Electronic Supplementary Material (ESI) for ChemComm.

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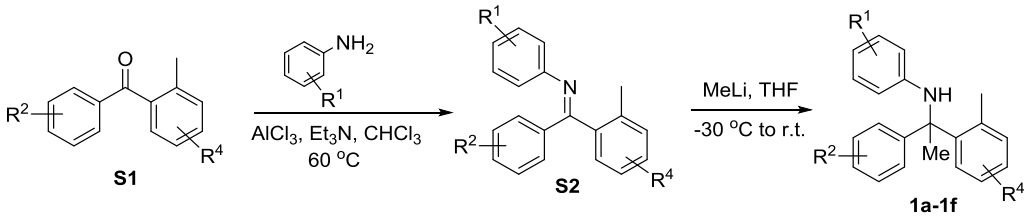
General Information:

Unless otherwise noted, all commercial reagents were used without further purification. Chloroform, toluene, ether, THF were purified by passage through an activated alumina column under argon. Thin-layer chromatography (TLC) analysis of reaction mixtures was performed using Huanghai silica gel HSGF254 TLC plates, and visualized under UV or by staining with ceric ammonium molybdate. Flash column chromatography was carried out on Huanghai Silica Gel HHGJ-300, 300-400 mesh. Nuclear magnetic resonance (NMR) spectra were recorded using Bruker Avance III HD spectrometer (FT, 500 MHz for ^{1}H, 126 MHz for ^{13}C, 471 MHz for ^{19}F, or 400 MHz for ^{1}H, 101 MHz for ^{13}C, 376 MHz for ^{19}F. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield of tetramethylsilane and referenced to residual solvent peak ($CDCl_3$, δH = 7.26 and δC = 77.16; d6-Acetone, δH = 2.05 and δC = 29.84). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance. FT-IR spectra were recorded on ThermoFisher Scientific Nicolet iS5 Spectrometer, and absorption frequencies are reported in reciprocal centimeters (cm^{-1}).Mass spectral data were obtained from the Agilent Technologies 6230 TOF LC/MS spectrometer in electrospray ionization (ESI^{+}) mode. Optical rotations were measured with an Autopol V Plus/VI digital polarimeter. X-Ray structure analyses were performed using a Bruker D8 Venture X-ray single crystal diffractometer and D8 Venture metalJet X-Ray single crystal diffractometer. Enantiomeric excesses were determined on an Agilent 1260 Chiral HPLC using IA, IB, IC, ID, IG columns. Racemic products were synthesized by carrying out the reactions using **(±)-TMEP** as catalyst.

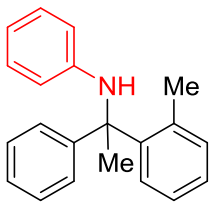
Synthesis of the racemicα-tertiary amine substrates



Under N_2 atmosphere, a solution of arylamines (1.2 eq) in Et_3N (12.0 eq) was added dropwisely to a solution of **S1** (10 mmol, 1.0 eq) and $AlCl_3$ (4.0 eq) in chloroform (40 mL) at 0 ^oC. After stirring at 60 ^oC (by oil bath) overnight, the reaction mixture was quenched with 1 N NaOH solution and filtered through celite. Then the filtrate was extracted with DCM for three times. The combined organic layer was dried over Na_2SO_4 and concentrated under vacuum to give a residue, which was purified by silica gel column chromatography (petroleoum:EtOAc:Et_3N, 400:2:1) to give product **S2**.

Under N_2 atmosphere, MeLi (12.0 mmol, 1.6 M, 4.0 eq) was added dropwisely into a solution of **S2** (3.0 mmol, 1.0 eq) in THF (20 mL) at -30 ^oC. After completion of the addition, the mixture was stirred overnight and slowly warmed up to room temperature. After the consumption of **S2** as monitored by TLC analysis, the reaction was quenched with saturated aqueous solution of NH_4Cl, and the mixture was extracted with EtOAc for 3 times. The combined organic layers were dried over Na_2SO, filtered and concentrated under vacuum to give a residue, which was purified by silica gel column chromatography (petroleoum:EtOAc, 200:1) to give the product **1** (**1a**-**1f**).

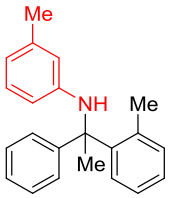
N-(1-phenyl-1-(*o*-tolyl)ethyl)aniline (**1a**)



1a was prepared in 2.3 mmol scale of **S2** and obtained as a white solid (660 mg, 98% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.33 – 7.27 (m, 4H), 7.27 – 7.19 (m,

3H), 7.08 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.05 – 6.97 (m, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.48 (d, *J* = 8.0 Hz, 2H), 4.46 (s, 1H), 2.10 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 145.9, 143.4, 137.2, 132.9, 128.8, 128.6, 128.4, 127.5, 127.0, 126.0, 125.8, 117.6, 115.8, 63.4, 29.2, 22.4. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{22}F_3N^+$ 288.1747; Found 288.1762.

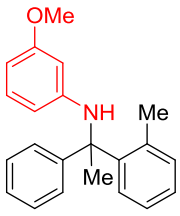
3-methyl-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline (**1b**)



^{13}C NMR (101 MHz, $CDCl_3$)

1b was prepared in 3.0 mmol scale of **S2** and obtained as a brown solid (810 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.31 – 7.18 (m, 7H), 7.08 (dd, *J* = 7.3, 1.8 Hz, 1H), 6.89 (t, *J* = 7.8 Hz, 1H), 6.47 (d, *J* = 7.5 Hz, 1H), 6.34 (s, 1H), 6.29 – 6.22 (m, 1H), 4.41 (s, 1H), 2.16 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 145.9, 143.5, 138.5, 137.2, 132.9, 128.7, 128.5, 128.4, 127.4, 126.9, 126.0, 125.8, 118.6, 116.8, 112.7, 63.3, 29.2, 22.4, 21.7. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{24}N^+$ 302.1904; Found 302.1922.

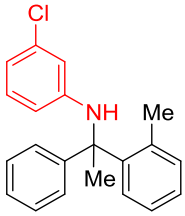
3-methoxy-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline (**1c**)



1c was prepared in 3 mmol scale of **S2** and obtained as yellow oil (937 mg, 98% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.27 – 7.09 (m, 7H), 7.00 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.84 (t, *J* = 8.1 Hz, 1H), 6.12 (dd, *J* = 8.1, 2.3 Hz, 1H), 6.04 (dd, *J* = 8.1, 2.2 Hz, 1H), 5.92 (t, *J* = 2.3 Hz, 1H), 4.42 (s, 1H), 3.49 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 148.2, 147.3, 143.3, 137.4, 132.9, 129.5, 128.6, 128.3, 127.5, 127.0,

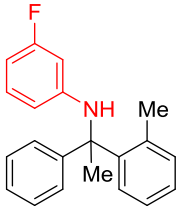
125.9, 125.9, 108.8, 103.2, 101.2, 63.4, 55.0, 29.5, 22.4. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{28}NO^+$ 322.2166; Found 322.2175.

3-chloro-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline (**1d**)



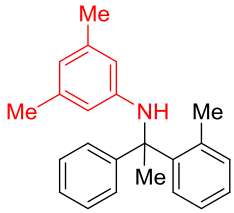
1d was prepared in 3.0 mmol scale as a white solid (892 mg, 93% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.26 – 7.10 (m, 7H), 7.00 (d, *J* = 7.3 Hz, 1H), 6.80 (t, *J* = 8.0 Hz, 1H), 6.49 (dd, *J* = 7.9, 2.0 Hz, 1H), 6.38 (q, *J* = 2.0 Hz, 1H), 6.23 (dd, *J* = 8.3, 2.2 Hz, 1H), 4.47 (s, 1H), 2.00 (s, 3H), 1.95 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 147.1, 142.7, 137.1, 134.4, 133.0, 129.8, 128.7, 128.3, 127.7, 127.2, 126.0, 125.8, 117.4, 115.2, 113.4, 63.4, 29.3, 22.4. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{21}ClN^+$ 322.1358; Found 322.1365.

3-fluoro-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline (**1e**)



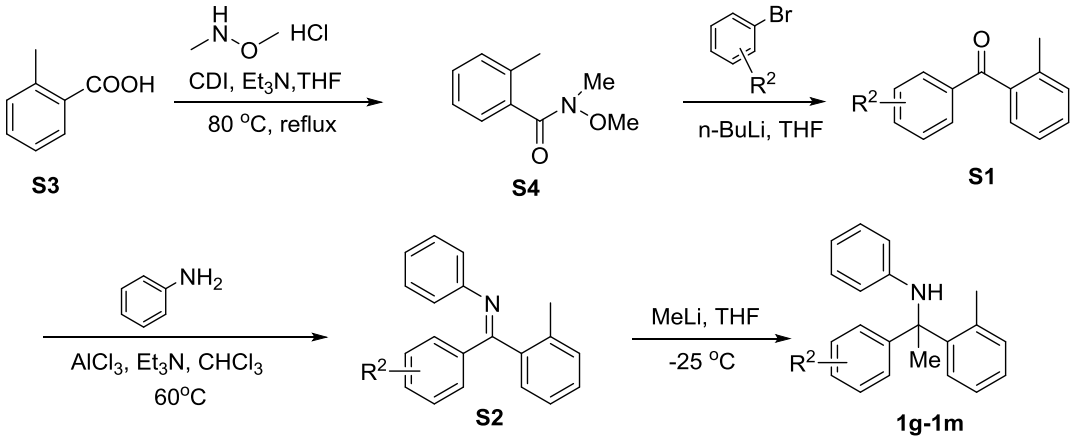
1e was prepared in 2 mmol scale of **S2** and obtained as a white solid (230 mg, 38% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 1H), 7.24-7.13 (m, 7H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.85 (q, *J* = 7.8 Hz, 1H), 6.22 (td, *J* = 8.2, 2.1 Hz, 1H), 6.19 – 6.14 (m, 1H), 6.05 (dd, *J* = 12.1, 2.4 Hz, 1H), 4.53 (s, 1H), 2.01 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6 (d, *J* = 242.0 Hz), 147.9, 147.6 (d, *J* = 10.9 Hz), 142.7, 137.2, 133.0, 129.8 (d, *J* = 10.4 Hz), 128.7, 128.3, 127.7, 127.2, 126.0, 125.9, 111.3, 103.9 (d, *J* = 21.7 Hz), 102.0 (d, *J* = 25.6 Hz), 63.4, 29.3, 22.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.9. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{21}FN^+$ 306.1653; Found 306.1657.

3,5-dimethyl-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline (**1f**)



1f was prepared in 3 mmol scale of **S2** and obtained as green oil (864 mg, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.25 – 7.09 (m, 7H), 6.99 (d, *J* = 7.3 Hz, 1H), 6.23 (s, 1H), 6.04 (s, 2H), 4.26 (s, 1H), 2.02 (s, 6H), 2.01 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 146.0, 143.7, 138.3, 137.2, 132.9, 128.5, 128.4, 127.4, 126.9, 126.0, 125.7, 119.7, 113.8, 63.3, 29.1, 22.4, 21.6. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{23}H_{26}N^+$ 316.2060; Found 316.2061.

Method B for the synthesis of substrate 1g-1m:

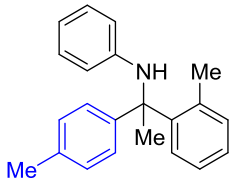


General Procedure of method B for Synthesis of substrate 1g-1m: To a stirred solution of commercially available benzoic acid **S3** (17.1 g, 100 mmol) in anhydrous THF (170 mL) was added 1,1′-carbonyldiimidazole (16.2 g, 100 mmol) at 65 °C (by oil bath) and stirred for 2 h. Then a suspension of *N*,*O*-dimethylhydroxylamine hydrochloride (9.7 g, 100 mmol) and Et_3N (14 mL, 100 mmol) in THF (30 mL) was added, and the reaction mixture was refluxed at 80 °C (by oil bath) overnight. When the reaction was completed as determined by TLC analysis, the reaction mixture was cooled to room temperature and filtered through Celite. Then the filtrate was concentrated in vacuo to give a residue, which was purified by flash column chromatography (petroleum ether/EtOAc = 10:1 to 5:1) to give the corresponding Weinreb amide **S4** (12.3 g, 69%).

Under N_2 atmosphere, n-BuLi (10 mmol 1.0 equiv) was added slowly to a solution of ArBr (10 mmol 1.0 equiv) in dry THF at -78 ^oC. After stirring for 30 min, the solution of **S4** (10 mmol in 10 mL THF, 1.0 equiv) was added slowly into the system. After stirring for 1 hour, the reaction mixture was quenched with saturated NH_4Cl solution, and the mixture was extracted with EtOAc for 3 times. The combined organic layer was washed with saturated NaCl solution, dried over with anhydrous Na_2SO_4, filtered and concentrated under vacuum to give a residue, which was purified by flash column chromatography (petroleum ether/EtOAc, 150:1 to 100:1) to yield the products **S1.**

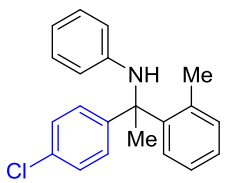
The same general procedures from **method A** were used for the synthesis substrates **1g-1m** starting from **S1**

N-(1-(o-tolyl)-1-(*p*-tolyl)ethyl)aniline (**1g**)



1g was prepared in 1.75 mmol scale of **S2** and obtained as a yellow solid (427 mg, 81% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.20 – 7.06 (m, 4H), 7.05 – 6.96 (m, 3H), 6.96 – 6.89 (m, 2H), 6.54 (t, *J* = 7.3 Hz, 1H), 6.43 – 6.32 (m, 2H), 4.35 (s, 1H), 2.24 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 146.0, 145.4, 143.5, 137.2, 136.5, 132.9, 129.2, 128.8, 128.4, 127.4, 125.9, 125.8, 117.5, 115.6, 63.1, 29.2, 22.5, 21.1. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{24}N^+$ 302.1904; Found 302.1919.

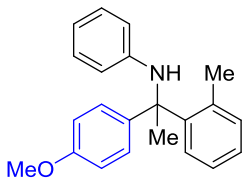
N-(1-(4-chlorophenyl)-1-(*o*-tolyl)ethyl)aniline (**1h**)



1h was prepared in 2.7 mmol scale of **S2** and obtained as yellow oil (509 mg, 59% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.46 (m, 1H), 7.25 – 7.08 (m, 6H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 2H), 6.57 (t, *J* = 7.3 Hz, 1H), 6.39 (t, *J* = 5.4 Hz, 2H), 4.26 (s, 1H), 2.00 (s,

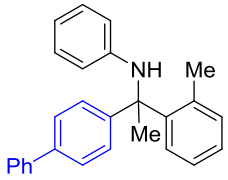
3H), 1.99 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.7, 145.7, 143.1, 137.0, 133.1, 132.7, 128.9, 128.6, 128.3, 127.7, 127.7, 126.0, 118.0, 116.1, 63.2, 29.1, 22.5. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{21}ClN^+$ 322.1358; Found 322.1362.

N-(1-(4-methoxyphenyl)-1-(*o*-tolyl)ethyl)aniline (**1i**)



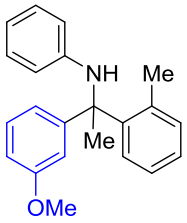
1i was prepared in 2.0 mmol scale of **S2** and obtained as a red solid (482 mg, 76% yield) with purified by flash neutral alumina (200-300 mesh) column chromatography. ^{1}H NMR (500 MHz, Acetone) δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.24 (dd, *J* = 7.8, 3.8 Hz, 3H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 6.91 (t, *J* = 7.7 Hz, 2H), 6.88 – 6.82 (m, 2H), 6.57 (d, *J* = 8.1 Hz, 2H), 6.51 (t, *J* = 7.3 Hz, 1H), 5.28 (s, 1H), 3.76 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, Acetone) δ 159.3, 147.5, 144.6, 140.9, 138.0, 133.4, 129.1, 129.1, 128.1, 128.0, 126.5, 117.5, 116.2, 114.2, 63.4, 55.5, 30.1, 22.5. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{24}NO^+$ 318.1853; Found 318.1851.

N-(1-([1,1'-biphenyl]-4-yl)-1-(*o*-tolyl)ethyl)aniline (**1j**)



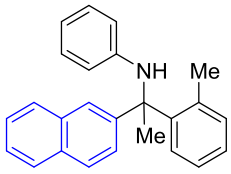
1j was prepared in 2.1mmol scale of **S2** and obtained as a yellow solid (672 mg, 88% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.47 – 7.40 (m, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.21 (m, 3H), 7.16 (dtd, *J* = 22.9, 7.4, 1.7 Hz, 2H), 7.01 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.97 – 6.90 (m, 2H), 6.56 (t, *J* = 7.3 Hz, 1H), 6.44 – 6.37 (m, 2H), 4.38 (s, 1H), 2.05 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.3, 145.9, 143.4, 140.6, 139.7, 137.2, 133.0, 128.9, 128.9, 128.4, 127.5, 127.4, 127.2, 127.1, 126.5, 125.9, 117.7, 115.8, 63.2, 29.2, 22.5. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{27}H_{26}N^+$ 364.2060; Found 364.2065.

N-(1-(3-methoxyphenyl)-1-(*o*-tolyl)ethyl)aniline (**1k**)



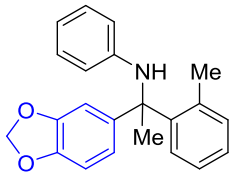
1k was prepared in 2.0 mmol scale of **S2** and obtained as a yellow solid (482 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.22 – 7.08 (m, 3H), 6.98 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.97 – 6.88 (m, 2H), 6.81 – 6.75 (m, 2H), 6.74 – 6.67 (m, 1H), 6.58 – 6.52 (m, 1H), 6.44 – 6.36 (m, 2H), 4.37 (s, 1H), 3.66 (s, 3H), 2.00 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 150.3, 145.9, 143.3, 137.2, 132.9, 129.5, 128.8, 128.4, 127.5, 125.8, 118.4, 117.6, 115.7, 112.7, 111.5, 63.3, 55.3, 29.2, 22.4. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{24}NO^+$ 318.1853; Found 318.1858.

N-(1-(naphthalen-2-yl)-1-(*o*-tolyl)ethyl)aniline (**1l**)



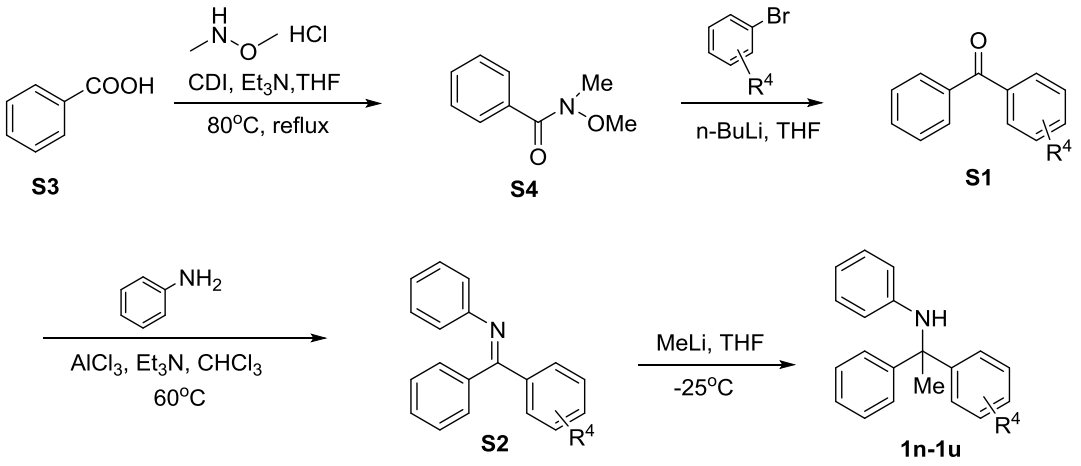
1l was prepared in 4.0 mmol scale of **S2** and obtained as yellow oil (170 mg) with the purification by flash column chromatography using neutral alumina (200-300 mesh). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.65 (m, 4H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.31 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.24 – 7.12 (m, 2H), 7.01 (d, *J* = 7.3 Hz, 1H), 6.94 (t, *J* = 7.7 Hz, 2H), 6.57 (t, *J* = 7.4 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 2H), 4.47 (s, 1H), 2.10 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.0, 145.5, 143.4, 137.2, 133.2, 133.0, 132.4, 128.9, 128.5, 128.4, 127.6, 127.6, 126.3, 126.1, 125.9, 124.9, 124.5, 117.8, 116.1, 63.6, 29.1, 22.5. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{25}H_{24}N^+$ 338.1904 ; Found 338.1901.

N-(1-(benzo[*d*][1,3]dioxol-5-yl)-1-(*o*-tolyl)ethyl)aniline (**1m**)

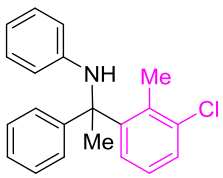


1m was prepared in 1.5 mmol scale of **S2** and obtained as a white solid (148 mg, 30% yield) with the purification by flash column chromatography using neutral alumina (200-300 mesh). ^{1}H NMR (500 MHz, Acetone) δ 7.64 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.25 (td, *J* = 7.7, 1.6 Hz, 1H), 7.19 (td, *J* = 7.4, 1.4 Hz, 1H), 7.10 – 7.05 (m, 1H), 6.95 – 6.89 (m, 2H), 6.84 (d, *J* = 1.9 Hz, 1H), 6.80 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.66 – 6.54 (m, 2H), 6.51 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.02 – 5.91 (m, 2H), 5.29 (s, 1H), 2.13 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, Acetone) δ 148.4, 147.2, 146.9, 144.4, 143.0, 137.8, 133.3, 129.0, 129.0, 127.9, 126.4, 120.0, 117.5, 116.1, 108.1, 107.7, 101.9, 63.6, 29.9, 22.4. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{22}NO_2^+$ 332.1646; Found 332.1643.

The same general procedures from method B were used for the synthesis substrates 1n-1u:

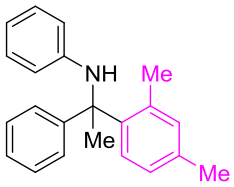


N-(1-(3-chloro-2-methylphenyl)-1-phenylethyl)aniline (**1n**)



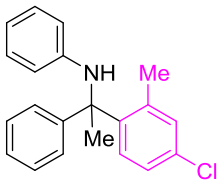
1n was prepared in 3.0 mmol scale of **S2** and obtained as a yellow solid (900 mg, 93% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.28 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.26 – 7.14 (m, 5H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.97 – 6.90 (m, 2H), 6.58 (t, *J* = 7.3 Hz, 1H), 6.41 – 6.33 (m, 2H), 4.32 (s, 1H), 2.02 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 145.8, 145.6, 137.1, 135.3, 128.9, 128.7, 127.2, 127.2, 126.3, 125.9, 118.1, 116.2, 63.8, 29.5, 18.8. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{21}ClN^+$ 322.1358; Found 322.1345.

N-(1-(2,4-dimethylphenyl)-1-phenylethyl)aniline (**1o**)



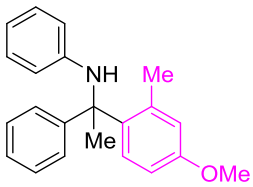
1o was prepared in 3.8 mmol scale of **S2** and obtained as yellow oil (873 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.18 (m, 4H), 7.18 – 7.12 (m, 1H), 6.99 – 6.95 (m, 1H), 6.95 – 6.88 (m, 2H), 6.81 (d, *J* = 1.9 Hz, 1H), 6.55 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.44 – 6.38 (m, 2H), 4.34 (s, 1H), 2.23 (s, 3H), 1.99 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 146.0, 140.5, 136.9, 136.9, 133.8, 128.8, 128.5, 128.4, 126.9, 126.4, 126.1, 117.5, 115.8, 63.2, 29.2, 22.3, 20.9. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{24}N^+$ 302.1904; Found 302.1901.

N-(1-(4-chloro-2-methylphenyl)-1-phenylethyl)aniline (**1p**)



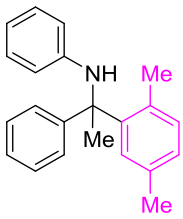
1p was prepared in 2.0mmol scale of **S2** and obtained as yellow oil (208 mg, 32% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.5 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.19 – 7.12 (m, 4H), 6.99 (s, 1H), 6.94 (t, *J* = 7.7 Hz, 2H), 6.58 (t, *J* = 7.3 Hz, 1H), 6.38 (d, *J* = 7.9 Hz, 2H), 4.30 (s, 1H), 1.98 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 145.6, 142.1, 139.3, 132.9, 132.6, 129.9, 128.9, 128.7, 127.2, 125.8, 125.8, 118.0, 115.9, 63.1, 29.2, 22.3. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{21}ClN^+$ 322.1358; Found 322.1348.

N-(1-(4-methoxy-2-methylphenyl)-1-phenylethyl)aniline (**1q**)



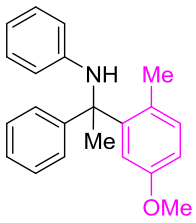
1q was prepared in 2.0 mmol scale of **S2** and obtained as a yellow solid (438 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.7 Hz, 1H), 7.29 (d, *J* = 4.3 Hz, 4H), 7.23 (q, *J* = 4.7 Hz, 1H), 7.05 – 6.97 (m, 2H), 6.77 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.69 – 6.58 (m, 2H), 6.56 – 6.42 (m, 2H), 4.42 (s, 1H), 3.80 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 148.7, 146.0, 138.8, 135.7, 129.5, 128.8, 128.5, 126.9, 126.0, 118.5, 117.6, 115.8, 110.3, 63.0, 55.2, 29.5, 22.6. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{24}NO^+$ 318.1853; Found 318.1838.

N-(1-(2,5-dimethylphenyl)-1-phenylethyl)aniline (**1r**)



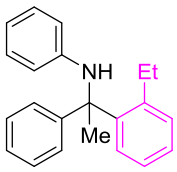
1r was prepared in 2.0 mmol scale of **S2** and obtained as a white solid (437 mg, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.21 (dt, *J* = 4.7, 1.5 Hz, 4H), 7.18 – 7.13 (m, 1H), 6.96 – 6.90 (m, 3H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.55 (t, *J* = 7.4 Hz, 1H), 6.43 – 6.38 (m, 2H), 4.34 (s, 1H), 2.30 (s, 3H), 2.00 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 146.0, 143.2, 135.1, 134.0, 132.8, 129.1, 128.8, 128.5, 128.0, 126.9, 126.1, 117.6, 115.8, 63.3, 29.2, 22.0, 21.6. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{24}N^+$ 302.1904; Found 302.1897.

N-(1-(5-methoxy-2-methylphenyl)-1-phenylethyl)aniline (**1s**)



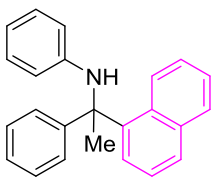
1s was prepared in 2.5 mmol scale of **S2** and obtained as a yellow solid (439 mg, 55% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 4.3 Hz, 4H), 7.23 (dd, *J* = 5.7, 2.6 Hz, 2H), 7.05 – 6.94 (m, 3H), 6.74 (dd, *J* = 8.3, 2.7 Hz, 1H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 2H), 4.43 (s, 1H), 3.80 (s, 3H), 2.07 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 148.1, 145.9, 144.8, 133.6, 129.1, 128.8, 128.6, 127.0, 126.0, 117.7, 115.8, 115.6, 111.3, 63.3, 55.4, 29.1, 21.5. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{24}NO^+$ 318.1853; Found 318.1841.

N-(1-(2-ethylphenyl)-1-phenylethyl)aniline (**1t**)

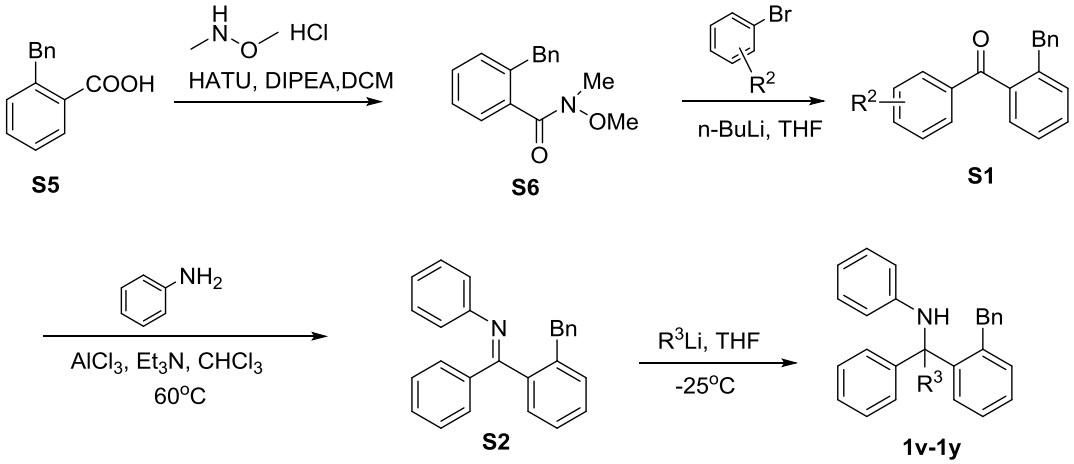


1t was prepared in 3.0 mmol scale of **S2** and obtained as yellow oil (790 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.30 (dt, *J* = 5.6, 2.7 Hz, 5H), 7.25 – 7.18 (m, 3H), 7.02 (ddd, *J* = 8.7, 7.3, 1.4 Hz, 2H), 6.64 (td, *J* = 7.3, 1.3 Hz, 1H), 6.52 – 6.44 (m, 2H), 4.40 (s, 1H), 2.49 (dddd, *J* = 12.8, 7.4, 4.6, 1.4 Hz, 2H), 2.08 (d, *J* = 1.4 Hz, 3H), 0.87 (td, *J* = 7.5, 1.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 146.2, 143.4, 143.3, 130.9, 128.8, 128.5, 128.1, 127.6, 126.8, 126.3, 125.5, 117.8, 116.3, 63.4, 29.3, 26.7, 15.1. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{24}N^+$ 302.1904; Found 302.1890.

N-(1-(naphthalen-1-yl)-1-phenylethyl)aniline (**1u**)



1u was prepared in 2 mmol scale of **S2** and obtained as yellow oil (512 mg, 79% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.8 Hz, 1H), 7.84 – 7.77 (m, 2H), 7.71 – 7.67 (m, 1H), 7.46 – 7.38 (m, 3H), 7.38 – 7.32 (m, 1H), 7.28 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.22 (qd, *J* = 7.9, 3.5 Hz, 2H), 7.03 – 6.95 (m, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.48 (d, *J* = 8.0 Hz, 2H), 4.57 (s, 1H), 2.24 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 146.0, 141.9, 135.1, 131.0, 129.2, 129.0, 128.7, 128.6, 127.4, 126.9, 126.9, 126.4, 125.3, 125.2, 125.0, 118.3, 117.2, 64.1, 29.1. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{24}H_{22}N^+$ 324.1747; Found 324.1736.



General Procedure of method C for the synthesis of substrate 1v-1y:

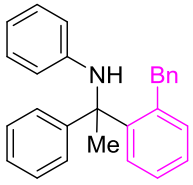
To a solution of 2-benzylbenzoic acid (2.12 g, 10 mmol, 1.0 eq) and N,O-dimethylhydroxylamine hydrochloride (1.94 g, 20 mmol, 2.0 eq) in DCM (50 mL) was added HATU (4.56 g, 12 mmol, 1.2 eq) and DIPEA (6.8 mL, 40 mmol, 4.0 eq) at rt. After stirring overnight, a saturated aqueous solution of sodium hydrogencarbonate was added to the reaction mixture, and the mixture was stirred for 30 minutes. The mixture was then extracted with DCM for three times, and the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to give a residue, which was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 6:1) to give **S6** (2.6g, 93%yield) as colorless oil.

The same general procedures from **method B** were used for the synthesis substrates **S2** starting from **S6.**

Under N_2 atmosphere, R^3Li (6.0 mmol, 2.0 eq) was added dropwisely into a solution of **S2** (3.0 mmol, 1.0 eq) in THF (20 mL) at -78 °C. After completion of the addition, the mixture was

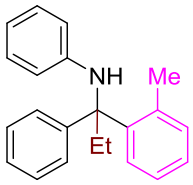
stirring for 3 hours at this temperature. Then the reaction was quenched with saturated aqueous solution of NH_4Cl, and the mixture was extracted with EtOAc for 3 times. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum at room temperature to give a residue, which was purified by column chromatography on neutral alumina (200-300 mesh) (petroleoum:EtOAc, 200:1) to give the product **1** (**1v**-**1y**).

N-(1-(2-benzylphenyl)-1-phenylethyl)aniline (**1v**)



1v was prepared in 2.0 mmol scale of **S2** and obtained as red oil (375 mg, 52% yield). ^{1}H NMR (500 MHz, Acetone) δ 7.75 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.35 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.31 – 7.23 (m, 2H), 7.18 (td, *J* = 7.5, 1.4 Hz, 1H), 7.10 (qd, *J* = 7.7, 3.7 Hz, 3H), 6.97 – 6.92 (m, 2H), 6.85 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.78 – 6.72 (m, 2H), 6.64 – 6.59 (m, 2H), 6.57 (td, *J* = 7.2, 1.2 Hz, 1H), 5.44 (s, 1H), 3.99 (d, *J* = 16.2 Hz, 1H), 3.86 (d, *J* = 16.1 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (126 MHz, Acetone) δ 149.2, 147.4, 144.6, 142.4, 141.5, 132.7, 130.2, 129.2, 129.1, 129.1, 128.9, 128.0, 127.5, 127.0, 126.6, 126.4, 117.9, 116.7, 63.9, 39.9, 30.5. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{27}H_{26}N^+$ 364.2060; Found 364.2056.

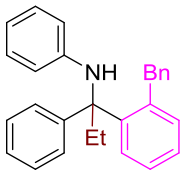
N-(1-phenyl-1-(*o*-tolyl)propyl)aniline (**1w**)



1w was prepared in 3 mmol scale of **S2** and obtained as a yellow solid (130 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.32 – 7.22 (m, 5H), 7.19 (qd, *J* = 6.9, 1.7 Hz, 2H), 7.05 – 6.91 (m, 3H), 6.62 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.51 – 6.39 (m, 2H), 4.59 (s, 1H), 2.78 (dq, *J* = 14.4, 7.3 Hz, 1H), 2.30 (dq, *J* = 14.2, 7.2 Hz, 1H), 2.02 (s, 3H), 0.71 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 145.3, 143.9, 137.8, 133.0, 128.8, 128.1, 127.6, 127.3,

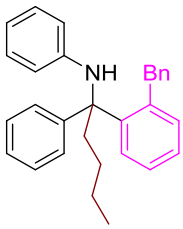
126.4, 126.3, 125.7, 117.9, 115.9, 65.4, 31.6, 22.1, 8.2. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{24}N^+$ 302.1904; Found 302.1894.

N-(1-(2-benzylphenyl)-1-phenylpropyl)aniline (**1x**)



1x was prepared in 4.0 mmol scale of **S2** and obtained as a yellow solid (90 mg). ^{1}H NMR (400 MHz, Acetone) δ 7.93 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.36 – 7.28 (m, 3H), 7.26 – 7.18 (m, 1H), 7.16 (td, *J* = 7.5, 1.3 Hz, 2H), 7.05 (dd, *J* = 5.1, 1.9 Hz, 3H), 6.97 – 6.88 (m, 2H), 6.80 – 6.74 (m, 1H), 6.67 – 6.52 (m, 5H), 5.52 (s, 1H), 4.02 (d, *J* = 16.1 Hz, 1H), 3.82 (d, *J* = 16.1 Hz, 1H), 2.87 (dq, *J* = 14.7, 7.4 Hz, 1H), 2.38 (dq, *J* = 14.2, 7.2 Hz, 1H), 0.71 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Acetone) δ 146.5, 145.7, 144.4, 141.9, 141.3, 131.9, 129.5, 128.5, 128.0, 127.9, 127.5, 127.0, 126.6, 126.3, 125.7, 125.5, 117.4, 115.9, 65.2, 38.5, 31.5, 7.5. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{28}H_{28}N^+$ 378.2217; Found 378.2204.

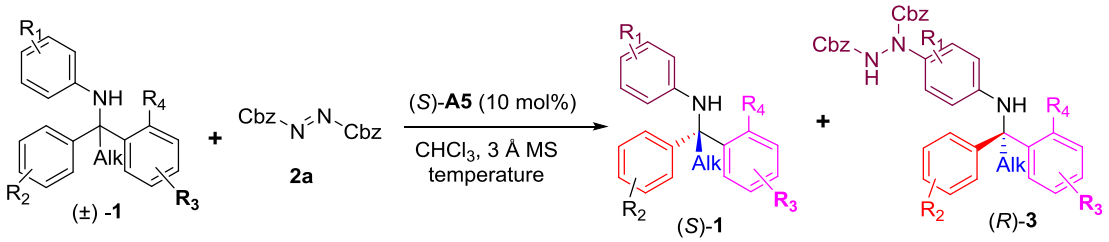
N-(1-(2-benzylphenyl)-1-phenylpentyl)aniline (**1y**)



1y was prepared in 4.0 mmol scale of **S2** and obtained as yellow oil (203 mg, 13% yield). ^{1}H NMR (400 MHz, Acetone) δ 7.93 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.49 (dd, *J* = 7.5, 1.7 Hz, 2H), 7.35 – 7.29 (m, 3H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.15 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.05 (dd, *J* = 5.1, 2.0 Hz, 2H), 6.95 – 6.89 (m, 2H), 6.80 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.66 – 6.59 (m, 4H), 6.56 (td, *J* = 7.3, 1.2 Hz, 1H), 5.52 (s, 1H), 4.02 (d, *J* = 16.1 Hz, 1H), 3.83 (d, *J* = 16.1 Hz, 1H), 2.82 – 2.75 (m, 1H), 2.37 (ddd, *J* = 13.2, 11.7, 4.1 Hz, 1H), 1.33 – 1.26 (m, 1H), 1.17 (qd, *J* = 7.0, 1.6 Hz, 2H), 1.06 – 0.93 (m, 1H), 0.72 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Acetone) δ 147.3, 146.8, 145.1, 142.6, 141.9, 132.8, 130.2, 129.2, 128.8, 128.7, 128.5, 127.8, 127.4, 127.0, 126.5, 126.3,

118.1, 116.8, 65.9, 39.9, 39.4, 26.5, 23.4, 14.3. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{30}H_{32}N^+$ 406.2530; Found 406.2516.

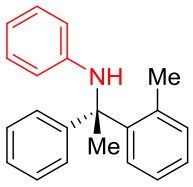
Kinetic resolution of α-tertiary amines 1



General procedure for kinetic resolution of α-tertiary amines 1: To a mixture of racemic **1** (0.2 mmol, 1.0 eq), dibenzyl azodicarboxylates **2a** (0.2 mmol, 1.0 eq), CPA (*S*)-**A5** (0.02 mmol, 10 mol%) and activated 3 Å MS (120 mg) was added anhydrous $CHCl_3$ (2 mL), which was precooled to the designated temperature. The reaction was allowed to stir at that temperature until achieving appropriate conversion as indicated by HPLC analysis of the reaction mixture. After adding several drops of Et_3N to quench the reaction, the mixture was concentrated under vacuum at 20 °C to give a residue, which was purified by column chromatography on silica gel or neutral alumina (200-300 mesh) to give the recovered SM (*S*)-**1** and product **3**.

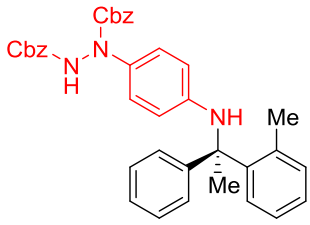
The reaction of **1a** was performed on 0.2 mmol scale for 23 h at -30 °C, which was purified by column chromatography on silica gel (petroleoum:EtOAc, 100:1 to 5:1) to give the recovered SM (*S*)-**1a** (25.4 mg, 44% yield) as a white solid and product **3a** (55.3 mg, 47% yield) as a yellow solid.

(*S*)-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1a**)



HPLC: Chiralpak IB column, 99:1 hexanes/isopropanol, 1 mL/min, t_R = 5.0 min (major), 6.3 min (minor), 94:6 er. $[\alpha]_D^{25}$ = +8.56 (c 1.0, CH_2Cl_2); m.p. 85-91 °C. IR (cm^{-1}): *f* = 3427, 2979, 1598, 1493, 746, 730, 701, 691.

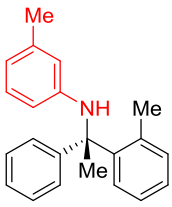
Dibenzyl-(*R*)-1-(4-((1-phenyl-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3a**)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 1H), 7.26 – 6.71 (m, 21H), 6.32 (d, *J* = 8.4 Hz, 2H), 5.06 (d, *J* = 14.8 Hz, 4H), 4.47 (s, 1H), 2.00 (s, 3H), 1.97 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 155.6, 148.0, 145.1, 143.0, 137.2, 136.1, 135.7, 133.0, 131.6, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.6, 127.0, 125.9, 115.3, 68.2, 67.9, 63.4, 29.1, 22.4. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{37}H_{34}N_3O_4^-$ 584.2554; Found 584.2567. HPLC: Chiralpak IB column, 80:20 hexanes/ isopropanol, 1 mL/min, t_R =25.8 min (major), 28.2 min (minor), 95:5 er. $[\alpha]_D^{25}$ = -3.04 (c 1.0, CH_2Cl_2) ; m.p. 70-75 °C. IR (cm^{-1}): *f* = 3364, 3290, 3031, 2852, 1715, 1609, 1513, 1489, 1219, 754, 730, 696.

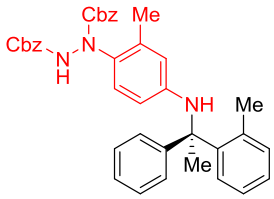
The reaction of **1b** was performed on 0.2 mmol scale for 22 h at -30 °C, which was purified by column chromatography on silica gel (petroleoum:EtOAc, 100:1 to 5:1) to give the recovered SM (*S*)-**1b** (27.6 mg, 46% yield) as green oil and product **3b** (59.6 mg, 50% yield) as a yellow solid.

(*S*)-3-methyl-N-(1-phenyl-1-(o-tolyl)ethyl)aniline ((*S*)-**1b**)



HPLC: Chiralpak IB column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 4.6 min (major), 5.2 min (minor), 98:2 er. $[\alpha]_D^{25}$ = +14.12 (c 1.0, CH_2Cl_2).

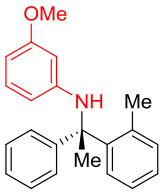
Dibenzyl(*R*)-1-(2-methyl-4-((1-phenyl-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3b**)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.35 – 7.03 (m, 19H), 6.26 (d, *J* = 20.4 Hz, 2H), 5.10 (t, *J* = 8.4 Hz, 4H), 4.52 (s, 1H), 2.07 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 155.2, 148.1, 145.9, 143.1, 139.6, 137.2, 136.2, 135.9, 135.7, 132.9, 130.7, 130.3, 128.6, 128.4, 128.4, 128.3, 128.0, 127.5, 127.5, 127.3, 127.0, 126.3, 125.9, 116.8, 113.1, 68.1, 67.8, 63.3, 29.1, 22.4, 17.9. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{38}H_{36}N_3O_4^-$ 598.2711; Found 598.2695. HPLC: Chiralpak IB column, 80:20 hexanes/ isopropanol, 1 mL/min, t_R = 16.9 min (minor), 20.1 min (major), 8:92 er. $[\alpha]_D^{25}$ = +0.58 (c 1.0, CH_2Cl_2) ; m.p. 80-87 ^{o}C.

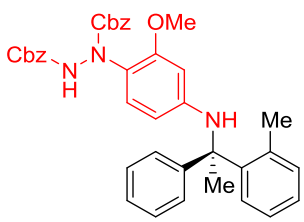
The reaction of **1c** was performed on 0.2 mmol scale for 21 h at -60 ^{o}C, which was purified by column chromatography on silica gel (petroleoum:EtOAc, 100:1 to 5:1) to give the recovered SM (*S*)-**1c** (25.7 mg, 40% yield) as red oil and product **3c** (66.5 mg, 54% yield) as a white solid.

(*S*)-3-methoxy-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1c**)



HPLC: Chiralpak IA column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 6.3 min (major), 6.7 min (minor), 96.5:3.5 er. $[\alpha]_D^{25}$ = -2.42 (c 1.0, CH_2Cl_2).

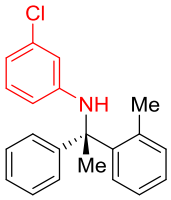
Dibenzyl-(*R*)-1-(2-methoxy-4-((1-phenyl-1-(o-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarb oxylate (**3c)**



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.6 Hz, 1H), 7.48 – 6.76 (m, 20H), 6.28 – 5.63 (m, 2H), 5.26 – 5.00 (m, 4H), 4.66 (s, 1H), 3.38 (d, *J* = 40.9 Hz, 3H), 2.08 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 155.9, 155.0, 154.9, 147.8, 147.2, 142.8, 137.6, 136.5, 135.8, 133.1, 129.9, 129.4, 128.6, 128.6, 128.3, 128.1, 127.8, 127.8, 127.7, 127.2, 127.1, 125.9, 125.7, 120.0, 119.5, 107.6, 107.3, 98.2, 98.1, 68.1, 67.8, 67.6, 63.3, 55.2, 55.0, 29.7, 22.3. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{38}H_{36}N_3O_5^-$ 614.2660; Found 614.2654. HPLC: Chiralpak IB column, 80:20 hexanes/ isopropanol, 1 mL/min, t_R = 16.7 min (minor), 19.5 min (major), 13.5:86.5 er. $[\alpha]_D^{25}$ = -1.46 (c 1.0, CH_2Cl_2) ; m.p. 75-82 °C.

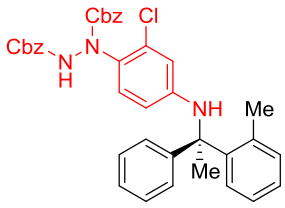
The reaction of **1d** was performed on 0.2 mmol scale for 60 h at -10 °C, which was purified by column chromatography on silica gel (petroleoum:EtOAc, 100:1 to 5:1) to give the recovered SM (*S*)-**1d** (30.5 mg, 48% yield) as a yellow solid and product **3d** (59.8 mg, 48% yield) as a white solid.

(*S*)-3-chloro-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1d**)



HPLC: Chiralpak IB column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 6.0 min (major), 9.5 min (minor), 93:7 er. $[\alpha]_D^{25}$ = +16.92 (c 1.0, CH_2Cl_2) ; m.p. 57-63 °C.

Dibenzyl-(*R*)-1-(2-chloro-4-((1-phenyl-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarbox ylate (**3d**)

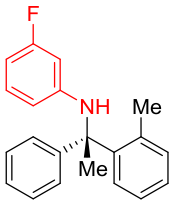


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (t, *J* = 5.7 Hz, 1H), 7.42 – 6.80 (m, 19H), 6.47 (d, *J* = 2.8 Hz, 1H), 6.41 – 6.12 (m, 1H), 5.33 – 5.01 (m, 4H), 4.73 (s, 1H), 2.07 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 155.8, 155.5, 155.2, 147.5, 146.9, 142.2, 142.2, 137.1, 136.0, 135.9, 135.6, 133.1, 133.1, 132.4, 130.8, 130.7, 130.2, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2,

128.0, 127.9, 127.8, 127.3, 127.3, 126.1, 125.7, 114.8, 113.9, 68.4, 68.2, 67.9, 67.8, 63.4, 63.4, 29.8, 29.1, 29.0, 22.4. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{37}H_{33}ClN_3O_4^-$ 618.2165; Found 618.2195. HPLC: Chiralpak IB column, 80:20 hexanes/ isopropanol, 1 mL/min, t_R = 18.4 min (minor), 21.4 min (major), 7.5:92.5 er. $[\alpha]_D^{25}$ = -3.24 (c 1.0, CH_2Cl_2) ; m.p. 72-77 °C.

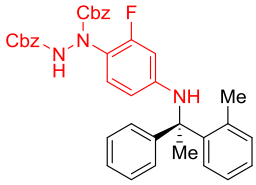
The reaction of **1e** was performed on 0.2 mmol scale for 120 h at -20 °C, which was purified by column chromatography on silica gel (petroleoum:EtOAc, 100:1 to 5:1) to give the recovered SM (*S*)-**1e** (28 mg, 46% yield) as a white solid and product **3e** (53.3 mg, 44% yield) as a yellow solid.

(*S*)-3-fluoro-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1e**)



HPLC: Chiralpak IB column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 5.7 min (major), 7.9 min (minor), 97.5:2.5 er. $[\alpha]_D^{25}$ = +7.36 (c 1.0, CH_2Cl_2) ; m.p. 80-87 °C.

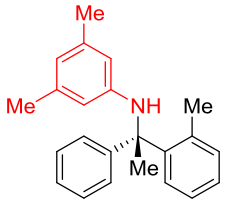
Dibenzyl-(*R*)-1-(2-fluoro-4-((1-phenyl-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarbox ylate (**3e**)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.41 – 6.77 (m, 19H), 6.22 (s, 1H), 6.11 (d, *J* = 13.0 Hz, 1H), 5.31 – 5.00 (m, 4H), 4.74 (s, 1H), 2.06 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0 (d, *J* = 246.8 Hz), 156.1, 155.7, 147.5, 147.3, 142.2, 137.1, 135.9, 135.6, 133.1, 129.7, 128.7, 128.6, 128.4, 128.2, 128.0, 127.8, 127.3, 127.2, 126.1, 125.7, 118.2, 110.9, 101.5 (d, *J* = 24.4 Hz), 68.3, 67.8, 63.4, 29.1, 22.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -120.8, -121.3, -121.5. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{37}H_{33}FN_3O_4^-$ 602.2460; Found 602.2506. HPLC: Chiralpak IB column, 80:20 hexanes/ isopropanol, 1 mL/min, t_R = 18.8 min (minor), 22.1 min (major), 10.5:89.5 er. $[\alpha]_D^{25}$ = -4.48 (c 1.0, CH_2Cl_2) ; m.p. 74-80 °C.

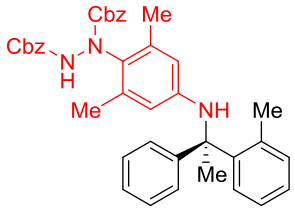
The reaction of **1f** was performed on 0.2 mmol scale for 130 h at -60 °C, which was purified by column chromatography on silica gel (petroleoum:EtOAc, 100:1 to 5:1) to give the recovered SM (*S*)-**1f** (30.7 mg, 49% yield) as green oil and product **3f** (57.9 mg, 47% yield) as a yellow solid.

(*S*)-3,5-dimethyl-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1f**)



HPLC: Chiralpak IB N-5 column, 100:0 hexanes/ isopropanol, 1 mL/min, t_R = 7.6 min (minor), 8.3 min (major), 11.5:88.5 er. $[\alpha]_D^{25}$ = -4.72 (c 1.0, CH_2Cl_2).

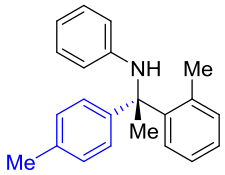
Dibenzyl-(*R*)-1-(2,6-dimethyl-4-((1-phenyl-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dica r-boxylate (**3f**)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (t, *J* = 6.6 Hz, 1H), 7.37 – 7.19 (m, 15H), 7.14 (dd, *J* = 6.6, 2.9 Hz, 1H), 7.08 (d, *J* = 6.7 Hz, 1H), 6.86 (d, *J* = 27.7 Hz, 1H), 6.14 (d, *J* = 6.2 Hz, 2H), 5.24 – 5.06 (m, 4H), 4.48 (s, 1H), 2.06 (d, *J* = 21.1 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5, 156.0, 155.0, 148.2, 145.7, 143.2, 137.2, 136.6, 136.2, 135.7, 133.0, 132.9, 129.2, 129.0, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.1, 128.0, 127.6, 127.5, 127.5, 127.0, 127.0, 125.9, 125.9, 125.8, 115.0, 114.9, 68.3, 68.2, 67.8, 63.3, 63.2, 29.2, 29.0, 22.4, 18.6, 18.5. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{39}H_{38}N_3O_4^-$ 612.2867; Found 612.2881. HPLC: Chiralpak IB N-5 column, 70:30 hexanes/ isopropanol, 1 mL/min, t_R = 21.1 min (minor), 25.2 min (major), 10.5:89.5 er. $[\alpha]_D^{25}$ = -1.12 (c 1.0, CH_2Cl_2) ; m.p. 71-79 °C.

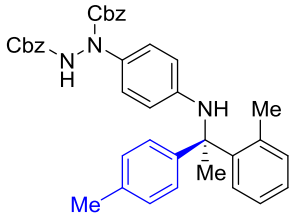
The reaction of **1g** was performed on 0.2 mmol scale for 86 h at -30 °C, which was purified by column chromatography on silica gel (petroleoum:EtOAc, 100:1 to 5:1) to give the recovered SM (*S*)-**1g** (30.1 mg, 50% yield) as yellow oil and product **3g** (53.7 mg, 45% yield) as a yellow solid.

(*S*)-*N*-(1-(*o*-tolyl)-1-(*p*-tolyl)ethyl)aniline ((*S*)-**1g**)



HPLC: Chiralpak IB column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 4.7 min (major), 5.9 min (minor), 90:10 er. $[\alpha]_D^{25}$ = +10.14 (c 1.0, CH_2Cl_2).

Dibenzyl (*R*)-1-(4-((1-(*o*-tolyl)-1-(*p*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3g)**

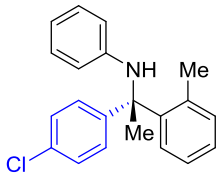


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.40 – 7.17 (m, 12H), 7.15 – 6.98 (m, 7H), 6.39 (d, *J* = 8.4 Hz, 2H), 5.13 (d, *J* = 14.8 Hz, 4H), 4.53 (s, 1H), 2.32 (s, 3H), 2.05 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 155.2, 145.1, 143.1, 137.2, 136.7, 136.1, 135.7, 132.9, 131.5, 129.3, 128.6, 128.5, 128.4, 128.3, 128.1, 127.5, 125.9, 125.8, 115.1, 68.2, 67.9, 63.1, 29.1, 22.5, 21.0. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{38}H_{36}N_3O_4^-$ 598.2711; Found 598.2706. HPLC: Chiralpak ID column, 80:20 hexanes/ isopropanol, 1 mL/min, t_R = 25.5 min (major), 28.6 min (minor), 94:6 er. $[\alpha]_D^{25}$ = -6.78 (c 1.0, CH_2Cl_2) ; m.p. 75-82 °C.

The reaction of **1h** was performed on 0.2 mmol scale for 35 h at -30 °C, which was purified by column chromatography on silica gel (petroleoum:EtOAc, 100:1 to 5:1) to give the

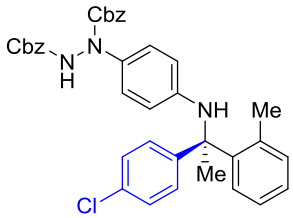
recovered SM (*S*)-**1h** (31.5 mg, 49% yield) as a yellow oil and product **3h** (60.5 mg, 49% yield) as a yellow solid.

(*S*)-*N*-(1-(4-chlorophenyl)-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1h**)



HPLC: Chiralpak IB column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 5.7 min (major), 9.5 min (minor), 97:3 er. $[\alpha]_D^{25}$ = +2.70 (c 1.0, CH_2Cl_2).

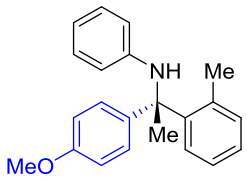
Dibenzyl-(*R*)-1-(4-((1-(4-chlorophenyl)-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarboxyl-ate (**3h)**



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.2 Hz, 1H), 7.38 – 6.83 (m, 20H), 6.38 (d, *J* = 8.4 Hz, 2H), 5.11 (d, *J* = 17.0 Hz, 4H), 4.46 (s, 1H), 2.05 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 155.5, 146.4, 144.7, 142.7, 136.9, 136.0, 135.6, 133.1, 132.8, 131.9, 128.6, 128.6, 128.5, 128.4, 128.3, 128.1, 127.7, 127.6, 126.0, 115.5, 68.2, 67.8, 63.1, 29.0, 22.4. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{37}H_{33}ClN_3O_4^-$ 618.2165; Found 618.2188. HPLC: Chiralpak IB column, 80:20 hexanes/ isopropanol, 1 mL/min, t_R = 17.7 min (minor), 20.2 min (major), 7:93 er. $[\alpha]_D^{25}$ = +0.90 (c 1.0, CH_2Cl_2) ; m.p. 74-81 ^{o}C.

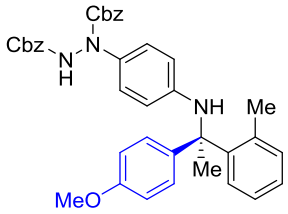
The reaction of **1i** was performed on 0.2 mmol scale for 83 h at -20 ^{o}C, which was purified by column chromatography on neutral alumina (200-300 mesh) (petroleoum:EtOAc, 100:1, 2:1 to 1:1) to give the recovered SM (*S*)-**1i** (30.3 mg, 48% yield) as a white solid and product **3i** (55.6 mg, 45% yield) as a yellow solid.

(*S*)-*N*-(1-(4-methoxyphenyl)-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1i**)



HPLC: Chiralpak IB N-5 column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 7.6 min (major), 9.4 min (minor), 95.5:4.5 er. $[\alpha]_D^{25}$ = +14.60 (c 1.0, CH_2Cl_2) ; m.p. 96-103 °C.

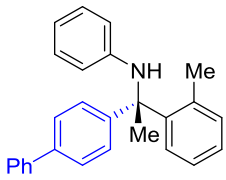
Dibenzyl-(*R*)-1-(4-((1-(4-methoxyphenyl)-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3i**)



^{1}H NMR (500 MHz, Acetone) δ 8.86 (m, *J* = 185.4 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.18 (m, 14H), 7.06 (m, 3H), 6.89 – 6.80 (m, 2H), 6.54 (d, *J* = 8.7 Hz, 2H), 5.50 (s, 1H), 5.12 (d, *J* = 3.7 Hz, 4H), 3.76 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, Acetone) δ 159.2, 157.0, 146.2, 144.3, 140.6, 137.9, 137.6, 137.5, 133.4, 132.8, 129.7, 129.2, 129.2, 129.1, 128.8, 128.7, 128.6, 128.2, 128.0, 126.5, 115.4, 114.2, 68.0, 67.5, 63.4, 55.4, 29.9, 22.6. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{38}H_{36}N_3O_5^-$ 614.2660; Found 614.2657. HPLC: Chiralpak IA column, 80:20 hexanes/ isopropanol, 1 mL/min, t_R = 20.0 min (major), 23.8 min (minor), 94:6 er. $[\alpha]_D^{25}$ = -3.74 (c 1.0, CH_2Cl_2) ; m.p. 67-73 °C.

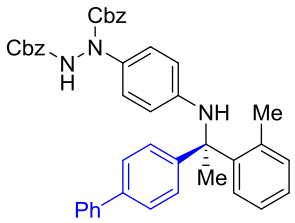
The reaction of **1j** was performed on 0.2 mmol scale for 59 h at -30 °C, which was purified by column chromatography on silica gel (petroleoum:EtOAc, 100:1, 5:1) to give the recovered SM (*S*)-**1j** (35.1 mg, 48% yield) as a yellow oil and product **3j** (62.5 mg, 47% yield) as a white solid.

(*S*)-*N*-(1-([1,1'-biphenyl]-4-yl)-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1j**)



HPLC: Chiralpak IB column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 7.9 min (major), 9.9 min (minor), 92.5:7.5 er. $[\alpha]_D^{25}$ = +6.80 (c 1.0, CH_2Cl_2).

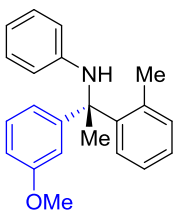
Dibenzyl-(*R*)-1-(4-((1-([1,1'-biphenyl]-4-yl)-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dic ar-boxylate (**3j**)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.28 (m, 15H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.06 (s, 1H), 6.42 (d, *J* = 8.4 Hz, 2H), 5.13 (d, *J* = 16.4 Hz, 4H), 4.58 (s, 1H), 2.10 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 155.6, 147.0, 145.0, 143.0, 140.5, 139.8, 137.2, 136.1, 135.7, 133.0, 131.7, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.6, 127.5, 127.2, 127.1, 126.4, 126.0, 115.3, 68.2, 67.9, 63.2, 29.1, 22.5. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{43}H_{38}N_3O_4^-$ 660.2867; Found 660.2865. HPLC: Chiralpak IA column, 70:30 hexanes/ isopropanol, 1 mL/min, t_R = 14.7 min (major), 22.0 min (minor), 95.5:4.5 er. $[\alpha]_D^{25}$ = -2.50 (c 1.0, CH_2Cl_2) ; m.p. 82-89 ^oC.

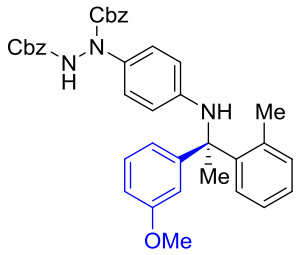
The reaction of **1k** was performed on 0.2 mmol scale for 59 h at -30 ^oC, which was purified by column chromatography on silica gel (petroleoum:EtOAc, 100:1, 5:1) to give the recovered SM (*S*)-**1k** (30.3 mg, 48% yield) as green oil and product **3k** (59.2 mg, 48% yield) as yellow oil.

(*S*)-*N*-(1-(3-methoxyphenyl)-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1k**)



HPLC: Chiralpak IB column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 7.2 min (major), 8.7 min (minor), 93.5:6.5 er. $[\alpha]_D^{25}$ = +7.2 (c 1.0, CH_2Cl_2).

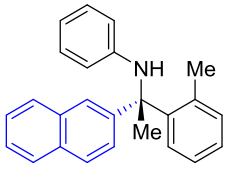
Dibenzyl-(*R*)-1-(4-((1-(3-methoxyphenyl)-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3k**)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.44 – 6.88 (m, 17H), 6.88 – 6.72 (m, 3H), 6.39 (d, *J* = 8.4 Hz, 2H), 5.12 (d, *J* = 16.0 Hz, 4H), 4.56 (s, 1H), 3.71 (s, 3H), 2.05 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 156.2, 155.5, 149.9, 145.0, 142.9, 137.2, 136.1, 135.7, 132.9, 131.6, 129.6, 128.6, 128.5, 128.4, 128.3, 128.1, 127.6, 126.7, 125.9, 118.3, 115.2, 112.6, 111.5, 68.2, 67.8, 63.3, 55.3, 29.0, 22.4. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{38}H_{36}N_3O_5^-$ 614.2660; Found 614.2664. HPLC: Chiralpak IB column, 80:20 hexanes/ isopropanol, 1 mL/min, t_R = 20.9 min (major), 22.8 min (minor), 94.5:5.5 er. $[\alpha]_D^{25}$ = +0.56 (c 1.0, CH_2Cl_2).

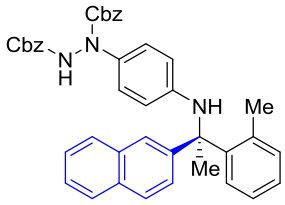
The reaction of **1l** was performed on 0.2 mmol scale for 59 h at -30 °C, which was purified by column chromatography on neutral alumina (200-300 mesh) (petroleoum:EtOAc, 200:1, 2:1 to 1:1) to give the recovered SM (*S*)-**1l** (32.8 mg, 48% yield) as yellow oil and product **3l** (57.4 mg, 45% yield) as a pink solid.

(*S*)-*N*-(1-(naphthalen-2-yl)-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1l**)



HPLC: Chiralpak IB column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 7.0 min (major), 8.0 min (minor), 95.5:4.5 er. $[\alpha]_D^{25}$ = -9.74 (c 1.0, CH_2Cl_2).

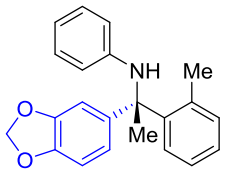
Dibenzyl-(*R*)-1-(4-((1-(naphthalen-2-yl)-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarboxyl-ate (**3l**)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dq, *J* = 19.1, 3.3 Hz, 4H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.45 (dt, *J* = 6.0, 2.9 Hz, 2H), 7.37 – 6.81 (m, 17H), 6.45 (d, *J* = 8.4 Hz, 2H), 5.12 (d, *J* = 17.7 Hz, 4H), 4.65 (d, *J* = 6.4 Hz, 1H), 2.15 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 155.3, 145.2, 143.0, 137.2, 136.0, 135.7, 133.2, 133.0, 132.4, 131.8, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 128.1, 127.7, 127.6, 127.1, 126.3, 126.2, 125.9, 124.7, 124.4, 115.5, 68.2, 67.8, 63.5, 28.9, 22.4. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{41}H_{36}N_3O_4^-$ 634.2711; Found 634.2708. HPLC: Chiralpak IA column, 80:20 hexanes/ isopropanol, 1 mL/min, t_R = 20.8 min (major), 27.7 min (minor), 92.5:7.5 er. $[\alpha]_D^{25}$ = +7.26 (c 1.0, CH_2Cl_2) ; m.p. 84-88 °C.

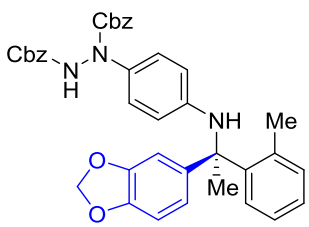
The reaction of **1m** was performed on 0.2 mmol scale for 125 h at -30 °C, which was purified by column chromatography on neutral alumina (200-300 mesh) (petroleoum:EtOAc, 100:1, 2:1 to 1:1) to give the recovered SM (*S*)-**1m** (29.8 mg, 45% yield) as red oil and product **3m** (59.2 mg, 47% yield) as a yellow solid.

(*S*)-*N*-(1-(benzo[d][1,3]dioxol-5-yl)-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1m**)



HPLC: Chiralpak IB column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 7.1 min (major), 8.3 min (minor), 91:9 er. $[\alpha]_D^{25}$ = +11.54 (c 1.0, CH_2Cl_2).

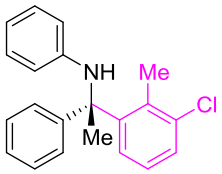
Dibenzyl-(*R*)-1-(4-((1-(benzo[d][1,3]dioxol-5-yl)-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1, 2-di-carboxylate (**3m**)



^{1}H NMR (500 MHz, Acetone) δ 8.86 (m, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.23 (m, 10H), 7.23 – 7.17 (m, 1H), 7.07 (dd, *J* = 15.2, 7.8 Hz, 3H), 6.84 (d, *J* = 1.9 Hz, 1H), 6.81 – 6.72 (m, 2H), 6.56 (d, *J* = 8.7 Hz, 2H), 5.96 (q, *J* = 1.1 Hz, 2H), 5.51 (s, 1H), 5.12 (d, *J* = 3.9 Hz, 4H), 2.12 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, Acetone) δ 157.1, 155.7, 148.6, 147.1, 145.9, 144.3, 142.9, 137.9, 137.6, 137.5, 133.5, 132.9, 129.2, 129.2, 129.1, 128.8, 128.8, 128.6, 128.3, 128.2, 126.6, 120.1, 115.6, 108.3, 107.8, 107.8, 102.1, 68.0, 67.5, 63.8, 30.0, 22.6. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{38}H_{34}N_3O_6^-$ 628.2453; Found 628.2453. HPLC: Chiralpak IB column, 60:40 hexanes/ isopropanol, 1 mL/min, t_R = 11.1 min (major), 13.2 min (minor), 92.5:7.5 er. $[\alpha]_D^{25}$ = -2.26 (c 1.0, CH_2Cl_2) ; m.p. 80-85 °C.

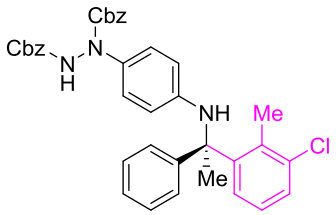
The reaction of **1n** was performed on 0.2 mmol scale for 59 h at -30 °C, which was purified by column chromatography on neutral alumina (200-300 mesh) (petroleoum:EtOAc, 100:1, 2:1 to 1:1) to give the recovered SM (*S*)-**1n** (31.6 mg, 49% yield) as a white solid and product **3n** (57.2 mg, 46% yield) as yellow oil.

(*S*)-*N*-(1-(3-chloro-2-methylphenyl)-1-phenylethyl)aniline ((*S*)-**1n**)



HPLC: Chiralpak IB column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 5.8 min (major), 8.3 min (minor), 94.5:5.5 er. $[\alpha]_D^{25}$ = -14.92 (c 1.0, CH_2Cl_2) ; m.p. 87-92 °C.

Dibenzyl-(*R*)-1-(4-((1-(3-chloro-2-methylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-di-carboxylate (**3n**)

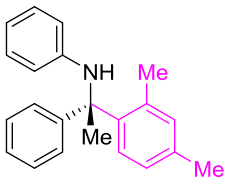


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.35 – 7.21 (m, 15H), 7.18 (t, *J* = 7.9 Hz, 1H), 7.14 – 6.84 (m, 3H), 6.38 (d, *J* = 8.4 Hz, 2H), 5.14 (d, *J* = 13.8 Hz,

4H), 4.52 (s, 1H), 2.09 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 155.4, 147.5, 145.4, 144.7, 137.1, 136.0, 135.7, 135.2, 132.0, 128.8, 128.8, 128.6, 128.5, 128.4, 128.3, 128.1, 127.6, 127.2, 127.1, 126.3, 125.8, 115.6, 68.2, 67.8, 63.8, 29.4, 18.8. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{37}H_{33}ClN_3O_4^-$ 618.2165; Found 618.2151. HPLC: Chiralpak IB column, 80:20 hexanes/isopropanol, 1 mL/min, t_R = 18.4 min (minor), 19.7 min (major), 5.5:94.5 er. $[\alpha]_D^{25}$ = +23.76 (c 1.0, CH_2Cl_2).

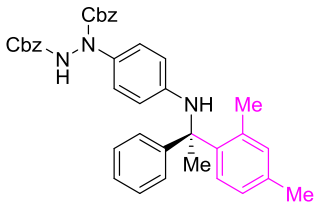
The reaction of **1o** was performed on 0.2 mmol scale for 183 h at -30 °C, which was purified by column chromatography on neutral alumina (200-300 mesh) (petroleoum:EtOAc, 100:1, 2:1 to 1:1) to give the recovered SM (*S*)-**1o** (28.4 mg, 47% yield) as yellow oil and product **3o** (55 mg, 45% yield) as a yellow solid.

(*S*)-*N*-(1-(2,4-dimethylphenyl)-1-phenylethyl)aniline ((*S*)-**1o**)



HPLC: Chiralpak IB column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 4.7 min (major), 6.2 min (minor), 91.5:8.5 er. $[\alpha]_D^{25}$ = +2.68 (c 1.0, CH_2Cl_2).

Dibenzyl-(*R*)-1-(4-((1-(2,4-dimethylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-dicar-boxylate (**3o**)

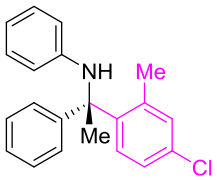


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 1H), 7.25 – 6.74 (m, 20H), 6.33 (d, *J* = 8.4 Hz, 2H), 5.05 (d, *J* = 16.0 Hz, 4H), 4.45 (s, 1H), 2.23 (s, 3H), 1.97 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 155.5, 155.2, 148.2, 145.2, 140.0, 137.0, 136.9, 136.1, 135.7, 133.8, 131.5, 128.6, 128.6, 128.5, 128.4, 128.3, 128.1, 126.9, 126.5, 125.9, 115.2, 68.2, 67.9, 63.1, 29.1, 22.3, 20.9. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{38}H_{36}N_3O_4^-$ 598.2711; Found

598.2700. HPLC: Chiralpak IB column, 80:20 hexanes/ isopropanol, 1 mL/min, t_R = 14.7 min (minor), 16.4 min (major), 4.5:95.5 er. $[\alpha]_D^{25}$ = +6.48 (c 1.0, CH_2Cl_2) ; m.p. 70-75 ^oC.

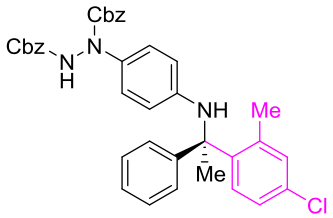
The reaction of **1p** was performed on 0.2 mmol scale for 34 h at -20 ^oC, which was purified by column chromatography on neutral alumina (200-300 mesh) (petroleoum:EtOAc, 100:1, 2:1 to 1:1) to give the recovered SM (*S*)-**1p** (29.1mg, 45% yield) as yellow oil and product **3p** (53.2 mg, 43% yield) as a yellow solid.

(*S*)-*N*-(1-(4-chloro-2-methylphenyl)-1-phenylethyl)aniline ((*S*)-**1p**)



HPLC: Chiralpak IB N-5 column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 7.0 min (major), 12.2 min (minor), 90:10 er. $[\alpha]_D^{25}$ = +1.84 (c 1.0, CH_2Cl_2).

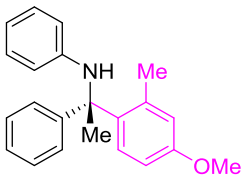
Dibenzyl-(*R*)-1-(4-((1-(4-chloro-2-methylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-di-carboxylate (**3p**)



^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.4 Hz, 1H), 7.33 – 7.16 (m, 17H), 7.06 (m, 3H), 6.38 (d, *J* = 8.4 Hz, 2H), 5.12 (d, *J* = 16.6 Hz, 4H), 4.49 (s, 1H), 2.04 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 155.2, 147.4, 144.7, 141.6, 139.3, 136.0, 135.6, 133.0, 132.6, 131.9, 129.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.7, 127.2, 126.2, 125.8, 125.7, 115.3, 68.2, 67.8, 63.0, 29.1, 22.2. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{37}H_{33}ClN_3O_4^-$ 618.2165; Found 618.2162. HPLC: Chiralpak IB N-5 column, 70:30 hexanes/ isopropanol, 1 mL/min, t_R = 18.9 min (minor), 22.3 min (major), 11.5:88.5 er. $[\alpha]_D^{25}$ = +6.92 (c 1.0, CH_2Cl_2) ; m.p. 69-75 ^oC.

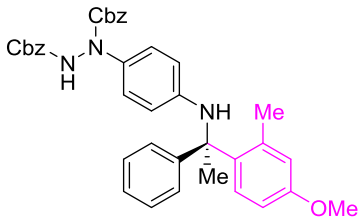
The reaction of **1q** was performed on 0.2 mmol scale for 65 h at -30 °C, which was purified by column chromatography on neutral alumina (200-300 mesh) (petroleoum:EtOAc, 100:1, 2:1 to 1:1) to give the recovered SM (*S*)-**1q** (30.2mg, 48% yield) as a white solid and product **3q** (54.4 mg, 44% yield) as a yellow solid.

(*S*)-*N*-(1-(4-methoxy-2-methylphenyl)-1-phenylethyl)aniline ((*S*)-**1q**)



HPLC: Chiralpak IB N-5 column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 7.9 min (major), 11.4 min (minor), 93:7 er. $[\alpha]_D^{25}$ = +6.2 (c 1.0, CH_2Cl_2) ; m.p. 85-92 °C.

Dibenzyl(*R*)-1-(4-((1-(4-methoxy-2-methylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1, 2-di-carboxylate (**3q**)

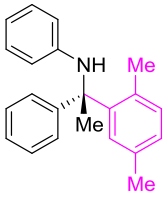


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.7 Hz, 1H), 7.26 (m, 15H), 7.12 – 6.71 (m, 4H), 6.64 (d, *J* = 2.8 Hz, 1H), 6.41 (d, *J* = 8.4 Hz, 2H), 5.14 (d, *J* = 14.1 Hz, 4H), 4.53 (s, 1H), 3.80 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 156.2, 155.2, 148.3, 145.1, 138.8, 136.0, 135.7, 135.2, 131.5, 129.4, 128.6, 128.5, 128.5, 128.4, 128.2, 128.1, 127.4, 126.9, 125.8, 118.5, 115.2, 110.3, 68.2, 67.8, 62.9, 55.1, 29.4, 22.5. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{38}H_{36}ClN_3O_5^-$ 614.2660; Found 614.2649. HPLC: Chiralpak IB N-5 column, 80:20 hexanes/ isopropanol, 1 mL/min, t_R = 36.2 min (minor), 39.8 min (major), 5:95 er. $[\alpha]_D^{25}$ = +16.56 (c 1.0, CH_2Cl_2) ; m.p. 74-78 °C.

The reaction of **1r** was performed on 0.2 mmol scale for 83 h at -30 °C, which was purified by column chromatography on neutral alumina (200-300 mesh) (petroleoum:EtOAc, 100:1, 2:1

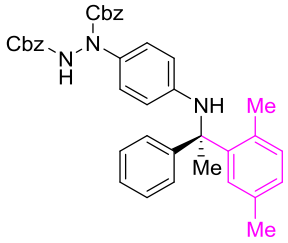
to 1:1) to give the recovered SM (*S*)-**1r** (29.3mg, 49% yield) as a white solid and product **3r** (59.5 mg, 49% yield) as yellow solid.

(*S*)-*N*-(1-(2,5-dimethylphenyl)-1-phenylethyl)aniline ((*S*)-**1r**)



HPLC: Chiralpak IB column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 5.2 min (major), 6.0 min (minor), 95.5:4.5 er. $[\alpha]_D^{25}$ = +61.4 (c 1.0, CH_2Cl_2) ; m.p. 91-98 ^oC.

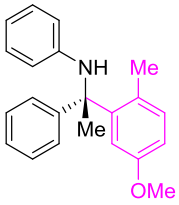
Dibenzyl-(*R*)-1-(4-((1-(2,5-dimethylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-dicar -boxylate (**3r**)



^1H NMR (500 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.28 – 6.74 (m, 20H), 6.32 (d, *J* = 8.4 Hz, 2H), 5.05 (d, *J* = 15.8 Hz, 4H), 4.45 (s, 1H), 2.29 (s, 3H), 1.97 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 155.0, 148.1, 145.1, 142.8, 136.1, 135.7, 135.1, 134.0, 132.9, 131.5, 129.0, 128.6, 128.5, 128.5, 128.4, 128.3, 128.1, 127.7, 127.1, 126.9, 125.9, 115.2, 68.2, 67.8, 63.3, 29.1, 21.9, 21.5. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{38}H_{36}N_3O_4^-$ 598.2711; Found 598.2688. HPLC: Chiralpak IB column, 80:20 hexanes/ isopropanol, 1 mL/min, t_R = 13.5 min (minor), 14.4 min (major), 2.5:97.5 er. $[\alpha]_D^{25}$ = -31.32 (c 1.0, CH_2Cl_2) ; m.p. 65-70 ^oC.

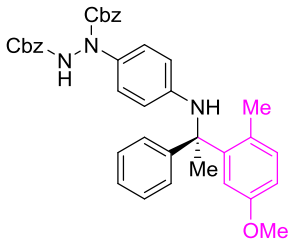
The reaction of **1s** was performed on 0.2 mmol scale for 82 h at -20 ^oC, which was purified by column chromatography on neutral alumina (200-300 mesh) (petroleoum:EtOAc, 100:1, 2:1 to 1:1) to give the recovered SM (*S*)-**1s** (30.0mg, 47% yield) as yellow oil and product **3s** (51.8 mg, 42% yield) as a yellow solid.

(*S*)-*N*-(1-(5-methoxy-2-methylphenyl)-1-phenylethyl)aniline ((*S*)-**1s**)



HPLC: Chiralpak IB N-5 column, 99:1 hexanes/ethanol, 1 mL/min, t_R = 8.3 min (major), 8.8 min (minor), 93:7 er. $[\alpha]_D^{25}$ = +57.92 (c 1.0, CH_2Cl_2).

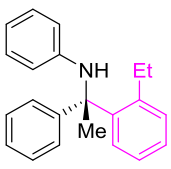
Dibenzyl(*R*)-1-(4-((1-(5-methoxy-2-methylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1, 2-di-carboxylate (**3s**)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 6.84 (m, 20H), 6.74 (dd, *J* = 8.2, 2.7 Hz, 1H), 6.42 (d, *J* = 8.4 Hz, 2H), 5.13 (d, *J* = 14.7 Hz, 4H), 4.54 (s, 1H), 3.78 (s, 3H), 2.04 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 156.2, 155.2, 147.8, 145.0, 144.4, 136.1, 135.7, 133.7, 131.6, 129.0, 128.6, 128.6, 128.5, 128.4, 128.3, 128.1, 127.7, 127.1, 125.9, 115.6, 115.2, 111.3, 68.2, 67.8, 63.3, 55.3, 29.0, 21.4. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{38}H_{36}N_3O_5^-$ 614.2660; Found 614.2648. HPLC: Chiralpak IA column, 80:20 hexanes/ ethanol, 1 mL/min, t_R = 23.9 min (minor), 34.8 min (major), 4:96 er. $[\alpha]_D^{25}$ = -33.32 (c 1.0, CH_2Cl_2) ; m.p. 73-79 ^{o}C.

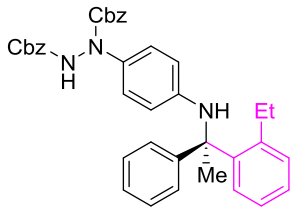
The reaction of **1t** was performed on 0.2 mmol scale for 65 h at -20 ^{o}C, which was purified by column chromatography on neutral alumina (200-300 mesh) (petroleoum:EtOAc, 100:1, 2:1 to 1:1) to give the recovered SM (*S*)-**1t** (28.0mg, 47% yield) as pink oil and product **3t** (53.4 mg, 45% yield) as a yellow solid.

(*S*)-*N*-(1-(2-ethylphenyl)-1-phenylethyl)aniline ((*S*)-**1t**)



HPLC: Chiralpak IB N-5 column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 5.6 min (major), 6.9 min (minor), 93.5:6.5 er. $[\alpha]_D^{25}$ = +12.68 (c 1.0, CH_2Cl_2).

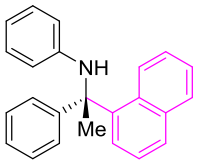
Dibenzyl-(*R*)-1-(4-((1-(2-ethylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-dicarboxyl ate (**3t**)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.9 Hz, 1H), 7.39 – 6.80 (m, 21H), 6.40 (d, *J* = 8.4 Hz, 2H), 5.12 (d, *J* = 15.3 Hz, 4H), 4.51 (s, 1H), 2.54 – 2.39 (m, *J* = 7.3 Hz, 2H), 2.05 (s, 3H), 0.85 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 155.2, 148.4, 145.2, 143.3, 143.0, 136.0, 135.7, 131.7, 130.9, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.7, 127.5, 127.1, 126.9, 126.1, 125.5, 115.7, 68.2, 67.8, 63.4, 29.2, 26.6, 15.1. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{38}H_{36}N_3O_4^-$ 598.2711; Found 598.2689. HPLC: Chiralpak IB N-5 column, 80:20 hexanes/ isopropanol, 1 mL/min, t_R = 28.7 min (minor), 31.4 min (major), 10.5:89.5 er. $[\alpha]_D^{25}$ = +9.44 (c 1.0, CH_2Cl_2) ; m.p. 66-71 ^{o}C.

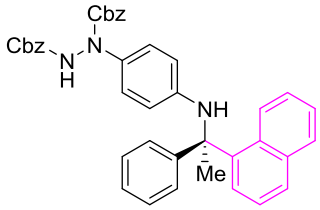
The reaction of **1u** was performed on 0.2 mmol scale for 95 h at -10 ^{o}C, which was purified by column chromatography on neutral alumina (200-300 mesh) (petroleoum:EtOAc, 100:1, 2:1 to 1:1) to give the recovered SM (*S*)-**1u** (31.6 mg, 49% yield) as a yellow oil and product **3u** (60.4 mg, 49% yield) as a yellow solid.

(*S*)-*N*-(1-(naphthalen-1-yl)-1-phenylethyl)aniline ((*S*)-**1u**)



HPLC: Chiralpak IB N-5 column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 7.9 min (major), 8.9 min (minor), 88.5:11.5 er. $[\alpha]_D^{25}$ = -24.00 (c 1.0, CH_2Cl_2).

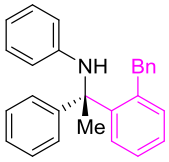
Dibenzyl-(*R*)-1-(4-((1-(naphthalen-1-yl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-dicarbox ylate (**3u**)



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 1H), 7.80 (t, *J* = 8.6 Hz, 2H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.39 – 7.31 (m, 3H), 7.31 – 7.15 (m, 14H), 7.13 – 6.81 (m, 3H), 6.40 (d, *J* = 8.5 Hz, 2H), 5.10 (d, *J* = 17.5 Hz, 4H), 4.66 (s, 1H), 2.22 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 155.4, 147.5, 145.0, 141.5, 136.0, 135.6, 135.1, 132.1, 130.9, 129.2, 129.1, 128.6, 128.5, 128.4, 128.3, 128.1, 127.7, 127.2, 127.0, 126.8, 126.4, 125.8, 125.6, 125.3, 125.2, 124.9, 116.5, 68.2, 67.8, 64.1, 28.9. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{40}H_{34}N_3O_4^-$ 620.2554; Found 620.2539. HPLC: Chiralpak IG column, 70:30 hexanes/ isopropanol, 1 mL/min, t_R = 21.1 min (minor), 30.6 min (major), 11.5:88.5 er. $[\alpha]_D^{25}$ = +44.20 (c 1.0, CH_2Cl_2) ; m.p. 83-91 °C.

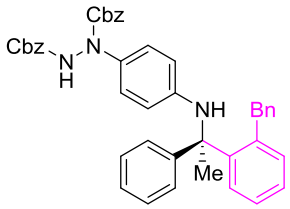
The reaction of **1v** was performed on 0.2 mmol scale for 71 h at -30 °C, which was purified by column chromatography on neutral alumina (200-300 mesh) (petroleoum:EtOAc, 100:1, 2:1 to 1:1) to give the recovered SM (*S*)-**1v** (34.6 mg, 48% yield) as a yellow oil and product **3v** (59.4 mg, 45% yield) as a yellow solid.

(*S*)-*N*-(1-(2-benzylphenyl)-1-phenylethyl)aniline ((*S*)-**1v**)



HPLC: Chiralpak IB N-5 column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 8.1 min (major), 9.9 min (minor), 99:1 er. $[\alpha]_D^{25}$ = -46.88 (c 1.0, CH_2Cl_2).

Dibenzyl-(*R*)-1-(4-((1-(2-benzylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3v**)

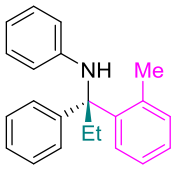


^{1}H NMR (400 MHz, Acetone)

^{1}H NMR (400 MHz, Acetone) δ 8.95 (m, 1H), 7.75 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.42 – 7.23 (m, 14H), 7.23 – 7.17 (m, 1H), 7.09 (q, *J* = 7.3 Hz, 5H), 6.85 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.76 – 6.68 (m, 2H), 6.63 – 6.45 (m, 2H), 5.67 (s, 1H), 5.15 (d, *J* = 3.8 Hz, 4H), 4.05 – 3.75 (m, 2H), 2.10 (s, 3H). ^{13}C NMR (126 MHz, Acetone) δ 157.1, 155.7, 149.0, 146.1, 144.3, 142.3, 141.5, 137.6, 137.5, 133.1, 132.8, 130.2, 129.2, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3, 128.1, 127.6, 126.9, 126.6, 126.4, 125.9, 115.9, 68.0, 67.5, 63.9, 39.9, 30.5. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{43}H_{38}N_3O_4^-$ 660.2867; Found 660.2847. HPLC: Chiralpak IB N-5 column, 80:20 hexanes/ isopropanol, 1 mL/min, t_R = 30.9 min (minor), 33.8 min (major), 1.5:98.5 er. $[\alpha]_D^{25}$ = +67.48 (c 1.0, CH_2Cl_2) ; m.p. 67-74 °C.

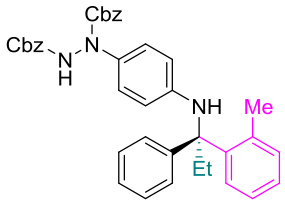
The reaction of **1w** was performed on 0.2 mmol scale for 24 h at -30°C, which was purified by column chromatography on neutral alumina (200-300 mesh) (petroleoum:EtOAc, 100:1, 2:1 to 1:1) to give the recovered SM (*S*)-**1w** (27.1 mg, 45% yield) as a white solid and product **3w** (52.6 mg, 44% yield) as yellow solid.

(*S*)-*N*-(1-phenyl-1-(*o*-tolyl)propyl)aniline ((*S*)-**1w**)



HPLC: Chiralpak IB N-5 column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 4.8 min (major), 5.6 min (minor), 94.5:5.5 er. $[\alpha]_D^{25}$ = -35.68 (c 1.0, CH_2Cl_2) ; m.p. 87-95 °C.

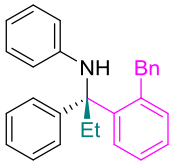
Dibenzyl (*R*)-1-(4-((1-phenyl-1-(*o*-tolyl)propyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3w**)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 1H), 7.38 – 6.75 (m, 21H), 6.38 (d, *J* = 8.5 Hz, 2H), 5.11 (d, *J* = 14.3 Hz, 4H), 4.69 (s, 1H), 2.75 (dq, *J* = 14.3, 7.3 Hz, 1H), 2.28 (dq, *J* = 14.1, 7.1 Hz, 1H), 1.99 (s, 3H), 0.69 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 155.2, 145.0, 143.6, 137.8, 136.0, 135.7, 133.0, 131.8, 128.6, 128.5, 128.4, 128.3, 128.1, 127.7, 127.5, 127.4, 127.1, 126.5, 126.3, 126.2, 125.9, 125.7, 115.4, 68.2, 67.8, 65.4, 31.4, 22.0, 8.2. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{38}H_{36}N_3O_4^-$ 598.2711; Found 598.2687. HPLC: Chiralpak IB N-5 column, 80:20 hexanes/ ethanol, 1 mL/min, t_R = 12.5 min (minor), 13.6 min (major), 10:90 er. $[\alpha]_D^{25}$ = +36.40 (c 1.0, CH_2Cl_2) ; m.p. 70-77 °C.

The reaction of **1x** was performed on 0.17 mmol scale for 31 h at -30 °C, which was purified by column chromatography on neutral alumina (200-300 mesh) (petroleoum:EtOAc, 100:1, 2:1 to 1:1) to give the recovered SM (*S*)-**1x** (26.3 mg, 41% yield) as a yellow solid and product **3x** (51.8 mg, 45% yield) as a yellow solid.

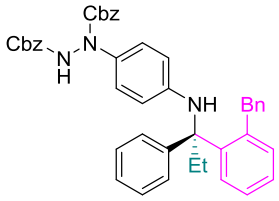
(*S*)-*N*-(1-(2-benzylphenyl)-1-phenylpropyl)aniline ((*S*)-**1x**)



$[\alpha]_D^{25}$ = -128.48(c 1.0, CH_2Cl_2) ; m.p. 97-102 °C.

Due to the low polarity of compound (*S*)-**1x**, its er value could not be determined precisely by direct chiral HPLC analysis. As a consequence, (*S*)-**1x** was converted into the corresponding (*S*)-**3x** through the achiral phosphoric acid catalyzed amination with azodicarboxylate **2a**, and er value of (*S*)-**3x** was determined instead. HPLC date of (*S*)-**3x**: Chiralpak ID column, 80:20 hexanes/ isopropanol, 1 mL/min, t_R = 24.8 min (major), > 99.5:0.5 er.

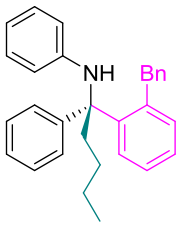
Dibenzyl-(*R*)-1-(4-((1-(2-benzylphenyl)-1-phenylpropyl)amino)phenyl)hydrazine-1,2-dicarbo xyl-ate (**3x**)



^{1}H NMR (400 MHz, Acetone) δ 8.92 (m, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.43 – 7.20 (m, 14H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.13 – 6.92 (m, 5H), 6.79 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.66 – 6.50 (m, 4H), 5.73 (s, 1H), 5.15 (d, *J* = 3.4 Hz, 4H), 3.98 (dd, *J* = 16.1, 2.6 Hz, 1H), 3.83 (d, *J* = 16.1 Hz, 1H), 2.89 (dq, *J* = 14.1, 7.1 Hz, 1H), 2.37 (dq, *J* = 14.1, 7.1 Hz, 1H), 0.71 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Acetone) δ 157.1, 155.7, 146.3, 144.9, 142.5, 142.0, 137.6, 137.5, 133.3, 132.8, 130.2, 129.2, 129.2, 128.8, 128.8, 128.7, 128.6, 128.4, 128.2, 127.9, 127.4, 127.1, 126.6, 126.3, 116.0, 68.0, 67.5, 66.0, 66.0, 39.3, 8.3. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{44}H_{40}N_3O_4^-$ 674.3024; Found 674.3008. HPLC: Chiralpak ID column, 80:20 hexanes/ isopropanol, 1 mL/min, t_R = 22.6 min (major), 25.1 min (minor), 95:5 er. $[\alpha]_D^{25}$ = +122.60 (c 1.0, CH_2Cl_2) ; m.p. 66-74 °C.

The reaction of **1y** was performed on 0.17 mmol scale for 31 h at -30 °C, which was purified by column chromatography on neutral alumina (200-300 mesh) (petroleoum:EtOAc, 100:1, 2:1 to 1:1) to give the recovered SM (*S*)-**1y** (28.8 mg, 42% yield) as a yellow oil and product **3y** (48 mg, 40% yield) as a yellow solid.

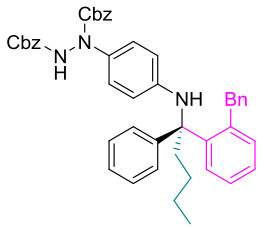
(*S*)-*N*-(1-(2-benzylphenyl)-1-phenylpentyl)aniline ((*S*)-**1y**)



$[\alpha]_D^{25}$ = -62.88 (c 1.0, CH_2Cl_2).

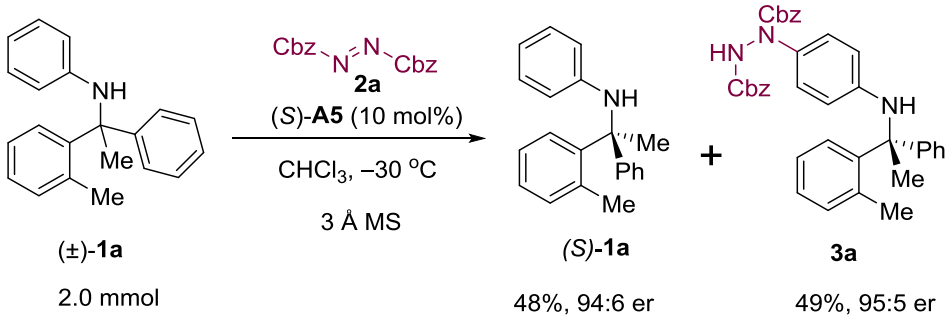
Due to the low polarity of compound (*S*)-**1y**, its er value could not be determined precisely by direct chiral HPLC analysis. As a consequence, (*S*)-**1y** was converted into the corresponding (*S*)-**3y** through the achiral phosphoric acid catalyzed amination with azodicarboxylate **2a**, and er value of (*S*)-**3y** was determined instead. HPLC date for (*S*)-**3y**: Chiralpak IA column, 80:20 hexanes/ isopropanol, 1 mL/min, t_R = 8.7 min (major) , > 99.5:0.5 er.

Dibenzyl-(*R*)-1-(4-((1-(2-benzylphenyl)-1-phenylpentyl)amino)phenyl)hydrazine-1,2-dicarbo xyl-ate (**3y**)



^{1}H NMR (500 MHz, Acetone) δ 9.05-8.68 (m, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.41 – 7.19 (m, 14H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.03 (q, *J* = 10.8 Hz, 5H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 4H), 5.70 (s, 1H), 5.14 (s, 4H), 3.97 (d, *J* = 16.1 Hz, 1H), 3.82 (d, *J* = 16.1 Hz, 1H), 2.82 – 2.69 (m, 1H), 2.37 (m, 1H), 1.29 (m, 1H), 1.17 (m, 2H), 0.98 (m, 1H), 0.72 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, Acetone) δ 157.1, 155.7, 146.7, 146.0, 144.8, 142.5, 141.8, 137.6, 137.5, 133.3, 132.9, 130.2, 129.2, 129.2, 128.9, 128.8, 128.7, 128.6, 128.6, 128.3, 127.9, 127.4, 127.3, 127.1, 126.6, 126.3, 125.8, 116.1, 68.1, 67.5, 65.9, 40.0, 39.4, 26.6, 23.5, 14.4. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{46}H_{44}N_3O_4^-$ 702.3337; Found 702.3315. HPLC: Chiralpak IA column, 80:20 hexanes/ isopropanol, 1 mL/min, t_R = 9.2 min (minor), 9.9 min (major), 10:90 er. $[\alpha]_D^{25}$ = +100.08 (c 1.0, CH_2Cl_2) ; m.p. 66-73 °C.

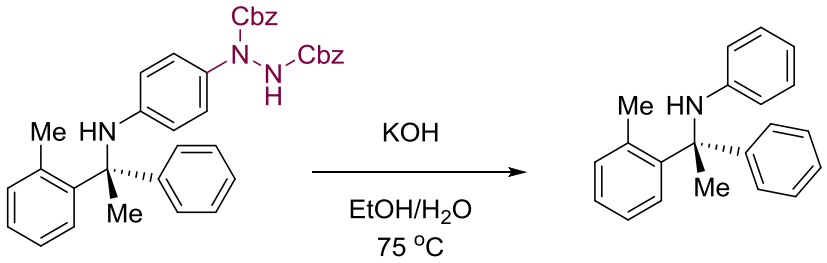
Large-scale kinetic resolution of racemic 1a



To a mixture of racemic **1a** (2 mmol, 1.0 eq), dibenzyl azodicarboxylate **2a** (2 mmol, 1.0 eq), CPA (*S*)-**A5** (0.2 mmol, 10 mol%) and activated 3 Å MS (800 mg) was added $CHCl_3$ (20 mL), which was precooled to −30 ℃. After achieving appropriate conversion as indicated by HPLC analysis of the reaction mixture, the mixture was quenched with a few drops of Et_3N. Then the mixture was filtered through Celite and concentrated under vacuum to give a residue,

which was purified by silica gel column chromatography (petroleoum:EtOAc, 100:1 to 5:1) to give the recovered SM (*S*)-**1a** (276 mg, 48% yield, 94:6 er) and product (*R*)-**3a** (567 mg, 49% yield, 95:5 er).

Transformations of the chiral products

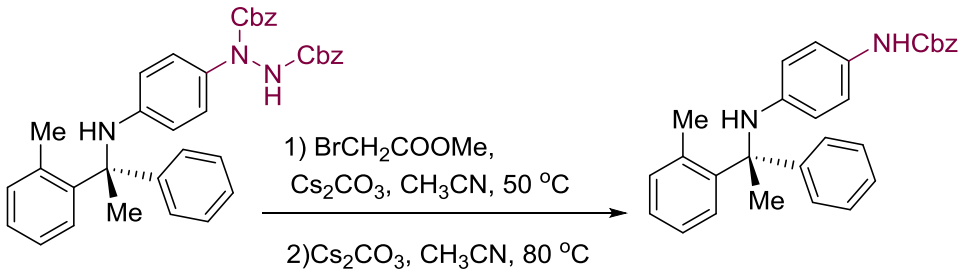


3a, 95:5 er

(R)-**1a**
80%, 94.5:5.5 er

To a solution of **3a** (58.5 mg, 0.1 mmol) in EtOH (2 mL) was added a solution of KOH (56 mg, 10 eq) in H_2O (1 mL) at rt. After stirring at 75 ℃ overnight, the mixture was cooled to rt and extracted with ether (5 x 2 mL). The combined organic layer was then washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to give a residue, which was purified by silica gel column chromatography to give (*R*)-**1a** (23 mg, 80%, 94.5:5.5 er) as a white solid. $[\alpha]^{D}_{25}$ = -22.36 (c 1.0, CH_2Cl_2) ; m.p. 85-91 °C. HPLC: Chiralpak IB column, 99:1 hexanes/ isopropanol, 1mL/min; t_R = 5.0 min (minor), 6.2 min (major); 5.5:94.5 er.

Benzyl (*R*)-(4-((1-phenyl-1-(*o*-tolyl)ethyl)amino)phenyl)carbamate (**4a**)



3a, 95:5 er

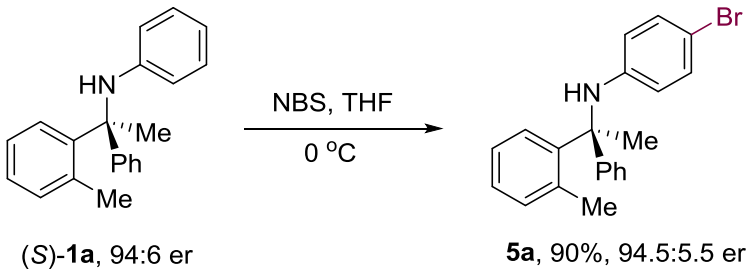
4a
62%, 94.5:5.5 er

To a solution of **3a** (58.5 mg, 0.1 mmol) in acetonitrile (1.0 mL) was added methyl bromoacetate (18 μL, 31 mg, 2.0 equiv.) and Cs_2CO_3 (82 mg, 0.25 mmol, 2.5 equiv.) at rt. After

stirring at 50 ℃ for 12 h, the reaction mixture was diluted with EtOAc (30 mL) and washed with brine 15 mL ×2. The combined organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo to give a residue.

To a solution of the above residue in acetonitrile (1 mL) was added Cs_2CO_3 (98 mg, 0.3 mmol, 3.0 equiv.) at rt. After stirring at 80 ℃ for 18 h, the reaction mixture was diluted with 30 mL EtOAc and washed with brine 15 mL ×2. The combined organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo to give a residue, which was purified by flash column chromatography (300~400 mesh silica gel, petroleum ether/EA = 10/1) to afford the product **4a** (26.0 mg, 62%, 94.5:5.5 er) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.40 – 7.17 (m, 12H), 7.10 – 6.93 (m, 3H), 6.48 – 6.29 (m, 3H), 5.14 (s, 2H), 4.35 (s, 1H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 148.2, 143.4, 142.5, 137.2, 136.5, 132.9, 128.7, 128.6, 128.4, 128.4, 127.5, 126.9, 126.0, 125.8, 120.7, 116.7, 66.9, 63.5, 29.3, 22.4. HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{29}H_{27}N_2O_2^-$ 435.2078; Found 435.2028. HPLC: Chiralpak IA column, 80:20 hexanes/ isopropanol, 1 mL/min, t_R = 10.0 min (major), 10.9 min (minor), 94.5:5.5 er. $[\alpha]_D^{25}$ = +14.68 (c 1.0, CH_2Cl_2).

(*S*)-4-bromo-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline (**5a**)



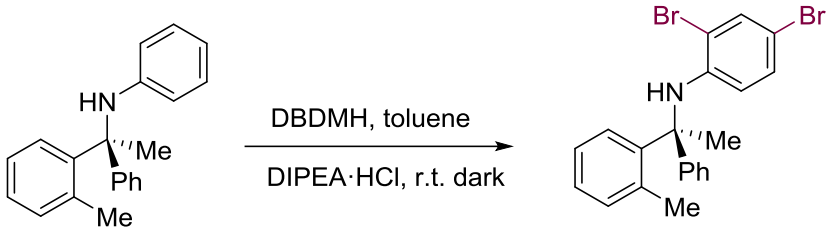
(*S*)-**1a**, 94:6 er

5a, 90%, 94.5:5.5 er

To a solution of the (*S*)-**1a** (28.7 mg, 0.1 mmol, 1.0 eq) in THF (0.5 mL) was added a solution of NBS (17 mg, 0.1 mmol) in THF (0.5 mL) slowly at 0 ℃. After stirring at this temperature for 1 h, the mixture was concentrated under vacuum to give a residue, which was purified by flash column chromatography (300~400 mesh silica gel, petroleum ether/EA = 100/1) to yield the corresponding *para*-brominated product **4a** (32.9 mg, 90% yield, 94.5:5.5 er). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.35 – 7.18 (m, 7H), 7.11 – 7.03 (m, 3H), 6.51 – 6.18 (m, 2H), 4.50 (s, 1H), 2.07 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 144.9, 142.8, 137.2, 133.0, 131.6, 128.7, 128.4, 127.7, 127.1, 126.0, 125.9, 117.1, 109.4, 63.4,

29.3, 22.4. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{21}BrN^+$ 366.0852; Found 366.0845. HPLC: Chiralpak IB N-5 column, 99:1 hexanes/ isopropanol, 1 mL/min, t_R = 7.8 min (major), 8.8 min (minor), 94.5:5.5 er. $[\alpha]_D^{25}$ = -4.04 (c 1.0, CH_2Cl_2).

(*S*)-2,4-dibromo-N-(1-phenyl-1-(o-tolyl)ethyl)aniline (**6a**)



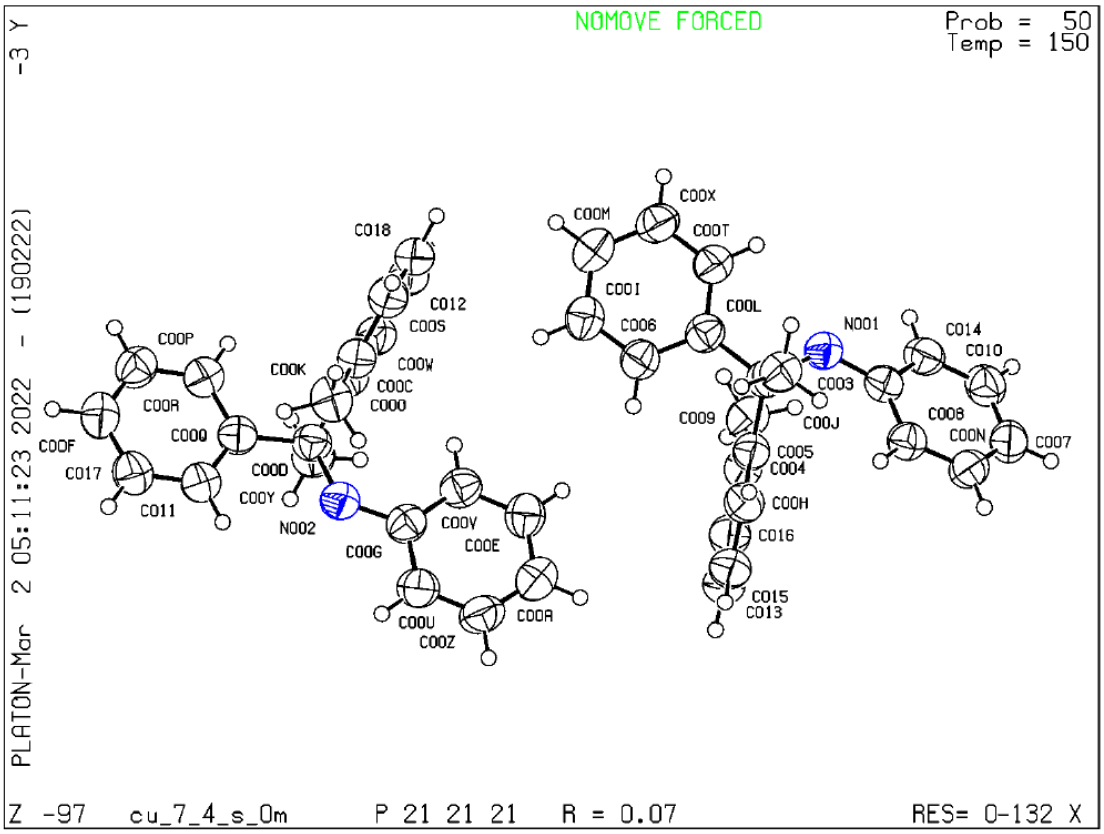
(*S*)-**1a** **6a**, 82%

To a solution of the (*S*)-**1a** (28.7 mg, 0.1 mmol, 1.0 eq), DIPEA·HCl (3 mg, 0.02 mmol, 0.2 eq) in toluene (1 mL) was added DBDMH (27 mg, 0.095 mmol, 0.95 eq) at 25°C in the absence of light. The mixture was stirred at 25°C overnight and then quenched by adding saturated aqueous Na_2SO_3 (5 mL). The solution was diluted with water (5 mL) and extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with brine, dried with anhydrous Na_2SO_4, filtered and concentrated under vacuum to give a residue, which was purified by flash column chromatography (300~400 mesh silica gel, petroleum ether/EtOAc = 100/1) to yield the corresponding dibrominated product **6a** (36.3 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.52 (d, *J* = 2.3 Hz, 1H), 7.37 – 7.19 (m, 7H), 7.08 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.91 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.20 (d, *J* = 8.9 Hz, 1H), 5.46 (s, 1H), 2.06 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 141.9, 141.7, 137.6, 134.4, 133.2, 130.6, 128.9, 128.3, 127.9, 127.3, 126.1, 125.4, 114.6, 111.5, 108.1, 63.5, 29.8, 22.1. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{20}Br_2N^+$ 445.9937; Found 445.9911. $[\alpha]_D^{25}$ = +30.34 (c 1.0, CH_2Cl_2).

X-Ray Crystal Structure

Hexane (0.5 mL) was added to dissolve the compound (*S*)-**1a** (10 mg) in a sample tube at room temperature. Then the mixture was filtered through the filter membrane into the vial. The single crystal of (*S*)-**1a** was obtained by slowly evaporating solvent at room temperature under the air conditions.

Crystal measurement: X-ray crystal structures of (*S*)-**1a** were determined at 150 K by using D8 VENTURE dual sources single crystal X-ray diffractometer. ORTEP representation with 50% probability thermal ellipsoids.



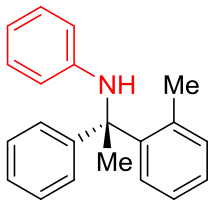
X-Ray structure of (*S*)-**1a** (with CCDC number 2240486)

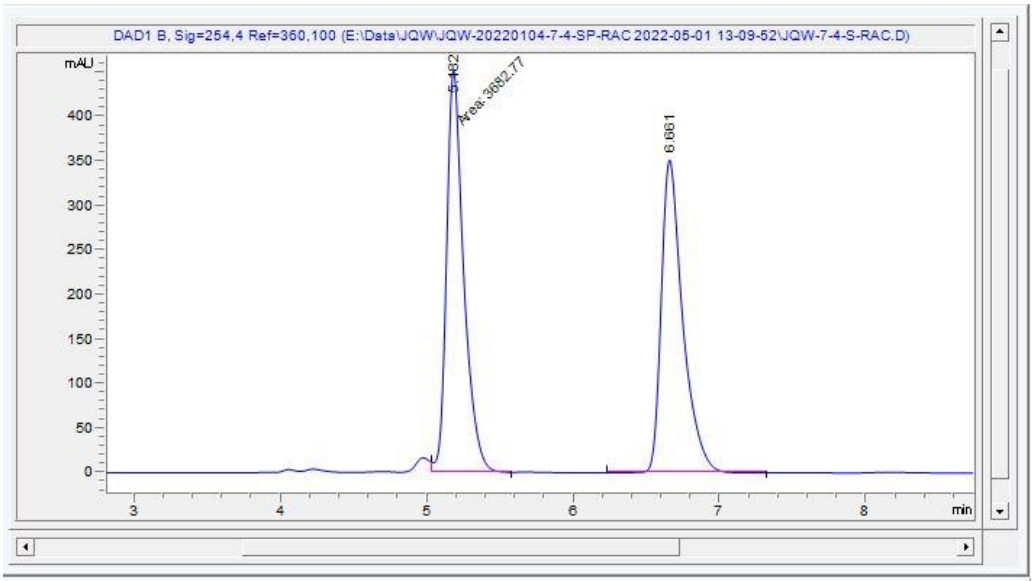
Single crystallography data for (*S*)-**1a**

Identification code	jqw_7_78_s_0m
Empirical formula	$C_{21}H_{21}N$
Formula weight	287.39
Temperature/K	150.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	11.3037(5)
b/Å	14.5967(7)
c/Å	19.5380(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3223.7(3)
Z	8
ρcalcg/cm^3	1.184
μ/mm^{-1}	0.328
F(000)	1232.0
Crystal size/mm^3	0.15 × 0.15 × 0.15
Radiation	GaKα (λ = 1.34138)
2Θ range for data collection/°	6.576 to 118.63
Index ranges	$-14 \leq h \leq 13$, $-18 \leq k \leq 18$, $-17 \leq l \leq 25$
Reflections collected	41671
Independent reflections	7042 [R_{int} = 0.0555, R_{sigma} = 0.0400]
Data/restraints/parameters	7042/6/401
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0387, wR_2 = 0.0895
Final R indexes [all data]	R_1 = 0.0471, wR_2 = 0.0932
Largest diff. peak/hole / e Å^{-3}	0.25/-0.25
Flack parameter	0.0(3)

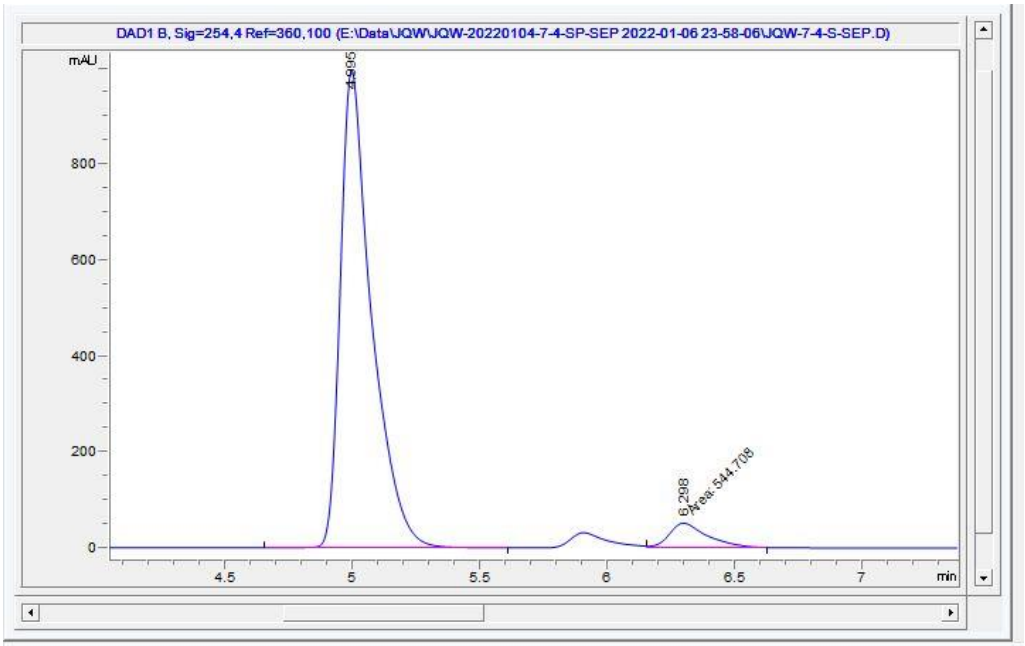
HPLC traces:

(*S*)-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1a**)



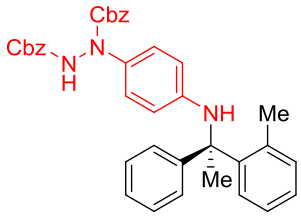


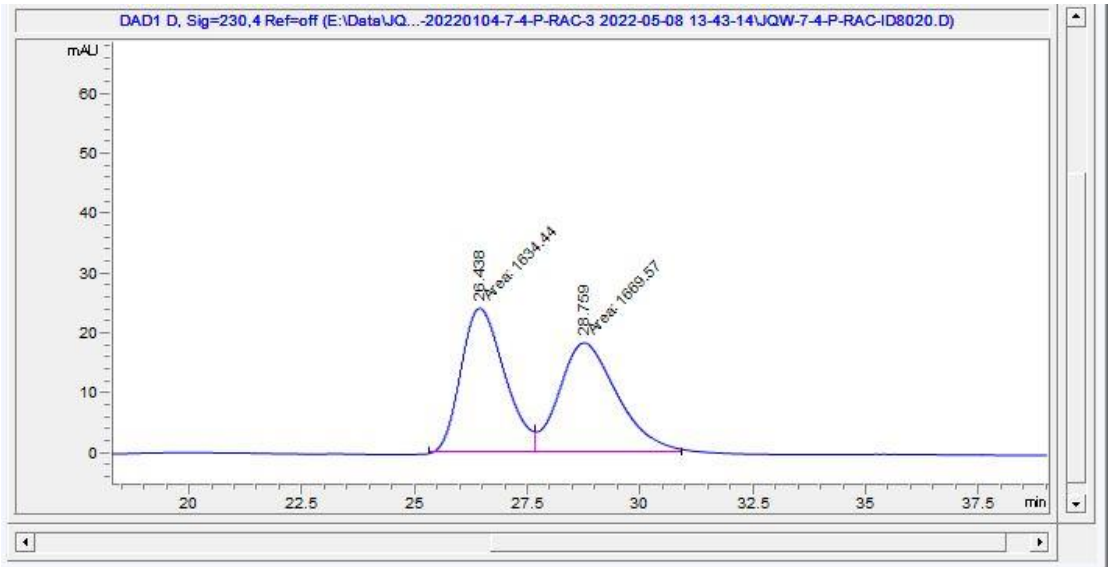
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.182	FM	3682.8	452.5	0.1356	50.611	0.664
2	6.661	BB	3593.9	351.8	0.1512	49.389	0.585



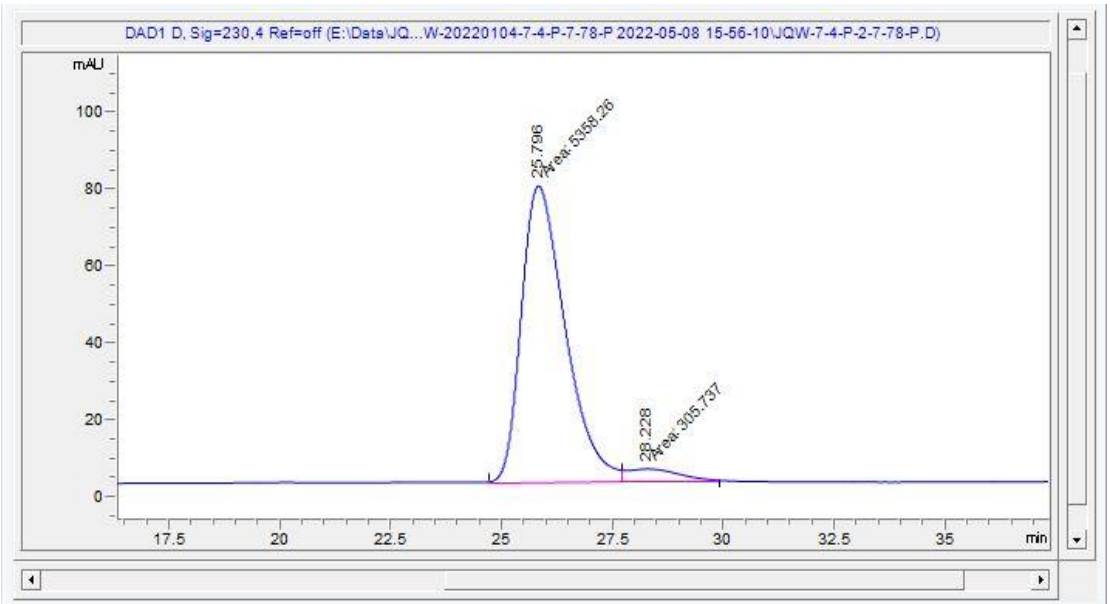
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.995	BB	8517.9	998.8	0.1235	93.989	0.522
2	6.298	MF	544.7	51.7	0.1757	6.011	0.583

Dibenzyl(*R*)-1-(4-((1-phenyl-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarboxylat (**3a**)



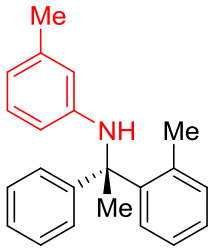


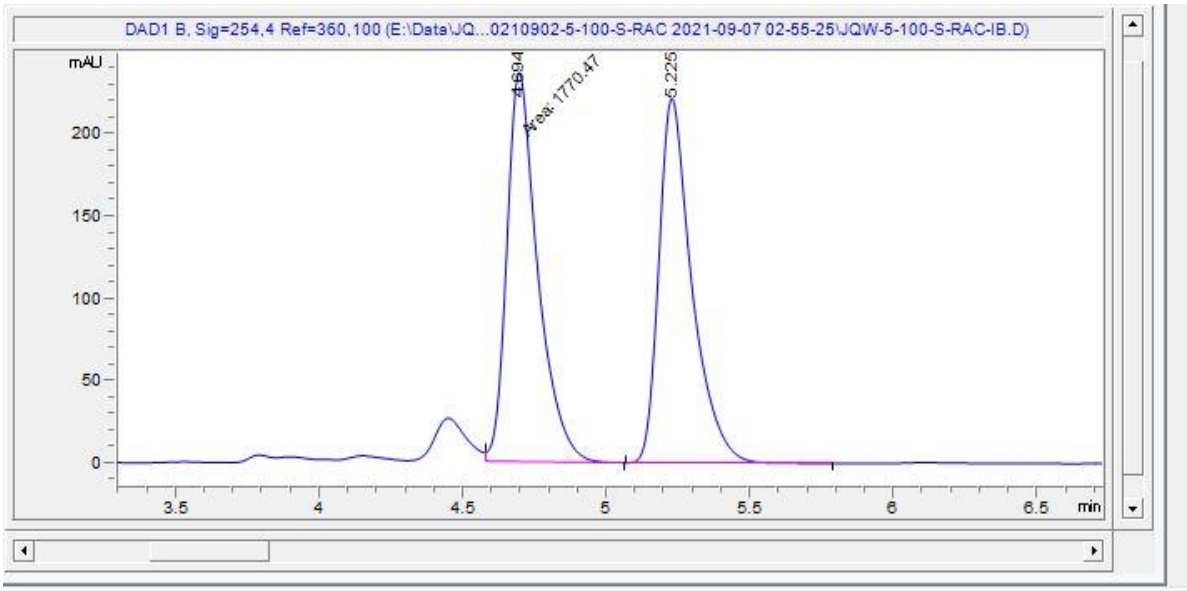
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	26.438	MF	1634.4	24.2	1.127	49.468	0.731
2	28.759	FM	1669.6	18.4	1.5138	50.532	0.724



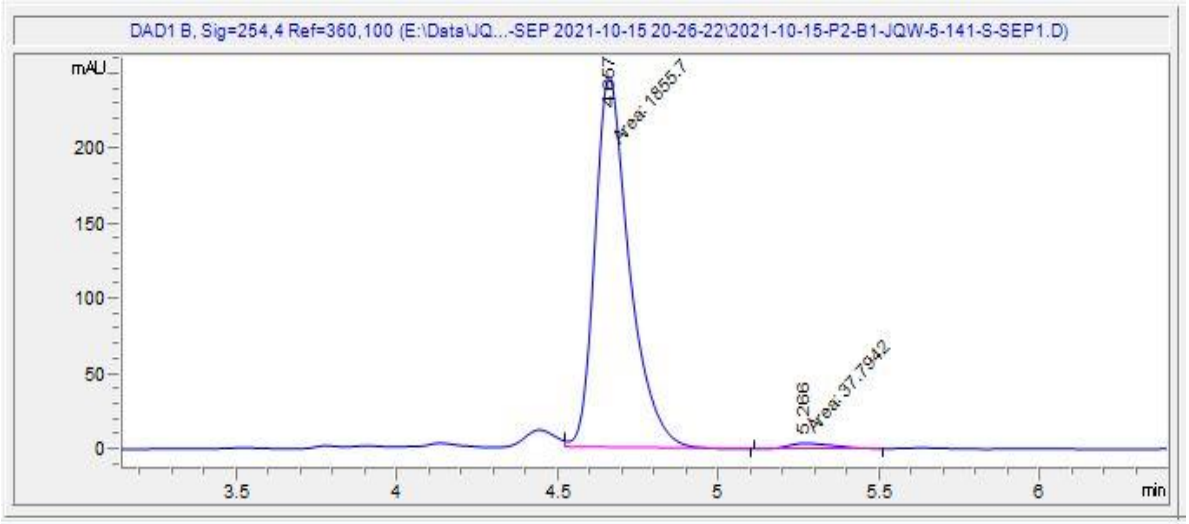
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	25.796	MF	5358.3	77.3	1.1549	94.602	0.622
2	28.228	FM	305.7	3.7	1.3926	5.398	0.495

(*S*)-3-methyl-N-(1-phenyl-1-(o-tolyl)ethyl)aniline ((*S*)-**1b**)





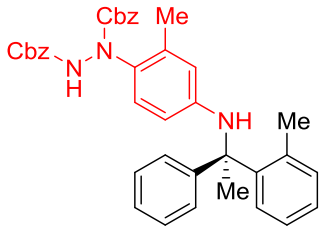
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.694	FM	1770.5	237	0.1245	49.980	0.64
2	5.225	BB	1771.9	222	0.1191	50.020	0.601

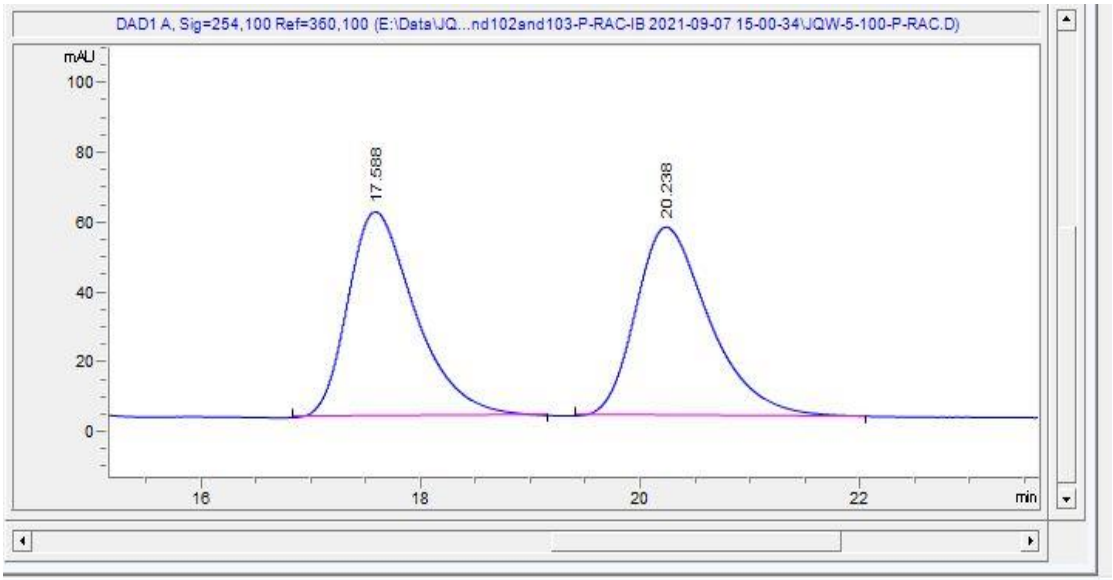


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.657	FM	1855.7	248.3	0.1245	98.004	0.675
2	5.266	MF	37.8	3.8	0.1652	1.996	0.53

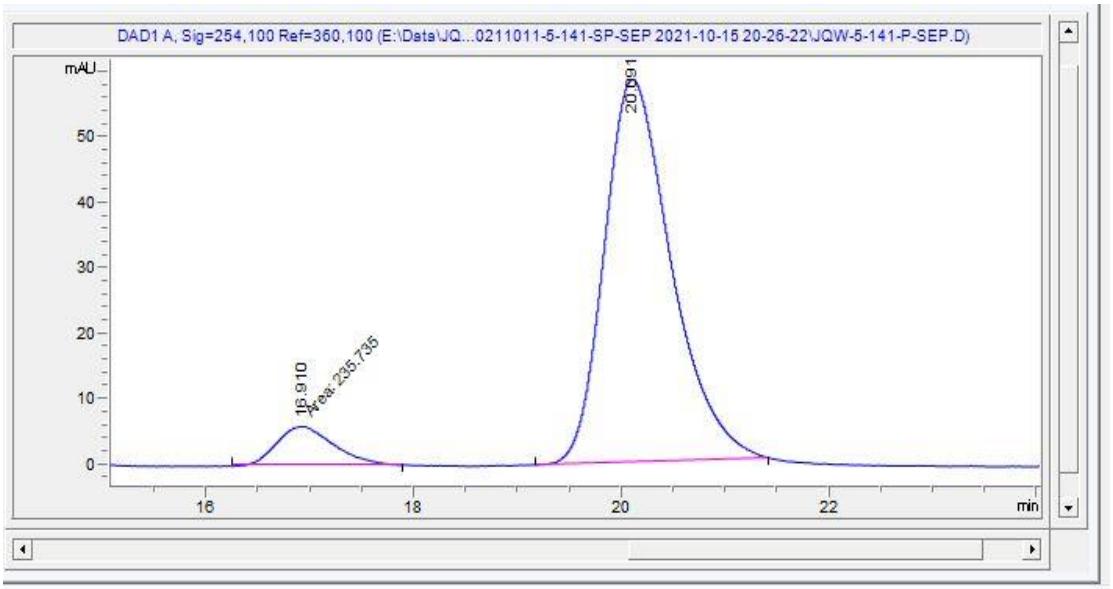
Dibenzyl(*R*)-1-(2-methyl-4-((1-phenyl-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarbox

ylate (**3b**)



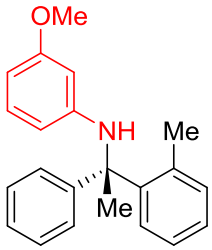


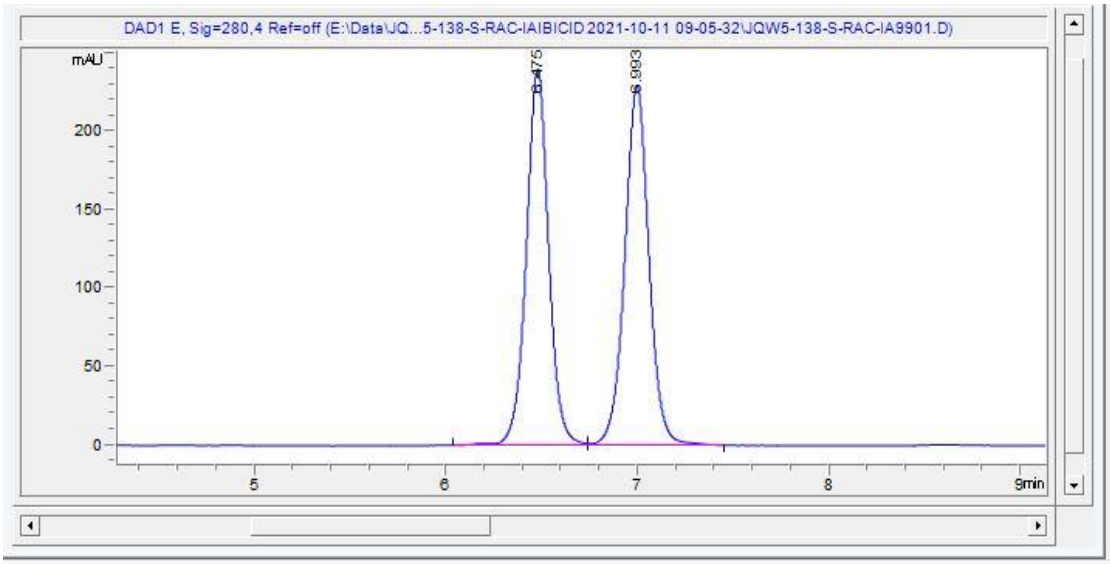
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.588	BB	2536.7	59	0.5257	49.921	0.657
2	20.238	BB	2544.7	54.3	0.5488	50.079	0.682



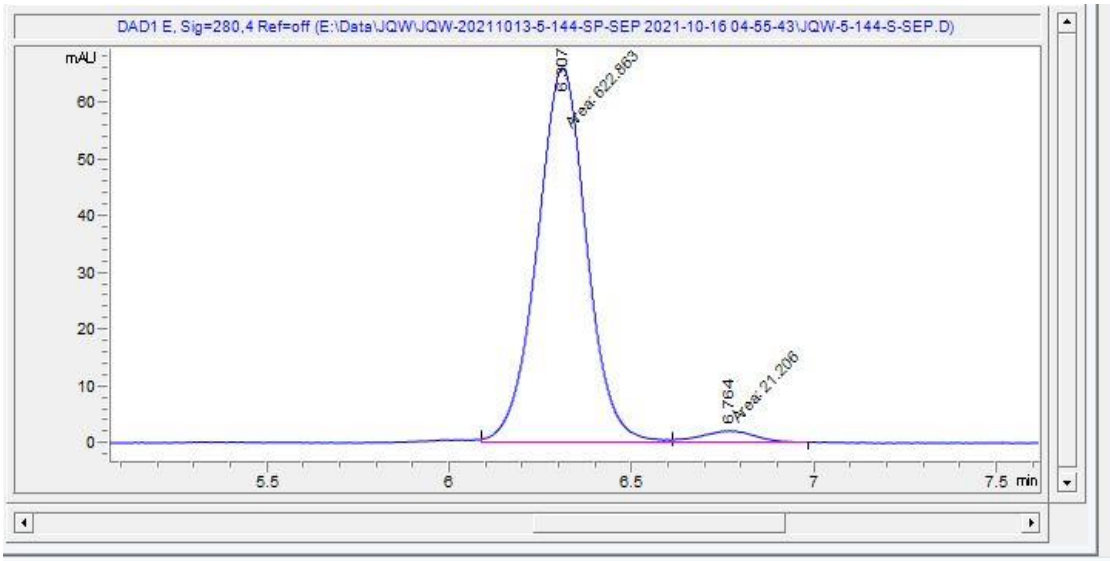
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	16.91	MM	235.7	6.1	0.6488	8.226	0.744
2	20.091	BV R	2630	58.7	0.5255	91.774	0.698

(*S*)-3-methoxy-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1c**)



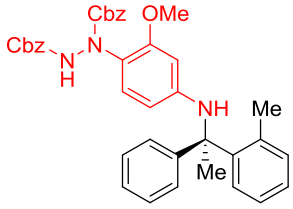


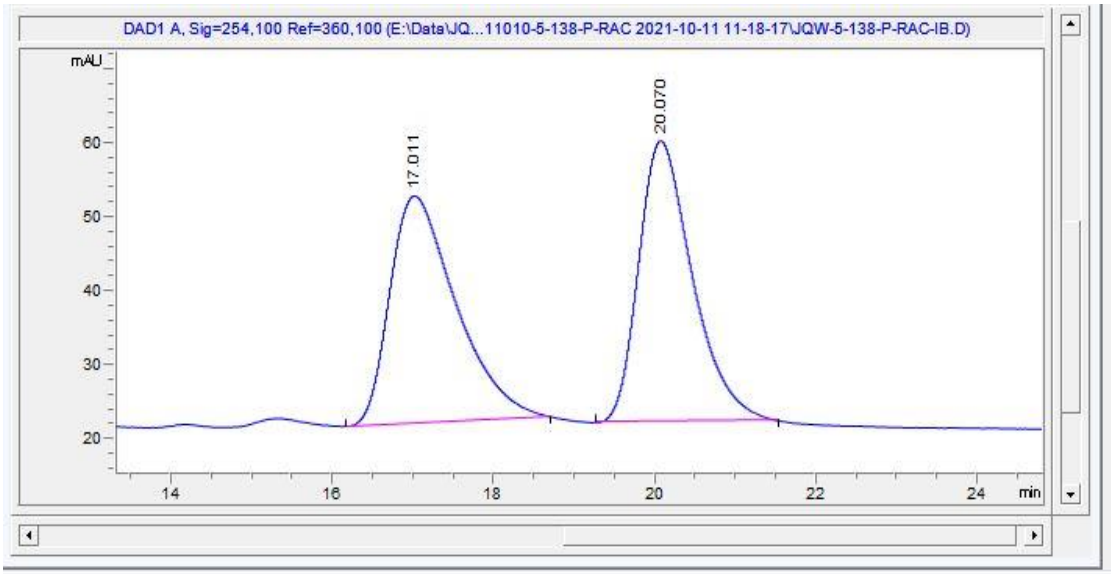
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.475	VV R	1948.3	239.7	0.1223	49.139	0.988
2	6.993	VB	2016.5	228.7	0.1349	50.861	0.967



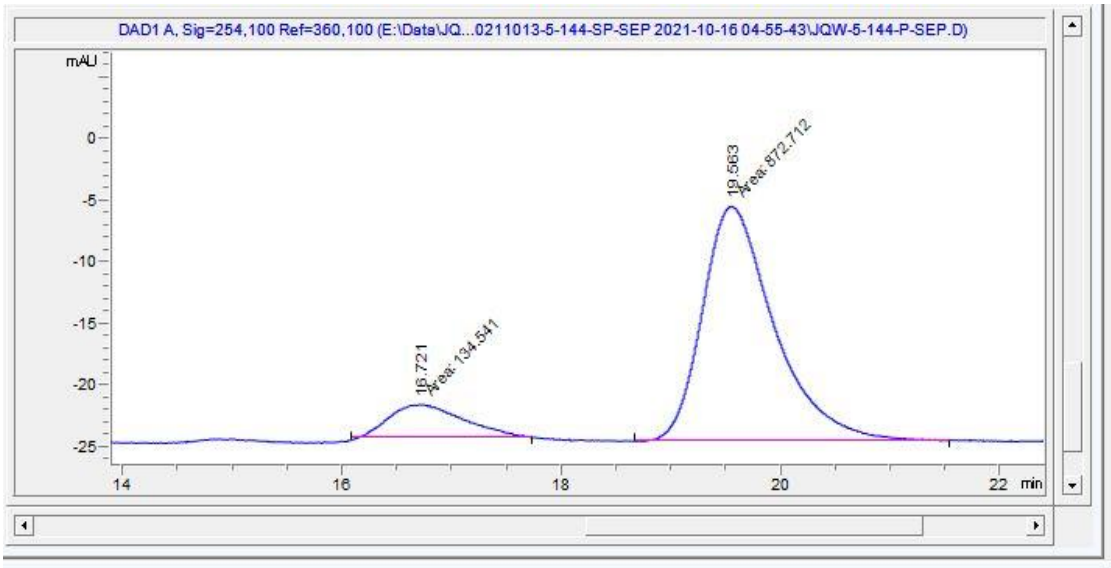
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.307	MF	622.9	65.9	0.1574	96.708	1.029
2	6.764	FM	21.2	2	0.1757	3.292	1.115

Dibenzyl-(*R*)-1-(2-methoxy-4-((1-phenyl-1-(o-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarb oxyl-ate (**3c)**



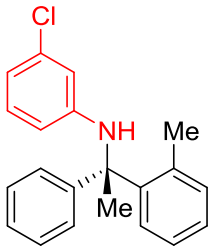


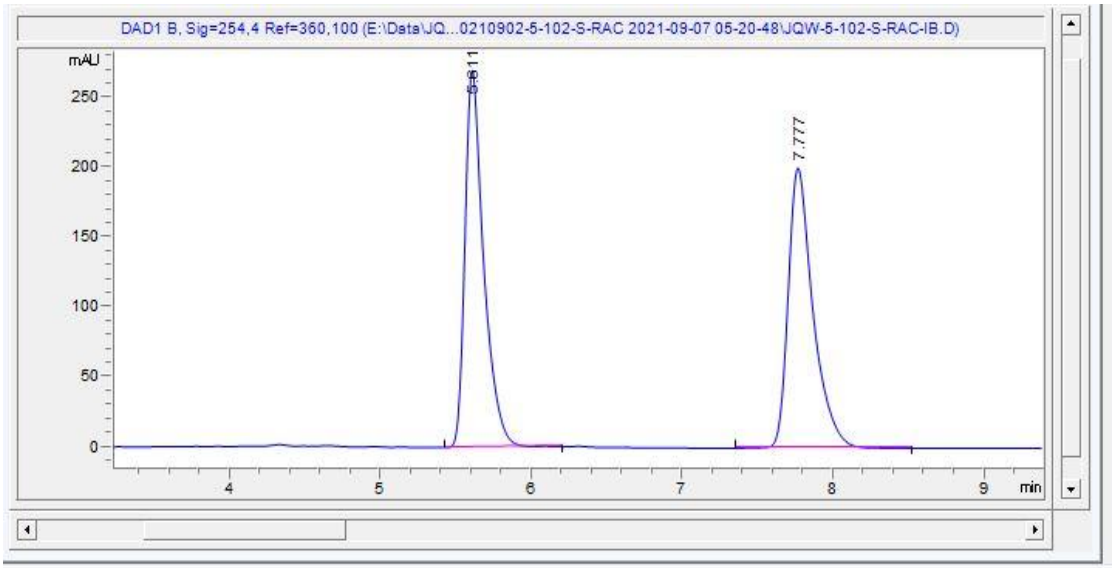
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.011	BB	1749.7	30.7	0.6677	49.806	0.573
2	20.07	BV R	1763.3	38	0.5433	50.194	0.667



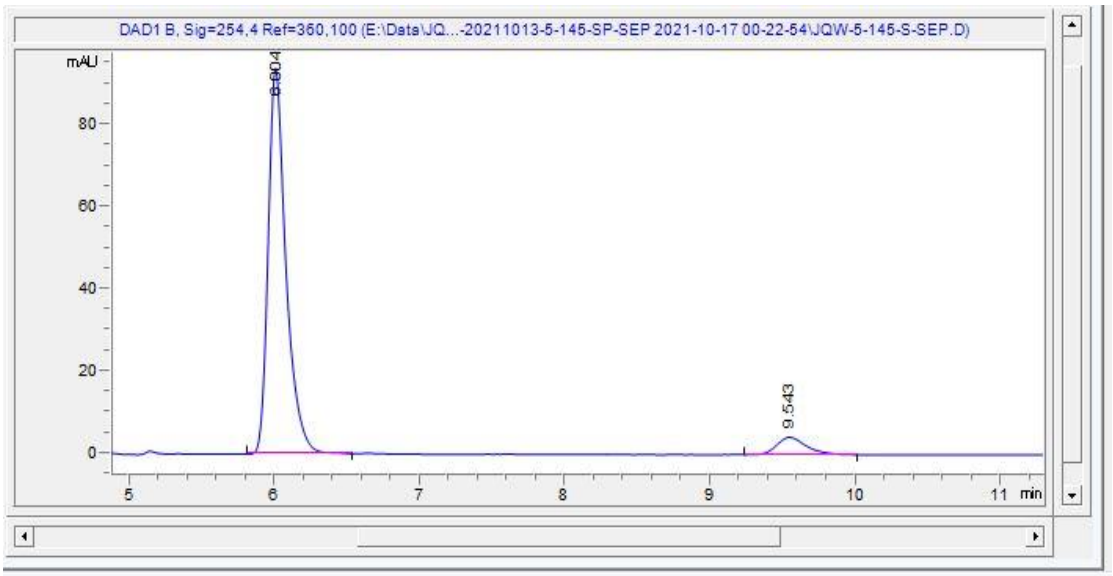
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	16.721	MM	134.5	2.8	0.8056	13.357	0.722
2	19.563	MM	872.7	19.1	0.7614	86.643	0.698

(*S*)-3-chloro-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1d**)





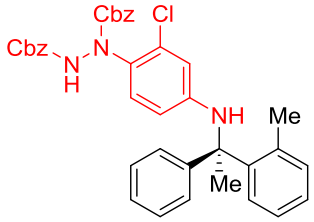
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.611	BV R	2339.7	270.5	0.1269	50.420	0.586
2	7.777	BB	2300.8	200.8	0.1717	49.580	0.605

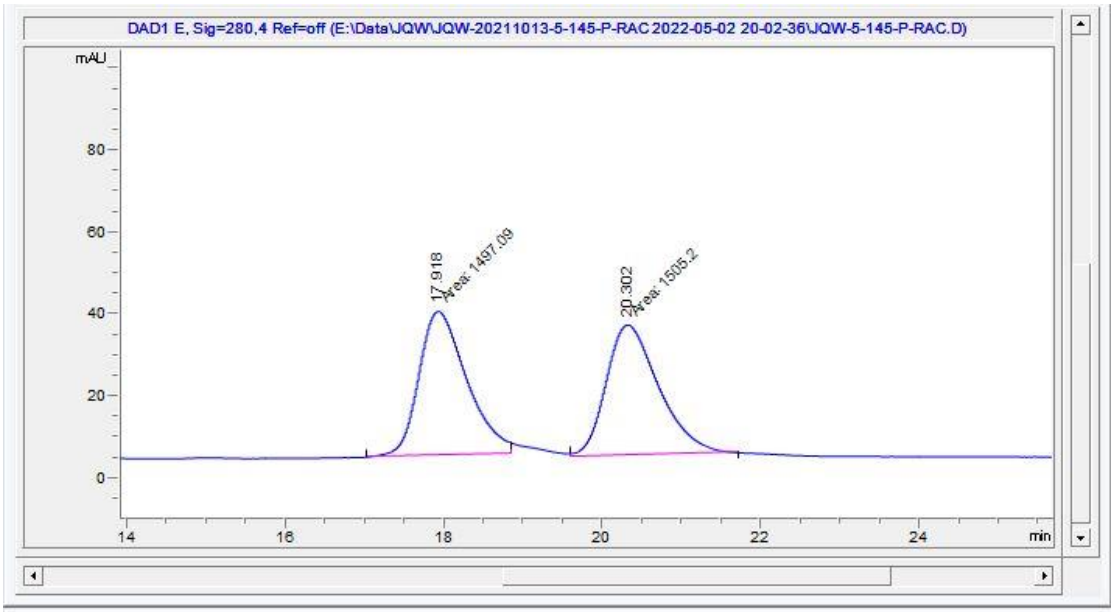


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.004	BB	804.6	94.5	0.1273	92.982	0.654
2	9.543	BB	60.7	4.3	0.2162	7.018	0.713

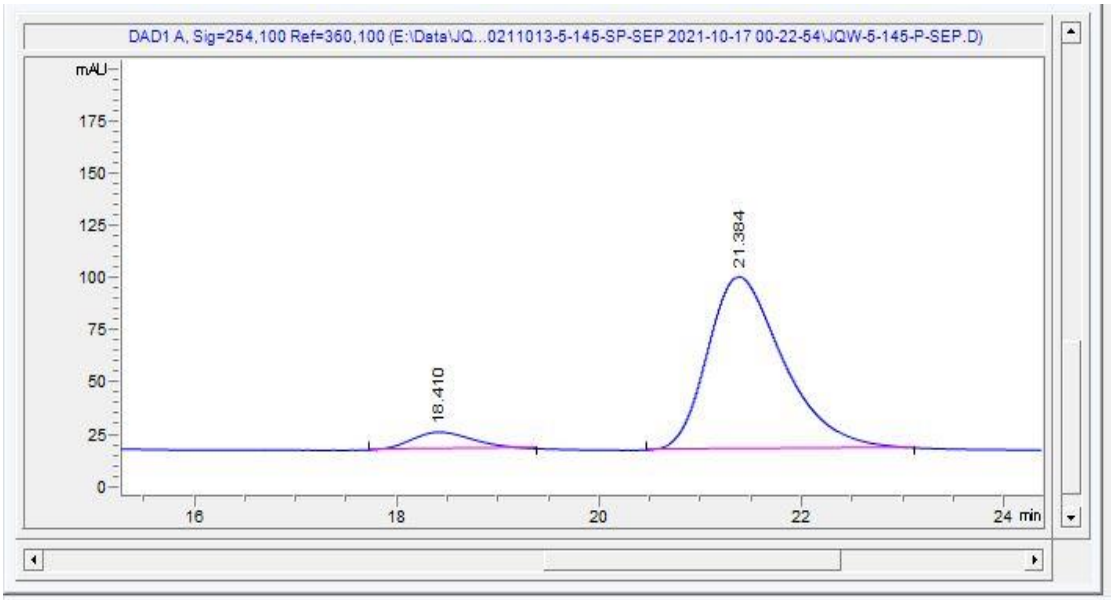
Dibenzyl-(*R*)-1-(2-chloro-4-((1-phenyl-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarbox

ylate (**3d**)



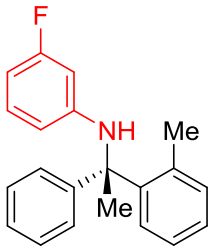


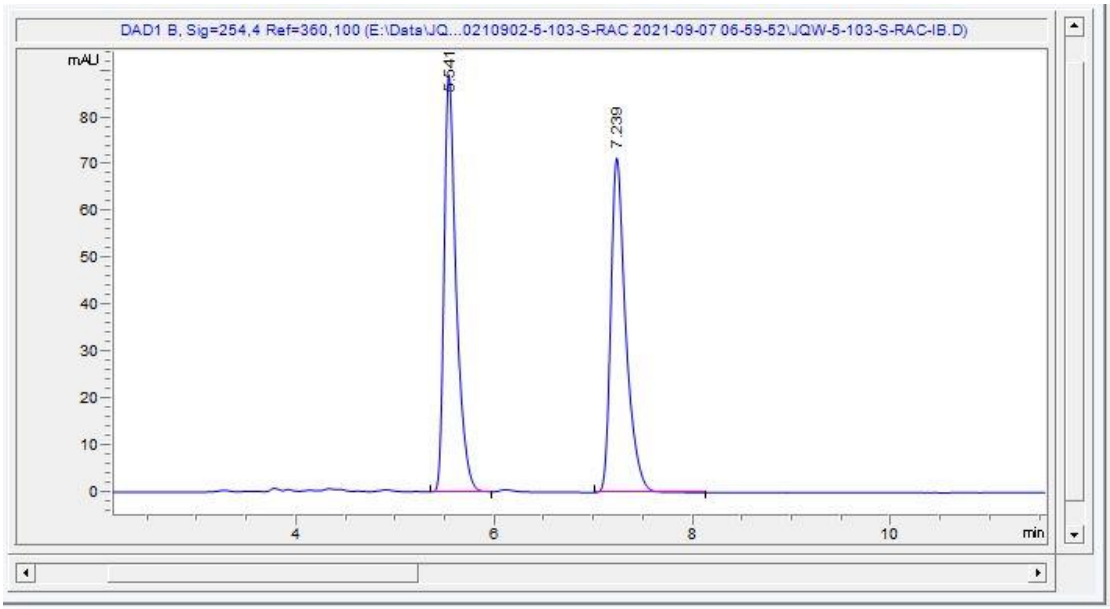
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.918	MF	1497.1	35.3	0.7061	49.865	0.667
2	20.302	MM	1505.2	32.2	0.78	50.135	0.666



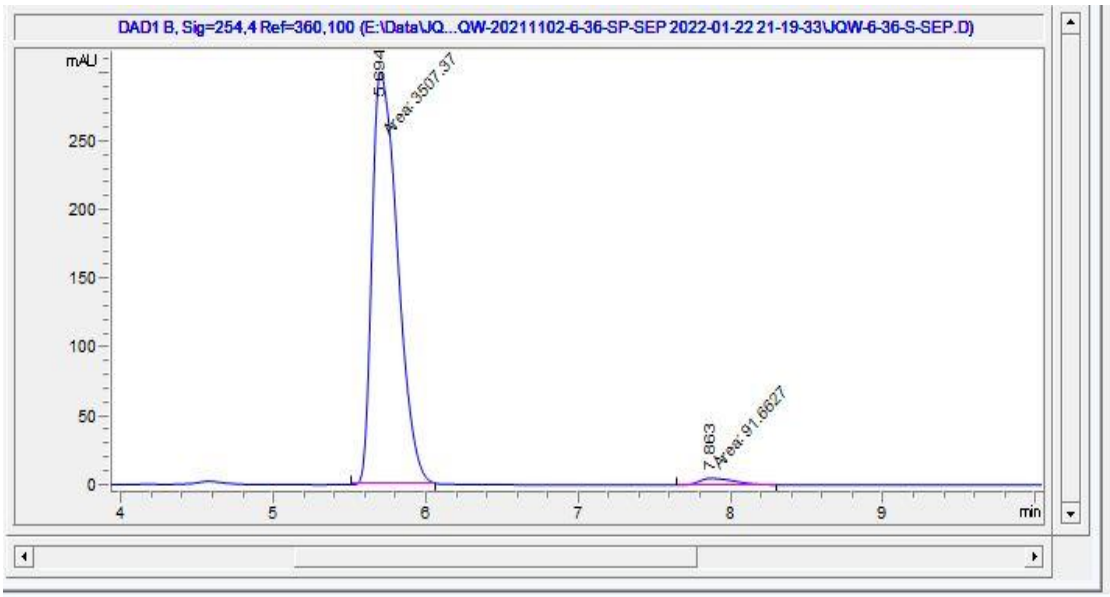
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.41	BB	360.4	8.3	0.5071	7.697	0.781
2	21.384	BV R	4322.1	82.9	0.6102	92.303	0.69

(*S*)-3-fluoro-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1e**)



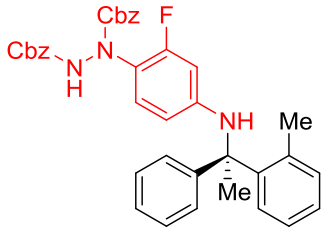


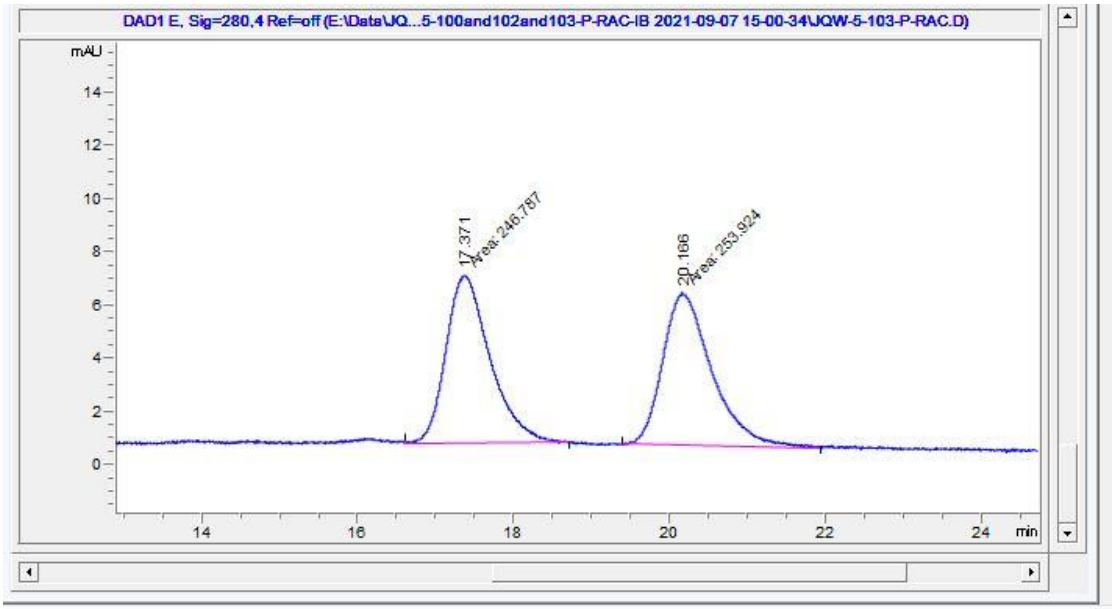
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.541	BB	759.6	89.5	0.125	50.080	0.6
2	7.239	BB	757.2	71.8	0.155	49.920	0.616



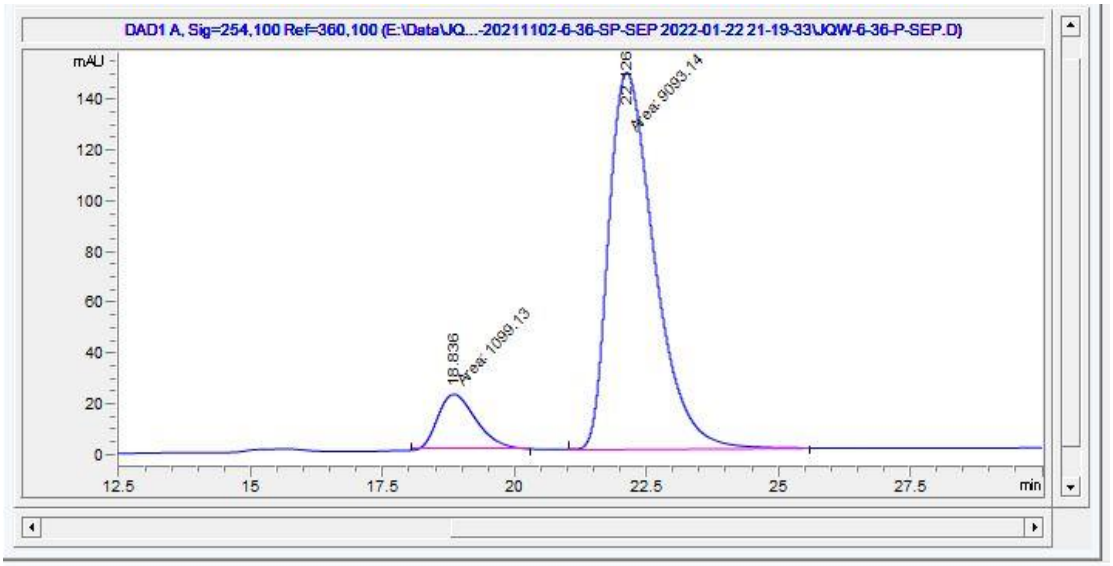
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.694	MF	3507.4	300.4	0.1946	97.453	0.489
2	7.863	MM	91.7	5.2	0.2925	2.547	0.474

dibenzyl-(*R*)-1-(2-fluoro-4-((1-phenyl-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3e**)



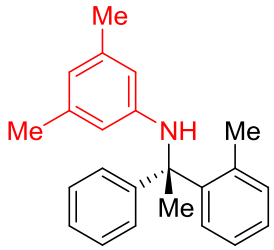


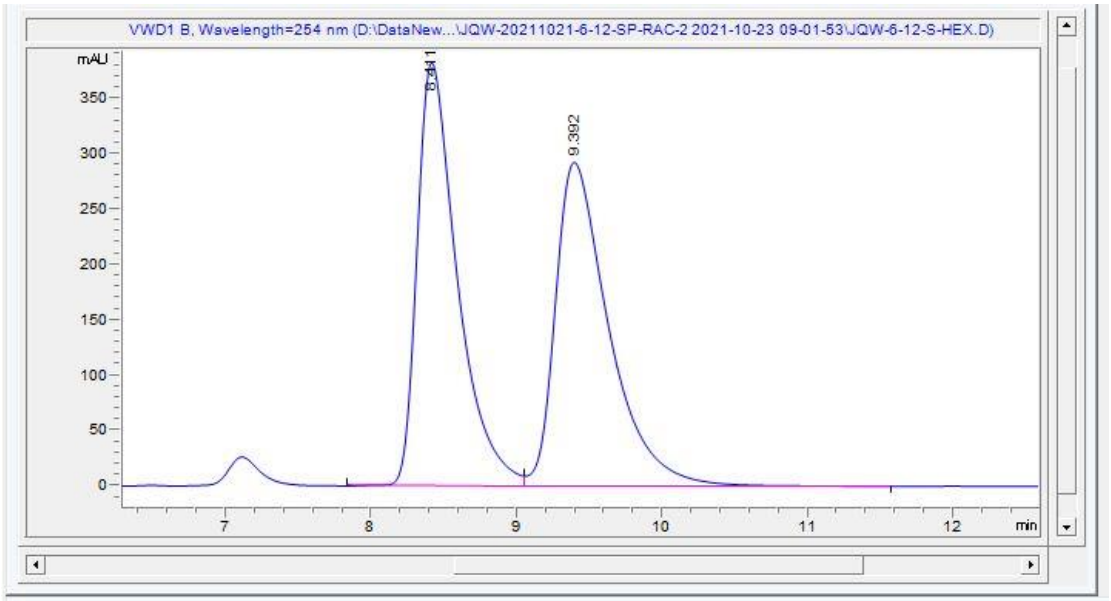
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.371	MM	246.8	6.3	0.6526	49.287	0.7
2	20.166	MM	253.9	5.7	0.7365	50.713	0.625



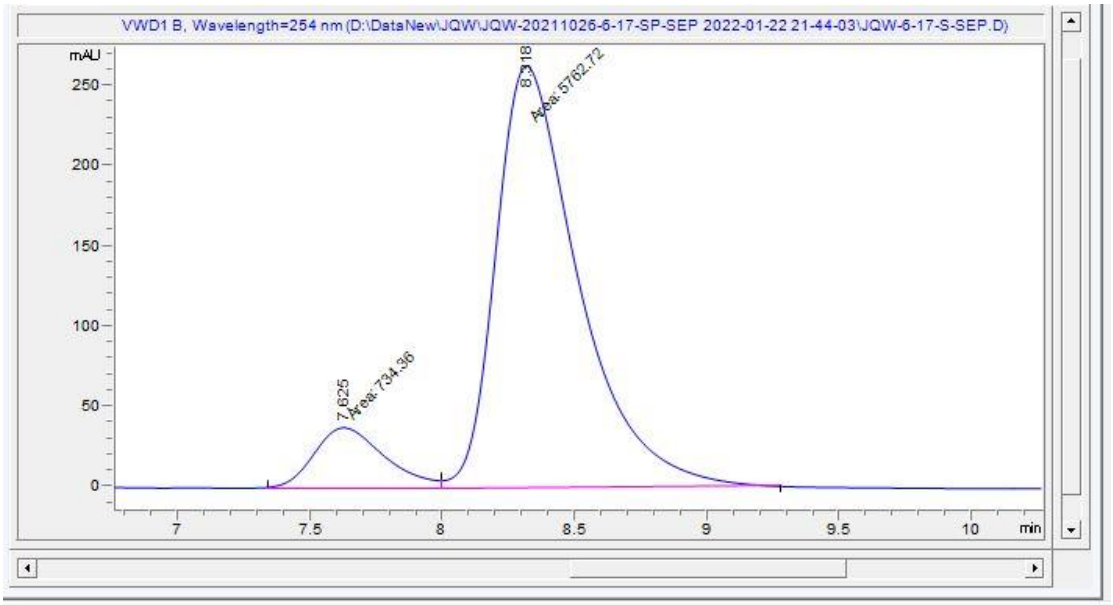
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.836	MM	1099.1	21.8	0.8407	10.784	0.677
2	22.126	MM	9093.1	149.3	1.0153	89.216	0.627

(*S*)-3,5-dimethyl-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1f**)



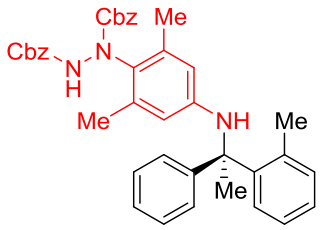


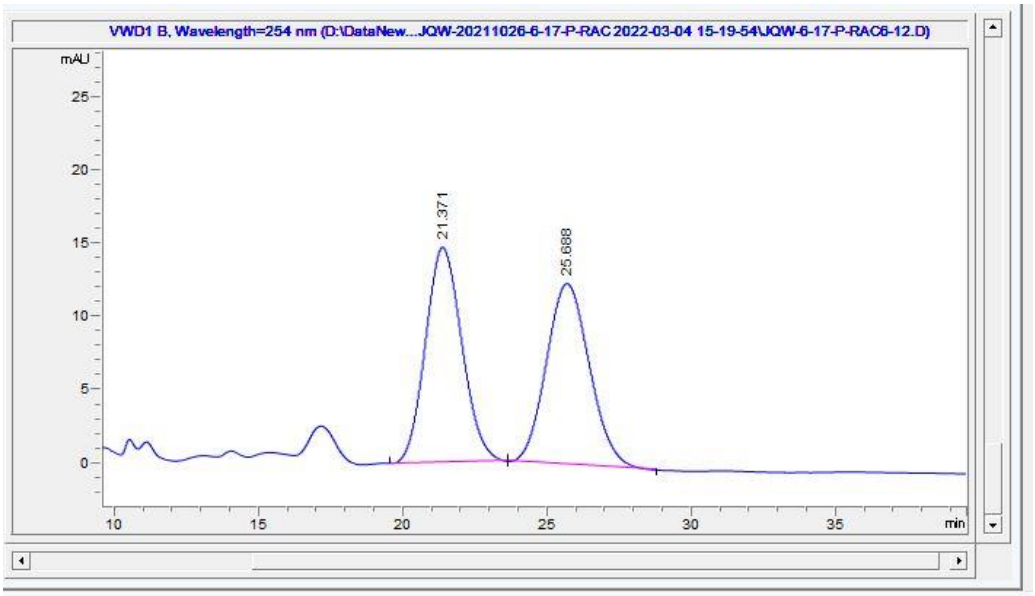
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.411	VV	7335.6	381.1	0.2866	49.563	0.529
2	9.392	VB	7465.1	291.6	0.3827	50.437	0.51



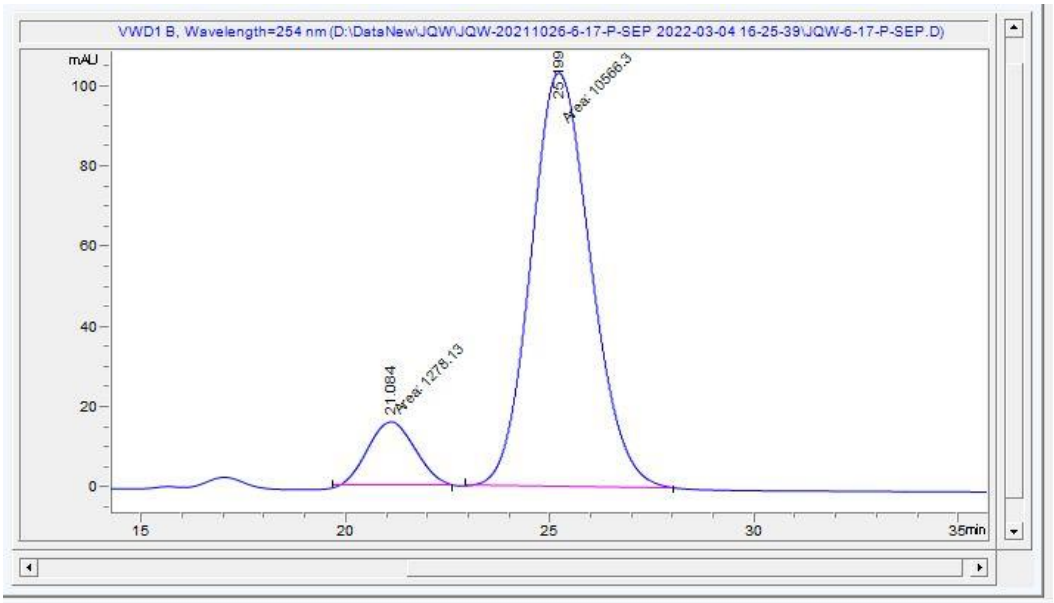
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.625	MF	734.4	38.5	0.3178	11.303	0.723
2	8.318	FM	5762.7	263.7	0.3643	88.697	0.571

Dibenzyl-(*R*)-1-(2,6-dimethyl-4-((1-phenyl-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dica r-boxylate (**3f**)



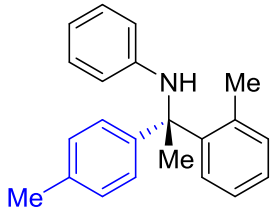


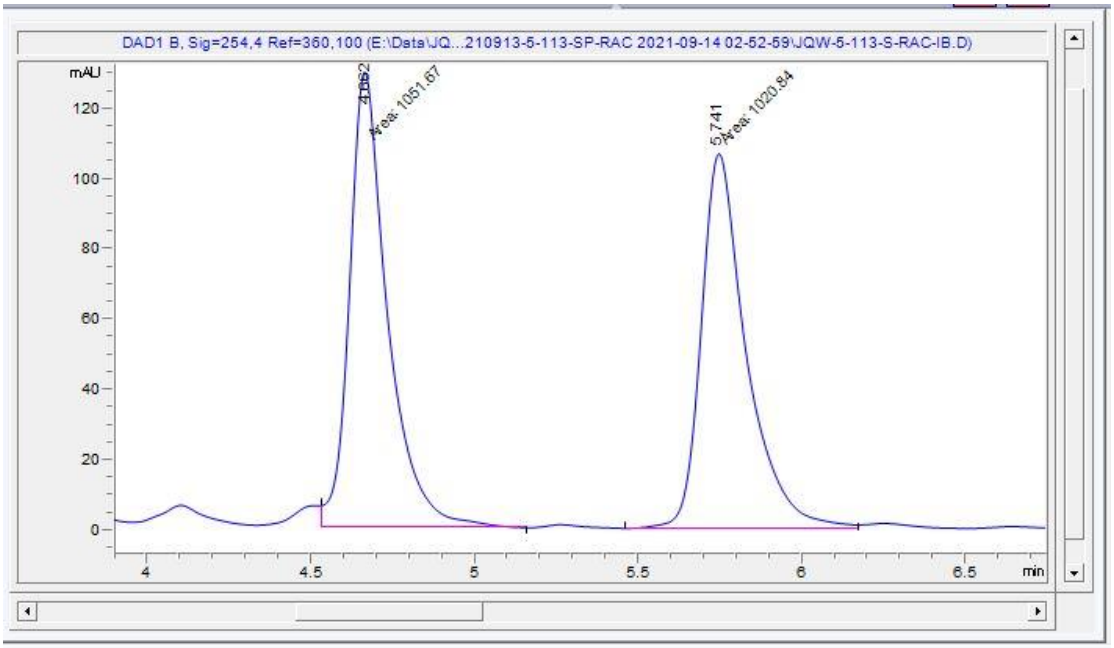
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	21.371	BB	1300.4	14.8	1.3605	50.018	0.86
2	25.688	BB	1299.5	12.4	1.59	49.982	0.875



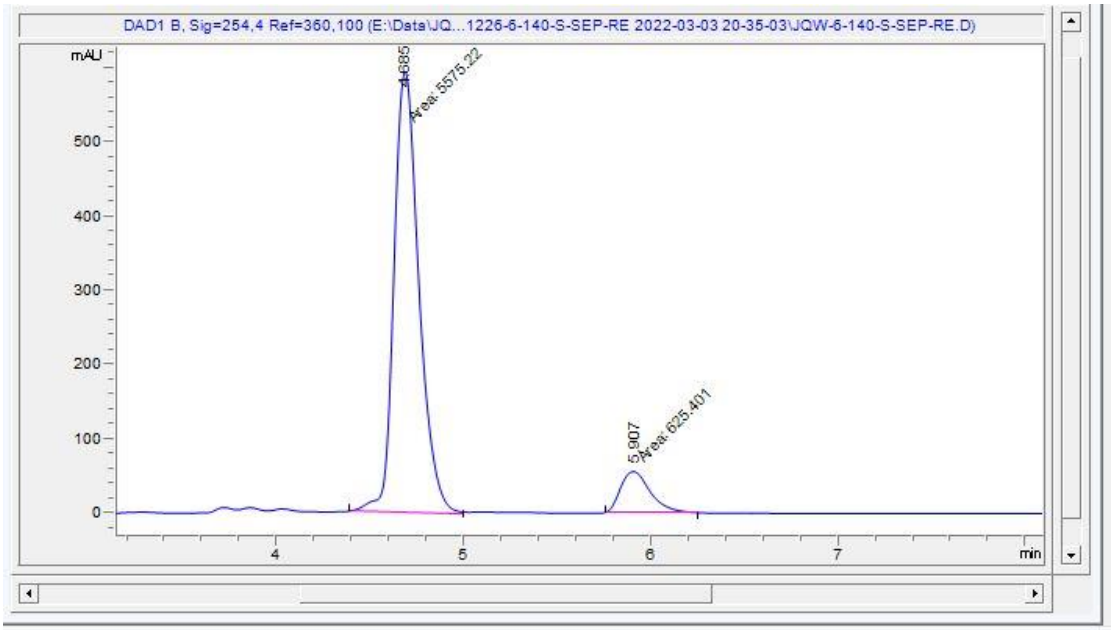
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	21.084	MM	1278.1	15.9	1.3379	10.791	0.94
2	25.199	MM	10566.3	103.2	1.706	89.209	0.847

(*S*)-*N*-(1-(*o*-tolyl)-1-(*p*-tolyl)ethyl)aniline ((*S*)-**1g**)



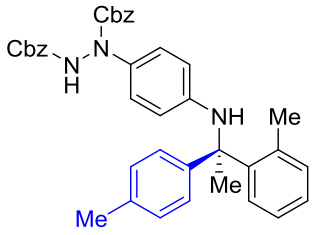


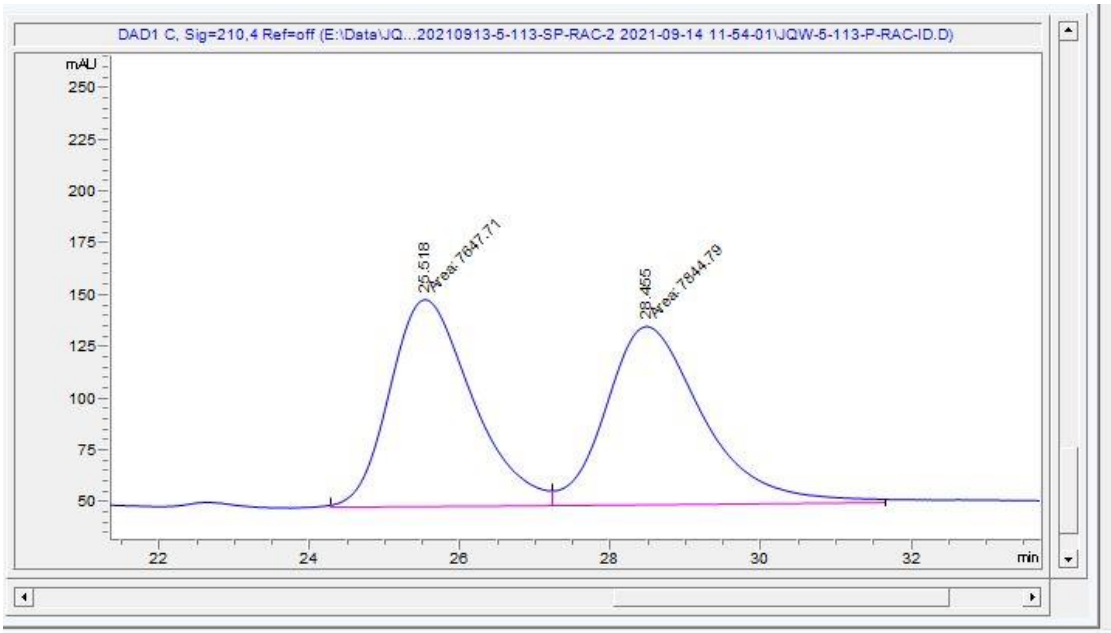
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.662	FM	1051.7	130.2	0.1347	50.744	0.64
2	5.741	MF	1020.8	106.9	0.1592	49.256	0.629



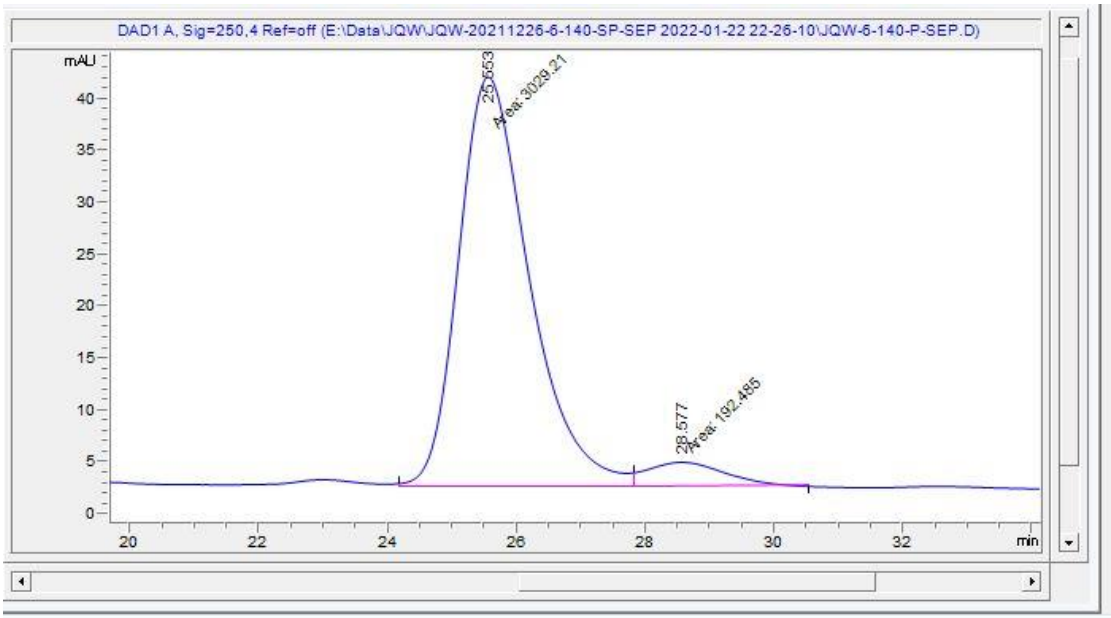
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.685	MM	5575.2	598.1	0.1554	89.914	0.775
2	5.907	MM	625.4	56.1	0.186	10.086	0.73

Dibenzyl (*R*)-1-(4-((1-(*o*-tolyl)-1-(*p*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3g)**



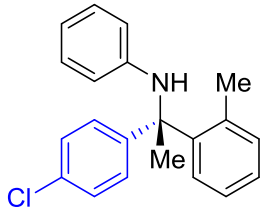


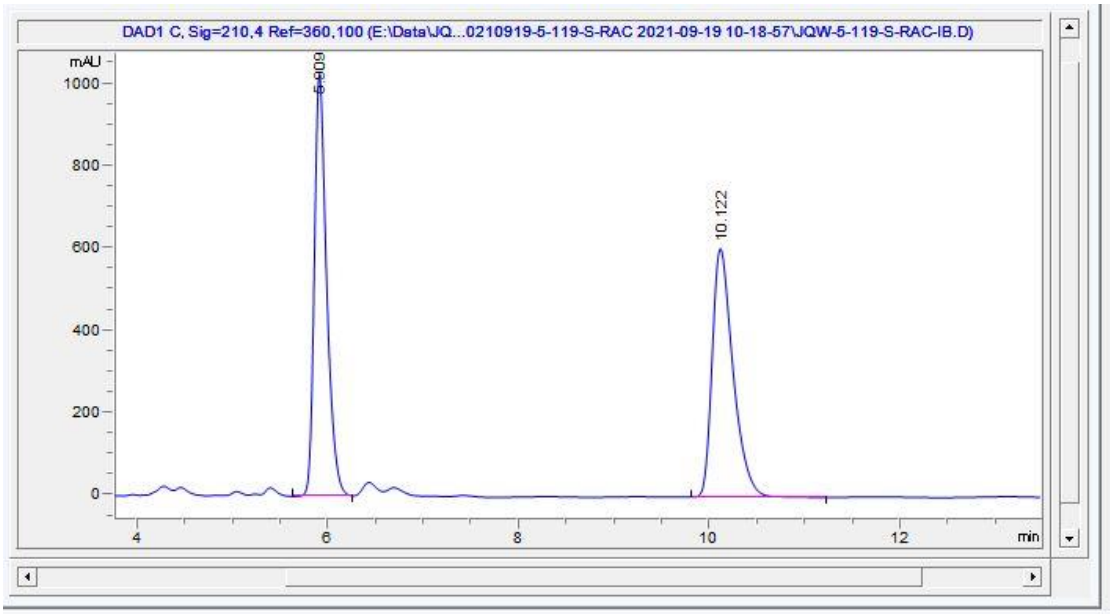
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	25.518	MF	7647.7	99.9	1.2757	49.364	0
2	28.455	FM	7844.8	86.4	1.5131	50.636	0.683



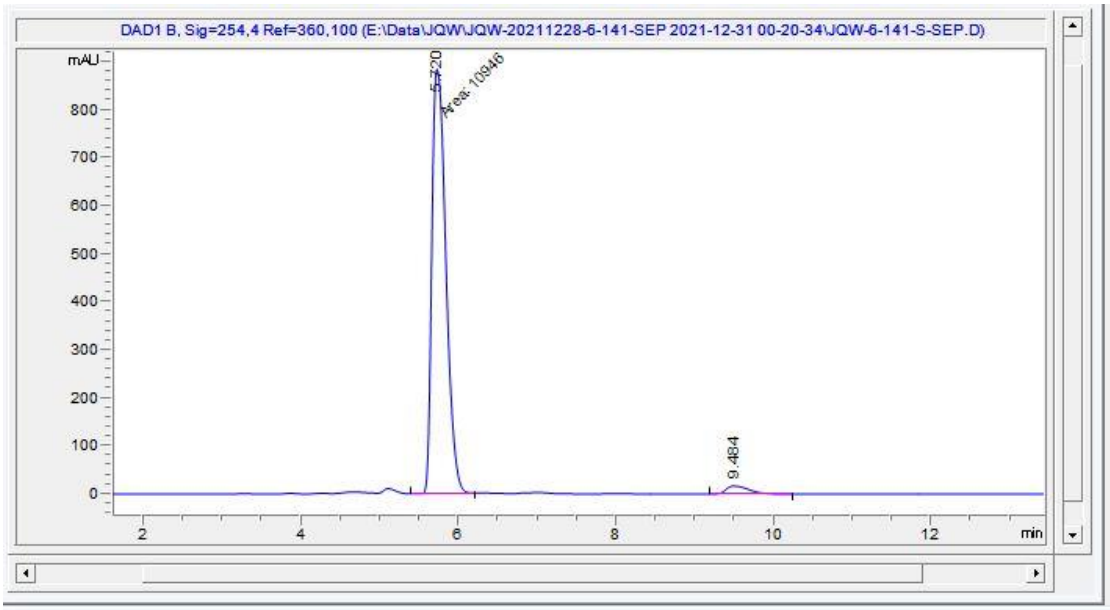
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	25.553	MF	3029.2	39.5	1.2769	94.025	0
2	28.577	FM	192.5	2.3	1.3832	5.975	0.806

(*S*)-*N*-(1-(4-chlorophenyl)-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1h**)



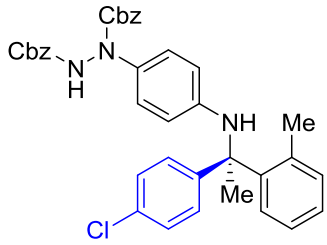


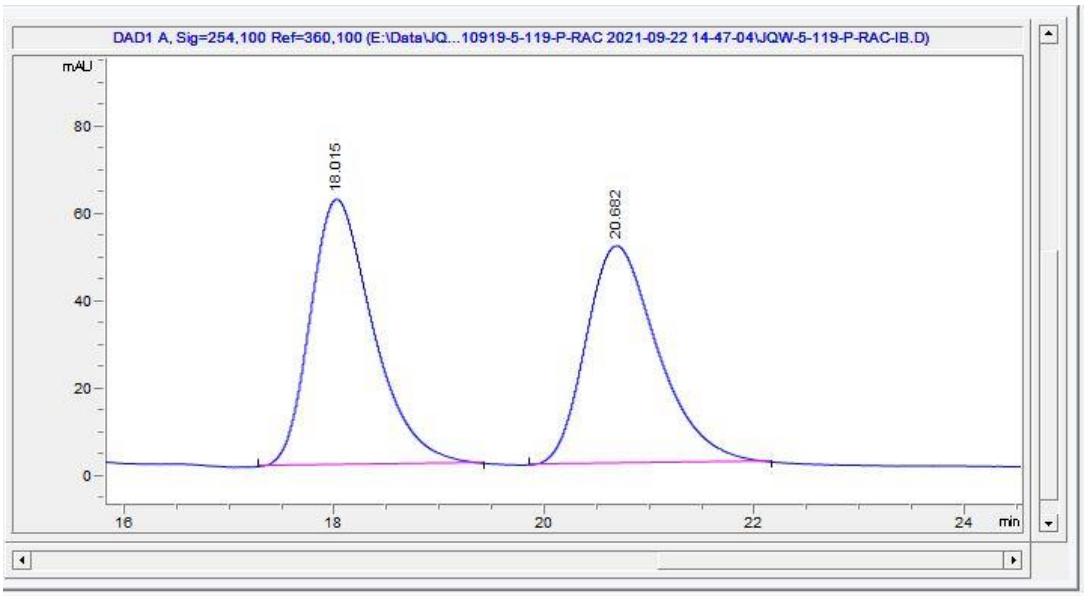
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.909	BB	9202.4	1024.5	0.1348	50.000	0.666
2	10.122	BB	9202.5	603.6	0.2299	50.000	0.603



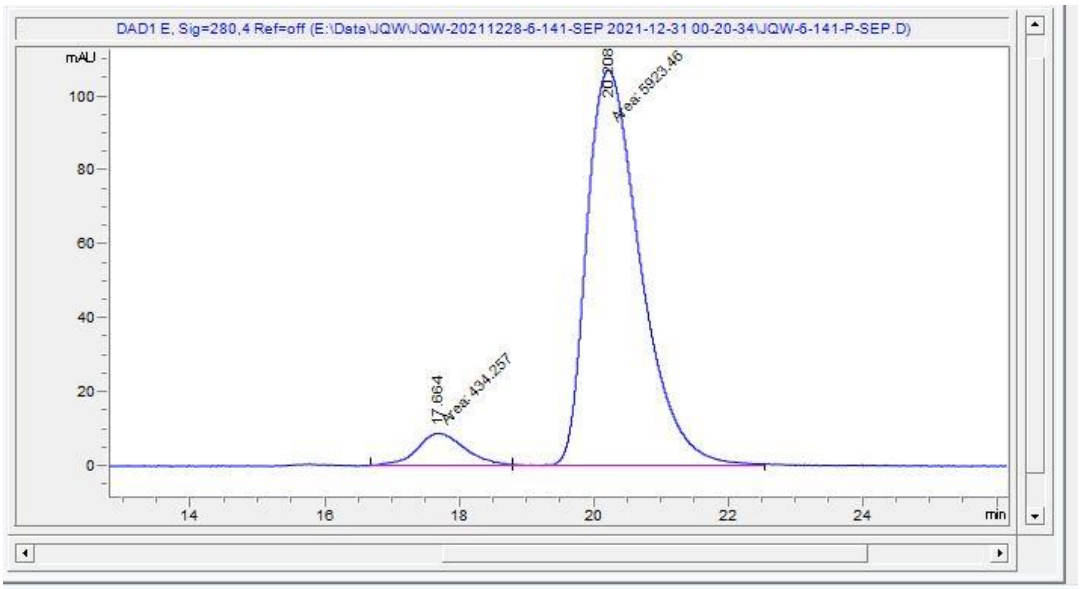
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.72	MF	10946	886.7	0.2058	97.016	0
2	9.484	BB	336.6	16.8	0.3159	2.984	0.494

Dibenzyl-(*R*)-1-(4-((1-(4-chlorophenyl)-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarbo xyl-ate (**3h)**



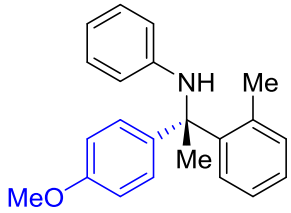


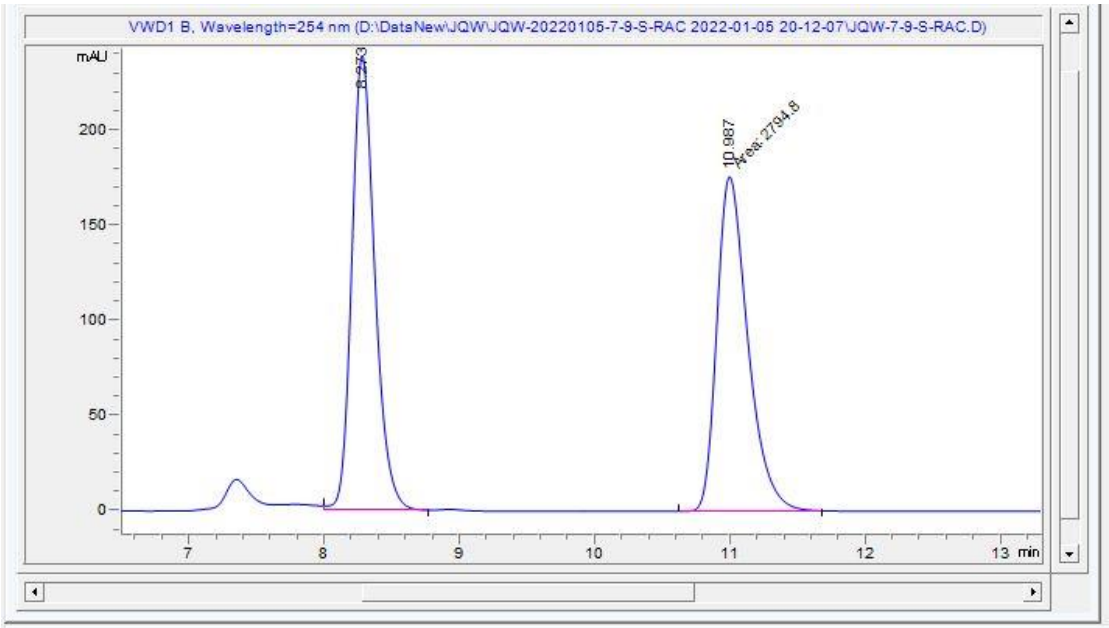
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.015	BV R	2525.4	60.7	0.4888	51.527	0.689
2	20.682	BB	2375.6	49.8	0.5584	48.473	0.712



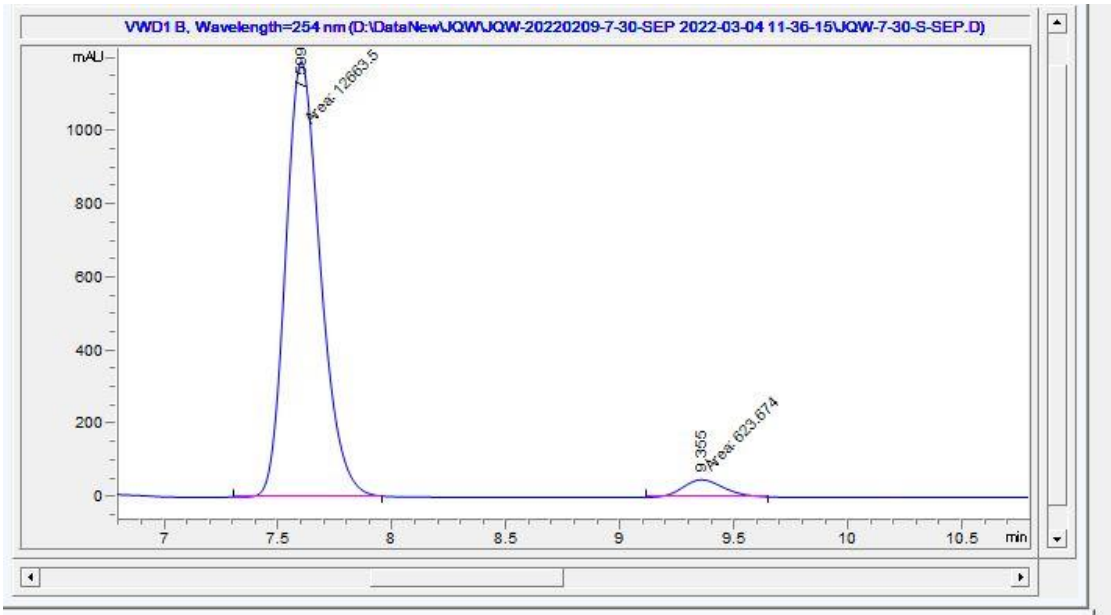
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.664	MF	434.3	8.7	0.8285	6.830	0
2	20.208	FM	5923.5	106.9	0.9236	93.170	0.65

(*S*)-*N*-(1-(4-methoxyphenyl)-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1i**)



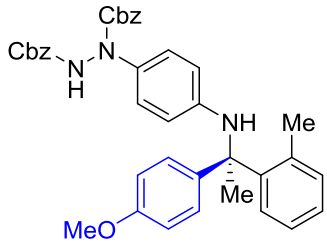


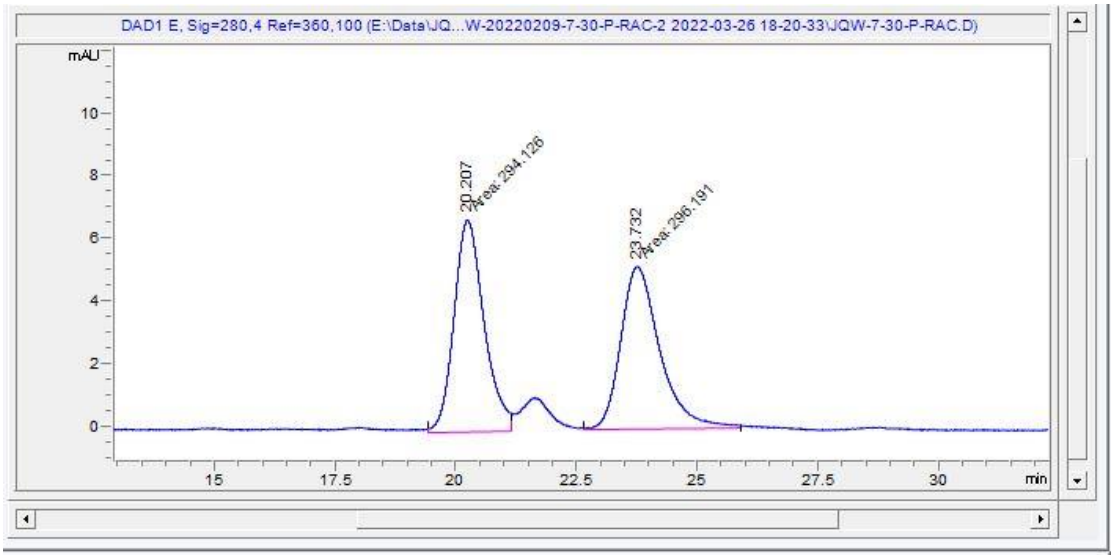
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.273	VB	2817	238.7	0.1817	50.198	0.779
2	10.987	MF	2794.8	175.5	0.2654	49.802	0.67



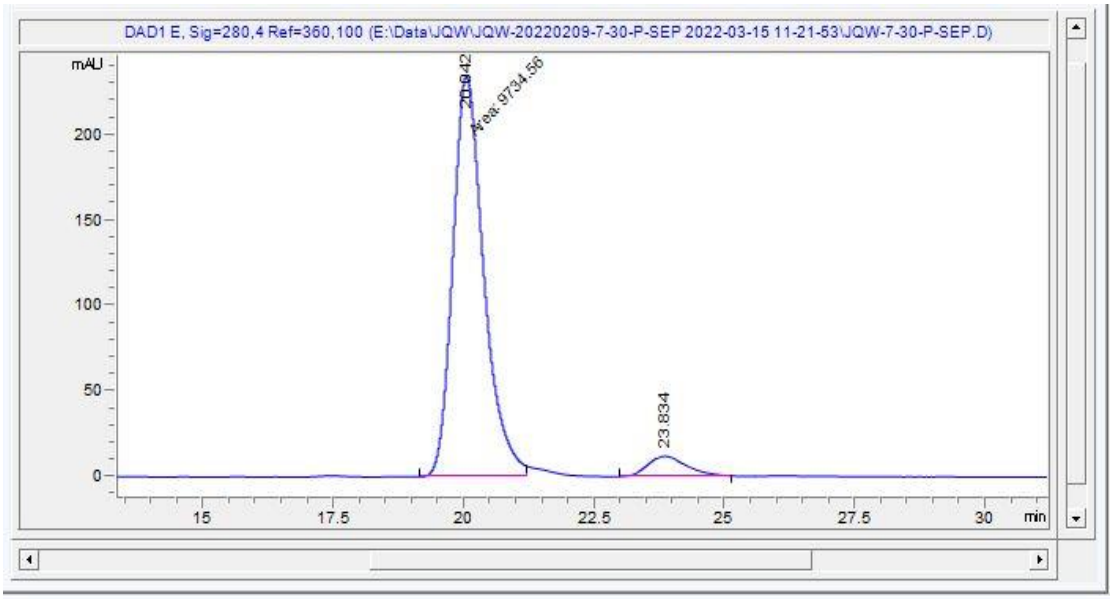
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.599	FM	12663.5	1190.7	0.1772	95.306	0.777
2	9.355	FM	623.7	48.2	0.2157	4.694	0.8

Dibenzyl-(*R*)-1-(4-((1-(4-methoxyphenyl)-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3i**)



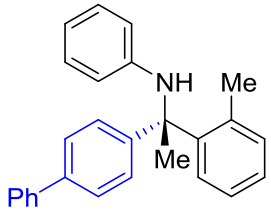


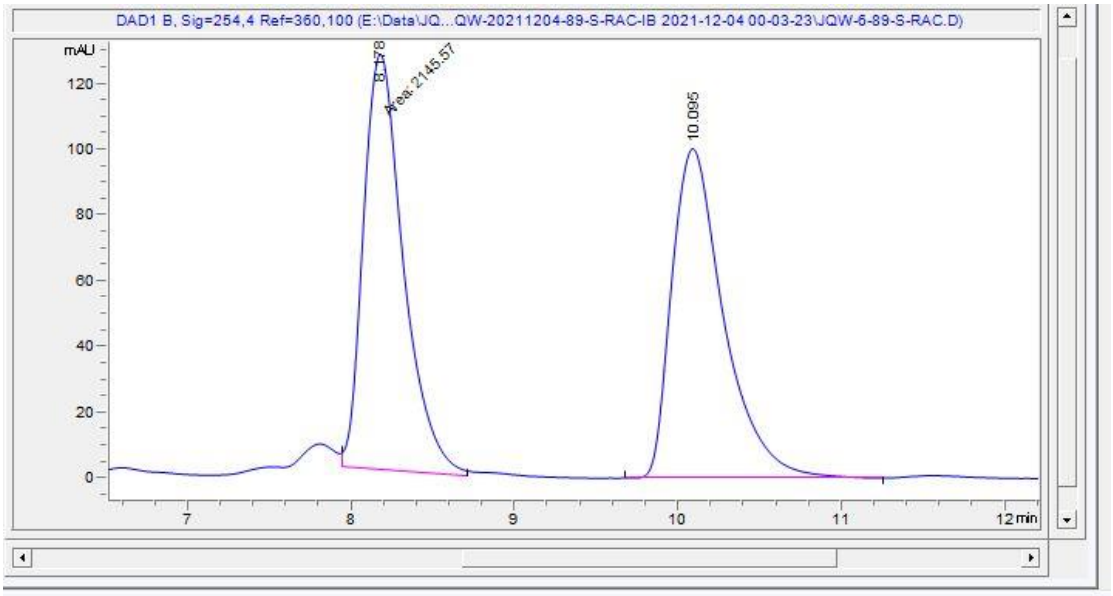
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	20.207	MF	294.1	6.8	0.7244	49.825	0.731
2	23.732	FM	296.2	5.2	0.9477	50.175	0.709



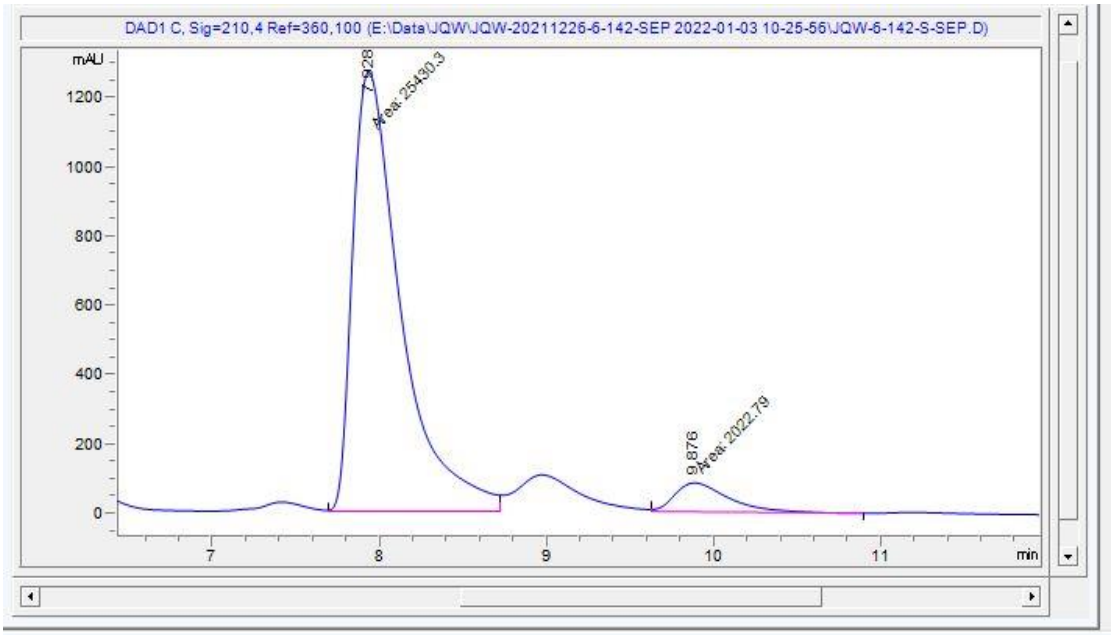
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	20.042	MF	9734.6	234.5	0.6919	94.193	0.753
2	23.834	BB	600.1	11.7	0.6001	5.807	0.742

(*S*)-*N*-(1-([1,1'-biphenyl]-4-yl)-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1j**)



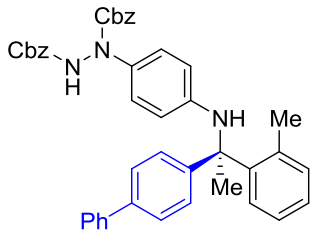


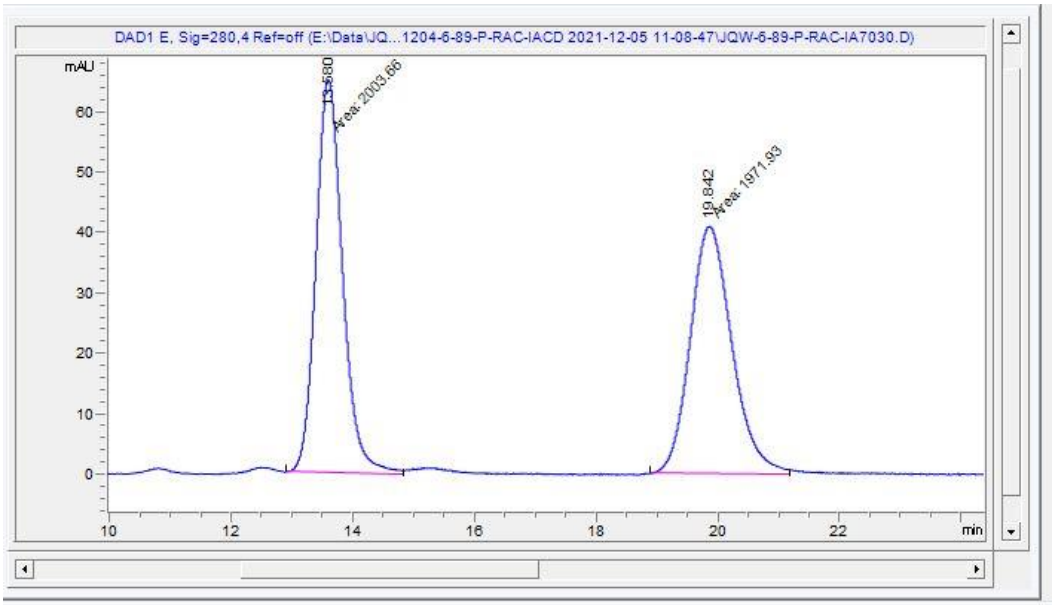
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.178	MM	2145.6	125.9	0.2839	49.196	0.704
2	10.095	BB	2215.7	99.9	0.3407	50.804	0.623



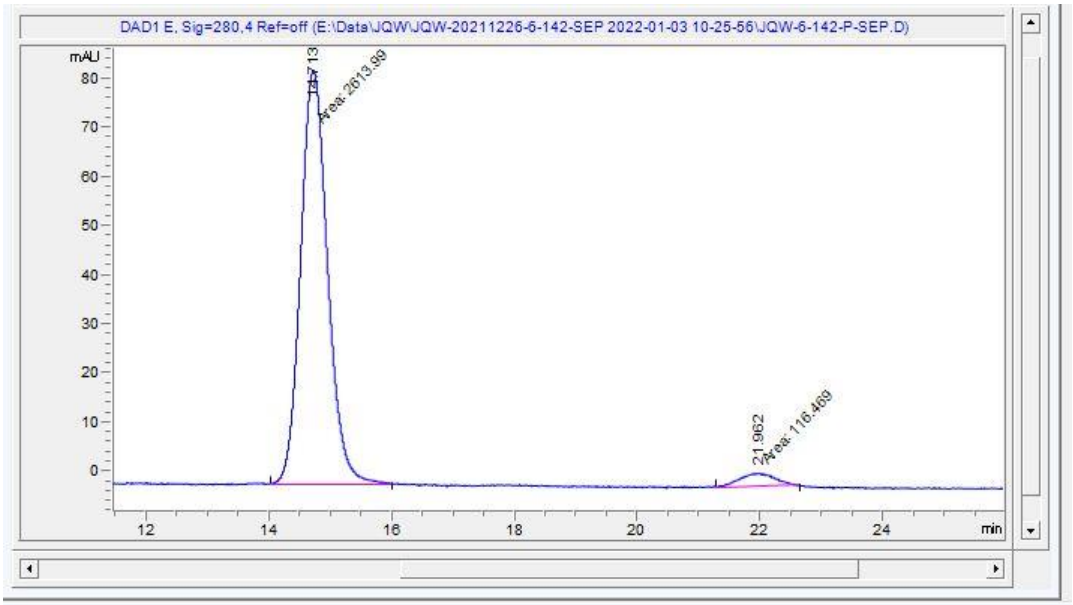
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.928	MF	25430.3	1266.4	0.3347	92.632	0.471
2	9.876	FM	2022.8	86.3	0.3906	7.368	0.555

Dibenzyl-(*R*)-1-(4-((1-([1,1'-biphenyl]-4-yl)-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dic ar-boxylate (**3j**)



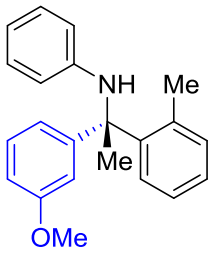


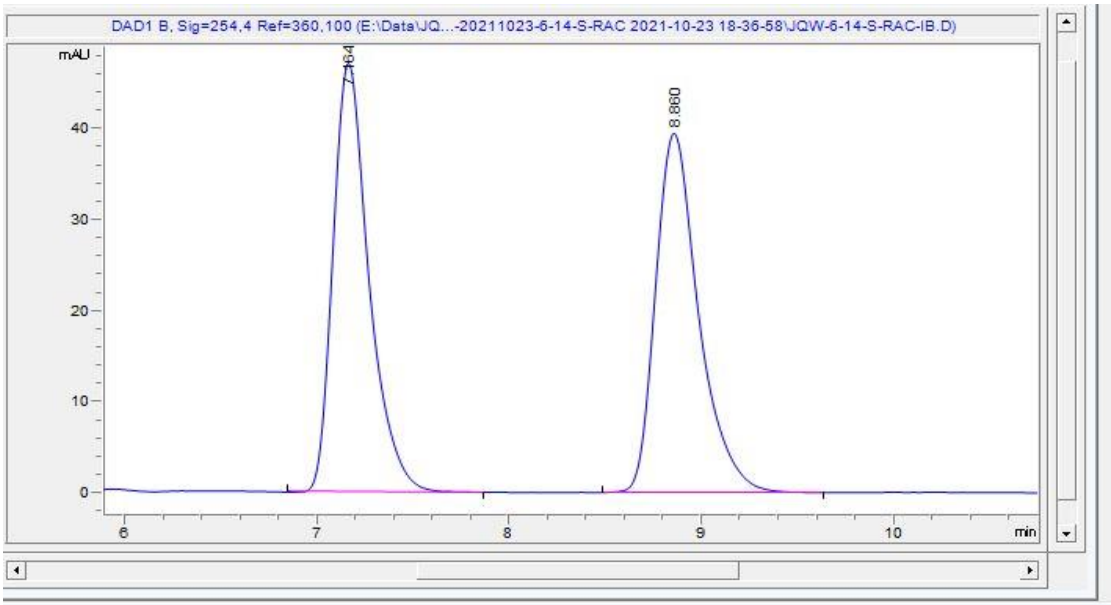
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	13.58	MM	2003.7	65.3	0.5117	50.399	0.846
2	19.842	MM	1971.9	41.2	0.7983	49.601	0.859



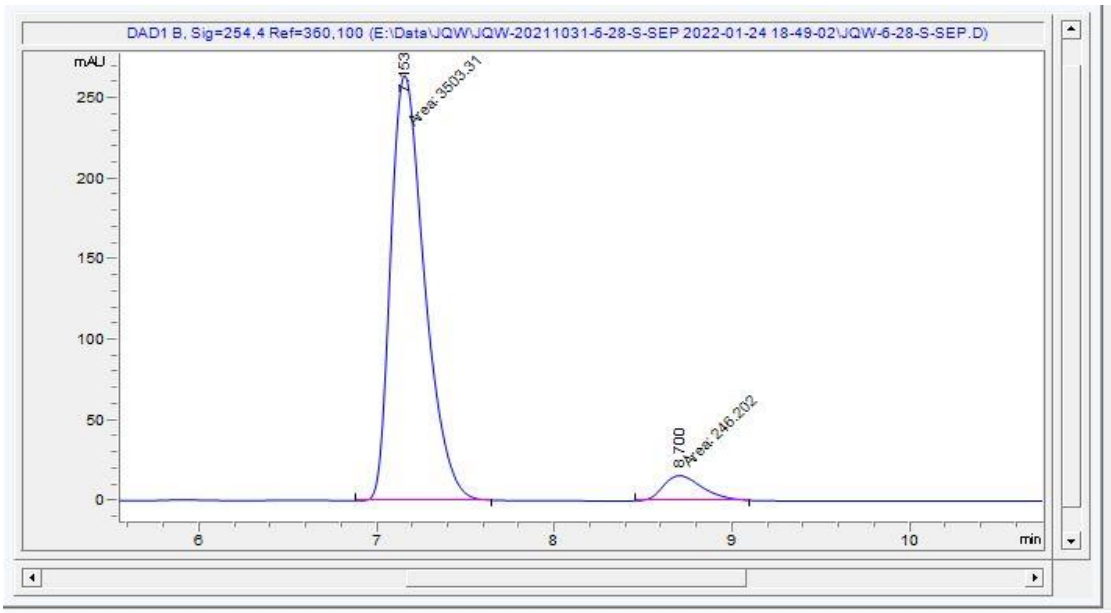
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.713	MM	2614	84.8	0.514	95.734	0.882
2	21.962	MM	116.5	2.8	0.6842	4.266	1.208

(*S*)-*N*-(1-(3-methoxyphenyl)-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1k**)



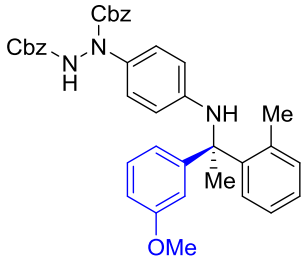


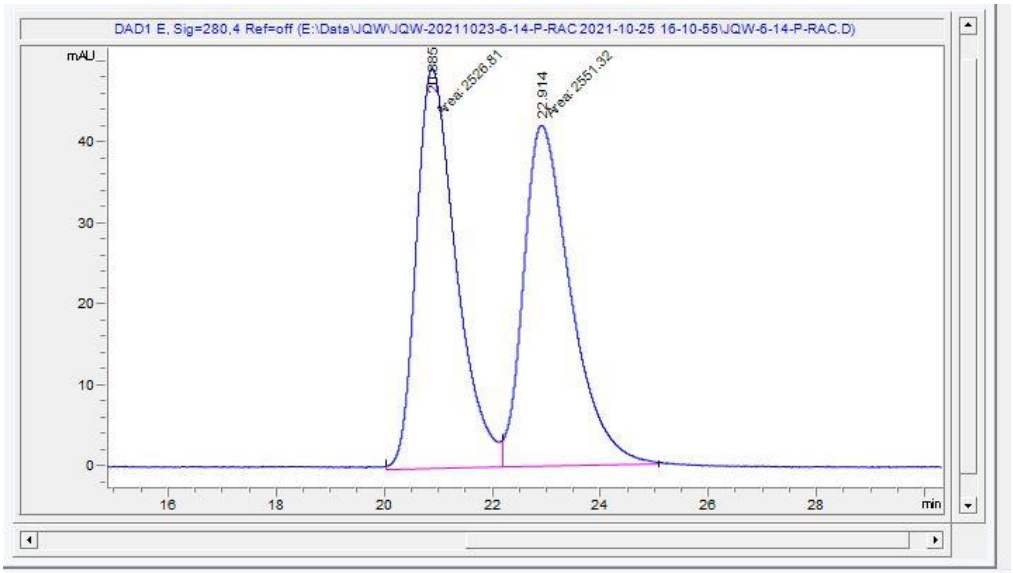
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.164	BB	613.8	47.1	0.1982	49.913	0.692
2	8.86	BB	616	39.4	0.2364	50.087	0.7



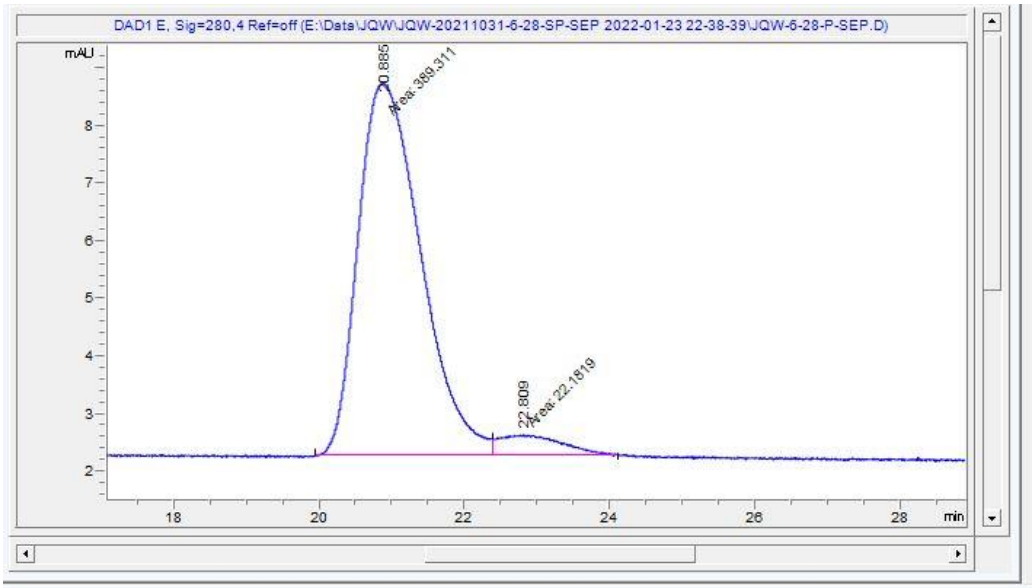
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.153	MF	3503.3	264.3	0.2209	93.434	0.669
2	8.7	MM	246.2	15.7	0.2611	6.566	0.689

Dibenzyl-(*R*)-1-(4-((1-(3-methoxyphenyl)-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicar-boxylate (**3k**)



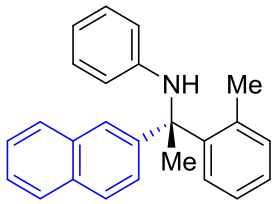


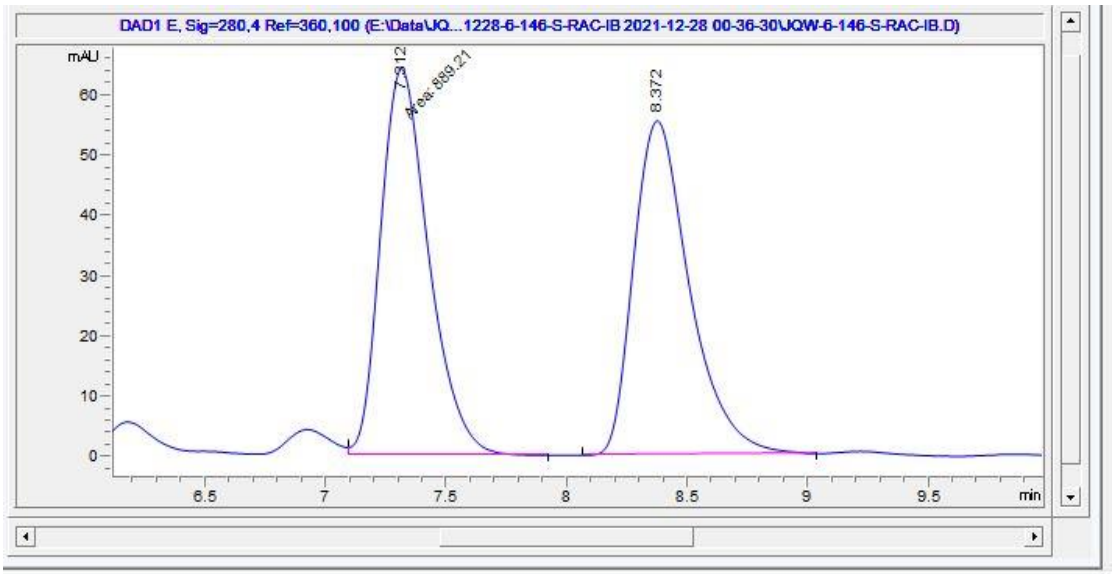
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	20.885	MF	2526.8	49.4	0.8531	49.759	0.649
2	22.914	FM	2551.3	42	1.0115	50.241	0.613



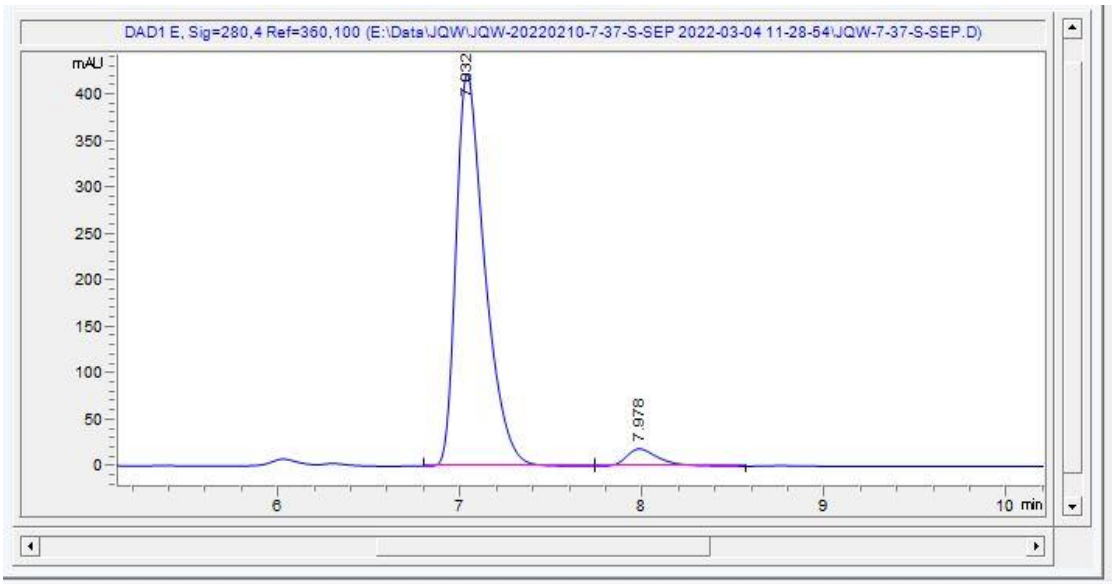
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	20.885	MF	389.3	6.5	1.005	94.609	0
2	22.809	FM	22.2	3.7E-1	0.9966	5.391	0.56

(*S*)-*N*-(1-(naphthalen-2-yl)-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1l**)



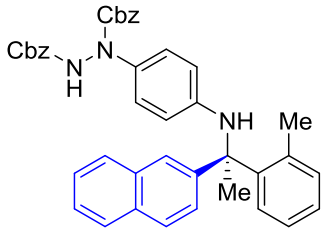


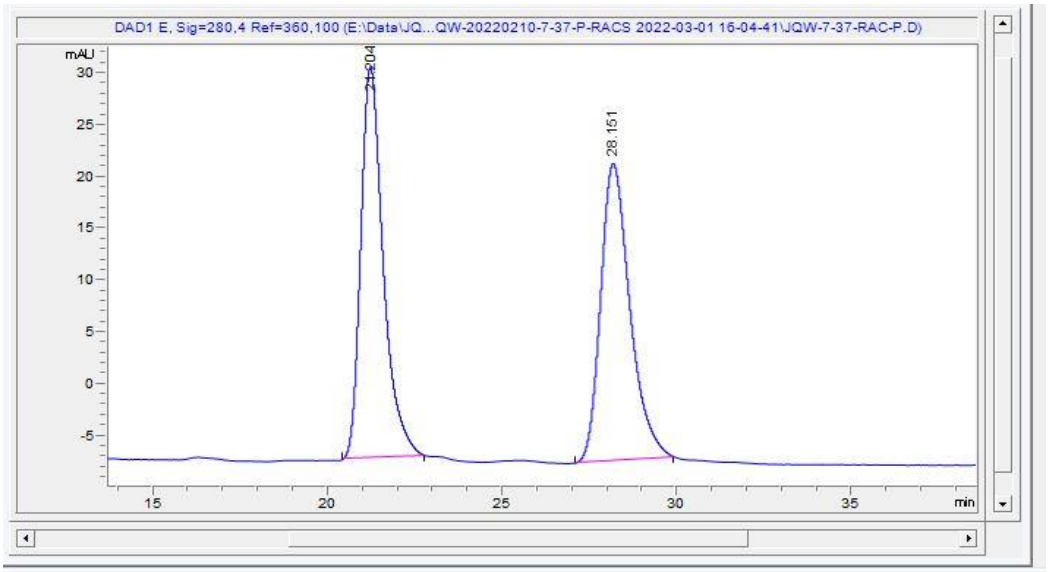
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.312	FM	889.2	64.2	0.2307	49.790	0.742
2	8.372	BB	896.7	55.6	0.2481	50.210	0.681



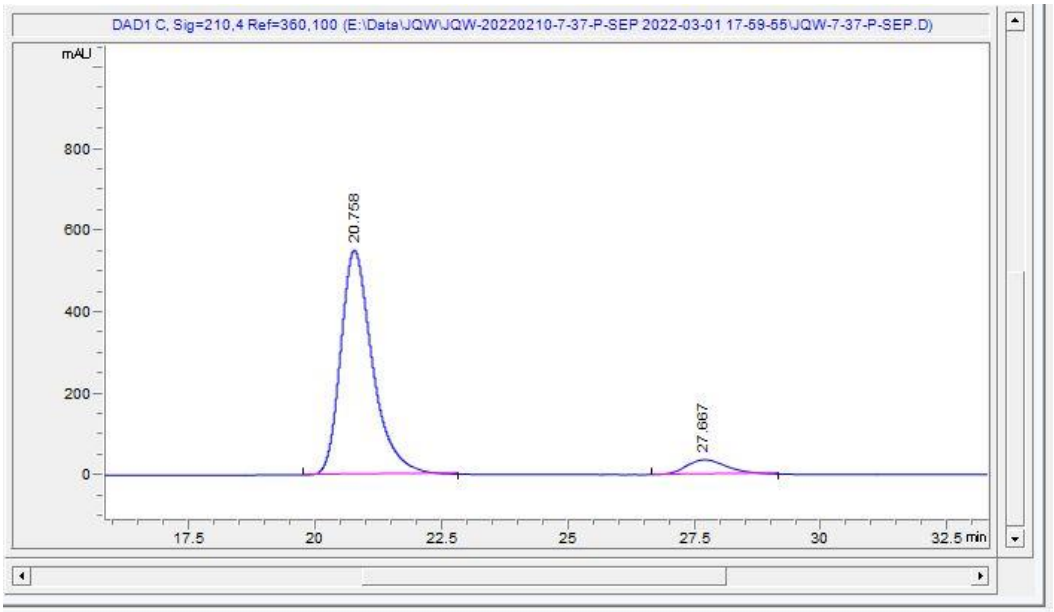
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.032	BB	4614.5	421.4	0.1637	95.250	0.582
2	7.978	BB	230.1	18.6	0.1843	4.750	0.612

Dibenzyl-(*R*)-1-(4-((1-(naphthalen-2-yl)-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarbo xyl-ate (**3l**)



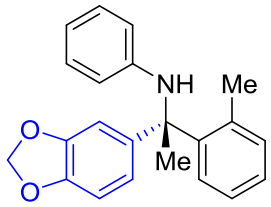


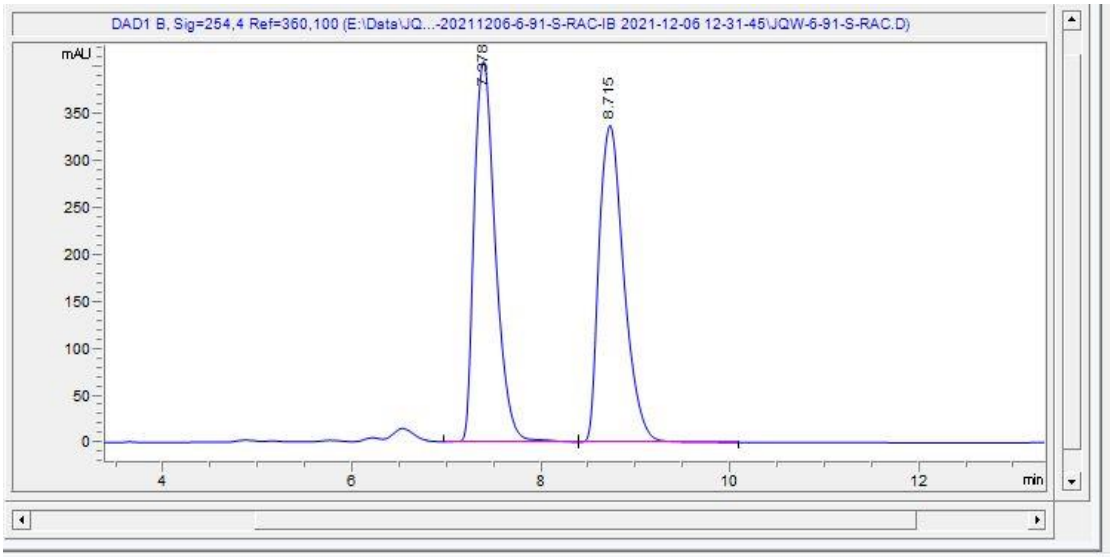
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	21.204	BB	1680.3	37.8	0.5226	50.134	0.713
2	28.151	BB	1671.3	28.7	0.6811	49.866	0.737



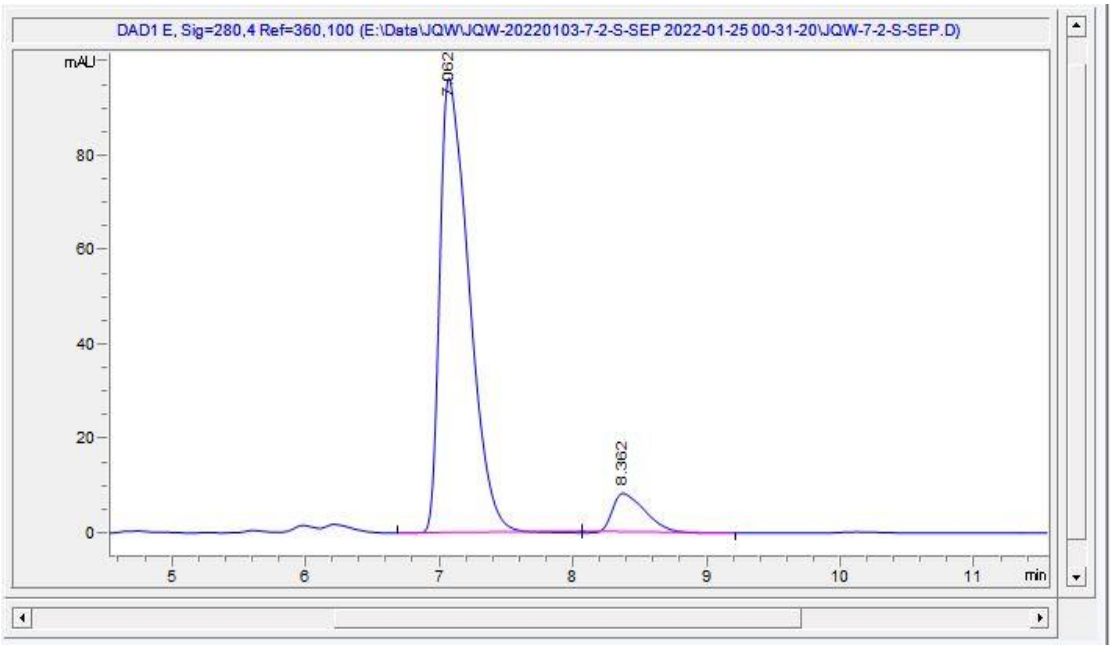
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	20.758	BB	24215.2	551.5	0.5202	92.231	0.738
2	27.667	BB	2039.7	36	0.6632	7.769	0.788

(*S*)-*N*-(1-(benzo[d][1,3]dioxol-5-yl)-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1m**)



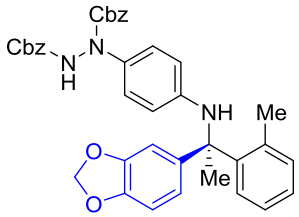


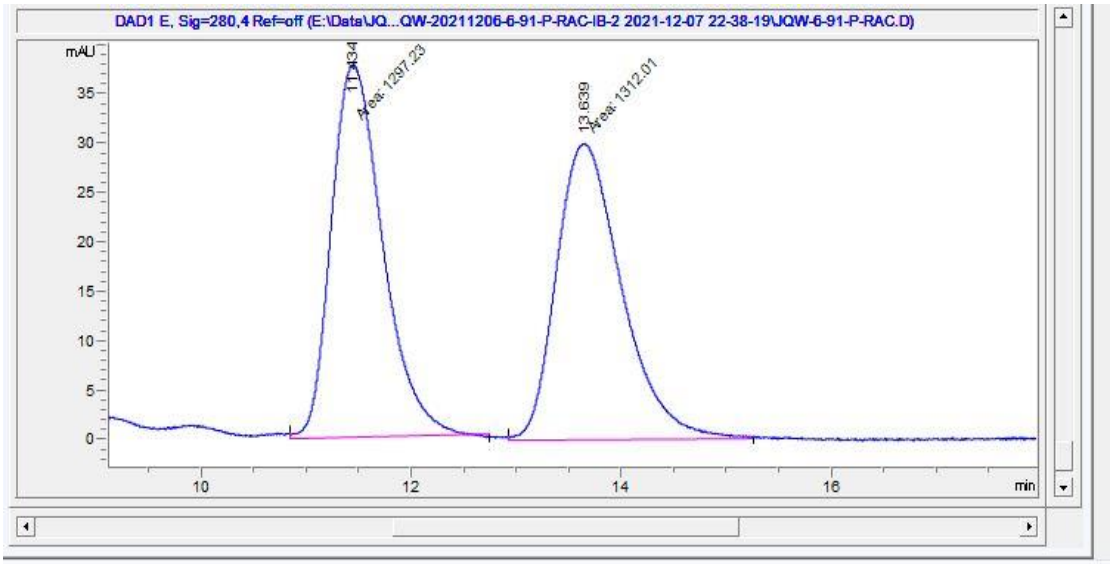
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.378	BB	6285.6	403.5	0.2417	50.602	0.725
2	8.715	BB	6135.9	335.9	0.2851	49.398	0.73



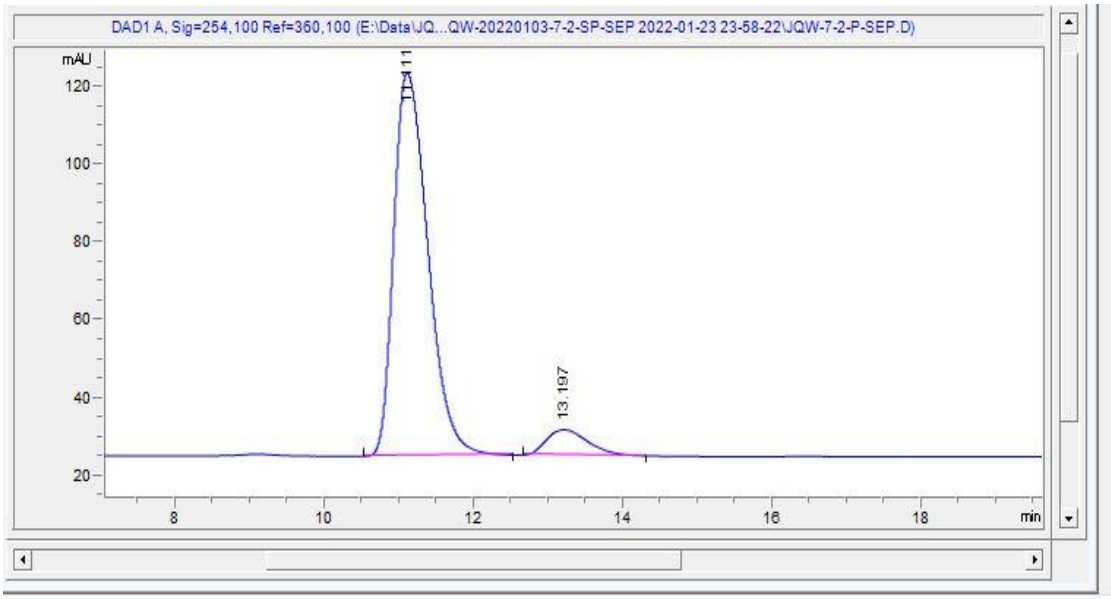
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.062	BB	1463.7	96.7	0.2405	90.994	0.426
2	8.362	BB	144.9	8.4	0.2406	9.006	0.453

Dibenzyl-(*R*)-1-(4-((1-(benzo[d][1,3]dioxol-5-yl)-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1, 2-di-carboxylate (**3m**)



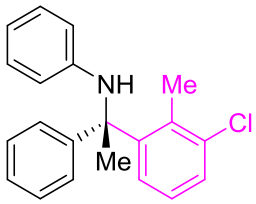


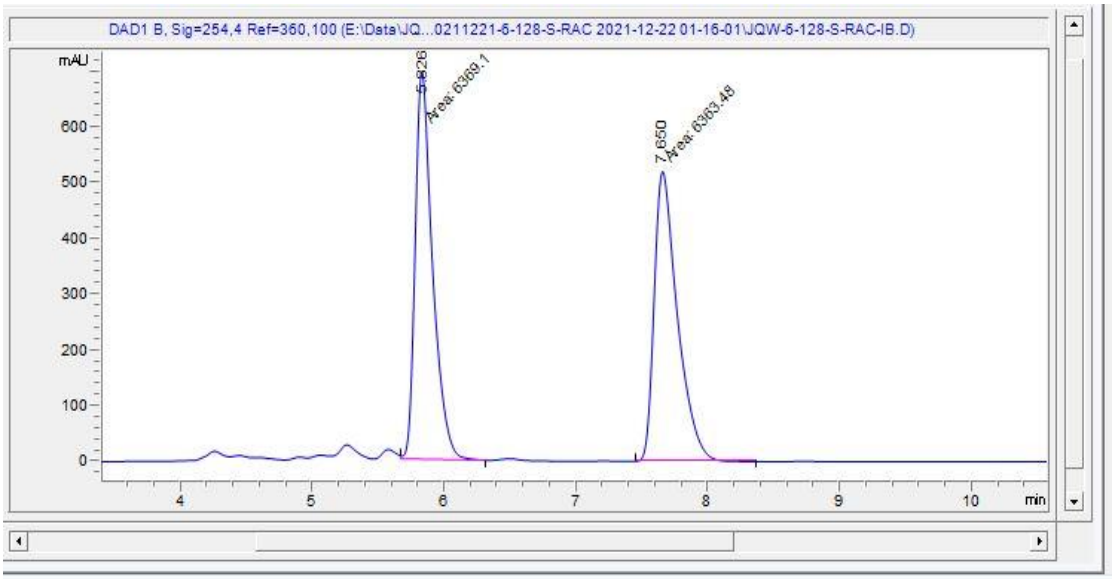
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.434	MM	1297.2	38	0.5692	49.717	0.696
2	13.639	MM	1312	30.2	0.723	50.283	0.723



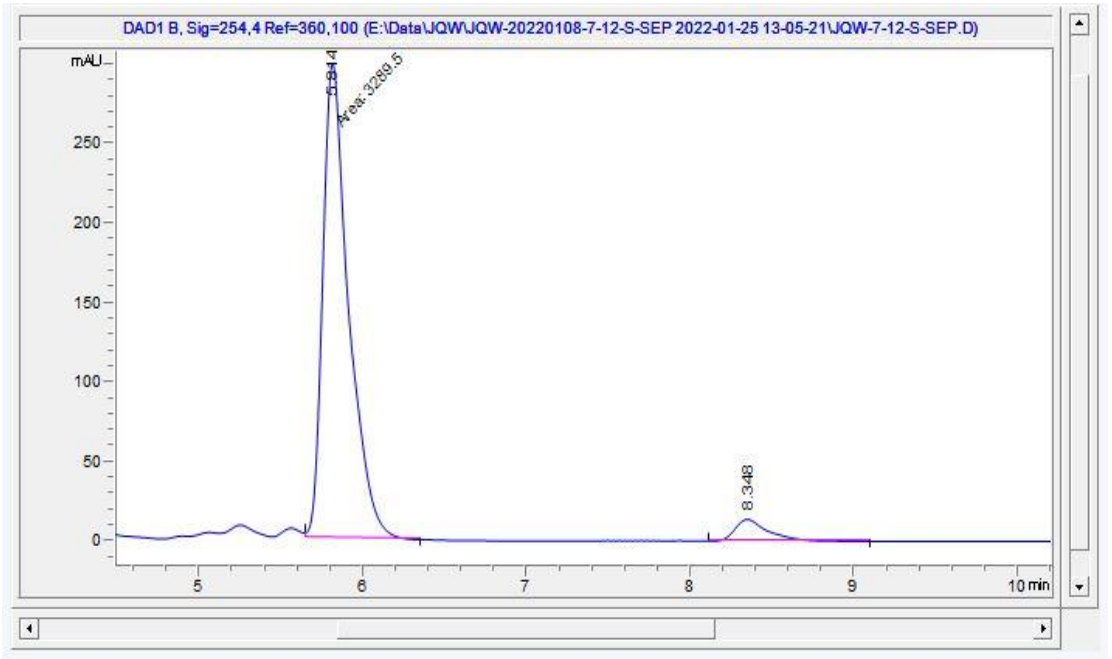
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.111	BB	3135.1	98.6	0.3884	92.464	0.65
2	13.197	BB	255.5	6.6	0.454	7.536	0.655

(*S*)-*N*-(1-(3-chloro-2-methylphenyl)-1-phenylethyl)aniline ((*S*)-**1n**)



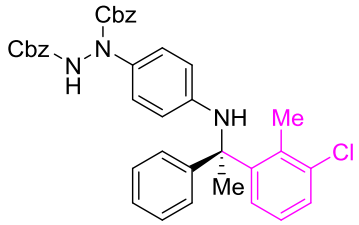


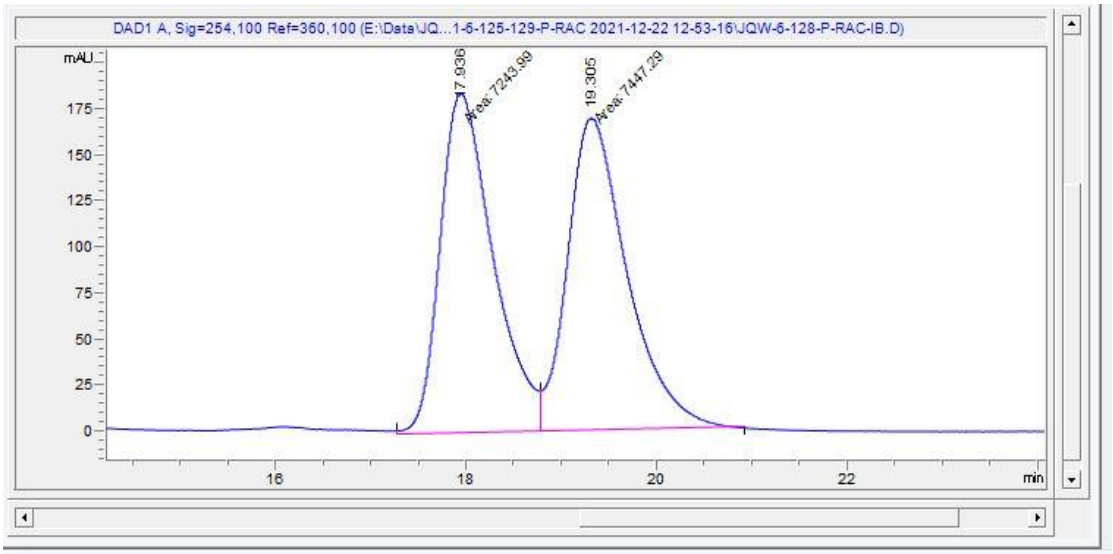
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.826	FM	6369.1	697.2	0.1523	50.022	0.608
2	7.65	FM	6363.5	520.4	0.2038	49.978	0.551



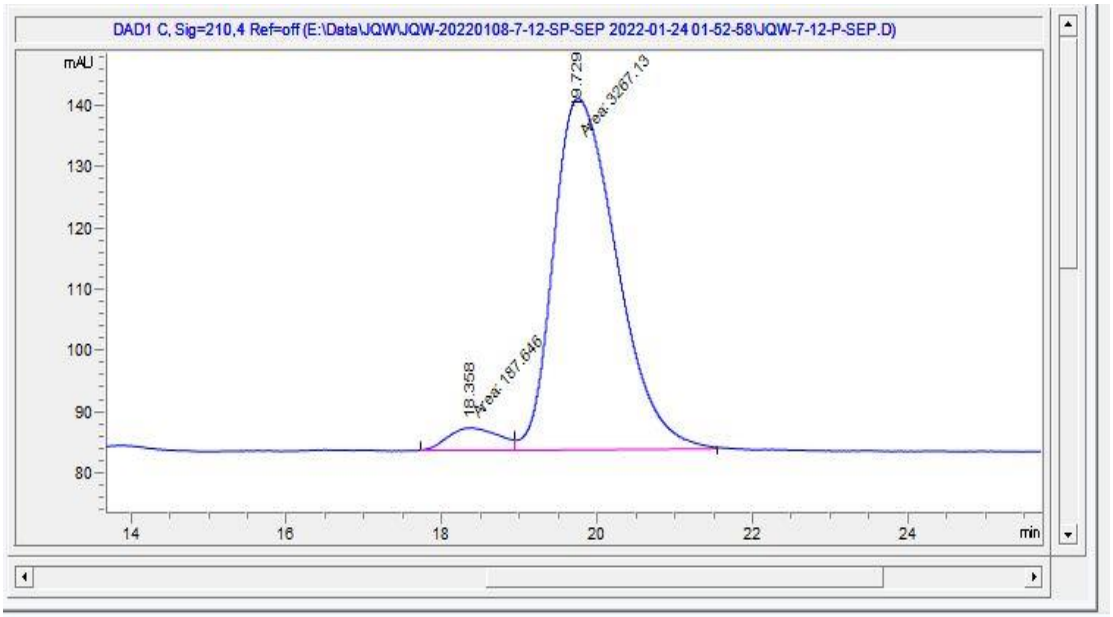
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.814	FM	3289.5	300.1	0.1827	94.446	0.586
2	8.348	BB	193.4	13.7	0.2043	5.554	0.541

Dibenzyl-(*R*)-1-(4-((1-(3-chloro-2-methylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-di-carboxylate (**3n**)



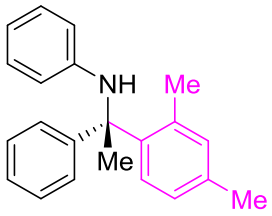


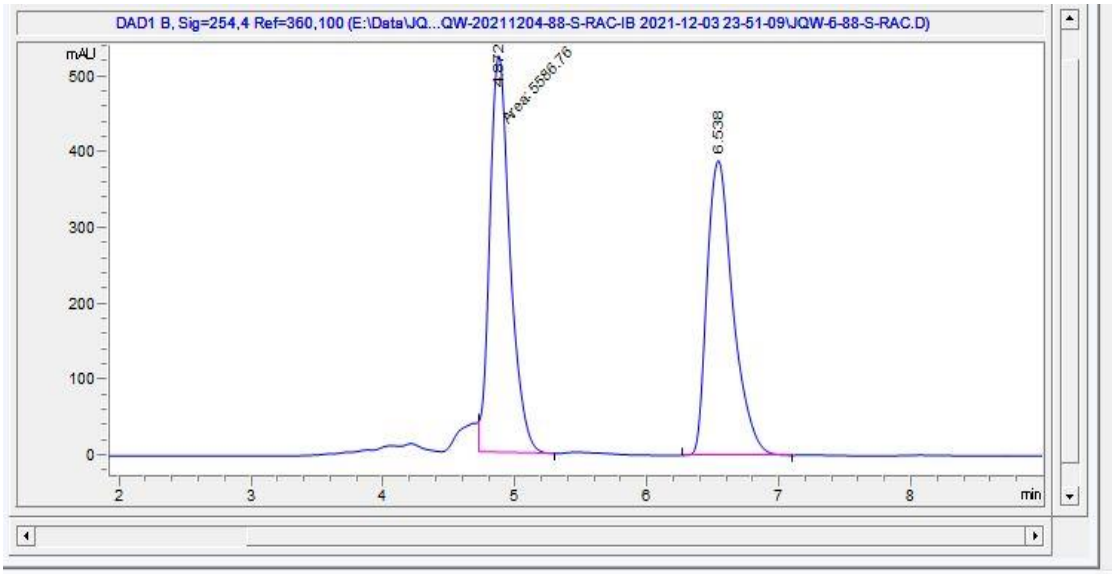
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.936	MF	7244	186.1	0.6488	49.308	0.631
2	19.305	FM	7447.3	171.2	0.7249	50.692	0.654



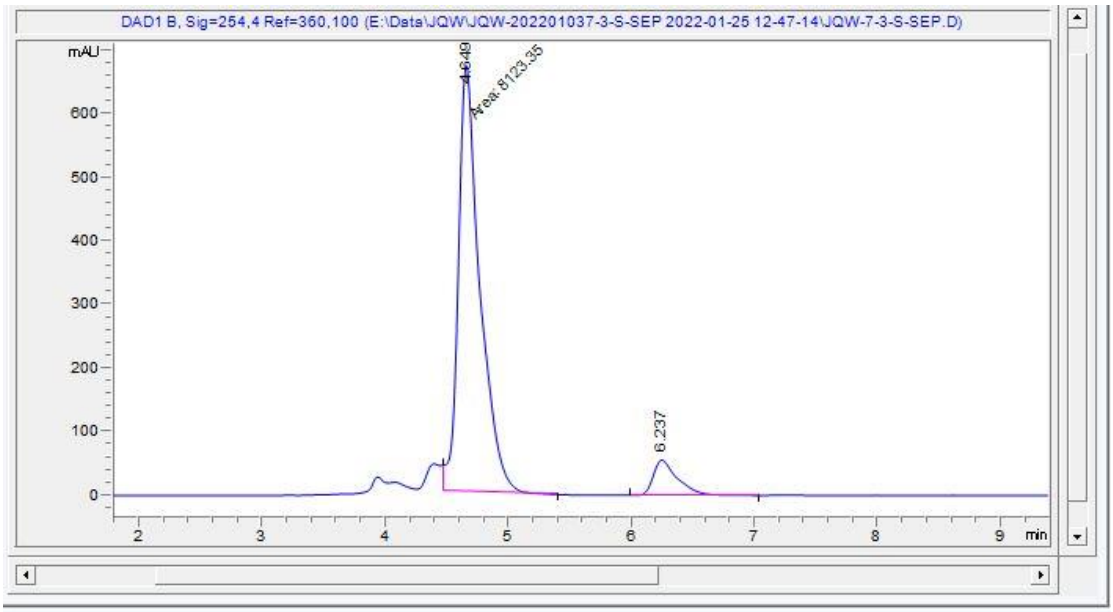
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.358	MF	187.6	3.9	0.795	5.431	0
2	19.729	FM	3267.1	57.7	0.9437	94.569	0.614

(*S*)-*N*-(1-(2,4-dimethylphenyl)-1-phenylethyl)aniline ((*S*)-**1o**)





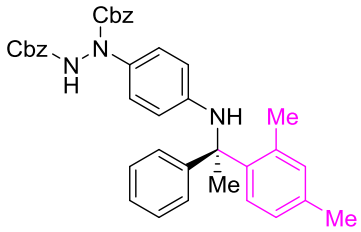
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.872	FM	5586.8	522.3	0.1783	51.273	0.764
2	6.538	BB	5309.3	387.6	0.2098	48.727	0.698

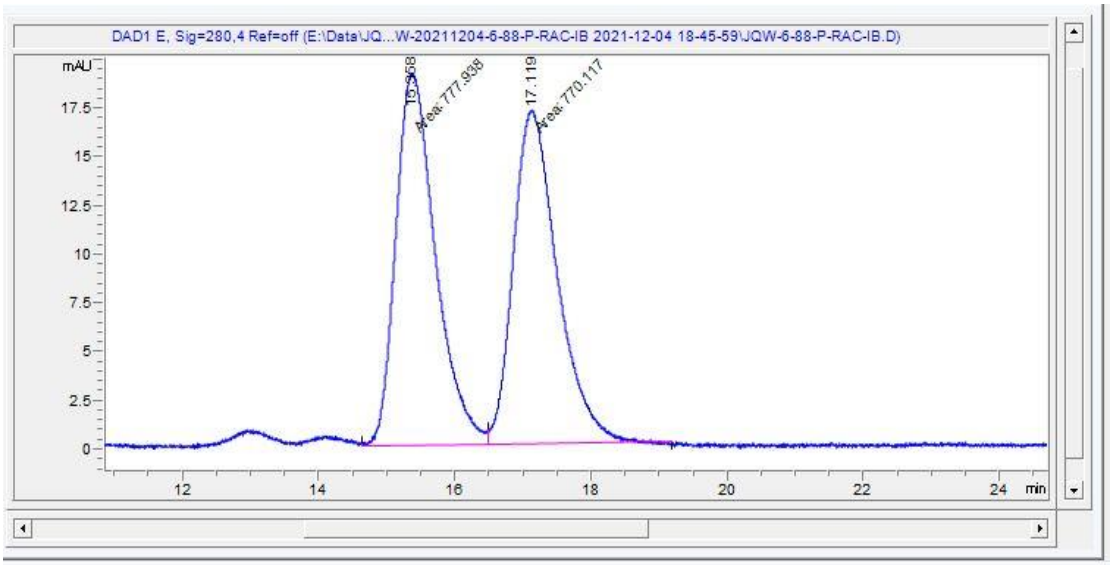


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.649	FM	8123.3	670.5	0.2019	91.550	0.562
2	6.237	BB	749.8	55.3	0.1961	8.450	0.509

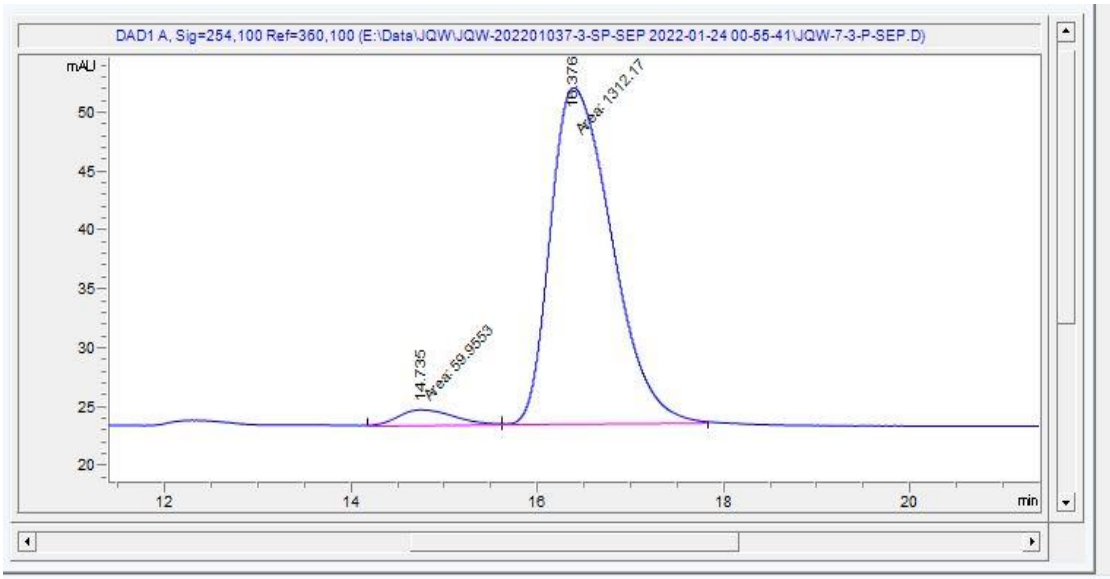
Dibenzyl-(*R*)-1-(4-((1-(2,4-dimethylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-dicar

-boxylate (**3o**)



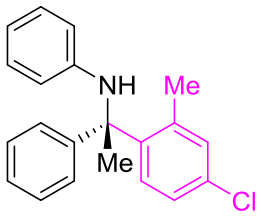


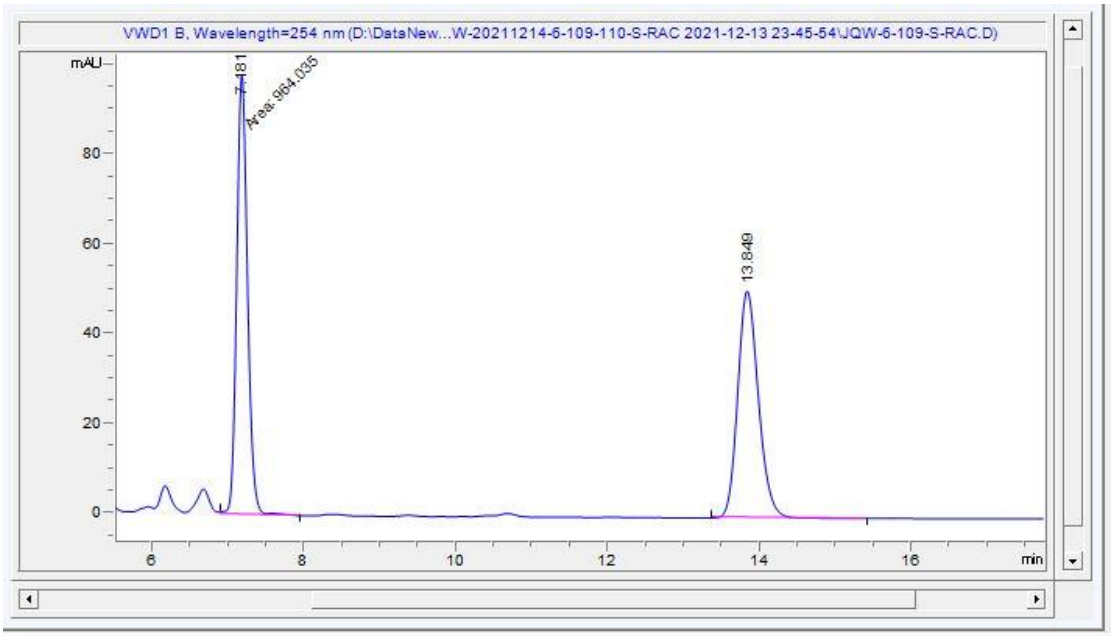
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.358	MF	777.9	19.1	0.6779	50.253	0
2	17.119	FM	770.1	17.1	0.7492	49.747	0.719



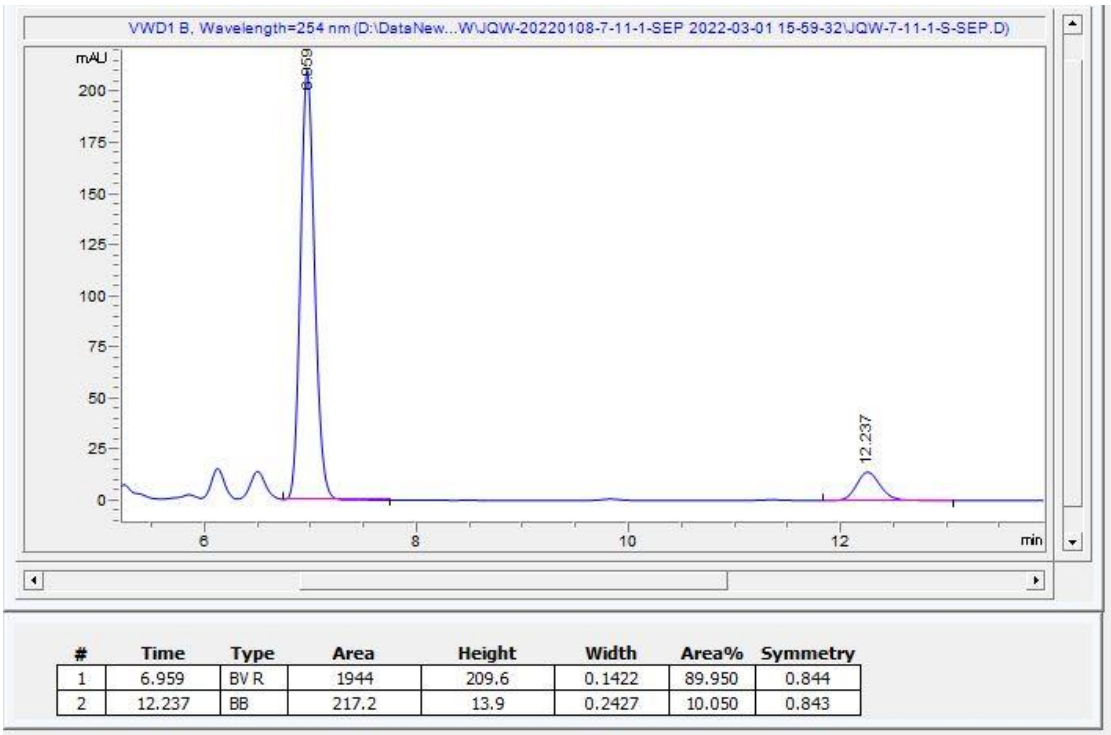
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.735	MF	60	1.4	0.722	4.370	0
2	16.376	FM	1312.2	28.6	0.7651	95.630	0.606

(*S*)-*N*-(1-(4-chloro-2-methylphenyl)-1-phenylethyl)aniline ((*S*)-**1p**)



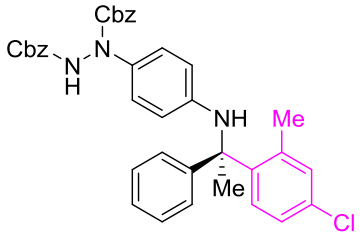


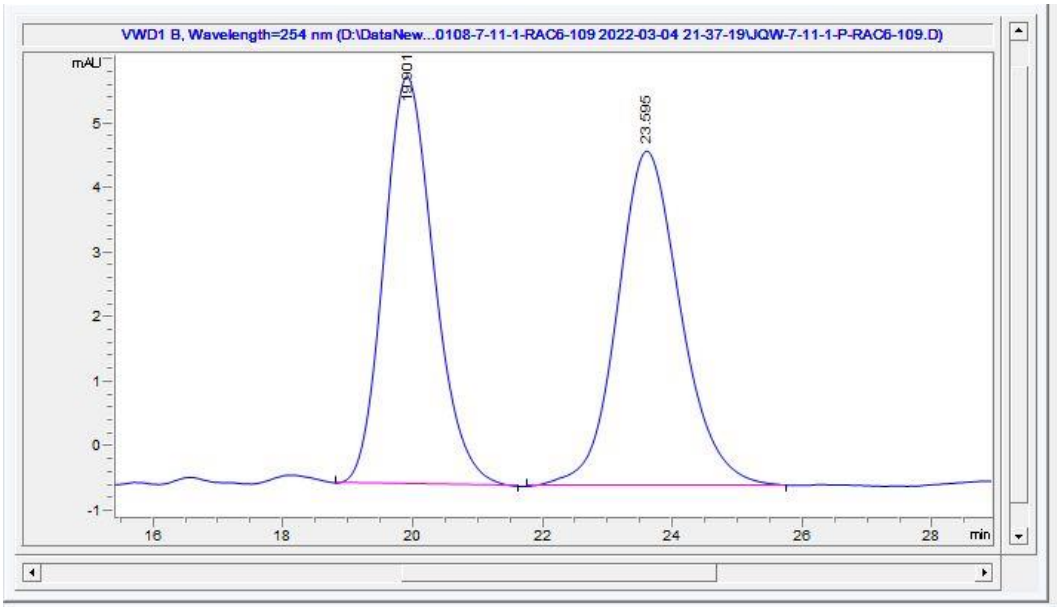
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.181	FM	964	97.8	0.1643	50.169	0.858
2	13.849	BB	957.5	50.5	0.2913	49.831	0.8



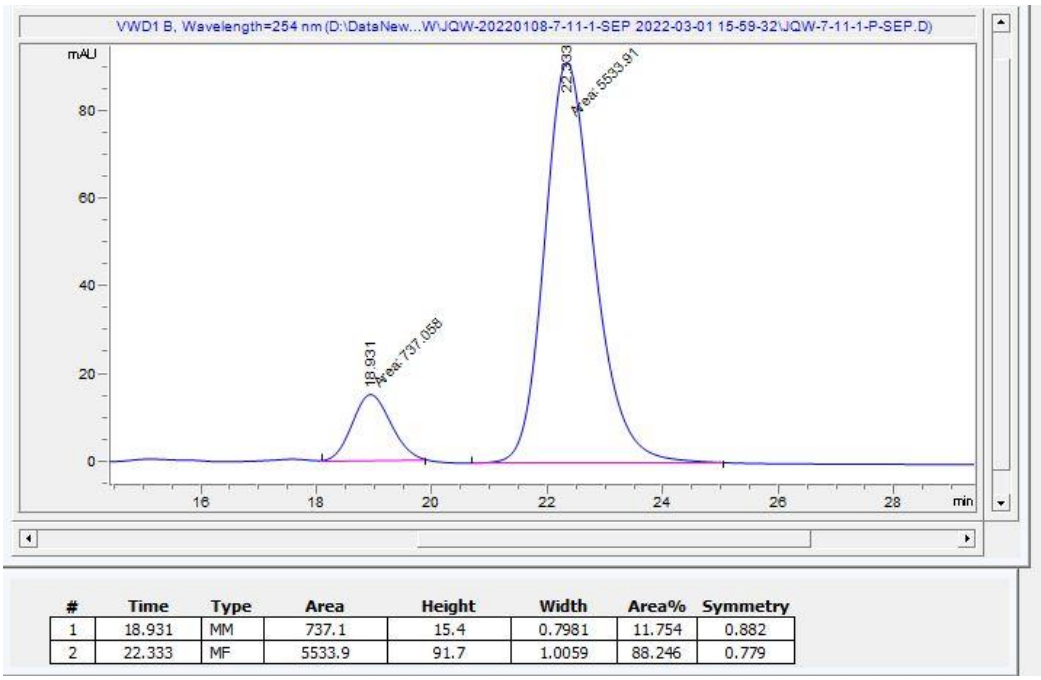
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.959	BV R	1944	209.6	0.1422	89.950	0.844
2	12.237	BB	217.2	13.9	0.2427	10.050	0.843

Dibenzyl-(*R*)-1-(4-((1-(4-chloro-2-methylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-di-carboxylate (**3p**)



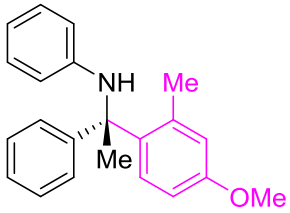


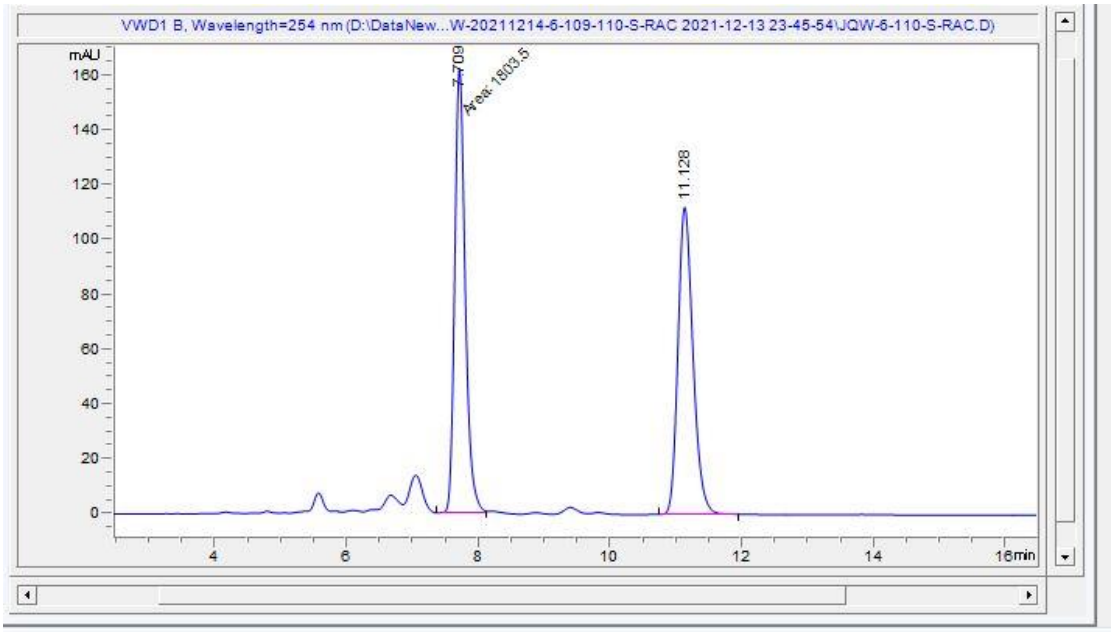
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.901	BB	338.9	6.3	0.8199	48.993	0.817
2	23.595	BB	352.8	5.2	1.0314	51.007	0.846



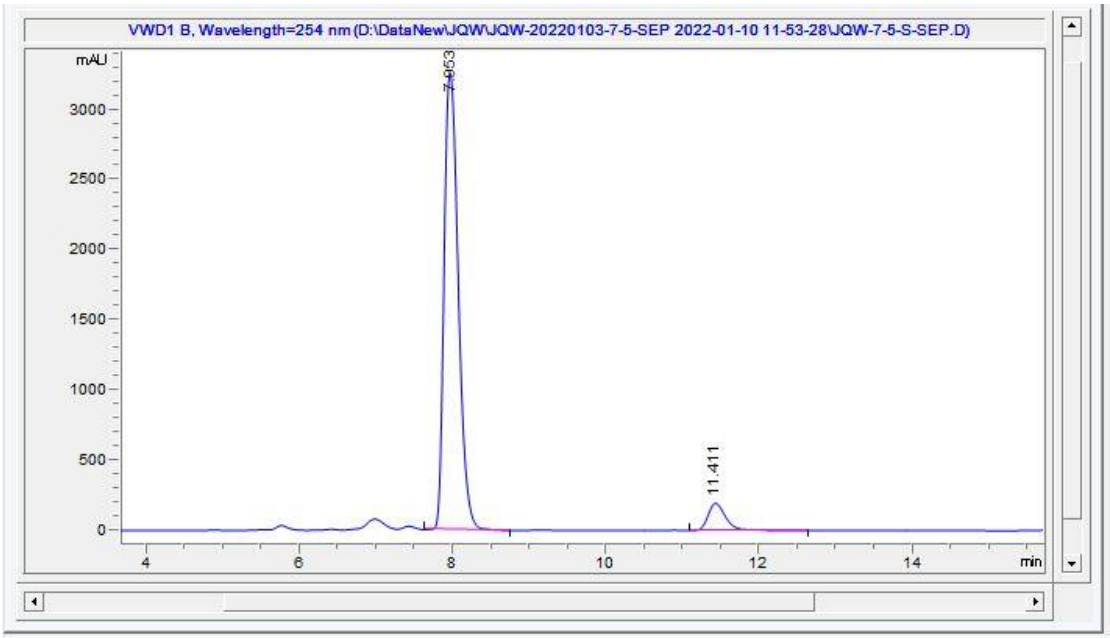
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.931	MM	737.1	15.4	0.7981	11.754	0.882
2	22.333	MF	5533.9	91.7	1.0059	88.246	0.779

(*S*)-*N*-(1-(4-methoxy-2-methylphenyl)-1-phenylethyl)aniline ((*S*)-**1q**)



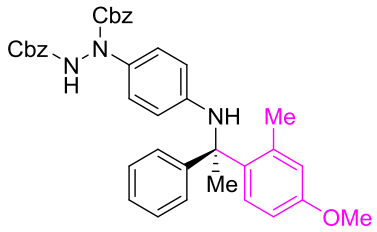


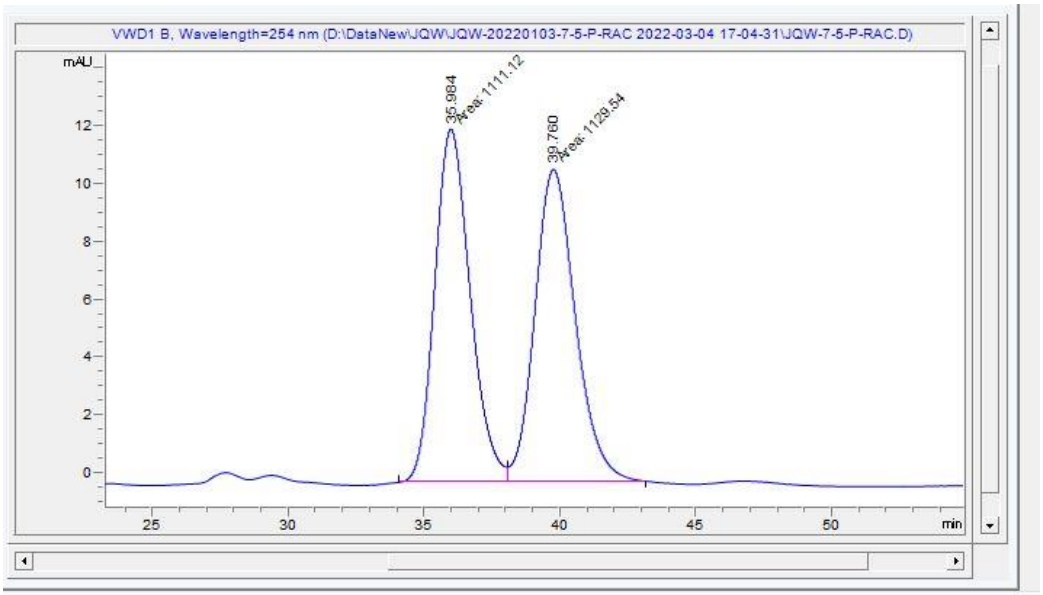
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.709	MF	1803.5	162.2	0.1853	50.488	0.788
2	11.128	BB	1768.6	112.1	0.2421	49.512	0.763



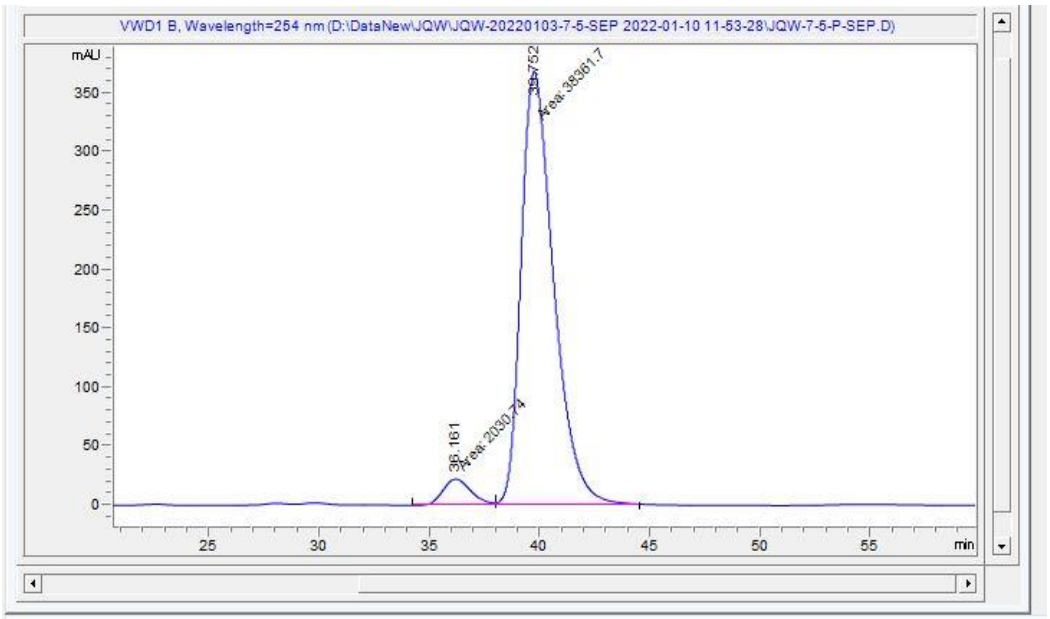
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.953	BB	41539.3	3246.8	0.2013	92.979	0.673
2	11.411	BV R	3136.7	193.9	0.2421	7.021	0.69

Dibenzyl(*R*)-1-(4-((1-(4-methoxy-2-methylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1, 2-di-carboxylate (**3q**)



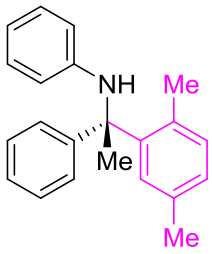


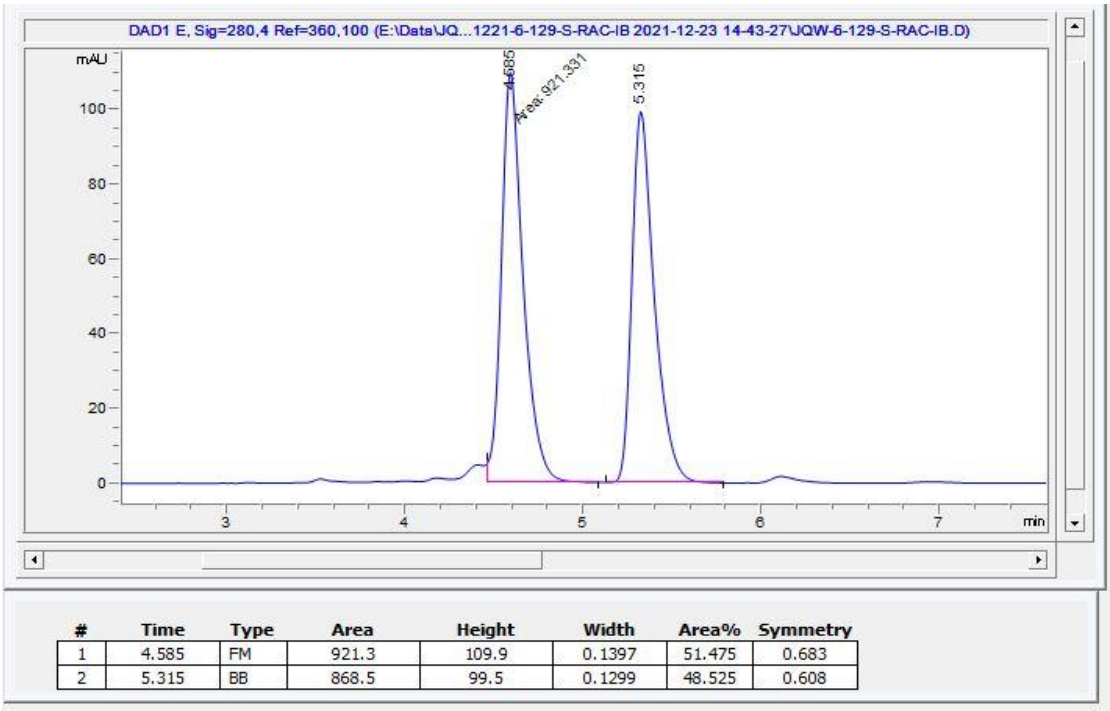
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	35.984	MF	1111.1	12.2	1.5189	49.589	0
2	39.76	FM	1129.5	10.8	1.7431	50.411	0.809



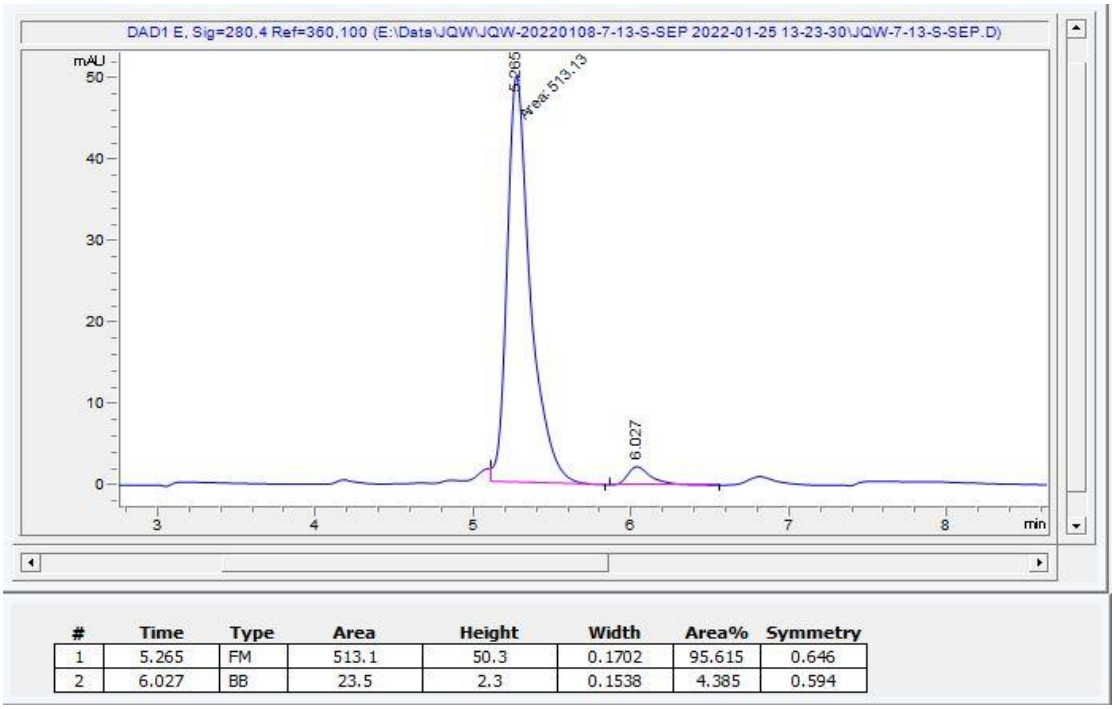
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	36.161	MF	2030.7	22.4	1.5086	5.028	0
2	39.752	MF	38361.7	370.8	1.7243	94.972	0.645

(*S*)-*N*-(1-(2,5-dimethylphenyl)-1-phenylethyl)aniline ((*S*)-**1r**)





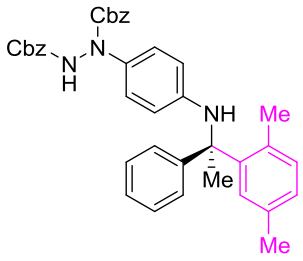
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.585	FM	921.3	109.9	0.1397	51.475	0.683
2	5.315	BB	868.5	99.5	0.1299	48.525	0.608

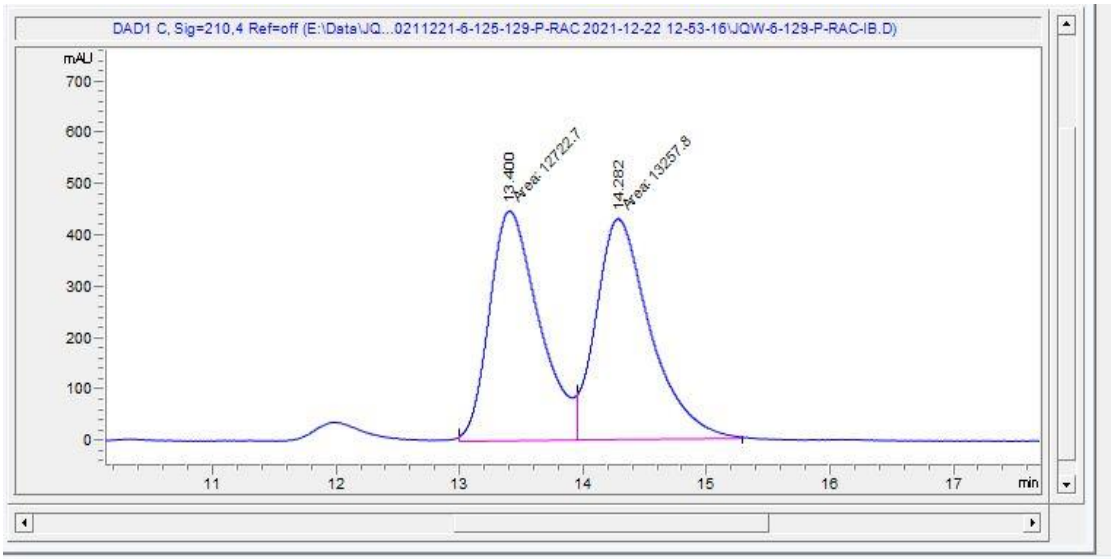


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.265	FM	513.1	50.3	0.1702	95.615	0.646
2	6.027	BB	23.5	2.3	0.1538	4.385	0.594

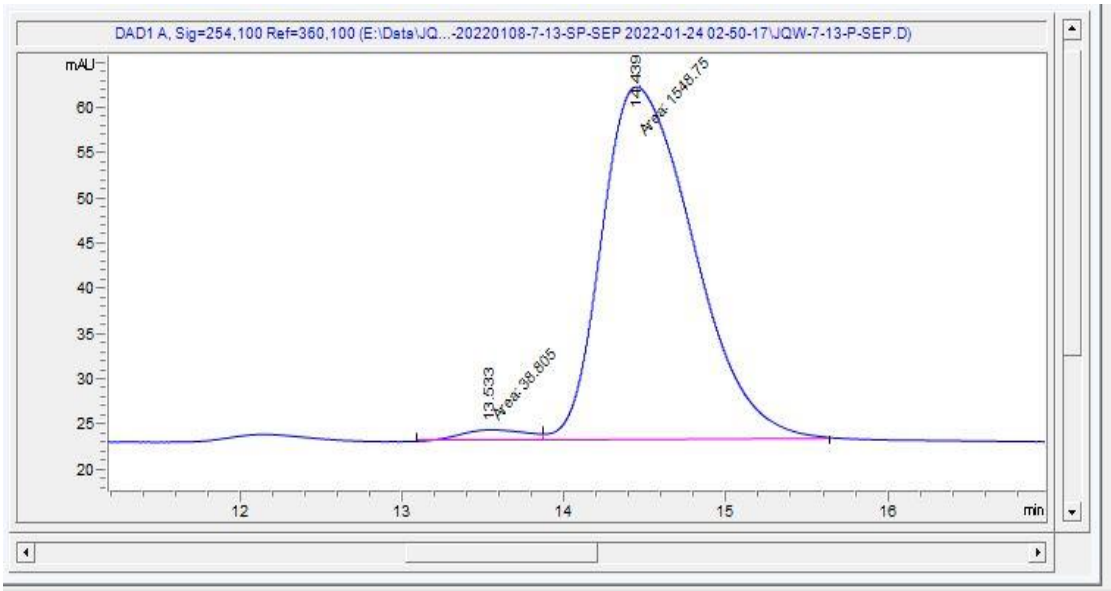
Dibenzyl-(*R*)-1-(4-((1-(2,5-dimethylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-dicar

-boxylate (**3r**)



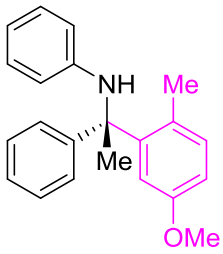


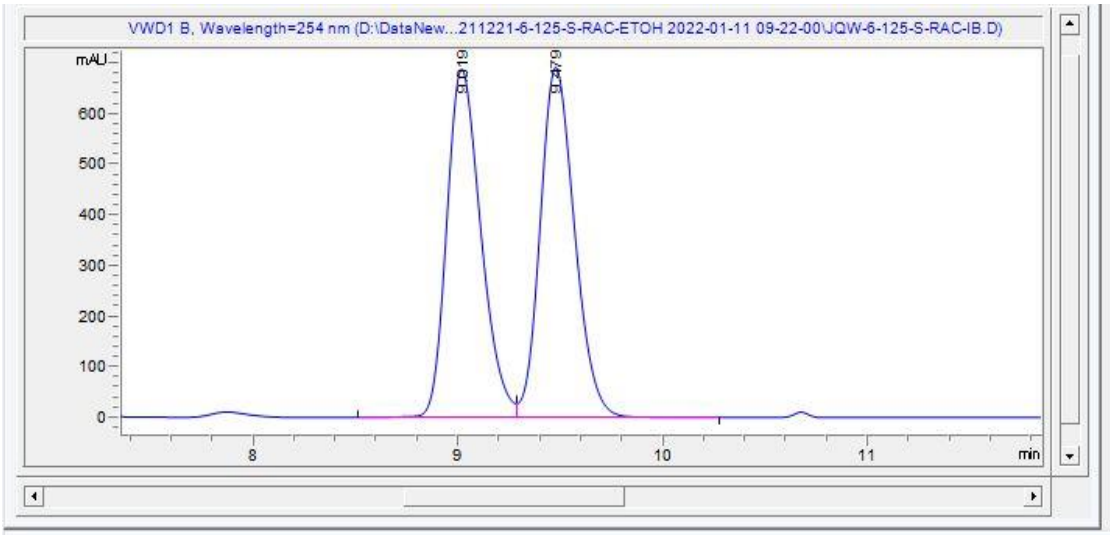
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	13.4	MF	12722.7	449.7	0.4716	48.970	0
2	14.282	FM	13257.8	433.6	0.5097	51.030	0.632



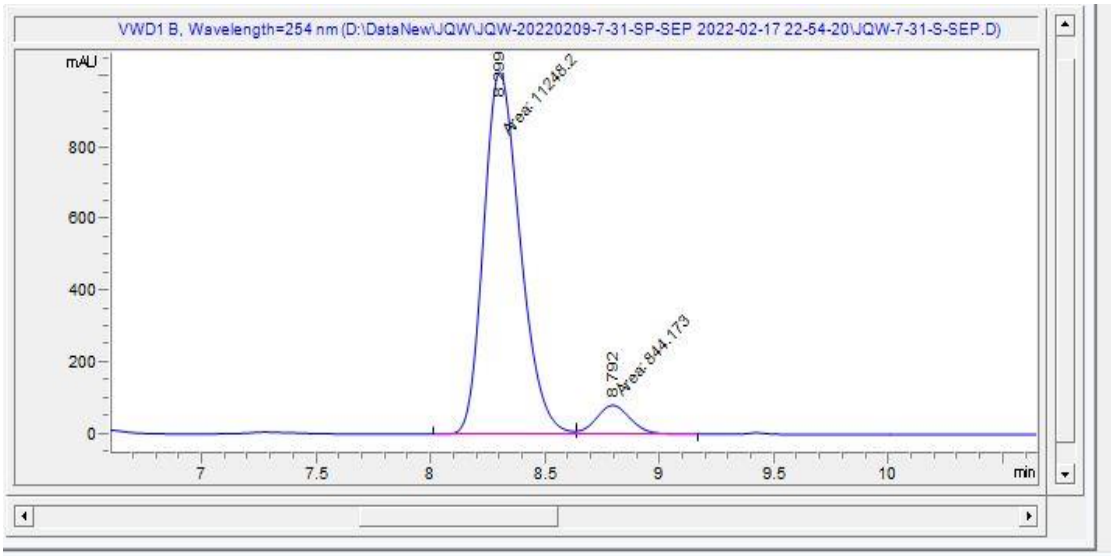
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	13.533	MF	38.8	1.3	0.5056	2.444	0.835
2	14.439	FM	1548.7	39.3	0.6572	97.556	0.59

(*S*)-*N*-(1-(5-methoxy-2-methylphenyl)-1-phenylethyl)aniline ((*S*)-**1s**)



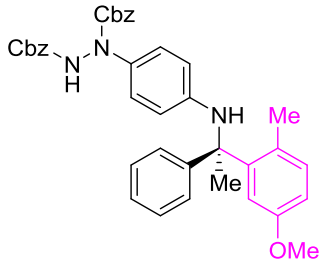


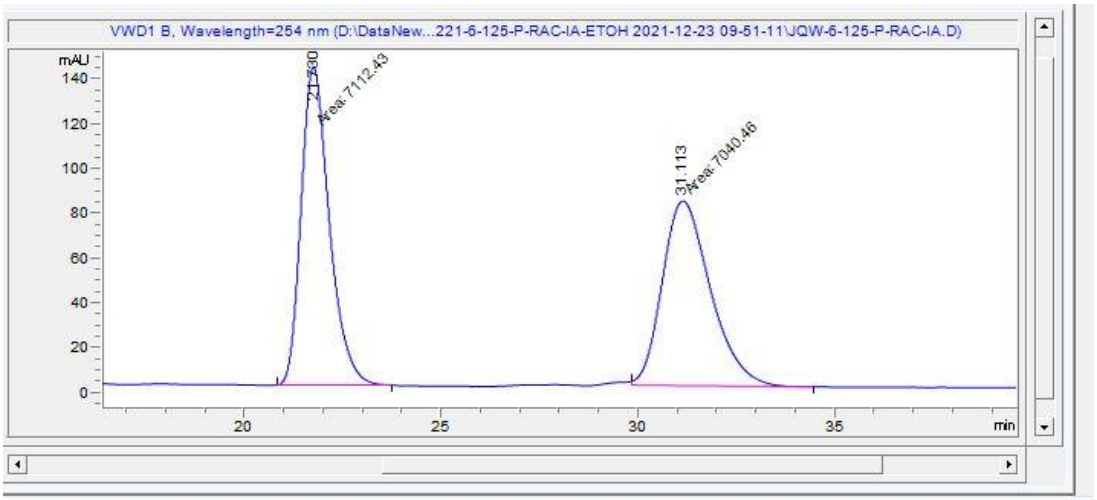
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.019	BV	7958	686.2	0.1773	49.686	0.736
2	9.479	VB	8058.5	689.6	0.1823	50.314	0.78



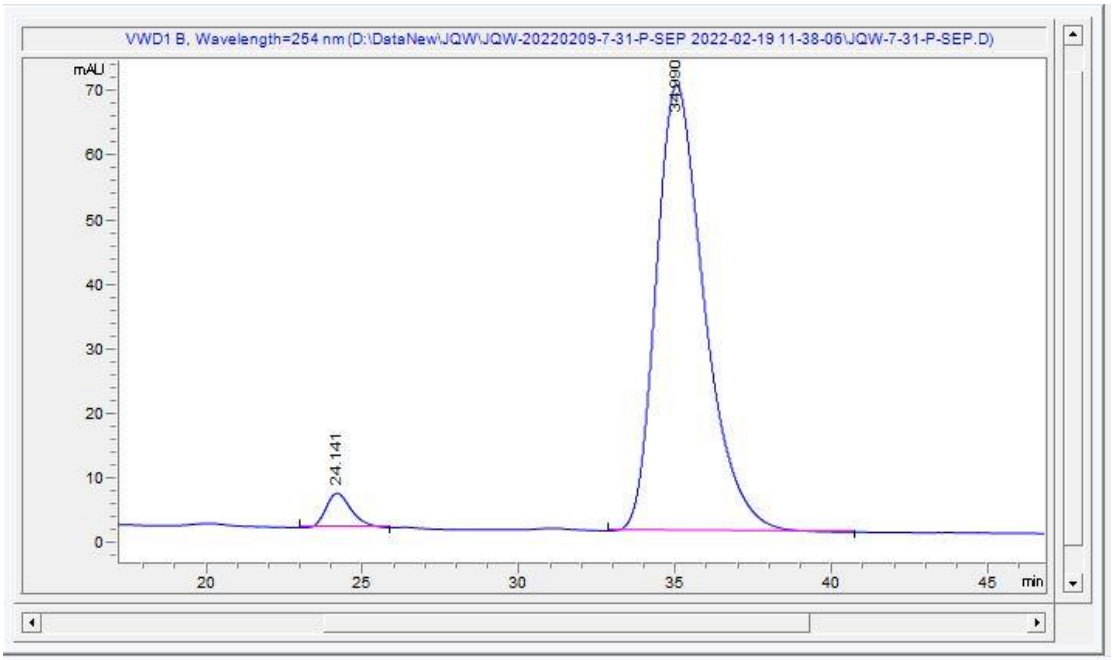
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.299	MF	11248.2	1015.6	0.1846	93.019	0.755
2	8.792	MF	844.2	81.4	0.1729	6.981	0.892

Dibenzyl(*R*)-1-(4-((1-(5-methoxy-2-methylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1, 2-di-carboxylate (**3s**)



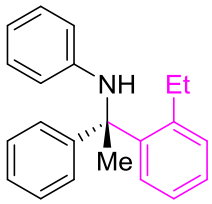


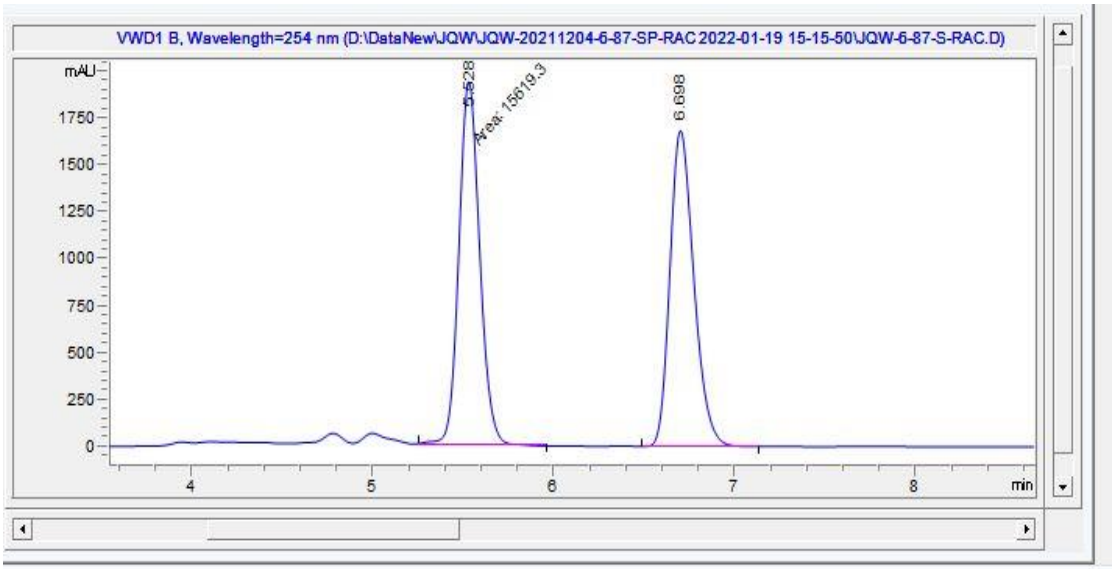
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	21.73	MM	7112.4	141.8	0.8358	50.254	0.73
2	31.113	MM	7040.5	82.3	1.4258	49.746	0.723



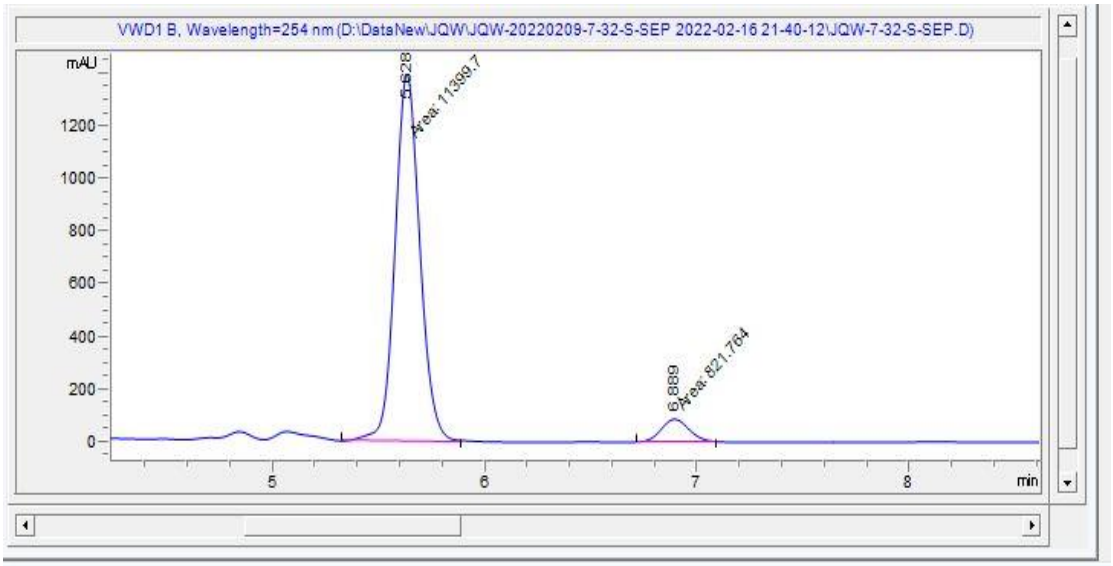
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	24.141	BB	304.8	5.4	0.8685	3.932	0.722
2	34.99	BB	7445.9	69.4	1.6322	96.068	0.695

(*S*)-*N*-(1-(2-ethylphenyl)-1-phenylethyl)aniline ((*S*)-**1t**)



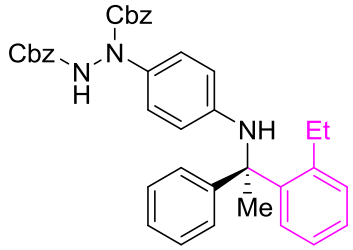


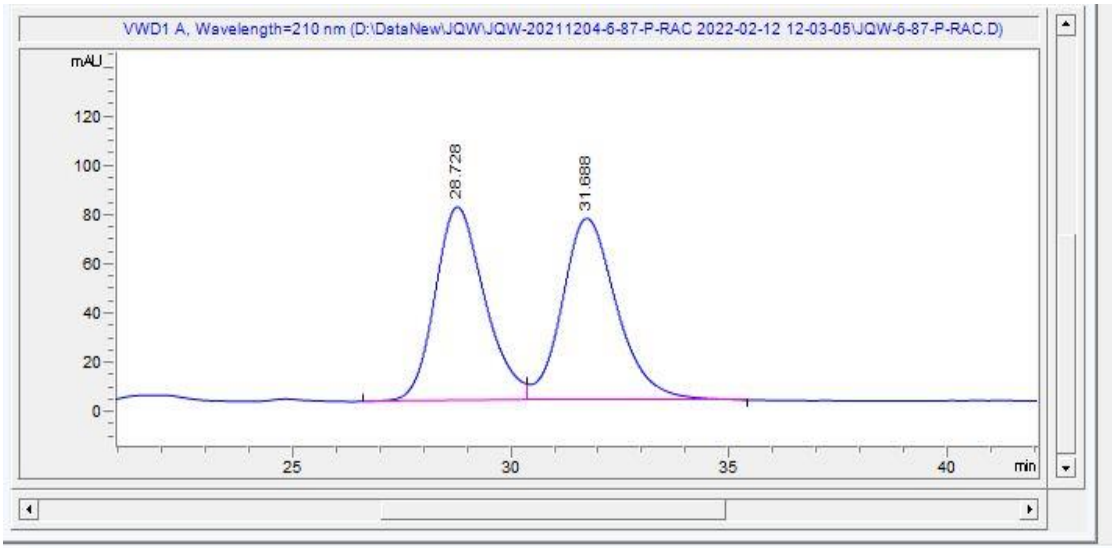
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.528	FM	15619.3	1948.9	0.1336	50.154	0.878
2	6.698	VB	15523.1	1691.5	0.1411	49.846	0.741



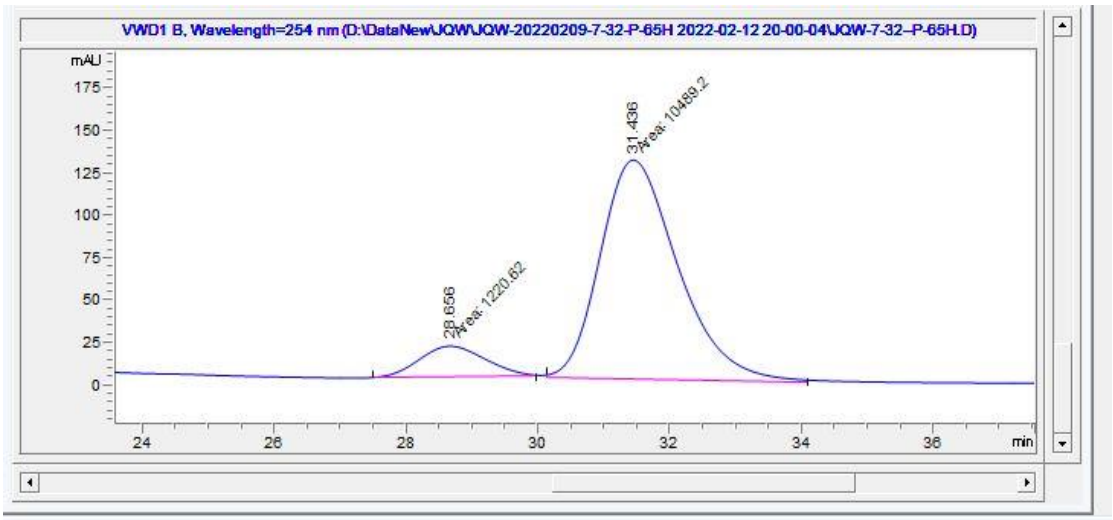
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.628	MF	11399.7	1403.5	0.1354	93.276	0.895
2	6.889	FM	821.8	88.1	0.1554	6.724	0.878

Dibenzyl-(*R*)-1-(4-((1-(2-ethylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3t**)



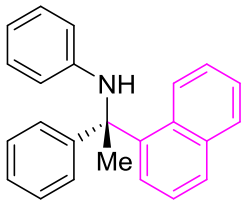


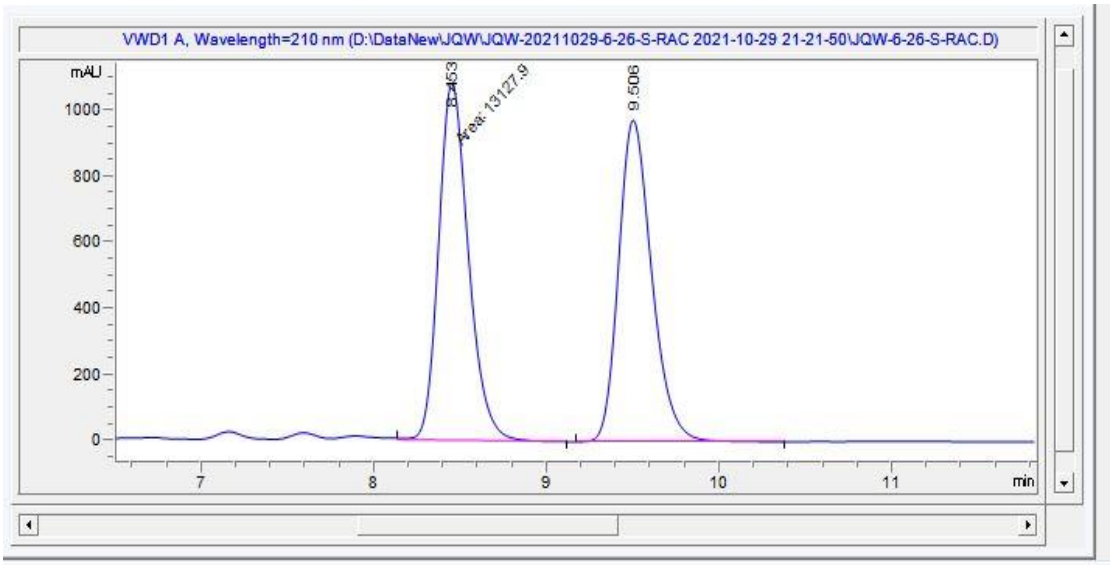
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	28.728	BV	6250.8	78.7	1.2149	49.224	0.77
2	31.688	VB	6447.9	73.9	1.3235	50.776	0.771



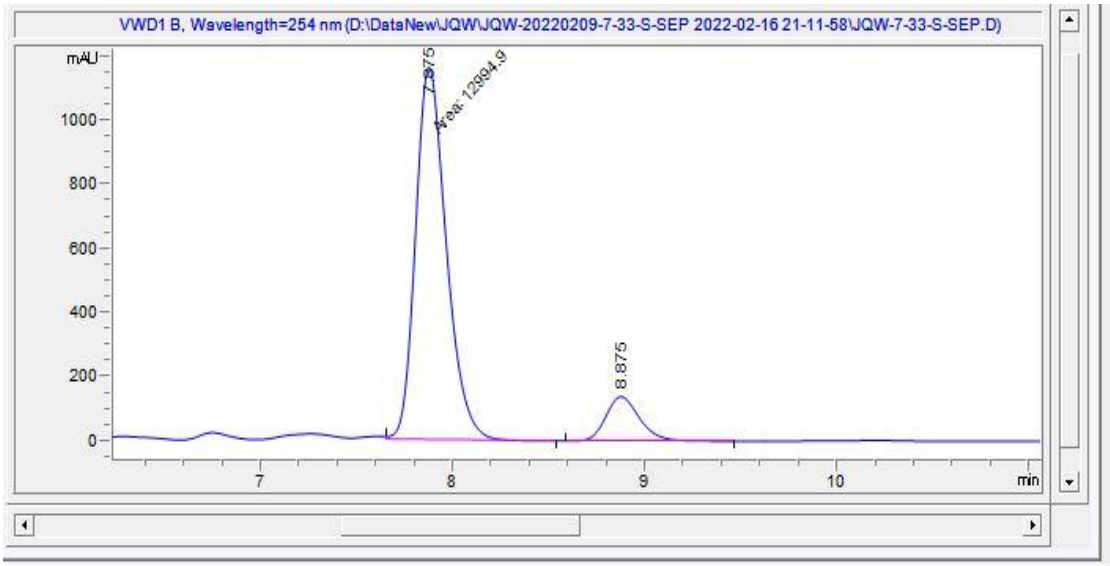
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	28.656	MM	1220.6	17.7	1.1466	10.424	0.859
2	31.436	MM	10489.2	128	1.3655	89.576	0.717

(*S*)-*N*-(1-(naphthalen-1-yl)-1-phenylethyl)aniline ((*S*)-**1u**)





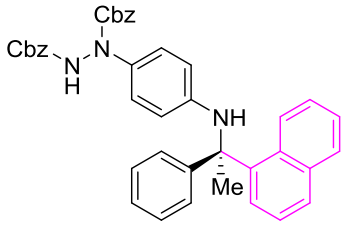
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.453	FM	13127.9	1088.7	0.201	50.071	0.784
2	9.506	BB	13090.4	979.1	0.206	49.929	0.741

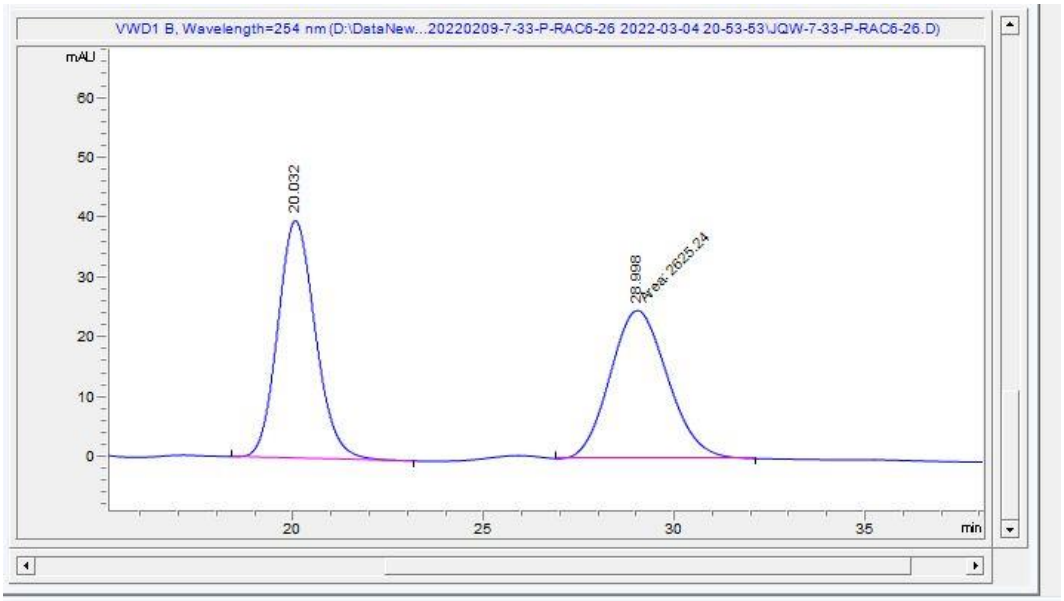


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.875	FM	12994.9	1163.6	0.1861	88.576	0.749
2	8.875	BB	1676	137.9	0.1858	11.424	0.777

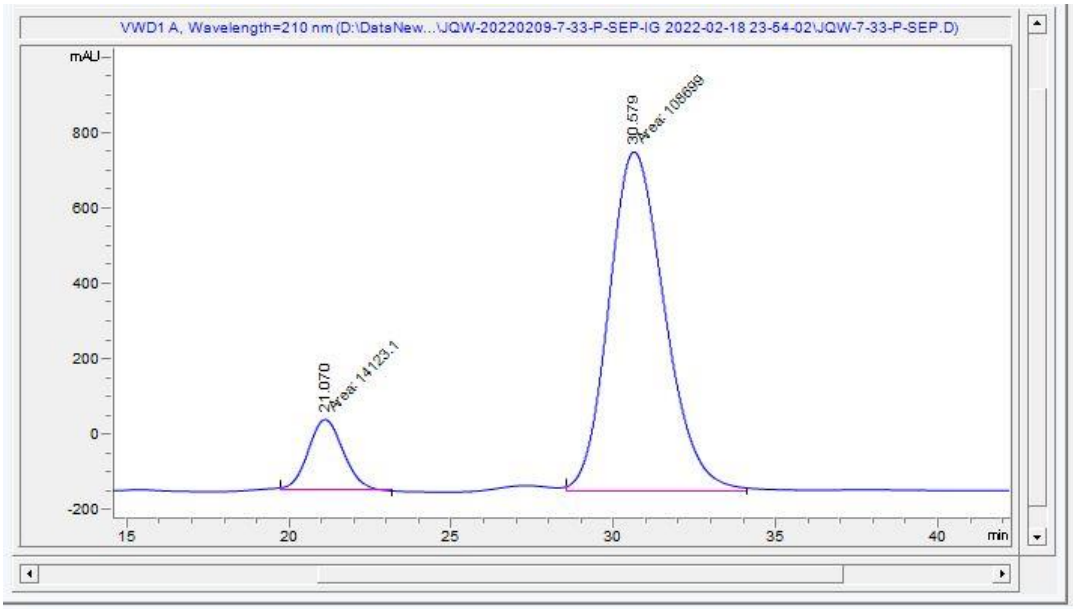
Dibenzyl-(*R*)-1-(4-((1-(naphthalen-1-yl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-dicarbox

ylate (**3u**)



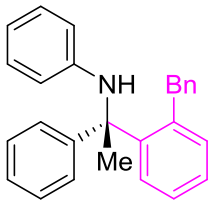


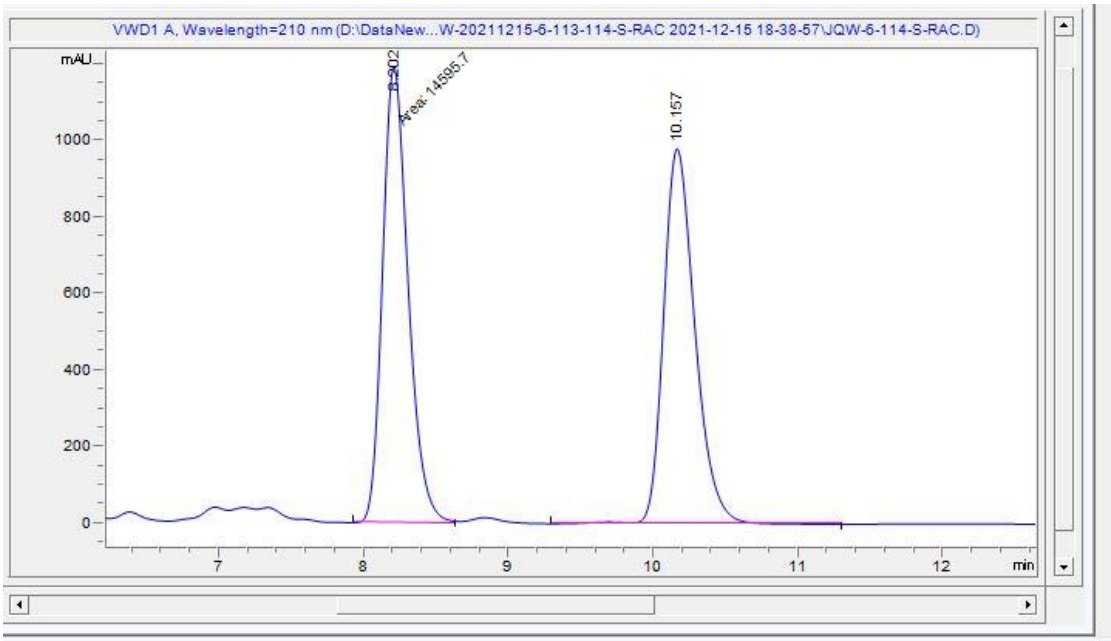
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	20.032	BB	2722.7	39.8	1.0585	50.911	0.836
2	28.998	MF	2625.2	24.9	1.7584	49.089	0.869



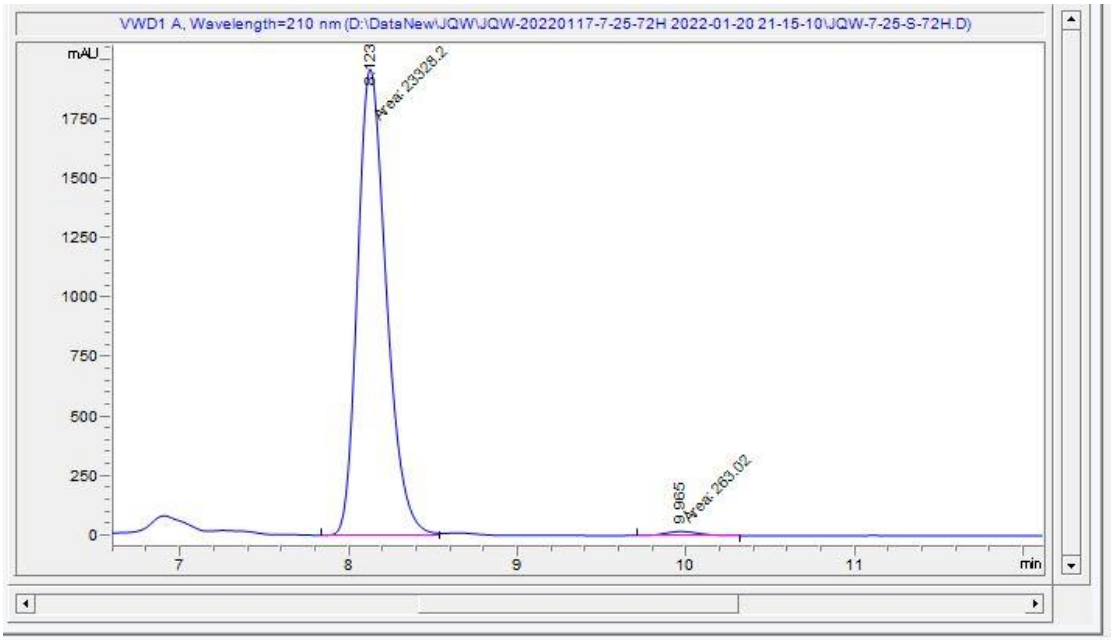
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	21.07	MM	14123.1	187.7	1.2538	11.499	0.904
2	30.579	MM	108699.4	904.5	2.003	88.501	0.796

(*S*)-*N*-(1-(2-benzylphenyl)-1-phenylethyl)aniline ((*S*)-**1v**)





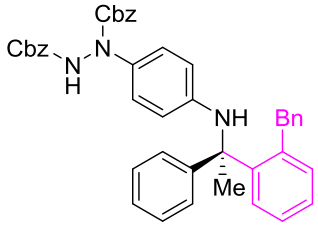
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.202	MF	14595.7	1189.8	0.2045	49.768	0.764
2	10.157	VB R	14731.6	978.2	0.2308	50.232	0.729

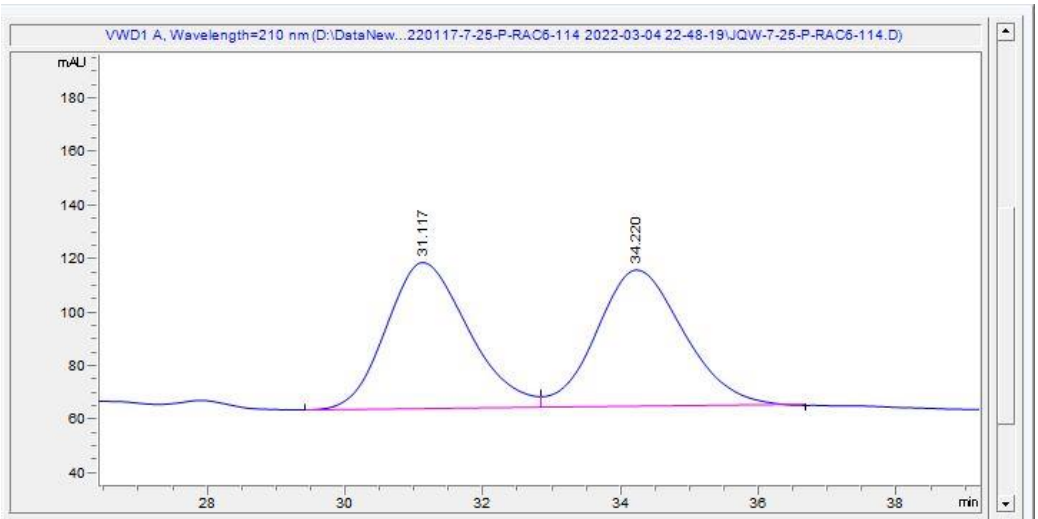


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.123	MF	23328.2	1968.4	0.1975	98.885	0.748
2	9.965	FM	263	18.3	0.2397	1.115	0.828

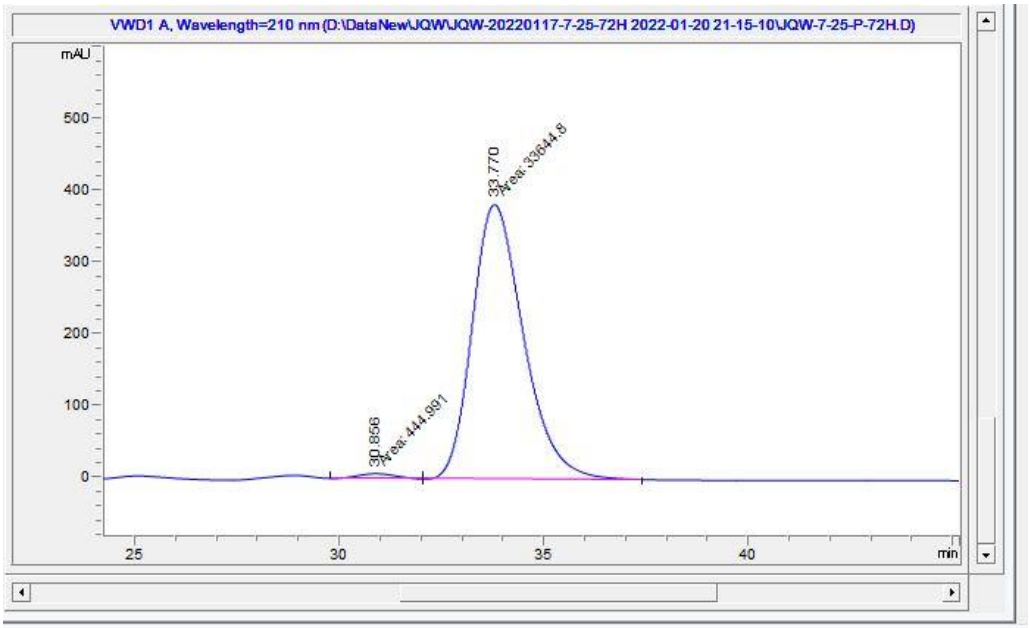
Dibenzyl-(*R*)-1-(4-((1-(2-benzylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-dicarbox

ylate (**3v**)



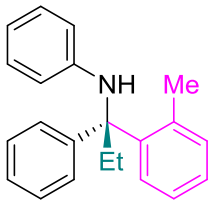


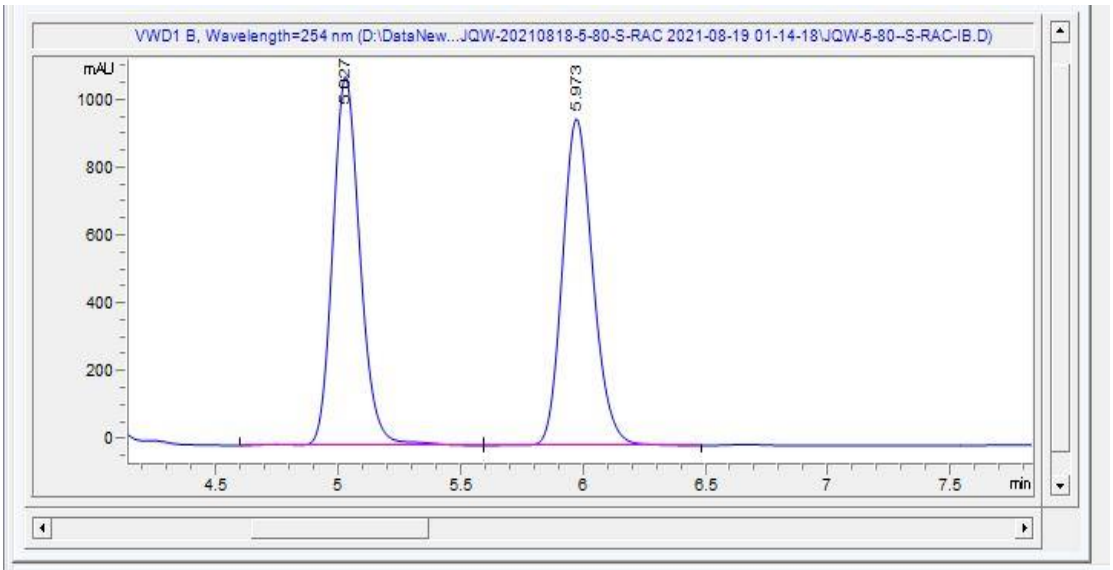
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	31.117	BV	4542.7	54.6	1.2709	50.073	0.773
2	34.22	VB	4529.5	51.1	1.3685	49.927	0.829



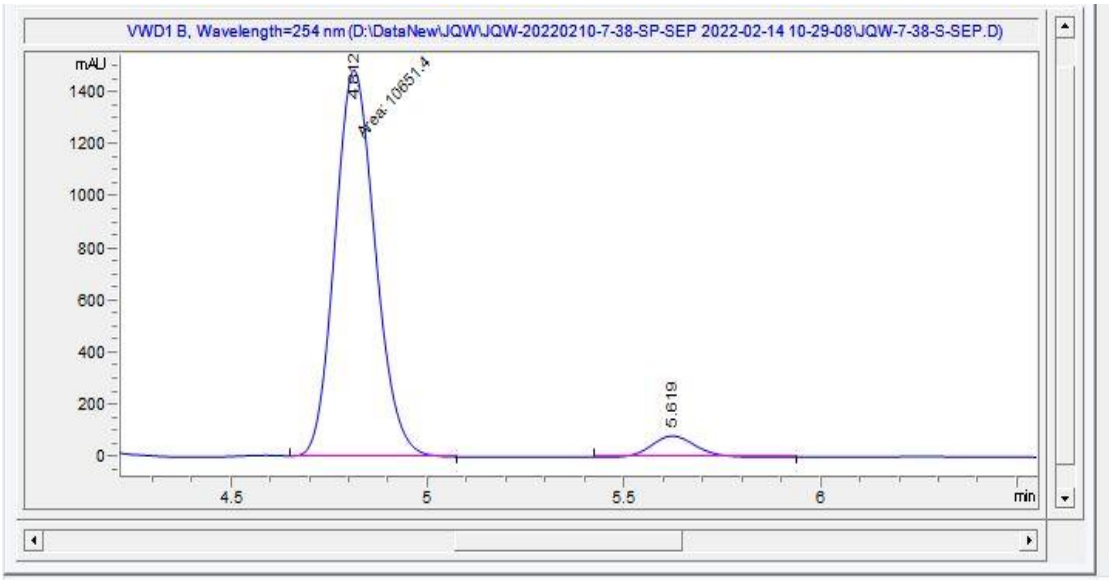
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	30.856	MF	445	7	1.0642	1.305	0.878
2	33.77	FM	33644.8	384.3	1.459	98.695	0.74

(*S*)-*N*-(1-phenyl-1-(*o*-tolyl)propyl)aniline ((*S*)-**1w**)



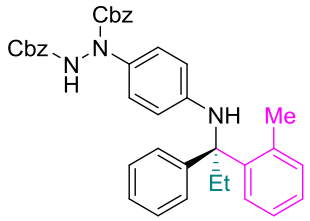


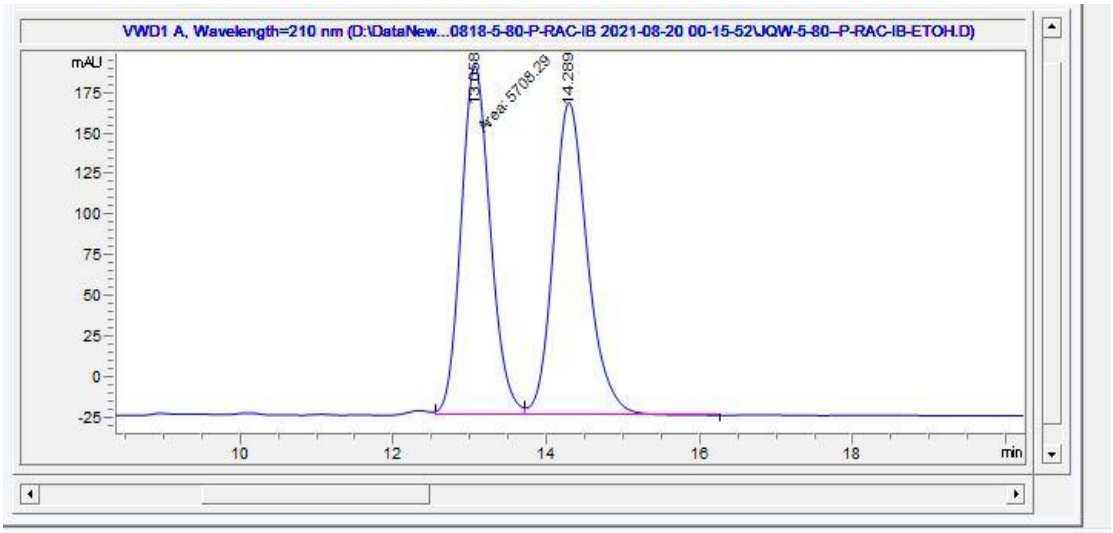
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.027	VB R	8422	1085.1	0.1183	50.311	0.822
2	5.973	VV R	8317.9	961.1	0.133	49.689	0.812



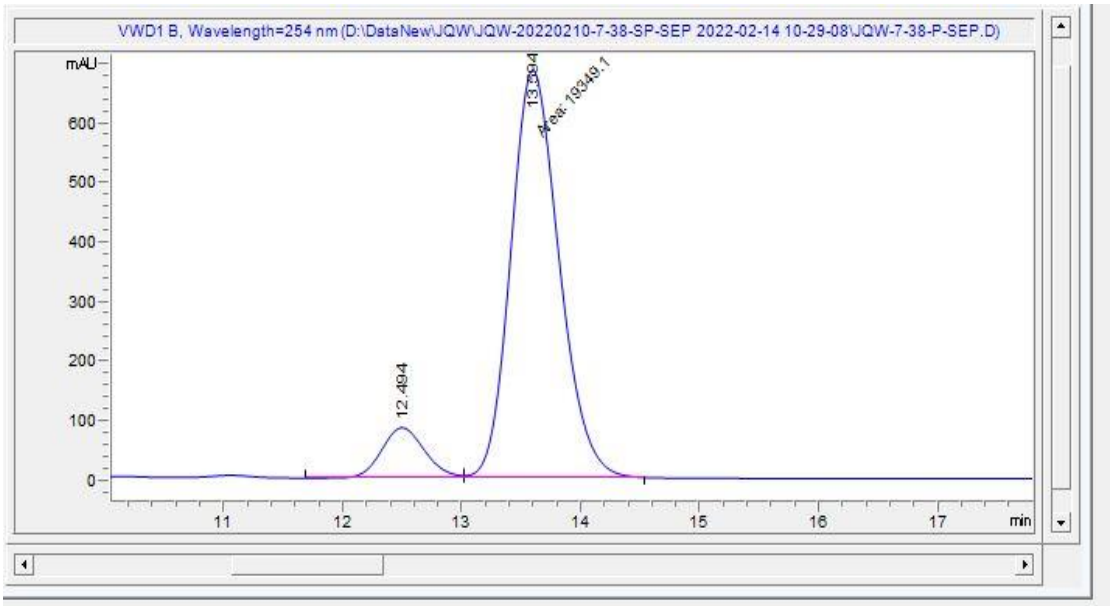
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.812	MF	10651.4	1496.7	0.1186	94.345	0.865
2	5.619	BB	638.4	81.7	0.1212	5.655	0.856

Dibenzyl (*R*)-1-(4-((1-phenyl-1-(*o*-tolyl)propyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3w**)



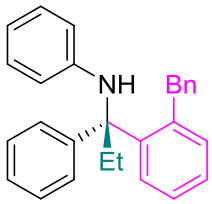


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	13.058	FM	5708.3	214.4	0.4438	48.985	0.857
2	14.289	VB	5944.8	191.8	0.4736	51.015	0.801

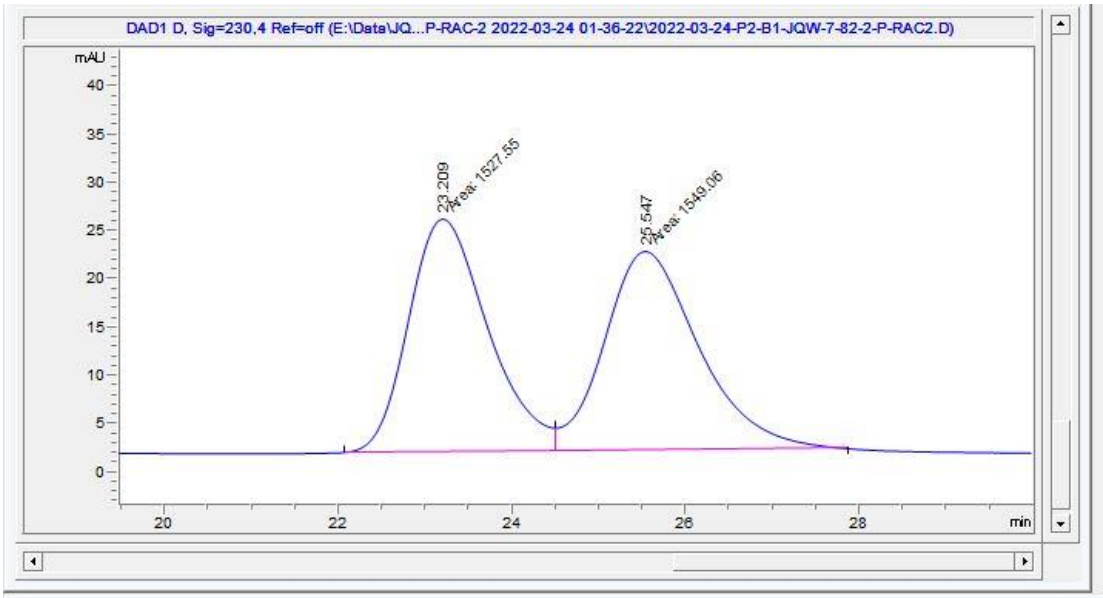


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.494	BV	2139.3	84.4	0.3917	9.956	0.865
2	13.594	MF	19349.1	683.4	0.4719	90.044	0.809

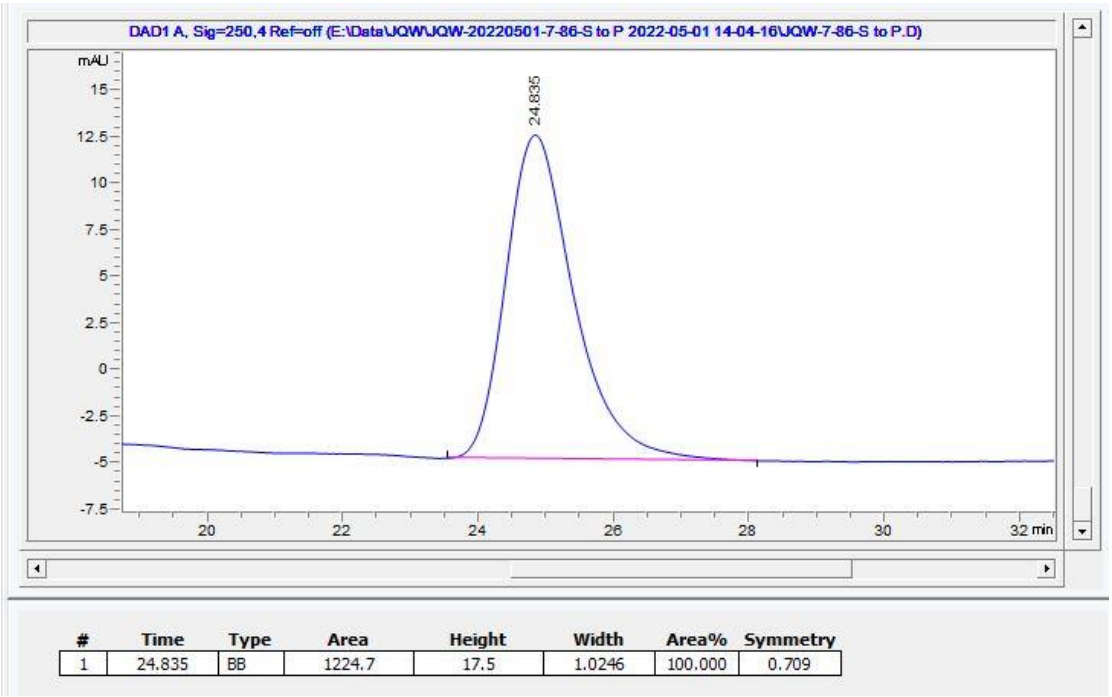
(*S*)-*N*-(1-(2-benzylphenyl)-1-phenylpropyl)aniline ((*S*)-**1x**)



The er value of (*S*)-**1x** was determined by converting it into (*S*)-**3x** through achiral phosphoric acid catalyzed amination with azodicarboxylate **2a**.

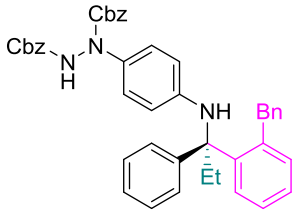


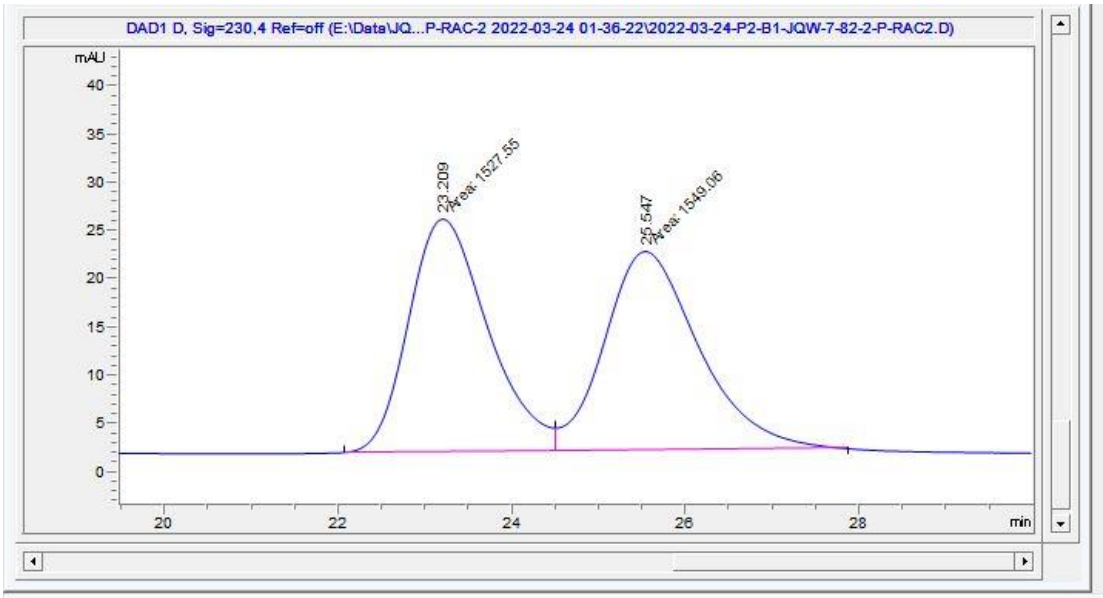
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	23.209	MF	1527.6	24	1.0591	49.650	0.74
2	25.547	FM	1549.1	20.5	1.2605	50.350	0.755



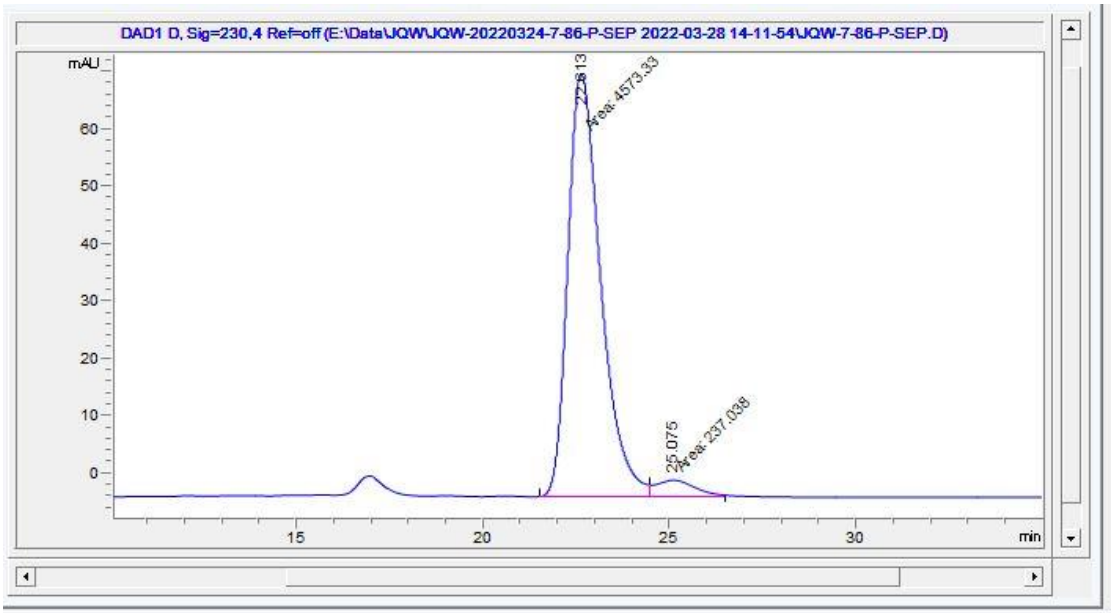
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	24.835	BB	1224.7	17.5	1.0246	100.000	0.709

Dibenzyl-(*R*)-1-(4-((1-(2-benzylphenyl)-1-phenylpropyl)amino)phenyl)hydrazine-1,2-dicarbo xyl-ate ((*R*)-**3x**)



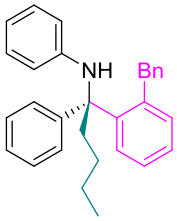


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	23.209	MF	1527.6	24	1.0591	49.650	0.74
2	25.547	FM	1549.1	20.5	1.2605	50.350	0.755

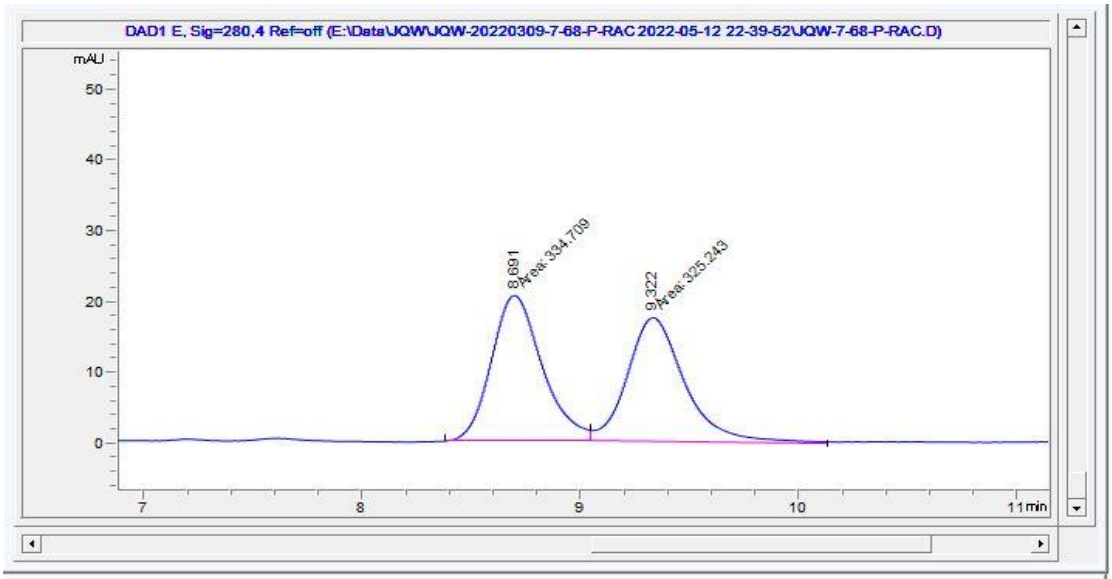


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	22.613	MF	4573.3	74	1.0294	95.072	0
2	25.075	FM	237	3.1	1.2565	4.928	0.67

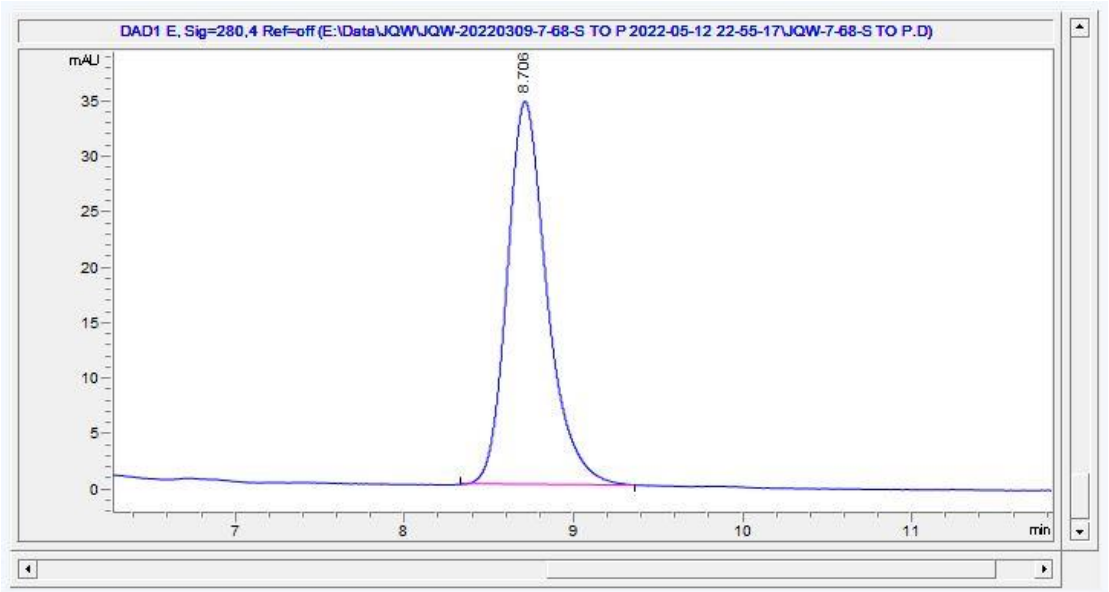
(*S*)-*N*-(1-(2-benzylphenyl)-1-phenylpentyl)aniline ((*S*)-**1y**)



The er value of (*S*)-**1y** was determined by converting it into (*S*)-**3y** through achiral phosphoric acid catalyzed amination with azodicarboxylate **2a**.

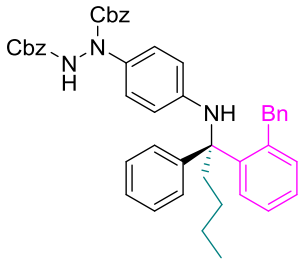


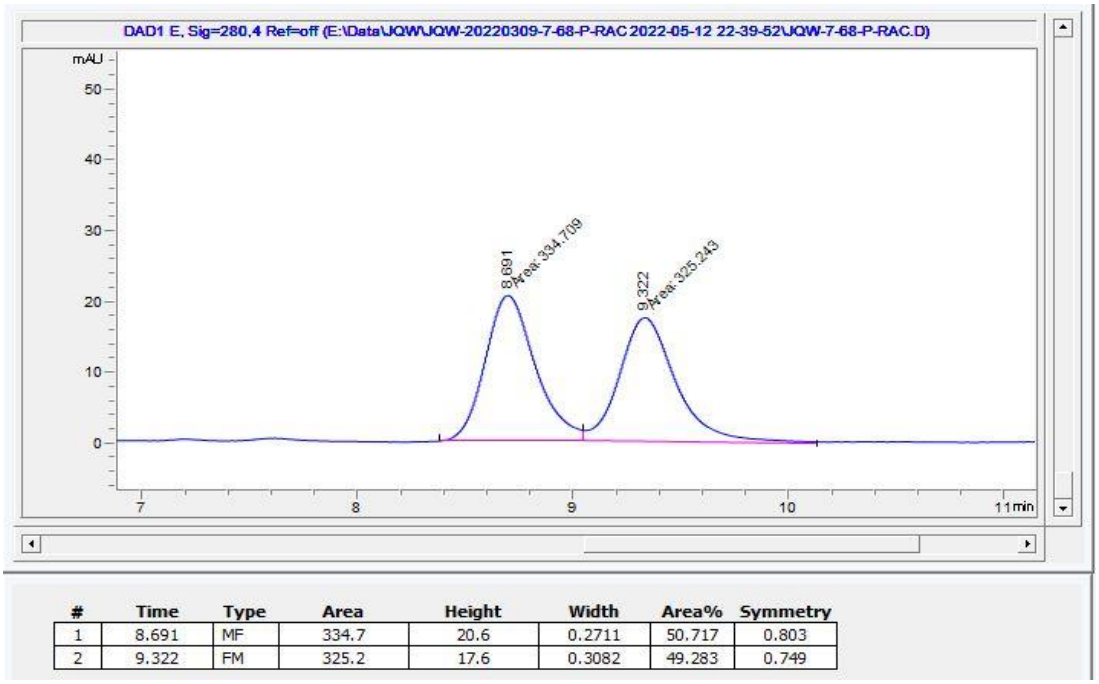
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.691	MF	334.7	20.6	0.2711	50.717	0.803
2	9.322	FM	325.2	17.6	0.3082	49.283	0.749



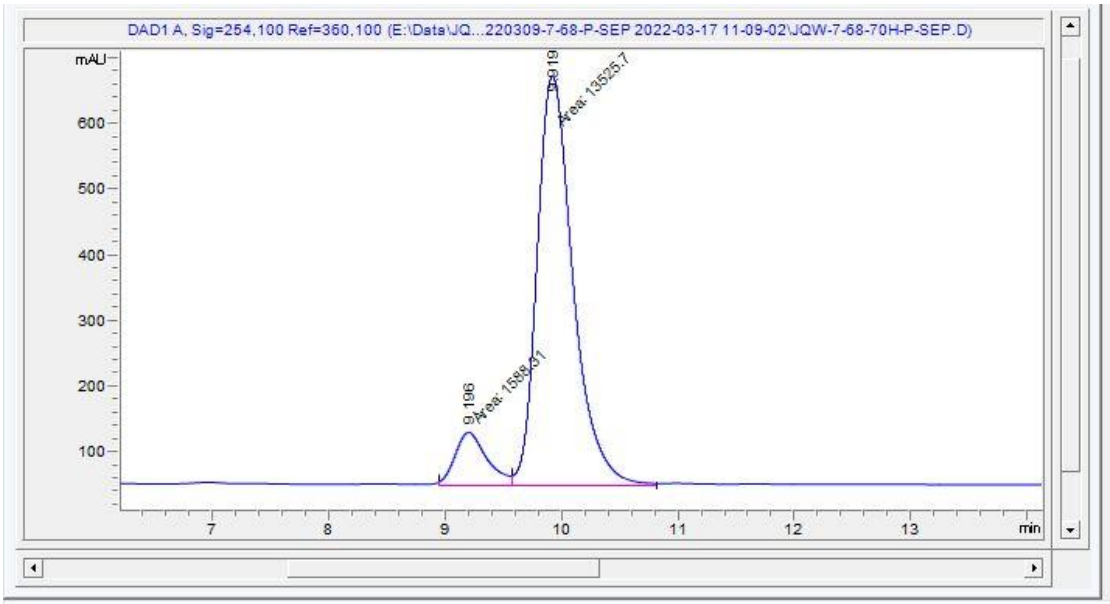
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.706	BB	568	34.7	0.2306	100.000	0.771

Dibenzyl-(*R*)-1-(4-((1-(2-benzylphenyl)-1-phenylpentyl)amino)phenyl)hydrazine-1,2-dicarboxyl-ate (**3y**)



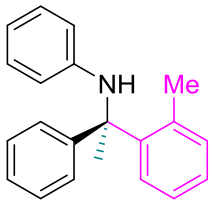


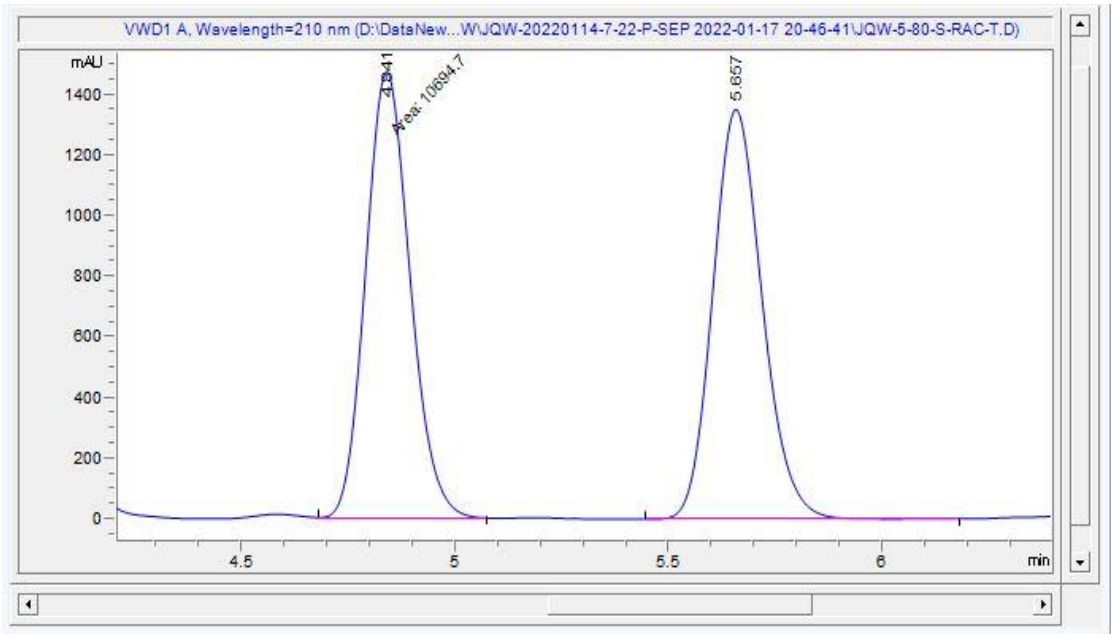
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.691	MF	334.7	20.6	0.2711	50.717	0.803
2	9.322	FM	325.2	17.6	0.3082	49.283	0.749



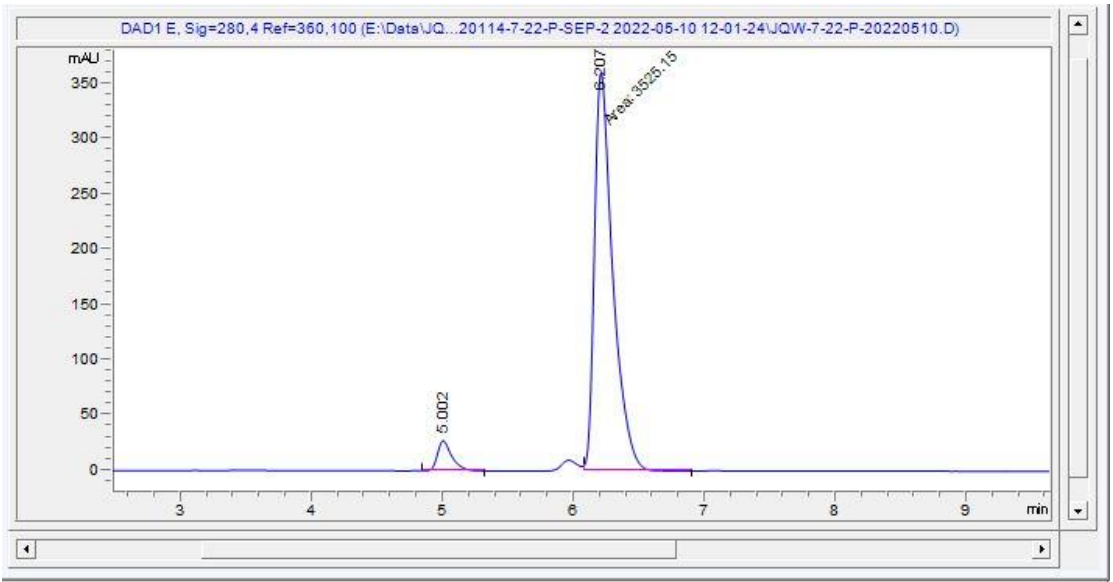
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.196	MF	1588.3	81.6	0.3244	10.509	0
2	9.919	FM	13525.7	627.3	0.3594	89.491	0.715

(*R*)-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline ((*R*)-**1a**)



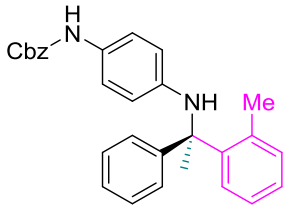


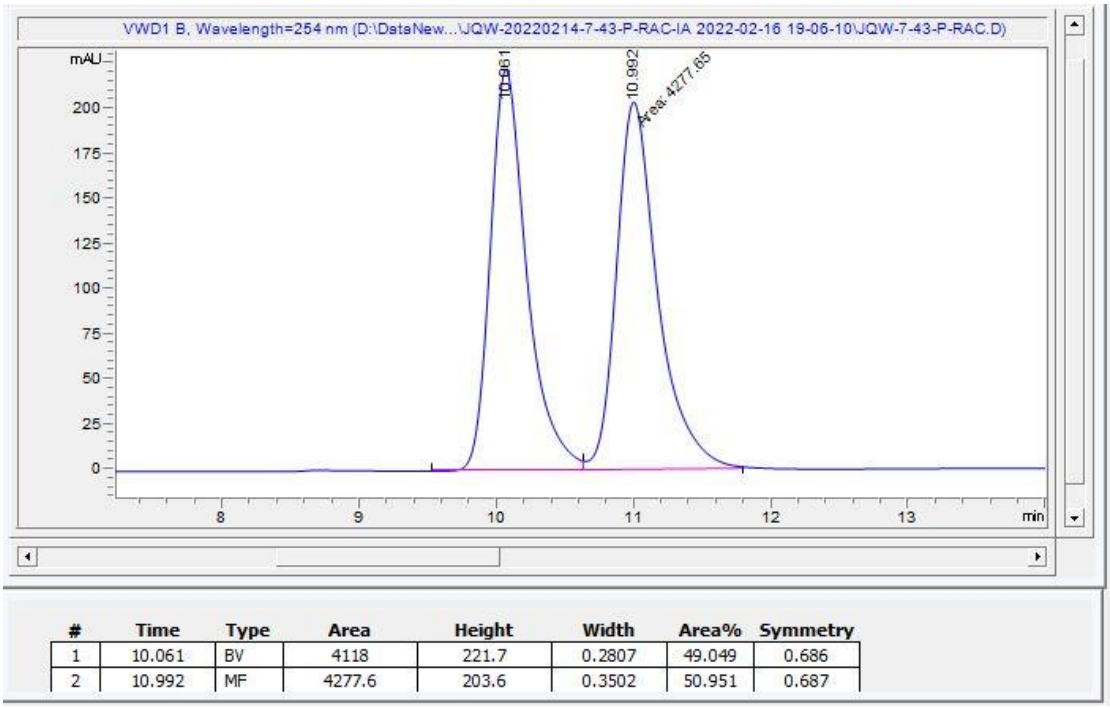
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.841	FM	10694.7	1477.9	0.1206	49.582	0.862
2	5.657	BV R	10874.8	1352.1	0.1258	50.418	0.831



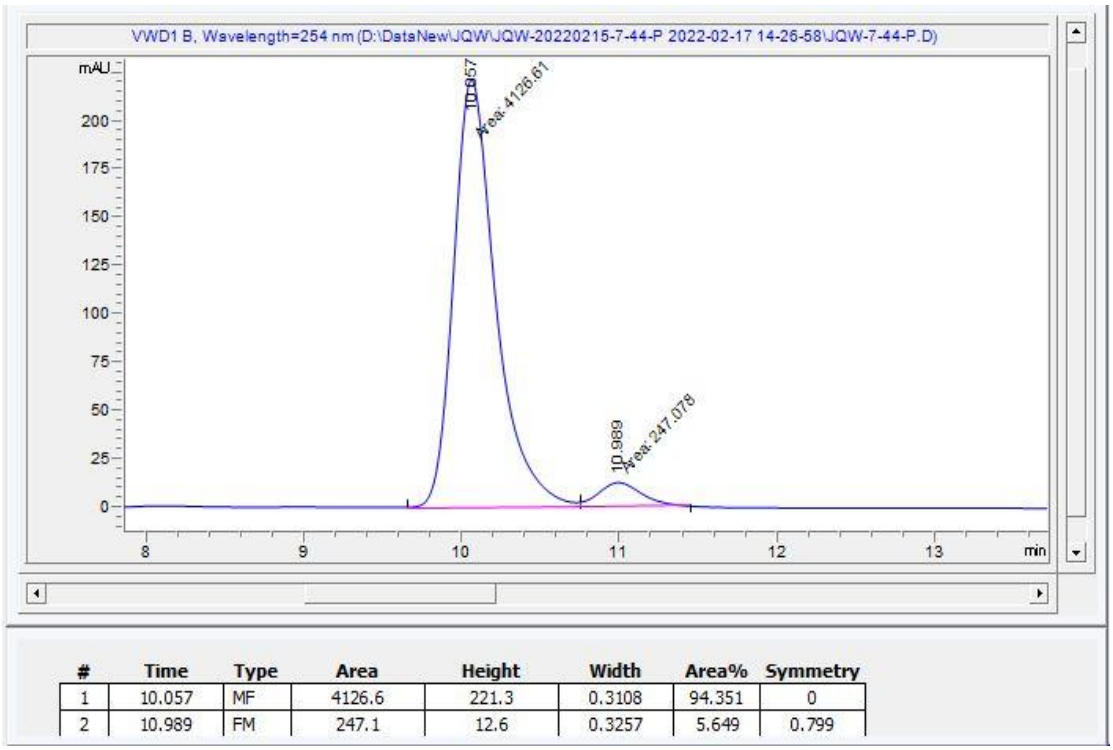
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.002	BB	207.8	27.5	0.1122	5.566	0.609
2	6.207	FM	3525.1	363.1	0.1618	94.434	0.537

Benzyl (*R*)-(4-((1-phenyl-1-(*o*-tolyl)ethyl)amino)phenyl)carbamate (**4a**)



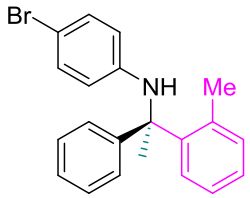


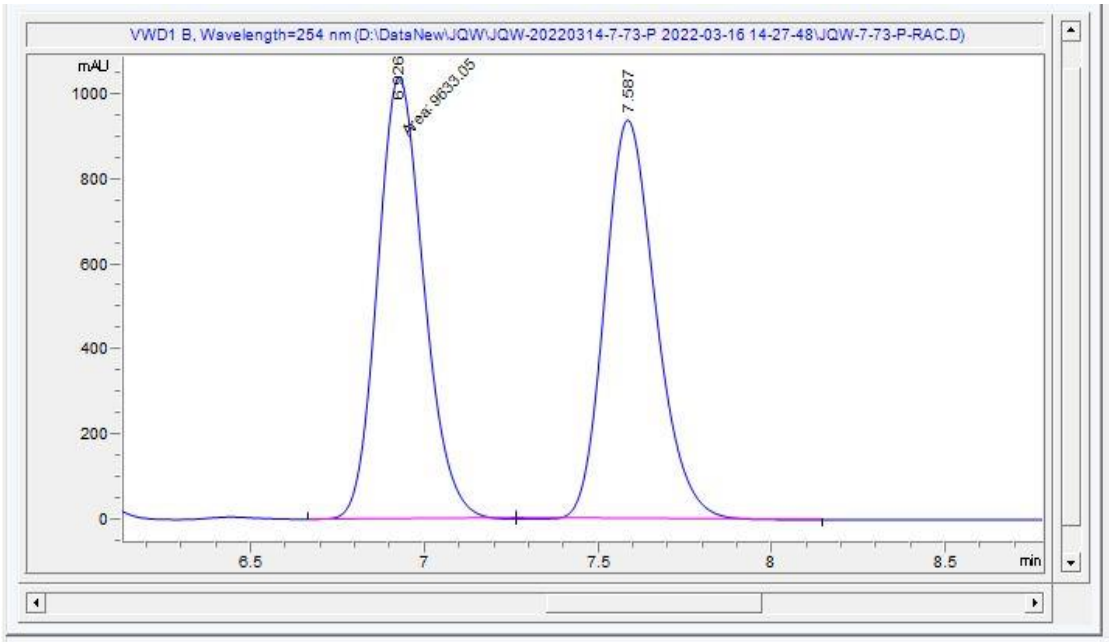
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.061	BV	4118	221.7	0.2807	49.049	0.686
2	10.992	MF	4277.6	203.6	0.3502	50.951	0.687



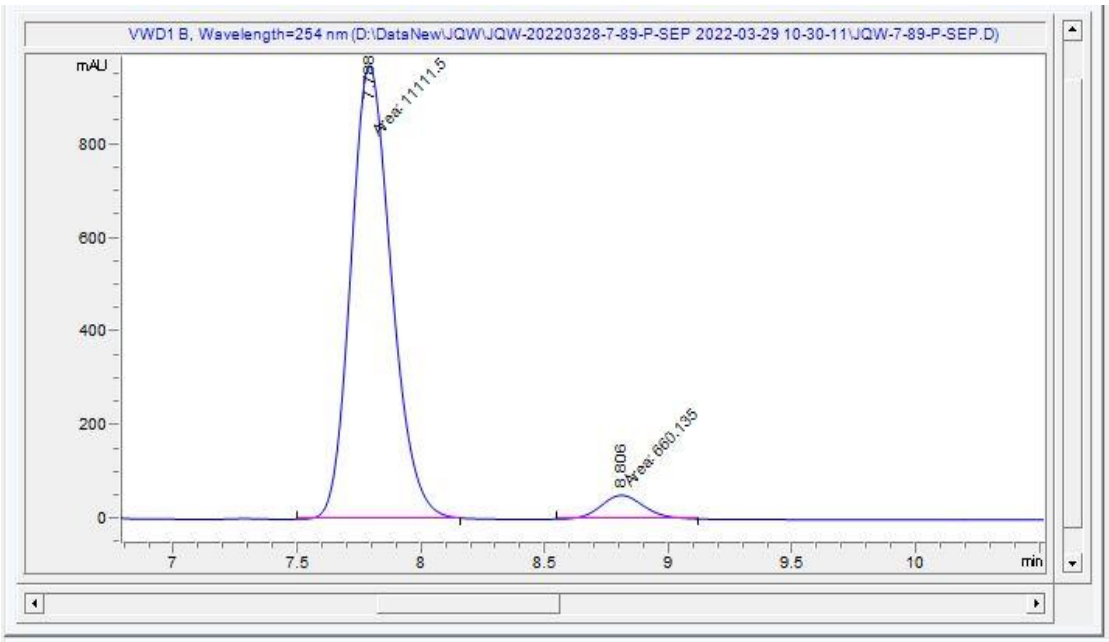
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.057	MF	4126.6	221.3	0.3108	94.351	0
2	10.989	FM	247.1	12.6	0.3257	5.649	0.799

(*R*)-4-bromo-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline (**5a**)





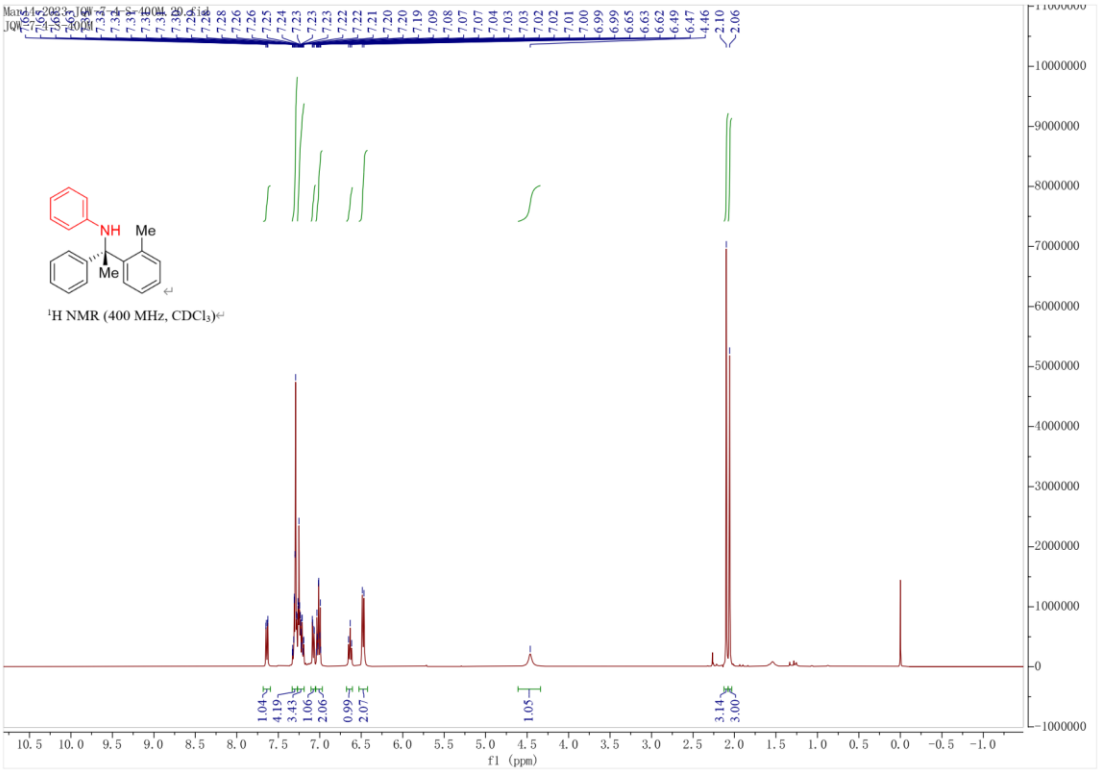
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.926	FM	9633.1	1037	0.1548	50.092	0.842
2	7.587	BB	9597.5	935.4	0.1577	49.908	0.784

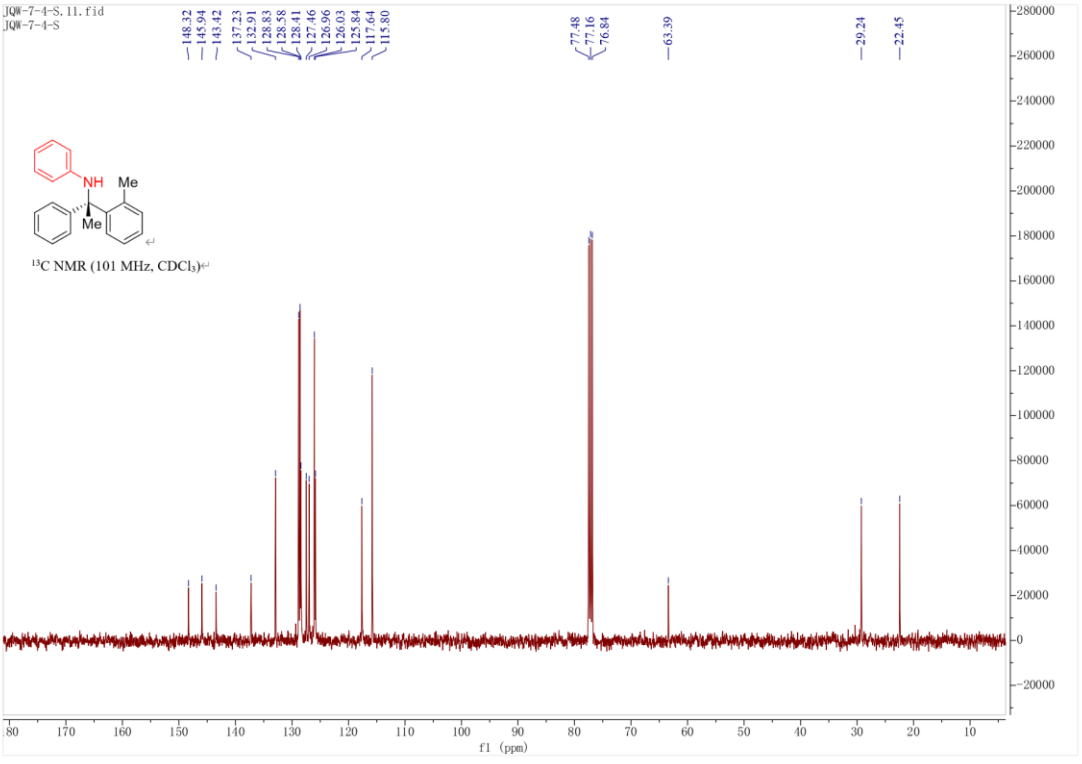


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.788	FM	11111.5	971.9	0.1906	94.392	0.814
2	8.806	FM	660.1	52	0.2117	5.608	0.868

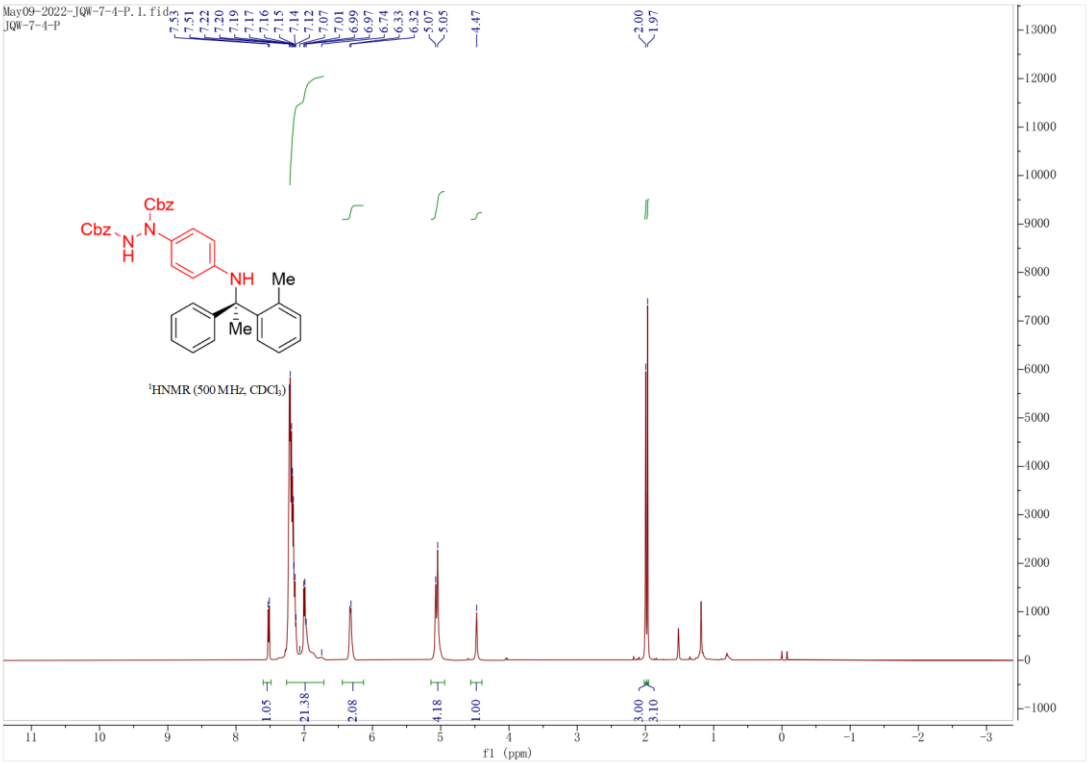
NMR spectrums:

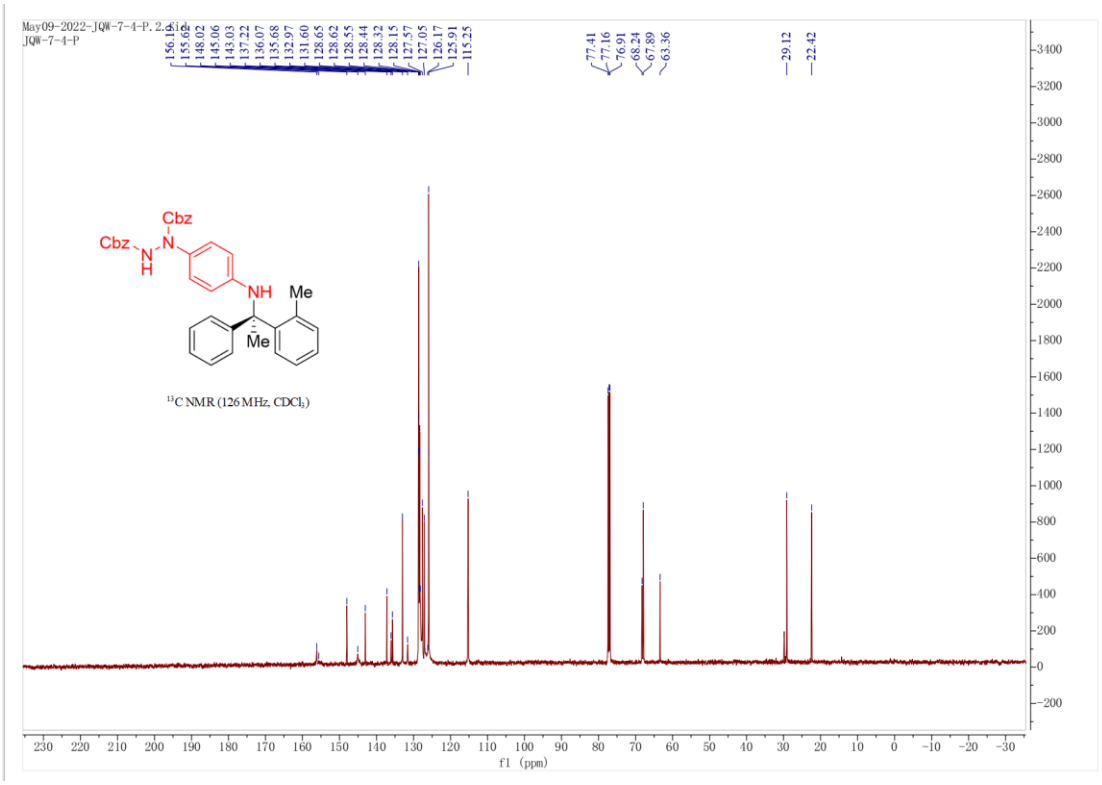
(*S*)-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1a**)



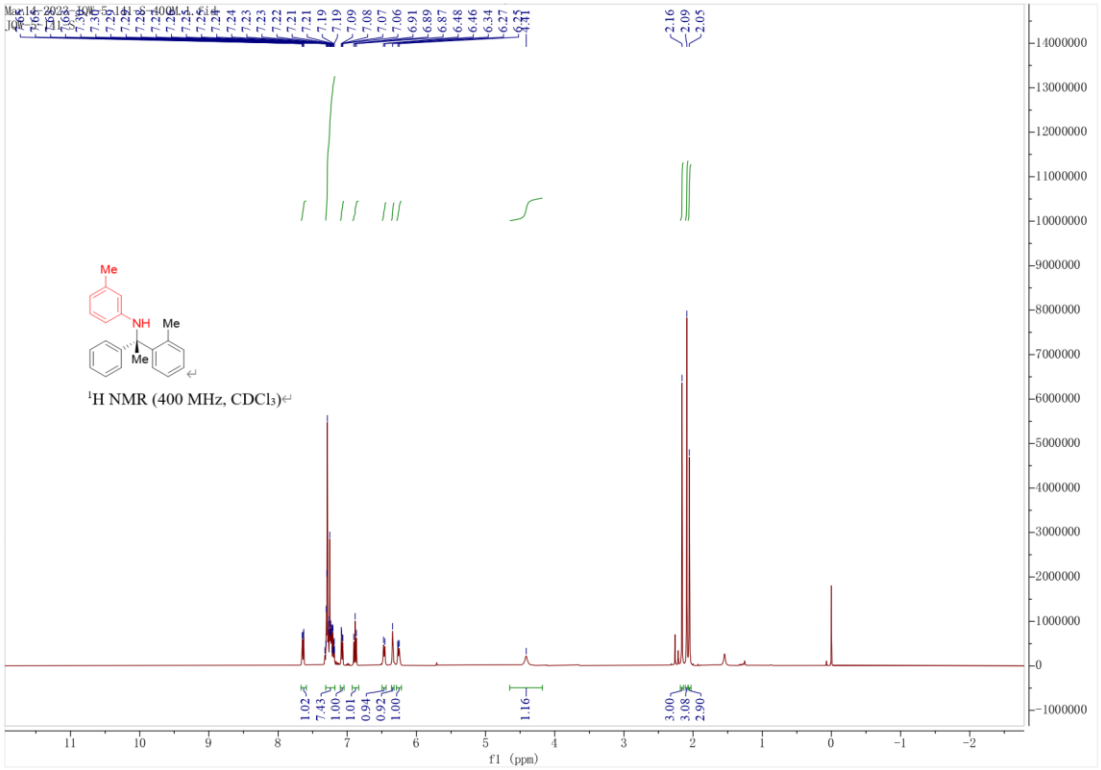


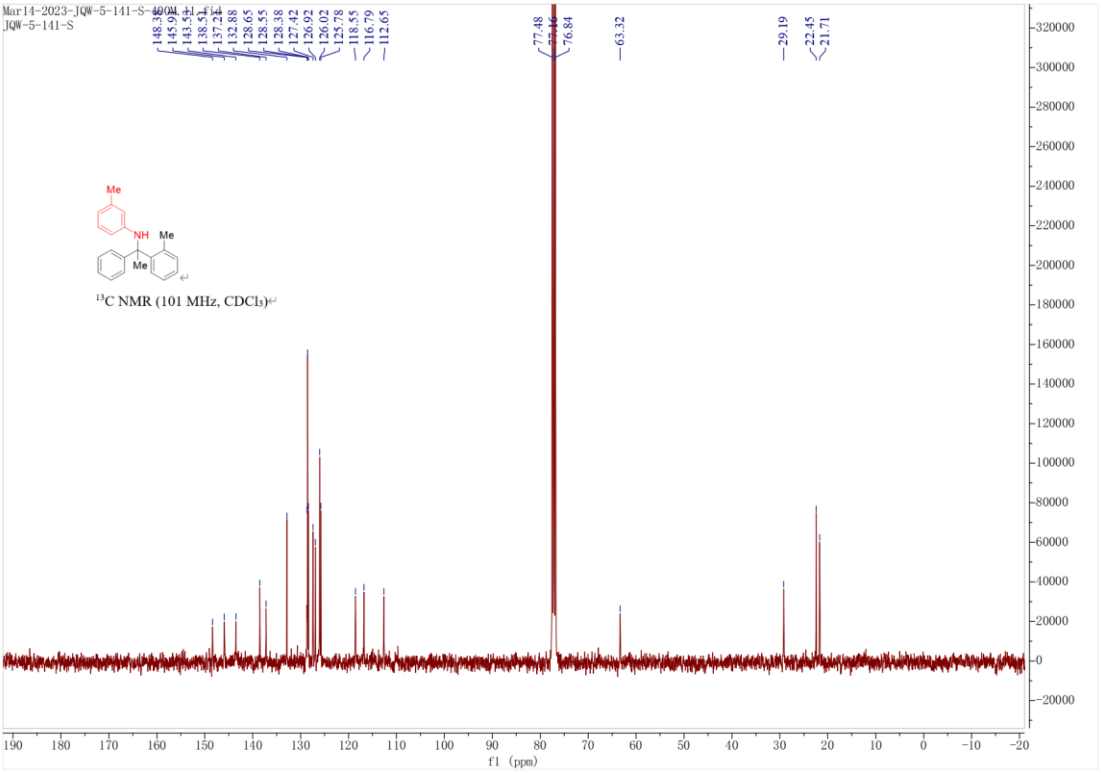
Dibenzyl(*R*)-1-(4-((1-phenyl-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarboxylat (**3a**)



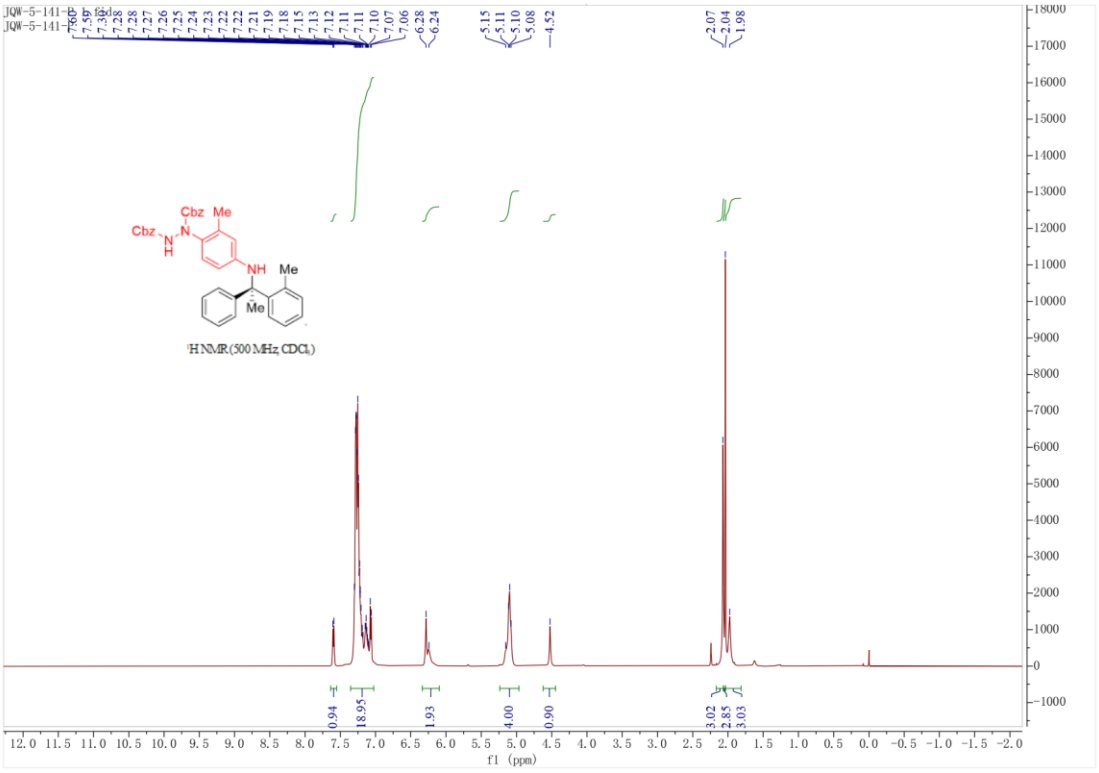


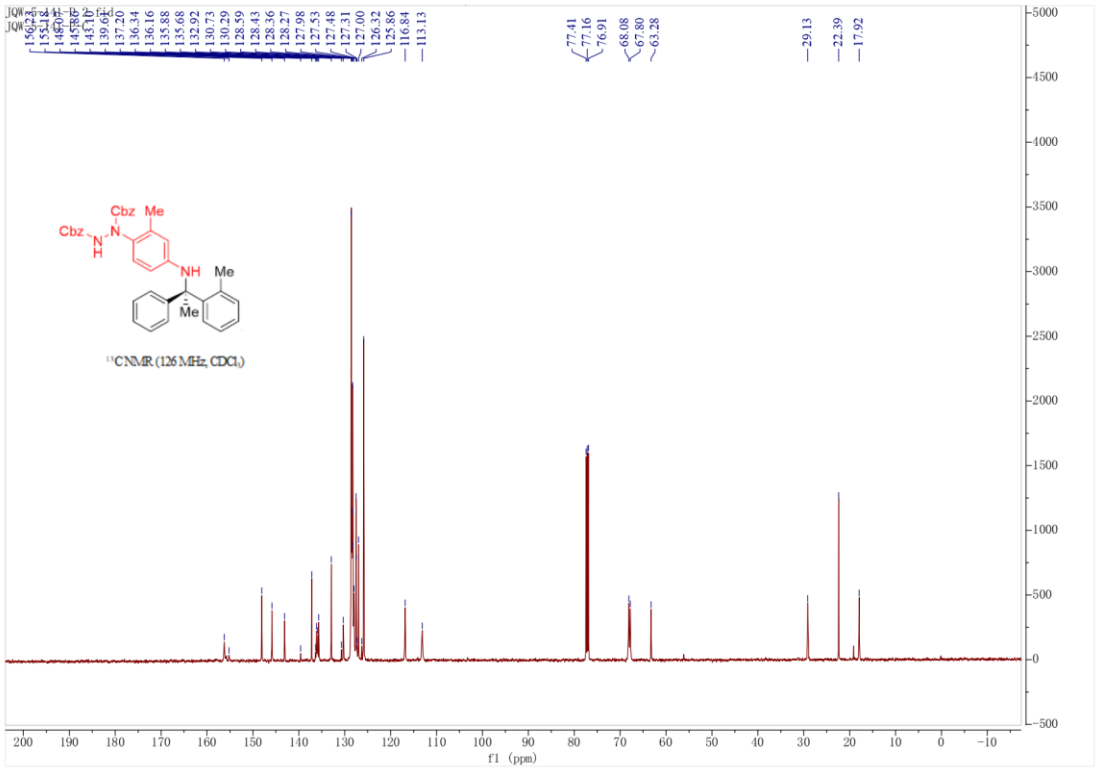
(*S*)-3-methyl-N-(1-phenyl-1-(o-tolyl)ethyl)aniline ((*S*)-**1b**)



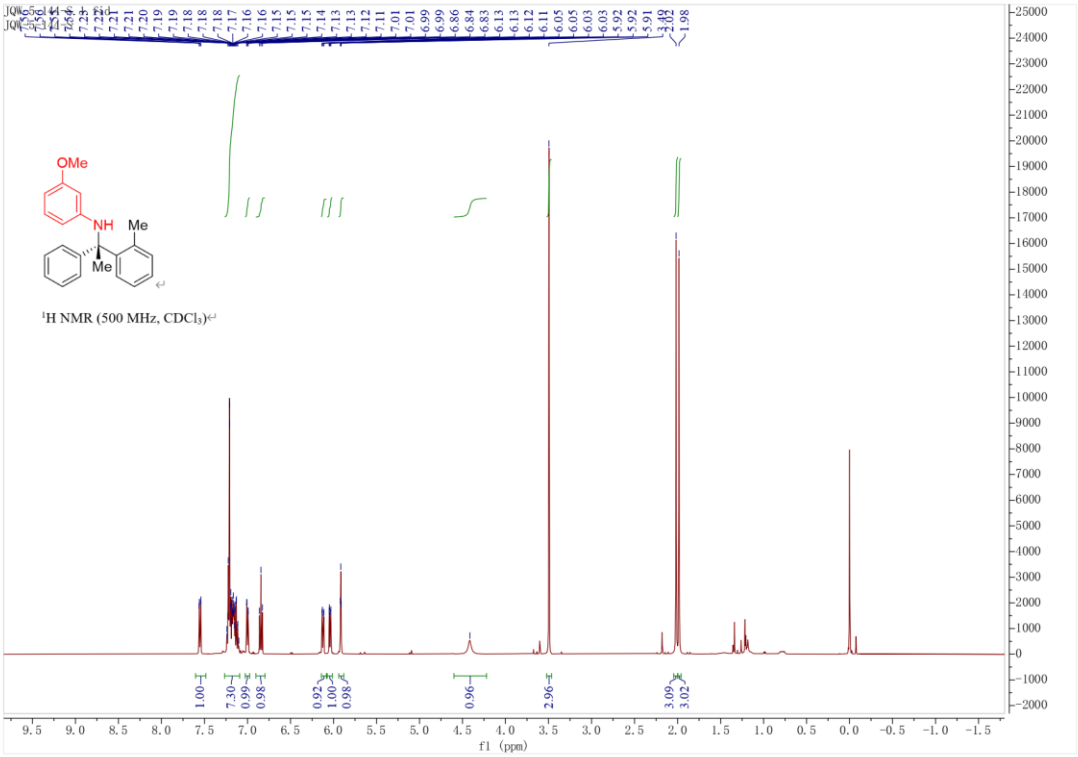


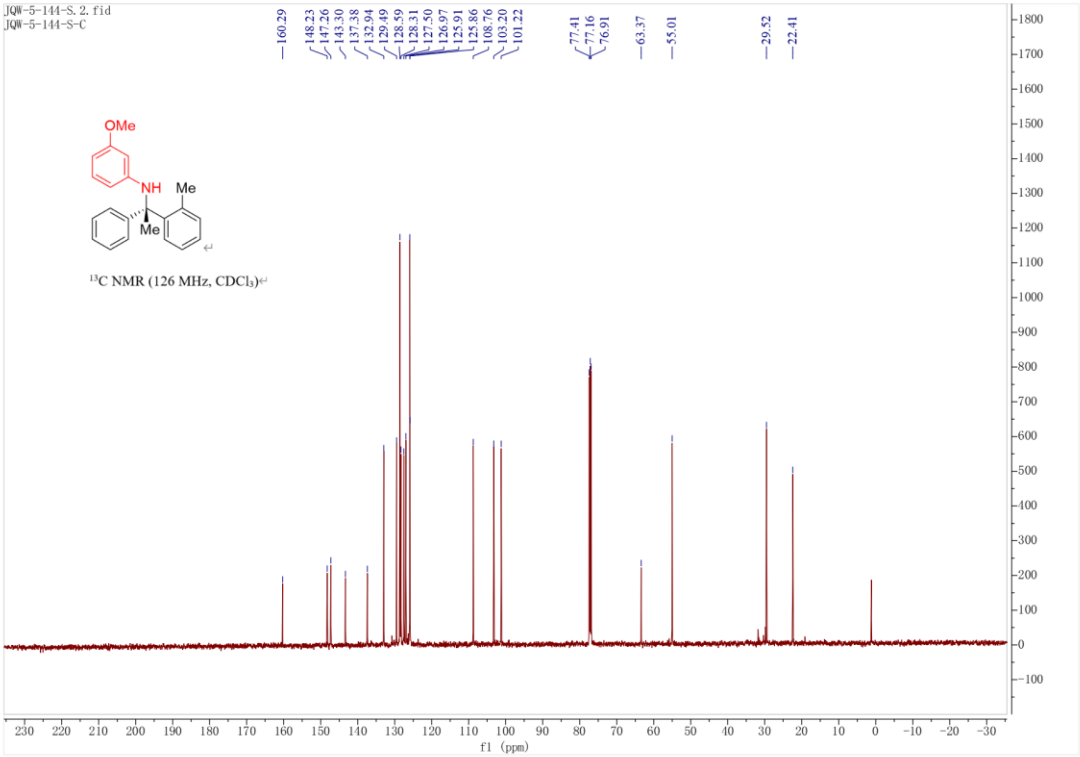
Dibenzyl(*R*)-1-(2-methyl-4-((1-phenyl-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3b**)



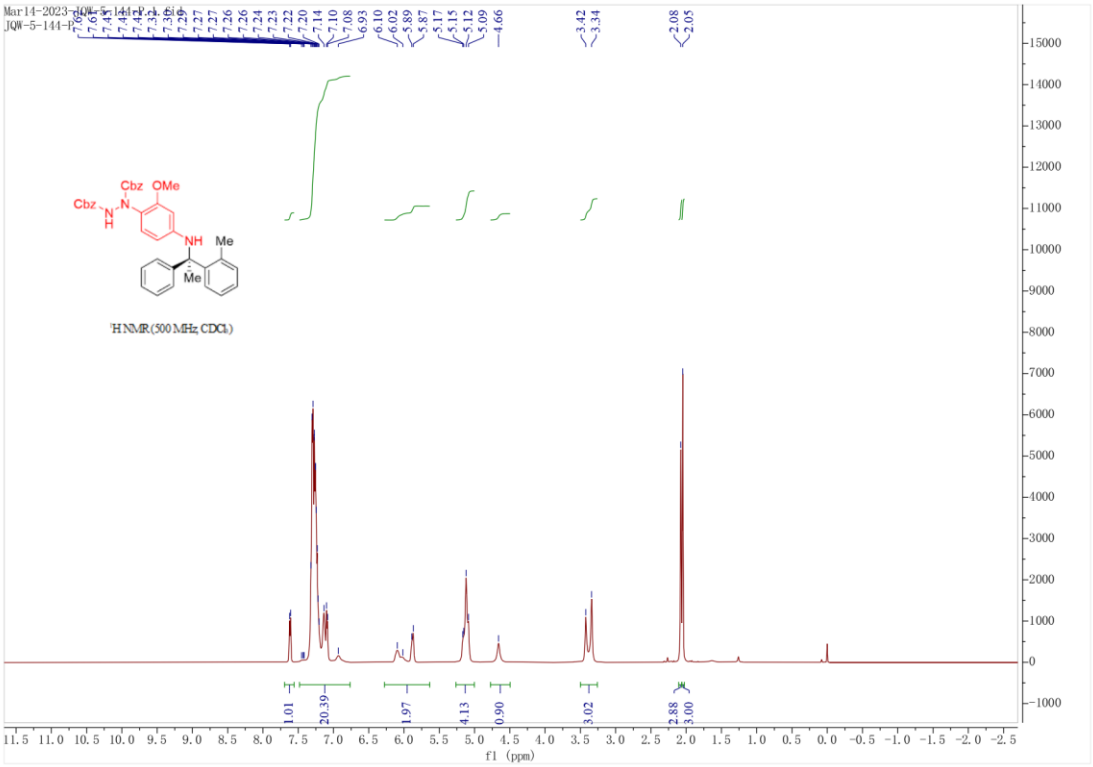


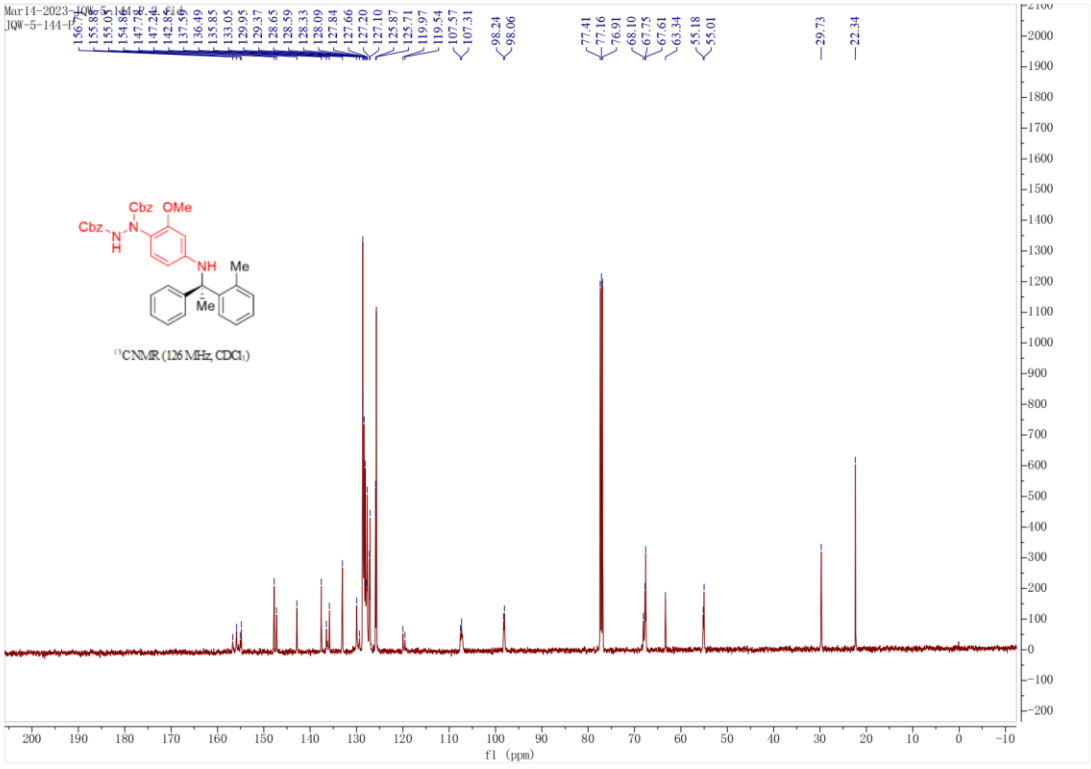
(*S*)-3-methoxy-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1c**)



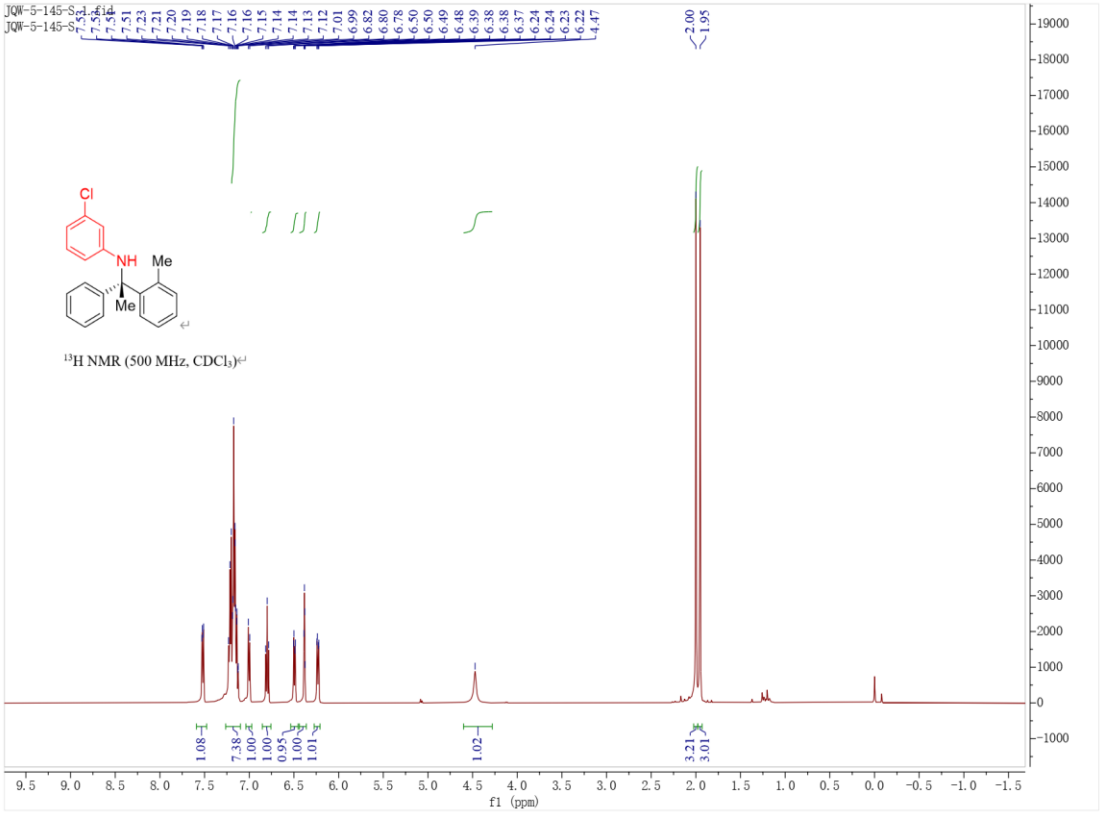


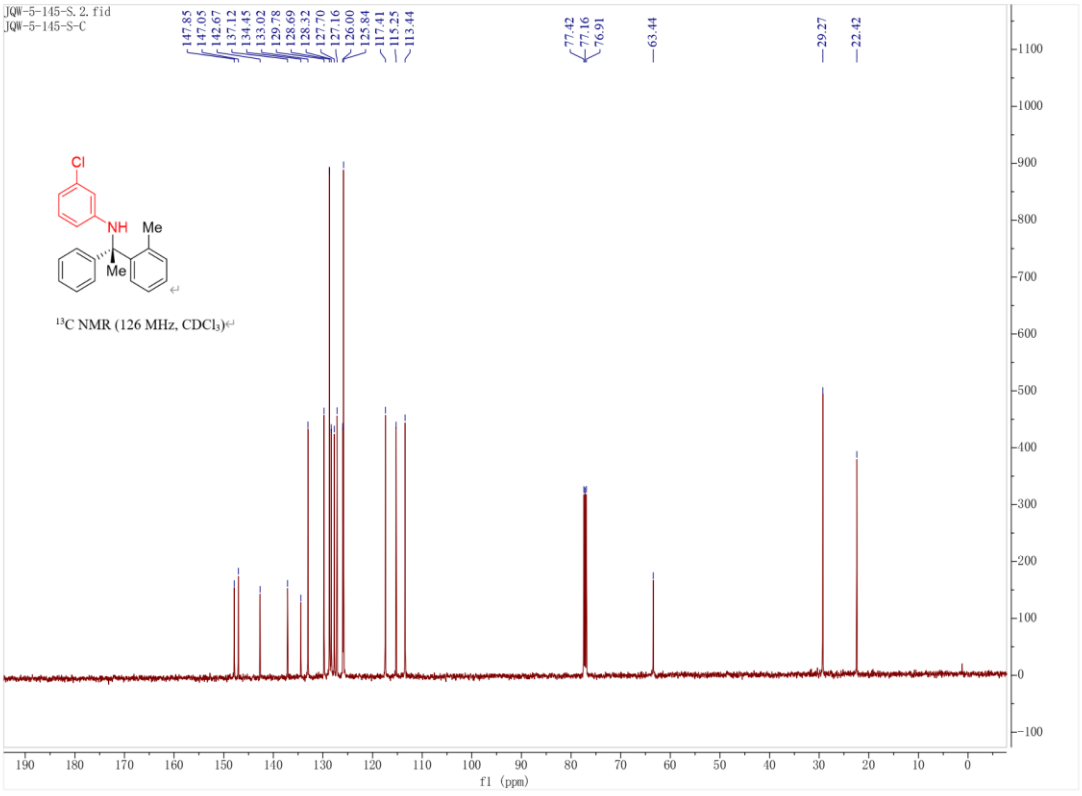
Dibenzyl-(*R*)-1-(2-methoxy-4-((1-phenyl-1-(o-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarb oxyl-ate (**3c)**



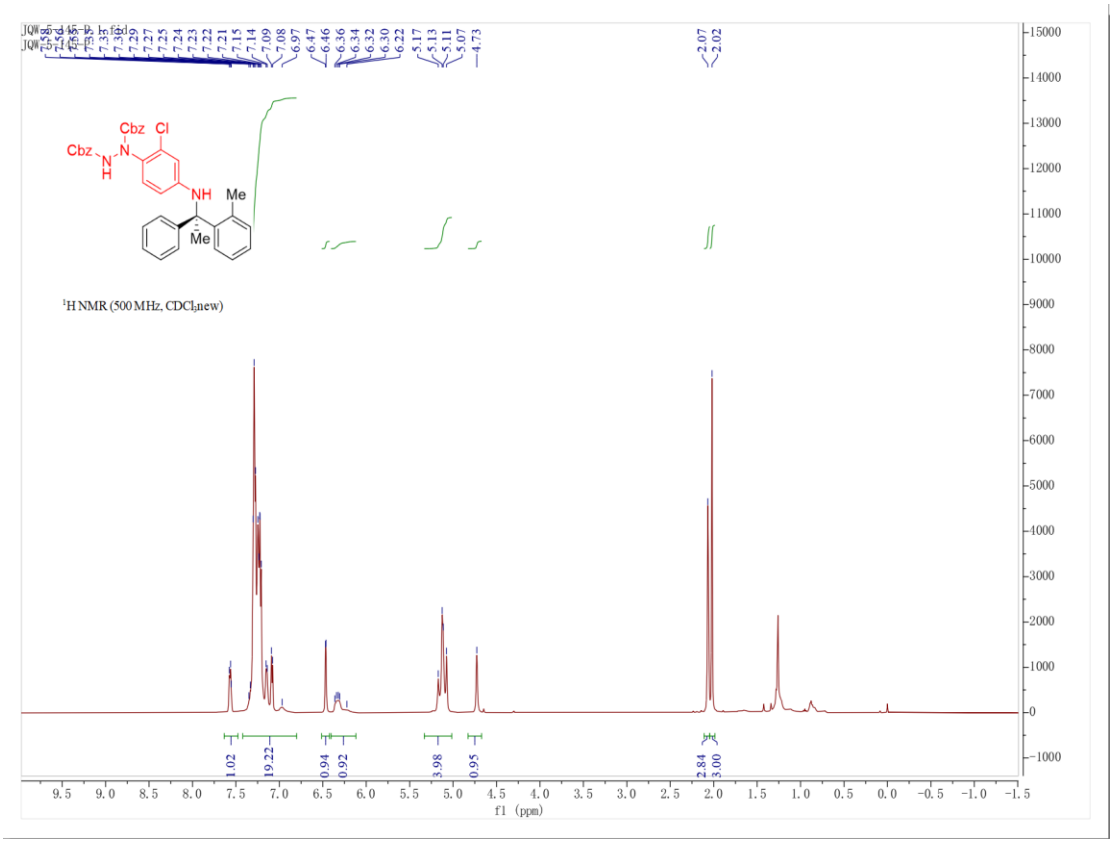


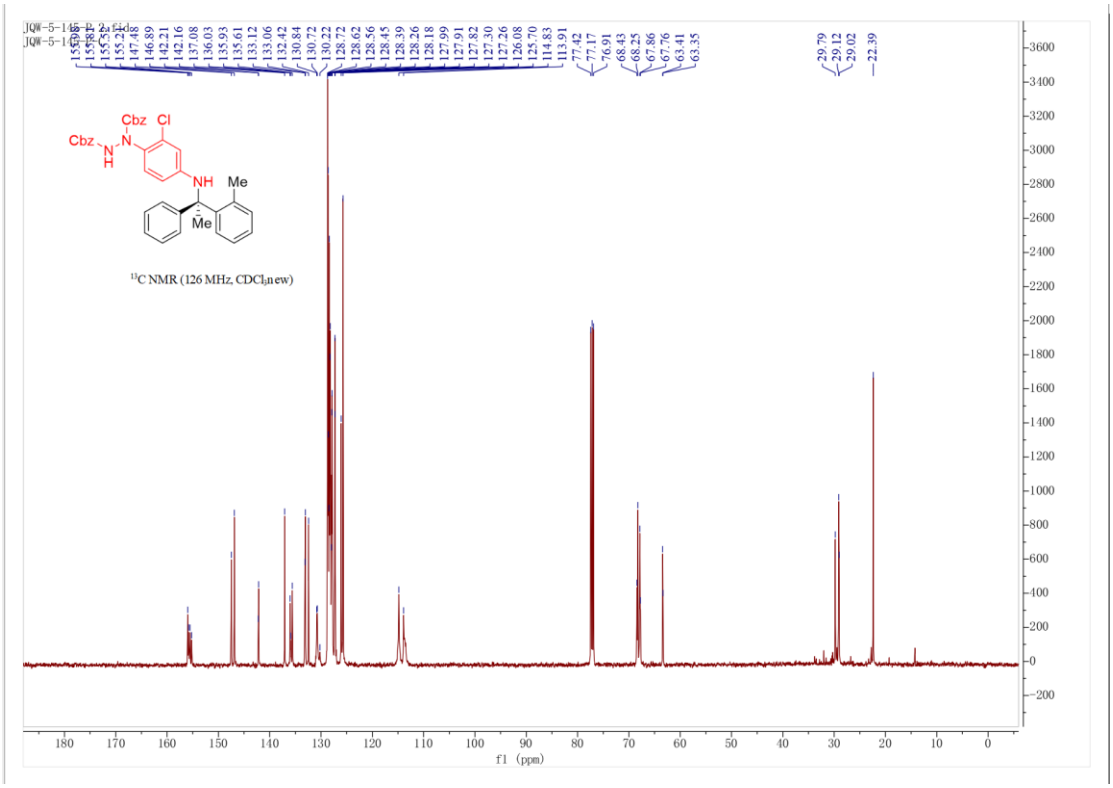
(*S*)-3-chloro-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1d**)



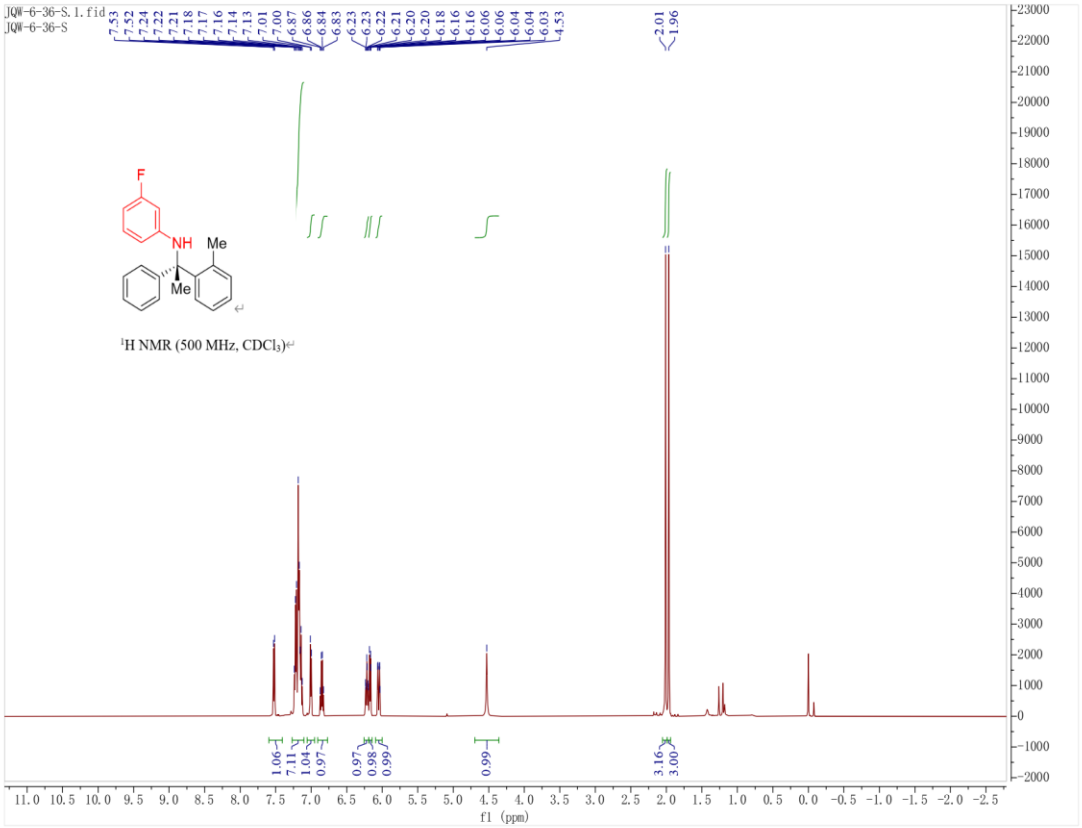


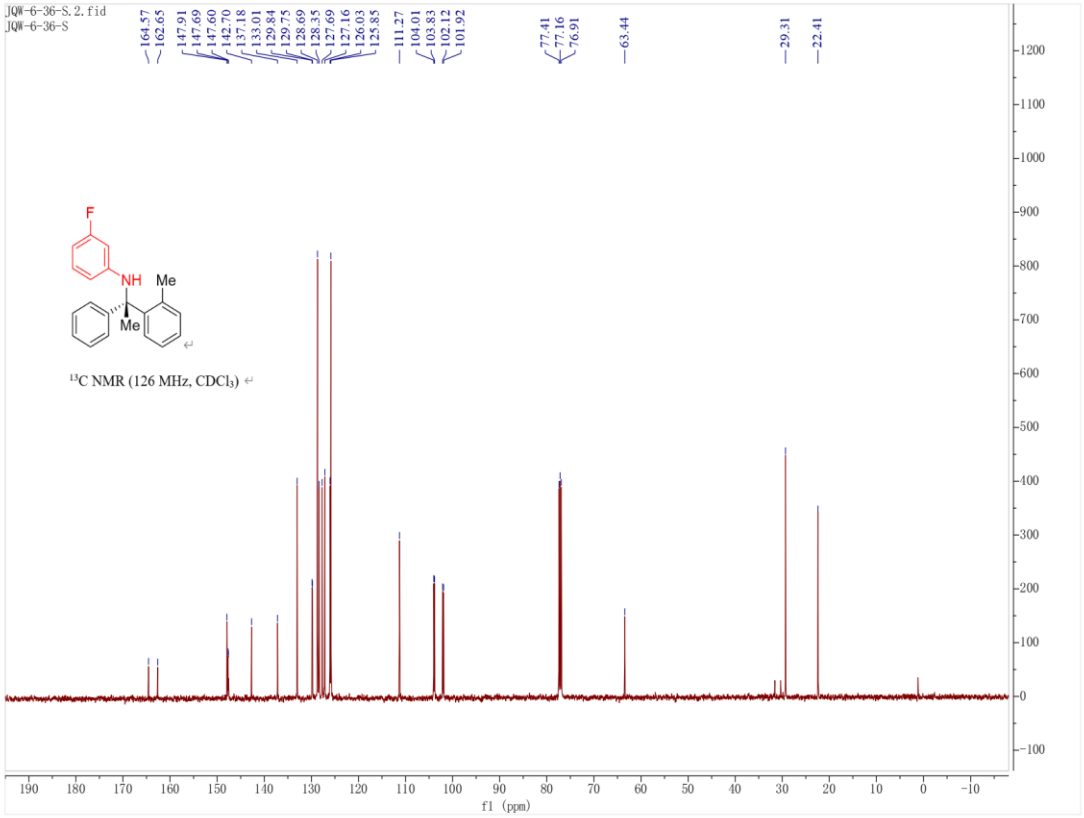
Dibenzyl-(*R*)-1-(2-chloro-4-((1-phenyl-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3d**)

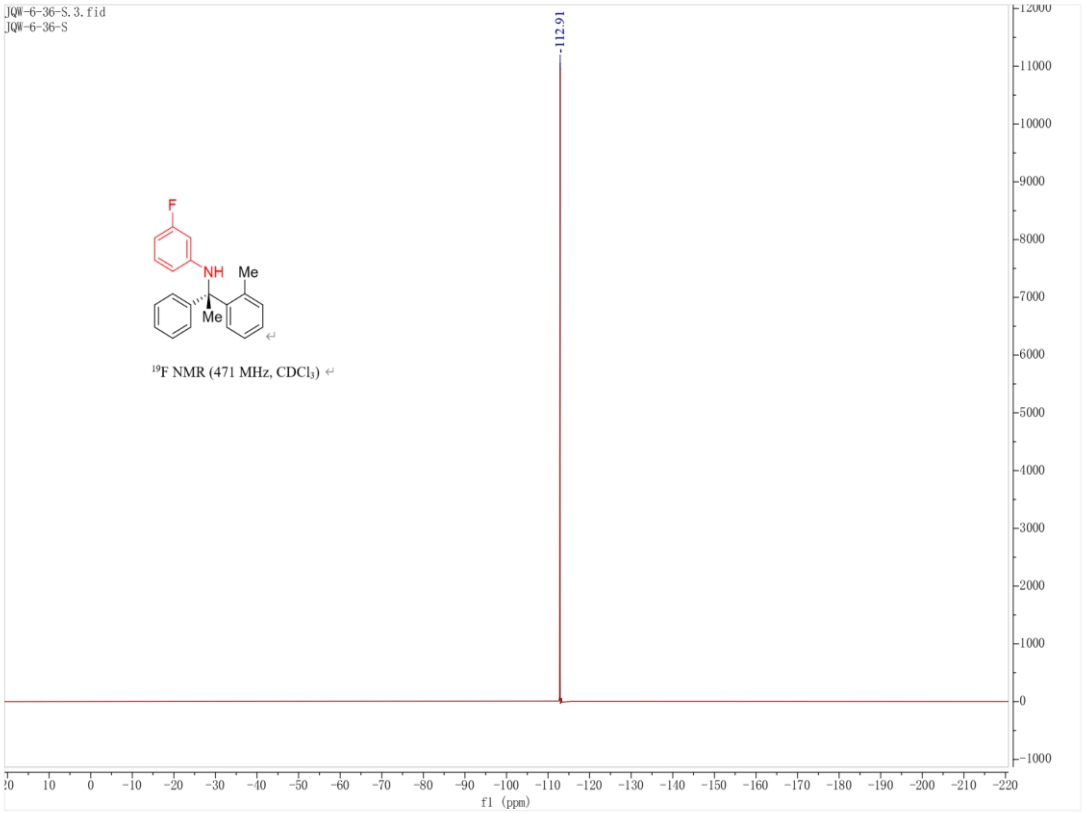




(*S*)-3-fluoro-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1e**)

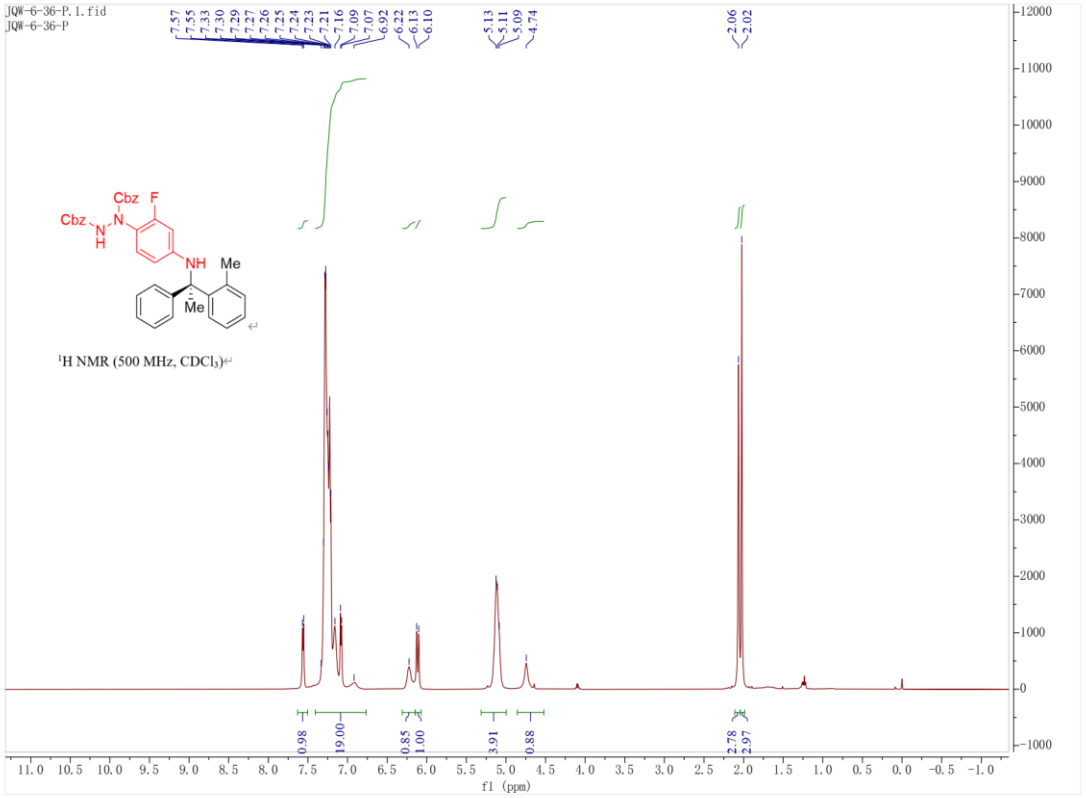


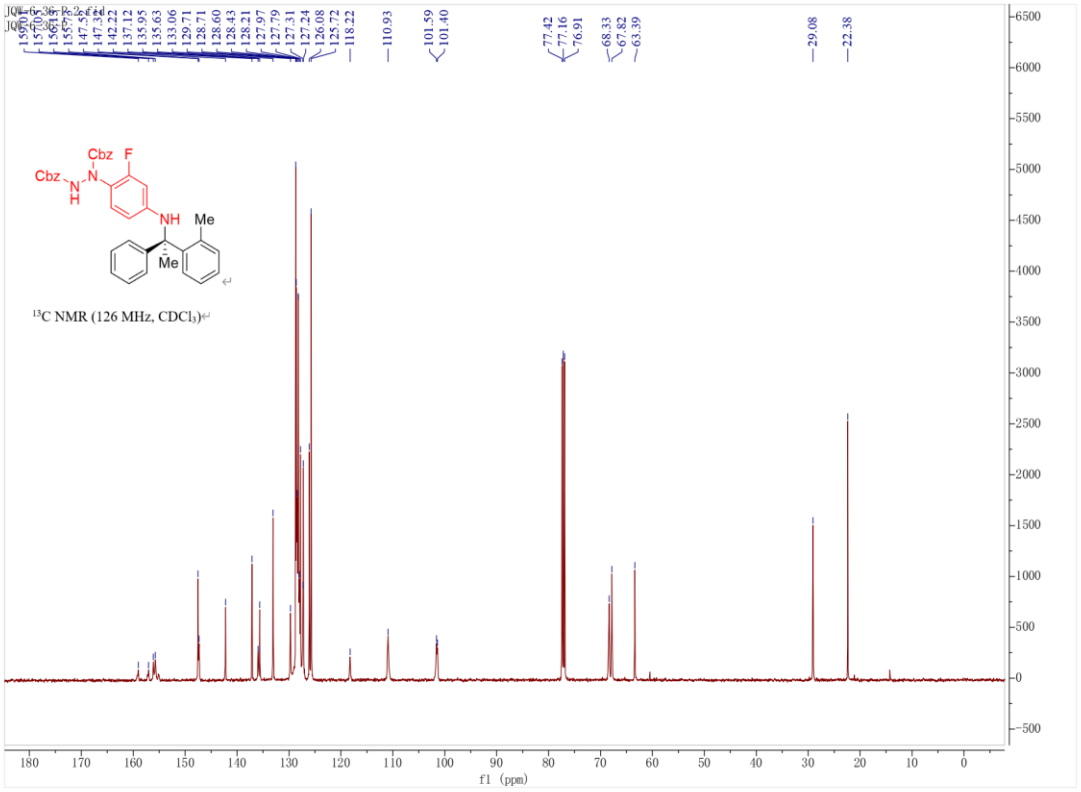




^{19}F NMR (471 MHz, $CDCl_3$)

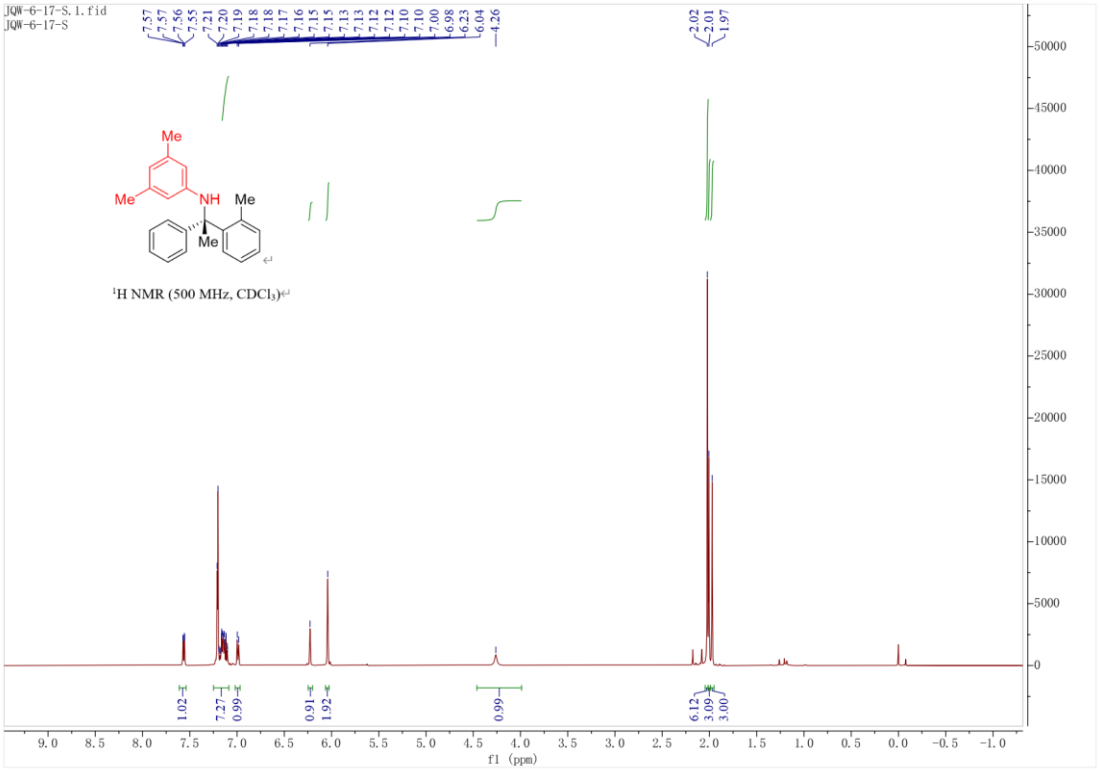
Dibenzyl-(*R*)-1-(2-fluoro-4-((1-phenyl-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3e**)

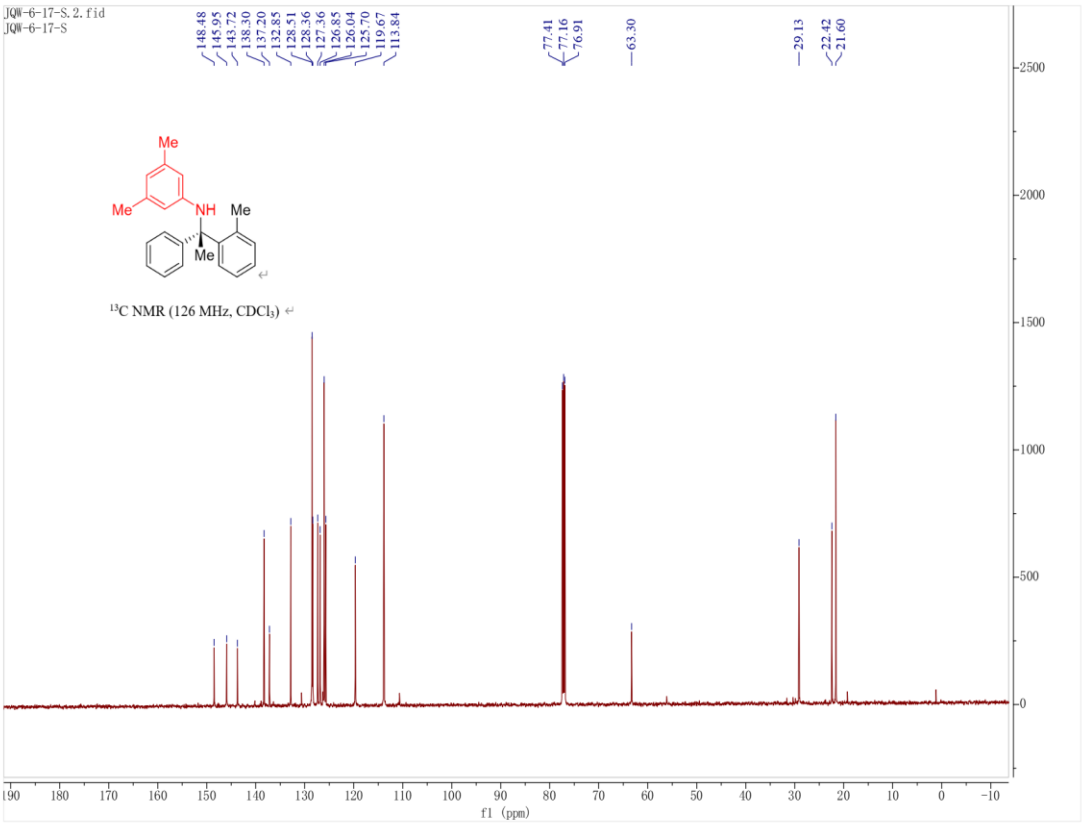




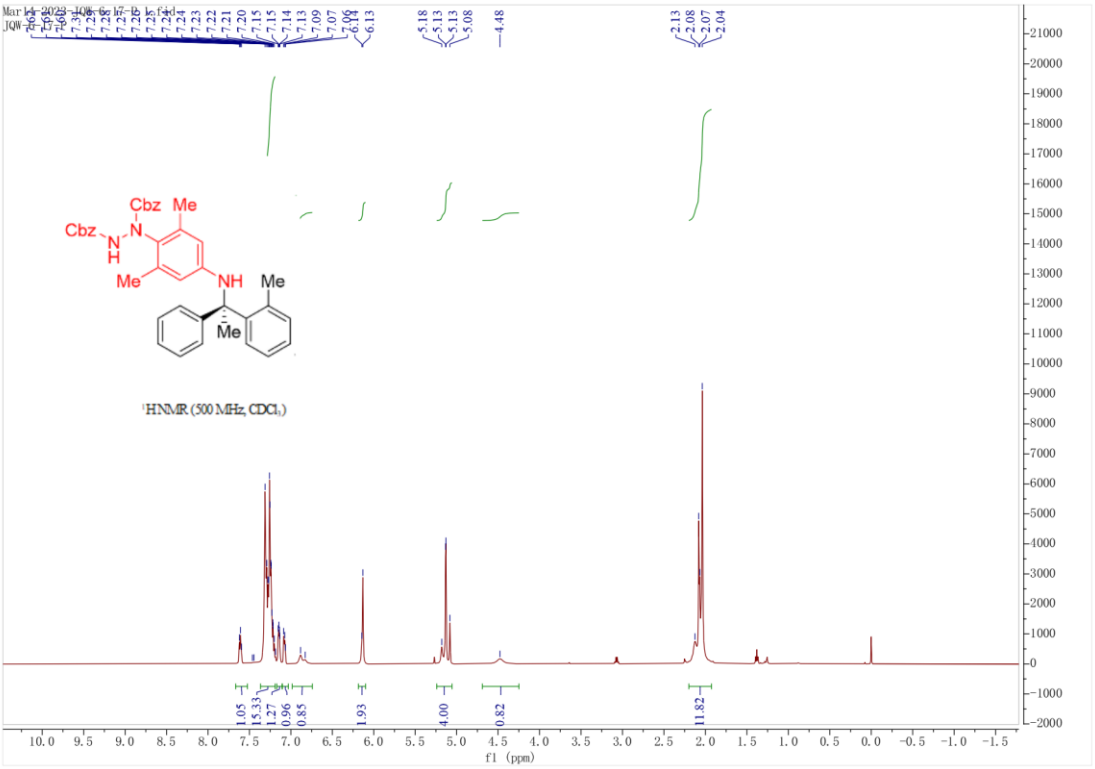
^{19}F NMR (471 MHz, $CDCl_3$)

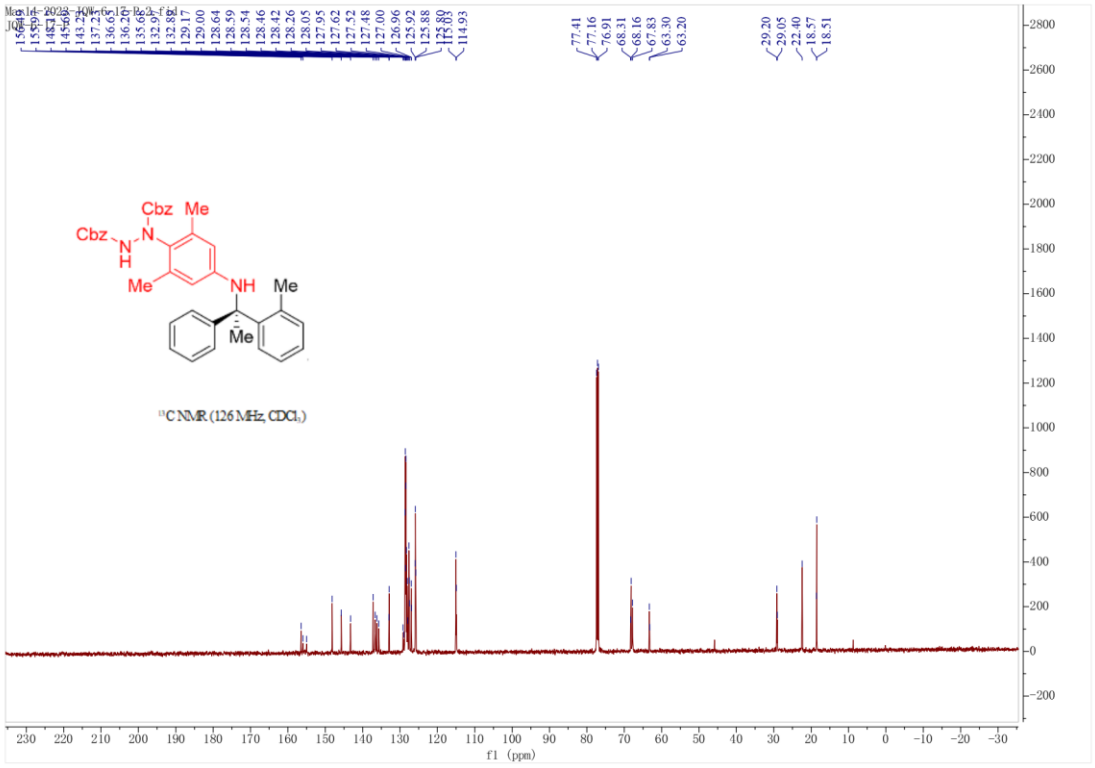
(*S*)-3,5-dimethyl-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1f**)



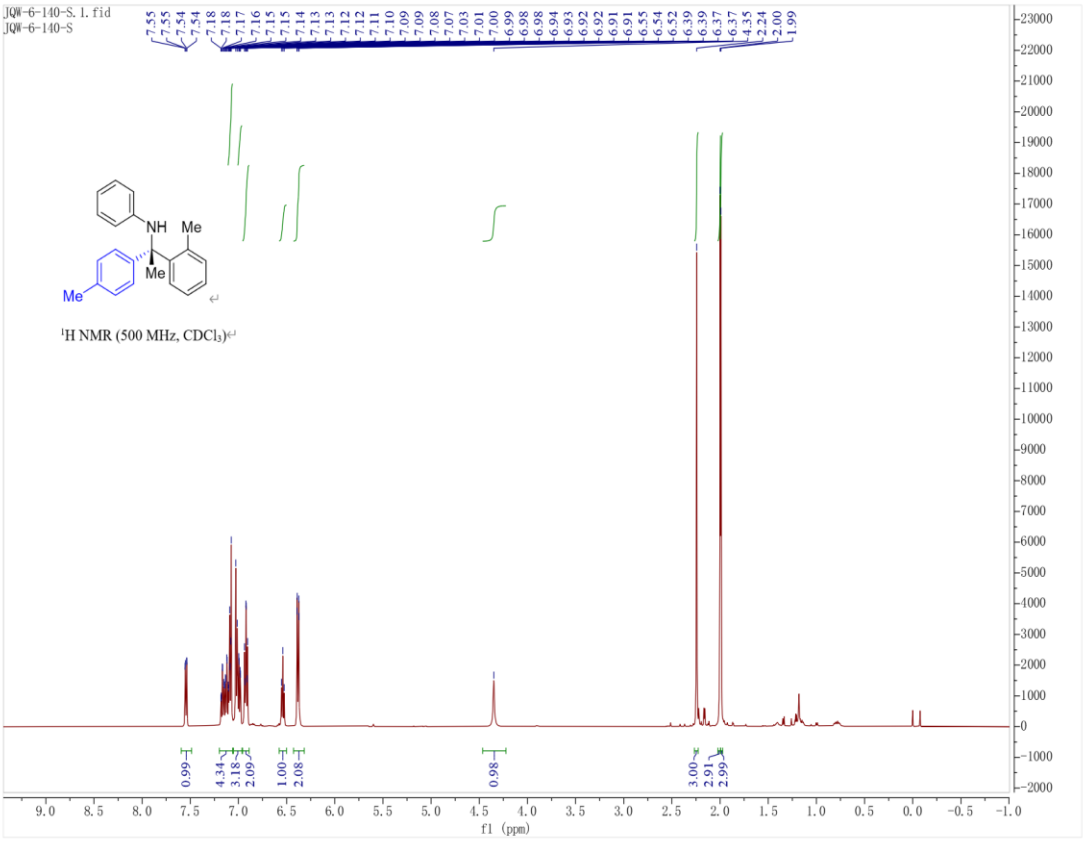


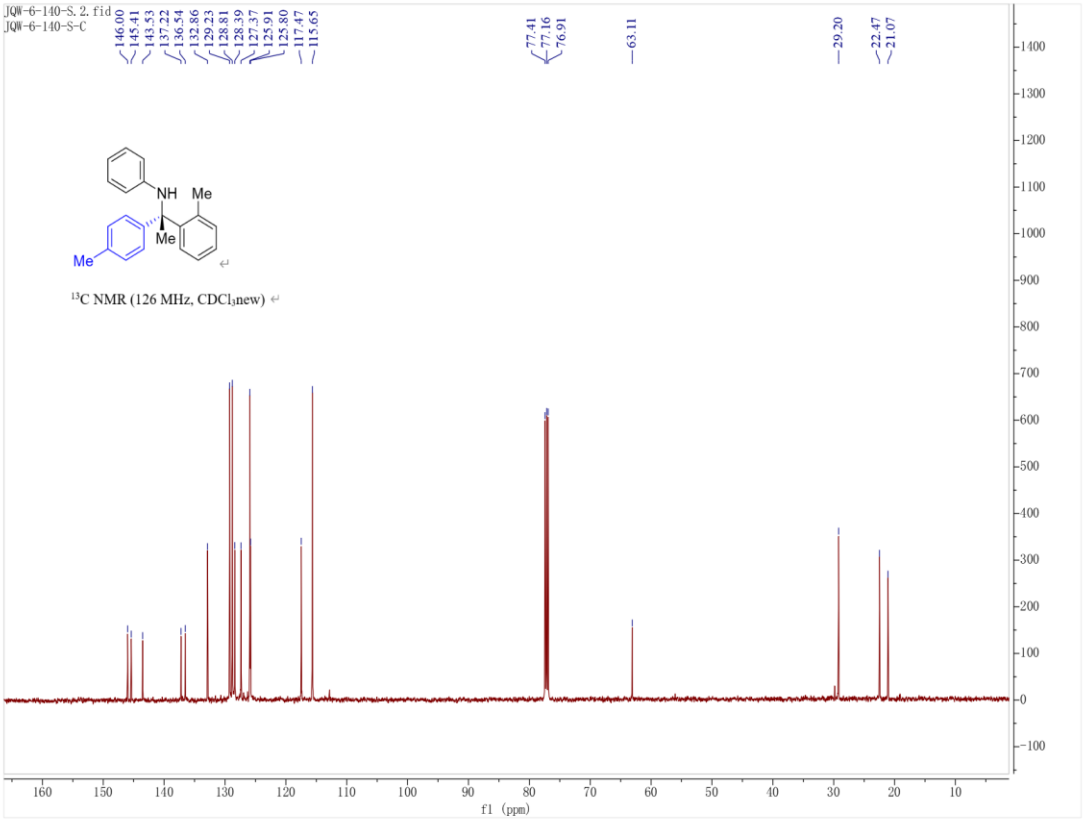
Dibenzyl-(*R*)-1-(2,6-dimethyl-4-((1-phenyl-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dica r-boxylate (**3f**)



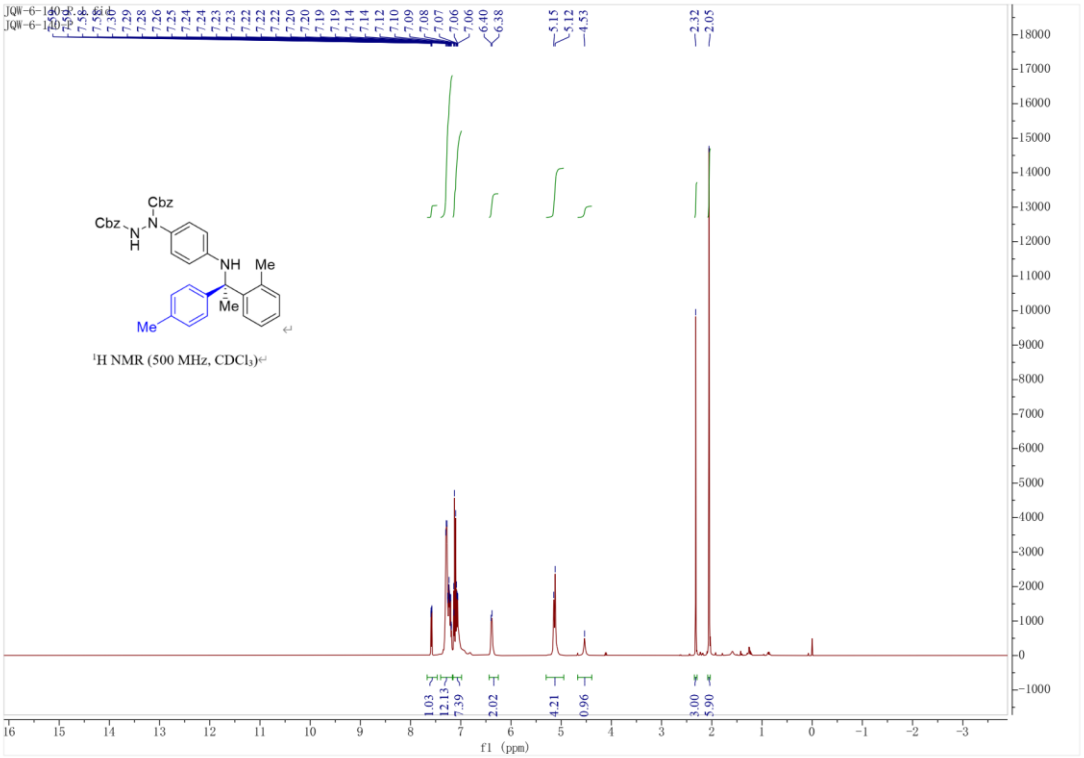


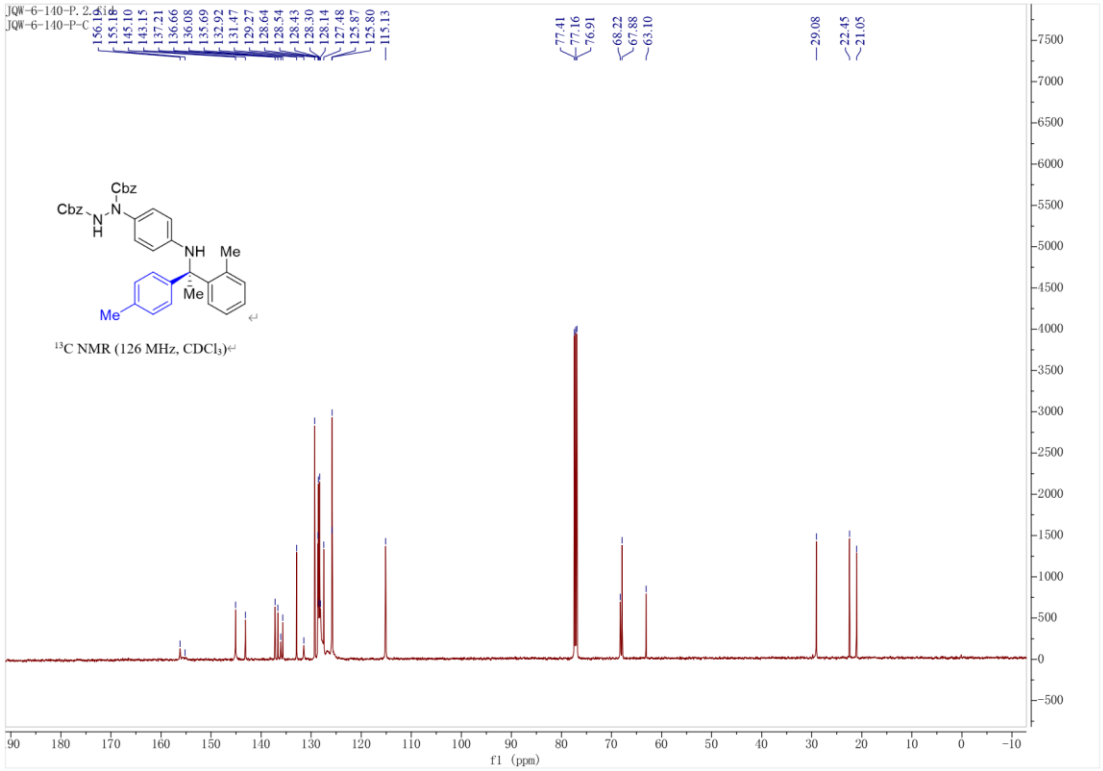
(*S*)-*N*-(1-(*o*-tolyl)-1-(*p*-tolyl)ethyl)aniline ((*S*)-**1g**)



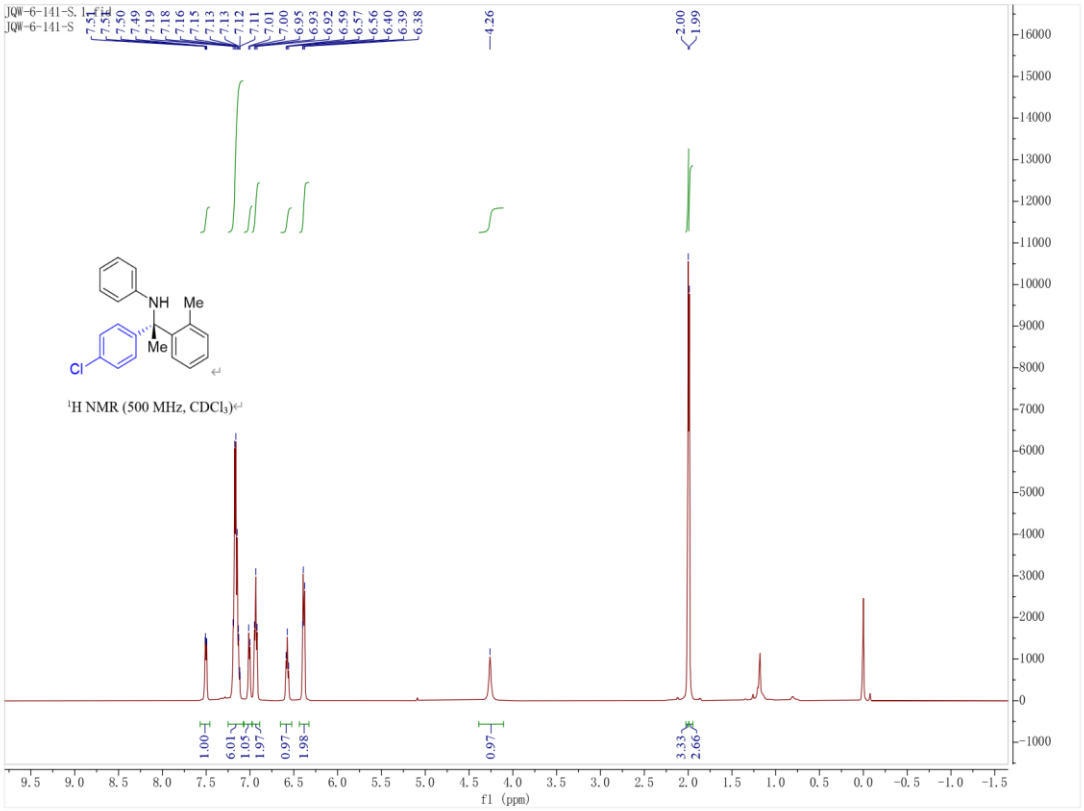


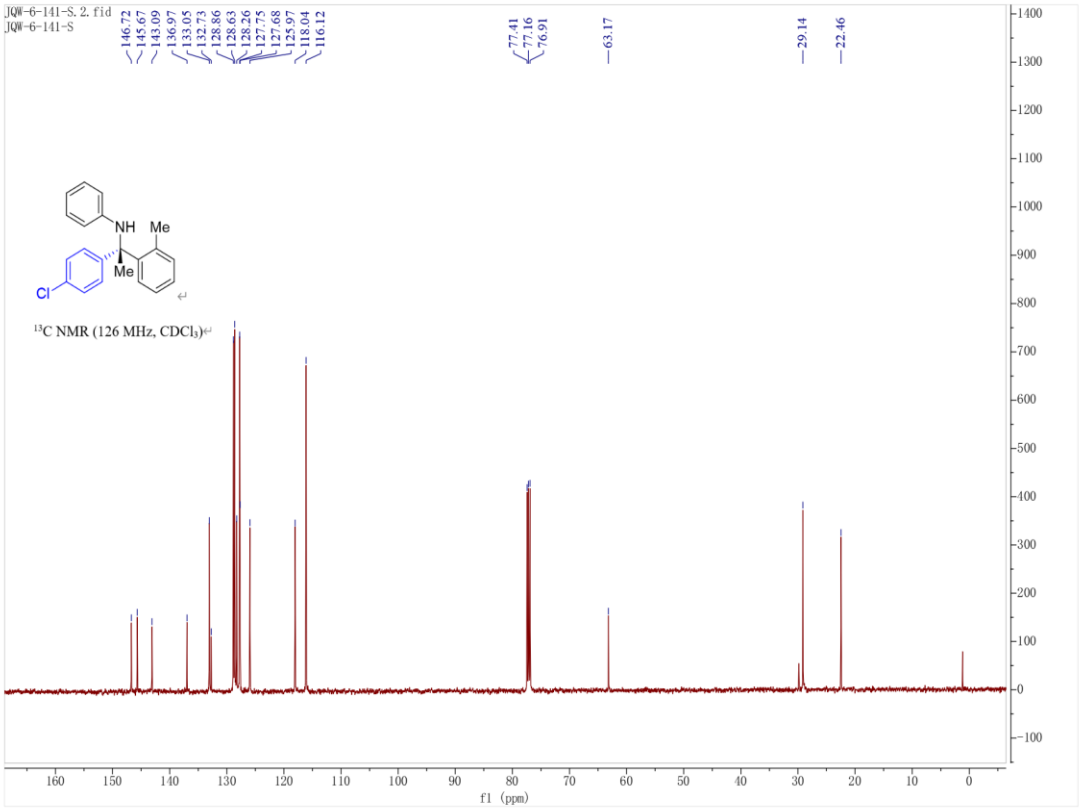
Dibenzyl (*R*)-1-(4-((1-(*o*-tolyl)-1-(*p*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3g**)



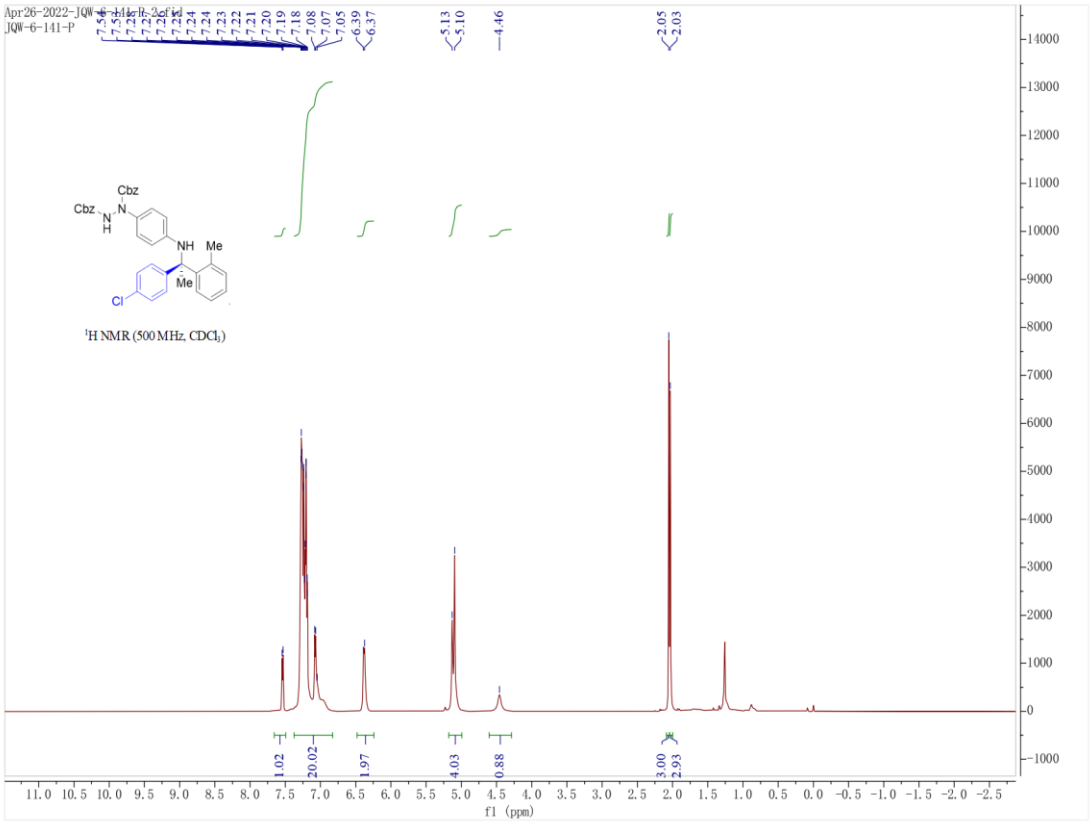


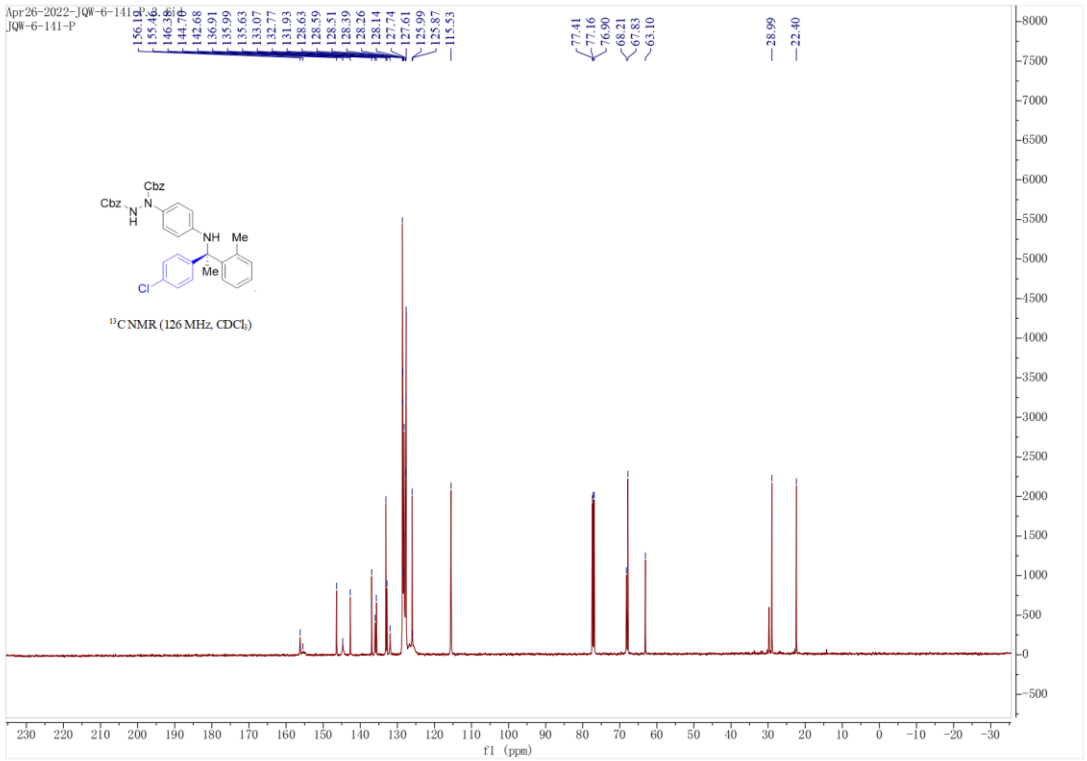
(*S*)-*N*-(1-(4-chlorophenyl)-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1h**)



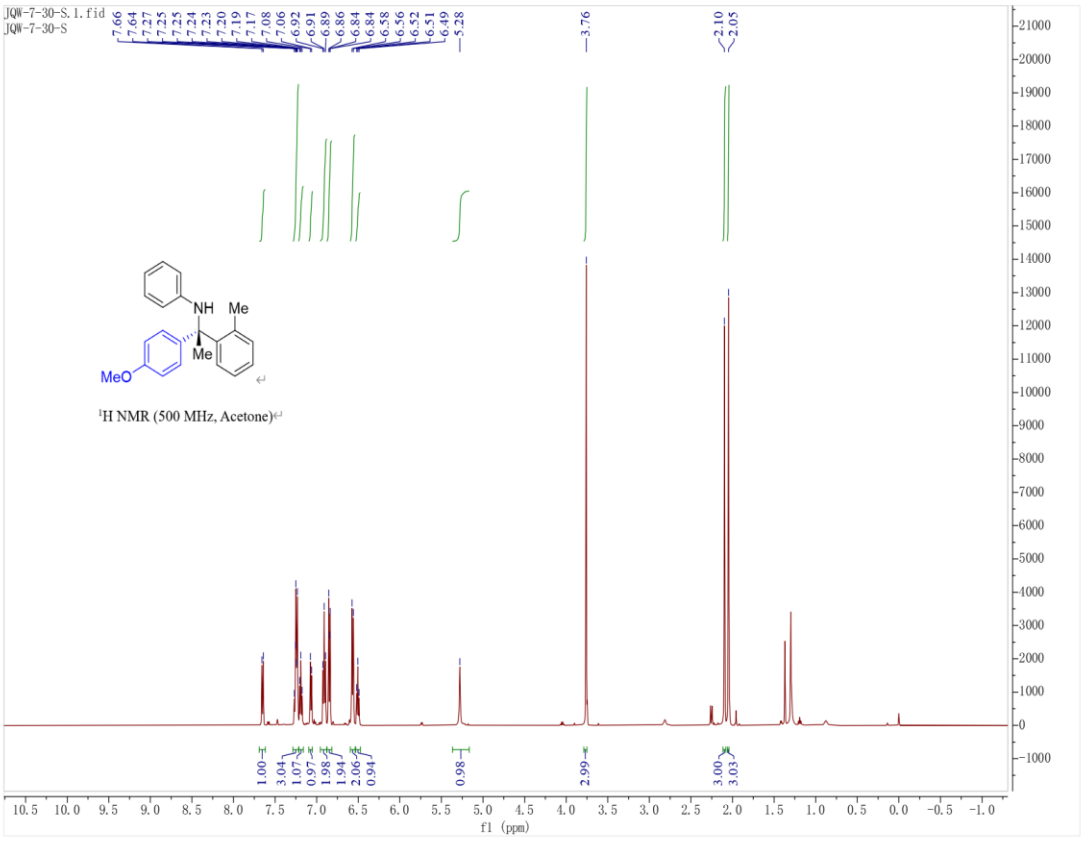


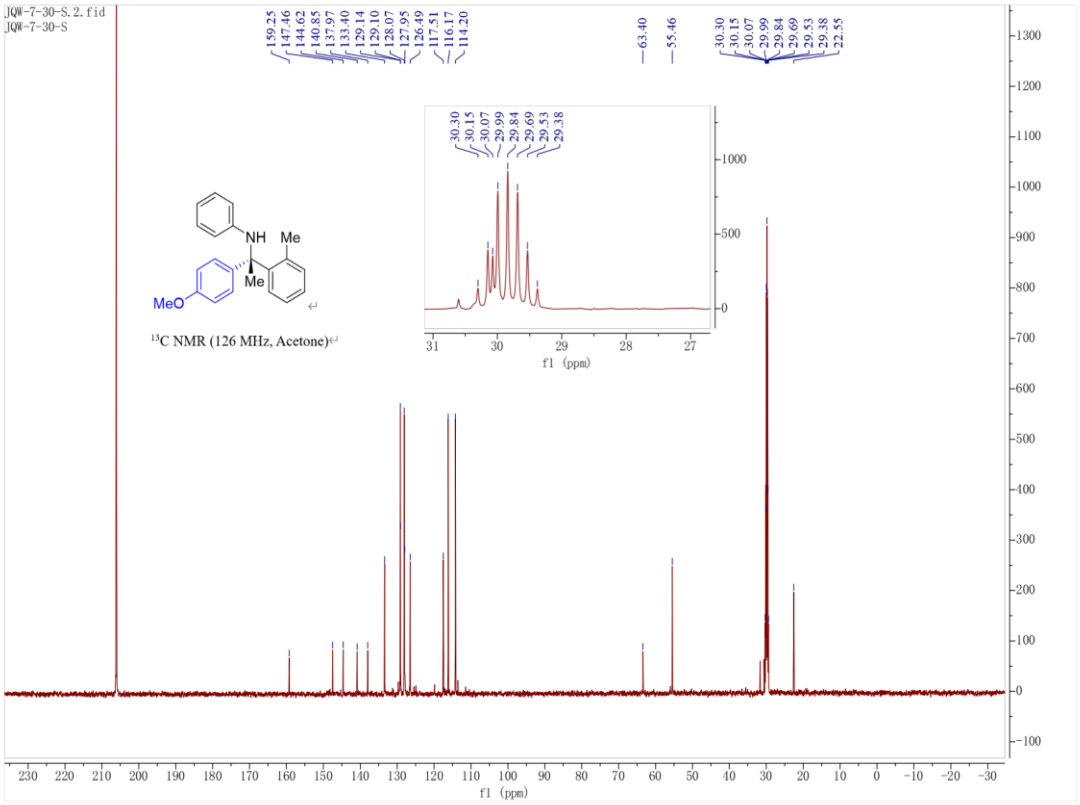
Dibenzyl-(*R*)-1-(4-((1-(4-chlorophenyl)-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarbo xyl-ate (**3h)**



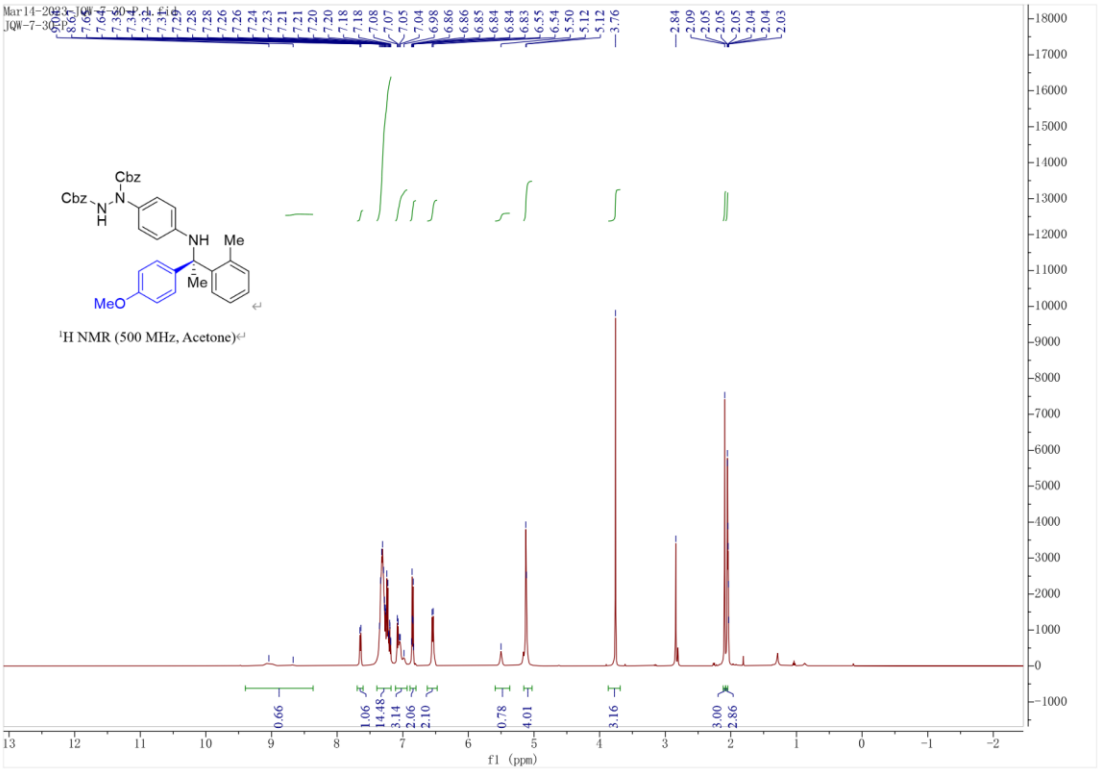


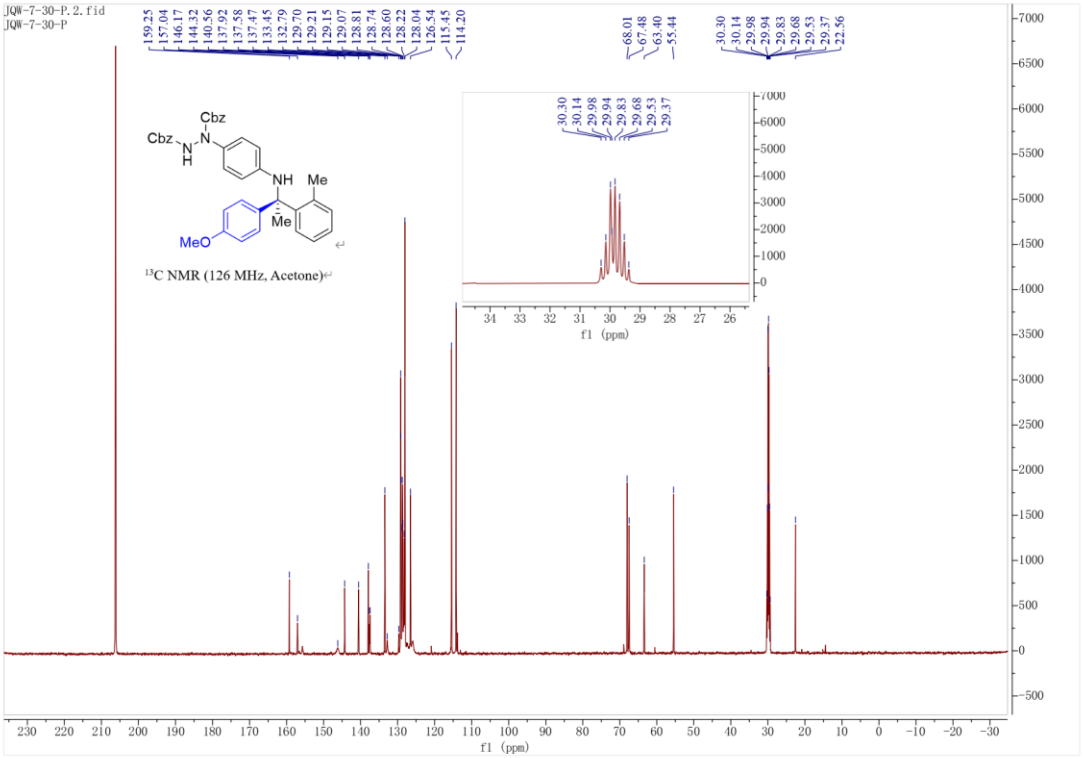
(*S*)-*N*-(1-(4-methoxyphenyl)-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1i**)



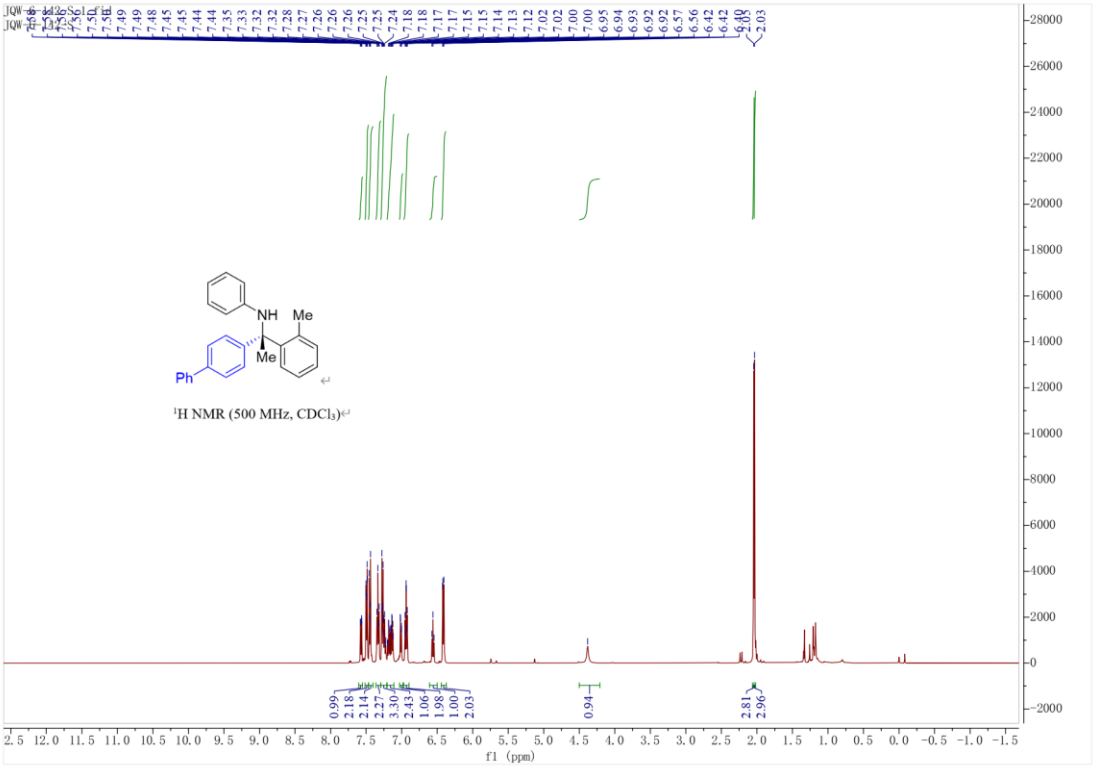


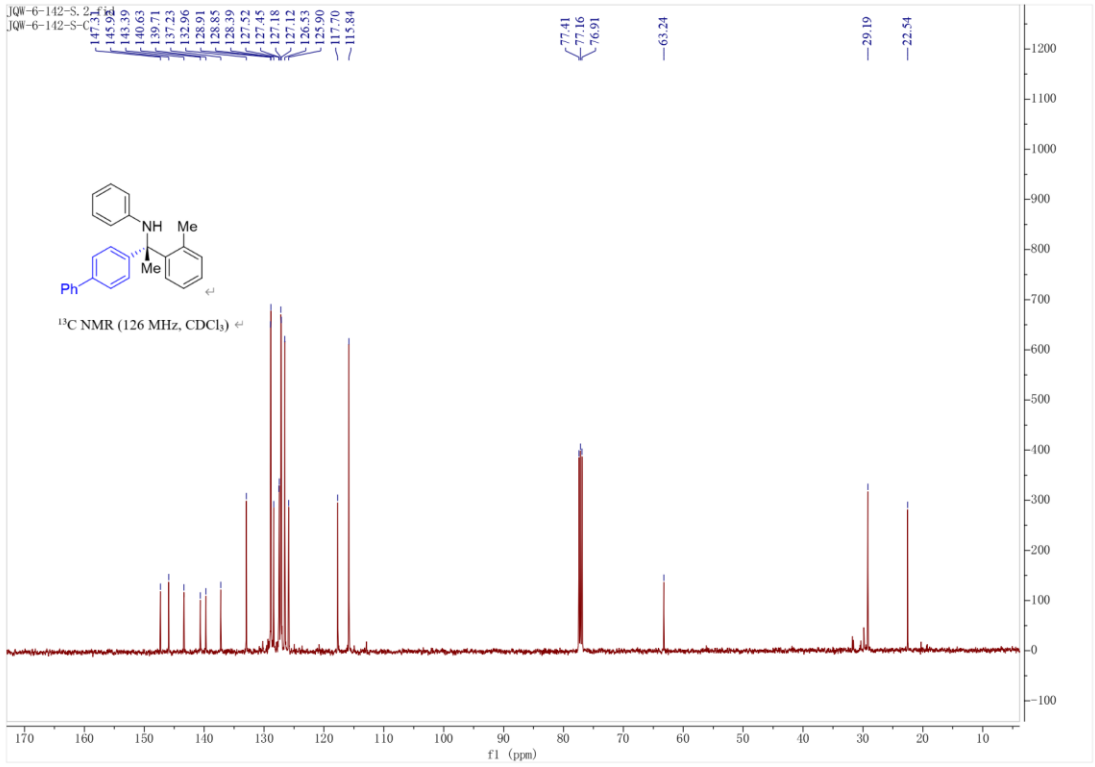
Dibenzyl-(*R*)-1-(4-((1-(4-methoxyphenyl)-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3i**)



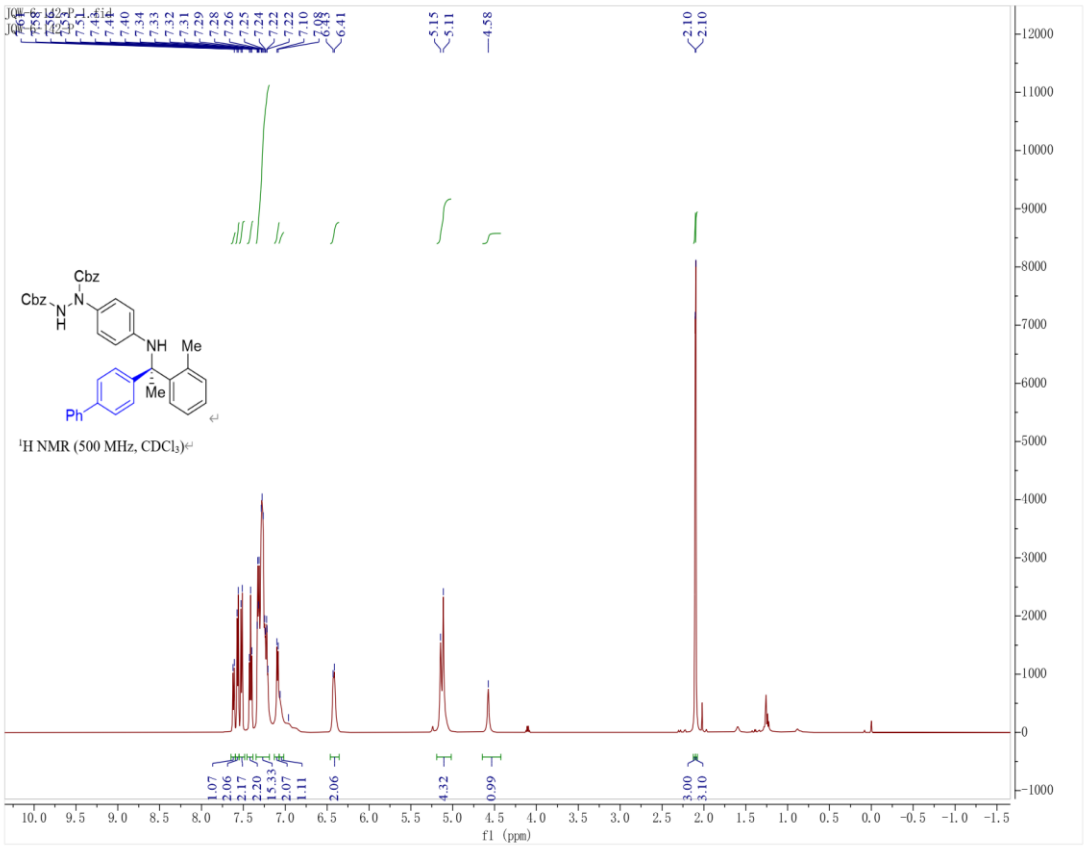


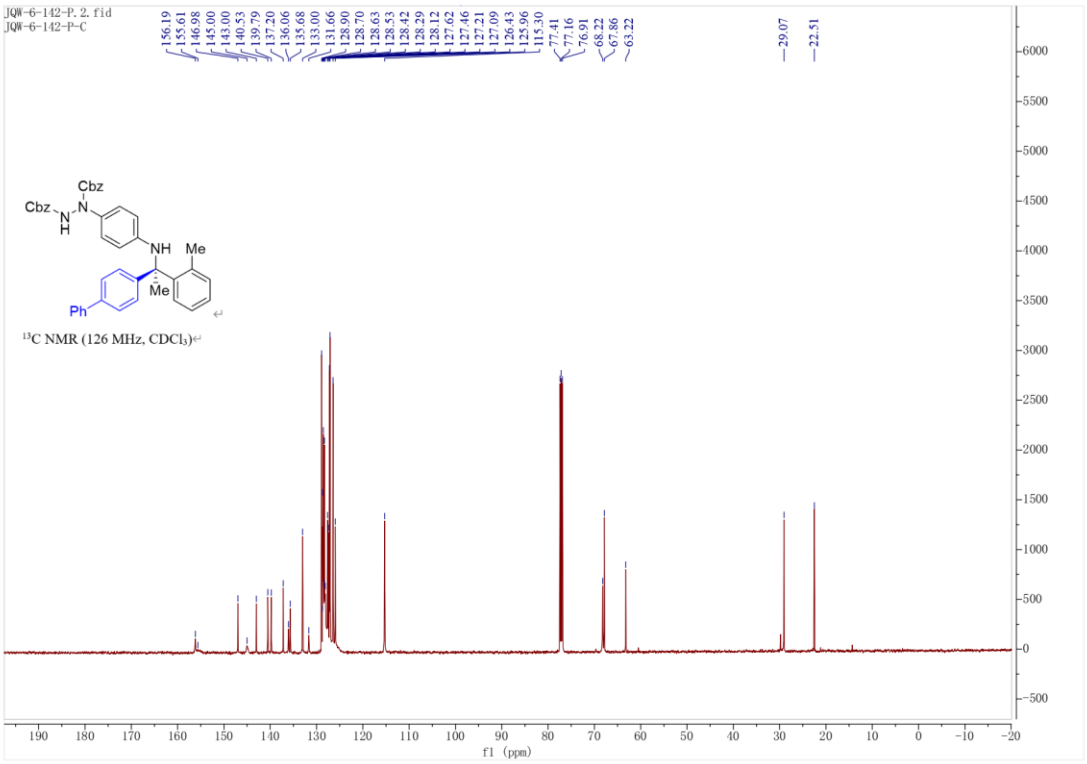
(*S*)-*N*-(1-([1,1'-biphenyl]-4-yl)-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1j**)



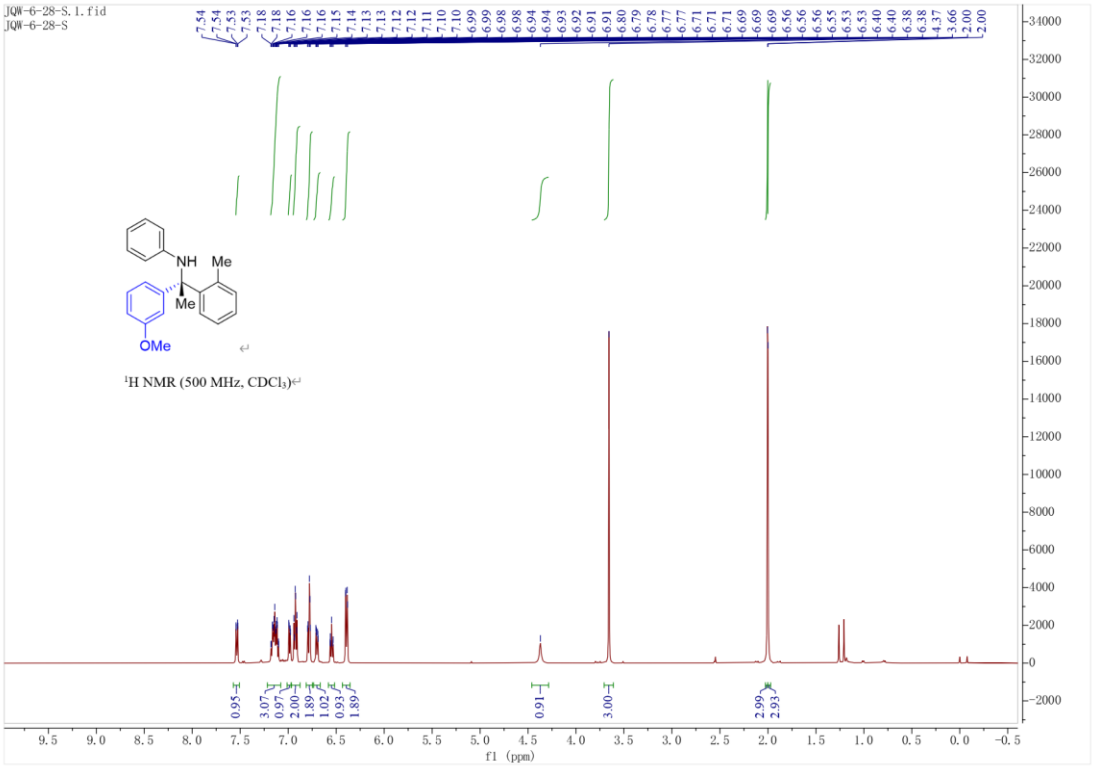


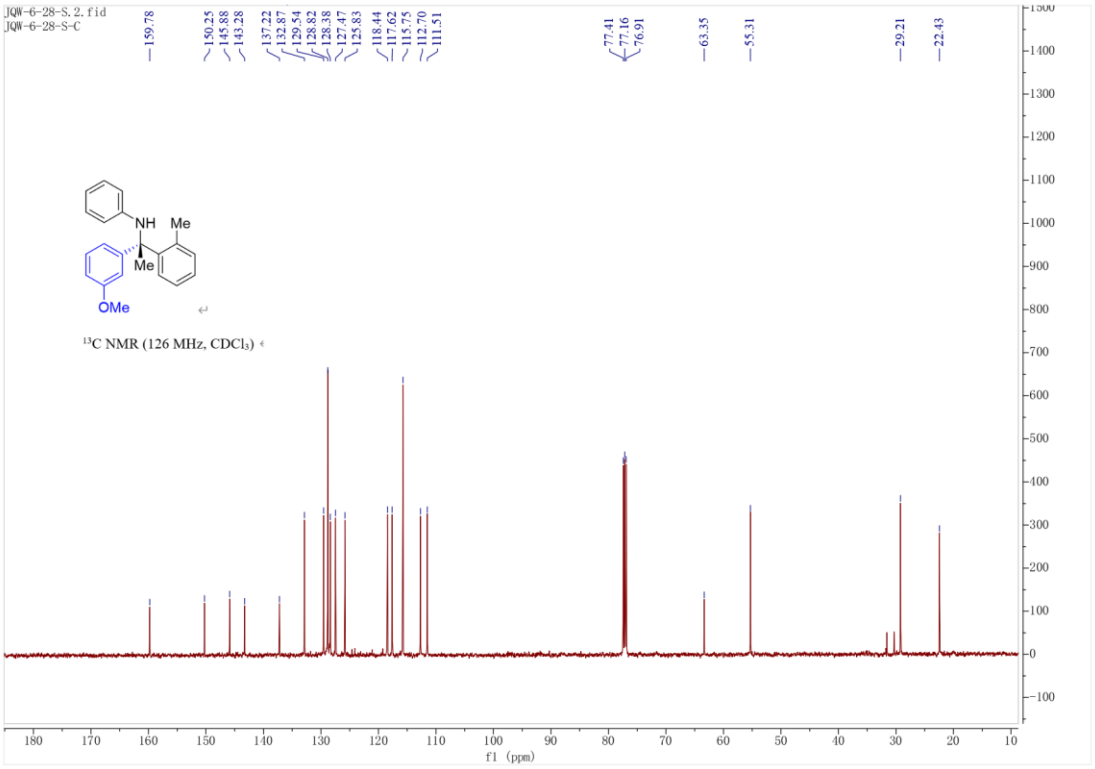
Dibenzyl-(*R*)-1-(4-((1-([1,1'-biphenyl]-4-yl)-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dic ar-boxylate (**3j**)



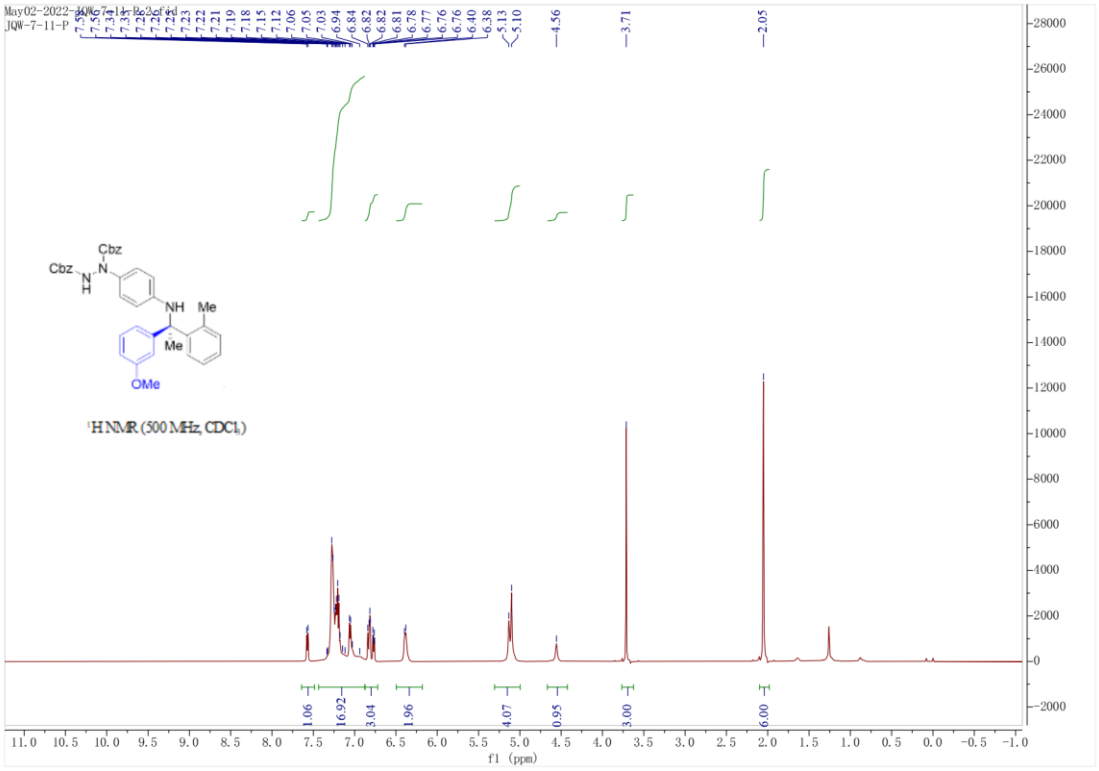


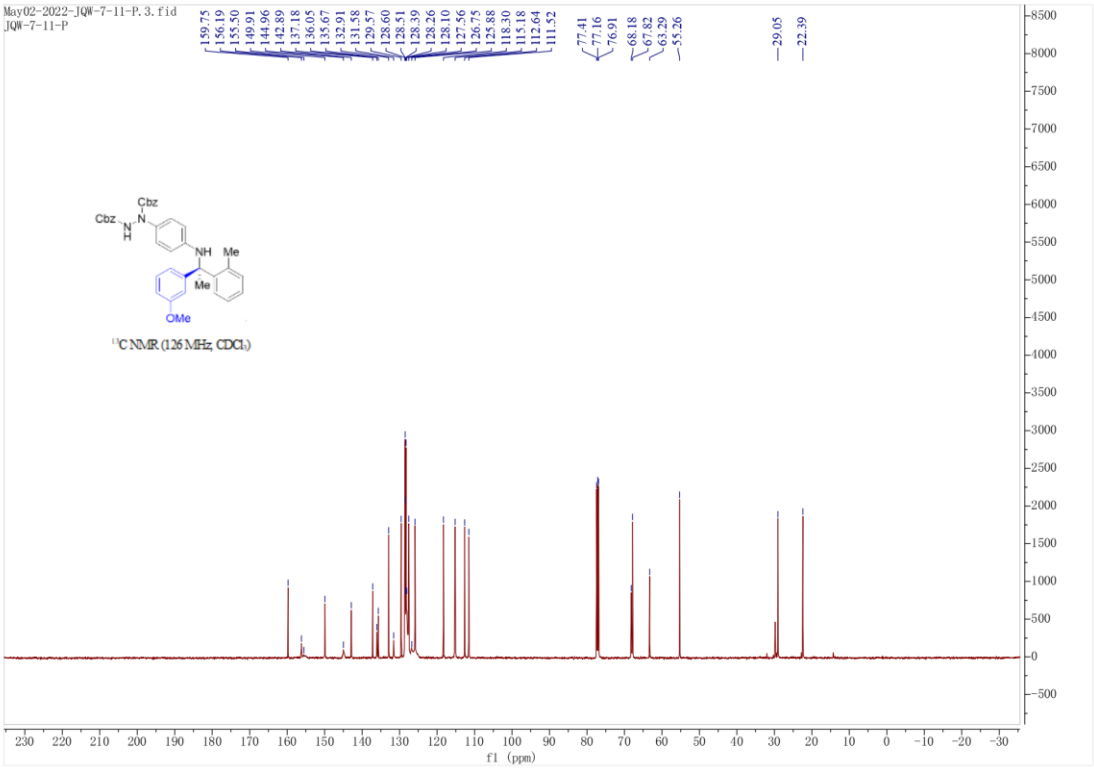
(*S*)-*N*-(1-(3-methoxyphenyl)-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1k**)



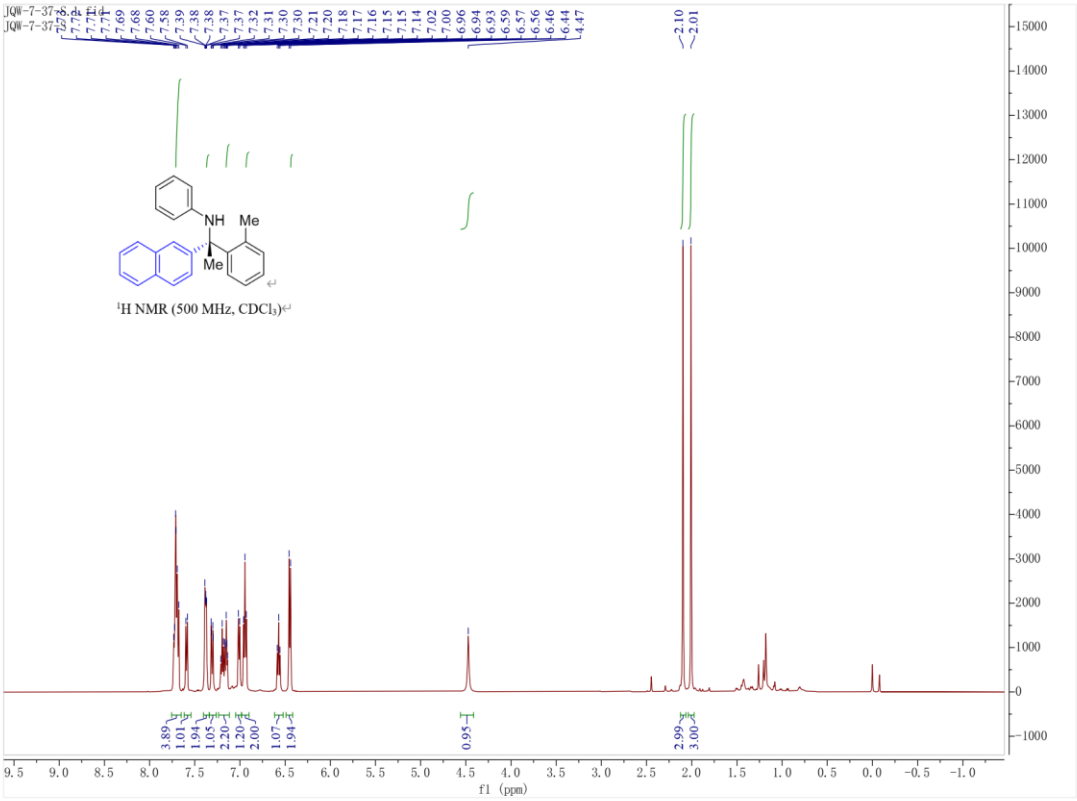


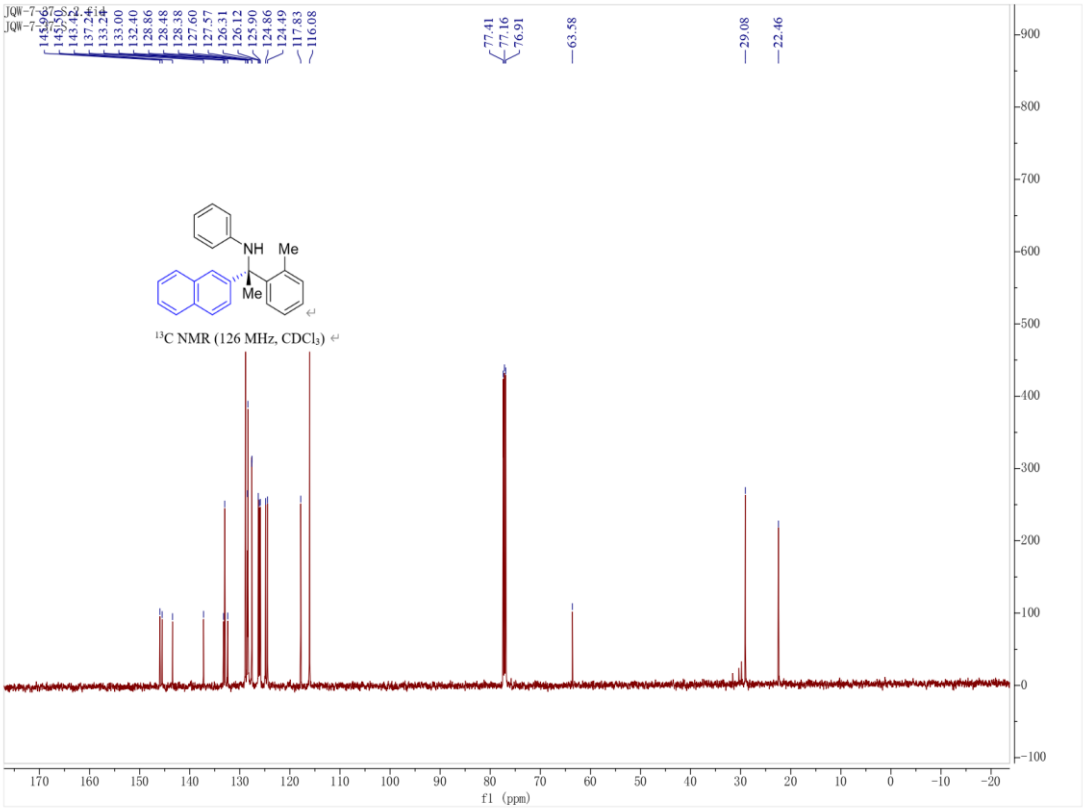
Dibenzyl-(*R*)-1-(4-((1-(3-methoxyphenyl)-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3k**)



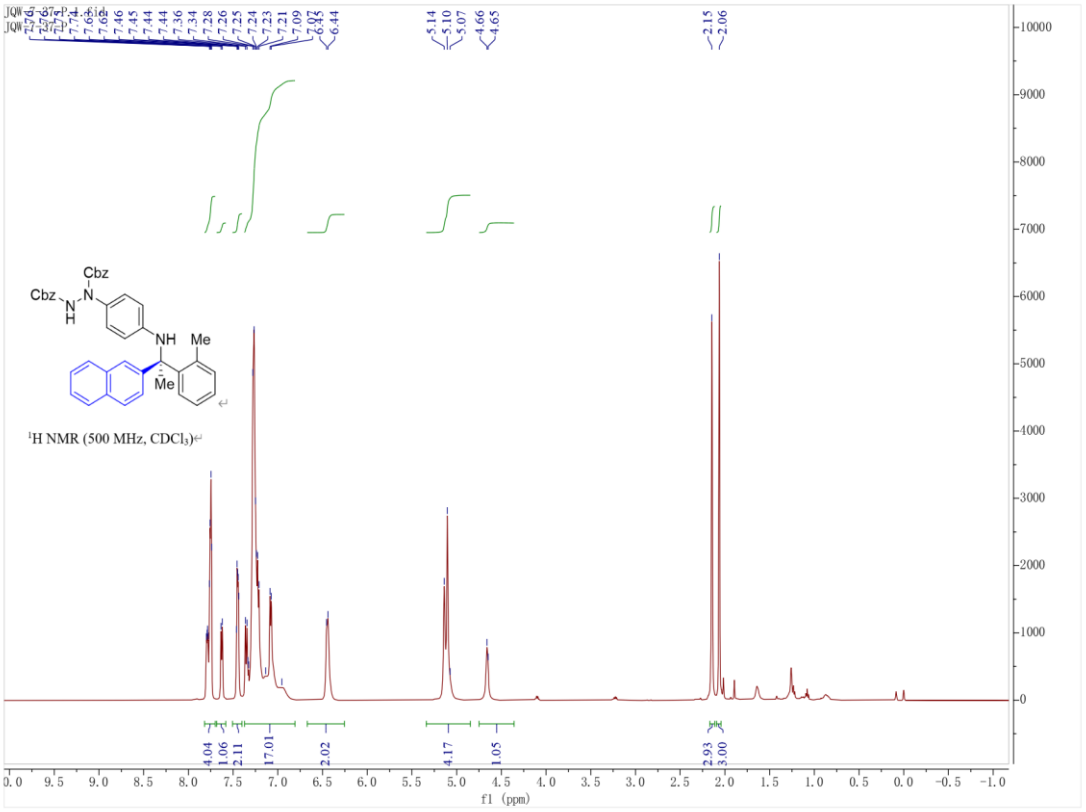


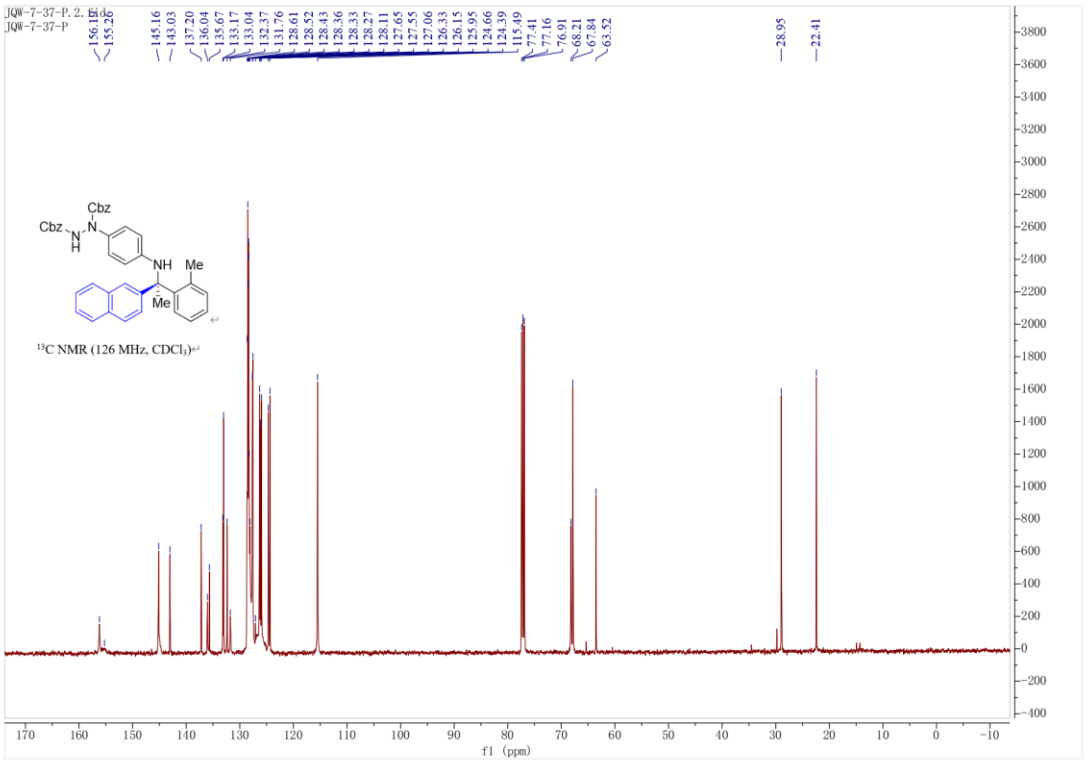
(*S*)-*N*-(1-(naphthalen-2-yl)-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1l**)



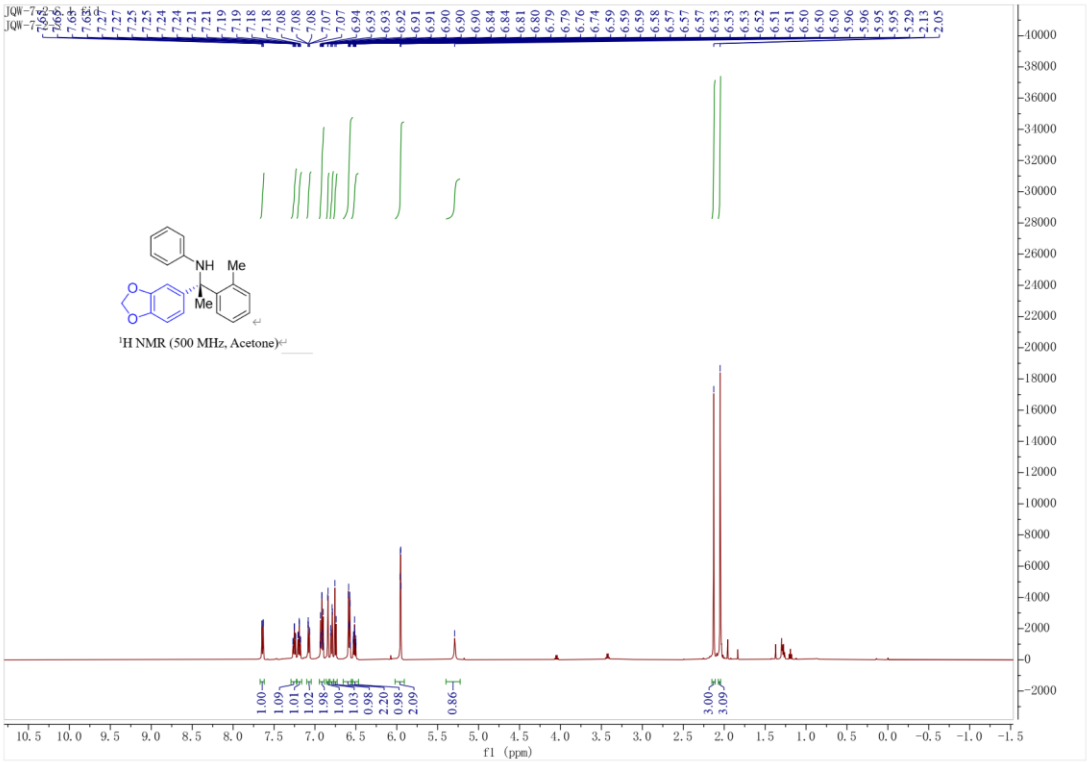


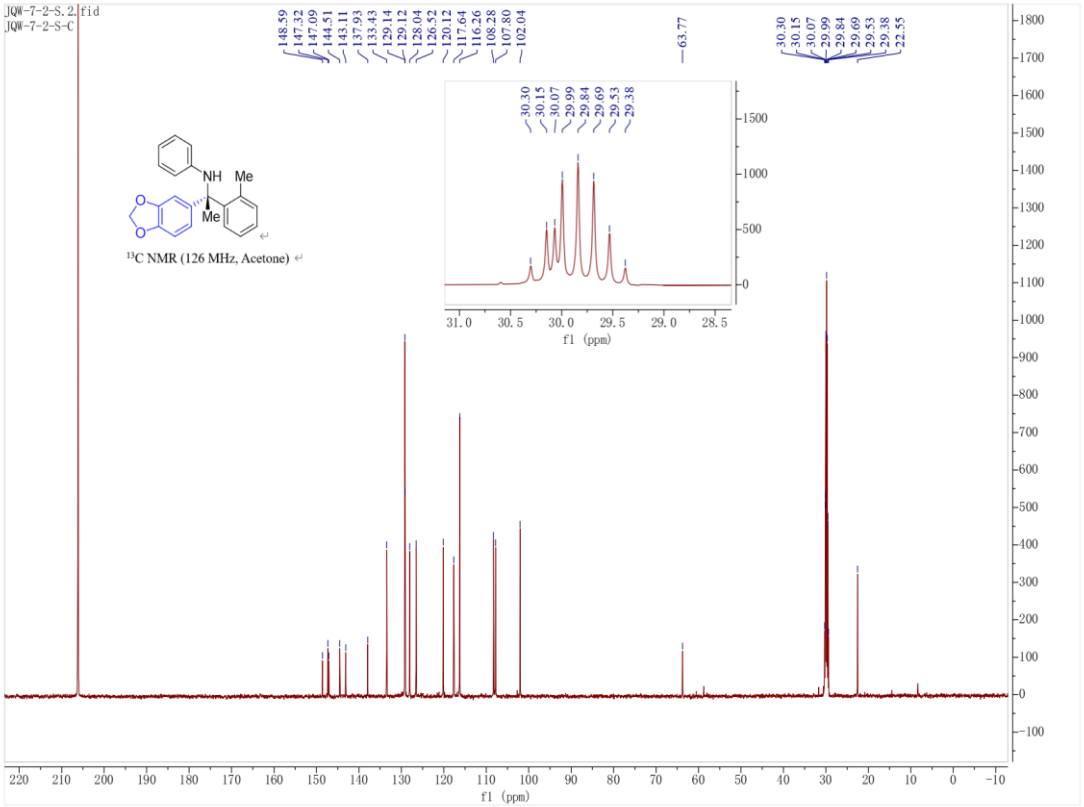
Dibenzyl-(*R*)-1-(4-((1-(naphthalen-2-yl)-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1,2-dicarbo xyl-ate (**3l**)



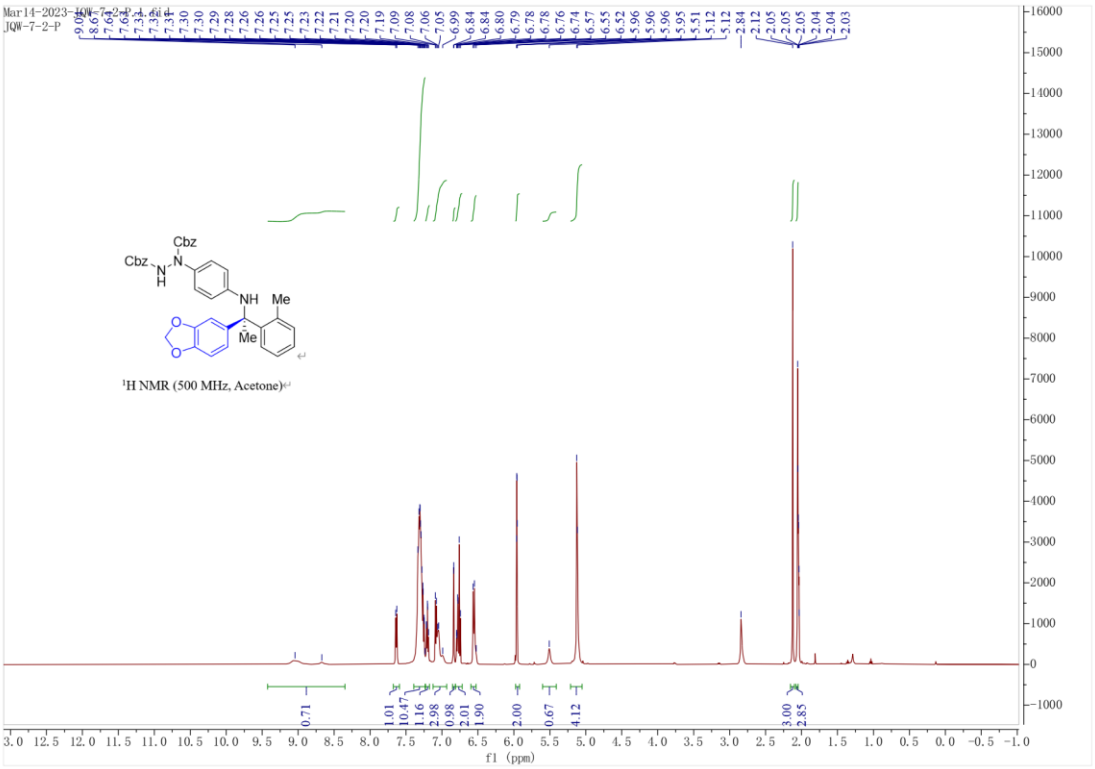


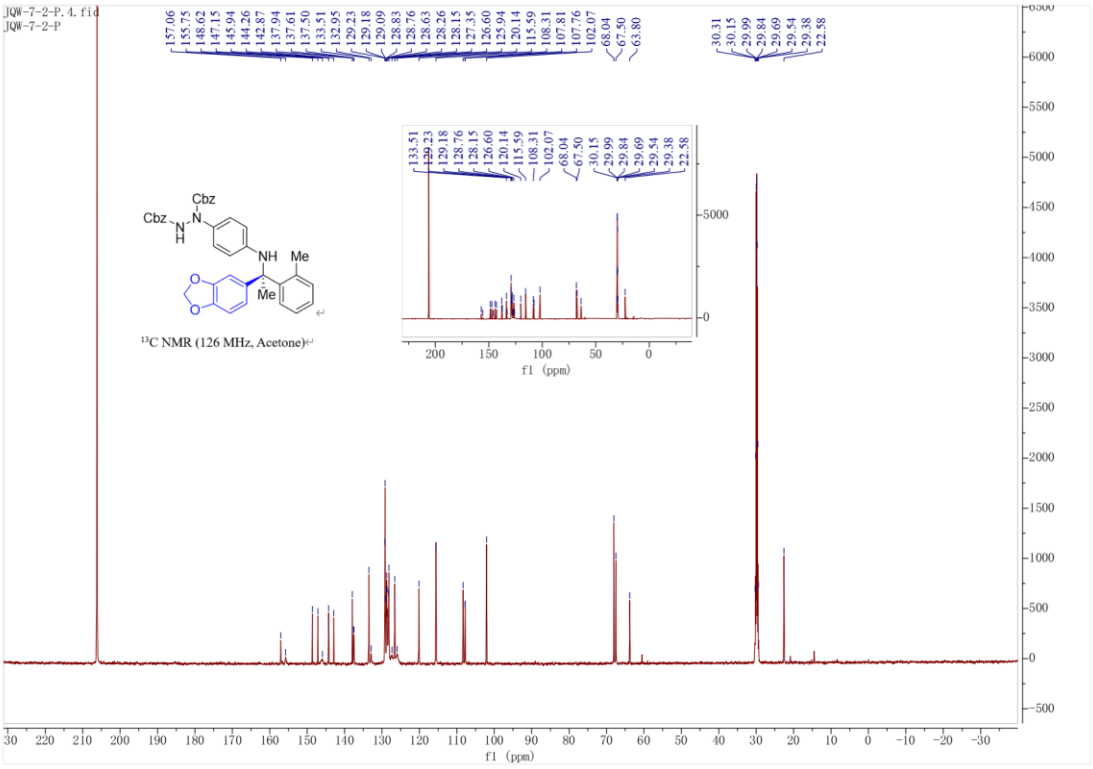
(*S*)-*N*-(1-(benzo[d][1,3]dioxol-5-yl)-1-(*o*-tolyl)ethyl)aniline ((*S*)-**1m**)



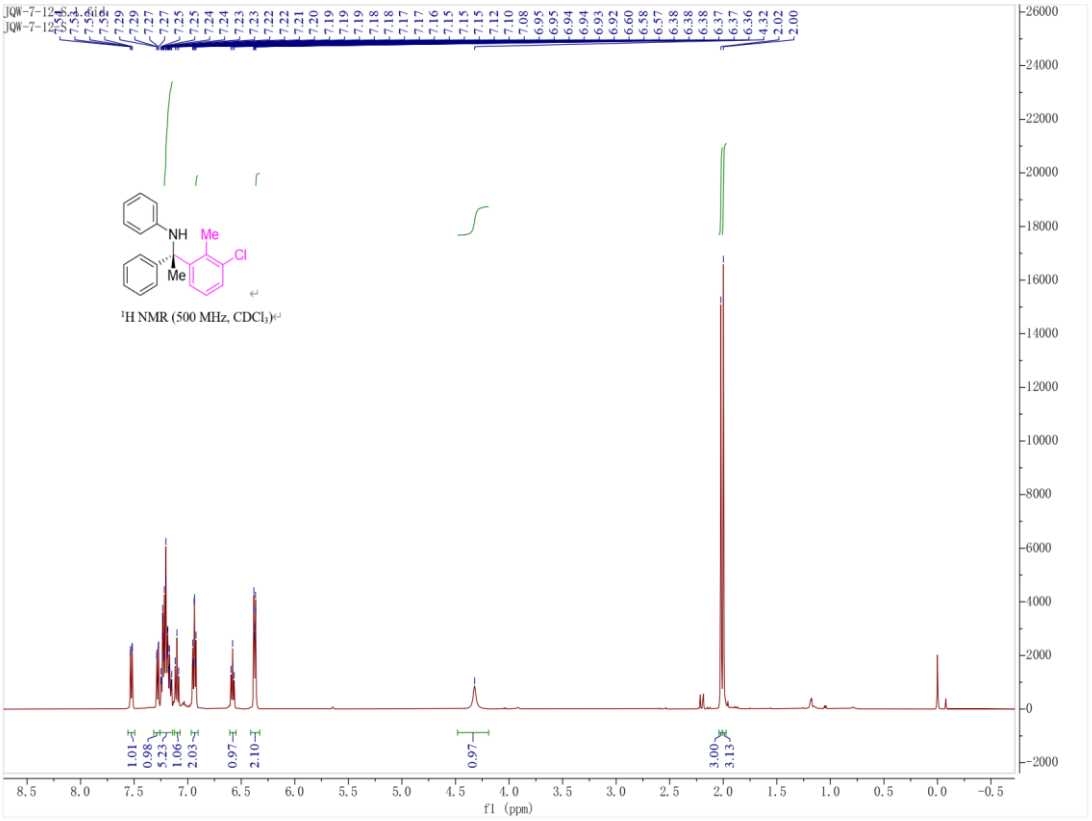


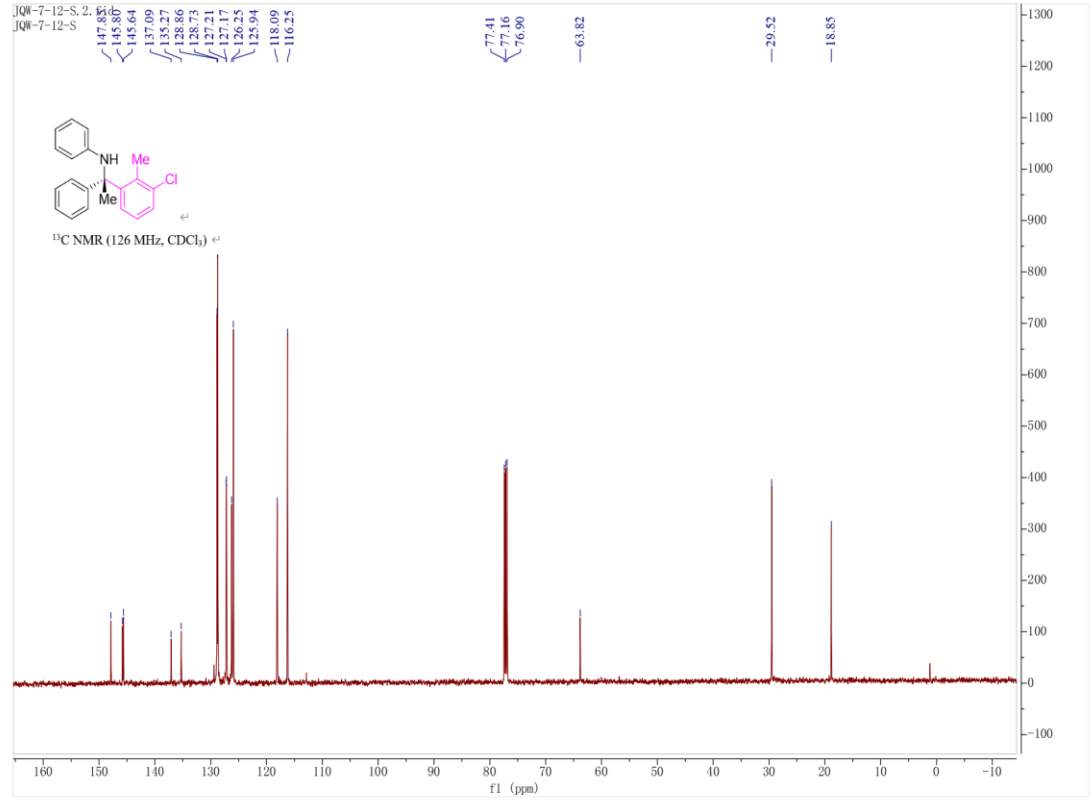
Dibenzyl-(*R*)-1-(4-((1-(benzo[d][1,3]dioxol-5-yl)-1-(*o*-tolyl)ethyl)amino)phenyl)hydrazine-1, 2-di-carboxylate (**3m**)



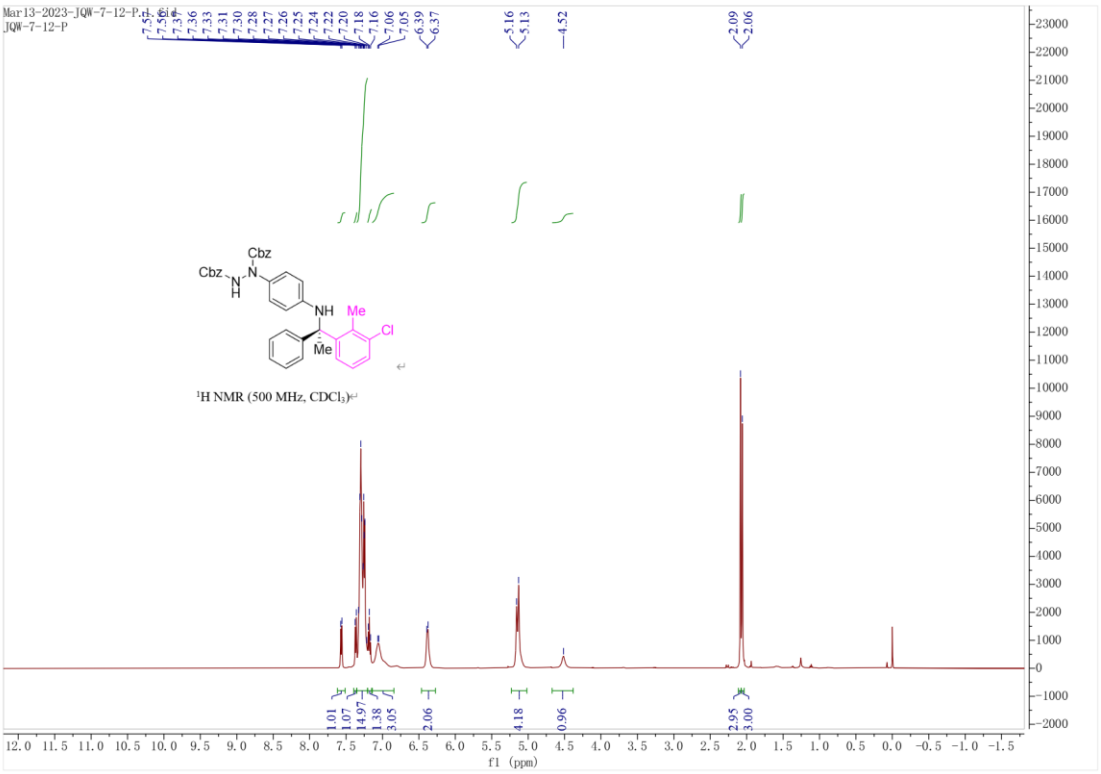


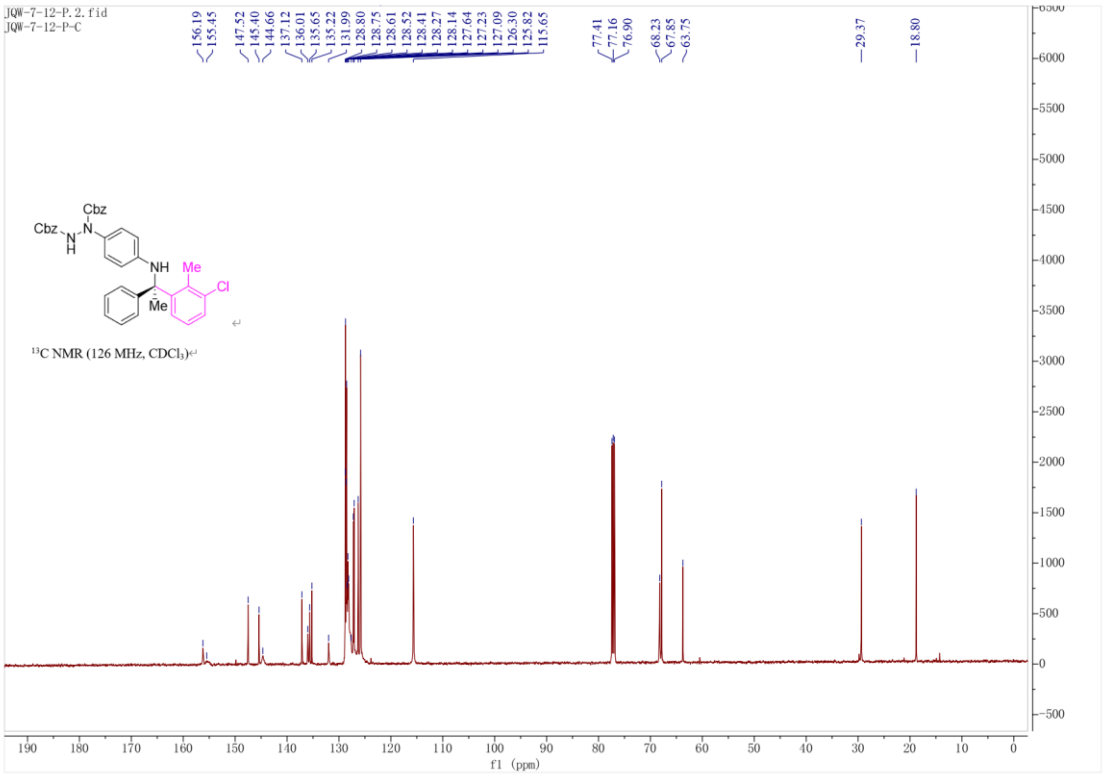
(*S*)-*N*-(1-(3-chloro-2-methylphenyl)-1-phenylethyl)aniline ((*S*)-**1n**)



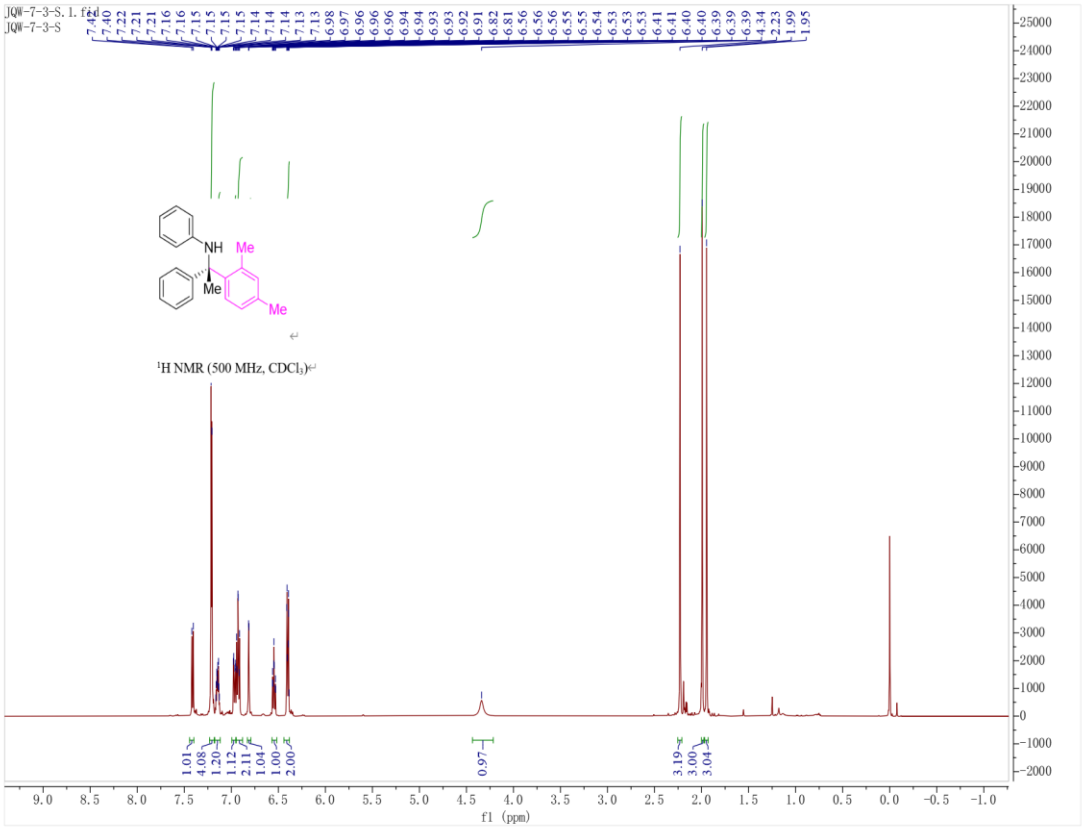


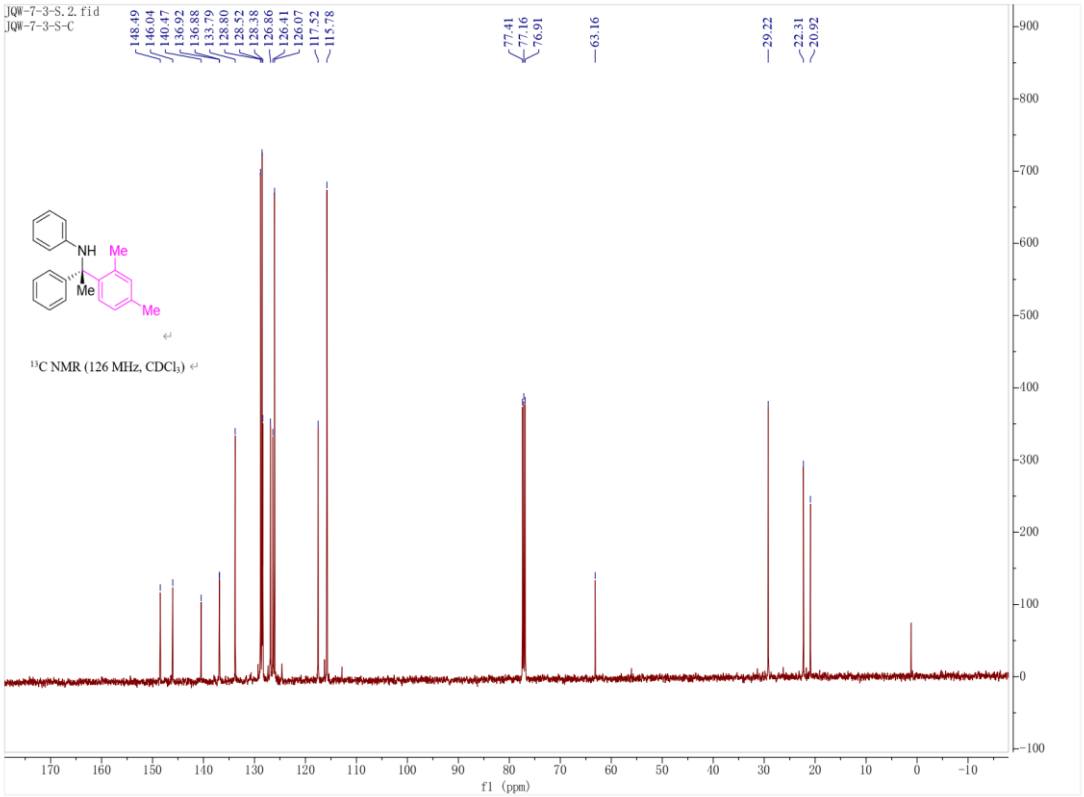
Dibenzyl-(*R*)-1-(4-((1-(3-chloro-2-methylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-di-carboxylate (**3n**)





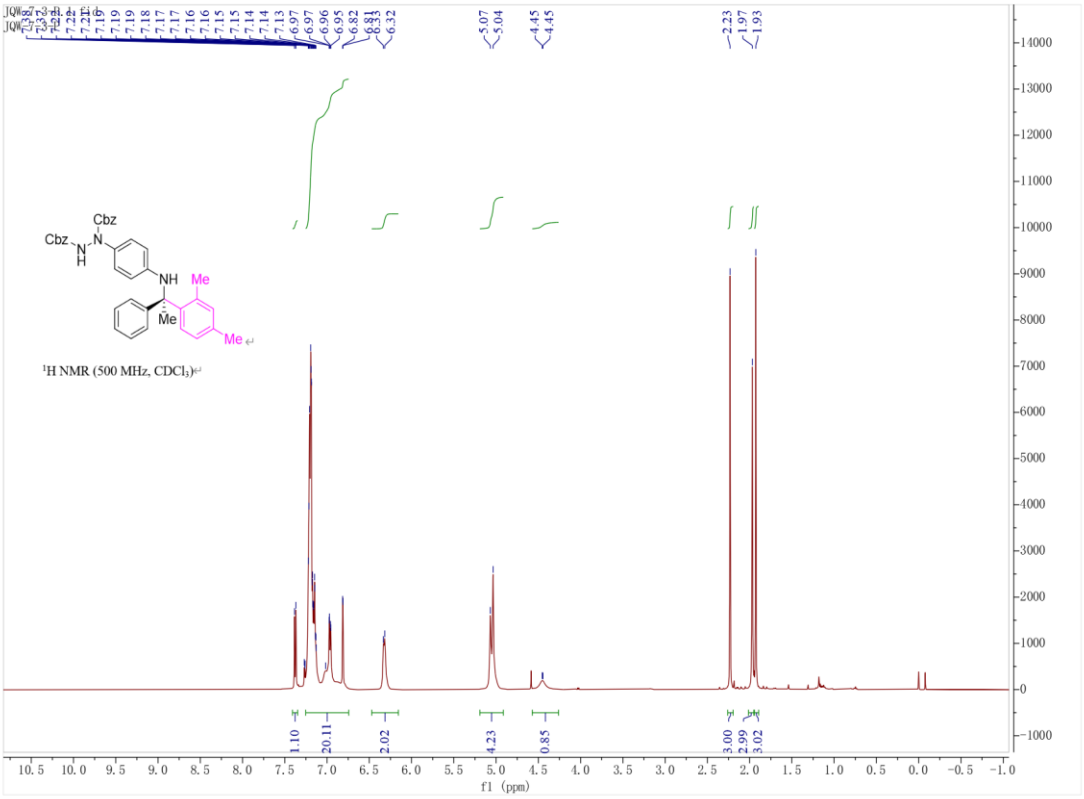
(*S*)-*N*-(1-(2,4-dimethylphenyl)-1-phenylethyl)aniline ((*S*)-**1o**)

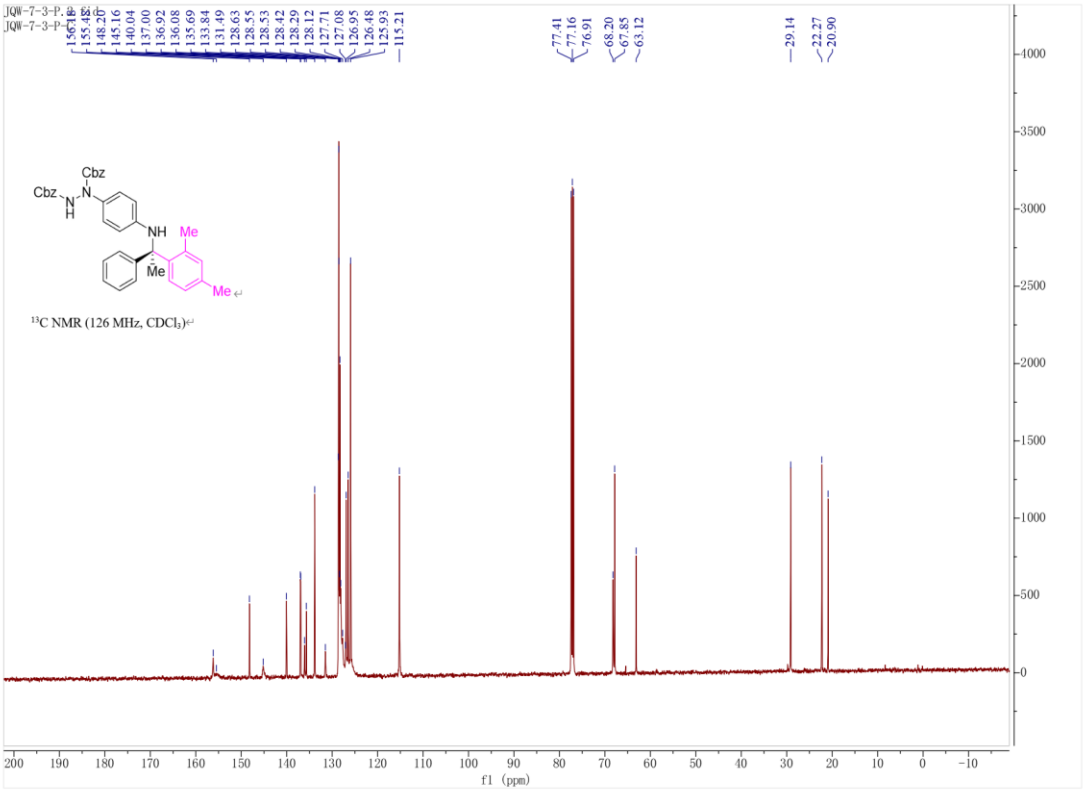




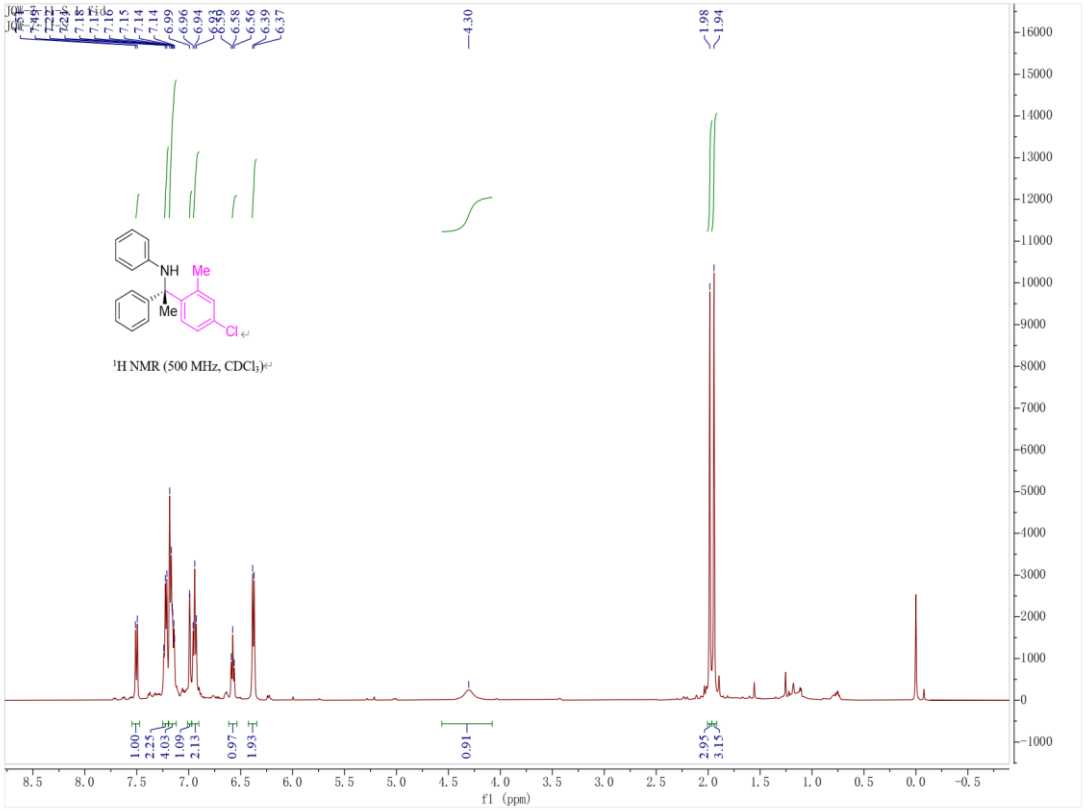
Dibenzyl-(*R*)-1-(4-((1-(2,4-dimethylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-dicar

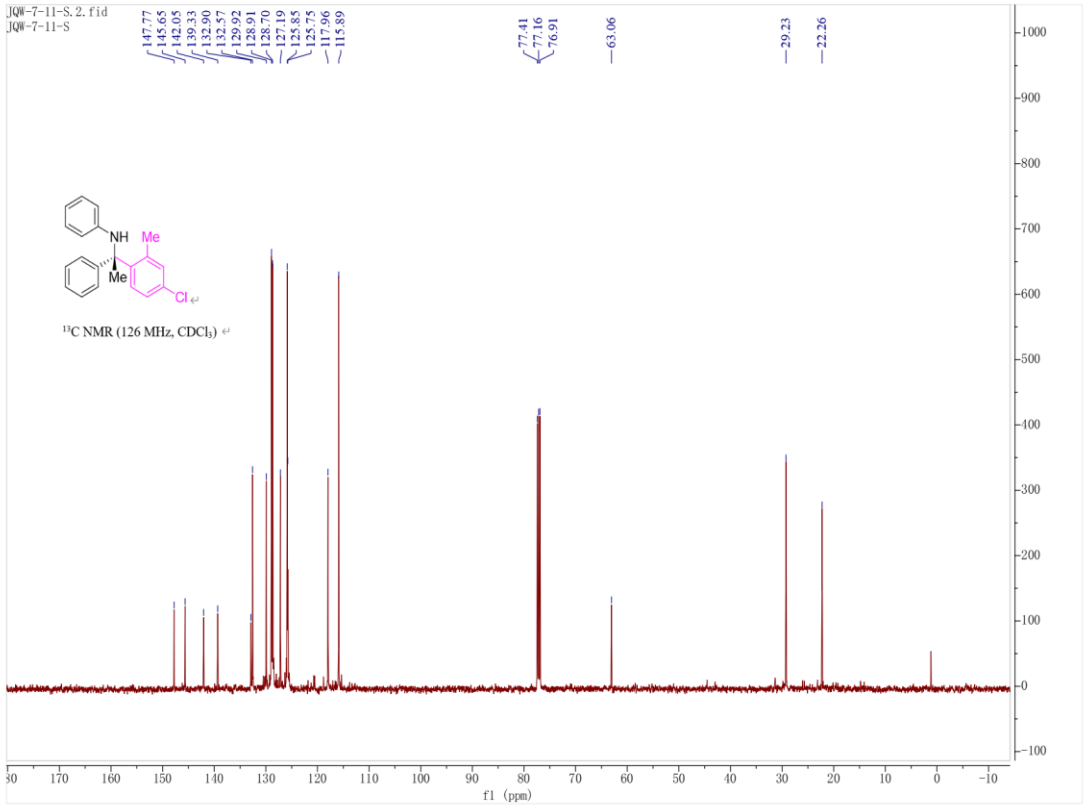
-boxylate (**3o**)



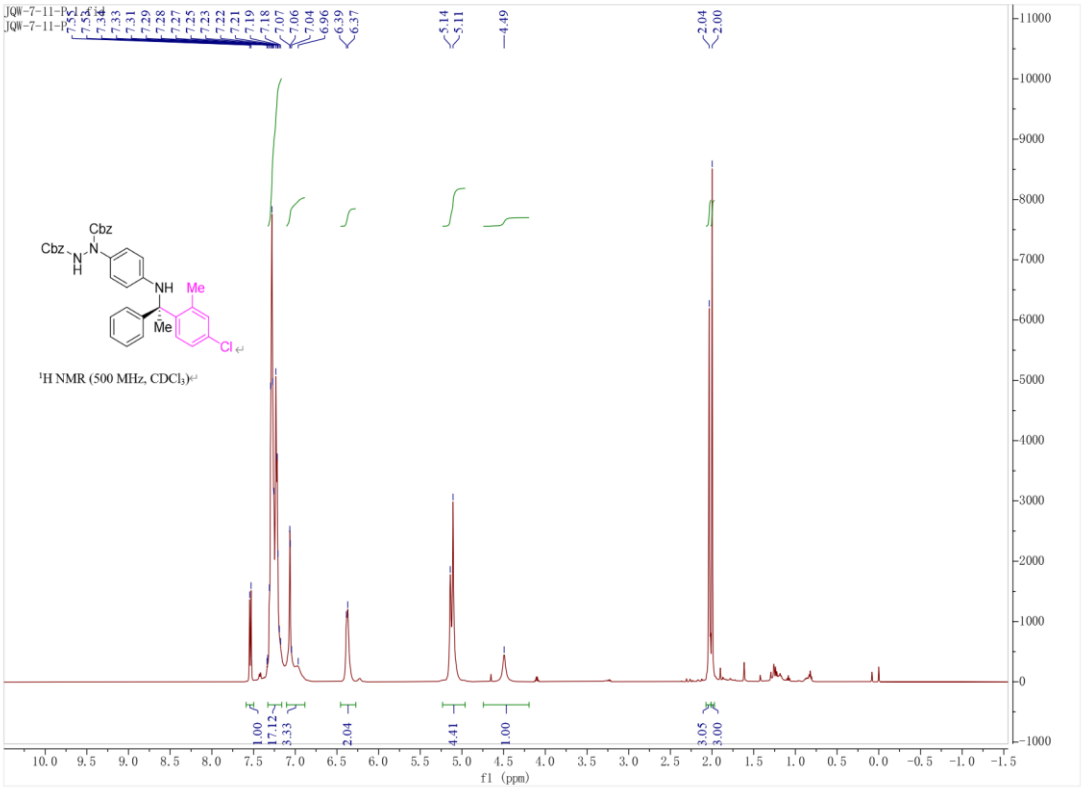


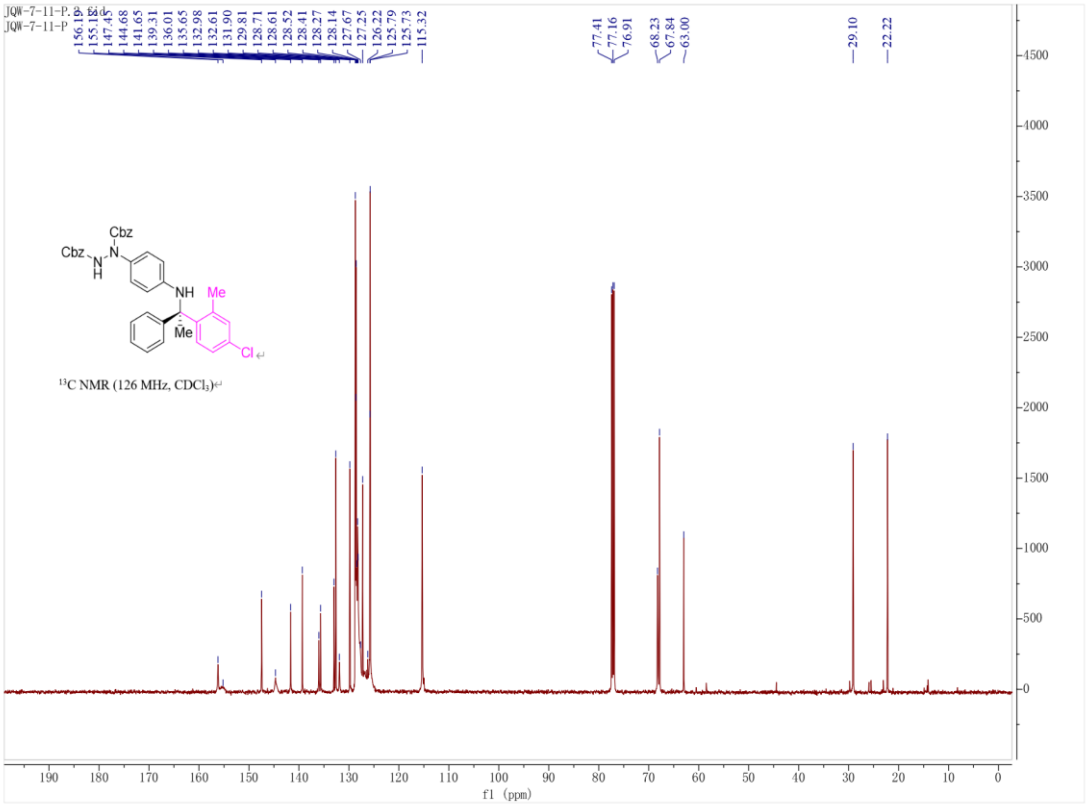
(*S*)-*N*-(1-(4-chloro-2-methylphenyl)-1-phenylethyl)aniline ((*S*)-**1p**)



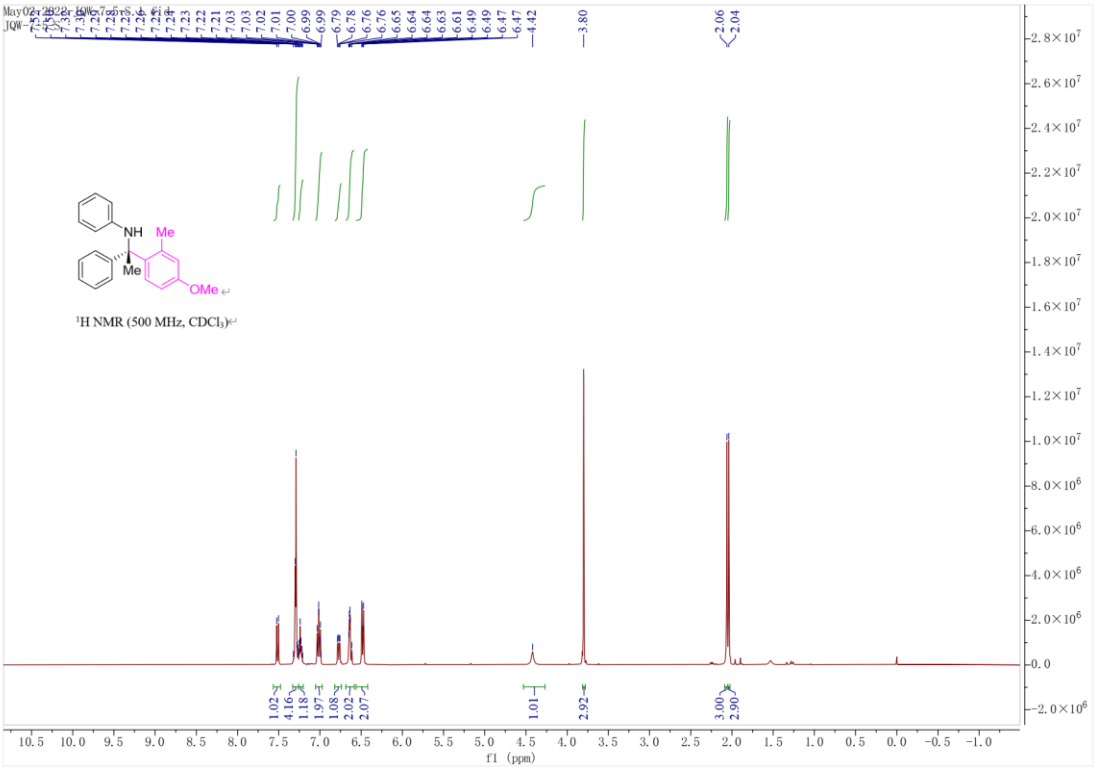


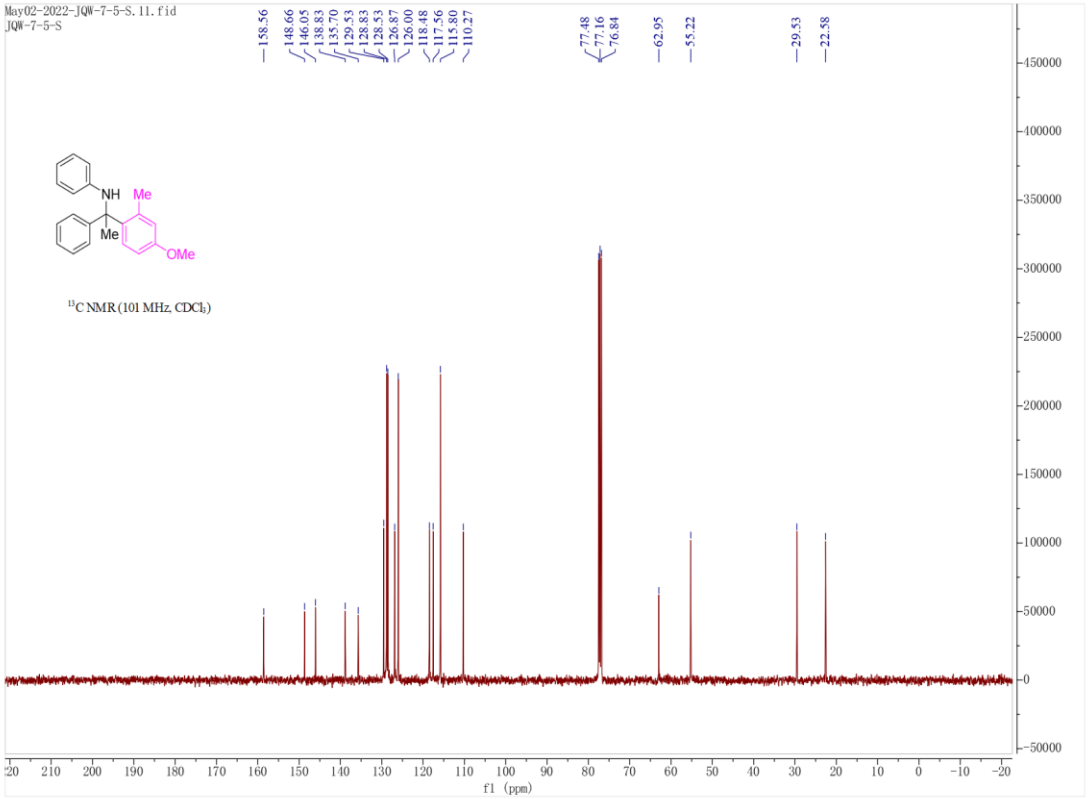
Dibenzyl-(*R*)-1-(4-((1-(4-chloro-2-methylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-di-carboxylate (**3p**)



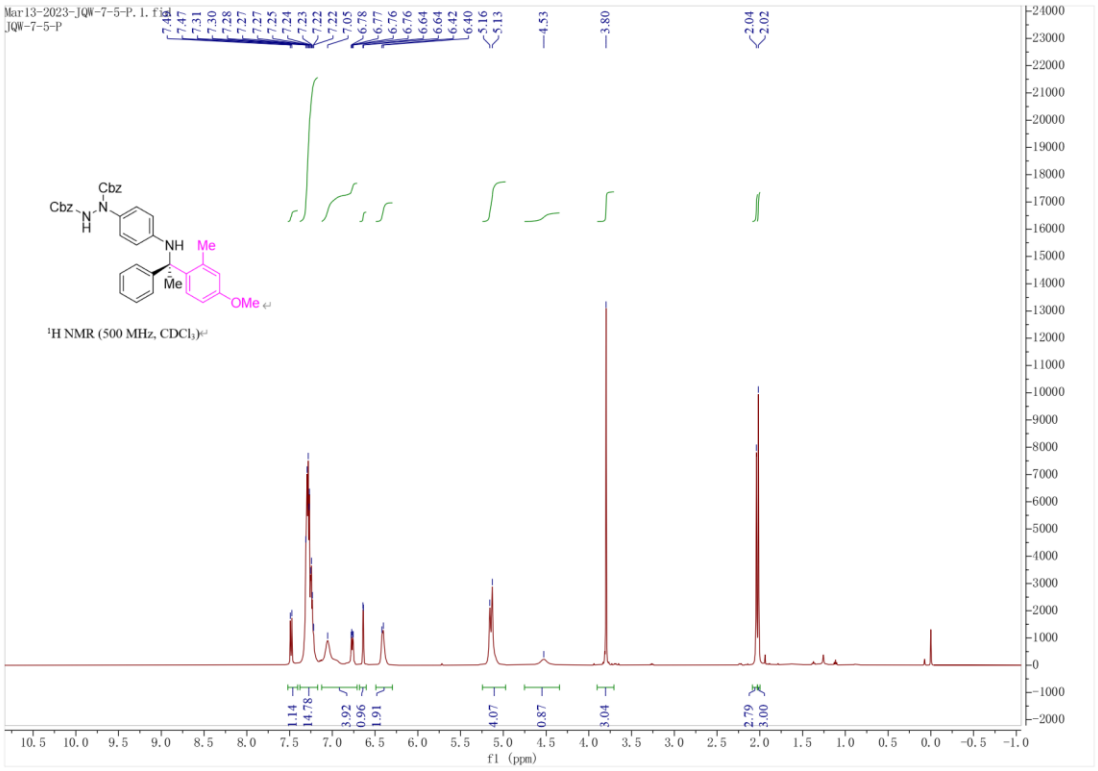


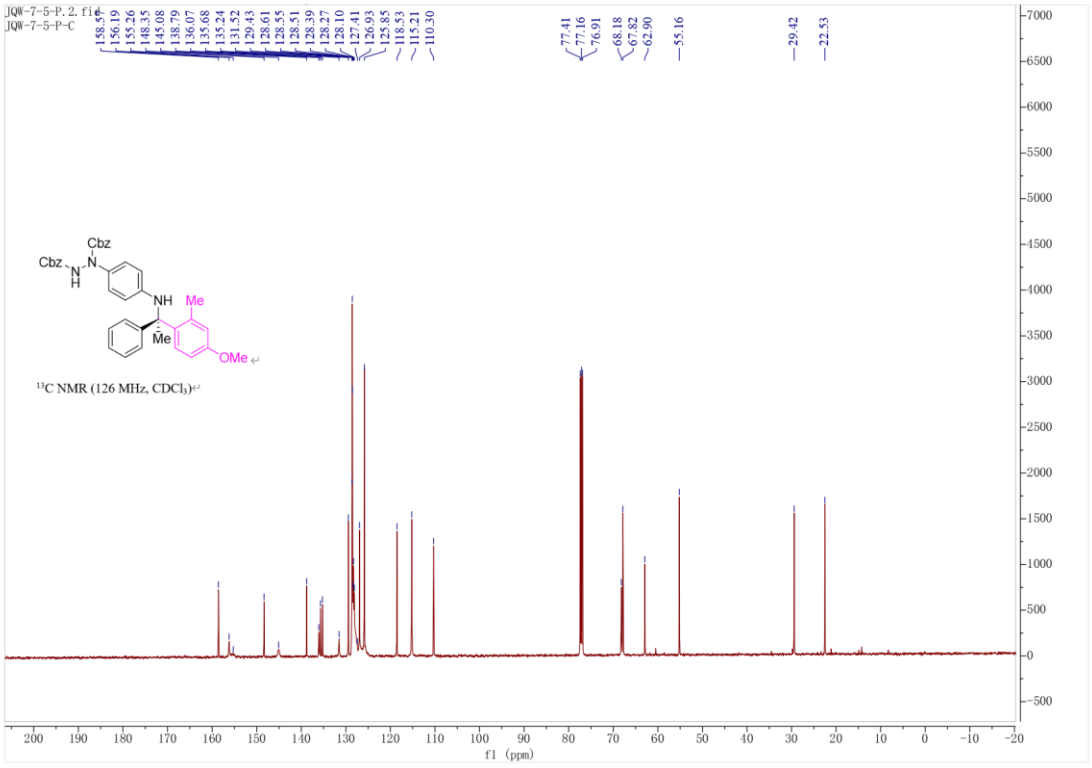
(*S*)-*N*-(1-(4-methoxy-2-methylphenyl)-1-phenylethyl)aniline ((*S*)-**1q**)



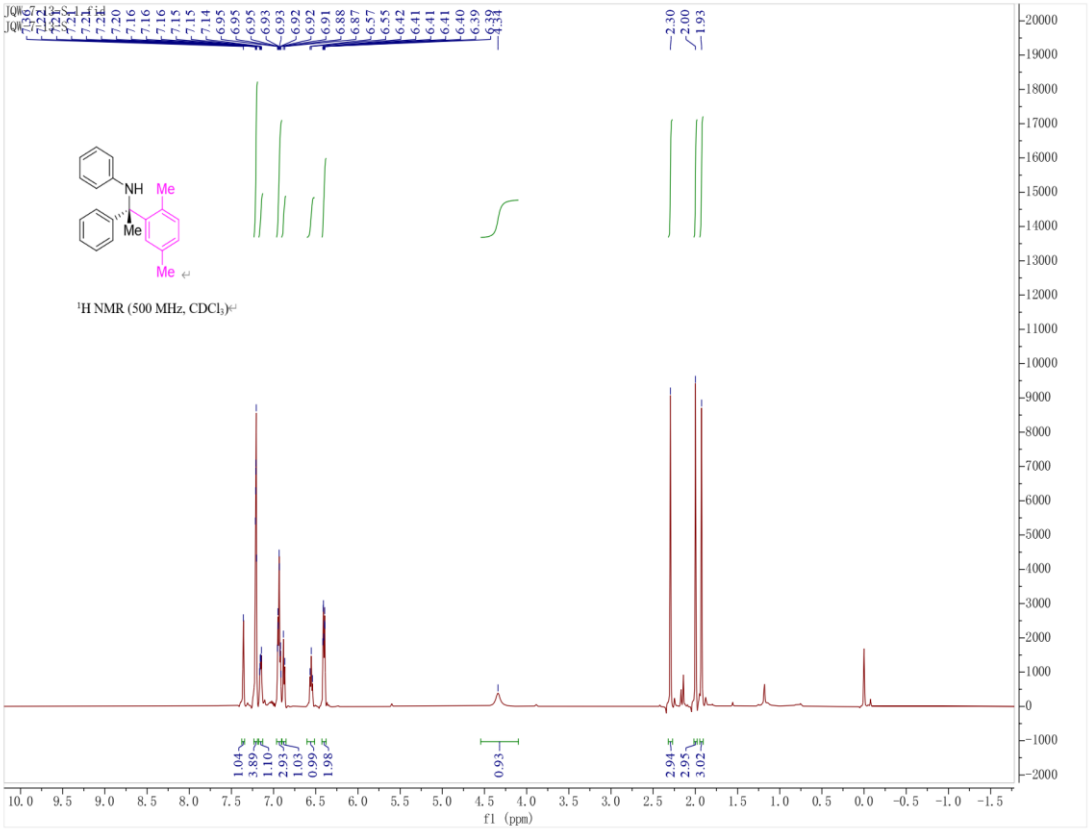


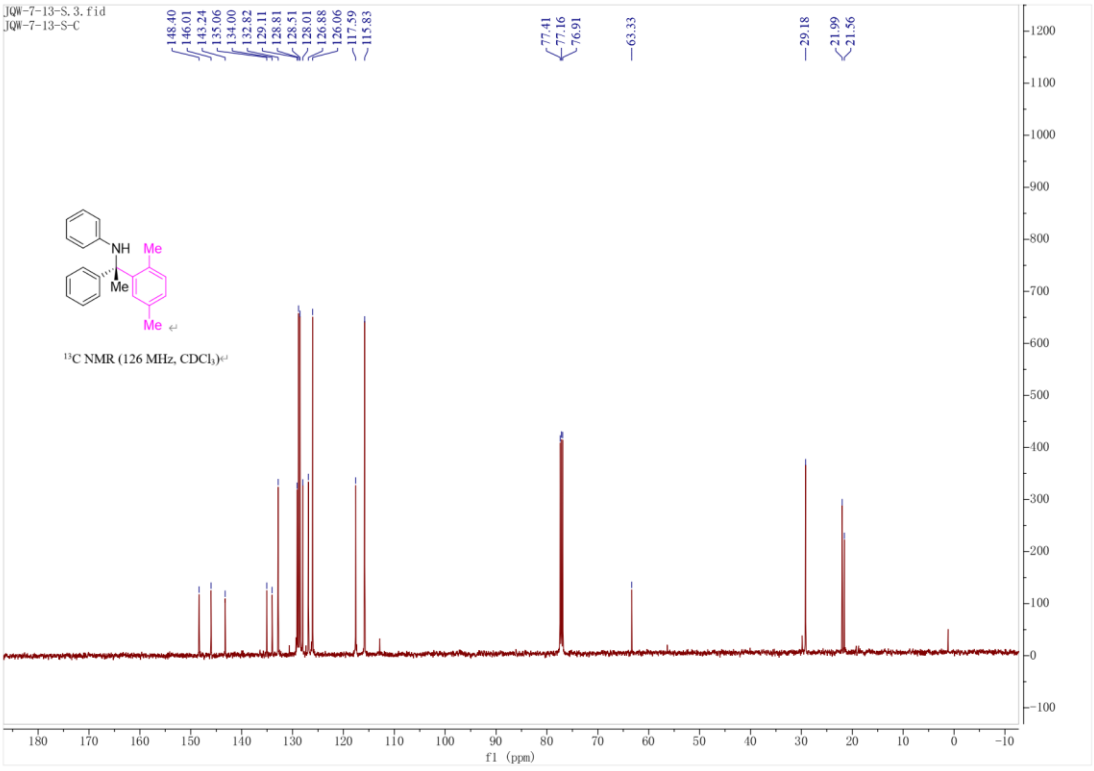
Dibenzyl(*R*)-1-(4-((1-(4-methoxy-2-methylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1, 2-di-carboxylate (**3q**)





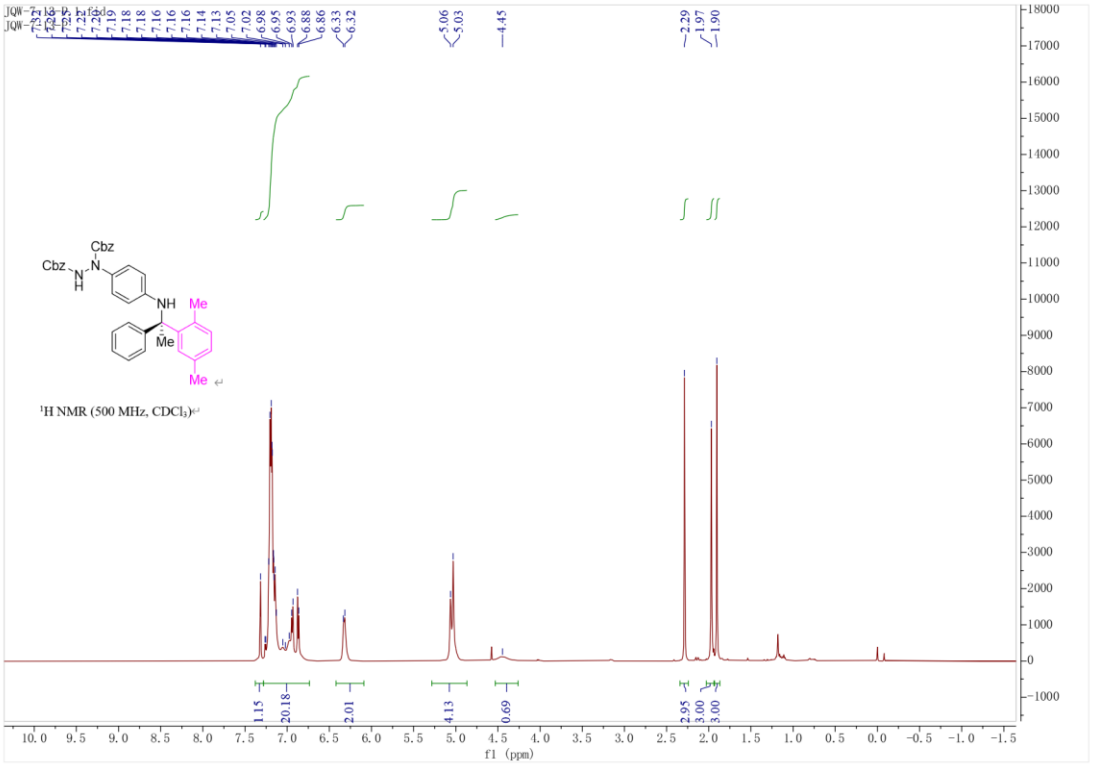
(*S*)-*N*-(1-(2,5-dimethylphenyl)-1-phenylethyl)aniline ((*S*)-**1r**)

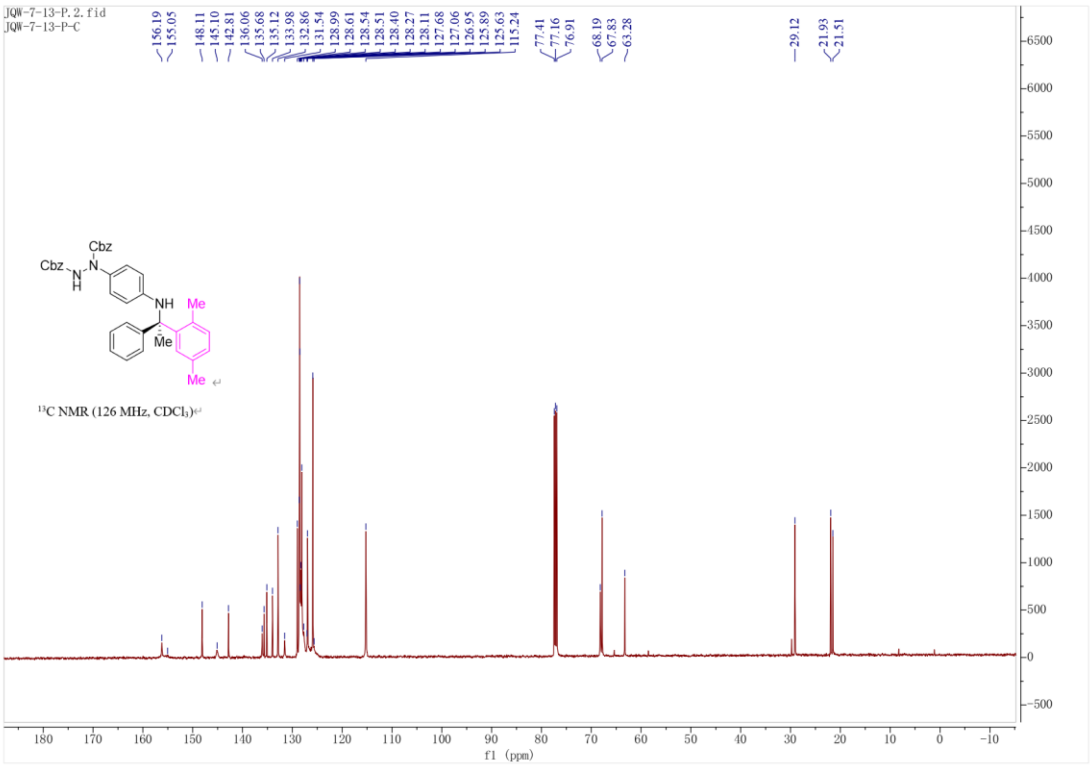




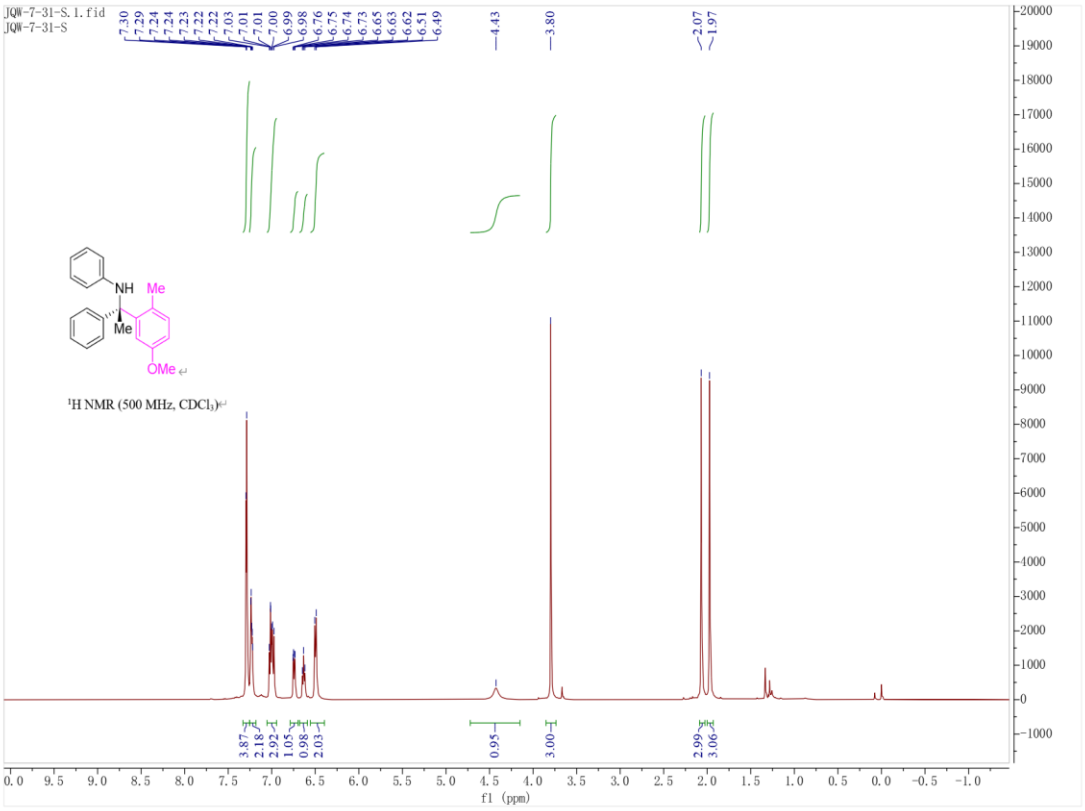
Dibenzyl-(*R*)-1-(4-((1-(2,5-dimethylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-dicar

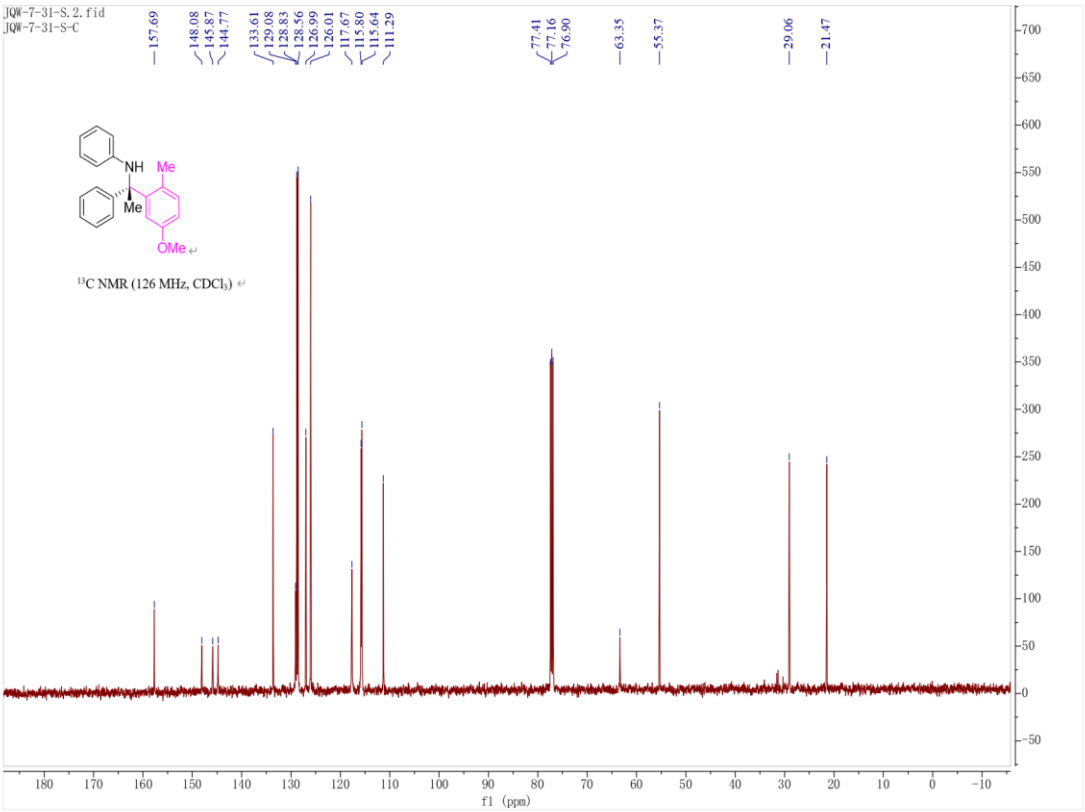
-boxylate (**3r**)



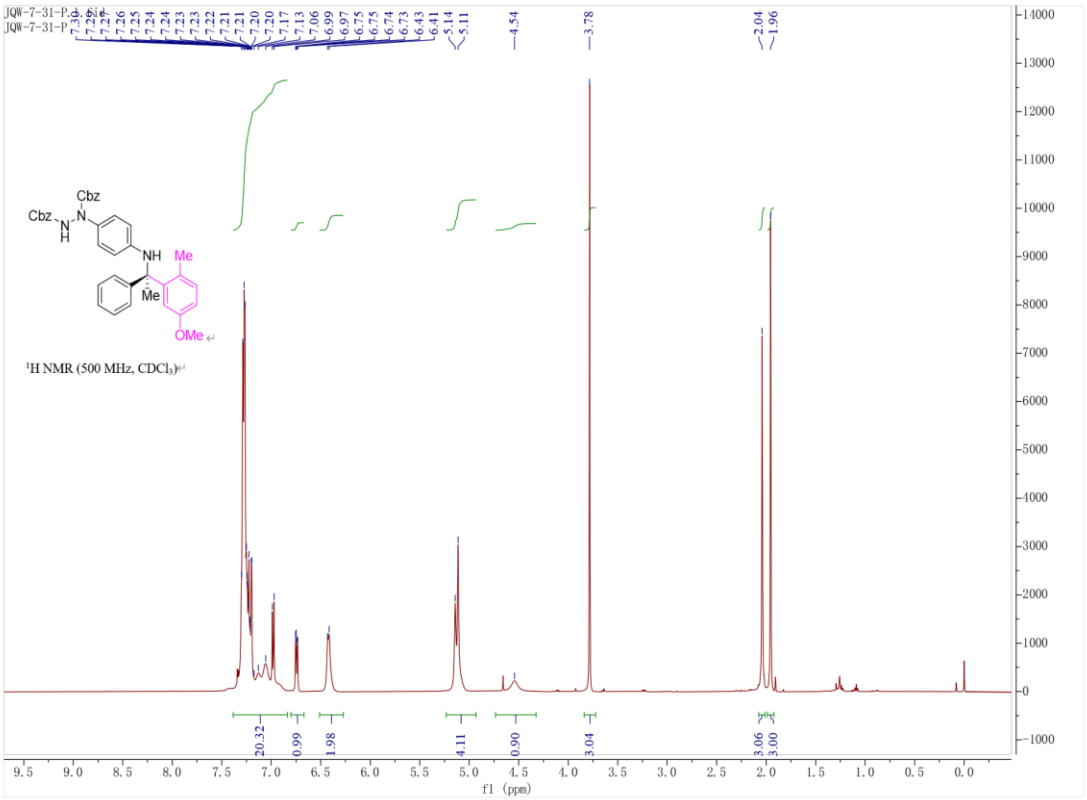


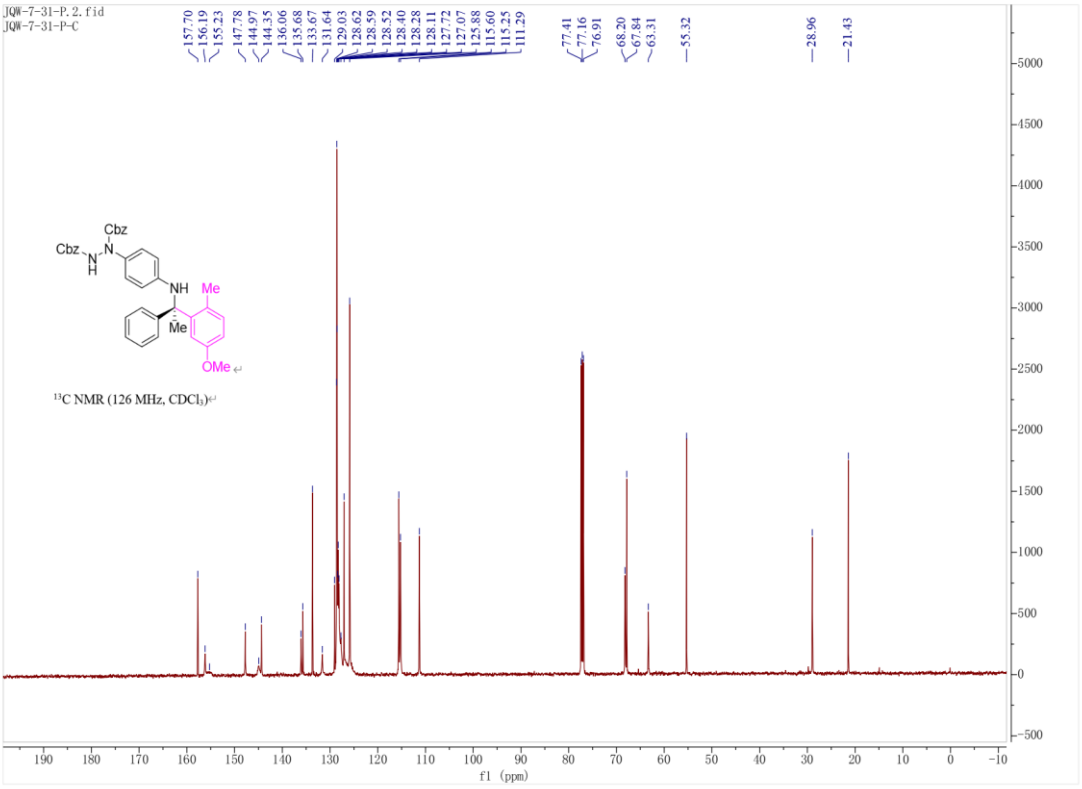
(*S*)-*N*-(1-(5-methoxy-2-methylphenyl)-1-phenylethyl)aniline ((*S*)-**1s**)



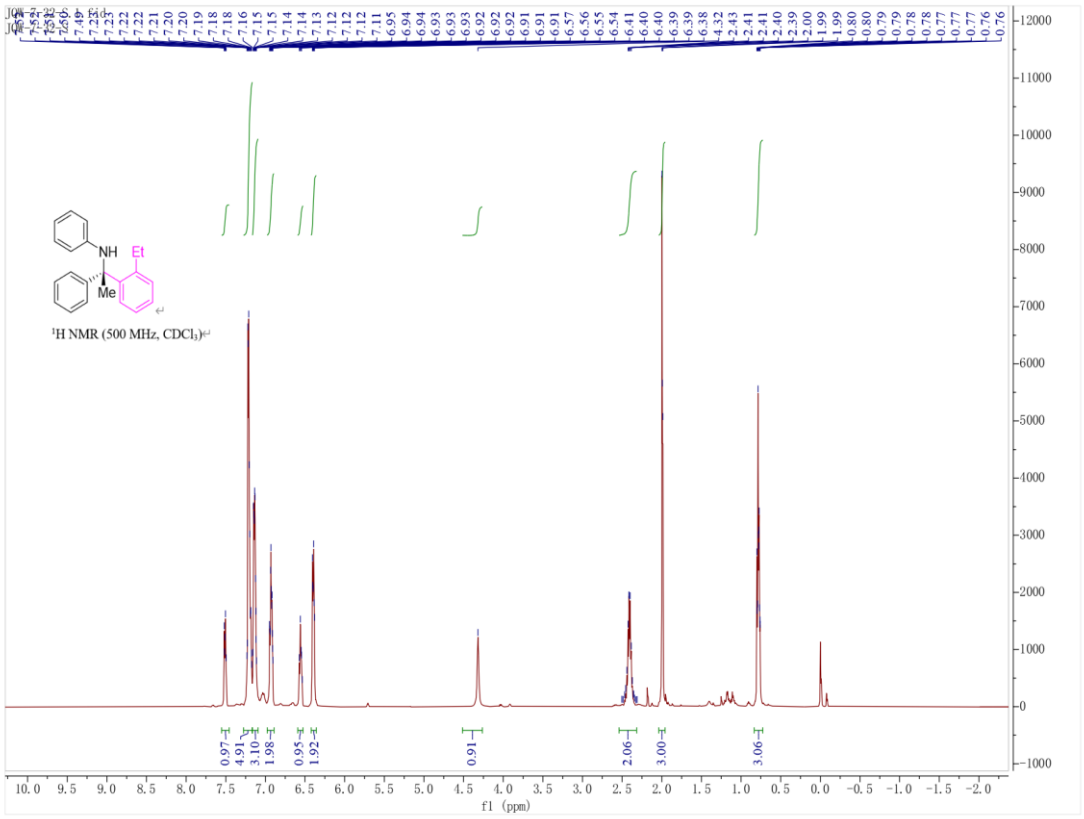


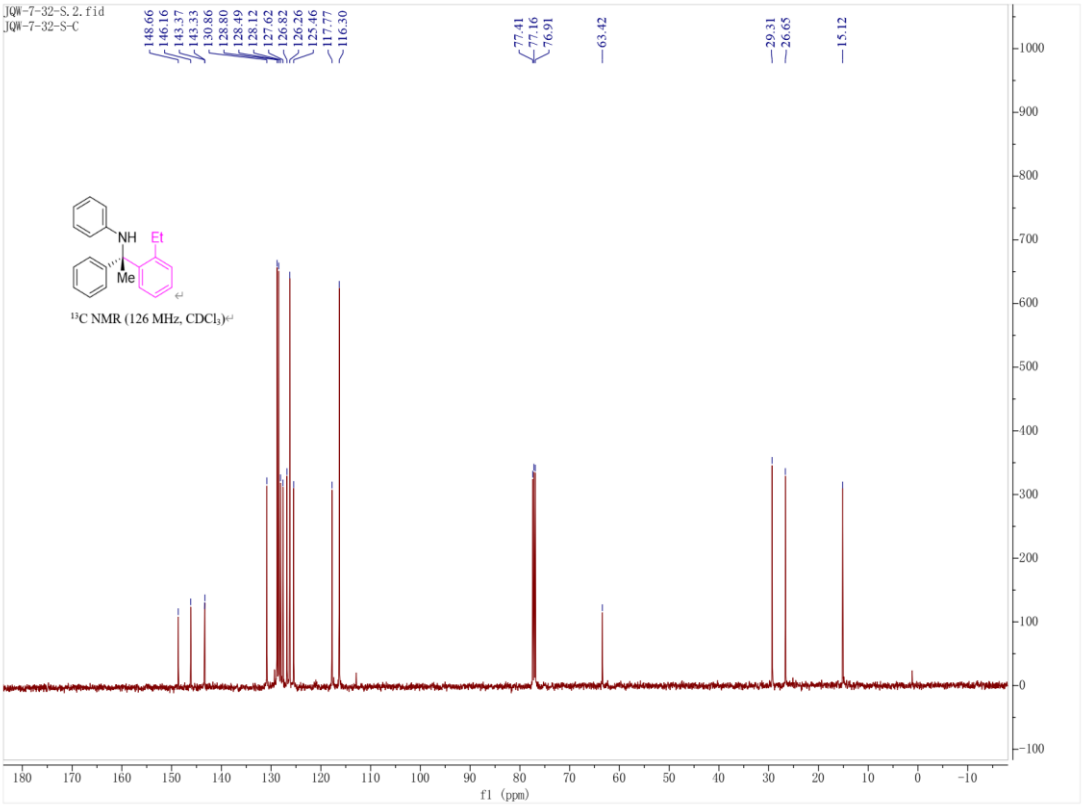
Dibenzyl(*R*)-1-(4-((1-(5-methoxy-2-methylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1, 2-di-carboxylate (**3s**)



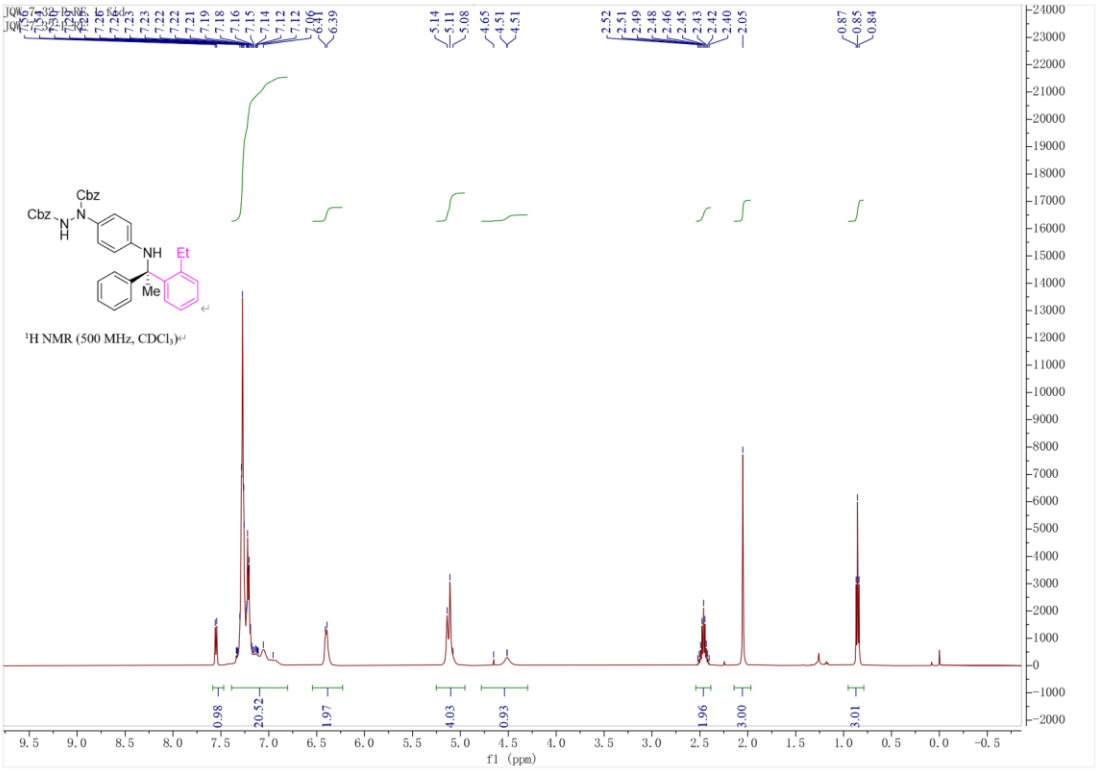


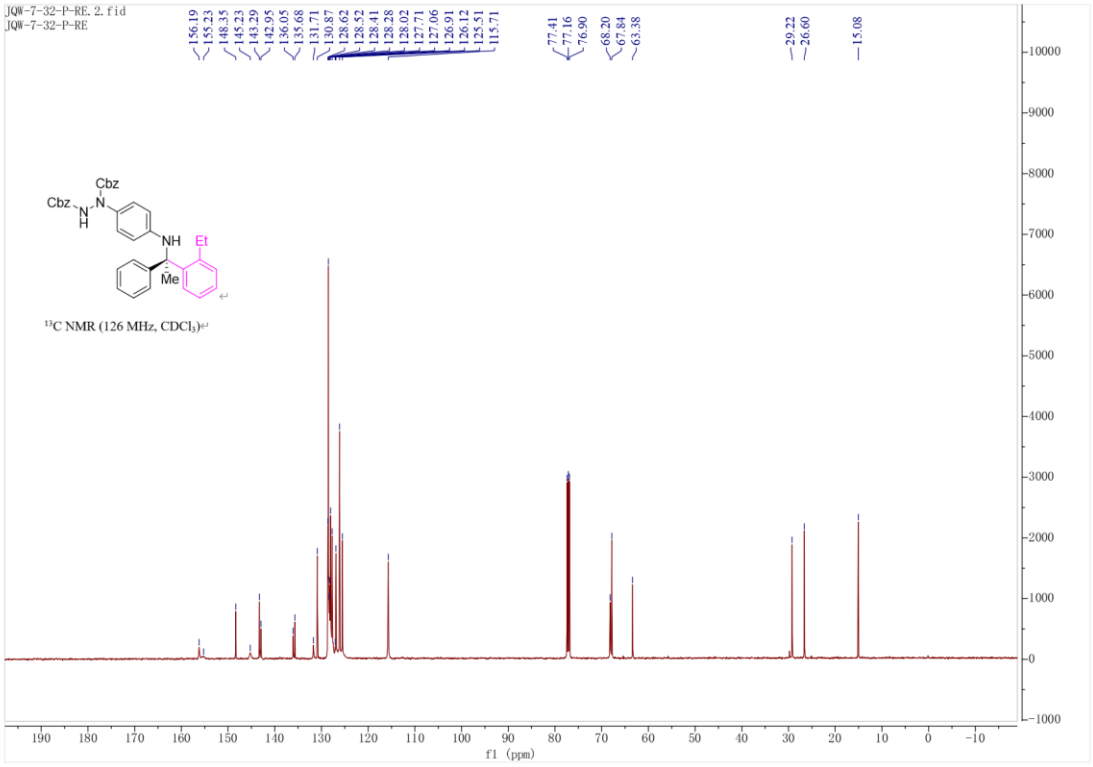
(*S*)-*N*-(1-(2-ethylphenyl)-1-phenylethyl)aniline ((*S*)-**1t**)



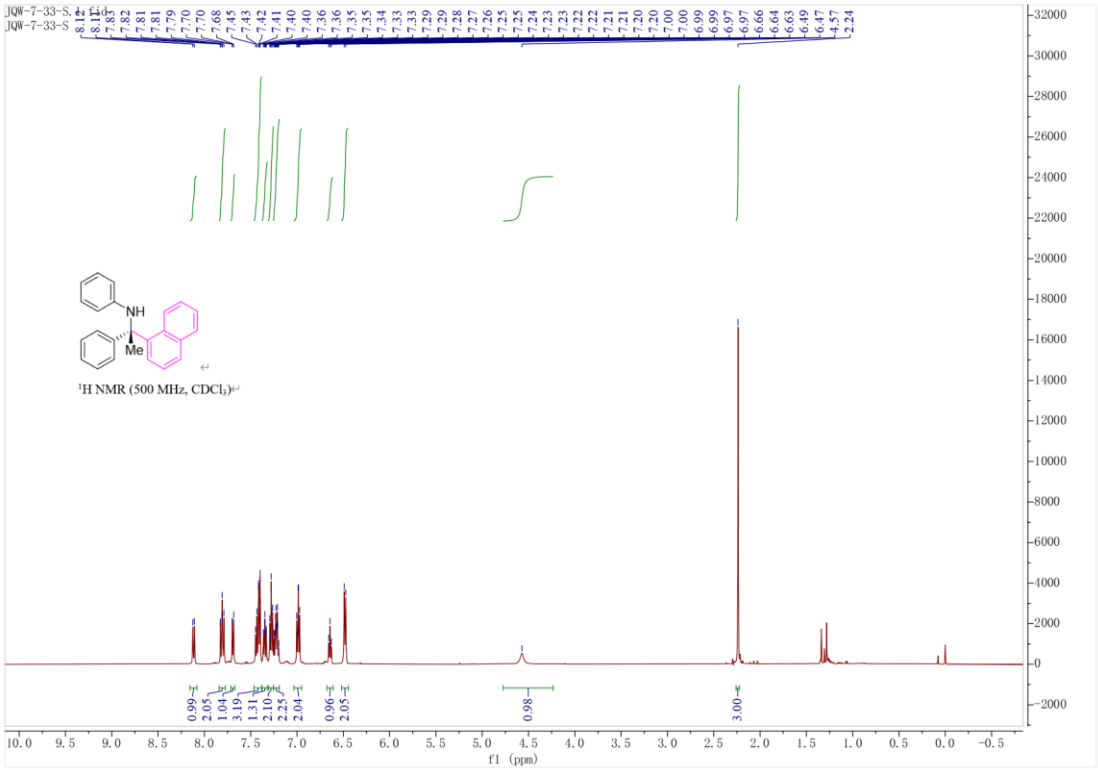


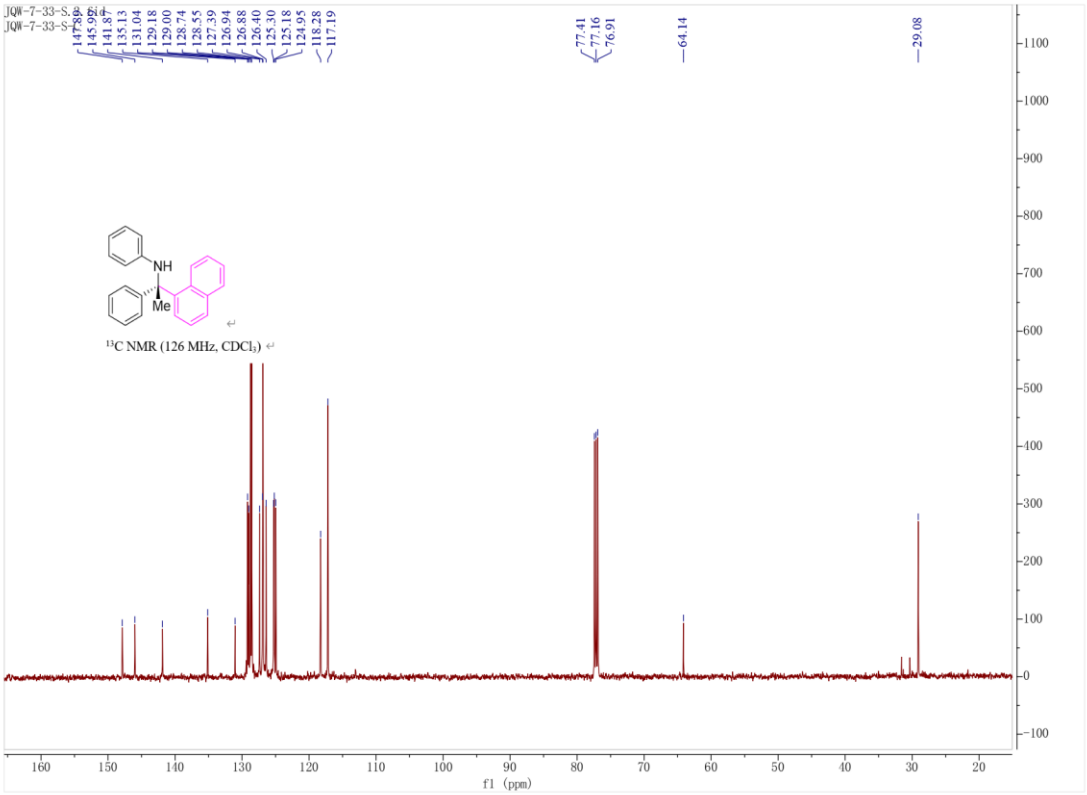
Dibenzyl-(*R*)-1-(4-((1-(2-ethylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3t**)



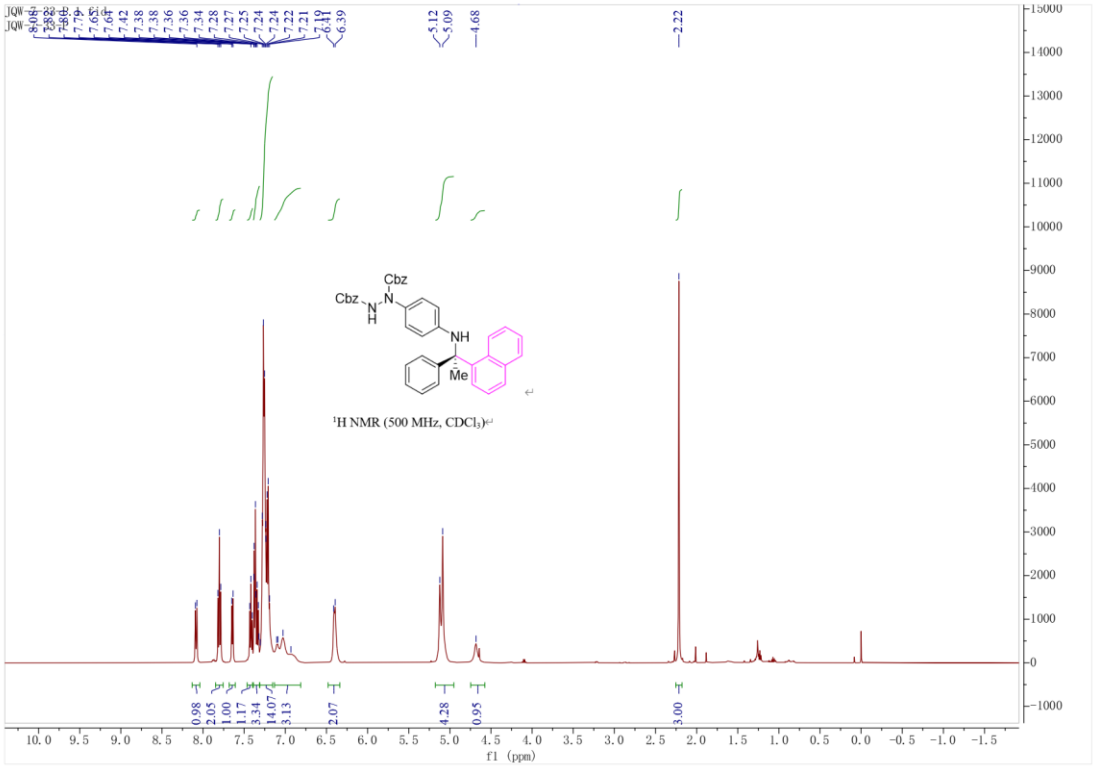


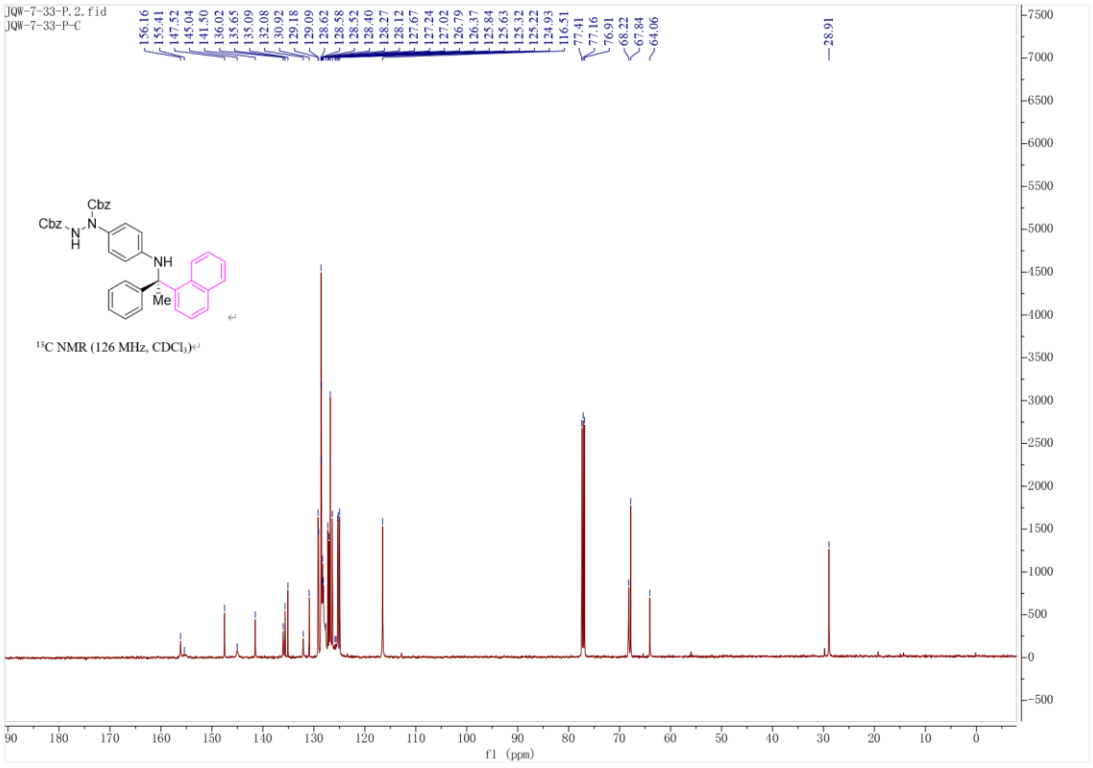
(*S*)-*N*-(1-(naphthalen-1-yl)-1-phenylethyl)aniline ((*S*)-**1u**)



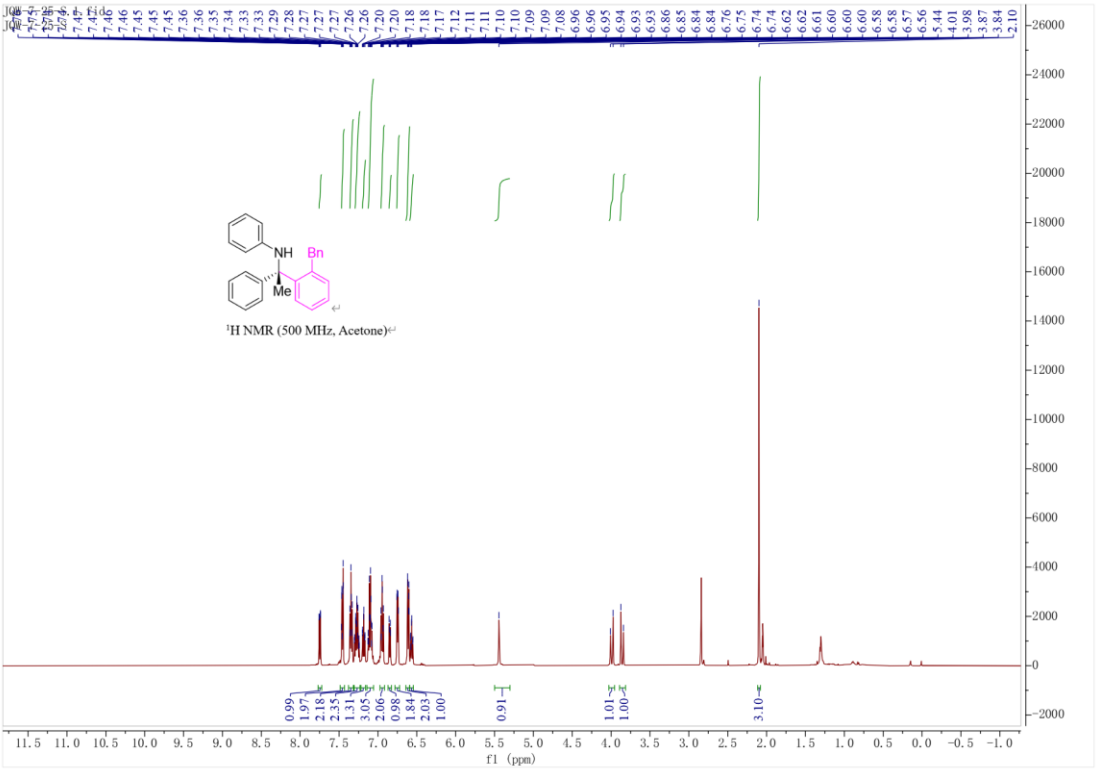


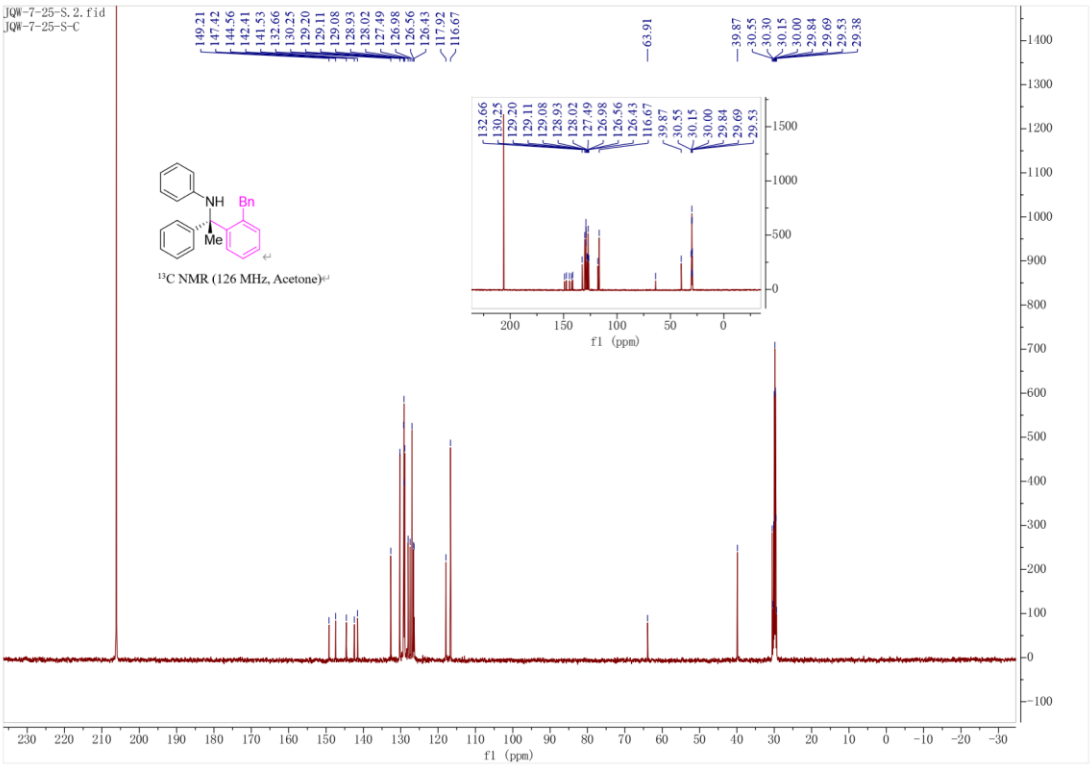
Dibenzyl-(*R*)-1-(4-((1-(naphthalen-1-yl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3u**)



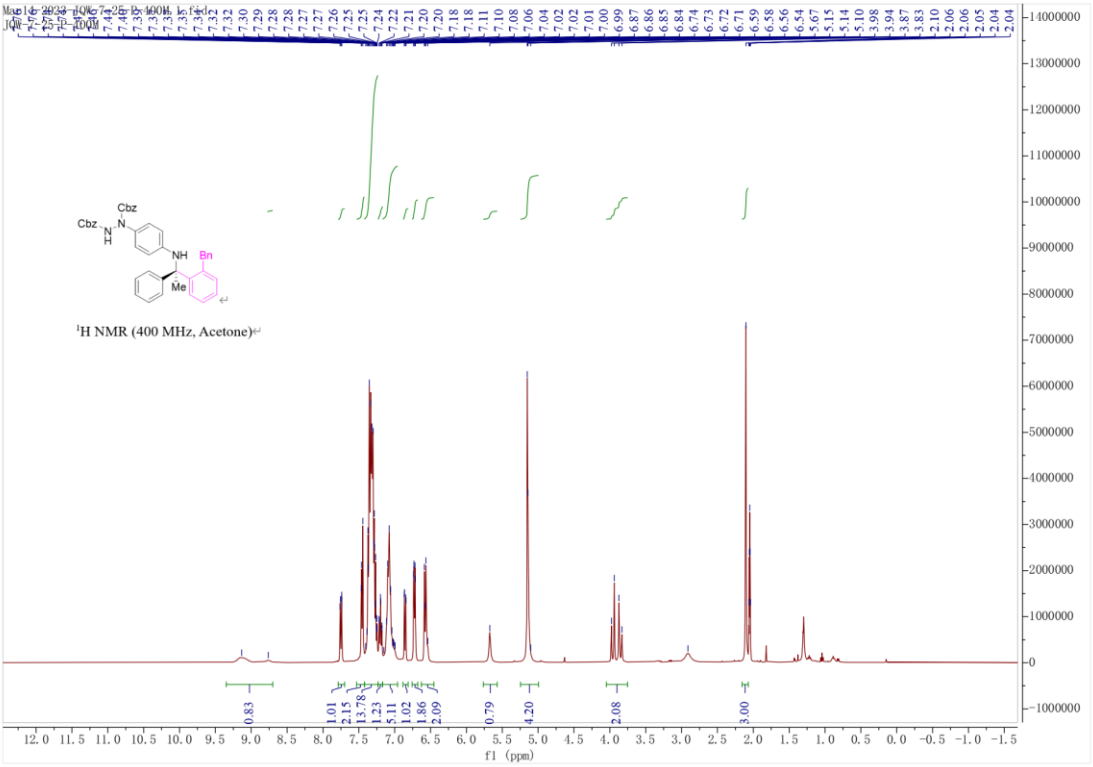


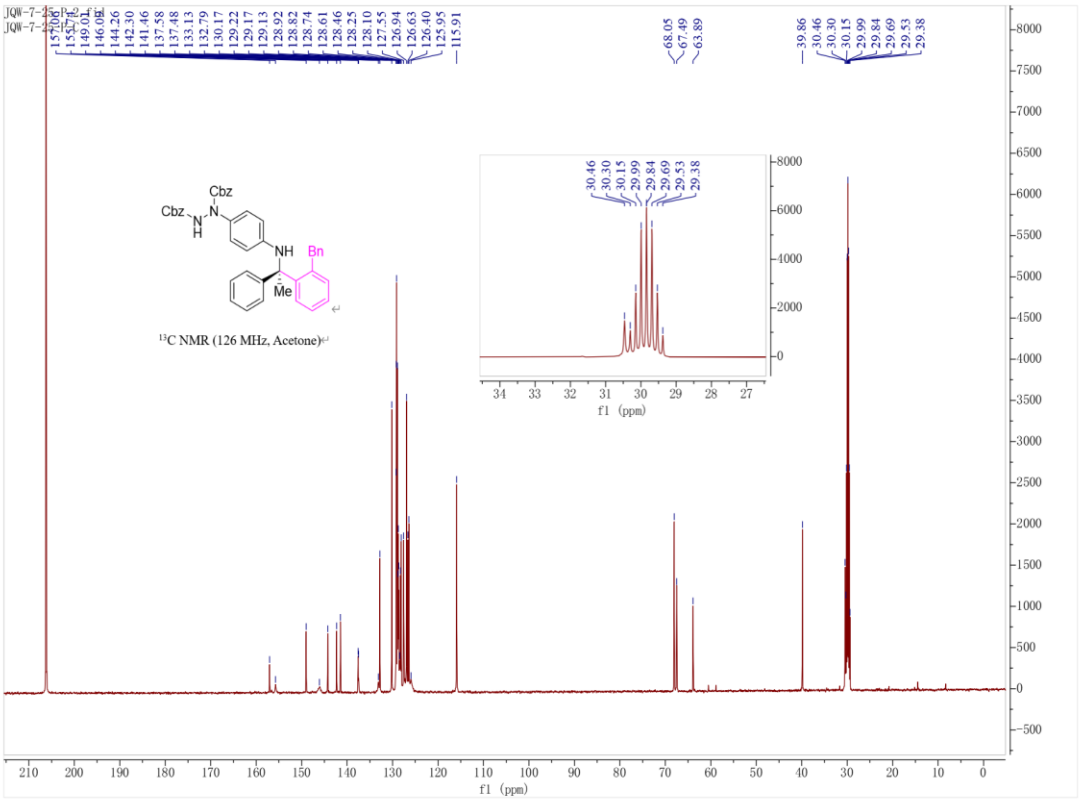
(*S*)-*N*-(1-(2-benzylphenyl)-1-phenylethyl)aniline ((*S*)-**1v**)



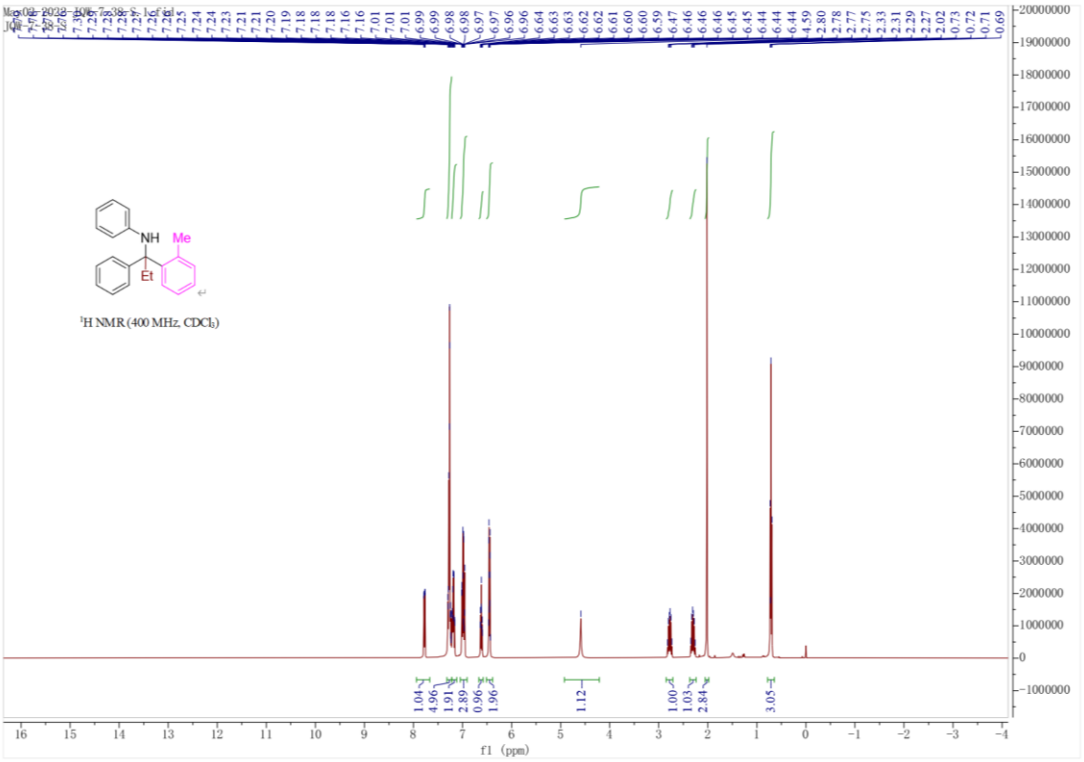


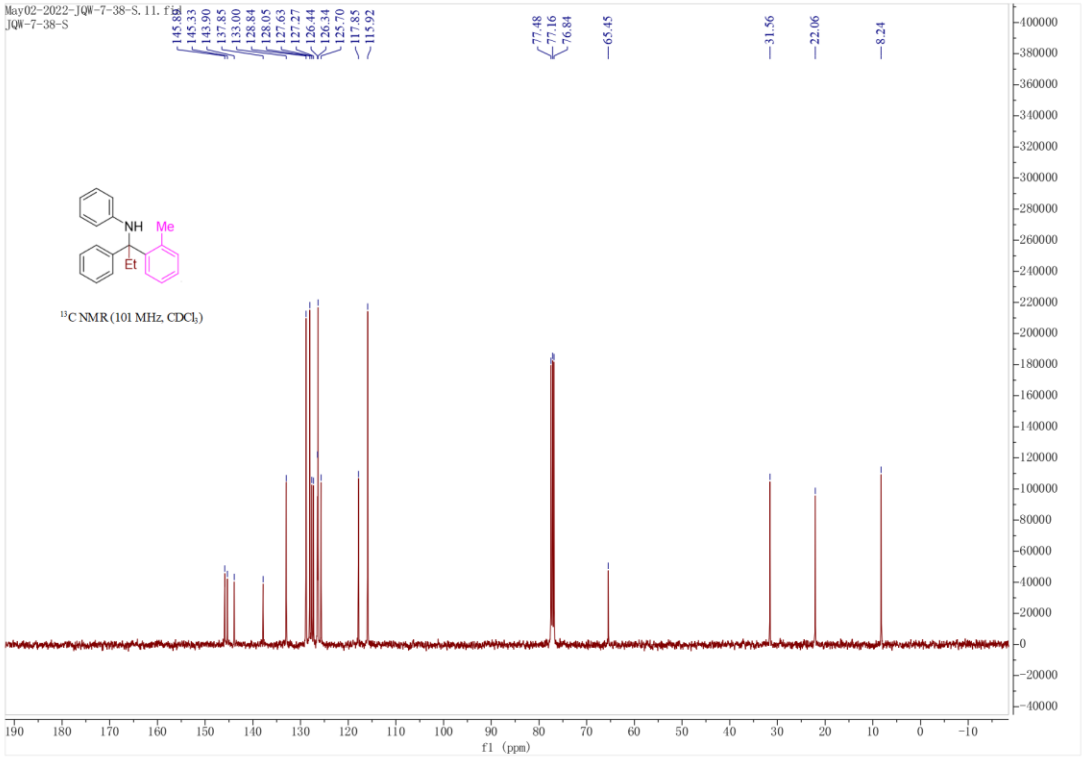
Dibenzyl-(*R*)-1-(4-((1-(2-benzylphenyl)-1-phenylethyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3v**)



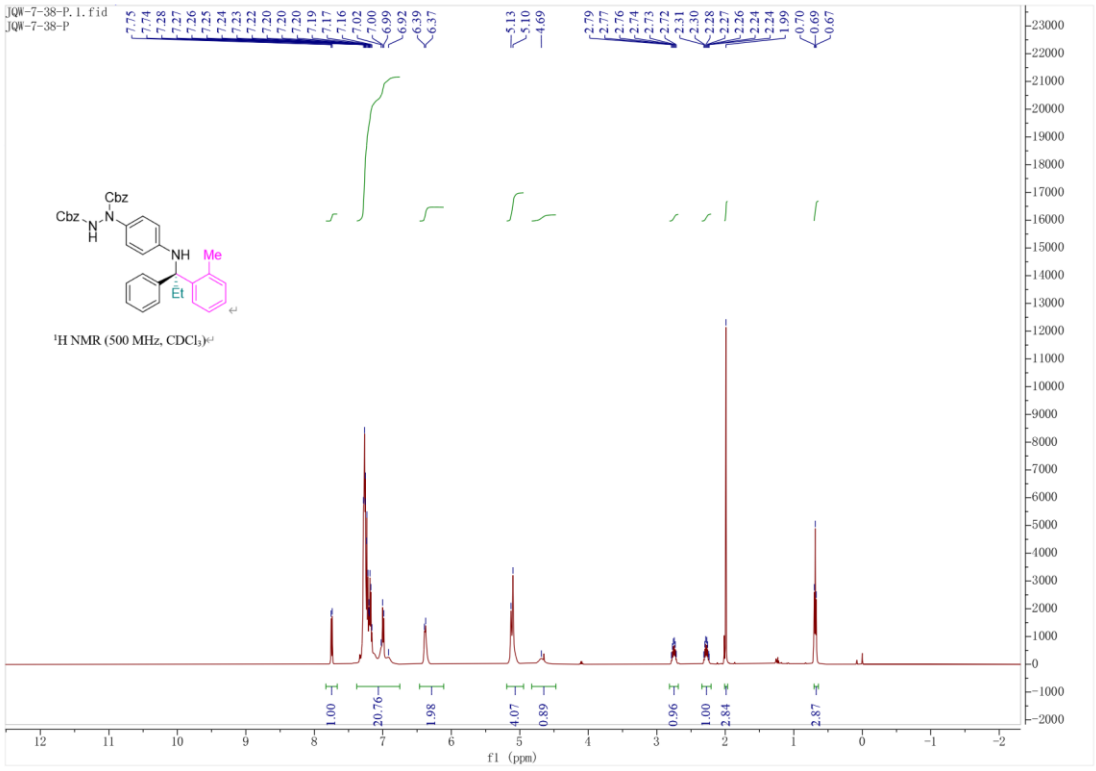


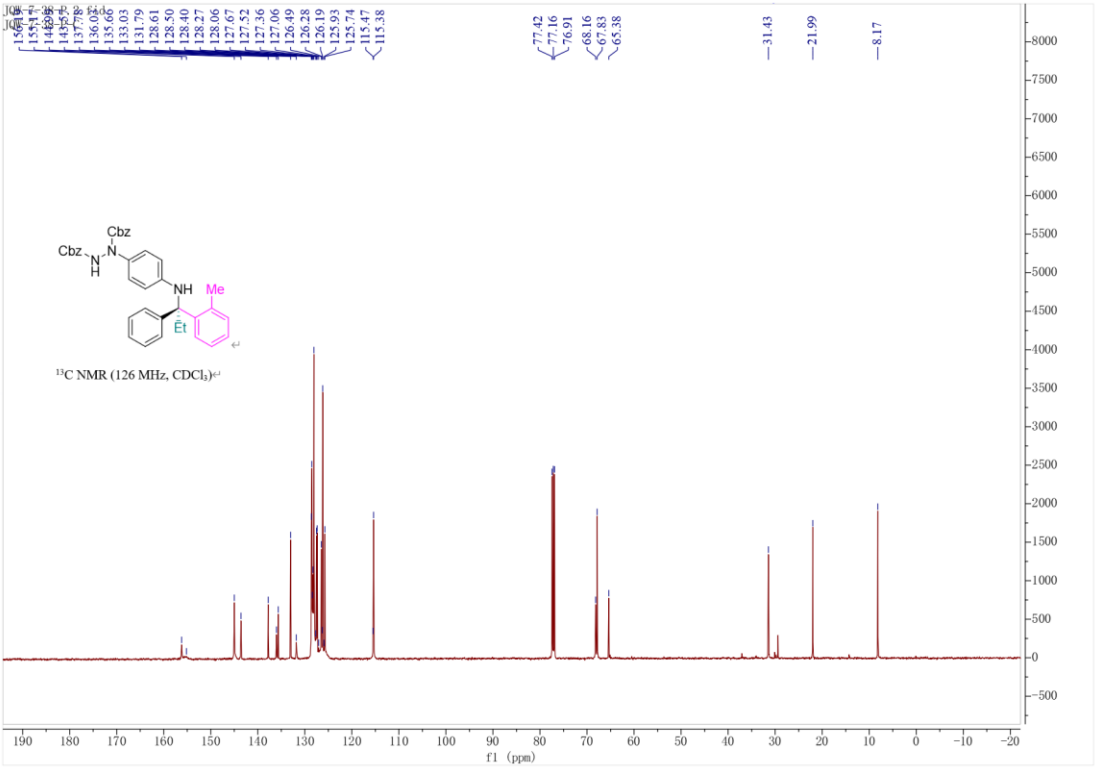
(*S*)-*N*-(1-phenyl-1-(*o*-tolyl)propyl)aniline ((*S*)-**1w**)



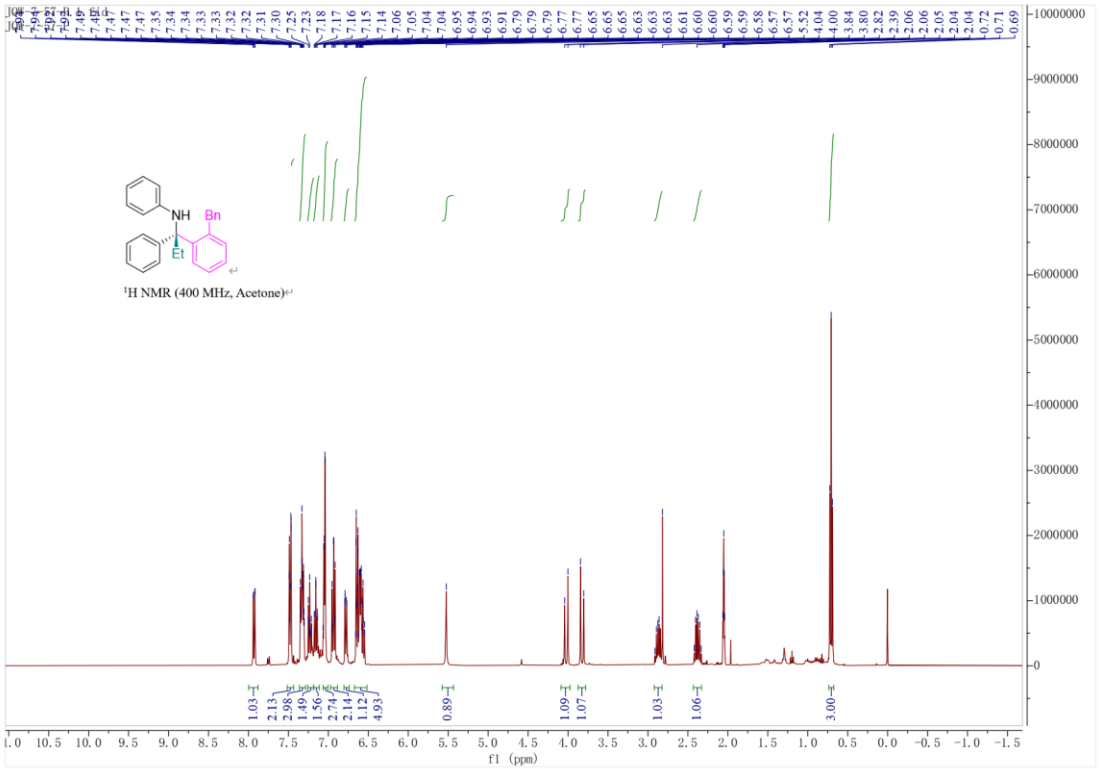


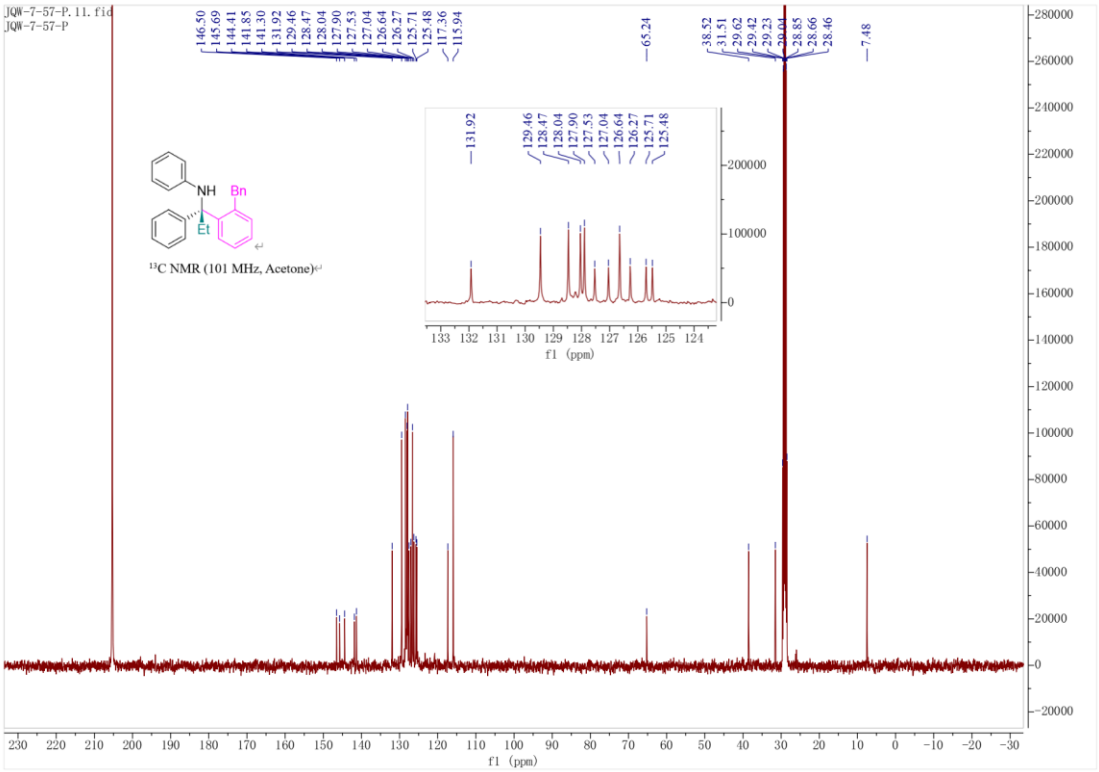
Dibenzyl (*R*)-1-(4-((1-phenyl-1-(*o*-tolyl)propyl)amino)phenyl)hydrazine-1,2-dicarboxylate (**3w**)



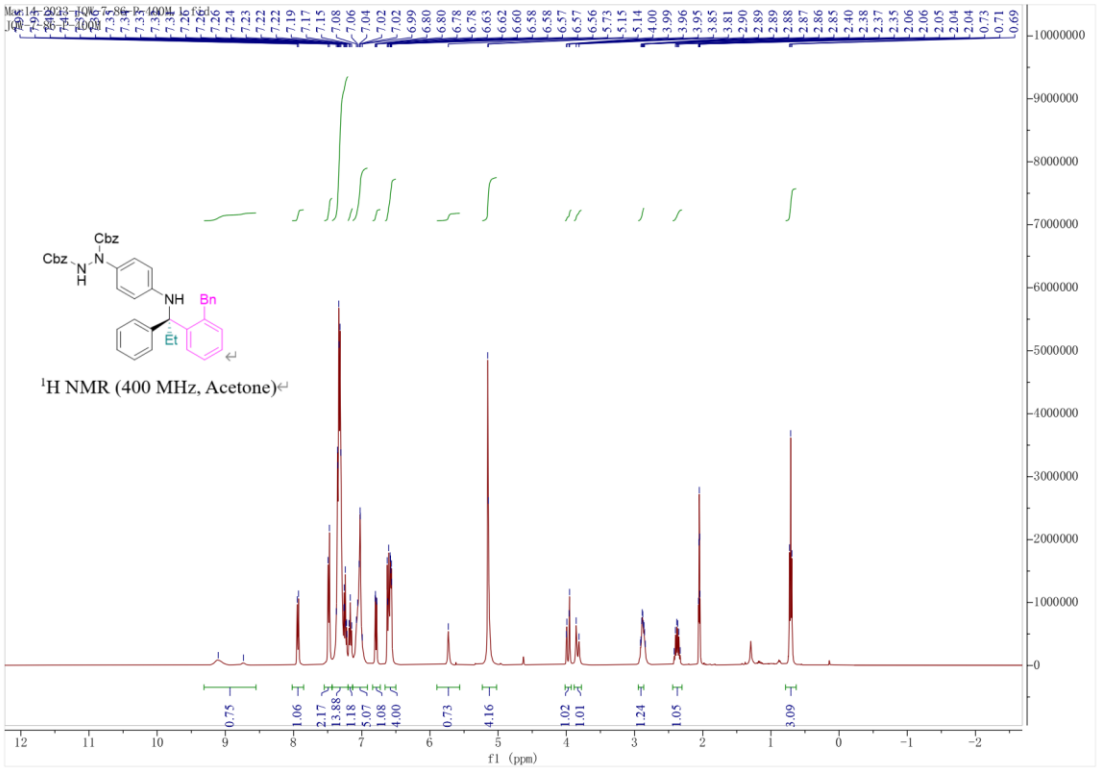


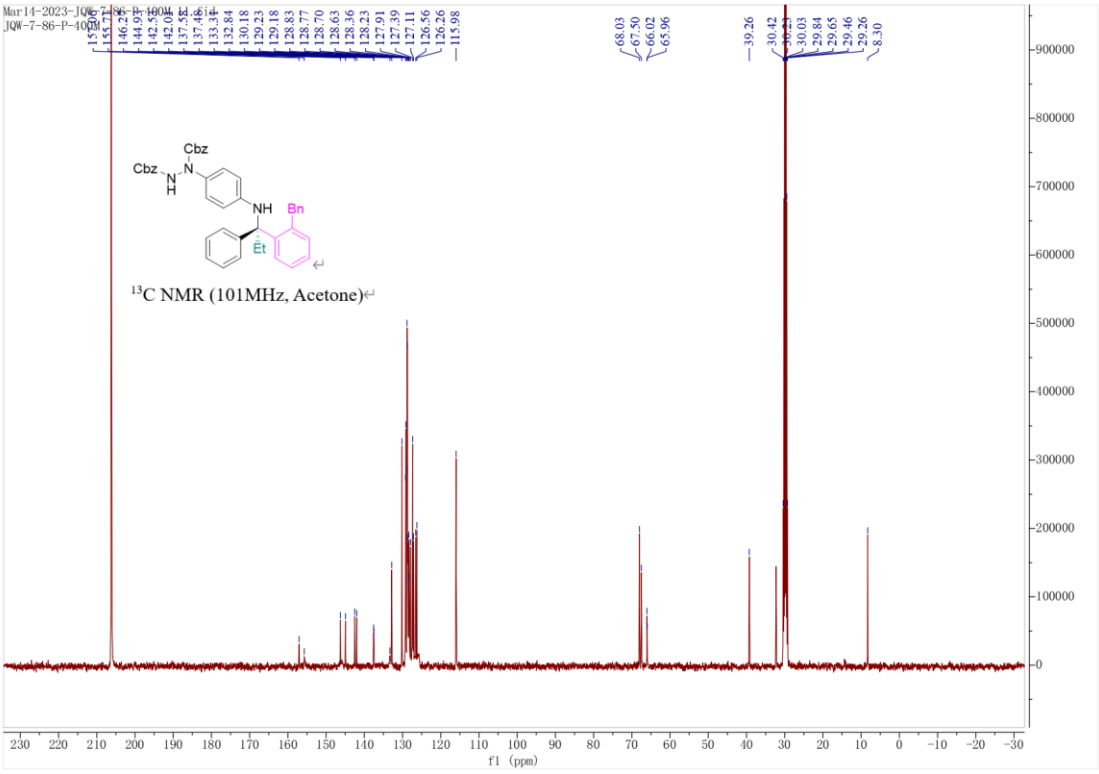
(*S*)-*N*-(1-(2-benzylphenyl)-1-phenylpropyl)aniline ((*S*)-**1x**)



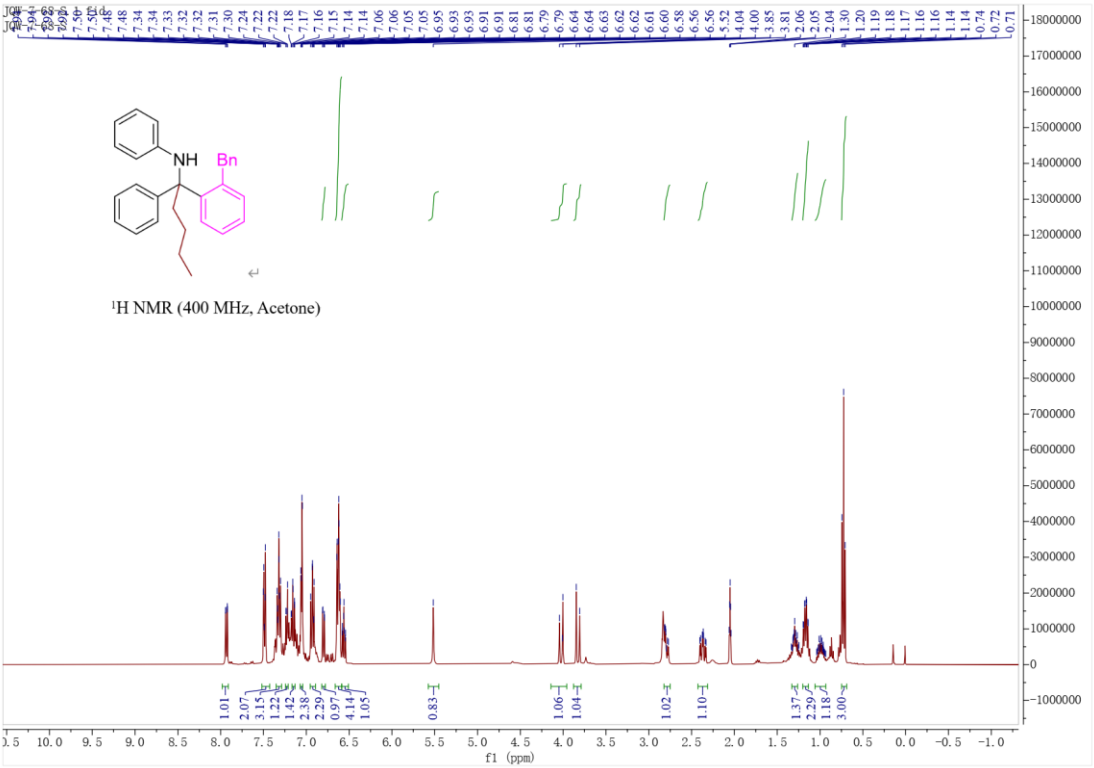


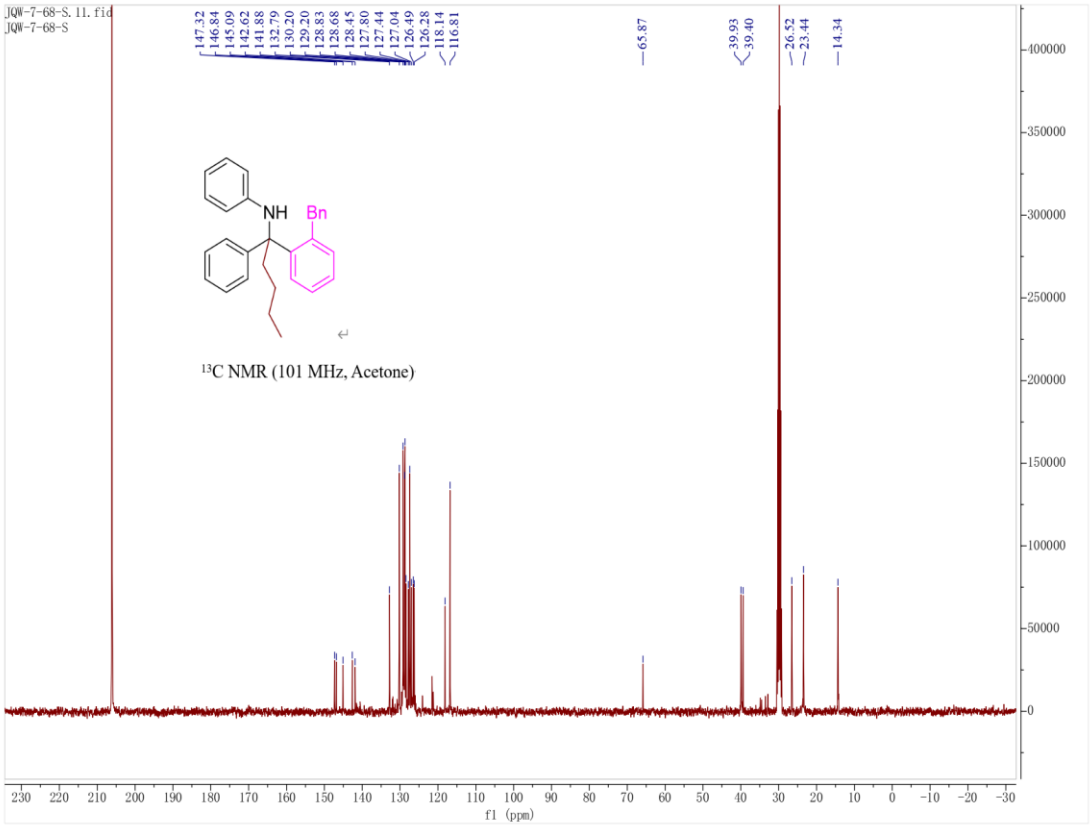
Dibenzyl-(*R*)-1-(4-((1-(2-benzylphenyl)-1-phenylpropyl)amino)phenyl)hydrazine-1,2-dicarboxyl-ate (**3x**)



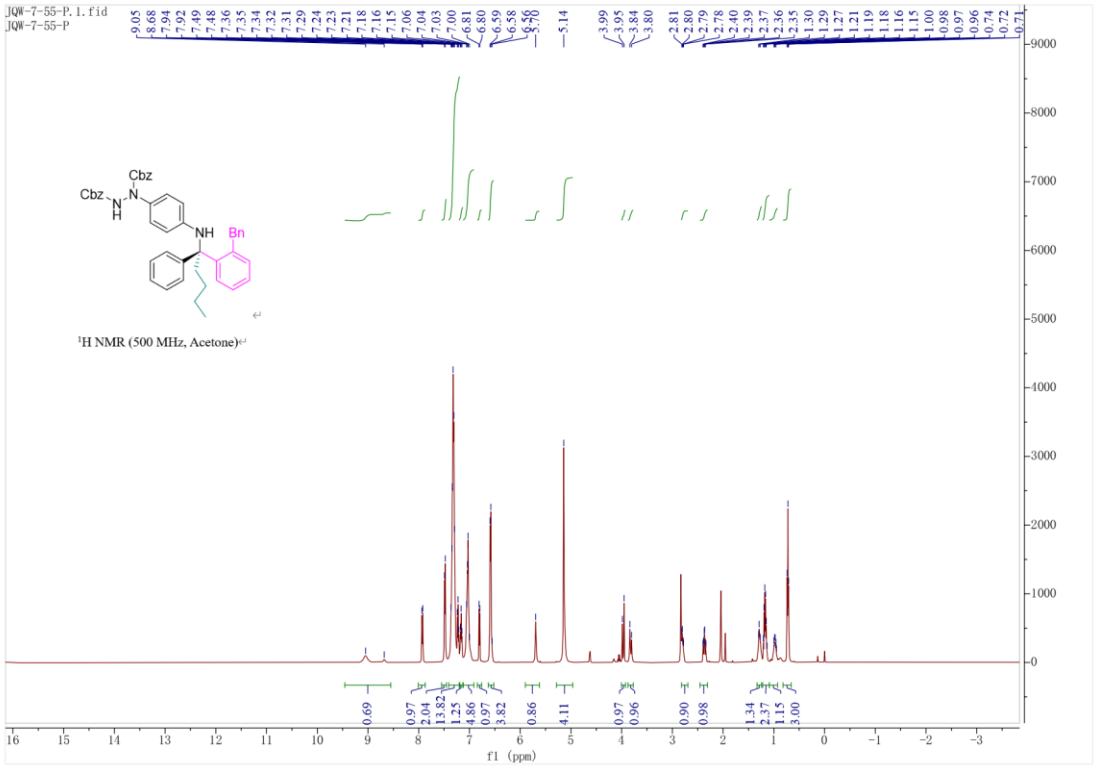


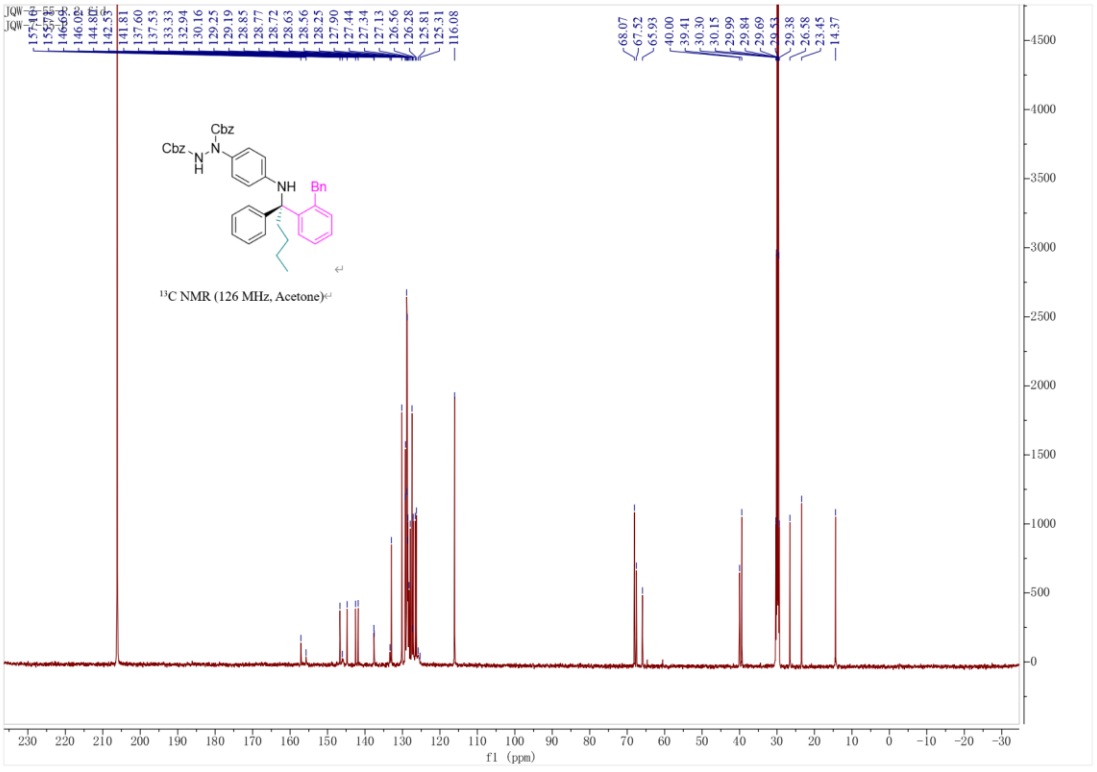
(*S*)-*N*-(1-(2-benzylphenyl)-1-phenylpentyl)aniline ((*S*)-**1y**)



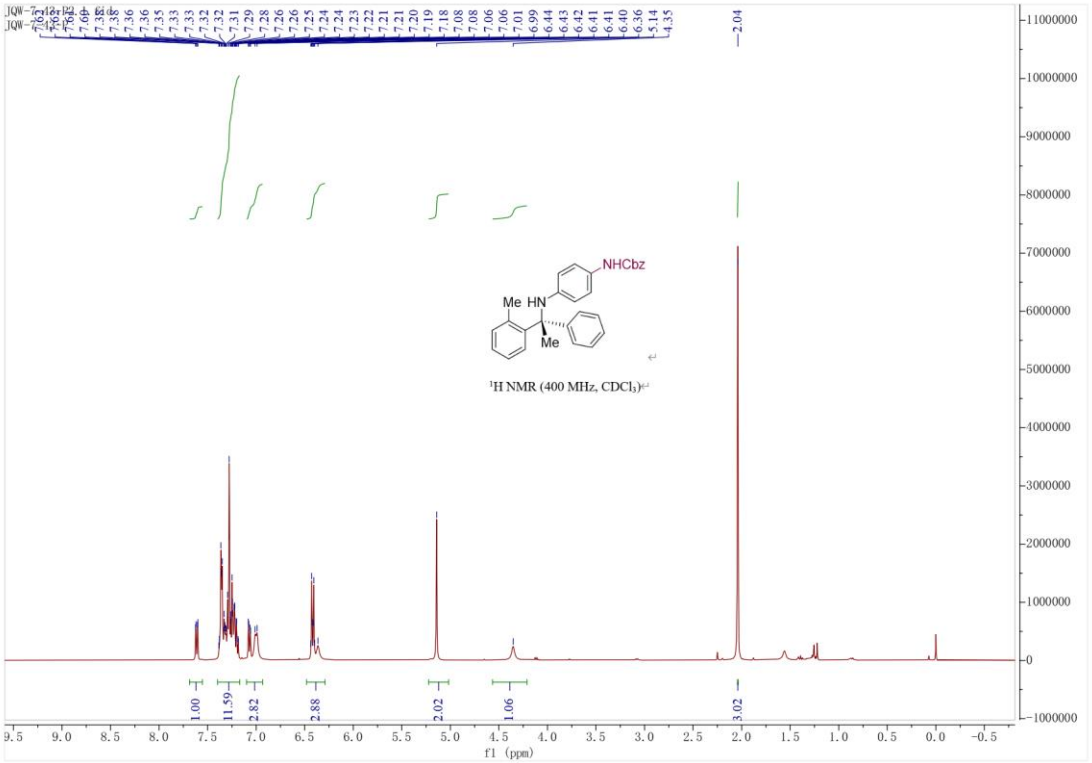


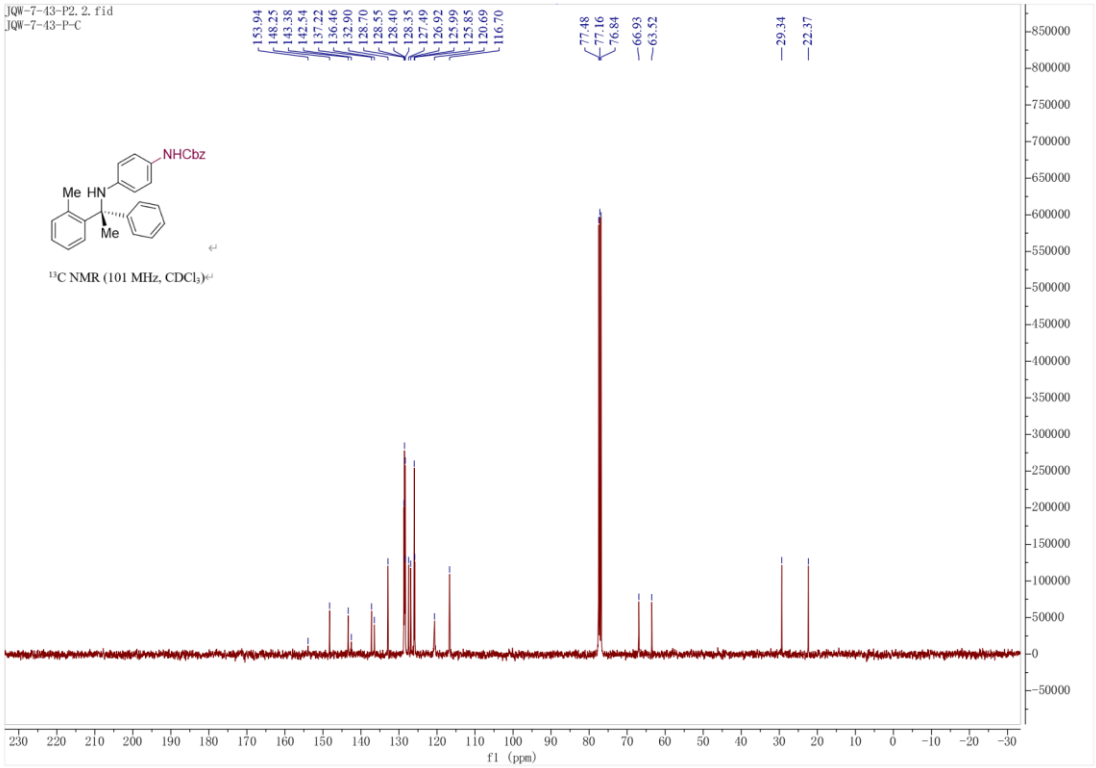
Dibenzyl-(*R*)-1-(4-((1-(2-benzylphenyl)-1-phenylpentyl)amino)phenyl)hydrazine-1,2-dicarbo xyl-ate (**3y**)



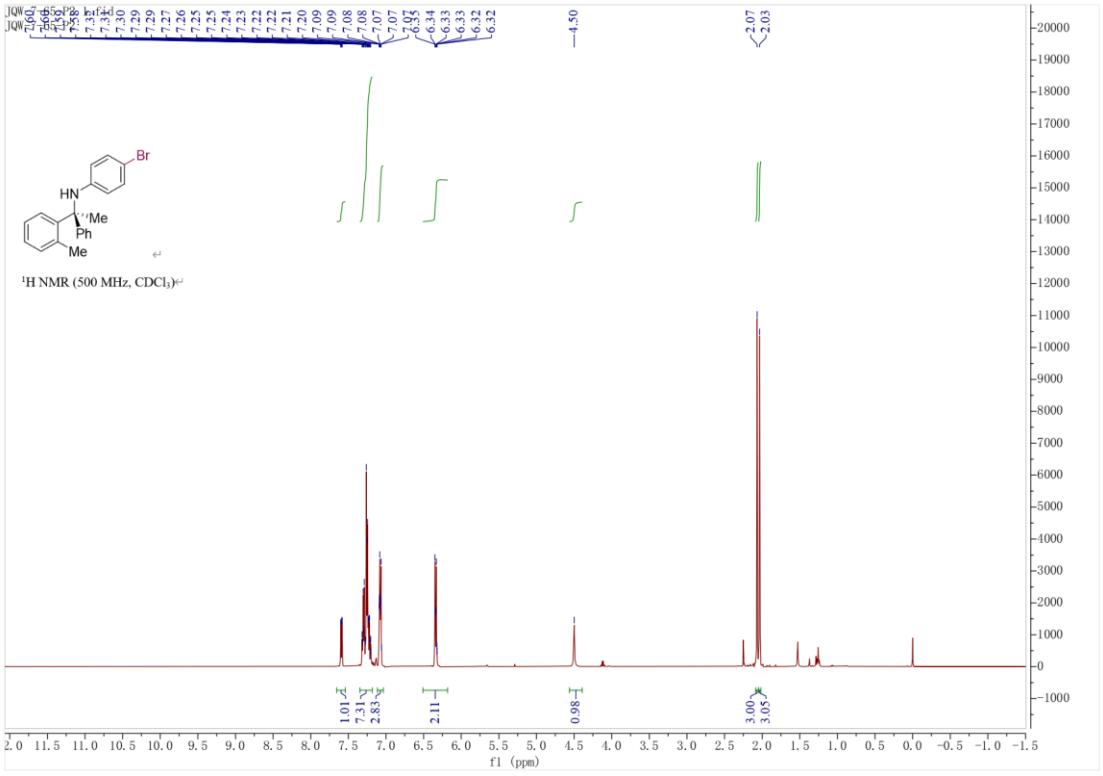


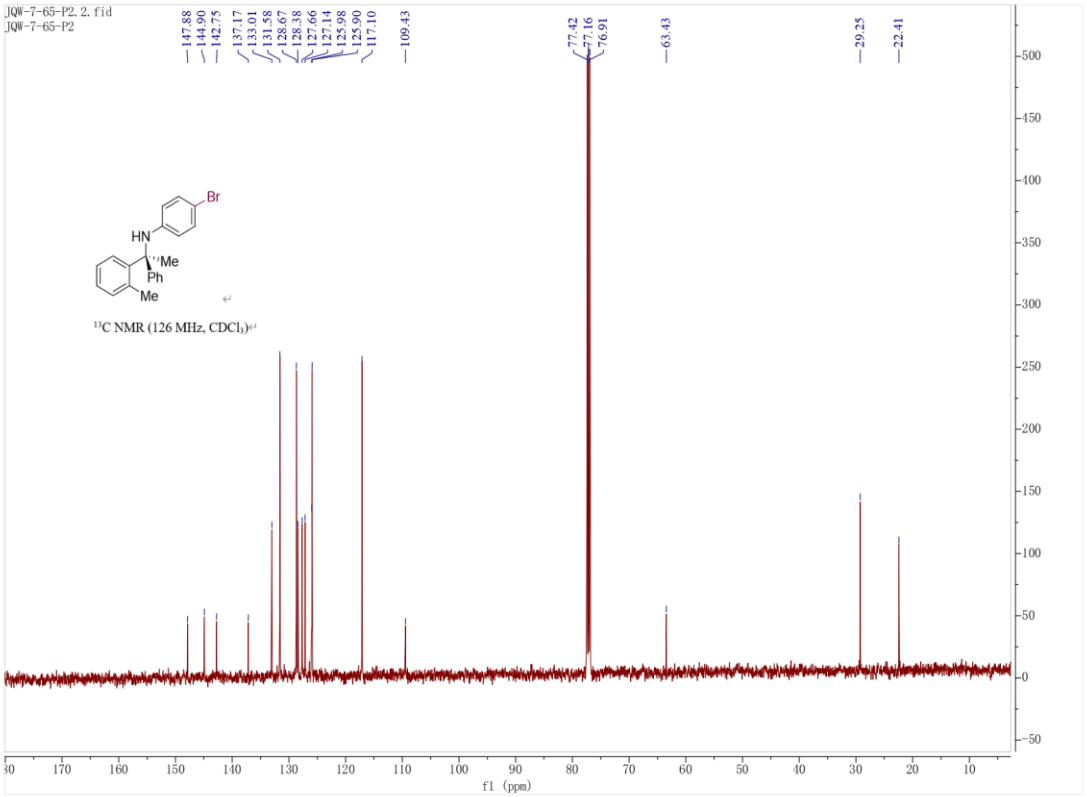
Benzyl (*R*)-(4-((1-phenyl-1-(*o*-tolyl)ethyl)amino)phenyl)carbamate (**4a**)





(*S*)-4-bromo-*N*-(1-phenyl-1-(*o*-tolyl)ethyl)aniline (**5a**)





(*S*)-2,4-dibromo-N-(1-phenyl-1-(o-tolyl)ethyl)aniline (**6a**)