Electronic Supporting Information

Facile one-pot fabrication of silica gel-supported chiral phase-transfer catalyst—*N*-(2-cyanobenzyl)-*O*(9)-allyl-cinchonidinium salt

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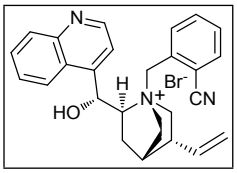
Preparation of chiral phase-transfer catalyst CDPTC

General procedure for *N*-(2-cyanobenzyl)cinchonidinium bromide

In the 250 mL round-bottomed flask, a mixture of cinchonidine (2.9 g, 10.0 mmol) and 2-cyanobenzyl bromide (2.1 g, 11.0 mmol) in toluene (100 mL) was stirred at 65℃ for 12 h. The reaction mixture was filtered, washed with toluene (15 mL×3). The crude solid was recrystallized from methanol/ether (225 mL, *v*/*v* =1/8) to afford the white ***N*-(2-cyanobenzyl)cinchonidinium bromide** (4.7 g, 95%).



^{1}H NMR (300.1 MHz, $CDCl_3$, TMS) δ 8.86 (d, ^3J = 4.3 Hz, 1H, Ar-H), 8.47 (d, ^3J = 7.6 Hz, 1H, Ar-H), 8.21 (d, ^3J = 7.5 Hz, 1H, Ar-H), 7.95 (d, ^3J = 7.8 Hz, 1H, Ar-H), 7.78 (d, ^3J = 4.3 Hz, 1H, Ar-H), 7.63 (dd, ^3J = 9.6, 5.6 Hz, 2H, Ar-H), 7.56 – 7.43 (m, 3H, Ar-H), 6.68 (s, 1H, OCH), 6.08 (d, ^3J = 10.0 Hz, 1H, -CH=), 5.49 (ddd, ^3J = 16.8, 10.4, 6.1 Hz, 2H, =CH_2), 5.17 (d, ^3J = 17.2 Hz, 1H, N^+-CH), 4.95 (d, ^3J = 10.4 Hz, 2H, N^+-CH_2), 4.02 (d, ^3J = 9.5 Hz, 2H, N^+-CH_2), 3.17 – 2.98 (m, 2H, N^+-CH_2), 2.54 (s, 1H, -OH), 2.17 (t, ^3J = 11.1 Hz, 1H, CH), 2.01 (dd, ^3J = 22.5, 9.5 Hz, 3H, CH, CH_2), 1.60 – 1.76 (m, 2H, CH_2).

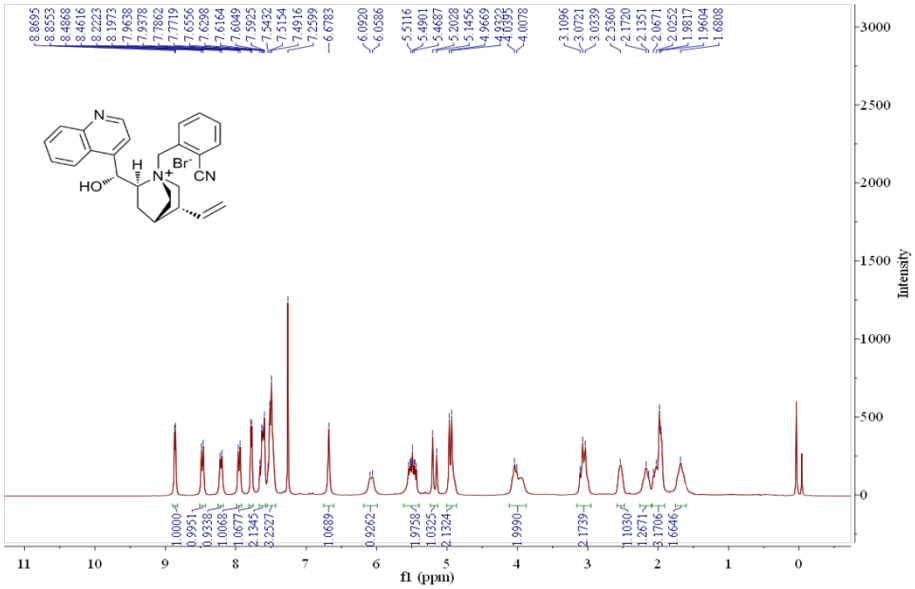
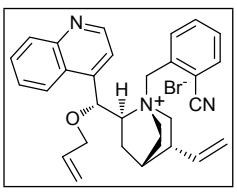


Fig. 1 ^{1}H NMR spectra of *N*-(2-cyanobenzyl)cinchonidinium bromide

General procedure for *N*-(2-cyanobenzyl)-O(9)-allylcinchonidinium bromide (CDPTC)

In 250 mL of round-bottomed flask was added *N*-(2-cyanobenzyl)cinchonidinium bromide (4.8 g, 9.8 mmol), CH_2Cl_2 (100 mL), allyl bromide (3.6 g, 29.4 mmol) and 50% aqueous KOH solution (5.5 mL, 49.0 mmol), successively. The resulting mixture was stirred vigorously at 25℃ for 24 h. Then the mixture was diluted with water (20 mL) and extracted with dichloromethane (50 mL×3). The combined organic phase was dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude solid was recrystallized from dichloromethane/hexane (220 mL, *v*/*v*=1/10) to obtain the light yellow solid ***N*-(2-cyanobenzyl)-O(9)-allylcinchonidinium bromide** (4.7 g, 90%).



^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.96 (d, ^3J = 4.3 Hz, 2H, Ar-H), 8.84 (d, ^3J = 8.5 Hz, 1H, Ar-H), 8.13 (d, ^3J = 8.3 Hz, 1H, Ar-H), 7.92 (d, ^3J = 6.4 Hz, 1H, Ar-H), 7.89 –7.73 (m, 3H, Ar-H), 7.65 (t, ^3J = 7.6 Hz, 2H, Ar-H),

6.91 (d, ^3J = 12.1 Hz, 1H, OCH), 6.28–6.09 (m, 2H, -CH=, -CH=), 5.70 (ddd, ^3J = 16.8, 10.4, 6.2 Hz, 1H, =CH_2), 5.41 (d, ^3J = 17.2 Hz, 1H, =CH_2), 5.31 (dd, ^3J = 13.6, 8.0 Hz, 2H, =CH_2), 5.22 (d, ^3J = 12.5 Hz, 1H, N^+-CH), 4.98 (dd, ^3J = 23.9, 11.3 Hz, 2H, N^+-CH_2), 4.83 – 4.56 (m, 2H, OCH_2), 4.16 (d, ^3J = 6.1 Hz, 2H, N^+-CH_2), 3.16 (dd, ^3J = 15.4, 7.0 Hz, 2H, N^+-CH_2), 2.63 (s, 1H, CH), 2.17 (dd, ^3J = 16.7, 6.2 Hz, 1H, CH), 2.06 (d, ^3J = 7.0 Hz, 3H, CH_2, CH_2), 1.82 (d, ^3J = 6.6 Hz, 1H, CH_2).

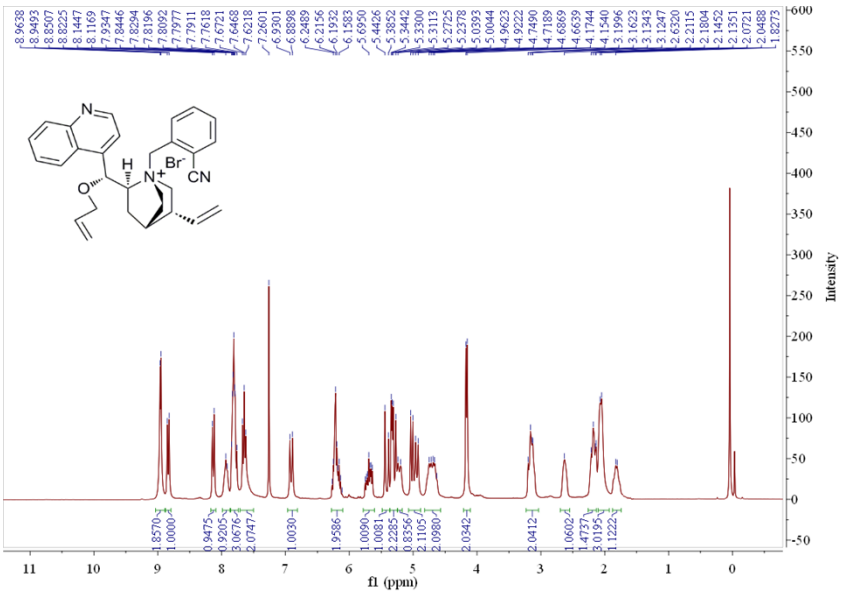
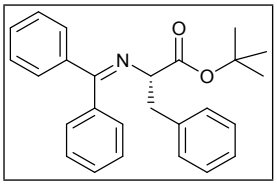


Fig. 2 ^{1}H NMR of *N*-(2-cyanobenzyl)-O(9)-allylcinchonidinium bromide

Characterization data of *α*-alkylation products

***tert*-Butyl 3-phenyl-2-(diphenylmethyleneamino)propanoate (Table 1).**



^{1}H NMR (300.1 MHz, $CDCl_3$, TMS) δ 7.52 (d, ^3J = 7.0 Hz, 2H, Ph-H), 7.30−7.00 (m, 11H, Ph-H), 6.54 (d, ^3J = 6.4 Hz, 2H, Ph-H), 4.06 (dd, ^3J = 4.4 Hz, 4.4 Hz, 1H, NCH), 3.22−3.07 (m, 2H, CH_2), 1.39 (s, 9H, CH_3); ^{13}C NMR (75.0 MHz, $CDCl_3$, TMS): δ 170.8, 170.2 (C=N, C=O), 139.5, 138.3, 137.5, 136.3, 132.4, 130.0, 129.8, 129.3, 128.6, 128.4, 128.2, 128.1, 128.0, 128.0, 127.9, 127.6, 126.6, 126.1(Ph), 81.1 (O-C), 67.9 (NCH), 39.5 (CH_2), 28.0 (CH_3); HPLC analysis: Phenomenex Lux 5u Amylose-2, hexane/dioxane = 95/5, 254 nm, flow rate = 0.5 ml/min, retention times: 12.8 min (R), 15.3 min (S).

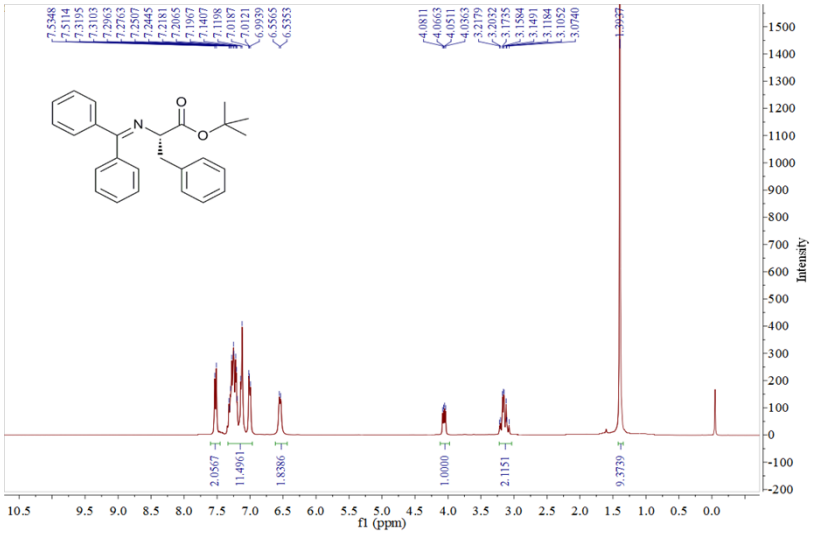


Fig.3 ^{1}H NMR spectra of *tert*-butyl 3-phenyl-2-(diphenylmethyleneamino)propanoate

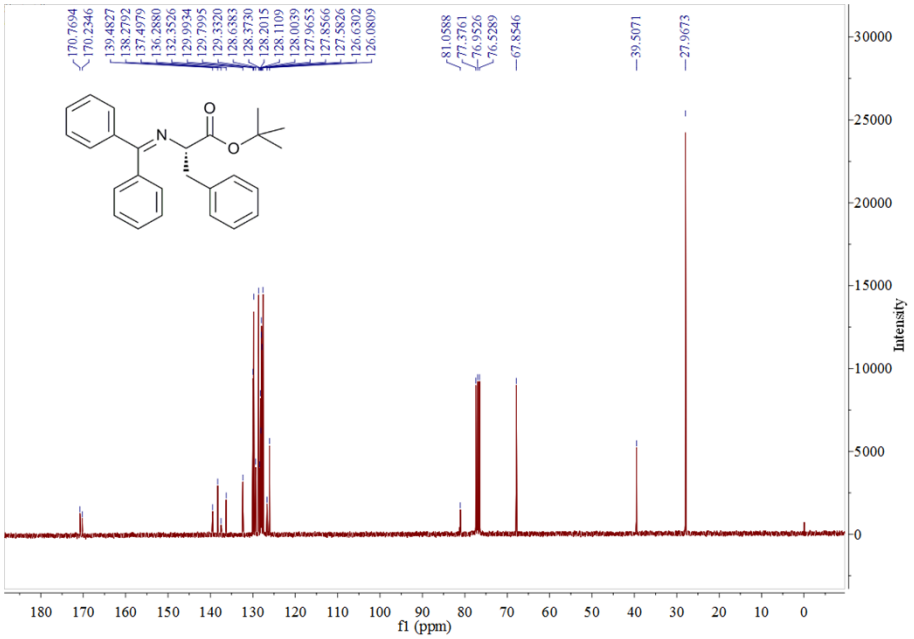
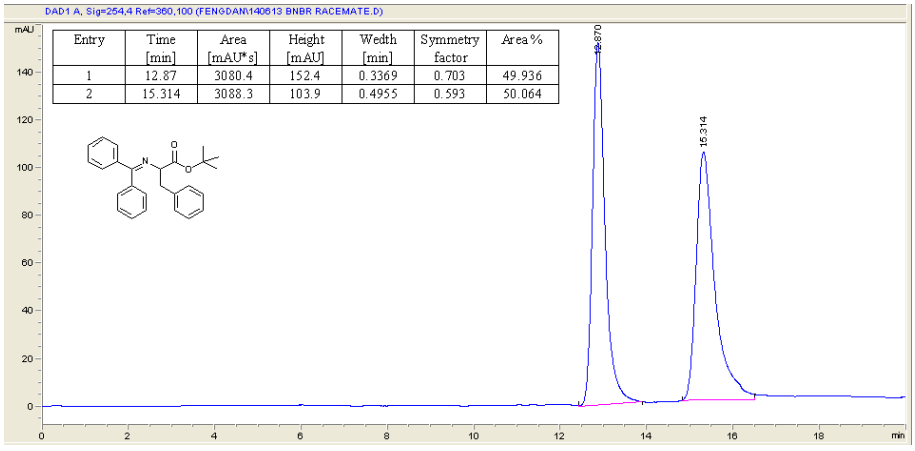
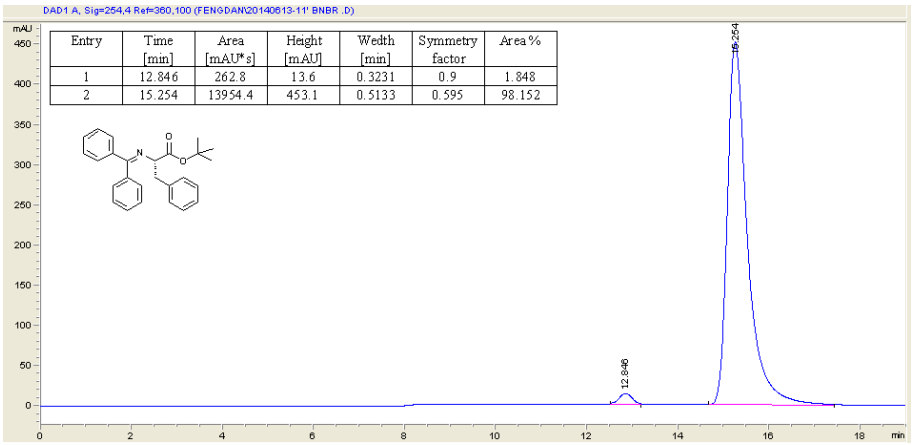


Fig.4 ^{13}C NMR spectra of *tert*-butyl 3-phenyl-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	12.87	3080.4	152.4	0.3369	0.703	49.936
2	15.314	3088.3	103.9	0.4955	0.593	50.064

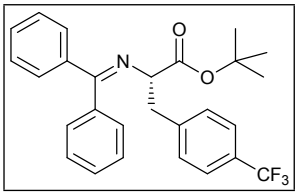
Fig.5 The HPLC chromatogram of racemic *tert*-butyl 3-phenyl-2-(diphenylmethyleneamino) propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	12.846	262.8	13.6	0.3231	0.9	1.848
2	15.254	13954.4	453.1	0.5133	0.595	98.152

Fig.6 The HPLC chromatogram of *tert*-butyl 3-phenyl-2-(diphenylmethyleneamino)propanoate catalyzed by **SiO_2@CDPTC**

***tert*-Butyl 3-(4-trifluoromethylphenyl)-2-(diphenylmethyleneamino)propanoate (Entry 1 in Table 2).**



^{1}H NMR (300.1 MHz, $CDCl_3$, TMS): δ 7.54 (d, ^3J = 7.1 Hz, 2H, Ph-H), 7.40 (d, ^3J = 7.9 Hz, 2H, Ph-H), 7.37−7.21 (m, 6H, Ph-H), 7.13 (d, ^3J = 7.9 Hz, 2H, Ph-H), 6.58 (d, ^3J = 6.4 Hz, 2H, Ph-H), 4.10 (dd, ^3J = 4.4 Hz, 4.4 Hz, 1H, NCH), 3.27−3.14 (m, 2H, CH_2), 1.41 (s, 9H, CH_3); ^{13} C NMR (75.0 MHz, $CDCl_3$, TMS): δ 170.7, 170.4 (C=N, C=O), 142.6 (q, $^3J_{C\text{-}F}$ = 1.3 Hz), 139.2, 137.5, 136.0, 132.4, 130.3, 130.1, 130.0, 130.0, 129.7, 128.6, 128.3, 128,2, 128.1, 128.0, 127.4, 126.0 (Ph), 125.2 (q, $^2J_{C\text{-}F}$ = 3.8 Hz), 124.9 (q, $^1J_{C\text{-}F}$ = 3.8 Hz, CF_3), 81.4 (O-C), 67.4 (NCH), 39.2 (CH_2), 27.9 (CH_3); HPLC analysis: Phenomenex Lux 5u Amylose-2, hexane/dioxane = 95/5, 254 nm, flow rate = 0.5 ml/min, retention times: 12.2 min (R), 13.9 min (S).

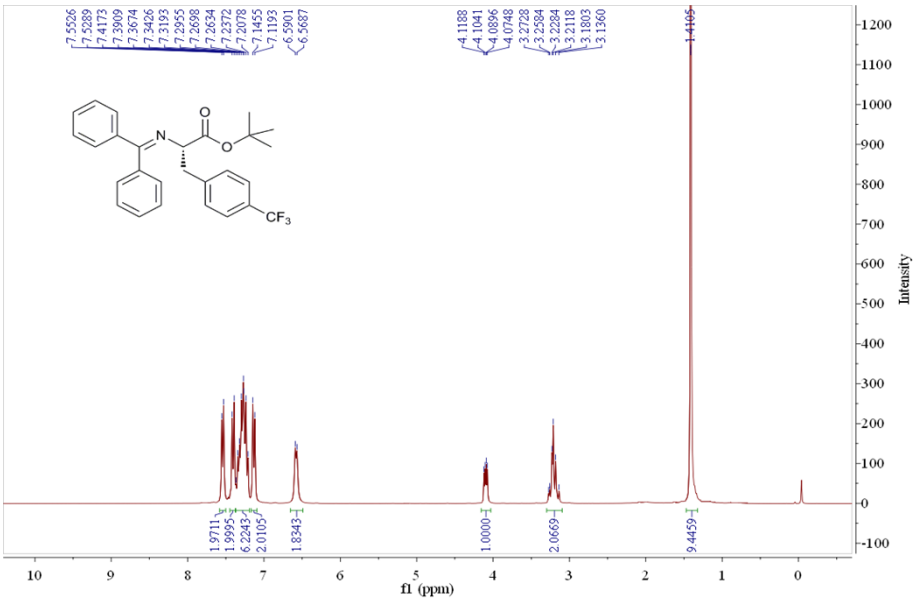


Fig.7 ^{1}H NMR spectra of *tert*-butyl 3-(4-trifluoromethylphenyl)-2-(diphenylmethyleneamino)propanoate

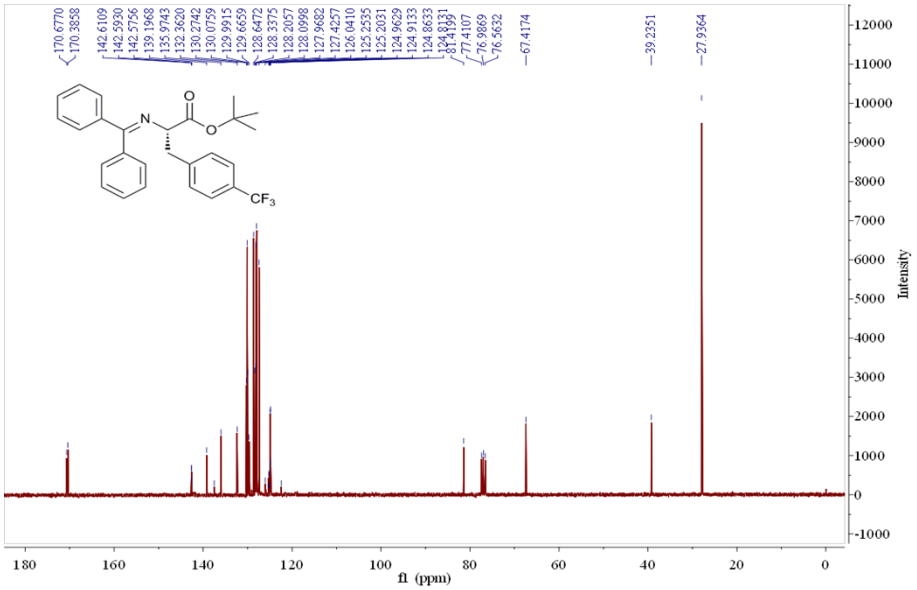
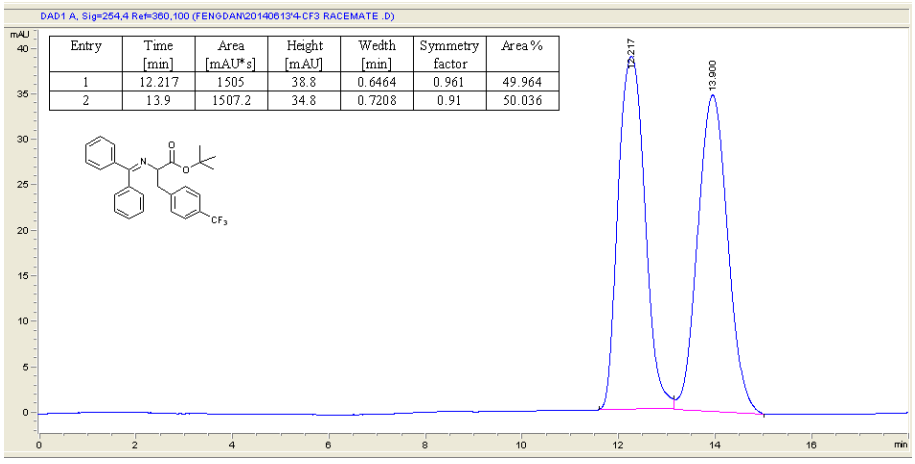
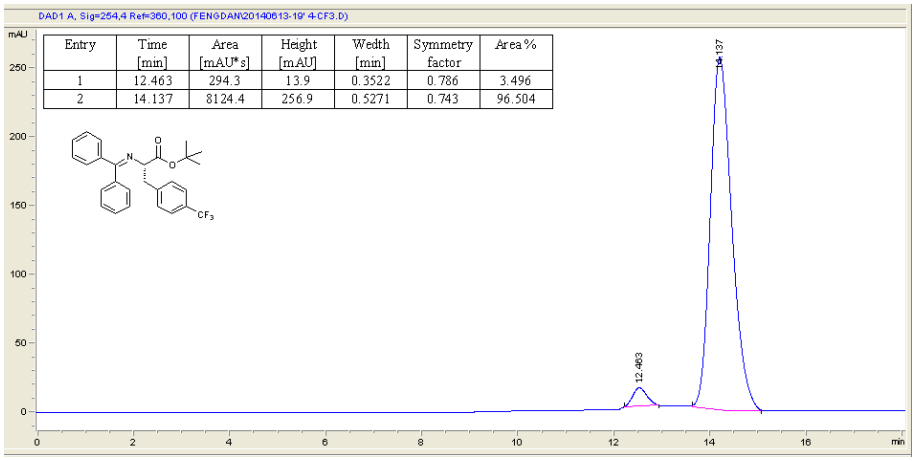


Fig.8 ^{13}C NMR spectra of *tert*-butyl 3-(4-trifluoromethylphenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	12.217	1505	38.8	0.6464	0.961	49.964
2	13.9	1507.2	34.8	0.7208	0.91	50.036

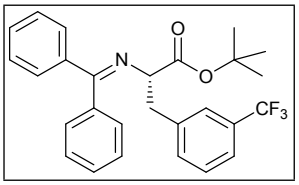
Fig.9 The HPLC chromatogram of racemic *tert*-butyl 3-(4-trifluoromethylphenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	12.463	294.3	13.9	0.3522	0.786	3.496
2	14.137	8124.4	256.9	0.5271	0.743	96.504

Fig.10 The HPLC chromatogram of *tert*-butyl 3-(4-trifluoromethylphenyl)-2-(diphenylmethyleneamino)propanoate catalyzed by **SiO_2@CDPTC**

***tert*-Butyl 3-(3-trifluoromethylphenyl)-2-(diphenylmethyleneamino)propanoate (Entry 2 in Table 2).**



^{1}H NMR (300.1 MHz, $CDCl_3$, TMS): δ 7.52 (d, ^{3}J = 7.0 Hz, 2H, Ph-H), 7.40−7.21 (m, 10H, Ph-H), 6.57 (d, ^{3}J = 6.6 Hz, 2H, Ph-H), 4.09 (dd, ^{3}J = 5.6 Hz, 5.6 Hz, 1H, NCH), 3.23−3.21 (m, 2H, CH_2), 1.41 (s, 9H, CH_3); ^{13}C NMR (75.0 MHz, $CDCl_3$, TMS): δ 170.8, 170.3 (C=N, C=O), 139.3, 139.2, 136.1, 133.4, 133.4, 132.4, 130.5, 130.2, 130.1, 130.0, 128.6, 128.4, 128.3, 128.2, 128,1, 127.9, 127.4, 126.4 (q, $^{2}J_{C\text{-}F}$ = 3.7 Hz, CF_3), 125.9 (Ph), 123.0 (q, $^{1}J_{C\text{-}F}$ = 3.8 Hz, CF_3), 81.4 (O-C), 67.3 (NCH), 39.2 (CH_2), 27.9 (CH_3); HPLC analysis: Daicel Chiralpak OD-H column, hexane/dioxane = 95/5, 254 nm, flow rate = 0.5 ml/min, retention times: 13.4 min (S), 15.0 min (R).

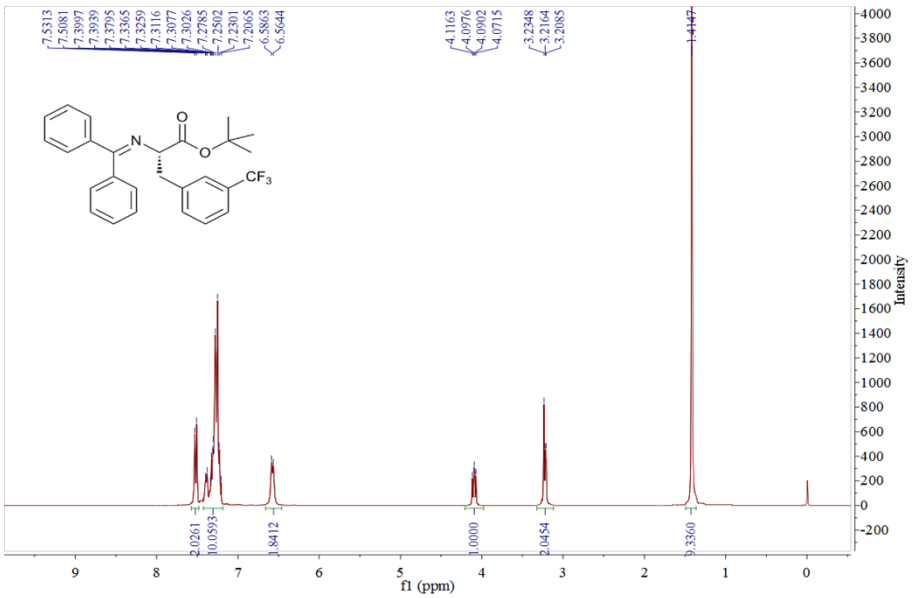


Fig.11 ^{1}H NMR spectra of *tert*-butyl 3-(3-trifluoromethylphenyl)-2-(diphenylmethyleneamino)propanoate

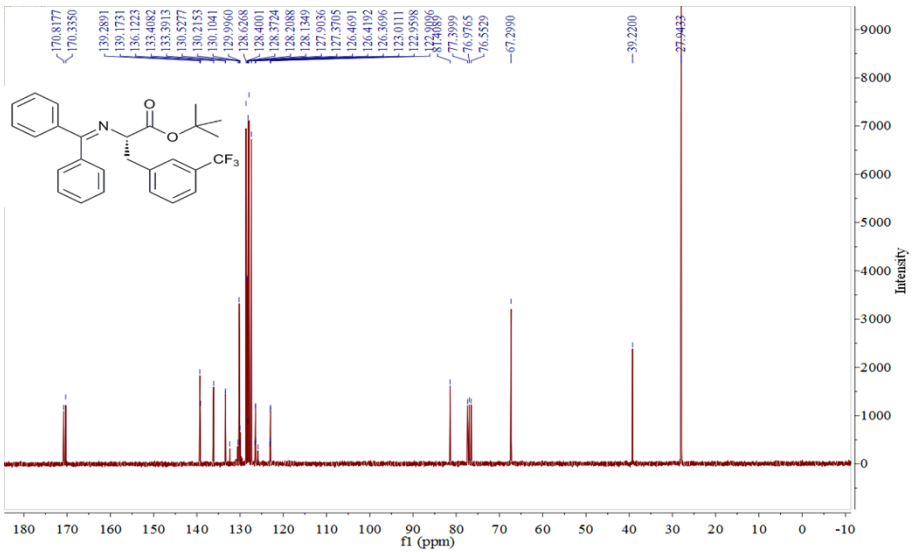
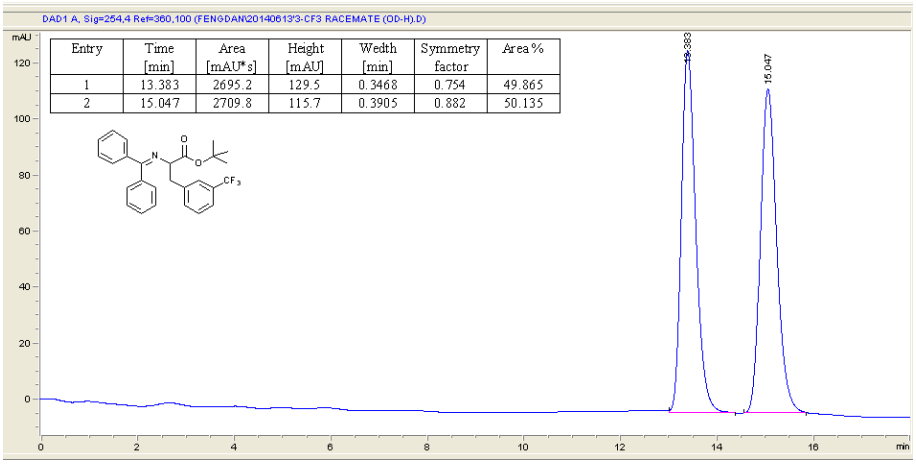
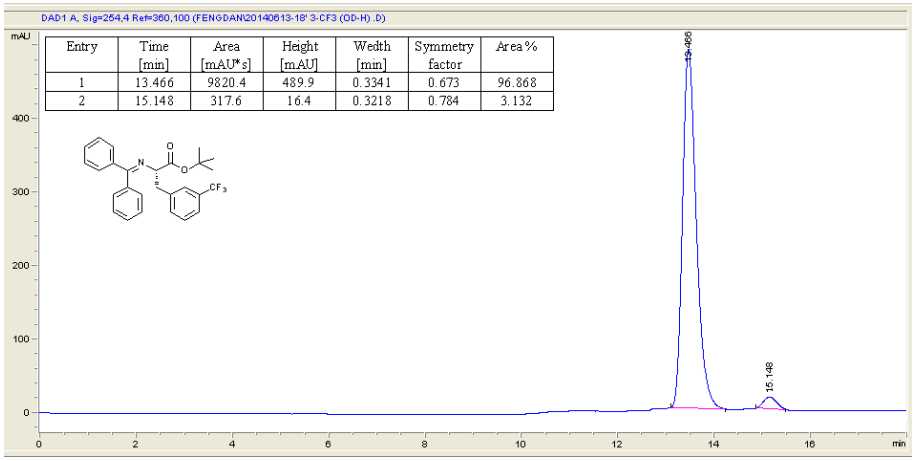


Fig.12 ^{13}C NMR spectra of *tert*-butyl 3-(3-trifluoromethylphenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	13.383	2695.2	129.5	0.3468	0.754	49.865
2	15.047	2709.8	115.7	0.3905	0.882	50.135

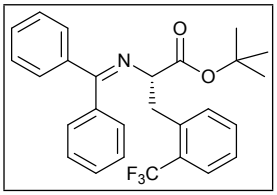
Fig.13 The HPLC chromatogram of racemic *tert*-butyl 3-(3-trifluoromethylphenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	13.466	9820.4	489.9	0.3341	0.673	96.868
2	15.148	317.6	16.4	0.3218	0.784	3.132

Fig.14 The HPLC chromatogram of *tert*-butyl 3-(3-trifluoromethylphenyl)-2-(diphenylmethyleneamino)propanoate catalyzed by **SiO_2@CDPTC**

***tert*-Butyl 3-(2-trifluoromethylphenyl)-2-(diphenylmethyleneamino)propanoate (Entry 3 in Table 2)**.



^{1}H NMR (300.1 MHz, $CDCl_3$, TMS): δ 7.76 (d, ^3J = 7.1 Hz, 1H, Ph-H), 7.57−7.41 (m, 4H, Ph-H), 7.35−7.15 (m, 7H, Ph-H), 6.43 (d, ^3J = 6.4 Hz, 2H, Ph-H), 4.13 (dd, ^3J = 3.5 Hz, 3.5 Hz, 1H, NCH), 3.50−3.22 (m, 2H, CH_2), 1.39 (s, 9H, CH_3); ^{13}C NMR (75.0 MHz, $CDCl_3$, TMS): δ 170.7, 170.5 (C=N, C=O), 139.2, 136.8 (q, $^2J_{C\text{-}F}$ = 1.6 Hz), 136.0, 133.3, 132.4, 131.1, 130.2, 131.0, 129.6, 128.7, 128.2, 128,1, 127.9, 127.9, 127.3, 126.3, 126.0 (Ph), 125.7 (q, $^1J_{C\text{-}F}$ = 5.7 Hz, CF_3), 81.2 (O-C), 66.5 (NCH), 36.0 (CH_2), 27.9 (CH_3); HPLC analysis: Phenomenex Lux 5u Amylose-2, hexane/dioxane = 95/5, 254 nm, flow rate = 0.5 ml/min, retention times: 12.2 min (R), 14.8 min (S).

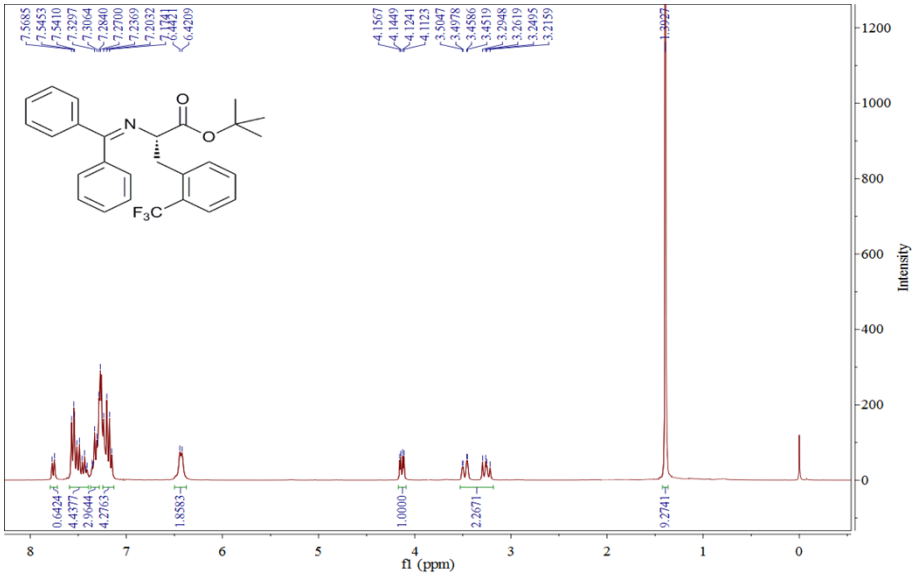


Fig.15 ^{1}H NMR spectra of *tert*-butyl 3-(2-trifluoromethylphenyl)-2-(diphenylmethyleneamino)propanoate

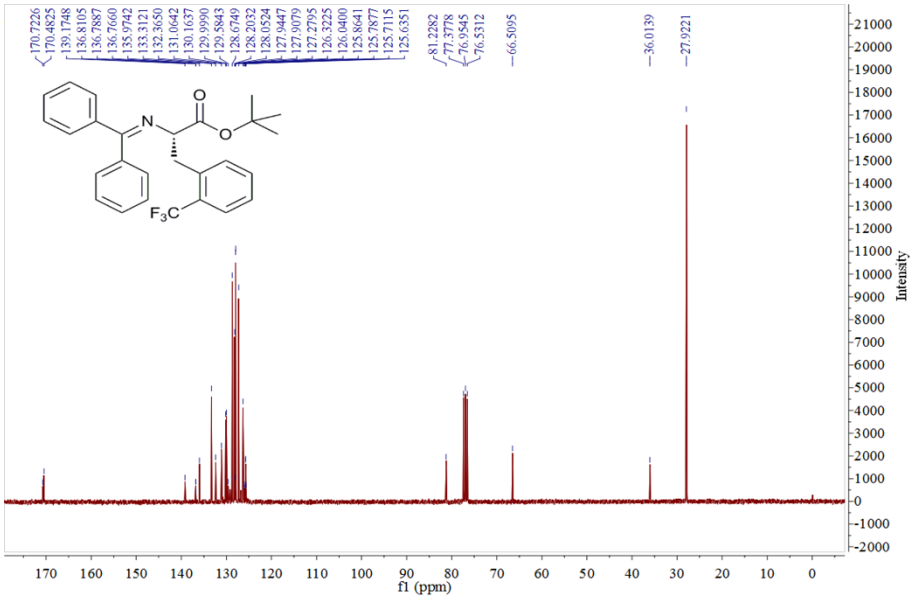
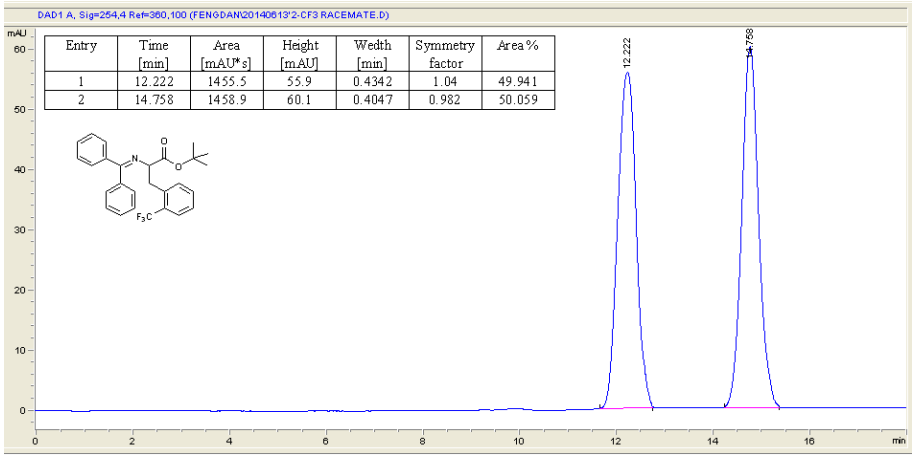
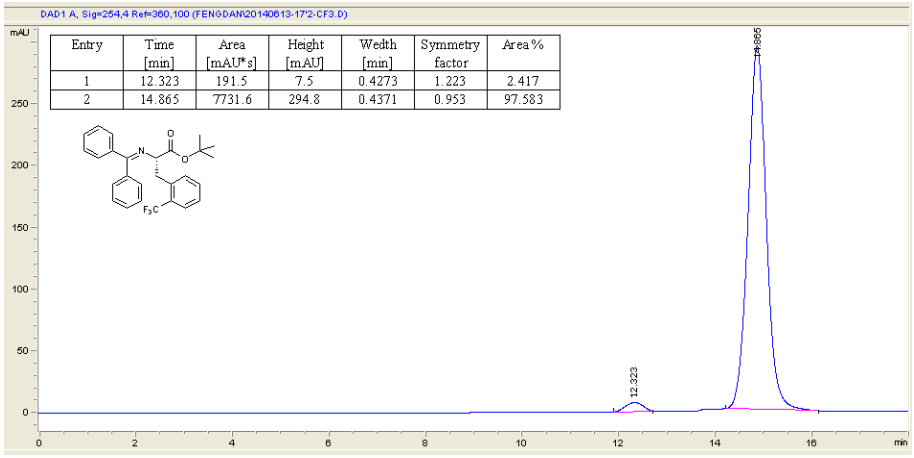


Fig.16 ^{13}C NMR spectra of *tert*-butyl 3-(2-trifluoromethylphenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	12.222	1455.5	55.9	0.4342	1.04	49.941
2	14.758	1458.9	60.1	0.4047	0.982	50.059

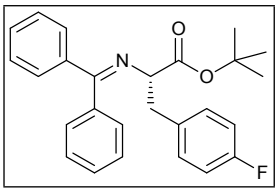
Fig.17 The HPLC chromatogram of racemic *tert*-butyl 3-(2-trifluoromethylphenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	12.323	191.5	7.5	0.4273	1.223	2.417
2	14.865	7731.6	294.8	0.4371	0.953	97.583

Fig.18 The HPLC chromatogram of *tert*-butyl 3-(2-trifluoromethylphenyl)-2-(diphenylmethyleneamino)propanoate catalyzed by **SiO_2@CDPTC**

***tert*-Butyl 3-(4-fluorophenyl)-2-(diphenylmethyleneamino)propanoate (Entry 4 in Table 2)**.



^{1}H NMR (300.1 MHz, $CDCl_3$, TMS): δ 7.53 (d, ^3J = 6.9 Hz, 2H, Ph-H), 7.35−7.21 (m, 6H, Ph-H), 7.00−6.80 (m, 4H, Ph-H), 6.62 (d, ^3J = 6.5 Hz, 2H, Ph-H), 4.04 (dd, ^3J = 4.6 Hz, 4.7 Hz, 1H, NCH), 3.19−3.05 (m, 2H, CH_2), 1.40 (s, 9H, CH_3); ^{13}C NMR (75.0 MHz, $CDCl_3$, TMS): δ 170.6, 170.4 (C=N, C=O), 163.1, 160.0, 139.3, 134.0, 132.4, 131.2 (d, $^2J_{C\text{-}F}$ = 7.8 Hz, F), 131.1, 130.9, 130.2, 130.0, 128.6, 128.3, 128.2, 128.1, 128,0, 127.5 (Ph), 114.7, (d, $^1J_{C\text{-}F}$ = 20.9 Hz, F), 81.2 (O-C), 67.7 (NCH), 38.7 (CH_2), 28.0 (CH_3); HPLC anal- ysis: Phenomenex Lux 5u Amylose-2, hexane/dioxane = 95/5, 254 nm, flow rate = 0.5 ml/min, retention times: 12.7 min (R), 14.7 min (S).

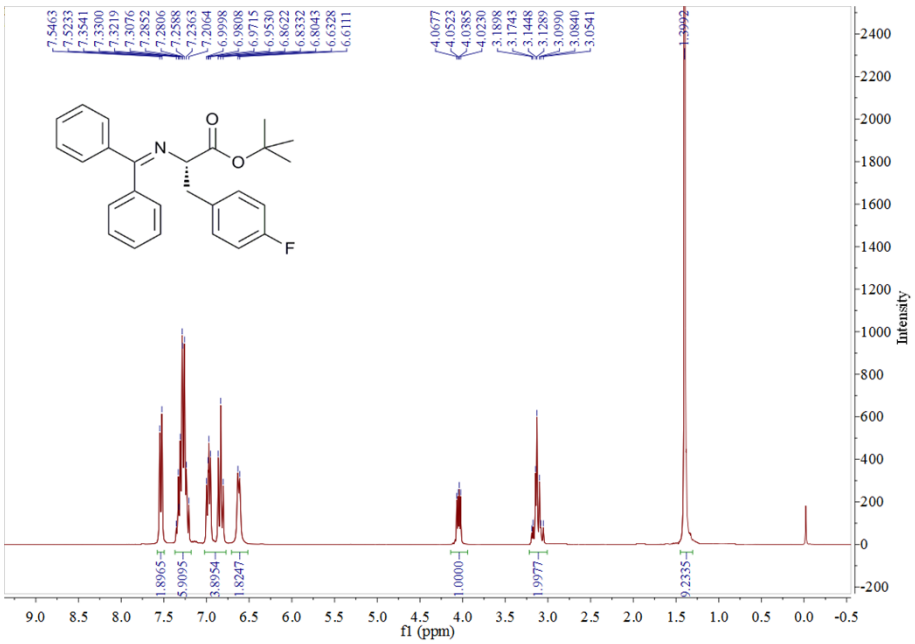


Fig.19 ^{1}H NMR spectra of *tert*-butyl 3-(4-fluorophenyl)-2-(diphenylmethyleneamino)propanoate

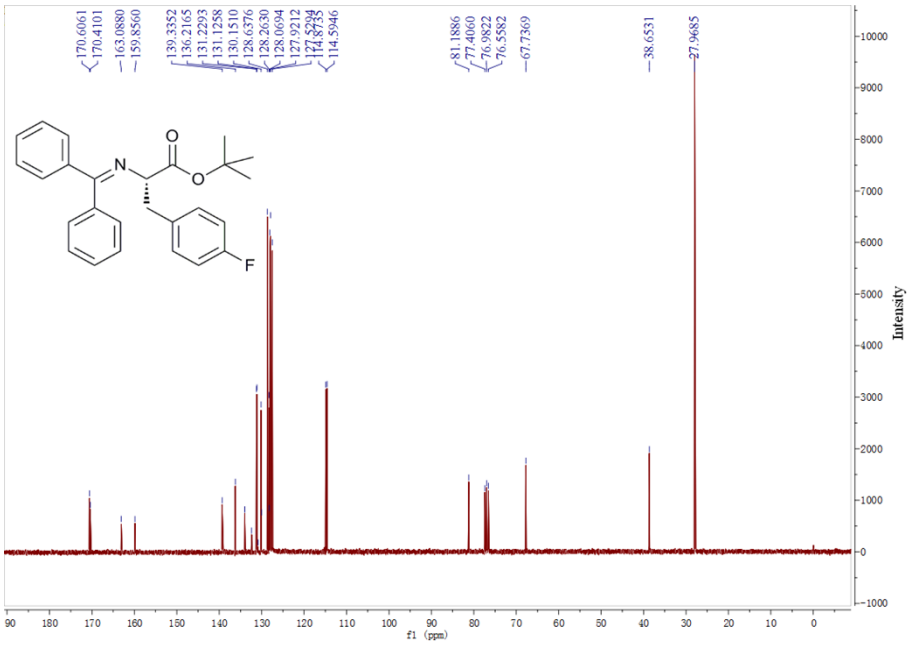
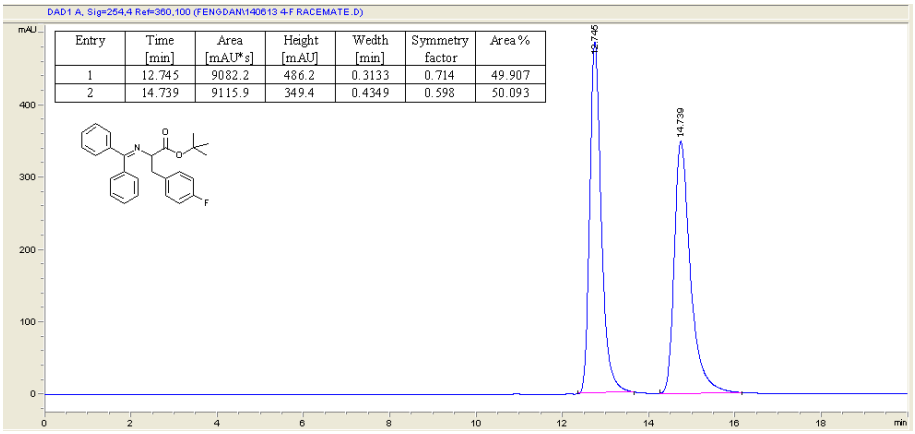
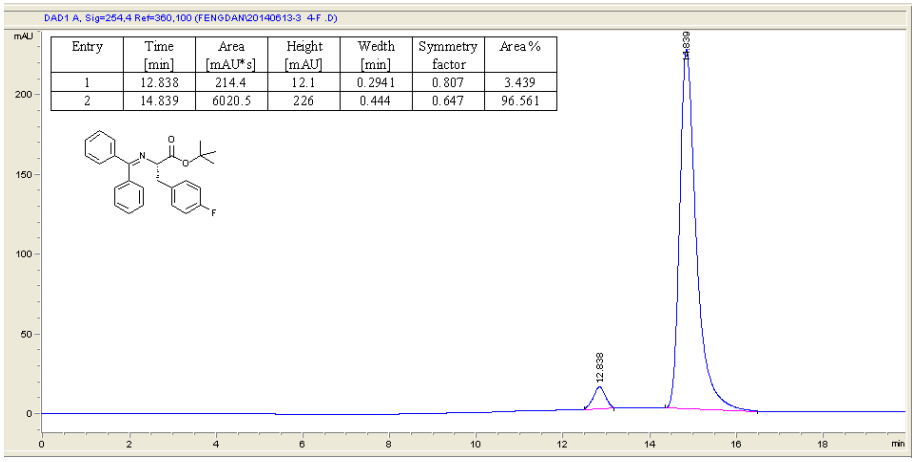


Fig.20 ^{13}C NMR spectra of *tert*-butyl 3-(4-fluorophenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	12.745	9082.2	486.2	0.3133	0.714	49.907
2	14.739	9115.9	349.4	0.4349	0.598	50.093

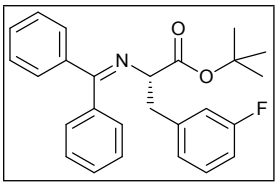
Fig.21 The HPLC chromatogram of racemic *tert*-butyl 3-(4-fluorophenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	12.838	214.4	12.1	0.2941	0.807	3.439
2	14.839	6020.5	226	0.444	0.647	96.561

Fig.22 The HPLC chromatogram of *tert*-butyl 3-(4-fluorophenyl)-2-(diphenylmethyleneamino)propanoate catalyzed by **SiO_2@CDPTC**

***tert*-Butyl 3-(3-fluorophenyl)-2-(diphenylmethyleneamino)propanoate (Entry 5 in Table 2)**.



^{1}H NMR (300.1 MHz, $CDCl_3$, TMS): δ 7.49 (d, ^{3}J = 6.7 Hz, 2H, Ph-H), 7.26−7.19 (m, 7H, Ph-H), 7.08 (q, ^{3}J = 6.6 Hz, 1H, Ph-H), 6.79−6.62 (m, 4H, Ph-H), 6.66 (d, ^{3}J = 6.6 Hz, 2H, Ph-H), 4.04 (dd, ^{3}J = 3.8 Hz, 3.8 Hz, 1H, NCH), 3.17−3.04 (m, 2H, CH_2), 1.37 (s, 9H, CH_3); ^{13}C NMR (75.0 MHz, $CDCl_3$, TMS): δ 170.5, 170.4 (C=N, C=O), 164.2, 160.9, 140.8 (d, $^{3}J_{C\text{-}F}$ = 7.4 Hz, F), 139.3, 136.2, 132.3, 130.1, 130.0, 128.6, 128.3, 128.2, 128.1, 127.9, 127.5, 125.5, 125.4 (C-Ph), 116.4 (d, $^{2}J_{C\text{-}F}$ = 20.9 Hz, F), 112.9 (d, $^{1}J_{C\text{-}F}$ = 20.9 Hz, F), 81.2 (O-C), 67.4 (NCH), 39.2 (CH_2), 27.9 (CH_3); HPLC analysis: Phenomenex Lu5x 5u Amylose-2, hexane/dioxane = 95/5, 254 nm, flow rate = 0.5 ml/min, retent- ion times: 12.7 min (R), 14.8 min (S).

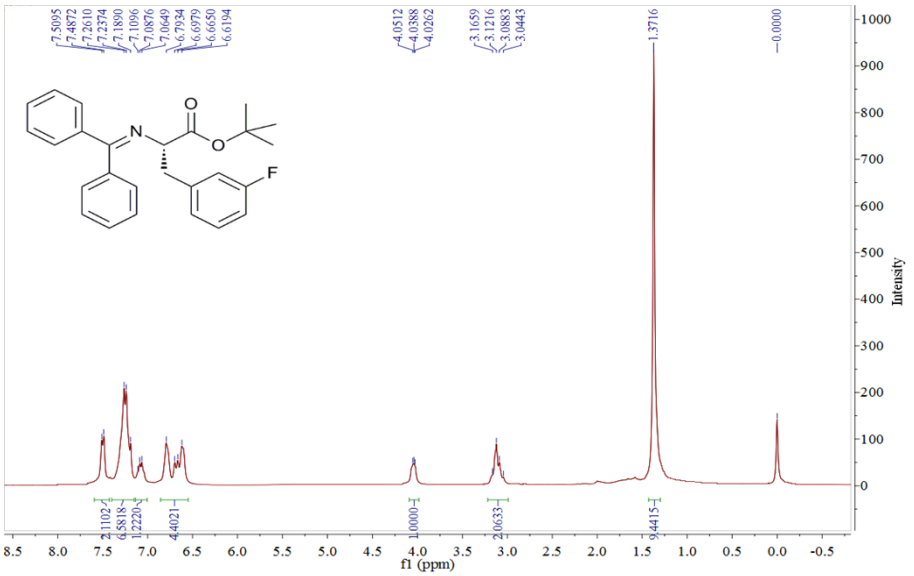


Fig.23 ^{1}H NMR spectra of *tert*-butyl 3-(3-fluorophenyl)-2-(diphenylmethyleneamino)propanoate

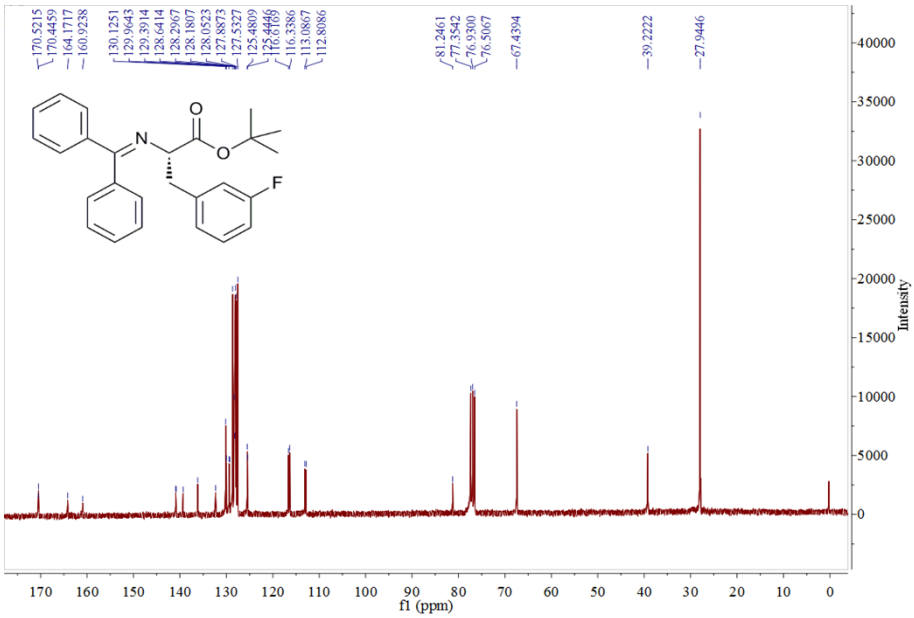
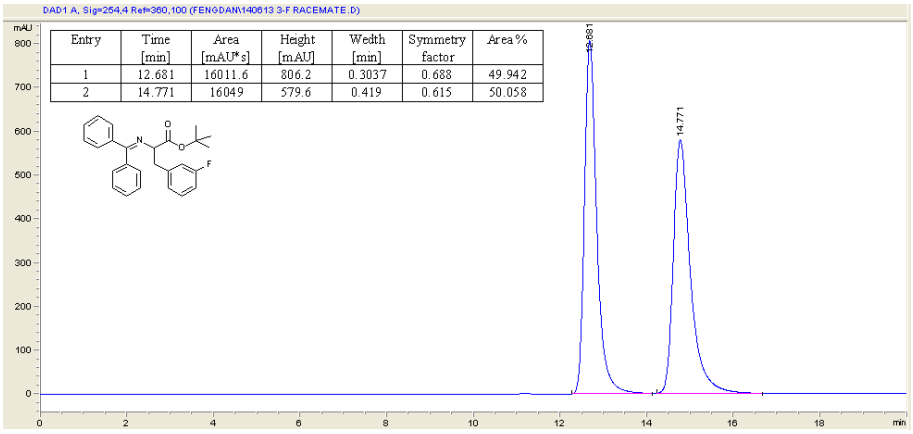
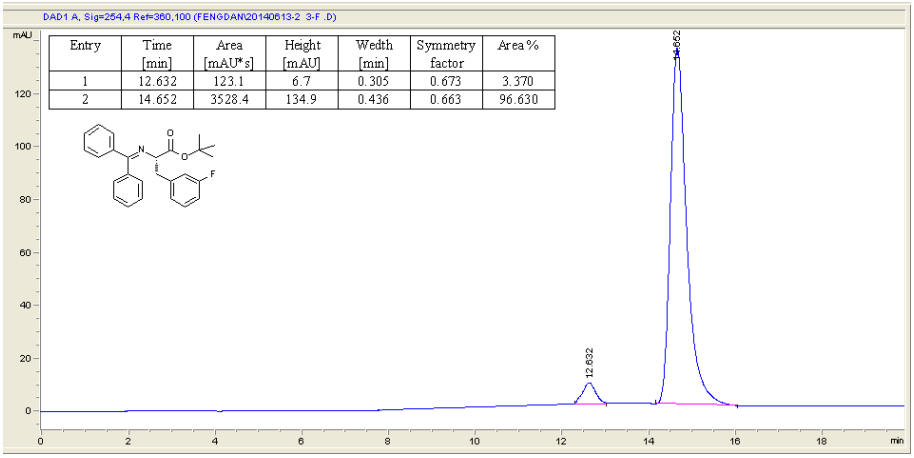


Fig.24 ^{13}C NMR spectra of *tert*-butyl 3-(3-fluorophenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	12.681	16011.6	806.2	0.3037	0.688	49.942
2	14.771	16049	579.6	0.419	0.615	50.058

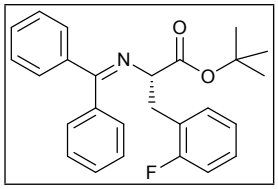
Fig.25 The HPLC chromatogram of racemic *tert*-butyl 3-(3-fluorophenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	12.632	123.1	6.7	0.305	0.673	3.370
2	14.652	3528.4	134.9	0.436	0.663	96.630

Fig.26 The HPLC chromatogram of *tert*-butyl 3-(3-fluorophenyl)-2-(diphenylmethyleneamino)propanoate catalyzed by **SiO_2@CDPTC**

***tert*-Butyl 3-(2-fluorophenyl)-2-(diphenylmethyleneamino)propanoate (Entry 6 in Table 2).**



^{1}H NMR (300.1 MHz, $CDCl_3$, TMS): δ 7.56 (d, ^3J = 7.1 Hz, 2H, Ph-H), 7.37−7.25 (m, 6H, Ph-H), 7.16−7.11 (m, 2H, Ph-H), 6.98−6.87 (m, 2H, Ph-H), 6.66 (d, ^3J = 6.6 Hz, 2H, Ph-H), 4.19 (dd, ^3J = 4.4 Hz, 4.4 Hz, 1H, NCH), 3.36−3.12 (m, 2H, CH_2), 1.44 (s, 9H, CH_3); ^{13}C NMR (75.0 MHz, $CDCl_3$, TMS): δ 170.6, 170.5 (C=N, C=O), 162.9, 159.7, 139.4, 136.1, 132.3, 130.1, 130.0, 128.7, 128.2, 128.2, 128.0, 128.0, 127.9, 127.9, 127.6 (C-Ph), 125.2 (d, $^3J_{C\text{-}F}$ = 15.5 Hz, F), 123.5 (d, $^2J_{C\text{-}F}$ = 3.5 Hz, F), 114.9 (d, $^1J_{C\text{-}F}$ = 21.9 Hz, F), 81.2 (O-C), 66.0 (NCH), 32.6 (CH_2), 27.9 (CH_3); HPLC analysis: Phenomenex Lux 5u Amylose-2, hexane/dioxane = 95/5, 254 nm, flow rate = 0.5 ml/min, retention times: 13.2 min (R), 15.6 min (S).

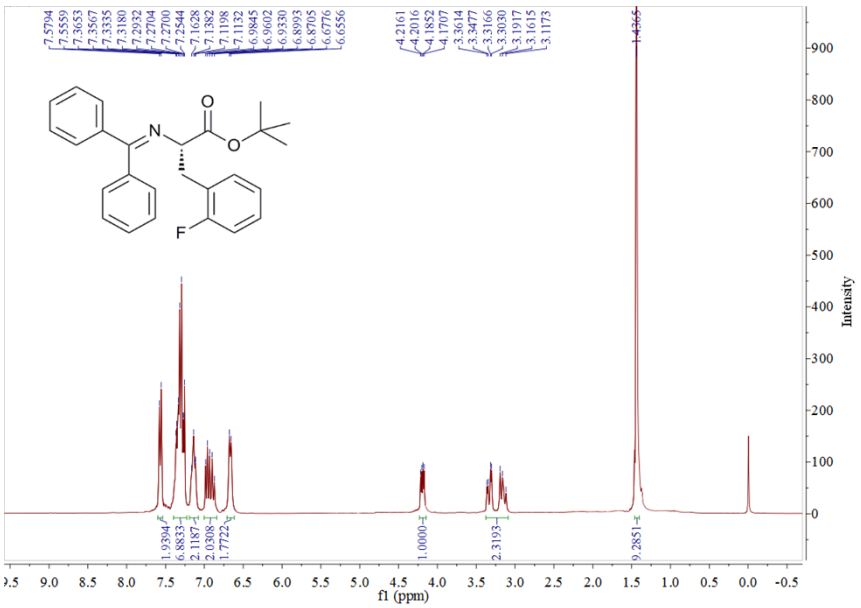


Fig.27 ^{1}H NMR spectra of *tert*-butyl 3-(2-fluorophenyl)-2-(diphenylmethyleneamino)propanoate

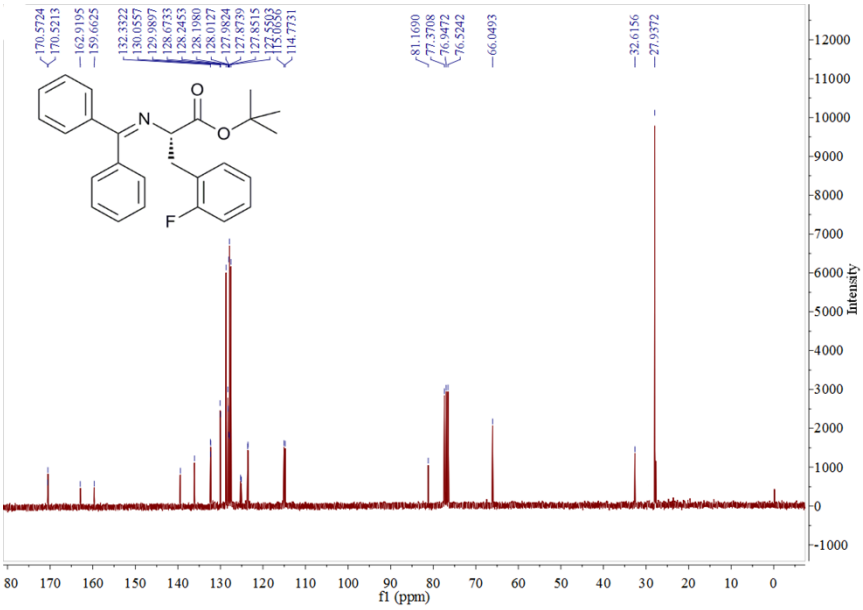
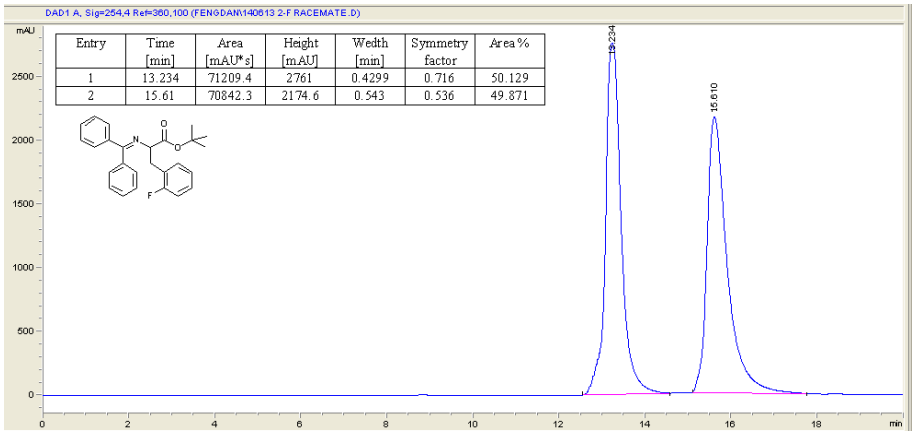


Fig.28 ^{13}C NMR spectra of *tert*-butyl 3-(2-fluorophenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	13.234	71209.4	2761	0.4299	0.716	50.129
2	15.61	70842.3	2174.6	0.543	0.536	49.871

Fig.29 The HPLC chromatogram of racemic

tert-butyl 3-(2-fluorophenyl)-2-(diphenylmethyleneamino)propanoate

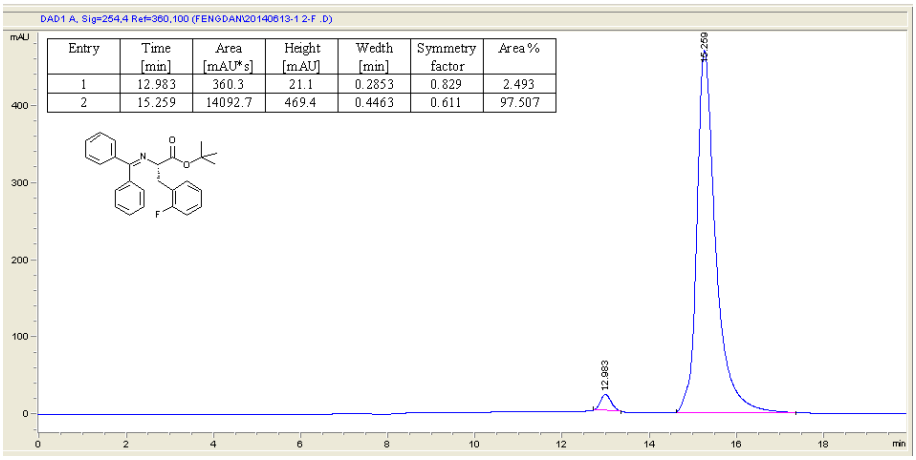
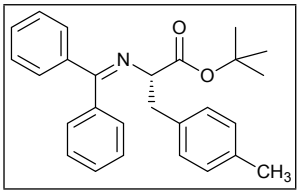


Fig.30 The HPLC chromatogram of *tert*-butyl 3-(2-fluorophenyl)-2-(diphenylmethyleneamino)propanoate catalyzed by **SiO_2@CDPTC**

***tert*-Butyl 3-(4-methylphenyl)-2-(diphenylmethyleneamino)propanoate (Entry 7 in Table 2).**



^{1}H NMR (300.1 MHz, $CDCl_3$, TMS): δ 7.81 (d, ^3J = 7.2 Hz, 1H, Ph-H), 7.58 (d, ^3J = 7.1 Hz, 2H, Ph-H), 7.39−7.25 (m, 6H, Ph-H), 6.96 (q, ^3J = 7.9 Hz, 4H, Ph-H), 6.62 (d, ^3J = 6.6 Hz, 2H, Ph-H), 4.09 (dd, ^3J = 4.4 Hz, 4.4 Hz, 1H, NCH), 3.23−3.07 (m, 2H, CH_2), 2.28 (s, 3H, Ph-CH_3), 1.44 (s, 9H, CH_3); ^{13}C NMR (75.0 MHz, $CDCl_3$, TMS): δ 170.9, 170.1 (C=N, C=O), 139.5, 137.5, 136.3, 135.5, 135.1, 132.4, 130.0, 129.6, 128.7, 128.2, 128.1, 128.0, 127.9, 127.6 (C-Ph), 81.0 (O-C), 68.0 (N-CH), 39.1 (CH_2), 28.0 (CH_3), 21.0 (Ph-CH_3); HPLC analysis: Phenomenex Lux 5u Amylose-2, hexane/dioxane = 95/5, 254 nm, flow rate = 0.5 ml/min, retention times: 13.0 min (R), 15.4 min (S).

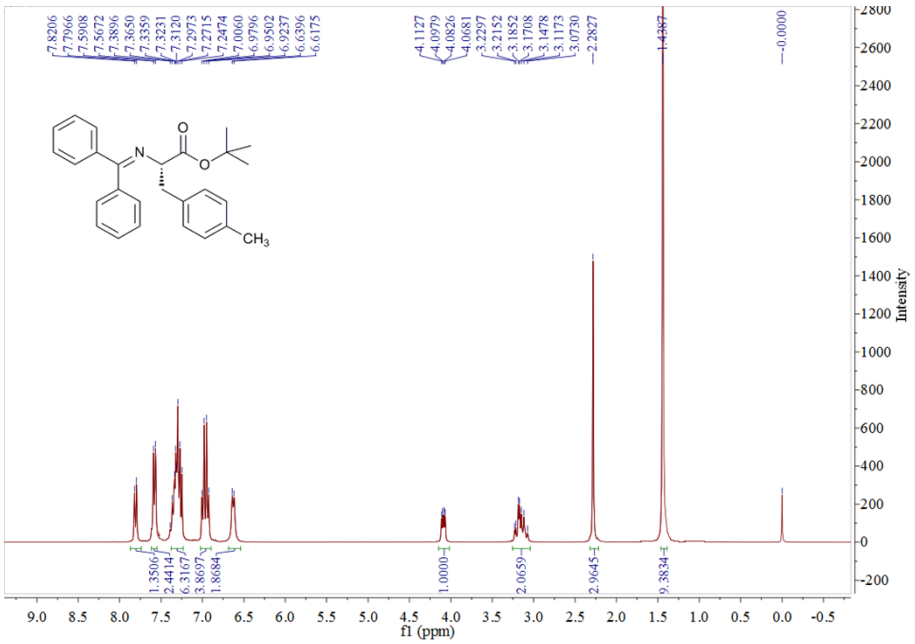


Fig.31 ^{1}H NMR spectra of *tert*-butyl 3-(4-methylphenyl)-2-(diphenylmethyleneamino)propanoate

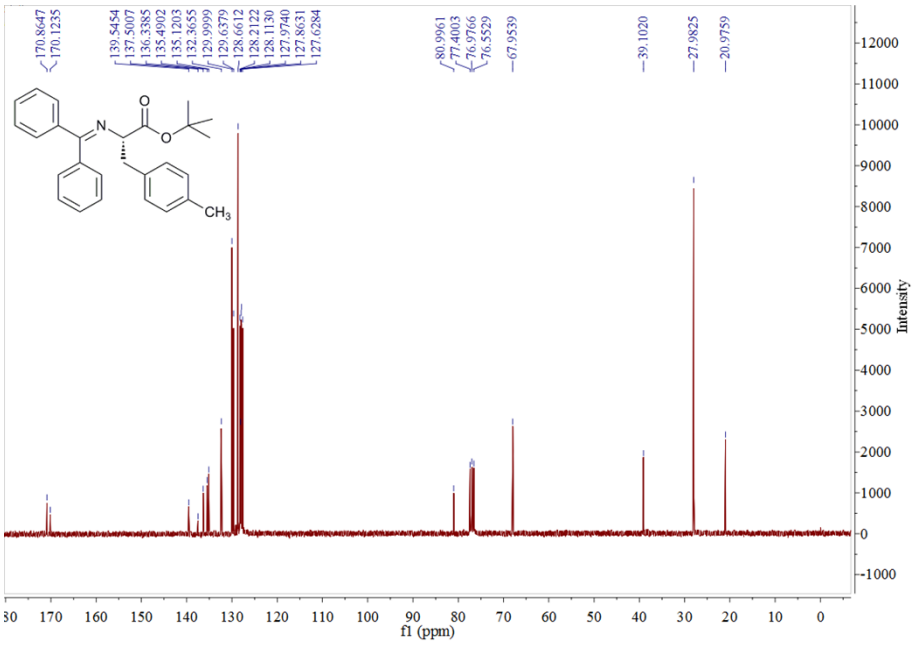
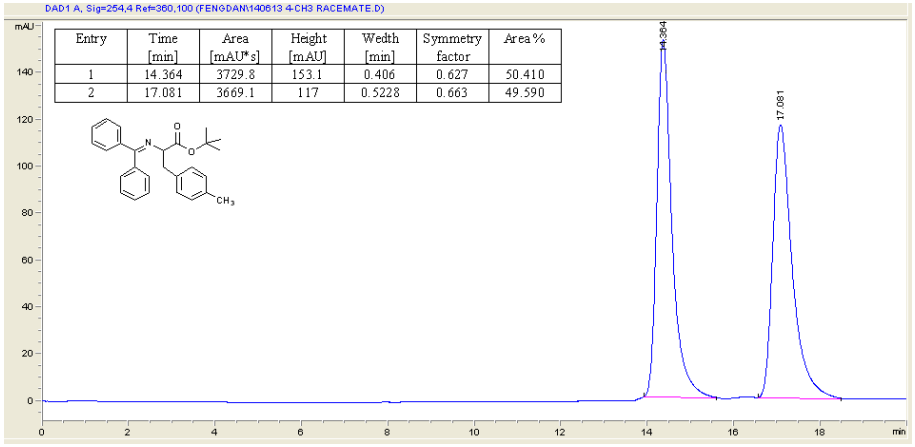
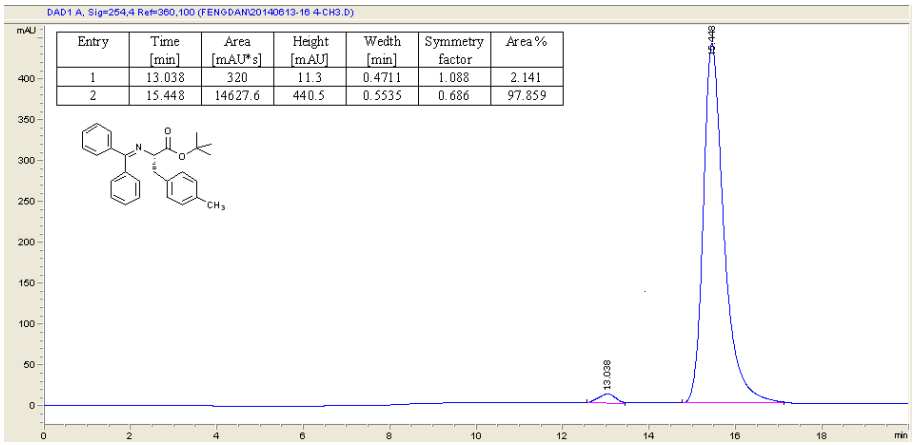


Fig.32 ^{13}C NMR spectra of *tert*-butyl 3-(4-methylphenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	14.364	3729.8	153.1	0.406	0.627	50.410
2	17.081	3669.1	117	0.5228	0.663	49.590

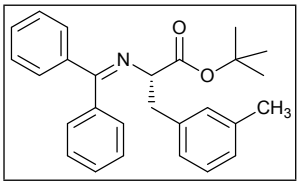
Fig.33 The HPLC chromatogram of racemic *tert*-butyl 3-(4-methylphenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	13.038	320	11.3	0.4711	1.088	2.141
2	15.448	14627.6	440.5	0.5535	0.686	97.859

Fig.34 The HPLC chromatogram of *tert*-butyl 3-(4-methylphenyl)-2-(diphenylmethyleneamino)propanoate catalyzed by **SiO_2@CDPTC**

***tert*-Butyl 3-(3-methylphenyl)-2-(diphenylmethyleneamino)propanoate (Entry 8 in Table 2).**



^{1}H NMR (300.1 MHz, $CDCl_3$, TMS): δ 7.81 (d, ^{3}J = 7.2 Hz, 1H, Ph-H), 7.62−7.46 (m, 4H, Ph-H), 7.38−7.26 (m, 7H, Ph-H), 6.59 (d, ^{3}J = 6.5 Hz, 2H, Ph-H), 4.09 (dd, ^{3}J = 4.5 Hz, 4.3 Hz, 1H, NCH), 3.23−3.08 (m, 2H, CH_2), 2.22 (s, 3H, Ph-CH_3), 1.45 (s, 9H, CH_3); ^{13}C NMR (75.0 MHz, $CDCl_3$, TMS): δ 170.8, 170.2 (C=N, C=O), 139.5, 138.1, 137.4, 136.3, 132.4, 132.3, 130.6, 130.0, 130.0, 128.6, 128.2, 128.2, 128.1, 127.9, 127.8, 127.7, 126.8, 126.7 (C-Ph), 81.0 (O-C), 67.8 (NCH), 39.4 (CH_2), 28.0 (CH_3), 21.1 (Ph-CH_3); HPLC analysis: Phenomenex Lux 5u Amylose-2, hexane/dioxane = 95/5, 254 nm, flow rate = 0.5 ml/min, retention times: 14.0 min (R), 16.3 min (S).

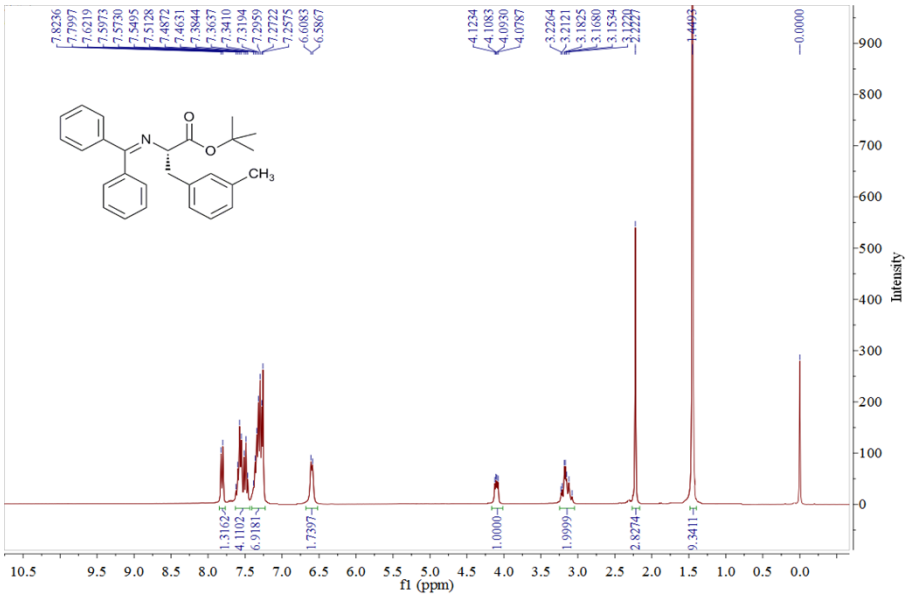


Fig.35 ^{1}H NMR spectra of *tert*-butyl 3-(3-methylphenyl)-2-(diphenylmethyleneamino)propanoate

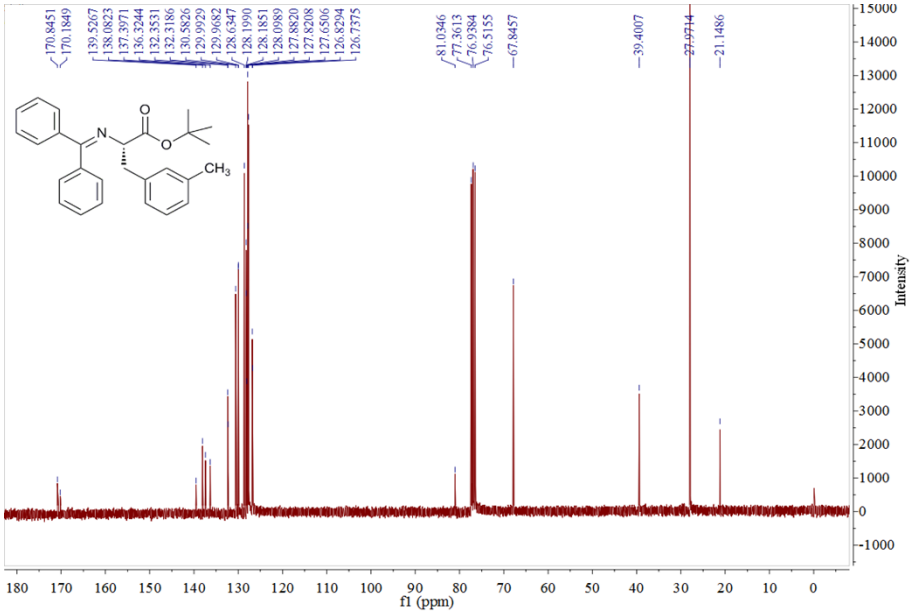
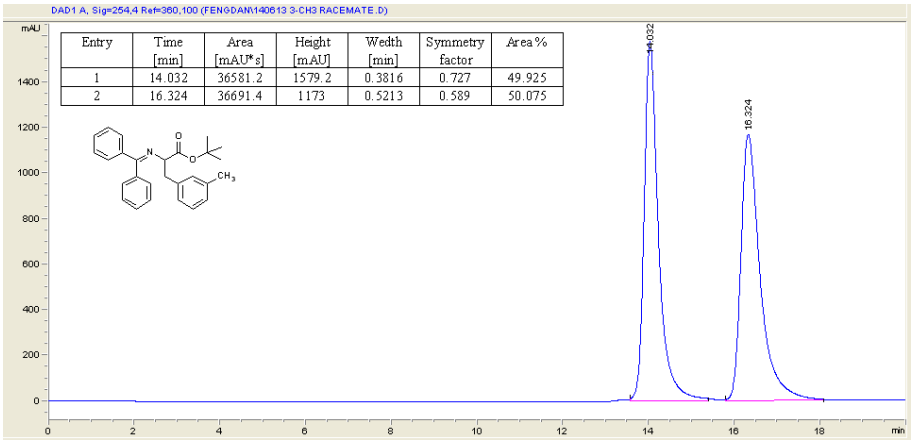
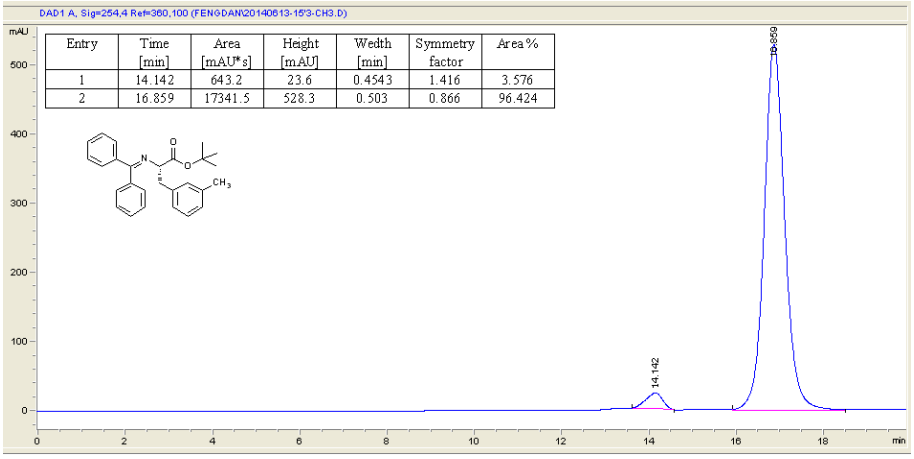


Fig.36 ^{13}C NMR spectra of *tert*-butyl 3-(3-methylphenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	14.032	36581.2	1579.2	0.3816	0.727	49.925
2	16.324	36691.4	1173	0.5213	0.589	50.075

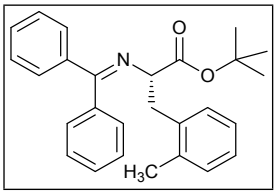
Fig.37 The HPLC chromatogram of racemic *tert*-butyl 3-(3-methylphenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	14.142	643.2	23.6	0.4543	1.416	3.576
2	16.859	17341.5	528.3	0.503	0.866	96.424

Fig.38 The HPLC chromatogram of *tert*-butyl 3-(3-methylphenyl)-2-(diphenylmethyleneamino)propanoate catalyzed by **SiO_2@CDPTC**

***tert*-Butyl 3-(2-methylphenyl)-2-(diphenylmethyleneamino)propanoate (Entry 9 in Table 2).**



^{1}H NMR (300.1 MHz, $CDCl_3$, TMS): δ 7.60 (d, ^3J = 7.2 Hz, 2H, Ph-H), 7.35−7.23 (m, 6H, Ph-H), 7.09−7.04 (m, 4H, Ph-H), 6.52 (d, ^3J = 4.1 Hz, 2H, Ph-H), 4.15 (dd, ^3J = 3.9 Hz, 3.9 Hz, 1H, NCH), 3.33−3.15 (m, 2H, CH_2), 2.06 (s, 3H, Ph-CH_3), 1.39 (s, 9H, CH_3); ^{13}C NMR (75.0 MHz, $CDCl_3$, TMS): δ 171.0, 170.1 (C=N, C=O), 139.3, 136.9, 136.3, 136.2, 132.4, 131.0, 130.0, 130.0, 129.9, 128.7, 128.2, 128.1, 127.9, 127.8, 127.6, 126.3, 125.9, 125.5 (Ph-C), 81.0 (O-C), 66.4 (NCH), 36.7 (CH_2), 28.0 (CH_3), 19.2 (Ph-CH_3); HPLC analysis: Phenomenex Lux 5u Amylose-2, hexane/dioxane = 95/5, 254 nm, flow rate = 0.5 ml/min, retention times: 12.3 min (R), 14.6 min (S).

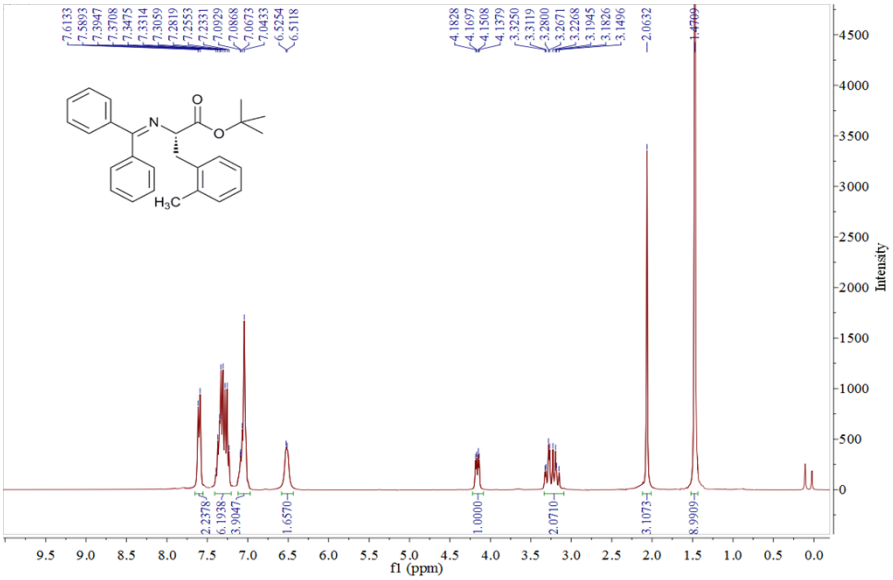


Fig.39 ^{1}H NMR spectra of *tert*-butyl 3-(2-methylphenyl)-2-(diphenylmethyleneamino)propanoate

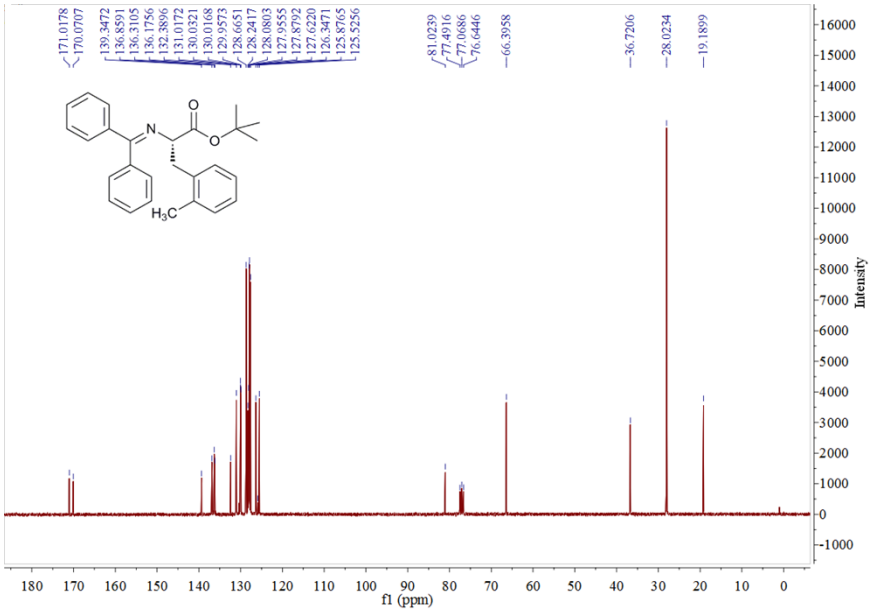
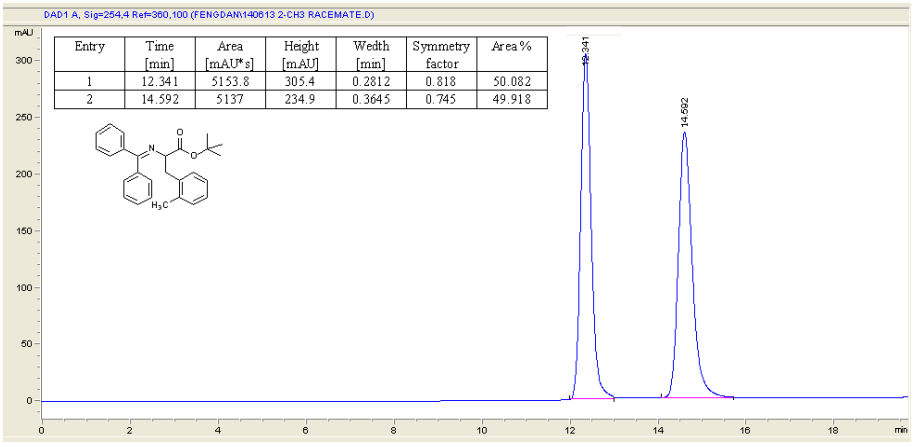
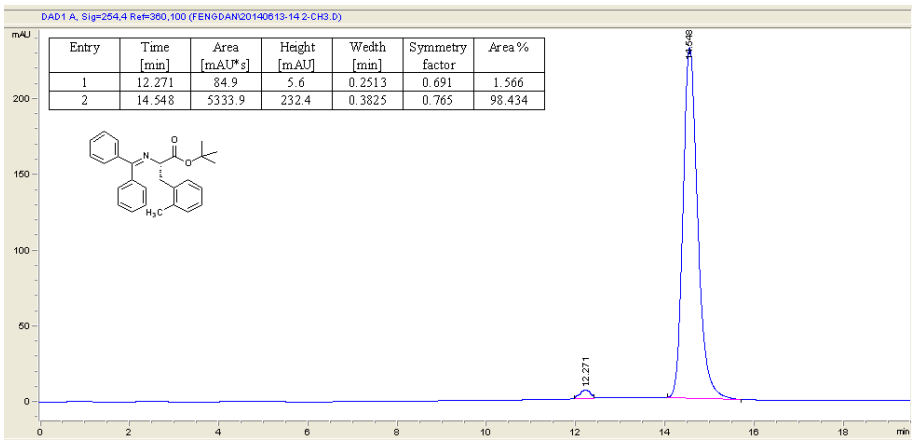


Fig.40 ^{13}C NMR spectra of *tert*-butyl 3-(2-methylphenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	12.341	5153.8	305.4	0.2812	0.818	50.082
2	14.592	5137	234.9	0.3645	0.745	49.918

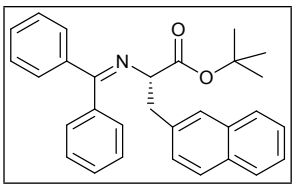
Fig.41 The HPLC chromatogram of racemic *tert*-butyl 3-(2-methylphenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	12.271	84.9	5.6	0.2513	0.691	1.566
2	14.548	5333.9	232.4	0.3825	0.765	98.434

Fig.42 The HPLC chromatogram of *tert*-butyl 3-(2-methylphenyl)-2-(diphenylmethyleneamino)propanoate catalyzed by **SiO_2@CDPTC**

tert-Butyl 3-(2-naphthyl)-2-(diphenylmethyleneamino)propanoate (Entry 10 in Table 2).



^{1}H NMR (600.1 MHz, $CDCl_3$, TMS): δ 7.78 (d, ^3J = 7.6 Hz, 1H, Ar-H), 7.73 (d, ^3J = 7.2 Hz, 1H, Ar-H), 7.64 (dd, ^3J = 17.6, 12.3 Hz, 2H, Ar-H), 7.54 (t, ^3J = 8.0 Hz, 2H, Ar-H), 7.45 (dd, ^3J = 19.8, 12.2 Hz, 2H, Ar-H), 7.40 – 7.35 (m, 2H, Ar-H), 7.32 (dd, ^3J = 15.5, 8.1 Hz, 1H, Ar-H), 7.22 – 7.11 (m, 4H, Ar-H), 6.52 (s, 2H, Ar-H), 4.22 (dd, ^3J = 9.2, 4.2 Hz, 1H, NCH), 3.34 (ddd, ^3J = 22.7, 13.5, 6.8 Hz, 2H, CH_2), 1.42 (s, 9H, CH_3); ^{13}C NMR (150.9 MHz, $CDCl_3$, TMS): δ 170.85, 170.39(C=N, C=O), 139.62, 137.71, 136.37, 135.99, 133.51, 132.38, 132.19, 130.10, 130.05, 128.75, 128.42, 128.29, 128.24, 128.02, 127.94, 127.72, 127.62, 127.56, 127.51, 126.15, 125.77, 125.25, 81.18 (O-C), 67.94 (N-C), 39.83 (CH_2), 28.11 (CH_3); HPLC analysis: Phenomenex Lux 5u Amylose-2, hexane/
/dioxane = 95/5, 254 nm, flow rate = 0.5 ml/min, retention times: 17.3 min (R), 21.1 min (S).

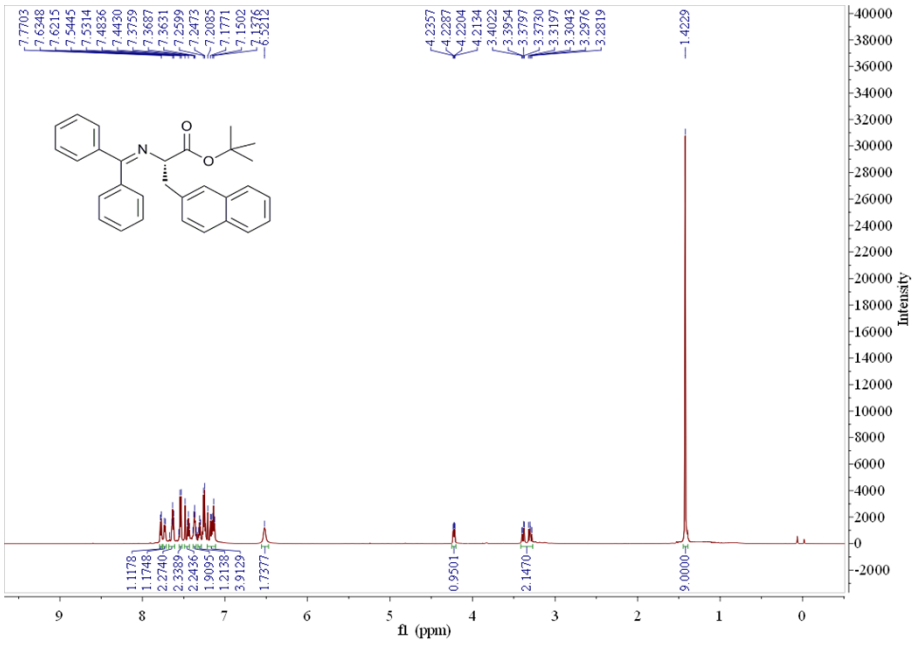


Fig.43 ^{1}H NMR spectra of *tert*-butyl 3-(2-naphthyl)-2-(diphenylmethyleneamino)propanoate

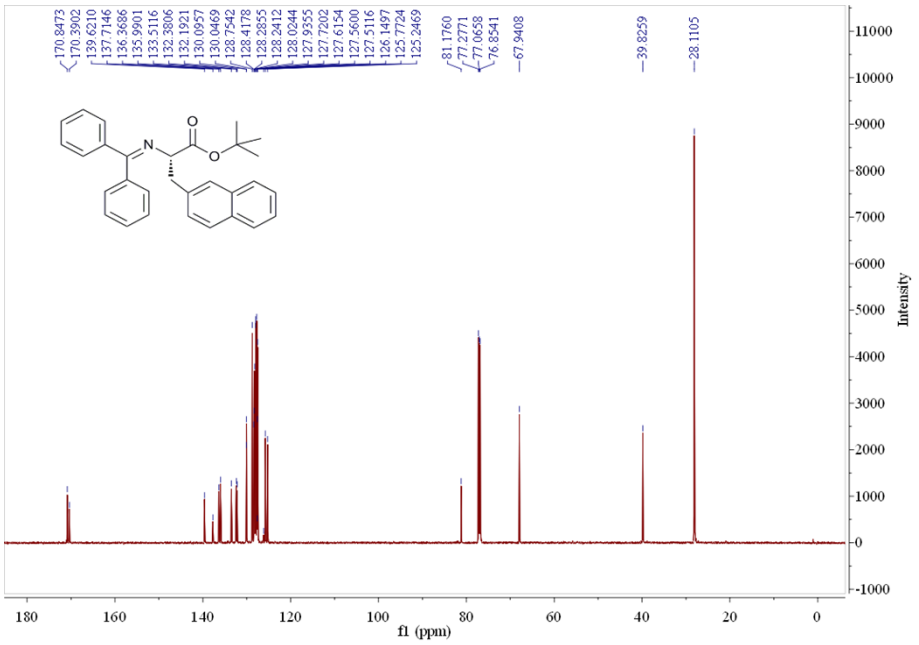
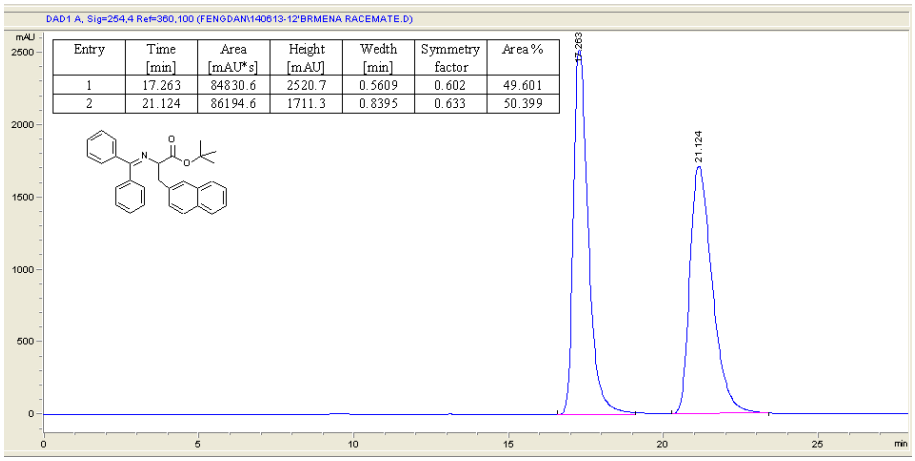
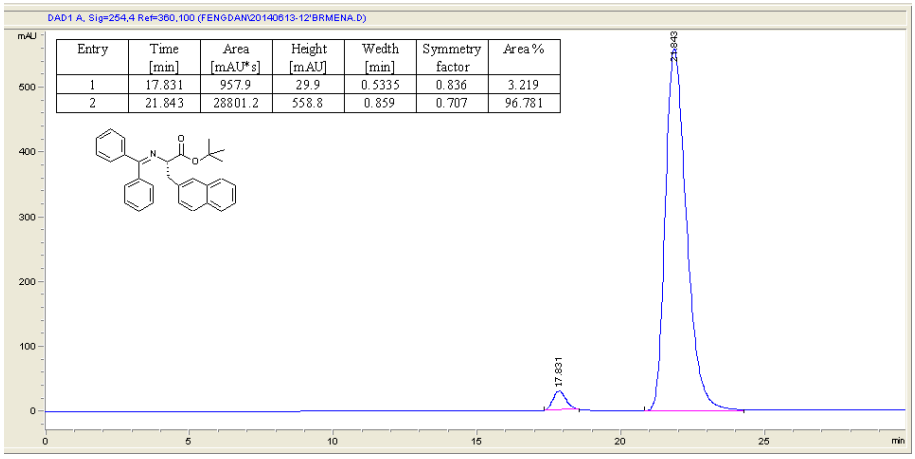


Fig.44 ^{13}C NMR spectra of *tert*-butyl 3-(2-naphthyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Wedth [min]	Symmetry factor	Area %
1	17.263	84830.6	2520.7	0.5609	0.602	49.601
2	21.124	86194.6	1711.3	0.8395	0.633	50.399

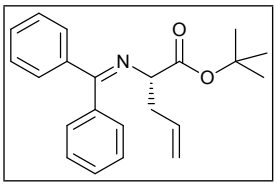
Fig.45 The HPLC chromatogram of racemic *tert*-butyl 3-(2-naphthyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Wedth [min]	Symmetry factor	Area %
1	17.831	957.9	29.9	0.5335	0.836	3.219
2	21.843	28801.2	558.8	0.859	0.707	96.781

Fig.46 The HPLC chromatogram of *tert*-butyl 3-(2-naphthyl)-2-(diphenylmethyleneamino)propanoate catalyzed by **SiO_2@CDPTC**

***tert*-Butyl 3-vinyl-2-(diphenylmethyleneamino)propanoate (Entry 11 in Table 2).**



^{1}H NMR (600.1 MHz, $CDCl_3$, TMS): δ 7.72 – 7.68 (m, 2H, Ph-H), 7.56 (d, ^3J = 7.3 Hz, 1H, Ph-H), 7.46 (t, ^3J = 7.4 Hz, 1H, Ph-H), 7.36 (t, ^3J = 7.8 Hz, 2H, Ph-H), 7.32 (dd, ^3J = 8.8, 6.2 Hz, 1H, Ph-H), 7.20 (dt, ^3J = 5.2, 3.8 Hz, 2H, Ph-H), 7.08 (dd, ^3J = 7.5, 1.6 Hz, 1H, Ph-H), 5.64 (ddt, ^3J = 17.2, 10.2, 7.1 Hz, 1H, -CH=), 4.95 (ddd, ^3J = 13.6, 11.2, 1.1 Hz, 2H, $=CH_2$), 3.93 (dd, ^3J = 7.6, 5.3 Hz, 1H, NCH), 2.62 – 2.50 (m, 2H, CH_2), 1.35 (s, 9H, CH_3); ^{13}C NMR (150.9 MHz, $CDCl_3$, TMS): 170.85, 170.08 (C=O, C=N), 139.79, 137.70, 136.72, 134.78, 132.38, 130.02, 128.84, 128.54, 128.41, 128.29, 127.99, 127.98, 117.22, 80.97(O-C), 65.92 (N-CH), 38.17 (CH_2), 28.12 (CH_3); HPLC analysis: Phenomenex Lux 5u Amylose-2, hexane/dioxane = 95/5, 254 nm, flow rate = 0.5 ml/min, retention times: 12.1 min (R), 13.6 min (S).

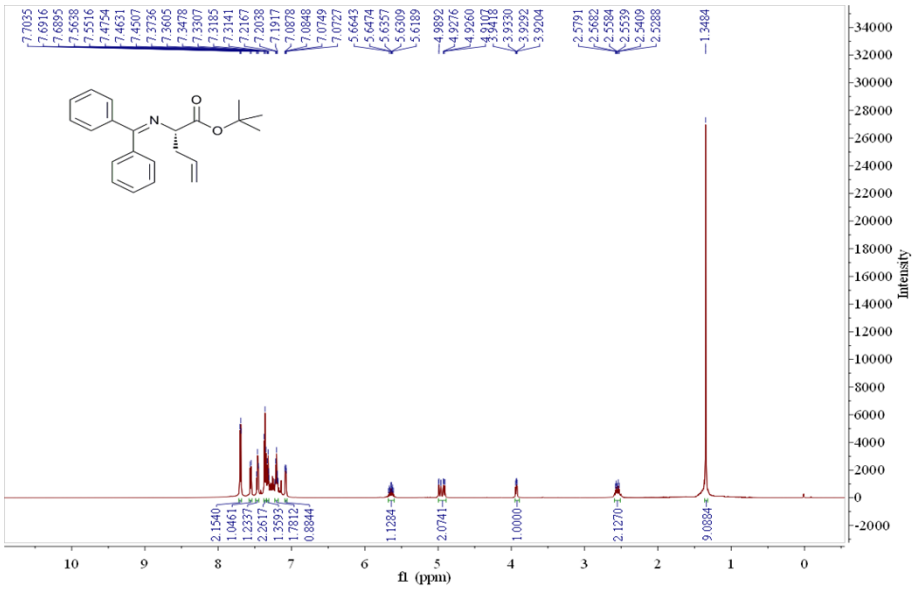


Fig.47 ^{1}H NMR spectra of *tert*-butyl 3-**vinyl**-2-(diphenylmethyleneamino)propanoate

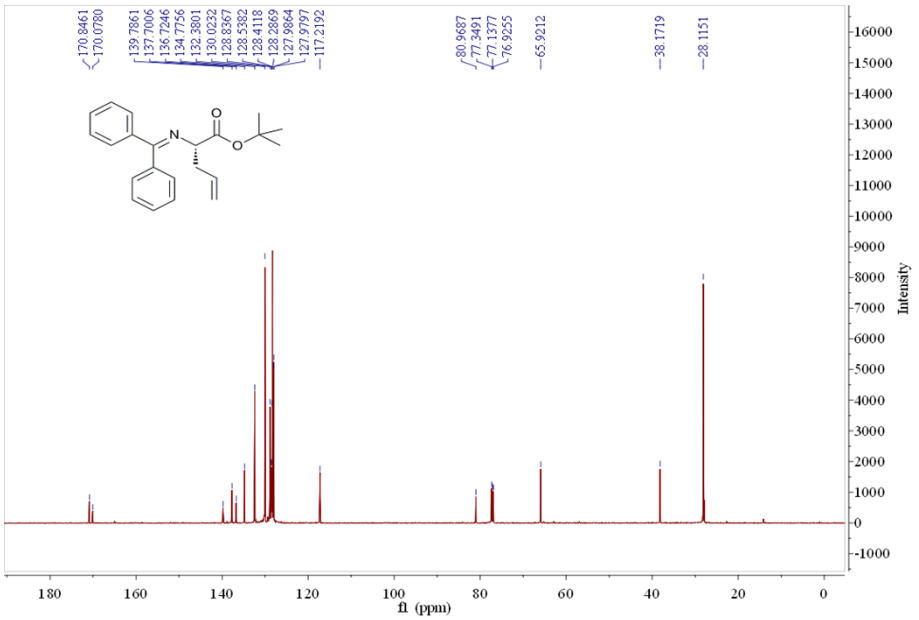
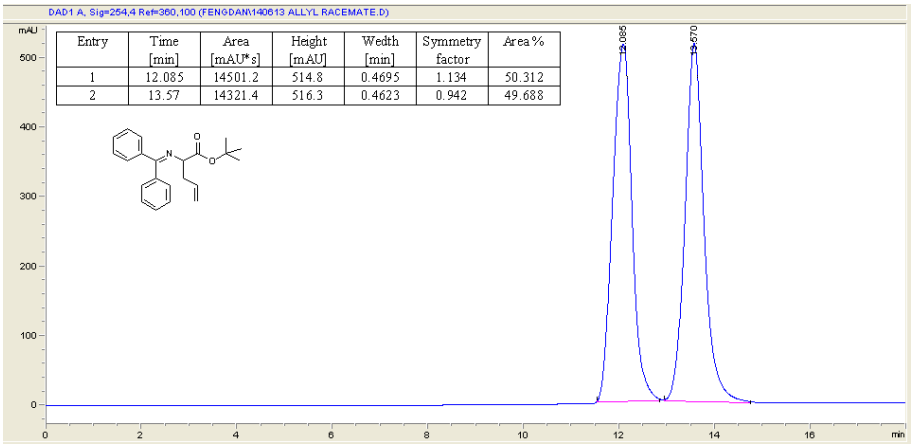
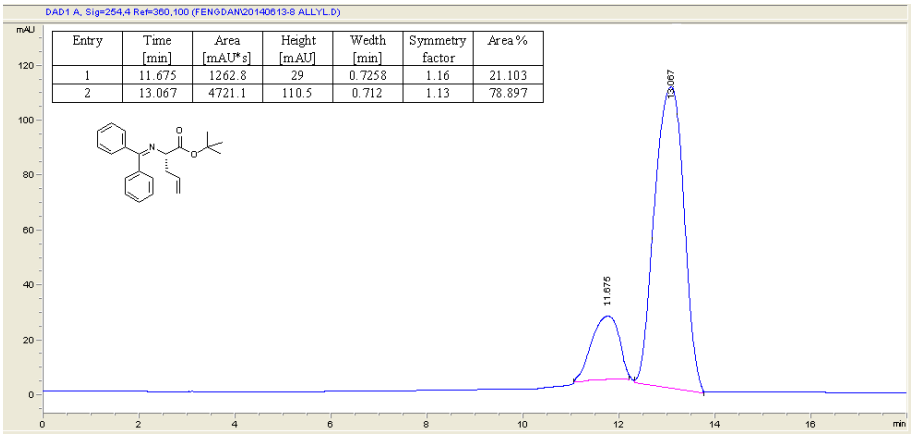


Fig.48 ^{13}C NMR spectra of *tert*-butyl 3-**vinyl**-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	12.085	14501.2	514.8	0.4695	1.134	50.312
2	13.57	14321.4	516.3	0.4623	0.942	49.688

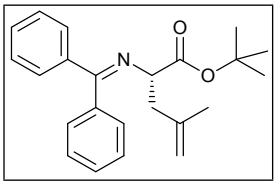
Fig.49 The HPLC chromatogram of racemic *tert*-butyl 3-vinyl-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	11.675	1262.8	29	0.7258	1.16	21.103
2	13.067	4721.1	110.5	0.712	1.13	78.897

Fig.50 The HPLC chromatogram of *tert*-butyl 3-vinyl-2-(diphenylmethyleneamino)propanoate catalyzed by **SiO_2@CDPTC**

***tert*-Butyl 3-(1-methylvinyl)-2-(diphenylmethyleneamino)propanoate (Entry 12 in Table 2).**



^{1}H NMR (600.1 MHz, $CDCl_3$, TMS): δ 7.66 (dd, ^3J = 26.3, 7.8 Hz, 2H, Ph-H), 7.49 – 7.41 (m, 3H, Ph-H), 7.38 – 7.34 (m, 1H, Ph-H), 7.30 (t, ^3J = 7.4 Hz, 2H, Ph-H), 7.19 (t, ^3J = 14.0 Hz, 2H, Ph-H), 4.72 (d, ^3J = 14.0 Hz, 2H, $=CH_2$), 4.08 (dd, ^3J = 7.9, 5.3 Hz, 1H, NCH), 2.67 – 2.54 (m, 2H, CH_2), 1.52 (s, 3H, CH_3), 1.45 (s, 9H, CH_3); ^{13}C NMR (150.9 MHz, $CDCl_3$, TMS): δ 171.17, 169.84 (C=N, C=O), 141.92, 139.83, 136.56, 132.36, 130.09, 130.03, 128.83, 128.50, 128.30, 128.11, 127.94, 113.27, 80.98 (O-C), 64.91 (N-CH), 41.90 (CH_2), 28.08 (CH_3), 22.61 (CH_3); HPLC analysis: Phenomenex Lux 5u Amylose-2, hexane/dioxane = 95/5, 254 nm, flow rate = 0.5 ml/min, retention times: 12.2 min (R), 13.8 min (S).

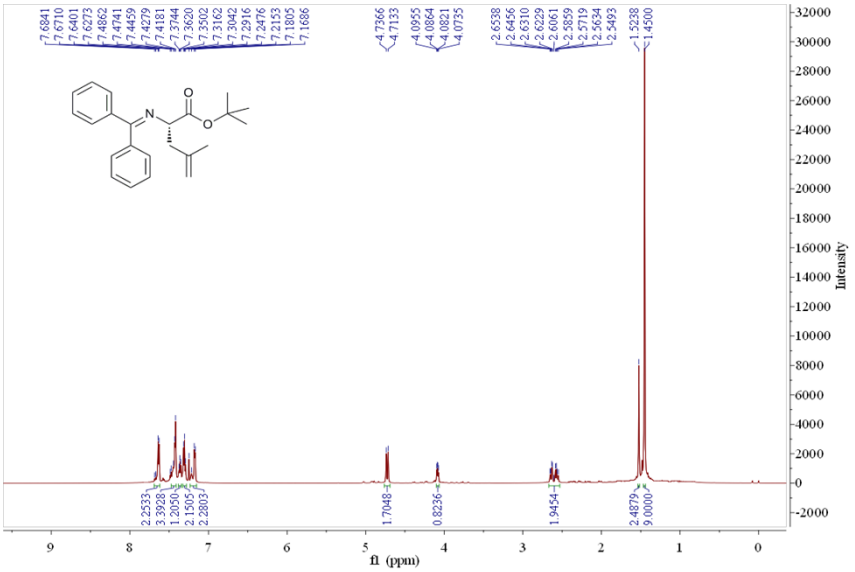


Fig.51 ^{1}H NMR spectra of *tert*-butyl 3-**(1-methylvinyl)**-2-(diphenylmethyleneamino)propanoate

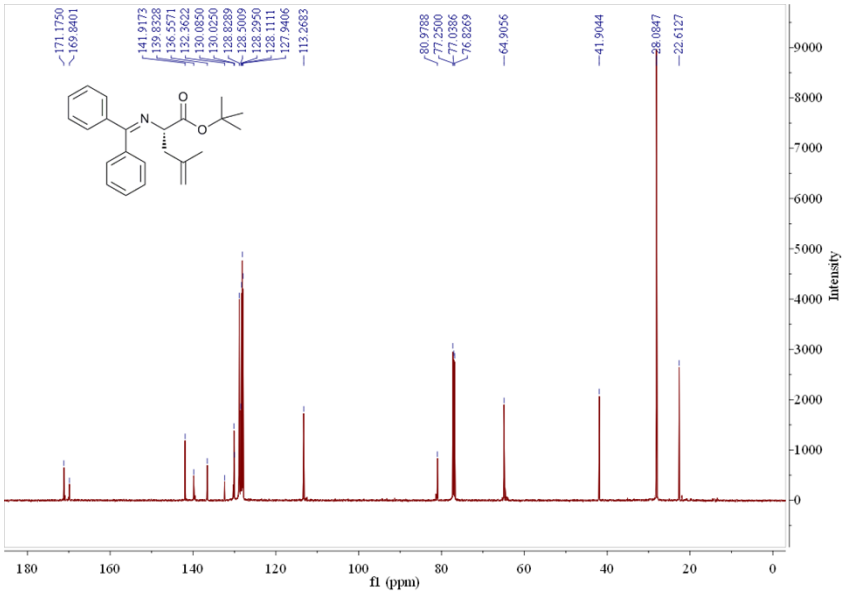
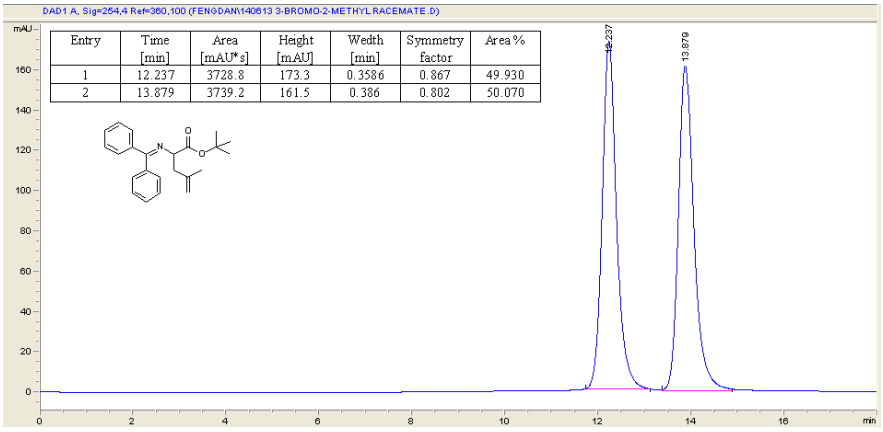
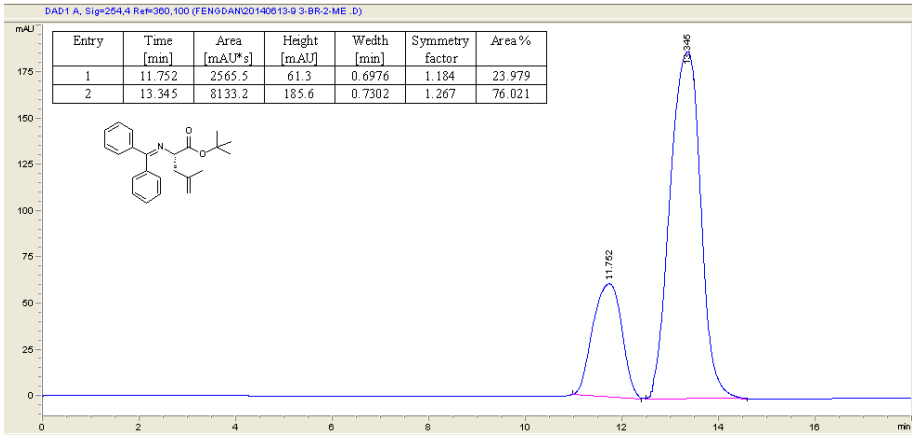


Fig.52 ^{13}C NMR spectra of *tert*-butyl 3-**(1-methylvinyl)**-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	12.237	3728.8	173.3	0.3586	0.867	49.930
2	13.879	3739.2	161.5	0.386	0.802	50.070

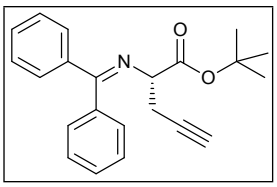
Fig.53 The HPLC chromatogram of racemic *tert*-butyl 3-(1-methylvinyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	11.752	2565.5	61.3	0.6976	1.184	23.979
2	13.345	8133.2	185.6	0.7302	1.267	76.021

Fig.54 The HPLC chromatogram of *tert*-butyl 3-(1-methylvinyl)-2-(diphenylmethyleneamino)propanoate catalyzed by **SiO_2@CDPTC**

***tert*-Butyl 3-ethynyl-2-(diphenylmethyleneamino)propanoate (Entry 13 in Table 2).**



^{1}H NMR (600.1 MHz, $CDCl_3$, TMS): δ 7.81 (d, ^3J = 7.2 Hz, 1H, Ph-H), 7.66 (d, ^3J = 7.4 Hz, 2H, Ph-H), 7.51 – 7.43 (m, 4H, Ph-H), 7.40 (t, ^3J = 7.3 Hz, 1H, Ph-H), 7.33 (t, ^3J = 7.6 Hz, 2H, Ph-H), 4.18 (dd, ^3J = 8.1, 5.2 Hz, 1H, NCH), 2.84 – 2.76 (m, 2H, CH_2), 1.95 (t, ^3J = 2.6 Hz, 1H, ≡CH), 1.45 (s, 9H, CH_3); ^{13}C NMR (150.9 MHz, $CDCl_3$, TMS) δ 171.4, 169.5 (C=N, C=O), 139.6, 137.7, 136.3, 132.4, 130.3, 130.0, 129.0, 128.6, 128.3, 128.3, 128.0 (Ph-C), 81.6 (≡CH), 81.3 (O-C), 70.0 (≡C-), 64.8 (N-C), 28.0 (CH_3), 23.4 (CH_2); HPLC analysis: Phenomenex Lux 5u Amylose-2, hexane/dioxane = 95/5, 254 nm, flow rate = 0.5 ml/min, retention times: 13.6 min (R), 16.3 min (S).

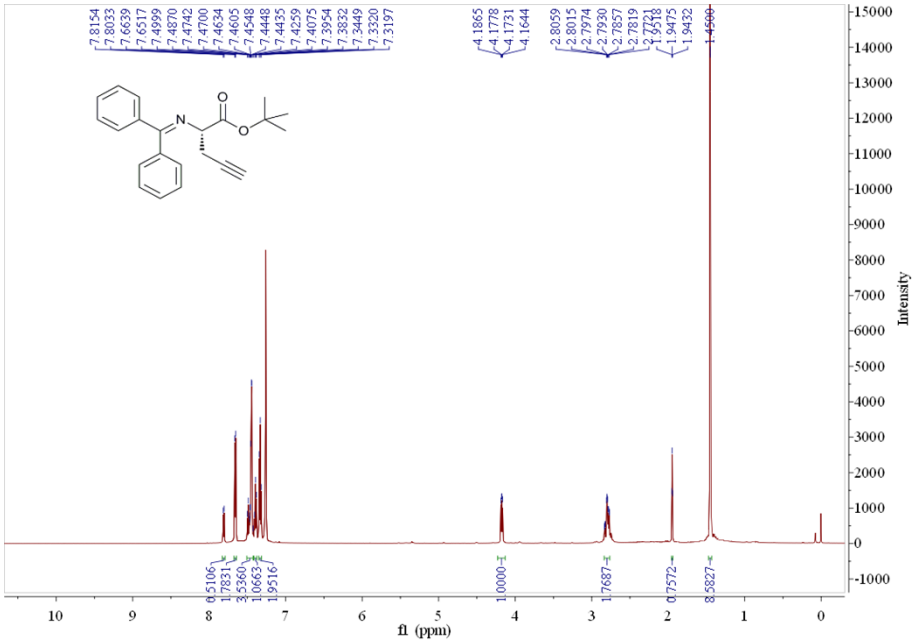


Fig.55 ^{1}H NMR spectra of *tert*-butyl 3-ethynyl-2-(diphenylmethyleneamino)propanoate

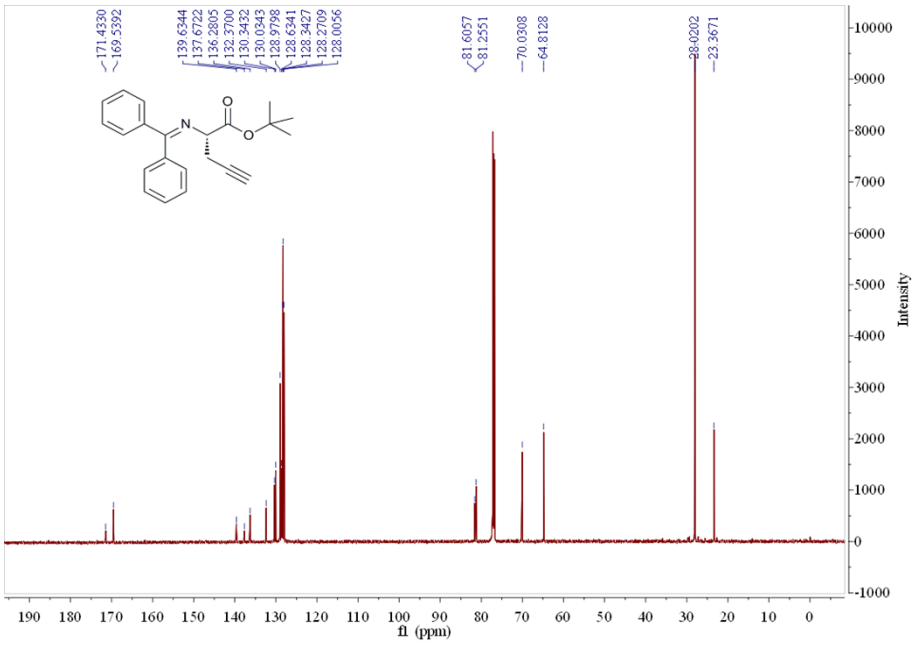
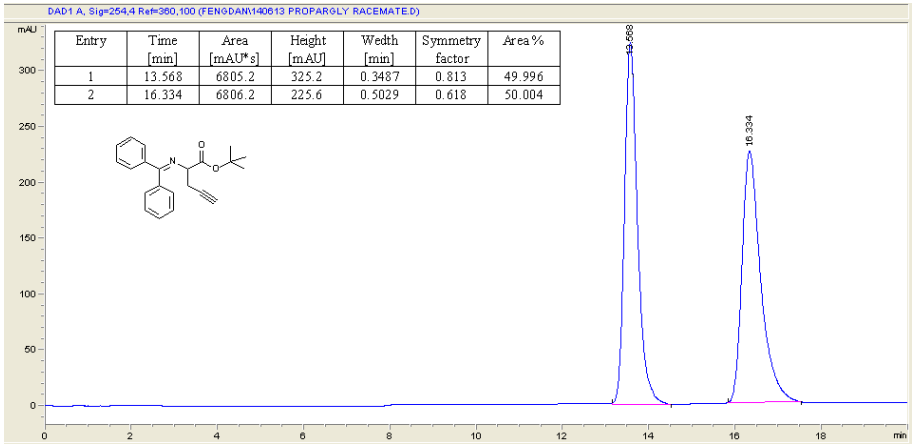
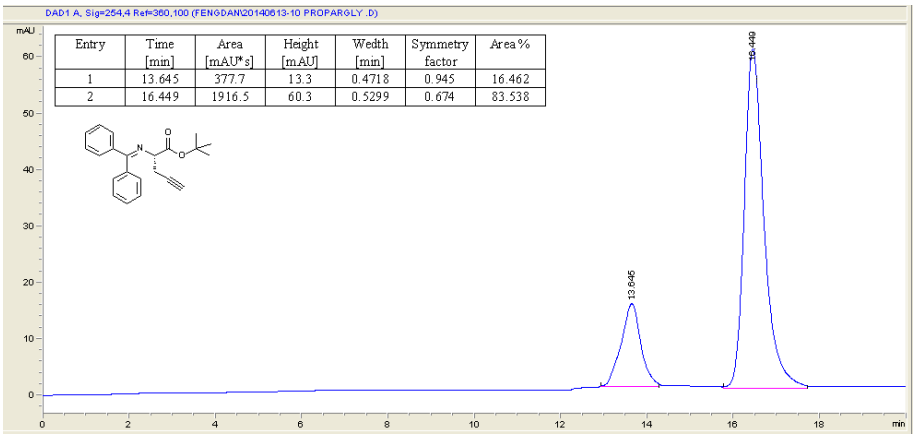


Fig.56 ^{13}C NMR spectra of *tert*-butyl 3-ethynyl-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	13.568	6805.2	325.2	0.3487	0.813	49.996
2	16.334	6806.2	225.6	0.5029	0.618	50.004

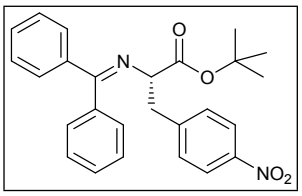
Fig.57 The HPLC chromatogram of racemic
tert-butyl 3-ethynyl-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	13.645	377.7	13.3	0.4718	0.945	16.462
2	16.449	1916.5	60.3	0.5299	0.674	83.538

Fig.58 The HPLC chromatogram of *tert*-butyl
3-ethynyl-2-(diphenylmethyleneamino)propanoate catalyzed by **SiO_2@CDPTC**

***tert*-Butyl 3-(4-nitrophenyl)-2-(diphenylmethyleneamino)propanoate (Entry 14 in Table 2).**



^{1}H NMR (600.1 MHz, $CDCl_3$, TMS) δ 8.00 (d, ^3J = 8.7 Hz, 2H, Ph-H), 7.76 – 7.73 (m, 1H, Ph-H), 7.52 (dd, ^3J = 17.6, 7.4 Hz, 2H, Ph-H), 7.42 (t, ^3J = 7.7 Hz, 1H, Ph-H), 7.33 (dd, ^3J = 14.3, 7.3 Hz, 2H, Ph-H), 7.19 (d, ^3J = 7.4 Hz, 4H, Ph-H), 6.65 (d, ^3J = 6.1 Hz, 2H, Ph-H), 4.14 – 4.10 (m, 1H, NCH), 3.25 (d, ^3J = 5.7 Hz, 2H, CH_2), 1.38 (s, 9H, CH_3); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 170.0, 169.1 (C=N, C=O), 145.7, 145.5, 138.1, 136.7, 135.0, 131.4, 129.7, 129.5, 129.0, 127.7, 127.6, 127.3, 127.3, 127.1, 126.5, 122.9, 122.8, 122.2 (Ph-C), 80.7 (O-C), 66.0 (N-C), 38.4 (CH_2), 27.0 (CH_3); HPLC analysis: Phenomenex Lux 5u Amylose-2, hexane/dioxane = 90/10, 254 nm, flow rate = 0.5 ml/min, retention times: 19.6 min (R), 24.1 min (S).

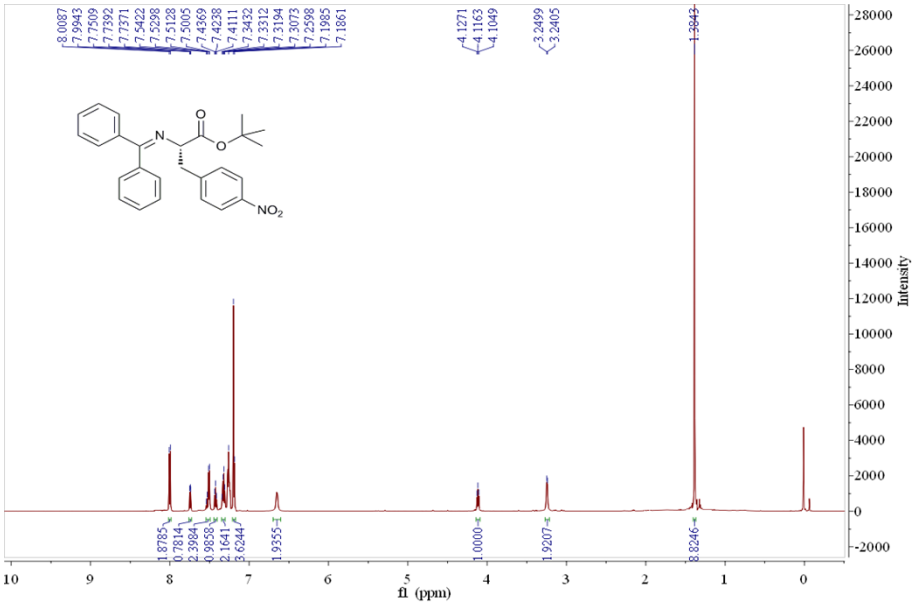


Fig.59 ^{1}H NMR spectra of *tert*-butyl 3-(4-nitrophenyl)-2-(diphenylmethyleneamino)propanoate

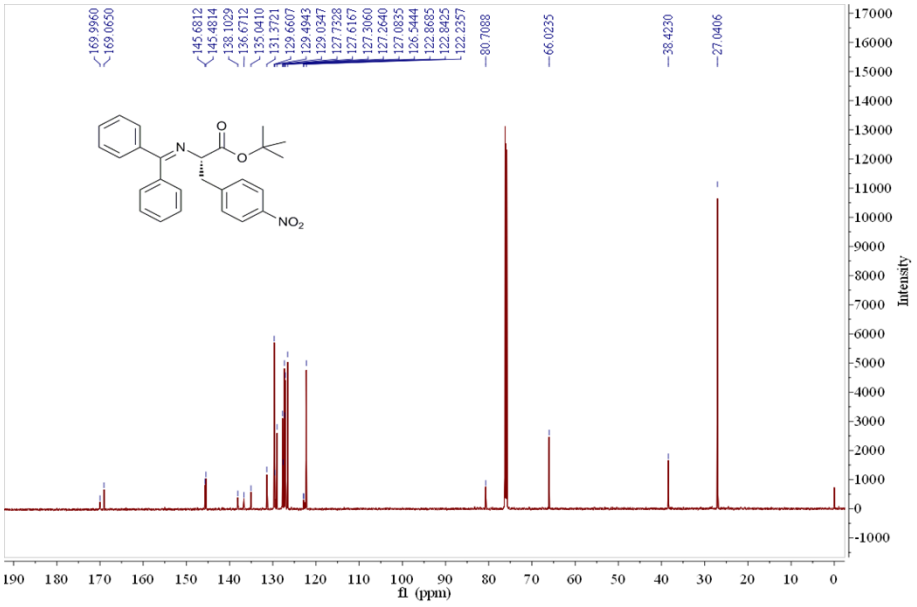
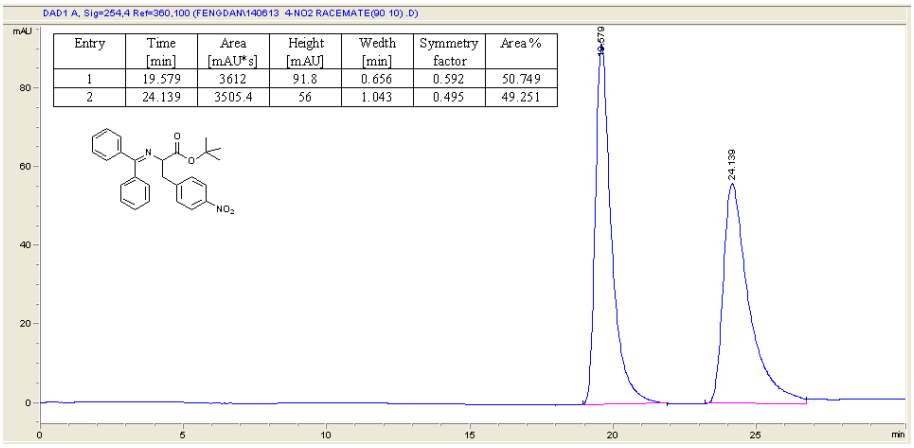
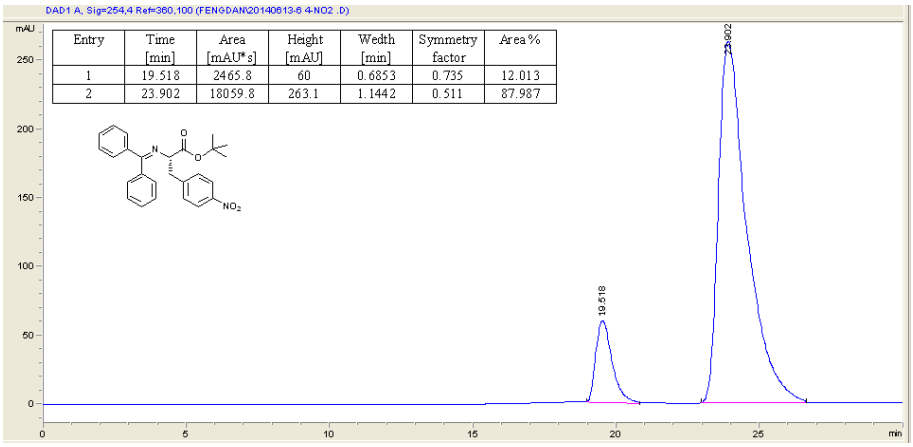


Fig.60 ^{13}C NMR spectra of *tert*-butyl 3-(4-nitrophenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	19.579	3612	91.8	0.656	0.592	50.749
2	24.139	3505.4	56	1.043	0.495	49.251

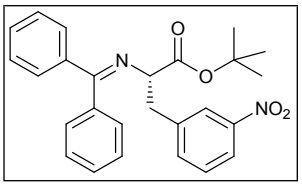
Fig.61 The HPLC chromatogram of racemic *tert*-butyl 3-(4-nitrophenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	19.518	2465.8	60	0.6853	0.735	12.013
2	23.902	18059.8	263.1	1.1442	0.511	87.987

Fig.62 The HPLC chromatogram of *tert*-butyl 3-(4-nitrophenyl)-2-(diphenylmethyleneamino)propanoate catalyzed by **SiO_2@CDPTC**

***tert*-Butyl 3-(3-nitrophenyl)-2-(diphenylmethyleneamino)propanoate (Entry 15 in Table 2).**



^{1}H NMR (600.1 MHz, $CDCl_3$, TMS): δ 8.04 (ddd, ^3J = 8.1, 2.2, 0.9 Hz, 1H, Ph-H), 7.95 – 7.94 (m, 1H, Ph-H), 7.82 – 7.80 (m, 1H, Ph-H), 7.59 – 7.56 (m, 2H, Ph-H), 7.48 (dd, ^3J = 18.0, 7.8 Hz, 1H, Ph-H), 7.37 (dd, ^3J = 6.8, 5.3 Hz, 2H, Ph-H), 7.34 – 7.29 (m, 4H, Ph-H), 6.72 (d, ^3J = 6.1 Hz, 2H, Ph-H), 4.19 (dd, ^3J = 8.2, 5.1 Hz, 1H, NCH), 3.35 – 3.26 (m, 2H, CH_2), 1.45 (s, 9H, CH_3); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 171.1, 170.1 (C=N, C=O), 148.1, 140.6, 139.1, 137.7, 136.2, 136.1, 132.4, 130.5, 130.0, 128.9, 128.8, 128.7, 128.3, 128.3, 128.1, 127.5, 124.7, 121.4 (Ph-C), 81.7 (O-C), 67.0 (N-C), 39.2 (CH_2), 28.0 (CH_3); HPLC analysis: Phenomenex Lux 5u Amylose-2, hexane/dioxane = 90/10, 254 nm, flow rate = 0.5 ml/min, retention times: 20.0 min (R), 25.2 min (S).

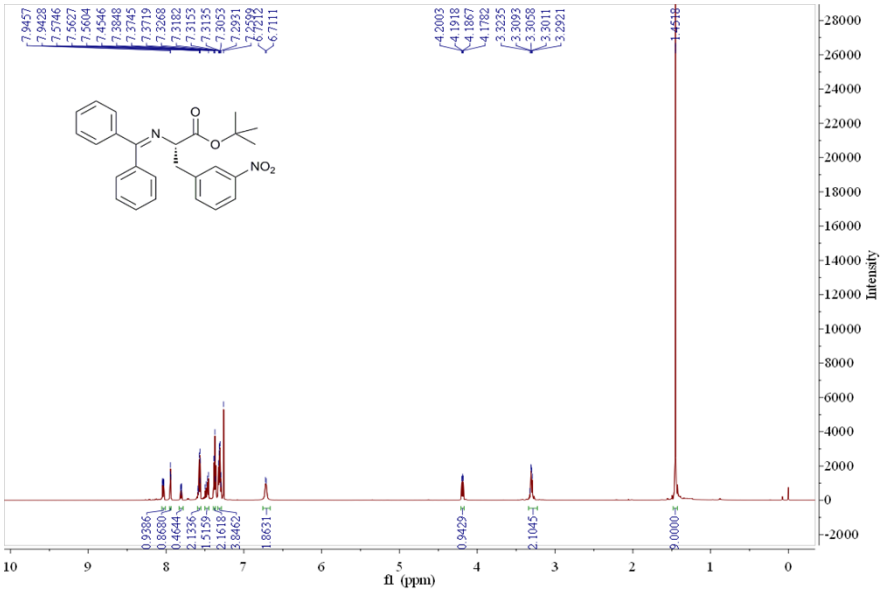


Fig.63 [1]H NMR spectra of *tert*-butyl 3-(3-nitrophenyl)-2-(diphenylmethyleneamino)propanoate

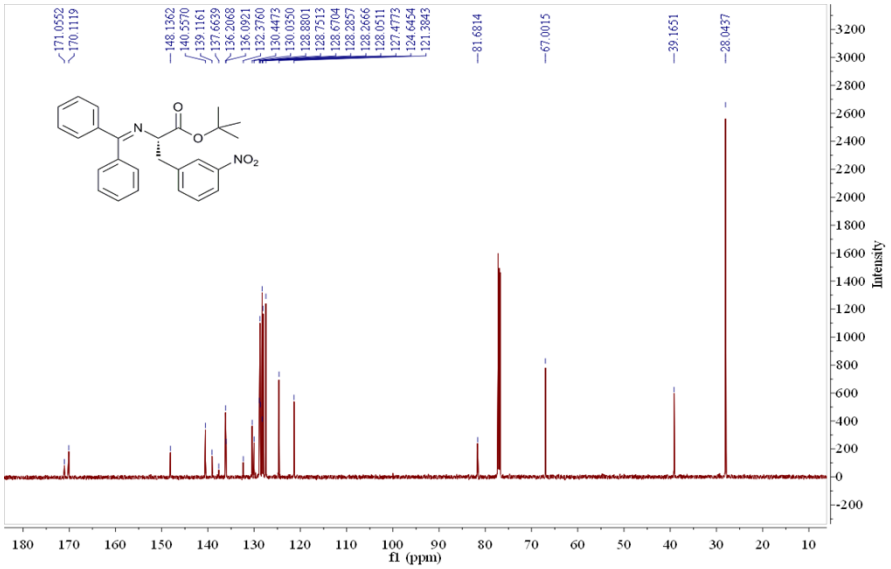
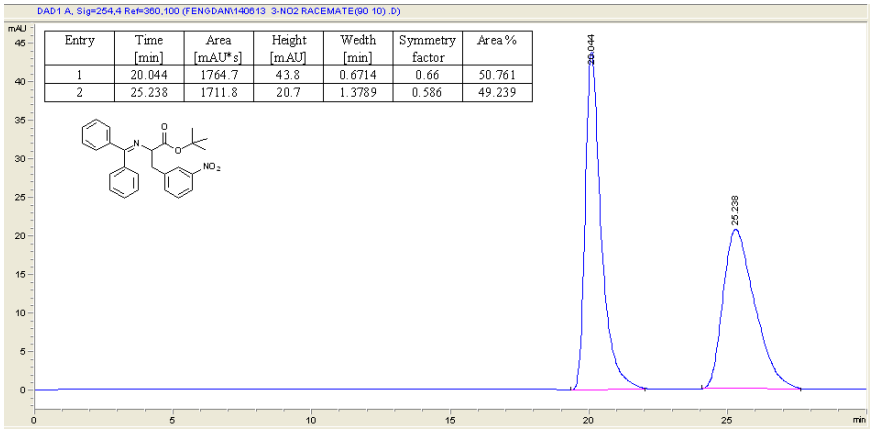
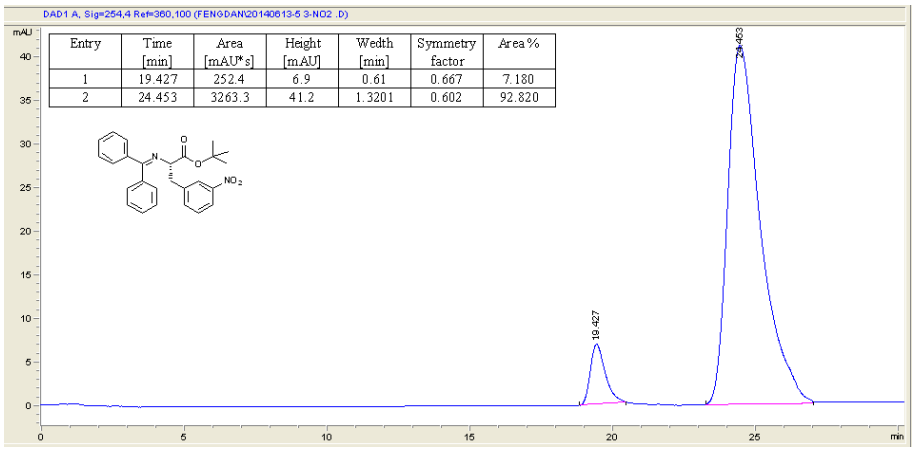


Fig.64 [13]C NMR spectra of *tert*-butyl 3-(3-nitrophenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	20.044	1764.7	43.8	0.6714	0.66	50.761
2	25.238	1711.8	20.7	1.3789	0.586	49.239

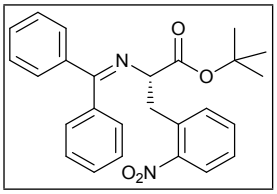
Fig.65 The HPLC chromatogram of racemic *tert*-butyl 3-(3-nitrophenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	19.427	252.4	6.9	0.61	0.667	7.180
2	24.453	3263.3	41.2	1.3201	0.602	92.820

Fig.66 The HPLC chromatogram of *tert*-butyl 3-(3-nitrophenyl)-2-(diphenylmethyleneamino)propanoate catalyzed by **SiO_2@CDPTC**

***tert*-Butyl 3-(2-nitrophenyl)-2-(diphenylmethyleneamino)propanoate (Entry 7 in Table 2).**



^{1}H NMR (600.1 MHz, $CDCl_3$, TMS): δ 8.05 – 7.98 (m, 1H, Ph-H), 7.97 – 7.88 (m, 1H, Ph-H), 7.80 (dd, ^3J = 8.2, 3.4 Hz, 1H, Ph-H), 7.76 – 7.74 (m, 1H, Ph-H), 7.66 – 7.60 (m, 1H, Ph-H), 7.51 (dd, ^3J = 7.0, 4.3 Hz, 2H, Ph-H), 7.45 – 7.36 (m, 2H, Ph-H), 7.32 (d, ^3J = 6.8 Hz, 2H, Ph-H), 7.20 (d, ^3J = 4.7 Hz, 2H, Ph-H), 6.56 (s, 1H, Ph-H), 4.29 – 4.24 (m, 1H, NCH), 3.48 – 3.32 (m, 2H, CH_2), 1.38 (s, 9H, CH_3); ^{13}C NMR (150.9 MHz, $CDCl_3$, TMS): δ 170.04, 169.19 (C=N, C=O), 148.70, 138.22, 136.68, 135.00, 133.10, 131.41, 131.36, 129.29, 129.02, 128.32, 127.78, 127.47, 127.26, 127.17, 126.94, 126.42, 123.62, 123.58, 80.43 (O-C), 64.96 (N-C), 35.40 (CH_2), 27.02 (CH_3); HPLC analysis: Phenomenex Lux 5u Amylose-2, hexane/dioxane = 90/10, 254 nm, flow rate = 0.5 ml/min, retention times: 19.1 min (R), 23.7 min (S).

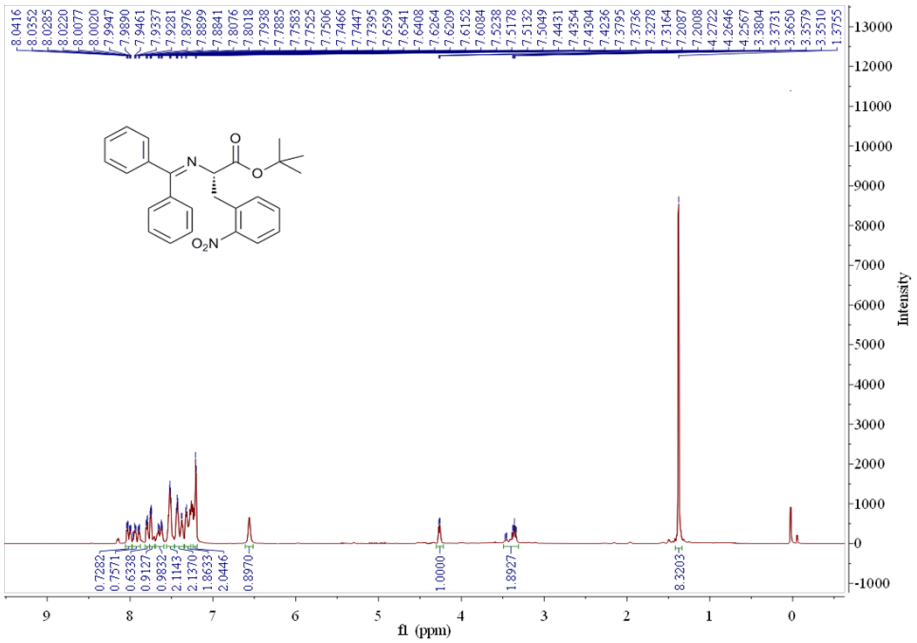


Fig.67 ^{1}H NMR spectra of *tert*-butyl 3-(2-nitrophenyl)-2-(diphenylmethyleneamino)propanoate

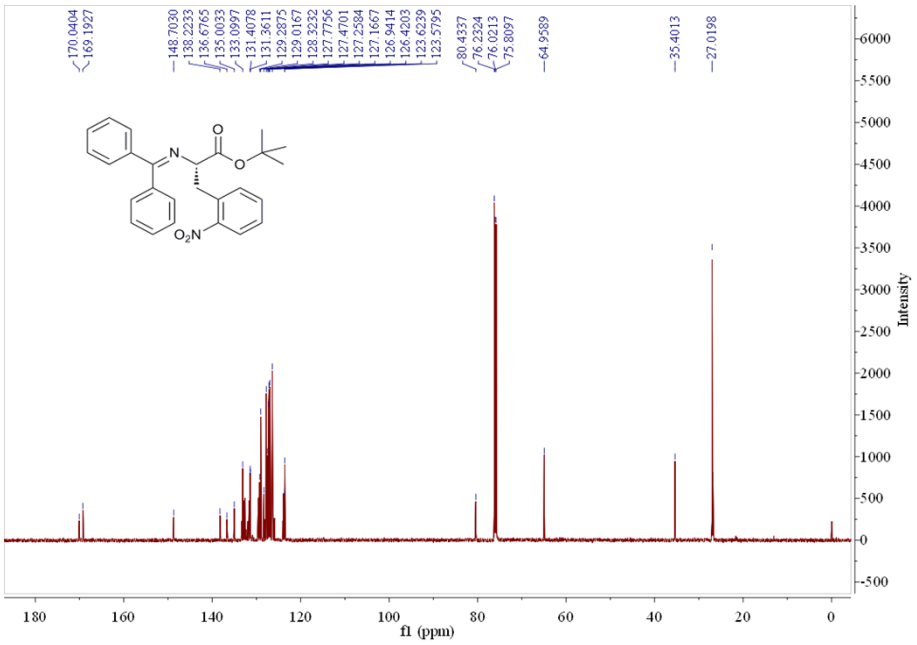
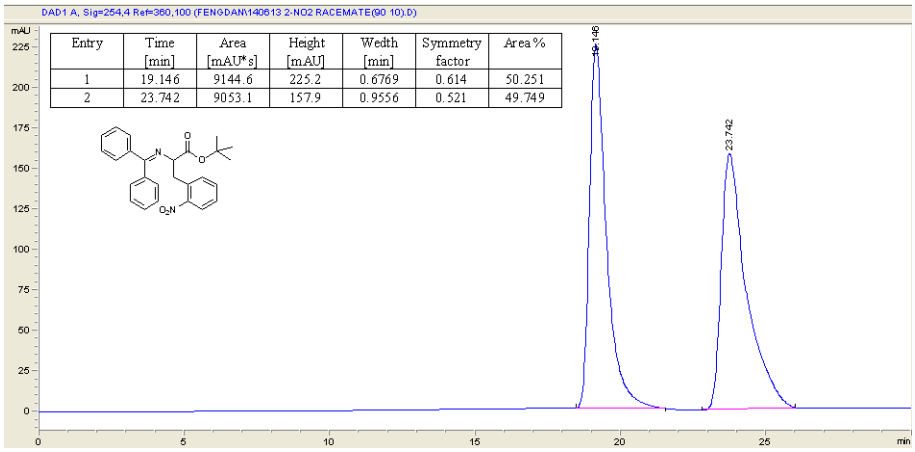
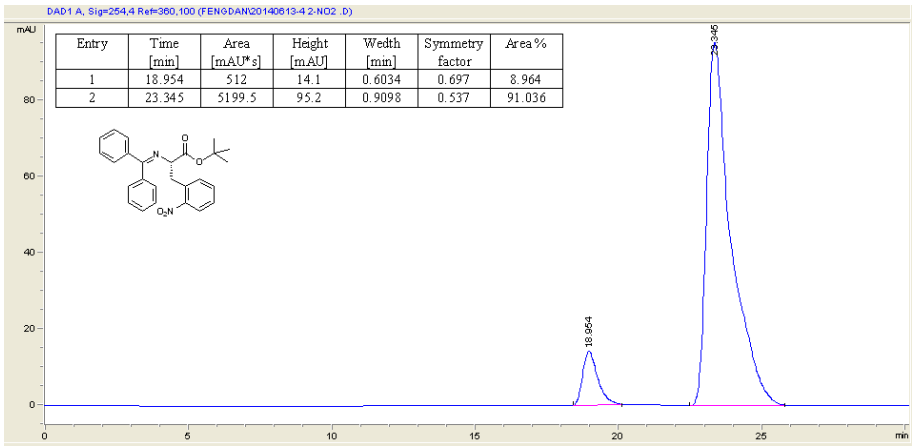


Fig.68 ^{13}C NMR spectra of *tert*-butyl 3-(2-nitrophenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	19.146	9144.6	225.2	0.6769	0.614	50.251
2	23.742	9053.1	157.9	0.9556	0.521	49.749

Fig.69 The HPLC chromatogram of racemic *tert*-butyl 3-(2-nitrophenyl)-2-(diphenylmethyleneamino)propanoate



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	18.954	512	14.1	0.6034	0.697	8.964
2	23.345	5199.5	95.2	0.9098	0.537	91.036

Fig.70 The HPLC chromatogram of *tert*-butyl 3-(2-nitrophenyl)-2-(diphenylmethyleneamino)propanoate catalyzed by **SiO_2@CDPTC**

X-ray diffraction and elemental analysis of SiO_2@CDPTC

X-ray powder diffractions were carried out on an XRD-7000 S/L instrument: Cu-Kα radiation, X-ray tube settings of 40.0kV/30.0 mA, a scan speed of 2º /min in the 10–100º (2θ) range. X-ray diffraction of **SiO_2@CD/PTC** (**Fig. 71**) indicate that the structure is amorphous.

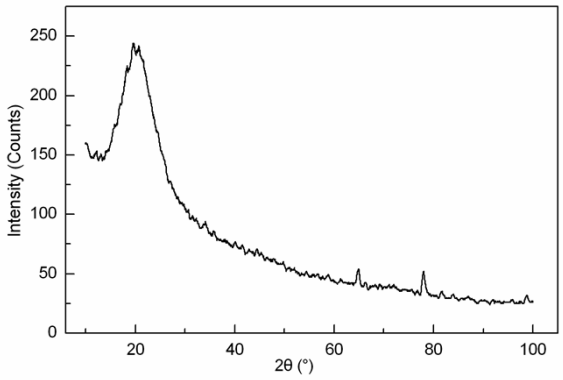


Fig.71 X-ray diffraction patterns of **SiO_2@CDPTC**

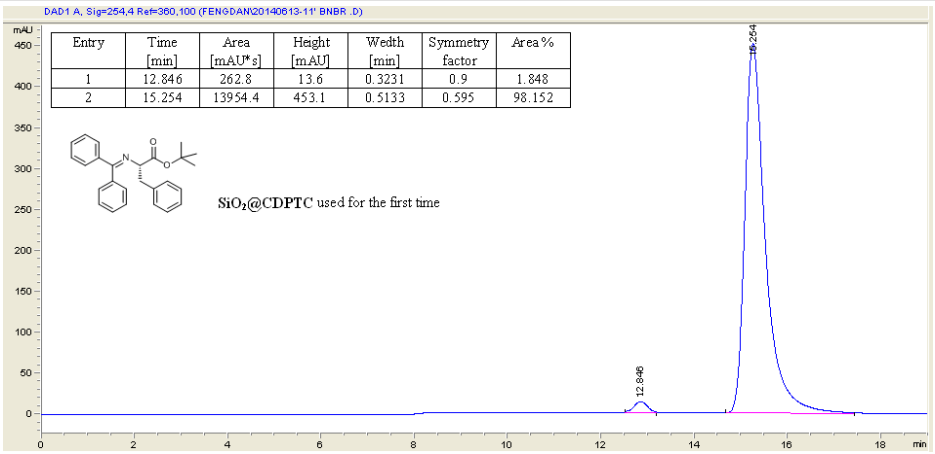
The recovery and reuse of catalyst

The data of the yields and enantioselectivities of *α*-alkylation product *tert*-Butyl 3-phenyl-2-(diphen- ylmethyleneamino)propanoate in reused process were shown in the following **Table 1** and **Fig. 72**.

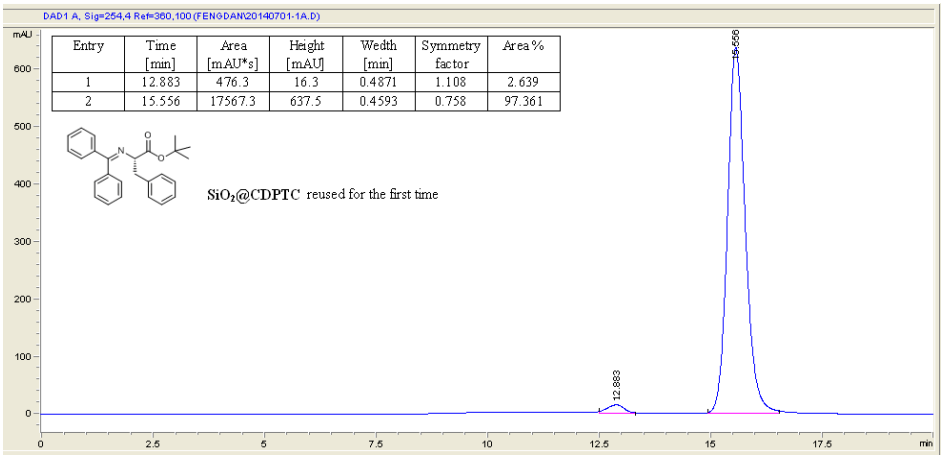
Table 1 Reusability of **SiO_2@CDPTC** under optimized reaction conditions

Entry	Temp.(°C)	Reaction times	Yield[a] (%)	%ee [b]
1	-40	1	95	96.3
2	-40	2	93	94.7
3	-40	3	92	94.0
4	-40	4	90	93.0
5	-40	5	88	91.6
6	-40	6	80	91.2

Reaction conditions: 20 mol% **SiO_2@CDPTC**, -40 °C, benzyl bromide (2.5 mmol), *N*-(diphenylmethylene)glycine ethyl ester (150.0 mg, 0.51 mmol), 50% aq KOH (1.0 mL, 13.4 mmol), 4.0 mL toluene. [a] Isolated yield. [b] Determined by chiral HPLC with Phenomenex Lux 5u Amylose-2 chiral column.

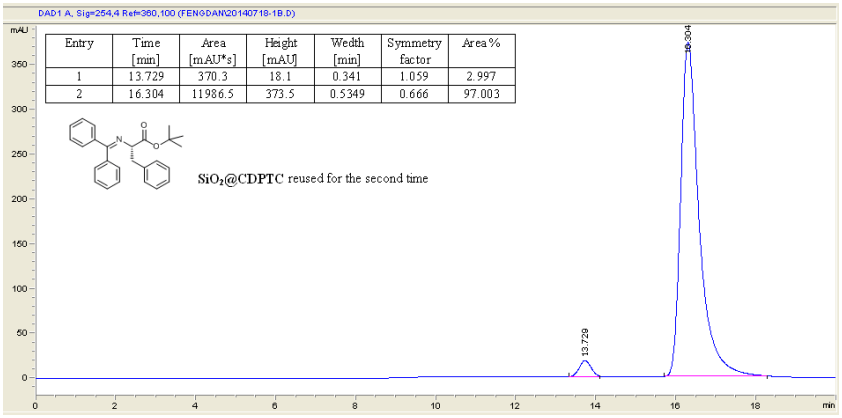


Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	12.846	262.8	13.6	0.3231	0.9	1.848
2	15.254	13954.4	453.1	0.5133	0.595	98.152



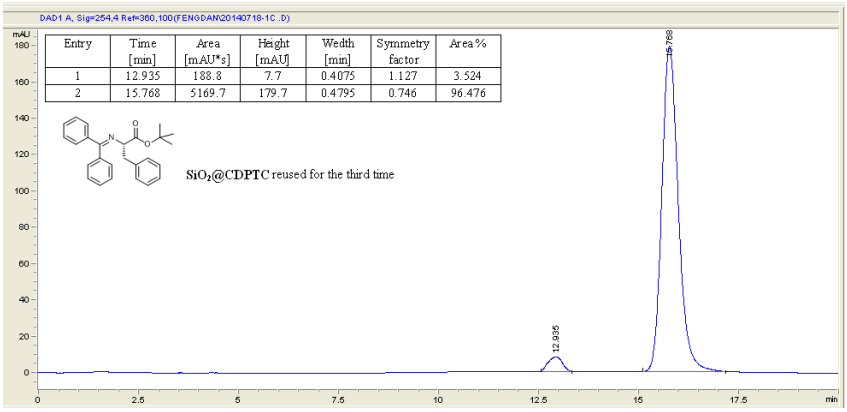
Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	12.883	476.3	16.3	0.4871	1.108	2.639
2	15.556	17567.3	637.5	0.4593	0.758	97.361

SiO_2@CDPTC reused for the first time



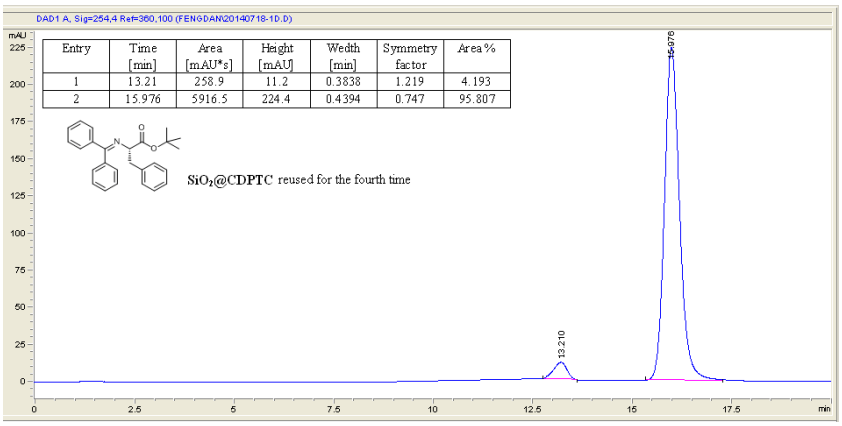
Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	13.729	370.3	18.1	0.341	1.059	2.997
2	16.304	11986.5	373.5	0.5349	0.666	97.003

SiO_2@CDPTC reused for the second time



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	12.935	188.8	7.7	0.4075	1.127	3.524
2	15.768	5169.7	179.7	0.4795	0.746	96.476

SiO_2@CDPTC reused for the third time



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	13.21	258.9	11.2	0.3838	1.219	4.193
2	15.976	5916.5	224.4	0.4394	0.747	95.807

SiO_2@CDPTC reused for the fourth time

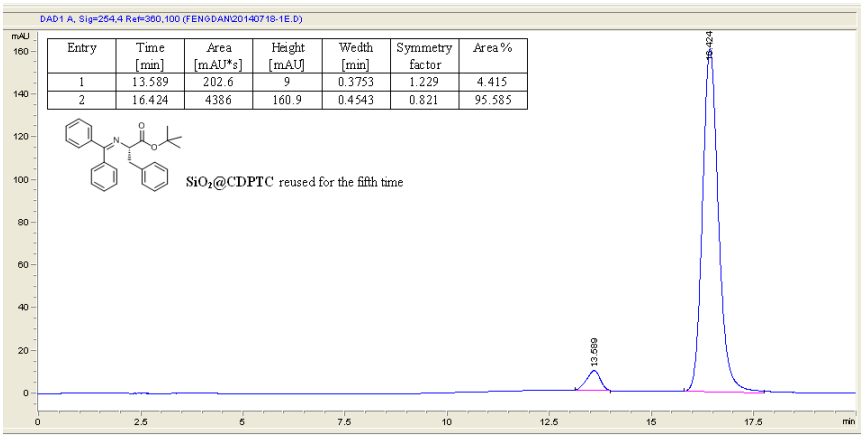
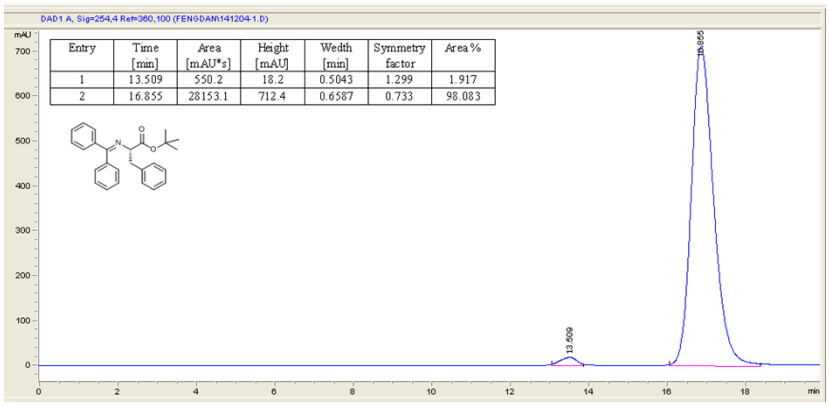
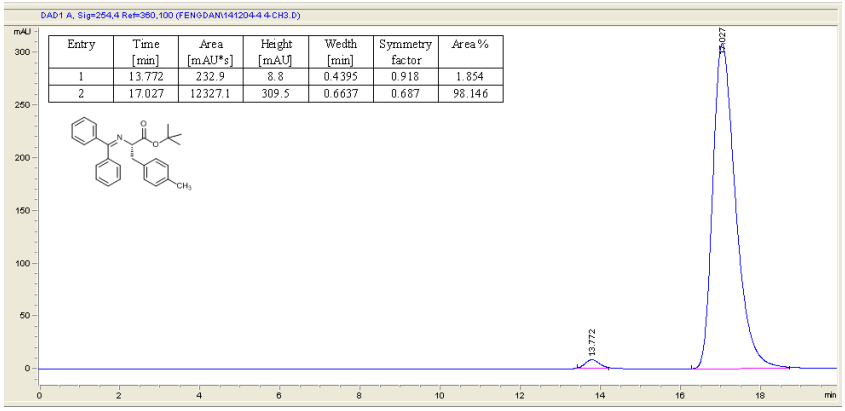
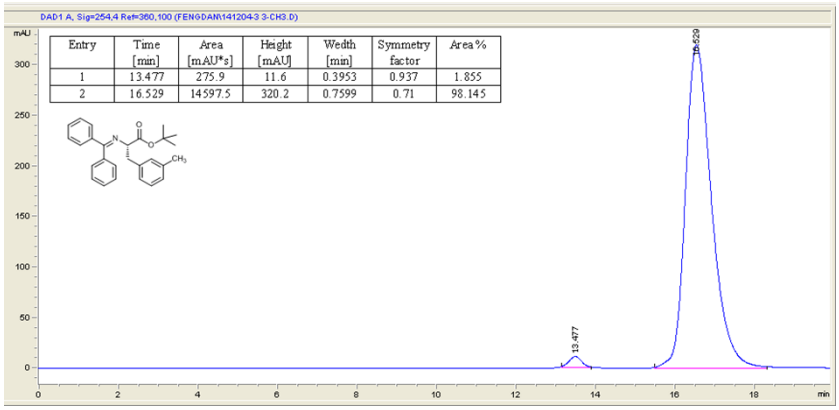


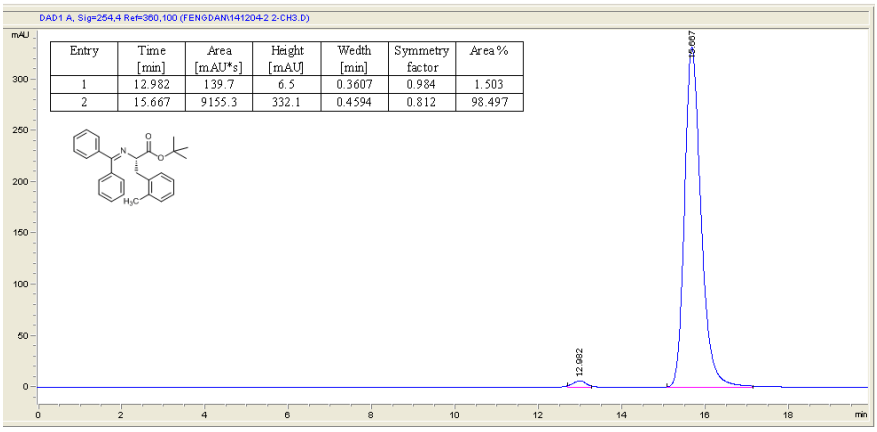
Fig.72 The HPLC chromatogram of *tert*-butyl 3-phenyl-2-(diphenylmethyleneamino)propanoate in the six times

HPLC chromatogram of homogeneous CDPTC

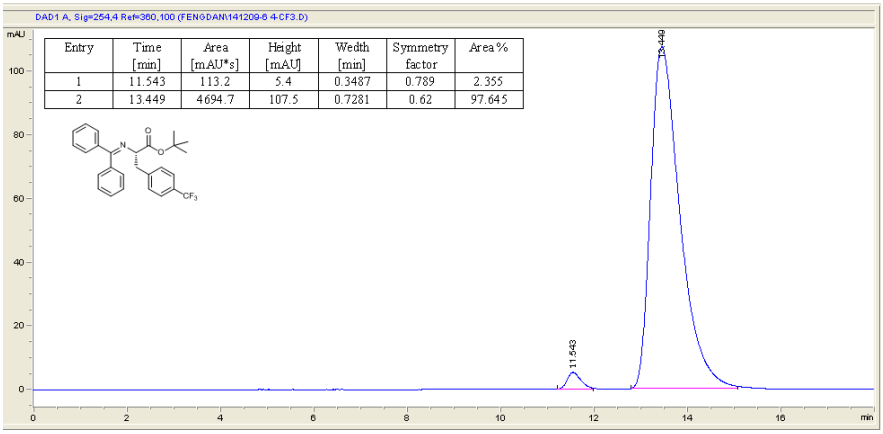




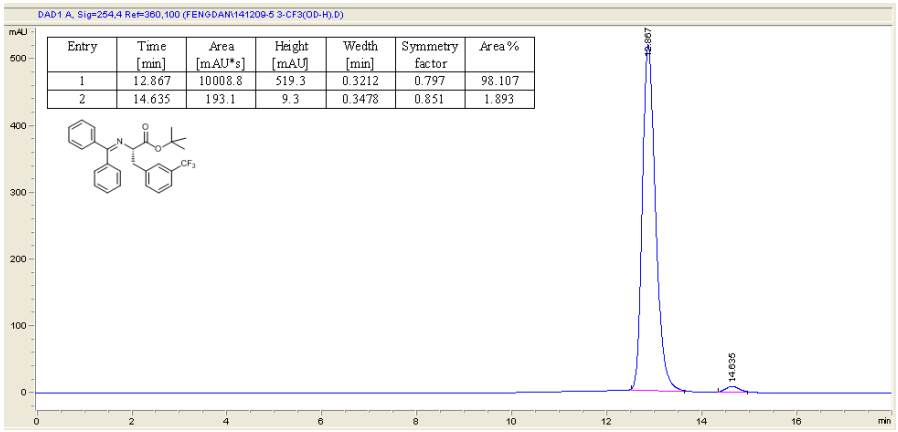




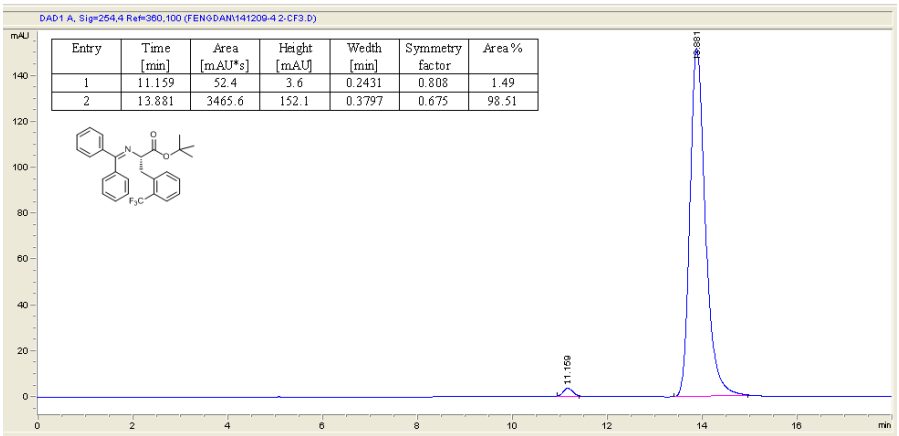
Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	12.982	139.7	6.5	0.3607	0.984	1.503
2	15.667	9155.3	332.1	0.4594	0.812	98.497



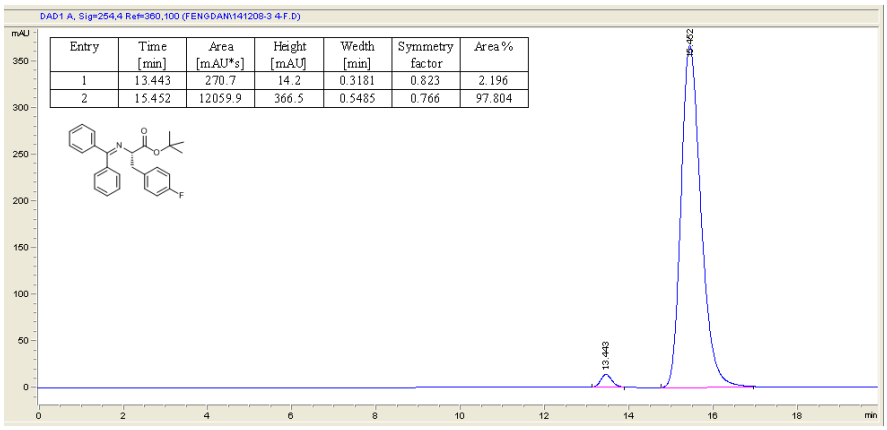
Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	11.543	113.2	5.4	0.3487	0.789	2.355
2	13.449	4694.7	107.5	0.7281	0.62	97.645



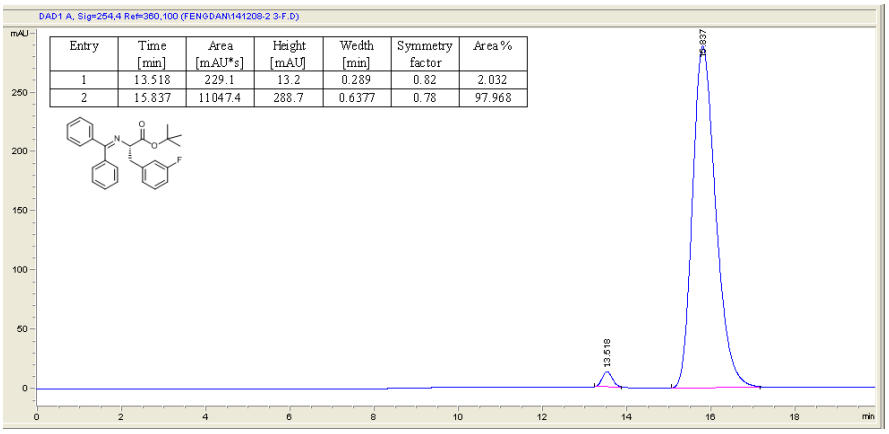
Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	12.867	10008.8	519.3	0.3212	0.797	98.107
2	14.635	193.1	9.3	0.3478	0.851	1.893



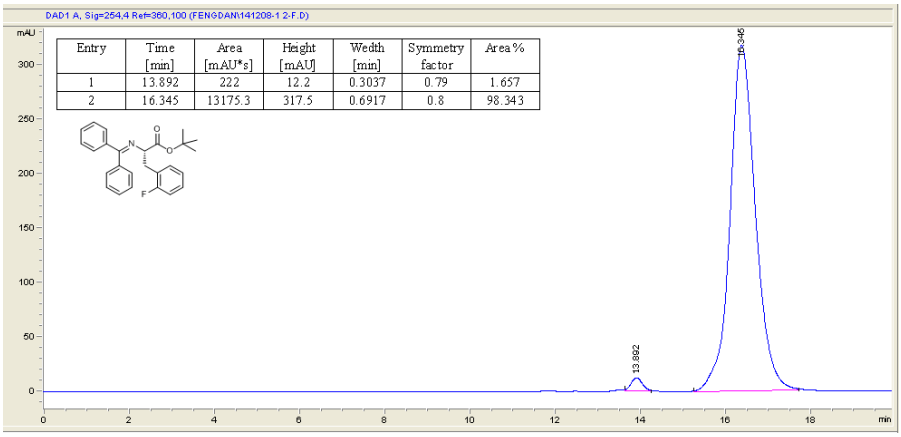
Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	11.159	52.4	3.6	0.2431	0.808	1.49
2	13.881	3465.6	152.1	0.3797	0.675	98.51



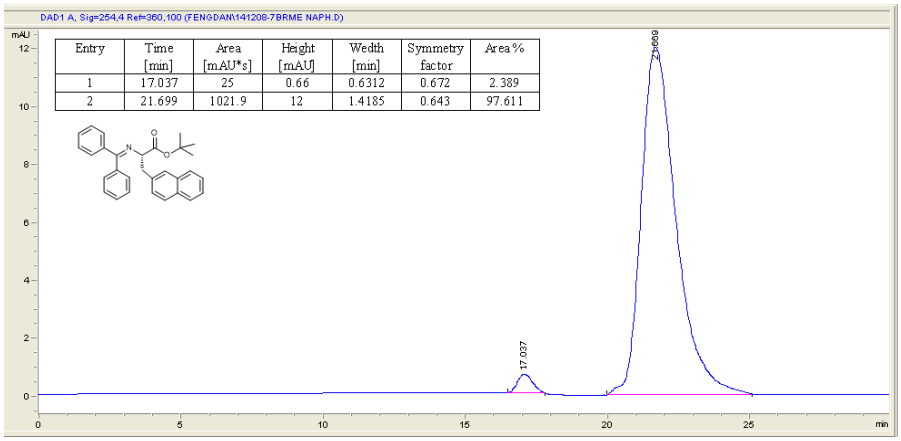
Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	13.443	270.7	14.2	0.3181	0.823	2.196
2	15.452	12059.9	366.5	0.5485	0.766	97.804



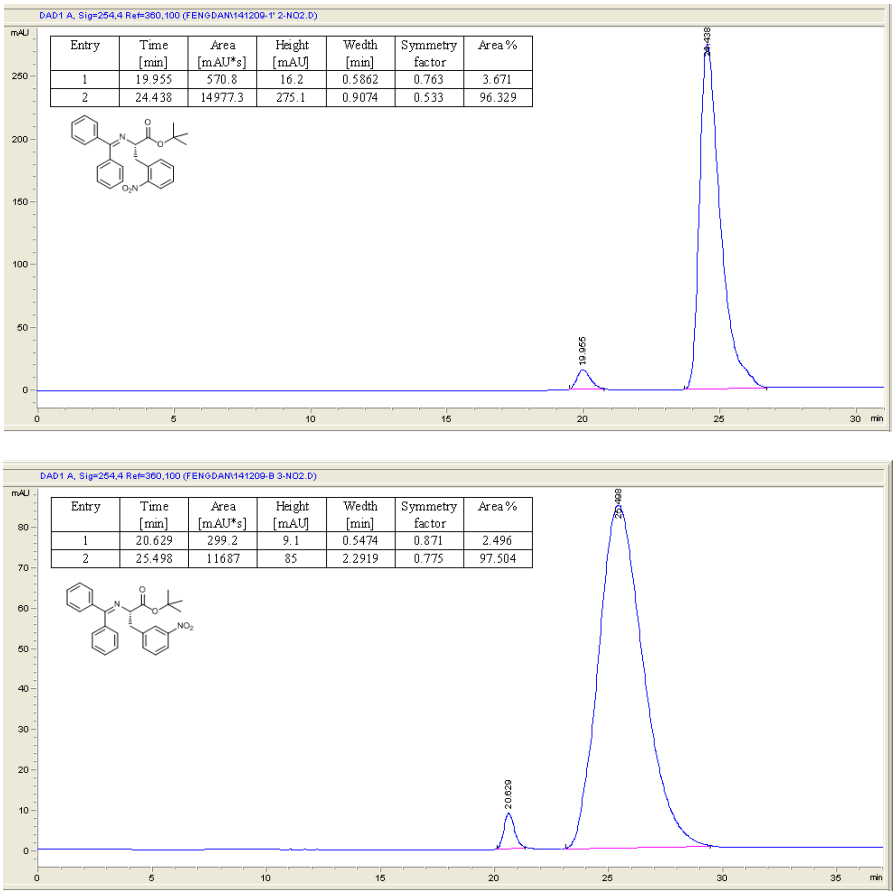
Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	13.518	229.1	13.2	0.289	0.82	2.032
2	15.837	11047.4	288.7	0.6377	0.78	97.968



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	13.892	222	12.2	0.3037	0.79	1.657
2	16.345	13175.3	317.5	0.6917	0.8	98.343



Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	17.037	25	0.66	0.6312	0.672	2.389
2	21.699	1021.9	12	1.4185	0.643	97.611

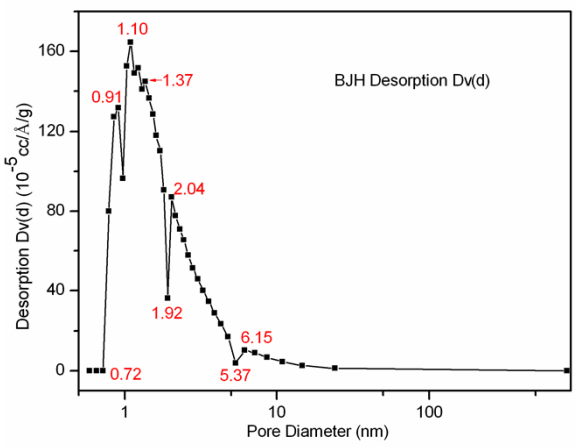


Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	19.955	570.8	16.2	0.5862	0.763	3.671
2	24.438	14977.3	275.1	0.9074	0.533	96.329

Entry	Time [min]	Area [mAU*s]	Height [mAU]	Width [min]	Symmetry factor	Area %
1	20.629	299.2	9.1	0.5474	0.871	2.496
2	25.498	11687	85	2.2919	0.775	97.504

Fig.73 HPLC chromatogram of various electrophiles catalyzed by homogeneous **CDPTC**

N_2 adsorption–desorption isotherm of deeply hydrolytic SiO_2@CDPTC



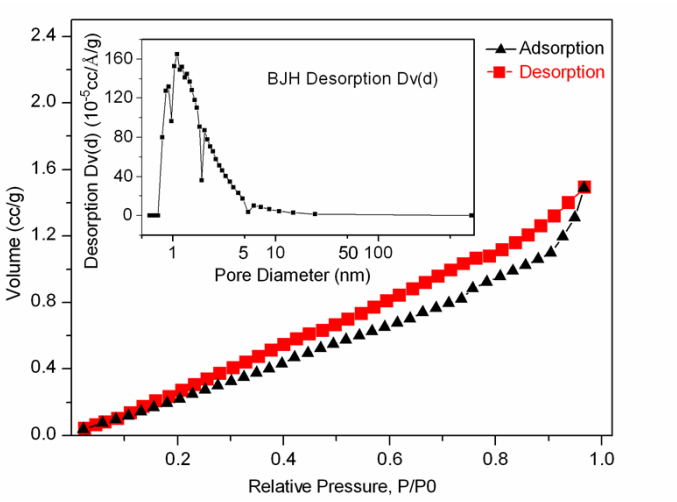
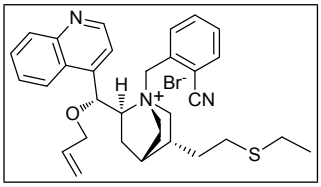


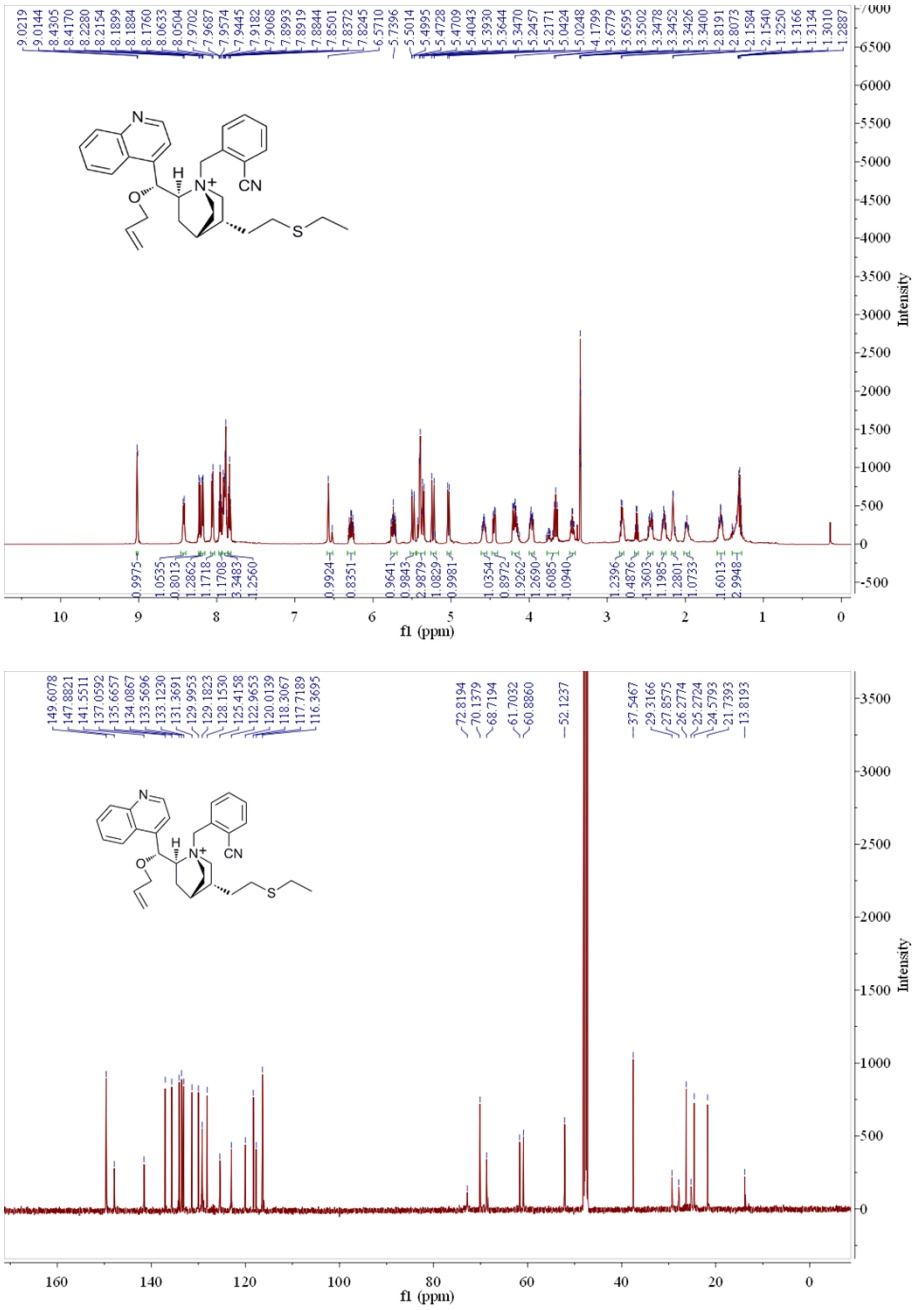
Fig.74 N_2 adsorption–desorption isotherms of deeply hydrolytic **SiO_2@CDPTC** and pore size distributions from BJH analysis based on desorption isotherm

An analogues of CDPTC

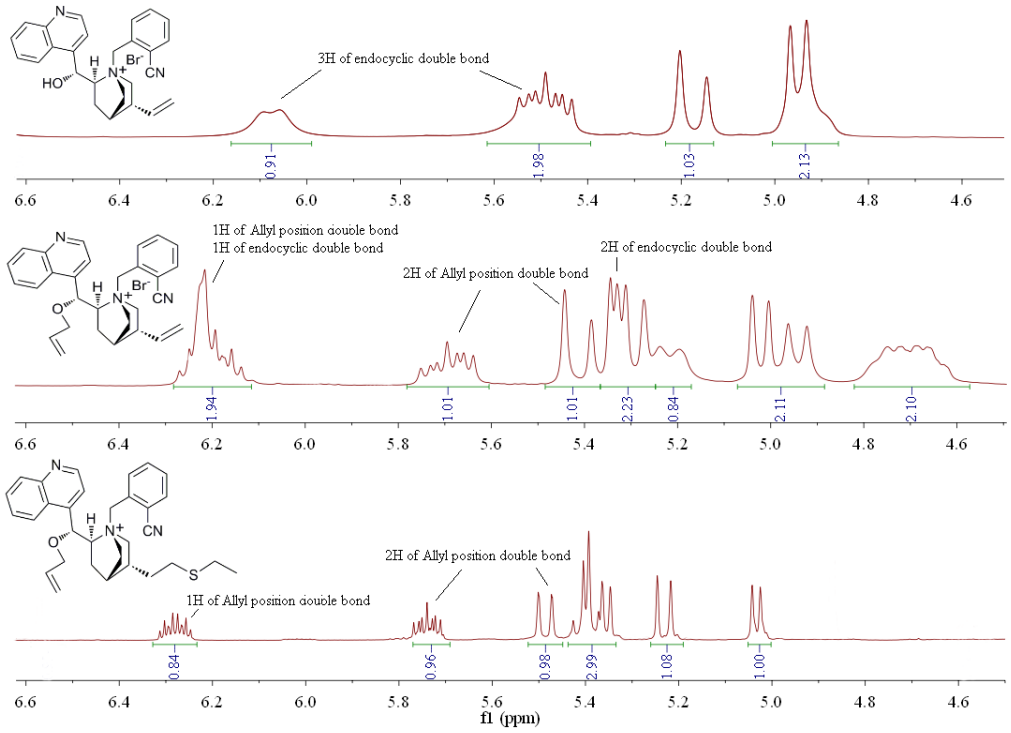
To a round-bottomed flask (100 mL) was charged with *N*-(2-cyanobenzyl)-*O*(9)-allyl- cinchonidinium bromide (265.3 mg, 0.5 mmol), mercaptan (124.3 mg, 2.0 mmol) and AIBN (16.4 mg, 0.1 mmol), flushed three times with Ar atmosphere and sealed. Then $CHCl_3$ (30 mL) was added by a syringe and the reaction mixture was refluxed for 72 h at 80 °C with the tracking of TLC. During the reaction, AIBN (16.4 mg, 0.1 mmol) was added once per 24 hours. After the solvent was evaporated under reduced pressure, the residue was subjected to flash column chromatography by gradient elution with $CHCl_3/CH_3OH$ (*v*/*v*= 60/1→30/1→15/1) to obtain the pale yellow solid **(**474.1 mg, 80%**)**.



^{1}H NMR (600.1 MHz, CD_3OD, TMS) δ 9.02 (d, ^3J = 4.5 Hz, 1H, Ph-H), 8.42 (d, ^3J = 8.1 Hz, 1H, Ph-H), 8.22 (d, ^3J = 7.6 Hz, 1H, Ph-H), 8.19 (dd, ^3J = 7.5, 6.7 Hz, 1H, Ph-H), 8.06 (d, ^3J = 7.7 Hz, 1H, Ph-H), 7.96 (dd, ^3J = 11.1, 4.3 Hz, 1H, Ph-H), 7.94 – 7.86 (m, 3H, Ph-H), 7.84 (t, ^3J = 7.7 Hz, 1H, Ph-H), 6.55 (d, ^3J = 18.7 Hz, 1H, O-CH), 6.33 – 6.24 (m, 1H, -CH=), 5.78 – 5.69 (m, 1H, =CH_2), 5.49 (dd, ^3J = 17.2, 1.1 Hz, 1H, =CH_2), 5.38 (dt, ^3J = 14.9, 11.7 Hz, 3H, N^+-CH, N^+-CH_2), 5.22 (dd, ^3J = 16.5, 8.3 Hz, 1H, O-CH_2), 5.03 (t, ^3J = 9.2 Hz, 1H, O-CH_2), 4.58 (ddd, ^3J = 16.3, 11.3, 5.0 Hz, 1H, N^+-CH_2), 4.45 (dd, ^3J = 11.9, 5.9 Hz, 1H, N^+-CH_2), 4.17 (ddd, ^3J = 25.7, 14.2, 7.2 Hz, 2H, N^+-CH_2), 3.97 (ddd, ^3J = 12.5, 8.6, 4.4 Hz, 1H, S-CH_2), 3.77 – 3.63 (m, 2H, S-CH_2), 3.45 (td, ^3J = 11.3, 4.3 Hz, 1H, S-CH_2), 2.84 – 2.77 (m, 1H, CH), 2.62 (q, ^3J = 7.4 Hz, 1H, CH), 2.48 – 2.41 (m, 1H, CH_2), 2.31 – 2.24 (m, 1H, CH_2), 2.15 (t, ^3J = 8.8 Hz, 1H, CH_2), 2.02 – 1.94 (m, 1H, CH_2), 1.58 – 1.51 (m, 2H, CH_2), 1.33 (ddd, ^3J = 23.4, 16.8, 7.1 Hz, 3H, CH_3); ^{13}C NMR (150.9 MHz, CD_3OD, TMS) δ 149.61, 147.88, 141.55, 137.06, 135.67, 134.09, 133.57, 133.12, 131.37, 130.00, 129.18, 128.15, 125.42, 122.97, 120.01, 118.31, 117.72, 116.37, 72.82, 70.14, 68.72, 61.70, 60.89, 52.12, 37.55, 29.32, 27.86, 26.28, 25.27, 24.58, 21.74, 13.82.



By comparison of ^{1}H NMR spectra, it was found that the peaks of hydrogens attached to endocyclic carbon-carbon double bond disappeared, which demonstrated that the free radical addition of sulfydryl in 3-MPTS was added to endocyclic carbon-carbon double bond.


3H of endocyclic double bond
1H of Allyl position double bond
1H of endocyclic double bond
2H of Allyl position double bond
2H of endocyclic double bond
2H of Allyl position double bond
1H of Allyl position double bond
f1 (ppm)