Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Highly Stereoselective Intramolecular α-Arylation of Self-Stabilized Non-Racemic Enolates: Synthesis of α-Quaternary α-Amino Acid Derivatives

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CONTENTS

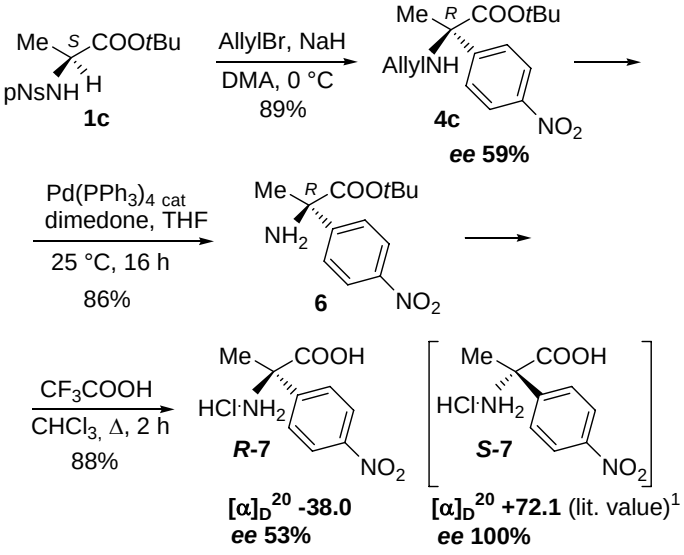
Synthesis of Quaternary α-Amino Acid Derivatives

Materials and Methods.

All reactions were carried out in flame-dried glassware with magnetic stirring. Isolated yields refer to homogeneous materials (TLC, HPLC, NMR). Reagent-grade commercially available reagents and solvents were used; anhydrous solvents were used as purchased. TLC was performed using 0.25 mm silica-gel pre-coated plates and visualized by UV-254 light and CAM staining. Silica-gel (particle size 0.040–0.063 mm) was used for flash column chromatography (FCC) and medium pressure liquid chromatographic (MPLC). Melting points are corrected. Chiral HPLC analyses were performed using CHIRALPAK AD (250/4.6) or CHIRALCEL OD (250/4.6) columns. IR spectra are reported in frequency of absorption (cm^{-1}). $[\alpha]_D$'s were measured at 589 nm, using a (10 cm X 5 ml) cell and *c* is in g/100 ml. NMR spectra were recorded at: 300.13 MHz for ^1H and 75.00 MHz for ^{13}C; TMS was used as external reference; δ are in ppm and *J* are in Hz.

Discussion of Migration Stereochemical Outcome

The stereochemical outcome of the aryl migration was determined by transforming the α-quaternary alanine derivative **4c** into the corresponding α-amino acid ***R*-7** (Scheme 1): **4c** was *N*-deallylated and the resulting α-amino *t*-butyl ester **6** was then reacted with trifluoroacetic acid to give ***R*-7**. The comparison with ***S*-7** showed that 4-nitrophenyl group preferentially rearranges to give the retention product, notwithstanding this step occurs with inversion of absolute configuration.

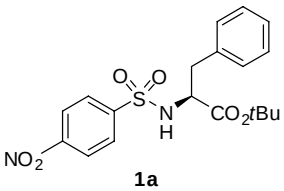


Scheme 1. Synthesis of α-quaternary α-amino acid ***R*-7**.[1]

1 Literature for enantiomer ***S*-7**: (*a*) F. A. Davis, S. Lee, H. Zhang and D. L. Fanelli, *J. Org. Chem.*, 2000, **65**, 8704; (*b*) L. Ferron, F. Guillen, S. Coste, G. Coquerel and J.-C. Plaquevent, *Chirality*, 2006, **18**, 662.

Synthesis of 2-(4-nitrophenylsulphonamido)carboxylic esters 1. General Procedure

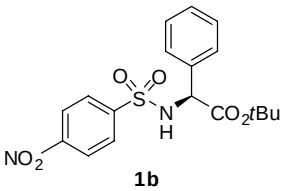
To a suspension of the α-amino acid *tert*-butyl ester hydrochloride (10 mmol) in dry dichloromethane (40 mL), DIPEA (21 mmol) was added dropwise (10 min) at 25 °C. The reaction mixture was stirred for further 10 min, then cooled to 0 °C, and (4-nitrobenzene)sulphonyl chloride (10 mmol) was added dropwise (10 min). The resulting solution was stirred until completion (TLC control), then was diluted with dichloromethane (20 mL), washed with saturated NH_4Cl solution (2×15 mL), saturated $NaHCO_3$ solution (2×15 mL) and brine (20 mL), dried over $MgSO_4$, and filtered. After evaporation of the solvent under vacuum (RV), the crude was purified by FCC to afford sulphonamides **1**. Starting material, product, yield, chromatographic eluant, physical and analytical data are as follows.



1a

(*S*)-*tert*-Butyl 2-(4-nitrophenylsulphonamido)-3-phenylpropanoate (1a)

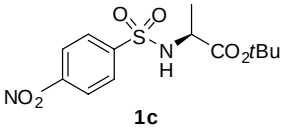
L-Phenylalanine *tert*-butyl ester hydrochloride, 2.58 g; sulphonamide **1a** (4.02 g, 99%, 2 h); FCC - AcOEt/hexane (1:6); white solid, mp 79-81°C, $[\alpha]_D^{20}$ = +5.74 (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, 2H, *J* = 8.7), 7.87 (d, 2H, *J* = 8.7), 7.22-7.20 (m, 3H), 7.11-7.08 (m, 2H), 5.35 (d, 1H, *J* = 9.4), 4.16-4.09 (m, 1H), 3.09-2.92 (m, 2H), 1.28 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7 (CO), 149.9 ($C_{Ar}NO_2$), 145.7 ($C_{Ar}SO_2$), 135.1 ($C_{Ar}CH_2$), 129.5, 128.5, 128.3, 127.3, 124.1 (9 CH_{Ar}), 83.3 ($C_{t\mathrm{Bu}}$), 57.4 (CH*N*), 39.4 (CH_2Ph), 27.7 (3 $CH_{3\text{-}t\mathrm{Bu}}$). IR (nujol) 3297, 1754, 1549, 1365, 1342, 1302, 1261, 1172, 1154, 1089, 1066, 949, 856, 835, 746 cm^{-1}. Anal. Calcd. for $C_{19}H_{22}N_2O_6S$: C, 56.15; H, 5.46; N, 6.89. Found: C, 56.18; H, 5.49; N, 6.85.



1b

(*S*)-*tert*-Butyl 2-(4-nitrophenylsulphonamido)-2-phenylacetate (1b).

L-Phenylglycine *tert*-butyl ester hydrochloride, 2.44 g; sulphonamide **1b** (3.68 g, 94%, 2 h); FCC - AcOEt/hexane (1:8); white solid, mp 131-132°C, $[\alpha]_D^{20}$ = -68.3 (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, 2H, *J* = 8.7), 7.79 (d, 2H, *J* = 8.7), 7.25-7.14 (m, 5H), 5.91 (d, 1H, *J* = 7.3), 5.03 (d, 1H, *J* = 7.3), 1.28 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7 (CO), 149.8 ($C_{Ar}NO_2$), 146.3 ($C_{Ar}SO_2$), 135.2 ($C_{Ar}CH$), 128.7, 128.6, 128.3, 127.1, 123.8 (9 CH_{Ar}), 83.7 ($C_{t\mathrm{Bu}}$), 60.0 (CH*N*), 27.6 (3 $CH_{3\text{-}t\mathrm{Bu}}$). IR (nujol) 3276, 1719, 1529, 1354, 1308, 1263, 1172, 1151, 1089, 1066, 931, 856, 835, 742 cm^{-1}. Anal. Calcd. for $C_{18}H_{20}N_2O_6S$: C, 55.09; H, 5.17; N, 7.14. Found: C, 55.03; H, 5.14; N, 7.10.

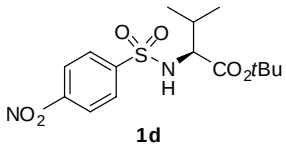


1c

(*S*)-*tert*-Butyl 2-(4-nitrophenylsulphonamido)propanoate (1c).

L-Alanine *tert*-butyl ester hydrochloride, 1.81 g; sulphonamide **1c** (3.26 g, 99%, 2 h); FCC - AcOEt/hexane (1:8); white solid, mp 75-76°C, $[\alpha]_D^{20}$ = +26.8 (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (d, 2H, *J* = 8.7), 8.03 (d, 2H, *J* = 8.7), 5.37 (d, 1H, *J* = 8.6), 3.98-3.89 (m, 1H), 1.38 (d, 3H, *J* = 7.1), 1.30 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3 (CO), 150.5 ($C_{Ar}NO_2$), 146.6 ($C_{Ar}SO_2$), 128.9,

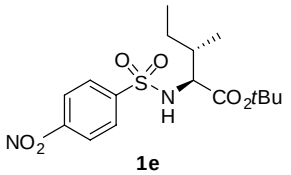
124.7 (4 CH_{Ar}), 83.4 (C_{tBu}), 52.6 (CH*N*), 28.1 (3 $CH_{3\text{-}tBu}$), 20.3 (CH_3*CH*). IR (nujol) 3264, 1722, 1523, 1350, 1309, 1226, 1180, 1160, 1130, 1089, 859, 739 cm^{-1}. Anal. Calcd. for $C_{13}H_{18}N_2O_6S$: C, 47.23; H, 5.49; N, 8.48. Found: C, 47.26; H, 5.49; N, 8.52.



1d

(*S*)-*tert*-Butyl 3-methyl-2-(4-nitrophenylsulphonamido)butanoate (1d).

L-Valine *tert*-butyl ester hydrochloride, 2.10 g; sulphonamide **1d** (3.44 g, 96%, 2 h); FCC - AcOEt/hexane (1:8); white solid, mp 94-95°C, $[\alpha]_D^{20}$ = +54.1 (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, 2H, *J* = 9.0), 8.03 (d, 2H, *J* = 9.0), 5.38 (d, 1H, *J* = 9.9), 3.68 (dd, 1H, *J* = 9.9, 4.4), 2.13-2.02 (m, 1H), 1.22 (s, 9H), 0.98 (d, 3H, *J* = 6.8), 0.83 (d, 3H, *J* = 6.8). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.9 (CO), 150.0 (C_{Ar}*NO*$_2$), 145.9 (C_{Ar}*SO*$_2$), 128.6, 124.1 (4 CH_{Ar}), 82.7 (C_{tBu}), 61.5 (CH*N*), 31.5 (CH_{iPr}), 27.6 (3 $CH_{3\text{-}tBu}$), 18.9, 17.0 (2 $CH_{3\text{-}iPr}$). IR (nujol) 3301, 1721, 1698, 1524, 1363, 1347, 1310, 1248, 1182, 1158, 1081, 913, 856, 790, 739, 684 cm^{-1}. Anal. Calcd. for $C_{15}H_{22}N_2O_6S$: C, 50.27; H, 6.19; N, 7.82. Found: C, 50.31; H, 6.23; N, 7.79.



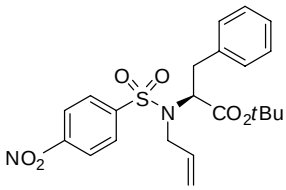
1e

(*2S,3S*)-*tert*-Butyl 3-methyl-2-(4-nitrophenylsulphonamido)pentanoate (1e).

L-Isoleucine *tert*-butyl ester hydrochloride, 2.24 g; sulphonamide **1e** (3.39 g, 91%, 2 h); FCC - AcOEt/hexane (1:9); white solid, mp 71-73°C, $[\alpha]_D^{20}$ = +51.0 (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, 2H, *J* = 8.7), 8.02 (d, 2H, *J* = 8.7), 5.37 (d, 1H, *J* = 9.8), 3.73 (dd, 1H, *J* = 9.8, 4.9), 1.84-1.76 (m, 1H), 1.40-1.27 (m, 1H), 1.23 (s, 9H), 1.13-1.08 (m, 1H), 0.94 (d, 3H, *J* = 6.8), 0.88 (t, 3H, *J* = 7.4). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.9 (CO), 150.1 (C_{Ar}*NO*$_2$), 145.9 (C_{Ar}*SO*$_2$), 128.6, 124.2 (4 CH_{Ar}), 82.9 (C_{tBu}), 60.9 (CH*N*), 38.6 (CH_{sBu}), 27.7 (3 $CH_{3\text{-}tBu}$), 24.6 (CH_2*CH*$_3$), 15.5 (CH_3*CH*), 11.5 (CH_3*CH*$_2$). IR (nujol) 3285, 2970, 2935, 2878, 1729, 1607, 1531, 1457, 1350, 1309, 1253, 1164, 1138, 1092, 915, 855, 789, 736, 686 cm^{-1}. Anal. Calcd. for $C_{16}H_{24}N_2O_6S$: C, 51.60; H, 6.50; N, 7.52. Found: C, 51.64; H, 6.52; N, 7.49.

Synthesis of Quaternary α-Amino Acid Derivatives

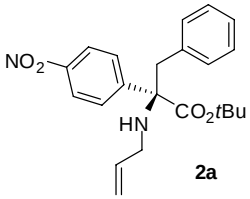
Synthesis of (*S*)-*tert*-butyl 2-(*N*-allyl-4-nitrophenylsulphonamido)-3-phenylpropanoate (3a) under SL-PTC conditions



3a

In a screw cap vial, a heterogeneous mixture of starting sulphonamido ester **1a** (4.06 g, 10 mmol), TEBA (0.23 g, 1 mmol), and allyl bromide (3.63 g, 30 mmol) solution in anhydrous acetonitrile (30 mL) and anhydrous potassium carbonate (2.21 g, 16 mmol) was vigorously stirred at 25 °C until completion (13 h, TLC analysis). The crude was then diluted with AcOEt (30 mL) and filtered through a celite pad. After evaporation of the solvent under reduced pressure (RV), purification of the crude by FCC - AcOEt/hexane (1:10) - on silica gel gave the *N*-alkyl sulphonamido ester **3a** (4.11 g, 92%); $[\alpha]_D^{20}$ = -11.3 (*c* 0.4, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, 2H, *J* = 9.0), 7.74 (d, 2H, *J* = 8.7), 7.28-7.20 (m, 5H), 5.73-5.64 (m, 1H), 5.23 (dd, 1H, *J* = 17.1, 1.2), 5.11 (dd, 1H, *J* = 10.2, 1.2), 4.81 (dd, 1H, *J* = 8.7, 6.9), 4.02 (ddt, 1H, *J* = 16.5, 6.3, 1.5), 3.87 (ddt, 1H, *J* = 16.5, 6.9, 1.5), 3.32 (dd, 1H, *J* = 14.1, 6.6), 2.97 (dd, 1H, *J* = 14.4, 8.7), 1.33 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9 (CO), 149.6 ($C_{Ar}NO_2$), 146.2 ($C_{Ar}SO_2$), 135.2 ($C_{Ar}CH_2$), 134.0 (CH_{All}), 129.1, 128.5, 128.4, 126.8, 123.7 (9 CH_{Ar}), 118.6 ($CH_{2\text{-}All}$), 82.5 ($C_{t\text{Bu}}$), 62.2 (CH*N*), 48.3 ($CH_{2\text{-}All}$), 36.6 (CH_2Ph), 27.6 (3 $CH_{3\text{-}t\text{Bu}}$). IR (neat) 3299, 3030, 1731, 1530, 1349, 1164, 930 cm^{-1}. Anal. Calcd. for $C_{22}H_{26}N_2O_6S$: C, 59.18; H, 5.87; N, 6.27. Found: C, 59.22; H, 5.89; N, 6.23.

Rearrangement of *N*-allyl-4-nitrophenylsulphonamido ester 3a



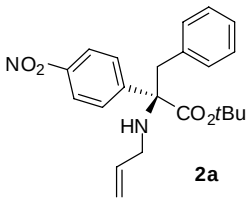
2a

In a flame-dried round bottomed flask, 60% sodium hydride (120 mg, 3 mmol) was rinsed with anhydrous *n*-pentane and, after cooling at 0°C, a solution of *N*-alkyl-sulphonamido ester **3a** (447 mg, 1 mmol) in anhydrous *N,N*-dimethylacetamide (7 mL) was added under nitrogen atmosphere. The reaction mixture was stirred at 0 °C until completion (2 h, TLC analysis), then was quenched with saturated NH_4Cl solution (1 mL). After extraction with AcOEt (2 X 10 mL) and evaporation of the solvent under reduced pressure (RV), the crude was purified by FCC - AcOEt/hexane (1:15) - on silica gel. Product **2a** (333 mg, 87%) was isolated as yellow oil, $[\alpha]_D^{20}$ = +6.0 (*c* 1, $CHCl_3$), *ee* 62% [CHIRALPAK AD, hexane/*i*PrOH (95:5), flow rate 1 mL/min, P l8 bar, t_1 5.08, t_2 6.19]. For physical and spectroscopic data see the corresponding section in**'One-pot' alkylation/rearrangement**.

Synthesis of Quaternary α-Amino Acid Derivatives

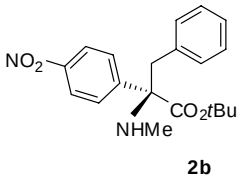
'One-pot' alkylation/rearrangement of 4-nitrophenylsulphonamido esters 1: General Procedure

In a flame-dried round bottomed flask, 60% sodium hydride (120 mg, 3 mmol) was rinsed with anhydrous *n*-pentane, under nitrogen. After cooling at 0 °C, a solution of sulphonamido ester **1** (1 mmol) in anhydrous DMA (3 mL) was added dropwise. The reaction mixture was stirred until hydrogen evolution ended (ca. 30 min), then a solution of the alkylating agent RX (3 mmol) in anhydrous DMA (1 mL) was added by syringe. The resulting solution was stirred at 0 °C until completion (TLC analysis), then it was quenched with saturated NH_4Cl solution (1 mL). After dilution with AcOEt (20 mL) and water (20 mL), the organic phase was separated, dried on $MgSO_4$, evaporated under reduced pressure (RV), and the crude was purified by FCC on silica gel.



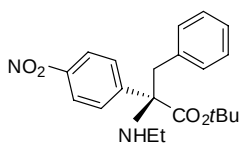
2a

(*R*)-*tert*-Butyl 2-(allylamino)-2-(4-nitrophenyl)-3-phenylpropanoate (2a). Sulphonamide **1a**, 406 mg; allyl bromide, 363 mg; **2a** (333 mg, 87%, 5 h); FCC - AcOEt/hexane (1:15); yellow oil, $[\alpha]_D^{20}$ = +13.5 (*c* 0.3, $CHCl_3$), *ee* 62% [CHIRALPAK AD, hexane/*i*PrOH (95:5), flow rate 1 mL/min, P 18 bar, t_1 5.08, t_2 6.19]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, 2H, *J* = 8.7), 7.56 (d, 2H, *J* = 8.7), 7.21-7.18 (m, 3H), 6.97-6.93 (m, 2H), 6.03-5.92 (m, 1H), 5.30 (dd, 1H, *J* = 16.9, 1.2), 5.17 (d, 1H, *J* = 10.3), 3.38 (s, 2H), 3.28 (dd, 1H, *J* = 13.7, 5.4), 3.16 (dd, 1H, *J* = 13.7, 5.7), 1.97 (br, 1H), 1.48 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1 (CO), 148.8 (C_{Ar}), 147.0 ($C_{Ar}NO_2$), 136.1 (CH_{All}), 135.5 (C_{Ar}), 130.5, 128.0, 127.9, 126.7, 122.9 (9 CH_{Ar}), 115.9 ($CH_{2\text{-}All}$), 82.4 ($C_{t\text{Bu}}$), 69.7 (C_α), 46.2 (CH_2N), 42.6 (CH_2Ph), 27.9 (3 $CH_{3\text{-}t\text{Bu}}$). IR (neat) 3348, 3084, 3065, 3031, 1725, 1496, 1249, 842, 749 cm^{-1}. Anal. Calcd. for $C_{22}H_{26}N_2O_4$: C, 69.09, H, 6.85; N, 7.32. Found: C, 69.07, H, 6.83; N, 7.30.



2b

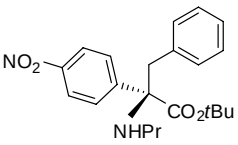
(*R*)-*tert*-Butyl 2-(methylamino)-2-(4-nitrophenyl)-3-phenylpropanoate (2b). Sulphonamide **1a**, 406 mg; methyl iodide, 426 mg; **2b** (342 mg, 96%, 7 h); FCC - AcOEt/hexane (1:6); yellow oil, $[\alpha]_D^{20}$ = +21.4 (*c* 1.5, $CHCl_3$), *ee* 80% [CHIRALPAK AD, hexane/*i*PrOH (8:2), flow rate 0.7 mL/min, P 15 bar, t_1 7.89, t_2 10.18]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, 2H, *J* = 9.0), 7.54 (d, 2H, *J* = 9.0), 7.21-7.19 (m, 3H), 6.97-6.94 (m, 2H), 3.42 (d, 1H, *J* = 13.8), 3.25 (d, 1H, *J* = 13.8), 2.43 (s, 3H), 2.20 (br, 1H), 1.48 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1 (CO), 148.7 (C_{Ar}), 147.0 ($C_{Ar}NO_2$), 135.5 (C_{Ar}), 130.4, 128.0, 127.8, 126.7, 122.9 (9 CH_{Ar}), 82.4 ($C_{t\text{Bu}}$), 70.3 (C_α), 41.3 (CH_2Ph), 30.1 (CH_3N), 27.9 (3 $CH_{3\text{-}t\text{Bu}}$). IR (neat) 3354, 2803, 1943, 1726, 1603, 1520, 1347, 1031, 800 cm^{-1}. Anal. Calcd. for $C_{20}H_{24}N_2O_4$: C, 67.40; H, 6.79; N, 7.86. Found: C, 67.37; H, 6.77; N, 7.82.



2c

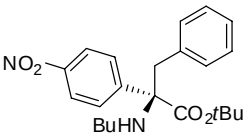
(*R*)-*tert*-Butyl 2-(ethylamino)-2-(4-nitrophenyl)-3-phenylpropanoate (2c). Sulphonamide **1a**, 406 mg; ethyl iodide, 468 mg; **2c** (367 mg, 99%, 5 h); FCC - AcOEt/hexane (1:6); yellow oil, $[\alpha]_D^{20}$ = +12.1(*c* 0.87, $CHCl_3$), *ee* 56% [CHIRALPAK AD, hexane/*i*PrOH (95:5), flow rate 0.7 mL/min, P 12 bar, t_1 7.16, t_2 8.45]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, 2H, *J* = 9.0 Hz), 7.49

(d, 2H, *J* = 9.0 Hz), 7.15-7.12 (m, 3H), 6.90-6.87 (m, 2H), 3.31 (s, 2H), 2.65-2.50 (m, 2H), 1.77 (br, 1H), 1.42 (s, 9H), 1.15 (t, 3H, *J* = 7.0 Hz) . ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.3 (CO), 149.1 (C_{Ar}), 147.0 ($C_{Ar}NO_2$), 135.7 (C_{Ar}), 130.4, 128.0, 127.8, 126.7, 122.9 (9 CH_{Ar}), 82.3 ($C_{t\mathrm{Bu}}$), 70.0 (C_α), 42.0 (CH_2Ph), 37.9 (CH_2N), 27.9 (3 $CH_{3\text{-}t\mathrm{Bu}}$), 15.5 ($CH_3$). IR (neat) 3348, 3076, 3029, 2927, 1730, 1597, 851 cm^{-1}. Anal. Calcd. for $C_{21}H_{26}N_2O_4$: C, 68.09; H, 7.07; N, 7.56. Found: C, 68.13; H, 7.10; N, 7.52.



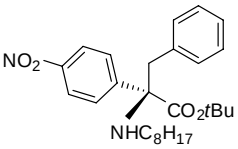
2d

(*R*)-*tert*-Butyl 2-(4-nitrophenyl)-3-phenyl-2-(propylamino)propanoate (2d).
Sulphonamide **1a**, 406 mg; propyl iodide, 510 mg; **2d** (308 mg, 80%, 5 h); FCC - AcOEt/hexane (1:6); yellow oil, $[\alpha]_D^{20}$ = +13.3(*c* 0.91, $CHCl_3$), *ee* 56% [CHIRALPAK AD, hexane/*i*PrOH (95:5), flow rate 0.7 mL/min, P 12 bar, t_1 7.20, t_2 8.49]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, 2H, *J* = 9.0 Hz), 7.48 (d, 2H, *J* = 9.0 Hz), 7.15-7.13 (m, 3H), 6.90-6.88 (m, 2H), 3.31 (s, 2H), 2.60-2.41 (m, 2H), 1.80 (br, 1H), 1.63-1.52 (m, 2H), 1.42 (s, 9H), 0.96 (t, 3H, *J* = 7.4 Hz) . ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4 (CO), 149.2 (C_{Ar}), 146.9 ($C_{Ar}NO_2$), 135.7 (C_{Ar}), 130.5, 128.0, 127.8, 126.7, 122.9 (9 CH_{Ar}), 82.3 ($C_{t\mathrm{Bu}}$), 69.9 (C_α), 45.4 (CH_2Ph), 42.1 (CH_2N), 27.9 (3 $CH_{3\text{-}t\mathrm{Bu}}$), 23.6 ($CH_2CH_3$), 11.8 ($CH_3CH_2$). IR (neat) 3354, 3093, 3033, 2931, 1726, 1574, 843, 715 cm^{-1}. Anal. Calcd. for $C_{22}H_{28}N_2O_4$: C, 68.73; H, 7.34; N, 7.29. Found: C, 68.76; H, 7.36; N, 7.25.



2e

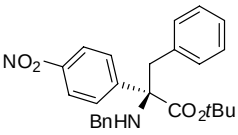
(*R*)-*tert*-Butyl 2-(butylamino)-2-(4-nitrophenyl)-3-phenylpropanoate (2e).
Sulphonamide **1a**, 406 mg; butyl iodide, 552 mg; **2e** (343 mg, 86%, 4 h); FCC - AcOEt/hexane (1:15); yellow oil, $[\alpha]_D^{20}$ = +12.7 (*c* 1, $CHCl_3$), *ee* 62% [CHIRALPAK AD, hexane/*i*PrOH (95:5), flow rate 0.6 mL/min, P 10 bar, t_1 7.41, t_2 8.76]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, 2H, *J* = 9.0), 7.53 (d, 2H, *J* = 9.0), 7.19-7.17 (m, 3H), 6.94-6.93 (m, 2H), 3.35 (s, 2H), 2.66-2.51 (m, 2H), 1.87 (br, 1H), 1.60-1.30 (m, 4H), 1.47 (s, 9H), 0.97 (t, 3H *J* = 7.2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4 (CO), 149.1 (C_{Ar}), 146.8 ($C_{Ar}NO_2$), 135.8 (C_{Ar}), 130.4, 127.9, 127.7, 126.6, 122.7 (9 CH_{Ar}), 82.1 ($C_{t\mathrm{Bu}}$), 69.8 (C_α), 43.1 (CH_2Ph), 42.1, 32.6 (2 CH_2), 27.8 (3 $CH_{3\text{-}t\mathrm{Bu}}$), 20.4 ($CH_2CH_3$), 13.9 ($CH_3CH_2$). IR (neat) 3341, 3087, 3031, 2930, 1725, 1604, 843, 735 cm^{-1}. Anal. Calcd. for $C_{23}H_{30}N_2O_4$: C, 69.32; H, 7.59; N, 7.03. Found: C, 69.29; H, 7.57; N, 7.06.



2f

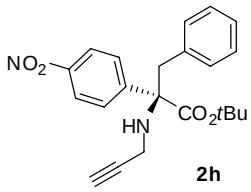
(*R*)-*tert*-Butyl 2-(octylamino)-2-(4-nitrophenyl)-3-phenylpropanoate (2f).
Sulphonamide **1a**, 406 mg; octyl iodide, 720 mg; **2f** (332 mg, 73%, 6 h); FCC - AcOEt/hexane (1:15); yellow oil, $[\alpha]_D^{20}$ = +9.7 (*c* 0.3, $CHCl_3$), *ee* 61% [CHIRALPAK AD, hexane/*i*PrOH (98:2), flow rate 0.7 mL/min, P 11 bar, t_1 6.44, t_2 8.15]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, 2H, *J* = 8.8 Hz), 7.47 (d, 2H, *J* = 8.8 Hz), 7.14-7.12 (m, 3H), 6.88-6.86 (m, 2H), 3.29 (s, 2H), 2.62-2.42 (m, 2H), 1.79 (br, 1H), 1.52-1.27 (m, 21H), 0.88 (t, 3H *J* = 10.3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1 (CO), 149.7 (C_{Ar}), 147.3 ($C_{Ar}NO_2$), 136.1 (C_{Ar}), 130.8, 128.3, 128.1, 127.0, 123.2 (9 CH_{Ar}), 82.3 ($C_{t\mathrm{Bu}}$), 68.1 (C_α), 43.3 (CH_2Ph), 41.8, 31.5, 30.2, 29.2, 28.9(5 CH_2), 27.6 (3 $CH_{3\text{-}t\mathrm{Bu}}$), 27.0, 22.3 (2 CH_2), 13.7 (CH_3CH_2). IR (neat) 3368, 3063, 3031, 2928, 1726, 1521, 842, 737, 702 cm^{-1}. Anal. Calcd. for $C_{27}H_{38}N_2O_4$: C, 71.33; H, 8.43; N, 6.16. Found: C, 71.38; H, 8.45; N, 6.12.

Synthesis of Quaternary α-Amino Acid Derivatives



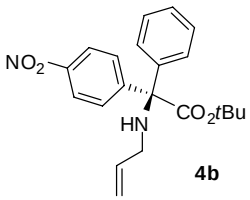
2g

(*R*)-*tert*-Butyl 2-(benzylamino)-2-(4-nitrophenyl)-3-phenylpropanoate (2g). Sulphonamide **1a**, 406 mg**;** benzyl bromide, 513 mg; **2g** (324 mg, 75%, 5 h); FCC - AcOEt/hexane (1:15); yellow oil, $[\alpha]_D^{20}$ = +6.7 (*c* 1.2, $CHCl_3$), *ee* 51% [CHIRALPAK AD, hexane/*i*PrOH (95:5), flow rate 0.7 mL/min, P 12 bar, t_1 9.26, t_2 10.24]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, 2H, *J* = 8.9 Hz), 7.56 (d, 2H, *J* = 8.9 Hz), 7.38-7.29 (m, 5H), 7.18-7.13 (m, 3H), 6.95-6.92 (m, 2H), 3.83 (d, 1H, *J* = 12.3 Hz), 3.66 (d, 1H, *J* = 12.3 Hz), 3.45 (d, 1H, *J* = 13.8), 3.37 (d, 1H, *J* = 13.8), 2.24 (br, 1H), 1.47 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7 (CO), 149.2 (C_{Ar}), 147.4 ($C_{Ar}NO_2$), 140.2 (C_{Ar}), 136.0 (C_{Ar}), 130.9, 129.0, 128.8, 128.4, 128.3, 127.7, 127.3, 123.4 (14 CH_{Ar}), 82.9 ($C_{t\text{Bu}}$), 70.4 (C_α), 48.3 (NCH_2Ph), 42.9 (CH_2Ph), 28.5 (3 $CH_{3\text{-}t\text{Bu}}$). IR (neat) 3343, 3030, 1725, 1604, 1369, 843, 734 cm^{-1}. Anal. Calcd. for $C_{26}H_{28}N_2O_4$: C, 72.20; H, 6.53; N, 6.48. Found: C, 72.23; H, 6.55; N, 6.45.



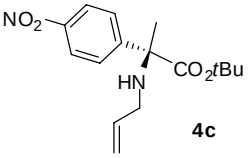
2h

(*R*)-*tert*-Butyl 2-(4-nitrophenyl)-3-phenyl-2-(prop-2-ynylamino)propanoate (2h). Sulphonamide **1a**, 406 mg; propargyl bromide, 357 mg; **2h** (335 mg, 88%, 8 h); FCC - AcOEt/hexane (1:15); yellow oil, $[\alpha]_D^{20}$ = +3.7 (*c* 0.2, $CHCl_3$), *ee* 80% [CHIRALPAK AD, hexane/*i*PrOH (95:5), flow rate 0.8 mL/min, P 14 bar, t_1 10.48, t_2 12.26]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, 2H, *J* = 9.0), 7.62 (d, 2H, *J* = 9.0), 7.24-7.22 (m, 3H), 7.05-7.01 (m, 2H), 3.50-3.29 (m, 4H), 2.28 (t, 1H, *J* = 2.7), 1.48 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4 (CO), 147.7 ($C_{Ar}NO_2$), 147.0, 135.0 (2 C_{Ar}), 130.3, 127.9, 127.8, 126.8, 123.0 (9 CH_{Ar}), 82.8 ($C_{propargyl}$), 81.3 ($C_{t\text{Bu}}$), 71.5 ($CH_{propargyl}$), 69.6 (C_α), 42.8 (CH_2Ph), 33.2 (CH_2N), 27.8 (3 $CH_{3\text{-}t\text{Bu}}$). IR (neat) 3342, 3296, 2130, 1723, 1604, 1523, 856, 735 cm^{-1}. Anal. Calcd. for $C_{22}H_{24}N_2O_4$: C, 69.46; H, 6.36; N, 7.36. Found: C, 69.44; H, 6.32; N, 7.40.



4b

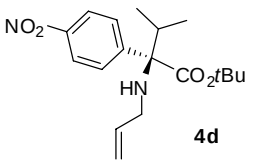
(*R*)-*tert*-Butyl 2-(allylamino)-2-(4-nitrophenyl)-2-phenylacetate (4b). Sulphonamide **1b**, 392 mg; allyl bromide, 363 mg; **4b** (339 mg, 92%, 26 h); FCC - AcOEt/hexane (1:12); yellow oil, $[\alpha]_D^{20}$ = +12.5 (*c* 1, $CHCl_3$), *ee* 50% [CHIRALCEL OD, hexane/*i*PrOH (99:1), flow rate 0.7 mL/min, P 11 bar, t_1 11.96, t_2 12.88]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, 2H, *J* = 9.0), 7.75 (d, 2H, *J* = 9.0), 7.37-7.25 (m, 5H), 5.99-5.86 (m, 1H), 5.23 (dd, 1H, *J* = 17.1, 1.5), 5.09 (dd, 1H, *J* = 10.2, 1.5), 2.90-2.87 (m, 2H), 2.43 (br, 1H), 1.40 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8 (CO), 149.5 ($C_{Ar}NO_2$), 147.3, 141.4 (2 C_{Ar}), 136.6 (CH_{All}), 130.0, 128.7, 128.2, 128.1, 123.3 (9 CH_{Ar}), 116.2 ($CH_{2\text{-}All}$), 83.3 ($C_{t\text{Bu}}$), 73.1 (C_α), 47.1 (CH_2N), 28.2 (3 $CH_{3\text{-}t\text{Bu}}$). IR (neat) 3331, 2979, 2932, 1726, 1644, 1604, 1520, 1368, 1348, 1246, 1153, 991, 918, 852, 733, 703 cm^{-1}. Anal. Calcd. for $C_{21}H_{24}N_2O_4$: C, 68.46; H, 6.57; N, 7.60. Found: C, 68.41; H, 6.55; N, 7.63.



4c

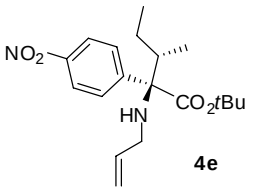
(*R*)-*tert*-Butyl 2-(allylamino)-2-(4-nitrophenyl)propanoate (4c). Sulphonamide **1c**, 330 mg; allyl bromide, 363 mg; **4c** (273 mg, 89%, 6 h); FCC - AcOEt/hexane (1:7); yellow oil, $[\alpha]_D^{20}$ = -2.0 (*c* 1, $CHCl_3$), *ee* 59% [CHIRALPAK AD, hexane/*i*PrOH (95:5), flow rate 1 mL/min, P 17 bar, t_1 5.49, t_2 6.18]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, 2H, *J* = 8.7), 7.73 (d, 2H, *J* = 8.7), 6.04-5.93 (m, 1H), 5.28 (dd, 1H, *J* = 17.1, 1.5), 5.16 (dd, 1H, *J* = 10.2, 1.2), 3,23-3,11 (m, 2H), 2.05 (br, 1H), 1.70 (s, 3H), 1.48 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0 (CO), 151.1 (C_{Ar}), 147.0 ($C_{Ar}NO_2$), 136.4 (CH_{All}), 126.9, 123.3 (4 CH_{Ar}), 115.8 ($CH_{2\text{-}All}$), 82.0 ($C_{t\text{Bu}}$), 65.6 (C_α), 46.5 (CH_2N), 27.7 (3

$CH_{3\text{-}t\text{Bu}}$), 24.3 (CH_3). IR (neat) 3346, 2979, 2928, 1727, 1604, 1522, 1456, 1369, 1349, 1253, 1145, 1111, 855 cm^{-1}. Anal. Calcd. for $C_{16}H_{22}N_2O_4$: C, 62.73; H, 7.24; N, 9.14. Found: C, 62.76; H, 7.26; N, 9.11.



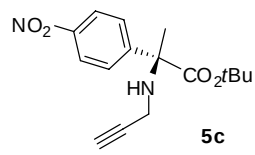
4d

(*R*)-*tert*-Butyl 2-(allylamino)-3-methyl-2-(4-nitrophenyl)butanoate (4d).
Sulphonamide **1d**, 358 mg; allyl bromide, 363 mg (331 mg, 99%, 24 h); FCC - AcOEt/hexane (1:12); yellow oil, $[\alpha]_D^{20}$ = -60.1 (*c* 1.1, $CHCl_3$), *ee* 95% [CHIRALPAK AD, hexane/*i*PrOH (9:1), flow rate 0.8 mL/min, P 14 bar, t_1 5.04, t_2 6.61]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, 2H, *J* = 9.0), 7.78 (d, 2H, *J* = 9.0), 6.03-5.91 (m, 1H), 5.29 (d, 1H, *J* = 17.4), 5.16 (dd, 1H, *J* = 10.2, 1.5), 3.12 (dd, 1H, *J* = 13.5, 5.4), 2.98 (dd, 1H, *J* = 14.0, 4.2), 2.43-2.40 (m, 1H), 1.70 (br, 1H), 1.56 (s, 9H), 0.90 (d, 3H, *J* = 5.7), 0.80 (d, 3H, *J* = 6.9). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0 (CO), 146.8 (C_{Ar}), 145.1 ($C_{Ar}NO_2$), 136.4 (CH_{All}), 130.2, 121.9 (4 CH_{Ar}), 115.3 ($CH_{2\text{-}All}$), 81.8 ($C_{t\text{Bu}}$), 72.6 (C_α), 46.5 (CH_2N), 35.6 ($CH_{i\text{Pr}}$), 28.0 (3 $CH_{3\text{-}t\text{Bu}}$), 18.4, 16.7 (2 $CH_{3\text{-}i\text{Pr}}$). IR (neat) 3341, 2974, 2934, 1723, 1644, 1520, 1349, 1244, 1160, 885 cm^{-1}. Anal. Calcd. for $C_{18}H_{26}N_2O_4$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.69; H, 7.86; N, 8.35.



4e

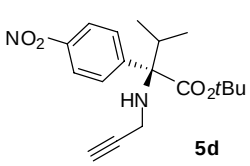
(2*R*,3*S*)-*tert*-Butyl 2-(allylamino)-3-methyl-2-(4-nitrophenyl)pentanoate (4e).
Sulphonamide **1e**, 372 mg; allyl bromide, 363 mg; **4e** (345 mg, 99%, 26h); FCC - AcOEt/hexane (1:8); yellow oil, $[\alpha]_D^{20}$ = -53.2 (*c* 1.2, $CHCl_3$), *de* 96% [CHIRALCEL OD, hexane/*i*PrOH (98:2), flow rate 0.8 mL/min, P 13 bar, t_1 5.04, t_2 5.63]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, 2H, *J* = 8.7), 7.74 (d, 2H, *J* = 9.0), 5.97-5.86 (m, 1H), 5.25 (d, 1H, *J* = 17.1), 5.09 (d, 1H, *J* = 10.2), 3.05 (dd, 1H, *J* = 13.8, 5.7), 2.94 (dd, 1H, *J* = 13.8, 4.5), 2.06-2.02 (m, 1H), 1.88-1.81 (m, 1H), 1.71 (br, 1H), 1.52 (s, 9H), 0.87-0.80 (m, 6H), 0.46-0.32 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1 (CO), 146.8 (C_{Ar}), 145.5 ($C_{Ar}NO_2$), 136.4 (CH_{All}), 130.0, 122.0 (4 CH_{Ar}), 115.4 ($CH_{2\text{-}All}$), 81.8 ($C_{t\text{Bu}}$), 72.9 (C_α), 46.6 (CH_2N), 43.0 ($CH_{s\text{Bu}}$), 28.0 (3 $CH_{3\text{-}t\text{Bu}}$), 23.5 (CH_2CH_3), 14.8 (CH_3CH), 12.2 (CH_3CH_2). IR (neat) 3338, 1743, 1639, 1525, 1298, 1217, 1106, 988, 889 cm^{-1}. Anal. Calcd. for $C_{19}H_{28}N_2O_4$: C, 65.49; H, 8.10; N, 8.04. Found C, 65.53; H, 8.14; N, 8.00.



5c

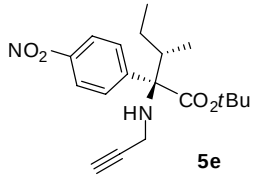
(*R*)-*tert*-Butyl 2-(4-nitrophenyl)-2-(prop-2-ynylamino)propanoate (5c).
Sulphonamide **1c**, 330 mg; propargyl bromide, 357 mg; **5c** (283 mg, 93%, 5h); FCC - AcOEt/hexane (1:7); yellow oil, $[\alpha]_D^{20}$ = -15.2 (*c* 1, $CHCl_3$), *ee* 68% [CHIRALPAK AD, hexane/*i*PrOH (9:1), flow rate 0.8 mL/min, P 14 bar, t_1 8.31, t_2 13.53]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, 2H, *J* = 9.0), 7.73 (d, 2H, *J* = 9.0), 3.46 (dd, 1H, *J* = 16.5, 2.4), 3.35 (dd, 1H, *J* = 16.2, 2.4), 2.26 (t, 1H, *J* = 2.4), 1.72 (s, 3H), 1.48 (s, 9H); NH signal is not visible. ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6 (CO), 150.4 ($C_{Ar}NO_2$), 147.1 (C_{Ar}), 126.9, 123.4 (4 CH_{Ar}), 82.4 ($C_{propargyl}$), 81.8 ($C_{t\text{Bu}}$), 71.6 ($CH_{propargyl}$), 65.4 (C_α), 33.1 ($CH_{2\text{-}propargyl}$), 27.7 (3 $CH_{3\text{-}t\text{Bu}}$), 23.8 (CH_3). IR (neat) 3299, 2980, 2935, 1724, 1605, 1520, 1477, 1457, 1369, 1348, 1253, 1164, 1128, 1087, 1014, 856, 845, 739, 700 cm^{-1}. Anal. Calcd. for $C_{16}H_{20}N_2O_4$: C, 63.14; H, 6.62; N, 9.20. Found: C, 63.18; H, 6.65; N, 9.17.

Synthesis of Quaternary α-Amino Acid Derivatives



5d

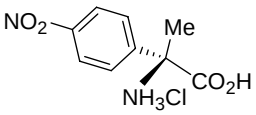
(*R*)-*tert*-Butyl 3-methyl-2-(4-nitrophenyl)-2-(prop-2-ynylamino)butanoate (5d). Sulphonamide **1d**, 358 mg; propargyl bromide, 357 mg; **5d** (326 mg, 98%, 20 h); FCC - AcOEt/hexane (1:9); yellow oil, $[\alpha]_D^{20}$= -77.0 (*c* 1, $CHCl_3$), *ee* 96% [CHIRALPAK AD, hexane/*i*PrOH (9:1), flow rate 0.8 mL/min, P 14 bar, t_1 5.649, t_2 6.288]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, 2H, *J* = 9.0), 7.81 (d, 2H, *J* = 9.0), 3.32 (dd, 1H, *J* = 16.2, 2.4), 3.17 (dd, 1H, *J* = 16.2, 2.4), 2.49-2.40 (m, 1H), 2.28 (t, 1H, *J* = 2.4), 1.58 (s, 9H), 0.93 (d, 3H, *J* = 6.8), 0.82 (d, 3H, *J* = 6.9); NH signal is not visible. ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5 (CO), 147.0 (C_{Ar}), 144.5 ($C_{Ar}NO_2$), 130.1, 122.3 (4 C_{Ar}), 82.4 ($C_{propargyl}$), 81.7 (C_{tBu}), 72.8 ($CH_{propargyl}$), 71.3 (C_α), 36.0 (CH_{iPr}), 33.8 ($CH_{2\text{-}propargyl}$), 28.0 (3 $CH_{3\text{-}tBu}$), 18.2 , 16.9 ($CH_{2\text{-}iPr}$). IR (neat) 3303, 2974, 2934, 1720, 1604, 1522, 1459, 1369, 1350, 1249, 1160, 1136, 1108, 1015, 856, 822, 735 cm^{-1}. Anal. Calcd. for $C_{18}H_{24}N_2O_4$: C, 65.04; H, 7.28; N, 8.43. Found: C, 65.00; H, 7.26; N, 8.47.



5e

(2*R*,3*S*)-*tert*-butyl 3-methyl-2-(4-nitrophenyl)-2-(prop-2-ynylamino)pentanoate (5e). Sulphonamide **1e**, 372 mg; propargyl bromide, 357 mg; **5e** (336 g, 97%, 26 h); FCC - AcOEt/hexane (1:10); yellow oil, $[\alpha]_D^{20}$ = -61.7 (*c* 1, $CHCl_3$) *de* 98% [CHIRALCEL OD, hexane/*i*PrOH (98:2), flow rate 0.8 mL/min, P 13 bar, t_1 7.156, t_2 7.613]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12-8.09 (m, 2H), 7.71-7.68 (m, 2H), 3.19 (dd, 1H, *J* = 16.1, 2.4), 3.03 (dd, 1H, *J* = 16.1, 2.5), 2.19 (t, 1H, *J* = 2.2), 1.98 (br, 1H), 1.97-1.92 (m, 1H), 1.65-1.75 (m, 1H), 1.46 (s, 9H), 0.81-0.74 (m, 6H), 0.45-0.34 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0 (CO), 147.4 (C_{Ar}), 145.3 ($C_{Ar}NO_2$), 130.4, 122.7 (4 C_{Ar}), 82.8 ($C_{propargyl}$), 82.2 (C_{tBu}), 73.5 ($CH_{propargyl}$), 71.7 (C_α), 43.7 (CH_{sBu}), 34.2 ($CH_{2\text{-}propargyl}$), 28.4 (3 $CH_{3\text{-}tBu}$), 24.1 (CH_2CH_3), 15.0 (CH_3CH), 12.7 (CH_3CH_2). IR (neat) 3336, 2971, 2944, 1715, 1612, 1525, 1451, 1369, 1355, 1237, 1164, 1131, 1111, 1010, 851, 828, 731 cm^{-1}. Anal. Calcd. for $C_{19}H_{26}N_2O_4$: C, 65.87; H, 7.56; N, 8.09. Found: C, 65.90; H, 7.59; N, 8.05.

Synthesis of (*R*)-2-amino-2-(4-nitrophenyl)propanoic acid (*R*-7)

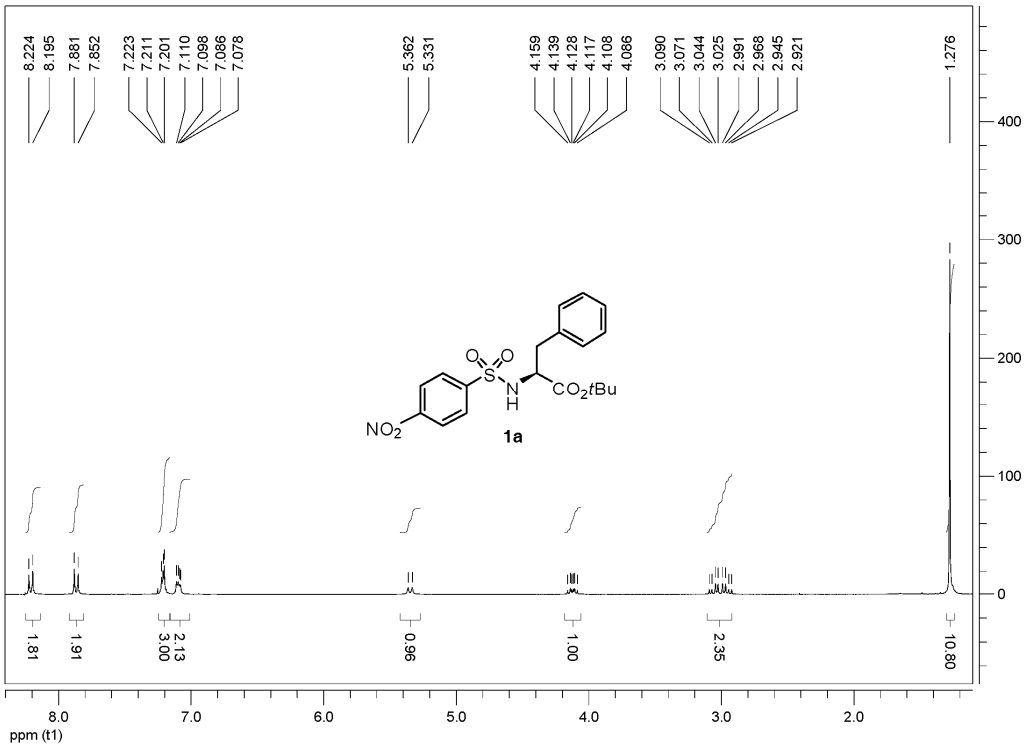


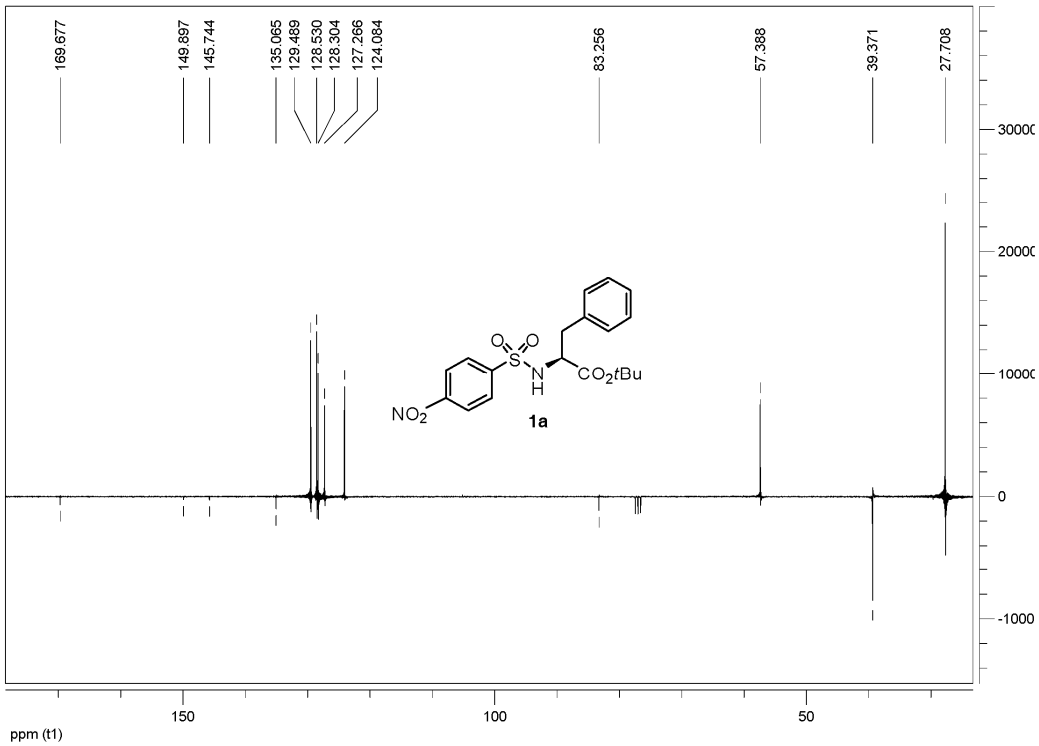
***R*-7**

Tetrakis(triphenylphosphine)palladium(0) (81 mg, 0.07mmol) was added to a solution of **(*R*)-*tert*-**butyl 2-(allylamino)-2-(4-nitrophenyl)propanoate (**4c**) (306 mg, 1 mmol) and dimedone (178 mg, 1.2 mmol) in THF (5 mL) previously purged with nitrogen through three freeze-pump-thaw cycles. The reaction mixture was stirred at 25 °C overnight; the crude, after solvent evaporation, was purified by FCC - AcOEt/hexane (1:4) on silica gel. The isolated product **6** (229 mg, 0.86 mmol, 86%) was dissolved in $CHCl_3$ (6 ml), TFA (1.96 g, 17.2 mmol,) was added, and this solution was stirred at 62 °C for 2 h. After evaporation under reduced pressure (RV), the crude was diluted with 10% HCl_{aq} (20 mL) and extracted with Et_2O (2 X 20 ml). The aqueous layer was evaporated (RV) and the product ***R*-7** (187 mg, 88%) was isolated as a white solid, mp 148-149 °C (lit.[1] 152-153 °C). $[\alpha]_D^{20}$ = -38.0 (*c* 0.44, 1 N HCl) *ee* 53% [lit. [1] ***S*-7**: $[\alpha]_D^{20}$ = +79.2 (*c* 0.6, 1 N HCl); ^{1}H NMR (300 MHz, D_2O) δ 8.37 (d, 2H, *J* = 8.7), 7.81 (d, 2H, *J* = 8.7), 2.07 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 175.3 (CO), 148.3 ($C_{Ar}NO_2$), 145.3 (C_{Ar}), 127.9, 124.8 (4 CH_{Ar}), 63.3 (C_α), 22.1 (CH_3).

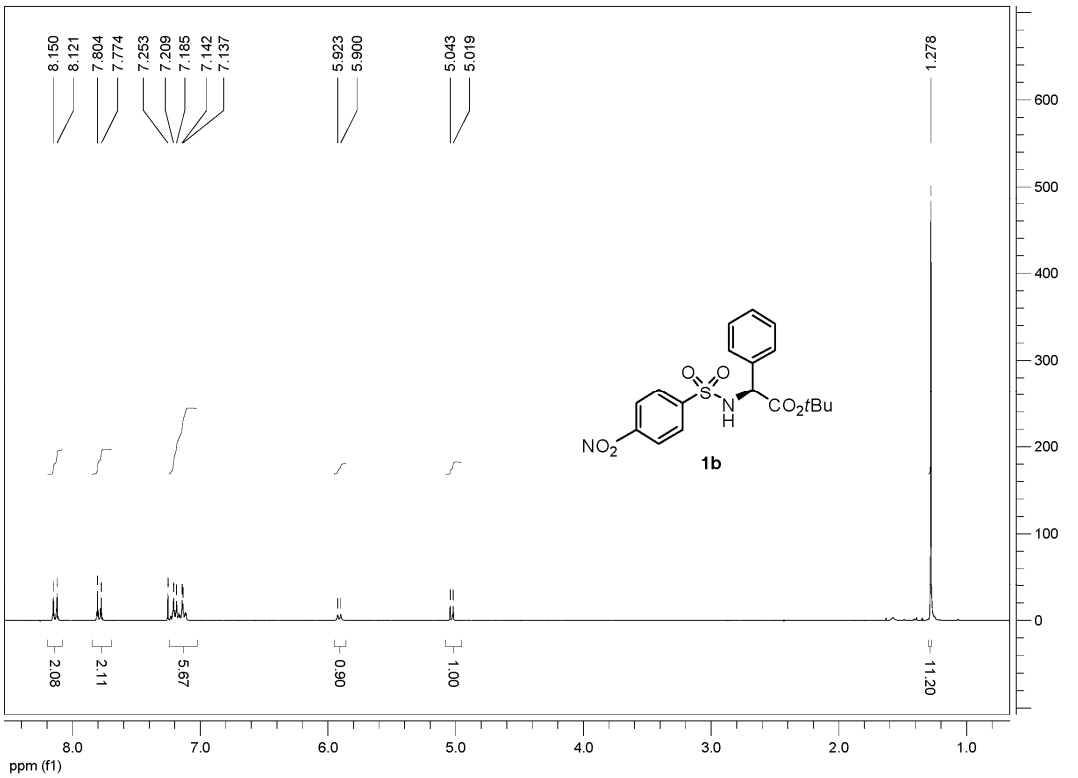
[1] F. A. Davis, S. Lee, H. Zhang, D. L. Fanelli *J. Org. Chem.* **2000***, 65*, 8704.

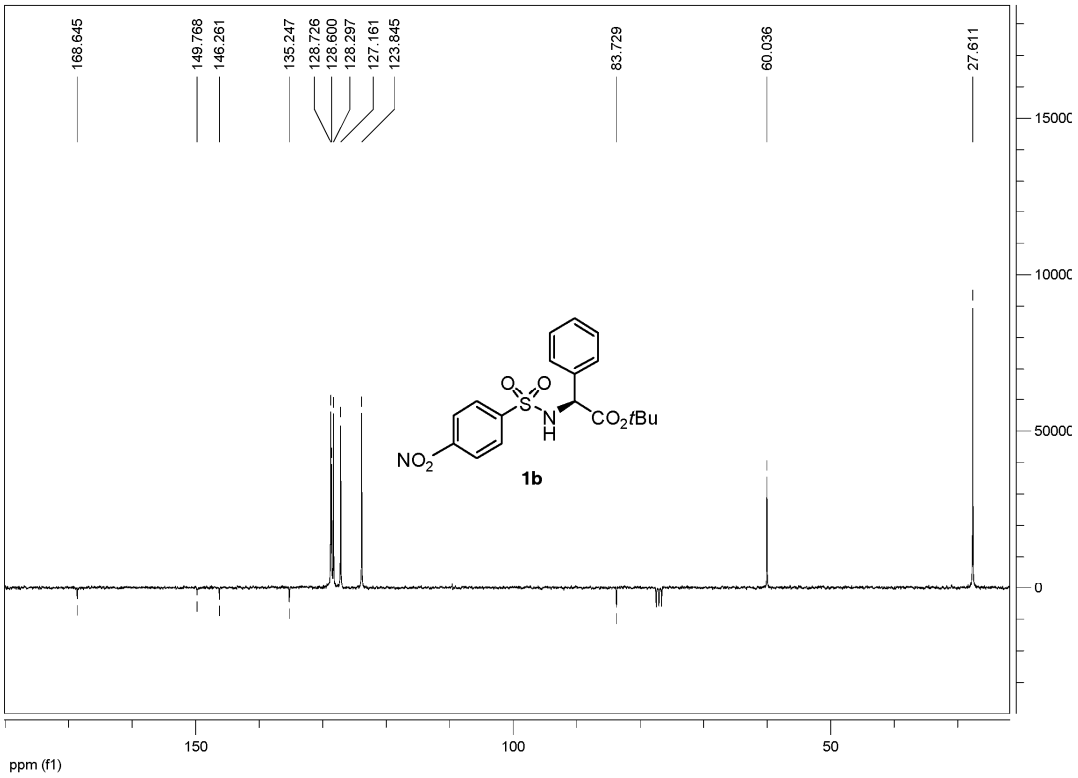
Synthesis of Quaternary α-Amino Acid Derivatives





Synthesis of Quaternary α-Amino Acid Derivatives





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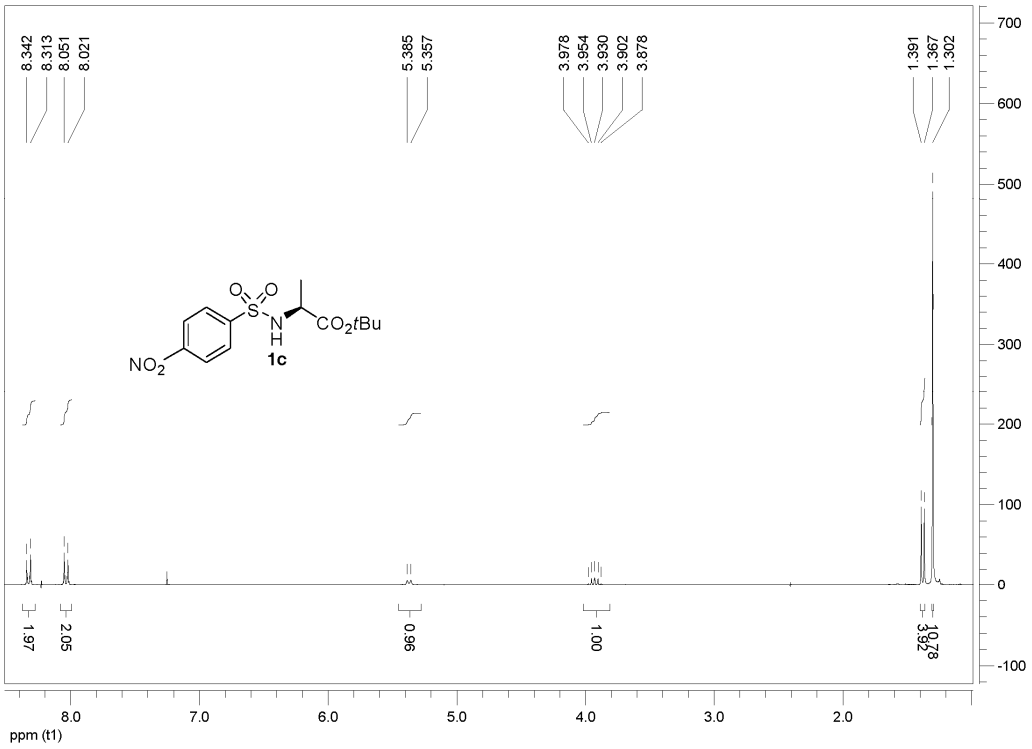

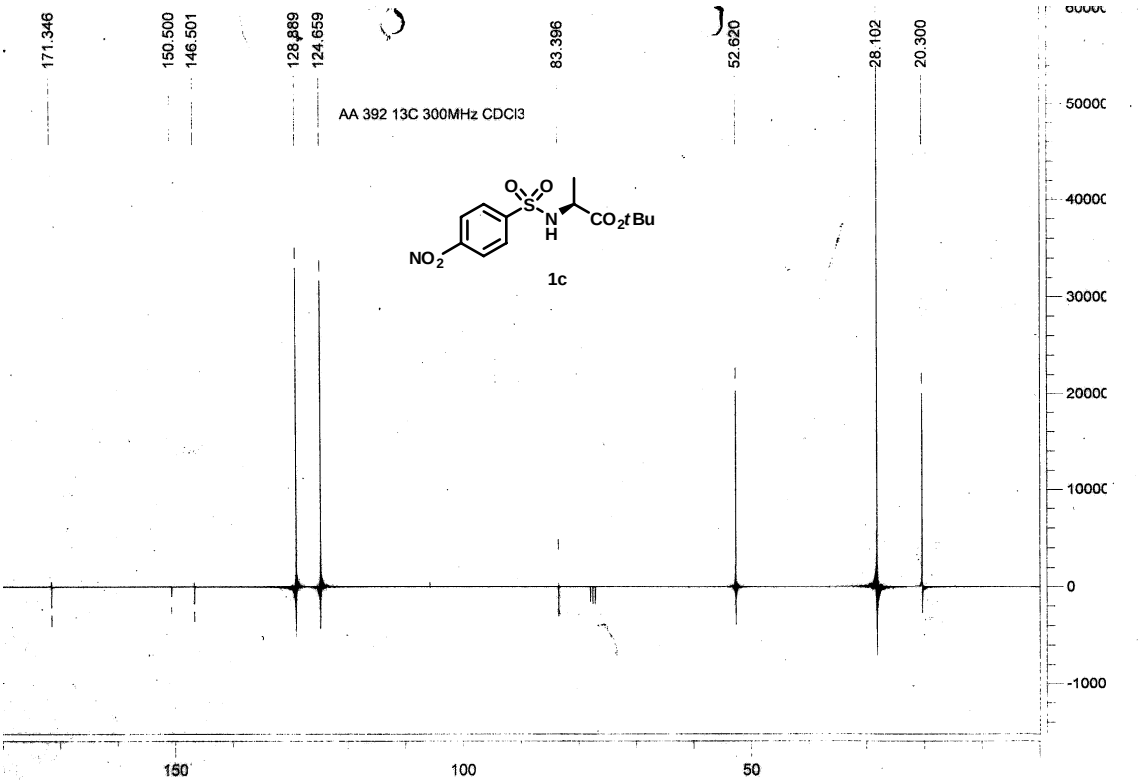

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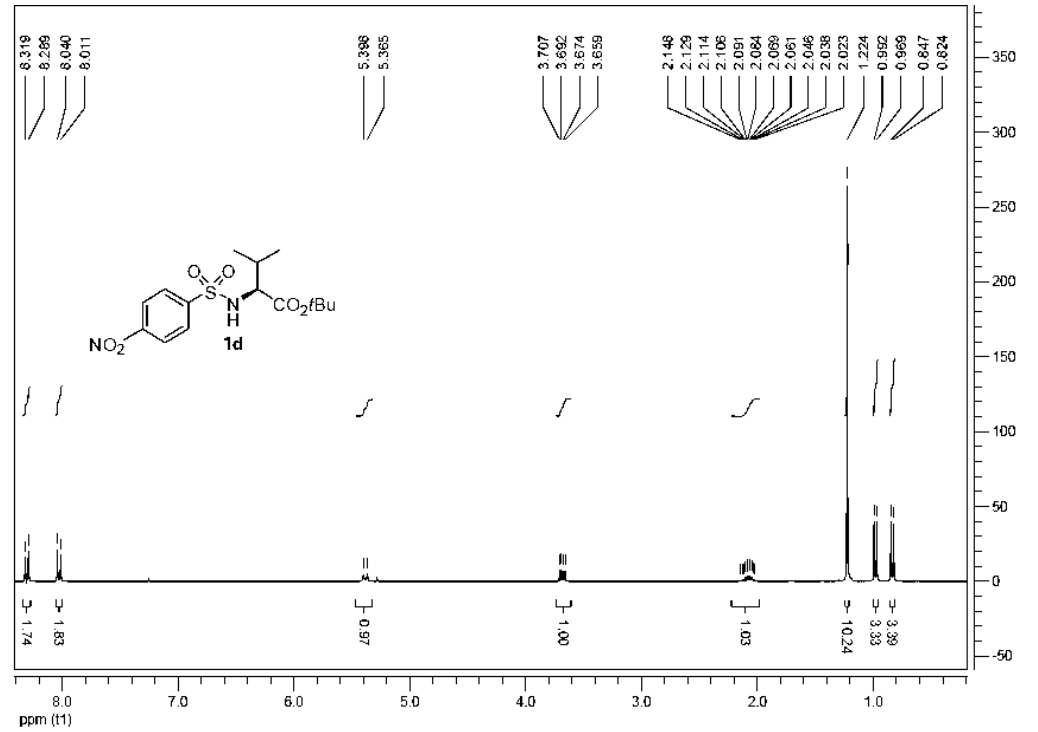

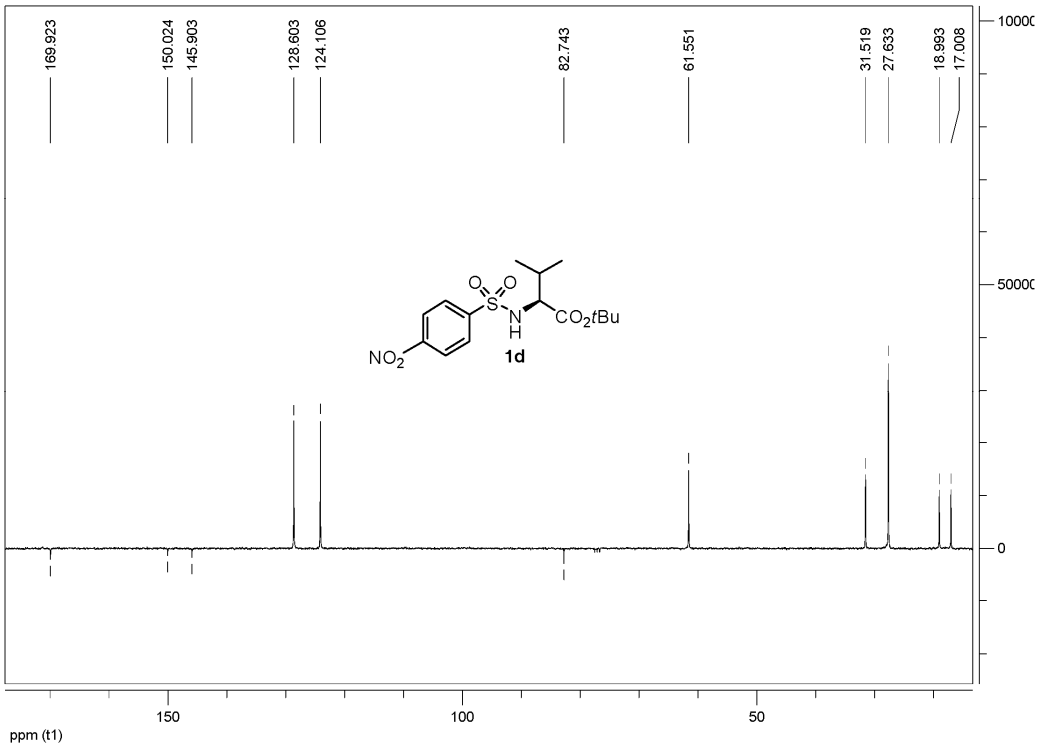

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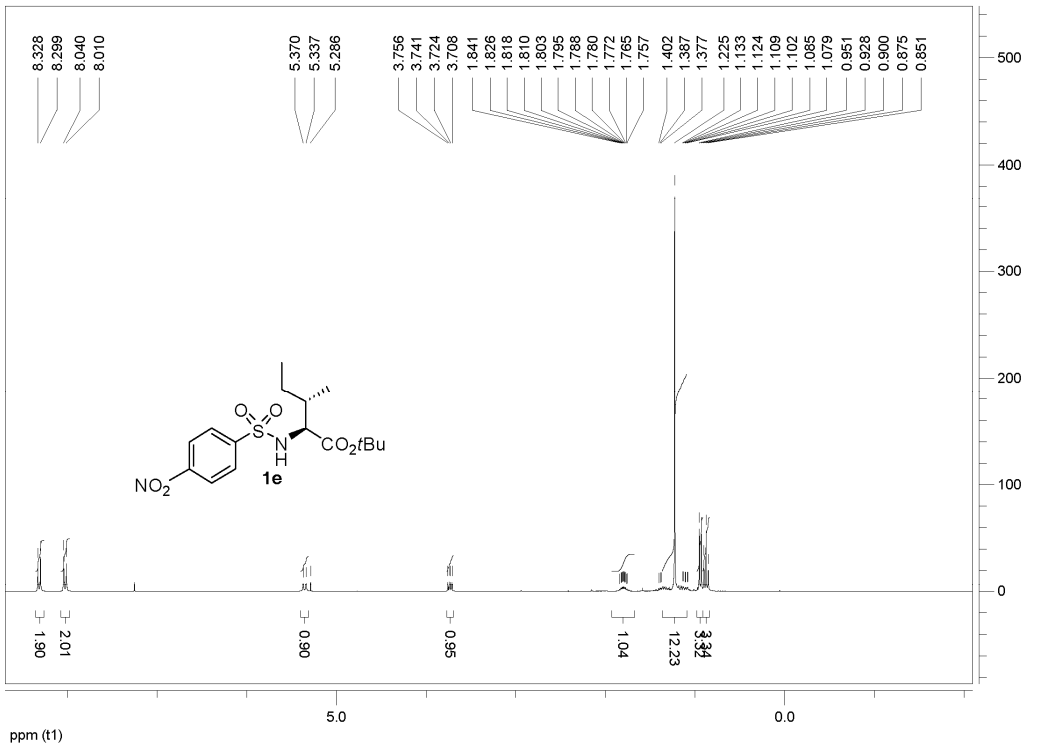

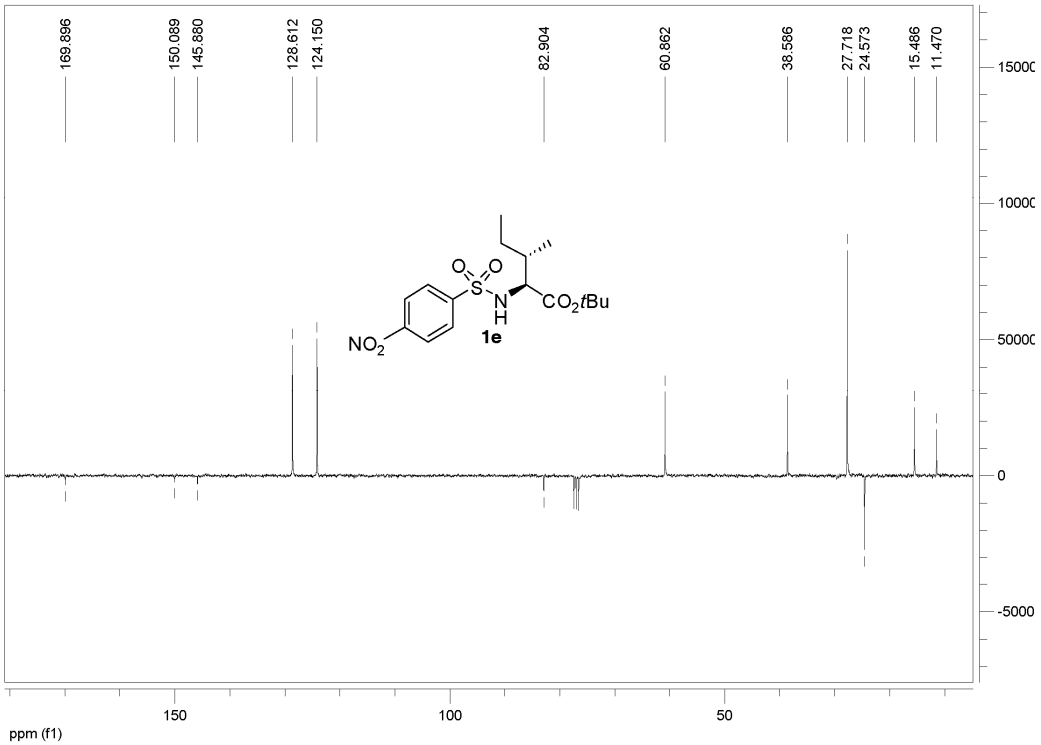

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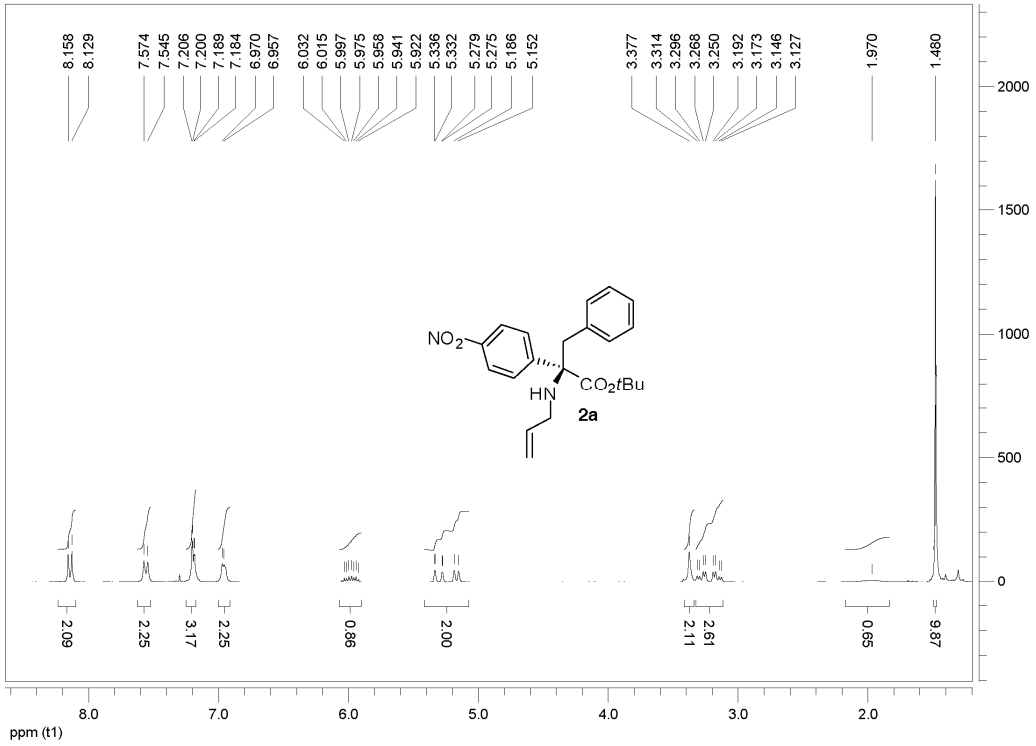

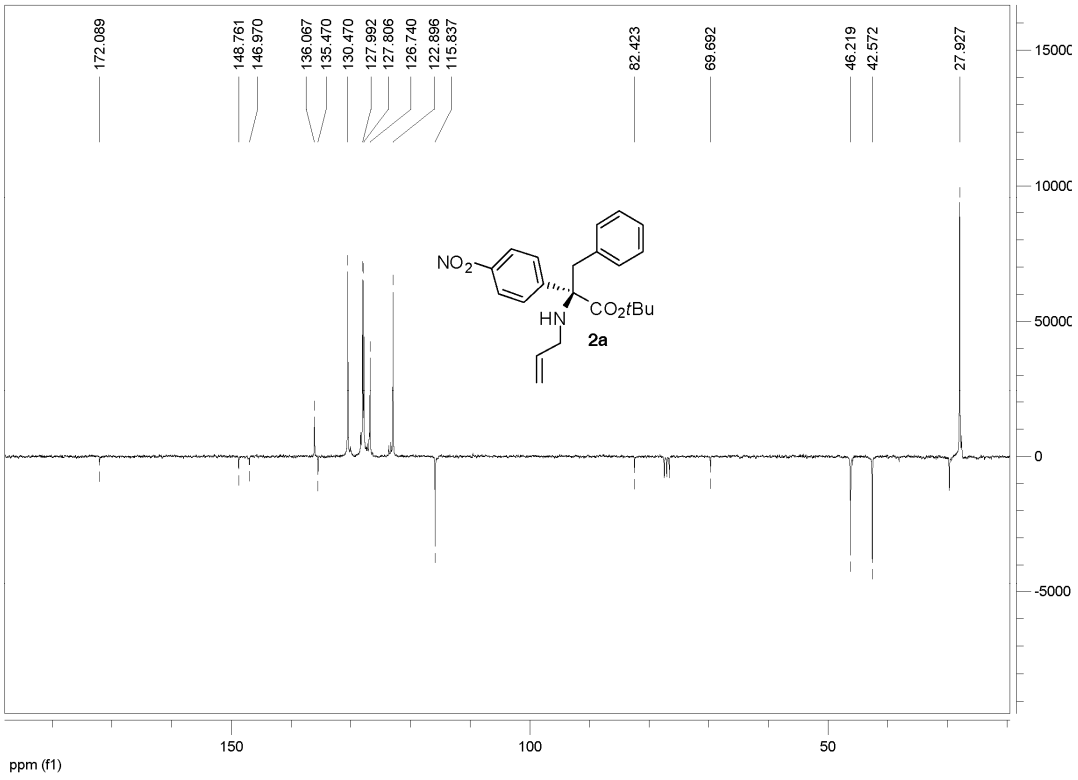

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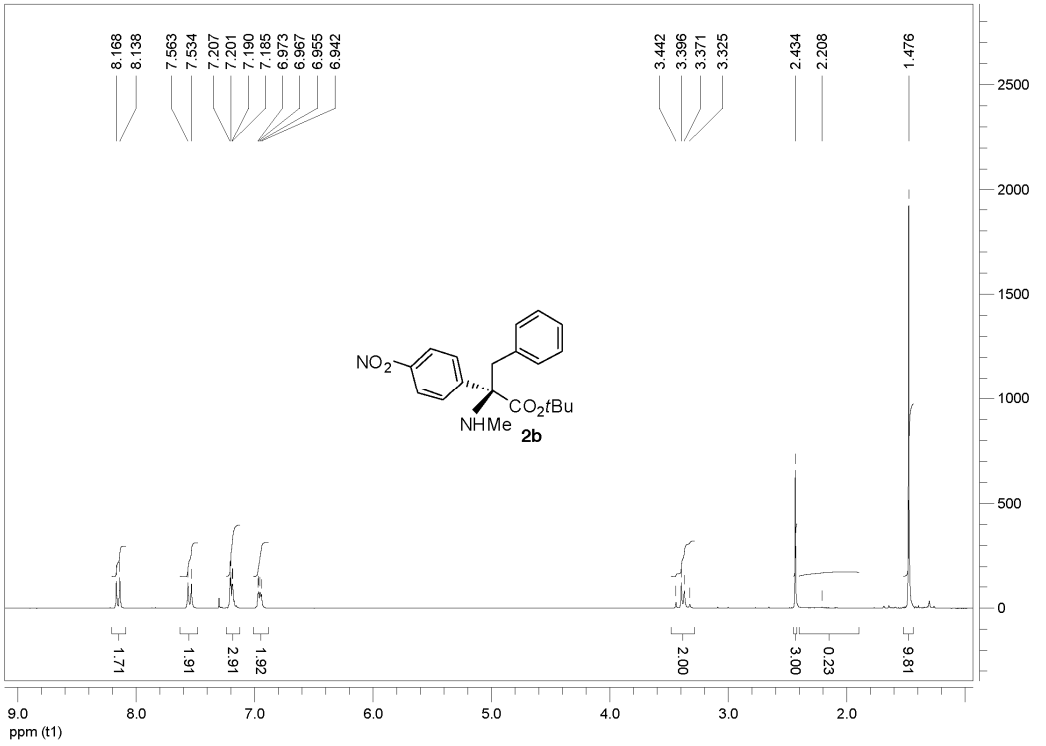

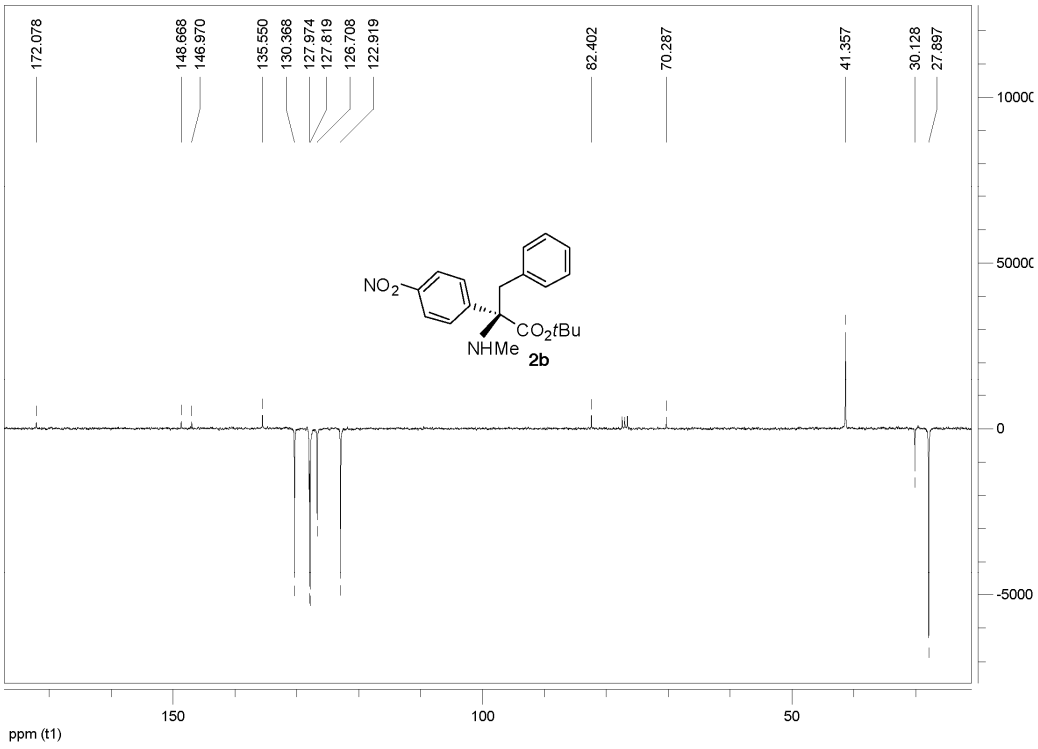

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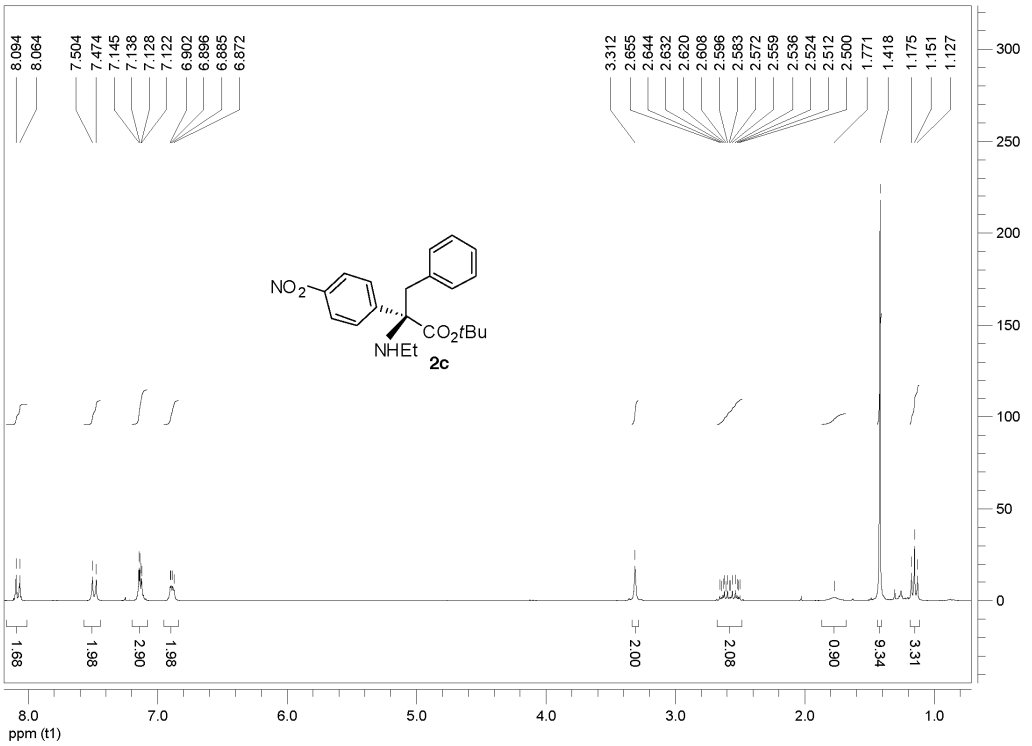

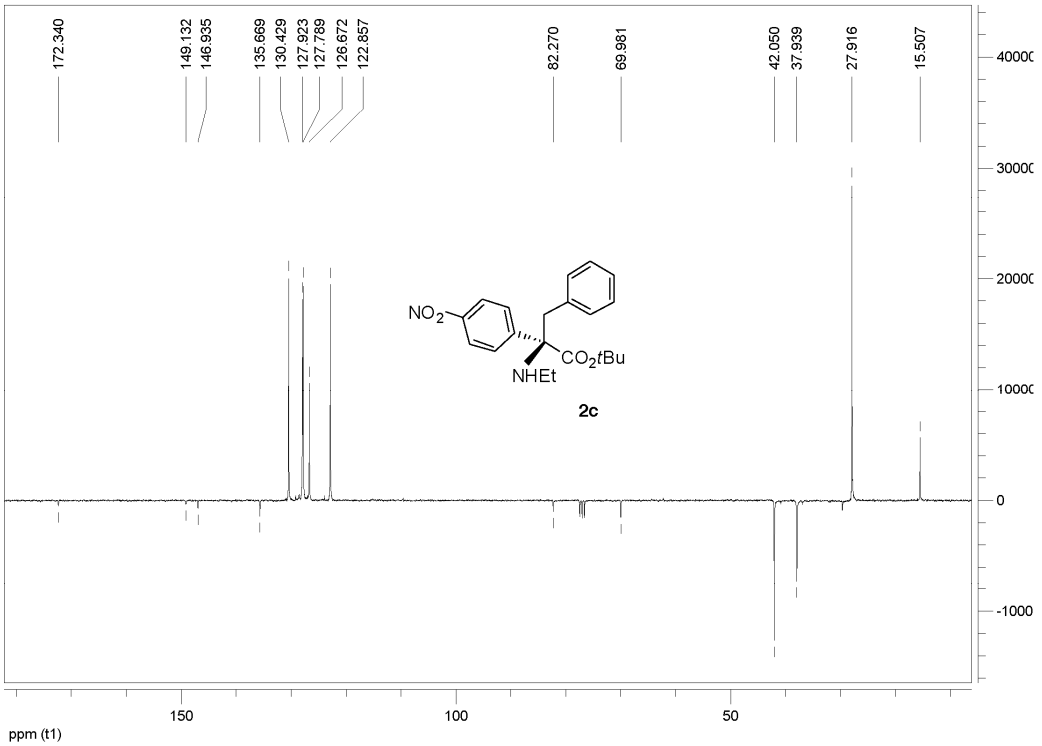

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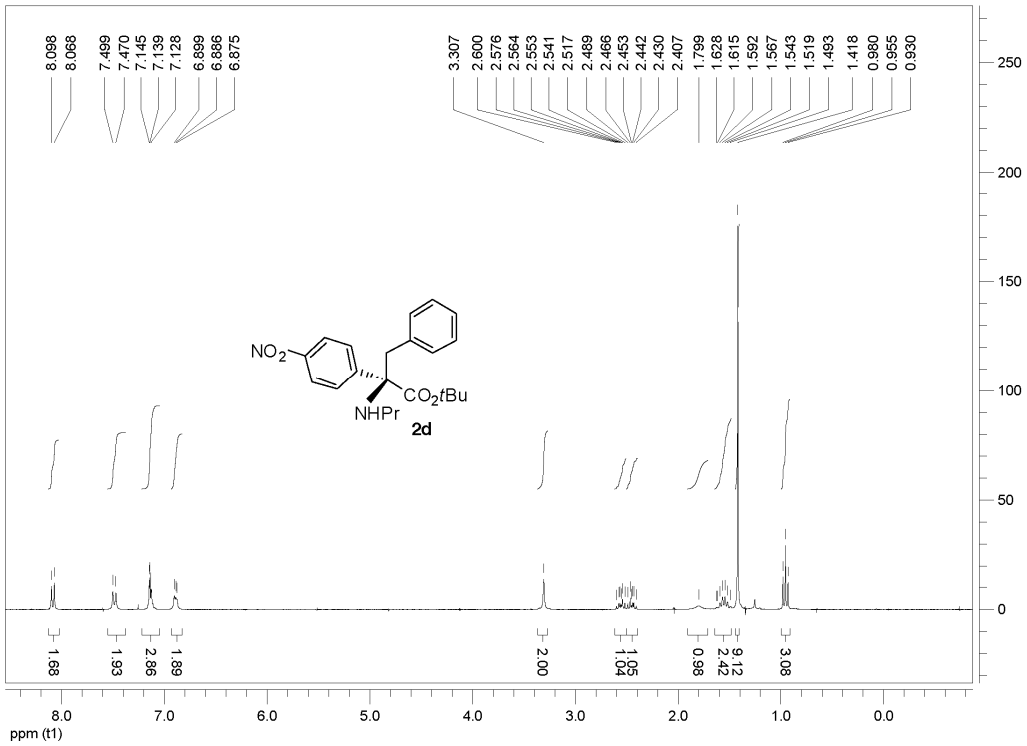

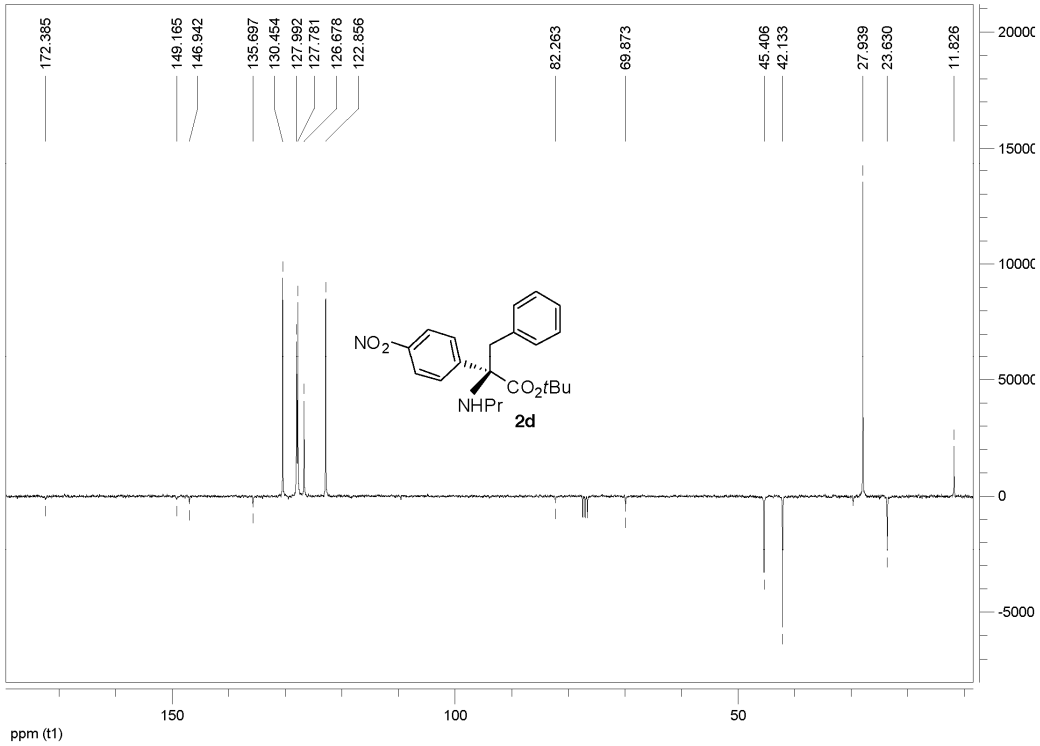

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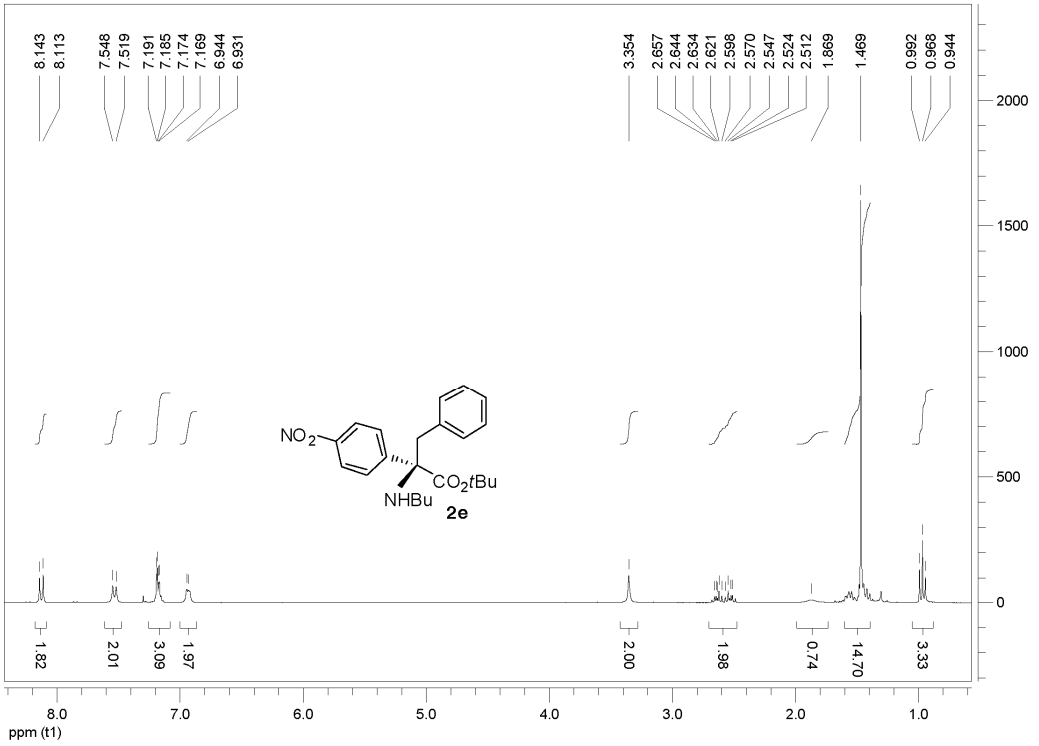

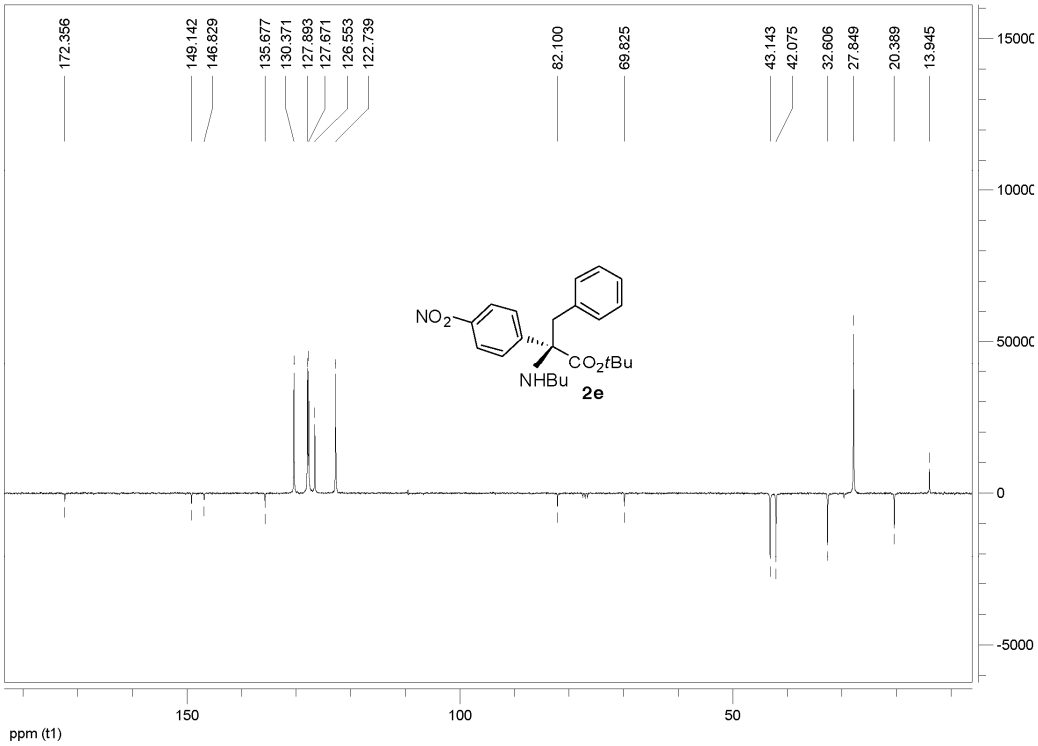

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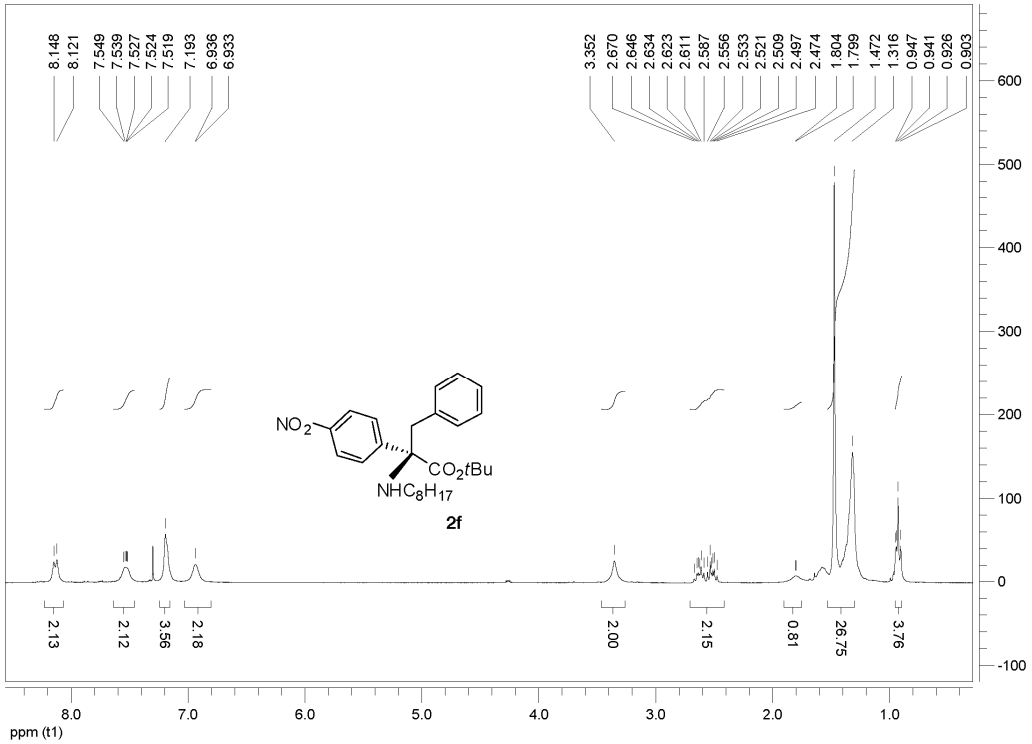

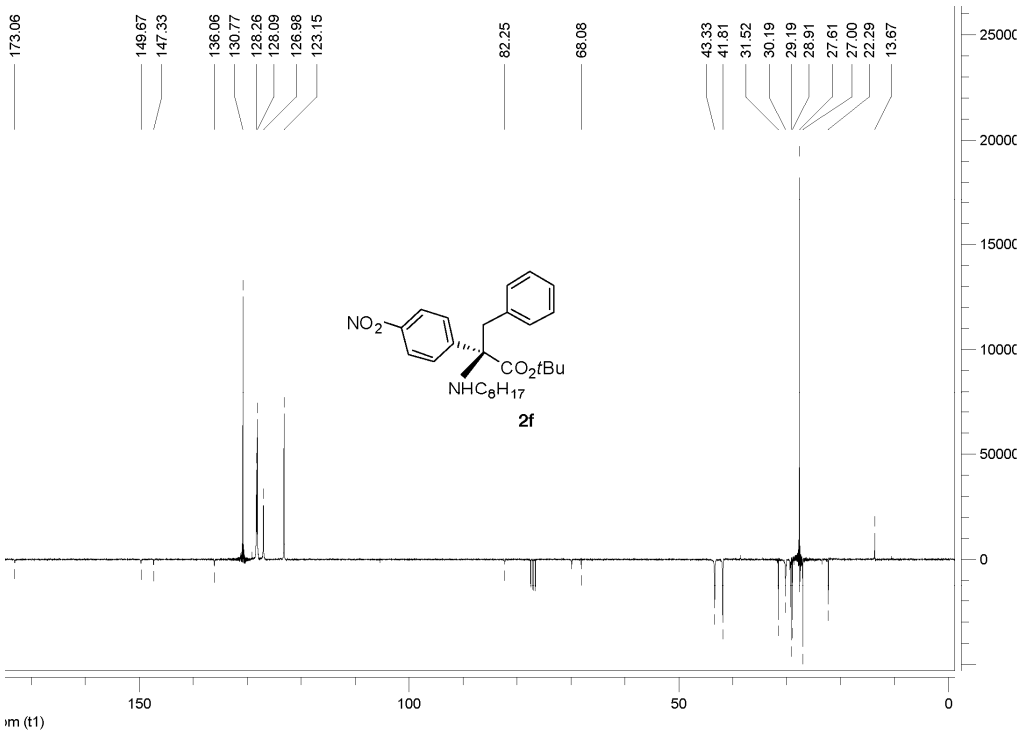

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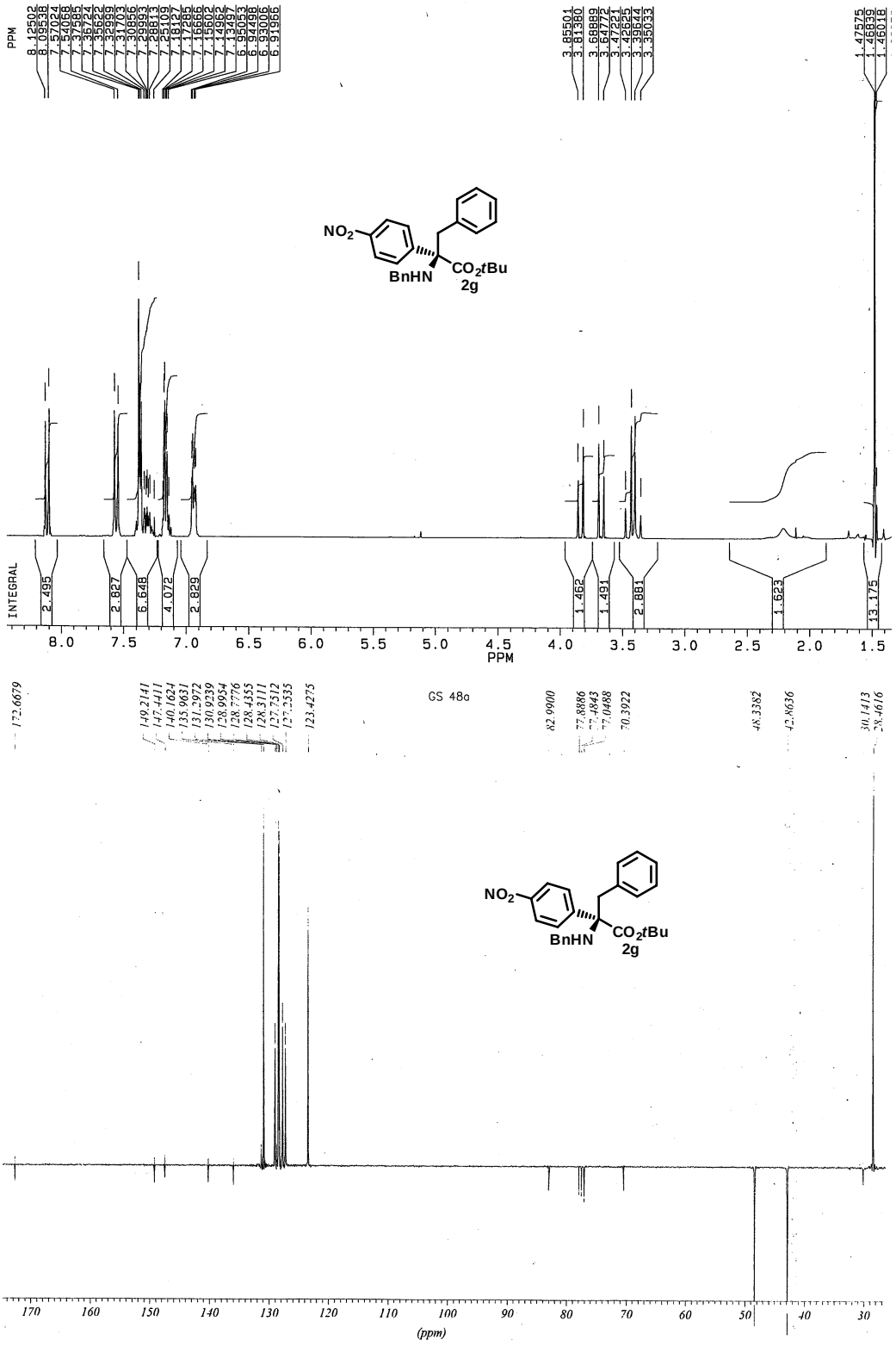

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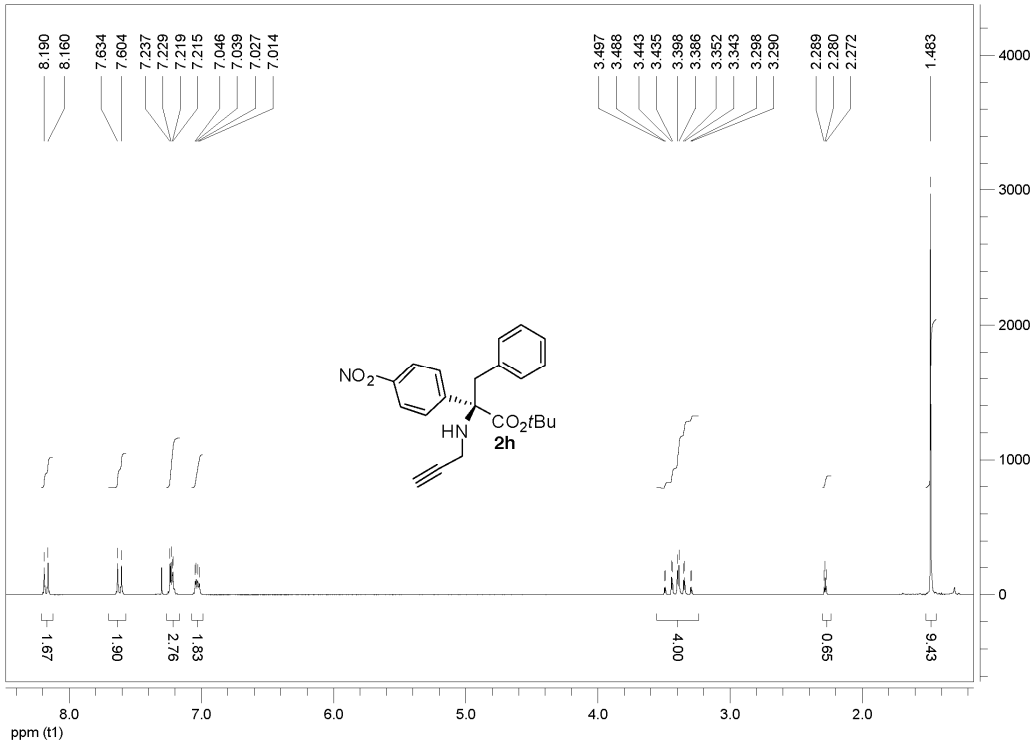

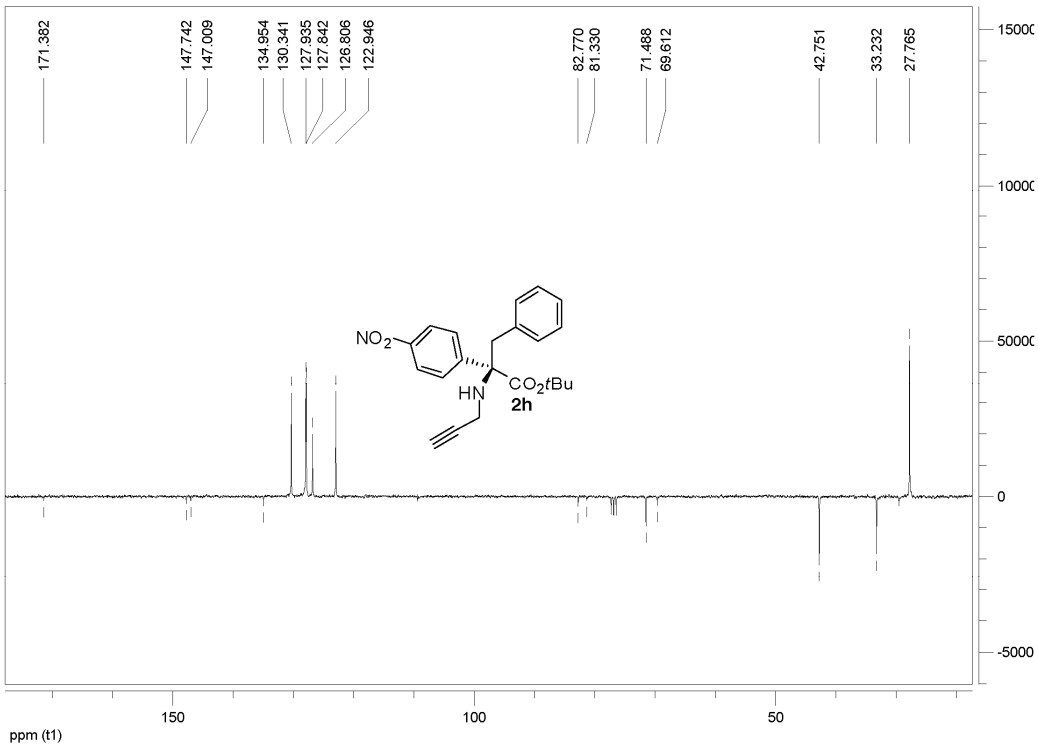

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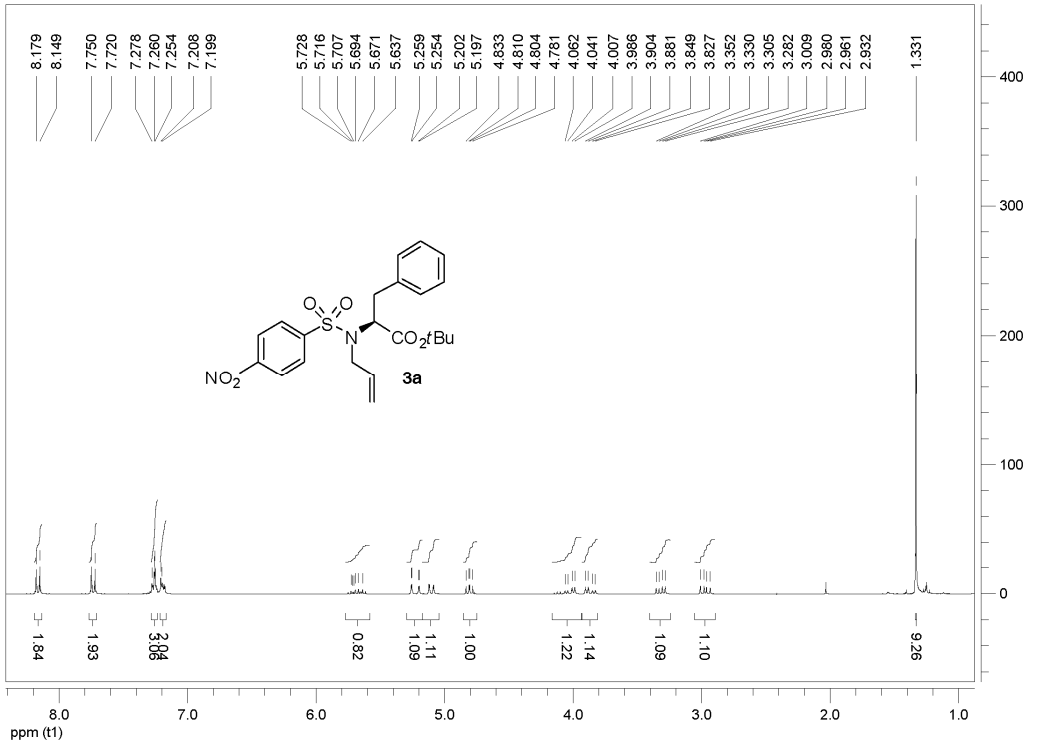

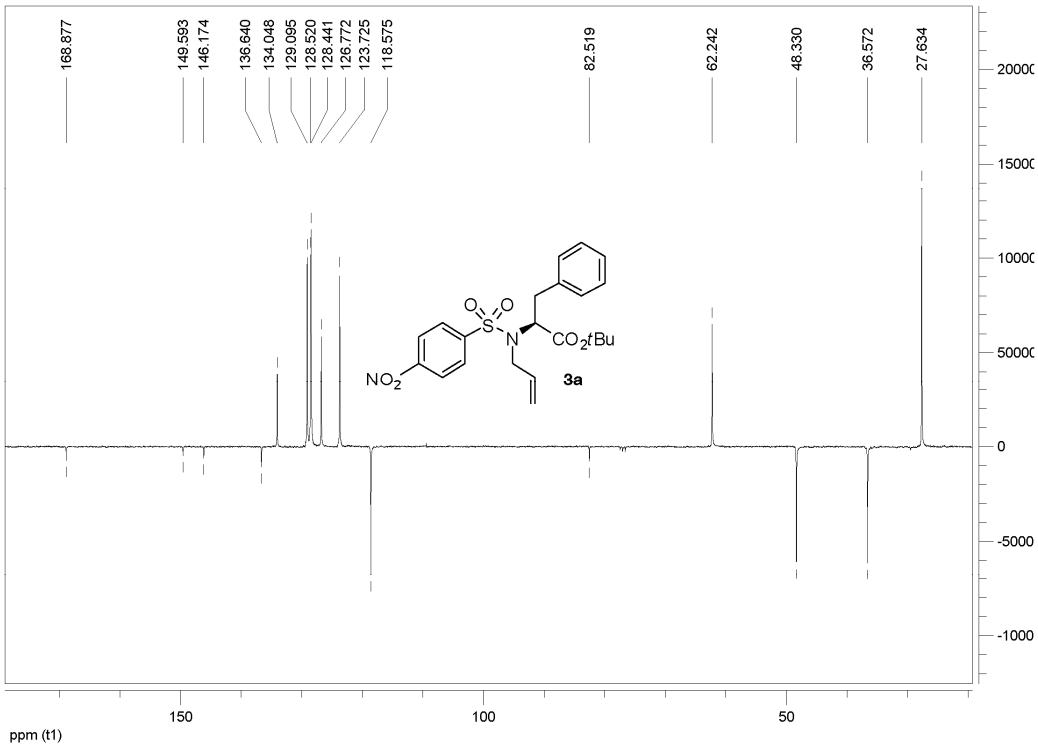

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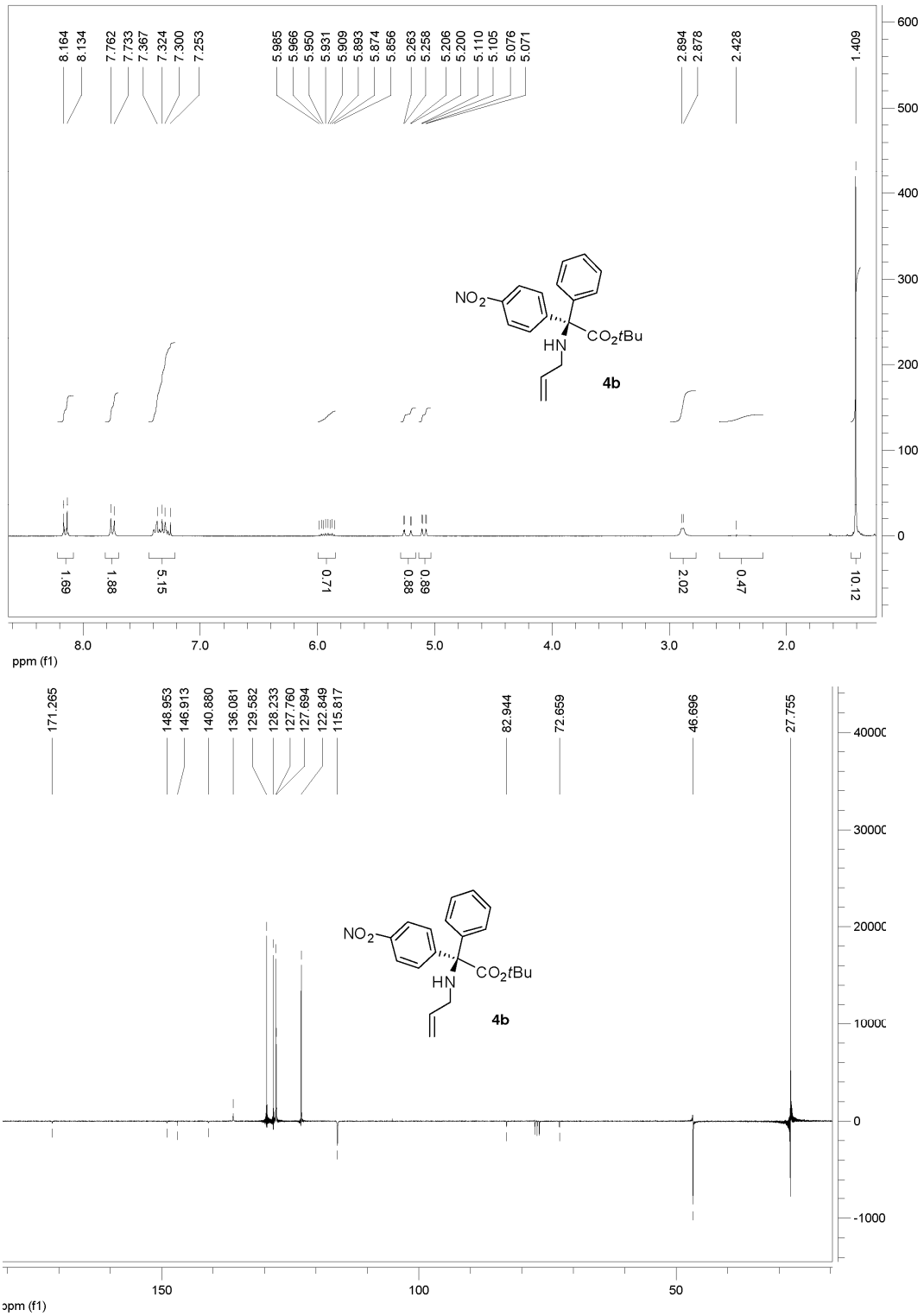

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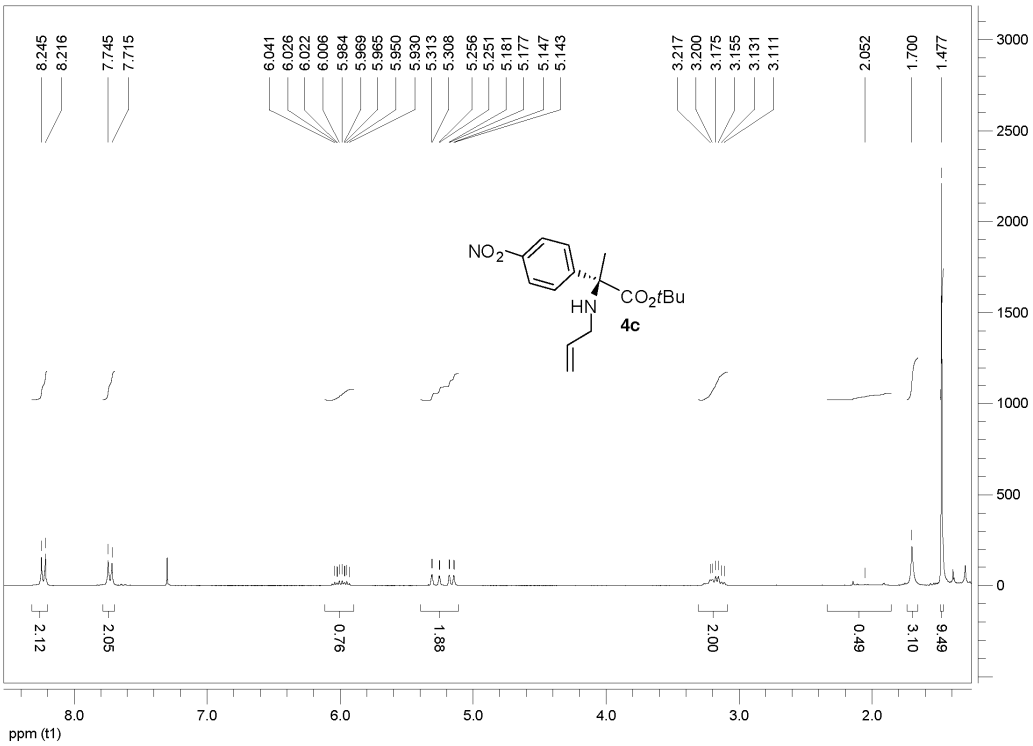

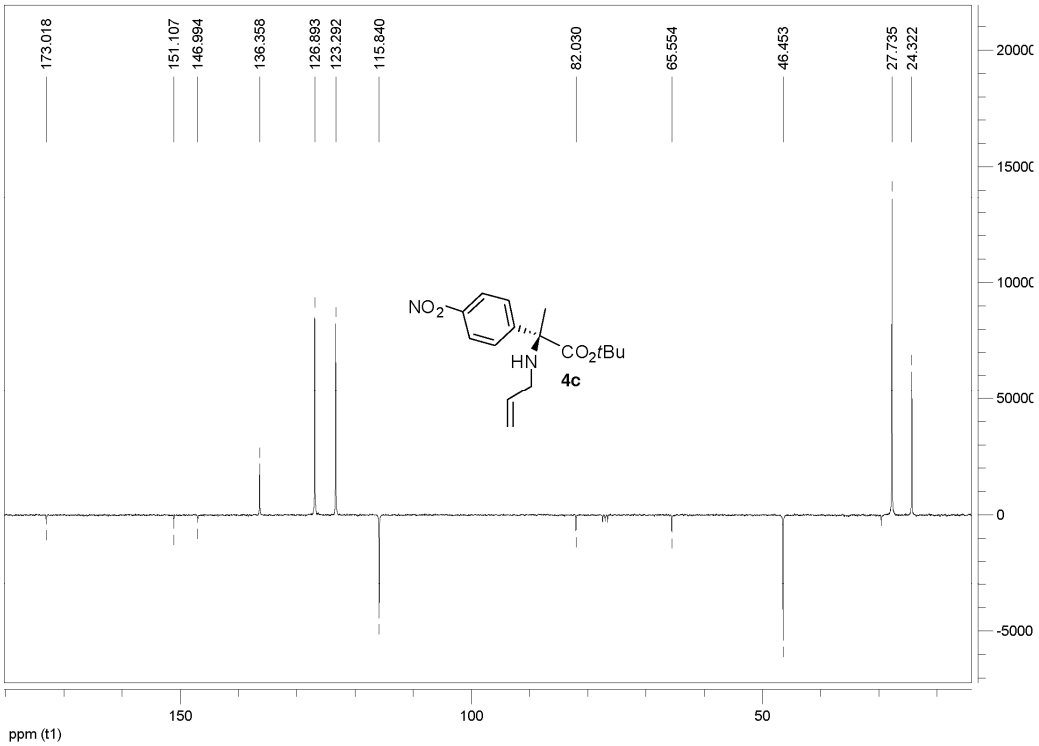

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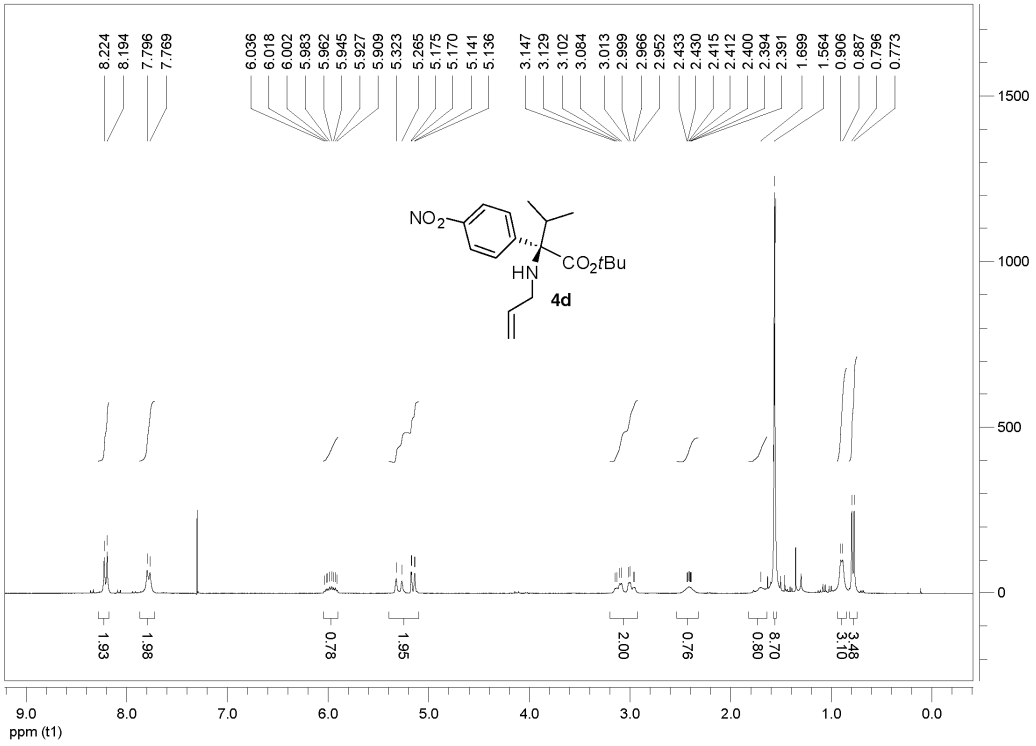

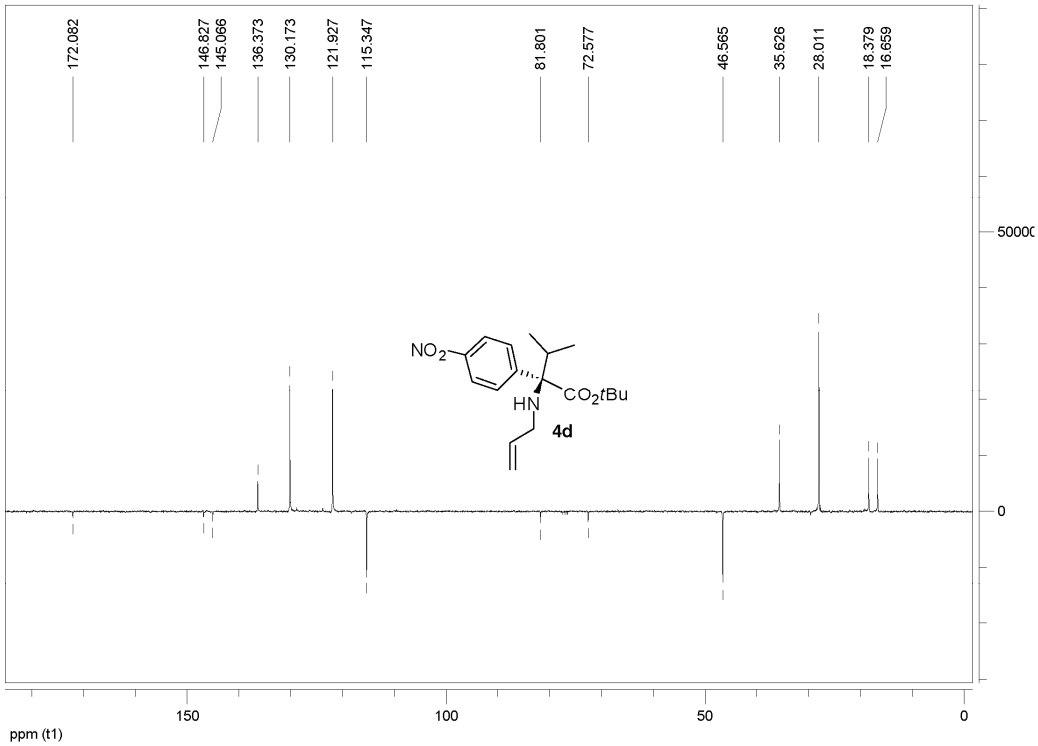

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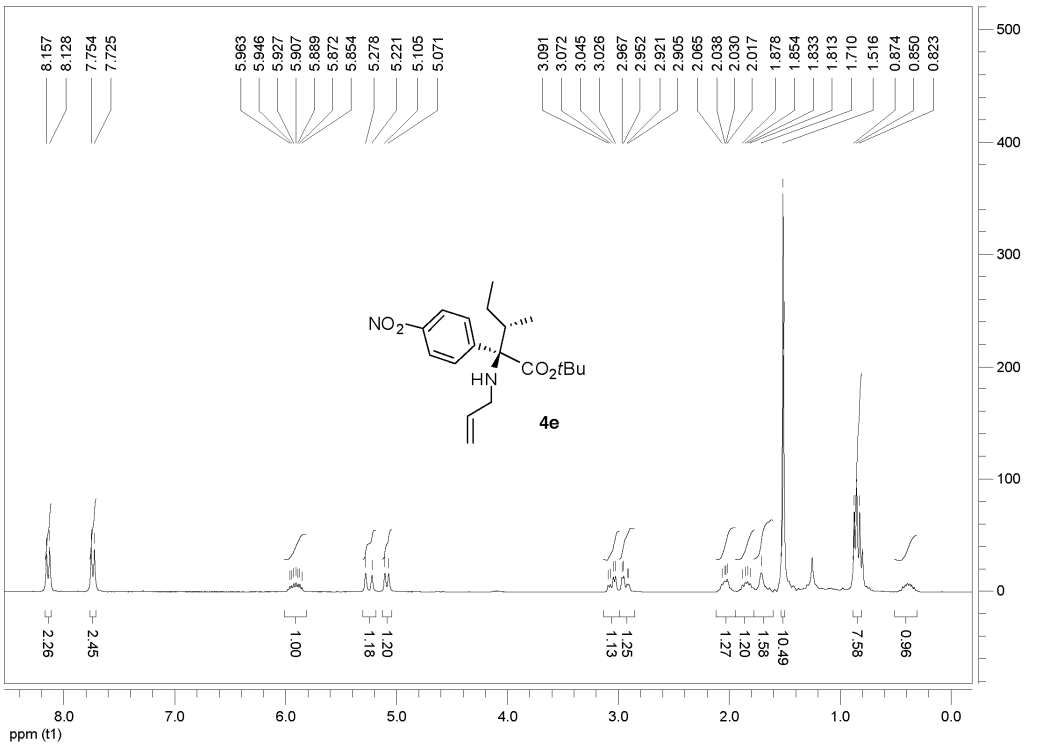

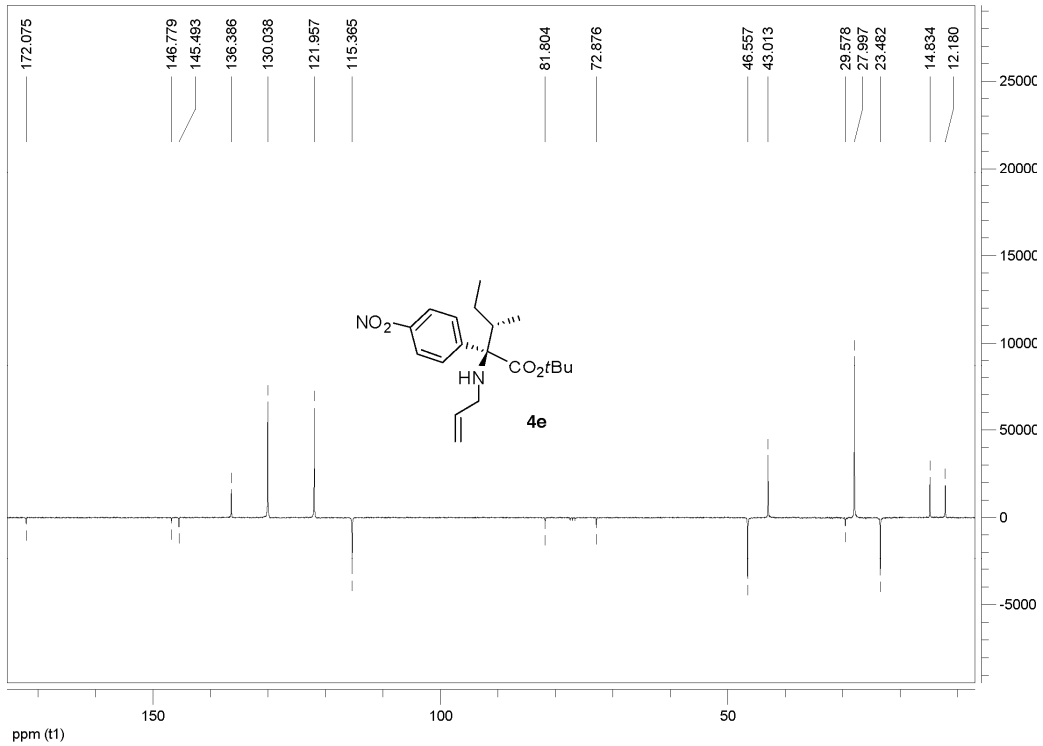

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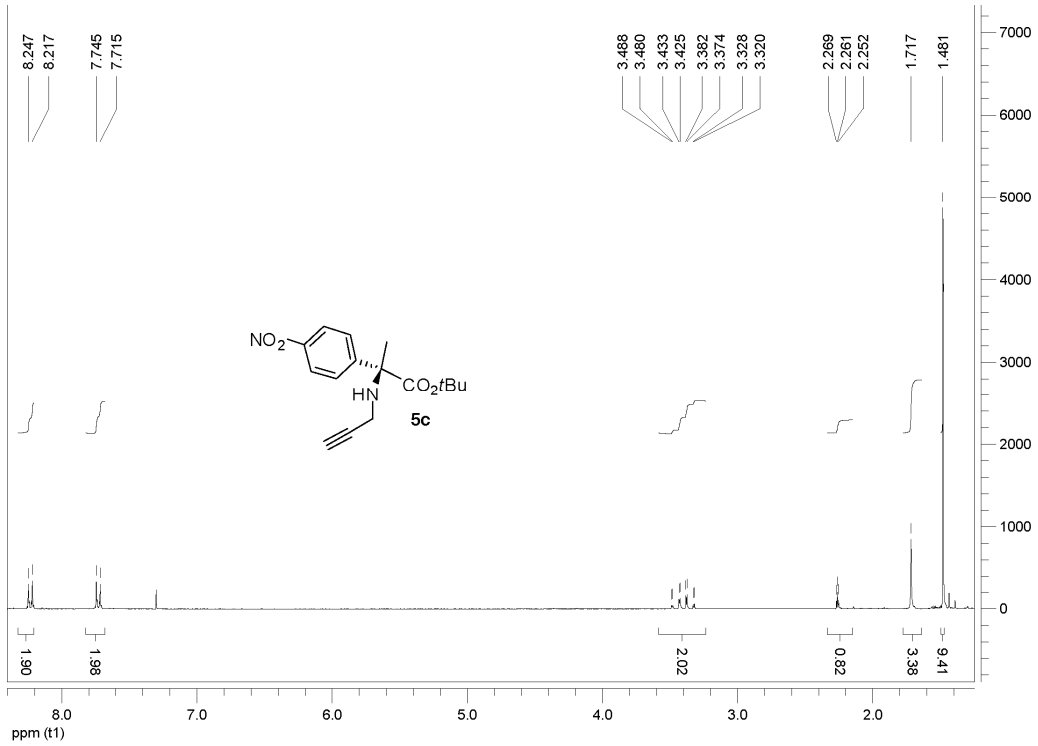

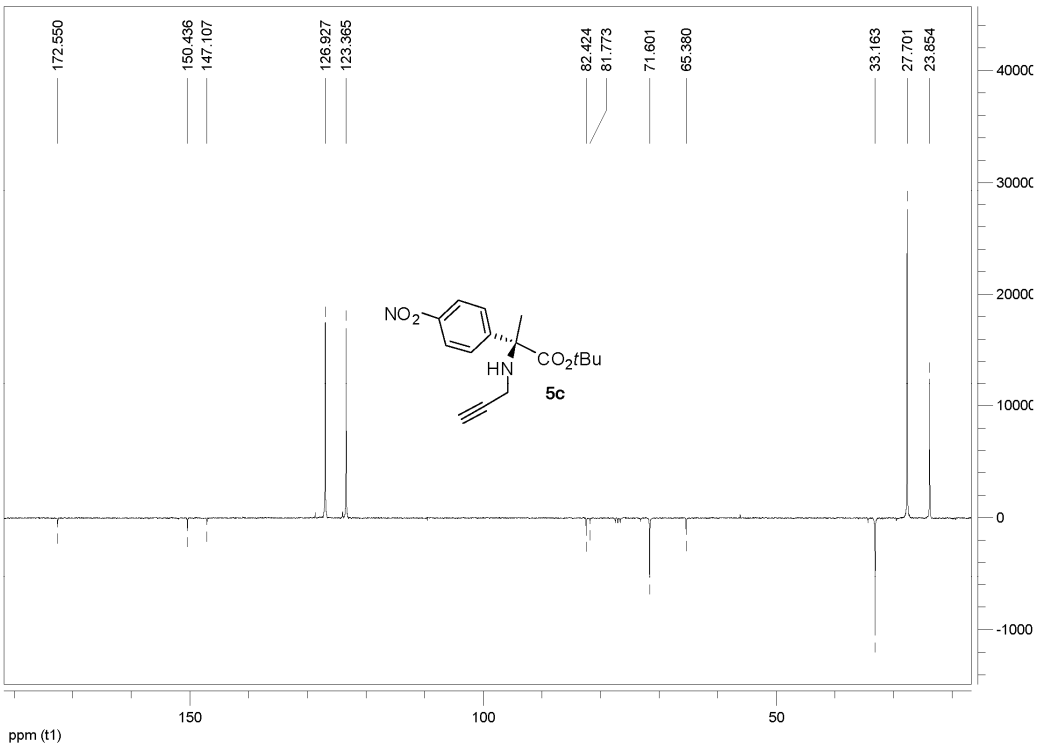

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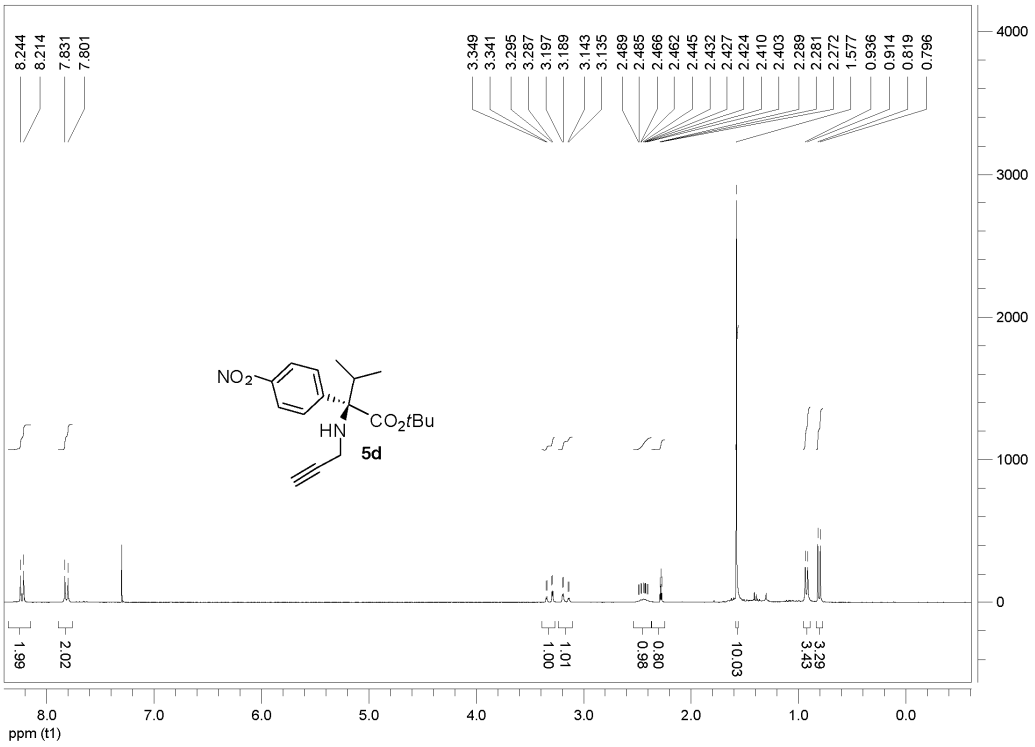

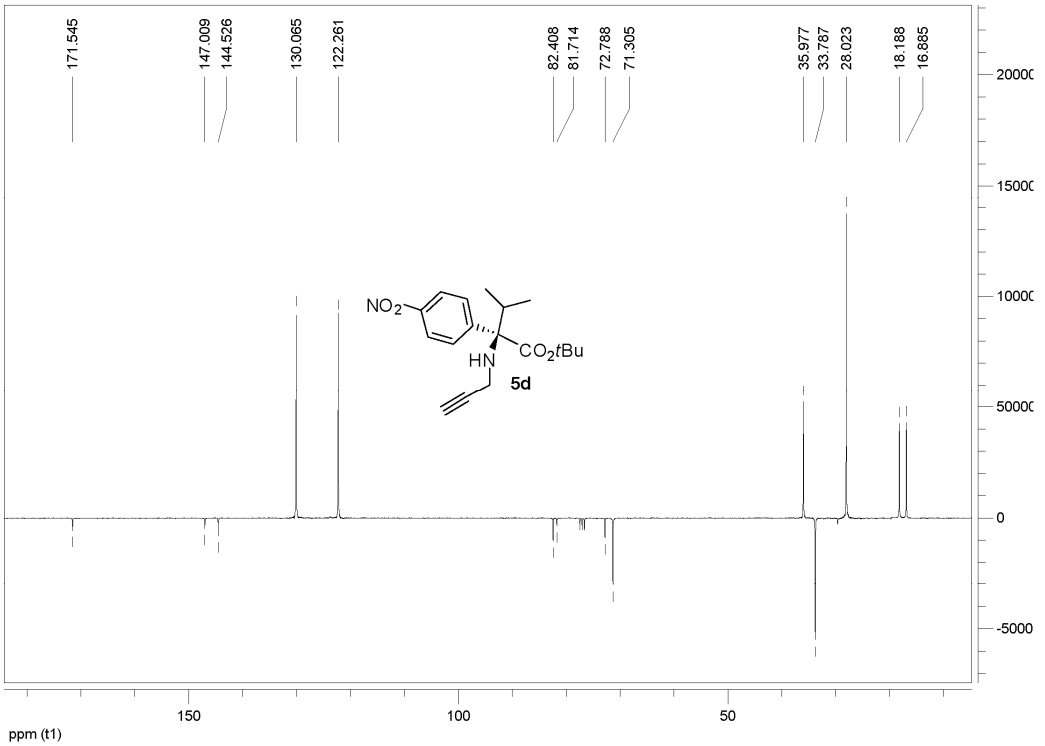

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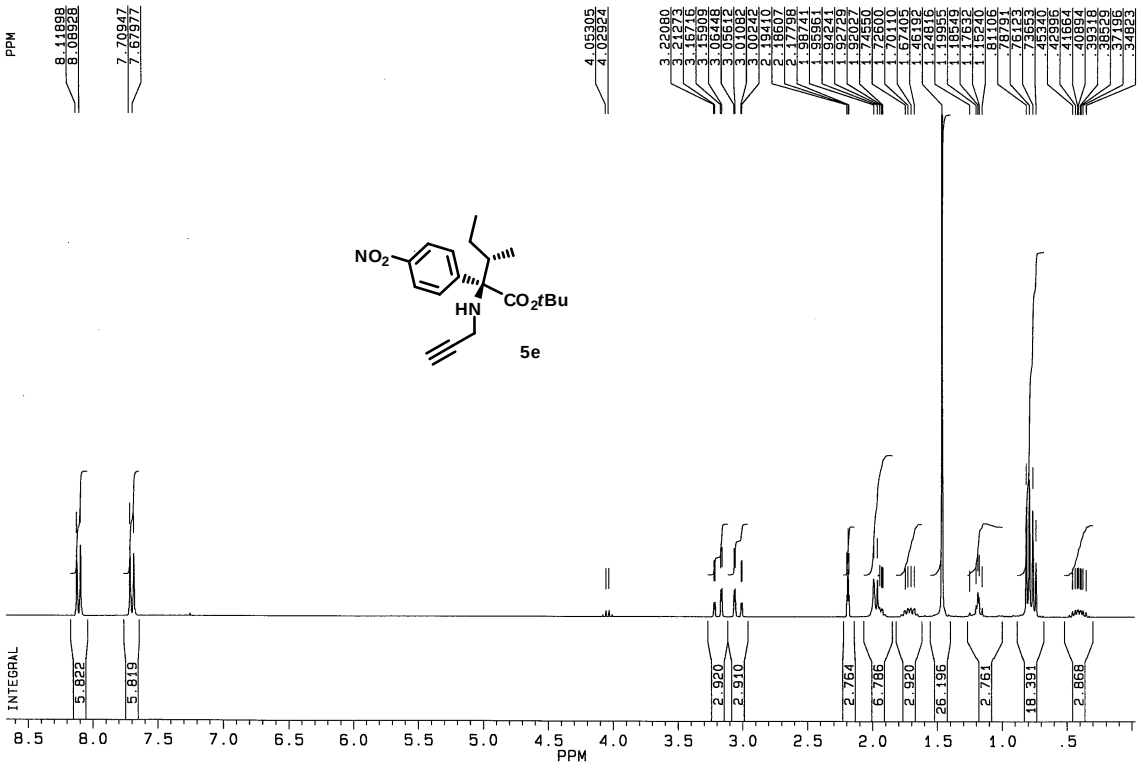

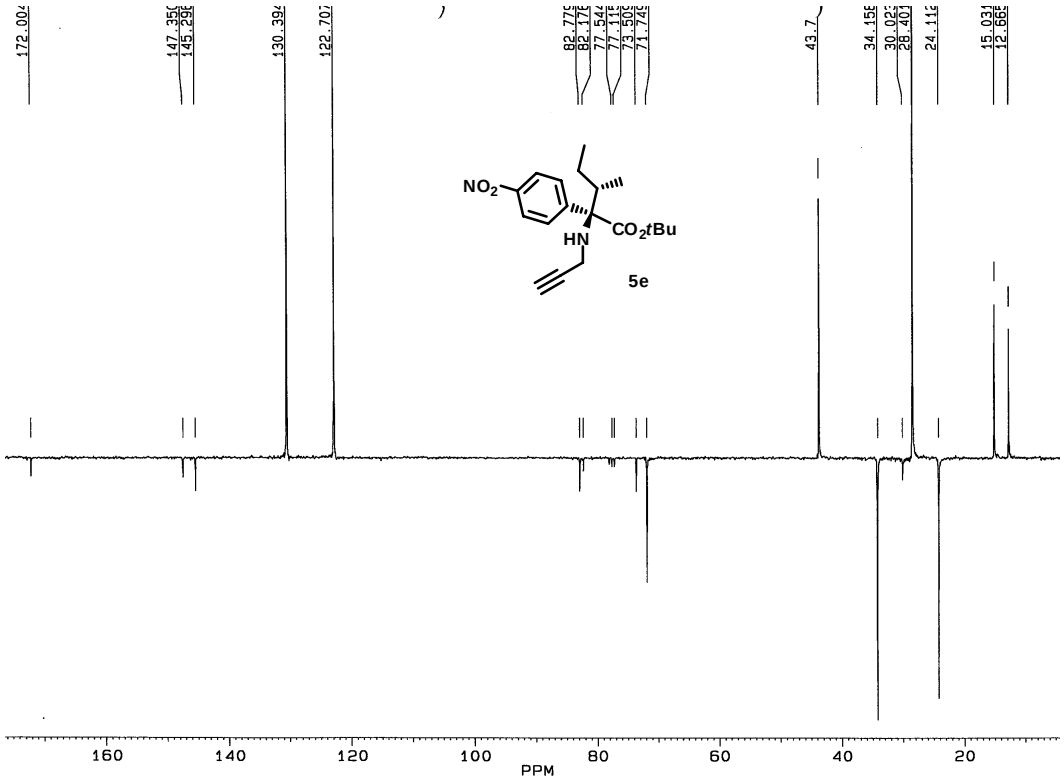

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