 mmol, 30 mol%). The mixture was refluxed (2 h) and allowed to cool. The solvent was removed by rotary evaporation. The red oily residue was dissolved in a minimum of DCM, and loaded onto a silica column that was packed and eluted with EtOAc/hexanes (15:85 v/v). The solvent was removed from the combined product containing fractions by rotary evaporation and oil-pump vacuum (rt, 14 h) to give **6o** as an oily residue that slowly became a vermillion semi-solid (0.174 g, 1.00 mmol, 50%).[s4]

NMR ($CDCl_3$, δ/ppm): ^1H (500 MHz) 7.78 (ddd, $^3J_{HH}$ = 13.0, 11.6 Hz, $^4J_{HH}$ = 0.7 Hz, 1H), 7.55-7.47 (m, 2H), 7.44-7.37 (m, 3H), 7.24 (d, $^3J_{HH}$ = 13.1 Hz, 1H), 7.16 (d, $^3J_{HH}$ = 15.5 Hz, 1H), 6.87 (ddd, $^3J_{HH}$ = 15.5, 11.6 Hz, $^4J_{HH}$ = 0.6 Hz, 1H); $^{13}C\{^1H\}$ (100 MHz) 146.2, 139.3, 138.8, 135.3, 130.5, 129.2, 127.9, 120.7 (8 × s).

Syntheses of catalysts

Λ-(*S*,*S*)-2^{3+} $4a^-Cl^-BAr_f^-{\cdot}2H_2O$. Isolated according to the general procedure (main text) from Λ-(*S*,*S*)-2^{3+} $2Cl^-BAr_f^-{\cdot}2H_2O$ and isonicotinic acid (0.011 g) as an orange solid (0.048 g, 0.027 mmol, 91%), mp 125.7-129.6 ˚C (open capillary, dec to green liquid). Anal. Calcd. for $C_{80}H_{64}BClCoF_{24}N_7O_2{\cdot}2H_2O$ (1752.62): C 54.83, H 3.91, N, 5.59; found C 54.98, H 3.91, N 5.36. IR (powder film, cm^{-1}): 3068, 1681, 1609, 1539, 1385, 1354, 1273, 1119, 679.

NMR (acetone-d_6, δ/ppm):[s5] ^1H (500 MHz) isonicotinate at 8.69-8.63 (d, $^3J_{HH}$ = 5.8 Hz, 2H), 7.92-7.86 (d, $^3J_{HH}$ = 5.8 Hz, 2H); BAr_f^- at 7.84-7.77 (m, 8H, *o*), 7.68 (s, 4H, *p*); dpen at

8.54 (br s, 4H, NHH', overlapping isonicotinate), 7.63-7.46 (m, 12H), 7.36-7.16 (m, 18H), 5.26 (br s, 4H, NHH'), 5.17 (br s, 6H, CHNH$_2$); ^{13}C{^{1}H} (125 MHz) BAr$_f^-$ at 162.6 (q, $^1J_{BC}$ = 50.0 Hz, *i*), 135.5 (br s, *o*), 130.0 (qq, $^2J_{CF}$ = 31.5 Hz, $^4J_{CF}$ = 2.9 Hz, *m*), 125.4 (q, $^1J_{CF}$ = 271.6 Hz, CF$_3$), 118.4 (sept, $^3J_{CF}$ = 4.0 Hz, *p*); dpen at 137.6 (s, *i*-Ph), 129.8, 129.7, 129.6 (3 × s, *o*-, *m*-, *p*-Ph), 63.5 (s, CHNH$_2$); isonicotinate at 172.8 (s, COO$^-$), 150.7, 145.9, 124.2 (5 × s).

Λ-(*S*,*S*)-2^{3+} 4b$^-$Cl$^-$BAr$_f^-$·2H$_2$O. Isolated according to the general procedure from Λ-(*S*,*S*)-2^{3+} 2Cl$^-$BAr$_f^-$·2H$_2$O and nicotinic acid (0.011 g) as an orange solid (0.046 g, 0.026 mmol, 88%), mp 119.1-122.2 °C (open capillary, dec to green liquid). Anal. Calcd. for C$_{80}$H$_{64}$BClCoF$_{24}$N$_7$O$_2$·2H$_2$O (1752.62): C 54.83, H 3.91, N, 5.59, Cl, 2.00; found C 54.56, H 3.98, N 5.39. IR (powder film, cm^{-1}): 3063, 1609, 1539, 1387, 1354, 1275, 1119.

NMR (acetone-d_6, δ/ppm):[s5] ^{1}H (500 MHz) nicotinate at 9.24 (dd, $^4J_{HH}$ = 2.1 Hz, $^5J_{HH}$ = 0.9 Hz, 1H), 8.65 (dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.8 Hz, 1H), 8.34 (dt, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 2.0 Hz, 1H), 7.40 (ddd, $^3J_{HH}$ = 7.7 Hz, 4.8 Hz, $^5J_{HH}$ = 0.9, 1H); BAr$_f^-$ at 7.85-7.78 (m, 8H, *o*), 7.70 (s, 4H, *p*); dpen at 8.68 (br s, 5H, NHH', overlapping nicotinate), 7.62-7.46 (m, 12H), 7.35-7.22 (m, 18H), 5.25 (br s, 5H, NHH'), 5.18 (s, 6H, CHNH$_2$); ^{13}C{^{1}H} (125 MHz) BAr$_f^-$ at 162.6 (q, $^1J_{BC}$ = 50.0 Hz, *i*), 135.5 (br s, *o*), 130.0 (qq, $^2J_{CF}$ = 31.5 Hz, $^4J_{CF}$ = 2.9 Hz, *m*), 125.4 (q, $^1J_{CF}$ = 271.9 Hz, CF$_3$), 118.4 (sept, $^3J_{CF}$ = 4.0 Hz, *p*); dpen at 137.6 (s, *i*-Ph), 129.72, 129.71, 129.6 (3 × s, *o*-, *m*-, *p*-Ph), 63.5 (s, CHNH$_2$); nicotinate at 173.1 (s, COO$^-$), 152.1, 151.8, 137.4, 133.7, 123.6 (5 × s); ^{19}F{^{1}H} (470 MHz, CDCl$_3$ vs. internal C$_6$H$_5$CF$_3$ at –63.72) –63.2 (s).

Δ-(*S*,*S*)-2^{3+} 4b$^-$Cl$^-$BAr$_f^-$·2H$_2$O. Isolated according to the general procedure from Δ-(*S*,*S*)-2^{3+} 2Cl$^-$BAr$_f^-$·H$_2$O and nicotinic acid (0.011 g) as an orange solid (0.051 g, 0.029 mmol, 88%), mp 117.5 °C (open capillary; dec to green liquid with gradual darkening at lower temperatures). Anal. Calcd. for C$_{80}$H$_{64}$BClCoF$_{24}$N$_7$O$_2$·2H$_2$O (1752.62): C 54.83, H 3.91, N, 5.59; found C 55.38, H 4.08, N 5.70. IR (powder film, cm^{-1}): 3067, 1684, 1596, 1457, 1382, 1354, 1275, 1120, 682.

NMR (acetone-d_6, δ/ppm):[s5] ^{1}H (500 MHz) nicotinate at 9.14 (apparent s, 1H), 8.59 (dd, $^3J_{HH}$ = 5.0 Hz, $^4J_{HH}$ = 1.8 Hz, 1H), 8.23 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 7.36-7.29 (m, 1H); BAr$_f^-$ at

7.82-7.74 (m, 8H, *o*), 7.68 (s, 4H, *p*); dpen at 7.87 (br s, 1H, N**H**H', overlapping nicotinate), 7.58-7.46 (m, 12H), 7.28-7.13 (m, 18H), 5.98 (br s, 1H, NH**H**'), 5.08 (s, 6H, C**H**NH$_2$); ^{13}C{^{1}H} (125 MHz) BAr$_f^-$ at 162.6 (q, $^1J_{BC}$ = 49.8 Hz, *i*), 135.5 (br s, *o*), 130.0 (qq, $^2J_{CF}$ = 31.5 Hz, $^4J_{CF}$ = 2.9 Hz, *m*), 125.3 (q, $^1J_{CF}$ = 271.8 Hz, **C**F$_3$), 118.4 (sept, $^3J_{CF}$ = 4.0 Hz, *p*); dpen at 137.7 (s, *i*-Ph), 129.6, 129.4, 129.2 (3 × s, *o*-, *m*-, *p*-Ph), 66.0 (s, **C**HNH$_2$); nicotinate at[s6] 152.0, 151.5, 137.2, 129.7, 123.6 (5 × s).

Λ-(*S*,*S*)-2^{3+} 4c$^-$Cl$^-$BAr$_f^-$. Isolated according to the general procedure from Λ-(*S*,*S*)-2^{3+} 2Cl$^-$BAr$_f^-$·2H$_2$O and picolinic acid (0.011 g) as an orange solid (0.051 g, 0.029 mmol, 98%), mp 129.9 °C (open capillary; dec to green liquid with gradual darkening at lower temperatures). Anal. Calcd. for $C_{80}H_{64}BClCoF_{24}N_7O_2$ (1716.59): C 55.98, H 3.76, N, 5.71; found C 56.27, H 3.88, N 5.71. IR (powder film, cm^{-1}): 3029, 1609, 1579, 1549, 1387, 1354, 1274, 1118, 696.

NMR (acetone-d_6, δ/ppm):[s5] ^{1}H (500 MHz) picolinate at 8.66 (br s, 1H), 8.15 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.85 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 7.43-7.35 (m, 1H); BAr$_f^-$ at 7.83-7.79 (m, 8H, *o*), 7.69 (br s, 4H, *p*); dpen at 8.40 (br s, 4H, N**H**H'), 7.57-7.44 (m, 12H), 7.31-7.09 (m, 18H), 5.68 (br s, 4H, NH**H**'), 5.15 (s, 6H, C**H**NH$_2$); ^{13}C{^{1}H} (125 MHz) BAr$_f^-$ at 162.6 (q, $^1J_{BC}$ = 50.0 Hz, *i*), 135.5 (br s, *o*), 130.0 (qq, $^2J_{CF}$ = 31.5 Hz, $^4J_{CF}$ = 2.9 Hz, *m*), 125.3 (q, $^1J_{CF}$ = 271.8 Hz, **C**F$_3$), 118.4 (sept, $^3J_{CF}$ = 4.0 Hz, *p*); dpen at 137.6 (s, *i*-Ph), 129.63 (double intensity), 129.58, (2 × s, *o*-, *m*-, *p*-Ph), 63.6 (s, **C**HNH$_2$); picolinate at 172.7 (s, **C**OO$^-$), 156.5, 149.7, 137.3, 125.4, 125.1 (5 × s).

Λ-(*S*,*S*)-2^{3+} 4d$^-$Cl$^-$BAr$_f^-$·2H$_2$O. Isolated according to the general procedure from Λ-(*S*,*S*)-2^{3+} 2Cl$^-$BAr$_f^-$·2H$_2$O and pyridine-2-sulfonic acid (0.014 g) as an orange solid (0.051 g, 0.029 mmol, 96%), mp 126.4-136.7 °C (open capillary; dec to green liquid). Anal. Calcd. for $C_{79}H_{64}BClCoF_{24}N_7O_3S{\cdot}2H_2O$ (1788.67): C 53.05, H 3.83, N, 5.48; found C 53.31, H 3.73, N 5.39. IR (powder film, cm^{-1}): 3216, 3079, 1610, 1457, 1354, 1274, 1118, 1024, 681.

NMR (acetone-d_6, δ/ppm):[s5] ^{1}H (500 MHz) 2-pyridinesulfonate at 8.55 (d, $^3J_{HH}$ = 4.7 Hz, 1H), 8.10-7.99 (m, 2H), 7.56-7.48 (m, 1H); BAr$_f^-$ at 7.81-7.78 (m, 8H, *o*), 7.67 (s, 4H, *p*); dpen at ca. 7.5 (N**H**H', overlapping Ar-C**H**, 2H), 7.49-7.39 (m, 12H), 7.31-7.12 (m, 18H), 5.25

(br s, 4H, NHH'), 5.05 (s, 6H, CHNH$_2$); ^{13}C{^{1}H} (125 MHz) BAr$_f^-$ at 162.6 (q, $^1J_{BC}$ = 50.0 Hz, *i*), 135.5 (br s, *o*), 130.0 (qq, $^2J_{CF}$ = 31.5 Hz, $^4J_{CF}$ = 2.9 Hz, *m*), 125.4 (q, $^1J_{CF}$ = 274.5 Hz, CF$_3$), 118.4 (sept, $^3J_{CF}$ = 4.0 Hz, *p*); dpen at 136.9 (s, *i*-Ph), 129.8, 129.64, 129.62 (3 × s, *o-, m-*, *p*-Ph), 63.4 (s, CHNH$_2$); 2-pyridinesulfonate at 162.7, 150.2, 139.2, 126.1, 121.8 (6 × s).

Λ-(*S*,*S*)-2^{3+} 4e$^-$Cl$^-$BAr$_f^-$·2H$_2$O. Isolated according to the general procedure from Λ-(*S*,*S*)-**2**$^{3+}$ 2Cl$^-$BAr$_f^-$·2H$_2$O and 3-(dimethylamino)benzoic acid (0.015 g) as an orange solid (0.053 g, 0.030 mmol, 99%), mp 99.8-106.9 ˚C (open capillary; dec to green liquid). Anal. Calcd. for C$_{83}$H$_{70}$BClCoF$_{24}$N$_7$O$_2$·2H$_2$O (1793.45): C 55.55, H 4.16, N, 5.46; found C 56.39, H 4.39, N 5.42. IR (powder film, cm^{-1}): 1597, 1525, 1382, 1353, 1123, 696, 682.

NMR (acetone-d_6, δ/ppm):[s5] ^{1}H (500 MHz) 3-(dimethylamino)benzoate at 7.51-7.39 (m, 3H), 6.9-6.82 (m, 1H), 2.98 (s, 6H, overlapping with H$_2$O); BAr$_f^-$ at 7.83-7.78 (m, 8H, *o*), 7.69 (br s, 4H, *p*); dpen at 8.96 (br s, 4H, NHH'), 7.63-7.51 (m, 12H), 7.33-7.19 (m, 18H), 5.11 (br s, 9H, NHH' and CHNH$_2$); ^{13}C{^{1}H} (125 MHz) BAr$_f^-$ at 162.6 (q, $^1J_{BC}$ = 50.0 Hz, *i*), 135.5 (br s, *o*), 130.0 (qq, $^2J_{CF}$ = 31.5 Hz, $^4J_{CF}$ = 2.9 Hz, *m*), 125.3 (q, $^1J_{CF}$ = 271.8 Hz, CF$_3$), 118.4 (sept, $^3J_{CF}$ = 4.0 Hz, *p*); dpen at 137.9 (s, *i*-Ph), 129.7, 129.67, 129.61, (3 × s, *o-, m-*, *p*-Ph), 63.5 (s, CHNH$_2$); 3-(dimethylamino)benzoate at 175.2 (s, COO$^-$), 151.4, 139.4, 128.9, 128.2, 119.0, 115.0 (6 × s).

Λ-(*S*,*S*)-2^{3+} 4f$^-$Cl$^-$BAr$_f^-$·2H$_2$O. Isolated according to the general procedure from Λ-(*S*,*S*)-**2**$^{3+}$ 2Cl$^-$BAr$_f^-$·2H$_2$O (0.100 g, 0.060 mmol), 6-chloronicotinic acid (0.028 g, 0.180 mmol), and Na$_2$CO$_3$ (0.021 g, 0.198 mmol) as an orange solid (0.103 g, 0.058 mmol, 96%), mp 129.4-133.3˚C (open capillary; dec to green liquid). Anal. Calcd. for C$_{83}$H$_{70}$BClCoF$_{24}$N$_7$O$_2$·H$_2$O (1769.05): C 54.32, H 3.70, N, 5.54; found C 54.32, H 3.73, N 5.52. IR (powder film, cm^{-1}): 3040, 1609, 1585, 1537, 1393, 1354, 1275, 1119.

NMR (acetone-d_6, δ/ppm):[s5] ^{1}H (500 MHz) 6-chloronicotinate at 8.99-8.94 (m, 1H), 8.37 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 2.3 Hz, 1H), 7.49 (dd, $^3J_{HH}$ = 8.2 Hz, $^5J_{HH}$ = 0.7 Hz, 1H); BAr$_f^-$ at 7.89-7.77 (m, 8H, *o*), 7.70 (s, 4H, *p*); dpen at 8.55 (br s, 5H, NHH'), 7.60-7.52 (m, 12H), 7.39-7.23 (m, 18H), 5.29 (br s, 5H, NHH'), 5.20 (s, 6H, CHNH$_2$); 3.01 (br s, 4H, H$_2$O); ^{13}C{^{1}H} (125

MHz) BAr_f^- at 162.6 (q, $^1J_{BC}$ = 50.0 Hz, *i*), 135.5 (br s, *o*), 130.0 (qq, $^2J_{CF}$ = 31.5 Hz, $^4J_{CF}$ = 2.9 Hz, *m*), 125.4 (q, $^1J_{CF}$ = 271.9 Hz, **C**F_3), 118.4 (sept, $^3J_{CF}$ = 4.0 Hz, *p*); dpen at 137.6 (s, *i*-Ph), 129.8, 129.7, 129.6 (3 × s, *o*-, *m*-, *p*-Ph), 63.5 (s, **C**HNH_2); 6-chloronicotinate at 171.9 (s, **C**OO^-), 153.3, 152.2, 140.8, 133.1, 124.1 (5 × s).

Λ-(*S*,*S*)-2^{3+} 4g$^-$Cl$^-$$BAr_f^-$·2$H_2O$. Isolated according to the general procedure from Λ-(*S*,*S*)-2^{3+} 2$Cl^-$$BAr_f^-$·2$H_2O$ and 2-methoxynicotinic acid (0.014 g) as an orange solid (0.053 g, 0.030 mmol, 99%), mp 102.7-106.7 ˚C (open capillary; dec to green liquid). Anal. Calcd. for $C_{81}H_{66}BClCoF_{24}N_7O_3·2H_2O$ (1782.65): C 54.58, H 3.96, N, 5.50; found C 55.14, H 3.90, N 5.46. IR (powder film, cm^{-1}): 3067, 1593, 1580, 1499, 1354, 1275, 1119.

NMR (acetone-d_6, δ/ppm):[s5] ^{1}H (500 MHz) 2-methoxynicotinate at 8.22-8.13 (m, 1H), 8.07-7.97 (m, 1H), 7.01-6.90 (m, 1H), 3.96 (s, 3H); BAr_f^- at 7.85-7.79 (m, 8H, *o*), 7.70 (s, 4H, *p*); dpen at 8.69 (br s, 4H, N**H**H'), 7.64-7.46 (m, 12H), 7.36-7.17 (m, 18H), 5.21 (br s, 4H, NH**H**'), 5.14 (s, 6H, C**H**NH_2); ^{13}C{^{1}H} (125 MHz) BAr_f^- at 162.6 (q, $^1J_{BC}$ = 49.8 Hz, *i*), 135.5 (br s, *o*), 130.0 (qq, $^2J_{CF}$ = 31.0 Hz, $^4J_{CF}$ = 2.8 Hz, *m*), 125.4 (q, $^1J_{CF}$ = 271.8 Hz, **C**F_3), 118.4 (sept, $^3J_{CF}$ = 3.9 Hz, *p*); dpen at 137.7 (s, *i*-Ph), 129.7 (double intensity), 129.6 (2 × s, *o*-, *m*-, *p*-Ph), 63.5 (s, **C**HNH_2); 2-methoxynicotinate at 173.8 (s, **C**OO^-), 162.5, 147.8, 139.9, 123.9, 117.0 (5 × s), 53.5 (s, O**C**H_3).

Λ-(*S*,*S*)-2^{3+} 4h$^-$Cl$^-$$BAr_f^-$·$H_2O$. Isolated according to the general procedure from Λ-(*S*,*S*)-2^{3+} 2$Cl^-$$BAr_f^-$·2$H_2O$ (0.100 g, 0.060 mmol), 6-methylnicotinic acid (0.025 g, 0.180 mmol), and Na_2CO_3 (0.021 g, 0.20 mmol) as an orange solid (0.096 g, 0.055 mmol, 91%), mp 121.6-134.1 ˚C (open capillary; dec to green liquid). Anal. Calcd. for $C_{83}H_{70}BClCoF_{24}N_7O_2·H_2O$ (1748.64): C 55.64, H 3.92, N, 5.61; found C 55.56, H 3.96, N 5.61. IR (powder film, cm^{-1}): 3034, 1607, 1533, 1389, 1354, 1275, 1119.

NMR (acetone-d_6, δ/ppm):[s5] ^{1}H (500 MHz) 2-methylnicotinate at 9.08 (apparent s, 1H), 8.21 (dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 2.1 Hz, 1H), 7.24, (m, 1H, overlapping with dpen), 2.54 (s, 3H); BAr_f^- at 7.85-7.77 (m, 8H, *o*), 7.69 (s, 4H, *p*); dpen at 8.72 (br s, 4H, N**H**H'), 7.62-7.46 (m, 12H), 7.36-7.19 (m, 18H), 5.16 (m, 10H, C**H**NH_2, NH**H**'); ^{13}C{^{1}H} (125 MHz) BAr_f^- at 162.6

(q, $^1J_{BC}$ = 50.5 Hz, *i*), 135.5 (br s, *o*), 130.0 (qq, $^2J_{CF}$ = 31.5 Hz, $^4J_{CF}$ = 2.8 Hz, *m*), 125.3 (q, $^1J_{CF}$ = 271.8 Hz, **C**F_3), 118.4 (sept, $^3J_{CF}$ = 4.0 Hz, *p*); dpen at 137.7 (s, *i*-Ph), 130.9 (s, *o*-, *m*-, *p*-Ph), 63.5 (s, **C**HNH_2); 2-methylnicotinate at 173.4 (s, **C**OO^-), 160.7, 151.6, 137.8, 130.9, 122.8 (5 × s), 24.5 (s, **C**H_3).

Λ-(*S*,*S*)-2^{3+} 4i$^-$Cl$^-$BAr_f^-·2H_2O. Isolated according to the general procedure from Λ-(*S*,*S*)-2^{3+} 2Cl$^-$BAr_f^-·2H_2O (0.100 g, 0.060 mmol), 6-aminonicotinic acid (0.025 g, 0.180 mmol), and Na_2CO_3 (0.021 g, 0.20 mmol) as an orange solid (0.095 g, 0.054 mmol, 90%), mp 118.4 °C (open capillary; dec to green liquid with gradual darkening at lower temperatures). Anal. Calcd. for $C_{83}H_{70}BClCoF_{24}N_7O_2$·2$H_2O$ (1767.64): C 54.36 H 3.93, N, 6.34; found C 54.34, H 3.87, N 6.11. IR (powder film, cm^{-1}): 3069, 1609, 1375, 1354, 1275, 1119.

NMR (acetone-d_6, δ/ppm):[s5] ^{1}H (500 MHz) 6-aminonicotinate at 8.67 (d, $^4J_{HH}$ = 1.7 Hz, 1H), 8.00 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2.2 Hz, 1H), 6.51, (dd, $^3J_{HH}$ = 8.5 Hz, $^5J_{HH}$ = 0.8 Hz, 1H), 5.70 (br s, 2H, N**H**$_2$); BAr_f^- at 7.86-7.74 (m, 8H, *o*), 7.68 (s, 4H, *p*); dpen at 8.89 (br s, 2H, N**H**H'), 7.60-7.41 (m, 12H), 7.34-7.13 (m, 18H), 5.08 (br s, 8H, C**H**NH_2, NH**H**'); ^{13}C{^{1}H} (125 MHz) BAr_f^- at 162.6 (q, $^1J_{BC}$ = 49.7 Hz, *i*), 135.5 (br s, *o*), 130.0 (qq, $^2J_{CF}$ = 31.5 Hz, $^4J_{CF}$ = 2.8 Hz, *m*), 125.3 (q, $^1J_{CF}$ = 271.6 Hz, **C**F_3), 118.4 (sept, $^3J_{CF}$ = 4.0 Hz, *p*); dpen at 137.7 (s, *i*-Ph), 129.7 (double intensity), 129.6 (2 × s, *o*-, *m*-, *p*-Ph), 63.3 (s, **C**HNH_2); 6-aminonicotinate at 174.2 (s, **C**OO^-), 161.8, 151.8, 139.4, 123.2, 107.1 (5 × s); ^{19}F{^{1}H} (470 MHz, $CDCl_3$ vs. internal $C_6H_5CF_3$ at –63.72) –63.2 (s).

Δ-(*S*,*S*)-2^{3+} 4i$^-$Cl$^-$BAr_f^-·2H_2O. Isolated according to the general procedure from Δ-(*S*,*S*)-2^{3+} 2Cl$^-$BAr_f^-·H_2O (0.200 g, 0.120 mmol), 6-aminonicotinic acid (0.050 g, 0.360 mmol), and Na_2CO_3 (0.042 g, 0.396 mmol) as an orange solid (0.202 g, 0.11 mmol, 95%), mp 110.5 °C (open capillary; dec to green liquid with gradual darkening at lower temperatures). Anal. Calcd. for C_{83}–$H_{70}BClCoF_{24}N_7O_2$·2H_2O (1767.64): C 54.36, H 3.93, N, 6.34; found C 54.02, H 3.97, N 6.37. IR (powder film, cm^{-1}): 3042, 1609, 1456, 1354, 1275, 1119.

NMR (acetone-d_6, δ/ppm):[s5] ^{1}H (500 MHz) 6-aminonicotinate at 8.79 (apparent s, 1H), 7.94 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 2.2 Hz, 1H), 6.48, (d, $^3J_{HH}$ = 8.4 Hz, 1H), 5.85 (br s, 2H, N**H**$_2$);

BAr_f^- at 7.84-7.79 (m, 8H, *o*), 7.69 (s, 4H, *p*); dpen at 7.75 (br s, 2H, NHH'), 7.57-7.42 (m, 12H), 7.32-7.09 (m, 18H), 6.18 (br s, 4H, NHH') 5.07 (br s, 6H, CHNH$_2$); $^{13}C\{^1H\}$ (125 MHz) BAr_f^- at 162.6 (q, $^1J_{BC}$ = 50.0 Hz, *i*), 135.5 (br s, *o*), 130.0 (qq, $^2J_{CF}$ = 31.5 Hz, $^4J_{CF}$ = 2.8 Hz, *m*), 125.4 (q, $^1J_{CF}$ = 271.8 Hz, CF_3), 118.4 (sept, $^3J_{CF}$ = 4.0 Hz, *p*); dpen at 137.8 (s, *i*-Ph), 129.5, 129.4, 129.2 (3 × s, *o*-, *m*-, *p*-Ph), 66.1 (s, CHNH$_2$); 6-aminonicotinate at 173.5 (s, COO^-), 161.7, 151.8, 139.4, 123.6, 107.2 (5 × s).

Nitroolefin addition products accessed by the general procedure for Chart 4

Dimethyl 2-(2-nitro-1-phenylethyl)malonate (7a). This known compound was obtained as a colorless oil, 95%. NMR ($CDCl_3$, δ/ppm): ^1H (400 MHz) 7.35-7.26 (m, 3H), 7.23-7.18 (m, 2H), 4.97-4.80 (m, 2H), 4.23 (td, $^3J_{HH}$ = 8.9, 5.3 Hz, 1H), 3.85 (d, $^3J_{HH}$ = 9.0 Hz, 1H), 3.75 (s, 3H), 3.55 (s, 3H). $^{13}C\{^1H\}$ (100 MHz) 168.0, 167.4, 136.3, 129.2, 128.6, 128.0, 77.5, 54.9, 53.2, 53.0, 43.0 (11 × s). The enantiomeric excess was determined by HPLC with a Chiralcel AD column (98:2 v/v hexane/isopropanol, 1 mL/min, λ = 220 nm); t_R = 32.9 min (major), 43.6 min (minor), 86% ee.[s1]

Diethyl 2-(2-nitro-1-phenylethyl)malonate (7a-Et). This known compound was obtained as a colorless oil, 90%. NMR ($CDCl_3$, δ/ppm): ^1H (500 MHz) 7.34-7.26 (m, 3H), 7.25-7.21 (m, 2H), 5.05-4.74 (m, 2H), 4.34-4.12 (m, 3H), 4.00 (q, $^3J_{HH}$ = 7.1 Hz, 2H), 3.82 (d, $^3J_{HH}$ = 9.4 Hz, 1H), 1.26 (t, $^3J_{HH}$ = 7.1 Hz, 3H), 1.04 (t, $^3J_{HH}$ = 7.1 Hz, 3H). The enantiomeric excess was determined by HPLC with a Chiralcel AD column (90:10 v/v hexane/isopropanol, 1 mL/min, λ = 230 nm); t_R = 11.4 min (major), 24.4 min (minor), 80% ee.[s7]

Diisopropyl 2-(2-nitro-1-phenylethyl)malonate (7a-*i*Pr). This known compound was obtained as a colorless oil, 29%. NMR ($CDCl_3$, δ/ppm): ^1H (500 MHz). 7.34-7.27 (m, 3H), 7.26-7.21 (m, 2H), 5.08 (sept, $^3J_{HH}$ = 6.3 Hz, 1H), 4.92 (dd, $^2J_{HH}$ = 12.9 Hz, $^3J_{HH}$ = 4.6 Hz, 1H), 4.87-4.79 (m, 2H), 4.20 (td, $^3J_{HH}$ = 9.5, 4.6 Hz, 1H), 3.76 (d, $^3J_{HH}$ = 9.6 Hz, 1H), 1.244 (d, $^3J_{HH}$ = 6.3 Hz, 3H), 1.242 (d, $^3J_{HH}$ = 6.3 Hz, 3H), 1.06 (d, $^3J_{HH}$ = 6.3 Hz, 3H), 1.01 (d, $^3J_{HH}$ = 6.3 Hz, 3H). The enantiomeric excess was determined by HPLC with a Chiralcel OD column (95:5

v/v hexane/isopropanol, 1 mL/min, λ = 220 nm); t_R = 10.5 min (major), 12.4 min (minor), 65% ee.[s1]

Dimethyl 2-(2-nitro-1-β-naphthylethyl)malonate (7b). This known compound was obtained as a colorless oil, 90%. NMR ($CDCl_3$, δ/ppm): ^{1}H (500 MHz) 8.18 (d, $^3J_{HH}$ = 8.6 Hz, 1H), 7.87 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.80 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.62 (ddd, $^3J_{HH}$ = 8.4, 6.8 Hz, $^4J_{HH}$ = 1.4 Hz, 1H), 7.53 (ddd, $^3J_{HH}$ = 8.0, 6.8 Hz, $^4J_{HH}$ = 1.1 Hz, 1H), 7.46-7.40 (m, 1H), 7.38 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 5.27-5.20 (m, 1H), 5.18 (dd, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 8.2 Hz, 1H), 5.07 (dd, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 4.5 Hz, 1H), 4.11 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 3.72 (s, 3H), 3.54 (s, 3H). The enantiomeric excess was determined by HPLC with a Chiralcel OD column (70:30 v/v hexane/isopropanol, 1 mL/min, λ = 254 nm); t_R = 12.5 min (major), 35.5 min (minor), 84% ee.[s1]

Dimethyl 2-(2-nitro-1-α-naphthylethyl)malonate (7c). This known compound was obtained as a colorless oil, 95%. NMR ($CDCl_3$, δ/ppm): ^{1}H (500 MHz) 8.18 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 7.87 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.80 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 7.62 (ddd, $^3J_{HH}$ = 8.4, 6.9 Hz, $^4J_{HH}$ = 1.3 Hz, 1H), 7.58-7.48 (m, 1H), 7.47-7.35 (m, 2H), 5.27-5.24 (m, 1H), 5.18 (dd, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 8.2 Hz, 1H), 5.07 (dd, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 4.5 Hz, 1H), 4.11 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 3.72 (s, 3H), 3.54 (s, 3H). The enantiomeric excess was determined by HPLC with a Chiralcel AD column (90:10 v/v hexane/isopropanol, 1 mL/min, λ = 254 nm); t_R = 14.4 min (major), 19.1 min (minor), 90% ee.[s1]

Dimethyl 2-(2-nitro-1-(4-methoxyphenyl)ethyl)malonate (7d). This known compound was obtained as a colorless oil, 99%. NMR ($CDCl_3$, δ/ppm): ^{1}H (500 MHz) 7.17-7.10 (m, 2H), 6.88-6.79 (m, 2H), 4.89 (dd, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 5.0 Hz, 1H), 4.82 (dd, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 9.2 Hz, 1H), 4.19 (td, $^3J_{HH}$ = 9.2, 5.0 Hz, 1H), 3.82 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.57 (s, 3H). The enantiomeric excess was determined by HPLC with a Chiralcel AD column (80:20 v/v hexane/isopropanol, 1 mL/min, λ = 254 nm); t_R = 12.4 min (major), 18.0 min (minor), 71% ee.[s1]

Dimethyl 2-(2-nitro-1-(4-nitrophenyl)phenylethyl)malonate (7e). This known compound was obtained as a colorless oil, 85%. NMR ($CDCl_3$, δ/ppm): ^{1}H (500 MHz) 8.24-8.17 (m, 2H),

7.61-7.36 (m, 2H), 5.07-4.82 (m, 2H), 4.37 (td, $^3J_{HH}$ = 8.9, 5.2 Hz, 1H), 3.88 (d, $^3J_{HH}$ = 8.8 Hz, 1H), 3.78 (s, 3H), 3.61 (s, 3H). The enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (90:10 v/v hexane/isopropanol, 1 mL/min, λ = 220 nm); t_R = 22.7 min (minor), 35.1 min (major), 76% ee.

Dimethyl 2-(2-nitro-1-(3,4-dioxolophenyl)ethyl)malonate (7f). This known compound was obtained as a colorless oil, 90%. NMR ($CDCl_3$, δ/ppm): ^{1}H (500 MHz) 6.85-6.59 (m, 3H), 5.95 (s, 2H), 5.01-4.58 (m, 2H), 4.15 (td, $^3J_{HH}$ = 9.3, 4.9 Hz, 1H), 3.80 (d, $^3J_{HH}$ = 9.1 Hz, 1H), 3.76 (s, 3H), 3.61 (s, 3H). The enantiomeric excess was determined by HPLC with a Chiralcel AS-H column (90:10 v/v hexane/isopropanol, 1 mL/min, λ = 220 nm); t_R = 44.8 min (major), 53.3 min (minor), 97% ee.[s8]

Dimethyl 2-(2-nitro-1-(4-methoxycarbonyl)phenylethyl)malonate (7g). This known compound was obtained as a colorless oil, 73%. NMR ($CDCl_3$, δ/ppm): ^{1}H (500 MHz) 8.00 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.32 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 5.25-4.71 (m, 2H), 4.31 (td, $^3J_{HH}$ = 8.8, 5.3 Hz, 1H), 3.90 (s, 3H), 3.87 (d, $^3J_{HH}$ = 8.9 Hz, 1H), 3.77 (s, 3H), 3.57 (s, 3H). The enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (90:10 v/v hexane/isopropanol, 1 mL/min, λ = 210 nm); t_R = 28.5 min (major), 42.8 min (minor), 67% ee.[s9]

Dimethyl 2-(2-nitro-1-(2-(trifluoromethyl)phenylethyl)malonate (7h). This known compound was obtained as a colorless oil, 99%. NMR ($CDCl_3$, δ/ppm): ^{1}H (500 MHz). 7.72 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.53 (t, $^3J_{HH}$ = 8.1 Hz, 1H), 7.43 (ddt, $^3J_{HH}$ = 7.7, 6.7 Hz, $^4J_{HH}$ = 1.0 Hz, 1H), 7.37 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 5.16 (dd, $^2J_{HH}$ = 13.3 Hz, $^3J_{HH}$ = 7.7 Hz, 1H), 4.94 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 4.5 Hz, 1H), 4.64 (td, $^3J_{HH}$ = 7.6, 4.5 Hz, 1H), 4.10 (d, $^3J_{HH}$ = 7.4 Hz, 1H), 3.75 (s, 3H), 3.64 (s, 3H). The enantiomeric excess was determined by HPLC with a Chiralcel OD column (95:5 v/v hexane/isopropanol, 1 mL/min, λ = 220 nm); t_R = 12.0 min (minor), 22.6 min (major), 91% ee.[s1]

Dimethyl 2-(2-nitro-1-(2-acetoxyphenyl)ethyl)malonate (7i). This known compound was obtained as a colorless oil, 82%. NMR ($CDCl_3$, δ/ppm): ^{1}H (500 MHz) 7.32 (ddd, $^3J_{HH}$ = 8.1, 7.2 Hz, $^4J_{HH}$ = 1.8 Hz, 1H), 7.26 (dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.8 Hz, 1H), 7.23-7.18 (m, 1H),

7.14 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.2 Hz, 1H), 5.00-4.82 (m, 2H), 4.49 (td, $^3J_{HH}$ = 8.1, 5.3 Hz, 1H), 3.92 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 3.74 (s, 3H), 3.59 (s, 3H), 2.39 (s, 3H). The enantiomeric excess was determined by HPLC with a Chiralcel OD column (90:10 v/v hexane/isopropanol, 1 mL/min, λ = 210 nm); t_R = 17.3 min (minor), 24.5 min (major), 91%ee.[s1]

Dimethyl 2-(2-nitro-1-(2-benzoyloxyphenyl)ethyl)malonate (7j). This known compound was obtained as a colorless oil, 99%. NMR ($CDCl_3$, δ/ppm): ^{1}H (500 MHz) 8.36-8.22 (m, 2H), 7.75-7.63 (m, 1H), 7.60-7.53 (m, 2H), 7.42-7.31 (m, 2H), 7.29-7.21 (m, 2H), 4.98 (dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 8.6 Hz, 1H), 4.91 (dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 4.9 Hz, 1H), 4.59 (td, $^3J_{HH}$ = 8.5, 4.9 Hz, 1H), 3.96 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 3.72 (s, 3H), 3.52 (s, 3H). The enantiomeric excess was determined by HPLC with a Chiralcel AD column (90:10 v/v hexane/isopropanol, 1 mL/min, λ = 220 nm); t_R = 16.1 min (major), 25.7 min (minor), 91% ee.[s1]

Dimethyl 2-(2-nitro-1-(2-benzyloxyphenyl)ethyl)malonate (7k). This known compound was obtained as a colorless oil, 95%. NMR ($CDCl_3$, δ/ppm): ^{1}H (500 MHz) 7.53-7.46 (m, 2H), 7.45-7.40 (m, 2H), 7.39-7.34 (m, 1H), 7.24 (ddd, $^3J_{HH}$ = 8.3, 7.4 Hz, $^4J_{HH}$ = 1.7 Hz, 1H), 7.17 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.7 Hz, 1H), 6.93 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.0 Hz, 1H), 6.90 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.1 Hz, 1H), 5.14 (d, $^2J_{HH}$ = 11.8 Hz, 1H), 5.11 (d, $^2J_{HH}$ = 11.8 Hz, 1H) 5.05 (dd, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 9.4 Hz, 1H), 4.84 (dd, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 4.6 Hz, 1H), 4.44 (td, $^3J_{HH}$ = 9.6, 4.5 Hz, 1H), 4.17 (d, $^3J_{HH}$ = 9.9 Hz, 1H), 3.72 (s, 3H), 3.50 (s, 3H). The enantiomeric excess was determined by HPLC with a Chiralcel OD column (90:10 v/v hexane/ isopropanol, 1 mL/min, λ = 220 nm); t_R = 10.8 min (minor), 17.9 min (major), 91% ee.[s1]

Dimethyl 2-(2-nitro-1-(2-bromophenyl(ethyl)malonate (7l). This known compound was obtained as a colorless oil, 99%. NMR ($CDCl_3$, δ/ppm): ^{1}H (500 MHz) 7.61 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.0 Hz, 1H), 7.33-7.20 (m, 2H), 7.16 (td, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.8 Hz, 1H), 5.13 (dd, $^2J_{HH}$ = 13.7 Hz, $^3J_{HH}$ = 8.5 Hz, 1H), 4.96 (dd, $^2J_{HH}$ = 13.7 Hz, $^3J_{HH}$ = 4.5 Hz, 1H), 4.77 (td, $^3J_{HH}$ = 8.2, 4.5 Hz, 1H), 4.11 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 3.73 (s, 3H), 3.66 (s, 3H). The enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (70:30 v/v hexane/isopropanol, 1 mL/min, λ = 220 nm); t_R = 8.3 min (minor), 14.1 min (minor), 87% ee.[s10]

Dimethyl 2-(2-nitro-1-(2-methylphenyl)ethyl)malonate (7m). This known compound was obtained as a colorless oil, 74%. NMR ($CDCl_3$, δ/ppm): ^1H (500 MHz) 7.20-7.08 (m, 4H), 4.90 (dd, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 5.2 Hz, 1H), 4.85 (dd, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 8.8 Hz, 1H), 4.57 (td, $^3J_{HH}$ = 9.0, 5.2 Hz, 1H), 3.83 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 3.76 (s, 3H), 3.54 (s, 3H), 2.44 (s, 3H). The enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (75:25 v/v hexane/isopropanol, 1 mL/min, λ = 210 nm); t_R = 9.8 min (major), 19.1 min (minor), 82% ee.[s11]

Dimethyl 2-(2-nitro-1-furylethyl)malonate (7n). This known compound was obtained as a colorless oil, 87%. NMR ($CDCl_3$, δ/ppm): ^1H (500 MHz) 7.34 (dd, $^3J_{HH}$ = 1.9 Hz, $^4J_{HH}$ = 0.8 Hz, 1H), 6.29 (dd, $^3J_{HH}$ = 3.3, 1.9 Hz, 1H), 6.22 (dt, $^3J_{HH}$ = 3.3 Hz, $^4J_{HH}$ = 0.7 Hz, 1H), 4.98-4.84 (m, 2H), 4.38 (td, $^3J_{HH}$ = 8.2, 5.2 Hz, 1H), 3.94 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 3.76 (s, 3H), 3.69 (s, 3H). The enantiomeric excess was determined by HPLC with a Chiralcel OD column (90:10 v/v hexane/isopropanol, 1 mL/min, λ = 220 nm); t_R = 10.7 min (minor), 21.4 min (major), 84% ee.[s1]

(*E*)-Dimethyl 2-(1-nitro-4-phenylbut-3-en-2-yl)malonate (7o). This known compound was obtained as a colorless oil, 14%. The ^1H NMR spectrum matches those reported earlier.[s9] NMR ($CDCl_3$, δ/ppm): ^1H (500 MHz) 7.35-7.28 (m, 5H), 6.58 (d, $^3J_{HH}$ = 15.7 Hz, 1H), 6.10 (dd, $^3J_{HH}$ = 15.8, 9.0 Hz, 1H), 4.83-4.62 (m, 2H), 3.77 (s, 3H), 3.73 (s, 3H), 3.73-3.71 (m, 2H). The enantiomeric excess was determined by HPLC with a Chiralcel IC column (99:1 v/v hexane/isopropanol, 1 mL/min, λ = 210 nm); t_R = 46.2 min (minor), 55.4 min (major), 73% ee.[s9]

Di-*t*-butyl azodicarboxylate addition products accessed by the general procedure for Chart 5

***N,N*-Bis(t-butoxycarbonyl)-1-hydrazino-2-oxocyclopentanecarboxylic acid methyl ester (10a).** This known compound was obtained as a colorless oil, 99%. NMR ($CDCl_3$, δ/ppm): ^1H (500 MHz) 6.70-6.03 (m, 1H), 3.76 (s, 3H), 2.97-2.03 (m, 5 H), 2.03-1.81 (s, 1H), 1.53-1.29 (m, 18H). The enantiomeric excess was determined by HPLC with a Chiralcel AD column (96:4 v/v hexane/isopropanol, 1 mL/min, λ = 210 nm); t_R = 13.6 min (major), 20.0 min (minor), 82% ee.[s12]

***N,N*-Bis(t-butoxycarbonyl)-1-hydrazino-2-oxocyclopentanecarboxylic acid ethyl ester (10b).** This known compound was obtained as a colorless oil, 91%. NMR ($CDCl_3$, δ/ppm): ^1H (500 MHz) 6.69-6.02 (m, 1H), 4.34-4.11 (m, 2H), 2.92-2.04 (m, 5H), 2.05-1.82 (m, 1H), 1.54-1.35 (m, 18H), 1.34-1.22 (m, 3H). The enantiomeric excess was determined by HPLC with a Chiralcel AD column (96:4 v/v hexane/isopropanol, 1 mL/min, λ = 210 nm); t_R = 10.6 min (major), 15.8 min (minor), 81% ee.[s12]

***N,N*-Bis(t-butoxycarbonyl)-1-acetyl-1-hydrazino-2-oxocyclopentane (10c).** This known compound was obtained as a colorless oil, 99%. NMR ($CDCl_3$, δ/ppm): ^1H (500 MHz) 6.55-5.99 (m, 1H), 2.93-1.58 (m, 9H), 1.52-1.36 (m, 18H). The enantiomeric excess was determined by HPLC with a Chiralcel AS-H column (90:10 v/v hexane/isopropanol, 1 mL/min, λ = 210 nm); t_R = 5.8 min (major), 11.0 min (minor), 81% ee.[s13]

***N,N*-Bis(t-butoxycarbonyl)-2-hydrazino-2-methyl-3-oxobutyric acid ethyl ester (10d).** This known compound was obtained as a colorless oil, 95%. NMR ($CDCl_3$, δ/ppm): ^1H (500 MHz) 6.44-5.84 (m, 1H), 4.35-4.08 (m, 2H), 3.76 (s, 3H), 2.47-2.17 (m, 3 H), 1.65-1.56 (m, 3H), 1.55-1.36 (m, 18H), 1.29 (t, $^3J_{HH}$ = 7.2 Hz, 3H). The enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (95:5 v/v hexane/isopropanol, 1 mL/min, λ = 210 nm); t_R = 14.0 min (minor), 19.4 min (major), 79% ee.[s12]

***N,N*-Bis(t-butoxycarbonyl)-1-acetyl-1-hydrazino-2-oxocyclohexane (10e).** This known compound was obtained as a colorless oil, 92%. NMR ($CDCl_3$, δ/ppm): ^1H (500 MHz) 6.30-5.66 (m, 1H), 3.19-1.7 (m, 2H), 1.53-1.31 (m, 18H). The enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (95:5 v/v hexane/isopropanol, 1 mL/min, λ = 210 nm); t_R = 15.6 min (minor), 41.6 min (major), 86% ee.[s12]

***N,N'*-Bis(t-butoxycarbonyl)-1-hydrazino-1,2,3,4-tetrahydro-1-oxonaphthalene-2-carboxylic acid ethyl ester (10f).** This known compound was obtained as a colorless oil, 90%. NMR ($CDCl_3$, δ/ppm): ^1H (500 MHz) 7.95-7.84 (m, 1H), 7.54-7.38 (m, 1H), 7.37-7.17 (m, 2H), 6.38-6.01 (m, 1H), 4.38-4.17 (m, 2H), 3.63-2.54 (m, 4H), 1.54-1.09 (m, 21H). The enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (80:20 v/v hexane/isopropanol,

1 mL/min, λ = 220 nm); t_R = 9.3 min (minor), 11.6 min (major), 51% ee.[s12]

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(s5) (a) For nearly all catalysts, the NHH' ^{1}H NMR signals integrated to less than the theoretical value of 6H (a determination sometimes complicated by overlapping peaks). Complexes of this type can undergo H/D exchange with appropriate NMR solvents: Ghosh, S. K.; Lewis, K. G.; Kumar, A.; Gladysz, J. A. Syntheses of Families of Enantiopure and Diastereopure Cobalt Catalysts Derived from Trications of the Formula $[Co(NH_2CHArCHArNH_2)_3]^{3+}$. *Inorg. Chem.* **2017**, 56, 2304-2320. (b) The following reference was helpful in assigning the NMR signals associated with BAr_f^-: Filippou, A. C.; Weidemann, N.; Schnakenburg, G.; Rohde, H.; Philippopoulos, A. L. Tungten-Lead Triple Bonds: Syntheses, Structures, and Coordination Chemistry of the Plumbylidyne Complexes *trans*-$[X(PMe_3)_4W{\equiv}P(2,6\text{-}Trip)_2C_6H_3)]$. *Angew. Chem. Int. Ed.* **2004**, *43*, 6512-6516 and *Angew. Chem.* **2004**, *116*, 6674-6678.

(s6) The carboxylate ^{13}C NMR signal, normally observed near 172 ppm, was not detected.

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Eutectic Mixtures: Recyclable Organocatalysts for the Enantioselective Michael Addition of 1,3-Dicarbonyl Compounds to β-Nitroalkenes. *ACS Sustainable Chem. Eng.* **2017**, *5*, 10649-10656.

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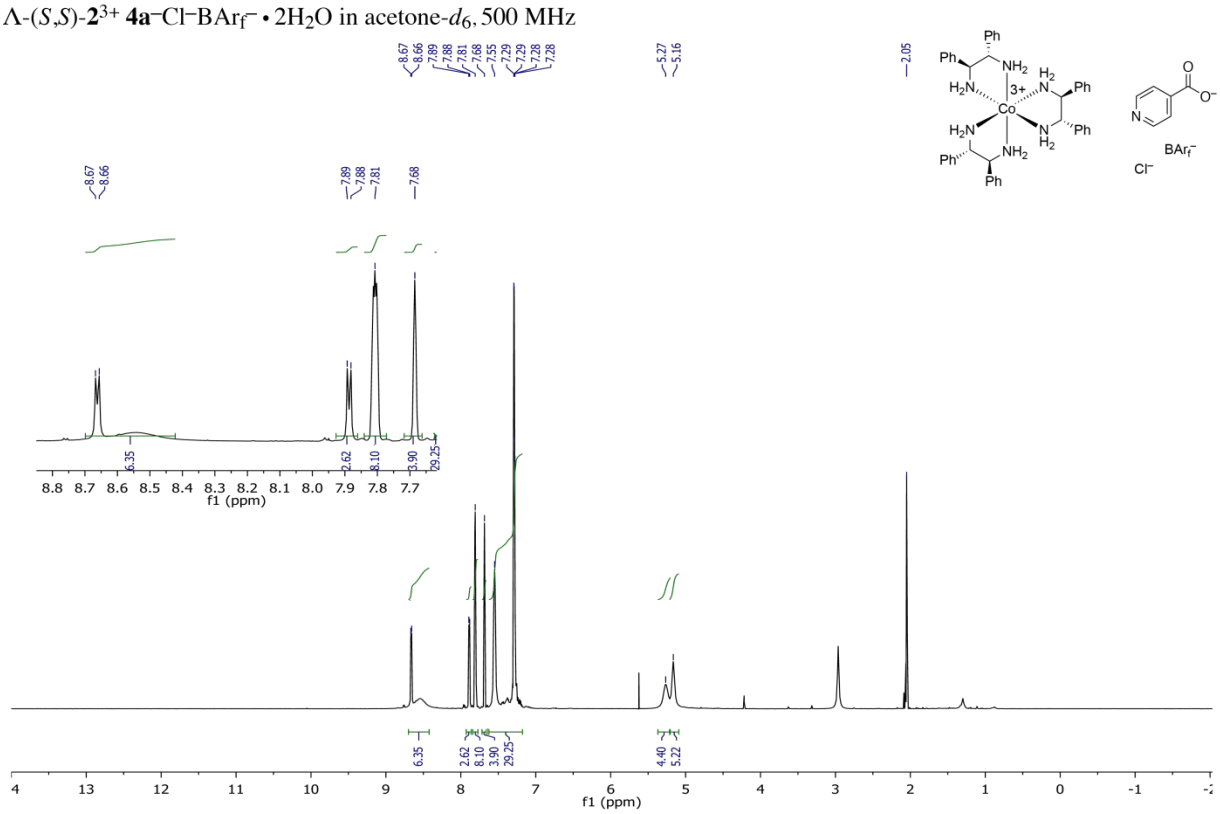
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of catalysts

Λ-(*S*,*S*)-$\mathbf{2}^{3+}$ **4a**$^{-}$Cl^{-}BAr$_f^{-}$ • 2H$_2$O in acetone-d_6, 500 MHz



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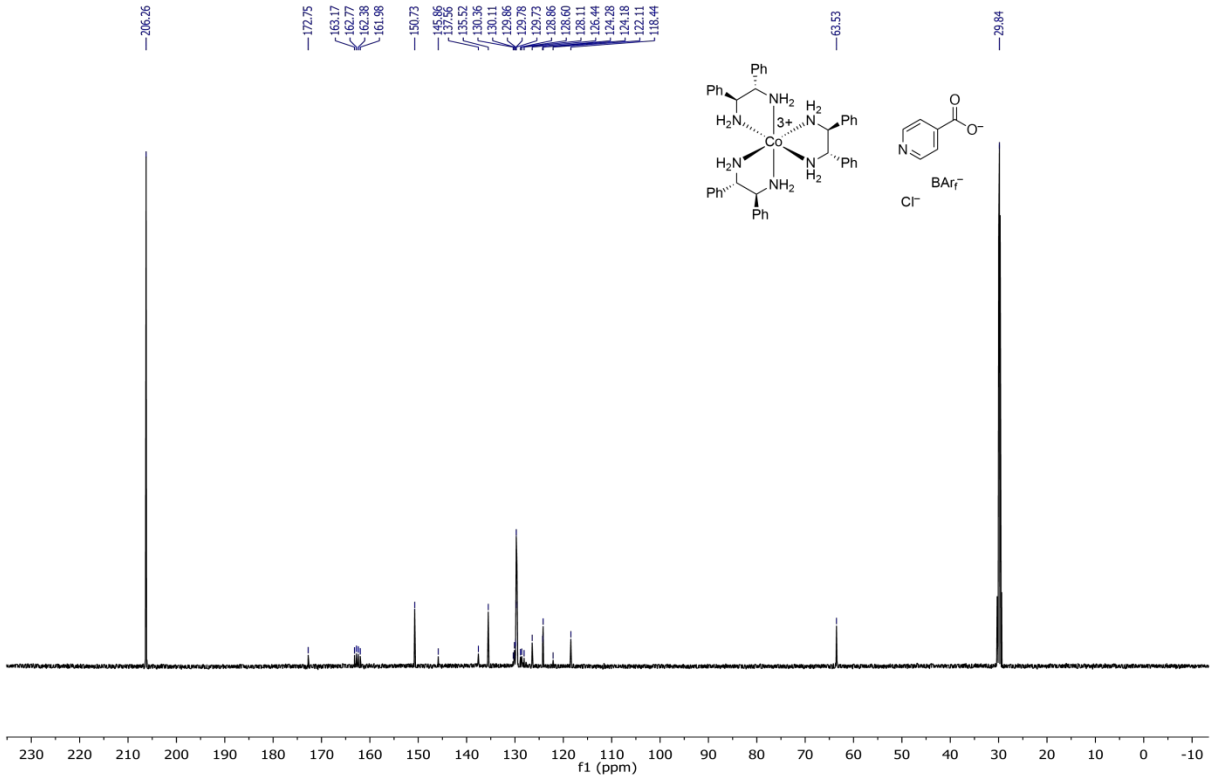

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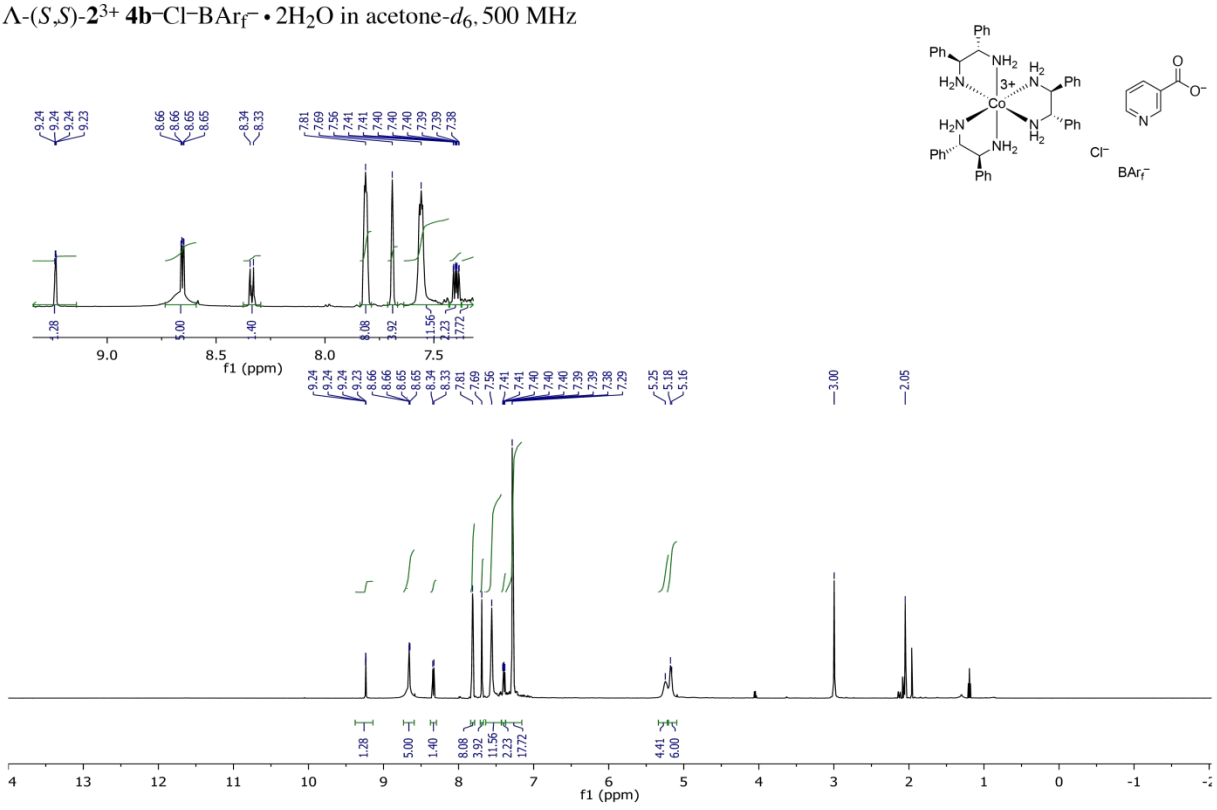

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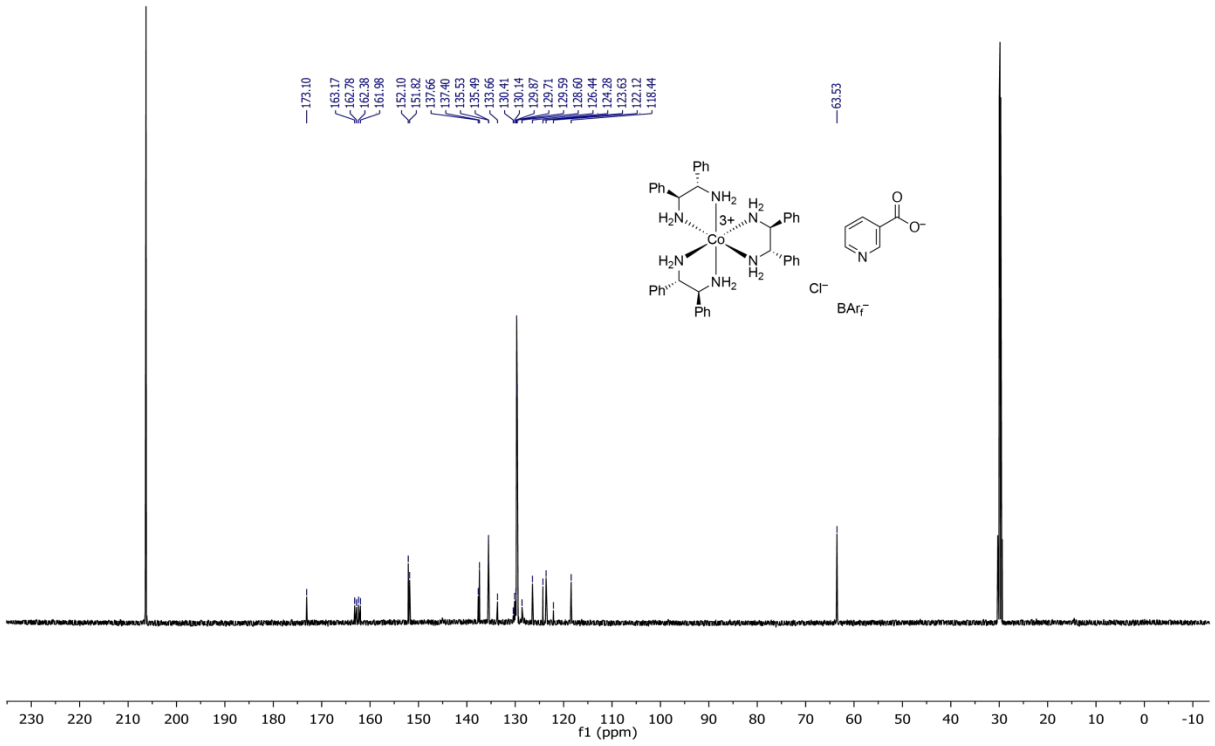

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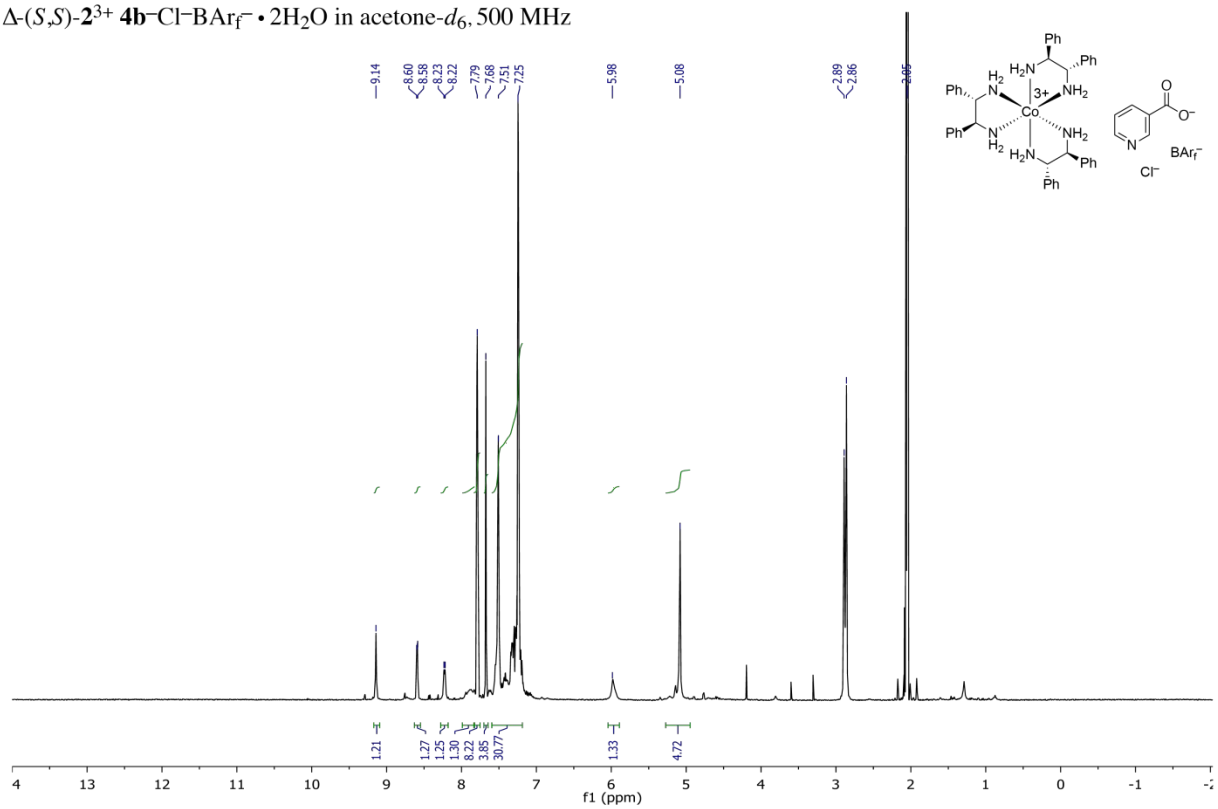

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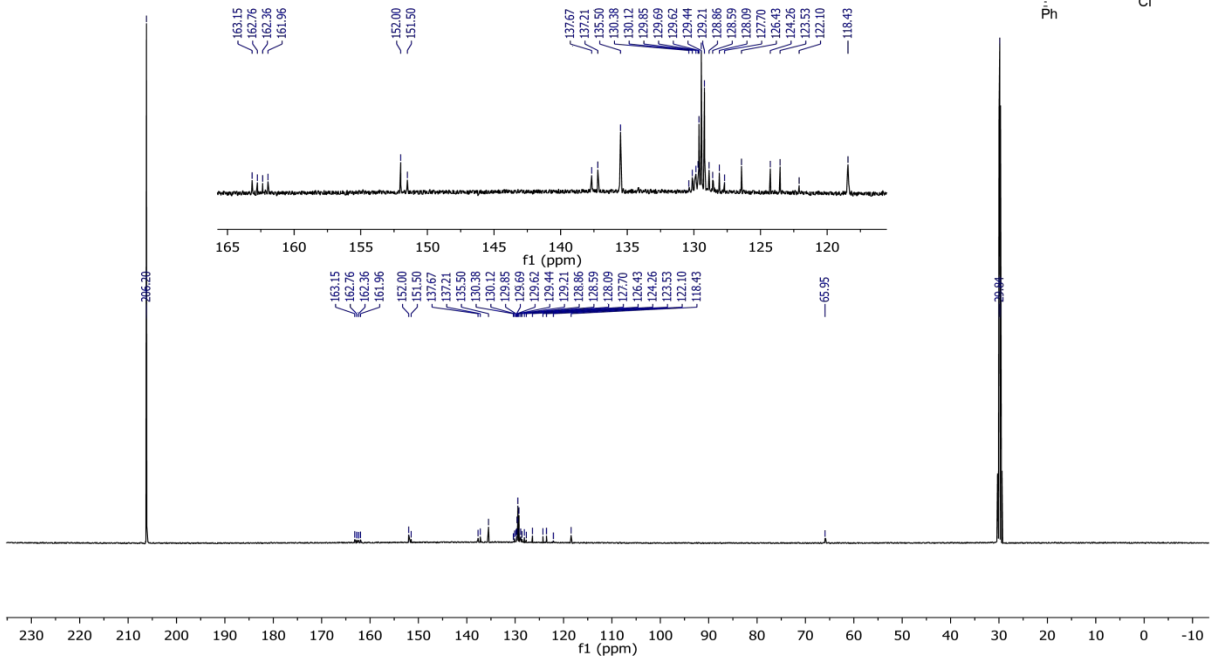

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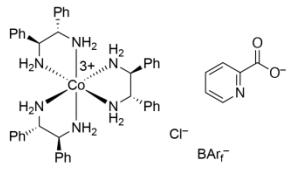

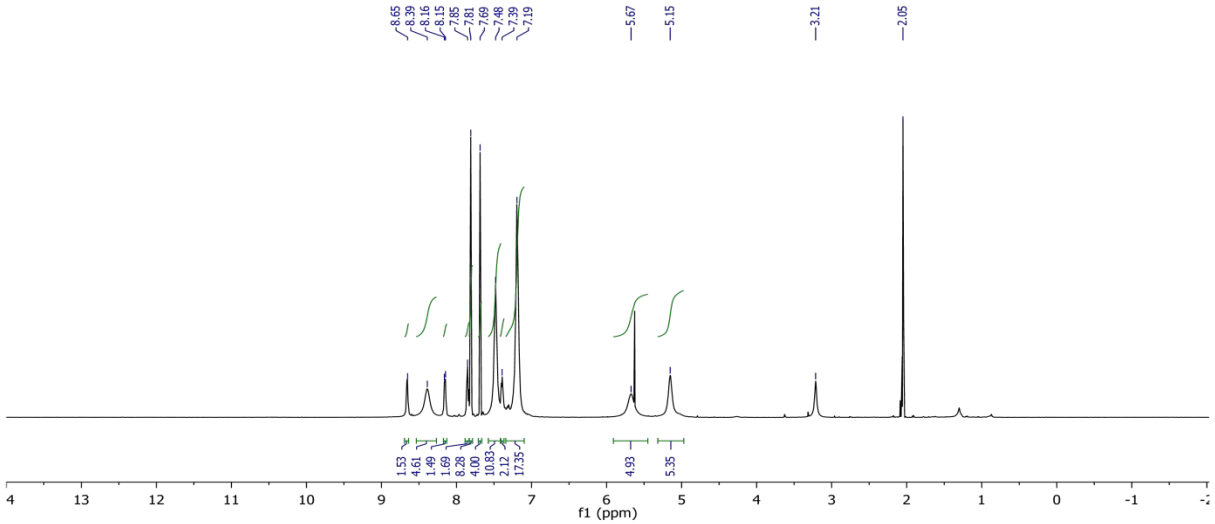

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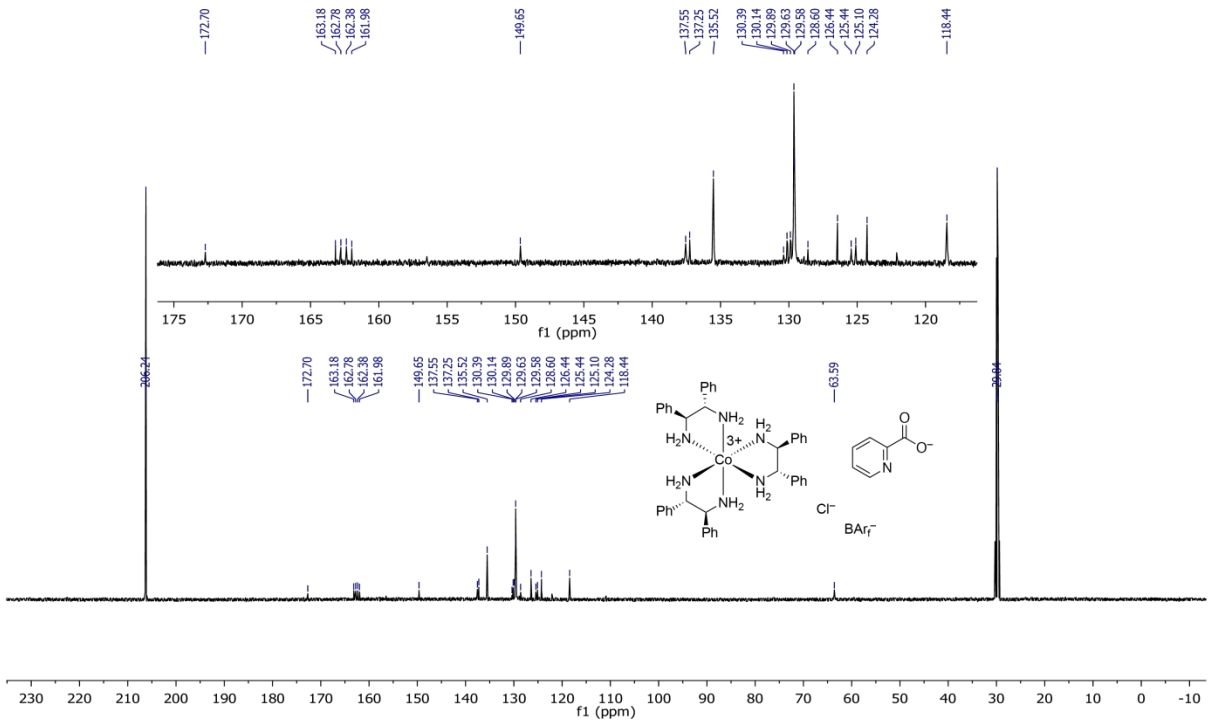

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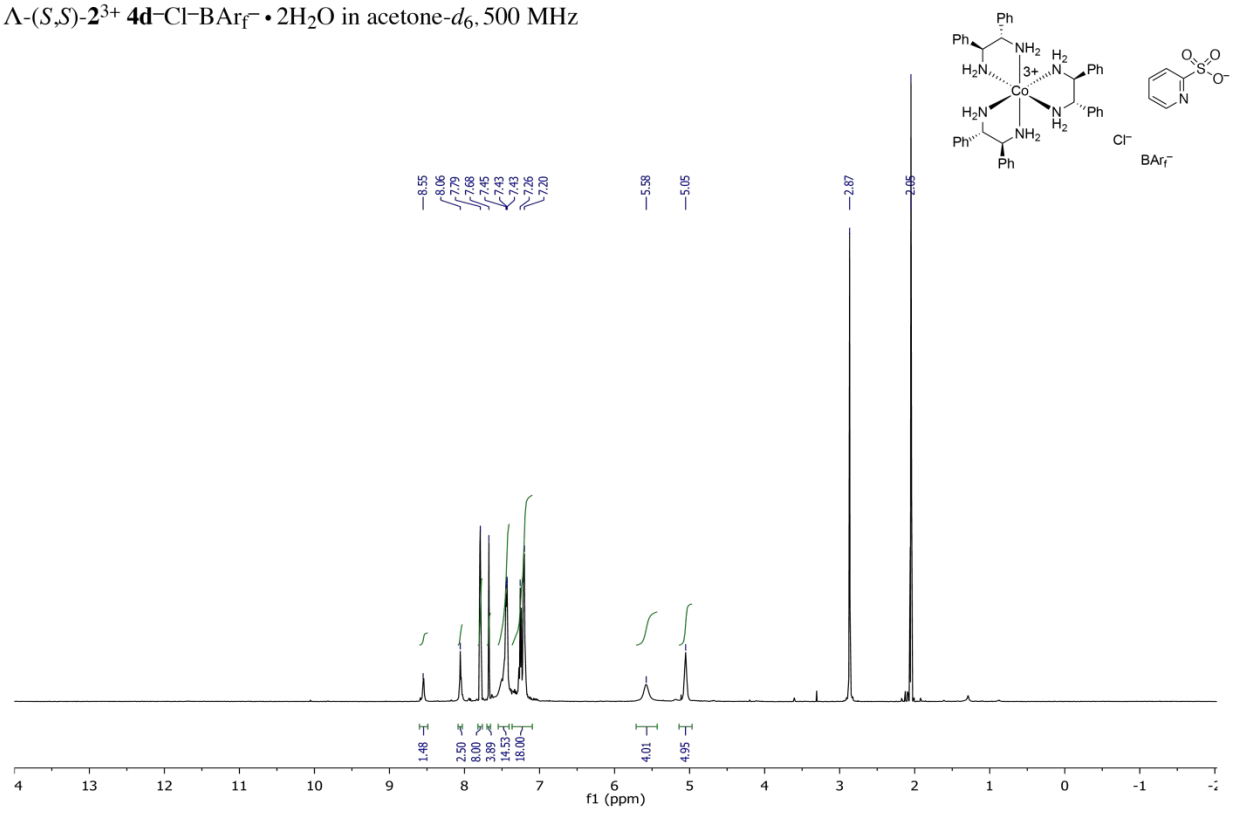

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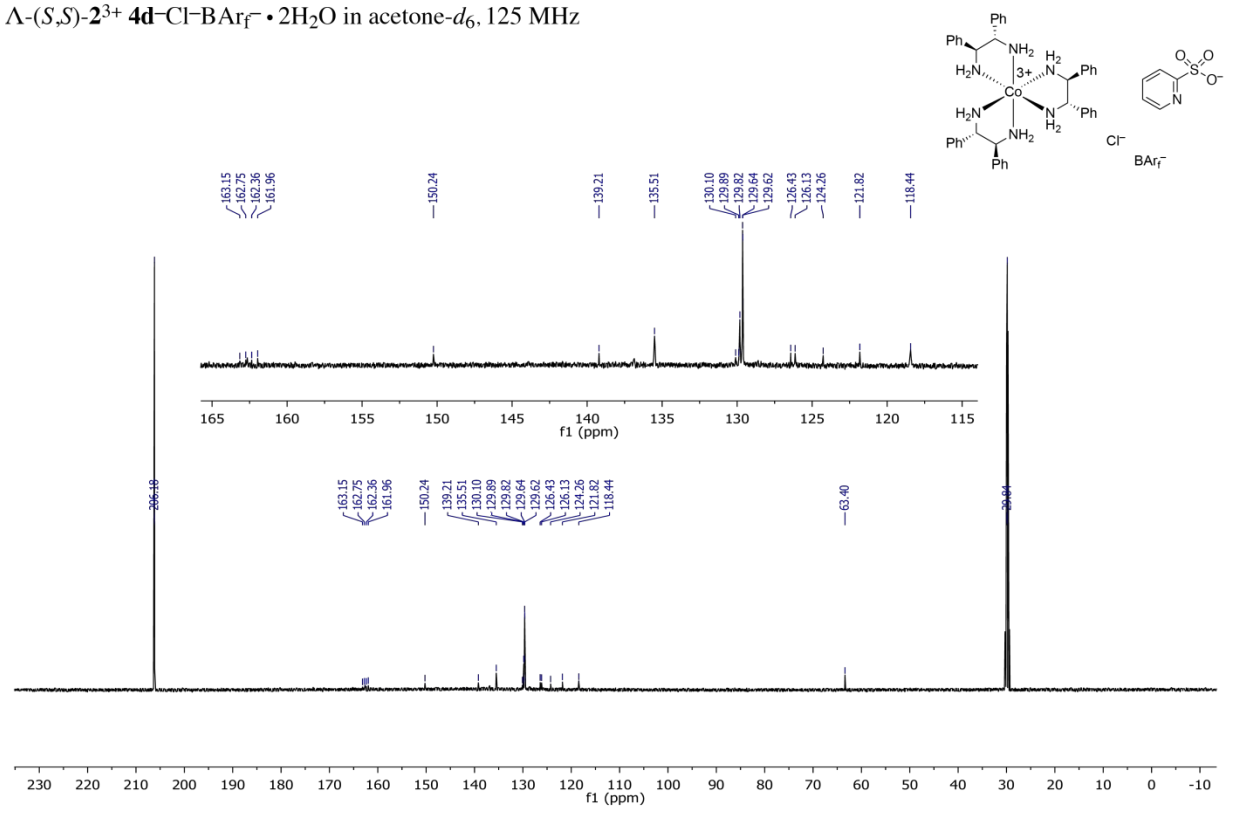

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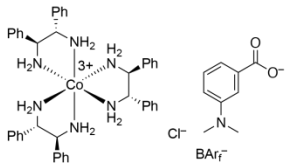

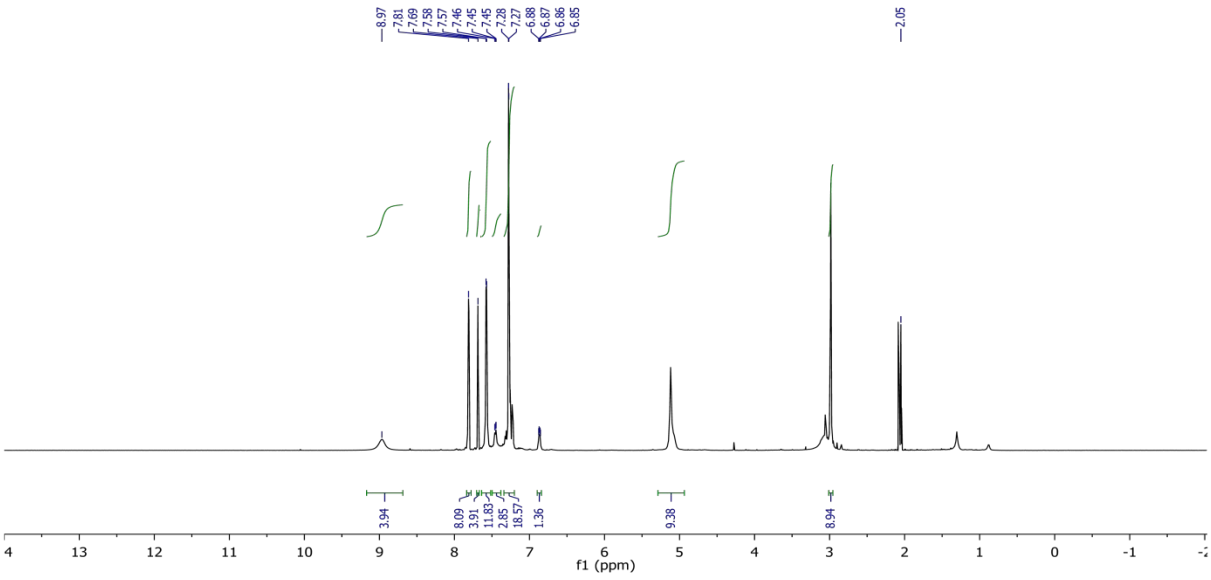

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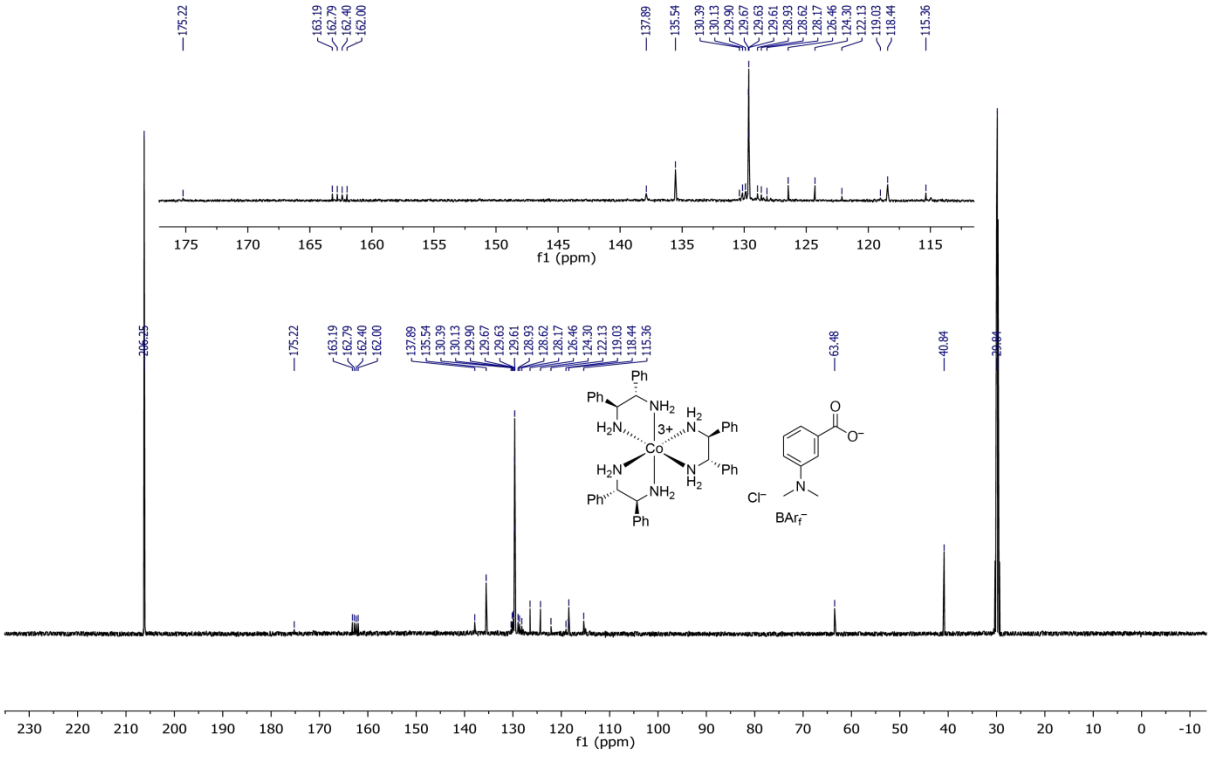

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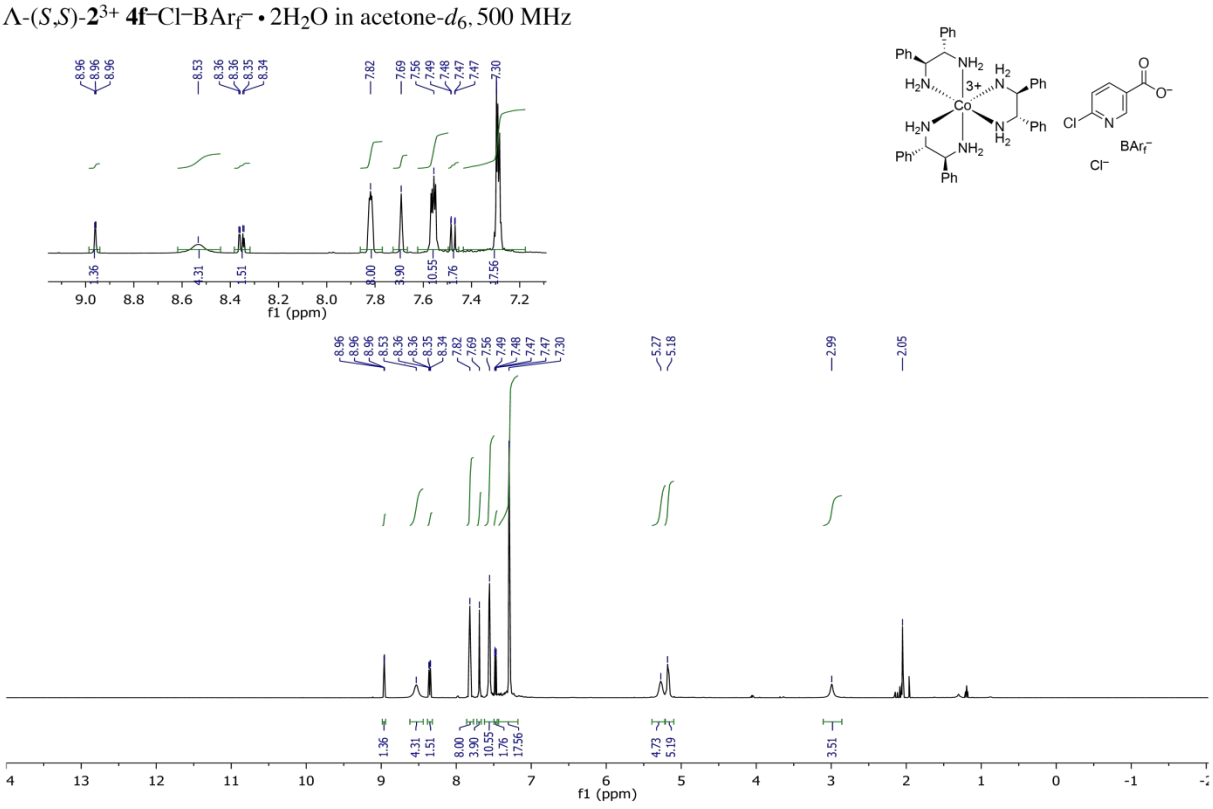

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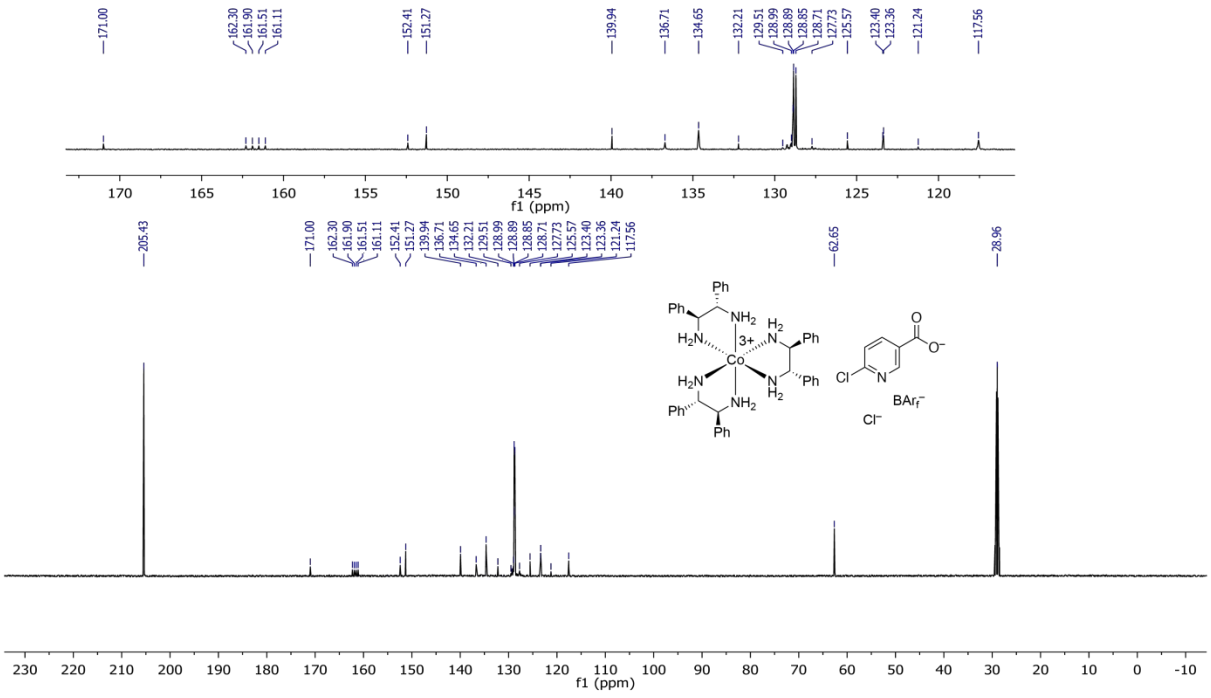

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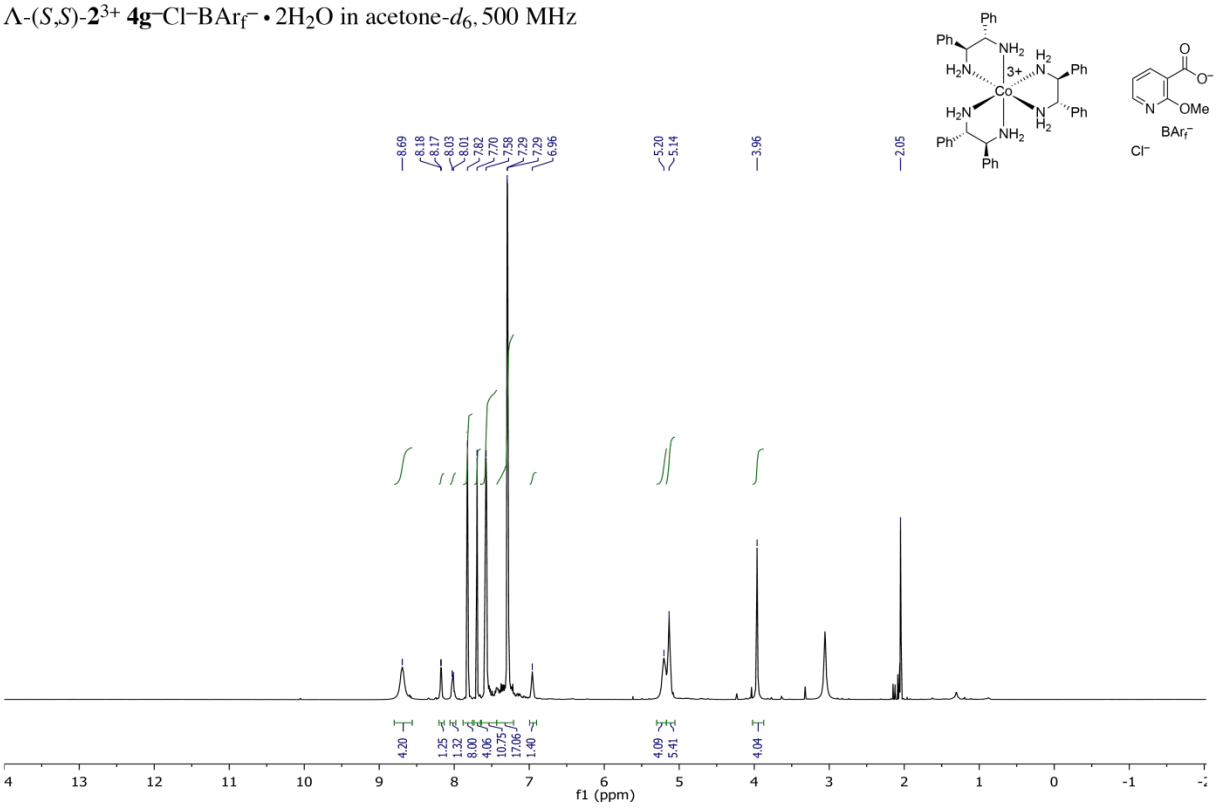

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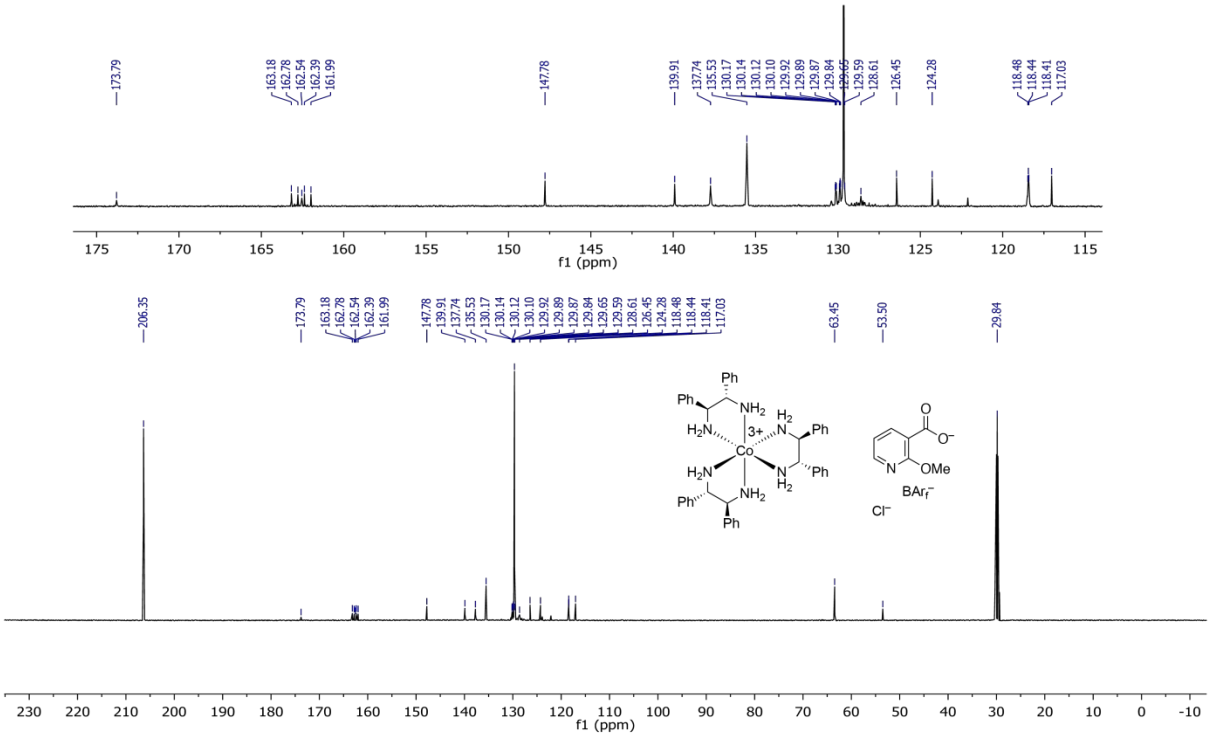

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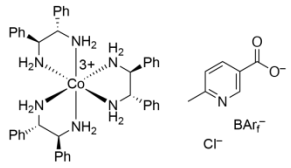

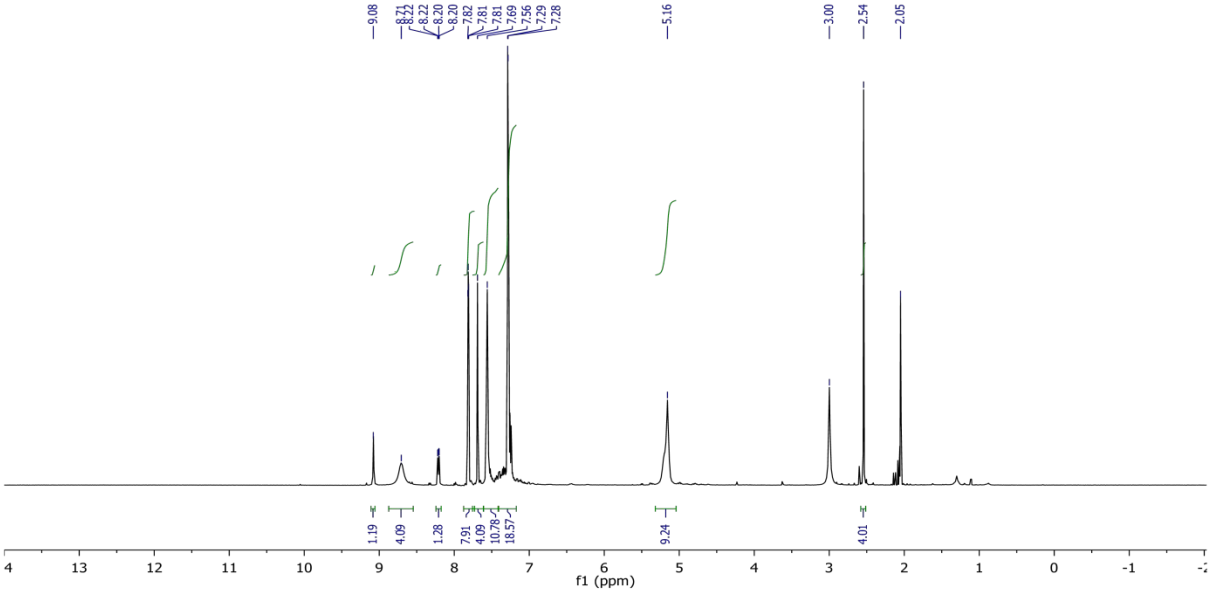

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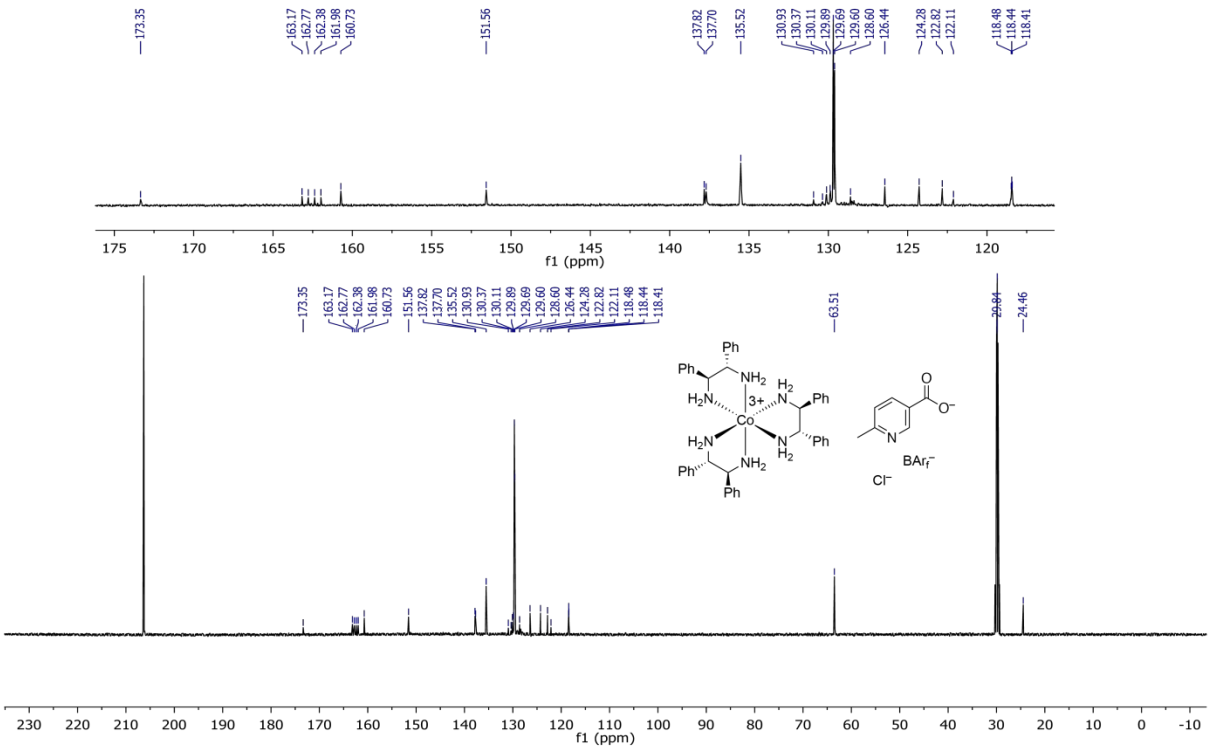

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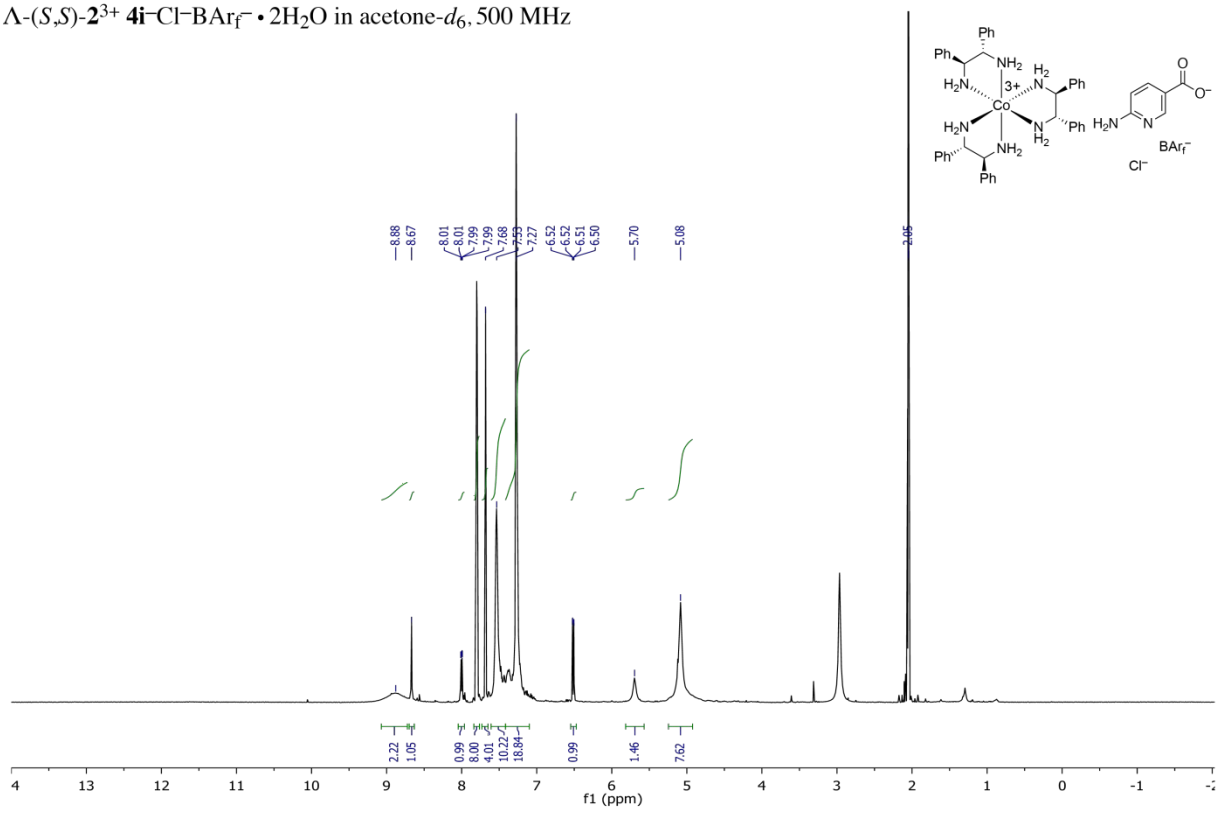

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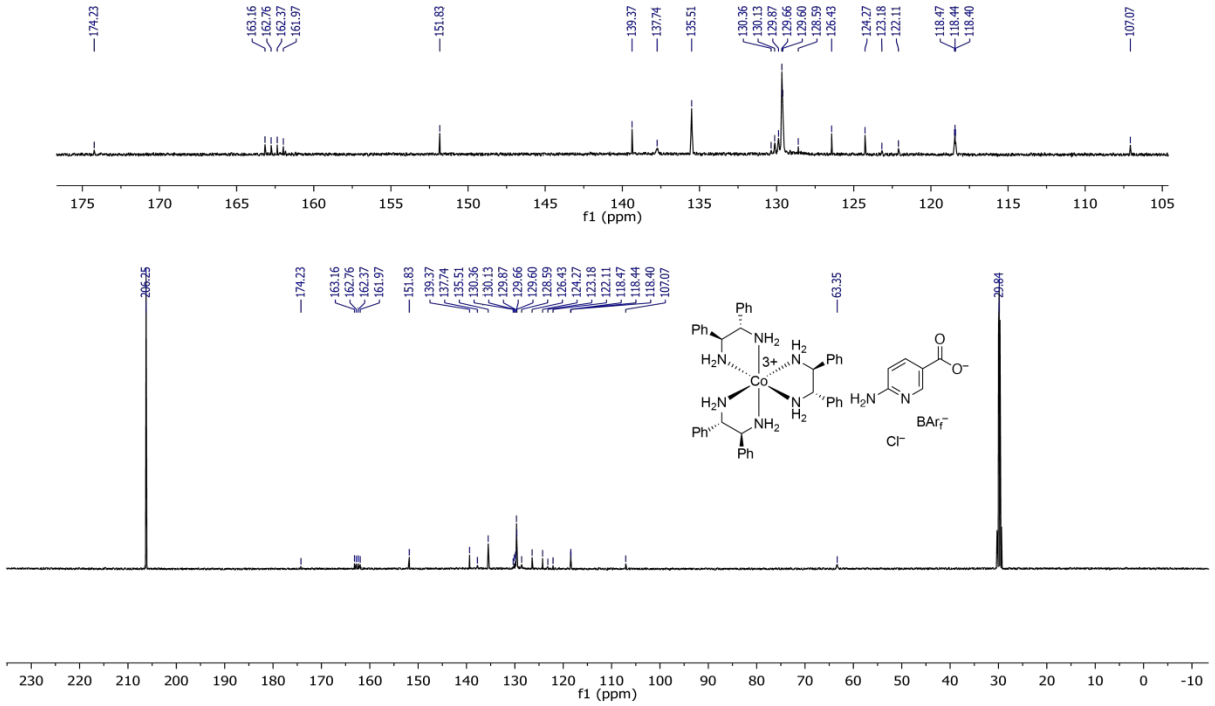

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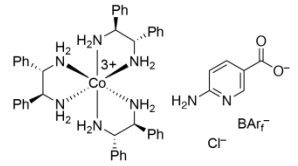

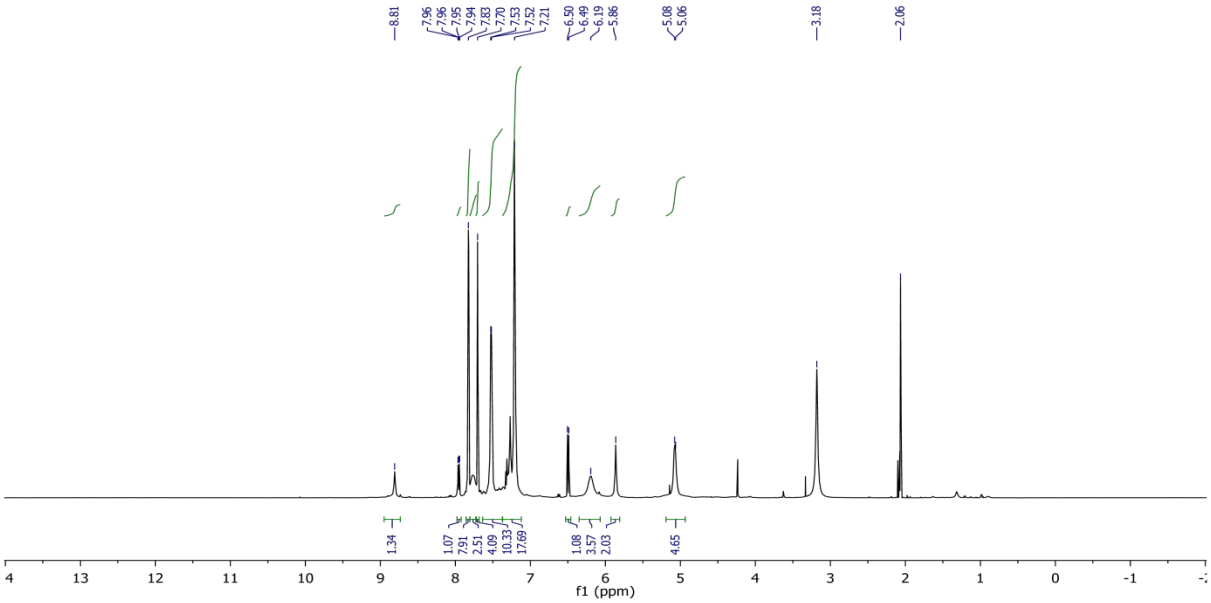

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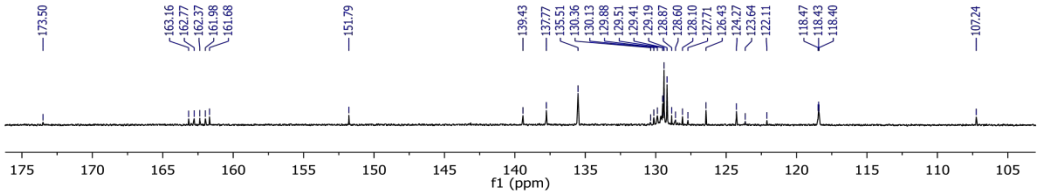
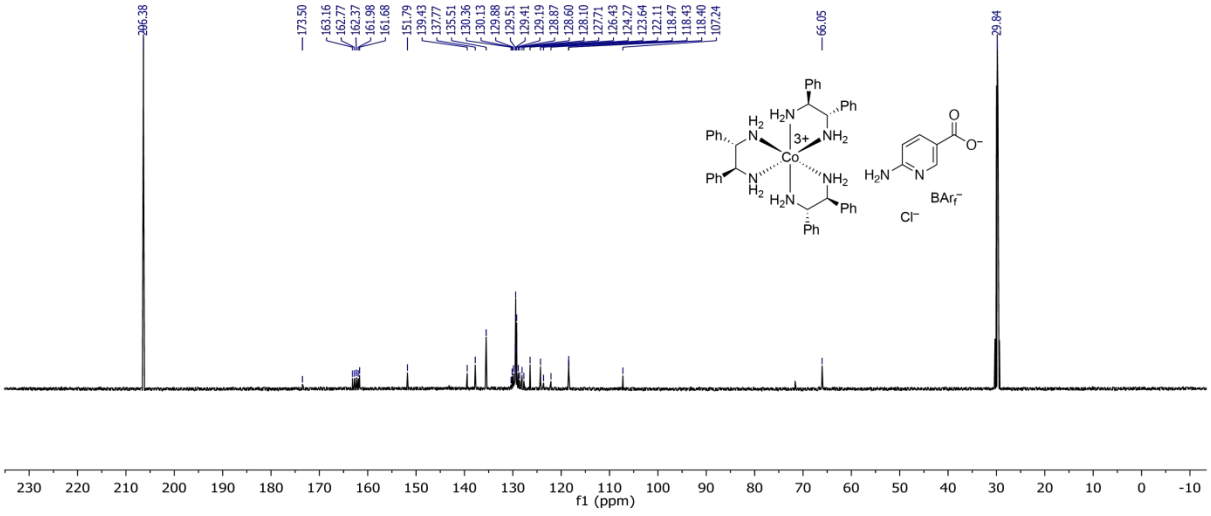
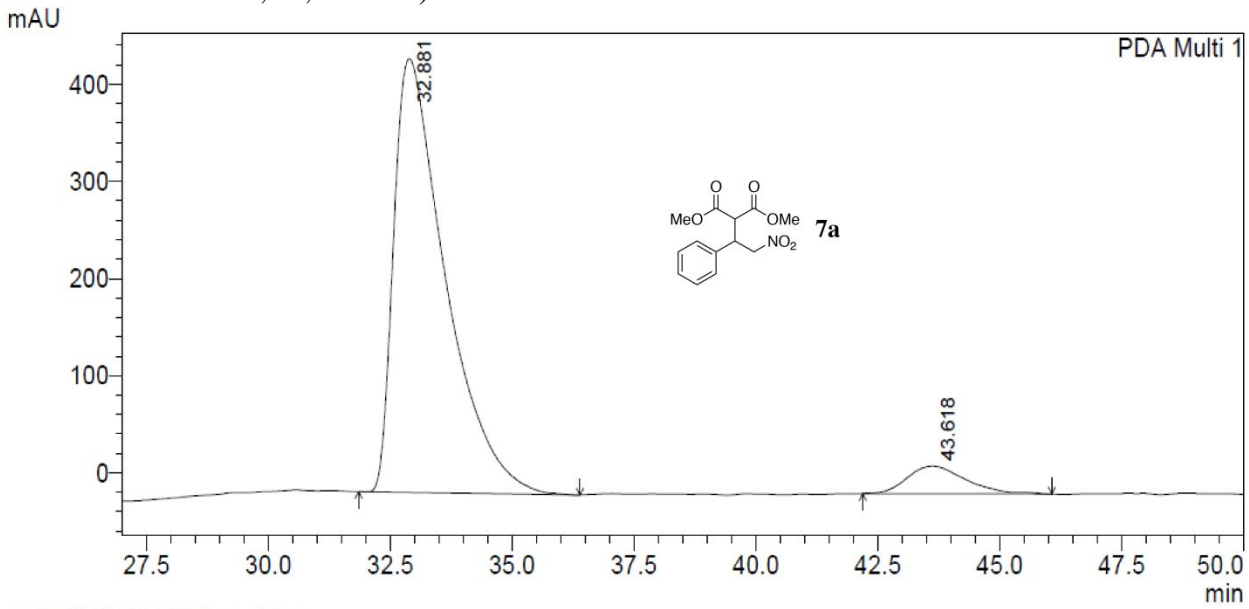




HPLC Traces (traces for racemates of nearly all of the following compounds can be found in the earlier references s1, s8, and s12).



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PDA Ch1 220nm 4nm

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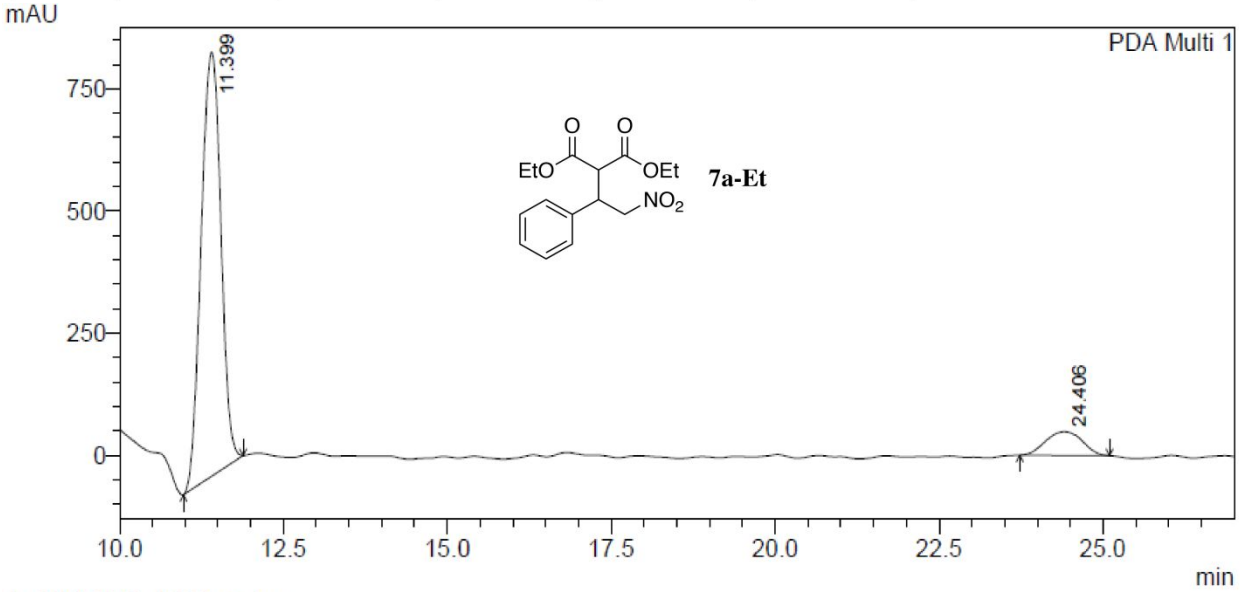

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PeakTable

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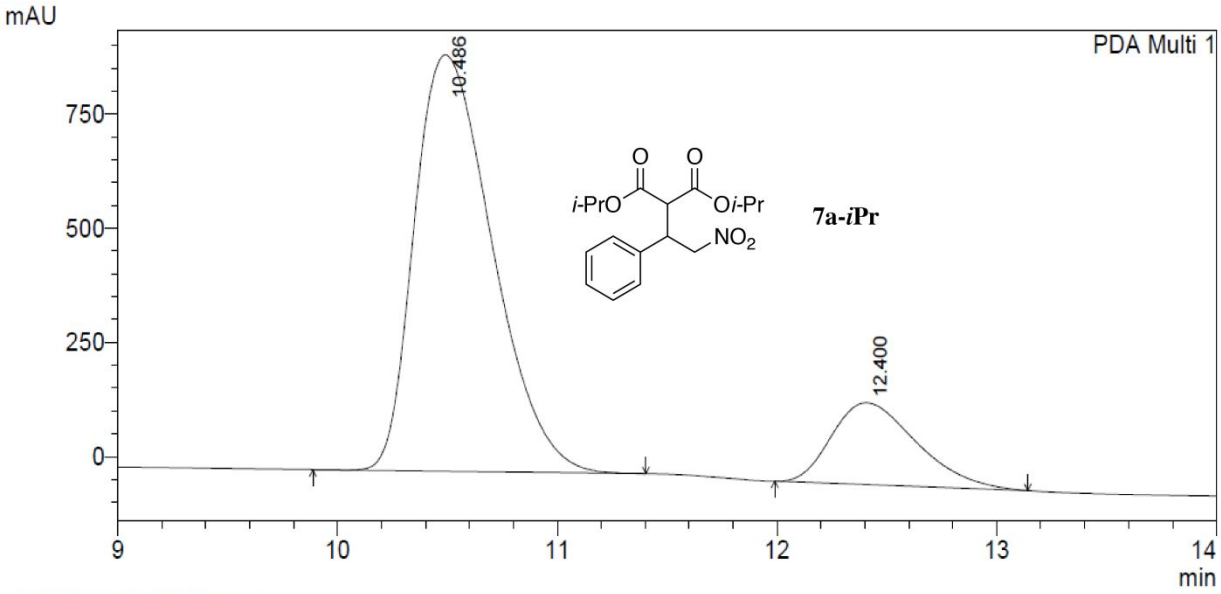

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PeakTable

PDA Ch1 220nm 4nm

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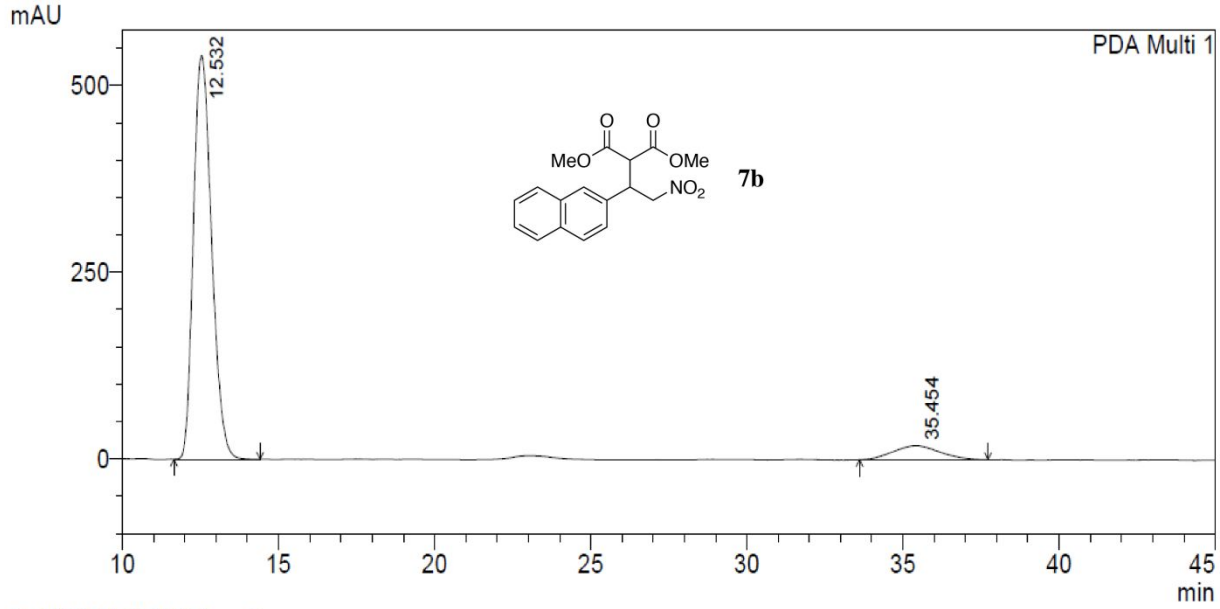

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PeakTable

PDA Ch1 254nm 4nm

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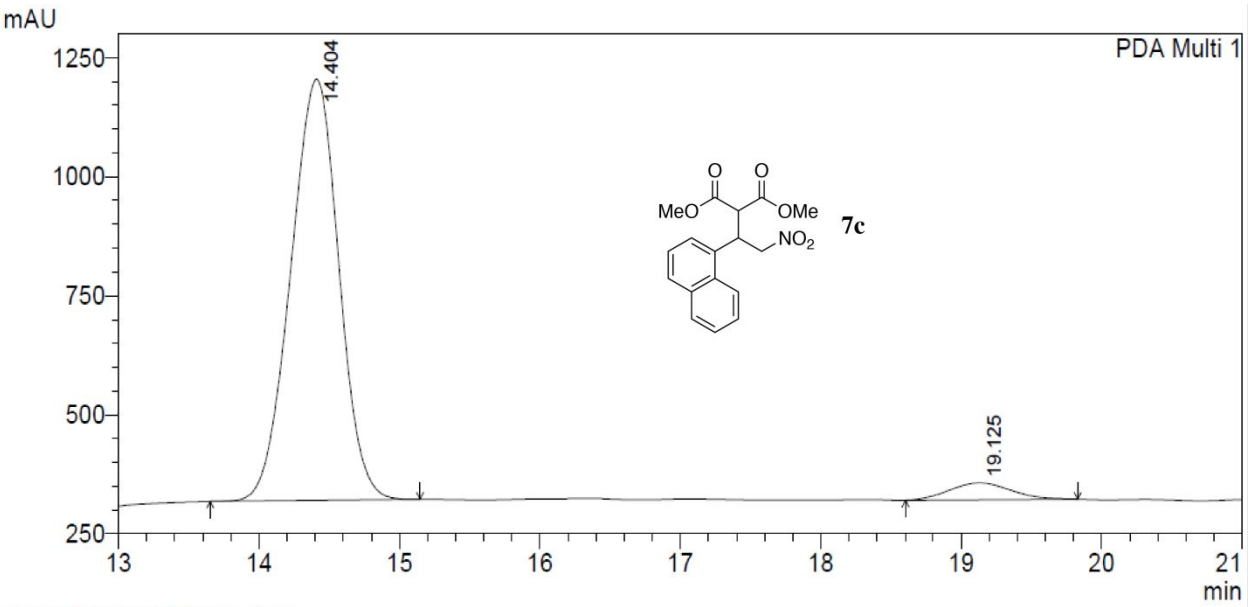

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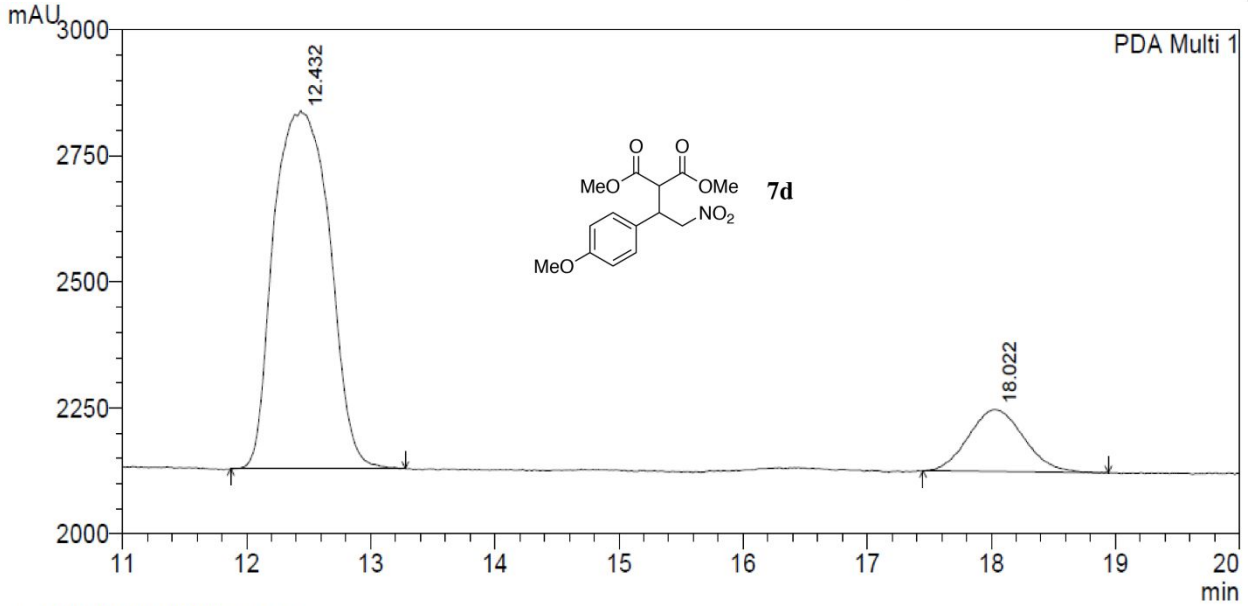
2	19.125	1069249	35341	4.823	3.842
Total		22171200	919920	100.000	100.000

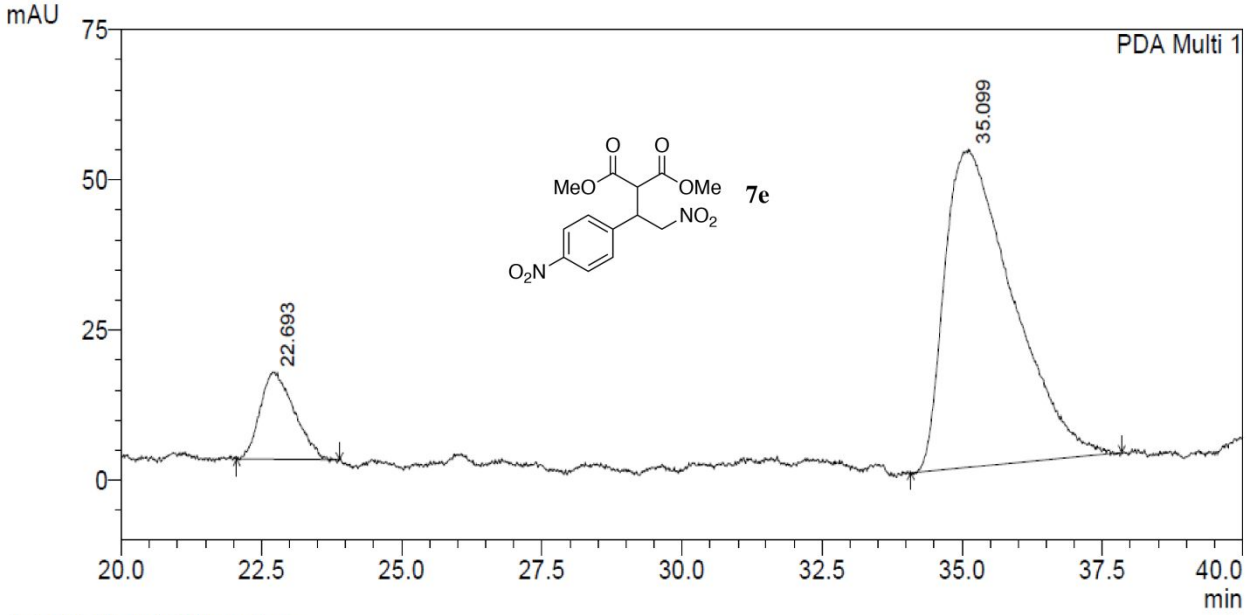


1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.432	22262060	710105	85.509	85.321
2	18.022	3772708	122166	14.491	14.679
Total		26034767	832271	100.000	100.000

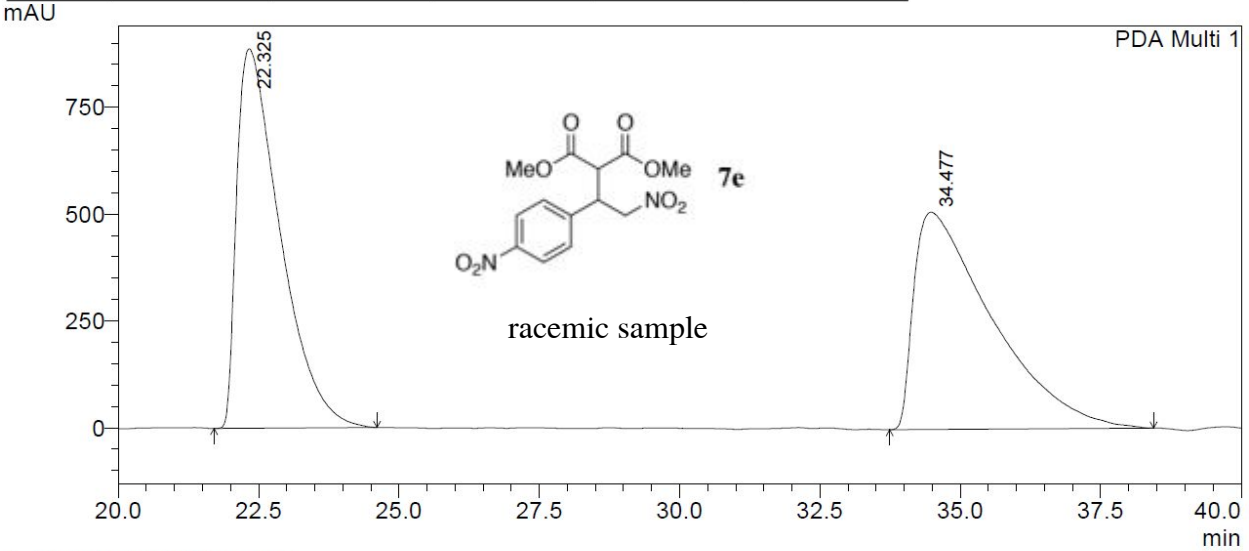


1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.693	613772	14494	12.114	21.477
2	35.099	4453059	52992	87.886	78.523
Total		5066830	67486	100.000	100.000

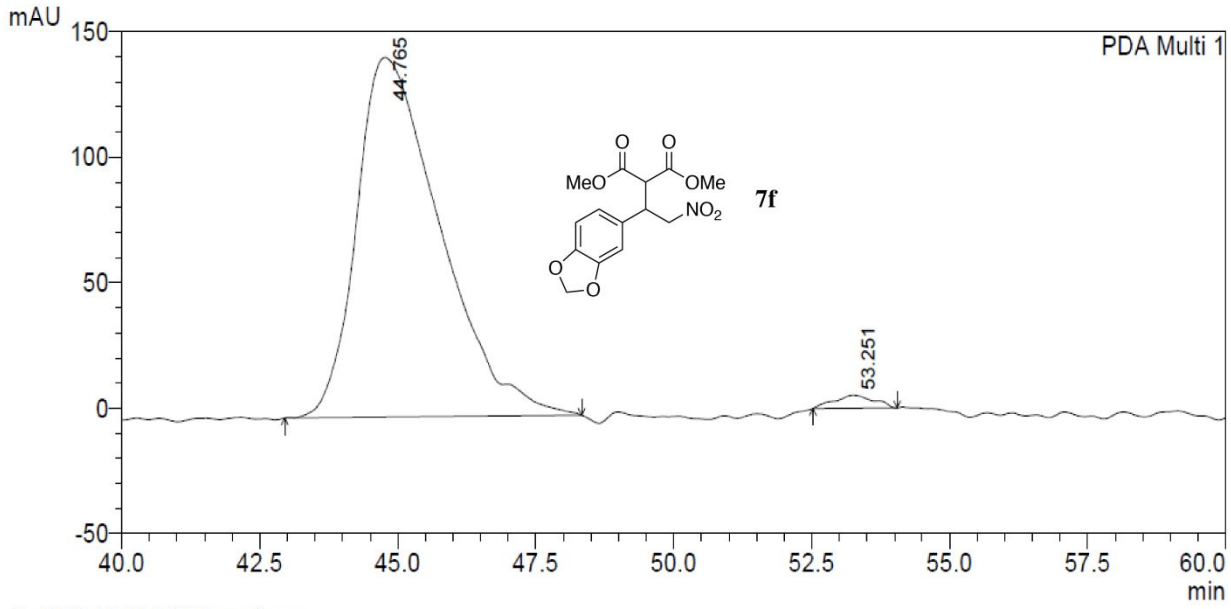


1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.325	47762796	887994	49.232	63.584
2	34.477	49253418	508575	50.768	36.416
Total		97016214	1396569	100.000	100.000

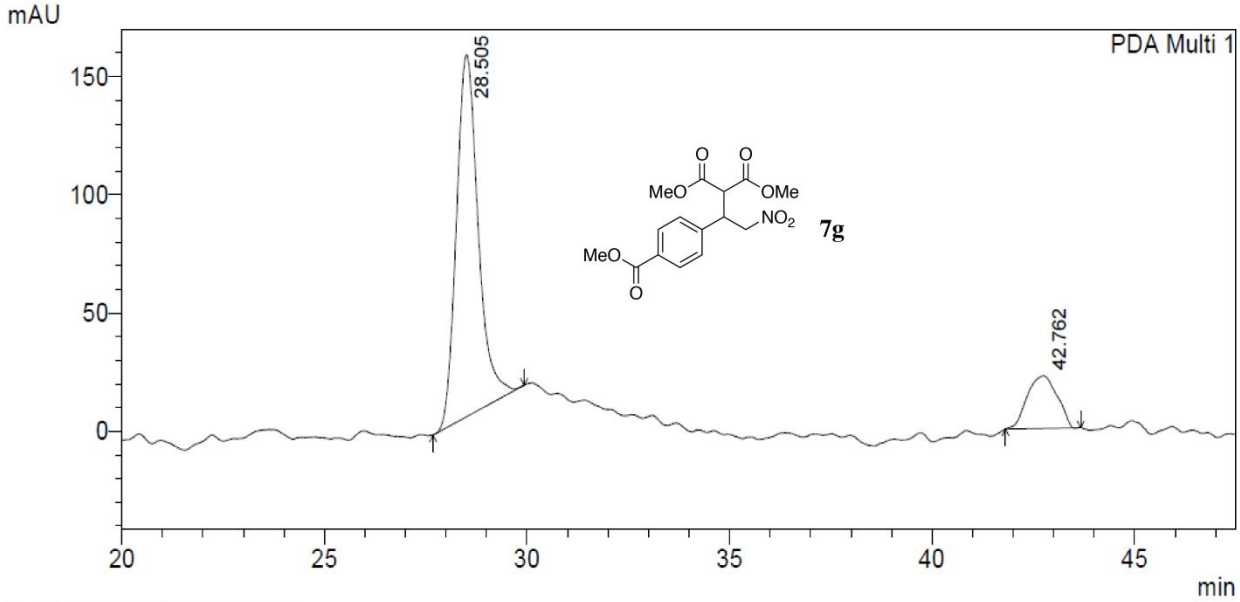


1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.765	15100824	143230	98.312	96.516
2	53.251	259286	5171	1.688	3.484
Total		15360109	148401	100.000	100.000

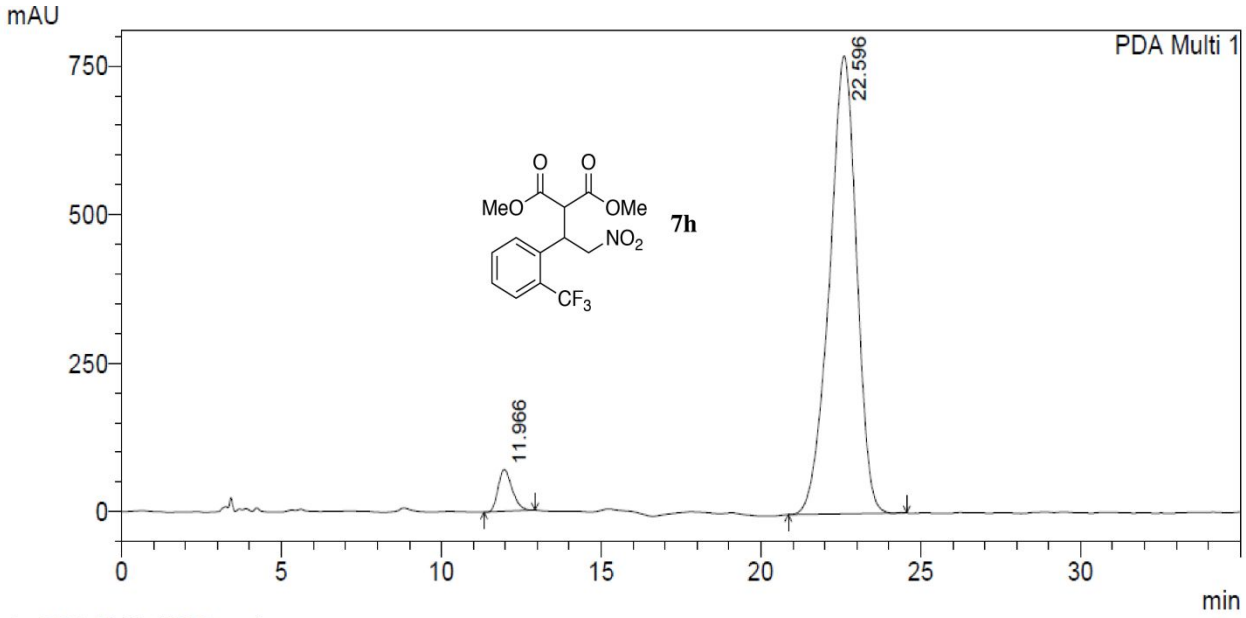


1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.505	5756305	153144	83.368	87.296
2	42.762	1148382	22286	16.632	12.704
Total		6904687	175430	100.000	100.000

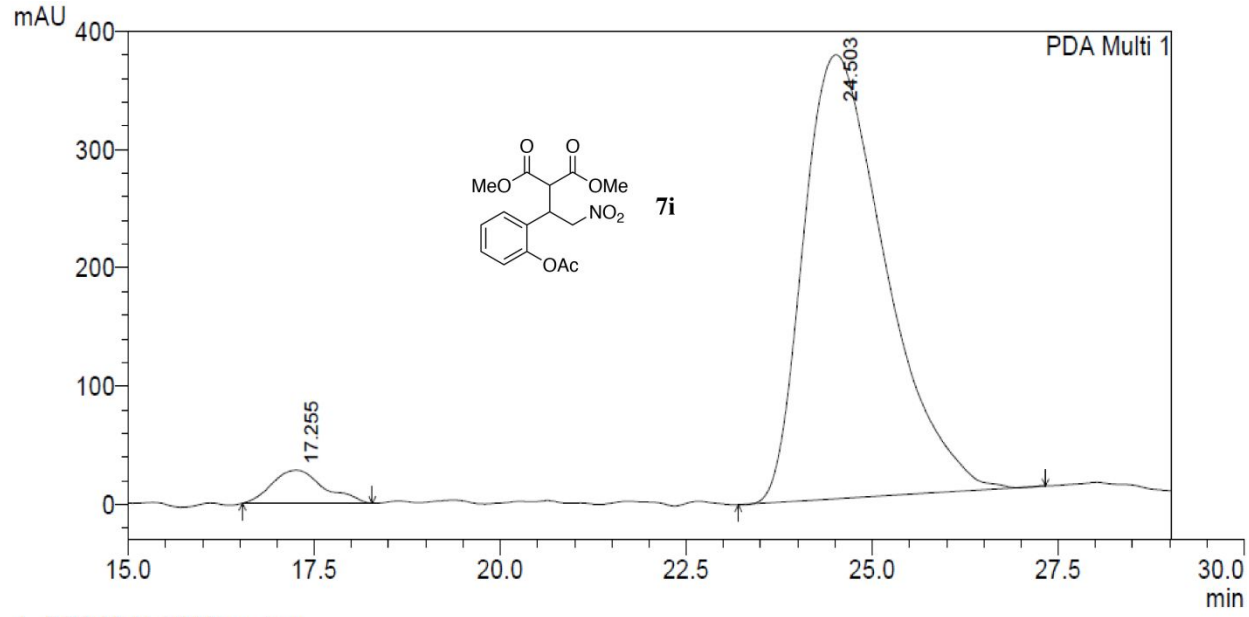


1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.966	2141166	70585	4.490	8.393
2	22.596	45542705	770372	95.510	91.607
Total		47683871	840957	100.000	100.000

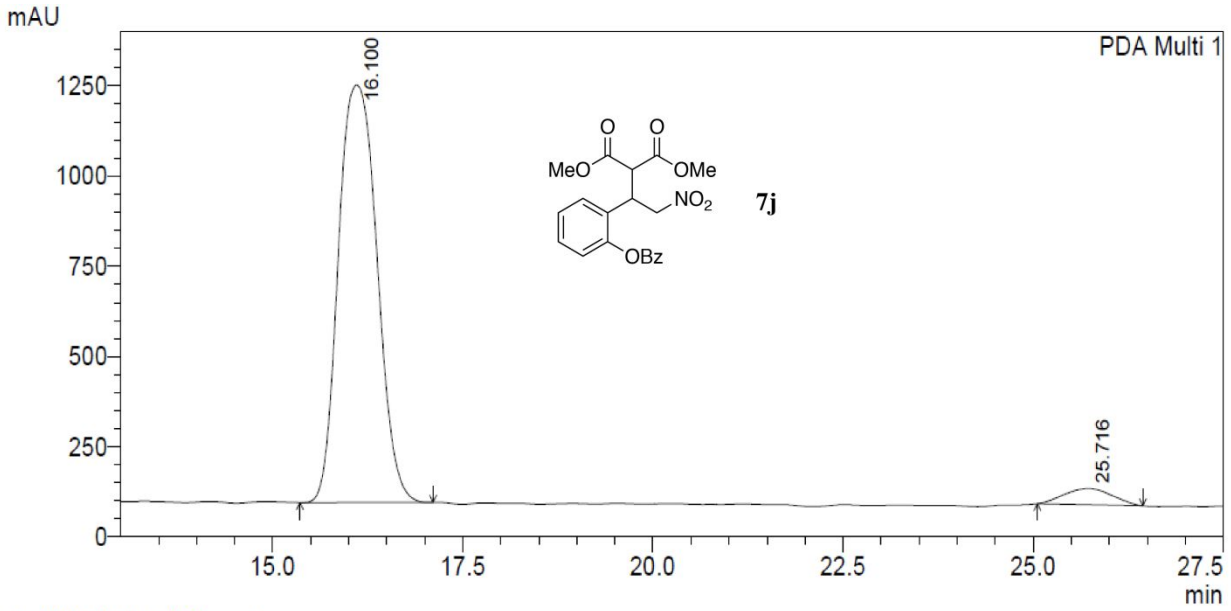


1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.255	1375710	28163	4.560	6.975
2	24.503	28791723	375596	95.440	93.025
Total		30167433	403759	100.000	100.000

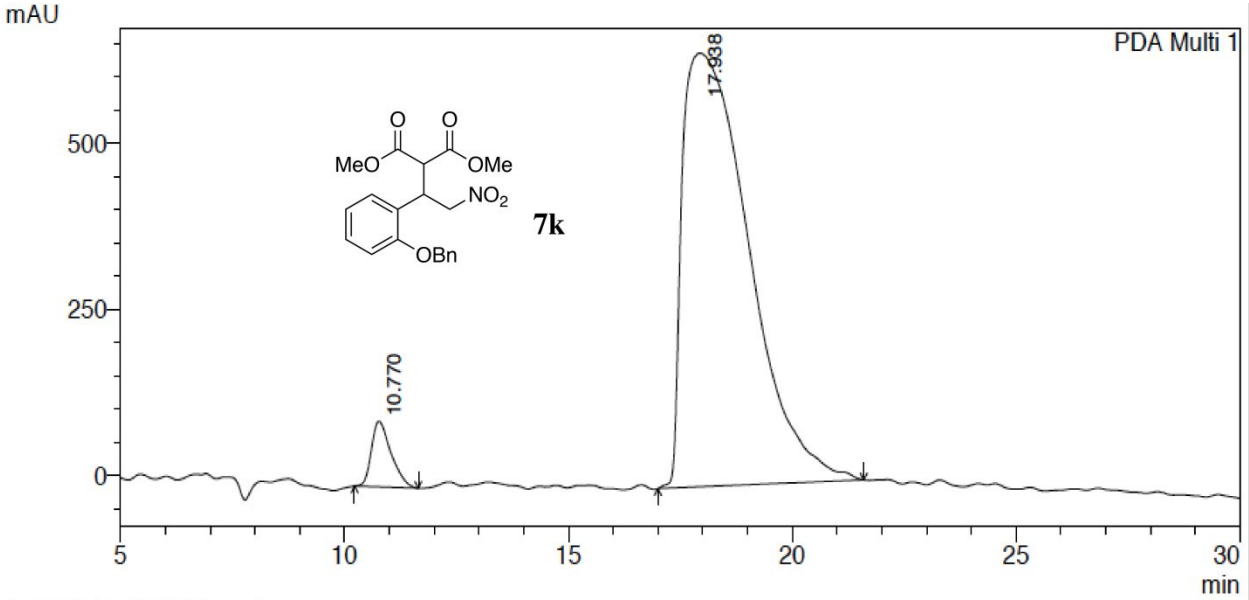


1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.100	40843400	1156471	95.462	96.274
2	25.716	1941795	44760	4.538	3.726
Total		42785195	1201231	100.000	100.000

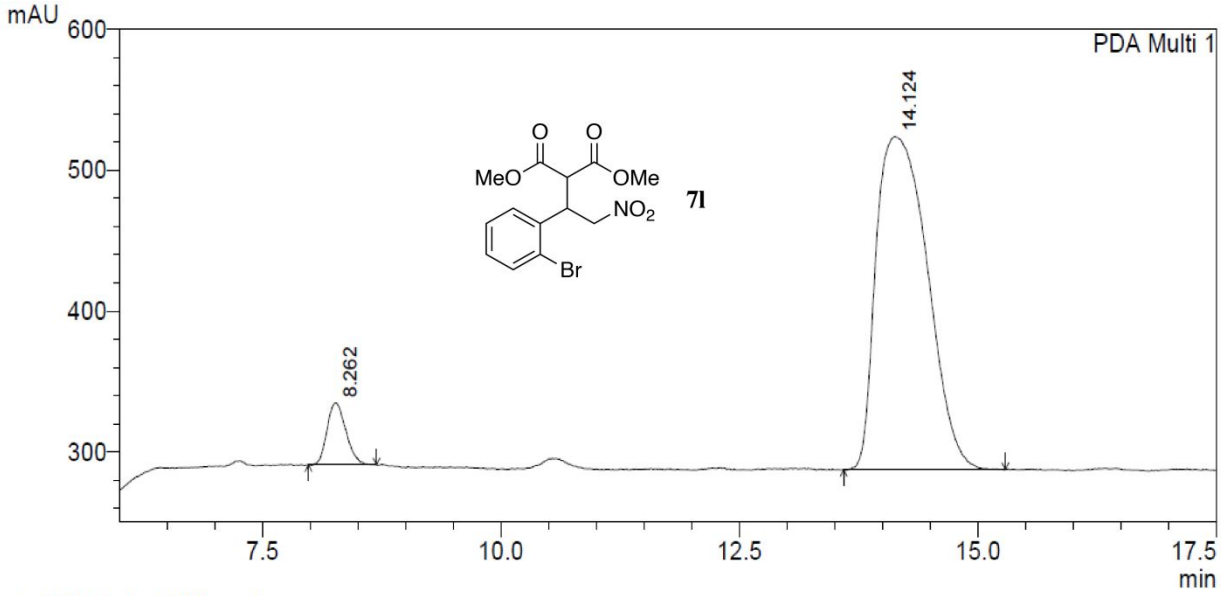


1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.770	3007142	98777	4.264	13.143
2	17.938	67524994	652767	95.736	86.857
Total		70532135	751544	100.000	100.000



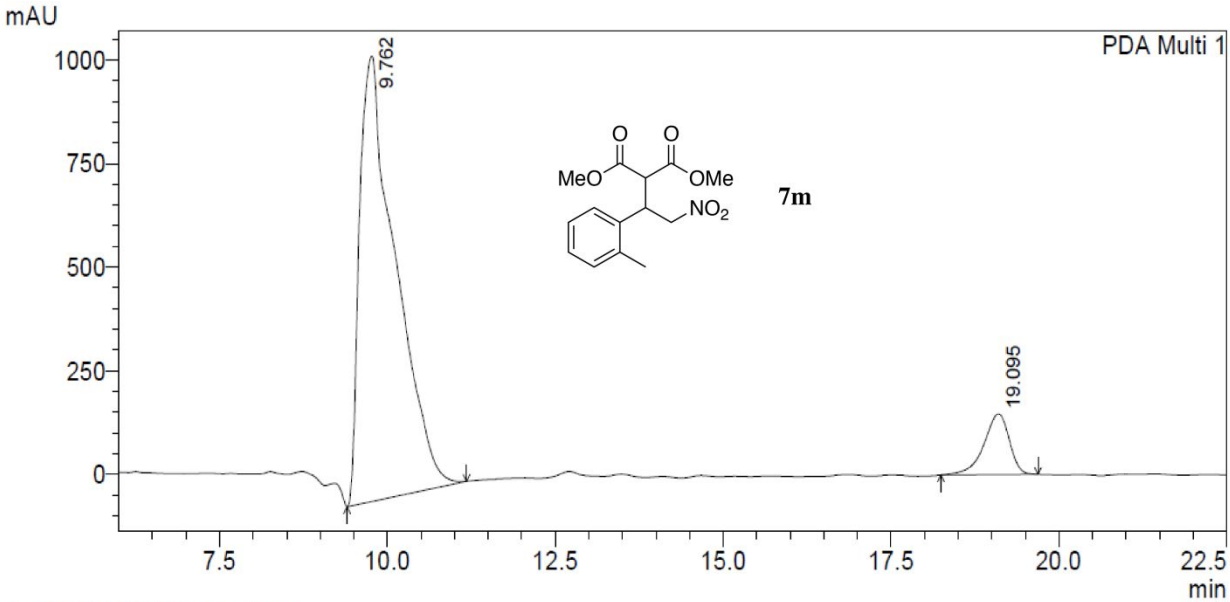
7l

1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.262	606589	44047	6.410	15.705
2	14.124	8855877	236412	93.590	84.295
Total		9462466	280459	100.000	100.000



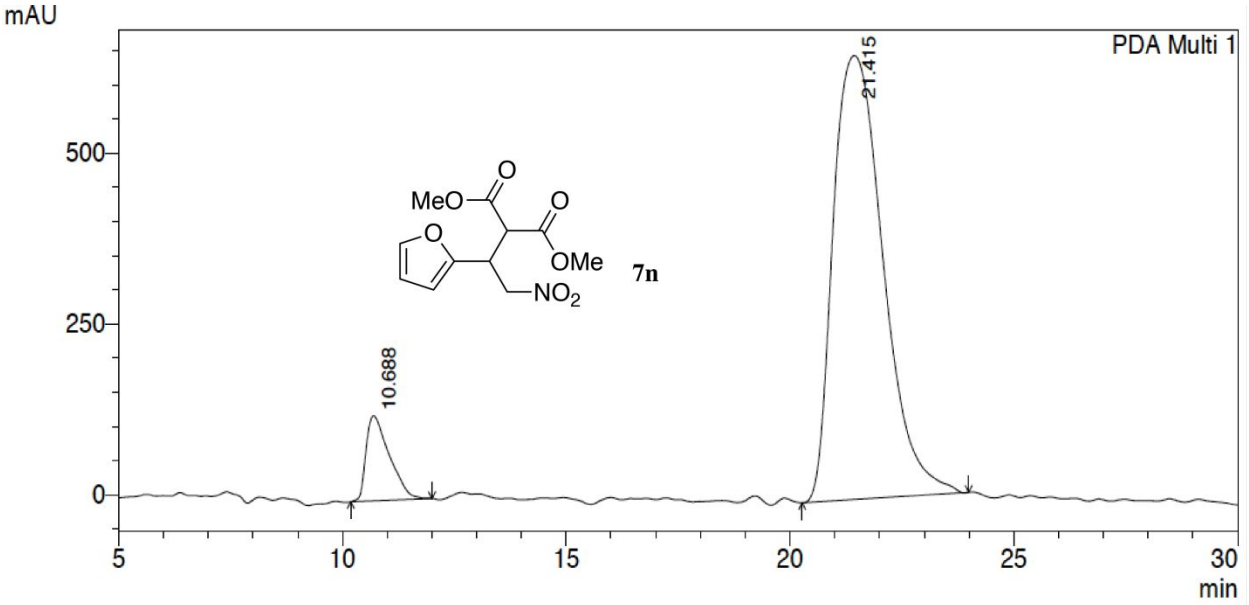
7m

1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.762	40142061	1075203	91.179	88.002
2	19.095	3883720	146590	8.821	11.998
Total		44025781	1221793	100.000	100.000

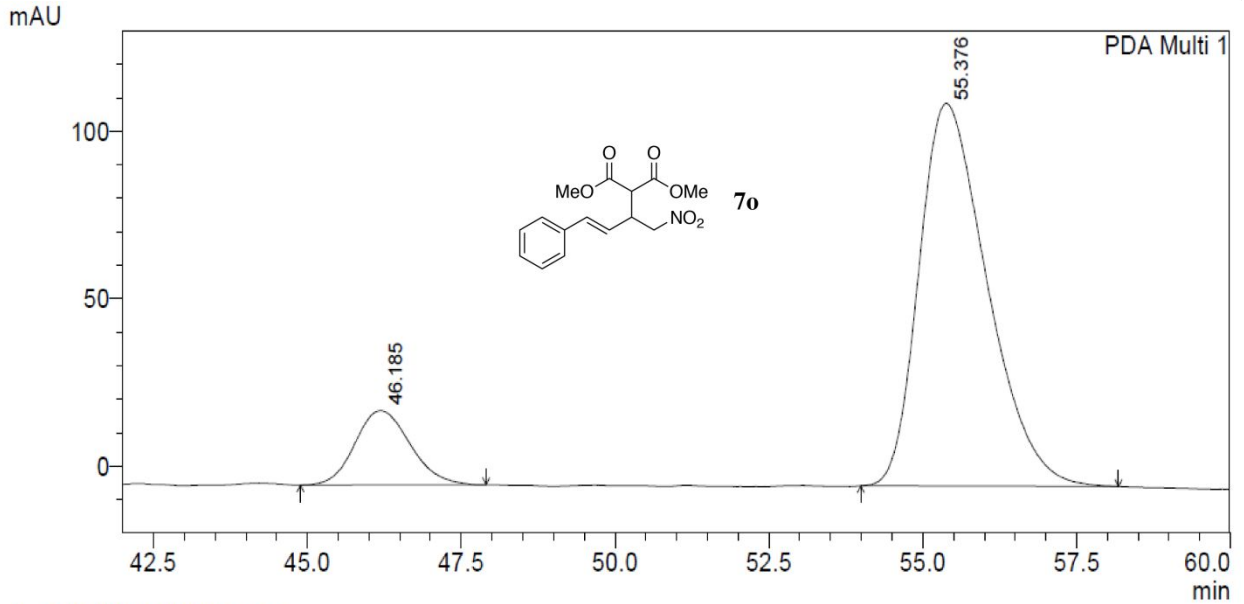


1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.688	4501488	124344	8.196	16.073
2	21.415	50423476	649299	91.804	83.927
Total		54924964	773643	100.000	100.000

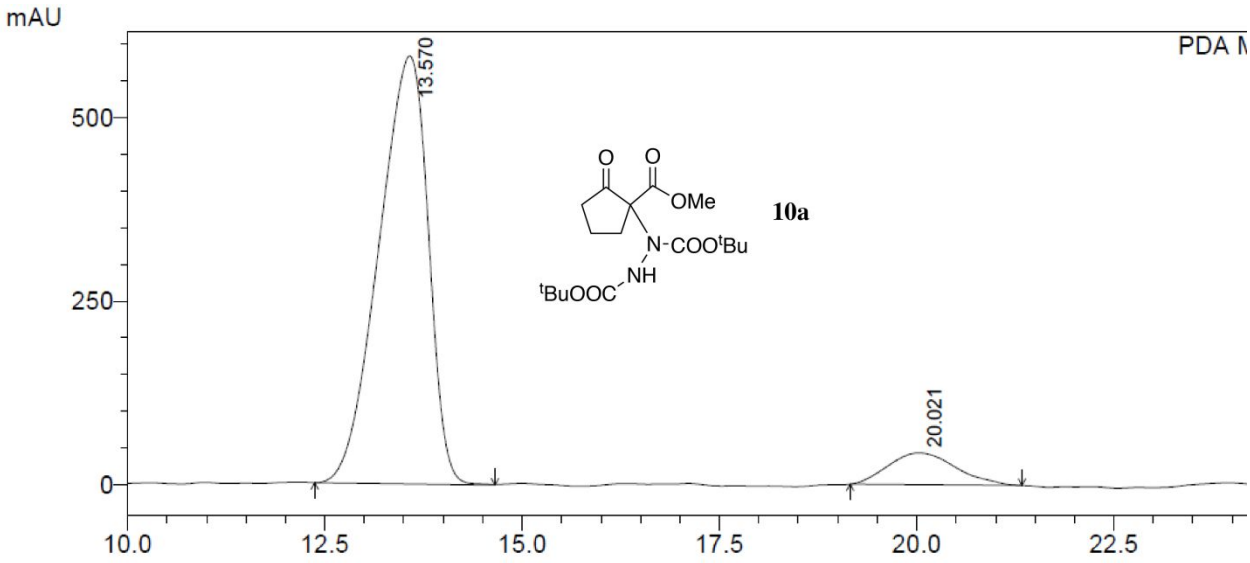


1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	46.185	1385094	22211	13.593	16.267
2	55.376	8804661	114324	86.407	83.733
Total		10189755	136534	100.000	100.000

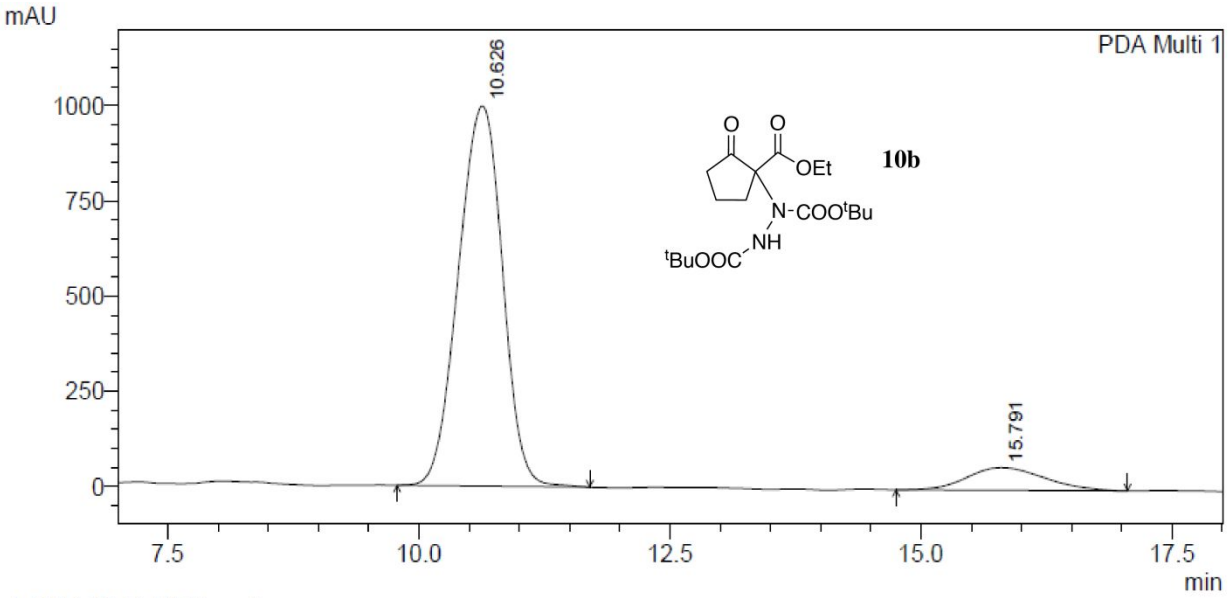


1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.570	25405995	583120	90.747	93.079
2	20.021	2590411	43358	9.253	6.921
Total		27996406	626478	100.000	100.000

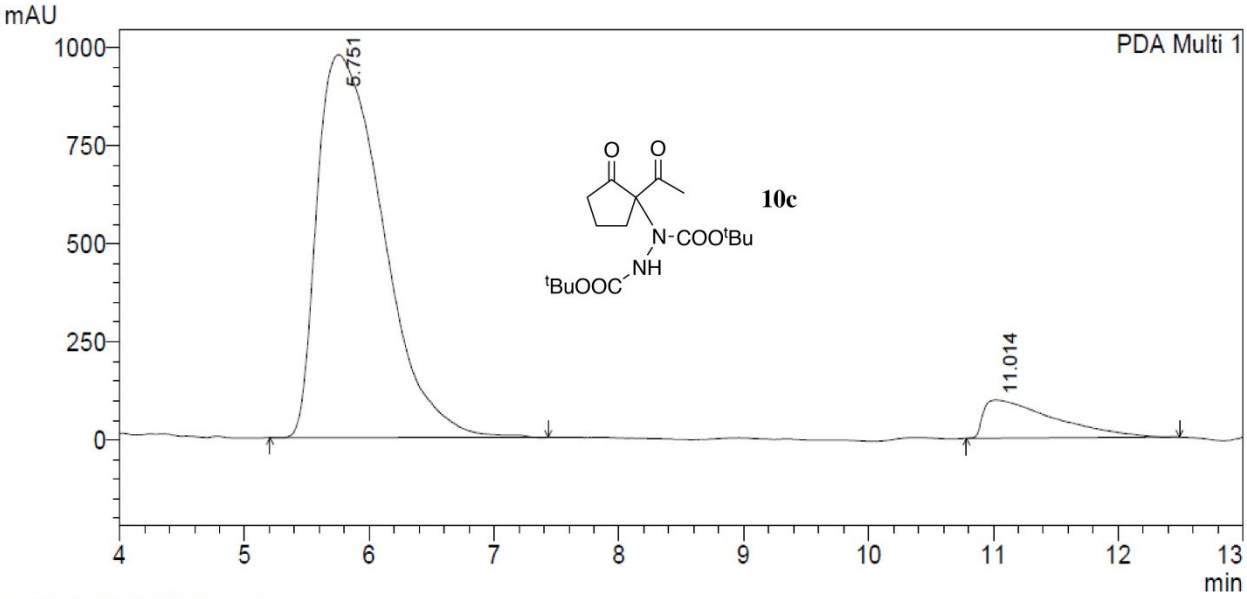


1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.626	30473749	998531	90.547	94.426
2	15.791	3181424	58947	9.453	5.574
Total		33655173	1057478	100.000	100.000

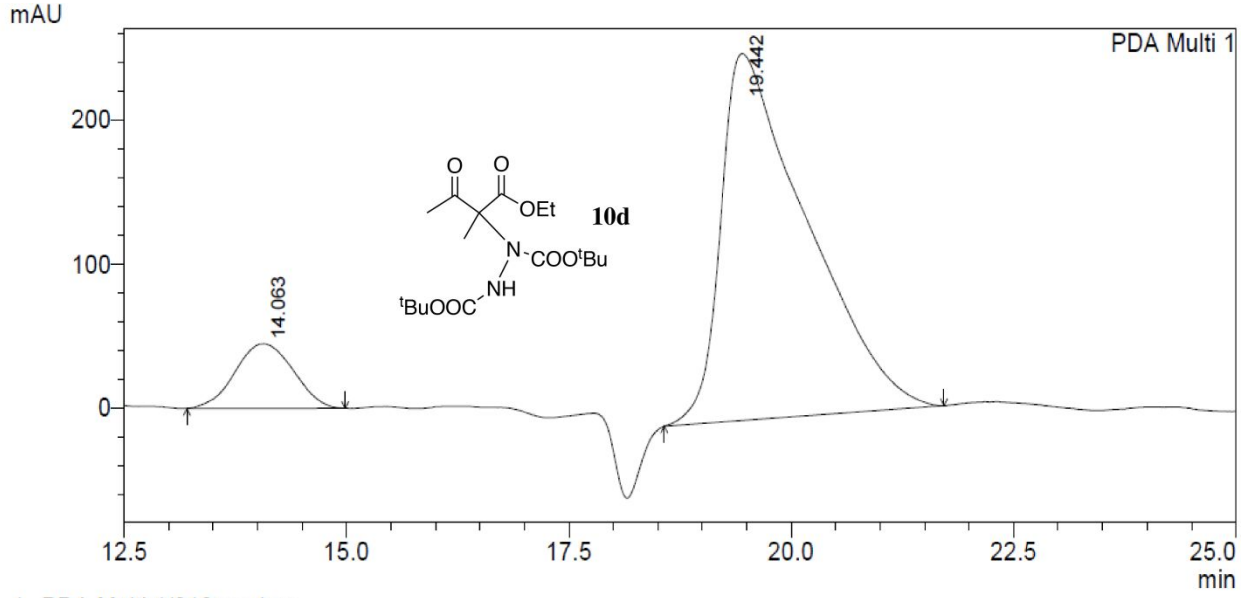


1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.751	35826029	976164	90.376	90.950
2	11.014	3815109	97136	9.624	9.050
Total		39641139	1073300	100.000	100.000

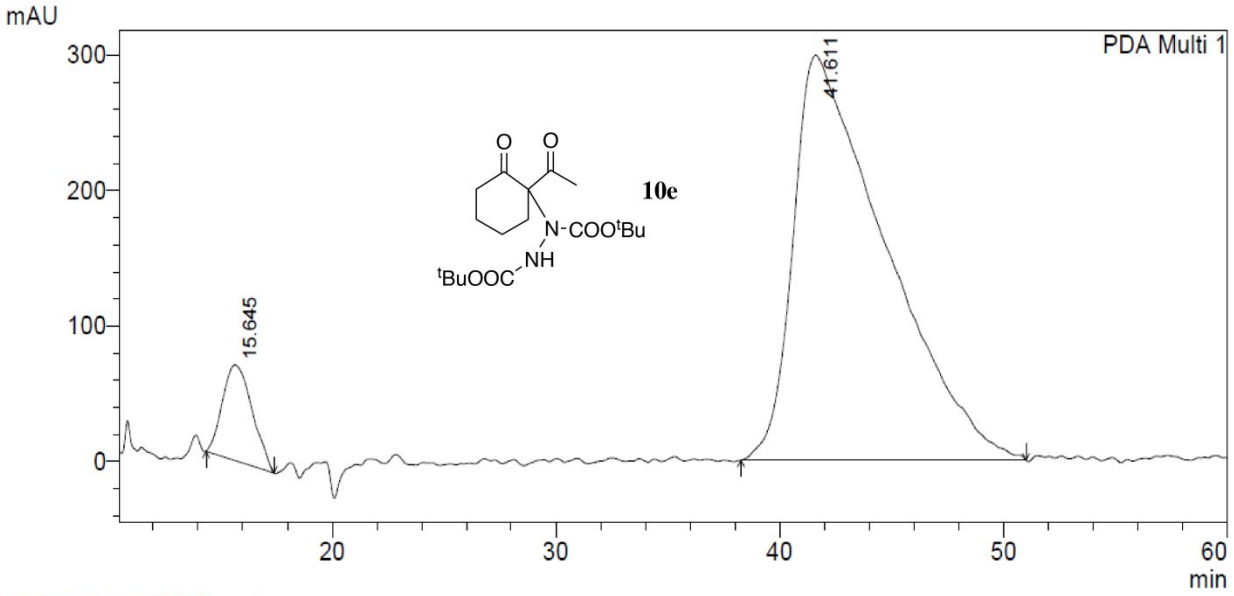


1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.063	2052636	44962	10.682	15.010
2	19.442	17162791	254582	89.318	84.990
Total		19215427	299544	100.000	100.000

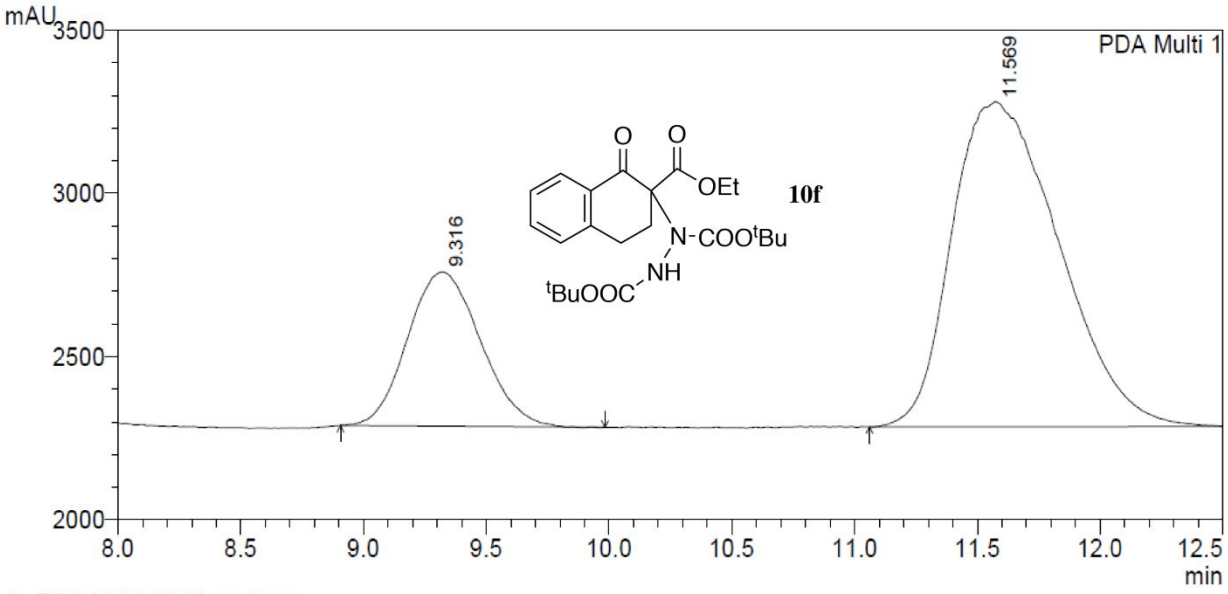


1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.645	6546369	70564	7.087	19.104
2	41.611	85825411	298801	92.913	80.896
Total		92371780	369365	100.000	100.000



1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.316	9744256	472899	24.366	32.157
2	11.569	30246826	997711	75.634	67.843
Total		39991081	1470610	100.000	100.000