Chemical Communications

Supporting Information

Enhanced Reactivity and Selectivity of Asymmetric oxa-Michael addition of 2'-Hydroxychalcone in Carbon Confined Space

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1. Experimental section:

Characterization Techniques: Transmission electron microscopy (TEM) studies of the particles were carried out at an accelerated voltage of 197 kV using a Philips CM200 TEM equipped with a LaB₆ source. The X-ray diffraction (XRD) patterns were recorded on a Shimadzu XD-3A X-ray diffractometer operating at 20 kV using Cu K α radiation (λ = 0.1542) nm) for CNTs and its composites. For ferrites, Cr K α radiation (λ = 0.2 nm) radiation source was used. X-ray photoelectron spectroscopic analysis (XPS) was performed using an ESCALAB250 instrument by Thermo VG Scientific. Unless stated otherwise, monochromatic Al K_a-radiation was used (15kV, 150W, ~500 μ m spot diameter) with the transmission function of the analyzer having been calibrated using a standard copper sample; when necessary, charge compensation was achieved using a "Flood-Gun" (~6eV/ 0.05mA). Spectra were recorded with pass energy of 80 eV for survey spectra, and 30 eV for core level spectra. For non-magnetic samples, a magnetic lens was used to enhance the signal/noise ratio. Infrared spectra were recorded on a Varian Associated FT-IR 3100 Excalibur with ATR unit. The wave numbers (n) of recorded IR-signals are quoted in cm⁻¹. Enantiomeric excess (ee) was determined using HPLC, Shimadzu with UV-detector using chiralcel AD-H column with flow rate of 1.2 mL/min and 5% isopropanal: hexane system. The ACME silica gel (100-200 mesh) was used for column chromatography and thin layer chromatography was performed on Merck precoated silica gel 60-F₂₅₄ plates.

2. Synthesis of MNPs (Fe₃O₄): The MNPs were prepased by the so called wet-impregnation method as reported in literature. The ultra-fine MNPs were prepared by co-precipitating aqueous solutions of ferrous ammonium sulphate $(NH_4)_2Fe(SO_4)_2$ $6H_2O$ and ferric chloride (FeCl₃) mixture, respectively, in alkaline medium. Ferrous ammonium sulphate 0.98g (2.5 mmol) was added to 0.81 g (5 mmol) of ferric chloride in 200 mL of water (*i.e.*, stoichiometry ratio Fe²⁺:Fe³⁺= 1: 2) and the resultant mixture was kept at 80 °C for 30 min

under inert atmosphere. To this solution, 0.02N NH₄OH was added drop by drop till the complete precipitation occurs under constant stirring. Magnetite formed by conversion of metal chloride into hydroxides (which takes place immediately), and hydroxides into ferrites. The resultant solution was maintained at 80 °C for another 2h. Then the brown colour precipitate, obtained is washed several times with distilled water. The precipitate is then separated with the help of external magnet and is kept for drying at 80 °C. Finally thus prepared MNPs were calcinated at 400°C for 2h to get free flowing powder.

2.1. Synthesis of CPA (L1) modified MNPs (Chiral Solid):

In a typical experiment, magnetite (0.1 g) was added into the round bottom flask containing toluene (3.0 mL) and (*R*)-(–)-1,1'-Binaphthyl-2,2'-diyl hydrogen phosphate (0.02 mmol, 7.0 mg) was sonicated for 1 h at 80 °C. Then chiral magnetite nanoparticles (MNP/L1) collected via magnetic decantination was directly used in asymmetric cyclization of 2'-hydroxychalcone. Various concentrations of L1 (5, 7.5, 10, 15 mol % of L 1) on MNPs were prepared. Similarly MNP/L2 was synthesized using L2 ligand.

2.2 Synthesis of CNPs (CoFe₂O₄):

Cobalt ferrite nanoparticles were synthesized similar to that of MNPs, using cobalt chloride 0.59g (2.5 mmol) (CoCl₂ $6H_2O$) instead of ferrous ammonium sulphate. The samples were designated as CNP/L1 with ligand L1 and CNP/L2 with ligand L2 respectively.

2.3 Preparation of MNP-L1-CNT (inside the CNT channel):

The pristine CNTs, present a specific surface area 40m²/g, a mesoporous volume of 0.15 cm³/g, a mean pore diameter of 14 nm, an average external diameter of 60 nm and internal diameter of 40 nm were purchased from UNITECH, Bangalore. Pure CNTs (250 mg) (CNT) were dispersed in xylene (10.0 mL) and ultra sonicated for 30 min at room temperature. To the resultant suspension, MNP/L1 (30 mg, dispersed in 15.0 mL of xylene) were added and

further sonicated for 6 h. Then the suspension was washed several times thoroughly with ethanol (20 mL) and finally with water till the neutral pH is attained and dried at 50 °C overnight to get the functionalized CNTs (M/CNT-L1). Similarly M/CNT-L2 and (C/CNT-L1; C/CNT-L2) were prepared.

2.4 Preparation of MNP/L1-CNT (out) Catalyst:

Pure CNTs (5.0 g) were dispersed in a solution of conc. HNO₃ (4.0 mL) and conc. H₂SO₄ (16.0 mL). The suspension was ultra sonicated for 3 h at room temperature. Later pure water (100 mL) was added and further sonicated for 10 min. Then the suspension was washed several times thoroughly with water till the neutral pH is attained and dried at 50 °C overnight to get the –COOH functionalized CNTs. (**z**. Wang, M. D. Shirley, S. T. Meikle, R. L. D. Whitby, S. V. Mikhalovsky, *Carbon*, 2009, 47, 73-79. And B. Scheibe, E. B.- Palen, R. J. Kalenczuk, *J. Mat. Char*, 2010, 61, 185-191.) Thus prepared acid functionalized CNTs (360 mg) were dispersed in 200 ml DMF-water mixture [DMF/water: 20/80 (v/v)]. To this dispersed solution, MNP-L1 (50.0 mg) in toluene (3.0 mL of H₂O) were added slowly and sonicated for further 12 h. The resultant mixture was washed thoroughly with water, followed by methanol and dried at 80 °C for 24 h to get the magnetite functionalized CNTs.

2.5 Asymmetric cyclization of 2'-hydroxychalcone to flavanone:

In an oven dried flask, 2'-hydroxychalcone (0.5 mmol) were stirred in chlorobenzene (3.0 mL) containing a catalyst (20.0 mg) to give a yellow color suspension. The temperature increased to 100 °C and further allowed to stir for the required time. After completion of the reaction, (monitored by TLC), the catalyst was removed with the help of external magnet and washed with ethanol (2 X 10 mL). Later, the reaction mixture was quenched with addition of (1.0 mL) 0.1 N HCl followed by EtOAC. After evaporation of the organic phase, the residue was purified by column chromatography (Hexane: EtOAC, 9:1 as eluent) to give colorless crystals.

3. Characterization of the catalyst

3.1. XPS of MNP-L1/CNT (inside)



Fig. S1. XPS surface scan survey of catalyst

3.2 . FT-IR of MNP/L1-CNT (inside)



Fig. S2. (a) As received CNT (b) M/CNT/L1 (c) C/CNT-L1

4. Mass spectra of Fe-CPA

(a)



Fig. S3. Mass spectra of Fe²⁺-CPA



Fig. S4. Mass spectra of Fe²⁺-CPA

5. Recycling of the catalyst



Fig. S5. Recycling of M-L1/CNT (inside) in the asymmetric cyclization of 2'hydroxychalcones



6. Effect of the chiral ligand

Fig. S6. Effect of the ligand concentration in reactivity and selectivity for asymmetric cyclization (A) inside of the CNT channel and (B) outside of the CNT surface [HPLC data for MNP-LI inside CNT channel (Fig. S20-S24) and outside of the CNT surface (Fig. S30-S34).

entry	catalyst	solvent	temp (°C)	Yield (%)
1	MNPs	Ethanol	100	10
2	MNPs	Methanol	100	10<
3	MNPs	toluene	100	N.R
4	MNPs	DMF	100	80
5	MNPs	Dichlomethane	60	16
6	MNPs	Chlorobenzene	100	92
7	MNPs	Chlorobenzene	80	85
8	MNPs	Chlorobenzene	60	75
9	MNPs	DMF	100	60
10	CNT	DMF	100	<10
11	CNT	Chlorobenzene	100	N.R
12	CNPs	Chlorobenzene	100	63
13	CNPS	Chlorobenzene	80	38

7. Table S1. Optimization conditions cyclization of 2'-hydroxychalcone (in the absence of chiral phosphoric acid).

Reaction condition: 0.5 mmol of reactant, 3.0 mL of solvent, 20 mg of the catalyst

entry	Fe: CPA		Fe ₃ O ₄ -CPA ^a		Fe ₃ O ₄ -C	PA confin CNT ^b	ement in
		Yield (%)	ee (%)	HPLC spectrum	Yield (%)	ee (%)	HPLC spectrum
1	40	80	17	Fig. S25	87	-80	Fig. S20
2	20	81	39	Fig. S26	86	-82	Fig. S21
3	13.3	79	47	Fig. S27	88	-91	Fig. S22
4	10	75	54	Fig.S28	87	-95	Fig. S23
5	8	74	61	Fig. S29	85	-97	Fig. S24

Table S2: Asymmetric oxa-Michael addition reaction of various ratios of Fe: CPA.

Reaction condition: Reactant (0.5 mmol): ^acatalyst (20.0 mg of Fe₃O₄-CPA): ^b (20.0 mg of CNT-Fe₃O₄-CPA)

8. (a) Previous reports for the asymmetric Oxa-Michael addition of 2'-hydroxychalcone:



Yield 65%, Selectivity 96% ee

Wang et al, Tetrahedron Lett., **2014**, 55, 3255.

(b) Reported Metal-CPA catalysts for Various Reactions



- 1. D. Parmar, E. Sugiono, S. Raja and M. Rueping, Chem. Rev. 2014, 114, 9047-9153.
- 2. S. Mukherjee, B. List, J. Am. Chem. Soc., 2007, 129, 11336.
- 3. G. L. Hamilton, E. J. Kang, M. Mba, F. D. Toste, Science, 2007, 317, 496.
- 4. A. Parra, S. Reboredo, A. M. Martín Castro, J. Alemán, Org. Biomol. Chem., 2012, 10, 5001.
- 5. R. J. Phipps, G. L. Hamilton, F. D. Toste, Nat. Chem., 2012, 4, 603.
- 6. M. Mahlau, B. List, Angew. Chem.Int. Ed., 2013, 52, 518.

(c) Our catalyst (heterogeneous catalyst)



9. TOF Calculation:



Fig. S7. TOF of (A) MNP-L1/CNT (in) and (B) MNP-L1/CNT (out)

10. ¹H-NMR Spectra of flavanones



Fig. S8. ¹H NMR of the 2-(4-bromophenyl) chroman-4-one



Fig. S9. ¹H NMR of the 2-(4-methoxyphenyl) chroman-4-one.



Fig. S10. ¹H NMR of the 2-(4-methylphenyl) chroman-4-one



Fig. S11. ¹H NMR of the 2-Phenylchroman-4-one (flavanone)



Fig. S12. ¹H NMR of the 2-(4-chlorophenyl) chroman-4-one



Fig. S13. ¹H NMR of the 2-(3-chlorophenyl) chroman-4-one



Fig. S14. ¹H NMR of the 2-(3-nitrophenyl) chroman-4-one



Fig. S15. ¹³C NMR of the 2-Phenylchroman-4-one (flavanone)



Fig. S16. ¹³C NMR of the 2-(4-chlorophenyl) chroman-4-one



Fig. S17. ¹³C NMR of the 2-(3-chlorophenyl) chroman-4-one



Fig. S18. ¹³C NMR of the 2-(3-nitrophenyl) chroman-4-one

11. Chiral HPLC traces



<Sample Information>

Sample Name	: Comp c ch9		
Sample ID	: Comp c ch9		
Data Filename	: Comp c ch 9.lcd		
Method Filename	: Fav 2.lcm		
Batch Filename	:		
Vial #	: 1-2	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 11/21/2016 4:02:11 PM	Acquired by	: System Administrator
Date Processed	: 11/21/2016 4:23:01 PM	Processed by	: System Administrator



Fig. S19. HPLC of 2-Phenylchroman-4-one racemic



<Sample Information>

Sample Name Sample ID Data Filename	: FLAB : FLAB : c72.lcd			
Method Filename	: Fav 2.lcm			
Batch Filename	:			
Vial #	: 1-2	Sample Type	: Unknown	
Injection Volume	: 1 uL			
Date Acquired	: 4/25/2017 11:02:25 AM	Acquired by	: System Administrator	
Date Processed	: 4/25/2017 11:25:08 AM	Processed by	: System Administrator	





Fig. S20. HPLC of 2-Phenylchroman-4-one using M/CNT/L1-(inside) (5 mol%)





Fig. S21. HPLC of 2-Phenylchroman-4-one using M/CNT/L1-inside (7.5 mol%)



<Sample Information>

Sample Name	: Comp c ch1		
Sample ID	. comp c cm		
Data Filename	: Comp c ch1.lcd		
Method Filename	: Fav 2.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 0.4 uL	1 11	
Date Acquired	· 11/21/2016 12:35:23 PM	Acquired by	System Administrator
Date Processed	· 11/21/2016 1:34:40 PM	Processed by	: System Administrator
Date Freesseu	. 102 02010 1.04.40 110	r roccoscu by	. Oyotom Administrator



Detector A	204000			
Ret. Time	Area	Height	Area%	Height%
8.399	2189666	194890	94.727	93.641
11.412	121900	13234	5.273	6.359
	2311566	208124	100.000	100.000

Fig. S22. HPLC of 2-Phenylchroman-4-one ssing M/CNT/L1-inside (10 mol%)

<Sample Information>

Sample Name	: Comp c ch8 : Comp c ch8			
Data Filename	: Comp c ch 8.lcd			
Method Filename	: Fav 2.lcm			
Batch Filename				
Vial #	: 1-2	Sample Type	: Unknown	
Injection Volume	:1uL			
Date Acquired	: 11/21/2016 3:46:11 PM	Acquired by	: System Administrator	
Date Processed	: 11/21/2016 4:07:09 PM	Processed by	: System Administrator	

<Chromatogram>



<Peak Table>

Detector A	254nm		X	1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.
Ret. Time	Area	Height	Area%	Height%
8.225	21841684	1412655	97.427	96.421
11.129	576730	52430	2.573	3.579
	22418414	1465084	100.000	100.000

Fig. S23. HPLC of 2-Phenylchroman-4-one using M/CNT/L1-inside (12.5 mol%)



Fig. S24. HPLC of 2-Phenylchroman-4-one using M/CNT/L1-inside (15 mol%)



<Sample Information>

Sample Name Sample ID Data Filename Method Filename	: Ferrite @ 5 mol% CPA : Ferrite @ 5 mol% CPA : Ferrite @ 5 mol% CPA : Fav 2.lcm		
Vial #	1-2	Sample Type	: Unknown
Date Acquired	: 1 uL : 4/26/2017 1:22:12 PM : 4/26/2017 1:38:15 PM	Acquired by	: System Administrator
Date 1100essed		r tobessed by	. cystem rightinistrator

<Chromatogram> mV



Ret. Time	Area	Height	Area%	Height%
7.908	8106732	404281	41.819	32.315
10.880	11278596	846767	58.181	67.685
0.00000000	19385328	1251048	100.000	100.000

Fig. S25. HPLC of 2-Phenylchroman-4-one using MNP/L1(5 mol%) (in the absence of CNT)



<Sample Information>

Sample Name	: Comp c ch12 : Comp c ch12		
Data Filename	: Comp c ch 12.lcd		
Method Filename	: Fav 2.lcm		
Batch Filename	:		
Vial #	: 1-2	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 11/21/2016 4:47:34 PM	Acquired by	: System Administrator
Date Processed	: 2/2/2017 4:43:54 PM	Processed by	: System Administrator



7.894	9005468	812137	30.619	31.240
10.918	20406272	1787538	69.381	68.760
	29411740	2599675	100.000	100.000

Fig. S26. HPLC of 2-Phenylchroman-4-one using MNP/L1 (7.5 mol%) (in the absence of CNTs)



21335321

LabSolutions Analysis Report

<Sample Information>

Sample Name Sample ID	: Ferrite@ 10 mole% CPA : Ferrite@ 10 mole% CPA		
Data Filename	: Femtel@ 10 mole% CPA		
Method Filename	: Fav 2.lcm		
Batch Filename	1		
Vial #	: 1-2	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 4/26/2017 11:34:27 AM	Acquired by	: System Administrator
Date Processed	: 4/26/2017 11:49:31 AM	Processed by	: System Administrator

<Chromatogram>



80.121

100.000

Fig. S27. HPLC of 2-Phenylchroman-4-one using MNP/L1 (10 mol%) (in the absence of CNTs)

100.000



Fig. S28. HPLC of 2-Phenylchroman-4-one using MNP/L1 (12.5 mol%) (in the absence of CNT)

Batch Filename			
Vial #	: 1-2	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 4/26/2017 10:28:19 AM	Acquired by	: System Administrator
Date Processed	: 4/26/2017 10:43:20 AM	Processed by	: System Administrator





Fig. S29. HPLC of 2-Phenylchroman-4-one using MNP/L1 (15 mol%) (in absence of CNTs)

LabSo	lutions	Analys	sis Repo	rt
<sample inform<="" th=""><th>nation></th><th></th><th></th><th></th></sample>	nation>			
Sample Name Sample ID Data Filename Method Filename Batch Filename	: 5 mole % C : 5 mole % C : 5 mole % C : 5 mole % C : Fav 2.lcm	PA OUT side CNT PA OUT side CNT PA OUT side CNT		
Vial # Injection Volume	: 1-2 : 1 uL		Sample Type	: Unknown
Date Acquired Date Processed	: 4/21/2017 1 : 4/21/2017 1	2:38:56 PM 2:56:23 PM	Acquired by Processed by	: System Administrator : System Administrator

<Chromatogram>





<Peak Table>

Detector A	254nm			
Ret. Time	Area	Height	Area%	Height%
8.057	2643456	116207	21.500	13.474
11.188	9651564	746227	78.500	86.526
1	12295020	862434	100.000	100.000

Fig. S30. HPLC of 2-Phenylchroman-4-one using M/CNT/L1-outside (5 mol%)







Detector A.	294nm		201 - D. 1	c
Ret. Time	Area	Height	Area%	Height%
8.102	3220315	148704	20.684	14.275
11.130	12348756	892991	79.316	85.725
	15569071	1041695	100.000	100.000

Fig. S31. HPLC of 2-Phenylchroman-4-one Using M/CNT/L1-outside (7.5 mol%)



Fig. S32. HPLC of 2-Phenylchroman-4-one using M/CNT/L1-outside (10 mol%)



Fig. S33. HPLC of 2-Phenylchroman-4-one Using M/CNT/L1-outside (12.5 mol%)

LabSo	lutions	Analys	is Repo	ort	
<sample inforr<="" th=""><th>nation></th><th></th><th></th><th></th><th></th></sample>	nation>				
Sample Name Sample ID Data Filename Method Filename Batch Filename	: 15 mole % : 15 mole % : 15 mole % : Fav 2.lcm	CPA OUT side CNT CPA OUT side CNT CPA OUT side CNT			
Vial #	: 1-2		Sample Type	: Unknown	
Date Acquired Date Processed	: 4/21/2017 1 : 4/21/2017 1	2:56:12 PM :31:24 PM	Acquired by Processed by	: System Administrator : System Administrator	
<chromatogra< td=""><td>m></td><td></td><td></td><td></td><td>_</td></chromatogra<>	m>				_
1000-				Detector A 258	im
500-					

8.431

10.0

min

7.5

Fig. S34. HPLC of 2-Phenylchroman-4-one Using M/CNT/L1-outside (15 mol%)

Height% 8.623 91.377 100.000

5.0

Area% 12.166 87.834 100.000

2.5

Height 95943 1016661 1112604

250

0-

<Peak Table>
Detector A 254nm
Ret. Time Ar
8.431 17

11.685

0.0

Area 1714061 12374835 14088896

<Sample Information>

Sample Name	: c18 : c18		
Data Filename	: c20.lcd		
Method Filename	: Fav 2.lcm		
Batch Filename	:		
Vial #	: 1-2	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 2/2/2017 5:53:33 PM	Acquired by	: System Administrator
Date Processed	: 2/2/2017 6:25:28 PM	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A	254nm	2012 (Contractor)		A CONTRACT OF STATE
Ret. Time	Area	Height	Area%	Height%
6.184	18840747	989507	77.450	72.472
8.275	4652580	315814	19.126	23.130
11.161	832906	60050	3.424	4.398
	24326233	1365371	100.000	100.000

Fig. S35. HPLC of 2-Phenylchroman-4-one using M/CNT/L1 with reactant.

<Sample Information>

Sample Name Sample ID	: Com b2 : Com b2		
Data Filename	: Com b2.lcd		
Method Filename	: Fav.lcm		
Batch Filename	1		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 4 uL		
Date Acquired	: 11/17/2016 11:20:45 AM	Acquired by	: System Administrator
Date Processed	: 11/17/2016 12:30:56 PM	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A 2	254nm			
Ret. Time	Area	Height	Area%	Height%
7.987	13255884	778362	57.297	46.515
11.339	9879637	894982	42.703	53.485
	23135521	1673344	100.000	100.000

Fig. S36. HPLC of 2-(4-Bromophenyl) chroman-4-one racemic

	SHIMADZU LabSolutions	Analysis Report
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<Sample Information>

Sample Name Sample ID Data Filename Method Filename	: Comp b ch4 : Comp b ch4 : Comp b ch4.lcd : Fay 2 lcm		
Batch Filename	1.2	Sample Type	Unknown
Injection Volume	: 1 ūL	eanipie type	
Date Acquired Date Processed	: 11/21/2016 5:53:40 PM : 11/21/2016 6:11:33 PM	Acquired by Processed by	: System Administrator : System Administrator



Detector A	254nm	a secondaria da		a second second
Ret. Time	Area	Height	Area%	Height%
8.463	1891228	204417	75.290	78.104
12.210	620691	57307	24.710	21.896
	2511919	261724	100.000	100.000

Fig. S37. HPLC of 2-(4-Bromophenyl) chroman-4-one using M/CNT/L1(inside)

<Sample Information>

Sample Name Sample ID Data Filename Method Filename	: Comp b ch2 : Comp b ch2 : Comp b ch2.lcd : Fav 2.lcm			
Batch Filename Vial #	1-2	Sample Type	: Unknown	
Injection Volume Date Acquired Date Processed	: 1 uL : 11/21/2016 5:21:15 PM : 11/21/2016 5:40:31 PM	Acquired by Processed by	: System Administrator : System Administrator	

<Chromatogram>



<Peak Table>

Detector A	254nm			
Ret. Time	Area	Height	Area%	Height%
8.432	5855214	396738	15.177	14.114
12.199	32724817	2414224	84.823	85.886
	38580031	2810962	100.000	100.000

Fig. S38. HPLC of 2-(4-Bromophenyl) chroman-4-one using MNP/L1 (in absence of CNT)

SHIMADZU abSolutions Analysis Report

<Sample Information>

: Comp d5 : Comp d5 : Comp d5.lcd : Fav 2.lcm		
2		
: 1-1	Sample Type	: Unknown
: 1 uL		
: 11/18/2016 6:01:39 PM	Acquired by	: System Administrator
: 11/18/2016 6:23:19 PM	Processed by	: System Administrator
	: Comp d5 : Comp d5 : Comp d5.lcd : Fav 2.lcm : : 1-1 : 1 uL : 11/18/2016 6:01:39 PM : 11/18/2016 6:23:19 PM	: Comp d5 : Comp d5 : Comp d5.lcd : Fav 2.lcm : : 1 uL : 11/18/2016 6:01:39 PM : 11/18/2016 6:23:19 PM Processed by

<Chromatogram>



<Peak Table>

Detector A	254nm			
Ret. Time	Area	Height	Area%	Height%
9.648	8597231	789365	48.629	48.857
12.289	9081876	826312	51.371	51.143
	17679107	1615677	100.000	100.000

Fig. S39. HPLC of 2-(4-methoxyphenyl) chroman-4-one racemic

<Sample Information>

Sample Name Sample ID Data Filename Method Filename Batch Filename Vial #	: Comp d ch6 : Comp d ch6 : Comp d ch6.lcd : Fav 2.lcm : : 1-1	Sample Type	: Unknown	
Date Acquired	: 11/21/2016 12:16:07 PM	Acquired by	: System Administrator	
Date Processed	: 11/21/2016 12:41:40 PM	Processed by	: System Administrator	



CICCION A 2041111				
Ret. Time	Area	Height	Area%	Height%
9.727	18208969	1734642	82.872	82.167
12.579	3763541	376474	17.128	17.833
	21972510	2111116	100.000	100.000

Fig. S40. HPLC of 2-(4-methoxyphenyl) chroman-4-one using M/CNT/L1 (inside)

<Sample Information>

Sample Name Sample ID Data Filename Method Filename Batch Eilename	: Comp d4 : Comp d4 : Comp d4.lcd : Fav 2.lcm		
Vial #	1-1 1 ul	Sample Type	: Unknown
Date Acquired Date Processed	: 11/18/2016 5:46:51 PM : 11/21/2016 11:06:24 AM	Acquired by Processed by	: System Administrator : System Administrator



Detector A	254nm			
Ret. Time	Area	Height	Area%	Height%
9.853	4438145	426078	41.386	39.496
12.712	6285703	652722	58.614	60.504
i i i ann	10723848	1078800	100.000	100.000

Fig. S41. HPLC of 2-(4-methoxyphenyl) chroman-4-one using MNP/L1 (in absence of CNT)

<Sample Information>

Sample Name Sample ID Data Filename Method Filename	: Racemic flavanone : Racemic flavanone : Racemic flavanone : Fav.lcm			
Batch Filename Vial #	: : 1-1 : 1 ul	Sample Type	: Unknown	
Date Acquired Date Processed	: 11/16/2016 2:06:38 PM : 11/22/2016 12:45:31 PM	Acquired by Processed by	: System Administrator : System Administrator	



Detector A:	254nm			
Ret. Time	Area	Height	Area%	Height%
2.769	27305	4598	0.861	1.423
3.358	77579	12169	2.445	3.767
6.261	1544968	159763	48.689	49.458
10.116	1523269	146501	48.005	45.352
	3173121	323030	100.000	100.000

Fig. S42. HPLC of 2-(4-methylphenyl) chroman-4-one racemic

<Sample Information>

Sample Name Sample ID Data Filename Method Filename	: CHIRAL 2 : CHIRAL 2 : CHIRAL 1.lcd : Fav.lcm		
Vial # Injection Volume	: 1-1 1 uL	Sample Type	: Unknown
Date Acquired Date Processed	: 11/16/2016 2:22:22 PM : 11/16/2016 2:55:41 PM	Acquired by Processed by	: System Administrator : System Administrator

<Chromatogram>



<Peak Table>

Detector A	254nm	CONTRACTOR DESCRIPTION		
Ret. Time	Area	Height	Area%	Height%
2.761	24754	4417	1.220	2.130
6.276	1798663	183458	88.650	88.487
10.153	205540	19454	10.130	9.383
	2028957	207329	100.000	100.000

Fig. S43. HPLC of 2-(4-methylphenyl) chroman-4-one M/CNT/L1 (inside)



<Sample Information>

Sample Name Sample ID Data Filename Method Filename	: FE CPA2 : FE CPA2 : FE CPA2.lcd : Fav.lcm			
Batch Filename Vial #	1-1	Sample Type	: Unknown	
Injection Volume Date Acquired Date Processed	: 1 uL : 11/16/2016 4:44:47 PM : 11/16/2016 5:16:39 PM	Acquired by Processed by	: System Administrator : System Administrator	

<Chromatogram>



<Peak Table>

Detector A:	254nm			
Ret. Time	Area	Height	Area%	Height%
2.764	29157	4740	0.648	1.069
3.347	38300	5822	0.852	1.313
6.268	1176411	121702	26.159	27.445
10.110	3253303	311175	72.341	70.173
	4497171	443440	100.000	100.000

Fig. S44. HPLC of 2-(4-methylphenyl) chroman-4-one MNP/L1 (in absence of CNT)



Fig. S45. HPLC of 2-(4-chlorophenyl) chroman-4-one racemic



Fig. S46. HPLC of 2-(4-chlorophenyl) chroman-4-one M/CNT/L1 (inside CNT)



Fig. S47. HPLC of 2-(4-chlorophenyl) chroman-4-one MNP/L1 (in absence of CNT)



Fig. S48. HPLC of 2-(3-chlorophenyl) chroman-4-one racemic



Fig. S49. HPLC of 2-(3-chlorophenyl) chroman-4-one M/CNT/L1(inside CNT)





3416769 5179101

11.105



289997 401566 65.972

Fig. S50. HPLC of 2-(3-chlorophenyl) chroman-4-one MNP/L1 (in absence of CNT)



Fig. S51. HPLC of 2-(3-nitrophenyl) chroman-4-one racemic





Detector A	294nm			Contraction and a second s
Ret. Time	Area	Height	Area%	Height%
9.897	1924699	226230	82.264	83.859
12.150	414954	43543	17.736	16.141
	2339653	269773	100.000	100.000

Fig. S52. HPLC of 2-(3-nitrophenyl) chroman-4-one M/CNT/L1(inside CNT)



Fig. S53. HPLC of 2-(3-nitrophenyl) chroman-4-one MNP/L1 (in absence of CNT)