Supporting Information

Highly Stereoselective Modifications of Peptides *via* Pd-catalyzed Allylic Alkylation

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Analytical data of compounds 1–19

***N*-Trifluoroacetylglycyl-(*S*)-prolinanilide (1a)**. $[\alpha]_D^{20}$ = –68.7° (c = 0.5, $CHCl_3$). M.p. 142–143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (bs, 1 H), 7.67 (bs, 1 H), 7.47 (d, *J* = 7.6 Hz, 2 H), 7.28 (t, *J* = 7.6 Hz, 2 H), 7.07 (t, *J* = 7.6 Hz, 1 H), 4.62 (dd, *J* = 8.0, 2.4 Hz, 1 H), 4.16 (dd, *J* = 17.6, 5.2 Hz, 1 H), 3.97 (dd, *J* = 17.6, 4.0 Hz, 1 H), 3.50 (m, 1 H), 3.39 (m, 1 H), 2.36 (m, 1 H), 2.20 (m, 1 H), 2.06–1.94 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 166.7, 157.2 (q, $^2J_{C,F}$ = 37.4 Hz), 137.6, 128.8, 124.4, 119.9, 115.6 (q, $^1J_{C,F}$ = 285.4 Hz), 61.2, 46.5, 41.8, 27.8, 24.7. HRMS (CI) *m/z* calcd for $C_{15}H_{17}F_3N_3O_3$ $[M+H]^+$ 344.1222; found 344.1193. $C_{15}H_{16}F_3N_3O_3$ (343.31) calcd C 52.48, H 4.70, N 12.24; found: C 52.83, H 4.90, N 12.01.

***N*-Benzyloxycarbonylglycyl-(*S*)-prolinanilide (1b)**. $[\alpha]_D^{20}$ = –147.3° (c = 1.0, $CHCl_3$). M.p. 137–139 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.22 (bs, 1 H), 7.48 (d, *J* = 8.0 Hz, 2 H), 7.34–7.29 (m, 5 H), 7.24 (t, *J* = 8.0 Hz, 2 H), 7.04 (t, *J* = 8.0 Hz, 1 H), 5.83 (bs, 1 H), 5.18 (d, *J* = 12.4 Hz, 1 H), 5.08 (d, *J* = 12.4 Hz, 1 H), 4.69 (d, *J* = 7.6 Hz, 1 H), 4.05 (dd, *J* = 17.2, 5.2 Hz, 1 H), 3.95 (dd, *J* = 17.2, 7.6 Hz, 1 H), 2.44 (m, 1 H), 2.20 (m, 1 H), 2.01 (m, 1 H), 1.87 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 168.6, 156.3, 138.0, 136.2, 128.7, 128.4, 128.1, 127.9, 123.9, 119.7, 66.9, 61.0, 46.4, 43.4, 27.1, 24.8. HRMS (CI) *m/z* calcd for $C_{21}H_{24}N_3O_4$ $[M+H]^+$ 382.1767; found: 382.1790. $C_{21}H_{23}N_3O_4$ (381.43) calcd C 66.13, H 6.08, N 11.02; found C 66.14, H 5.96, N 10.88.

***N*-Trifluoroacetyl-(*R*/*S*)-alanyl-(*S*)-prolinanilide (2a)**. According to a slightly modified procedure for palladium-catalyzed allylic alkylations of dipeptides **2a** was obtained from **1a** (100 mg, 0.270 mmol) and MeI (25 μL, 0.404 mmol) in 90% yield (87.0 mg, 0.243 mmol). Major diastereomer (57%): $[\alpha]_D^{20}$ = –99.6° (c = 1.0, $CHCl_3$). M.p. 197–198 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (bs, 1 H), 7.46 (d, *J* = 7.6 Hz, 2 H), 7.43 (bs, 1 H), 7.28 (t, *J* = 7.6 Hz, 2 H), 7.08 (t, *J* = 7.6 Hz, 1 H), 4.80–4.73 (m, 2 H), 3.69–3.58 (m, 2 H), 2.50 (m, 1 H), 2.24 (m, 1 H), 2.09 (m, 1 H), 1.97 (m, 1 H), 1.46 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 168.1, 156.3 (q, $^2J_{C,F}$ = 37.3 Hz), 137.8, 128.9, 124.3, 119.7, 115.6 (q, $^1J_{C,F}$ = 285.7 Hz), 61.0, 47.4, 47.4, 26.8, 25.1, 17.9. HRMS (CI) *m/z* calcd for $C_{16}H_{19}F_3N_3O_3$ $[M+H]^+$ 358.1379; found: 358.1334. Minor diastereomer (43%): $[\alpha]_D^{20}$ = –42.5° (c = 0.5, $CHCl_3$). M.p. 186–188 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (bs, 1 H), 7.54 (d, *J* = 7.6 Hz, 2 H), 7.41 (d, *J* = 7.6 Hz, 1 H), 7.32 (t, *J* = 7.6 Hz, 2 H), 7.11 (t, *J* = 7.6 Hz, 1 H), 4.76–4.71 (m, 2 H), 3.83 (td, *J* = 8.8, 2.8 Hz, 1 H), 3.55 (m, 1 H), 2.57 (m, 1 H), 2.26 (m, 1 H), 2.11 (m, 1 H), 2.00 (m, 1 H), 1.49 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0, 168.1, 156.6 (q, $^2J_{C,F}$ = 37.7 Hz), 137.8, 128.9, 124.3, 119.8, 115.6 (q, $^1J_{C,F}$ = 285.7 Hz), 61.4, 48.0, 47.3, 27.6, 24.6, 17.1. HRMS (CI) *m/z* calcd for $C_{16}H_{19}F_3N_3O_3$ $[M+H]^+$ 358.1379; found: 358.1314. HPLC (silica, hexane/EtOAc 60:40, 1 mL/min, 254 nm): t_R (57%) = 9.42 min, t_R (43%) = 29.79 min.

***N*-Trifluoroacetyl-(*S*)-phenylalanyl-glycyl-(*S*)-prolinanilide (3)**. $[\alpha]_D^{20}$ = –71.6° (c = 1.0, CH_3OH). M.p. 239–240 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.6 Hz, 2 H), 7.28–7.20 (m, 6 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 7.06 (t, *J* = 7.6 Hz, 1 H), 4.80 (td, *J* = 7.8, 1.6 Hz, 1 H), 4.63 (dd, *J* = 8.0, 2.4 Hz, 1 H), 4.05 (d, *J* = 17.2 Hz, 1 H), 3.95 (d, *J* = 17.2 Hz, 1 H), 3.63 (m, 1 H), 3.17 (m, 1 H), 3.16 (dd, *J* = 14.0, 6.4 Hz, 1 H), 3.00 (dd, *J* = 14.0, 7.6 Hz, 1 H), 2.34 (m, 1 H), 2.16 (m, 1 H), 2.06–1.98 (m, 2 H). ^{13}C NMR (125 MHz, DMSO-d_6, 353 K): δ 169.8, 169.2, 166.5, 155.7 (q, $^2J_{C,F}$ = 36.4 Hz), 138.5, 136.9, 128.6, 128.1, 127.6, 125.9, 122.9, 119.3, 115.3 (q, $^1J_{C,F}$ = 286.8 Hz), 60.1, 54.3, 45.8, 41.2, 37.8, 36.4, 28.7, 23.9. HRMS (CI) *m/z* calcd for $C_{24}H_{26}F_3N_4O_4$ $[M+H]^+$ 491.1906; found 491.1840.

***N*-Trifluoroacetyl-(*S*)-leucyl-glycyl-(*S*)-prolinanilide (4)**. $[\alpha]_D^{20}$ = –120.1° (c = 1.0, $CHCl_3$). M.p. 103–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (bs, 1 H), 7.73 (bs, 1 H), 7.48 (bs, 1 H), 7.50 (d, *J* = 8.0 Hz, 2 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 7.07 (t, *J* = 7.6 Hz, 1 H), 4.76 (bs, 1 H), 4.66 (d, *J* = 7.0 Hz, 1 H), 4.09 (m, 1 H), 3.94 (d, *J* = 16.0 Hz, 1 H), 3.66–3.62 (m, 1 H), 3.36 (m, 1 H), 2.30–2.14 (m, 2 H), 2.04–1.99 (m, 2 H), 1.66–1.56 (m, 2 H), 1.26 (m, 1 H), 0.87 (d, *J* = 6.0 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 169.1, 168.3, 137.9, 128.8, 124.3, 119.7, 115.7 (q, $^1J_{C,F}$ = 285.8 Hz), 61.2, 52.0, 46.8, 41.9, 41.6, 28.4, 24.7, 24.6, 22.8, 21.7. HRMS (CI) *m/z* calcd for $C_{21}H_{28}F_3N_4O_4$ $[M+H]^+$ 457.2063; found 457.2058.

***N*-Trifluoroacetyl-(*S*)-*tert.*-leucyl-glycyl-(*S*)-prolinanilide (5)**. $[\alpha]_D^{20}$ = –87.8° (c = 1.0, $CHCl_3$). M.p. 228–230 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (bs, 1 H), 7.49 (d, *J* = 8.0 Hz, 2 H), 7.48 (bs, 1 H), 7.27 (t, *J* = 8.0 Hz, 2 H), 7.22 (bs, 1 H), 7.06 (t, *J* = 7.6 Hz, 1 H), 4.80 (d, *J* = 7.6 Hz, 1 H), 4.55 (d, *J* = 8.0 Hz, 1 H), 4.16 (m, 1 H), 4.01 (dd, *J* = 18.0, 2.8 Hz, 1 H) 3.62 (t, *J* = 7.2 Hz, 1 H), 3.42 (m, 1 H), 2.38 (m, 1 H), 2.22 (m, 1 H), 2.04–1.94 (m, 2 H), 0.99 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 168.8, 167.8, 157.2 (q, $^2J_{C,F}$ = 35.4 Hz), 137.9, 128.8, 124.2, 119.7, 115.8 (q, $^1J_{C,F}$ = 286.0 Hz), 60.9, 60.7, 46.7, 42.2, 35.3, 28.1, 26.4, 24.6. HRMS (CI) *m/z* calcd for $C_{21}H_{28}F_3N_4O_4$ $[M+H]^+$ 457.2063; found 457.2056.

***N*-Trifluoroacetyl-(*S*)-(4-methoxy)-phenylalanyl-glycyl-(*S*)-prolinanilide (6)**. $[\alpha]_D^{20}$ = –41.5° (c = 1.0, CH_3OH). M.p. 253–255 °C. ^{1}H NMR (400 MHz, CD_3OD): δ 7.55 (d, *J* = 8.4 Hz, 2 H), 7.29 (t, *J* = 8.4 Hz, 2 H), 7.14 (d, *J* = 7.2 Hz, 2 H), 7.09 (t, *J* = 7.2 Hz, 1 H), 6.80 (d, *J* = 7.2 Hz, 2 H), 4.73 (dd, *J* = 10.0, 5.2 Hz, 1 H), 4.55 (dd, *J* = 8.4, 4.0 Hz, 1 H), 4.13 (d, *J* = 16.8 Hz, 1 H), 4.04 (d, *J* = 16.8 Hz, 1 H), 3.73 (s, 3 H), 3.70–3.58 (m, 2 H), 3.21 (dd, *J* = 14.0, 5.2 Hz, 1 H), 2.90 (dd, *J* = 14.0, 10.0 Hz, 1 H), 3.62 (t, *J* = 7.2 Hz, 1 H), 2.26 (m, 1 H), 2.13–2.02 (m, 3 H). ^{13}C NMR (100 MHz, CD_3OD): δ 172.8, 172.6, 169.5, 158.7 (q, $^2J_{C,F}$ = 37.0 Hz), 139.5, 131.3, 129.9, 129.8, 125.4, 121.5, 117.3 (q, $^1J_{C,F}$ = 285.7 Hz), 114.9, 62.5, 56.4, 55.6, 47.9, 43.0, 37.6, 33.5, 30.8, 25.8. HRMS (CI) *m/z* calcd for $C_{25}H_{28}F_3N_4O_5$ $[M+H]^+$ 521.2012. found 521.1971.

***N*-Trifluoroacetyl-(*S*)-phenylalanyl-(*R*)-(2-phenylallyl)-glycyl-(*S*)-prolinanilide (7b)**. According to the general procedure for palladium-catalyzed allylic alkylations of tripeptides **7b** was obtained from **3** (100 mg, 0.204 mmol) in 73% yield (90.4 mg, 0.148 mmol). Major diastereomer (88%): $[\alpha]_D^{20}$ = –76.5° (c = 1.0, $CHCl_3$). M.p. 82–84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 1 H), 7.50 (d, *J* = 7.6 Hz, 2 H), 7.42–7.33 (m, 6 H), 7.24–7.20 (m, 5 H), 7.13 (m, 1 H), 7.08–7.02 (m, 3 H), 5.42 (s, 1 H), 5.13 (s, 1 H), 4.79 (m, 1 H), 4.51 (m, 1 H), 4.47 (dd, *J* = 8.0, 2.4 Hz, 1 H), 3.62 (m, 1 H), 3.13 (m, 1 H), 3.08 (dd, *J* = 14.0, 6.8 Hz, 1 H), 3.00 (dd, *J* = 14.0, 6.4 Hz, 1 H), 2.91 (dd, *J* = 14.0, 8.0 Hz, 1 H), 2.76 (dd, *J* = 14.0, 6.8 Hz, 1 H), 2.27 (m, 1 H), 1.96–1.77 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 169.7, 169.0, 156.6 (q, $^2J_{C,F}$ = 37.4 Hz), 142.4, 138.9, 137.7, 135.1, 129.2, 128.7, 128.7, 128.6, 128.3, 127.3, 125.8, 124.2, 120.0, 116.8, 115.5 (q, $^1J_{C,F}$ = 286.8 Hz), 61.2, 54.2, 51.0, 47.1, 38.3, 37.2, 28.7, 24.1. HRMS (CI) *m/z* calcd for $C_{33}H_{34}F_3N_4O_4$ $[M+H]^+$ 607.2532; found 607.2562. Minor diastereomer (12%): $[\alpha]_D^{20}$ = –28.7° (c = 1.0, $CHCl_3$). M.p. 100–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (s, 1 H), 7.54 (d, *J* = 7.2 Hz, 2 H), 7.43 (bs, 1 H), 7.30–7.25 (m, 7 H), 7.21–7.20 (m, 3 H), 7.15–7.02 (m, 4 H), 4.94 (s, 1 H), 4.94 (s, 1 H), 4.89 (s, 1 H), 4.87–4.79 (m, 2 H), 4.68 (dd, *J* = 8.0, 3.2 Hz, 1 H), 3.52 (m, 1 H), 3.25 (m, 1 H), 3.02 (dd, *J* = 14.0, 6.0 Hz, 1 H), 2.98 (dd, *J* = 13.6, 6.0 Hz, 1 H), 2.90 (dd, *J* = 13.6, 7.2 Hz, 1 H), 2.79 (dd, *J* = 14.0, 8.0 Hz, 1 H), 2.36 (m, 1 H), 2.13 (m, 1 H), 2.01–1.91 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 168.7, 168.6, 142.3, 139.6, 138.2, 135.2, 129.1, 128.9, 128.6, 128.5, 127.9, 127.4, 126.1, 124.1, 119.5, 117.3, 60.7, 54.0, 49.8, 47.6, 39.1, 39.0, 27.7, 24.9. HRMS

(CI) *m/z* calcd for $C_{33}H_{34}F_3N_4O_4$ $[M+H]^+$ 607.2532; found 607.2530. HPLC (silica, silica, hexane/EtOAc = 50:50, 1 mL/min, 254 nm): t_R (12%) = 6.49 min, t_R (88%) = 10.29 min.

***N*-Trifluoroacetyl-(*S*)-phenylalanyl-(*R*)-[2(*E*)-hexenyl]-glycyl-(*S*)-prolinanilide (7e$_l$)**. According to the general procedure for palladium-catalyzed allylic alkylations of tripeptides **7e$_l$** was obtained as major regioisomer from **3** (200 mg, 0.409 mmol) in 65% yield (152.1 mg, 0.266 mmol). Major diastereomer (90%): $[\alpha]_D^{20}$ = –72.9° (c = 0.5, $CHCl_3$). M.p. 74–78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 1 H), 7.53 (d, *J* = 7.6 Hz, 2 H), 7.37 (d, *J* = 7.6 Hz, 1 H), 7.28–7.23 (m, 5 H), 7.13 (dd, *J* = 7.6, 1.6 Hz, 2 H), 7.05 (t, *J* = 7.6 Hz, 1 H), 7.00 (d, *J* = 6.0 Hz, 1 H), 5.53 (dt, *J* = 15.2, 6.8 Hz, 1 H), 5.25 (dt, *J* = 15.2, 7.2 Hz, 1 H), 4.84 (m, 1 H), 4.69 (dd, *J* = 8.0, 1.9 Hz, 1 H), 4.55 (m, 1 H), 3.87 (td, *J* = 8.8, 2.4 Hz, 1 H), 3.54 (m, 1 H), 3.08 (dd, *J* = 13.6, 6.8 Hz, 1 H), 3.04 (dd, *J* = 13.6, 6.8 Hz, 1 H), 2.44–2.23 (m, 3 H), 2.13 (m, 1 H), 2.05–1.93 (m, 4 H), 1.39–1.30 (m, 2 H), 0.88 (t, *J* = 7.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 169.4, 168.8, 156.6 (q, $^2J_{C,F}$ = 37.6 Hz), 137.8, 136.0, 135.2, 129.1, 128.7, 128.6, 127.4, 124.2, 122.8, 119.9, 115.5 (q, $^1J_{C,F}$ = 285.9 Hz), 61.2, 54.3, 51.6, 47.4, 38.6, 34.8, 34.5, 28.7, 24.3, 22.3, 13.6. HRMS (CI) *m/z* calcd for $C_{30}H_{36}F_3N_4O_4$ $[M+H]^+$ 573.2689; found 573.2604. $C_{30}H_{35}F_3N_4O_4$ (572.62) calcd C 62.93, H 6.16, N 9.48; found C 62.67, H 6.49, N 9.42. Minor diastereomer (10%): $[\alpha]_D^{20}$ = –33.1° (c = 0.5, $CHCl_3$). M.p. 80–83 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.05 (s, 1 H), 7.48 (d, *J* = 7.5 Hz, 2 H), 7.46 (bs, 1 H), 7.30–7.26 (m, 5 H), 7.16 (dd, *J* = 8.0, 1.4 Hz, 2 H), 7.06 (t, *J* = 7.5 Hz, 1 H), 6.72 (bs, 1 H), 5.35 (dt, *J* = 15.5, 7.0 Hz, 1 H), 5.17 (dt, *J* = 15.5, 7.5 Hz, 1 H), 4.79–4.75 (m, 2 H), 4.68 (m, 1 H), 3.68–3.62 (m, 2 H), 3.07 (d, *J* = 7.0 Hz, 2 H), 2.52 (m, 1 H), 2.43 (m, 1 H), 2.29 (m, 1 H), 2.20 (m, 1 H), 2.08 (m, 1 H), 1.94 (m, 1 H), 1.73–1.69 (m, 2 H), 1.15–1.08 (m, 2 H), 0.72 (t, *J* = 5.7 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.4, 168.4, 168.3, 138.1, 136.3, 135.1, 129.3, 128.9, 128.7, 127.5, 124.1, 122.2, 119.5, 60.7, 54.3, 50.9, 47.7, 38.7, 35.8, 34.3, 29.6, 25.1, 22.1, 13.5. HRMS (CI) *m/z* calcd for $C_{30}H_{36}F_3N_4O_4$ $[M+H]^+$ 573.2689; found 573.2665. $C_{30}H_{35}F_3N_4O_4$ (572.62) calcd C 62.93, H 6.16, N 9.48; found C 62.30, H 6.24, N 9.24. HPLC (silica, hexane/EtOAc = 70:30, 1 mL/min, 254 nm): t_R (10%) = 36.75 min, t_R (90%) = 41.72 min.

***N*-Trifluoroacetyl-(*S*)-phenylalanyl-(*R*)-(1-propylallyl)-glycyl-(*S*)-prolinanilide (7e$_b$)**. According to the general procedure for palladium-catalyzed allylic alkylations of tripeptides **7g$_b$** was obtained as minor regioisomer from **3** (200 mg, 0.409 mmol) in 10% yield (23.3 mg, 0.041 mmol). $[\alpha]_D^{20}$ = –67.0° (c = 0.5, $CHCl_3$). M.p. 70–72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (s, 1 H), 7.50 (d, *J* = 7.6 Hz, 2 H), 7.33–7.24 (m, 5 H), 7.18 (d, *J* = 7.8 Hz, 2 H), 7.16 (bs, 1 H), 7.05 (t, *J* = 7.6 Hz, 1 H), 6.53 (d, *J* = 6.9 Hz, 1 H), 5.54 (m, 1 H), 5.10 (dd, *J* = 10.4, 1.6 Hz, 1 H), 4.99 (dd, *J* = 16.8, 1.6 Hz, 1 H), 4.72 (m, 1 H), 4.64 (dd, *J* = 8.0, 1.3 Hz, 1 H), 4.44 (dd, *J* = 7.6, 6.9 Hz, 1 H), 3.91 (td, *J* = 9.0, 2.8 Hz, 1 H), 3.56 (m, 1 H), 3.13 (dd, *J* = 13.6, 6.0 Hz, 1 H), 3.02 (dd, *J* = 13.6, 8.0 Hz, 1 H), 2.46 (m, 1 H), 2.22 (m, 1 H), 2.10 (m, 1 H), 2.02 (m, 1 H), 1.91 (m, 1 H), 1.38–1.19 (m, 4 H), 0.85 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 169.6, 168.7, 156.6 (q, $^2J_{C,F}$ = 37.5 Hz), 137.8, 136.5, 135.3, 129.1, 128.9, 128.8, 127.5, 124.3, 119.9, 118.9, 115.4 (q, $^1J_{C,F}$ = 287.5 Hz), 61.2, 54.8, 54.7, 47.6, 46.4, 38.5, 31.8, 28.4, 24.4, 19.9, 13.7. HRMS (CI) *m/z* calcd for $C_{30}H_{36}F_3N_4O_4$ $[M+H]^+$ 573.2689; found 573.2594. $C_{30}H_{35}F_3N_4O_4$ (572.62) calcd C 62.93, H 6.16, N 9.48; found C 62.83, H 6.14, N 9.49.

***N*-Trifluoroacetyl-(*S*)-phenylalanyl-(*R*)-[(*E*)-3-phenylallyl]-glycyl-(*S*)-prolinanilide (7f$_l$)**. According to the general procedure for palladium-catalyzed allylic alkylations of tripeptides **7f$_l$** was obtained from **3** (200 mg, 0.409 mmol) as the major regioisomer in 82% yield (196.7 mg, 0.335 mmol). Major diastereomer (92%): $[\alpha]_D^{20}$ = –72.0° (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (s, 1 H), 7.51 (d, *J* = 7.6 Hz, 2 H), 7.31–7.03 (m, 15 H), 6.41 (d, *J* = 16.0 Hz, 1 H), 6.02 (m, 1 H), 4.82 (m, 1 H), 4.73–4.68 (m, 2 H), 3.84 (m, 1 H), 3.54 (m, 1 H), 3.04 (d, *J* = 6.8 Hz, 2 H), 2.56–2.42 (m, 2 H), 2.34

(m, 1 H), 2.12 (m, 1 H), 1.96–1.86 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 169.4, 168.7, 156.6 (q, $^2J_{C,F}$ = 37.4 Hz), 137.8, 136.6, 135.2, 134.5, 129.2, 128.8, 128.7, 128.6, 127.9, 127.4, 126.1, 124.2, 12.6, 119.9, 115.5 (q, $^1J_{C,F}$ = 287.0 Hz), 61.3, 54.3, 51.6, 47.5, 38.7, 35.5, 28.5, 20.4. Minor diastereomer (8%, selected peaks): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (s, 1 H), 7.47 (d, *J* = 7.6 Hz, 2 H), 6.29 (d, *J* = 16.0 Hz, 1 H), 5.08 (m, 1 H), 4.90 (m, 1 H), 3.72–3.65 (m, 2 H), 2.99–2.89 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 169.0, 168.8, 138.0, 136.5, 135.2, 134.3, 129.1, 128.9, 128.5, 128.4, 126.2, 124.1, 122.5, 119.9, 60.9, 54.3, 50.9, 47.8, 38.9, 36.3, 27.6, 25.1. HRMS (CI) *m/z* calcd for $C_{33}H_{34}F_3N_4O_4$ $[M+H]^+$ 607.2532; found 607.2577. $C_{30}H_{33}F_3N_4O_4$ (570.61) calcd C 65.34, H 5.48, N 9.24; found C 64.78, H 5.80, N 8.94. HPLC (Reprosil, hexane/isopropanol = 90:10, 2 mL/min, 254 nm): t_R (8%) = 21.84 min, t_R (92%) = 30.75 min.

N*-Trifluoroacetyl-(*S*)-phenylalanyl-(*R*)-(1-phenylallyl)-glycyl-(*S*)-prolinanilide (7f*b*)**. According to the general procedure for palladium-catalyzed allylic alkylations of tripeptides **7f*b was obtained from **3** (200 mg, 0.409 mmol) as the minor regioisomer in 3.5% yield (8.0 mg, 0.014 mmol). $[\alpha]_D^{20}$ = –20.0° (c = 0.3, $CHCl_3$). M.p. 100–102 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.15 (s, 1 H), 7.49 (d, *J* = 7.5 Hz, 2 H), 7.34–7.29 (m, 6 H), 7.20 (dd, *J* = 8.0, 1.5 Hz, 2 H), 7.12 (t, *J* = 7.5 Hz, 1 H), 7.05–7.03 (m, 3 H), 6.89 (t, *J* = 8.0 Hz, 2 H), 6.19 (d, *J* = 7.5 Hz, 1 H), 5.98 (m, 1 H), 5.10 (dd, *J* = 10.0, 1.2 Hz, 1 H), 5.07 (dd, *J* = 16.4, 1.2 Hz, 1 H), 4.80 (dd, *J* = 10.3, 7.5 Hz, 1 H), 4.70–4.67 (m, 1 H) 4.65 (dd, *J* = 7.8, 1.9 Hz, 1 H), 3.58 (dd, *J* = 10.3, 9.7 Hz, 1 H), 3.49 (m, 1 H), 3.14 (dd, *J* = 13.6, 6.0 Hz, 1 H), 3.10 (dd, *J* = 13.6, 7.6 Hz, 1 H), 2.82 (m, 1 H), 2.46 (m, 1 H), 1.87–1.67 (m, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.9, 168.5, 167.2, 138.2, 137.9, 135.8, 135.0, 129.4, 128.9, 128.8, 128.7, 127.8, 127.7, 127.6, 124.0, 119.9, 118.9, 60.5, 54.8, 54.4, 53.5, 47.5, 38.1, 25.9, 24.8. HRMS (CI) *m/z* calcd for $C_{33}H_{34}F_3N_4O_4$ $[M+H]^+$ 607.2532; found 607.2533.

N*-Trifluoroacetyl-(*S*)-phenylalanyl-(*R*)-[(4-*tert*.-butyldimethylsilyloxy)-2(*E*)-butenyl]-glycyl-(*S*)-prolinanilide (7g*l*)**. According to the general procedure for palladium-catalyzed allylic alkylations of tripeptides **7g*l was obtained as major regioisomer from **3** (200 mg, 0.409 mmol) in 65% yield (179 mg, 0.266 mmol). Major diastereomer (97%): $[\alpha]_D^{20}$ = –70.0° (c = 0.5, $CHCl_3$). M.p. 67–68 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (s, 1 H), 7.51 (d, *J* = 7.6 Hz, 2 H), 7.31–7.23 (m, 6 H), 7.14 (dd, *J* = 7.8, 1.5 Hz, 2 H), 7.05 (t, *J* = 7.6 Hz, 1 H), 6.70 (d, *J* = 6.4 Hz, 1 H), 5.63 (dt, *J* = 15.2, 4.6 Hz, 1 H), 5.51 (dt, *J* = 15.2, 7.2 Hz, 1 H), 4.76 (m, 1 H), 4.66 (dd, *J* = 7.8, 2.0 Hz, 1 H), 4.57 (m, 1 H), 4.12–4.04 (m, 2 H), 3.83 (m, 1 H), 3.54 (m, 1 H), 3.08 (dd, *J* = 13.6, 6.5 Hz, 1 H), 3.04 (dd, *J* = 13.6, 7.5 Hz, 1 H), 2.42 (m, 1 H), 2.37–2.27 (m, 2 H), 2.11 (m, 1 H), 2.01–1.91 (m, 2 H), 0.89 (s, 9 H), 0.06 (s, 3 H), 0.05 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 169.3, 168.7, 156.6 (q, $^2J_{C,F}$ = 37.5 Hz), 137.8, 135.2, 134.6, 129.2, 128.8, 127.5, 124.2, 122.7, 119.9, 115.5 (q, $^1J_{C,F}$ = 285.8 Hz), 62.9, 61.2, 54.4, 51.5, 47.4, 38.6, 34.6, 28.4, 25.8, 24.4, 18.3, –5.3. HRMS (CI) *m/z* calcd for $C_{30}H_{36}F_3N_4O_5Si$ $[M–C_4H_9]^+$ 617.2407; found 617.2382. $C_{34}H_{45}F_3N_4O_5Si$ (674.83) calcd C 60.51, H 6.72, N 8.30; found C 60.37, H 6.64, N 8.62. Minor diastereomer (3%): $[\alpha]_D^{20}$ = –18.0° (c = 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03 (s, 1 H), 7.48 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.31–7.27 (m, 5 H), 7.17 (dd, *J* = 7.6, 1.6 Hz, 2 H), 7.12–7.06 (m, 2 H), 6.48 (d, *J* = 6.4 Hz, 1 H), 5.47–5.45 (m, 2 H), 4.75 (dd, *J* = 8.0, 2.2 Hz, 1 H), 4.74–4.66 (m, 2 H), 3.83–3.81 (m, 2 H), 3.67–3.60 (m, 2 H), 3.10–3.08 (m, 2 H), 2.55 (m, 1 H), 2.46 (m, 1 H), 2.34 (m, 1 H), 2.20 (m, 1 H), 2.07 (m, 1 H), 1.92 (m, 1 H), 0.84 (s, 9 H), 0.03 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 168.3, 167.0, 138.0, 135.1, 134.7, 129.3, 128.9, 128.7, 127.5, 124.1, 122.4, 119.5, 62.7, 60.7, 54.4, 50.8, 47.7, 38.5, 35.5, 26.4, 25.8, 25.1, 21.0, –5.3. HRMS (CI) *m/z* calcd for $C_{33}H_{34}F_3N_4O_4$ $[M+H]^+$ 617.2407; found 617.2388. HPLC (silica, hexane/EtOAc = 60:40, 1 mL/min, 254 nm): t_R (3%) = 14.09 min, t_R (97%) = 16.72 min.

***N*-Trifluoroacetyl-(*S*)-phenylalanyl-(*R*)-[1-(*tert.*-butyldimethylsilyloxymethyl)-allyl]-glycyl-(*S*)-prolinanilide (7g$_b$)**. According to the general procedure for palladium-catalyzed allylic alkylations of tripeptides **7g$_l$** was obtained as minor regioisomer from **3** (200 mg, 0.409 mmol) in 5% yield (13.8 mg, 0.020 mmol). $[\alpha]_D^{20}$ = –59.4° (c = 0.5, $CHCl_3$). M.p. 85–87 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.81 (s, 1 H), 7.55 (d, *J* = 7.5 Hz, 2 H), 7.34–7.24 (m, 6 H), 7.20 (d, *J* = 5.0 Hz, 1 H), 7.15 (dd, *J* = 7.6, 1.5 Hz, 2 H), 7.06 (t, *J* = 7.5 Hz, 1 H), 7.01 (d, *J* = 7.0 Hz, 1 H), 5.70 (ddd, *J* = 17.3, 10.2, 9.2 Hz 1 H), 5.16 (dd, *J* = 10.2, 1.1 Hz, 1 H), 5.10 (dd, *J* = 17.3, 1.1 Hz, 1 H), 4.67 (dd, *J* = 8.1, 1.4 Hz, 1 H), 4.63 (m, 1 H), 4.52 (dd, *J* = 7.0, 5.0 Hz, 1 H), 3.93 (m, 1 H), 3.79 (dd, *J* = 10.6, 3.1 Hz, 1 H), 3.64 (m, 1 H), 3.58 (dd, *J* = 10.6, 6.7 Hz, 1 H), 3.10 (d, *J* = 7.0 Hz, 2 H), 2.47–2.44 (m, 2 H), 2.09–2.13 (m, 3 H), 0.93 (s, 9 H), 0.10 (s, 3 H), 0.08 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.1, 169.7, 168.9, 156.4 (q, $^2J_{C,F}$ = 37.5 Hz), 137.9, 135.1, 133.5, 129.2, 128.8, 128.7, 127.5, 124.2, 120.1, 119.4, 64.0, 61.3, 54.6, 54.4, 47.3, 47.2, 38.5, 29.6, 28.8, 25.8, 24.3, –5.4, –5.5. HRMS (CI) *m/z* calcd for $C_{30}H_{36}F_3N_4O_5Si$ $[M–C_4H_9]^+$ 617.2407; found 617.2380.

***N*-Trifluoroacetyl-(*S*)-phenylalanyl-(*R*)-(3-methyl-2-butenyl)-glycyl-(*S*)-prolinanilide (7h$_l$)**. According to the general procedure for palladium-catalyzed allylic alkylations of tripeptides **7h$_l$** was obtained as minor regioisomer from **3** (150 mg, 0.306 mmol) in 24% yield (41.0 mg, 0.073 mmol). Major diastereomer (92%): $[\alpha]_D^{20}$ = –69.3° (c = 1.0, $CHCl_3$). M.p. 72–74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (s, 1 H), 7.53 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.33 (d, *J* = 7.6 Hz, 1 H), 7.27–7.23 (m, 5 H), 7.14 (dd, *J* = 7.6, 1.6 Hz, 2 H), 7.05 (t, *J* = 7.6 Hz, 1 H), 6.77 (d, *J* = 6.0 Hz, 1 H), 4.98 (m, 1 H), 4.79 (m, 1 H), 4.67 (dd, *J* = 8.4, 2.0 Hz, 1 H), 4.50 (m, 1 H), 3.84 (m, 1 H), 3.52 (m, 1 H), 3.11–3.01 (m, 2 H), 2.43 (m, 1 H), 2.36–2.23 (m, 2 H), 2.10 (m, 1 H), 2.02–1.94 (m, 2 H), 1.69 (s, 3 H), 1.58 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 169.5, 168.8, 156.7 (q, $^2J_{C,F}$ = 37.5 Hz), 137.8, 137.0, 137.3, 129.2, 128.8, 128.7, 127.4, 124.2, 119.9, 117.1, 115.5 (q, $^1J_{C,F}$ = 288.3 Hz), 61.3, 54.4, 51.6, 47.4, 38.5, 30.2, 28.6, 25.7, 24.4, 17.8. HRMS (CI) *m/z* calcd for $C_{29}H_{34}F_3N_4O_4$ $[M+H]^+$ 559.2532; found 559.2537. Minor diastereomer (8%): $[\alpha]_D^{20}$ = –22.1° (c = 0.5, $CHCl_3$). M.p. 93–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1 H), 8.01 (bs, 1 H), 7.49–7.46 (m, 3 H), 7.27–7.19 (m, 5 H), 7.06–7.02 (m, 3 H), 5.14 (m, 1 H), 4.98 (m, 1 H), 4.88 (m, 1 H), 4.69 (m, 1 H), 3.77–3.74 (m, 2 H), 3.02 (dd, *J* = 13.5, 5.2 Hz, 1 H), 2.92 (dd, *J* = 13.5, 8.1 Hz, 1 H), 2.49 (ddd, *J* = 14.3, 6.5. 6.5 Hz, 1 H), 2.35 (ddd, *J* = 14.3, 7.5, 7.5 Hz, 1 H), 2.31–2.25 (m, 2 H), 2.10–2.00 (m, 2 H), 1.44 (s, 3 H), 1.36 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 169.0, 156.9 (q, $^2J_{C,F}$ = 37.5 Hz), 138.2, 136.9, 135.3, 129.1, 128.8, 128.5, 127.3, 123.9, 119.3, 116.7, 115.6 (q, $^1J_{C,F}$ = 285.4 Hz), 60.7, 54.1, 50.9, 47.7, 39.5, 31.2, 28.2, 25.4, 24.9, 17.5. HRMS (CI) *m/z* calcd for $C_{29}H_{34}F_3N_4O_4$ $[M+H]^+$ 559.2532; found 559.2599. $C_{29}H_{33}F_3N_4O_4$ (558.60) calcd C 62.36, H 5.95, N 10.03; found C 62.60, H 5.77, N 9.33. HPLC (silica, hexane/EtOAc = 70:30, 1 mL/min, 254 nm): t_R (8%) = 27.13 min, t_R (92%) = 28.55 min.

***N*-Trifluoroacetyl-(*S*)-phenylalanyl-(*R*)-(1,1-dimethylallyl)-glycyl-(*S*)-prolinanilide (7h$_b$)**. According to the general procedure for palladium-catalyzed allylic alkylations of tripeptides **7h$_b$** was obtained as major regioisomer from **3** (150 mg, 0.306 mmol) in 30% yield (51.1 mg, 0.091 mmol). $[\alpha]_D^{20}$ = –83.4° (c = 1.0, $CHCl_3$). Major diastereomer (92%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.07 (s, 1 H), 7.54 (dd, *J* = 7.6, 1.2 Hz, 2 H), 7.33–7.23 (m, 6 H), 7.17 (dd, *J* = 8.4, 1.6 Hz, 2 H), 7.06 (t, *J* = 7.6 Hz, 1 H), 6.20 (d, *J* = 6.8 Hz, 1 H), 5.86 (dd, *J* = 13.6, 10.8 Hz, 1 H), 5.07 (dd, *J* = 10.8, 1.0 Hz, 1 H), 4.93 (dd, *J* = 13.6, 1.0 Hz, 1 H), 4.74–4.69 (m, 2 H), 4.31 (d, *J* = 6.8 Hz, 1 H), 3.99 (m, 1 H), 3.65 (m, 1 H), 3.07 (dd, *J* = 14.0, 6.4 Hz, 1 H), 3.03 (dd, *J* = 14.0, 7.2 Hz, 1 H), 2.45 (m, 1 H), 2.16–1.93 (m, 3 H), 1.05 (s, 3 H), 0.95 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 169.9, 168.9, 156.6 (q, $^2J_{C,F}$ = 37.3 Hz), 142.3, 137.8, 135.3, 129.0, 128.9, 128.7, 127.5, 124.3, 120.1, 115.3 (q, $^1J_{C,F}$ = 285.9 Hz), 114.8, 61.3, 58.0, 54.6, 48.1, 41.0, 38.2, 28.7, 24.4, 23.8, 23.3. Minor diastereomer (8%, selected peak):

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.07 (s, 1 H), 7.49 (dd, *J* = 8.4, 1.0 Hz, 2 H), 6.74 (d, *J* = 8.4 Hz, 1 H), 5.01 (dd, *J* = 10.8, 0.6 Hz, 1 H), 4.86–4.80 (m, 2 H), 4.31 (d, *J* = 8.0 Hz, 1 H), 3.57 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 129.2, 128.6, 127.4, 124.1, 119.6, 114.5, 61.0, 56.7. HRMS (CI) *m/z* calcd for $C_{29}H_{34}F_3N_4O_4Si$ $[M+H]^+$ 559.2532; found 559.2532. HPLC (silica, hexane/EtOAc = 70:30, 1 mL/min, 254 nm): t_R (8%) = 43.43 min, t_R (92%) = 47.72 min.

***N*-Trifluoroacetyl-(*S*)-leucyl-(*R*)-(2-methylallyl)-glycyl-(*S*)-prolinanilide (8a)**. According to the general procedure for palladium-catalyzed allylic alkylations of tripeptides **8a** was obtained from **4** (91 mg, 0.201 mmol) in 80% yield (81.6 mg, 0.160 mmol). Major diastereomer (88%): $[\alpha]_D^{20}$ = –91.4° (c = 0.5, $CHCl_3$). M.p. 77–79 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 1 H), 7.58 (d, *J* = 7.6 Hz, 2 H), 7.31 (d, *J* = 7.6 Hz, 1 H), 7.26 (t, *J* = 7.6 Hz, 2 H), 7.06 (t, *J* = 7.6 Hz, 1 H), 6.96 (d, *J* = 6.0 Hz, 1 H), 4.91 (s, 1 H), 4.82 (s, 1 H), 4.69 (dd, *J* = 8.4, 2.4 Hz, 1 H), 4.67–4.57 (m, 2 H), 3.97 (m, 1 H), 3.52 (m, 1 H), 2.46 (m, 3 H), 2.13–2.01 (m, 3 H), 1.46 (s, 3 H), 1.58–1.51 (m, 3 H), 0.87 (d, *J* = 6.0 Hz, 3 H), 0.84 (d, *J* = 6.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 171.1, 168.9, 157.0 (q, $^2J_{C,F}$ = 37.2 Hz), 139.6, 137.9, 128.7, 124.2, 120.1, 115.6 (q, $^1J_{C,F}$ = 285.8 Hz), 115.3, 61.4, 52.0, 49.9, 47.4, 41.4, 39.4, 28.7, 24.7, 24.4, 22.7, 21.9, 21.8. HRMS (CI) *m/z* calcd for $C_{25}H_{34}F_3N_4O_4$ $[M+H]^+$ 511.2532; found 511.2485. $C_{25}H_{33}F_3N_4O_4$ (510.56) calcd C 58.81, H 6.51, N 10.97; found C 58.91, H 6.57, N 10.67. Minor diastereomer (12%): $[\alpha]_D^{20}$ = –44.9° (c = 0.5, $CHCl_3$). M.p. 93–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1 H), 8.40 (bs, 1 H), 7.53–7.47 (m, 3 H), 7.25 (d, *J* = 7.6 Hz, 2 H), 7.05 (t, *J* = 7.6 Hz, 1 H), 5.03–4.95 (m, 2 H), 4.83 (dd, *J* = 8.4, 2.8 Hz, 1 H), 4.48 (s, 1 H), 4.38 (s, 1 H), 3.76 (m, 1 H), 2.42 (dd, *J* = 14.0, 4.0 Hz, 1 H), 2.32–2.17 (m, 3 H), 2.13–2.01 (m, 3 H), 1.76–1.54 (m, 2 H), 1.59 (s, 3 H), 1.44 (m, 1 H), 0.86 (d, *J* = 7.8 Hz, 3 H), 0.83 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 170.5, 169.4, 157.1 (q, $^2J_{C,F}$ = 37.2 Hz), 139.2, 138.1, 128.7, 123.9, 119.4, 115.8 (q, $^1J_{C,F}$ = 285.9 Hz), 115.1, 60.7, 51.5, 49.1, 47.5, 42.4, 41.2, 28.7, 24.8, 24.5, 23.1, 21.9, 21.5. HRMS (CI) *m/z* calcd for $C_{25}H_{34}F_3N_4O_4$ $[M+H]^+$ 511.2532; found 511.2516. $C_{25}H_{33}F_3N_4O_4$ (510.56) calcd C 58.81, H 6.51, N 10.97, found: C 58.11, H 6.45, N 10.83. HPLC (Reprosil, hexane/isopropanol = 90:10, 0.5 mL/min, 254 nm): t_R (12%) = 37.05 min, t_R (88%) = 42.00 min.

***N*-Trifluoroacetyl-(*S*)-(4-methoxy)-phenylalanyl-(*R*)-(2-methylallyl)-glycyl-(*S*)-prolinanilide (10a)**. According to the general procedure for palladium-catalyzed allylic alkylations of tripeptides **10a** was obtained from **6** (100 mg, 0.203 mmol) in 85% yield (99.2 mg, 0.173 mmol). Major diastereomer: $[\alpha]_D^{20}$ = –49.5° (c = 0.5, $CHCl_3$). M.p. 93–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1 H), 7.56 (d, *J* = 7.6 Hz, 2 H), 7.25 (t, *J* = 7.6 Hz, 2 H), 7.20 (bs, 1 H), 7.06 (t, *J* = 7.6 Hz, 1 H), 7.03 (d, *J* = 8.4 Hz, 2 H), 6.79 (d, *J* = 8.4 Hz, 2 H), 6.59 (bs, 1 H), 4.85 (s, 1 H), 4.76 (s, 1 H), 4.69–3.68 (m, 2 H), 4.54 (m, 1 H), 3.98–3.94 (m, 1 H), 3.76 (s, 3 H), 3.51 (m, 1 H), 2.98 (d, *J* = 6.7 Hz, 2 H), 2.43 (m, 1 H), 2.35 (dd, *J* = 14.0, 1.2 Hz, 1 H), 2.26 (dd, *J* = 14.0, 9.2 Hz, 1 H), 2.16–1.98 (m, 3 H), 1.72 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 169.8, 168.9, 158.9, 139.4, 137.8, 130.2, 128.8, 12.6.9, 124.3, 120.1, 115.5, 114.2, 61.4, 55.2, 54.5, 49.9, 47.4, 39.3, 37.5, 28.7, 24.4, 21.9. HRMS (CI) *m/z* calcd for $C_{29}H_{34}F_3N_4O_5$ $[M+H]^+$ 575.2481; found 575.2461. Minor diastereomer: $[\alpha]_D^{20}$ = –18.0° (c = 1.0, $CHCl_3$). M.p. 94–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1 H), 8.39 (bs, 1 H), 7.61 (d, *J* = 8.5 Hz, 1 H), 7.45 (d, *J* = 7.6 Hz, 2 H), 7.25 (t, *J* = 7.6 Hz, 2 H), 7.06 (t, *J* = 7.6 Hz, 1 H), 6.49 (d, *J* = 7.2 Hz, 2 H), 6.71 (d, *J* = 7.2 Hz, 2 H), 5.20 (ddd, *J* = 8.5, 8.4, 4.8 Hz, 1 H),), 5.03 (m, 1 H), 4.67 (dd, *J* = 7.8, 2.9 Hz, 1 H), 4.47 (s, 1 H), 4.37 (s, 1 H), 3.87–3.76 (m, 2 H), 3.73 (s, 3 H), 2.99 (dd, *J* = 13.6, 4.8 Hz, 1 H), 2.84 (dd, *J* = 13.6, 8.4 Hz, 1 H), 2.49 (dd, *J* = 14.0, 7.6 Hz, 1 H), 2.34–2.08 (m, 5 H), 1.63 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171, 169.3, 169.2, 158.7, 156.9 (q, $^2J_{C,F}$ = 37.7 Hz), 139.0, 138.1, 130.1, 128.8, 127.3, 124.0, 119.3, 115.9 (q, $^1J_{C,F}$ = 285.7 Hz), 115.4, 113.8, 60.8, 55.1, 54.1, 49.3, 47.6, 41.1, 38.6, 28.7, 24.9, 21.9. HRMS (CI) *m/z* calcd for $C_{29}H_{34}F_3N_4O_5$ $[M+H]^+$ 575.2481; found

575.2464. HPLC (Reprosil, hexane/isopropanol = 90:10, 0.5 mL/min, 254 nm): t_R (4%) = 72.44 min, t_R (96%) = 83.31 min.

***N*-Trifluoroacetyl-(*S*)-phenylalanyl-glycyl-(*S*)-*N*-methyl-leucineanilide (11)**. $[\alpha]_D^{20}$ = –110.3° (c = 1.0, $CHCl_3$). M.p. 86–88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1 H), 7.46 (d, *J* = 7.6 Hz, 2 H), 7.40 (d, *J* = 8.0 Hz, 1 H),7.30–7.12 (m, 8 H), 7.06 (t, *J* = 7.4 Hz, 1 H), 5.18 (dd, *J* = 8.8, 6.6 Hz, 1 H), 4.94 (td, *J* = 8.0, 8.0 Hz, 1 H), 4.06 (d, *J* = 4.1 Hz, 2 H), 3.12 (m, 2 H), 2.96 (s, 3 H), 1.82 (ddd, *J* = 14.6, 8.3, 6.6 Hz, 1 H), 1.70 (ddd, *J* = 14.2, 8.9, 5.6 Hz, 1 H), 1.57–1.42 (m, 1 H), 0.97 (d, *J* = 6.6 Hz, 3 H), 0.91 (d, *J* = 6.5 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 169.1, 168.2, 155.9 (q, $^2J_{C,F}$ = 38.1 Hz), 137.6, 135.2, 129.1, 129.0, 128.7, 127.4, 124.5, 119.8, 115.6 (q, $^1J_{C,F}$ = 287.5 Hz), 55.9, 54.4, 41.7, 38.6, 36.6, 29.9, 25.0, 22.9, 22.0. HRMS (CI) *m/z* calcd for $C_{26}H_{31}F_3N_4O_4$ $[M–PhNH_2]^+$ 428.1797; found 428.1759. $C_{26}H_{31}F_3N_4O_4$ (520.54) calcd C 59.99, H 6.00, N 10.76; found C 59.94, H 6.02, N 10.50.

***N*-Trifluoroacetyl-(*S*)-phenylalanyl-glycyl-(*R*)-*N*-methyl-leucineanilide (12)**. $[\alpha]_D^{20}$ = +73.0° (c = 1.0, $CHCl_3$). M.p. 86–88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1 H), 7.51–7.43 (m, 3 H), 7.36 (t, *J* = 3.9 Hz, 1 H), 7.32–7.25 (m, 3 H), 7.20–7.01 (m, 5 H), 5.24 (dd, *J* = 8.6, 7.0 Hz, 1 H), 5.09 (dd, *J* = 14.7, 7.1 Hz, 1 H), 4.24 (dd, *J* = 17.7, 5.0 Hz, 1 H), 4.01 (dd, *J* = 17.7, 3.7 Hz, 1 H), 3.18–3.02 (m, 2 H), 3.05 (s, 3 H), 1.80–1.72 (m, 2 H), 1.51–1.41 (m, 1 H), 0.95 (d, *J* = 6.6 Hz, 3 H), 0.87 (d, *J* = 6.5 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 169.2, 168.7, 156.7 (q, $^2J_{C,F}$ = 37.7 Hz), 137.7, 135.0, 129.1, 128.9, 128.7, 127.4, 124.4, 119.8, 115.6 (q, $^1J_{C,F}$ = 287.3 Hz), 55.7, 54.4, 41.7, 39.1, 37.1, 30.1, 25.0, 22.9, 21.8. HRMS (CI) *m/z* calcd for $C_{26}H_{31}F_3N_4O_4$ $[M+H]^+$ 521.2370; found 521.2388. $C_{26}H_{31}F_3N_4O_4$ (520.54) calcd C 59.99, H 6.00, N 10.76; found C 59.79, H 6.18, N 10.34.

***N*-Trifluoroacetyl-(*S*)-phenylalanyl-glycyl-(*S*)-*N*-benzyl-leucineanilide (13)**. $[\alpha]_D^{20}$ = –95.4° (c = 1.0, $CHCl_3$). M.p. 87–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1 H), 7.42 (d, *J* = 7.6 Hz, 2 H), 7.36–7.20 (m, 11 H), 7.14 (d, *J* = 7.8 Hz, 2 H), 7.09 (t, *J* = 7.4 Hz, 1 H), 6.88 (t, *J* = 4.2 Hz, 1 H), 5.07 (dd, *J* = 8.0, 6.2 Hz, 1 H), 4.81 (td, *J* = 7.0, 6.9 Hz, 1 H), 4.64 (s, 2 H), 3.96 (m, 2 H), 3.09 (d, *J* = 6.8 Hz, 2 H), 1.97 (m, 1 H), 1.53 (m, 2 H), 0.89 (d, *J* = 6.5 Hz, 3 H), 0.87 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 169.2, 168.1, 156.8 (q, $^2J_{C,F}$ = 37.8 Hz), 137.5, 135.8, 135.2, 129.1, 129.1, 128.9, 128.8, 127.9, 127.4, 126.0, 124.5, 119.9, 115.6 (q, $^1J_{C,F}$ = 287.8 Hz), 57.9, 54.5, 48.2, 42.0, 38.5, 37.0, 25.2, 22.7, 22.3. HRMS (CI) *m/z* calcd for $C_{32}H_{35}F_3N_4O_4$ $[M+H]^+$ 597.2683; found 597.2668. $C_{32}H_{35}F_3N_4O_4$ (596.64) calcd C 64.42, H 5.91, N 9.39; found C 64.50, H 5.87, N 9.30.

***N*-Trifluoroacetyl-(*S*)-alanyl-glycyl-(*S*)-*N*-methylleucineanilide (14)**. $[\alpha]_D^{20}$ = –145.9° (c = 1.0, $CHCl_3$). M.p. 78–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1 H), 7.54 (d, *J* = 7.5 Hz, 1 H), 7.51–7.46 (m, 3 H), 7.28 (m, 2 H), 7.09 (t, *J* = 7.4 Hz, 1 H), 5.24 (dd, *J* = 9.1, 6.5 Hz, 1 H), 4.81 (qd, *J* = 7.0, 7.0 Hz, 1 H), 4.22 (dd, *J* = 17.7, 5.3 Hz, 1 H), 4.05 (dd, *J* = 17.7, 3.4 Hz, 1 H), 3.01 (s, 3 H), 1.85–1.70 (m, 2 H), 1.51 (m, 1 H), 1.46 (d, *J* = 7.0 Hz, 3 H), 0.96 (d, *J* = 6.6 Hz, 3 H), 0.91 (d, *J* = 6.5 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 170.9, 168.4, 156.7 (q, $^2J_{C,F}$ = 37.9 Hz), 139.5, 128.8, 124.3, 119.9, 115.6 (q, $^1J_{C,F}$ = 287.4 Hz), 56.0, 49.0, 40.5, 36.5, 31.1, 25.0, 23.2, 21.9, 18.9. HRMS (CI) *m/z* calcd for $C_{20}H_{27}F_3N_4O_4$ $[M+H]^+$ 445.1984; found 445.2058. $C_{20}H_{27}F_3N_4O_4$ (444.45) calcd C 54.05, H 6.12, N 12.61; found C 54.06, H 6.23, N 12.24.

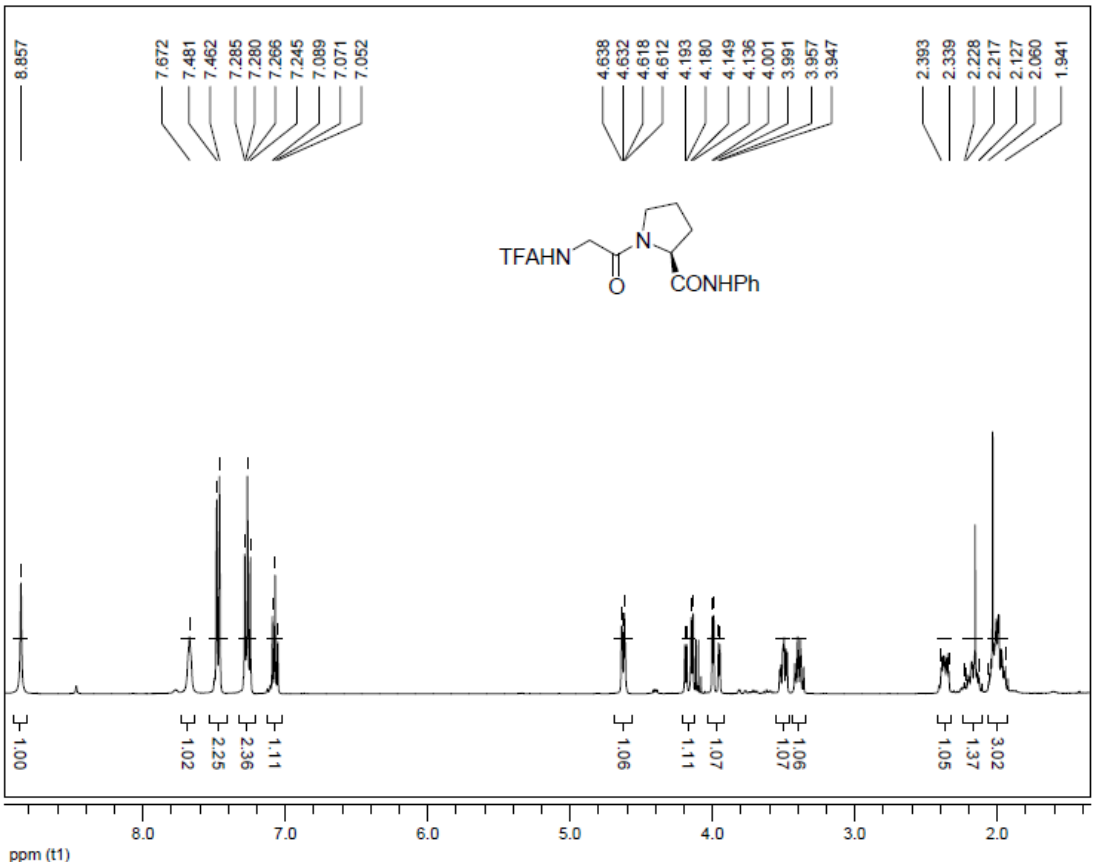
***N*-Trifluoroacetyl-(*S*)-valyl-glycyl-(*S*)-*N*-methylleucineanilide (15)**. $[\alpha]_D^{20}$ = –131.6° (c = 1.0, $CHCl_3$). M.p. 87–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1 H), 7.62 (dd, *J*=5.2, 2.9 Hz, 1 H), 7.55-7.47 (m, 2 H), 7.39 (d, *J*=8.9 Hz, 1 H), 7.32 (d, *J*=7.5 Hz, 2 H), 7.11 (t, *J*=7.4, 1 H), 5.28 (dd,

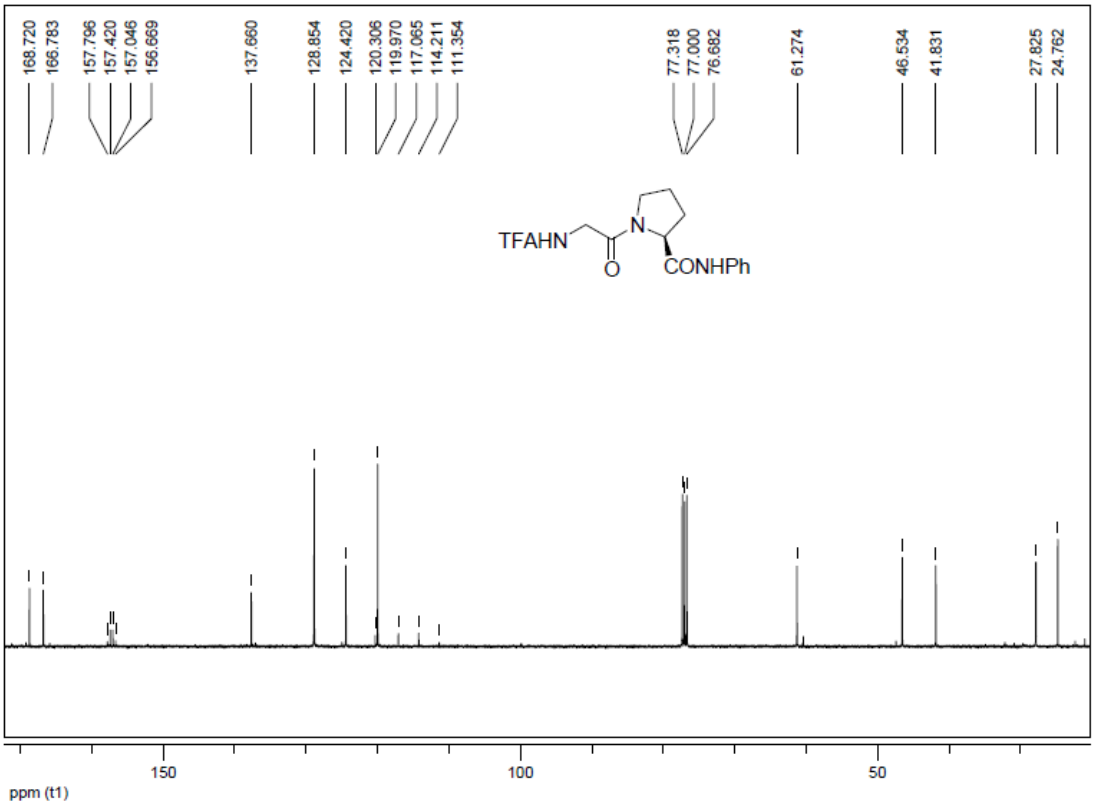
J=9.0, 6.6 Hz, 1 H), 4.69 (dd, *J*=8.8, 6.7 Hz, 1 H), 4.36 (dd, *J*=17.8, 5.7 Hz, 1 H), 4.01 (dd, *J*=17.8, 3.1 Hz, 1 H), 3.05 (s, 3 H), 2.16 (m, 1 H), 1.88-1.72 (m, 2 H), 1.54 (m, 1 H), 1.02-0.96 (m, 9 H), 0.94 (d, *J* = 6.6 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 169.4, 168.6, 157.3 (q, $^2J_{C,F}$ = 37.5 Hz), 137.6, 128.9, 124.4, 119.8, 115.8 (q, $^1J_{C,F}$ = 287.6 Hz), 58.4, 55.8, 41.6, 37.0, 31.6, 30.1, 25.0, 22.9, 22.0, 19.0, 17.9. HRMS (CI) *m/z* calcd for $C_{22}H_{31}F_3N_4O_4$ $[M+H]^+$ 473.2297; found 473.2360. $C_{22}H_{31}F_3N_4O_4$ (472.50) calcd C 55.92, H 6.61, N 11.86; found C 55.54, H 6.63, N 11.59.

***N*-Trifluoroacetyl-(*S*)-phenylalanyl-(*R*)-(2-(*tert*-butyldimethylsilyloxy)methylallyl)-glycyl-(*S*)-*N*-methylleucineanilide (16b)**. According to the general procedure for palladium-catalyzed allylic alkylations of tripeptides **16b** was obtained from **11** (208 mg, 0.400 mmol) in 56% yield (157 mg, 0.223 mmol). Major diastereomer (98%): $[\alpha]_D^{20}$ = –108.9° (c = 1.0, $CHCl_3$). M.p. 63–64 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1 H), 7.58 (d, *J* = 7.6 Hz, 2 H), 7.35–7.20 (m, 6 H), 7.15 (d, *J* = 6.1 Hz, 2 H), 7.08 (t, *J* = 7.4 Hz, 1 H), 6.67 (d, *J* = 5.3 Hz, 1 H), 5.32 (dd, *J*=10.2, 5.3 Hz, 1 H), 5.06 (s, 1 H), 4.87 (s, 1 H), 4.80–4.70 (m, 2 H), 4.14 (d, *J* = 13.1 Hz, 1 H), 4.04 (d, *J* = 13.2 Hz, 1 H), 3.12 (s, 1 H), 3.10 (s, 1 H), 3.06 (s, 3 H), 2.51 (dd, *J* = 14.0, 5.0 Hz, 1 H), 2.25 (dd, *J* = 14.1, 9.7 Hz, 1 H), 1.93 (m, 1 H), 1.67 (ddd, *J* = 14.6, 10.3, 4.6 Hz, 1 H), 1.44 (m, 1 H), 0.96 (d, *J* = 6.7 Hz, 3 H), 0.92 (s, 9 H), 0.90 (d, *J* = 6.5 Hz, 3 H), 0.10 (s, 3 H), 0.10 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.8, 169.6, 168.4, 156.6 (q, $^2J_{C,F}$ = 37.8 Hz), 142.7, 138.0, 135.1, 129.2, 128.8, 128.8, 127.5, 124.2, 119.9, 115.5 (q, $^1J_{C,F}$ = 287.7 Hz), 114.7, 65.9, 56.0, 54.2, 49.2, 38.3, 35.9, 34.6, 30.9, 25.8, 24.9, 23.3, 21.6, 18.4, –5.3. HRMS (CI) *m/z* calcd for $C_{36}H_{51}F_3N_4O_5Si$ $[M+H]^+$ 705.3654; found: 705.3659. $C_{36}H_{51}F_3N_4O_5Si$ (704.89) calcd C 61.34, H 7.29, N 7.95; found C 61.25, H 7.35, N 7.78. HPLC (Reprosil, hexane/*i*PrOH = 9:1 to 7:3, 40 min, 1 mL/min, 252 nm): t_R (3%) = 15.81 min, t_R (97%) = 21.65 min.

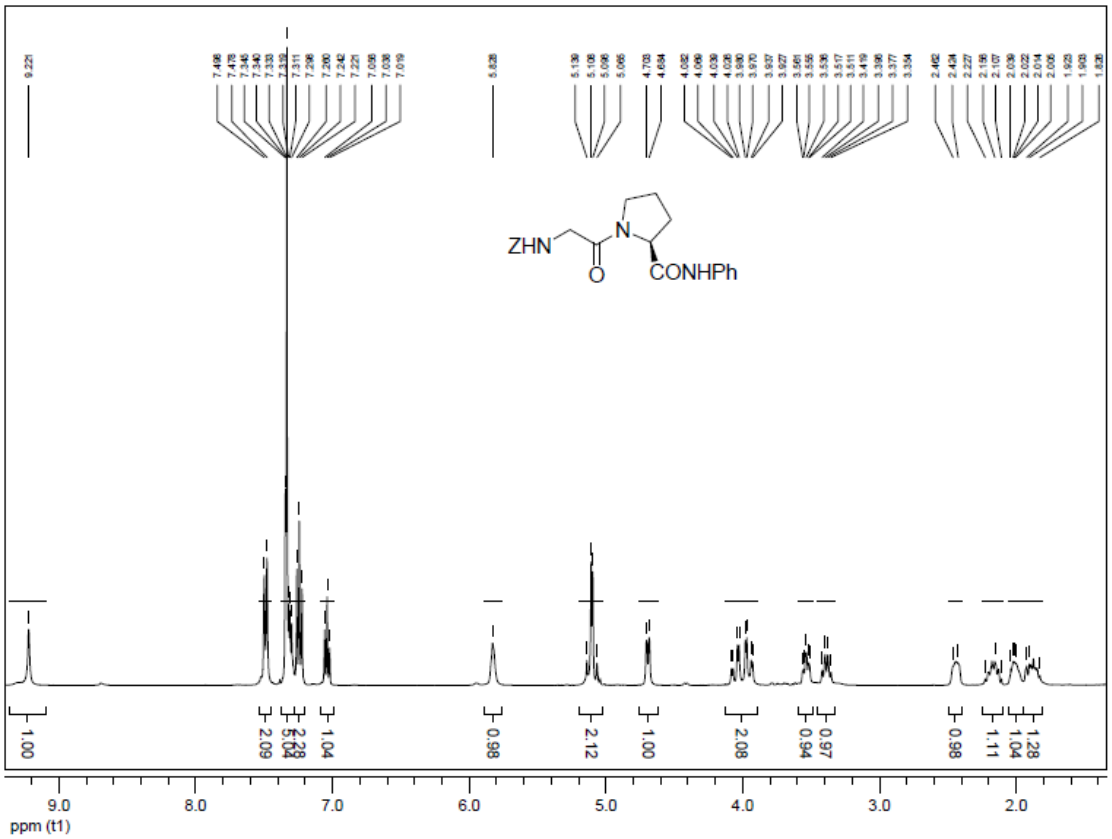
***N*-Trifluoroacetyl-(*S*)-alanyl-(*R*)-(2-methylallyl)-glycyl-(*S*)-*N*-methylleucineanilide (19)**. According to the general procedure for palladium-catalyzed allylic alkylations of tripeptides **19** was obtained from **14** (178 mg, 0.400 mmol) in 70% yield (152 mg, 0.265 mmol). Major diastereomer (91%): $[\alpha]_D^{20}$ = –145.8° (c = 1.0, $CHCl_3$). M.p. 63–64 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1 H), 7.57 (d, *J* = 7.7 Hz, 2 H), 7.40 (m, 1 H), 7.29 (m, 2 H), 7.07 (t, *J* = 7.4 Hz, 1 H), 6.99 (d, *J* = 6.6 Hz, 1 H), 5.29 (dd, *J* = 9.9, 5.6 Hz, 1 H), 4.97 (ddd, *J* = 9.1, 6.5, 5.5 Hz, 1 H), 4.92 (dd, *J* = 1.7, 1.2 Hz, 1 H), 4.83 (s, 1 H), 4.66 (ddd, *J* = 12.5, 6.9, 6.9 Hz, 1 H), 3.13 (s, 3 H), 2.50–2.30 (m, 2 H), 1.90 (m, 1 H), 1.81 (s, 3 H), 1.72 (ddd, *J* = 14.5, 10.0, 4.8 Hz, 1 H), 1.50 (m, 1 H), 1.44 (d, *J* = 6.9 Hz, 3 H), 0.98 (d, *J* = 6.7 Hz, 3 H), 0.92 (d, *J* = 6.5 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 171.0, 168.4, 156.7 (q, $^2J_{C,F}$ = 37.6 Hz), 139.5, 137.9, 128.8, 124.3, 119.9, 115.6 (q, $^1J_{C,F}$ = 287.6 Hz), 115.5, 56.0, 49.0, 48.1, 40.5, 36.5, 31.1, 25.0, 23.2, 21.9, 21.7, 18.9. HRMS (CI) *m/z* calcd for $C_{24}H_{33}F_3N_4O_4$ $[M+H]^+$ 499.2454; found: 499.2453. HPLC (Reprosil, hexane/*i*PrOH = 9:1 to 7:3, 40 min, 1 mL/min, 252 nm): t_R (11%) = 19.87 min, t_R (89%) = 24.95 min.

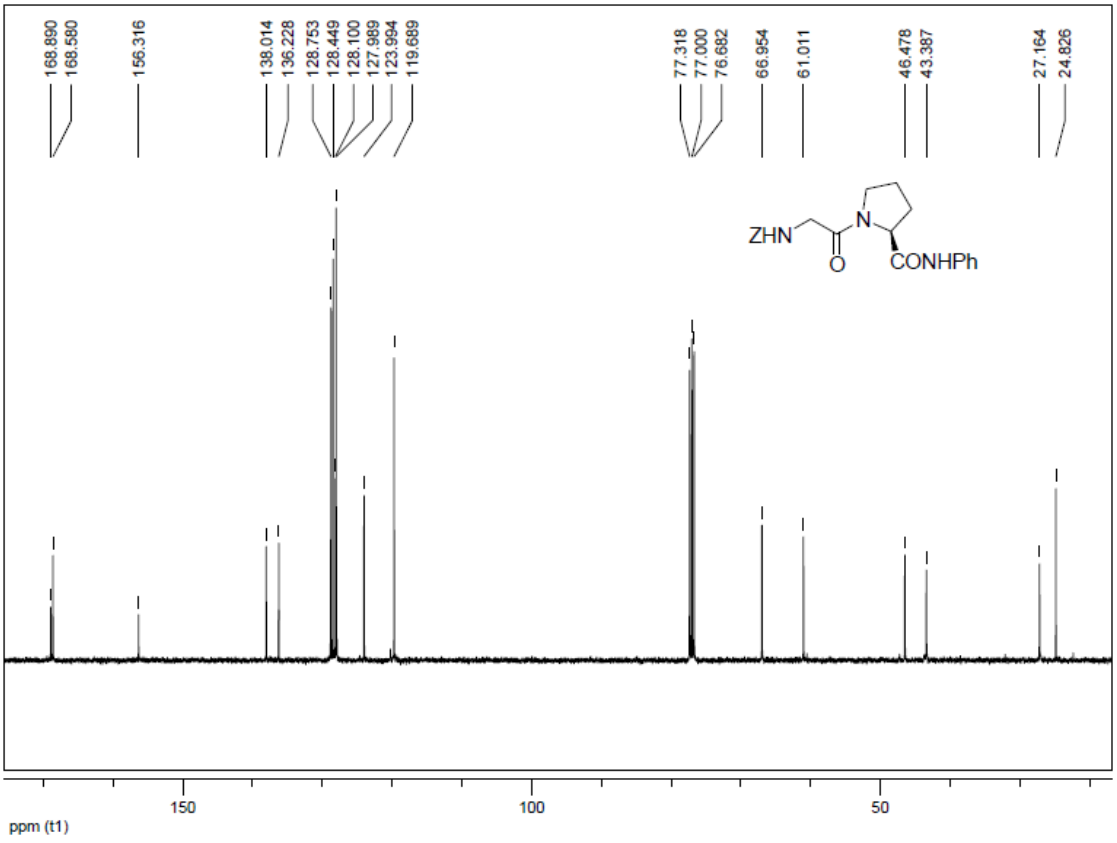
NMR spectra of compound **1a**



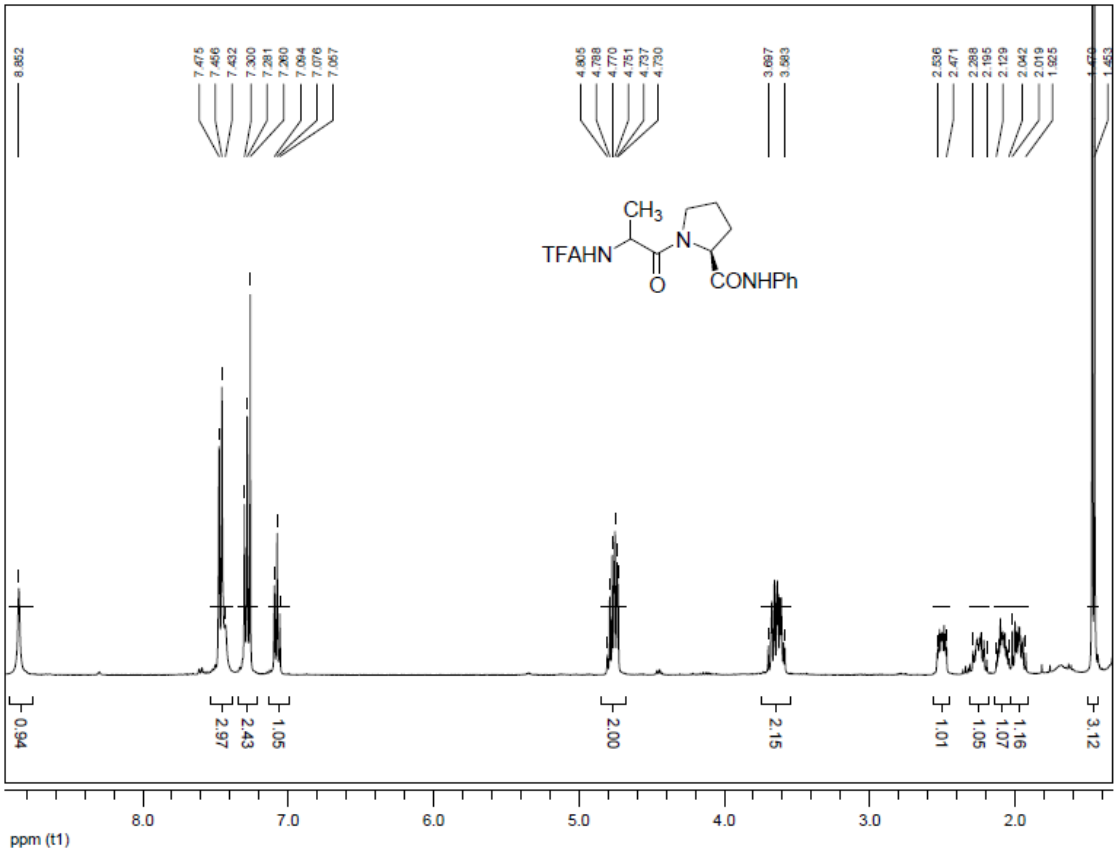


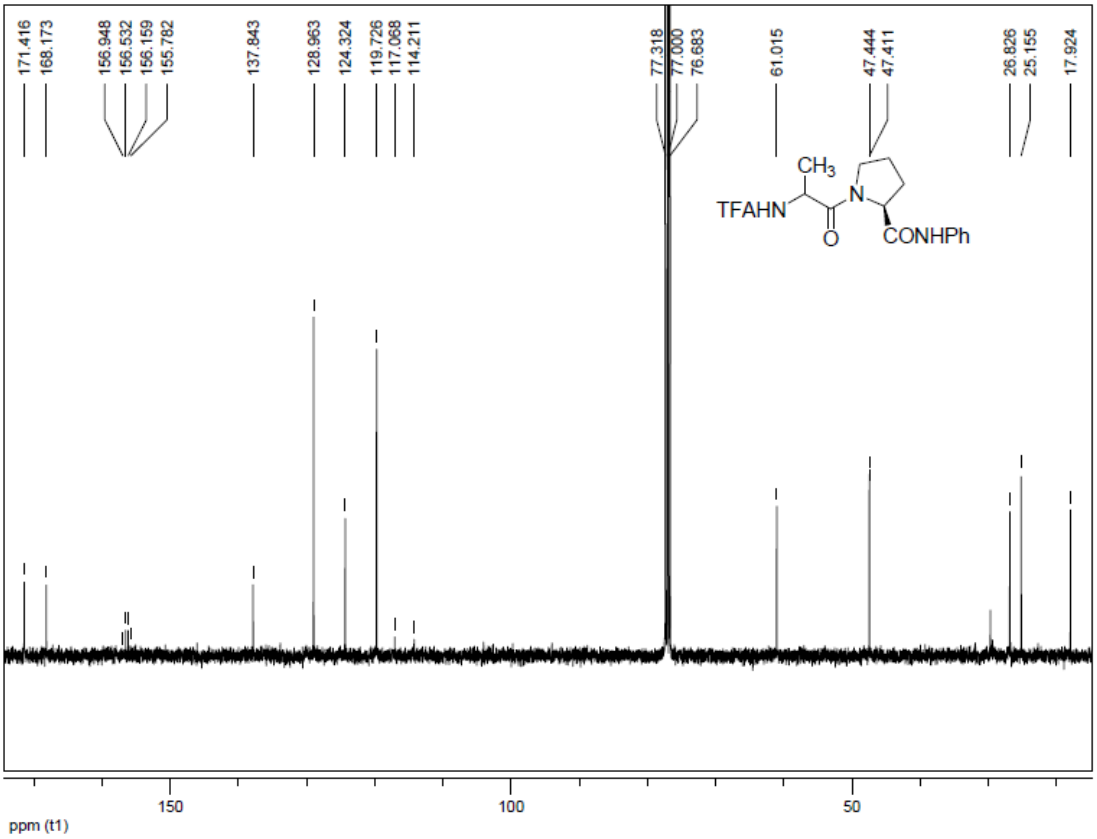
NMR spectra of compound **1b**



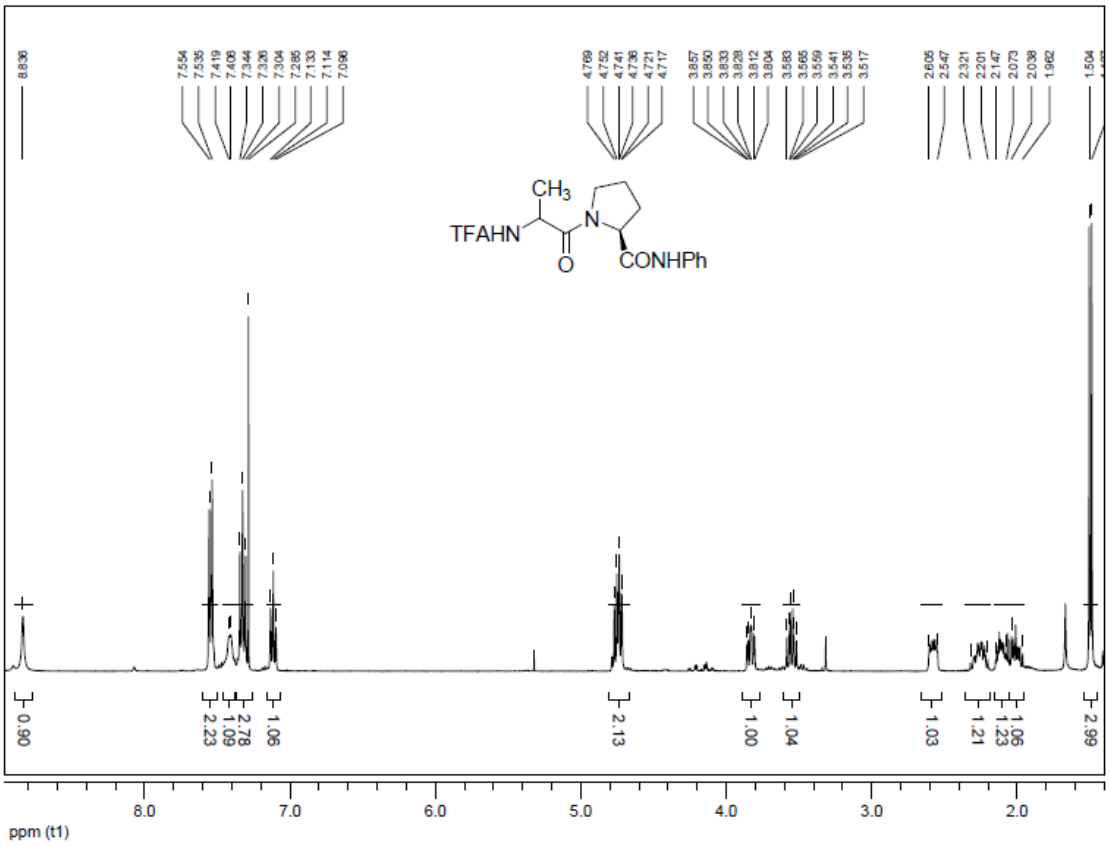


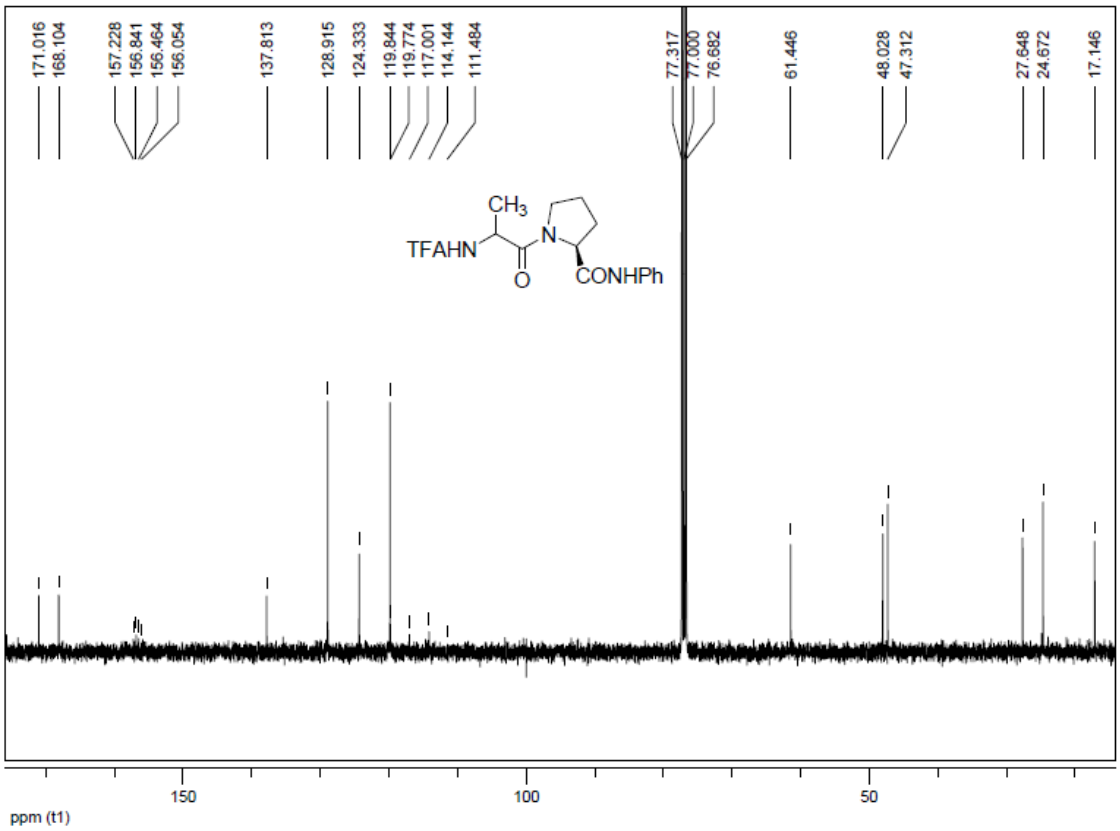
NMR spectra of compound **2a** (major diastereomer)



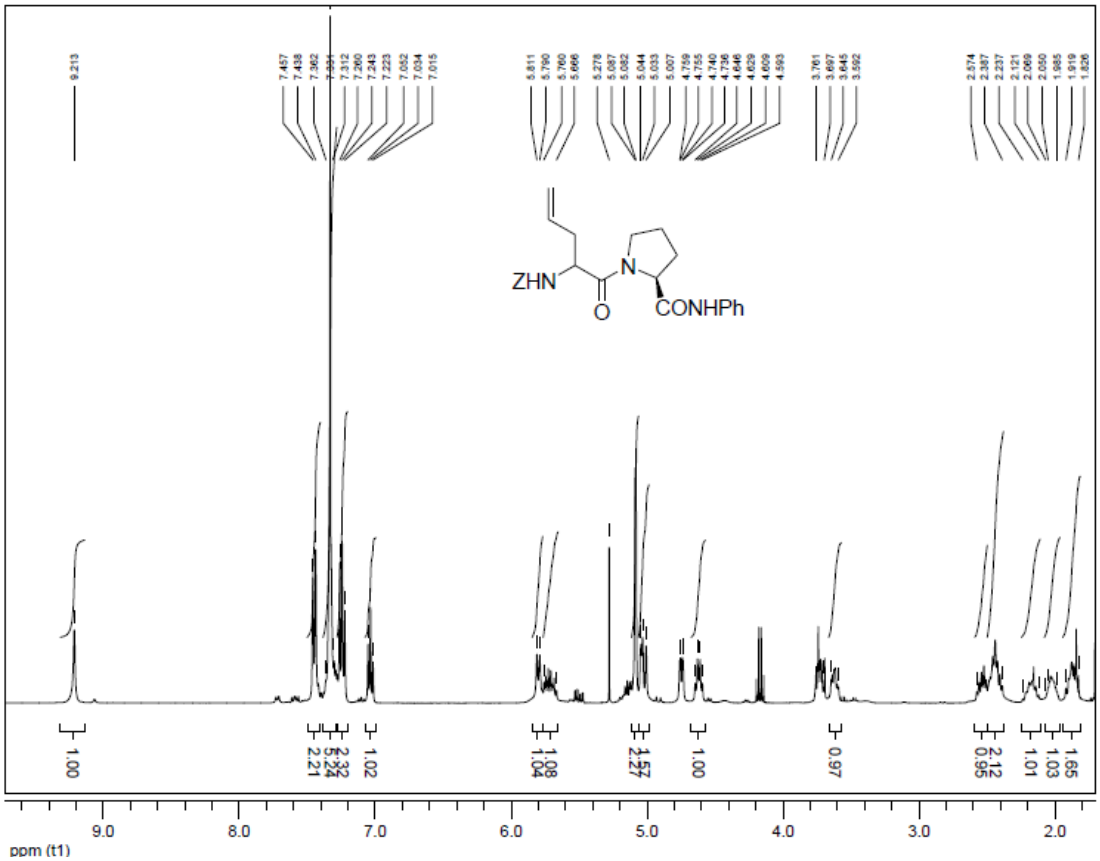


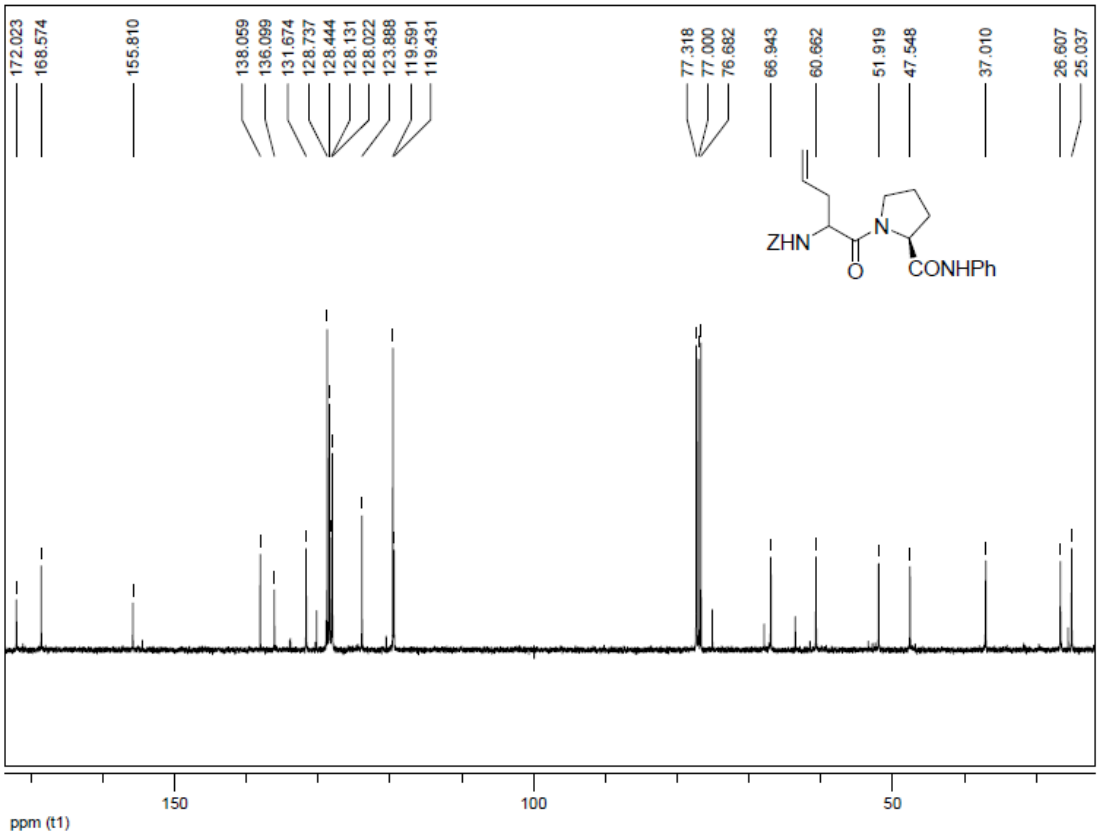
NMR spectra of compound **2a** (minor diastereomer)



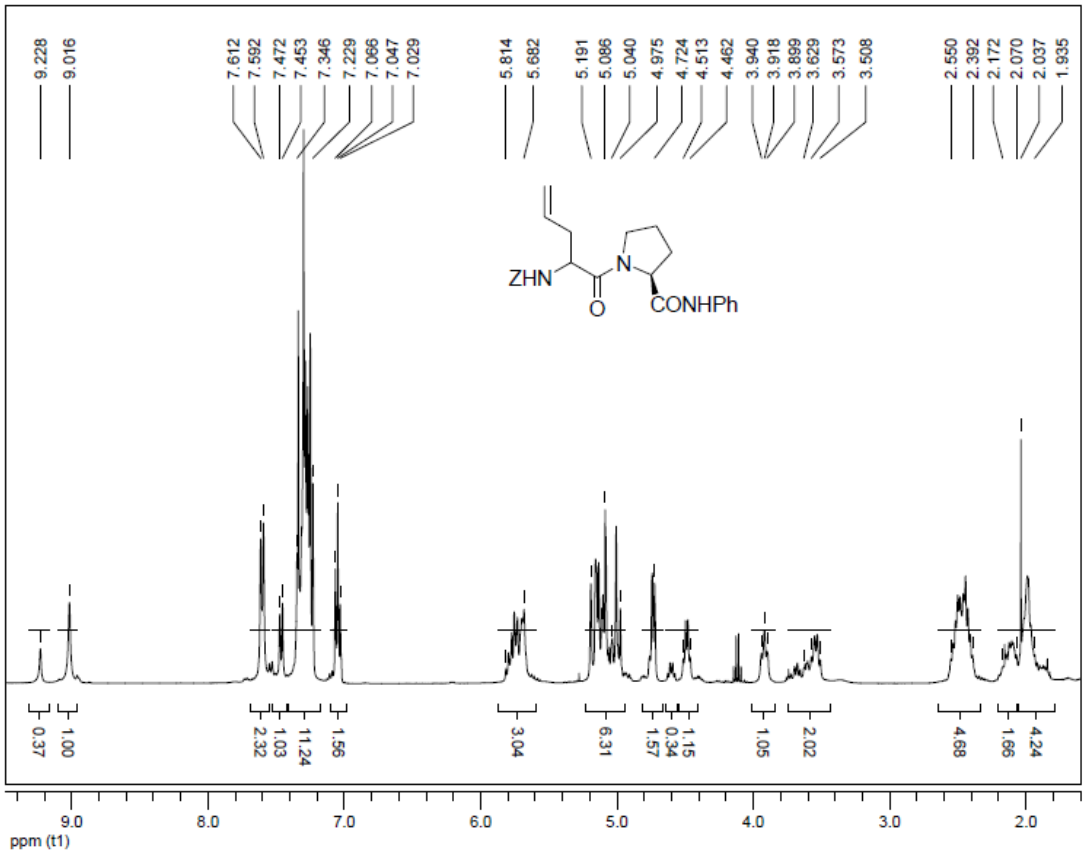


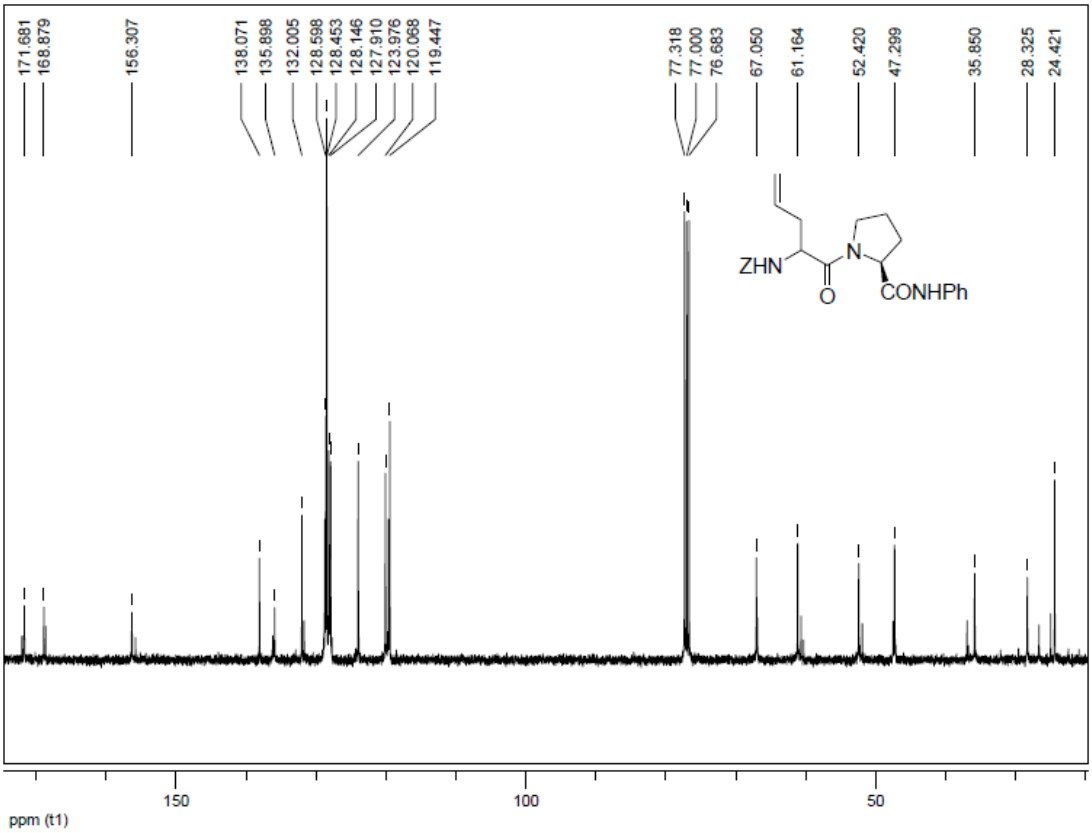
NMR spectra of compound **2b** (major diastereomer)



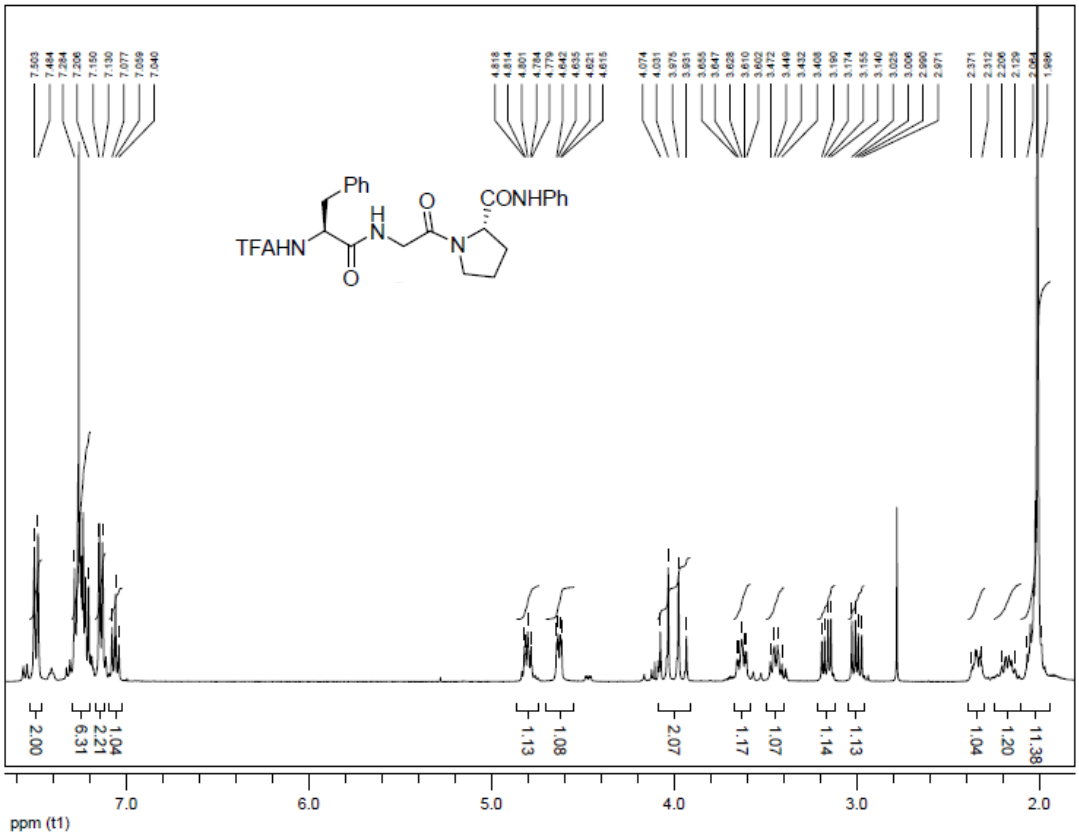


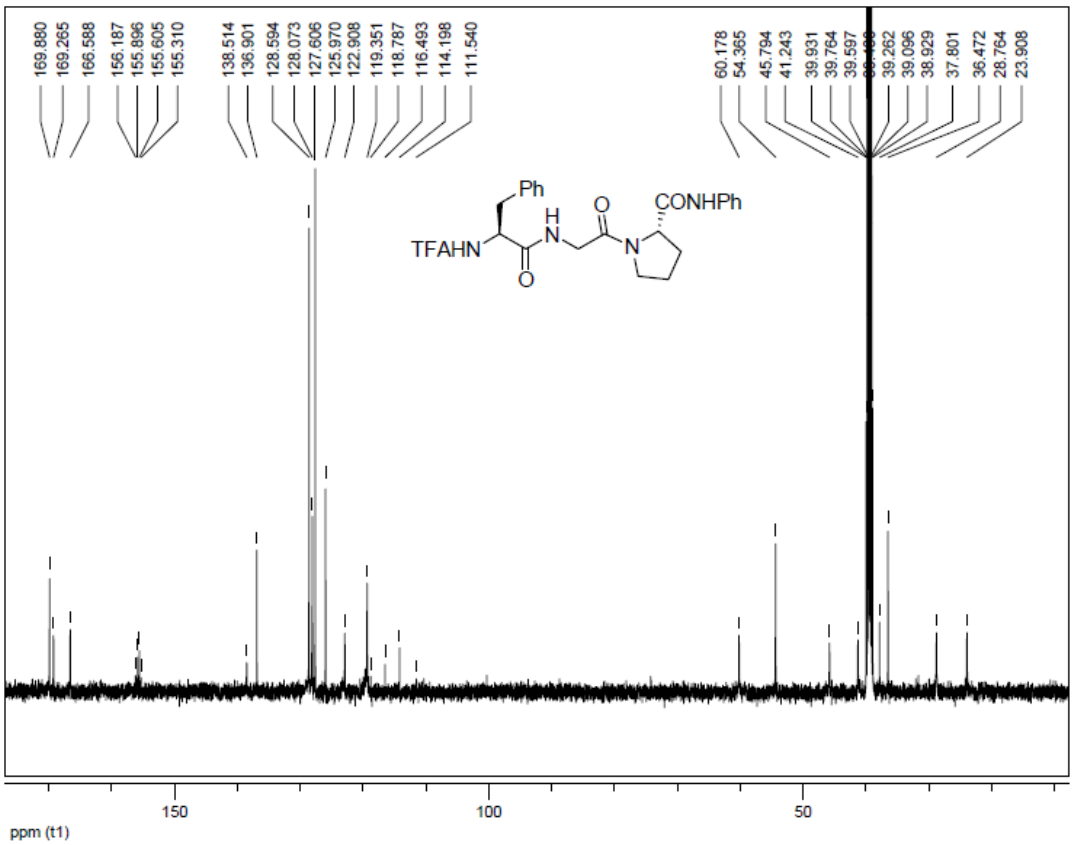
NMR spectra of compound **2b** (minor + major diastereomer)



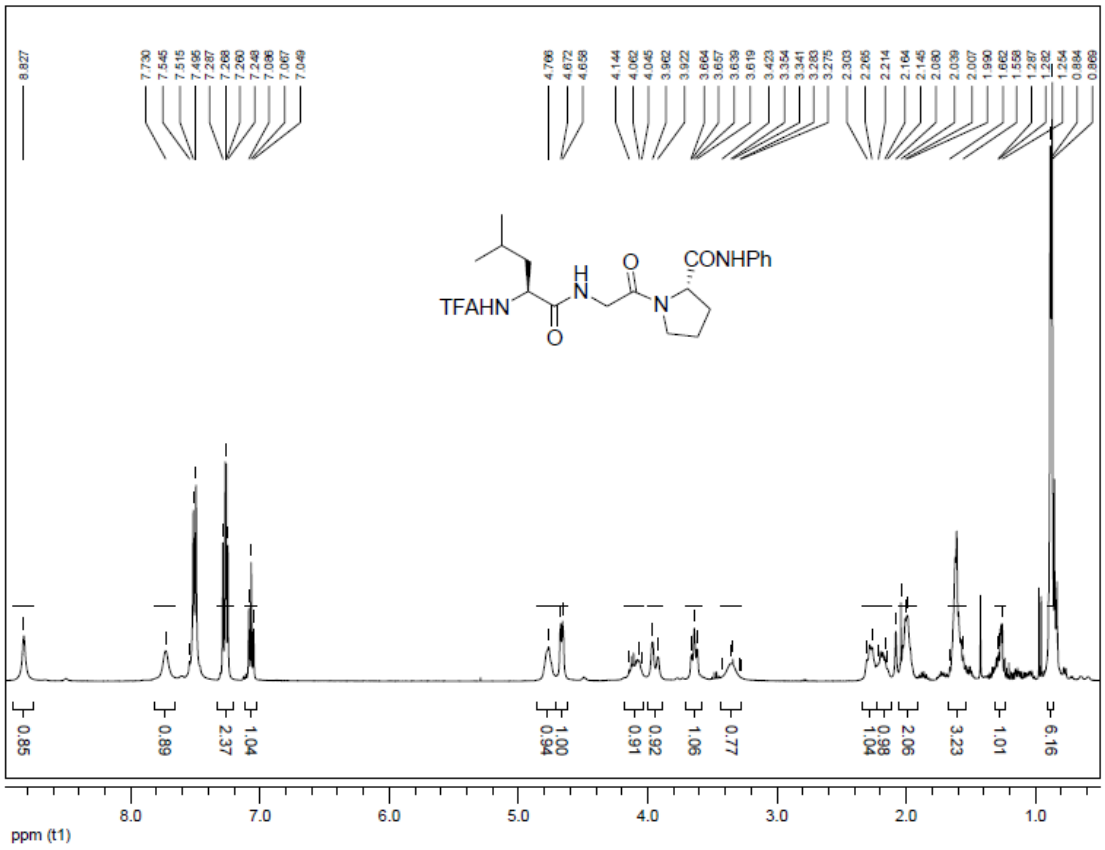


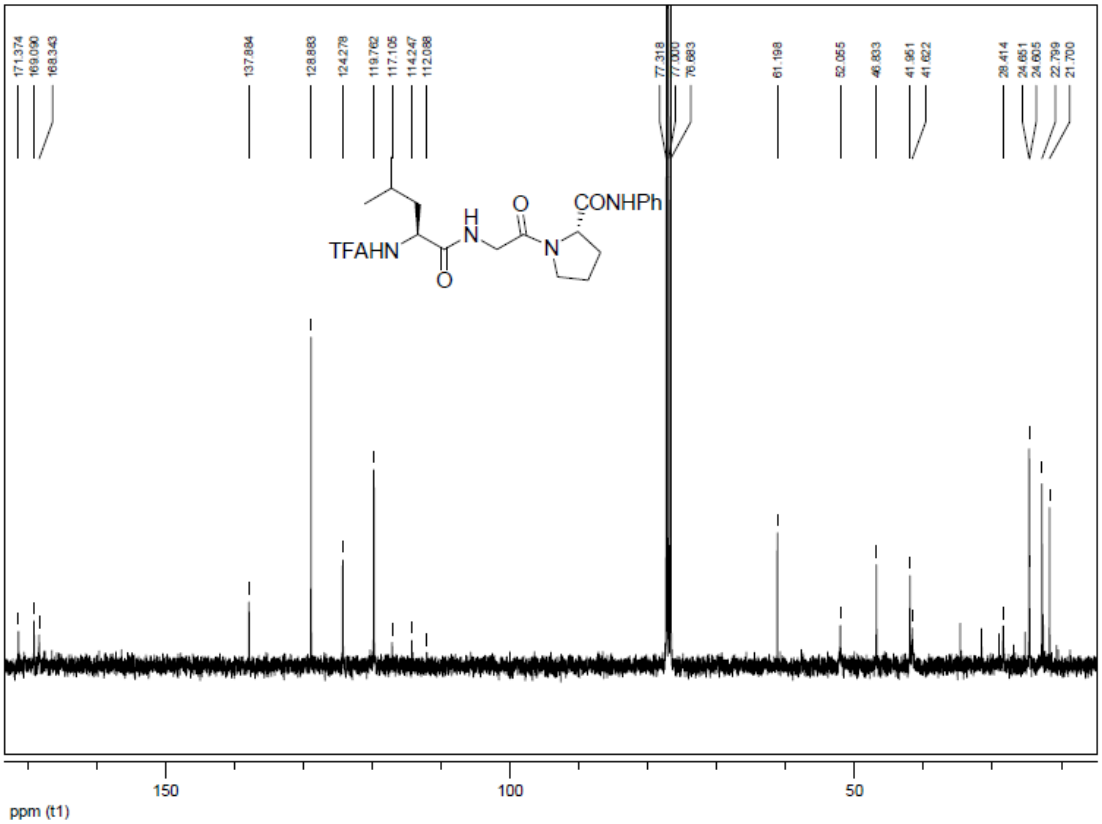
NMR spectra of compound **3**



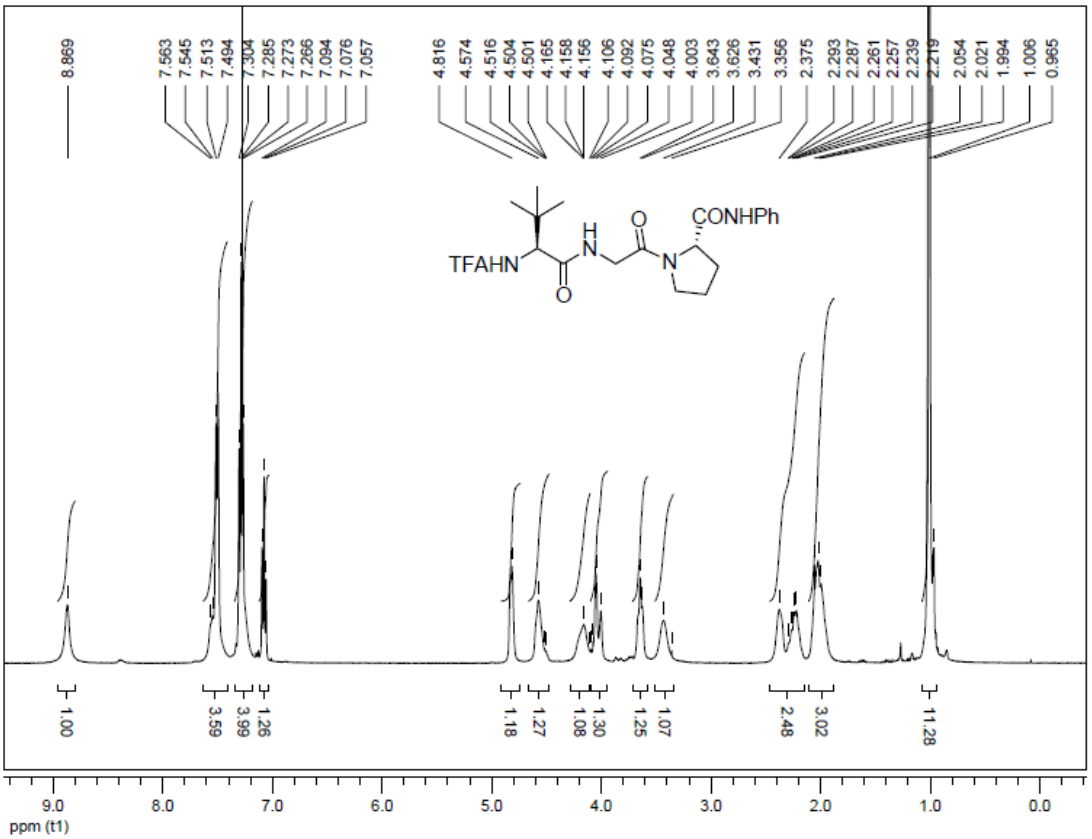


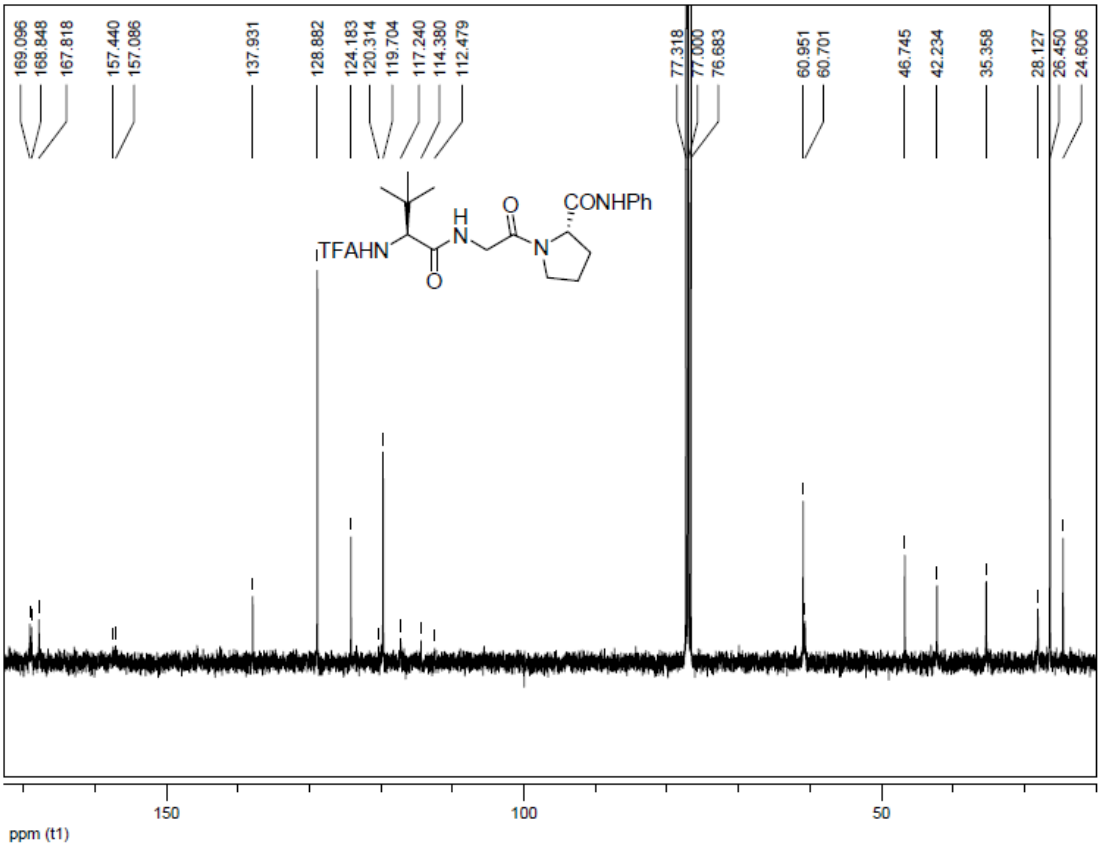
NMR spectra of compound **4**



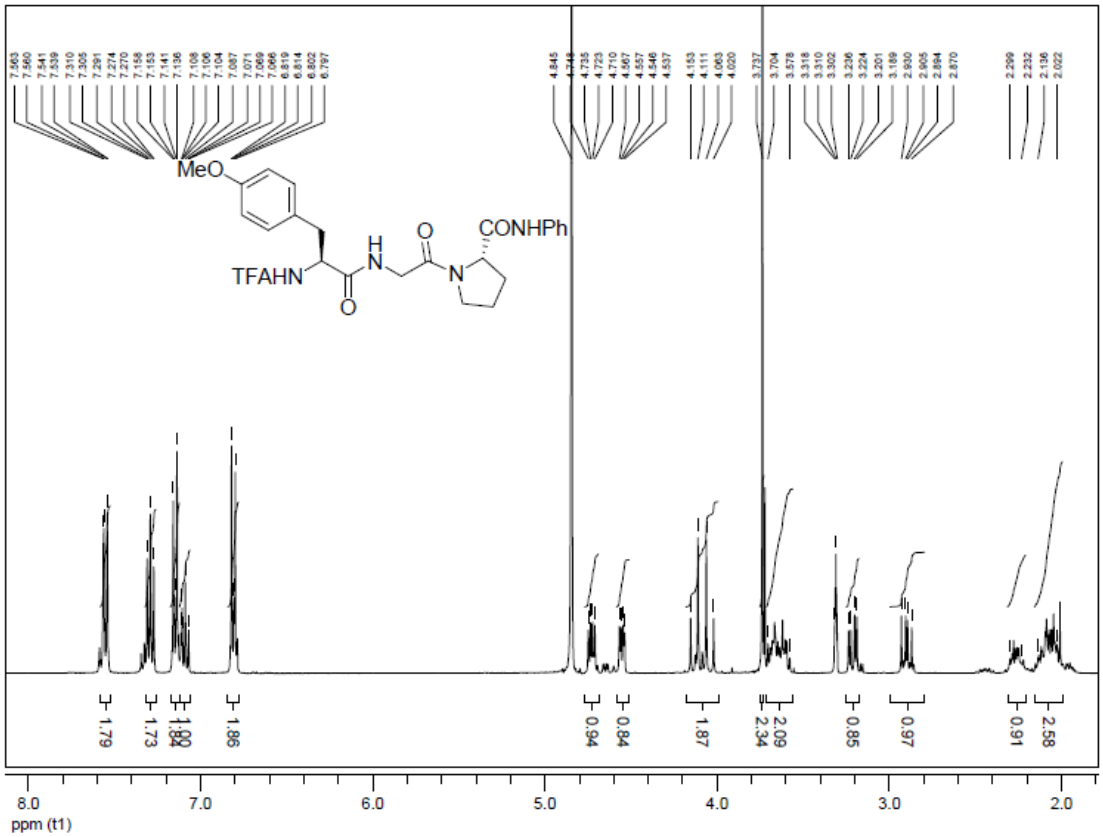


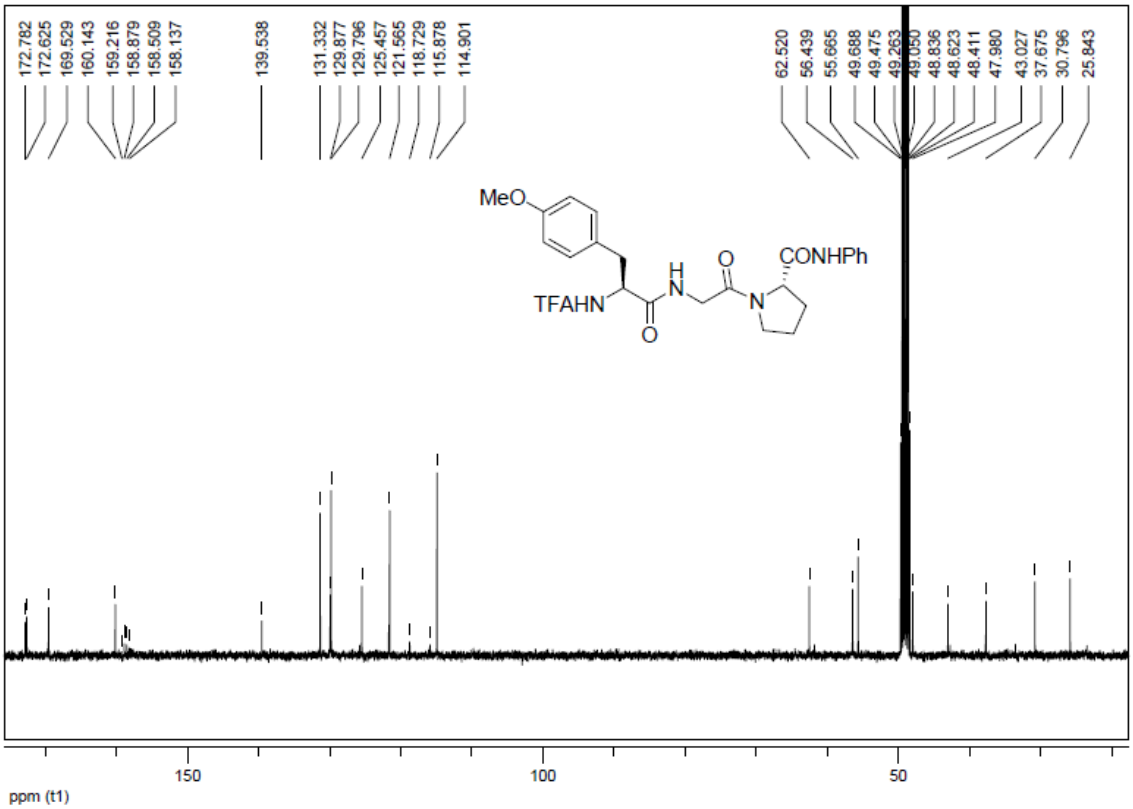
NMR spectra of compound **5**



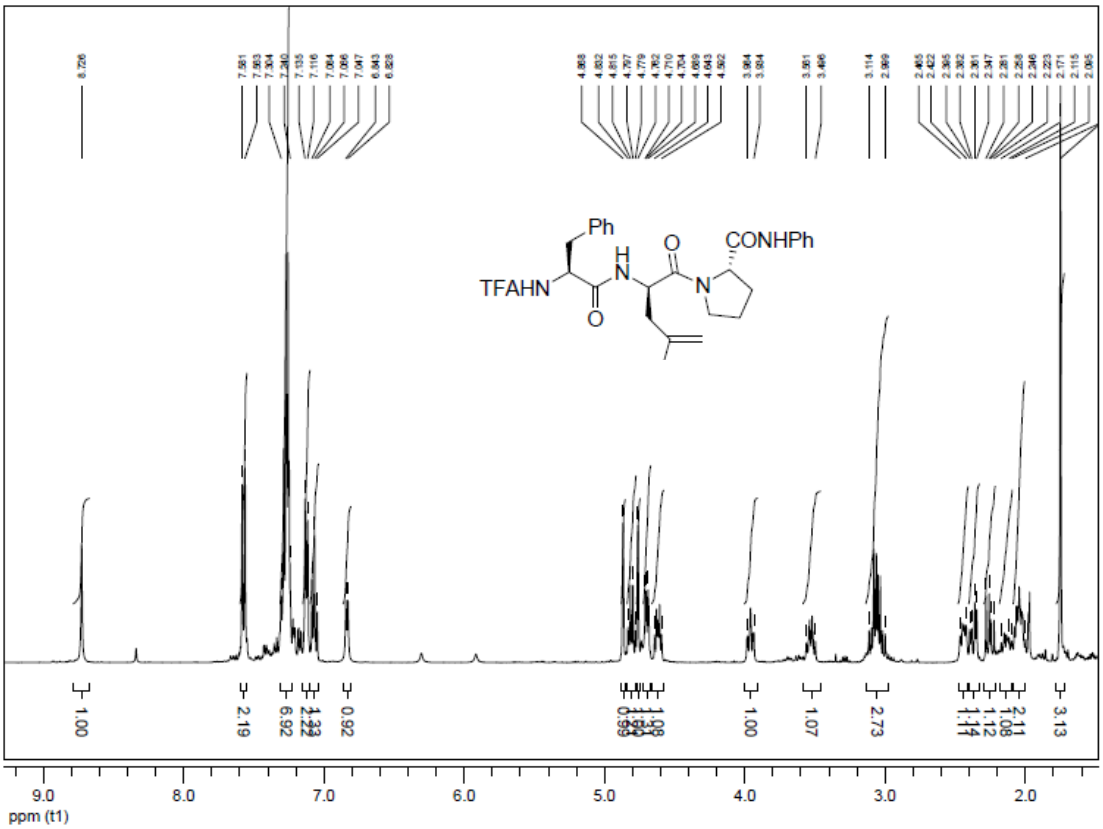


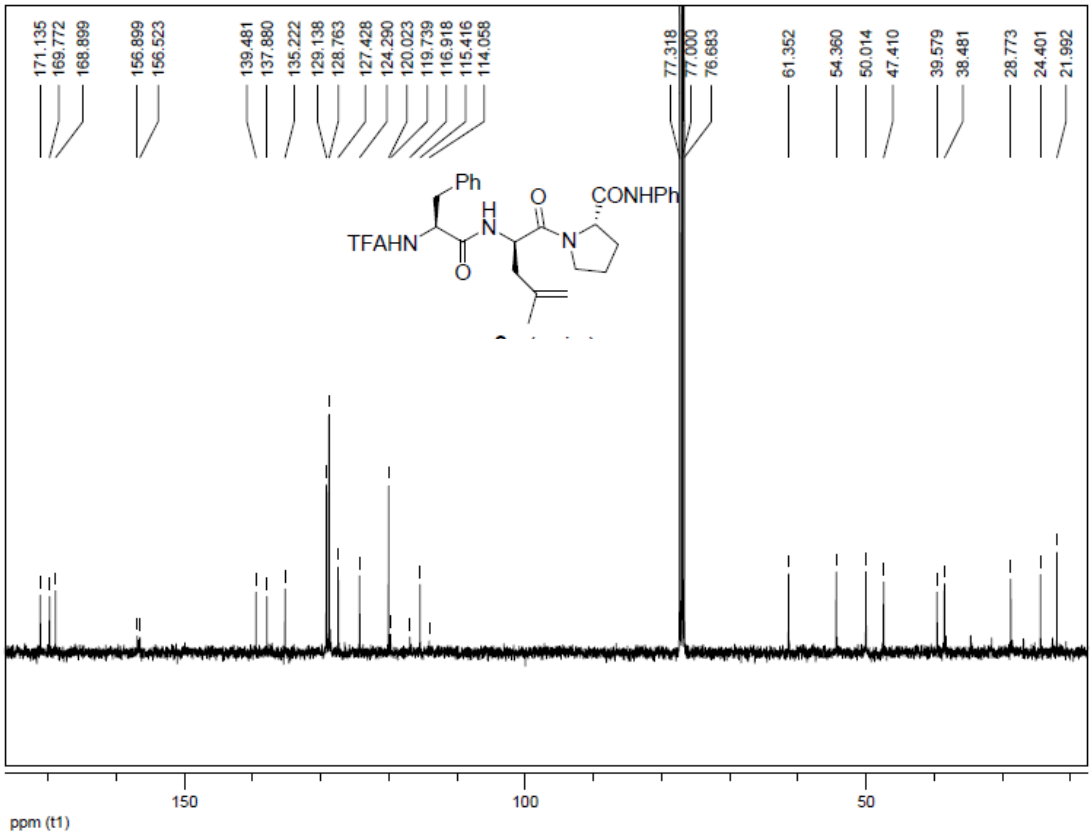
NMR spectra of compound **6**



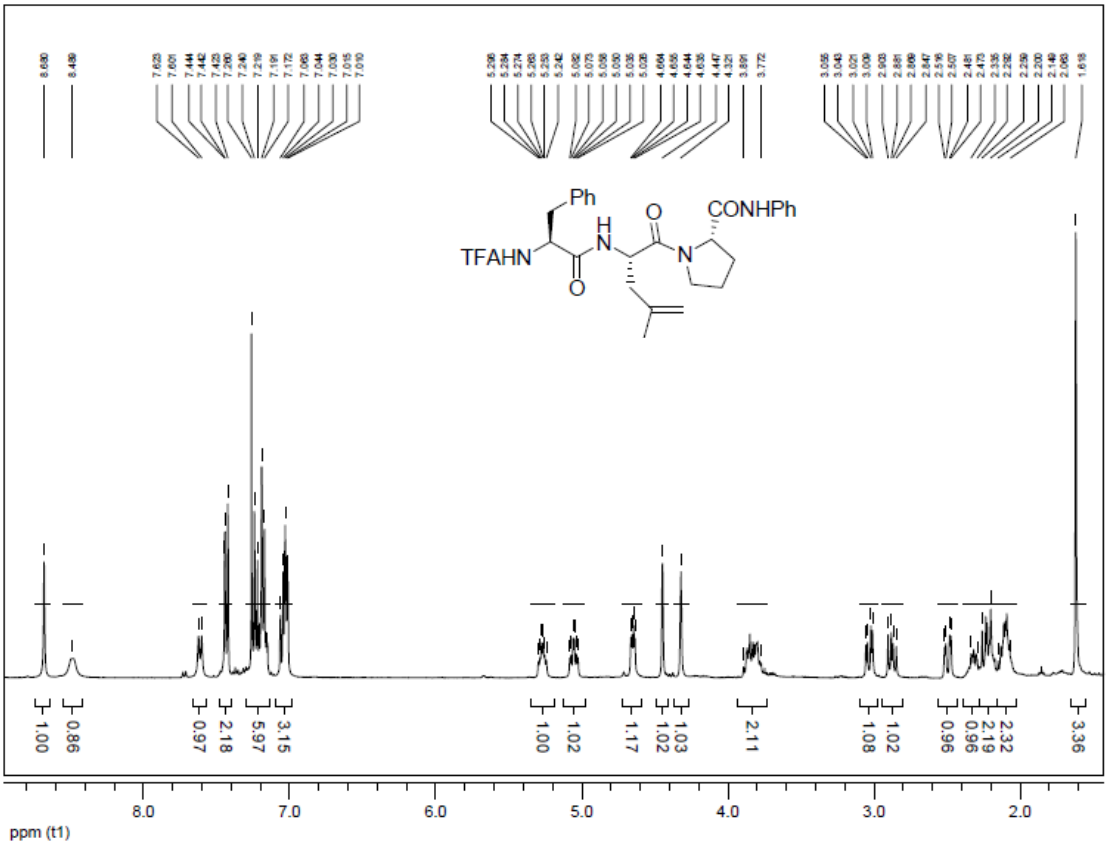


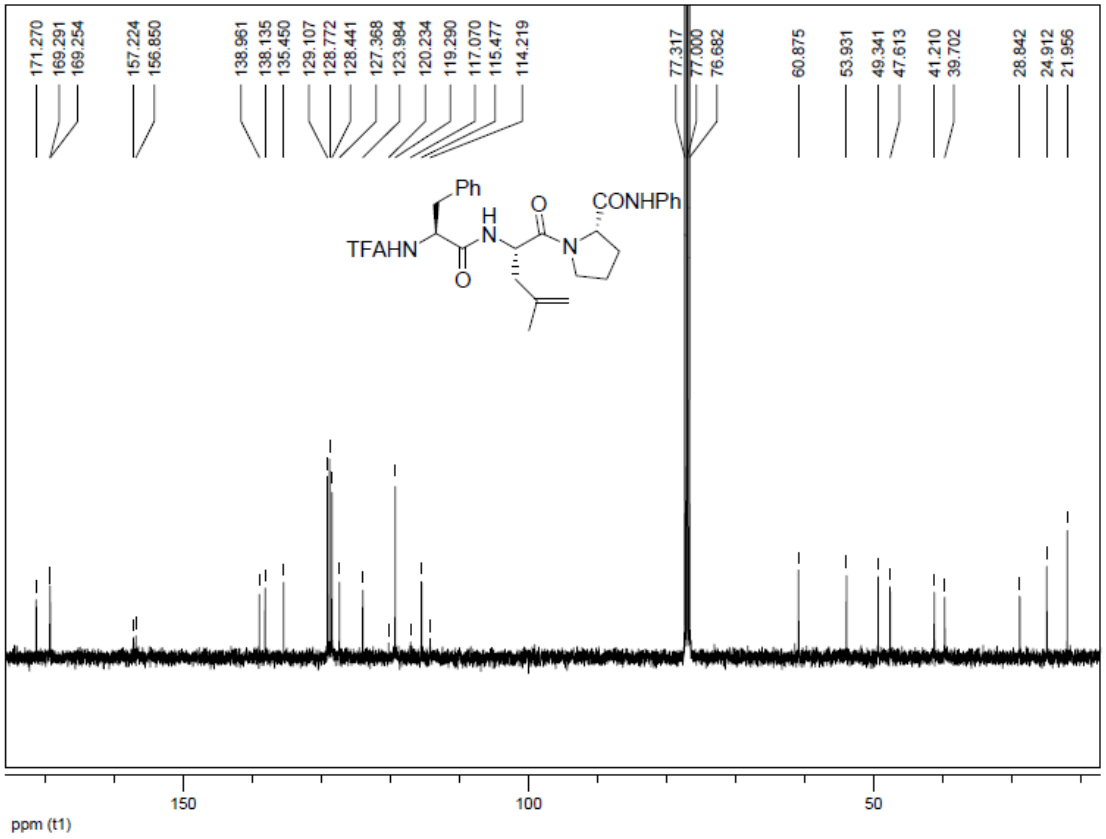
NMR spectra of compound **7a** (major diastereomer)



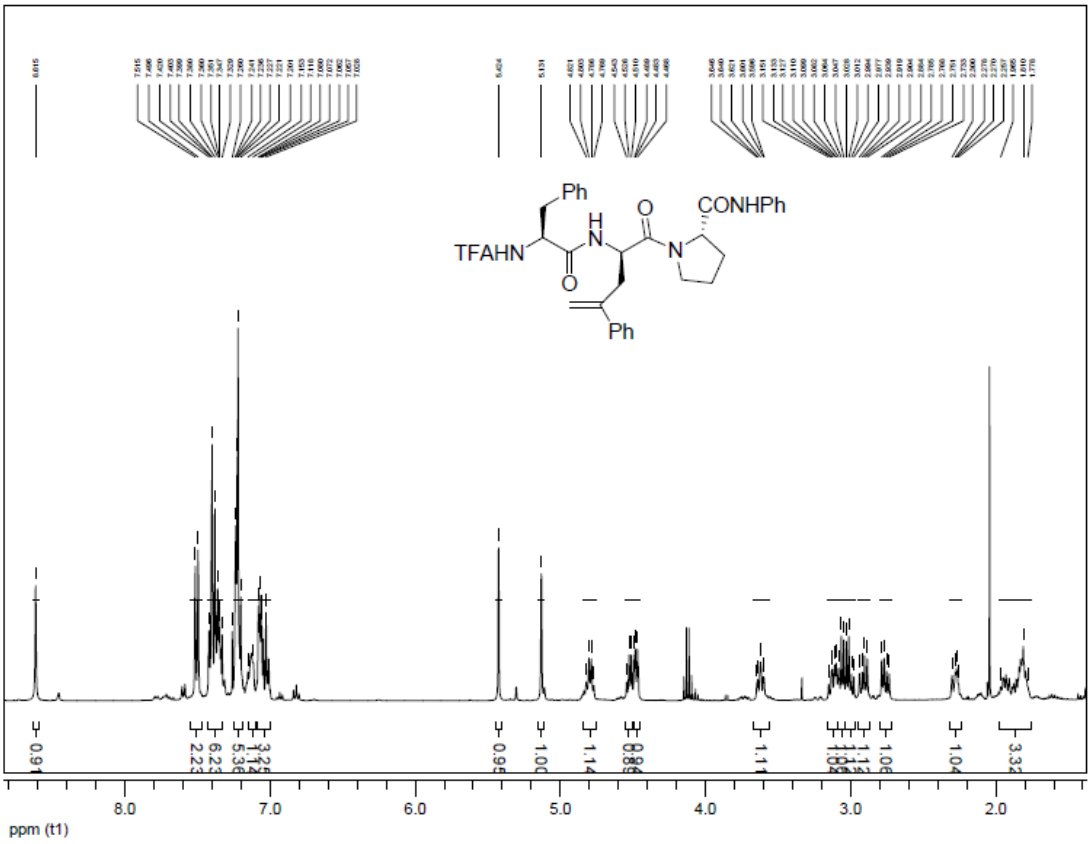


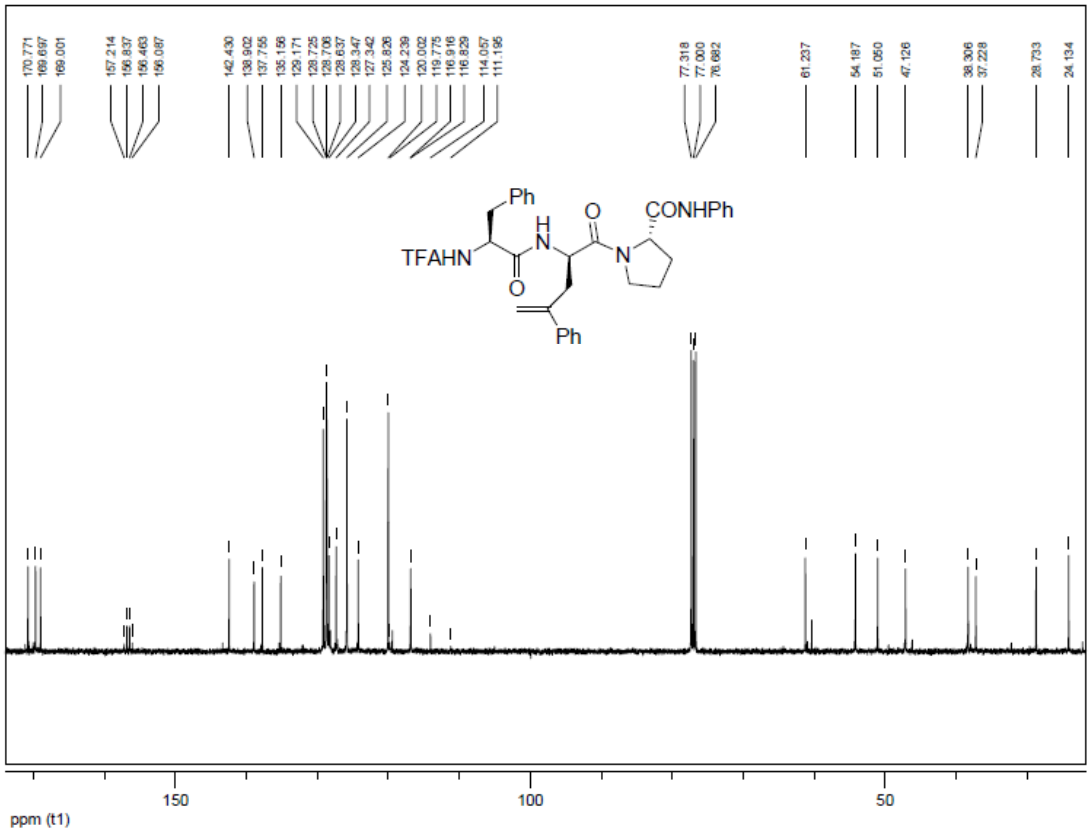
NMR spectra of compound **7a** (minor diastereomer)



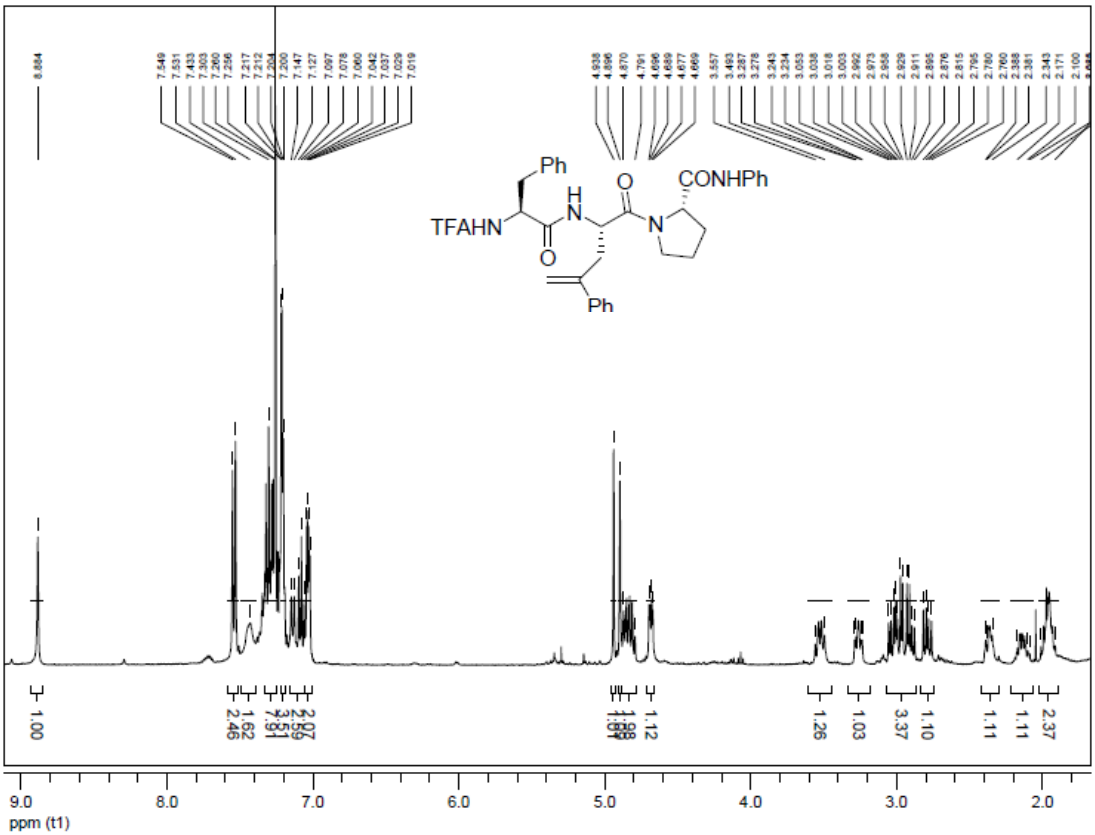


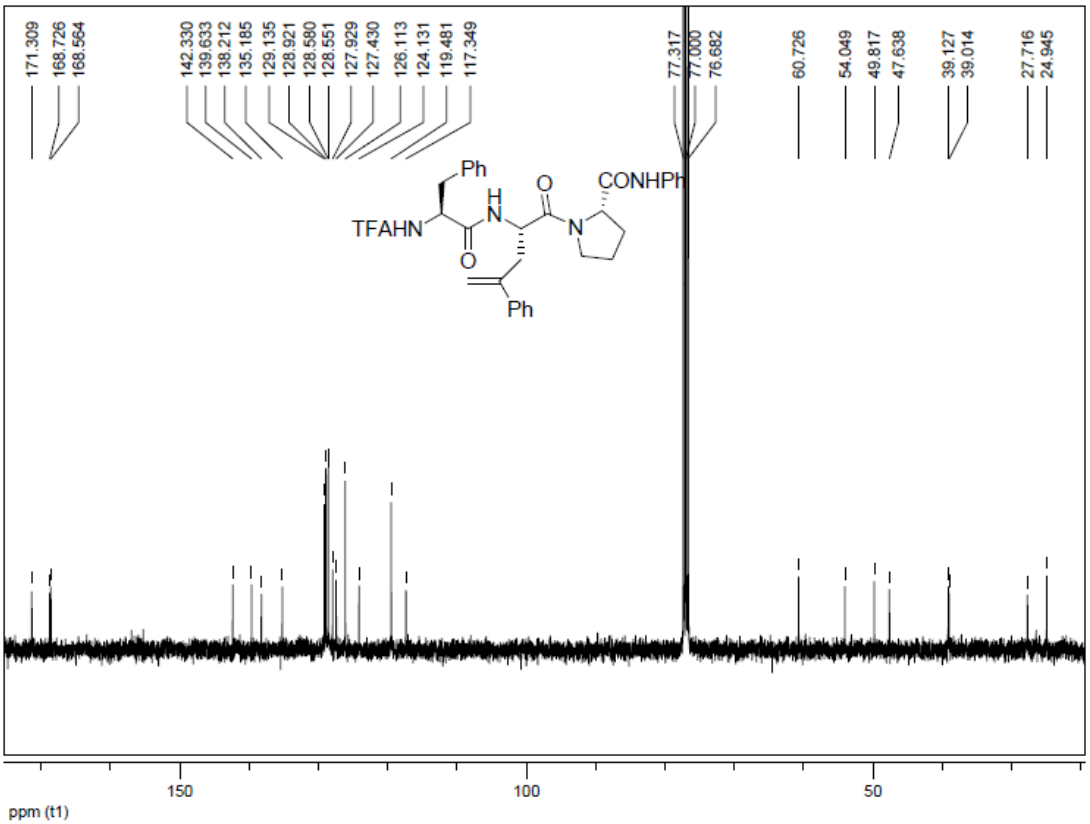
NMR spectra of compound **7b** (major diastereomer)



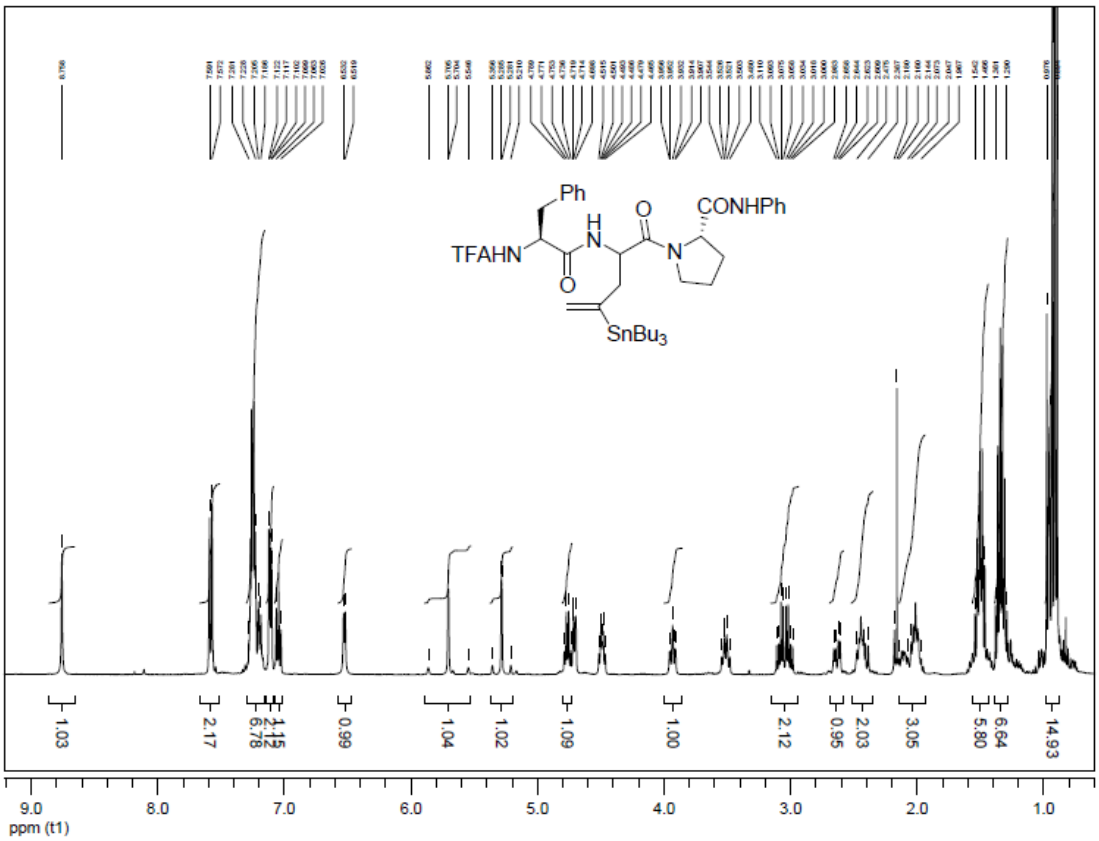


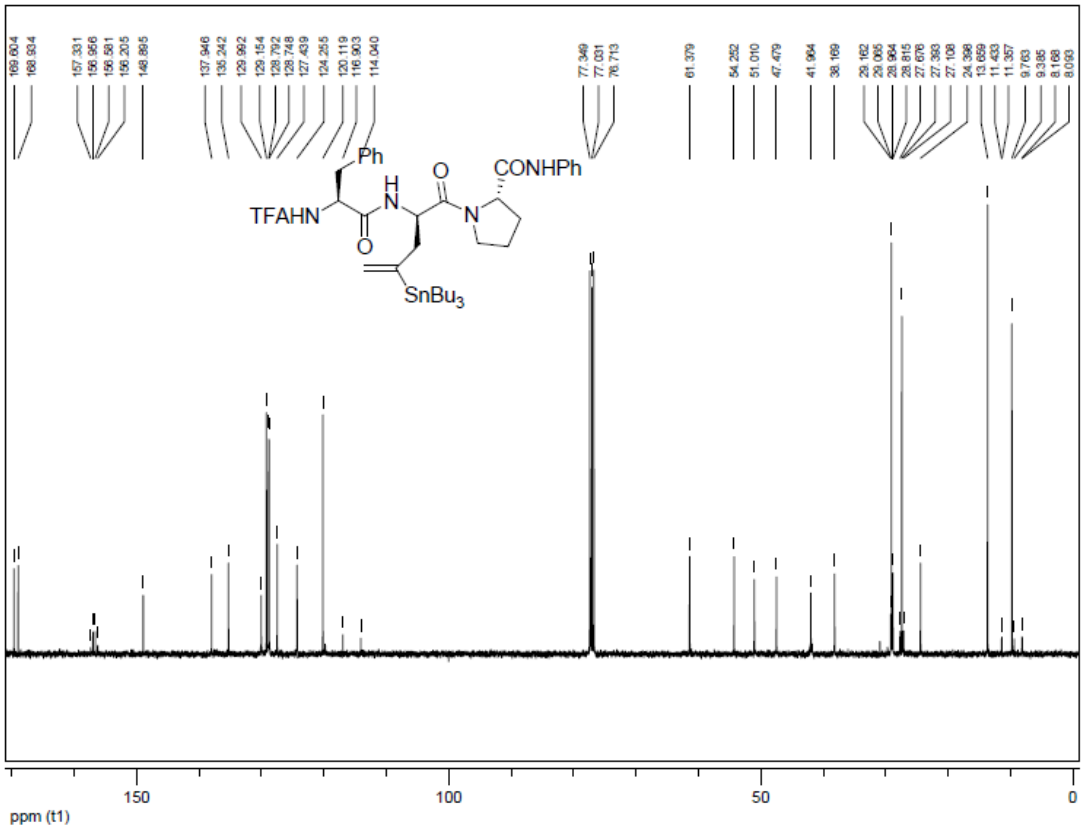
NMR spectra of compound **7b** (minor diastereomer)



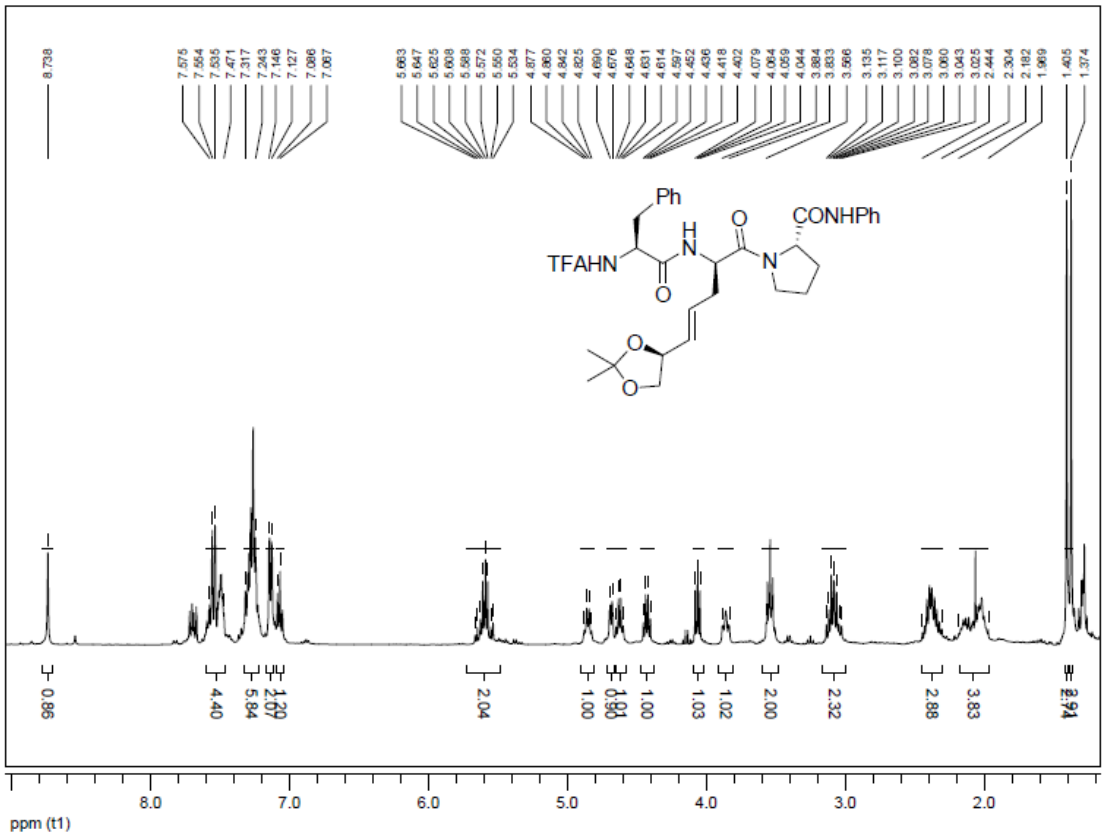


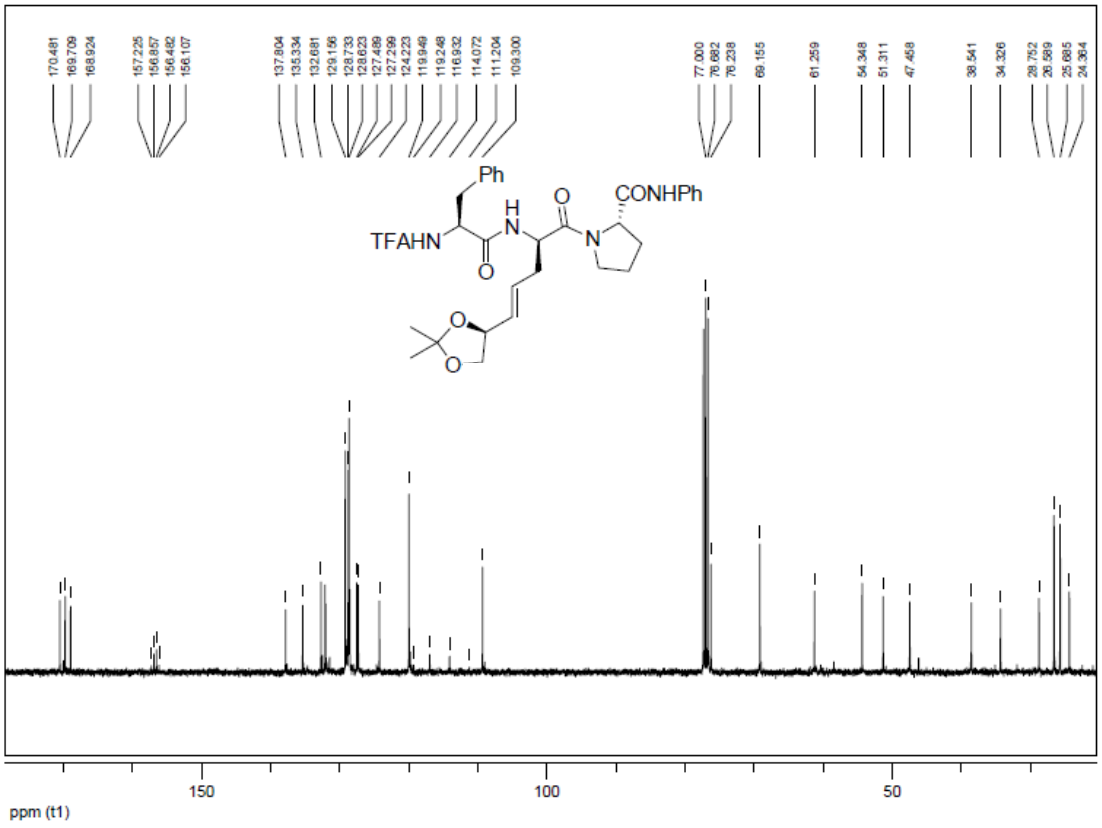
NMR spectra of compound **7c**



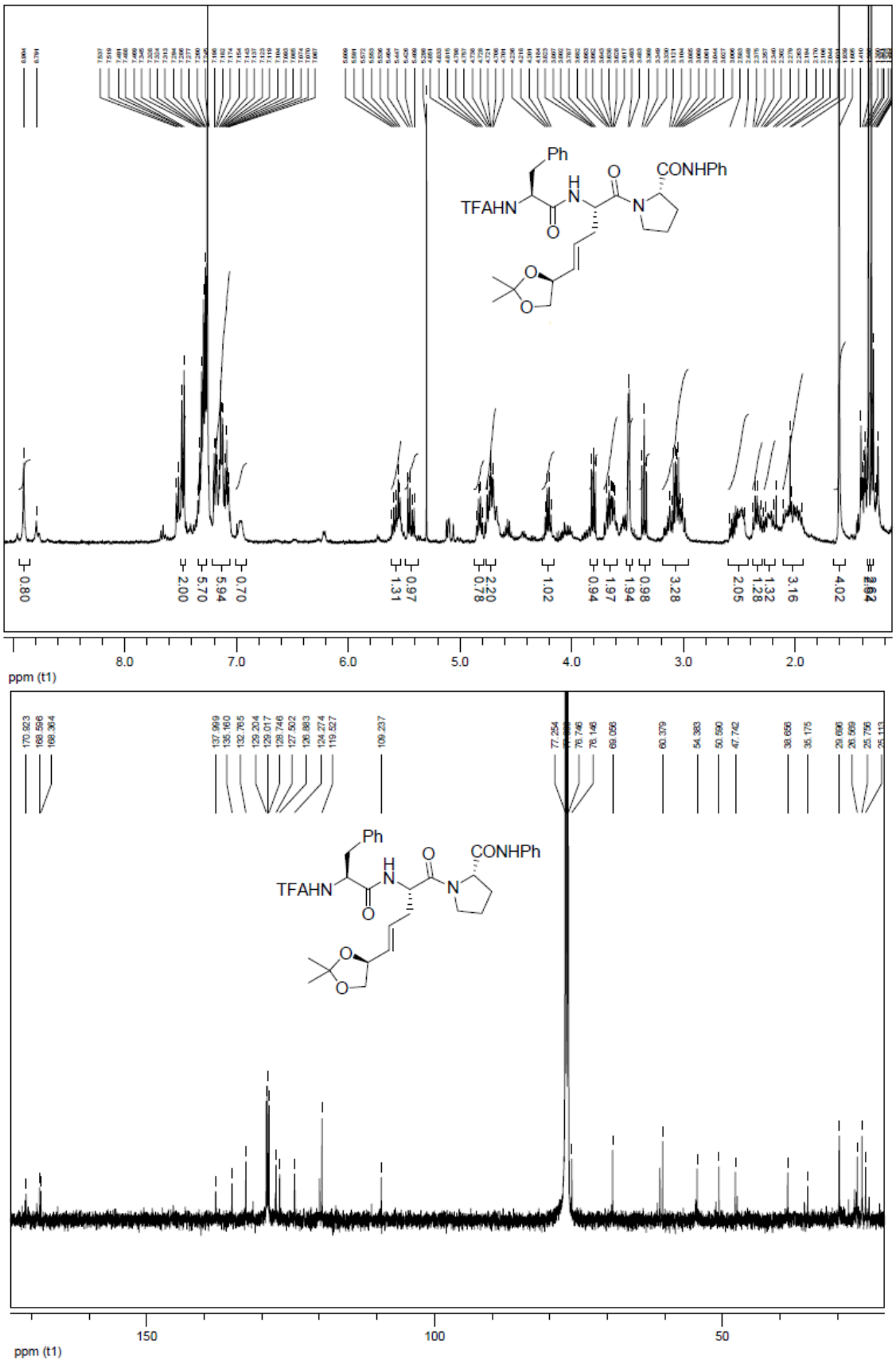


NMR spectra of compound **7d** (major diastereomer)

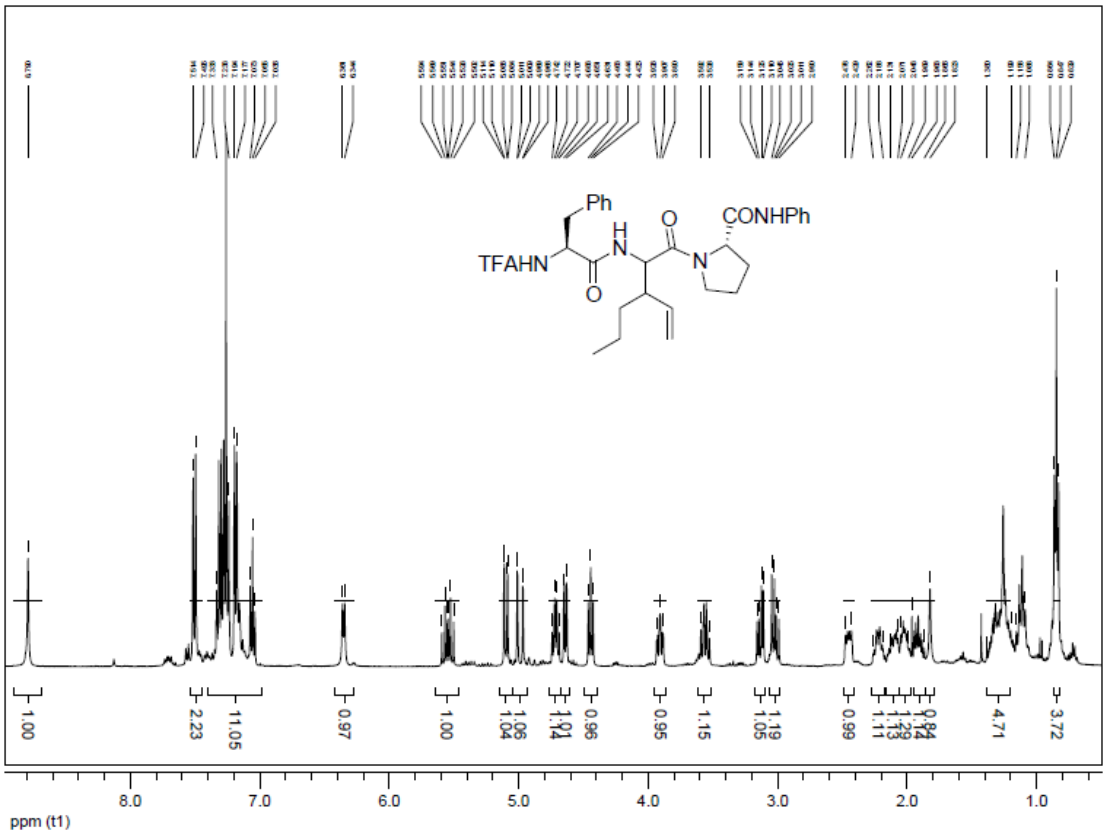


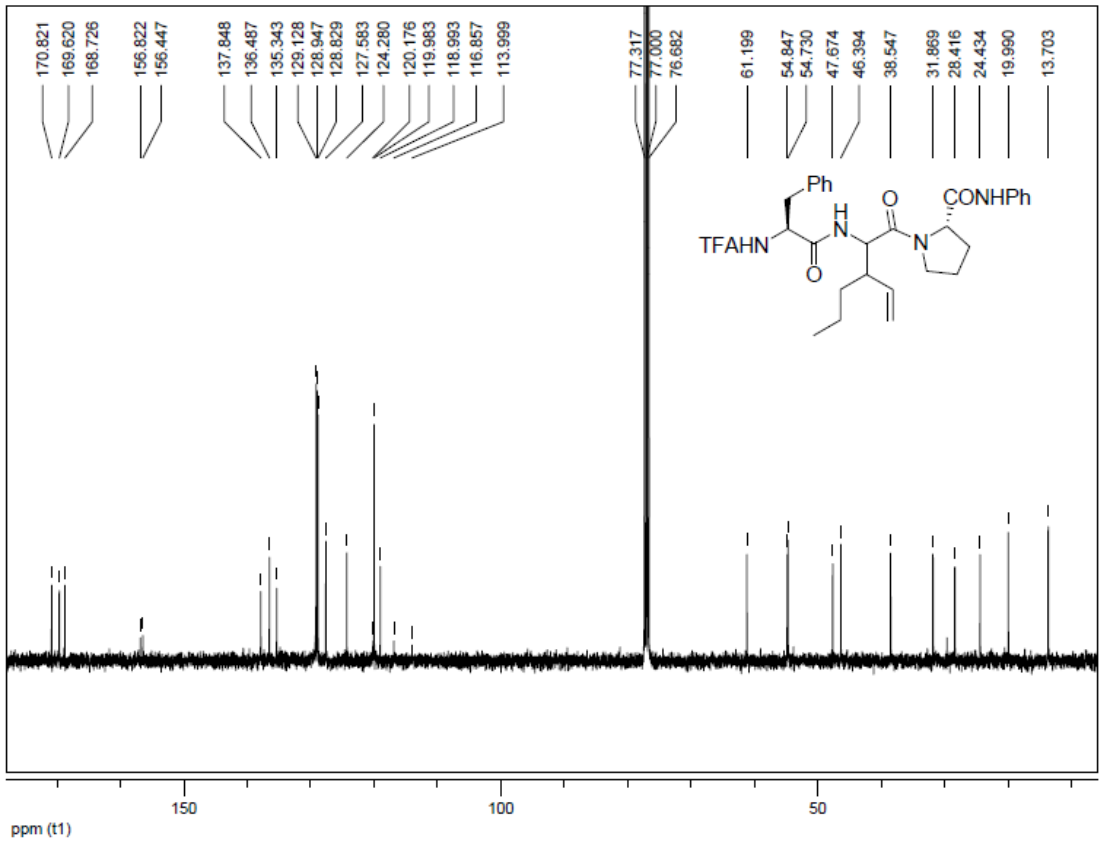


NMR spectra of compound **7d** (minor diastereomer)

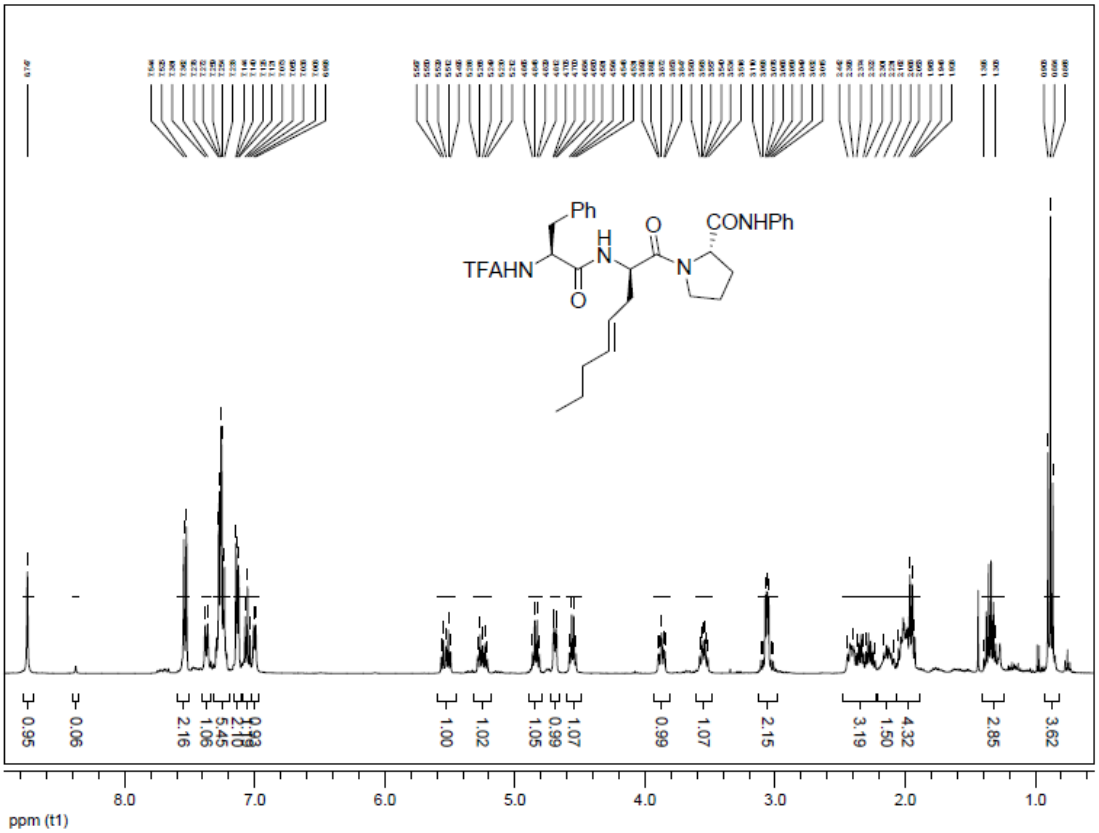


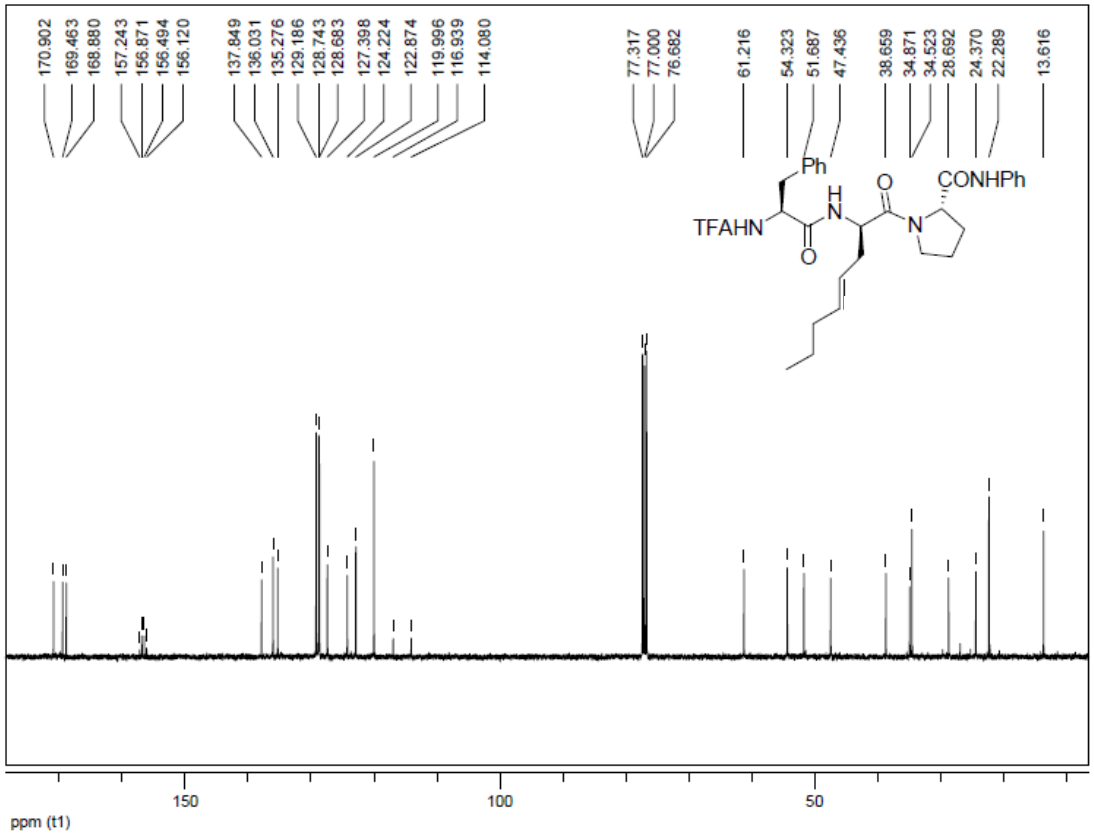
NMR spectra of compound **7e*b***



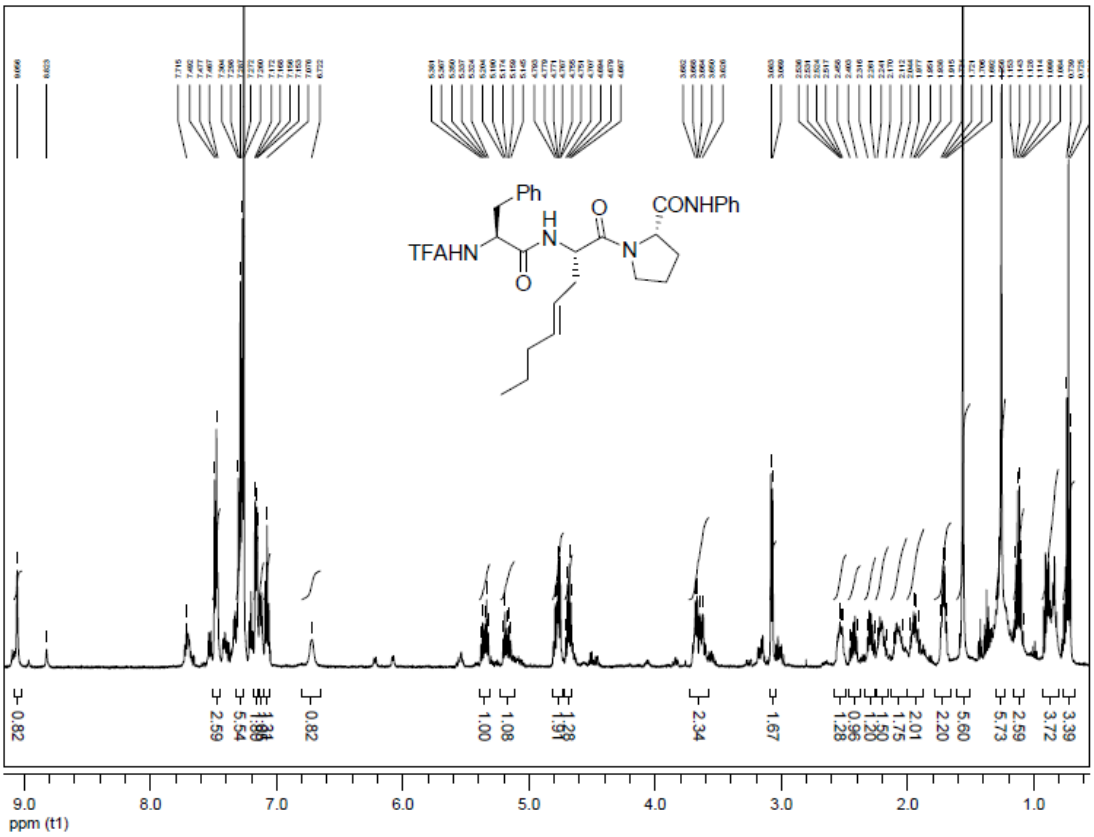


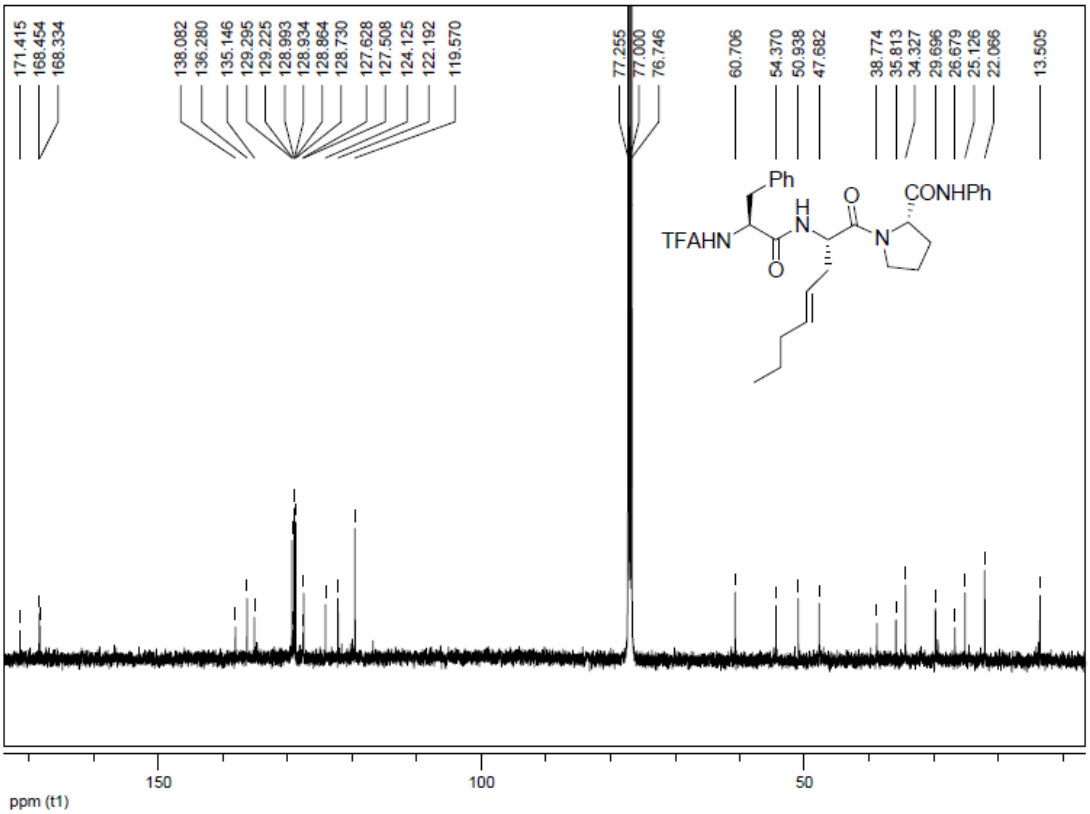
NMR spectra of compound **7e$_I$** (major product)



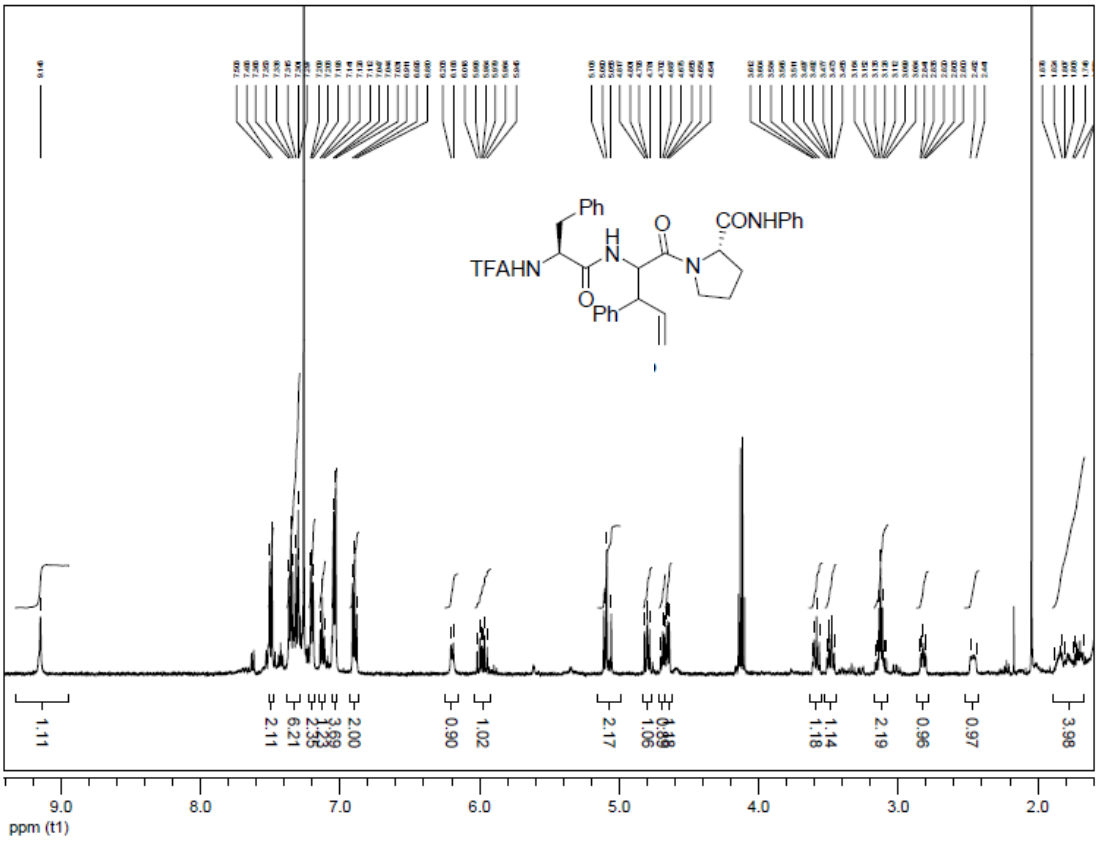


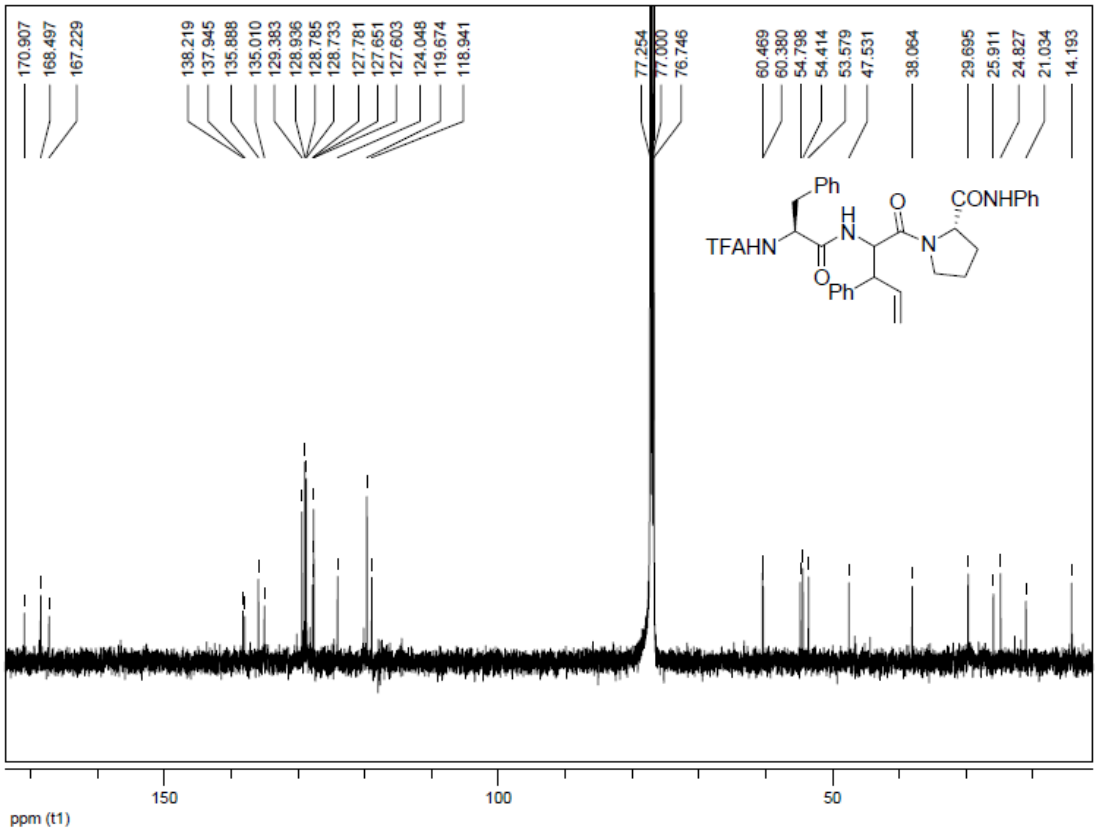
NMR spectra of compound **7e$_I$** (minor product)



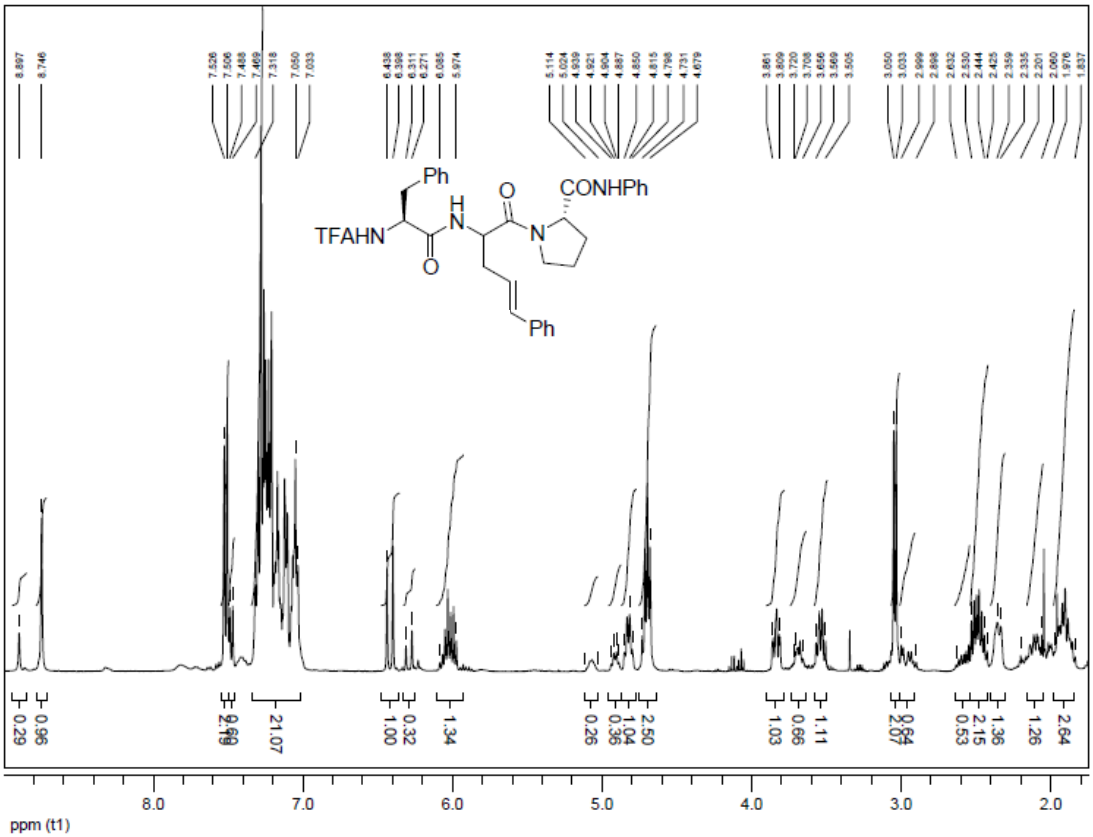


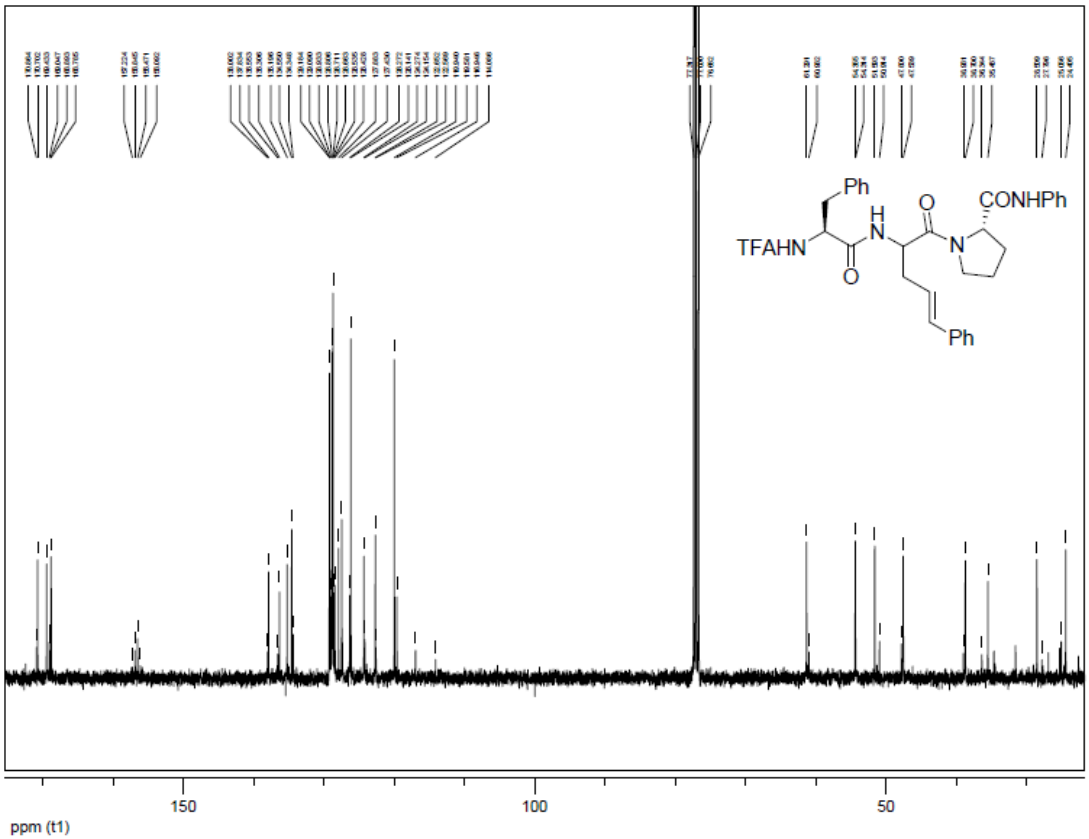
NMR spectra of compound **7f$_b$**



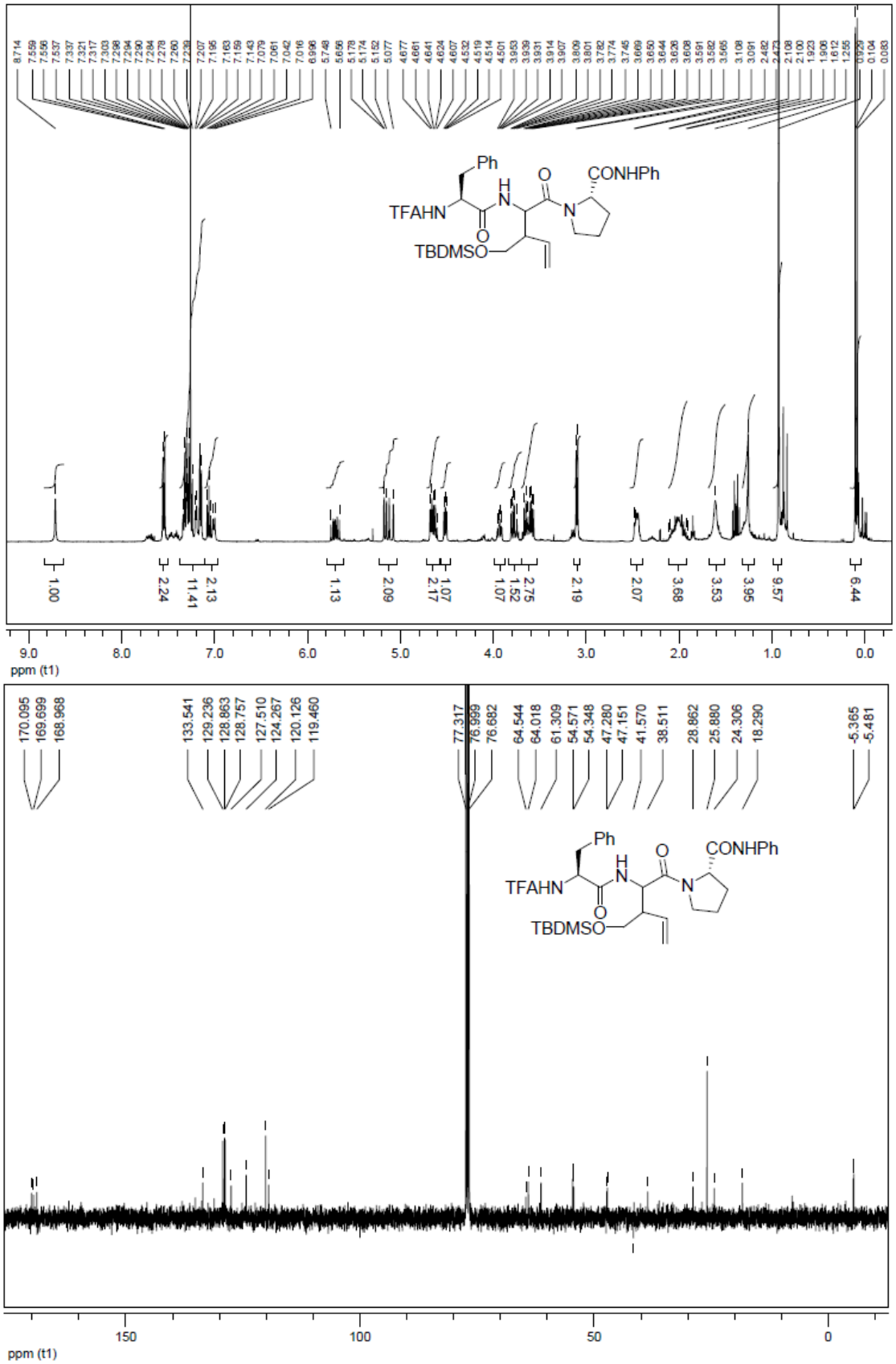


NMR spectra of compound **7f$_l$**

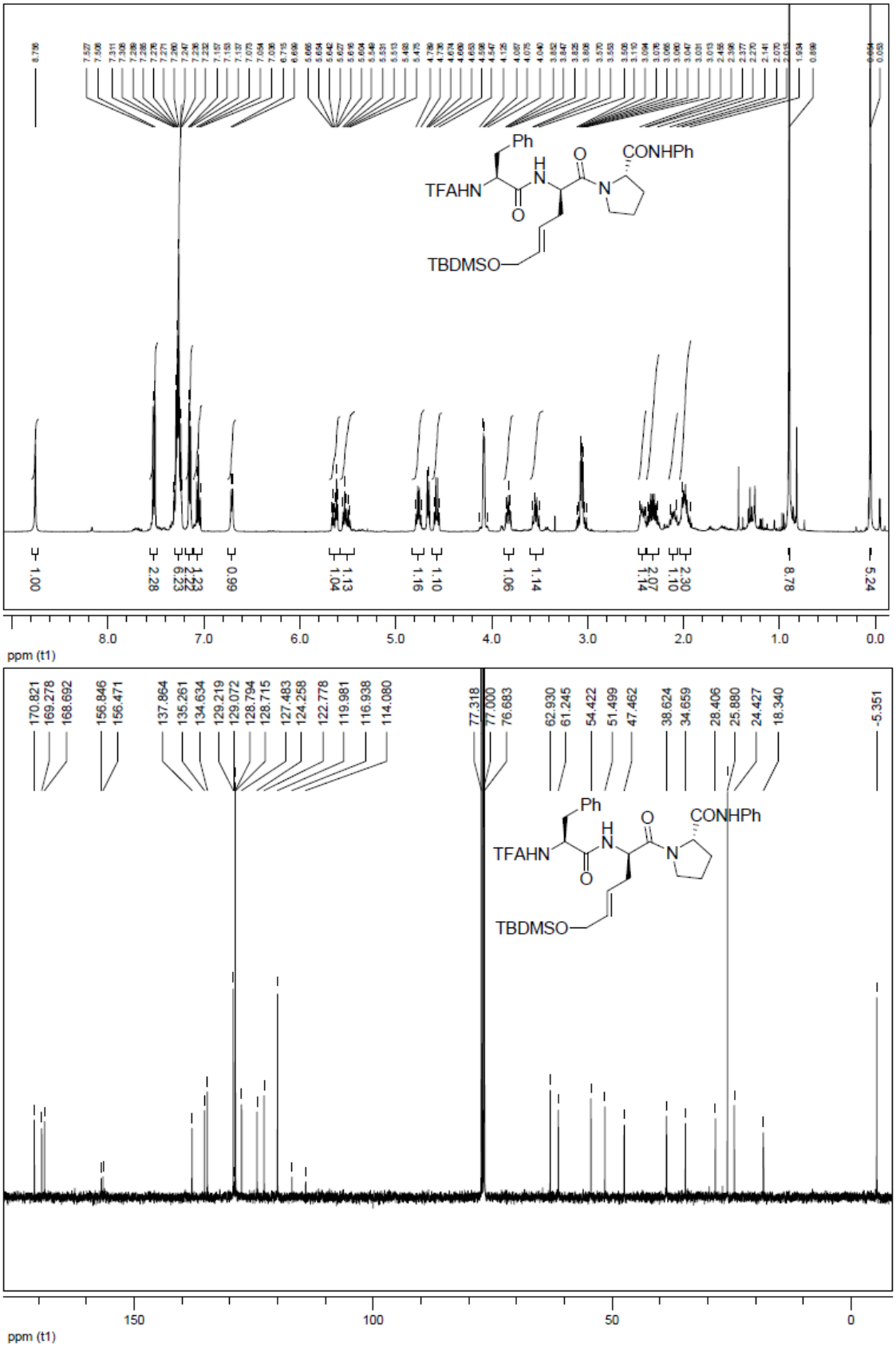




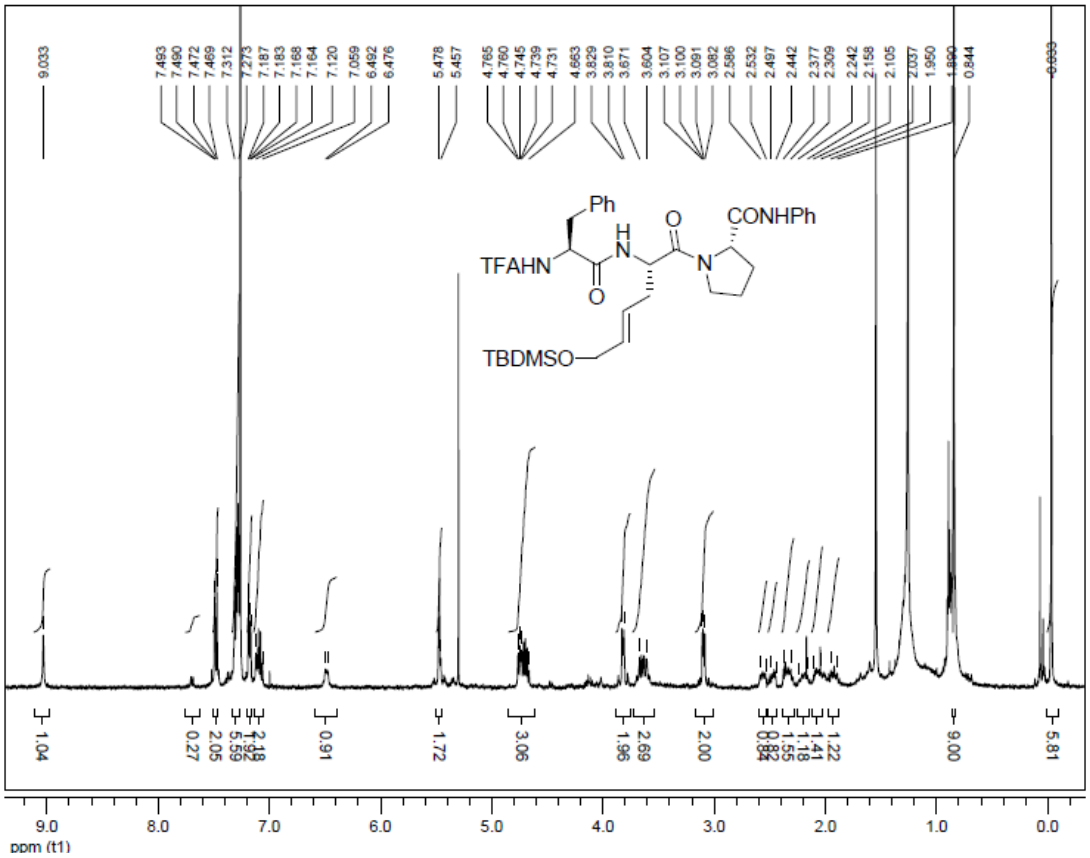
NMR spectra of compound **7g*b***

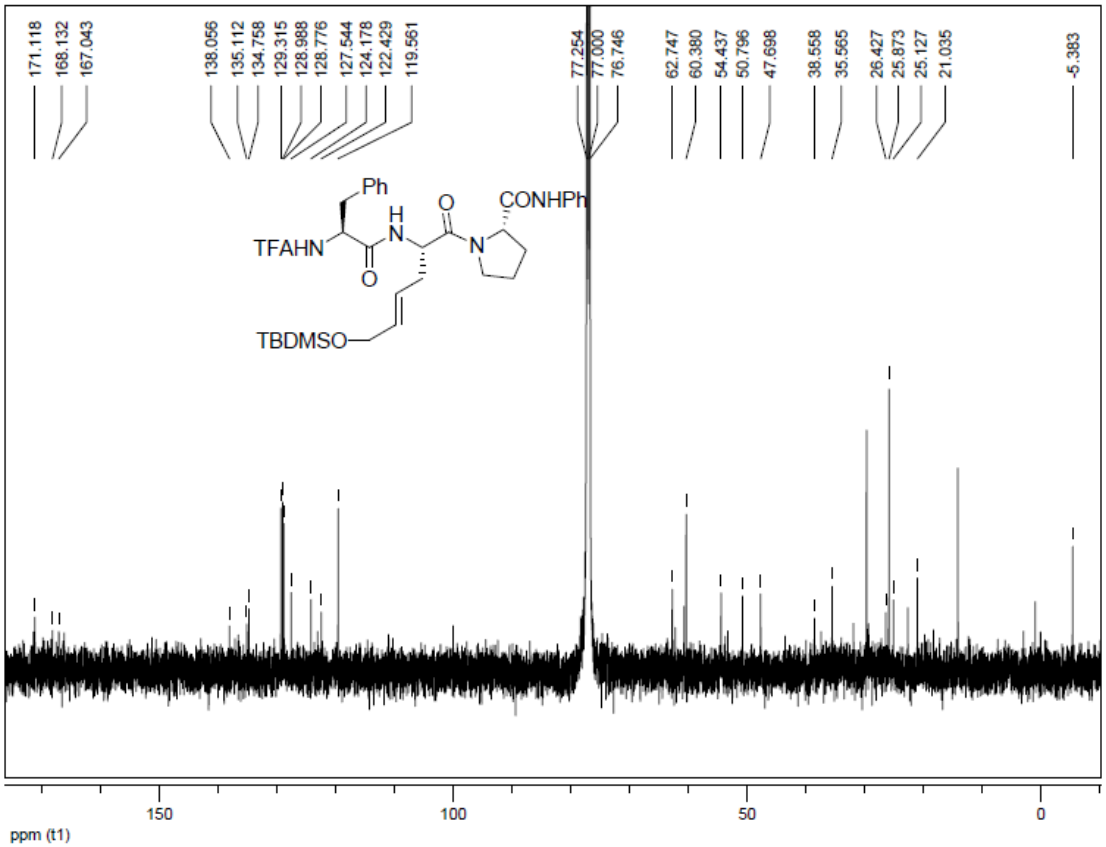


NMR spectra of compound **7g*l*** (major diastereomer)

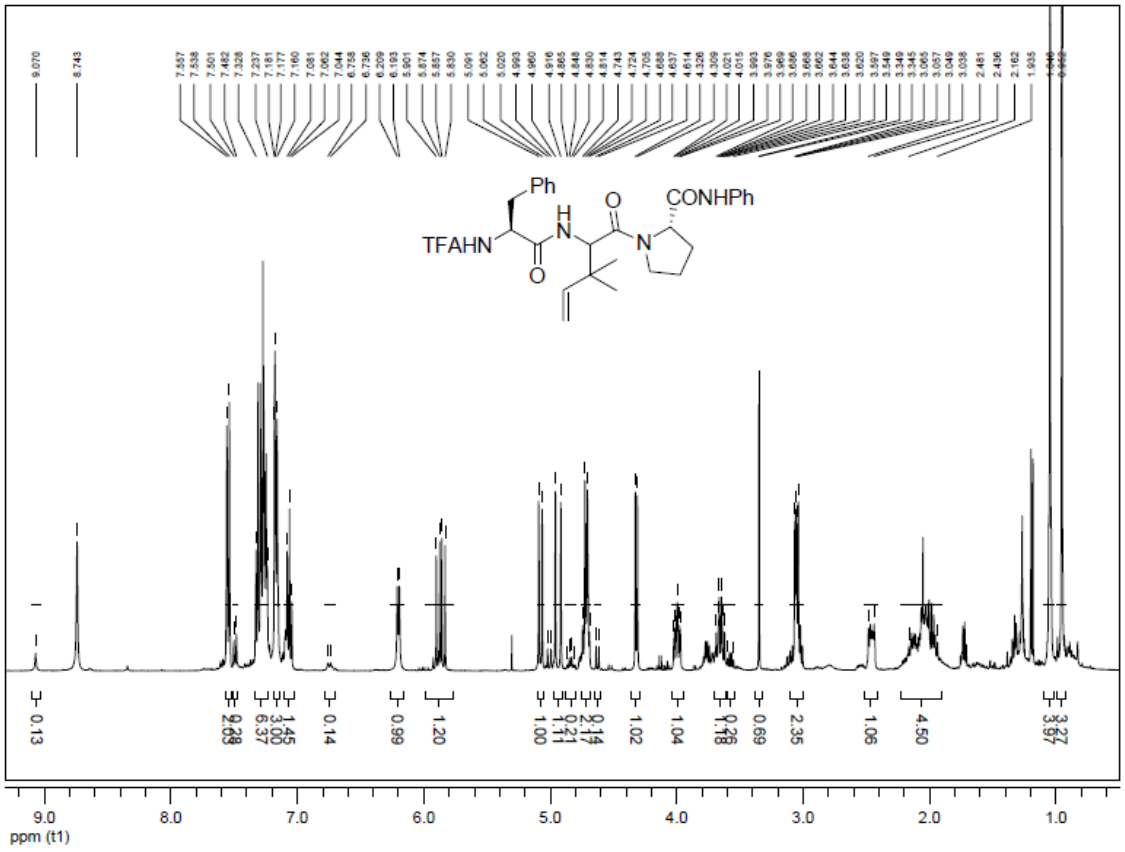


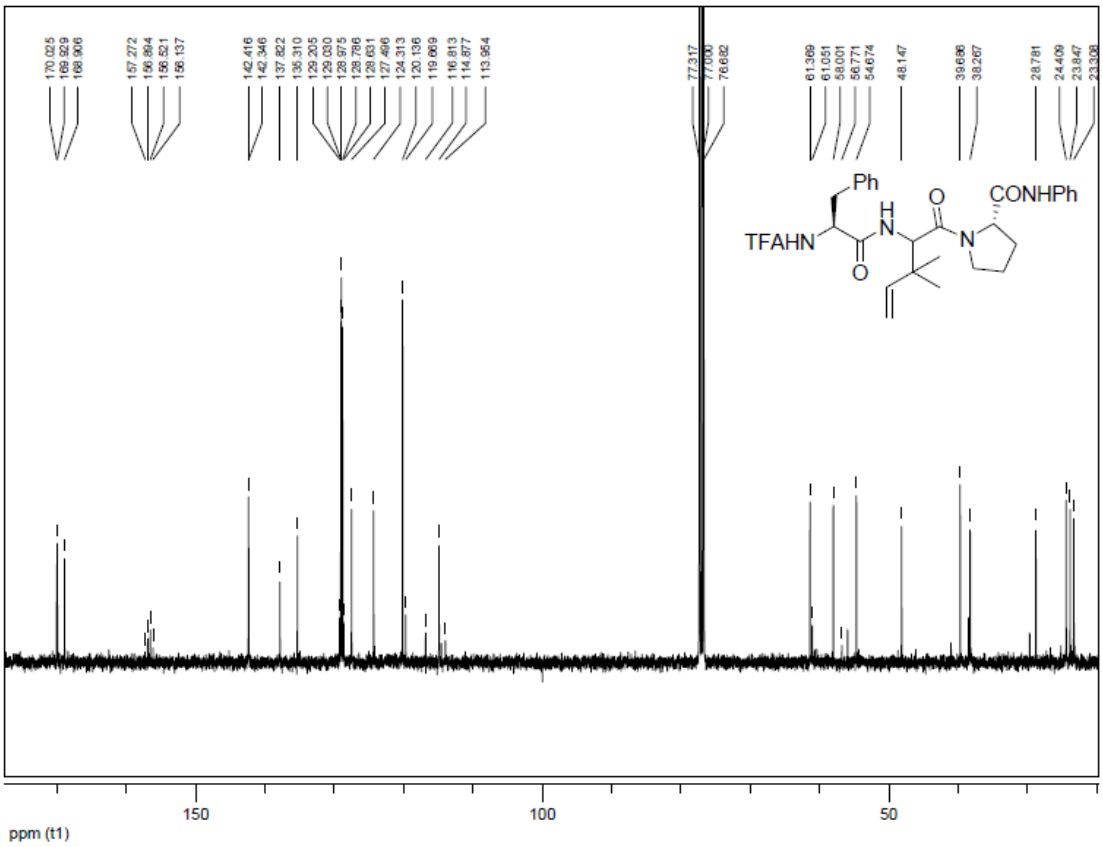
NMR spectra of compound **7g$_I$** (minor diastereomer)



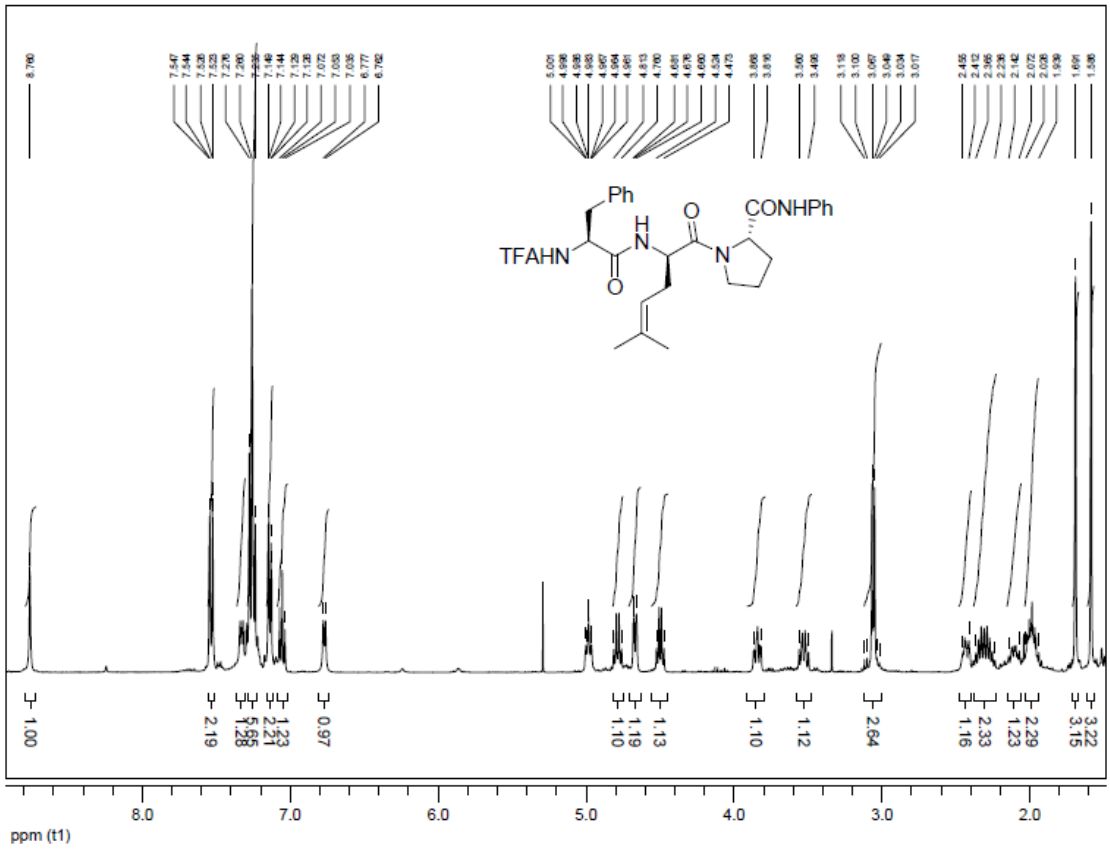


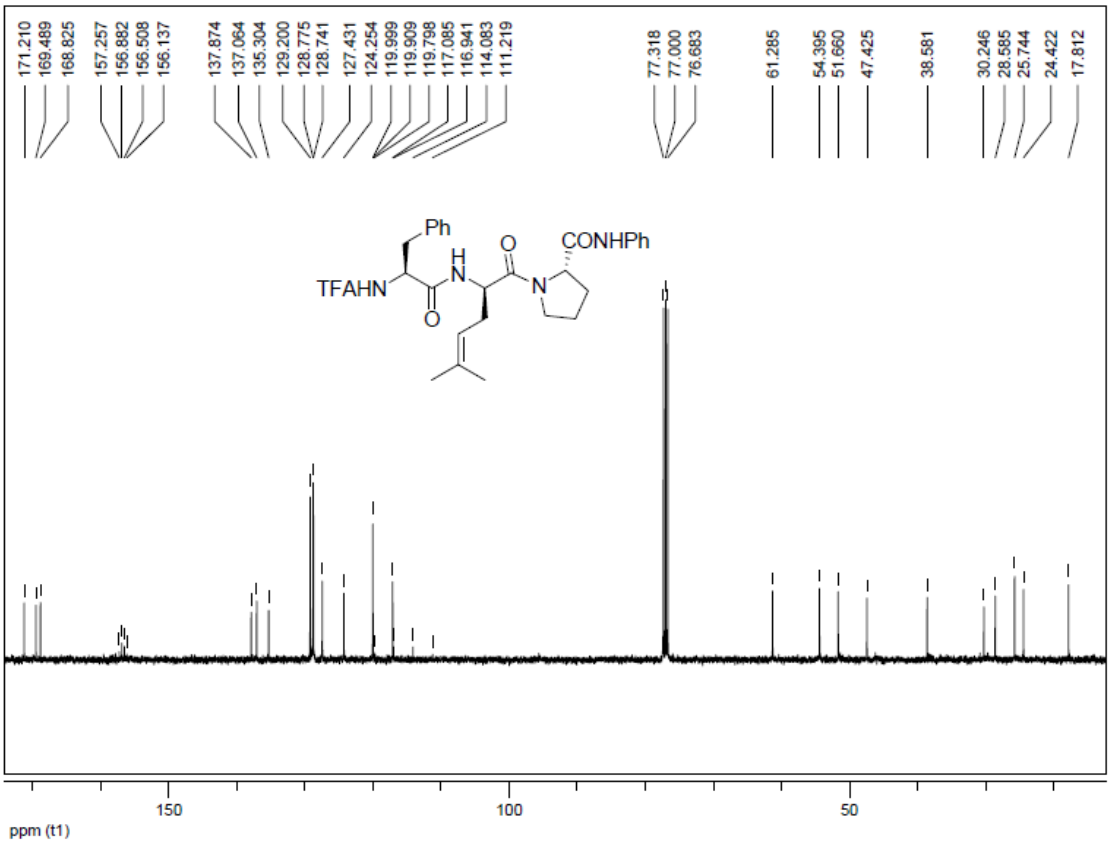
NMR spectra of compound **7h*b***



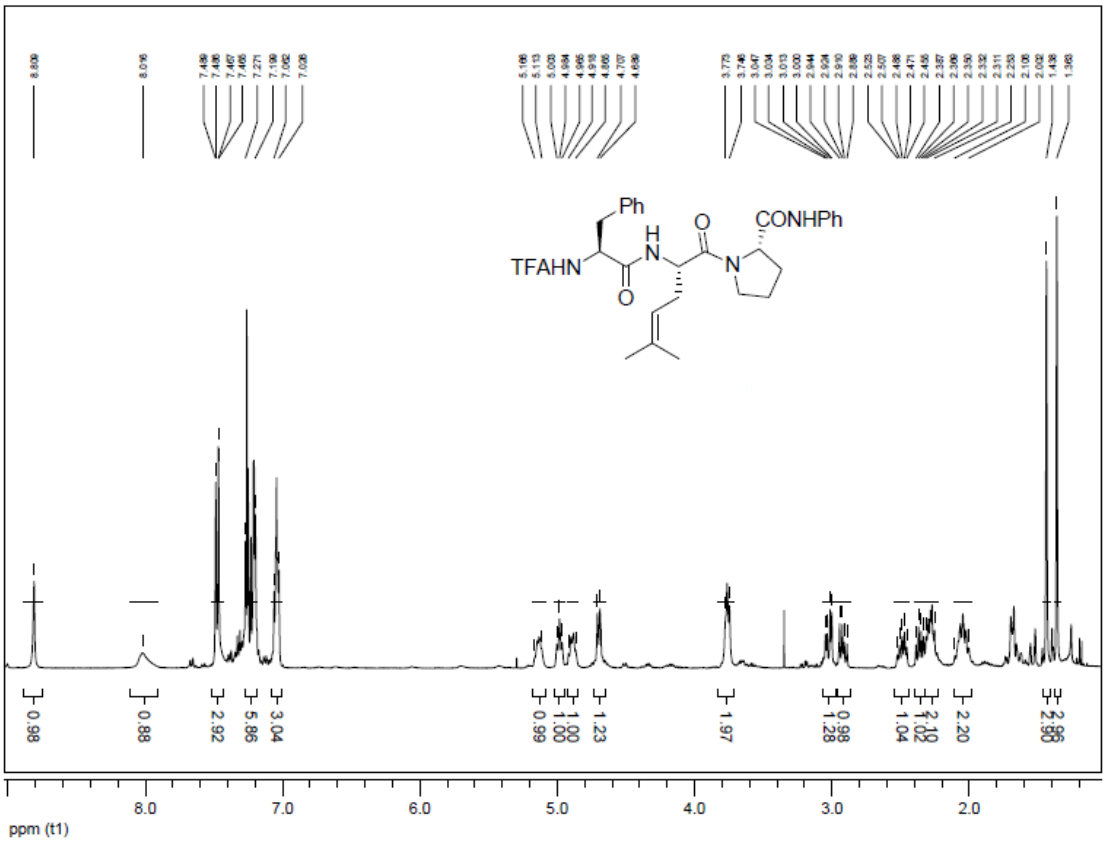


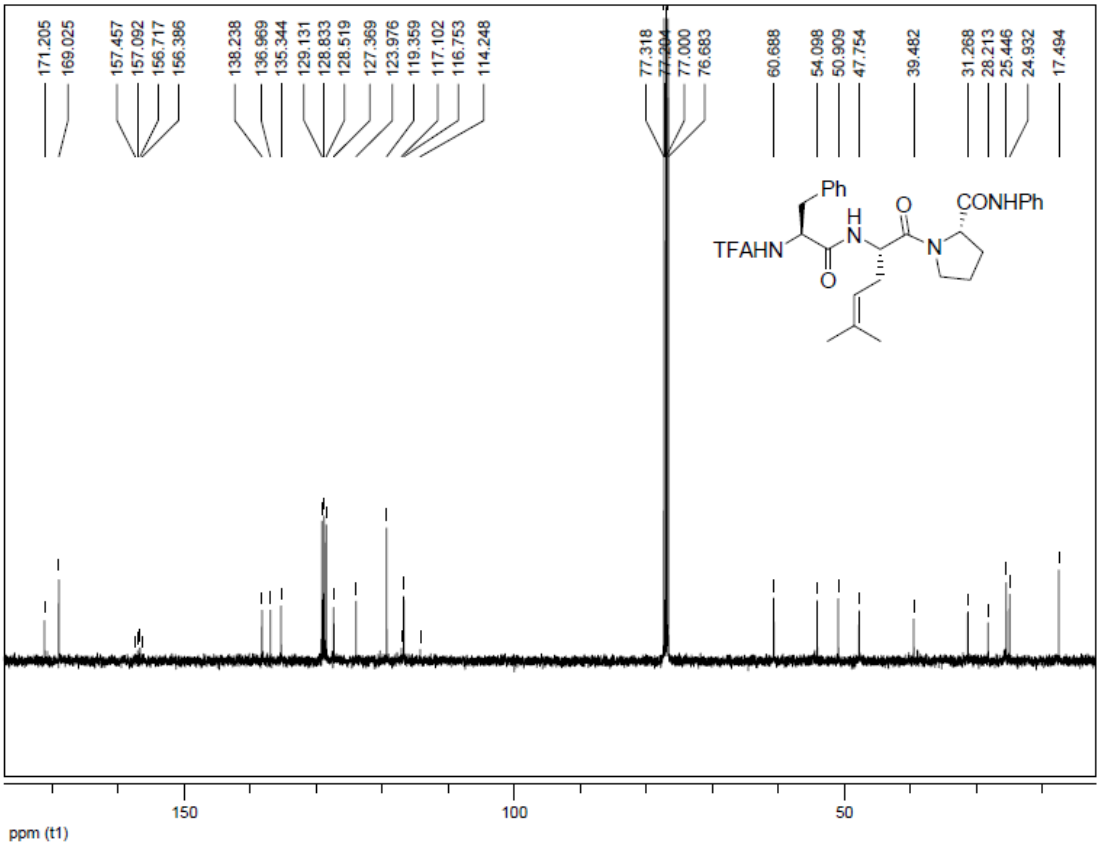
NMR spectra of compound **7h$_l$** (major diastereomer)



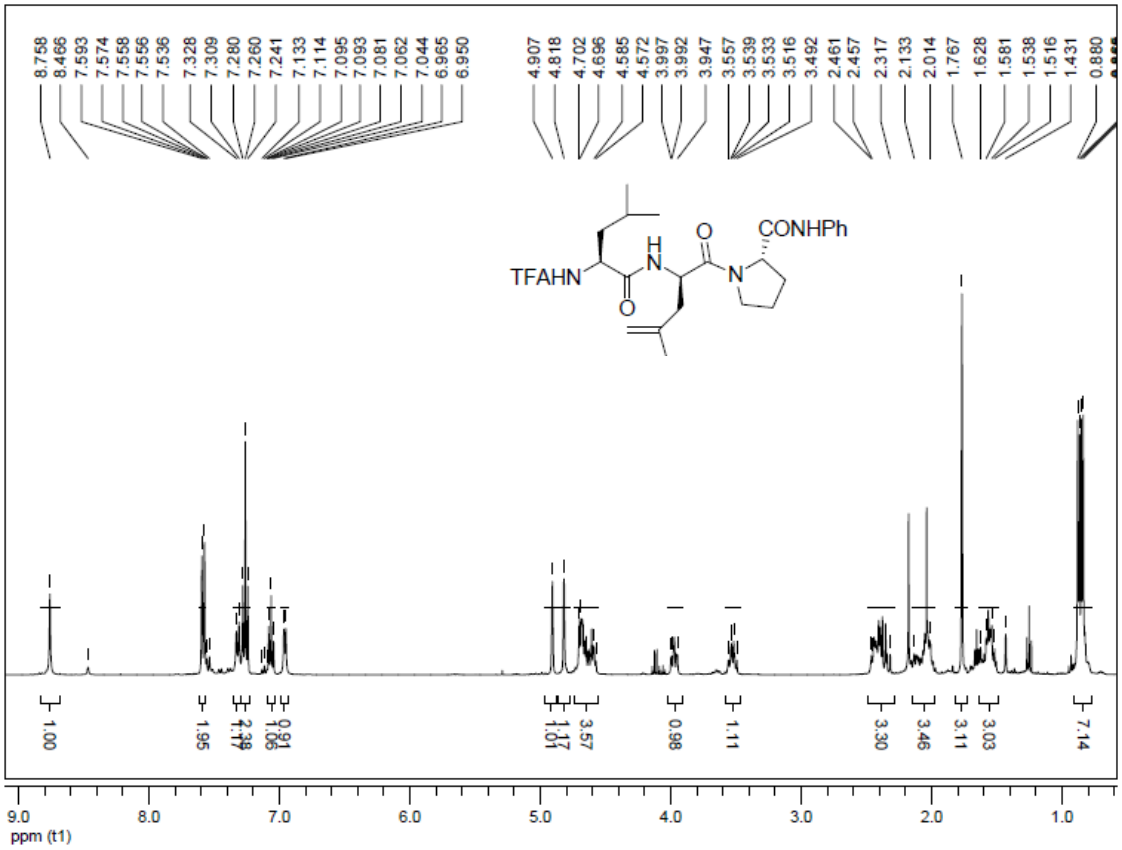


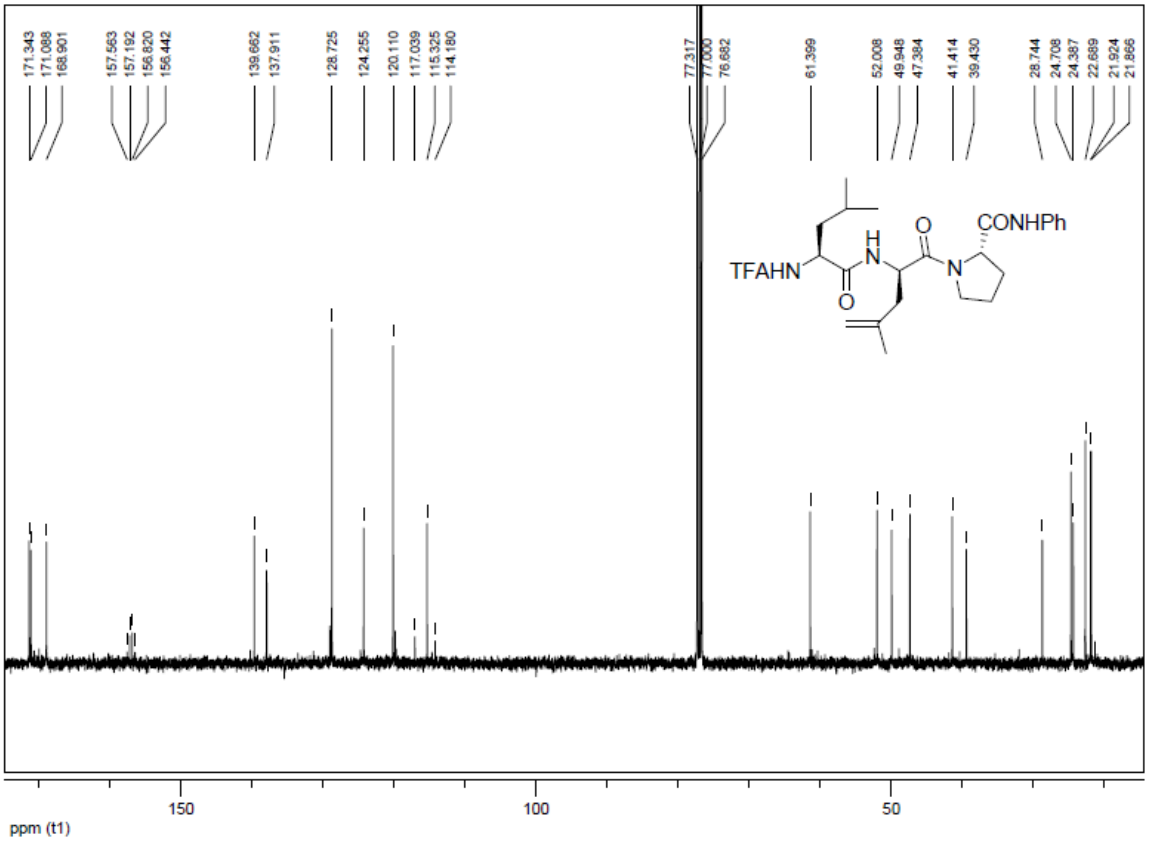
NMR spectra of compound **7h$_I$** (minor diastereomer)



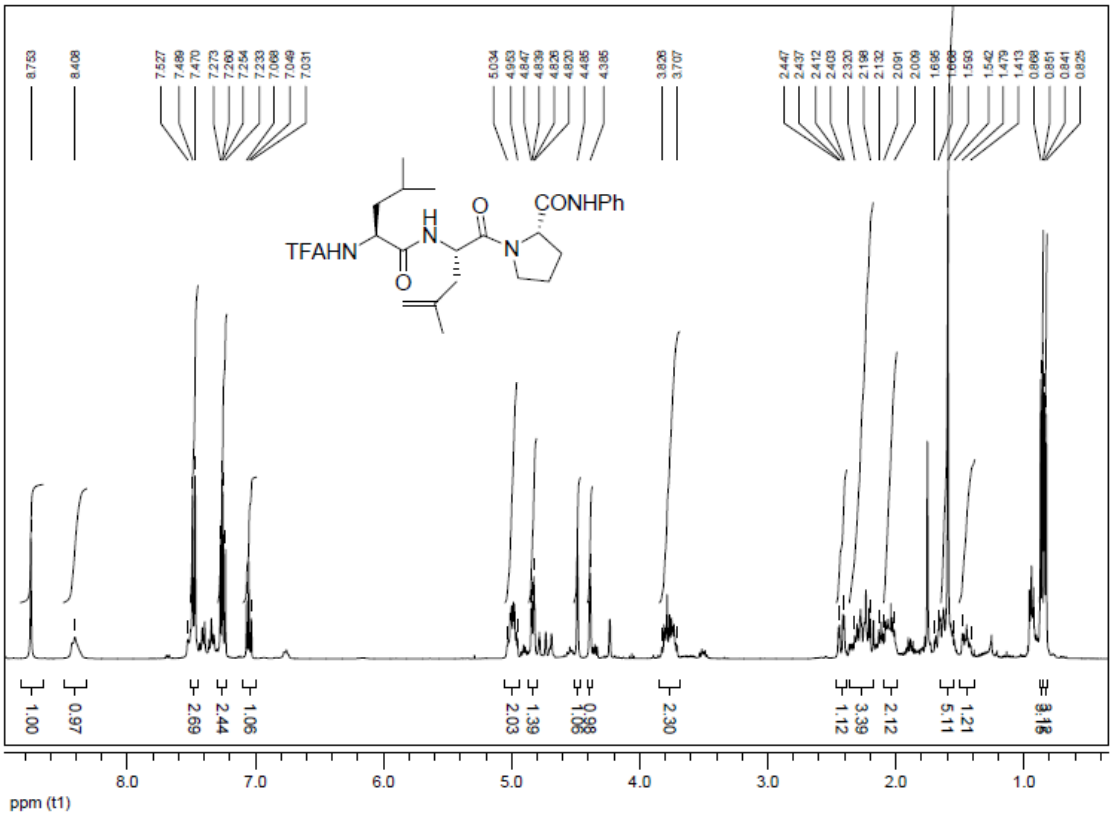


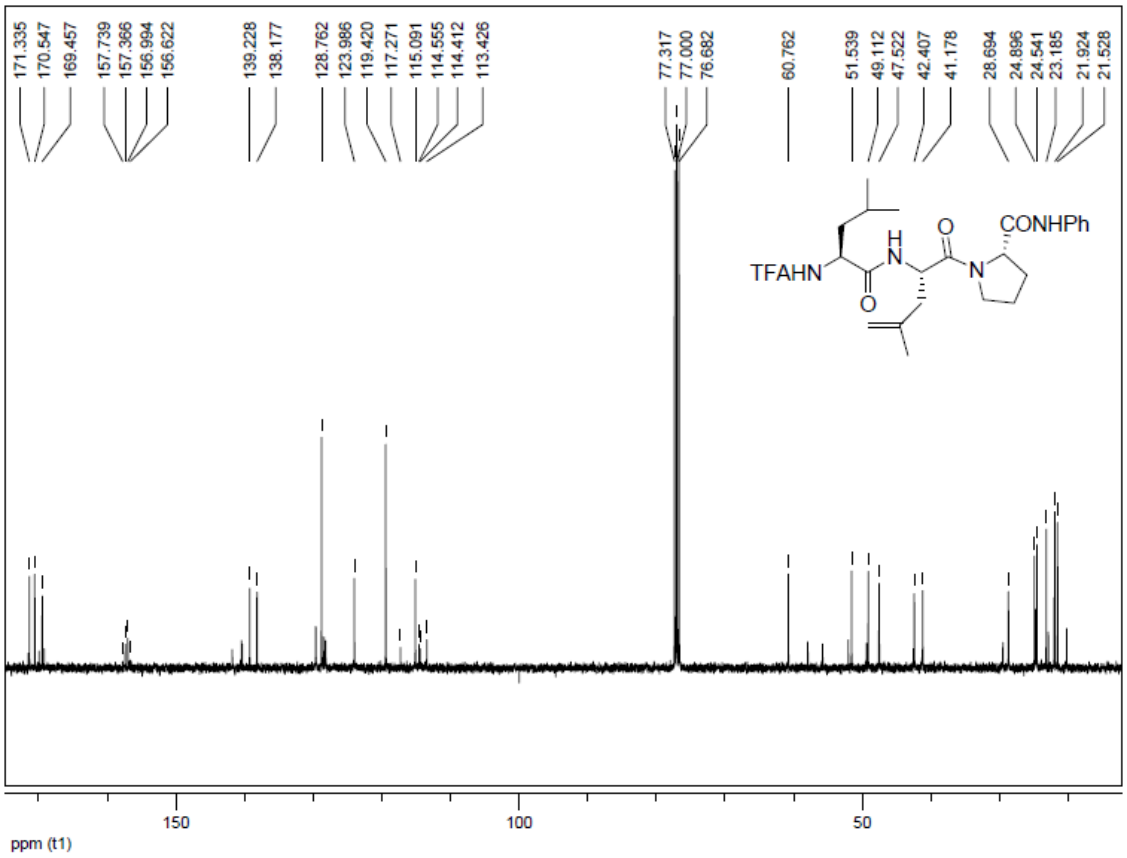
NMR spectra of compound **8a** (major diastereomer)



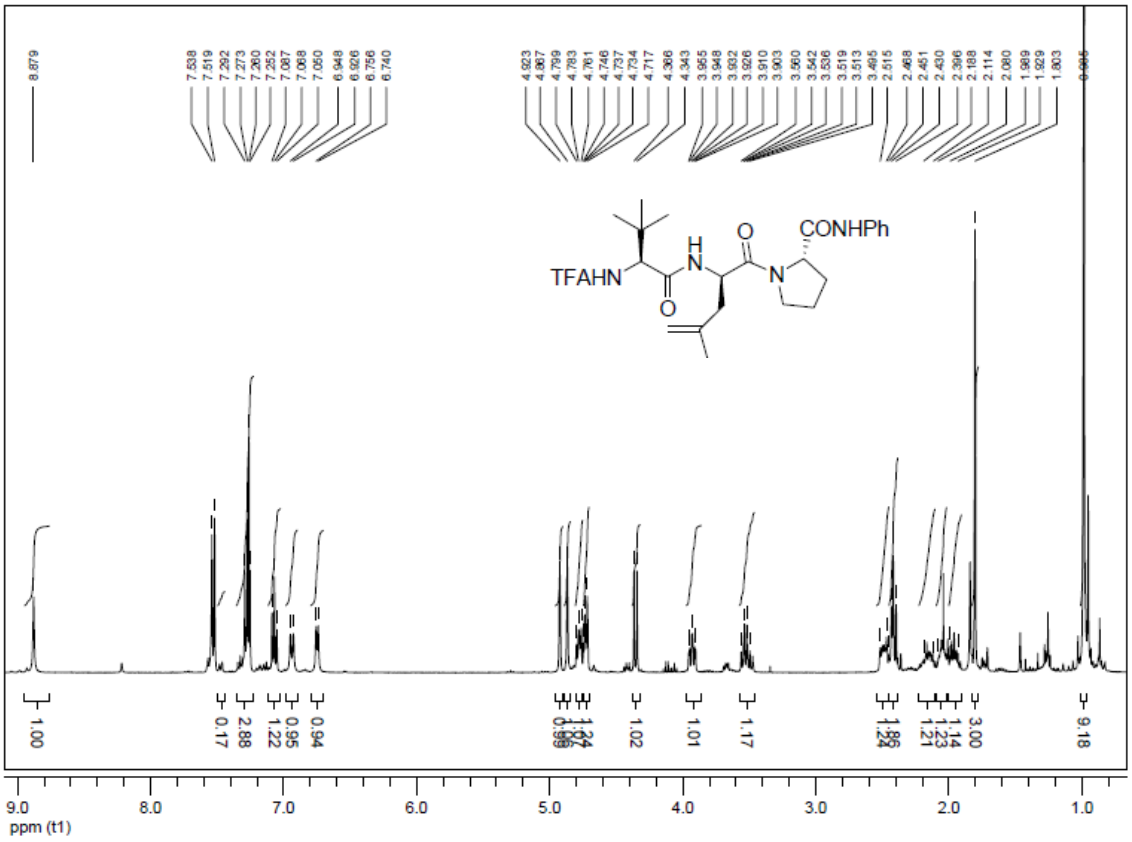


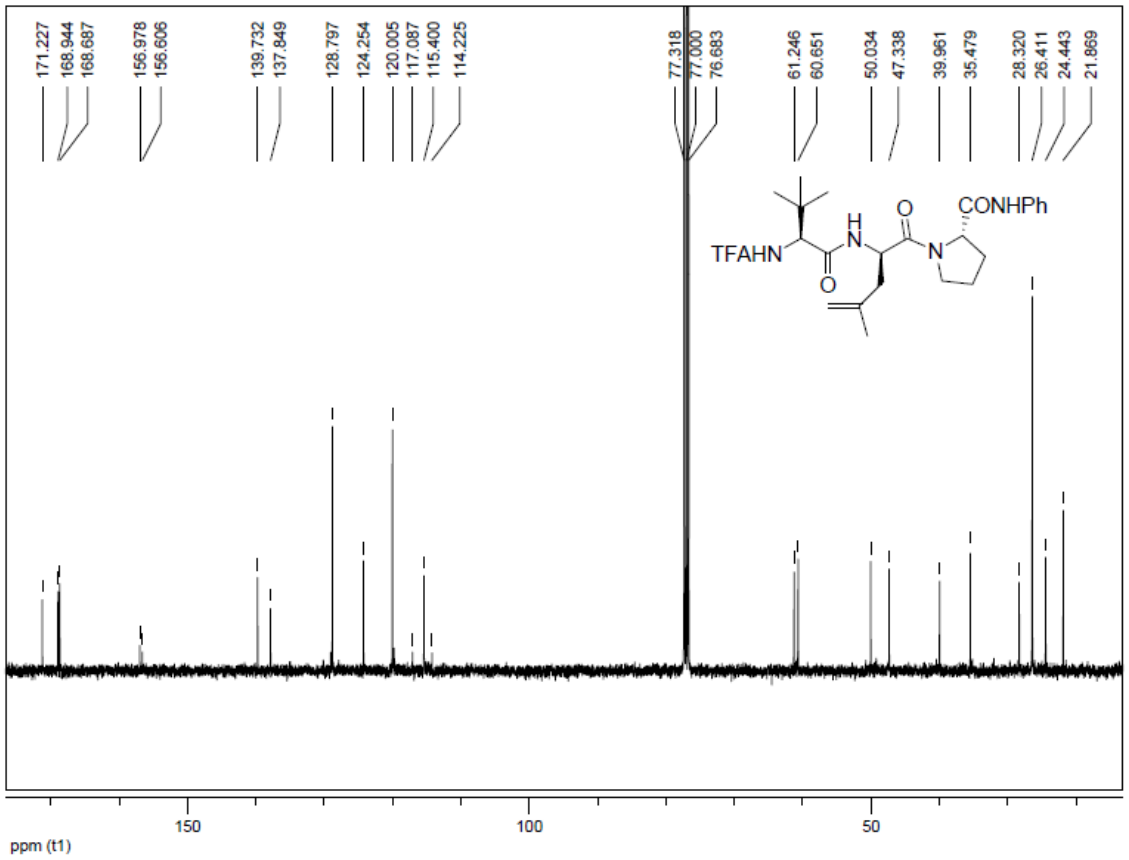
NMR spectra of compound **8a** (minor diastereomer)



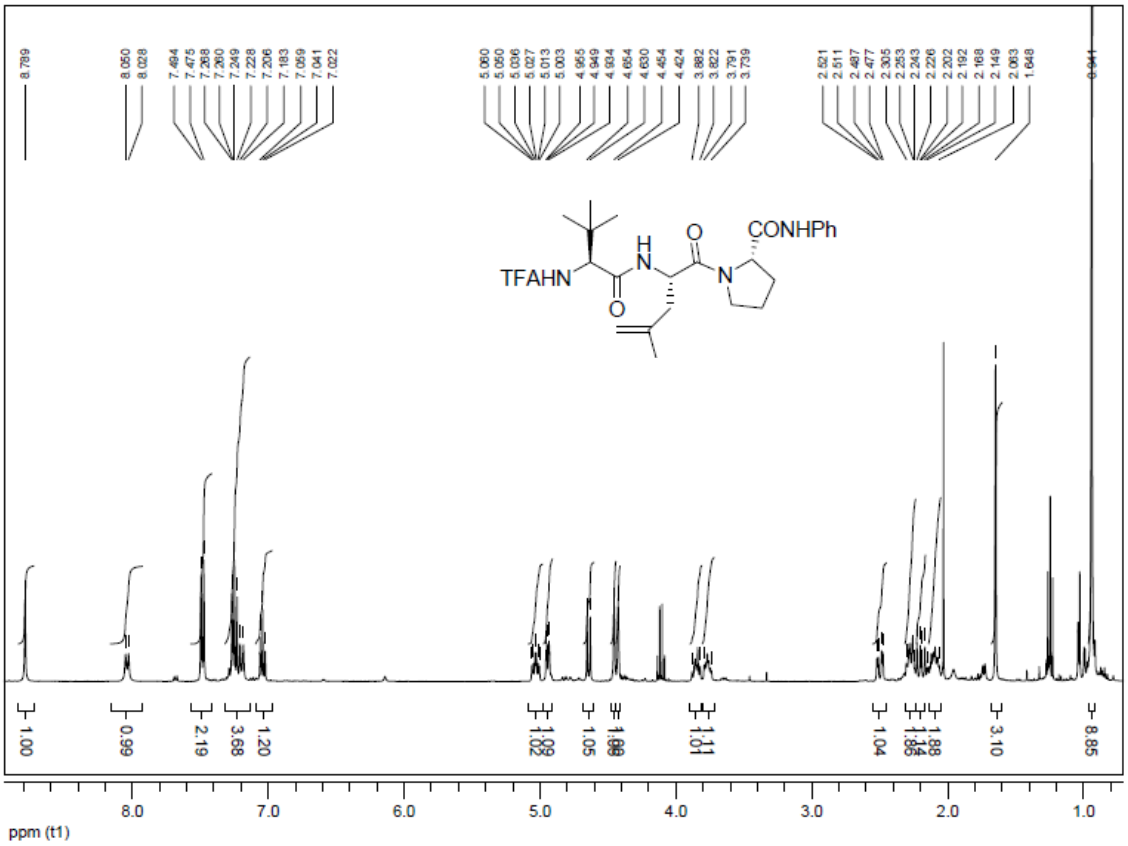


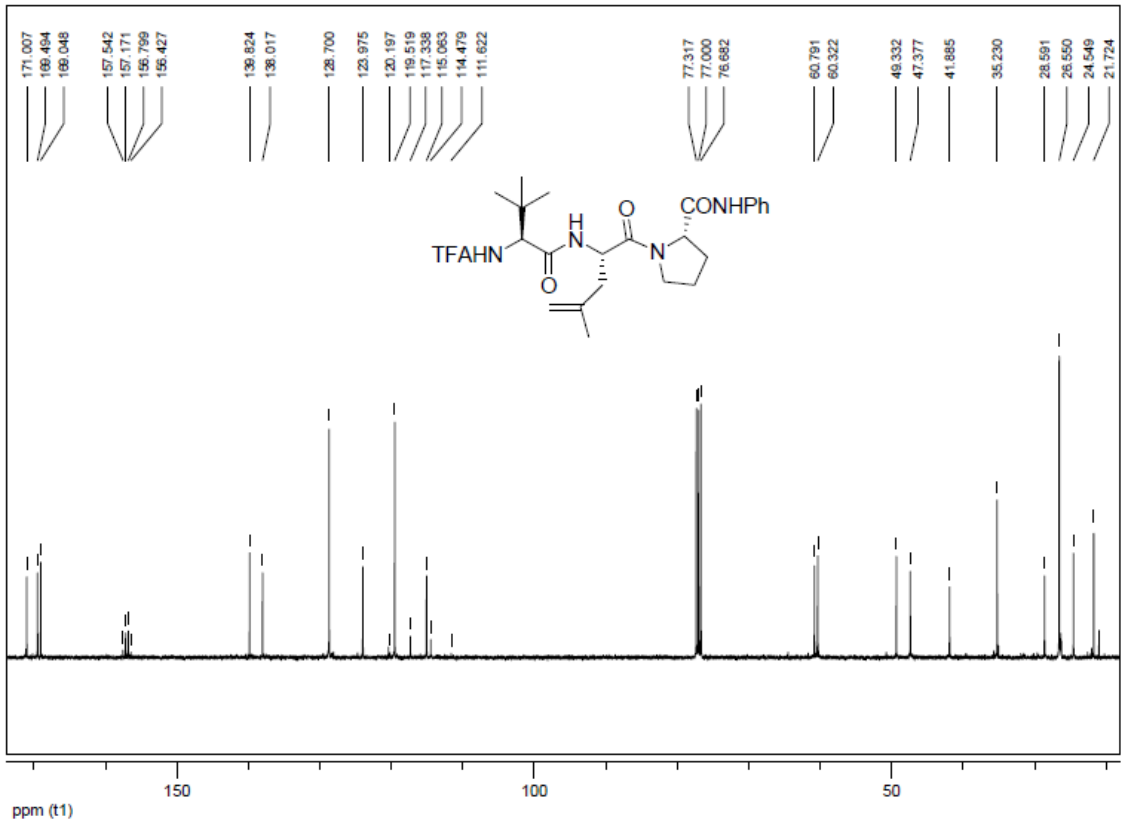
NMR spectra of compound **9a** (major diastereomer)



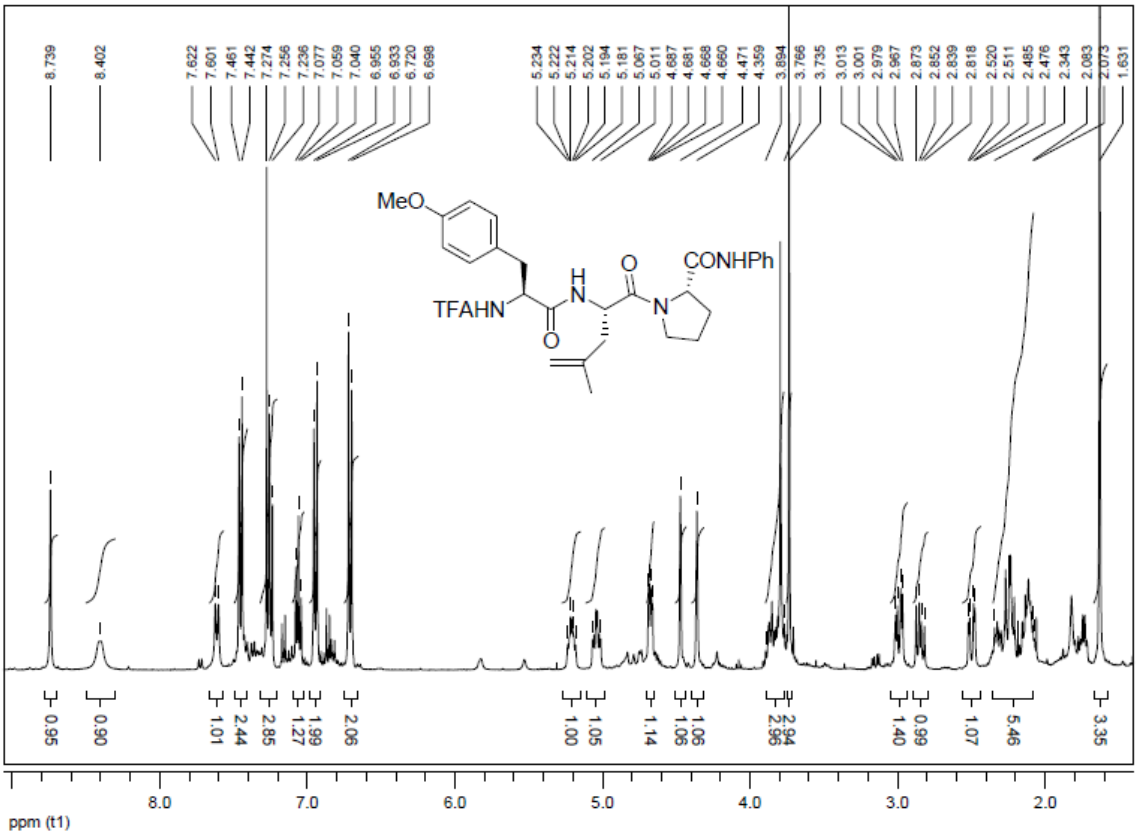


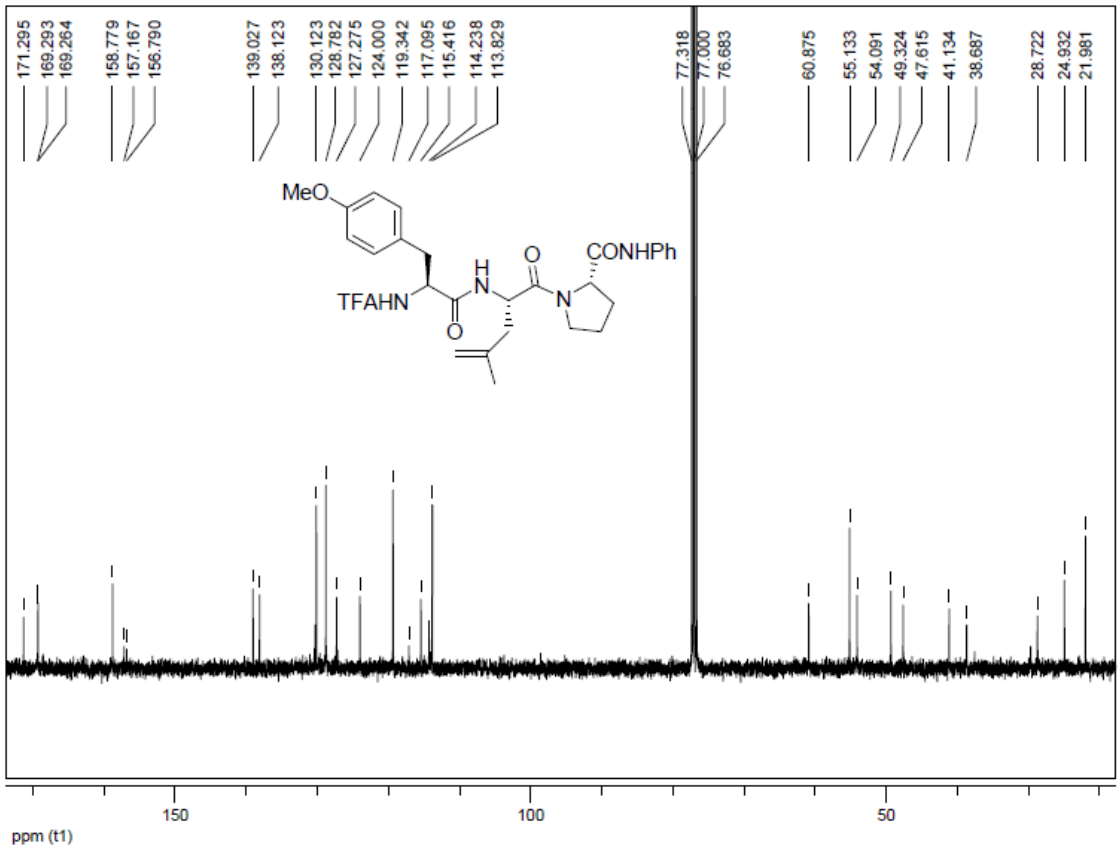
NMR spectra of compound **9a** (minor diastereomer)



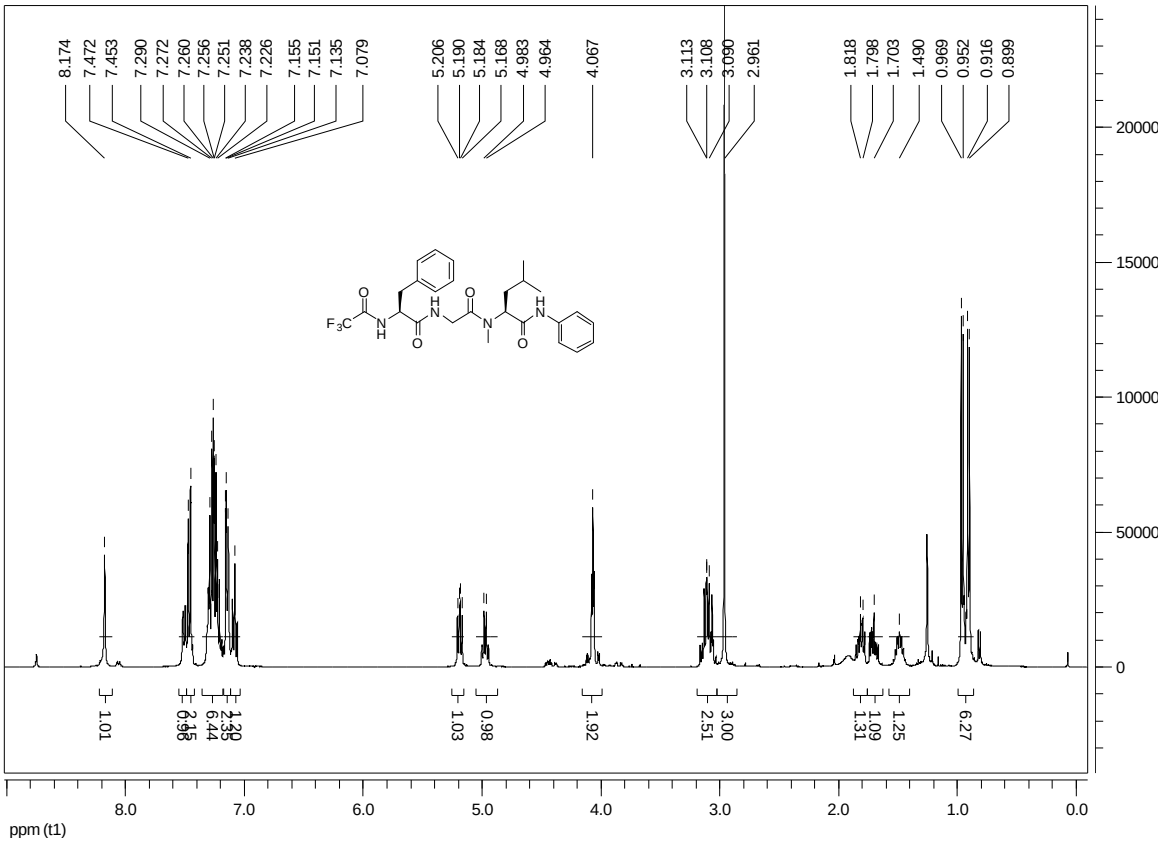


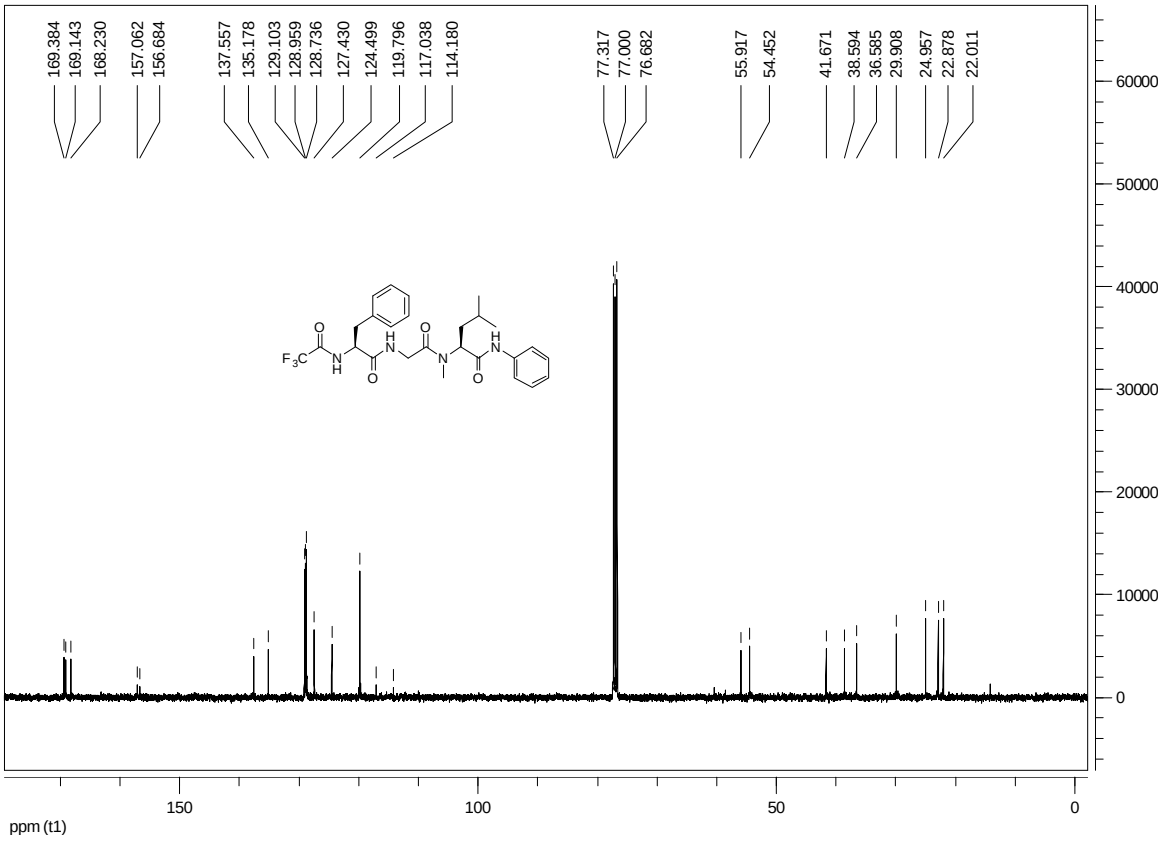
NMR spectra of compound **10a** (minor diastereomer)



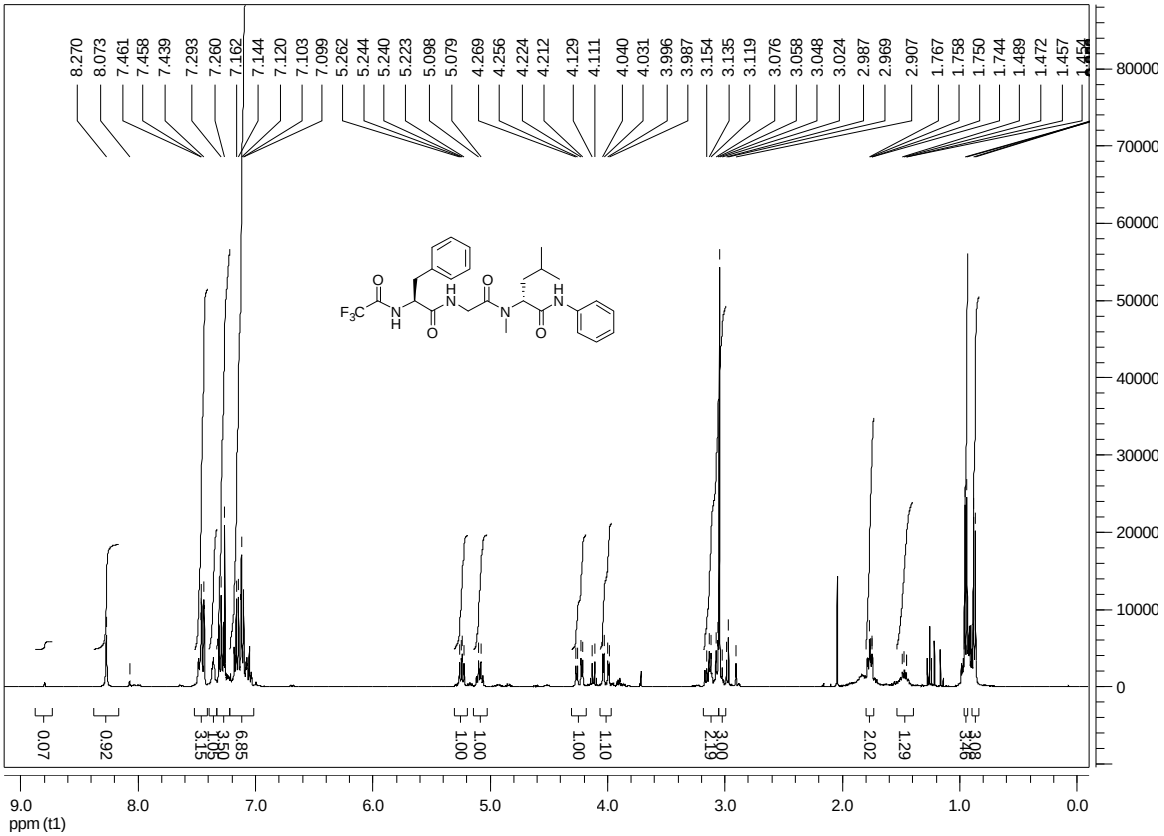


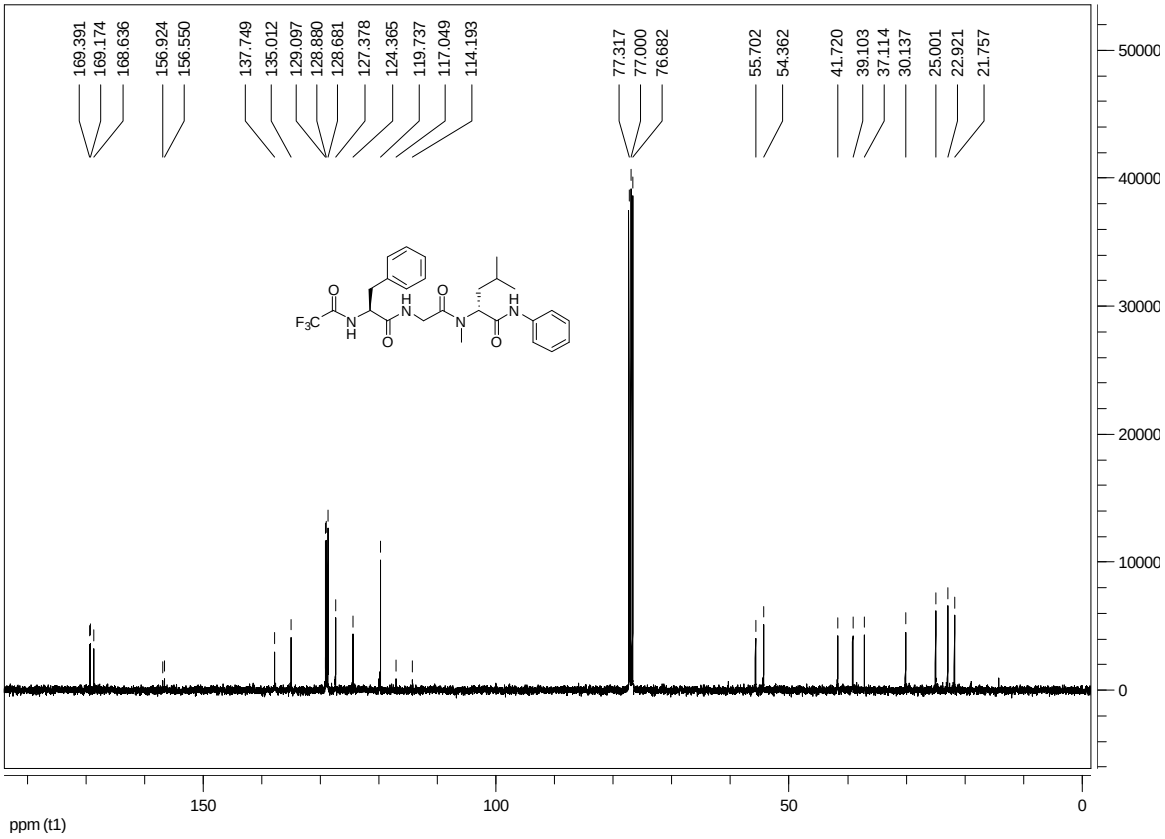
NMR spectra of compound **11**



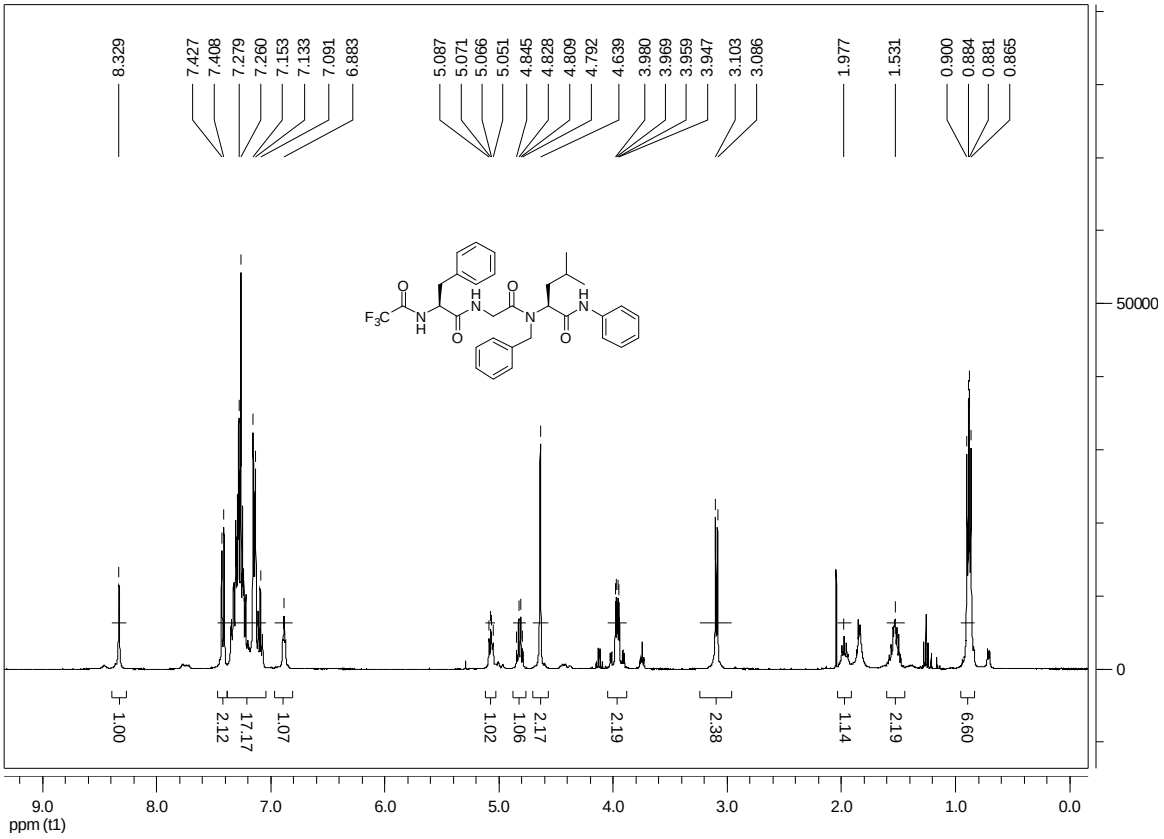


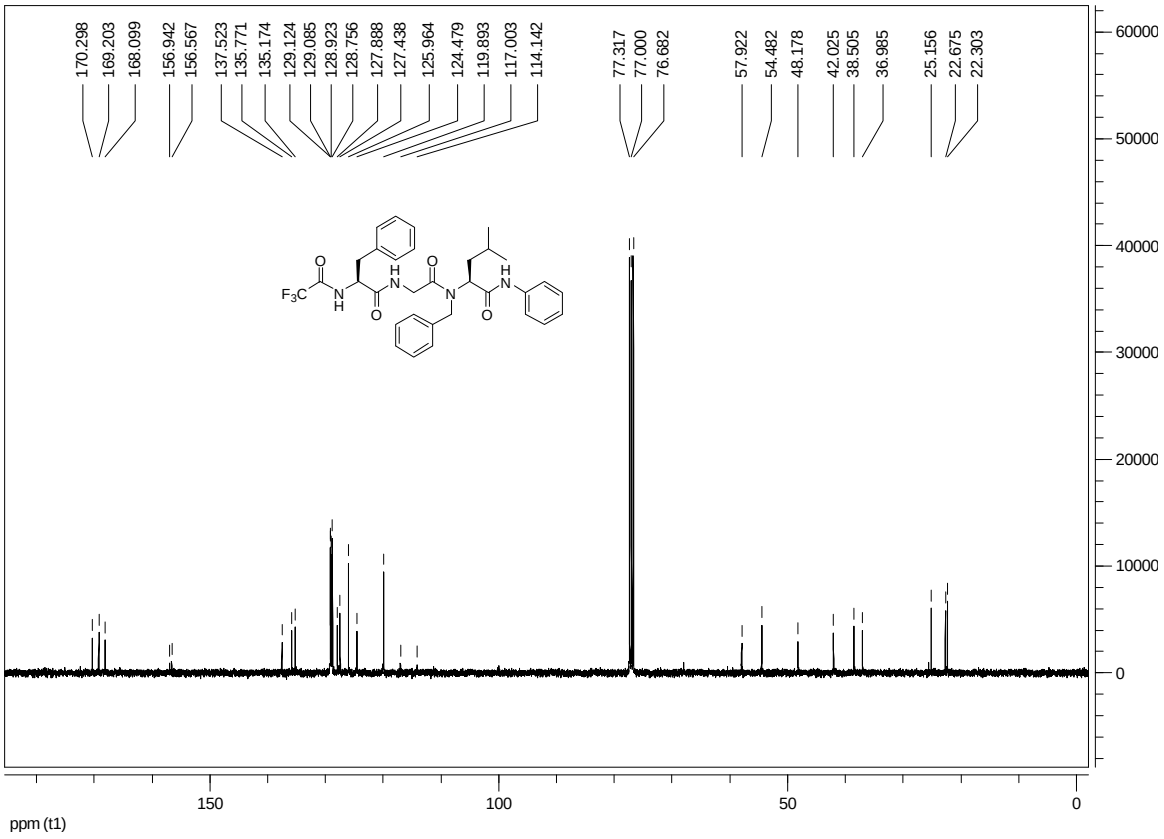
NMR spectra of compound **12**



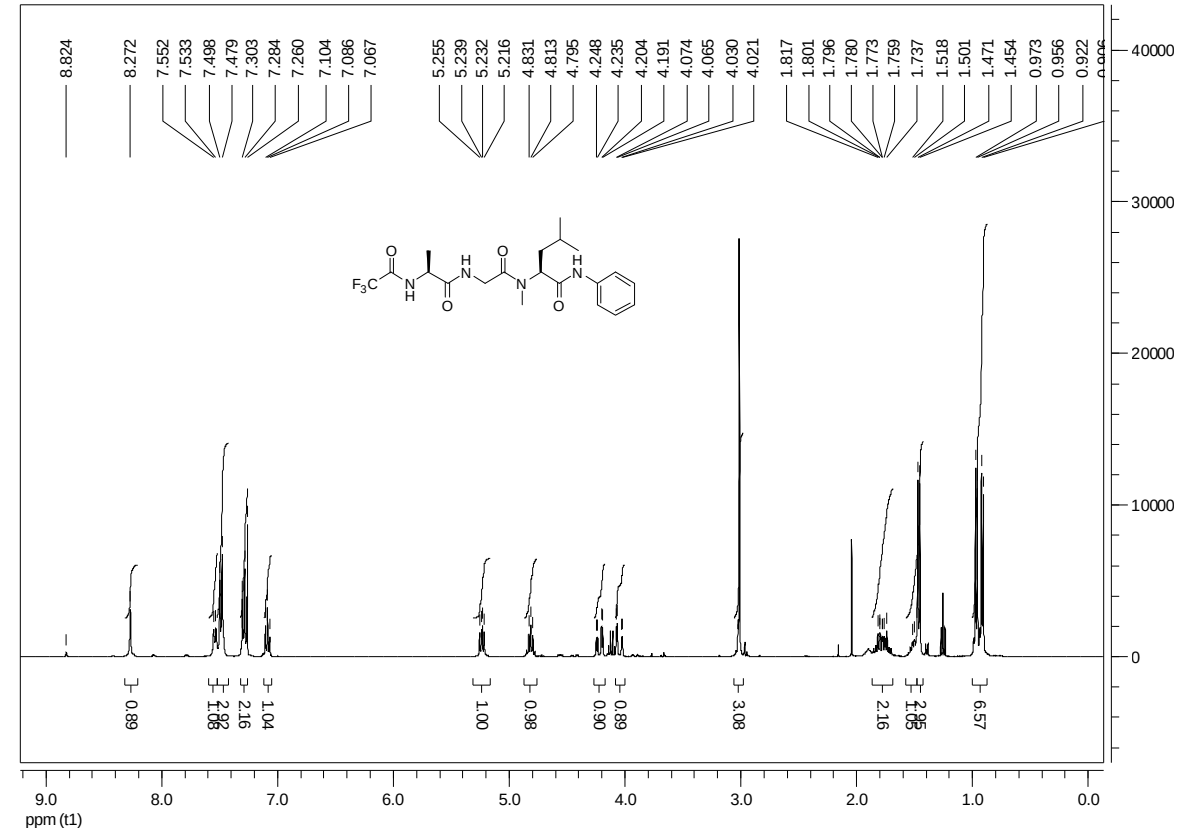


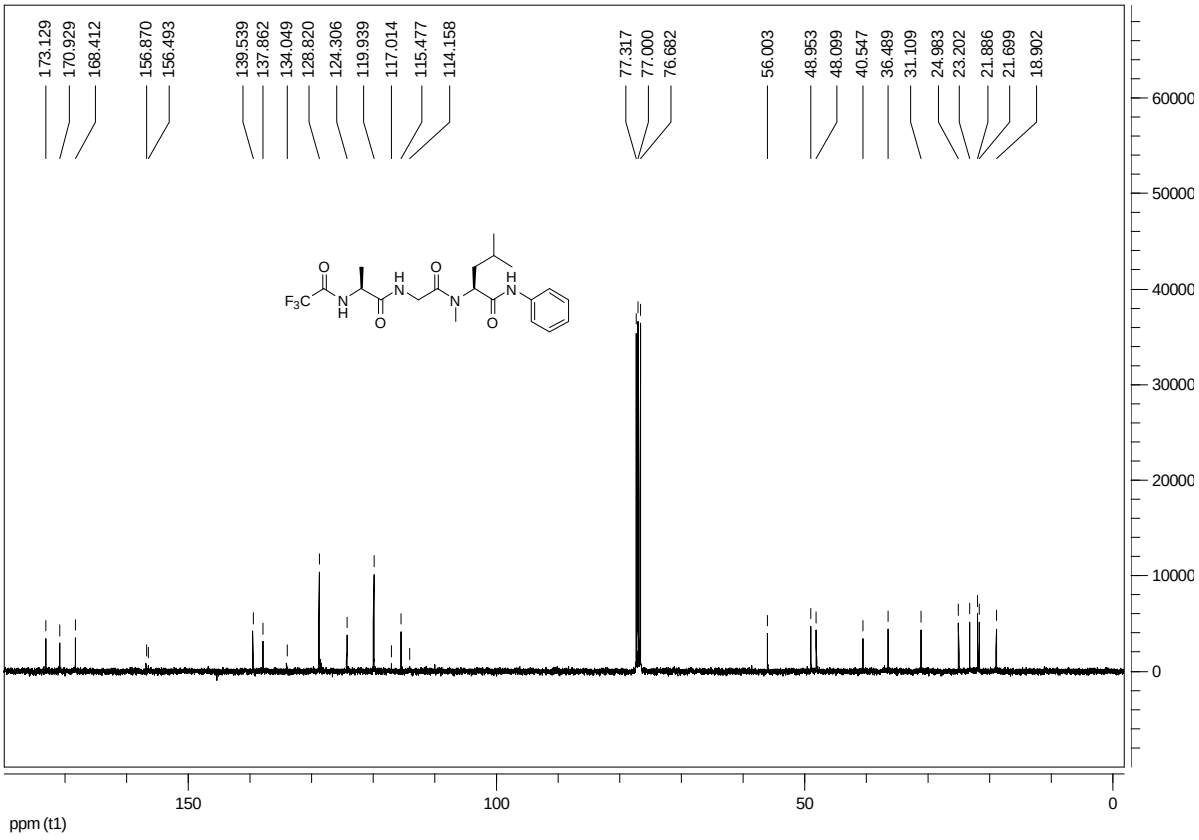
NMR spectra of compound **13**



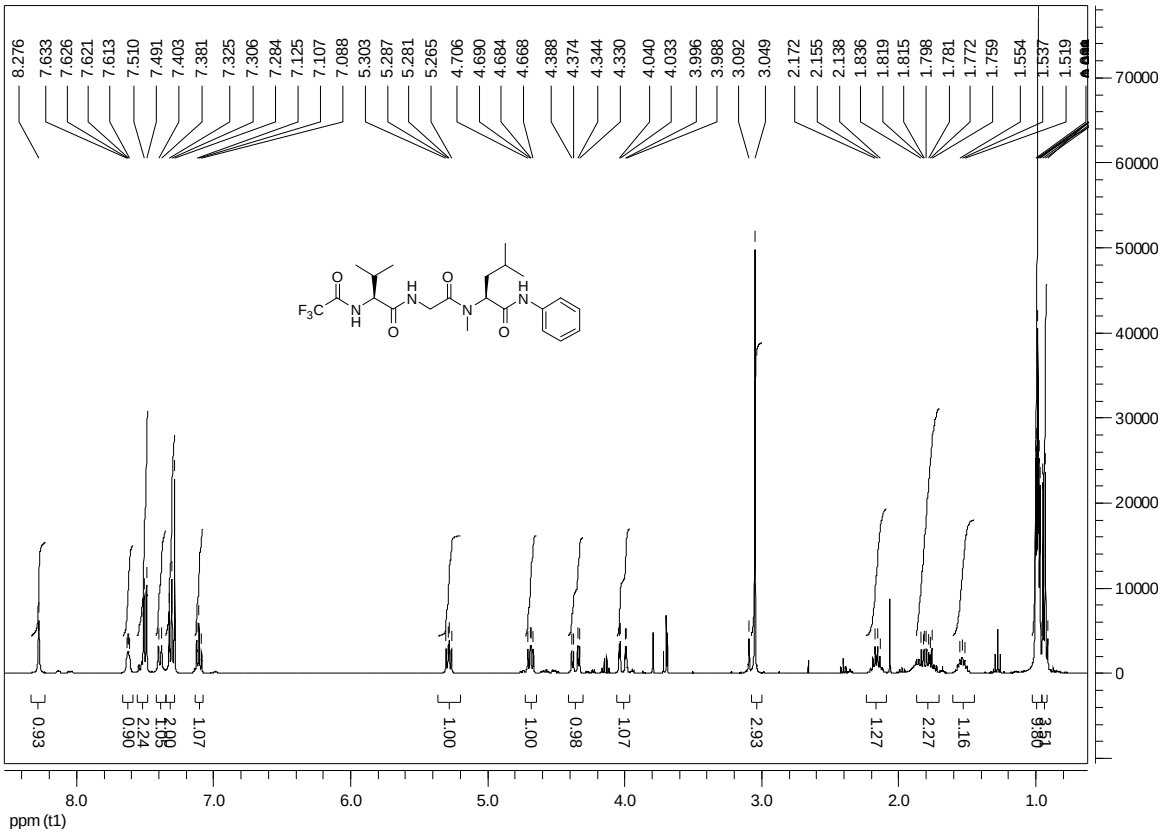


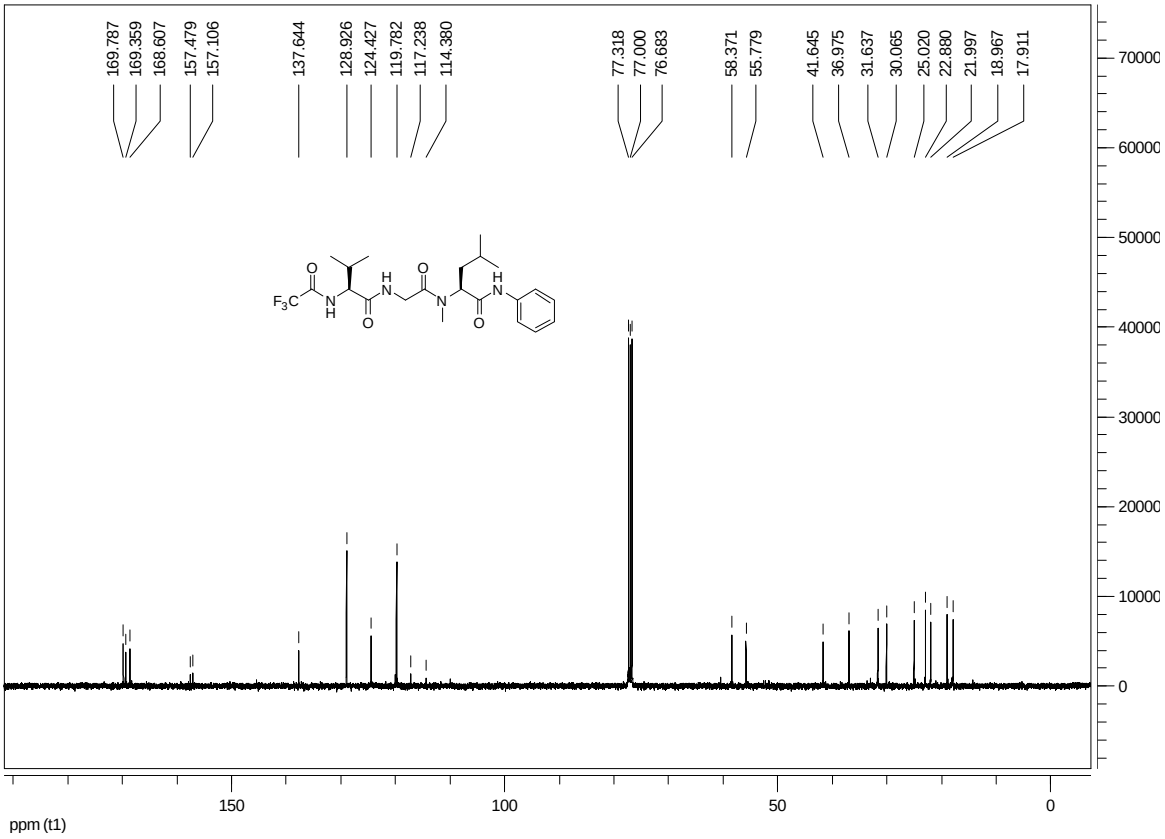
NMR spectra of compound **14**



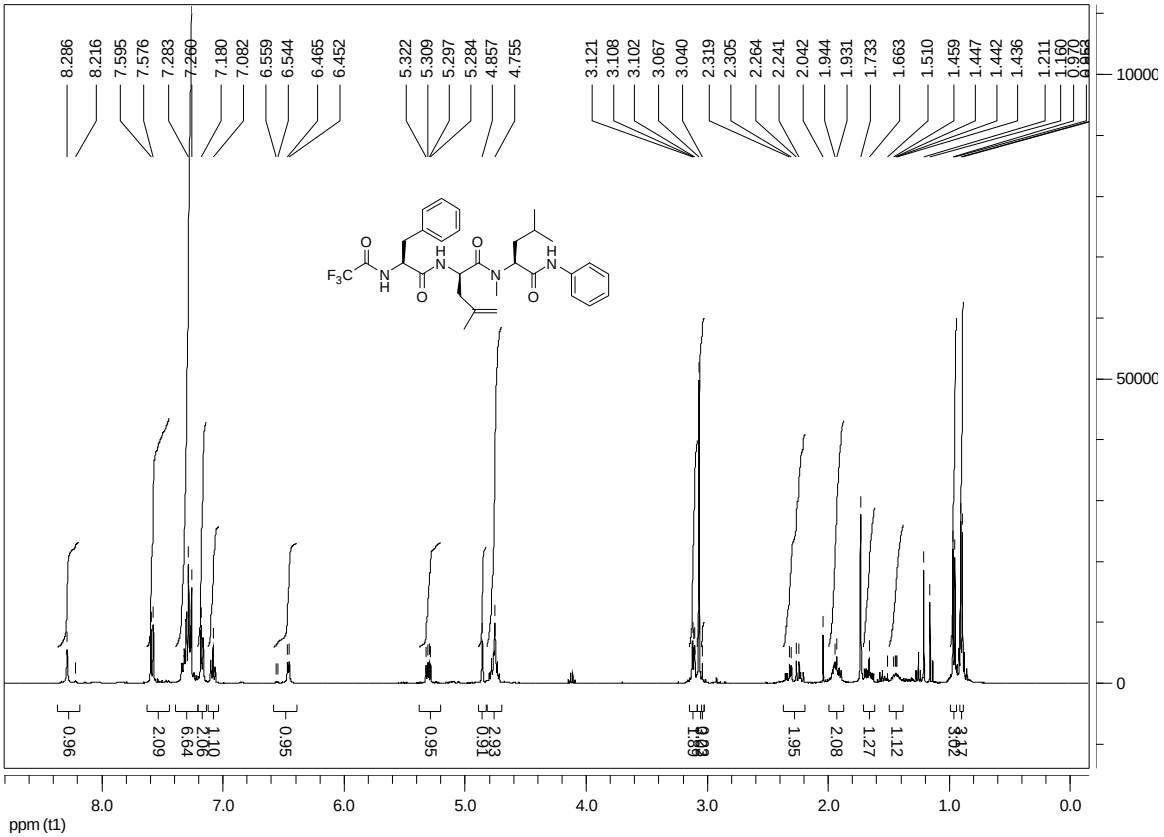


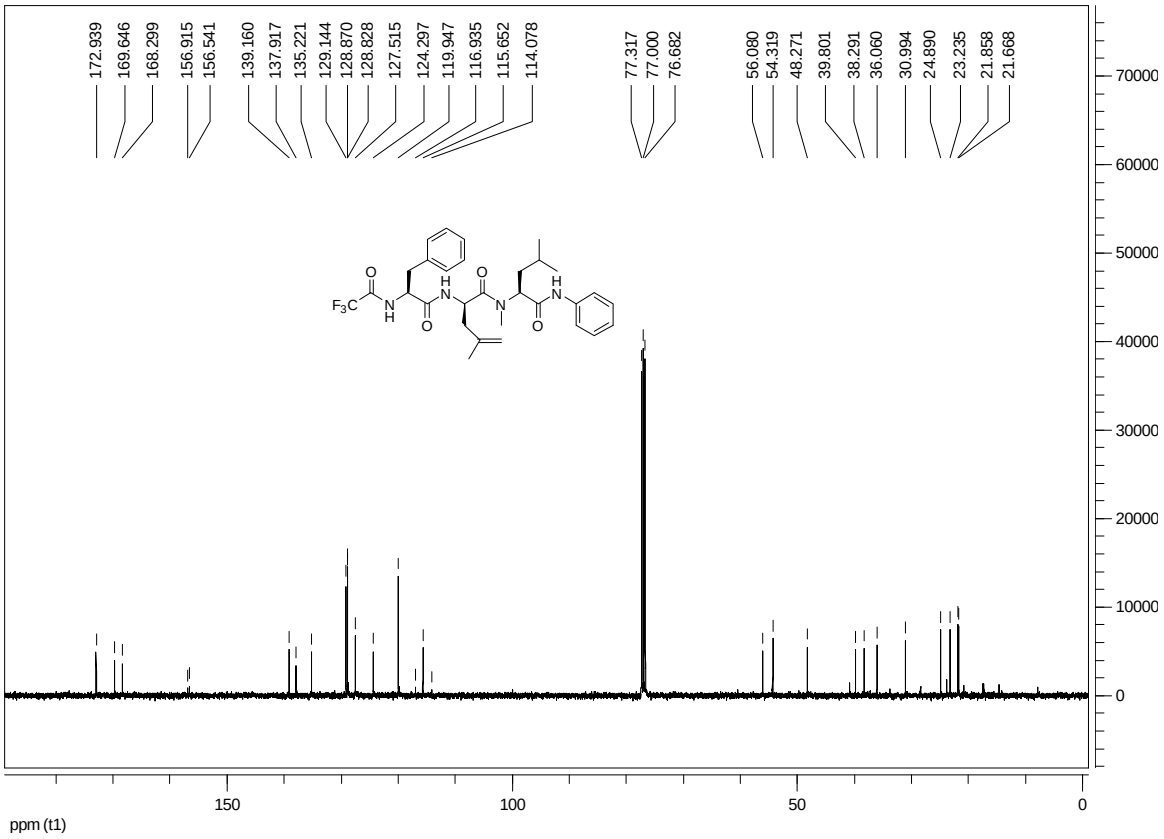
NMR spectra of compound **15**



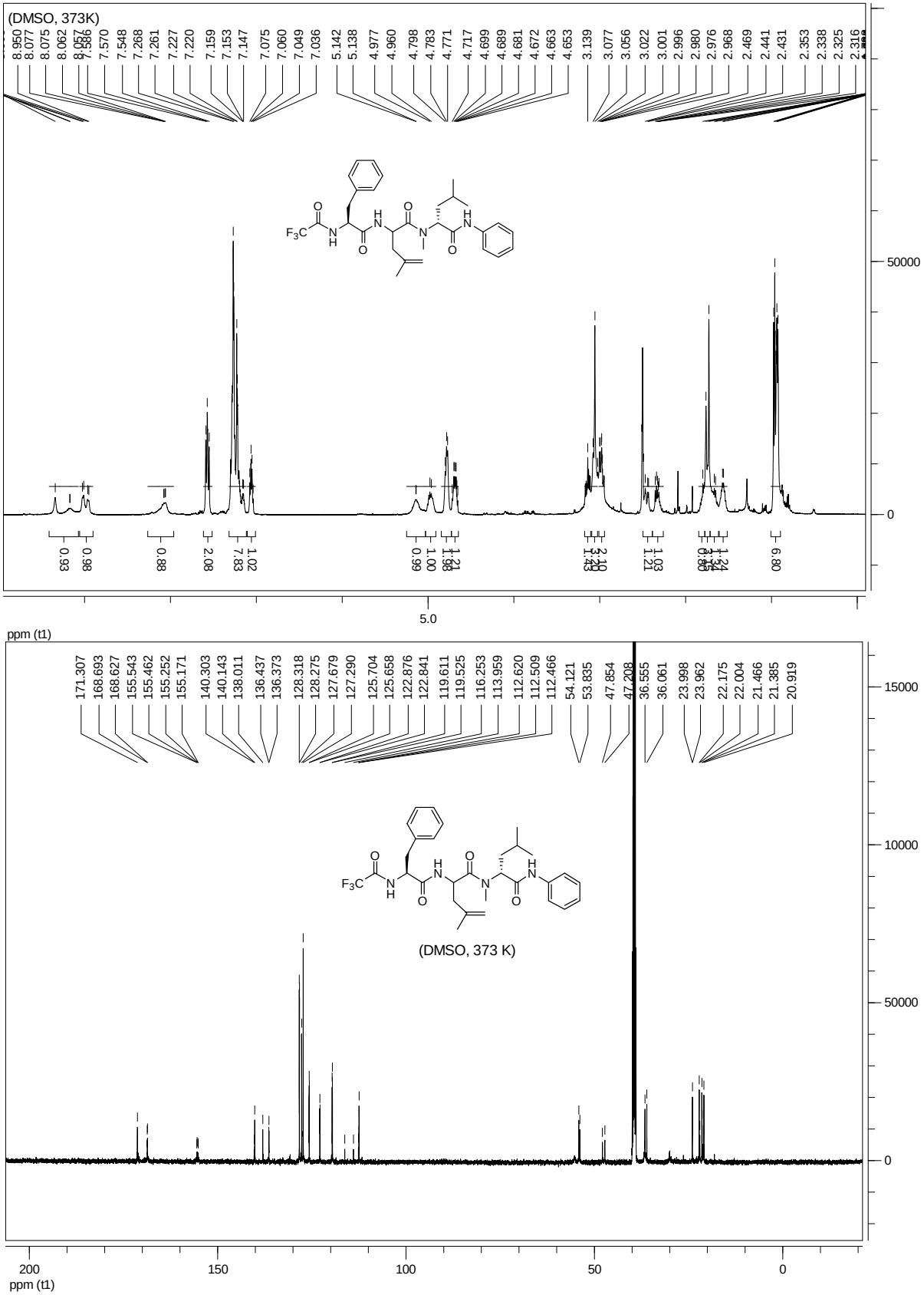


NMR spectra of compound **16a**

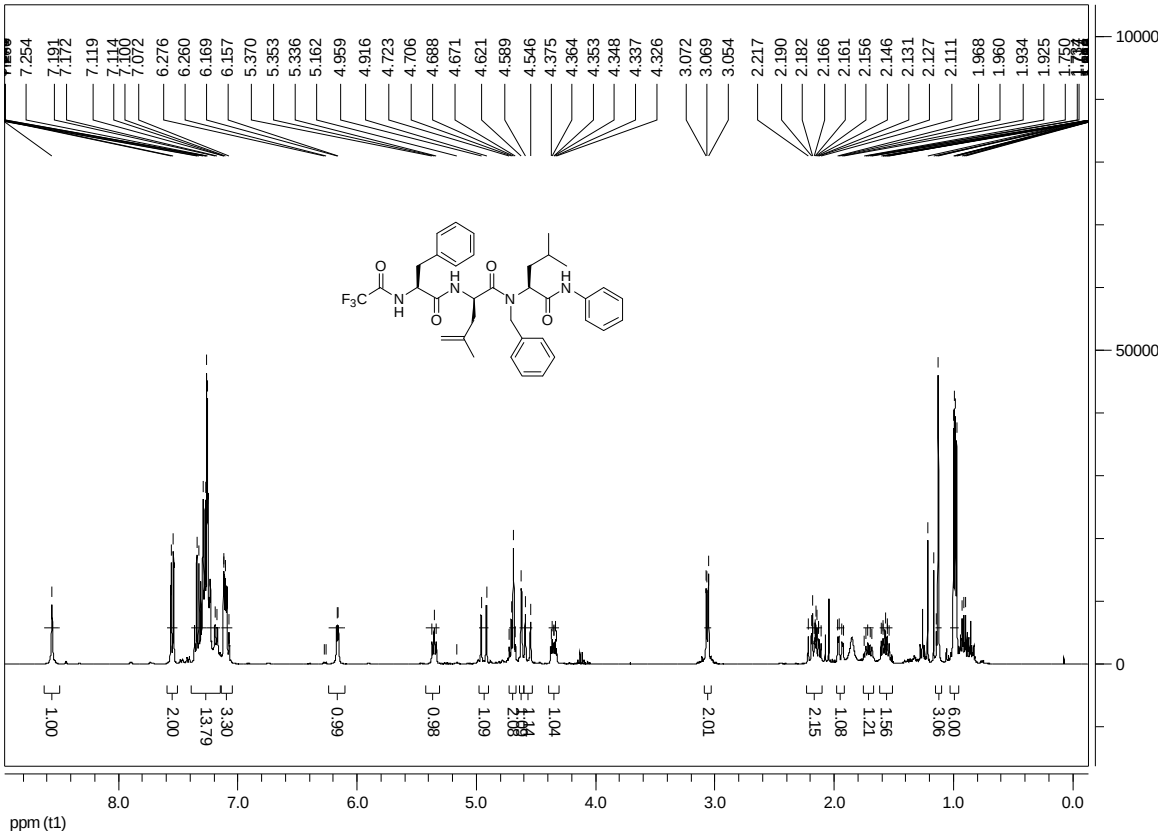


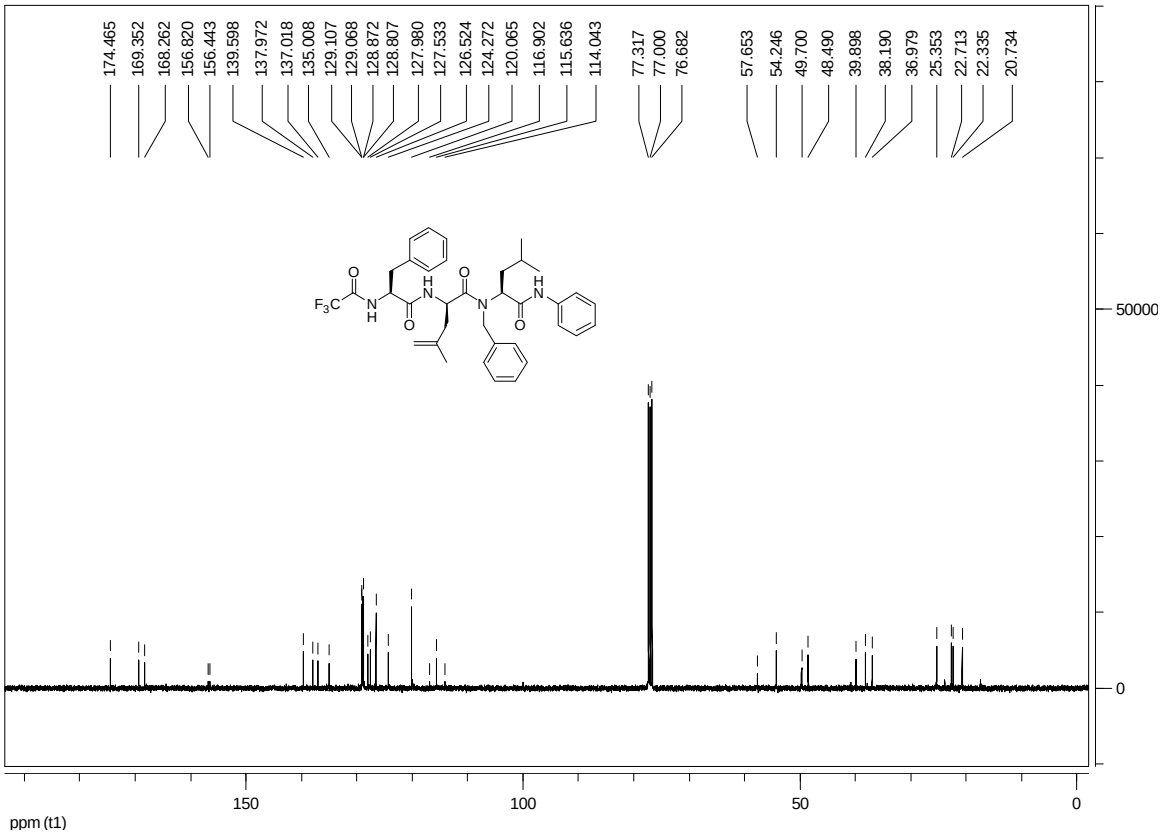


NMR spectra of compound **17**

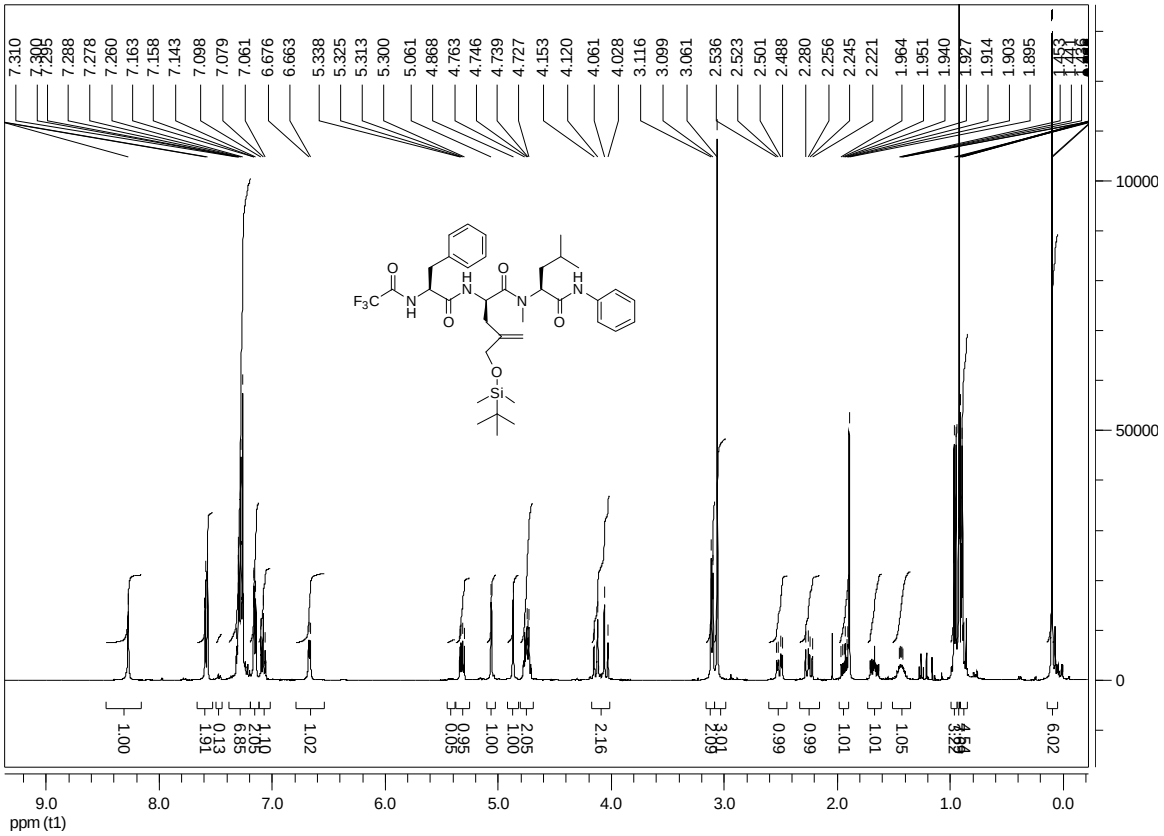


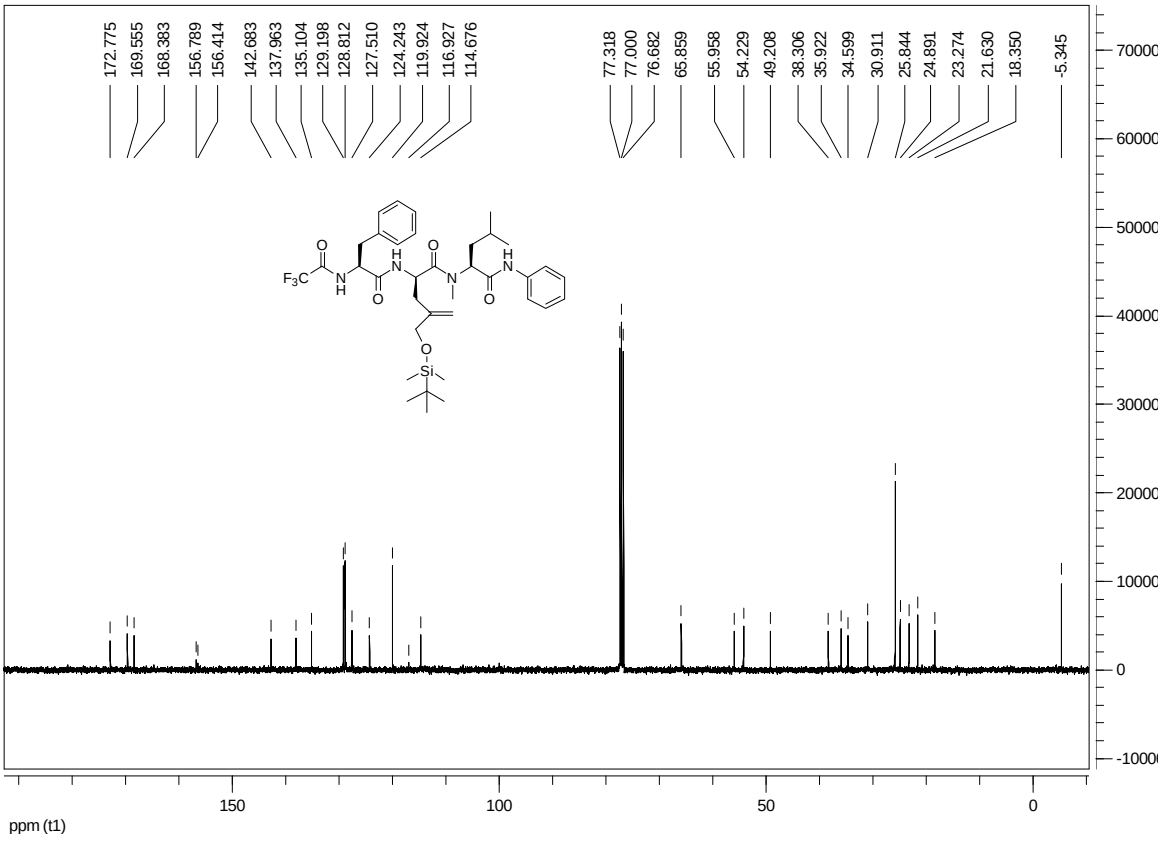
NMR spectra of compound **18**



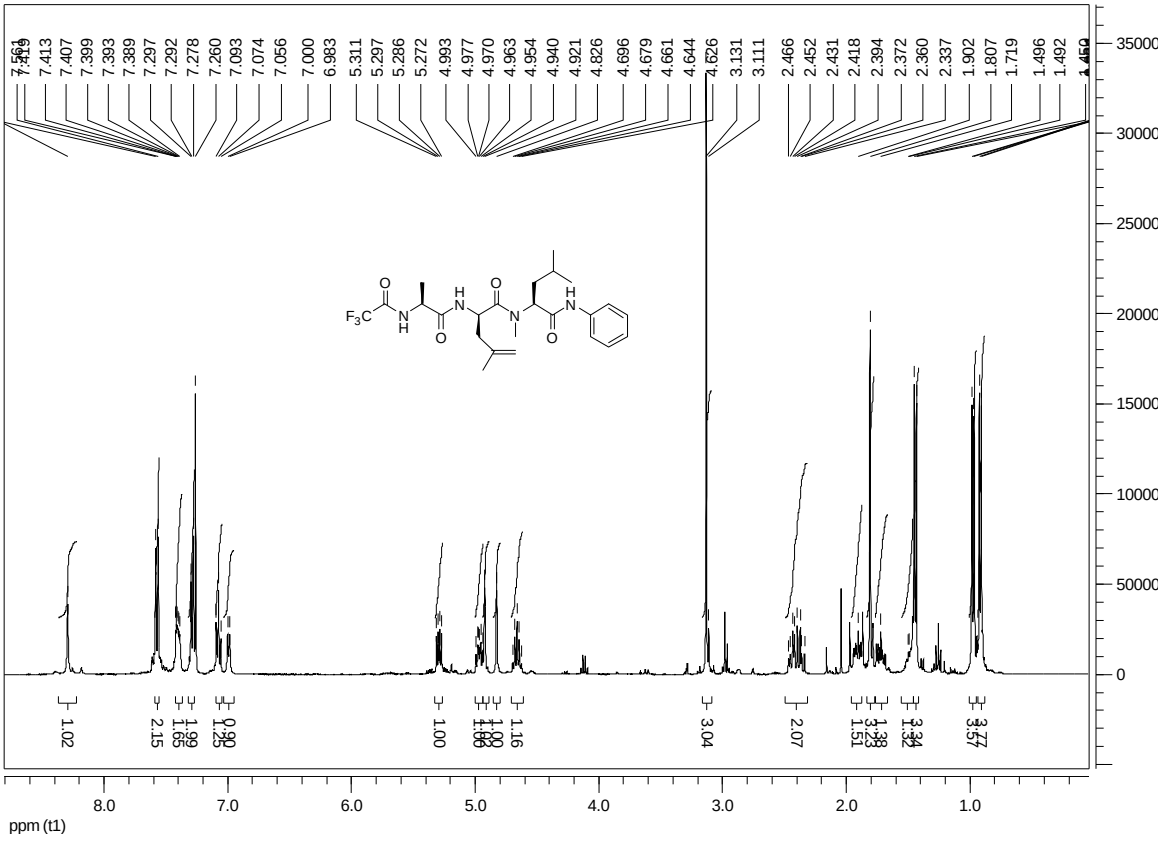


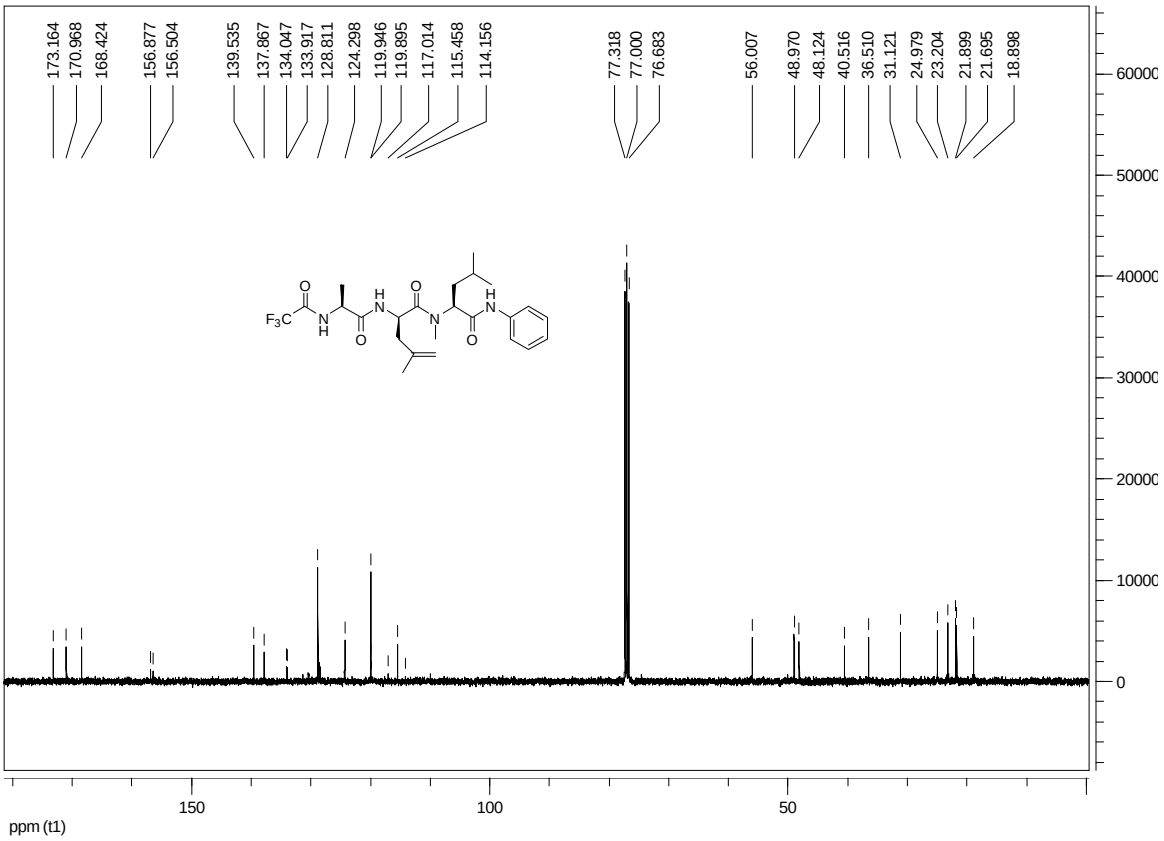
NMR spectra of compound **16b**



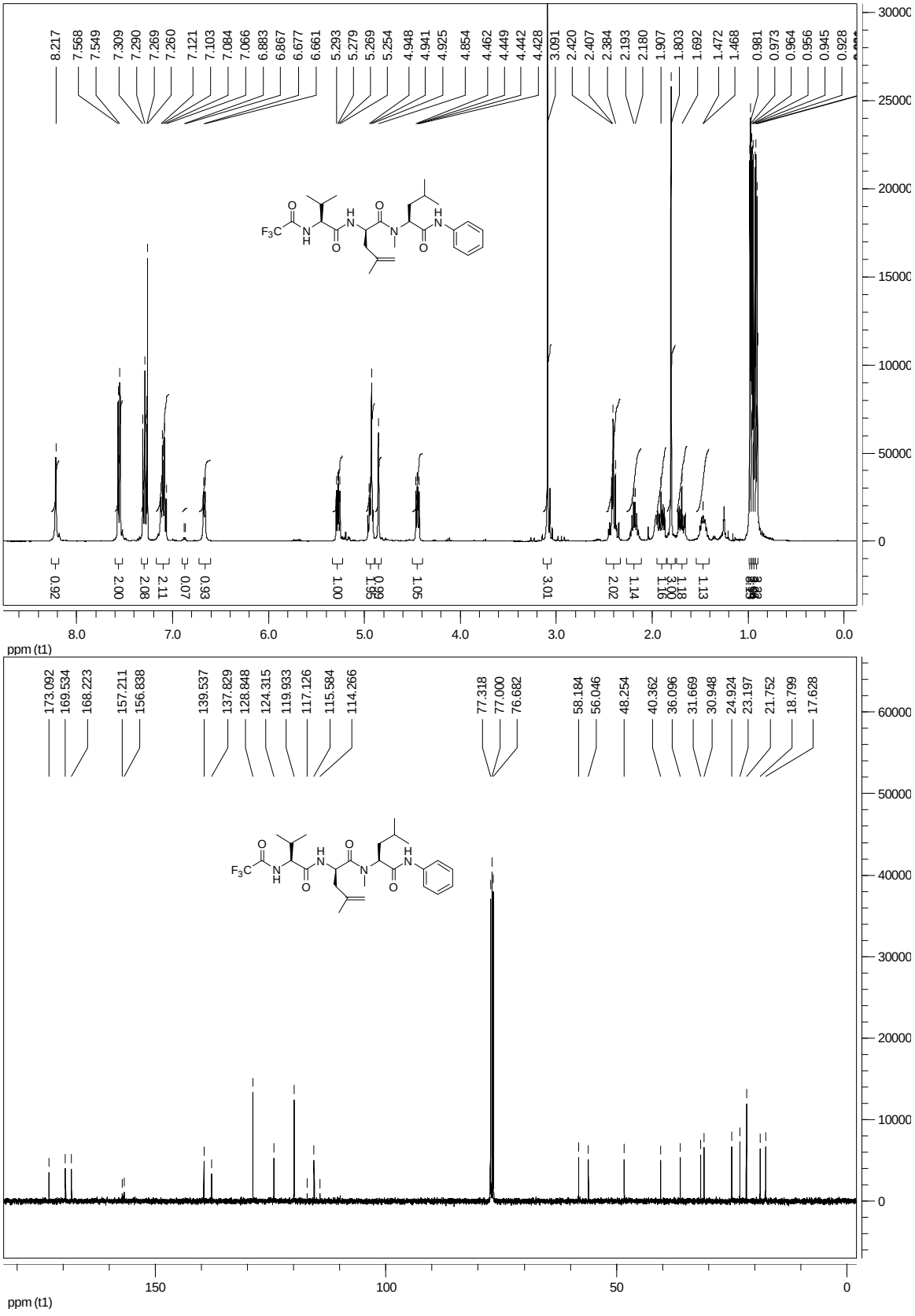


NMR spectra of compound **19**





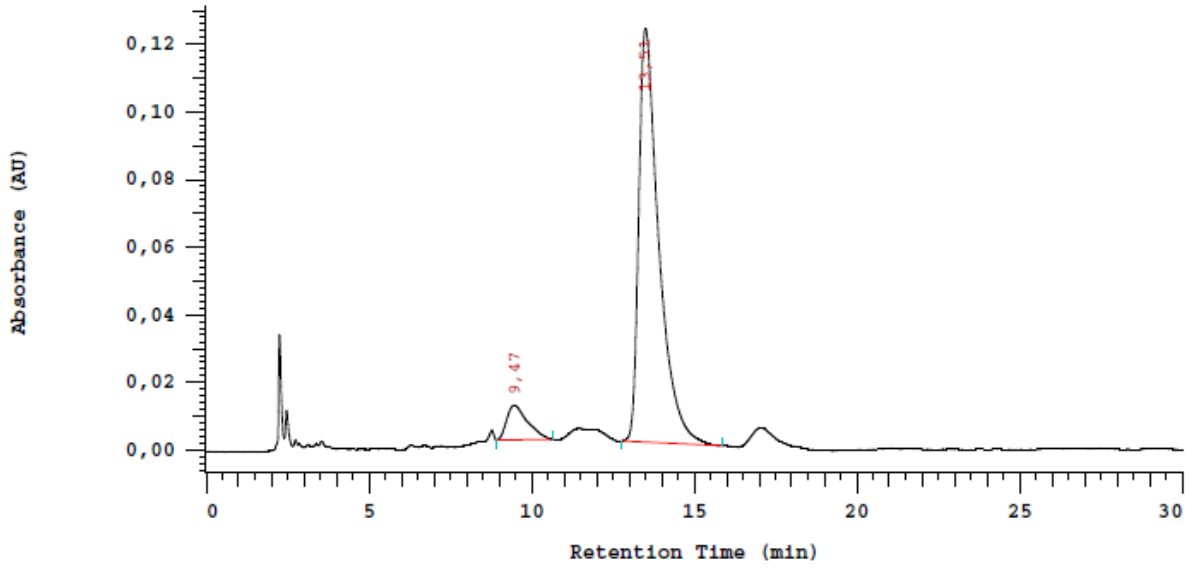
NMR spectra of compound **20**



HPLC chromatogram of crude compound **7a**

Sample Name: sd-345-cr_1 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description: silica HEX:EA 50:50 1ml/min

Chrom Type: Fixed WL Chromatogram, 254 nm



Acquisition Method: swarup,silica 50:50,100 min1ml
Column Type: RP-18 Developed by: Rudi
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: EE Solvent D:
Method Description: silicagel, Hexan/EE 50:50, 1,000 mL/min 30 min

Chrom Type: Fixed WL Chromatogram, 254 nm

Peak Quantitation: AREA
Calculation Method: AREA%

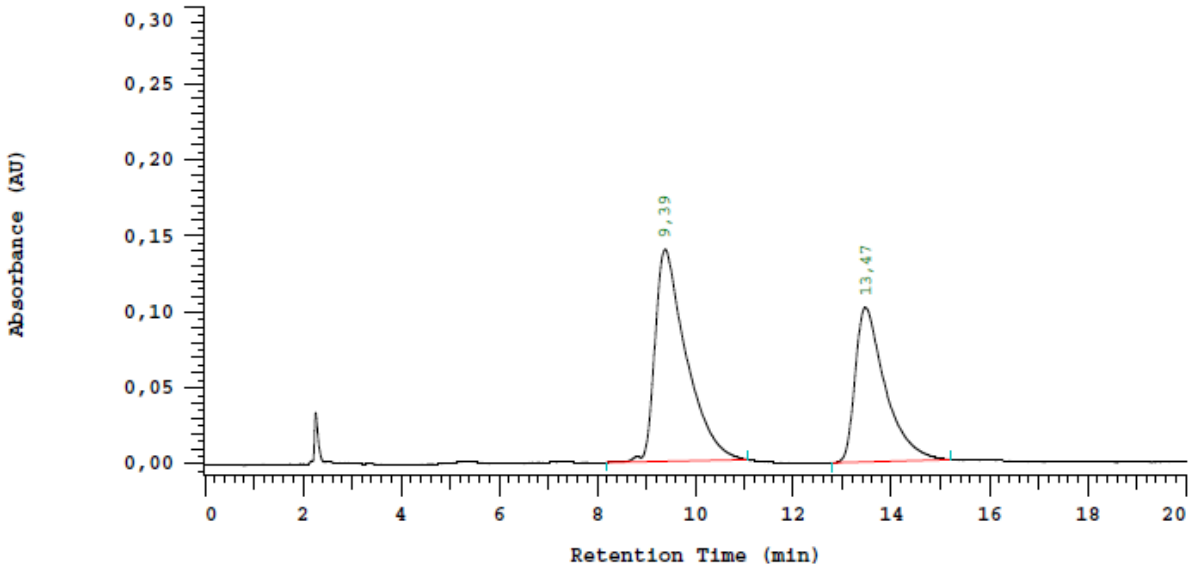
No.	RT	Area	Area %
1	9,47	225959	7,945
2	13,51	2618211	92,055
		2844170	100,000

1: (*S*,*S*,*S*)-**7a**; 2: (*S*,*R*,*S*)-**7a**.

HPLC chromatogram of crude compound **7a** (from allylation without Pd)

Sample Name: sd-344-cr_7 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description: silica HEX:EA 50:50

Chrom Type: Fixed WL Chromatogram, 254 nm



Acquisition Method: swarup, silica hex:ea 50:50
Column Type: RP-18 Developed by: Rudi
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: EE Solvent D:
Method Description: silicagel, Hexan/EE 50:50, 1,000 mL/min

Chrom Type: Fixed WL Chromatogram, 254 nm

Peak Quantitation: AREA
Calculation Method: AREA%

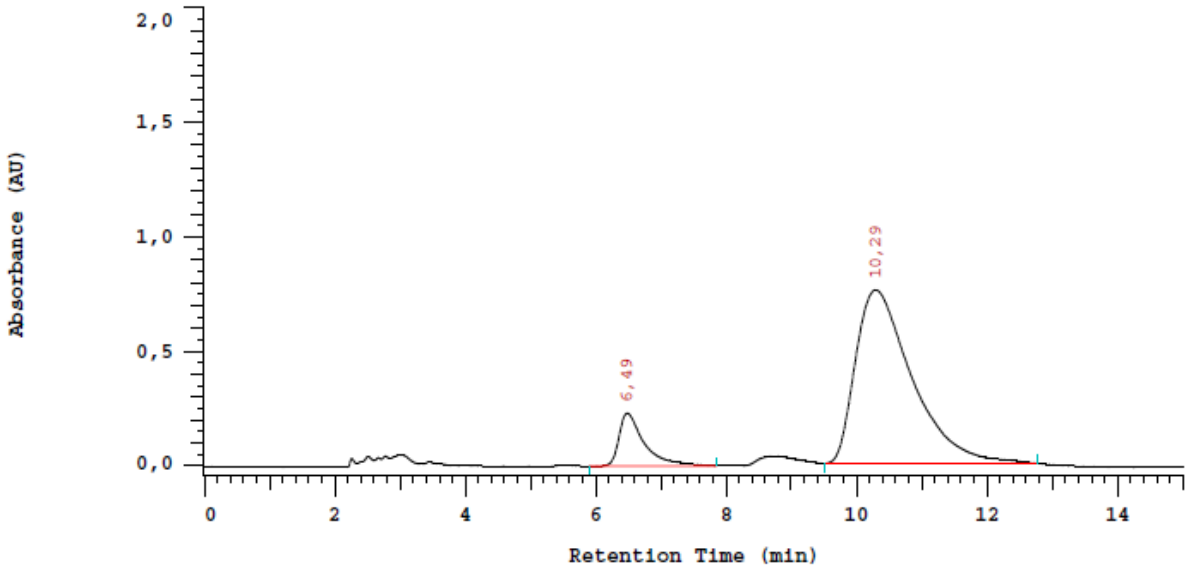
No.	RT	Area	Area %
1	9,39	3106849	58,929
2	13,47	2165355	41,071
		5272204	100,000

1: (*S*,*S*,*S*)-**7a**; 2: (*S*,*R*,*S*)-**7a**.

HPLC chromatogram of crude compound **7b**

Sample Name: sd-408-cr_2 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description: silica hex:ea 50:50

Chrom Type: Fixed WL Chromatogram, 254 nm



Acquisition Method: swarup , silica 50:50 15 min
Column Type: RP-18 Developed by: Rudi
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: EE Solvent D:
Method Description: silicagel, Hexan/EE 50:50, 1,000 mL/min 15 min

Chrom Type: Fixed WL Chromatogram, 254 nm

Peak Quantitation: AREA
Calculation Method: AREA%

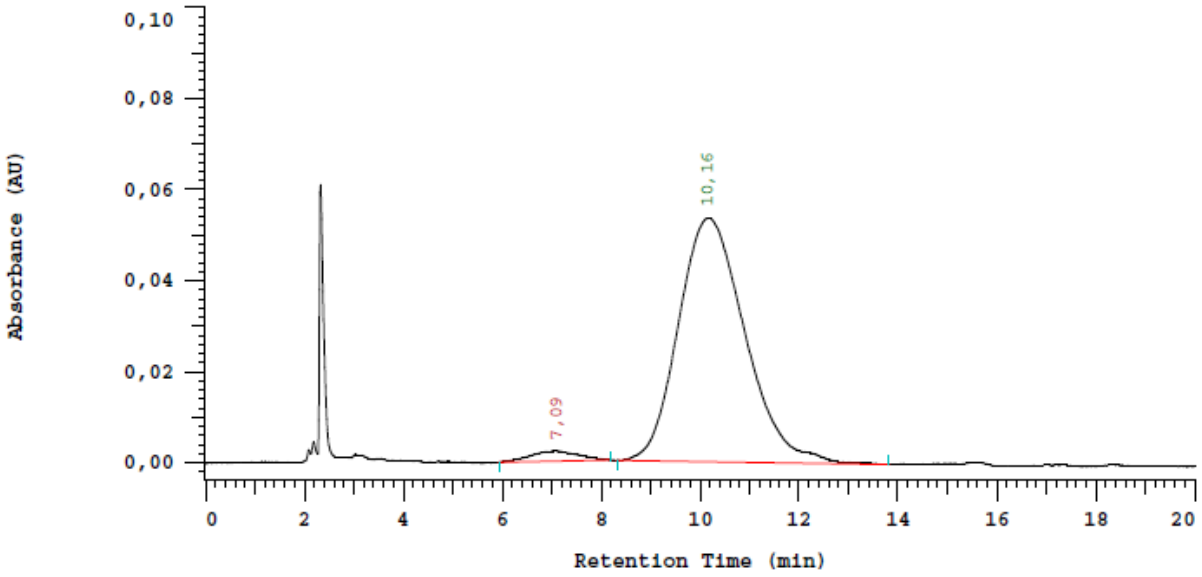
No.	RT	Area	Area %
1	6,49	3118238	12,032
2	10,29	22798377	87,968
		25916615	100,000

1: (*S*,*S*,*S*)-**7b**; 2: (*S*,*R*,*S*)-**7b**.

HPLC chromatogram of crude compound **7c**

Sample Name: sd-350-cr_1 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description: silicage HEX:EA 70:30 1ml/min

Chrom Type: Fixed WL Chromatogram, 254 nm



Acquisition Method: swarup,silicahex:ea 70:30 180m
Column Type: RP-18 Developed by: Rudi
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: EE Solvent D:
Method Description: silicagel, Hexan/EE 70:30, 1,000 mL/min

Chrom Type: Fixed WL Chromatogram, 254 nm

Peak Quantitation: AREA
Calculation Method: AREA%

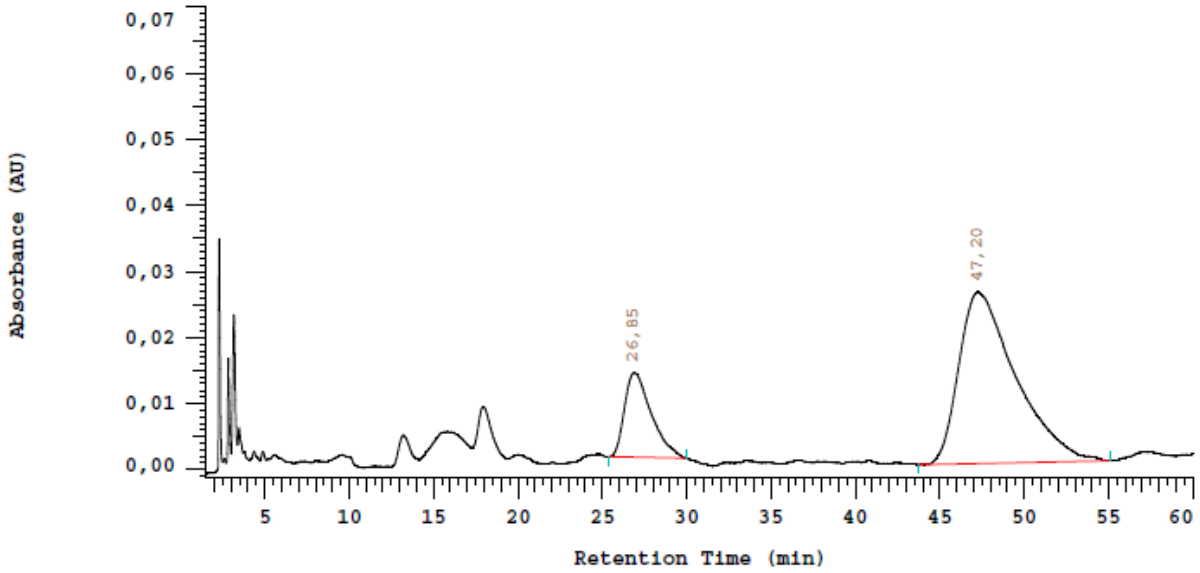
No.	RT	Area	Area %
1	7,09	75384	2,932
2	10,16	2495945	97,068
		2571329	100,000

2: (*S*,*R*,*S*)-**7c**.

HPLC chromatogram of crude compound **7d**

Sample Name: sd-351-cr_1 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description: silicage HEX:EA 50:50 1ml/min

Chrom Type: Fixed WL Chromatogram, 254 nm



Acquisition Method: swarup,silica 50:50,100 min1ml
Column Type: RP-18 Developed by: Rudi
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: EE Solvent D:
Method Description: silicagel, Hexan/EE 50:50, 1,000 mL/min 100 min

Chrom Type: Fixed WL Chromatogram, 254 nm

Peak Quantitation: AREA
Calculation Method: AREA%

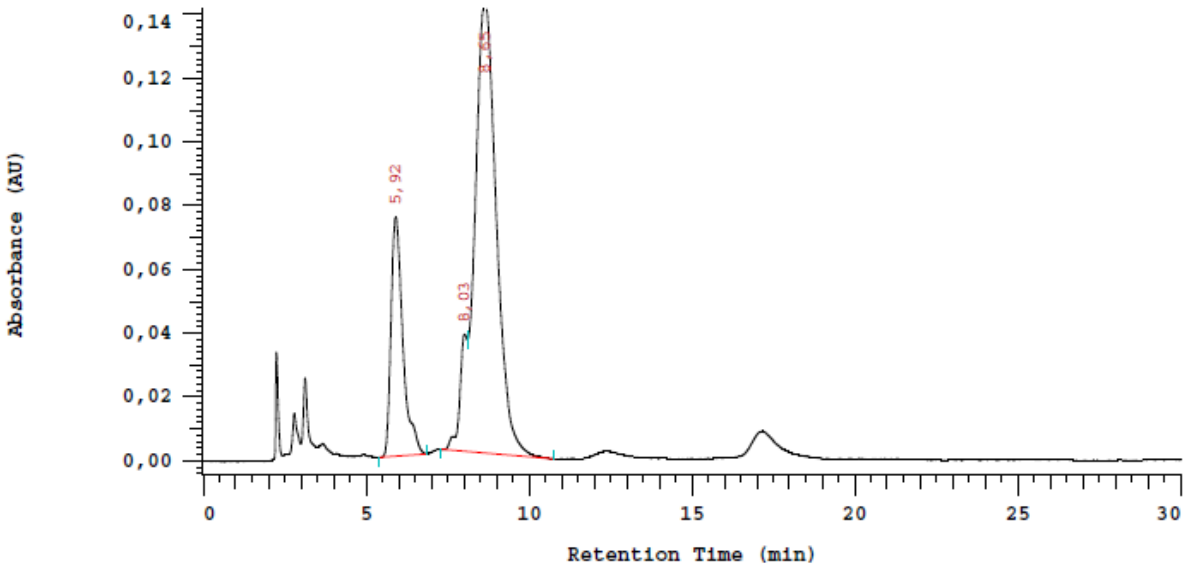
No.	RT	Area	Area %
1	26,85	701592	18,825
2	47,20	3025276	81,175
		3726868	100,000

1: (*S*,*S*,*S*)-**7d**; 2: (*S*,*R*,*S*)-**7d**.

HPLC chromatogram of crude compound **7e**

Sample Name: sd-348-cr_1 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description: silica HEX:EA 50:50 1ml/min

Chrom Type: Fixed WL Chromatogram, 254 nm



Acquisition Method: swarup,silica 50:50,100 min1ml
Column Type: RP-18 Developed by: Rudi
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: EE Solvent D:
Method Description: silicagel, Hexan/EE 50:50, 1,000 mL/min 100 min

Chrom Type: Fixed WL Chromatogram, 254 nm

Peak Quantitation: AREA
Calculation Method: AREA%

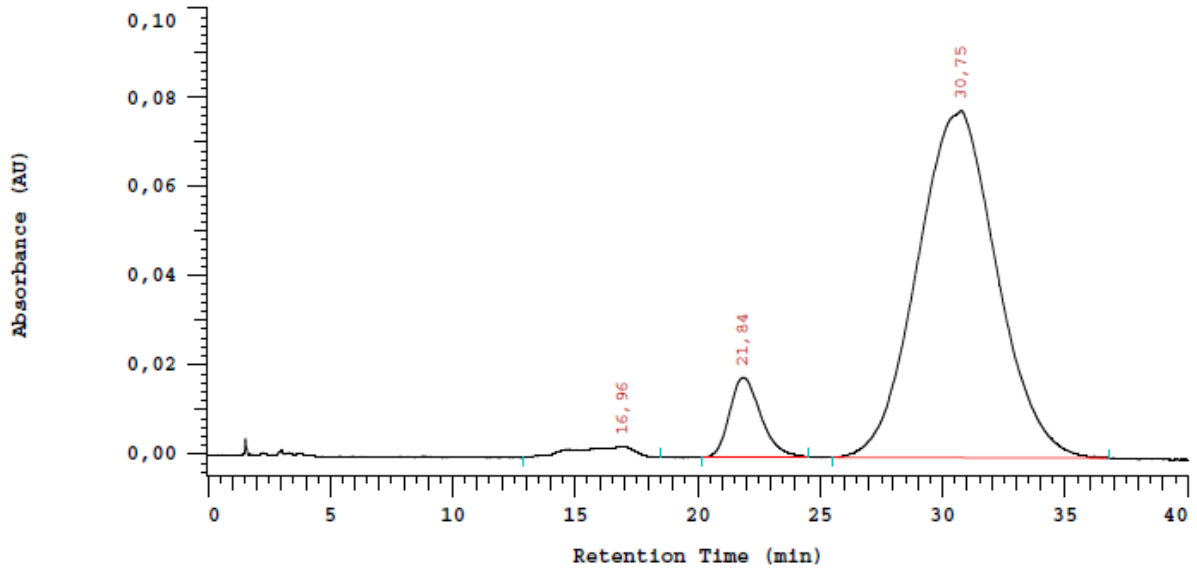
No.	RT	Area	Area %
1	5,92	946941	11,117
2	8,03	279257	3,278
3	8,65	3180023	37,332
4	75,24	4111937	48,273
		8518158	100,000

1: (*S*,*R*,*S*)-**7e**$_b$ 2: (*S*,*S*,*S*)-**7e**$_l$; 3: (*S*,*R*,*S*)-**7e**$_l$.

HPLC chromatogram of crude compound **7f**

Sample Name: sd-346-cr_5 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description: repro HEX:IPA 90:10 2,0 ml/min

Chrom Type: Fixed WL Chromatogram, 254 nm



Acquisition Method: swarup-repro9010 2mL/min
Column Type: RP-18 Developed by: Rudi
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: EE Solvent D: IPA
Method Description: reprosil, Hexan/IPA 90:10, 2,0 mL/min

Chrom Type: Fixed WL Chromatogram, 254 nm

Peak Quantitation: AREA
Calculation Method: AREA%

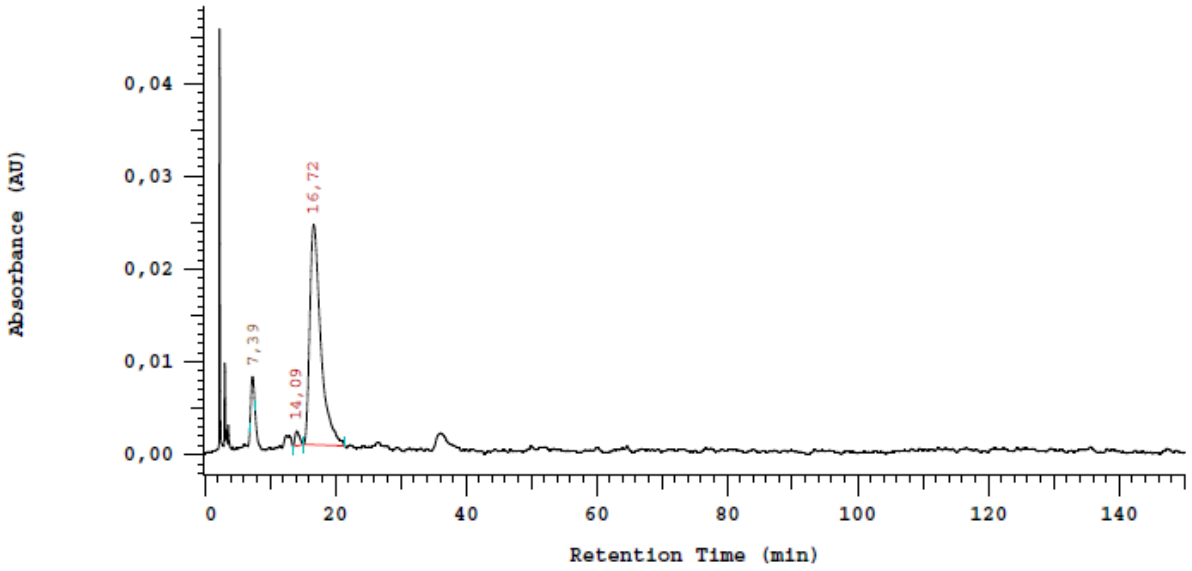
No.	RT	Area	Area %
1	16,96	0	0,000
2	21,84	784412	8,226
3	30,75	8751748	91,774
		9536160	100,000

1: (*S*,*S*,*S*)-**7f**; 2: (*S*,*R*,*S*)-**7f**.

HPLC chromatogram of crude compound **7g**

Sample Name: sd-352-cr_1 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description: silicage HEX:EA 60:40 1ml/min

Chrom Type: Fixed WL Chromatogram, 254 nm



Acquisition Method: swarup , silica 60:40 150 min
Column Type: RP-18 Developed by: Rudi
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: EE Solvent D:
Method Description: silicagel, Hexan/EE 60:40, 1,000 mL/min 150 min

Chrom Type: Fixed WL Chromatogram, 254 nm

Peak Quantitation: AREA
Calculation Method: AREA%

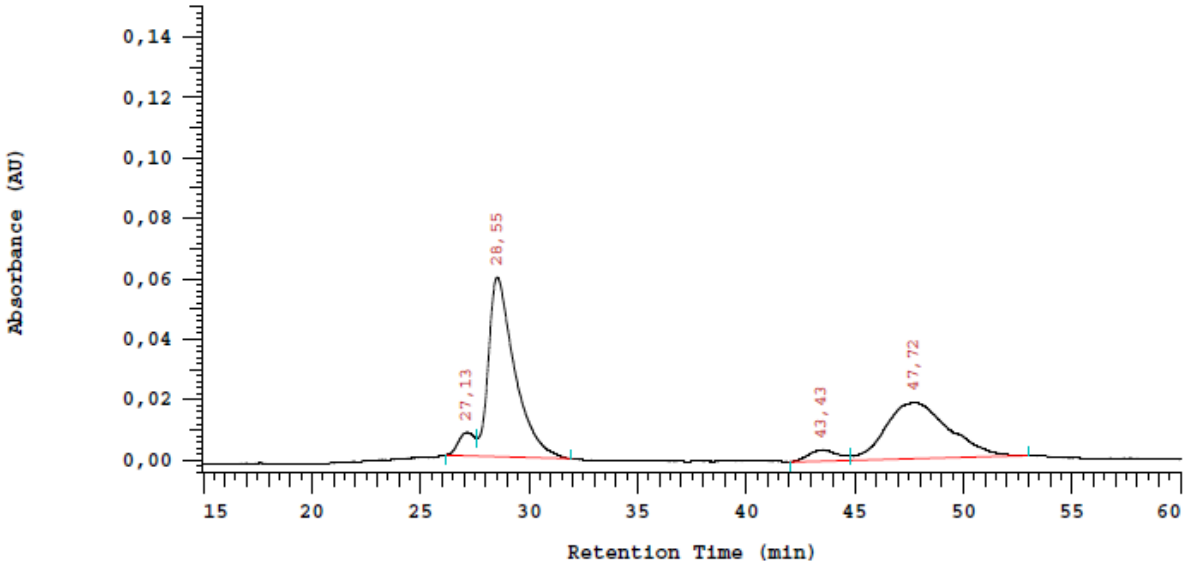
No.	RT	Area	Area %
1	7,39	0	0,000
2	14,09	36042	2,572
3	16,72	1365486	97,428
		1401528	100,000

1: (*S*,*S*,*S*)-**7g**; 2: (*S*,*R*,*S*)-**7g**.

HPLC chromatogram of crude compound **7h**

Sample Name: sd-355-cr_1 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description: silicage HEX:EA 70:30 1ml/min

Chrom Type: Fixed WL Chromatogram, 254 nm



Acquisition Method: swarup, silica hex:ea 70:30
Column Type: RP-18 Developed by: Rudi
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: EE Solvent D:
Method Description: silicagel, Hexan/EE 70:30, 1,000 mL/min

Chrom Type: Fixed WL Chromatogram, 254 nm

Peak Quantitation: AREA
Calculation Method: AREA%

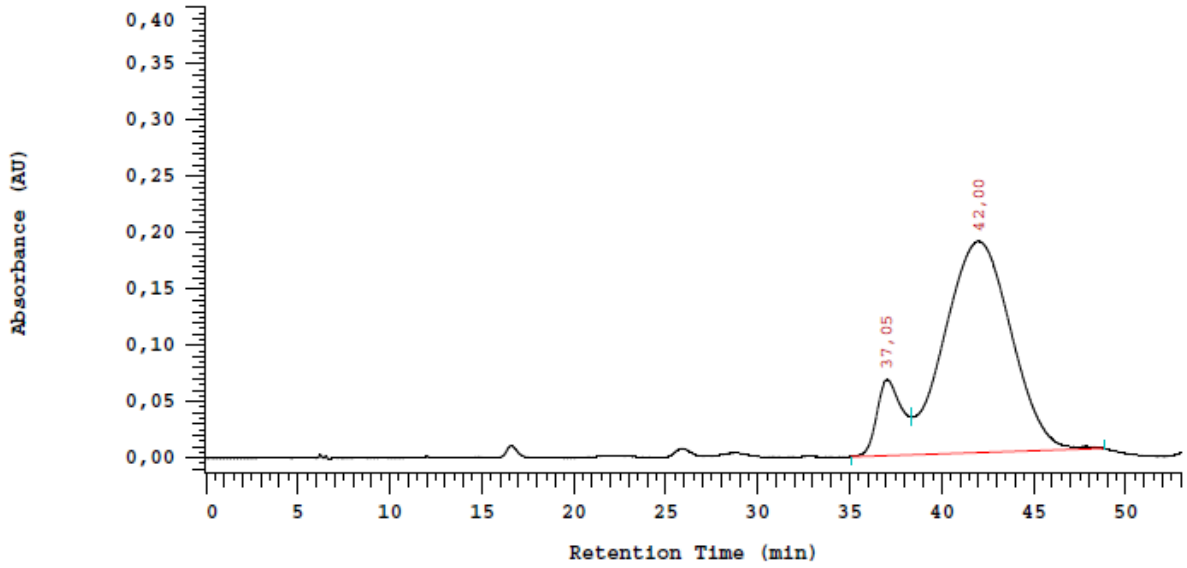
No.	RT	Area	Area %
1	27,13	201693	4,255
2	28,55	2483369	52,388
3	43,43	172975	3,649
4	47,72	1882284	39,708
		4740321	100,000

1: (*S*,*S*,*S*)-**7h**$_b$; 2: (*S*,*R*,*S*)-**7h**$_b$; 3: (*S*,*S*,*S*)-**7h**$_l$, 4: (*S*,*R*,*S*)-**7h**$_l$.

HPLC chromatogram of crude compound **8a**

Sample Name: sd-388-cr_2 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description: reprosilhex:ipa90:10 0,5ml/min

Chrom Type: Fixed WL Chromatogram, 254 nm



Acquisition Method: swarup-repro9010
Column Type: RP-18 Developed by: Rudi
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: EE Solvent D: IPA
Method Description: reprosil, Hexan/IPA 90:10, 0,500 mL/min

Chrom Type: Fixed WL Chromatogram, 254 nm

Peak Quantitation: AREA
Calculation Method: AREA%

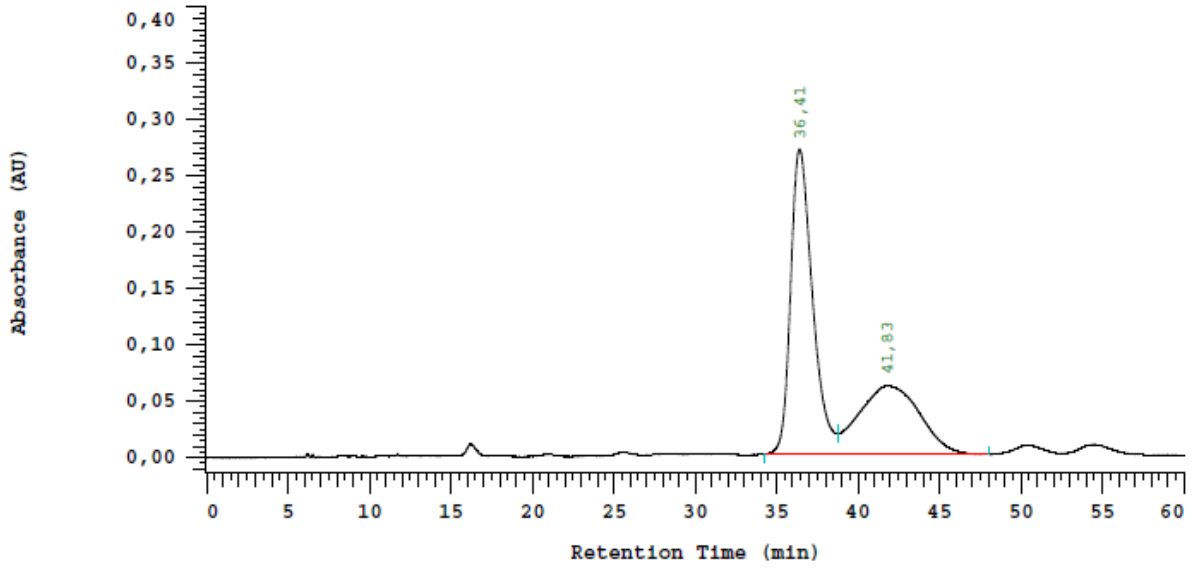
No.	RT	Area	Area %
1	37,05	3184857	11,864
2	42,00	23660384	88,136
		26845241	100,000

1: (*S*,*S*,*S*)-**8a**; 2: (*S*,*R*,*S*)-**8a**.

HPLC chromatogram of crude compound **8a** (from allylation without Pd)

Sample Name: sd-389_cr_5 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description: reprosilhex:ipa90:10 0,5ml/min

Chrom Type: Fixed WL Chromatogram, 254 nm



Acquisition Method: swarup-repro9010
Column Type: RP-18 Developed by: Rudi
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: EE Solvent D: IPA
Method Description: reprosil, Hexan/IPA 90:10, 0,500 mL/min

Chrom Type: Fixed WL Chromatogram, 254 nm

Peak Quantitation: AREA
Calculation Method: AREA%

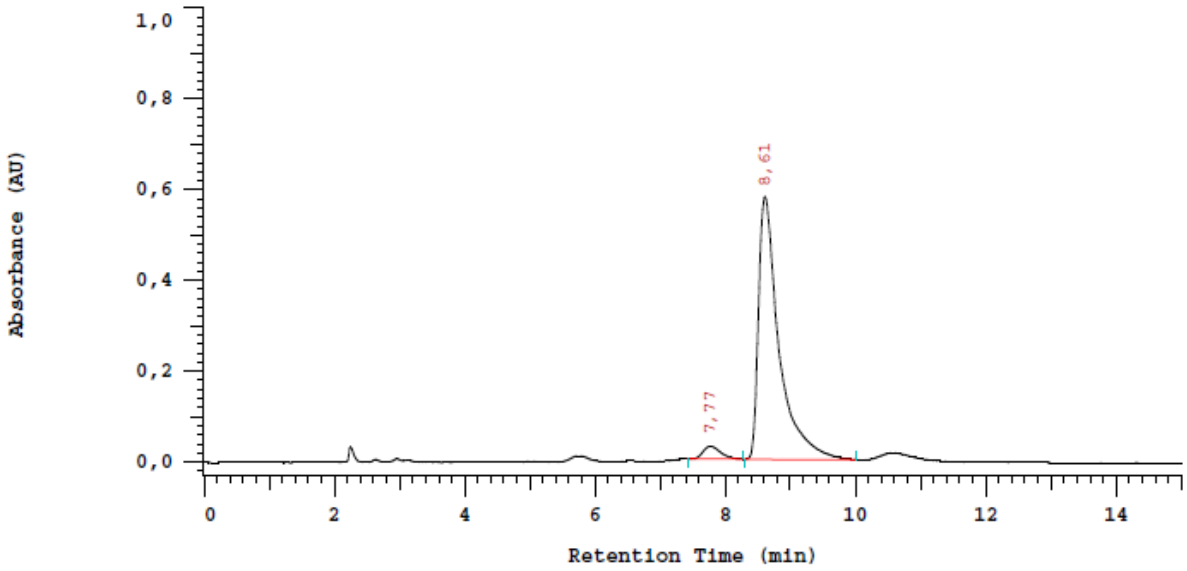
No.	RT	Area	Area %
1	36,41	12639211	61,511
2	41,83	7908764	38,489
		20547975	100,000

1: (*S*,*S*,*S*)-**8a**; 2: (*S*,*R*,*S*)-**8a**.

HPLC chromatogram of crude compound **9a**

Sample Name: sd-385-cr_1 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description: silicage HEX:EA 50:50 1ml/min

Chrom Type: Fixed WL Chromatogram, 254 nm



Acquisition Method: swarup,silica 50:50,100 min1ml
Column Type: RP-18 Developed by: Rudi
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: EE Solvent D:
Method Description: silicagel, Hexan/EE 50:50, 1,000 mL/min 100 min

Chrom Type: Fixed WL Chromatogram, 254 nm

Peak Quantitation: AREA
Calculation Method: AREA%

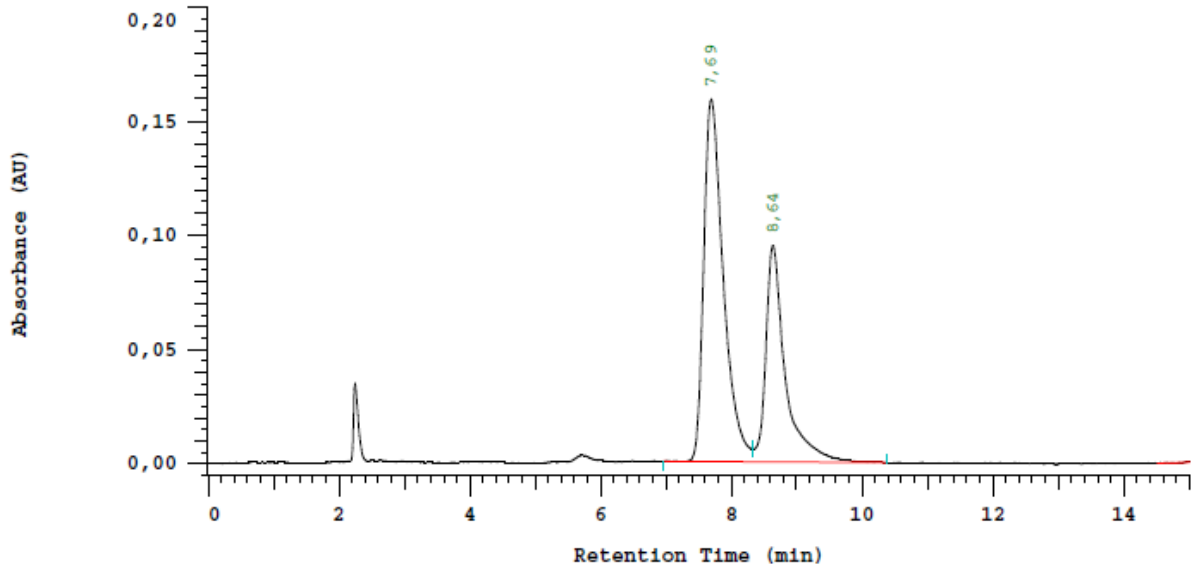
No.	RT	Area	Area %
1	7,77	258957	3,923
2	8,61	6341757	96,077
		6600714	100,000

1: (*S*,*S*,*S*)-**9a**; 2: (*S*,*R*,*S*)-**9a**.

HPLC chromatogram of crude compound **9a** (from allylation without Pd)

Sample Name: sd-386-cr_1 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description: silicage HEX:EA 50:50 1ml/min

Chrom Type: Fixed WL Chromatogram, 254 nm



Acquisition Method: swarup,silica 50:50,100 min1ml
Column Type: RP-18 Developed by: Rudi
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: EE Solvent D:
Method Description: silicagel, Hexan/EE 50:50, 1,000 mL/min 100 min

Chrom Type: Fixed WL Chromatogram, 254 nm

Peak Quantitation: AREA
Calculation Method: AREA%

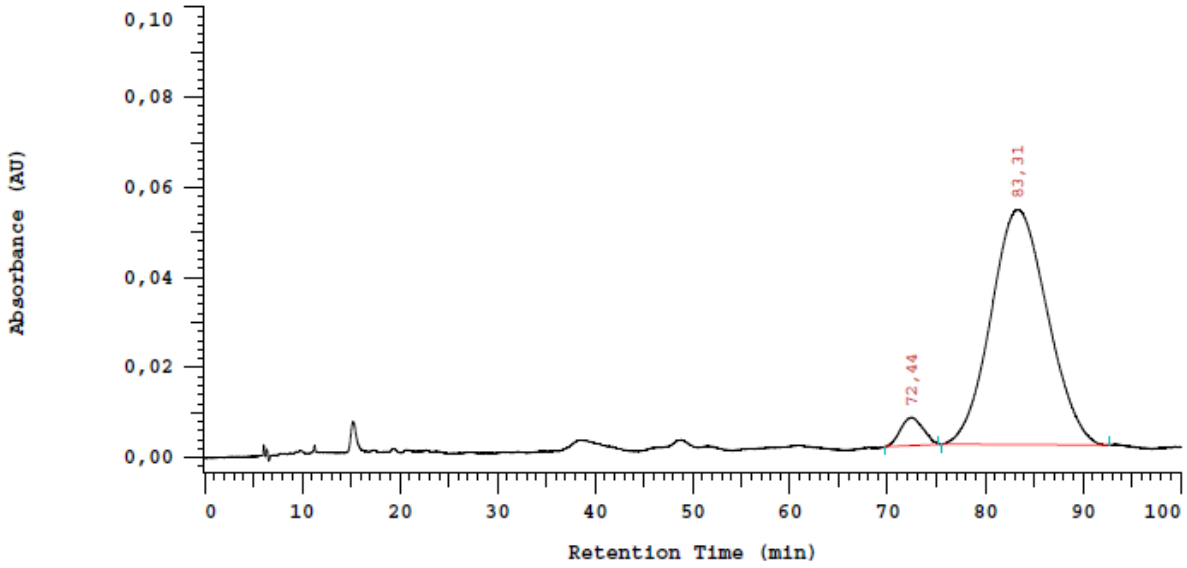
No.	RT	Area	Area %
1	7,69	1656552	62,524
2	8,64	992914	37,476
		2649466	100,000

1: (*S*,*S*,*S*)-**9a**; 2: (*S*,*R*,*S*)-**9a**.

HPLC chromatogram of crude compound **10a**

Sample Name: sd-390-cr_2 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description: reprosilhex:ipa90:10 0,5ml/min

Chrom Type: Fixed WL Chromatogram, 254 nm



Acquisition Method: swarup-repro9010
Column Type: RP-18 Developed by: Rudi
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: EE Solvent D: IPA
Method Description: reprosil, Hexan/IPA 90:10, 0,500 mL/min

Chrom Type: Fixed WL Chromatogram, 254 nm

Peak Quantitation: AREA
Calculation Method: AREA%

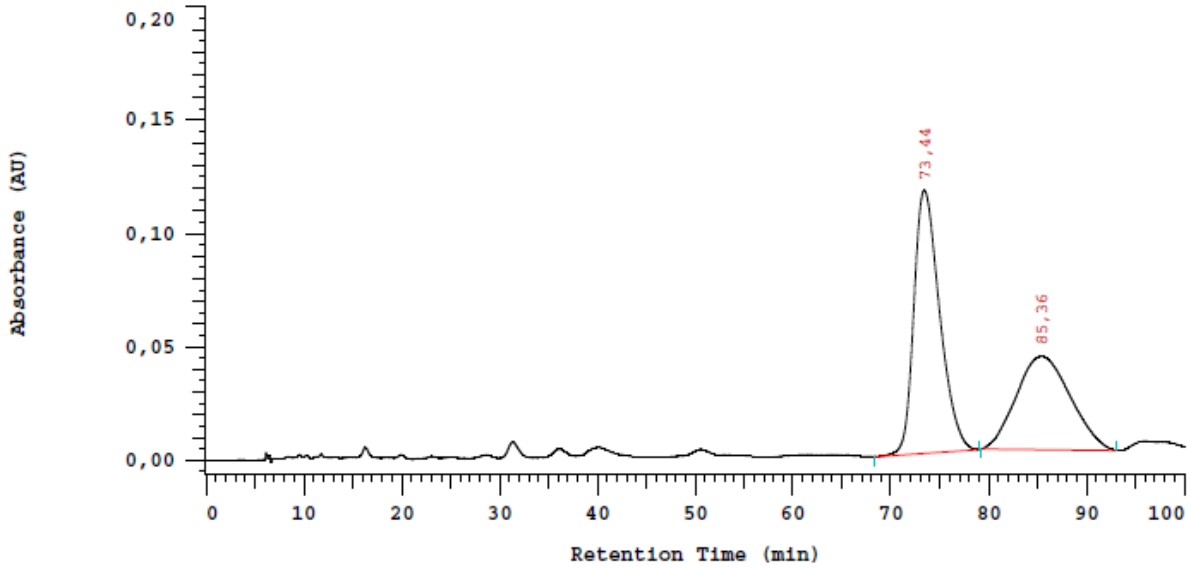
No.	RT	Area	Area %
1	72,44	489199	4,476
2	83,31	10439817	95,524
		10929016	100,000

1: (*S*,*S*,*S*)-**10a**; 2: (*S*,*R*,*S*)-**10a**.

HPLC chromatogram of crude compound **10a** (from allylation without Pd)

Sample Name: sd-391-cr_2 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description: reprosilhex:ipa90:10 0,5ml/min

Chrom Type: Fixed WL Chromatogram, 254 nm



Acquisition Method: swarup-repro9010
Column Type: RP-18 Developed by: Rudi
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: EE Solvent D: IPA
Method Description: reprosil, Hexan/IPA 90:10, 0,500 mL/min

Chrom Type: Fixed WL Chromatogram, 254 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %
1	73,44	10543728	57,305
2	85,36	7855568	42,695
		18399296	100,000

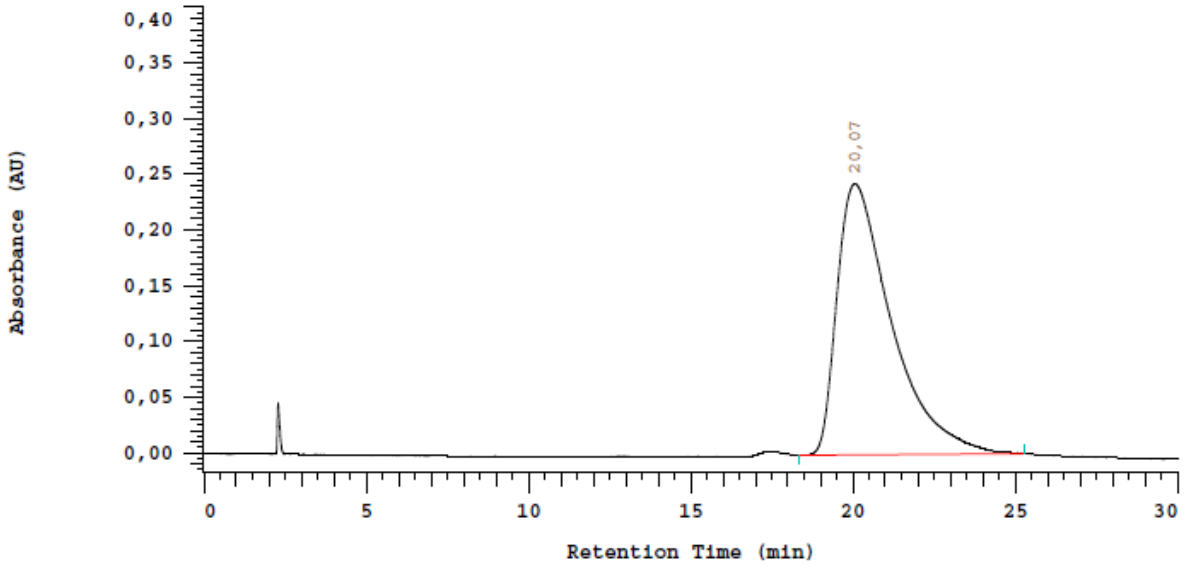
1: (*S*,*S*,*S*)-**10a**; 2: (*S*,*R*,*S*)-**10a**.

Determination of configuration of **7a**

HPLC chromatogram of compound **7a** (major diastereomer) after hydrogenation

Sample Name: sd-401_2 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description: silicage HEX:EA 60:40 1ml/min

Chrom Type: Fixed WL Chromatogram, 254 nm



Acquisition Method: swarup , silica 60:40 30 min
Column Type: RP-18 Developed by: Rudi
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: EE Solvent D:
Method Description: silicagel, Hexan/EE 60:40, 1,000 mL/min 30 min

Chrom Type: Fixed WL Chromatogram, 254 nm

Peak Quantitation: AREA
Calculation Method: AREA%

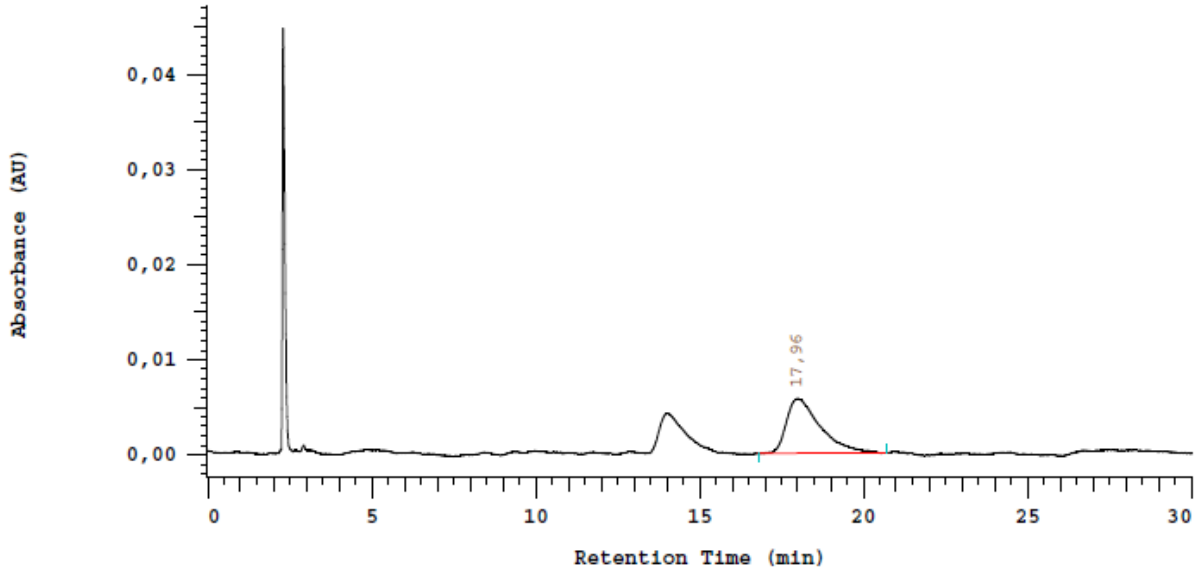
No.	RT	Area	Area %
1	20,07	14208003	100,000
		14208003	100,000

1: (*S*,*R*,*S*)-TFA-Phe-Leu-ProNHPh.

HPLC chromatogram of compound **7a** (minor diastereomer) after hydrogenation

Sample Name: sd-403_1 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description: silicage HEX:EA 60:40 1ml/min

Chrom Type: Fixed WL Chromatogram, 254 nm



Acquisition Method: swarup , silica 60:40 60 min
Column Type: RP-18 Developed by: Rudi
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: EE Solvent D:
Method Description: silicagel, Hexan/EE 60:40, 1,000 mL/min 60 min

Chrom Type: Fixed WL Chromatogram, 254 nm

Peak Quantitation: AREA
Calculation Method: AREA%

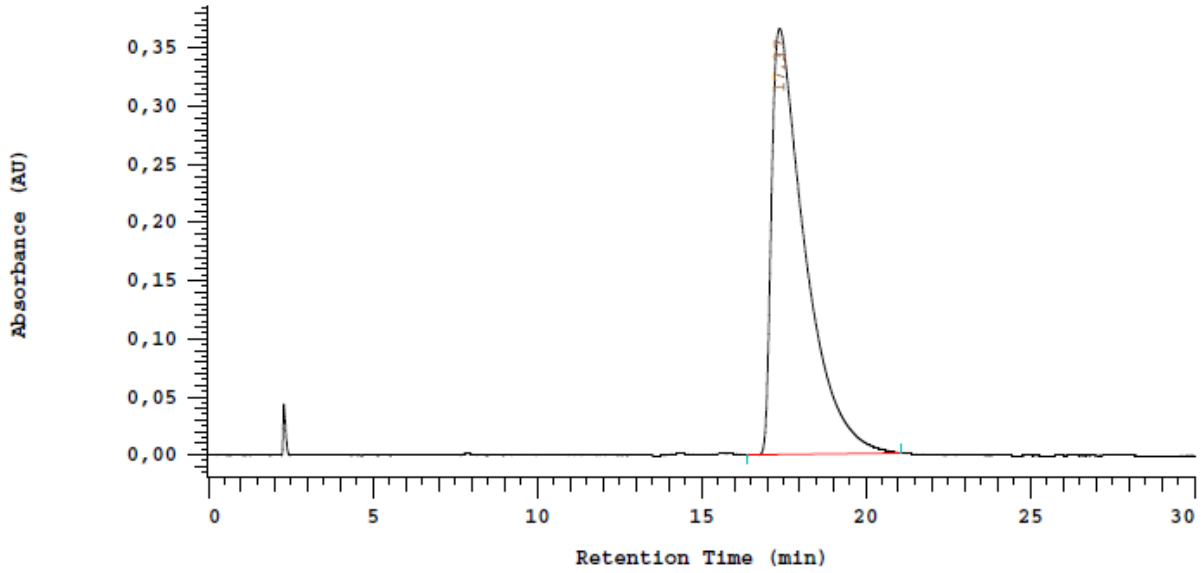
No.	RT	Area	Area %
1	17,96	204499	100,000
		204499	100,000

1: (*S*,*S*,*S*)-TFA-Phe-Leu-ProNHPh.

HPLC chromatogram of authentic TFA-(*S*)-Phe-(*S*)-Leu-(*S*)-ProNHPh from standard peptide coupling

Sample Name: sd-399-p_1 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description: silicage HEX:EA 60:40 1ml/min

Chrom Type: Fixed WL Chromatogram, 254 nm



Acquisition Method: swarup , silica 60:40 60 min
Column Type: RP-18 Developed by: Rudi
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: EE Solvent D:
Method Description: silicagel, Hexan/EE 60:40, 1,000 mL/min 60 min

Chrom Type: Fixed WL Chromatogram, 254 nm

Peak Quantitation: AREA
Calculation Method: AREA%

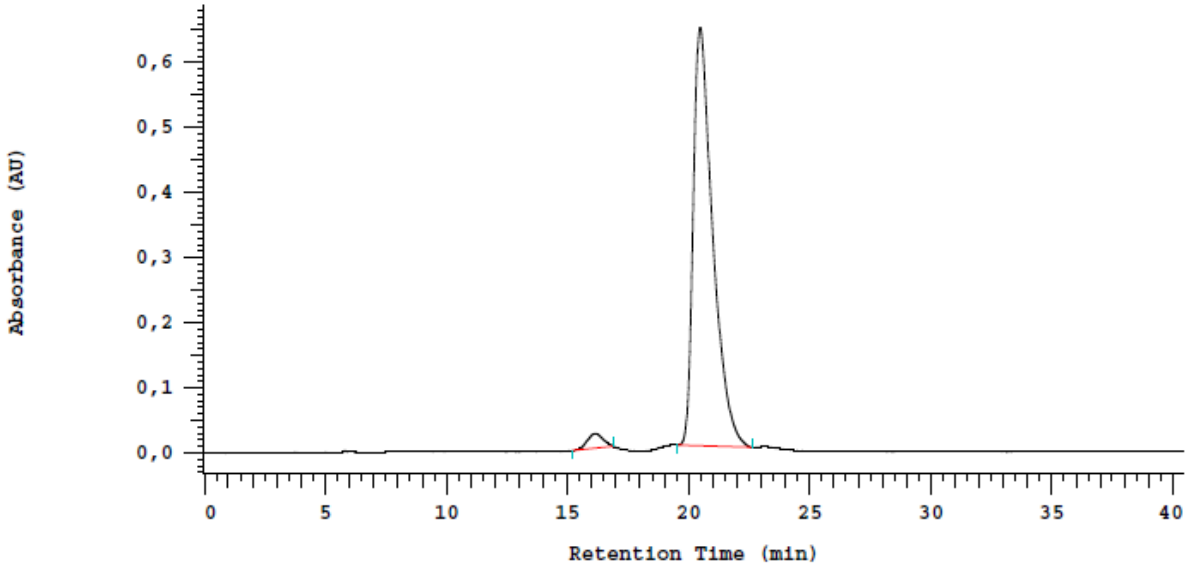
No.	RT	Area	Area %
1	17,37	12966679	100,000
		12966679	100,000

1: (*S*,*S*,*S*)-TFA-Phe-Leu-ProNHPh.

HPLC chromatogram of compound **16a**

Sample Name: AB312B Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description:

Chrom Type: Fixed WL Chromatogram, 252 nm



Acquisition Method: Anton R Hex:iPrOH 9-1 50m
Column Type: RP-18 Developed by: Anton
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: Solvent D: iPrOH
Method Description: Repro, Hexan:iPrOH 9:1 -> 7:3 1 mL/min, 60 min

Chrom Type: Fixed WL Chromatogram, 252 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %
1	16,16	505235	2,738
2	20,48	17944566	97,262
		18449801	100,000

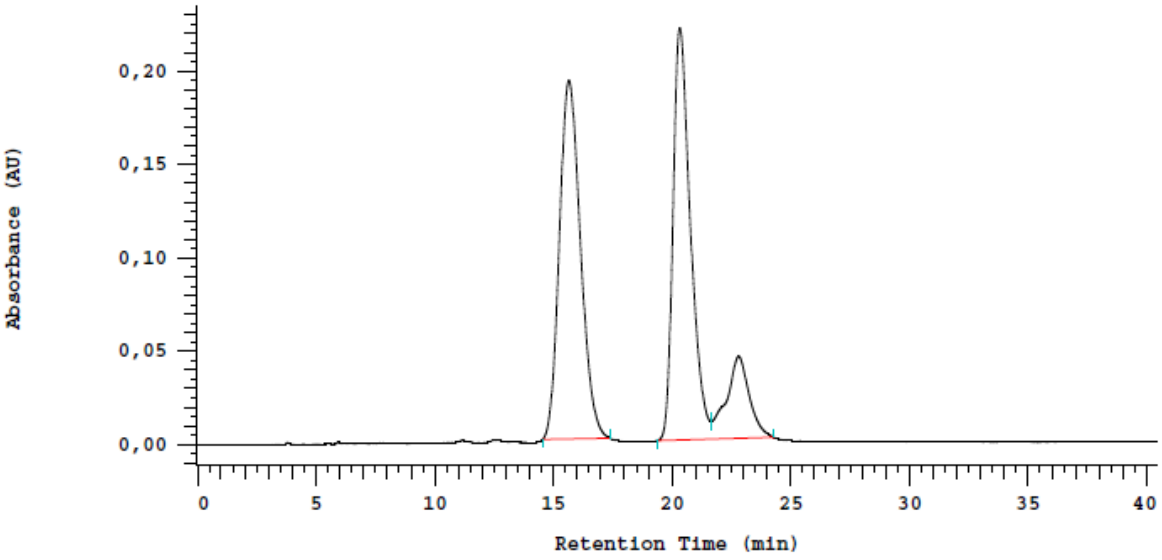
1: (*S*,*S*,*S*)-**16a**; 2: (*S*,*R*,*S*)-**16a**.

HPLC chromatogram of compound **17**

Sample Name: AB313A
Injection from this vial: 1 of 1
Sample Description:

Vial Type: UNK
Volume: 10,0 ul

Chrom Type: Fixed WL Chromatogram, 252 nm



Acquisition Method: Anton R Hex:iPrOH 9-1 50m
Column Type: RP-18
Developed by: Anton
Pump A Type: L-7100
Solvent A:
Solvent B: Hexan
Solvent C:
Solvent D: iPrOH
Method Description: Repro, Hexan:iPrOH 9:1 -> 7:3 1 mL/min, 60 min

Chrom Type: Fixed WL Chromatogram, 252 nm

Peak Quantitation: AREA
Calculation Method: AREA%

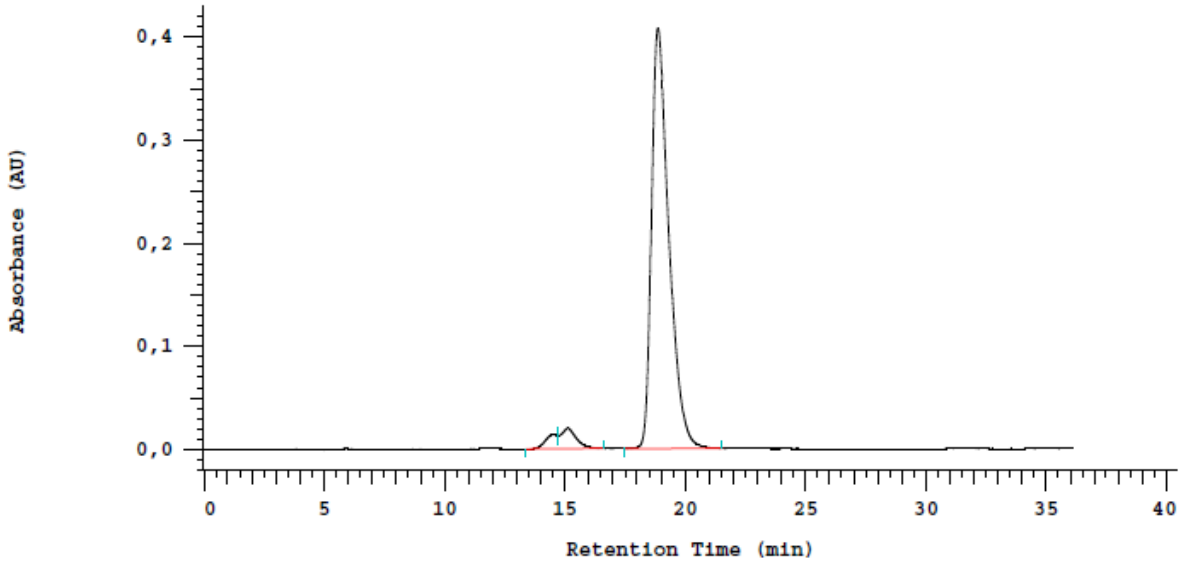
No.	RT	Area	Area %
1	15,67	5919900	45,551
2	20,33	5599845	43,089
3	22,79	1476315	11,360
		12996060	100,000

1: (*S*,*S*,*S*)-**17**; 2: (*S*,*R*,*S*)-**17**; 3: unreacted **12**.

HPLC chromatogram of compound **18**

Sample Name: AB313B Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description:

Chrom Type: Fixed WL Chromatogram, 252 nm



Acquisition Method: Anton R Hex:iPrOH 9-1 50m
Column Type: RP-18 Developed by: Anton
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: Solvent D: iPrOH
Method Description: Repro, Hexan:iPrOH 9:1 -> 7:3 1 mL/min, 60 min

Chrom Type: Fixed WL Chromatogram, 252 nm

Peak Quantitation: AREA
Calculation Method: AREA%

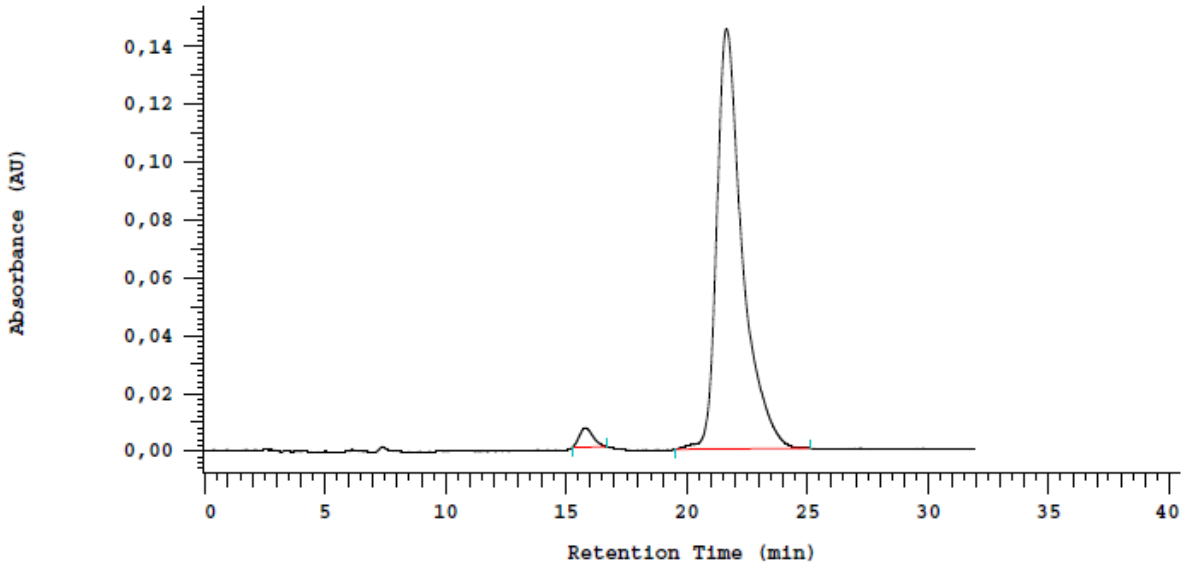
No.	RT	Area	Area %
1	14,51	248196	2,246
2	15,13	451155	4,083
3	18,87	10348956	93,670
		11048307	100,000

1/2: (*S*,*S*,*S*)-**18**; 3: (*S*,*R*,*S*)-**18**.

HPLC chromatogram of compound **16b**

Sample Name: AB315A Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description:

Chrom Type: Fixed WL Chromatogram, 252 nm



Acquisition Method: Anton R Hex:iPrOH 9-1 50m
Column Type: RP-18 Developed by: Anton
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: Solvent D: iPrOH
Method Description: Repro, Hexan:iPrOH 9:1->7:3 1 mL/min, 60 min

Chrom Type: Fixed WL Chromatogram, 252 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %
1	15,81	131772	2,408
2	21,65	5341318	97,592
		5473090	100,000

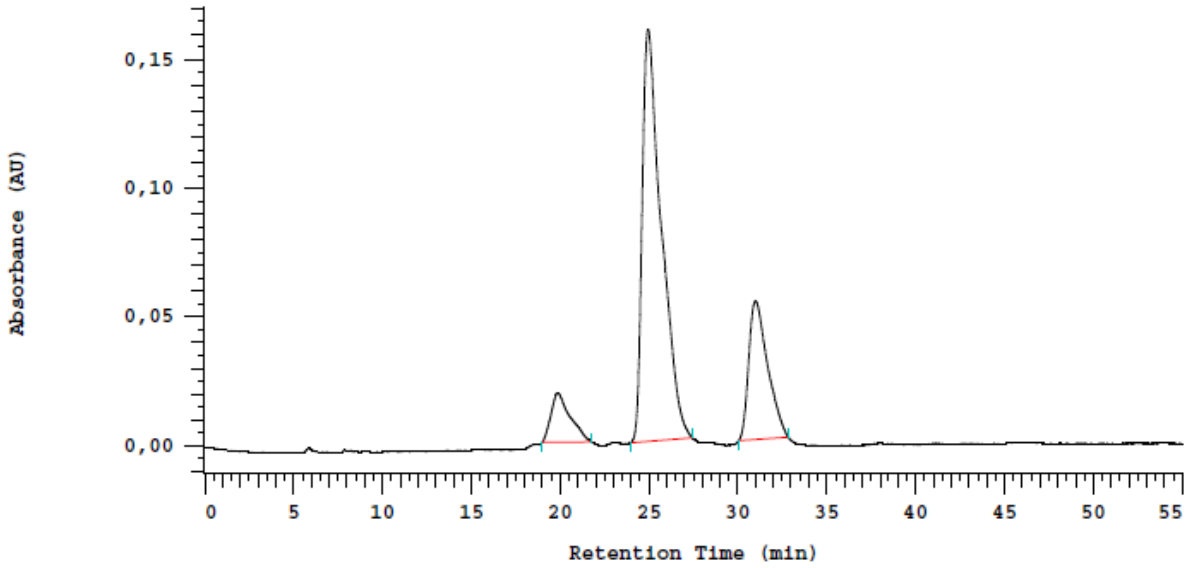
1: (*S*,*S*,*S*)-**16b**; 2: (*S*,*R*,*S*)-**16b**.

HPLC chromatogram of crude compound **19**

Sample Name: AB356B_roh
Injection from this vial: 1 of 1
Sample Description:

Vial Type: UNK
Volume: 10,0 ul

Chrom Type: Fixed WL Chromatogram, 252 nm



Acquisition Method: Anton R Hex:iPrOH 9-1 50m
Column Type: RP-18
Developed by: Anton
Pump A Type: L-7100
Solvent A:
Solvent B: Hexan
Solvent C:
Solvent D: iPrOH
Method Description: Repro, Hexan:iPrOH 9:1->7:3 1 mL/min, 60 min

Chrom Type: Fixed WL Chromatogram, 252 nm

Peak Quantitation: AREA
Calculation Method: AREA%

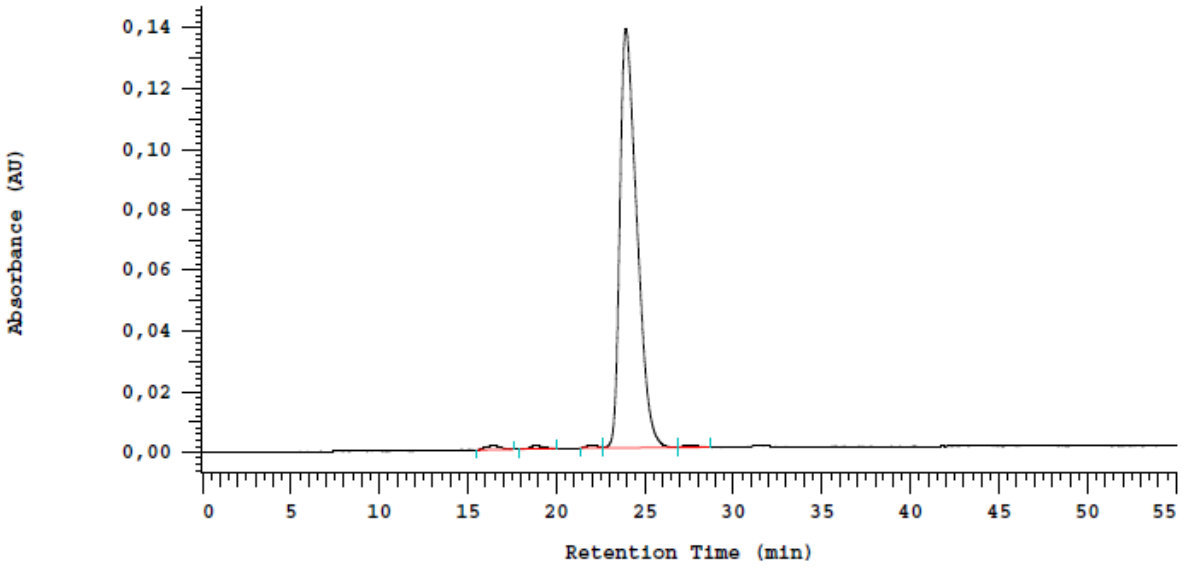
No.	RT	Area	Area %
1	19,87	716759	8,219
2	24,95	6022205	69,059
3	30,99	1981441	22,722
		8720405	100,000

1: (*S*,*S*,*S*)-**19**; 2: (*S*,*R*,*S*)-**19**; 3: unreacted **14**.

HPLC chromatogram of compound **20**

Sample Name: AB353B_F1 Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10,0 ul
Sample Description:

Chrom Type: Fixed WL Chromatogram, 252 nm



Acquisition Method: Anton R Hex:iPrOH 9-1 50m
Column Type: RP-18 Developed by: Anton
Pump A Type: L-7100
Solvent A: Solvent B: Hexan
Solvent C: Solvent D: iPrOH
Method Description: Repro, Hexan:iPrOH 9:1->7:3 1 mL/min, 60 min

Chrom Type: Fixed WL Chromatogram, 252 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %
1	16,44	40262	0,856
2	18,81	26826	0,570
3	21,95	23707	0,504
4	23,93	4594426	97,660
5	27,51	19266	0,410
		4704487	100,000

4: (*S*,*R*,*S*)-**20**.