Electronic Supporting Information

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

Dandan Feng, a Jinghan Xu, a Jingwei Wan, a Bing Xie * b and Xuebing Ma* a

Table of contents

Preparation of chiral phase-transfer catalyst CDPTC ..............................S2

General procedure for \( N\text{-}(2\text{-}\text{cyanobenzyl})\text{cinchonidinium bromide} \) .........................S2
General procedure for \( N\text{-}(2\text{-}\text{cyanobenzyl})\text{-}O(9)\text{-}\text{allyl}\text{cinchonidinium bromide} \) (CDPTC) .................................................................S2

Characterization data of \( \alpha \)-alkylation products .................................S3

X-ray diffraction of SiO\(_2\)@CDPTC ..........................................................S32

The recovery and reuse of catalyst ..........................................................S32

HPLC chromatogram of various electrophiles catalyzed by homogeneous CDPTC ........................................................................ S34

\( \text{N}_2 \) adsorption–desorption isotherm of deeply hydrolytic SiO\(_2\)@CDPTC ..................................................................................S37
An analogues of CDPTC
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-cyano- benzyl bromide (2.1 g, 11.0 mmol) in toluene (100 mL) was stirred at 65°C 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%).

\[ ^1 \text{H NMR (300.1 MHz, CDCl}_3, \text{TMS)} \delta 8.86 (d, ^3J = 4.3 Hz, 1H, Ar-H), 8.47 (d, ^3J = 7.6 Hz, 1H, Ar-H), 8.21 (d, ^3J = 7.5 Hz, 1H, Ar-H), 7.95 (d, ^3J = 7.8 Hz, 1H, Ar-H), 7.78 (d, ^3J = 4.3 Hz, 1H, Ar-H), 7.63 (dd, ^3J = 9.6, 5.6 Hz, 2H, Ar-H), 7.56 – 7.43 (m, 3H, Ar-H), 6.68 (s, 1H, OCH), 6.08 (d, ^3J = 10.0 Hz, 1H, -CH=), 5.49 (ddd, ^3J = 16.8, 10.4, 6.1 Hz, 2H, =CH\_2), 5.17 (d, ^3J = 17.2 Hz, 1H, N^+\text{-CH}), 4.95 (d, ^3J = 10.4 Hz, 2H, N^+\text{-CH}_2), 4.02 (d, ^3J = 9.5 Hz, 2H, N^+\text{-CH}_2), 3.17 – 2.98 (m, 2H, N^+\text{-CH}_2), 2.54 (s, 1H, -OH), 2.17 (t, ^3J = 11.1 Hz, 1H, CH), 2.01 (dd, ^3J = 22.5, 9.5 Hz, 3H, CH, CH\_2), 1.60 – 1.76 (m, 2H, CH\_2). \]

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

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°C 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\textsubscript{2}SO\textsubscript{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%).

\[ ^1 \text{H NMR (300 MHz, CDCl}_3, \text{TMS)} \delta 8.96 (d, ^3J = 4.3 Hz, 2H, Ar-H), 8.84 (d, ^3J = 8.5 Hz, 1H, Ar-H), 8.13 (d, ^3J = 8.3 Hz, 1H, Ar-H), 7.92 (d, ^3J = 6.4 Hz, 1H, Ar-H), 7.89 – 7.73 (m, 3H, Ar-H), 7.65 (t, ^3J = 7.6 Hz, 2H, Ar-H), \]
6.91 (d, $J = 12.1$ Hz, 1H, OCH), 6.28–6.09 (m, 2H, -CH=, -CH=), 5.70 (ddd, $J = 16.8$, 10.4, 6.2 Hz, 1H, =CH2), 5.41 (d, $J = 17.2$ Hz, 1H, =CH2), 5.31 (dd, $J = 13.6$, 8.0 Hz, 2H, =CH2), 5.22 (d, $J = 12.5$ Hz, 1H, N+-CH), 4.98 (ddd, $J = 23.9$, 11.3 Hz, 2H, N+-CH2), 4.83 – 4.56 (m, 2H, OCH2), 4.16 (d, $J = 6.1$ Hz, 2H, N+-CH3), 3.16 (dd, $J = 15.4$, 7.0 Hz, 2H, N+-CH2), 2.63 (s, 1H, CH), 2.17 (dd, $J = 16.7$, 6.2 Hz, 1H, CH), 2.06 (d, $J = 7.0$ Hz, 3H, CH2, CH3), 1.82 (d, $J = 6.6$ Hz, 1H, CH2).

Fig. 2 $^1$H NMR of N-(2-cyanobenzyl)-O(9)-allylecinchinidinium bromide

Characterization data of $\alpha$-alkylation products

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

$^1$H NMR (300.1 MHz, CDCl3, TMS) δ 7.52 (d, $J = 7.0$ Hz, 2H, Ph-H), 7.30–7.00 (m, 11H, Ph-H), 6.54 (d, $J = 6.4$ Hz, 2H, Ph-H), 4.06 (dd, $J = 4.4$ Hz, 4.4 Hz, 1H, NCH), 3.22–3.07 (m, 2H, CH2), 1.39 (s, 9H, CH3);

$^{13}$C NMR (75.0 MHz, CDCl3, 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, 127.9, 127.6, 126.6, 126.1(PH), 81.1 (O-C), 67.9 (NCH), 39.5 (CH2), 28.0 (CH3); 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

Fig. 5 The HPLC chromatogram of racemic tert-butyl 3-phenyl-2-(diphenylmethyleneamino) propanoate
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): $\delta$ 7.54 (d, $^3$J = 7.1 Hz, 2H, Ph-H), 7.40 (d, $^3$J = 7.9 Hz, 2H, Ph-H), 7.37–7.21 (m, 6H, Ph-H), 7.13 (d, $^3$J = 7.9 Hz, 2H, Ph-H), 6.58 (d, $^3$J = 6.4 Hz, 2H, Ph-H), 4.10 (dd, $^3$J = 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): $\delta$ 170.7, 170.4 (C=N, C=O), 142.6 (q, $^1$J$_{C,F}$ = 1.3 Hz), 139.2, 137.5, 136.0, 132.4, 130.3, 130.1, 130.0, 129.7, 128.6, 128.3, 128.2, 128.1, 128.0, 127.4, 126.0 (Ph), 125.2 (q, $^2$J$_{C,F}$ = 3.8 Hz), 124.9 (q, $^2$J$_{C,F}$ = 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

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

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, $^3J = 7.0$ Hz, 2H, Ph-H), 7.40–7.21 (m, 10H, Ph-H), 6.57 (d, $^3J = 6.6$ Hz, 2H, Ph-H), 4.09 (dd, $^3J = 5.6$ 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, $^2J_{C,F} = 3.7$ Hz, CF$_3$), 125.9 (Ph), 123.0 (q, $^1J_{C,F} = 3.8$ 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
**Fig. 13** The HPLC chromatogram of racemic tert-butyl 3-(3-trifluoromethylphenyl)-2-(diphenylmethyleneamino)propanoate

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**Fig. 14** The HPLC chromatogram of tert-butyl 3-(3-trifluoromethylphenyl)-2-(diphenylmethyleneamino)propanoate catalyzed by SiO₂@CDPTC

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

\[
\text{H}_\text{NMR} \ (300.1 \text{ MHz, CDCl}_3, \ TMS): \delta 7.76 (\text{d, } ^3J = 7.1 \text{ Hz, 1H, Ph-H}), 7.57-7.41 \text{ (m, 4H, Ph-H}), 7.35-7.15 \text{ (m, 7H, Ph-H), 6.43 (d, } ^3J = 6.4 \text{ Hz, 2H, Ph-H), 4.13 (dd, } ^3J = 3.5 \text{ Hz, 3.5 Hz, 1H, NCH), 3.50-3.22 \text{ (m, 2H, CH}_2\text{), 1.39 (s, 9H, CH}_3\text{); } ^{13}\text{C NMR (75.0 MHz, CDCl}_3, \ TMS): \delta 170.7, 170.5 \text{ (C=O, C=N), 139.2, 136.8 (q, } ^2J_{C,F} = 1.6 \text{ Hz), 136.0, 133.3, 132.4, 131.1, 130.2, 131.0, 129.6, 128.7, 128.2, 128.1, 127.9, 127.9, 127.3, 126.3, 126.0 (Ph), 125.7 (q, } ^1J_{C,F} = 5.7 \text{ Hz, CF}_3\text{), 81.2 (O-C), 66.5 (NCH), 36.0 (CH}_2\text{), 27.9 (CH}_3\text{); HPLC analysis: Phenomenex Lux 5u Amylose-2, hexane/dioxane = 95/5, 254 \text{ nm, flow rate = 0.5 ml/min, retention times: 12.2 min (R), 14.8 min (S).} \]
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
**Fig. 17** The HPLC chromatogram of racemic tert-butyl 3-(2-trifluoromethylphenyl)-2-(diphenylmethyleneamino)propanoate

**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): $\delta$ 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): $\delta$ 170.6, 170.4 (C=N, C=O), 163.1, 160.0, 139.3, 134.0, 132.4, 131.2 (d, $^2J_{C,F} = 7.8$ 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, $^1J_{C,F} = 20.9$ Hz, F), 81.2 (O-C), 67.7 (NCH), 38.7 (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: 12.7 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

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

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): $\delta$ 7.49 (d, $^3J = 6.7$ Hz, 2H, Ph-H), 7.26–7.19 (m, 7H, Ph-H), 7.08 (q, $^3J = 6.6$ Hz, 1H, Ph-H), 6.79–6.62 (m, 4H, Ph-H), 6.66 (d, $^3J = 6.6$ Hz, 2H, Ph-H), 4.04 (dd, $^3J = 3.8$ 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): $\delta$ 170.5, 170.4 (C=N, C=O), 164.2, 160.9, 140.8 (d, $^3J_{C,F} = 7.4$ 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, $^3J_{C,F} = 20.9$ Hz, F), 112.9 (d, $^1J_{C,F} = 20.9$ 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
**Fig. 25** The HPLC chromatogram of racemic tert-butyl 3-(3-fluorophenyl)-2-(diphenylmethyleneamino)propanoate

**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): $\delta$ 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): $\delta$ 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, $^3J_{C-F} = 15.5$ Hz, F), 123.5 (d, $^2J_{C-F} = 3.5$ Hz, F), 114.9 (d, $^1J_{C,F} = 21.9$ 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/di-octane = 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

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

**Table 2**

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**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, $^3$J = 7.2 Hz, 1H, Ph-H), 7.58 (d, $^3$J = 7.1 Hz, 2H, Ph-H), 7.39–7.25 (m, 6H, Ph-H), 6.96 (q, $^3$J = 7.9 Hz, 4H, Ph-H), 6.62 (d, $^3$J = 6.6 Hz, 2H, Ph-H), 4.09 (dd, $^3$J = 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 Su 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

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

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): $\delta$ 7.81 (d, $^3J = 7.2$ Hz, 1H, Ph-H), 7.62–7.46 (m, 4H, Ph-H), 7.38–7.26 (m, 7H, Ph-H), 6.59 (d, $^3J = 6.5$ Hz, 2H, Ph-H), 4.09 (dd, $^3J = 4.5$ 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): $\delta$ 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
Fig. 37 The HPLC chromatogram of racemic tert-butyl 3-(3-methylphenyl)-2-(diphenylmethyleneamino)propanoate

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): $\delta$ 7.60 (d, $^3$J = 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, $^3$J = 4.1 Hz, 2H, Ph-H), 4.15 (dd, $^3$J = 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): $\delta$ 171.0, 170.1 (C=N, C=O), 139.3, 136.9, 136.3, 136.2, 132.4, 131.0, 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

Fig. 41 The HPLC chromatogram of racemic tert-butyl 3-(2-methylphenyl)-2-(diphenylmethyleneamino)propanoate
Fig. 42 The HPLC chromatogram of tert-buty 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): $\delta$ 7.78 (d, $^3$J = 7.6 Hz, 1H, Ar-H), 7.73 (d, $^3$J = 7.2 Hz, 1H, Ar-H), 7.64 (dd, $^3$J = 17.6, 12.3 Hz, 2H, Ar-H), 7.54 (t, $^3$J = 8.0 Hz, 2H, Ar-H), 7.45 (dd, $^3$J = 19.8, 12.2 Hz, 2H, Ar-H), 7.40 – 7.35 (m, 2H, Ar-H), 7.32 (dd, $^3$J = 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, $^3$J = 9.2, 4.2 Hz, 1H, NCH), 3.34 (ddd, $^3$J = 27.7, 13.5, 6.8 Hz, 2H, CH$_2$), 1.42 (s, 9H, CH$_3$); $^{13}$C NMR (150.9 MHz, CDCl$_3$, TMS): $\delta$ 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-(diphenylmethylenedioxyamino)propanoate

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

Fig. 46 The HPLC chromatogram of tert-butyl 3-(2-naphthyl)-2-(diphenylmethylenedioxyamino)propanoate catalyzed by $\text{SiO}_2@\text{CDPTC}$
**tert-Butyl 3-vinyl-2-(diphenylmethyleneamino)propanoate (Entry 11 in Table 2).**

1H NMR (600.1 MHz, CDCl₃, 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, =CH₂), 3.93 (dd, ³J = 7.6, 5.3 Hz, 1H, NCH), 2.62 – 2.50 (m, 2H, CH₂), 1.35 (s, 9H, CH₃); ¹³C NMR (150.9 MHz, CDCl₃, 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 (CH₂), 28.12 (CH₃); 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. 49** The HPLC chromatogram of racemic tert-butyl 3-vinyl-2-(diphenylmethyleneamino)propanoate.

**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): $\delta$ 7.66 (dd, $^3$J = 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, $^3$J = 7.4 Hz, 2H, Ph-H), 7.19 (t, $^3$J = 14.0 Hz, 2H, Ph-H), 4.72 (d, $^3$J = 14.0 Hz, 2H, =CH$_2$), 4.08 (dd, $^3$J = 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): $\delta$ 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

Fig. 53 The HPLC chromatogram of racemic tert-butyl 3-(1-methylvinyl)-2-(diphenylmethyleneamino)propanoate
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): $\delta$ 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, $\equiv$CH), 1.45 (s, 9H, CH$_3$); $^{13}$C NMR (150.9 MHz, CDCl$_3$, TMS) $\delta$ 171.4, 169.5 (C=N, C=O), 139.6, 137.7, 136.3, 132.4, 130.0, 129.0, 128.6, 128.3, 128.0 (Ph-C), 81.6 ($\equiv$CH), 81.3 (O-C), 70.0 ($=\equiv$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

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

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) $\delta$ 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$_3$) $\delta$ 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, 127.1, 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
**Fig. 61** The HPLC chromatogram of racemic tert-butyl 3-(4-nitrophenyl)-2-(diphenylmethyleneamino)propanoate

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**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): \(\delta\) 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\(_3\)) \(\delta\) 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, 128.1, 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

Fig. 65 The HPLC chromatogram of racemic tert-butyl 3-(3-nitrophenyl)-2-(diphenylmethyleneamino)propanoate
**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): $\delta$ 8.05 – 7.98 (m, 1H, Ph-H), 7.97 – 7.88 (m, 1H, Ph-H), 7.80 (dd, $^3$J = 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, $^3$J = 7.0, 4.3 Hz, 2H, Ph-H), 7.45 – 7.36 (m, 2H, Ph-H), 7.32 (d, $^3$J = 6.8 Hz, 2H, Ph-H), 7.20 (d, $^3$J = 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): $\delta$ 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, 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

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

**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-K$_\alpha$ radiation, X-ray tube settings of 40.0kV/30.0 mA, a scan speed of 2°/min in the 10–100° (2θ) range. X-ray diffraction of SiO$_2$@CD/PTC (Fig. 71) indicate that the structure is amorphous.

![X-ray diffraction patterns of SiO$_2$@CDPTC](image)

**Fig.71** X-ray diffraction patterns of SiO$_2$@CDPTC

The recovery and reuse of catalyst

The data of the yields and enantioselectivities of $\alpha$-alkylation product tert-Butyl 3-phenyl-2-(diphenylmethyleneamino)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

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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. *Isolated yield. $^b$Determined by chiral HPLC with Phenomenex Lux 5u Amylose-2 chiral column.

![Reusability of SiO$_2$@CDPTC](image)

**Table 2** X-ray diffraction data of SiO$_2$@CDPTC used for the first time

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SiO₂@CDTC reused for the first time

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SiO₂@CDTC reused for the second time

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SiO₂@CDTC reused for the third time

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SiO₂@CDTC reused for the fourth time

S34
Fig. 72 The HPLC chromatogram of tert-butyl 3-phenyl-2-(diphenylmethyleneamino)propanoate in the six times

HPLC chromatogram of homogeneous CDPTC
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S37
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$_3$OH (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$_3$OD, TMS) δ 9.02 (d, $^3$J = 4.5 Hz, 1H, Ph-H), 8.42 (d, $^3$J = 8.1 Hz, 1H, Ph-H), 8.22 (d, $^3$J = 7.6 Hz, 1H, Ph-H), 8.19 (dd, $^3$J = 7.5, 6.7 Hz, 1H, Ph-H), 8.06 (d, $^3$J = 7.7 Hz, 1H, Ph-H), 7.96 (dd, $^3$J = 11.1, 4.3 Hz, 1H, Ph-H), 7.94 – 7.86 (m, 3H, Ph-H), 7.84 (t, $^3$J = 7.7 Hz, 1H, Ph-H), 7.84 (t, $^3$J = 7.7 Hz, 1H, Ph-H), 6.55 (d, $^3$J = 18.7 Hz, 1H, O-CH), 6.33 – 6.24 (m, 1H, -CH=), 5.78 – 5.69 (m, 1H, =CH$_2$), 5.49 (dd, $^3$J = 17.2, 1.1 Hz, 1H, =CH$_2$), 5.38 (dt, $^3$J = 14.9, 11.7 Hz, 3H, N$^\text{+}$-CH, N$^\text{+}$-CH$_2$), 5.22 (dd, $^3$J = 16.5, 8.3 Hz, 1H, O-CH$_2$), 5.03 (t, $^3$J = 9.2 Hz, 1H, O-CH$_2$), 4.58 (ddd, $^3$J = 16.3, 11.3, 5.0 Hz, 1H, N$^\text{+}$-CH$_2$), 4.45 (dd, $^3$J = 11.9, 5.9 Hz, 1H, N$^\text{+}$-CH$_2$), 4.17 (ddd, $^3$J = 25.7, 14.2, 7.2 Hz, 2H, N$^\text{+}$-CH$_2$), 3.97 (ddd, $^3$J = 12.5, 8.6, 4.4 Hz, 1H, S-CH$_3$), 3.77 – 3.63 (m, 2H, S-CH$_3$), 3.45 (td, $^3$J = 11.3, 4.3 Hz, 1H, S-CH$_2$), 2.84 – 2.77 (m, 1H, CH), 2.62 (q, $^3$J = 7.4 Hz, 1H, CH), 2.48 – 2.41 (m, 1H, CH$_2$), 2.31 – 2.24 (m, 1H, CH$_2$), 2.15 (t, $^3$J = 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, $^3$J = 23.4, 16.8, 7.1 Hz, 3H, CH$_3$); $^{31}$C NMR (150.9 MHz, CD$_3$OD, 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.