Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Synthesis of Indoles and Tryptophan Derivatives *via* Photoinduced Nitrene C-H-Insertion

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Supporting Information

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1. Experimental Section

1.1. Preparation of Starting Materials

Unless otherwise stated, all starting materials were purchased from *Acros Organics*, *ABCR* or *Sigma-Aldrich* and used without further purification.

2-(tributylstannyl)allyl ethyl carbonate and stannylated amino acid **1** were prepared according to a procedure by Kazmaier *et al.*[1]

2-Iodo-4-methylaniline[2], 4-chloro-2-iodoaniline[2], 2-iodo-4-methoxyaniline[3], 2-iodo-3-methoxyaniline[4], 3-iodobenzocaine[5] and 2-iodo-1-naphthylamin[4] were prepared according to published procedures.

1.2. General procedures (GP)

GP1: Stille cross coupling (Method A)[8]

A dried Schlenk tube was charged with the organotin compound and the (substituted) *o*-iodoaniline in DMF (2 mL/mmol). CsF (2.0 eq), CuI (10 mol-%) and $Pd(PPh_3)_4$ were added and the mixture was stirred at 45 °C. After reaching full conversion (TLC) EtOAc and H_2O were added. Upon vigorous shaking (in the Schlenk tube) a colorless precipitate formed and the mixture was filtered through a pad of Celite® with EtOAc. The filtrate was dried over Na_2SO_4 and concentrated. The residue was purified by (automated) flash chromatography.

GP2: Stille cross coupling (Method B)

An oven dried Schlenk tube was charged with LiCl (2.0 eq) and heated with a heat gun under vacuum (< 0.1 mbar). After cooling to r.t. CuI (2.0 eq), (substituted) *o*-iodoaniline (1.0 eq) and $Pd(PPh_3)_4$ (5 mol-%) were added and the flask was evacuated and refilled with Ar three times. DMF (10 mL/mmol), which was previously degassed by bubbling with Ar, and the organotin compound (1.2 eq) was added and the mixture was heated to 80 °C for 18 h. After reaching full conversion (TLC) the mixture was diluted with EtOAc and 5 mL of 1 M KF-solution were added. Upon vigorous shaking (in the Schlenk tube) a colorless precipitate formed and the mixture was filtered through a pad of Celite® with EtOAc. The layers were separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by (automated) flash chromatography.

GP3: Diazotation/azidation of anilines

The aniline derivative was dissolved in a mixture of MeCN and 0.5 M HCl (1:1, 0.05 M). Subsequently, $NaNO_2$ (1.6 equiv) was added at 0 °C. After stirring for 5 min NaN_3 (1.6 equiv) was added. After stirring for another 5 min, saturated $NaHCO_3$ solution was added and the aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, concentrated *in vacuo* and the residue was purified by (automated) flash chromatography.

GP4: Photocyclisation of azides

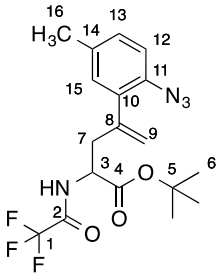
The corresponding azide was dissolved in MeCN (10 mL/mmol) in a round bottom flask, which was then wrapped with aluminium foil and irradiated with an UV-LED lamp at 25% (6.25 W cm^{-2}) of the maximum irradiance for the specified time at room temperature under laboratory atmosphere. The solvent was removed *in vacuo* and the residue was purified by (automated) flash chromatography.

Figure 1. Setup for the photocyclisation of azides.

1.3. Synthesis of tryptophan derivates

***tert*-Butyl 4-(2-azido-5-methylphenyl)-2-(2,2,2-trifluoroacetamido)pent-4-enoate (3b)**

According to **GP3** 143 mg (0.383 mmol) of **4b** were reacted with $NaNO_2$ (42.3 mg, 0.614 mmol) and NaN_3 (39.9 mg, 0.614 mmol). Flash chromatography (hexanes/EtOAc 95:5) afforded 141 mg (0.354 mmol, 92%) of azide **3b** as a colorless oil. $\mathbf{R_f}$ = 0.46 (hexanes/EtOAc 90:10).



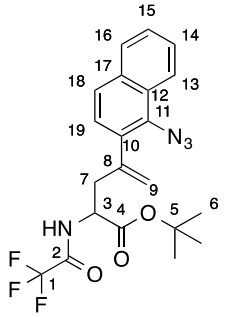
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.39 (s, 9 H, 6-H), 2.31 (s, 3 H, 16-H), 2.93 (ddd, *J* = 14.5, 6.3, 0.6 Hz, 1 H, 7-H_a), 3.22 (ddd, *J* = 14.5, 5.3, 0.7 Hz, 1 H, 7-H_b), 4.47 (m, 1 H, 3-H), 5.13 (d, *J* = 1.4 Hz, 1 H, 9-H_a), 5.24 (m, 1 H, 9-H_b), 6.81 (d, *J* = 6.7 Hz, 1 H, TFAN-H), 6.94 (d, *J* = 1.7 Hz, 1 H, 15-H), 7.03 (d, *J* = 8.1 Hz, 1 H, 12-H), 7.14 (dd, *J* = 8.2, 1.5 Hz, 1 H, 13-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 20.7 (C-16), 27.8 (C-6), 38.1 (C-7), 52.3 (C-3), 83.1 (C-5), 118.3 (C-12), 120.3 (C-9), 129.9 (C-13), 131.0 (C-12), 132.7 (C-10), 134.2 (C-11), 134.8 (C-14), 141.9 (C-8), 169.0 (C-4). Signals of the TFA group could not be observed.

HRMS (CI)	calculated	found
$C_{18}H_{21}F_3NO_3$ $[M\text{-}N_3\text{-}H_2]^+$	355.1390	355.1392

***tert*-Butyl 4-(1-azidonaphthalen-2-yl)-2-(2,2,2-trifluoroacetamido)pent-4-enoate (3g)**

According to **GP3** 50 mg of **4g** (0.122 mmol) were reacted with $NaNO_2$ (14 mg, 0.196 mmol) and NaN_3 (13 mg, 0.196 mmol). Automated flash chromatography (hexanes/EtOAc 100:0, 90:10) afforded 48 mg (0.110 mmol, 91%) of azide **3g** as a brown resin. $\mathbf{R_f}$ = 0.79 (hexanes/EtOAc 90:10).



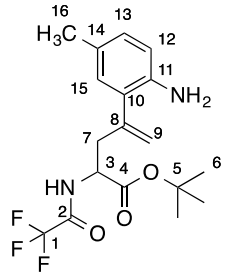
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.30 (s, 9 H, 6-H), 3.10 (ddd, *J* = 14.6, 6.1, 0.8 Hz, 1 H, 7-H_a), 3.33 (ddd, *J* = 14.6, 5.1, 0.9 Hz, 1 H, 7-H_b), 4.55 (m, 1 H, 3-H), 5.38 (d, *J* = 1.2 Hz, 1 H, 9-H_a), 5.50 (m, 1 H, 9-H_b), 6.81 (d, *J* = 7.2 Hz, 1 H, TFAN-H), 7.24 (d, *J* = 8.4 Hz, 1 H, 19-H), 7.50–7.59 (m, 2 H, 14-H, 15-H), 7.68 (d, *J* = 8.3 Hz, 1 H, 18-H), 7.82 (m, 1 H, 16-H), 8.20 (m, 1 H, 13-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 27.7 (C-6), 37.9 (C-7), 52.3 (C-3), 83.5 (C-5), 121.7 (C-9), 122.9, 126.2 (C-18), 126.8, 127.0 (C-14, C-15), 127.5 (C-19), 127.9 (C-16), 128.0 (C-12), 131.7 (C-17), 131.9 (C-10), 133.8 (C-11), 141.1 (C-8), 156.4 (q, $^2J_{C2\text{-}F}$ = 38.7 Hz, 168.8 (C-4). The signal of C-1 could not be observed.

HRMS (CI)	calculated	found
$C_{21}H_{21}F_3N_2O_3$ $[M\text{-}N_2]^+$	406.1499	406.1482

***tert*-Butyl 4-(2-amino-5-methylphenyl)-2-(2,2,2-trifluoroacetamido)pent-4-enoate (4b)**

According to **GP2** 136 mg (0.584 mmol) of 2-iodo-4-methylaniline were reacted with **1** (390 mg, 0.701 mmol), LiCl (42 mg, 1.00 mmol), CuI (190 mg, 1.00 mmol) and $Pd(PPh_3)_4$ (28.9 mg, 25 µmol). Automated flash chromatography (hexanes/EtOAc 100:0, 80:20) afforded 161 mg (0.432 mmol, 74%) of **4b** as a brown oil. $\mathbf{R_f}$ = 0.29 (hexanes/EtOAc 80:20).



^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.42 (s, 9 H, 6-H), 2.21 (s, 3 H, 16-H), 2.96 (dd, *J* = 14.0, 5.1 Hz, 1 H, 7-H_a), 3.05 (ddd, *J* = 14.1, 5.3, 0.7 H, 7-H_b), 3.70 (bs, 2 H, NH_2), 4.59 (m, 1 H, 3-H), 5.19 (d, *J* = 1.8 Hz, 1 H, 9-H_a), 5.33 (m,1 H, 9-H_b), 6.62 (d, *J* = 8.1 Hz, 1 H, 12-H),6.77 (d, *J* = 1.8 Hz, 15-H), 6.89 (dd, *J* = 8.1, 1.5 Hz, 1 H, 13-H), 7.57 (d, *J* = 7.2 Hz, 1 H, TFAN-H).

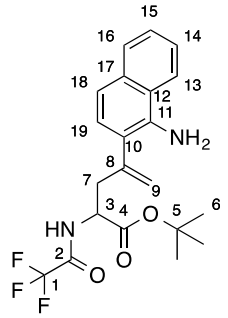
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 20.4 (C-16), 27.9 (C-6), 38.8 (C-7), 52.6 (C-3), 83.1 (C-5), 116.7 (C-12), 119.5 (C-9), 127.6 (C-10), 128.4 (C-14), 128.9 (C-15), 129.3 (C-13), 139.8 (C-11), 142.4 (C-8), 168.9 (C-4). Signals of the TFA group could not be observed.

HRMS (CI)	calculated	found

$C_{18}H_{23}F_3N_2O_3$ [M]$^+$	372.1655	372.1660

tert-Butyl 4-(1-aminonaphthalen-2-yl)-2-(2,2,2-trifluoroacetamido)pent-4-enoate (4g)

According to **GP2** 51 mg (0.190 mmol) of 2-amino-3-iodonaphthalene were reacted with **1** (127 mg, 0.228 mmol), LiCl (16 mg, 0.380 mmol), CuI (72 mg, 0.380 mol) and $Pd(PPh_3)_4$ (11 mg, 9.5 µmol). Automated flash chromatography (hexanes/EtOAc 100:0, 80:20, 70:30) yielded 51 mg (0.125 mmol, 66%) of **4g** as a purple resin. $\mathbf{R_f}$ = 0.31 (hexanes/EtOAc 80:20).



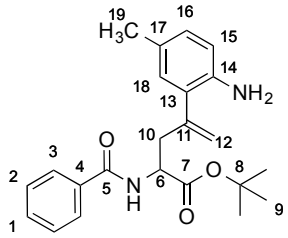
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.38 (s, 9 H, 6-H), 3.02 (ddd, *J* = 14.2, 5.3, 0.7 Hz, 1 H, 7-H_a), 3.19 (ddd, *J* = 14.2, 5.3, 1.0 Hz, 1 H, 7-H_b), 4.45 (bs, 2 H, NH_2), 4.58 (m, 1 H, 3-H), 5.34 (d, *J* = 1.8 Hz, 1 H, 9-H_a), 5.48 (m, 1 H, 9-H_b), 7.11 (d, *J* = 8.4 Hz, 1 H, 19-H), 7.17 (d, *J* = 7.3 Hz, 1 H, TFAN-H), 7.30 (d, *J* = 8.4 Hz, 1 H, 18-H), 7.43–7.50 (m, 2 H, 14-H, 15-H), 7.75–7.82 (m, 2 H, 13-H, 16-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 27.9 (C-6), 39.0 (C-7), 52.7 (C-3), 83.4 (C-5), 118.9 (C-18), 120.2 (C-9), 121.0, 121.1 (C-10, C-13), 123.7 (C-12), 125.4, 126.0, 126.1 (C-14, C-15, C-19), 128.5 (C-16), 133.7 (C-17), 137.9 (C-11), 142.5 (C-8),169.0 (C-4). Signals of the TFA group could not be observed.

HRMS (CI)	calculated	found
$C_{21}H_{23}F_3N_2O_3$ [M]$^+$	408.1655	408.1661

tert-Butyl 4-(2-amino-5-methylphenyl)-2-benzamidopent-4-enoate (5b)

According to **GP1** 2-iodo-4-methylaniline (128 mg, 0.550 mmol) were reacted with **2** (282 mg, 0.500 mmol), CsF (152 mg, 1.00 mmol), CuI (9.5 mg, 0.05 mmol) and $Pd(PPh_3)_4$ (12 mg, 10 µmol). The reaction was worked up after 18 h. Automated flash chromatography (hexanes/EtOAc 100:0, 70:30) afforded 134 mg (0.352 mmol, 70%) of **5b** as a brown resin. $\mathbf{R_f}$ = 0.26 (hexanes/EtOAc 70:30).



^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.46 (s, 9 H, 9-H), 2.15 (s, 3 H, 19-H), 2.96 (ddd, *J* = 14.0, 5.2, 0.7 Hz, 1 H, 10-H_a), 3.14 (ddd, *J* = 14.0, 5.1, 1.1 Hz, 1 H, 10-H_b), 3.75 (bs, 2 H, NH_2), 4.84 (ddd, *J* = 8.2, 5.1, 5.1 Hz, 1 H, 6-H), 5.21 (d, *J* = 2.0 Hz, 1 H, 12-H_a), 5.36 (m, 1 H, 12-H_b), 6.57

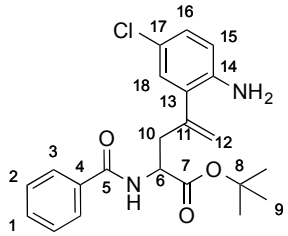
(dd, *J* = 6.5, 2.1 Hz, 1 H, 16-H), 6.80–6.84 (m, 3 H, BzN-H, 15-H, 18-H), 7.31 (m, 2 H, 2-H), 7.41–7.48 (m, 3 H, 1-H, 3-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 20.3 (C-19), 28.1 (C-9), 39.5 (C-10), 53.0 (C-6), 82.2 (C-8), 116.3 (C-16), 119.1 (C-12), 126.9 (C-3), 127.9 (C-13, C-18), 128.2 (C-2), 128.9, 129.1 (C-15, C-17), 131.3 (C-1), 133.9 (C-4), 140.4 (C-14), 142.8 (C-11), 166.5 (C-5), 170.8 (C-7).

HRMS (CI)	calculated	found
$C_{23}H_{28}N_2O_3$ $[M]^+$	380.2094	380.2092

tert-Butyl 4-(2-amino-5-chlorophenyl)-2-benzamidopent-4-enoate (5c)

According to **GP1** 4-chloro-2-iodoaniline (120 mg, 0.473 mmol) was reacted with **2** (282 mg, 0.500 mmol), CsF (152 mg, 1.00 mmol), CuI (9.5 mg, 0.05 mmol) and $Pd(PPh_3)_4$ (12 mg, 10 µmol). The reaction was worked up after 18 h. Automated flash chromatography (hexanes/EtOAc 100:0, 70:30) afforded 137 mg (0.341 mmol, 72%) of **5c** as a brown resin. **R_f** = 0.20 (hexanes/EtOAc 70:30).



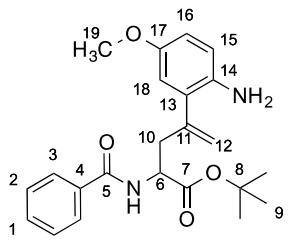
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.46 (s, 9 H, 9-H), 2.91 (ddd, *J* = 14.0, 5.3, 0.7 Hz, 1 H, 10-H_a), 3.13 (ddd, *J* = 14.0, 5.3, 1.1 Hz, 1 H, 10-H_b), 3.88 (bs, 2 H, NH_2), 4.82 (ddd, *J* = 7.9, 5.3, 5.3 Hz, 1 H, 6-H), 5.22 (d, *J* = 1.7 Hz, 1 H, 12-H_a), 5.39 (m, 1 H, 12-H_b), 6.53 (d, *J* = 8.5 Hz, 1 H, 15-H), 6.79 (d, *J* = 7.9 Hz, 1 H, BzN-H), 6.93 (dd, *J* = 8.5, 2.5 Hz, 1 H, 16-H), 6.99 (d, *J* = 2.5 Hz, 1 H, 18-H), 7.36 (m, 2 H, 2-H), 7.46 (m, 1 H, 1-H), 7.56 (m, 2 H, 3-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 28.0 (C-9), 39.3 (C-10), 52.8 (C-6), 82.6 (C-8), 117.1 (C-15), 119.9 (C-12), 123.2 (C-17), 126.9 (C-3), 128.0 (C-16), 128.3 (C-2), 128.4 (C-18), 129.1 (C-13), 131.5 (C-1), 133.8 (C-4), 141.7, 141.8 (C-11, C-14), 166.6 (C-5), 170.7 (C-7).

HRMS (CI)	calculated	found
$C_{22}H_{25}N_2O_3Cl$ $[M]^+$	400.1548	400.1554

tert-Butyl 4-(2-amino-5-methoxyphenyl)-2-benzamidopent-4-enoate (5d)

According to **GP1** 2-iodo-4-methoxyaniline (137 mg, 0.550 mmol) was reacted with **2** (201 mg, 0.356 mmol), CsF (108 mg, 0.712 mmol), CuI (6.8 mg, 35.6 µmol) and $Pd(PPh_3)_4$ (8.2 mg, 7.1 µmol). The reaction was worked up after 6 h. Automated flash chromatography



(hexanes/EtOAc 100:0, 70:30) afforded 108 mg (0.272 mmol, 77%) of **5d** as a brown resin. $\mathbf{R_f}$ = 0.19 (hexanes/EtOAc 70:30).

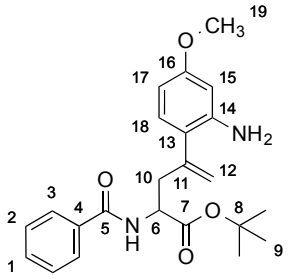
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.45 (s, 9 H, 9-H), 2.96 (ddd, *J* = 14.0, 5.3, 0.6 Hz, 1 H, 10-H_a), 3.14 (ddd, *J* = 14.0, 5.2, 1.0 Hz, 1 H, 10-H_b), 3.67 (s, 3 H, 19-H), 3.88 (bs, 2 H, NH_2), 4.84 (ddd, *J* = 8.1, 5.2, 5.2 Hz, 1 H, 6-H), 5.21 (d, *J* = 1.9 Hz, 1 H, 12-H_a), 5.37 (m, 1 H, 12-H_b), 6.57–6.62 (m, 3 H, 15-H, 16-H, 18-H), 6.93 (d, *J* = 8.1 Hz, 1 H, BzN-H), 7.33 (m, 2 H, 2-H), 7.44 (m, 1 H, 1-H), 7.51 (m, 2 H, 3-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 28.1 (C-9), 39.4 (C-10), 52.8 (C-6), 55.6 (C-19), 82.3 (C-8), 114.1–114.2 (C-16, C-18), 117.3 (C-15) 119.4 (C-12), 126.9 (C-3), 128.2 (C-2), 129.0 (C-13), 131.4 (C-1), 133.9 (C-4), 136.4 (C-14), 142.8 (C-11), 152.7 (C-17), 166.6 (C-5), 170.7 (C-7).

HRMS (CI)	calculated	found
$C_{23}H_{30}N_2O_4$ $[M]^+$	396.2044	396.2084

tert-Butyl 4-(2-amino-4-methoxyphenyl)-2-benzamidopent-4-enoate (5e)

According to **GP1** 2-iodo-5-methoxyaniline (149 mg, 0.600 mmol) was reacted with **2** (339 mg, 0.600 mmol), CsF (182 mg, 1.20 mmol), CuI (11 mg, 0.06 mmol) and $Pd(PPh_3)_4$ (14 mg, 12 µmol). The reaction was worked up after 22 h. Automated flash chromatography (hexanes/EtOAc 100:0, 70:30) afforded 170 mg (0.429 mmol, 71%) of **5e** as a brown resin. $\mathbf{R_f}$



= 0.18 (hexanes/EtOAc 70:30).

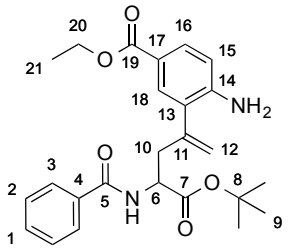
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.47 (s, 9 H, 9-H), 2.91 (ddd, *J* = 14.0, 5.1, 0.7 Hz, 1 H, 10-H_a), 3.14 (ddd, *J* = 14.0, 5.1, 1.0 Hz, 1 H, 10-H_b), 3.70 (s, 3 H, 19-H), 3.90 (bs, 2 H, NH_2), 4.81 (ddd, *J* = 8.1, 5.1, 5.1 Hz, 1 H, 6-H), 5.19 (d, *J* = 2.0 Hz, 1 H, 12-H_a), 5.34 (m, 1 H, 12-H_b), 6.18 (d, *J* = 2.5 Hz, 1 H, 15-H), 6.28 (dd, *J* = 8.4, 2.5 Hz, 1 H, 17-H), 6.70 (d, *J* = 8.1 Hz, 1 H, BzN-H), 6.93 (d, *J* = 8.4 Hz, 1 H, 18-H), 7.32 (m, 2 H, 2-H), 7.42–7.49 (m, 3 H, 1-H, 3-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 28.1 (C-9), 39.7 (C-10), 53.0 (C-6), 55.1 (C-19), 82.3 (C-8), 101.4 (C-15), 104.3 (C-17), 118.9 (C-12), 120.5 (C-13), 126.9 (C-3), 128.2 (C-2), 129.7 (C-18), 131.4 (C-1), 133.9 (C-4), 142.3 (C-11), 144.3 (C-14), 159.9 (C16), 166.5 (C-5), 170.8 (C-7).

HRMS (CI)	calculated	found
$C_{23}H_{29}N_2O_4$ $[M+H]^+$	397.2122	397.2145

Ethyl 4-amino-3-[4-benzamido-5-(*tert*-butoxy)-5-oxopent-1-en-2-yl]benzoate (5f)

According to **GP1** 3-iodobenzocaine (87 mg, 0.300 mmol) was reacted with **2** (169 mg, 0.300 mmol), CsF (91 mg, 0.600 mmol), CuI (5.7 mg, 0.03 mmol) and $Pd(PPh_3)_4$ (7 mg, 6 µmol). The reaction was worked up after 16 h. Automated flash chromatography (hexanes/EtOAc 100:0, 70:30) afforded 78 mg (0.178 mmol, 59%) of **5f** as a brown resin. $\mathbf{R_f}$ = 0.20 (hexanes/EtOAc 70:30).



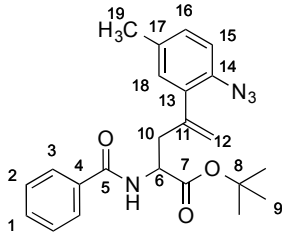
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.34 (t, *J* = 7.1 Hz, 3 H, 21-H), 1.46 (s, 9 H, 9-H), 2.93 (ddd, *J* = 14.1, 5.7, 0.8 Hz, 1 H, 10-H_a), 3.17 (ddd, *J* = 14.1, 5.2, 1.0 Hz, 1 H, 10-H_b), 4.29 (m, 2 H, 20-H), 4.39 (bs, 2 H, NH_2), 4.81 (ddd, *J* = 7.9, 5.5, 5.5 Hz, 1 H, 6-H), 5.25 (d, *J* = 1.7 Hz, 1 H, 12-H_a), 5.42 (m, 1 H, 12-H_b), 6.60 (d, *J* = 8.3 Hz, 1 H, 15-H), 6.68 (d, *J* = 7.8 Hz, 1 H, BzN-H), 7.34 (m, 2 H, 2-H), 7.45 (m, 1 H, 1-H), 7.53 (m, 2 H, 3-H), 7.70 (dd, *J* = 8.3, 2.0 Hz, 1 H, 16-H), 7.73 (d, *J* = 2.0 Hz, 1 H, 18-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.4 (C-21), 28.0 (C-9), 39.7 (C-10), 52.9 (C-6), 60.3 (C-20), 82.7 (C-8), 114.9 (C-15), 119.7 (C-12), 120.0 (C-17), 126.4 (C-13), 126.8 (C-3), 128.4 (C-2), 130.3 (C-16), 130.6, (C-18), 131.5 (C-1), 133.8 (C-4), 141.8 (C-11), 147.6 (C-14), 166.4 (C-19), 166.6 (C-5), 170.8 (C-7).

HRMS (CI)	calculated	found
$C_{25}H_{30}N_2O_5$ $[M]^+$	438.2149	438.2114

tert-Butyl 4-(2-azido-5-methylphenyl)-2-benzamidopent-4-enoate (6b)

According to **GP3** 113 mg (0.270 mmol) of **5b** were reacted with $NaNO_2$ (33 mg, 0.475 mmol) for 15 min and NaN_3 (31 mg, 0.475 mmol) for 15 min. Automated flash chromatography (hexanes/EtOAc 100:0, 80:20) afforded 107 mg (0.256 mmol, 95%) of **6b** as a yellow resin. $\mathbf{R_f}$ = 0.56 (hexanes/EtOAc 70:30).



^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.41 (s, 9 H, 9-H), 2.25 (s, 3 H, 19-H), 2.97 (ddd, *J* = 14.3, 6.2, 0.6 Hz, 1 H, 10-H_a), 3.26 (ddd, *J* = 14.3, 5.2, 0.8 Hz, 1 H, 10-H_b), 4.71 (ddd, *J* = 7.8, 6.2, 5.3 Hz, 1 H, 6-H), 5.11 (d, *J* = 1.7 Hz, 1 H, 12-H_a), 5.27 (m, 1 H, 12-H_a), 6.57 (d, *J* = 7.7 Hz, 1 H, BzN-H), 6.97 (d, *J* = 8.1 Hz, 1 H, 15-H), 6.99 (m, 1 H, 18-H), 7.05 (m, 1 H, 16-H), 7.36 (m, 2 H, 2-H), 7.46 (m, 1 H, 1-H), 7.58 (m, 2 H, 3-H).

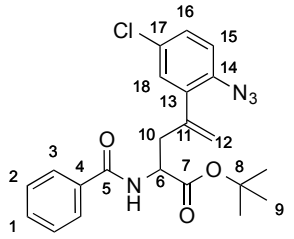
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 20.6 (C-19), 27.9 (C-9), 38.7 (C-10), 52.4 (C-6), 82.1 (C-8), 118.3 (C-15), 119.7 (C-12), 126.8 (C-3), 128.3 (C-2), 129.4 (C-16), 131.0 (C-18), 131.4 (C-1), 133.5 (C-13), 134.0, 134.1 (C-4, C-14), 134.6 (C-17), 142.8 (C-11), 166.4 (C-5), 170.7 (C-7).

HRMS (CI)	calculated	found
$C_{23}H_{27}N_4O_3$ $[M+H]^+$	407.2078	407.2091

tert-Butyl 4-(2-azido-5-chlorophenyl)-2-benzamidopent-4-enoate (6c)

According to **GP3** 71 mg (0.177 mmol) of **5c** were reacted with $NaNO_2$ (20 mg, 0.283 mmol) and NaN_3 (18 mg, 0.283 mmol). Automated flash chromatography (hexanes/EtOAc 100:0,

80:20) afforded 67 mg (0.157 mmol, 89%) of **6c** as a yellow resin. $\mathbf{R_f}$ = 0.29 (hexanes/EtOAc 80:20).



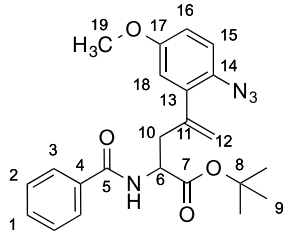
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.42 (s, 9 H, 9-H), 2.96 (ddd, *J* = 14.4, 5.9, 0.8 Hz, 1 H, 10-H_a), 3.26 (ddd, *J* = 14.4, 5.7, 0.9 Hz, 1 H, 10-H_b), 4.71 (ddd, *J* = 7.6, 5.8, 5.8 Hz, 1 H, 6-H), 5.12 (d, *J* = 1.4 Hz, 1 H, 12-H_a), 5.30 (m, 1 H, 12-H_b), 6.60 (d, *J* = 7.6 Hz, 1 H, BzN-H), 6.95 (m, 1 H, 15-H), 7.18–7.20 (m, 2 H, 16-H, 18-H), 7.38 (m, 2 H, 2-H), 7.47 (m, 1 H, 1-H), 7.62 (m, 2 H, 3-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 27.9 (C-9), 38.5 (C-10), 52.3 (C-6), 82.4 (C-8), 119.6 (C-15), 120.6 (C-12), 126.7 (C-3), 128.4 (C-2), 128.6 (C-16), 130.0 (C-17), 130.3 (C-18), 131.5 (C-1), 133.8 (C-4), 135.2 (C-13), 135.7 (C-14), 141.8 (C-11), 166.3 (C-5), 170.7 (C-7).

HRMS (CI)	calculated	found
$C_{18}H_{16}N_4O_3Cl$ [M+2H-*t*Bu]$^+$	371.0905	371.0940

***tert*-Butyl 4-(2-azido-5-methoxyphenyl)-2-benzamidopent-4-enoate (6d)**

According to **GP3** 51 mg (0.129 mmol) of **5d** were reacted with $NaNO_2$ (14 mg, 0.206 mmol) and NaN_3 (13 mg, 0.206 mmol). Automated flash chromatography (hexanes/EtOAc 100:0, 80:20) afforded 46 mg (0.157 mmol, 89%) of **6d** as a yellow resin. $\mathbf{R_f}$ = 0.49 (hexanes/EtOAc 70:30).



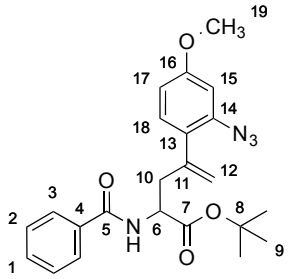
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.42 (s, 9 H, 9-H), 2.95 (ddd, *J* = 14.4, 6.3, 0.7 Hz, 1 H, 10-H_a), 3.27 (ddd, *J* = 14.4, 5.3, 0.9 Hz, 1 H, 10-H_b), 3.74 (s, 3 H, 19-H), 4.72 (ddd, *J* = 7.7, 6.3, 5.3 Hz, 1 H, 6-H), 5.13 (d, *J* = 1.6 Hz, 1 H, 12-H_a), 5.29 (m, 1 H, 12-H_b), 6.57 (d, *J* = 7.7 Hz, 1 H, BzN-H), 6.74 (d, *J* = 2.9 Hz, 1 H, 18-H), 6.79 (dd, *J* = 8.7, 2.9 Hz, 1 H, 16-H), 6.96 (d, *J* = 8.7 Hz, 1 H, 16-H), 7.37 (m, 2 H, 2-H), 7.47 (m, 1 H, 1-H), 7.60 (m, 2 H, 3-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 27.9 (C-9), 38.8 (C-10), 52.3 (C-6), 55.5 (C-19), 82.2 (C-8), 114.2 (C-16), 115.9 (C-18), 119.4 (C-15), 119.9 (C-12), 126.8 (C-3), 128.4 (C-2), 129.3 (C-14), 131.5 (C-1), 134.0 (C-4), 134.7 (C-13), 142.7 (C-11), 156.7 (C-17), 166.4 (C-5), 170.7 (C-7).

HRMS (CI)	calculated	found
$C_{23}H_{28}N_2O_4$ [M-N_2+2H]$^+$	396.2044	396.2072

***tert*-Butyl 4-(2-azido-4-methoxyphenyl)-2-benzamidopent-4-enoate (6e)**

According to **GP3** 59 mg (0.150 mmol) of **5e** were reacted with $NaNO_2$ (17 mg, 0.240 mmol) for 15 seconds (!) and NaN_3 (16 mg, 0.240 mmol) for 30 min. Automated flash chromatography (hexanes/EtOAc 100:0, 80:20) afforded 45 mg (0.107 mmol, 71%) of azide **6e** as a colorless solid, mp: 67–68 °C. $\mathbf{R_f}$ = 0.27 (hexanes/EtOAc 80:20).



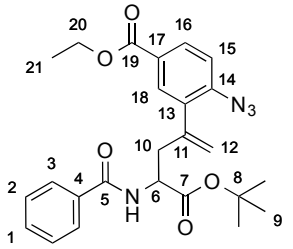
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.43 (s, 9 H, 9-H), 2.93 (dd, *J* = 14.3, 6.2 Hz, 1 H, 10-H_a), 3.29 (dd, *J* = 14.0, 5.2 Hz, 1 H, 10-H_b), 3.75 (s, 3 H, 19-H), 4.69 (m, 1 H, 6-H), 5.08 (d, *J* = 1.7 Hz, 1 H, 12-H_a), 5.24 (m, 1 H, 12-H_b), 6.49 (d, *J* = 7.5 Hz, 1 H, BzN-H), 6.53 (d, *J* = 2.4 Hz, 1 H, 15-H), 6.63 (dd, *J* = 8.5, 2.4 Hz, 1 H, 17-H), 7.10 (d, *J* = 8.5 Hz, 1 H, 18-H), 7.36 (m, 2 H, 2-H), 7.46 (m, 1 H, 1-H), 7.58 (m, 2 H, 3-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 28.0 (C-9), 39.0 (C-10), 52.3 (C-6), 55.4 (C-19), 82.1 (C-8), 104.3 (C-15), 110.4 (C-17), 119.5 (C-12), 126.2 (C-13), 126.8 (C-3), 128.3 (C-2), 131.4 (C-1, C-18), 134.0 (C-4), 138.0 (C-14), 142.5 (C-11), 160.1 (C-16), 166.3 (C-5), 170.8 (C-7).

HRMS (CI)	calculated	found
$C_{23}H_{27}N_4O_4$ $[M+H]^+$	423.2027	423.2034

Ethyl 4-azido-3-[4-benzamido-5-(*tert*-butoxy)-5-oxopent-1-en-2-yl]benzoate (6f)

According to **GP3** 38.0 mg (86.7 µmol) of **5f** were reacted with $NaNO_2$ (11 mg, 0.160 mmol) for 15 min and with NaN_3 (10 mg, 0.160 mmol) for 15 min. Automated flash chromatography (hexanes/EtOAc 100:0, 80:20) yielded 35 mg (75.3 µmol, 87%) of azide **6f** as a yellow resin.



$\mathbf{R_f}$ = 0.23 (hexanes/EtOAc 80:20).

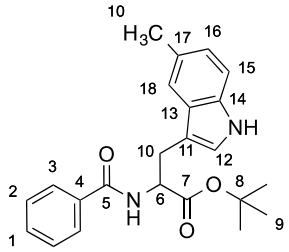
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.36 (t, *J* = 7.1 Hz, 3 H, 21-H), 1.42 (s, 9 H, 9-H), 3.02 (dd, *J* = 14.4, 5.9 Hz, 1 H, 10-H_a), 3.26 (dd, *J* = 14.4, 5.8 Hz, 1 H, 10-H_b), 3.74 (s, 3 H, 9-H), 4.34 (q, *J* = 7.1 Hz, 2 H, 20-H), 4.67 (ddd, *J* = 7.5, 5.9, 5.9 Hz, 1 H, 6-H), 5.16 (d, *J* = 1.3 Hz, 1 H, 12-H_a), 5.33 (m, 1 H, 12-H_b), 6.58 (d, *J* = 7.5 Hz, 1 H, BzN-H), 7.08 (d, *J* = 8.4 Hz, 1 H, 15-H), 7.37 (m, 2 H, 2-H), 7.47 (m, 1 H, 1-H), 7.61 (m, 2 H, 3-H), 7.87 (d, *J* = 2.0 Hz, 1 H, 18-H), 7.93 (dd, *J* = 8.4, 2.0 Hz, 1 H, 16-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.3 (C-21), 27.9 (C-9), 38.7 (C-10), 52.2 (C-6), 61.0 (C-20), 82.4 (C-8), 118.2 (C-15), 120.5 (C-12), 126.8 (C-3), 126.9 (C-17), 128.4 (C-2), 130.1 (C-16), 131.5 (C-1), 131.8 (C-18), 133.5 (C-13), 133.9 (C-4), 141.7 (C-14), 142.1 (C-11), 165.5 (C-19), 166.4 (C-5), 170.7 (C-7).

HRMS (CI)	calculated	found
$C_{25}H_{29}N_4O_5$ [M+H]$^+$	465.2132	465.2138

tert-Butyl 2-benzamido-3-(5-methyl-1*H*-indol-3-yl)propanoate (7b)

According to **GP4** 70 mg (0.172 mmol) of azide **6b** were irradiated for 8.5 h (12.5 W cm^{-2}) through the pyrex glass of a flask. Automated flash chromatography (hexanes/EtOAc 100:0, 70:30) afforded 51 mg (0.135 mmol, 78%) of indole **7b** as a colorless solid, mp: 71–72 °C. $\mathbf{R_f}$ = 0.26 (hexanes/EtOAc 70:30).



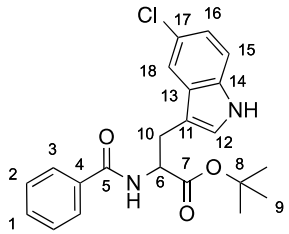
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.43 (s, 9 H, 9-H), 2.31 (s, 3 H, 19-H), 3.36 (ddd, *J* = 14.8, 5.0, 0.5 Hz, 1 H, 10-H_a), 3.44 (ddd, *J* = 14.8, 5.5, 0.7 Hz, 1 H, 10-H_b), 5.05 (ddd, *J* = 7.7, 5.2, 5.2 Hz, 1 H, 6-H), 6.71 (d, *J* = 7.6 Hz, 1 H, BzN-H), 6.97–7.00 (m, 2 H, 12-H, 16-H), 7.23 (d, *J* = 8.3 Hz, 1 H, 15-H), 7.35–7.39 (m, 3 H, 2-H, 18-H), 7.47 (m, 1 H, 1-H), 7.70 (m, 2 H, 3-H), 8.07 (bs, 1 H, N_{indole}-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.2 (C-19), 27.6 (C-10), 28.0 (C-9), 54.0 (C-6), 82.2 (C-8), 109.9 (C-11), 110.8 (C-15), 118.8 (C-18), 122.9 (C-12), 123.7 (C-16), 127.0 (C-3), 128.1 (C-14), 128.4 (C-2), 128.8 (C-17), 131.5 (C-1), 134.1 (C-4), 134.4 (C-13), 166.8 (C-5), 171.0 (C-7).

HRMS (CI)	calculated	found
$C_{23}H_{26}N_2O_3$ [M]$^+$	378.1938	378.1940

tert-Butyl 2-benzamido-3-(5-chloro-1*H*-indol-3-yl)propanoate (7c)

According to **GP4** 63 mg (0.148 mmol) of azide **6c** were irradiated for 9 h. Automated flash chromatography (hexanes/EtOAc 100:0, 70:30) afforded 3 mg (7 µmol, 5%) of azide **6c** as well as 39 mg (0.098 mmol, 66%) of indole **7c** as a colorless solid, mp: 146–147 °C. $\mathbf{R_f}$ = 0.21 (hexanes/EtOAc 70:30).



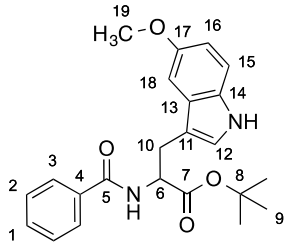
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.41 (s, 9 H, 9-H), 3.33 (dd, *J* = 14.9, 5.2 Hz, 1 H, 10-H_a), 3.40 (dd, *J* = 14.8, 5.5 Hz, 1 H, 10-H_b), 5.02 (ddd, *J* = 7.5, 5.3, 5.3 Hz, 1 H, 6-H), 6.75 (d, *J* = 7.5 Hz, 1 H, BzN-H), 7.03 (d, *J* = 2.4 Hz, 1 H, 12-H), 7.09 (dd, *J* = 8.6, 1.9 Hz, 1 H, 16-H), 7.21 (d, *J* = 8.6 Hz, 1 H, 15-H), 7.39 (m, 2 H, 2-H), 7.48 (m, 1 H, 1-H), 7.57 (d, *J* = 1.9 Hz, 1 H, 18-H), 7.72 (m, 2 H, 3-H), 8.45 (bs, 1 H, N_{indole}-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 27.5 (C-10), 27.9 (C-9), 53.8 (C-6), 82.6 (C-8), 110.2 (C-11), 112.2 (C-15), 118.5 (C-18), 122.4 (C-16), 124.3 (C-12), 125.3 (C-17), 127.0 (C-3), 128.6 (C-13), 128.9 (C-2), 131.6 (C-1), 134.0 (C-4), 134.3 (C-14), 167.0 (C-5), 171.0 (C-7).

HRMS (CI)	calculated	found
$C_{22}H_{24}N_2O_3Cl$ $[M+H]^+$	399.1470	399.1480

tert-Butyl 2-benzamido-3-(5-methoxy-1*H*-indol-3-yl)propanoate (7d)

According to **GP4** 44 mg (0.104 mmol) of **6d** were irradiated for 11 h. Automated flash chromatography (hexanes/EtOAc 100:0, 80:20, 70:30) afforded 1 mg (2 µmol, 2%) of azide **6d** and 23 mg (58.3 µmol, 56%) of **7d** as a colorless solid, mp: 72–73 °C. $\mathbf{R_f}$ = 0.20 (hexanes/EtOAc 70:30).



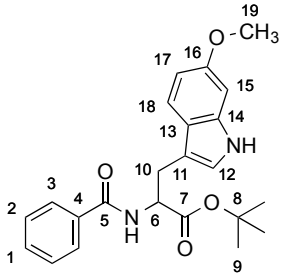
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.43 (s, 9 H, 9-H), 3.35 (ddd, *J* = 14.9, 5.0, 0.6 Hz, 1 H, 10-H_a), 3.43 (ddd, *J* = 14.9, 5.5, 0.7 Hz, 1 H, 10-H_b), 3.59 (s, 3 H, 19-H), 5.06 (ddd, *J* = 7.6, 5.3, 5.3 Hz, 1 H, 6-H), 6.74 (d, *J* = 7.6 Hz, 1 H, BzN-H), 6.81 (dd, *J* = 8.8, 2.4 Hz, 1 H, 16-H), 6.98 (d, *J* = 2.4 Hz, 1 H, 18-H), 7.01 (d, *J* = 2.4 Hz, 1 H, 12-H), 7.22 (d, *J* = 8.8 Hz, 1 H, 15-H), 7.37 (m, 2 H, 2-H), 7.47 (m, 1 H, 1-H), 7.69 (m, 2 H, 3-H), 8.11 (bs, 1 H, N_{indole}-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 27.7 (C-10), 28.0 (C-9), 54.0 (C-6), 55.5 (C-19) 82.2 (C-8), 100.4 (C-18), 110.2 (C-11), 111.9 (C-15), 112.8 (C-16), 123.5 (C-12), 127.0 (C-3), 128.3 (C-13) 128.5 (C-2), 131.1 (C-14), 131.6 (C-1), 134.0 (C-4), 154.1 (C-17), 167.0 (C-5), 171.0 (C-7).

HRMS (CI)	calculated	found
$C_{23}H_{27}N_2O_4$ $[M+H]^+$	395.1965	395.1970

tert-Butyl 2-benzamido-3-(1*H*-6-methoxyindol-3-yl)-propanoate (7e)

According to **GP4** 41 mg (97.0 µmol) of azide **6e** were irradiated for 12 h. Automated flash chromatography (hexanes/EtOAc 100:0, 70:30) afforded 8 mg (19 µmol, 20%) of azide **6e** as well as 13 mg (33.0 µmol, 34%) of indole **7e** as a colorless solid, mp: 127–128 °C. $\mathbf{R_f}$ = 0.15 (hexanes/EtOAc 70:30).



^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.41 (s, 9 H, 9-H), 3.34 (dd, *J* = 14.8, 5.2 Hz, 1 H, 10-H_a), 3.44 (dd, *J* = 14.8, 5.4 Hz, 1 H, 10-H_b), 3.82 (s, 3 H, 19-H), 5.03 (m, 1 H, 6-H), 6.69 (d, *J* = 7.6 Hz, 1 H, BzN-H), 6.73 (dd, *J* = 8.7, 2.2 Hz, 1 H, 17-H), 6.82 (d, *J* = 2.2 Hz, 1 H, 15-H), 6.92 (d, *J* =

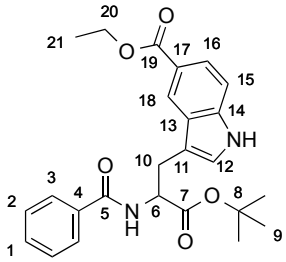
2.2 Hz, 1 H, 12-H), 7.38 (m, 2 H, 2-H), 7.45–7.49 (m, 2 H, 1-H, 18-H), 7.70 (m, 2 H, 3-H), 8.00 (bs, 1 H, N_{indole}-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 27.7 (C-10), 28.0 (C-9), 53.8 (C-6), 55.6 (C-19), 82.2 (C-8), 94.5 (C-15) 109.6 (C-17), 110.4 (C-11), 119.7 (C-18), 121.4 (C-12), 122.3 (C-13), 127.0 (C-3), 128.5 (C-2), 131.5 (C-1), 134.1 (C-4), 136.8 (C-14), 156.6 (C-16), 166.8 (C-5), 171.1 (C-7).

HRMS (CI)	calculated	found
$C_{23}H_{27}N_2O_4$ $[M+H]^+$	395.1965	395.1940

Ethyl 3-[2-benzamido-3-(*tert*-butoxy)-3-oxopropyl]-1*H*-indole-5-carboxylate (7f)

According to **GP4** 30 mg (64.6 µmol) of azide **6f** were irradiated for 9.5 h. Automated flash chromatography (hexanes/EtOAc 100:0, 70:30) yielded 19 mg (43.5 µmol, 67%) of indole **7f** as a colorless solid, mp: 79–80 °C. $\mathbf{R_f}$ = 0.12 (hexanes/EtOAc 70:30).



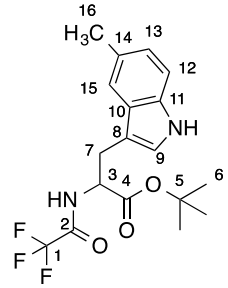
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.1 Hz, 3 H, 21-H), 1.41 (s, 9 H, 9-H), 3.42 (dd, *J* = 15.0, 5.3 Hz, 1 H, 10-H_a), 3.50 (dd, *J* = 15.0, 5.4 Hz, 1 H, 10-H_b), 4.31 (m, 2 H, 20-H), 5.05 (ddd, *J* = 7.5, 5.3, 5.3 Hz, 1 H, 6-H), 6.76 (d, *J* = 7.5 Hz, 1 H, BzN-H), 7.10 (d, *J* = 2.3 Hz, 1 H, 12-H), 7.32 (d, *J* = 8.6 Hz, 1 H, 15-H), 7.36 (m, 2 H, 2-H), 7.46 (m, 1 H, 1-H), 7.70 (m, 2 H, 3-H), 7.89 (dd, *J* = 8.6, 1.6 Hz, 1 H, 16-H), 8.37 (m, 1 H, 18-H), 8.54 (bs, 1 H, N_{indole}-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.4 (C-21), 27.4 (C-10), 27.9 (C-9), 53.8 (C-6), 60.5 (C-20) 82.6 (C-8), 110.9 (C-15), 111.9 (C-11), 121.9 (C-18), 122.0 (C-17), 123.6 (C-16), 124.1 (C-12), 127.0 (C-3), 127.5 (C-13), 128.5 (C-2), 131.6 (C-1), 134.0 (C-4), 138.5 (C-14), 166.9 (C-5), 167.5 (C-19), 171.0 (C-7).

HRMS (CI)	calculated	found
$C_{25}H_{28}N_2O_5$ $[M]^+$	436.1993	436.1976

***tert*-Butyl 3-(5-methyl-1*H*-indol-3-yl)-2-(2,2,2-trifluoroacetamido)propanoate (8b)**

According to **GP4** 125 mg (0.314 mmol) of azide **3b** were irradiated for 20 h. Flash chromatography (hexanes/EtOAc 90:10) afforded 94 mg (0.254 mmol, 81%) of the indole **8b** as an



off-white solid, mp: 130–131 °C. $\mathbf{R_f}$ = 0.34 (hexanes/EtOAc 80:20).

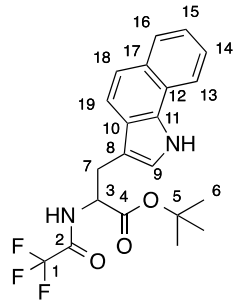
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.43 (s, 9 H, 6-H), 2.46 (s, 3 H, 16-H), 3.38 (m, 2 H, 7-H), 4.83 (m, 1 H, 3-H), 6.88 (d, *J* = 6.5 Hz, 1 H, TFAN-H), 6.98 (d, *J* = 2.4 Hz, 1 H, 9-H), 7.05 (dd, *J* = 8.3, 1.3 Hz, 1 H, 13-H), 7.28 (s, 1 H, 12-H), 7.35 (m, 1 H, 15-H), 8.01 (bs, 1 H, N_{indole}-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.3 (C-16), 27.0 (C-7), 27.9 (C-6), 53.9 (C-3), 82.2 (C-5), 108.8 (C-8), 110.9 (C-12), 118.3 (C-15), 122.9 (C-9), 124.1 (C-13), 127.8 (C-10), 129.2 (C-14), 134.4 (C-11), 169.3 (C-4). Signals of the TFA group could not be observed.

HRMS (CI)	calculated	found
$C_{18}H_{21}F_3N_2O_3$ $[M]^+$	370.1499	370.1501

***tert*-Butyl 3-(1*H*-benzo[*g*]indol-3-yl)-2-(2,2,2-trifluoroacetamido)propanoate (8g)**

According to **GP4** 47 mg (0.108 mmol) of azide **3g** were irradiated for 8:30 h. Automated flash chromatography (hexanes/EtOAc 100:0, 80:20) afforded 31 mg (76.3 µmol, 71%) of indole **8g**



as an off-white solid, mp: 139–142 °C. $\mathbf{R_f}$ = 0.28 (hexanes/EtOAc 80:20).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.41 (s, 9 H, 6-H), 3.45 (m, 2 H, 7-H), 4.86 (m, 1 H, 3-H), 6.91 (d, *J* = 7.8 Hz, 1 H, TFAN-H), 7.07 (d, *J* = 2.5 Hz, 1 H, 9-H), 7.44 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1 H, 15-H), 7.51–7.55 (m, 2 H, 14-H, 18-H), 7.64 (d, *J* = 8.7 Hz, 1 H, 19-H), 7.93 (d, *J* = 8.0 Hz, 1 H, 16-H), 7.98 (m, 1 H, 13-H), 8.89 (bs, 1 H, N_{indole}-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 27.0 (C-7), 27.9 (C-6), 53.9 (C-3), 83.4 (C-5), 111.0 (C-8), 118.5 (C-19), 119.3 (C-13), 120.8 (C-9, C-18), 121.6 (C-12), 123.4 (C-10), 124.2 (C-15), 125.6 (C-14), 128.9 (C-16), 130.6, 130.7 (C-11, C-17), 169.3 (C-4). Signals of the TFA group could not be observed.

HRMS (CI)	calculated	found
$C_{21}H_{21}F_3N_2O_3$ $[M]^+$	406.1499	406.1521

2 Literature

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[2] K. S. K. Reddy, N. Narender, C. N. Rohitha, S. J. Kulkarni, *Synth. Commun.* **2008**, *38*, 3894–3902.

[3] P. P. Sharp, M. G. Banwell, J. Renner, K. Lohmann, A. C. Willis, *Org. Lett.* **2013**, *15*, 2616–2619.

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[8] C. Bukovec, A. O. Wesquet, U. Kazmaier, *Eur. J. Org. Chem.* **2011**, *2011*, 1047–1056.

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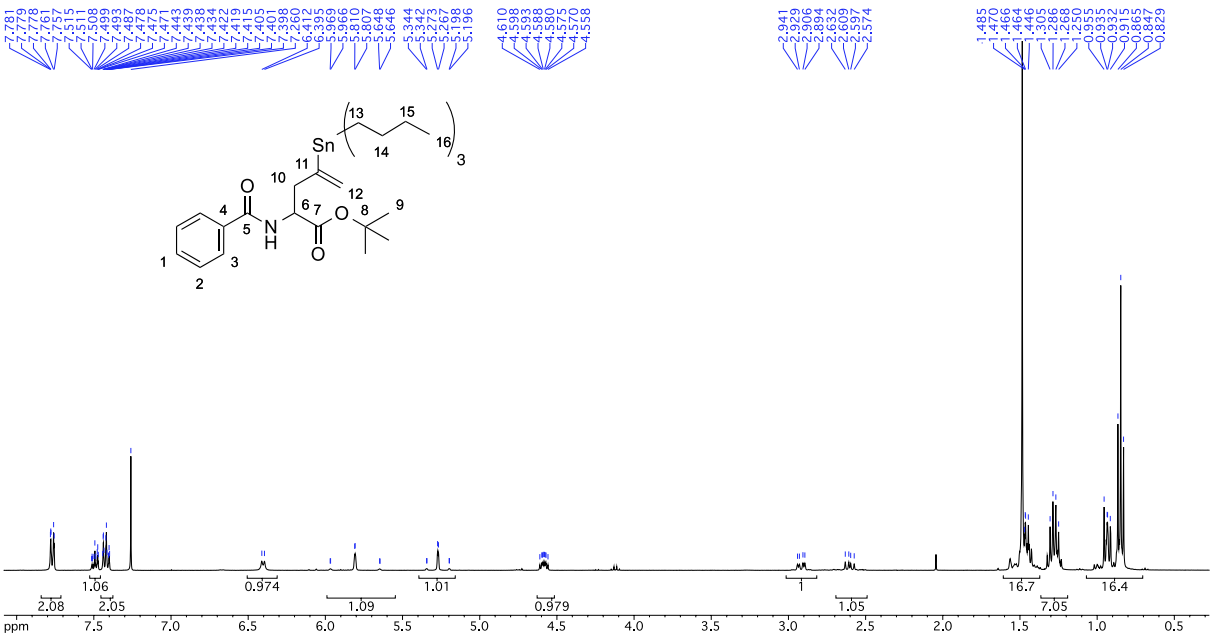
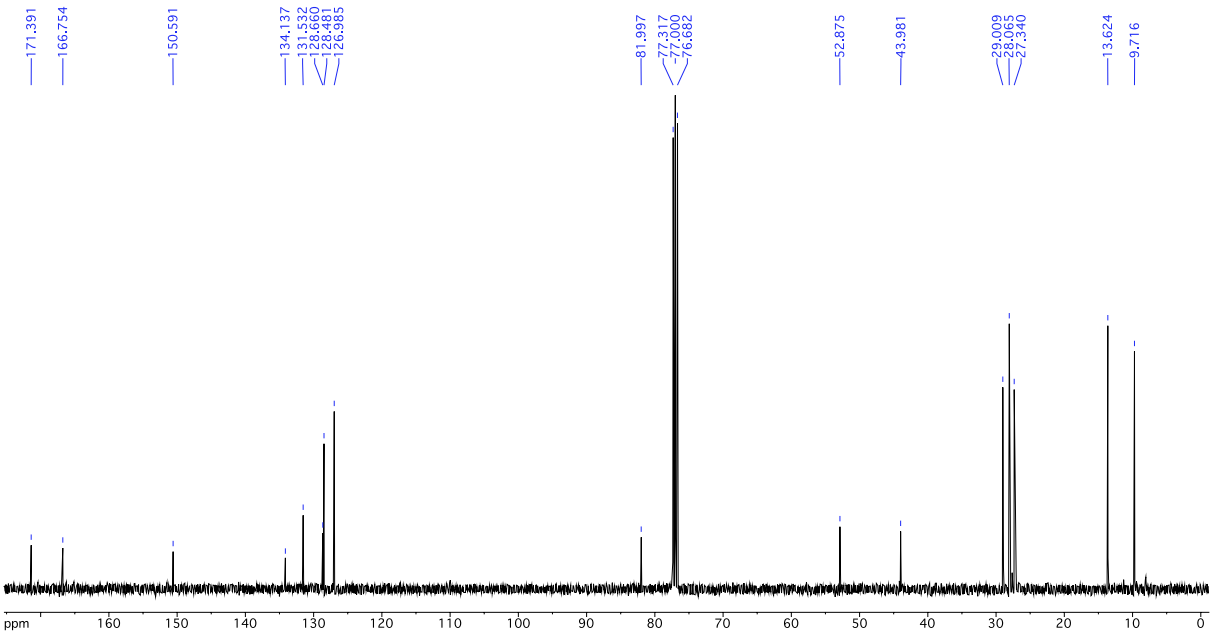
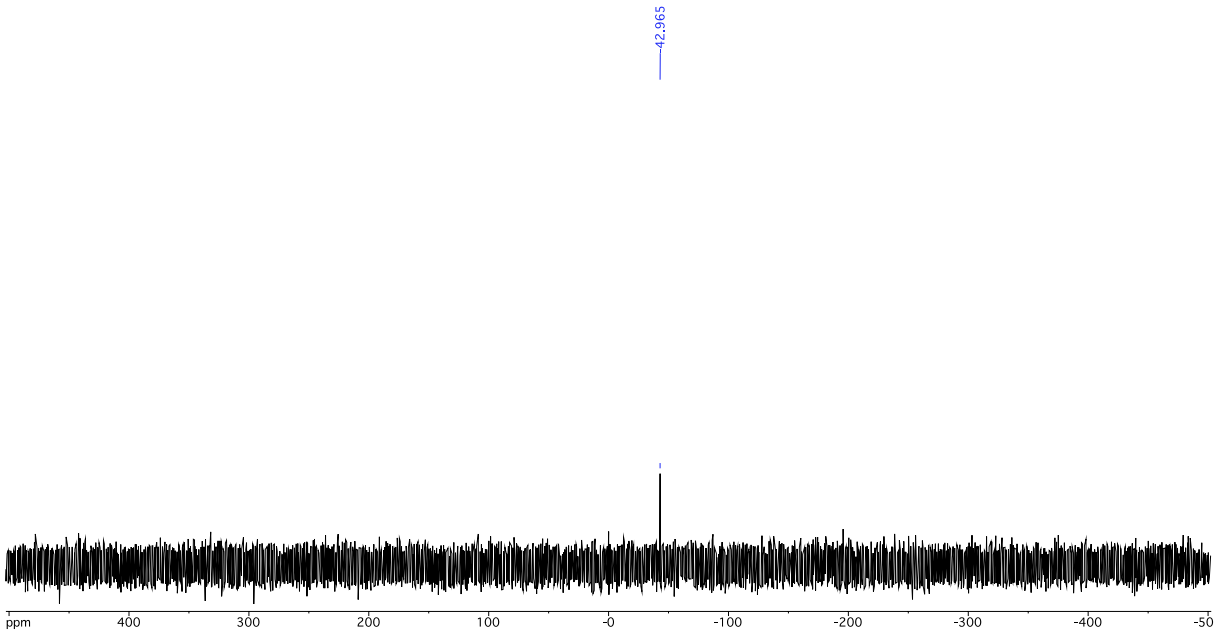
3 Copies of NMR spectra and chromatograms

tert-Butyl 2-benzoylamino-4-tributylstannyl-pent-4-enoate (2)






42.965
ppm
400
300
200
100
-0
-100
-200
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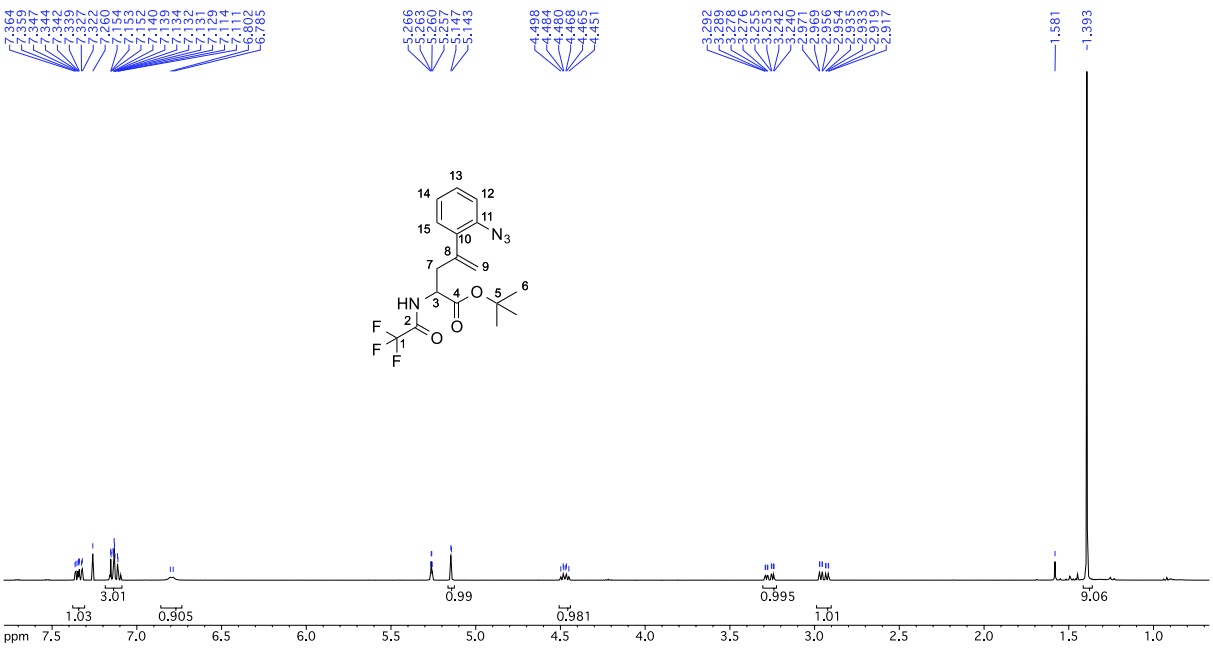
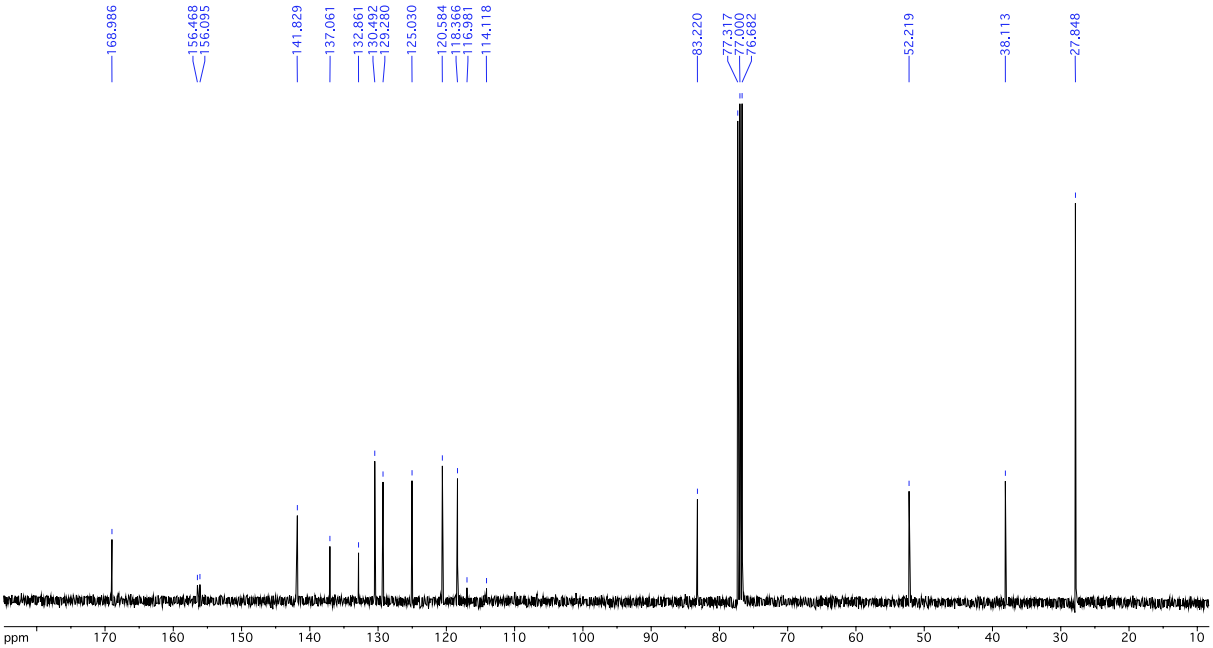
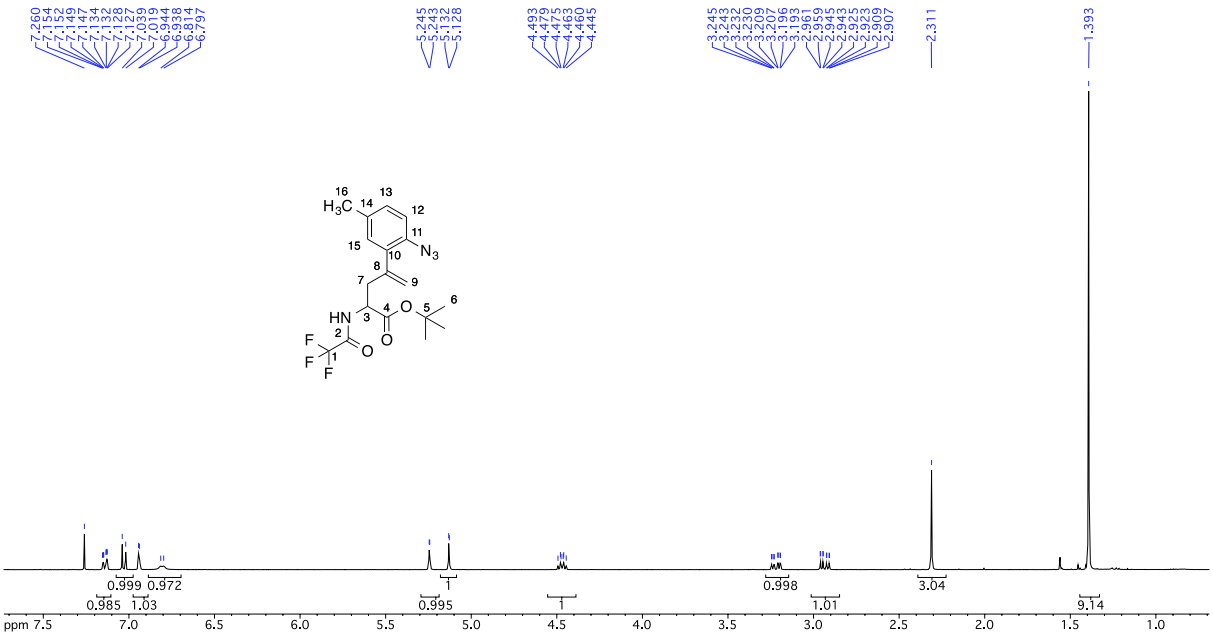
-400
-50

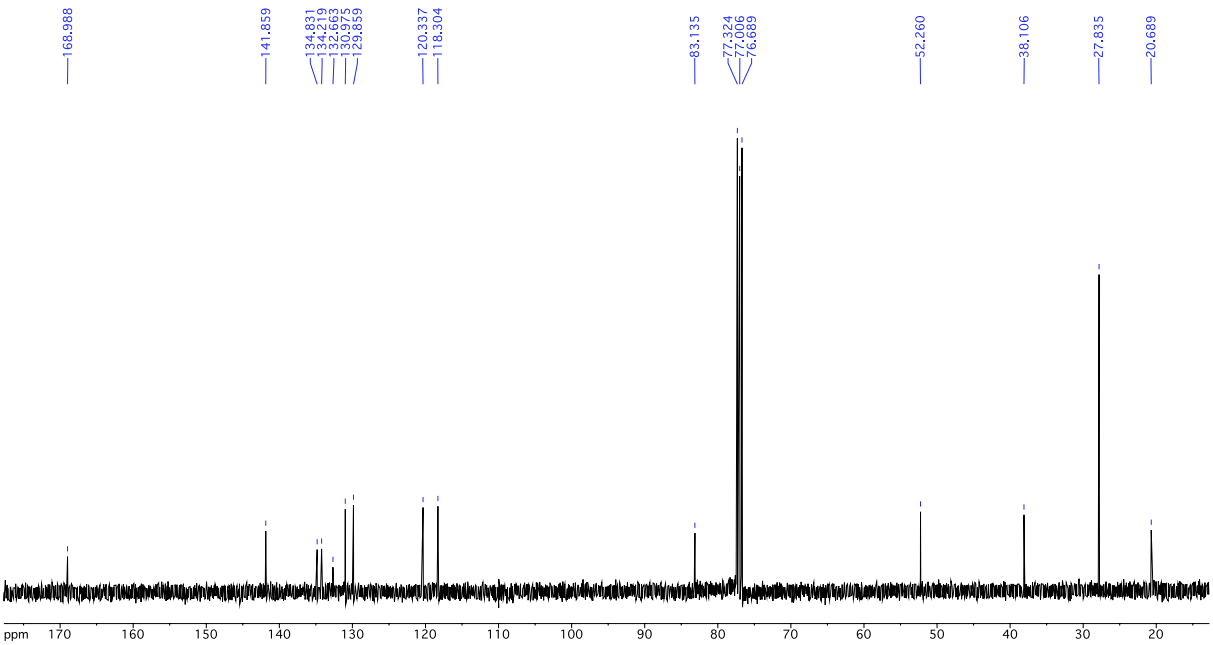
tert-Butyl 4-(2-azidophenyl)-2-(2,2,2-trifluoroacetamido)pent-4-enoate (3a)



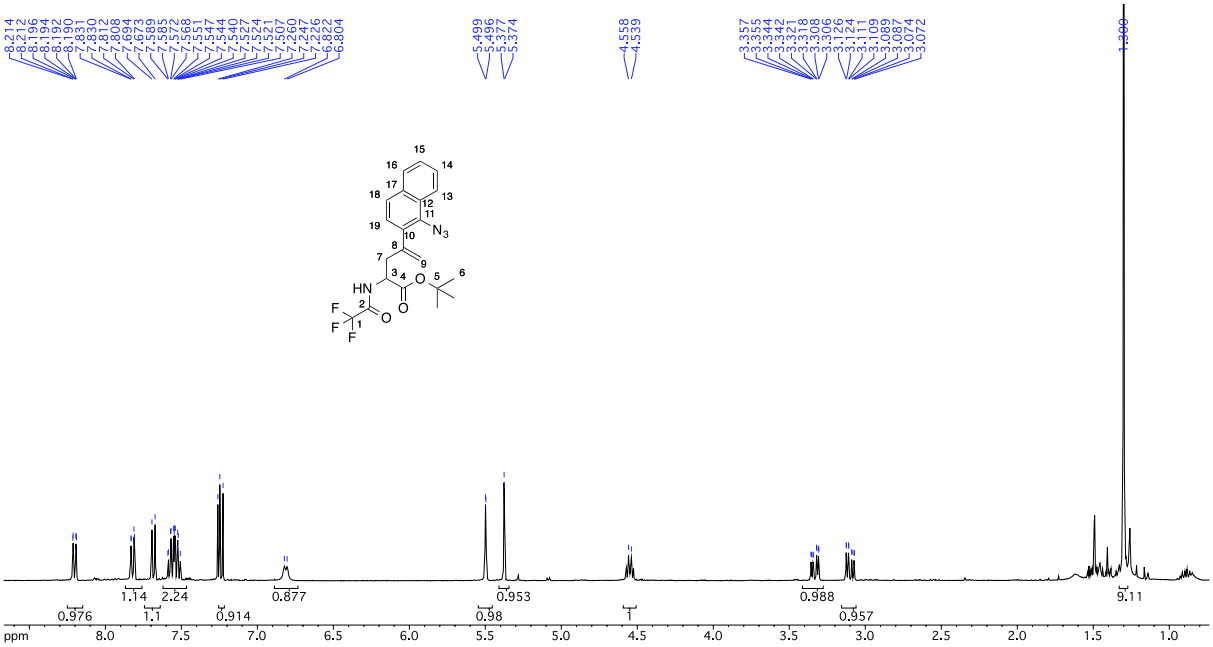


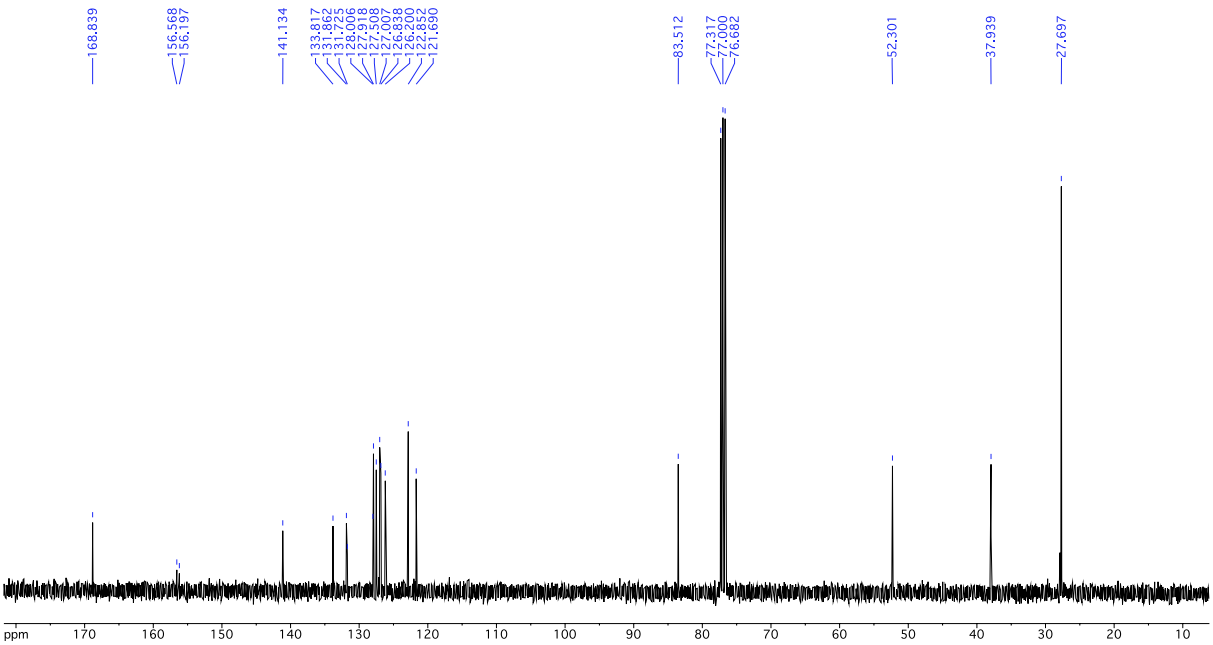
tert-Butyl 4-(2-azido-5-methylphenyl)-2-(2,2,2-trifluoroacetamido)pent-4-enoate (3b)



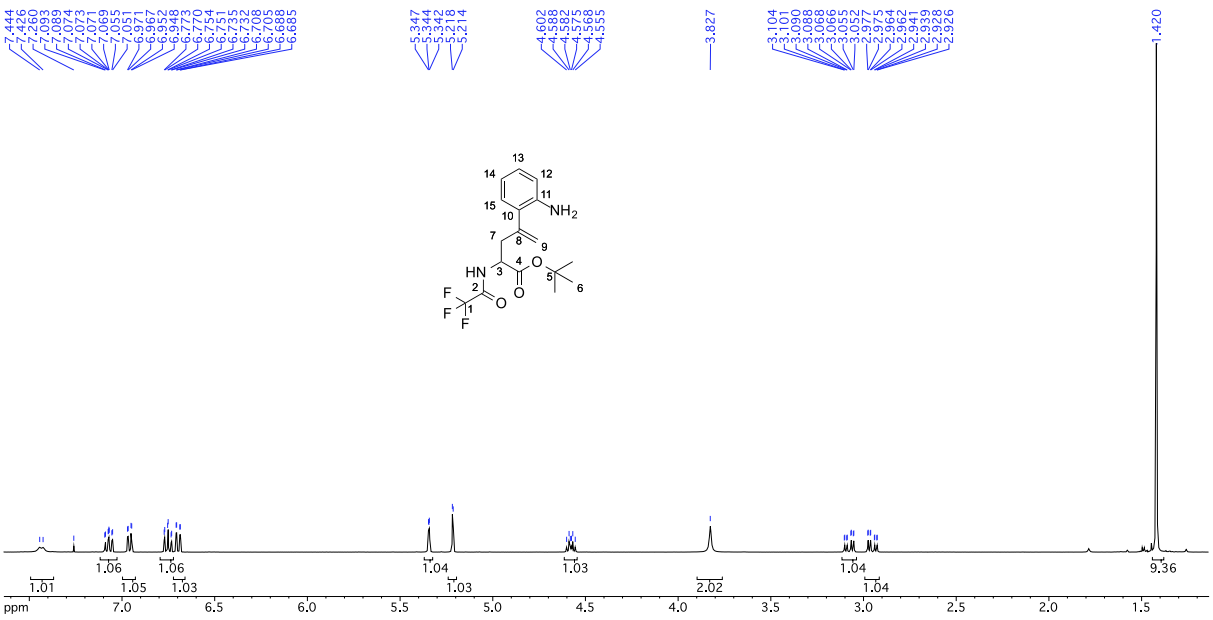


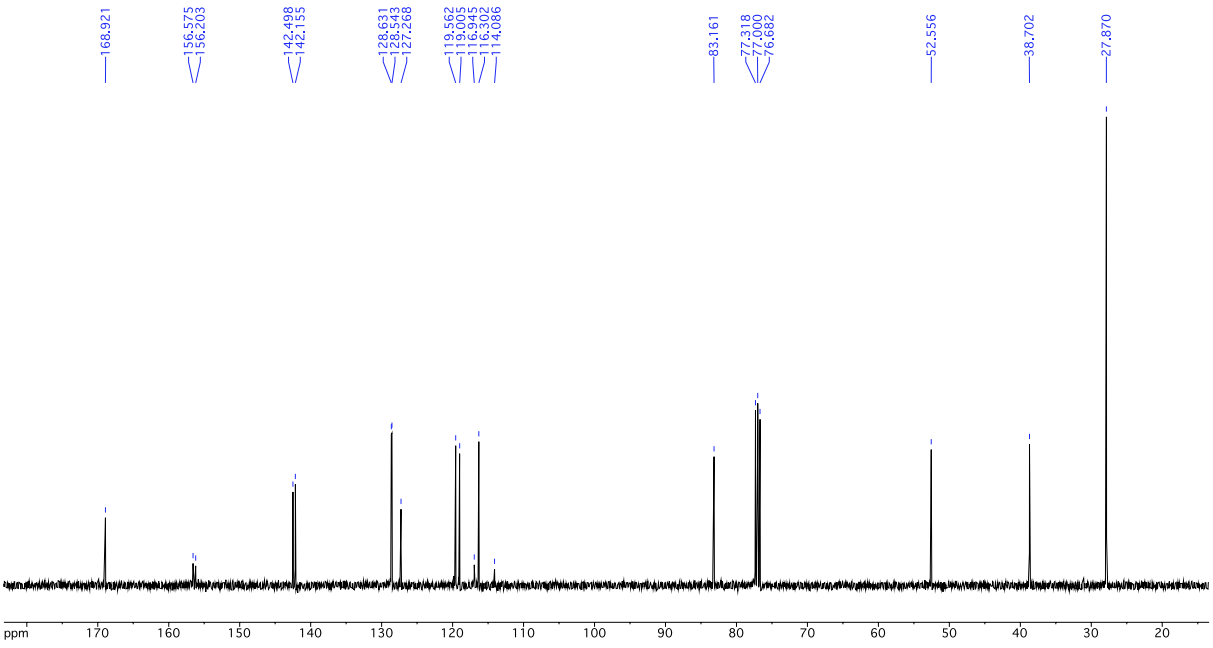
tert-Butyl 4-(1-azidonaphthalen-2-yl)-2-(2,2,2-trifluoroacetamido)pent-4-enoate (3g)



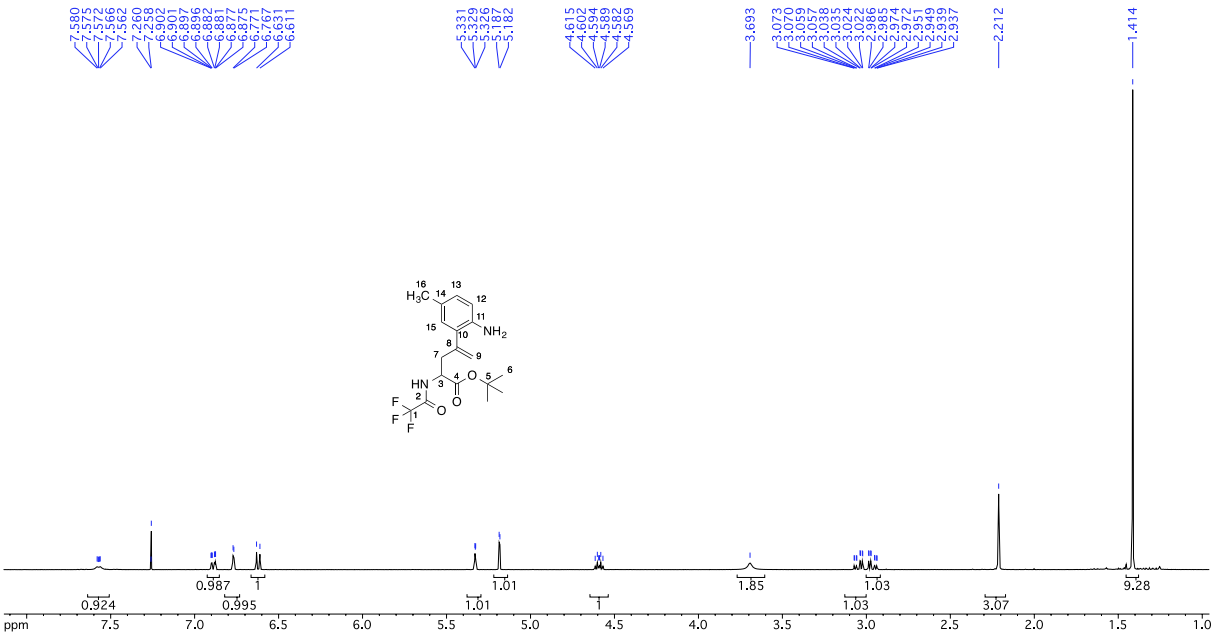


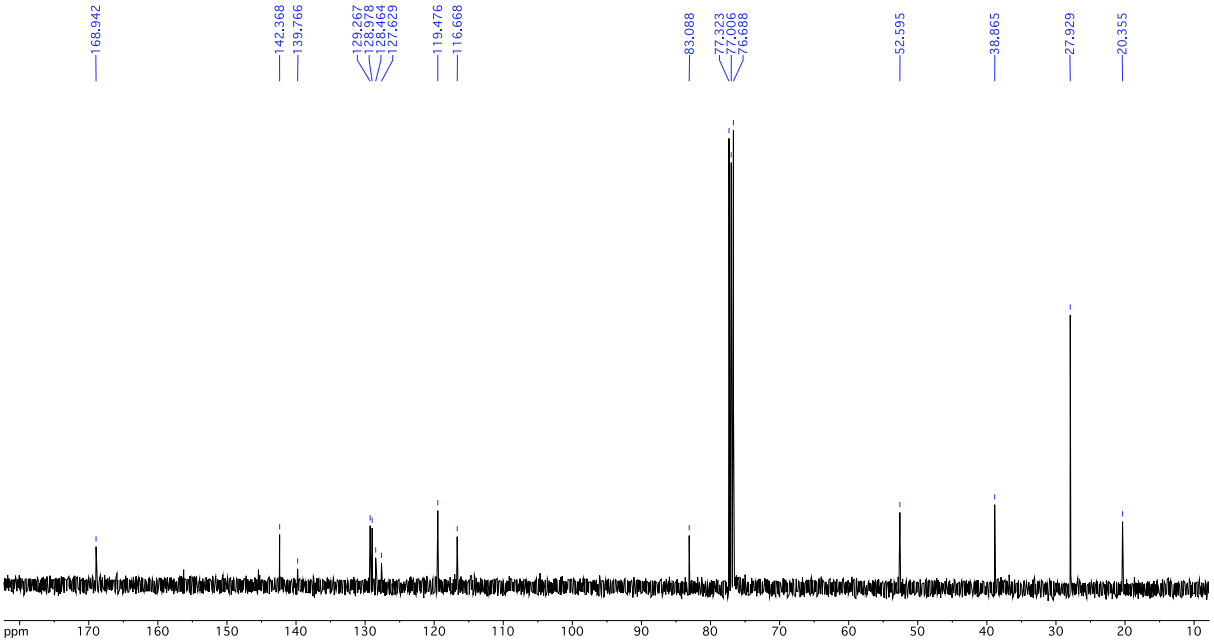
tert-Butyl 4-(2-aminophenyl)-2-(2,2,2-trifluoroacetamido)pent-4-enoate (4a)



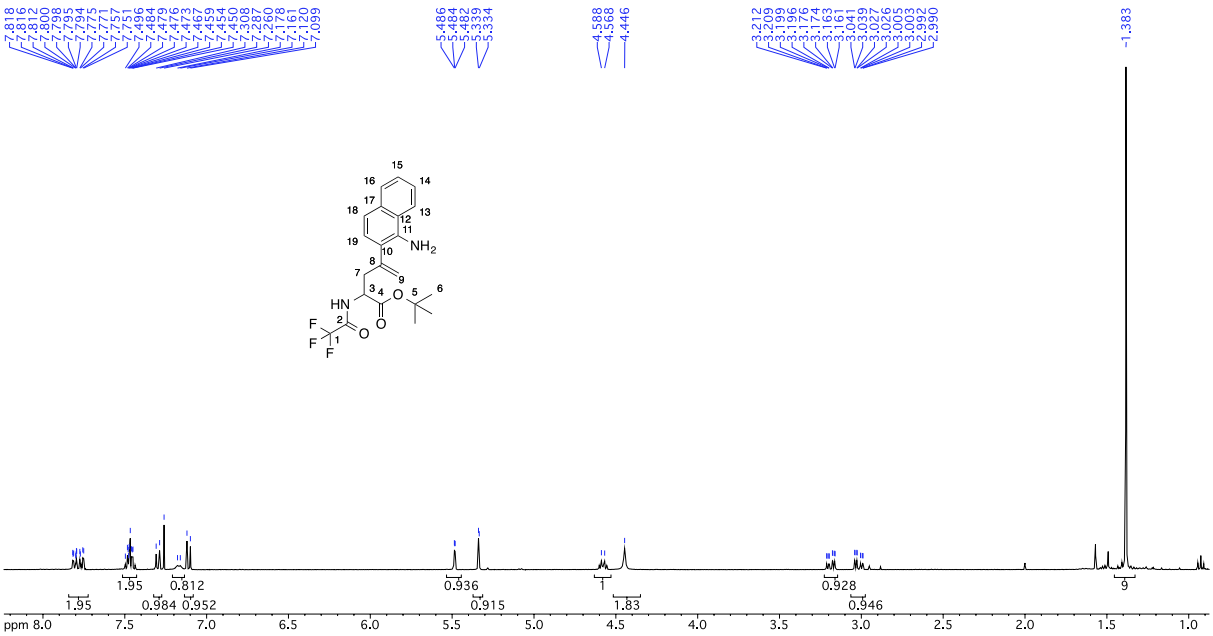


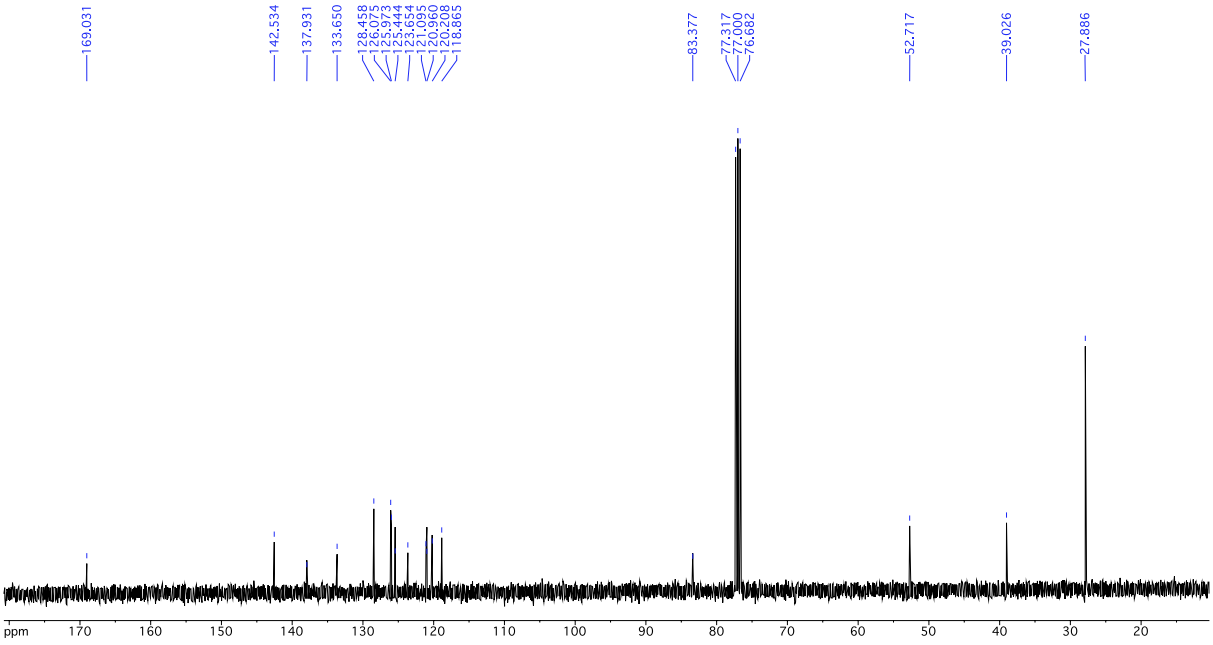
tert-Butyl 4-(2-amino-5-methylphenyl)-2-(2,2,2-trifluoroacetamido)pent-4-enoate (4b)



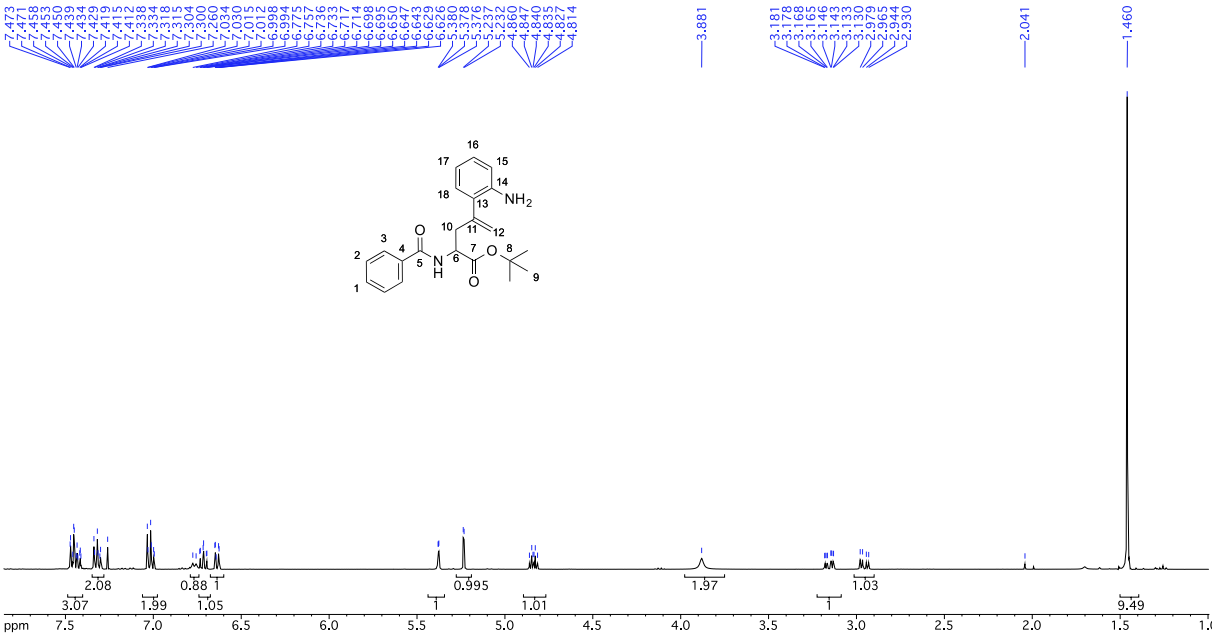


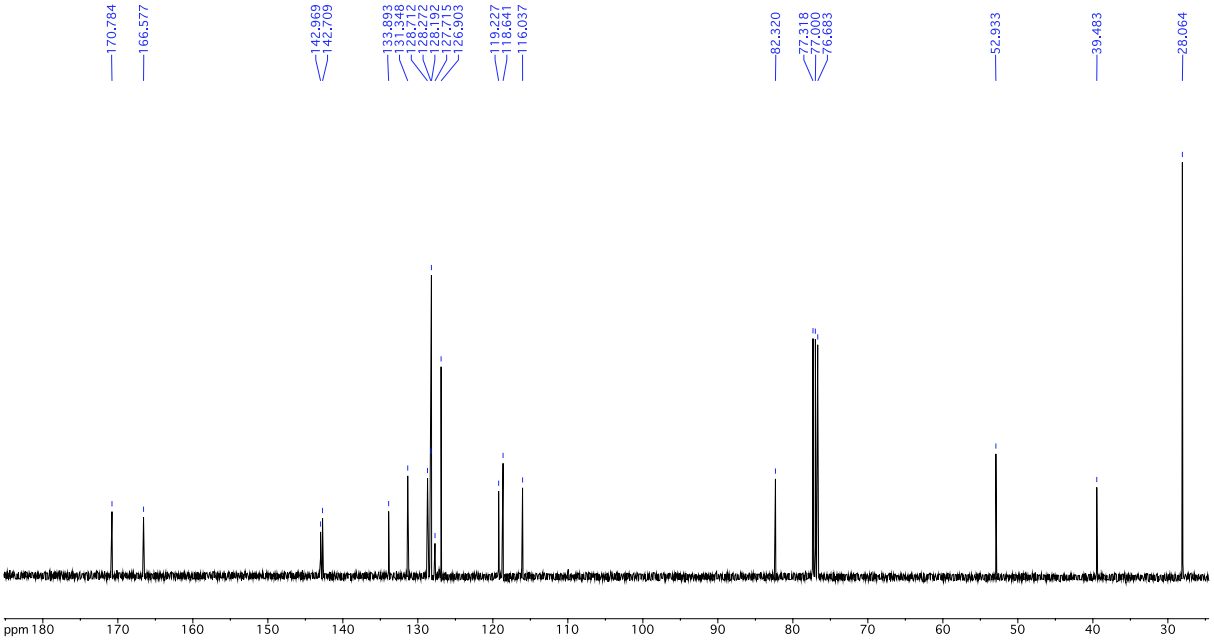
tert-Butyl 4-(1-aminonaphthalen-2-yl)-2-(2,2,2-trifluoroacetamido)pent-4-enoate (4g)



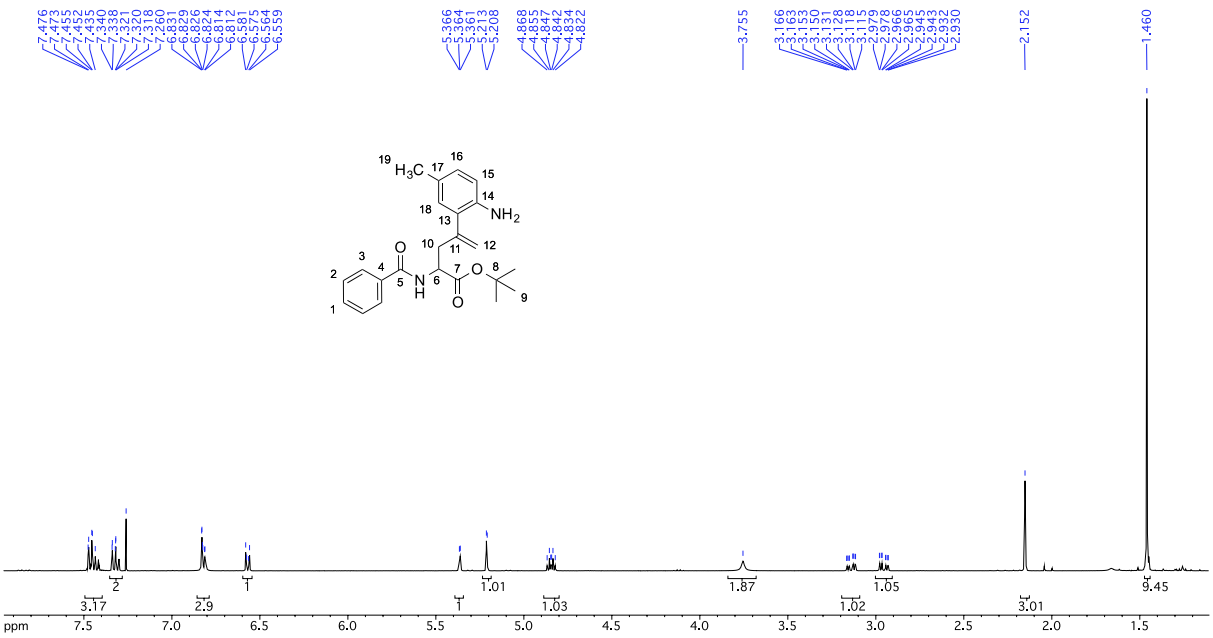


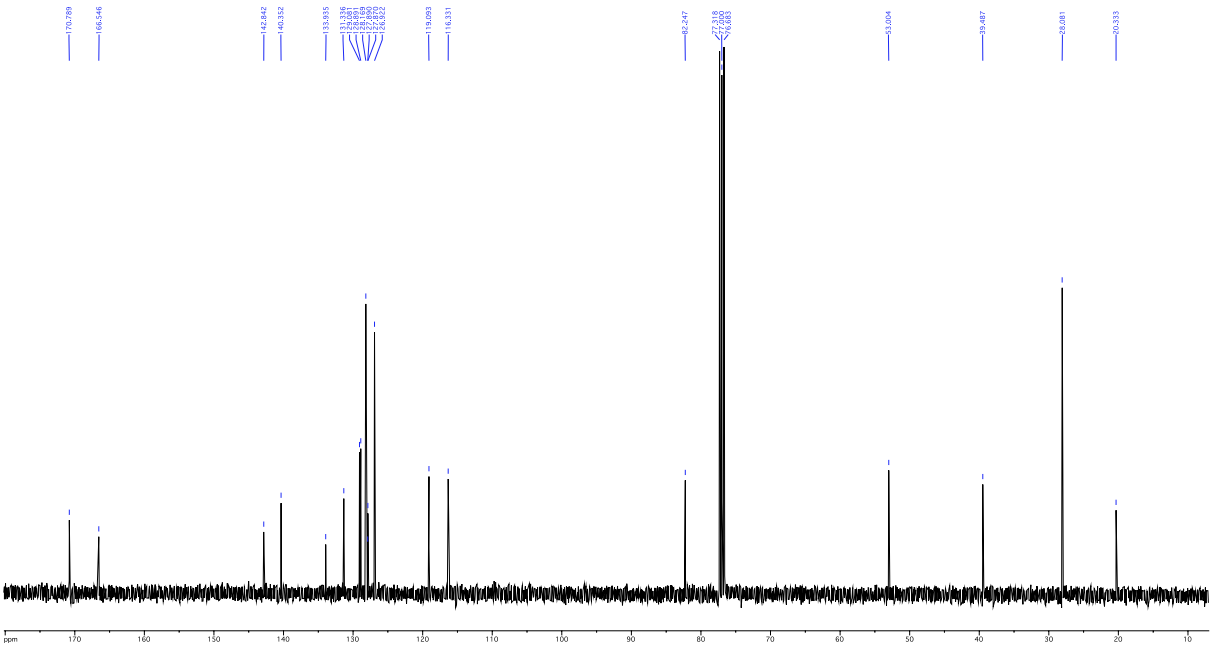
tert-Butyl 4-(2-aminophenyl)-2-benzamidopent-4-enoate (5a)



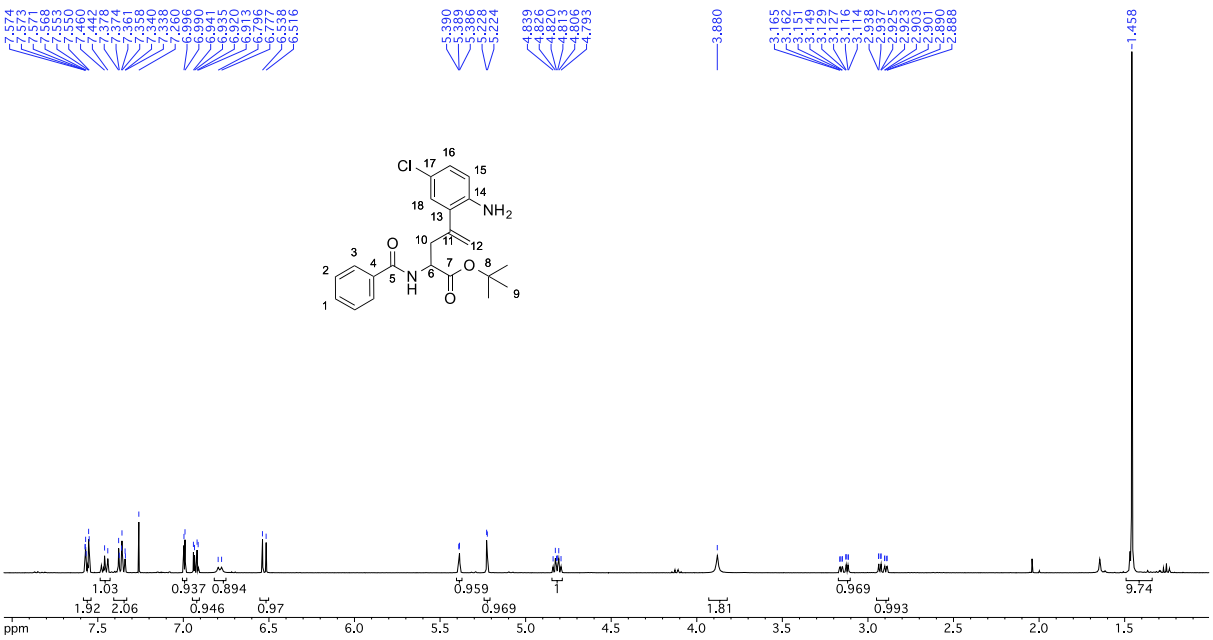


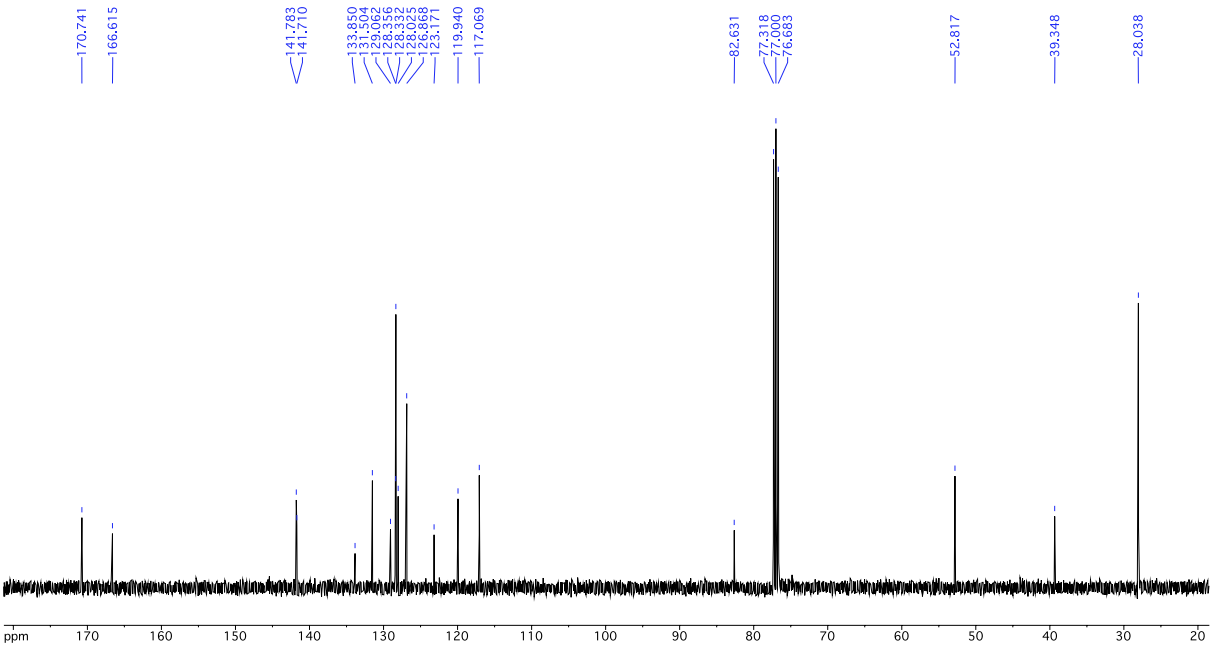
tert-Butyl 4-(2-amino-5-methylphenyl)-2-benzamidopent-4-enoate (5b)



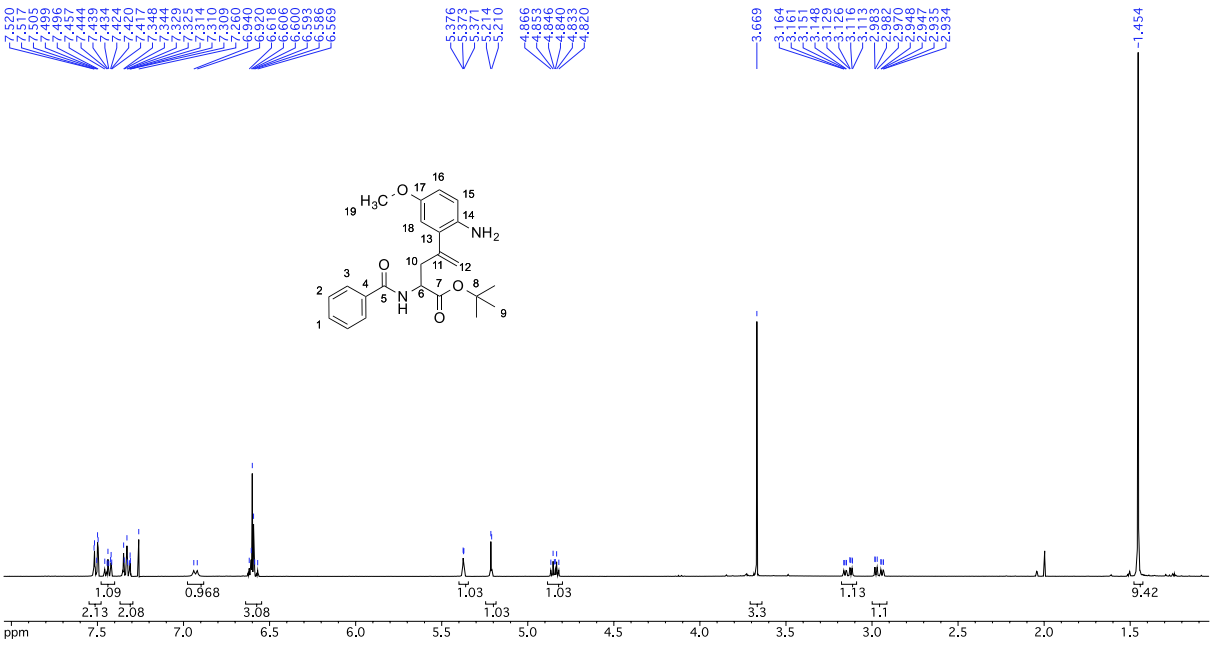


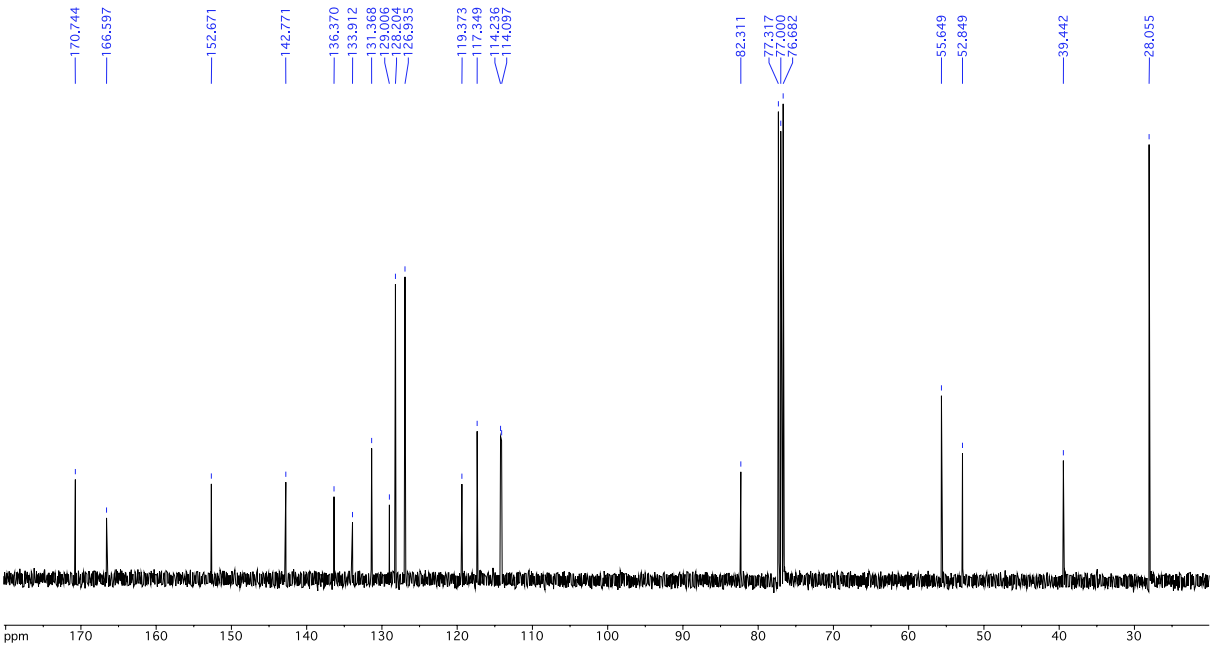
tert-Butyl 4-(2-amino-5-chlorophenyl)-2-benzamidopent-4-enoate (5c)



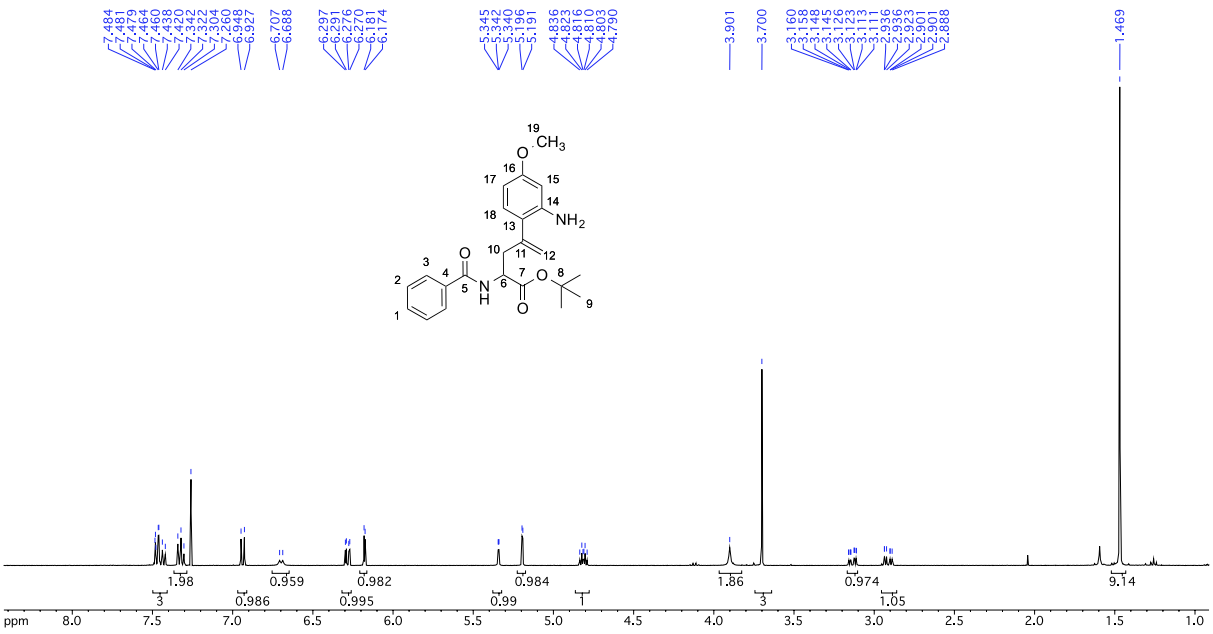


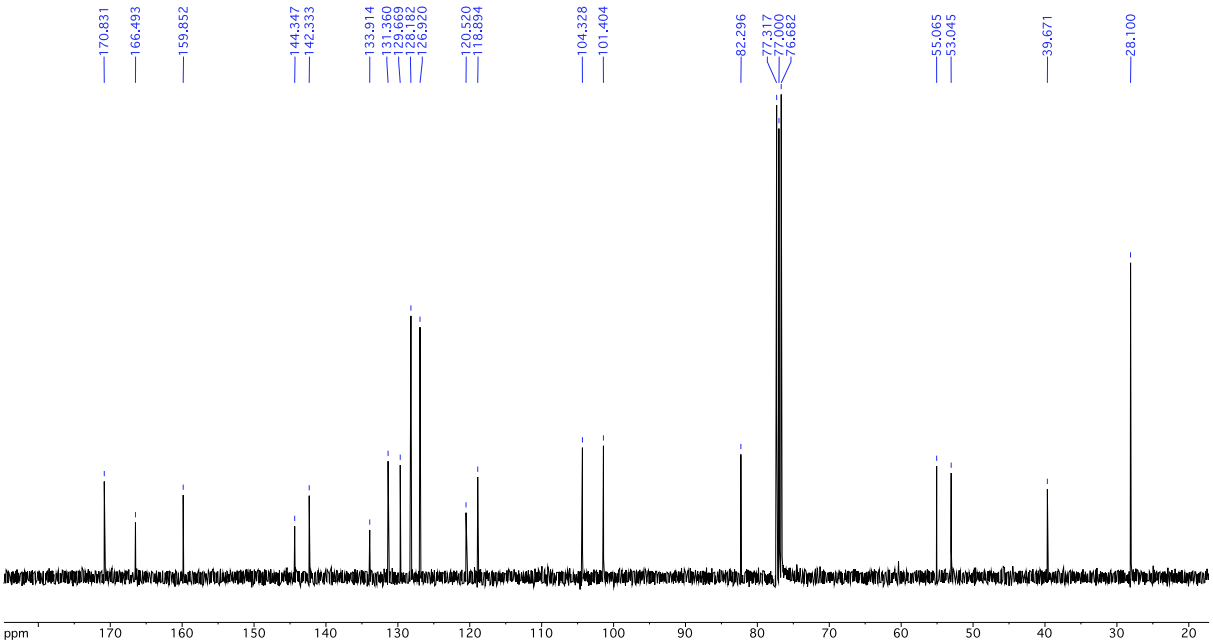
tert-Butyl 4-(2-amino-5-methoxyphenyl)-2-benzamidopent-4-enoate (5d)



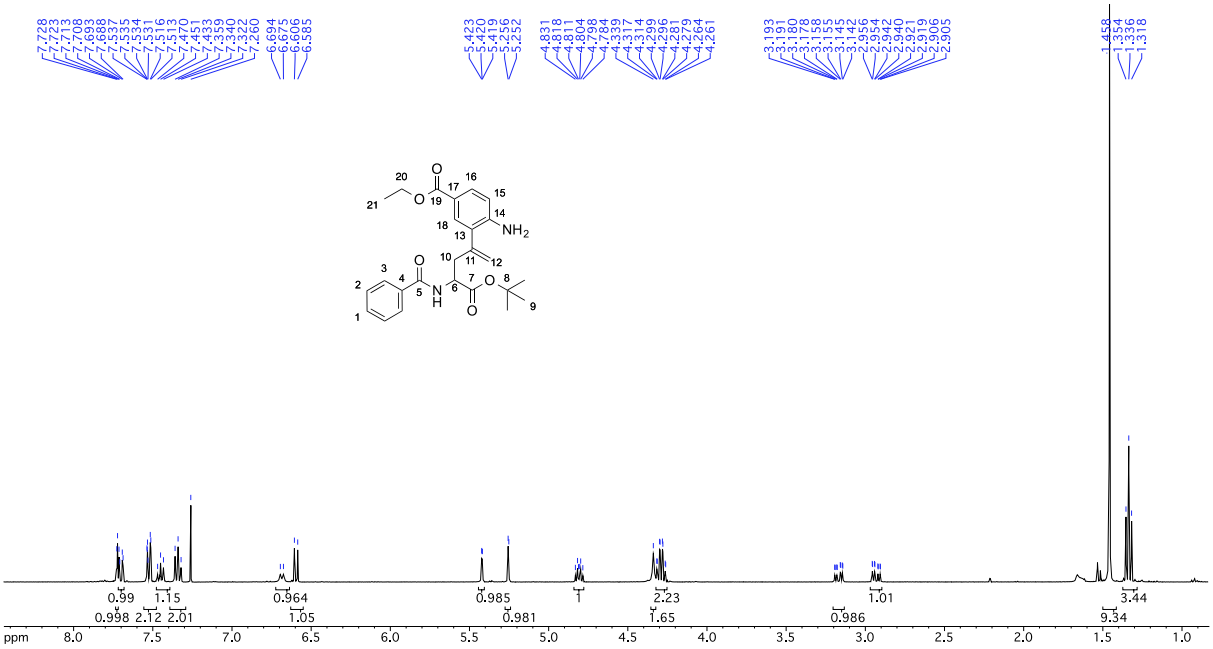


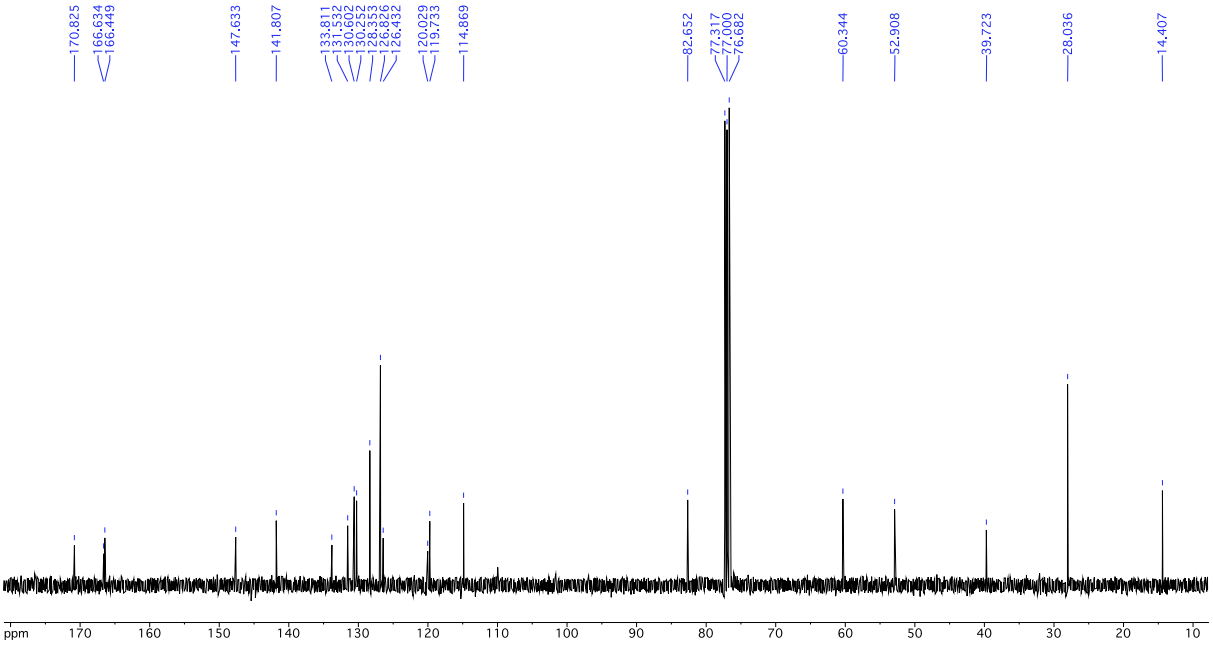
tert-Butyl 4-(2-amino-4-methoxyphenyl)-2-benzamidopent-4-enoate (5e)



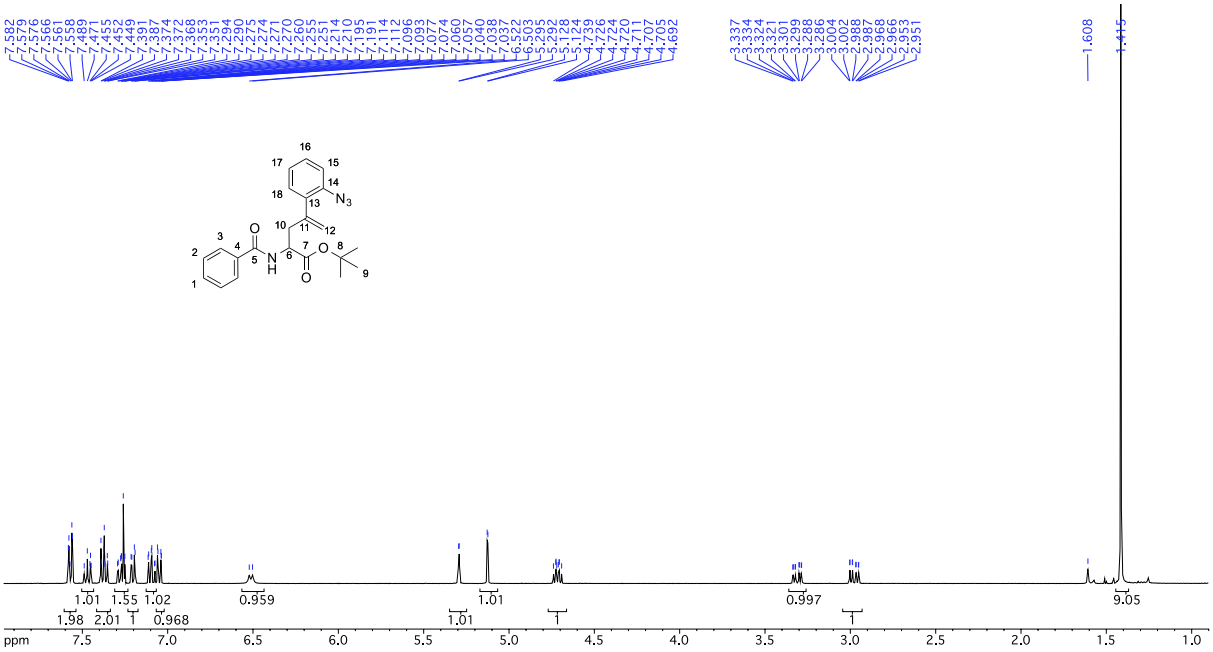


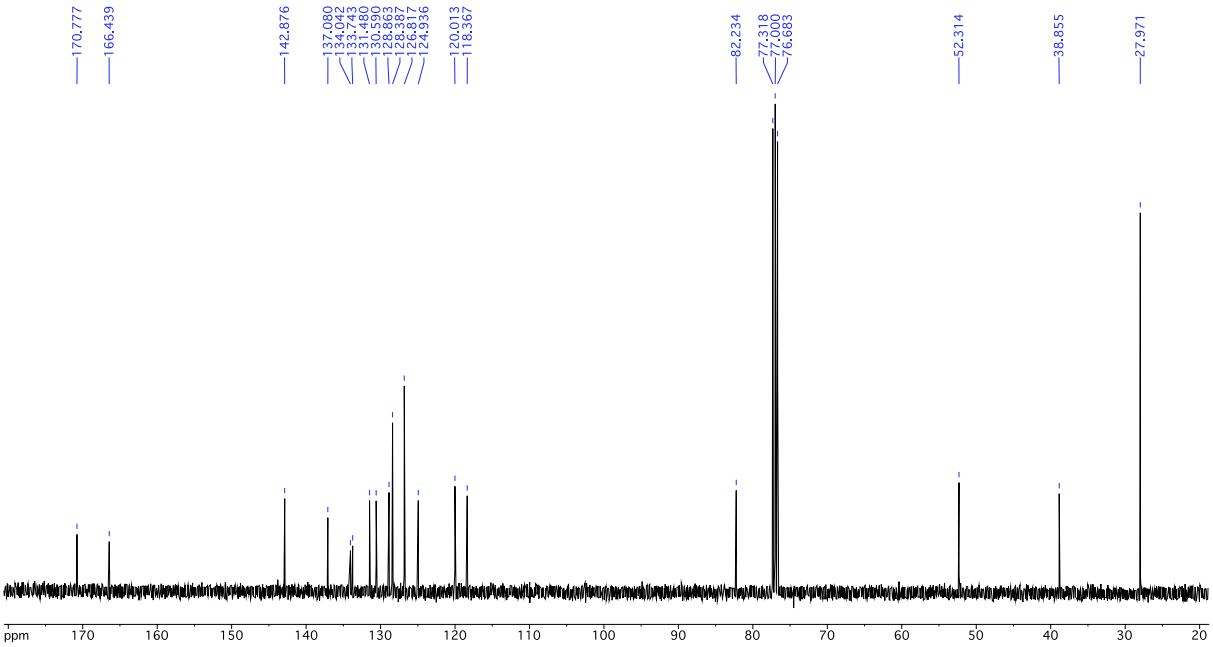
Ethyl 4-amino-3-[4-benzamido-5-(*tert*-butoxy)-5-oxopent-1-en-2-yl]benzoate (5f)



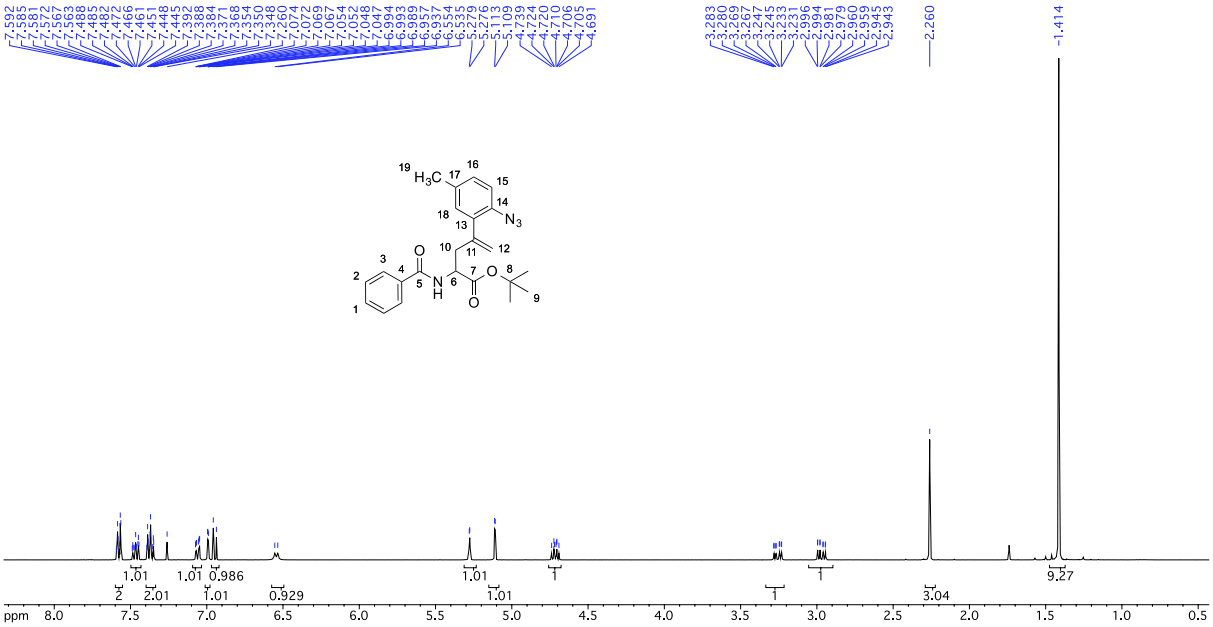


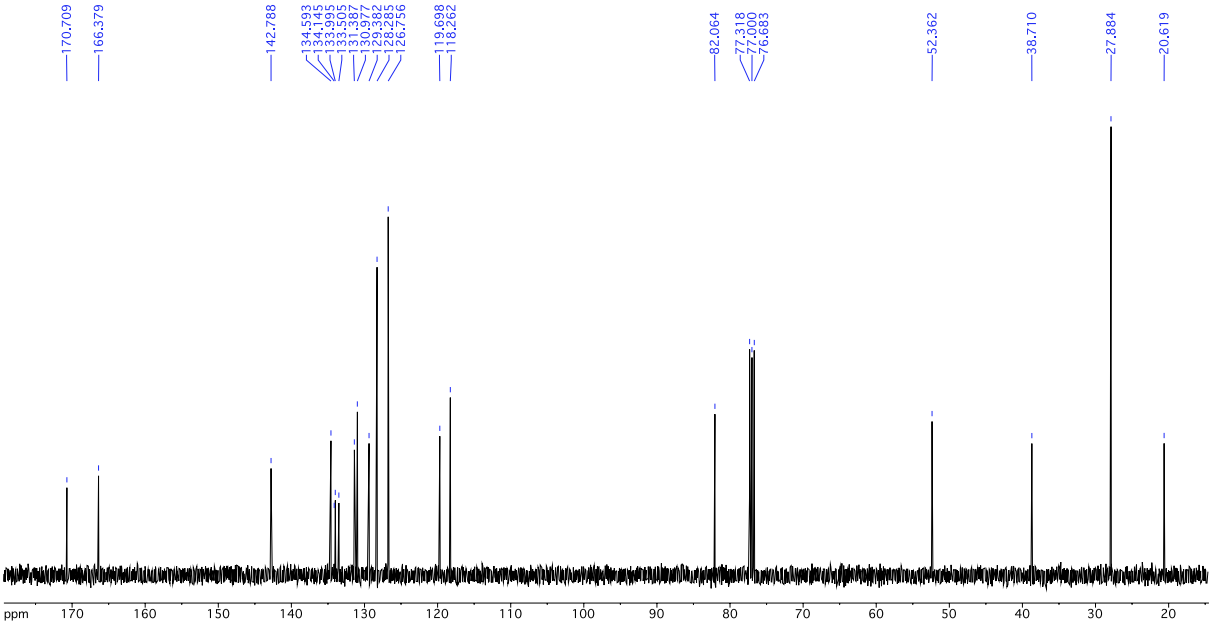
tert-Butyl 4-(2-azidophenyl)-2-benzamidopent-4-enoate (6a)



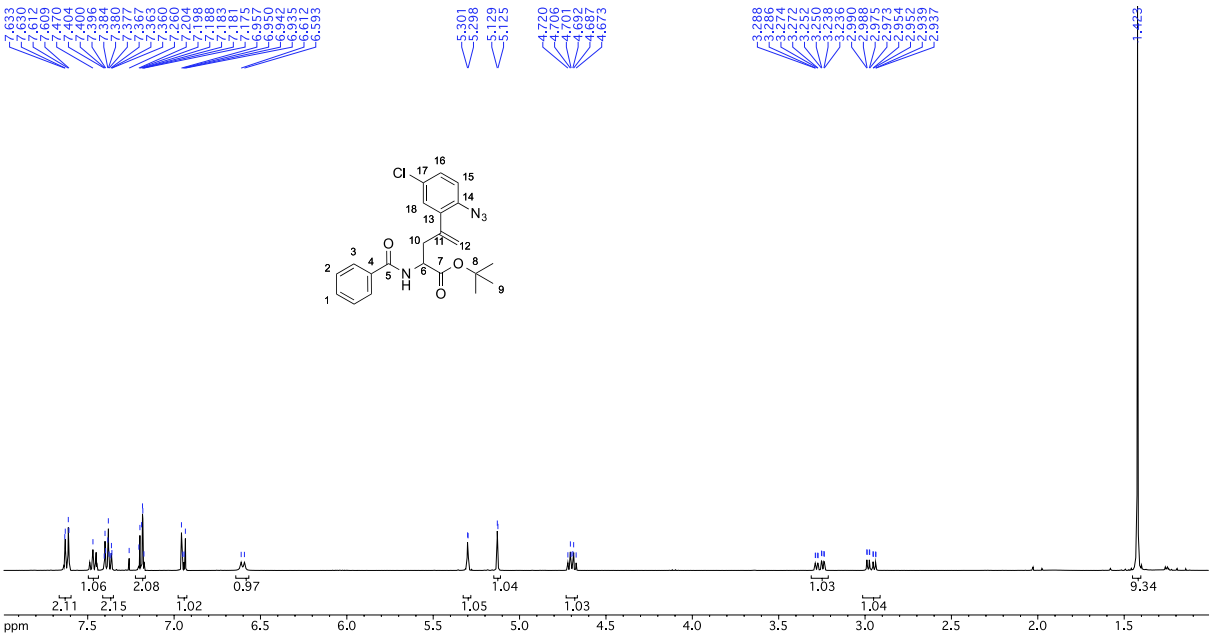


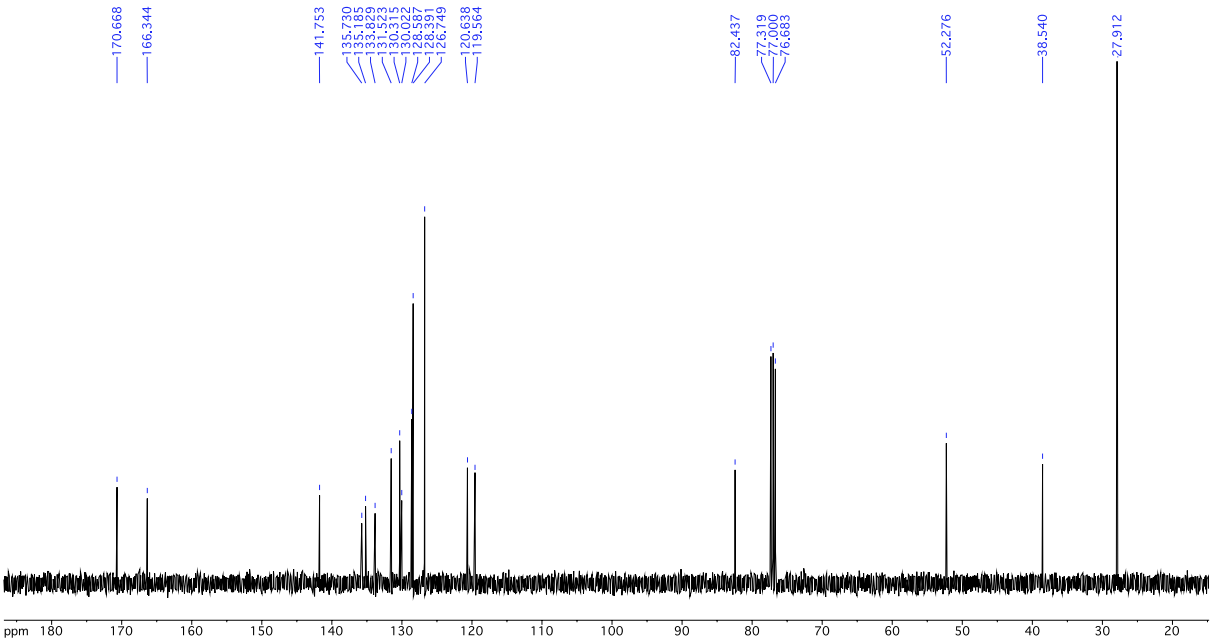
tert-Butyl 4-(2-azido-5-methylphenyl)-2-benzamidopent-4-enoate (6b)



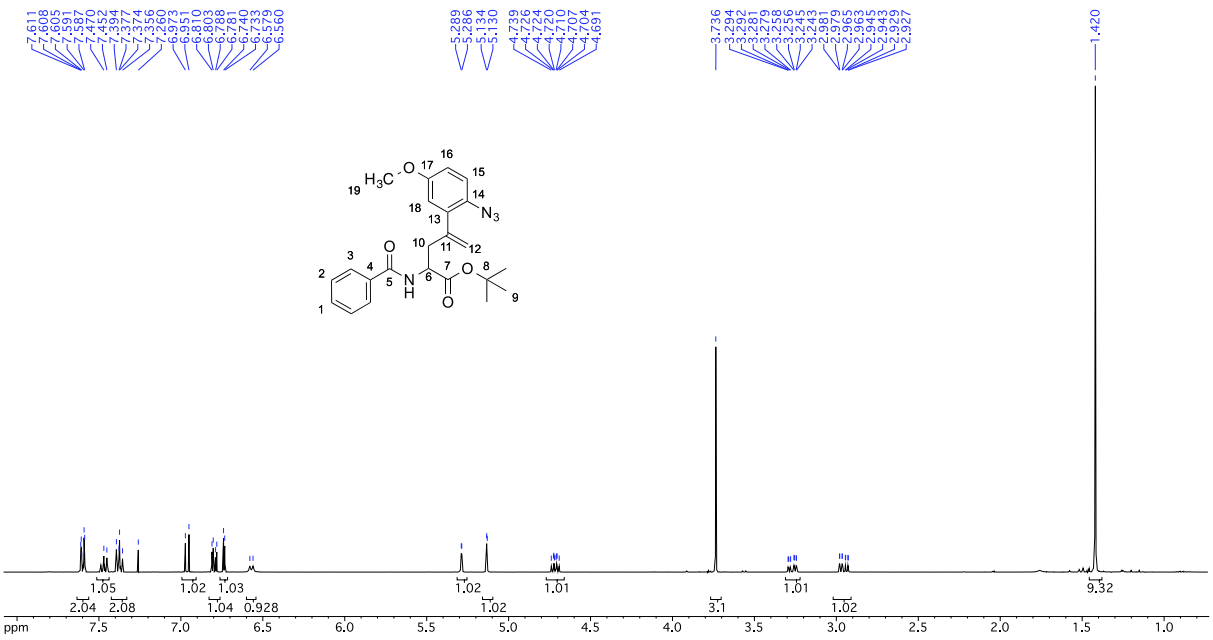


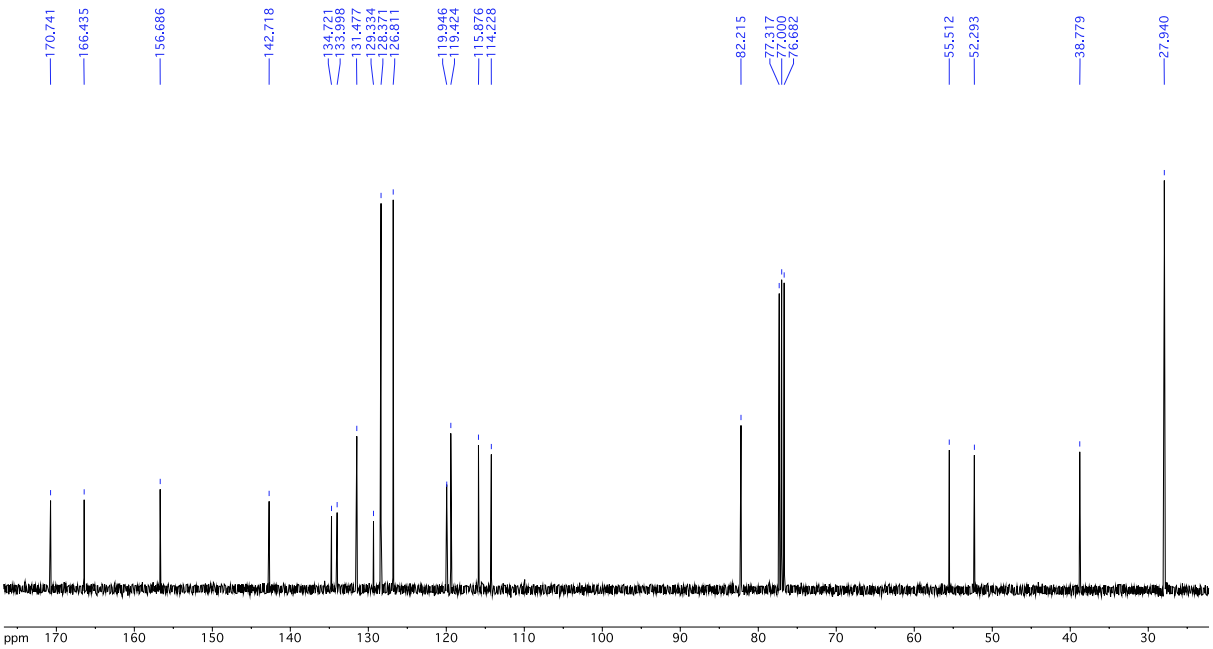
tert-Butyl 4-(2-azido-5-chlorophenyl)-2-benzamidopent-4-enoate (6c)



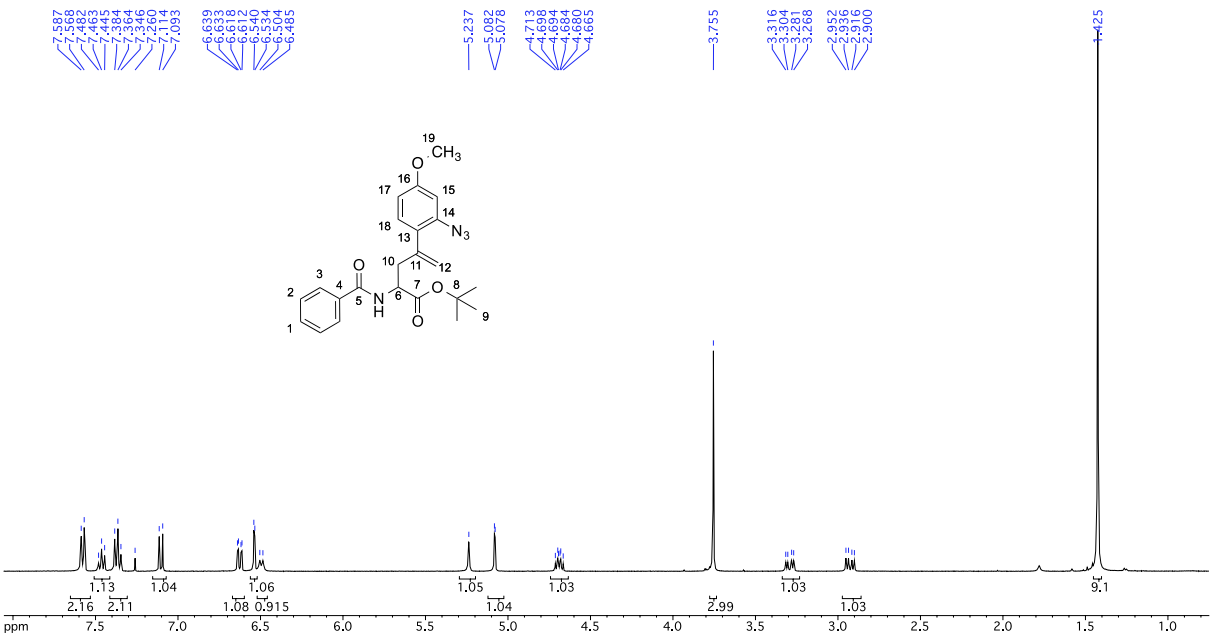


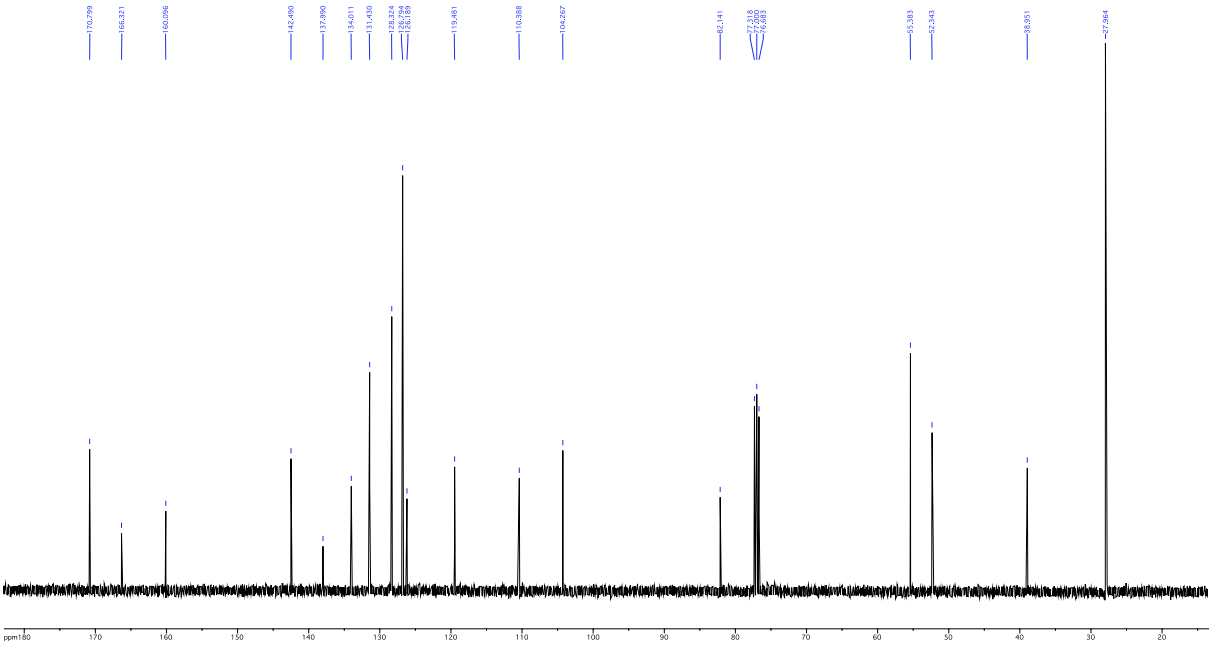
tert-Butyl 4-(2-azido-5-methoxyphenyl)-2-benzamidopent-4-enoate (6d)



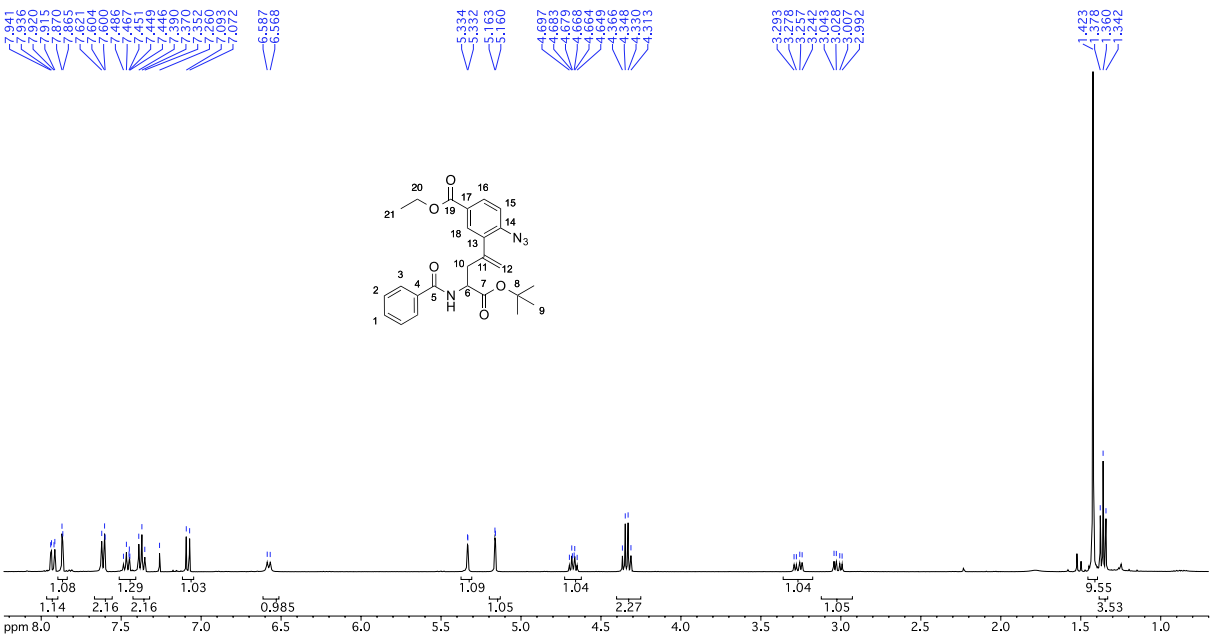


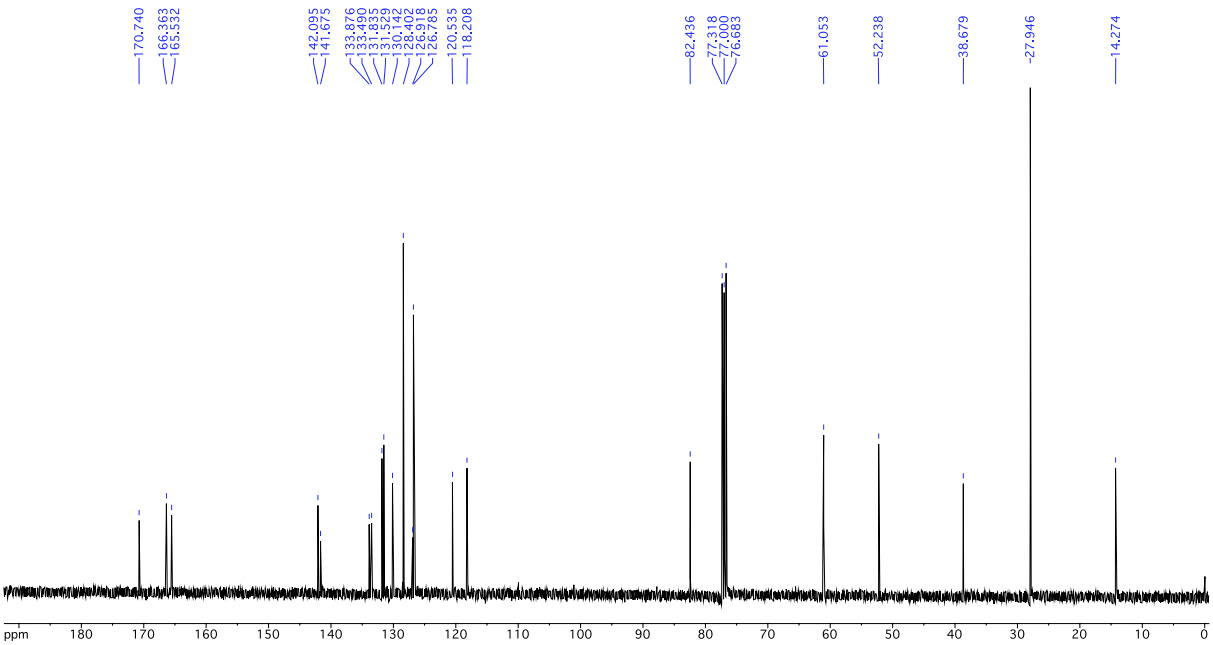
tert-Butyl 4-(2-azido-4-methoxyphenyl)-2-benzamidopent-4-enoate (6e)



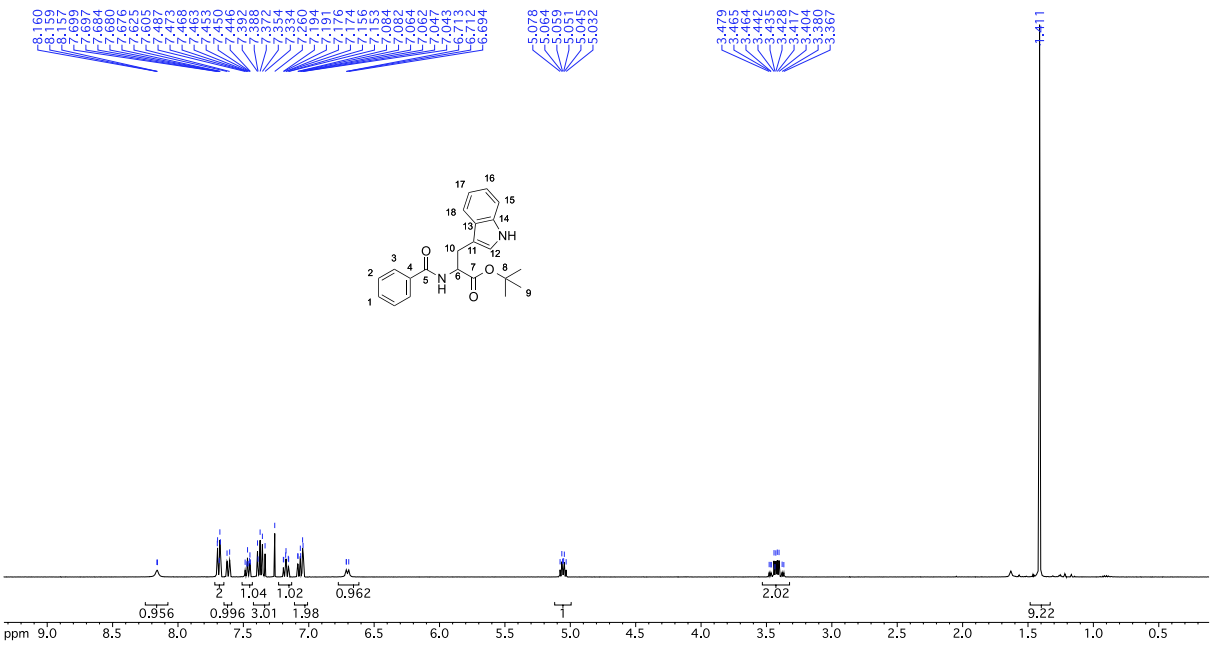


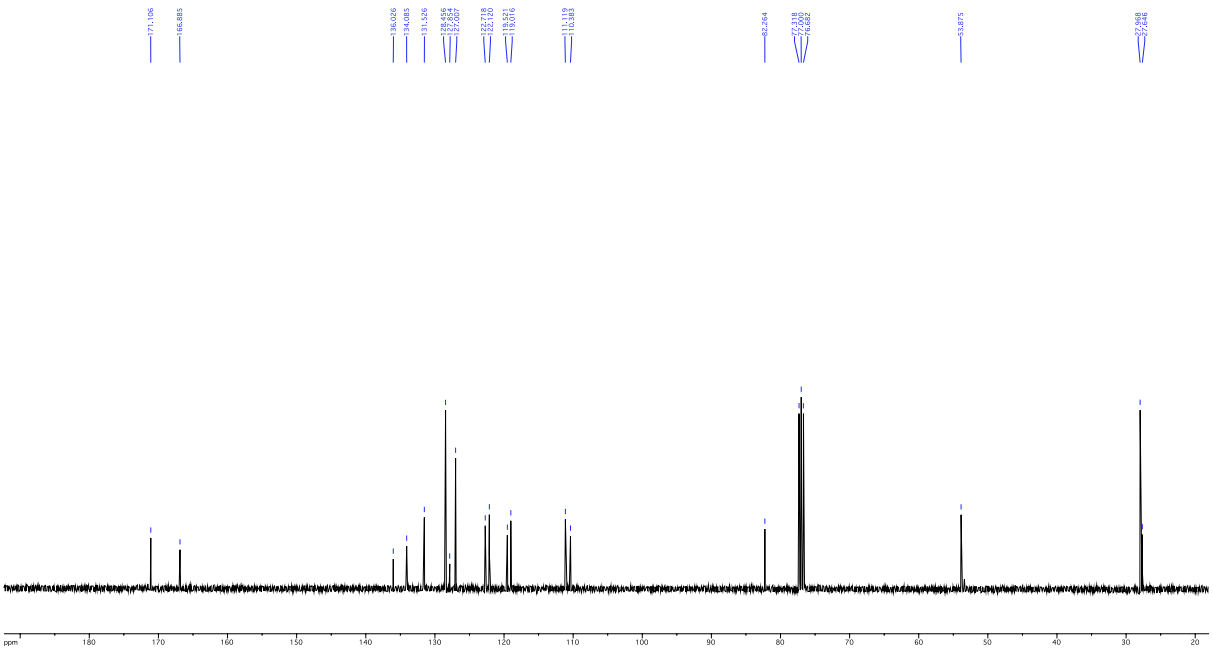
Ethyl 4-azido-3-[4-benzamido-5-(*tert*-butoxy)-5-oxopent-1-en-2-yl]benzoate (6f)



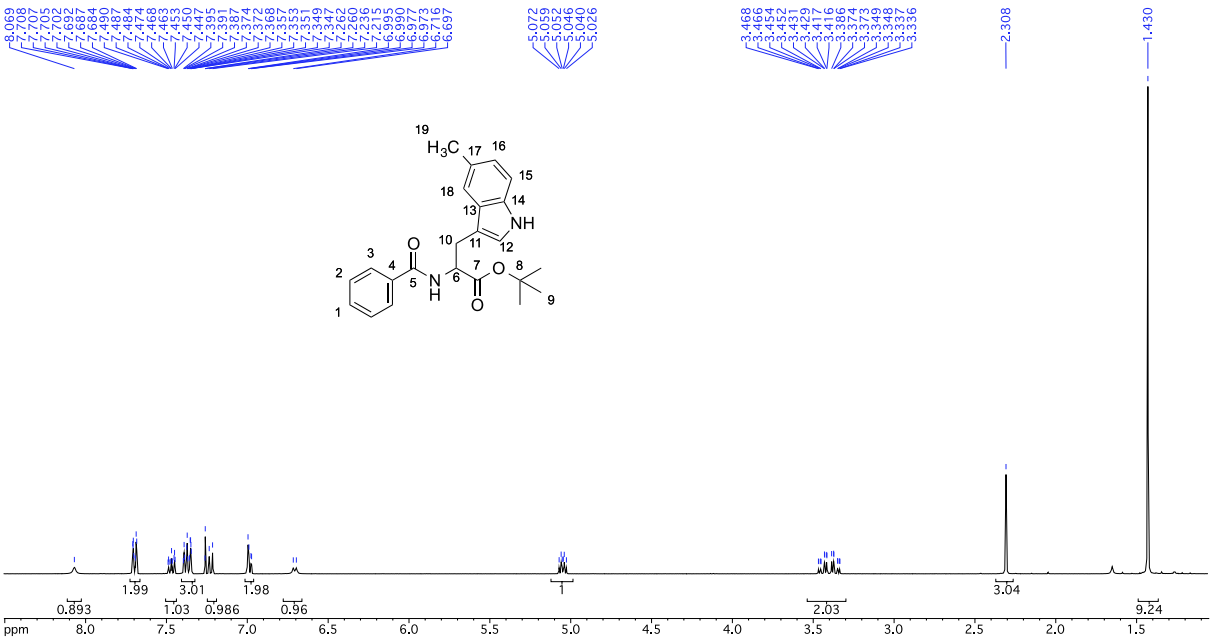


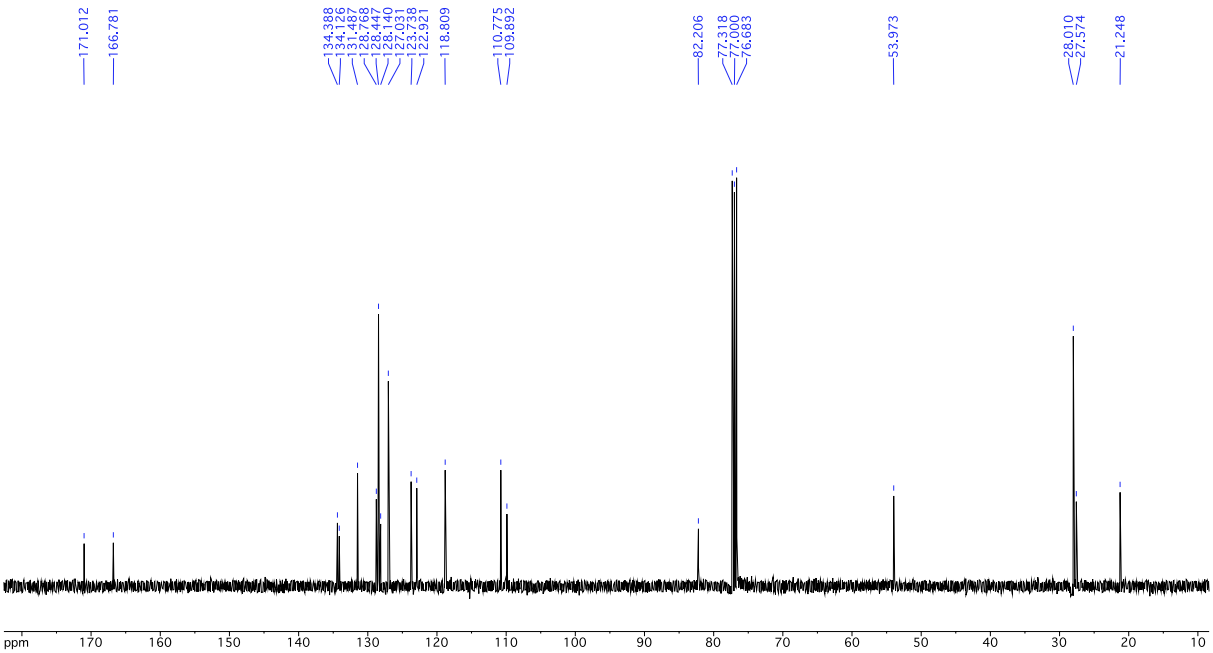
tert-Butyl benzoyltryptophanate (7a)



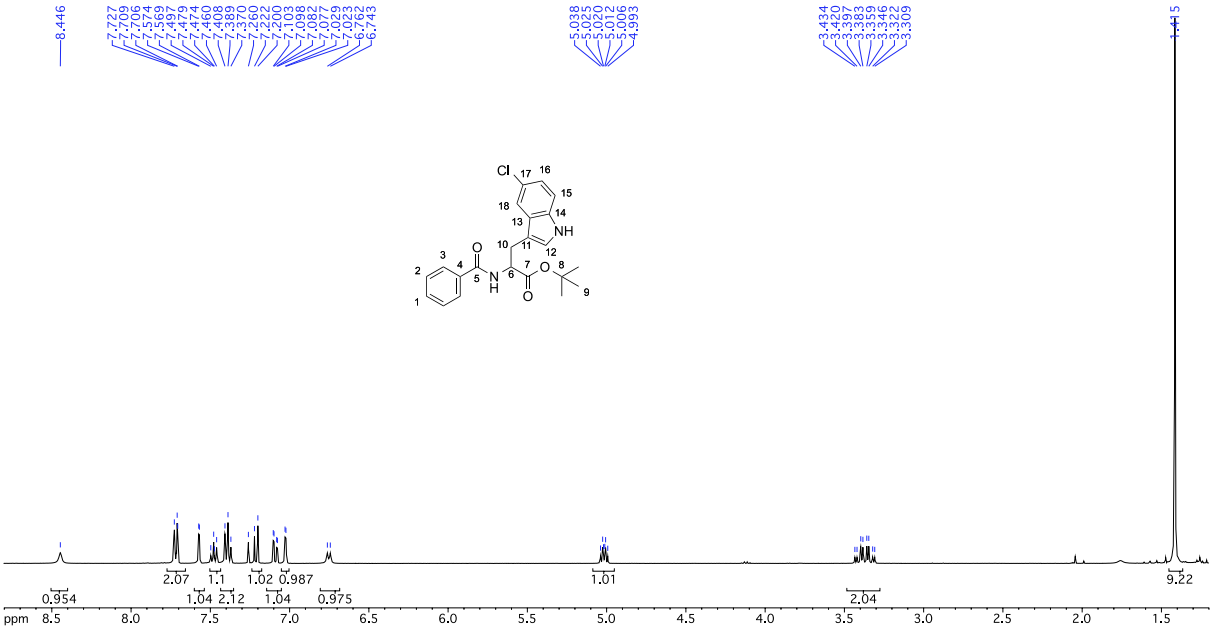


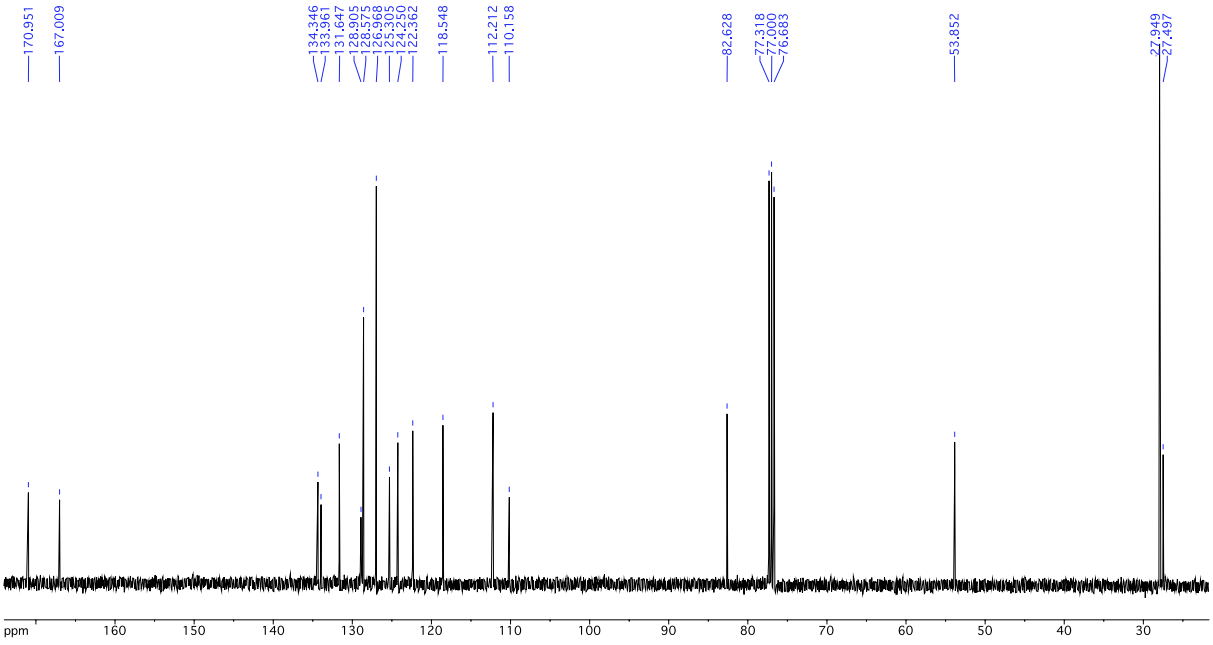
tert-Butyl 2-benzamido-3-(5-methyl-1*H*-indol-3-yl)propanoate (7b)



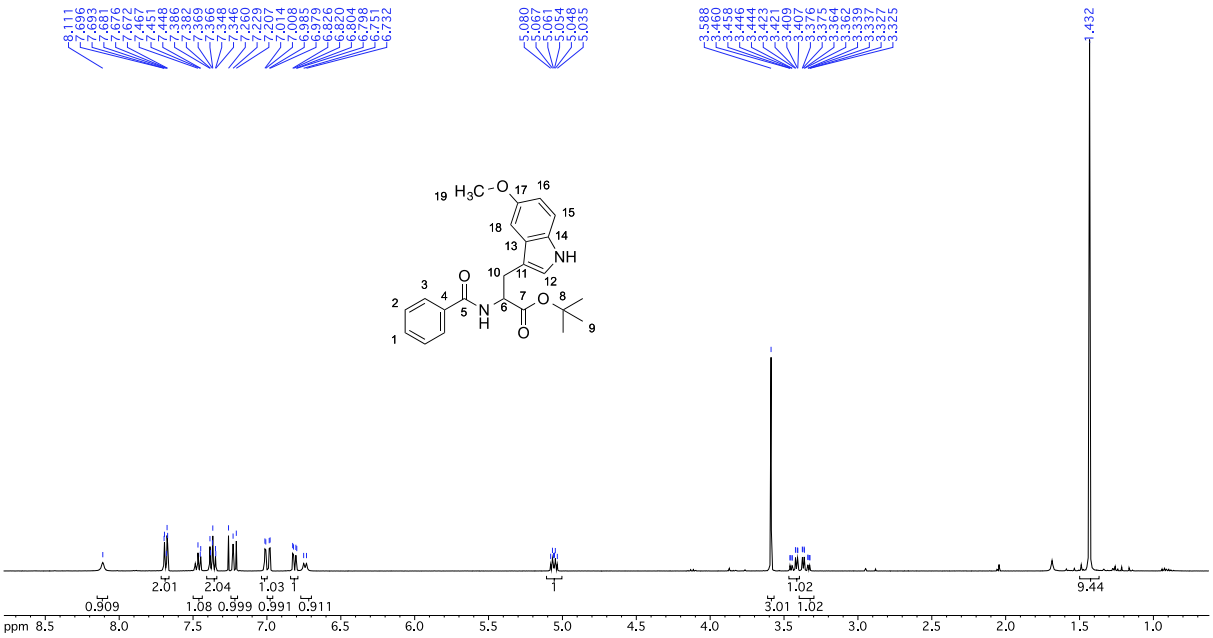


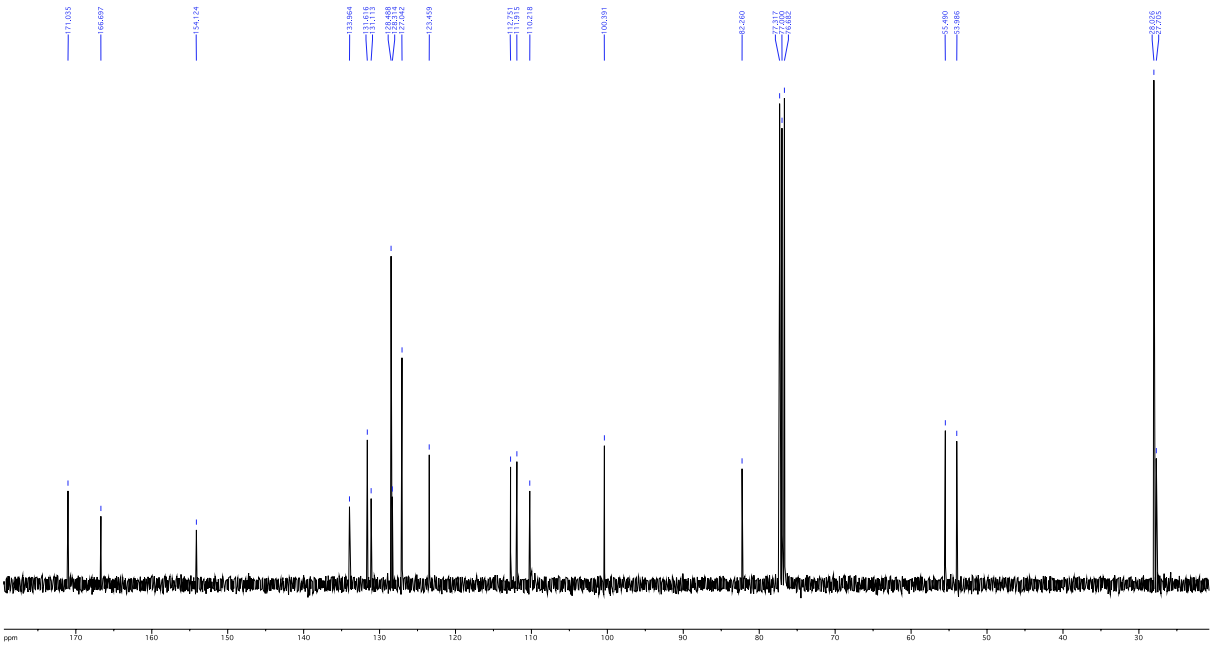
tert-Butyl 2-benzamido-3-(5-chloro-1*H*-indol-3-yl)propanoate (7c)



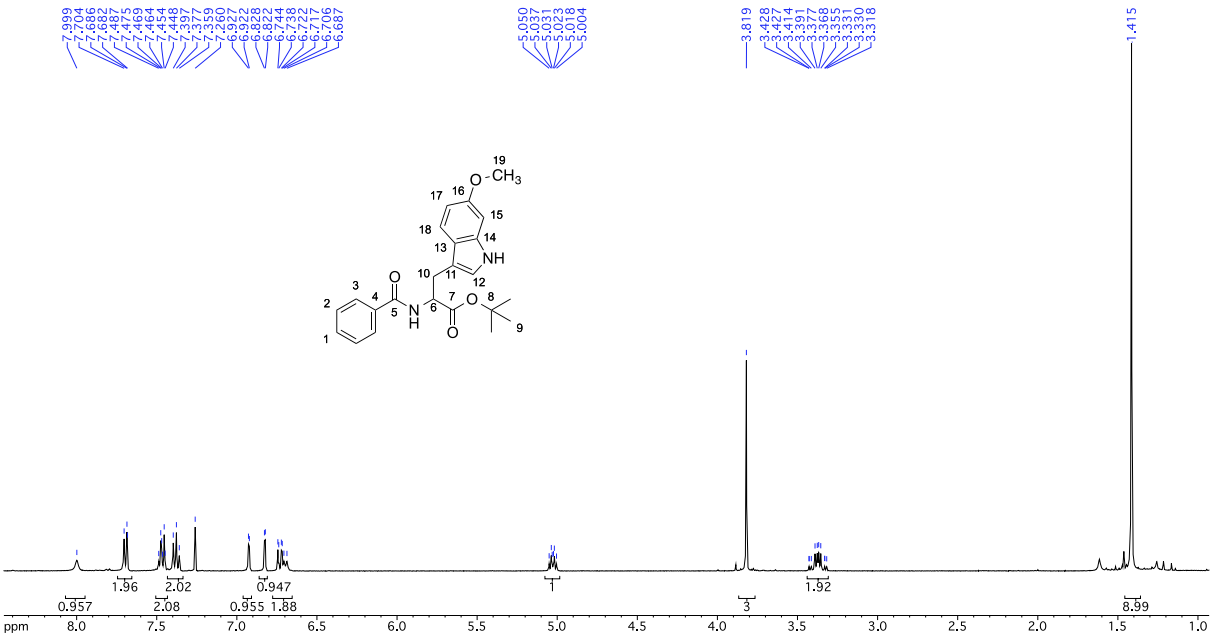


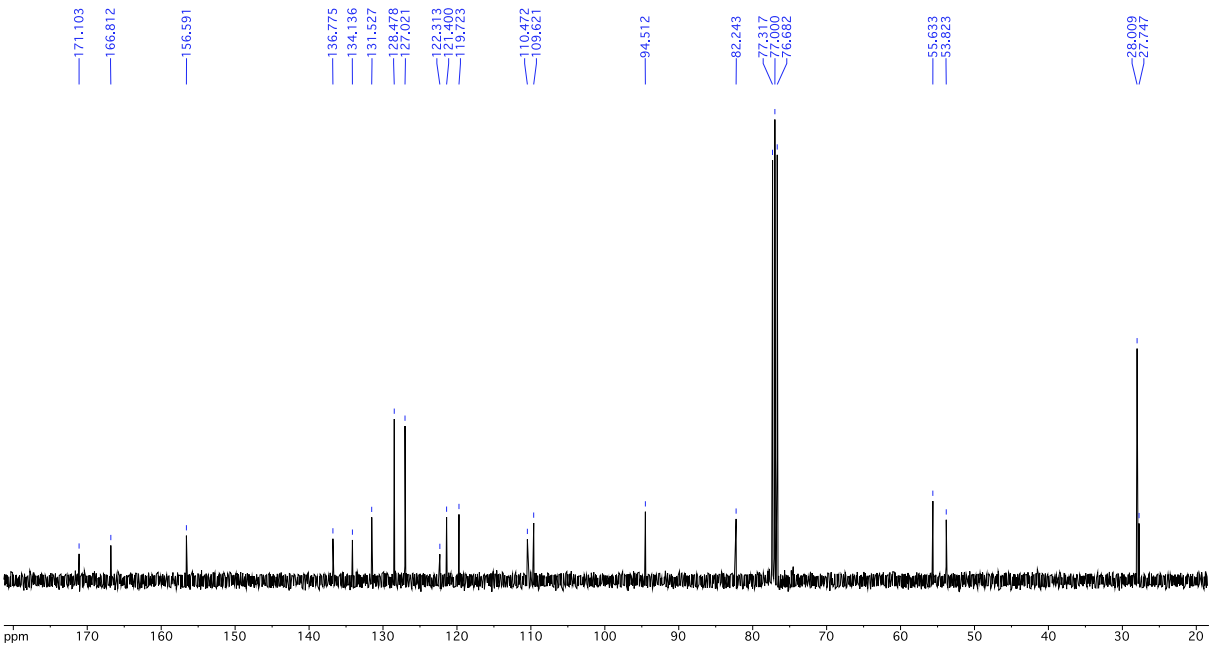
tert-Butyl 2-benzamido-3-(5-methoxy-1*H*-indol-3-yl)propanoate (7d)



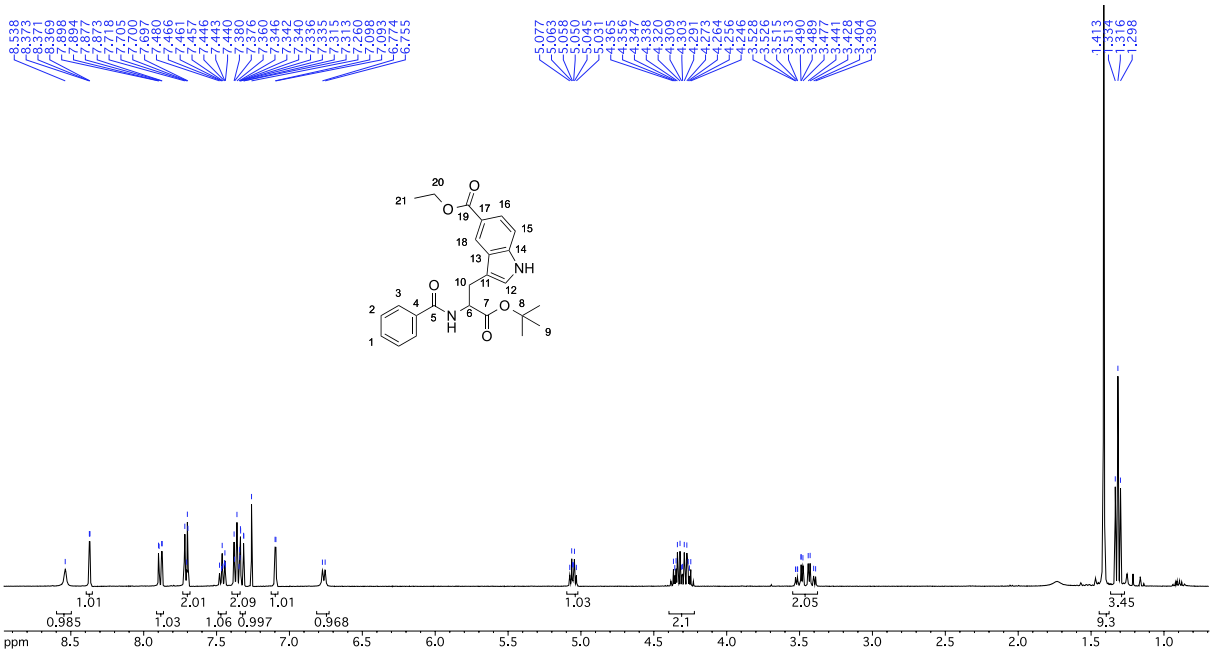


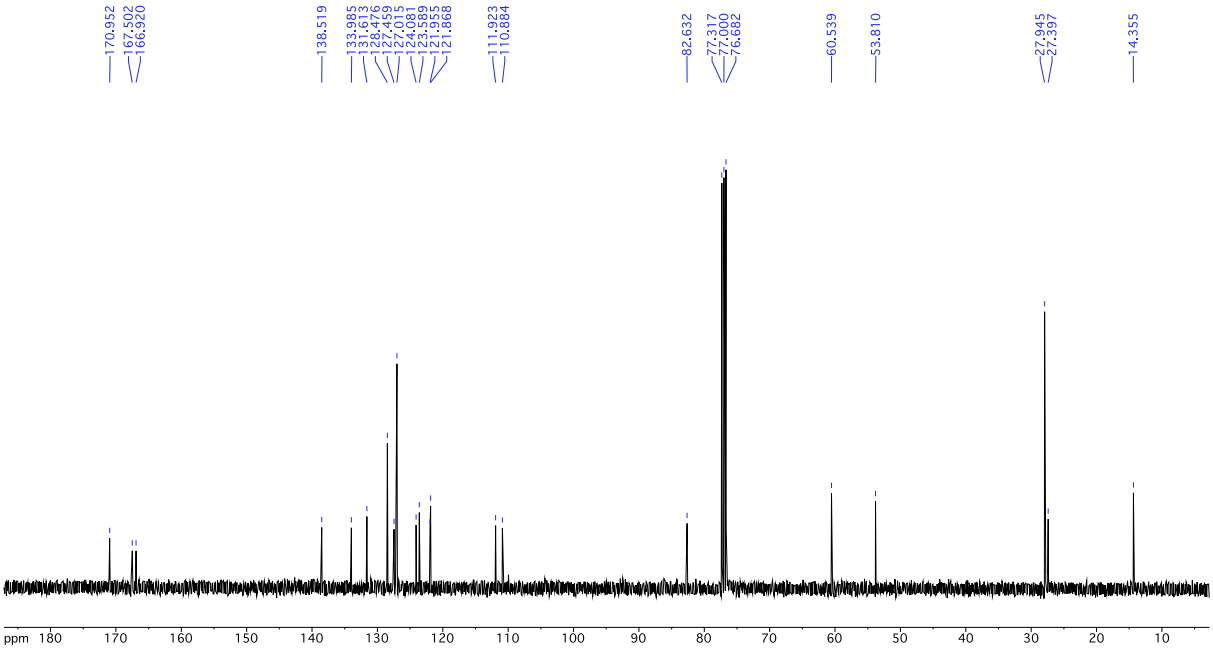
tert-Butyl 2-benzamido-3-(6-methoxy-1*H*-indol-3-yl)propanoate (7e)



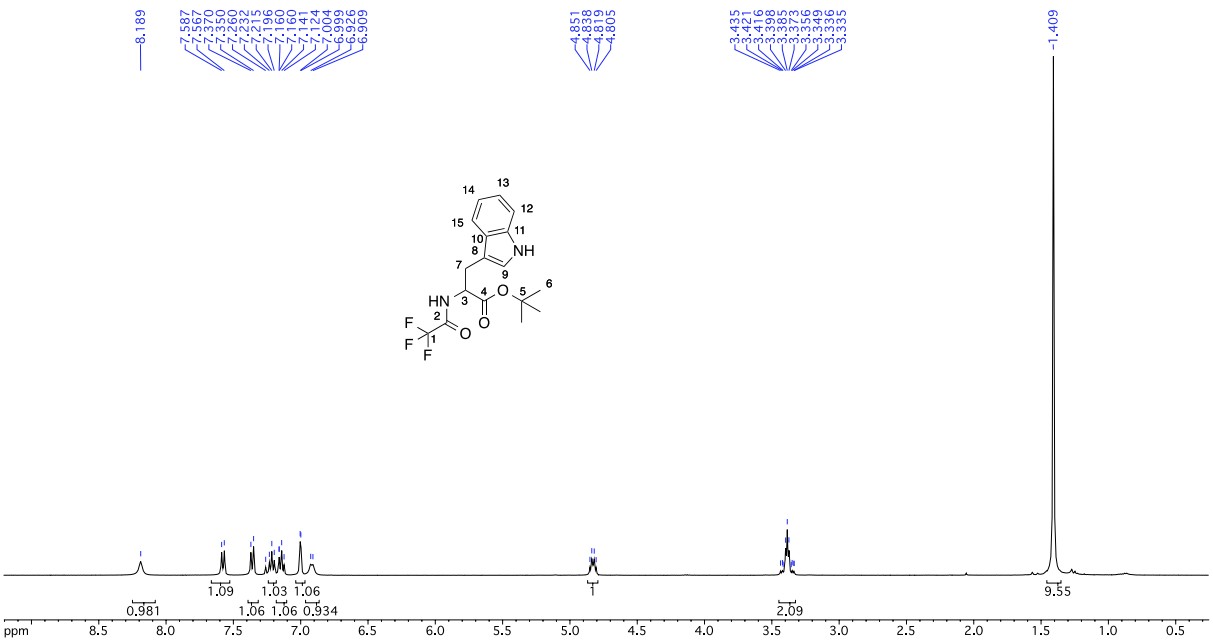


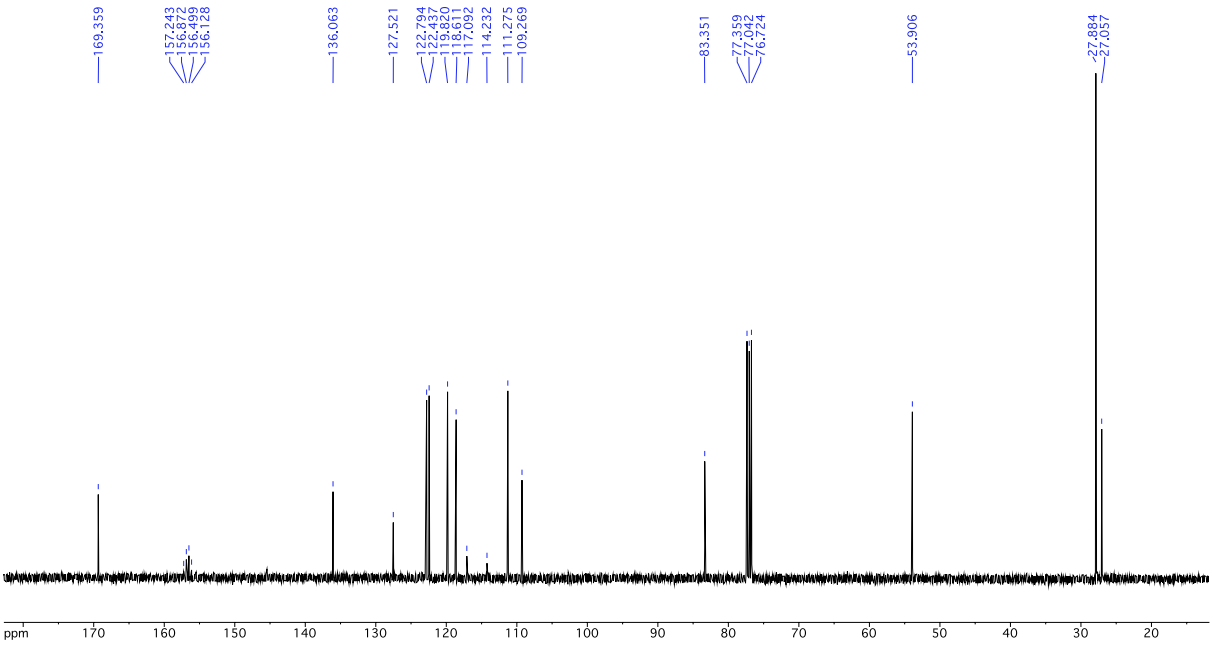
Ethyl 3-[2-benzamido-3-(*tert*-butoxy)-3-oxopropyl]-1*H*-indole-5-carboxylate (7f)



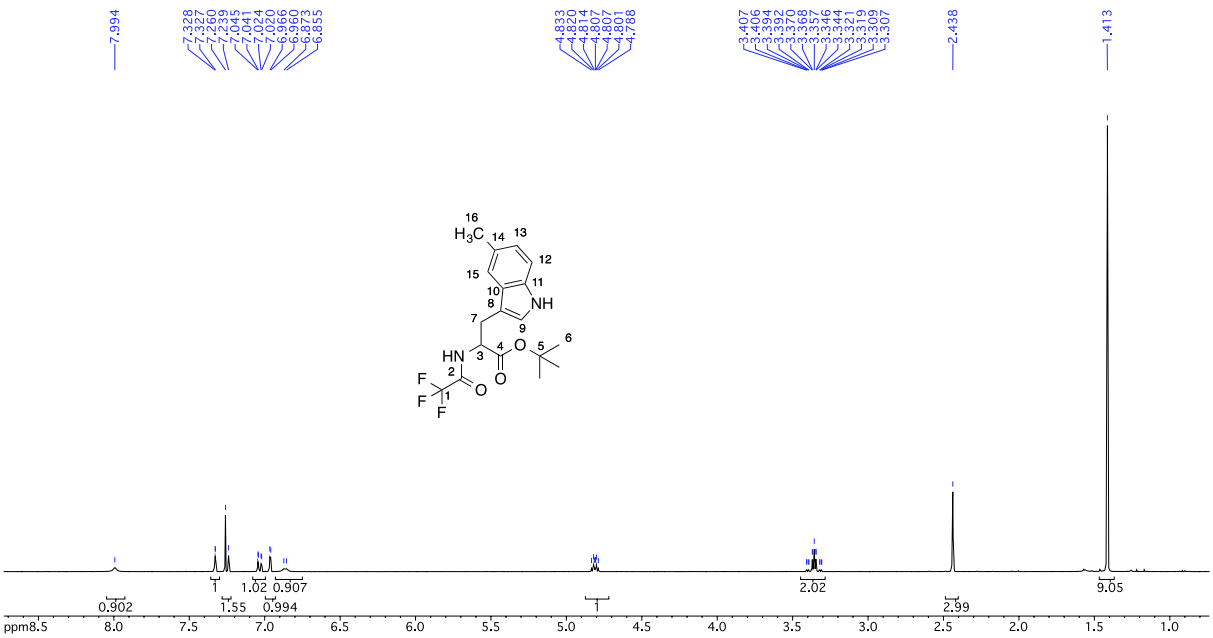


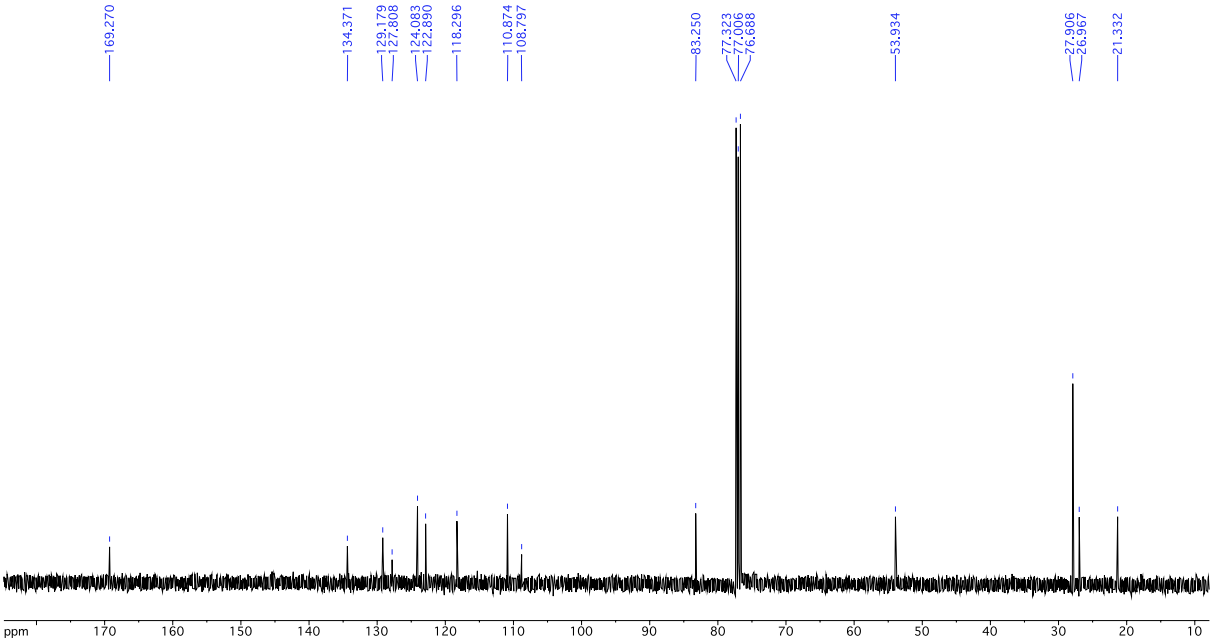
tert-Butyl (2,2,2-trifluoroacetyl)tryptophanate (8a)



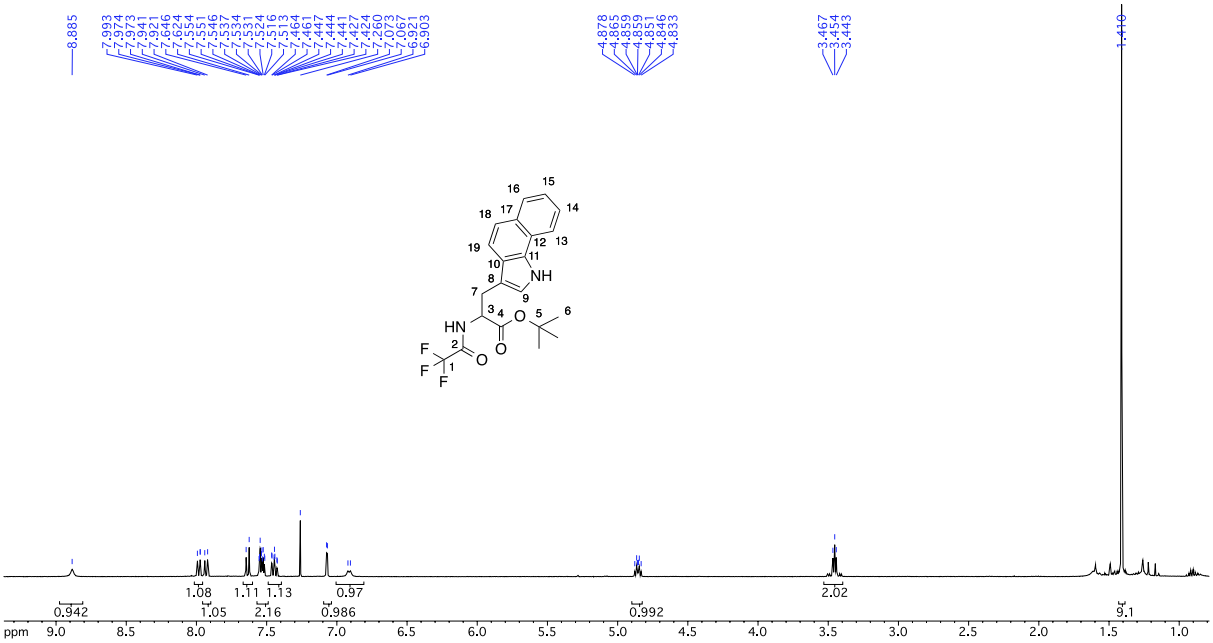


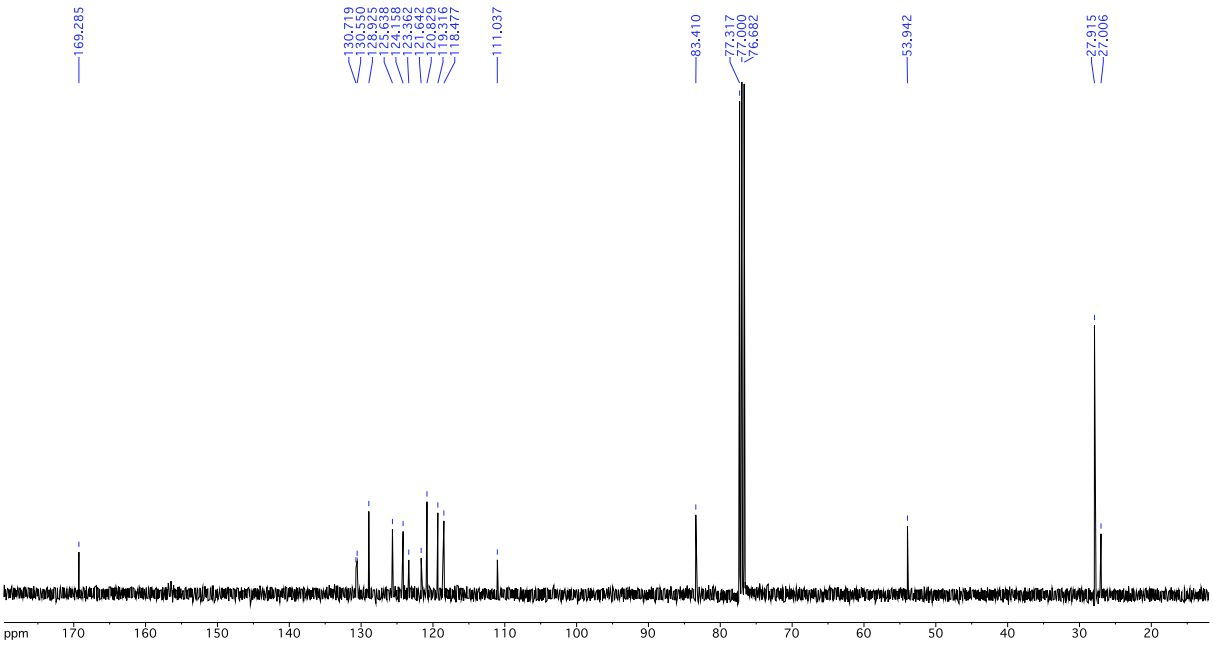
tert-Butyl 3-(5-methyl-1*H*-indol-3-yl)-2-(2,2,2-trifluoroacetamido)propanoate (8b)



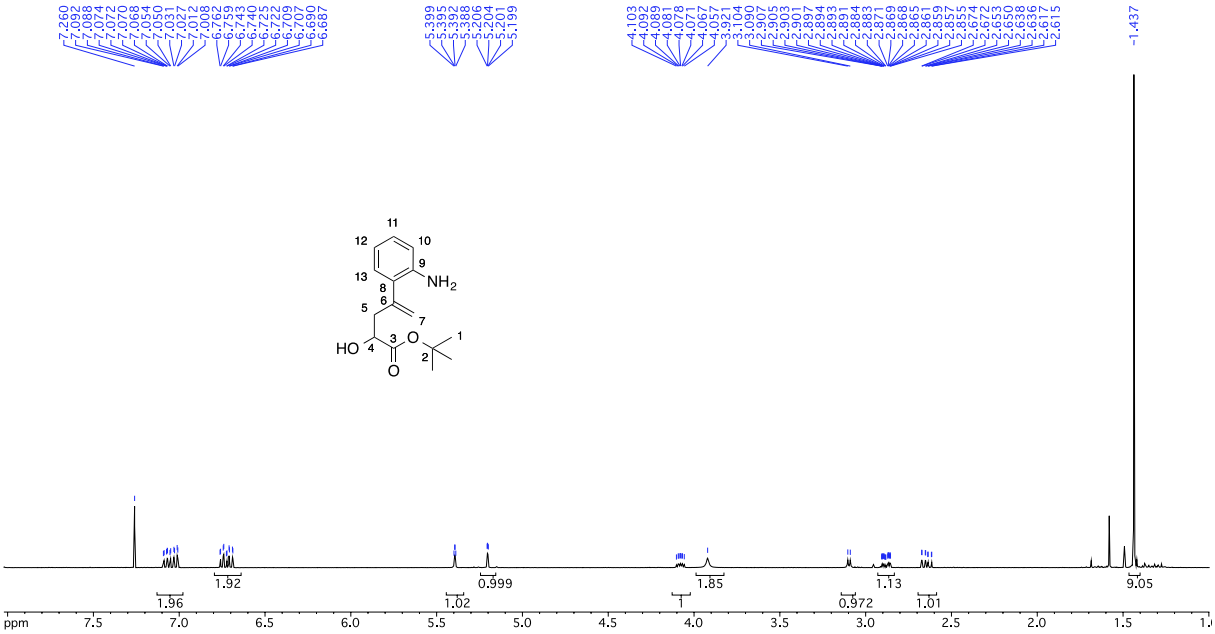


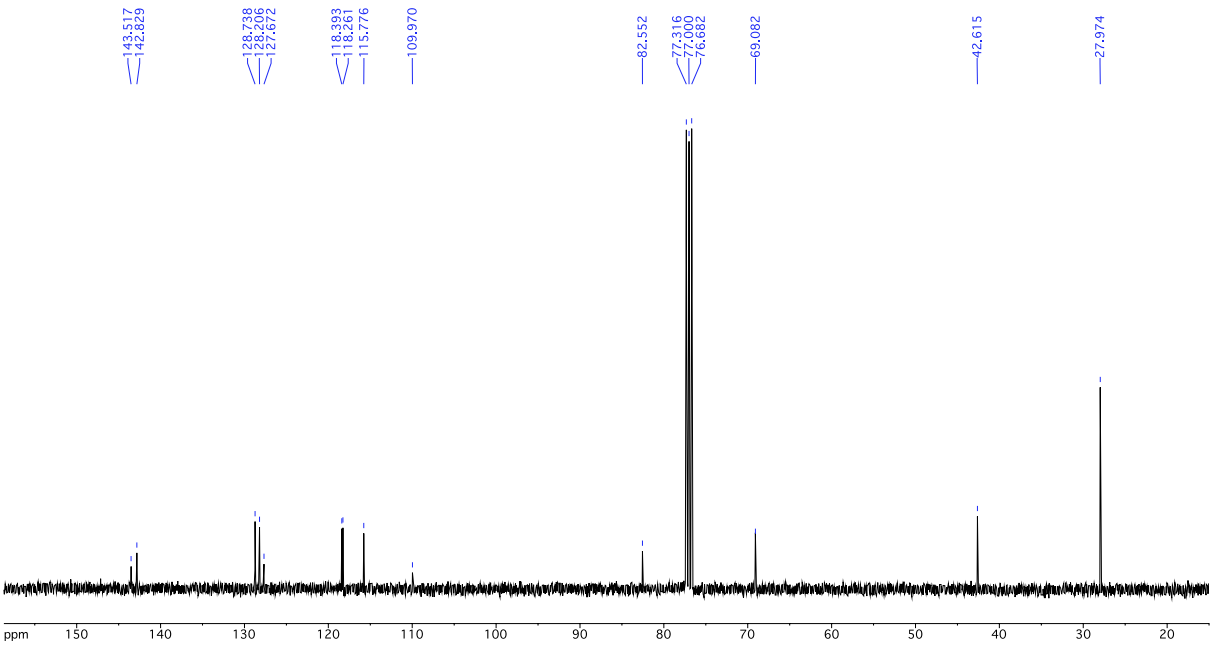
tert-Butyl 3-(1*H*-benzo[*g*]indol-3-yl)-2-(2,2,2-trifluoroacetamido)propanoate (8g)



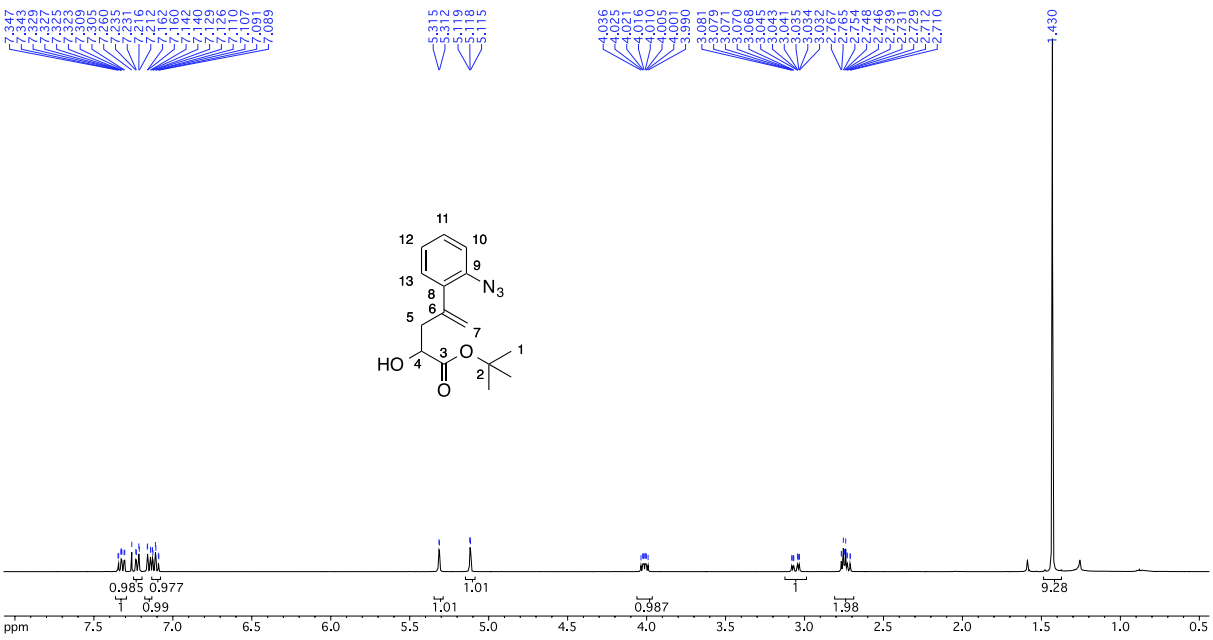


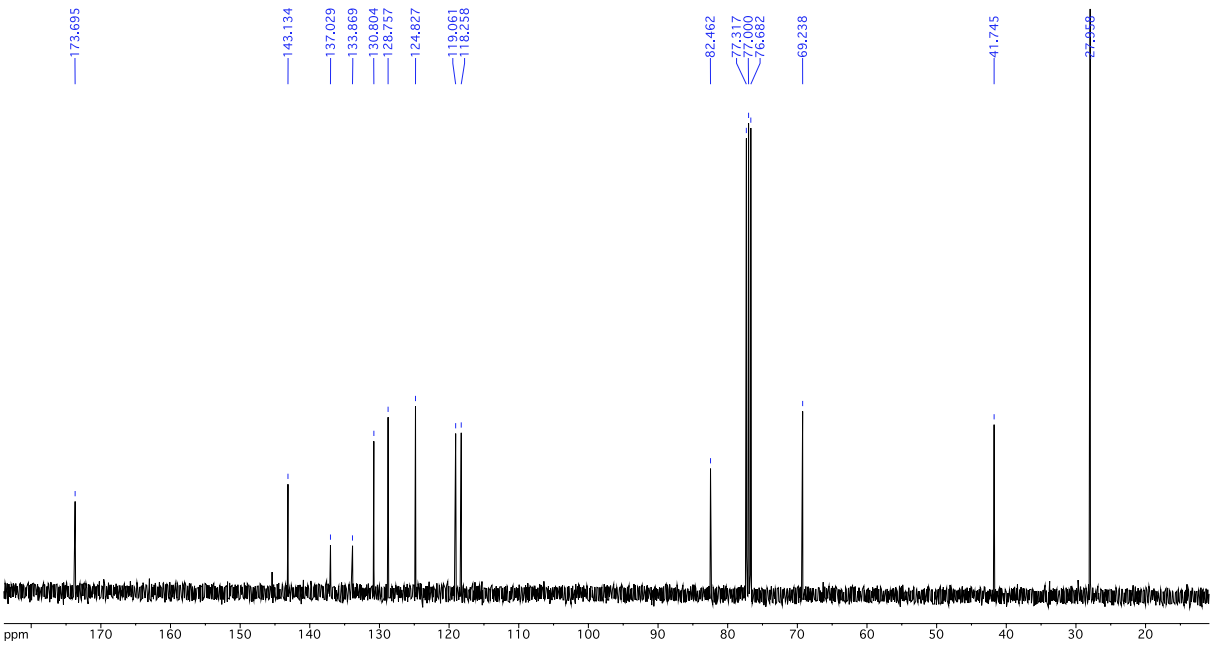
tert-Butyl 4-(2-aminophenyl)-2-hydroxypent-4-enoate (10a)



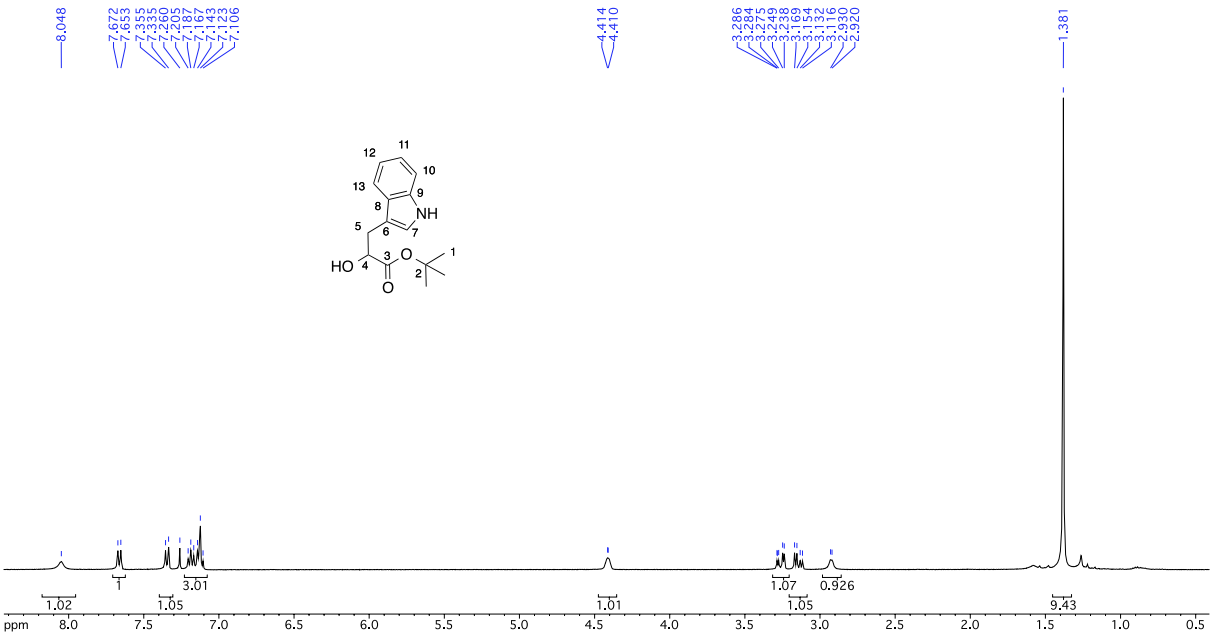


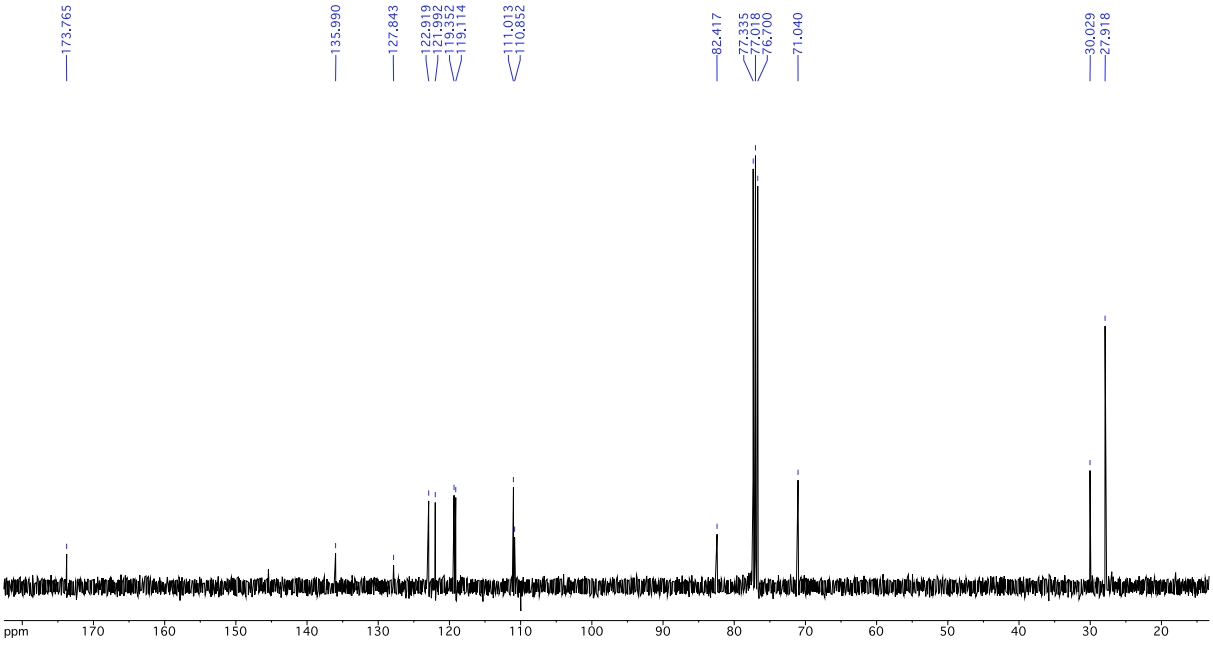
tert-Butyl 4-(2-azidophenyl)-2-hydroxypent-4-enoate (11a)



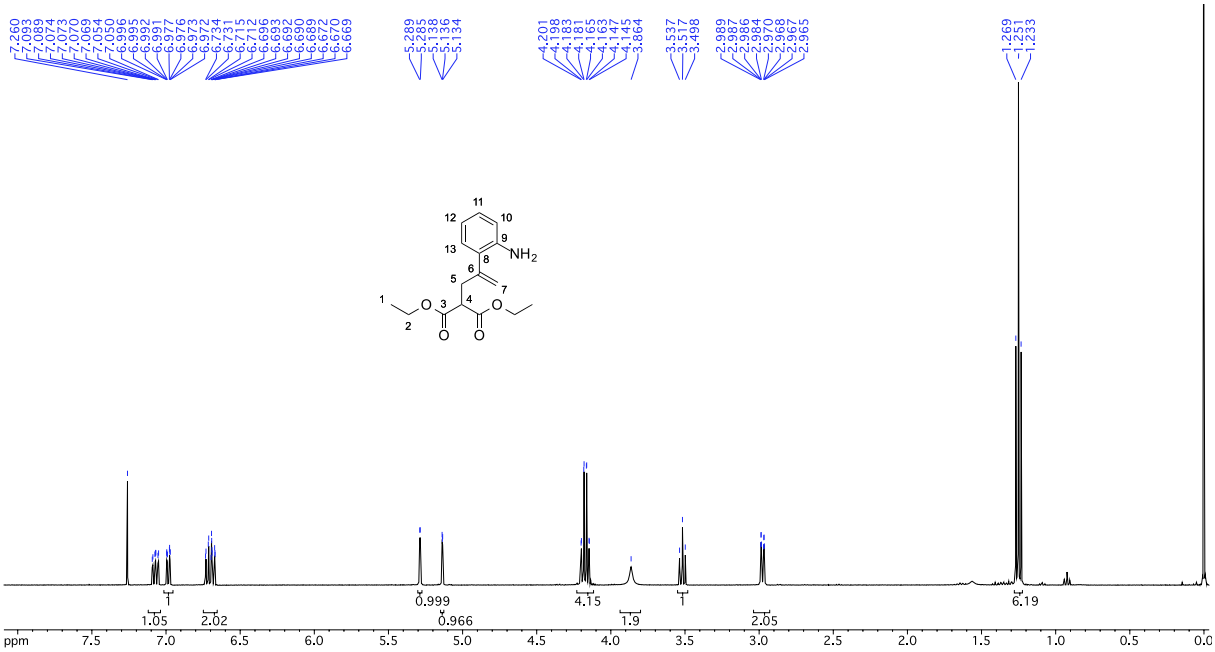


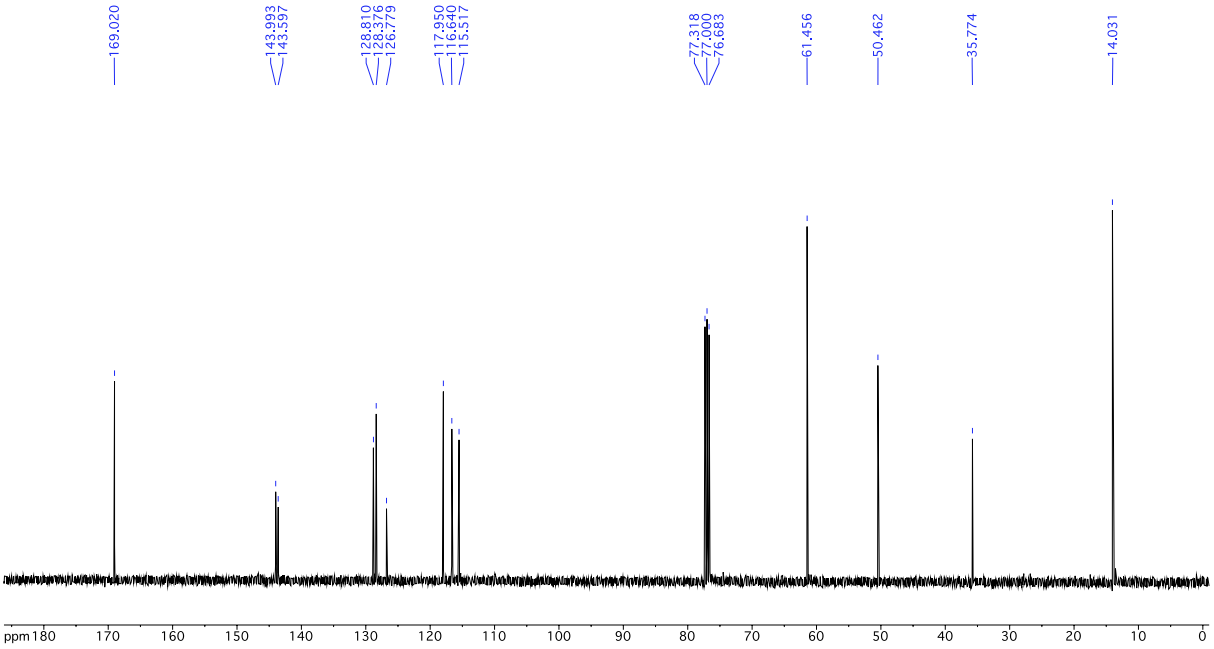
tert-Butyl 2-hydroxy-3-(1*H*-indol-3-yl)propanoate (12a)



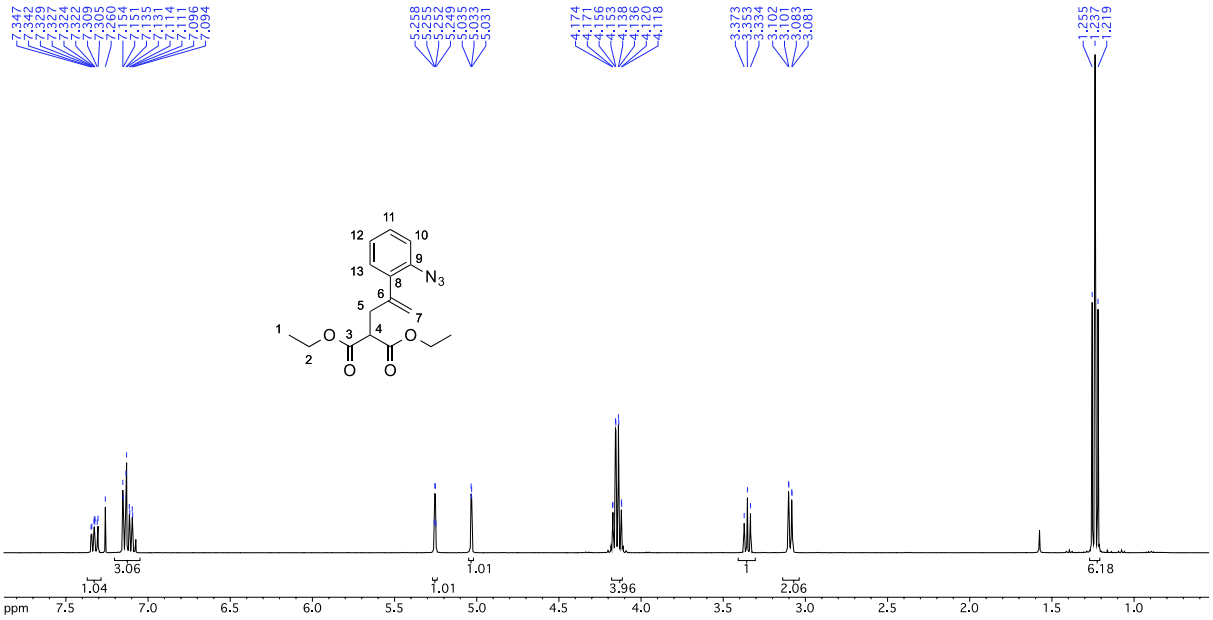


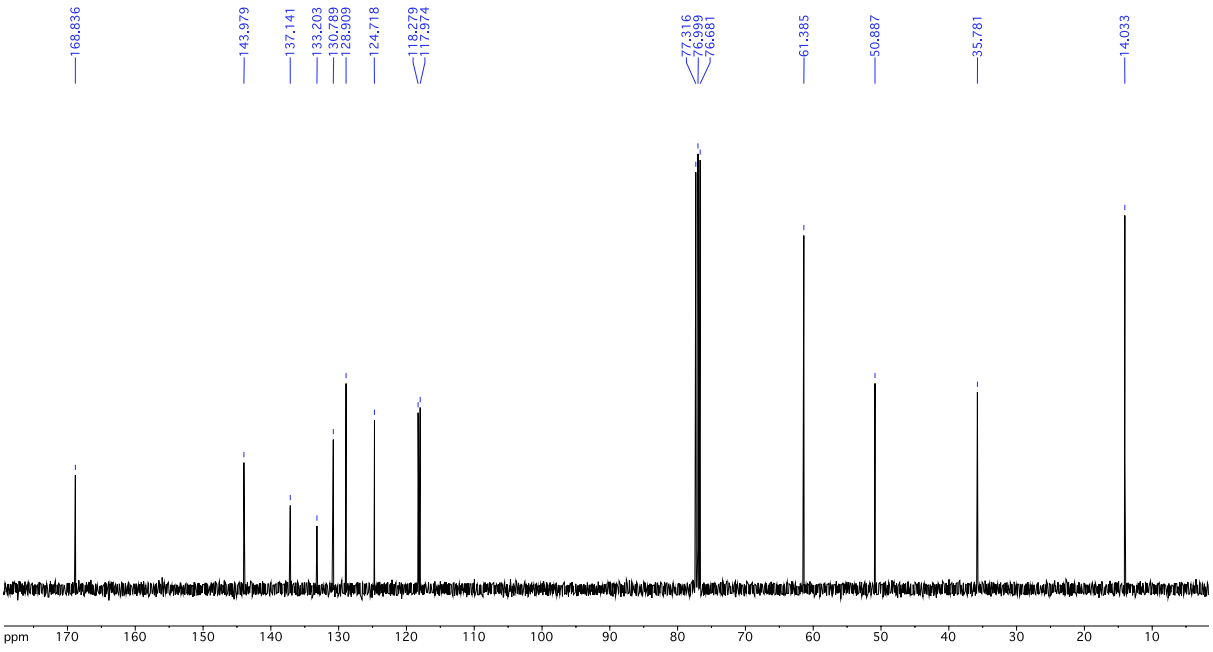
Diethyl 2-(2-(2-aminophenyl)allyl)malonate (10b)



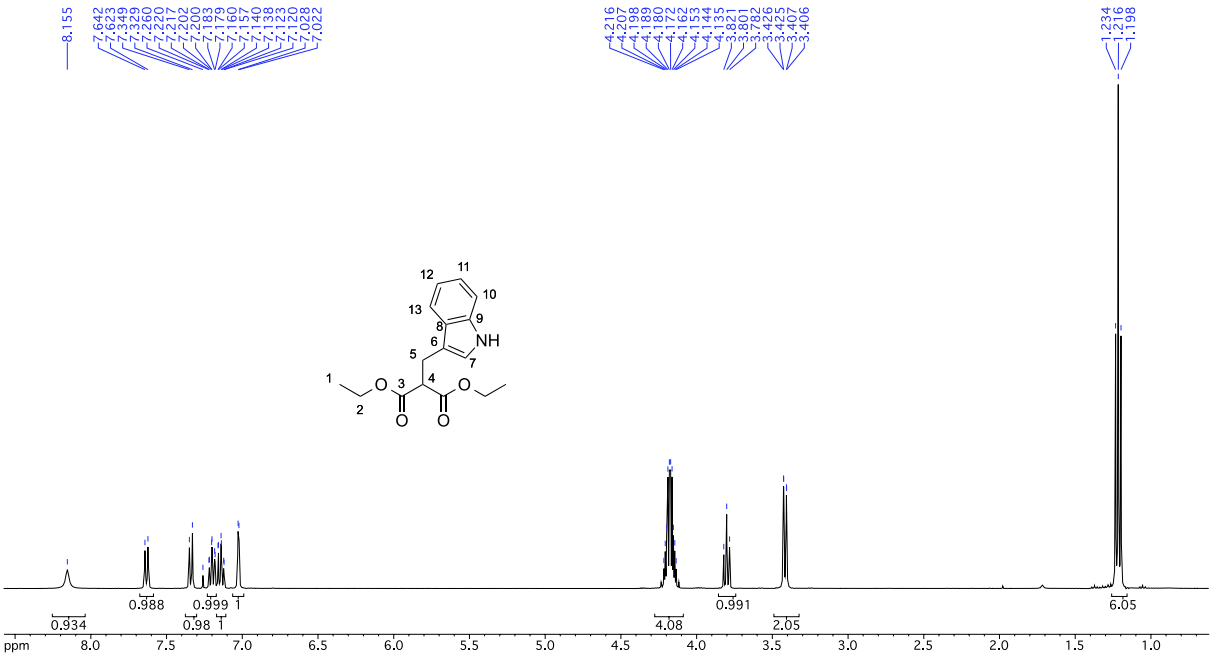


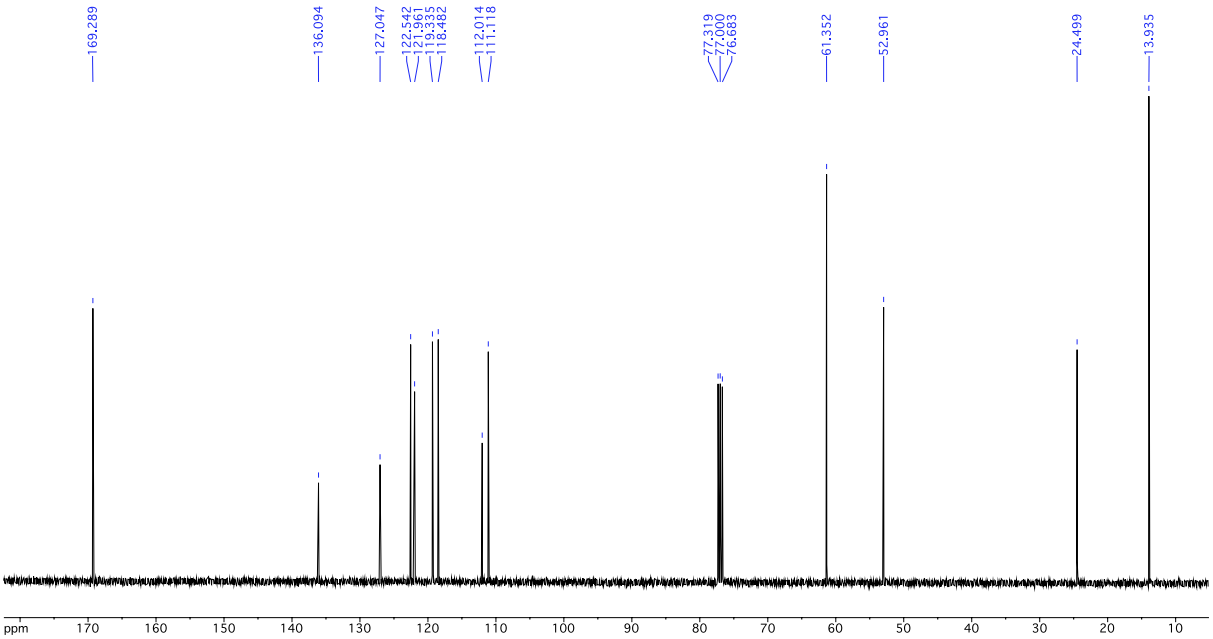
Diethyl 2-(2-(2-azidophenyl)allyl)malonate (11b)



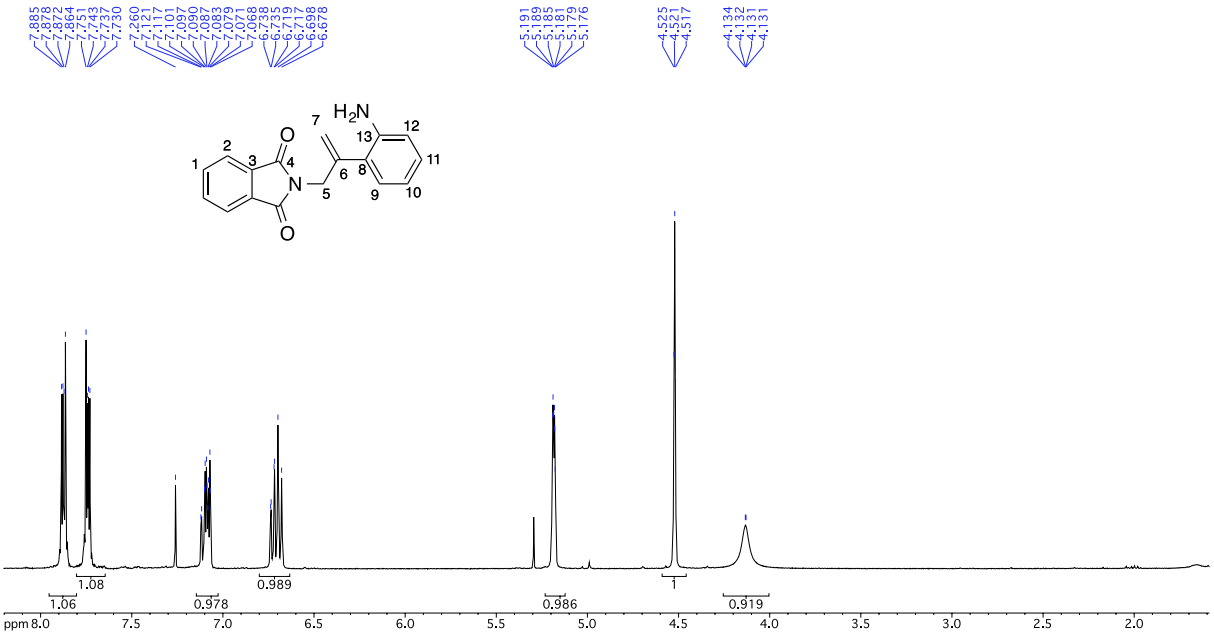


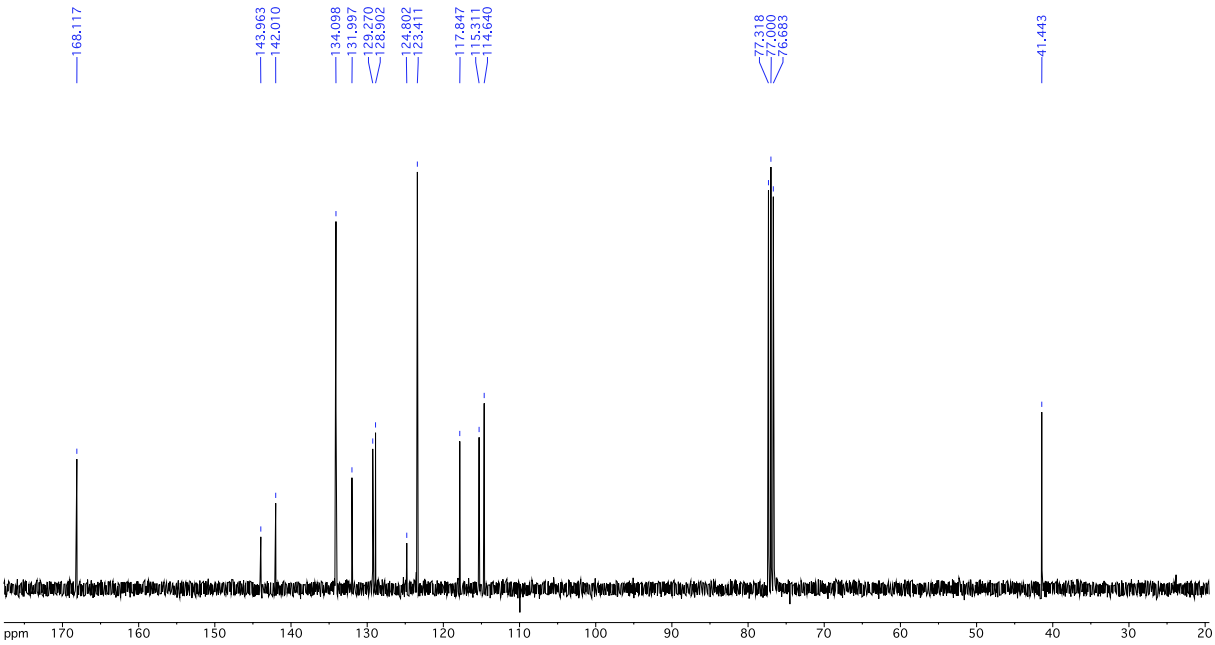
Diethyl 2-[(1*H*-indol-3-yl)methyl]malonate (12b)



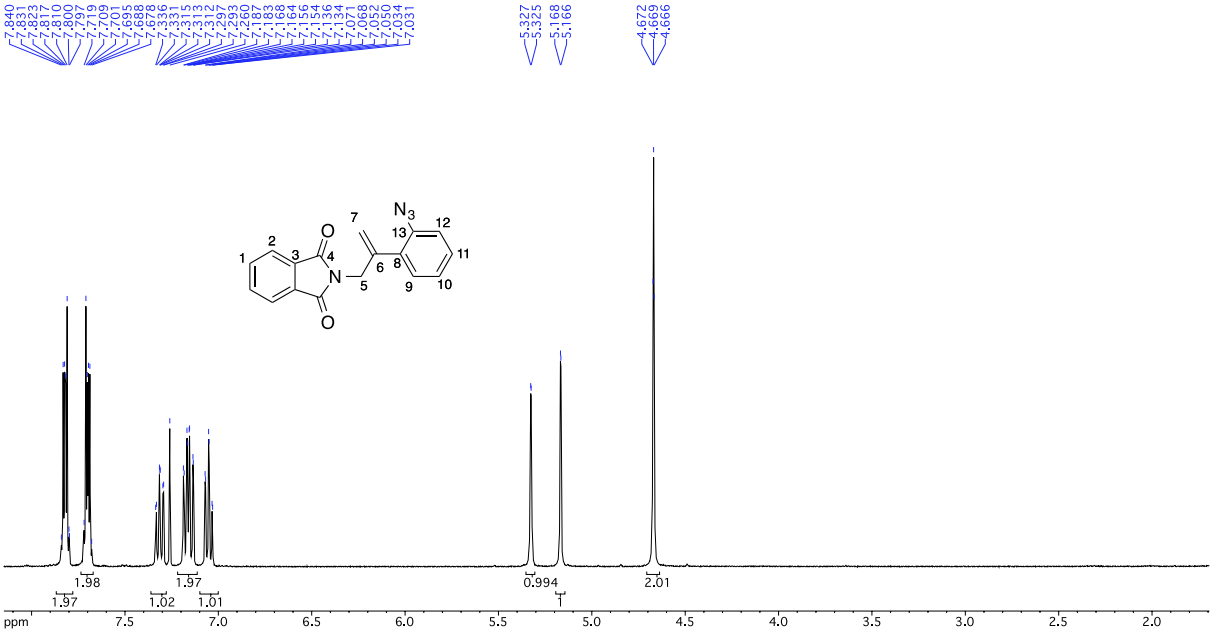


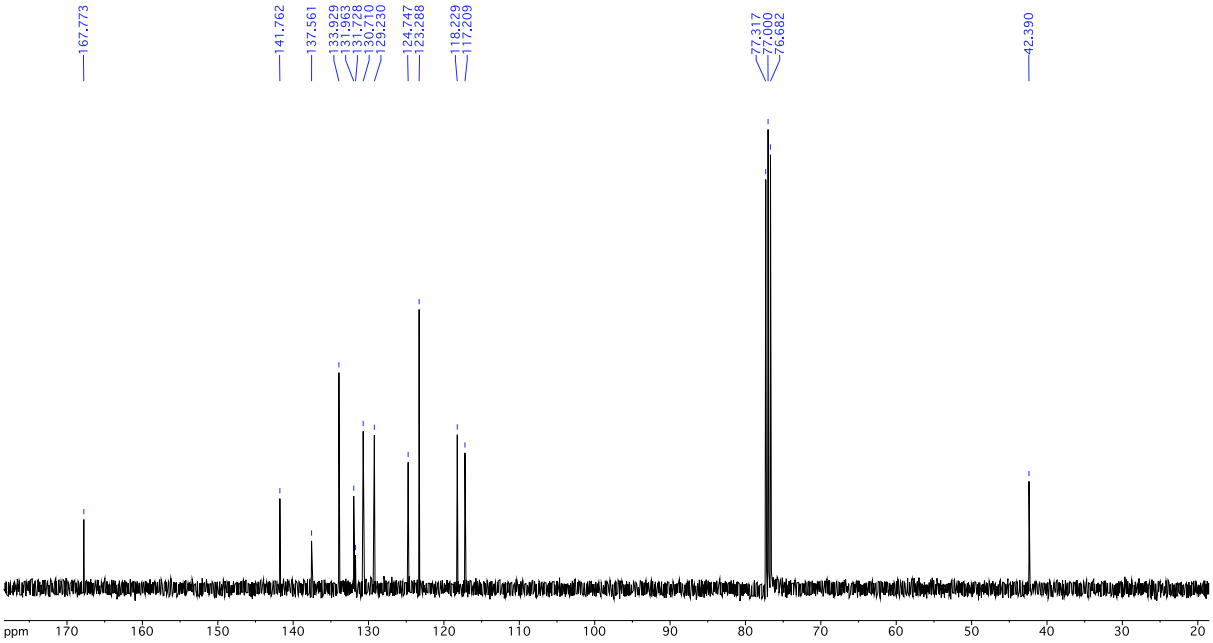
2-[2-(2-Aminophenyl)allyl]isoindoline-1,3-dione (10c)





2-[2-(2-Azidophenyl)allyl]isoindoline-1,3-dione (11c)





2-[(1*H*-Indol-3-yl)methyl]isoindoline-1,3-dione (12c)