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VII *. STUDY ON HPLC OF BIS- AND MONO-(SUBSTITUTED CYCLOPENTADIENYL)TITANIUM DERIVATIVES

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Summary

The high-performance liquid chromatographic behavior of 56 bis- and mono-(substituted cyclopentadienyl)titanium dichlorides was investigated. According to their capacity factors (K') and separation efficiencies (N), the relationship between chromatographic behavior and structure of titanium complexes was discussed.

Introduction

The low valent titanium catalytic systems consisting of Cp_2TiCl_2 and a reducing agent has attracted increasing attention during recent years because of their effective catalytic activity in a series of reactions. Recently we and Nakamura et al. have used Cp_2TiCl_2 or Cp'_2TiCl_2 ***/i-C_3H_7MgBr systems for isomerization of some unconjugated dienes, such as 1,4-pentadiene [1], 1,5-hexadiene [1–3], 1,7-octadiene [1], 1,5-cyclooctadiene [4] and 4-vinylcyclohexene [5], and hydrogenation of 1,5-cyclooctadiene [6]. We have found that introduction of a substituent into the cyclopentadienyl ring sometimes leads to a large change in catalytic activity and selectivity [3,6]. For example, catalytic isomerization of 1,5-hexadiene strongly depends on the nature of the substituent on the cyclopentadienyl ring. Some alkenyl

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*** $Cp = \eta^5$-C_5H_5; Cp′ = substituted cyclopentadienyl group.

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groups, such as allyl or substituted allyl were favorable to the formation of linear conjugated isomers with about 95% yield. In contrast to the allyl group, an alkoxyethyl group, such as methoxyethyl, leads to cyclization with a yield as high as 90%. In order to understand the effect of substitution on the whole steric bulk and the electronic effect of titanocene complexes, we have carried out research on relationship between chromatographic behavior and structure of a substituent on the Cp ring.

HPLC analysis of organometallic compounds was first reported in 1969 [7]. Normal-phase and reversed-phase HPLC have been extensively used in the analysis of Fe-, Ni-, Co-, Cr- and Mo-containing organometallic compounds [8,9]. However, only a few papers on HPLC separation of organotitanium compounds have appeared in the literature [10,11]. Recently paper-chromatographic analysis of substituted titanocene dichloride has been reported [12]. Here we report the results of normal-phase HPLC of 56 bis- and mono-(substituted cyclopentadienyl)titanium dichlorides, $(R{-}Cp)_2TiCl_2$ and $(R{-}Cp)CpTiCl_2$ (R = alkyl and alkenyl group).

Experimental

All substituted titanocene derivatives were prepared by ourselves [13,14]. A microprocessor-controlled liquid chromatograph, model SY 5000 (Beijing Analytical Instrument Factory, China), was used. The instrument was equipped with 3 solvent flasks, a pump system, UV-100 variable wavelength detector and 3390-A reporting intergrator, and fitted with a Varian micropak analytical column CN-10 (4.0 i.d. × 6.35 o.d. × 300 mm length, particle size: 10 μm). All solvents were HPLC grade and dried by 5Å molecular sieves. All samples were first dissolved in chloroform with a content 20–30 ng/μl. All chromatograms were obtained at a flow rate of 1.5 ml/min, at 25°C. UV detection was at 254 nm. Void time (t_0) was determined with benzene as solvent. The retention volume (V_R) of each compound was obtained by multiplying the compound retention time (t_R) by the flow-rate. Column void volume (V_0) was determined as the retention volume of the solvent employed, i.e. benzene. The capacity factor (K') for all the compounds was calculated from $K' = (V_R - V_0)/V_0$, where V_R is the apparent compound retention volume and V_0 is as defined above. Column efficiency (N) was determined using $N = 16\,(t_R/t_w)^2$, where t_R is the compound retention time and t_w is the peak width at half peak height. Resolution (R) of adjacent peaks was obtained by dividing the distance between peak centers by the average peak width; $R = 2(t_2 - t_1)/(t_{w1} + t_{w2})$.

Results and discussion

The chromatographic behavior of the 56 titanium complexes was investigated and their retention volumes (V_R), capacity factors (K') and separation efficiencies (N) are listed in Table 1. From these results, the following points can be summarized:

(1) As shown in Fig. 1, when a mixture of n-hexane and methylene chloride was used as the mobile phase (or eluent), log K' values decreased linearly with decrease in the number of C atoms in the substituent on the Cp ring. The use of polar solvents, however, led to smaller K' values.

(2) The order of polarity of the substituted titanocene dichloride is dependent on the number of C atoms in the substituent on the Cp ring and is as follows: Cp_2TiCl_2 > $(CH_3Cp)_2TiCl_2$ > $(C_2H_5Cp)_2TiCl_2$ > (n-$C_3H_7Cp)_2TiCl_2$ > (n-$C_4H_9Cp)_2TiCl_2$ > (n-$C_5H_{11}Cp)_2TiCl_2$. This was not surprising since the electron donating ability of alkyl group decreased the polarity between the cyclopentadienyl group and the titanium atom, and the larger the alkyl group, the stronger is the electron donating ability.

(3) Due to asymmetry in the molecule, log K' of (R–Cp)$CpTiCl_2$ was greater than that of (R–Cp)$_2TiCl_2$ (lines 1 and 5 in Fig. 1).

(4) In the case of substituents with the same number of C atoms, the steric effect of a bulky group may lead to an increase in retention volume, for example, the following order of K' (**10–12, 14** in Table 1) was found: Et–C(Me_2)–Cp ∼ cyclo-C_5H_9Cp > n-$C_5H_{11}Cp$ ∼ i-$C_5H_{11}Cp$.

(5) K' for (allylCp)$_2TiCl_2$ was apparently higher than that for (n-$C_3H_7Cp)_2TiCl_2$, but K' for (substituted allyl Cp)$_2TiCl_2$ and (allyl alkyl Cp)$_2TiCl_2$ were exclusively lower than that for (allylCp)$_2TiCl_2$ (**15–23** in Table 1, Fig. 2 and Fig. 3).

(6) For the [H_2C=C(R)Cp]$_2TiCl_2$ series of complexes, log K' was proportional to the number of C atoms in R (**24–29** in Table 1, Fig. 4 and 5).

(7) For the [H_2C=$CHCH_2$C(Me)(R)Cp]$_2TiCl_2$ series of complexes, there was a similar trend, that is, log K' decreased with decrease in the number of C atoms in R. Due to asymmetry, the retention volume for all the monosubstituted samples was higher than that for bis-substituted samples (**45–56** in Table 1, Fig. 4, 6 and Fig. 7).

(8) In the case of [n-C_4H_9-C(R_1)(R_2)Cp]$_2TiCl_2$, the retention volume probably depends on both electron donating ability and on the steric effect of R_1 and R_2 (**30–33** in Table 1).

(9) For the bridged titanocene complexes (**34** and **35** in Table 1), the K' value for the sample where $n = 1$ was higher than that for sample where $n = 2$.

(10) In the case of [Ph-C(R_1)(R_2)Cp]$_2TiCl_2$, the main factor of influence was the electron donating ability of R_1 and R_2 (**36–38** in Table 1 and Fig. 8).

(*Continued on p. 35*)

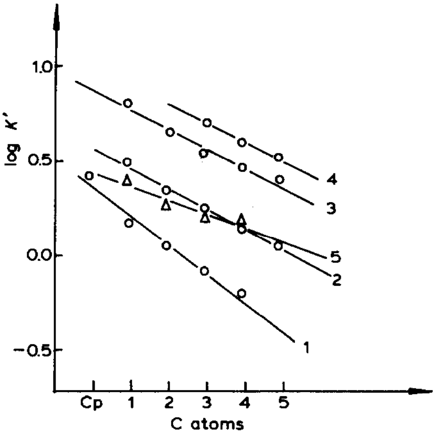


Fig. 1. The dependence of log K' on the number of C atoms in R on the Cp ring. Lines 1–4: (R–Cp)$_2TiCl_2$; line 5: (R–Cp)$CpTiCl_2$. Line 1: n-hexane: methylene chloride = 70:30. Line 2: n-hexane: methylene chloride = 80:20. Line 3: n-hexane: methylene chloride = 85:15. Line 4: n-hexane: methylene chloride = 90:10. Line 5: n-hexane: methylene chloride = 70:30.

$(R{-}Cp)_2TiCl_2$ and $(R{-}Cp)CpTiCl_2$

Cp_2TiCl_2
(1)

$(CH_3Cp)CpTiCl_2$
(2)

$(C_2H_5Cp)CpTiCl_2$
(3)

$(n{-}C_3H_7Cp)CpTiCl_2$
(4)

$(n{-}C_4H_9Cp)CpTiCl_2$
(5)

$(CH_3Cp)_2TiCl_2$
(6)

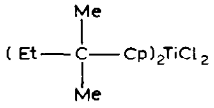
$(C_2H_5Cp)_2TiCl_2$
(7)

$(n{-}C_3H_7Cp)_2TiCl_2$
(8)

$(n{-}C_4H_9Cp)_2TiCl_2$
(9)

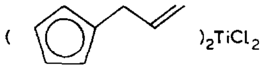
$(n{-}C_5H_{11}Cp)_2TiCl_2$
(10)

$(i{-}C_5H_{11}Cp)_2TiCl_2$
(11)


(12)

$(Me_5Cp)_2TiCl_2$
(13)

$(cyclo{-}C_5H_9Cp)_2TiCl_2$
(14)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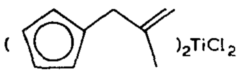
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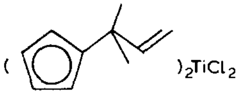
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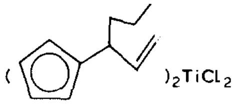
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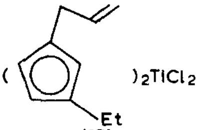
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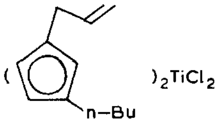
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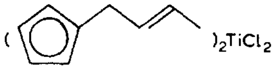
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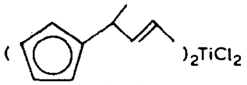
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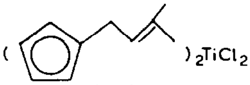
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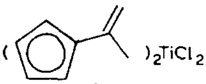
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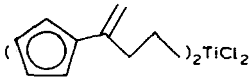
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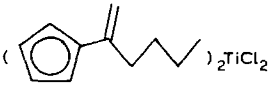
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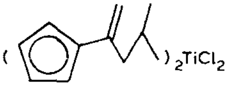
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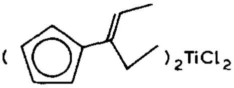
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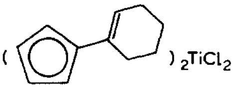
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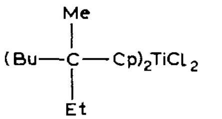
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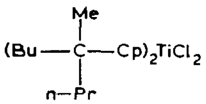
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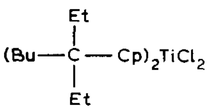
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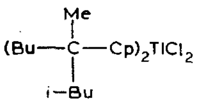
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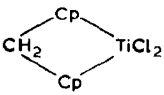
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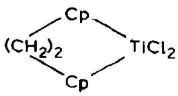
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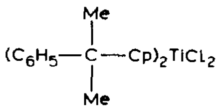
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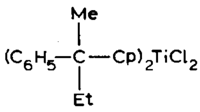

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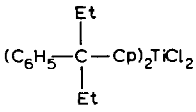

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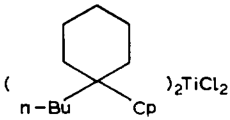

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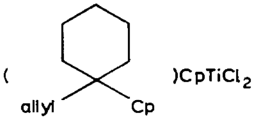

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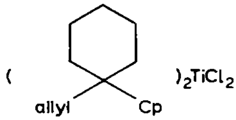

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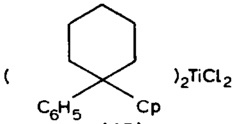

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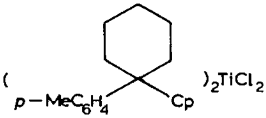

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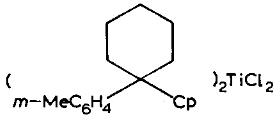

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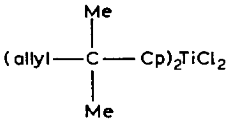

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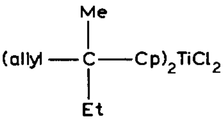

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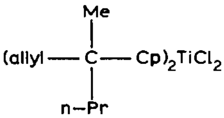

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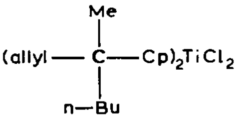

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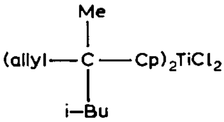

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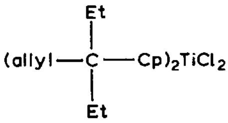

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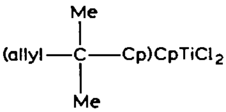

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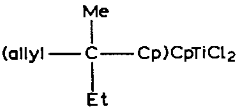

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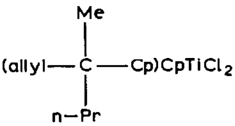

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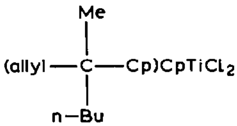

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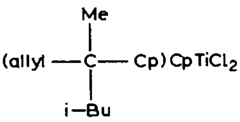

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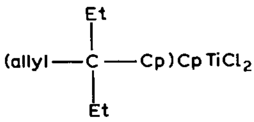

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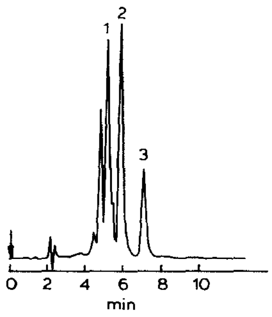

Fig. 2. Chromatogram of (substituted allylCp)$_2$TiCl$_2$. Peak 1: compound **18**. Peak 2: compound **17**. Peak 3: compound **15**.

TABLE 1

CHROMATOGRAPHIC PARAMETERS FOR COMPOUNDS **1–56** [a]

Compound	V_R (ml)	K'	N
1 [b]	10.98	2.73	
2 [b]	10.28	2.49	
3 [b]	8.24	1.80	
4 [b]	7.76	1.64	
5 [b]	7.29	1.48	
6	12.62	3.10	
7	9.81	2.19	
8	8.28	1.69	
9	7.32	1.38	
10	6.56	1.13	
11	6.41	1.08	
12	7.76	1.52	
13	6.47	1.10	
14	7.71	1.51	
15	10.22	2.32	14400
16	8.82	1.87	12500
17	8.40	1.70	10000
18	7.20	1.34	6400
19	6.09	0.98	7500
20	5.67	0.84	7000
21 [c]	8.45	1.75	11600
	9.06	1.95	
22	7.02	1.28	6400
23	8.27	1.69	10800
24	9.86	2.20	14400
25	8.67	1.82	14500
26	7.80	1.54	7300
27	7.74	1.52	10000
28	9.60	2.12	11600
29	8.81	1.86	10800
30	5.37	0.75	7000
31	5.81	0.89	10000
32	6.59	1.14	8400
33	7.02	1.28	10800
34	16.74	4.44	
35	10.62	2.45	
36	10.14	2.30	
37	8.60	1.80	

TABLE 1 (continued)

Compound	V_R (ml)	K'	N
38	7.25	1.36	
39	6.38	1.07	
40	14.20	3.62	
41	6.65	1.16	
42	8.04	1.61	
43	7.65	1.48	
44	7.28	1.37	
45	7.65	1.49	11600
46	6.91	1.25	10800
47	6.23	1.02	10500
48	5.70	0.85	9200
49	5.64	0.83	9200
50	6.39	1.08	8000
51	14.94	3.86	14000
52	14.31	3.65	13000
53	13.85	3.50	14400
54	13.28	3.32	12500
55	13.08	3.25	12500
56	13.62	3.43	14400

[a] n-Hexane: methylene chloride = 80:20 as mobile phase. [b] n-Hexane: methylene chloride = 70:30 as mobile phase. [c] Mixture of *cis*- and *trans*-isomers.

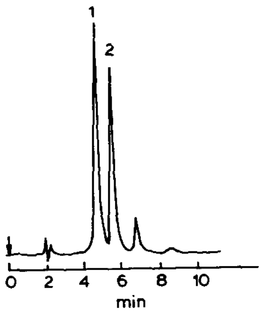

Fig. 3. Chromatogram of (substituted allylCp)$_2$TiCl$_2$. Peak 1: compound **22**. Peak 2: compound **23**.

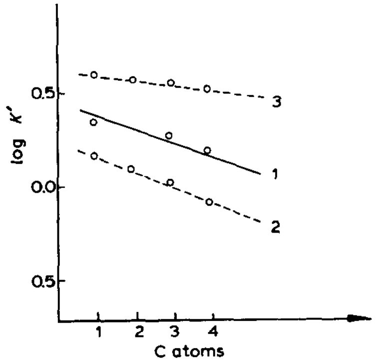

Fig. 4. The dependence of log K' on the number of C atoms in R on the Cp ring. Line 1: [H_2C=C(R)Cp]$_2$TiCl$_2$. Line 2: [allyl–C(Me)(R)Cp]$_2$TiCl$_2$. Line 3: [allyl–C(Me)(R)Cp]CpTiCl$_2$.

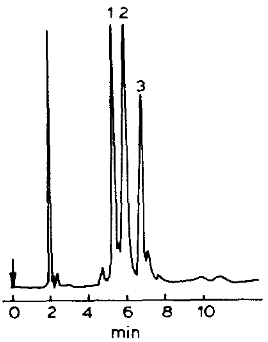

Fig. 5. Chromatogram of $[H_2C{=}C(R)Cp]_2TiCl_2$. Peak 1: compound **27** ($R = i\text{-}C_4H_9$). Peak 2: compound **25** ($R = n\text{-}C_3H_7$). Peak 3: compound **24** ($R = CH_3$).

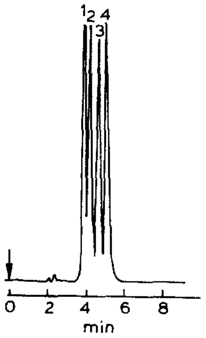

Fig. 6. Chromatogram of $[allyl\text{-}C(Me)(R)Cp]_2TiCl_2$. Peak 1: compound **48** ($R = n\text{-}C_4H_9$). Peak 2: compound **47** ($R = n\text{-}C_3H_7$). Peak 3: compound **46** (R = Et). Peak 4: compound **45** (R = Me).

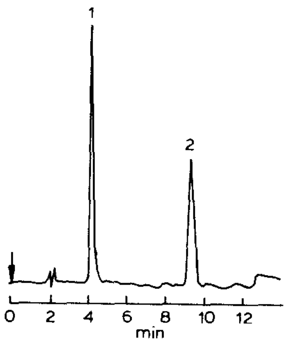

Fig. 7. Chromatogram of compound **47** and **53**. Peak 1: compound **47**. Peak 2: compound **53**.

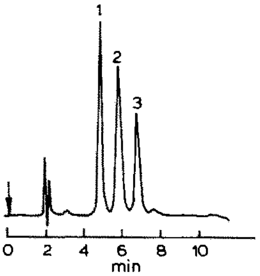

Fig. 8. Chromatogram of $[Ph-C(R_1)(R_2)Cp]_2TiCl_2$. Peak 1: compound **38** ($R_1 = R_2 = Et$). Peak 2: compound **37** ($R_1 = Me$; $R_2 = Et$). Peak 3: compound **36** ($R_1 = R_2 = Me$).

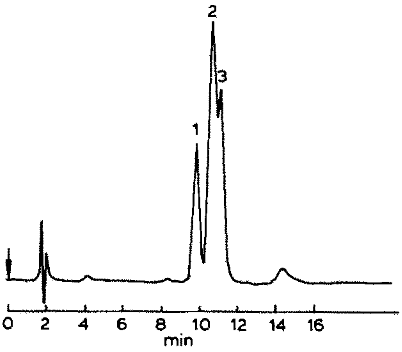

Fig. 9. Chromatogram of compounds **42–44**. n-Hexane: methylene chloride = 90:10. Peak 1: compound **44**. Peak 2: compound **43**. Peak 3: compound **42**.

(11) For the [R-substituted cyclohexyl $Cp]_2TiCl_2$ series of complexes (**39–44**), the K' value depends on the substituent R, and gives the following order for K': Ph > *p*-Ph > *m*-Ph > allyl > n-Bu. For compounds **42–44** in Table 1, a mixture of n-hexane and methylene chloride (9:1) was used as the mobile phase and $R_s = 2$ for *p*- and *m*-$CH_3C_6H_4$-substituted samples and $R_s = 0.9$ for C_6H_5- and *p*-$CH_3C_6H_5$-substituted samples (Fig. 9).

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