Enantioselective β-C(sp^3)–H arylation of amides via synergistic nickel and photoredox catalysis

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Supporting Information

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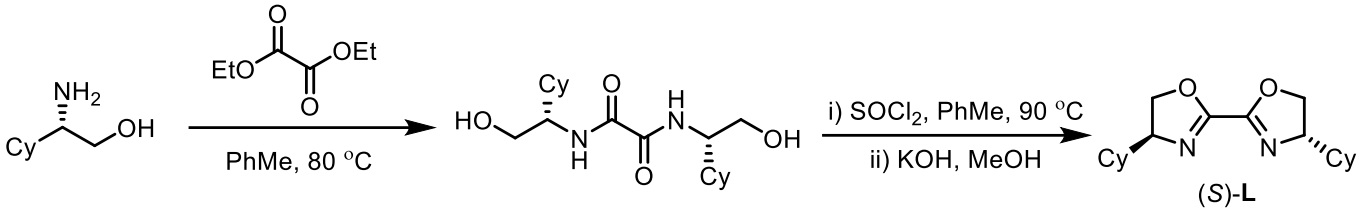
I. General Information

Unless otherwise noted, reactions were performed with rigorous exclusion of air and moisture. *N*-Phenylpropanamide derivatives were prepared according to a literature procedure, and all analytical data matched that report.[1] Anhydrous EtOAc (>99.6%, Sigma-Aldrich) was dried using freshly activated 4Å MS. $NiBr_2$·glyme (>97%, Strem), Na_3PO_4 (>96.0%, Sigma-Aldrich), and all starting materials and reagents were purchased from commercial sources and used as received. NMR spectra were collected on a Bruker 400 MHz, a Bruker 500 MHz spectrometer at ambient temperature. Chemical shifts (δ) are given in in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane (^{1}H NMR: $CDCl_3$ at 7.26 ppm. ^{13}C NMR: $CDCl_3$ at 77.00 ppm). The data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet, br = broad), coupling constant *J* (Hz) and integration. HPLC analyses were carried out on an Agilent 1260 series system with Daicel CHIRALPAK® or Daicel CHIRALCEL® columns (4.6 × 250 mm, particle size 3 μm). FT-IR measurements were carried out on a Nicolet AVATER FTIR330 spectrometer. High resolution mass spectra (ESI) were recorded by the instrumentation center of Department of Chemistry, Xiamen University, on a high-resolution LC/MS instrument. Optical rotation data were obtained with an Anton Paar MCP 500 polarimeter at 589 nm and at 25 °C, using a 50 mm path-length cell in the solvent and at the concentration indicated. GC analyses were obtained on an Agilent 6890A GC. Blue LED lamps (40 W; Kessil PR160L) were used to irradiate the reaction mixtures. The chiral bisoxazoline,[2–4] bisimidazole,[4] and pydine-oxazole ligands[5] are prepared according to the previously reported procedures. $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ photocatalyst is synthesized by the previously reported method.[6]

II. Preparation of chiral ligand (*S*)-L



The synthesis of (*S*)-**L** was according to a similar procedure.[2] (*S*)-2-amino-2-cyclohexylethan-1-ol (2.0 equiv., 30 mmol, 4.3 g) and diethyl oxalate (1.0 equiv., 15 mmol, 2.0 mL) were dissolved in toluene (250 mL) and heated to 80 °C. The reaction was allowed to stir overnight with the diamide precipitating out of solution as a white solid. Reaction was cooled to room temperature and concentrated in vacuo. The crude diol was dissolved in toluene (150 mL) and heated to 70 °C whereupon thionyl chloride (2.0 equiv., 30 mmol, 2.4 mL) was added. Reaction was stirred at 70 °C for 30 minutes then heated to 90 °C for 2 h. The reaction was cooled to room temperature and poured into 20% KOH solution at 0 °C. The aqueous layer was separated and extracted three times with DCM and the combined organic layers were washed with 20% KOH solution, saturated $NaHCO_3$ solution and brine. The organic layer was dried with Na_2SO_4, filtered, and concentrated under reduced pressure to afford the dichloro-intermediate as a sticky yellow solid. The crude dichloro-intermediate was immediately dissolved in MeOH (150 mL) and KOH (37.5 mmol, 2.1 g) was added. The reaction was heated to reflux for 14 hours. The reaction was cooled to room temperature and concentrated. The residue was purified by flash column chromatography (1:2 EtOAc/Petroleum ether) to give (*S*)-**L** (1.82 g, 6.0 mmol) in 40% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.46 – 4.37 (m, 2H), 4.19 – 4.01 (m, 4H), 1.96 (d, *J* = 12.9 Hz, 2H), 1.80 – 1.70 (m, 4H), 1.69 – 1.62 (m, 2H), 1.61 – 1.44 (m, 4H), 1.31 – 1.13 (m, 6H), 1.12 – 0.95 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 72.3, 71.2, 42.3, 29.5, 28.9, 26.3, 25.88, 25.85.

FT-IR (film): 2920, 1654, 1613, 1451, 1356, 1106, 1069, 953, 716 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{18}H_{28}N_2O_2Na$: 327.2043, found: 327.2043.

III. Effect of Reaction Parameters

General Procedure A (GP-A): In a glovebox, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.1 mg, 0.001 mmol, 1%), $NiBr_2$·glyme (3.1 mg, 0.01 mmol, 10%), (*S*)-**L** (4.0 mg, 0.013 mmol, 13%), Na_3PO_4 (24.6 mg, 0.15 mmol, 1.5 equiv), *N*,3-diphenylpropanamide (0.3 mmol, 3.0 equiv.), a Teflon stir bar, and anhydrous EtOAc (1.0 mL) were added sequentially to a 4-mL vial. The vial was closed with a PTFE septum cap and wrapped with electrical tape. After the reaction mixture was stirred at room temperature for 30 min, 4-bromobenzotrifluoride (14 μL, 0.10 mmol, 1.0 equiv) was added via a microsyringe. Next, the vial was transferred out of the glovebox, and then vacuum grease was liberally applied to cover the entrie top of the septum cap. Then, the reaction mixture was stirred at 10 °C in an EtOH bath for 1 min before being irradiated with a 40 W the blue LED lamp (Kessil PR160L, 427 nm, a single lamp was used for setup of two reactions as depicted below, and the distance between vials and the lamp is approximately 4cm.). The reaction was stirred under blue LED irradiation at 10 °C for 48 hours. Next, the lamp was turned off and the resulting mixture was allowed to warm to room temperature, and then dodecane (23 μL, 0.10 mmol) was added as an internal standard. The mixture was filtered through a small plug of silica gel, which was flushed with Et_2O (~6 mL). A portion of the filtrate (0.1 mL) was diluted with acetone (total volume: ~1 mL) and analyzed via GC, and the remainder of the filtrate was concentrated via rotary evaporation, and the pure product was isolated by preparative TLC on silica gel (5:1 Dichloromethane/Petroleum ether).

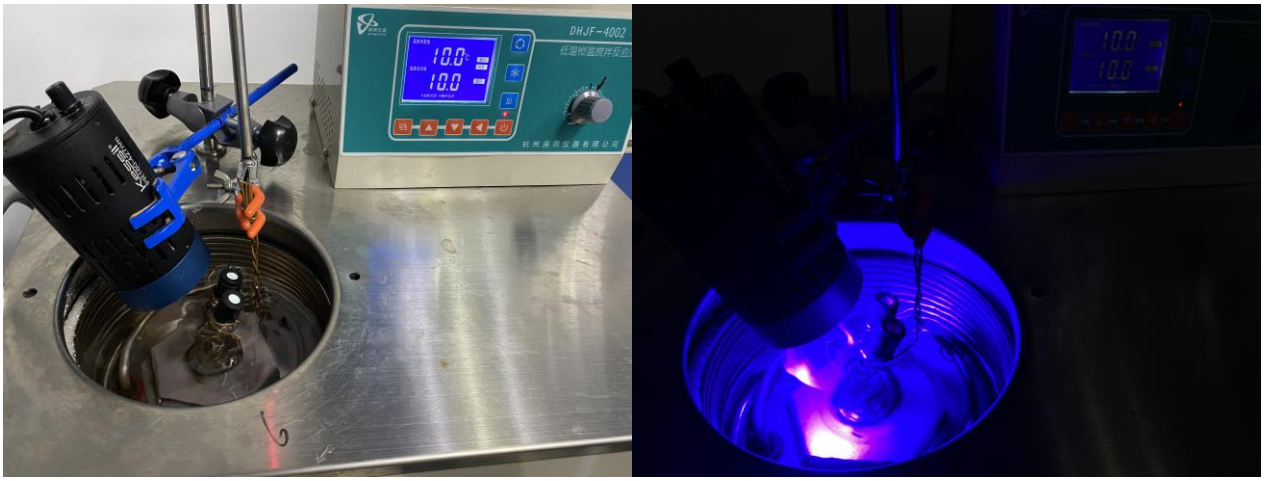
The results for the effect of reaction parameters were shown in Fig. 1. **GP-A** was followed for the experiments set-up, using *N*,3-diphenylpropanamide (0.30 mmol) and 4-bromobenzotrifluoride (0.10 mmol), the yield was determined via GC analysis with dodecane as an internal standard. The ee values were determined via HPLC analysis after purification by preparative thin-layer chromatography.

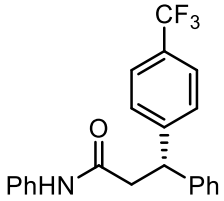
IV. Catalytic Enantioselective C(sp^3)–H Arylation

General Procedure B (GP-B): In a glovebox, Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.2 mg, 0.002mmol, 1%), $NiBr_2$·glyme (6.2 mg, 0.02 mmol, 10%), (*S*)-**L** (8.0 mg, 0.026 mmol, 13%), Na_3PO_4 (49.2 mg, 0.30 mmol, 1.5 equiv), Phenylpropanamide derivative (0.6 mmol, 3.0 equiv.), a Teflon stir bar, and anhydrous EtOAc (2.0 mL) was added sequentially to 4-mL vial. The vial was closed with a PTFE septum cap and wrapped with electrical tape. After the reaction mixture was stirred at room temperature for 30 min, aryl bromide (0.20 mmol, 1.0 equiv) was added. Next, the vial was transferred out of the glovebox, and then vacuum grease was liberally applied to cover the entire top of the septum cap. Then, the reaction mixture was stirred at 10 °C in an EtOH bath for 1 min before being irradiated with a 40 W the blue LED lamp (Kessil PR160L, 427 nm, a single lamp was used for setup of two reactions as depicted below, and the distance between vials and the lamp is approximately 4cm.). The reaction was stirred under blue LED irradiation at 10 °C for 48 hours. The reaction mixture was then passed through a short pad of silica gel, with Et_2O as the eluent (~15 mL). The resulting mixture was concentrated, and the residue was purified by preparative thin-layer chromatography (PTLC) on silica gel.

General Procedure C (GP-C): Unless otherwise noted, the racemic products were synthesized according to **GP-A** except for changes in the following conditions: using dtbbpy (3.5 mg, 0.13 mmol, 13%) as ligand and the reaction was stirred for 16 hours under room temperature.

Exemplary reaction setup:





(*S*)-*N*,3-Diphenyl-3-(4-(trifluoromethyl)phenyl)propanamide (Figure 2, compound 1). The title compound was synthesized according to **GP-B** from *N*,3-diphenylpropanamide and 4-bromobenzotrifluoride. The product was purified by preparative thin-layer chromatography (PTLC) on silica gel (5:1 Dichloromethane/Petroleum ether). White solid.

(*S*)-**L**: 71 mg, 96% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (15.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 14.8 min (major), 20.6 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.29 (m, 4H), 7.28 – 7.20 (m, 5H), 7.08 (t, *J* = 7.1 Hz, 1H), 7.03 (brs, 1H), 4.74 (t, *J* = 7.6 Hz, 1H), 3.16 – 3.02 (m, 2H).

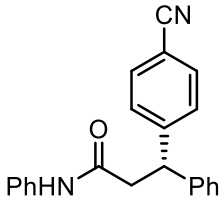
^{19}F NMR (471 MHz, $CDCl_3$) δ −62.4 (s, 3F).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 147.6, 142.6, 137.4, 128.9, 128.87, 128.88 (q, J_{C-F} = 32.5 Hz), 128.0, 127.7, 127.0, 125.56 (q, J_{C-F} = 3.7 Hz), 124.6, 124.10 (q, J_{C-F} = 272.3 Hz), 120.2, 47.0, 43.7.

FT-IR (film): 3233, 2922, 1644, 1540, 1498, 1456, 1326, 1113, 1069, 743, 697 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{22}H_{19}F_3NO$: 370.1413, found:370.1414.

$[\alpha]^{25}_D$ = +0.5 (*c* 1.0, CH_2Cl_2).



(*S*)-3-(4-Cyanophenyl)-*N*,3-diphenylpropanamide (Figure 2, compound 2). The title compound was synthesized according to **GP-B** from *N*,3-diphenylpropanamide and 4-bromobenzonitrile. The product was purified by PTLC on silica gel (1:3 EtOAc/Petroleum ether). White solid.

(*S*)-**L**: 56 mg, 86% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (25.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 11.0 min (major), 16.3 min (minor).

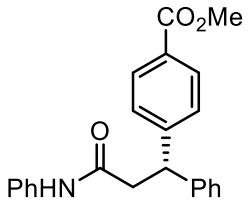
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (brs, 1H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.37 – 7.30 (m, 4H), 7.29 – 7.20 (m, 5H), 7.18 (d, *J* = 7.3 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 1H), 4.70 (t, *J* = 7.6 Hz, 1H), 3.04 (d, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 149.2, 142.1, 137.4, 132.4, 128.9, 128.6, 127.6, 127.1, 124.5, 120.1, 118.8, 110.2, 47.1, 43.1.

FT-IR (film): 3307, 2929, 2227, 1658, 1599, 1545, 1498, 1442, 1308, 1066, 751, 693 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{22}H_{19}N_2O$: 327.1492, found: 327.1496.

$[\alpha]^{25}_D = -11.4$ (*c* 1.0, CH_2Cl_2).



Methyl (*S*)-4-(3-oxo-1-phenyl-3-(phenylamino)propyl)benzoate (Figure 2, compound 3). The title compound was synthesized according to **GP-B** from *N*,3-diphenylpropanamide and methyl 4-bromobenzoate. The product was purified by PTLC on silica gel (1:3 EtOAc/Petroleum ether). White solid.

(*S*)-**L**: 62 mg, 87% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (25.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 10.5 min (major), 13.9 min (minor).

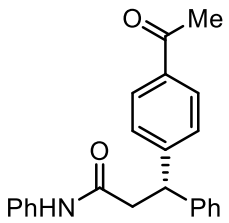
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.69 (brs, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.20 (m, 4H), 7.20 – 7.15 (m, 3H), 7.04 (t, *J* = 7.3 Hz, 1H), 4.70 (t, *J* = 7.7 Hz, 1H), 3.86 (s, 3H), 3.04 (d, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 167.0, 148.9, 142.7, 137.5, 129.9, 128.8, 128.7, 128.3, 127.8, 127.7, 126.8, 124.4, 120.2, 52.0, 47.1, 43.4.

FT-IR (film):3301, 3029, 2926, 1721, 1662, 1600, 1545, 1498, 1442, 1282, 1183, 754, 696 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{22}NO_3$: 360.1594, found: 360.1595.

$[\alpha]^{25}_D = -3.5$ (*c* 1.0, CH_2Cl_2).



(*S*)-3-(4-Acetylphenyl)-*N*,3-diphenylpropanamide (Figure 2, compound 4). The title compound was synthesized according to **GP-B** from *N*,3-diphenylpropanamide and 4'-bromoacetophenone. The product was purified by PTLC on silica gel (1:3 EtOAc/Petroleum ether). White solid.

(*S*)-**L**: 57 mg, 83% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (25.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 10.7 min (major), 15.7 min (minor).

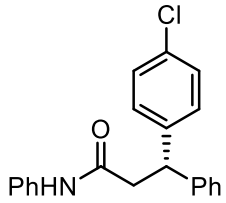
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.60 (brs, 1H), 7.33 (d, *J* = 7.2 Hz, 4H), 7.30 – 7.24 (m, 3H), 7.23 – 7.17 (m, 4H), 7.05 (t, *J* = 7.3 Hz, 1H), 4.72 (t, *J* = 7.7 Hz, 1H), 3.08 (d, *J* = 7.7 Hz, 2H), 2.53 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 169.0, 149.2, 142.7, 137.6, 135.5, 128.9, 128.8, 128.7, 128.0, 127.7, 126.9, 124.4, 120.1, 47.1, 43.5, 26.6.

FT-IR (film): 3321, 3053, 2923, 1734, 1668, 1600, 1544, 1498, 1443, 1269, 756, 700 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{22}NO_2$: 344.1645, found: 344.1648.

$[\alpha]^{25}_D$ = –2.8 (*c* 1.0, CH_2Cl_2).



(*S*)-3-(4-Chlorophenyl)-*N*,3-diphenylpropanamide (Figure 2, compound 5). The title compound was synthesized according to **GP-B** from *N*,3-diphenylpropanamide and 4-bromochlorobenzene. The product was purified by PTLC on silica gel (1:400 CH_3OH/ Dichloromethane). White solid.

(*S*)-**L**: 49 mg, 73% yield, 93% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OJ-3 column (15.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 15.5 min (major), 19.2 min (minor).

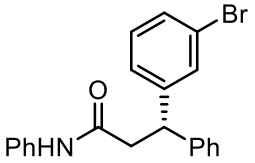
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 4H), 7.29 – 7.23 (m, 7H), 7.22 – 7.18 (m, 2H), 7.15 – 7.06 (m, 2H), 4.66 (t, *J* = 7.6 Hz, 1H), 3.12 – 2.98 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 143.0, 142.1, 137.4, 132.4, 129.1, 128.9, 128.8, 128.8, 127.7, 126.9, 124.5, 120.1, 46.6, 44.1.

FT-IR (film): 3238, 2926, 1641, 1595, 1534, 1488, 1446, 1281, 753, 696 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{21}H_{19}ClNO$: 336.1150, found: 336.1153.

$[\alpha]^{25}_D$ = +6.8 (*c* 1.0, CH_2Cl_2).



(*S*)-3-(3-Bromophenyl)-*N*,3-diphenylpropanamide (Figure 2, compound 6). The title compound was synthesized according to **GP-B** from *N*,3-diphenylpropanamide and 1,3-dibromobenzene. The product was purified by PTLC on silica gel (1:400 CH_3OH/Dichloromethane). The corresponding racemic product was synthesized according to **GP-C** using (4*S*,4′*S*)-4,4'-diphenyl-4,4',5,5'-tetrahydro-2,2'-bioxazole as ligand instead. White solid.

(*S*)-**L**: 41 mg, 54% yield, 95% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OJ-3 column (15.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 17.3 min (major), 22.9 min (minor).

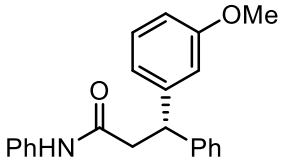
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.36 – 7.29 (m, 5H), 7.28 – 7.19 (m, 6H), 7.18 – 7.12 (m, 1H), 7.11 – 7.03 (m, 2H), 4.63 (t, *J* = 7.6 Hz, 1H), 3.04 (d, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 145.9, 142.7, 137.4, 130.7, 130.2, 129.8, 128.9, 128.8, 127.7, 126.9, 126.5, 124.5, 122.7, 120.2, 46.9, 43.8.

FT-IR (film): 3293, 2923, 1655, 1599, 1544, 1498, 1443, 1311, 1257, 1074, 755, 701 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{21}H_{19}BrNO$: 380.0645, found: 380.0648.

$[\alpha]^{25}_D$ = –0.5 (*c* 1.0, CH_2Cl_2).



(*S*)-3-(3-Methoxyphenyl)-*N*,3-diphenylpropanamide (Figure 2, compound 7). The title compound was synthesized according to **GP-B** from *N*,3-diphenylpropanamide and 3-bromoanisole. The product was purified by PTLC on silica gel (1:3 Acetone/Petroleum ether). White solid.

(*S*)-**L**: 41 mg, 62% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (15.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 18.8 min (major), 24.2 min (minor).

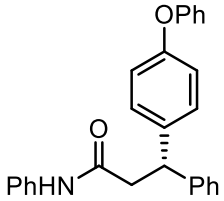
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 6H), 7.23 – 7.17 (m, 3H), 7.11– 7.00 (m, 2H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.81 (s, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 4.59 (t, *J* = 7.6 Hz, 1H), 3.73 (s, 3H), 3.04 (d, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 159.8, 145.2, 143.4, 137.6, 129.7, 128.8, 128.7, 127.7, 126.7, 124.3, 120.07, 120.05, 113.9, 111.7, 55.1, 47.4, 44.3.

FT-IR (film): 3300, 3060, 2929, 1660, 1599, 1548, 1497, 1443, 1312, 1258, 1051, 755, 695 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{22}H_{22}NO_2$: 332.1645, found: 332.1647.

$[\alpha]^{25}_D$ = –0.1 (*c* 1.0, CH_2Cl_2).



(*S*)-3-(4-Phenoxyphenyl)-*N*,3-diphenylpropanamide (Figure 2, compound 8). The title compound was synthesized according to **GP-B** from *N*,3-diphenylpropanamide and 4-bromophenoxybenzene. The product was purified by PTLC on silica gel (1:400 CH_3OH/Dichloromethane). White solid.

(*S*)-**L**: 42 mg, 53% yield, 86% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK **ID**-3 column (15.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 19.5 min (major), 21.8 min (minor).

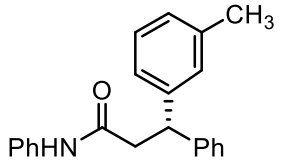
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.2 Hz, 6H), 7.26 – 7.17 (m, 7H), 7.10 – 7.02 (m, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 4.62 (t, *J* = 7.6 Hz, 1H), 3.03 (d, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 157.1, 155.9, 143.5, 138.3, 137.5, 129.7, 129.0, 128.9, 128.7, 127.7, 126.7, 124.4, 123.2, 120.1, 119.0, 118.8, 46.8, 44.4.

FT-IR (film): 3296, 2924, 1656, 1598, 1544, 1489, 1443, 1240, 1169, 753, 693 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{27}H_{24}NO_2$: 394.1802, found: 394.1804.

$[\alpha]^{25}_D$ = –14.4 (*c* 1.0, CH_2Cl_2).



(*S*)-*N*,3-Diphenyl-3-(*m*-tolyl)propanamide (Figure 2, compound 9). The title compound was synthesized according to **GP-B** from *N*,3-diphenylpropanamide and 3-bromotoluene. The product was purified by PTLC on silica gel (1:400 CH_3OH/Dichloromethane). White solid.

(*S*)-**L**: 27 mg, 44% yield, 89% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-3 column (15.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 12.4 min (minor), 14.3 min (major).

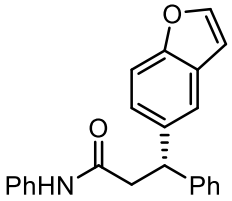
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 7H), 7.22 – 7.15 (m, 2H), 7.11 – 6.99 (m, 4H), 6.94 (s, 1H), 4.58 (t, *J* = 7.6 Hz, 1H), 3.06 (d, *J* = 7.6 Hz, 2H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 143.6, 143.4, 138.3, 137.5, 128.9, 128.7, 128.6, 128.6, 127.7, 127.5, 126.6, 124.6, 124.3, 120.1, 47.5, 44.4, 21.5.

FT-IR (film): 3294, 3026, 2922, 1659, 1600, 1548, 1498, 1443, 1311, 1175, 754, 698 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{22}H_{22}NO$: 316.1696, found: 316.1700.

$[\alpha]^{25}_D$ = +3.1 (*c* 1.0, CH_2Cl_2).



(*S*)-3-(Benzofuran-5-yl)-*N*,3-diphenylpropanamide (Figure 2, compound 10). The title compound was synthesized according to **GP-B** stirring for 63 h from *N*,3-diphenylpropanamide and 5-bromobenzofuran. The product was purified by PTLC on silica gel (1:3 Acetone/Petroleum ether). White solid.

(*S*)-**L**: 30 mg, 44% yield, 93% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (15.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 20.4 min (major), 24.4 min (minor).

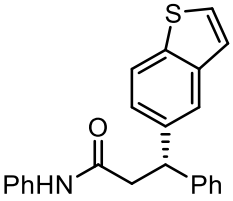
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 2.2 Hz, 1H), 7.50 (s, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.33 – 7.28 (m, 4H), 7.26 – 7.23 (m, 3H), 7.23 – 7.17 (m, 3H), 7.05 (t, *J* = 6.6 Hz, 1H), 6.96 (brs, 1H), 6.73 – 6.67(m, 1H), 4.75 (t, *J* = 7.7 Hz, 1H), 3.21 – 3.05 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 153.8, 145.4, 143.9, 138.2, 137.5, 128.9, 128.7, 127.72, 127.68, 126.6, 124.34, 124.25, 120.06, 120.03, 111.5, 106.6, 47.3, 44.7.

FT-IR (film): 3293, 2924, 1659, 1600, 1541, 1498, 1443, 1258, 1030, 738, 698 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{20}NO_2$: 342.1489, found:342.1492.

$[\alpha]^{25}_D$ = –13.3 (*c* 1.0, CH_2Cl_2).



(*S*)-3-(Benzo[*b*]thiophen-5-yl)-*N*,3-diphenylpropanamide (Figure 2, compound 11). The title compound was synthesized according to **GP-B** stirring for 63 h from *N*,3-diphenylpropanamide and 5-bromobenzo[*b*]thiophene. The product was purified by PTLC on silica gel (Dichloromethane). White solid.

(*S*)-**L**: 29 mg, 41% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL AD-3 column (15.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 24.7 min (minor), 27.0 min (major).

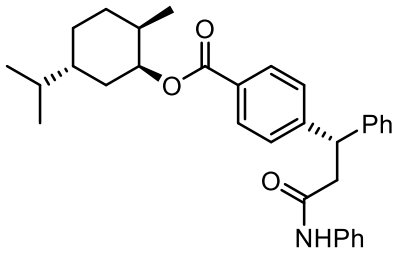
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 1H), 7.73 (s, 1H), 7.42 (d, *J* = 5.4 Hz, 1H), 7.30 (d, *J* = 4.4 Hz, 4H), 7.28 – 7.19 (m, 7H), 7.05 (t, *J* = 6.8 Hz, 1H), 7.01 (brs, 1H), 4.78 (t, *J* = 7.7 Hz, 1H), 3.14 (d, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 143.7, 140.0, 139.8, 138.1, 137.5, 128.8, 128.7, 127.8, 126.9, 126.7, 124.5, 124.4, 123.8, 122.7, 122.4, 120.1, 47.3, 44.5.

FT-IR (film): 3288, 2923, 1656, 1599, 1543, 1497, 1443, 1307, 1080, 754, 695 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{20}NOS$: 358.1260, found: 358.1260.

$[\alpha]^{25}_D$ = –11.6 (*c* 1.0, CH_2Cl_2).



(1*S*,2*R*,5*R*)-5-Isopropyl-2-methylcyclohexyl 4-((*S*)-3-oxo-1-phenyl-3-(phenylamino)propyl)benzoate (Figure 2, compound 12). The title compound was synthesized according to **GP-B** from *N*,3-diphenylpropanamide and (1*S*,2*R*,5*R*)-5-isopropyl-2-methylcyclohexyl 4-bromobenzoate prepared by known procedure.[7] The product was purified by PTLC on silica gel (1:3 EtOAc/Petroleum ether). White solid.

(*S*)-**L**: 52 mg, 54% yield, 95:5 dr.

HPLC analysis: The dr was determined via HPLC on a CHIRALCEL OD-3 column (15.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 11.5 min (major), 15.1 min (minor).

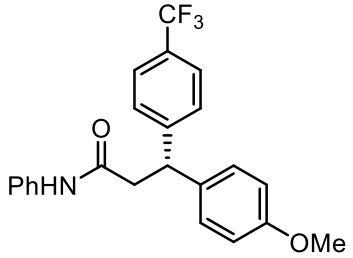
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.28 (m, 5H), 7.27 – 7.15 (m, 6H), 7.06 (t, *J* = 7.2 Hz, 1H), 4.90 (td, *J* = 10.9, 4.4 Hz, 1H), 4.72 (t, *J* = 7.6 Hz, 1H), 3.09 (d, *J* = 7.6 Hz, 2H), 2.11 – 2.03 (m, 1H), 1.98 – 1.87 (m, 1H), 1.75 – 1.66 (m, 2H), 1.58 – 1.46 (m, 2H), 1.16 – 1.00 (m, 2H), 0.94 – 0.86 (m, 7H), 0.76 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 165.9, 148.7, 142.8, 137.5, 130.0, 129.3, 128.9, 128.8, 127.7, 127.7, 126.9, 124.4, 120.1, 74.8, 47.3, 47.2, 43.8, 41.0, 34.3, 31.4, 26.5, 23.6, 22.0, 20.7, 16.5.

FT-IR (film): 3314, 3061, 2955, 1712, 1663, 1600, 1541, 1498, 1443, 1276, 1107, 752, 696 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{32}H_{37}NO_3Na$: 506.2666, found: 506.2670.

$[\alpha]^{25}_D$ = –54.7 (*c* 1.0, CH_2Cl_2).



(*R*)-3-(4-Methoxyphenyl)-*N*-phenyl-3-(4-(trifluoromethyl)phenyl)propanamide (Figure 3, compound 13). The title compound was synthesized according to **GP-B** from 3-(4-methoxyphenyl)-*N*-phenylpropanamide and 4-bromobenzotrifluoride. The product was purified by PTLC on silica gel (Dichloromethane). White solid.

(*S*)-**L**: 53 mg, 66% yield, 93% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (15.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 15.8 min (major), 18.2 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.1 Hz, 2H), 7.44 (brs, 1H), 7.35 – 7.27 (m, 4H), 7.25 – 7.18 (m, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 2H), 4.65 (t, *J* = 7.7 Hz, 1H), 3.74 (s, 3H), 3.01 (d, *J* = 7.7 Hz, 2H).

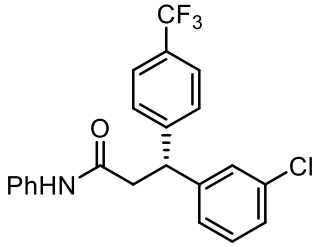
^{19}F NMR (471 MHz, $CDCl_3$) δ −62.4 (s, 3F).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 158.5, 148.0, 137.4, 134.6, 128.9, 128.74 (q, $J_{C–F}$ = 32.5 Hz), 128.67, 127.9, 125.51 (q, $J_{C–F}$ = 3.7 Hz), 124.5, 124.11 (q, $J_{C–F}$ = 272.4 Hz), 120.2, 114.2, 55.2, 46.2, 43.8.

FT-IR (film): 3297, 3062, 2933, 1659, 1600, 1548, 1512, 1444, 1326, 1251, 1116, 830, 757 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{23}H_{20}F_3NO_2Na$: 422.1338, found: 422.1339.

$[\alpha]^{25}_D$ = +8.7 (*c* 1.0, CH_2Cl_2).



(*R*)-3-(3-Chlorophenyl)-*N*-phenyl-3-(4-(trifluoromethyl)phenyl)propanamide (Figure 3, compound 14). The title compound was synthesized according to **GP-B** from 3-(3-chlorophenyl)-*N*-phenylpropanamide and 4-bromobenzotrifluoride. The product was purified by PTLC on silica gel (5:1 Dichloromethane/Petroleum ether). White solid.

(*S*)-**L**: 36 mg, 45% yield, 88% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (15.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 12.8 min (major), 17.9 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.31 (m, 4H), 7.30 – 7.27 (m, 1H), 7.24 – 7.18 (m, 3H), 7.16 – 7.07 (m, 3H), 4.74 (t, *J* = 7.6 Hz, 1H), 3.05 (d, *J* = 7.6 Hz, 2H).

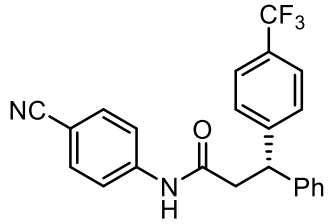
^{19}F NMR (471 MHz, $CDCl_3$) δ −62.5 (s, 3F).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 146.9, 144.7, 137.2, 134.7, 130.1, 129.23 (q, $J_{C–F}$ = 33.0 Hz), 129.0, 128.1, 127.8, 127.3, 126.1, 125.76 (q, $J_{C–F}$ = 3.8 Hz), 124.7, 124.03 (q, $J_{C–F}$ = 272.7 Hz), 120.1, 46.5, 43.4.

FT-IR (film): 3296, 2926, 1660, 1597, 1553, 1499, 1444, 1326, 1126, 1070, 759, 695 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{22}H_{18}ClF_3NO$: 404.1024, found: 404.1020.

$[\alpha]^{25}_D$ = +1.3 (*c* 1.0, CH_2Cl_2).



(*S*)-*N*-(4-Cyanophenyl)-3-phenyl-3-(4-(trifluoromethyl)phenyl)propanamide (Figure 3, compound 15). The title compound was synthesized according to **GP-B** from *N*-(4-cyanophenyl)-3-phenylpropanamide and 4-bromobenzotrifluoride. The product was purified by PTLC on silica gel (Dichloromethane). White solid.

(*S*)-**L**: 43 mg, 54% yield, 90%.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (25.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 8.7 min (major), 12.2 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 4H), 7.50 – 7.44 (m, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.28 – 7.21 (m, 4H), 4.72 (t, *J* = 7.6 Hz, 1H), 3.20 – 3.08 (m, 2H).

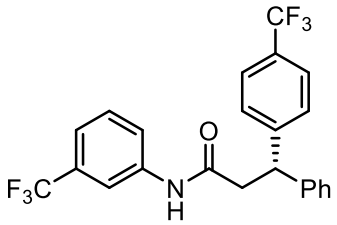
^{19}F NMR (471 MHz, $CDCl_3$) δ -62.5 (s, 3F).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3, 147.3, 142.3, 141.6, 133.2, 129.05 (q, $J_{C–F}$ = 32.5 Hz), 128.98, 128.0, 127.6, 127.2, 125.66 (q, $J_{C–F}$ = 3.8 Hz), 124.03 (q, $J_{C–F}$ = 272.6 Hz), 119.6, 118.8, 107.1, 46.9, 43.7.

FT-IR (film): 3324, 2927, 2227, 1675, 1595, 1526, 1453, 1409, 1325, 1164, 1018, 837, 700 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{23}H_{17}F_3N_2ONa$: 417.1185, found: 417.1185.

$[\alpha]^{25}_D$ = +0.9 (*c* 1.0, CH_2Cl_2).



(*S*)-3-Phenyl-*N*-(3-(trifluoromethyl)phenyl)-3-(4-(trifluoromethyl)phenyl)propanamide (Figure 3, compound 16). The title compound was synthesized according to **GP-B** from 3-phenyl-*N*-(3-(trifluoromethyl)phenyl)propanamide and 4-bromobenzotrifluoride. The product was purified by PTLC on silica gel (Dichloromethane). White solid.

(*S*)-**L**: 67 mg, 77% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (15.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 8.3 min (major), 12.4 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.56 – 7.48 (m, 3H), 7.40 – 7.33 (m, 4H), 7.32 – 7.27 (m, 3H), 7.27 – 7.21 (m, 3H), 4.72 (t, *J* = 7.7 Hz, 1H), 3.19 – 2.99 (m, 2H).

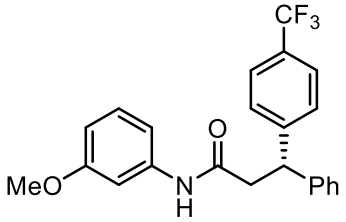
^{19}F NMR (471 MHz, $CDCl_3$) δ -62.5 (s, 3F), -62.8 (s, 3F).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3, 147.4, 142.3, 137.8, 131.29 (q, $J_{C–F}$ = 32.6 Hz), 129.5, 129.0 (q, $J_{C–F}$ = 32.6 Hz), 128.97, 128.0, 127.6, 127.2, 125.64 (q, $J_{C–F}$ = 3.7 Hz), 124.05 (q, $J_{C–F}$ = 272.5 Hz), 123.69 (q, $J_{C–F}$ = 273.0 Hz), 123.1, 121.09 (q, $J_{C–F}$ = 3.5 Hz), 116.73 (q, $J_{C–F}$ = 3.5 Hz), 46.9, 43.6.

FT-IR (film): 3297, 2927, 1663, 1618, 1557, 1493, 1449, 1328, 1126, 1018, 798, 698 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{18}F_6NO$: 438.1287, found: 438.1291.

$[\alpha]^{25}_D$ = +0.2 (*c* 1.0, CH_2Cl_2).



(*S*)-*N*-(3-Methoxyphenyl)-3-phenyl-3-(4-(trifluoromethyl)phenyl)propanamide (Figure 3, compound 17). The title compound was synthesized according to **GP-B** from *N*-(3-methoxyphenyl)-3-phenylpropanamide and 4-bromobenzotrifluoride. The product was purified by PTLC on silica gel (Dichloromethane). White solid.

(*S*)-**L**: 17 mg, 21% yield, 86% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (25.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 10.2 min (major), 12.3 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.26 – 7.21 (m, 3H), 7.15 (t, *J* = 8.1 Hz, 1H), 7.09 (s, 1H), 7.03 (brs, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 4.74 (t, *J* = 7.6 Hz, 1H), 3.76 (s, 3H), 3.15 – 3.00 (m, 2H).

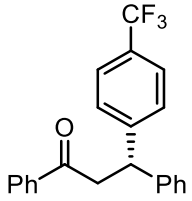
^{19}F NMR (471 MHz, $CDCl_3$) δ -62.5 (s, 3F).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 160.1, 147.6, 142.6, 138.6, 129.6, 128.91 (q, J_{C-F} = 32.6 Hz), 128.92, 128.1, 127.7, 127.1, 125.61 (q, J_{C-F} = 3.7 Hz), 124.09 (q, J_{C-F} = 272.4 Hz), 112.1, 110.3, 105.8, 55.3, 46.9, 43.9.

FT-IR (film): 3295, 3059, 2925, 1660, 1609, 1546, 1493, 1454, 1326, 1164, 1069, 699 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{23}H_{20}F_3NO_2Na$: 422.1338, found: 422.1339.

$[\alpha]^{25}_D$ = +0.1 (*c* 1.0, CH_2Cl_2).



(*S*)-1,3-Diphenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (Figure 3, compound 18). The known compound[8] was synthesized according to **GP-B** from 1,3-diphenylpropan-1-one prepared by the reported literature,[9] and 4-bromobenzotrifluoride. The product was purified by PTLC on silica gel (1:20 EtOAc/Petroleum ether). White solid.

(*S*)-**L**: 43 mg, 60% yield, 60% ee.

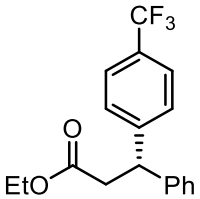
HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (15.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 6.4 min (major), 7.6 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.27 – 7.23 (m, 2H), 7.22 – 7.17 (m, 1H), 4.89 (t, *J* = 7.3 Hz, 1H), 3.82 – 3.69 (m, 2H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.4 (s, 3F).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.4, 148.2, 143.3, 136.8, 133.3, 128.8, 128.7, 128.67 (q, J_{C-F} = 32.3 Hz), 128.2, 128.0, 127.8, 126.8, 125.50 (q, J_{C-F} = 3.8 Hz), 124.17 (q, J_{C-F} = 272.5 Hz), 45.7, 44.4.

$[\alpha]^{25}_{D}$ = +5.8 (*c* 1.0, CH_2Cl_2).



Ethyl (*S*)-3-phenyl-3-(4-(trifluoromethyl)phenyl)propanoate (Figure 3, compound 19). The known compound[10] was synthesized according to **GP-B** from ethyl 3-phenylpropanoate and 4-bromobenzotrifluoride. The product was purified by PTLC on silica gel (1:10 EtOAc/Petroleum ether). Colorless oil.

(*S*)-**L**: 16 mg, 25% yield, 41% ee.

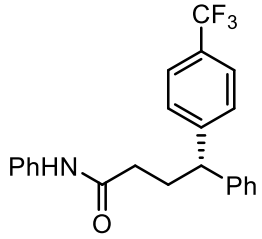
HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (10.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 4.8 min (minor), 5.5 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.33 – 7.26 (m, 2H), 7.24 – 7.19 (m, 3H), 4.61 (t, *J* = 8.0 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.06 (d, *J* = 8.0 Hz, 2H), 1.12 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.5 (s, 3F).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 147.5, 142.5, 128.87 (q, J_{C-F} = 32.5 Hz), 128.7, 128.1, 127.6, 126.9, 125.51 (q, J_{C-F} = 3.7 Hz), 124.14 (q, J_{C-F} = 272.2 Hz), 60.6, 46.9, 40.5, 14.0.

$[\alpha]^{25}_{D}$ = –0.9 (*c* 1.0, CH_2Cl_2).



(*S*)-*N*,4-Diphenyl-4-(4-(trifluoromethyl)phenyl)butanamide (Figure 3, compound 20). The title compound was synthesized according to **GP-B** from *N*,4-diphenylbutanamide and 4-bromobenzotrifluoride. The product was purified by PTLC on silica gel (5:1 Dichloromethane/Petroleum ether). White solid.

(*S*)-**L**: 41 mg, 53% yield, 65% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (15.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 16.2 min (minor), 24.7 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.25 – 7.21 (m, 3H), 7.18 (brs, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 4.05 (t, *J* = 7.9 Hz, 1H), 2.49 (q, *J* = 7.5 Hz, 2H), 2.35 – 2.21 (m, 2H).

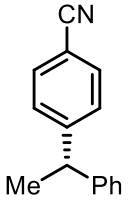
^{19}F NMR (471 MHz, $CDCl_3$) δ −62.4 (s, 3F).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 148.3, 143.0, 137.7, 129.0, 128.8, 128.68 (q, J_{C-F} = 32.7 Hz), 128.1, 127.9, 126.8, 125.49 (q, J_{C-F} = 3.7 Hz), 124.3, 124.17 (q, J_{C-F} = 272.4 Hz), 119.8, 50.1, 35.5, 30.6.

FT-IR (film): 3304, 2927, 1660, 1600, 1545, 1499, 1443, 1326, 1123, 1018, 757, 700 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{21}F_3NO$: 384.1570, found: 384.1572.

$[\alpha]^{25}_D$ = +0.3 (*c* 1.0, CH_2Cl_2).



(S)-4-(1-Phenylethyl)benzonitrile (Figure 3, compound 21). The known compound[4] was synthesized according to **GP-B** from ethylbenzene and 4-bromobenzonitrile. The product was purified by PTLC on silica gel (1:8 EtOAc/Petroleum ether). Colorless oil.

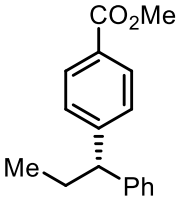
(*S*)-**L**: 28 mg, 68% yield, 44% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OJ-3 column (1.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 21.9 min (major), 23.7 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H), 7.35 – 7.28 (m, 4H), 7.25 – 7.16 (m, 3H), 4.20 (q, *J* = 7.2 Hz, 1H), 1.65 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 144.7, 132.2, 128.6, 128.4, 127.5, 126.6, 119.0, 109.9, 44.9, 21.4.

$[\alpha]^{25}_{D}$ = +3.0 (*c* 1.0, CH_2Cl_2).



Methyl (*S*)-4-(1-phenylpropyl)benzoate (Figure 3, compound 22). The known compound[4] was synthesized according to **GP-B** from propylbenzene and methyl 4-bromobenzoate. The product was purified by PTLC on silica gel (1:8 EtOAc/Petroleum ether). Colorless oil.

(*S*)-**L**: 26 mg, 51% yield, 34% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (1.0% 2-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L**: 7.5 min (major), 8.3 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.28 (m, 4H), 7.28 – 7.19 (m, 3H), 3.92 (s, 3H), 3.88 (t, *J* = 7.8 Hz, 1H), 2.13 (p, *J* = 7.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 150.5, 144.2, 129.7, 128.5, 128.0, 127.94, 127.87, 126.3, 53.22, 51.9, 28.3, 12.6.

$[\alpha]^{25}_{D}$ = +1.7 (*c* 1.0, CH_2Cl_2).

V. Assignment of Absolute Configuration

The stereochemistry of compound **18**,[8] **19**,[10] **21**,[4] and **22**[4] has been established in the literature. As described below, the (*S*) configuration was assigned for each compound by comparison with the published HPLC analysis and optical rotation.

Compound **18:**

Optical rotation:

$[\alpha]^{25}_{D}$ = +5.7 (*c* 1.0, $CHCl_3$); 60% ee, from (*S*)-**L**.

Lit.[8]: $[\alpha]^{28}_{D}$ = +8.4 (*c* 1.0, $CHCl_3$); 81% ee, for (*S*) configuration.

HPLC analysis:

6.4 min (major), 7.6 min (minor), CHIRALCEL OD-3 column (15.0% 2-PrOH in hexanes, 1.0 mL/min).

Lit.[8]: 20.2 min (major), 26.0 min (minor), for (*S*) configuration, CHIRALCEL OD-H column (1.0% 2-PrOH in hexanes, 0.8 mL/min).

Compound **19:**

Optical rotation:

$[\alpha]^{25}_{D}$ = –1.0 (*c* 1.0, $CHCl_3$); 41% ee, from (*S*)-**L**.

Lit.[10]: $[\alpha]^{25}_{D}$ = –2.3 (*c* 0.991, $CHCl_3$); 88% ee, for (*S*) configuration.

HPLC analysis:

4.8 min (minor), 5.5 min (major). CHIRALCEL OD-3 column (10.0% 2-PrOH in hexanes, 1.0 mL/min).

Lit.[10]: 7.5 min (minor), 9.2 min (major) for (*S*) configuration, CHIRALCEL OD-H column (1.0% 2-PrOH in hexanes, 1.0 mL/min)

Compound **21:**

Optical rotation:

$[\alpha]^{20}_{D}$ = +2.8 (*c* 1.0, $CHCl_3$); 44% ee, from (*S*)-**L**.

Lit.[4]: $[\alpha]^{20}_{D}$ = +5.9 (*c* 0.74, $CHCl_3$); 77% ee, for (*S*) configuration.

HPLC analysis:

21.9 min (major), 23.7 min (minor), CHIRALCEL OJ-3 column (1.0% 2-PrOH in hexanes, 1.0 mL/min).

Lit.[4]: 18.8 min (major), 20.1 min (minor), for (*S*) configuration, CHIRALCEL OJ-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min).

Compound **22:**

Optical rotation:

$[\alpha]^{20}_{D}$ = +1.5 (*c* 1.0, $CHCl_3$); 34% ee, from (*S*)-**L**.

Lit.[4]: $[\alpha]^{20}_{D}$ = +2.7 (*c* 0.85, $CHCl_3$); 80% ee, for (*S*) configuration.

HPLC analysis:

7.5 min (major), 8.3 min (minor), CHIRALCEL OD-3 column (1.0% 2-PrOH in hexanes, 1.0 mL/min).

Lit.[4]: 6.6 min (major), 7.0 min (minor) for (*S*) configuration, CHIRALCEL OD-H column (2.0% 2-PrOH in hexanes, 1.0 mL/min).

VI. References

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VII. ^{1}H-NMR and ^{13}C-NMR Spectra; Stereoselectivity Analysis

Figure S-1. ^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (*S*)-**L**.

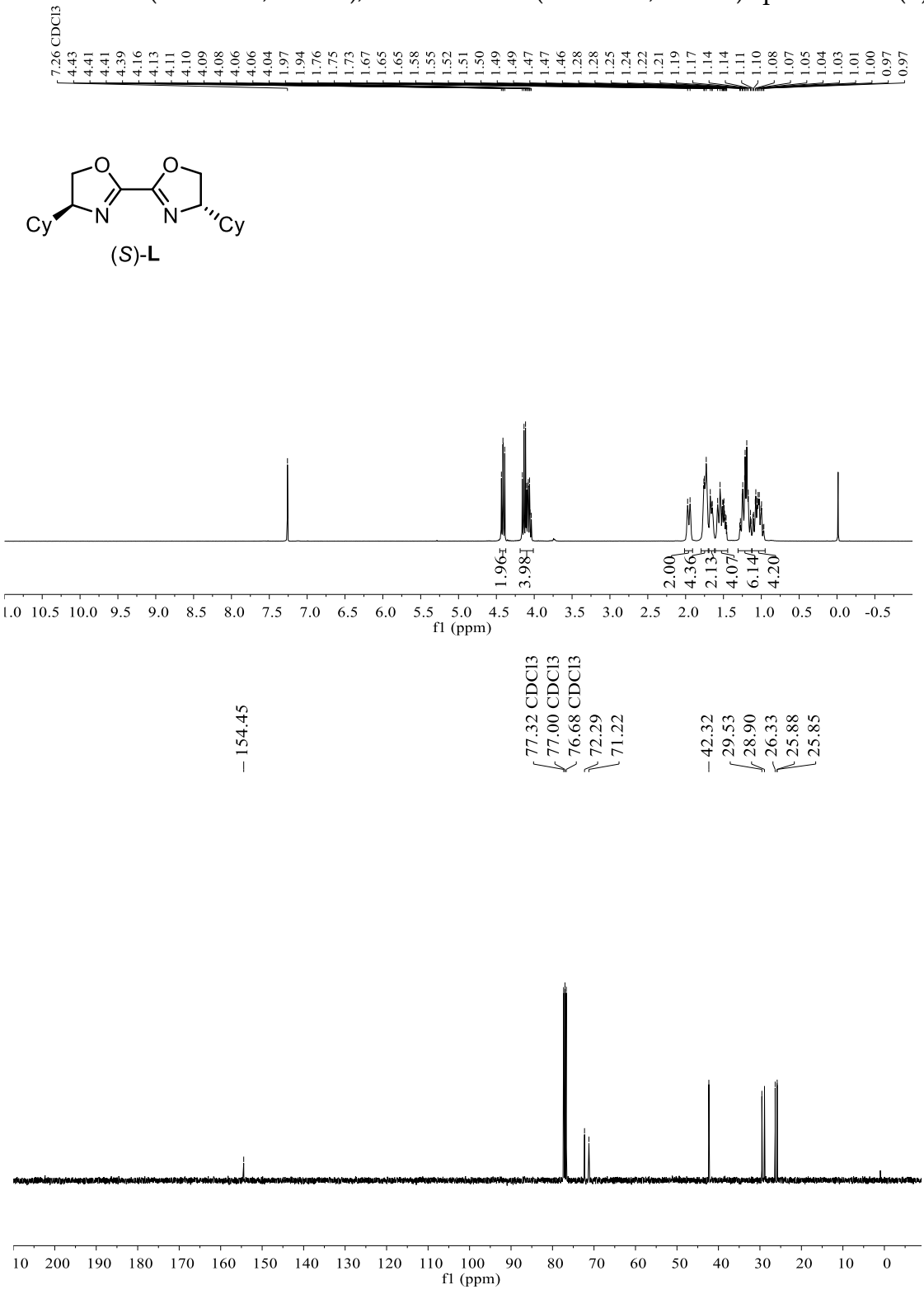
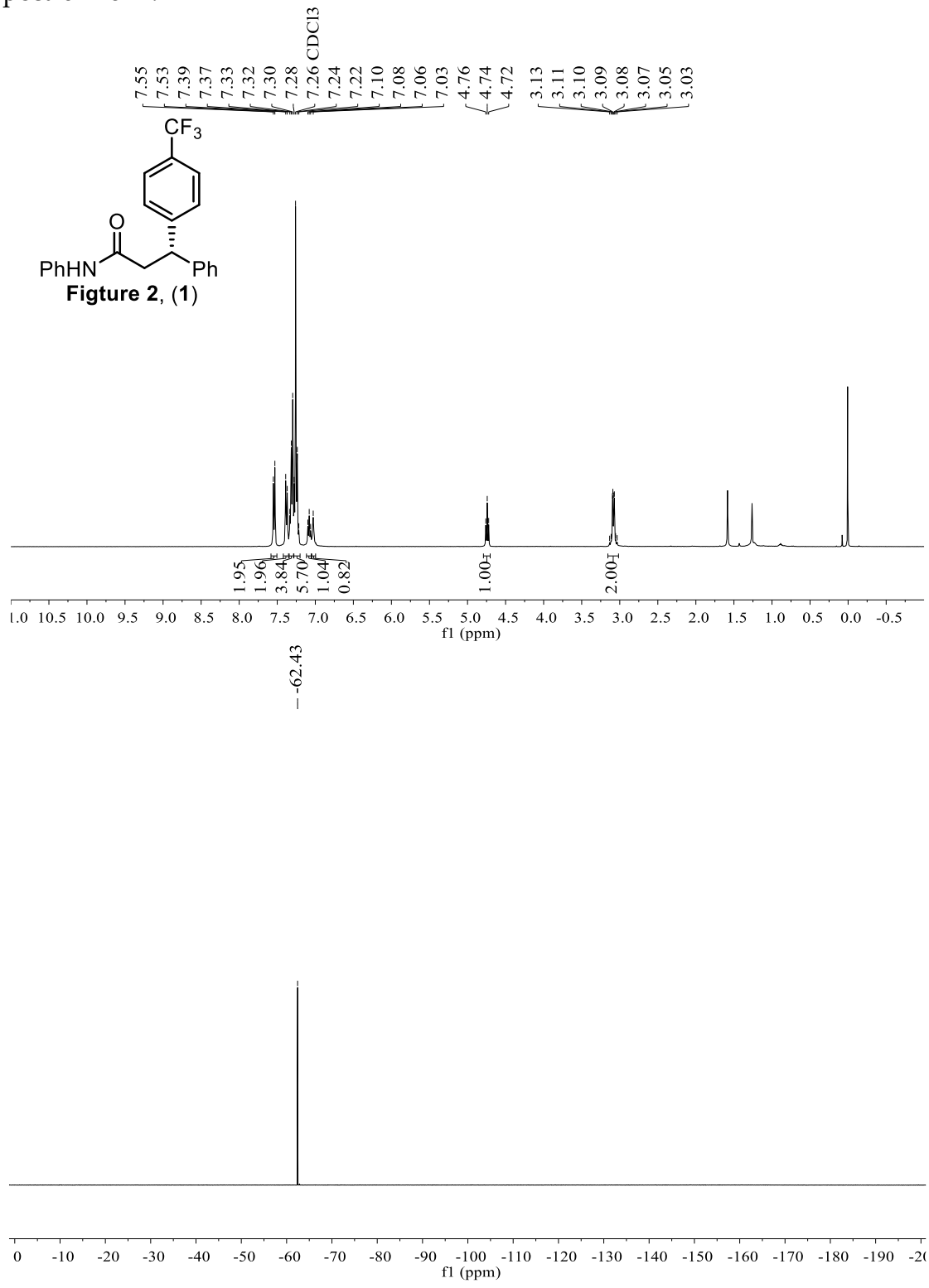


Figure S-2. ^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (471 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1**.



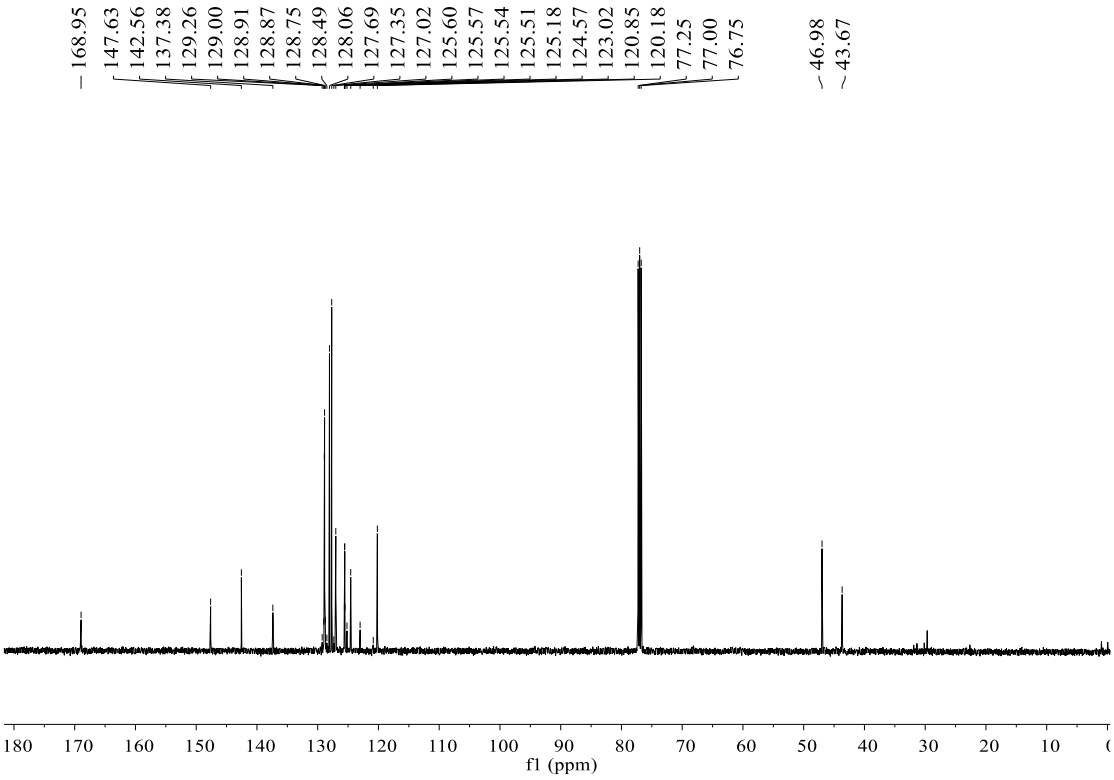

168.95
147.63
142.56
137.38
129.26
129.00
128.91
128.87
128.75
128.49
128.06
127.69
127.35
127.02
125.60
125.57
125.54
125.51
125.18
124.57
123.02
120.85
120.18
77.25
77.00
76.75
46.98
43.67
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Figure S-3. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **2**.

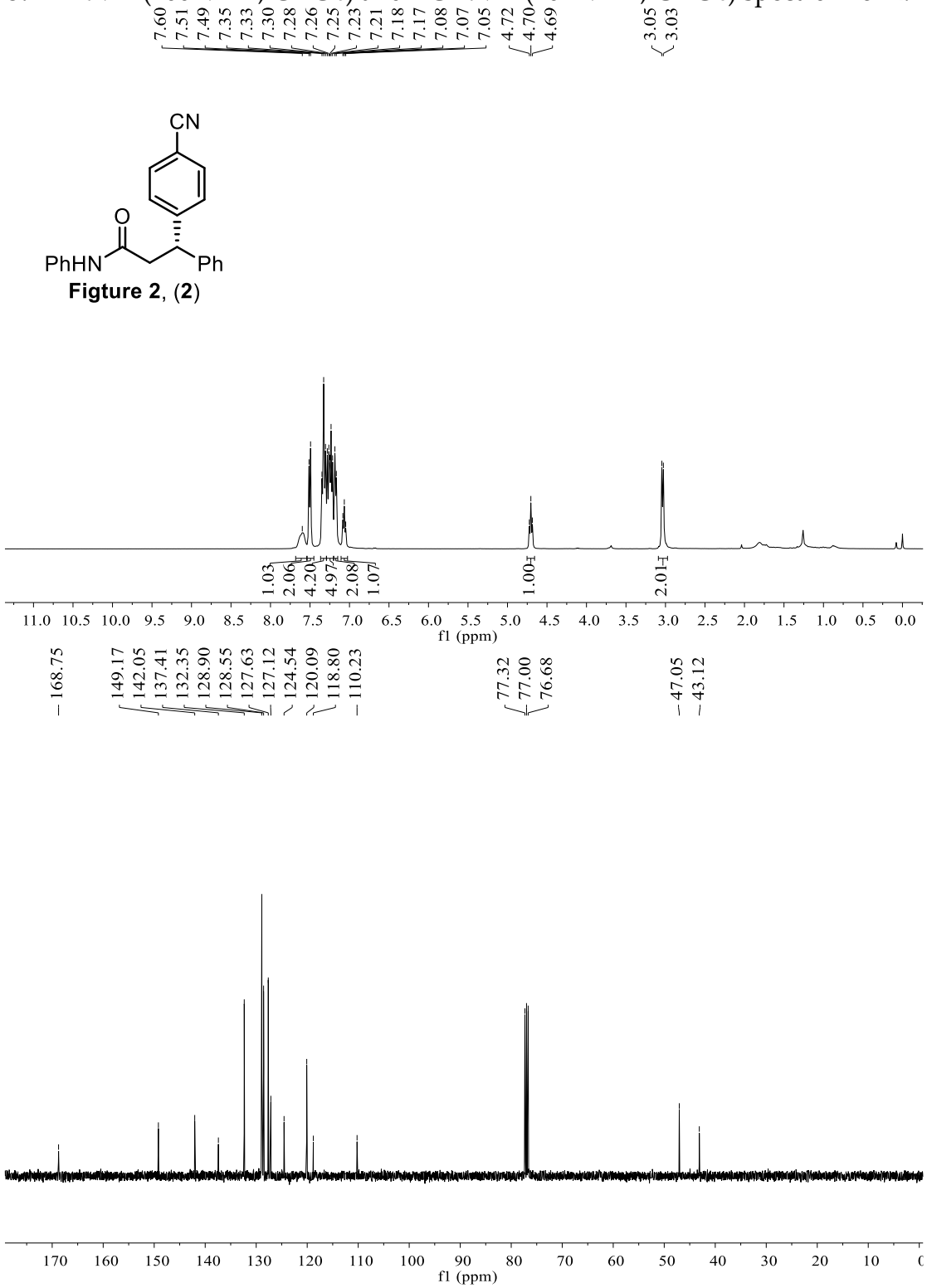


Figure S-4. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3**.

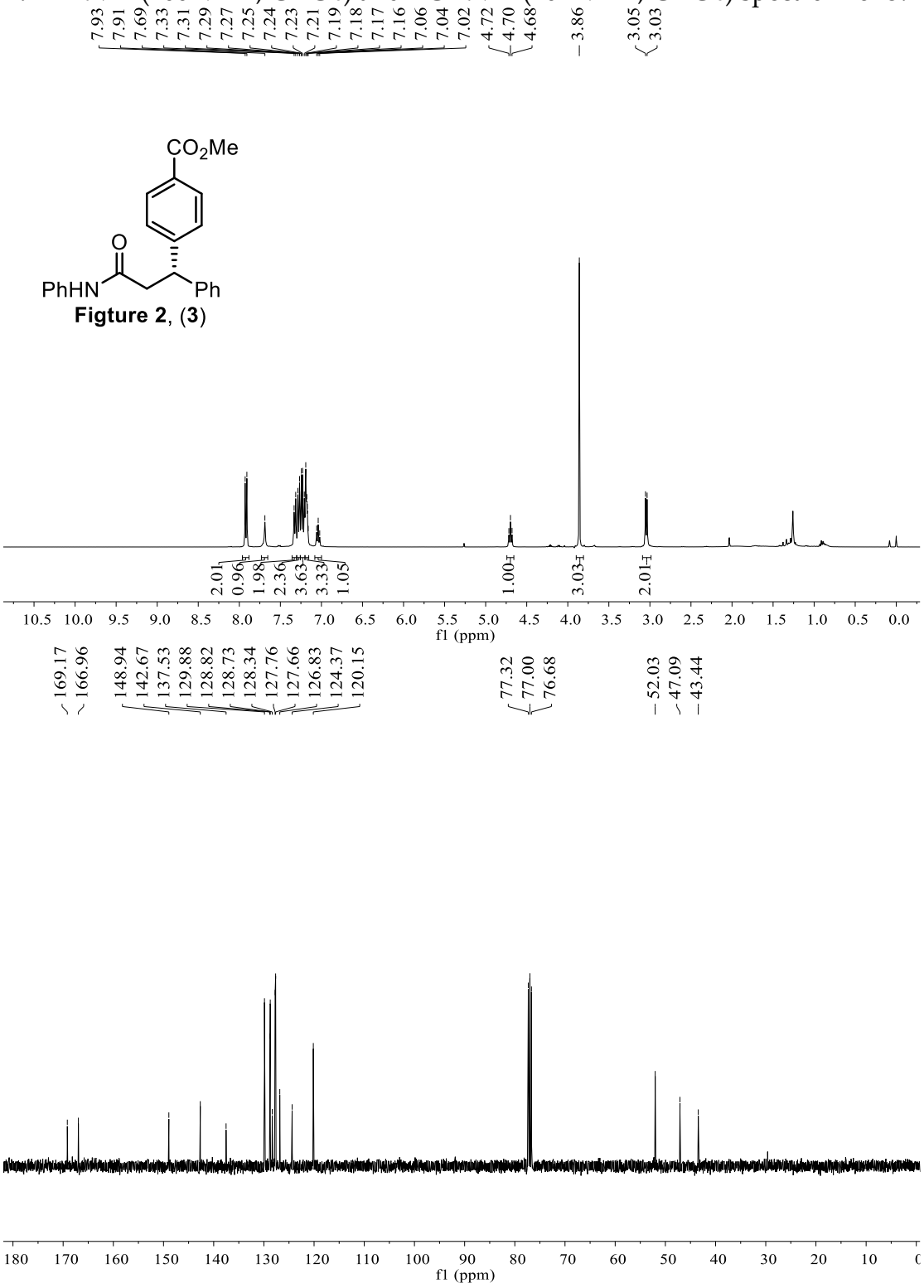


Figure S-5. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4**.

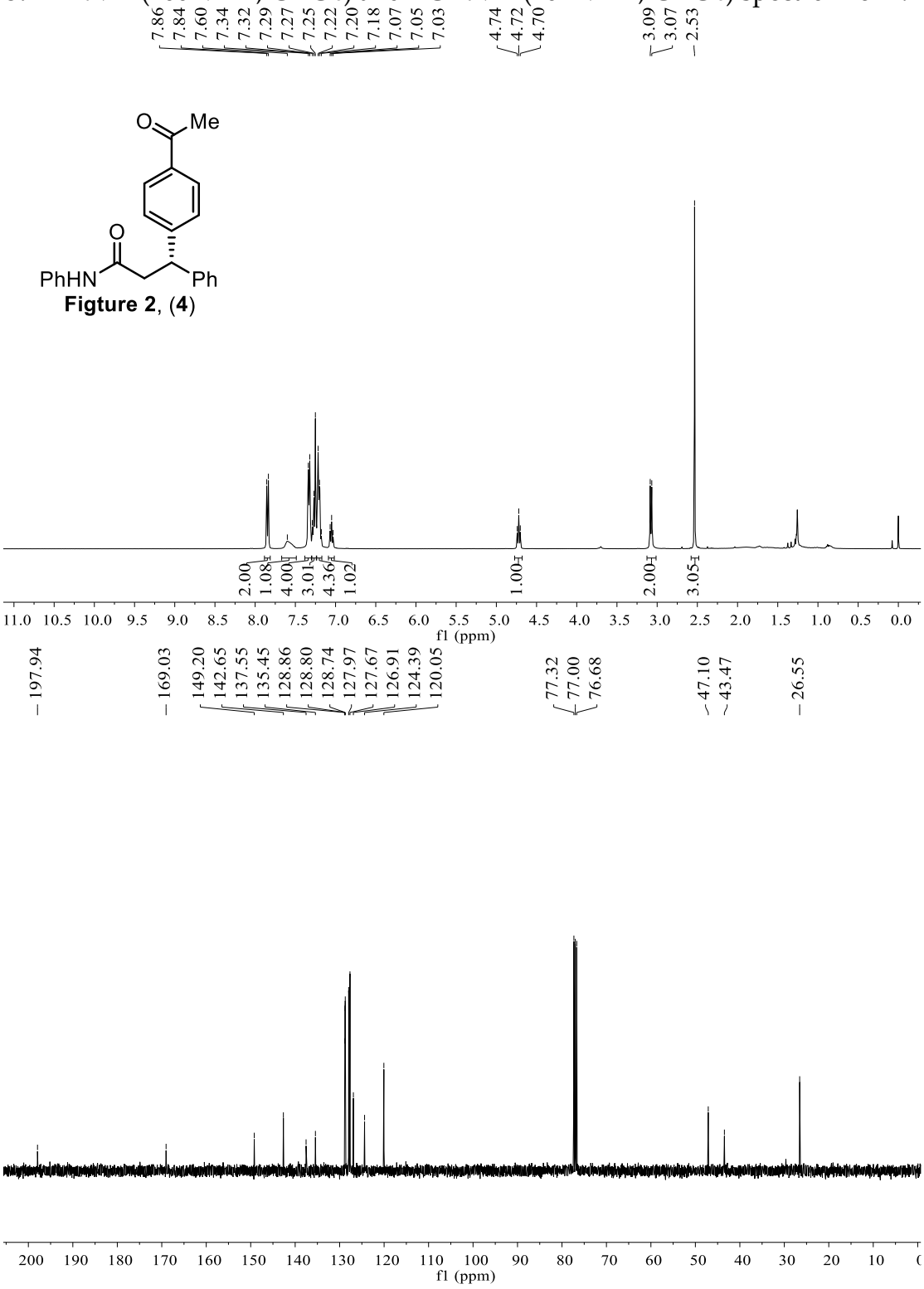


Figure S-6. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5**.

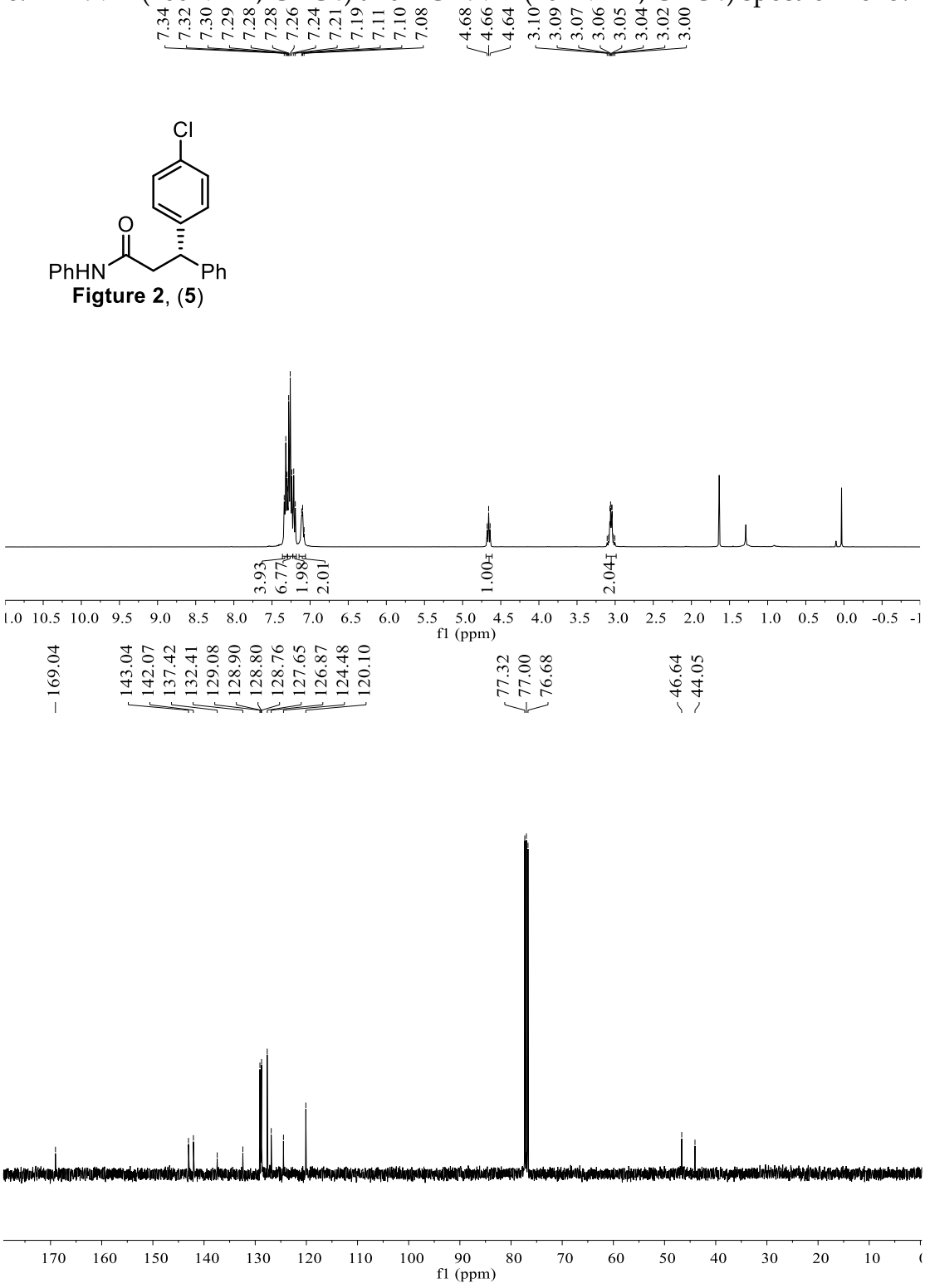


Figure S-7. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **6**.

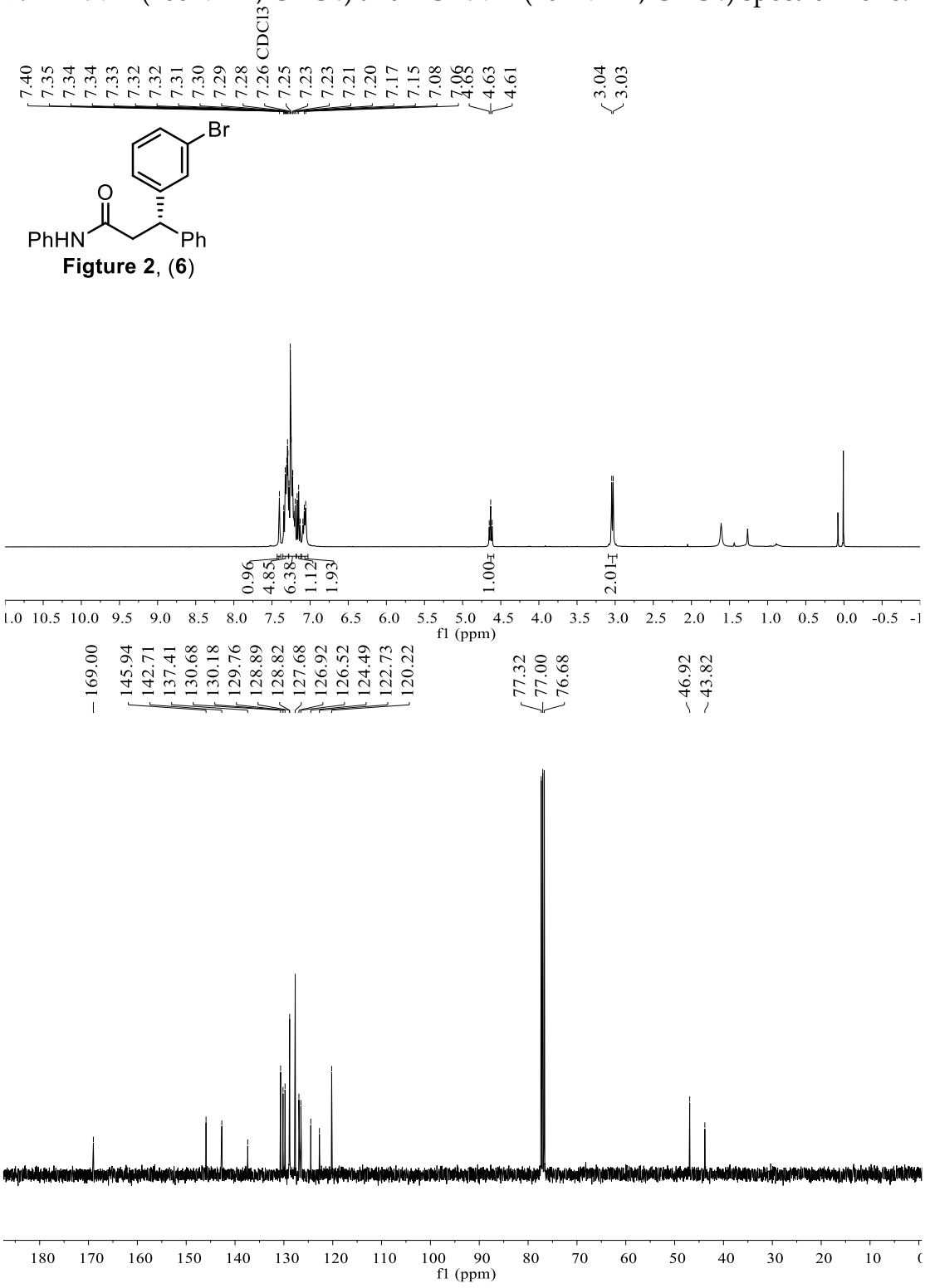


Figure S-8. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **7**.

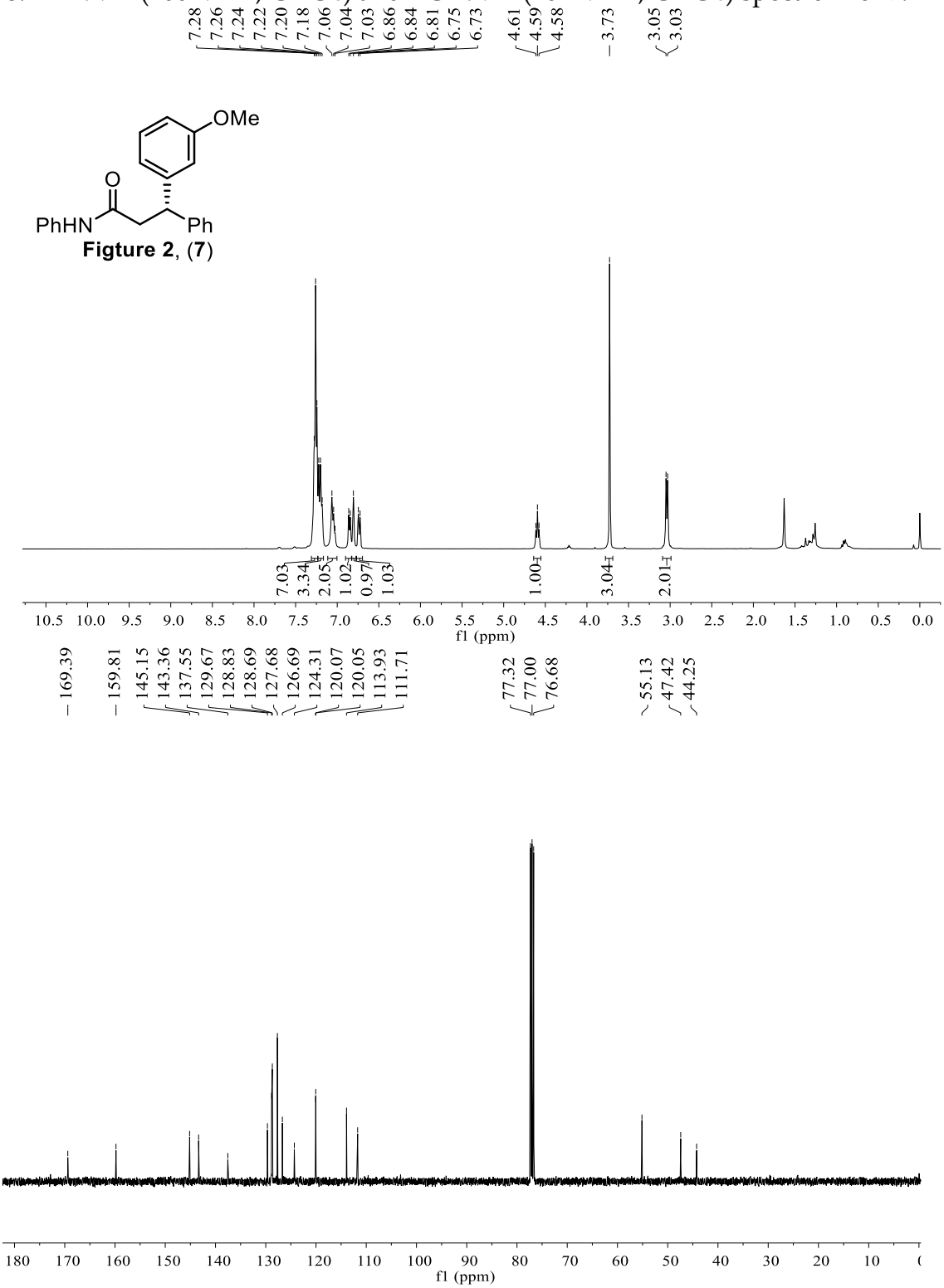


Figure S-9. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **8**.

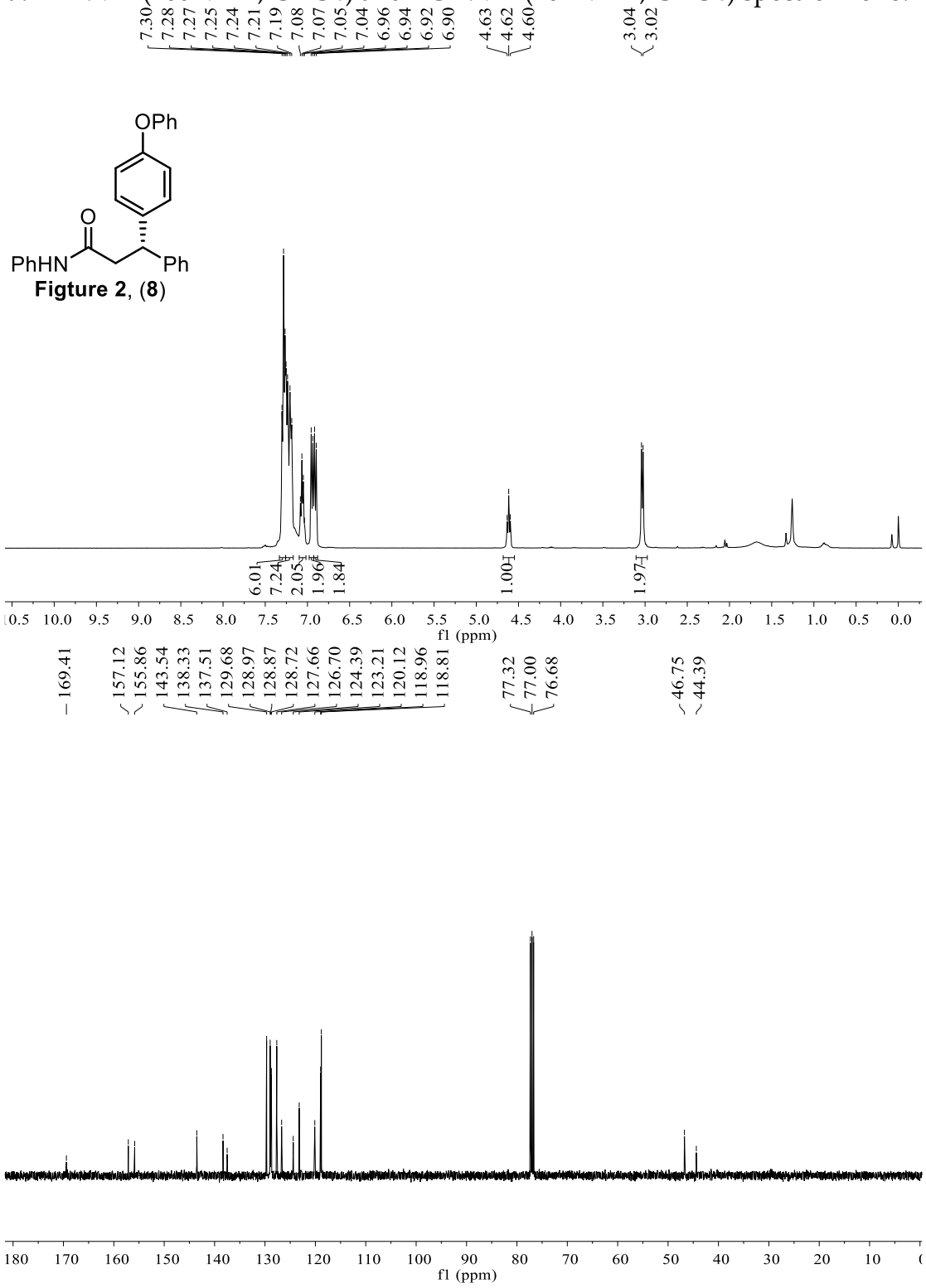


Figure S-10. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **9**.

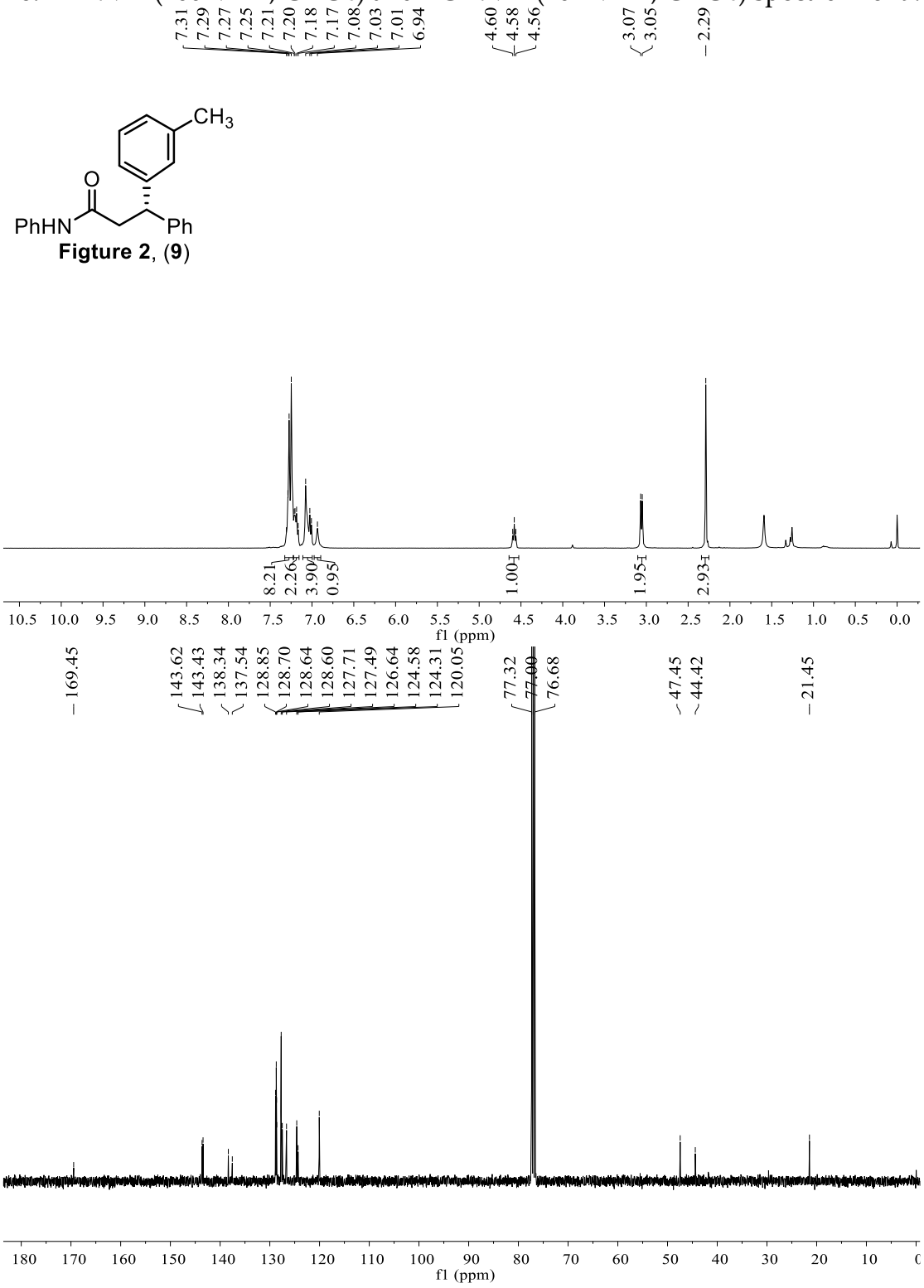


Figure S-11. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **10**.

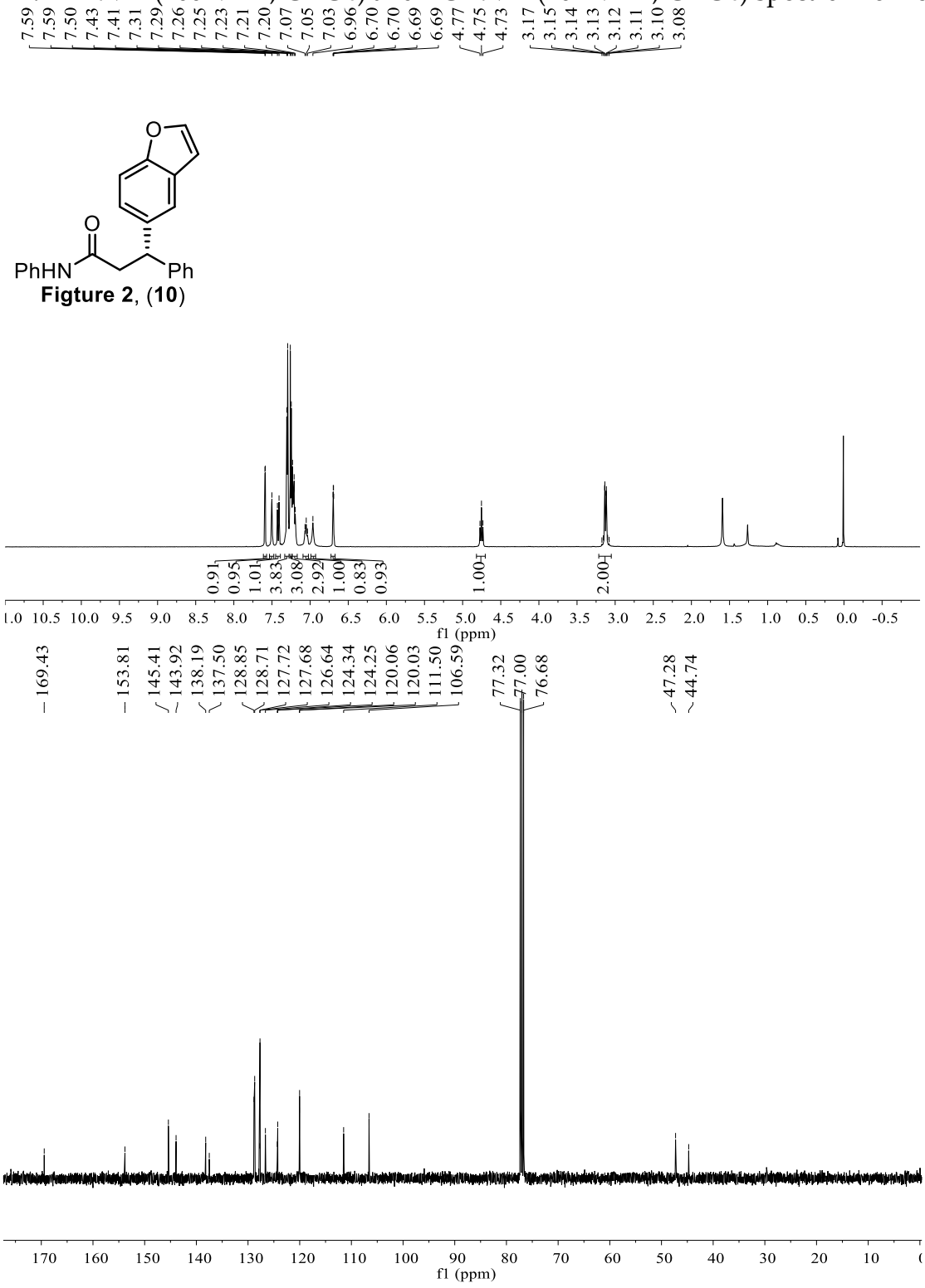


Figure S-12. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **11**.

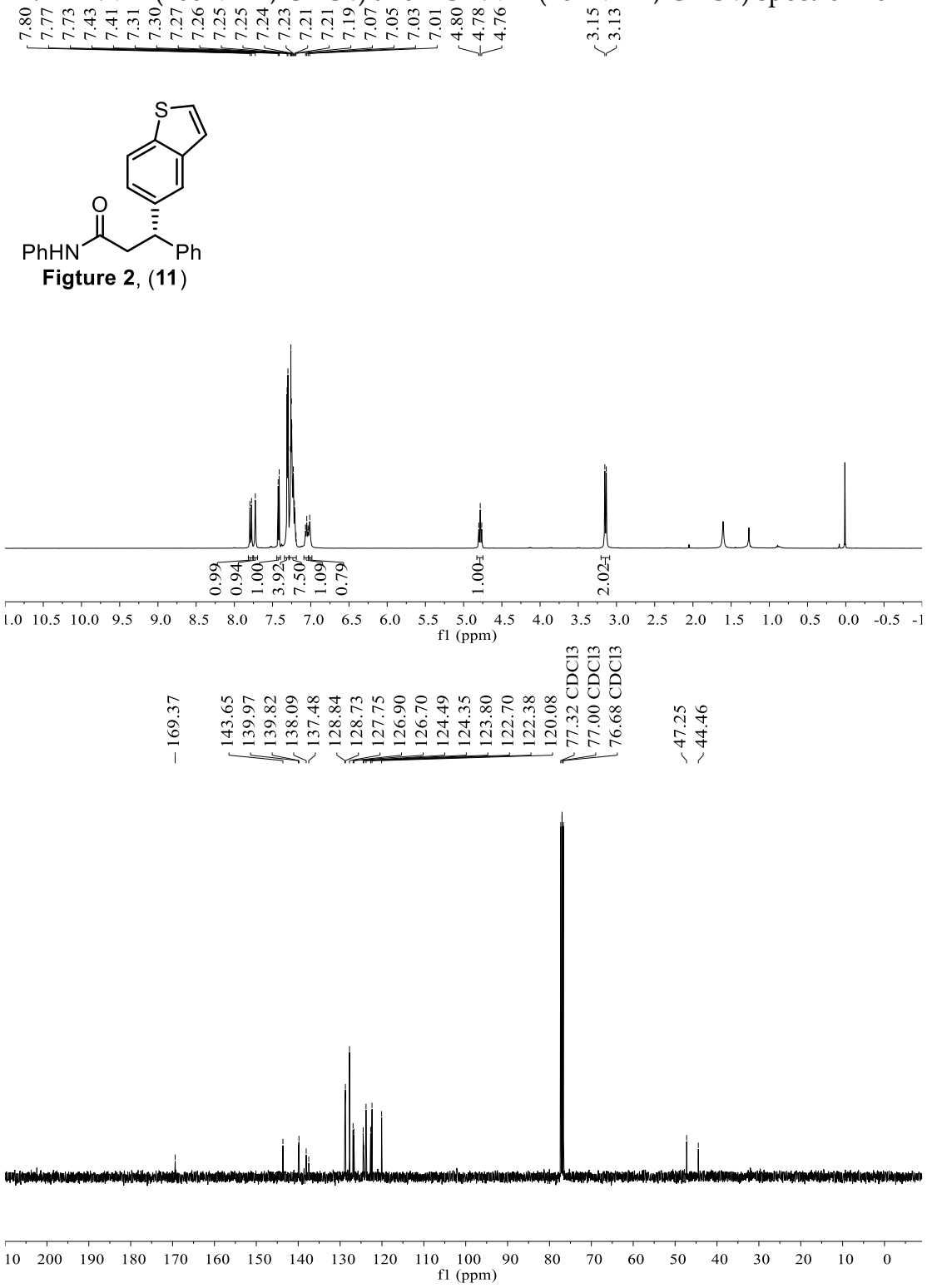


Figure S-13. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **12**.

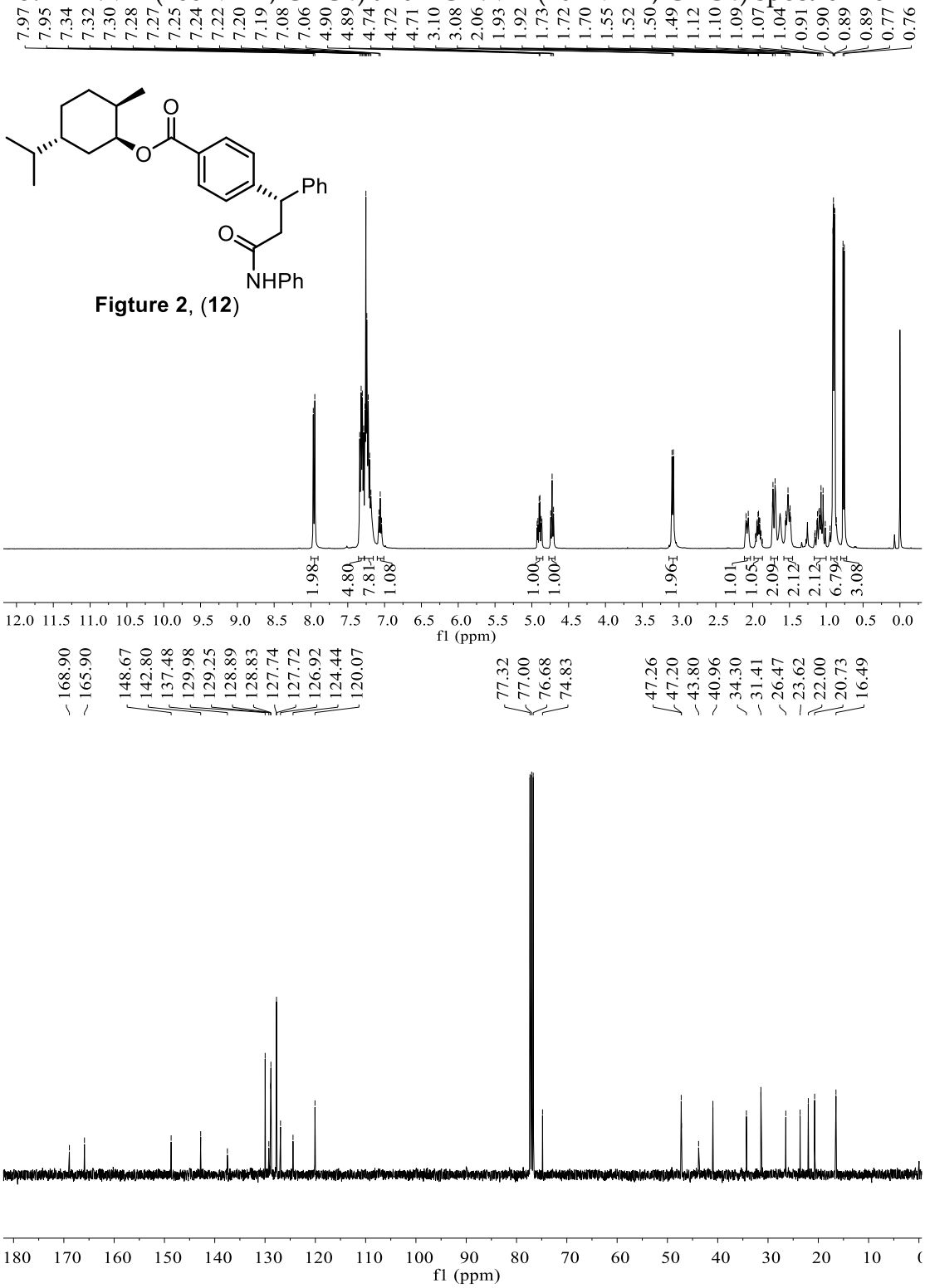
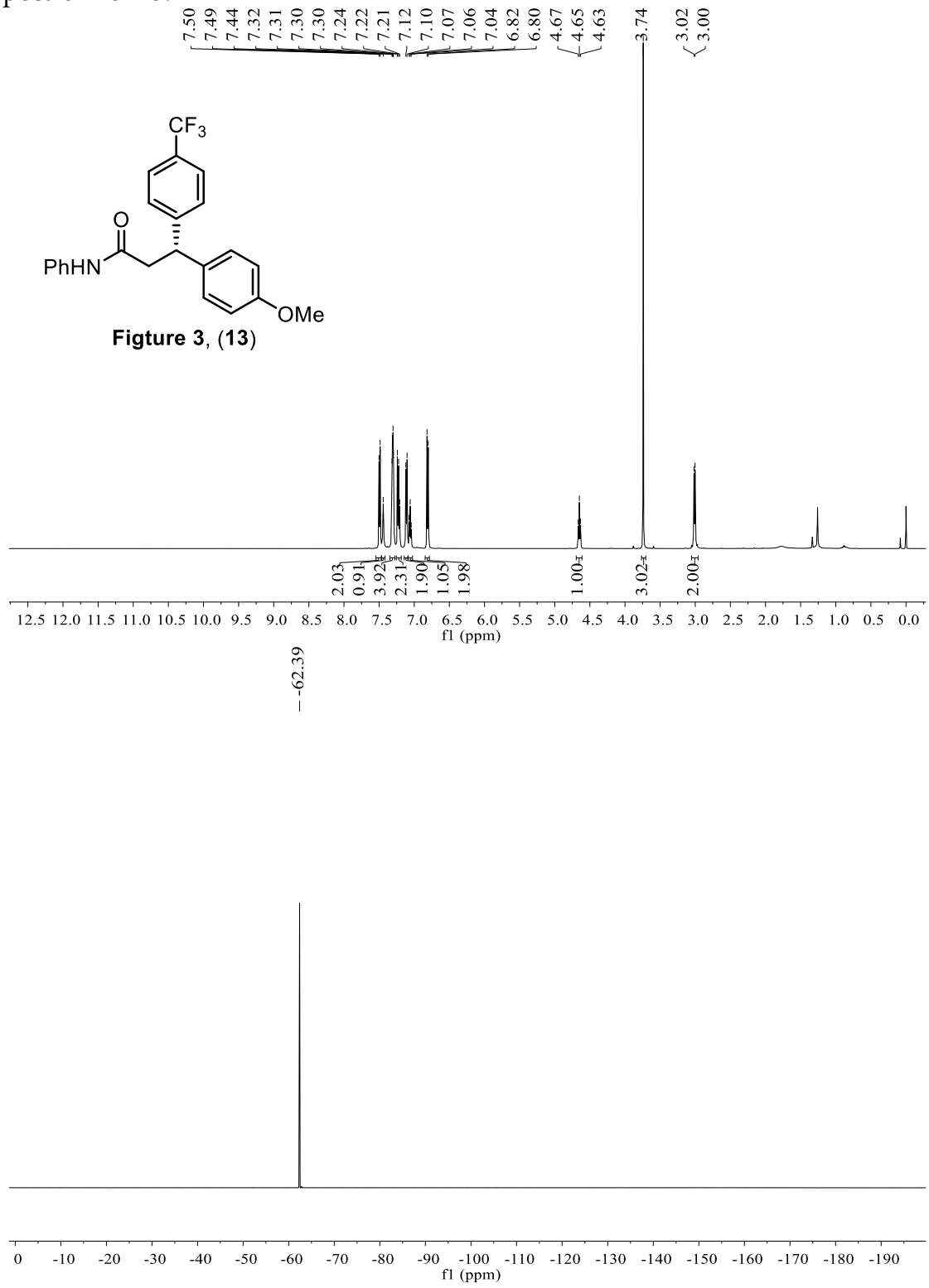
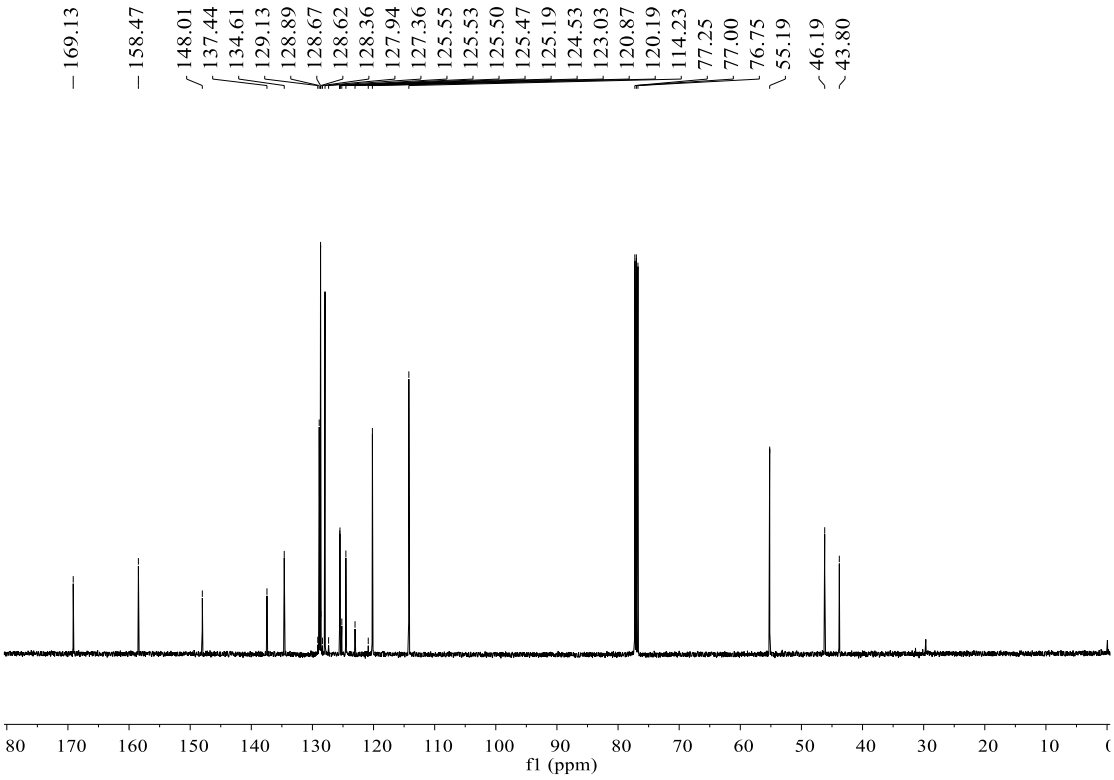


Figure S-14. ^{1}H NMR (500 MHz, $CDCl_3$), ^{19}F NMR (471 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **13**.

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128.67
128.62
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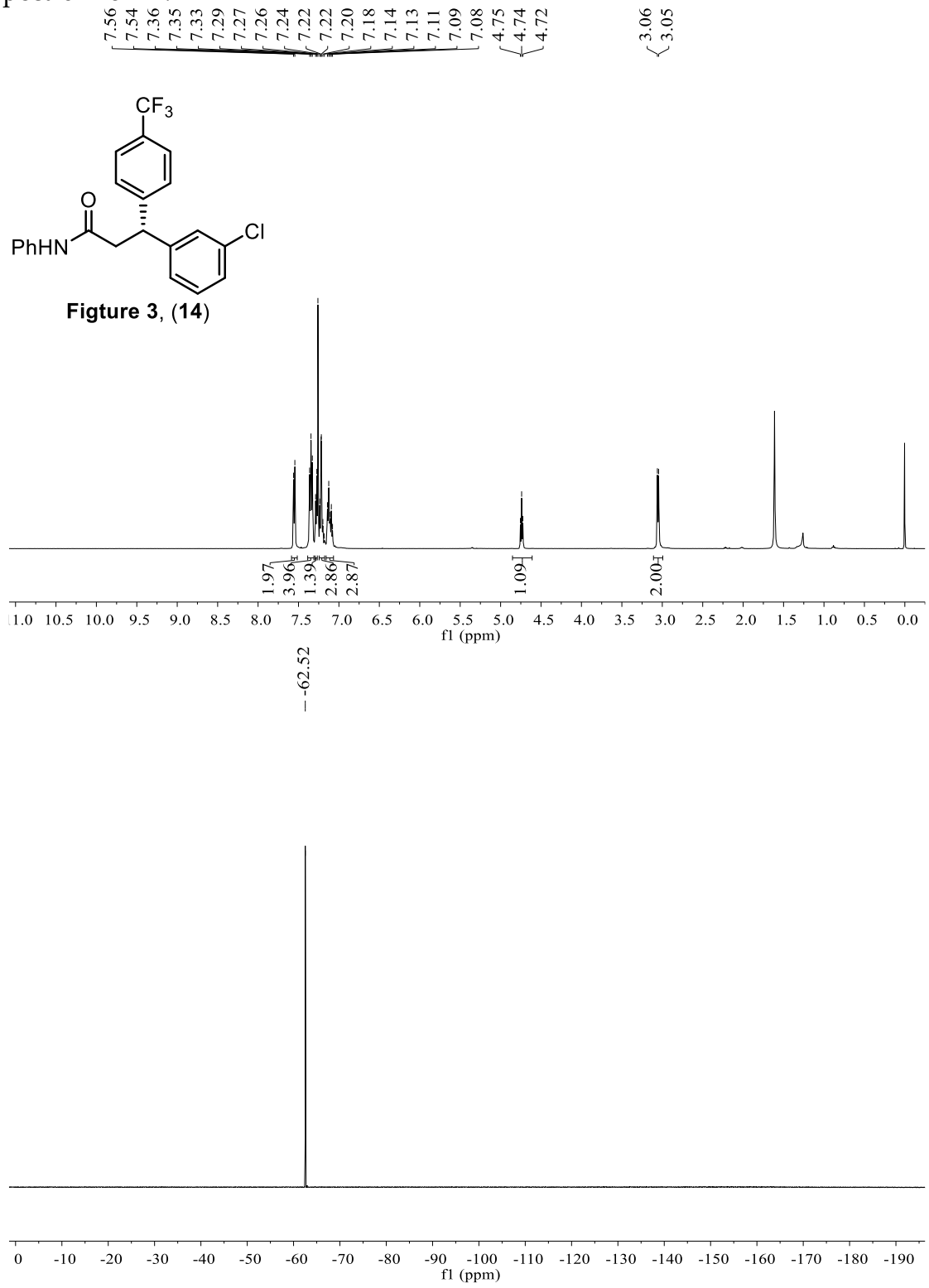
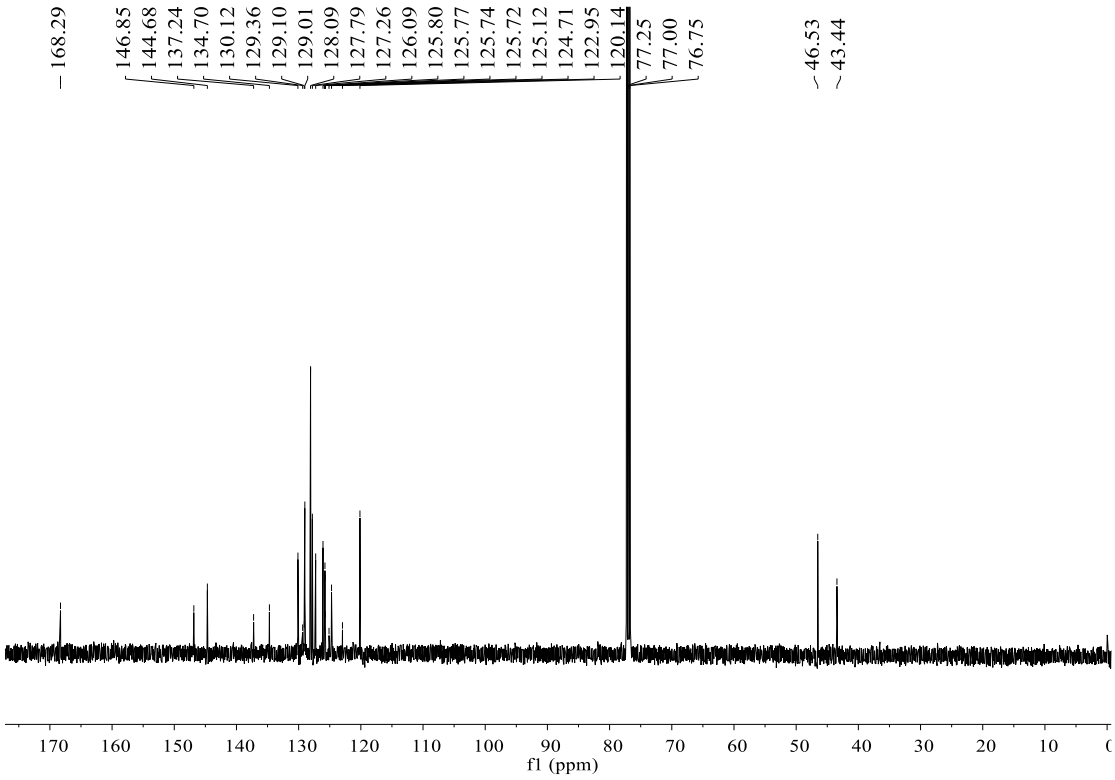
127.94
127.36
125.55
125.53
125.50
125.47
125.19
124.53
123.03
120.87
120.19
114.23
77.25
77.00
76.75
55.19
46.19
43.80
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Figure S-15. ^{1}H NMR (500 MHz, $CDCl_3$), ^{19}F NMR (471 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **14**.

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126.09
125.80
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125.74
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125.12
124.71
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120.14
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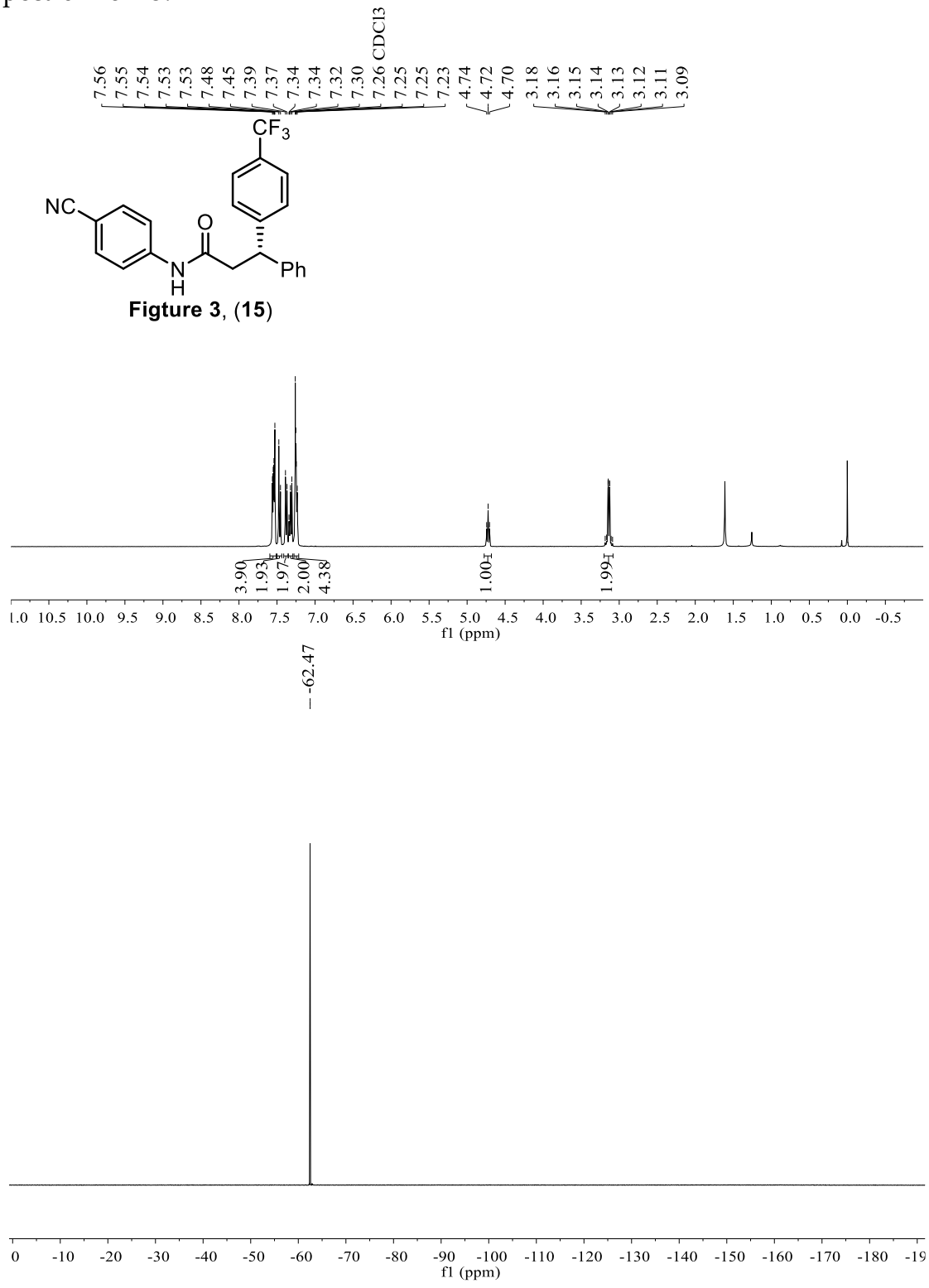
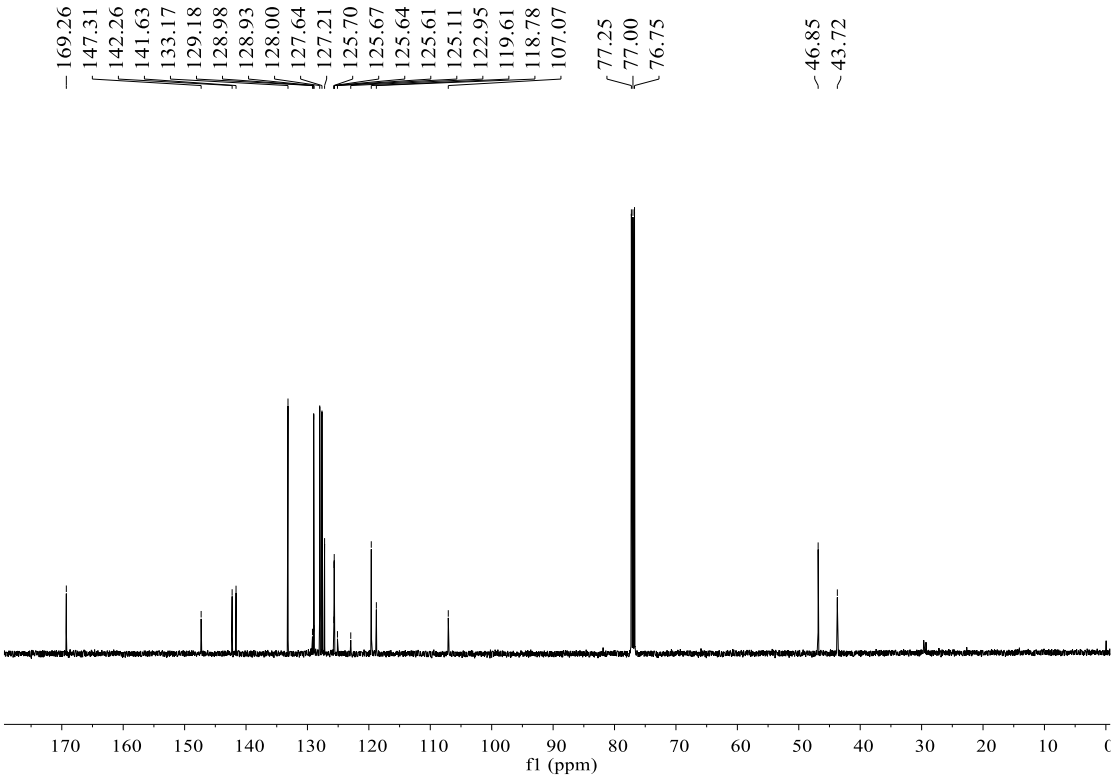
77.00
76.75
46.53
43.44
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Figure S-16. ^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (471 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **15**.




169.26
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133.17
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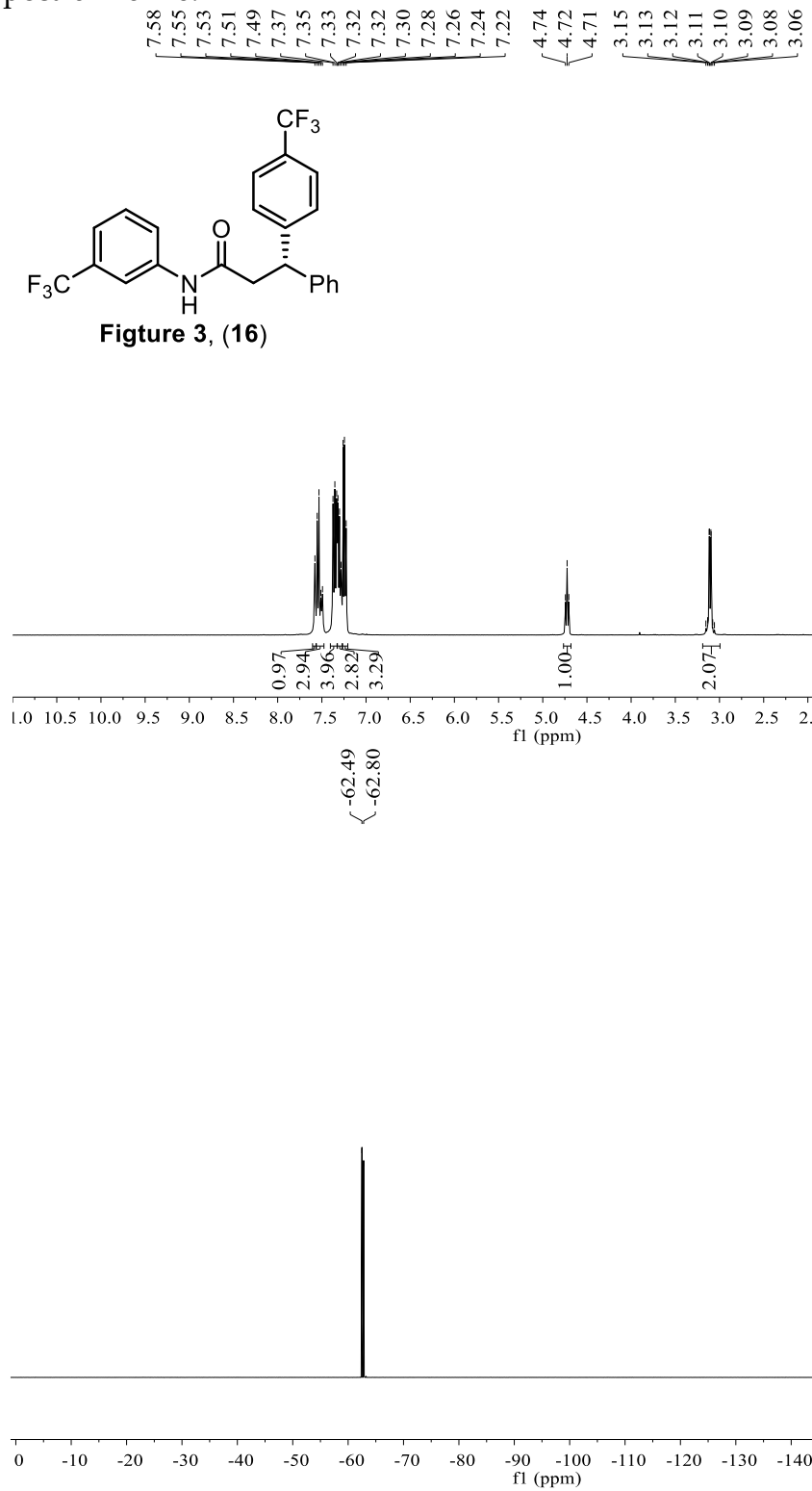
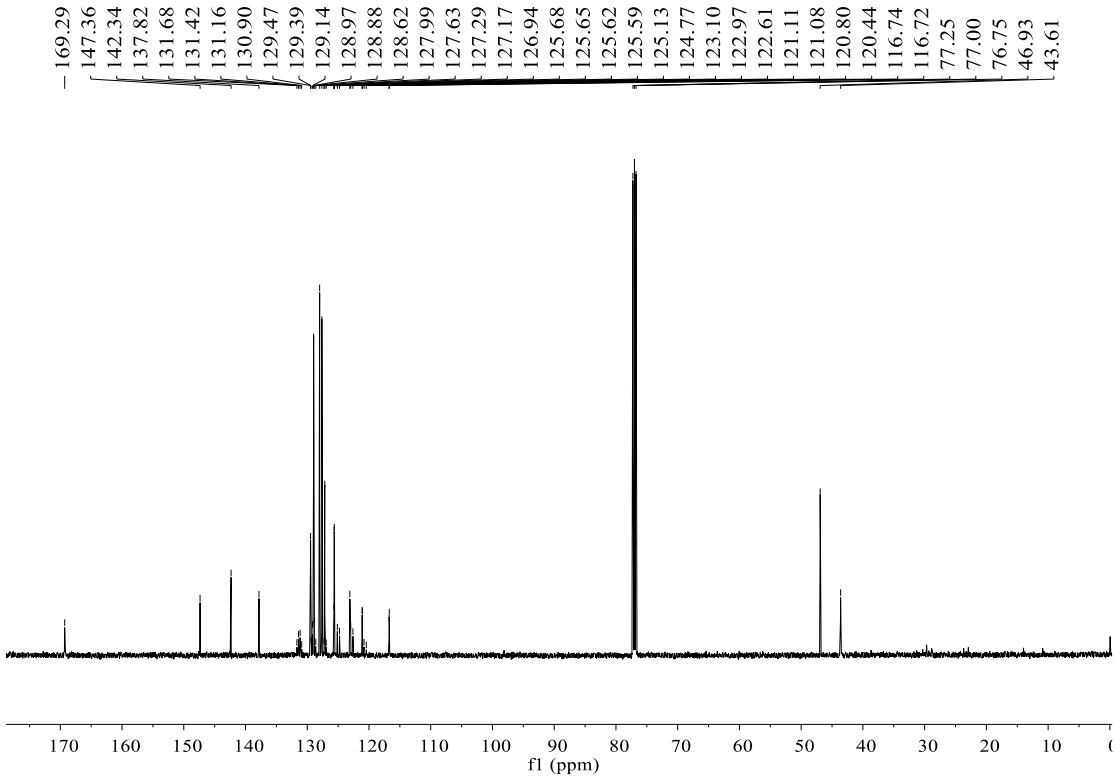
128.93
128.00
127.64
127.21
125.70
125.67
125.64
125.61
125.11
122.95
119.61
118.78
107.07
77.25
77.00
76.75
46.85
43.72
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Figure S-17. ^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (471 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **16**.

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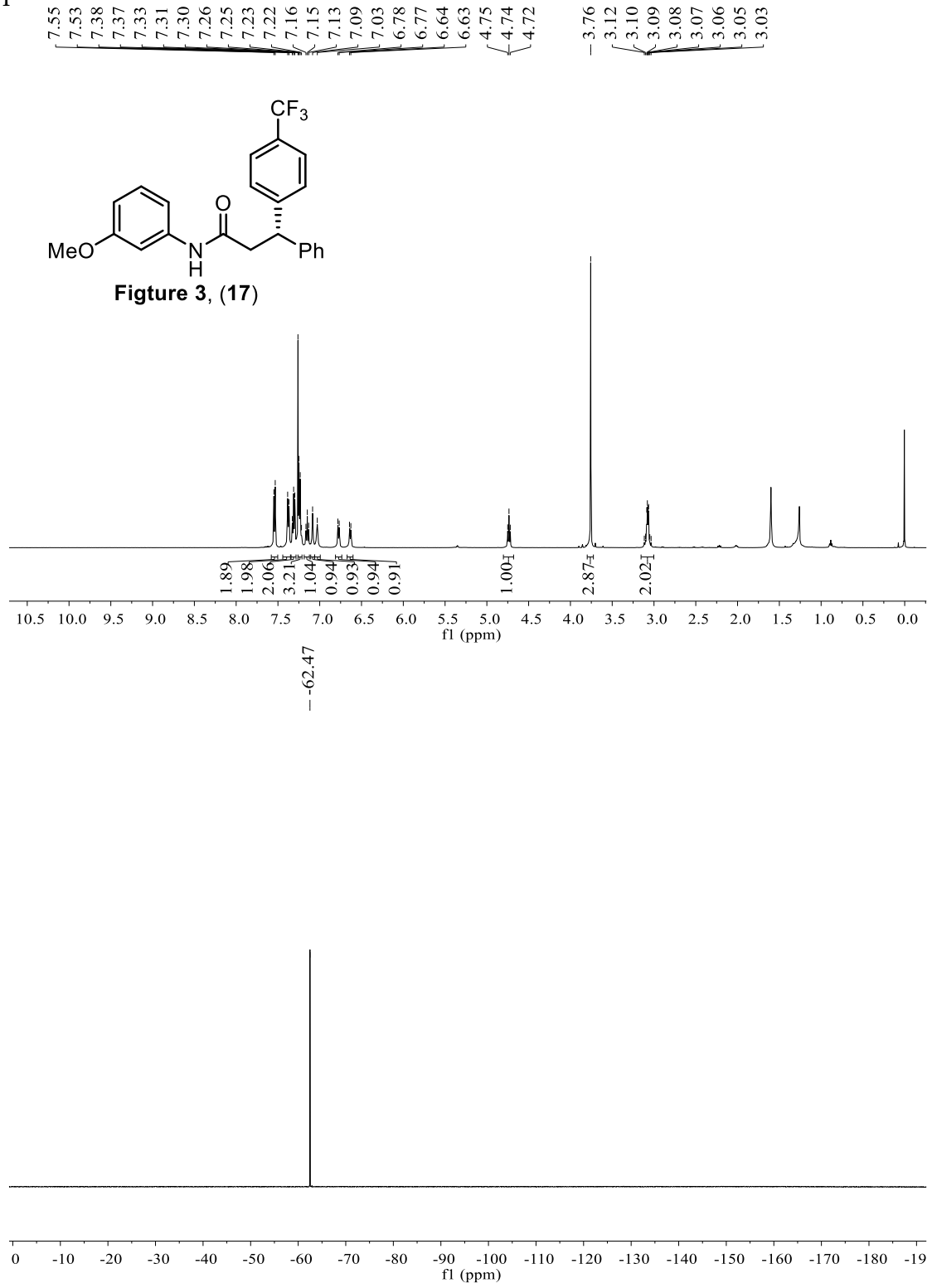
142.34
137.82
131.68
131.42
131.16
130.90
129.47
129.39
129.14
128.97
128.88
128.62
127.99
127.63
127.29
127.17
126.94
125.68
125.65
125.62
125.59
125.13
124.77
123.10
122.97
122.61
121.11
121.08
120.80
120.44
116.74
116.72
77.25
77.00
76.75
46.93
43.61
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Figure S-18. ^{1}H NMR (500 MHz, $CDCl_3$), ^{19}F NMR (471 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **17**.



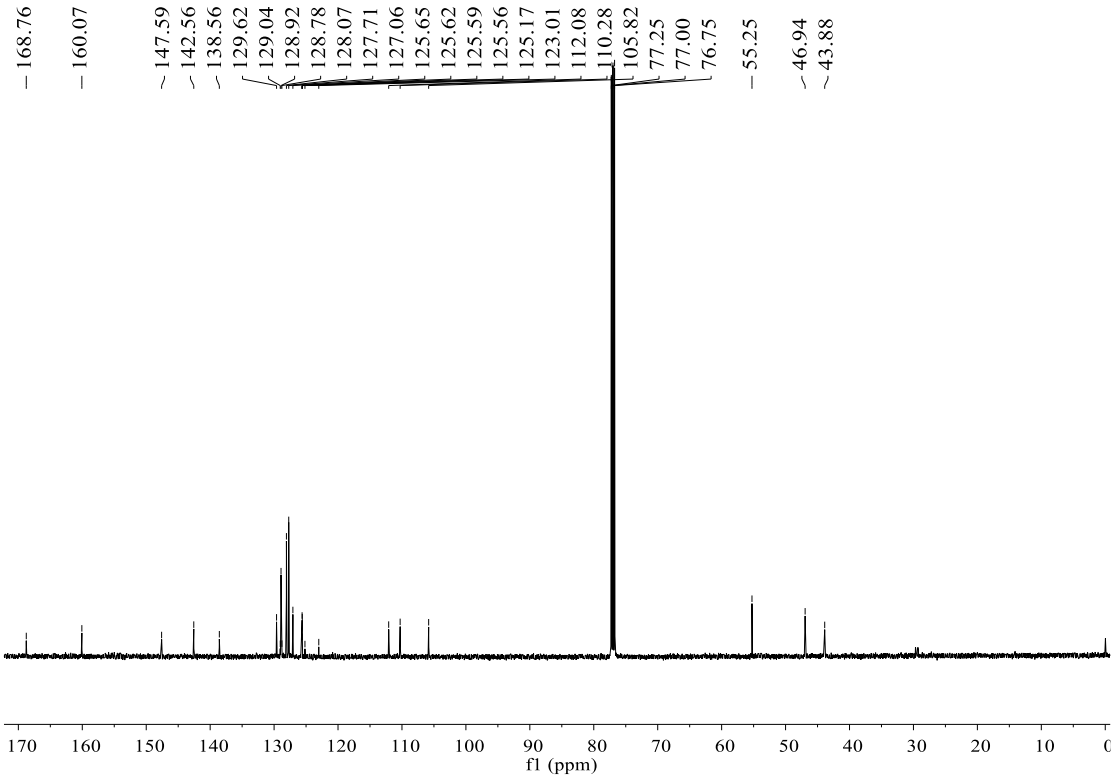
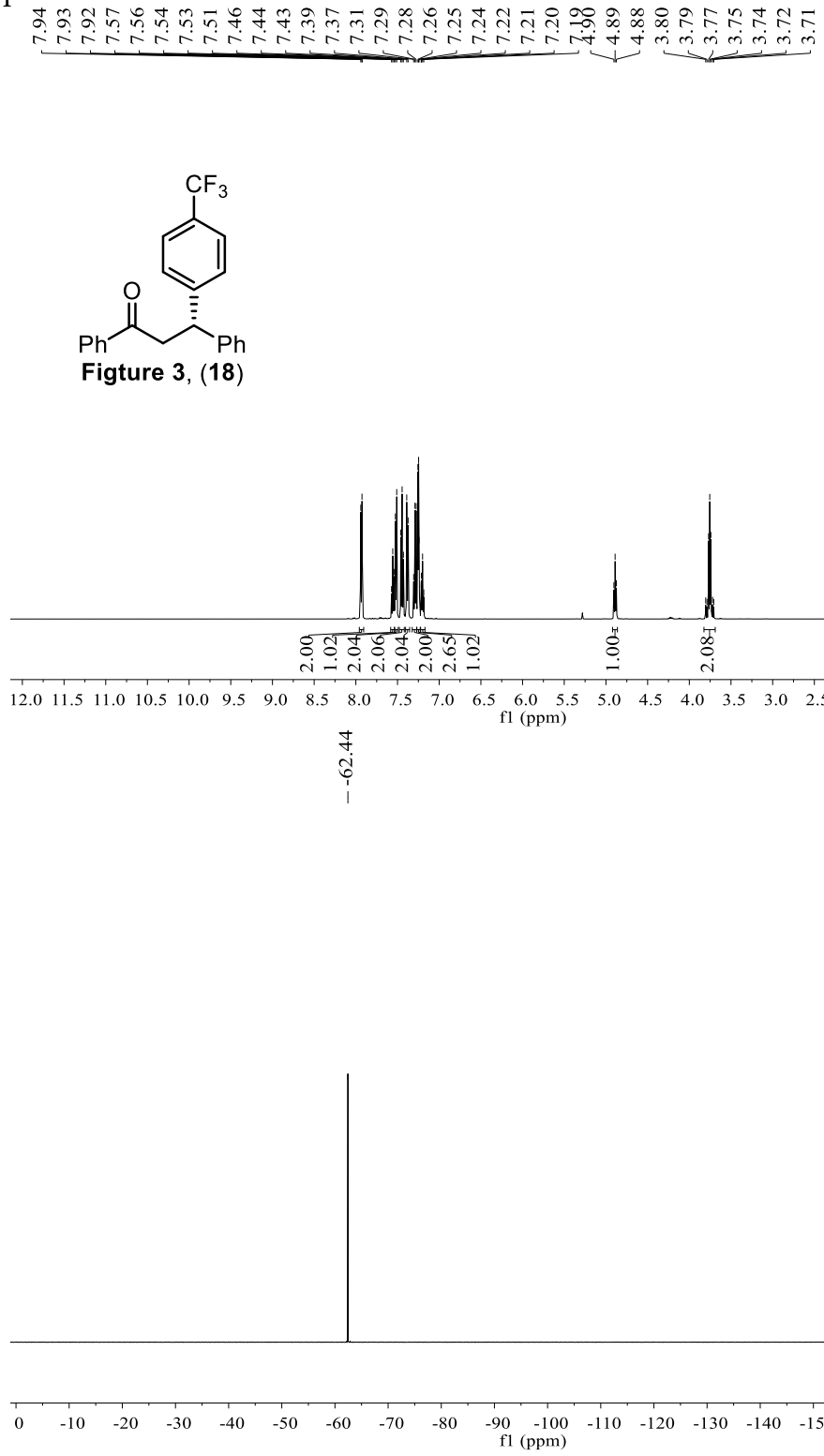

168.76
160.07
147.59
142.56
138.56
129.62
129.04
128.92
128.78
128.07
127.71
127.06
125.65
125.62
125.59
125.56
125.17
123.01
112.08
110.28
105.82
77.25
77.00
76.75
55.25
46.94
43.88
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Figure S-19. ^{1}H NMR (500 MHz, $CDCl_3$), ^{19}F NMR (471 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **18**.



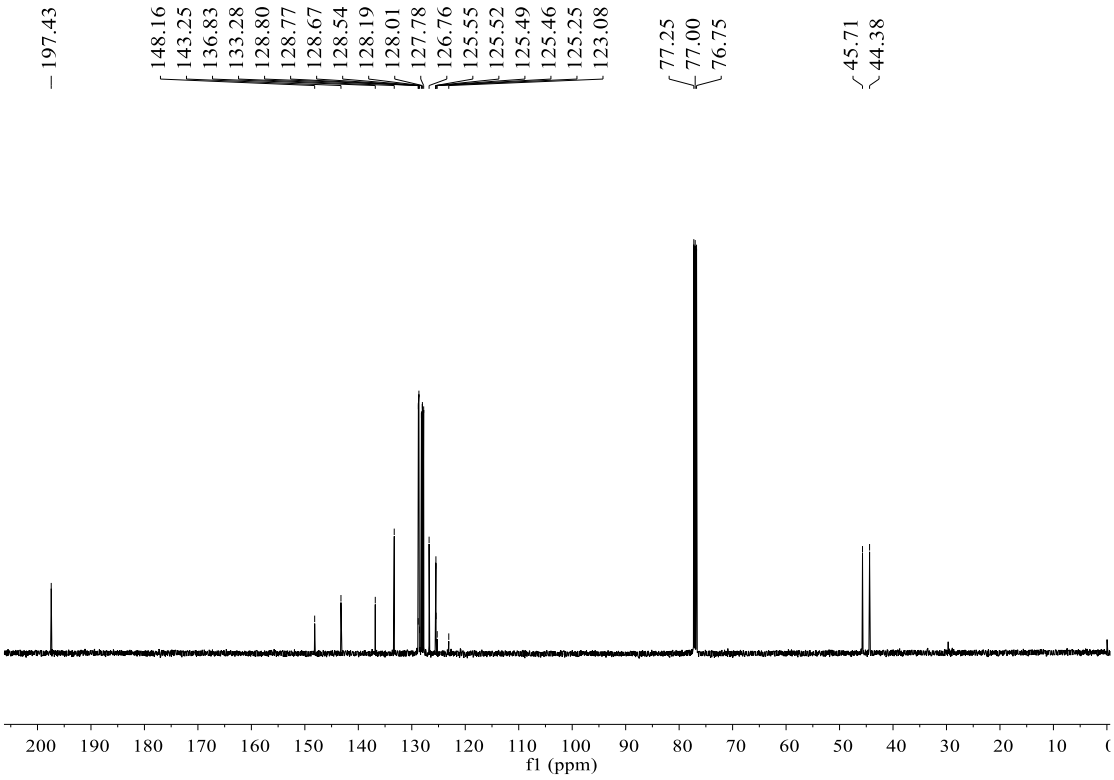
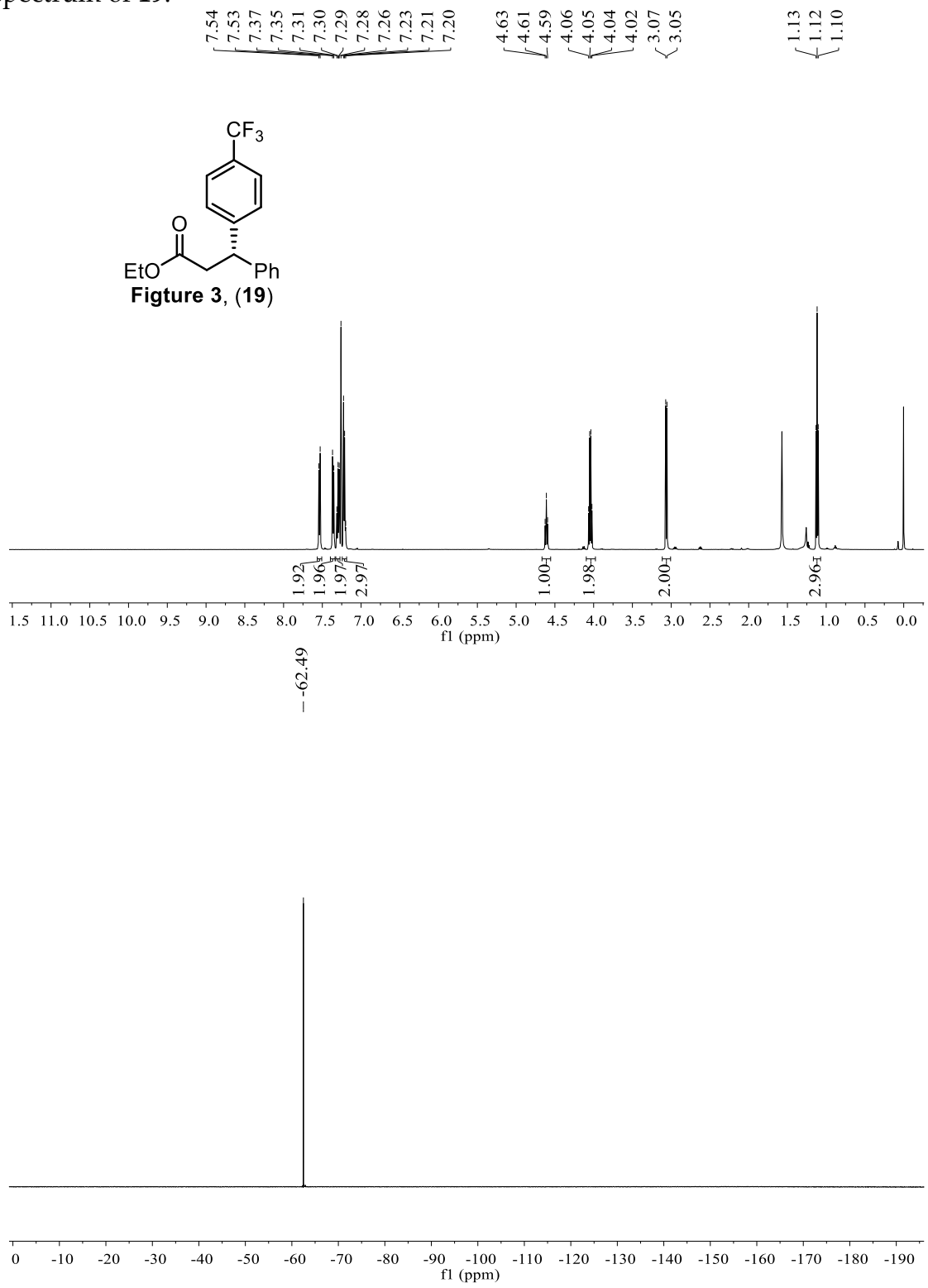

197.43
148.16
143.25
136.83
133.28
128.80
128.77
128.67
128.54
128.19
128.01
127.78
126.76
125.55
125.52
125.49
125.46
125.25
123.08
77.25
77.00
76.75
45.71
44.38
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Figure S-20. ^{1}H NMR (500 MHz, $CDCl_3$), ^{19}F NMR (471 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **19**.



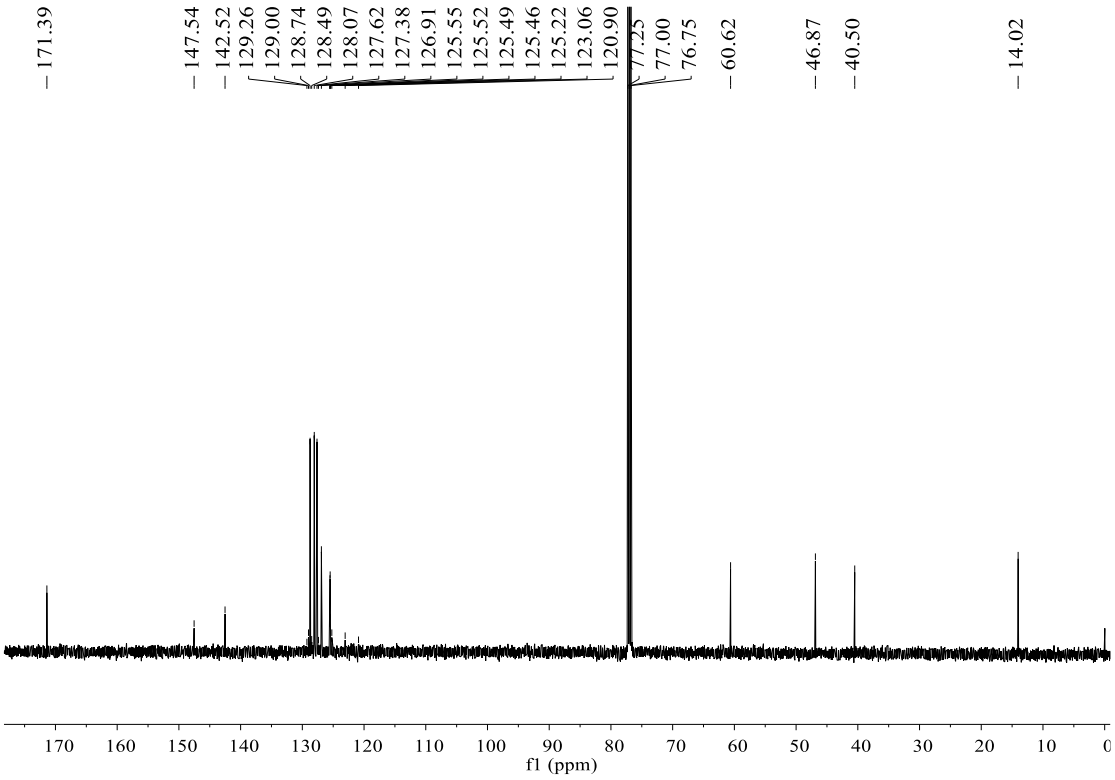
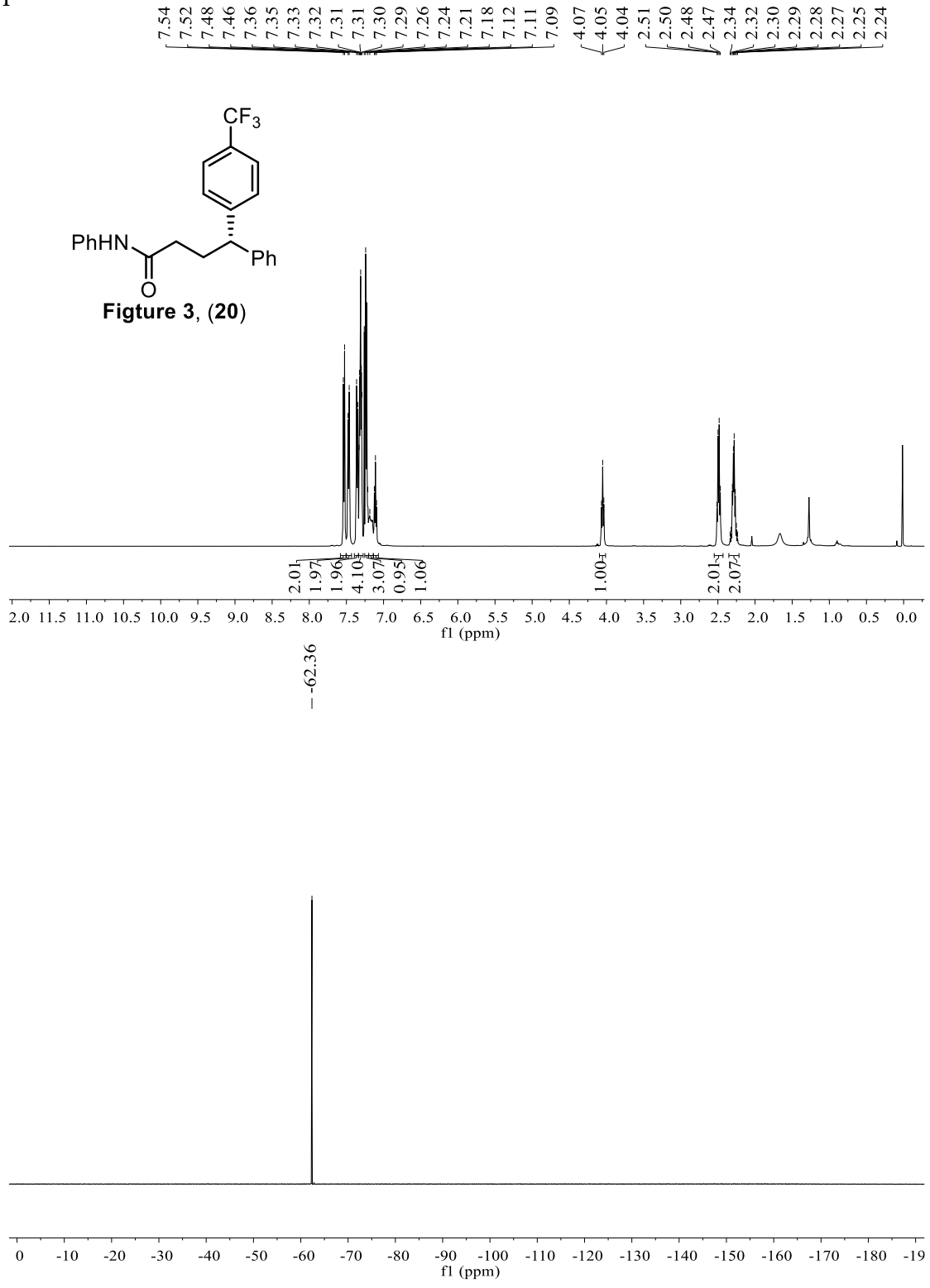

171.39
147.54
142.52
129.26
129.00
128.74
128.49
128.07
127.62
127.38
126.91
125.55
125.52
125.49
125.46
125.22
123.06
120.90
77.25
77.00
76.75
60.62
46.87
40.50
14.02
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Figure S-21. ^{1}H NMR (500 MHz, $CDCl_3$), ^{19}F NMR (471 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **20**.



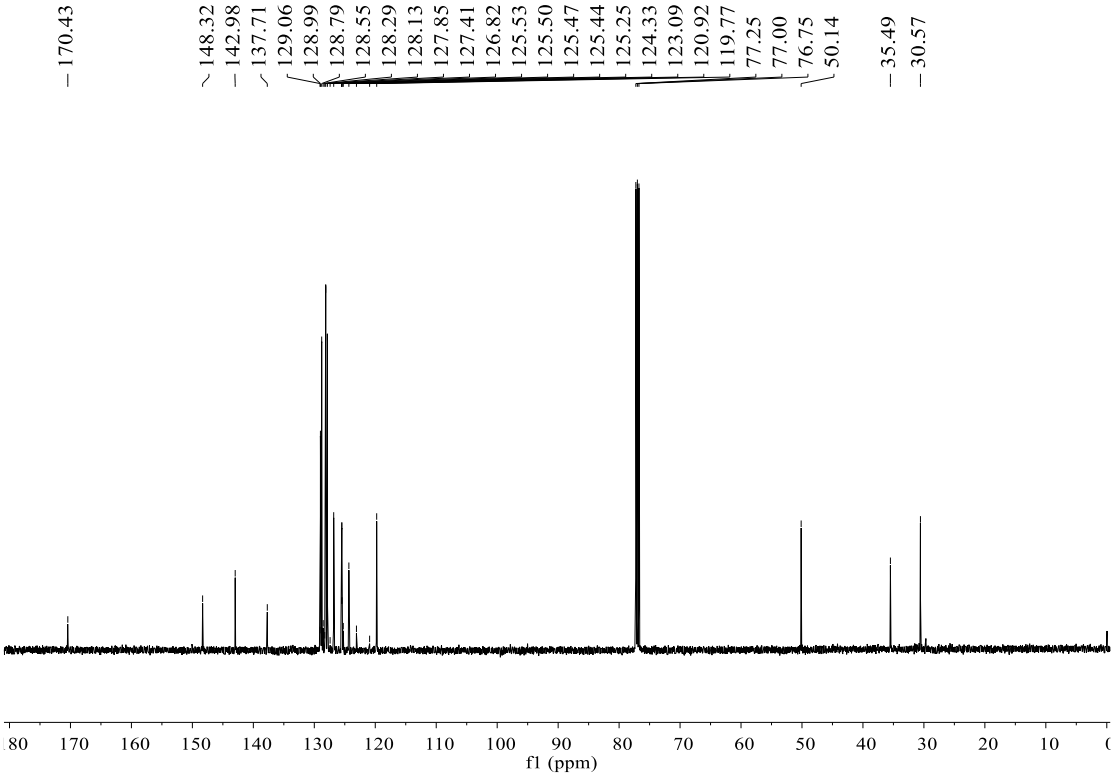

170.43
148.32
142.98
137.71
129.06
128.99
128.79
128.55
128.29
128.13
127.85
127.41
126.82
125.53
125.50
125.47
125.44
125.25
124.33
123.09
120.92
119.77
77.25
77.00
76.75
50.14
35.49
30.57
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Figure S-22. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **21**.

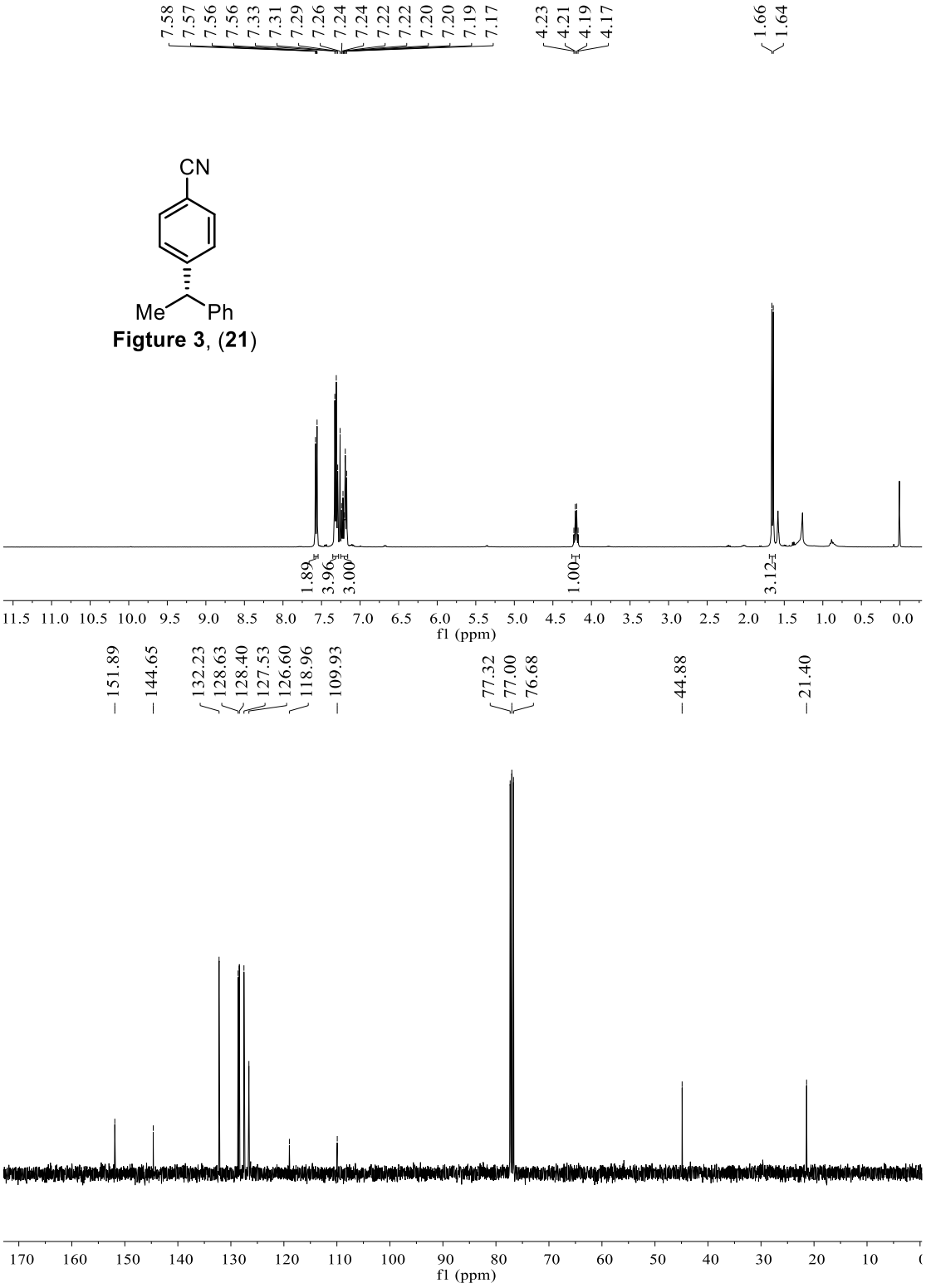
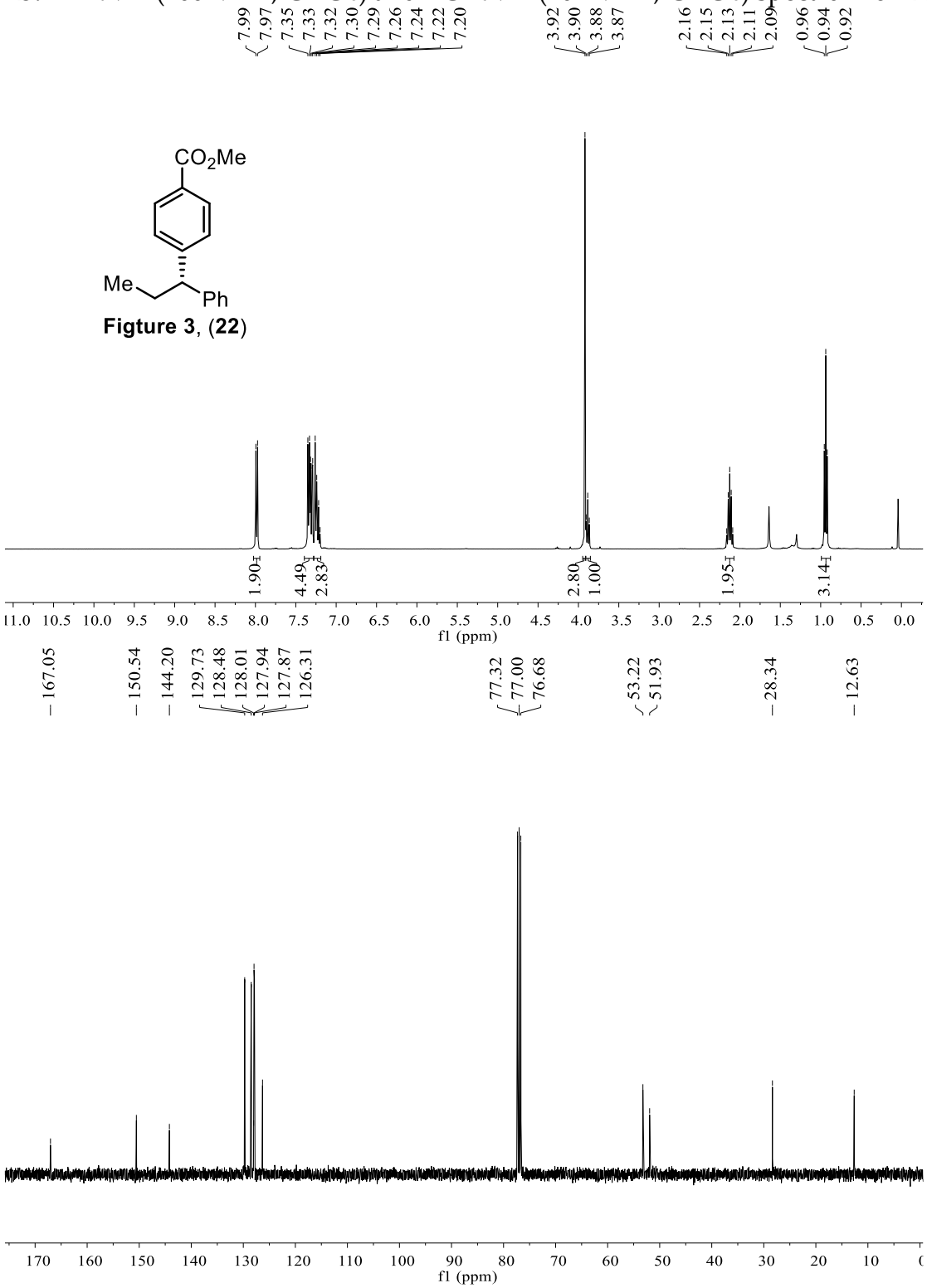
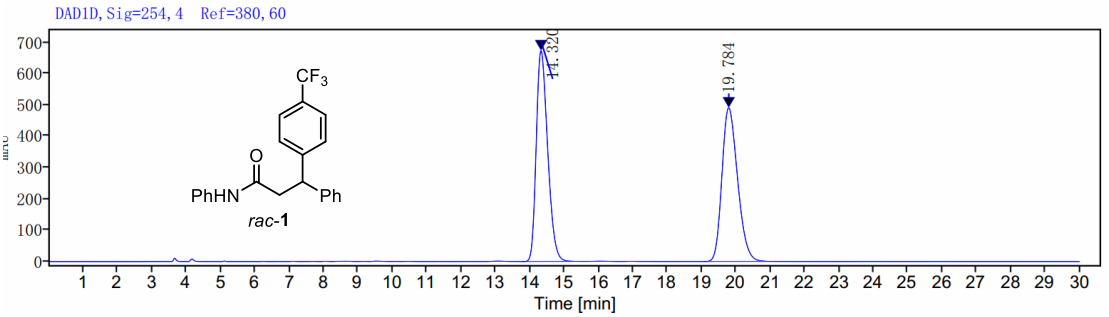


Figure S-23. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **22**.

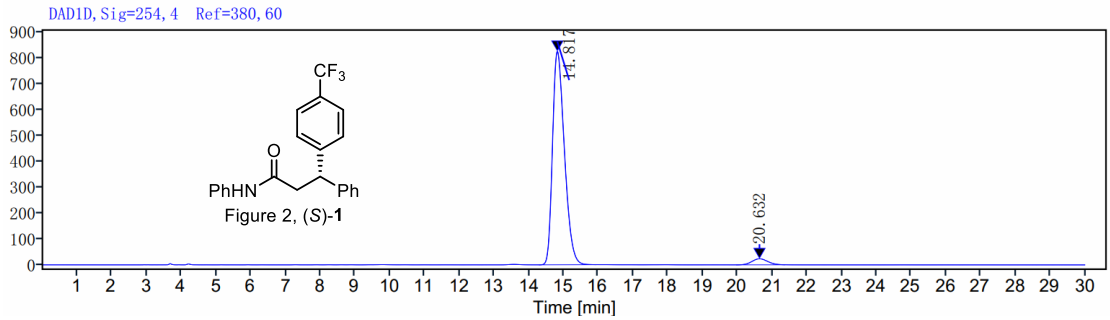


Stereoselectivity Analysis



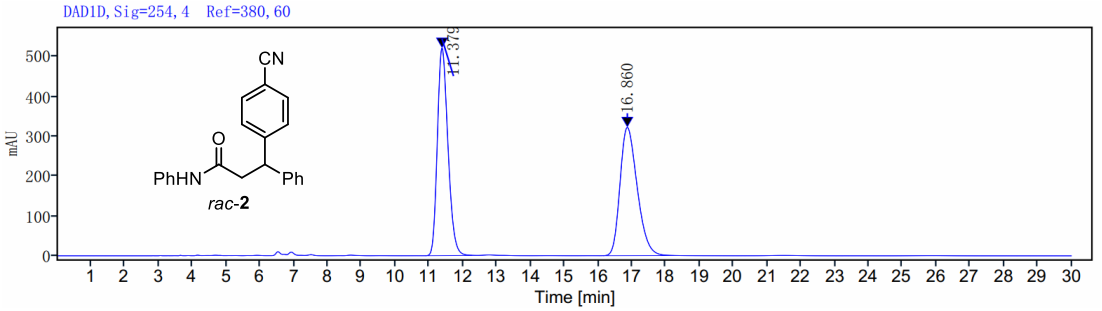
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
14.320	BV	1.48591	15518.98308	673.68148	49.9787
19.784	VV	1.98347	15532.24152	491.07964	50.0213
		Totals	31051.22461		



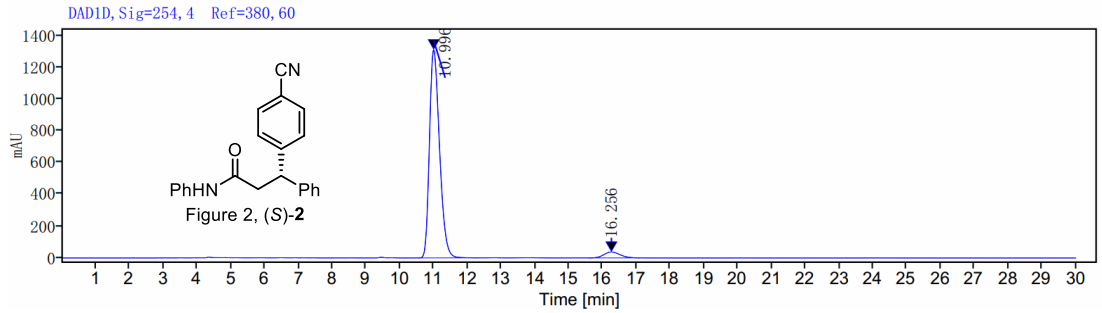
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
14.817	VV	1.65778	19705.60160	829.35339	96.3214
20.632	VV	1.40795	752.56651	23.66553	3.6786
		Totals	20458.16812		



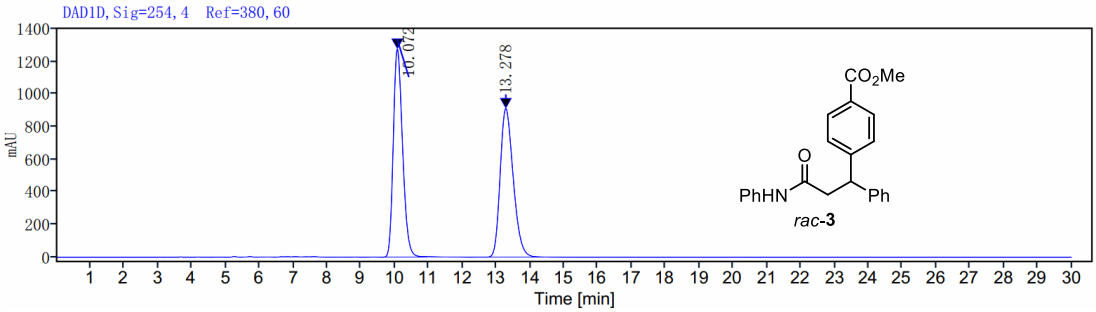
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
11.379	VV	1.38485	11372.25495	521.72878	49.9468
16.860	VV	2.09568	11396.50018	322.50223	50.0532
		Totals	22768.75513		



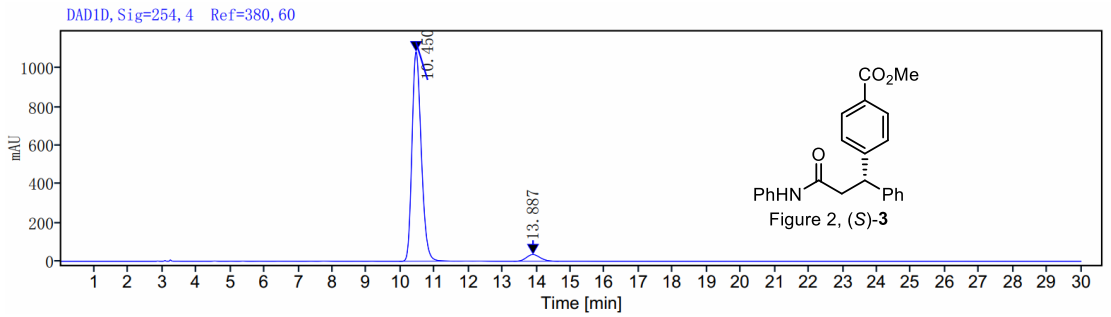
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
10.996	VV	1.78061	27110.84478	1309.63213	95.6312
16.256	BV	1.50979	1238.52823	37.38470	4.3688
		Totals	28349.37301		



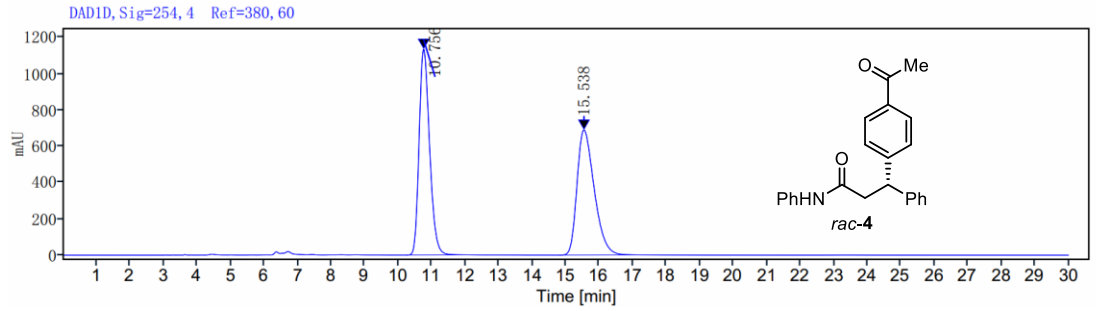
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
10.072	BV	1.35147	24343.43526	1277.32190	49.9018
13.278	VV	1.72275	24439.28550	912.15988	50.0982
		Totals	48782.72076		



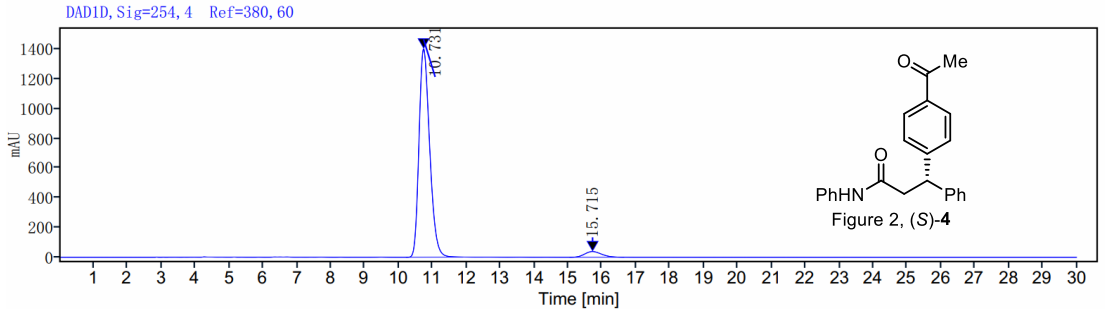
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
10.450	VV	1.63203	20610.60807	1088.16647	95.4552
13.887	VV	1.32305	981.30001	34.75820	4.5448
		Totals	21591.90808		



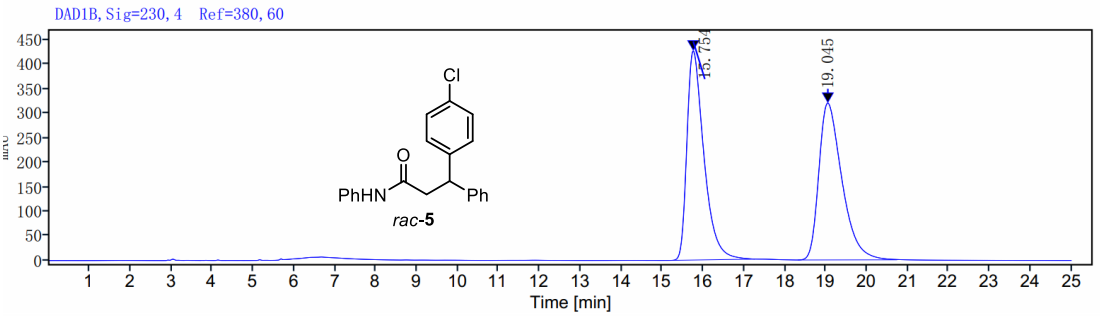
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
10.756	VV	1.65329	24609.23491	1135.67830	49.9875
15.538	VV	2.36668	24621.51224	690.23630	50.0125
		Totals	49230.74715		



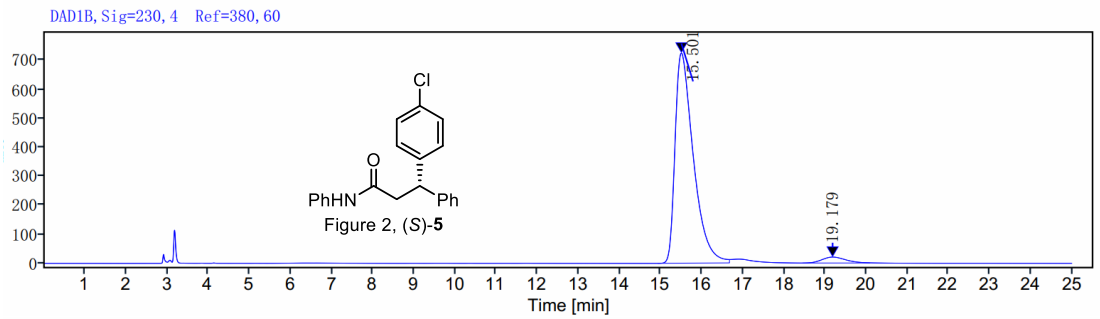
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
10.731	BV	1.68497	30654.59419	1403.88710	95.7724
15.715	VV	1.61296	1353.14550	38.63892	4.2276
		Totals	32007.73970		



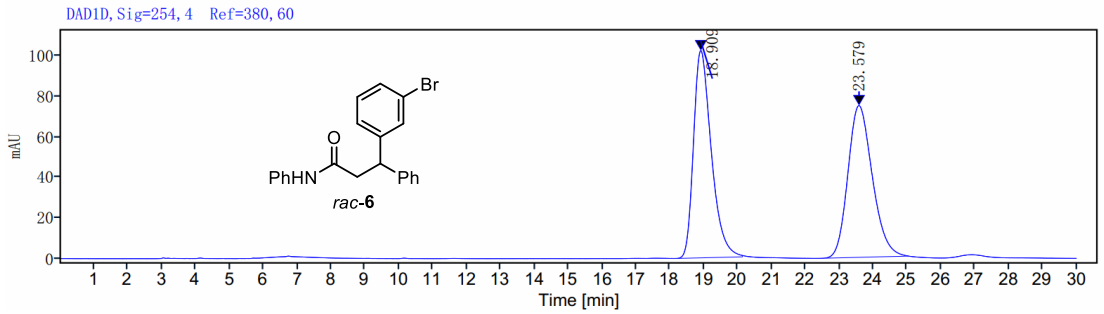
Signal: DAD1B, Sig=230, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
15.754	VV	2.05456	12330.81753	426.75818	49.5708
19.045	BV	2.42512	12544.35711	320.07727	50.4292
		Totals	24875.17464		



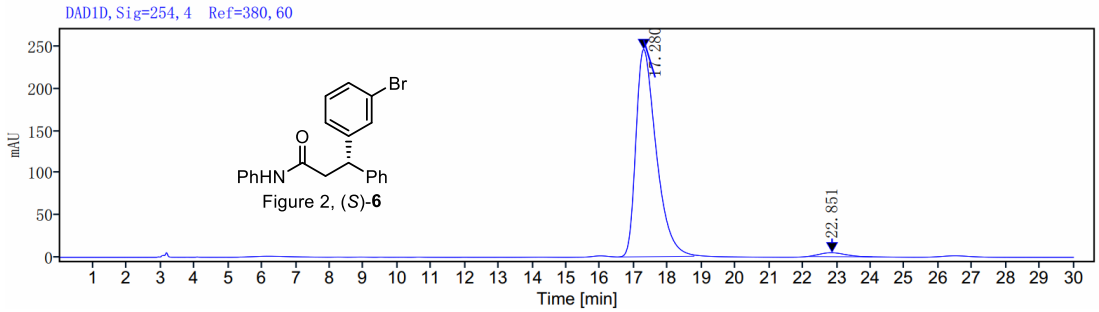
Signal: DAD1B, Sig=230, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
15.501	BV	1.74377	22377.55089	724.82930	96.4605
19.179	VV	1.63247	821.11943	20.46302	3.5395
		Totals	23198.67032		



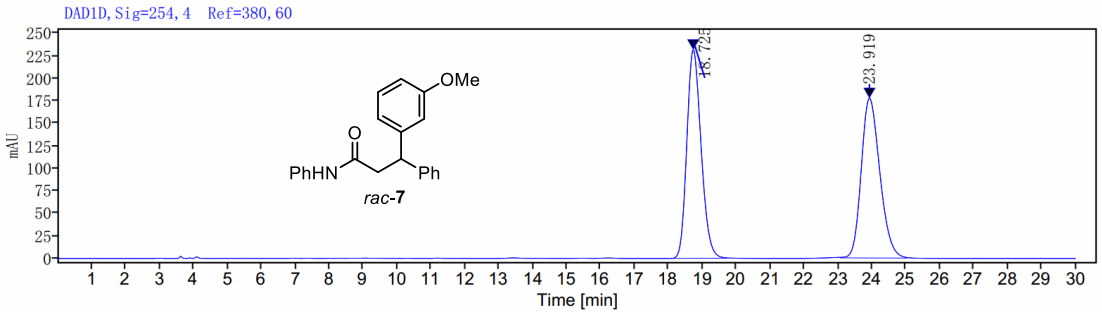
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
18.909	VV	1.92025	3738.25071	102.39640	49.9462
23.579	VV	2.43450	3746.30076	74.99918	50.0538
		Totals	7484.55147		



Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
17.280	VV	2.23128	10310.82566	246.81645	97.6602
22.851	MM m	1.92491	247.02981	4.68717	2.3398
		Totals	10557.85547		



Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
18.725	VV	1.63870	6765.72859	231.87251	50.0196
23.919	VV	1.98225	6760.43051	177.65379	49.9804
		Totals	13526.15909		

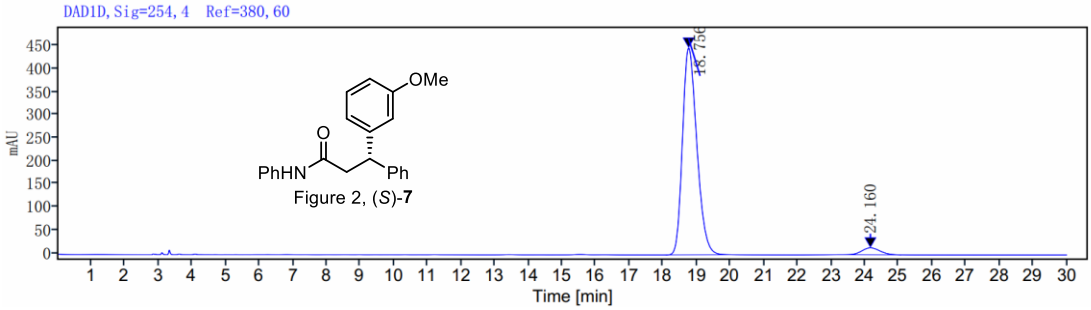
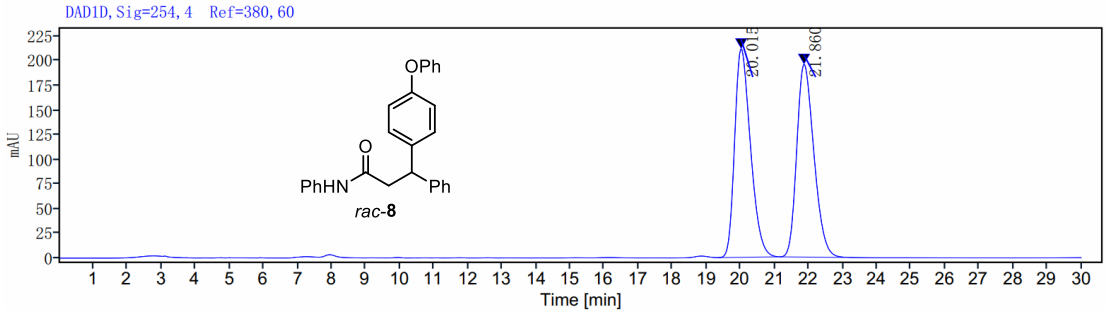


Figure 2, (*S*)-**7**

Signal: DAD1D, Sig=254, 4 Ref=380, 60

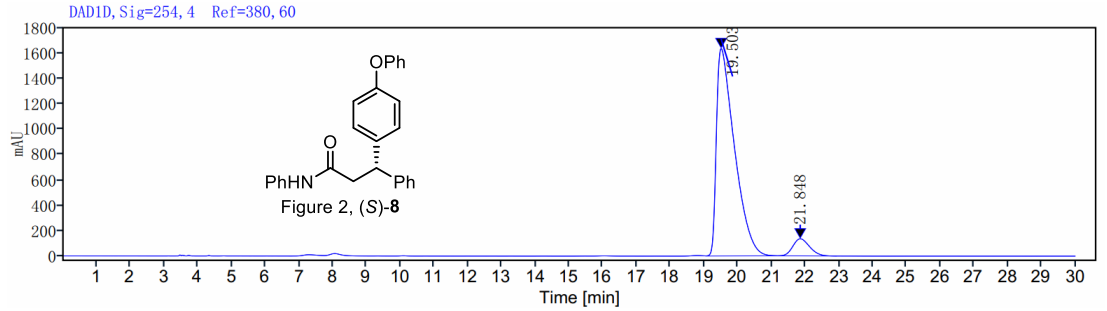
RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
18.756	VV	1.83501	13317.07252	449.07372	95.8825
24.160	VV	1.61240	571.87274	15.17424	4.1175
		Totals	13888.94525		

rac-



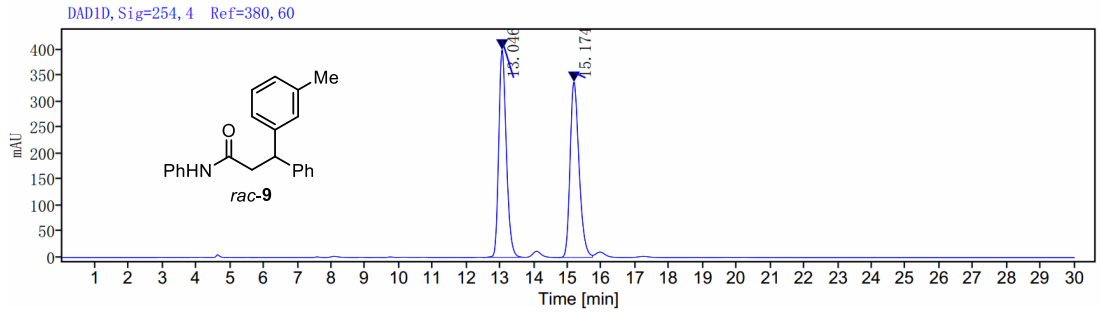
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
20.015	BV	1.76060	6836.02749	211.60337	49.9267
21.860	BV	1.90776	6856.10326	195.63240	50.0733
		Totals	13692.13074		



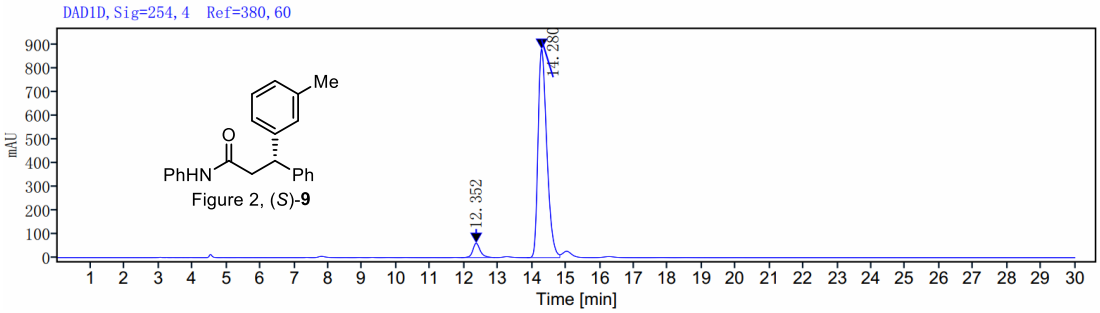
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
19.503	VB	2.12978	61048.26200	1645.28697	92.9173
21.848	VV	1.74683	4653.43009	135.50803	7.0827
		Totals	65701.69209		



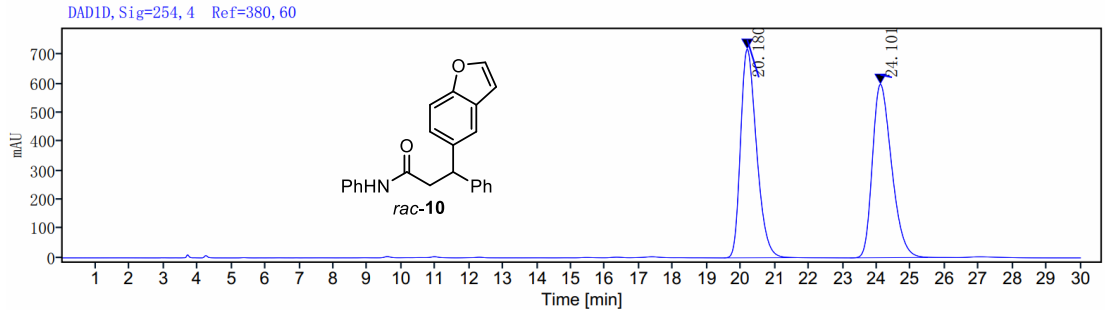
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
13.046	BV	1.21650	6235.50244	400.29949	49.9564
15.174	VV	0.99317	6246.39168	338.20977	50.0436
		Totals	12481.89412		



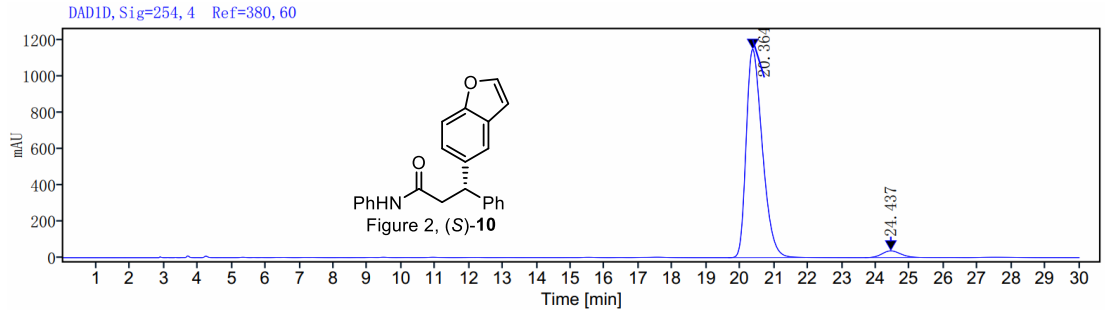
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
12.352	BV	0.99166	918.11288	60.54212	5.4712
14.280	BV	0.96944	15862.77319	881.82773	94.5288
		Totals	16780.88606		



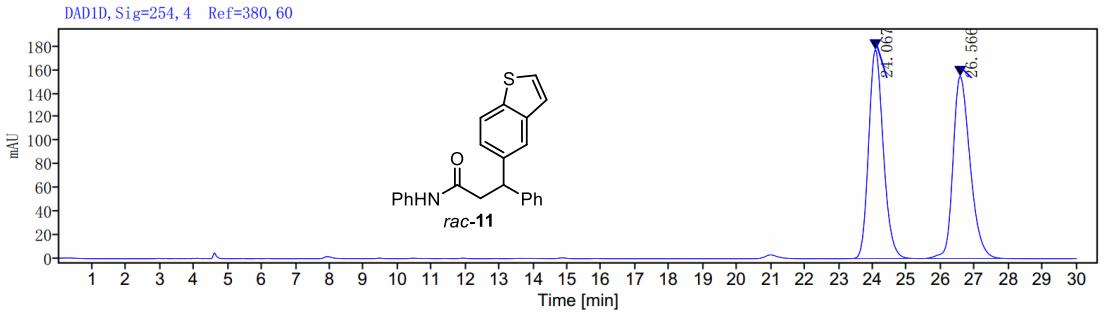
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
20.180	VV	2.12860	23483.11377	719.34018	50.0110
24.101	BV	2.28156	23472.79627	597.99512	49.9890
		Totals	46955.91004		



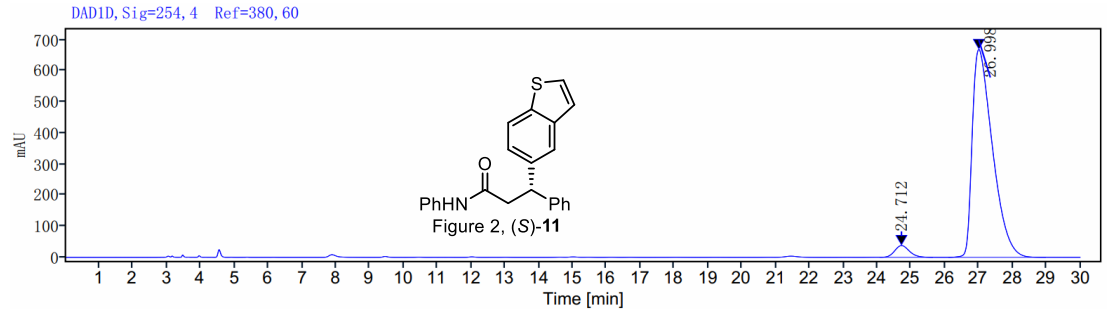
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
20.364	BV	2.27452	37983.06516	1149.53551	96.4630
24.437	VV	1.60698	1392.71755	36.63100	3.5370
		Totals	39375.78270		



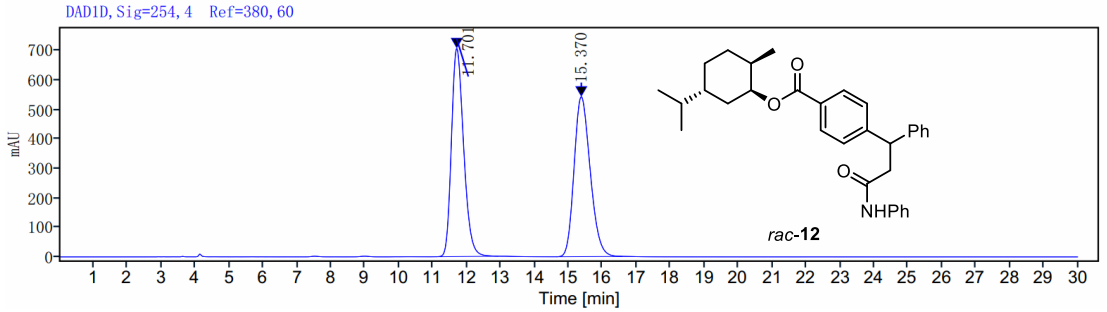
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
24.067	VV	1.68619	5316.12403	177.38529	49.5828
26.566	VV	2.26471	5405.59131	154.71479	50.4172
		Totals	10721.71534		



Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
24.712	VV	1.56819	1149.38166	37.97934	3.9772
26.998	VV	2.87485	27749.62635	669.06304	96.0228
		Totals	28899.00801		



Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
11.701	VV	1.84011	17668.46507	707.01925	49.6302
15.370	VV	1.95103	17931.75743	543.10062	50.3698
		Totals	35600.22250		

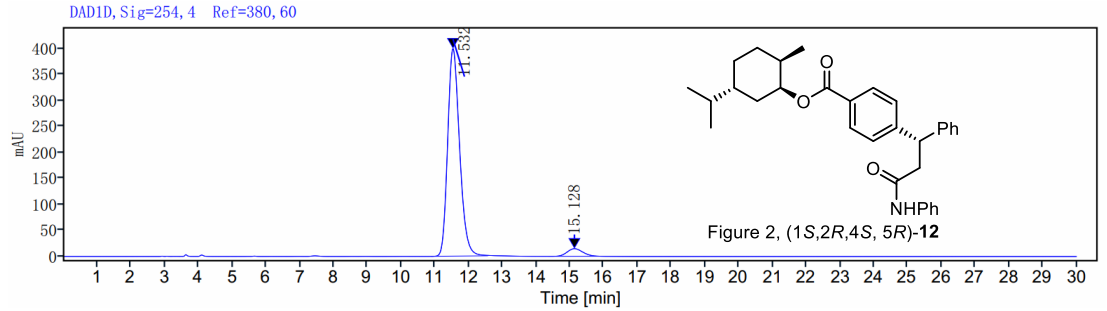
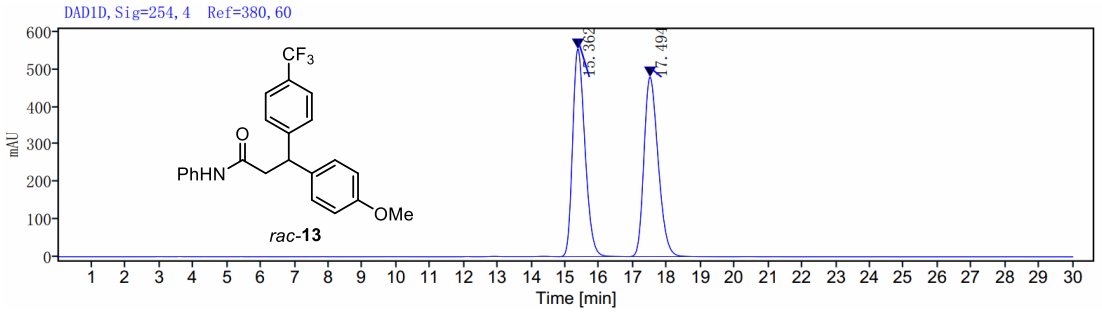


Figure 2, (1*S*,2*R*,4*S*, 5*R*)-**12**

Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
11.532	BV	1.67832	9799.76318	400.43881	95.4100
15.128	VV	1.29585	471.44917	14.73318	4.5900
		Totals	10271.21236		



Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
15.362	VV	1.64063	13963.89541	554.45639	49.9925
17.494	VV	1.82839	13968.10734	479.56678	50.0075
		Totals	27932.00275		

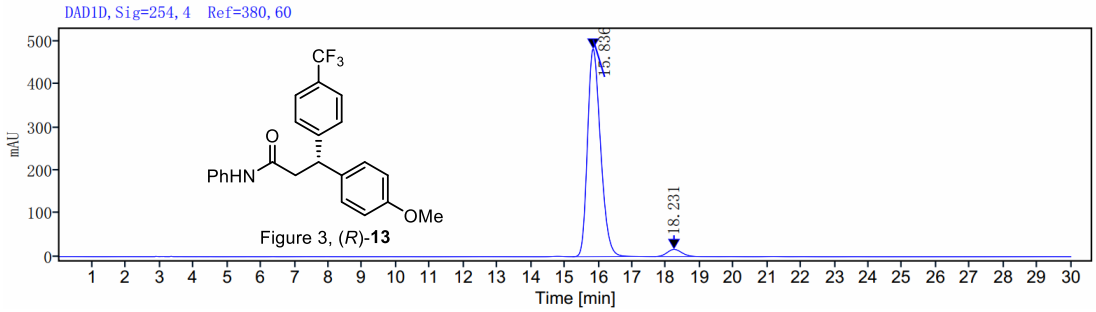
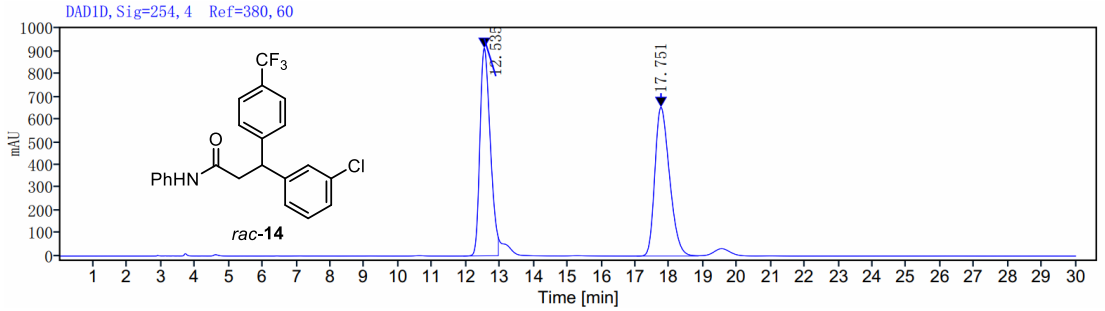


Figure 3, (*R*)-**13**

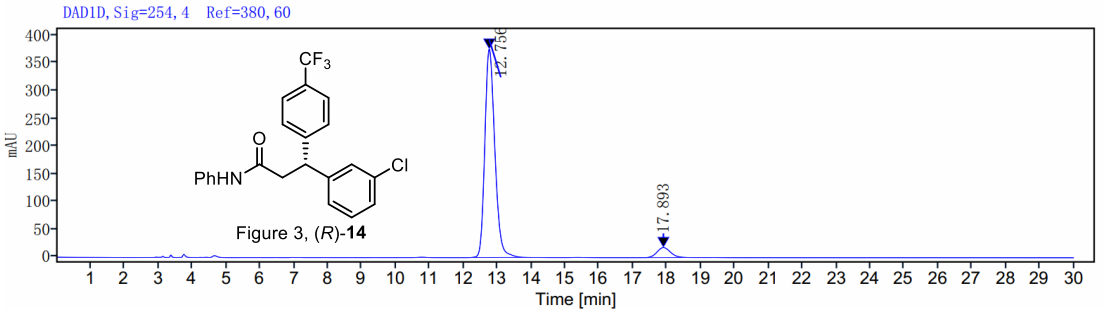
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
15.836	BV	1.69889	12932.31608	482.33116	96.2855
18.231	VV	1.27040	498.90186	16.55511	3.7145
		Totals	13431.21794		



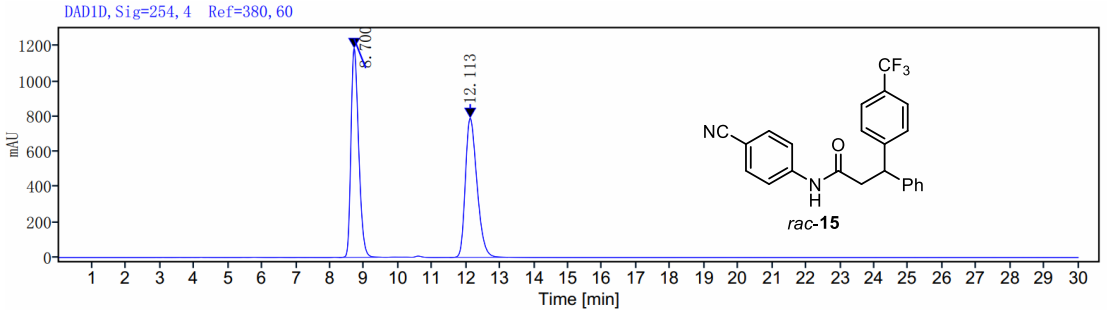
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
12.535	VM m	1.03103	19337.74721	912.57301	49.5402
17.751	BV	1.82584	19696.70265	653.56424	50.4598
		Totals	39034.44985		



Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
12.756	VV	1.48207	7681.79928	375.35815	94.0084
17.893	VV	1.15156	489.59637	17.94309	5.9916
		Totals	8171.39566		



Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
8.700	VV	1.12598	18636.62086	1186.24969	49.8787
12.113	VV	1.71285	18727.23041	789.66523	50.1213
		Totals	37363.85127		

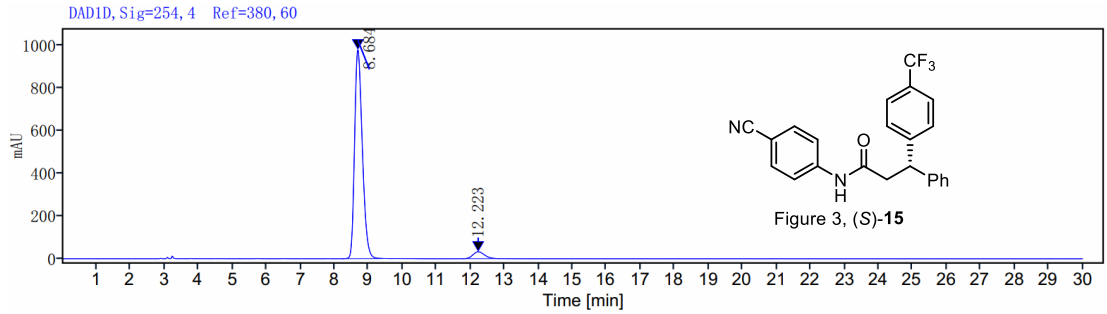
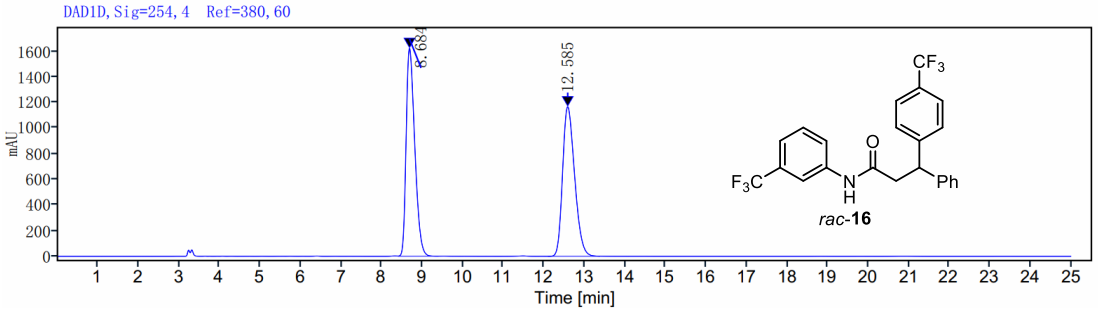


Figure 3, (*S*)-**15**

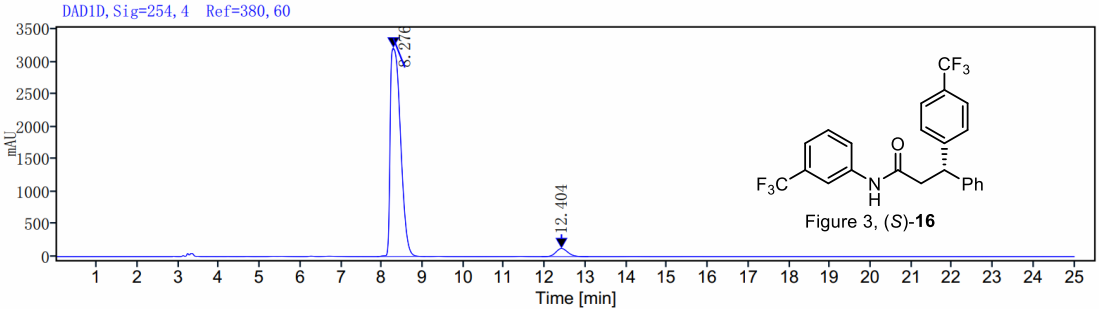
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
8.684	BV	1.17666	15496.74661	979.12143	95.2251
12.223	VV	1.10170	777.06378	32.41384	4.7749
		Totals	16273.81039		



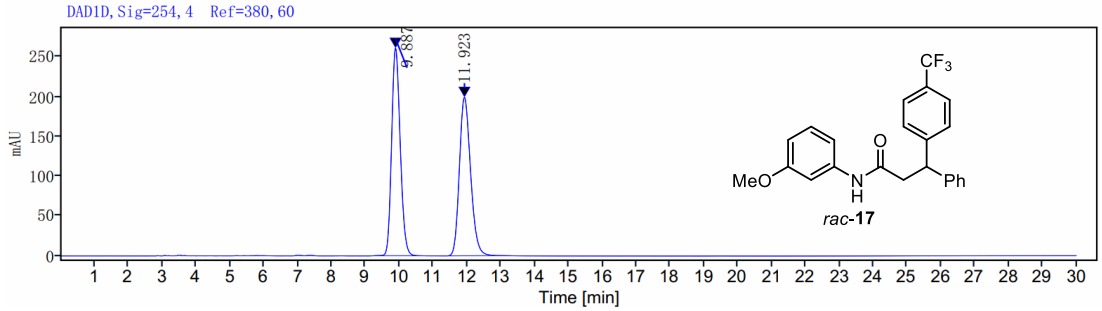
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
8.684	VB	0.99451	23957.29395	1621.58734	49.9045
12.585	BV	1.28346	24048.98386	1166.66980	50.0955
		Totals	48006.27782		



Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
8.276	MM m	1.18685	56398.70115	3214.87308	95.7557
12.404	VV	1.15041	2499.83873	124.04167	4.2443
		Totals	58898.53989		



Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
9.887	VV	1.04870	4605.51800	260.85759	50.1865
11.923	VV	1.42833	4571.28764	199.23810	49.8135
		Totals	9176.80564		

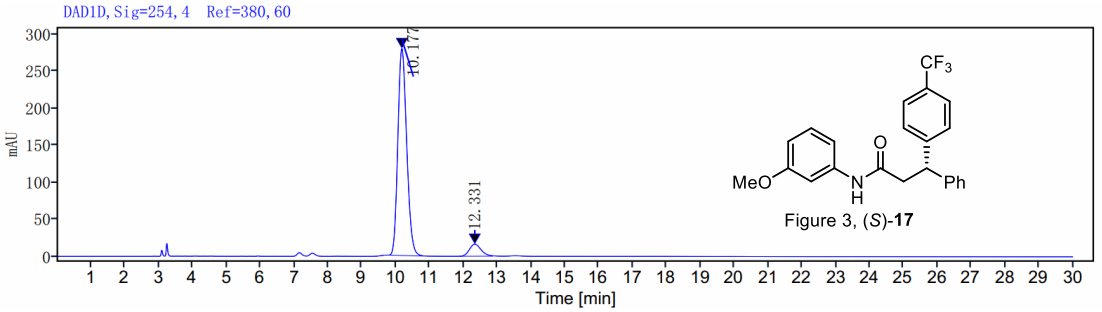
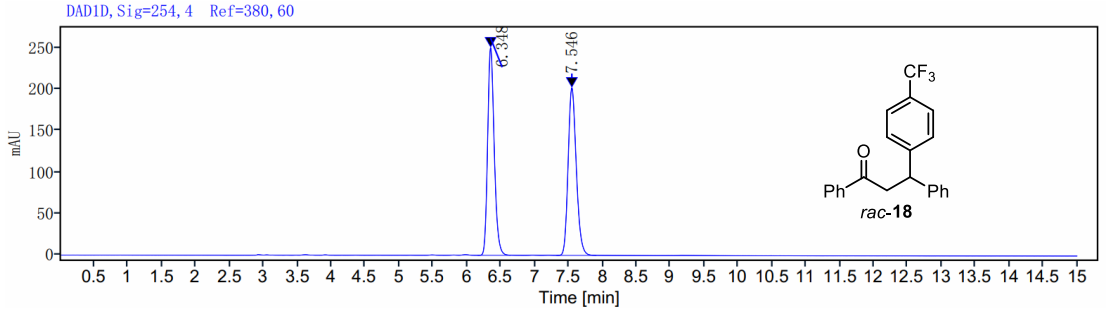


Figure 3, (*S*)-**17**

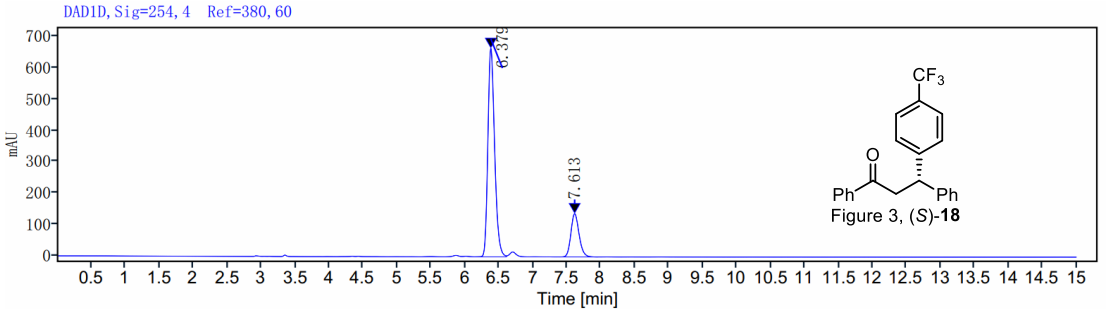
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
10.177	VV	1.03853	5086.43137	280.00130	92.8351
12.331	VV	0.97402	392.56207	16.36290	7.1649
		Totals	5478.99344		



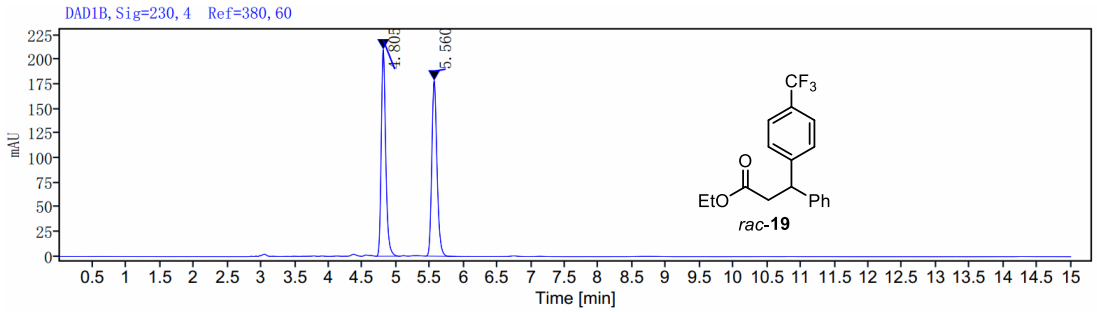
Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
6.348	VV	0.48645	1688.40488	250.33268	49.9861
7.546	BV	0.58625	1689.34425	202.09344	50.0139
		Totals	3377.74913		



Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
6.379	BV	0.46075	4565.64463	664.76146	79.8790
7.613	VV	0.56396	1150.05855	137.91353	20.1210
		Totals	5715.70318		



rac-**19**

Signal: DAD1B, Sig=230, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
4.805	VB	0.34940	973.77780	210.40093	50.2554
5.560	BB	0.45734	963.87931	178.64874	49.7446
		Totals	1937.65710		

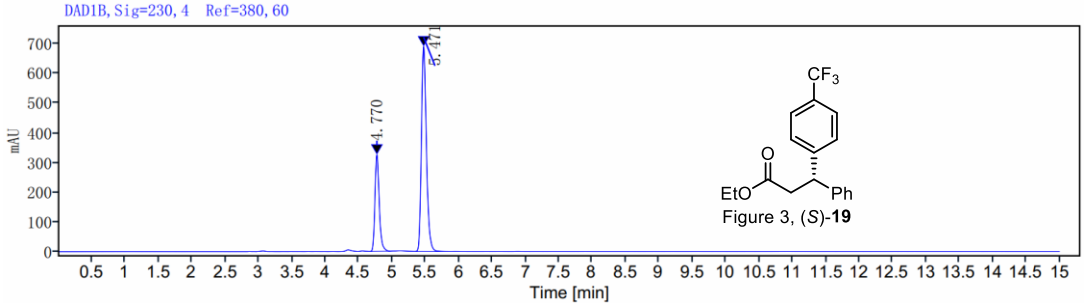
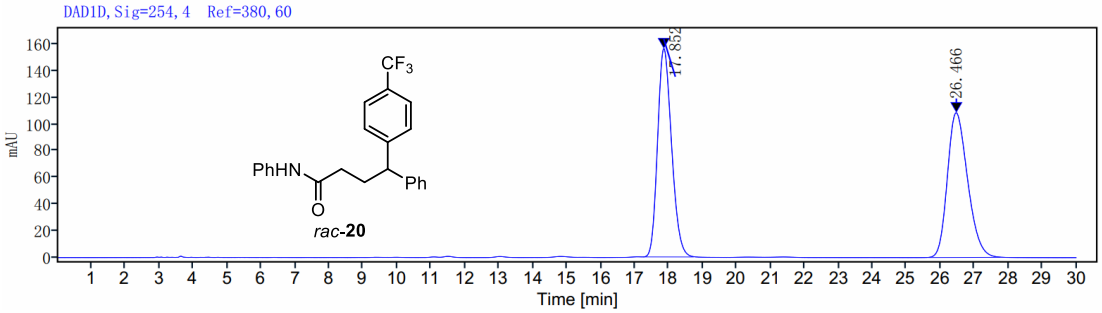


Figure 3, (*S*)-**19**

Signal: DAD1B, Sig=230, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
4.770	BB	0.30167	1453.64935	326.33322	28.7354
5.471	BB	0.52217	3605.09824	691.51992	71.2646
		Totals	5058.74760		



Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
17.852	BV	1.47892	4472.05536	156.47488	49.8888
26.466	VV	2.11636	4491.99824	108.66297	50.1112
		Totals	8964.05360		

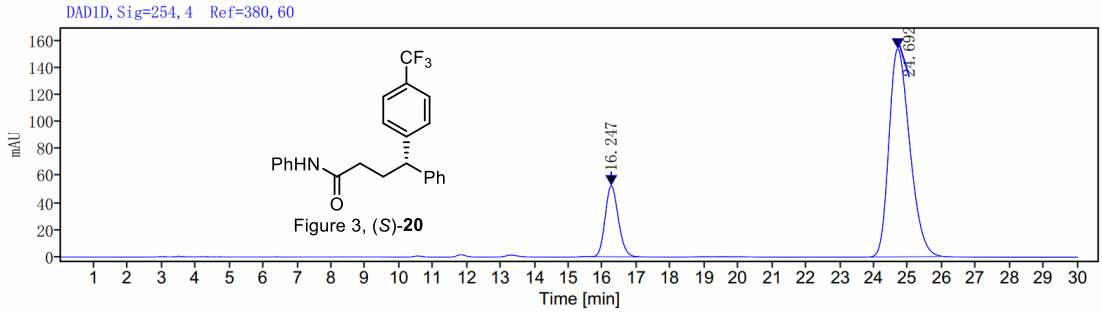
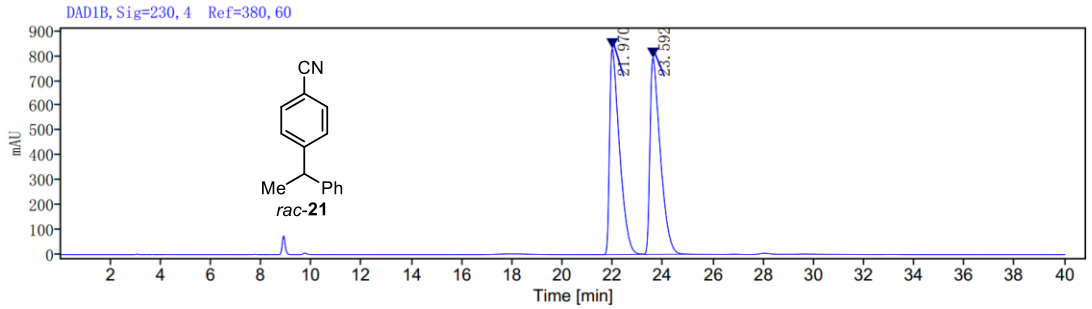


Figure 3, (*S*)-**20**

Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
16.247	VV	1.32411	1419.01156	52.70771	17.7406
24.692	VV	2.12370	6579.67127	154.31807	82.2594
		Totals	7998.68283		



Signal: DAD1B, Sig=230, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
21.970	BV	1.59637	22673.62474	831.00405	50.0341
23.592	VV	1.65939	22642.76017	792.40536	49.9659
		Totals	45316.38491		

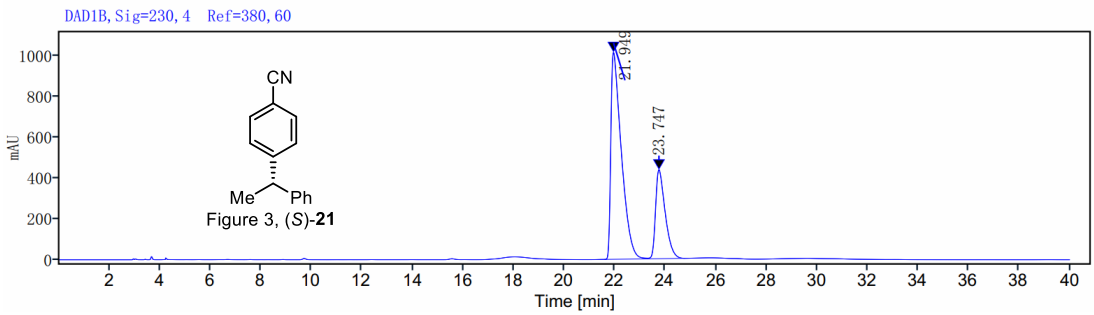
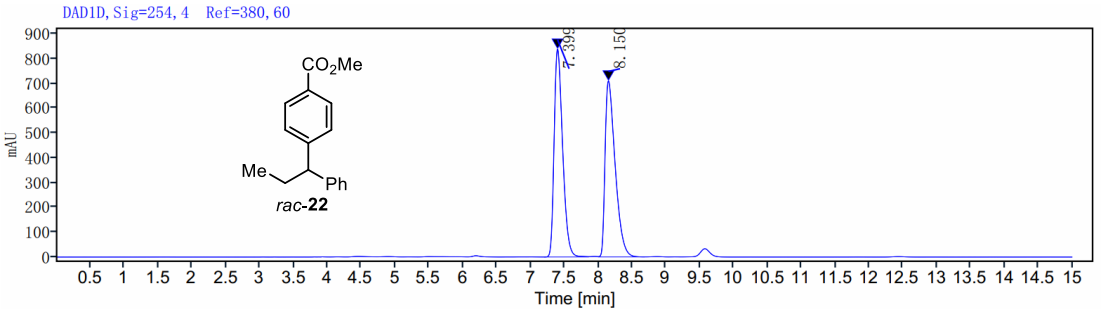


Figure 3, (*S*)-**21**

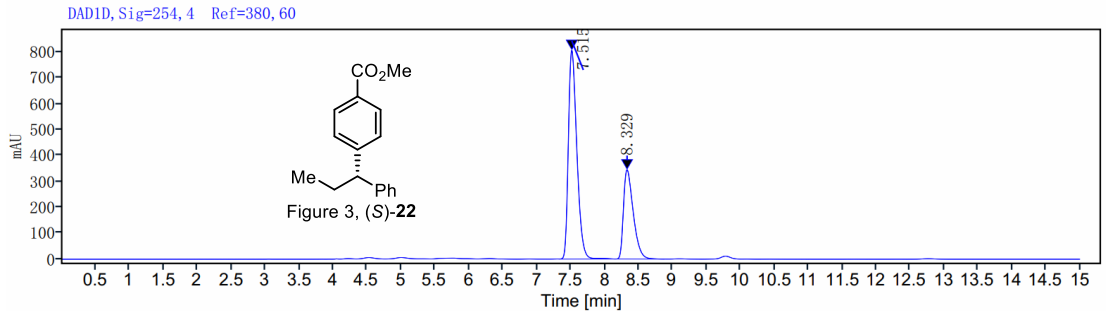
Signal: DAD1B, Sig=230, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
21.949	BV	1.70118	29135.74881	1011.67608	71.8008
23.747	VB	1.47044	11442.82644	434.55830	28.1992
		Totals	40578.57525		



Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
7.399	BV	0.65908	7317.16296	839.75958	49.9338
8.150	VB	0.68618	7336.57343	711.14238	50.0662
		Totals	14653.73639		



Signal: DAD1D, Sig=254, 4 Ref=380, 60

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
7.515	VB	0.83154	6992.58577	807.02014	66.9927
8.329	BV	0.72300	3445.24164	344.85400	33.0073
		Totals	10437.82741		