

Supplementary Information for:

Efficient Synthesis of Optically Active α -Quaternary Amino Acids by Highly Diastereoselective [2,3]-Rearrangement of Allylic Ammonium Ylides

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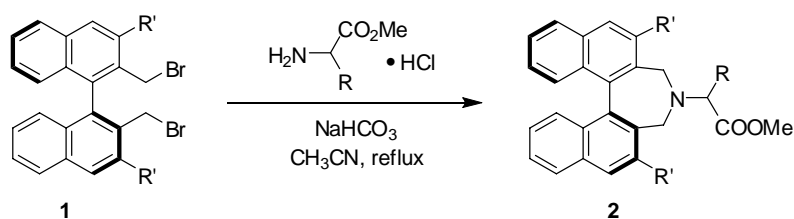
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1. General

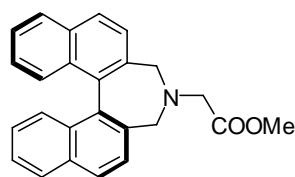
All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or argon. NMR spectra were recorded on a Mercury 300 spectrometer (300 MHz for ^1H), and Variant MR-400 (100 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal SiMe_4 standard for ^1H NMR and chloroform-*d* (δ 77.00) for ^{13}C NMR. Optical rotations were measured on a Perkin-Elmer 241 MC polarimeter. HPLC was performed on a JASCO 2000 instrument by using Daicel columns. LC-MS are performed on a Agilent 1100 instrument by column 20RBAX SB-C18 (4.6X30mm, 3.5 μm)

2. General Procedure for the Synthesis of Amines 2

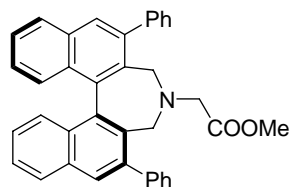
2.1 General Synthetic Procedure for Amines 2a-j



To a 50 mL flask was added dibromo compound **1**¹ (440 mg, 1 mmol), methyl amino acid hydrogen chloride (1.5 mmol), NaHCO_3 (330 mg, 3 mmol) and 20 mL of acetonitrile. The reaction was stirred under reflux for about 4 hours and monitored by TLC for completion. The mixture was then cooled to room temperature, diluted with CH_2Cl_2 , and filtrated through Celite. The filtrate was washed three times with water and brine, dried over anhydrous Na_2SO_4 , and concentrated. Purification by flash column chromatography on silica gel afforded the corresponding *N,N*-disubstituted amine product **2**.

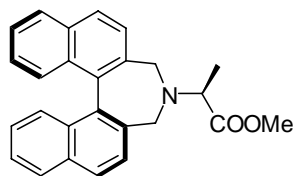


(*S*)-**2a**, light yellow solid, yield 99%;
 ^1H NMR (300 MHz, CDCl_3) δ 3.22 (d, 1H, $J = 16.2$ Hz, $\text{CH}_2\text{-COOMe}$), 3.30 (d, 2H, $J = 12.3$ Hz, Ar- CH_2), 3.44 (d, 1H, $J = 16.2$ Hz, $\text{CH}_2\text{-COOMe}$), 3.76 (d, 2H, $J = 12.3$ Hz, Ar- CH_2), 3.78 (s, 3H, COOCH_3), 7.26-7.29 (m, 2H, Ar-H), 7.44-7.49 (m, 4H, Ar-H), 7.57 (d, 2H, $J = 8.4\text{Hz}$, Ar-H), 7.95(d, 4H, $J = 8.1$ Hz, Ar-H).

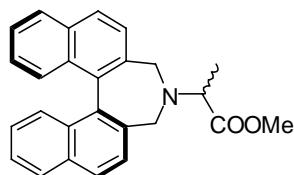


(*S*)-**2a'**, colorless oil yield 94%;
 ^1H NMR (300 MHz, CDCl_3) δ 2.81(dd, 2H, $J = 18.9\text{Hz}$, 16.2 Hz, $\text{CH}_2\text{-COOMe}$). 3.16(d, 2H, $J = 12.6$ Hz, Ar- CH_2), 3.42(s, 3H, COOCH_3), 4.01(d, 2H, $J = 12.6$ Hz, Ar- CH_2), 7.26-7.32 (m, 2H, Ar-H), 7.40-7.60 (m, 10H, Ar-H), 7.61 (d, 4H, $J = 6.9$ Hz, A-H), 7.95-7.98(m, 4H, Ar-H)

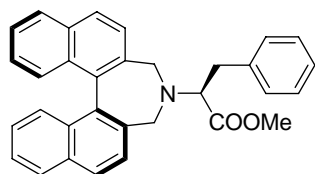
¹ T. Ooi, M. Kameda, K. Maruoka, *J. Am. Chem. Soc.*, **2003**, 125, 5139.



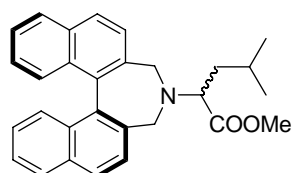
(*S, L*)-**2b** (*S* for the confirmation of Chiral auxiliary, *L* for the confirmation of amino acid), colorless oil, yield 95%;
 $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 1.54 (d, 3H, $J = 6.9$ Hz, $\text{CH}-\underline{\text{CH}_3}$), 3.42 (d, 2H, $J = 12.6$ Hz, Ar- CH_2), 3.40- 3.48 (m, 1H, $\underline{\text{CH}}-\text{CH}_3$), 3.67 (s, 3H, COOCH_3), 3.90 (d, 2H, $J = 12.6$ Hz, Ar- CH_2), 7.25-7.28 (m, 2H, Ar-H), 7.46-7.51 (m, 4H, Ar-H), 7.60 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.98 (d, 4H, $J = 8.4$ Hz, Ar-H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 16.6, 51.9, 53.2, 61.4, 125.4, 125.7, 127.4, 128.1, 128.2, 128.3, 131.2, 133.1, 135.0, 174.5 ppm.



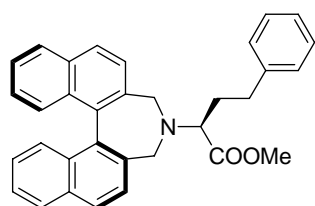
(*S, rac*)-**2b**, colorless oil, yield 94% (including two isomers);
 $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 1.39 and 1.54 (d, 3H, $J = 6.9$ Hz, $\text{CH}-\underline{\text{CH}_3}$), 3.37- 3.48 (m, 3H, Ar- $\underline{\text{CH}_2}$, $\underline{\text{CH}}-\text{CH}_3$), 3.66 and 3.74 (s, 3H, COOCH_3), 3.79 and 3.90 (d, 2H, $J = 12.6$ Hz, Ar- CH_2), 7.23-7.28 (m, 2H, Ar-H), 7.44-7.51 (m, 4H, Ar-H), 7.57-7.62 (m, 2H, Ar-H), 7.95-7.99 (m, 4H, Ar-H).



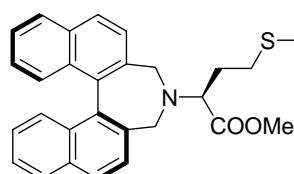
(*S, L*)-**2c**, colorless oil, yield 92%;
 $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 3.18 (d, 2H, $J = 7.5$ Hz, Ph- $\underline{\text{CH}_2}$), 3.42 (s, 3H, COOCH_3), 3.57 (d, 2H, $J = 12.0$ Hz, Ar- CH_2), 3.71 (t, 1H, $J = 7.5$ Hz, $\underline{\text{CH}}\text{COOMe}$), 3.92 (d, 2H, $J = 12.3$ Hz, Ar- CH_2), 7.20-7.28 (m, 7H, Ar-H), 7.42-7.48 (m, 4H, Ar-H), 7.55 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.94 (dd, 4H, $J = 8.1$ Hz, 8.1 Hz, Ar-H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 37.1, 51.4, 53.2, 68.4, 125.4, 125.7, 126.4, 127.5, 128.1, 128.2, 128.3, 128.4, 129.2, 131.2, 133.1, 133.2, 134.9, 137.7, 172.9 ppm



(*S, rac*)-**2d**, colorless oil, yield 99% (including two isomers);
 $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 0.86-1.01 (m, 6H, $\text{CH}(\underline{\text{CH}_3})_2$), 1.65-1.79 (m, 3H, $\underline{\text{CH}_2}\underline{\text{CH}}(\text{CH}_3)_2$), 3.30-3.40 (m, 1H, N-CH), 3.46 and 3.55 (d, 2H, $J = 12.3$ Hz, Ar- CH_2), 3.55 and 3.58 (s, 3H, COOCH_3), 3.80 and 3.84 (d, 2H, $J = 12.3$ Hz, Ar- CH_2), 7.22-7.28 (m, 2H, Ar-H), 7.43-7.48 (m, 4H, Ar-H), 7.54 and 7.58 (d, 2H, $J = 8.1$ Hz, Ar-H), 7.95 (d, 4H, $J = 8.1$ Hz, Ar-H).

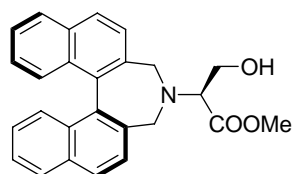


(*S, L*)-**2e**, colorless oil, yield 94%;
 $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 2.14-2.21 (m, 2H, Ph- $\text{CH}_2-\underline{\text{CH}_2}$), 2.73 (t, 2H, $J = 7.8$ Hz, Ph- CH_2), 3.31 (t, 1H, $J = 7.5$ Hz, N-CH), 3.55 (d, 2H, $J = 12.6$ Hz, Ar- CH_2), 3.58 (s, 3H, COOCH_3), 3.81 (d, 2H, $J = 12.6$ Hz, Ar- CH_2), 7.24-7.35 (m, 7H, Ar-H), 7.35-7.51 (m, 4H, Ar-H), 7.60 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.96-8.01 (m, 4H, Ar-H).
 $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 31.9, 32.0, 51.4, 51.7, 65.0, 125.4, 125.7, 126.0, 127.5, 128.2, 128.3, 128.4, 128.5, 131.2, 133.0, 133.4, 134.8, 141.5, 173.7 ppm.



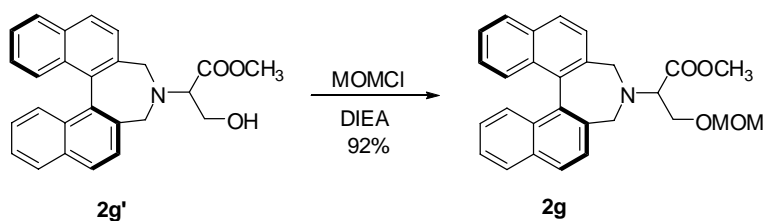
(*S, L*)-**2f**, light yellow powder, yield 90%;
 $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 2.06-2.11 (m, 2H, S- CH_2-CH_2), 2.11 (s, 3H, S- CH_3), 2.53-2.60 (m, 2H, S- CH_2-CH_2), 3.45-3.50 (m, 1H, N-CH), 3.51 (d, 2H, $J = 12.6$ Hz, Ar- CH_2), 3.54 (s, 3H, COOCH_3), 3.77 (d, 2H, $J = 12.6$ Hz, Ar- CH_2), 7.21-7.28 (m, 2H, Ar-H),

7.41-7.48 (m, 4H, Ar-H), 7.54 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.94 (d, 4H, $J = 8.4$ Hz, Ar-H). ^{13}C NMR (100 MHz, CDCl_3) δ 15.5, 29.6, 30.5, 51.5, 52.7, 64.4, 125.4, 125.7, 127.5, 128.1, 128.2, 128.4, 131.2, 133.0, 133.3, 134.8, 173.5 ppm.



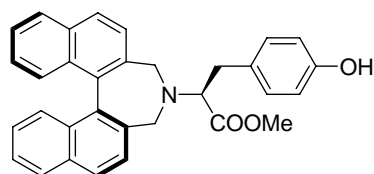
(*S,L*)-**2g'**, white solid, yield 96%;

^1H NMR (300 MHz, CDCl_3) δ 3.44-3.49 (m, 1H, N-CH), 3.49 (s, 3H, COOCH_3), 3.65 (d, 2H, $J = 12.6$ Hz, Ar- CH_2), 3.80 (d, 2H, $J = 12.3$ Hz, Ar- CH_2), 3.80-3.94 (m, 2H, CH_2OH), 7.23-7.28 (m, 2H, Ar-H), 7.41-7.49 (m, 2H, Ar-H), 7.52 (d, 2H, $J = 8.7$ Hz, Ar-H), 7.92-7.97 (m, 4H, Ar-H). ^{13}C NMR (100 MHz, CDCl_3) δ 51.5, 52.5, 59.6, 65.7, 125.6, 125.8, 127.5, 127.9, 128.2, 128.6, 131.3, 133.0, 133.1, 134.9, 172.4 ppm.



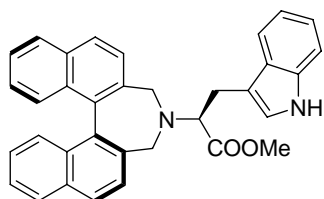
To a 25 mL flask was added **2g'** (40 mg, 0.1 mmol), DIEA (70 μL , 4 eq), MOMCl (12 μL , 1.5 eq) and CH_2Cl_2 (5 mL). The reaction was stirred under room temperature and monitored by TLC for completion. The mixture was then quenched with NH_4Cl (aq, saturated), extracted for three times with CH_2Cl_2 . The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4 , and concentrated. Purification by flash column chromatography on silica gel (eluted with 5:1 hexane/ethyl acetate) afforded the MOM-protected product **2g** (40 mg, 92%)

^1H NMR (300 MHz, CDCl_3) δ 3.39 (s, 3H, OCH_2OCH_3), 3.48 (d, 2H, $J = 12.0$ Hz, Ar- CH_2), 3.53-3.57 (m, 1H, CH_2OMOM), 3.68 (s, 3H, COOCH_3), 3.78 (d, 2H, Ar- CH_2), 3.79-3.84 (m, 1H, CH_2OMOM), 3.95-4.01 (m, 1H, N-CH), 4.62 (s, 1H, OCH_2OCH_3), 7.25-7.28 (m, 2H, Ar-H), 7.43-7.48 (m, 4H, Ar-H), 7.58 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.93-7.97 (m, 4H, Ar-H). ^{13}C NMR (100 MHz, CDCl_3) δ 51.8, 53.3, 55.3, 65.7, 66.7, 96.6, 125.5, 125.7, 127.4, 128.1, 128.2, 128.4, 131.2, 132.9, 133.1, 134.9, 172.2 ppm.



(*S,L*)-**2h**, white solid, yield 91%;

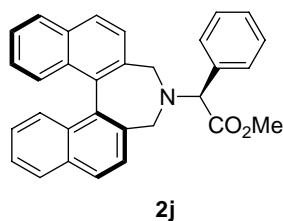
^1H NMR (300 MHz, CDCl_3) δ 3.03 (d, 2H, $J = 6$ Hz, Ph- CH_2), 3.46 (d, 2H, $J = 12.3$ Hz, Ar- CH_2), 3.48 (s, 3H, COOCH_3), 3.44-3.49 (m, 1H, N-CH), 3.85 (d, 2H, $J = 12.4$ Hz, Ar- CH_2), 6.70 (d, 2H, $J = 8.1$ Hz, Ph-H), 7.00 (d, 2H, $J = 8.1$ Hz, Ph-H), 7.23-7.29 (m, 2H, Ar-H), 7.44-7.49 (m, 4H, Ar-H), 7.57 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.97 (d, 4H, $J = 8.4$ Hz, Ar-H). ^{13}C NMR (100 MHz, CDCl_3) δ 36.2, 51.6, 53.3, 68.8, 115.3, 125.5, 125.7, 127.5, 128.15, 128.24, 128.4, 129.2, 130.3, 131.2, 133.0, 133.1, 134.9, 154.4, 173.1 ppm



(*S,L*)-**2i**, white solid, yield 92%;

^1H NMR (300 MHz, CDCl_3) δ 3.0-3.3 (m, 2H, Ph- CH_2), 3.47-3.50(m, 1H, N-CH) 3.42 and 3.45 (s, 3H, COOCH_3), 3.54-3.70 (m, 2H, Ar- CH_2), 3.86-4.01 (m, 2H, Ar- CH_2), 7.0-7.3 (m, 6H, Ar-H), 7.47-7.52 (m, 4H, Ar-H), 7.58-7.70 (m, 3H, Ar-H), 7.98 (d, 2H, $J = 8.4$ Hz, Ar-H), 8.17 (b, 1H, NH).

^{13}C NMR (100 MHz, CDCl_3) 26.5, 51.4, 53.2, 67.4, 111.0, 111.6, 118.7, 119.3, 121.9, 122.7, 125.4, 125.7, 127.4, 127.5, 128.2, 128.2, 128.4, 131.2, 133.0, 133.3, 134.9, 136.0, 173.4 ppm.



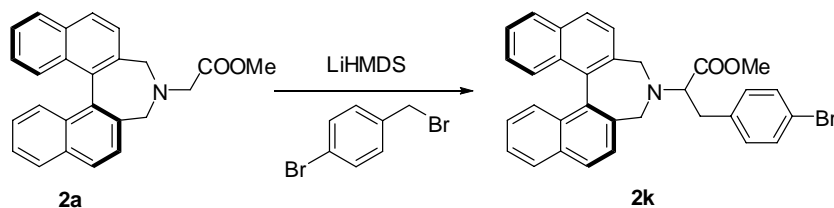
2j

(*S,L*)-**2j**, white solid, yield 93%;

^1H NMR (300 MHz, CDCl_3) δ 3.19 (d, 2H, $J = 12.3$ Hz, Ar CH_2), 3.63 (s, 3H, COOCH_3), 3.77 (d, 2H, $J = 12.0$ Hz, Ar CH_2), 4.01 (s, 1H, NCH COOCH_3), 7.21-7.27 (m, 2H, Ar-H), 7.38-7.48 (m, 9H, Ar-H), 7.65 (d, 2H, $J = 6.9$ Hz, ArH), 7.94 (d, 4H, $J = 8.1$ Hz, ArH). ^{13}C NMR (100 MHz, CDCl_3) 52.4, 53.9, 71.8, 125.5, 125.7, 125.5, 125.7, 127.4, 128.0, 128.3, 128.3, 128.6, 128.6, 128.9, 131.2, 132.8, 133.2, 135.1,

136.0, 172.5 ppm.

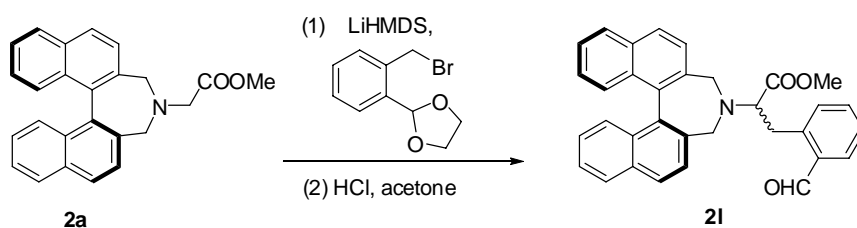
2.2 Synthetic Procedure for Amine **2k**



Under nitrogen atmosphere, to a solution of (*S*)-**2a** (36.5 mg, 0.1 mmol) in dry THF at -78°C was added LiHMDS (1.0 M in THF, 0.15 mL, 1.5 eq). The mixture was allowed to warm and stirred at 0°C for 1h, and then cooling to -78°C again, 1-bromo-4-(bromomethyl)-benzene (50 mg, 2 eq) was added and the mixture was allowed to warm to room temperature slowly and stirred for another 6h. The reaction was quenched with water, and extracted with ethyl acetate for 3 times. The organic layer was washed with NaHCO_3 (aq, saturated) and brine, dried over anhydrous Na_2SO_4 , and concentrated. Purification by flash column chromatography on silica gel (eluted with 10:1 hexane/ethyl acetate) afforded a colorless oil **2k** (36 mg, 67%).

^1H NMR (300 MHz, CDCl_3) δ 2.95-3.18 (m, 2H, Ph- CH_2), 3.44 (s, 3H, COOCH_3), 3.42-3.51 (m, 1H, N-CH), 3.50 (d, 2H, $J = 12.3$ Hz, Ar- CH_2), 3.82 (d, 2H, $J = 12.4$ Hz, Ar- CH_2), 7.05 (d, 2H, $J = 8.4$ Hz, Ph-H), 7.24-7.27 (m, 2H, Ar-H), 7.37 (d, 2H, $J = 8.4$ Hz, Ph-H), 7.42-7.47 (m, 4H, Ar-H), 7.54 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.94 (d, 2H, $J = 8.4$ Hz, Ar-H). ^{13}C NMR (100 MHz, CDCl_3) δ 36.4, 51.4, 53.0, 59.0, 67.9, 71.7, 120.3, 125.5, 125.7, 127.4, 127.6, 128.0, 128.2, 128.4, 130.8, 131.0, 131.2, 131.3, 131.5, 133.01, 133.04, 133.2, 134.8, 134.9, 136.8, 172.7 ppm.

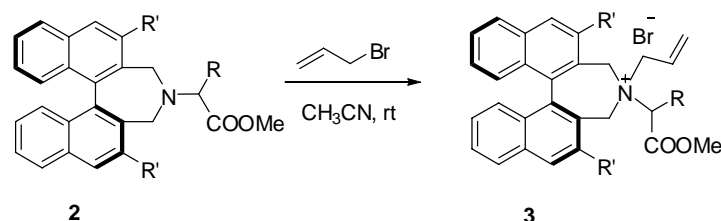
2.3 Synthetic Procedure for Amine 21



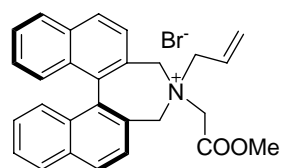
Under nitrogen atmosphere, to a solution of (S)-**2a** (36.5 mg, 0.1 mmol) in dry THF at -78°C was added LiHMDS (1.0 M in THF, 0.15 mL, 1.5 eq). The mixture was allowed to warm and stirred at 0°C for 1h, and then cooling to -78°C again, 2-(2-(bromomethyl)phenyl)-1,3-dioxolane (48 mg, 2 eq) was added and the mixture was allowed to warm to room temperature slowly and stirred for another 6h. The reaction was quenched with water, extracted with ethyl acetate for 3 times. The organic layer was washed with NaHCO₃ (aq, saturated) and brine, dried over anhydrous Na₂SO₄, and concentrated.

The above obtained residue was dissolved in acetone and drops of concentrated HCl was added. After further stirring at room temperature for 3h, the reaction was quenched with NaHCO₃ (aq, saturated), extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na₂SO₄, and concentrated. Purification by flash column chromatography on silica gel (eluted with 10:1 hexane/ethyl acetate) afforded a colorless oil **21** (30 mg, 62%). ¹H NMR (300 MHz, CDCl₃) δ 3.23-3.27 (m, 2H, Ph-CH₂), 3.39 (s, 3H, COOCH₃), 3.44-3.50 (m, 1H, N-CH), 3.62 (d, 2H, *J* = 12.3 Hz, Ar-CH₂), 3.92 (d, 2H, *J* = 12.4 Hz, Ar-CH₂), 7.26-7.30 (m, 2H, Ar-H), 7.43-7.59 (m, 10H, Ar-H), 7.96 (d, 4H, *J* = 7.8 Hz, Ar-H), 10.26 (s, 1H, -CHO)

3. General Procedure for the Synthesis of Ammonium Salts



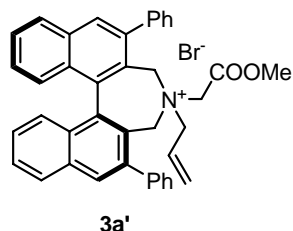
To a 25 mL flask was added the amine substrates **2** (0.2 mmol), allyl bromide (0.4 mmol) and 5 mL of acetonitrile. The reaction was stirred at room temperature for 1-2 days, monitored by TLC for completion. The mixture was then diluted with CH₂Cl₂, concentrated under vacuum, removing the solvent and allyl bromide. The residue was purified by flash column chromatography on silica gel afforded the corresponding ammonium salts **3**.



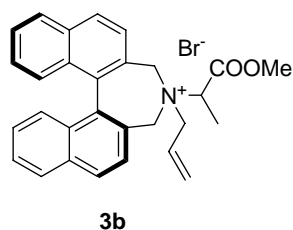
3a, white solid, yield 96%;

¹H NMR (300 MHz, CDCl₃) δ 3.77 (d, 2H, *J* = 12.0 Hz), 3.78 (s, 3H), 4.25 (dd, 1H, *J* = 7.2 Hz, 13.5 Hz), 4.44 (d, 1H, *J* = 17.4 Hz), 4.72 (dd, 1H, *J* = 7.5 Hz, 13.5 Hz), 5.30 (d, 1H, *J* = 13.2 Hz), 5.48 (d, 1H, *J* = 17.7 Hz), 5.66 (d, 1H, *J* = 17.7 Hz), 5.75 (d, 1H, *J* = 9.3 Hz), 5.87 (d, 1H, *J* = 12.9 Hz), 6.40-6.54 (m, 1H), 7.38-7.44 (m, 4H), 7.59-7.62 (m, 2H), 7.74 (d, 1H, *J* = 7.8

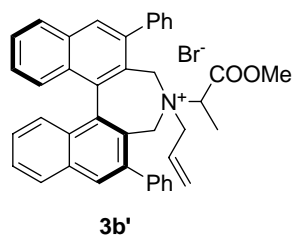
Hz), 8.01-8.05 (m, 2H), 8.13 (d, 2H, $J = 8.4$ Hz), 8.26 (d, 1H, $J = 7.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 53.2, 57.2, 62.6, 63.1, 64.2, 124.6, 125.6, 125.9, 127.2, 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 128.1, 128.5, 128.6, 129.2, 130.2, 130.6, 131.0, 131.1, 134.37, 134.44, 136.5, 137.0 ppm. ESI-MS: 408.1 (M^+ -Br); HRMS (ESI) for $\text{C}_{28}\text{H}_{26}\text{N}_1\text{O}_2$ (M^+ -Br): calcd 408.1964, found 408.1954.



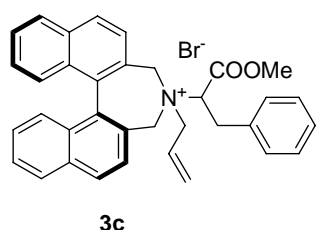
3a', white solid, yield 82%;
 ^1H NMR (300 MHz, CDCl_3) δ 3.28 (s, 3H), 3.34 (d, 1H, $J = 8.1$ Hz), 3.52-3.59 (m, 2H), 3.75-3.83 (m, 2H), 4.57-4.70 (m, 1H), 4.93 (dd, 2H, $J = 14.7$ Hz, 16.8 Hz), 5.11 (d, 1H, $J = 9.9$ Hz), 5.48 (d, 1H, $J = 12.9$ Hz), 5.70 (d, 1H, $J = 14.1$ Hz), 7.26-7.45 (m, 10H), 7.58-7.67 (m, 6H), 8.01-8.06 (m, 3H), 8.11 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 52.3, 54.1, 56.7, 58.6, 60.3, 123.0, 123.7, 123.8, 127.3, 127.5, 127.6, 127.7, 127.9, 128.0, 128.2, 128.4, 128.5, 130.0, 130.5, 130.7, 131.0, 131.4, 134.0, 137.8, 138.4, 138.6, 138.7, 139.7, 140.8, 164.9 ppm. ESI-MS: 560.2 (M^+ -Br); HRMS (ESI) for $\text{C}_{40}\text{H}_{34}\text{N}_1\text{O}_2$ (M^+ -Br): calcd 560.2590, found 560.2614.



3b, white solid, yield 91%;
 ^1H NMR (300 MHz, CDCl_3) δ 3.87 (d, 3H, $J = 7.2$ Hz), 3.92 (s, 3H), 3.98 (dd, 2H, $J = 6.0$ Hz, 6.9 Hz), 4.43-4.50 (m, 1H), 4.62-4.69 (m, 1H), 4.88 (d, 1H, $J = 7.2$ Hz), 5.55-5.69 (m, 3H), 5.82 (d, 2H, $J = 12.6$ Hz), 6.18-6.32 (m, 1H), 7.32-7.36 (m, 4H), 7.57-7.60 (m, 2H), 8.02 (d, 2H, $J = 8.4$ Hz), 8.06-8.13 (m, 3H), 8.25 (d, 1H, $J = 8.7$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 14.1, 53.6, 61.2, 62.3, 63.6, 67.0, 125.1, 126.2, 126.8, 126.9, 127.0, 127.2, 127.3, 127.4, 127.46, 127.54, 127.9, 128.2, 128.4, 128.5, 128.8, 130.0, 130.9, 131.0, 134.1, 134.2, 136.4, 136.5, 168.5 ppm. ESI-MS: 422.1 (M^+ -Br); HRMS (ESI) for $\text{C}_{29}\text{H}_{28}\text{N}_1\text{O}_2$ (M^+ -Br): calcd 422.2120, found 422.2134.

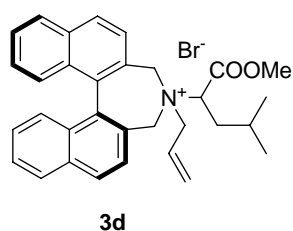


3b', white solid, yield 74%;
 ^1H NMR (300 MHz, CDCl_3) δ 1.14 (s, 3H), 3.48-3.54 (m, 4H), 3.80 (d, 2H, $J = 14.2$ Hz), 4.06-4.12 (m, 1H), 4.32 (d, 1H, $J = 14.7$ Hz), 4.53-4.59 (m, 1H), 4.99 (d, 1H, $J = 10.2$ Hz), 5.21-5.37 (m, 1H), 5.65 (d, 1H, $J = 16.2$ Hz), 5.83 (d, 1H, $J = 12.0$ Hz), 7.39-7.67 (m, 16H), 8.02-8.10 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.1, 22.6, 31.9, 53.0, 55.8, 65.6, 123.8, 124.7, 127.4, 127.5, 127.6, 127.7, 128.3, 128.4, 128.5, 129.5, 130.7, 131.1, 133.9, 140.0, 138.47, 138.53, 140.6 ppm. ESI-MS: 574.1 (M^+ -Br); HRMS (ESI) for $\text{C}_{41}\text{H}_{36}\text{N}_1\text{O}_2$ (M^+ -Br): calcd 574.2746, found 574.2740.



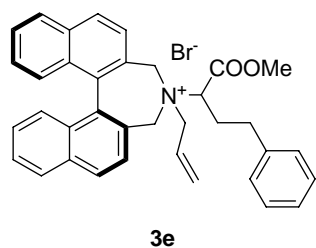
3c, white solid, yield 81%;
 ^1H NMR (300 MHz, CDCl_3) δ 3.20 (t, 1H, $J = 12.0$ Hz), 3.39 (s, 2H), 3.52 (s, 3H), 3.85-3.90 (m, 1H), 3.97 (d, 1H, $J = 13.5$ Hz), 4.16 (d, 1H, $J = 12.6$ Hz), 4.42-4.49 (m, 1H), 4.57-4.64 (m, 1H), 4.87 (dd, 1H, $J = 3.3$ Hz, 8.4 Hz), 5.54 (dd, 2H, $J = 11.1$ Hz, 15.0 Hz), 5.69 (d, 1H, $J = 13.8$ Hz), 5.82 (d, 1H, $J = 12.9$ Hz), 6.24-6.38 (m, 1H), 7.14-7.19 (m, 5H), 7.27-7.33 (m, 4H), 7.53-7.58 (m, 2H), 7.96-7.99 (m, 2H), 8.05 (dd, 2H, $J = 8.4$ Hz, 13.8 Hz), 8.20 (dd, 2H, $J = 8.7$ Hz, 12.3 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 33.6, 53.1, 61.1, 63.5, 64.9, 73.6, 125.1, 126.0, 127.0, 127.1, 127.4, 127.5, 127.6, 128.2, 128.5, 128.6, 128.8, 129.5,

130.0, 130.1, 131.01, 131.03, 132.8, 134.1, 134.2, 136.46, 136.54, 167.2 ppm. ESI-MS: 498.1 (M^+-Br); HRMS (ESI) for $C_{35}H_{32}N_1O_2$ (M^+-Br): calcd 498.2433, found 498.2441.



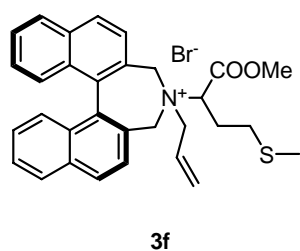
3d, white solid, yield 96%;

1H NMR (300 MHz, $CDCl_3$) δ 0.86 (d, 3H, $J = 6.3$ Hz), 0.93 (d, 3H, $J = 6.3$ Hz), 1.56 (br, 1H), 2.11-2.32 (m, 2H), 3.79 (d, 1H, $J = 12.3$ Hz), 4.03 (d, 1H, $J = 14.1$ Hz), 4.06 (s, 3H), 4.39 (d, 1H, $J = 11.1$ Hz), 4.50 (dd, 1H, $J = 7.2$ Hz, 13.8 Hz), 4.72 (dd, 1H, $J = 6.9$ Hz, 13.8 Hz), 5.24 (d, 1H, $J = 13.5$ Hz), 5.55 (d, 1H, $J = 9.9$ Hz), 5.63 (d, 1H, $J = 17.1$ Hz), 5.86 (d, 1H, $J = 12.3$ Hz), 6.26-6.40 (m, 1H), 7.33-7.37 (m, 4H), 7.59-7.62 (m, 2H), 7.98-8.16 (m, 5H), 8.33 (d, 1H, $J = 8.4$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1, 22.9, 25.7, 35.2, 53.3, 61.4, 63.1, 63.6, 71.3, 125.6, 126.1, 126.2, 126.7, 126.8, 127.2, 127.3, 127.4, 127.8, 128.0, 128.28, 128.32, 128.7, 129.6, 129.8, 130.7, 130.8, 133.9, 134.0, 136.3, 136.4, 167.5 ppm. ESI-MS: 464.1 (M^+-Br); HRMS (ESI) for $C_{32}H_{34}N_1O_2$ (M^+-Br): calcd 464.2590, found 464.2581.



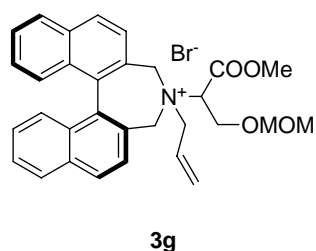
3e, white solid, yield 80%;

1H NMR (300 MHz, $CDCl_3$) δ 2.29-2.37 (m, 1H), 2.78-2.80 (m, 2H), 2.88-2.95 (m, 1H), 3.16 (d, 1H, $J = 12.6$ Hz), 3.90 (d, 1H, $J = 13.5$ Hz), 4.02 (s, 3H), 4.37-4.48 (m, 2H), 4.60 (dd, $J = 6.6$ Hz, 13.2 Hz), 5.33 (d, 1H, 13.5 Hz), 5.57 (dd, 2H, $J = 11.1$ Hz, 19.6 Hz), 5.74 (d, 1H, $J = 12.6$ Hz), 6.30-6.44 (m, 1H), 6.66 (d, 1H, $J = 6.6$ Hz), 6.80 (d, 2H, $J = 6.3$ Hz, 7.5 Hz), 7.04 (d, 2H, $J = 7.5$ Hz), 7.24-7.36 (m, 4H), 7.53-7.63 (m, 2H), 7.91-8.07 (m, 5H), 8.17 (d, 1H, $J = 7.5$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.9, 31.9, 53.8, 61.1, 62.6, 63.8, 70.0, 125.4, 126.0, 126.3, 126.8, 126.9, 127.2, 127.3, 127.4, 127.5, 127.6, 128.0, 128.2, 128.3, 128.4, 128.5, 128.8, 129.9, 130.9, 134.1, 136.2, 136.3, 138.0, 168.2 ppm. ESI-MS: 512.1 (M^+-Br); HRMS (ESI) for $C_{36}H_{34}N_1O_2$ (M^+-Br): calcd 512.2590, found 512.2583.



3f, light yellow solid; yield 95%; (contains some inseparable sulfur-allylation compounds);

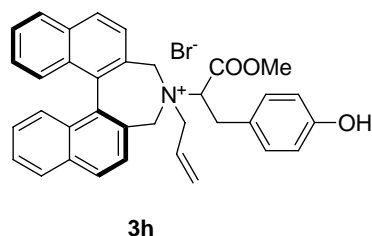
1H NMR (300 MHz, $CDCl_3$) δ 2.04 (s, 3H), 2.35-2.38 (m, 2H), 3.30 (s, 3H), 3.48-3.60 (m, 3H), 3.74-3.82 (m, 2H), 3.96 (d, 2H, $J = 12.3$ Hz), 4.09-4.13 (m, 2H), 4.50-4.73 (m, 1H), 5.55-5.61 (m, 1H), 5.78-5.87 (m, 1H), 7.23-7.25 (m, 2H), 7.35-7.46 (m, 4H), 7.56 (d, 2H, $J = 8.1$ Hz), 7.92-8.01, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 24.7, 31.3, 52.6, 60.3, 62.8, 62.9, 64.3, 123.5, 124.0, 125.3, 125.6, 125.8, 127.3, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.3, 128.5, 131.1, 132.5, 132.6, 132.9, 134.7, 172.3 ppm. ESI-MS: 482.2 (M^+-Br); HRMS (ESI) for $C_{31}H_{32}N_1O_2S_1$ (M^+-Br): calcd 482.2154, found 482.2162.



3g, white solid, yield 78%;

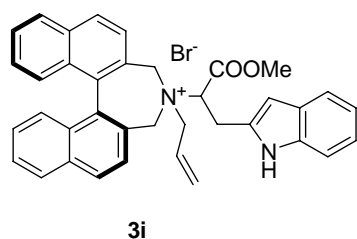
1H NMR (300 MHz, $CDCl_3$) δ 3.76-3.78 (m, 1H), 3.88 (s, 3H), 3.96-4.06 (m, 2H), 4.28 (s, 3H), 4.63-4.85 (m, 4H), 5.50 (d, 1H, $J = 16.2$ Hz), 5.57 (d, 1H, $J = 13.2$ Hz), 5.69 (d, 1H, $J = 9.9$ Hz), 6.05 (s, 2H), 6.29-6.38 (m, 1H), 6.48 (d, 1H, $J = 13.5$ Hz), 7.29-7.34 (m, 4H), 7.59-7.61 (m, 2H), 7.92 (d, 1H, $J = 8.7$ Hz), 8.04 (d, 2H, $J =$

8.1 Hz), 8.14 (d, 2H, $J = 8.4$ Hz), 8.49 (d, 1H, $J = 8.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 53.2, 55.2, 61.5, 64.9, 66.5, 71.1, 96.5, 124.9, 125.9, 126.9, 127.2, 127.4, 127.5, 127.7, 128.2, 128.3, 128.5, 128.6, 130.1, 130.2, 131.1, 131.3, 134.3, 136.2, 136.7, 166.8 ppm. ESI-MS: 482.0 ($\text{M}^+ - \text{Br}$); HRMS (ESI) for $\text{C}_{31}\text{H}_{32}\text{N}_1\text{O}_4$ ($\text{M}^+ - \text{Br}$): calcd 482.2331, found 482.2334.



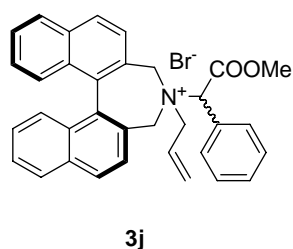
3h, white solid, yield 72%;

^1H NMR (300 MHz, CDCl_3) δ 3.11 (t, 1H, $J = 12.6$ Hz), 3.47-3.55 (m, 4H), 3.99 (dd, 2H, $J = 9.6$ Hz, 13.5 Hz), 4.34 (d, 1H, $J = 9.6$ Hz), 4.43-4.50 (m, 1H), 4.61-4.69 (m, 1H), 4.99 (d, 1H, $J = 12.3$ Hz), 5.48 (d, 1H, $J = 9.9$ Hz), 5.56 (d, 1H, $J = 16.5$ Hz), 5.82 (d, 1H, $J = 12.3$ Hz), 6.14-6.28 (m, 1H), 6.58 (d, 2H, $J = 8.1$ Hz), 6.77 (d, 2H, $J = 8.1$ Hz), 7.29-7.36 (m, 4H), 7.52-7.57 (m, 2H), 7.88-8.09 (m, 5H), 8.28 (d, 1H, $J = 8.4$ Hz), 8.71 (br, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 32.6, 53.3, 62.0, 63.2, 64.0, 74.0, 116.1, 122.5, 125.3, 125.7, 126.3, 127.0, 127.1, 127.4, 127.6, 128.0, 128.6, 128.7, 129.0, 130.1, 131.0, 131.1, 134.2, 134.3, 136.5, 156.8, 167.0 ppm. ESI-MS: 514.1 ($\text{M}^+ - \text{Br}$); HRMS (ESI) for $\text{C}_{35}\text{H}_{32}\text{N}_1\text{O}_3$ ($\text{M}^+ - \text{Br}$): calcd 514.2382, found 514.2388.



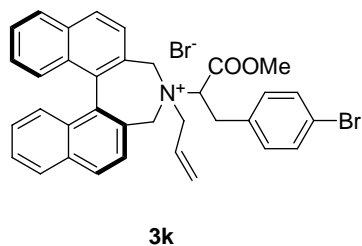
3i, white solid, yield 80%;

^1H NMR (300 MHz, CDCl_3) δ 3.34 (s, 3H), 3.41-3.52 (m, 2H), 3.80 (d, 1H, $J = 12.9$ Hz), 3.95 (d, 1H, $J = 13.2$ Hz), 4.36 (d, 1H, $J = 7.5$ Hz), 4.49-4.56 (m, 1H), 4.65-4.72 (m, 1H), 4.87 (d, 1H, $J = 13.2$ Hz), 5.50 (dd, 2H, $J = 11.1$ Hz, 17.4 Hz), 5.95 (d, 1H, $J = 12.6$ Hz), 6.10-6.19 (m, 1H), 6.56 (t, 1H, $J = 7.5$ Hz), 6.75 (t, 1H, $J = 7.8$ Hz), 6.85 (d, 1H, $J = 6.9$ Hz), 6.86 (s, 1H), 7.34-7.43 (m, 5H), 7.58 (dd, 2H, $J = 8.4$ Hz, 6.6 Hz), 7.79 (d, 1H, $J = 8.4$ Hz), 7.95-8.04 (m, 4H), 8.13 (d, 1H, $J = 8.4$ Hz), 8.41 (d, 1H, $J = 8.1$ Hz), 10.47 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 23.1, 53.3, 62.1, 62.8, 63.4, 72.6, 104.7, 112.0, 117.1, 118.6, 121.1, 124.9, 125.4, 126.0, 126.1, 126.4, 126.9, 127.0, 127.3, 127.4, 127.5, 127.6, 127.7, 128.1, 128.5, 128.9, 130.1, 130.9, 134.1, 134.2, 135.8, 136.4, 136.5, 167.2 ppm. ESI-MS: 537.1 ($\text{M}^+ - \text{Br}$); HRMS (ESI) for $\text{C}_{37}\text{H}_{33}\text{N}_2\text{O}_2$ ($\text{M}^+ - \text{Br}$): calcd 537.2542, found 537.2515.



3j, white solid, yield 85%;

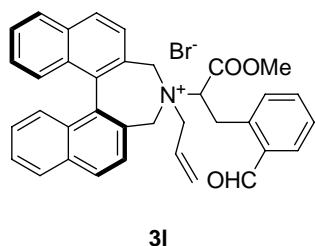
^1H NMR (300 MHz, CDCl_3) δ 3.64 (s, 3H), 4.00 (dd, 1H, $J = 14.7$ Hz, 14.4 Hz), 4.28-4.32 (m, 1H), 4.65 (d, 1H, $J = 12.6$ Hz), 5.29 (d, 1H, 6.3 Hz), 5.60 (d, 2H, $J = 12.6$ Hz), 5.85 (d, 1H, $J = 16.5$ Hz), 6.32 (d, 1H, $J = 14.1$ Hz), 6.49-6.60 (m, 2H), 7.16-7.57 (m, 10H), 7.76-8.15 (m, 7H); ^{13}C NMR (100 MHz, CDCl_3) δ 53.2, 53.3, 58.0, 59.6, 62.4, 66.0, 66.3, 66.8, 72.0, 73.2, 124.9, 125.2, 125.5, 126.0, 126.3, 126.6, 126.7, 126.9, 127.0, 127.1, 127.16, 127.2, 127.36, 127.40, 127.43, 127.5, 127.6, 127.8, 128.17, 128.20, 128.22, 128.33, 128.36, 128.39, 128.43, 128.5, 128.7, 128.8, 129.4, 130.1, 130.2, 130.4, 131.0, 131.2, 131.3, 131.5, 132.3, 133.3, 133.9, 134.12, 134.16, 135.4, 136.2, 136.4, 136.8, 167.3, 167.8 ppm. ESI-MS: 484.1 ($\text{M}^+ - \text{Br}$); HRMS (ESI) for $\text{C}_{34}\text{H}_{30}\text{N}_1\text{O}_2$ ($\text{M}^+ - \text{Br}$): calcd 484.2277, found 484.2299.



3k, light yellow solid, yield 84%;

^1H NMR (300 MHz, CDCl_3) δ 3.12 (t, 1H, $J = 12.0$ Hz), 3.53 (s, 3H), 3.87-4.67 (m, 5H), 5.17 (d, 1H, $J = 9.6$ Hz), 5.51 (d, 1H, $J = 16.8$ Hz), 5.59 (d, 1H, $J = 10.2$ Hz), 5.74 (d, 1H, $J = 12.6$ Hz), 5.99 (d, 1H, $J = 13.8$ Hz), 6.26-6.40 (m, 1H), 7.22-7.40 (m, 8H), 7.57-7.61 (m, 2H), 7.98-8.11 (m, 5H), 8.29 (d, 1H, $J = 8.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 33.2, 53.0, 60.8, 63.6, 65.5, 73.0,

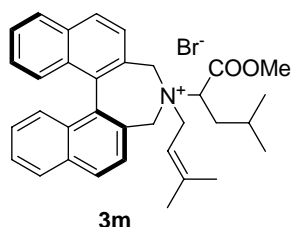
121.9, 124.8, 125.8, 127.1, 127.2, 127.5, 127.57, 127.61, 127.7, 127.8, 128.4, 128.6, 130.2, 130.3, 131.1, 131.6, 131.9, 131.96, 132.02, 134.3, 134.4, 136.7, 167.6 ppm. ESI-MS: 576.1 (M^+-Br); HRMS (ESI) for $\text{C}_{35}\text{H}_{31}\text{N}_1\text{O}_2\text{Br}_1$ (M^+-Br): calcd 576.1538, found 576.1530.



3l, light yellow solid, yield 67%;

^1H NMR (300 MHz, CDCl_3) δ 3.60 (s, 3H), 4.08 (d, 1H, $J = 13.2$ Hz), 4.23 (d, 1H, $J = 15.9$ Hz), 4.53 (d, 1H, $J = 12.6$ Hz), 4.67-4.85 (m, 3H), 5.51 (d, 1H, $J = 10.2$ Hz), 5.61 (d, 1H, $J = 16.8$ Hz), 5.97 (d, 1H, $J = 11.4$ Hz), 6.07-6.18 (m, 1H), 7.26-7.39 (m, 5H), 7.53-7.59 (m, 4H), 7.73 (dd, 2H, $J = 6.3$ Hz, 8.1 Hz), 7.98 (dd, 4H, $J = 7.5$ Hz, 8.4 Hz), 8.44 (d, 1H, $J = 8.1$ Hz), 9.70 (s, 1H); ^{13}C NMR

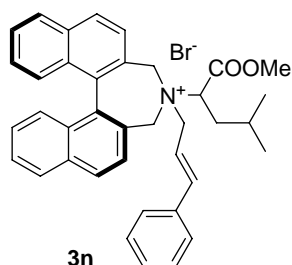
(100 MHz, CDCl_3) δ 31.5, 53.4, 61.6, 63.1, 63.9, 71.2, 125.6, 126.8, 127.0, 127.1, 127.4, 127.59, 127.63, 127.8, 128.4, 128.6, 128.8, 129.5, 129.9, 130.1, 131.0, 133.5, 134.2, 134.3, 136.9, 137.0, 175.0, 193.9 ppm. ESI-MS: 526.1 (M^+-Br); HRMS (ESI) for $\text{C}_{36}\text{H}_{32}\text{N}_1\text{O}_3$ (M^+-Br): calcd 526.2385, found 526.2382.



3m, white solid, yield 84%;

^1H NMR (300 MHz, CDCl_3) δ 0.90-0.98 (m, 6H), 1.66-1.76 (m, 7H) 2.22-2.32 (m, 2H), 3.80-3.86 (m, 1H), 4.02 (d, 1H, $J = 8.1$ Hz), 4.09 (s, 3H), 4.31 (br, 1H), 4.68 (br, 2H), 5.10 (br, 1H), 5.60-5.70 (m, 1H), 5.92 (br, 1H), 7.36 (d, 4H, $J = 8.4$ Hz), 7.61 (br, 2H), 8.02-8.27 (m, 5H), 8.47 (br, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 18.8, 20.7, 22.7,

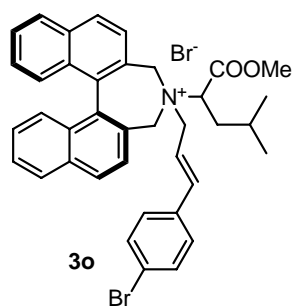
25.0, 25.9, 34.8, 54.7, 59.3, 62.1, 62.3, 70.3, 111.5, 125.6, 126.0, 126.1, 126.2, 126.6, 126.8, 127.7, 127.8, 128.7, 129.1, 129.2, 129.9, 130.1, 133.20, 133.23, 135.5, 135.6, 145.8, 166.9 ppm. ESI-MS: 492.1 (M^+-Br); HRMS (ESI) for $\text{C}_{34}\text{H}_{38}\text{N}_1\text{O}_2$ (M^+-Br): calcd 492.2903, found 492.2896.



3n, white solid, yield 87%;

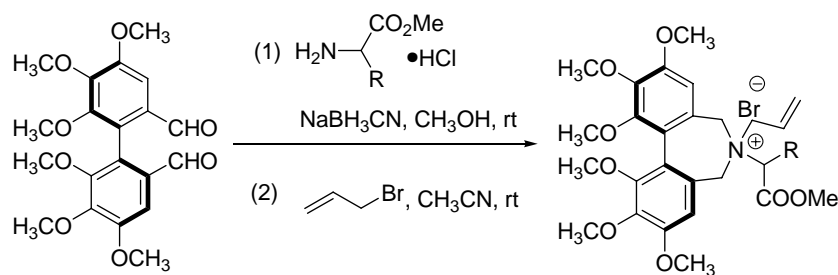
^1H NMR (300 MHz, CDCl_3) δ 0.85 (d, 3H, $J = 6.6$ Hz), 0.91 (d, 3H, $J = 6.6$ Hz), 1.53-1.61 (m, 1H), 2.20 (dd, 1H, $J = 10.2$ Hz, 10.5 Hz), 2.38 (dd, 1H, $J = 10.5$ Hz, 10.5 Hz), 3.80 (d, 1H, $J = 12.6$ Hz), 3.98 (s, 3H), 4.12 (d, 1H, $J = 13.8$ Hz), 4.41 (d, 1H, $J = 10.2$ Hz), 4.70 (dd, 1H, $J = 7.5$ Hz, 13.5 Hz), 4.90 (dd, 1H, $J = 7.2$ Hz, 13.8 Hz), 5.34 (d, 1H, $J = 13.5$ Hz), 6.07 (d, 1H, $J = 12.6$ Hz), 6.55-6.65 (m, 1H), 6.92 (d,

1H, $J = 16.2$ Hz), 7.22-7.62 (m, 9H), 7.55-7.63 (m, 2H), 7.94-7.98 (m, 2H), 8.01-8.06 (m, 2H), 8.14 (d, 1H, $J = 8.7$ Hz), 8.45 (d, 1H, $J = 8.1$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 20.9, 23.0, 25.7, 35.3, 53.8, 61.4, 62.8, 63.7, 71.2, 115.7, 125.3, 127.1, 127.2, 127.3, 127.4, 127.8, 127.9, 128.0, 128.2, 128.3, 133.9, 134.5, 141.9, 167.8 ppm. ESI-MS: 540.0 (M^+-Br); HRMS (ESI) for $\text{C}_{38}\text{H}_{38}\text{N}_1\text{O}_2$ (M^+-Br): calcd 540.2903, found 540.2886.

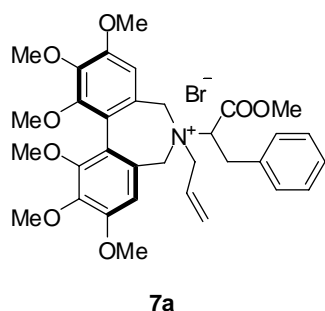


30, white solid, yield 81%;
 $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 0.86 (d, 3H, $J = 6.3$ Hz), 0.89 (d, 3H, $J = 6.6$ Hz), 1.56 (br, 1H), 2.11 (dd, 1H, $J = 12.9$ Hz, 12.0 Hz), 2.33 (dd, 1H, $J = 10.5$ Hz, 11.1 Hz), 3.85 (d, 1H, $J = 12.6$ Hz), 3.96 (s, 3H), 4.10 (d, 1H, $J = 13.5$ Hz), 4.52 (d, 1H, $J = 10.8$ Hz), 4.62 (dd, 1H, $J = 7.2$ Hz, 13.5 Hz), 4.83 dd (q, 1H, $J = 6.9$ Hz), 5.44 (d, 1H, $J = 13.5$ Hz), 6.00 (d, 1H, $J = 12.9$ Hz), 6.68-6.78 (m, 1H), 6.88 (d, 1H, $J = 15.3$ Hz), 7.30 (d, 1H, $J = 4.2$ Hz), 7.36 (br, 6H), 7.53-7.64 (m, 2H), 7.95-8.04 (m, 4H), 8.12 (d, 1H, $J = 8.1$ Hz), 8.37 (d, 1H, $J = 8.7$ Hz); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 21.1, 23.1, 25.8, 35.6, 53.8, 61.2, 63.2, 63.8, 71.4, 166.7, 122.9, 126.5, 126.8, 127.0, 127.2, 127.4, 127.5, 127.9, 128.3, 128.4, 128.9, 129.0, 129.7, 129.8, 130.8, 130.9, 131.5, 133.6, 134.0, 136.3, 136.5, 140.5, 168.0 ppm. ESI-MS: 618.0 (M^+-Br); HRMS (ESI) for $\text{C}_{38}\text{H}_{37}\text{N}_1\text{O}_2\text{Br}_1$ (M^+-Br): calcd 618.2008, found 618.2015.

3.1 Synthetic Procedure for 7a and 7b



To a 50 mL flask was added dialdehyde compound **6**² (440 mg, 1 mmol), methyl amino acids hydrogen chloride (1.5 mmol), NaBH_3CN (330 mg, 3 mmol) and 20 mL of methol. The reaction was stirred at rt for about 4 hours for completion. The mixture was diluted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4 , and concentrated. Purification by flash column chromatography on silica gel afforded the corresponding *N,N*-disubstituted amine. The amine (0.2 mmol) and allyl bromide (0.4 mmol) was dissolved in 5 mL of acetonitrile, and stirred at room temperature for about 2 days. The mixture was then diluted with CH_2Cl_2 , concentrated under vacuum, removing the solvent and allyl bromide. The residue was purified by flash column chromatography on silica gel (eluted with 10:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$) to afford the corresponding ammonium salts **7a** or **7b**.

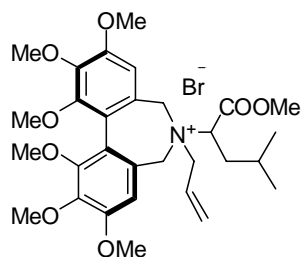


7a, white solid, yield 82%;

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 3.26 (t, 1H, $J = 12.0$ Hz), 3.61 (s, 3H), 3.72-3.81 (m, 7H), 3.90-4.00 (m, 14H), 4.51-4.66 (m, 2H), 4.80 (d, 1H, $J = 9.0$ Hz), 5.40 (d, 1H, $J = 13.2$ Hz), 5.56-5.64 (m, 3H), 6.30-6.43 (m, 1H), 7.24-7.30 (m, 5H), 7.53 (s, 1H), 7.67 (s, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 32.8, 52.8, 55.9, 56.4, 60.45, 60.46, 60.57, 60.62, 62.9, 64.1, 73.0, 110.3, 111.1, 121.9, 122.8,

² a) C. Zhu, Y. Shi, M.-H. Xu, G.-Q. Lin, *Org. Lett.* **2008**, *10*, 1243; b) W.-W. Chen, Q. Zhao, M.-H. Xu, G.-Q. Lin, *Org. Lett.*, **2010**, *12*, 1072.

124.8, 127.2, 127.6, 128.2, 129.0, 132.6, 143.2, 143.3, 151.18, 151.24, 153.3, 166.3 ppm. ESI-MS: 578.1 (M^+-Br); HRMS (ESI) for $C_{33}H_{40}N_1O_2$ (M^+-Br): calcd 578.2754, found 578.2754.

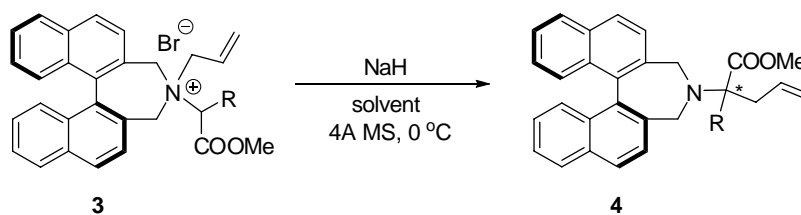


7b

7b, white solid, yield 92%;

1H NMR (300 MHz, $CDCl_3$) δ 0.68 (d, 3H, $J = 6.3$ Hz), 0.72 (d, 3H, $J = 6.6$ Hz), 1.37 (br, 1H), 1.85-2.05 (m, 2H), 3.31 (d, 1H, $J = 12.6$ Hz), 3.51 (s, 6H), 3.57 (d, 1H, 13.8 Hz), 3.73 (s, 3H), 3.75 (s, 6H), 3.80 (d, 6H, $J = 1.5$ Hz), 4.12 (d, 1H, $J = 12.9$ Hz), 4.22-4.29 (m, 1H), 4.39-4.46 (m, 1H), 4.67 (d, 1H, $J = 13.5$ Hz), 5.34-5.45 (m, 3H), 6.02-6.16 (m, 1H), 7.02 (s, 1H), 7.50 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 22.7, 25.4, 34.6, 53.6, 55.9, 56.5, 60.5, 60.56, 60.61, 62.7, 63.2, 70.9, 110.0, 111.3, 122.1, 122.3, 122.7, 123.0, 125.4, 127.5, 143.3, 143.4, 151.1, 151.3, 153.0, 153.4, 167.1 ppm. ESI-MS: 544.1 (M^+-Br); HRMS (ESI) for $C_{30}H_{42}N_1O_8$ (M^+-Br): calcd 544.2910, found 544.2896.

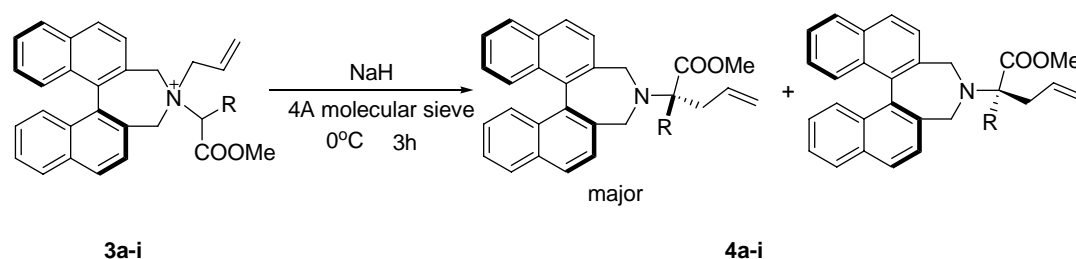
4. Optimization of the reaction conditions.



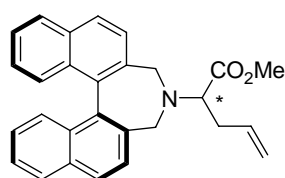
entry ^a	R	4	solvent	NaH (equiv)	yield ^b (%)	de ^c (%)
1	H (3a)	4a	CH_2Cl_2	1	80	64
2	H (3a)	4a	THF	1	74	62
3	H (3a)	4a	Et_2O	1	trace	-
4	H (3a)	4a	DME	1	76	76
5	H (3a)	4a	DME	1.5	97	34
6	Me (3b)	4b	DME	1	70	85
7	Me (3b)	4b	DME	1.5	92	85
8 ^d	Me (3b)	4b	DME	1.5	93	78
9 ^e	Me (3b)	4b	DME	1.5	89	85
10	Bn (3c)	4c	DME	1.5	92	98

^aUnless otherwise mentioned all reactions were performed on 0.1 mmol scale with 100 mg of 4Å molecular sieves in 5 mL of solvent at 0 °C. ^bYield of isolated product. ^cDetermined by crude 1H NMR. ^dReaction was proceeded at r.t.. ^eReaction was proceeded at -20 °C.

5. General Procedure for the Asymmetric [2,3]-Rearrangement

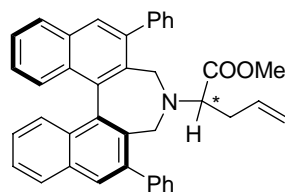


Under nitrogen atmosphere, the ammonium salts **3** (0.1 mmol), NaH (amounts as indicated in Table 2), and 4Å molecular sieves (100 mg) was added to a Schlenk flask. Dry DME (4 mL) was added at 0 °C and the reaction mixture was stirred at the same temperature for 1-3h. The mixture was then filtrated through Celite before warming to room temperature. The filtrate was washed with sat. aq. NaHCO₃ and brine, dried over anhydrous Na₂SO₄, and concentrated. Purification by flash column chromatography on silica gel afforded the corresponding rearrangement product **4** or **8**.



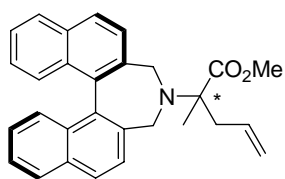
4a, colorless oil, yield 76%;

¹H NMR (300 MHz, CDCl₃) δ 2.45-2.64 (m, 2H, CH₂CH=CH₂), 3.32 (dd, 1H, *J* = 6 Hz, 9 Hz), 3.39 (d, 2H, *J* = 12.3 Hz, Ar-CH₂), 3.61 (s, 3H, COOCH₃), 3.76 (d, 2H, *J* = 12.3 Hz, Ar-CH₂), 5.08 (dd, 2H, *J* = 18.6 Hz, 11.1 Hz, CH₂CH=CH₂), 5.70-5.84 (m, 1H, CH₂CH=CH₂), 7.19 (dd, 2H, *J* = 7.8 Hz, 7.5 Hz, Ar-H), 7.37-7.45 (m, 4H, Ar-H), 7.55 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.90 (dd, 4H, *J* = 7.8 Hz, 6.4 Hz, Ar-H). ¹³C NMR (100 MHz, CDCl₃) δ 35.1, 51.5, 3.1, 66.3, 117.6, 125.4, 125.7, 127.4, 128.1, 128.2, 128.3, 128.4, 131.2, 133.06, 133.13, 133.8, 134.9, 173.1 ppm. ESI-MS: 408.0 [M+H]⁺, HRMS (ESI) for C₂₈H₂₆N₁O₂ [M+H]⁺: calcd 408.1964, found 408.1971.



4a', colorless oil, yield 68%;

¹H NMR (300 MHz, CDCl₃) δ 1.78-1.87 (m, 1H, CH₂CH=CH₂), 2.12-2.22 (m, 1H, CH₂CH=CH₂), 3.05 (dd, 1H, *J* = 5.4Hz, 4.8Hz, CHCOOMe), 3.29 (s, 3H, COOCH₃), 3.38 (d, 2H, *J* = 12.6Hz, Ar-CH₂), 4.08 (d, 2H, *J* = 12.6Hz, Ar-CH₂), 4.80 (dd, 2H, *J* = 17.1Hz, 10.5Hz, CH=CH₂), 5.37-5.51 (m, 1H, CH=CH₂), 7.26-7.30 (m, 2H, ArH), 7.39-7.51 (m, 10H, ArH), 7.59 (d, 4H, *J* = 6.9 Hz, ArH), 7.94-7.96 (m, 4H, ArH). ¹³C NMR (100 MHz, CDCl₃) δ 33.5, 48.5, 51.1, 66.0, 117.0, 125.7, 125.8, 127.1, 127.5, 128.1, 128.2, 129.4, 130.1, 130.7, 131.7, 132.5, 134.0, 136.2, 140.2, 141.0, 172.0. ESI-MS: 560.1 [M+H]⁺, HRMS (ESI) for C₄₀H₃₃N₁O₂ [M+H]⁺: calcd 560.2590, found 560.2605.

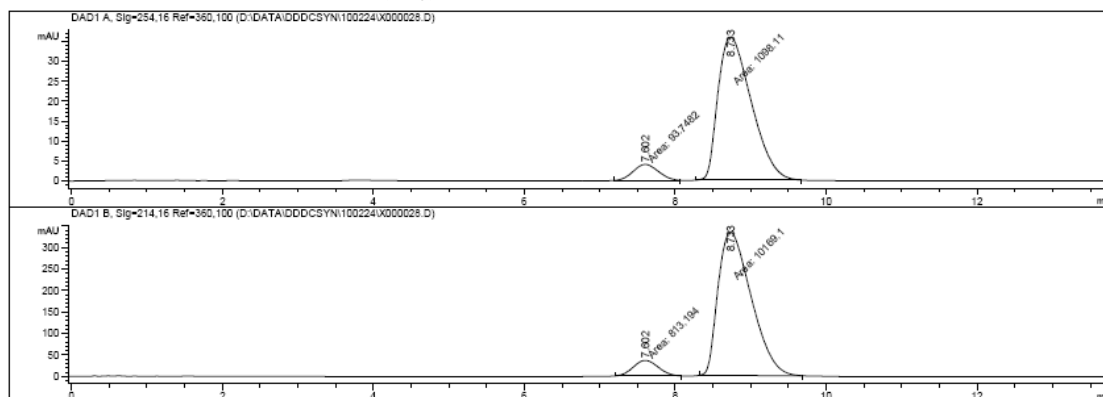


4b, colorless oil, yield 92%;

¹H NMR (300 MHz, CDCl₃) δ 1.37 (s, 3H, CCH₃), 2.58-2.78 (m, 2H, CH₂CH=CH₂), 3.47 (d, 2H, *J* = 12.6 Hz, Ar-CH₂), 3.52 (s, 3H, COOCH₃), 3.93 (d, 2H, *J* = 12.6 Hz, Ar-CH₂), 5.12 (dd, 2H, *J* = 18.6 Hz, 11.1 Hz, CH₂CH=CH₂), 5.75-5.87 (m, 1H, CH₂CH=CH₂), 7.21-7.28 (m, 2H, Ar-H), 7.41-7.48 (m, 4H, Ar-H), 7.54 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.94 (d, 4H, *J* =

8.4 Hz, Ar-H). ^{13}C NMR (100 MHz, CDCl_3) δ 20.8, 42.6, 49.4, 49.7, 51.4, 65.8, 117.8, 125.3, 125.6, 127.2, 127.5, 128.1, 128.3, 130.1, 131.2, 132.9, 134.1, 134.2, 135.0, 175.3 ppm. ESI-MS: 422.1 $[\text{M}+\text{H}]^+$, 444.0 $[\text{M}+\text{Na}]^+$; HRMS (ESI) for $\text{C}_{29}\text{H}_{28}\text{N}_1\text{O}_2$ $[\text{M}+\text{H}]^+$: calcd 422.2120, found 422.2120.

LC-MS: detected at both 254 nm and 214 nm; MeOH / H_2O = 80/20; flow = 1.0 mL/min, Retention time: 7.6 min, 8.7 min (maj).

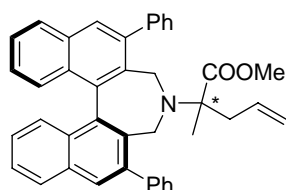


Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.602	MM	0.3885	93.74821	4.02141	7.8657
2	8.733	MM	0.5100	1098.10937	35.88855	92.1343

Signal 2: DAD1 B, Sig=214,16 Ref=360,100

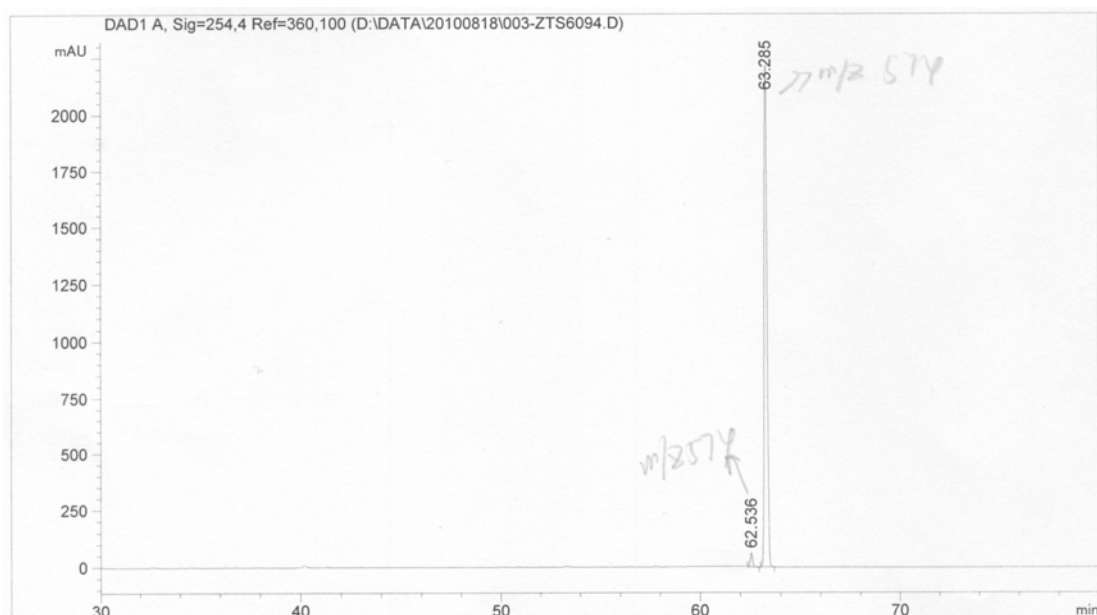
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.602	MM	0.3782	813.19409	35.83181	7.4046
2	8.733	MM	0.5091	1.01691e4	332.88657	92.5954



4b', colorless oil, yield 90%;

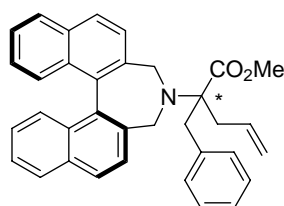
^1H NMR (300 MHz, CDCl_3) δ 0.832 (s, 3H, CCH_3), 1.74 (dd, 1H, $J = 6.9$ Hz, $J = 7.2$ Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.17 (dd, 1H, $J = 6.9$ Hz, $J = 6.6$ Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.16 (s, 3H, COOCH_3), 3.45 (d, 2H, $J = 12.9$ Hz, NCH_2), 4.19 (d, 2H, $J = 12.9$ Hz, NCH_2), 4.86 (dd, 2H, $J = 17.1$ Hz, 9.6 Hz, $\text{CH}=\text{CH}_2$), 5.42-5.56 (m, 1H, $\text{CH}=\text{CH}_2$), 7.22-7.27 (m, 2H, ArH), 7.36-7.49 (m, 10H, ArH), 7.58 (br, 4H, ArH), 7.94 (d, 4H, $J = 5.7$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 20.9, 40.7, 45.4, 51.1, 66.7, 117.6, 125.6, 125.7, 127.1, 127.5, 128.1, 129.3, 130.3, 132.2, 132.4, 133.9, 136.5, 140.3, 141.2, 174.8 ppm. ESI-MS: 574.3 $[\text{M}+\text{H}]^+$, 596.3 $[\text{M}+\text{Na}]^+$; HRMS (ESI) for $\text{C}_{41}\text{H}_{36}\text{N}_1\text{O}_2$ $[\text{M}+\text{H}]^+$: calcd 574.2741, found 574.2715.

LC-MS: detected at 254 nm, Retention time: 62.5 min, 63.3 min (maj).



信号 1: DAD1 A, Sig=254,4 Ref=360,100

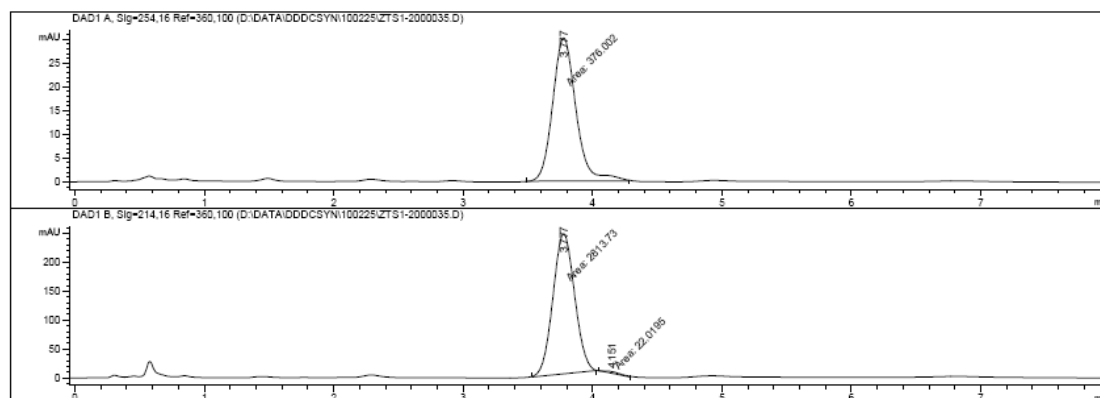
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	62.536	VB	0.1264	527.49365	63.81199	2.3518
2	63.285	BB	0.1573	2.19023e4	2216.26538	97.6482



4c, colorless oil, yield 92%;

^1H NMR (300 MHz, CDCl_3) δ 2.38-2.46 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.81-2.88 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.30 (d, 1H, $J = 13.5$ Hz, PhCH_2), 3.38, (s, 3H, COOCH_3), 4.45 (d, 1H, $J = 13.5$ Hz, PhCH_2), 3.53 (d, 2H, $J = 12.6$ Hz, Ar-CH_2), 4.13 (d, 2H, $J = 12.6$ Hz, Ar-CH_2), 5.04 (dd, 2H, $J = 18.3$ Hz, 12.3 Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.88-6.01 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.14-7.29 (m, 7H, Ar-H), 7.44-7.48 (m, 4H, Ar-H), 7.54 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.94 (d, 4H, $J = 8.4$ Hz, Ar-H). ^{13}C NMR (100 MHz, CDCl_3) δ 36.0, 39.2, 49.4, 50.8, 68.0, 117.7, 125.3, 125.6, 126.5, 127.5, 128.2, 128.3, 130.1, 131.2, 132.9, 134.0, 135.2, 137.2, 174.3 ppm. ESI-MS: 498.1 $[\text{M}+\text{H}]^+$, 520.1 $[\text{M}+\text{Na}]^+$; HRMS (ESI) for $\text{C}_{35}\text{H}_{32}\text{N}_1\text{O}_2$ $[\text{M}+\text{H}]^+$: calcd 498.2433, found 498.2437.

LC-MS: detected at both 254 nm and 214 nm; MeOH / $\text{H}_2\text{O} = 80/20$; flow = 1.0 mL/min, Retention time: 3.78 min (maj), 4.15min.

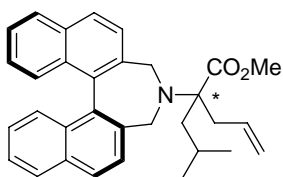


Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.777	MM	0.2082	376.00159	30.09663	100.0000

Signal 2: DAD1 B, Sig=214,16 Ref=360,100

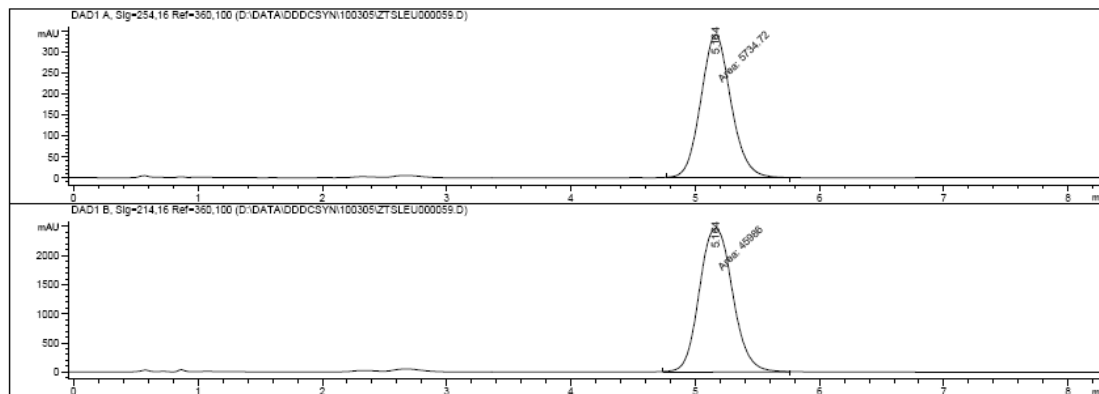
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.777	MM	0.1938	2813.73437	241.96638	99.2235
2	4.151	MM	0.1405	22.01950	2.61202	0.7765



Colorless oil **4d**, yield 95%;

^1H NMR (300 MHz, CDCl_3) δ 0.76 (d, 3H, $J = 6.3$ Hz, CHCH_3), 0.98 (d, 3H, $J = 6.3$ Hz, CHCH_3), 1.69-1.91 (m, 3H, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 2.53-2.61 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.01-3.08 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.30 (s, 3H, COOCH_3), 3.40 (d, 2H, $J = 12.6$ Hz, Ar- CH_2), 4.08 (d, 2H, $J = 12.6$ Hz, Ar- CH_2), 5.07 (dd, 2H, $J = 18.6$ Hz, 11.1 Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.78-5.92 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.23-7.27 (m, 2H, Ar-H), 7.41-7.45 (m, 4H, Ar-H), 7.51 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.92 (d, 4H, $J = 8.4$ Hz, Ar-H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.7, 24.4, 25.2, 36.1, 42.3, 48.6, 50.6, 65.7, 116.9, 125.3, 125.5, 127.5, 128.1, 128.2, 128.3, 131.2, 132.9, 134.3, 134.4, 135.1, 175.5 ppm. ESI-MS: 464.0 $[\text{M}+\text{H}]^+$; HRMS (ESI) for $\text{C}_{32}\text{H}_{34}\text{N}_1\text{O}_2$ $[\text{M}+\text{H}]^+$: calcd 464.2584, found 464.2567.

LC-MS: detected at both 254 nm and 214 nm; MeOH / H_2O = 80/20; flow = 1.0 mL/min, Retention time: 5.16 min (maj).

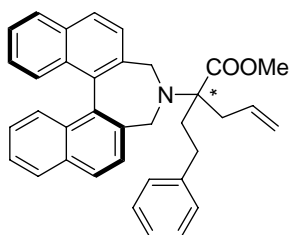


Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.164	MM	0.2814	5734.72021	339.68430	100.0000

Signal 2: DAD1 B, Sig=214,16 Ref=360,100

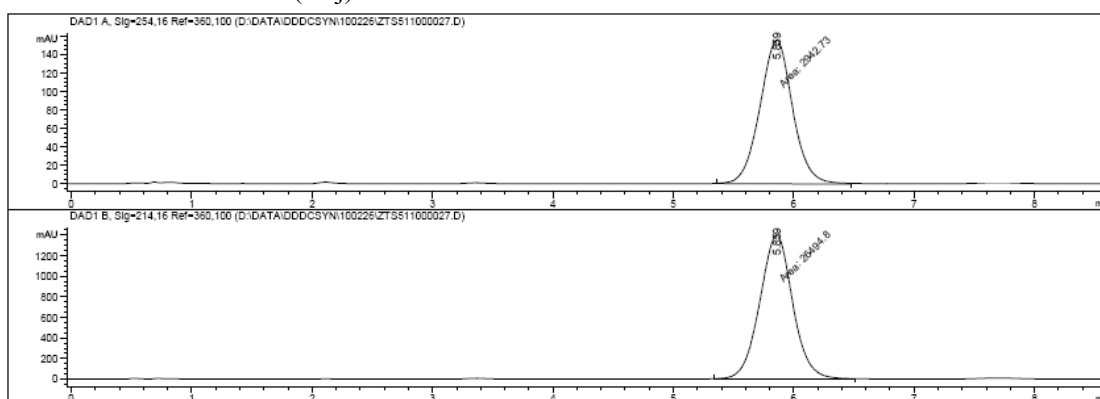
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.164	MM	0.3116	4.59860e4	2460.00952	100.0000



4e, colorless oil, yield 97%;

^1H NMR (300 MHz, CDCl_3) δ 2.18 (dd, 2H, $J = 7.5\text{Hz}$, 9.6Hz , PhCH_2CH_2), 2.24-2.52 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.78-3.00 (m, 3H, $\text{CH}_2\text{CH}=\text{CH}_2$, PhCH_2CH_2), 3.39 (s, 3H, COOCH_3), 3.49 (d, 2H, $J = 12.3\text{ Hz}$, Ar- CH_2), 4.12 (d, 2H, $J = 12.3\text{ Hz}$, Ar- CH_2), 5.04 (dd, 2H, $J = 17.1\text{ Hz}$, 10.5 Hz , $\text{CH}_2\text{CH}=\text{CH}_2$), 5.88-6.01 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.23-7.34 (m, 7H, Ar-H), 7.44-7.49 (m, 4H, Ar-H), 7.55 (d, 2H, $J = 8.4\text{ Hz}$, Ar-H), 7.96 (d, 4H, $J = 8.4\text{ Hz}$, Ar-H). ^{13}C NMR (100 MHz, CDCl_3) δ 29.7, 29.9, 35.3, 37.4, 48.9, 51.1, 66.5, 117.5, 125.3, 125.6, 126.0, 127.5, 128.1, 128.3, 128.4, 128.5, 131.1, 132.9, 134.1, 134.3, 135.1, 142.1, 174.6 ppm. ESI-MS: 512.0 $[\text{M}+\text{H}]^+$; HRMS (ESI) for $\text{C}_{36}\text{H}_{34}\text{N}_1\text{O}_2$ $[\text{M}+\text{H}]^+$: calcd 512.2584, found 512.2579.

LC-MS: detected at both 254 nm and 214 nm; MeOH / $\text{H}_2\text{O} = 80/20$; flow = 1.0 mL/min, Retention time: 5.86 min (maj).

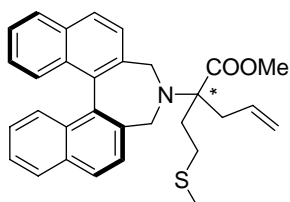


Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.859	MM	0.3150	2942.73389	155.71225	100.0000

Signal 2: DAD1 B, Sig=214,16 Ref=360,100

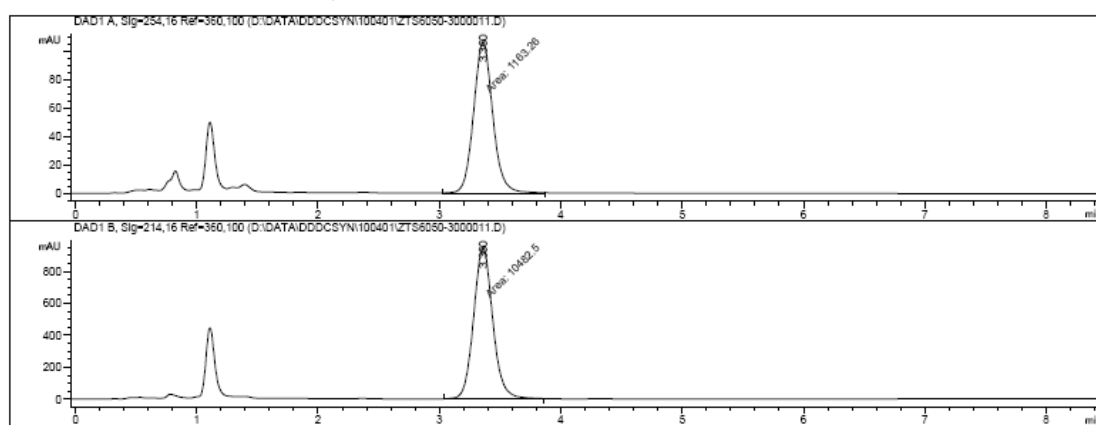
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.859	MM	0.3162	2.64948e4	1396.71497	100.0000



4f, light yellow oil, yield 88%;

^1H NMR (300 MHz, CDCl_3) δ 2.13 (s, 3H, SCH_3), 2.13-2.19 (m, 2H, $\text{CH}_2\text{CH}_2\text{S}$), 2.30-2.39 (m, 1H, $\text{CH}_2\text{CH}_2\text{S}$), 2.64-2.72 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$, $\text{CH}_2\text{CH}_2\text{S}$), 2.80-2.88 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.36 (s, 3H, COOCH_3), 3.41 (d, 2H, $J = 12.3\text{ Hz}$, Ar- CH_2), 4.03 (d, 2H, $J = 12.3\text{ Hz}$, Ar- CH_2), 5.14 (dd, 2H, $J = 18.3\text{ Hz}$, 10.5 Hz , $\text{CH}_2\text{CH}=\text{CH}_2$), 5.778-6.89 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.21-7.28 (m, 7H, Ar-H), 7.40-7.46 (m, 4H, Ar-H), 7.51 (d, 2H, $J = 8.4\text{ Hz}$, Ar-H), 7.93 (d, 4H, $J = 8.4\text{ Hz}$, Ar-H). ^{13}C NMR (100 MHz, CDCl_3) δ 15.6, 28.2, 33.1, 37.7, 48.9, 51.1, 66.6, 117.8, 125.4, 125.6, 127.5, 128.2, 128.2, 128.3, 131.2, 132.9, 133.9, 133.9, 135.2, 174.1 ppm. ESI-MS: 482.0 $[\text{M}+\text{H}]^+$, HRMS (ESI) for $\text{C}_{31}\text{H}_{32}\text{N}_1\text{O}_2\text{S}_1$ $[\text{M}+\text{H}]^+$: calcd 482.2154, found 482.2143.

LC-MS: detected at both 254 nm and 214 nm; MeOH / H₂O = 80/20; flow = 1.0 mL/min,
Retention time: 3.36 min (maj).

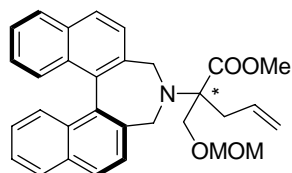


Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.360	MM	0.1826	1163.25940	106.17855	100.0000

Signal 2: DAD1 B, Sig=214,16 Ref=360,100

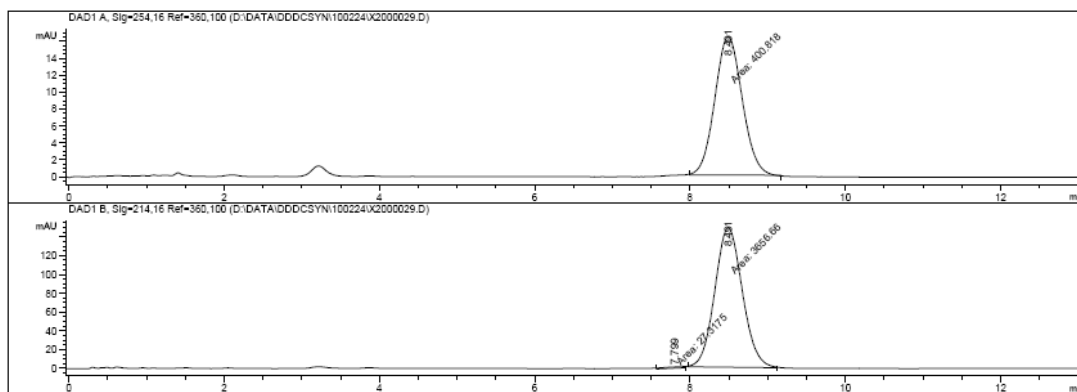
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.360	MM	0.1842	1.04825e4	948.66193	100.0000



4g, colorless oil, yield 78%;

¹H NMR (300 MHz, CDCl₃) δ 2.77-2.85 (m, 2H, CH₂CH=CH₂), 2.92-3.00 (m, 2H, CH₂CH=CH₂), 3.28 (s, 3H, OCH₂OCH₃), 3.41 (s, 3H, COOCH₃), 3.52 (d, 2H, *J* = 12.3 Hz, Ar-CH₂), 3.78 (d, 1H, *J* = 8.7 Hz, CH₂OMOM), 3.95 (d, 2H, *J* = 12.3 Hz, Ar-CH₂), 3.97 (d, 1H, *J* = 8.7 Hz, CH₂OMOM), 4.58 (2H, s, OCH₂OCH₃), 5.11 (dd, 2H, *J* = 17.1 Hz, 9.0 Hz, CH₂CH=CH₂), 5.78-5.91 (m, 1H, CH₂CH=CH₂), 7.21-7.28 (m, 2H, Ar-H), 7.41-7.44 (m, 4H, Ar-H), 7.51 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.92 (d, 4H, *J* = 8.4 Hz, Ar-H). ¹³C NMR (100 MHz, CDCl₃) δ 36.0, 49.4, 51.2, 55.4, 67.7, 68.2, 96.8, 117.8, 125.4, 125.6, 127.5, 128.1, 128.2, 128.3, 131.1, 132.9, 133.9, 134.0, 135.0, 173.5 ppm. ESI-MS: 482.2 [M+H]⁺, 504.0 [M+Na]⁺; HRMS (ESI) for C₃₁H₃₂N₁O₄ [M+H]⁺: calcd 482.2331, found 482.2343.

LC-MS: detected at both 254 nm and 214 nm; MeOH / H₂O = 80/20; flow = 1.0 mL/min,
Retention time: 7.80 min, 8.49 min (maj).

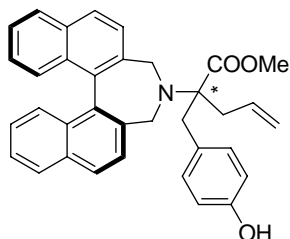


Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.491	MM	0.4079	400.81784	16.37694	100.0000

Signal 2: DAD1 B, Sig=214,16 Ref=360,100

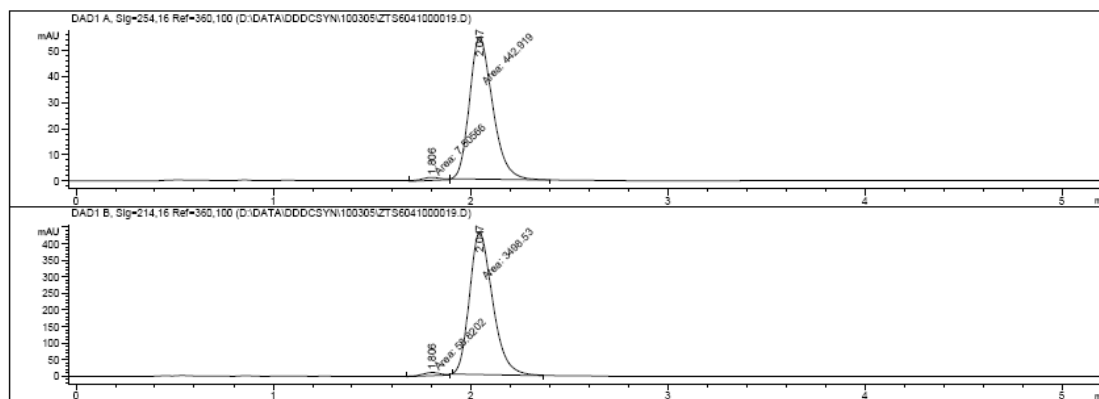
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.799	MM	0.3405	27.31749	1.33713	0.7415
2	8.491	MM	0.4109	3656.65503	148.30144	99.2585



4h, light yellow oil, yield 85%;

^1H NMR (300 MHz, CDCl_3) δ 2.41-2.49 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.83-2.88 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.94 (d, 1H, $J = 13.5$ Hz, PhCH_2), 3.40, (s, 3H, COOCH_3), 3.42 (d, 1H, $J = 13.5$ Hz, PhCH_2), 3.57 (d, 2H, $J = 12.6$ Hz, Ar- CH_2), 4.14 (d, 2H, $J = 12.6$ Hz, Ar- CH_2), 5.10 (dd, 2H, $J = 18.3$ Hz, 12.3 Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.92-6.01 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 6.69 (d, 2H, $J = 8.4$ Hz, Ph-H), 7.01 (d, 2H, $J = 8.4$ Hz, Ph-H), 7.25-7.30 (m, 2H, Ar-H), 7.44-7.0 (m, 4H, Ar-H), 7.55 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.96 (d, 4H, $J = 8.4$ Hz, Ar-H). ^{13}C NMR (100 MHz, CDCl_3) δ 35.8, 38.3, 49.1, 51.0, 68.1, 115.1, 117.7, 125.3, 125.6, 127.5, 128.1, 128.2, 128.3, 128.7, 131.1, 132.9, 133.97, 134.03, 135.1, 154.4, 175.0 ppm. ESI-MS: 514.1 $[\text{M}+\text{H}]^+$; HRMS (ESI) for $\text{C}_{35}\text{H}_{32}\text{N}_1\text{O}_3$ $[\text{M}+\text{H}]^+$: calcd 514.2382, found 514.2382.

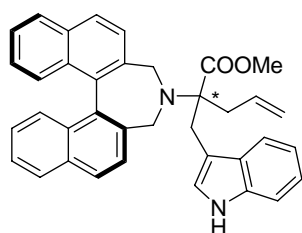
LC-MS: detected at both 254 nm and 214 nm; MeOH / H_2O = 80/20; flow = 1.0 mL/min, Retention time: 1.80 min, 2.05 min (maj).



Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.806	MM	0.1075	7.50566	1.16334	1.6664
2	2.047	MM	0.1357	442.91888	54.41439	98.3336

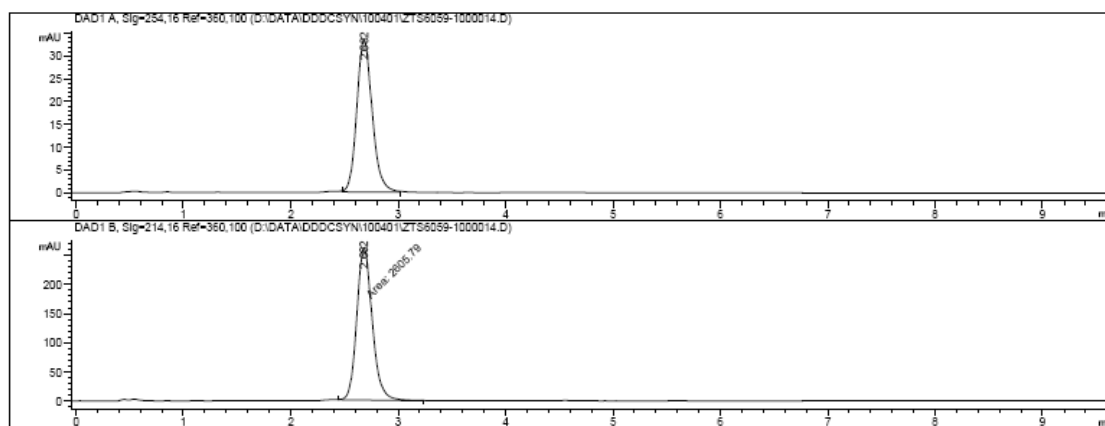
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.806	MM	0.1038	58.82017	9.44504	1.6535
2	2.047	MM	0.1360	3498.52710	428.89011	98.3465



4i, light yellow solid, yield 91%;

^1H NMR (300 MHz, CDCl_3): δ 2.80 (d, 2H, $J = 6.6$ Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.26 (d, 1H, $J = 15.0$ Hz, Indole- CH_2), 3.36 (s, 3H, COOCH_3), 3.48 (d, 1H, $J = 15.0$ Hz, Indole- CH_2), 3.56 (d, 2H, $J = 12.3$ Hz, Ar- CH_2), 4.21 (d, 2H, $J = 12.3$ Hz, Ar- CH_2), 4.98 (dd, 2H, $J = 17.4$ Hz, 10.2 Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.86-6.00 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.08 (dd, 1H, $J = 7.2$ Hz, 7.2 Hz, indole-H), 7.17 (dd, 1H, $J = 7.2$ Hz, 7.2 Hz, indole-H), 7.17 (s, 1H, indole-H), 7.25 (dd, 2H, $J = 5.1$ Hz, 9.3 Hz, Ar-H), 7.34 (d, 2H, $J = 8.1$ Hz, indole-H), 7.46 (dd, 2H, $J = 5.1$ Hz, 9.3 Hz, Ar-H), 7.53 (d, 2H, $J = 8.1$ Hz, Ar-H), 7.56 (d, 1H, $J = 8.1$ Hz, indole-H), 7.94 (d, 4H, $J = 8.1$ Hz, Ar-H), 8.04 (s, 1H, NH). ^{13}C NMR (100 MHz, CDCl_3): δ 28.4, 37.0, 49.1, 51.0, 68.3, 110.8, 110.9, 117.8, 119.0, 119.2, 121.8, 123.3, 125.3, 125.6, 127.5, 128.1, 128.2, 128.2, 128.3, 131.2, 132.9, 134.1, 134.3, 135.2, 135.5, 174.5 ppm. ESI-MS: 537.3 $[\text{M}+\text{H}]^+$; HRMS (ESI) for $\text{C}_{37}\text{H}_{33}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: calcd 537.2536, found 537.2534.

LC-MS: detected at both 254 nm and 214 nm; MeOH / $\text{H}_2\text{O} = 80/20$; flow = 1.0 mL/min, Retention time: 2.69 min (maj).

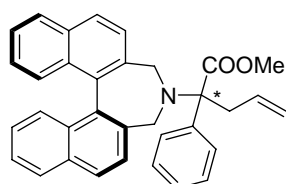


Signal 1: DAD1 A, Sig-254,16 Ref-360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.682	BB	0.1525	333.63248	33.40149	100.0000

Signal 2: DAD1 B, Sig-214,16 Ref-360,100

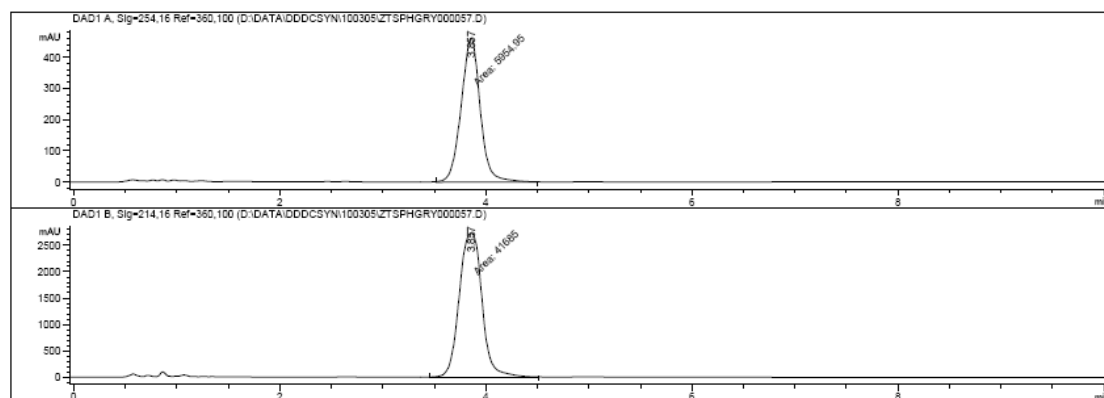
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.682	MM	0.1666	2605.78540	260.62408	100.0000



4j, white solid, yield 92%;

^1H NMR (300 MHz, CDCl_3): δ 2.97-3.15 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.42 (s, 3H, COOCH_3), 3.43 (d, 2H, $J = 12.6$ Hz, Ar- CH_2), 4.09 (d, 2H, $J = 12.6$ Hz, Ar- CH_2), 4.85 (dd, 2H, $J = 18.0$ Hz, 9.0 Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.46-5.60 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.23-7.28 (m, 2H, Ar-H), 7.31-7.53 (m, 11H, Ar-H), 7.95 (d, 4H, $J = 8.4$ Hz, Ar-H). ^{13}C NMR (100 MHz, CDCl_3): δ 44.2, 49.4, 51.1, 72.8, 118.0, 125.3, 125.6, 127.1, 127.5, 127.7, 127.9, 128.0, 128.2, 128.3, 131.2, 132.9, 133.4, 134.3, 135.1, 141.0, 172.9 ppm. ESI-MS: 483.9 $[\text{M}+\text{H}]^+$; HRMS (ESI) for $\text{C}_{34}\text{H}_{30}\text{N}_1\text{O}_2$ $[\text{M}+\text{H}]^+$: calcd 484.2271, found 474.2265.

LC-MS: detected at 254 nm and 214 nm; MeOH / H_2O = 80/20; flow = 1.0 mL/min, Retention time: 3.86 min (maj).

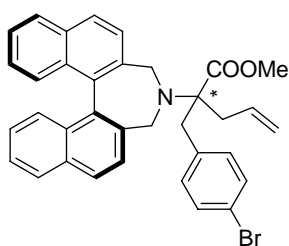


Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.857	MM	0.2149	5954.95020	461.73965	100.0000

Signal 2: DAD1 B, Sig=214,16 Ref=360,100

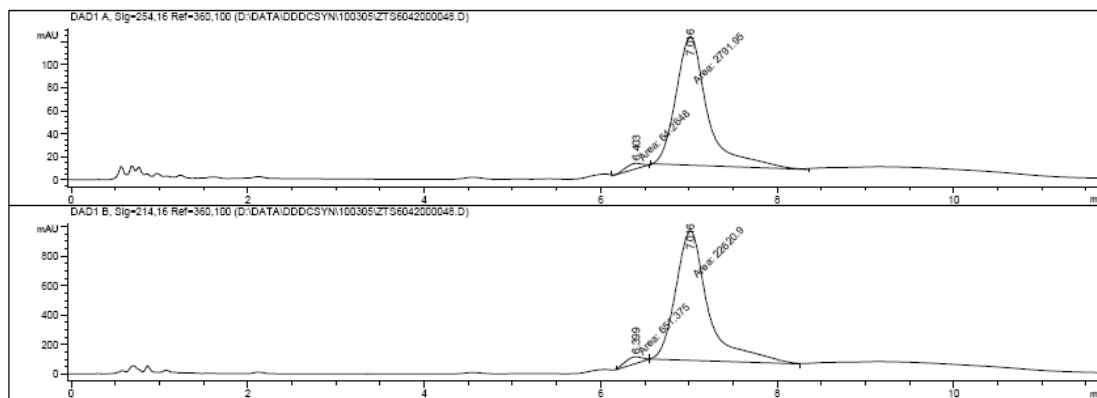
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.857	MM	0.2551	4.16850e4	2723.80493	100.0000



4k, colorless solid, yield 92%;

^1H NMR (300 MHz, CDCl_3) δ 2.41-2.49 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.77-2.85 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.01 (d, 1H, $J = 13.5$ Hz, PhCH_2), 3.37 (d, 1H, $J = 13.5$ Hz, PhCH_2), 3.39 (s, 3H, COOCH_3), 3.52 (d, 2H, $J = 12.6$ Hz, Ar-CH_2), 4.12 (d, 2H, $J = 12.6$ Hz, Ar-CH_2), 5.10 (dd, 2H, $J = 18.3$ Hz, 12.3 Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.85-5.97 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.08 (d, 2H, $J = 8.4$ Hz, Ph-H), 7.28-7.30 (m, 2H, Ar-H), 7.39 (d, 2H, $J = 8.4$ Hz, Ph-H), 7.45-7.50 (m, 4H, Ar-H), 7.54 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.96 (d, 2H, $J = 8.4$ Hz, Ar-H). ^{13}C NMR (100 MHz, CDCl_3) δ 38.1, 38.4, 49.1, 51.0, 67.8, 118.1, 120.5, 125.4, 125.7, 127.5, 128.1, 128.3, 131.1, 131.2, 131.9, 132.9, 133.7, 133.8, 135.1, 136.2, 173.9 ppm. ESI-MS: 576.2 $[\text{M}+\text{H}]^+$, HRMS (ESI) for $\text{C}_{35}\text{H}_{31}\text{Br}_1\text{N}_1\text{O}_2$ $[\text{M}+\text{H}]^+$: calcd 576.1533, found 576.1532.

LC-MS: detected at both 254 nm and 214 nm; MeOH / H_2O = 80/20; flow = 1.0 mL/min, Retention time: 6.4 min, 7.0 min (maj).

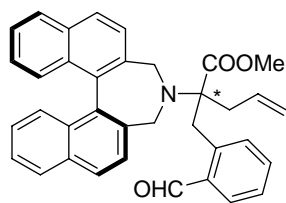


Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.403	MM	0.2335	64.26478	4.58751	2.2500
2	7.016	MM	0.4143	2791.95142	112.31408	97.7500

Signal 2: DAD1 B, Sig=214,16 Ref=360,100

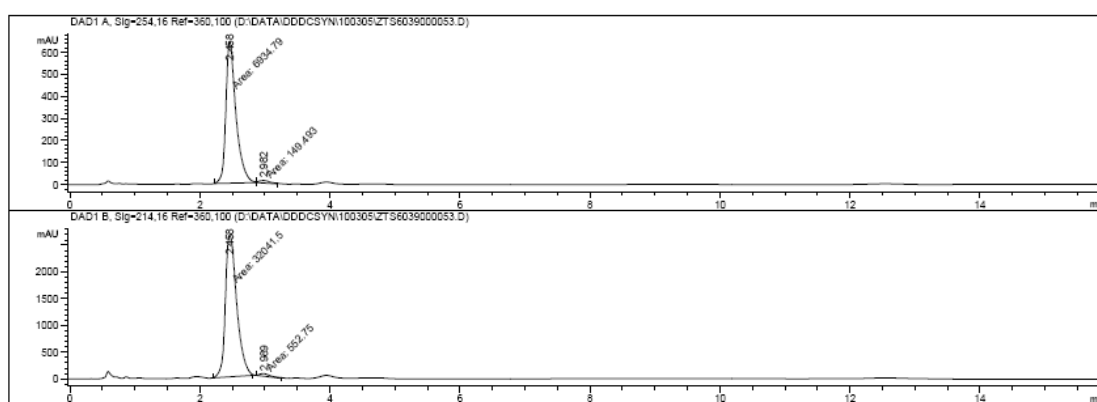
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.399	MM	0.2343	651.37463	46.32499	2.7989
2	7.016	MM	0.4284	2.26209e4	880.04199	97.2011



4l, light brown solid, yield 92%;

^1H NMR (300 MHz, CDCl_3): δ 2.57-2.72 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.36 (s, 3H, COOCH_3), 3.54 (d, 1H, $J = 14.4$ Hz, ArCH_2), 3.54 (d, 2H, $J = 12.6$ Hz, Ar-CH_2), 3.81 (d, 1H, $J = 14.4$ Hz, ArCH_2), 4.11 (d, 2H, $J = 12.6$ Hz, Ar-CH_2), 4.90 (d, 1H, $J = 17.1$ Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.10 (d, 1H, $J = 10.2$ Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.74-5.85 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.23-7.28 (m, 2H, Ar-H), 7.39-7.49 (m, 6H, Ar-H), 7.53-7.61 (m, 3H, Ar-H), 7.84 (d, 1H, $J = 7.5$ Hz, Ar-H), 7.93-7.97 (m, 4H, Ar-H). ^{13}C NMR (100 MHz, CDCl_3): δ 33.6, 37.9, 49.3, 51.2, 68.9, 118.4, 125.4, 125.6, 127.0, 127.5, 128.2, 128.4, 131.2, 131.7, 132.9, 133.0, 133.4, 133.7, 135.1, 135.3, 139.8, 173.9, 191.7 ppm. ESI-MS: 526.0 $[\text{M}+\text{H}]^+$; HRMS (ESI) for $\text{C}_{36}\text{H}_{32}\text{N}_1\text{O}_3$ $[\text{M}+\text{H}]^+$: calcd 526.2376, found 526.2355.

LC-MS: detected at both 254 nm and 214 nm; MeOH / H_2O = 80/20; flow = 1.0 mL/min, Retention time: 2.5 min (maj), 3.0 min.

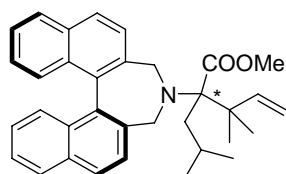


Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.458	MM	0.1793	6934.79297	644.44891	97.8898
2	2.982	MM	0.2053	149.49290	12.13869	2.1102

Signal 2: DAD1 B, Sig=214,16 Ref=360,100

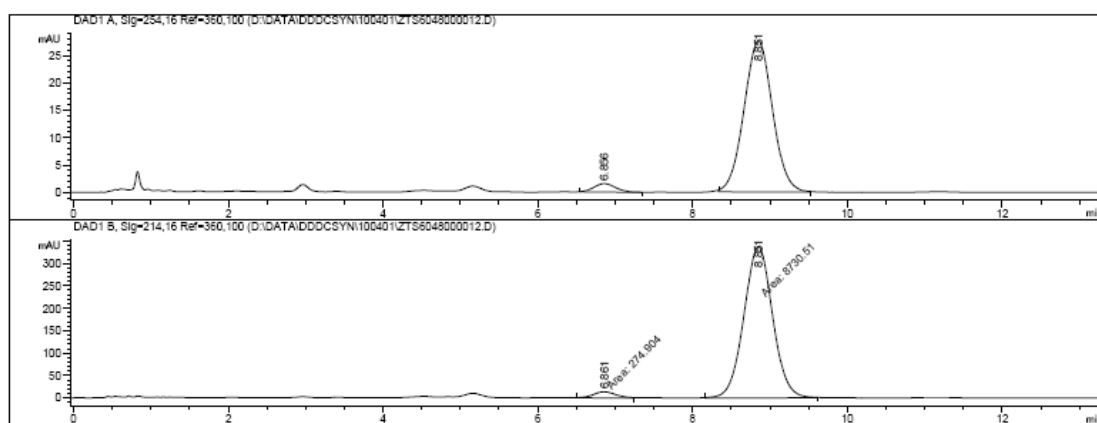
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.458	MM	0.2022	3.20415e4	2641.37842	98.3041
2	2.989	MM	0.1977	552.75043	46.58923	1.6959



4m, light yellow oil, yield 92%;

^1H NMR (300 MHz, CDCl_3) δ 0.71 (d, 3H, $J = 6.3$ Hz, CHCH_3), 0.85 (d, 3H, $J = 6.3$ Hz, CHCH_3), 1.11 (s, 3H, $\text{C}(\text{CH}_3)_2$), 1.16 (s, 3H, $\text{C}(\text{CH}_3)_2$), 1.62-1.93 (m, 3H, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 3.59 (d, 2H, $J = 12.6$ Hz, Ar-CH_2), 3.81 (s, 3H, COOCH_3), 4.12 (d, 2H, $J = 12.6$ Hz, Ar-CH_2), 4.91-4.97 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 6.11-6.21 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.21-7.27 (m, 2H, Ar-H), 7.42-7.47 (m, 4H, Ar-H), 7.69 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.93-7.98 (m, 2H, Ar-H). ^{13}C NMR (100 MHz, CDCl_3) δ 23.2, 23.5, 25.1, 25.6, 25.6, 44.2, 46.9, 51.1, 51.7, 111.6, 125.2, 125.4, 127.6, 128.1, 128.1, 129.0, 131.2, 132.7, 134.7, 134.8, 147.3, 176.0 ppm. ESI-MS: 492.1 $[\text{M}+\text{H}]^+$; HRMS (ESI) for $\text{C}_{34}\text{H}_{38}\text{N}_1\text{O}_2$ $[\text{M}+\text{H}]^+$: calcd 492.2903, found 492.2898.

LC-MS: detected at both 254 nm and 214 nm; MeOH / H₂O = 80/20; flow = 1.0 mL/min,
 Retention time: 6.86 min, 9.95 min (maj).

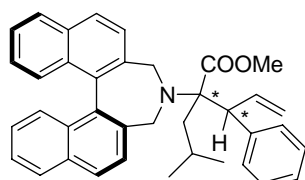


Signal 1: DAD1 A, Sig-254,16 Ref-360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.856	BB	0.2982	29.55830	1.52466	4.0108
2	9.951	BB	0.3977	707.40552	27.54036	95.9892

Signal 2: DAD1 B, Sig-214,16 Ref-360,100

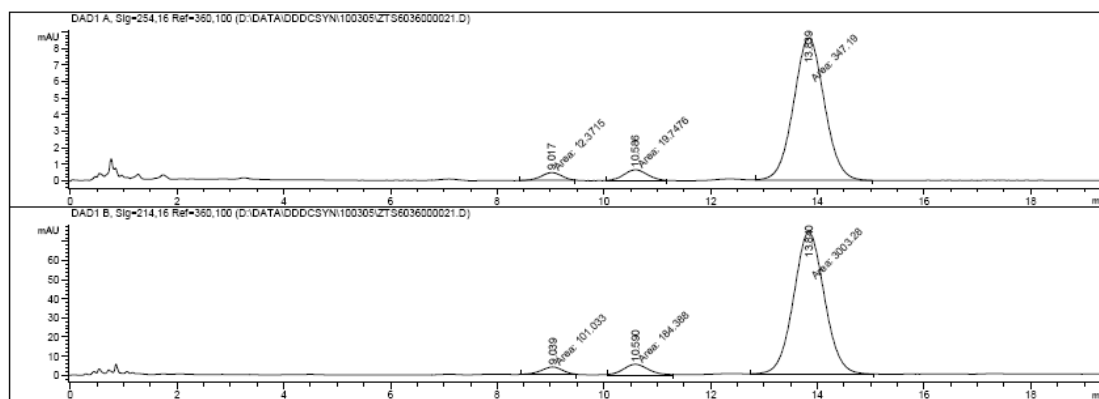
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.861	MM	0.3350	274.90417	13.67529	3.0527
2	9.951	MM	0.4312	9730.51367	337.47147	96.9473



4n, white solid, yield 90%;

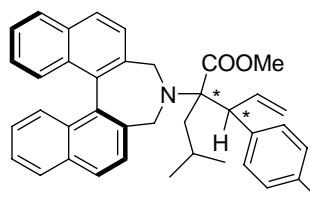
¹H NMR (300 MHz, CDCl₃): δ 0.69 (d, 3H, *J* = 6.3 Hz, CHCH₃), 0.75 (d, 3H, *J* = 6.3 Hz, CHCH₃), 1.26-1.63 (m, 3H, CH₂CH(CH₃)₂), 3.65 (s, 3H, COOCH₃), 3.67 (d, 2H, *J* = 12.3 Hz, Ar-CH₂), 4.06 (d, 2H, *J* = 12.3 Hz, Ar-CH₂), 4.17 (d, 1H, *J* = 8.1 Hz), 5.03 (dd, 2H, *J* = 16.8 Hz, 10.5 Hz, CH₂CH=CH₂), 6.21-6.34 (m, 1H, CH₂CH=CH₂), 7.23-7.37 (m, 7H, Ar-H), 7.44-7.50 (m, 6H, Ar-H), 7.96-8.01 (m, 4H, Ar-H). ¹³C NMR (100 MHz, CDCl₃): δ 24.2, 25.3, 46.1, 51.4, 52.7, 55.9, 71.8, 116.5, 125.3, 125.5, 126.2, 127.7, 128.2, 128.3, 128.9, 131.3, 131.5, 131.9, 132.7, 134.3, 134.8, 139.7, 140.4, 176.4 ppm. ESI-MS: 540.0 [M+H]⁺, 561.8 [M+Na]⁺; HRMS (ESI) for C₃₈H₃₈N₁O₂ [M+H]⁺: calcd 540.2897, found 540.2890.

LC-MS: detected at both 254 nm and 214 nm; MeOH / H₂O = 80/20; flow = 1.0 mL/min,
 Retention time: 9.0 min, 10.6 min, 13.8 min (maj).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.017	MM	0.4460	12.37148	4.62351e-1	3.2616
2	10.586	MM	0.5085	19.74756	6.47265e-1	5.2062
3	13.839	MM	0.6707	347.18954	8.62786	91.5322

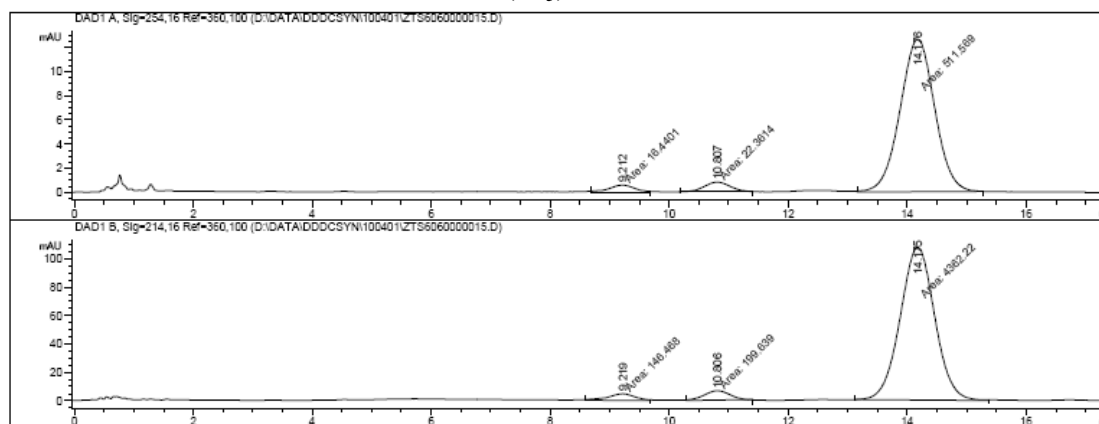
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.039	MM	0.4445	101.03299	3.78868	3.0721
2	10.590	MM	0.5465	184.38756	5.62339	5.6067
3	13.840	MM	0.6727	3003.27930	74.40588	91.3212



4o, white solid, yield 94%;

^1H NMR (300 MHz, CDCl_3): δ 0.70 (d, 3H, $J = 6.3$ Hz, CHCH_3), 0.75 (d, 3H, $J = 6.3$ Hz, CHCH_3), 1.29-1.63 (m, 3H, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 3.65 (s, 3H, COOCH_3), 3.66 (d, 2H, $J = 12.3$ Hz, Ar- CH_2), 4.02 (d, 2H, $J = 12.3$ Hz, Ar- CH_2), 4.13 (d, 1H, $J = 8.1$ Hz) 5.07 (dd, 2H, $J = 16.8$ Hz, 10.5 Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 6.19-6.31 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.24-7.29 (m, 4H, Ar-H), 7.41-7.50 (m, 8H, Ar-H), 7.96-8.01 (m, 4H, Ar-H). ^{13}C NMR (100 MHz, CDCl_3): δ 23.8, 25.1, 45.7, 51.1, 52.5, 55.6, 72.1, 116.3, 120.5, 125.4, 125.6, 127.5, 128.0, 128.1, 128.7, 131.1, 131.2, 131.9, 132.9, 134.3, 134.9, 139.9, 140.2, 176.1 ppm. ESI-MS: 617.8 $[\text{M}+\text{H}]^+$; HRMS (ESI) for $\text{C}_{38}\text{H}_{37}\text{Br}_1\text{N}_1\text{O}_2$ $[\text{M}+\text{H}]^+$: calcd 618.2002 found 618.2001.

LC-MS: detected at both 254 nm and 214 nm; MeOH / H_2O = 80/20; flow = 1.0 mL/min, Retention time: 9.2 min, 10.9 min, 14.2 min (maj).

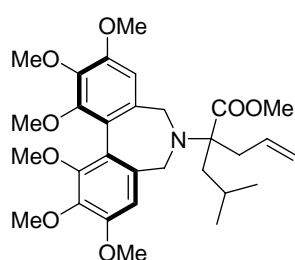


Signal 1: DAD1 A, Sig-254,16 Ref-360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.212	MM	0.4847	16.44015	5.65360e-1	2.9871
2	10.807	MM	0.4846	22.36142	7.69049e-1	4.0630
3	14.176	MM	0.6744	511.56903	12.64222	92.9499

Signal 2: DAD1 B, Sig-214,16 Ref-360,100

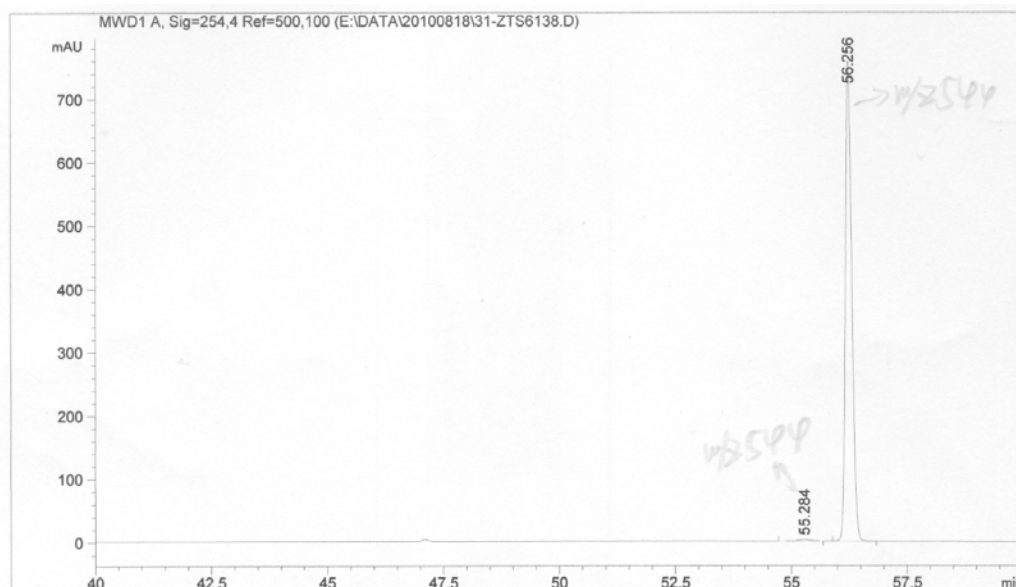
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.219	MM	0.5233	146.46814	4.66516	3.1108
2	10.806	MM	0.5057	199.63934	6.58008	4.2401
3	14.175	MM	0.6741	4362.21729	107.84634	92.6490



8a, colorless solid, yield 91%;

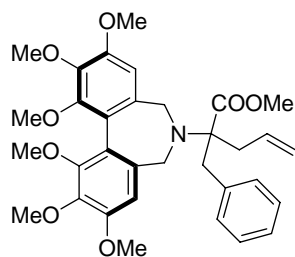
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 0.74 (d, 3H, $J = 6.3$ Hz, CHCH_3), 0.96 (d, 3H, $J = 6.3$ Hz, CHCH_3), 1.64-1.91 (m, 3H, CH_2CHCH_3), 2.51 (dd, 1H, $J = 8.4$ Hz, 8.1 Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.05 (dd, 1H, $J = 4.2$ Hz, 5.7 Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.30 (s, 3H, COOCH_3), 3.31 (d, 2H, $J = 12.6$ Hz, NCH_2), 3.68 (s, 6H, $2 \times \text{ArOCH}_3$), 3.82 (d, 2H, $J = 12.6$ Hz, NCH_2), 3.90 (s, 6H, $2 \times \text{ArOCH}_3$), 3.94 (s, 6H, $2 \times \text{ArOCH}_3$), 5.12 (dd, 2H, $J = 7.5$ Hz, 17.7 Hz, CHCH_2), 5.82-5.96 (m, 1H, CHCH_2), 6.61 (s, 2H, ArH). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 21.4, 24.4, 25.1, 35.6, 42.1, 48.5, 50.1, 55.9, 60.6, 60.8, 65.2, 108.4, 116.7, 122.9, 131.2, 134.4, 141.0, 150.9, 152.4, 175.6 ppm. ESI-MS: 544.3 $[\text{M}+\text{H}]^+$, 566.3 $[\text{M}+\text{Na}]^+$; HRMS (ESI) for $\text{C}_{30}\text{H}_{42}\text{N}_1\text{O}_8$ $[\text{M}+\text{H}]^+$: calcd 544.2905, found 544.2886.

LC-MS: detected at 254 nm, Retention time: 55.3 min, 56.3 min (maj).



信号 1: MWD1 A, Sig=254,4 Ref=500,100

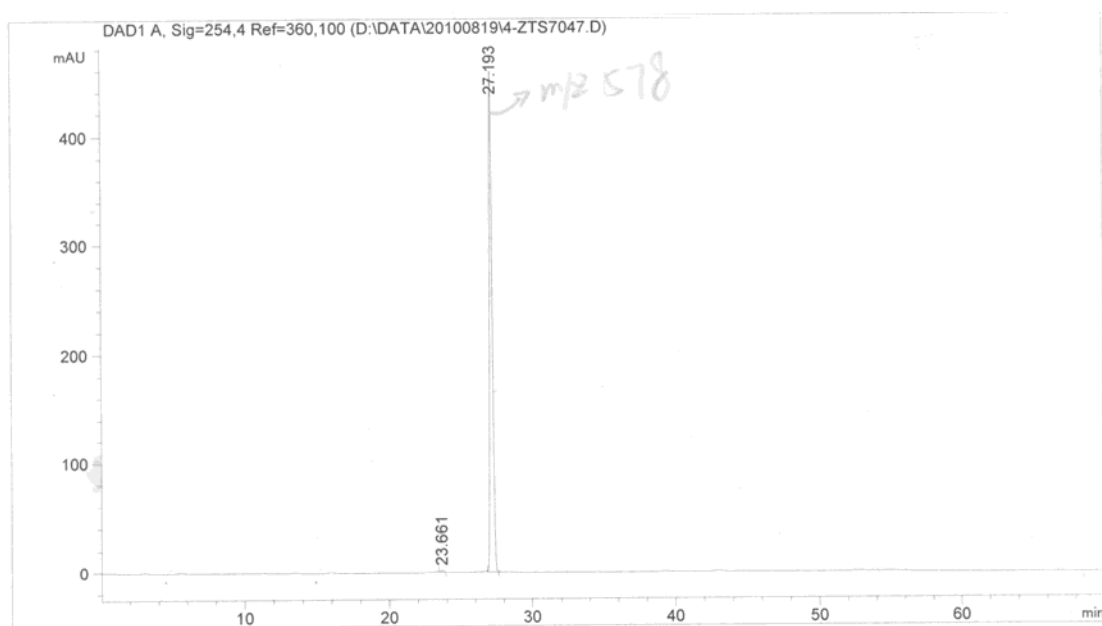
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	55.284	BV	0.3115	47.74992	2.32618	0.6472
2	56.256	BB	0.1509	7330.32910	757.25916	99.3528



8b, white solid, yield 92%;

^1H NMR (300 MHz, CDCl_3): δ 2.35 (dd, 1H, $J = 7.5$ Hz, 7.2 Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.82 (dd, 1H, $J = 5.7$ Hz, 5.7 Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.96 (d, 1H, $J = 13.8$ Hz, CH_2Ph), 3.38-3.47 (m, 6H, CH_2Ph , NCH_2 , COOCH_3), 3.68 (s, 6H, $2 \times \text{ArOCH}_3$), 3.84-3.91 (m, 14H, NCH_2 , $4 \times \text{ArOCH}_3$), 5.07 (dd, 2H, $J = 17.1$ Hz, 10.2 Hz, $\text{CH}=\text{CH}_2$), 5.90-6.03 (m, 1H, $\text{CH}=\text{CH}_2$), 6.61 (s, 2H, ArH), 7.12 (d, 2H, $J = 7.8$ Hz, Ph-H), 7.20 (t, 3H, $J = 7.5$ Hz, Ph-H), ^{13}C NMR (100 MHz, CDCl_3): δ 35.5, 38.9, 49.0, 50.3, 55.8, 60.5, 60.8, 67.5, 108.3, 117.5, 122.9, 126.5, 128.1, 129.9, 131.0, 133.9, 137.0, 141.1, 150.9, 152.5, 174.2 ppm. ESI-MS: 578.3 $[\text{M}+\text{H}]^+$; HRMS (ESI) for $\text{C}_{33}\text{H}_{40}\text{N}_1\text{O}_8$ $[\text{M}+\text{H}]^+$: calcd 578.2754, found 578.2737.

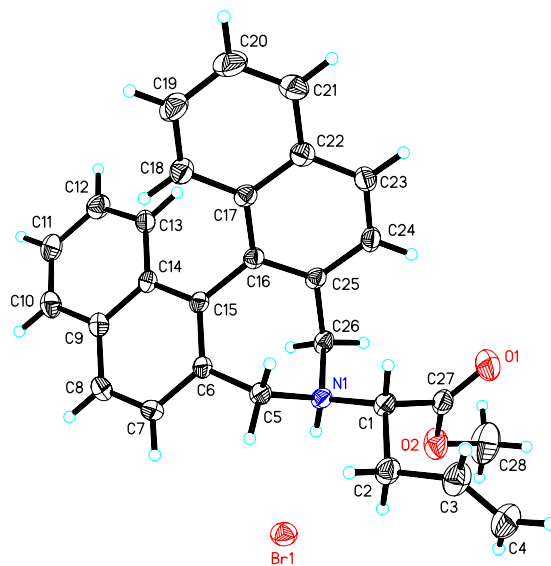
LC-MS: detected at 254 nm, Retention time: 27.2 min, 29.7 min (maj).



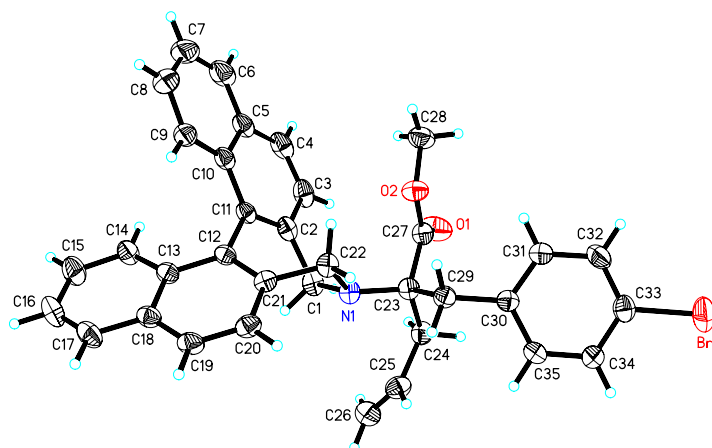
信号 1: MWD1 A, Sig=254,4 Ref=500,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	27.193	BB	0.2129	6259.97314	459.55725	0.8562
2	29.686	BB	0.3381	54.06723	2.48262	99.1438

6. X-ray Crystal Structure of Rearrangement Product 4a and 4k



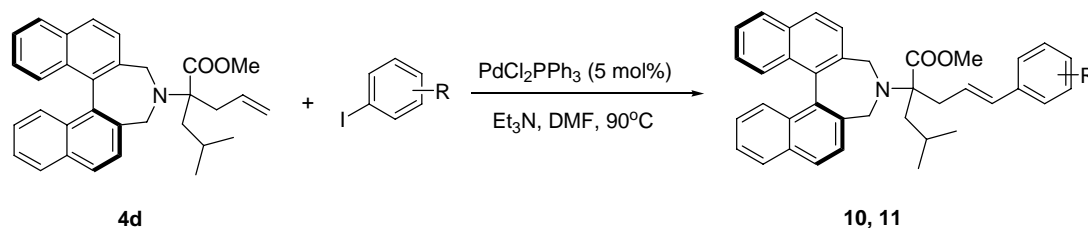
Compound 4a



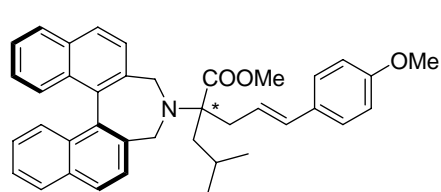
Compound 4k

CCDC 865414 (**4a**) & 865415 (**4k**) contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

7. General Procedure for Double Bond Elaboration via Heck Reaction

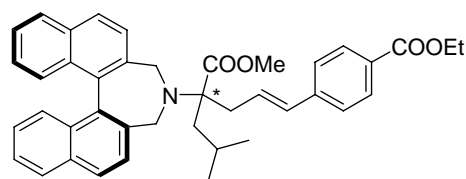


Under nitrogen atmosphere, the ammonium salts **4d** (46 mg, 0.1 mmol), aryl iodide (0.1 mmol), PdPPh₃Cl₂ (2.2 mg, 5 mol%), Et₃N (21 μL, 0.15 mmol) was mixed in dry DMF (5 mL). The mixture was heated to 90°C and stirred overnight. The solution was then diluted with EtOAc, washed with NaHCO₃ (aq, saturated) and brine, dried over anhydrous Na₂SO₄, and concentrated. Purification by flash column chromatography on silica gel afforded the corresponding products.



10, colorless oil, yield 84%;

¹H NMR (300 MHz, CDCl₃): δ 0.80 (d, 3H, *J* = 5.7 Hz, CH(CH₃)₂), 0.99 (d, 3H, *J* = 5.7 Hz, CH(CH₃)₂), 1.74-1.97 (m, 3H, CH₂CH(CH₃)₂), 2.71 (dd, 1H, *J* = 7.8 Hz, 8.4 Hz, CH₂CH=CH₂), 3.16 (dd, 1H, *J* = 5.1 Hz, 4.8 Hz, CH₂CH=CH₂), 3.34 (s, 3H, ArOCH₃), 3.47 (d, 2H, *J* = 12.3 Hz, NCH₂), 3.61 (s, 3H, COOCH₃), 4.12 (d, 2H, *J* = 12.6 Hz, NCH₂), 6.07-6.16 (m, 1H, ArCH=CH), 6.41 (d, 1H, *J* = 16.5 Hz, ArCH=CH), 6.83 (d, 2H, *J* = 8.4 Hz, ArH), 7.23-7.29 (m, 4H, ArH), 7.56 (dd, 4H, *J* = 6.3 Hz, 8.1 Hz, ArH), 7.53 (d, 2H, *J* = 7.8 Hz, ArH), 7.94 (d, 2H, *J* = 8.1 Hz, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 21.9, 24.4, 25.2, 35.5, 42.6, 48.7, 50.7, 55.2, 66.3, 113.8, 124.3, 125.3, 125.5, 127.1, 127.5, 128.1, 128.2, 128.3, 130.7, 131.1, 131.4, 132.9, 134.3, 135.1, 158.6, 175.6 ppm. ESI-MS: 570.3 [M+H]⁺; HRMS (ESI) for C₃₉H₄₀N₁O₃ [M+H]⁺: calcd 570.3008 found 570.3003.

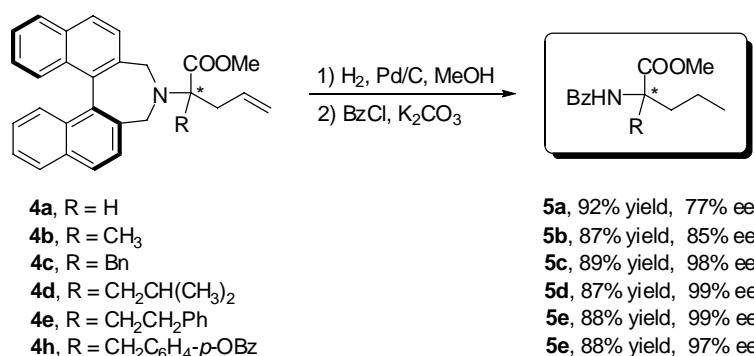


11, colorless oil, yield 82%;

¹H NMR (300 MHz, CDCl₃): δ 0.79 (d, 3H, *J* = 6.3 Hz, CH(CH₃)₂), 0.98 (d, 3H, *J* = 6.0 Hz, CH(CH₃)₂), 1.40 (t, 3H, *J* = 7.2 Hz, COOCH₂CH₃), 1.73-1.99 (m, 3H, CH₂CH(CH₃)₂), 2.74 (dd, 1H, *J* = 7.5 Hz, 7.2 Hz, CH₂CH=CH₂), 3.20 (dd, 1H, *J* = 4.2 Hz, 4.8 Hz, CH₂CH=CH₂), 3.35 (s, 3H, COOCH₃), 3.48 (d, 2H, *J* = 12.9 Hz, NCH₂), 4.10 (d, 2H, *J* = 12.3 Hz, NCH₂), 4.37 (q, 2H, *J* = 6.9 Hz, COOCH₂CH₃), 6.35-6.44 (m, 1H, ArCH=CH), 6.50 (d, 1H, *J* = 15.9 Hz, ArCH=CH), 7.23-7.28 (m, 2H, ArH), 7.33 (d, 2H, *J* = 8.4 Hz, ArH), 7.45 (dd, 4H, *J* = 8.7 Hz, 8.1 Hz, ArH), 7.52 (d, 2H, *J* = 8.4 Hz), 7.93-7.98 (m, 6H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 14.3, 21.8, 24.5, 25.2, 35.6, 42.7, 48.8, 50.8, 60.8, 66.2, 125.3, 125.6, 125.8, 127.5, 128.1, 128.2, 128.6, 128.6, 129.8, 131.1, 131.3, 132.9, 134.2, 135.1, 142.2, 166.5, 175.5 ppm. ESI-MS: 612.3 [M+H]⁺; HRMS (ESI) for C₄₁H₄₂N₁O₄ [M+H]⁺: calcd 612.3114 found 612.3107.

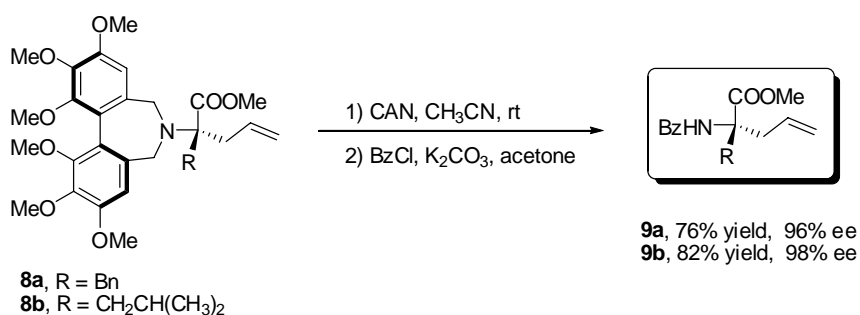
8. General Procedure for Removal of Chiral Auxiliary

6.1 Debenzylation via Hydrogenation

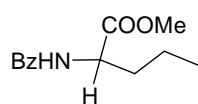


Amine **4** (0.1 mmol) and Pd/C (10%, 11mg) was added to 5 mL of methanol, and stirred under H₂ (4 atm) atmosphere at 30°C. After completion, the reaction mixture was filtrated, concentrated. The mixture was dissolved in 5 mL of acetone and to this solution was added K₂CO₃ (27.6 mg, 0.2 mmol), then stirred at room temperature for 1h. After filtration and concentration, the residue was purified via column chromatography on silica gel, affording corresponding benzoyl amino acids.

6.2 Debenzylation via Oxidation



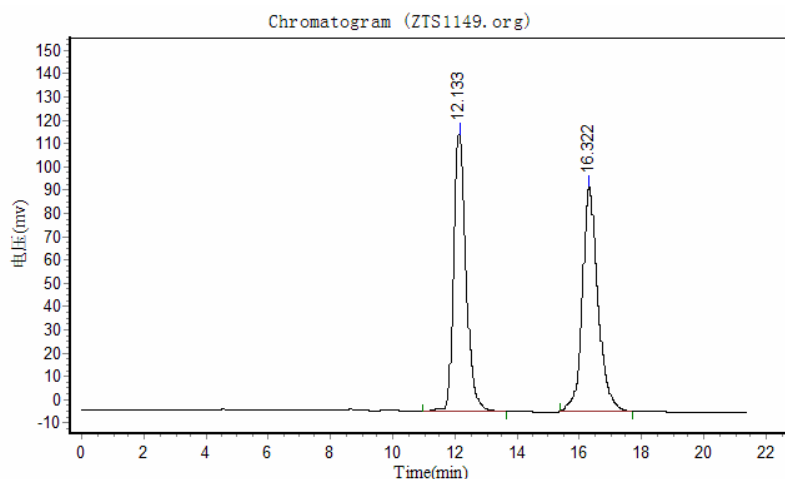
To a 25 mL flask was added amine **8** (0.1 mmol), CAN (0.6 mmol) and 5 mL of acetonitrile. The reaction was stirred at room temperature for about 2 hours for completion. The mixture was then diluted with EtOAc, washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated. The residue was dissolved in 5 mL of acetone and K₂CO₃ and BzCl was added. After stirring at room temperature for 1 hour, the mixture was diluted with EtOAc, and filtrated through Celite. The filtrate was washed three times with water and brine, dried over anhydrous Na₂SO₄, and concentrated. Purification by flash column chromatography on silica gel afforded the corresponding bezoylation product **9**.



5a, colorless oil, yield 92%, ee 77%;

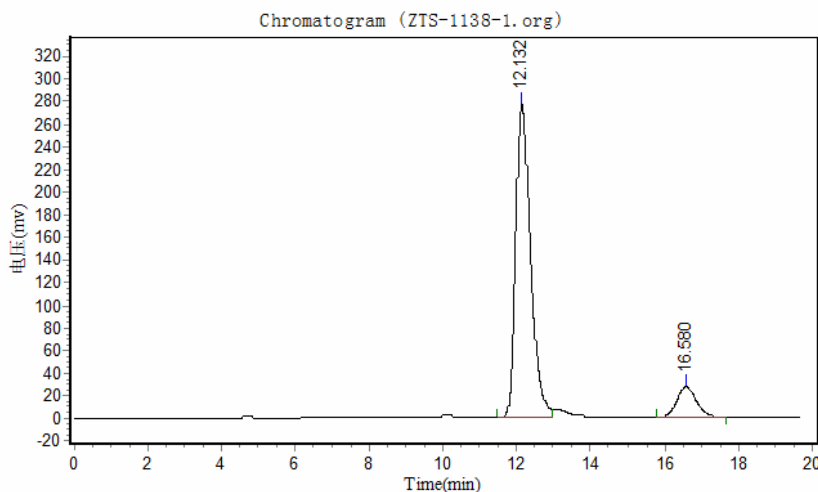
$[\alpha]_D^{14} = -20.0$ (c 0.4, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 0.92-0.98 (m, 3H, CH_2CH_3), 1.38-1.44 (m, 2H, CH_2CH_3), 1.65-1.82 (m, 1H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.85-1.98 (m, 1H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.77 (s, 3H, COOCH_3), 4.82-4.86 (m, 1H, N-CH), 6.74 (b, 1H, NH), 7.42-7.51 (m, 3H, Ph-H), 7.80 (d, 2H, $J = 8.1$ Hz, Ph-H).

HPLC: Chiral OD-H column (250 mm); detected at 214 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 12.1 min (maj), 16.6 min



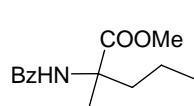
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.133	118400.977	3305446.250	49.6379
2		16.322	96330.977	3353677.750	50.3621
Total			214731.953	6659124.000	100.0000



Results

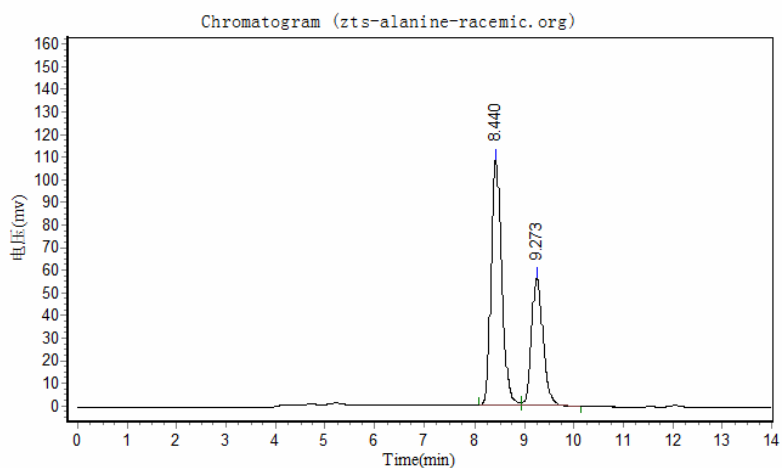
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.132	276716.219	7735855.500	88.7819
2		16.580	26313.008	977468.750	11.2181
Total			303029.227	8713324.250	100.0000



5b, white solid, yield 87%, ee 85%;

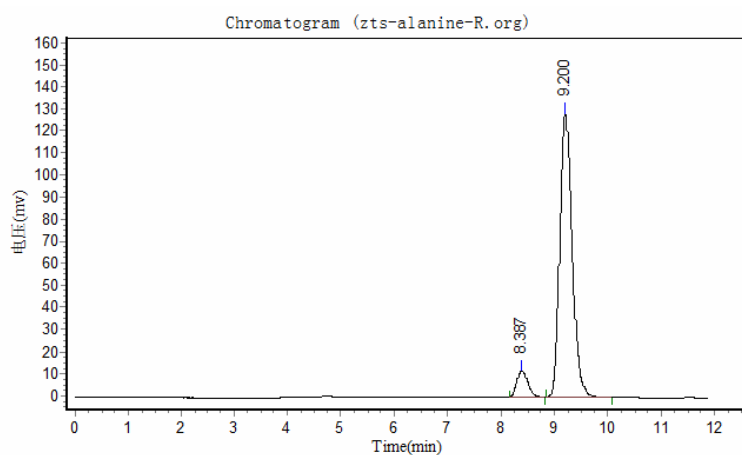
$[\alpha]_D^{25} = +12.7$ (c 0.3, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 0.88-0.92 (m, 3H, CH_2CH_3), 1.09-1.14 (m, 1H, CH_2CH_3), 1.28-1.35 (m, 1H, CH_2CH_3), 1.71 (s, 3H, NCCCH_3) 1.80-1.89 (m, 1H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.36-2.47 (m, 1H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.79 (s, 3H, COOCH_3), 7.06 (b, 1H, NH), 7.42-7.47 (m, 3H, Ph-H), 7.79 (d, 2H, $J = 8.1$ Hz, Ph-H).

HPLC: Chiral OD-H column (250 mm); detected at 214 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 8.4 min, 9.2 min (maj)



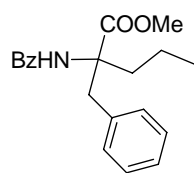
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.440	108815.727	1613260.375	63.6885
2		9.273	56307.598	919788.750	36.3115
Total			165123.324	2533049.125	100.0000



Results

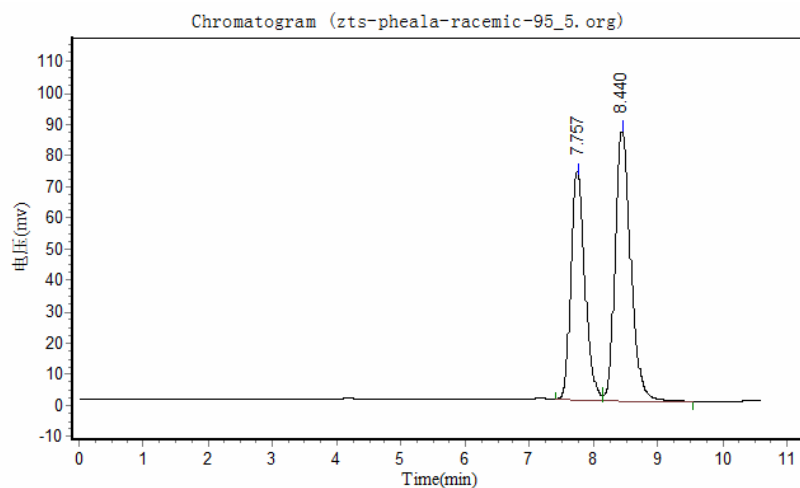
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.387	11870.838	169974.203	7.5713
2		9.200	128648.883	2074997.750	92.4287
Total			140519.721	2244971.953	100.0000



5c, colorless oil, yield 89%, ee 98%;

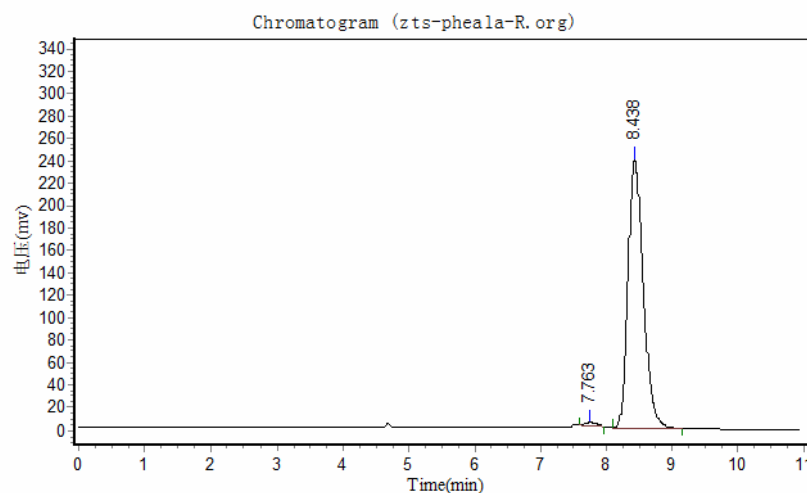
$[\alpha]_D^{25} = +102.7$. (c 0.5, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 0.89-0.94 (m, 3H, CH_2CH_3), 1.00-1.11 (m, 1H, CH_2CH_3), 1.30-1.41 (m, 1H, CH_2CH_3), 1.88-1.99 (m, 1H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.75-2.86 (m, 1H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.16 (d, 2H, $J = 13.5$ Hz, PhCH_2), 3.83 (s, 3H, COOCH_3), 3.94 (d, 2H, $J = 13.5$ Hz, PhCH_2), 6.96 (b, 1H, NH), 7.01-7.04 (m, 2H, Ph-H), 7.17-7.19 (m, 3H, Ph-H), 7.41 (q, 2H, $J = 7.2$ Hz, Ph-H), 7.49 (q, 1H, $J = 7.2$ Hz, Ph-H), 7.69 (d, 2H, $J = 8.4$ Hz, Ph-H).

HPLC: Chiral AD-H column (250 mm); detected at 214 nm; hexane/*i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 7.8 min, 8.4 min (maj)



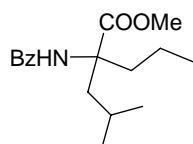
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.757	72843.484	1107720.250	43.2768
2		8.440	85836.477	1451896.750	56.7232
Total			158679.961	2559617.000	100.0000



Results

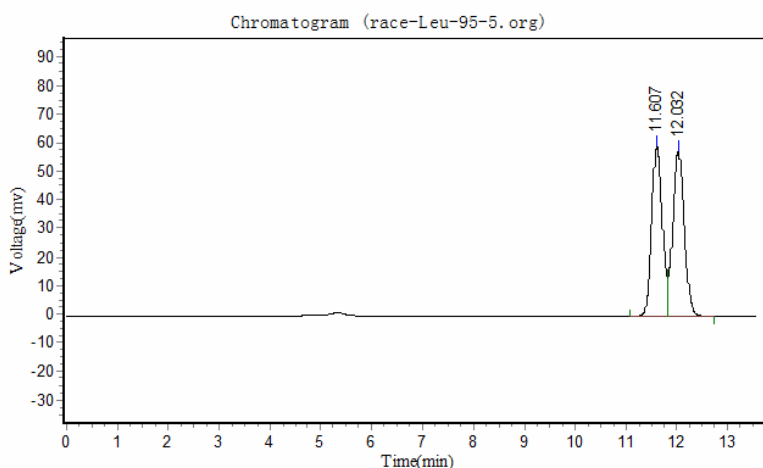
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.763	2692.691	30984.998	0.8012
2		8.438	238964.516	3836118.000	99.1988
Total			241657.207	3867102.998	100.0000



5d, colorless oil, yield 87%, ee 99%;

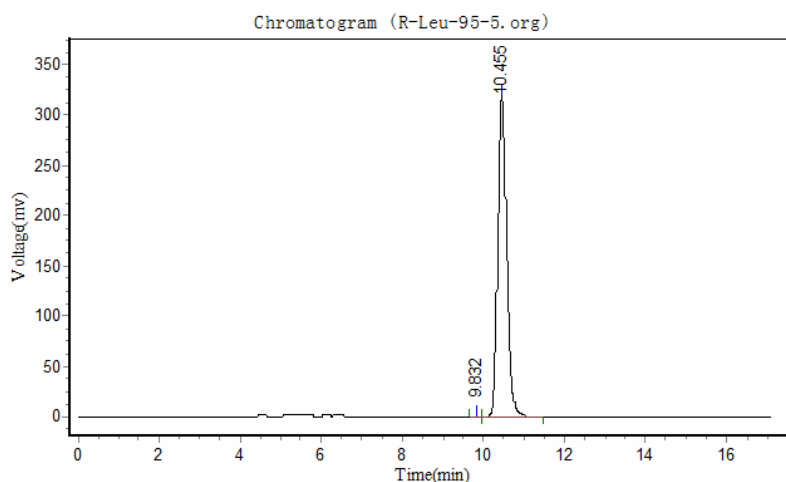
$[\alpha]_D^{20} = -14.7$ (c 1.25, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 0.77 (d, 3H, $J = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.85-0.89, (m, 6H, CH_2CH_3 , $\text{CH}(\text{CH}_3)_2$), 0.91-1.00 (m, 1H, CH_2CH_3), 1.24-1.33 (m, 1H, CH_2CH_3), 1.51-1.62 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 1.70-1.77 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 2.59-2.72 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 3.80 (s, 3H, COOCH_3), 7.35 (b, 1H, NH), 7.43-7.50 (m, 3H, Ph-H), 7.79 (d, 2H, $J = 8.4$ Hz, Ph-H).

HPLC: Chiral AD-H column (250 mm); detected at 214 nm; hexane/*i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 9.8 min, 10.4 min(maj)



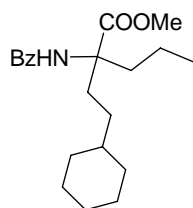
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.607	59684.266	880720.313	49.0877
2		12.032	58009.145	913456.125	50.9123
Total			117693.410	1794176.438	100.0000



Results

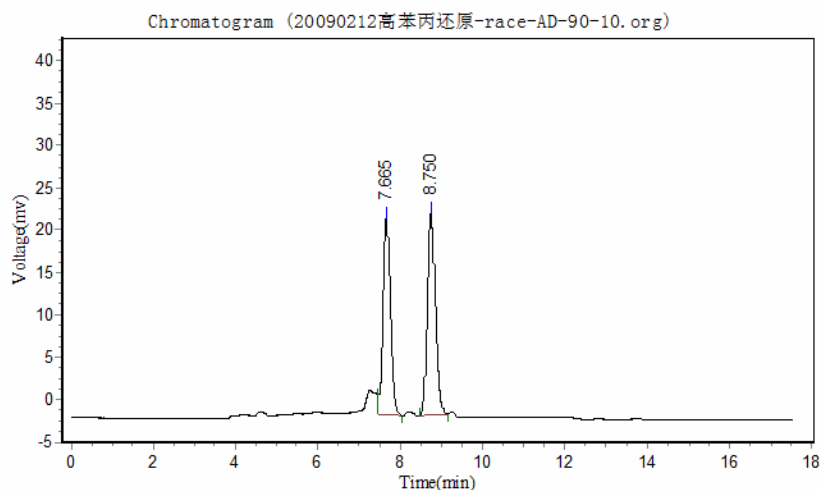
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.832	143.430	1678.633	0.0345
2		10.455	318386.563	4865164.000	99.9655
Total			318529.992	4866842.633	100.0000



5e, colorless oil, yield 88%, ee 99%;

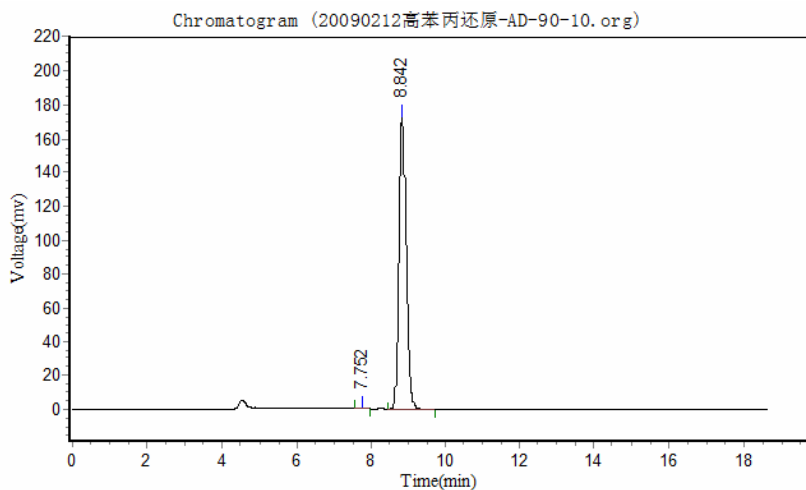
$[\alpha]_D^{20} = -10.7$ (c 0.6, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 0.78-0.89 (m, 6H), 1.12-1.19 (m, 6H), 1.25-1.40 (m, 2H), 1.61-1.83 (m, 6H), 2.58-2.65 (m, 2H), 3.81 (s, 3H, COOCH_3), 7.20 (b, 1H, NH), 7.43-7.49 (m, 3H, Ph-H), 7.80 (d, 2H, $J = 8.1$ Hz),

HPLC: Chiral AD-H column (250 mm); detected at 214 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 7.7 min, 8.8 min (maj)



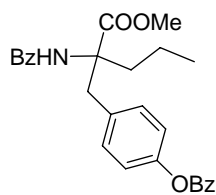
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.665	23029.877	290070.031	47.0056
2		8.750	23853.230	327027.188	52.9944
Total			46883.107	617097.219	100.0000



Results

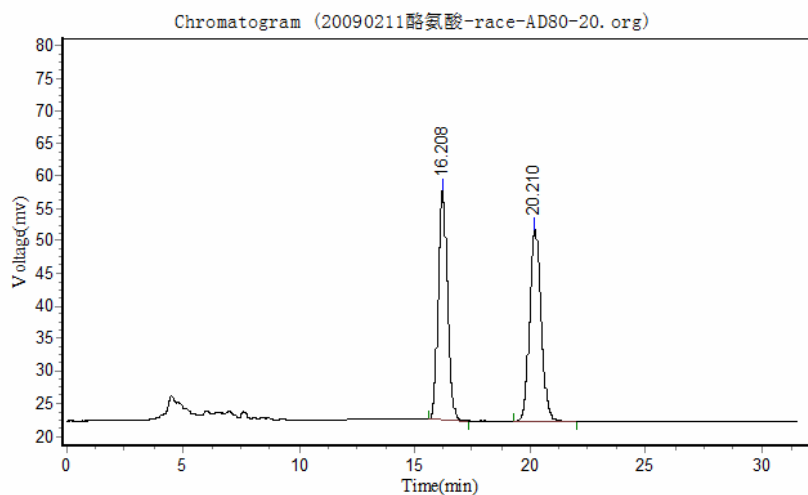
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.752	670.265	7796.100	0.3296
2		8.842	172482.172	2357718.750	99.6704
Total			173152.437	2365514.850	100.0000



5h, colorless oil, yield 88%, ee 97%;

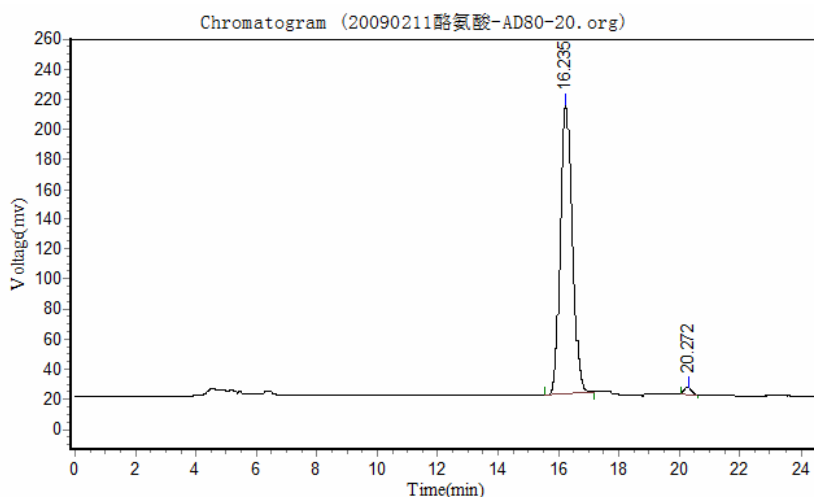
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 0.89-0.94 (m, 3H, CH_2CH_3), 1.04-1.16 (m, 1H, CH_2CH_3), 1.33-1.41 (m, 1H, CH_2CH_3), 1.88-1.99 (m, 1H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.75-2.86 (m, 1H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.21 (d, 2H, $J = 13.5$ Hz, PhCH_2), 3.84 (s, 3H, COOCH_3), 3.97 (d, 2H, $J = 13.5$ Hz, PhCH_2), 6.99 (b, 1H, NH), 7.06-7.08 (m, 4H, Ph-H), 7.43-7.52 (m, 5H, Ph-H), 7.62, (q, 1H, $J = 8.1$ Hz, Ph-H), 7.73 (q, 2H, $J = 8.1$ Hz, Ph-H), 8.17 (d, 2H, $J = 8.1$ Hz, Ph-H).

HPLC: Chiral AD-H column (250 mm); detected at 214 nm; hexane/*i*-propanol = 80/20; flow = 0.7 mL/min; Retention time: 16.2 min, 20.3 min (maj)



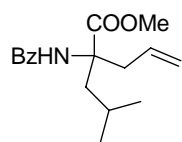
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.208	35159.871	984155.563	49.1780
2		20.210	29493.158	1017054.125	50.8220
Total			64653.029	2001209.688	100.0000



Results

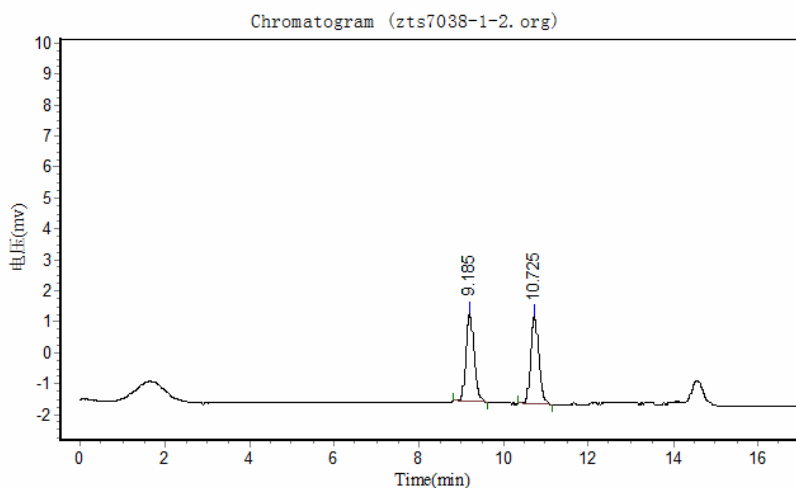
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.235	192599.984	5380005.000	98.4685
2		20.272	4177.874	83678.094	1.5315
Total			196777.858	5463683.094	100.0000



9a, colorless oil, yield 82%, ee 98%;

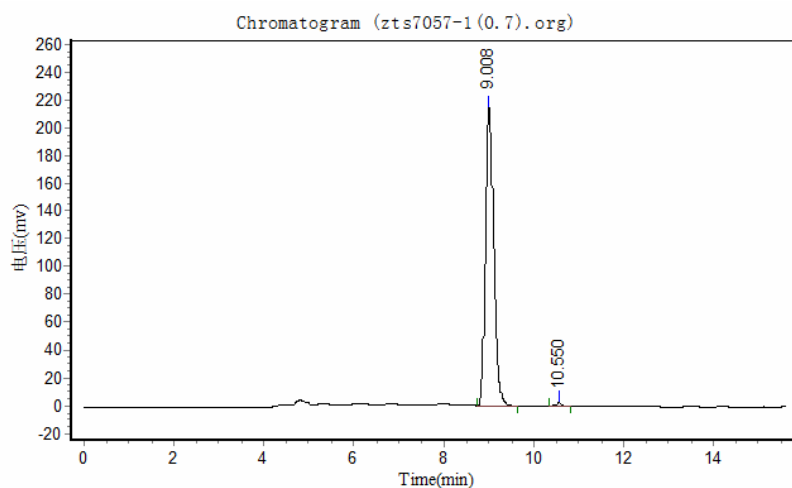
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 0.79 (d, 3H, $J = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.89 (d, 3H, $J = 7.2$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.56-1.65 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 1.73-1.80 (m, 1H, CH_2^iPr), 2.49 (dd, 1H, $J = 7.8$ Hz, 13.8 Hz, CH_2^iPr), 2.49 (dd, 1H, $J = 5.4$ Hz, 14.1 Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.44 (dd, 1H, $J = 7.2$ Hz, 13.8 Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.80 (s, 3H, COOCH_3), 5.04 (dd, 2H, $J = 9.9$ Hz, 18.6 Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.51-5.65 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.28 (br, 1H, BzNH), 7.41-7.50 (m, 3H, Ph-H), 7.78 (d, 2H, $J = 8.4$ Hz, Ph-H)

HPLC: Chiral AD-H column (250 mm); detected at 214 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 9.0 min (maj), 10.5 min



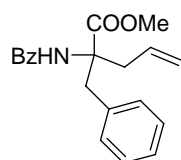
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.185	11187.462	39759.023	51.1179
2		10.725	2816.981	38020.004	48.8821
Total			14004.443	77779.027	100.0000



Results

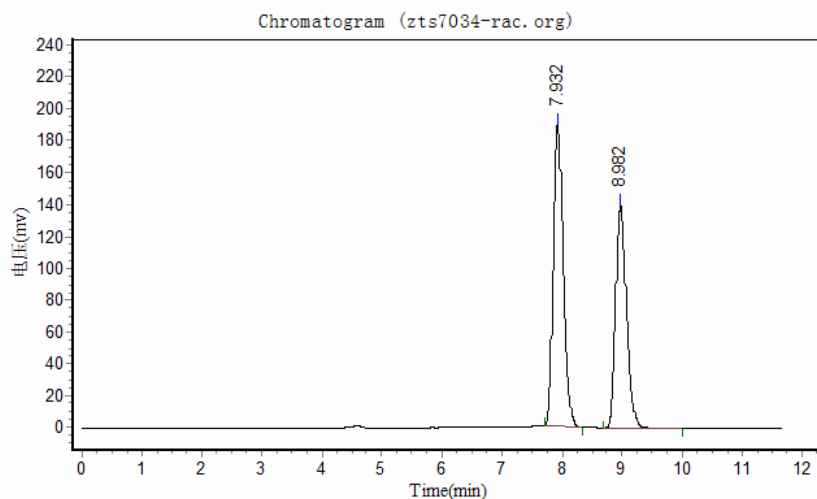
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.008	214384.766	2757203.750	99.0984
2		10.550	2008.821	25084.100	0.9016
Total			216393.586	2782287.850	100.0000



8b, white solid, yield 76%, ee 96%;

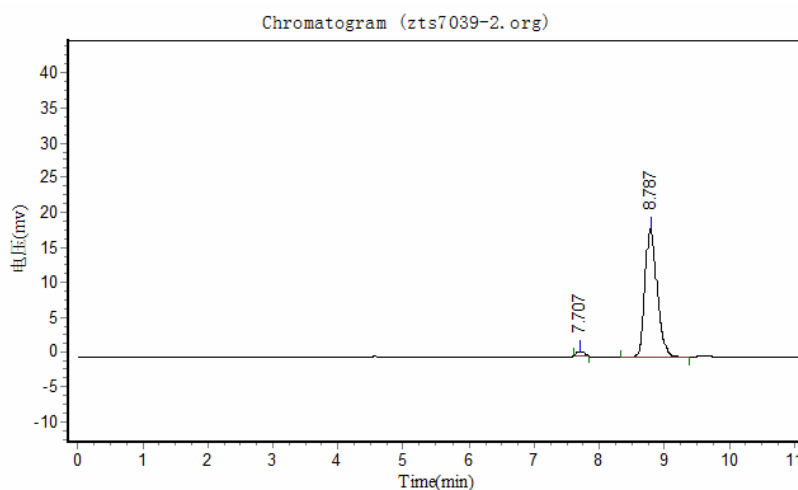
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 2.71 (dd, 1H, $J = 7.2$ Hz, 14.1 Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.21 (d, 1H, $J = 13.5$ Hz, CH_2Ph), 3.60 (dd, 1H, $J = 7.2$ Hz, 13.8 Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.82 (s, 3H, COOCH_3), 3.95 (d, 1H, $J = 13.5$ Hz, CH_2Ph), 5.09 (dd, 2H, $J = 10.5$ Hz, 17.4 Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.58-5.72 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 6.92 (br, 1H, BzNH), 7.04-7.06 (m, 2H, Ph-H), 7.18-7.20 (m, 3H, Ph-H), 7.38-7.51 (m, 3H, Ph-H), 7.68 (d, 2H, $J = 7.5$ Hz, Ph-H);

HPLC: Chiral AD-H column (250 mm); detected at 214 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 7.7 min, 8.8 min (maj)



Results

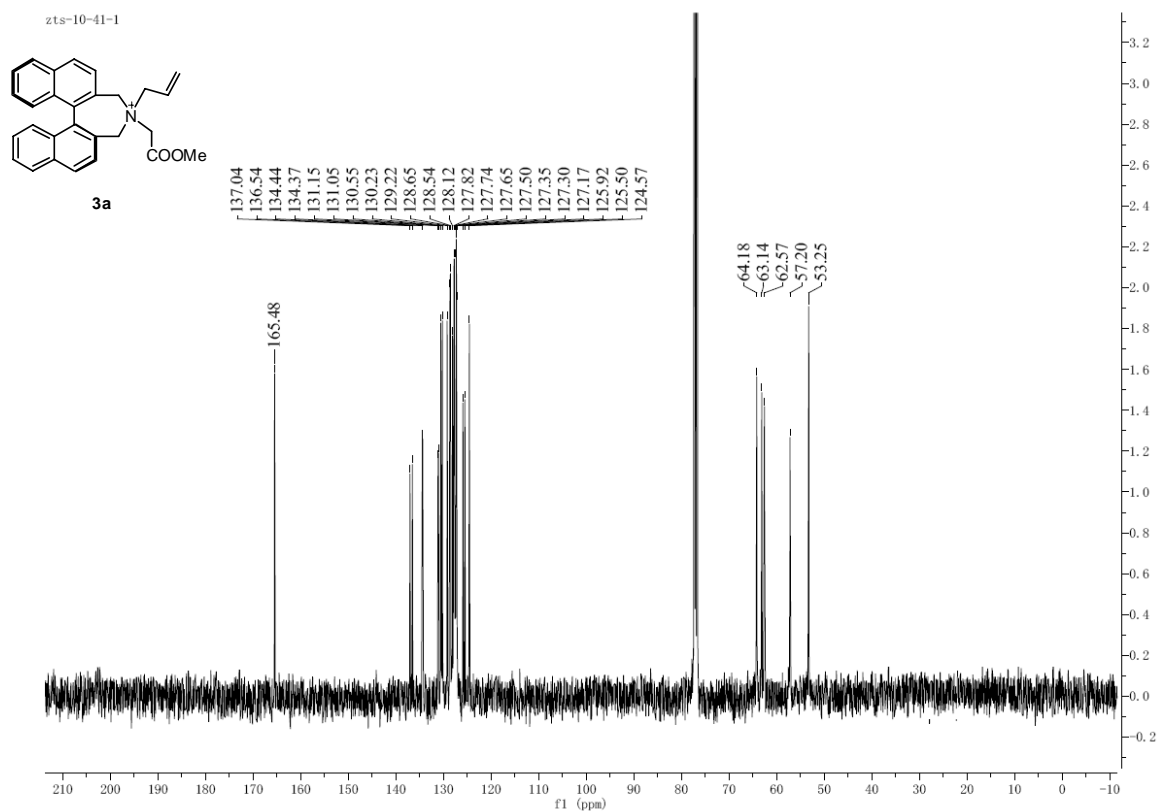
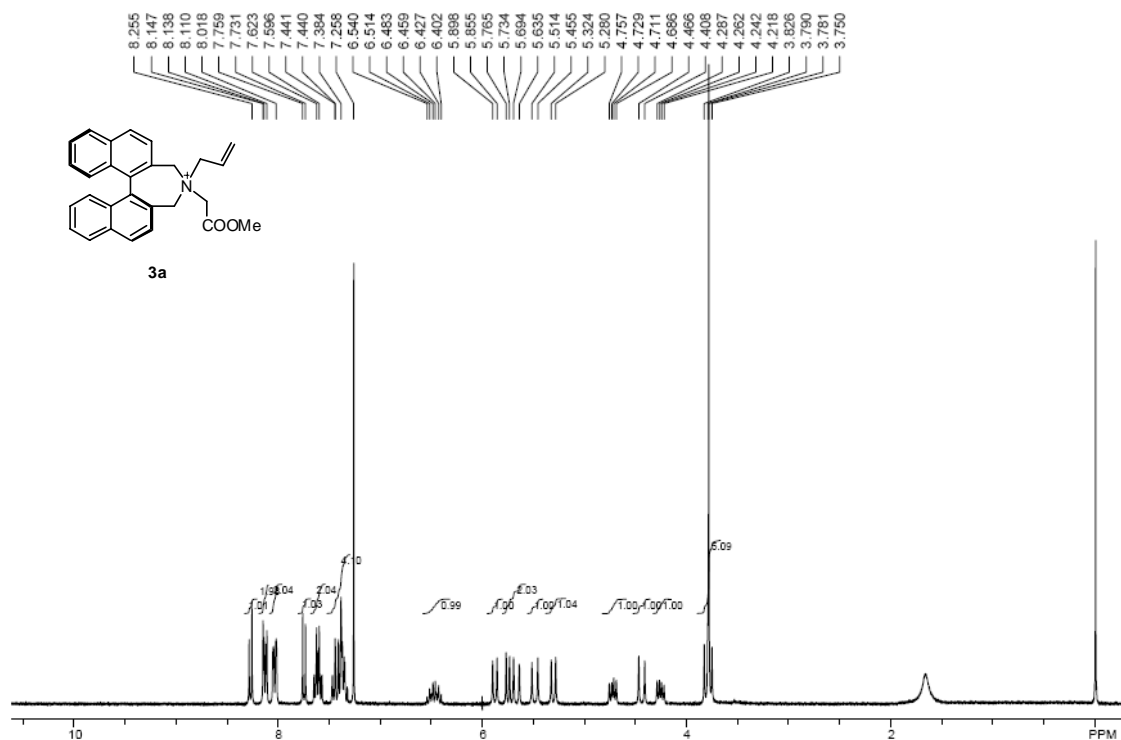
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.932	191094.906	2239411.250	55.8927
2		8.982	140245.250	1767217.375	44.1073
Total			331340.156	4006628.625	100.0000

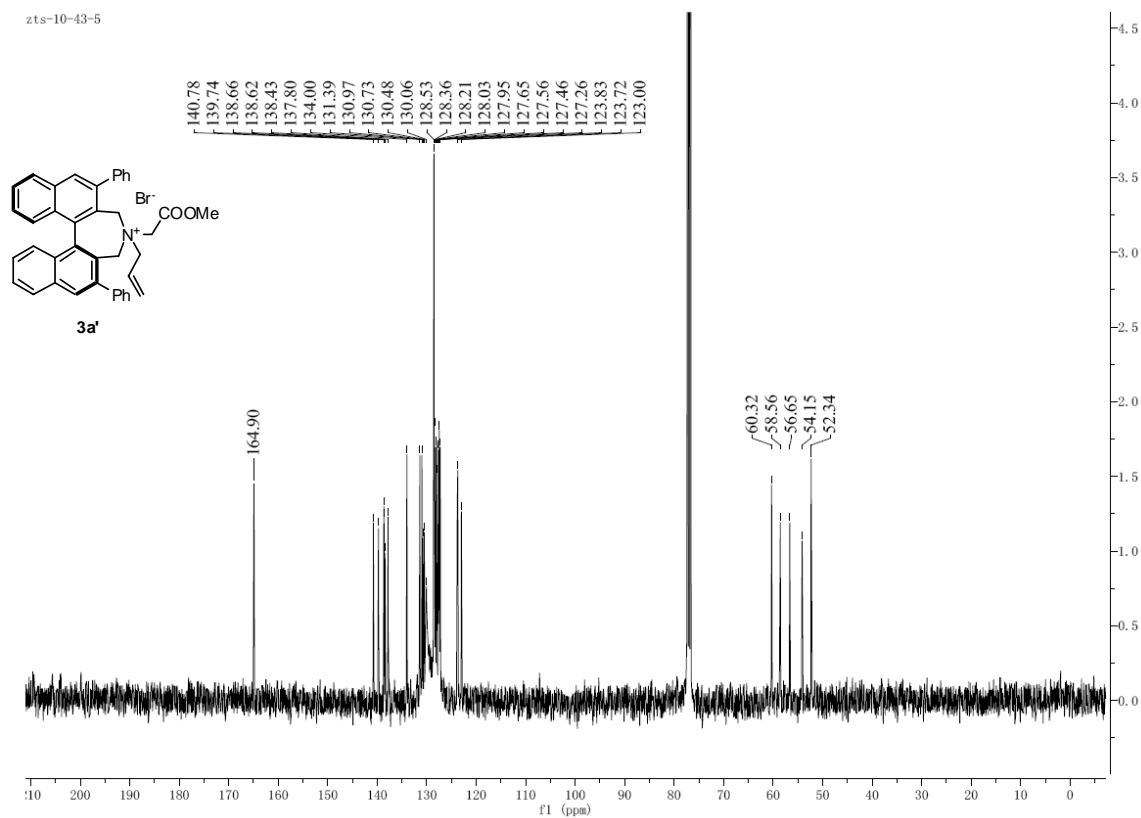
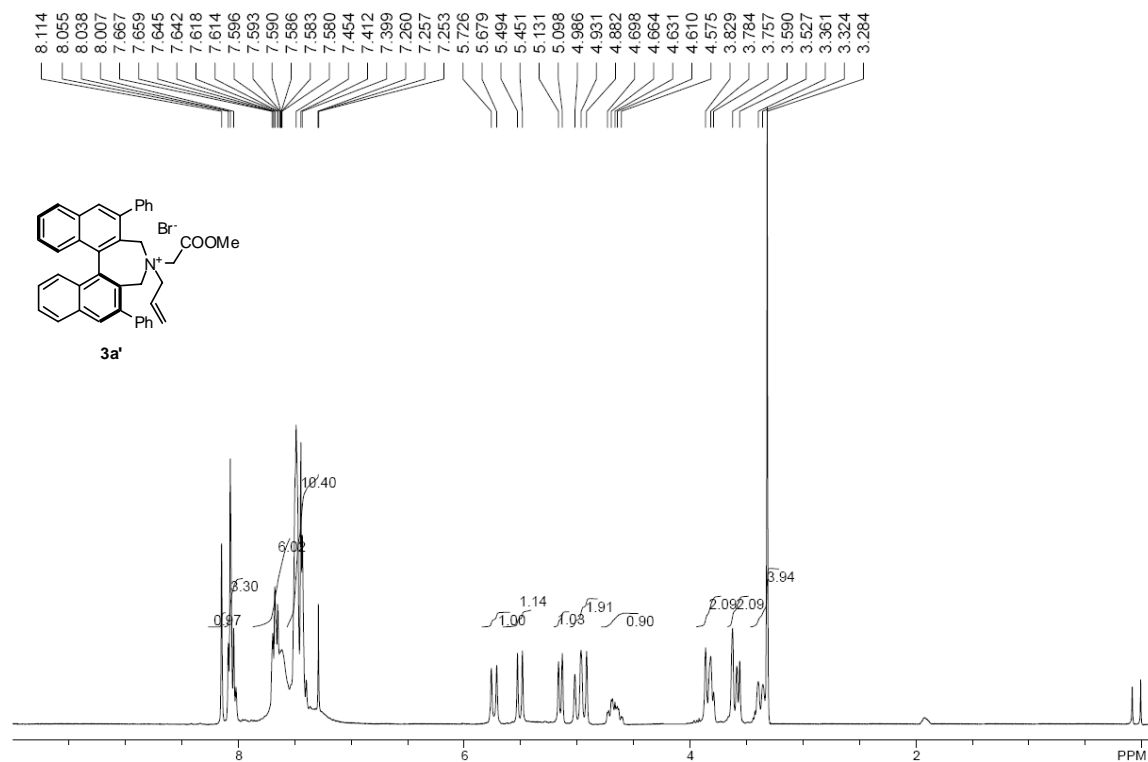


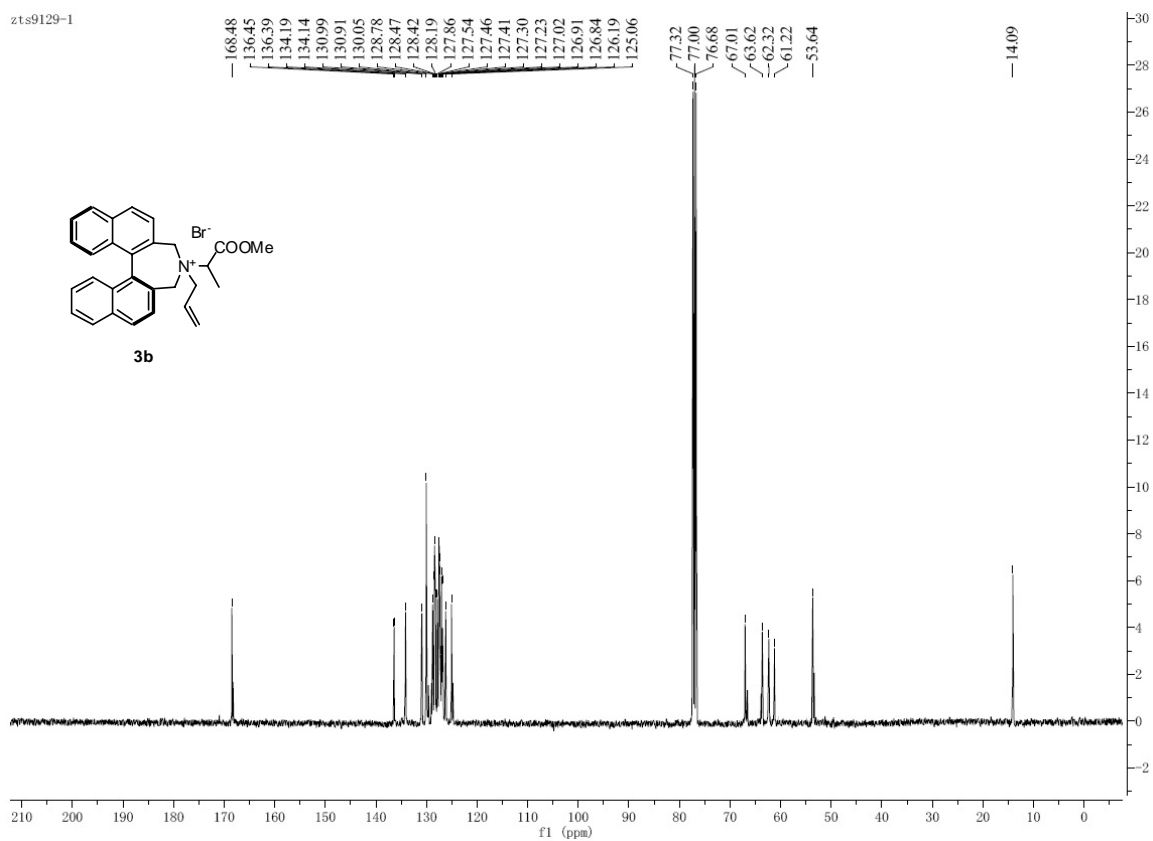
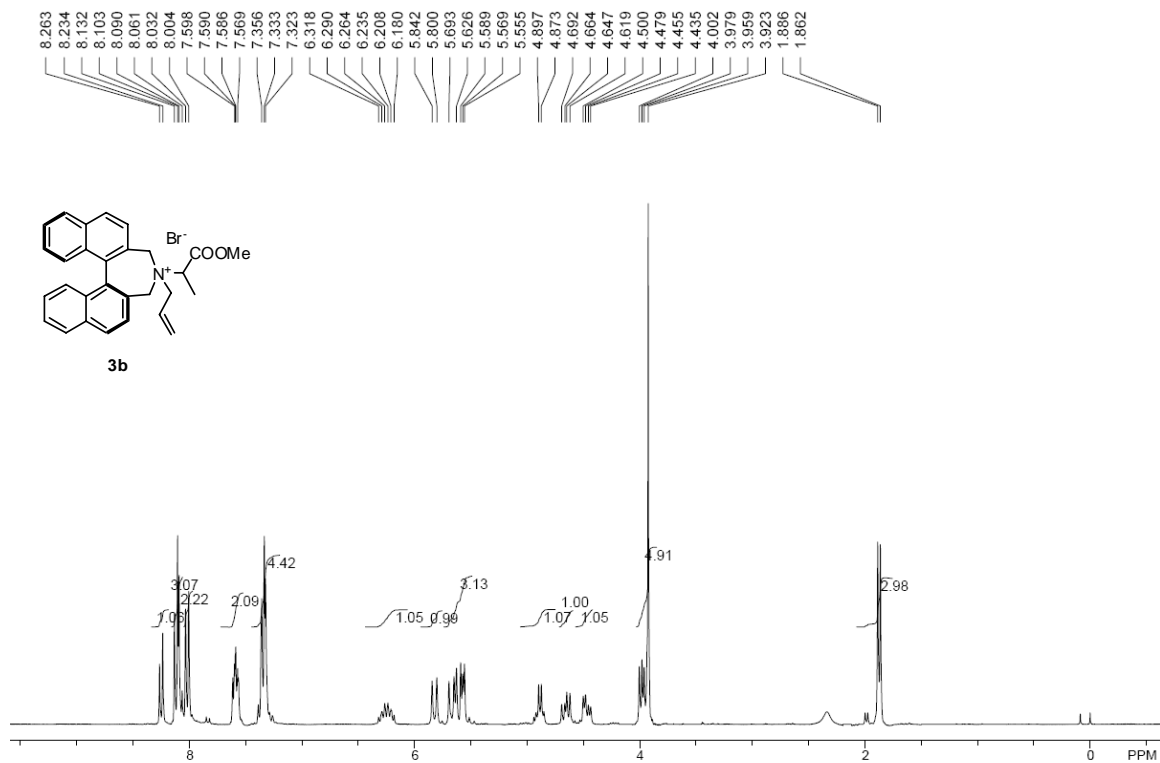
Results

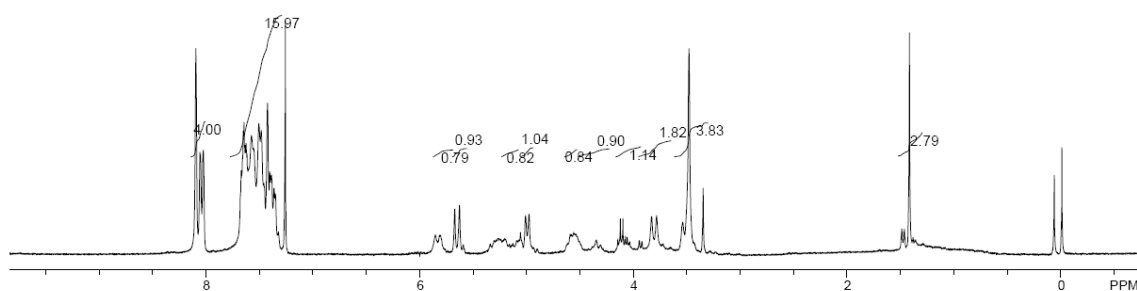
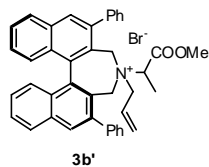
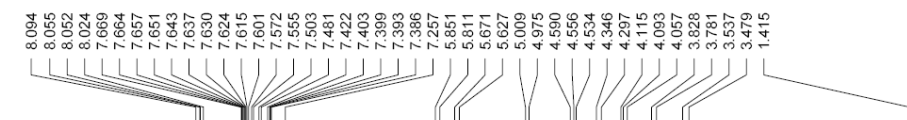
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.707	508.126	4399.950	1.7943
2		8.787	18304.143	240824.141	98.2057
Total			18812.268	245224.090	100.0000

9. Copies of ^1H NMR and ^{13}C NMR spectra

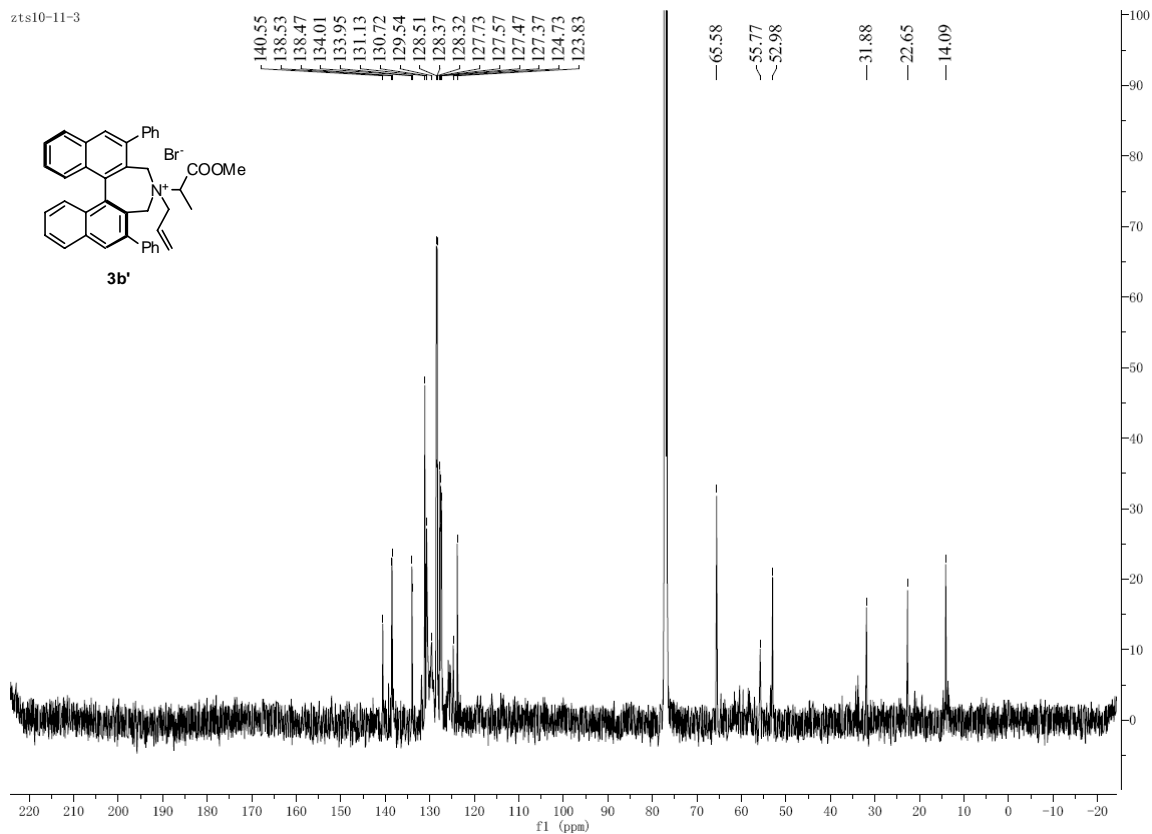


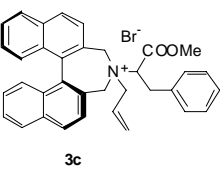
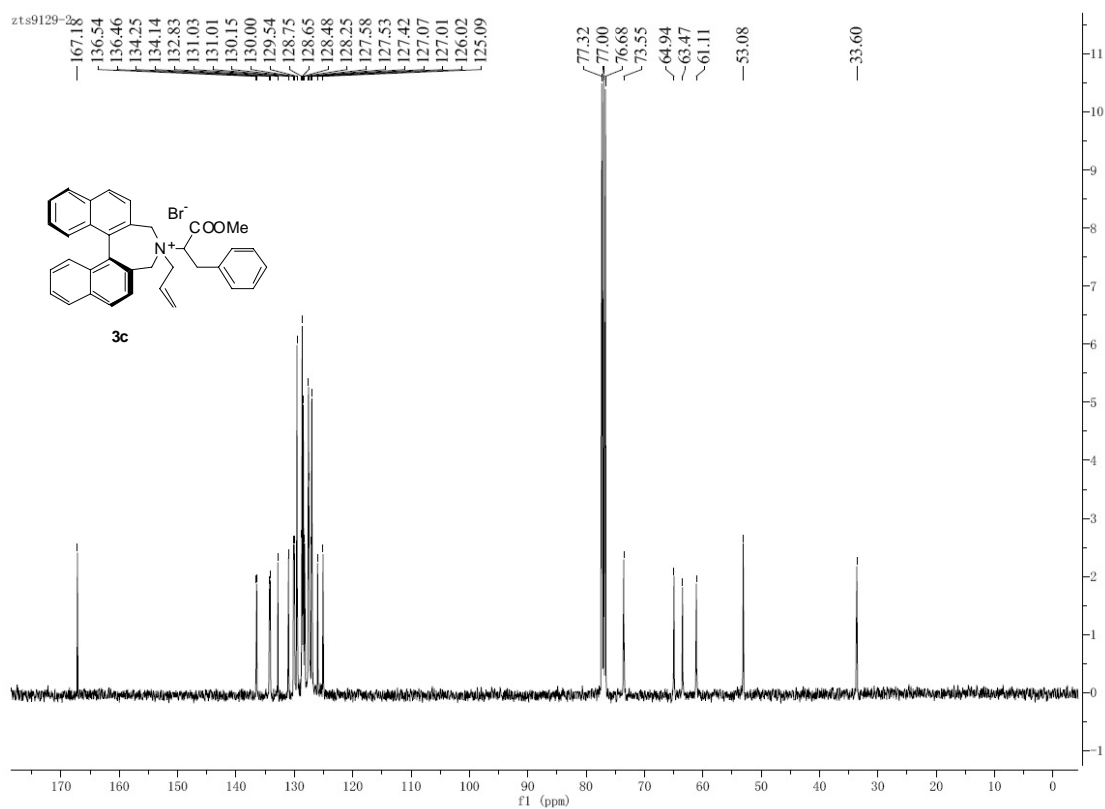
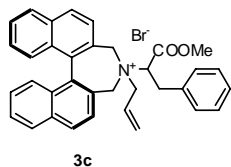
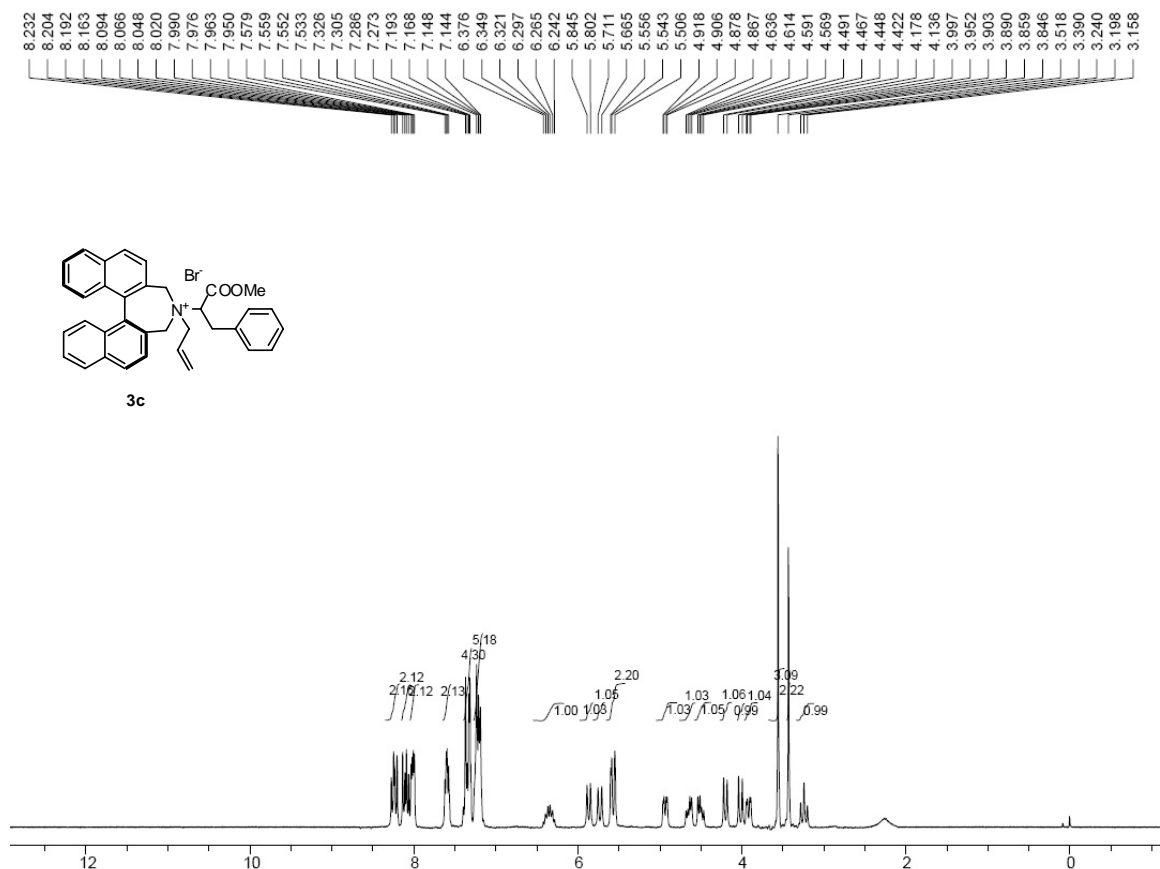


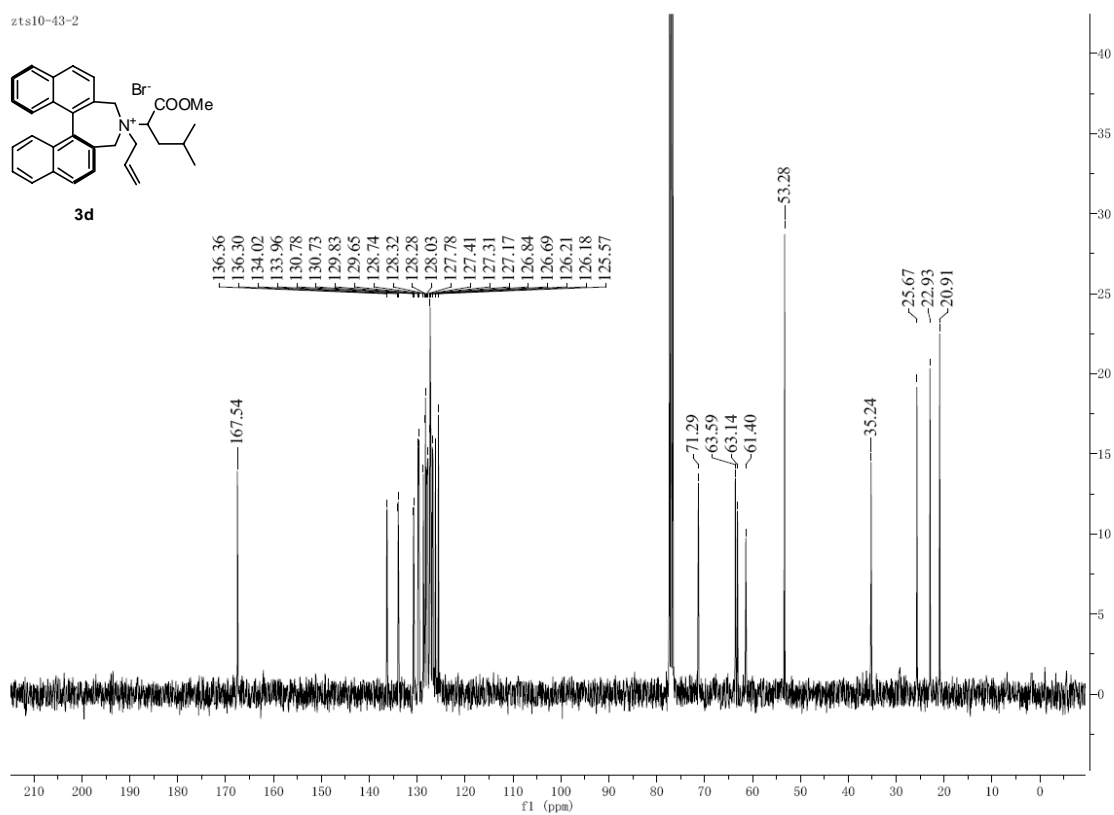
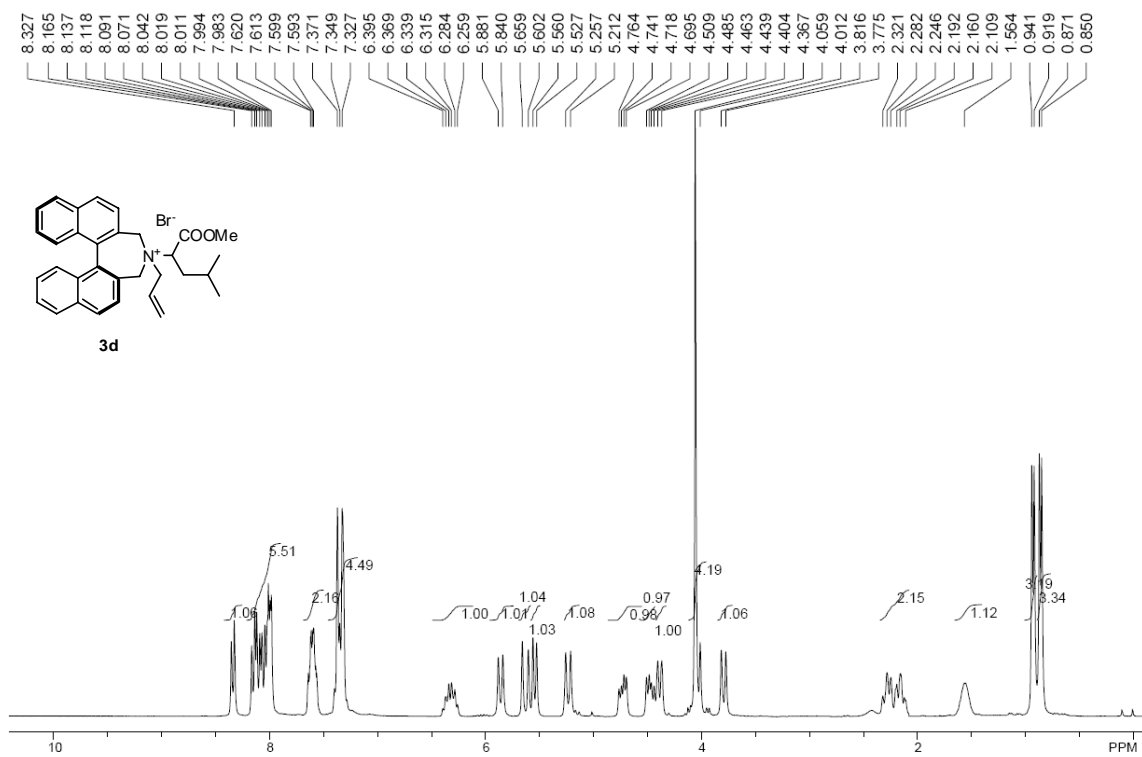


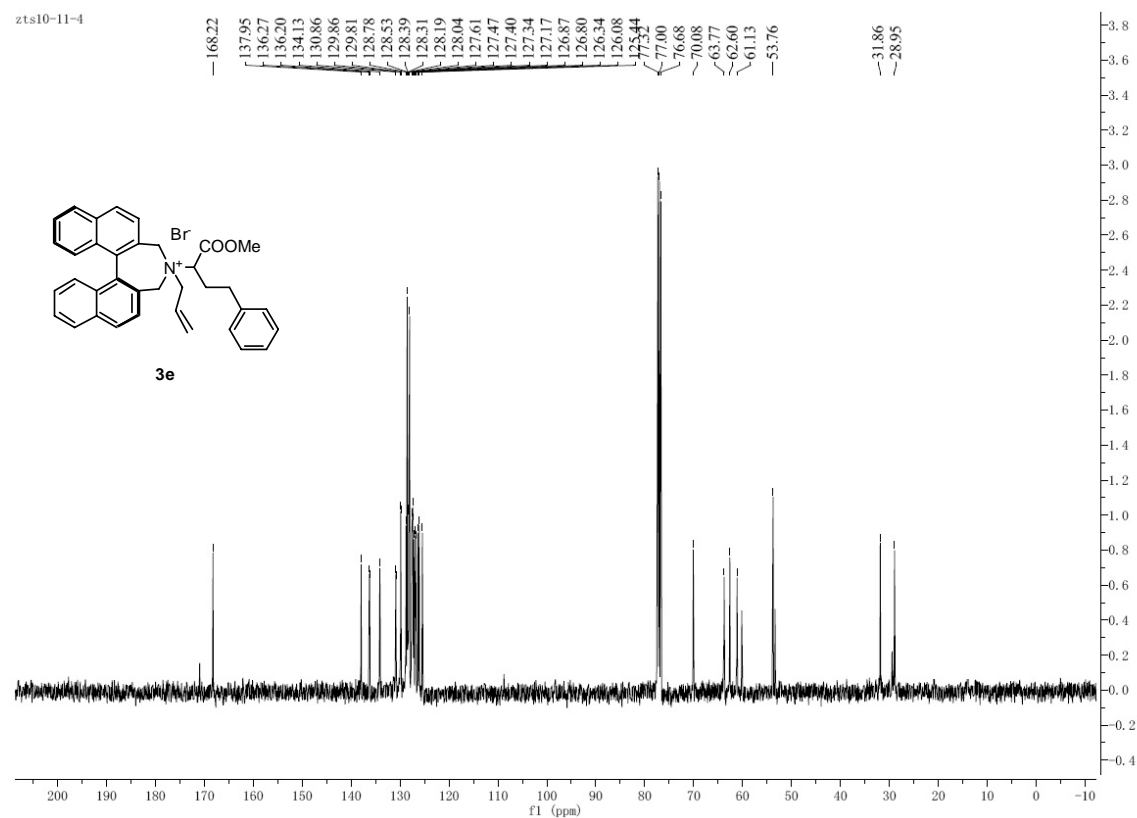
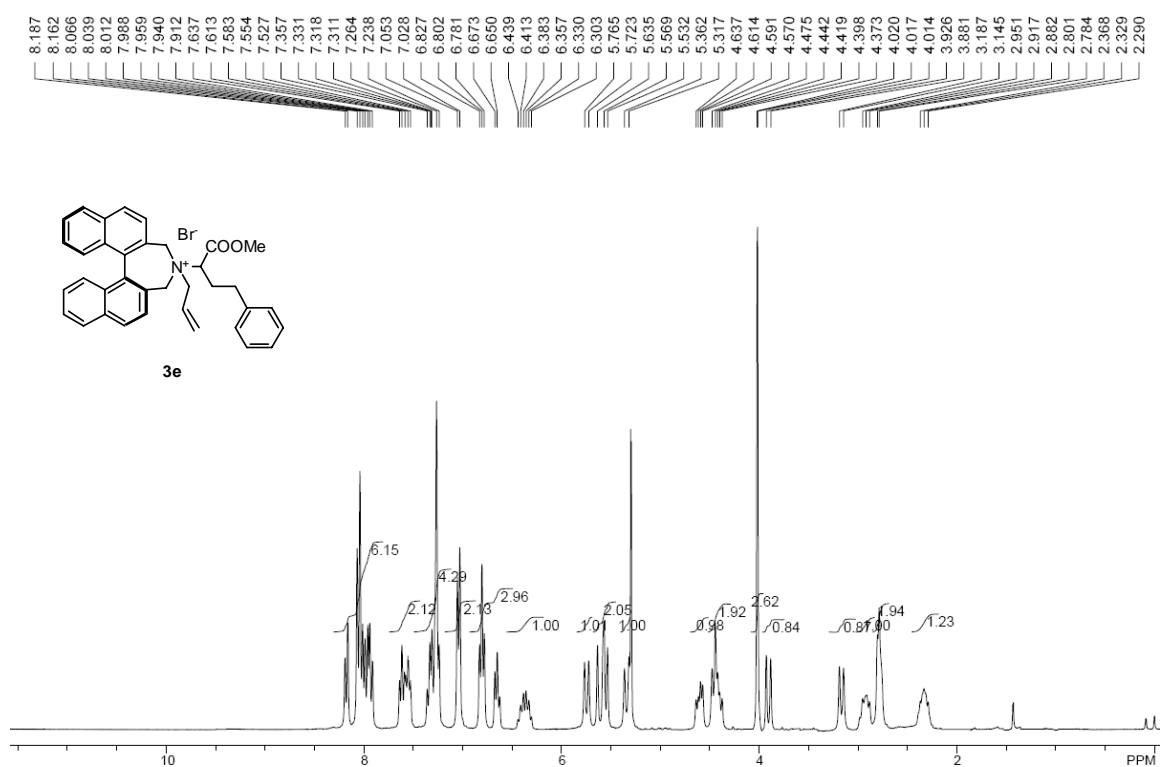


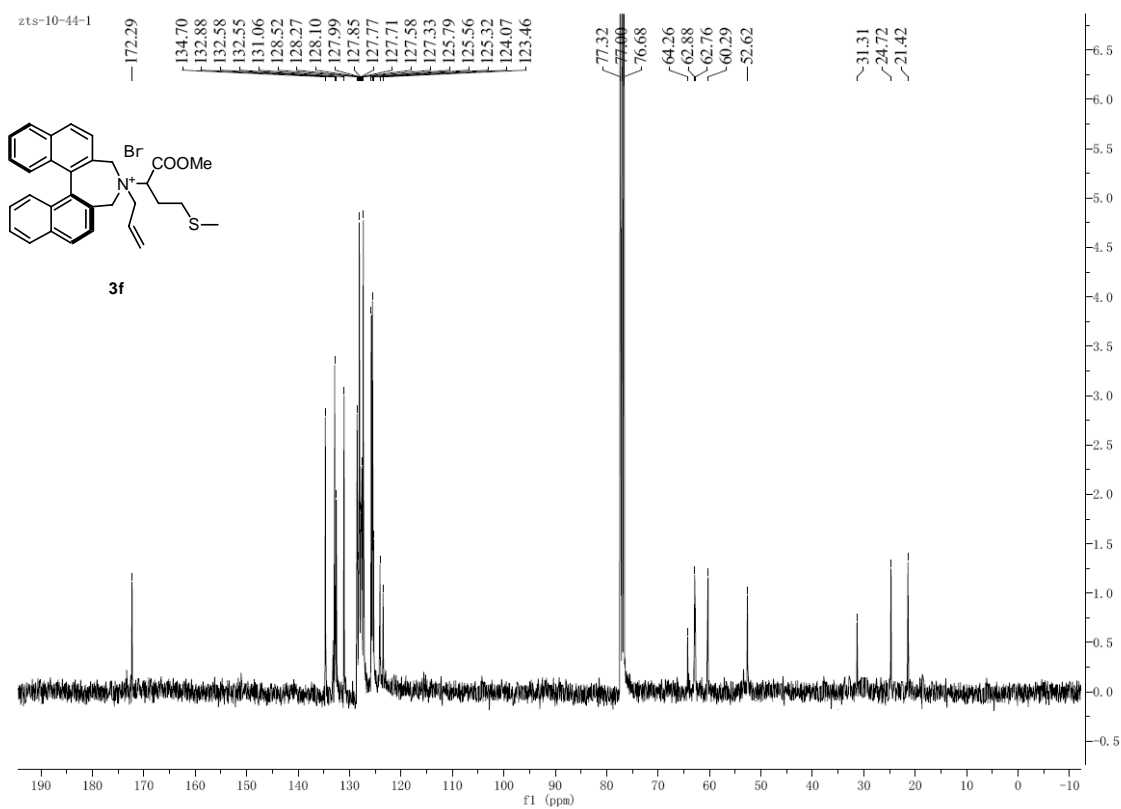
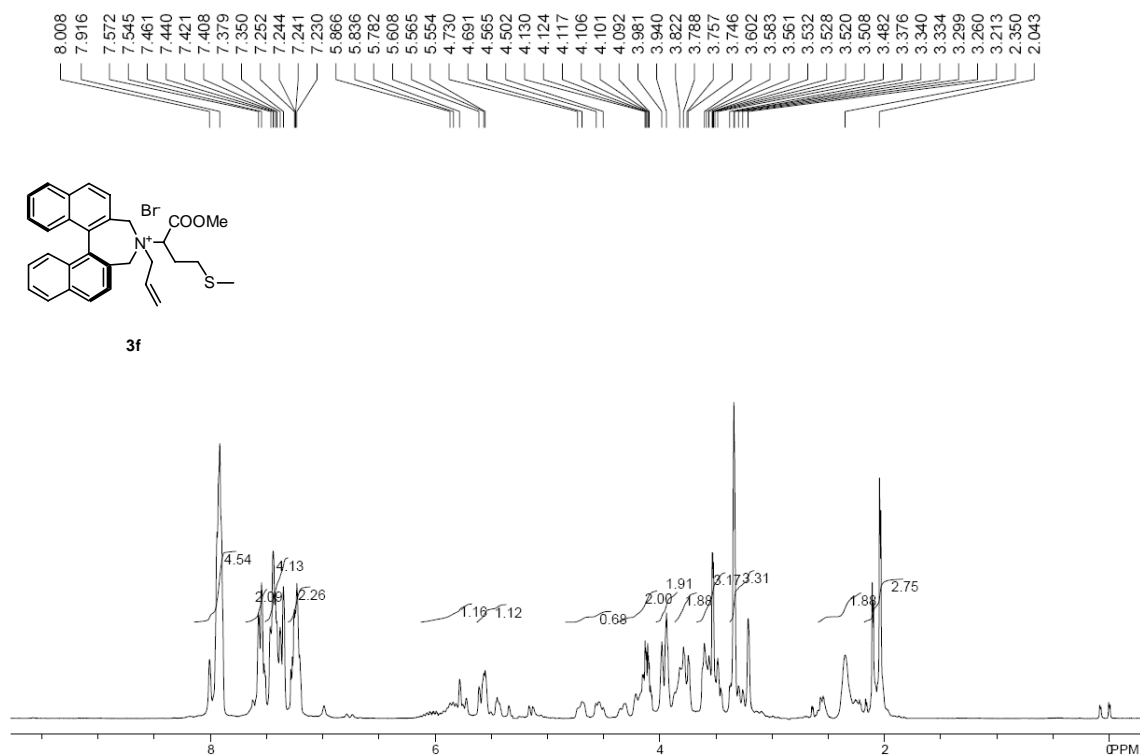
zts10-11-3

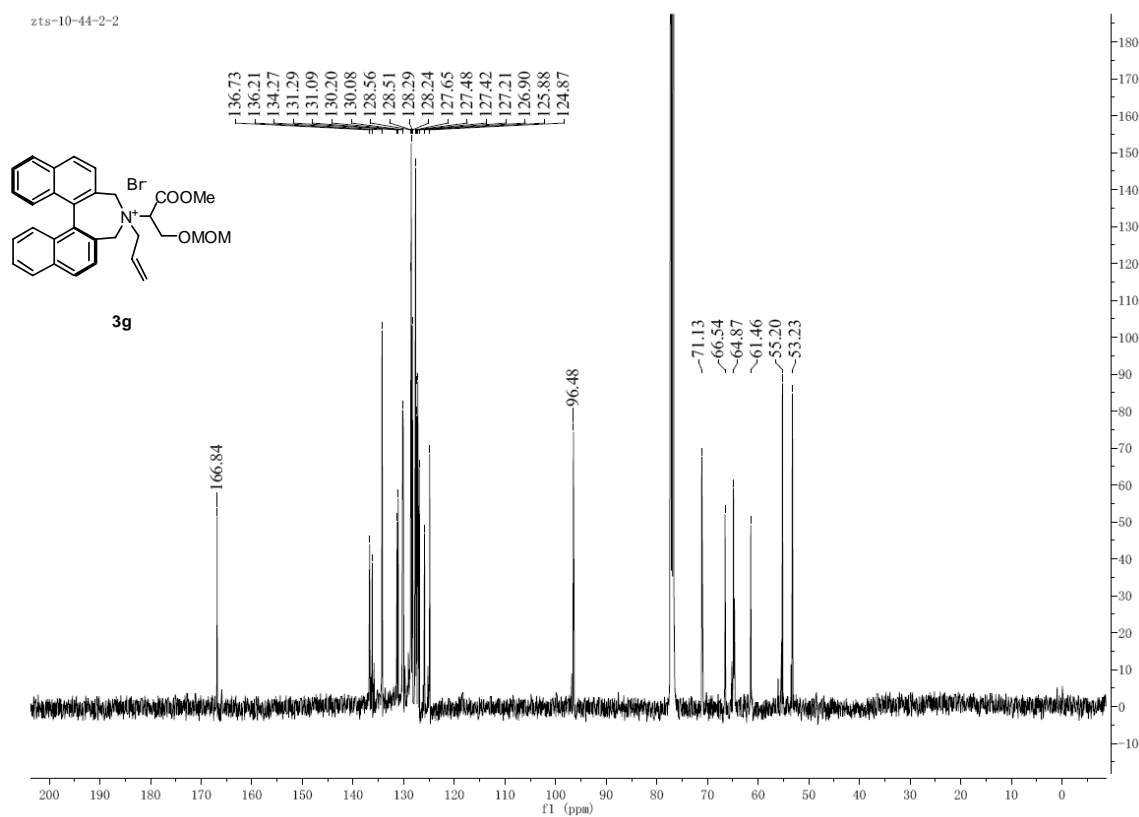
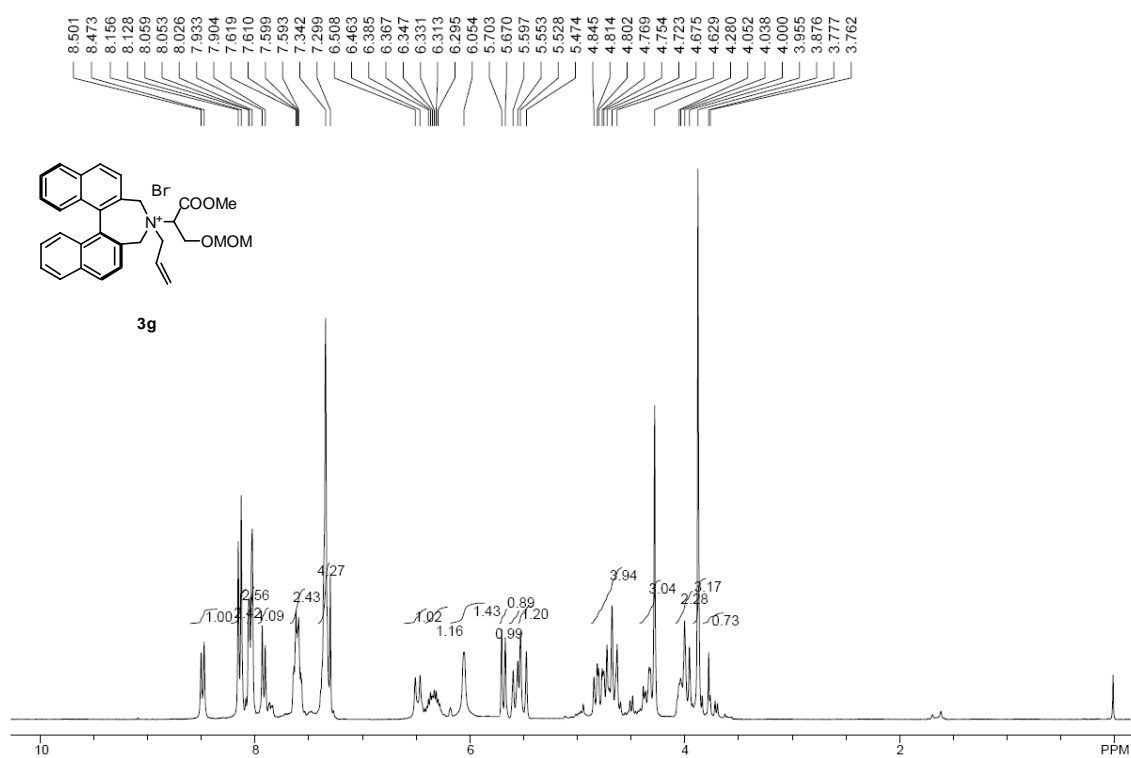


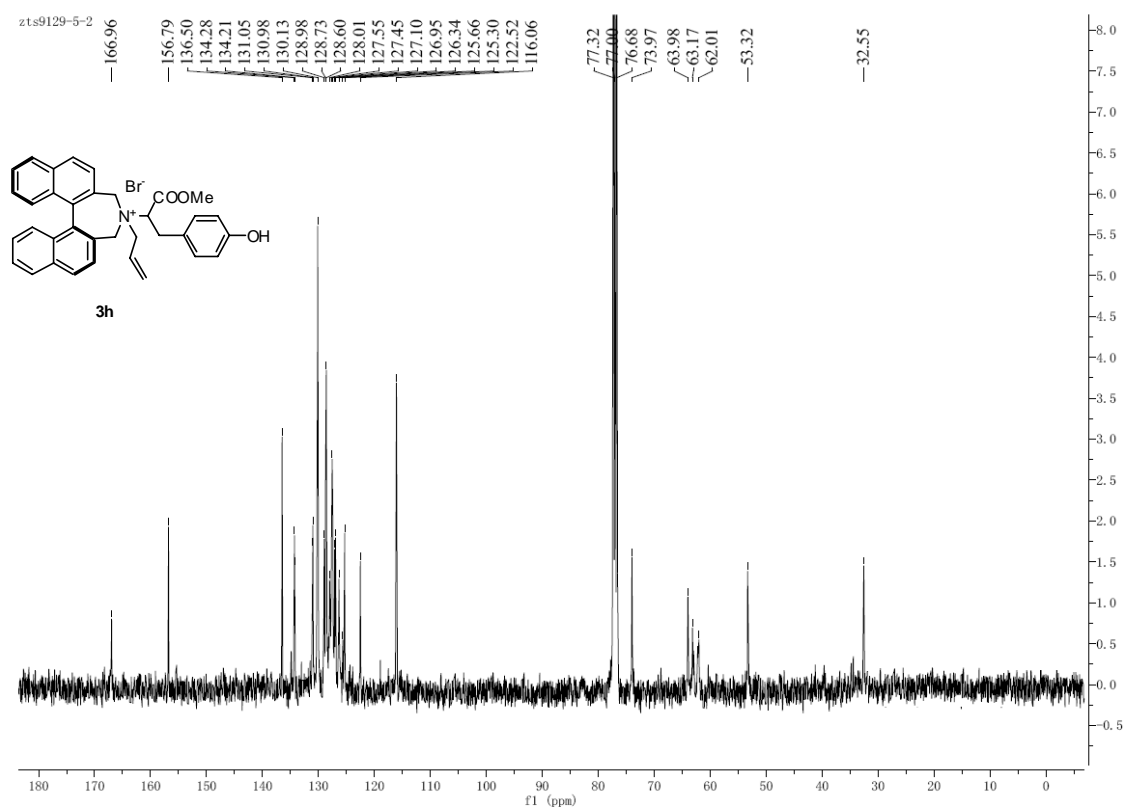
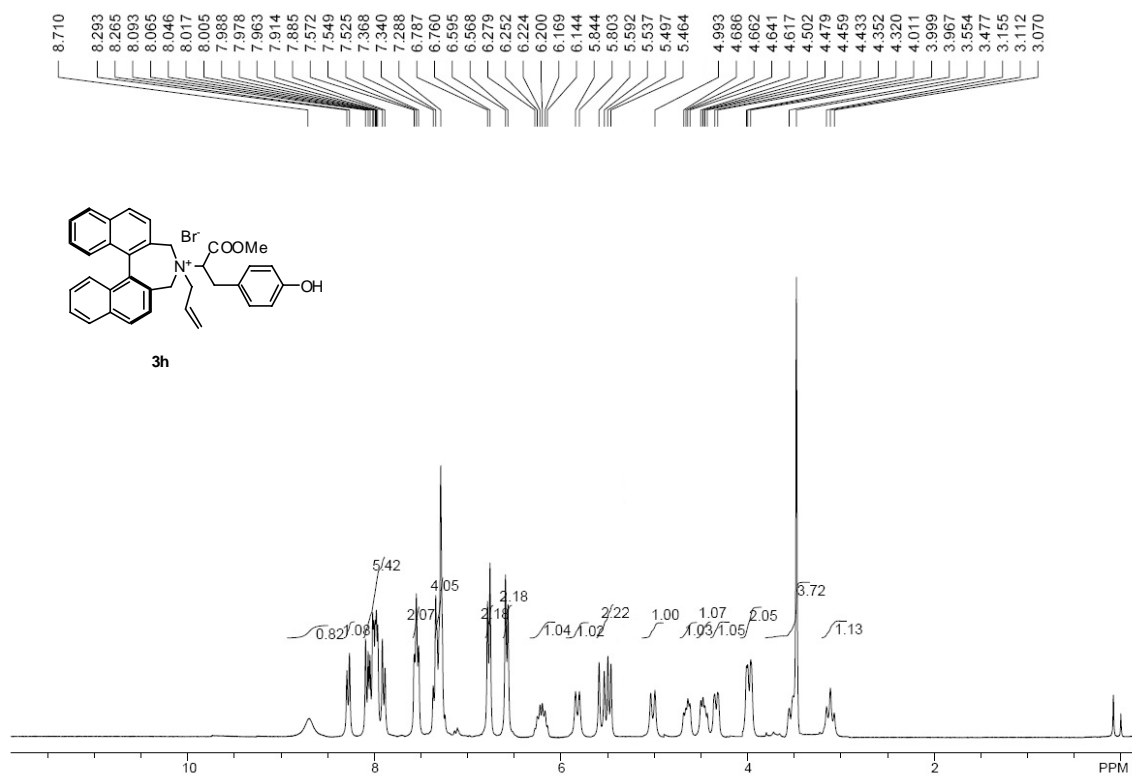


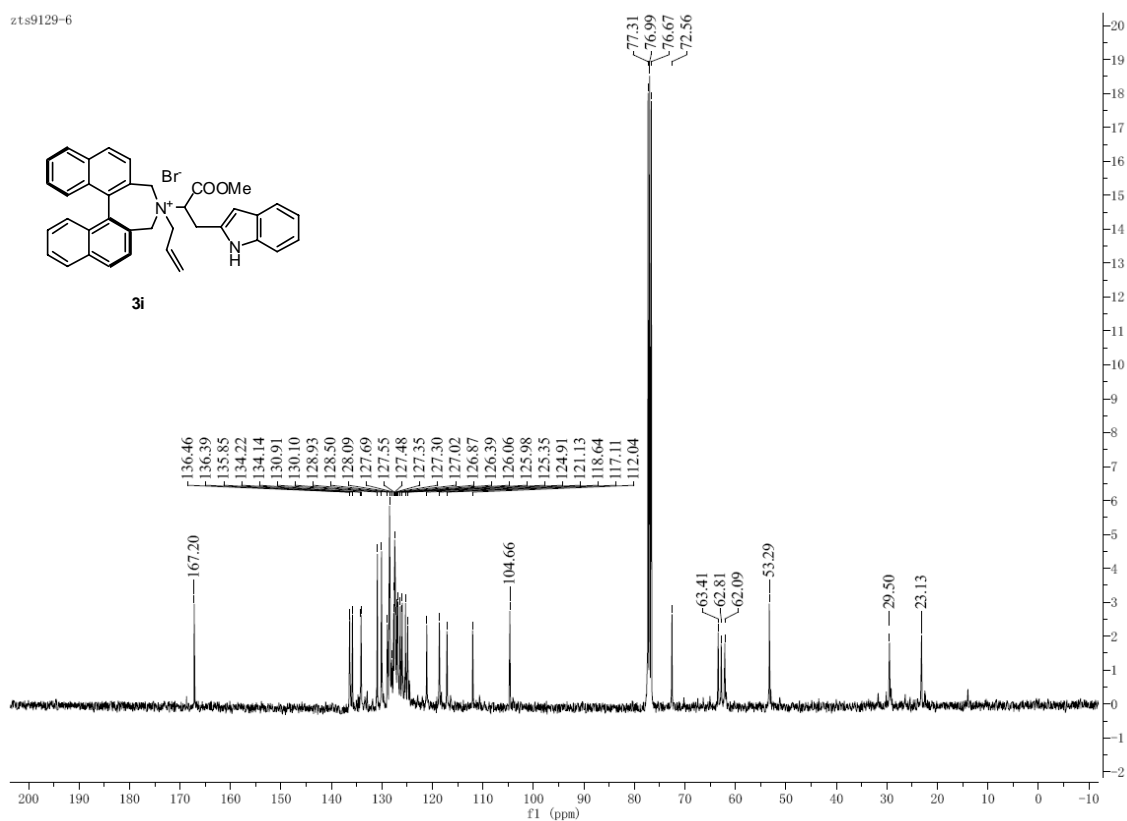
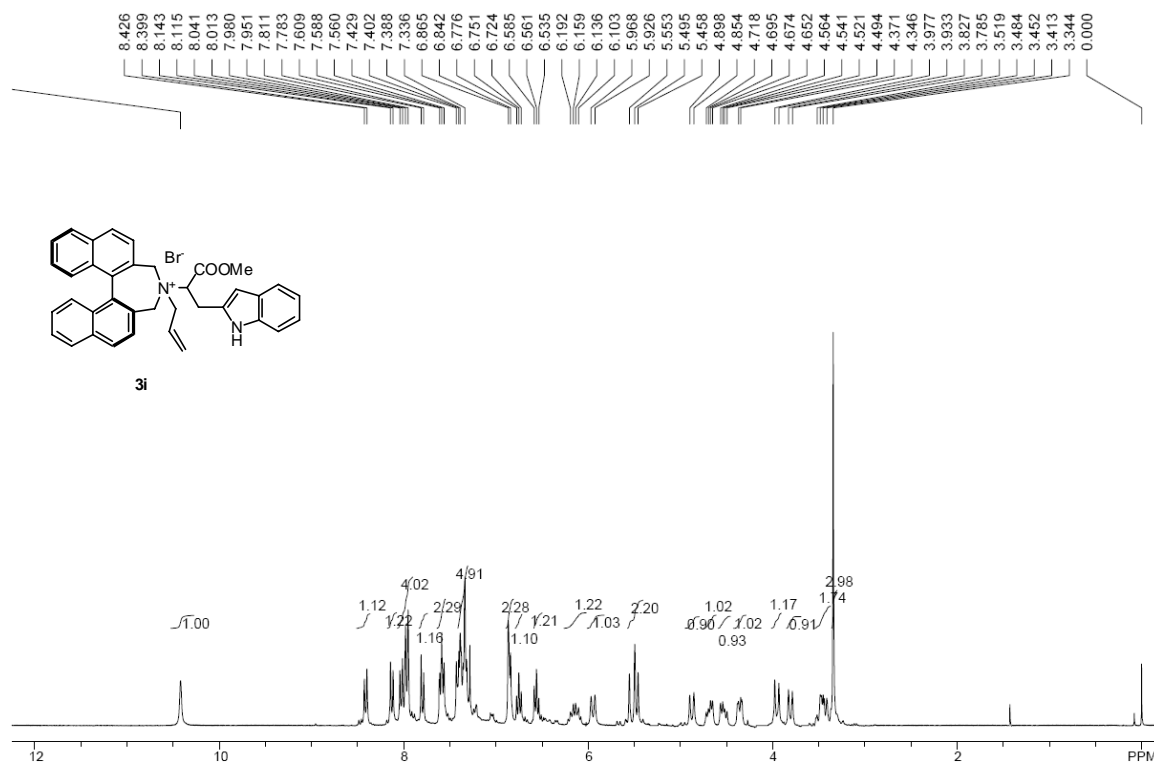


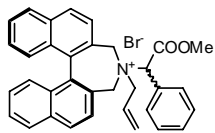
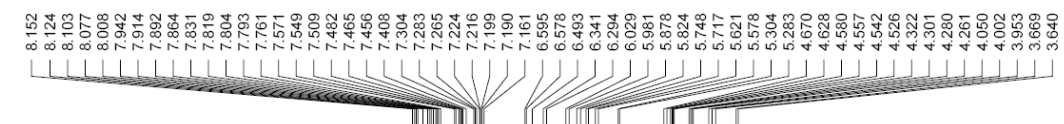




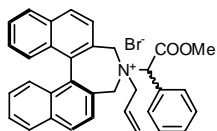
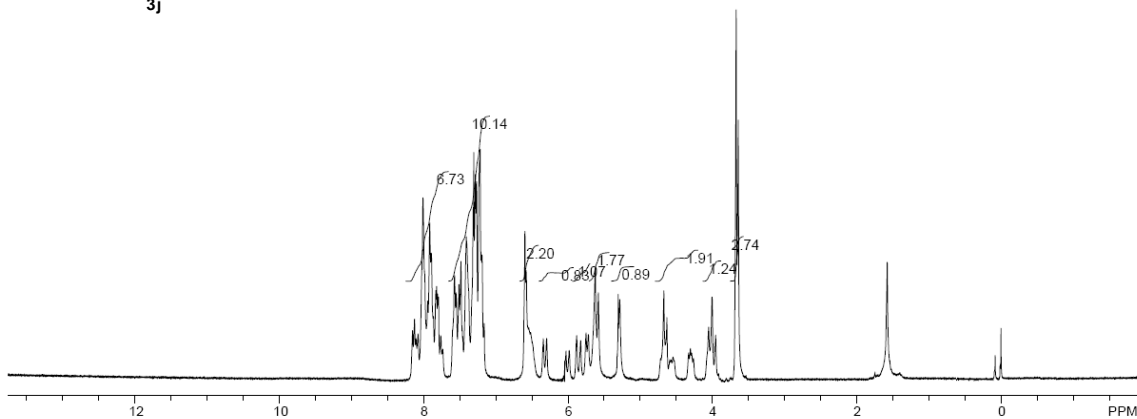




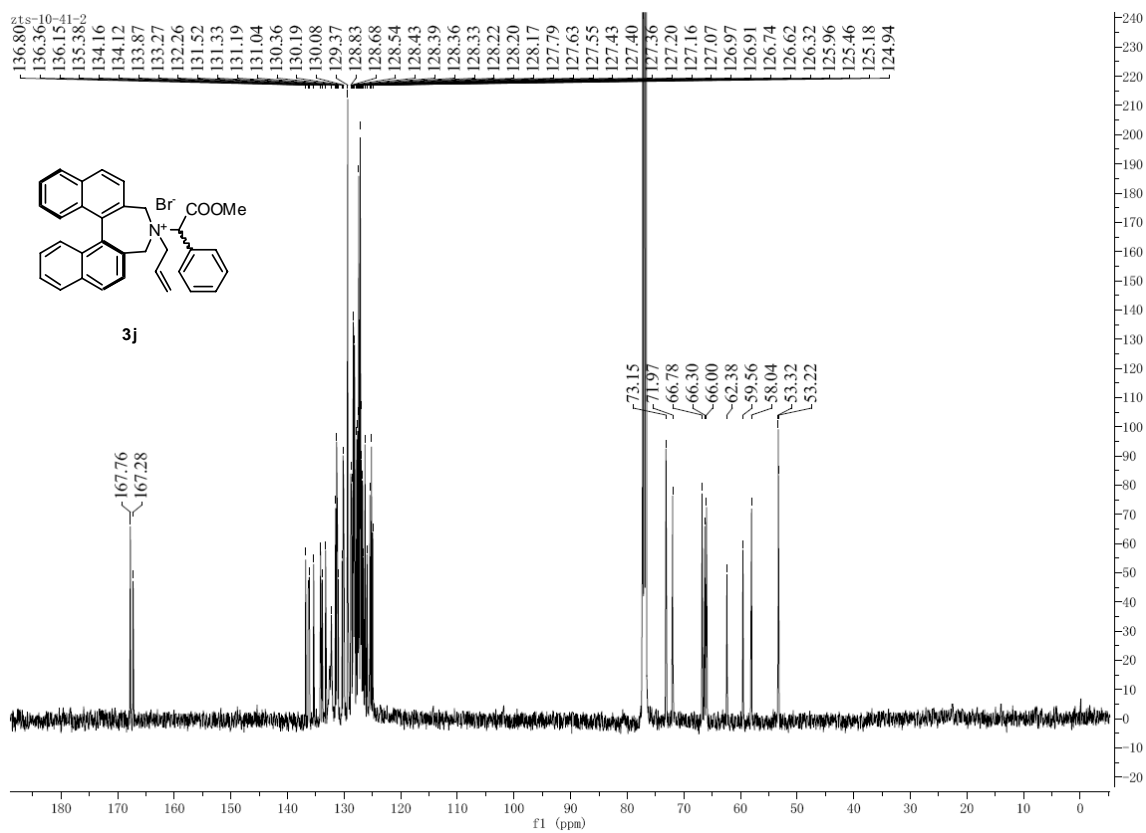


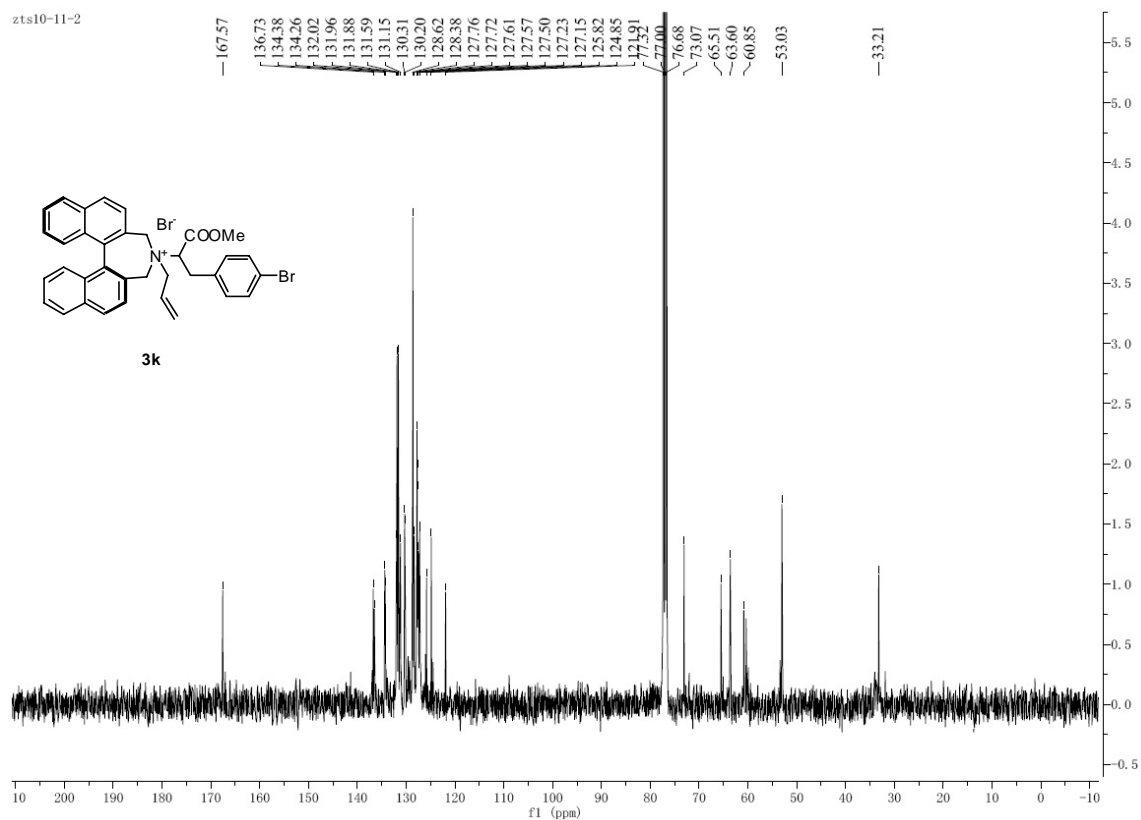
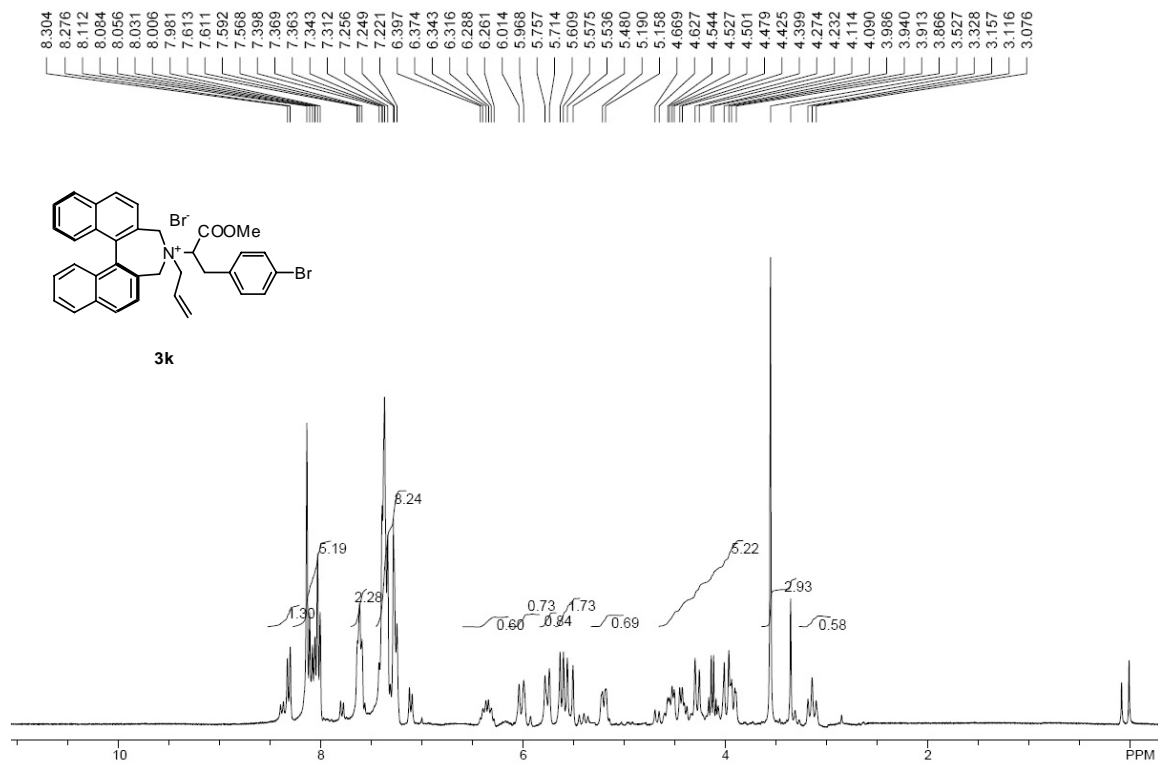


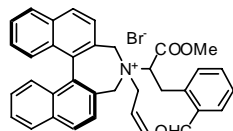
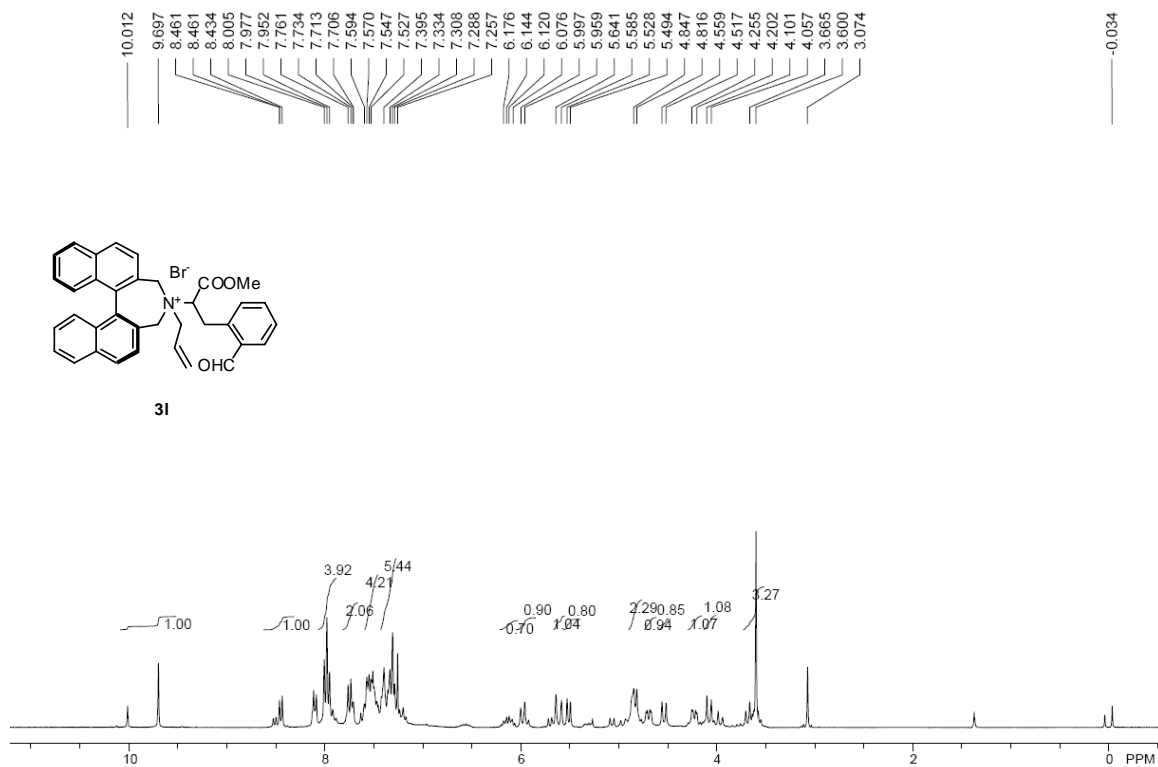
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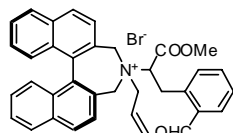
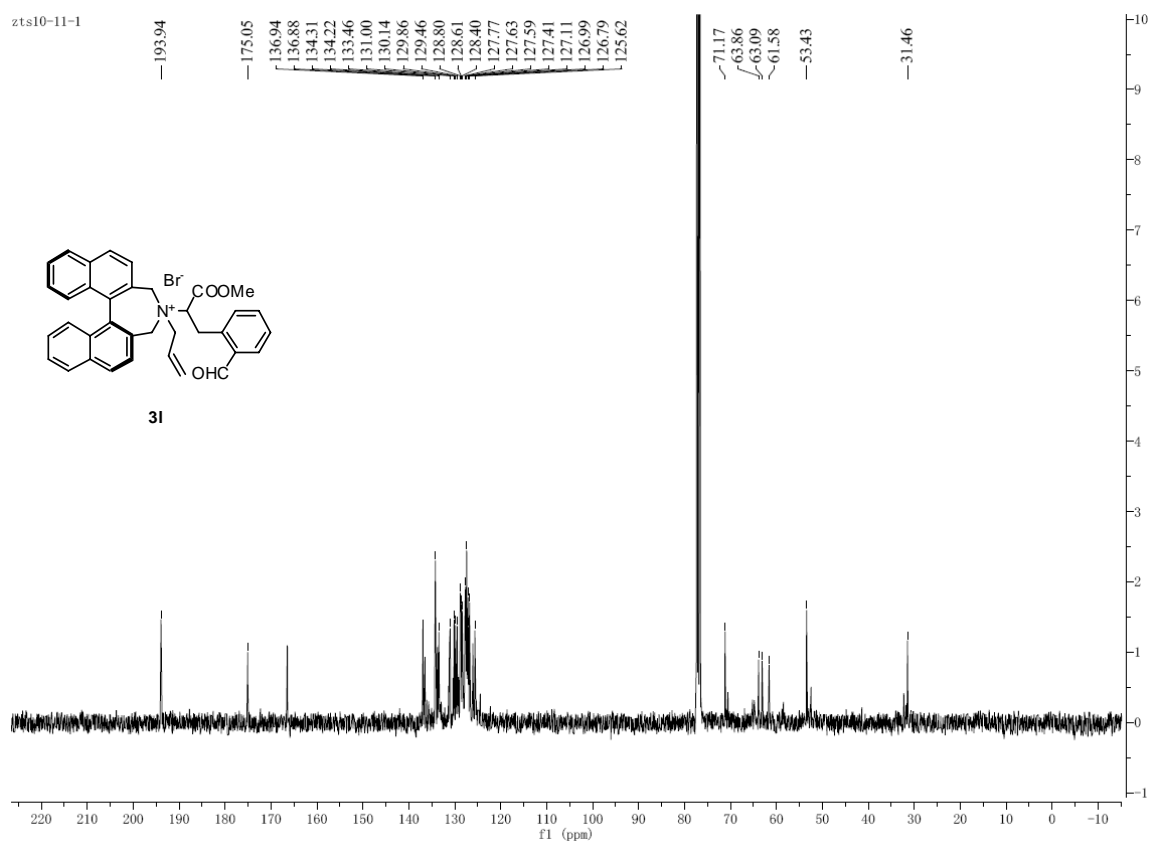
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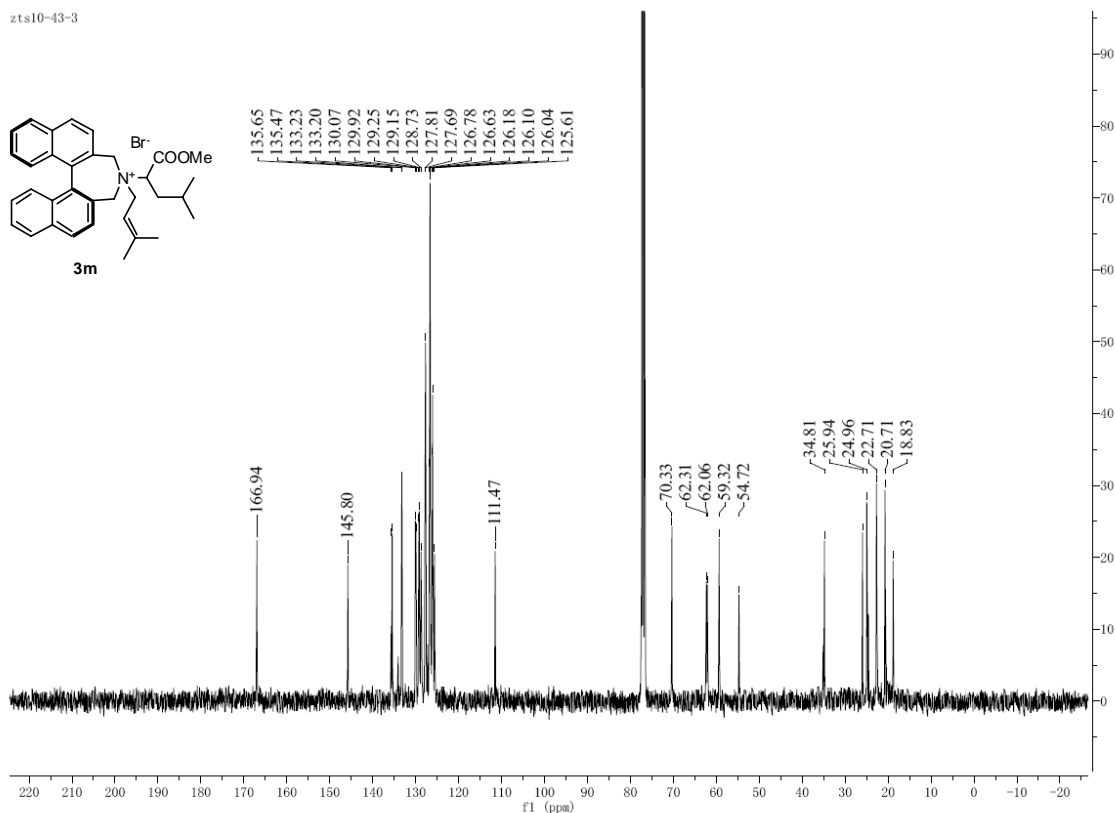
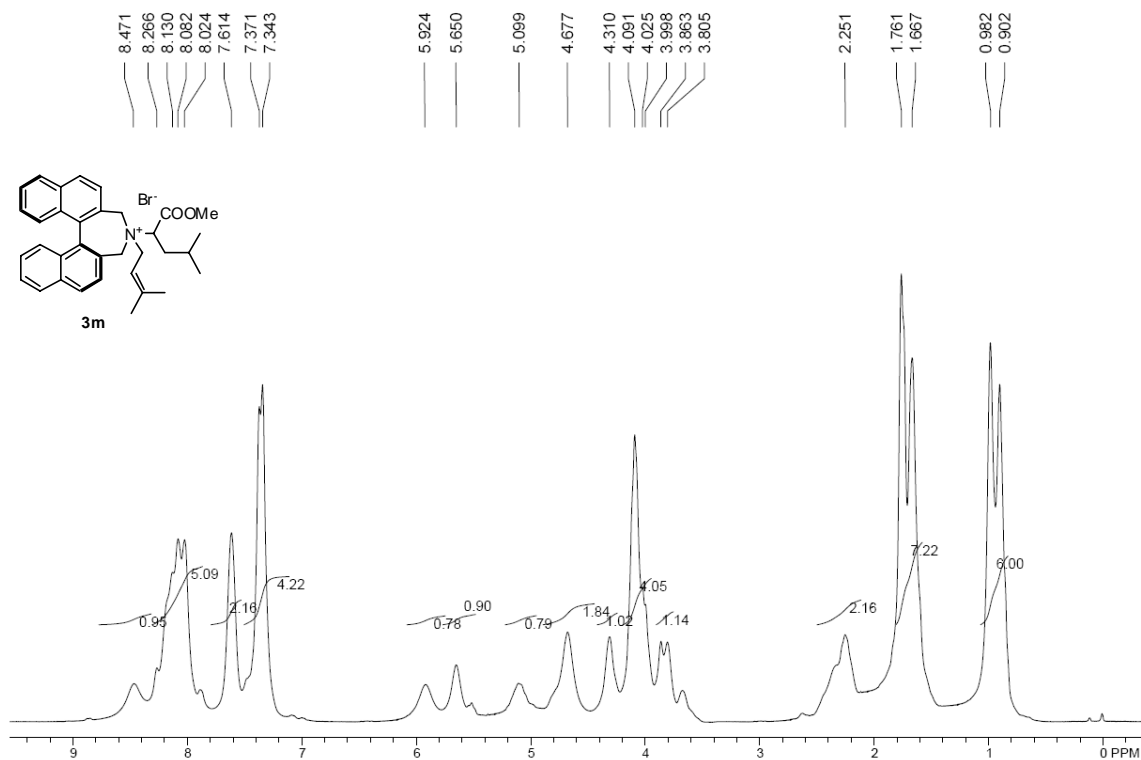


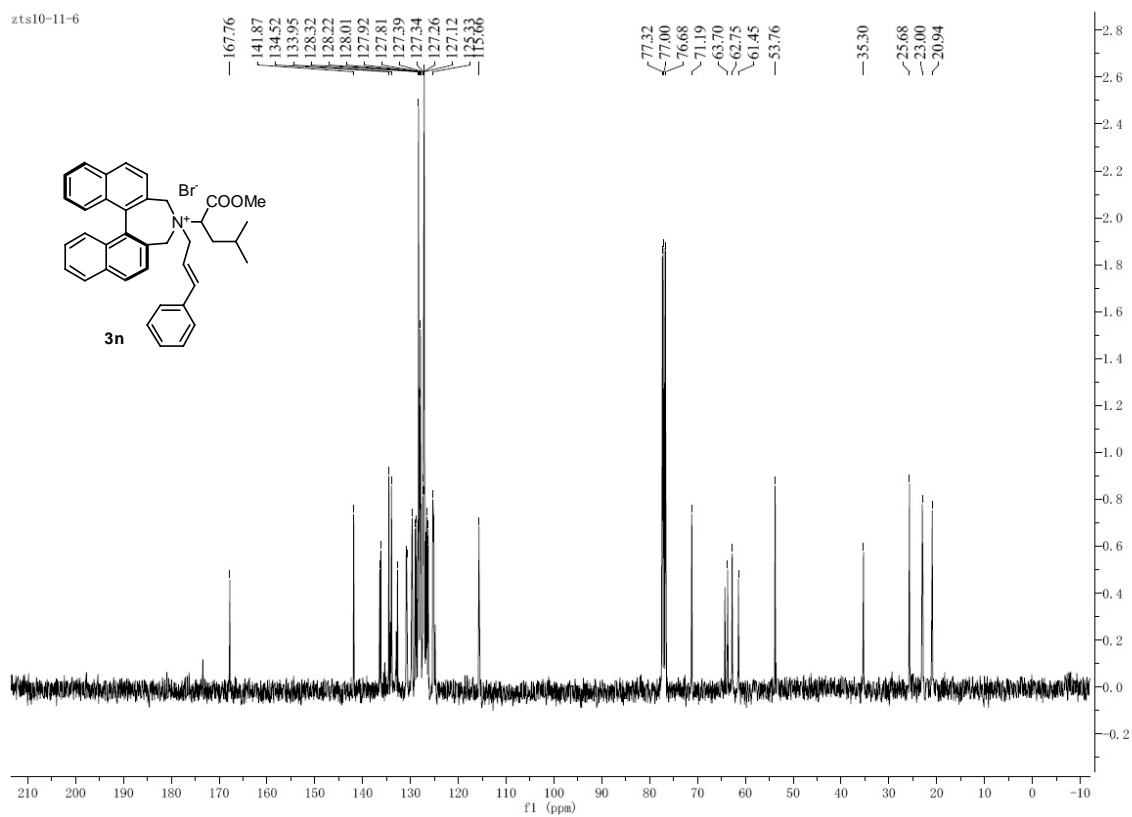
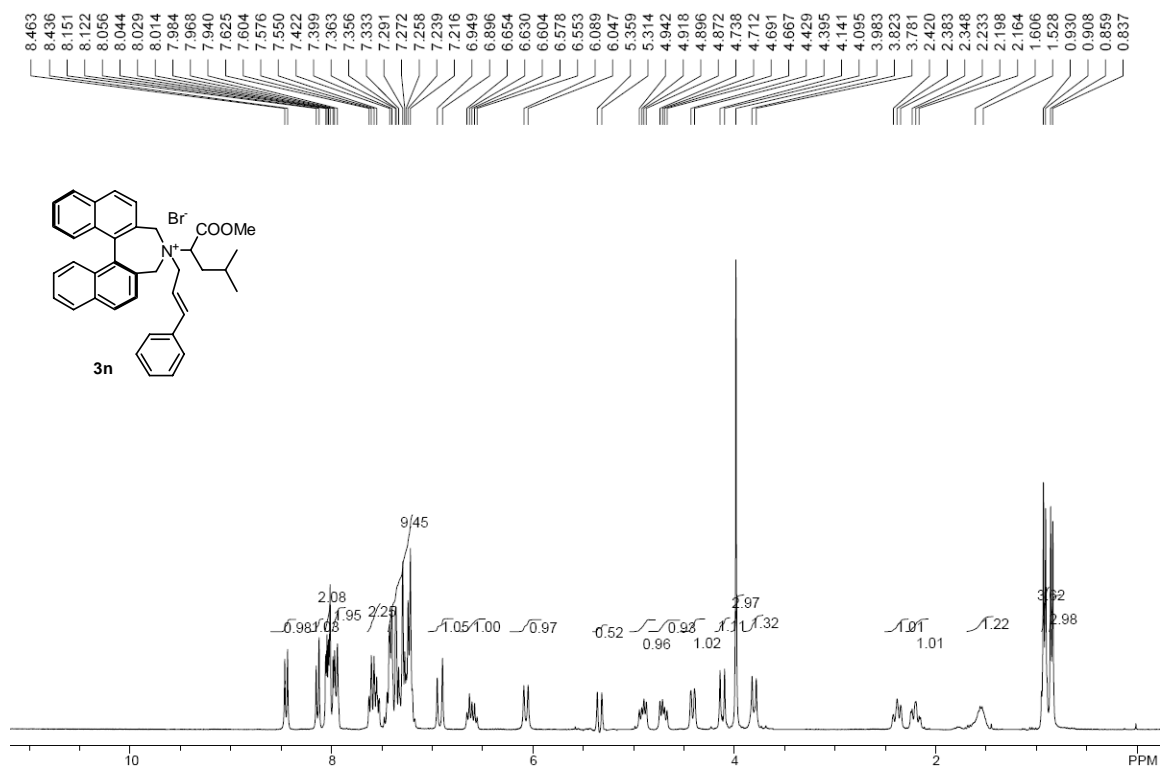


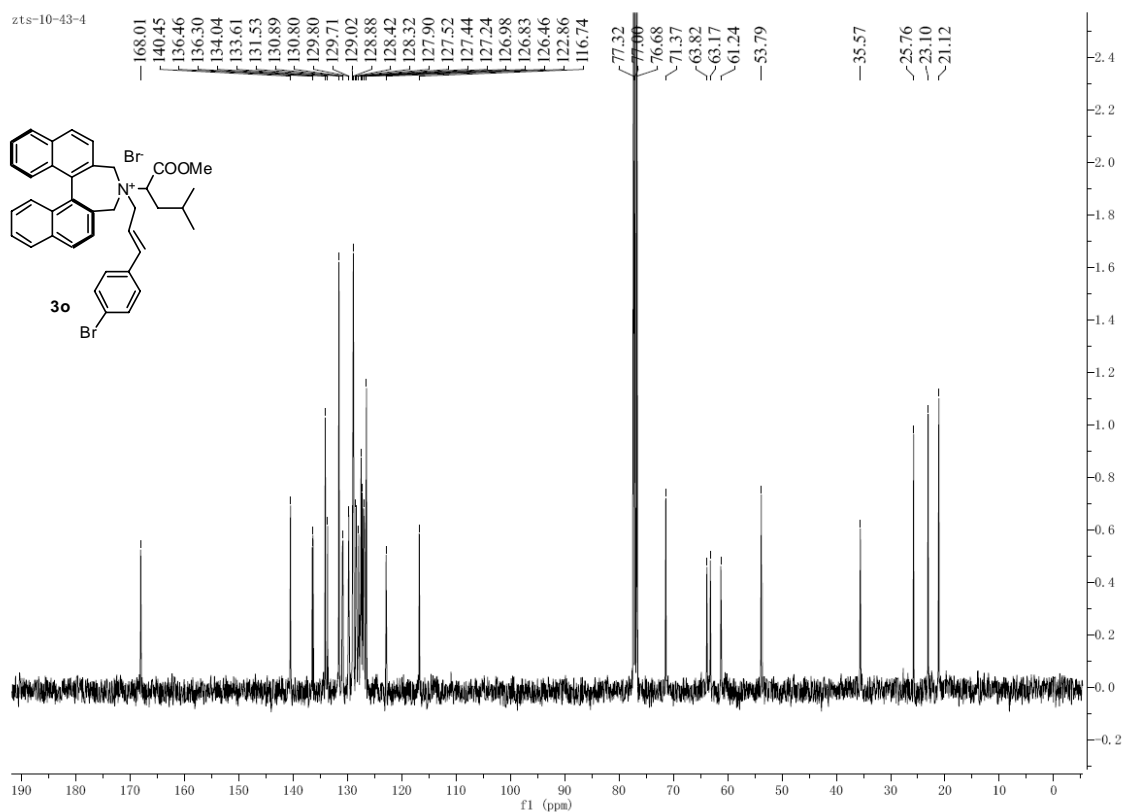
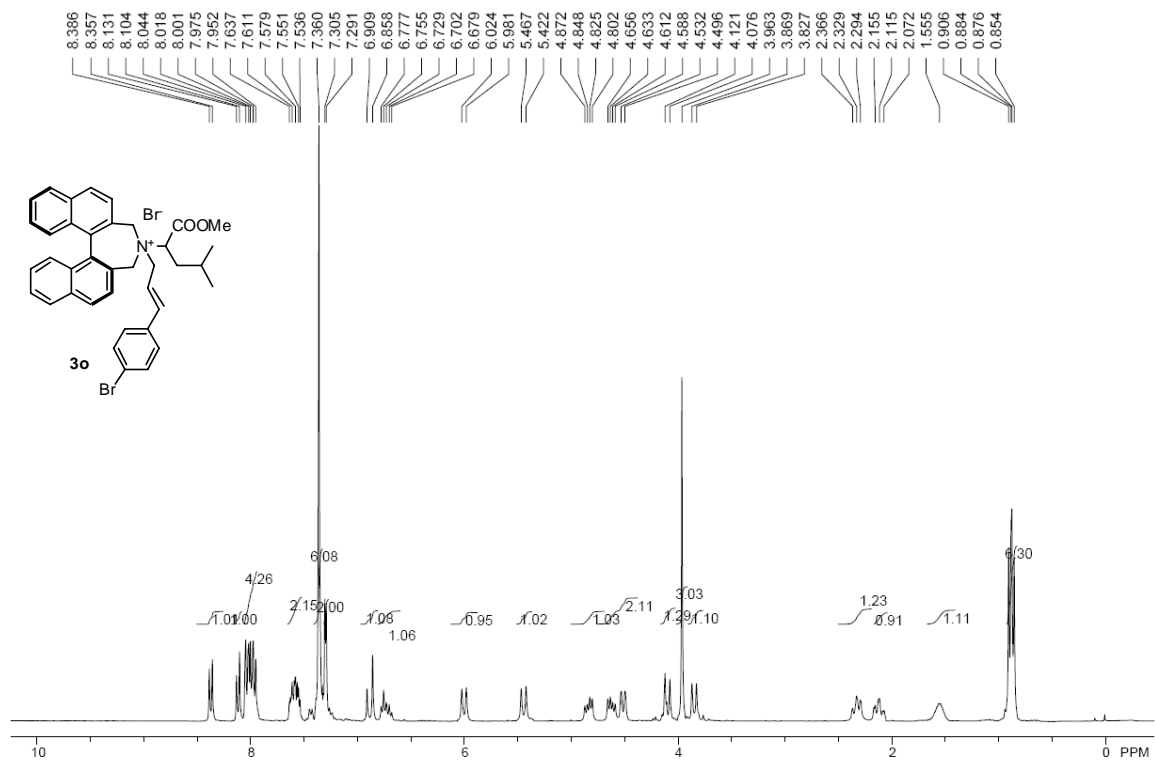
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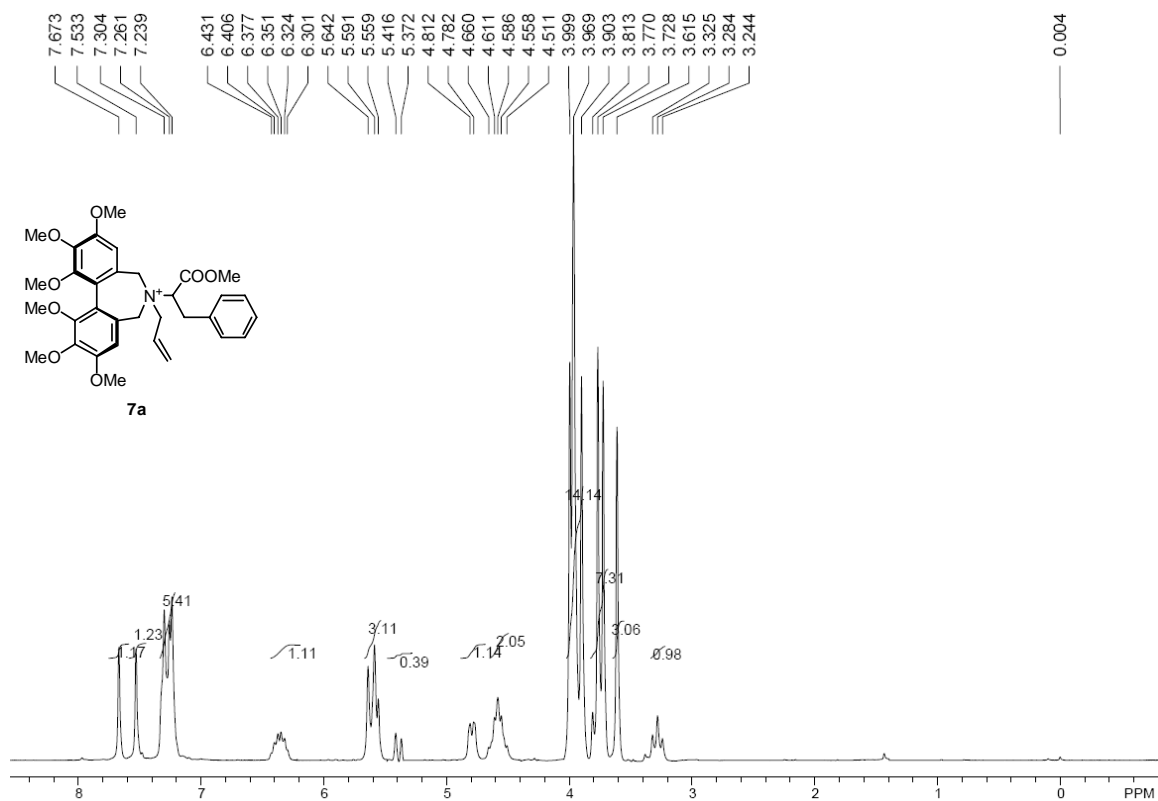


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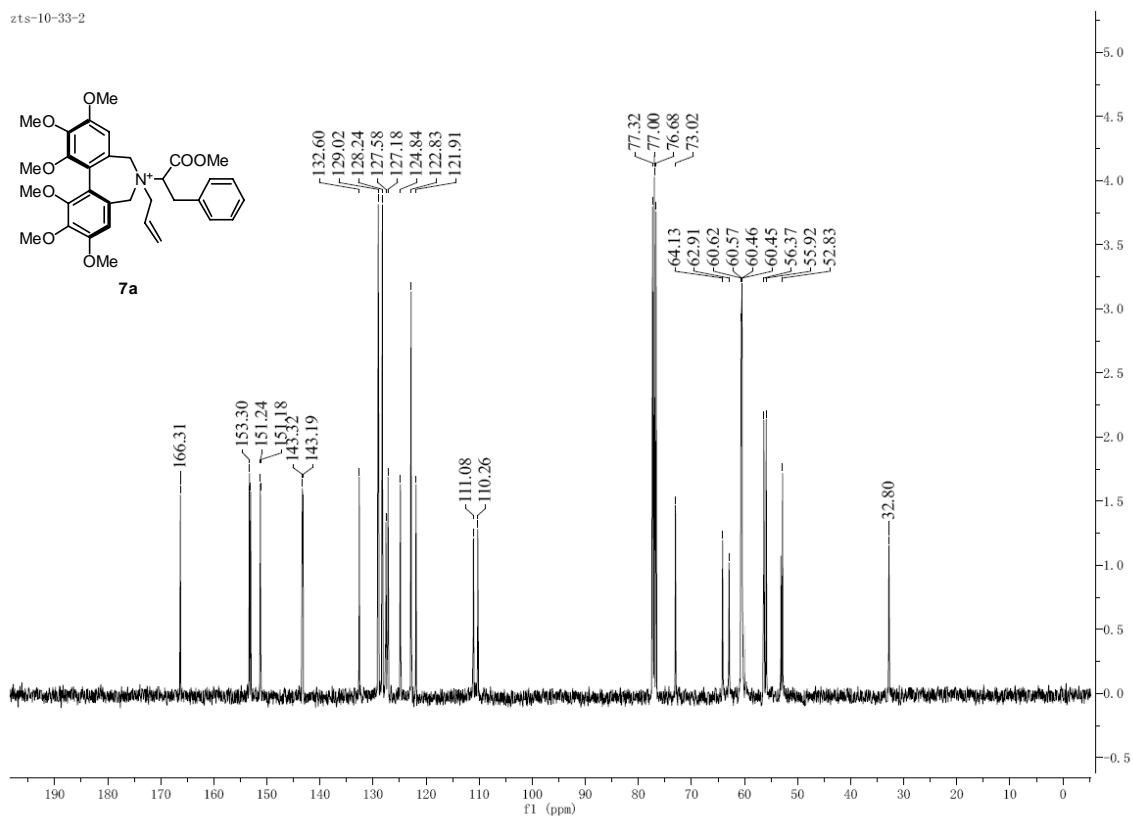


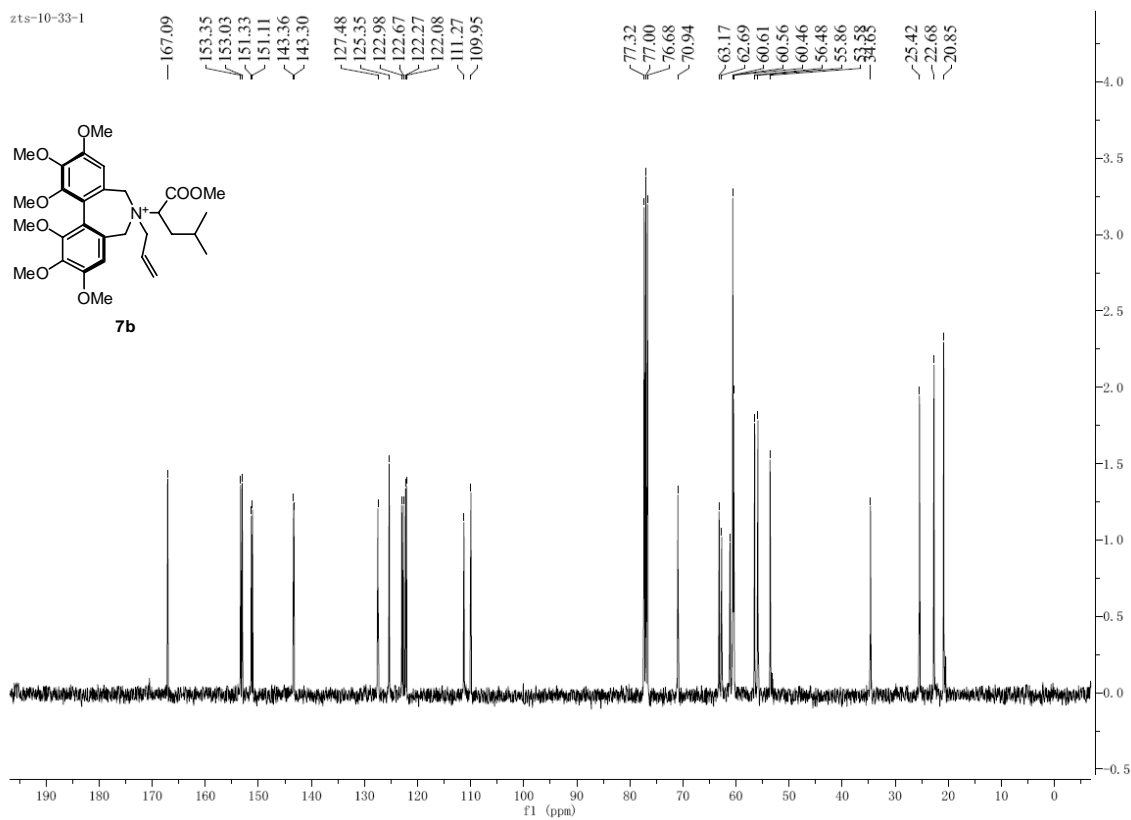
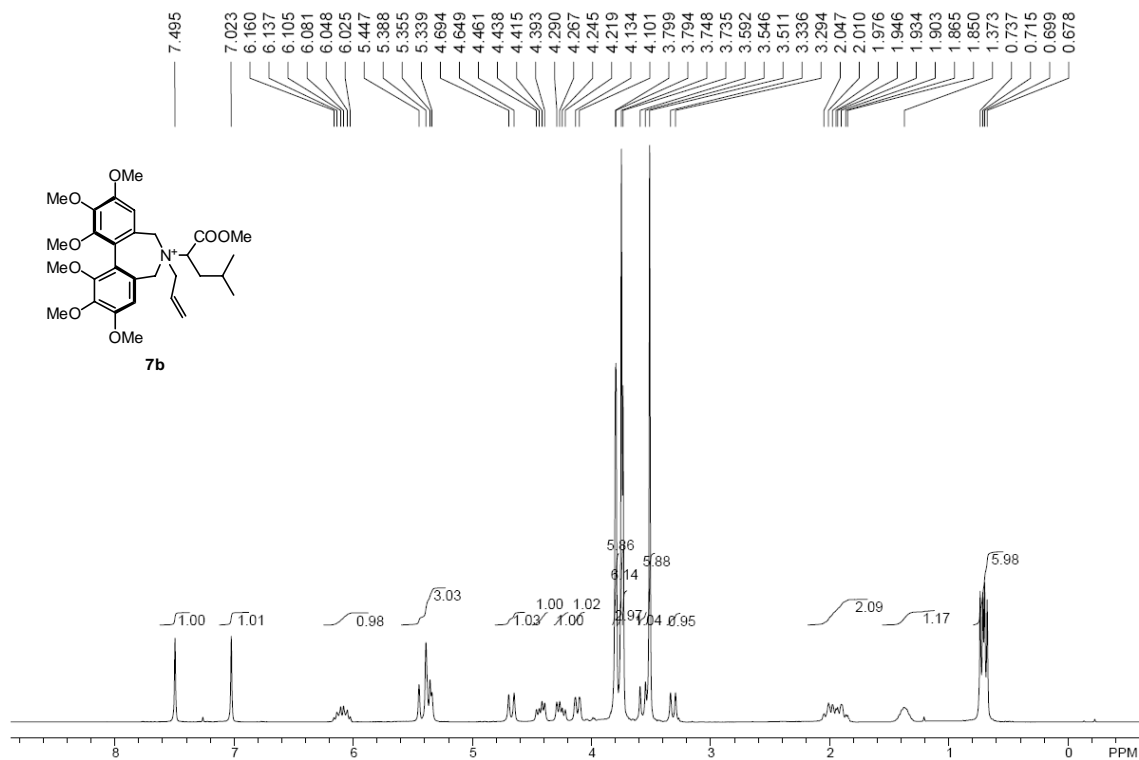


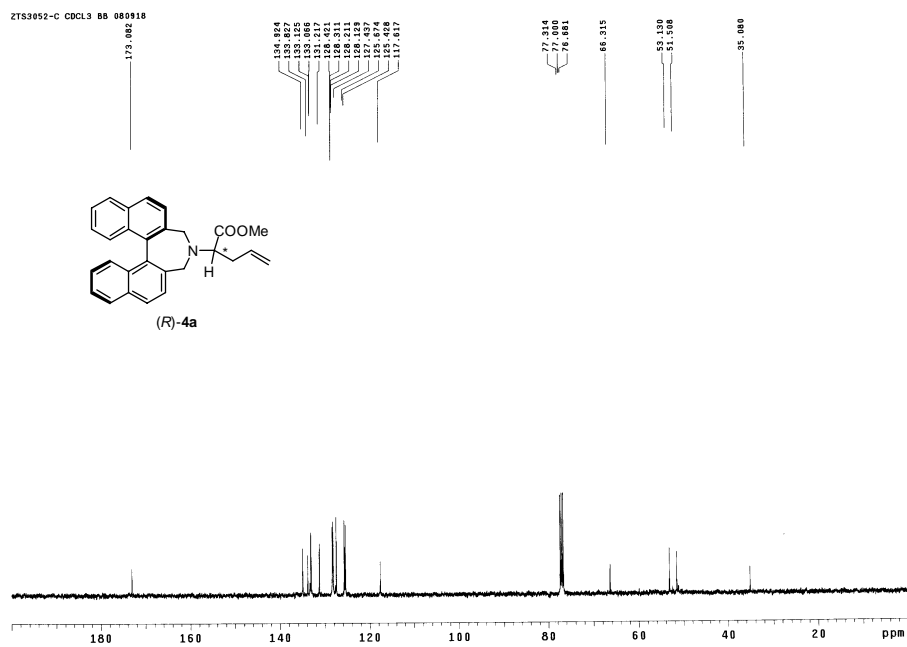
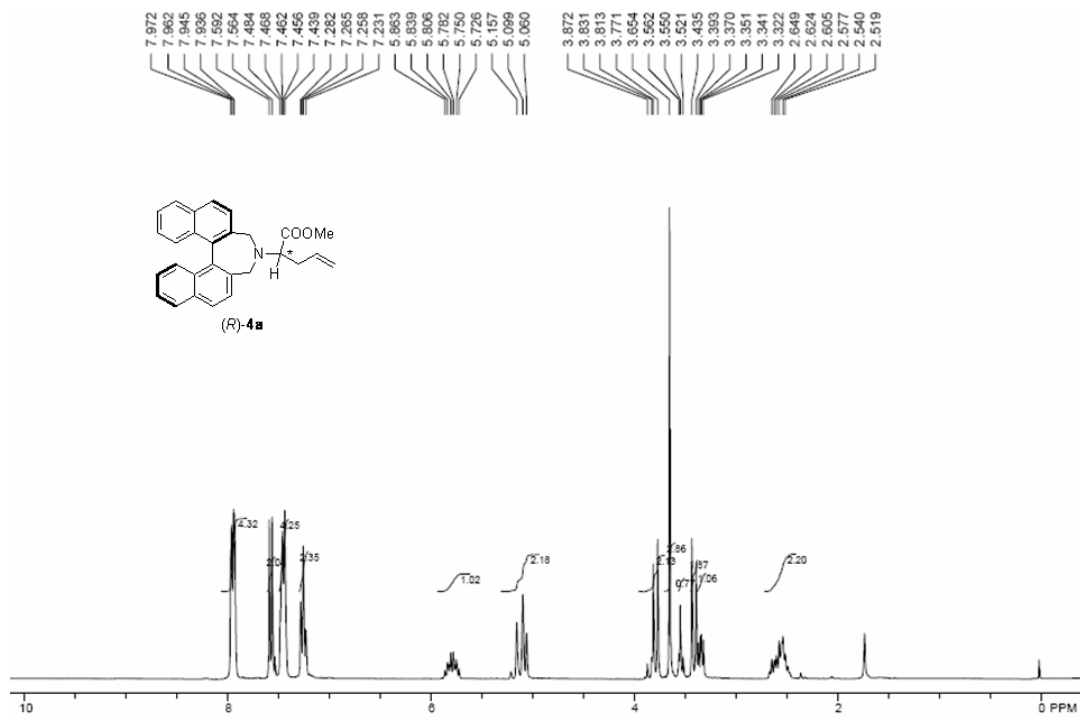


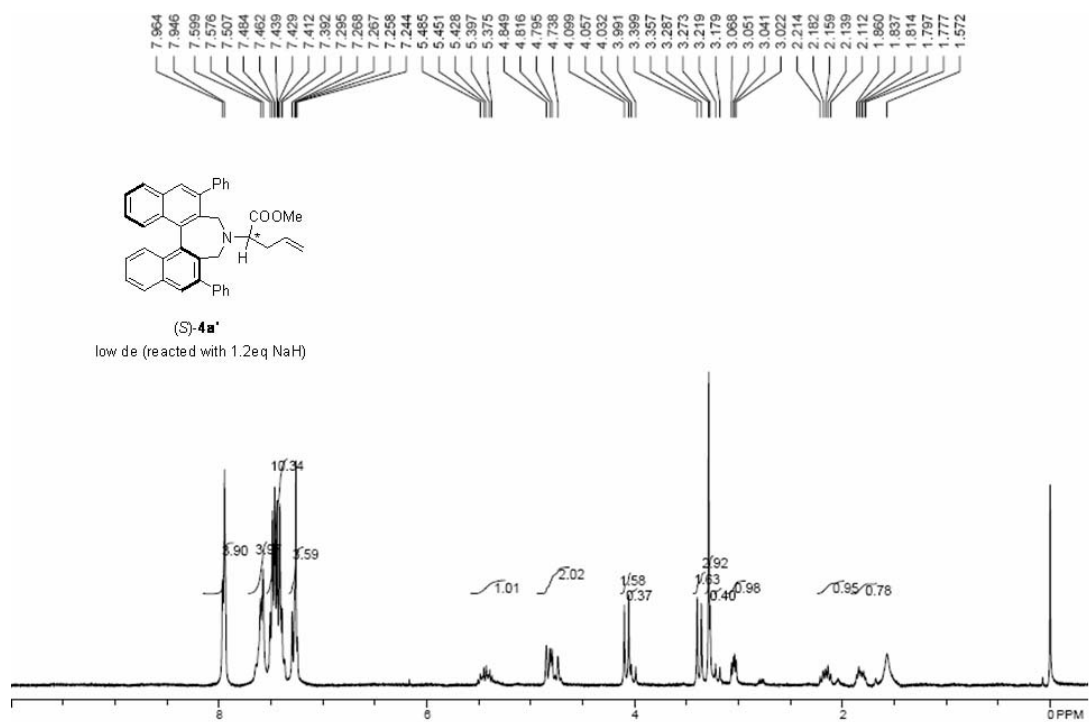
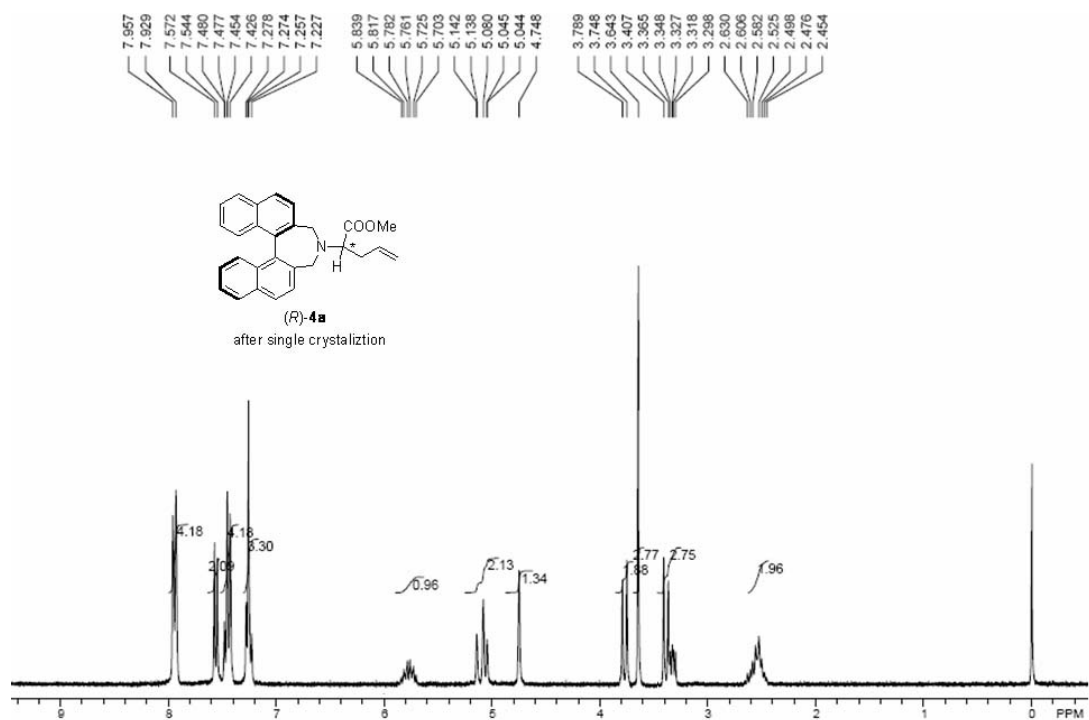


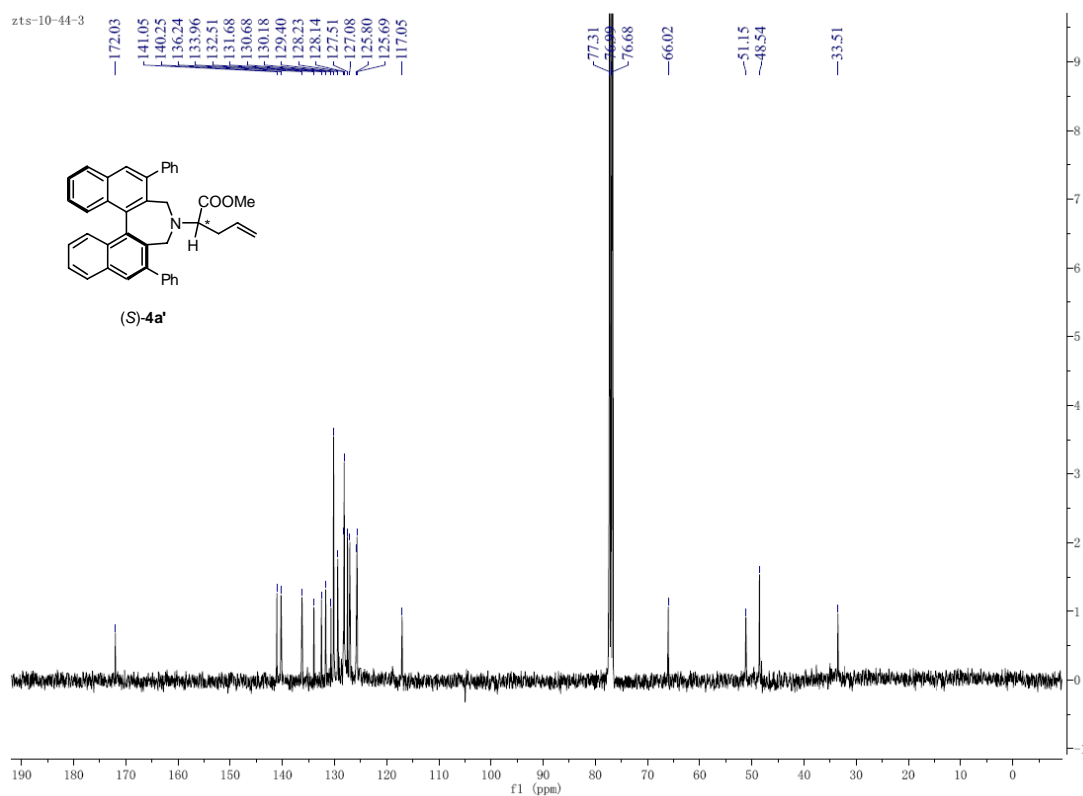
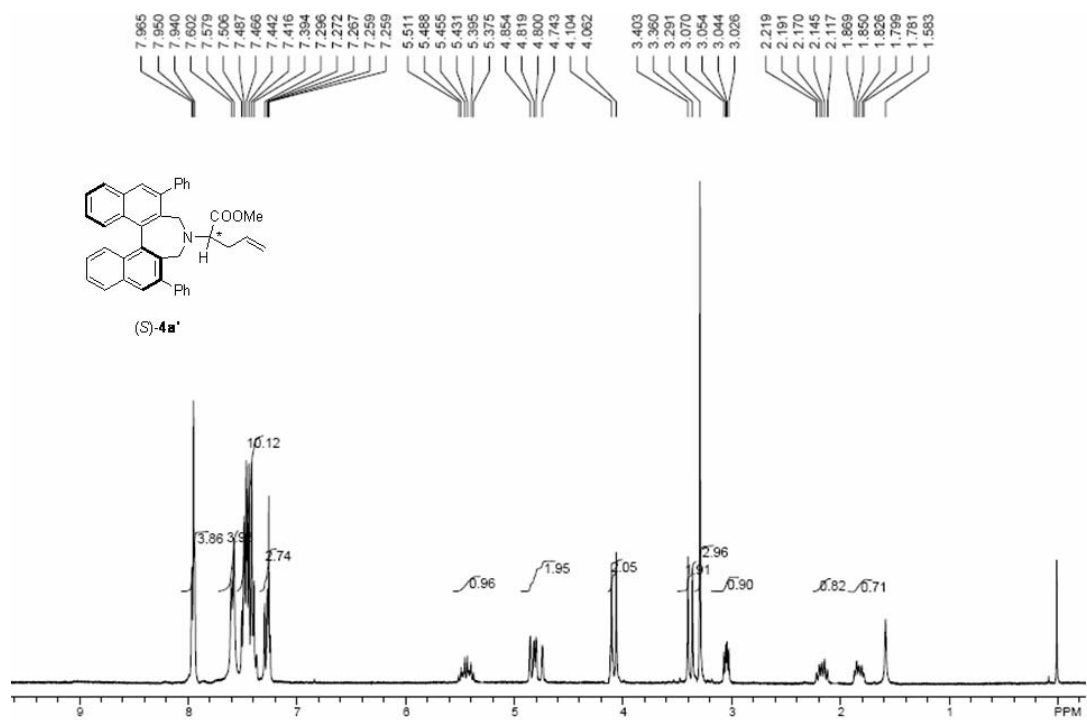
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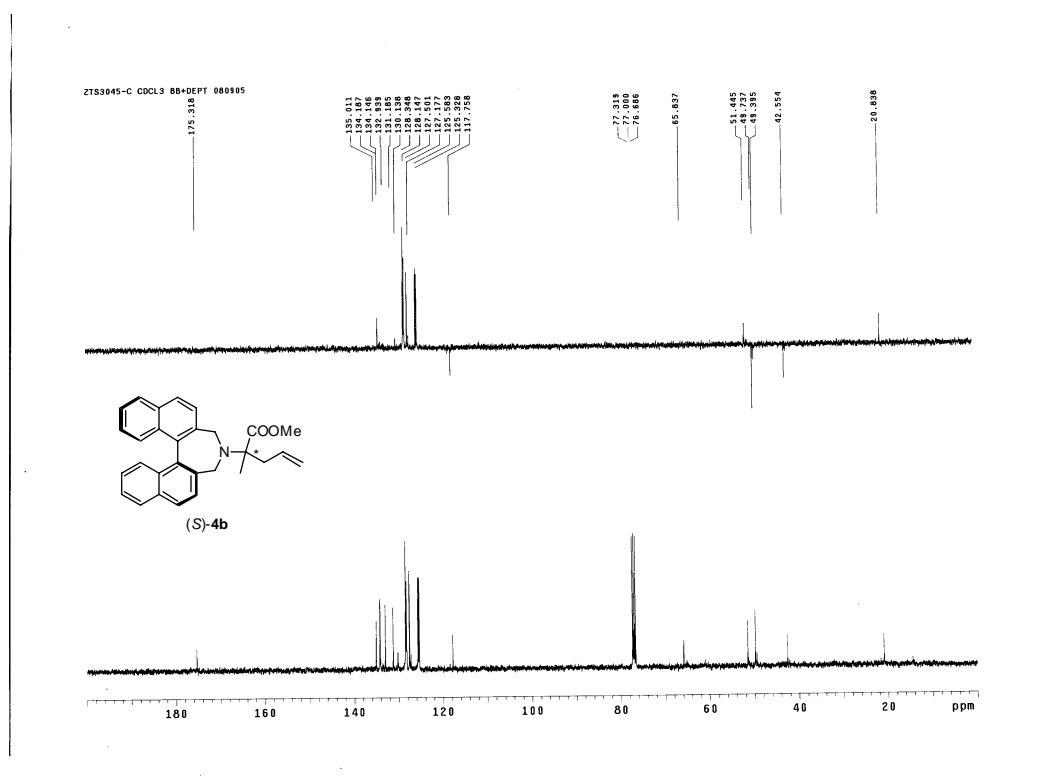
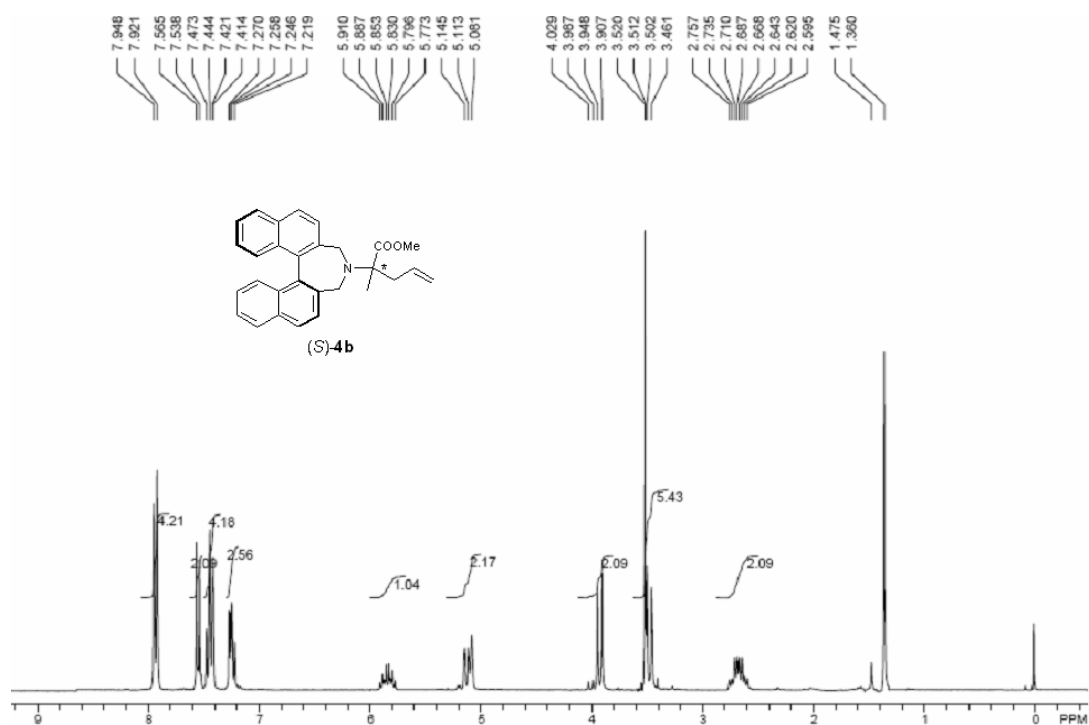


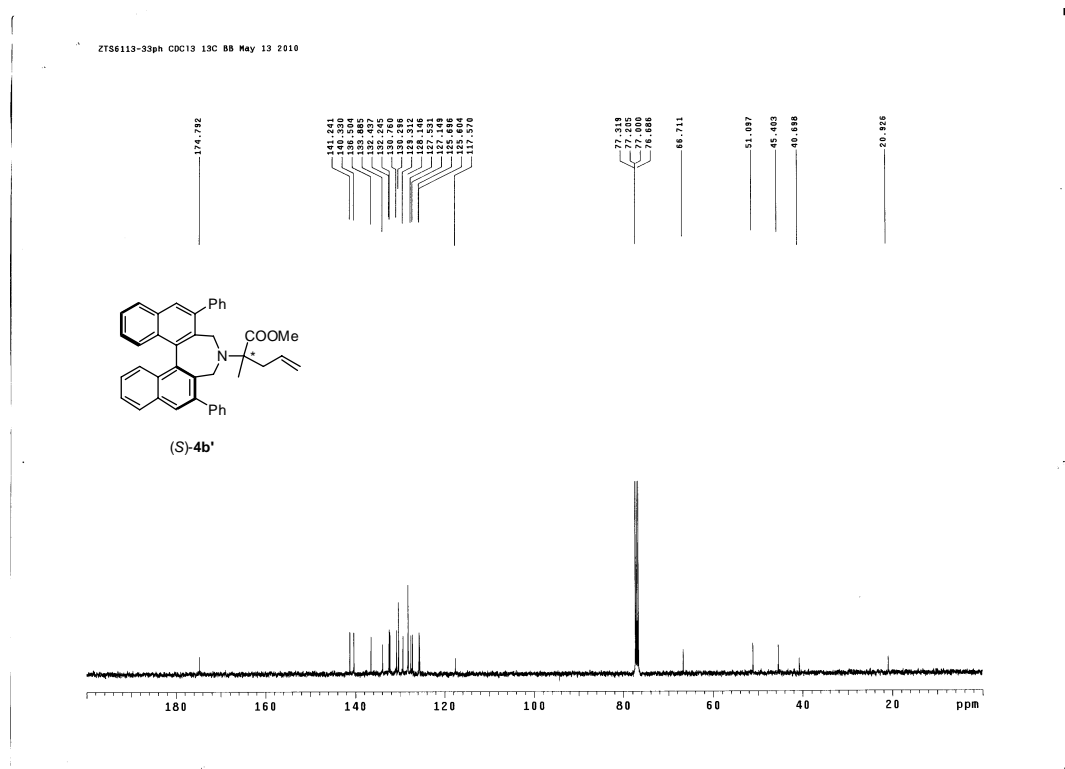
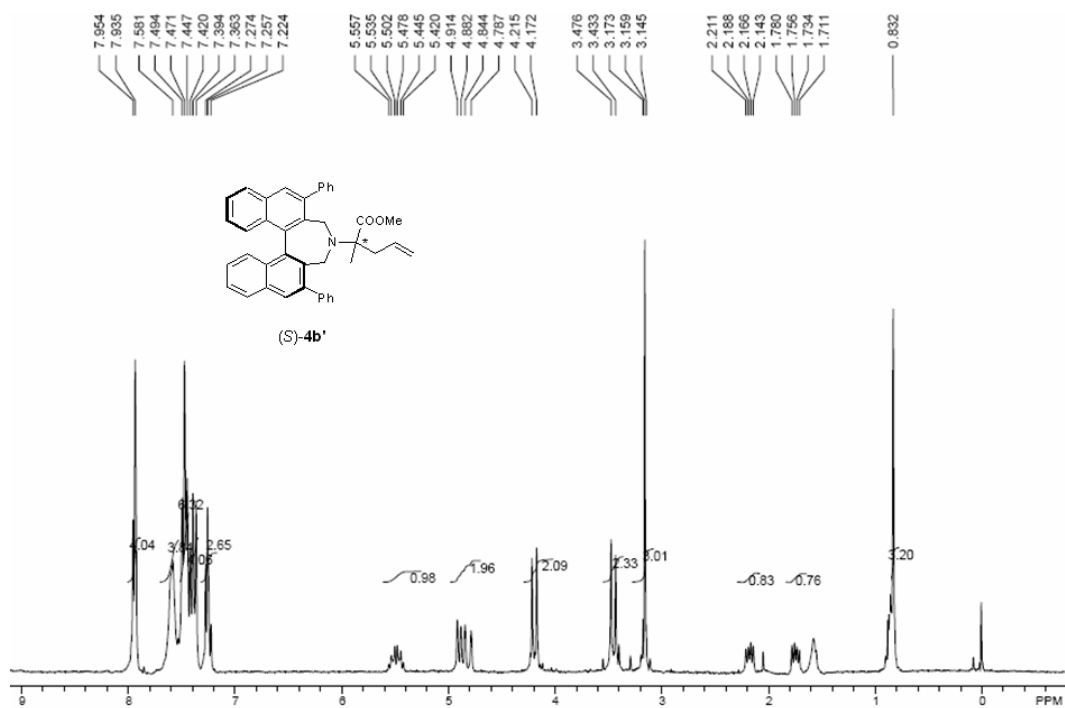


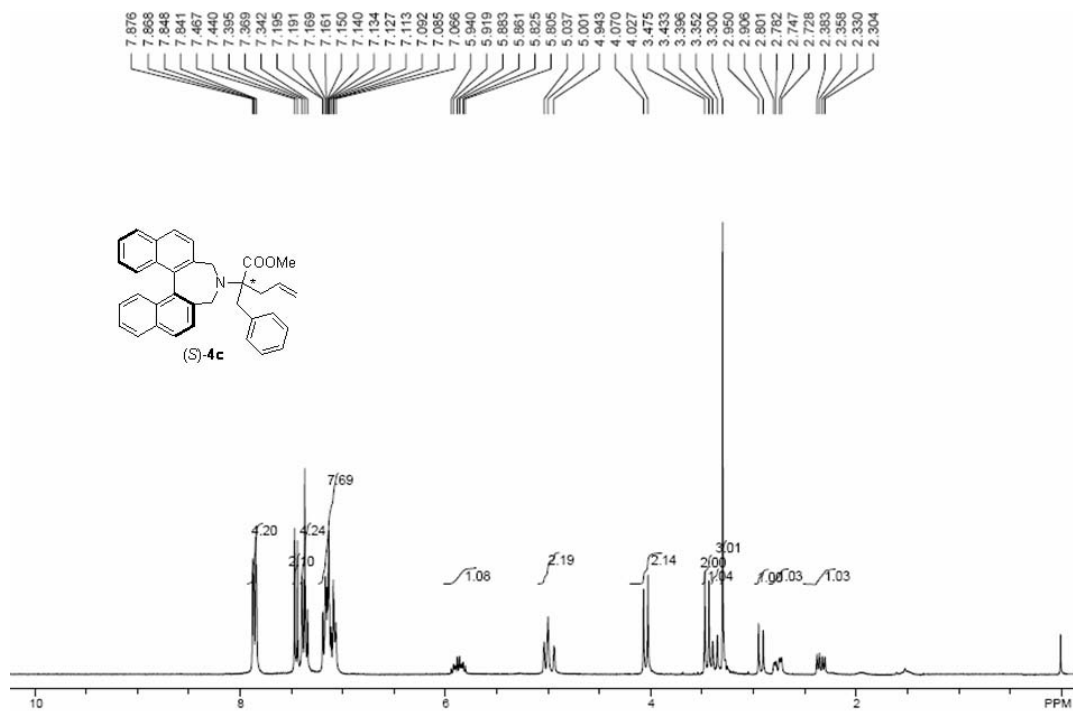




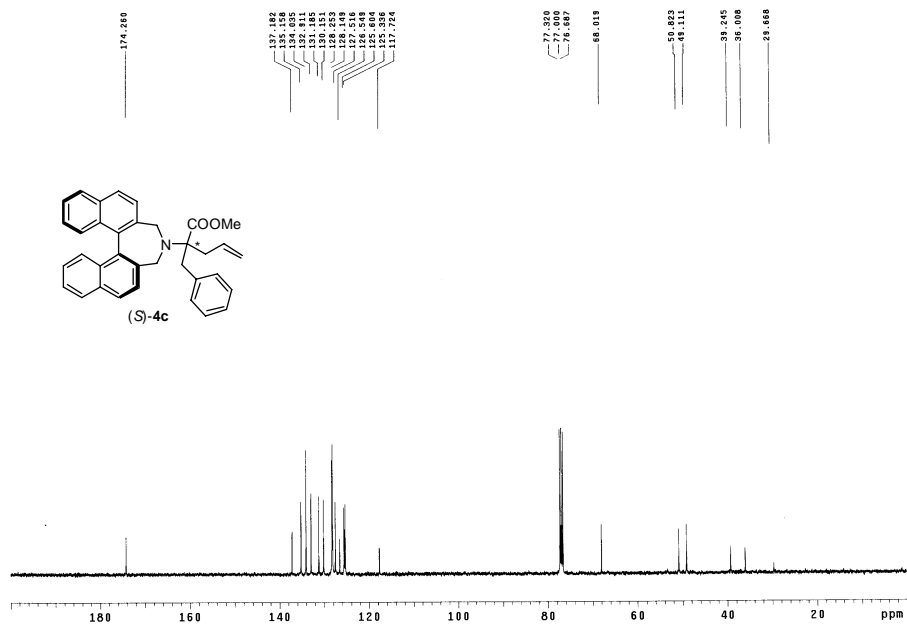


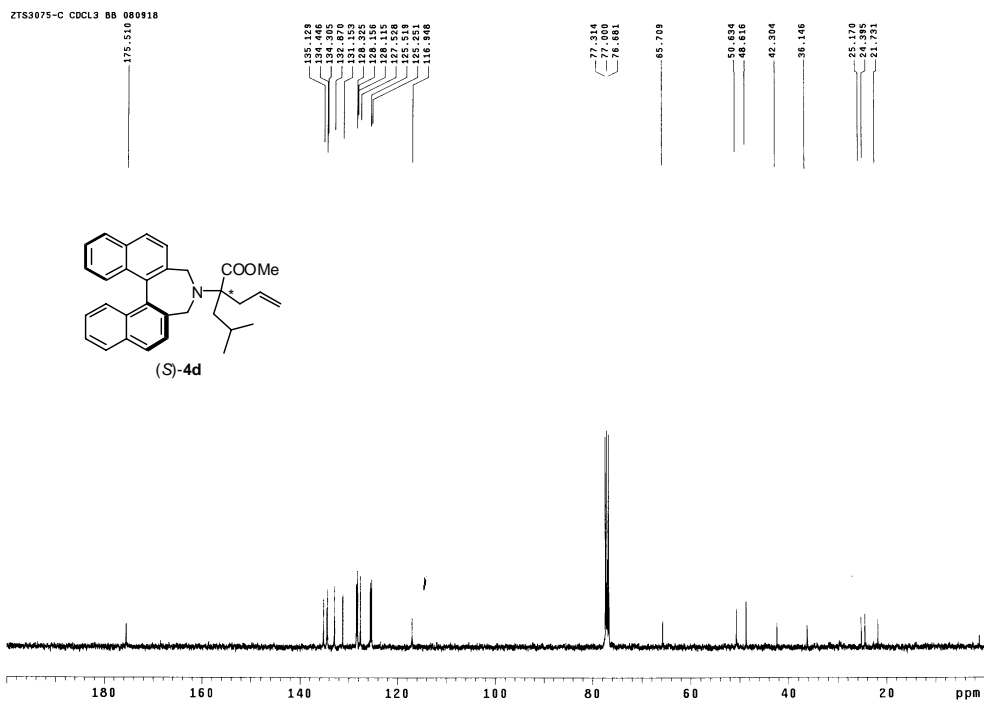
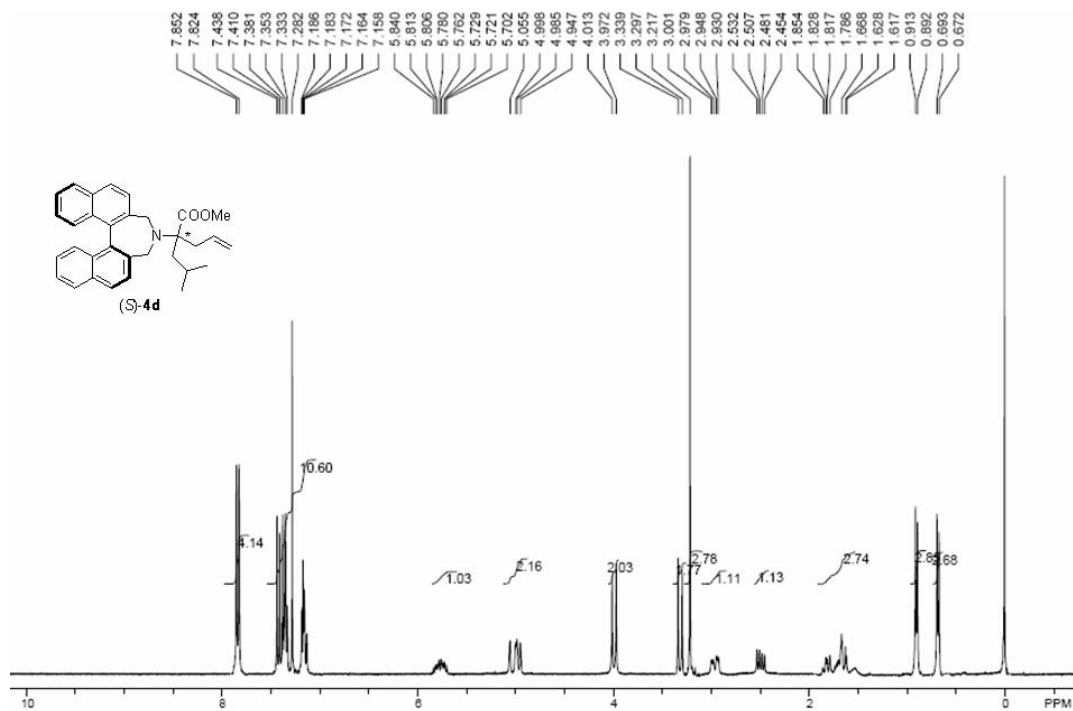


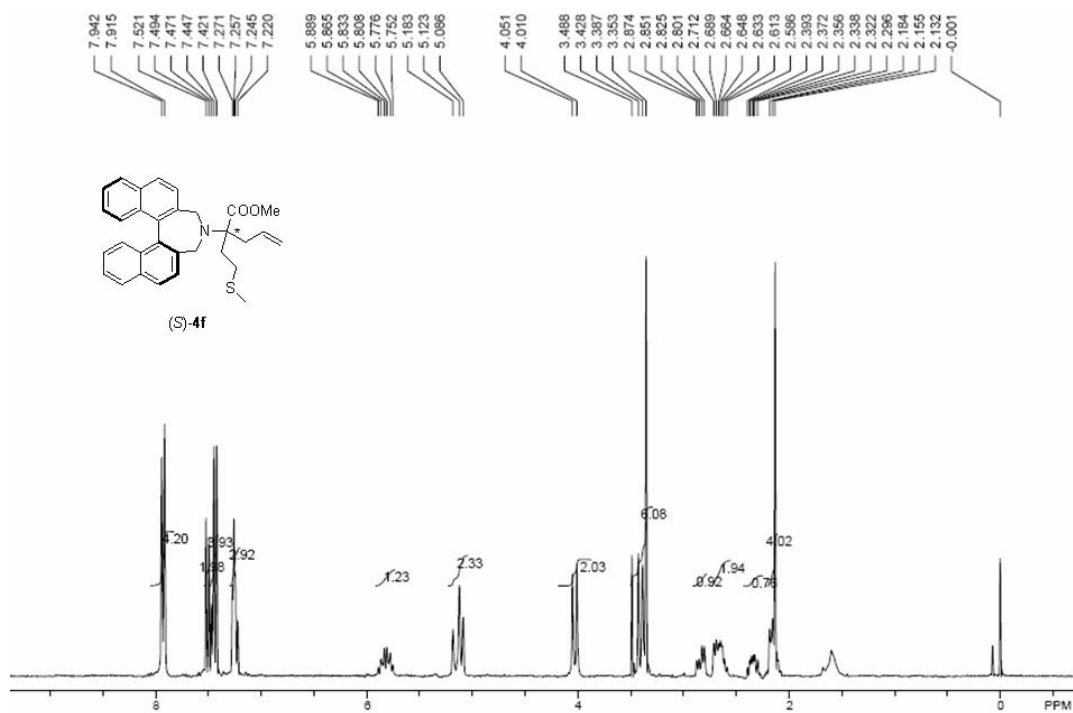




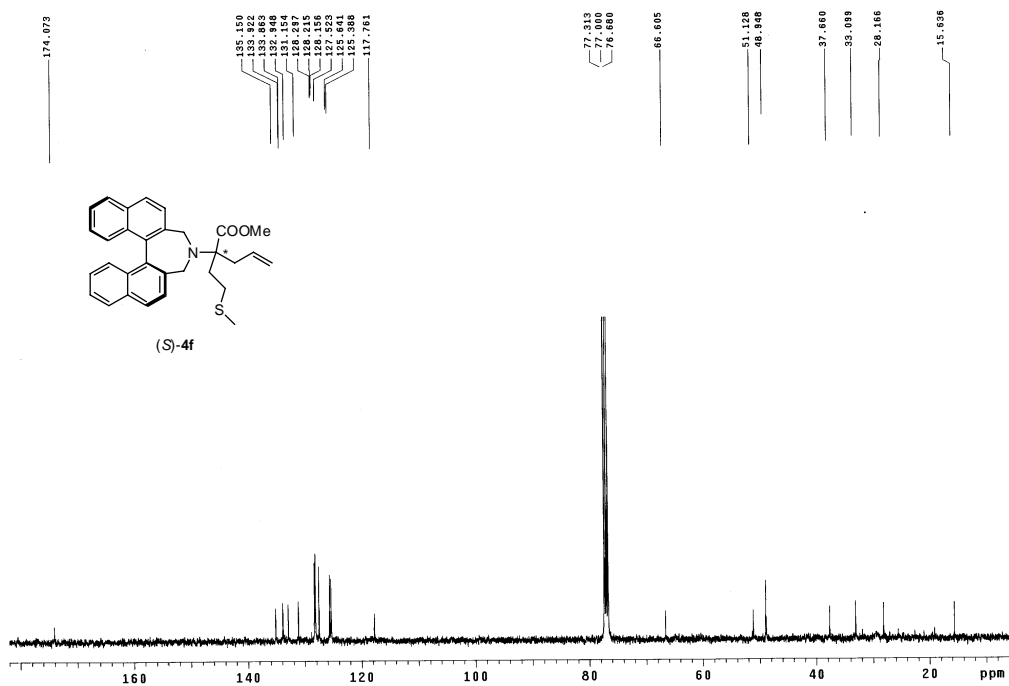
Z1S3087-C CDC13 13C NMR Sep 11 2008

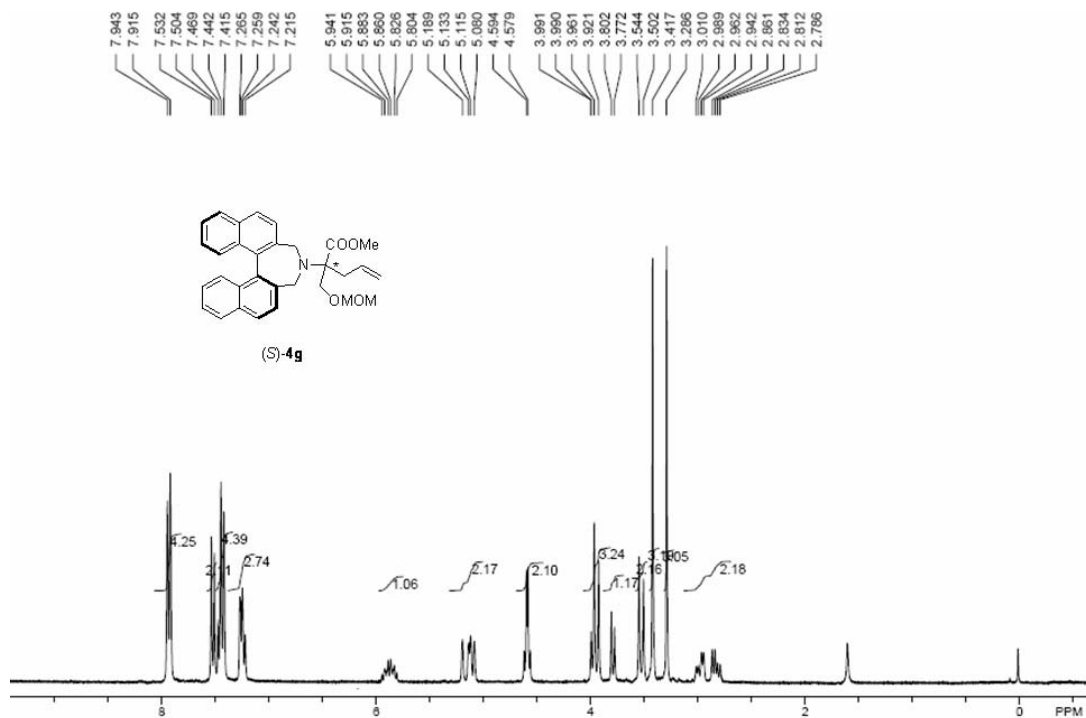




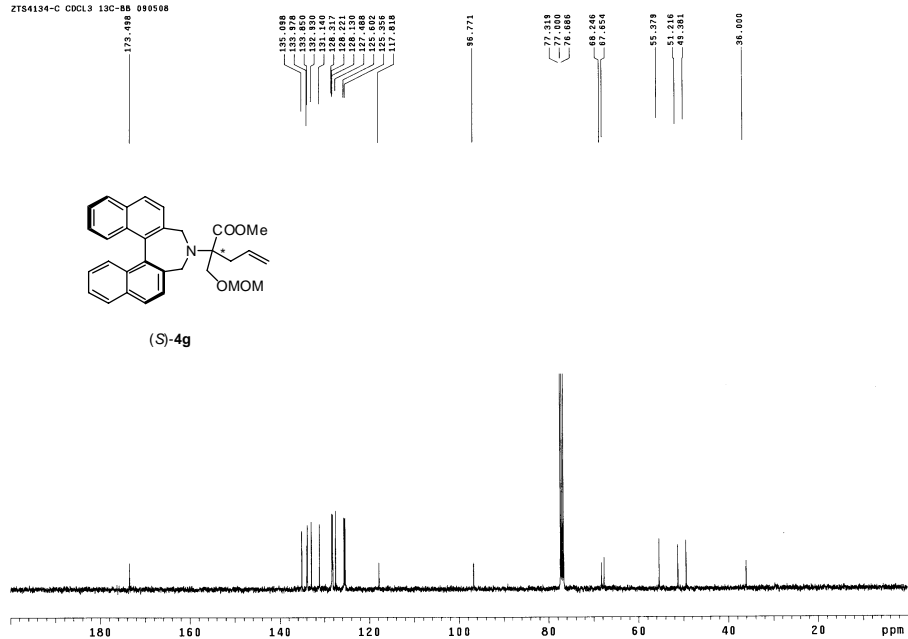


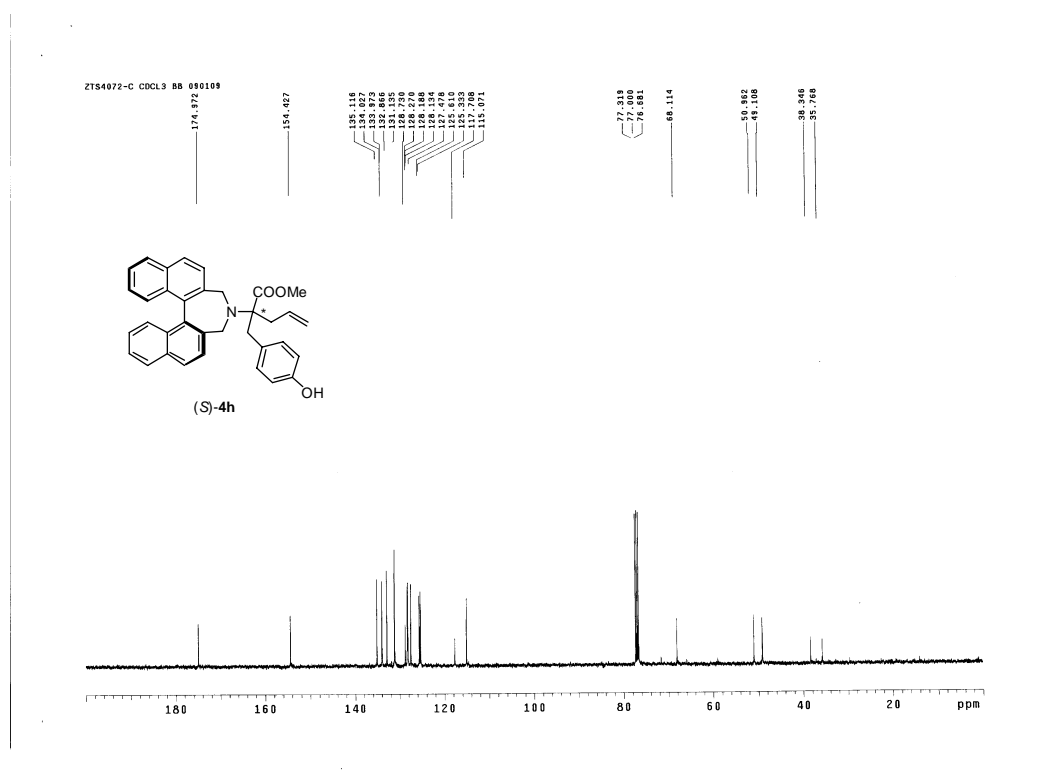
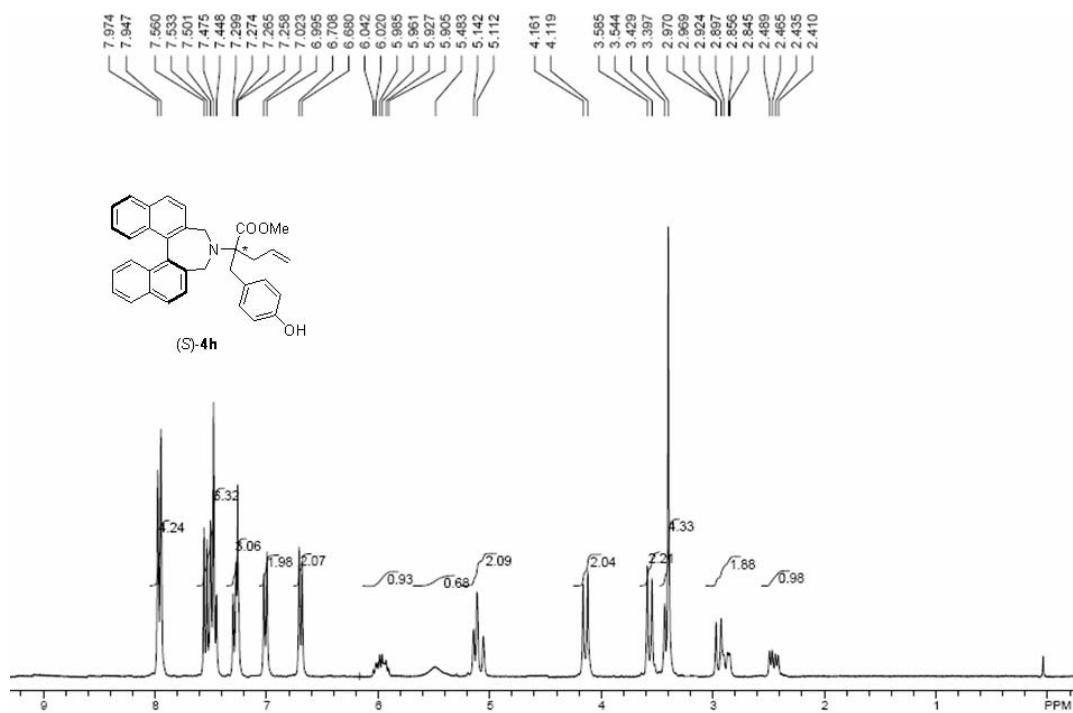
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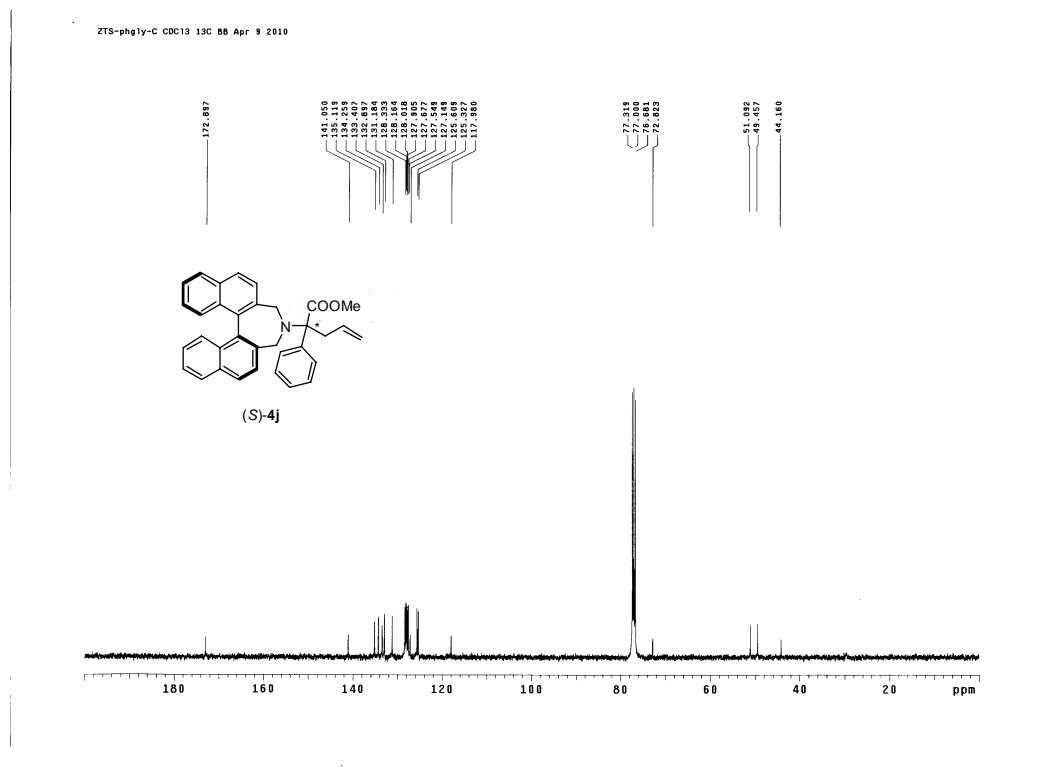
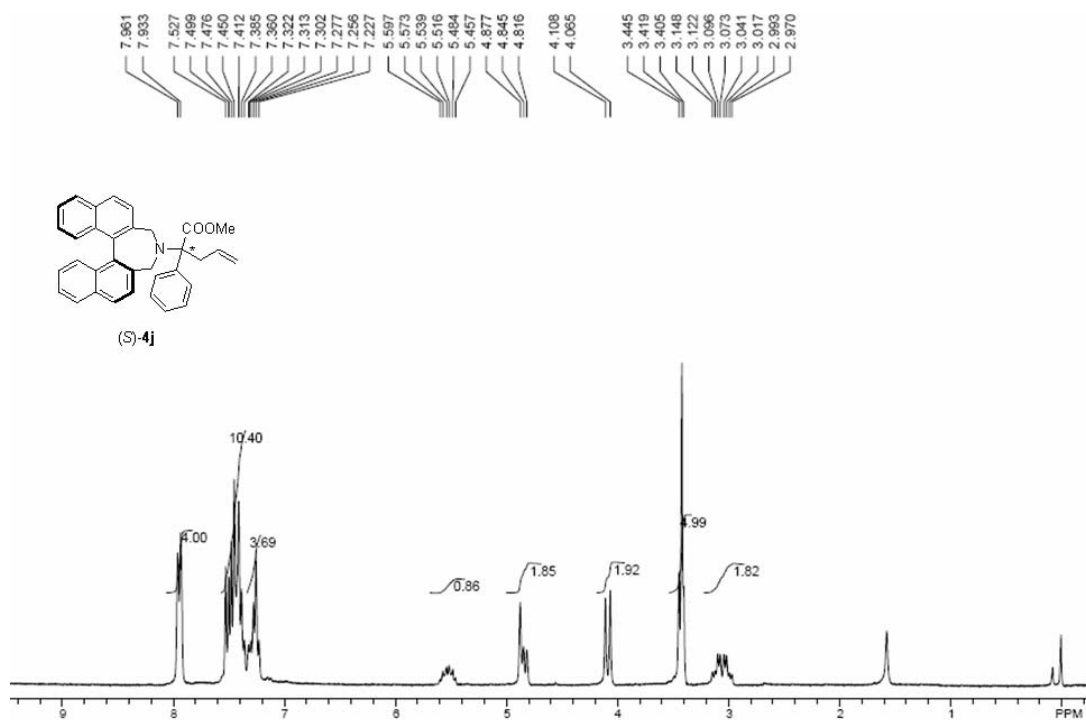


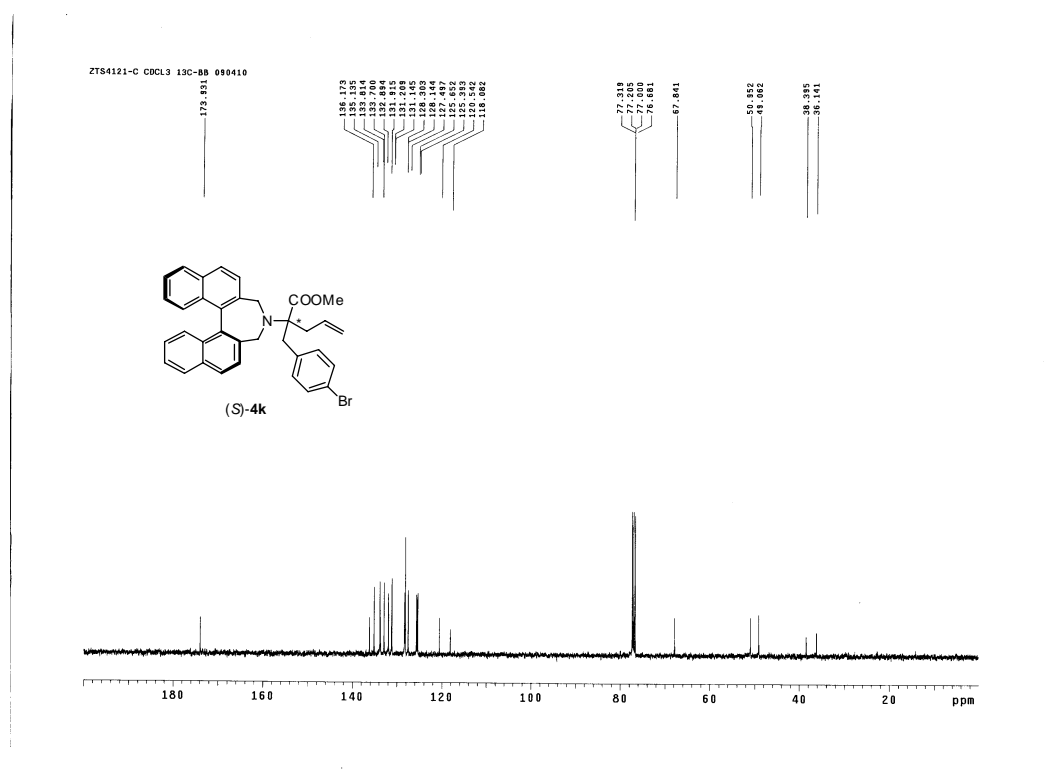
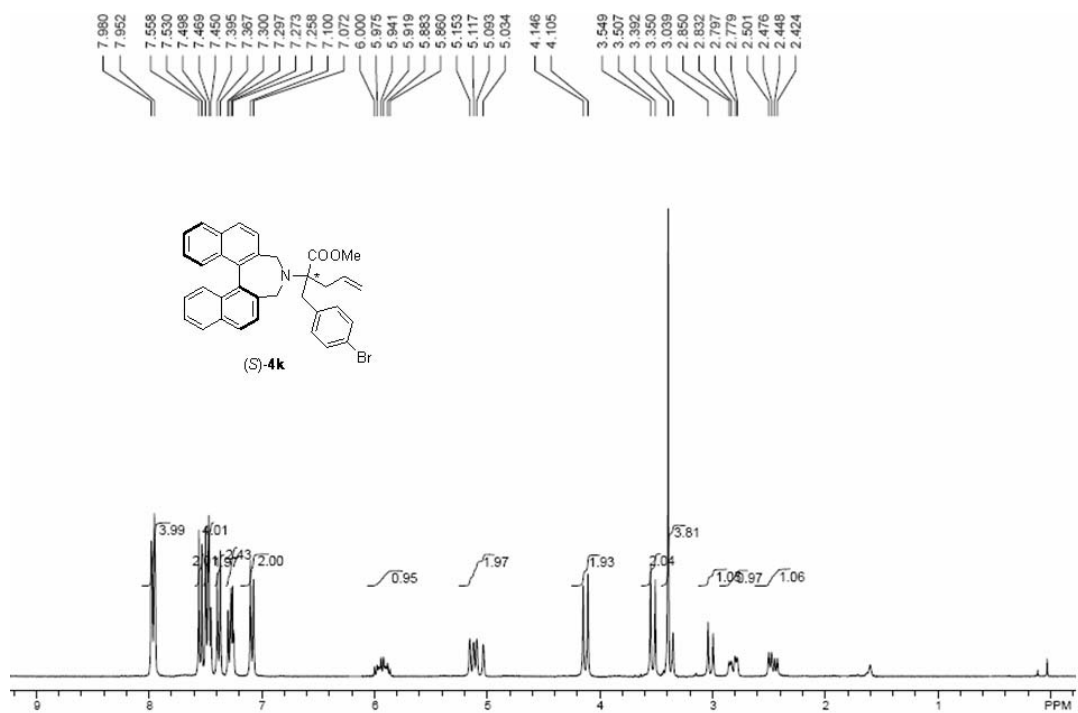


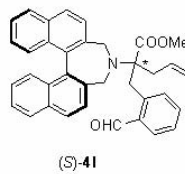
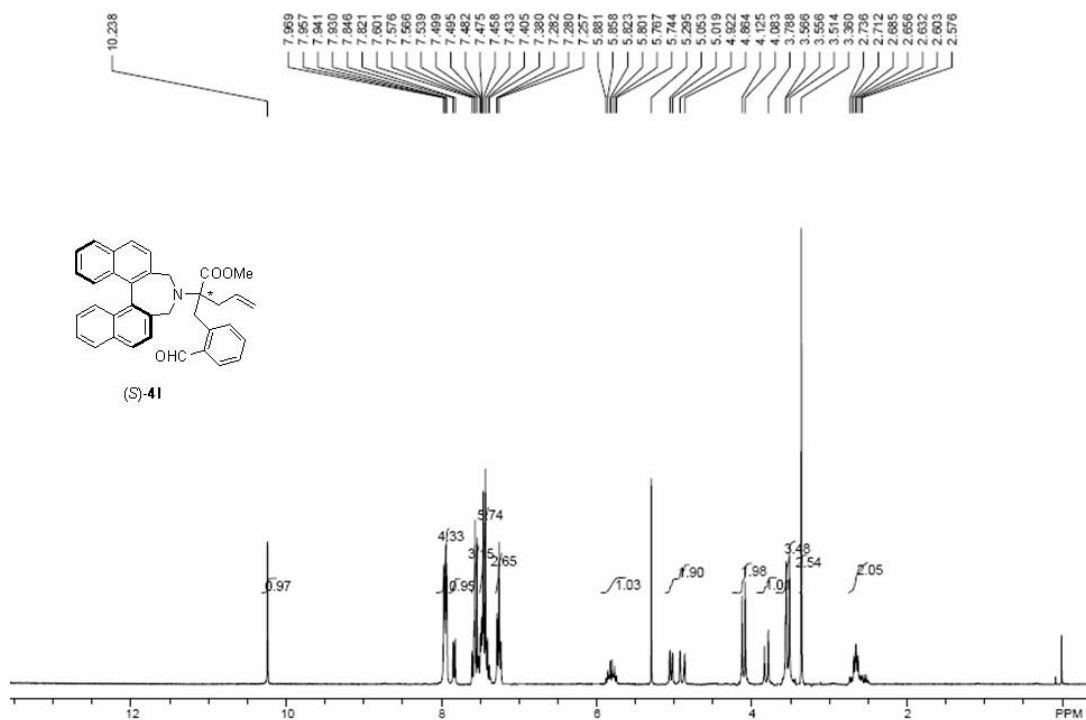
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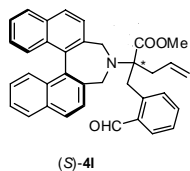
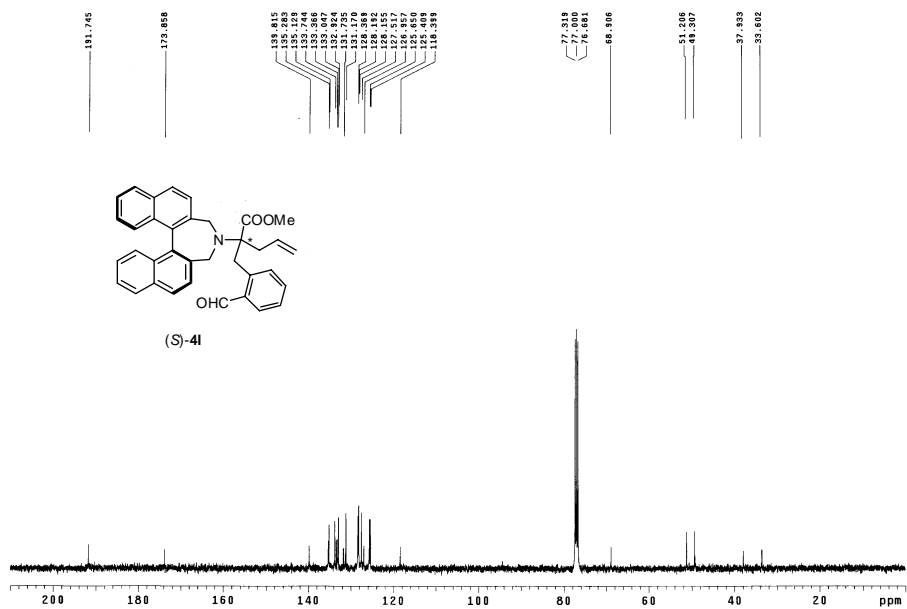


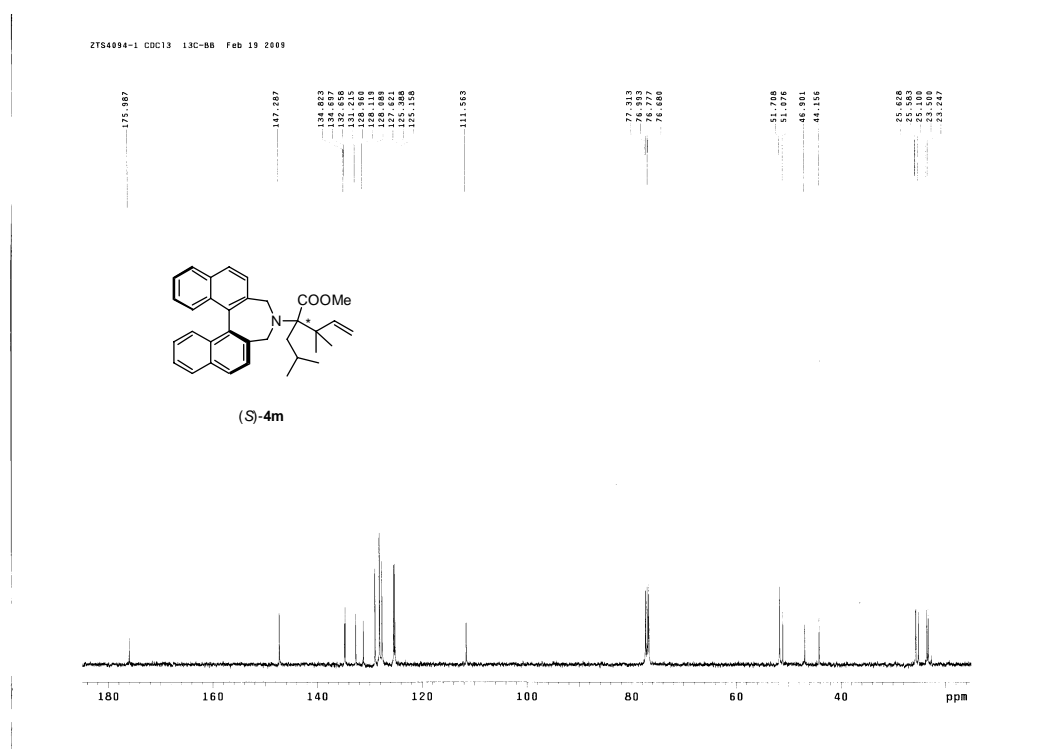
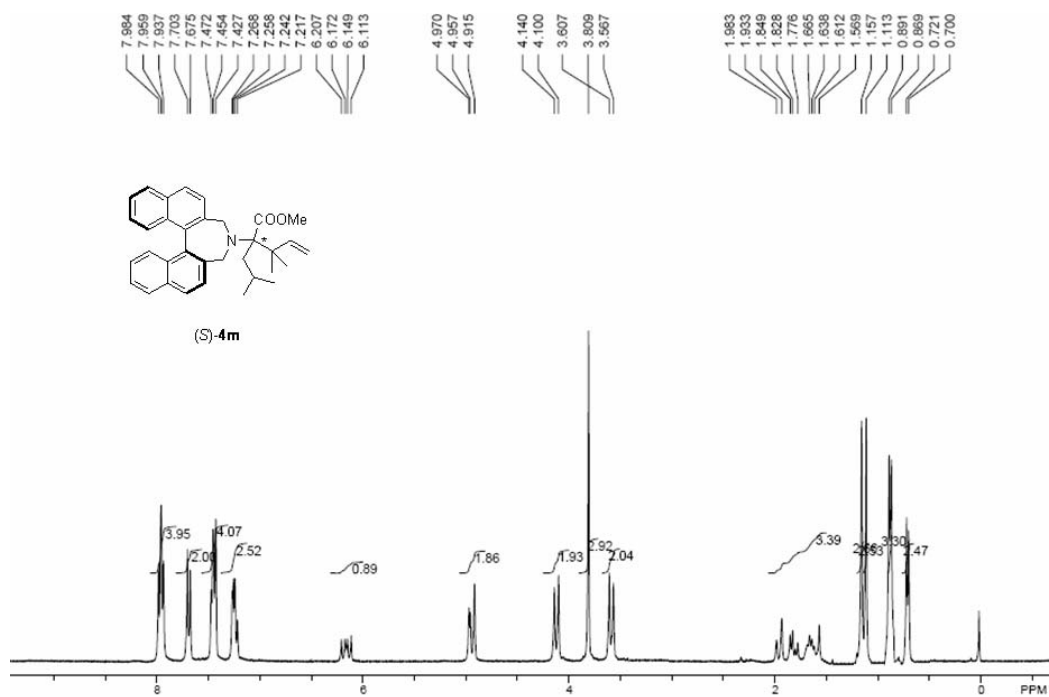


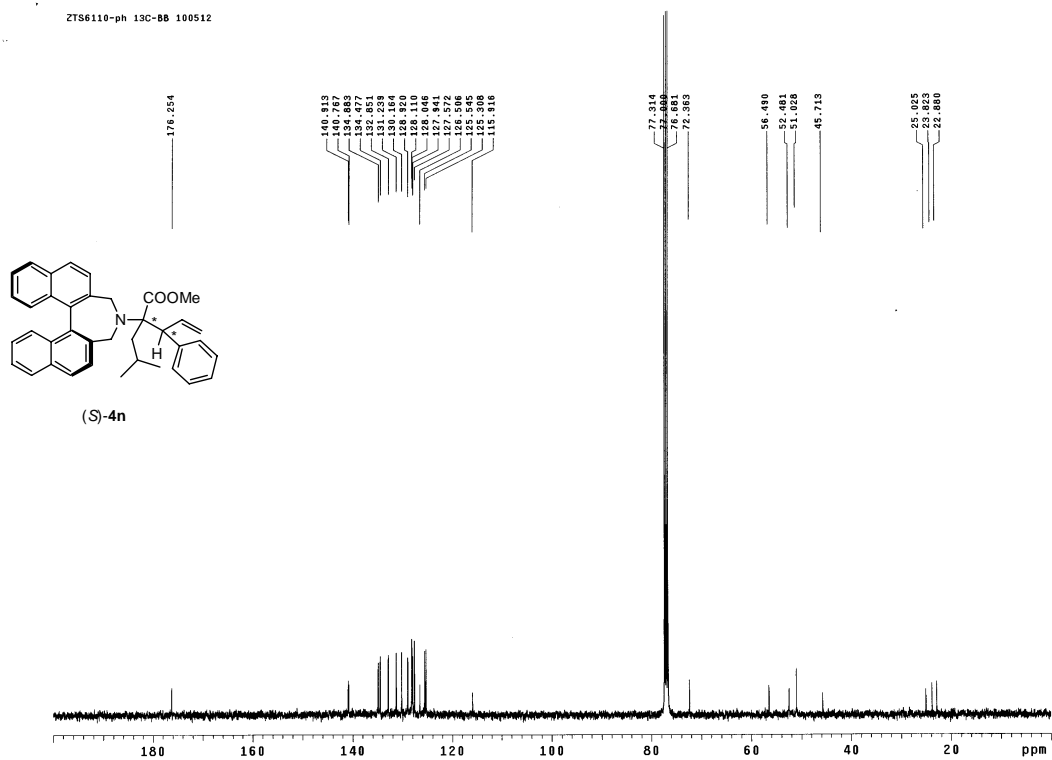
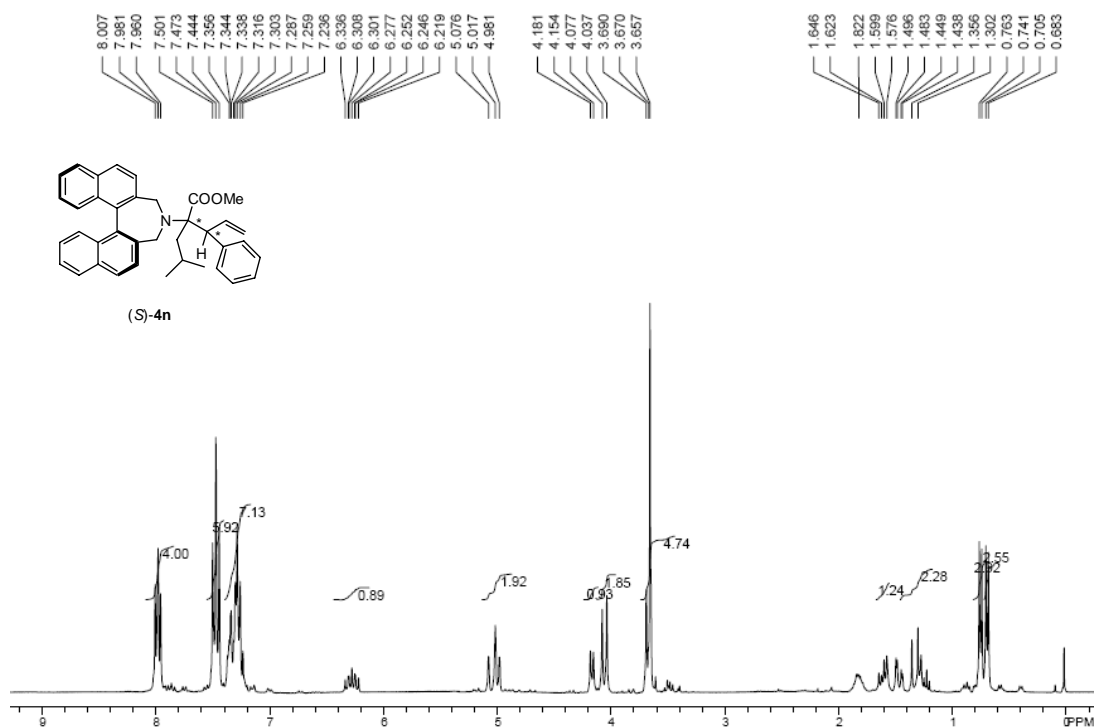


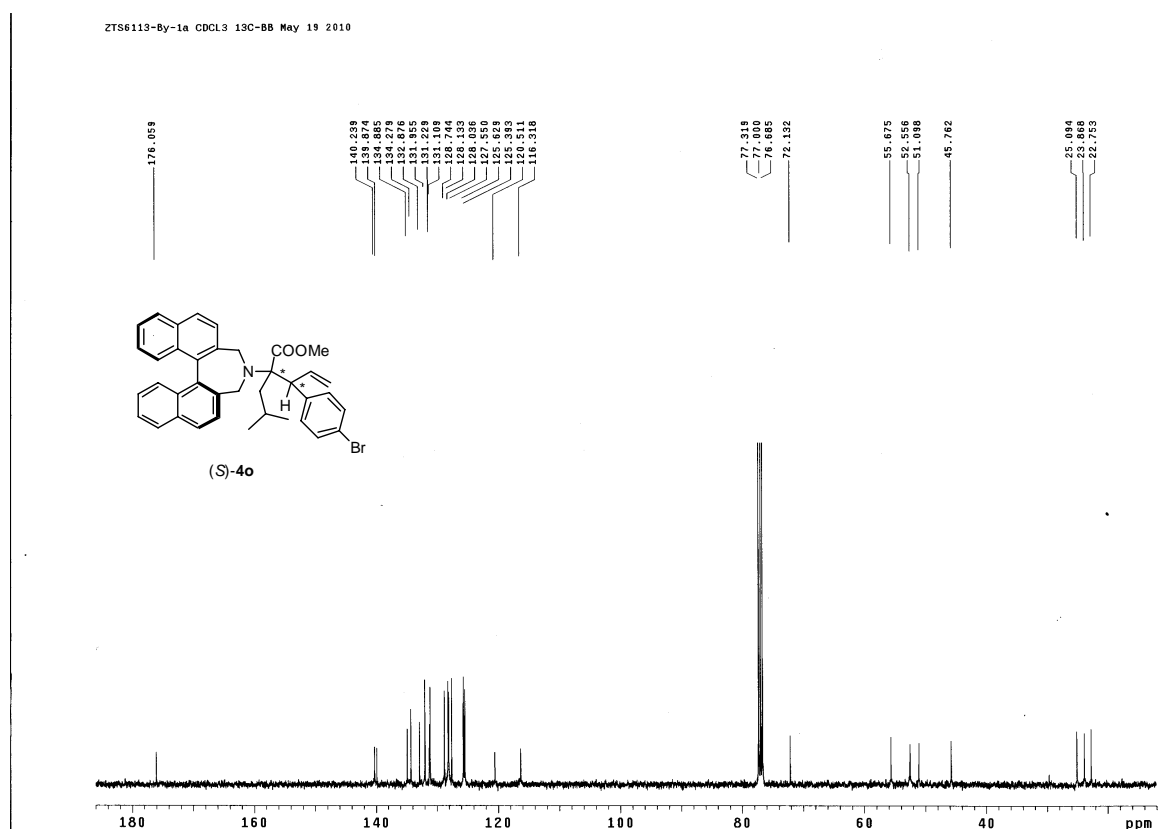
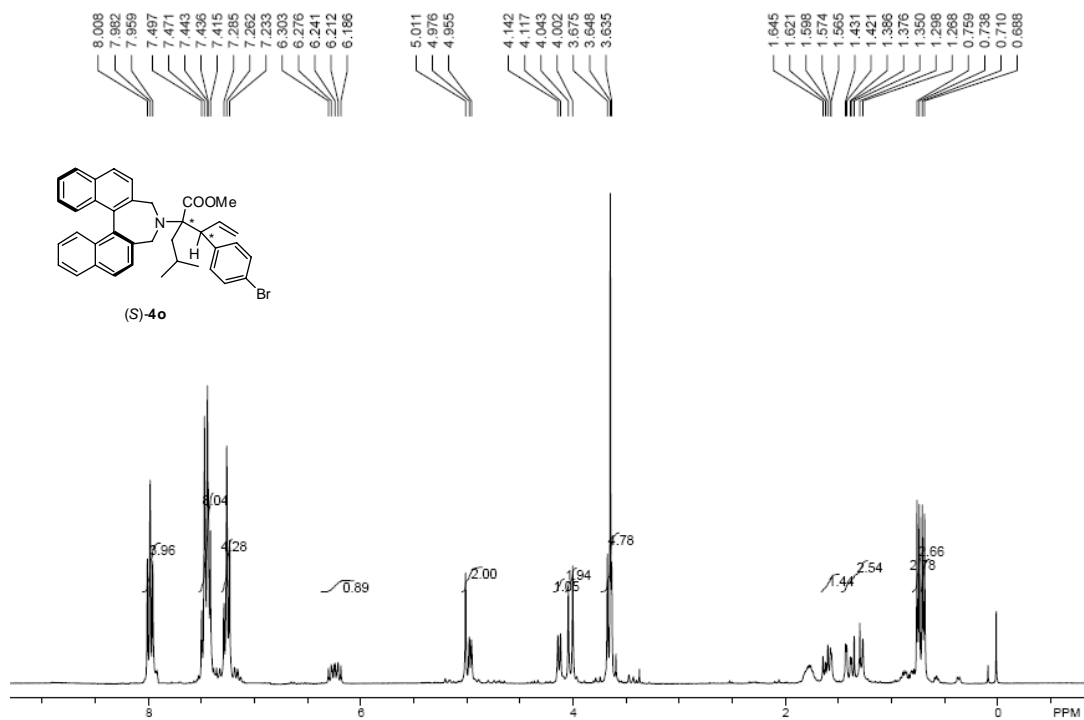


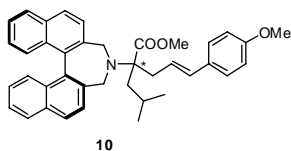
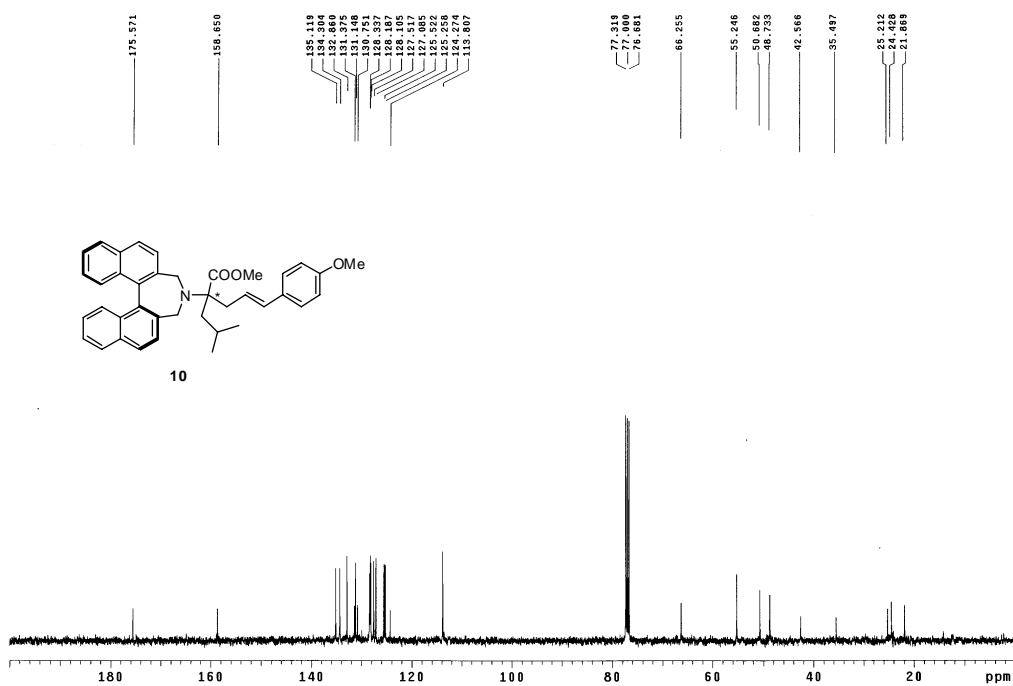
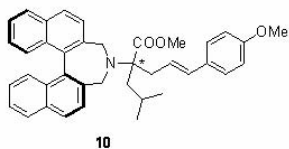
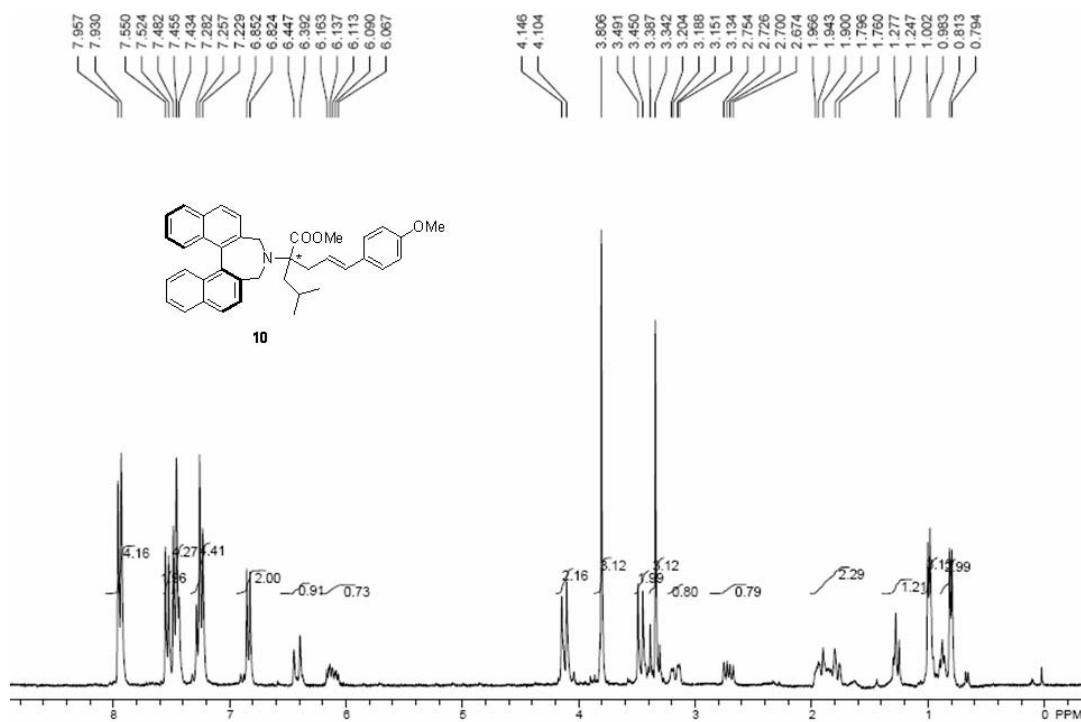
ZTC8039-C CDCl3 13C-NMR Apr 3 2010

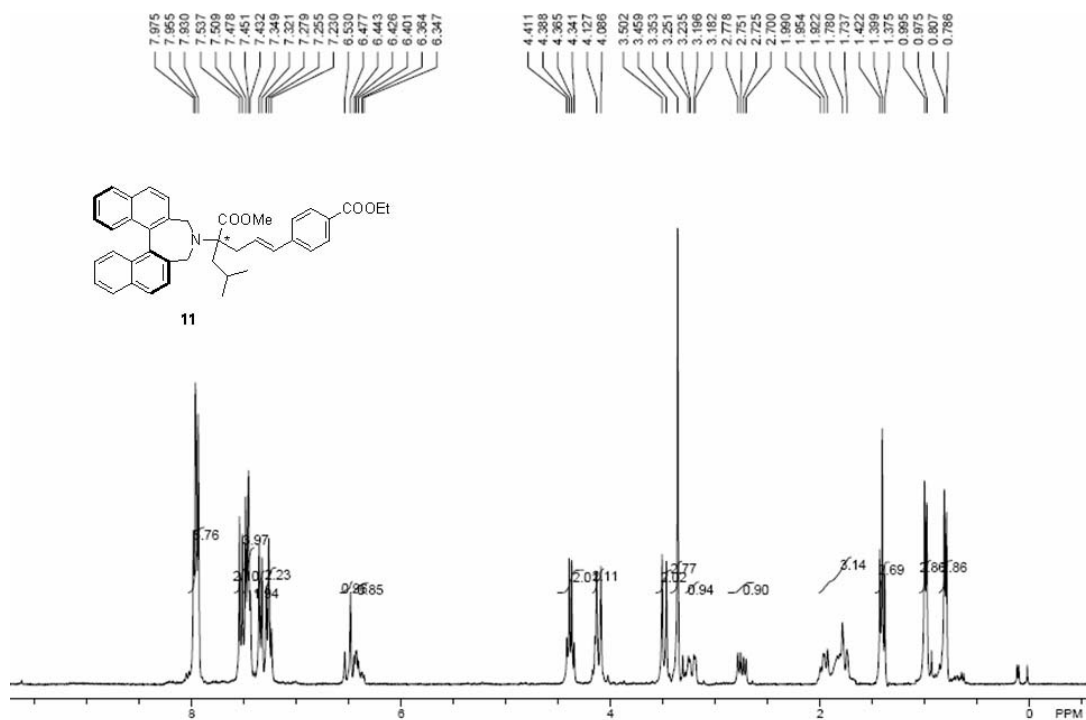




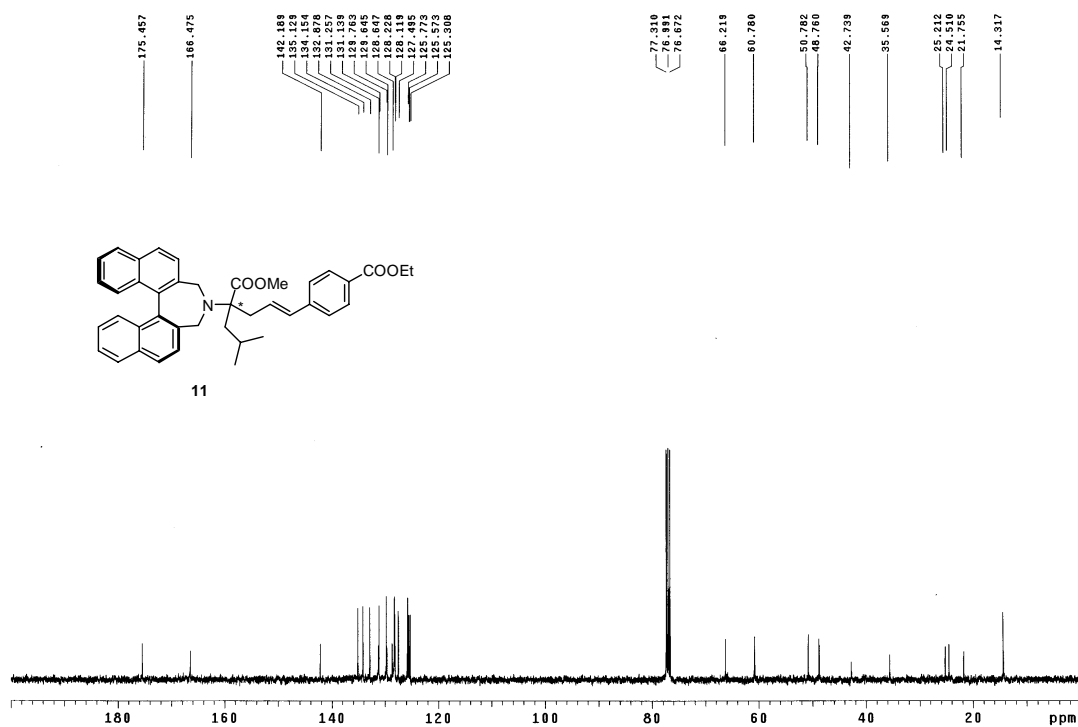


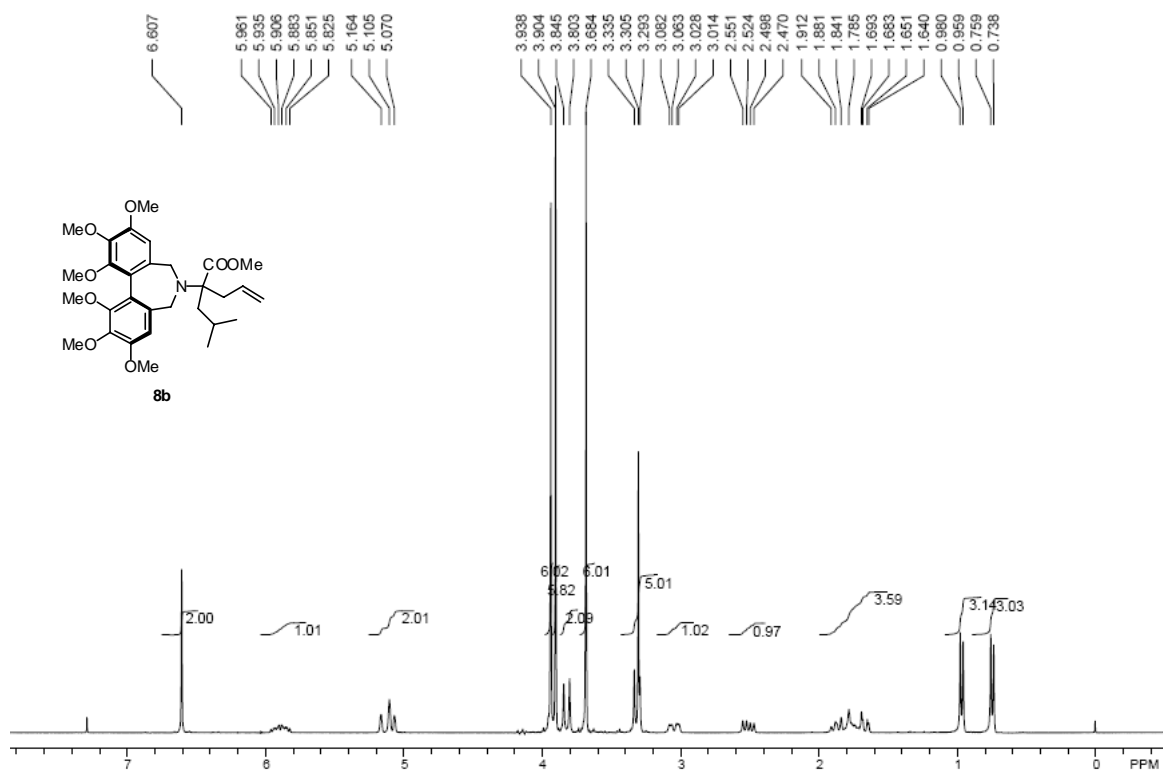






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