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Supporting Information

On the nature of organoindium intermediates: the formation of readily isolable difluoropropargyl indium reagents and their regioselectivity towards electrophilic substitutions

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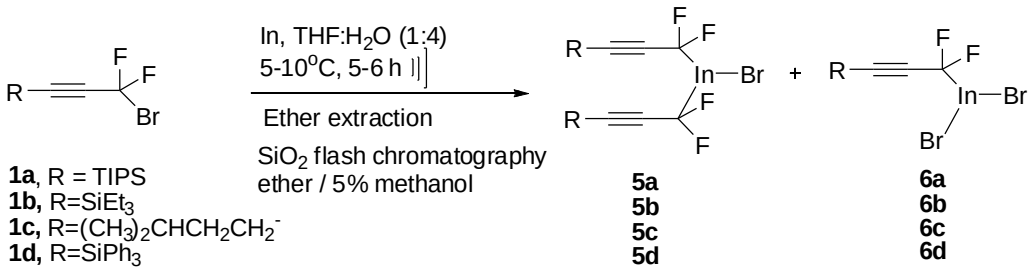
Experimental

General

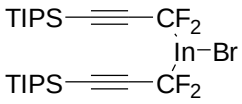
^{1}H, ^{13}C and ^{19}F NMR spectra were recorded at 500, 126 and 470 MHz respectively, using $CDCl_3$ as a solvent. The chemical shifts are reported in (ppm) values relative to $CHCl_3$ (7.26 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR) and $CFCl_3$ (0 ppm for ^{19}F NMR), multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. Coupling constants are reported in hertz (Hz). All air and/or moisture sensitive reactions were carried out under argon atmosphere. Solvents (tetrahydrofuran, ether, dichloromethane and DMF) were chemically dried using a commercial solvent purification system. All other reagents and solvents were employed without further purification. The products were purified using a Biotage flash+ system or Chromatotron apparatus or a regular glass column. TLC was developed on Merck silica gel 60 F254 aluminum sheets. Elemental analysis was performed at Atlantic Microlabs Inc., Norcross, Georgia 30091. When needed, reactions were monitored using ^{19}F NMR and the mixture percentage yield was obtained using α,α,α-trifluoromethylbenzene as internal reference.

Preparation and isolation of the indium complexes.



To a solution of (3-bromo-3,3-difluoroprop-1-ynyl)triisopropylsilane **1a** (1.55 g, 5.0 mmol) in a mixture of 2% NH_4Cl aqueous solution and THF (4:1) (35 mL) was added indium (570 mg, 5.0 mmol). This mixture was sonicated at 5-10 ^oC for 6-8h. The temperature in the ultrasound bath was adjusted by addition of ice periodically. An aliquot was analyzed in $CDCl_3$ by ^{19}F-NMR to monitor the completion of the reaction. After the starting material was consumed, the reaction mixture was extracted by ether and the organic layer was washed by brine and dried over $MgSO_4$. Then the solvent was removed in reduced pressure to almost complete dryness to give the crude indium complex. (Note: the indium complex is not stable when solvent was removed completely). Then the solution of crude indium complex in ether (5 mL) was charged into a column packed with SiO_2 (80 g) in ether, and eluted with ether (300 mL) followed by 5% methanol in ether (300 mL). DMSO (1 mL) was added to the two fractions collected, after evaporation of solvent two white solids were obtained, then they were filtered, washed with hexane, and dried in vacuum giving **5a** (750 mg, 37%) and **6a** (400 mg, 13%) as white solids.

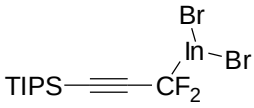
Bis(1,1-difluoro-3-(triisopropylsilyl)prop-2-ynyl)indium(III) bromide (5a)



5a

20a·3DMSO: mp 53-55 ^oC; ^1H NMR (500 MHz, $CDCl_3$) d 1.00-1.04 (m, 42 H); ^{13}C NMR (126 MHz, $CDCl_3$) d 11.3, 18.8, 92.5, 104.0 (t, *J* = 24.4 Hz), 131.0 (t, *J* = 285 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) d -88.8 (s, 2F); Anal. Calcd. for $C_{30}H_{60}BrF_4InO_3S_3Si_2$: C, 40.40; H, 6.78. Found: C, 40.59; H, 6.52.

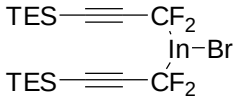
(1,1-Difluoro-3-(triisopropylsilyl)prop-2-ynyl)indium(III) bromide (6a)



6a

21a·3DMSO: mp 90-92 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) d 1.00-1.07 (m, 21 H); ^{13}C NMR (126 MHz, $CDCl_3$) d 11.3, 18.8, 93.5, 103.0 (m), 130.0 (m); ^{19}F NMR (470 MHz, $CDCl_3$) d -89.1 (s, 2F); Anal. Calcd. for $C_{18}H_{39}Br_2F_2InO_3S_3Si$: C, 29.20; H, 5.31. Found: C, 29.43; H, 5.23

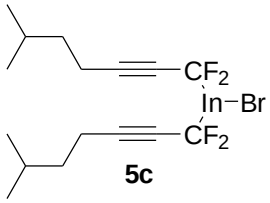
Bis(1,1-difluoro-3-(triethylsilyl)prop-2-ynyl)indium(III) bromide (5b)



5b

^{1}H NMR (500 MHz, $CDCl_3$) d 0.63 (q, *J* = 7.5 Hz, 12 H), 1.00 (t, *J* = 7.5 Hz, 18 H); ^{19}F NMR (470 MHz, $CDCl_3$) d -89.5 (s, 2F)

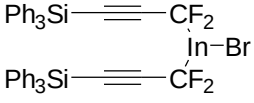
Bis(1,1-difluoro-6-methylhept-2-ynyl)indium(III) bromide (5c)



5c

^{13}C NMR (126 MHz, $CDCl_3$) *d* 17.0, 22.2, 27.1, 37.2, 78.6 (t, *J* = 25.7 Hz), 92.3, 132.2 (t, *J* = 285 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) *d* -86.9 (s, 2F)

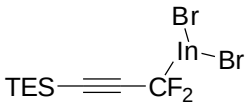
Bis(1,1-difluoro-3-(triphenyl)prop-2-ynyl)indium(III) bromide (5d)



5d

^{1}H NMR (500 MHz, $CDCl_3$) d 7.28-7.41 (m, 18 H), 7.69-7.71 (m, 12 H); ^{19}F NMR (470 MHz, $CDCl_3$) d -91.1 (s, 2F)

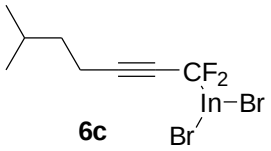
(1,1-difluoro-3-(triethylsilyl)prop-2-ynyl)indium(III) bromide (6b)



6b

^{1}H NMR (500 MHz, $CDCl_3$) d 0.62 (q, *J* = 8.0 Hz, 6 H), 0.99 (t, *J* = 8.0 Hz, 9 H); ^{19}F NMR (470 MHz, $CDCl_3$) d -89.8 (s, 2F)

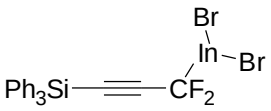
(1,1-difluoro-6-methylhept-2-ynyl)indium(III) bromide (6c)



6c

^{1}H NMR (500 MHz, $CDCl_3$) d 0.83 (d, *J* = 6.5 Hz, 6H), 1.39-1.42 (m, 2H), 1.60-1.68 (m, 1H), 2.26-2.28 (m, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) d -89.1 (s, 2F);

(1,1-difluoro-3-(triphenyl)prop-2-ynyl)indium(III) bromide (6d)



6d

^{1}H NMR (500 MHz, $CDCl_3$) d 7.28-7.41 (m, 9 H), 7.69-7.71 (m, 6H); ^{19}F NMR (470 MHz, $CDCl_3$) d -91.1 (s, 2F)

Table 1. Physical properties of isolated indium complexes.

Entry	Complexes	Mp ^{o}C	^{19}F-NMR ppm	? $_{max}$ nm	? $_{max}$ $dm^3mol^{-1}cm^{-1}$
1	**5a**	53-55	-88.8	284	6097
2	**5b**	67-69	-89.5	nd	nd
3	**5c**	nd[a]	-86.9	nd	nd
4	**5d**	136-138	-91.1	254, 290	5569, 3166
5	**6a**	90-92	-89.1	254, 290	4429, 2537
6	**6b**	72-75	-89.8	nd	nd
7	**6c**	nd[a]	-89.1	nd	nd
8	**6d**	120-123	-91.1	254, 290	1603, 993

[a] not determined because it is not solid at room temperature.

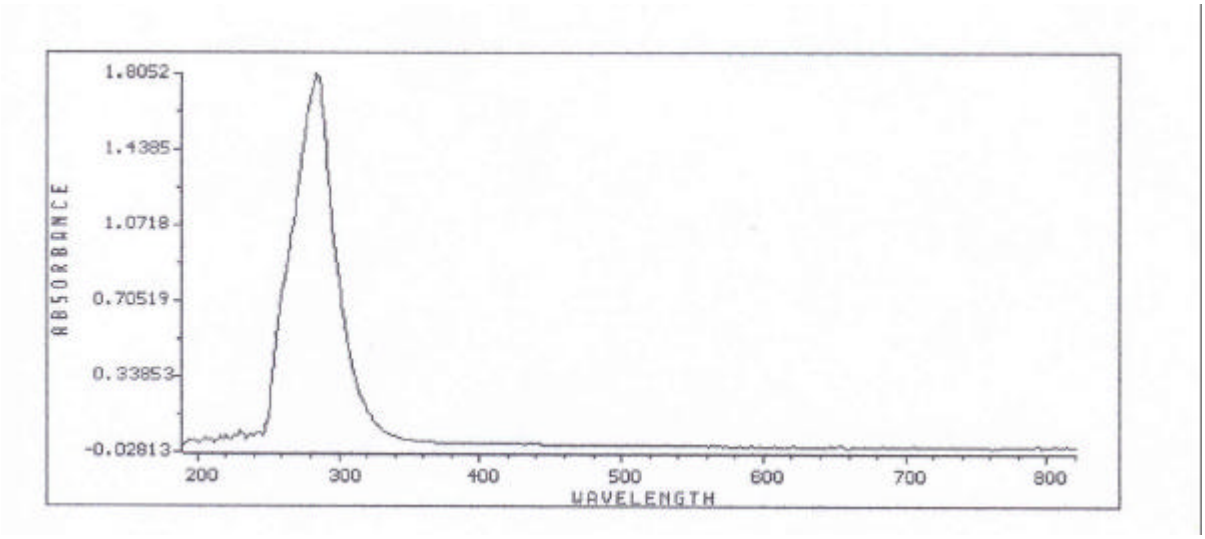


Figure 1. UV-Vis spectrum of **5a**.

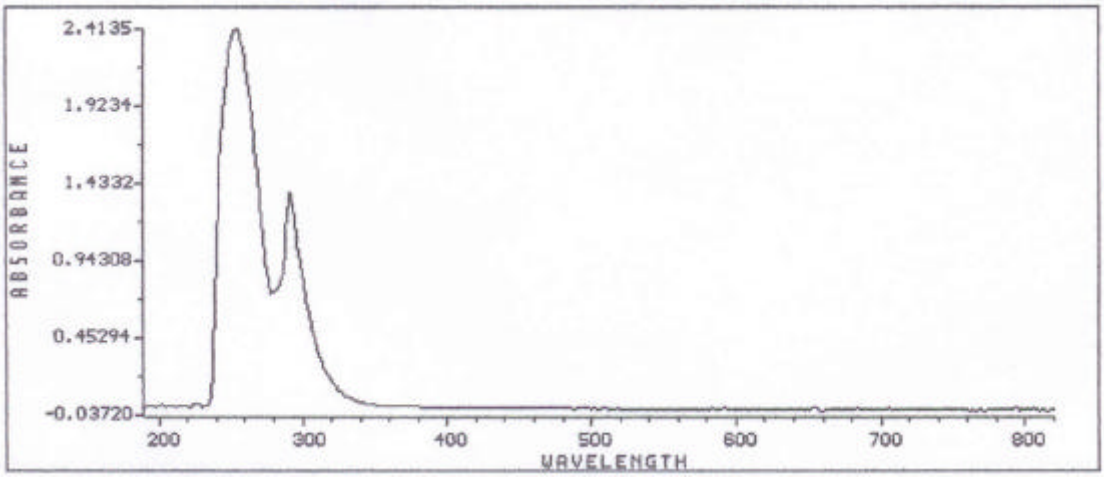


Figure 2. UV-Vis spectrum of **5d**.

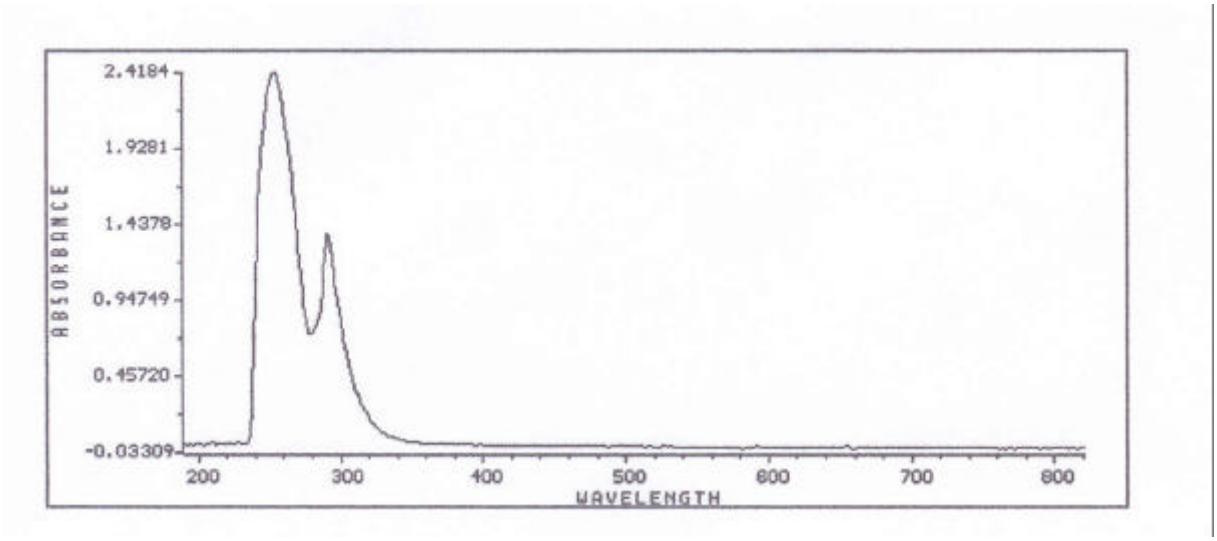


Figure 3. UV-Vis spectrum of **6a**.

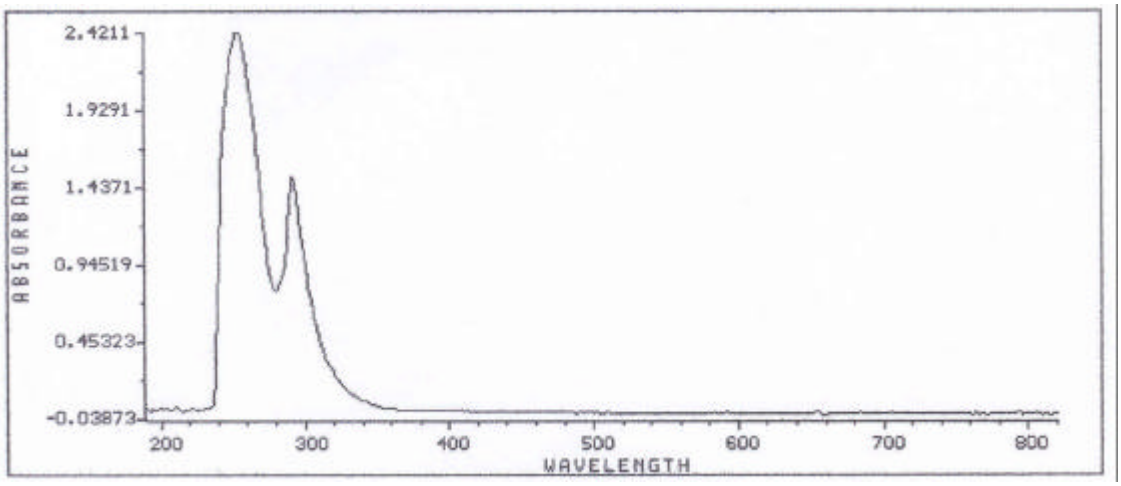
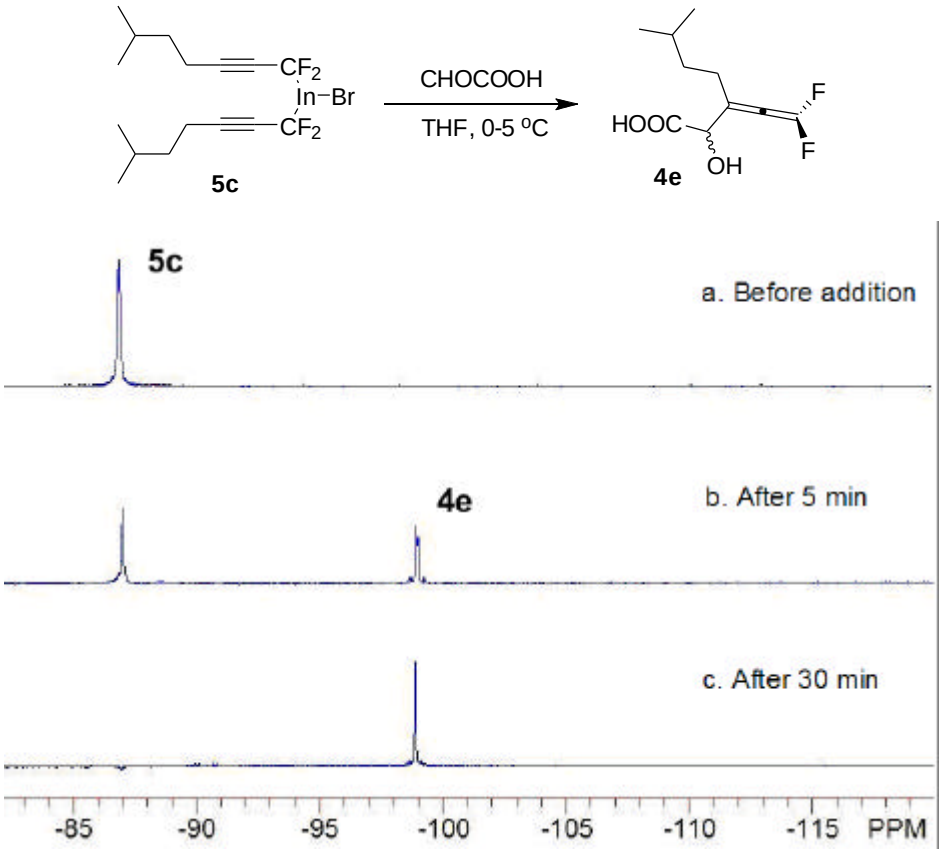


Figure 4. UV-Vis spectrum of **6d**.

General procedure for monitoring of reaction by ^{19}F NMR

The reaction was conducted in a NMR tube with screw cap, before reaction, the NMR tube was flushed with argon; a sealed capillary filled with d^6-benzene was used to facilitate lock and shimming when non-deuterated solvent was used. Variable temperature control (Varian Inova 500) was used to control temperature of reaction during ^{19}F NMR experiment.

Figure 5. Reaction of **5c** with CHOCOOH at RT monitored by ^{19}F-NMR.



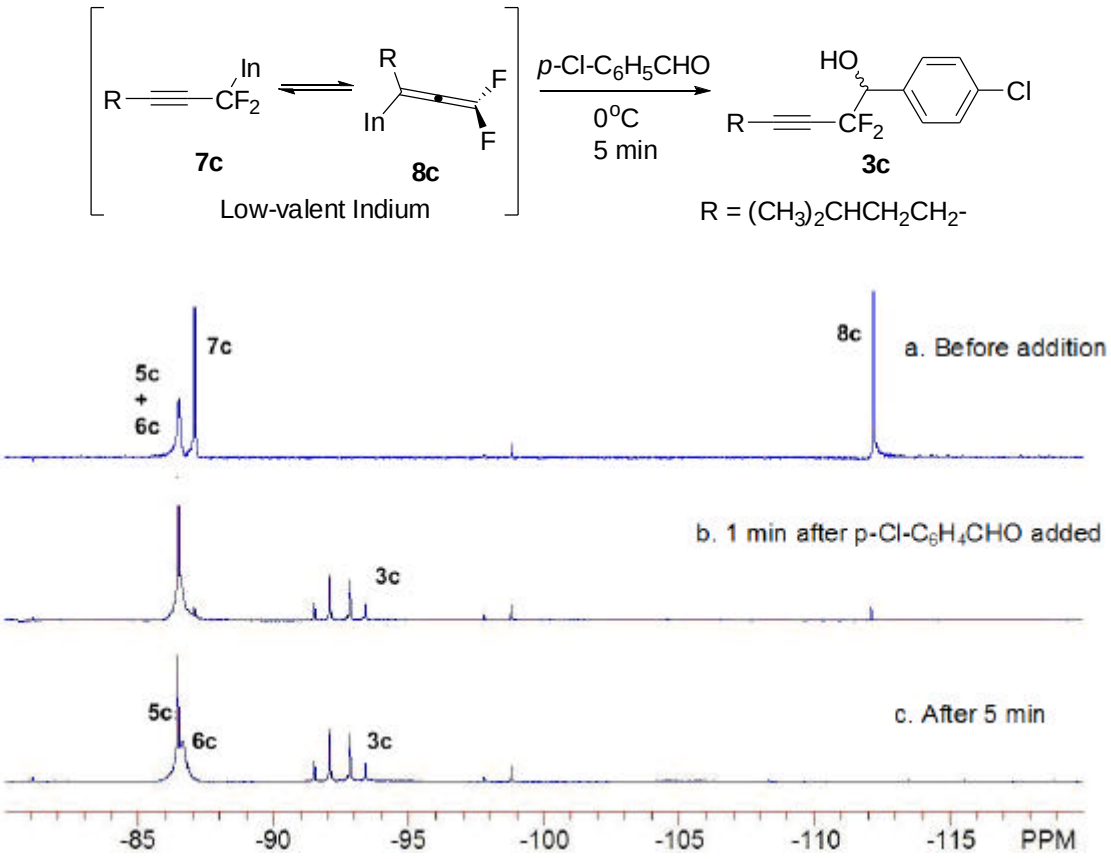


Figure 6. Reactivity of low valence indium species.

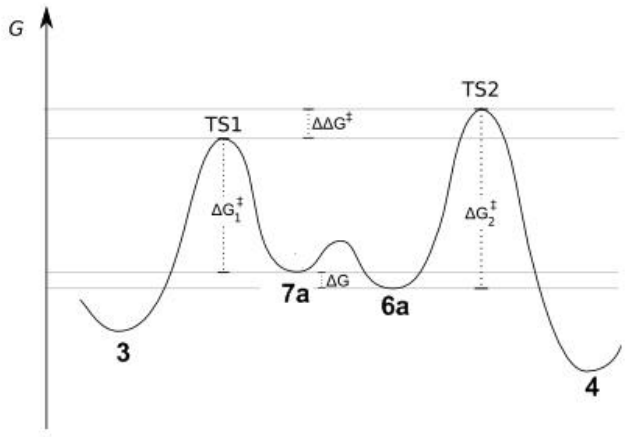


Figure 7. Potential energy diagram for reaction of **6a** with weak electrophiles.

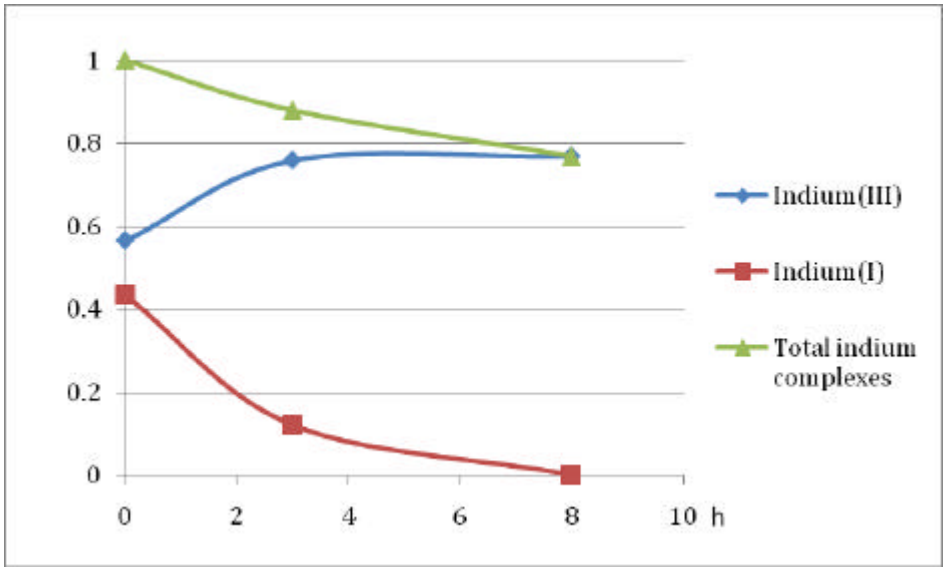


Figure 8. Increase of indium (III) complex intensity (repeated experiment).