Supporting information

Synthesis of *N*-Aryl β-Amino Acid Derivatives via Cu(II)-Catalyzed Asymmetric 1,4-Reduction in Air

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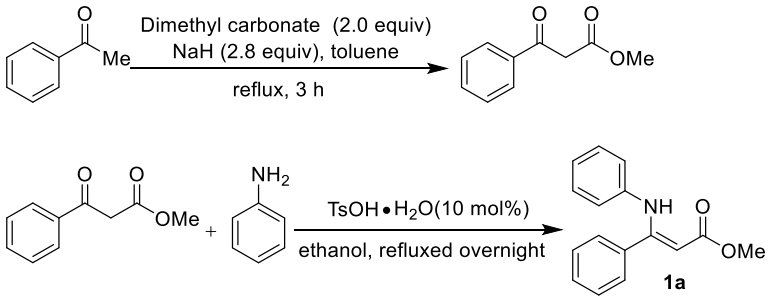
General

^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 on a Bruke advance spectrophotometer (400 or 500 MHz) at room temperature. Chemical shifts (δ) are given in ppm and are referenced to the residual solvent peaks. Fourier Transform Infrared (FT-IR) absorption spectra (diffuse reflectance spectroscopy) were performed on a Bruker TENSOR27 and only noteworthy absorptions (in cm^{-1}) are listed. Low resolution mass spectra were obtained with an Agilent Technologies 5975C with EI resource or Waters 2695 mass spectrometer with ESI resource. High resolution mass (HRMS) spectra were recorded on an Agilent Technologies 6530 Q-TOF mass spectrometer with ESI resource and are reported as *m*/*z* (relative intensity). Conversions were determined by ^{1}H NMR and gas chromatographic analyses. Enantiomeric excesses of the asymmetric hydrosilylation products were determined by chiral HPLC. GC analyses were conducted on an Agilent 7820A or a Fuli 9790 with an FID detector. HPLC analyses were performed using an Agilent 1200 with a UV detector. Optical rotations were measured on a Perkin-Elmer Model 341 or Anton Paar MCP 150 polarimeter in a 10 cm cell. Optically pure (*S*)-P-Phos, (*S*)-Xyl-P-Phos, (*S*)-BINAP, (*S*)-Tol-BINAP, (*S*)-H$_8$-BINAP, (*S*)-SEGPHOS, (*S*)-DM-SEGPHOS, and (*S*)-DTBM-SEGPHOS were purchased from Strem or Aldrich. (*S*)-Tol-P-Phos was prepared according to the previous reported procedure.[1] Substrates (**1a–s** and **3a–g**) were prepared and characterized according to the literature procedures.[2,3] All solvents were purified and dried according to standard methods prior to use. PMHS and other reagents were purchased from Aldrich, Alfa Aesar or Acros Organics and used as received without further purification unless otherwise stated.

Typical procedures for the synthesis of *N*-aryl β-substituted β-dehydroamino esters ((*Z*)-Methyl 3-phenyl-3-(phenylamino)acrylate 1a).[3]

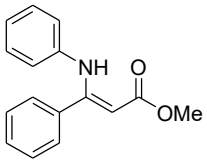


(1) To a dried three-necked flask equipped with a dropping funnel, a condenser, and a magnetic stirrer, NaH (4.5 g, 60 %, 112 mmol), dimethyl carbonate (7.2 g, 80 mmol), and toluene (60 mL) were added. The mixture was heated to reflux. A solution of ketone (4.8 g, 40 mmol) in toluene (20 mL) was added dropwise from the dropping funnel over 1−2 h. After the addition, the mixture was further refluxed until the evolution of hydrogen ceased (15−20 min). After the reaction mixture was cooled to room temperature, glacial acetic acid (12 mL) was added dropwise

and a heavy, pasty solid appeared. Ice-water was added until the solid was dissolved completely. The toluene layer was separated, and the aqueous layer was extracted with toluene (3 × 40 mL). The combined toluene solution was washed with water (40 mL) and brine (40 mL), and then dried over anhydrous Na_2SO_4, filtered, and evaporated in vacuo. The residue was purified by column chromatography on silica gel using ethyl acetate : petroleum ether (1 : 10) as eluent to give the pure product (Methyl benzoylacetate, 6.9 g, 97 % yield).

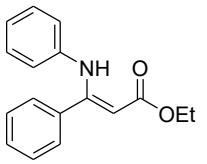
(2) A mixture of methyl benzoylacetate (4.3 g, 24 mmol), aniline (2.2 g, 24 mmol) and *p*-toluenesulfonic acid monohydrate (0.46 g, 2.4 mmol) was dissolved in 30 mL of methanol and refluxed overnight. The reaction mixture was cooled to room temperature and evaporated in vacuo. The crude product was dissolved in 60 mL ethyl acetate, washed with water (40 mL) and brine (40 mL), and then dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using ethyl acetate : petroleum ether (1 : 30) as eluent to give the pure product (**1a**, 4.5 g, 74 % yield).

(*Z*)-Methyl 3-phenyl-3-(phenylamino)acrylate (1a)[3]



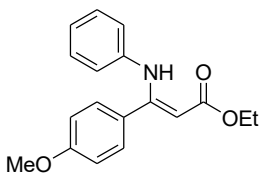
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.28 (br, 1H), 7.36–7.26 (m, 5H), 7.10–7.06 (m, 2H), 6.91 (t, J = 7.2 Hz, 1H), 6.66 (d, J = 8.0 Hz, 2H), 5.00 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.5, 159.3, 140.4, 136.0, 129.5, 128.6, 128.5, 128.3, 123.1, 122.3, 90.7, 50.7. IR (thin film): ν_{max} (cm^{-1}) = 3260, 3055, 2947, 1660, 1614, 1574, 1485, 1288, 1173, 771, 749, 700. MS (EI, *m*/*z*, relative intensity): 253 (M^+, 64), 222 (31), 193 (100), 178 (33), 165 (17), 97 (24), 97 (24), 77 (39), 57 (34).

(*Z*)-Ethyl 3-phenyl-3-(phenylamino)acrylate (1b)[4]



^{1}H NMR (500 MHz, $CDCl_3$): δ 10.30 (br, 1H), 7.36–7.26 (m, 5H), 7.09–7.06 (m, 2H), 6.91 (t, J = 7.5 Hz, 1H), 6.66 (d, J = 7.5 Hz, 2H), 5.00 (s, 1H), 4.22 (q, J = 7.2 Hz, 2H), 1.32 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.1, 159.1, 140.4, 136.0, 129.4, 128.6, 128.4, 128.2, 122.9, 122.2, 91.2, 59.3, 14.5. IR (thin film): ν_{max} (cm^{-1}) = 3260, 3030, 2979, 1659, 1614, 1596, 1504, 1485, 1362, 1286, 1177, 1039, 770, 749, 699. MS (EI, *m*/*z*, relative intensity): 267 (M^+, 50), 221 (29), 193 (100), 180 (30), 165 (18), 77 (39), 51 (18).

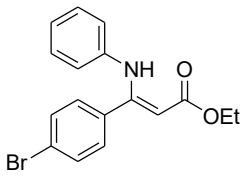
(*Z*)-Ethyl 3-(4-methoxyphenyl)-3-(phenylamino)acrylate (1c)[5]



^{1}H NMR (500 MHz, $CDCl_3$): δ 10.27 (br, 1H), 7.29 (d, J = 8.5 Hz, 2H), 7.11–7.08 (m, 2H), 6.91 (t, J = 7.3 Hz, 1H), 6.80 (d, J = 8.5 Hz, 2H), 6.69 (d, J = 8.0 Hz, 2H), 4.98 (s, 1H), 4.21 (q, J = 7.2 Hz, 2H). 3.79 (s, 3H), 1.32 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.2, 160.6, 158.8, 140.7, 129.7, 128.6, 128.2, 122.8, 122.2, 113.8, 90.5, 59.2, 55.3, 14.6. IR (thin film):

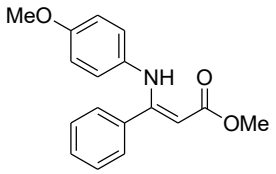
ν_{max} (cm^{-1}) = 3256, 3051, 2978, 1651, 1614, 1514, 1440, 1281, 1170, 1031, 839, 797, 751, 694. MS (EI, *m*/*z*, relative intensity): 297 (M^+, 100), 268 (18), 252 (28), 224 (94), 210 (43), 180 (16), 134 (20), 77 (30), 51 (8).

(*Z*)-Ethyl 3-(4-bromophenyl)-3-(phenylamino)acrylate (1d)



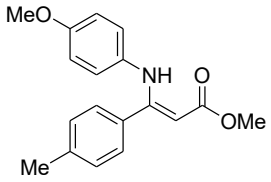
^{1}H NMR (500 MHz, $CDCl_3$): δ 10.25 (br, 1H), 7.42 (d, J = 8.5 Hz, 2H), 7.22 (d, J = 9.0 Hz, 2H), 7.11 (dd, J_1 = 8.0 Hz, J_2 = 7.5 Hz, 2H), 6.94 (t, J = 7.3 Hz, 1H), 6.67 (d, J = 7.5 Hz, 2H), 4.98 (s, 1H), 4.21 (q, J = 7.2 Hz, 2H), 1.32 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.9, 157.7, 140.2, 135.0, 131.7, 129.8, 128.8, 123.7, 123.3, 122.4, 91.6, 59.5, 14.5. IR (thin film): ν_{max} (cm^{-1}) = 3255, 3052, 2979, 1660, 1614, 1598, 1501, 1478, 1284, 1176, 1070, 1011, 835, 797, 749, 693. MS (EI, *m*/z, relative intensity): 345 (M^+, 81), 300 (29), 273 (100), 258 (22), 193 (61), 165 (30), 77 (49), 51 (17). HRMS (ESI) Calcd for $C_{17}H_{17}BrNO_2$ $[M + H]^+$: 346.0443, Found: 346.0449.

(*Z*)-Methyl 3-(4-methoxyphenylamino)-3-phenylacrylate (1e)[6]



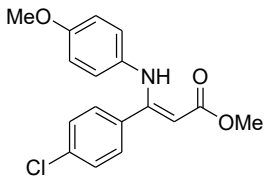
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.20 (br, 1H), 7.32–7.24 (m, 5H), 6.63 (br, 4H), 4.93 (s, 1H), 3.73 (s, 3H), 3.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7, 160.1, 155.9, 136.0, 133.4, 129.3, 128.4, 128.3, 124.4, 113.9, 89.1, 55.3, 50.7. IR (thin film): ν_{max} (cm^{-1}) = 3256, 2948, 1658, 1613, 1574, 1513, 1285, 1246, 1170, 1035, 829, 800, 775, 699. MS (EI, *m*/*z*, relative intensity): 283 (M^+, 100), 251 (50), 236 (15), 224 (17), 208 (21), 180 (18), 134 (14), 77 (13), 51 (6).

(*Z*)-Methyl 3-(4-methoxyphenylamino)-3-(*p*-tolyl)acrylate (1f)[6]



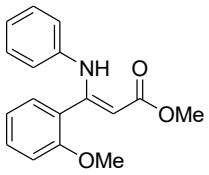
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.18 (br, 1H)，7.19 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.64 (br, 4H), 4.92 (s, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7, 160.1, 155.8, 139.4, 133.5, 133.0, 129.0, 128.3, 124.3, 113.9, 88.7, 55.3, 50.6, 21.3. IR (thin film): ν_{max} (cm^{-1}) = 3269, 2856, 1719, 1613, 1584, 1549, 1197, 1245, 1159, 1021, 821, 783, 687. MS (ESI) *m*/*z* 298 ($[M + H]^+$).

(*Z*)-Methyl 3-(4-chlorophenyl)-3-(4-methoxyphenylamino)acrylate (1g)[6]



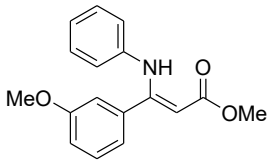
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.13 (br, 1H), 7.24 (br, 4H), 6.67–6.62 (m, 4H), 4.91 (s, 1H), 3.73 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.5, 158.7, 156.1, 135.3, 134.4, 133.1, 129.7, 128.6, 124.6, 114.0, 89.4, 55.3, 50.7. IR (thin film): ν_{max} (cm^{-1}) = 3256, 2948, 1660, 1614, 1513, 1476, 1286, 1246, 1171, 1089, 1034, 1013, 832, 794, 765. MS (EI, *m*/*z*, relative intensity): 317 (M^+, 100), 285 (66), 270 (18), 257 (20), 244 (28), 149 (21), 134 (25), 77 (11), 59 (8).

(*Z*)-Methyl 3-(2-methoxyphenyl)-3-(phenylamino)acrylate (1h)[6]



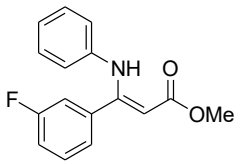
^{1}H NMR (500 MHz, $CDCl_3$): δ 10.48 (br, 1H), 7.35–7.31 (m, 2H), 7.06–7.03 (m, 2H), 6.99–6.96 (m, 1H), 6.90 (t, J = 7.3 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 6.66 (d, J = 8.0 Hz, 2H), 4.84 (s, 1H), 3.73 (s, 3H), 3.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.7, 157.7, 156.1, 140.4, 130.9, 130.2, 128.30, 125.1, 123.2, 121.5, 120.8, 111.1, 88.6, 55.2, 50.6. IR (thin film): ν_{max} (cm^{-1}) = 3256, 2946, 1657, 1614, 1597, 1584, 1486, 1292, 1172, 794, 753, 695. MS (EI, *m*/*z*, relative intensity): 283 (M^+, 100), 252 (20), 210 (15), 131 (33), 93 (20), 77 (18), 51 (7).

(*Z*)-Methyl 3-(3-methoxyphenyl)-3-(phenylamino)acrylate (1i)[7]



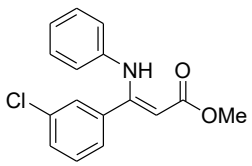
^{1}H NMR (500 MHz, $CDCl_3$): δ 10.28 (br, 1H), 7.21–7.17 (m, 1H), 7.11–7.08 (m, 2H), 6.93–6.88 (m, 4H), 6.70 (d, J = 8.0 Hz, 2H), 5.03 (s, 1H), 3.75 (s, 3H), 3.70 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.5, 159.5, 159.1, 140.3, 137.3, 129.5, 128.7, 123.1, 122.2, 120.7, 115.4, 113.5, 90.5, 55.3, 50.7. IR (thin film): ν_{max} (cm^{-1}) = 3262, 3001, 2948, 1660, 1615, 1597, 1580, 1445, 1293, 1248, 1169, 789, 758, 711. MS (EI, *m*/*z*, relative intensity): 283 (M^+, 85), 252 (20), 224 (100), 210 (36), 180 (25), 118 (12), 89 (8), 77 (21), 51 (7).

(*Z*)-Methyl 3-(3-fluorophenyl)-3-(phenylamino)acrylate (1j)



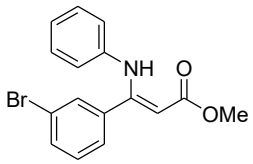
^{1}H NMR (500 MHz, $CDCl_3$): δ 10.26 (br, 1H), 7.30–7.28 (m, 1H), 7.16–7.05 (m, 5H), 6.97 (t, J = 7.3 Hz, 1H), 6.71 (d, J = 7.5 Hz, 2H), 5.04 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.3, 163.5, 161.6, 157.7, 140.0, 138.2, 128.8, 124.0, 123.4, 122.4, 116.4, 115.3, 91.3, 50.8. IR (thin film): ν_{max} (cm^{-1}) = 3260, 3065, 2948, 1663, 1620, 1597, 1581, 1480, 1290, 1207, 1169, 789, 746, 707. MS (EI, *m*/*z*, relative intensity): 271 (M^+, 62), 240 (26), 211 (100), 183 (13), 123 (19), 95 (15), 77 (28), 51 (8). HRMS (ESI) Calcd for $C_{16}H_{15}FNO_2$ $[M + H]^+$: 272.1087, Found: 272.1098.

(*Z*)-Methyl 3-(3-chlorophenyl)-3-(phenylamino)acrylate (1k)



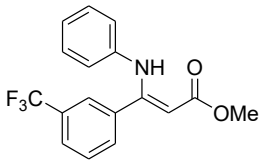
^{1}H NMR (500 MHz, $CDCl_3$): δ 10.22 (br, 1H), 7.38 (s, 1H), 7.32–7.30 (m, 1H), 7.21–7.17 (m, 2H), 7.11 (dd, J_1 = J_2 = 8.0 Hz, 2H), 6.95 (t, J = 7.5 Hz, 1H), 6.68 (d, J = 8.0 Hz, 2H), 5.00 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.3, 157.6, 140.0, 137.8, 134.5, 129.7, 129.6, 128.8, 128.2, 126.5, 123.4, 122.4, 91.3, 50.8. IR (thin film): ν_{max} (cm^{-1}) = 3260, 3061, 2948, 1664, 1615, 1586, 1565, 1472, 1287, 1176, 789, 753, 708. MS (EI, *m*/*z*, relative intensity): 287 (M^+, 100), 256 (28), 228 (18), 214 (17), 193 (10), 165 (5), 77 (6), 51 (3). HRMS (ESI) Calcd for $C_{16}H_{15}ClNO_2$ $[M + H]^+$: 288.0791, Found: 288.0798.

(*Z*)-Methyl 3-(3-bromophenyl)-3-(phenylamino)acrylate (1l)



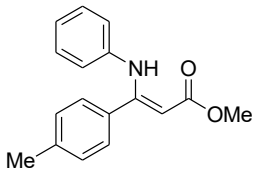
^{1}H NMR (500 MHz, $CDCl_3$): δ 10.22 (br,1H), 7.55 (s, 1H), 7.47–7.46 (m, 1H), 7.22 (d, J = 7.5 Hz, 1H), 7.14–7.10 (m, 3H), 6.95 (t, J = 7.3 Hz, 1H), 6.68 (d, J = 7.5 Hz, 2H), 4.99 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.2, 157.4, 139.9, 138.1, 132.5, 131.1, 129.9, 128.8, 127.0, 123.4, 122.5, 122.4, 91.4, 50.8. IR (thin film): ν_{max} (cm^{-1}) = 3259, 3058, 2947, 1663, 1615, 1585, 1559, 1470, 1445, 1284, 1175, 787, 752, 707. MS (EI, *m*/*z*, relative intensity): 331 (M^+, 18), 317 (34), 301 (44), 273 (100), 258 (33), 220 (29), 193 (58), 165 (37), 104 (81), 77 (79), 51 (25). HRMS (ESI) Calcd for $C_{16}H_{15}BrNO_2$ $[M + H]^+$: 332.0286, Found: 332.0295.

(*Z*)-Methyl 3-(phenylamino)-3-(3-(trifluoromethyl)phenyl)acrylate (1m)



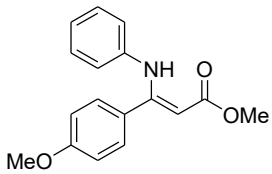
^{1}H NMR (500 MHz, $CDCl_3$): δ 10.25 (br, 1H), 7.64 (s, 1H), 7.59 (d, J = 7.5 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.40–7.37 (m, 1H), 7.12–7.09 (m, 2H), 6.95 (t, J = 7.5 Hz, 1H), 6.66 (d, J = 8.0 Hz, 2H), 5.03 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.2, 157.5, 139.8, 136.8, 131.6, 131.2, 130.9, 128.9, 128.8, 126.1, 125.1, 123.6, 122.7, 91.5, 50.9. IR (thin film): ν_{max} (cm^{-1}) = 3262, 3036, 2950, 1667, 1621, 1598, 1502, 1485, 1331, 1290, 1174, 1128, 798, 760, 707. MS (EI, *m*/*z*, relative intensity): 321 (M^+, 56), 290 (35), 261 (100), 193 (21), 173 (35), 145 (21), 77 (42), 57 (16). HRMS (ESI) Calcd for $C_{17}H_{15}F_3NO_2$ $[M + H]^+$: 322.1055, Found: 322.1054.

(*Z*)-Methyl 3-(phenylamino)-3-(*p*-tolyl)acrylate (1n)[4]



^{1}H NMR (500 MHz, $CDCl_3$): δ 10.27 (br, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.10–7.08 (m, 4H), 6.92 (t, J = 7.5 Hz, 1H), 6.69 (d, J = 7.5 Hz, 2H), 5.00 (s, 1H), 3.74 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.5, 159.4, 140.5, 139.7, 133.0, 129.2, 128.6, 128.2, 123.0, 122.3, 90.3, 55.7, 21.4. IR (thin film): ν_{max}(cm^{-1}) = 3256, 3029, 2947, 1660, 1615, 1597, 1500, 1486, 1445, 1289, 827, 796, 757, 693. MS (EI, *m*/*z*, relative intensity): 267 (M^+, 79), 236 (31), 207 (100), 194 (41), 118 (21), 103 (8), 91(13), 77 (25), 51 (7).

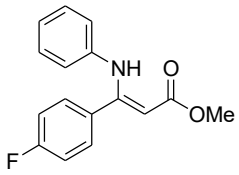
(*Z*)-Methyl 3-(4-methoxyphenyl)-3-(phenylamino)propanoate (1o)



^{1}H NMR (400 MHz, $CDCl_3$): δ 10.23 (br, 1H), 7.28 (d, J = 8.4 Hz, 2H), 7.11–7.08 (m, 2H), 6.92 (t, J = 7.4 Hz, 1H), 6.80 (d, J = 8.4 Hz, 2H), 6.68 (d, J = 7.6 Hz, 2H), 4.97 (s, 1H), 3.80 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.5, 160.6, 159.0, 140.6, 129.7, 128.7, 128.1, 122.9, 122.3, 113.8, 90.0, 55.3, 50.6. IR (thin film): ν_{max} (cm^{-1}) = 3266, 3003, 2947, 1659, 1614, 1514, 1499, 1486, 1444, 1283, 1253, 1170, 1023, 838, 796, 761, 694. MS (EI, *m*/*z*, relative intensity): 283 (M^+, 100), 252 (25), 223 (77), 208 (41), 180 (16), 150 (14), 135 (18), 118

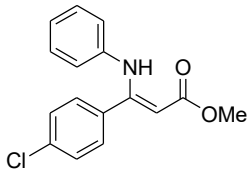
(17), 89 (12), 77 (33), 51 (11). HRMS (ESI) Calcd for $C_{17}H_{18}NO_3$ $[M + H]^+$: 284.1287, Found: 284.1292.

(*Z*)-Methyl 3-(4-fluorophenyl)-3-(phenylamino)acrylate (1p)[4]



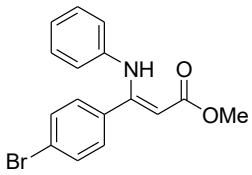
^{1}H NMR (500 MHz, $CDCl_3$): δ 10.25 (br, 1H), 7.34–7.32 (m, 2H), 7.10 (dd, $J_1 = J_2 = 8.0$ Hz, 2H), 6.99–6.92 (m, 3H), 6.67 (d, $J = 8.0$ Hz, 2H), 4.98 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.3, 163.3, 158.1, 140.2, 132.0, 130.2, 128.8, 123.3, 122.5, 115.7, 90.8, 50.8. IR (thin film): ν_{max} (cm^{-1}) = 3262, 3053, 2948, 1667, 1652, 1614, 1504, 1446, 1290, 1227, 1178, 1102, 883, 797, 762, 694. MS (EI, *m*/*z*, relative intensity): 271 (M^+, 61), 240 (28), 211 (100), 198 (33), 123 (19), 95 (10), 77 (21), 51 (7).

(*Z*)-Methyl 3-(4-chlorophenyl)-3-(phenylamino)acrylate (1q)



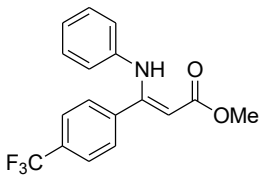
^{1}H NMR (500 MHz, $CDCl_3$): δ 10.24 (br, 1H), 7.30–7.27 (m, 4H), 7.13–7.10 (m, 2H), 6.95 (t, $J = 7.5$ Hz, 1H), 6.68 (d, $J = 7.5$ Hz, 2H), 5.00 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.3, 157.9, 140.1, 135.5, 134.4, 129.6, 128.8, 128.7, 123.4, 122.5, 91.1, 50.8. IR (thin film): ν_{max} (cm^{-1}) = 3258, 3054, 2948, 1661, 1614, 1598, 1502, 1480, 1287, 1174, 1091, 1013, 836, 798, 751, 693. MS (EI, *m*/*z*, relative intensity): 287 (M^+, 64), 256 (30), 228 (100), 214 (37), 193 (27), 77 (35), 51 (12). HRMS (ESI) Calcd for $C_{16}H_{15}ClNO_2$ $[M + H]^+$: 288.0791, Found: 288.0798.

(*Z*)-Methyl 3-(4-bromophenyl)-3-(phenylamino)acrylate (1r)



^{1}H NMR (400 MHz, $CDCl_3$): δ 10.21 (br, 1H), 7.42 (d, $J = 8.8$ Hz, 2H), 7.21 (d, $J = 8.4$ Hz, 2H), 7.13–7.09 (m, 2H), 6.95 (t, $J = 7.4$ Hz, 1H), 6.66 (d, $J = 8.4$ Hz, 2H), 4.97 (s, 1H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 157.9, 140.1, 134.9, 131.7, 129.8, 128.8, 123.8, 123.4, 122.5, 91.0, 50.8. IR (thin film): ν_{max} (cm^{-1}) = 3257, 3032, 2947, 1661, 1614, 1598, 1478, 1286, 1174, 1070, 1010, 833, 797, 750, 693. MS (EI, *m*/*z*, relative intensity): 331 (M^+, 100), 300 (25), 273 (70), 258 (20), 193 (36), 165 (22), 77 (34), 51 (15). HRMS (ESI) Calcd for $C_{16}H_{15}BrNO_2$ $[M + H]^+$: 332.0286, Found: 332.0288.

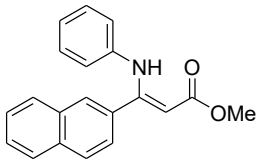
(*Z*)-Methyl 3-(phenylamino)-3-(4-(trifluoromethyl)phenyl)acrylate (1s)



^{1}H NMR (500 MHz, $CDCl_3$): δ 10.26 (br, 1H), 7.55 (d, $J = 8.0$ Hz, 2H), 7.47 (d, $J = 8.0$ Hz, 2H), 7.13–7.09 (m, 2H), 6.95 (t, $J = 7.5$ Hz, 1H), 6.67 (d, $J = 8.0$ Hz, 2H), 5.02 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.3, 157.6, 139.9, 139.7, 131.4, 128.9, 128.7, 125.6, 123.9, 123.7, 122.6, 91.9, 50.9. IR (thin film): ν_{max} (cm^{-1}) = 3259, 3033, 2950, 1666, 1613, 1598, 1447,

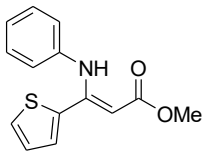
1324, 1282, 1175, 1126, 1066, 1017, 849, 799, 749, 695. MS (EI, *m*/*z*, relative intensity): 321 (M^+, 60), 290 (25), 261 (100), 248 (25), 193 (8), 77 (28), 57 (8). HRMS (ESI) Calcd for $C_{17}H_{15}F_3NO_2$ $[M + H]^+$: 322.1055, Found: 322.1052.

(*Z*)-Methyl 3-(naphthalen-2-yl)-3-(phenylamino)acrylate (3a)



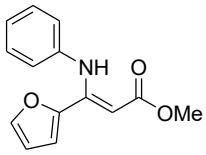
^{1}H NMR (500 MHz, $CDCl_3$): δ 10.39 (br, 1H), 7.99 (s, 1H), 7.84–7.80 (m, 2H), 7.71 (d, J = 8.5 Hz, 1H), 7.54–7.49 (m, 2H), 7.36–7.34 (m, 1H), 7.06 (dd, J_1 = J_2 = 8.0 Hz, 2H), 6.90 (t, J = 7.5 Hz, 1H), 6.73 (d, J = 8.0 Hz, 2H), 5.15 (s, 1H), 3.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.5, 159.1, 140.4, 133.7, 133.7, 133.1, 128.8, 128.4, 128.0, 127.9, 127.8, 127.0, 126.5, 125.6, 123.1, 122.2, 91.2, 50.8. IR (thin film): ν_{max} (cm^{-1}) = 3258, 3055, 2947, 1660, 1614, 1503, 1445, 1287, 1170, 1066, 822, 798, 749, 702. MS (EI, *m*/*z*, relative intensity): 303 (M^+, 80), 272 (21), 244 (100), 230 (27), 152 (21), 127 (16), 77 (27), 57 (9). HRMS (ESI) Calcd for $C_{20}H_{18}NO_2$ $[M + H]^+$: 304.1338, Found: 304.1342.

(*Z*)-Methyl 3-(phenylamino)-3-(thiophen-2-yl)acrylate (3b)



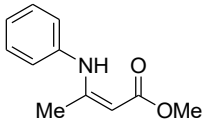
^{1}H NMR (500 MHz, $CDCl_3$): δ 10.09 (br, 1H), 7.30 (d, J = 5.0 Hz, 1H), 7.18–7.15 (m, 2H), 7.04 (d, J = 4.0 Hz, 1H), 7.00 (t, J = 7.3 Hz, 1H), 6.92 (dd, J_1 = 5.0 Hz, J_2 = 3.5 Hz, 1H), 6.83 (d, J = 8.0 Hz, 2H), 5.20 (s, 1H), 3.74 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.2, 152.2, 140.6, 137.6, 128.9, 127.7, 127.3, 123.8, 123.1, 119.8, 90.8, 50.8. IR (thin film): ν_{max} (cm^{-1}) = 3252, 3030, 2947, 1667, 1614, 1520, 1445, 1495, 1433, 1275, 1221, 1173, 796, 751, 697. MS (EI, *m*/*z*, relative intensity): 259 (M^+, 93), 227 (75), 199 (100), 186 (58), 167 (15), 77 (46), 63 (11), 57 (21). HRMS (ESI) Calcd for $C_{14}H_{14}NO_2S$ $[M + H]^+$: 260.0745, Found: 260.0749.

(*Z*)-Methyl 3-(furan-2-yl)-3-(phenylamino)acrylate (3c)



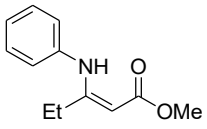
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.90 (br, 1H), 7.36 (s, 1H), 7.21 (dd, J_1 = 8.3 Hz, J_2 = 7.8 Hz, 2H), 7.04 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 7.5 Hz, 2H), 6.37–6.35 (m, 2H), 5.33 (s, 1H), 3.74 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.6, 148.3, 147.7, 143.6, 141.0, 128.8, 123.9, 115.1, 111.5, 88.6, 50.9, 45.2. IR (thin film): ν_{max} (cm^{-1}) = 3268, 3033, 2948, 1660, 1615, 1496, 1445, 1287, 1196, 1026, 797, 746, 707, 692. MS (EI, *m*/*z*, relative intensity): 243 (M^+, 79), 212 (19), 184 (100), 170 (56), 154 (59), 128 (22), 95 (23), 77 (65), 51 (21). HRMS (ESI) Calcd for $C_{14}H_{14}NO_3$ $[M + H]^+$: 244.0974, Found: 244.0982.

(*Z*)-Methyl 3-(phenylamino)but-2-enoate (3d)[8]



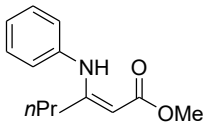
^{1}H NMR (500 MHz, $CDCl_3$): δ 10.37 (s, 1H), 7.32 (dd, J_1 = 8.0 Hz, J_2 = 7.5 Hz, 2H), 7.15 (t, J = 7.3 Hz, 1H), 7.08 (d, J = 8.0 Hz, 2H), 4.70 (s, 1H), 3.68 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.7, 159.1, 139.3, 129.1, 125.0, 124.5, 85.6, 50.2, 20.3. IR (thin film): ν_{max} (cm^{-1}) = 3256, 3189, 2990, 1657, 1615, 1490, 1441, 1274, 1166, 1030, 788, 746, 698, 496. MS (ESI) *m*/*z* 192 ($[M + H]^+$).

(*Z*)-Methyl 3-(phenylamino)pent-2-enoate (3e)



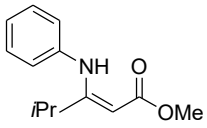
^{1}H NMR (500 MHz, $CDCl_3$): δ 10.31 (s, 1H), 7.34–7.31 (m, 2H), 7.17 (t, J = 7.3 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 4.74 (s, 1H), 3.69 (s, 3H), 2.32 (q, J = 7.5 Hz, 2H), 1.03 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.1, 164.9, 139.2, 129.1, 125.3, 125.1, 83.7, 50.3, 25.5, 12.4. IR (thin film): ν_{max} (cm^{-1}) = 3463, 3034, 2978, 2836, 1746, 1613, 1500, 1267, 1003, 751, 643, 494. MS (ESI) *m*/*z* 206 ($[M + H]^+$). HRMS (ESI) Calcd for $C_{12}H_{16}NO_2$ $[M + H]^+$: 206.1181, Found: 206.1181.

(*Z*)-Methyl 3-(phenylamino)hex-2-enoate (3f)



^{1}H NMR (500 MHz, $CDCl_3$): δ 10.29 (s, 1H), 7.34–7.31 (m, 2H), 7.17 (t, J = 7.3 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 4.73 (s, 1H), 3.70 (s, 3H), 2.28 (t, J = 7.8 Hz, 2H), 1.47–1.43 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.0, 163.4, 139.3, 129.1, 125.2, 125.1, 84.7, 50.2, 34.2, 21.3, 13.7. IR (thin film): ν_{max} (cm^{-1}) = 3248, 3185, 2963, 1744, 1653,1338, 1230, 1043, 789, 668, 648, 505. MS (ESI) *m*/*z* 220 ($[M + H]^+$). HRMS (ESI) Calcd for $C_{13}H_{18}NO_2$ $[M + H]^+$: 220.1338, Found: 220.1332.

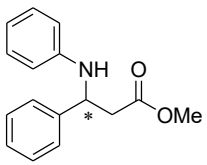
(*Z*)-Methyl 4-methyl-3-(phenylamino)pent-2-enoate (3g)



^{1}H NMR (500 MHz, $CDCl_3$): δ 10.31 (br, 1H), 7.34 (dd, J_1 = J_2 = 8.0 Hz, 2H), 7.19 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 4.78 (s, 1H), 3.69 (s, 3H), 2.87–2.82 (m, 1H), 1.09 (d, J = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.5, 171.4, 139.2, 129.1, 125.8, 125.5, 81.3, 50.2, 28.4, 22.0. IR (thin film): ν_{max} (cm^{-1}) = 3241, 3180, 2873, 1743, 1613, 1500, 1365, 1176, 1028, 916, 749, 490. MS (ESI) *m*/*z* 220 ($[M + H]^+$). HRMS (ESI) Calcd for $C_{13}H_{18}NO_2$ $[M + H]^+$: 220.1338, Found: 220.1332.

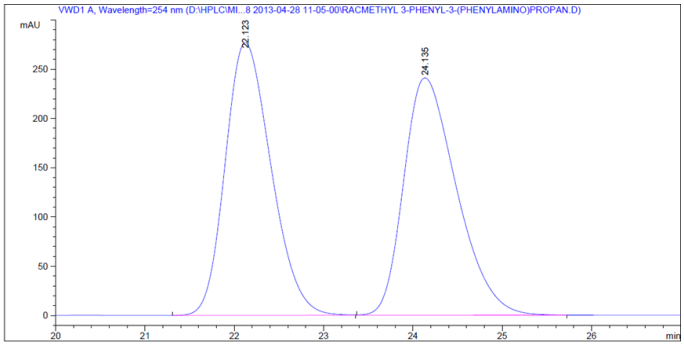
Analytical data and HPLC spectra for chiral *N*-aryl β-substituted β-amino esters

(–)-Methyl 3-phenyl-3-(phenylamino)propanoate (2a)[6]

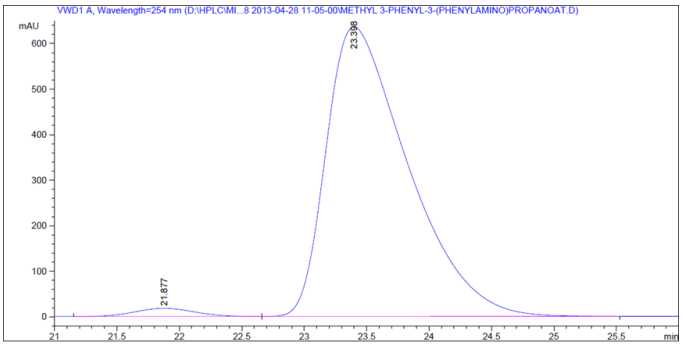


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.23 (m, 5H), 7.13–7.09 (m, 2H), 6.67 (t, J = 7.4 Hz, 1H), 6.56 (d, J = 7.6 Hz, 2H), 4.84 (t, J = 6.6 Hz, 1H), 4.55 (s, 1H), 3.65 (s, 3H), 2.83–2.81 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.6, 146.8, 142.2, 129.2, 128.8, 127.5, 126.2, 117.9, 113.7, 55.0, 51.9, 42.7. IR (thin film): ν_{max} (cm^{-1}) = 3388, 2950, 1731, 1505, 1314, 1168, 750. MS (EI, *m*/*z*, relative intensity): 255 (M^+, 11), 182 (100), 121 (9), 104 (15), 77 (27), 51 (4).

The conversion was determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 170 °C; isothermal; t_R (**1a**) = 18.63 min; t_R (**2a**) = 16.39 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 3 : 97; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (minor) = 21.88 min; t_R (major) = 23.40 min. $[\alpha]_D^{20}$ = –4.9 (c = 0.2 in $CHCl_3$) for a sample with 96 % *ee*. Literature data: $[\alpha]_D^{20}$ = –5.1 (c = 0.2 in $CHCl_3$) for an (–)-enantiomer sample with the optical value of 95 % *ee*. Chromatograms are illustrated below for a 96 % *ee* sample:

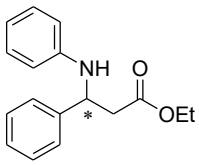


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.123	BB	0.5567	9889.57520	276.76123	49.9509
2	24.135	BB	0.6327	9909.01172	240.91078	50.0491



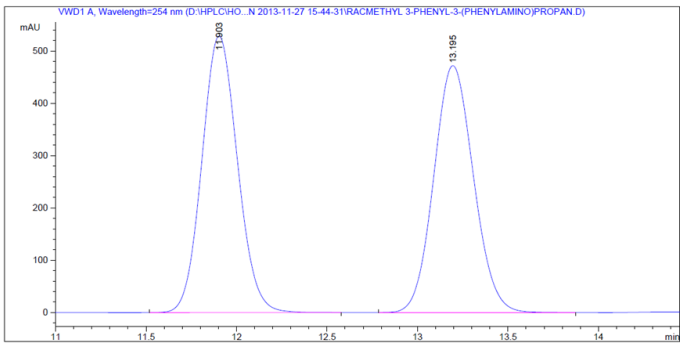
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.877	BV	0.5257	608.88220	18.06518	2.0603
2	23.398	VB	0.6886	2.89436e4	635.46033	97.9397

(+)-Ethyl 3-phenyl-3-(phenylamino)propanoate (2b)[4]

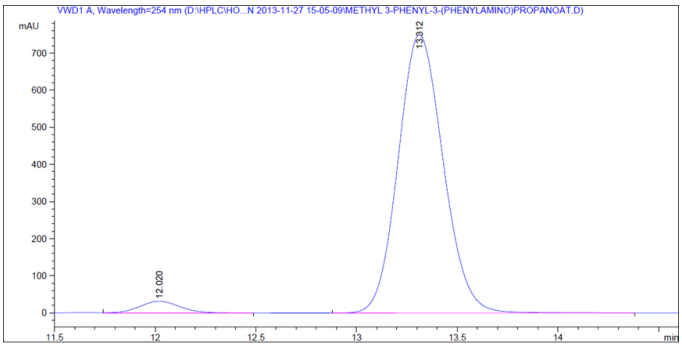


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.25 (m, 5H), 7.11–7.08 (m, 2H), 6.68–6.65 (m, 1H), 6.55 (d, J = 7.2 Hz, 2H), 4.84–4.82 (m, 1H), 4.55 (br, 1H), 4.11–4.09 (m, 2H), 2.80–2.78 (m, 2H), 1.19–1.15 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.2, 146.8, 142.2, 129.2, 128.8, 127.4, 126.3, 117.8, 113.7, 60.8, 55.0, 42.9, 14.2. IR (thin film): ν_{max} (cm^{-1}) = 3400, 2981, 1728, 1602, 1505, 1263, 1179, 1029, 750, 693. MS (EI, *m*/*z*, relative intensity): 269 (M^+, 12), 264 (35), 182 (40), 112 (50), 97 (44), 83 (49), 71 (71), 57 (100).

The conversion was determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 130 °C; isothermal; t_R (**1b**) = 12.31 min; t_R (**2b**) = 8.95 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel AD-H column (eluent, 2-propanol/hexane 5 : 95; flow rate, 1.0 mL•min^{-1}; detection, 254 nm light); t_R (minor) = 12.02 min; t_R (major) = 13.31 min. $[\alpha]_D^{20}$ = + 1.5 (c = 1.0, $CHCl_3$) for a 93 % *ee* sample. Literature data: $[\alpha]_D^{20}$ = –1.3 (c = 1.0 in $CHCl_3$) for an (–)-enantiomer sample with the optical value of 92 % *ee*. Chromatograms are illustrated below for a 93 % *ee* sample:

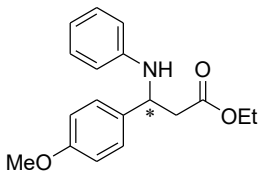


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.903	BB	0.2119	7232.54639	528.99963	50.0678
2	13.195	BB	0.2380	7212.96484	471.98837	49.9322



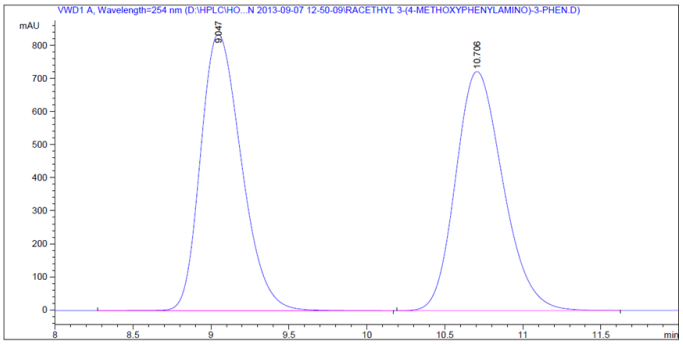
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.020	VB	0.2145	439.26248	31.61575	3.6348
2	13.312	BB	0.2424	1.16457e4	749.55463	96.3652

(+)-Ethyl 3-(4-methoxyphenyl)-3-(phenylamino)propanoate (2c)[5]

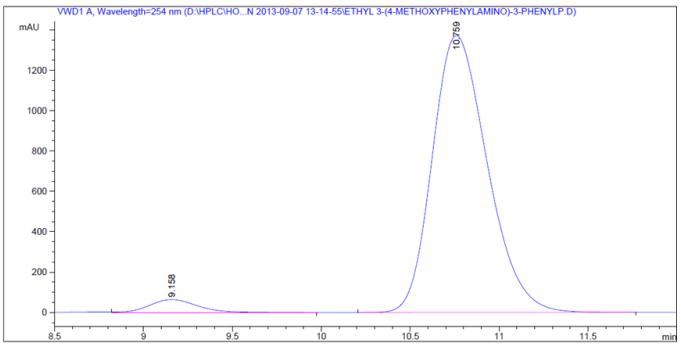


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, J = 8.5 Hz, 2H), 7.12 (dd, J_1 = 8.3 Hz, J_2 = 7.8 Hz, 2H), 6.86 (d, J = 9.0 Hz, 2H), 6.68 (t, J = 7.5 Hz, 1H), 6.57 (d, J = 8.0 Hz, 2H), 4.80 (t, J = 6.5 Hz, 1H), 4.53 (br, 1H), 4.14–4.09 (m, 2H), 3.78 (s, 3H), 2.79 (d, J = 6.5 Hz, 2H), 1.21 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.2, 158.9, 146.9, 134.2, 129.2, 127.4, 117.8, 114.1, 113.7, 60.8, 55.3, 54.5, 43.0, 14.2. IR (thin film): ν_{max} (cm^{-1}) = 3398, 2981, 2836, 1731, 1603, 1511, 1245, 1178, 1033, 751, 693. MS (EI, *m/z*, relative intensity): 299 (M^+, 10), 212 (100), 165 (25), 121 (57), 105 (31), 91 (17), 77 (15), 57 (13).

The conversion was determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 180 °C; isothermal; t_R (**1c**) = 36.81 min; t_R (**2c**) = 28.91 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 10 : 90; flow rate, 1.0 mL•min^{-1}; detection, 254 nm light); t_R (minor) = 9.16 min; t_R (major) = 10.76 min. $[\alpha]_D^{20}$ = +2.0 (c = 0.50, $CHCl_3$) for a 92 % *ee* sample. Chromatograms are illustrated below for a 92 % *ee* sample:

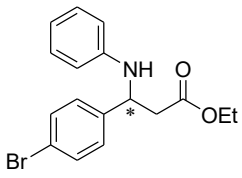


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.047	VB	0.2836	1.52048e4	835.57153	49.9624
2	10.706	BB	0.3258	1.52277e4	722.94427	50.0376



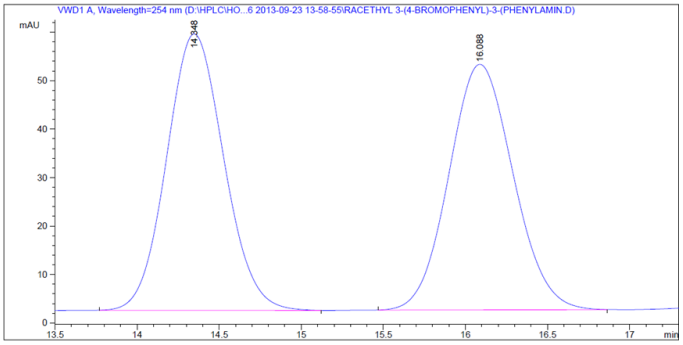
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.158	VB	0.2878	1181.36279	63.68672	3.8554
2	10.759	BB	0.3337	2.94601e4	1370.97144	96.1446

(+)-Ethyl 3-(4-bromophenyl)-3-(phenylamino)propanoate (2d)

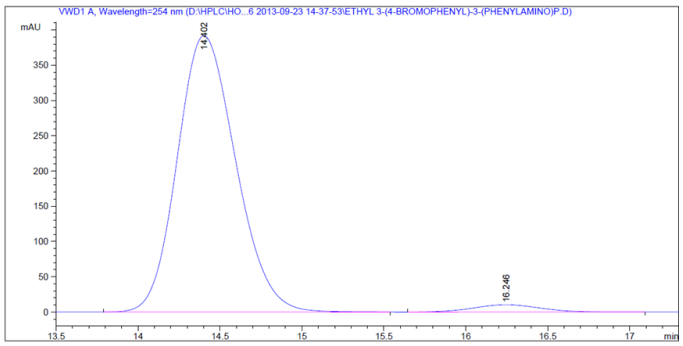


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.11 (dd, J_1 = 8.3 Hz, J_2 = 7.3 Hz, 2H), 6.70 (t, J = 7.5 Hz, 1H), 6.53 (d, J = 7.5 Hz, 2H), 4.81–4.77 (m, 1H), 4.60 (br, 1H), 4.15–4.09 (m, 2H), 2.82–2.74 (m, 2H), 1.21 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.9, 146.5, 141.3, 131.9, 129.2, 128.1, 121.2, 118.1, 113.7, 60.9, 54.5, 42.7, 14.2. IR (thin film): ν_{max} (cm^{-1}) = 3400, 2980, 2360, 1727, 1603, 1505, 1261, 1180, 1010, 750, 692. MS (ESI) m/z 348 ($[M + H]^+$). HRMS (ESI) Calcd for $C_{17}H_{19}BrNO_2$ $[M + H]^+$: 348.0599, Found: 348.0604.

The conversion was determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 210 °C; isothermal; t_R (**1d**) = 11.64 min; t_R (**2d**) = 9.91 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 4 : 96; flow rate, 1.0 mL•min^{-1}; detection, 254 nm light); t_R (major) = 14.40 min; t_R (minor) = 16.25 min. $[\alpha]_D^{20}$ = +1.4 (c = 0.50, $CHCl_3$) for a 94 % *ee* sample. Chromatograms are illustrated below for a 94 % *ee* sample:

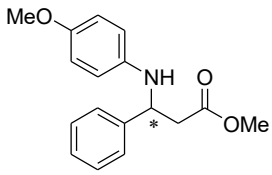


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.348	BB	0.3762	1384.25208	57.06599	50.0715
2	16.088	BB	0.4239	1380.29614	50.69947	49.9285



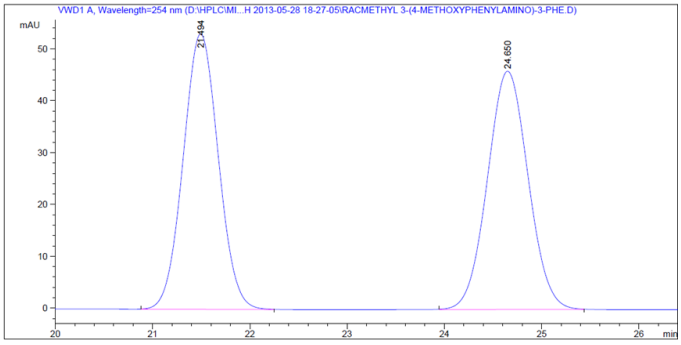
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.402	BB	0.3855	9719.64844	391.82440	97.1428
2	16.246	BB	0.4341	285.88107	10.26583	2.8572

(+)-Methyl 3-(4-methoxyphenylamino)-3-phenylpropanoate (2e)[6]

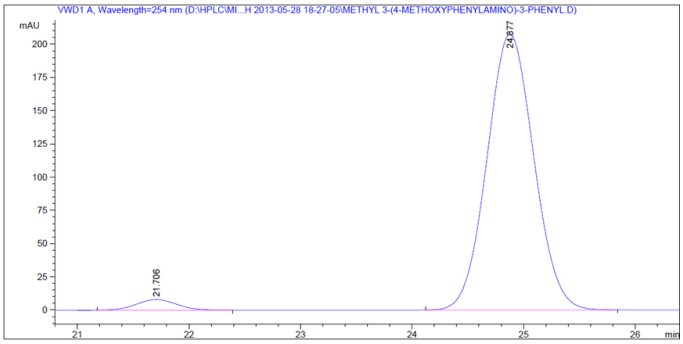


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.30 (m, 4H), 7.26–7.22 (m, 1H), 6.70 (d, J = 8.8 Hz, 2H), 6.52 (d, J = 8.8 Hz, 2H), 4.76 (t, J = 6.8 Hz, 1H), 4.27 (br, 1H), 3.69 (s, 3H), 3.65 (s, 3H), 2.80–2.78 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.7, 152.4, 142.4, 141.0, 128.8, 127.4, 126.3, 115.2, 114.8, 55.9, 55.7, 51.9, 42.7. IR (thin film): ν_{max} (cm^{-1}) = 3383, 2952, 2834, 1732, 1512, 1241, 1176, 1034, 821. MS (EI, *m/z*, relative intensity): 285 (M^+, 48), 212 (100), 134 (11), 121 (26), 108 (11), 91 (7), 77 (13), 59 (6), 51 (4).

The conversion was determined by NMR analysis. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel AD-H column (eluent, 2-propanol/hexane 5 : 95; flow rate, 1.0 mL•min^{-1}; detection, 254 nm light); t_R (minor) = 21.71 min; t_R (major) = 24.88 min. $[\alpha]_D^{20}$ = +5.4 (c = 0.20, $CHCl_3$) for a 94 % *ee* sample. Literature data: $[\alpha]_D^{20}$ = –6.2 (c = 0.2 in $CHCl_3$) for an (–)-enantiomer sample with the optical value of 95 % *ee*: Chromatograms are illustrated below for a 94 % *ee* sample:

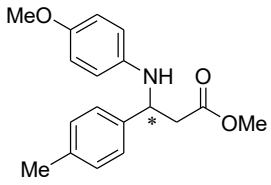


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.494	BB	0.3921	1335.24829	53.14352	49.9745
2	24.650	BB	0.4543	1336.60950	45.95763	50.0255



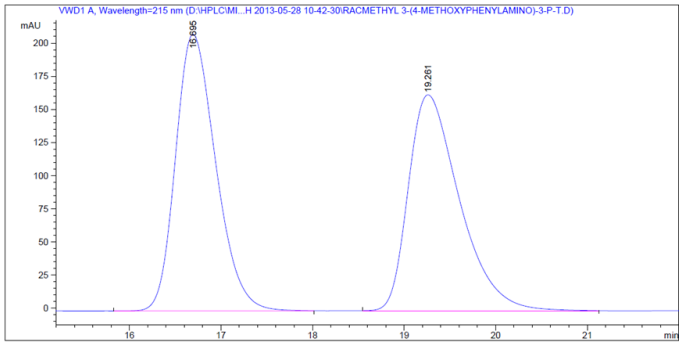
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.706	BB	0.3948	200.68672	7.95376	3.2071
2	24.877	BB	0.4554	6056.93018	207.61821	96.7929

(+)-Methyl 3-(4-methoxyphenylamino)-3-(*p*-tolyl)propanoate (2f)[6]

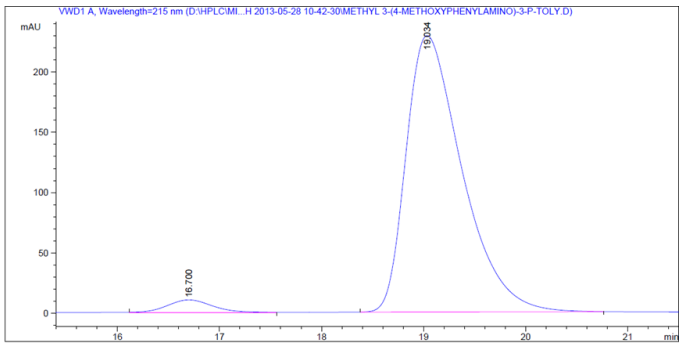


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.72 (d, J = 9.0 Hz, 2H), 6.55 (d, J = 8.5 Hz, 2H), 4.75 (t, J = 6.5 Hz, 1H), 4.24 (br, 1H), 3.72 (s, 3H), 3.67 (s, 3H), 2.81 (d, J = 7.0 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.7, 152.4, 141.1, 139.4, 137.0, 129.4, 126.2, 115.2, 114.8, 55.8, 55.7, 51.8, 42.7, 21.1. IR (thin film): ν_{max} (cm^{-1}) = 3459, 2888, 2856, 1776, 1599, 1427, 1249, 1156, 1035, 845, 723. MS (ESI) *m*/*z* 300 ([M + H]$^+$).

The conversion was determined by NMR analysis. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 5 : 95; flow rate, 1.0 mL•min^{-1}; detection, 254 nm light); t_R (minor) = 16.70 min; t_R (major) = 19.03 min. $[\alpha]_D^{20}$ = +3.8 (c = 0.50, $CHCl_3$) for a 93 % *ee* sample. Chromatograms are illustrated below for a 93 % *ee* sample:

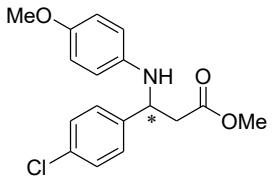


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.695	BB	0.4710	6369.14502	208.71675	50.1993
2	19.261	BB	0.5937	6318.58398	162.93169	49.8007



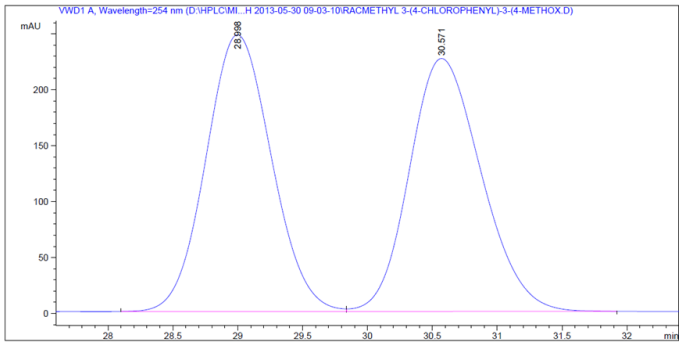
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.700	BB	0.4654	309.52448	10.30683	3.4236
2	19.034	BB	0.5816	8731.40332	229.06335	96.5764

(–)-Methyl 3-(4-chlorophenyl)-3-(4-methoxyphenylamino)propanoate (2g)[6]

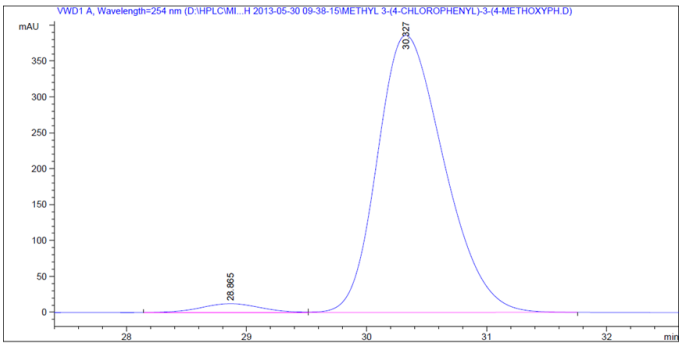


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.26 (m, 4H), 6.70 (d, J = 8.8 Hz, 2H), 6.52 (d, J = 8.8 Hz, 2H), 4.76 (t, J = 6.8 Hz, 1H), 4.27 (br, 1H), 3.69 (s, 3H), 3.65 (s, 3H), 2.79 (d, J = 6.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.4, 152.5, 141.0, 140.6, 133.1, 128.9, 127.8, 115.3, 114.8, 55.7, 55.3, 51.9, 42.5. IR (thin film): ν_{max} (cm^{-1}) = 3386, 2952, 2834, 1611, 1512, 1242, 1176, 1034, 822. MS (EI, *m*/*z*, relative intensity): 319 (M^+, 46), 246 (100), 155 (22), 122 (24), 108 (11), 95 (6), 77 (7), 59 (8).

The conversion was determined by NMR analysis. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel AD-H column (eluent, 2-propanol/hexane 5 : 95; flow rate, 1.0 mL•min^{-1}; detection, 254 nm light); t_R (minor) = 28.87 min; t_R (major) = 30.33 min. $[\alpha]_D^{20}$ = –3.2 (c = 0.50, $CHCl_3$) for a 95 % *ee* sample. Chromatograms are illustrated below for a 95 % *ee* sample:

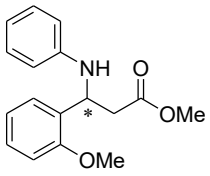


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.998	BV	0.5503	8706.64746	247.40907	49.9858
2	30.571	VB	0.5994	8711.60840	226.16017	50.0142



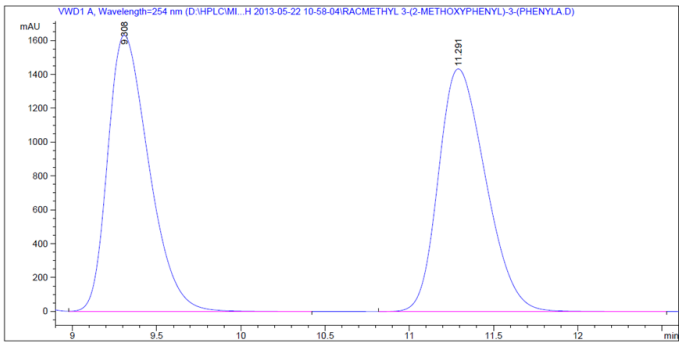
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.865	BV	0.5337	416.05621	12.18766	2.7213
2	30.327	VB	0.5949	1.48727e4	386.16104	97.2787

(–)-Methyl 3-(2-methoxyphenyl)-3-(phenylamino)propanoate (2h)[5]

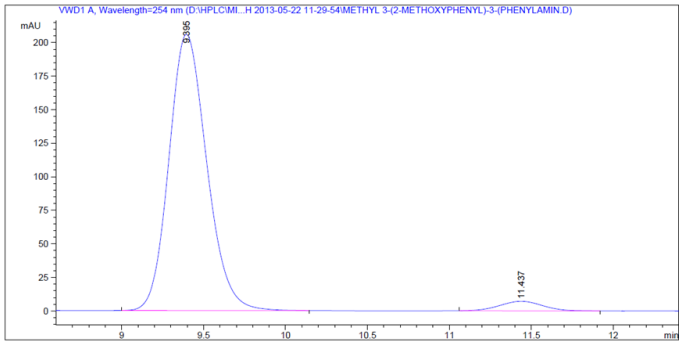


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32–7.30 (m, 1H), 7.24–7.21 (m, 1H), 7.11 (dd, J_1 = 8.5 Hz, J_2 = 7.5 Hz, 2H), 6.91–6.87 (m, 2H), 6.66 (t, J = 7.3 Hz, 1H), 6.59 (d, J = 7.5 Hz, 2H), 5.16–5.13 (m, 1H), 4.77 (s, 1H), 3.92 (s, 3H), 3.64 (s, 3H), 2.95–2.80 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.1, 156.9, 147.0, 129.3, 129.1, 128.3, 127.6, 120.8, 117.6, 113.7, 110.6, 55.4, 51.7, 50.7, 40.3. IR (thin film): ν_{max} (cm^{-1}) = 3397, 2950, 2838, 1732, 1602, 1505, 1262, 1167, 750, 693. MS (EI, *m*/*z*, relative intensity): 285 (M^+, 46), 212 (100), 196 (13), 151 (27), 91 (13), 77 (13), 65 (6), 51 (4).

The conversion was determined by Capillary GC with a 25m × 0.25 mm HP-5 column (Varian, carrier gas, N_2); 180 °C; isothermal; t_R (**1h**) = 19.41 min; t_R (**2h**) = 16.57 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel AS-H column (eluent, 2-propanol/hexane 10 : 90; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (major) = 9.40 min; t_R (minor) = 11.44 min. $[\alpha]_D^{20}$ = –2.0 (*c* = 0.50, $CHCl_3$) for a sample with 92 % *ee*. Literature data: $[\alpha]_D^{20}$ = –1.7 (*c* = 0.50, $CHCl_3$) for an (–)-enantiomer sample with the optical value of 90 % *ee*. Chromatograms are illustrated below for a 92 % *ee* sample:

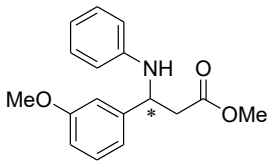


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.308	VB	0.2622	2.77158e4	1632.04590	49.8292
2	11.291	BB	0.3043	2.79059e4	1433.42212	50.1708



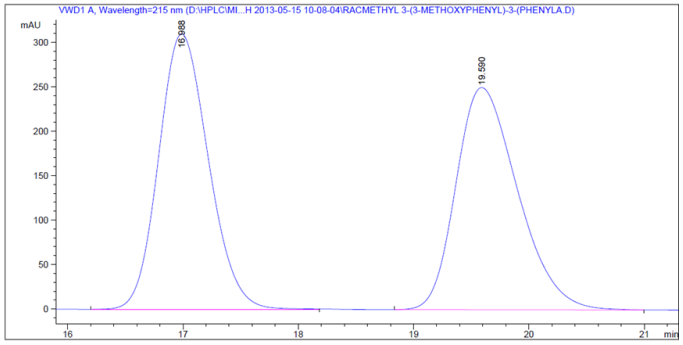
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.395	BB	0.2470	3303.68994	205.81419	96.2467
2	11.437	BB	0.2816	128.83168	7.09776	3.7533

(–)-Methyl 3-(3-methoxyphenyl)-3-(phenylamino)propanoate (2i)[4]

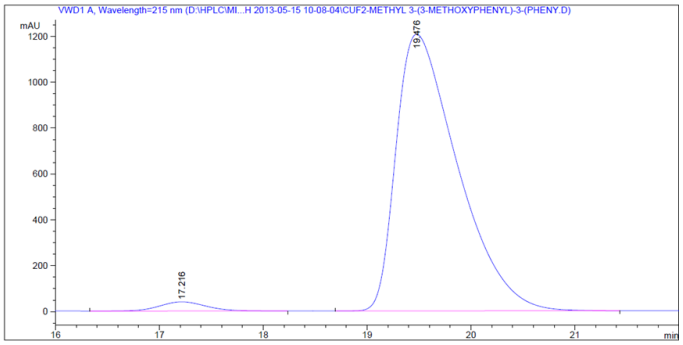


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29–7.26 (m, 1H), 7.16–7.13 (m, 2H), 7.01–6.97 (m, 2H), 6.82 (d, J = 7.5 Hz, 1H), 6.82 (t, J = 6.8 Hz, 1H), 6.10 (d, J = 7.5 Hz, 2H), 4.85–4.84 (m, 1H), 4.56 (s, 1H), 3.81 (s, 3H), 3.69 (s, 3H), 2.85–2.80 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.6, 160.0, 146.8, 144.1, 129.9, 129.2, 118.5, 117.9, 113.7, 112.7, 112.0, 55.2, 55.0, 52.9, 42.7. IR (thin film): ν_{max} (cm^{-1}) = 3397, 2951, 2836, 1732, 1602, 1506, 1256, 1155, 751, 693. MS (EI, *m*/*z*, relative intensity): 285 (M^+, 63), 212 (100), 151 (30), 104 (19), 91 (9), 77 (19), 65 (6), 51 (4).

The conversion was determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 180 °C; isothermal; t_R (**1i**) = 23.00 min; t_R (**2i**) = 20.27 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 10 : 90; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (minor) = 17.22 min; t_R (major) = 19.48 min. $[\alpha]_D^{20}$ = –2.2 (*c* = 0.50, $CHCl_3$) for a sample with 95 % *ee*. Chromatograms are illustrated below for a 95 % *ee* sample:

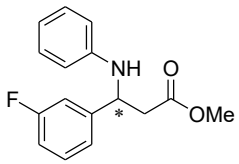


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.988	BB	0.4675	9283.57324	309.86343	49.9896
2	19.590	BB	0.5762	9287.44629	249.96921	50.0104



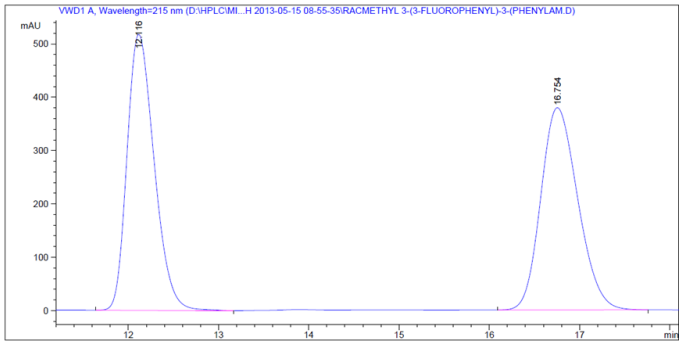
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.216	VB	0.4806	1243.60254	40.00307	2.4419
2	19.476	BB	0.6247	4.96849e4	1206.24854	97.5581

(+)-Methyl 3-(3-fluorophenyl)-3-(phenylamino)propanoate (2j)

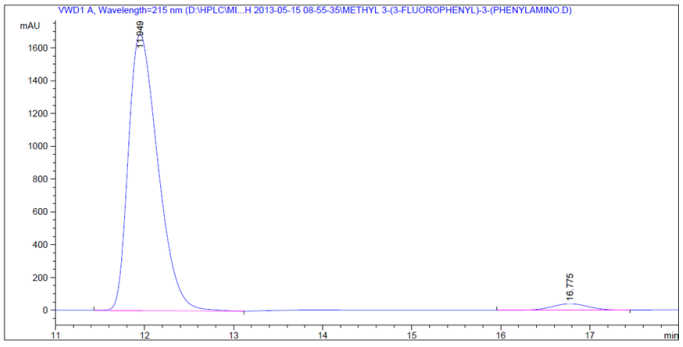


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32–7.28 (m, 1H), 7.18–7.10 (m, 4H), 6.97–6.93 (m, 1H), 6.71 (t, J = 7.0 Hz, 1H), 6.56 (d, J = 8.0 Hz, 2H), 4.84 (t, J = 6.5 Hz, 1H), 4.60 (s, 1H), 3.67 (s, 3H), 2.86–2.77 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.3, 164.2, 162.2, 146.5, 145.2, 130.4, 129.2, 121.9, 118.1, 113.9, 113.7, 54.6, 52.0, 42.5. IR (thin film): ν_{max} (cm^{-1}) = 3400, 2952, 1732, 1603, 1506, 1251, 1179, 751, 693. MS (ESI) m/z 273 (M^+). HRMS (ESI) Calcd for $C_{16}H_{17}FNO_2$ $[M + H]^+$: 274.1243, Found: 274.1234.

The conversion was determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 180 °C; isothermal; t_R (**1j**) = 9.71 min; t_R (**2j**) = 8.99 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 10 : 90; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (major) = 11.95 min; t_R (minor) = 16.78 min. $[\alpha]_D^{20}$ = +2.8 (c = 0.50, $CHCl_3$) for a sample with 94 % *ee*. Chromatograms are illustrated below for a 94 % *ee* sample:

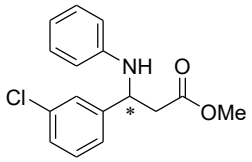


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.116	BV	0.3257	1.08212e4	517.13660	50.0544
2	16.754	BB	0.4460	1.07977e4	378.97525	49.9456



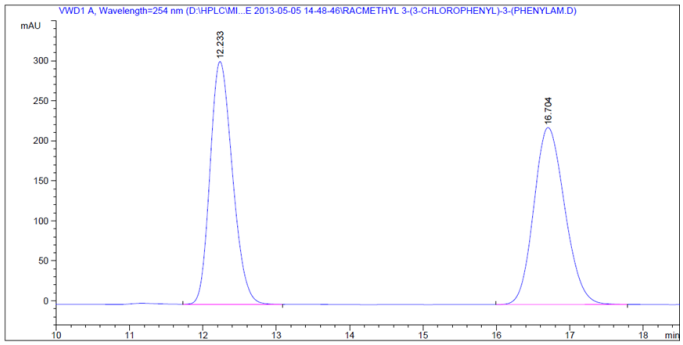
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.949	VV	0.3590	3.88147e4	1685.34302	97.2043
2	16.775	BV	0.4368	1116.36304	39.75764	2.7957

(–)-Methyl 3-(3-chlorophenyl)-3-(phenylamino)propanoate (2k)

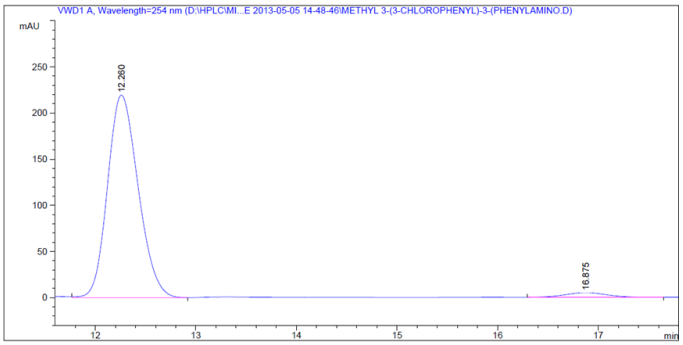


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (s, 1H), 7.26–7.21 (m, 3H), 7.13–7.09 (m, 2H), 6.69 (t, J = 7.4 Hz, 1H), 6.53 (d, J = 8.0 Hz, 2H), 4.78 (t, J = 6.6 Hz, 1H), 4.58 (s, 1H), 3.65 (s, 3H), 2.83–2.73 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.3, 146.4, 144.5, 134.7, 130.2, 129.3, 127.8, 126.5, 124.5, 118.1, 113.7, 54.6, 52.1, 42.6. IR (thin film): ν_{max} (cm^{-1}) = 3401, 2951, 1732, 1603, 1506, 1290, 1170, 751, 693. MS (ESI) *m/z* 290 ($[M + H]^+$). HRMS (ESI) Calcd for $C_{16}H_{17}ClNO_2$ $[M + H]^+$: 290.0948, Found: 290.0942.

The conversion was determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 200 °C; isothermal; t_R (**1k**) = 8.69 min; t_R (**2k**) = 8.13 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 10 : 90; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (major) = 12.26 min; t_R (minor) = 16.88 min. $[\alpha]_D^{20}$ = –2.0 (c = 0.50, $CHCl_3$) for a sample with 94 % *ee*. Chromatograms are illustrated below for a 94 % *ee* sample:

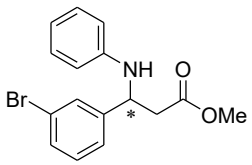


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.233	VB	0.3309	6445.82910	303.38910	49.8408
2	16.704	BB	0.4574	6486.99951	221.06792	50.1592



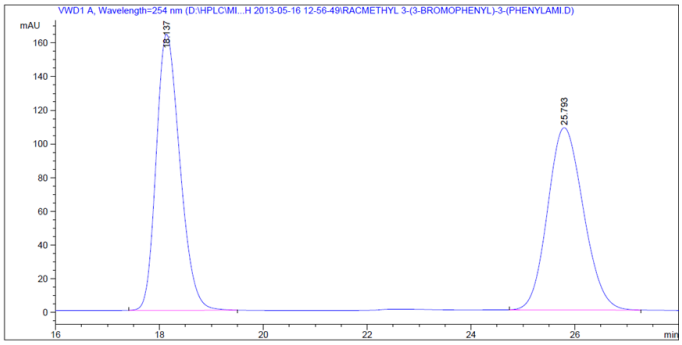
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.260	VV	0.3281	4637.97021	219.47231	97.0049
2	16.875	BB	0.4499	143.20076	5.01145	2.9951

(+)-Methyl 3-(3-bromophenyl)-3-(phenylamino)propanoate (2l)

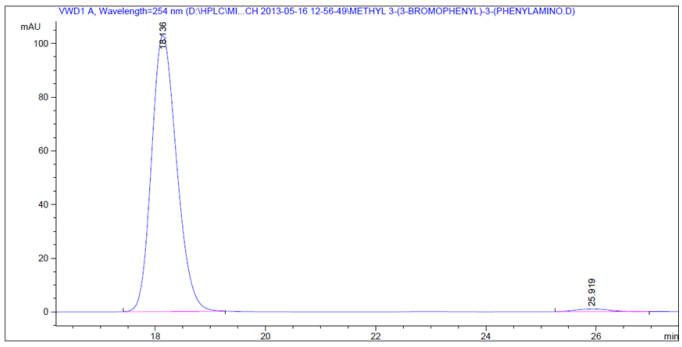


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (s, 1H),7.38–7.24 (m, 2H), 7.20–7.09 (m, 3H), 6.69 (t, J = 7.2 Hz, 1H), 6.53 (d, J = 7.2 Hz, 2H), 4.77 (br, 1H), 4.57 (br, 1H), 3.65 (s, 3H), 2.83–2.72 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.3, 146.4, 144.8, 130.7, 130.5, 129.4, 129.3, 124.9, 123.0, 118.1, 113.7, 54.5, 52.1, 42.6. IR (thin film): ν_{max} (cm^{-1}) = 3401, 2951, 1732, 1603, 1506, 1290, 1170, 750, 693. MS (ESI) m/z 334 ($[M + H]^+$). HRMS (ESI) Calcd for $C_{16}H_{17}BrNO_2$ $[M + H]^+$: 334.0443, Found: 334.0440.

The conversion was determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 180 °C; isothermal; t_R (**1l**) = 25.72 min; t_R (**2l**)= 23.98 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 5 : 95; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (major) = 18.14 min; t_R (minor)= 25.92 min. $[\alpha]_D^{20}$ = +2.3 (c = 1.0, $CHCl_3$) for a sample with 98 % *ee*. Chromatograms are illustrated below for a 98 % *ee* sample:

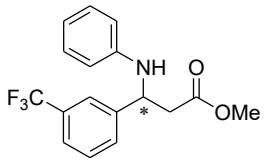


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.137	BB	0.4910	5197.60107	163.81725	50.0970
2	25.793	BB	0.7490	5177.47363	108.19547	49.9030



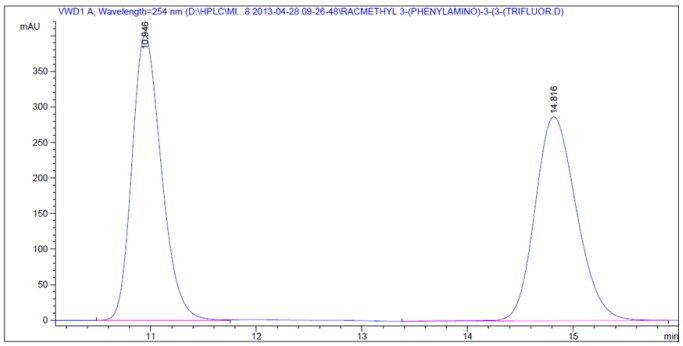
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.136	BB	0.4908	3250.23682	102.89220	98.7826
2	25.919	BB	0.5014	40.05657	9.86506e-1	1.2174

(+)-Methyl 3-(phenylamino)-3-(3-(trifluoromethyl)phenyl)propanoate (2m)

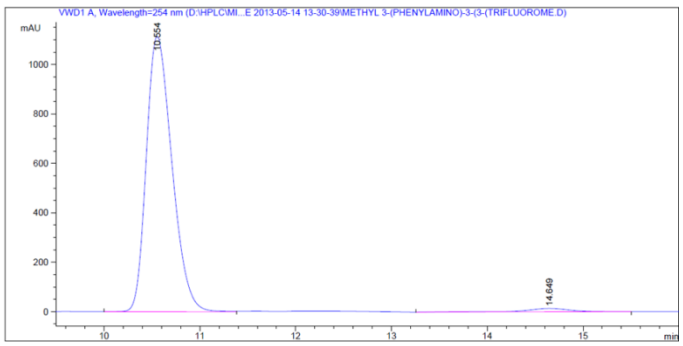


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.45 (dd, $J_1 = J_2$ = 7.6 Hz, 1H), 7.15–7.11 (m, 2H), 6.72 (t, J = 7.2 Hz, 1H), 6.55 (d, J = 8.0 Hz, 2H), 4.89 (t, J = 6.6 Hz, 1H), 4.64 (s, 1H), 3.67 (s, 3H), 2.84–2.82 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.2, 146.3, 143.4, 129.7, 129.4, 129.3, 124.5, 124.5, 123.1, 123.1, 118.2, 113.7, 54.7, 52.1, 42.5. IR (thin film): ν_{max} (cm^{-1}) = 3400, 2954, 1732, 1603, 1507, 1328, 1167, 750, 693. MS (ESI) m/z 324 ($[M + H]^+$). HRMS (ESI) Calcd for $C_{17}H_{17}F_3NO_2$ $[M + H]^+$: 324.1211, Found: 324.1210.

The conversion was determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 180 °C; isothermal; t_R (**1m**) = 9.43 min; t_R (**2m**) = 7.61 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 10 : 90; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (major) = 10.55min; t_R (minor) = 14.65min. $[\alpha]_D^{20}$ = +5.5 (c = 1.0, $CHCl_3$) for a sample with 96 % *ee*. Chromatograms are illustrated below for a 96 % *ee* sample:

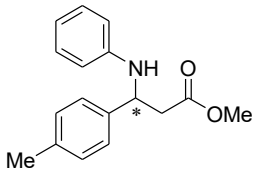


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.946	BV	0.3000	7752.09863	400.67834	49.7191
2	14.816	BB	0.4250	7839.68066	286.94281	50.2809



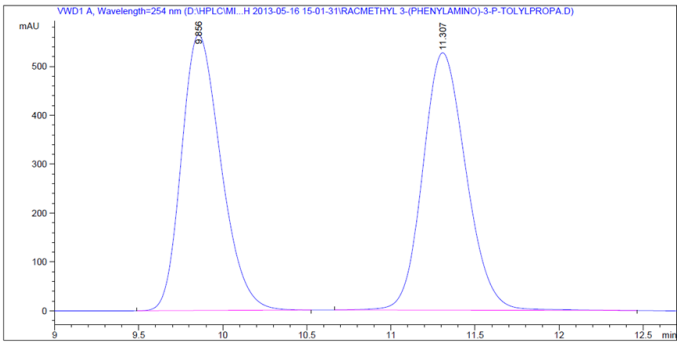
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.554	VV	0.2883	2.07242e4	1114.31836	97.8992
2	14.649	VB	0.4849	444.72098	13.49631	2.1008

(+)-Methyl 3-(phenylamino)-3-(*p*-tolyl)propanoate (2n)[4]

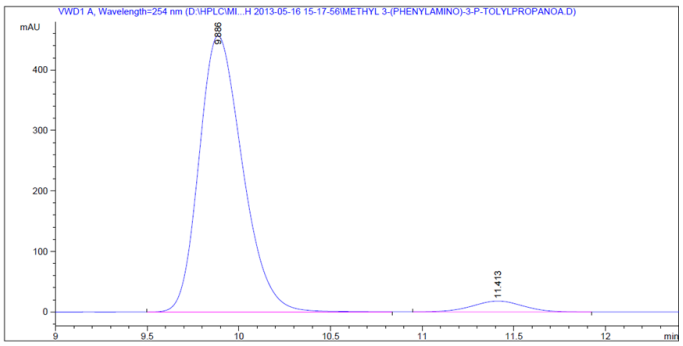


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28–7.26 (m, 2H), 7.15–7.10 (m, 4H), 6.68 (t, J = 7.5 Hz, 1H), 6.58 (d, J = 7.5 Hz, 2H), 4.82 (t, J = 6.5 Hz, 1H), 4.49 (s, 1H), 3.66 (s, 3H), 2.82 (d, J = 7.0 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.6, 146.9, 139.2, 137.1, 129.5, 129.2, 126.1, 117.8, 113.7, 54.7, 51.9, 42.7, 21.1. IR (thin film): ν_{max} (cm^{-1}) = 3400, 2950, 1731, 1603, 1504, 1261, 1165, 750, 692. MS (EI, *m*/*z*, relative intensity): 269 (M^+, 43), 196 (100), 135 (51), 117 (17), 104 (26), 93 (20), 77 (29), 51 (4).

The conversion was determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 180 °C; isothermal; t_R (**1n**) = 15.56 min; t_R (**2n**) = 13.20 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 10 : 90; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (major) = 9.89 min; t_R (minor) = 11.41 min. $[\alpha]_D^{20}$ = +16.8 (c = 0.50, $CHCl_3$) for a sample with 91 % *ee*. Literature data: $[\alpha]_D^{20}$ = –16.9 (c = 0.50, $CHCl_3$) for an (–)-enantiomer sample with the optical value of 91 % *ee*. Chromatograms are illustrated below for a 91 % *ee* sample:

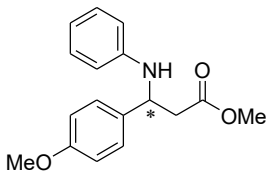


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.856	BB	0.2527	9190.32910	563.96637	49.3680
2	11.307	BB	0.2773	9425.63867	526.53851	50.6320



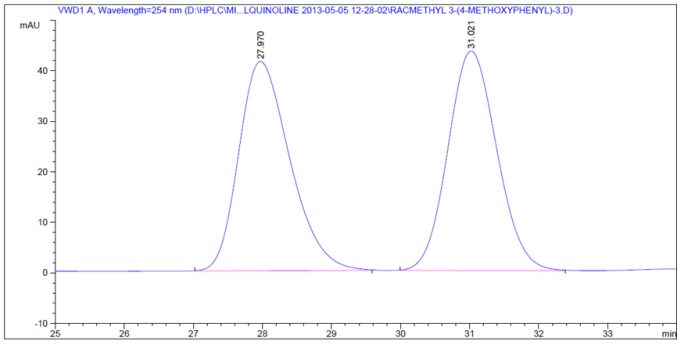
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.886	BB	0.2556	7496.83252	456.61099	95.5653
2	11.413	BB	0.2990	347.88623	17.94588	4.4347

(–)-Methyl 3-(4-methoxyphenyl)-3-(phenylamino)propanoate (2o)

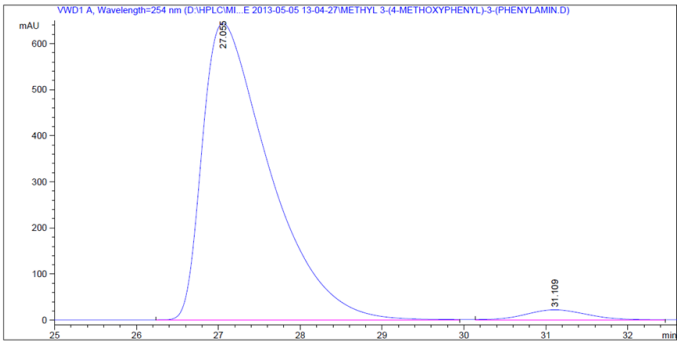


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 8.8 Hz, 2H), 7.14–7.10 (m, 2H), 6.86 (d, J = 8.4 Hz, 2H), 6.68 (t, J = 7.4 Hz, 1H), 6.57 (d, J = 8.0 Hz, 2H), 4.81 (t, J = 6.8 Hz, 1H), 4.52 (s, 1H), 3.79 (s, 3H), 3.66 (s, 3H), 2.81 (d, J = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.7, 158.9, 146.8, 134.1, 129.2, 127.4, 117.8, 114.2, 113.7, 55.3, 54.3, 52.0, 42.7. IR (thin film): ν_{max} (cm^{-1}) = 3398, 2952, 2836, 1732, 1603, 1511, 1248, 1177, 751, 693. MS (ESI) m/z 286 ($[M + H]^+$). HRMS (ESI) Calcd for $C_{17}H_{20}NO_3$ $[M + H]^+$: 286.1443, Found: 286.1451.

The conversion was determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 180 °C; isothermal; t_R (**1o**) = 28.40 min; t_R (**2o**) = 23.88 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 3 : 97; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (major) = 27.06 min; t_R (minor)=31.11 min. $[\alpha]_D^{20}$ = –9.0 (c = 0.50, $CHCl_3$) for a sample with 94 % *ee*. Chromatograms are illustrated below for a 94 % *ee* sample:

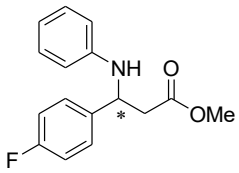


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.970	BB	0.7940	2130.99731	41.41405	49.9488
2	31.021	BB	0.7646	2135.36475	43.41473	50.0512



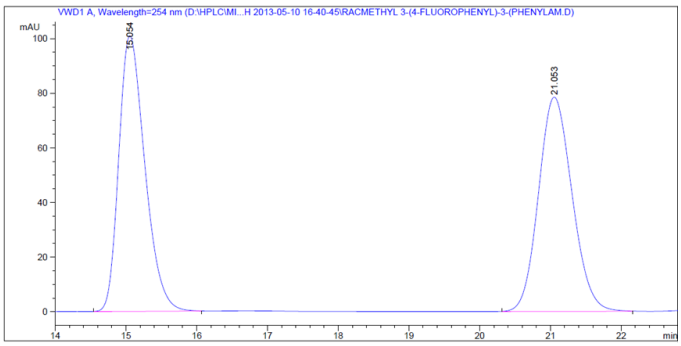
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.055	BB	0.8511	3.66575e4	643.35193	97.0362
2	31.109	BB	0.7992	1119.63367	21.72919	2.9638

(+)-Methyl 3-(4-fluorophenyl)-3-(phenylamino)propanoate (2p)[4]

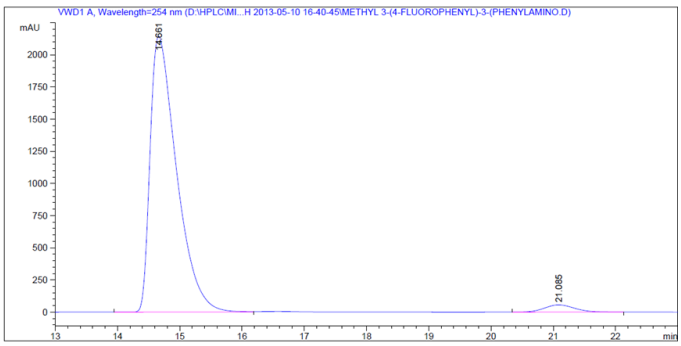


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37–7.34 (m, 2H), 7.14–7.11 (m, 2H), 7.03–7.00 (m, 2H), 6.70 (t, J = 7.3 Hz, 1H), 6.55 (d, J = 8.0 Hz, 2H), 4.83 (t, J = 6.5 Hz, 1H), 4.58 (s, 1H), 3.66 (s, 3H), 2.81 (d, J = 6.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.4, 163.1, 161.1 146.6, 137.9, 129.2, 127.9, 118.0, 115.8, 113.7, 54.3, 52.0, 42.7. IR (thin film): ν_{max} (cm^{-1}) =3400, 2952, 1732, 1603, 1508, 1221, 1157, 834, 751, 693. MS (EI, *m/z*, relative intensity): 273 (M^+, 19), 212 (30), 200 (100), 151 (25), 139 (18), 123 (19), 104 (11), 93 (11), 77 (7), 51 (10).

The conversion was determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 180°C; isothermal; t_R (**1p**) = 10.22 min; t_R (**2p**) = 9.28 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 5 : 95; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (major) = 14.66 min; t_R (minor) = 21.09 min. $[\alpha]_D^{20}$ = +7.6 (c = 1.0, $CHCl_3$) for a sample with 94 % *ee*. Literature data: $[\alpha]_D^{20}$ = –12.2 (c = 0.50, $CHCl_3$) for an (–)-enantiomer sample with the optical value of 95 % *ee*. Chromatograms are illustrated below for a 94 % *ee* sample:

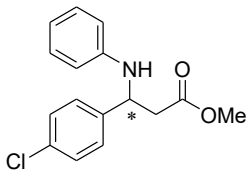


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.054	BB	0.3942	2578.06396	100.88611	49.9351
2	21.053	BB	0.5141	2584.76782	78.41945	50.0649



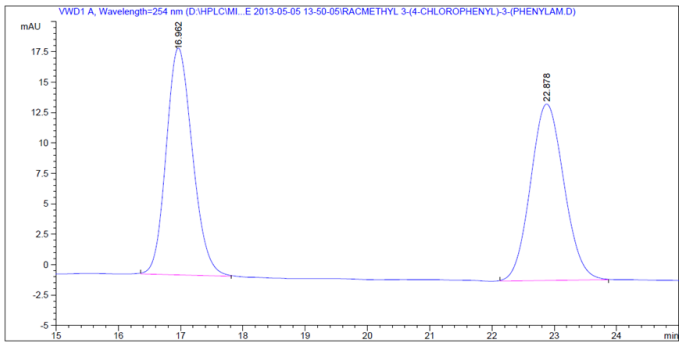
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.661	BV	0.4453	6.31121e4	2144.54980	97.1585
2	21.085	BB	0.5170	1845.78894	55.58536	2.8415

(–)-Methyl 3-(4-chlorophenyl)-3-(phenylamino)propanoate (2q)

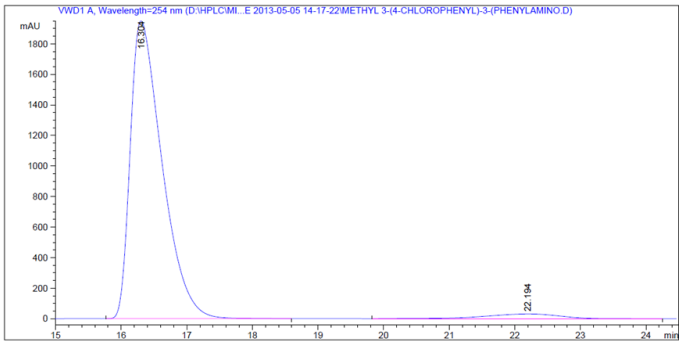


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33–7.29 (m, 4H), 7.12 (dd, $J_1 = J_2 =$ 8.0 Hz, 2H), 6.70 (t, $J = 7.3$ Hz, 1H), 6.54 (d, $J = 8.0$ Hz, 2H), 4.81 (t, $J =$ 6.5 Hz, 1H), 4.57 (s, 1H), 3.66 (s, 3H), 2.81–2.80 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.3, 146.5, 140.7, 133.2, 129.2, 129.0, 127.7, 118.1, 113.7, 54.4, 52.0, 42.5. IR (thin film): ν_{max} (cm^{-1}) =3401, 2951, 1732, 1603, 1505, 1287, 1166, 750, 693. MS (ESI) *m/z* 290 ($[M + H]^+$). HRMS (ESI) Calcd for $C_{16}H_{17}ClNO_2$ $[M + H]^+$: 290.0948, Found: 290.0943.

The conversion was determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 180 °C; isothermal; t_R (**1q**) = 20.40 min; t_R (**2q**) = 18.52 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 5 : 95; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (major) = 16.30 min; t_R (minor) = 22.19 min. $[\alpha]_D^{20}$ = –3.5 (c = 1.0, $CHCl_3$) for a sample with 93 % *ee*. Chromatograms are illustrated below for a 93 % *ee* sample:

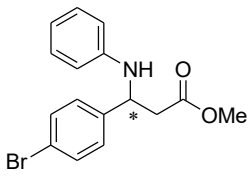


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.962	BB	0.4545	547.74719	18.66565	50.2672
2	22.878	BB	0.5840	541.92365	14.51643	49.7328



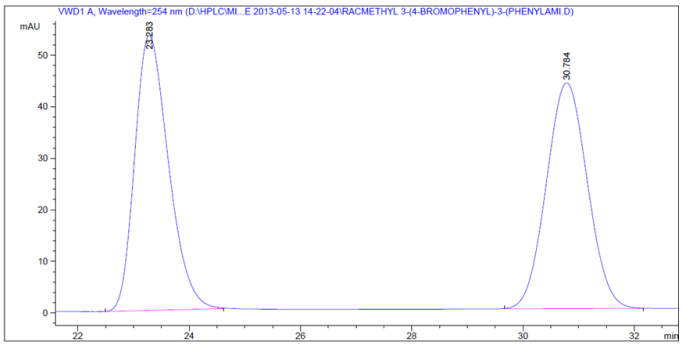
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.304	VB	0.5094	6.56585e4	1949.71692	96.4789
2	22.194	VB	1.2003	2396.28149	30.80117	3.5211

(–)-Methyl 3-(4-bromophenyl)-3-(phenylamino)propanoate (2r)

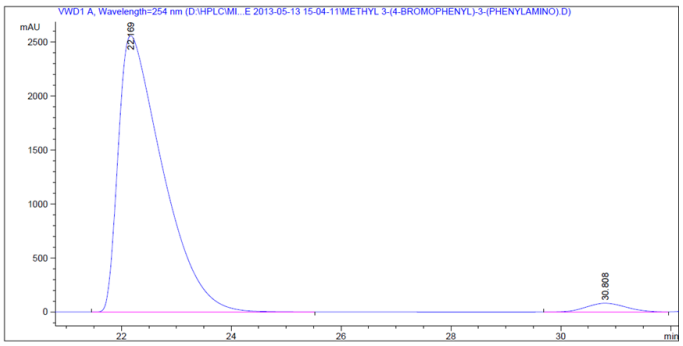


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.42 (m, 2H), 7.25 (d, J = 8.5 Hz, 2H), 7.10 (dd, J_1 = 8.3, J_2 = 7.8 Hz, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.52 (d, J = 8.0 Hz, 2H), 4.78 (t, J = 6.5 Hz, 1H), 3.64 (s, 3H), 2.79–2.77 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.2, 146.4, 141.3, 131.9, 129.2, 128.1, 121.3, 118.1, 113.8, 54.4, 52.0, 42.4. IR (thin film): ν_{max} (cm^{-1}) =3401, 2950, 1732, 1603, 1504, 1259, 1166, 751, 692. MS (ESI) m/z 334 ($[M + H]^+$). HRMS (ESI) Calcd for $C_{16}H_{17}BrNO_2$ $[M + H]^+$: 334.0443, Found: 334.0438.

The conversion was determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 190 °C; isothermal; t_R (**1r**) = 18.98 min; t_R (**2r**) = 17.56 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 5 : 95; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (major) = 22.17 min; t_R (minor) = 30.81 min. $[\alpha]_D^{20}$ = –9.9 (c = 1.0, $CHCl_3$) for a sample with 95 % *ee*. Chromatograms are illustrated below for a 95 % *ee* sample:

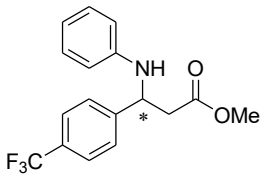


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.283	BB	0.6505	2241.67529	53.33689	49.9712
2	30.784	BB	0.8049	2244.26245	43.77210	50.0288



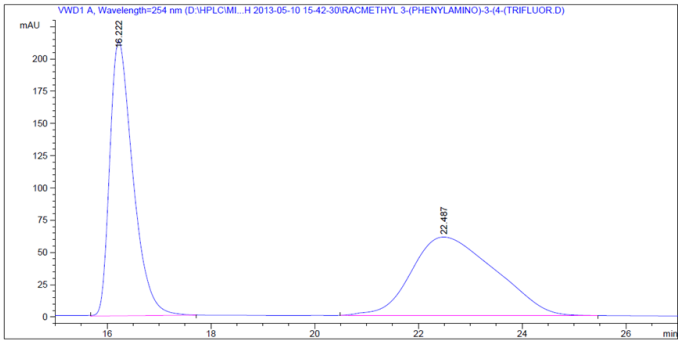
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.169	BB	0.8442	1.43367e5	2559.44702	97.2538
2	30.808	BV	0.7792	4048.37500	80.86743	2.7462

(+)-Methyl 3-(phenylamino)-3-(4-(trifluoromethyl)phenyl)propanoate (2s)

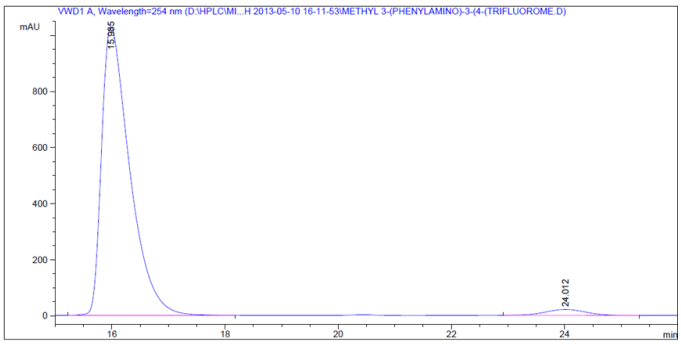


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J = 7.5 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.14–7.11 (m, 2H), 6.72 (t, J = 7.0 Hz, 1H), 6.54 (d, J = 8.0 Hz, 2H), 4.91–4.89 (m, 1H), 4.65 (s, 1H), 3.67 (s, 3H), 2.88–2.79 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.2, 146.4, 146.3, 129.3, 126.7, 125.9, 125.8, 125.7, 118.3, 113.7, 54.6, 52.1, 42.4. IR (thin film): ν_{max} (cm^{-1}) = 3401, 2954, 1732, 1603, 1506, 1326, 1165, 1121, 1067, 752, 693. MS (ESI) m/z 324 ($[M + H]^+$). HRMS (ESI) Calcd for $C_{17}H_{17}F_3NO_2$ $[M + H]^+$: 324.1211, Found: 324.1216.

The conversion was determined by Capillary GC with a 30 m×0.25 mm J & W Scientific INNOWAX column (Varian, carrier gas, N_2); 220 °C; isothermal; t_R (**1s**) = 15.67 min; t_R (**2s**) = 9.90 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 5 : 95; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (major) = 15.99 min; t_R (minor) = 24.01 min. $[\alpha]_D^{20}$ = +4.3 (c = 1.0, $CHCl_3$) for a sample with 94 % *ee*. Chromatograms are illustrated below for a 94 % *ee* sample:

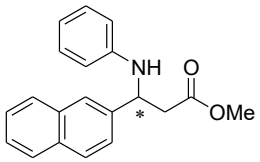


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.222	BB	0.4723	6596.14746	212.80885	49.1696
2	22.487	BB	1.6507	6818.93652	60.86326	50.8304



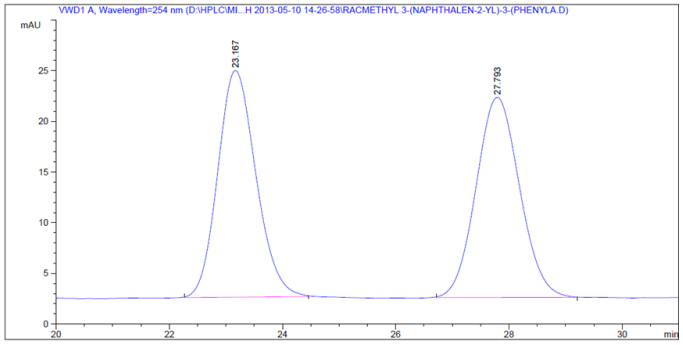
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.985	BB	0.5206	3.55503e4	1029.98145	97.1676
2	24.012	BB	0.7700	1036.26233	21.03020	2.8324

(+)-Methyl 3-(naphthalen-2-yl)-3-(phenylamino)propanoate (4a)

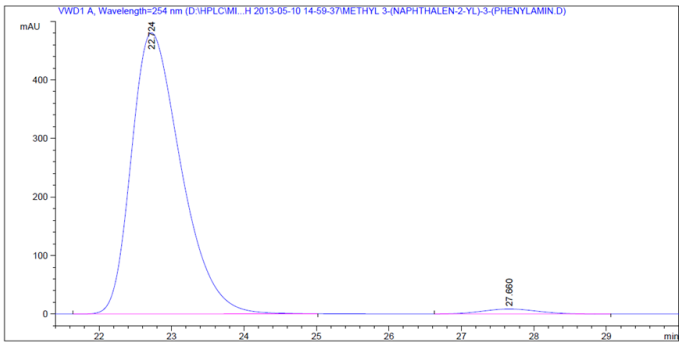


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88–7.82 (m, 4H), 7.54–7.48 (m, 3H), 7.15–7.11 (m, 2H), 6.70 (t, J = 7.2 Hz, 1H), 6.64 (d, J = 8.0 Hz, 2H), 5.03 (t, J = 6.6 Hz, 1H), 4.71 (s, 1H), 3.67 (s, 3H), 2.96–2.91 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.6, 146.8, 139.7, 133.5, 133.0, 129.2, 128.8, 128.0, 127.8, 126.3, 125.9, 125.1, 124.4, 117.9, 113.8, 55.2, 52.1, 42.7. IR (thin film): ν_{max} (cm^{-1}) = 3401, 2951,1732, 1602, 1505, 1286, 1178, 748, 692. MS (ESI) m/z 306 ($[M + H]^+$). HRMS (ESI) Calcd for $C_{20}H_{20}NO_2$ $[M + H]^+$: 306.1494, Found: 306.1496.

The conversion was determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 220 °C; isothermal; t_R (**3a**) = 13.61 min; t_R (**4a**) = 12.24 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 10 : 90; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (major) = 22.72 min; t_R (minor) = 27.66 min. $[\alpha]_D^{20}$ = +2.9 (c = 1.0, $CHCl_3$) for a sample with 96 % *ee*. Chromatograms are illustrated below for a 96 % *ee* sample:

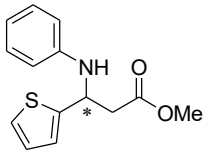


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.167	BB	0.7253	1047.73755	22.37990	49.7831
2	27.793	BB	0.8303	1056.86633	19.77370	50.2169



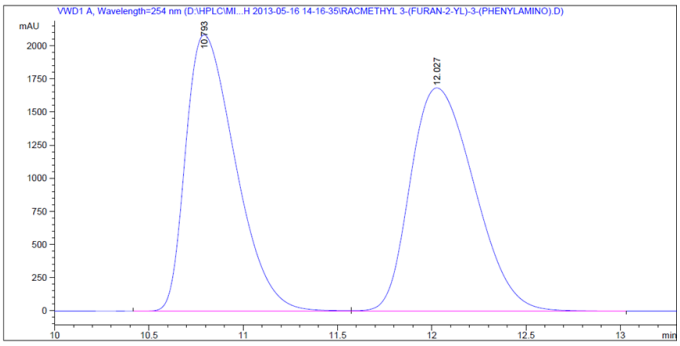
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.724	VB	0.7303	2.28031e4	480.10318	98.0478
2	27.660	BB	0.8282	454.02310	8.50358	1.9522

(–)-Methyl 3-(phenylamino)-3-(thiophen-2-yl)propanoate (4b)

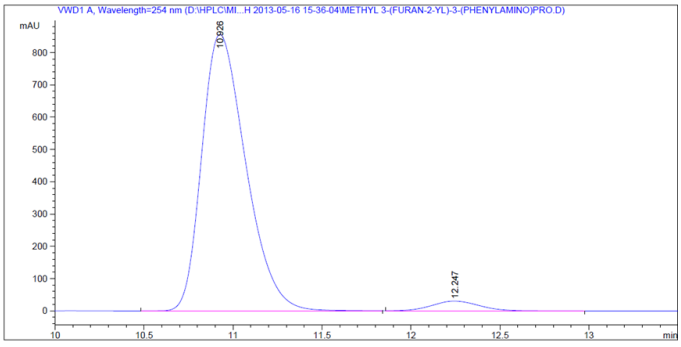


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20–7.16 (m, 3H), 7.00–6.94 (m, 2H), 6.75 (t, J = 6.8 Hz, 1H), 6.68 (d, J = 7.0 Hz, 2H), 5.19–5.17 (m, 1H), 4.46 (s, 1H), 3.68 (s, 3H), 2.99–2.91 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.3, 146.8, 146.4, 129.3, 126.9, 124.4, 123.9, 118.5, 114.0, 52.0, 51.1, 42.3. IR (thin film): ν_{max} (cm^{-1}) = 3367, 2950, 2360, 1724, 1601, 1504, 1281, 1170, 750, 691. MS (ESI) m/z 262 ($[M + H]^+$). HRMS (ESI) Calcd for $C_{14}H_{16}NO_2S$ $[M + H]^+$: 262.0902, Found: 262.0906.

The conversion was determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 180 °C; isothermal; t_R (**3b**) = 6.83 min; t_R (**4b**) = 5.20 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 10 : 90; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (major) = 10.93 min; t_R (minor) = 12.25 min. $[\alpha]_D^{20}$ = –2.4 (c = 0.50, $CHCl_3$) for a sample with 93 % *ee*. Chromatograms are illustrated below for a 93 % *ee* sample:

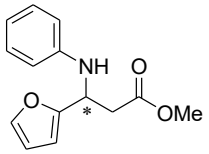


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.793	BV	0.2863	3.81894e4	2087.15088	49.0244
2	12.027	VV	0.3781	3.97094e4	1686.27295	50.9756



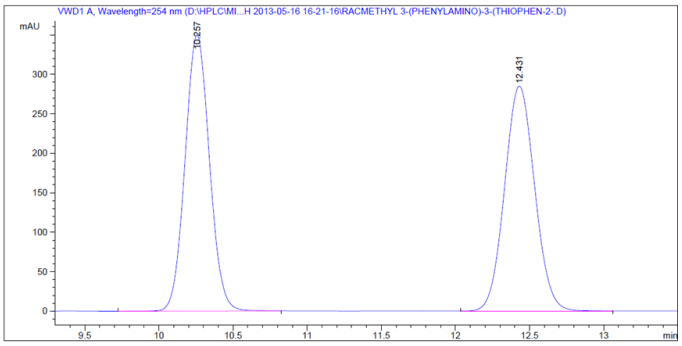
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.926	VB	0.2663	1.47363e4	856.48584	96.2582
2	12.247	BB	0.2907	572.83075	30.47333	3.7418

(–)-Methyl 3-(furan-2-yl)-3-(phenylamino)propanoate (4c)

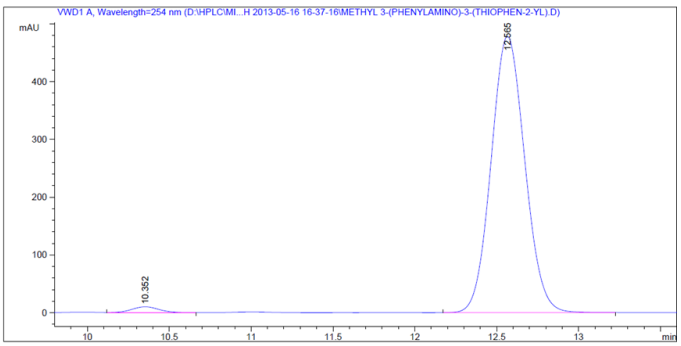


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, J = 1.0 Hz, 1H), 7.17 (dd, J_1 = 8.0 Hz, J_2 = 7.5 Hz, 2H), 6.74 (t, J = 7.3 Hz, 1H), 6.68 (d, J = 8.0 Hz, 2H), 6.28 (dd, J_1 = 3.3 Hz, J_2 = 1.8 Hz, 1H), 6.20 (d, J = 3.5 Hz, 1H), 5.01 (t, J = 6.5 Hz, 1H), 4.29 (s, 1H), 3.67 (s, 3H), 2.92–2.91 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.4, 154.4, 146.5, 141.9, 129.3, 118.5, 114.0, 110.3, 106.4, 51.9, 49.1, 39.1. IR (thin film): ν_{max} (cm^{-1}) = 3389, 2952, 2847, 1732, 1603, 1505, 1285, 1169, 1011, 750, 693. MS (ESI) m/z 246 ([M + H]$^+$). HRMS (ESI) Calcd for $C_{14}H_{16}NO_3$ [M + H]$^+$: 246.1130, Found: 246.1137.

The conversion was determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 180 °C; isothermal; t_R (**3c**) = 11.51 min; t_R (**4c**) = 9.63 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel AD-H column (eluent, 2-propanol/hexane 10 : 90; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (minor) = 10.35 min; t_R (major) = 12.57 min. $[\alpha]_D^{20}$ = –21.0 (c = 1.0, $CHCl_3$) for a sample with 97 % *ee*. Chromatograms are illustrated below for a 97 % *ee* sample:

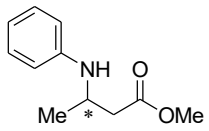


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.257	BB	0.1789	4011.12964	349.80295	49.9120
2	12.431	BB	0.2202	4025.27588	284.88156	50.0880



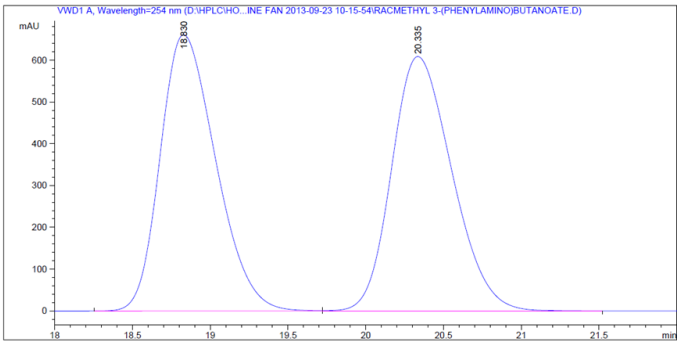
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.352	VB	0.1778	114.34129	10.05388	1.6471
2	12.565	BB	0.2234	6827.54688	478.07129	98.3529

(–)-Methyl 3-(phenylamino)butanoate (4d)[8]

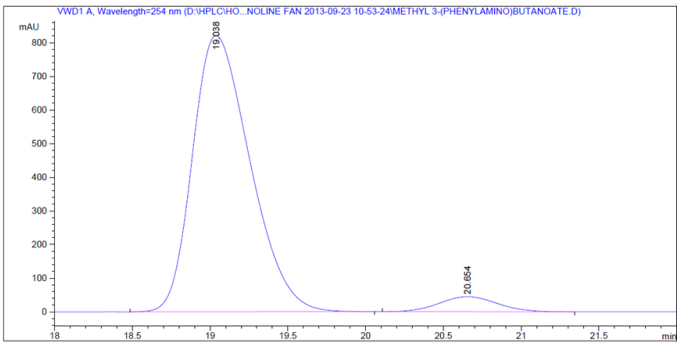


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20–7.17 (m, 2H), 6.71 (t, J = 7.5 Hz, 1H), 6.63 (t, J = 8.0 Hz, 2H), 3.99–3.92 (m, 1H), 3.75 (br, 1H), 3.69 (s, 3H), 2.67–2.42 (m, 2H), 1.29 (d, J = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.2, 146.8, 129.4, 117.7, 113.7, 51.6, 46.0, 40.8, 20.7. IR (thin film): ν_{max} (cm^{-1}) = 3391, 3088, 2952, 1731, 1602, 1435, 1256, 1195, 1029, 751, 694, 516. MS (ESI) *m/z* 194 ($[M + H]^+$).

The conversion was determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 110 °C; isothermal; t_R (**3d**) = 31.76 min; t_R (**4d**) = 21.82 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 1 : 99; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (major) = 19.04 min; t_R (minor) = 20.65 min. $[\alpha]_D^{20}$ = –1.7 (c = 1.0, $CHCl_3$) for a sample with 90 % *ee*. Chromatograms are illustrated below for a 90 % *ee* sample:

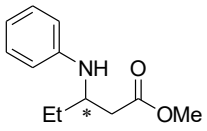


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.830	BV	0.3876	1.64374e4	661.18036	50.0244
2	20.335	VB	0.4209	1.64214e4	608.86176	49.9756



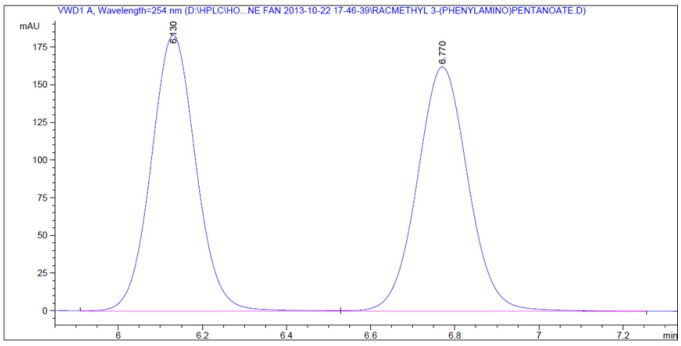
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.038	BB	0.3984	2.10888e4	821.70392	94.8111
2	20.654	BB	0.4051	1154.15320	44.62528	5.1889

(+)-Methyl 3-(phenylamino)pentanoate (4e)

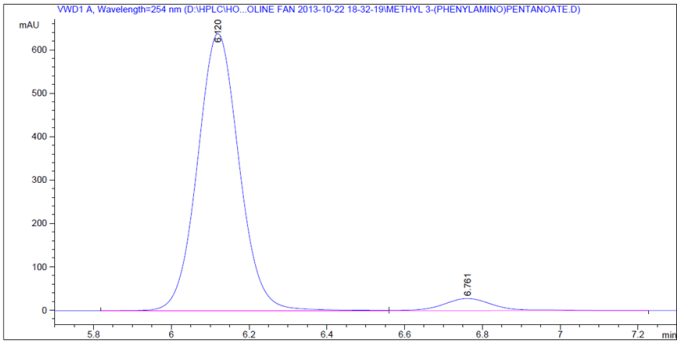


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18–7.15 (m, 2H), 6.69 (t, J = 7.3 Hz, 1H), 6.62 (d, J = 8.0 Hz, 2H), 3.76–3.73 (m, 2H), 3.66 (s, 3H), 2.60–2.48 (m, 2H), 1.66–1.59 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.4, 147.3, 129.3, 117.5, 113.5, 51.9, 51.6, 38.8, 27.8, 10.5. IR (thin film): ν_{max} (cm^{-1}) = 3392, 3052, 2964, 1731, 1603, 1505, 1317, 1185, 1176, 1004, 750, 509. MS (ESI) m/z 208 ($[M + H]^+$). HRMS (ESI) Calcd for $C_{12}H_{18}NO_2$ $[M + H]^+$: 208.1338, Found: 208.1332.

The conversion were determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 110 °C; isothermal; t_R (**3e**) = 45.35 min t_R (**4e**) = 32.85 min;. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel AS-H column (eluent, 2-propanol/hexane 1 : 99; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (major) = 6.12 min; t_R (minor) = 6.76 min. $[\alpha]_D^{20}$ = +5.9 (c = 1.0, $CHCl_3$) for a sample with 90 % *ee*. Chromatograms are illustrated below for a 90 % *ee* sample:

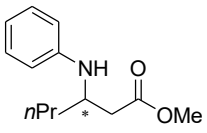


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.130	VV	0.1136	1350.63025	183.34409	49.9020
2	6.770	VB	0.1281	1355.93298	162.19971	50.0980



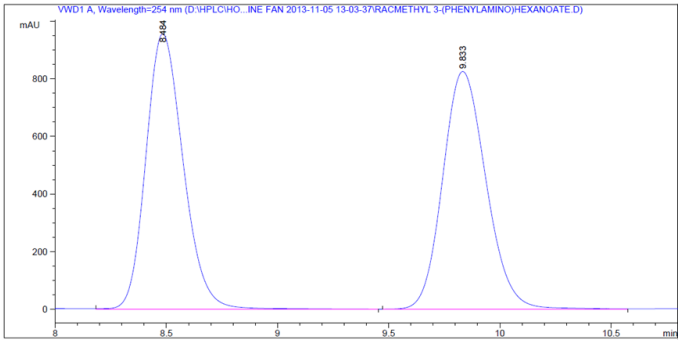
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.120	VV	0.1141	4733.38672	638.72345	95.0713
2	6.761	VB	0.1336	245.38737	27.78563	4.9287

(–)-Methyl 3-(phenylamino)hexanoate (4f)

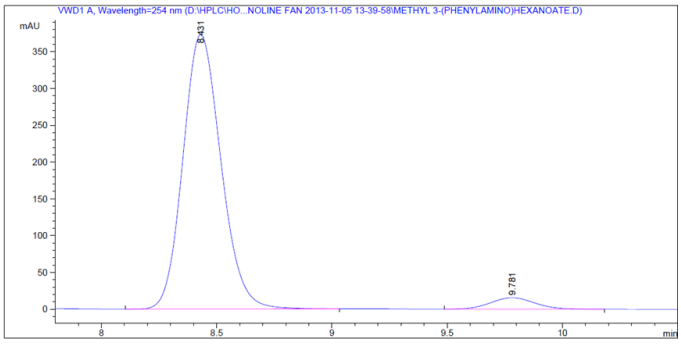


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18–7.15 (m, 2H), 6.69 (t, J = 7.3 Hz, 1H), 6.62 (d, J = 8.0 Hz, 2H), 3.82 (t, J = 6.0 Hz, 1H), 3.70 (s, 1H), 3.66 (s, 3H), 2.60–2.47 (m, 2H), 1.59–1.55 (m, 2H), 1.49–1.37 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.4, 147.3, 129.4, 117.5, 113.4, 51.5, 50.2, 39.2, 37.3, 19.3, 14.0. IR (thin film): ν_{max} (cm^{-1}) = 3394, 3053, 2957, 2872, 1731, 1602, 1504, 1367, 1106, 750, 693, 510. MS (ESI) m/z 222 ($[M + H]^+$). HRMS (ESI) Calcd for $C_{13}H_{20}NO_2$ $[M + H]^+$: 222.1494, Found: 222.1489.

The conversion was determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 110 °C; isothermal; t_R (**3f**) = 64.90 min; t_R (**4f**) = 48.11 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 5 : 95; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (major) = 8.43 min; t_R (minor)= 9.78 min. $[\alpha]_D^{20}$ = –5.1 (c = 1.0, $CHCl_3$) for a sample with 91 % *ee*. Chromatograms are illustrated below for a 91 % *ee* sample:

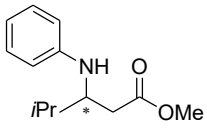


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.484	VB	0.1813	1.11761e4	957.43188	49.9200
2	9.833	BV	0.2108	1.12119e4	825.99487	50.0800



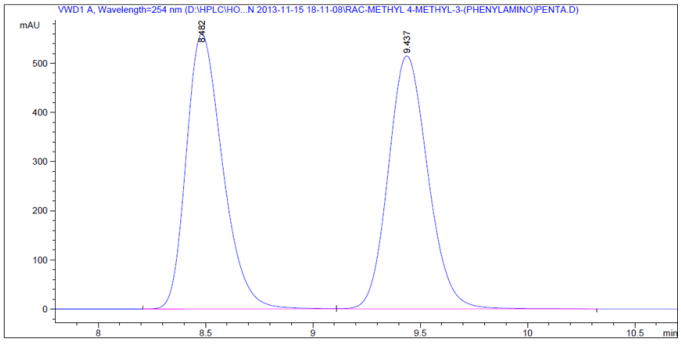
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.431	VB	0.1773	4274.55029	373.29935	95.3890
2	9.781	BB	0.2063	206.62872	15.51873	4.6110

(–)-Methyl 4-methyl-3-(phenylamino)pentanoate (4g)

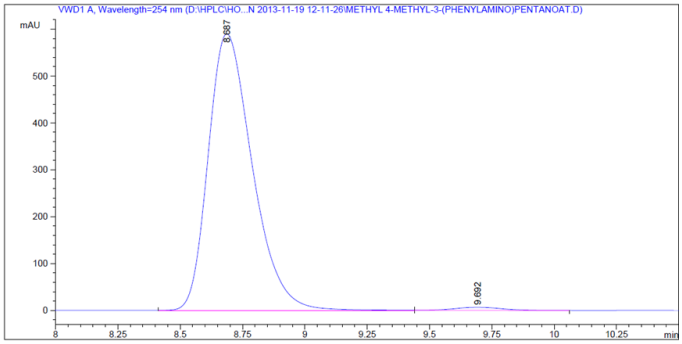


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17–7.14 (m, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.63 (d, J = 8.0 Hz, 2H), 3.72–3.71 (m, 2H), 3.63 (s, 3H), 2.56–2.45 (m, 2H), 1.95–1.91 (m, 1H), 0.99 (d, J = 7.0 Hz, 3H), 0.95 (d, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.7, 147.6, 129.3, 117.4, 113.5, 56.0, 51.6, 36.7, 31.7, 18.7, 18.6. IR (thin film): ν_{max} (cm^{-1}) = 3394, 3088, 2959, 1731, 1602, 1387, 1174, 992, 870, 749, 664, 506. MS (ESI) m/z 222 ($[M + H]^+$). HRMS (ESI) Calcd for $C_{13}H_{20}NO_2$ $[M + H]^+$: 222.1494, Found: 222.1489.

The conversion was determined by Capillary GC with a 25m×0.25 mm HP-5 column (Varian, carrier gas, N_2); 110 °C; isothermal; t_R (**3g**) = 9.63 min; t_R (**4g**) = 11.51 min. The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 10 : 90; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (major) = 8.69 min; t_R (minor) = 9.69 min. $[\alpha]_D^{20}$ = –1.1 (c = 1.0, $CHCl_3$) for a sample with 98 % *ee*. Chromatograms are illustrated below for a 98 % *ee* sample:

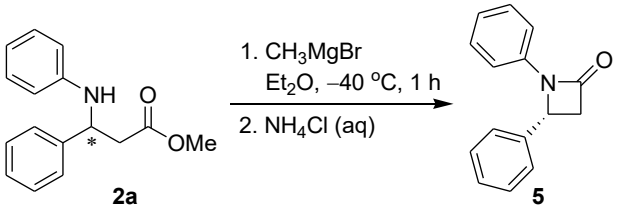


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.482	BV	0.1820	6566.42480	559.55200	49.9320
2	9.437	VB	0.1989	6584.30615	514.31073	50.0680



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.687	BV	0.1884	7249.95410	590.40741	98.7968
2	9.692	VB	0.2054	88.29195	6.60545	1.2032

Procedure for the synthesis of β-lactam (*R*)-1,4-diphenylazetidin-2-one (5).[9]

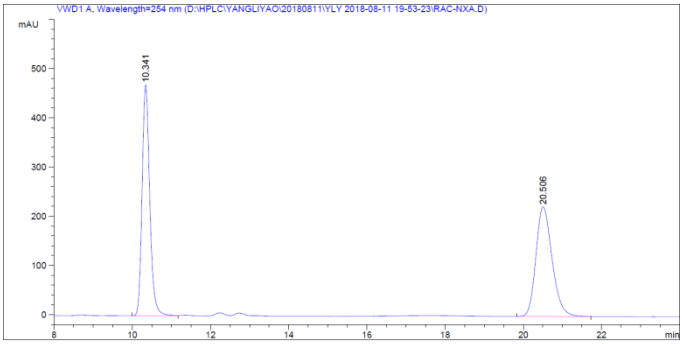


2a
95% *ee* (–)

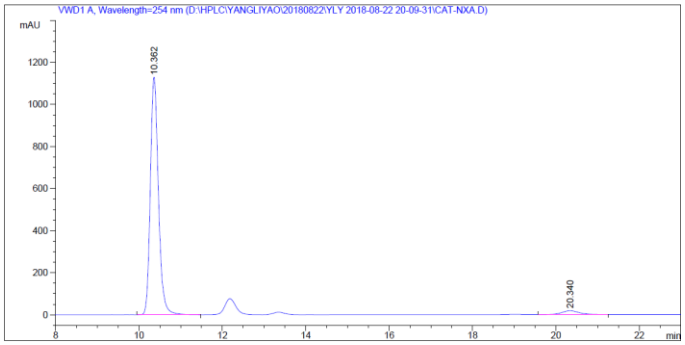
5
70% yield, 94% *ee* (*R*)
$[\alpha]_D^{20}$ = –55.9° (*c* = 0.85, in $CHCl_3$)

To a solution of compound (–)-**2a** (95 % *ee*, 50 mg, 0.20 mmol) in anhydrous Et_2O (5 mL) was added dropwise a solution of 1M CH_3MgBr in Et_2O (0.4 mL, 0.40 mmol) at –40 °C under nitrogen atmosphere. After stirring at –40 °C for 1h, the reaction was quenched by adding an excess amount of saturated aqueous NH_4Cl solution, followed by extracting with Et_2O (2 × 10 mL). The organic phase was washed with brine and then dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 15) to afford the chiral *β*-lactam **5** (31 mg, 70 %) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.36 (m, 4H), 7.35–7.32 (m, 1H), 7.30–7.28 (m, 2H), 7.26–7.22 (m, 2H), 7.03 (t, J = 7.3 Hz, 1H), 5.01 (dd, J_1 = 5.8 Hz, J_2 = 2.8 Hz, 1 H), 3.56 (dd, J_1 = 15.3 Hz, J_2 = 5.8 Hz, 1 H), 2.94 (dd, J_1 = 15.3 Hz, J_2 = 2.8 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 164.6, 138.3, 137.8, 129.2, 129.1, 128.5, 125.9, 123.8, 116.8, 54.1, 47.1. MS (ESI) *m/z* 224 ($[M + H]^+$). MS (ESI) Calcd for $C_{15}H_{14}NO$ $[M + H]^+$: 224.10, Found: 224.23.

The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 4 : 96; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light); t_R (*R*) = 10.36 min; t_R (*S*) = 20.34 min.[10] $[\alpha]_D^{20}$ = –55.9 (*c* = 0.85, $CHCl_3$). Literature data: $[\alpha]^{25}_D$ = –47.3 (*c* = 0.5, $CHCl_3$) for a (*R*)-product with 80 % *ee*.[10] Chromatograms are illustrated below for a 94 % *ee* sample:

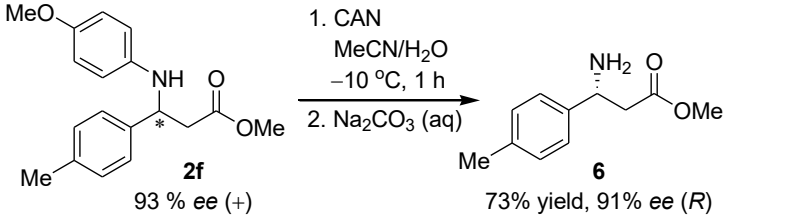


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.341	BB	0.2080	6375.56641	469.18045	50.0119
2	20.506	BB	0.4419	6372.52148	222.47406	49.9881



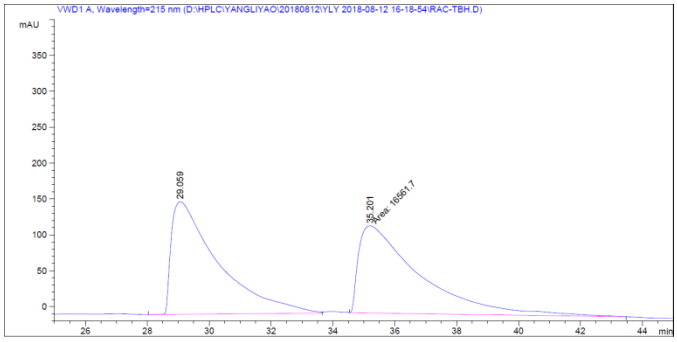
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.362	VB	0.2064	1.51881e4	1129.03943	96.8065
2	20.340	VB	0.4365	501.03278	17.47137	3.1935

Procedure for the synthesis of (*R*)-methyl 3-amino-3-(*p*-tolyl)propanoate (6).[11]

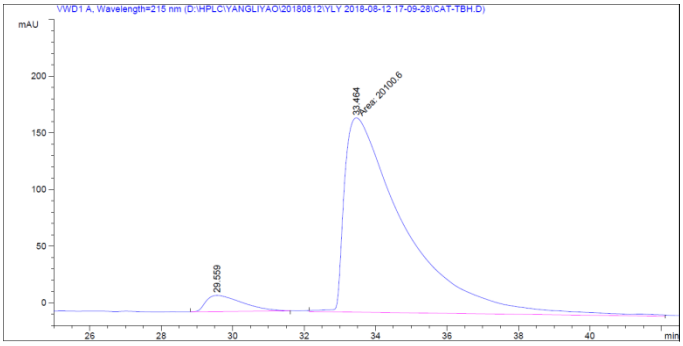


To a solution of compound (+)-**2f** (93 % *ee*, 50 mg, 0.17 mmol) in acetonitrile (5 mL) was added dropwise a solution of ceric ammonium nitrate (280 mg, 0.51 mmol) in water (5 mL) at –10 °C over 10 min. After the mixture was stirred for 1 h, water (5 mL) was added and MeCN was evaporated under vacuum. The residue was washed with Et_2O (2 × 10 mL) and added 10 % aqueous Na_2CO_3 solution until pH = 6. The mixture was further washed with Et_2O (2 × 10 mL). After the pH of the aqueous solution was tuned to be 8 by adding 10 % aqueous Na_2CO_3 solution, the mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 1) to give **6** (24 mg, 73 %) as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (d, J = 7.5 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 4.39 (t, J = 6.8 Hz, 1H), 3.68 (s, 3H), 2.67 (d, J = 7.0 Hz, 2H), 2.36 (br, 2H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 171.5, 141.2, 136.2, 128.3, 125.3, 51.6, 50.7, 43.2, 20.0. HRMS (ESI) Calcd for $C_{11}H_{16}NO_2$ $[M + H]^+$: 194.1176, Found: 194.1169.

The *ee* value was determined by chiral HPLC analysis with a 25 cm×4.6 mm Daicel Chiralcel OD-H column (eluent, 2-propanol/hexane 1 : 99; flow rate: 1.0 mL•min^{-1}; detection: 215 nm light); t_R (*S*) = 29.56 min; t_R (*R*) = 33.46 min.[12] $[\alpha]_D^{20}$ = +20.3 (c = 0.36, $CHCl_3$) for a sample with 91 % *ee*. $[\alpha]_D^{20}$ = +20.3 (c = 0.36, $CHCl_3$). Literature data: $[\alpha]^{20}_D$ = +21.8 (c = 1.0, $CHCl_3$) for a (*R*)-enantiomer with 99 % *ee*.[12] Chromatograms are illustrated below for a 91 % *ee* sample:



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.059	BV	1.4643	1.64535e4	157.00252	49.8362
2	35.201	MM	2.2713	1.65617e4	121.53043	50.1638



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.559	BB	1.0939	999.53815	14.19266	4.7371
2	33.464	MM	1.9543	2.01006e4	171.42188	95.2629

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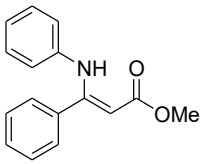
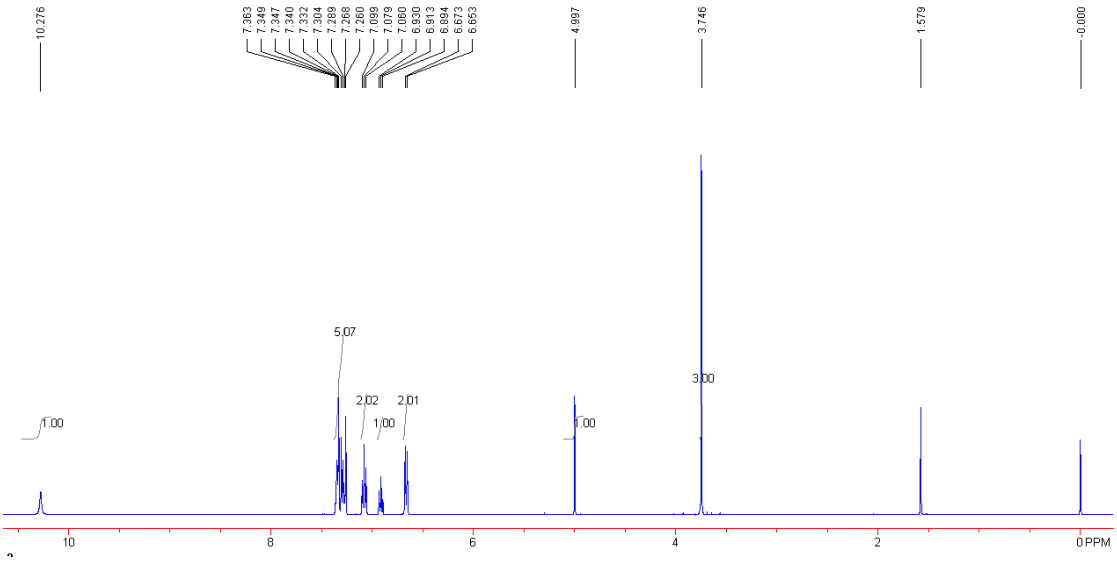
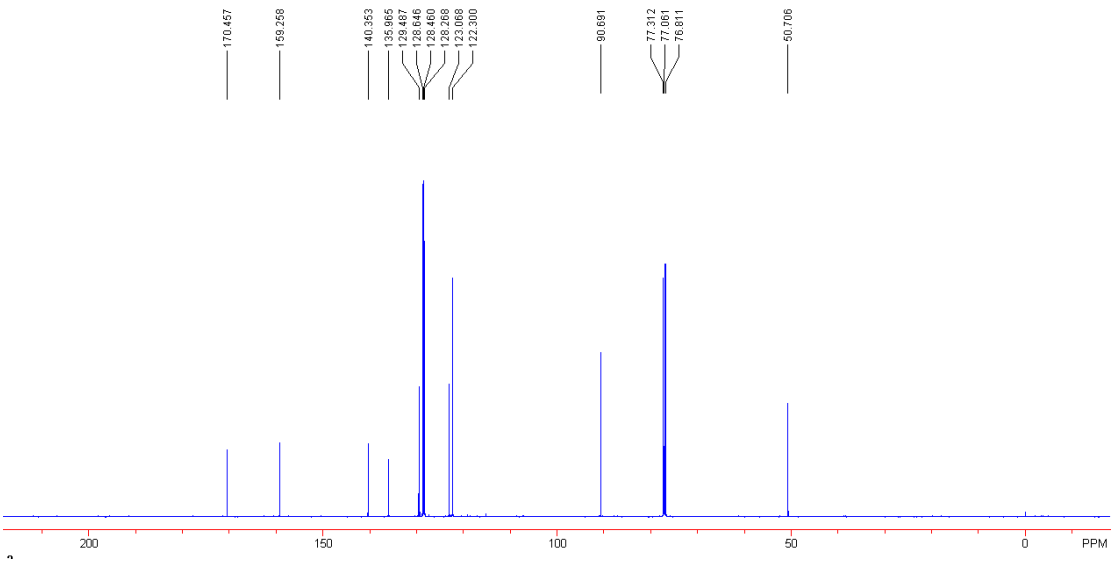
^{1}H NMR and ^{13}C NMR spectra of substrates and chiral products

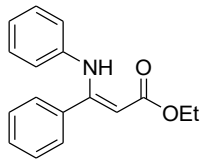
(*Z*)-Methyl 3-phenyl-3-(phenylamino)acrylate (1a)

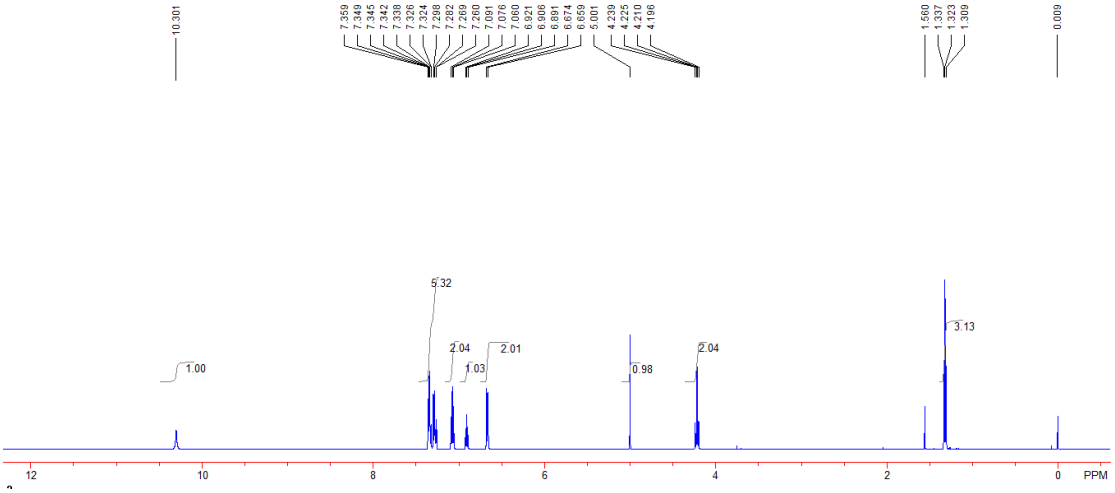


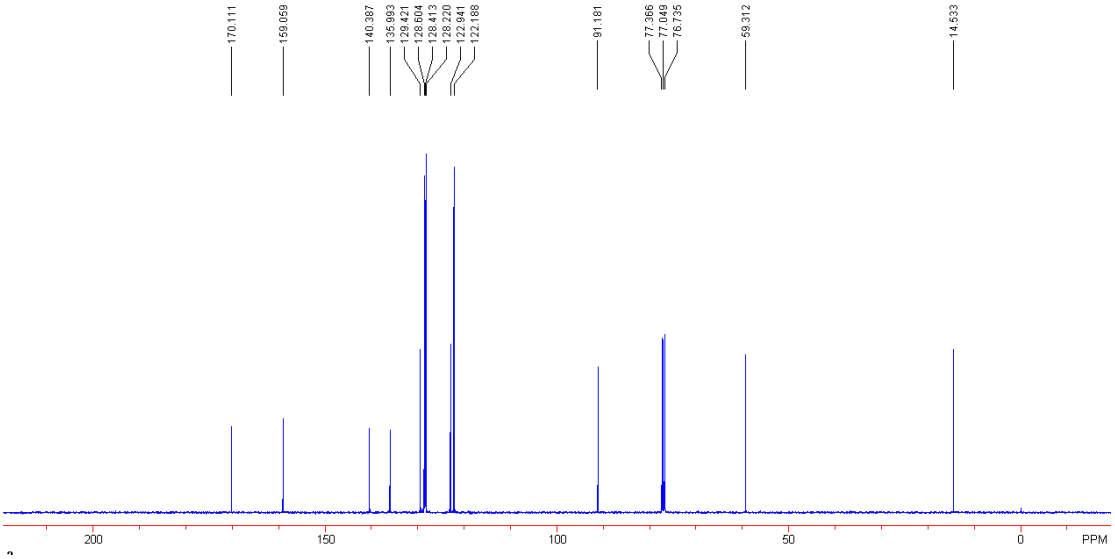




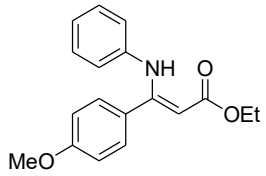
(*Z*)-Ethyl 3-phenyl-3-(phenylamino)acrylate (1b)

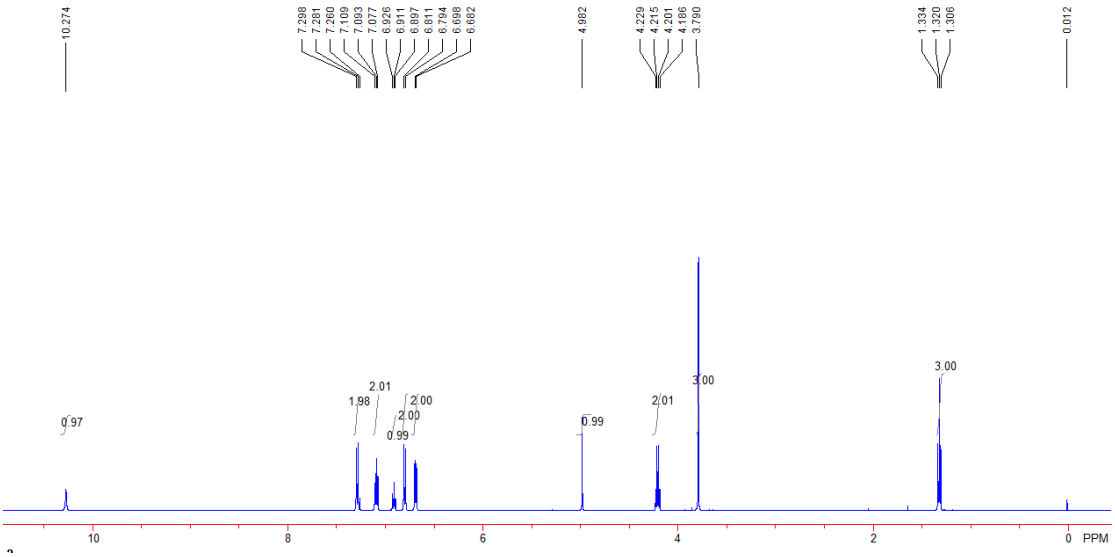


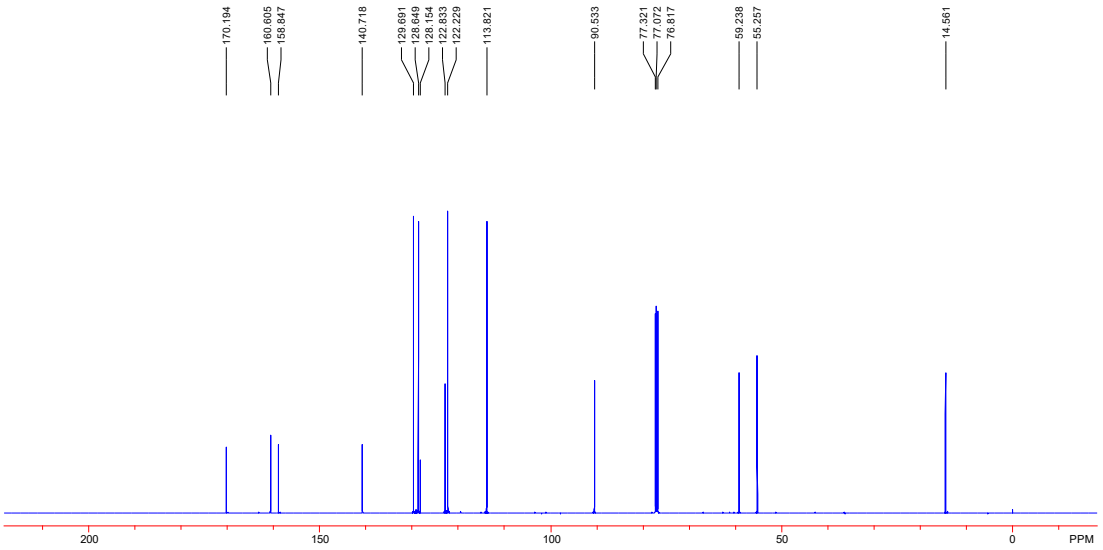




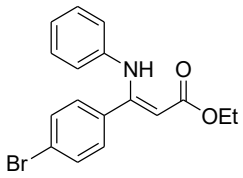
(*Z*)-Ethyl 3-(4-methoxyphenyl)-3-(phenylamino)acrylate (1c)

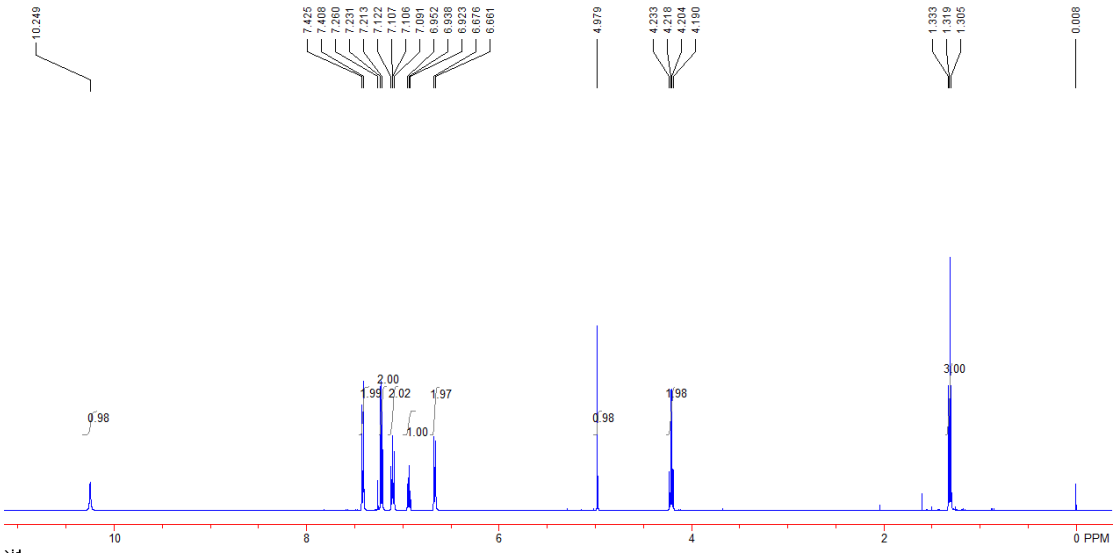


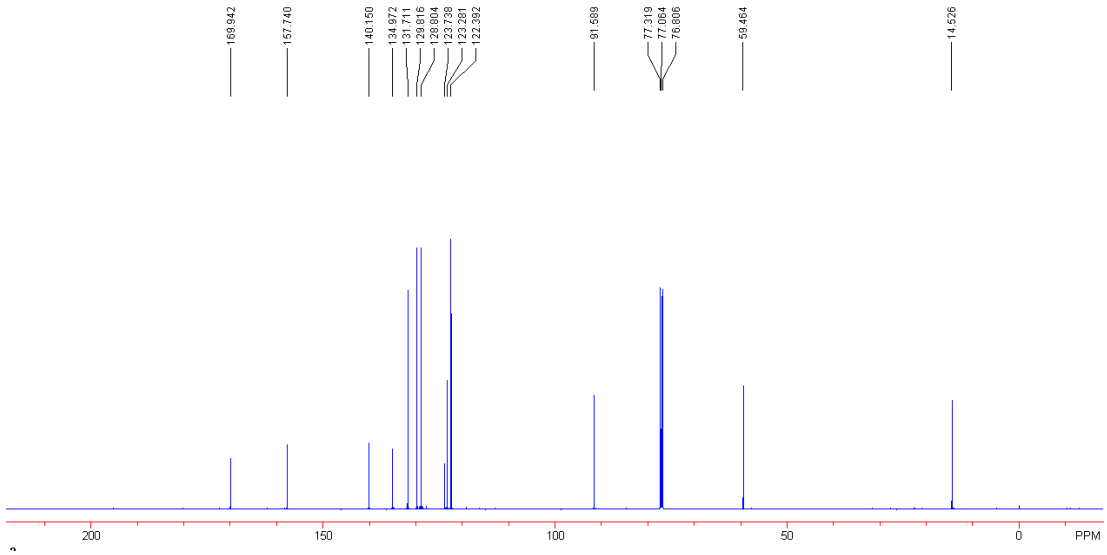




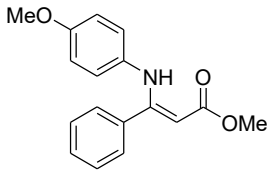
(*Z*)-Ethyl 3-(4-bromophenyl)-3-(phenylamino)acrylate (1d)

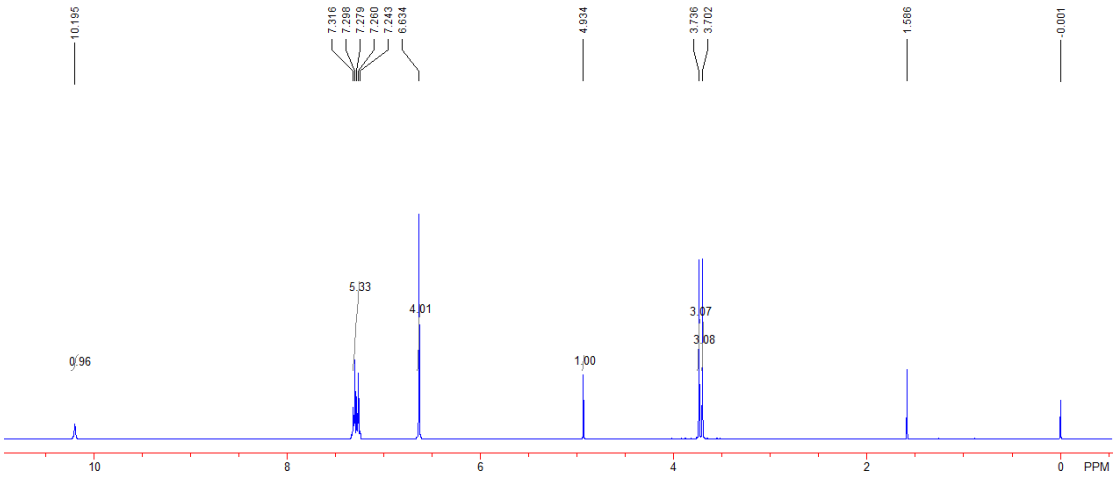


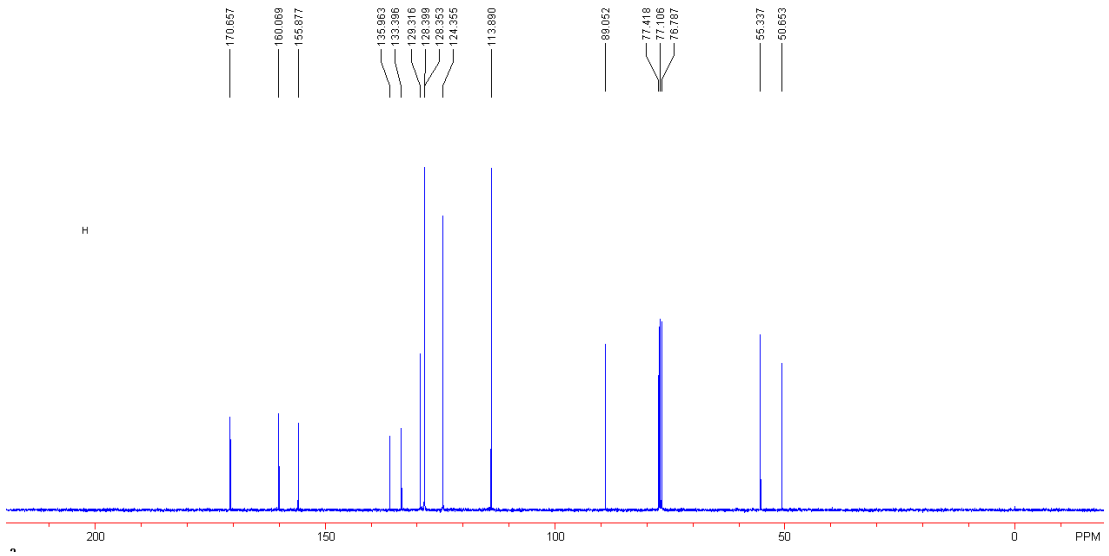




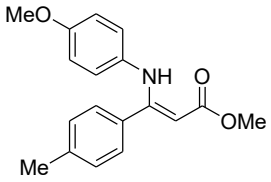
(*Z*)-Methyl 3-(4-methoxyphenylamino)-3-phenylacrylate (1e)

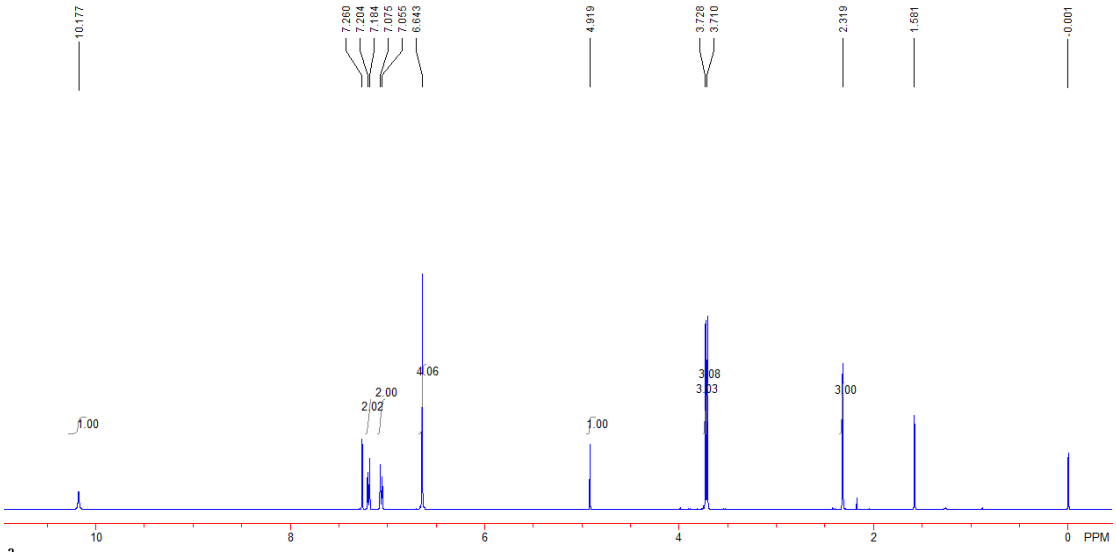


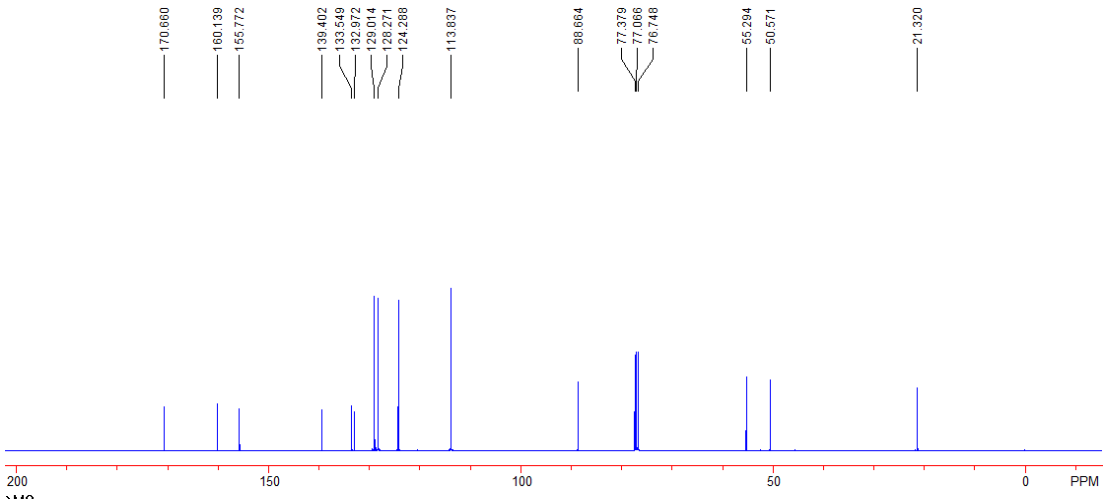




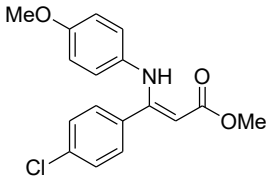
(*Z*)-Methyl 3-(4-methoxyphenylamino)-3-(*p*-tolyl)acrylate (1f)

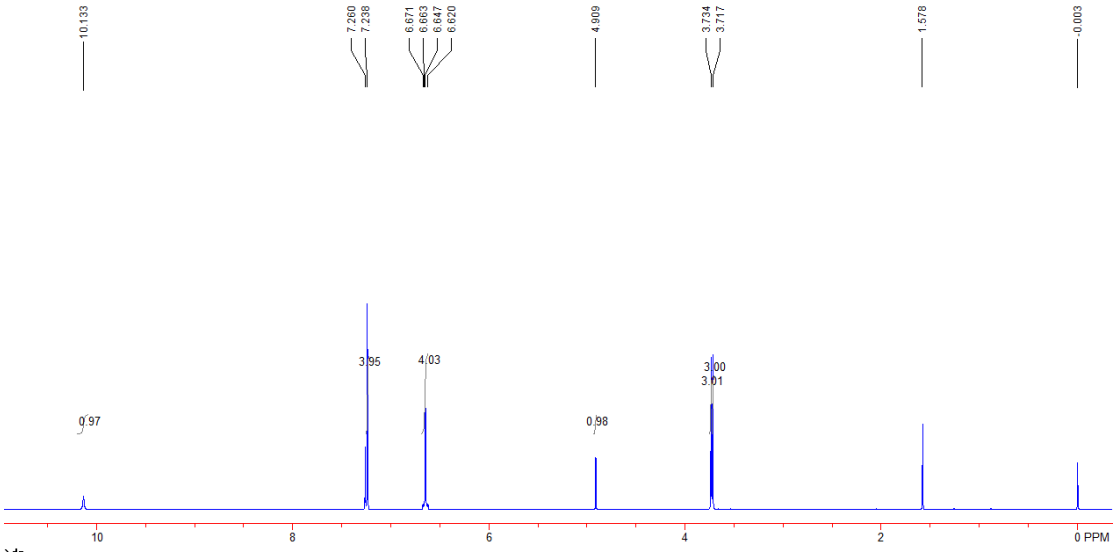


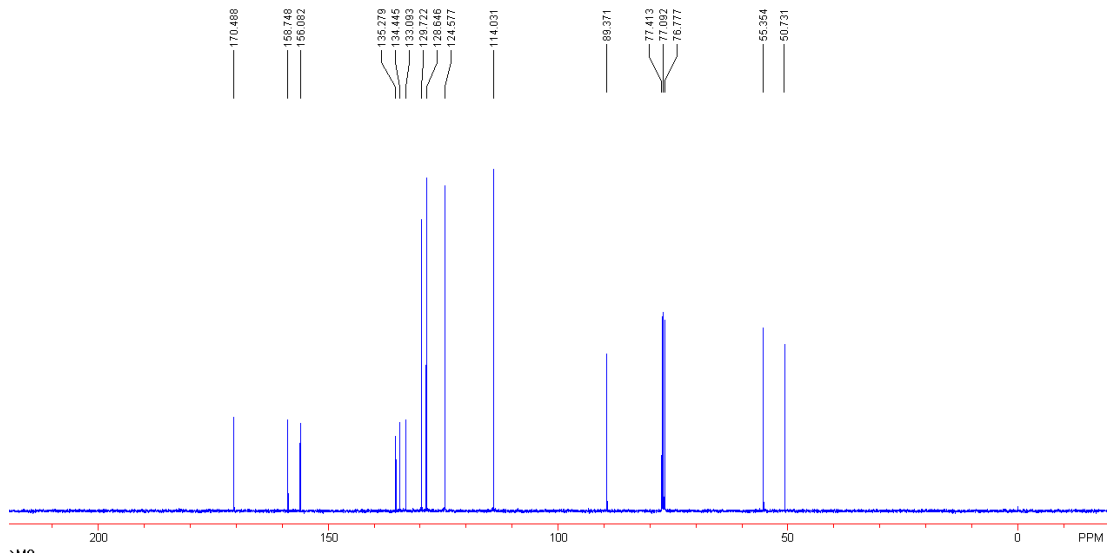




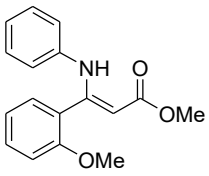
(*Z*)-Methyl 3-(4-chlorophenyl)-3-(4-methoxyphenylamino)acrylate (1g)

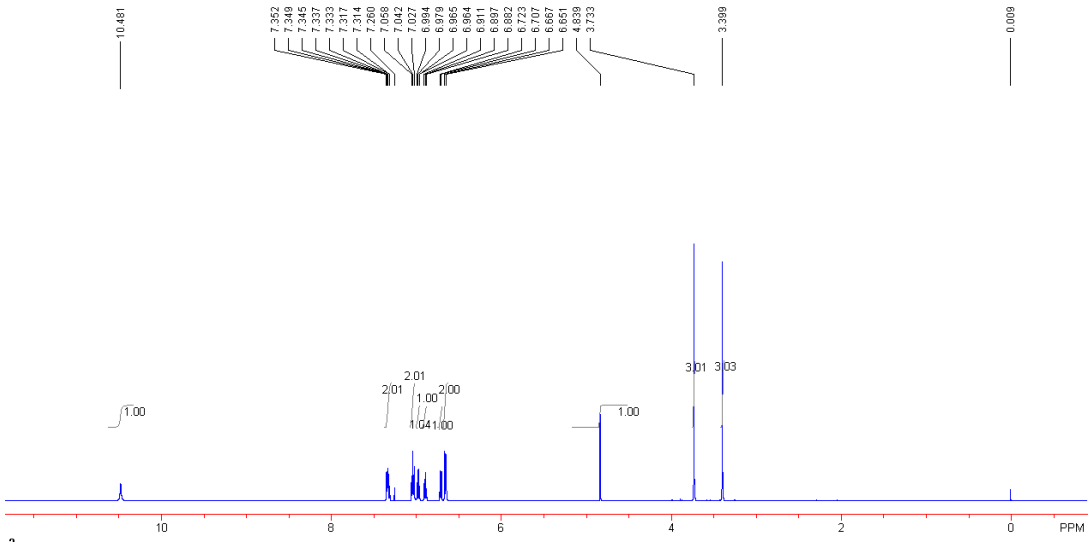


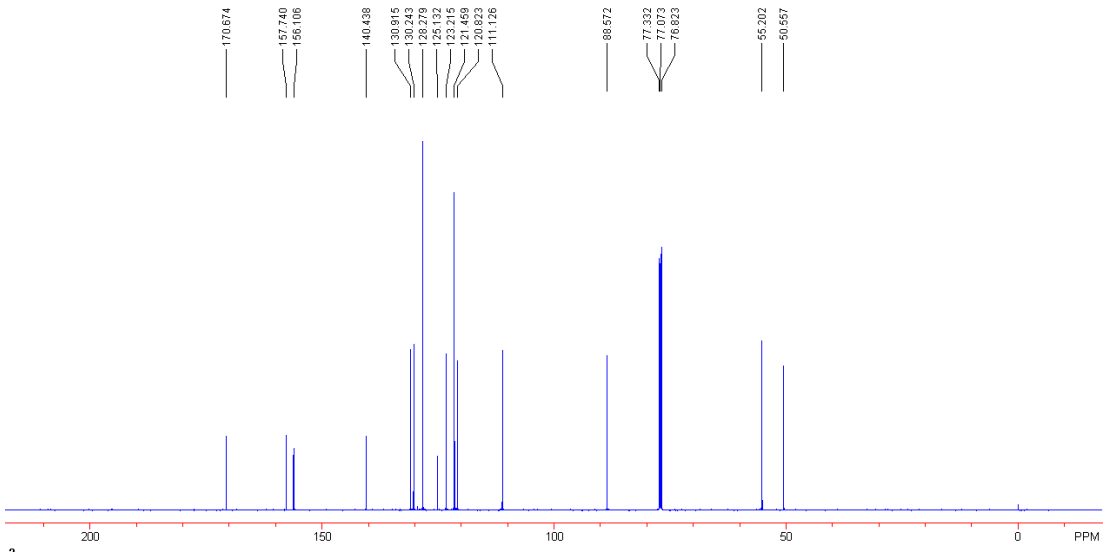




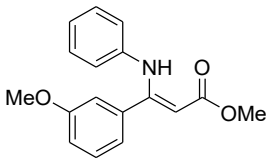
(*Z*)-Methyl 3-(2-methoxyphenyl)-3-(phenylamino)acrylate (1h)

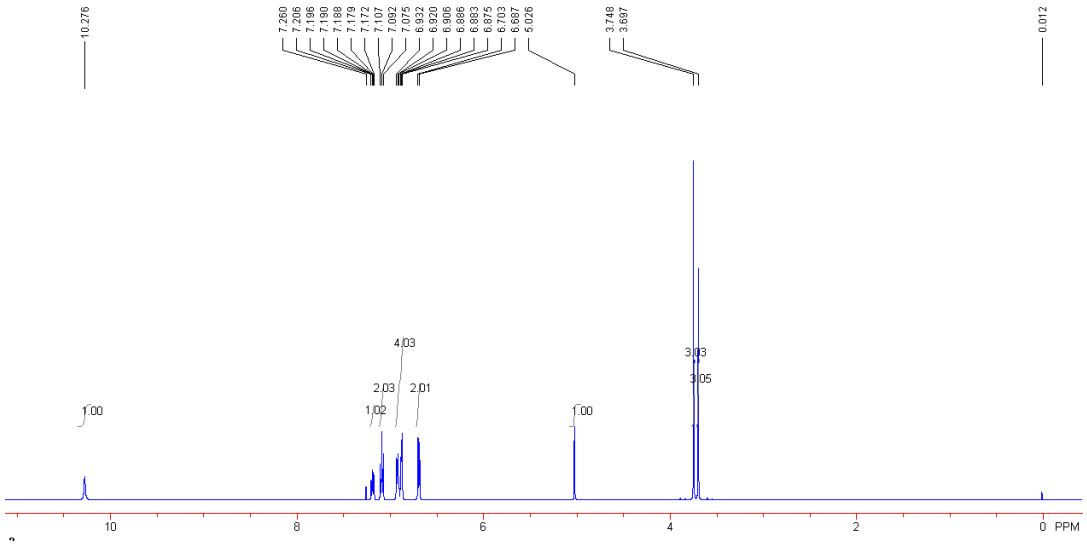


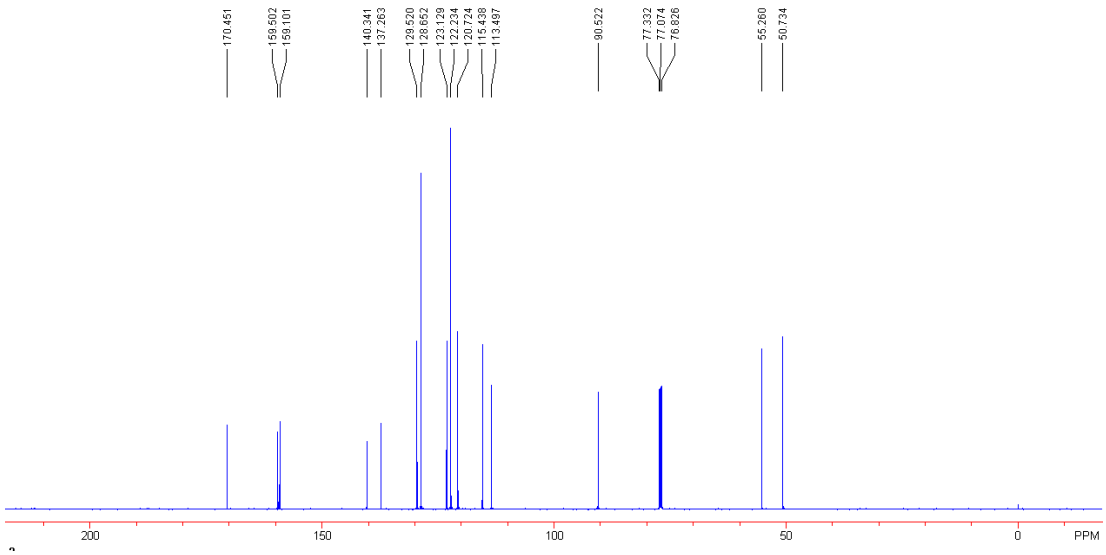




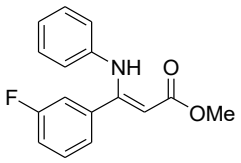
(*Z*)-Methyl 3-(3-methoxyphenyl)-3-(phenylamino)acrylate (1i)

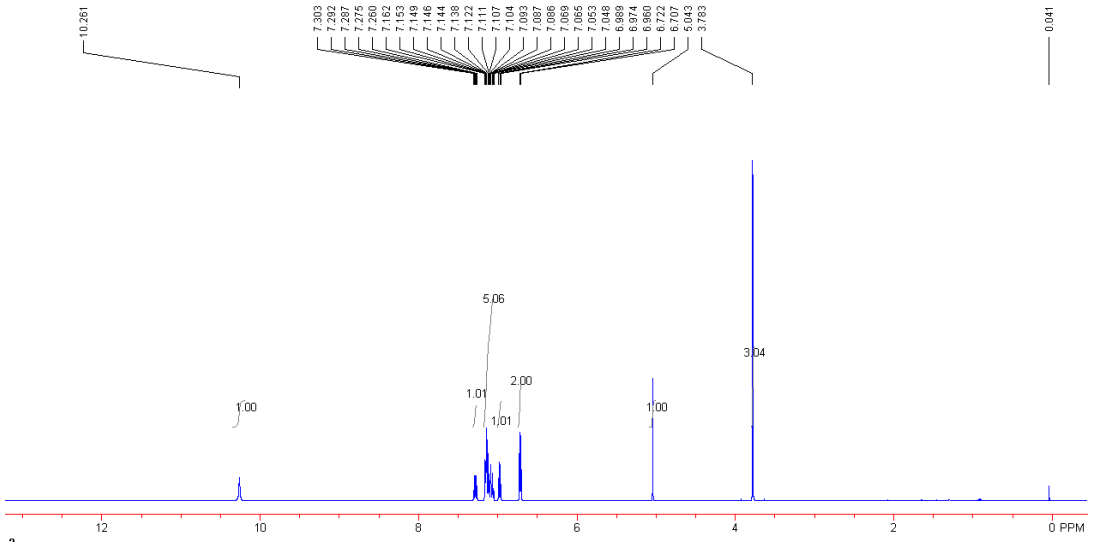


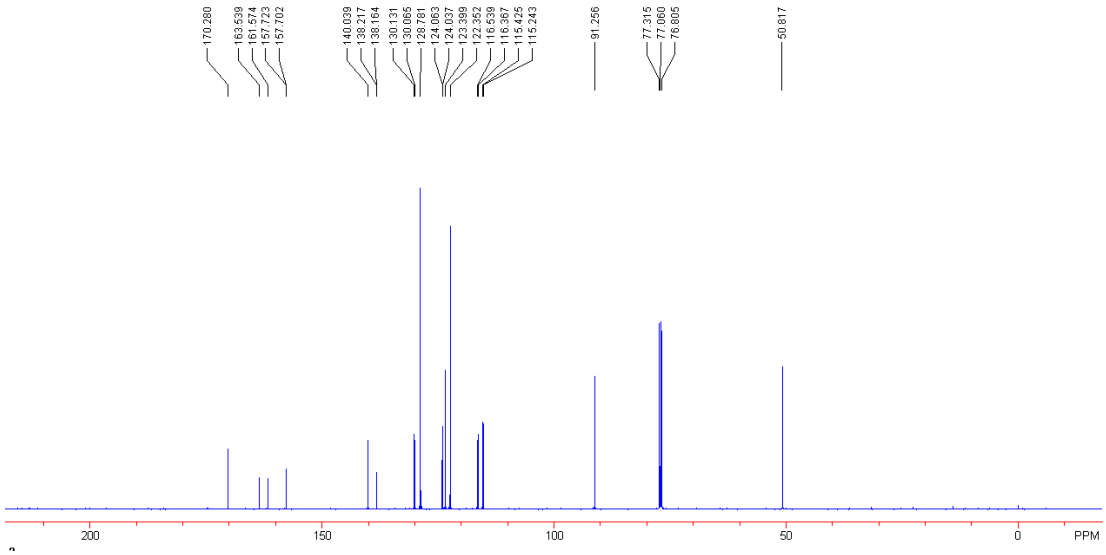




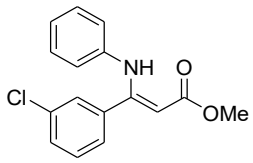
(*Z*)-Methyl 3-(3-fluorophenyl)-3-(phenylamino)acrylate (1j)

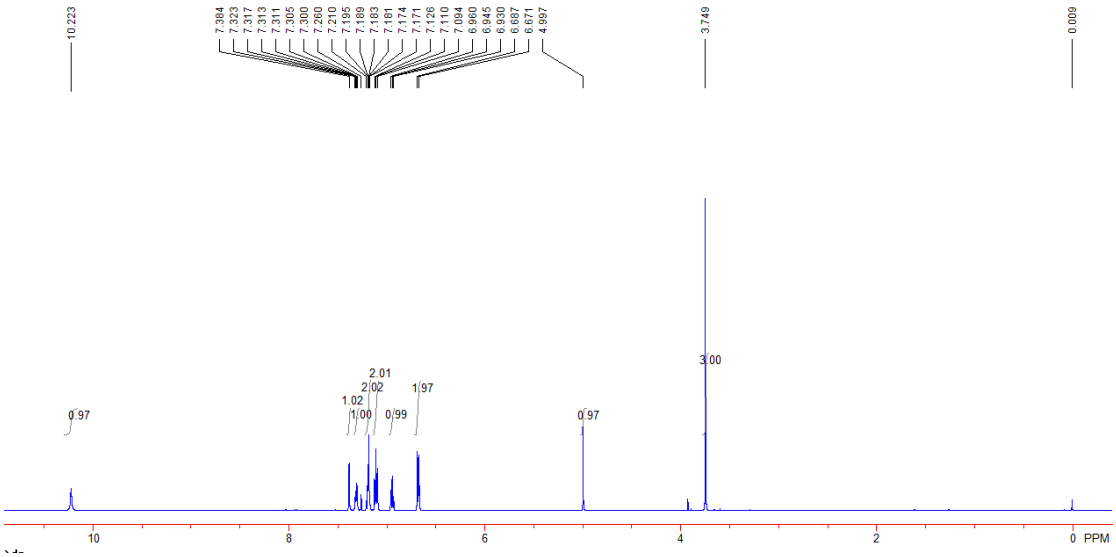


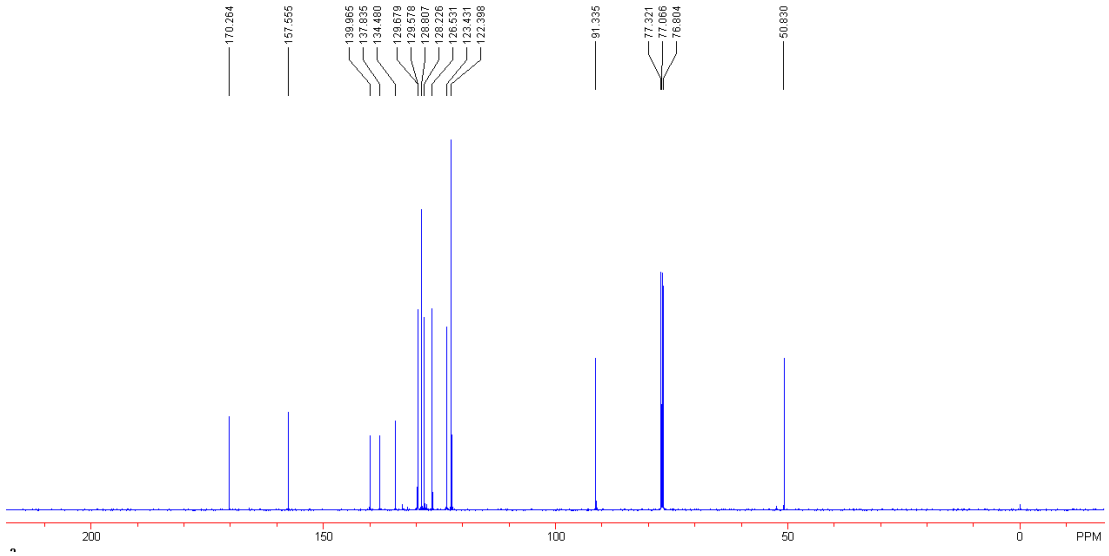




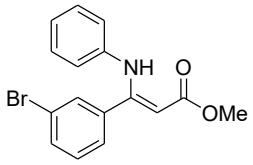
(*Z*)-Methyl 3-(3-chlorophenyl)-3-(phenylamino)acrylate (1k)

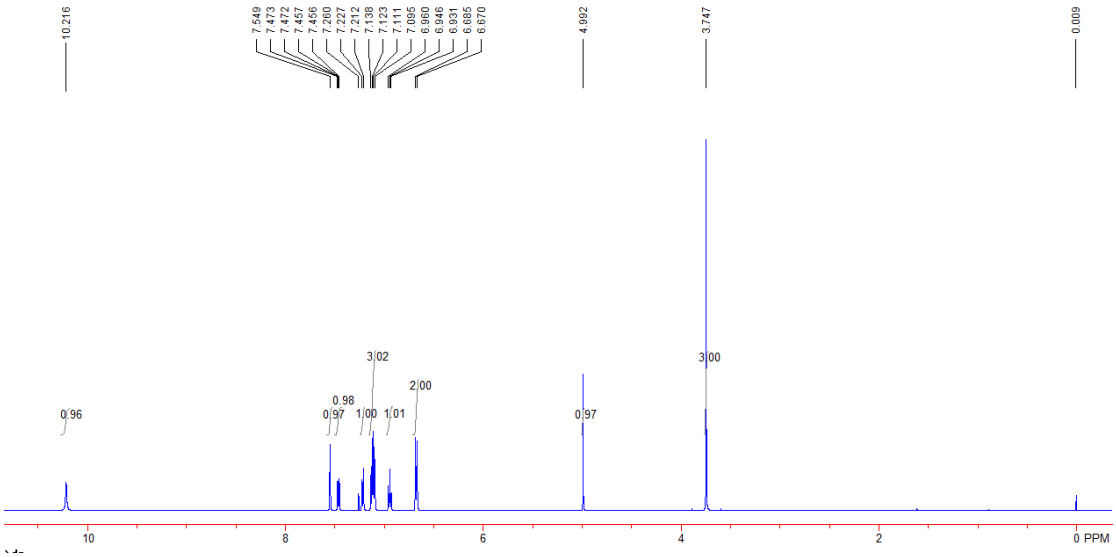


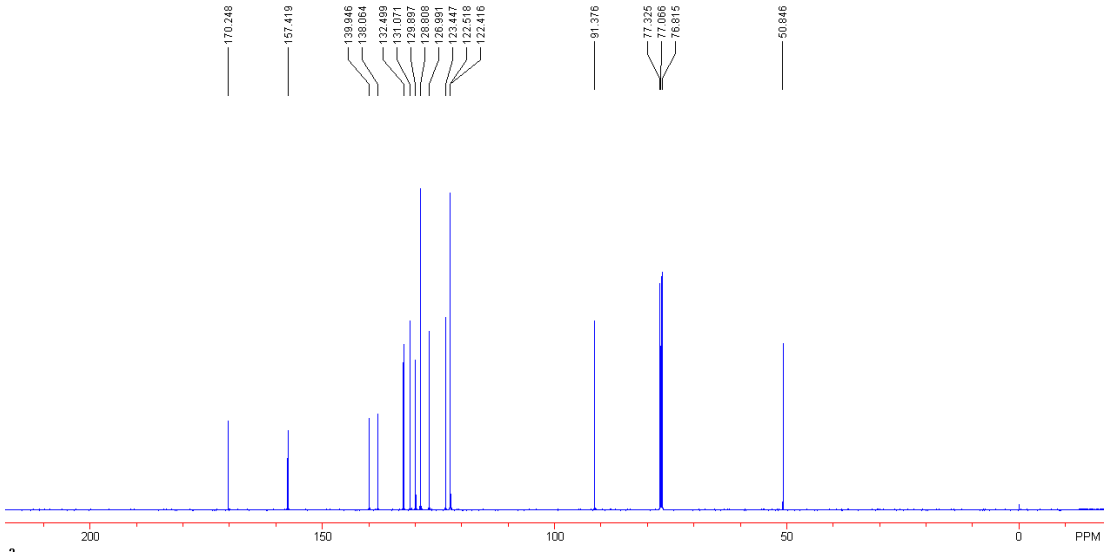




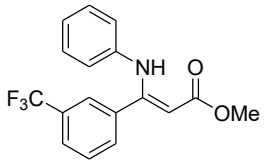
(*Z*)-Methyl 3-(3-bromophenyl)-3-(phenylamino)acrylate (1l)

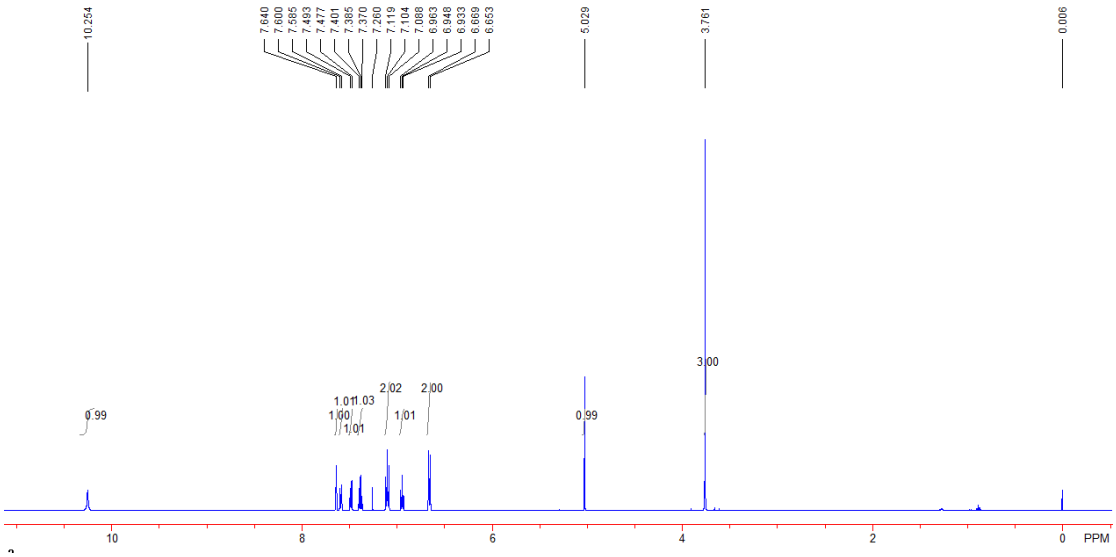


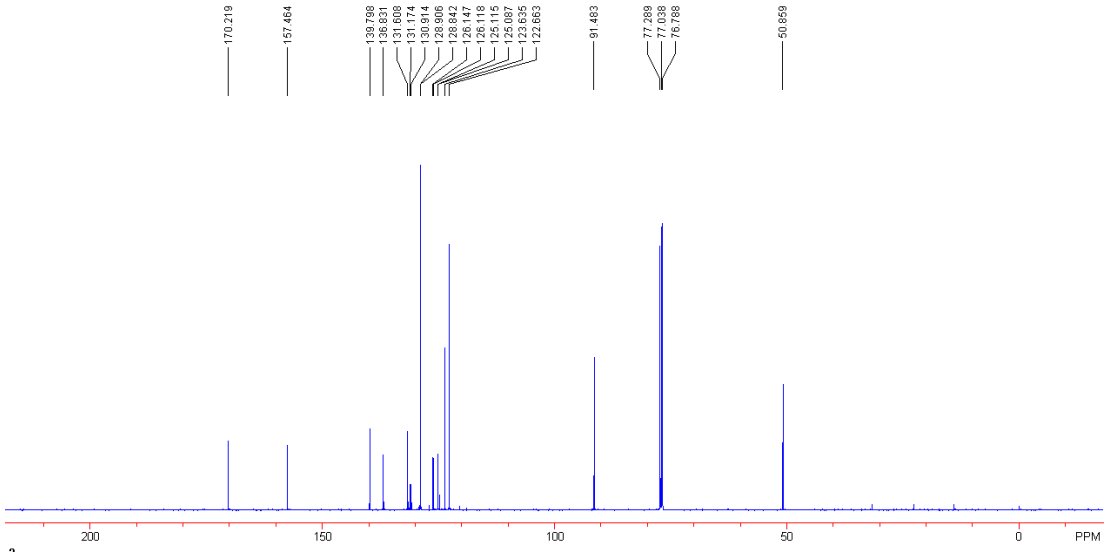




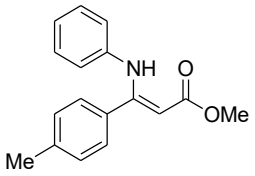
(*Z*)-Methyl 3-(phenylamino)-3-(3-(trifluoromethyl)phenyl)acrylate (1m)

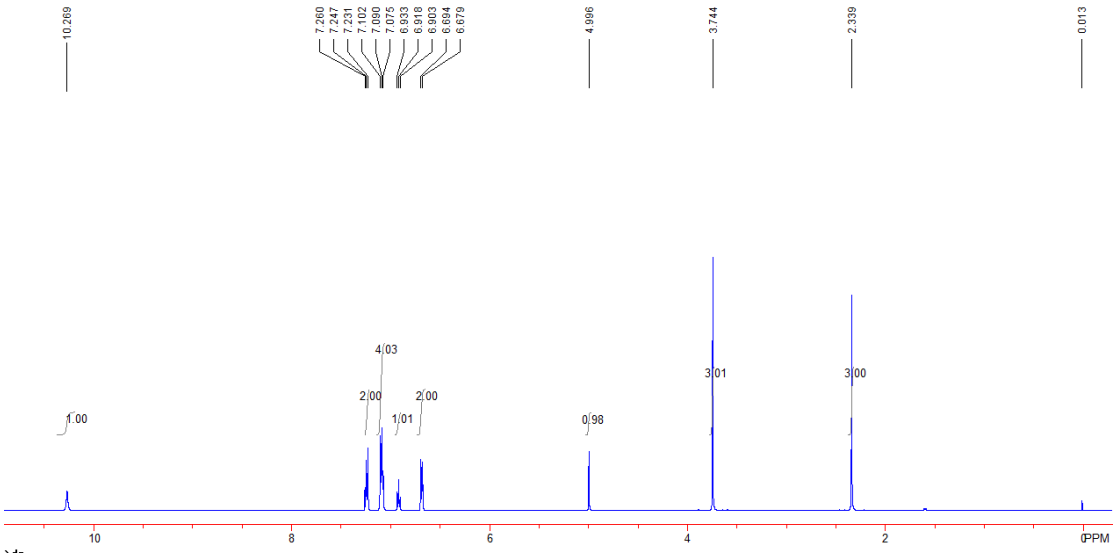


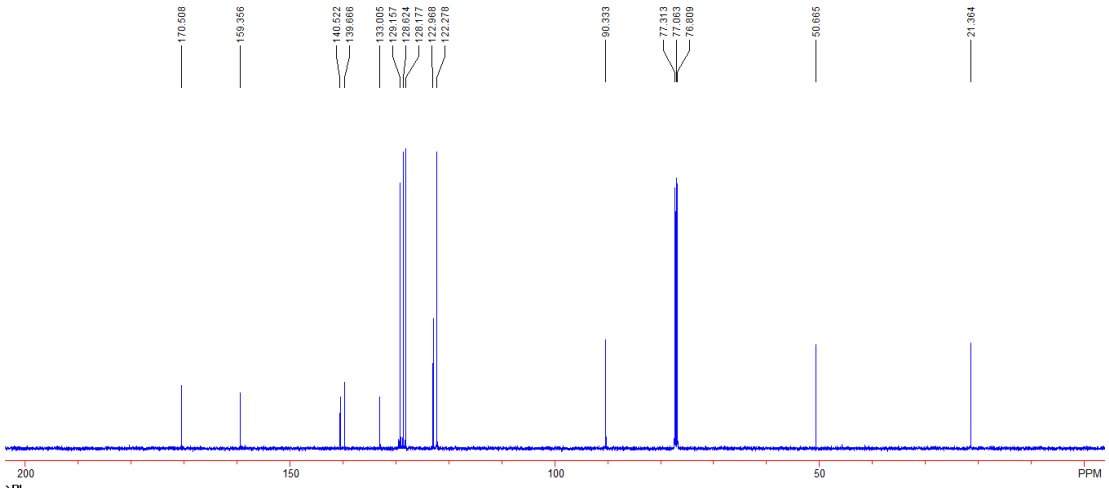




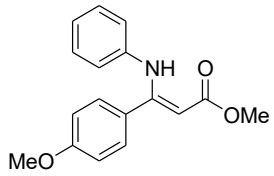
(*Z*)-Methyl 3-(phenylamino)-3-(*p*-tolyl)acrylate (1n)

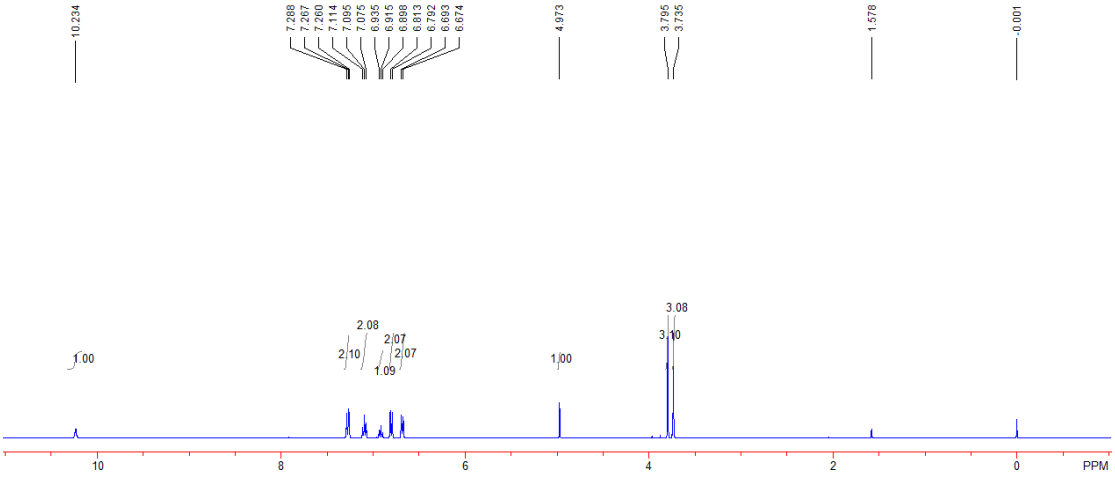


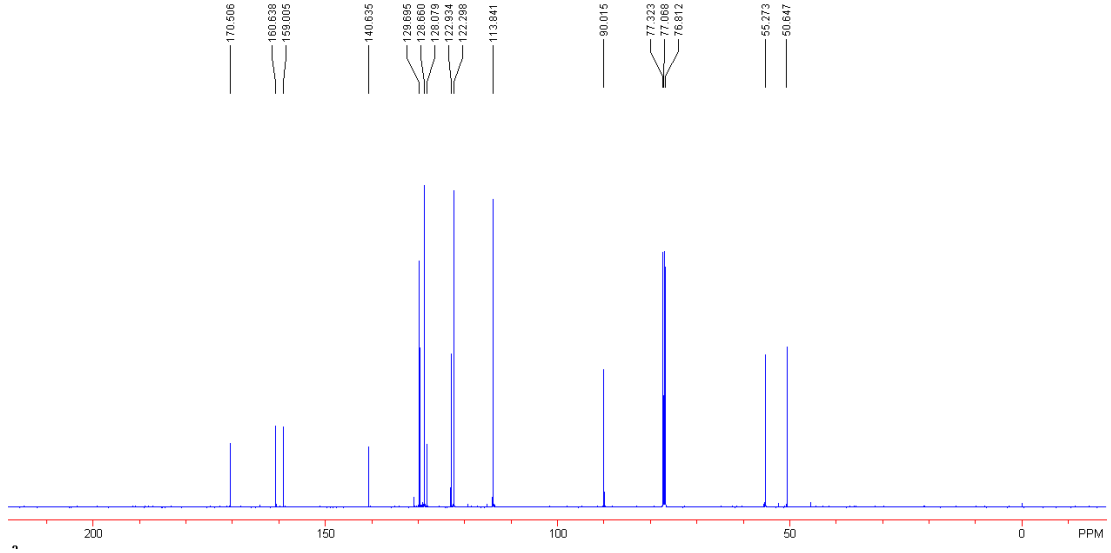




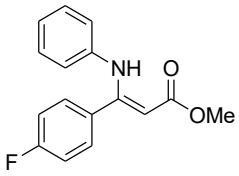
(*Z*)-Methyl 3-(4-methoxyphenyl)-3-(phenylamino)propanoate (1o)

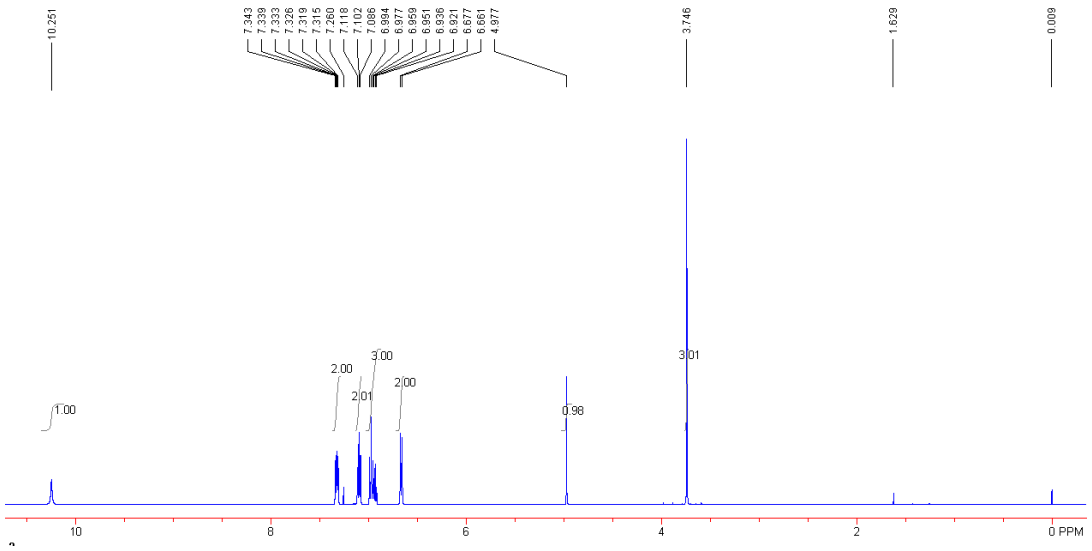


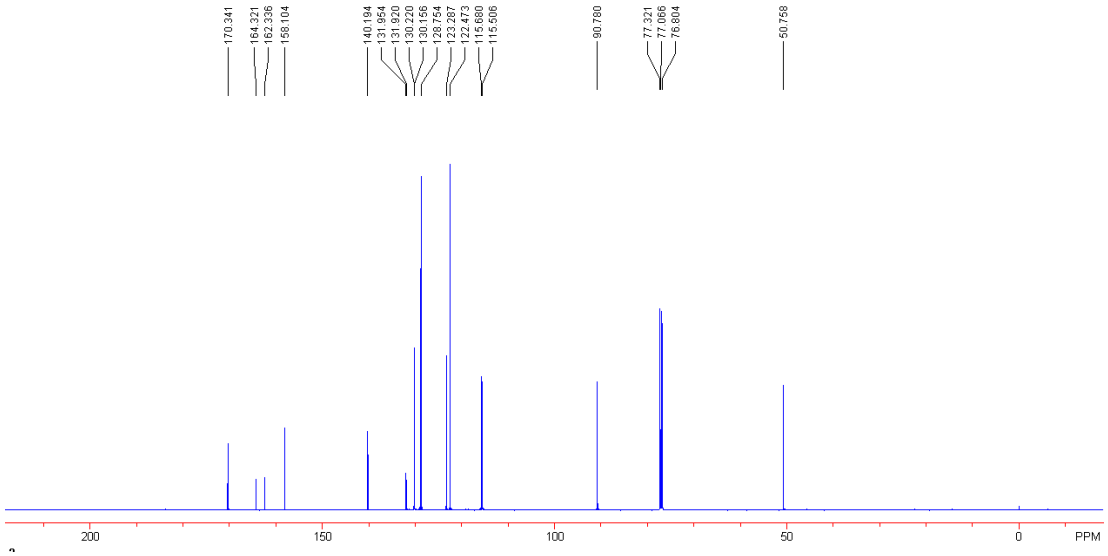




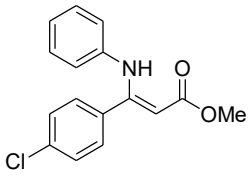
(*Z*)-Methyl 3-(4-fluorophenyl)-3-(phenylamino)acrylate (1p)

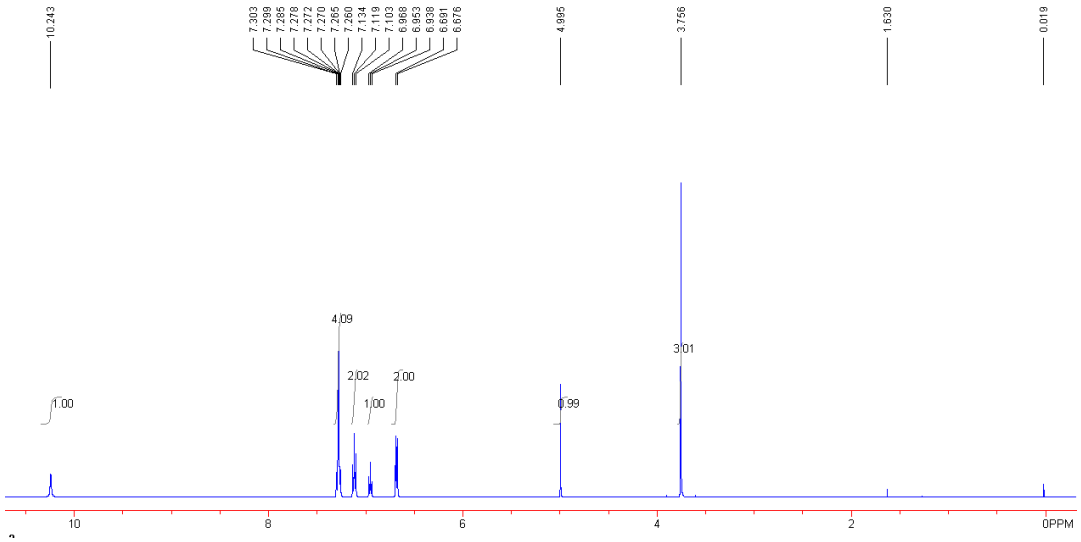


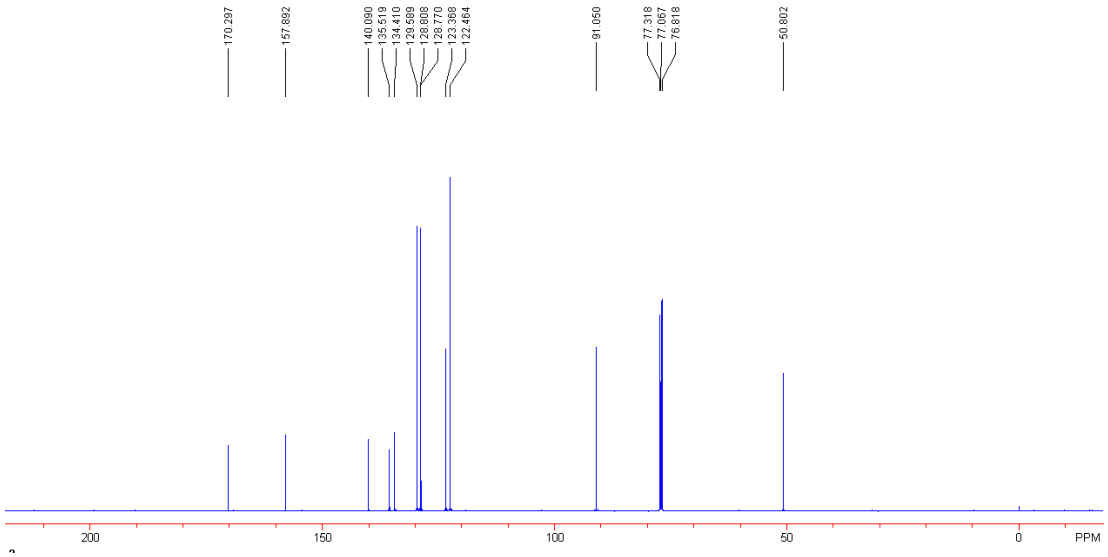




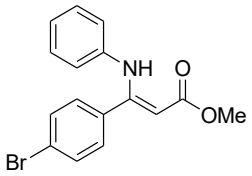
(*Z*)-Methyl 3-(4-chlorophenyl)-3-(phenylamino)acrylate (1q)

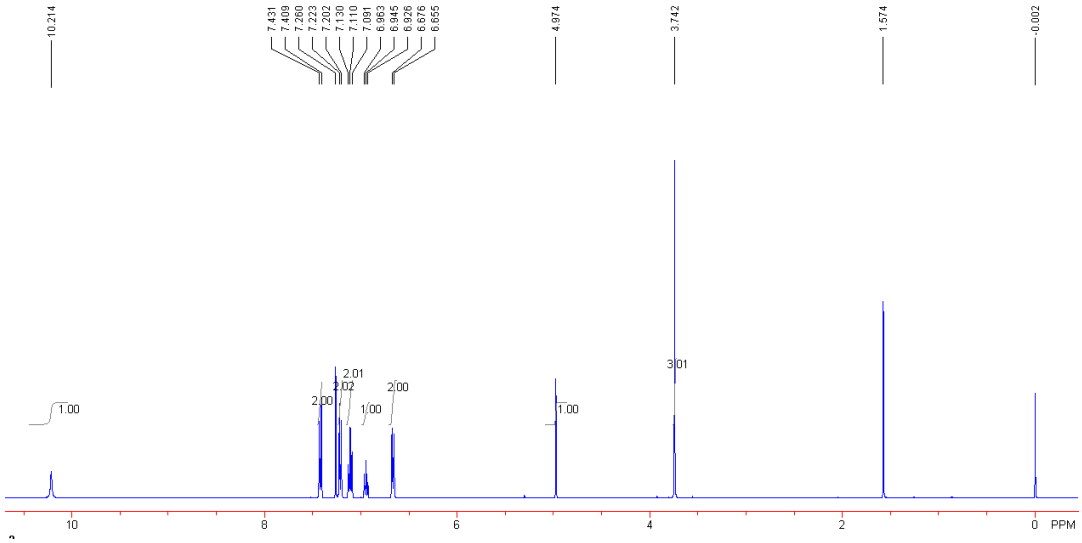


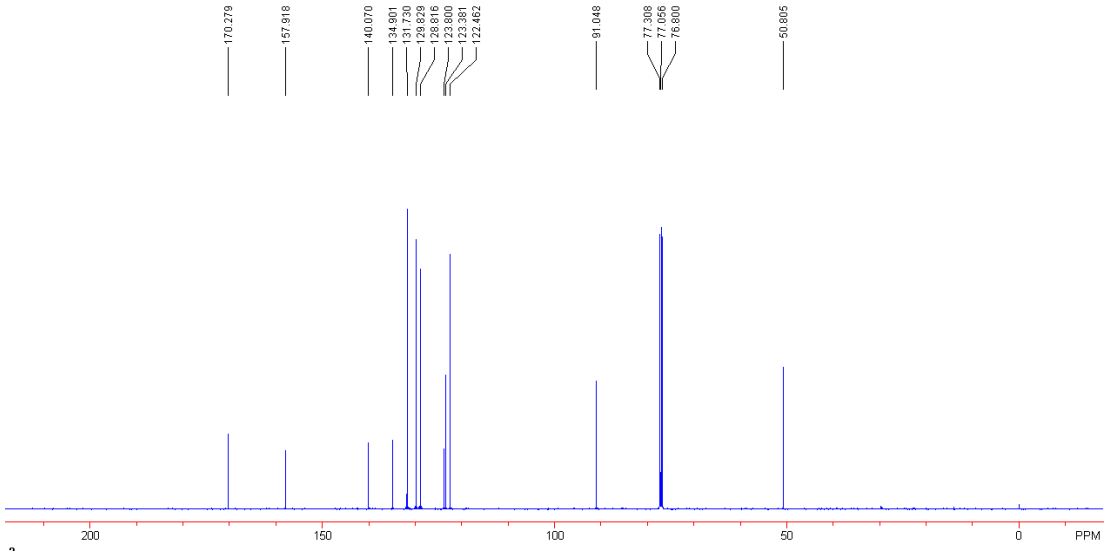




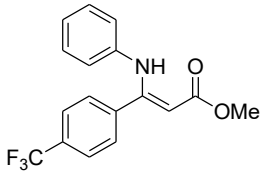
(*Z*)-Methyl 3-(4-bromophenyl)-3-(phenylamino)acrylate (1r)

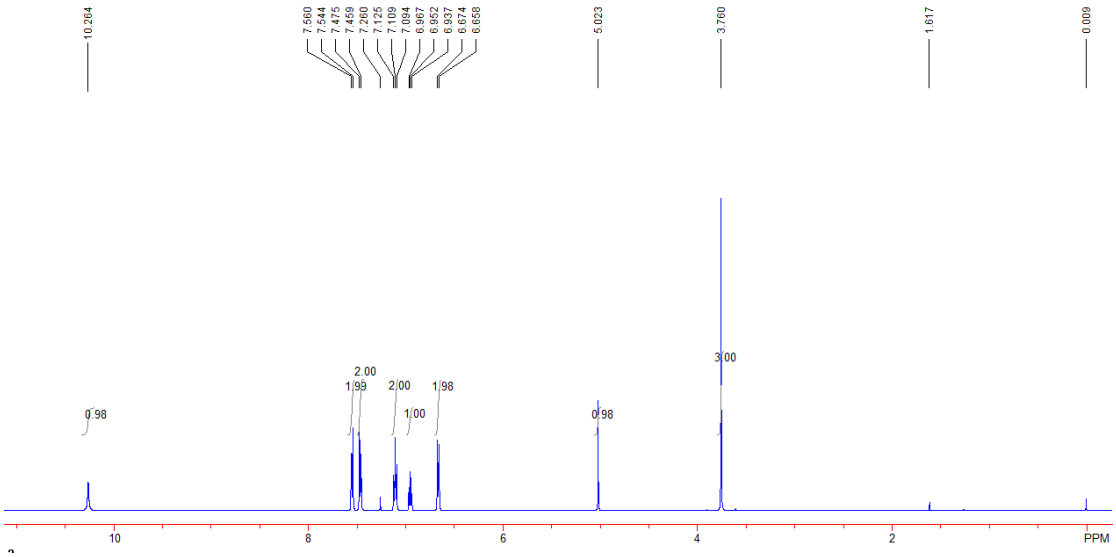


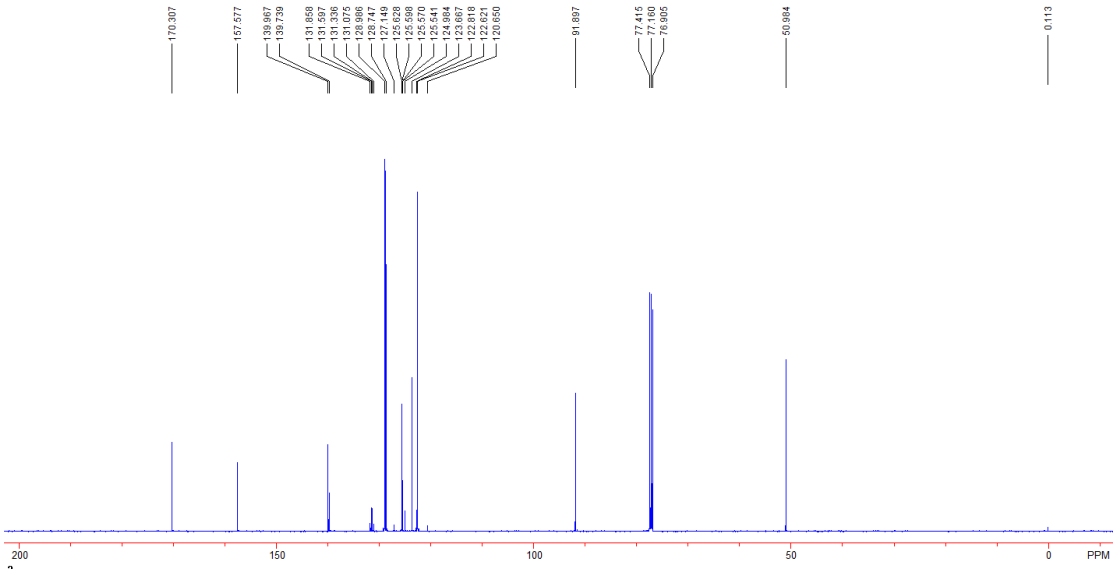




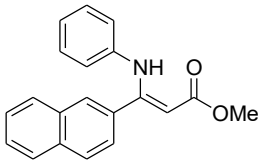
(*Z*)-Methyl 3-(phenylamino)-3-(4-(trifluoromethyl)phenyl)acrylate (1s)

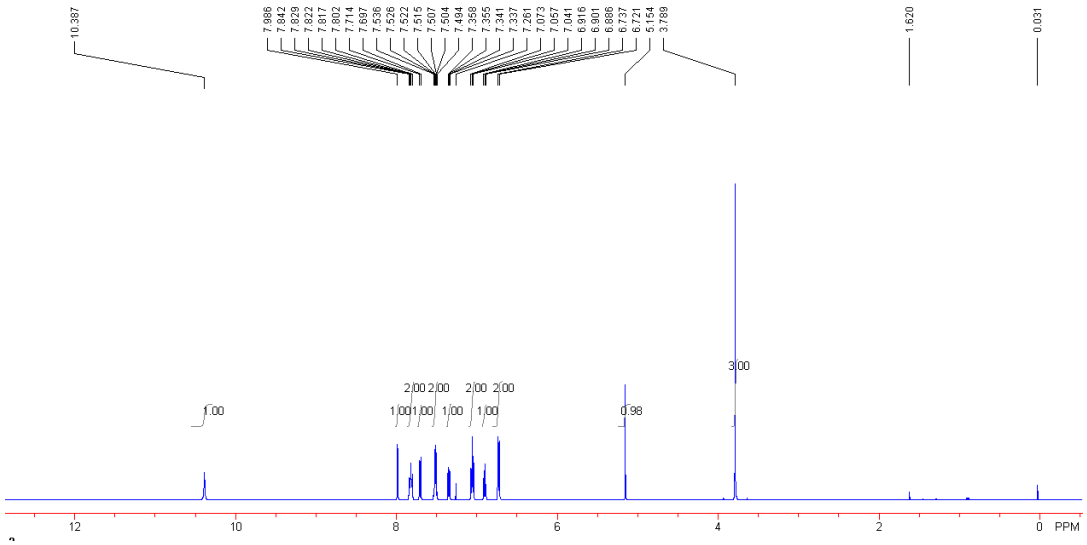


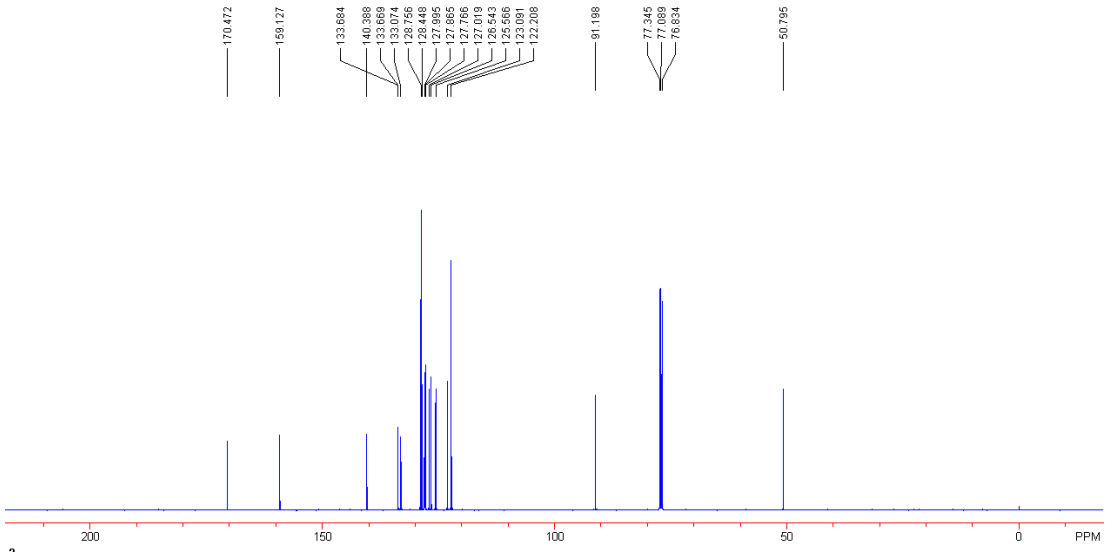




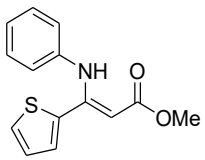
(*Z*)-Methyl 3-(naphthalen-2-yl)-3-(phenylamino)acrylate (3a)

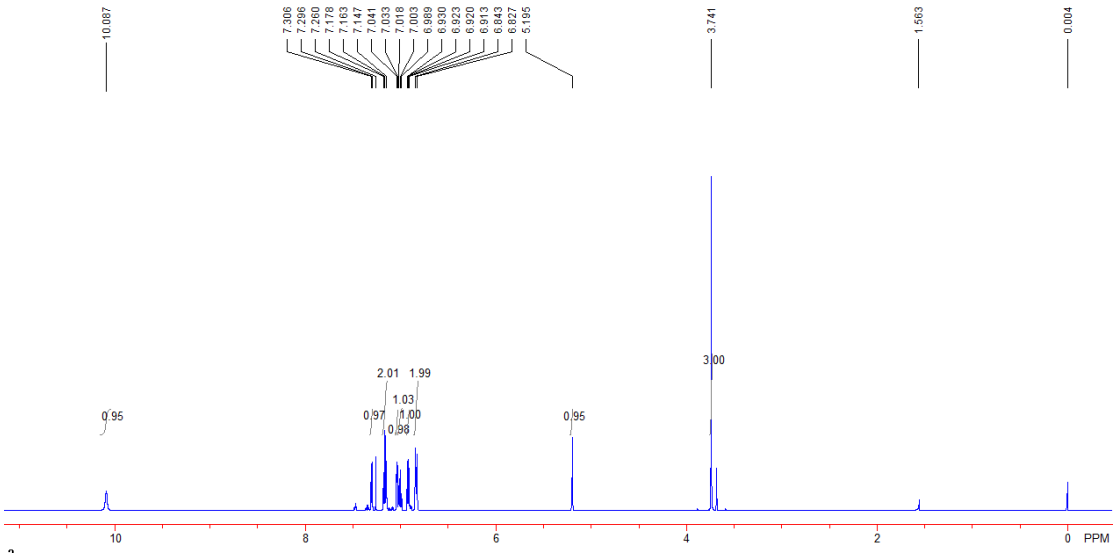


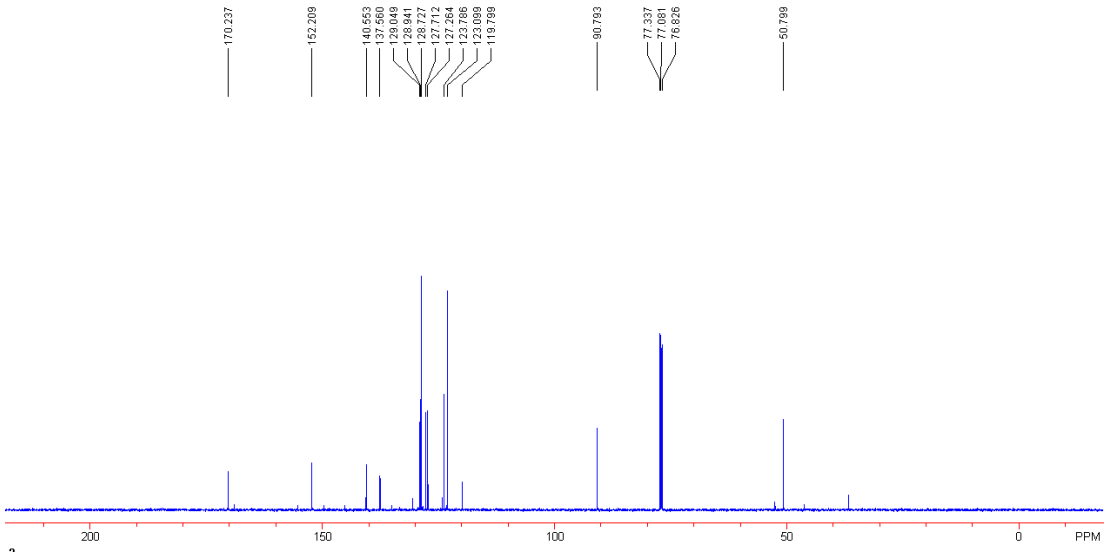




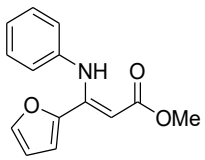
(*Z*)-Methyl 3-(phenylamino)-3-(thiophen-2-yl)acrylate (3b)

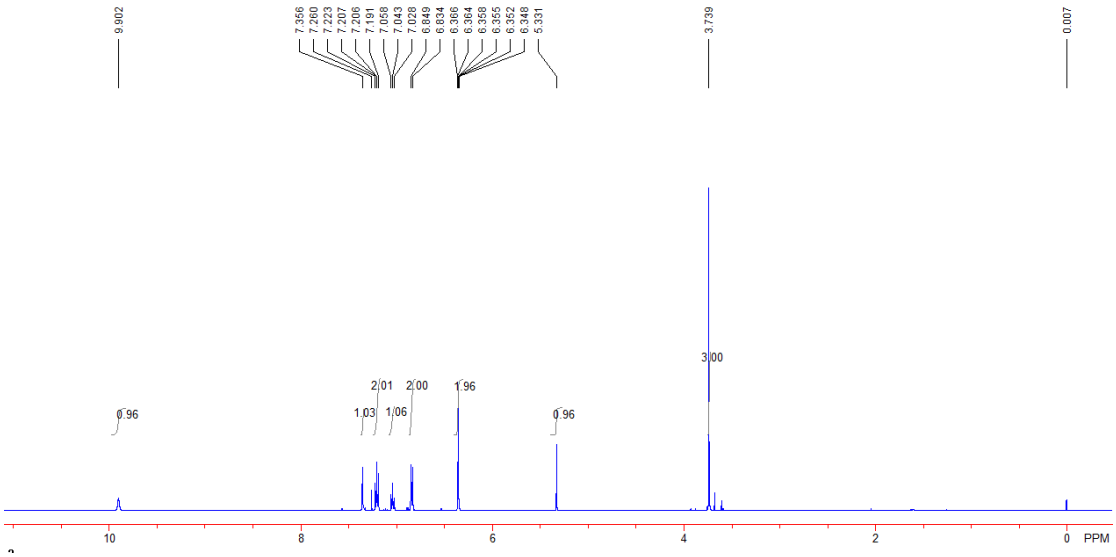


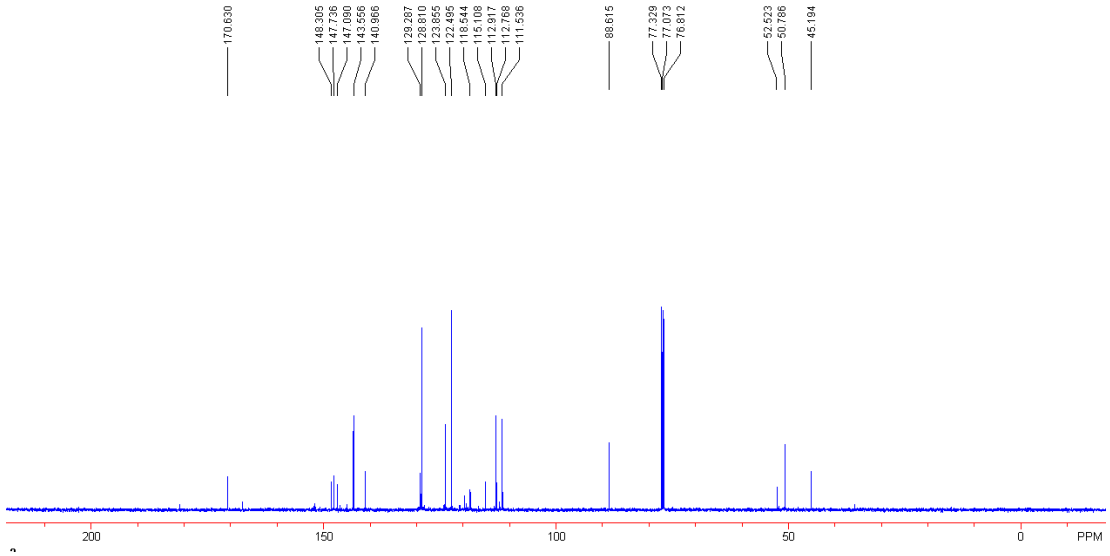




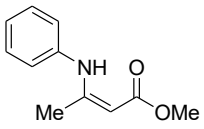
(*Z*)-Methyl 3-(furan-2-yl)-3-(phenylamino)acrylate (3c)

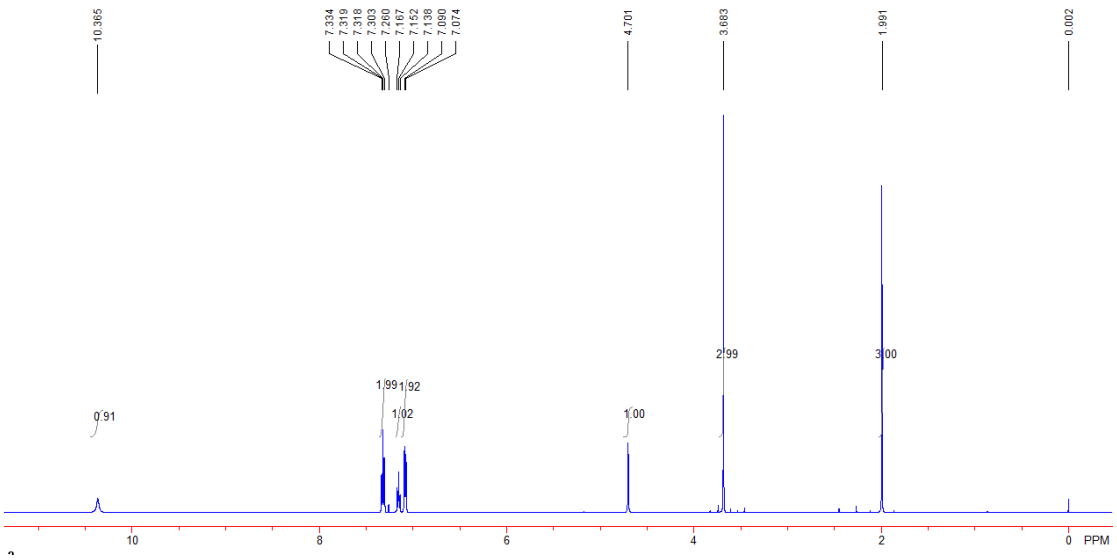


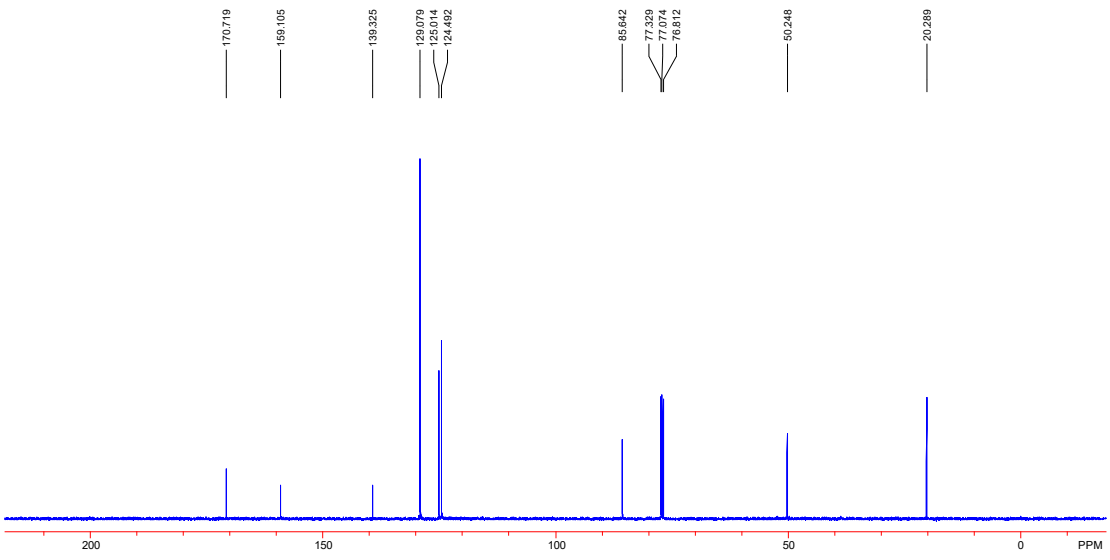




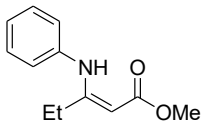
(*Z*)-Methyl 3-(phenylamino)but-2-enoate (3d)

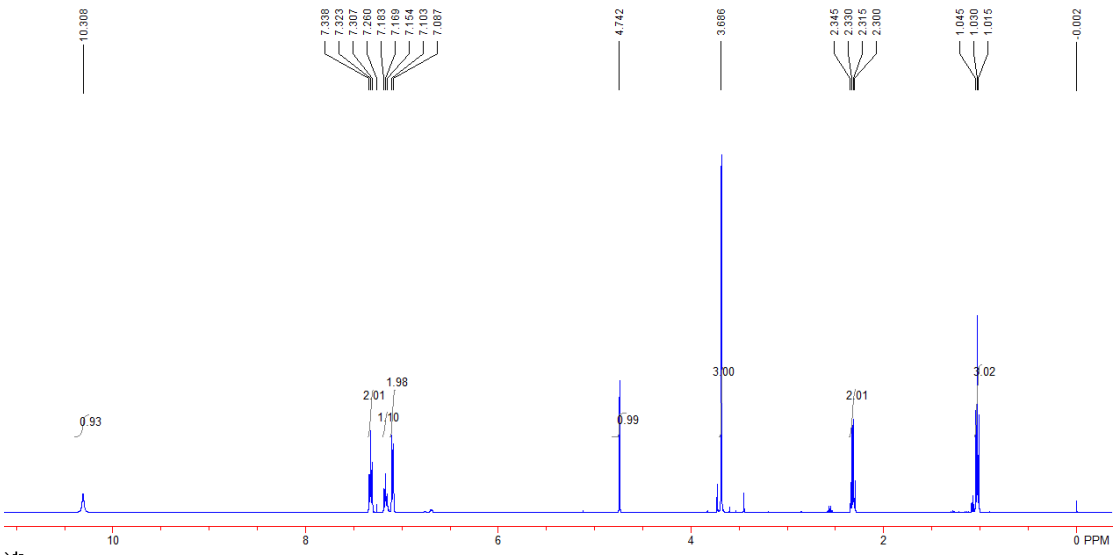


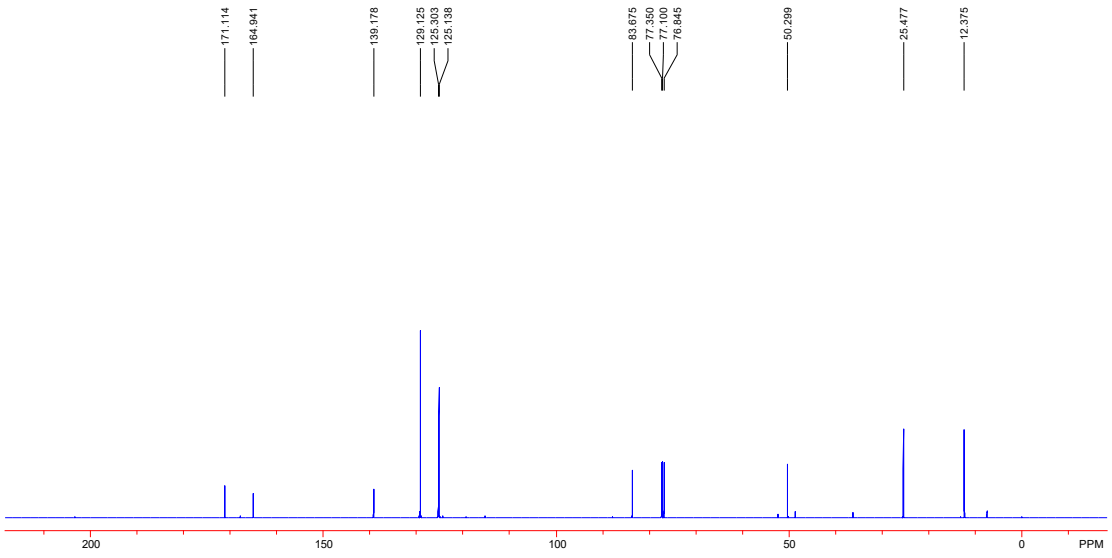




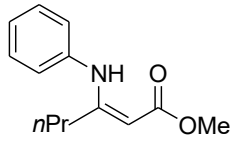
(*Z*)-Methyl 3-(phenylamino)pent-2-enoate (3e)

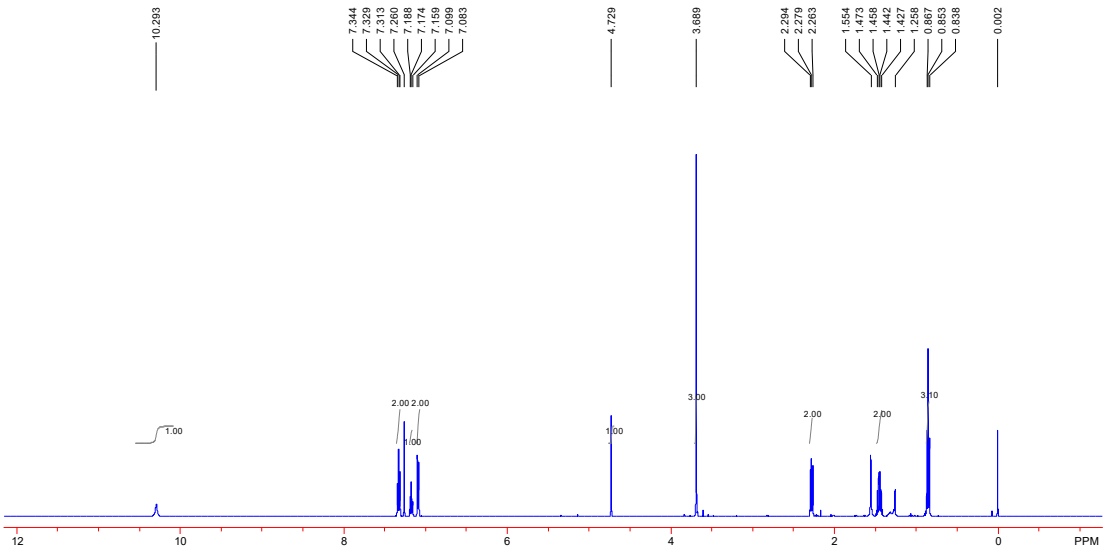


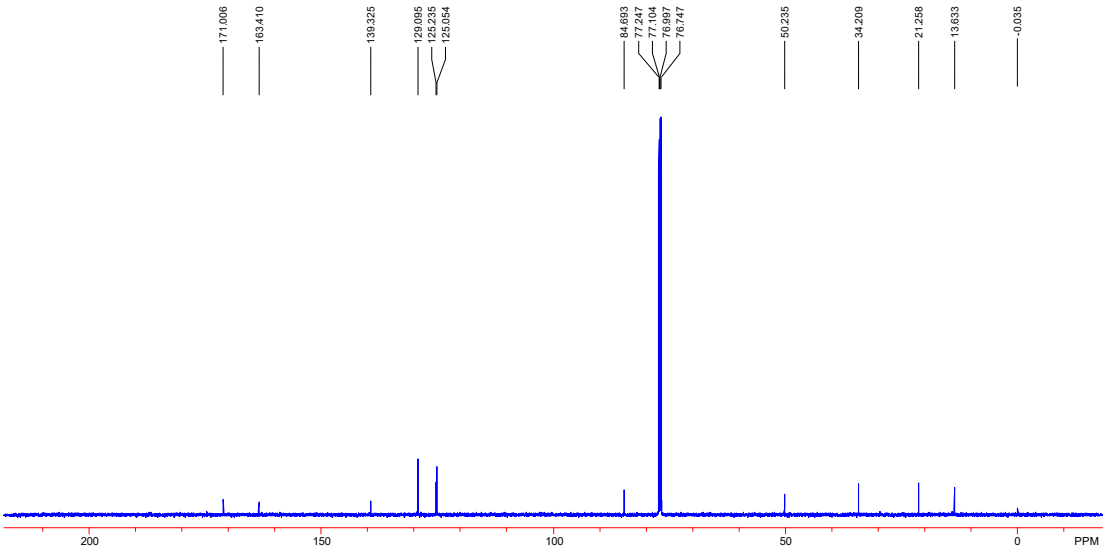




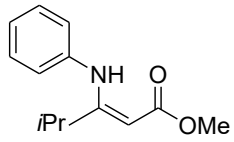
(*Z*)-Methyl 3-(phenylamino)hex-2-enoate (3f)

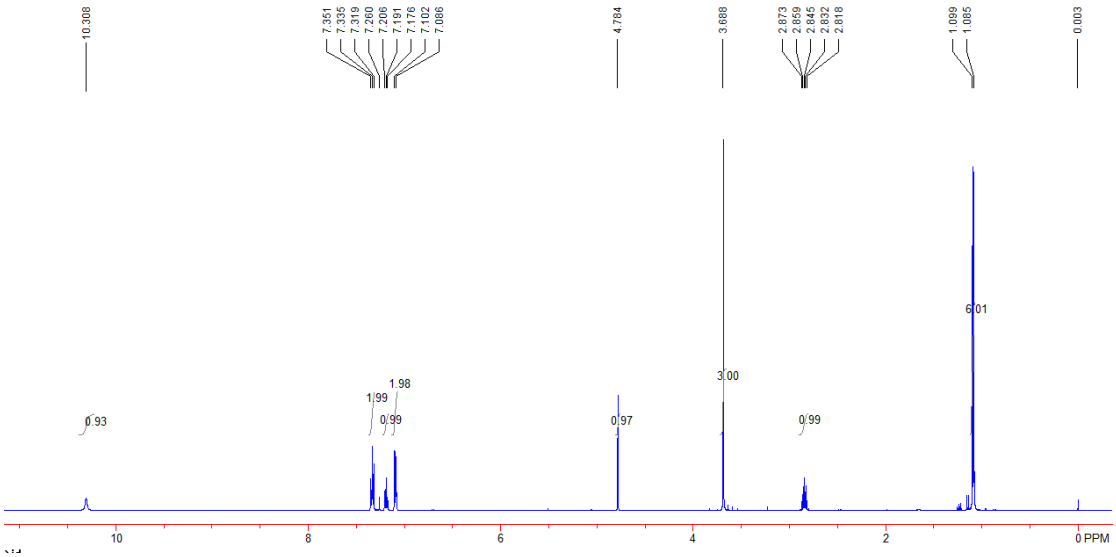


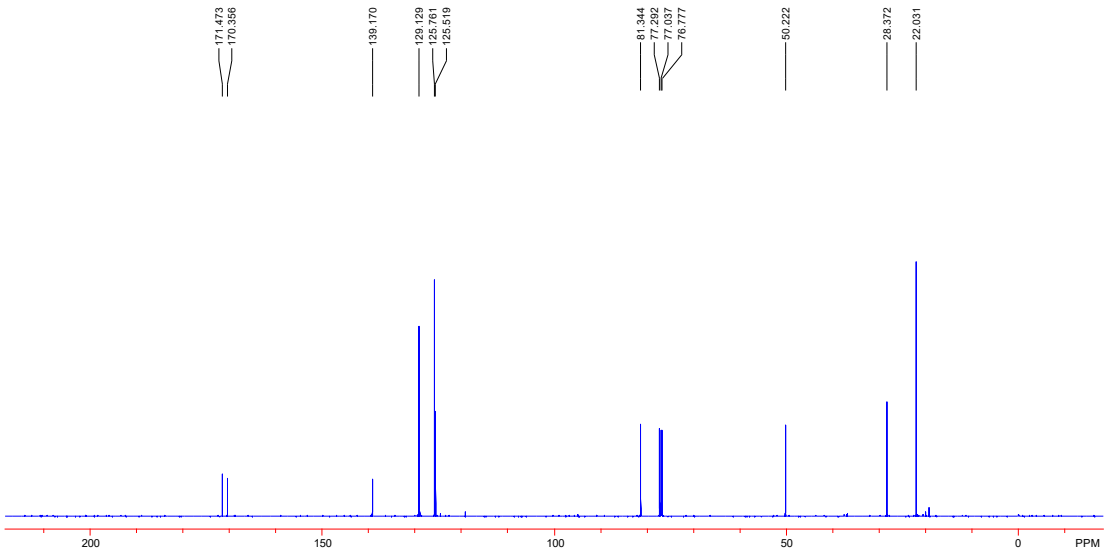




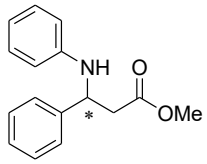
(*Z*)-Methyl 4-methyl-3-(phenylamino)pent-2-enoate (3g)

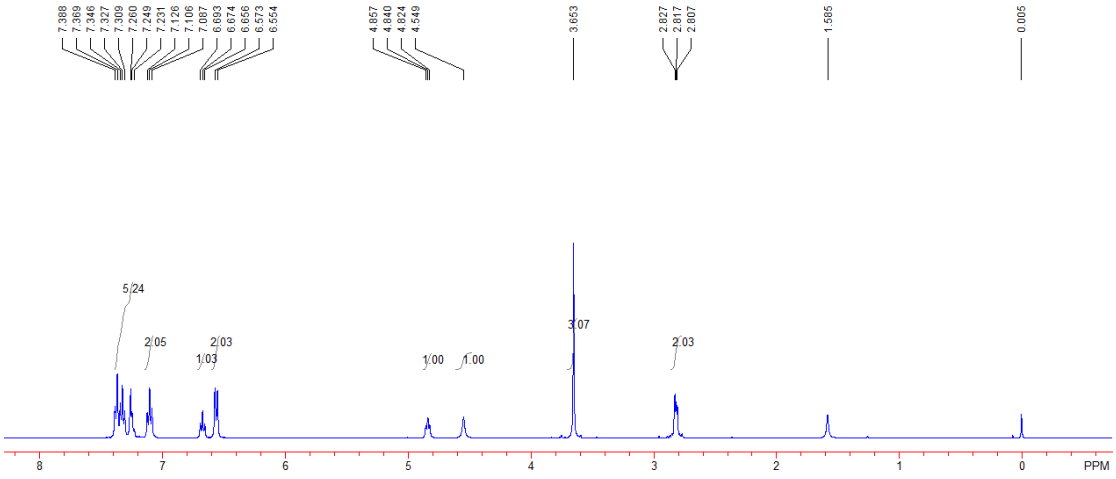


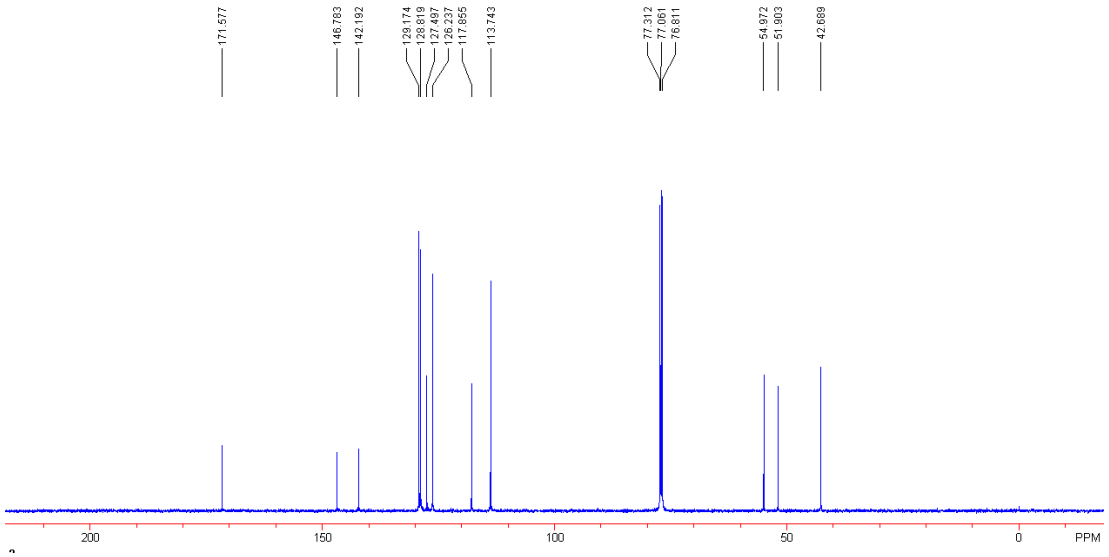




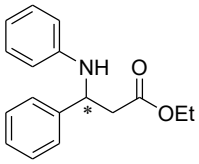
(–)-Methyl 3-phenyl-3-(phenylamino)propanoate (2a)

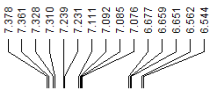


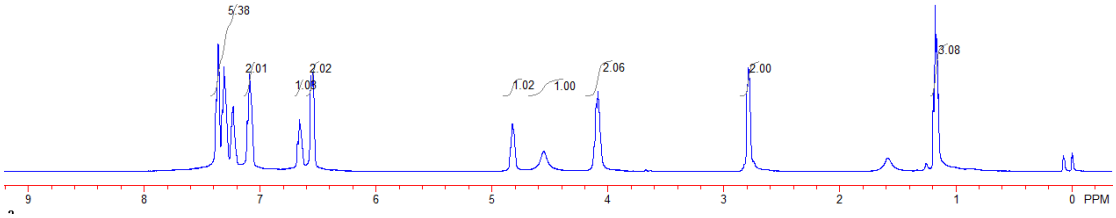


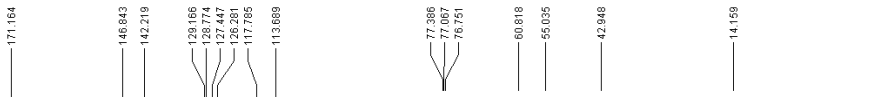


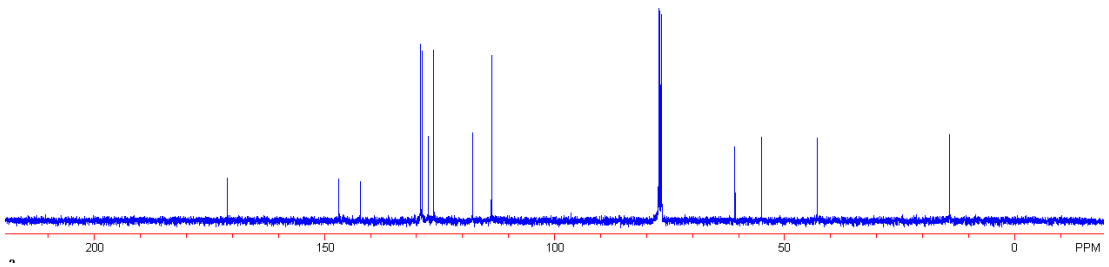
(+)-Ethyl 3-phenyl-3-(phenylamino)propanoate (2b)



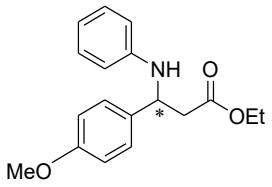


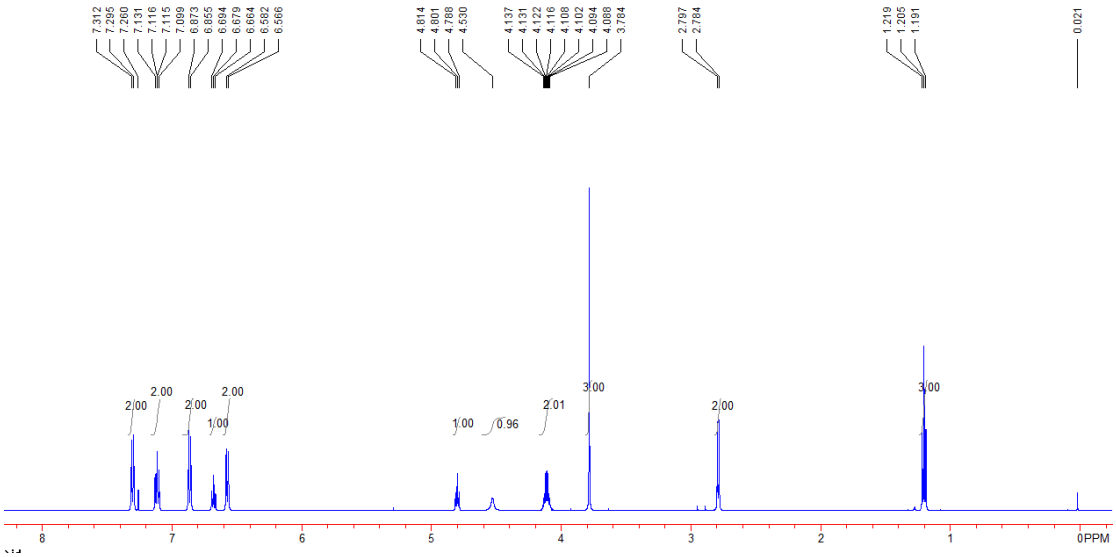


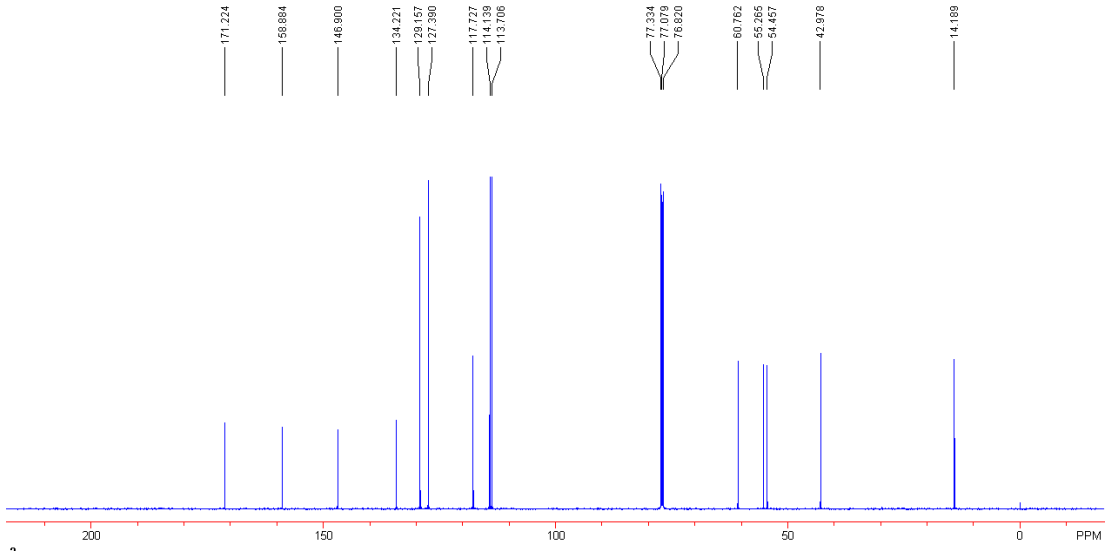




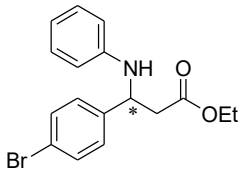
(+)-Ethyl 3-(4-methoxyphenyl)-3-(phenylamino)propanoate (2c)

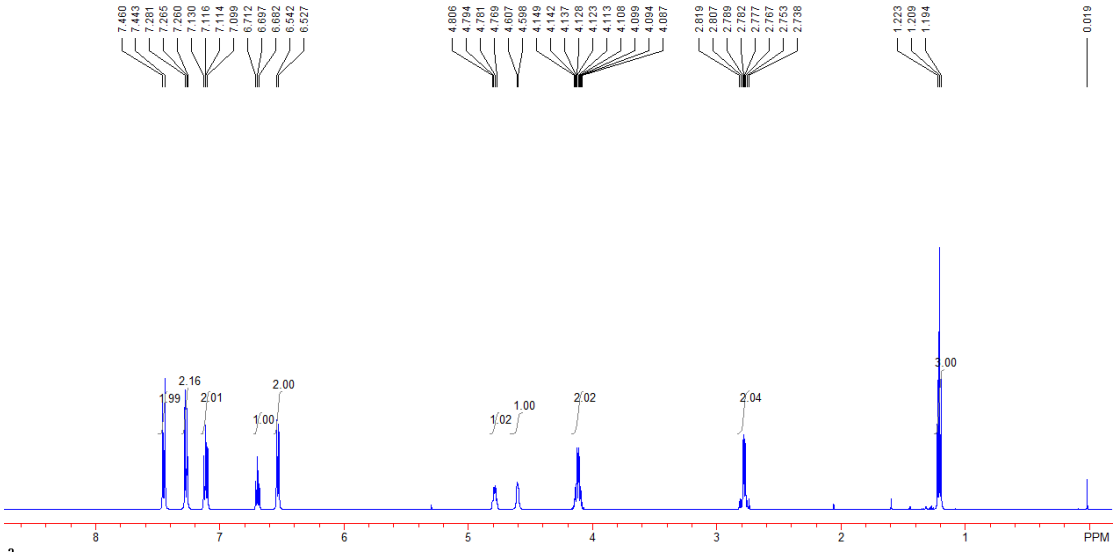


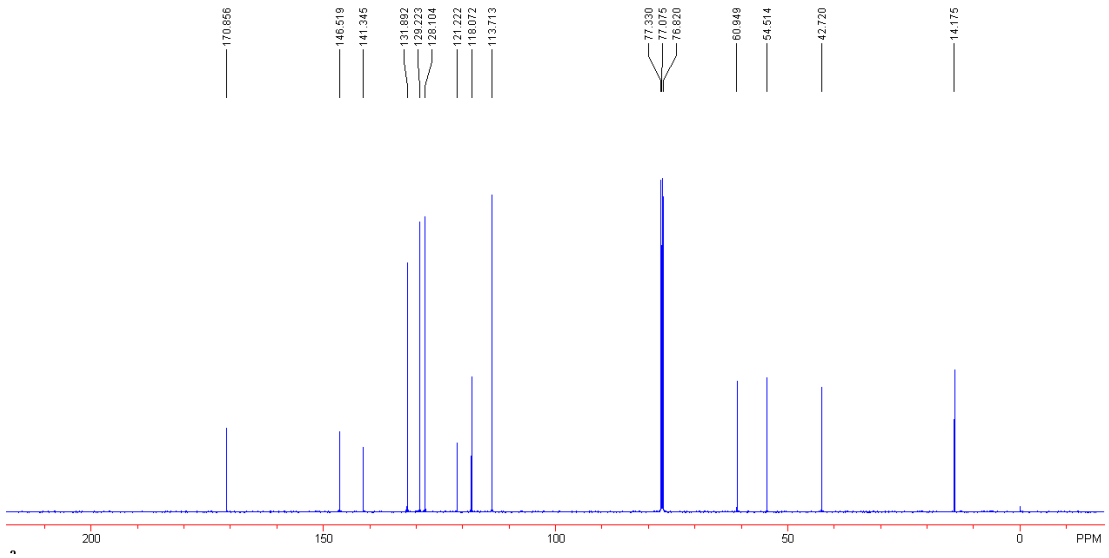




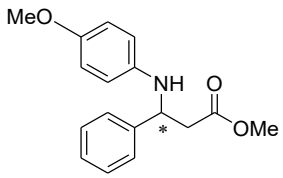
(+)-Ethyl 3-(4-bromophenyl)-3-(phenylamino)propanoate (2d)

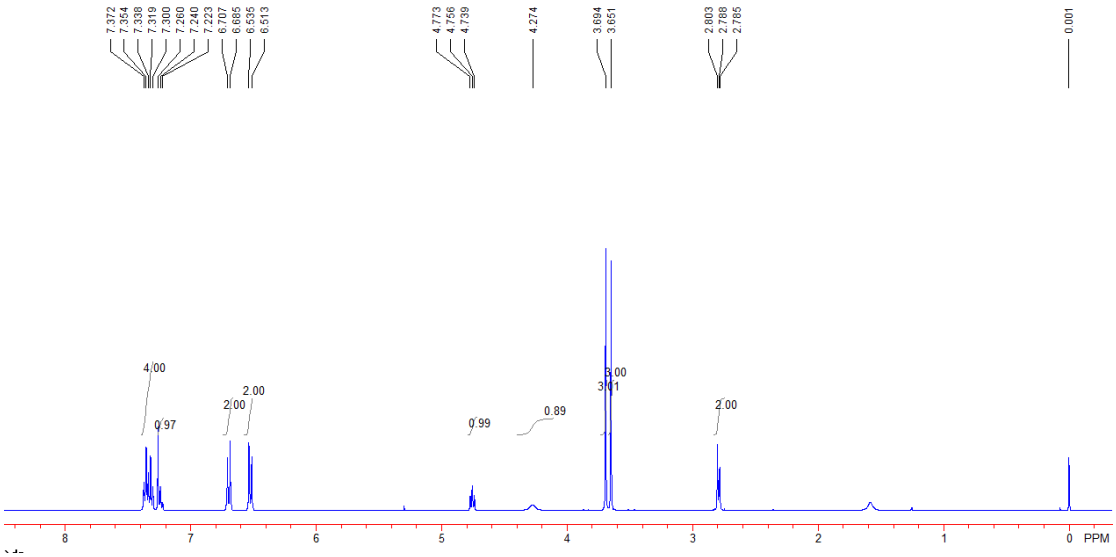


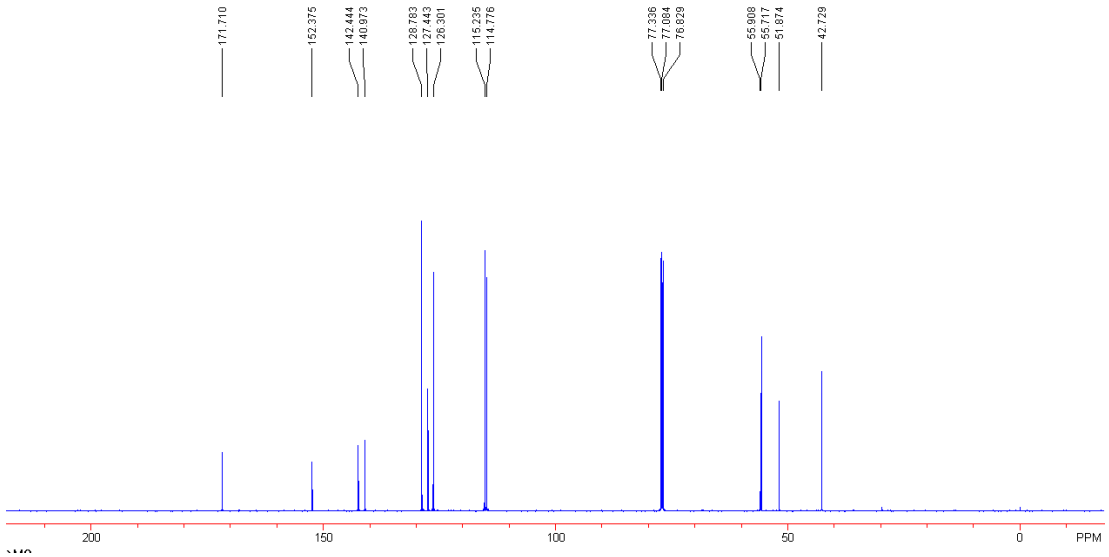




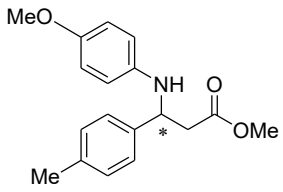
(+)-Methyl 3-(4-methoxyphenylamino)-3-phenylpropanoate (2e)

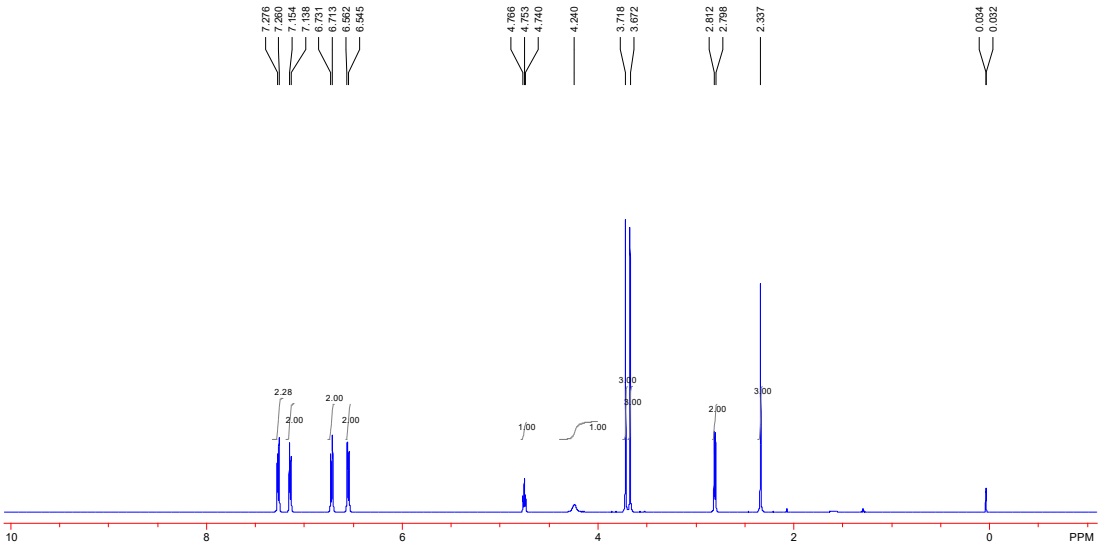


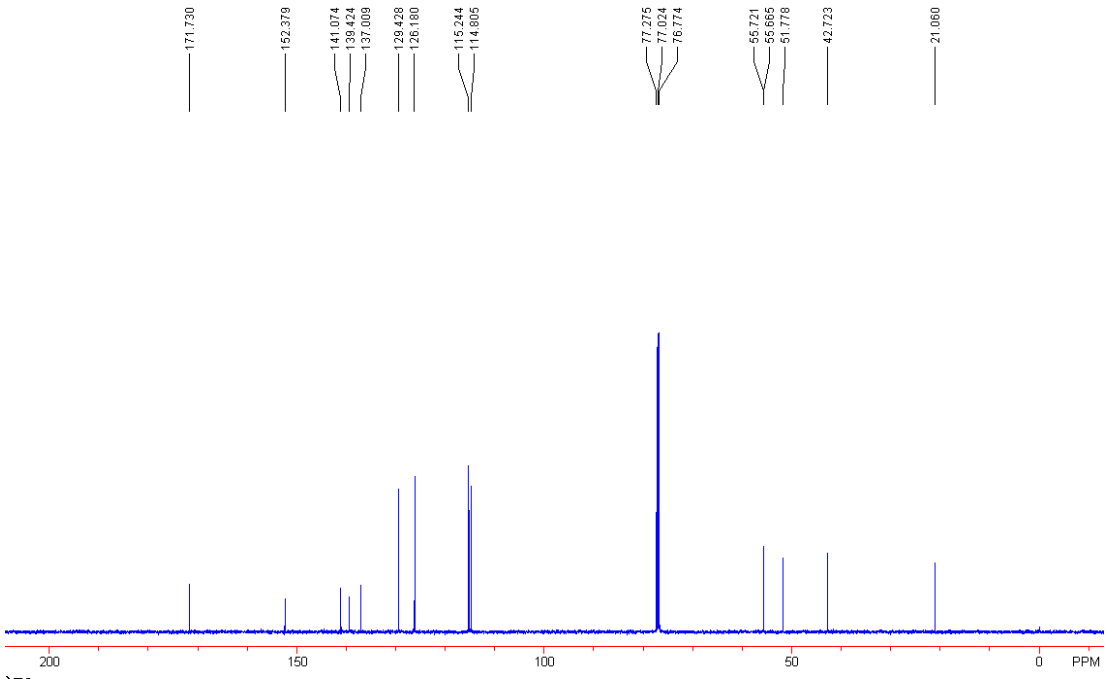




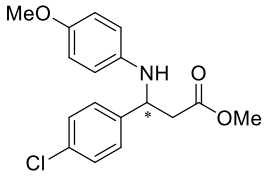
(+)-Methyl 3-(4-methoxyphenylamino)-3-(*p*-tolyl)propanoate (2f)

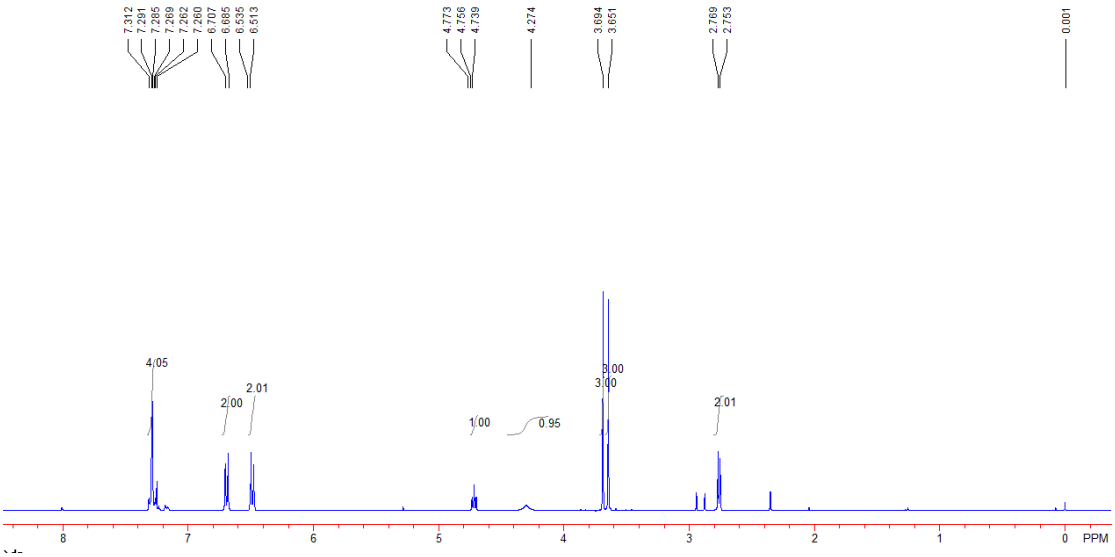


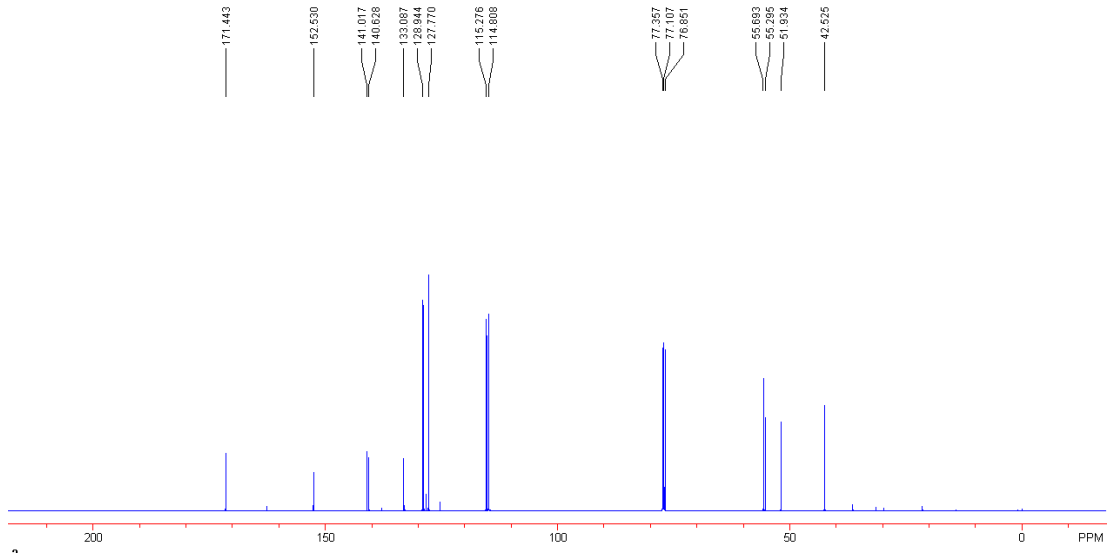




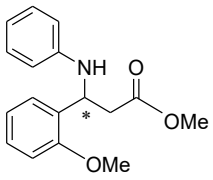
(–)-Methyl 3-(4-chlorophenyl)-3-(4-methoxyphenylamino)propanoate (2g)

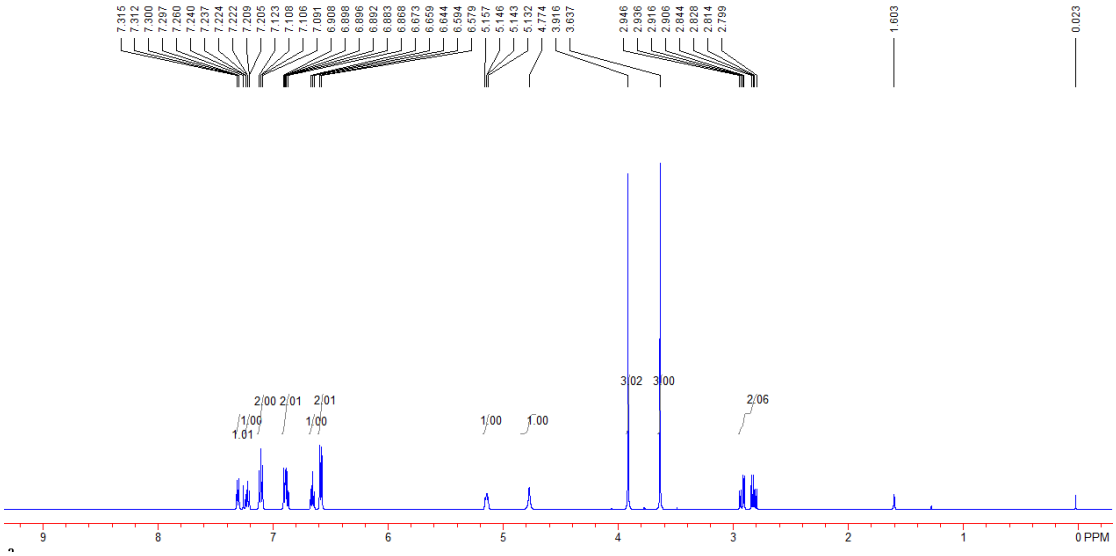


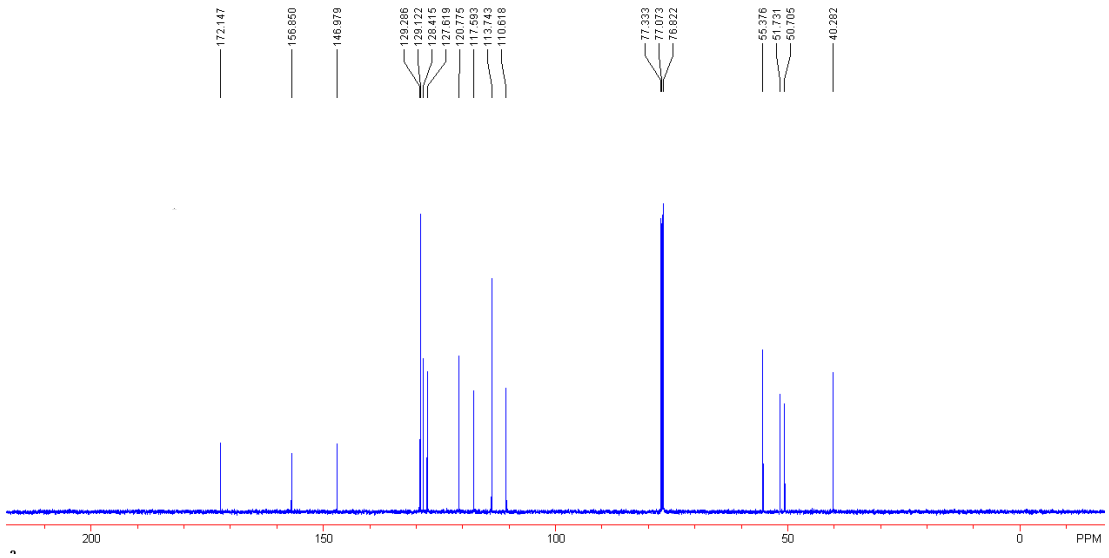




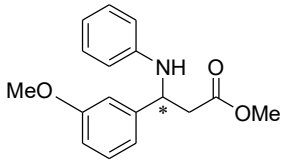
(–)-Methyl 3-(2-methoxyphenyl)-3-(phenylamino)propanoate (2h)

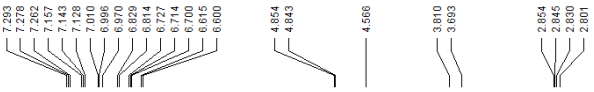


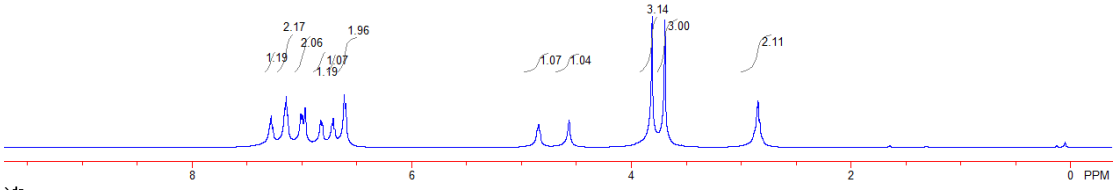


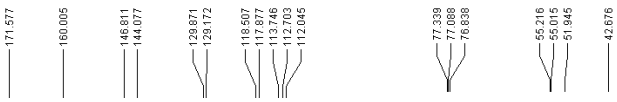


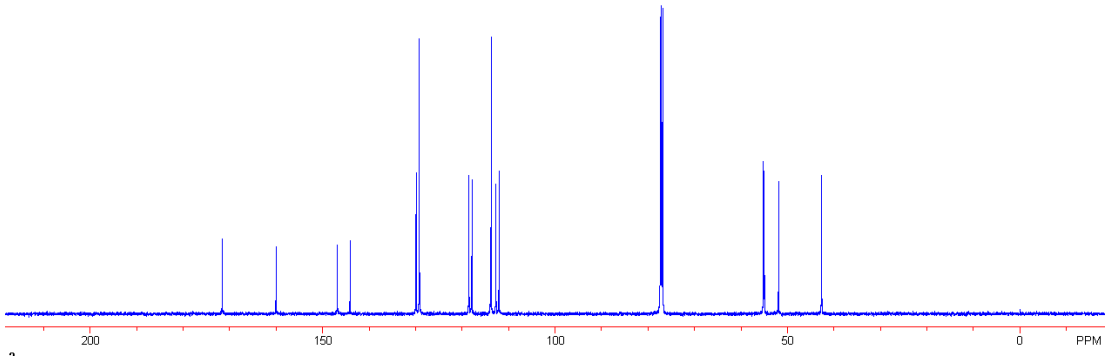
(–)-Methyl 3-(3-methoxyphenyl)-3-(phenylamino)propanoate (2i)



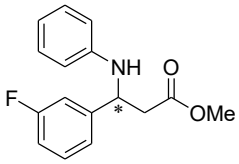


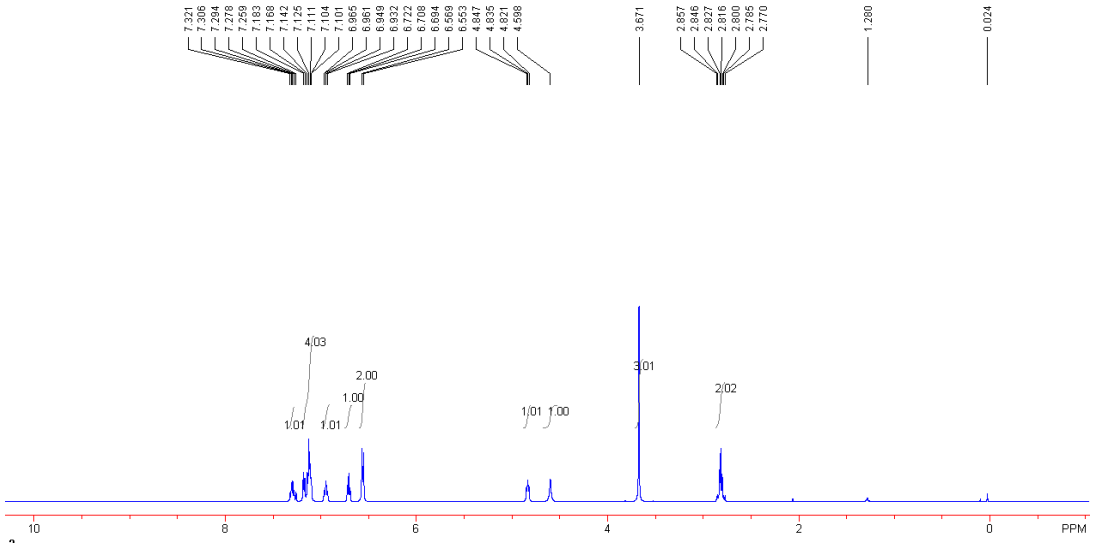


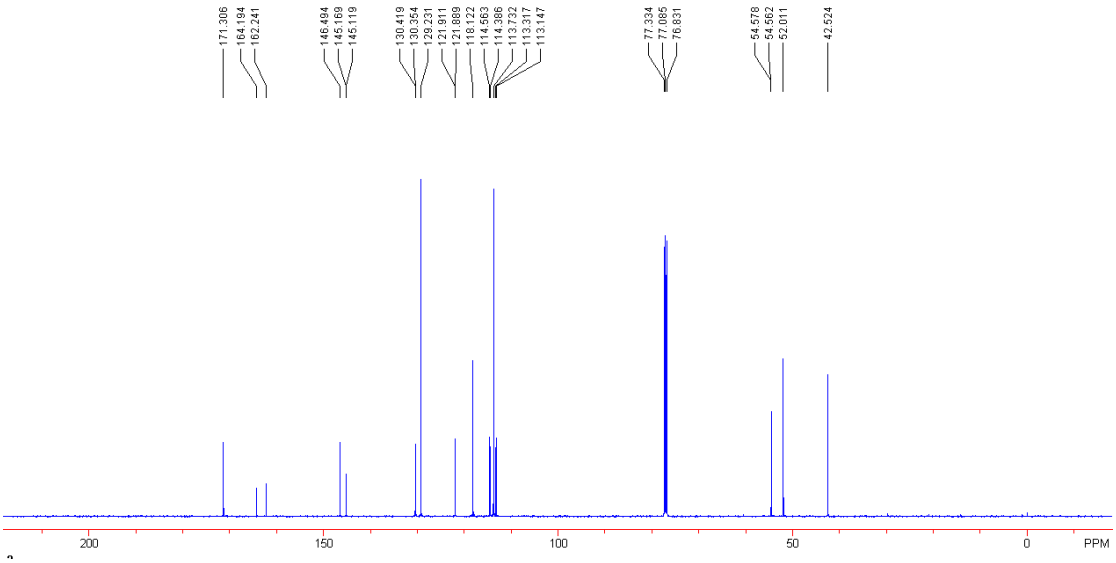




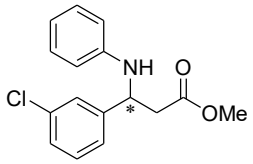
(+)-Methyl 3-(3-fluorophenyl)-3-(phenylamino)propanoate (2j)

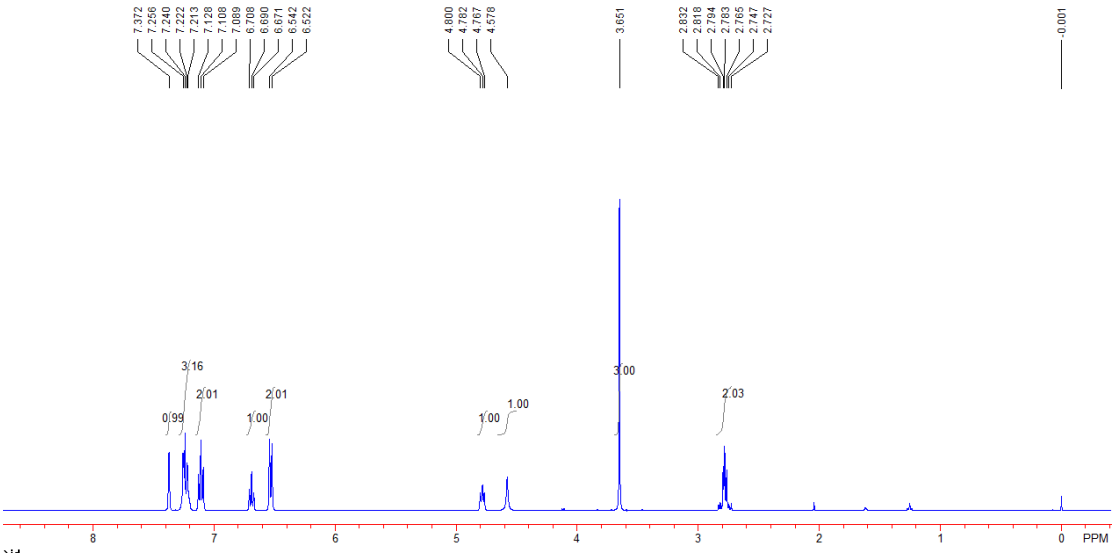


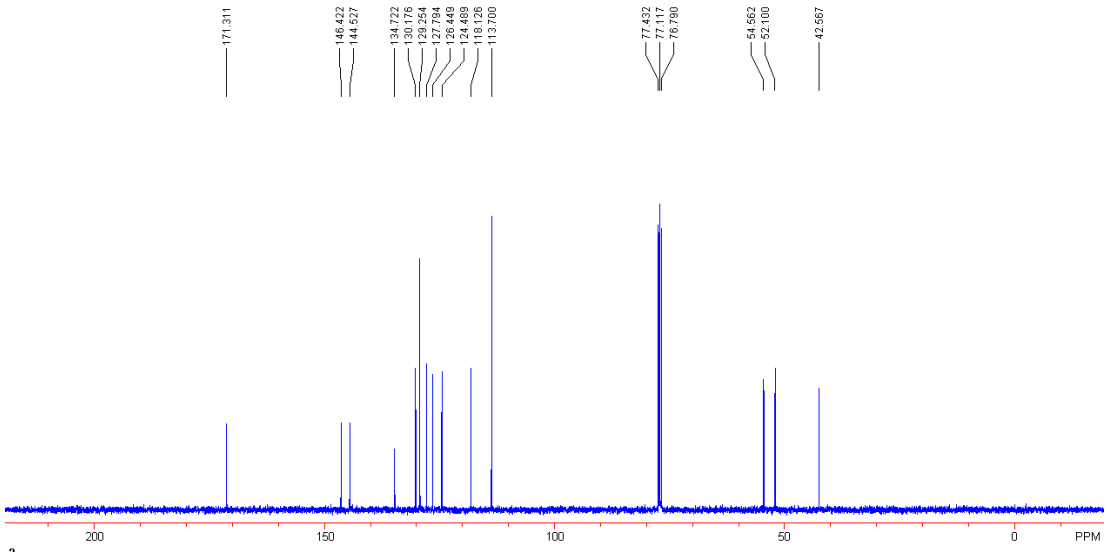




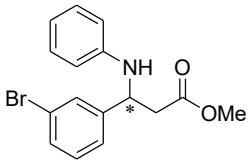
(–)-Methyl 3-(3-chlorophenyl)-3-(phenylamino)propanoate (2k)

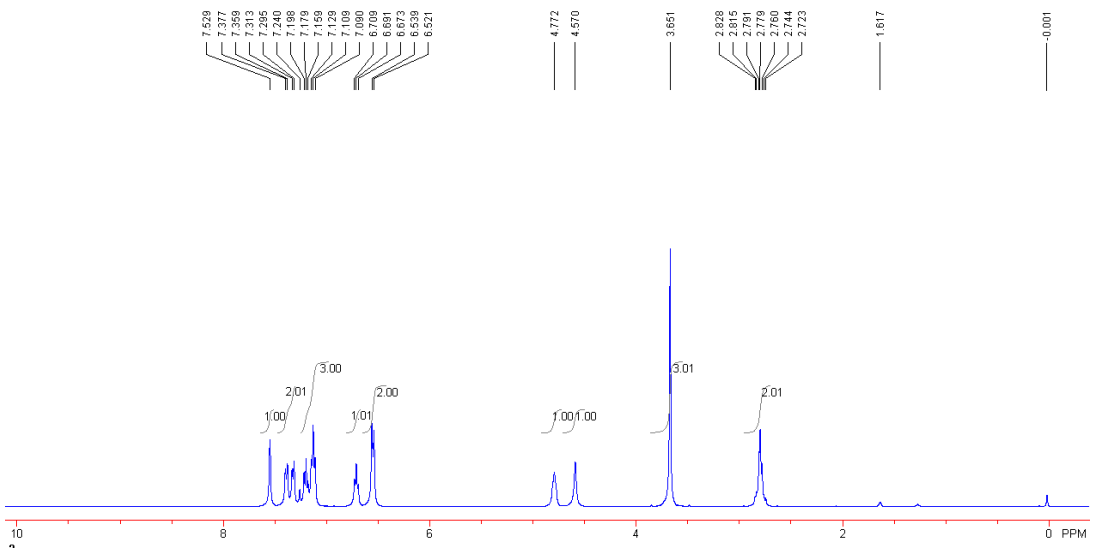


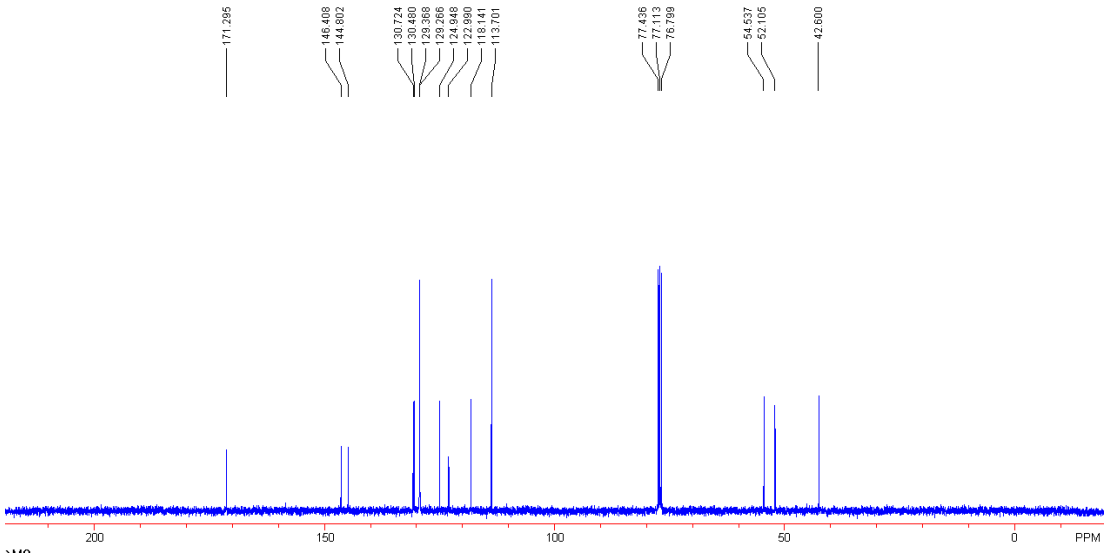




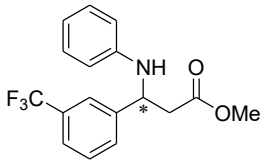
(+)-Methyl 3-(3-bromophenyl)-3-(phenylamino)propanoate (2l)

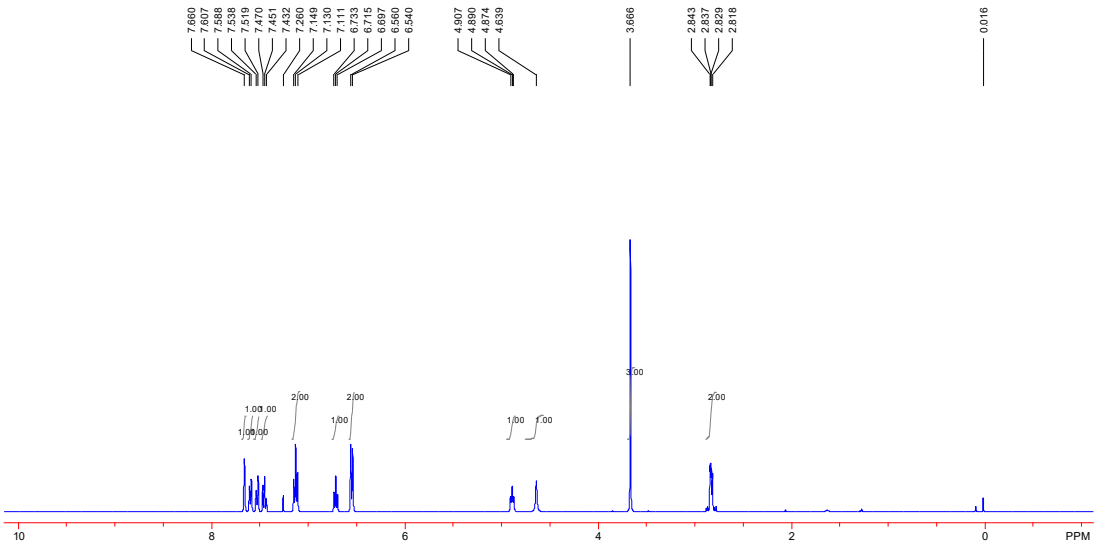


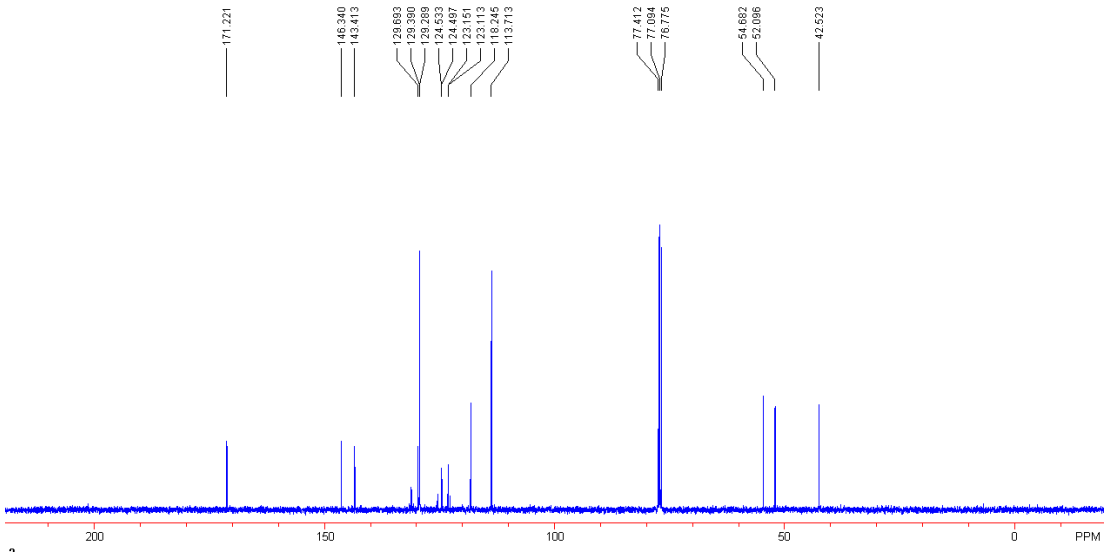




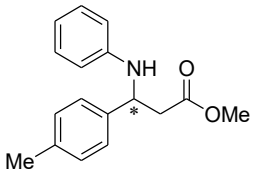
(+)-Methyl 3-(phenylamino)-3-(3-(trifluoromethyl)phenyl)propanoate (2m)

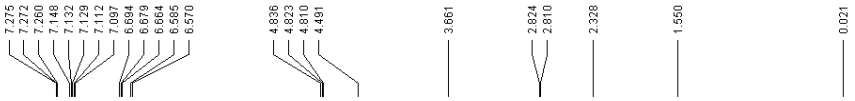


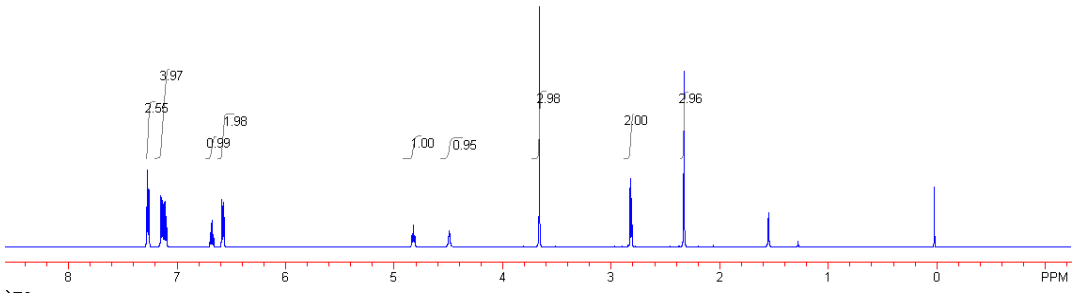


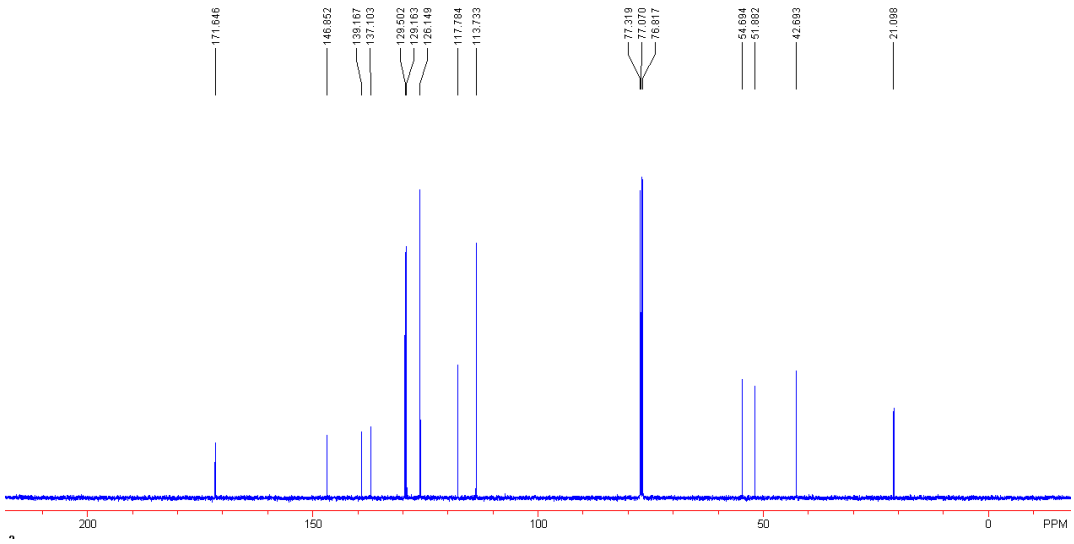


(+)-Methyl 3-(phenylamino)-3-(*p*-tolyl)propanoate (2n)

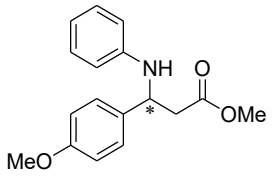


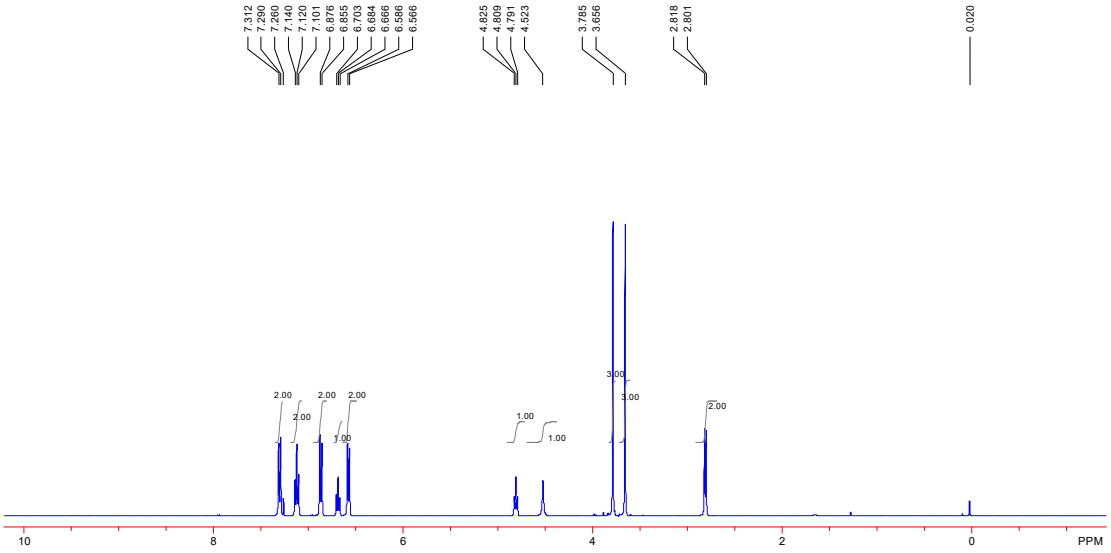


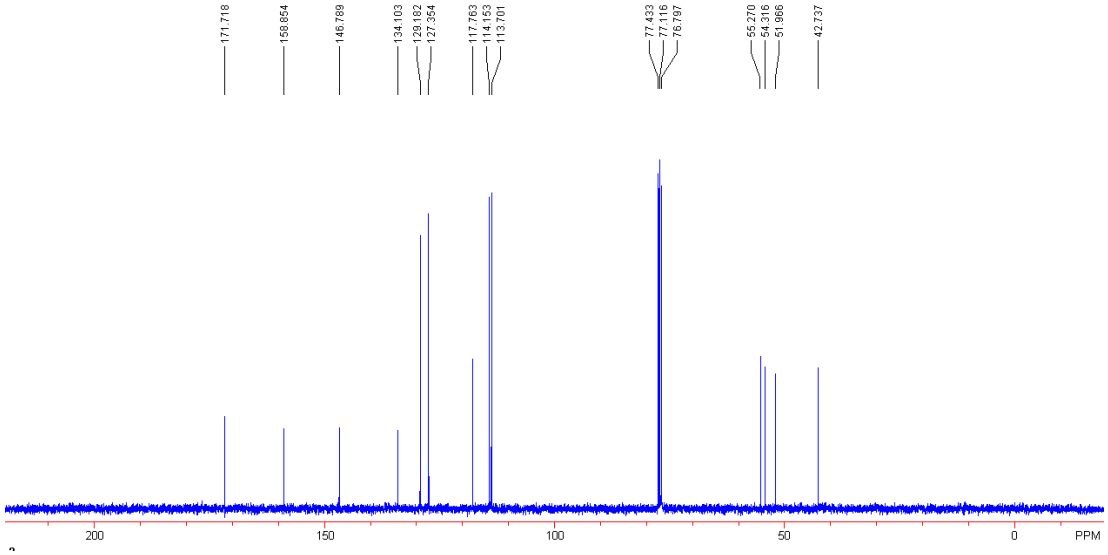




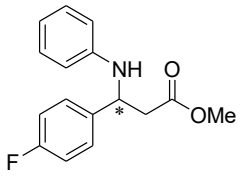
(–)-Methyl 3-(4-methoxyphenyl)-3-(phenylamino)propanoate (2o)

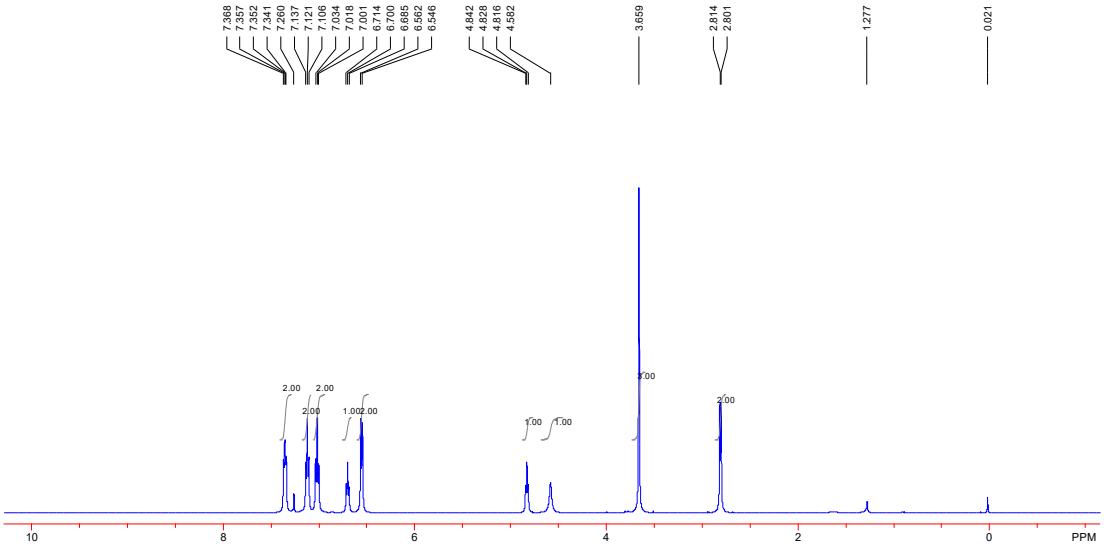


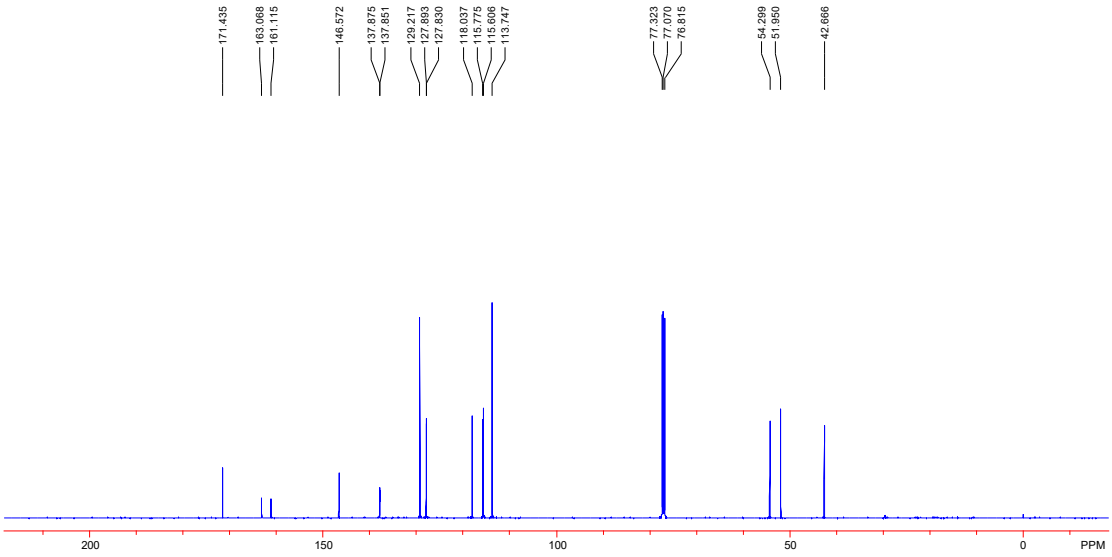




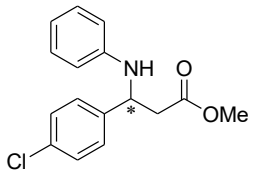
(+)-Methyl 3-(4-fluorophenyl)-3-(phenylamino)propanoate (2p)

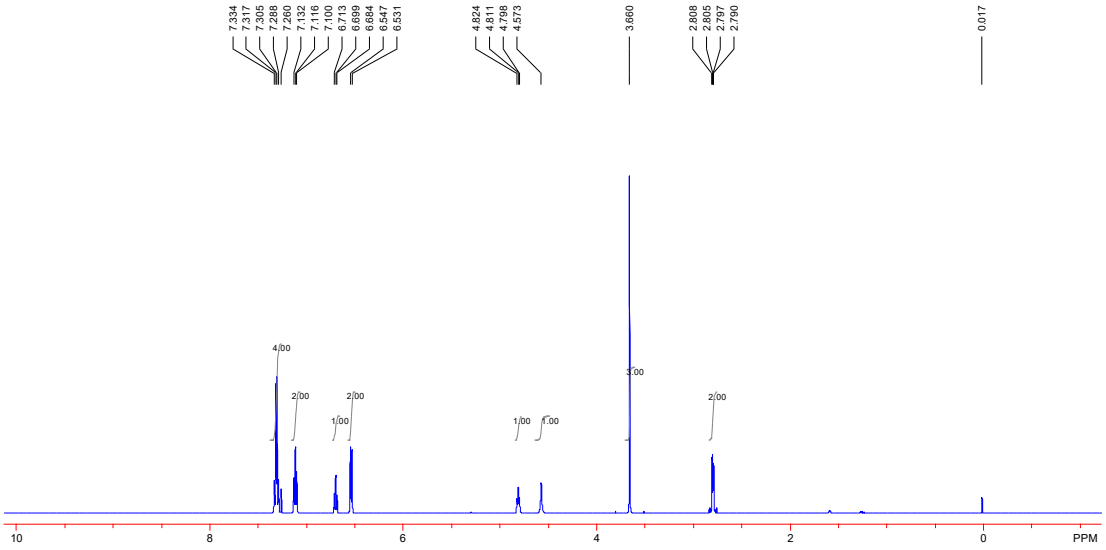


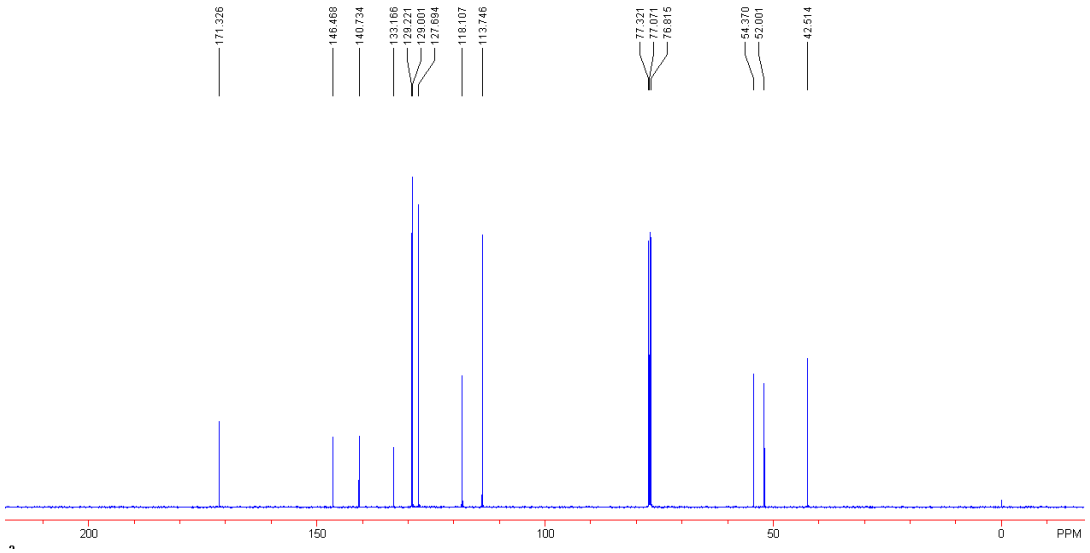




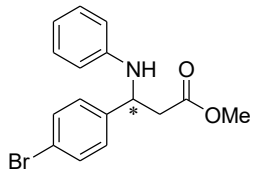
(–)-Methyl 3-(4-chlorophenyl)-3-(phenylamino)propanoate (2q)

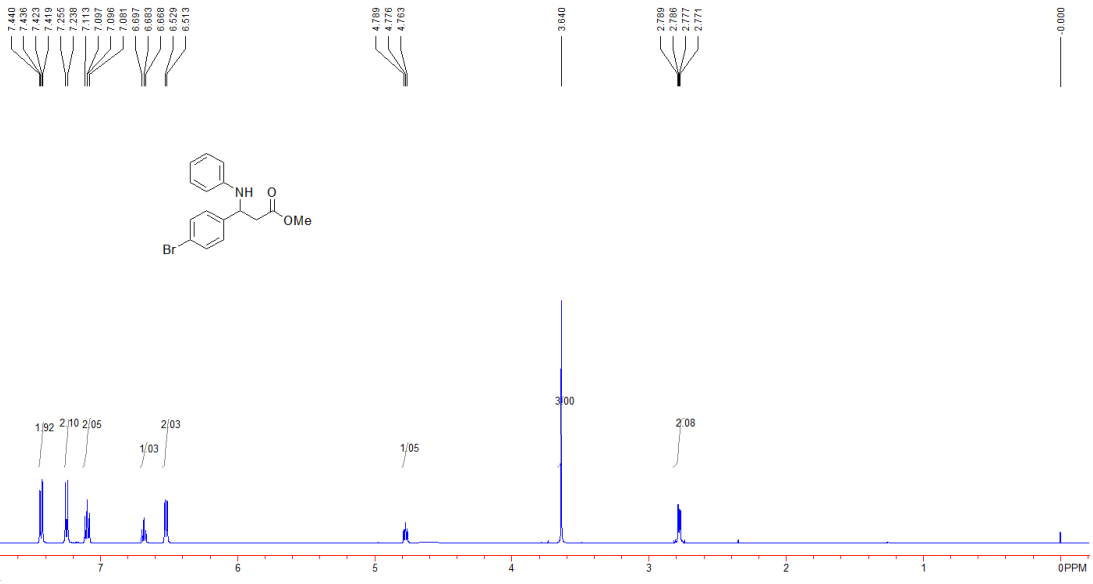


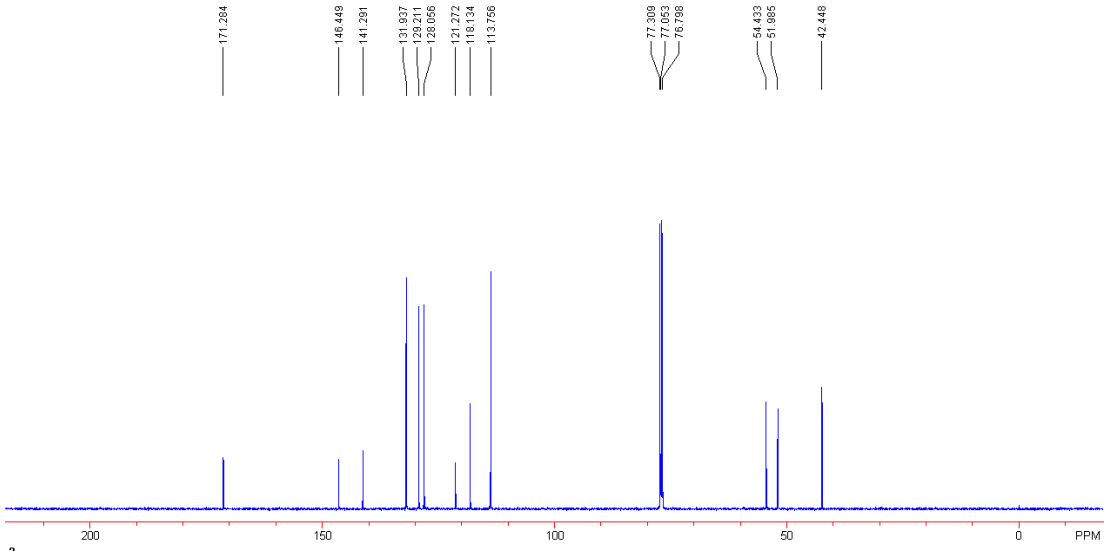




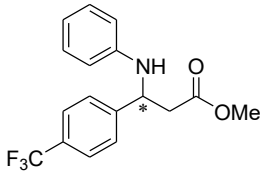
(–)-Methyl 3-(4-bromophenyl)-3-(phenylamino)propanoate (2r)

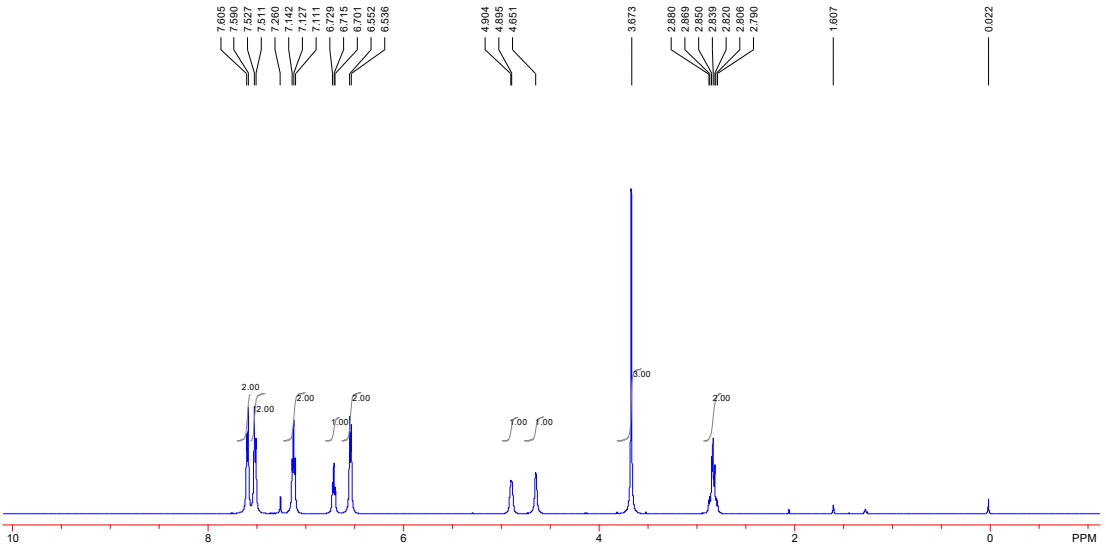


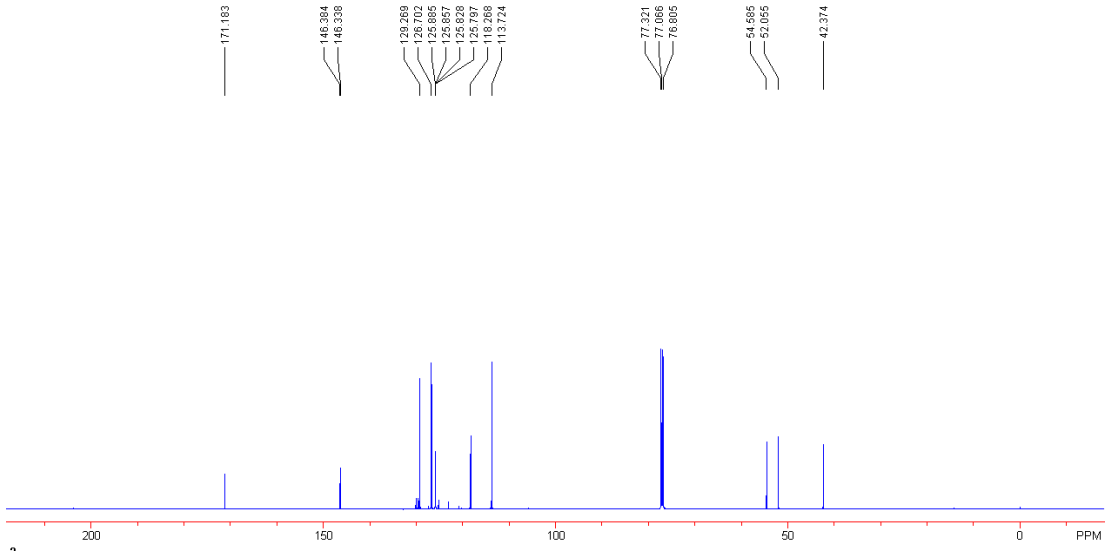




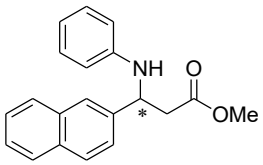
(+)-Methyl 3-(phenylamino)-3-(4-(trifluoromethyl)phenyl)propanoate (2s)

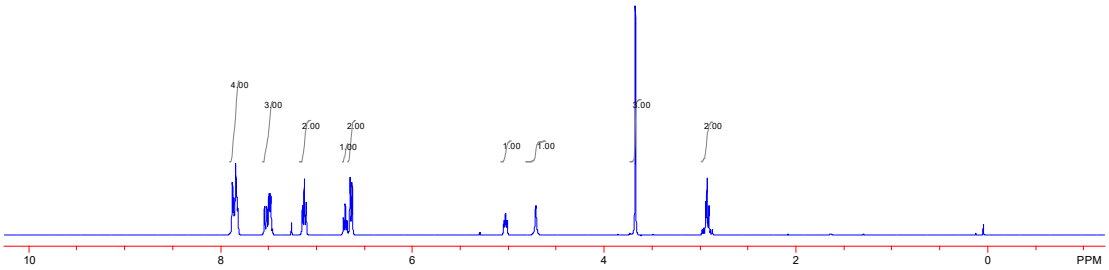


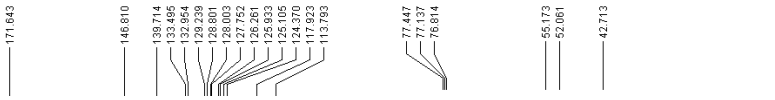


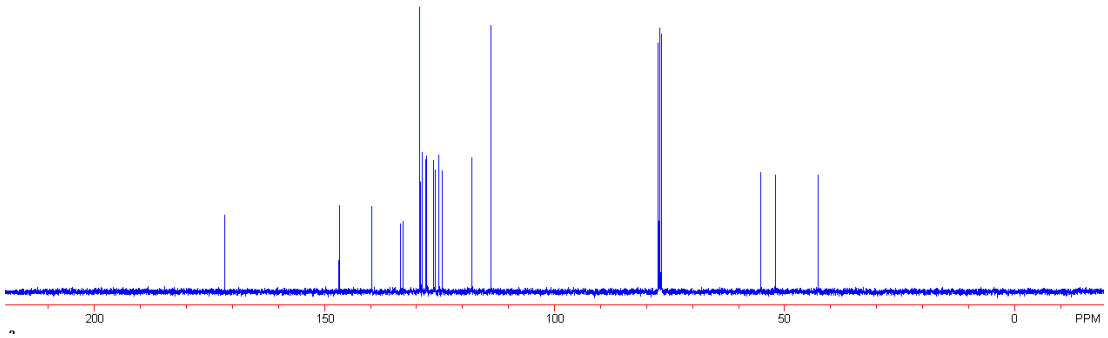


(+)-Methyl 3-(naphthalen-2-yl)-3-(phenylamino)propanoate (4a)

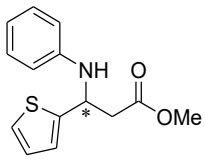


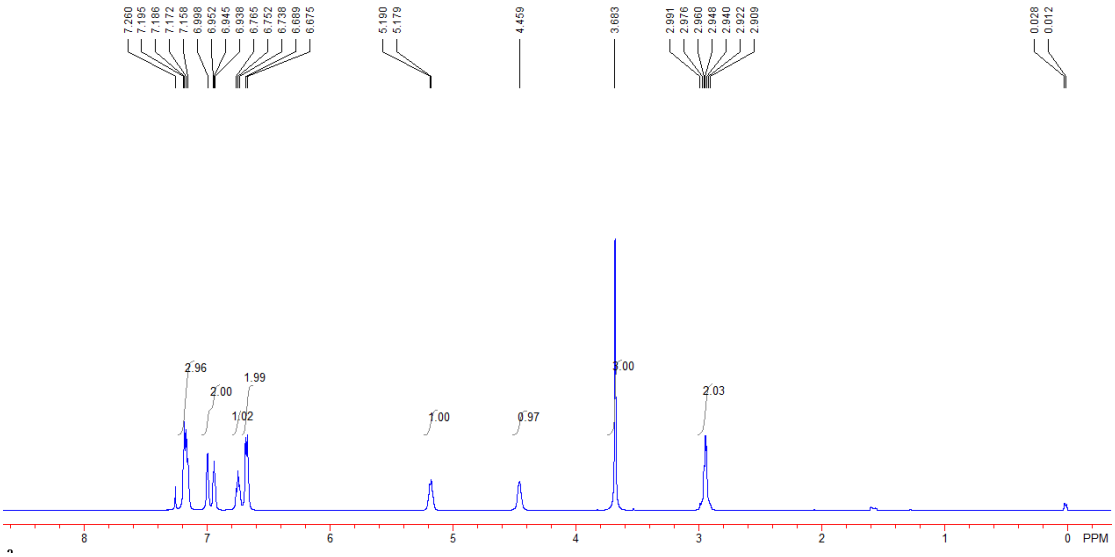


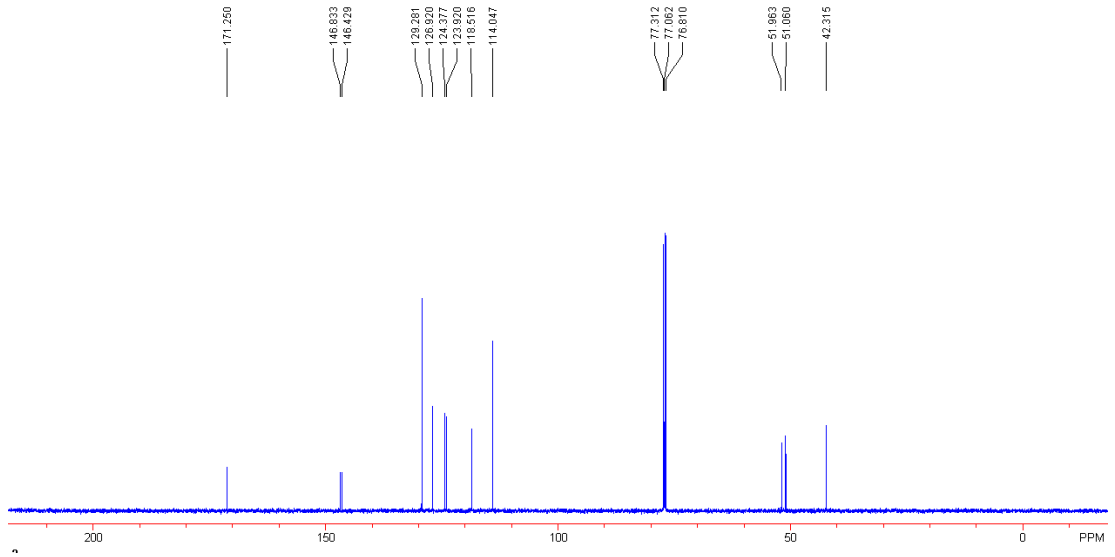




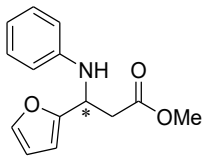
(–)-Methyl 3-(phenylamino)-3-(thiophen-2-yl)propanoate (4b)

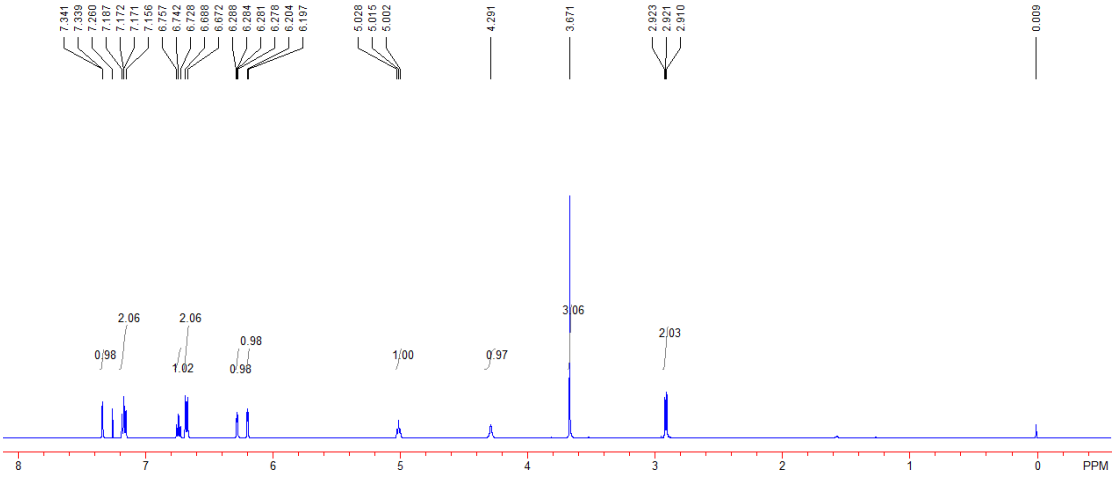


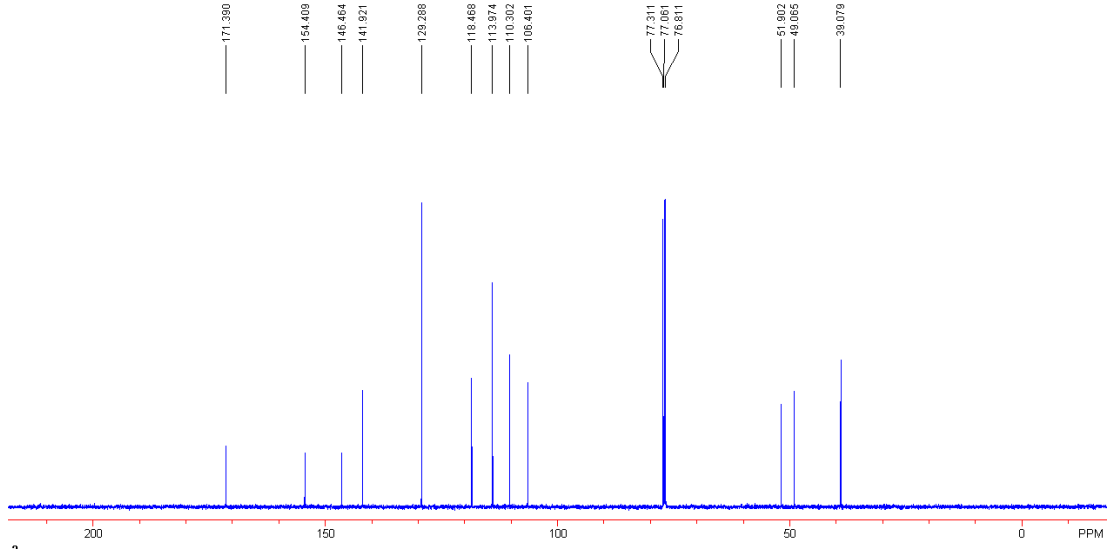




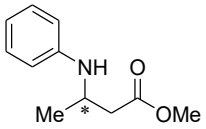
(–)-Methyl 3-(furan-2-yl)-3-(phenylamino)propanoate (4c)

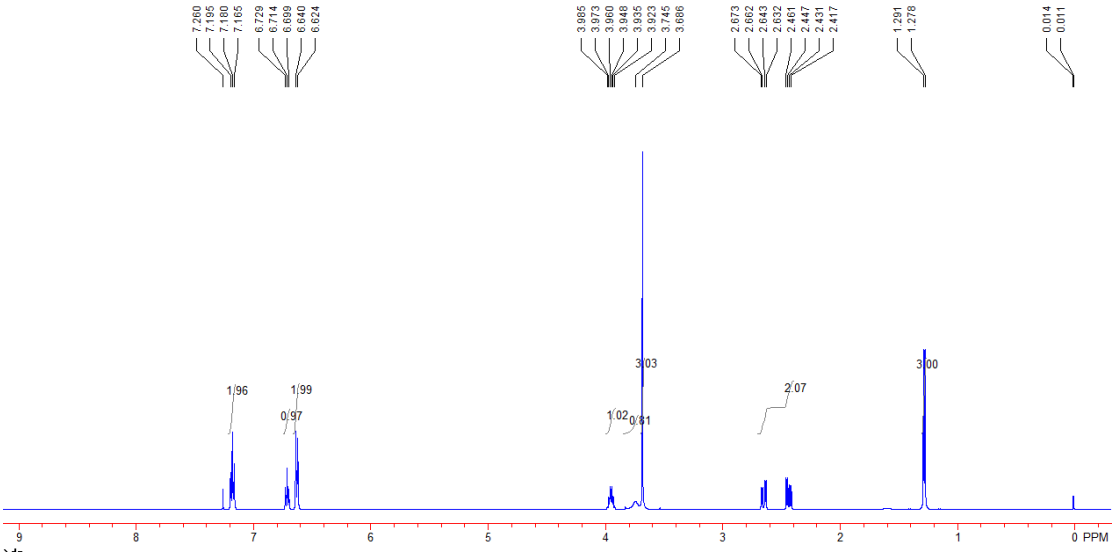


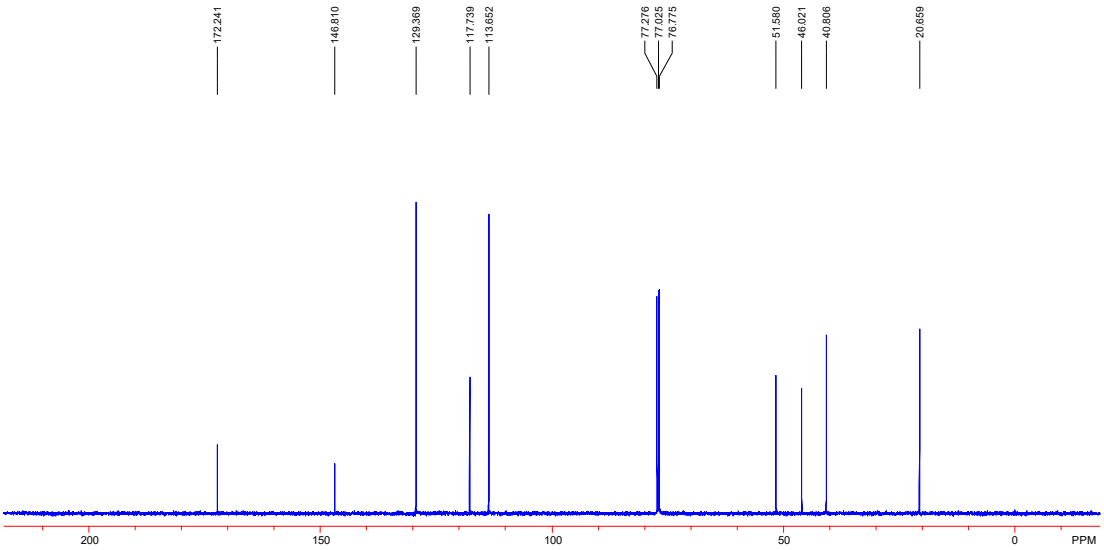




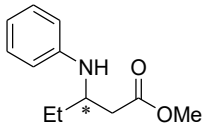
(–)-Methyl 3-(phenylamino)butanoate (4d)

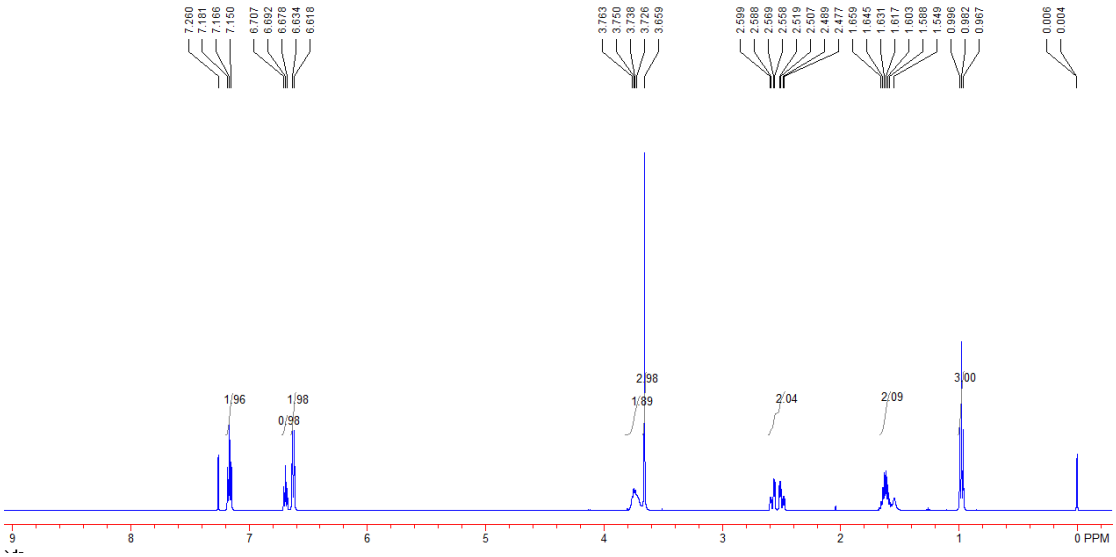


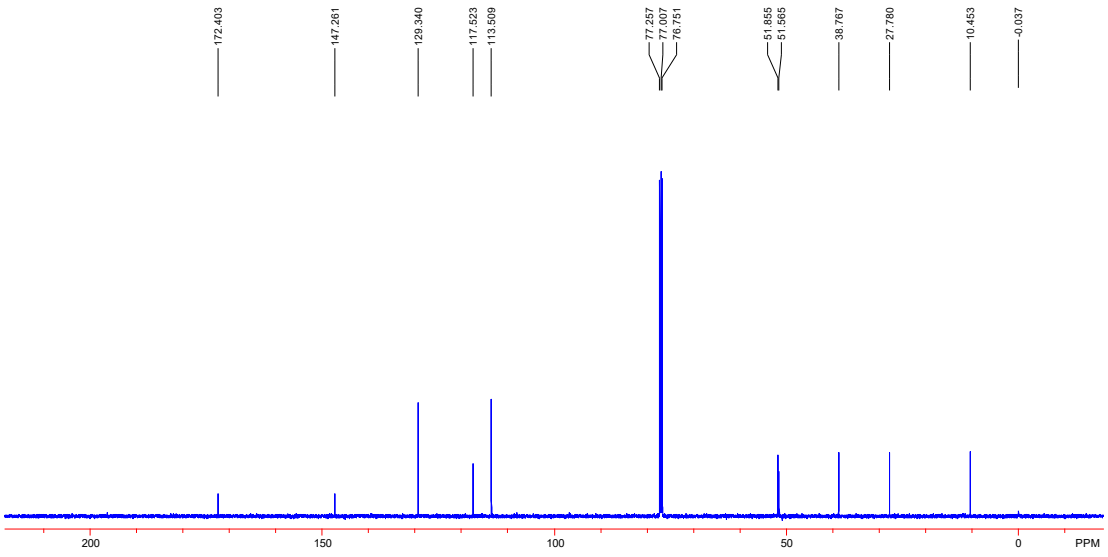




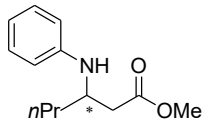
(+)-Methyl 3-(phenylamino)pentanoate (4e)

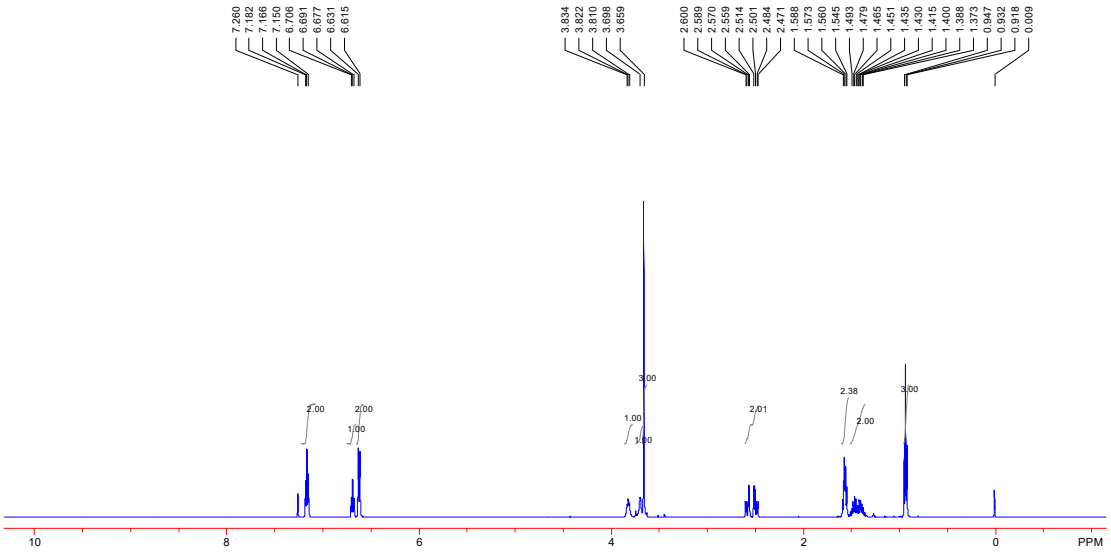


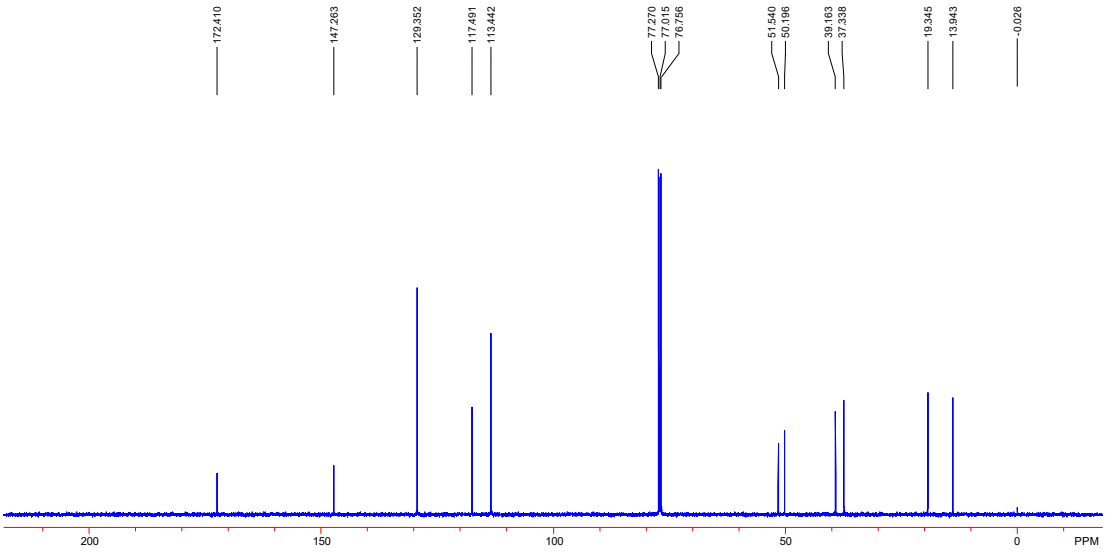




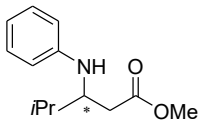
(–)-Methyl 3-(phenylamino)hexanoate (4f)

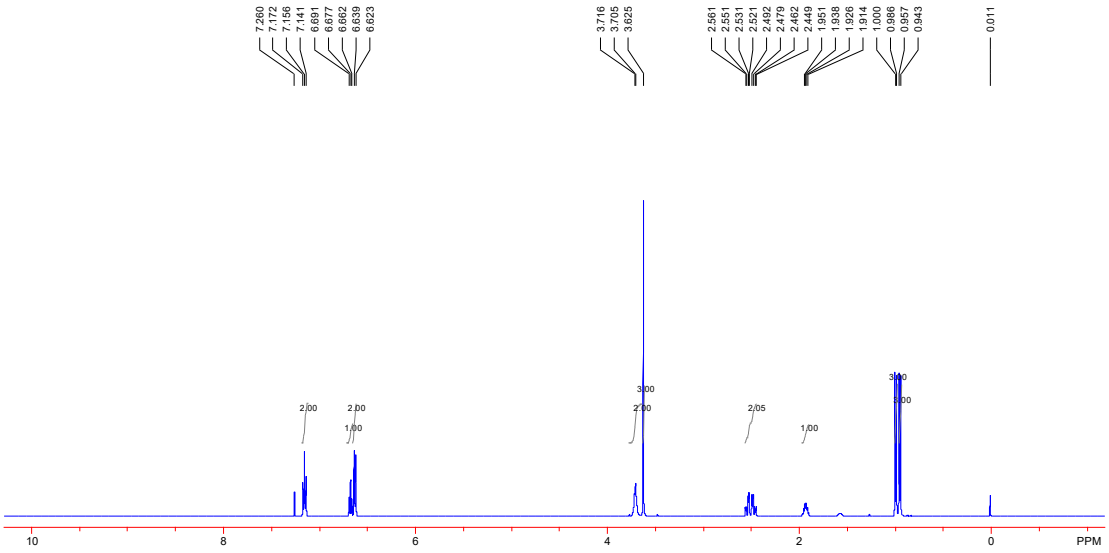


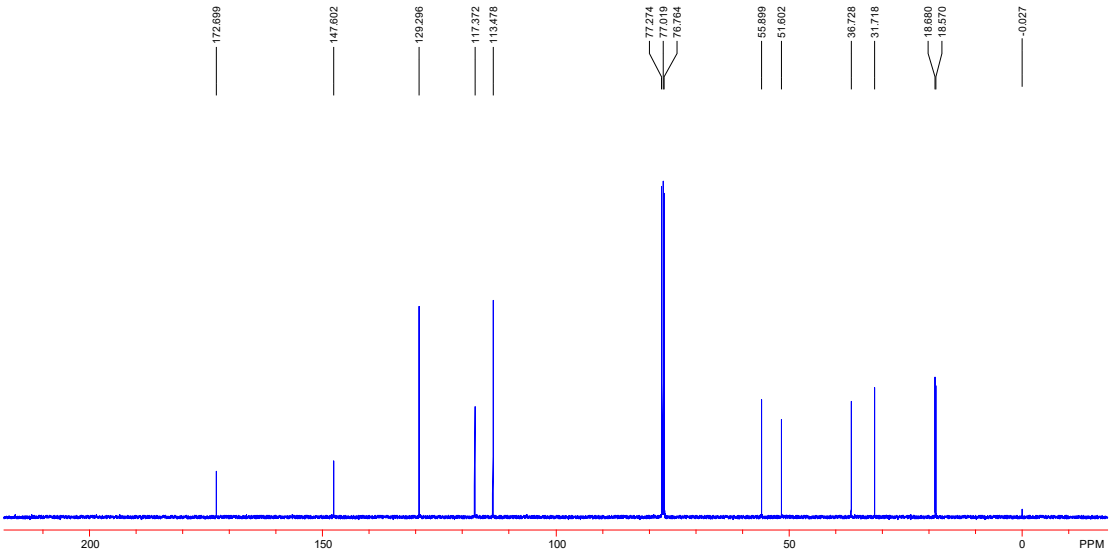




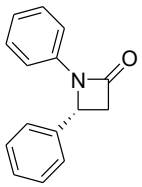
(–)-Methyl 4-methyl-3-(phenylamino)pentanoate (4g)

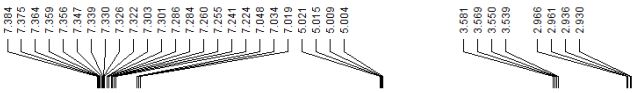


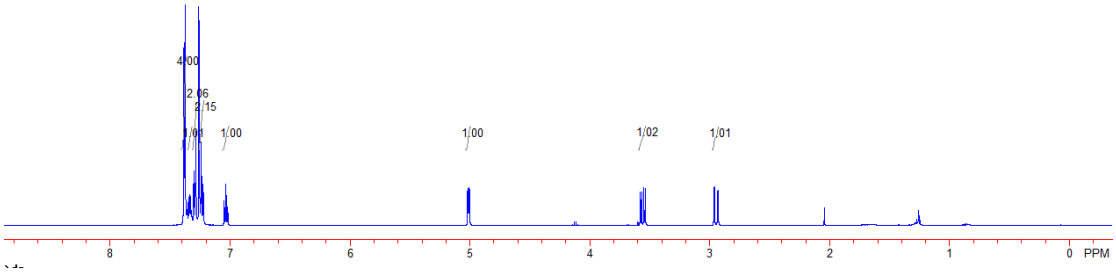


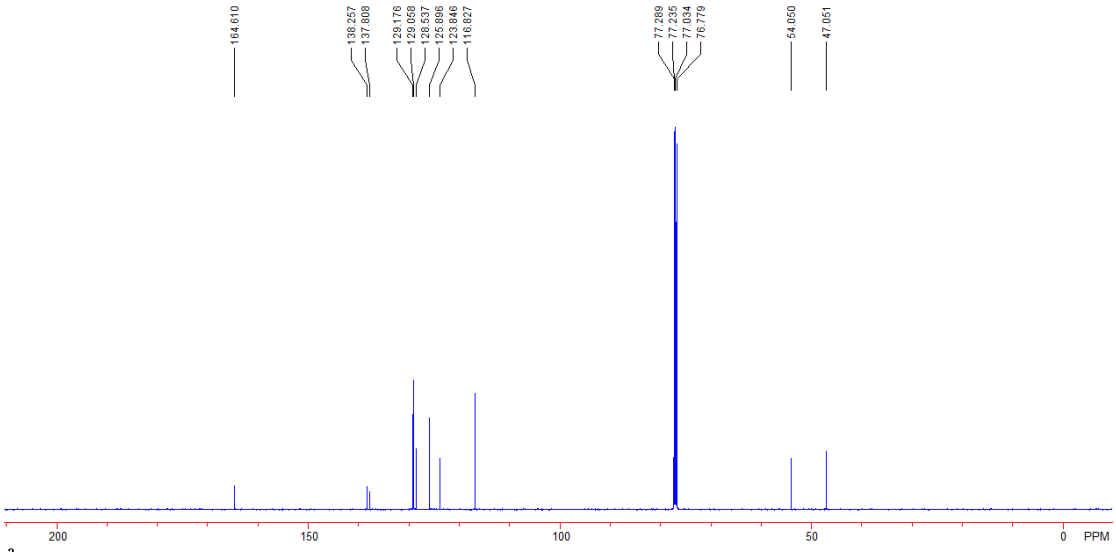


(*R*)-1,4-Diphenylazetidin-2-one (5)









(*R*)-Methyl 3-amino-3-(*p*-tolyl)propanoate (6)