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Supplementary Information

for

Decorated Single-Enantiomer Phosphoramide-Based Silica/Magnetic Nanocomposites for Direct Enantioseparation

Fatemeh Karimi Ahmadabad, [a] Mehrdad Pourayoubi*[a] and Hadi Bakhshi [b]

[a]Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran

[b]Macromolecular Chemistry II, University of Bayreuth, Universitätsstraße 30, 95440 Bayreuth, Germany

*For correspondence: pourayoubi@um.ac.ir (M. Pourayoubi)

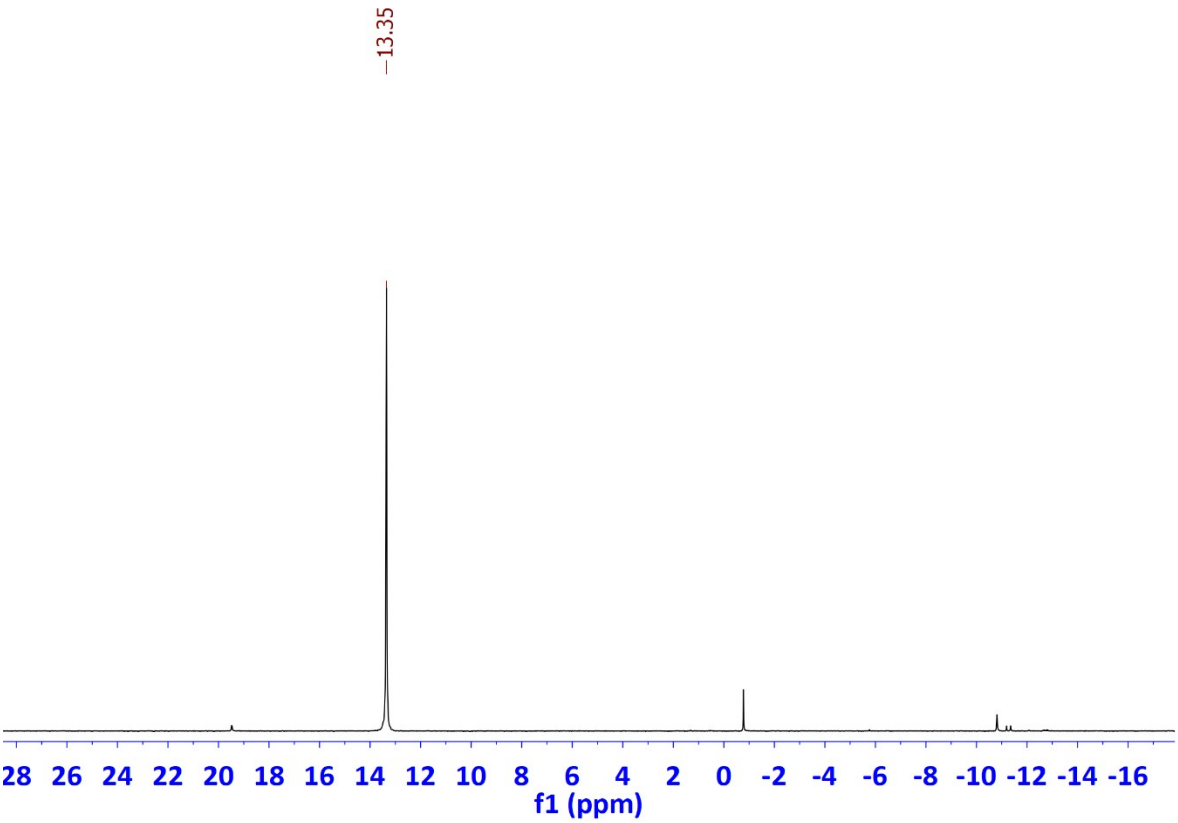


Figure S1. The $^{31}P\{^{1}H\}$NMR spectrum of P(=O)(NH-*R*-(+)CH(CH_3)C_6H_5)$_2$(NH$(CH_2)_3$Si$(OCH_3)_3$).

Assignments of NMR signals for P(=O)(NH-*R*-(+)CH(CH_3)C_6H_5)$_2$(NH$(CH_2)_3$Si$(OCH_3)_3$) (PTA(+))

The assignments of NMR signals of NH$(CH_2)_3$Si$(OCH_3)_3$ and two NH-*R*-(+)CH(CH_3)C_6H_5 fragments in the title compound were carried out by the comparative study of NMR spectra with those in closely related compounds.

The suitable compound for study of NH$(CH_2)_3$Si$(OCH_3)_3$ segment was not found in the literature; thus, we decided to synthesize a new phosphoramide compound including this fragment, *i.e*. P(O)$(OC_6H_5)_2$(NH$(CH_2)_3$Si$(OCH_3)_3$) (PA). In this compound (figure. S2), the aliphatic groups are merely related to the NH$(CH_2)_3$Si$(OCH_3)_3$ fragment, which allow to easy assignments of signals related to this silicon-based amine fragment.

The phosphoric triamide [2,6-F_2-C_6H_3C(O)NH][R-(+)(C_6H_5)CH(CH_3)NH]$_2$P(O)[S1] (FPTA(+)) was chosen for the assignments of signals related to the chiral amine. In this compound, two sets of signals appear for two chiral amines (for both in ^{1}HNMR and ^{13}C-NMR spectra), typically two triplets for two NH units, similar to what was observed in the title compound.

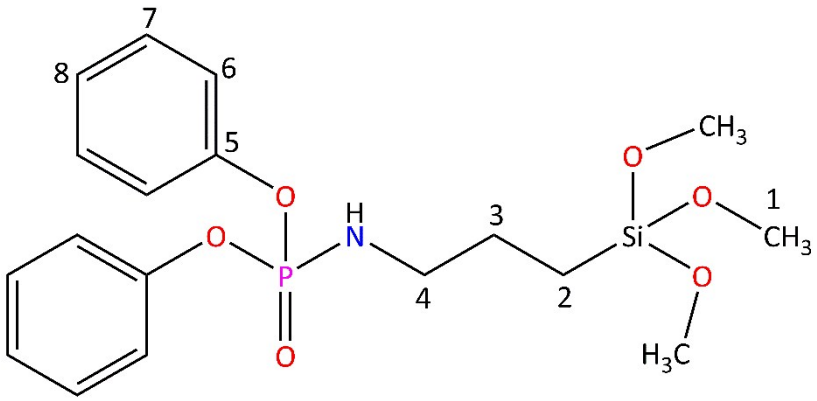


Figure S2. The chemical structure of $P(O)(OC_6H_5)_2(NH(CH_2)_3Si(OCH_3)_3)$.

According to the aliphatic region of the ^{1}H-NMR spectrum of PA, the signals at 0.45, 1.45 and 2.90 ppm correspond to the three CH_2 groups and the signals at 3.31 and 4.16 ppm are related to CH_3 and NH groups, respectively. Therefore, the signals at 0.56, 1.57, 2.02, 3.48 and 4.28 ppm in the ^{1}HNMR spectrum of PTA(+) are respectively assigned to three methylene of $CH_2CH_2CH_2$ segment, methyl and NH. The appearance of NH peaks in both PA and PTA(+) is the same and both of them are broad.

In the ^{13}C-NMR spectrum of PA, the signals in the aliphatic region are three singlets at 5.93, 44.01 and 50.18 ppm and a doublet at 24.50 ppm ($^3J_{P\text{-}C}$ = 6.0 Hz). Comparatively, the two singlets at 6.42 and 46.22 ppm and the doublet at 25.09 ppm ($^3J_{P\text{-}C}$ = 6.5 Hz) for PTA(+) correspond to the CH_2 carbon atoms of $CH_2CH_2CH_2$ fragment. The other signal is in the region that the signals of two CH units of two chiral segments also appear (50.10-50.90 ppm).

In the ^{1}H-NMR spectrum of PTA(+), the remaining signals in the aliphatic region are related to two CH and two CH_3 groups. Therefore, the overlapped signals at 1.38 ppm and within 3.98-4.22 ppm correspond to two CH and two CH_3 groups, respectively. Similar signals in the ^{1}H-NMR spectrum of FPTA(+) appear at 1.38-1.40 and 4.29-4.45 ppm, respectively. The triplets at 3.40 and 3.88 ppm for PTA(+) assign to two NH protons, in comparison with the triplets at 4.88 and 4.97 ppm in FPTA(+).

In the ^{13}C-NMR spectrum of PTA(+), the signals at 21.63 and 23.76 ppm are related to the carbon atoms of two CH_3 groups. Similar signals for FPTA(+) appear as doublets at 24.92 and 25.48 ppm, however in PTA(+) the intensity of signals are low and decision about the fine structure is impossible. The two signals related to two CH units appear in the range of 50.10-50.90 ppm, where the signal of OCH_3 of silicon-based amine fragment also appears. The two CH units in the literature compound appear as singlets at 49.68 and 50.03 ppm. Also, the ^{13}C-

NMR of Fe_3O_4@SiO_2@(-O_2(OCH_3)Si[(CH_2)$_3$$NH_2$ in solid state has been confirm the assignment of ^{13}C-NMR of PA and PTA.[S2]

The assignment of ^{1}H and ^{13}C signals of aromatic segments in the title compound are not difficult, as there is no crowding in this region.

The phosphoramide P(O)(OC_6H_5)$_2$(NH(CH_2)$_3$Si(OCH_3)$_3$) does not show the triethylamine-hydrochloride salt in the THF solution, in opposite with this impurity in the solution of P(=O)(NH-*R*-(+)CH(CH_3)C_6H_5)$_2$(NH(CH_2)$_3$Si(OCH_3)$_3$) phosphoric triamide. The amount of impurity was estimated according to the integration in the ^{1}H-NMR spectrum. For this aim, the overlapped signals related to two methyl groups of two chiral amines were adjusted for 6H and in this case, the signal of 9 methyl protons of triethylamine shows an integration about 2.30, showing about 13% impurity of triethylamine hydrochloride. The position of one H atom attached to N in Et_3NHCl was not identified, as the integration of about 0.26 probably was overlapped in the aromatic region or exchange with some exchangeable mobile protons.

Synthesis of P(O)(OC_6H_5)$_2$(NH(CH_2)$_3$Si(OCH_3)$_3$)

A solution of RMBA (2.5 mmol) and TEA (2.5 mmol) in dry THF (5 ml) was added dropwise to a stirring solution of PO(OC_6H_5)$_2$Cl (2.5 mmol) in the same solvent (10 ml) at 0°C. After stirring for 4 h, the obtained white solid (triethylamine-hydrochloride salt) was filtered off and the filtrate was concentrated in vacuum, and a few amounts of this solution was directly used for the NMR experiments, after adding two droplets of $CDCl_3$ to the NMR tube for adjustment requirement. ^{31}P{^{1}H}-NMR (THF/$CDCl_3$, ppm): –0.23. ^{13}C{^{1}H}-NMR (THF/$CDCl_3$, ppm): 5.93 (*s*, C_2), 24.50 (*d*, C_3, $^3J_{P\text{-}C}$ = 6.0 Hz), 44.01 (*s*, C_4), 50.18 (*s*, C_1), 120.07 (*d*, C_6, $^3J_{P\text{-}C}$ = 4.9 Hz), 124.48 (*s*, C_8), 129.36 (*s*, C_7), 150.91 (*d*, C_5, $^2J_{P\text{-}C}$ = 6.7 Hz). ^{1}H-NMR (THF/$CDCl_3$, ppm): 0.45 (*m*, 2H, CH_2), 1.45 (*m*, 2H, CH_2), 2.90 (*m*, 2H, CH_2), 3.31 (*m*, 9H, CH_3), 4.16 (*b*, 1H, NH), 6.99-7.19 (*m*, 10H, $CH_{aromatic}$).

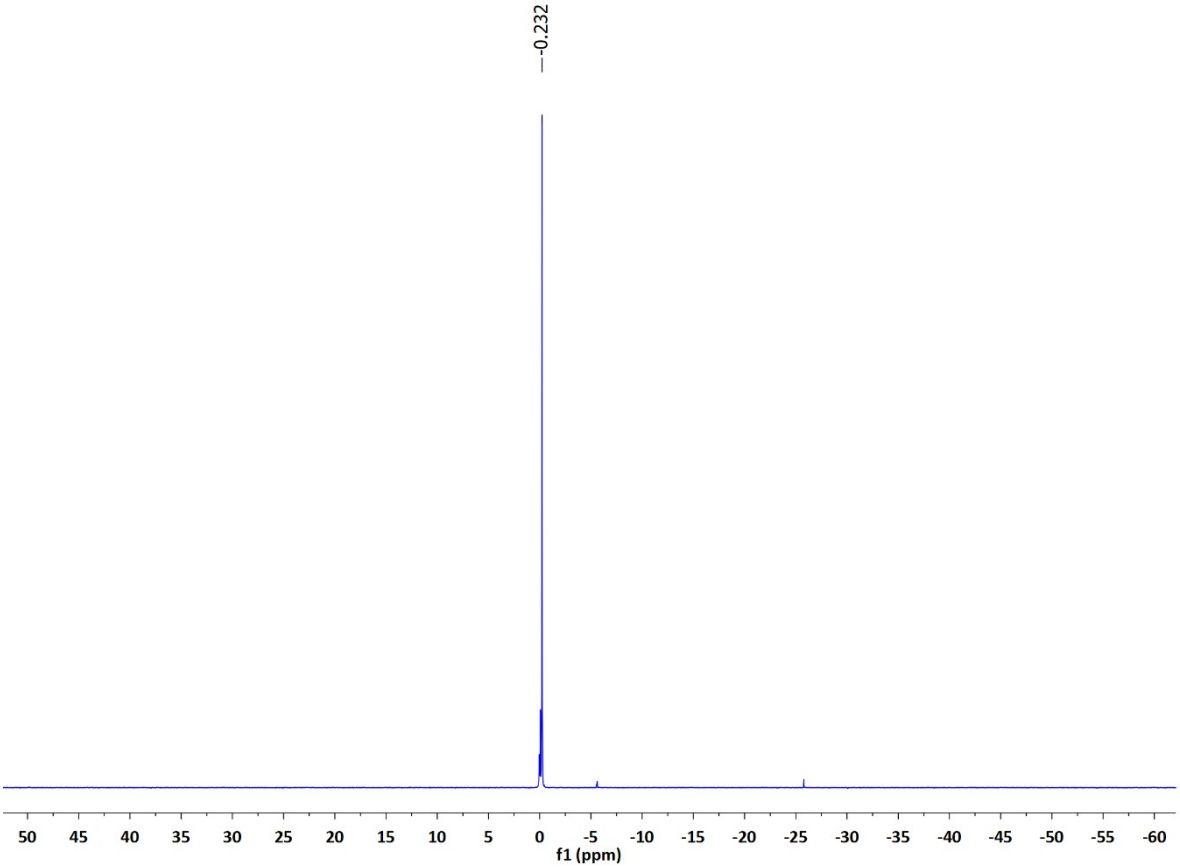


Figure S3. The $^{31}P\{^{1}H\}$NMR spectrum of $P(O)(OC_6H_5)_2(NH(CH_2)_3Si(OCH_3)_3)$

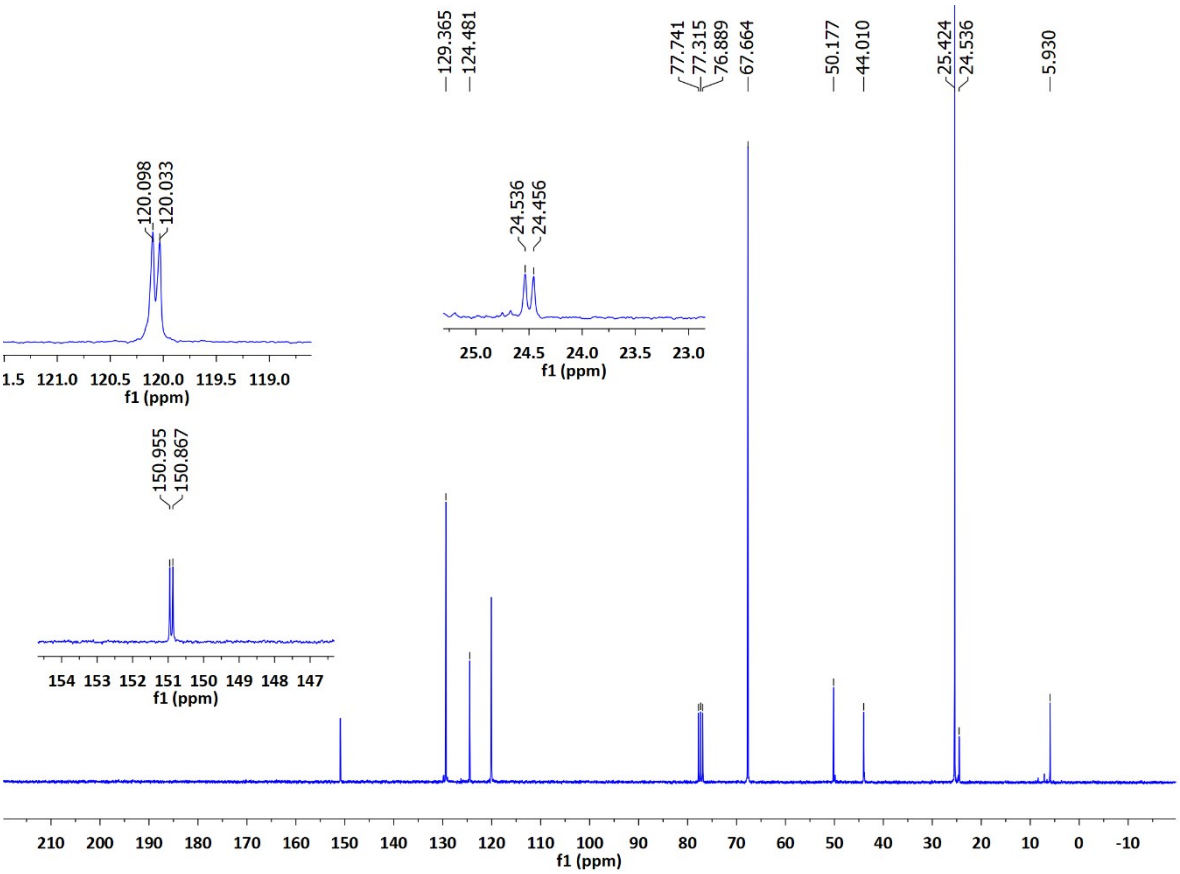


Figure S4. The $^{13}C\{^{1}H\}$NMR spectrum of $P(O)(OC_6H_5)_2(NH(CH_2)_3Si(OCH_3)_3)$.

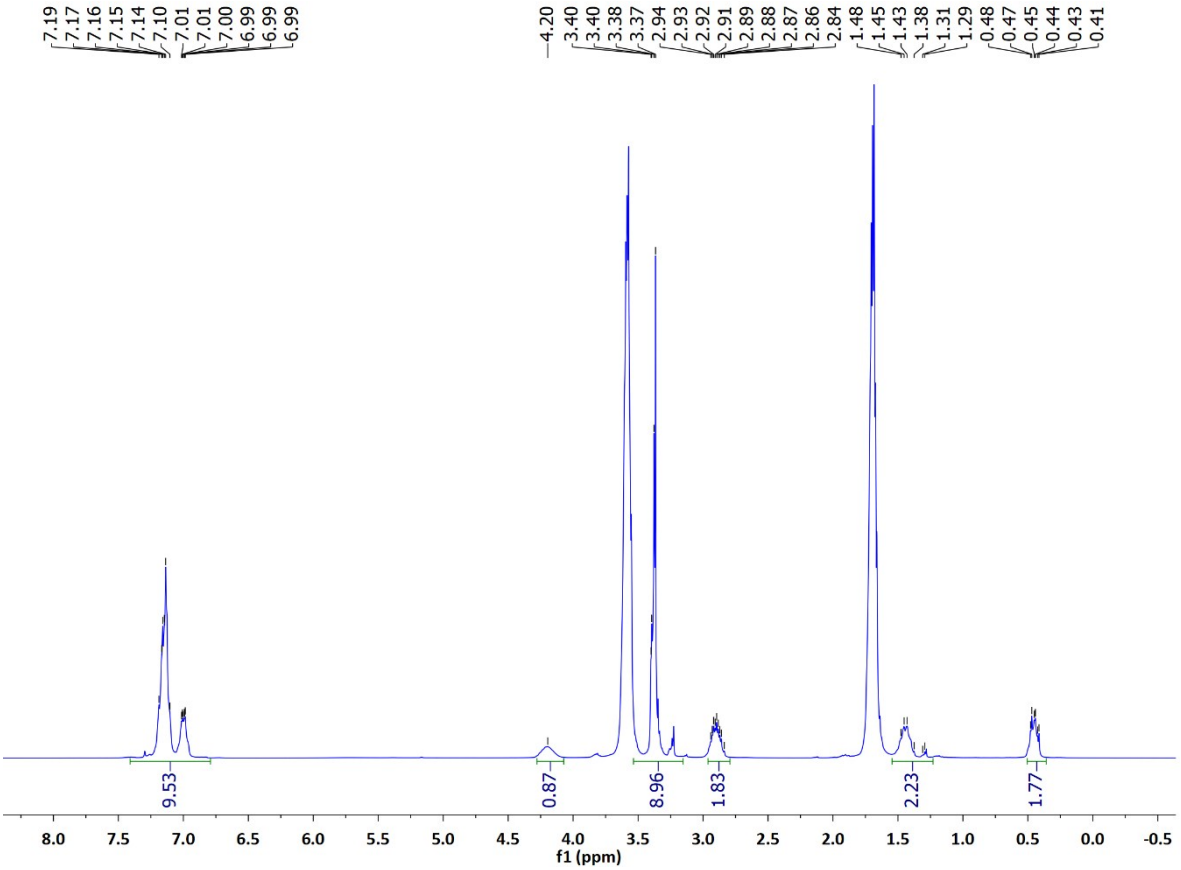


Figure S5. The ^{1}H-NMR spectrum of $P(O)(OC_6H_5)_2(NH(CH_2)_3Si(OCH_3)_3)$.

No.	2theta [°]	d [Å]	I/I0	FWHM	Matched
1	19.91	4.4553	140.04	0.5000	
2	30.11	2.9655	239.89	0.5000	A
3	32.62	2.7431	135.11	0.5000	
4	35.44	2.5309	1000.00	0.5000	A
5	35.79	2.5069	202.37	0.5000	
6	38.56	2.3327	167.49	0.5000	
7	43.15	2.0946	257.45	0.5000	A
8	43.80	2.0651	82.85	0.5000	
9	48.45	1.8774	98.17	0.5000	
10	53.59	1.7088	134.25	0.5000	A
11	56.41	1.6298	149.53	0.5000	
12	56.98	1.6150	413.61	0.5000	A
13	57.26	1.6076	156.44	0.5000	
14	58.49	1.5767	82.31	0.5000	
15	61.06	1.5163	94.82	0.5000	
16	62.60	1.4828	642.27	0.5000	A
17	62.98	1.4748	240.54	0.5000	
18	64.03	1.4531	82.16	0.5000	
19	66.91	1.3974	85.28	0.5000	
20	68.32	1.3718	136.15	0.5000	
21	69.27	1.3553	101.21	0.5000	
22	69.79	1.3464	88.36	0.5000	
23	71.05	1.3257	104.68	0.5000	A
24	74.04	1.2794	159.18	0.5000	A
25	74.41	1.2740	103.58	0.5000	
26	75.28	1.2614	92.03	0.5000	
27	77.70	1.2280	100.11	0.5000	
28	79.81	1.2008	344.04	0.5000	

Index	Amount (%)	Name
A	100.0	Magnetite
	52.8	*Unidentified peak area*

A: Magnetite (100.0 %)	
Formula sum	Fe_3O_4
Entry number	96-900-5838
Figure-of-Merit (FoM)	0.877435
Total number of peaks	34
Peaks in range	15
Peaks matched	8
Intensity scale factor	1.10
Space group	F d -3 m
Crystal system	cubic
Unit cell	a= 8.3862 Å
I/Ic	6.04
Calc. density	5.214 g/cm³

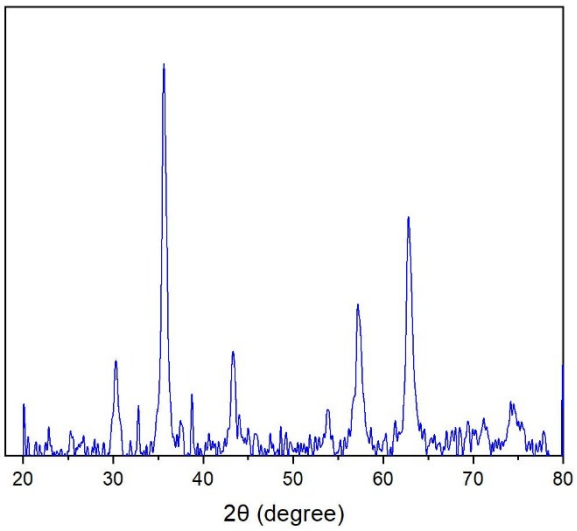
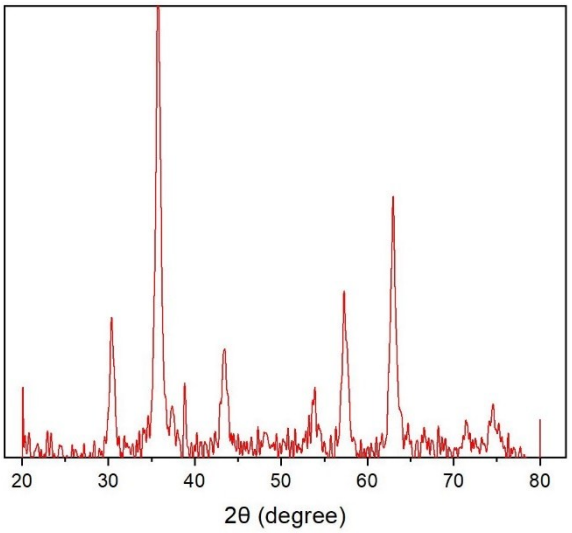


Figure S6. The XRD spectrum and related details of Fe_3O_4.

No.	2theta [°]	d [Å]	I/I0	FWHM	Matched
1	20.07	4.4242	142.36	0.5800	
2	22.93	3.8788	54.10	0.5800	B
3	30.36	2.9440	287.19	0.5800	A,B
4	30.69	2.9137	124.33	0.5800	
5	33.57	2.6699	53.76	0.5800	
6	34.02	2.6357	54.45	0.5800	
7	34.60	2.5926	81.45	0.5800	
8	35.74	2.5122	1000.00	0.5800	A
9	36.02	2.4931	425.05	0.5800	
10	36.04	2.4925	246.81	0.5800	
11	36.65	2.4524	59.53	0.5800	
12	37.37	2.4063	93.36	0.5800	A
13	38.83	2.3191	150.81	0.5800	
14	42.35	2.1343	53.25	0.5800	
15	42.95	2.1057	111.22	0.5800	
16	43.45	2.0826	213.34	0.5800	A
17	43.90	2.0627	90.84	0.5800	
18	47.32	1.9209	61.12	0.5800	
19	50.79	1.7977	59.82	0.5800	
20	51.61	1.7710	56.61	0.5800	
21	52.87	1.7317	53.84	0.5800	B
22	53.22	1.7211	78.32	0.5800	
23	53.65	1.7083	106.86	0.5800	
24	53.92	1.7006	115.89	0.5800	A
25	56.35	1.6328	62.16	0.5800	
26	57.29	1.6081	341.88	0.5800	A
27	57.64	1.5994	177.36	0.5800	B
28	57.88	1.5933	72.77	0.5800	B
29	62.98	1.4759	539.50	0.5800	A,B
30	63.36	1.4681	171.21	0.5800	B
31	63.80	1.4590	62.24	0.5800	
32	64.69	1.4409	65.12	0.5800	B
33	66.57	1.4047	61.19	0.5800	B
34	68.21	1.3749	64.29	0.5800	B
35	71.41	1.3210	76.88	0.5800	A
36	74.11	1.2793	75.06	0.5800	
37	74.58	1.2726	100.61	0.5800	A
38	75.21	1.2633	63.79	0.5800	

Index	Amount (%)	Name
A	93.4	Iron Oxide Magnetite
B	6.6	Silicon Oxide
	42.2	*Unidentified peak area*



A: Iron Oxide Magnetite (93.4 %)

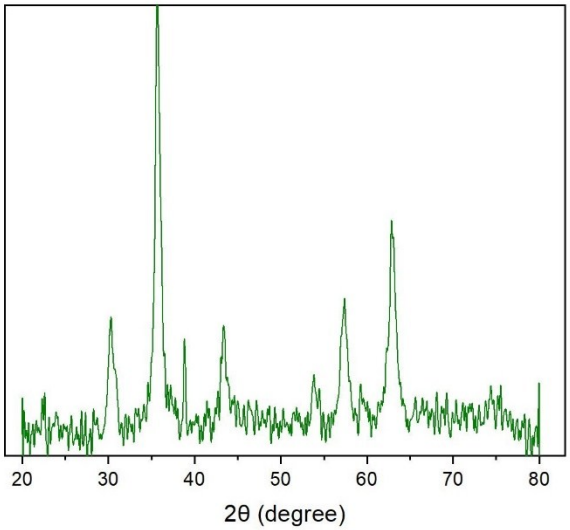
Formula sum	Fe3 O4
Entry number	01-075-0449
Figure-of-Merit (FoM)	0.833960
Total number of peaks	62
Peaks in range	24
Peaks matched	14
Intensity scale factor	0.73

B: Silicon Oxide (6.6 %)

Formula sum	Si O2
Entry number	01-075-3163
Figure-of-Merit (FoM)	0.725273
Total number of peaks	220
Peaks in range	64
Peaks matched	12
Intensity scale factor	0.04

Figure S7. The XRD spectrum and related details of Fe_3O_4@SiO_2.

No.	2theta [°]	d [Å]	I/I0	FWHM	Matched
1	25.26	3.5254	273.95	0.2400	
2	41.45	2.1786	272.30	0.2400	
3	42.67	2.1192	257.14	0.2400	B
4	43.04	2.1015	341.21	0.2400	
5	43.25	2.0919	269.10	0.2400	A
6	43.47	2.0820	307.96	0.2400	A,B
7	43.76	2.0686	253.58	0.2400	
8	48.66	1.8713	197.92	0.2400	
9	53.64	1.7088	214.69	0.2400	A
10	53.86	1.7022	213.48	0.2400	A
11	56.95	1.6169	313.45	0.2400	
12	57.19	1.6109	280.91	0.2400	A
13	57.38	1.6059	376.01	0.2400	A
14	57.75	1.5966	304.10	0.2400	
15	62.21	1.4924	257.92	0.2400	
16	62.50	1.4861	263.72	0.2400	B
17	62.66	1.4827	301.15	0.2400	B
18	62.76	1.4806	375.95	0.2400	
19	62.88	1.4781	442.34	0.2400	A
20	63.01	1.4753	287.36	0.2400	A
21	63.17	1.4720	322.69	0.2400	
22	63.36	1.4681	254.87	0.2400	
23	66.95	1.3977	197.46	0.2400	
24	67.49	1.3878	202.77	0.2400	B
25	70.37	1.3380	266.81	0.2400	B
26	71.15	1.3251	216.18	0.2400	
27	72.27	1.3074	228.07	0.2400	
28	73.07	1.2950	232.19	0.2400	
29	73.76	1.2846	213.39	0.2400	
30	74.17	1.2785	252.84	0.2400	
31	75.57	1.2583	220.93	0.2400	A



Index	Amount (%)	Name
A	61.7	Iron Oxide Magnetite, syr
B	38.3	Silicon Oxide
	50.1	*Unidentified peak area*

A: Iron Oxide Magnetite, syn (61.7 %)

Formula sum	Fe3 O4
Entry number	01-084-2782
Figure-of-Merit (FoM)	0.883094
Total number of peaks	62
Peaks in range	26
Peaks matched	9
Intensity scale factor	1.10

B: Silicon Oxide (38.3 %)

Formula sum	Si O2
Entry number	01-070-2539
Figure-of-Merit (FoM)	0.758020
Total number of peaks	98
Peaks in range	28
Peaks matched	7
Intensity scale factor	0.27

Figure S8. The XRD spectrum and related details of Fe_3O_4@SiO_2@PTA(+).

No.	2theta [°]	d [Å]	I/I0	FWHM	Matched
1	20.79	4.2730	250.40	0.2400	
2	21.08	4.2146	245.84	0.2400	
3	23.99	3.7098	251.51	0.2400	B
4	24.30	3.6625	268.71	0.2400	
5	26.14	3.4088	232.74	0.2400	B
6	29.74	3.0037	268.92	0.2400	
7	30.15	2.9643	368.93	0.2400	A
8	30.34	2.9461	312.23	0.2400	A
9	31.71	2.8221	273.14	0.2400	
10	33.44	2.6798	276.09	0.2400	
11	33.95	2.6407	398.82	0.2400	
12	34.40	2.6073	289.71	0.2400	
13	34.87	2.5733	371.79	0.2400	
14	35.15	2.5532	483.43	0.2400	
15	35.25	2.5458	309.61	0.2400	
16	35.38	2.5374	504.35	0.2400	
17	35.49	2.5298	623.23	0.2400	
18	35.65	2.5184	1000.00	0.2400	A,B
19	35.79	2.5092	818.39	0.2400	B
20	35.90	2.5015	420.51	0.2400	
21	36.01	2.4945	382.00	0.2400	
22	36.11	2.4875	274.09	0.2400	
23	36.24	2.4788	290.60	0.2400	
24	36.56	2.4577	296.17	0.2400	
25	37.12	2.4219	271.81	0.2400	
26	38.78	2.3221	270.57	0.2400	
27	42.89	2.1085	254.66	0.2400	
28	43.25	2.0919	364.74	0.2400	A
29	43.41	2.0848	258.72	0.2400	A
30	44.18	2.0500	235.09	0.2400	
31	47.17	1.9269	205.39	0.2400	
32	48.44	1.8791	235.27	0.2400	B
33	49.44	1.8434	229.52	0.2400	
34	49.83	1.8300	220.78	0.2400	
35	53.07	1.7255	255.91	0.2400	
36	53.45	1.7144	237.16	0.2400	
37	53.74	1.7057	239.51	0.2400	A
38	53.95	1.6997	252.07	0.2400	
39	56.58	1.6265	265.94	0.2400	
40	56.97	1.6166	336.93	0.2400	
41	57.17	1.6112	406.91	0.2400	A
42	57.38	1.6058	544.81	0.2400	A
43	57.68	1.5983	336.97	0.2400	
44	62.09	1.4950	329.06	0.2400	
45	62.45	1.4871	337.49	0.2400	B
46	62.61	1.4836	311.09	0.2400	
47	62.80	1.4797	473.11	0.2400	A
48	62.99	1.4757	464.36	0.2400	A
49	63.14	1.4725	370.10	0.2400	
50	63.28	1.4697	277.87	0.2400	
51	63.58	1.4635	267.32	0.2400	
52	67.89	1.3807	221.08	0.2400	
53	68.79	1.3648	248.52	0.2400	B
54	70.16	1.3414	248.51	0.2400	
55	70.46	1.3365	229.59	0.2400	
56	70.78	1.3312	227.08	0.2400	
57	71.37	1.3217	230.62	0.2400	A,B
58	71.97	1.3121	246.37	0.2400	
59	72.57	1.3028	280.58	0.2400	
60	73.26	1.2921	262.77	0.2400	
61	73.96	1.2816	261.73	0.2400	
62	74.30	1.2766	353.70	0.2400	A
63	74.64	1.2716	258.81	0.2400	A
64	74.87	1.2683	256.53	0.2400	
65	75.11	1.2649	305.12	0.2400	
66	75.36	1.2612	295.98	0.2400	A
67	75.67	1.2569	348.04	0.2400	A
68	75.95	1.2530	280.78	0.2400	
69	76.47	1.2457	301.56	0.2400	B
70	79.43	1.2066	240.47	0.2400	A

Index	Amount (%)	Name
A		Iron Oxide Magnetite, syn
B		Silicon Oxide
	58.9	*Unidentified peak area*

A: Iron Oxide Magnetite, syn

Formula sum	Fe3 O4
Entry number	01-084-2782
Figure-of-Merit (FoM)	0.863358
Total number of peaks	62
Peaks in range	27
Peaks matched	18
Intensity scale factor	0.84

B: Silicon Oxide

Formula sum	Si O2
Entry number	00-013-0026
Figure-of-Merit (FoM)	0.691727
Total number of peaks	54
Peaks in range	54
Peaks matched	12
Intensity scale factor	0.20

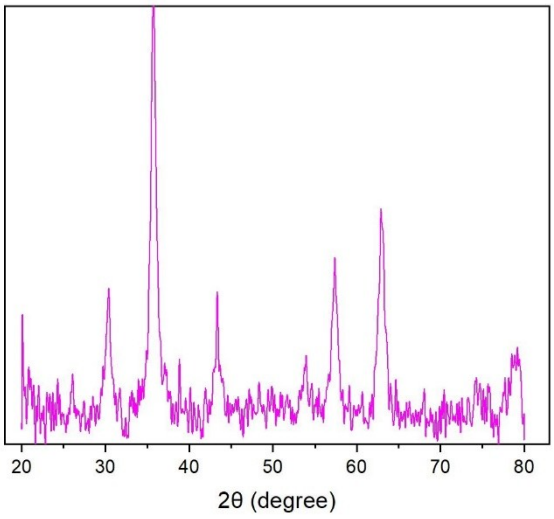


Figure S9. The XRD spectrum and related details of Fe_3O_4@SiO_2@PTA(-).

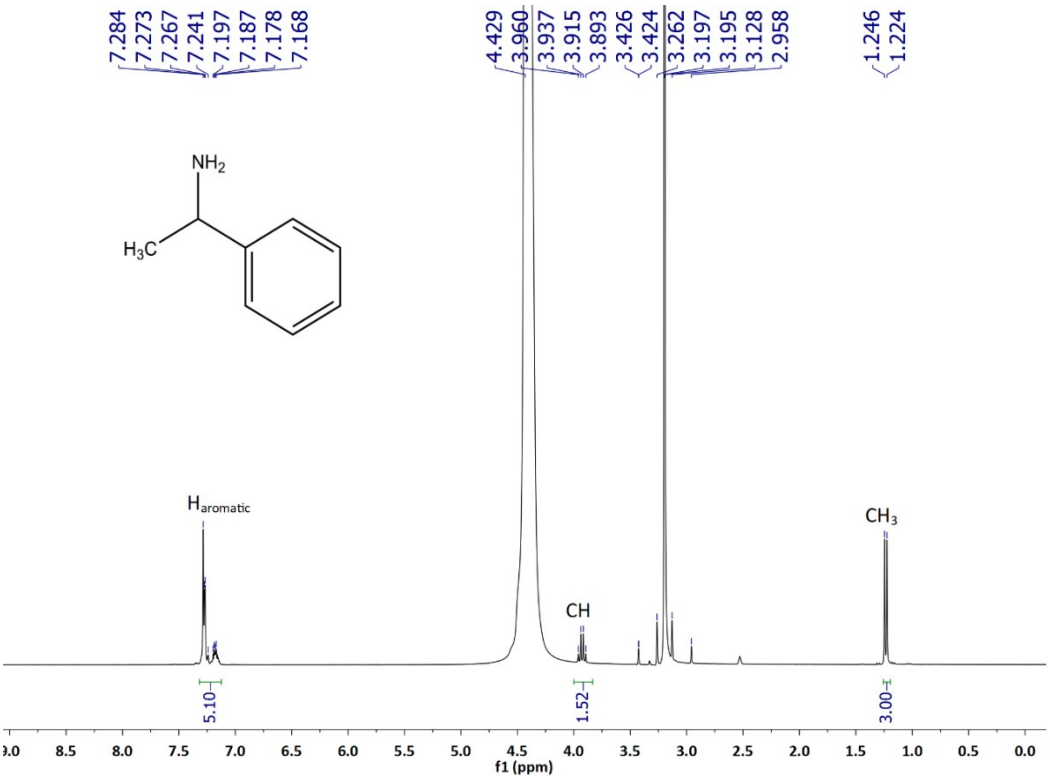


Figure S10. The ^{1}H-NMR spectrum of (±)-MBA solution(H_2O/CH_3OH) after enantioseparation.

References

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