Deconstructing Quinine. Part 1. Toward an Understanding of the Remarkable Performance of *Cinchona* Alkaloids in Asymmetric Phase Transfer Catalysis

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SUPPORTING INFORMATION

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General Experimental

All reactions were performed in oven-dried (145 °C) or flame-dried glassware under an inert atmosphere of dry argon. Reaction solvents THF (Fisher, HPLC grade), Et_2O (Fisher, BHT stabilized ACS grade) and methylene chloride (Fisher, unstabilized HPLC grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Reaction solvents hexane (Fisher, OPTIMA grade) and toluene (Fisher, ACS grade) were dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant, a supported copper catalyst for scavenging oxygen, under a positive pressure of argon. Reactions were carried out at the temperature indicated (external temperature) as measured by an thermocouple device unless otherwise indicated.

Column chromatography was performed using Merck grade 9385, 60 Å silica gel and column diameter (∅) was expressed in mm. Visualization was accomplished by UV light, permanganate ($KMnO_4$), or iodine (I_2) as indicated. Analytical and preparative thin-layer chromatography was performed on Merck silica gel plates with F-254 indicator. Chromatography solvents EtOAc (Honeywell, HPLC grade), CH_2Cl_2 (Sigma-Aldrich, ACS grade), TBME (Sigma-Aldrich, ACS grade), and MeOH (Fisher, Optima grade) were used as supplied.

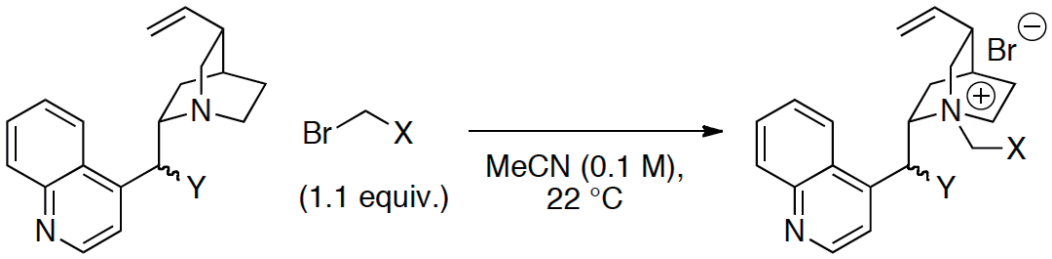
^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra were acquired at 500 MHz, 126 MHz, and 376 MHz, respectively, and referenced to residual solvent [$CHCl_3$ at 7.26 (^{1}H) and 77.00 (^{13}C) or MeOH 3.31 (^{1}H), 49.00 (^{13}C) or DMSO at 2.50 (^{1}H) and 39.5 (^{13}C) ppm]. Chemical shifts are reported in ppm; multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p,

(pentet), m (multiplet) and br (broad). Coupling constants, *J,* are reported in Hertz. Mass Spectrometry was performed by the University of Illinois Mass Spectrometer Center. ESI mass spectra were performed on a Waters Q-Tof Ultima or a Waters ZMD Quadrupole instrument. Data are reported in the form of *m/z* (intensity relative to base peak = 100). Analytical high pressure liquid chromatography (HPLC) was performed using a Hewlett Packard 1090L Chromatograph equipped with a variable wavelength diode array detector and an autosampler. The chromatograph was equipped with a reverse phase Agilent Zorbax 300SB-C8 column (5 μm, 4. 6x 200mm, lamp current = 1). Method 1: Linear Gradient; flow rate = 1.0 mL/min, l = 254 nm, solvent = CH_3CN/H_2O (30:70) to CH_3CN/H_2O (90:10) over 10 min, then isocratic for 7 min. A 3 min re-equilibration time was utilized between runs. The water eluent contained 0.1% v/v acetic acid. Chiral stationary phase HPLC (CSP-HPLC) Method 2: *R,R*-Welk-O, 1.0 mL/min, IPA/hexanes 5:95. Melting points were obtained in vacuum-sealed glass tubes using a Thomas-Hoover Uni-Melt™ melting point apparatus and are corrected.

Fitting of kinetic data was done with OriginPro 8 SR4 version 8.0951 (B951). Interpolation of kinetic plots was done with Microsoft Excel 2008.

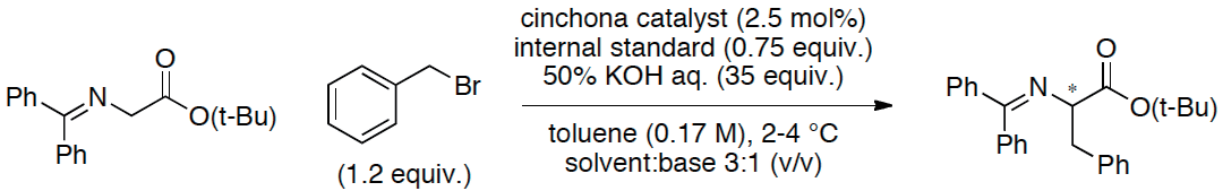
Cinchonidine and benzyl bromide were purchased from Acros Organics and Aldrich, respectively, 3,5-bis(trifluoromethyl)benzyl bromide was purchased from Alfa-Aesar, 9-bromomethylanthracene [i], 2-bromomethylnaphthalene [ii], 1-bromomethylnaphthalene[2], *N*-(diphenylmethylene)glycine *tert*-butyl ester,[iii,iv] and phenylchlorothionoformate[v] were prepared as described in the literature.

General Procedure I. *N*-Quaternization of Cinchona Alkaloids



The cinchona alkaloid was placed in a single-neck,, round-bottomed flask containing a magnetic stir bar and the arylmethylene bromide was then added (1.1 equiv). The flask was then purged with dry argon and the contents were dissolved in MeCN (0.1 M). The reaction mixture was allowed to stir until the starting material was consumed. Reactions were typically monitored by ^{1}H NMR spectroscopy of reaction aliquots (~100 μL). Solvent was removed on a rotavap (20 mm Hg, 25 °C) and the residue was purified either by washing, chromatography or recrystallization. On occasion the reaction mixtures could be diluted with CH_2Cl_2 and purified directly by silica gel flash chromatography.

General Procedure II. PTC Alkylation of *N*-(Diphenylmethylene)glycine *tert*-Butyl Ester



A 2 mL scintillation vial was fitted with a Teflon lined rubber septum and *tert*-butyl 2-(diphenylmethyleneamino)acetate (100 mg, 0.34 mmol), and the phase transfer catalyst (8.48 μmol, 0.025 equiv) were added. The liquid reagents, benzyl bromide (800 μL, 0.51 M in toluene, 1.2 equiv), internal standard (790 μL, 0.32 M in toluene, 0.75 equiv), and toluene (410 μL) were added via syringe. Then, a 1.5 cm egg-shaped magnetic stir bar was placed in the vial and the contents were briefly agitated in an ultrasonic bath (10-20 s). Reaction vials were then transferred to a cold room maintained at 2-4 ^{o}C and were allowed to equilibrate for at least 1 h with stirring while immersed in a water bath to control temperature fluctuations. Lastly, 50% aq. (w/w) KOH solution (670 μL, 11.9 mmol, 17.8 M, 35.0 equiv) was added to the rapidly stirred (1600 rpm) organic phase. Aliquots were taken at the indicated times and analyzed as follows.

The internal standard employed in these reactions was 1,1-diphenyl-1-heptene.

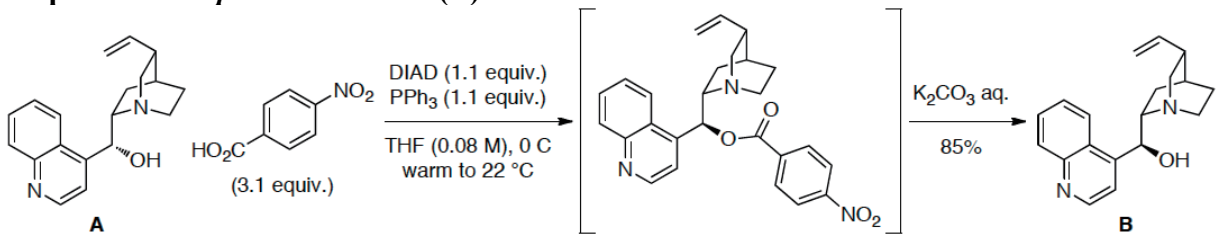
General Procedure III. Performing Kinetics and Enantioselectivity Measurements on PTC Alkylations

Three seconds prior to the indicated time interval, the stirrer was turned off. At the indicated time interval a 10-μL aliquot of the organic layer was removed and then was injected into MeCN (2.0 mL) containing glacial acetic acid (several drops). This clear solution was filtered through a small plug of silica gel (0.5 x 1 cm) and the filtrate was analyzed by Reverse Phase-HPLC Method 1.

For the PTC alkylations that reached near to full completion (70-85% conversion to product), a 10-μL aliquot was taken from the organic phase and injected into *i*-PrOH (2 mL). This aliquot was filtered through a small plug of silica gel (0.5 x 1 cm) and the filtrate was analyzed by CSP-HPLC Method 2

For the PTC alkylations that did not reach full completion (<70% conversion to product), the organic phase was first separated from the aqueous base *via* pipette. The alkylation product was obtained by preparative thin-layer chromatography (8 x 10 cm plate) using 0.5 - 1.0 mL of the organic phase directly. The product was eluted with 5:95 TBME/hexane. The product band was removed, suspended in *i*-PrOH (4 mL), and the silica gel was removed by filtration. The solvent was removed on a rotavap (20 mm Hg, 35-40 °C). The product was then dissolved in an appropriate amount of *i*-PrOH (1 mg/mL) and then analyzed by CSP-HPLC Method 2.

Preparation of *epi*-Cinchonidine (B)



Cinchonidine (2.94 g, 10.0 mmol), triphenylphosphine (2.89 g, 11.0 mmol, 1.1 equiv), and 4-nitrobenzoic acid (5.18 g, 31.0 mmol, 3.1 equiv) were dissolved in THF (125 mL, 0.08 M) in a 250-mL, three-neck round-bottomed flask fitted with an argon inlet, septum, and thermocouple. The suspension was cooled to 0 °C (internal) in an ice-bath over 1 h, whereupon diisopropyl azodicarboxylate (2.17 mL, 11.0 mmol, 1.1 equiv) was then added slowly over the course of several minutes. The reaction mixture was stirred for an additional hour at 0 °C then was allowed to warm to 22 °C over 1 h. The reaction mixture was diluted with Et_2O (50 mL), then was transferred to a 250-mL separatory funnel and was extracted with 1 N HCl aq. (3 x 50 mL). The combined aqueous extracts were basified with solid K_2CO_3 to pH 9-11. This aqueous phase was extracted with Et_2O (3 x 50 mL) then CH_2Cl_2 (50 mL). The combined organic extracts were dried over Na_2SO_4 and then the solvent was removed on a rotavap (20 mm Hg, 25 °C) to afford 2.50 g (85%) of **B** as a light-yellow solid. The entire product was further purified by recrystallization from boiling *i*-PrOH (~150 mL) to afford **B** as a white, crystalline solid.

Data for **B**:

mp: 203-205 °C

^{1}H-NMR: (500 MHz, $CDCl_3$)

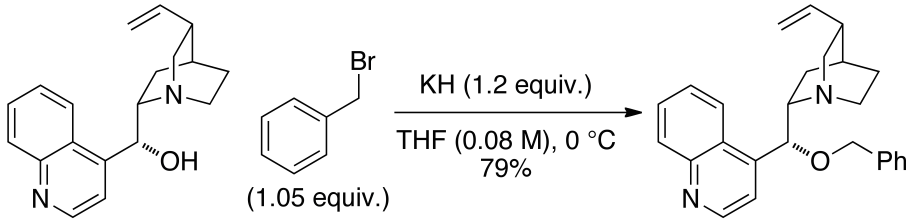
8.73 (d, J = 4.5 Hz, 1 H), 8.04 (dd, J = 8.5, 0.8 Hz, 1 H), 7.92 (d, J = 8.2 Hz, 1 H), 7.60 (ddd, J = 8.3, 6.9, 1.2 Hz, 1 H), 7.55 (d, J = 4.4 Hz, 1 H), 7.30 (ddd, J = 8.3, 6.9, 1.2 Hz, 1 H), 5.74 - 5.58 (m, 2 H), 5.12 (s, 1 H), 4.89 (ddt, J = 17.6, 10.3, 1.4 Hz, 2 H), 3.48 (tdd, J = 10.0, 4.8, 2.3 Hz, 1 H), 3.11 - 2.95 (m, 2 H), 2.66 - 2.47 (m, 2 H), 2.22 (s, 1 H), 1.82 - 1.66 (m, 3 H), 1.52 - 1.40 (m, 2 H).

^{13}C-NMR: (126 MHz, $CDCl_3$)

149.99, 149.61, 148.06, 141.77, 130.10, 128.95, 126.52, 125.61, 122.94, 118.19, 114.27, 71.76, 60.34, 56.95, 43.16, 39.90, 27.88, 27.58, 21.45.

Analysis:	$C_{19}H_{22}N_2O$ (294.39)			
	Calcd:	C, 77.52;	H, 7.53;	N, 9.52
	Found:	C, 77.38;	H, 7.67;	N, 9.47
LRMS:	(ESI^+, Q-tof)			
	295.2 (100, M-Br+)			
HRMS:	$C_{19}H_{23}N_2O^+$ (ESI^+, Q-tof)			
	Calcd:	295.1810		
	Found:	295.1814		
TLC:	R_f 0.11 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]			

Preparation of *O*-Benzylcinchonidine (C)



Potassium hydride (164 mg, 4.08 mmol, 1.2 equiv) was placed in a 100-mL, single-neck,, round-bottomed flask fitted with an argon inlet adapter and septum in a glove box. This flask was then removed from the glove box and a solution of cinchonidine (1.00 g, 3.40 mmol) in THF (43 mL, 0.08 M) was then added *via* syringe under argon. The reaction mixture was stirred for 15 min at 22 °C until it became a light orange solution and no further gas evolution was observed. The mixture was cooled to 0 °C (external) on an ice bath over 2 h. Benzyl bromide (420 μL, 3.57 mmol, 1.05 equiv) was then added *via* syringe and the mixture was stirred for 4 h at 0 °C.

The reaction mixture was quenched with sat. aq. NH_4Cl solution (~2 mL), and then was diluted with Et_2O (30 mL). The quenched reaction mixture was transferred to a 125-mL separatory funnel and then was extracted with 1 N aq. HCl solution (3 x 30 mL). The combined aqueous extracts were washed with Et_2O (3 x 30 mL) then were basified with solid K_2CO_3 until a white suspension persisted with a pH of 9-11. The aqueous suspension was diluted with H_2O (20 mL) and then was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were washed with brine (30 mL), dried over $MgSO_4$, and then concentrated on a rotavap (20 mm Hg, 25 °C) to afford 1.41 g of crude **C** as a light-amber oil. The product was purified by silica gel

flash chromatography (50 g SiO_2, ∅ = 30, 20:1 to 5:1, EtOAc/MeOH gradient elution) to afford 1.03 g (79%) of **C** as an off-white amorphous solid.

Data for **C:**

^{1}H-NMR: (500 MHz, $CDCl_3$)

8.91 (d, *J* = 4.4 Hz, 1H), 8.22-8.09 (s, 1H), 8.17 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.74 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.53 (d, *J* = 4.3 Hz, 1H), 7.40 – 7.28 (m, 5H), 5.79 – 5.68 (m, 1H), 5.32 (s, 1H), 4.93 (ddd, *J* = 17.5, 9.5, 5.9 Hz, 2H), 4.43 (q, *J* = 11.5 Hz, 2H), 3.47 – 3.33 (m, 1H), 3.22 – 3.02 (m, 2H), 2.76 – 2.54 (m, 2H), 2.26 (s, 1H), 1.90 – 1.68 (m, 3H), 1.64 (s, 1H), 1.57 – 1.43 (m, 1H).

^{13}C-NMR: (126 MHz, $CDCl_3$)

150.17, 148.60, 146.38, 141.84, 137.81, 130.52, 129.09, 128.42, 127.73, 127.64, 126.69, 126.52, 123.21, 118.59, 114.25, 71.31, 60.80, 57.03, 43.15, 39.99, 27.92, 27.73.

LRMS: (ESI^+, Q-tof)

385.2 (100, $M+H^+$)

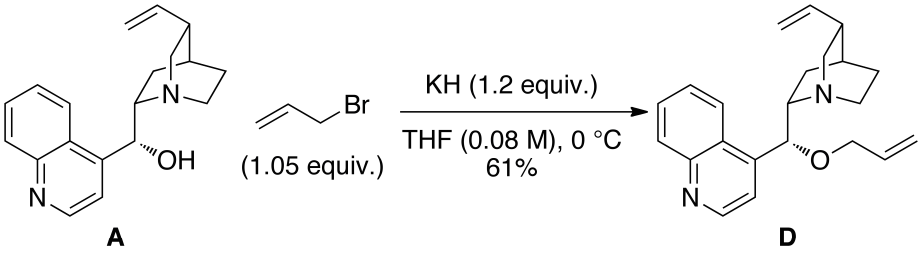
HRMS: $C_{26}H_{29}N_2O^+$ (ESI^+, Q-tof)

Calcd: 385.2280

Found: 385.2278

TLC: R_f 0.38 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of *O*-Allylcinchonidine (D)



Potassium hydride (164 mg, 4.08 mmol, 1.2 equiv) was placed in a 100-mL, single-neck,, round-bottomed flask fitted with an argon inlet adapter and septum in a glove box. This flask was then removed from the glove box and a solution of cinchonidine (1.00 g, 3.40 mmol) in THF (43 mL, 0.08 M) was then added *via* syringe under argon. The reaction mixture was stirred for 15 min at 22 °C until it became a light orange solution and no further gas evolution was observed.

The reaction mixture was cooled to 0 °C (external) on an ice bath over 2 h. Allyl bromide (310 μL, 3.57 mmol, 1.05 equiv) was then added *via* syringe and the mixture was stirred for 4 h at 0 °C.

The reaction mixture was quenched with sat. aq. NH_4Cl solution (~2 mL), and then was diluted with Et_2O (30 mL). The quenched reaction mixture was transferred to a 125-mL separatory funnel and then was extracted with 1 N aq. HCl solution (3 x 30 mL). The combined aqueous extracts were washed with Et_2O (3 x 30 mL) then were basified with solid K_2CO_3 until a white suspension persisted with a pH of 9-11. The aqueous suspension was diluted with H_2O (20 mL) and then was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were washed with brine (30 mL), dried over $MgSO_4$, and then concentrated on a rotavap (20 mm Hg, 25 °C) to afford 1.13 g (99+%) of crude **D** as a light-brown oil. The product was purified by silica gel flash chromatography (40 g SiO_2, ∅ = 30, 20:1 to 10:1, EtOAc/MeOH) to afford 1.03 g (79%) of **D** as a light-amber oil.

Data for **D**:

^{1}H-NMR: (500 MHz, $CDCl_3$)

8.90 (d, *J* = 4.4 Hz, 1 H), 8.13 (dd, *J* = 13.3, 8.5 Hz, 2 H), 7.72 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1 H), 7.57 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1 H), 7.49 (d, *J* = 4.4 Hz, 1 H), 5.93 (ddt, *J* = 17.1, 10.6, 5.4 Hz, 1 H), 5.77 - 5.65 (m, 1 H), 5.36 - 5.21 (m, 2 H), 5.21 - 5.13 (m, 1 H), 4.99 - 4.84 (m, 2 H), 3.95 (ddt, *J* = 12.8, 5.1, 1.4 Hz, 1 H), 3.87 (dd, *J* = 12.8, 5.7 Hz, 1 H), 3.44 (s, 1 H), 3.10 (dd, *J* = 13.5, 10.1 Hz, 2 H), 2.71 (dd, *J* = 17.0, 7.3 Hz, 1 H), 2.63 (d, *J* = 13.4 Hz, 1 H), 2.27 (s, 1 H), 1.88 - 1.74 (m, 3 H), 1.53 (ddd, *J* = 15.4, 12.7, 8.7 Hz, 2 H).

^{13}C-NMR: (126 MHz, $CDCl_3$)

150.14, 148.54, 146.31, 141.73, 134.31, 130.49, 129.05, 126.68, 126.41, 123.12, 118.39, 116.95, 114.27, 70.14, 60.65, 57.09, 43.27, 39.98, 27.93, 27.69, 22.04.

Analysis: $C_{22}H_{26}N_2O$ (334.45)

Calc:	C, 79.00;	H, 7.84;	N, 8.38
Found:	C, 78.76;	H, 8.21;	N, 8.11

LRMS: (ESI^+, Q-tof)

335.2 (100, $M+H^+$)

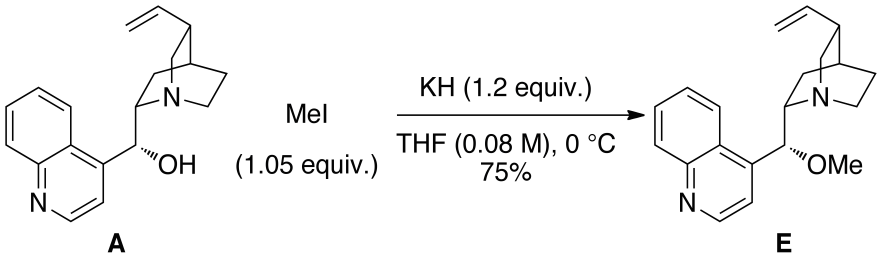
HRMS: $C_{22}H_{27}N_2O^+$ (ESI^+, Q-tof)

Calcd: 335.2123

Found: 335.2117

TLC: R_f 0.34 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of *O*-Methylcinchonidine (E)



Potassium hydride (164 mg, 4.08 mmol, 1.2 equiv) was placed in a 100-mL, single-neck,, round-bottomed flask fitted with an argon inlet adapter and septum in a glove box. This flask was then removed from the glove box and a solution of cinchonidine (1.00 g, 3.40 mmol) in THF (43 mL, 0.08 M) was then added *via* syringe under argon. The reaction mixture was stirred for 15 min at 22 °C until it became a light orange solution and no further gas evolution was observed. The reaction mixture was cooled to 0 °C (external) on an ice bath over 2 h. Methyl iodide (220 μL, 3.57 mmol, 1.05 equiv) was then added *via* syringe and the mixture was stirred for 4 h at 0 °C.

The reaction mixture was quenched with sat. aq. NH_4Cl solution (~2 mL), and then was diluted with Et_2O (30 mL). The quenched reaction mixture was transferred to a 125-mL separatory funnel and then was extracted with 1 N aq. HCl solution (3 x 30 mL). The combined aqueous extracts were washed with Et_2O (3 x 30 mL) then were basified with solid K_2CO_3 until a white suspension persisted with a pH of 9-11. The aqueous suspension was diluted with H_2O (20 mL) and then was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were washed with brine (30 mL), dried over $MgSO_4$, and then concentrated on a rotavap (20 mm Hg, 25 °C) to afford 1.17 g of crude **E** as a light-yellow, crystalline solid.

The product was purified by silica gel flash chromatography (40 g SiO_2, ∅ = 30, 20:1 to 10:1, CH_2Cl_2/MeOH) to afford 781 mg (75%) of **E** as a white, crystalline solid. The entire product was further purified by recrystallization from boiling hexane.

Data for **E**:

m.p.: 125-126 °C

^{1}H-NMR: (500 MHz, $CDCl_3$)

8.90 (d, *J* = 4.4 Hz, 1 H), 8.12 (dd, *J* = 21.0, 8.4 Hz, 2 H), 7.72 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1 H), 7.57 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1 H), 7.46 (d, *J* = 4.4 Hz, 1 H), 5.71 (ddd, *J* = 17.7, 10.3, 7.7 Hz, 1 H), 5.07 (s, 1 H), 4.91 (ddt, *J* = 20.2, 10.3, 1.4 Hz, 2 H), 3.39 (t, *J* = 9.0 Hz, 1 H), 3.30 (s, 3 H), 3.09 (dd, *J* = 13.5, 10.2 Hz, 2 H), 2.75 - 2.65 (m, 1 H), 2.65 - 2.55 (m, 1 H), 2.25 (s, 1 H), 1.84 - 1.69 (m, 3 H), 1.51 (ddd, *J* = 16.8, 12.5, 7.7 Hz, 2 H).

^{13}C-NMR: (126 MHz, $CDCl_3$)

150.14, 148.56, 146.07, 141.67, 130.49, 129.04, 126.69, 126.52, 123.16, 118.34, 114.34, 82.83, 60.57, 57.18, 56.96, 43.21, 39.92, 27.88, 27.59, 21.90.

Analysis: $C_{20}H_{24}N_2O$ (308.42)

Calcd:	C, 77.89;	H, 7.84;	N, 9.08
Found:	C, 77.96;	H, 7.95;	N, 9.17

LRMS: (ESI^+, Q-tof)

309.2 (100, $M+H^+$)

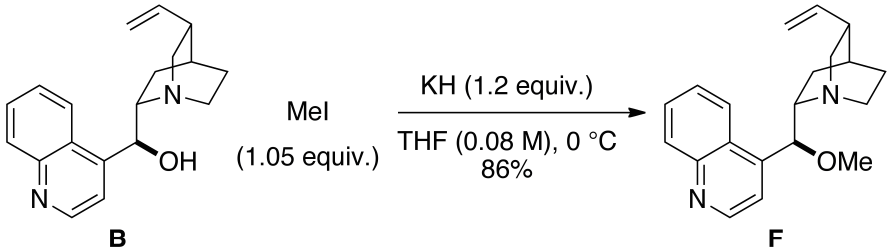
HRMS: $C_{20}H_{25}N_2O^+$ (ESI^+, Q-tof)

Calcd: 309.1967

Found: 309.1960

TLC: R_f 0.29 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of *O*-Methyl-*epi*-cinchonidine (F)



Potassium hydride (120 mg, 3.00 mmol, 1.2 equiv) was placed in a 50-mL, single-neck, round-bottomed flask fitted with an argon inlet adapter and septum in a glove box. This flask was then removed from the glove box and a solution of *epi*-cinchonidine (736 mg, 2.50 mmol) in THF (31.0 mL, 0.08 M) was then added *via* syringe under argon. The reaction mixture was

stirred for 15 min at 22 °C until it became a light orange solution and no further gas evolution was observed. The reaction mixture was cooled to 0 °C (external) on an ice bath over 2 h. Methyl iodide (164 μL, 2.63 mmol, 1.05 equiv) was then added *via* syringe and the mixture was stirred for 4 h at 0 °C.

The reaction mixture was quenched with sat. aq. NH_4Cl solution (~2 mL), and then was diluted with Et_2O (30 mL). The quenched reaction mixture was transferred to a 125-mL separatory funnel and then was extracted with 1 N aq. HCl solution (3 x 30 mL). The combined aqueous extracts were washed with Et_2O (3 x 30 mL) then were basified with solid K_2CO_3 until a white suspension persisted with a pH of 9-11. The aqueous suspension was diluted with H_2O (20 mL) and then was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were washed with brine (30 mL), dried over $MgSO_4$, and then concentrated on a rotavap (20 mm Hg, 25 °C) to afford 1.04 g of crude **F** as a light-yellow, crystalline solid.

The product was purified by silica gel flash chromatography (50 g SiO_2, ∅ = 30, 20:1 to 5:1, CH_2Cl_2/MeOH, gradient elution) to afford 665 mg (86%) of **F** as a white, crystalline solid. The entire product was further purified by recrystallization from boiling hexane.

Data for **F**:

m.p.: 125-126 °C

^{1}H-NMR: (500 MHz, $CDCl_3$)

8.90 (d, *J* = 4.4 Hz, 1 H), 8.18 - 8.06 (m, 2 H), 7.72 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1 H), 7.57 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1 H), 7.46 (d, *J* = 4.4 Hz, 1 H), 5.76 - 5.66 (m, 1 H), 5.07 (s, 1 H), 4.91 (ddt, *J* = 20.2, 10.3, 1.4 Hz, 2 H), 3.43 - 3.33 (m, 1 H), 3.30 (s, 3 H), 3.08 (dt, *J* = 18.9, 9.6 Hz, 2 H), 2.75 - 2.64 (m, 1 H), 2.64 - 2.57 (m, 1 H), 2.26 (s, 1 H), 1.83 - 1.69 (m, 3 H), 1.51 (ddd, *J* = 16.4, 12.1, 7.7 Hz, 2 H).

^{13}C-NMR: (126 MHz, $CDCl_3$)

150.14, 148.51, 146.25, 141.85, 130.46, 129.00, 126.61, 126.51, 123.10, 118.33, 114.20, 83.09, 60.55, 57.17, 57.03, 43.16, 40.03, 27.87, 27.67, 21.98.

analysis: $C_{20}H_{24}N_2O$ (308.42)

Calcd:	C, 77.89;	H, 7.84;	N, 9.08
Found:	C, 77.90;	H, 7.95;	N, 9.14

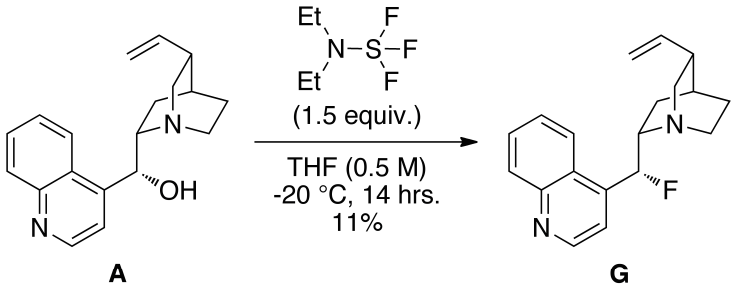
LRMS: (ESI^+, Q-tof)

309.2 (100, $M+H^+$)

HRMS: $C_{20}H_{25}N_2O^+$ (ESI$^+$, Q-tof)
Calcd: 309.1967
Found: 309.1965

TLC: R_f 0.30 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of Deoxyfluorocinchondine (G)



Cinchonidine (2.36 g, 8.00 mmol) was placed in a 50-mL, single-neck,, PTFE round-bottomed flask fitted with a septum and was then suspended in THF (16.0 mL, 0.50 M). The suspension was cooled to -20 °C (external) with a refrigerator unit in an *i*-PrOH bath over 2-3 h. Diethylaminosulfur trifluoride (1.58 mL, 12.0 mmol, 1.50 equiv) was then added slowly over several minutes *via* a polypropylene syringe under an argon atmosphere, and the mixture was then stirred for 14 h at -20 °C. The reaction was quenched by transferring the brown solution to a 250-mL separatory funnel containing a sat. aq. $NaHCO_3$ solution (60 mL) which was then extracted with CH_2Cl_2 (3 x 60 mL). The combined organic extracts were washed with brine (60 mL), dried over $MgSO_4$, and then were concentrated on a rotavap (20 mm Hg, 25 °C) to afford 2.75 g (116%) of **G** as an orange-amber, viscous oil.

The crude product was purified by three successive chromatographic separations on silica gel. The first column (100 g SiO_2, ∅ = 40, 20:1 to 5:1, CH_2Cl_2/MeOH gradient elution) afforded 1.42 g (60%) of crude **G** as a brown-amber oil. The second column (40 g SiO_2, ∅ = 30, 20:1 to 5:1, EtOAc/MeOH gradient elution) afforded 521 mg (22%) of crude **G** as a yellow oil. The third column (50 g SiO_2, ∅ = 30, 10:1 to 8:1, TBME/MeOH) afforded 253 mg (11%) of **G** as a white, crystalline solid. The entire product was further purified by recrystallization from boiling pentane.

Data for **G**:

m.p.: 78-81 °C

^{1}H-NMR: (500 MHz, CD_3OD)

8.81 (d, J = 4.6 Hz, 1 H), 8.03 (d, J = 8.3 Hz, 1 H), 7.98 (d, J = 8.4 Hz, 1 H), 7.75 (ddd, J = 8.4, 6.9, 1.3 Hz, 1 H), 7.63 (ddd, J = 8.3, 6.9, 1.2 Hz, 1 H), 7.58 (d, J = 4.6 Hz, 1 H), 6.40 (dd, J = 48.5, 2.2 Hz, 1 H), 5.70 (ddd, J = 17.6, 10.4, 7.5 Hz, 1 H), 4.91 (dd, J = 17.1, 1.5 Hz, 1 H), 4.87 - 4.81 (m, 1 H), 3.39 - 3.28 (m, 1 H), 3.10 (dd, J = 13.7, 10.2 Hz, 1 H), 2.80 - 2.70 (m, 1 H), 2.65 (ddd, J = 13.7, 5.1, 2.5 Hz, 1 H), 2.32 (s, 1 H), 1.80 - 1.69 (m, 3 H), 1.62 - 1.52 (m, 1 H), 1.46 (td, J = 10.4, 5.1 Hz, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

150.89, 148.81, 145.79 (d, J = 20.5 Hz), 142.31, 131.13, 130.33, 128.78, 125.91 (d, J = 5.3 Hz), 124.09, 118.93 (d, J = 11.6 Hz), 115.15, 93.76 (d, J = 178.9 Hz), 60.81 (d, J = 21.9 Hz), 57.27, 44.22 (d, J = 5.4 Hz), 40.66, 29.03, 27.99, 21.27 (d, J = 5.8 Hz).

^{19}F-NMR: (376 MHz, CD_3OD)

-199.29 (dd, $J_{H\text{-}F}$ = 48.4, 27.4 Hz).

analysis: $C_{19}H_{21}FN_2$ (296.38)

Calcd:	C, 77.00;	H, 7.14;	N, 9.45
Found:	C, 77.04;	H, 7.33;	N, 9.47

LRMS: (ESI^+, Q-tof)

297.2 (100, $M+H^+$)

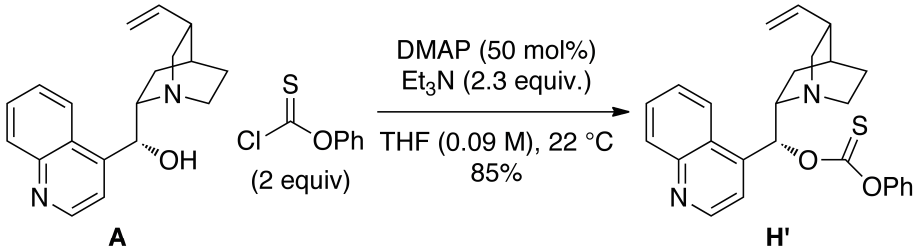
HRMS: $C_{19}H_{22}FN_2^+$ (ESI^+, Q-tof)

Calcd: 297.1767

Found: 297.1776

TLC: R_f 0.42 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of Cinchonan-9-ol, 9-(phenol thiocarbonate) (H')



Cinchonidine (1.77 g, 6.00 mmol) and 4-dimethylaminopyridine (367 mg, 3.00 mmol, 0.50 equiv) were added to a 100-mL, single-neck, round-bottomed flask fitted with an argon inlet adapter and septum and followed by THF (67.0 mL, 0.09 M). Triethylamine (1.92 mL, 13.8 mmol, 2.30 equiv) was then added and the mixture was stirred until it became homogeneous. Phenyl chlorothionoformate (1.67 mL, 12.0 mmol, 2.0 equiv) was then added *via* syringe to afford a suspension with a yellow precipitate and the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was transferred to 125-mL separatory funnel followed by the addition of a sat. aq. $NaHCO_3$ solution (70 mL) and the suspension was extracted with EtOAc (3 x 70 mL). The combined organic extracts were washed with brine (70 mL), dried over Na_2SO_4, and concentrated on a rotavap (20 mm Hg, 30 - 35 °C) to afford 6.07 g of crude **H'** as a dark-brown liquid. The product was purified by silica gel flash chromatography (100 g SiO_2, ∅ = 40, 20:1 to 10:1, EtOAc/MeOH) to afford 2.18 g (85%) of **H'** as an brown, amorphous solid.

Data for **H'**:

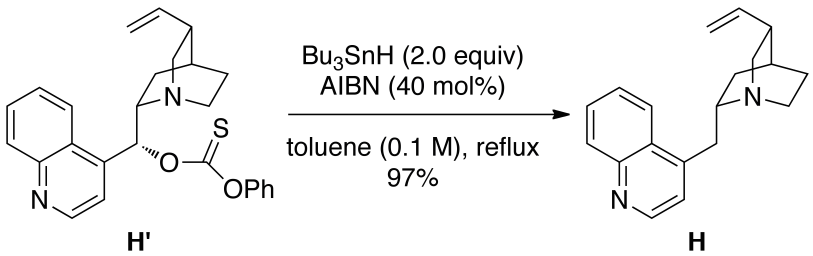
^{1}H-NMR: (500 MHz, $CDCl_3$)

8.94 (d, *J* = 4.5 Hz, 1 H), 8.20 (d, *J* = 8.2 Hz, 1 H), 8.16 (dd, *J* = 8.5, 0.8 Hz, 1 H), 7.74 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1 H), 7.61 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1 H), 7.48 (d, *J* = 4.5 Hz, 1 H), 7.42 - 7.35 (m, 2 H), 7.31 - 7.23 (m, 1 H), 7.09 - 7.00 (m, 3 H), 5.81 (ddd, *J* = 17.6, 10.4, 7.5 Hz, 1 H), 4.99 (ddt, *J* = 10.3, 6.4, 1.4 Hz, 2 H), 3.43 (dd, *J* = 16.9, 7.8 Hz, 1 H), 3.28 - 3.16 (m, 1 H), 3.07 (dd, *J* = 13.9, 10.1 Hz, 1 H), 2.78 - 2.67 (m, 1 H), 2.60 (ddd, *J* = 13.7, 4.5, 2.4 Hz, 1 H), 2.30 (s, 1 H), 1.96 - 1.85 (m, 2 H), 1.85 - 1.76 (m, 1 H), 1.76 - 1.68 (m, 1 H), 1.64 - 1.52 (m, 1 H).

LRMS: (ESI^+, ZMD)

277.2 (47), 431.1 (100, $M+H^+$)

Preparation of Deoxycinchonidine (H)



H' **H**

Azo bis(isobutyrodinitrile) (333 mg, 2.00 mmol, 0.40 equiv) and a solution of

Cinchonan-9-ol, 9-(phenol thiocarbonate) (2.15 g, 5.00 mmol) in toluene (50 mL, 0.10 M) were combined in a 100-mL, single-neck, round-bottomed flask fitted with a condenser and argon inlet. Tributyltin hydride (2.73 mL, 10.0 mmol, 2.00 equiv) was then added *via* syringe and the reaction mixture was stirred at reflux for 1 h. The reaction mixture was allowed to cool to 22 °C and was then concentrated on a rotavap (20 mm Hg, 35-40 °C) to afford a yellow liquid.

The product was purified by silica gel flash chromatography [50 g SiO_2, ∅ = 30, 10:1, EtOAc : (10% aq. NH_4OH in MeOH)] to afford 1.38 g (97%) of **H** as a light-brown, crystalline solid. The product was further purified by recrystallization from concentrated pentane solution and cooling overnight in a freezer to afford an off-white, crystalline solid.

Data for **H:**

m.p.: 58 – 59 °C

^{1}H-NMR: (500 MHz, $CDCl_3$)

8.81 (d, *J* = 4.4 Hz, 1 H), 8.09 (dd, *J* = 19.7, 8.4 Hz, 2 H), 7.74 - 7.66 (m, 1 H), 7.61 - 7.52 (m, 1 H), 7.28 (d, *J* = 4.4 Hz, 1 H), 5.79 (ddd, *J* = 17.8, 10.3, 7.6 Hz, 1 H), 4.97 (ddd, *J* = 13.7, 11.3, 1.2 Hz, 2 H), 3.41 (dd, *J* = 13.8, 5.8 Hz, 1 H), 3.28 - 3.15 (m, 3 H), 3.08 (dd, *J* = 13.8, 8.5 Hz, 1 H), 2.85 - 2.74 (m, 1 H), 2.70 (ddd, *J* = 13.8, 4.9, 2.4 Hz, 1 H), 2.33 - 2.22 (m, 1 H), 1.87 - 1.72 (m, 2 H), 1.71 - 1.62 (m, 1 H), 1.62 - 1.51 (m, 1 H), 1.17 (dd, *J* = 13.2, 6.6 Hz, 1 H).

^{13}C-NMR: (126 MHz, $CDCl_3$)

150.04, 148.37, 145.40, 141.77, 130.31, 128.95, 127.76, 126.38, 123.44, 121.52, 114.29, 56.25, 56.05, 41.06, 39.54, 38.18, 28.87, 27.96, 27.90.

analysis: $C_{19}H_{22}N_2O$ (278.39)

Calcd:	C, 81.97;	H, 7.97;	N, 10.06
Found:	C, 82.13;	H, 8.11;	N, 10.13

LRMS: (ESI^+, Q-tof)

279.2 (100, $M+H^+$)

HRMS: $C_{19}H_{23}N_2O^+$ (ESI^+, Q-tof)

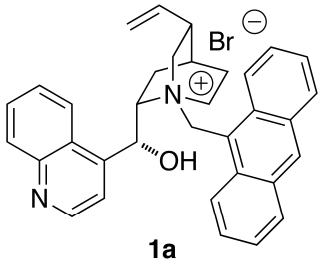
Calcd: 279.1861

Found: 279.1864

TLC: R_f 0.28 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of Cinchonidinium Salts in Series A

Preparation of *N*-9-Anthracenylmethylcinchonidinium Bromide (1a)



1a

Following General Procedure I, cinchonidine (1.31 g, 4.4 mmol), MeCN (25 mL), and 9-bromomethylanthracene (1.32 g, 4.84 mmol, 1.1 equiv) were combined in a 50-mL, single-neck, round-bottomed flask fitted with an argon inlet, wrapped in aluminum foil and the mixture was stirred overnight. Care was taken to avoid light exposure. The solvent was removed on a rotavap (20 mm Hg, 25 °C) and yellow solid residue was triturated with Et_2O (25-mL) and filtered to afford 2.16 g (86%) of **1a** as a light-yellow, crystalline solid. The entire product was further purified by recrystallization from a concentrated CH_2Cl_2 solution by slow diffusion of Et_2O in a chamber.

Data for **1a**:

m.p.: 154 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

9.01 (d, *J* = 4.6 Hz, 1 H), 8.86 - 8.77 (m, 2 H), 8.66 - 8.56 (m, 2 H), 8.22 (d, *J* = 8.5 Hz, 2 H), 8.20 - 8.14 (m, 1 H), 8.08 (d, *J* = 4.5 Hz, 1 H), 7.96 - 7.88 (m, 2 H), 7.83 - 7.75 (m, 2 H), 7.63 (ddd, *J* = 8.4, 6.6, 4.1 Hz, 2 H), 7.11 (d, *J* = 1.8 Hz, 1 H), 6.50 (d, *J* = 14.0 Hz, 1 H), 5.93 (d, *J* = 14.0 Hz, 1 H), 5.71 (ddd, *J* = 17.4, 10.4, 7.2 Hz, 1 H), 5.01 (dd, *J* = 26.2, 13.8 Hz, 2 H), 4.74 - 4.63 (m, 1 H), 4.48 (t, *J* = 9.0 Hz, 1 H), 3.86 (ddd, *J* = 12.5, 4.9, 3.2 Hz, 1 H), 3.24 (dd, *J* = 12.4, 10.9 Hz, 1 H), 2.80 (td, *J* = 11.7, 4.6 Hz, 1 H), 2.45 (s, 1 H), 2.30 (dd, *J* = 13.4, 8.2 Hz, 1 H), 2.18 - 2.07 (m, 1 H), 1.93 (d, *J* = 2.7 Hz, 1 H), 1.62 - 1.50 (m, 1 H), 1.50 - 1.39 (m, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

151.03, 148.72, 147.83, 138.79, 134.80, 134.71, 133.72, 133.04, 133.00, 131.35, 131.16, 131.08, 130.29, 129.29, 126.59, 126.32, 125.60, 125.12, 124.51, 121.55, 121.52, 119.25, 117.63, 69.95, 67.24, 63.74, 56.84, 53.37, 39.66, 27.29, 26.26,

23.04.

LRMS: (ESI^+, Q-tof)

191.1 (35), 295.2 (25), 485.3 m/z (100, M-Br+)

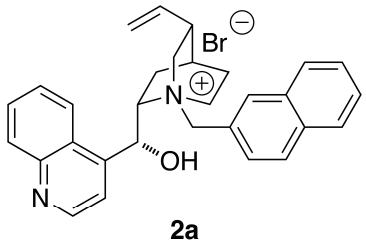
HRMS: $C_{34}H_{33}N_2O^+$ (ESI^+, Q-tof)

Calcd: 485.2593

Found: 485.2598

TLC: R_f 0.31 (CH_2Cl_2/MeOH, 5:1) [silica gel, I_2]

Preparation of *N*-(2-Naphthylmethyl)cinchonidinium Bromide (2a)



2a

Following General Procedure I, cinchonidine (1.47 g, 5 mmol), MeCN (50 mL), and 2-bromomethylnaphthalene (2.35 g, 10.5 mmol, 2.1 equiv) were combined in a 100-mL, single-neck, round-bottomed flask and the mixture was stirred overnight. The solvent was removed on a rotavap (20 mm Hg, 25 °C) and the remaining off-white solid was triturated in Et_2O (3 x 25 mL) then was filtered three times separately to afford 2.27 g (88%) of **2a** as a white, crystalline solid.

Data for **2a**:

m.p.: 236 °C (decomp.)

^{1}H-NMR: (500 MHz, d_6-DMSO)

9.00 (d, J = 4.4 Hz, 1 H), 8.37 - 8.28 (m, 2 H), 8.12 (dd, J = 7.9, 6.0 Hz, 2 H), 8.08 - 8.01 (m, 2 H), 7.89 - 7.80 (m, 3 H), 7.79 - 7.72 (m, 1 H), 7.69 - 7.61 (m, 2 H), 6.78 (d, J = 4.3 Hz, 1 H), 6.62 (s, 1 H), 5.69 (ddd, J = 17.2, 10.5, 6.5 Hz, 1 H), 5.31 (d, J = 12.4 Hz, 1 H), 5.17 (dd, J = 14.5, 13.3 Hz, 2 H), 4.96 (d, J = 10.5 Hz, 1 H), 4.35 (t, J = 10.6 Hz, 1 H), 3.98 (t, J = 8.9 Hz, 1 H), 3.81 (dd, J = 8.9, 3.7 Hz, 1 H), 3.46 - 3.34 (m, 2 H), 2.64 (s, 1 H), 2.11 (dt, J = 22.9, 10.9 Hz, 2 H), 1.99 (d, J = 2.3 Hz, 1 H), 1.79 (t, J = 10.4 Hz, 1 H), 1.31 (dd, J = 12.9, 10.3 Hz, 1 H).

^{13}C-NMR: (126 MHz, d_6-DMSO)

150.17, 147.62, 145.26, 138.13, 133.91, 133.27, 132.55, 130.15, 129.88, 129.45,

128.38, 128.33, 127.65, 127.54, 127.17, 126.83, 125.41, 124.30, 123.64, 120.06, 116.36, 67.57, 64.20, 62.92, 59.29, 50.67, 36.93, 25.87, 24.25, 20.92.

LRMS: (ESI^+, Q-tof)

295.2 (10), 435.2 (100, M-Br+)

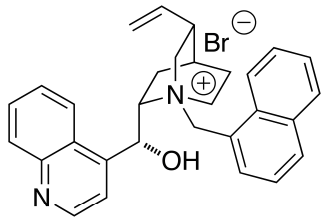
HRMS: $C_{30}H_{31}N_2O^+$ (ESI^+, Q-tof)

Calcd: 435.2436

Found: 435.2439

TLC: R_f 0.25 (CH_2Cl_2/MeOH, 5:1) [silica gel, I_2]

Preparation of *N*-(1-Naphthylmethyl)cinchonidinium Bromide (3a)



3a

Following General Procedure I, cinchonidine (1.47 g, 5.00 mmol), MeCN (50.0 mL), and 1-bromomethylnaphthalene (1.22 g, 5.50 mmol, 1.1 equiv) were combined in a 100-mL, single-neck, round-bottomed flask fitted with an argon inlet and the reaction mixture was stirred overnight. The solvent was removed on a rotavap (20 mm Hg, 25 °C) and remaining solid was triturated with Et_2O (50 mL) then was filtered to afford 2.33 g (90%) of **3a** as a white, crystalline solid. The entire crude product was further purified by recrystallization from a concentrated CH_2Cl_2 solution by slow diffusion of Et_2O in a chamber.

Data for **3a**:

m.p.: 200 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

8.98 (d, *J* = 4.6 Hz, 1 H), 8.40 (d, *J* = 8.2 Hz, 2 H), 8.20 - 8.11 (m, 2 H), 8.09 - 7.99 (m, 3 H), 7.87 (dtd, *J* = 16.5, 6.9, 1.2 Hz, 2 H), 7.79 - 7.73 (m, 1 H), 7.73 - 7.67 (m, 1 H), 7.65 (t, *J* = 7.5 Hz, 1 H), 6.87 (s, 1 H), 5.91 (d, *J* = 13.1 Hz, 1 H), 5.70 (ddd, *J* = 17.3, 10.5, 6.8 Hz, 1 H), 5.37 (d, *J* = 13.1 Hz, 1 H), 5.14 (d, *J* = 17.2 Hz, 1 H), 5.00 (d, *J* = 10.5 Hz, 1 H), 4.68 - 4.57 (m, 1 H), 4.22 (t, *J* = 9.1 Hz, 1 H), 3.88 - 3.78 (m, 1 H), 3.56 (dd, *J* = 12.5, 10.8 Hz, 1 H), 3.16 (td, *J* = 11.4, 3.7

Hz, 1 H), 2.65 (s, 1 H), 2.35 - 2.25 (m, 1 H), 2.24 - 2.14 (m, 1 H), 2.04 (s, 1 H), 1.80 - 1.69 (m, 1 H), 1.42 (td, *J* = 10.2, 3.2 Hz, 1 H).

^{13}C-NMR: (126 MHz, $CDCl_3$)

149.28, 146.89, 144.85, 135.77, 134.29, 133.01, 132.77, 130.27, 129.31, 128.64, 128.06, 127.41, 126.88, 125.70, 124.74, 124.11, 123.45, 123.25, 122.09, 119.48, 117.78, 65.92, 65.80, 59.49, 57.22, 50.99, 37.89, 25.93, 25.31, 22.81

LRMS: (ESI^+, Q-tof)

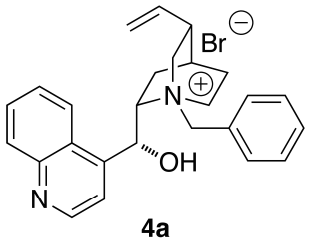
435.2 (100, M-Br^+)

HRMS: $C_{30}H_{31}N_2O^+$ (ESI^+, Q-tof)
Calcd: 435.2436

Found: 435.2436

TLC: R_f 0.31 (CH_2Cl_2/MeOH, 5:1) [silica gel, I_2]

Preparation of *N*-(Benzyl)cinchonidinium Bromide (4a)



4a

Following General Procedure I, cinchonidine (1.47 g, 5.00 mmol), MeCN (50.0 mL), and benzyl bromide (650 µL, 5.50 mmol, 1.1 equiv) were combined in a 100-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred overnight. The reaction mixture was filtered and the filter cake washed several times with MeCN (50 mL). The filtrate was concentrated on a rotavap (20 mm Hg, 25 °C) and the solid residue triturated with Et_2O (50 mL) then filtered. Both filter cakes were combined to afford 2.25 g (97%) of **4a** as a white, crystalline solid. The entire crude product was further purified by recrystallization from a concentrated CH_2Cl_2 solution by slow diffusion of Et_2O in a chamber.

Data for **4a**:

m.p.: 164 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

8.95 (d, *J* = 4.6 Hz, 1 H), 8.28 (d, *J* = 8.2 Hz, 1 H), 8.13 (d, *J* = 8.2 Hz, 1 H), 7.97 (d, *J* = 4.6 Hz, 1 H), 7.90 - 7.84 (m, 1 H), 7.84 - 7.77 (m, 1 H), 7.74 (dd, *J* = 6.5,

2.9 Hz, 2 H), 7.62 - 7.55 (m, 3 H), 6.66 (s, 1 H), 5.69 (ddd, *J* = 17.3, 10.5, 6.8 Hz, 1 H), 5.17 (dd, *J* = 21.7, 14.8 Hz, 2 H), 5.00 (d, *J* = 11.9 Hz, 2 H), 4.50 - 4.40 (m, 1 H), 4.00 (t, *J* = 9.1 Hz, 1 H), 3.66 (ddd, *J* = 12.7, 4.7, 3.3 Hz, 1 H), 3.48 (dd, *J* = 12.7, 10.8 Hz, 1 H), 3.41 (td, *J* = 11.3, 3.8 Hz, 1 H), 2.72 (s, 1 H), 2.33 - 2.19 (m, 2 H), 2.08 (d, *J* = 2.8 Hz, 1 H), 1.88 (ddd, *J* = 15.1, 5.2, 2.6 Hz, 1 H), 1.42 (ddd, *J* = 13.4, 6.5, 3.4 Hz, 1 H).

^{13}C-NMR: (126 MHz, $CDCl_3$)

149.42, 147.14, 144.42, 135.97, 134.02, 129.92, 129.58, 128.62, 128.34, 127.28, 126.90, 123.57, 122.88, 119.76, 117.77, 66.96, 65.06, 62.16, 60.04, 50.28, 37.79, 26.44, 25.08, 22.36

LRMS: (ESI^+, Q-tof)

385.2 (100, M-Br^+)

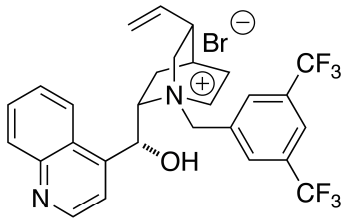
HRMS: $C_{26}H_{29}N_2O^+$ (ESI^+, Q-tof)

Calcd: 385.2280

Found: 385.2282

TLC: R_f 0.27 (CH_2Cl_2/MeOH, 5:1) [silica gel, I_2]

Preparation of *N*-(3,5-Bis-trifluoromethylbenzyl)cinchonidinium Bromide (5a)



5a

Following General Procedure I, cinchonidine 589 mg (2.00 mmol), MeCN (20.0 mL), and bis-(3,5-trifluoromethyl)benzyl bromide (404 μL, 2.20 mmol, 1.1 equiv) were combined in a 50-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred for 72 hours. The solvent was removed on a rotavap (20 mm Hg, 25 °C) and the solid residue was triturated with Et_2O (30 mL) then filtered to afford 1.04 g (87%) of **5a** as a white, crystalline solid. The product was further purified by recrystallization from a concentrated CH_2Cl_2 solution by slow diffusion of Et_2O in a chamber.

Data for **5a**:

m.p.: 173 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

8.95 (d, *J* = 4.6 Hz, 1 H), 8.45 (s, 2 H), 8.33 (d, *J* = 8.1 Hz, 1 H), 8.24 (s, 1 H), 8.13 (dd, *J* = 8.4, 1.0 Hz, 1 H), 7.96 (d, *J* = 4.5 Hz, 1 H), 7.85 (dddd, *J* = 16.5, 8.2, 6.9, 1.3 Hz, 2 H), 6.66 (s, 1 H), 5.69 (ddd, *J* = 17.3, 10.5, 6.8 Hz, 1 H), 5.34 (dd, *J* = 63.7, 12.6 Hz, 2 H), 5.17 (d, *J* = 17.2 Hz, 1 H), 5.01 (d, *J* = 10.5 Hz, 1 H), 4.64 - 4.52 (m, 1 H), 4.05 (t, *J* = 8.4 Hz, 1 H), 3.83 - 3.70 (m, 1 H), 3.47 (dd, *J* = 12.3, 10.8 Hz, 1 H), 3.39 (td, *J* = 11.3, 3.8 Hz, 1 H), 2.74 (s, 1 H), 2.38 - 2.20 (m, 2 H), 2.10 (d, *J* = 2.4 Hz, 1 H), 1.96 - 1.84 (m, 1 H), 1.50 - 1.38 (m, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

151.06, 148.76, 147.28, 138.52, 135.45, 133.68 (q, $J_{C\text{-}F}$ = 33.8 Hz), 132.03, 131.22, 130.41, 129.25, 126.06, 125.50 (m), 124.10, 123.43, 121.31, 117.69, 70.34, 66.32, 63.43, 61.93, 53.02, 39.13, 27.92, 25.86, 22.51.

LRMS: (ESI^+, Q-tof)

521.2 (100, M-Br^+)

HRMS: $C_{28}H_{27}N_2OF_6^+$ (ESI^+, Q-tof)

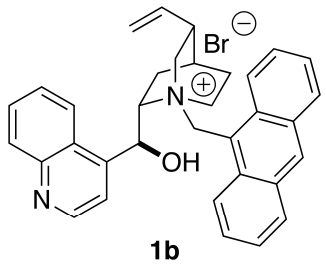
Calcd: 521.2028

Found: 521.2029

TLC: R_f 0.28 (CH_2Cl_2/MeOH, 5:1) [silica gel, I_2]

Preparation of Cinchonidinium Salts in Series B

Preparation of *N*-(9-Anthracenylmethyl)-*epi*-cinchonidinium Bromide (1b)



1b

Following General Procedure I, epi-cinchonidine (100 mg, 0.340 mmol), MeCN (3.4 mL), and 9-bromomethylanthracene (101 mg, 0.374 mmol, 1.10 equiv) were combined in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet, wrapped in aluminum foil and the

mixture was stirred overnight. Care was taken to avoid light exposure. The reaction mixture was diluted with CH_2Cl_2 (~5 mL) then was loaded directly on a silica gel column (15 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH gradient elution) to afford 169 mg (88%) of **1b** as a light-yellow, crystalline solid. The entire product was further purified by recrystallization from a concentrated CH_2Cl_2 solution by slow diffusion of Et_2O in a chamber.

Data for **1b**:

mp: 154-162 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

9.01 (d, *J* = 4.6 Hz, 1 H), 8.85 (s, 1 H), 8.80 (d, *J* = 9.0 Hz, 1 H), 8.63 (d, *J* = 9.0 Hz, 1 H), 8.61 - 8.56 (m, 1 H), 8.23 (d, *J* = 8.5 Hz, 2 H), 8.20 - 8.15 (m, 1 H), 8.08 (d, *J* = 4.5 Hz, 1 H), 7.95 - 7.88 (m, 2 H), 7.80 (dtd, *J* = 7.7, 6.2, 1.1 Hz, 2 H), 7.67 - 7.59 (m, 2 H), 7.11 (d, *J* = 1.9 Hz, 1 H), 6.51 (d, *J* = 14.0 Hz, 1 H), 5.93 (d, *J* = 14.0 Hz, 1 H), 5.70 (ddd, *J* = 17.4, 10.4, 7.2 Hz, 1 H), 5.01 (dd, *J* = 23.7, 13.8 Hz, 2 H), 4.74 - 4.64 (m, 1 H), 4.46 (t, *J* = 9.0 Hz, 1 H), 3.85 (ddd, *J* = 12.5, 4.9, 3.2 Hz, 1 H), 3.24 (dd, *J* = 12.4, 10.9 Hz, 1 H), 2.81 (td, *J* = 11.3, 4.2 Hz, 1 H), 2.45 (s, 1 H), 2.30 (dd, *J* = 13.6, 8.1 Hz, 1 H), 2.19 - 2.08 (m, 1 H), 1.93 (d, *J* = 2.7 Hz, 1 H), 1.62 - 1.52 (m, 1 H), 1.47 (ddd, *J* = 13.3, 8.3, 3.3 Hz, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

151.10, 148.88, 147.65, 138.76, 134.82, 134.73, 133.74, 133.07, 133.03, 131.28, 131.17, 131.09, 130.44, 129.30, 129.25, 129.22, 126.60, 126.56, 126.32, 125.50, 125.07, 124.38, 121.50, 119.23, 117.61, 70.06, 67.24, 63.80, 56.89, 53.42, 39.66, 27.29, 26.27, 23.04

LRMS: (ESI^+, Q-tof)

485.2 (100, M-Br^+)

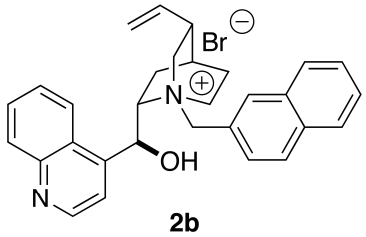
HRMS: $C_{34}H_{33}N_2O^+$ (ESI^+, Q-tof)

Calcd: 485.2593

Found: 485.2594

TLC: R_f 0.58 (CH_2Cl_2/MeOH, 5:1) [silica gel, I_2]

Preparation of *N*-(2-Naphthylmethyl)-*epi*-cinchonidinium Bromide (2b)



2b

Following General Procedure I, epi-cinchonidine (100 mg, 0.340 mmol), MeCN (3.4 mL), and 2-bromomethylnaphthalene (83.0 mg, 0.374 mmol, 1.1 equiv) were combined in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred overnight. Reaction was diluted with CH_2Cl_2 (~5 mL) and MeOH (several drops) then was loaded directly on a silica gel column (15 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH gradient elution) to afford 125 mg (71%) of **2b** as a pale-yellow, crystalline solid.

Data for **2b**

m.p.: 198-210 °C (decomp.)

^{1}H-NMR: (500 MHz, d_6-DMSO)

9.00 (d, *J* = 4.5 Hz, 1 H), 8.37 - 8.29 (m, 2 H), 8.15 - 8.08 (m, 2 H), 8.08 - 8.00 (m, 2 H), 7.85 (ddd, *J* = 11.4, 8.3, 2.5 Hz, 3 H), 7.76 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1 H), 7.69 - 7.60 (m, 2 H), 6.82 (d, *J* = 4.3 Hz, 1 H), 6.62 (d, *J* = 2.9 Hz, 1 H), 5.69 (ddd, *J* = 17.2, 10.6, 6.5 Hz, 1 H), 5.33 (d, *J* = 12.4 Hz, 1 H), 5.17 (t, *J* = 14.5 Hz, 2 H), 4.96 (d, *J* = 10.5 Hz, 1 H), 4.36 (t, *J* = 10.6 Hz, 1 H), 3.98 (t, *J* = 8.9 Hz, 1 H), 3.86 - 3.76 (m, 1 H), 3.39 (ddd, *J* = 18.8, 12.1, 7.8 Hz, 2 H), 2.65 (d, *J* = 3.7 Hz, 1 H), 2.19 - 2.02 (m, 2 H), 1.99 (d, *J* = 2.5 Hz, 1 H), 1.79 (t, *J* = 9.3 Hz, 1 H), 1.31 (dd, *J* = 12.9, 10.2 Hz, 1 H).

^{13}C-NMR: (126 MHz, d_6-DMSO)

150.11, 147.60, 145.21, 138.08, 133.86, 133.24, 132.51, 130.10, 129.84, 129.38, 128.33, 128.28, 127.60, 127.49, 127.12, 126.77, 125.38, 124.28, 123.59, 120.03, 116.31, 67.58, 64.14, 62.88, 59.33, 50.64, 36.90, 25.85, 24.22, 20.90, 19.27.

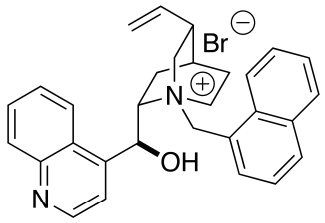
LRMS: (ESI^+, Q-tof)

435.2 (100, M-Br^+)

HRMS: $C_{30}H_{31}N_2O^+$ (ESI^+, Q-tof)
Calcd: 435.2436
Found: 435.2432

TLC: R_f 0.51 (CH_2Cl_2/MeOH, 5:1) [silica gel, I_2]

Preparation of *N*-(1-Naphthylmethyl)-*epi*-cinchonidinium Bromide (3b)



3b

Following General Procedure I, *epi*-cinchonidine (100 mg, 0.340 mmol), MeCN (3.4 mL), and 1-bromomethylnaphthalene (83.0 mg, 0.374 mmol, 1.1 equiv) were combined in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred overnight. The reaction mixture was diluted with CH_2Cl_2 (~5 mL) and then was loaded directly on a silica gel column (15 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH gradient elution) to afford 141 mg (81%) of **3b** as a white, crystalline solid.

Data for **3b**:

m.p.: 189-197 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)
8.98 (d, *J* = 4.5 Hz, 1 H), 8.41 (dd, *J* = 8.0, 4.6 Hz, 2 H), 8.21 - 8.10 (m, 2 H), 8.10 - 7.99 (m, 3 H), 7.93 - 7.80 (m, 2 H), 7.76 (t, *J* = 7.6 Hz, 1 H), 7.72 - 7.67 (m, 1 H), 7.64 (t, *J* = 7.5 Hz, 1 H), 6.87 (s, 1 H), 5.91 (d, *J* = 13.1 Hz, 1 H), 5.70 (ddd, *J* = 17.2, 10.5, 6.8 Hz, 1 H), 5.39 (d, *J* = 13.1 Hz, 1 H), 5.14 (d, *J* = 17.2 Hz, 1 H), 5.00 (d, *J* = 10.5 Hz, 1 H), 4.63 (t, *J* = 10.2 Hz, 1 H), 4.22 (t, *J* = 8.9 Hz, 1 H), 3.89 - 3.79 (m, 1 H), 3.61 - 3.51 (m, 1 H), 3.16 (td, *J* = 11.3, 3.8 Hz, 1 H), 2.65 (s, 1 H), 2.35 - 2.24 (m, 1 H), 2.24 - 2.13 (m, 1 H), 2.04 (s, 1 H), 1.81 - 1.68 (m, 1 H), 1.42 (td, *J* = 10.0, 2.8 Hz, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)
151.07, 148.81, 147.54, 138.73, 135.81, 135.65, 134.80, 133.10, 131.20, 130.64, 130.42, 129.18, 128.96, 127.60, 126.41, 126.16, 124.53, 124.14, 121.35, 117.52,

69.68, 66.74, 62.70, 61.28, 53.30, 39.36, 27.64, 26.08, 22.74.

LRMS: (ESI^+, Q-tof)

435.2 (100, $M\text{-}Br^+$)

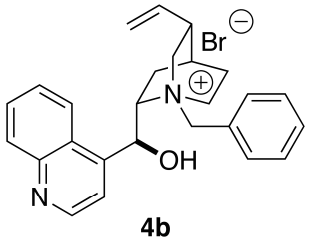
HRMS: $C_{30}H_{31}N_2O^+$ (ESI^+, Q-tof)

Calcd: 435.2436

Found: 435.2444

TLC: R_f 0.55 (CH_2Cl_2/MeOH, 5:1) [silica gel, I_2]

Preparation of *N*-(Benzyl)-*epi*-cinchonidinium Bromide (4b)



4b

Following General Procedure I, *epi*-cinchonidine (100 mg, 0.340 mmol), MeCN (3.4 mL), and benzyl bromide (44.0 μL, 0.374 mmol, 1.10 equiv) were combined in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred overnight. The reaction mixture was diluted with CH_2Cl_2 (~5 mL) and then was loaded directly on a silica gel column (15 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH gradient elution) to afford 137 mg (87%) of **4b** as a white, crystalline solid.

Data for **4b**:

m.p.: 165-169 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

8.95 (d, *J* = 4.6 Hz, 1 H), 8.29 (d, *J* = 7.9 Hz, 1 H), 8.13 (dd, *J* = 8.4, 0.9 Hz, 1 H), 7.97 (d, *J* = 4.4 Hz, 1 H), 7.84 (dtd, *J* = 16.5, 7.0, 1.2 Hz, 2 H), 7.75 (dd, *J* = 6.4, 2.9 Hz, 2 H), 7.59 (dd, *J* = 4.7, 1.8 Hz, 3 H), 6.66 (s, 1 H), 5.69 (ddd, *J* = 17.2, 10.5, 6.8 Hz, 1 H), 5.17 (dd, *J* = 22.4, 14.8 Hz, 2 H), 5.01 (t, *J* = 11.5 Hz, 2 H), 4.46 (t, *J* = 10.5 Hz, 1 H), 4.01 (t, *J* = 9.1 Hz, 1 H), 3.68 (ddd, *J* = 12.7, 4.5, 3.1 Hz, 1 H), 3.48 (dd, *J* = 12.6, 10.9 Hz, 1 H), 3.41 (td, *J* = 11.2, 3.5 Hz, 1 H), 2.72 (s, 1 H), 2.26 (ddd, *J* = 25.9, 14.7, 6.5 Hz, 2 H), 2.07 (s, 1 H), 1.94 - 1.81 (m, 1 H), 1.42 (td, *J* = 10.1, 2.8 Hz, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

151.04, 148.78, 147.52, 138.73, 134.90, 131.76, 131.15, 130.40, 129.15, 128.72, 126.11, 124.08, 121.32, 117.50, 69.70, 66.32, 65.26, 62.10, 52.75, 39.13, 28.04, 25.95, 22.51.

LRMS: (ESI^+, Q-tof)

295.2 (40), 385.2 m/z (100, M-Br^+)

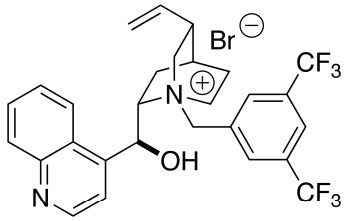
HRMS: $C_{26}H_{29}N_2O^+$ (ESI^+, Q-tof)

Calcd: 385.2280

Found: 385.2285

TLC: R_f 0.51 (CH_2Cl_2/MeOH, 5:1) [silica gel, I_2]

Preparation of *N*-(3,5-Bis-trifluoromethylbenzyl)-*epi*-cinchonidinium Bromide (5b)



5b

Following General Procedure I, *epi*-cinchonidine (100 mg, 0.340 mmol), MeCN (3.4 mL), and bis-(3,5-trifluormethyl)-benzyl bromide (69.0 μL, 0.374 mmol, 1.10 equiv) were combined in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred overnight. The reaction mixture was diluted with CH_2Cl_2 (~5 mL) and then was loaded directly on a silica gel column (15 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH gradient elution) to afford 200 mg (98%) of **5b** as a white, crystalline solid.

Data for **5b**:

m.p.: 200-212 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

8.96 (d, *J* = 4.6 Hz, 1 H), 8.45 (s, 2H), 8.32 (d, *J* = 8.5 Hz, 1 H), 8.25 (s, 1 H), 8.14 (dd, *J* = 8.4, 1.0 Hz, 1 H), 7.96 (d, *J* = 4.4 Hz, 1 H), 7.85 (dddd, *J* = 24.2, 8.2, 6.9, 1.3 Hz, 2H), 6.66 (s, 1 H), 5.69 (ddd, *J* = 17.3, 10.5, 6.8 Hz, 1 H), 5.40 (d, *J* = 12.6 Hz, 1 H), 5.27 (d, *J* = 12.6 Hz, 1 H), 5.17 (d, *J* = 17.2 Hz, 1 H), 5.01 (d, *J* = 10.5 Hz, 1 H), 4.63 - 4.52 (m, 1 H), 4.05 (t, *J* = 9.1 Hz, 1 H), 3.81 - 3.69 (m, 1 H),

3.48 (dd, J = 12.3, 10.8 Hz, 1 H), 3.39 (td, J = 11.3, 4.2 Hz, 1 H), 2.74 (s, 1 H), 2.37 - 2.21 (m, 2H), 2.10 (d, J = 2.3 Hz, 1 H), 1.97 - 1.85 (m, 1 H), 1.45 (td, J = 10.3, 3.3 Hz, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

151.07, 148.80, 147.24, 138.51, 135.43, 133.71 (q, $J_{C\text{-}F}$ = 33.7 Hz), 132.02, 131.21, 130.45, 129.23, 126.07, 125.59, 124.05, 123.42, 121.30, 117.70, 70.39, 66.34, 63.48, 62.00, 53.04, 39.14, 27.92, 25.87, 22.51.

LRMS: (ESI^+, Q-tof)

261.1 (15), 521.2 (100, M-Br^+)

HRMS: $C_{28}H_{27}N_2OF_6^+$ (ESI^+, Q-tof)

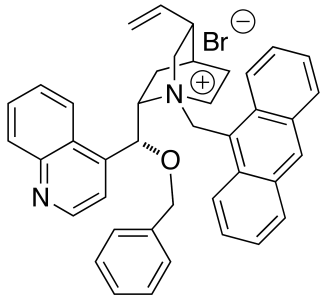
Calcd: 521.2028

Found: 521.2023

TLC: R_f 0.55 (CH_2Cl_2/MeOH, 5:1) [silica gel, I_2]

Preparation of Cinchonidinium Salts in Series C

Preparation of *O*-Benzyl-*N*-(9-Anthracenylmethyl)cinchonidinium Bromide (1c)



1c

Following General Procedure I, a solution *O*-benzyl-cinchonidine (100 mg, 0.260 mmol) in MeCN (2.60 mL, 0.1 M) was combined with 9-bromomethylanthracene (82.0 mg, 0.286 mmol, 1.1 equiv) in a 5-mL, single-neck, round-bottomed flask fitted with an argon inlet, wrapped in aluminum foil and the mixture was stirred overnight. Care was taken to avoid light exposure. The reaction mixture was diluted with CH_2Cl_2 (~5 mL) and then was loaded directly on a silica gel column (15 g SiO_2, ∅ = 20, 100:0 to 2.5:1, TBME/MeOH, gradient elution) to afford 140 mg (82%) of **1c** as a light-yellow, crystalline solid. The entire product was further purified by recrystallization from a concentrated CH_2Cl_2 solution via Et_2O slow diffusion in a chamber.

Data for **1c**:

m.p.: 185-188 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

9.08 (d, *J* = 4.5 Hz, 1 H), 8.87 (s, 1 H), 8.69 (d, *J* = 9.0 Hz, 1 H), 8.59 (s, 1 H), 8.28 - 8.16 (m, 3 H), 8.09 (dd, *J* = 10.3, 6.8 Hz, 2 H), 8.01 - 7.90 (m, 2 H), 7.79 (ddd, *J* = 8.9, 6.6, 1.2 Hz, 1 H), 7.72 (d, *J* = 7.3 Hz, 2 H), 7.66 - 7.47 (m, 5 H), 7.41 - 7.32 (m, 1 H), 7.06 (s, 1 H), 6.27 (d, *J* = 13.7 Hz, 1 H), 5.87 (d, *J* = 13.9 Hz, 1 H), 5.67 (ddd, *J* = 17.4, 10.2, 7.4 Hz, 1 H), 4.99 (ddd, *J* = 17.6, 14.9, 8.0 Hz, 4 H), 4.47 (t, *J* = 8.8 Hz, 1 H), 4.43 - 4.34 (m, 1 H), 3.69 (ddd, *J* = 12.6, 5.6, 3.0 Hz, 1 H), 3.21 - 3.09 (m, 1 H), 2.85 (td, *J* = 11.4, 5.6 Hz, 1 H), 2.61 - 2.50 (m, 1 H), 2.40 (s, 1 H), 2.19 - 2.07 (m, 1 H), 1.97 (d, *J* = 2.8 Hz, 1 H), 1.71 - 1.50 (m, 2H).

^{13}C-NMR: (126 MHz, CD_3OD)

150.46, 148.26, 144.28, 138.46, 138.11, 134.78, 134.43, 133.91, 133.02, 132.96, 132.15, 131.21, 131.15, 130.29, 129.86, 129.77, 129.45, 129.31, 129.17, 126.63, 126.44, 125.33, 124.75, 118.74, 117.82, 79.47, 72.73, 70.28, 63.31, 57.62, 53.82, 39.48, 27.33, 26.17, 23.31.

LRMS: (ESI^+, Q-tof)

575.3 (100, M-Br^+)

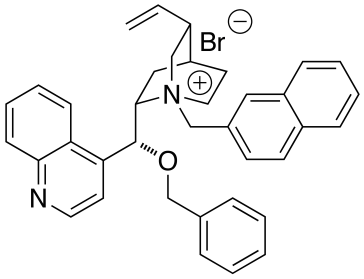
HRMS: $C_{41}H_{39}N_2O^+$ (ESI^+, Q-tof)

Calcd: 575.3062

Found: 575.3059

TLC: R_f 0.24 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of *O*-Benzyl-*N*-(2-Naphthylmethyl)cinchonidinium Bromide (2c)



2c

Following General Procedure I, a solution of *O*-benzyl-cinchonidine (100 mg, 0.260 mmol) in MeCN (2.60 mL, 0.1 M) was combined with 2-bromomethylnaphthalene (63.0 mg, 0.286 mmol, 1.10 equiv) in a 5-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred overnight. The reaction mixture was diluted with CH_2Cl_2 (~5 mL) and then was loaded directly on a silica gel column (15 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH, gradient elution) to afford 146 mg (93%) of **2c** as a pale-yellow, crystalline solid. The entire product was further purified by recrystallization from a CH_2Cl_2 solution via Et_2O slow diffusion in a chamber.

Data for **2c**:

m.p.: 167-175 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

9.03 (d, *J* = 4.4 Hz, 1 H), 8.26 (d, *J* = 7.6 Hz, 1 H), 8.20 (d, *J* = 8.4 Hz, 1 H), 8.08 - 7.95 (m, 5 H), 7.95 - 7.87 (t, *J* = 7.5 Hz, 1 H), 7.83 (t, *J* = 7.4 Hz, 1 H), 7.63 (ddd, *J* = 21.1, 11.3, 6.2 Hz, 4 H), 7.58 - 7.49 (m, 3 H), 7.45 (t, *J* = 7.3 Hz, 1 H), 6.51 (s, 1 H), 5.68 (ddd, *J* = 17.3, 10.4, 6.9 Hz, 1 H), 5.11 (d, *J* = 17.2 Hz, 1 H), 5.00 (d, *J* = 10.5 Hz, 1 H), 4.93 (dd, *J* = 13.9, 12.1 Hz, 2 H), 4.80 (d, *J* = 12.3 Hz, 1 H), 4.67 (d, *J* = 11.5 Hz, 1 H), 4.20 (dd, *J* = 14.5, 7.2 Hz, 1 H), 4.01 (t, *J* = 9.0 Hz, 1 H), 3.63 (ddd, *J* = 12.6, 5.0, 3.0 Hz, 1 H), 3.57 - 3.46 (m, 1 H), 3.40 (td, *J* = 11.3, 4.8 Hz, 1 H), 2.65 (s, 1 H), 2.47 (dd, *J* = 13.1, 7.9 Hz, 1 H), 2.20 (dd, *J* = 18.9, 8.0 Hz, 1 H), 2.07 (d, *J* = 2.6 Hz, 1 H), 1.83 (t, *J* = 9.6 Hz, 1 H), 1.59 (dd, *J* = 13.2, 10.7 Hz, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

151.11, 149.29, 142.99, 138.50, 137.75, 135.37, 135.35, 134.44, 131.45, 130.72, 130.55, 130.49, 130.32, 130.12, 130.10, 129.47, 129.45, 129.02, 128.85, 128.26,

126.95, 125.47, 123.85, 121.75, 117.67, 79.46, 72.48, 69.59, 65.56, 62.24, 52.88, 38.95, 27.97, 25.84, 22.82.

LRMS: (ESI^+, Q-tof)

525.3 (100, $M\text{-}Br^+$)

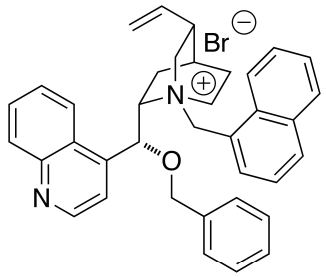
HRMS: $C_{37}H_{37}N_2O^+$ (ESI^+, Q-tof)

Calcd: 525.2906

Found: 525.2910

TLC: R_f 0.28 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of *O*-Benzyl-l-*N*-(1-Naphthylmethyl)cinchonidinium Bromide (3c)



3c

Following General Procedure I, a solution of *O*-benzyl-cinchonidine (100 mg, 0.260 mmol) in MeCN (2.6 mL, 0.1 M) was combined with 1-bromomethylnaphthalene (63.0 mg, 0.286 mmol, 1.10 equiv) in a 5-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred overnight. The reaction mixture was diluted with CH_2Cl_2 (~5 mL) and then was loaded directly on a silica gel column (15 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH, gradient elution) to afford 144 mg (92%) of **3c** as a pale-yellow, crystalline solid. The entire product was further purified by recrystallization from a concentrated CH_2Cl_2 solution via Et_2O slow diffusion in a chamber.

Data for **3c**:

m.p.: 164-173 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

9.05 (d, J = 4.5 Hz, 1 H), 8.43 (d, J = 5.2 Hz, 1 H), 8.21 (d, J = 7.8 Hz, 1 H), 8.14 (d, J = 8.2 Hz, 1 H), 8.03 (dd, J = 11.0, 5.8 Hz, 3 H), 7.98 - 7.80 (m, 3 H), 7.67 (dd, J = 13.4, 7.5 Hz, 3 H), 7.60 (t, J = 7.5 Hz, 1 H), 7.51 (ddd, J = 23.2, 14.8, 7.3 Hz, 4 H), 6.75 (s, 1 H), 5.68 (ddd, J = 17.3, 10.4, 7.0 Hz, 1 H), 5.49 (d, J = 12.9

Hz, 1 H), 5.30 (d, *J* = 13.0 Hz, 1 H), 5.09 (d, *J* = 17.1 Hz, 1 H), 4.97 (dd, *J* = 22.8, 10.9 Hz, 2 H), 4.81 (d, *J* = 11.3 Hz, 1 H), 4.33 - 4.16 (m, 2 H), 3.79 - 3.67 (m, 1 H), 3.44 (t, *J* = 11.7 Hz, 1 H), 3.15 (td, *J* = 11.2, 4.8 Hz, 1 H), 2.59 (s, 1 H), 2.55 - 2.42 (m, 1 H), 2.16 (dd, *J* = 19.2, 7.9 Hz, 1 H), 2.05 (d, *J* = 2.5 Hz, 1 H), 1.73 (t, *J* = 9.4 Hz, 1 H), 1.59 (dd, *J* = 13.0, 10.6 Hz, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

151.10, 149.35, 142.89, 138.47, 137.98, 135.76, 134.53, 133.23, 131.50, 130.70, 130.65, 130.26, 129.94, 129.84, 129.50, 128.91, 127.57, 127.00, 126.36, 124.38, 124.16, 124.08, 121.78, 117.72, 79.46, 72.62, 69.90, 62.63, 61.89, 53.44, 39.17, 27.65, 25.96, 23.07.

LRMS: (ESI^+, Q-tof)

525.3 (100, M-Br^+)

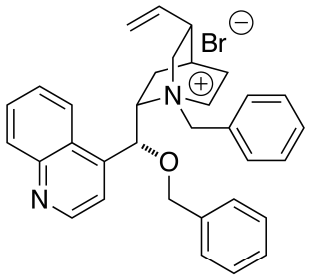
HRMS: $C_{37}H_{37}N_2O^+$ (ESI^+, Q-tof)

Calcd: 525.2906

Found: 525.2914

TLC: R_f 0.31 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of *O*-Benzyl-*N*-(Benzyl)cinchonidinium Bromide (4c)



4c

Following General Procedure I, a solution of *O*-benzyl-cinchonidine (100 mg, 0.260 mmol) in MeCN (2.6 mL, 0.1 M) was combined with benzyl bromide (34 μL, 0.286 mmol, 1.1 equiv) in a 5-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred overnight. The reaction mixture was diluted with CH_2Cl_2 (~5 mL) and then was loaded directly on a silica gel column (15 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH, gradient elution) to afford 134 mg (93%) of **4c** as a white, crystalline solid. The entire product was further purified by recrystallization from a concentrated CH_2Cl_2 solution via Et_2O slow

diffusion in a chamber.

Data for **4c**:

m.p.: 201 - 205 °C(decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

9.02 (d, *J* = 4.5 Hz, 1 H), 8.25 (d, *J* = 7.6 Hz, 1 H), 8.19 (dd, *J* = 8.4, 0.9 Hz, 1 H), 7.95 (d, *J* = 4.5 Hz, 1 H), 7.91 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1 H), 7.85 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1 H), 7.61 - 7.45 (m, 9 H), 7.44 - 7.38 (m, 1 H), 6.46 (s, 1 H), 5.67 (ddd, *J* = 17.3, 10.5, 6.9 Hz, 1 H), 5.11 (d, *J* = 17.2 Hz, 1 H), 4.99 (d, *J* = 10.5 Hz, 1 H), 4.90 - 4.76 (m, 2 H), 4.65 (dd, *J* = 11.8, 7.1 Hz, 2 H), 4.17 - 4.06 (m, 1 H), 3.97 (dd, *J* = 9.8, 8.4 Hz, 1 H), 3.57 (ddd, *J* = 12.8, 5.3, 3.1 Hz, 1 H), 3.43 (dd, *J* = 12.8, 10.7 Hz, 1 H), 3.32 (dd, *J* = 16.6, 10.6 Hz, 1 H), 2.72 - 2.61 (m, 1 H), 2.49 - 2.38 (m, 1 H), 2.24 - 2.12 (m, 1 H), 2.07 (dd, *J* = 6.0, 2.9 Hz, 1 H), 1.84 (ddd, *J* = 14.4, 4.7, 2.3 Hz, 1 H), 1.61 - 1.49 (m, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

151.09, 149.26, 142.99, 138.51, 137.69, 134.83, 131.83, 131.46, 130.65, 130.41, 130.37, 130.24, 130.04, 129.50, 128.25, 126.93, 123.95, 121.75, 117.66, 73.17, 72.41, 69.59, 65.33, 61.98, 52.70, 38.91, 27.99, 25.79, 22.80.

LRMS: (ESI^+, Q-tof)

475.3 (100, M-Br^+)

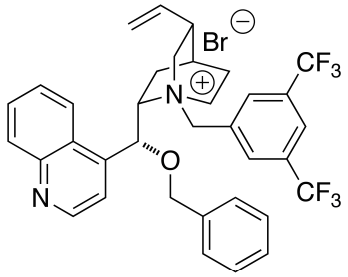
HRMS: $C_{33}H_{35}N_2O^+$ (ESI^+, Q-tof)

Calcd: 475.2749

Found: 475.2756

TLC: R_f 0.26 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of *O*-Benzyl-*N*-(3,5-Bis-trifluoromethylbenzyl)cinchonidinium Bromide (5c)



5c

Following General Procedure I, a solution of *O*-benzyl-cinchonidine (100 mg, 0.260 mmol) in MeCN (2.60 mL, 0.1 M) was combined with benzyl bromide (34.0 μL, 0.286 mmol, 1.10 equiv) in a 5-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred overnight. The reaction mixture was diluted with CH_2Cl_2 (~5 mL) and then was loaded directly on a silica gel column (15 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH, gradient elution) to afford 166 mg (92%) of **5c** as a white, crystalline solid. The entire product was further purified by trituration in hexane then filtered.

Data for **5c**:

m.p.: 164-170 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

9.02 (d, *J* = 4.5 Hz, 1 H), 8.31 (d, *J* = 7.8 Hz, 1 H), 8.24 (s, 1 H), 8.21 - 8.12 (m, 3 H), 7.96 (d, *J* = 4.5 Hz, 1 H), 7.92 (t, *J* = 7.2 Hz, 1 H), 7.87 (dd, *J* = 11.2, 3.9 Hz, 1 H), 7.60 (d, *J* = 7.2 Hz, 2 H), 7.48 (t, *J* = 7.5 Hz, 2 H), 7.41 (t, *J* = 7.4 Hz, 1 H), 6.46 (s, 1 H), 5.67 (ddd, *J* = 17.3, 10.5, 6.9 Hz, 1 H), 5.12 (t, *J* = 14.8 Hz, 2 H), 5.00 (d, *J* = 10.5 Hz, 1 H), 4.88 (d, *J* = 11.5 Hz, 1 H), 4.75 (d, *J* = 12.5 Hz, 1 H), 4.68 (d, *J* = 11.4 Hz, 1 H), 4.19 (dd, *J* = 12.4, 8.7 Hz, 1 H), 4.02 (t, *J* = 9.0 Hz, 1 H), 3.68 (ddd, *J* = 12.3, 4.7, 3.2 Hz, 1 H), 3.47 - 3.37 (m, 1 H), 3.36 - 3.21 (m, 1 H), 2.70 (s, 1 H), 2.53 - 2.41 (m, 1 H), 2.28 - 2.15 (m, 1 H), 2.10 (d, *J* = 2.6 Hz, 1 H), 1.87 (t, *J* = 9.5 Hz, 1 H), 1.58 (dd, *J* = 13.2, 10.6 Hz, 1 H).

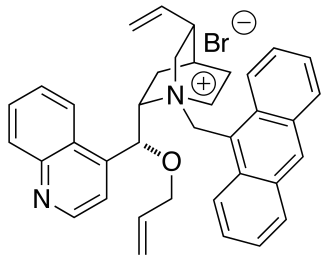
^{13}C-NMR: (126 MHz, CD_3OD)

151.11, 149.27, 142.81, 138.25, 137.86, 135.29, 133.68 (q, $J_{C\text{-}F}$ = 33.8 Hz), 131.46 (d, $J_{C\text{-}F}$ = 4.3 Hz), 130.71, 130.41, 130.23, 130.09, 129.59, 126.87, 125.76 (d, $J_{C\text{-}F}$ = 3.7 Hz), 125.52, 123.95, 123.35, 121.68, 117.86, 73.37 (d, $J_{C\text{-}F}$ = 11.2 Hz), 72.52, 70.28, 63.61, 61.91, 52.97, 38.90, 27.85, 25.74, 22.79.

LRMS: (ESI^+, Q-tof)
611.2 (100, M-Br^+)
HRMS: $C_{35}H_{33}N_2OF_6^+$ (ESI^+, Q-tof)
Calcd: 611.2497
Found: 611.2499
TLC: R_f 0.29 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of Cinchonidinium Salts in Series D

Preparation of *O*-Allyl-*N*-(9-Anthracenylmethyl)cinchonidinium Bromide (1d)



1d

Following General Procedure I, a solution of *O*-allyl-cinchonidine (190 mg, 0.568 mmol) in MeCN (5.70 mL, 0.1 M) was combined with 9-bromomethylanthracene (169 mg, 0.620 mmol, 1.10 equiv) in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet, wrapped in aluminum foil and the mixture was stirred overnight. Care was taken to avoid light exposure. The solvent was removed on a rotavap (20 mm Hg, 25 °C) and the yellow, solid residue was purified by silica gel flash chromatography (20 g SiO_2, ∅=20, 100:0 to 10:1, CH_2Cl_2/MeOH, gradient elution) to afford 197 mg (57%) of **1d** as a yellow, crystalline solid.

Data for **1d**:

m.p.: 102 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)
9.04 (d, *J* = 4.5 Hz, 1 H), 8.89 (s, 1 H), 8.77 (d, *J* = 9.0 Hz, 1 H), 8.59 (d, *J* = 5.8 Hz, 1 H), 8.45 (d, *J* = 9.0 Hz, 1 H), 8.30 - 8.17 (m, 3 H), 7.94 (dt, *J* = 12.5, 5.7 Hz, 3 H), 7.85 - 7.71 (m, 2 H), 7.69 - 7.59 (m, 2 H), 6.95 (s, 1 H), 6.41 (ddd, *J* = 15.4, 10.7, 5.3 Hz, 2 H), 5.91 (d, *J* = 14.0 Hz, 1 H), 5.75 - 5.62 (m, 2 H), 5.55 (d, *J* = 10.5 Hz, 1 H), 4.99 (t, *J* = 13.3 Hz, 2 H), 4.60 - 4.36 (m, 4 H), 3.80 (dd, *J* = 7.5, 3.2 Hz, 1 H), 3.24 (t, *J* = 11.6 Hz, 1 H), 2.90 (td, *J* = 11.2, 4.9 Hz, 1 H), 2.54 -

2.35 (m, 2 H), 2.18 (t, J = 11.2 Hz, 1 H), 1.97 (d, J = 2.5 Hz, 1 H), 1.61 (dd, J = 24.9, 12.3 Hz, 2 H).

^{13}C NMR: (126 MHz, CD_3OD)

151.05, 149.35, 142.99, 138.54, 134.81, 134.71, 134.62, 133.92, 133.10, 133.03, 131.53, 131.30, 131.15, 130.60, 129.45, 129.43, 129.25, 127.09, 126.66, 126.56, 125.42, 124.94, 124.45, 121.68, 119.05, 118.91, 117.80, 71.42, 70.04, 63.50, 57.41, 53.65, 39.50, 27.32, 26.26, 23.34.

LRMS: (ESI^+, Q-tof)

191.1 (10), 335.2 (5), 525.3 (100, M-Br^+)

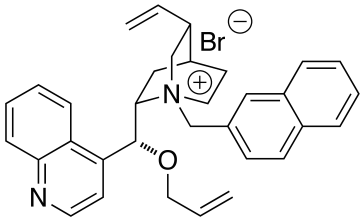
HRMS: $C_{37}H_{37}N_2O^+$ (ESI^+, Q-tof)

Calcd: 525.2906

Found: 525.2906

TLC: R_f 0.32 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of *O*-Allyl-*N*-(*2*-Naphthylmethyl)cinchonidinium Bromide (2d)



2d

Following General Procedure I, a solution of *O*-allyl-cinchonidine (201 mg, 0.598 mmol) in MeCN (6.00 mL, 0.1 M) was combined with 2-bromomethylnaphthalene (146 mg, 0.660 mmol, 1.10 equiv) in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred overnight. The solvent was removed on a rotavap (20 mm Hg, 25 °C) and the solid residue was triturated with Et_2O (10 mL) and then filtered. The filter cake was purified by silica gel flash chromatography (20 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH, gradient elution) to afford 215 mg (64%) of **2d** as an off-white, crystalline solid.

Data for **2d**:

m.p.: 133 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

8.99 (d, *J* = 4.4 Hz, 1 H), 8.31 (d, *J* = 6.4 Hz, 2 H), 8.17 (d, *J* = 8.4 Hz, 1 H), 8.07 (dd, *J* = 18.2, 8.2 Hz, 2 H), 7.99 (d, *J* = 7.6 Hz, 1 H), 7.94 - 7.80 (m, 3 H), 7.77 (d, *J* = 8.4 Hz, 1 H), 7.68 - 7.59 (m, 2 H), 6.53 (s, 1 H), 6.28 (dq, *J* = 10.5, 5.8 Hz, 1 H), 5.71 (ddd, *J* = 17.3, 10.4, 7.0 Hz, 1 H), 5.52 (d, *J* = 17.2 Hz, 1 H), 5.41 (d, *J* = 10.4 Hz, 1 H), 5.28 (d, *J* = 12.4 Hz, 1 H), 5.14 (d, *J* = 14.7 Hz, 2 H), 5.01 (d, *J* = 10.5 Hz, 1 H), 4.41 - 4.19 (m, 3 H), 4.06 (t, *J* = 8.6 Hz, 1 H), 3.77 - 3.65 (m, 1 H), 3.63 - 3.45 (m, 2 H), 2.69 (s, 1 H), 2.51 - 2.37 (m, 1 H), 2.28 (t, *J* = 11.6 Hz, 1 H), 2.10 (d, *J* = 2.1 Hz, 1 H), 1.90 (t, *J* = 10.1 Hz, 1 H), 1.58 (dd, *J* = 13.1, 10.9 Hz, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

151.04, 149.22, 143.33, 138.54, 135.49, 135.42, 134.76, 134.56, 131.43, 130.75, 130.58, 130.17, 129.54, 129.41, 129.00, 128.86, 128.22, 126.87, 125.79, 124.10, 121.39, 119.40, 117.69, 73.98, 71.34, 69.77, 66.05, 62.13, 53.10, 39.02, 28.08, 25.95, 22.80.

LRMS: (ESI^+, Q-tof)

475.3 (100, M-Br^+)

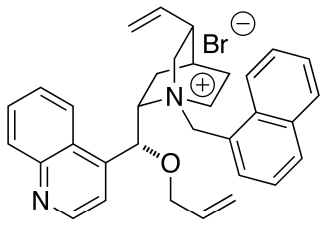
HRMS: $C_{33}H_{35}N_2O^+$ (ESI^+, Q-tof)

Calcd: 475.2749

Found: 475.2758

TLC: R_f 0.33 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of *O*-Allyl-*N*-(1-Naphthylmethyl)cinchonidinium Bromide (3d)



3d

Following General Procedure I, a solution of *O*-allyl-cinchonidine (201 mg, 0.598 mmol) in MeCN (6.00 mL, 0.1 M) was combined with 1-bromomethylnaphthalene (146 mg, 0.660

mmol, 1.10 equiv) in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred overnight. The solvent was removed on a rotavap (20 mm Hg, 25 °C) and the solid residue was triturated with Et_2O (10 mL) then filtered. The filter cake was purified by silica gel flash chromatography (20 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH, gradient elution) to afford 280 mg (84%) of **3d** as a white, crystalline solid.

Data for **3d**:

m.p.: 119 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

9.01 (d, *J* = 4.5 Hz, 1 H), 8.42 (d, *J* = 8.1 Hz, 1 H), 8.30 (d, *J* = 8.5 Hz, 1 H), 8.18 (t, *J* = 7.3 Hz, 2 H), 8.06 (dd, *J* = 15.2, 7.6 Hz, 2 H), 7.95 - 7.83 (m, 3 H), 7.72 (dd, *J* = 15.4, 8.0 Hz, 2 H), 7.65 (t, *J* = 7.5 Hz, 1 H), 6.69 (s, 1 H), 6.35 (ddd, *J* = 22.2, 10.9, 5.6 Hz, 1 H), 5.71 (ddd, *J* = 17.3, 15.9, 10.1 Hz, 2 H), 5.60 (dd, *J* = 17.2, 1.2 Hz, 1 H), 5.49 (d, *J* = 10.5 Hz, 1 H), 5.38 (d, *J* = 13.0 Hz, 1 H), 5.12 (d, *J* = 17.2 Hz, 1 H), 4.99 (d, *J* = 10.5 Hz, 1 H), 4.38 (ddd, *J* = 17.4, 12.3, 5.6 Hz, 3 H), 4.23 (t, *J* = 9.1 Hz, 1 H), 3.90 - 3.75 (m, 1 H), 3.55 (t, *J* = 11.7 Hz, 1 H), 3.24 (td, *J* = 11.4, 4.5 Hz, 1 H), 2.65 (s, 1 H), 2.44 (dd, *J* = 13.2, 8.3 Hz, 1 H), 2.23 (dd, *J* = 19.5, 7.7 Hz, 1 H), 2.07 (d, *J* = 2.4 Hz, 1 H), 1.79 (t, *J* = 9.3 Hz, 1 H), 1.55 (dd, *J* = 13.1, 10.6 Hz, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

151.04, 149.27, 143.04, 138.51, 135.76, 134.72, 134.67, 133.21, 131.45, 130.71, 130.60, 129.42, 128.92, 127.64, 126.91, 126.47, 124.45, 124.32, 124.17, 121.43, 119.28, 117.69, 71.40, 69.73, 62.60, 61.86, 53.49, 39.19, 27.67, 26.04, 23.07.

LRMS: (ESI^+, Q-tof)

335.2 (5), 475.3 (100, M-Br^+)

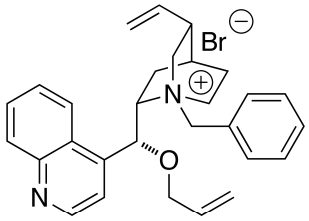
HRMS: $C_{33}H_{35}N_2O^+$ (ESI^+, Q-tof)

Calcd: 475.2749

Found: 475.2758

TLC: R_f 0.28 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of *O*-Allyl-*N*-(Benzyl)cinchonidinium Bromide (4d)



4d

Following General Procedure I, a solution of *O*-allyl-cinchonidine (201 mg, 0.598 mmol) in MeCN (6.00 mL, 0.1 M) was combined with benzyl bromide (78.5 μL, 0.660 mmol, 1.10 equiv) in a 10-mL, single-neck, round bottom flask fitted with an argon inlet and the mixture was stirred overnight. The solvent was removed on a rotavap (20 mm Hg, 25 °C) and the solid residue was triturated with hexane then filtered. The filter cake was purified by silica gel flash chromatography (20 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH, gradient elution) to afford 222 mg (73%) of **4d** as a white, crystalline solid.

Data for **4d**:

m.p.: 123 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

8.98 (d, *J* = 4.5 Hz, 1 H), 8.28 (d, *J* = 8.3 Hz, 1 H), 8.16 (d, *J* = 8.4 Hz, 1 H), 7.94 - 7.80 (m, 3 H), 7.73 (dd, *J* = 6.3, 2.7 Hz, 2 H), 7.65 - 7.55 (m, 3 H), 6.47 (s, 1 H), 6.24 (ddd, *J* = 22.9, 11.0, 5.8 Hz, 1 H), 5.69 (ddd, *J* = 17.3, 10.5, 6.9 Hz, 1 H), 5.49 (dd, *J* = 17.2, 1.3 Hz, 1 H), 5.38 (d, *J* = 10.4 Hz, 1 H), 5.12 (t, *J* = 14.9 Hz, 2 H), 4.99 (dd, *J* = 18.8, 11.4 Hz, 2 H), 4.26 (ddd, *J* = 17.5, 12.3, 5.7 Hz, 3 H), 4.01 (t, *J* = 9.0 Hz, 1 H), 3.63 (ddd, *J* = 12.6, 5.1, 3.1 Hz, 1 H), 3.56 - 3.38 (m, 2 H), 2.72 (s, 1 H), 2.42 (dd, *J* = 13.1, 7.9 Hz, 1 H), 2.32 - 2.19 (m, 1 H), 2.10 (d, *J* = 2.8 Hz, 1 H), 1.92 (t, *J* = 9.5 Hz, 1 H), 1.61 - 1.48 (m, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

151.02, 149.22, 143.25, 138.52, 134.91, 134.69, 131.87, 131.40, 130.59, 130.47, 129.39, 128.51, 126.84, 124.07, 121.37, 119.43, 117.68, 73.99, 71.33, 69.76, 65.86, 62.02, 52.94, 38.98, 28.08, 25.92, 22.80.

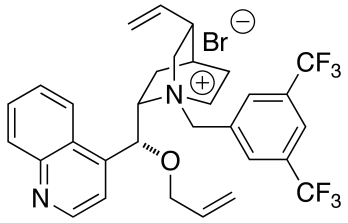
LRMS: (ESI^+, Q-tof)

425.3 (100, M-Br^+)

HRMS: $C_{29}H_{33}N_2O^+$ (ESI^+, Q-tof)
Calcd: 425.2593
Found: 425.2603

TLC: R_f 0.28 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of *O*-Allyl-*N*-(3,5-Bistrifluoromethylbenzyl)cinchonidinium Bromide (5d)



5d

Following General Procedure I, a solution of *O*-allyl-cinchonidine (201 mg, 0.598 mmol) in MeCN (6.00 mL, 0.1 M) was combined with bis-(3,5-trifluoromethyl)benzyl bromide (121 μL, 0.660 mmol, 1.10 equiv) in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred overnight. The solvent was removed on a rotavap (20 mm Hg, 25 °C) and the solid residue was triturated with hexane then filtered. The filter cake was purified by silica gel flash chromatography (20 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH, gradient elution) to afford 307 mg (85%) of **5d** as a white, crystalline solid.

Data for **5d:**

m.p.: 140 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)
8.98 (d, *J* = 4.6 Hz, 1 H), 8.46 (s, 2 H), 8.31 (d, *J* = 8.2 Hz, 1 H), 8.26 (s, 1 H), 8.20 - 8.13 (m, 1 H), 7.94 - 7.81 (m, 3 H), 6.45 (s, 1 H), 6.24 (ddd, *J* = 22.9, 10.9, 5.7 Hz, 1 H), 5.70 (ddd, *J* = 17.3, 10.5, 7.0 Hz, 1 H), 5.49 (dd, *J* = 17.2, 1.5 Hz, 1 H), 5.36 (dd, *J* = 10.5, 1.2 Hz, 1 H), 5.27 (dd, *J* = 36.6, 12.6 Hz, 2 H), 5.15 (d, *J* = 17.2 Hz, 1 H), 5.02 (d, *J* = 10.5 Hz, 1 H), 4.37 (td, *J* = 11.8, 4.7 Hz, 2 H), 4.19 (dd, *J* = 12.2, 5.5 Hz, 1 H), 4.10 - 3.98 (m, 1 H), 3.71 (ddd, *J* = 12.3, 5.0, 3.1 Hz, 1 H), 3.54 - 3.40 (m, 2 H), 2.74 (s, 1 H), 2.48 (dd, *J* = 13.1, 7.8 Hz, 1 H), 2.35 - 2.23 (m, 1 H), 2.13 (d, *J* = 2.9 Hz, 1 H), 1.95 (t, *J* = 9.5 Hz, 1 H), 1.59 (td, *J* = 10.5, 3.1 Hz, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

151.02, 149.25, 143.04, 138.29, 135.50, 134.81, 133.74 (q, $J_{C\text{-}F}$ = 33.9 Hz), 131.81, 131.43, 130.62, 129.48, 126.79, 125.77, 125.58, 124.08, 123.41, 121.35, 119.05, 117.89, 73.95, 71.30, 70.58, 64.18, 61.95, 53.27, 39.00, 27.97, 25.87, 22.76.

LRMS: (ESI^+, Q-tof)

561.2 (100, M-Br^+)

HRMS: $C_{31}H_{31}N_2OF_6^+$ (ESI^+, Q-tof)

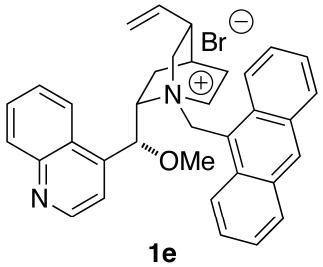
Calcd: 561.2341

Found: 561.2344

TLC: R_f 0.32 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of Cinchonidinium Salts in Series E

Preparation of *O*-Methyl-*N*-(9-Anthracenylmethyl)cinchonidinium Bromide (1e)



1e

Following General Procedure I, *O*-methyl-cinchonidine (100 mg, 0.324 mmol), MeCN (3.2 mL, 0.1 M), and 9-bromomethylanthracene (97.0 mg, 0.360 mmol, 1.10 equiv) were combined in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet, wrapped in aluminum foil and the mixture was stirred overnight. Care was taken to avoid light exposure. The solvent was removed on a rotavap (20 mm Hg, 25 °C) and the yellow solid residue was then purified by silica gel flash chromatography (15 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH, gradient elution) to afford 141 mg (75%) of **1e** as a light-yellow, crystalline solid.

Data for **1e**:

m.p.: 120 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

9.05 (d, *J* = 4.5 Hz, 1 H), 8.89 (s, 1 H), 8.75 (d, *J* = 9.0 Hz, 1 H), 8.57 (d, *J* = 8.7 Hz, 1 H), 8.52 (d, *J* = 9.0 Hz, 1 H), 8.23 (ddd, *J* = 9.2, 7.7, 4.6 Hz, 3 H), 7.98 -

7.89 (m, 3 H), 7.85 (ddd, *J* = 8.9, 6.6, 1.2 Hz, 1 H), 7.80 (ddd, *J* = 8.9, 6.5, 1.2 Hz, 1 H), 7.65 (ddd, *J* = 11.6, 8.3, 6.8 Hz, 2 H), 6.82 (s, 1 H), 6.42 (d, *J* = 14.0 Hz, 1 H), 5.90 (d, *J* = 14.0 Hz, 1 H), 5.69 (ddd, *J* = 17.4, 10.4, 7.3 Hz, 1 H), 5.04 - 4.93 (m, 2 H), 4.55 - 4.40 (m, 2 H), 3.85 (s, 3 H), 3.78 (ddd, *J* = 12.5, 5.4, 3.1 Hz, 1 H), 3.24 (dd, *J* = 12.4, 10.9 Hz, 1 H), 2.95 - 2.85 (m, 1 H), 2.42 (dd, *J* = 15.6, 5.0 Hz, 2 H), 2.20 - 2.08 (m, 1 H), 1.95 (d, *J* = 2.8 Hz, 1 H), 1.58 (ddd, *J* = 13.8, 13.4, 8.4 Hz, 2 H).

^{13}C-NMR: (126 MHz, CD_3OD)

151.06, 149.35, 142.98, 138.54, 134.79, 134.66, 133.90, 133.09, 133.05, 131.50, 131.28, 131.17, 130.59, 129.43, 129.41, 129.36, 127.23, 126.65, 126.61, 125.37, 124.81, 124.44, 121.67, 119.00, 117.77, 70.22, 63.45, 57.51, 57.48, 53.77, 39.53, 27.31, 26.22, 23.13.

LRMS: (ESI^+, Q-tof)

191.1 (15), 499.3 (100, M-Br^+)

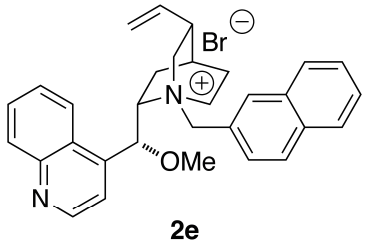
HRMS: $C_{35}H_{35}N_2O^+$ (ESI^+, Q-tof)

Calcd: 499.2749

Found: 499.2739

TLC: R_f 0.34 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of *O*-Methyl-*N*-(2-Naphthylmethyl)cinchonidinium Bromide (2e)



2e

Following General Procedure I, *O*-methyl-cinchonidine (185 mg, 0.600 mmol), MeCN (6.0 mL, 0.1 M), and 2-bromomethylnaphthalene (146 mg, 0.660 mmol, 1.10 equiv) were combined in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred overnight. The solvent was removed on a rotavap (20 mm Hg, 25 °C) and the solid residue was then purified by silica gel flash chromatography (15 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH, gradient elution) to afford 265 mg (83%) of **2e** as an off-white, crystalline

solid.

Data for **2e**:

m.p.: 144 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

9.00 (d, *J* = 4.5 Hz, 1 H), 8.39 - 8.28 (m, 2 H), 8.17 (d, *J* = 8.4 Hz, 1 H), 8.07 (dd, *J* = 16.9, 7.8 Hz, 2 H), 8.00 (d, *J* = 8.3 Hz, 1 H), 7.93 - 7.87 (m, 1 H), 7.87 - 7.77 (m, 3 H), 7.68 - 7.59 (m, 2 H), 6.39 (s, 1 H), 5.70 (ddd, *J* = 17.3, 10.4, 6.9 Hz, 1 H), 5.27 (d, *J* = 12.4 Hz, 1 H), 5.14 (dd, *J* = 15.1, 4.8 Hz, 2 H), 5.01 (d, *J* = 10.5 Hz, 1 H), 4.33 (t, *J* = 10.8 Hz, 1 H), 4.04 (t, *J* = 9.0 Hz, 1 H), 3.78 - 3.69 (m, 1 H), 3.65 (s, 3 H), 3.54 (dd, *J* = 22.1, 9.9 Hz, 2 H), 2.69 (s, 1 H), 2.39 (dd, *J* = 13.1, 8.1 Hz, 1 H), 2.25 (t, *J* = 11.6 Hz, 1 H), 2.08 (d, *J* = 2.5 Hz, 1 H), 1.88 (t, *J* = 9.4 Hz, 1 H), 1.54 (dd, *J* = 13.3, 10.6 Hz, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

151.04, 149.23, 143.10, 138.58, 135.54, 135.42, 134.57, 131.39, 130.81, 130.55, 130.10, 129.53, 129.36, 128.97, 128.86, 128.19, 127.01, 125.88, 124.15, 121.34, 117.65, 76.06, 69.81, 66.04, 62.04, 57.42, 53.03, 39.03, 28.05, 25.90, 22.74.

LRMS: (ESI^+, Q-tof)

449.2 (100, M-Br^+)

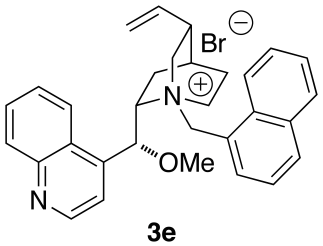
HRMS: $C_{31}H_{33}N_2O^+$ (ESI^+, Q-tof)

Calcd: 449.2593

Found: 449.2594

TLC: R_f 0.38 (CH_2Cl_2:MeOH, 10:1) [silica gel, I_2]

Preparation of *O*-Methyl-N-(1-Naphthylmethyl)cinchonidinium Bromide (3e)



3e

Following General Procedure I, *O*-methyl-cinchonidine (185 mg, 0.600 mmol), MeCN (6.0 mL, 0.1 M), and 1-bromomethylnaphthalene (146 mg, 0.660 mmol, 1.10 equiv) were combined in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet and the

mixture was stirred overnight. The solvent was removed on a rotavap (20 mm Hg, 25 °C) and the solid residue was triturated with Et_2O then filtered. The filter cake was purified by silica gel flash chromatography (15 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH, gradient elution) to afford 287 mg (90%) of **3e** as a white, crystalline solid.

Data for **3e**:

m.p.: 132 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

9.02 (d, *J* = 4.5 Hz, 1 H), 8.40 (d, *J* = 8.2 Hz, 1 H), 8.34 (d, *J* = 8.6 Hz, 1 H), 8.21 - 8.14 (m, 2 H), 8.06 (dd, *J* = 11.3, 7.7 Hz, 2 H), 7.94 - 7.83 (m, 3 H), 7.79 (dd, *J* = 11.3, 4.1 Hz, 1 H), 7.75 - 7.69 (m, 1 H), 7.66 (t, *J* = 7.5 Hz, 1 H), 6.55 (s, 1 H), 5.70 (ddd, *J* = 17.3, 16.5, 10.0 Hz, 2 H), 5.37 (d, *J* = 13.1 Hz, 1 H), 5.10 (d, *J* = 17.2 Hz, 1 H), 4.99 (d, *J* = 10.5 Hz, 1 H), 4.39 (ddd, *J* = 11.7, 8.0, 4.6 Hz, 1 H), 4.21 (t, *J* = 9.0 Hz, 1 H), 3.78 (ddd, *J* = 12.7, 5.0, 3.2 Hz, 1 H), 3.74 (s, 3 H), 3.56 - 3.45 (m, 1 H), 3.30 - 3.21 (m, 1 H), 2.63 (s, 1 H), 2.40 (dd, *J* = 13.3, 8.0 Hz, 1 H), 2.21 (dd, *J* = 19.5, 8.4 Hz, 1 H), 2.05 (d, *J* = 2.9 Hz, 1 H), 1.86 - 1.71 (m, 1 H), 1.54 (td, *J* = 10.5, 3.1 Hz, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

151.05, 149.30, 143.00, 138.51, 135.82, 135.77, 134.71, 133.22, 131.42, 130.71, 130.60, 129.37, 129.07, 127.65, 127.07, 126.45, 124.39, 124.37, 124.18, 121.42, 117.69, 76.30, 69.98, 62.55, 62.03, 57.43, 53.53, 39.24, 27.70, 26.03, 22.87.

LRMS: (ESI^+, Q-tof)

449.2 (100, M-Br^+)

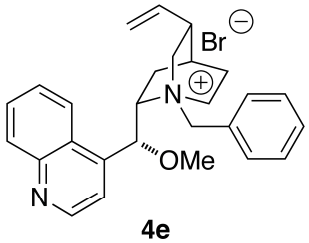
HRMS: $C_{31}H_{33}N_2O^+$ (ESI^+, Q-tof)

Calcd: 449.2593

Found: 449.2574

TLC: R_f 0.38 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of *O*-Methyl-*N*-(Benzyl)cinchonidinium Bromide (4e)



4e

Following General Procedure I, *O*-methyl-cinchonidine (185 mg, 0.60 mmol), MeCN (6.0 mL, 0.1 M), and benzyl bromide (78.0 μL, 0.660 mmol, 1.10 equiv) were combined in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred for 41 h. The solvent was removed on a rotavap (20 mm Hg, 25 °C) and the solid residue was triturated with hexanes then filtered. The filter cake was purified by silica gel flash chromatography (15 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH, gradient elution) to afford 211 mg (73%) of **4e** as a white, crystalline solid.

Data **4e**:

m.p.: 140 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

8.98 (d, *J* = 4.5 Hz, 1 H), 8.28 (d, *J* = 8.3 Hz, 1 H), 8.19 - 8.12 (m, 1 H), 7.93 - 7.86 (m, 1 H), 7.84 (dd, *J* = 11.4, 3.1 Hz, 2 H), 7.76 (dd, *J* = 6.6, 2.9 Hz, 2 H), 7.60 (dd, *J* = 4.0, 1.8 Hz, 3 H), 6.33 (s, 1 H), 5.68 (ddd, *J* = 17.3, 10.5, 6.9 Hz, 1 H), 5.18 - 5.06 (m, 2 H), 4.98 (dd, *J* = 16.9, 11.4 Hz, 2 H), 4.28 - 4.16 (m, 1 H), 3.98 (t, *J* = 9.1 Hz, 1 H), 3.69 - 3.56 (m, 4 H), 3.53 - 3.38 (m, 2 H), 2.71 (s, 1 H), 2.42 - 2.31 (m, 1 H), 2.23 (tdd, *J* = 10.9, 6.9, 4.3 Hz, 1 H), 2.08 (d, *J* = 2.9 Hz, 1 H), 1.96 - 1.83 (m, 1 H), 1.58 - 1.45 (m, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

151.02, 149.24, 143.03, 138.56, 134.95, 131.83, 131.36, 130.56, 130.43, 129.33, 128.59, 126.98, 124.10, 121.32, 117.64, 76.03, 69.85, 65.90, 61.95, 57.36, 52.90, 39.00, 28.05, 25.88, 22.72.

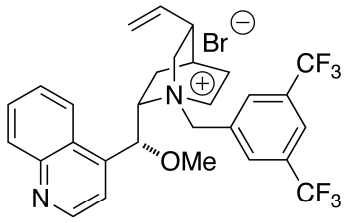
LRMS: (ESI^+, Q-tof)

399.2 (100, M-Br^+)

HRMS: $C_{27}H_{31}N_2O^+$ (ESI^+, Q-tof)
Calcd: 399.2436
Found: 399.2420

TLC: R_f 0.38 (CH_2Cl_2:MeOH, 10:1) [silica gel, I_2]

Preparation of *O*-Methyl-*N*-(3,5-Bistrifluoromethylbenzyl)cinchonidinium Bromide (5e)



5e

Following General Procedure I, *O*-methyl-cinchonidine (185 mg, 0.600 mmol), MeCN (6.0 mL, 0.1 M), and bis-(3,5-trifluoromethyl)benzyl bromide (121 μL, 0.660 mmol, 1.10 equiv) were combined in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred for 41 h. The solvent was removed on a rotavap (20 mm Hg, 25 °C) and the solid residue was triturated with hexane then filtered. The filter cake was purified by silica gel flash chromatography (15 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH, gradient elution) to afford 249 mg (67%) of **5e** as a white, crystalline solid.

Data for **5e**:

m.p.: 154 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)
8.99 (d, *J* = 4.5 Hz, 1 H), 8.51 (s, 2 H), 8.32 (d, *J* = 8.3 Hz, 1 H), 8.26 (s, 1 H), 8.16 (d, *J* = 8.4 Hz, 1 H), 7.94 - 7.78 (m, 3 H), 6.30 (s, 1 H), 5.68 (ddd, *J* = 17.3, 10.5, 6.9 Hz, 1 H), 5.25 (q, *J* = 12.6 Hz, 2 H), 5.15 (d, *J* = 17.2 Hz, 1 H), 5.01 (d, *J* = 10.5 Hz, 1 H), 4.39 (t, *J* = 11.2 Hz, 1 H), 4.01 (t, *J* = 9.1 Hz, 1 H), 3.76 - 3.68 (m, 1 H), 3.62 (s, 3 H), 3.45 (t, *J* = 11.5 Hz, 2 H), 2.73 (s, 1 H), 2.40 (dd, *J* = 12.3, 9.1 Hz, 1 H), 2.24 (dd, *J* = 19.5, 8.4 Hz, 1 H), 2.11 (s, 1 H), 1.93 (t, *J* = 11.7 Hz, 1 H), 1.54 (t, *J* = 11.8 Hz, 1 H).

^{13}C NMR: (126 MHz, CD_3OD)
151.03, 149.27, 142.72, 138.36, 135.55, 133.72 (q, $J_{C\text{-}F}$ = 33.9 Hz). 131.90, 131.40, 130.62, 129.43, 126.94, 125.69, 125.61, 124.08, 123.44, 121.35, 117.83,

76.01, 70.52, 64.05, 61.90, 57.49, 53.21, 39.01, 27.92, 25.81, 22.79

LRMS: (ESI^+, Q-tof)

535.2 (100, $M\text{-}Br^+$)

HRMS: $C_{29}H_{29}N_2OF_6^+$ (ESI^+, Q-tof)

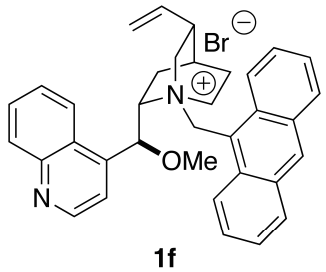
Calcd: 535.2184

Found: 535.2187

TLC: R_f 0.34 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of Cinchonidinium Salts in Series F

Preparation of *O*-Methyl-*N*-(9-Anthracenylmethyl)-*epi*-cinchonidinium Bromide (1f)



1f

Following General Procedure I, *O*-methyl-*epi*-cinchonidine (81 mg, 0.26 mmol), MeCN (2.6 mL, 0.1 M), and 9-bromomethylanthracene (78 mg, 0.29 mmol, 1.1 equiv) were combined in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet, wrapped in aluminum foil and the mixture was stirred overnight. Care was taken to avoid light exposure. The reaction mixture was diluted with CH_2Cl_2 (~5 mL) and then was loaded directly on a silica gel column (15 g SiO_2, ∅ = 20, 100:0 to 2.5:1, TBME/MeOH, gradient elution) to afford 136 mg (90%) of **1f** as a light-yellow, crystalline solid.

Data for **1f**:

m.p.: 143 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

9.04 (d, *J* = 4.5 Hz, 1 H), 8.89 (s, 1 H), 8.76 (d, *J* = 9.0 Hz, 1 H), 8.58 (d, *J* = 7.4 Hz, 1 H), 8.51 (d, *J* = 9.0 Hz, 1 H), 8.22 (ddd, *J* = 9.5, 7.5, 4.6 Hz, 3 H), 7.98 - 7.89 (m, 3 H), 7.88 - 7.76 (m, 2 H), 7.65 (ddd, *J* = 11.8, 8.3, 6.7 Hz, 2 H), 6.82 (s, 1 H), 6.42 (d, *J* = 14.0 Hz, 1 H), 5.91 (d, *J* = 14.0 Hz, 1 H), 5.69 (ddd, *J* = 17.4, 10.4, 7.3 Hz, 1 H), 4.99 (m, 2 H), 4.53 - 4.40 (m, 2 H), 3.85 (s, 3 H), 3.79 (ddd, *J* = 12.5, 5.4, 3.0 Hz, 1 H), 3.23 (dd, *J* = 12.4, 10.9 Hz, 1 H), 2.90 (td, *J* = 11.0, 4.7

Hz, 1 H), 2.41 (dd, *J* = 15.4, 4.6 Hz, 2 H), 2.20 - 2.08 (m, 1 H), 1.95 (d, *J* = 3.0 Hz, 1 H), 1.66 - 1.49 (m, 2 H).

^{13}C-NMR: (126 MHz, CD_3OD)

151.05, 149.37, 142.95, 138.54, 134.79, 134.66, 133.89, 133.09, 133.05, 131.48, 131.27, 131.16, 130.61, 129.43, 129.41, 129.36, 127.23, 126.64, 126.60, 125.39, 124.80, 124.45, 121.67, 118.99, 117.76, 76.76, 70.24, 63.48, 57.53, 53.79, 39.52, 27.31, 26.23, 23.15.

LRMS: (ESI^+, Q-tof)
191.1 (10), 499.3 (100, M-Br^+)

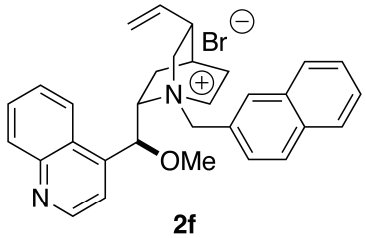
HRMS: $C_{35}H_{35}N_2O^+$ (ESI^+, Q-tof)

Calcd: 499.2749

Found: 499.2741

TLC: R_f 0.36 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of *O*-Methyl-*N*-(2-Naphthylmethyl)-*epi*-cinchonidinium Bromide (2f)



2f

Following General Procedure I, *O*-methyl-*epi*-cinchonidine (90 mg, 0.29 mmol), MeCN (2.9 mL, 0.1 M), and 2-bromomethylnaphthalene (71 mg, 0.32 mmol, 1.1 equiv) were combined in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred overnight. The reaction mixture was diluted with CH_2Cl_2 (~5 mL) and then was loaded directly on a silica gel column (15 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH, gradient elution) to afford 170 mg of **2f** as an off-white, crystalline solid. The entire product was further purified by trituration in Et_2O (~10 mL) then filtered to afford 115 mg (74%) of **2f** as an off-white crystalline solid.

Data for **2f**:

m.p.: 163 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

9.00 (d, *J* = 4.4 Hz, 1 H), 8.38 - 8.26 (m, 2 H), 8.17 (d, *J* = 8.3 Hz, 1 H), 8.12 -

8.02 (m, 2 H), 7.99 (d, J = 6.9 Hz, 1 H), 7.93 - 7.76 (m, 4 H), 7.70 - 7.58 (m, 2 H), 6.38 (s, 1 H), 5.70 (ddd, J = 17.3, 10.5, 6.9 Hz, 1 H), 5.27 (d, J = 12.4 Hz, 1 H), 5.19 - 5.08 (m, 2 H), 5.01 (d, J = 10.4 Hz, 1 H), 4.33 (t, J = 10.4 Hz, 1 H), 4.04 (t, J = 8.7 Hz, 1 H), 3.77 - 3.68 (m, 1 H), 3.65 (s, 3 H), 3.61 - 3.45 (m, 3 H), 2.68 (s, 1 H), 2.46 - 2.33 (m, 1 H), 2.24 (dd, J = 18.6, 8.0 Hz, 1 H), 2.08 (s, 1 H), 1.88 (t, J = 11.6 Hz, 1 H), 1.54 (t, J = 10.5 Hz, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

151.04, 149.25, 143.07, 138.57, 135.52, 135.42, 134.57, 131.37, 130.79, 130.58, 130.11, 129.53, 129.35, 128.97, 128.85, 128.19, 127.01, 125.86, 124.12, 121.34, 117.65, 76.08, 69.84, 66.07, 62.10, 57.42, 53.05, 39.03, 28.05, 25.91, 22.75.

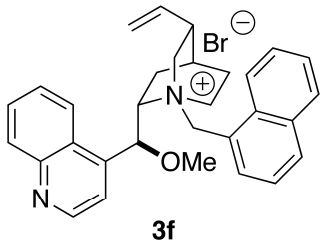
LRMS: (ESI^+, Q-tof)

142.0 (10), 449.2 (100, M-Br^+)

HRMS: $C_{31}H_{33}N_2O^+$ (ESI^+, Q-tof)
Calcd: 449.2593
Found: 449.2576

TLC: R_f 0.36 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of *O*-Methyl-*N*-(1-Naphthylmethyl)-*epi*-cinchonidinium bromide (3f)



3f

Following General Procedure I, *O*-methyl-*epi*-cinchonidine (90 mg, 0.29 mmol), MeCN (2.9 mL, 0.1 M), and 1-bromomethylnaphthalene (71 mg, 0.32 mmol, 1.1 equiv) were combined in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred overnight. The reaction mixture was diluted with CH_2Cl_2 (~5 mL) then loaded directly on a silica gel column (15 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH, gradient elution) to afford 176 mg of **3f** as an off-white, crystalline solid. The entire product was further purified by trituration in Et_2O (~10 mL) the filtered to afford 111 mg (72%) of **3f** as an off-white, crystalline solid.

Data for **3f**:

m.p.: 158 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

9.01 (d, *J* = 4.5 Hz, 1 H), 8.40 (d, *J* = 8.2 Hz, 1 H), 8.34 (d, *J* = 8.5 Hz, 1 H), 8.22 - 8.14 (m, 2 H), 8.06 (t, *J* = 8.4 Hz, 2 H), 7.95 - 7.83 (m, 3 H), 7.78 (ddd, *J* = 8.4, 6.9, 1.2 Hz, 1 H), 7.72 (dd, *J* = 8.1, 7.3 Hz, 1 H), 7.66 (t, *J* = 7.2 Hz, 1 H), 6.55 (s, 1 H), 5.80 - 5.62 (m, 2 H), 5.38 (d, *J* = 13.1 Hz, 1 H), 5.10 (d, *J* = 17.2 Hz, 1 H), 4.99 (d, *J* = 10.5 Hz, 1 H), 4.45 - 4.34 (m, 1 H), 4.21 (t, *J* = 9.0 Hz, 1 H), 3.83 - 3.69 (m, 4 H), 3.56 - 3.47 (m, 1 H), 3.29 - 3.21 (m, 1 H), 2.63 (s, 1 H), 2.46 - 2.34 (m, 1 H), 2.21 (ddd, *J* = 10.8, 8.7, 4.8 Hz, 1 H), 2.05 (d, *J* = 2.9 Hz, 1 H), 1.85 - 1.73 (m, 1 H), 1.54 (td, *J* = 10.3, 3.0 Hz, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

151.05, 149.26, 143.03, 138.52, 135.79, 134.71, 133.20, 131.43, 130.70, 130.56, 129.38, 129.07, 127.64, 127.07, 126.45, 124.40, 124.39, 124.22, 121.42, 117.69, 76.26, 69.93, 62.48, 61.99, 57.42, 53.51, 39.25, 27.70, 26.02, 22.86.

LRMS: (ESI^+, Q-tof)

449.2 m/z (100, M-Br^+)

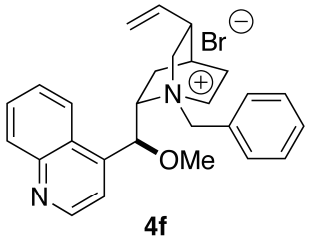
HRMS: $C_{31}H_{33}N_2O^+$ (ESI^+, Q-tof)

Calcd: 449.2593

Found: 449.2580

TLC: R_f 0.33 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of *O*-Methyl-*N*-(Benzyl)-*epi*-cinchonidinium Bromide (4f)



4f

Following General Procedure I, *O*-methyl-*epi*-cinchonidine (90 mg, 0.29 mmol), MeCN (2.9 mL, 0.1 M), and benzyl bromide (38 μL, 0.32 mmol, 1.1 equiv) were combined in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred

overnight. The reaction mixture was diluted with CH_2Cl_2 (~5 mL) and then was loaded directly on a silica gel column (15 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH, gradient elution) to afford 156 mg of **4f** as a light-yellow, crystalline solid. The entire product was further purified by trituration in Et_2O (~10 mL) and then filtered to afford 136 mg (97%) of **4f** as an off-white, crystalline solid.

Data for **4f**:

m.p.: 176 – 180 °C (decomp.)

^{1}H-NMR: (500 MHz, $CDCl_3$)

8.98 (d, *J* = 4.5 Hz, 1 H), 8.93 (d, *J* = 8.6 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.02 - 7.93 (m, 3 H), 7.82 (t, *J* = 7.2 Hz, 1 H), 7.54 - 7.50 (m, 3 H), 6.74 (d, *J* = 11.8 Hz, 1 H), 6.06 (d, *J* = 3.2 Hz, 1 H), 5.74 (ddd, *J* = 17.0, 10.5, 6.3 Hz, 1 H), 5.41 (dd, *J* = 17.2, 1.3 Hz, 1 H), 5.05 (dd, *J* = 10.6, 1.3 Hz, 2 H), 4.79 (s, 1 H), 4.51 (d, *J* = 11.8 Hz, 1 H), 4.33 - 4.23 (m, 1 H), 3.54 (s, 3 H), 3.51 - 3.39 (m, 1 H), 3.19 (dd, *J* = 12.9, 10.8 Hz, 1 H), 2.59 (s, 1 H), 2.10 (ddd, *J* = 31.5, 20.0, 9.3 Hz, 3 H), 1.78 (dd, *J* = 19.3, 11.5 Hz, 1 H), 1.40 (t, *J* = 14.3 Hz, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

LRMS: (ESI^+, Q-tof)

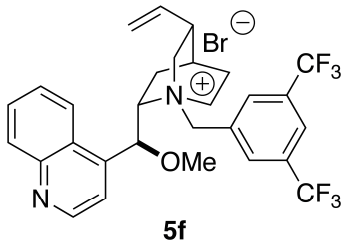
142.0 (20), 178.9 (10), 309.2 (5), 329.9 (10), 399.2 (100, M-Br^+), 449.3 (5)

HRMS: $C_{27}H_{31}N_2O^+$ (ESI^+, Q-tof)

Calcd: 399.2436

Found: 399.2421

Preparation of *O*-Methyl-*N*-(3,5-Bistrifluoromethylbenzyl)-*epi*-cinchonidinium Bromide (5f)



5f

Following General Procedure I, *O*-methyl-*epi*-cinchonidine (90 mg, 0.29 mmol), MeCN (2.9 mL, 0.1 M), and bis-(3,5-trifluoromethyl)benzyl bromide (59 μL, 0.32 mmol, 1.1 equiv) were combined in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet and the

mixture was stirred overnight. The reaction mixture was diluted with CH_2Cl_2 (~5 mL) and then was loaded directly on a silica gel column (15 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH, gradient elution) to afford 168 mg (93%) of **5f** as a white, crystalline solid.

Data for **5f**:

m.p.: 165 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

8.99 (d, *J* = 4.5 Hz, 1 H), 8.51 (s, 2 H), 8.32 (d, *J* = 8.1 Hz, 1 H), 8.25 (s, 1 H), 8.16 (dd, *J* = 8.4, 1.0 Hz, 1 H), 7.92 - 7.80 (m, 3 H), 6.30 (s, 1 H), 5.68 (ddd, *J* = 17.3, 10.5, 6.9 Hz, 1 H), 5.30 - 5.20 (m, 2 H), 5.15 (d, *J* = 17.2 Hz, 1 H), 5.00 (d, *J* = 10.5 Hz, 1 H), 4.44 - 4.33 (m, 1 H), 4.01 (dd, *J* = 9.8, 8.5 Hz, 1 H), 3.73 (ddd, *J* = 12.4, 4.8, 3.2 Hz, 1 H), 3.63 (s, 3 H), 3.45 (dd, *J* = 14.9, 8.2 Hz, 2 H), 2.73 (d, *J* = 1.5 Hz, 1 H), 2.46 - 2.34 (m, 1 H), 2.31 - 2.19 (m, 1 H), 2.11 (d, *J* = 2.8 Hz, 1 H), 1.93 (ddd, *J* = 15.2, 5.0, 2.4 Hz, 1 H), 1.59 - 1.47 (m, 1 H).

^{13}C NMR: (126 MHz, CD_3OD)

151.03, 149.27, 142.73, 138.36, 135.56, 133.72 (q, $J_{C\text{-}F}$ = 33.8 Hz), 131.91, 131.40, 130.61, 129.43, 126.94, 125.61, 124.10, 123.44, 121.35, 117.83, 76.02, 70.51, 64.05, 61.90, 57.49, 53.21, 39.01, 27.92, 25.81, 22.80.

LRMS: (ESI^+, Q-tof)

535.2 (100, M-Br^+)

HRMS: $C_{29}H_{29}N_2OF_6^+$ (ESI^+, Q-tof)

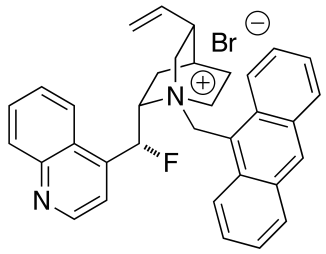
Calcd: 535.2184

Found: 535.2179

TLC: R_f 0.34 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of Cinchonidinium Salts in Series G

Preparation of *N*-(9-Anthracenylmethyl)deoxyfluorocinchonidinium Bromide (1g)



1g

Following General Procedure I, deoxyfluorocinchonidine (50 mg, 0.17 mmol), MeCN (1.7 mL, 0.1 M), and 9-bromomethylanthracene (48 mg, 0.18 mmol, 1.05 equiv) were combined in a 5-mL, single-neck, round-bottomed flask fitted with an argon inlet, wrapped in aluminum and the mixture was stirred for 2 days. Care was taken to avoid light exposure. The reaction mixture was cooled to 0 °C (external) in an ice bath and the product was then precipitated with ice-cold Et_2O (3-4 mL). The reaction mixture was filtered and the filter cake was washed several times with cold Et_2O (5-10 mL) to afford 84 mg (88%) of **1g** as a yellow, crystalline solid. The entire product was further purified by recrystallization from a concentrated CH_2Cl_2 solution (2-4 mL), layering Et_2O (6-12 mL), and then cooling overnight at -20 °C.

Data for **1g**:

m.p.: 183 – 186 °C (decomp.)

^{1}H-NMR: (500 MHz, $CDCl_3$)

9.68 (d, J = 9.0 Hz, 1 H), 9.03 (d, J = 4.4 Hz, 1 H), 8.93 (d, J = 8.4 Hz, 1 H), 8.67 (s, 1 H), 8.35 (d, J = 9.0 Hz, 1 H), 8.18 (dd, J = 8.4, 0.9 Hz, 1 H), 8.12 (d, J = 8.3 Hz, 1 H), 8.07 (d, J = 8.4 Hz, 1 H), 7.96 - 7.90 (m, 2 H), 7.88 (ddd, J = 8.9, 6.5, 1.2 Hz, 1 H), 7.83 (ddd, J = 8.2, 6.9, 1.1 Hz, 1 H), 7.73 (dd, J = 49.6, 1.9 Hz, 1 H), 7.72 (ddd, J = 8.9, 6.5, 1.2 Hz, 1 H), 7.57 (ddd, J = 13.3, 8.2, 6.6 Hz, 2 H), 7.25 (d, J = 13.5 Hz, 1 H), 6.26 - 6.09 (m, 2 H), 5.99 (ddd, J = 17.3, 10.5, 7.1 Hz, 1 H), 5.33 - 5.20 (m, 2 H), 5.14 (d, J = 9.9 Hz, 1 H), 4.14 (t, J = 11.7 Hz, 1 H), 3.23 (dd, J = 12.8, 10.7 Hz, 1 H), 2.67 (td, J = 12.4, 4.9 Hz, 1 H), 2.39 (s, 1 H), 2.08 - 1.90 (m, 3 H), 1.84 (td, J = 10.6, 3.2 Hz, 1 H), 1.54 (s, 3H), 1.25 (s, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

151.06, 149.06, 141.87 (d, $^2J_{C\text{-}F}$ = 20.0 Hz), 137.94, 134.86, 134.62, 134.12, 133.13, 133.05, 131.68, 131.22 (d, $^3J_{C\text{-}F}$ = 6.3 Hz), 130.75, 129.59, 129.51, 126.66

(d, J = 3.4 Hz), 125.15, 124.95, 124.32, 120.43 (d, $^3J_{C\text{-}F}$ = 12.5 Hz), 118.68, 118.10, 87.83 (d, $^1J_{C\text{-}F}$ = 182.0 Hz), 70.41 (d, $^2J_{C\text{-}F}$ = 20.3 Hz), 62.68, 58.47, 54.15 (d, $^3J_{C\text{-}F}$ = 7.4 Hz), 39.49, 27.30, 25.95, 22.17.

^{19}F-NMR: (376 MHz, $CDCl_3$)

198.65 (dd, J = 48.8, 33.7 Hz).

LRMS: (ESI^+, Q-tof)

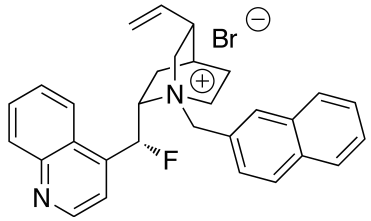
150 (20), 191.1 (70), 487.2 (100, M-Br^+)

HRMS: $C_{34}H_{32}N_2F^+$ (ESI^+, Q-tof)
Calcd: 487.2550

Found: 487.2551

TLC: R_f 0.60 (CH_2Cl_2/MeOH, 5:1) [silica gel, I_2]

Preparation of *N*-(2-Naphthylmethyl)deoxyfluorocinchonidinium Bromide (2g)



2g

Following General Procedure I, deoxyfluorocinchonidine (100 mg, 0.337 mmol), MeCN (3.4 mL, 0.1 M), and 1-bromomethylnaphthalene (82.0 mg, 0.371 mmol, 1.10 equiv) were combined in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred for 2 days. The reaction mixture was diluted with CH_2Cl_2 (~5 mL) and MeOH (<1 mL) and then was loaded directly on a silica gel column (20 g SiO_2, ∅ = 20, 100:0 to 5:1, CH_2Cl_2/MeOH, gradient elution) to afford 126 mg (72%) of **2g** as a light-orange, crystalline solid.

The entire product was further purified by recrystallization from a CH_2Cl_2 solution (2-4 mL), layered with Et_2O (6-12 mL), and then was allowed to cool overnight in a freezer to afford **2g** as an off-white, crystalline solid.

Data for **2g**:

m.p.: 210-213 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

9.01 (d, J = 4.6 Hz, 1 H), 8.27 (s, 1 H), 8.18 (dd, J = 12.9, 8.3 Hz, 2 H), 8.08 (d, J

= 8.5 Hz, 1 H), 8.00 (d, J = 8.1 Hz, 2 H), 7.95 - 7.89 (m, 1 H), 7.87 - 7.79 (m, 2 H), 7.73 (d, $J_{H\text{-}F}$ = 48.0 Hz, 1 H), 7.76 (m, 1 H), 7.64 (pd, J = 7.0, 1.4 Hz, 2 H), 5.79 (ddd, J = 17.4, 10.4, 7.2 Hz, 1 H), 5.54 (d, J = 12.5 Hz, 1 H), 5.22 - 5.05 (m, 3 H), 4.35 (ddd, J = 30.6, 10.9, 6.3 Hz, 1 H), 4.17 - 4.07 (m, 1 H), 3.78 - 3.54 (m, 3 H), 2.75 (dd, J = 15.9, 7.6 Hz, 1 H), 2.42 - 2.21 (m, 2 H), 2.15 (d, J = 2.7 Hz, 1 H), 1.99 (t, J = 11.4 Hz, 1 H), 1.86 (dd, J = 13.7, 11.1 Hz, 1 H)

^{13}C-NMR: (126 MHz, CD_3OD)

151.05, 148.97, 141.69 (d, $^2J_{C\text{-}F}$ = 19.7 Hz), 138.09, 135.47, 134.56, 131.63, 130.73, 130.56, 130.29, 129.56, 129.50, 129.09, 128.89, 128.29, 125.55, 125.24 (d, $^3J_{C\text{-}F}$ = 5.2 Hz), 124.04, 121.34, 120.24 (d, $^3J_{C\text{-}F}$ = 12.5 Hz), 118.08, 87.26 (d, $^1J_{C\text{-}F}$ = 182.3 Hz), 69.28 (d, $^2J_{C\text{-}F}$ = 20.4 Hz), 66.22, 61.84, 53.18, 39.15, 28.10, 25.68, 21.87

^{19}F-NMR: (376 MHz, CD_3OD)

-199.46 (dd, J = 48.0, 30.8 Hz)

LRMS: (ESI^+, Q-tof)

150 (8), 437.2 (100, M-Br^+)

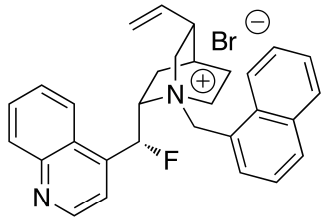
HRMS: $C_{30}H_{30}N_2F^+$ (ESI^+, Q-tof)

Calcd: 437.2393

Found: 437.2400

TLC: R_f 0.60 (CH_2Cl_2/MeOH, 5:1) [silica gel, I_2]

Preparation of *N*-(1-Naphthylmethyl)deoxyfluorocinchonidinium Bromide (3g)



3g

Following General Procedure I, deoxyfluorocinchonidine (100 mg, 0.337 mmol), MeCN (3.4 mL, 0.1 M), and 1-bromomethylnaphthalene (82.0 mg, 0.371 mmol, 1.10 equiv) were combined in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred for 2 days. The reaction mixture was diluted with CH_2Cl_2 (~5 mL) and then

was loaded directly on a silica gel column (15 g SiO_2, ∅ = 20, 100:0 to 10:1, CH_2Cl_2/MeOH, gradient elution) to afford 90 mg (52%) of **3g** as a light-orange, crystalline solid. The entire product was further purified by recrystallization from a CH_2Cl_2 solution (2-4 mL), layered with Et_2O (6-12 mL), and then was allowed to cool overnight in a freezer to afford **3g** as an light-amber, crystalline solid.

Data for **3g**:

m.p.: 150 – 155 °C (decomp.)

^{1}H-NMR: (500 MHz, CD_3OD)

9.03 (d, *J* = 4.5 Hz, 1 H), 8.40 (d, *J* = 8.6 Hz, 1 H), 8.27 - 8.16 (m, 3 H), 8.07 (d, *J* = 8.2 Hz, 1 H), 7.99 (d, *J* = 6.8 Hz, 1 H), 7.96 - 7.79 (m, 4 H), 7.77 - 7.68 (m, 2 H), 7.65 (t, *J* = 7.3 Hz, 1 H), 5.94 (d, *J* = 13.1 Hz, 1 H), 5.77 (ddd, *J* = 17.4, 10.4, 7.2 Hz, 1 H), 5.38 (d, *J* = 13.0 Hz, 1 H), 5.08 (dd, *J* = 18.8, 13.8 Hz, 2 H), 4.57 (ddd, *J* = 30.7, 10.6, 6.0 Hz, 1 H), 4.17 (dd, *J* = 16.0, 7.5 Hz, 1 H), 3.71 (ddd, *J* = 12.5, 6.7, 3.0 Hz, 1 H), 3.60 - 3.41 (m, 2 H), 2.65 (d, *J* = 8.3 Hz, 1 H), 2.38 (d, *J* = 13.7 Hz, 1 H), 2.32 - 2.20 (m, 1 H), 2.11 (d, *J* = 2.6 Hz, 1 H), 1.90 (dd, *J* = 27.2, 13.6 Hz, 2 H)

^{13}C-NMR: (126 MHz, CD_3OD)

151.05, 148.99, 141.79 (d, $^2J_{C\text{-}F}$ = 19.8 Hz), 137.97, 135.85, 135.73, 134.67, 133.40, 131.65, 130.71 (d, $^3J_{C\text{-}F}$ = 4.1 Hz), 129.59, 129.10, 127.72, 126.44, 125.30, 125.26, 124.52, 124.19, 124.10, 120.32 (d, $^3J_{C\text{-}F}$ = 12.4 Hz), 118.10, 87.40 (d, $^1J_{C\text{-}F}$ = 182.2 Hz), 69.95 (d, $^2J_{C\text{-}F}$ = 20.1 Hz), 62.62, 62.12, 53.50, 39.29, 27.75, 25.78, 21.94

^{19}F-NMR: (376 MHz, CD_3OD)

-199.38 (dd, *J* = 48.0, 31.0 Hz)

LRMS: (ESI^+, Q-tof)

437.2 (100, M-Br^+)

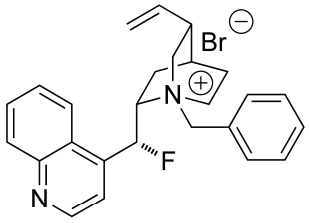
HRMS: $C_{30}H_{30}N_2F^+$ (ESI^+, Q-tof)

Calcd: 437.2393

Found: 437.2400

TLC: R_f 0.60 (CH_2Cl_2/MeOH, 5:1) [silica gel, I_2]

Preparation of *N*-(Benzyl)deoxyfluorocinchonidinium Bromide (4g)



4g

Following General Procedure I, deoxyfluorocinchonidine (50.0 mg, 0.170 mmol), MeCN (1.70 mL, 0.10 M), and benzyl bromide (21.0 μL, 0.180 mmol, 1.05 equiv) were combined in a 5-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred for 2 days. The mixture was cooled to 0 °C (external) in an ice bath and then the product was precipitated with ice-cold Et_2O (3-4 mL). The suspension was filtered and then washed several times with cold Et_2O (~5 mL) to afford 65 mg (82%) of **4g** as a light-yellow, crystalline solid. The entire product was further purified by recrystallization from a concentrated CH_2Cl_2 solution (2-4 mL), layered with Et_2O (6-12 mL), and was then allowed to cool in a freezer overnight.

Data for **4g**:

m.p.: 150-155 °C (decomp.)

^{1}H-NMR: (500 MHz, $CDCl_3$)

8.98 (d, J = 4.5 Hz, 1 H), 8.77 (d, J = 8.4 Hz, 1 H), 8.15 (d, J = 8.4 Hz, 1 H), 7.94 (dt, J = 5.4, 3.2 Hz, 3 H), 7.82 (t, J = 7.2 Hz, 1 H), 7.64 (d, J = 4.4 Hz, 1 H), 7.56 - 7.46 (m, 4 H), 7.32 (d, J = 49.8 Hz, 2 H), 6.73 (d, J = 11.8 Hz, 1 H), 5.82 (ddd, J = 17.1, 10.6, 6.5 Hz, 1 H), 5.43 (dd, J = 17.2, 1.2 Hz, 1 H), 5.28 (dt, J = 20.2, 9.8 Hz, 1 H), 5.21 - 5.15 (m, 1 H), 5.13 (dd, J = 10.6, 1.2 Hz, 1 H), 4.78 (d, J = 11.8 Hz, 1 H), 3.97 (t, J = 11.4 Hz, 1 H), 3.54 - 3.47 (m, 1 H), 3.32 (dd, J = 13.0, 10.7 Hz, 1 H), 2.65 (s, 1H), 2.22 - 2.13 (m, 1 H), 2.11 (d, J = 2.3 Hz, 1 H), 1.99 (dd, J = 13.6, 8.8 Hz, 1 H), 1.88 (t, J = 14.2 Hz, 1 H), 1.68 (td, J = 10.3, 3.1 Hz, 1 H)

^{13}C-NMR: (126 MHz, CD_3OD)

151.04, 148.98, 141.63 (d, $^2J_{C\text{-}F}$ = 20.3 Hz), 138.08, 134.82, 132.02, 131.61, 130.74, 130.56, 129.54, 128.29, 125.21 (d, $^3J_{C\text{-}F}$ = 5.3 Hz), 123.99, 120.21 (d, $^3J_{C\text{-}F}$ = 12.5 Hz), 118.06, 87.20 (d, $^1J_{C\text{-}F}$ = 182.3 Hz), 69.37 (d, $^2J_{C\text{-}F}$ = 20.3 Hz), 66.04, 61.68, 52.99 (d, $^3J_{C\text{-}F}$ = 7.2 Hz), 39.10, 28.10, 25.64, 21.84 (d, $^4J_{C\text{-}F}$ = 3.9 Hz)

^{19}F-NMR: (376 MHz, $CDCl_3$)

-201.07 (dd, J = 48.9, 32.7 Hz)

LRMS: (ESI^+, Q-tof)

367.2 (5), 387.2 (100, M-Br^+)

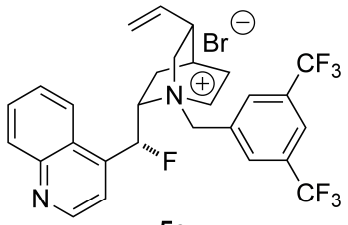
HRMS: $C_{26}H_{28}N_2F^+$ (ESI^+, Q-tof)

Calcd: 387.2237

Found: 387.2246

TLC: R_f 0.49 (CH_2Cl_2/MeOH, 5:1) [silica gel, I_2]

Preparation of *N*-(9-Anthracenylmethyl)deoxyfluorocinchonidinium Bromide (5g)



5g

Following General Procedure I, deoxyfluorocinchonidine (44 mg, 0.15 mmol), MeCN (1.5 mL), and bis-(3,5-trifluoromethyl)benzyl bromide (28 μL, 0.16 mmol, 1.05 equiv) were combined in a 5-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred for 4 days. The reaction mixture was cooled to 0 °C (external) in an ice bath and then the product was precipitated with ice-cold Et_2O (3-4 mL) then filtered. The filter cake was washed several times with ice-cold Et_2O (~5 mL) to afford 68 mg (76%) of **5g** as a light-orange, crystalline solid. The entire product was further purified by recrystallization from a CH_2Cl_2 solution (2-4 mL), layered with Et_2O (6-12 mL), and then was allowed to cool overnight in a freezer.

Data for **5g**:

m.p.: 150-155 °C (decomp.)

^{1}H-NMR: (500 MHz, $CDCl_3$)

8.98 (d, J = 4.5 Hz, 1 H), 8.80 (d, J = 8.4 Hz, 1 H), 8.56 (s, 2 H), 8.14 (d, J = 8.3 Hz, 1 H), 8.06 (s, 1 H), 7.92 (t, J = 7.7 Hz, 1 H), 7.81 (t, J = 7.6 Hz, 1 H), 7.63 (d, J = 4.4 Hz, 1 H), 7.33 (dd, J = 30.5, 23.3 Hz, 2 H), 5.81 (ddd, J = 17.1, 10.6, 6.4 Hz, 1 H), 5.54 - 5.30 (m, 4 H), 5.16 (d, J = 10.5 Hz, 1 H), 4.92 (d, J = 12.1 Hz, 1 H), 4.10 (s, 1 H), 3.36 (td, J = 11.8, 4.3 Hz, 1 H), 3.14 (dd, J = 12.5, 10.8 Hz, 1 H),

2.71 (s, 1 H), 2.23 (dd, J = 19.2, 8.6 Hz, 1 H), 2.17 (s, 1 H), 2.08 - 1.99 (m, 1 H), 1.94 (t, J = 15.2 Hz, 1 H), 1.69 (dd, J = 13.1, 10.1 Hz, 1 H)

^{13}C-NMR: (126 MHz, CD_3OD)

151.06, 149.00, 141.32 (d, $^2J_{C\text{-}F}$ = 20.7 Hz), 137.87, 135.35, 133.72 (dd, $J_{C\text{-}F}$ = 36.5, 31.1 Hz), 131.66, 131.53, 130.80, 129.65, 125.92, 125.54, 125.14 (d, $^3J_{C\text{-}F}$ = 5.3 Hz), 123.91, 120.21 (d, $^3J_{C\text{-}F}$ = 12.5 Hz), 118.27, 87.10 (d, $^1J_{C\text{-}F}$ = 182.9 Hz), 70.00 (d, $^2J_{C\text{-}F}$ = 20.4 Hz), 64.14, 61.75, 53.16, 39.11, 27.95, 25.56, 21.87

^{19}F-NMR: (376 MHz, $CDCl_3$)

-63.03 (s, 6 F), -200.89 (dd, J = 48.1, 32.3 Hz, 1 F)

LRMS: (ESI^+, Q-tof)

503.2 (5), 523.2 (100, M-Br^+)

HRMS: $C_{28}H_{26}N_2F_7^+$ (ESI^+, Q-tof)

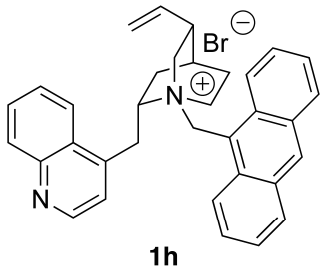
Calcd: 523.1984

Found: 523.1984

TLC: R_f 0.49 (CH_2Cl_2/MeOH, 5:1) [silica gel, I_2]

Preparation of Cinchonidinium Salts in Series H

Preparation of *N*-(9-Anthracenylmethyl)deoxycinchonidinium Bromide (1h)



1h

Following General Procedure I, deoxycinchonidine (100 mg, 0.359 mmol), MeCN (3.6 mL), and 9-bromomethylanthracene (107 mg, 0.390 mmol, 1.10 equiv) were combined in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet, wrapped in aluminum foil and the mixture was stirred for 4 h. Care was taken to avoid light exposure. The solvent was removed on a rotavap (20 mm Hg, 25 °C) and the yellow, solid residue was sonicated in Et_2O (10 mL) then filtered. The entire product was purified by recrystallization from a concentrated CH_2Cl_2 solution by a slow diffusion of Et_2O in a chamber stored in a freezer. The first crop of recrystallized product afforded 29.0 mg (15%) of **1h** as a light-yellow, crystalline solid.

Data for **1h**:

m.p.: 132 °C (decomp.)

^{1}H-NMR: (500 MHz, $CDCl_3$)

9.16 (d, *J* = 9.0 Hz, 1 H), 8.80 (d, *J* = 8.9 Hz, 1 H), 8.45 (d, *J* = 8.2 Hz, 1 H), 8.40 (s, 1 H), 8.04 (s, 2 H), 7.98 (d, *J* = 8.2 Hz, 1 H), 7.81 (d, *J* = 8.2 Hz, 1 H), 7.77 - 7.68 (m, 2 H), 7.55 - 7.38 (m, 4 H), 7.33 - 7.27 (m, 1 H), 6.74 (d, *J* = 14.2 Hz, 1 H), 6.04 (d, *J* = 14.2 Hz, 1 H), 5.60 (ddd, *J* = 17.2, 10.5, 6.8 Hz, 1 H), 5.45 - 5.32 (m, 1 H), 4.98 (dd, *J* = 32.1, 13.8 Hz, 2 H), 4.75 (dd, *J* = 13.4, 4.7 Hz, 1 H), 4.55 (t, *J* = 11.5 Hz, 1 H), 4.43 (t, *J* = 12.5 Hz, 1 H), 3.75 (dd, *J* = 11.7, 5.0 Hz, 1 H), 2.94 (td, *J* = 11.9, 6.1 Hz, 1 H), 2.84 (dd, *J* = 13.0, 10.7 Hz, 1 H), 2.13 (d, *J* = 7.3 Hz, 1 H), 1.99 - 1.87 (m, 1 H), 1.81 (dd, *J* = 13.6, 10.7 Hz, 1 H), 1.66 (d, *J* = 2.5 Hz, 1 H), 1.52 (t, *J* = 10.0 Hz, 1 H), 1.21 (dd, *J* = 18.2, 11.2 Hz, 1 H).

LRMS: (ESI^+, Q-tof)

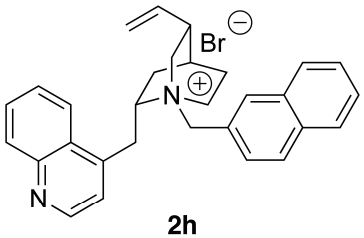
191.1 (80), 279.2 (35), 469.3 (100, M-Br^+)

HRMS: $C_{34}H_{33}N_2^+$ (ESI^+, Q-tof)

Calcd: 469.2644

Found: 469.2639

Preparation of *N*-(*2*-Naphthylmethyl)deoxycinchonidinium Bromide (2h)



2h

Following General Procedure I, deoxycinchonidine (100 mg, 0.359 mmol), MeCN (3.60 mL, 0.1 M), and 2-bromomethylnaphthalene (87.0 mg, 0.390 mmol, 1.10 equiv) were combined in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred for 3 h. The solvent was removed on a rotavap (20 mm Hg, 25 °C) and the solid residue was triturated with Et_2O (10 mL) then filtered. The filter cake was then sonicated in TBME (10 mL) and then filtered to afford 156 mg (87%) of **2h** as an off-white, crystalline solid.

Data for **2h**:

m.p.: 165 °C (decomp.)

^{1}H-NMR: (500 MHz, $CDCl_3$)

8.61 (d, *J* = 4.4 Hz, 1 H), 8.44 - 8.37 (m, 1 H), 8.09 (s, 1 H), 8.02 - 7.95 (m, 1 H), 7.72 - 7.57 (m, 5 H), 7.52 (d, *J* = 8.4 Hz, 1 H), 7.48 - 7.43 (m, 1 H), 7.43 - 7.36 (m, 2 H), 5.88 (d, *J* = 12.8 Hz, 1 H), 5.65 (ddd, *J* = 17.2, 14.4, 9.9 Hz, 2 H), 5.12 (dd, *J* = 13.7, 9.2 Hz, 2 H), 4.52 (dt, *J* = 13.9, 8.4 Hz, 2 H), 4.37 (dd, *J* = 14.5, 3.7 Hz, 1 H), 3.97 - 3.79 (m, 3 H), 3.50 - 3.39 (m, 1 H), 2.65 (dd, *J* = 16.6, 7.5 Hz, 1 H), 2.08 (dd, *J* = 18.4, 11.5 Hz, 1 H), 1.96 - 1.77 (m, 3 H), 1.61 (s (br), 1 H), 1.36 (d, *J* = 13.2 Hz, 1 H).

^{13}C-NMR: (126 MHz, CD_3OD)

150.90, 148.95, 143.86, 137.88, 135.41, 134.96, 134.54, 131.36, 130.26, 130.24, 129.42, 129.07, 128.95, 128.93, 128.85, 128.22, 125.91, 125.05, 123.30, 118.11, 66.03, 65.89, 61.41, 50.93, 39.22, 33.22, 28.38, 27.62, 25.54.

LRMS: (ESI^+, Q-tof)

419.2 (100, M-Br^+)

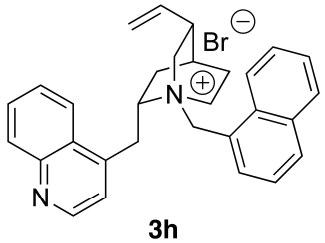
HRMS: $C_{30}H_{31}N_2^+$ (ESI^+, Q-tof)

Calcd: 419.2487

Found: 419.2491

TLC: R_f 0.55 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

Preparation of *N*-(*1*-Naphthylmethyl)deoxycinchonidinium Bromide (3h)



3h

Following General Procedure I, deoxycinchonidine (100 mg, 0.359 mmol), MeCN (3.60 mL, 0.1 M), and 2-bromomethylnaphthalene (87.0 mg, 0.390 mmol, 1.10 equiv) were combined in a 10-mL, single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred for 2 days. The solvent was removed on a rotavap (20 mm Hg, 25 °C) and the solid residue was triturated with Et_2O (10 mL) then filtered. The filter cake was then sonicated in

TBME (10 mL) in an ultrasonic bath and then filtered to afford 156 mg (87%) of **2h** as an off-white, crystalline solid.

Data for **3h**

m.p.: 165 °C (decomp.)

^{1}H-NMR: (500 MHz, $CDCl_3$)

8.64 (d, *J* = 8.6 Hz, 1 H), 8.30 (dd, *J* = 10.2, 6.4 Hz, 2 H), 8.02 (d, *J* = 7.0 Hz, 1 H), 7.90 (dd, *J* = 8.3, 1.1 Hz, 1 H), 7.69 - 7.53 (m, 5 H), 7.48 - 7.38 (m, 2 H), 6.96 - 6.88 (m, 1 H), 6.42 (d, *J* = 13.1 Hz, 1 H), 5.86 (d, *J* = 13.2 Hz, 1 H), 5.59 (ddd, *J* = 17.3, 10.5, 7.0 Hz, 1 H), 5.01 (dd, *J* = 27.1, 13.8 Hz, 2 H), 4.92 (dt, *J* = 15.7, 5.3 Hz, 1 H), 4.64 (t, *J* = 12.0 Hz, 1 H), 4.42 (dd, *J* = 13.8, 4.8 Hz, 1 H), 4.09 - 4.00 (m, 1 H), 3.53 - 3.35 (m, 2 H), 3.10 (dd, *J* = 13.0, 10.6 Hz, 1 H), 2.33 (d, *J* = 9.2 Hz, 1 H), 1.99 (dd, *J* = 17.1, 10.8 Hz, 1 H), 1.80 - 1.62 (m, 3 H), 1.19 (d, *J* = 10.3 Hz, 1 H)

^{13}C-NMR: (126 MHz, $CDCl_3$)

153.60, 141.23, 136.86, 136.67, 135.52, 134.41, 133.33, 132.72, 131.70, 130.65, 129.51, 128.25, 128.10, 126.94, 125.67, 124.88, 124.44, 122.84, 122.35, 121.78, 118.61, 66.25, 60.83, 59.68, 48.67, 37.76, 33.26, 27.16, 25.98, 24.94

LRMS: (ESI^+, Q-tof)

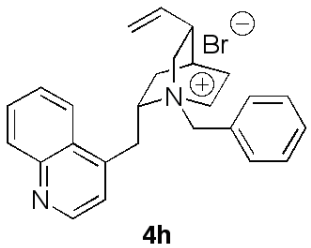
110.1 (20), 141.1 (80), 170.1 (8), 279.2 (100), 419.2 (50, M-Br^+)

HRMS: $C_{30}H_{31}N_2^+$ (ESI^+, Q-tof)

Calcd: 419.2487

Found: 419.2490

Preparation of *N*-(Benzyl)deoxycinchonidinium Bromide (4h)



4h

Following General Procedure I, deoxycinchonidine (101 mg, 0.362 mmol), MeCN (3.60 mL, 0.1 M), and benzyl bromide (47.0 μL, 0.400 mmol, 1.10 equiv) were combined in a 10-mL,

single-neck, round-bottomed flask fitted with an argon inlet and the mixture was stirred for 3 h. The solvent removed was removed on a rotavap (20 mm Hg, 25 °C) and the solid residue was then triturated with hexane and filtered. The filter cake sonicated twice with Et_2O (2 x 10 mL) and then filtered to afford 136 mg (84%) of **4h** as a pale-green, crystalline solid.

Data for **4h**:

m.p.: 113 °C (decomp)

^{1}H-NMR: (500 MHz, $CDCl_3$)

8.73 (d, *J* = 4.5 Hz, 1 H), 8.50 - 8.44 (m, 1 H), 8.06 (dd, *J* = 8.2, 1.2 Hz, 1 H), 7.75 - 7.62 (m, 4 H), 7.44 (d, *J* = 4.5 Hz, 1 H), 7.31 - 7.25 (m, 1 H), 7.22 (t, *J* = 7.3 Hz, 2 H), 5.75 - 5.59 (m, 2 H), 5.45 (d, *J* = 12.7 Hz, 1 H), 5.16 (dd, *J* = 17.8, 14.0 Hz, 2 H), 4.62 - 4.46 (m, 2 H), 4.27 (dd, *J* = 14.5, 3.6 Hz, 1 H), 3.86 (dd, *J* = 25.2, 12.8 Hz, 2 H), 3.79 - 3.69 (m, 1 H), 3.54 - 3.44 (m, 1 H), 2.69 (dd, *J* = 16.0, 7.6 Hz, 1 H), 2.15 - 2.03 (m, 1 H), 1.97 - 1.83 (m, 3 H), 1.44 - 1.34 (m, 1 H).

LRMS: (ESI^+, Q-tof)

91.1 (10), 110.1 (10), 279.2 (40), 369.2 (100, M-Br^+)

HRMS: $C_{26}H_{29}N_2^+$ (ESI^+, Q-tof)

Calcd: 369.2331

Found: 369.2337

TLC: R_f 0.54 (CH_2Cl_2/MeOH, 10:1) [silica gel, I_2]

References

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(i) H. Langhals, and S. Saulich, *Chem. Eur. J.* 2002, **8**(24), 5630-5643.

(ii) E. A. Dixon, A. Fischer, and F. P. Robinson, *Can. J. Chem*. 1981, **59**(17), 2629-2641.

(iii) P. L. Pickard, and T. L. Tolbert, *Org. Syn. Coll. Vol. 5* 1973, 520.

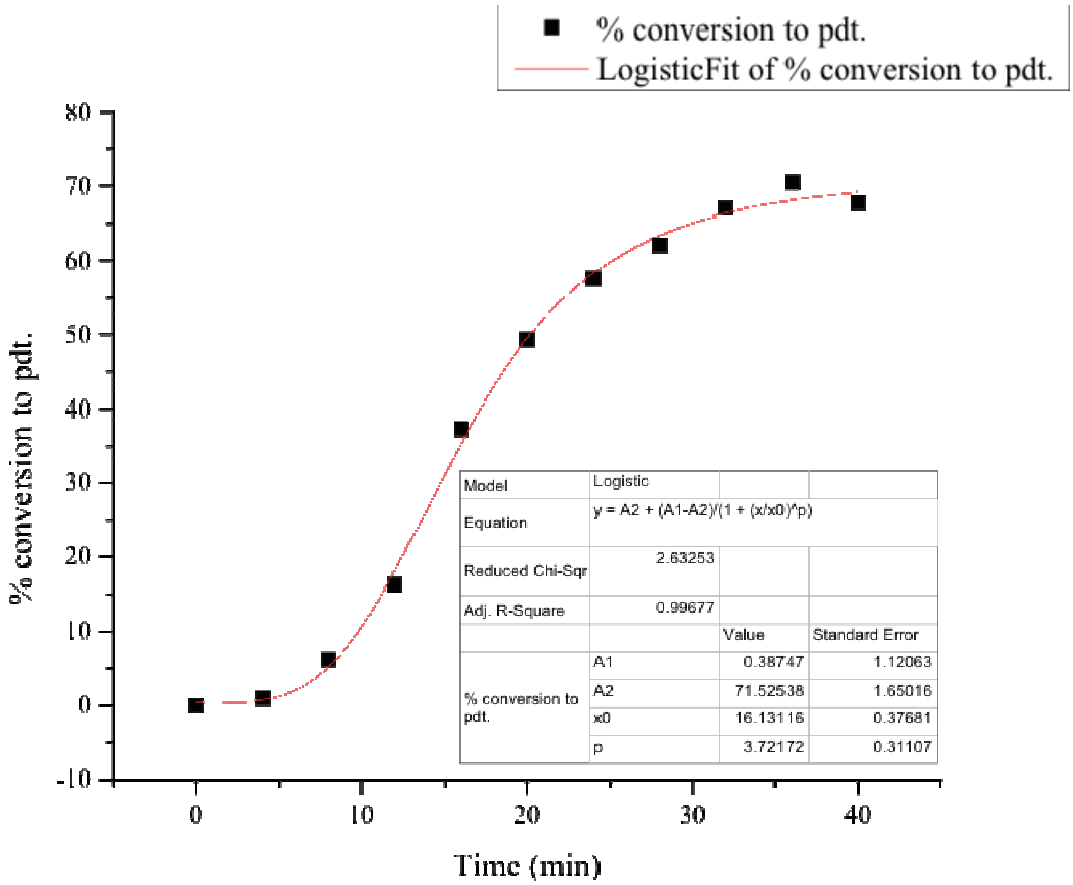
(iv) P. L. Dutton, B. R. Lichtenstein, J. F. Cerda, and R. L. Koder, *Chem. Comm.* 2009, 168-170.

(v) I. Lee, H. K. Oh, J. S. Ha, D. D. Sung, *J. Org. Chem.* 2004, **69**, 8219-8223

Kinetic Analyses of Catalysts in Series A

Catalyst **1a**: Run 1

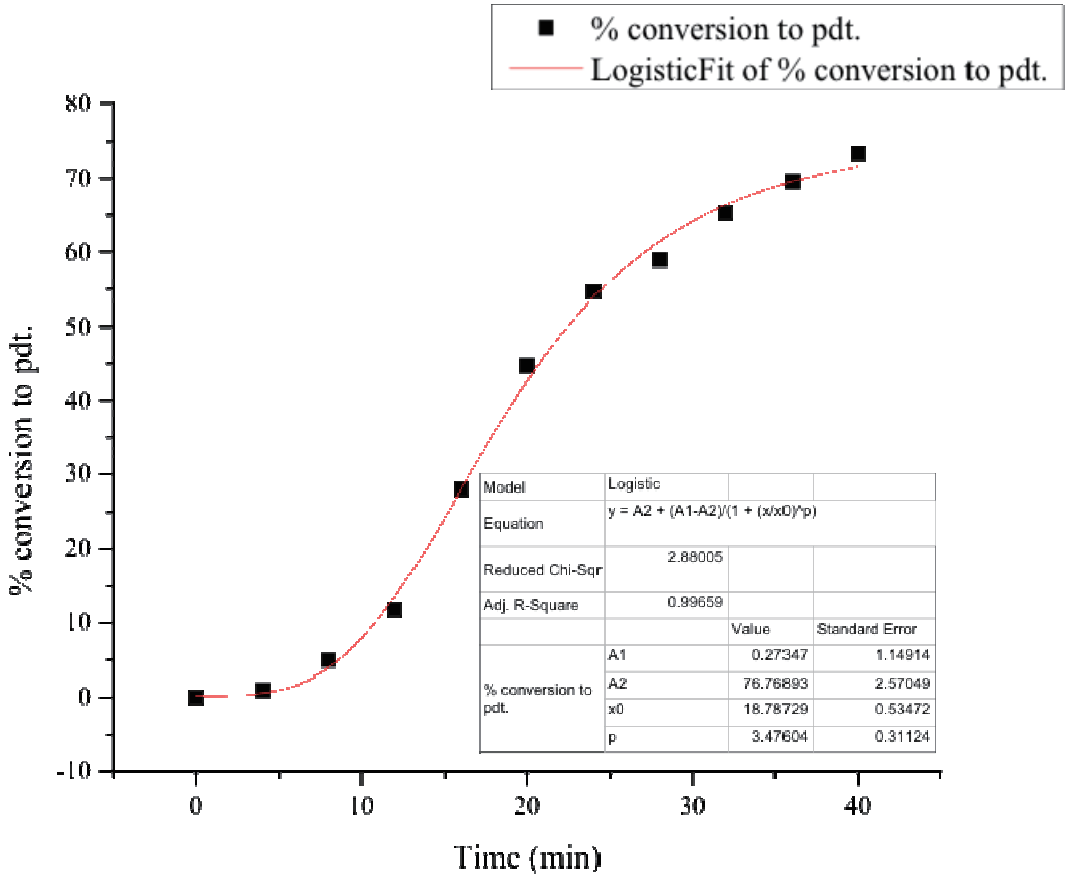
Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.00	0.0
4	254.0	6315.24	68.36	3.27	1.0
8	254.0	6655.10	462.93	21.03	6.2
12	254.0	6107.59	1115.00	55.20	16.3
16	254.0	5897.88	2466.57	126.45	37.3
20	254.0	6424.48	3549.97	167.08	49.3
24	254.0	7382.42	4765.74	195.19	57.6
28	254.0	6173.24	4297.34	210.48	62.1
32	254.0	6503.01	4885.58	227.16	67.0
36	254.0	7039.97	5559.75	238.79	70.4
40	254.0	6655.06	5052.67	229.56	67.7



Half-Life = 20 min

Catalyst **1a**: Run 2

Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
4	254.0	6525.65	70.70	3.3	1.0
8	254.0	6077.37	336.71	16.8	4.9
12	254.0	6667.15	879.72	39.9	11.8
16	254.0	6060.03	1905.65	95.1	28.0
20	254.0	6189.47	3102.61	151.6	44.7
24	254.0	6697.23	4101.86	185.2	54.6
28	254.0	7045.90	4652.70	199.7	58.9
32	254.0	6297.25	4608.70	221.3	65.3
36	254.0	8091.08	6307.97	235.7	69.5
40	254.0	7020.25	5777.23	248.8	73.4

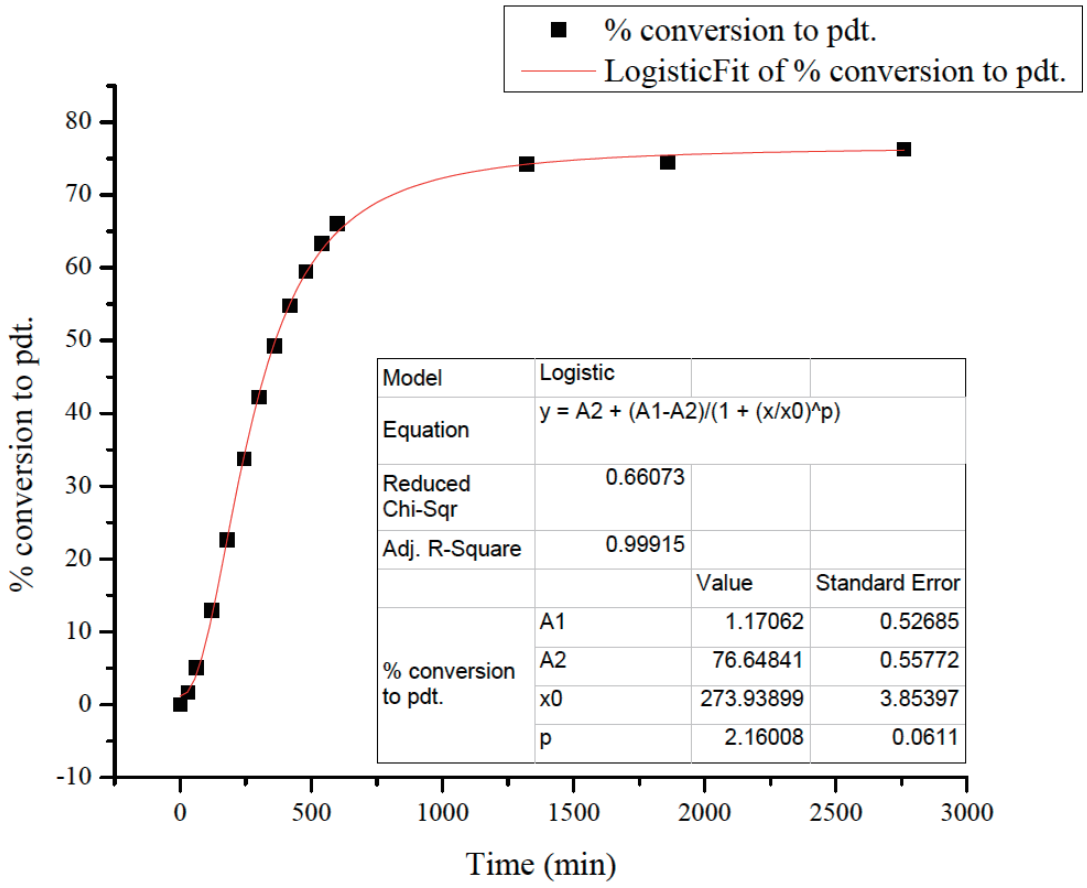


Half-Life = 22 min

Average Half-Life = 21 min

Catalyst **2a**: Run 1

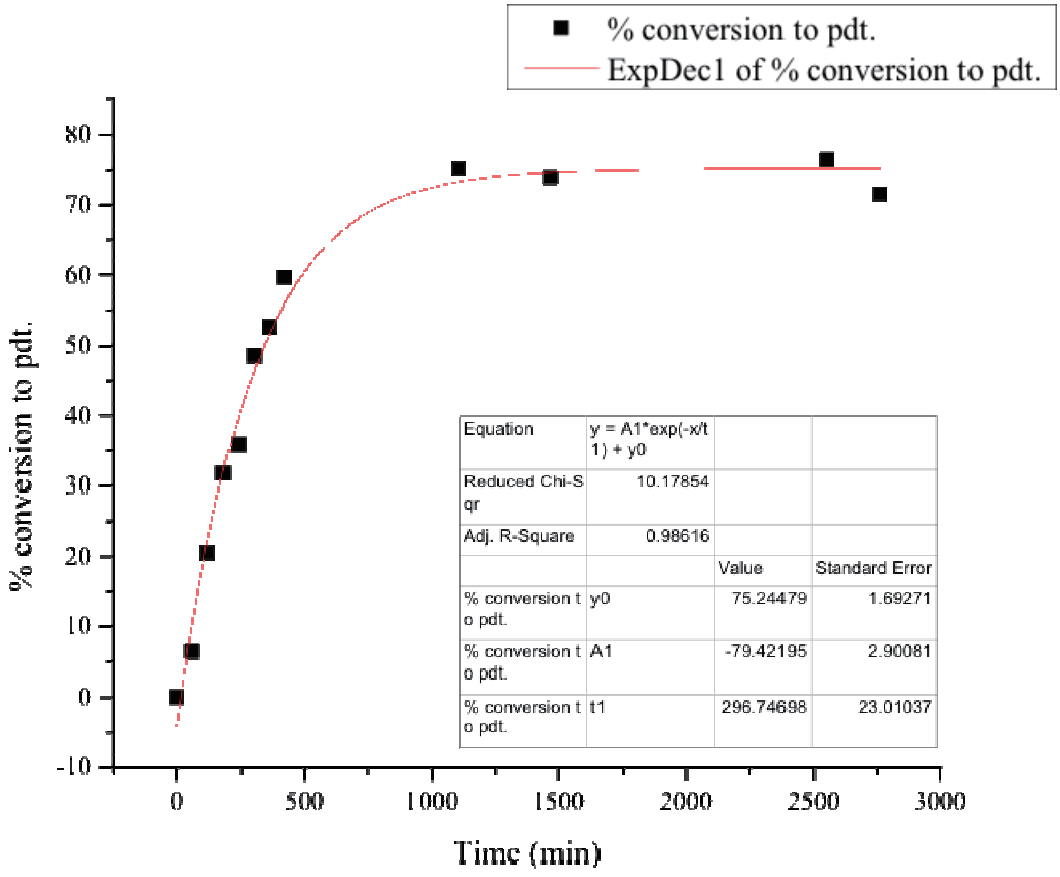
Time (min)	Standard (umol)	Standard Area	Product Area	Product (umol)	% Product
0	254.4	1.00	0.00	0.0	0.0
30	254.4	6090.60	113.01	5.6	1.7
61	254.4	6386.44	362.39	17.2	5.1
120	254.4	7553.15	1097.38	44.0	13.0
180	254.4	7437.62	1885.13	76.8	22.6
244	254.4	7170.76	2708.80	114.4	33.7
300	254.4	7017.54	3317.81	143.2	42.2
360	254.4	7163.19	3952.86	167.1	49.3
420	254.4	7223.67	4427.49	185.6	54.8
480	254.4	7401.25	4928.23	201.6	59.5
540	254.4	7653.35	5427.32	214.8	63.3
600	254.4	7117.47	5262.02	223.9	66.0
1320	254.4	7197.75	5979.38	251.6	74.2
1860	254.4	7042.44	5868.89	252.4	74.4
2760	254.4	7217.98	6162.11	258.5	76.3



Half-Life = 363 min

Catalyst **2a**: Run 2

Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.4	1.00	0.00	0.0	0.0
60	254.4	7764.86	557.63	21.7	6.4
120	254.4	7135.54	1641.45	69.7	20.5
180	254.4	7211.92	2565.60	107.7	31.8
240	254.4	7838.86	3141.89	121.4	35.8
300	254.4	7704.01	4191.80	164.8	48.6
360	254.4	7821.57	4611.86	178.6	52.7
420	254.4	7893.62	5272.90	202.3	59.7
1103	254.4	6816.47	5738.17	254.9	75.2
1468	254.4	7103.48	5878.89	250.6	73.9
2550	254.4	7509.56	6426.51	259.2	76.4

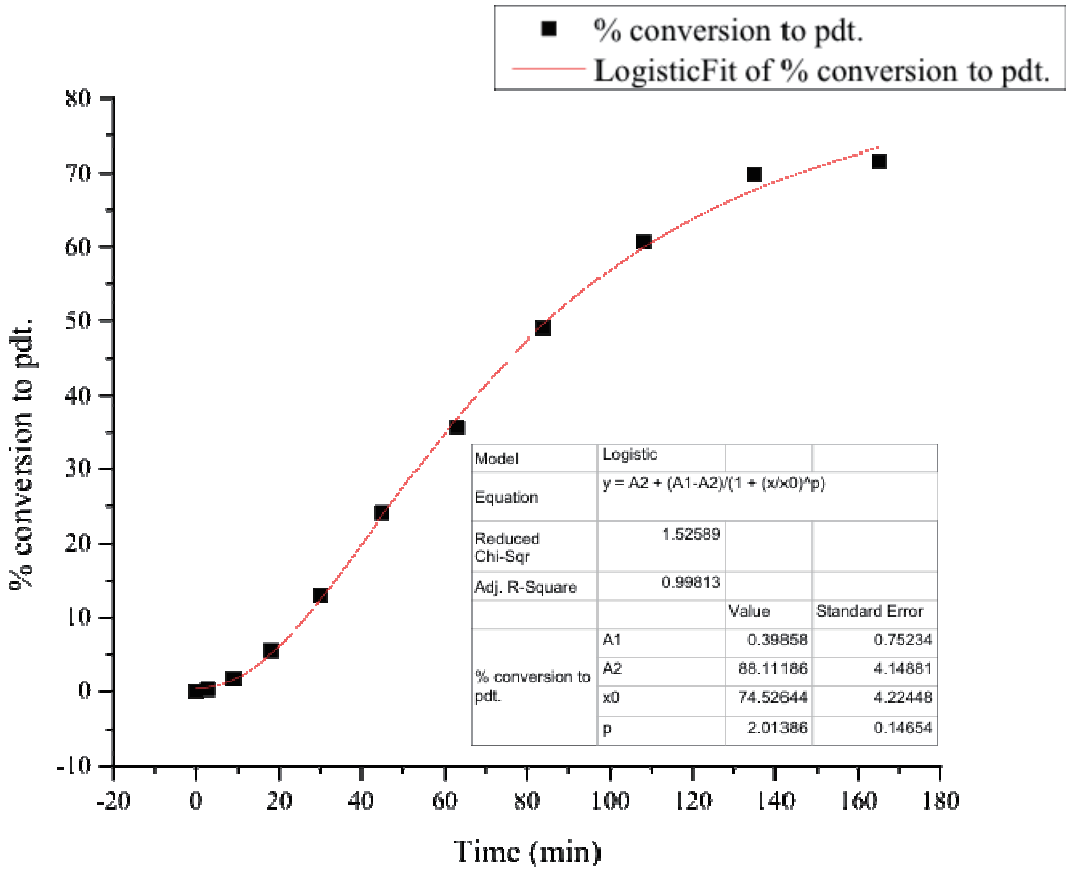


Half-Life = 340 min

Average Half-Life = 351 min

Catalyst **3a**: Run 1

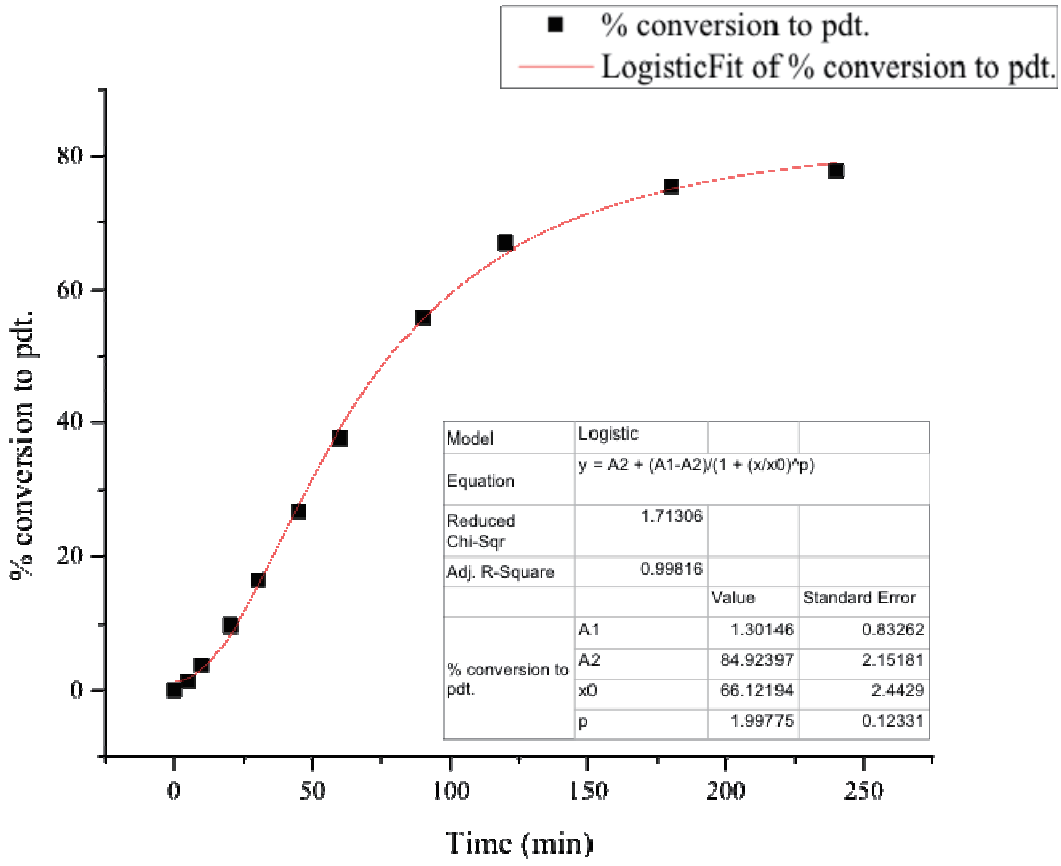
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
3	254.0	5724.09	20.61	1.1	0.3
9	254.0	5899.33	112.17	5.7	1.7
18	254.0	6511.32	404.84	18.8	5.5
30	254.0	6584.82	961.62	44.2	13.0
45	254.0	7436.89	2004.76	81.5	24.0
63	254.0	6987.36	2794.91	120.9	35.7
84	254.0	7502.23	4116.53	165.9	48.9
108	254.0	6968.71	4740.95	205.7	60.7
135	254.0	7027.91	5503.32	236.8	69.8
165	254.0	7938.40	6373.96	242.8	71.6



Half-Life = 85 min

Catalyst **3a**: Run 2

Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
5	254.0	7109.33	115.26	4.9	1.4
10	254.0	8054.54	347.28	13.0	3.8
20	254.0	7641.84	831.24	32.9	9.7
30	254.0	7735.89	1426.57	55.8	16.4
45	254.0	7214.04	2169.73	90.9	26.8
60	254.0	7402.72	3129.77	127.8	37.7
90	254.0	7277.34	4554.41	189.2	55.8
120	254.0	7206.75	5415.82	227.2	67.0
180	254.0	7633.05	6456.10	255.7	75.4
240	254.0	7413.94	6464.79	263.7	77.8
300	254.0	7155.78	6019.47	254.3	75.0
1020	254.0	8491.11	7208.87	256.7	75.7

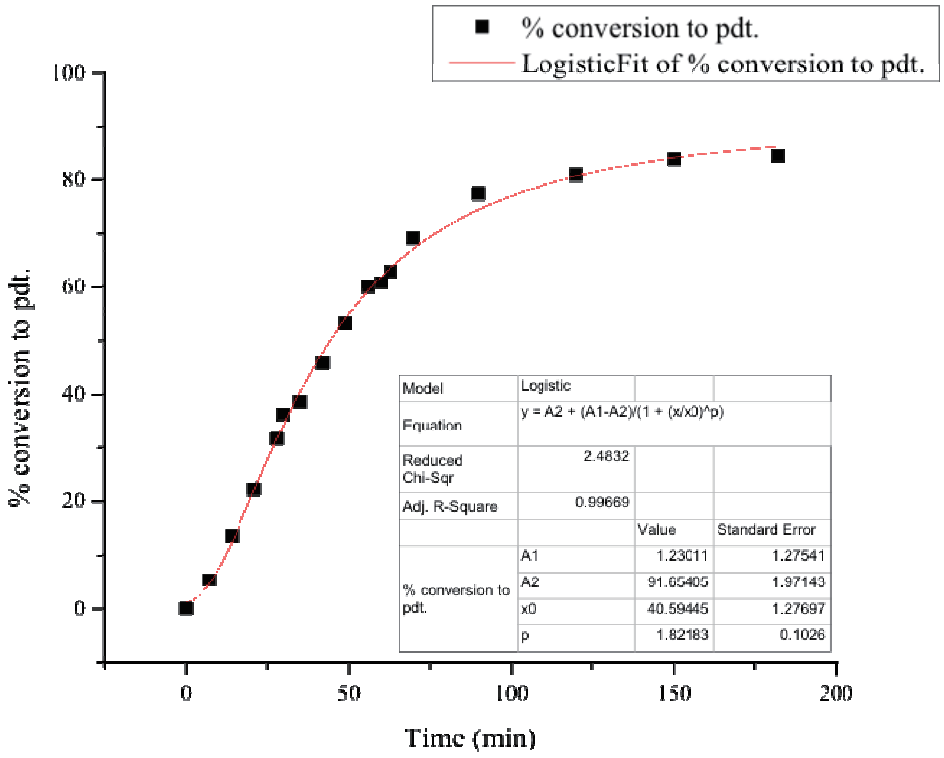


Half-Life = 78 min

Average Half-Life = 82 min

Catalyst **4a**: Run 1

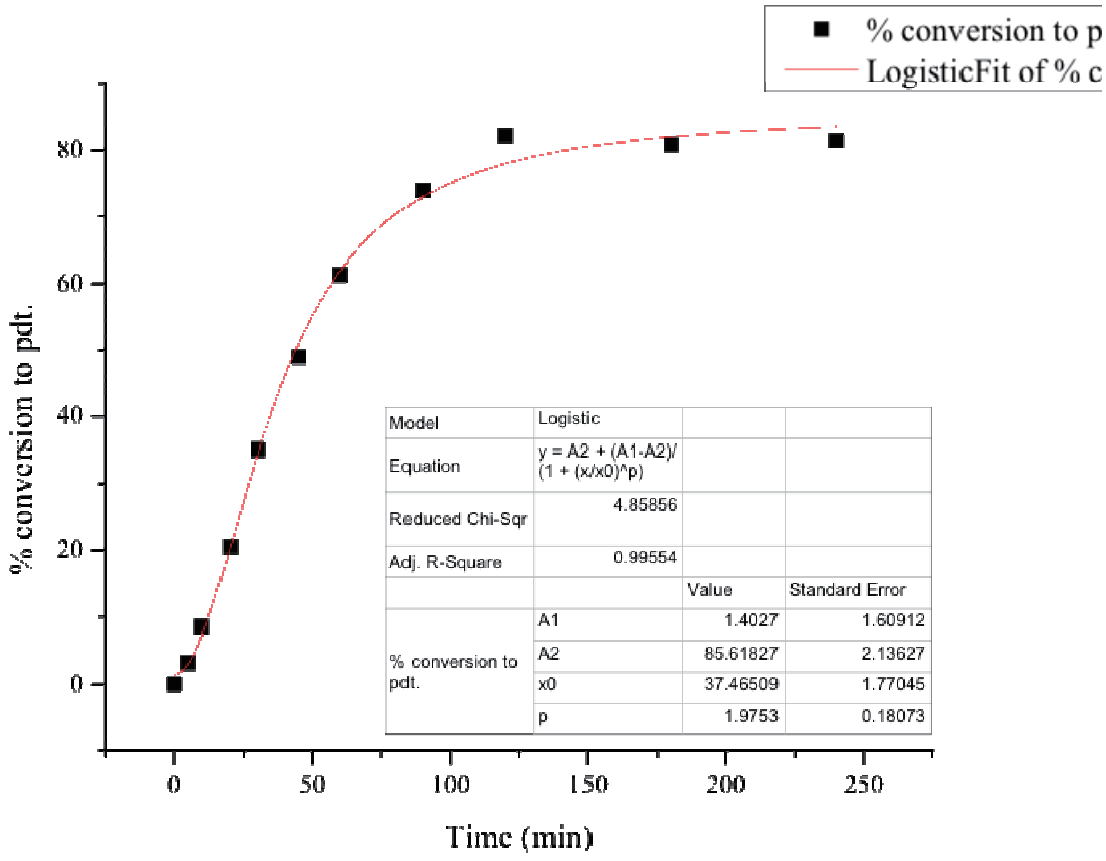
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
7	254.0	8099.77	491.92	18.4	5.4
14	254.0	6473.20	988.06	46.2	13.6
21	254.0	6481.47	1618.83	75.5	22.3
28	254.0	6848.23	2427.94	107.2	31.6
30	254.0	7449.53	3034.09	123.1	36.3
35	254.0	6195.73	2686.33	131.1	38.7
42	254.0	6774.26	3486.69	155.6	45.9
49	254.0	6132.76	3660.82	180.5	53.2
56	254.0	6327.44	4259.80	203.6	60.0
60	254.0	6343.97	4323.58	206.1	60.8
63	254.0	7591.06	5350.65	213.1	62.9
70	254.0	6811.49	5282.45	234.5	69.2
90	254.0	6360.96	5518.83	262.3	77.4
120	254.0	4711.11	4270.64	274.1	80.9
150	254.0	7115.57	6684.37	284.0	83.8
182	254.0	5451.71	5158.49	286.1	84.4



Half-Life = 44 min

Catalyst **4a**: Run 2

Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
5	254.0	6956.27	246.78	10.7	3.2
10	254.0	6983.71	671.26	29.1	8.6
20	254.0	7170.84	1646.42	69.4	20.5
30	254.0	7011.34	2755.72	118.8	35.1
45	254.0	6993.50	3834.21	165.8	48.9
60	254.0	6879.12	4722.85	207.6	61.2
90	254.0	6727.30	5568.84	250.3	73.8
120	254.0	7350.99	6770.02	278.5	82.1
180	254.0	7308.84	6618.29	273.8	80.8
240	254.0	7265.55	6626.65	275.8	81.3

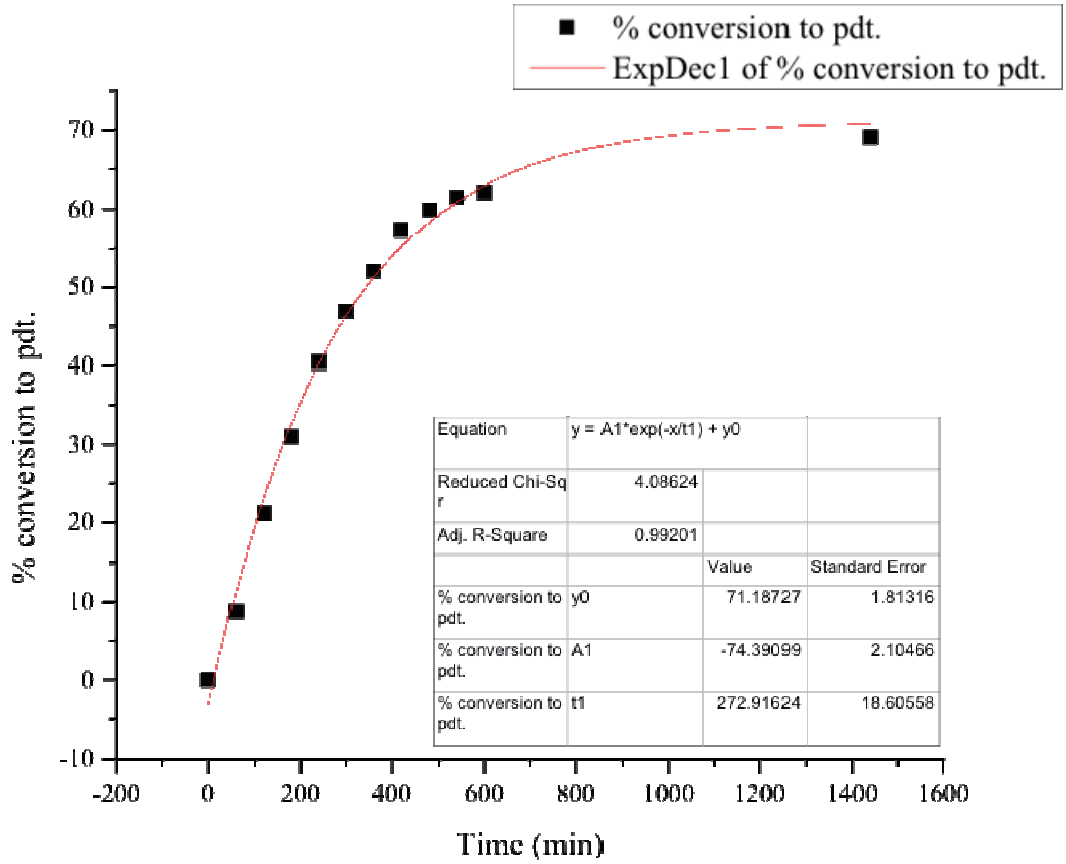


Half-Life = 44 min

Average Half-Life = 44 min

Catalyst **5a**: Run 1

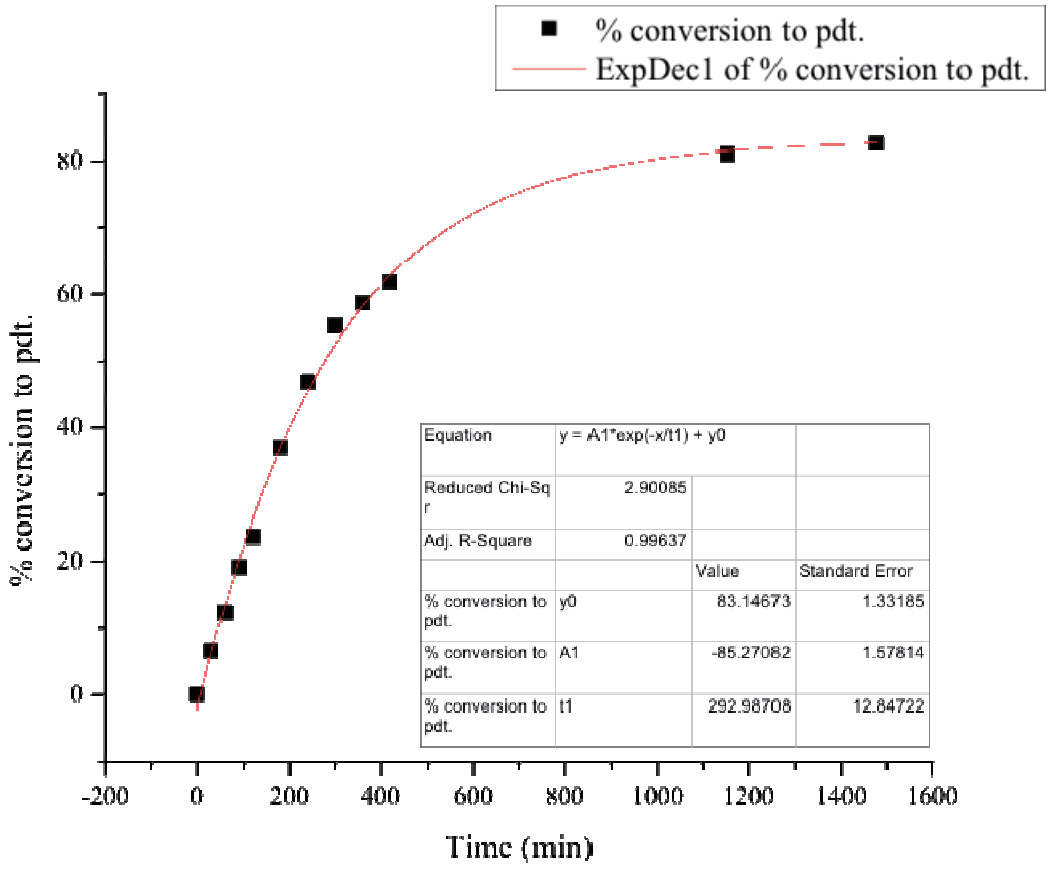
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.00	0.00
60	254.0	6551.96	646.15	29.82	8.80
120	254.0	6880.21	1634.19	71.82	21.19
180	254.0	6970.26	2422.03	105.06	30.99
240	254.0	6266.68	2842.73	137.16	40.46
300	254.0	6886.98	3625.36	159.17	46.95
360	254.0	7310.40	4273.93	176.77	52.15
420	254.0	7259.71	4668.02	194.42	57.35
480	254.0	7312.95	4913.18	203.14	59.92
540	254.0	7515.24	5182.03	208.49	61.50
600	254.0	6708.92	4674.66	210.68	62.15
1440.00	254.00	6427.62	4976.42	234.10	69.05



Half-Life = 343 min

Catalyst **5a**: Run 2

Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.4	1.00	0.00	0.0	0.0
30	254.4	6588.01	481.52	22.1	6.5
60	254.4	6964.99	963.41	41.9	12.4
90	254.4	6707.41	1436.32	64.8	19.1
120	254.4	6766.07	1799.51	80.5	23.8
180	254.4	6944.72	2876.93	125.5	37.0
240	254.4	6749.27	3543.57	159.0	46.9
300	254.4	7027.41	4341.94	187.1	55.2
360	254.4	6643.04	4358.22	198.7	58.6
420	254.4	6885.22	4763.41	209.5	61.8
1153	254.4	6768.02	6137.83	274.6	81.0
1478	254.4	6887.19	6364.26	279.8	82.5



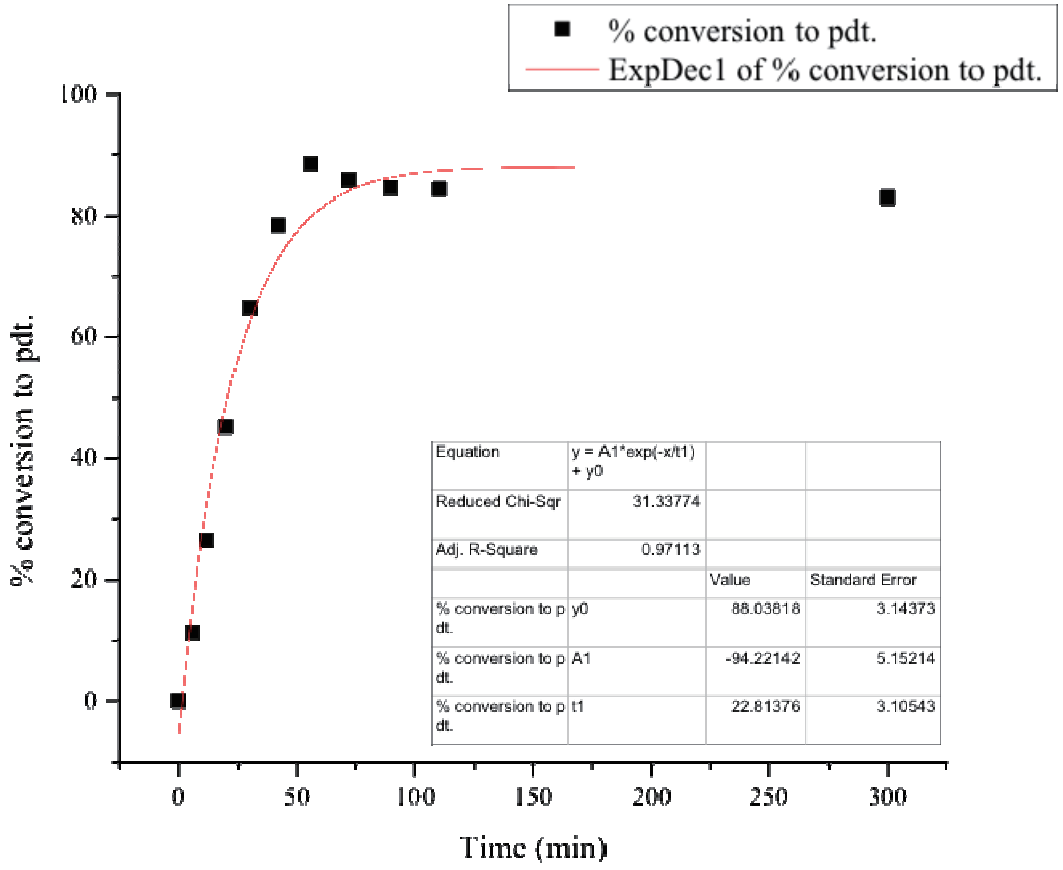
Half-Life = 277 min

Average Half-Life = 310 min

Kinetic Analyses of Catalysts in Series B

Catalyst **1b**: Run 1

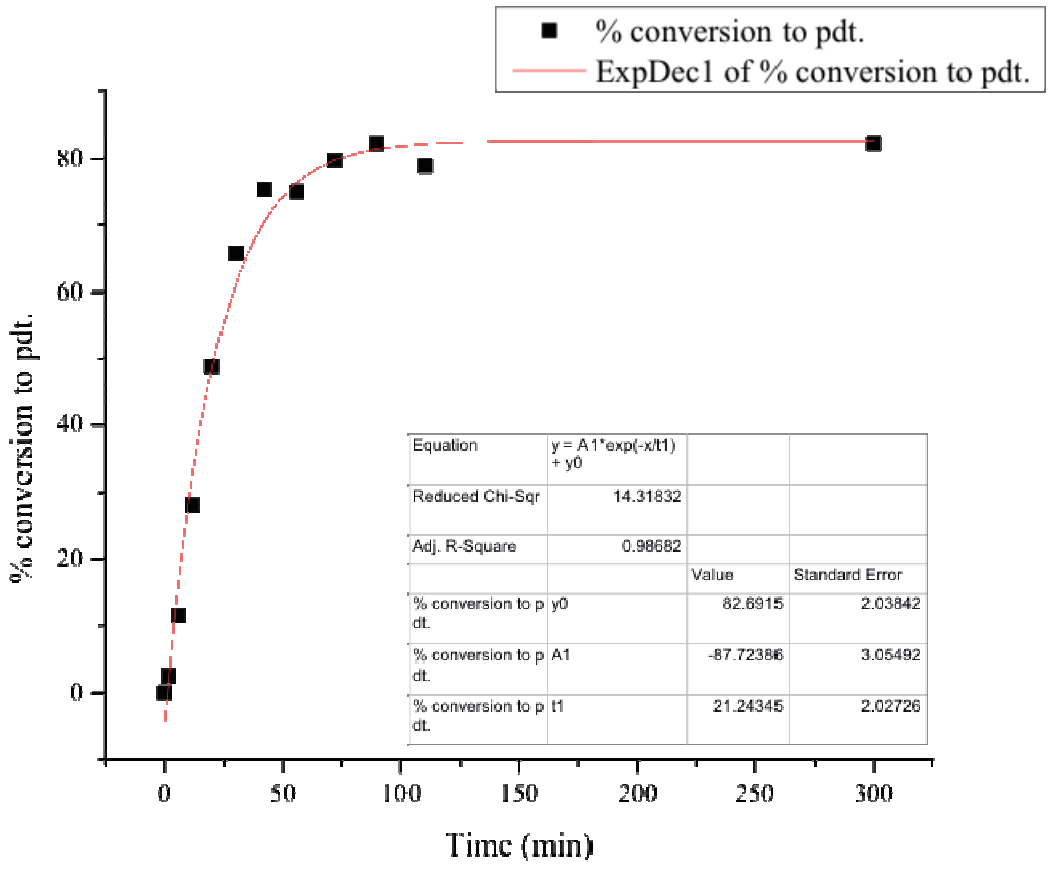
Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
6	254.0	7748.79	985.04	38.4	11.3
12	254.0	6567.97	1942.93	89.4	26.4
20	254.0	6318.09	3202.96	153.3	45.2
30	254.0	6684.17	4851.38	219.5	64.7
42	254.0	7460.54	6563.10	266.0	78.5
56	254.0	7489.41	7423.38	299.7	88.4
72	254.0	6878.57	6611.26	290.6	85.7
90	254.0	7598.74	7197.71	286.4	84.5
110	254.0	7548.24	7130.15	285.6	84.3
300	254.0	6857.69	6376.37	281.1	82.9



Half-Life = 21 min

Catalyst **1b**: Run 2

Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.00	0.0
2	254.0	6518.76	184.72	8.57	2.5
6	254.0	7542.25	970.35	38.90	11.5
12	254.0	6598.10	2082.50	95.43	28.2
20	254.0	6865.16	3758.28	165.53	48.8
30	254.0	6773.70	4987.07	222.61	65.7
42	254.0	7644.02	6455.82	255.36	75.3
56	254.0	6410.66	5388.35	254.14	75.0
72	254.0	7777.18	6948.31	270.14	79.7
90	254.0	7805.40	7196.24	278.76	82.2
110	254.0	6747.65	5967.86	267.42	78.9
300	254.0	6757.47	6230.80	278.80	82.2

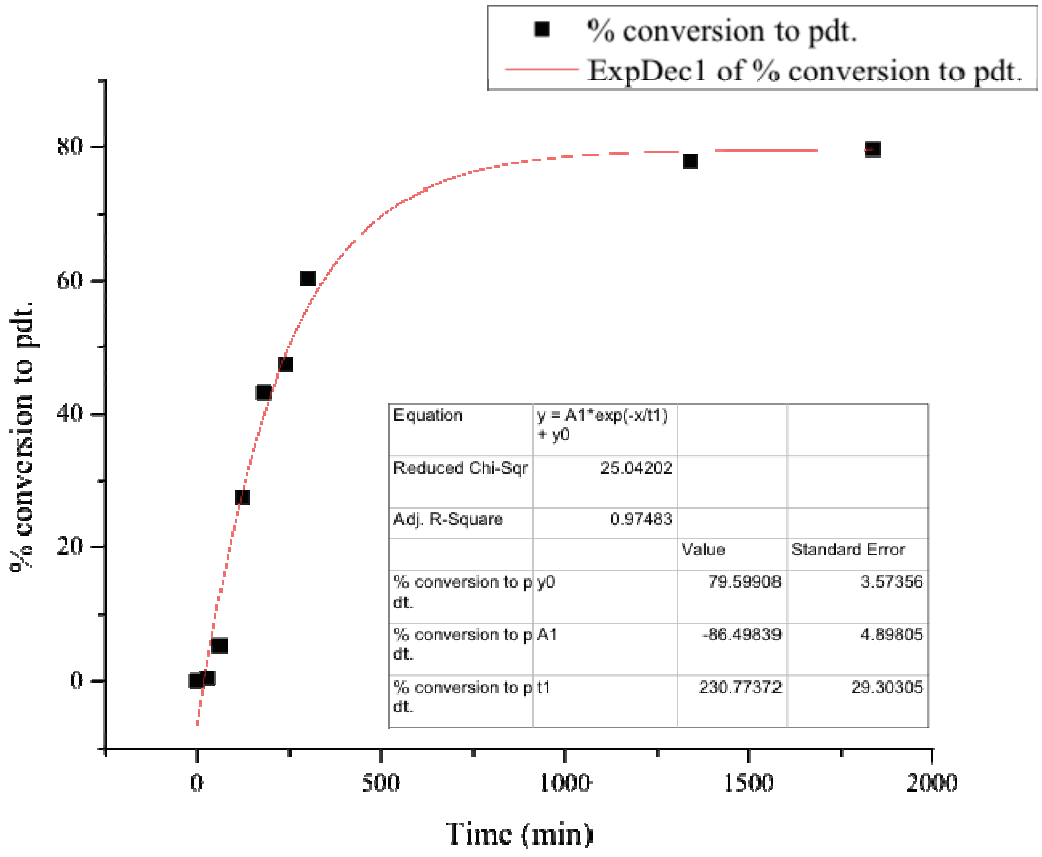


Half-Life = 21 min

Average Half-Life = 21 min

Catalyst **2b**: Run 1

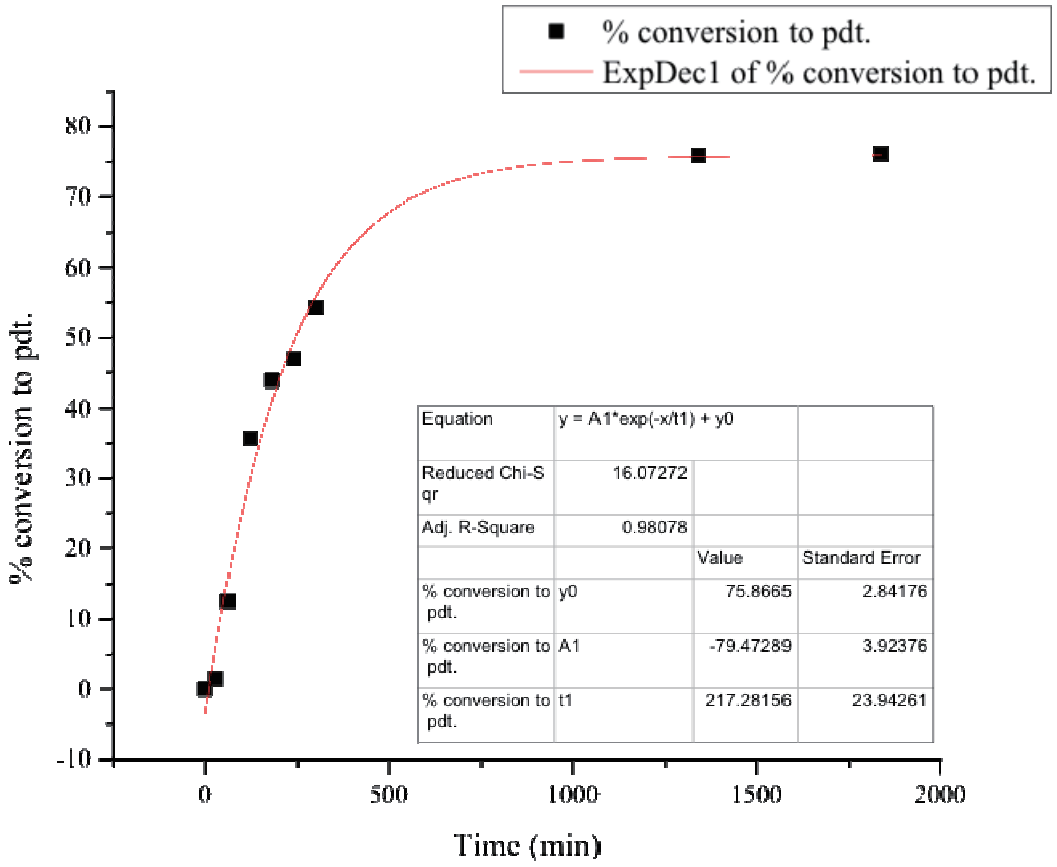
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
5	254.0	7879.88	0.00	0.0	0.0
30	254.0	7671.50	40.44	1.6	0.5
60	254.0	7635.95	456.30	18.1	5.3
120	254.0	7556.02	2331.50	93.3	27.5
180	254.0	7112.89	3454.01	146.8	43.3
240	254.0	7590.22	4029.87	160.5	47.4
300	254.0	7260.17	4909.52	204.5	60.3
1341	254.0	7782.06	6790.97	263.9	77.8
1837	254.0	8306.82	7412.94	269.8	79.6



Half-Life = 247 min

Catalyst **2b**: Run 2

Time (min)	Standard (umol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
5	254.0	7841.88	0.00	0.0	0.0
30	254.0	6461.39	107.85	5.0	1.5
60	254.0	6917.40	978.41	42.8	12.6
120	254.0	7423.29	2971.22	121.0	35.7
180	254.0	6886.53	3387.69	148.7	43.9
240	254.0	7504.17	3946.61	159.0	46.9
300	254.0	7686.25	4676.79	184.0	54.3
1341	254.0	7581.39	6448.81	257.2	75.9
1837	254.0	7969.25	6801.76	258.1	76.1

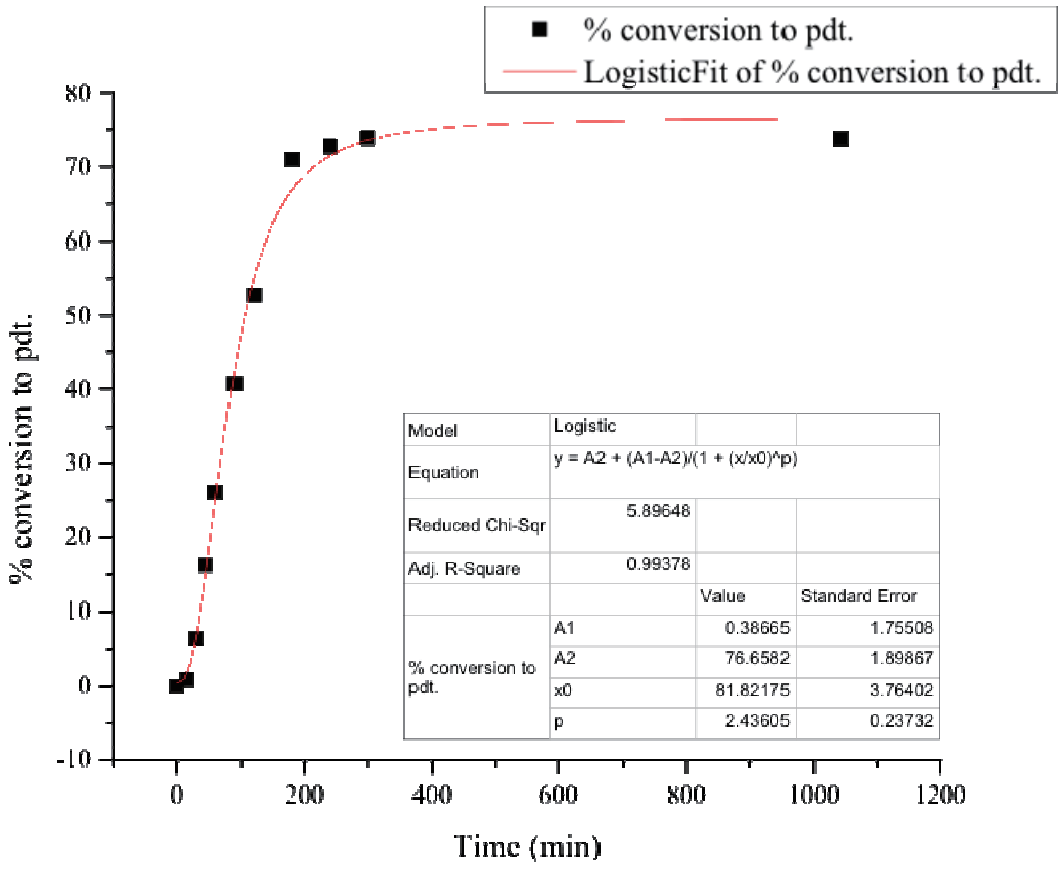


Half-Life = 244 min

Average Half-Life = 246 min

Catalyst **3b**: Run 1

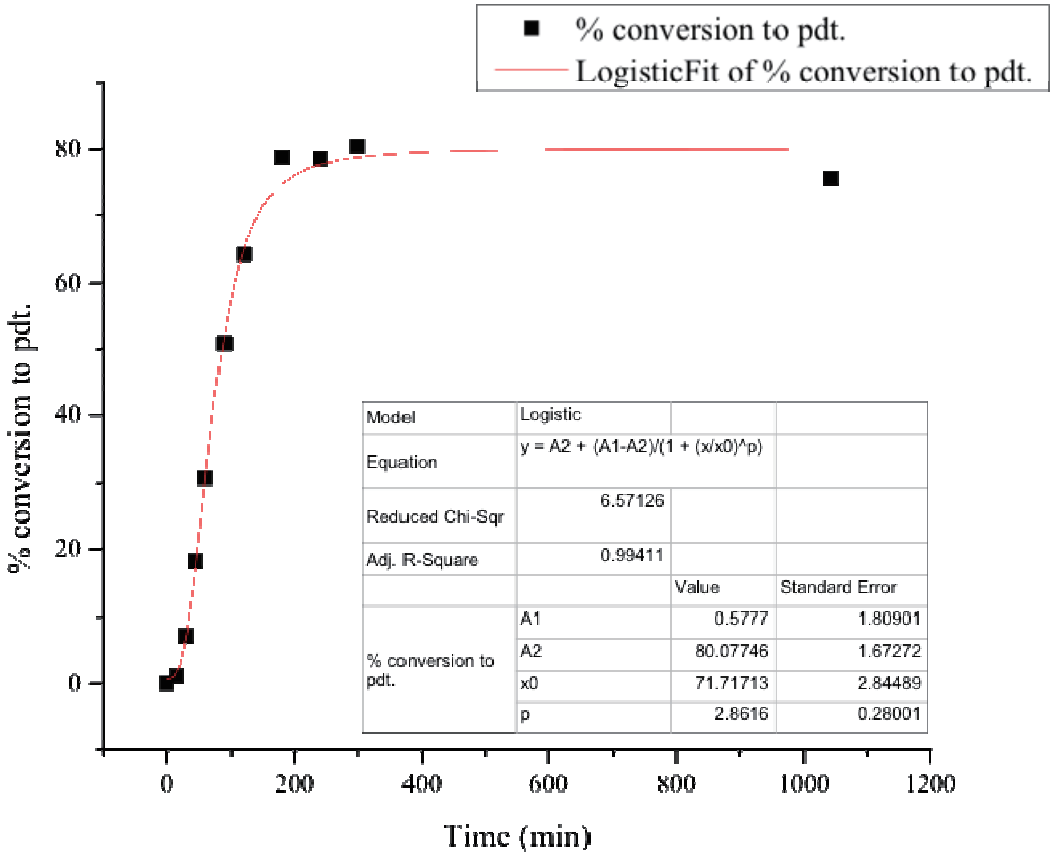
Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
5	254.0	7116.94	0.00	0.0	0.0
15	254.0	7529.49	78.86	3.2	0.9
30	254.0	6689.77	486.96	22.0	6.5
45	254.0	8134.10	1481.62	55.1	16.2
60	254.0	6632.84	1941.55	88.5	26.1
90	254.0	7293.13	3324.44	137.8	40.7
120	254.0	7563.81	4471.39	178.7	52.7
180	254.0	6919.37	5506.73	240.6	71.0
240	254.0	6872.94	5607.03	246.7	72.8
300	254.0	7407.61	6136.27	250.5	73.9
1042	254.0	6839.24	5655.01	250.0	73.7



Half-Life = 106 min

Catalyst **3b**: Run 2

Time (min)	Standard (μmol)	Product Area	Standard Area	Product (μmol)	% Product
0	254.0	0.00	1.00	0.0	0.0
5	254.0	0.00	7250.08	0.0	0.0
15	254.0	90.06	7390.36	3.7	1.1
30	254.0	579.70	7280.64	24.1	7.1
45	254.0	1385.53	6780.43	61.8	18.2
60	254.0	2690.50	7804.84	104.2	30.7
90	254.0	4150.43	7281.74	172.3	50.8
120	254.0	5310.07	7363.24	218.1	64.3
180	254.0	6169.84	6990.93	266.8	78.7
240	254.0	5813.56	6602.04	266.3	78.5
300	254.0	6631.58	7357.89	272.5	80.4
1042	254.0	6154.85	7266.25	256.1	75.5

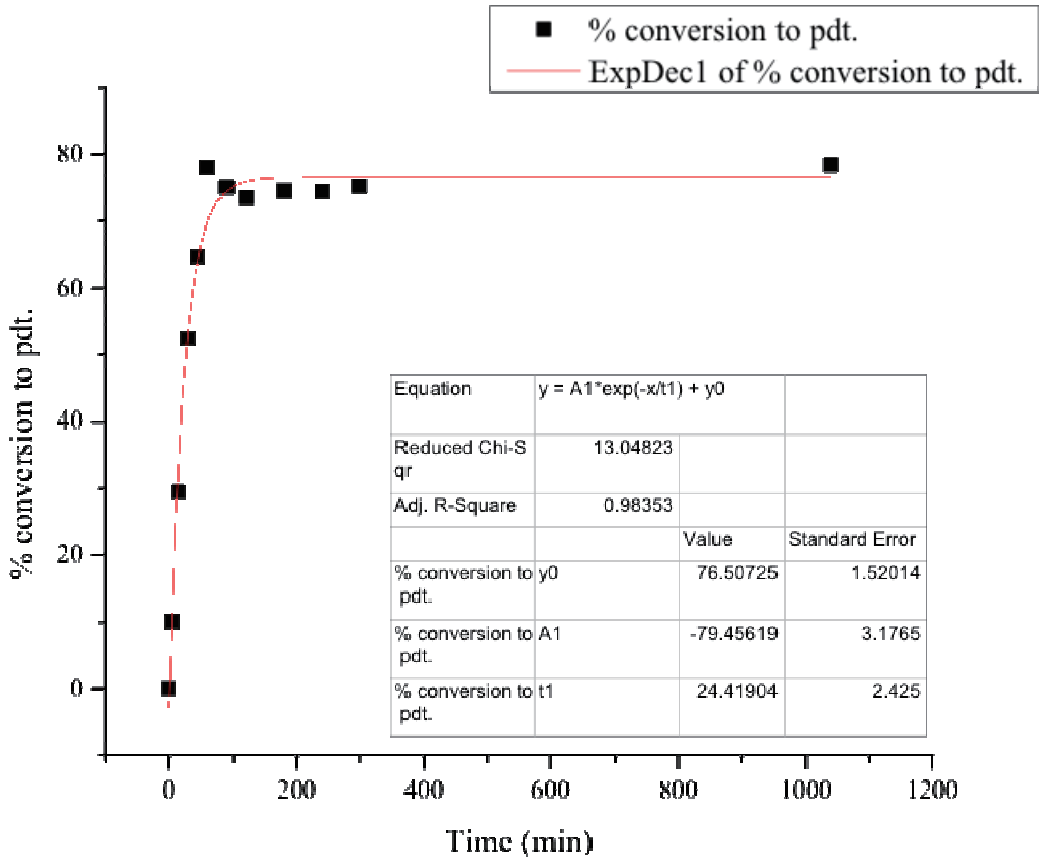


Half-Life = 85 min

Average Half-Life = 95 min

Catalyst **4b**: Run 1

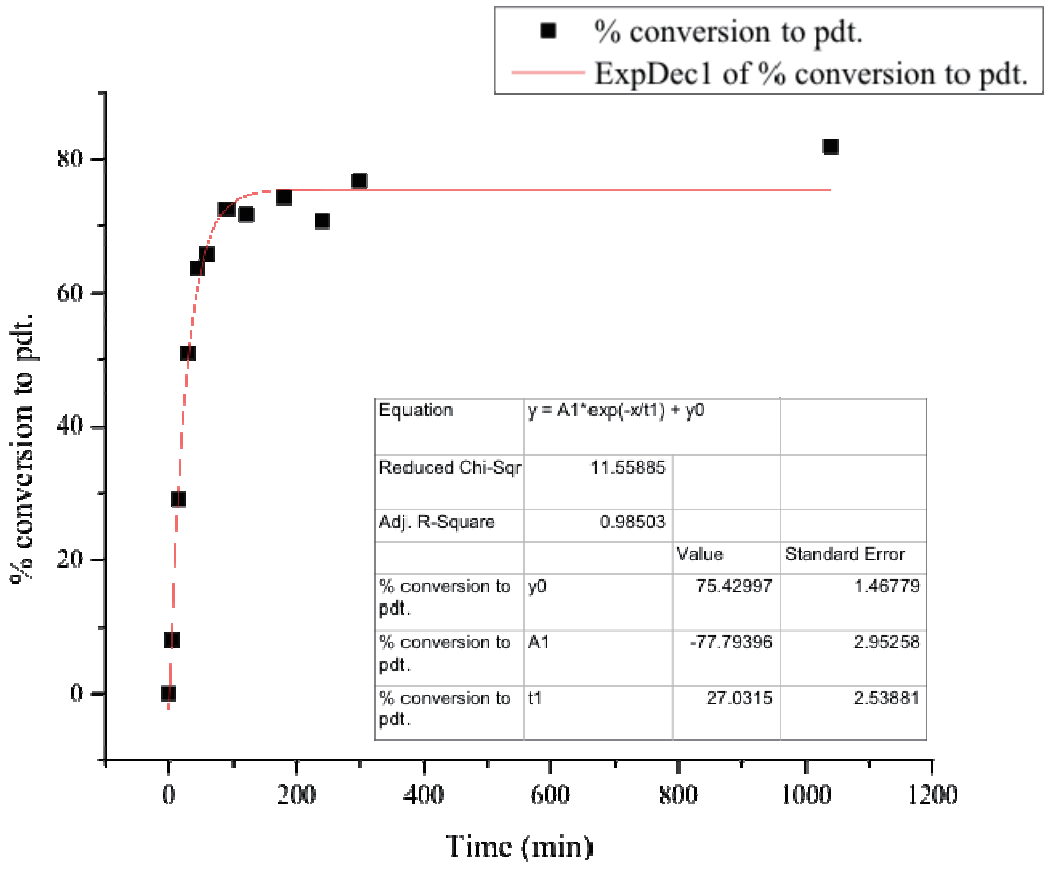
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
5	254.0	6915.34	783.53	34.3	10.1
15	254.0	6980.95	2308.70	100.0	29.5
30	254.0	6784.76	3985.27	177.6	52.4
45	254.0	7278.12	5281.28	219.4	64.7
60	254.0	7019.90	6137.38	264.3	78.0
90	254.0	7091.19	5962.76	254.2	75.0
120	254.0	6239.32	5139.75	249.1	73.5
180	254.0	7578.16	6326.69	252.4	74.5
240	254.0	6972.50	5818.39	252.3	74.4
300	254.0	7026.35	5921.27	254.8	75.2
1039	254.0	6420.38	5643.17	265.8	78.4



Half-Life = 27 min

Catalyst **4b**: Run 2

Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
5	254.0	8268.86	752.64	27.5	8.1
15	254.0	7168.00	2337.65	98.6	29.1
30	254.0	6913.03	3949.39	172.7	51.0
45	254.0	8533.48	6104.96	216.3	63.8
60	254.0	7106.51	5246.87	223.2	65.9
90	254.0	6864.22	5574.94	245.6	72.4
120	254.0	6501.38	5222.00	242.9	71.6
180	254.0	7052.11	5870.49	251.7	74.2
240	254.0	7260.77	5750.17	239.5	70.6
300	254.0	7612.69	6545.06	260.0	76.7
1039	254.0	6977.30	6410.19	277.8	81.9

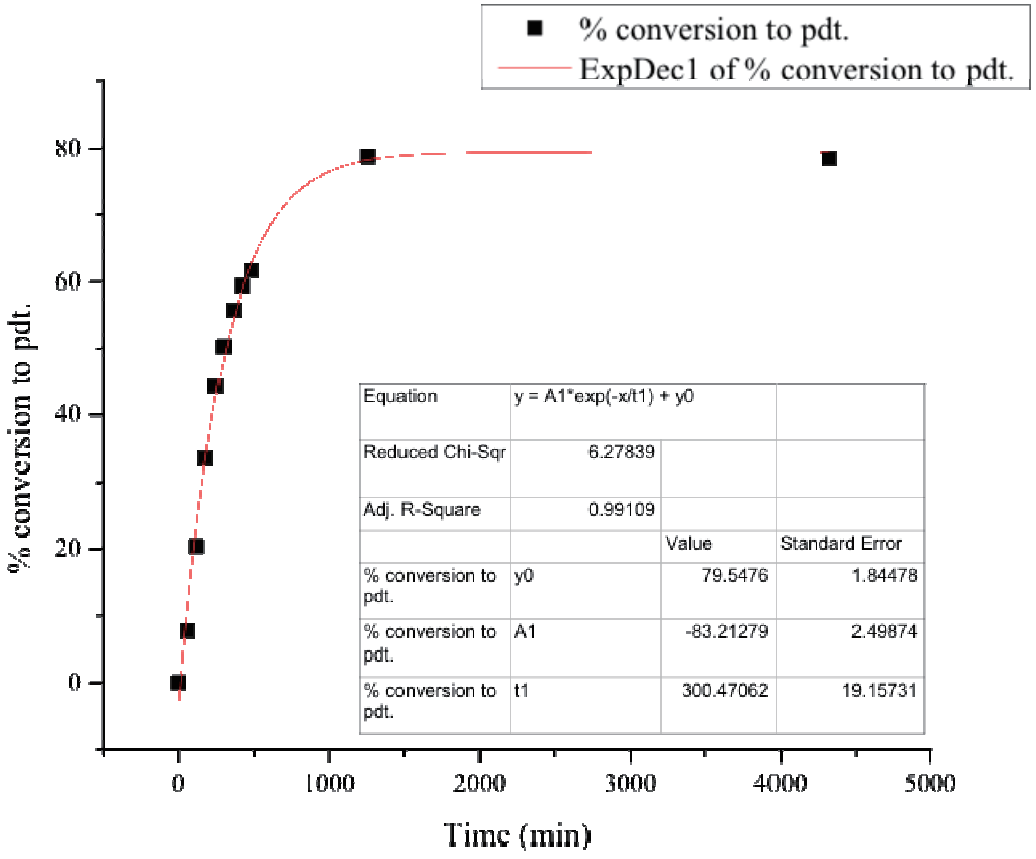


Half-Life = 30 min

Average Half-Life = 29 min

Catalyst **5b**: Run 1

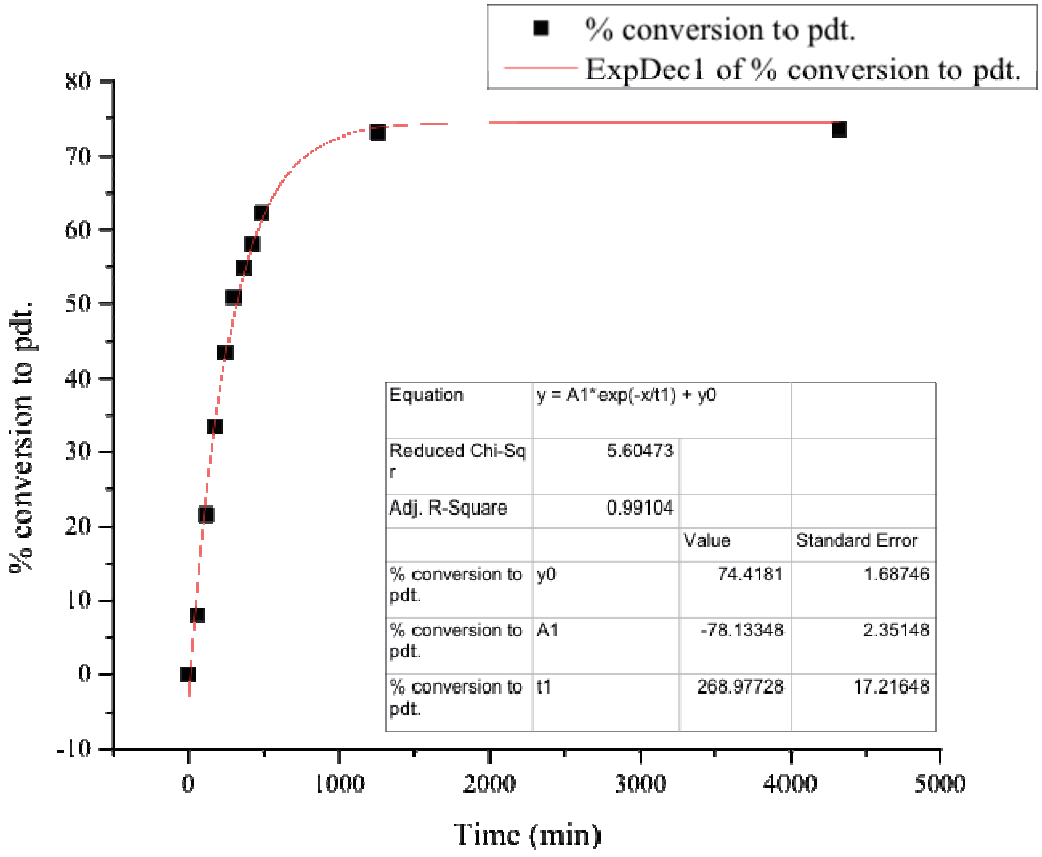
Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0	0.0
60	254.0	7515.93	648.02	26.06956273	7.7
120	254.0	7213.64	1646.44	69.01101463	20.4
180	254.0	7913.31	2972.46	113.5755569	33.5
240	254.0	6753.74	3360.49	150.4474812	44.4
300	254.0	8002.67	4513.40	170.5276886	50.3
360	254.0	7199.20	4499.93	188.9939234	55.8
420	254.0	7478.48	4977.12	201.229079	59.4
480	254.0	7621.79	5265.14	208.8716046	61.6
1260	254.0	7331.66	6477.10	267.1191093	78.8
4320	254.0	5576.05	4908.26	266.1507443	78.5



Half-Life = 311 min

Catalyst **5b**: Run 2

Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
60	254.0	7351.52	670.73	27.6	8.1
120	254.0	7540.39	1830.13	73.4	21.6
180	254.0	7364.30	2762.87	113.4	33.5
240	254.0	8103.71	3953.71	147.5	43.5
300	254.0	7115.94	4055.55	172.3	50.8
360	254.0	7554.33	4646.77	186.0	54.9
420	254.0	8041.56	5237.67	196.9	58.1
480	254.0	7699.79	5380.62	211.3	62.3
1260	254.0	8157.51	6690.44	248.0	73.2
4320	254.0	7505.50	6188.76	249.3	73.5



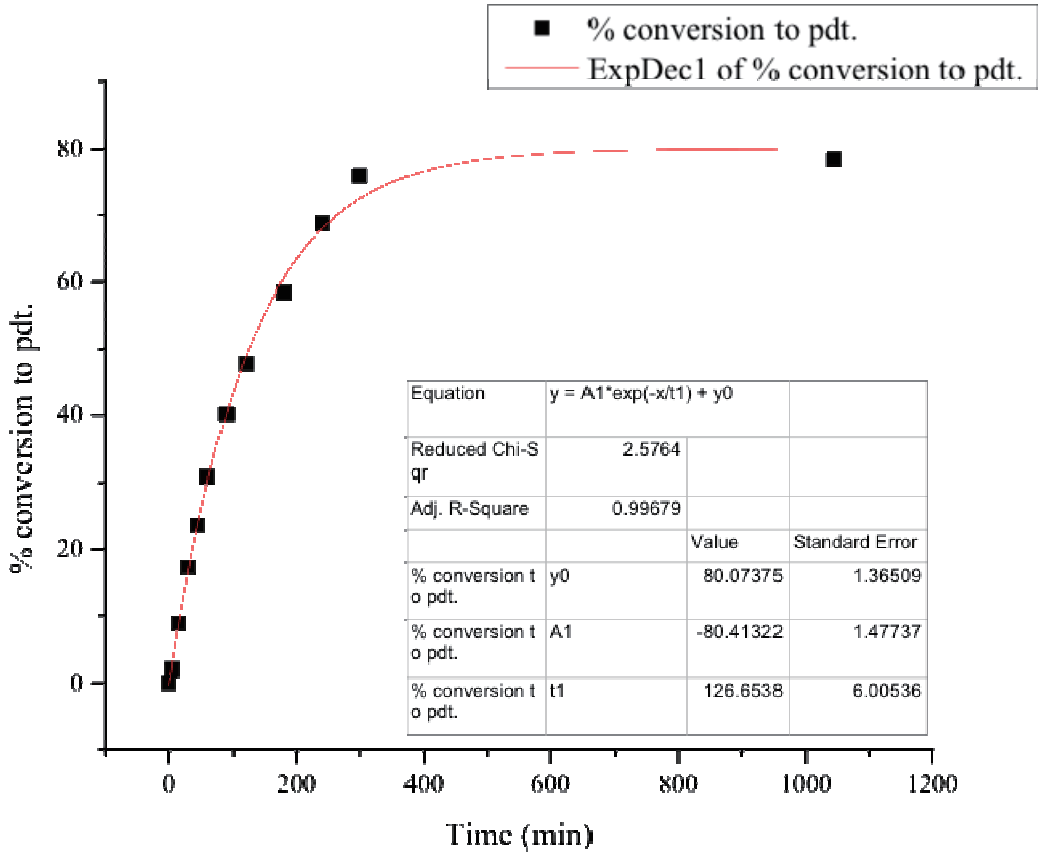
Half-Life = 313 min

Average Half-Life = 312 min

Kinetic Analyses of Catalysts in Series C

Catalyst **1c**: Run 1

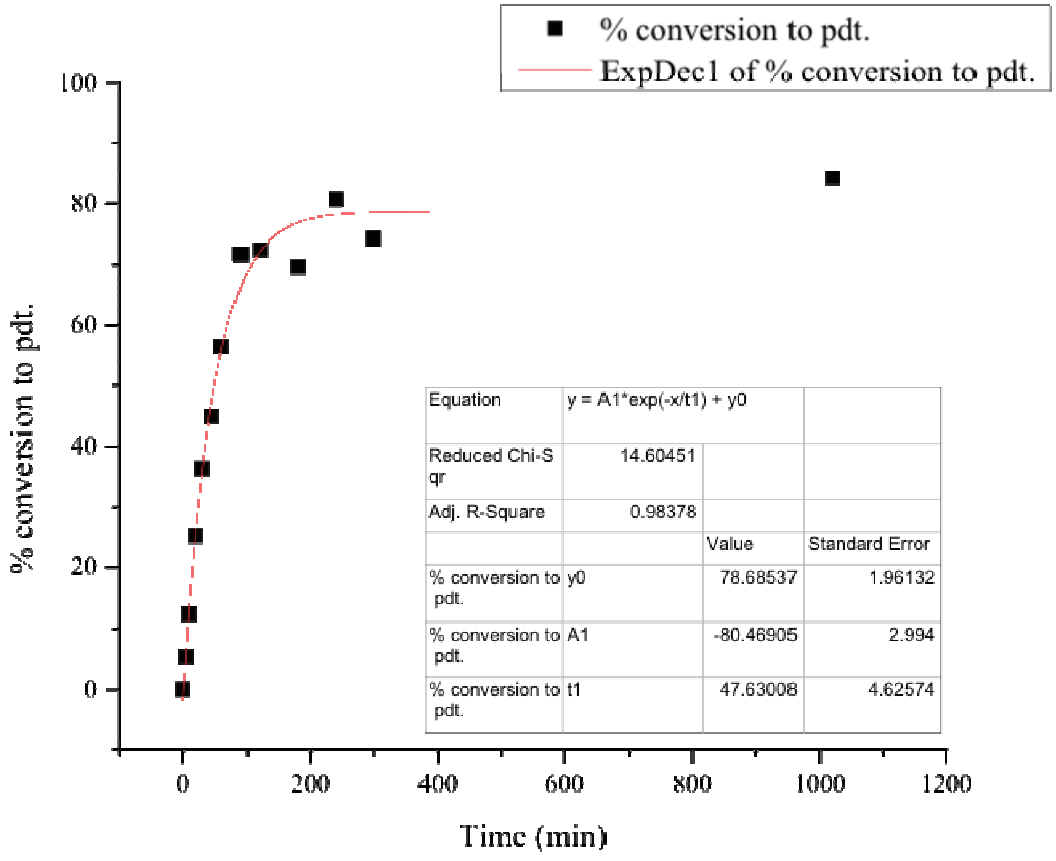
Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
5	254.0	7229.86	157.52	6.6	1.9
15	254.0	7227.43	715.20	29.9	8.8
30	254.0	6995.94	1360.21	58.8	17.3
45	254.0	6953.89	1844.50	80.2	23.7
60	254.0	5980.81	2065.91	104.4	30.8
90	254.0	6568.27	2955.29	136.0	40.1
120	254.0	7866.16	4215.99	162.1	47.8
180	254.0	6561.58	4296.26	198.0	58.4
240	254.0	5995.08	4624.01	233.2	68.8
300	254.0	6436.51	5480.08	257.4	75.9
1044	254.0	6175.21	5432.38	266.0	78.5



Half-Life = 125 min

Catalyst **1c**: Run 2

Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.4	1.00	0.00	0.0	0.0
5	254.4	7566.30	462.68	18.5	5.5
10	254.4	6850.47	952.01	42.1	12.4
20	254.4	7288.12	2061.08	85.6	25.3
30	254.4	6502.60	2648.20	123.3	36.4
45	254.4	6975.58	3500.42	152.0	44.8
60	254.4	7321.79	4625.62	191.3	56.4
90	254.4	6842.20	5492.58	243.1	71.7
120	254.4	7374.77	5984.07	245.7	72.5
180	254.4	7073.91	5517.55	236.2	69.7
240	254.4	6882.90	6210.53	273.3	80.6
300	254.4	7013.31	5829.00	251.7	74.2
1020	254.4	7014.34	6614.44	285.6	84.2

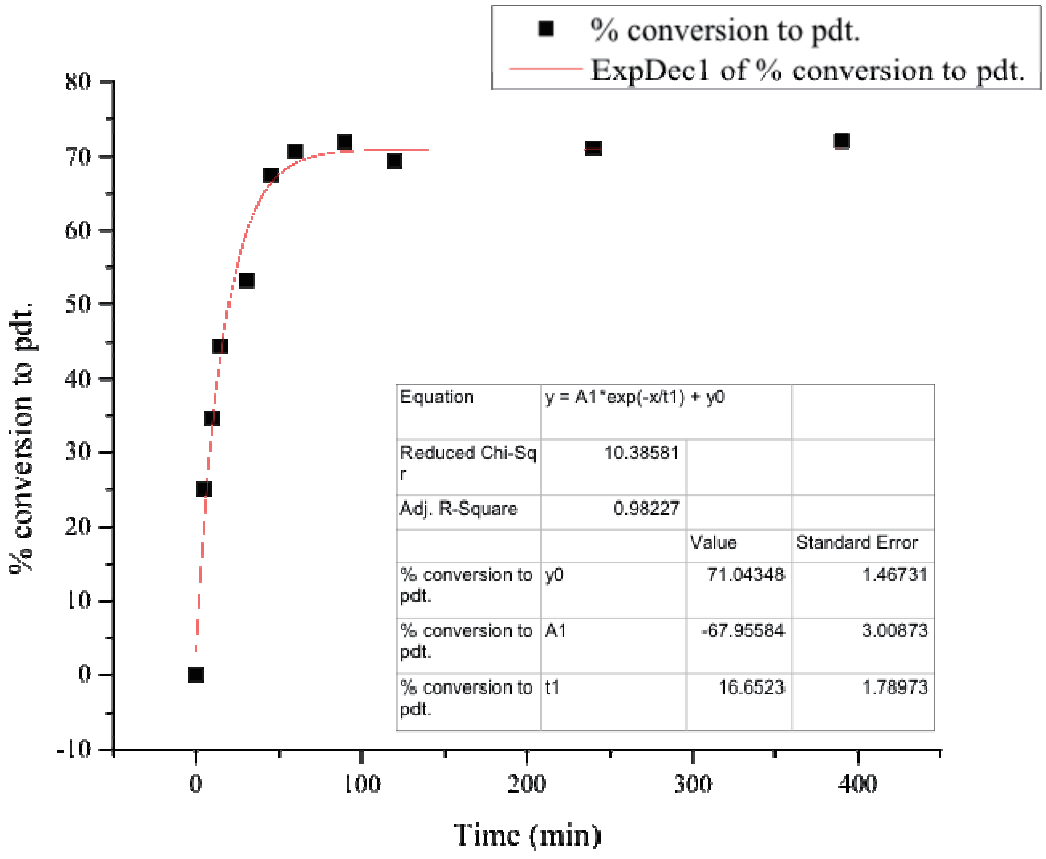


Half-Life = 49 min

Average Half = 87 min

Catalyst **2c**: Run 1

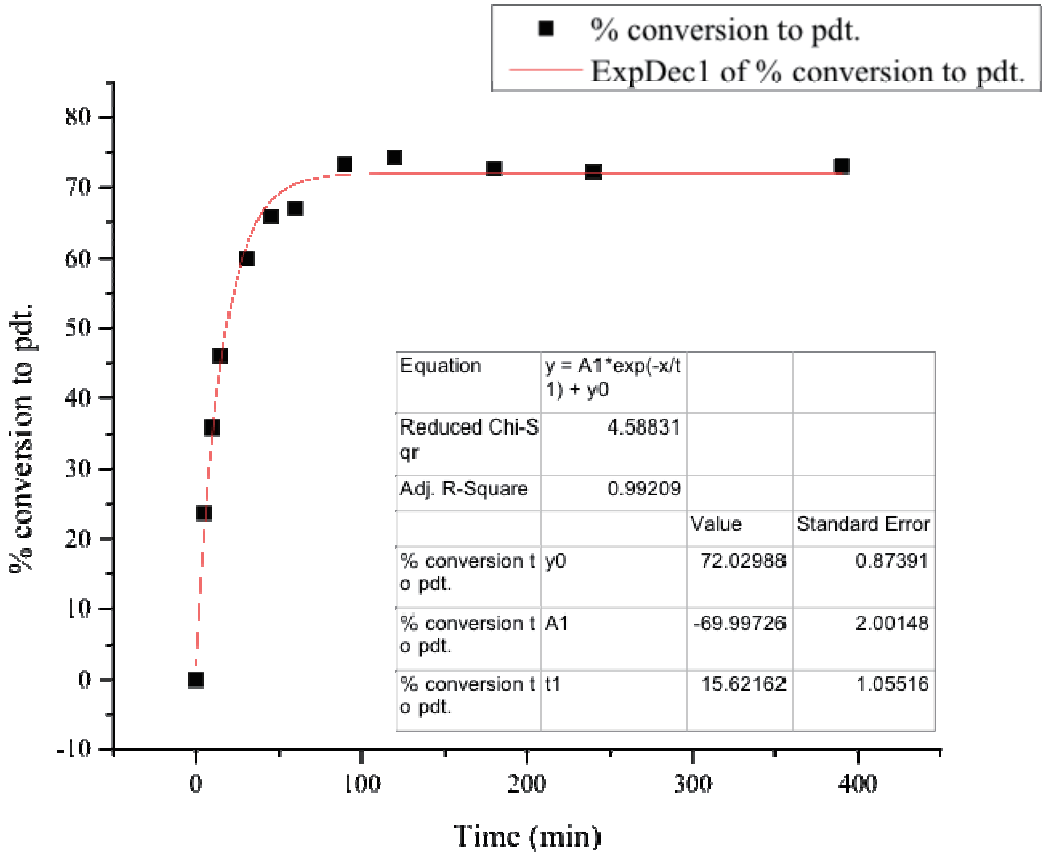
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
5	254.0	6948.18	1947.79	84.8	25.0
10	254.0	6930.96	2691.80	117.4	34.6
15	254.0	6307.47	3143.71	150.7	44.5
30	254.0	7164.98	4270.94	180.2	53.2
45	254.0	7140.67	5408.34	229.0	67.6
60	254.0	6757.77	5358.52	239.8	70.7
90	254.0	7322.81	5914.76	244.2	72.0
120	254.0	8230.17	6404.85	235.3	69.4
240	254.0	5617.81	4482.36	241.2	71.2
390	254.0	6697.65	5419.45	244.7	72.2



Half-Life = 20 min

Catalyst **2c**: Run 2

Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
5	254.0	6953.20	1845.14	80.2	23.7
10	254.0	6970.82	2801.66	121.5	35.8
15	254.0	6513.41	3364.79	156.2	46.1
30	254.0	5798.28	3899.58	203.4	60.0
45	254.0	6796.95	5018.23	223.2	65.9
60	254.0	7426.89	5575.46	227.0	67.0
90	254.0	6143.65	5050.34	248.6	73.3
120	254.0	7148.17	5951.79	251.8	74.3
180	254.0	7203.04	5868.43	246.3	72.7
240	254.0	6860.76	5555.94	244.9	72.2
390	254.0	6819.18	5583.45	247.6	73.0

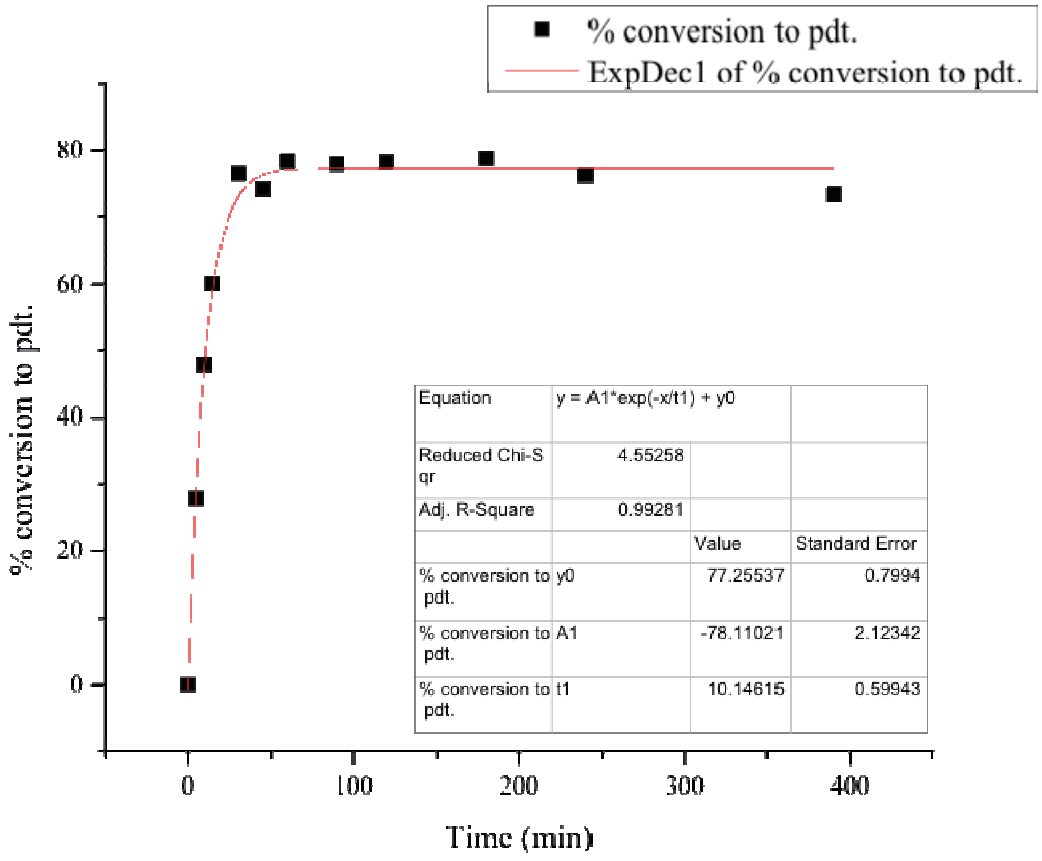


Half-Life = 18 min

Average Half-Life = 19 min

Catalyst **3c**: Run 1

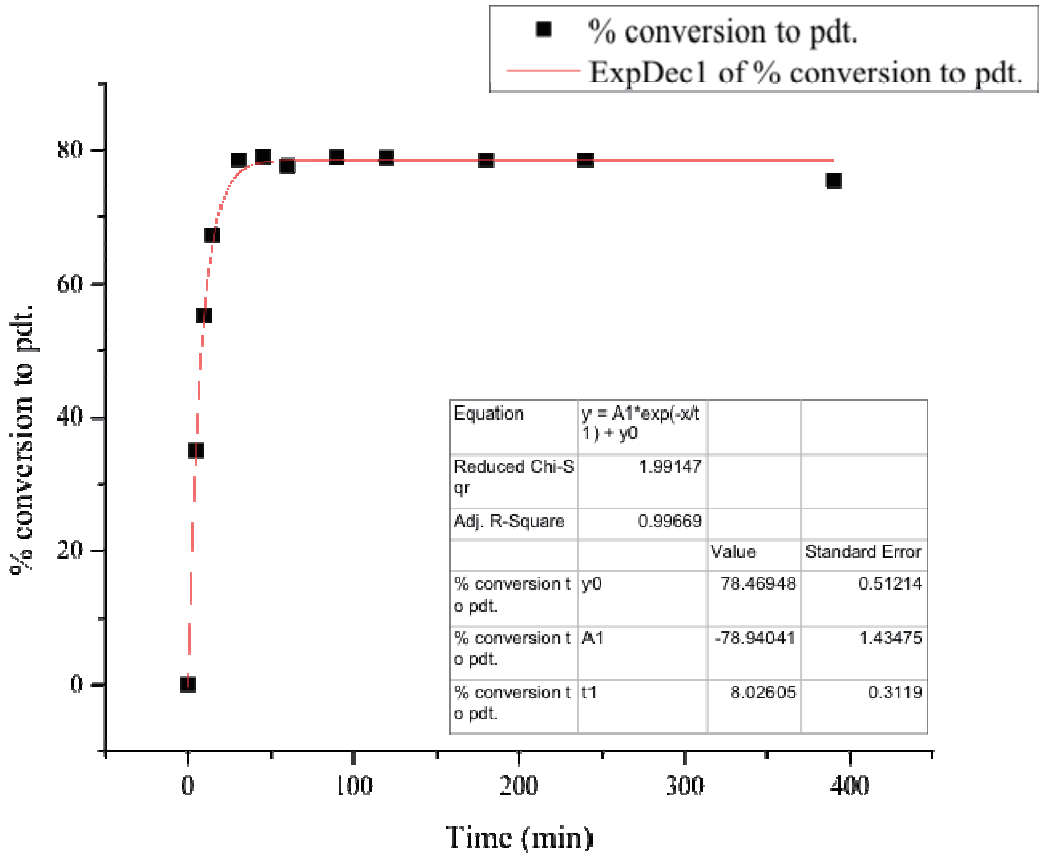
Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
5	254.0	6366.78	1987.10	94.4	27.8
10	254.0	7271.42	3898.83	162.1	47.8
15	254.0	6256.49	4213.33	203.6	60.1
30	254.0	7361.20	6309.61	259.2	76.5
45	254.0	6798.22	5649.22	251.3	74.1
60	254.0	6758.95	5936.93	265.6	78.3
90	254.0	6501.51	5679.15	264.1	77.9
120	254.0	7536.02	6606.41	265.1	78.2
180	254.0	6462.61	5706.41	267.0	78.8
240	254.0	7300.15	6235.80	258.3	76.2
390	254.0	6181.25	5085.59	248.8	73.4



Half-Life = 11 min

Catalyst **3c**: Run 2

Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
5	254.0	6497.60	2556.45	119.0	35.1
10	254.0	6409.23	3971.14	187.3	55.3
15	254.0	6714.73	5077.76	228.6	67.4
30	254.0	6316.60	5565.02	266.4	78.6
45	254.0	7164.22	6347.19	267.9	79.0
60	254.0	7023.72	6111.76	263.1	77.6
90	254.0	6812.49	6027.83	267.5	78.9
120	254.0	6956.38	6147.80	267.2	78.8
180	254.0	7296.56	6422.69	266.1	78.5
240	254.0	6965.82	6136.37	266.4	78.6
390	254.0	6369.80	5385.45	255.6	75.4

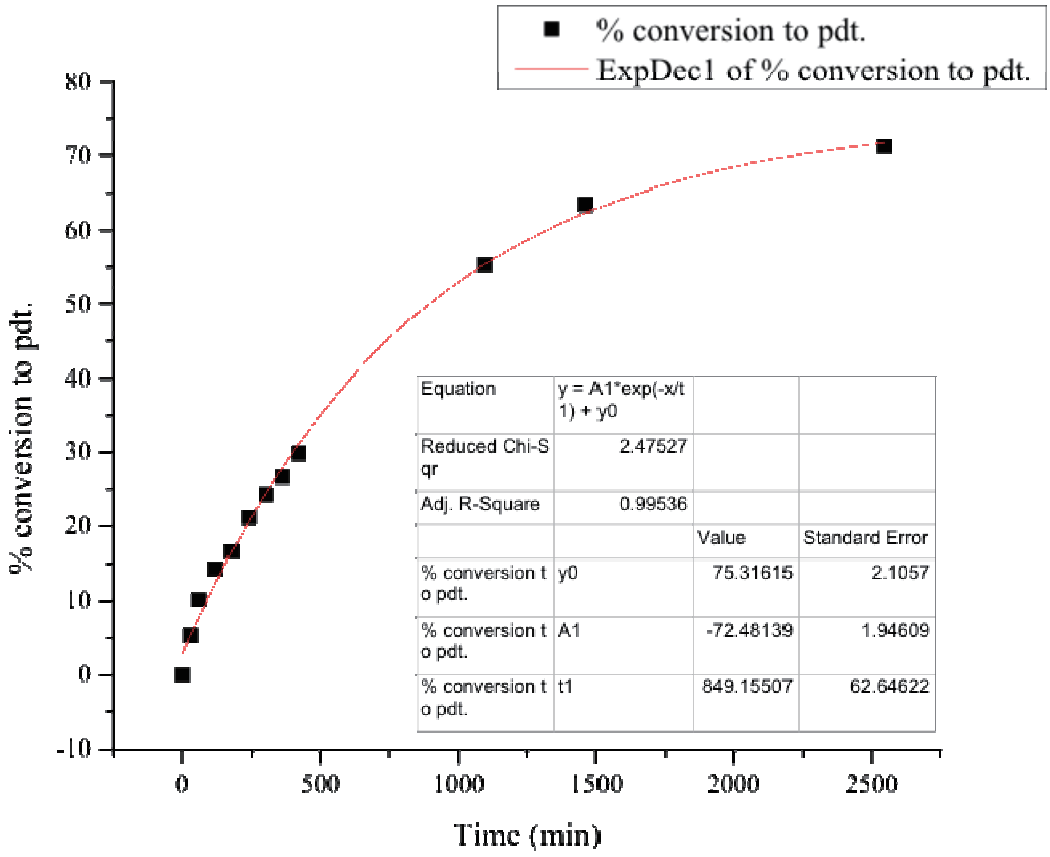


Half-Life = 8 min

Average Half-Life = 9 min

Catalyst **4c**: Run 1

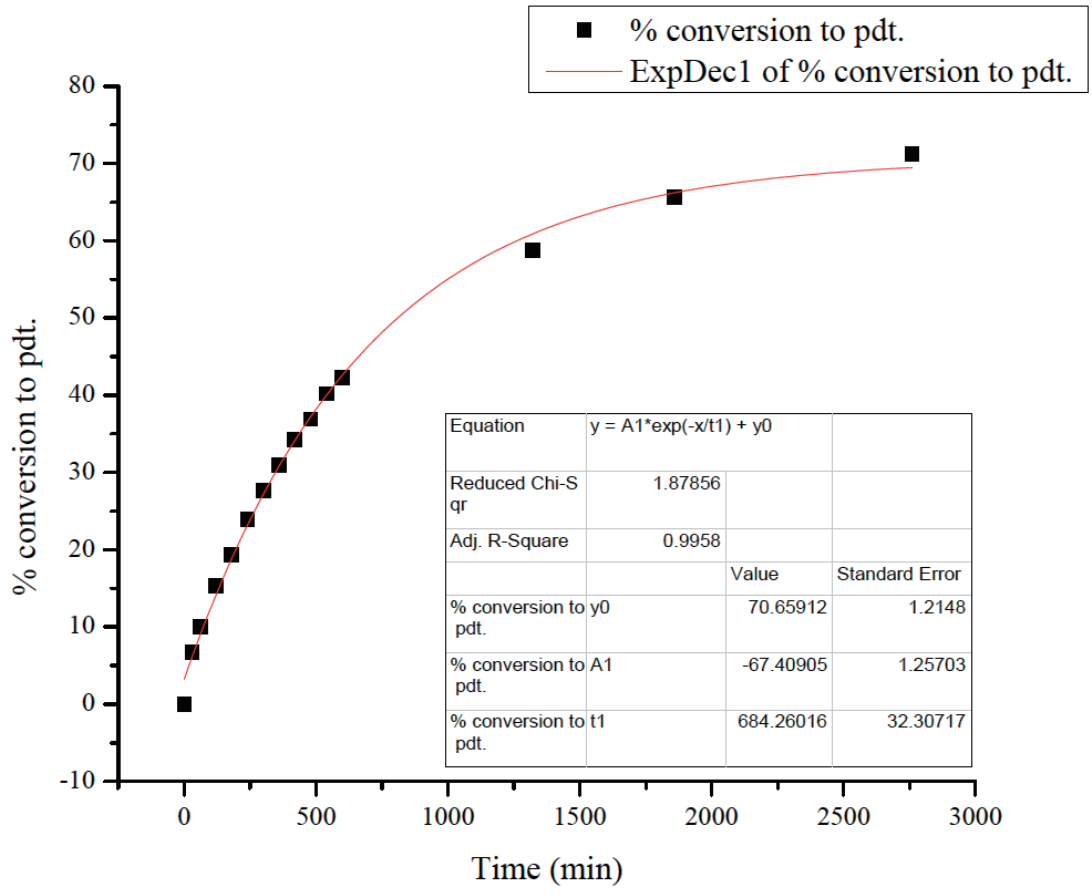
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.4	1.00	0.00	0.0	0.0
30	254.4	7863.59	474.71	18.3	5.4
60	254.4	7367.71	840.71	34.6	10.2
120	254.4	7404.97	1189.20	48.6	14.3
180	254.4	7649.45	1421.59	56.3	16.6
240	254.4	6730.51	1595.53	71.8	21.2
300	254.4	7201.13	1955.34	82.2	24.3
360	254.4	8112.84	2425.10	90.5	26.7
420	254.4	7489.21	2506.72	101.4	29.9
1096	254.4	7413.32	4588.50	187.4	55.3
1463	254.4	6053.13	4300.86	215.2	63.5
2546	254.4	6367.19	5077.05	241.5	71.2



Half-Life = 893 min

Catalyst **4c**: Run 2

Time (min)	Standard (umol)	Standard Area	Product Area	Product (umol)	% Product
0	254.4	1.00	0.00	0.0	0.0
30	254.4	10788.78	814.29	22.9	6.7
61	254.4	7527.68	843.86	33.9	10.0
120	254.4	7031.33	1206.67	52.0	15.3
180	254.4	8256.95	1782.66	65.4	19.3
240	254.4	7013.87	1877.42	81.1	23.9
300	254.4	8866.15	2744.85	93.8	27.7
360	254.4	7546.60	2610.97	104.8	30.9
420	254.4	7389.24	2834.78	116.2	34.3
480	254.4	7238.21	2989.89	125.1	36.9
540	254.4	7519.02	3385.00	136.3	40.2
600	254.4	8010.17	3787.29	143.2	42.2
1320	254.4	7710.55	5073.11	199.3	58.8
1860	254.4	7707.93	5663.60	222.5	65.6
2760	254.4	7732.30	6165.50	241.5	71.2

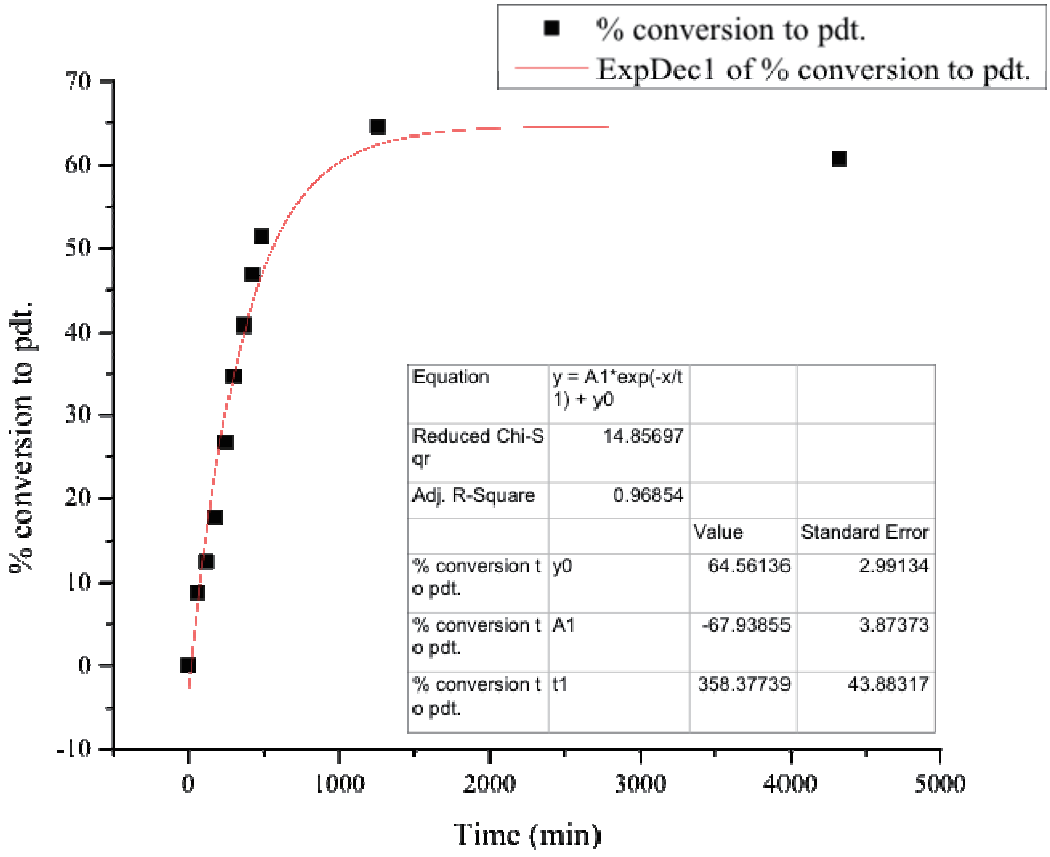


Half-Life = 809 min

Average Half-Life = 851 min

Catalyst **5c**: Run 1

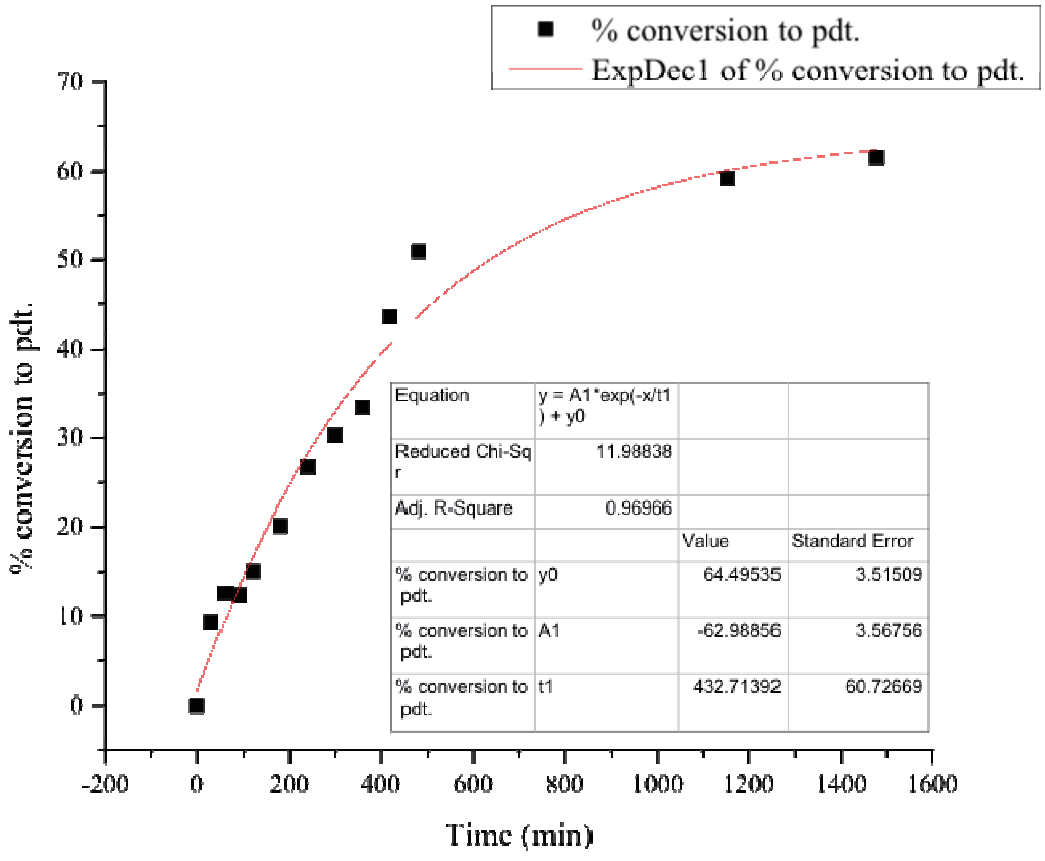
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
60	254.0	6368.39	629.97	29.9	8.8
120	254.0	8045.95	1132.05	42.5	12.5
180	254.0	8135.70	1627.98	60.5	17.8
240	254.0	7363.66	2208.14	90.7	26.7
300	254.0	8024.54	3125.56	117.8	34.7
360	254.0	7958.76	3637.38	138.2	40.8
420	254.0	7431.97	3903.86	158.8	46.9
480	254.0	7875.20	4543.85	174.5	51.5
1260	254.0	8115.78	5868.77	218.6	64.5
4320	254.0	7319.30	4992.20	206.2	60.8



Half-Life = 552 min

Catalyst **5c**: Run 2

Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.4	1.00	0.00	0.0	0.0
30	254.4	7941.61	824.43	31.4	9.3
60	254.4	7515.06	1058.79	42.7	12.6
90	254.4	7593.52	1051.55	41.9	12.4
120	254.4	7550.88	1271.89	51.0	15.0
180	254.4	7588.20	1711.40	68.3	20.1
240	254.4	7637.43	2287.61	90.7	26.8
300	254.4	7619.27	2586.18	102.8	30.3
360	254.4	8407.72	3149.90	113.5	33.5
420	254.4	7873.94	3838.21	147.6	43.5
480	254.4	8463.36	4825.66	172.7	50.9
1153	254.4	8061.29	5340.12	200.6	59.2
1478	254.4	7598.65	5239.92	208.8	61.6



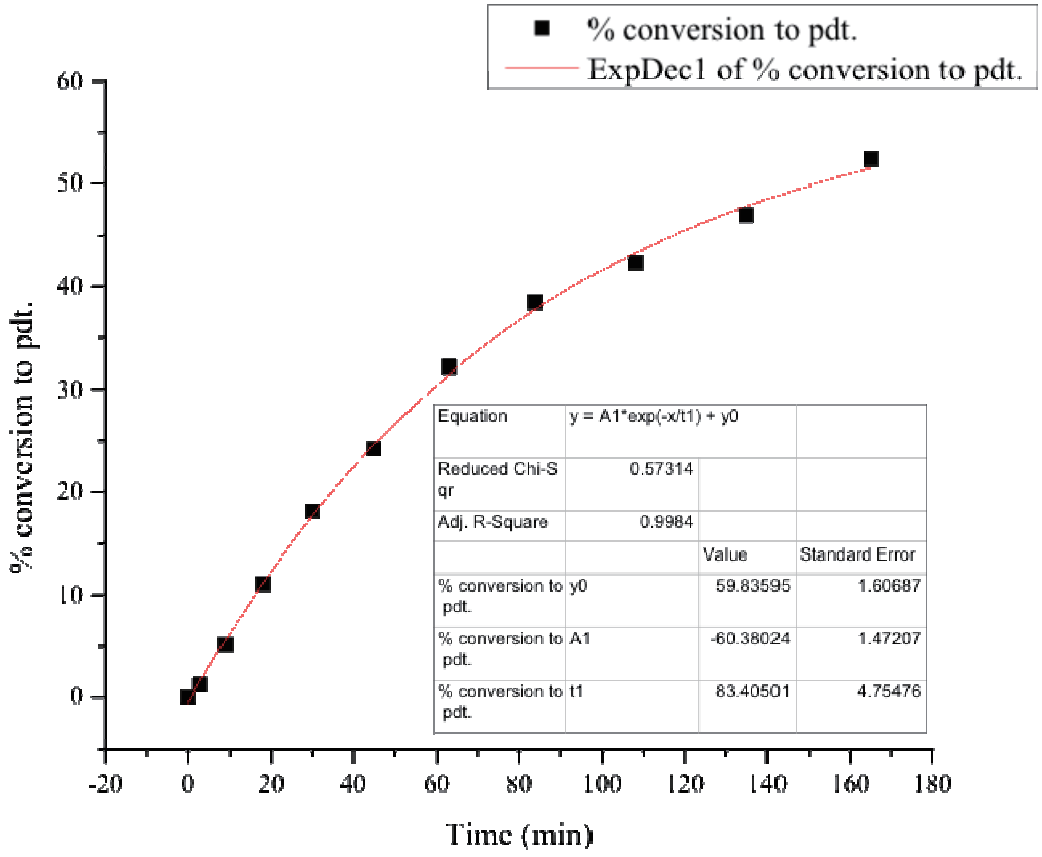
Half-Life = 636 min

Average Half-Life = 594 min

Kinetic Analyses of Catalysts in Series D

Catalyst **1d**: Run 1

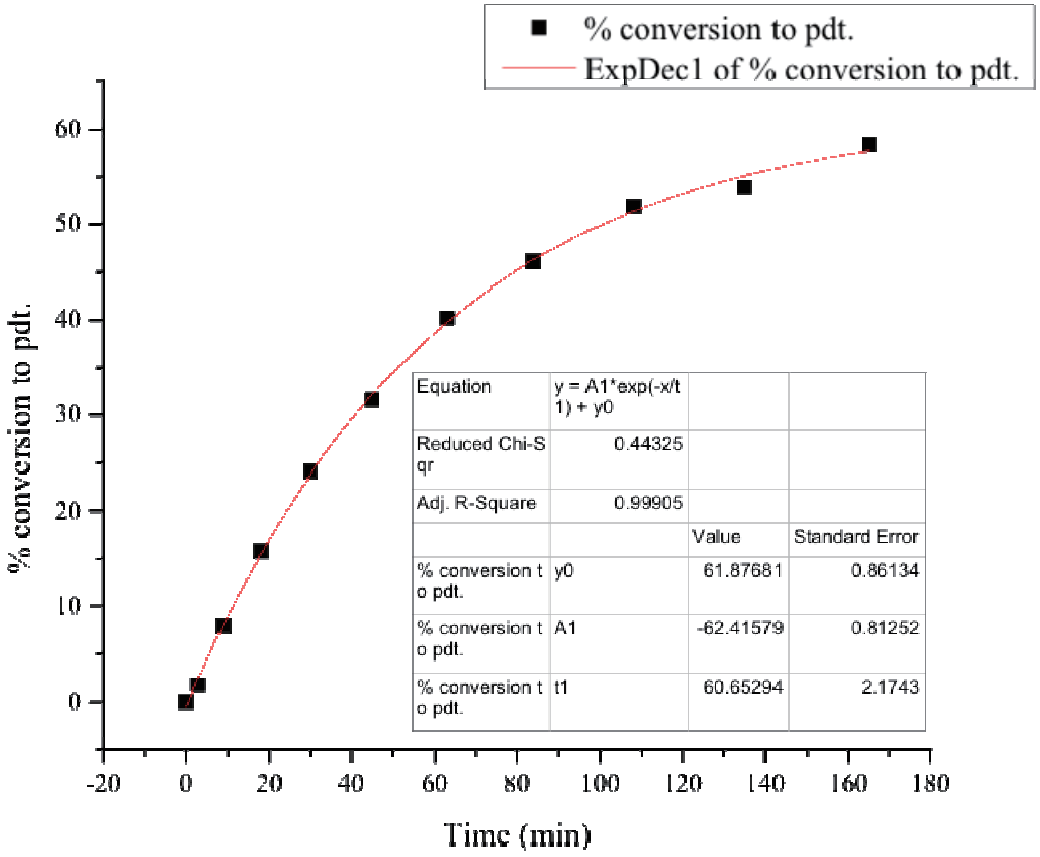
Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
30	254.0	5406.24	1359.20	76.0	22.4
60	254.0	5597.67	2322.44	125.4	37.0
90	254.0	6022.80	3061.08	153.7	45.3
120	254.0	5849.00	3388.52	175.2	51.7
150	254.0	6356.35	4236.60	201.5	59.4
180	254.0	6318.85	4449.16	212.9	62.8
210	254.0	7329.06	5406.82	223.1	65.8
240	254.0	7373.65	5588.14	229.1	67.6
270	254.0	6735.73	5379.98	241.5	71.2
300	254.0	7544.71	6096.67	244.3	72.1



Half-Life = 151 min

Catalyst **1d**: Run 2

Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
3	254.0	7510.25	152.92	6.2	1.8
9	254.0	7171.84	633.84	26.7	7.9
18	254.0	6894.65	1217.50	53.4	15.8
30	254.0	7108.05	1922.28	81.8	24.1
45	254.0	6914.86	2451.89	107.2	31.6
63	254.0	6219.46	2806.25	136.4	40.2
84	254.0	7238.37	3738.36	156.2	46.1
108	254.0	7818.04	4546.39	175.8	51.9
135	254.0	7537.11	4559.36	182.9	54.0
165	254.0	6789.20	4447.95	198.1	58.4

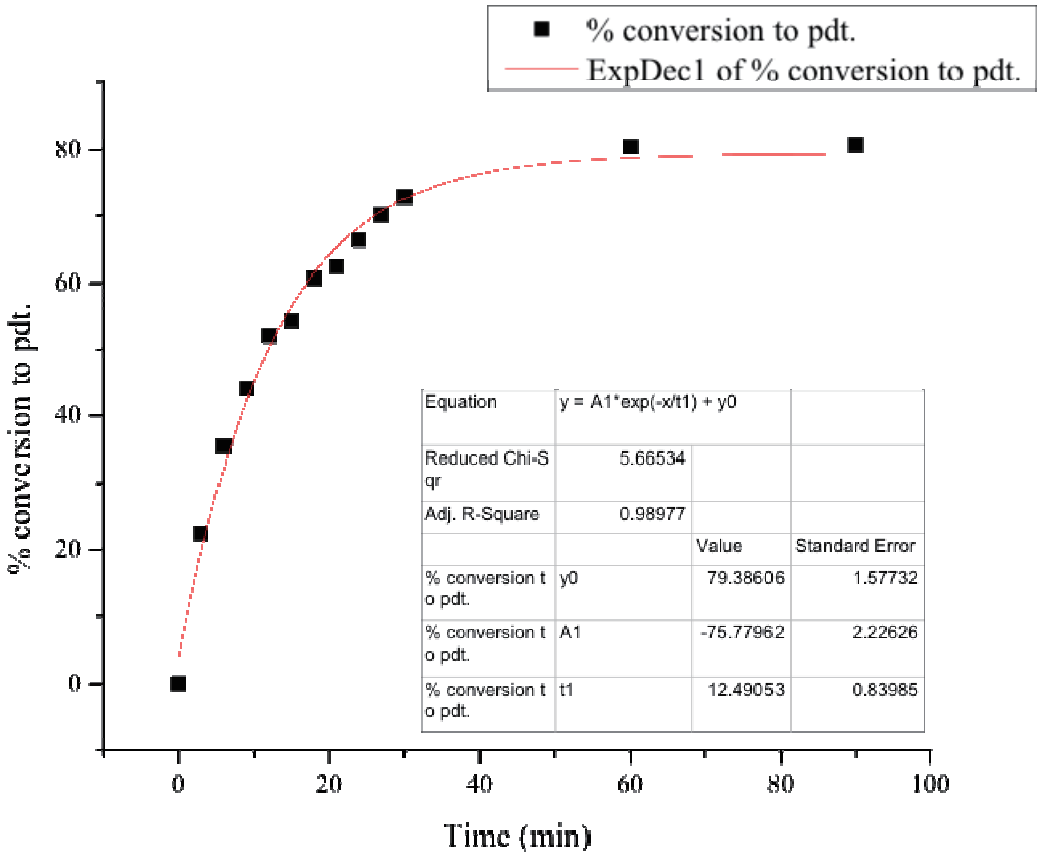


Half-Life = 101 min

Average Half-Life = 126 min

Catalyst **2d**: Run 1

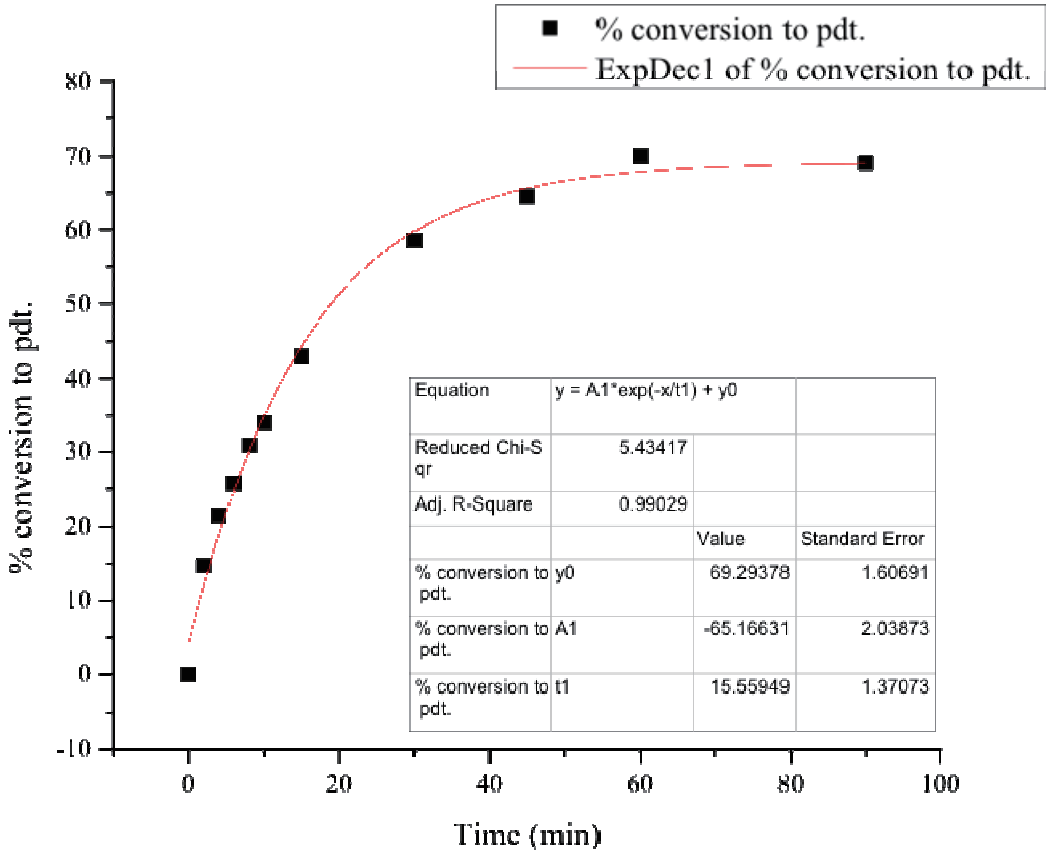
Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.00	0.00
3	254.0	7452.19	1874.83	76.07	22.44
6	254.0	6532.27	2598.15	120.26	35.48
9	254.0	7411.18	3663.17	149.45	44.09
12	254.0	6859.63	4003.37	176.46	52.05
15	254.0	7120.64	4338.85	184.24	54.35
18	254.0	7146.26	4860.47	205.65	60.66
21	254.0	6564.03	4590.67	211.46	62.38
24	254.0	6910.47	5137.96	224.81	66.31
27	254.0	6548.18	5147.46	237.68	70.11
30	254.0	6246.98	5100.82	246.89	72.83
60	254.0	6088.17	5485.47	272.43	80.36
90	254.0	6532.30	5906.09	273.38	80.64



Half-Life = 12 min

Catalyst **2d**: Run 2

Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
2	254.0	6657.24	1299.59	59.0	14.8
4	254.0	6625.67	1886.22	86.1	21.6
6	254.0	6654.65	2261.85	102.8	25.8
8	254.0	5937.63	2420.91	123.3	30.9
10	254.0	5945.19	2667.42	135.7	34.0
15	254.0	7215.81	4097.74	171.7	43.0
30	254.0	6335.24	4894.49	233.6	58.5
45	254.0	6563.80	5590.47	257.5	64.5
60	254.0	6914.90	6391.83	279.5	70.0
90	254.0	6598.44	6016.79	275.7	69.1

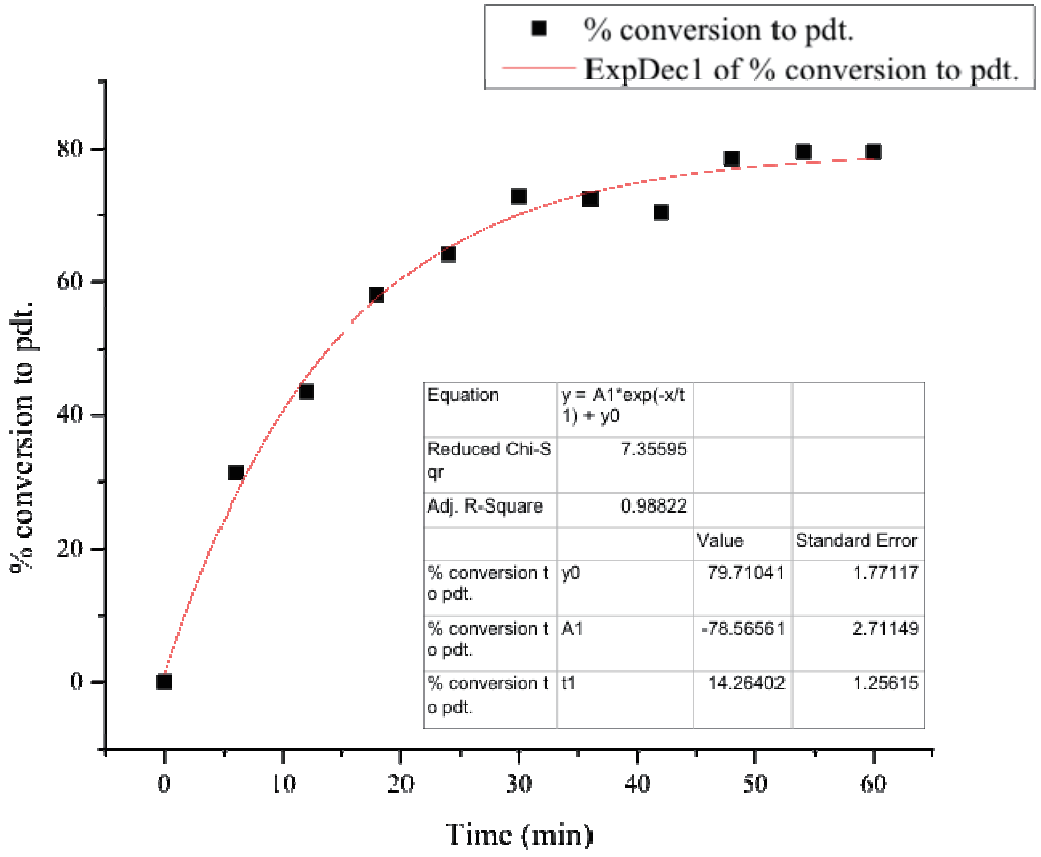


Half-Life = 19 min

Average Half-Life = 15 min

Catalyst **3d**: Run 1

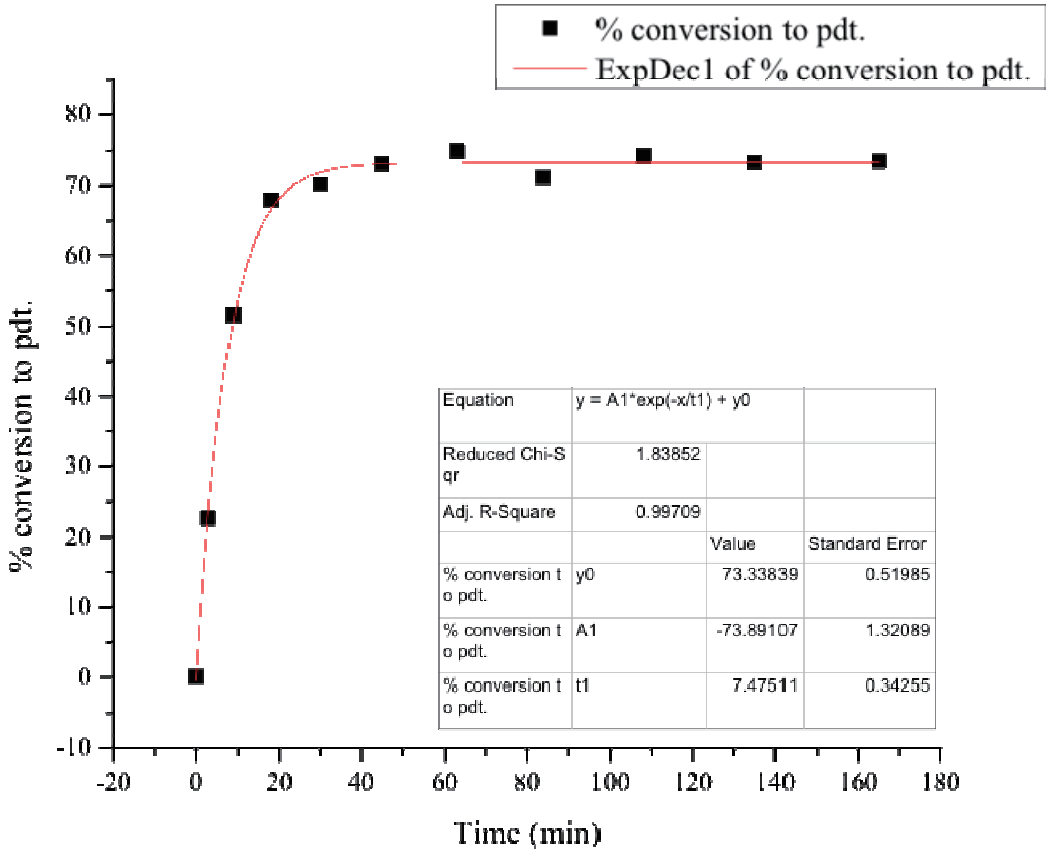
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
6	254.0	6734.66	2362.89	106.1	31.3
12	254.0	6056.31	2956.87	147.6	43.5
18	254.0	6426.49	4178.60	196.6	58.0
24	254.0	6750.96	4853.43	217.4	64.1
30	254.0	6287.08	5133.21	246.9	72.8
36	254.0	6644.98	5394.88	245.5	72.4
42	254.0	7858.06	6203.65	238.7	70.4
48	254.0	6605.05	5815.88	266.2	78.5
54	254.0	6342.74	5657.64	269.7	79.6
60	254.0	6043.27	5389.82	269.7	79.5



Half-Life = 14 min

Catalyst **3d**: Run 2

Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
3	254.0	6489.00	1653.27	77.0	22.7
9	254.0	5305.57	3070.89	175.0	51.6
18	254.0	6664.46	5076.20	230.3	67.9
30	254.0	6245.48	4917.91	238.1	70.2
45	254.0	6719.35	5513.31	248.1	73.2
63	254.0	6735.43	5660.49	254.1	75.0
84	254.0	7491.39	5979.50	241.3	71.2
108	254.0	6943.75	5782.35	251.8	74.3
135	254.0	7099.50	5840.60	248.7	73.4
165	254.0	7991.96	6587.32	249.2	73.5

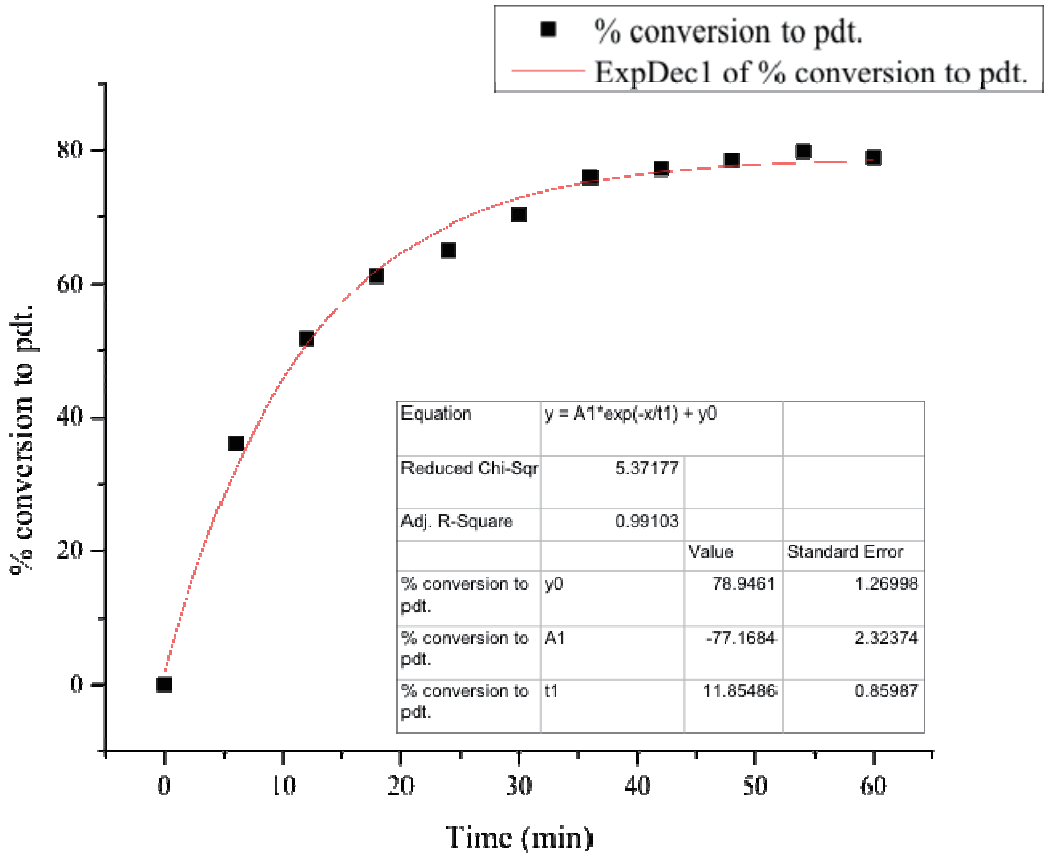


Half-Life = 9 min

Average Half-Life = 11 min

Catalyst **4d**: Run 1

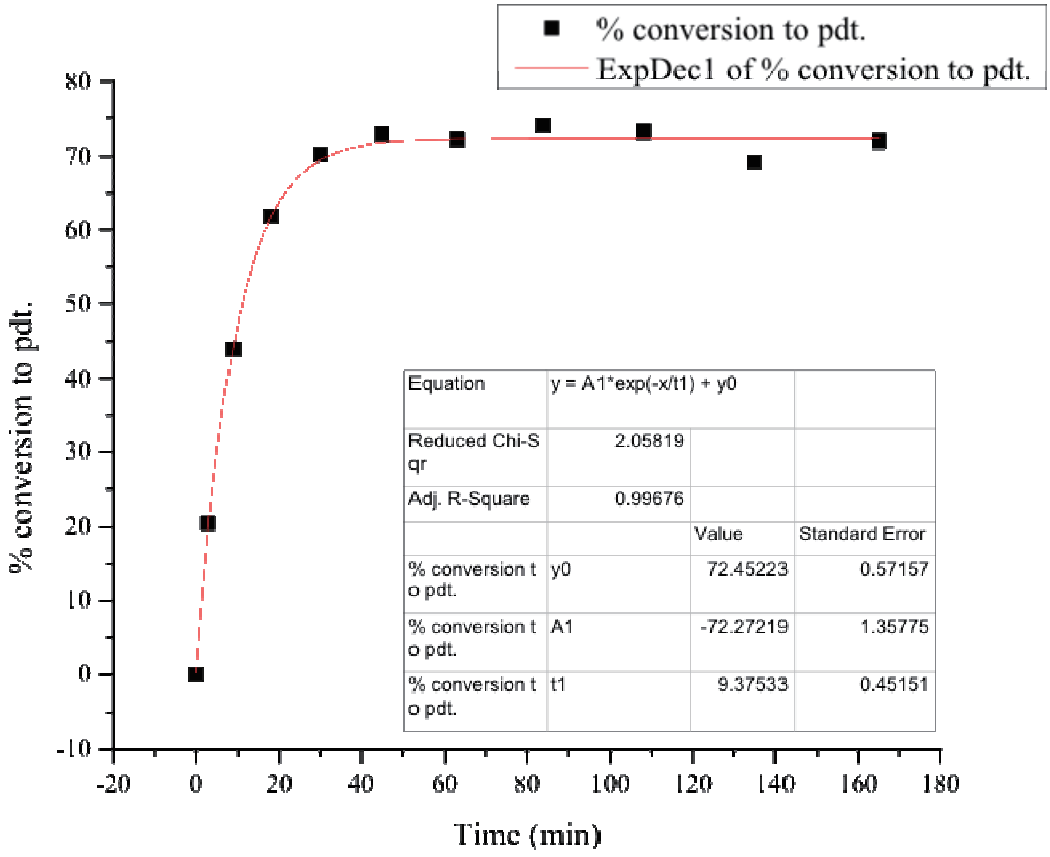
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
60	254.0	6546.90	774.40	35.8	10.6
120	254.0	7212.06	1150.39	48.2	14.2
180	254.0	7857.01	1744.91	67.1	19.8
240	254.0	7190.91	2047.66	86.1	25.4
300	254.0	8232.91	2921.40	107.3	31.6
360	254.0	7411.91	3252.86	132.7	39.1
420	254.0	7772.49	3857.10	150.0	44.3
480	254.0	7283.47	4225.35	175.4	51.7
540	254.0	7539.71	4745.14	190.3	56.1
600	254.0	7667.28	5138.08	202.6	59.8
1440	254.0	6692.90	5291.19	239.0	70.5



Half-Life = 12 min

Catalyst **4d**: Run 2

Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.4	1.00	0.00	0.0	0.0
30	254.4	7838.54	638.49	24.7	7.3
60	254.4	7546.78	975.79	39.2	11.6
90	254.4	7084.29	1143.68	48.9	14.4
120	254.4	7580.74	1380.32	55.1	16.3
180	254.4	7560.03	1557.28	62.4	18.4
240	254.4	8045.52	2350.86	88.5	26.1
300	254.4	7200.37	2371.19	99.7	29.4
480	254.4	8617.36	4650.85	163.4	48.2
1153	254.4	5196.10	4010.78	233.8	69.0
1478	254.4	7756.88	6064.77	236.8	69.8

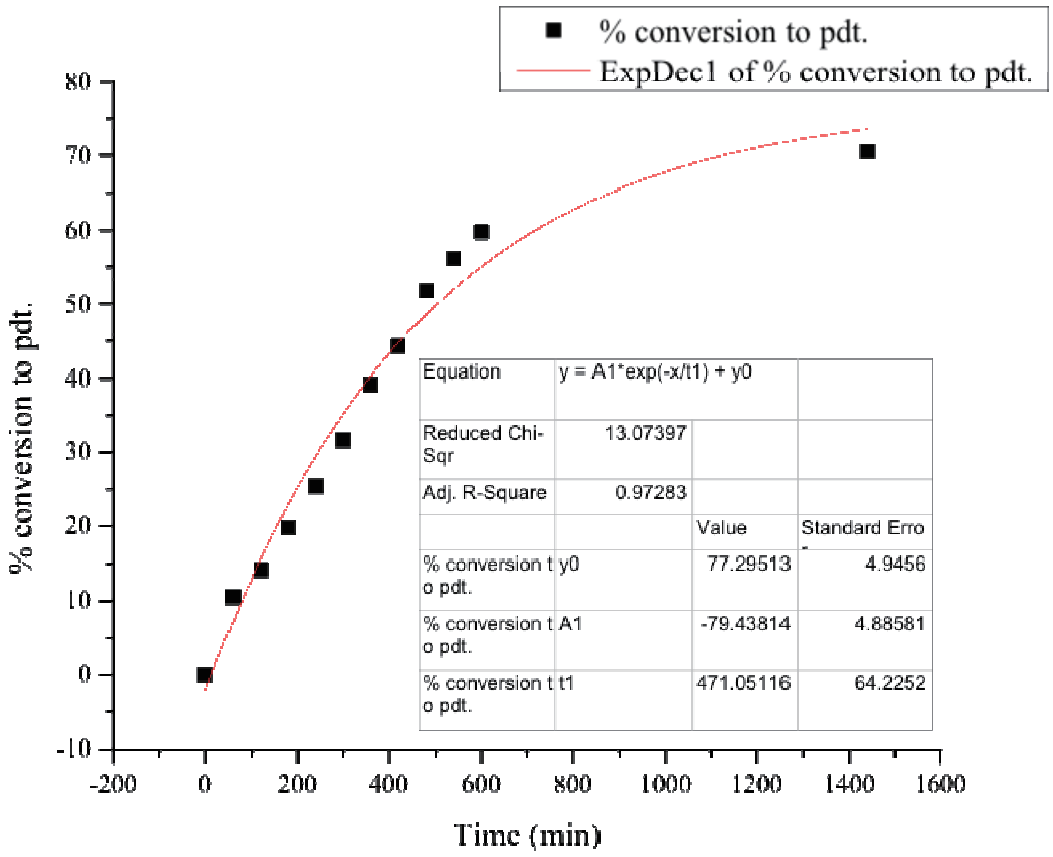


Half-Life = 11 min

Average Half-Life = 11 min

Catalyst **5d**: Run 1

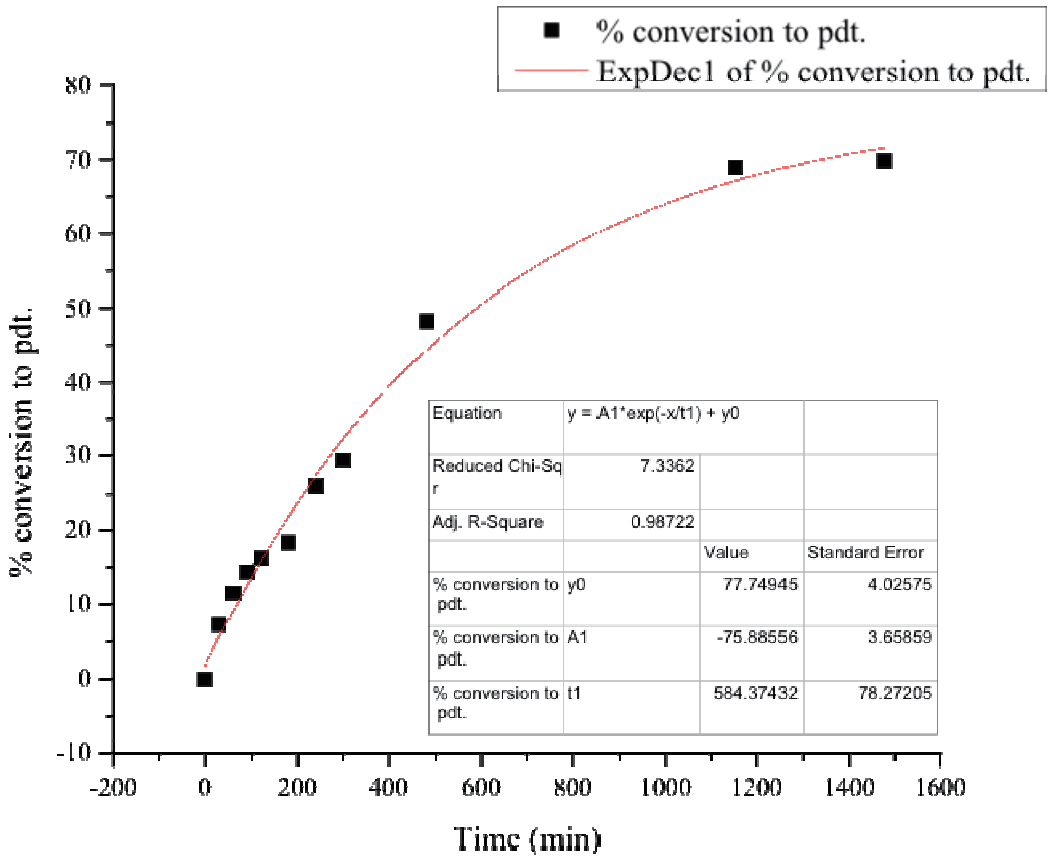
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
60	254.0	6546.90	774.40	35.8	10.6
120	254.0	7212.06	1150.39	48.2	14.2
180	254.0	7857.01	1744.91	67.1	19.8
240	254.0	7190.91	2047.66	86.1	25.4
300	254.0	8232.91	2921.40	107.3	31.6
360	254.0	7411.91	3252.86	132.7	39.1
420	254.0	7772.49	3857.10	150.0	44.3
480	254.0	7283.47	4225.35	175.4	51.7
540	254.0	7539.71	4745.14	190.3	56.1
600	254.0	7667.28	5138.08	202.6	59.8
1440	254.0	6692.90	5291.19	239.0	70.5



Half-Life = 503 min

Catalyst **5d**: Run 2

Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.4	1.00	0.00	0.0	0.0
30	254.4	7838.54	638.49	24.7	7.3
60	254.4	7546.78	975.79	39.2	11.6
90	254.4	7084.29	1143.68	48.9	14.4
120	254.4	7580.74	1380.32	55.1	16.3
180	254.4	7560.03	1557.28	62.4	18.4
240	254.4	8045.52	2350.86	88.5	26.1
300	254.4	7200.37	2371.19	99.7	29.4
480	254.4	8617.36	4650.85	163.4	48.2
1153	254.4	5196.10	4010.78	233.8	69.0
1478	254.4	7756.88	6064.77	236.8	69.8



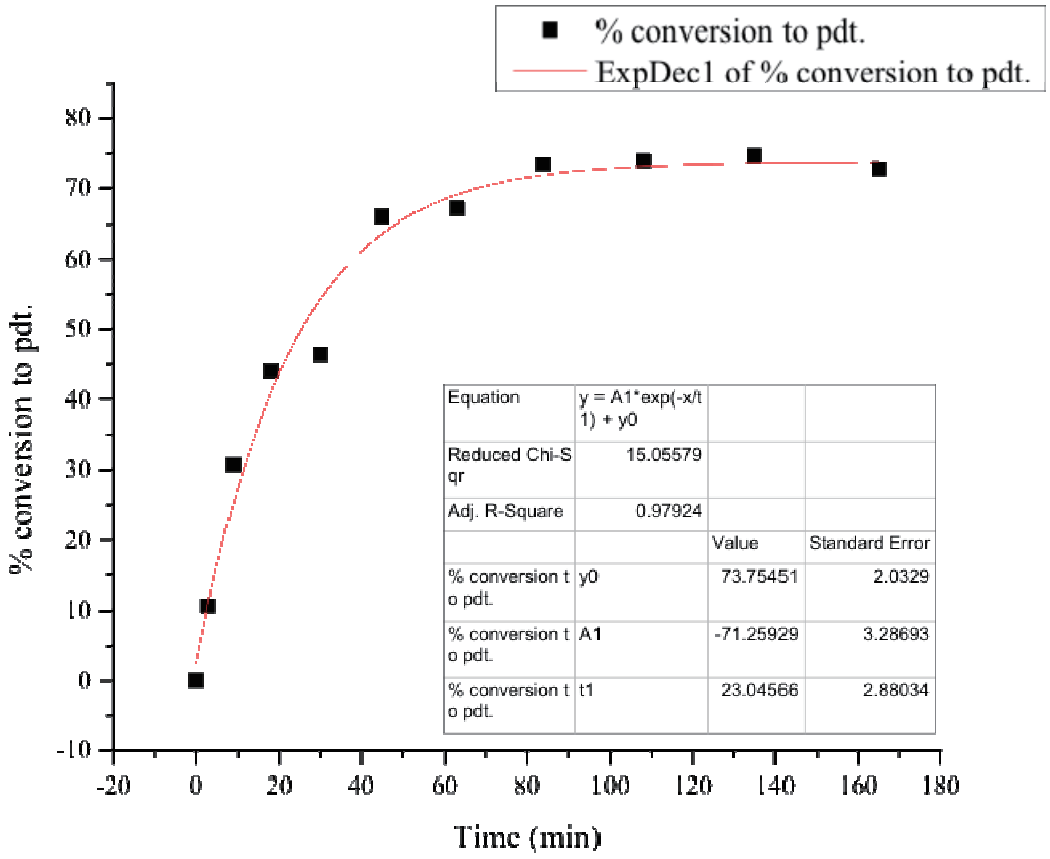
Half-Life = 588 min

Average Half-Life = 546 min

Kinetic Analyses of Catalysts in Series E

Catalyst **1e**: Run 1

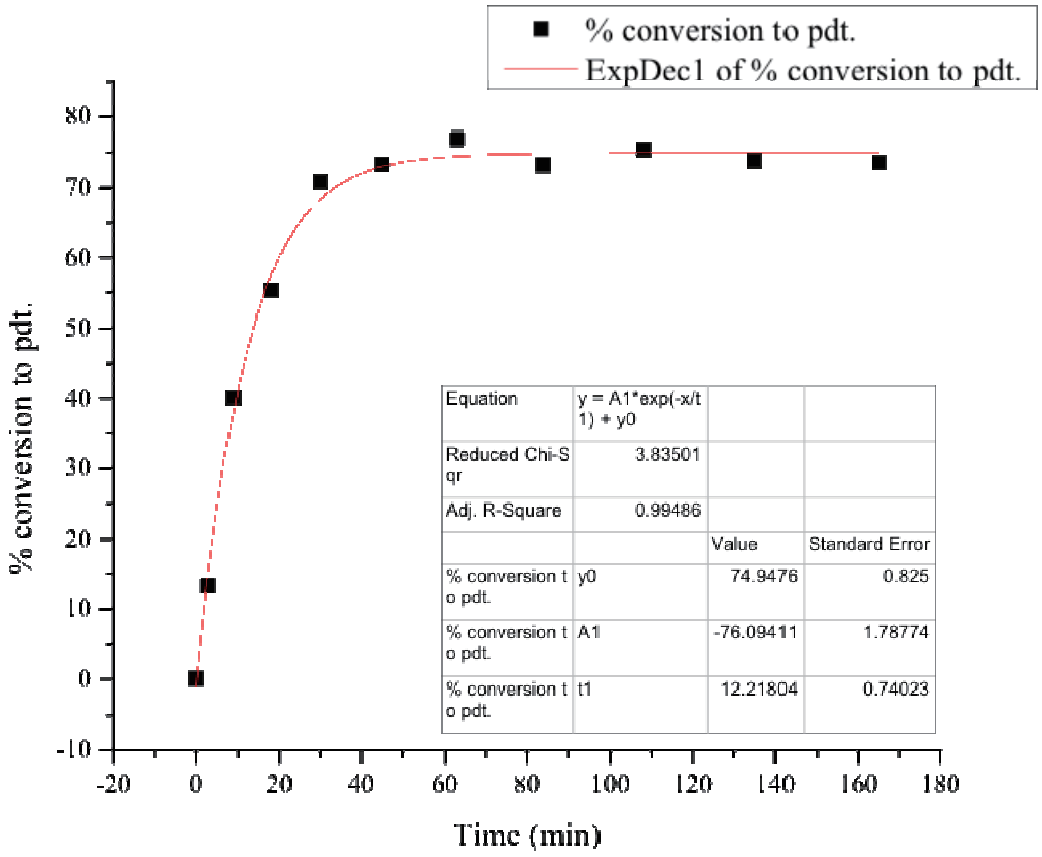
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
3	254.0	6882.99	828.49	36.4	10.7
9	254.0	8570.29	2953.49	104.2	30.7
18	254.0	5777.19	2847.38	149.0	44.0
30	254.0	7714.14	4008.40	157.1	46.3
45	254.0	6368.22	4712.73	223.8	66.0
63	254.0	6953.42	5236.57	227.7	67.2
84	254.0	7315.55	6023.74	249.0	73.4
108	254.0	6751.74	5595.77	250.6	73.9
135	254.0	6672.18	5583.20	253.0	74.6
165	254.0	6291.08	5132.58	246.7	72.8



Half-Life = 25 min

Catalyst **1e**: Run 2

Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
3	254.0	7234.79	1084.52	45.3	13.4
9	254.0	6823.99	3065.34	135.8	40.1
18	254.0	6804.85	4217.07	187.4	55.3
30	254.0	6794.97	5397.66	240.2	70.9
45	254.0	7175.81	5900.93	248.6	73.3
63	254.0	7830.53	6754.11	260.8	76.9
84	254.0	7106.46	5837.28	248.4	73.3
108	254.0	7390.44	6250.08	255.7	75.4
135	254.0	7153.57	5922.00	250.3	73.8
165	254.0	7339.00	6055.46	249.5	73.6

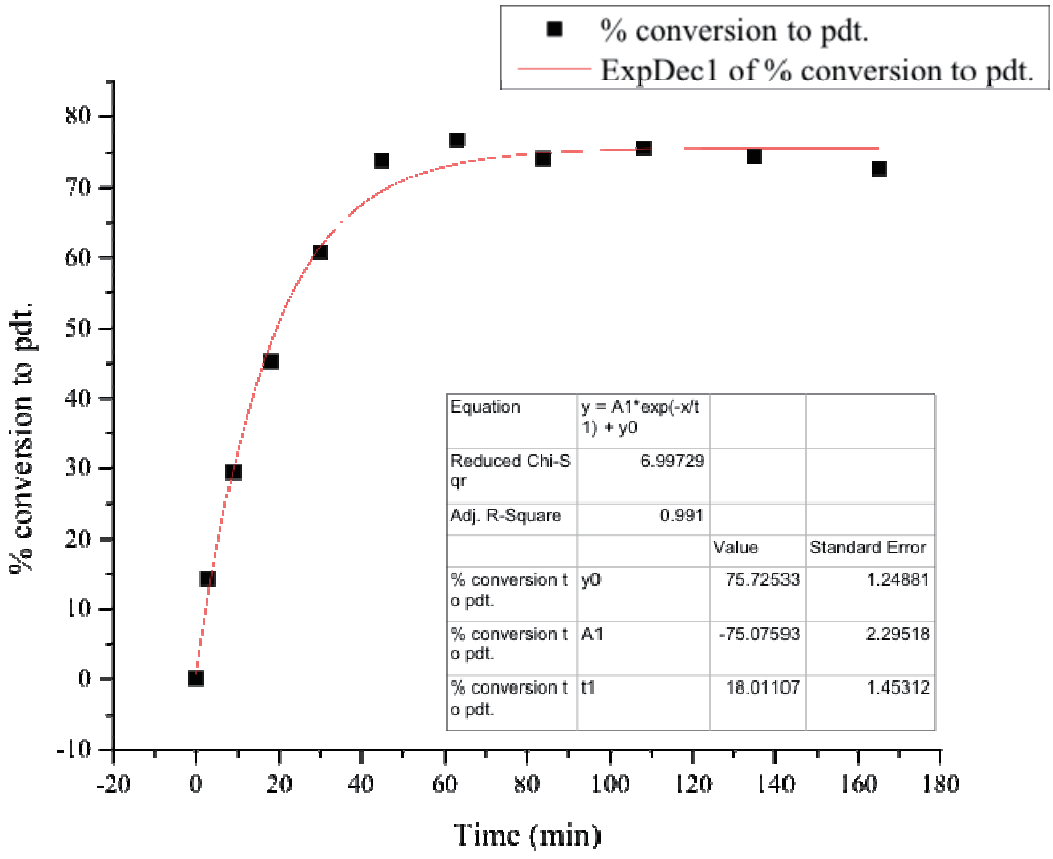


Half-Life = 14 min

Average Half-Life = 19 min

Catalyst **2e**: Run 1

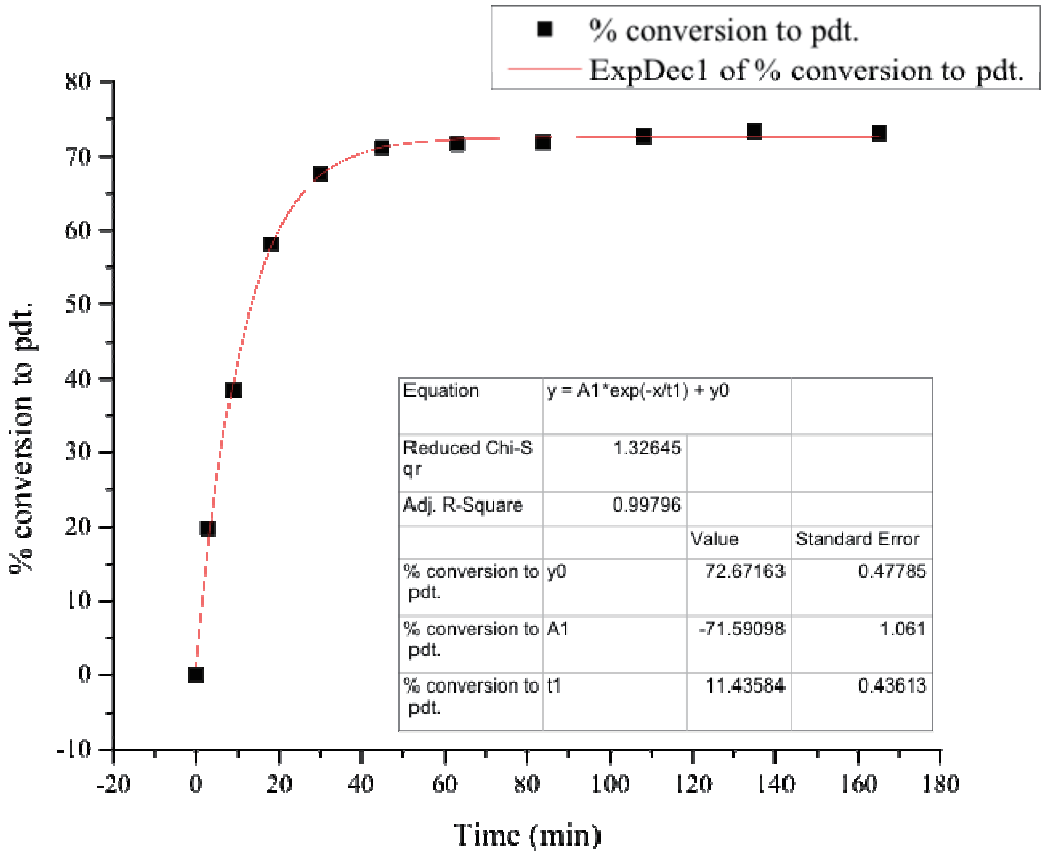
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
3	254.0	6239.34	1004.37	48.7	14.4
9	254.0	5956.21	1963.61	99.7	29.4
18	254.0	6389.58	3242.29	153.4	45.3
30	254.0	6714.18	4574.33	206.0	60.8
45	254.0	6706.44	5554.85	250.4	73.9
63	254.0	7280.79	6275.59	260.6	76.9
84	254.0	6529.20	5428.99	251.4	74.2
108	254.0	7678.27	6514.85	256.5	75.7
135	254.0	7619.53	6361.20	252.4	74.5
165	254.0	7499.82	6115.74	246.6	72.7



Half-Life = 19 min

Catalyst **2e**: Run 2

Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
3	254.0	7412.62	1650.78	67.3	19.9
9	254.0	6779.88	2923.76	130.4	38.5
18	254.0	7300.21	4759.80	197.1	58.2
30	254.0	7593.24	5761.56	229.4	67.7
45	254.0	7793.95	6227.00	241.6	71.3
63	254.0	8408.63	6764.48	243.2	71.8
84	254.0	8153.02	6578.51	244.0	72.0
108	254.0	7526.92	6135.04	246.4	72.7
135	254.0	7776.50	6397.54	248.7	73.4
165	254.0	8493.77	6966.35	248.0	73.2

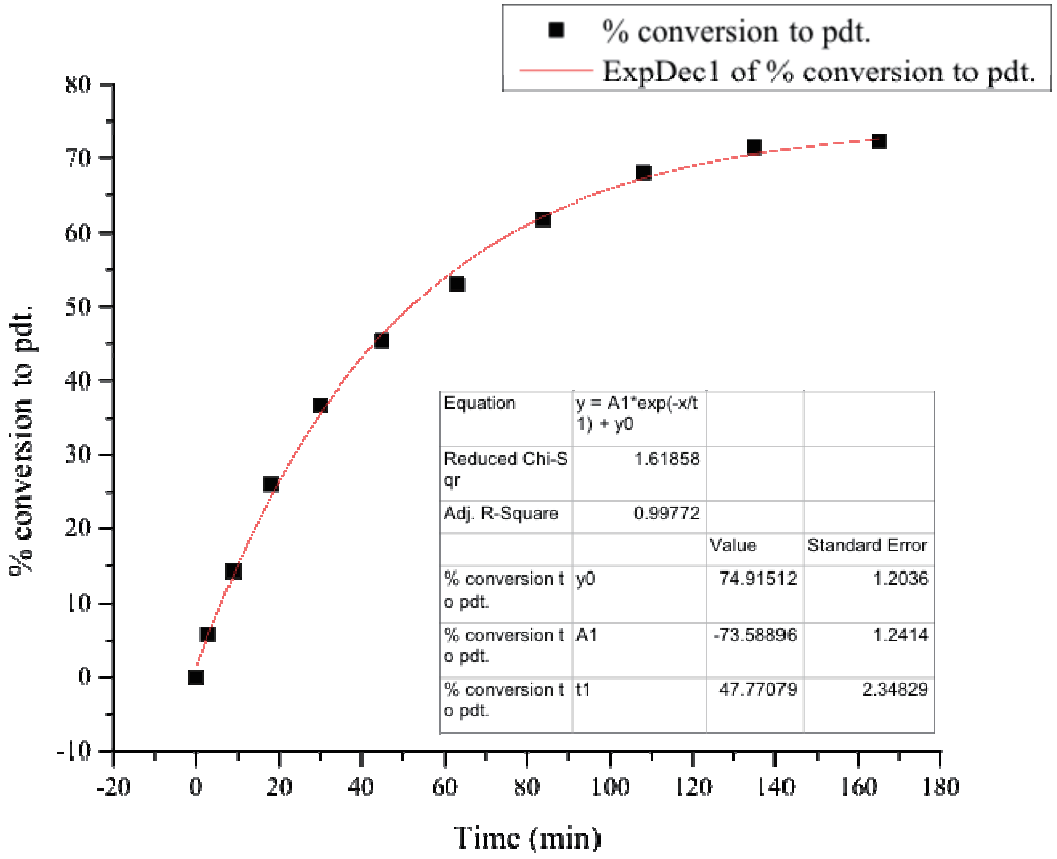


Half-Life = 13 min

Average Half-Life = 16 min

Catalyst **3e**: Run 1

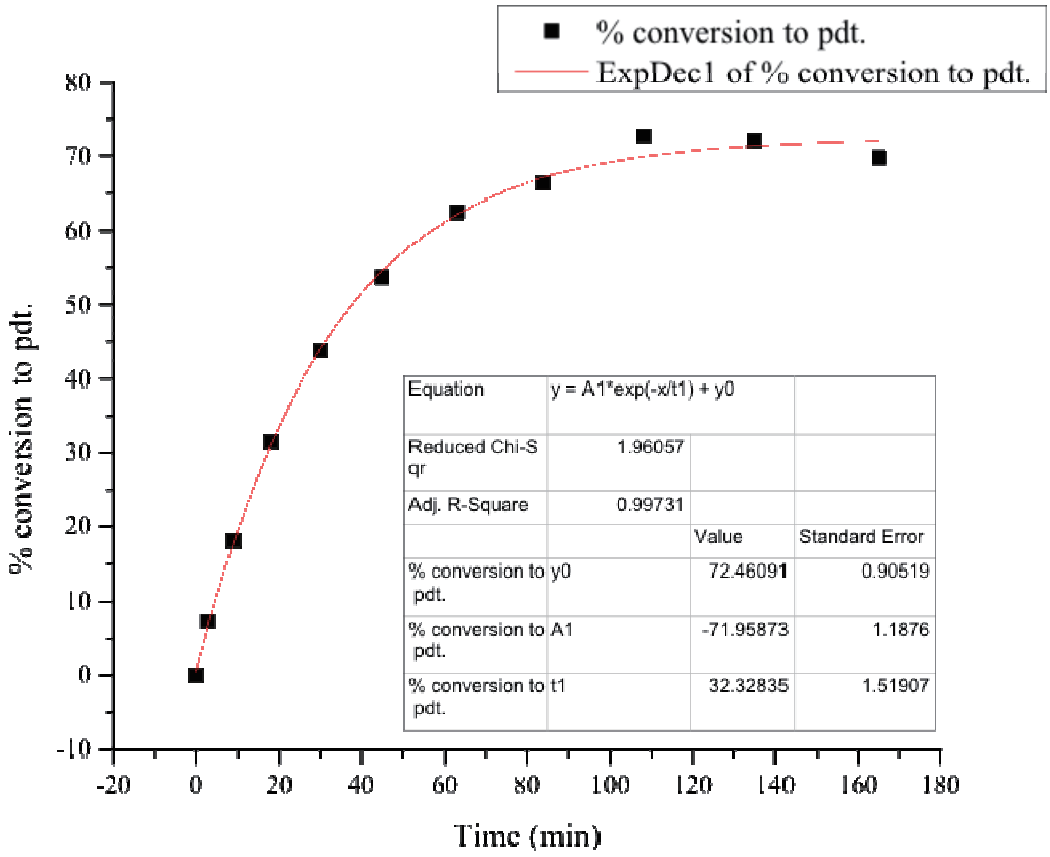
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
3	254.0	6120.53	404.98	20.0	5.9
9	254.0	6216.99	1002.48	48.8	14.4
18	254.0	6722.38	1963.40	88.3	26.1
30	254.0	6362.14	2626.00	124.8	36.8
45	254.0	6585.24	3349.33	153.8	45.4
63	254.0	6746.52	4015.37	180.0	53.1
84	254.0	6693.50	4643.27	209.7	61.9
108	254.0	6446.70	4914.72	230.5	68.0
135	254.0	6889.46	5521.58	242.3	71.5
165	254.0	7153.94	5798.73	245.1	72.3



Half-Life = 52 min

Catalyst **3e**: Run 2

Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
3	254.0	6604.29	547.47	25.1	7.4
9	254.0	6912.08	1403.08	61.4	18.1
18	254.0	6703.31	2373.20	107.0	31.6
30	254.0	7172.43	3515.76	148.2	43.7
45	254.0	6816.97	4103.24	182.0	53.7
63	254.0	6987.07	4896.22	211.9	62.5
84	254.0	7132.50	5304.48	224.9	66.3
108	254.0	7104.38	5790.27	246.4	72.7
135	254.0	7345.73	5933.77	244.2	72.0
165	254.0	8554.62	6688.04	236.4	69.7

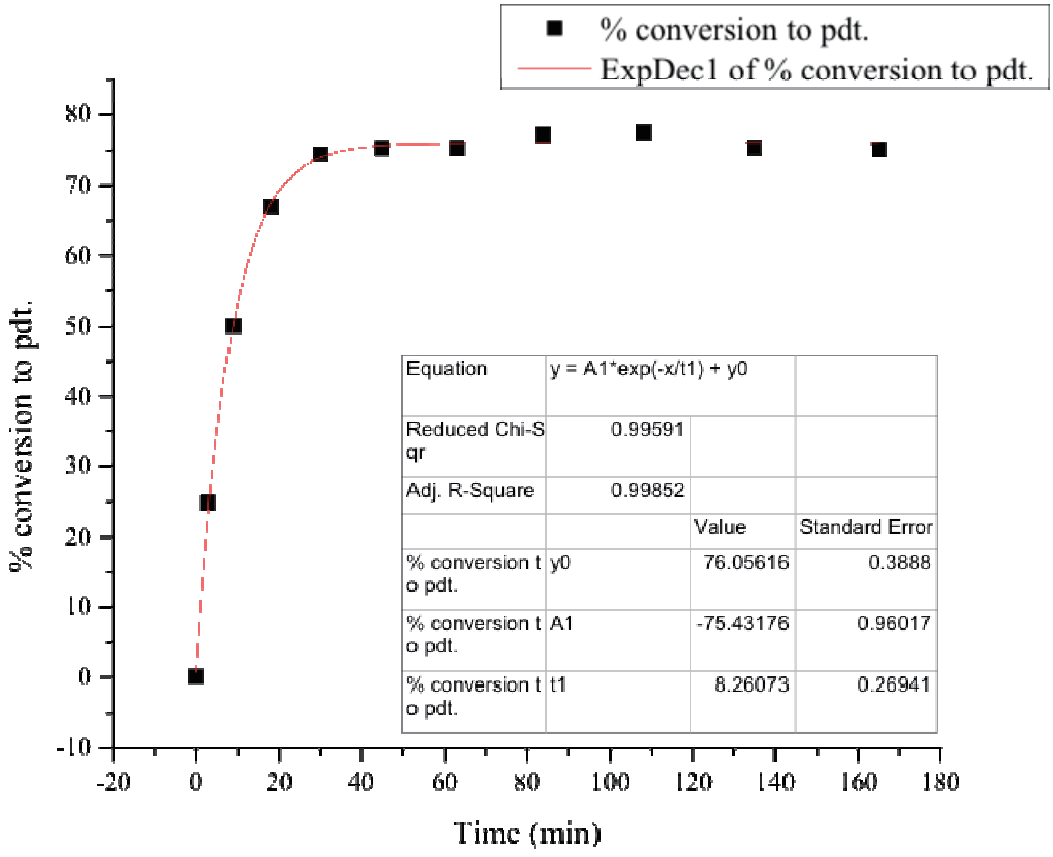


Half-Life = 38 min

Average Half-Life = 45 min

Catalyst **4e**: Run 1

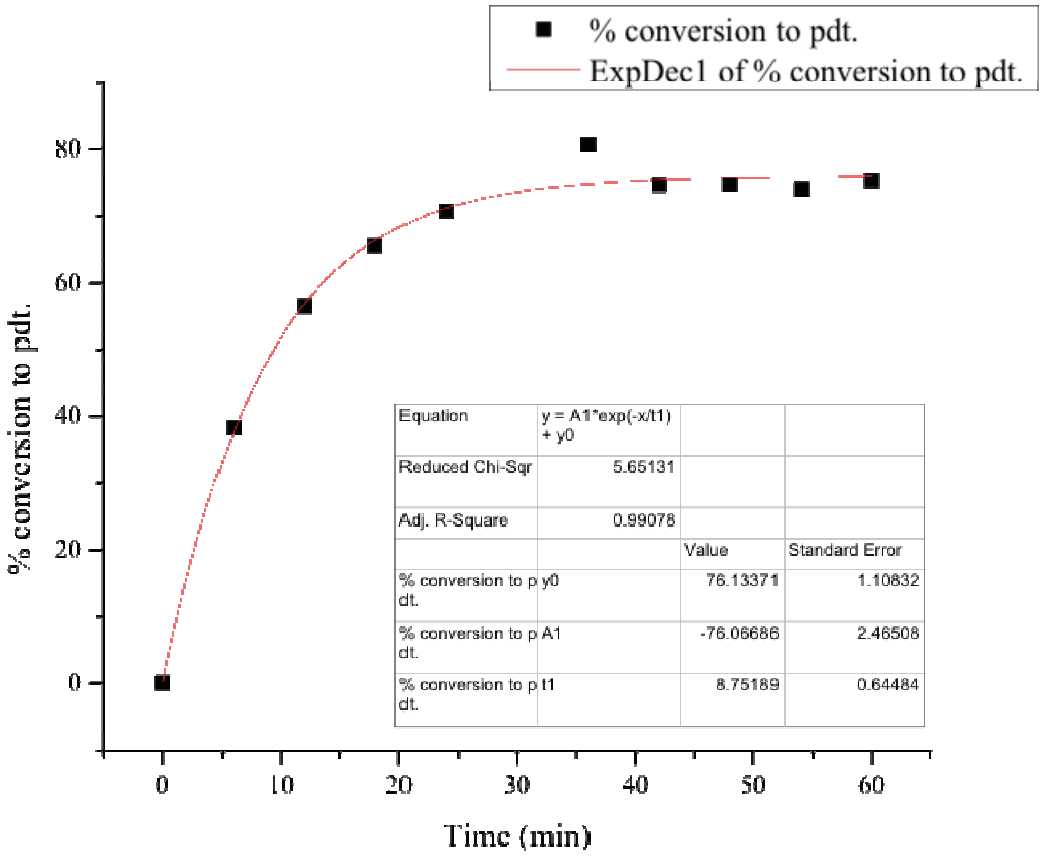
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
3	254.0	6034.20	1681.63	84.3	24.9
9	254.0	5815.10	3265.33	169.8	50.1
18	254.0	7693.56	5776.40	227.0	67.0
30	254.0	7152.44	5979.27	252.8	74.6
45	254.0	7464.03	6305.21	255.4	75.3
63	254.0	6860.98	5798.58	255.5	75.4
84	254.0	6520.74	5640.82	261.6	77.2
108	254.0	6816.84	5923.90	262.8	77.5
135	254.0	7308.24	6179.92	255.7	75.4
165	254.0	6008.21	5063.76	254.8	75.2



Half-Life = 9 min

Catalyst **4e**: Run 2

Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
6	254.0	7408.90	3181.06	129.8	38.3
12	254.0	6486.04	4100.11	191.1	56.4
18	254.0	9219.50	6773.80	222.2	65.5
24	254.0	6842.62	5428.10	239.9	70.8
36	254.0	14846.30	13414.10	273.2	80.6
42	254.0	6787.48	5690.50	253.5	74.8
48	254.0	6829.84	5728.66	253.6	74.8
54	254.0	6693.96	5558.16	251.1	74.1
60	254.0	6649.07	5620.00	255.6	75.4

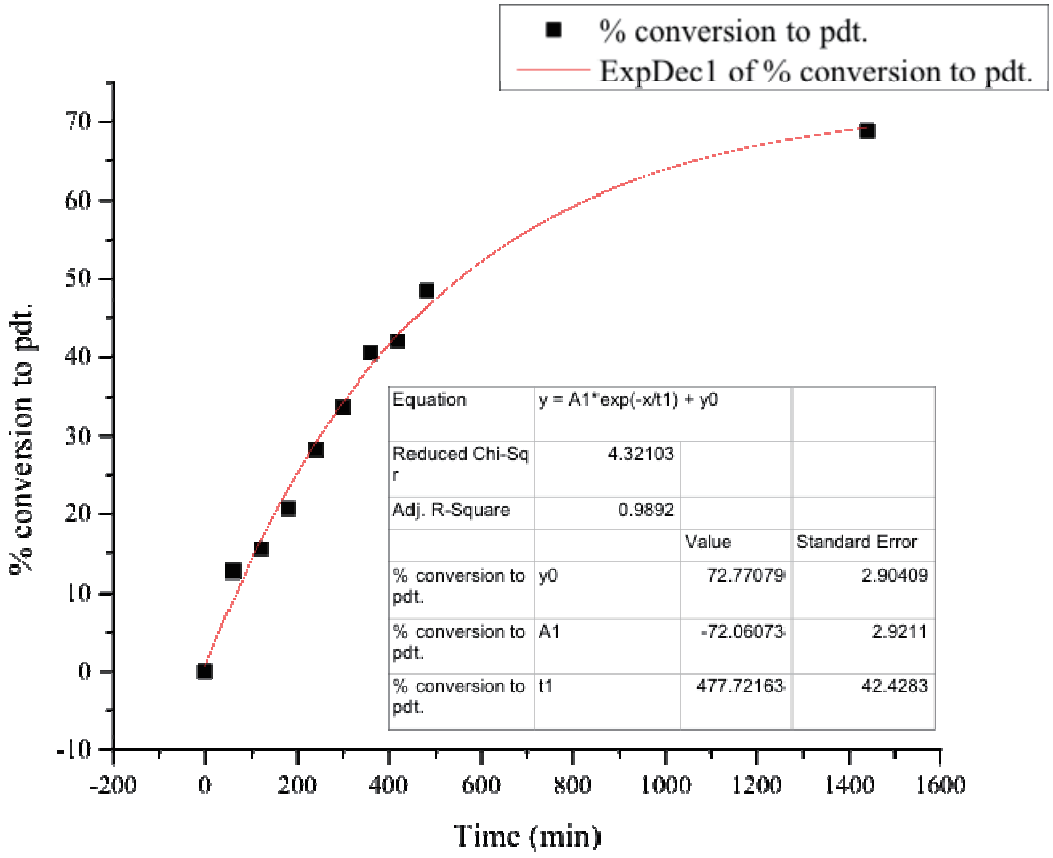


Half-Life = 9 min

Average Half-Life = 9 min

Catalyst **5e**: Run 1

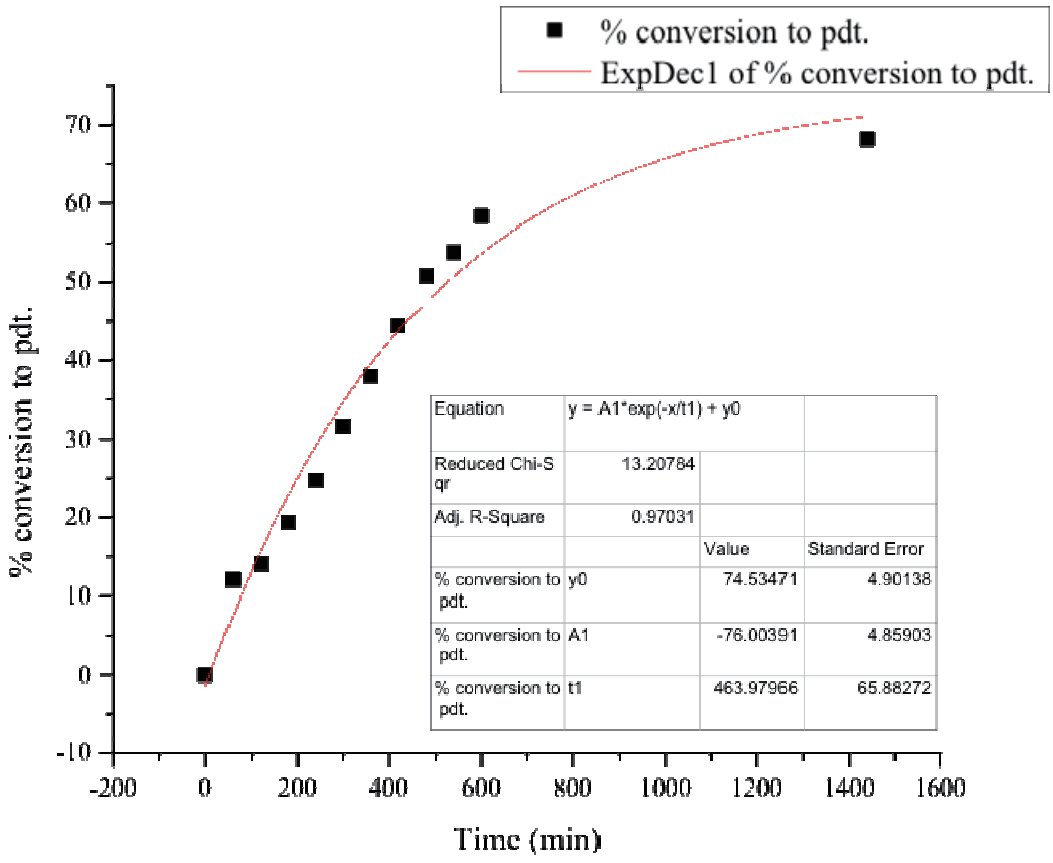
Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
60	254.0	7802.71	1114.30	43.2	12.7
120	254.0	8225.37	1433.34	52.7	15.5
180	254.0	6856.91	1591.42	70.2	20.7
240	254.0	7626.93	2416.44	95.8	28.3
300	254.0	8083.26	3058.24	114.4	33.7
360	254.0	7515.24	3412.32	137.3	40.5
420	254.0	4895.07	2307.47	142.5	42.0
480	254.0	8446.94	4589.99	164.3	48.5
1440	254.0	8084.39	6235.59	233.2	68.8



Half-Life = 550 min

Catalyst **5e**: Run 2

Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
60	254.0	5736.16	776.53	40.9	12.1
120	254.0	2850.93	449.61	47.7	14.1
180	254.0	4661.94	1013.96	65.8	19.4
240	254.0	6389.07	1775.61	84.0	24.8
300	254.0	9501.85	3374.84	107.4	31.7
360	254.0	5738.45	2442.08	128.7	38.0
420	254.0	5254.53	2615.95	150.5	44.4
480	254.0	3907.70	2226.49	172.3	50.8
540	254.0	5259.69	3173.95	182.5	53.8
600	254.0	4111.57	2688.67	197.7	58.3
1440	254.0	6744.83	5156.23	231.1	68.2



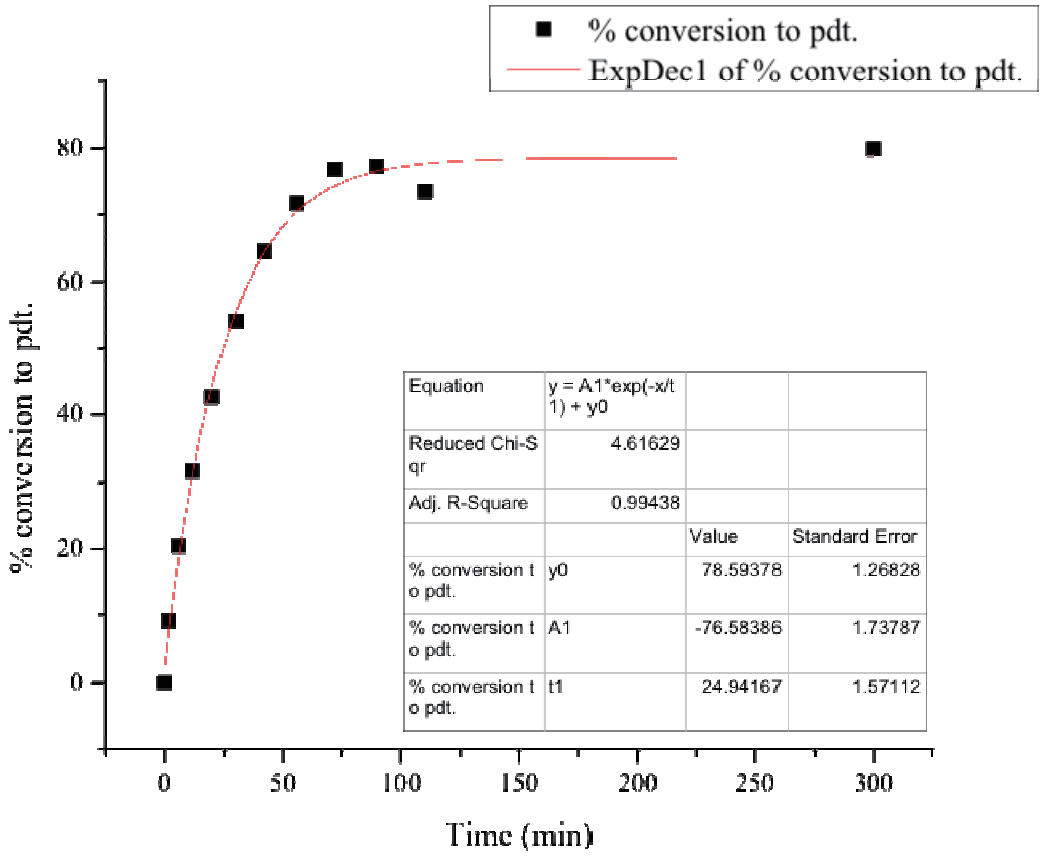
Half-Life = 525 min

Average Half-Life = 537 min

Kinetic Analyses of Catalysts in Series F

Catalyst **1f**: Run 1

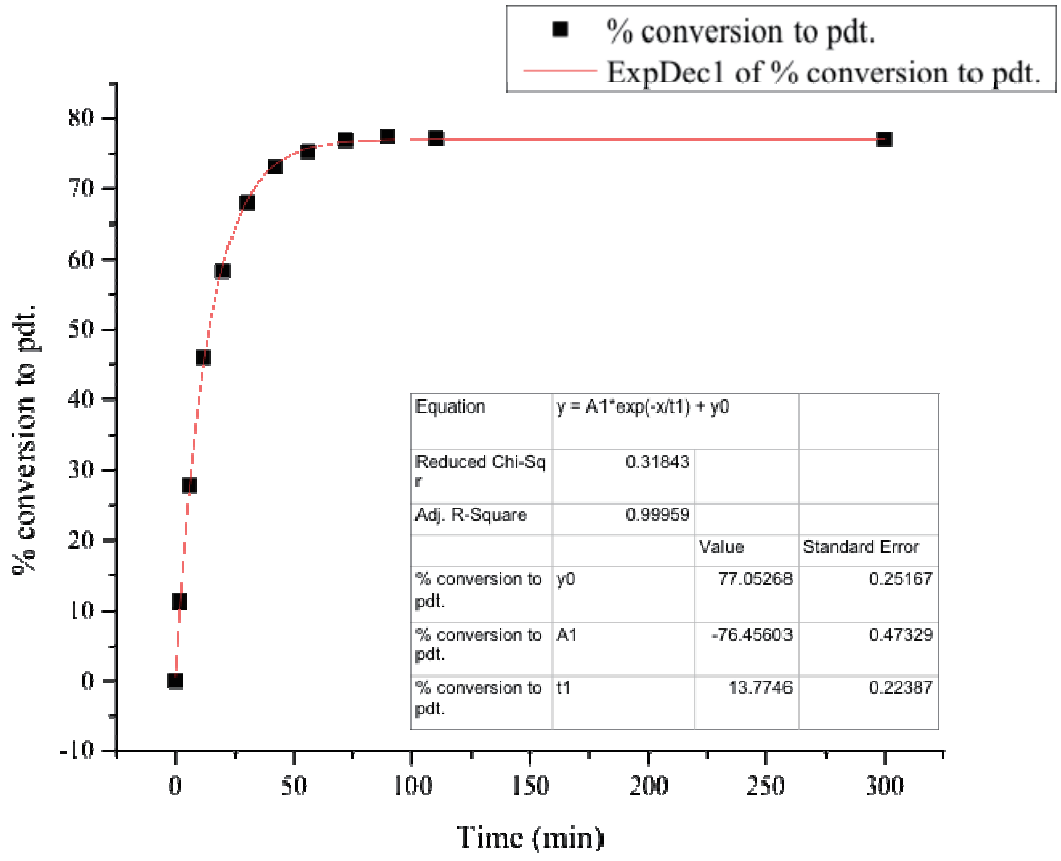
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
2	254.0	6746.20	689.73	30.9	9.1
6	254.0	6197.64	1415.62	69.1	20.4
12	254.0	6219.61	2211.64	107.5	31.7
20	254.0	6887.98	3290.58	144.4	42.6
30	254.0	6410.00	3887.26	183.4	54.1
42	254.0	6988.92	5046.74	218.3	64.4
56	254.0	7510.71	6032.30	242.8	71.6
72	254.0	7749.14	6671.50	260.3	76.8
90	254.0	6479.14	5612.92	261.9	77.3
110	254.0	7366.58	6070.10	249.1	73.5
300	254.0	7157.27	6408.50	270.7	79.9



Half-Life = 25 min

Catalyst **1f**: Run 2

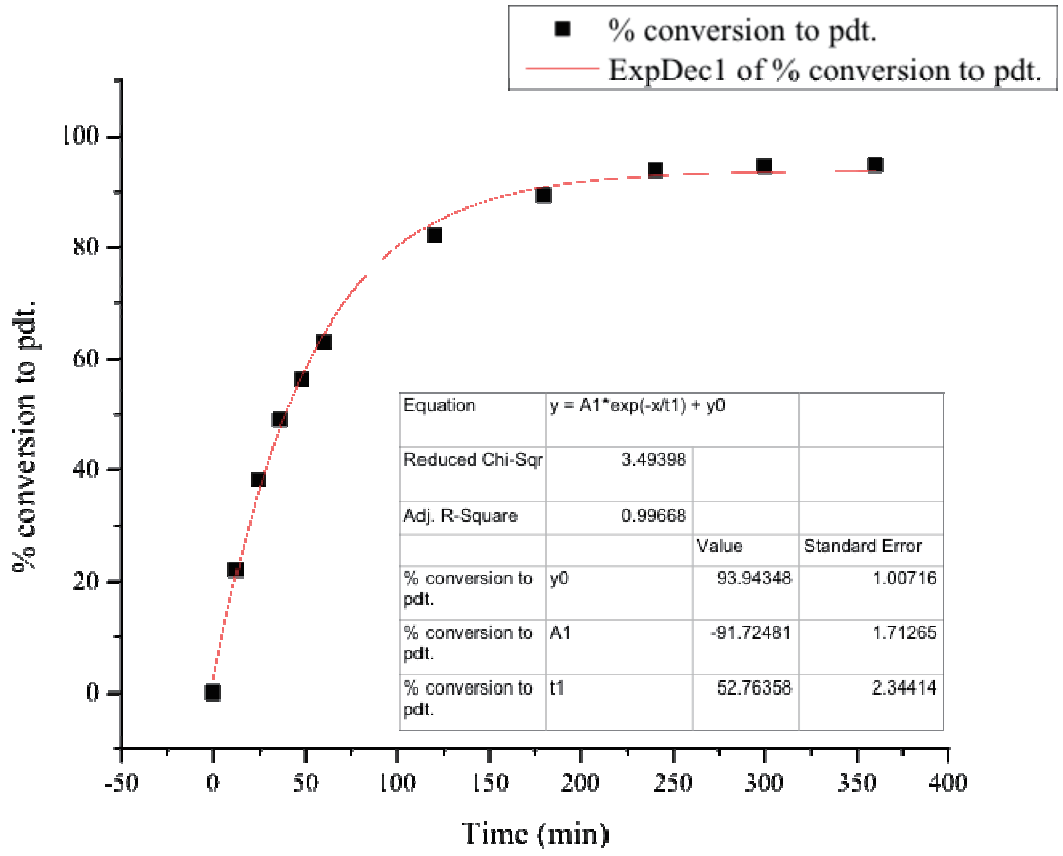
Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
2	254.0	5080.48	644.75	38.4	11.3
6	254.0	5237.71	1632.97	94.3	27.8
12	254.0	6424.64	3309.58	155.8	45.9
20	254.0	6994.52	4578.36	197.9	58.4
30	254.0	7068.22	5386.00	230.4	68.0
42	254.0	6840.88	5606.84	247.8	73.1
56	254.0	6560.04	5537.58	255.2	75.3
72	254.0	6075.60	5238.96	260.7	76.9
90	254.0	7615.96	6618.52	262.8	77.5
110	254.0	6549.97	5671.33	261.8	77.2
300	254.0	7417.62	6411.60	261.4	77.1



Half-Life = 14 min
Average Half-Life = 19 min

Catalyst **2f**: Run 1

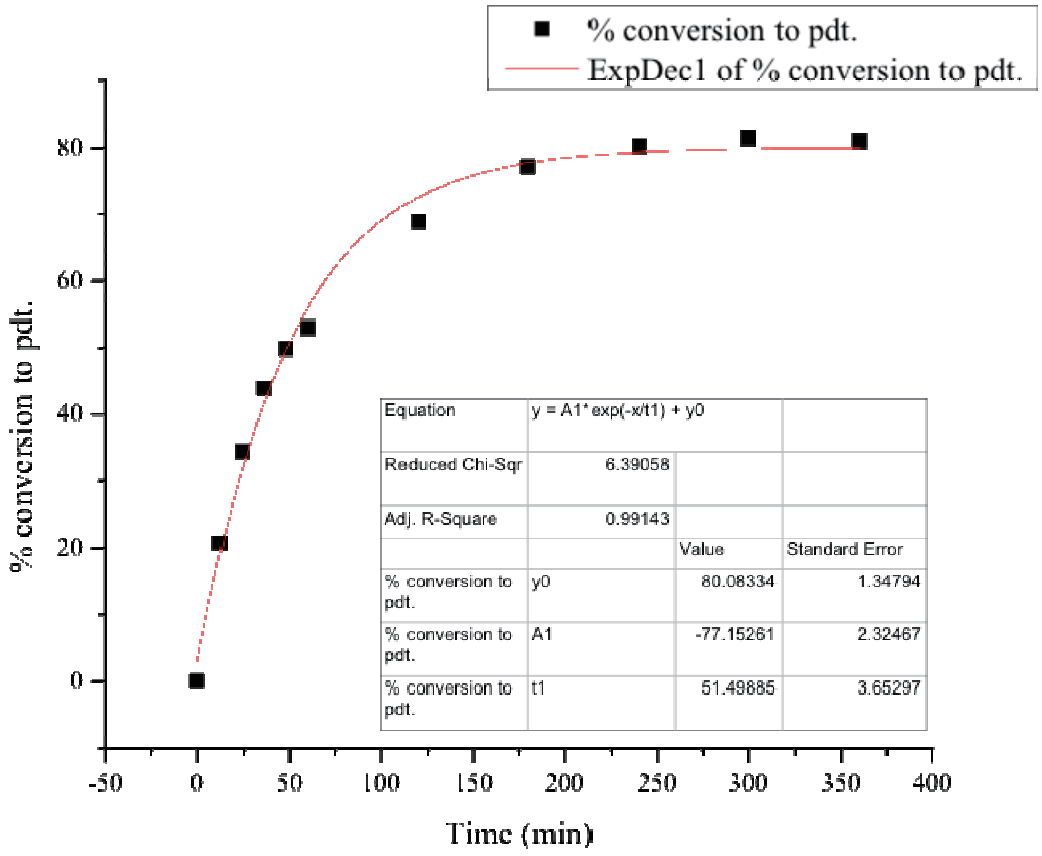
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
12	254.0	6324.66	1567.39	74.9	22.1
24	254.0	5366.03	2291.07	129.1	38.1
36	254.0	6418.06	3533.47	166.5	49.1
48	254.0	6675.58	4220.13	191.1	56.4
60	254.0	6671.54	4712.91	213.6	63.0
120	254.0	7093.22	6534.59	278.5	82.2
180	254.0	6775.49	6791.46	303.1	89.4
240	254.0	6865.26	7235.56	318.7	94.0
300	254.0	6482.36	6879.45	320.9	94.7
360	254.0	7270.22	7736.72	321.8	94.9



Half-Life = 39 min

Catalyst **2f**: Run 2

Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
12	254.0	6927.88	1612.46	70.4	20.8
24	254.0	7272.62	2798.99	116.4	34.3
36	254.0	6758.99	3329.83	149.0	43.9
48	254.0	6662.96	3724.54	169.0	49.9
60	254.0	7018.41	4168.07	179.6	53.0
120	254.0	7401.03	5717.94	233.6	68.9
180	254.0	7034.90	6083.71	261.5	77.1
240	254.0	6652.70	5988.91	272.2	80.3
300	254.0	7370.92	6729.16	276.0	81.4
360	254.0	7207.37	6541.66	274.4	81.0

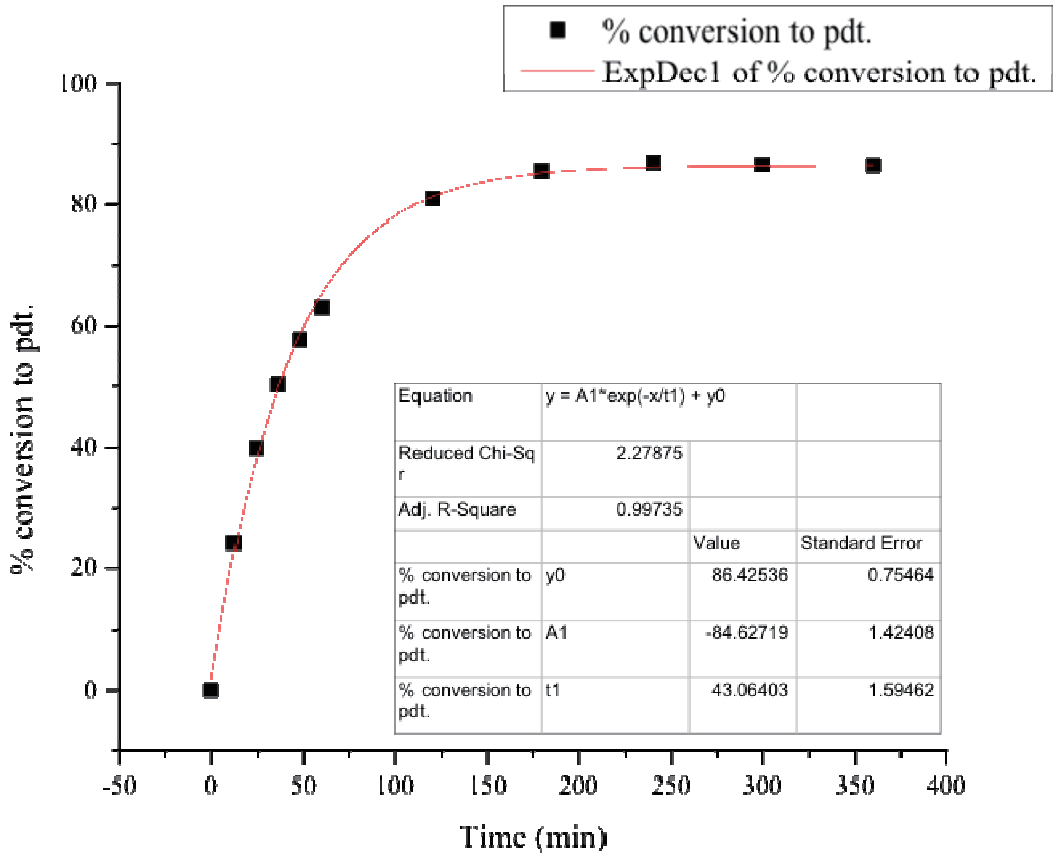


Half-Life = 49 min

Average Half-Life = 44 min

Catalyst **3f**: Run 1

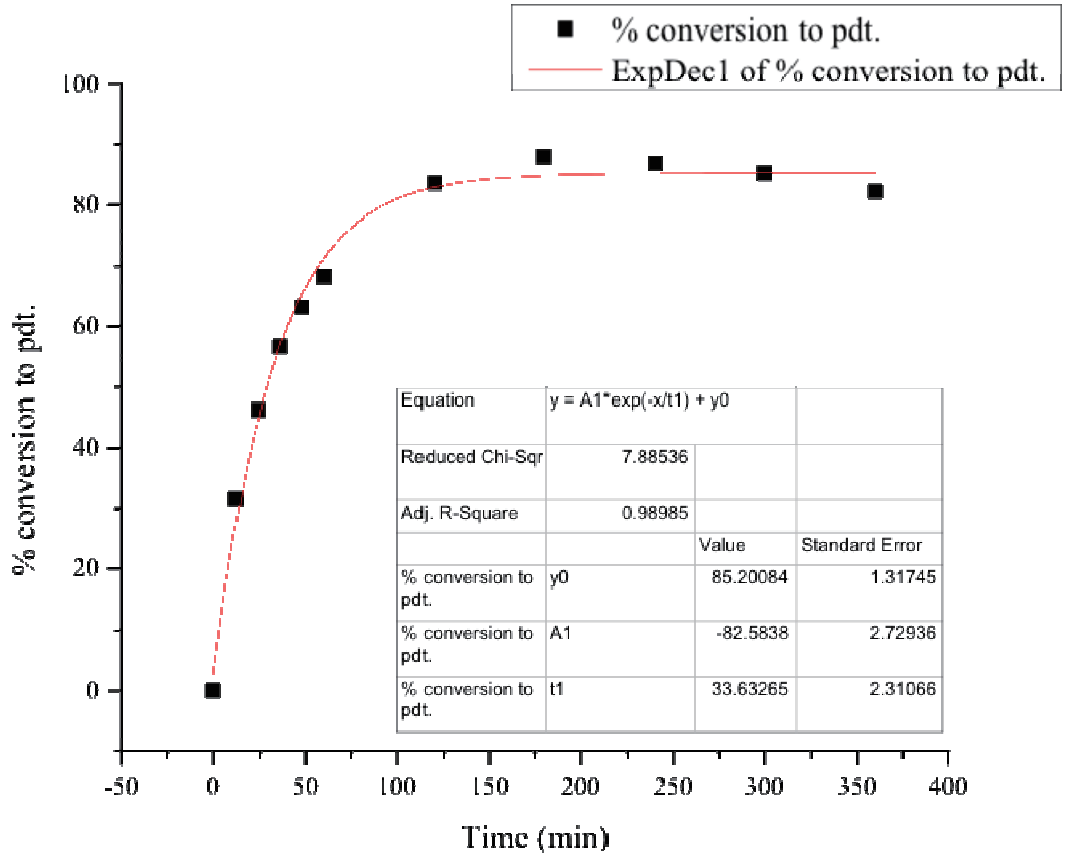
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
12	254.0	6696.54	1815.67	82.0	24.2
24	254.0	5904.32	2640.73	135.2	39.9
36	254.0	6676.11	3768.43	170.7	50.3
48	254.0	6494.00	4199.48	195.5	57.7
60	254.0	6996.87	4941.47	213.5	63.0
120	254.0	6669.55	6049.20	274.2	80.9
180	254.0	6278.46	6013.98	289.6	85.4
240	254.0	6974.64	6792.46	294.5	86.9
300	254.0	6438.08	6240.71	293.1	86.5
360	254.0	7661.69	7422.68	292.9	86.4



Half-Life = 36 min

Catalyst **3f**: Run 2

Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
12	254.0	7204.22	2552.93	107.1	31.6
24	254.0	5943.56	3083.08	156.8	46.3
36	254.0	6007.45	3816.28	192.1	56.7
48	254.0	6786.74	4810.62	214.3	63.2
60	254.0	7396.10	5661.89	231.5	68.3
120	254.0	6214.94	5820.62	283.2	83.5
180	254.0	6575.49	6480.29	298.0	87.9
240	254.0	6611.76	6435.94	294.3	86.8
300	254.0	6406.46	6114.86	288.6	85.1
360	254.0	6888.95	6344.32	278.5	82.1

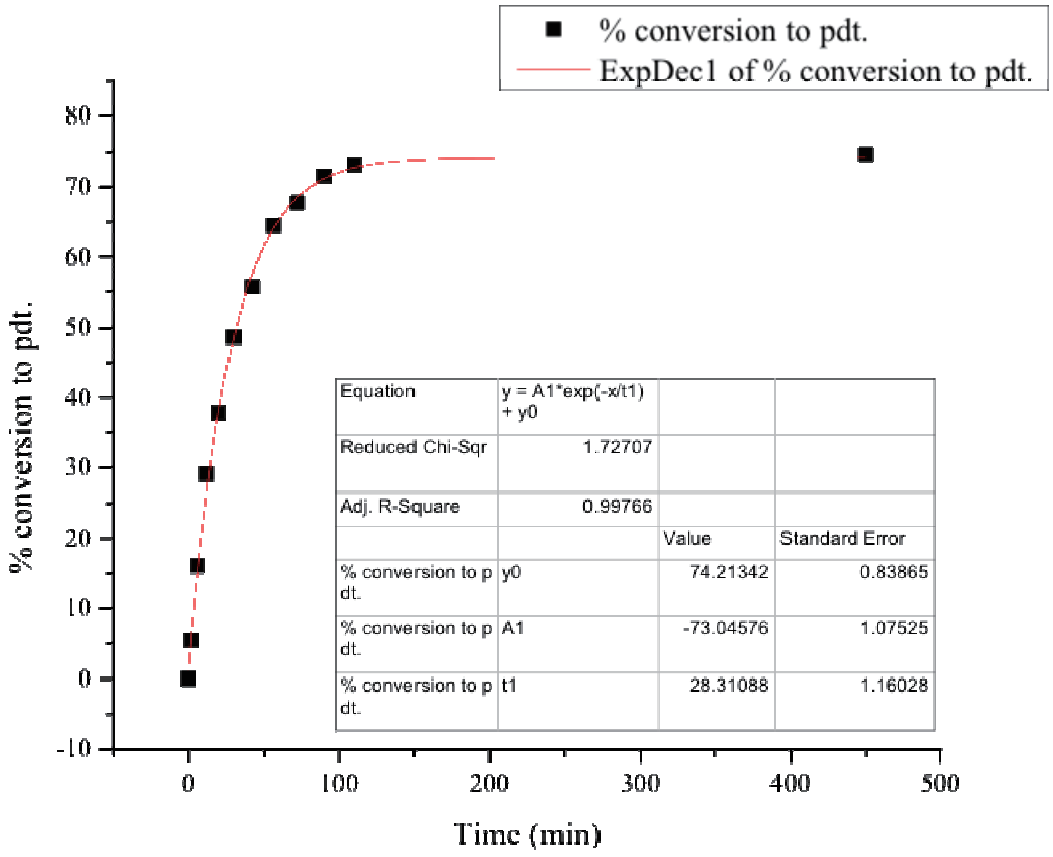


Half-Life = 29 min

Average Half-Life = 32 min

Catalyst **4f**: Run 1

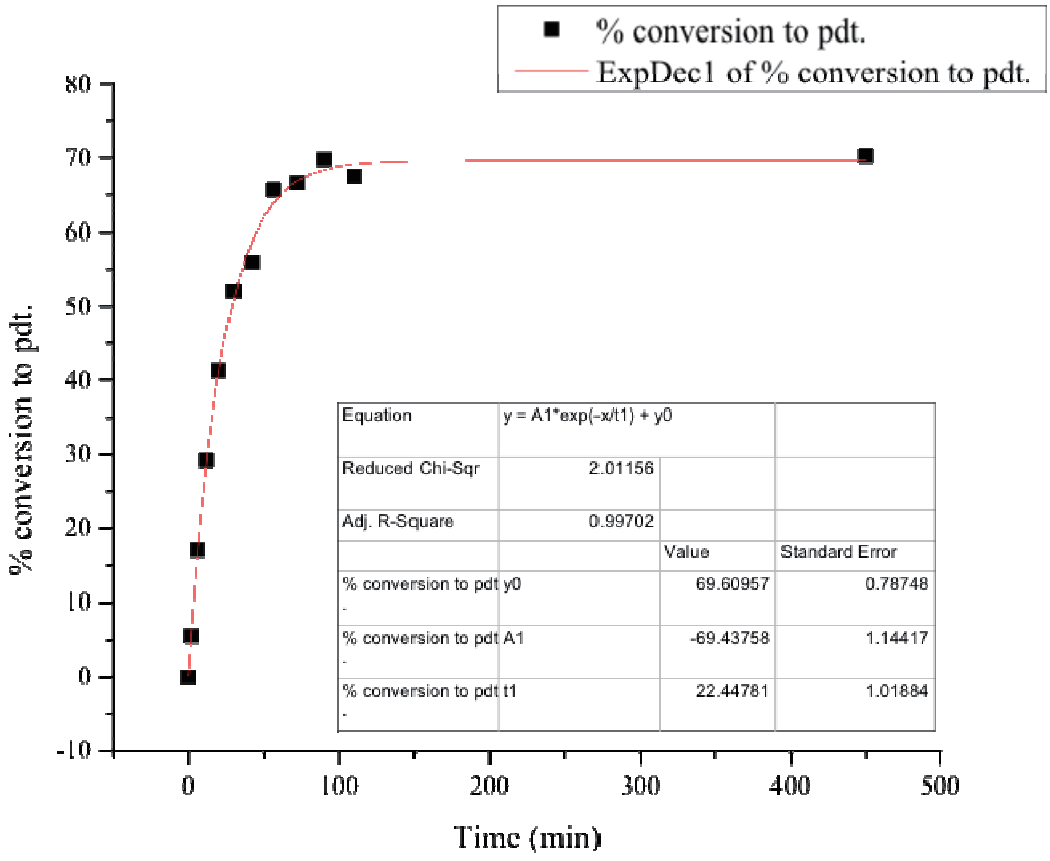
Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
2	254.0	8302.52	505.63	18.4	5.4
6	254.0	8506.73	1537.43	54.6	16.1
12	254.0	7923.75	2583.53	98.6	29.1
20	254.0	7614.71	3222.40	128.0	37.7
30	254.0	8226.42	4489.79	165.0	48.7
42	254.0	8094.67	5048.39	188.6	55.6
56	254.0	8570.60	6196.11	218.6	64.5
72	254.0	8062.57	6122.82	229.6	67.7
90	254.0	8202.17	6581.54	242.6	71.6
110	254.0	9014.30	7392.26	248.0	73.1
450	254.0	8553.64	7156.44	253.0	74.6



Half-Life = 31 min

Catalyst **4f**: Run 2

Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
2	254.0	8189.52	514.56	19.0	5.6
6	254.0	6596.58	1266.05	58.0	17.1
12	254.0	6805.55	2231.29	99.1	29.2
20	254.0	8318.14	3846.29	139.8	41.2
30	254.0	6211.89	3626.47	176.5	52.1
42	254.0	7508.75	4711.72	189.7	56.0
56	254.0	6662.03	4899.97	222.4	65.6
72	254.0	6309.02	4707.80	225.6	66.6
90	254.0	6673.20	5217.23	236.4	69.7
110	254.0	7273.48	5498.61	228.6	67.4
450	254.0	6265.72	4932.82	238.0	70.2

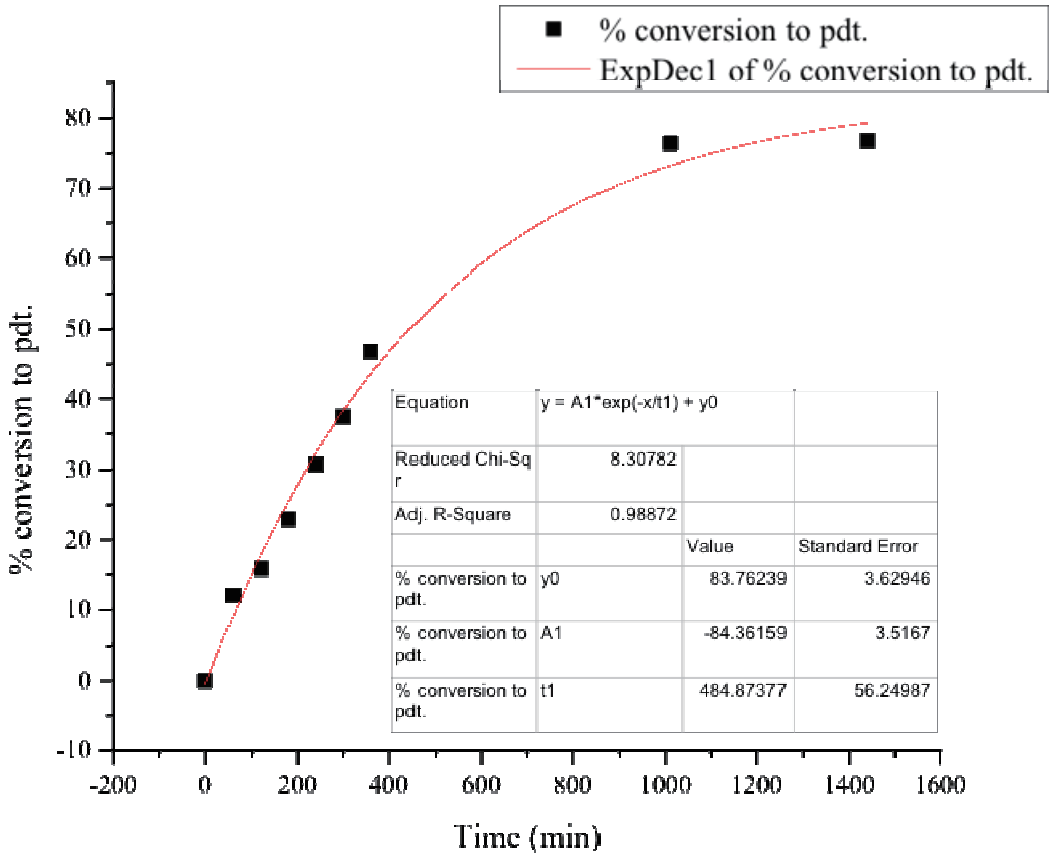


Half-Life = 28 min

Average Half-Life = 30 min

Catalyst **5f**: Run 1

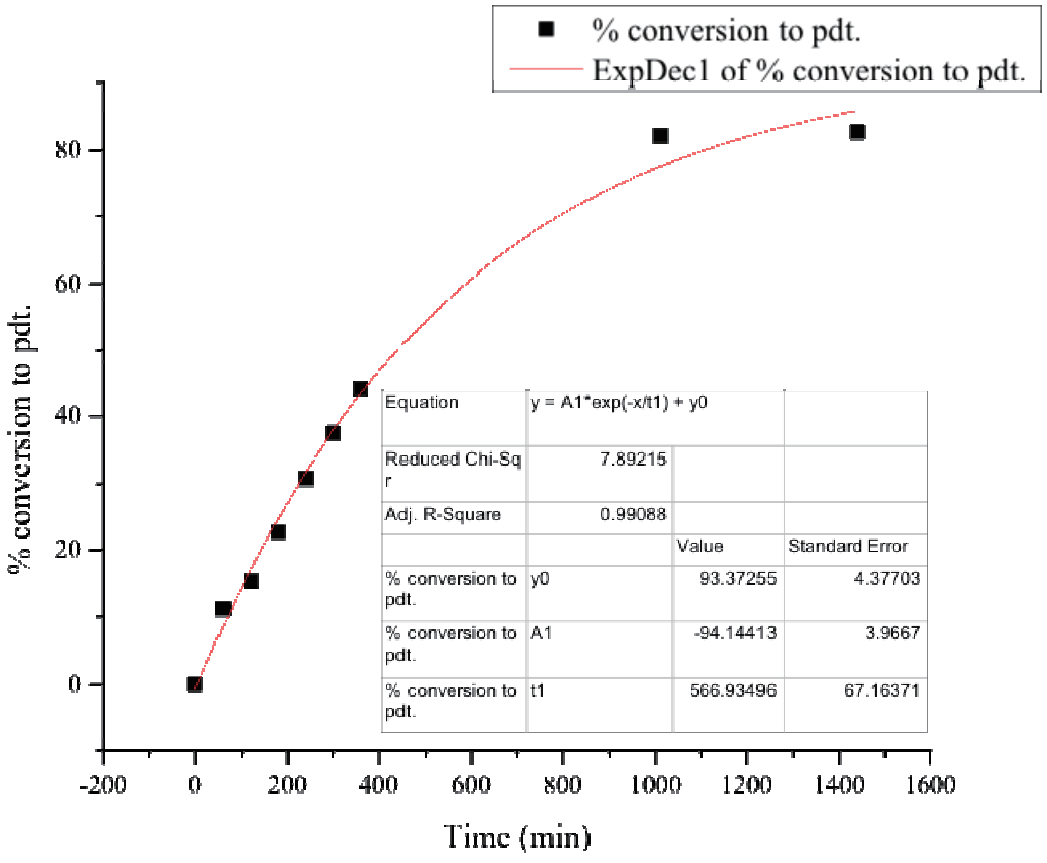
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
60	254.0	6608.52	893.80	40.9	12.1
120	254.0	6852.95	1218.56	53.8	15.9
180	254.0	7020.18	1806.02	77.8	22.9
240	254.0	6545.57	2252.42	104.0	30.7
300	254.0	6793.92	2850.32	126.9	37.4
360	254.0	6628.84	3477.13	158.6	46.8
1011	254.0	7481.96	6413.33	259.2	76.5
1440	254.0	7024.42	6051.69	260.5	76.8



Half-Life = 444 min

Catalyst **5f**: Run 2

Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
60	254.0	6451.04	808.15	37.9	11.2
120	254.0	6972.20	1199.07	52.0	15.3
180	254.0	6673.80	1702.65	77.1	22.8
240	254.0	7158.30	2469.27	104.3	30.8
300	254.0	6765.32	2842.87	127.1	37.5
360	254.0	6806.36	3370.52	149.7	44.2
1011	254.0	7313.61	6734.09	278.4	82.1
1440	254.0	6722.68	6236.44	280.5	82.7



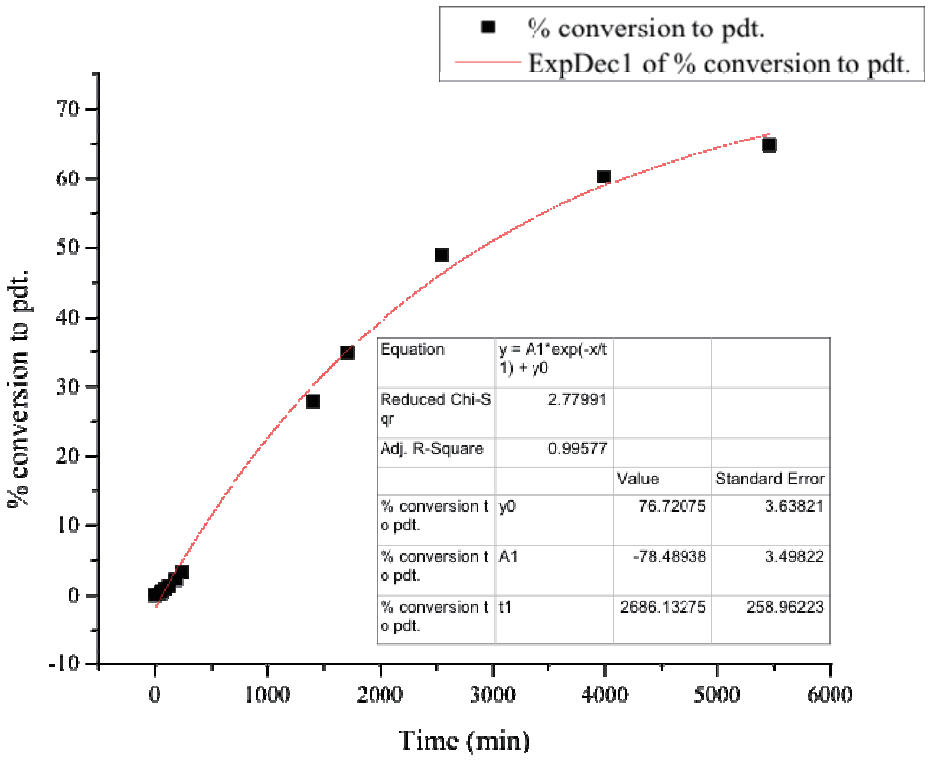
Half-Life = 439 min

Average Half-Life = 442 min

Kinetic Analyses of Catalysts in Series G

Catalyst **1g**: Run 1

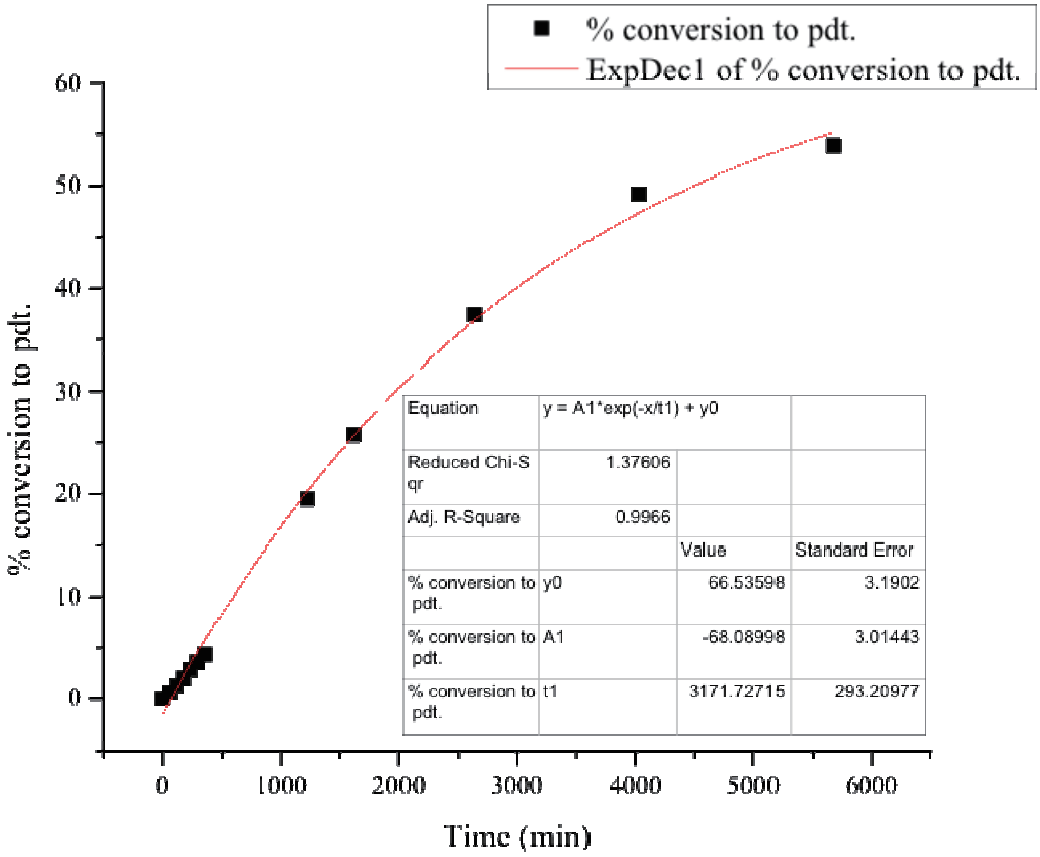
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
5	254.0	4785.40	0.00	0.0	0.0
10	254.0	6481.61	0.00	0.0	0.0
15	254.0	6278.11	0.00	0.0	0.0
30	254.0	6196.21	0.00	0.0	0.0
45	254.0	7055.98	29.33	1.3	0.4
60	254.0	7036.21	43.22	1.9	0.5
90	254.0	7040.81	70.43	3.0	0.9
120	254.0	6788.59	99.73	4.4	1.3
180	254.0	6166.88	155.59	7.6	2.3
240	254.0	7618.04	281.53	11.2	3.3
1407	254.0	3124.85	977.35	94.6	27.9
1705	254.0	7065.51	2760.89	118.1	34.9
2544	254.0	5809.74	3190.58	166.1	49.0
3993	254.0	6635.87	4481.06	204.2	60.2
5460	254.0	8019.76	5833.45	219.9	64.9



Half-Life = 2894 min

Catalyst **1g**: Run 2

Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
60	254.0	6226.14	44.30	2.2	0.6
120	254.0	6555.16	96.03	4.4	1.3
180	254.0	6917.37	158.11	6.9	2.0
240	254.0	6946.54	225.34	9.8	2.9
300	254.0	7093.78	286.27	12.2	3.6
360	254.0	7195.26	351.78	14.8	4.4
1224	254.0	6945.15	1515.48	66.0	19.5
1620	254.0	7602.57	2194.78	87.3	25.7
2640	254.0	6005.86	2518.23	126.8	37.4
4026	254.0	7049.26	3888.84	166.8	49.2
5673	254.0	7061.82	4263.06	182.5	53.8

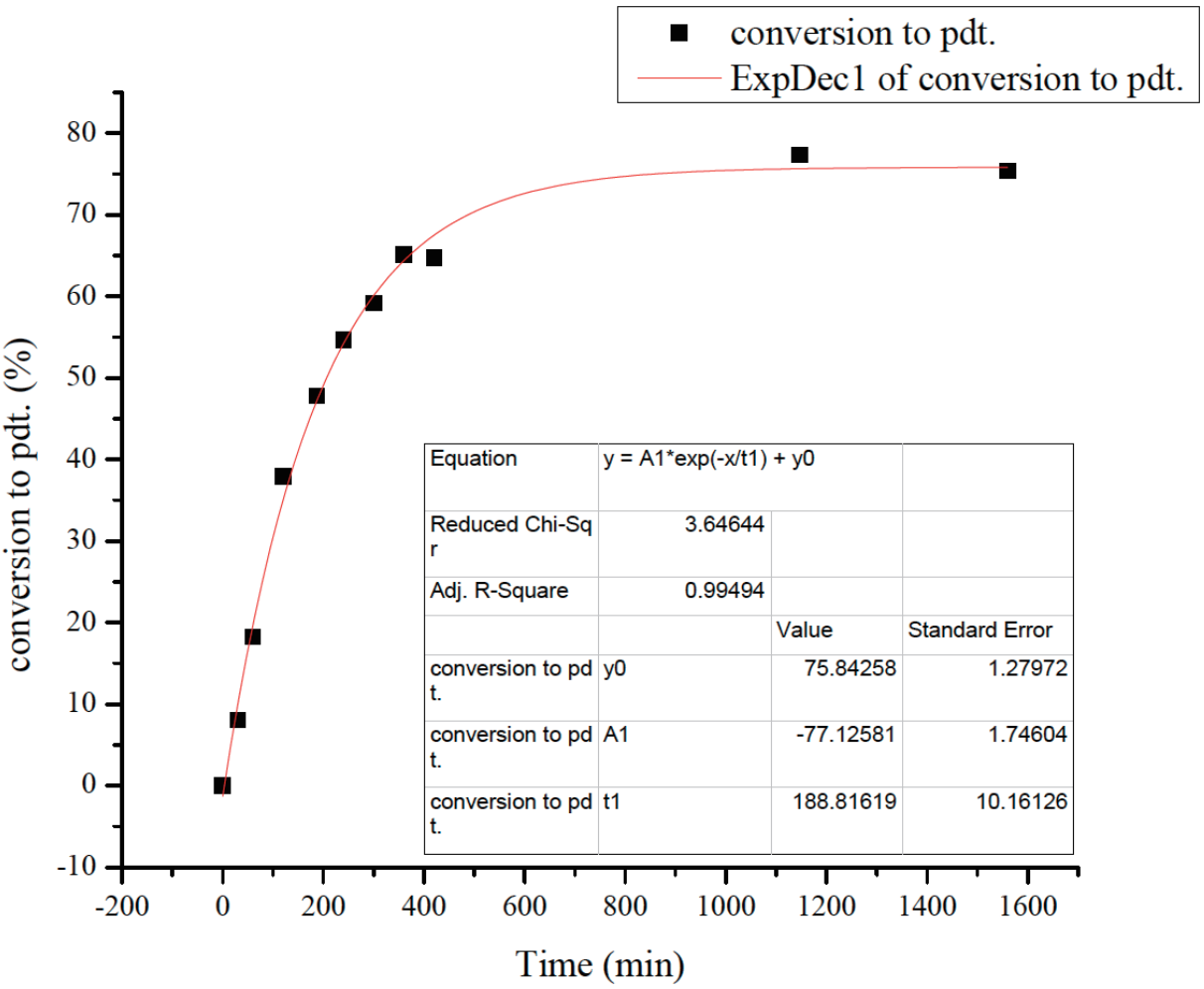


Half-Life = 4489 min

Average Half-Life = 3692 min

Catalyst **2g**: Run 1

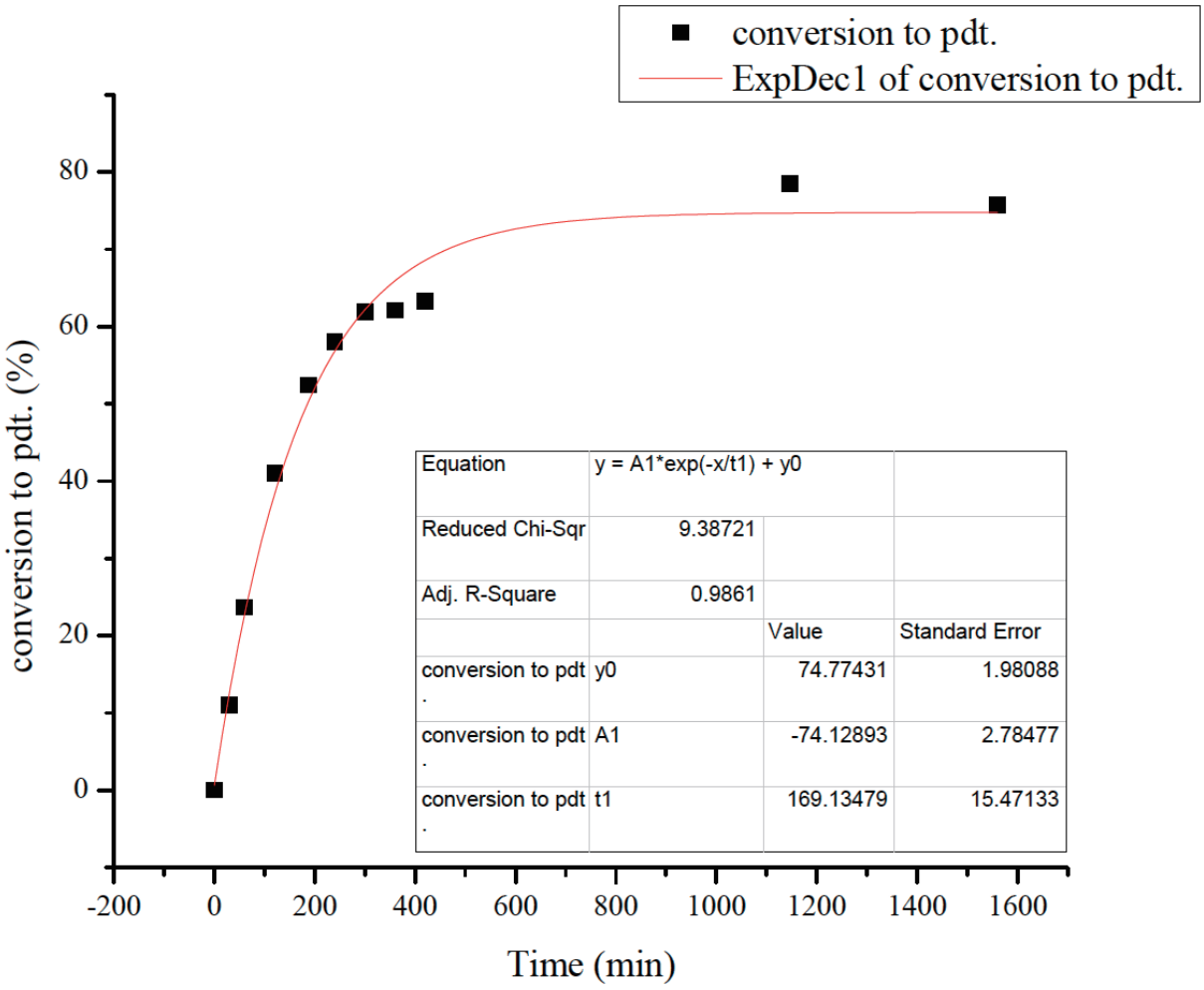
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.4	1.00	0.00	0.0	0.0
30	254.4	6787.93	609.88	27.2	8.0
60	254.4	7257.10	1481.89	61.8	18.2
120	254.4	7551.69	3204.37	128.5	37.9
187	254.4	7887.53	4220.36	162.0	47.8
240	254.4	7380.23	4514.83	185.3	54.6
300	254.4	8035.92	5323.30	200.6	59.2
360	254.4	8171.71	5955.57	220.7	65.1
420	254.4	7824.91	5666.78	219.3	64.7
1147	254.4	8168.60	7071.88	262.2	77.3
1560	254.4	7224.20	6097.69	255.6	75.4



Half-Life = 206 min

Catalyst **2g**: Run 2

Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.4	1.00	0.00	0.0	0.0
30	254.4	7879.70	974.28	37.4	11.0
60	254.4	7632.34	2021.67	80.2	23.7
120	254.4	7338.45	3373.79	139.2	41.1
187	254.4	7725.06	4531.65	177.6	52.4
240	254.4	7509.69	4875.33	196.6	58.0
300	254.4	7493.59	5189.88	209.7	61.9
360	254.4	8120.01	5647.67	210.6	62.1
420	254.4	7942.36	5629.66	214.7	63.3
1147	254.4	8318.25	7305.35	266.0	78.5
1560	254.4	7807.39	6619.81	256.8	75.7

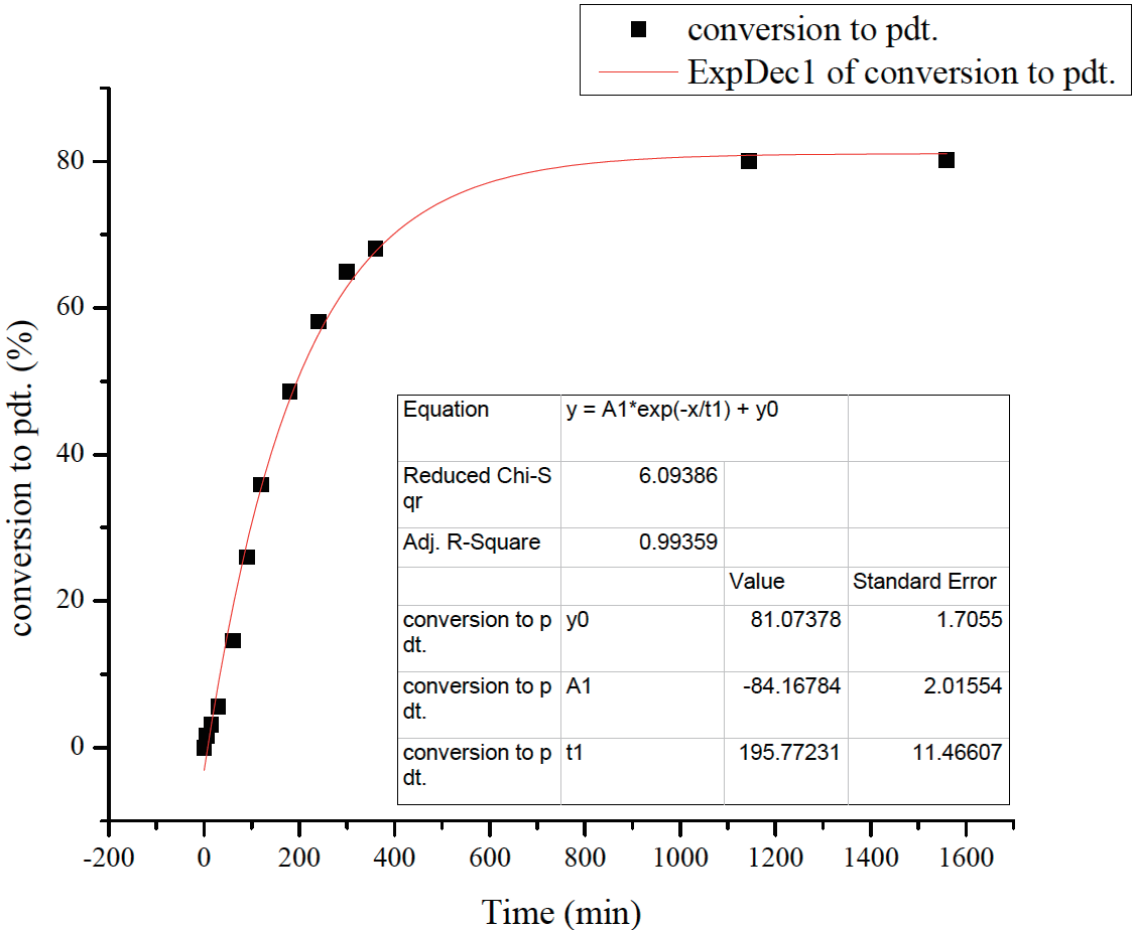


Half-Life = 185 min

Average Half-Life = 196 min

Catalyst **3g**: Run 1

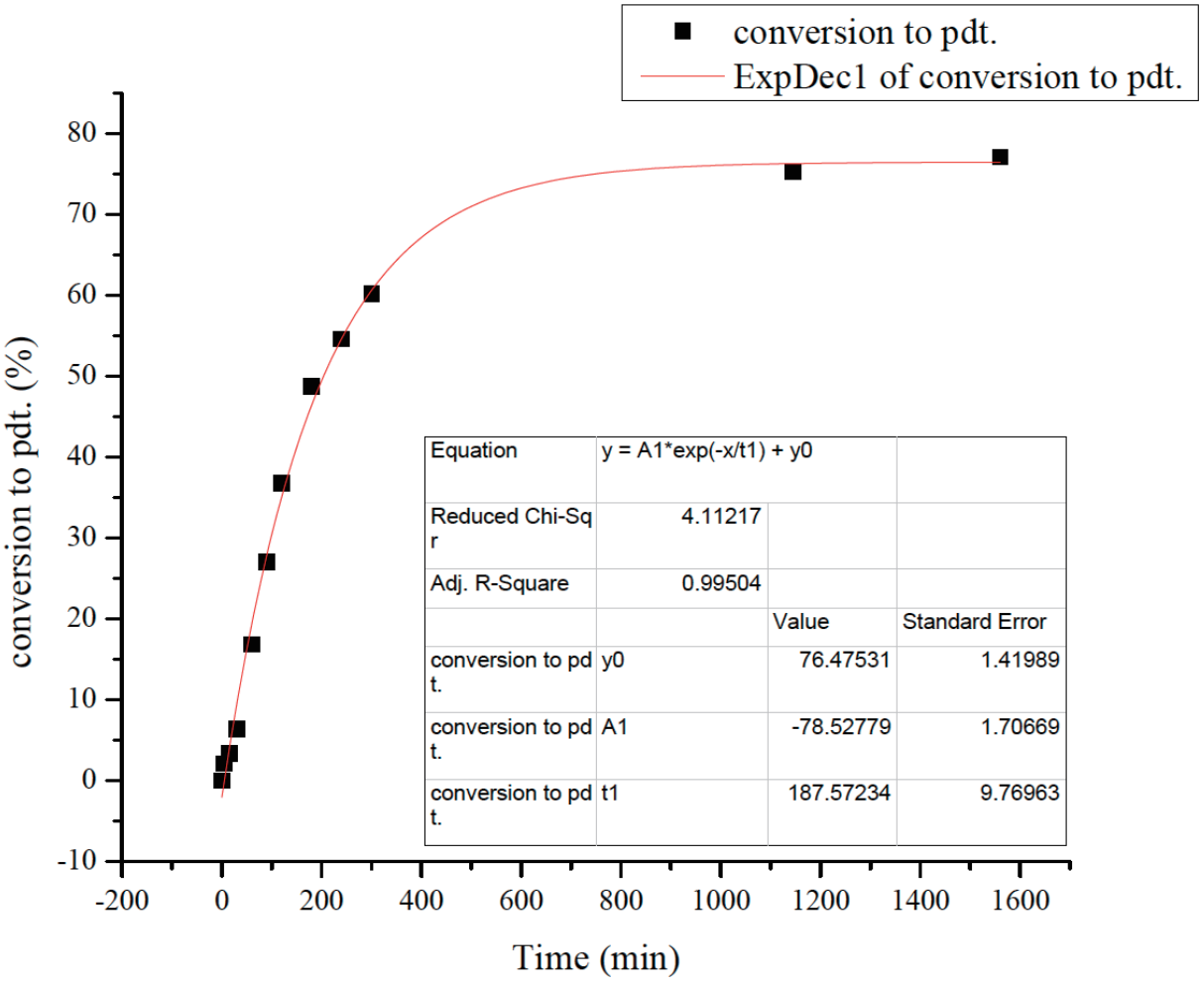
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.4	1.00	0.00	0.0	0.0
5	254.4	7555.78	137.60	5.5	1.6
15	254.4	7675.03	269.49	10.6	3.1
30	254.4	7437.46	467.38	19.0	5.6
60	254.4	8236.57	1348.06	49.6	14.6
90	254.4	7395.39	2152.72	88.2	26.0
120	254.4	7192.46	2890.21	121.7	35.9
180	254.4	8134.50	4423.51	164.7	48.6
240	254.4	7371.72	4797.26	197.1	58.1
300	254.4	7601.25	5521.92	220.0	64.9
360	254.4	8066.03	6149.84	230.9	68.1
1145	254.4	7824.90	7006.29	271.2	80.0
1560	254.4	7618.68	6837.57	271.8	80.2



Half-Life = 195 min

Catalyst **3g**: Run 2

Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.4	1.00	0.00	0.0	0.0
5	254.4	7015.07	161.58	7.0	2.1
15	254.4	8256.07	306.73	11.3	3.3
30	254.4	7499.40	535.31	21.6	6.4
60	254.4	7462.14	1404.07	57.0	16.8
90	254.4	7326.29	2214.59	91.5	27.0
120	254.4	7777.68	3203.36	124.7	36.8
180	254.4	8064.22	4403.38	165.4	48.8
240	254.4	7774.00	4752.02	185.1	54.6
300	254.4	7759.49	5227.26	204.0	60.2
1145	254.4	8132.78	6851.19	255.1	75.3
1560	254.4	7680.57	6628.07	261.3	77.1

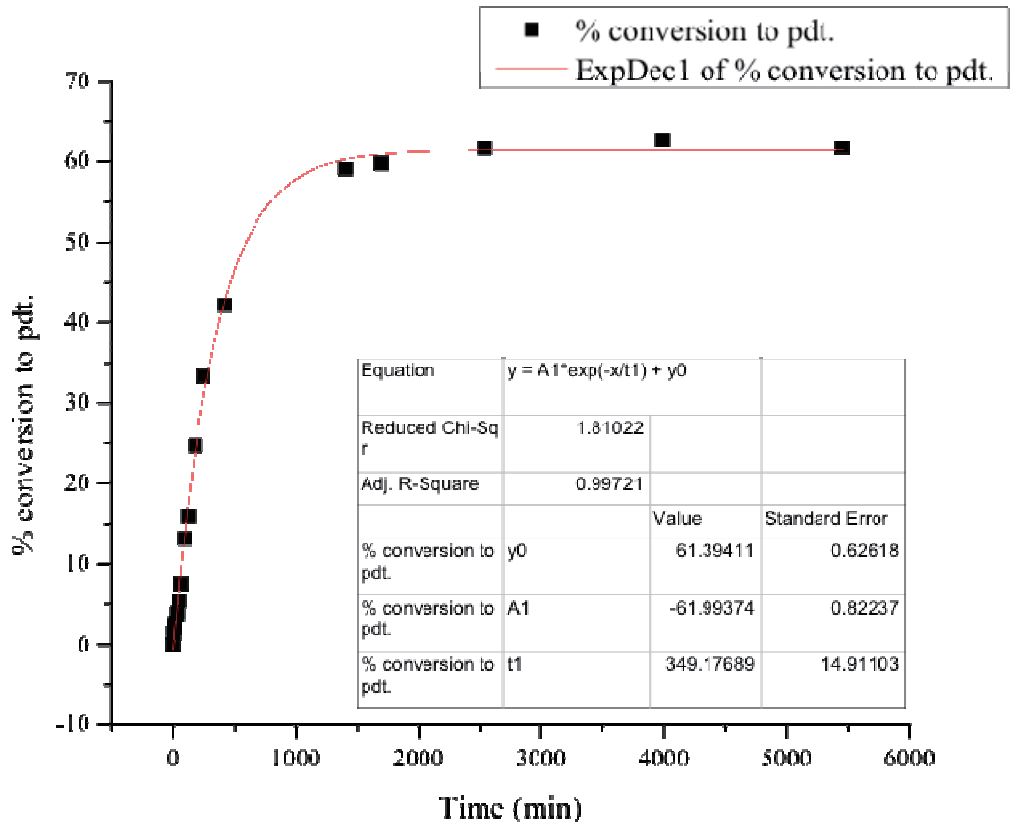


Half-Life = 204 min

Average Half-Life = 200 min

Catalyst **4g**: Run 1

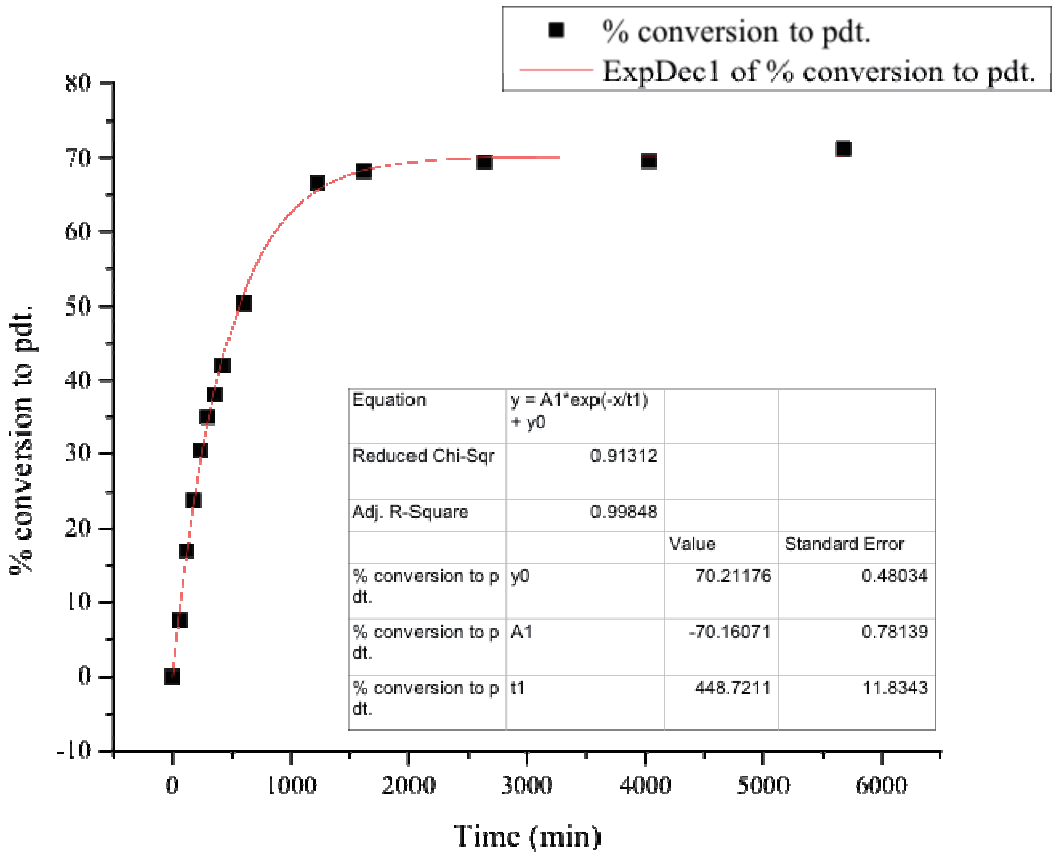
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
5	254.0	6852.17	110.72	4.9	1.4
10	254.0	6817.03	158.95	7.0	2.1
15	254.0	7699.92	215.54	8.5	2.5
30	254.0	6630.67	281.05	12.8	3.8
45	254.0	7347.50	441.68	18.2	5.4
60	254.0	7795.26	662.70	25.7	7.6
90	254.0	6685.08	986.00	44.6	13.2
120	254.0	3378.30	604.63	54.1	16.0
180	254.0	7588.50	2102.34	83.8	24.7
240	254.0	7529.30	2813.65	113.0	33.3
420	254.0	8020.55	3789.02	142.8	42.1
1402	254.0	7165.58	4748.75	200.4	59.1
1700	254.0	7360.62	4932.70	202.6	59.8
2540	254.0	7336.59	5072.65	209.1	61.7
3988	254.0	7775.68	5465.47	212.5	62.7
5455	254.0	7686.08	5322.10	209.4	61.8



Half-Life = 591 min

Catalyst **4g**: Run 2

Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
60	254.0	6065.59	515.52	25.7	7.6
120	254.0	6510.57	1245.10	57.8	17.1
180	254.0	6607.95	1771.45	81.1	23.9
240	254.0	6189.82	2115.38	103.3	30.5
300	254.0	6698.55	2625.93	118.5	35.0
360	254.0	7265.78	3099.91	129.0	38.1
420	254.0	7283.71	3425.02	142.2	41.9
595	254.0	8157.31	4603.36	170.6	50.3
1224	254.0	7028.87	5247.63	225.7	66.6
1620	254.0	7270.08	5561.25	231.3	68.2
2640	254.0	5815.63	4528.96	235.5	69.5
4026	254.0	6589.75	5139.52	235.8	69.6
5673	254.0	7112.28	5681.54	241.5	71.2

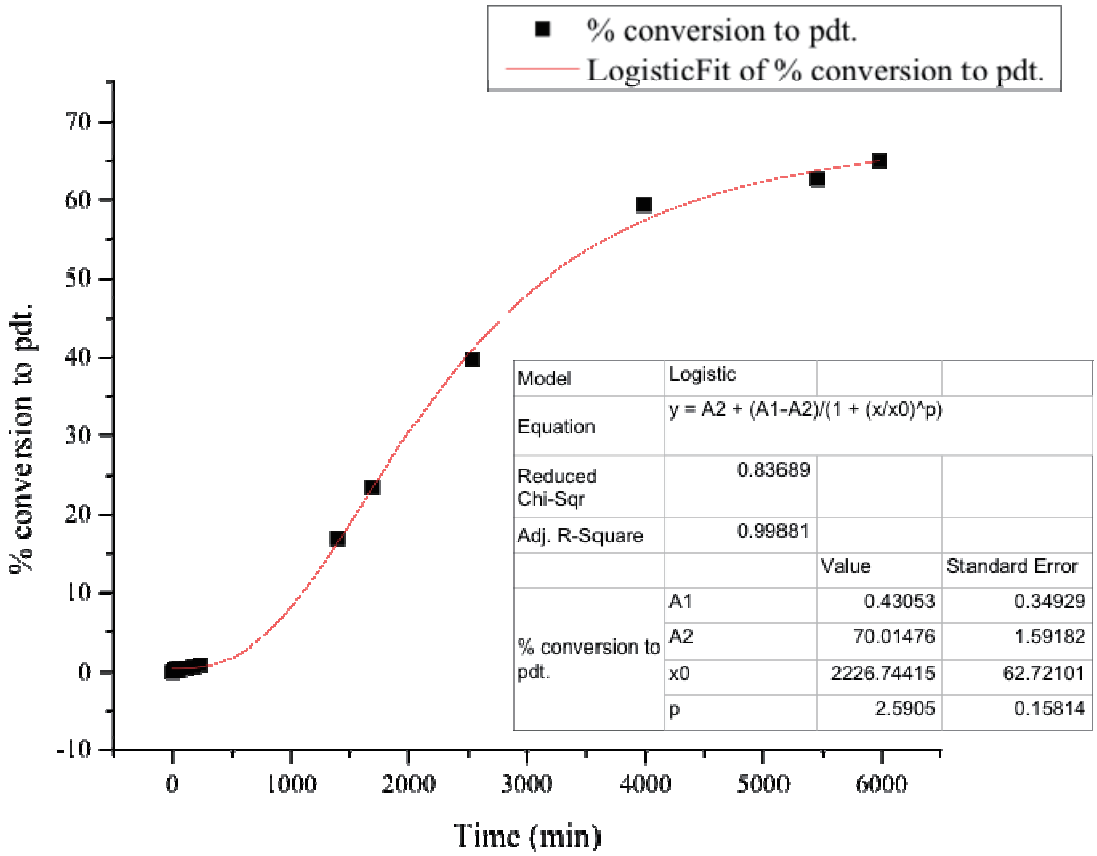


Half-Life = 558 min

Average Half-Life = 575 min

Catalyst **5g**: Run 1

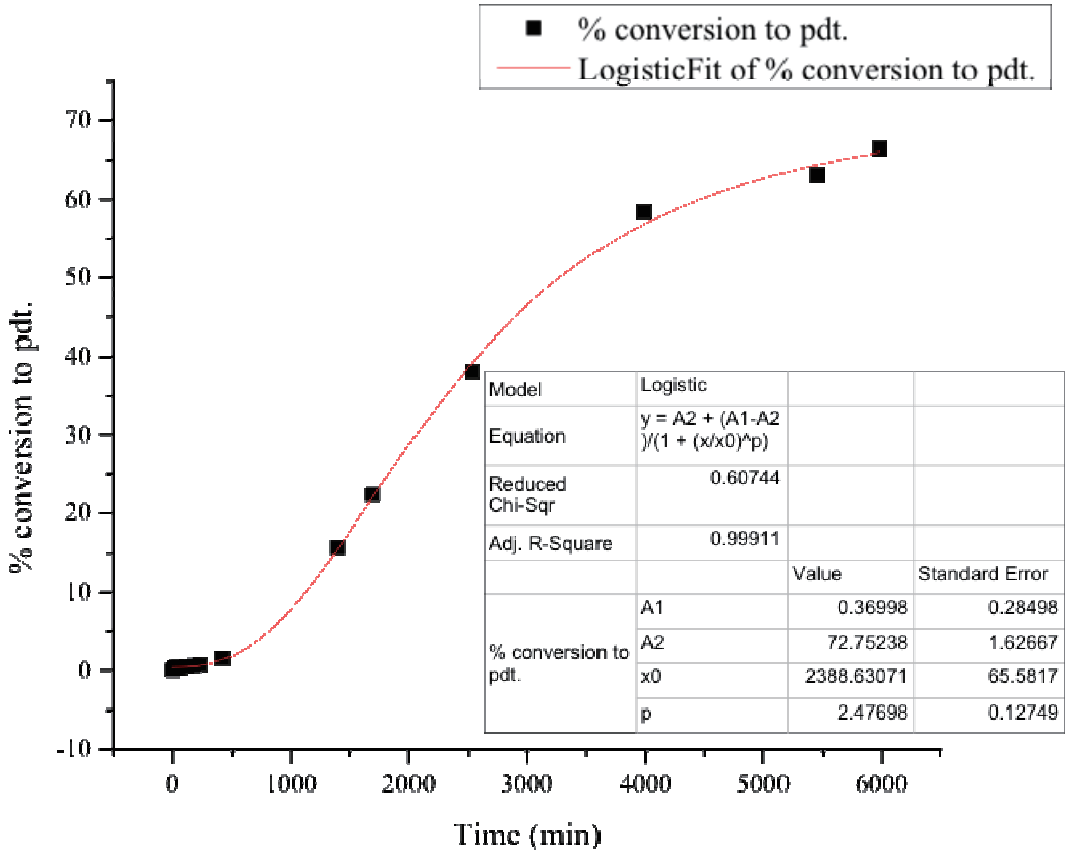
Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
20	254.0	6704.03	24.82	1.1	0.3
40	254.0	7061.44	29.39	1.3	0.4
60	254.0	6941.09	29.71	1.3	0.4
120	254.0	6517.55	37.89	1.8	0.5
180	254.0	7593.26	58.47	2.3	0.7
240	254.0	7134.07	73.46	3.1	0.9
1397	254.0	7796.78	1482.19	57.5	17.0
1695	254.0	7398.42	1949.06	79.7	23.5
2535	254.0	7565.42	3368.12	134.6	39.7
3983	254.0	7863.07	5236.10	201.3	59.4
5450	254.0	7261.97	5102.63	212.5	62.7
5982	254.0	6722.67	4899.27	220.4	65.0



Half-Life = 3160 min

Catalyst **5g**: Run 2

Time (min)	Standard (μmol)	Standard Area	Product Area	Product (μmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
20	254.0	6810.74	22.83	1.0	0.3
40	254.0	7555.66	31.60	1.3	0.4
60	254.0	7428.10	26.43	1.1	0.3
120	254.0	6894.61	34.74	1.5	0.4
180	254.0	7584.21	47.24	1.9	0.6
240	254.0	6978.06	54.40	2.4	0.7
420	254.0	7301.12	127.65	5.3	1.6
1397	254.0	7504.53	1322.42	53.3	15.7
1695	254.0	7643.58	1916.64	75.8	22.4
2535	254.0	7144.83	3052.49	129.2	38.1
3983	254.0	7119.85	4665.06	198.1	58.4
5450	254.0	7699.37	5449.40	214.0	63.1
5982	254.0	6928.39	5159.28	225.2	66.4



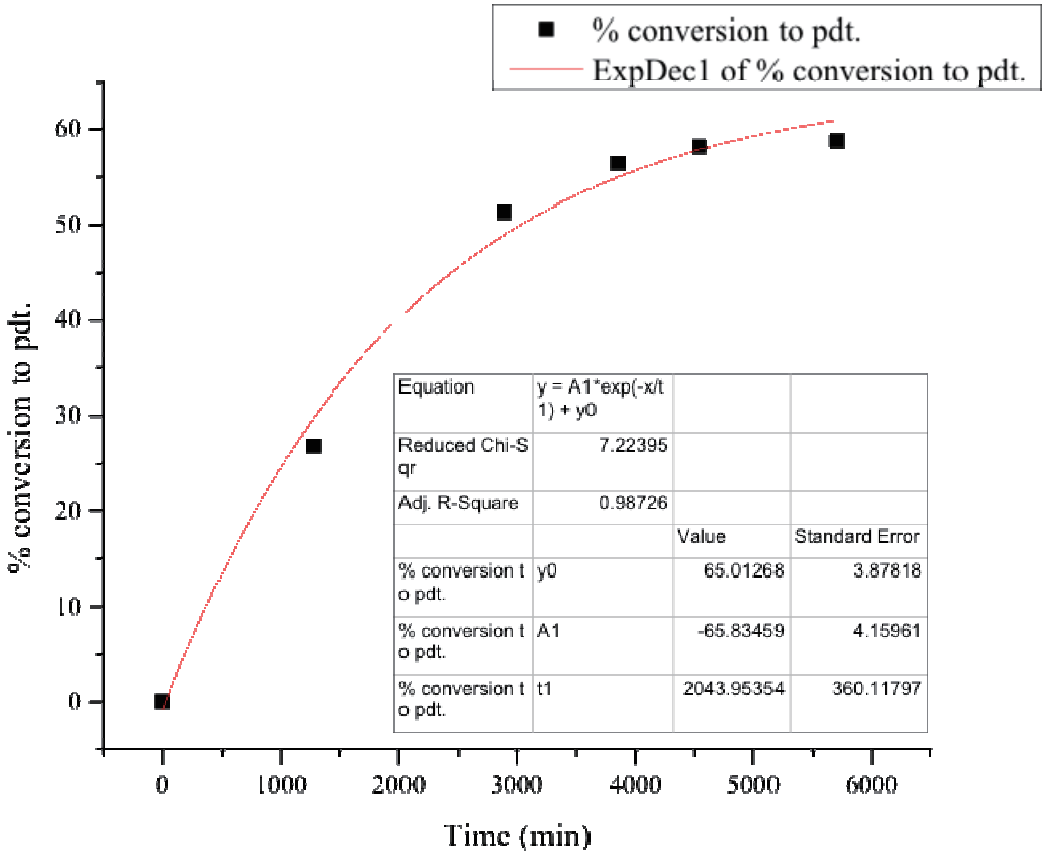
Half-Life = 3273 min

Average Half-Life = 3216 min

Kinetic Analyses of Catalysts in Series H

Catalyst **1h**: Run 1

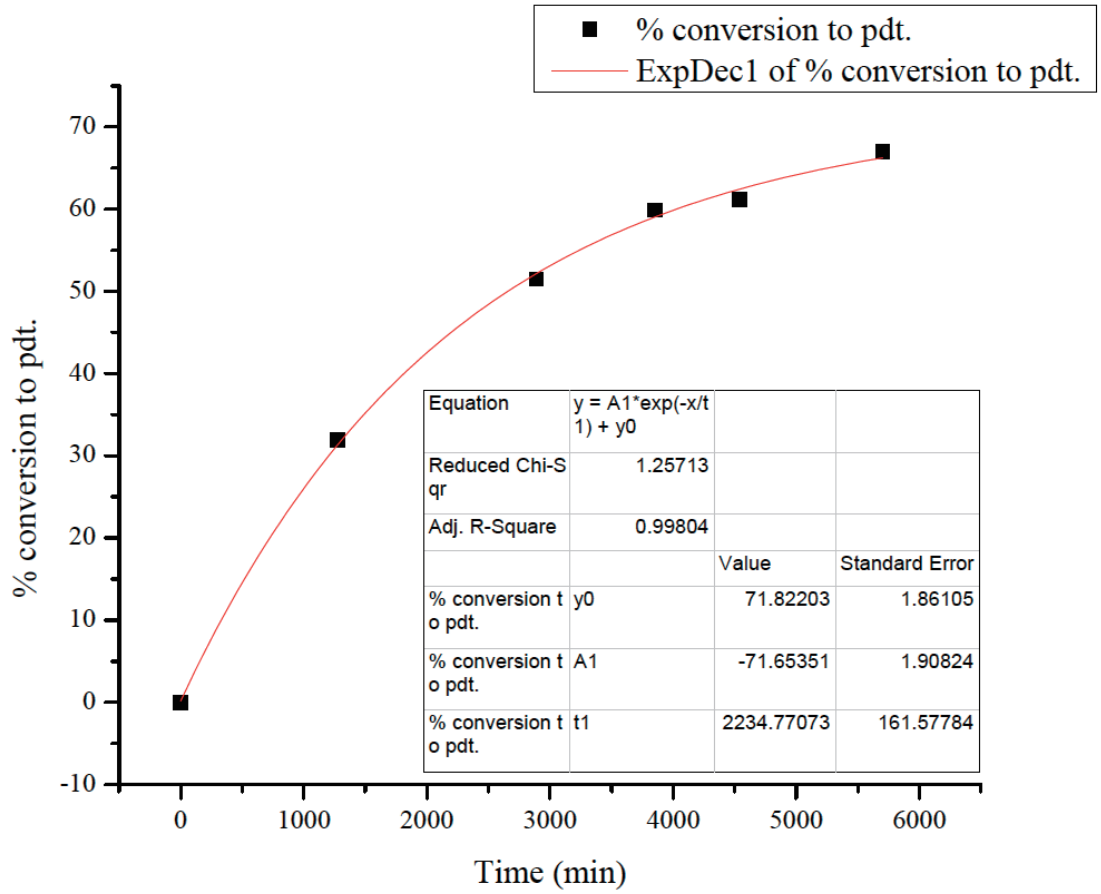
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
1276	254.0	5044.18	1520.27	91.1	26.9
2888	254.0	6706.97	3865.74	174.3	51.4
3852	254.0	5659.38	3583.60	191.5	56.5
4543	254.0	7840.04	5115.84	197.3	58.2
5702	254.0	6757.42	4455.41	199.4	58.8



Half-Life = 3021 min

Catalyst **1h**: Run 2

Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
1276	254.0	5857.86	2095.20	108.1	31.9
2888	254.0	6751.11	3896.04	174.5	51.5
3852	254.0	7596.78	5098.87	202.9	59.9
4543	254.0	7845.55	5377.01	207.2	61.1
5702	254.0	7161.18	5379.07	227.1	67.0

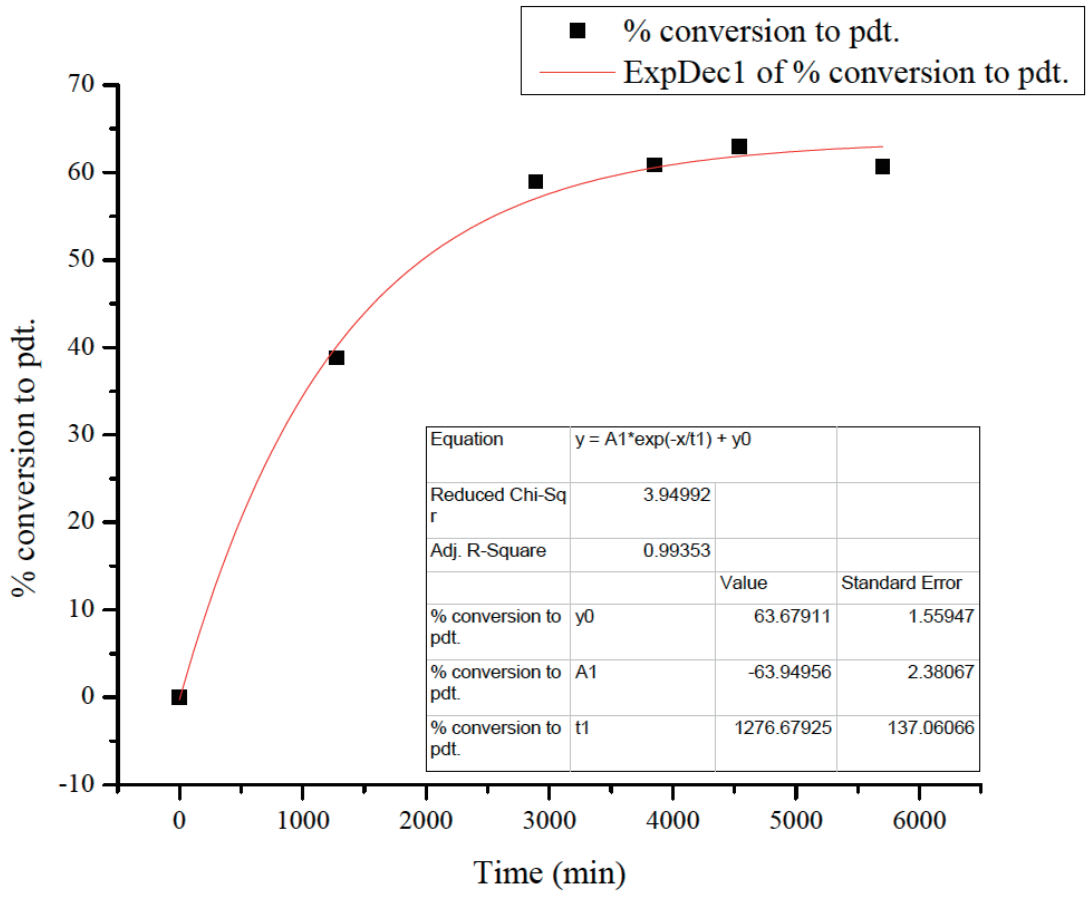


Half-Life = 2657 min

Average Half-Life = 2839 min

Catalyst **2h**: Run 1

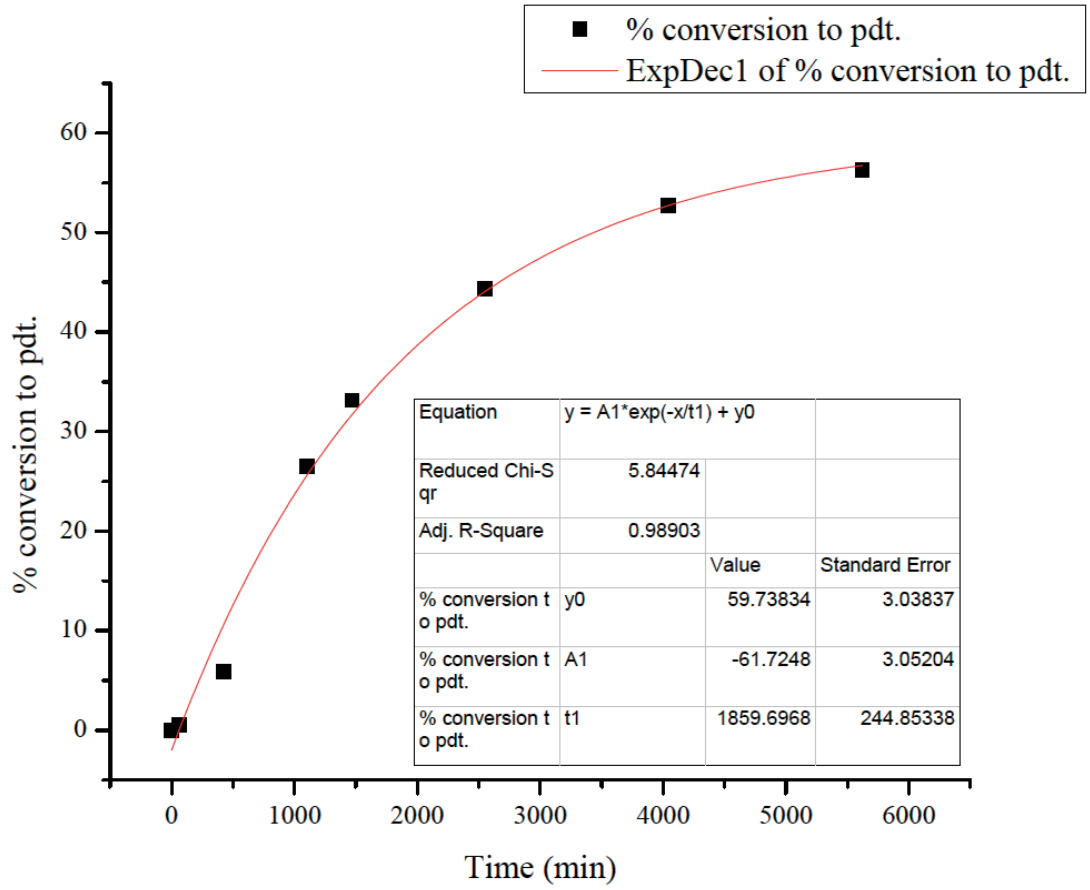
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
1276	254.0	6692.21	2912.20	131.6	38.8
2888	254.0	6891.21	4552.77	199.8	58.9
3852	254.0	6510.76	4440.45	206.2	60.8
4543	254.0	6905.02	4875.40	213.5	63.0
5702	254.0	6350.41	4321.55	205.8	60.7



Half-Life = 1969 min

Catalyst **2h**: Run 2

Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.4	1.00	0.00	0.0	0.0
60	254.4	7952.52	47.53	1.8	0.5
423	254.4	7724.03	510.09	20.0	5.9
1102	254.4	7640.90	2267.59	89.9	26.5
1468	254.4	7368.77	2733.70	112.3	33.1
2550	254.4	7712.36	3827.83	150.3	44.3
4042	254.4	9474.91	5588.37	178.6	52.7
5620	254.4	7859.00	4951.41	190.8	56.3

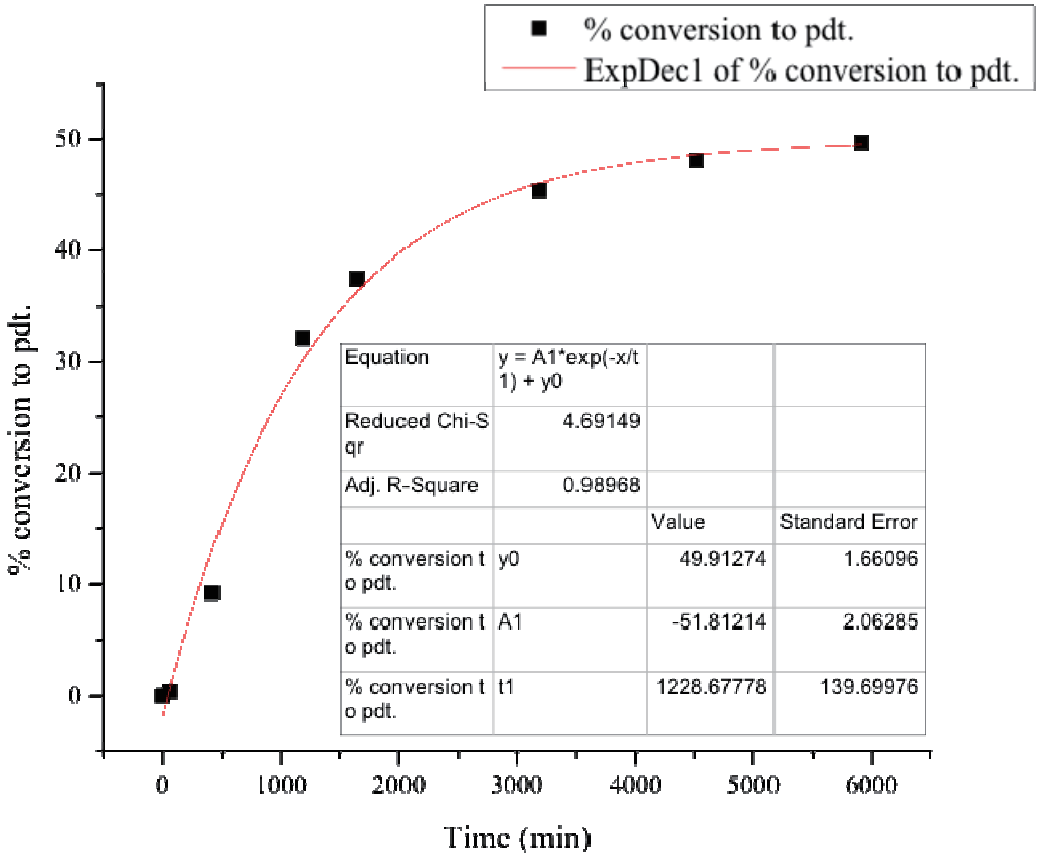


Half-Life = 3434 min

Average Half-Life = 2702 min

Catalyst **3h**: Run 1

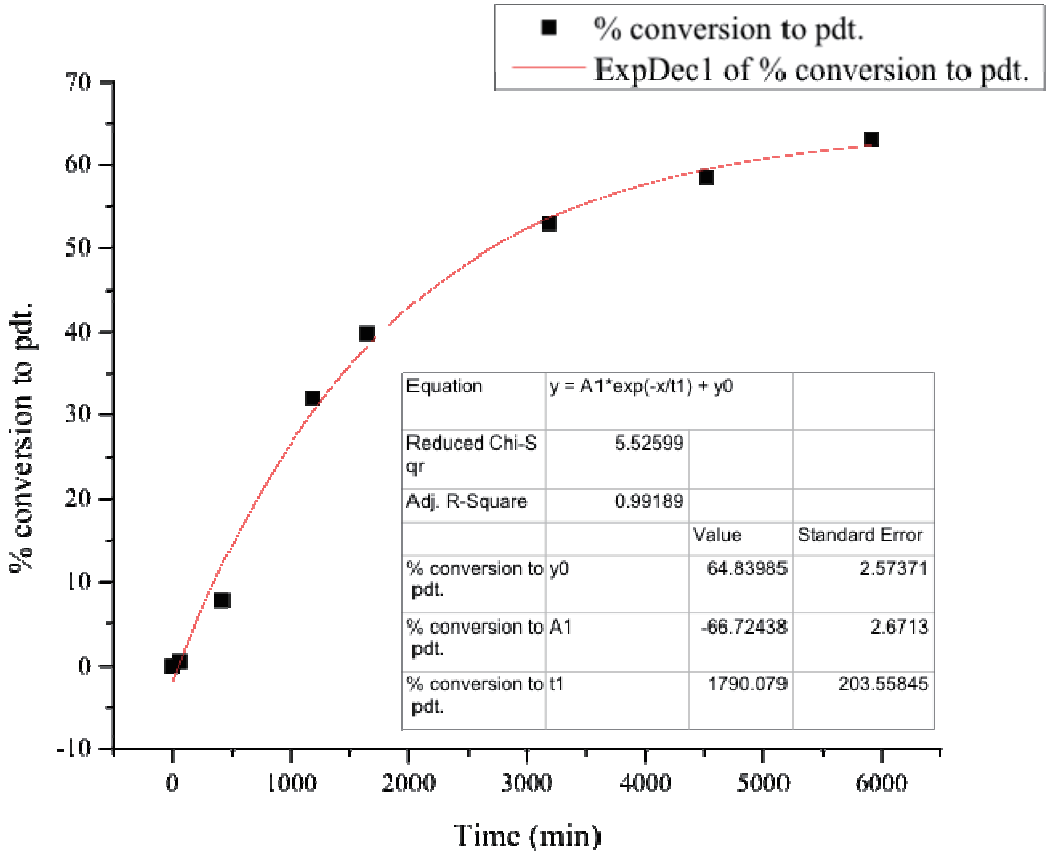
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
60	254.0	5737.46	26.01	1.4	0.4
414	254.0	6992.29	711.57	30.8	9.1
1187	254.0	6390.86	2281.63	107.9	32.1
1649	254.0	7496.73	3125.42	126.1	37.5
3188	254.0	5325.90	2687.77	152.6	45.4
4516	254.0	7979.26	4269.13	161.8	48.1
5912	254.0	7060.27	3903.97	167.2	49.7



Half-Life = 5912 min

Catalyst **3h**: Run 2

Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
60	254.0	6080.03	35.79	1.8	0.5
414	254.0	6877.12	590.05	25.9	7.7
1187	254.0	6898.09	2455.45	107.6	32.0
1649	254.0	6284.74	2781.60	133.8	39.8
3188	254.0	6769.44	3985.13	178.0	52.9
4516	254.0	6445.00	4194.09	196.8	58.5
5912	254.0	6846.86	4804.95	212.2	63.1

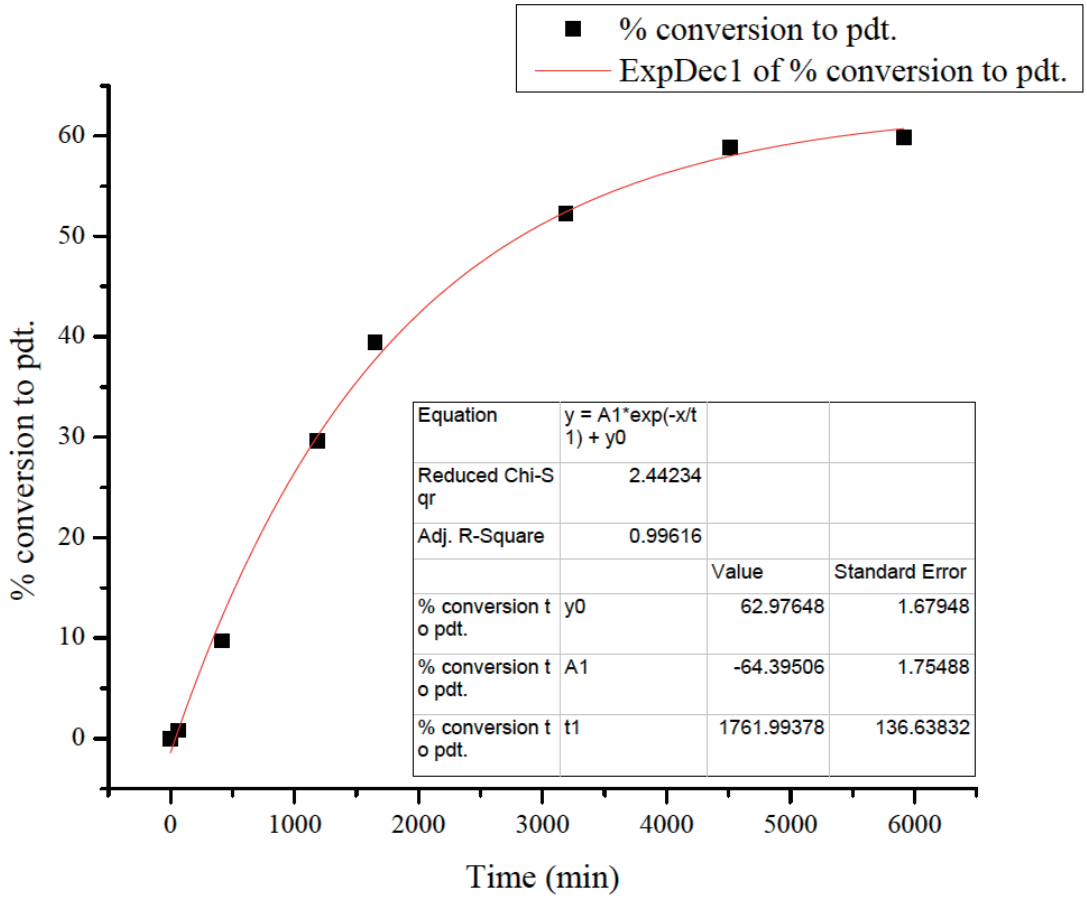


Half-Life = 2691 min

Average Half-Life = 4301

Catalyst **4h**: Run 1

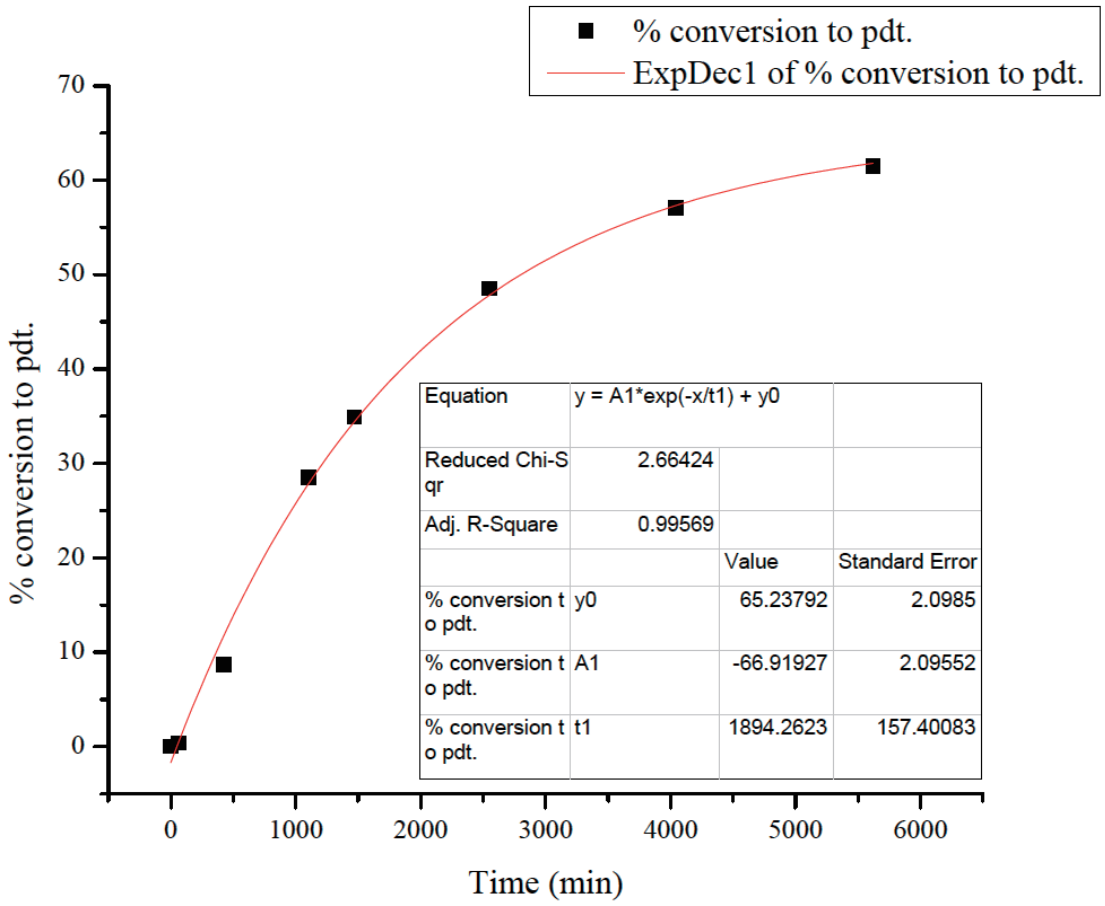
Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.0	1.00	0.00	0.0	0.0
60	254.0	6670.25	59.28	2.7	0.8
414	254.0	7258.66	790.51	32.9	9.7
1187	254.0	7639.41	2535.21	100.3	29.6
1649	254.0	6456.36	2853.02	133.6	39.4
3188	254.0	7128.59	4175.76	177.1	52.2
4516	254.0	6641.67	4380.18	199.4	58.8
5912	254.0	6893.22	4624.21	202.8	59.8



Half-Life = 2823 min

Catalyst **4h**: Run 2

Time (min)	Standard (µmol)	Standard Area	Product Area	Product (µmol)	% Product
0	254.4	1.00	0.00	0.0	0.0
60	254.4	7350.67	32.88	1.4	0.4
423	254.4	7464.41	725.62	29.4	8.7
1102	254.4	7208.55	2300.29	96.6	28.5
1468	254.4	7326.11	2862.31	118.3	34.9
2550	254.4	7321.29	3977.12	164.5	48.5
4042	254.4	9678.18	6186.04	193.6	57.1
5620	254.4	7968.50	5485.01	208.5	61.5



Half-Life = 2803 min

Average Half-Life = 2813 min

Tabular Summary of Kinetics Data

Catalyst	Run #	Fit Equation	A1	A2	x0	p	R^2	$t_{1/2}$	mean $t_{1/2}$
1a	1	y = A2 + (A1-A2)/(1+(x/x0)^p)	0.3875	71.5254	16.1312	3.7217	0.9968	20	21
1a	2	y = A2 + (A1-A2)/(1+(x/x0)^p)	0.2735	76.7689	18.7873	3.4760	0.9966	22	
2a	1	y = A2 + (A1-A2)/(1+(x/x0)^p)	1.1706	76.6484	273.9390	2.1601	0.9992	363	351
3a	1	y = A2 + (A1-A2)/(1+(x/x0)^p)	0.3986	88.1119	74.5264	2.0139	0.9981	85	82
3a	2	y = A2 + (A1-A2)/(1+(x/x0)^p)	1.3015	84.9240	66.1219	1.9978	0.9982	78	
4a	1	y = A2 + (A1-A2)/(1+(x/x0)^p)	1.2301	91.6541	40.5945	1.8218	0.9967	44	44
4a	2	y = A2 + (A1-A2)/(1+(x/x0)^p)	1.4027	85.6183	37.4651	1.9753	0.9955	44	
3b	1	y = A2 + (A1-A2)/(1+(x/x0)^p)	0.3867	76.6582	81.8218	2.4361	0.9938	106	95
3b	2	y = A2 + (A1-A2)/(1+(x/x0)^p)	0.5777	80.0775	71.7171	2.8616	0.9941	85	
5g	1	y = A2 + (A1-A2)/(1+(x/x0)^p)	0.4305	70.0148	2226.7442	2.5905	0.9988	3160	3216
5g	2	y = A2 + (A1-A2)/(1+(x/x0)^p)	0.3700	72.7524	2388.6307	2.4770	0.9991	3273	

Catalyst	Run #	Fit Equation	y0	A1	t1	R^2	$t_{1/2}$	mean $t_{1/2}$
2a	2	y = A1*exp(-x/t1) + y0	75.24479	-79.422	296.747	0.9862	340	351
5a	1	y = A1*exp(-x/t1) + y0	71.18727	-74.391	272.916	0.9920	343	310
5a	2	y = A1*exp(-x/t1) + y0	83.14673	-85.271	292.987	0.9964	277	
1b	1	y = A1*exp(-x/t1) + y0	88.03818	-94.221	22.814	0.9711	21	21
1b	2	y = A1*exp(-x/t1) + y0	82.6915	-87.724	21.243	0.9868	21	
2b	1	y = A1*exp(-x/t1) + y0	79.59908	-86.498	230.774	0.9748	247	246
2b	2	y = A1*exp(-x/t1) + y0	75.8665	-79.473	217.282	0.9808	244	
4b	1	y = A1*exp(-x/t1) + y0	76.50725	-79.456	24.419	0.9835	27	29
4b	2	y = A1*exp(-x/t1) + y0	75.42997	-77.794	27.032	0.9850	30	
5b	1	y = A1*exp(-x/t1) + y0	79.5476	-83.213	300.471	0.9911	311	312
5b	2	y = A1*exp(-x/t1) + y0	74.4181	-78.133	268.977	0.9910	313	
1c	1	y = A1*exp(-x/t1) + y0	80.07375	-80.413	126.654	0.9968	125	87
1c	2	y = A1*exp(-x/t1) + y0	78.68537	-80.469	47.630	0.9838	49	
2c	1	y = A1*exp(-x/t1) + y0	71.04348	-67.956	16.652	0.9823	20	19
2c	2	y = A1*exp(-x/t1) + y0	72.02988	-69.997	15.622	0.9921	18	
3c	1	y = A1*exp(-x/t1) + y0	77.25537	-78.110	10.146	0.9928	11	9
3c	2	y = A1*exp(-x/t1) + y0	78.46948	-78.940	8.026	0.9967	8	
4c	1	y = A1*exp(-x/t1) + y0	75.31615	-72.481	849.155	0.9954	893	851
4c	2	y = A1*exp(-x/t1) + y0	70.65912	-67.409	684.260	0.9958	809	
5c	1	y = A1*exp(-x/t1) + y0	64.56136	-67.939	358.377	0.9685	552	594
5c	2	y = A1*exp(-x/t1) + y0	64.49535	-62.989	432.714	0.9697	636	
1d	1	y = A1*exp(-x/t1) + y0	59.83595	-60.380	83.405	0.9984	151	126
1d	2	y = A1*exp(-x/t1) + y0	61.87681	-62.416	60.653	0.9991	101	
2d	1	y = A1*exp(-x/t1) + y0	79.38606	-75.780	12.491	0.9898	12	15
2d	2	y = A1*exp(-x/t1) + y0	69.29378	-65.166	15.559	0.9903	19	
3d	1	y = A1*exp(-x/t1) + y0	79.71041	-78.566	14.264	0.9882	14	11
3d	2	y = A1*exp(-x/t1) + y0	73.33839	-73.891	7.475	0.9971	9	
4d	1	y = A1*exp(-x/t1) + y0	78.9461	-77.168	11.855	0.9910	12	11
4d	2	y = A1*exp(-x/t1) + y0	72.45223	-72.272	9.375	0.9968	11	
5d	1	y = A1*exp(-x/t1) + y0	77.29513	-79.438	471.051	0.9728	503	546
5d	2	y = A1*exp(-x/t1) + y0	77.74945	-75.886	584.374	0.9872	588	
1e	1	y = A1*exp(-x/t1) + y0	73.75451	-71.259	23.046	0.9792	25	19
1e	2	y = A1*exp(-x/t1) + y0	74.9476	-76.094	12.218	0.9949	14	
2e	1	y = A1*exp(-x/t1) + y0	75.72533	-75.076	18.011	0.9910	19	16
2e	2	y = A1*exp(-x/t1) + y0	72.67163	-71.591	11.436	0.9980	13	

3e	1	y = A1*exp(-x/t1) + y0	74.91512	-73.589	47.771	0.9977	52	45
3e	2	y = A1*exp(-x/t1) + y0	72.46091	-71.959	32.328	0.9973	38	
4e	1	y = A1*exp(-x/t1) + y0	76.05616	-75.432	8.261	0.9985	9	9
4e	2	y = A1*exp(-x/t1) + y0	76.13371	-76.067	8.752	0.9908	9	
5e	1	y = A1*exp(-x/t1) + y0	72.77079	-72.061	477.722	0.9892	550	537
5e	2	y = A1*exp(-x/t1) + y0	74.53471	-76.004	463.980	0.9703	525	
1f	1	y = A1*exp(-x/t1) + y0	78.59378	-76.584	24.942	0.9944	25	19
1f	2	y = A1*exp(-x/t1) + y0	77.05268	-76.456	13.775	0.9996	14	
2f	1	y = A1*exp(-x/t1) + y0	93.94348	-91.725	52.764	0.9967	39	44
2f	2	y = A1*exp(-x/t1) + y0	80.08334	-77.153	51.499	0.9914	49	
3f	1	y = A1*exp(-x/t1) + y0	86.42536	-84.627	43.064	0.9974	36	32
3f	2	y = A1*exp(-x/t1) + y0	85.20084	-82.584	33.633	0.9899	29	
4f	1	y = A1*exp(-x/t1) + y0	74.21342	-73.046	28.311	0.9977	31	30
4f	2	y = A1*exp(-x/t1) + y0	69.60957	-69.438	22.448	0.9970	28	
5f	1	y = A1*exp(-x/t1) + y0	83.76239	-84.362	484.874	0.9887	444	442
5f	2	y = A1*exp(-x/t1) + y0	93.37255	-94.144	566.935	0.9909	439	
1g	1	y = A1*exp(-x/t1) + y0	76.72075	-78.489	2686.133	0.9958	2894	3692
1g	2	y = A1*exp(-x/t1) + y0	66.53598	-68.090	3171.727	0.9966	4489	
2g	1	y = A1*exp(-x/t1) + y0	75.84258	-77.126	188.816	0.9949	206	196
2g	2	y = A1*exp(-x/t1) + y0	74.77431	-74.129	169.135	0.9861	185	
3g	1	y = A1*exp(-x/t1) + y0	81.07378	-84.168	195.772	0.9936	195	200
3g	2	y = A1*exp(-x/t1) + y0	76.47531	-78.528	187.572	0.9950	204	
4g	1	y = A1*exp(-x/t1) + y0	61.39411	-61.994	349.177	0.9972	591	575
4g	2	y = A1*exp(-x/t1) + y0	70.21176	-70.161	448.721	0.9985	558	
1h	1	y = A1*exp(-x/t1) + y0	65.01268	-65.835	2043.954	0.9873	3021	2839
1h	2	y = A1*exp(-x/t1) + y0	71.82203	-71.654	2234.771	0.9980	2657	
2h	1	y = A1*exp(-x/t1) + y0	63.67911	-63.950	1276.679	0.9935	1969	2702
2h	2	y = A1*exp(-x/t1) + y0	59.73834	-61.725	1859.697	0.9890	3434	
3h	1	y = A1*exp(-x/t1) + y0	49.91274	-51.812	1228.678	0.9897	5912	4301
3h	2	y = A1*exp(-x/t1) + y0	64.83985	-66.724	1790.079	0.9919	2691	
4h	1	y = A1*exp(-x/t1) + y0	62.97648	-64.395	1761.994	0.9962	2823	2813
4h	2	y = A1*exp(-x/t1) + y0	65.23792	-66.919	1894.262	0.9957	2803	

References: