Electronic Supplementary Material (ESI) for ChemComm.

Synthesis of Homopropargylamines from 2-cyanoazetidines

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Supplementary information

Contents:

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded at 200 or 300 and 75 MHz, respectively; chemical shifts (δ) are reported in ppm and coupling constants (*J*) reported in Hertz and rounded up to 0.1 Hz. Splitting patterns are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), septuplet (sep), multiplet (m), broad (br), or a combination of these. Solvents were used as internal standard when assigning NMR spectra (δ H : $CDCl_3$ 7.26 ppm ; δ C: $CDCl_3$ 77.0 ppm).Assignments for signals from ^{1}H and ^{13}C in the NMR spectra were validated by two-dimensional correlated spectroscopy (2D COSY) and Heteronuclear Multiple Bond Correlation (HMBC). IR data were collected with an ATR-FT-IR spectrometer. All reactions were carried out under argon. Column chromatography was performed on silica gel (230–400 mesh) with use of various mixtures of CH_2Cl_2, EtOAc, petroleum ether (35-60°C fraction) (PE) and methanol. TLC was performed on Merck Kieselgel 60 F254 plates. Melting points are uncorrected. THF was distilled under argon from sodium using benzophenone as indicator. Dichloromethane was distilled from calcium hydride. Isomeric ratios were determined by NMR analysis of crude reaction mixtures before purification.

Synthesis of starting azetidines

Azetidines **4, 7**, **8**, **11-15**, **23**, **24** and **25**-**27** were synthesized following the procedure described in: Agami, C. ; Couty,F. ; Evano, G. *Tetrahedron: Asymmetry*, **2002**, *13*, 297-302. Data for new azetidines **11**-**13** and **41** are reported herein.

N-aryl azetidines **16**-**22** and **28-30** were synthesized following the procedure described in : Quinodoz, P.; Drouillat, B.; Wright, K.; Marrot, J.; Couty, F. *J. Org. Chem.***2016**, *81*, 2899-2910.

Synthesis of homopropargyl amines: general procedure

To a solution of aminonitrile (1 mmol) in toluene (7 mL) was added dibutyltin oxide (62 mg, 0.25 mmol) and $TMSN_3$ (197 µL, 1.5 mmol). The solution was stirred at 60°C for 96h and then submitted to one of the following treatments.

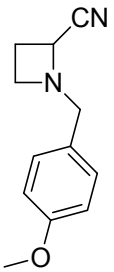
A : Boc_2O (1.1 mmol) was added. The mixture was heated at 60°C for 3h, cooled to rt and concentrated under reduced pressure. Residue was purified by flash chromatography (PE/EtOAc).

B : CBzCl (1.5 mmol) was added. The mixture was heated at 60°C for 3h, cooled to rt and concentrated under reduced pressure. Residue was purified by flash chromatography (PE/EtOAc).

C : The mixture was cooled to rt and concentrated under reduced pressure. Residue was purified by flash chromatography (PE/EtOAc).

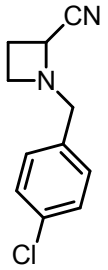
D : The mixture was cooled to rt and filtered on fritted glass, the solid washed with small quantities of chloroform and dried under vacuum.

1-(4-methoxybenzyl)azetidine-2-carbonitrile 11



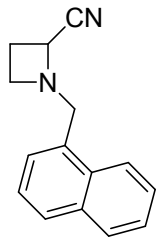
Colorless oil, Rf : 0.40 (PE/EtOAc 70/30), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24 (d, 2H, J=8.7 Hz, Ar), 6.88 (d, 2H, J=8.7 Hz, Ar), 3.90 (t, 1H, J=7.1 Hz, C***H***CN), 3.80 (s, 3H, O***Me***), 3.68 and 3.61 (two d, 2H, J=12.6 Hz, NC***H$_2$***Ar), 3.36 (q, 1H, J=6.7 Hz, CH_2C***H***HN), 3.13 (q, 1H, J=7.2 Hz, CH_2CH***H***N), 2.42 (q, 2H, J=7.2 Hz, NCH_2C***H$_2$***) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.13 (C_q), 130.06 (C_{Ar}), 128.14 (C_q), 118.92 (C_q), 113.90 (C_{Ar}), 60.16 (N***C***H_2Ar), 55.24 (O***Me***), 52.19 (N***C***H_2CH_2), 51.47 (***C***HCN), 22.88 (NCH_2***C***H_2) ppm. IR : νmax = 3325(b), 2969, 2835, 1610, 1511, 1244, 1171, 1031, 817, 792, 510 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{12}H_{15}N_2O$ $[MH]^+$: 203.1184; found : 203.1178.

1-(4-chlorobenzyl)azetidine-2-carbonitrile 12



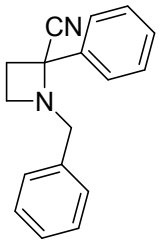
Colorless oil, Rf : 0.66 (PE/EtOAc 70/30), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 (d, 2H, J=8.1 Hz, Ar), 7.26 (d, 2H, J=8.1 Hz, Ar), 3.93 (t, 1H, J=7.2 Hz, C***H***CN), 3.77 (two d, 2H, J=13.2 Hz, NC***H$_2$***Ar), 3.38 (q, 1H, J=6.7 Hz, NC***H***HCH_2), 3.15 (q, 1H, J=7.2 Hz, NCH***H***CH_2), 2.53-2.36 (m, 2H, NCH_2C***H$_2$***) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.73 (C_q), 133.38 (C_q), 130.09 (C_{Ar}), 128.69 (C_{Ar}), 118.71 (CH***C***N), 59.99 (Ar***C***H_2N), 52.48 (N***C***H_2CH_2), 51.79 (***C***HCN), 22.88 (NCH_2***C***H_2) ppm. IR : νmax = 3322, 3189 (b), 2866, 1584, 1404, 1215, 1078, 1064, 787, 759 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{11}H_{11}ClN_2$ $[MH]^+$: 207.0689; found : 207.0687.

1-(naphthalen-1-ylmethyl)azetidine-2-carbonitrile 13



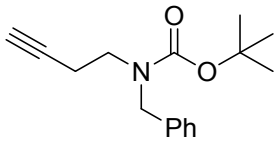
Colorless oil, Rf : 0.47 (PE/EtOAc 70/30), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.23 (d, 1H, J=8.1 Hz, Ar), 7.92-7.78 (m, 2H, Ar), 7.63-7.40 (m, 4H, Ar), 4.26 and 4.06 (two d, 2H, J=12.9 Hz, C***H*****$_2$**Napht), 4.00 (t, 1H, J=7.1 Hz, C***H***CN), 3.40 (q, 1H, J=6.6 Hz, NC***H***HCH_2), 3.20 (q, 1H, J=7.1 Hz, NCH***H***CH_2), 2.45 (q, 2H, J=7.0 Hz, NCH_2C***H*****$_2$**) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 133.86 (C_q), 132.04 (C_q), 131.89 (C_q), 128.63 (C_{Ar}), 128.59 (C_{Ar}), 127.14 (C_{Ar}), 126.26 (C_{Ar}), 125.88 (C_{Ar}), 125.21 (C_{Ar}), 124.08 (C_{Ar}), 118.94 (CH***C***N), 58.81 (N***C***H_2Napht), 52.58 (N***C***H_2CH_2), 51.99 (***C***HCN), 22.95 (NCH_2***C***H_2) ppm. IR : νmax = 3362 (b), 3048, 2968, 2837, 1172, 788, 773, 416 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{15}H_{15}N_2$ $[MH]^+$: 223.1235; found : 223.1239.

1-benzyl-2-phenylazetidine-2-carbonitrile 41



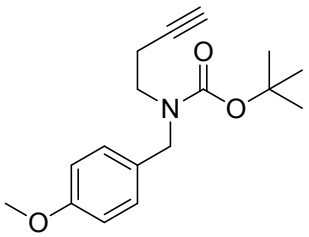
Colorless oil, Rf : 0.49 (PE/EtOAc 95/5), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72 (dd, *J* = 8.1, 1.5 Hz, 2H, Ph), 7.47-7.24 (m, 8H, Ph), 3.86 and 3.72 (two d, *J* = 12.9 Hz, 2H, NC***H*****$_2$**Ph), 3.43-3.36 (m, 1H, NC***H***HCH_2), 3.30 (dt, *J* = 9.6, 7.0 Hz, 1H, NCH***H***CH_2), 2.72 (ddd, *J* = 10.5, 7.3, 2.0 Hz, 1H, NCH_2C***H***H), 2.51 (td, *J* = 10.1, 8.1 Hz, 1H, NCH_2CH***H***) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.30 (C_q), 136.53 (C_q), 128.90 (C_{Ar}), 128.83 (C_{Ar}), 128.73 (C_{Ar}), 128.40 (C_{Ar}), 127.40 (C_{Ar}), 125.73 (C_{Ar}), 118.83 (C***C***N), 68.32 (***C***CN), 57.60 (N***C***H_2Ph), 49.54 (N***C***H_2CH_2), 34.60 (NCH_2***C***H_2) ppm. IR : νmax = 3026, 2965, 2836, 1495, 1448, 756, 694 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{17}H_{17}N_2$ $[MH]^+$: 249.1392; found : 249.1390.

***tert*-butyl benzyl(but-3-yn-1-yl)carbamate from 7**



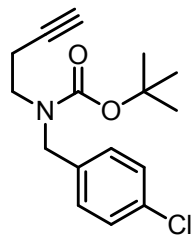
Treatment A, Yield: 179 mg, 69%. White solid, Mp : 34-36°C, Rf : 0.37 (PE/EtOAc 95/5), ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.20 (m, 5H, Ph), 4.54 (s, 2H, C***H*****$_2$**Ph), 3.42 and 3.32 (two s, 2H, NC***H*****$_2$**CH_2), 2.50-2.32 (m, 2H, NCH_2C***H*****$_2$**), 1.98 (t, J=2.6 Hz, 1H, CC***H***), 1.53 and 1.47 (two s, 9H, tBu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.61 and 155.43 (C_q), 138.40 and 138.21 (C_q), 128.53 (C_{Ar}), 127.75 (C_{Ar}), 127.24 (C_{Ar}), 80.03 (***C***CH), 69.56 (C***C***H), 51.41 and 50.46 (***C***H_2Ph), 45.82 and 45.51 (***C***H_2NBoc), 28.41 (tBu), 18.29 and 18.05 (***C***H_2CCH) ppm. IR : νmax = 3291, 2967, 1686, 1410, 1365, 1244, 1160, 1118, 879, 770, 733, 698, 634 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{16}H_{21}NNaO_2$ $[MNa]^+$: 282.1470; found : 282.1468.

***tert*-butyl but-3-yn-1-yl(4-methoxybenzyl)carbamate from 11**



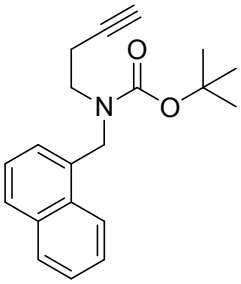
Treatment A, Yield: 216 mg, 75%. Colorless oil, Rf : 0.30 (PE/EtOAc 95/5), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18 (bs, 2H, Ar), 6.86 (d, 2H, J=5.7 Hz, Ar), 4.45 (s, 2H, C***H*****$_2$**Ar), 3.81 (s, 3H, O***Me***), 3.34 (m, 2H, NC***H*****$_2$**CH_2), 2.37 (m, 2H, NCH_2C***H*****$_2$**), 1.97 (t, 1H, J=2.6 Hz, CC***H***), 1.50 (s, 9H, tBu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.87 (C_q), 155.57 (C_q), 130.32 (C_q), 129.16 and 128.56 (C_{Ar}), 113.91 (C_{Ar}), 82.04 and 81.78 (***C***CH), 79.95 (O***C***Me_3), 69.52 (C***C***H), 55.26 (O***Me***), 50.72 and 49.83 (***C***H_2Ar), 45.46 and 45.21 (N***C***H_2CH_2), 28.43 (tBu), 18.28 and 17.99 (NCH_2***C***H_2) ppm. IR : νmax = 3294 (b), 2974, 2932, 1685, 1511, 1408, 1243, 1158, 1118, 1033, 632 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{15}H_{17}N_2O$ $[MH]^+$: 312.1576; found : 312.1576.

***tert*-butyl but-3-yn-1-yl(4-chlorobenzyl)carbamate from 12**



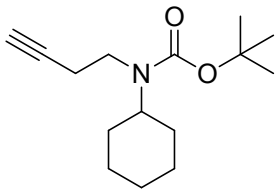
Treatment A,Yield: 221 mg, 75%. Colorless oil, Rf : 0.29 (PE/EtOAc 95/5), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34-7.26 (m, 2H, Ar), 7.18 (m, 2H, Ar), 4.48 (s, 2H, C***H*₂**Ar), 3.50-3.22 (m, 2H, NC***H*₂**CH_2), 2.52-2.18 (m, 2H, NCH_2C***H*₂**), 1.97 (s, 1H, CC***H***), 1.47 (two s, 9H, tBu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.61 and 155.21 (C_q), 137.01 and 136.78 (C_q), 133.01 (C_q), 129.09 and 128.42 (C_{Ar}), 128.69 (C_{Ar}), 81.90 and 81.61 (***C***CH), 80.26 (O***C***Me_3), 69.72 (C***C***H), 50.89 and 49.99 (***C***H_2Ar), 45.90 and 45.60 (N***C***H_2CH_2), 28.38 (tBu), 18.33 and 18.16 (NCH_2***C***H_2) ppm. IR : νmax = 3303, 2974, 1687, 1402, 1366, 1246, 1160, 1120, 1090, 798, 634 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{12}H_{13}ClNO_2$ $[M(-tBu)H]^+$: 238.0635; found : 238.0630.

***tert*-butyl but-3-yn-1-yl(naphthalen-1-ylmethyl)carbamate from 13**



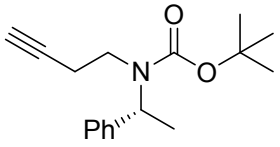
Treatment A, Yield: 216 mg, 70%. Colorless oil, Rf : 0.43 (PE/EtOAc 95/5), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20-7.98 (m, 1H, Ar), 7.96-7.77 (m, 2H, Ar), 7.60-7.30 (m, 4H, Ar), 5.04 (s, 2H, C***H*₂**Ar), 3.50-3.20 (m, 2H, NC***H*₂**CH_2), 2.57-2.15 (m, 2H, NCH_2C***H*₂**), 1.97 (t, 1H, J=2.6 Hz, CC***H***), 1.55 and 1.50 (two s, 9H, tBu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.36 (C_q), 133.85 (C_q), 133.24 (C_q), 131.28 (C_q), 128.68 and 128.42 (C_{Ar}), 126.60 and 126.38 (C_{Ar}), 125.86 (C_{Ar}), 125.26 (C_{Ar}), 124.82 (C_{Ar}), 123.91 (C_{Ar}), 123.05 (C_{Ar}), 82.07 and 81.76 (***C***CH), 80.20 (O***C***Me_3), 69.61 (C***C***H), 49.12 and 48.35 (***C***H_2Ar), 45.19 and 44.49 (N***C***H_2CH_2), 28.44 (tBu), 18.09 and 17.93 (NCH_2***C***H_2) ppm. IR : νmax = 3293 (b), 2977, 2929, 1682, 1411, 1365, 1247, 1156, 1115, 771, 634 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{20}H_{24}NO_2$ $[MH]^+$: 332.1626; found : 332.1623.

tert-butyl but-3-yn-1-yl(cyclohexyl)carbamate from 14



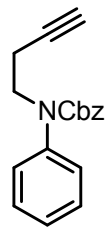
Treatment A, Yield: 152 mg, 60%. White solid, Mp : 64-66°C, Rf : 0.60 (PE/EtOAc 95/5), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.00-3.40 (m, 1H, $(CH_2)_2CHN$), 3.37-3.07 (m, 2H, NCH_2), 2.37 (t, 2H, J=6.5 Hz, CH_2CCH), 1.99-1.94 (m, 1H, CH_2CCH), 1.85-0.95 (m, 19H, N***Cy*** and N***Boc***) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.16 (C_q), 81.81 (C_q), 79.50 (CH_2CCH), 69.46 (CH_2CCH), 56.62 and 54.90 ($(CH_2)_2CHN$), 41.98 (NCH_2), 31.20 (N***Cy***), 28.46 (N***Boc***), 25.95 (N***Cy***), 25.51 (N***Cy***), 20.24 (CH_2CCH) ppm. IR : νmax = 3235, 2983, 2948, 2920, 2856, 1678, 1410, 1364, 1297, 1157, 709 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{15}H_{26}NO_2$ $[MH]^+$: . 274.1783; found : 274.1786.

(*R*)-*tert*-butyl but-3-yn-1-yl(1-phenylethyl)carbamate from 4



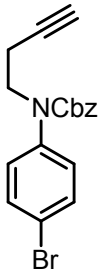
Treatment A, Yield: 177 mg, 64%. White solid, Mp : 38-40°C, Rf : 0.47 (PE/EtOAc 95/5), $[\alpha]_D^{20}$ +72 (*c* 1.3, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40-7.23 (m, 5H, Ph), 5.70-5.05 (m, 2H, C***H***Me), 3.40-2.90 (m, 2H, CH_2N), 2.50-1.97 (m, 2H, CH_2CCH), 1.92 (t, J=2.7 Hz, 1H, CH_2CCH), 1.55 (d, J=3.6 Hz, 3H, CH***Me***), 1.49 (s, 9H, tBu)) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.43 (C_q), 141.61 (C_q), 128.40 (C_{Ar}), 127.24 (C_{Ar}), 127.00 (C_{Ar}), 81.77 (***C***CH), 79.91 (O***C***Me_3), 69.46 (CH_2CCH), 53.07 (***C***HMe), 42.71 (CH_2N), 28.45 (tBu), 19.41 (CH_2CCH), 17.41 (CH***Me***) ppm. IR : νmax = 3244, 2972, 1670, 1408, 1365, 1300, 1156, 772, 696 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{17}H_{24}NO_2$ $[MH]^+$: 296.1626; found : 296.1635.

benzyl but-3-yn-1-yl(phenyl)carbamate from 16



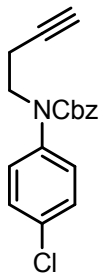
Treatment B, Yield: 189 mg, 68%. Colorless oil, Rf : 0.34 (PE/EtOAc 90/10), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47-7.12 (m, 10H, Ar), 5.18 (s, 2H, Cbz), 3.89 (t, *J* = 7.3 Hz, 2H, NC***H*****$_2$**CH_2), 2.47 (td, *J* = 7.3, 2.6 Hz, 2H, NCH_2C***H*****$_2$**), 1.96 (t, *J* = 2.7 Hz, 1H, CH_2CC***H***) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.31 (C_q), 141.30 (C_q), 136.57 (C_q), 129.12 (C_{Ar}), 128.42 (C_{Ar}), 127.90 (C_{Ar}), 127.60 (C_{Ar}), 127.48(C_{Ar}), 127.06(C_{Ar}), 81.13 (***C***CH), 70.03 (C***C***H), 67.28 (***C***H_2Ph), 49.09 (N***C***H_2CH_2), 18.25 (NCH_2***C***H_2) ppm. IR : νmax = 3287, 3062, 3031, 2952, 1697, 1493, 1400, 1292, 1197, 1134, 1061, 752, 695 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{18}H_{18}NO_2$ $[MH]^+$: 280.1338; found : 280.1333

benzyl (4-bromophenyl)(but-3-yn-1-yl)carbamate from 17



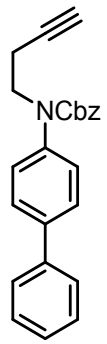
Treatment B, Yield: 253 mg, 71%. White solid, Mp : 83-85°C, Rf : 0.22 (PE/EtOAc 95/5), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.6 Hz, 2H, Ar), 7.43-7.22 (m, 5H, Ar), 7.14 (d, *J* = 8.4 Hz, 2H, Ar), 5.17 (s, 2H, Cbz), 3.85 (t, *J* = 7.1 Hz, 2H, NC***H*****$_2$**CH_2), 2.45 (td, *J* = 7.1, 2.5 Hz, 2H, NCH_2C***H*****$_2$**), 1.95 (t, *J* = 2.6 Hz, 1H, CC***H***) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.02 (C_q), 140.44 (C_q), 136.28 (C_q), 132.23 (C_{Ar}), 129.10 (C_{Ar}), 128.50 (C_{Ar}), 128.07 (C_{Ar}), 127.79 (C_{Ar}), 120.53 (C_q), 80.92 (C_q), 70.31 (C***C***H), 67.53 (***C***H_2Ph), 48.96 (N***C***H_2CH_2), 18.27 (NCH_2***C***H_2) ppm. IR : νmax = 3293, 1690, 1491, 1310, 1296, 855, 630cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{18}H_{17}BrNO_2$ $[MH]^+$: 358.0443; found : 358.1449.

benzyl but-3-yn-1-yl(4-chlorophenyl)carbamate from 18



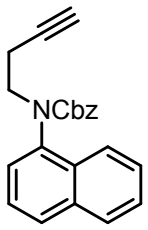
Treatment B, Yield: 219 mg, 69%. Colorless oil, Rf : 0.34 (PE/EtOAc 90/10), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43-7.12 (m, 9H, Ar), 5.17 (s, 2H, Cbz), 3.85 (t, *J* = 7.1 Hz, 2H, NC***H*****$_2$**CH_2), 2.46 (td, *J* = 7.1 and 2.5 Hz, 2H, NCH_2C***H*****$_2$**), 1.96 (t, *J* = 2.5 Hz, 1H,. CC***H***) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.09 (C_q), 139.90 (C_q), 136.30 (C_q), 132.59 (C_q), 129.25 (C_{Ar}), 128.76 (C_{Ar}), 128.49 (C_{Ar}), 128.06 (C_{Ar}), 127.76 (C_{Ar}), 80.93 (C_q), 70.28 (C***C***H), 67.50 (***C***H_2Ph), 49.00 (N***C***H_2CH_2), 18.26 (NCH_2***C***H_2) ppm. IR : νmax = 3268, 1708, 1492, 1284, 838, 694 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{18}H_{17}NO_2$ $[MH]^+$: 314.0948; found : 314.0943.

benzyl [1,1'-biphenyl]-4-yl(but-3-yn-1-yl)carbamate from 19



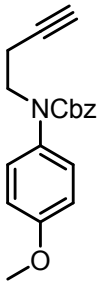
Treatment B, Yield: 211 mg, 60%. White solid, Mp : 74-76°C, Rf : 0.34 (PE/EtOAc 90/10), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.2 Hz, 4H, Ar), 7.47 (t, *J* = 7.4 Hz, 2H, Ar), 7.43-7.19 (m, 8H, Ar), 5.21 (s, 2H, Cbz), 3.93 (t, *J* = 7.3 Hz, 2H, NC***H*****$_2$**CH_2), 2.52 (td, *J* = 7.3, 2.5 Hz, 2H, NCH_2C***H*****$_2$**), 1.98 (t, *J* = 2.5 Hz, 1H, CC***H***) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.32 (C_q), 140.49 (C_q), 140.33 (C_q), 139.89 (C_q), 136.52 (C_q), 128.85 (C_{Ar}), 128.46 (C_{Ar}), 127.96 (C_{Ar}), 127.79 (C_{Ar}), 127.64 (C_{Ar}), 127.49 (C_{Ar}), 127.11 (C_{Ar}), 81.12 (***C***CH), 70.10 (C***C***H), 67.39 (C***H*****$_2$**Ph), 49.09 (N***C***H_2CH_2), 18.32 (NCH_2***C***H_2) ppm. IR : νmax = 3281, 1702, 1361, 1251, 1195, 829, 685 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{24}H_{22}NO_2$ $[MH]^+$: 356.1651; found : 356.1651.

benzyl but-3-yn-1-yl(naphthalen-1-yl)carbamate from 20



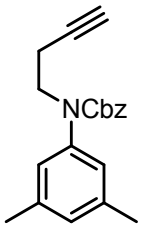
Treatment B, Yield: 143 mg, 44%. Colorless oil, Rf : 0.30 (PE/EtOAc 90/10), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03-7.76 (m, 3H, Ar), 7.62-7.35 (m, 5H, Ar), 7.33-7.12 (m, 2H, Ar), 7.10-6.95 (m, 2H, Ar), 5.34 and 5.10 (two s, 2H, Cbz), 4.37-4.15 (m, 1H, NC***H***HCH$_2$), 3.85-3.63 (m,1H, NCH***H***CH$_2$), 2.65-2.45 (m, 2H, NCH$_2$C***H$_2$***), 1.97 (t, *J* = 2.6 Hz, 1H, CC***H***) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.03 (C_q), 137.35 (C_q), 136.58 (C_q), 134.62 (C_q), 130.57 (C_q), 128.51 (C_{Ar}), 128.39 (C_{Ar}), 128.21 (C_{Ar}), 127.66 (C_{Ar}), 127.26 (C_{Ar}), 126.90 (C_{Ar}), 126.35 (C_{Ar}), 126.06 (C_{Ar}), 125.57 (C_{Ar}), 122.67 (C_{Ar}), 81.25 (***C***CH), 70.04 (C***C***H), 67.12 (***C***H$_2$Ph), 49.24 (N***C***H$_2$CH$_2$), 18.45 (NCH$_2$***C***H$_2$) ppm. IR : νmax = 3255, 2952, 2898, 1687, 1470, 1293, 962, 769, 699 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{22}H_{20}NO_2$ [MH]$^+$: 330.1494; found : 330.1487.

benzyl but-3-yn-1-yl(4-methoxyphenyl)carbamate from 21



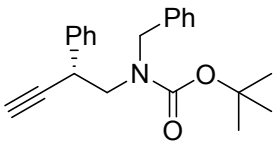
Treatment B, Yield: 102 mg, 33%. Colorless oil, Rf : 0.20 (PE/EtOAc 90/10), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51-7.05 (m, 7H, Ar), 6.90 (d, *J* = 8.8 Hz, 2H, Ar), 5.21 and 5.15 (two s, 2H, Cbz), 3.88-3.76 (m, 5H, NC***H$_2$***CH$_2$ and OMe), 2.45 (td, *J* = 7.2 and 2.5 Hz, 2H, NCH$_2$C***H$_2$***), 1.95 (t, *J* = 2.6 Hz, 1H, CC***H***) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.39 (C_q), 155.61 (C_q), 136.68 (C_q), 133.95 (C_q), 128.71 and 128.61 (C_{Ar}), 128.40 and 128.30 (C_{Ar}), 127.79 (C_{Ar}), 127.33 (C_{Ar}), 114.30 (C_{Ar}), 81.23 (***C***CH), 69.94 (C***C***H), 67.12 (***C***H$_2$Ph), 55.45 (O***Me***), 49.25 (N***C***H$_2$CH$_2$), 18.07 (NCH$_2$***C***H$_2$) ppm. IR : νmax = 3281, 2955, 1697, 1510, 1400, 1132, 1026, 696 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{19}H_{20}NO_3$ [MH]$^+$: 310.1443; found : 310.1456.

benzyl but-3-yn-1-yl(3,5-dimethylphenyl)carbamate from 22

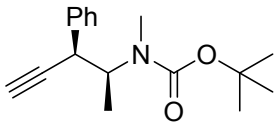


Treatment B, Yield: 100 mg, 31%. Colorless oil, Rf : 0.39 (PE/EtOAc 90/10), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48-7.22 (m, 5H, Ar), 6.95 (s, 1H, Ar), 6.88 (s, 2H, Ar), 5.20 (s, 2H, Cbz), 3.87 (t, *J* = 7.4 Hz, 2H, NC***H*****$_2$**CH_2), 2.50 (td, *J* = 7.5, 2.6 Hz, 2H, NCH_2C***H*****$_2$**), 2.35 (s, 6H, Me), 1.98 (t, *J* = 2.6 Hz, 1H, CC***H***)ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.40 (C_q), 141.09 (C_q), 138.75 (C_q), 136.71 (C_q), 128.81 (C_{Ar}), 128.42 (C_{Ar}), 127.90 (C_{Ar}), 127.69 (C_{Ar}), 125.12 (C_{Ar}), 81.26 (***C***CH), 69.95 (C***C***H), 67.21 (***C***H_2Ph), 49.13 (N***C***H_2CH_2), 21.25 (Me), 18.26 (NCH_2***C***H_2) ppm. IR : νmax = 3243, 2918, 1697, 1595, 1401, 1226, 1143, 6893243, 2918, 1697, 1595, 1401, 1226, 1143, 689 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{20}H_{22}NO_2$ $[MH]^+$: 308.1651; found : 308.1651.

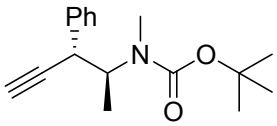
(*R*)-*tert*-butyl methyl(2-phenylbut-3-yn-1-yl)carbamate from 23



Treatment A, Yield: 230 mg, 69%. Colorless oil, Rf : 0.57 (PE/EtOAc 90/10), $[\alpha]_D^{20}$ +17 (*c* 0.9, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48-7.08 (m, 10H, Ph), 4.58-4.23 (m, 2H, C***H*****$_2$**Ph), 4.23-3.95 (two td, J=2.4 and 7.5 Hz, 1H, C***H***Ph), 3.44 (two d, J=7.5 Hz, 2H, CHPhC***H*****$_2$**NBoc), 2.30 (d, J=2.4 Hz, 1H, CC***H***), 1.48 (two s, 9H, tBu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.67 (C_q), 138.62 (C_q), 138.00 (C_q), 128.68 (C_{Ar}), 128.50 (C_{Ar}), 127.77 (C_{Ar}), 127.36 (C_{Ar}), 127.11 (C_{Ar}), 80.11 (***C***CH), 72.10 (C***C***H), 54.08 and 53.25 (***C***H_2NBoc), 52.07 and 50.68 (***C***H_2Ph), 37.31 and 36.72 (***C***HPh), 28.40 (tBu) ppm. IR : νmax = 3288, 2970, 1687, 1453, 1409, 1364, 1244, 1226, 1157, 1116, 749, 697, 639, 547 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{17}H_{18}N$ $[M(-Boc)H]^+$: 236.1439; found : 236.1439.

***tert*-butyl methyl((2*S*,3*S*)-3-phenylpent-4-yn-2-yl)carbamate from 8** 

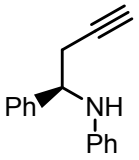
Treatment A, Yield: 235 mg, 86%. White solid, Mp : 95-97°C, Rf : 0.45 (PE/EtOAc 95/5), $[\alpha]_D^{20}$ +2 (*c* 1.3, $CHCl_3$), ^1H NMR (300 MHz, $CDCl_3$): δ = 7.45-7.20 (m, 5H, Ph), 4.67-4.47 and 4.45-4.24 (two m, 1H, C***H***Me), 3.76 and 3.72 (two d, J = 2.2 Hz, 1H, C***H***Ph), 2.83 and 2.76 (two s, 3H, N***Me***), 2.23 (t, J=3.2 Hz, 1H, CC***H***), 1.45 and 1.43 (two s, 9H, tBu), 1.11 and 1.06 (two d, J=7.0 Hz, 3H, CH***Me***) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.84 and 155.60 (C_q), 138.87 and 138.68 (C_q), 128.61 (C_{Ar}), 128.51 (C_{Ar}), 128.46 (C_{Ar}), 128.37 (C_{Ar}), 127.33 (C_{Ar}), 127.26 (C_{Ar}), 83.85 (***C***CH), 79.61 and 79.28 (O***C***Me_3), 72.01 and 71.51 (C***C***H), 55.84 and 55.03 (C***H***Me), 43.01 and 42.46 (C***H***Ph), 29.11 (N***Me***), 28.43 and 28.39 (tBu), 16.23 and 15.64 (CH***Me***) ppm. IR : νmax = 3222, 2967, 1681, 1137, 718, 699 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{17}H_{24}NO_2$ $[MH]^+$: 174.1283; found : 174.1283.

***tert*-butyl methyl((2*S*,3*R*)-3-phenylpent-4-yn-2-yl)carbamate from 26** 

Treatment A, Yield: 32 mg, 12%. Colorless oil, Rf : 0.33 (PE/EtOAc 95/5), $[\alpha]_D^{20}$ +19 (*c* 1.3, $CHCl_3$), ^1H NMR (300 MHz, $CDCl_3$): δ = 7.48-7.18 (m, 5H, Ph), 4.47-4.16 (m, 1H, C***H***Me), 4.00-3.90 and 3.89-3.78 (two m, 1H, C***H***Ph), 2.80 and 2.74 (two s, 3H, N***Me***), 2.33 (d, J=2.1 Hz, 1H, CC***H***), 1.41-1.27 (m, 12H, CH***Me*** and tBu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.35 and 155.10 (C_q), 138.84 (C_q), 128.37 and 128.28 (C_{Ar}), 127.96 (C_{Ar}), 127.16 and 126.99 (C_{Ar}), 83.86 (***C***CH), 79.65 and 79.29 (O***C***Me_3), 72.83 (C***C***H), 56.53 and 56.05 (***C***HMe), 42.38 and 42.27 (***C***HPh), 29.97 and 28.92 (N***Me***), 28.34 (tBu), 15.49 and 14.41 (CH***Me***) ppm. IR : νmax = 3298, 3240, 2977, 1682, 1333, 1143, 698, 638

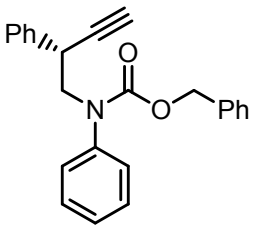
cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{17}H_{24}NO_2$ $[MH]^+$: 218.1181; found : 218.1175.

(*R*)-*N*-(1-phenylbut-3-yn-1-yl)aniline from 28



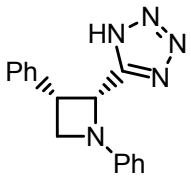
Treatment C, Yield: 135 mg, 61%. Colorless oil, Rf : 0.45 (PE/EtOAc 98/2), $[\alpha]_D^{20}$ +1 (*c* 1.1, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49-7.28 (m, 5H, Ph), 7.17 (dd, *J* = 8.5, 7.4 Hz, 2H, Ph), 6.75 (t, *J* = 7.4 Hz, 1H, Ph), 6.62 (dd, *J* = 8.5 Hz, 2H, Ph), 4.60 (t, *J* = 6.2 Hz, 1H, C***H***Ph), 4.47 (bs, 1H, NH), 2.83 (ddd, *J* = 16.5, 5.4, 2.7 Hz, 1H, C***H***HCCH), 2.71 (ddd, *J* = 16.5, 6.9, 2.7 Hz, 1H, CH***H***CCH), 2.12 (t, *J* = 2.6 Hz, 1H, CC***H***) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.05 (C_q), 142.15 (C_q), 129.20 (C_{Ar}), 128.70 (C_{Ar}), 127.56 (C_{Ar}), 126.45 (C_{Ar}), 117.95 (C_{Ar}), 113.84 (C_{Ar}), 80.37 (***C***CH), 71.47 (C***C***H), 56.55 (***C***HPh), 28.10 (***C***H_2) ppm. IR : νmax = 3411, 3281, 3037, 2911, 1599, 1502, 1313, 1264, 747, 692, 640 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{16}H_{16}N$ $[MH]^+$: 222.1283; found : 222.1286.

(*R*)-benzyl phenyl(2-phenylbut-3-yn-1-yl)carbamate from 29



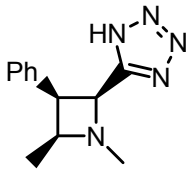
Treatment B, Yield: 121 mg, 55%. Colorless oil, Rf : 0.15 (PE/EtOAc 95/5), $[\alpha]_D^{20}$ -4 (*c* 1.2, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42-6.85 (m, 15H, Ph), 5.05 (s, 2H), 4.10-3.85 (m, 2H, C***H***Ph and NC***H***H), 3.74 (dd, *J* = 12.6, 6.2 Hz, 1H, NCH***H***), 2.12 (d, *J* = 2.2 Hz, 1H, CC***H***) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.45 (C_q), 141.75 (C_q), 138.16 (C_q), 136.58 (C_q), 128.90 (C_{Ar}), 128.63 (C_{Ar}), 128.40 (C_{Ar}), 127.96 (C_{Ar}), 127.48 (C_{Ar}), 127.42 (C_{Ar}), 126.87 (C_{Ar}), 83.64 (***C***CH), 72.33 (C***C***H), 67.29 (***C***H_2Ph), 56.73 (N***C***H_2), 36.79 (***C***HPh) ppm. IR : νmax = 3284, 3059, 3027, 1697, 1593, 1492, 1398, 1275, 1204, 1135, 749, 695 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{24}H_{22}NO_2$ $[MH]^+$: 356.1656; found : 356.1656.

5-((2*S*,3*R*)-1,3-diphenylazetidin-2-yl)-1H-tetrazole 32



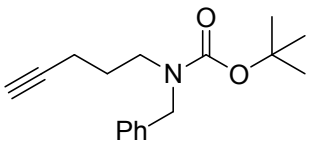
Treatment D, Yield: 88 mg, 65%. White solid, Rf : 0.15 (PE/EtOAc/AcOH 85/15/2), $[\alpha]_D^{20}$ -44 (*c* 1.3, EtOH), ^{1}H NMR (300 MHz, MeOD): δ = 7.22(d, *J* = 7.2 Hz, 2H, Ph), 7.15-6.97 (m, 5H, Ph), 6.72 (t, *J* = 7.4 Hz, 1H, Ph), 6.37 (d *J* = 8.4 Hz, 2H, Ph), 5.69-5.60 (m, 1H, C***H***Tet), 4.34-4.28 (m, 1H, NCH***H***), 4.24-4.12 (m, 2H, NC***H***H and C***H***Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.95 (C_q), 151.90 (C_q), 138.68 (C_q), 130.13 (C_{Ar}), 129.47 (C_{Ar}), 129.09 (C_{Ar}), 128.40 (C_{Ar}), 120.53 (C_{Ar}), 113.62 (C_{Ar}), 63.14 (***C***HTet), 56.52 (N***C***H_2), 41.21 (***C***HPh) ppm. IR : νmax = 3119, 3034, 2882, 2774, 1593, 1477, 1323, 1297, 1045, 742, 692 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{16}H_{16}N_5$ $[MH]^+$: 278.1406; found : 278.1407.

5-((2*S*,3*R*,4*S*)-1,4-dimethyl-3-phenylazetidin-2-yl)-1H-tetrazole 31



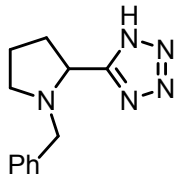
Treatment D, Yield: 138 mg, 60%. White solid, Mp : 188-190°C (degradation), $[\alpha]_D^{20}$ -65 (*c* 0.4, EtOH), ^{1}H NMR (300 MHz, MeOD): δ = 7.17 (s, 5H, Ar), 5.59 (d, *J* = 8.7 Hz, 1H, C***H***Tet), 4.51-4.39 (dd, *J* = 14.1, 7.2 Hz, 1H, C***H***Me), 4.32 (t, *J* = 8.6 Hz, 1H, C***H***Ph), 2.92 (s, 3H, N***Me***), 1.15 (d, *J* = 6.7 Hz, 3H, CH***Me***) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.23 (CH***C***N_4), 134.76 (C_q), 131.16 (C_{Ar}), 129.10 (C_{Ar}), 128.63 (C_{Ar}), 68.23 (***C***HMe), 65.59 (***C***HCN_4), 47.29 (***C***HPh), 41.64 (N***Me***), 13.94 (CH***Me***) ppm. IR : νmax = 2962, 2825, 1475, 1337, 1080, 926, 763, 700, 597, 489 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{12}H_{16}N_5$ $[MH]^+$: 230.1406; found : 230.1399.

***tert*-butyl benzyl(pent-4-yn-1-yl)carbamate 36**



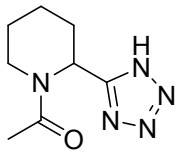
Treatment A, Yield: 64 mg, 23%. Colorless oil, Rf : 0.62 (PE/EtOAc 90/10), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40-7.20 (m, 5H, Ph), 4.46 (s, 2H, C***H*****$_2$**Ph), 3.29 (m, 2H, NC***H*****$_2$**CH_2), 2.18 (m, 2H, NCH_2C***H*****$_2$**), 1.96 (t, J=2.6 Hz, 1H, CC***H***), 1.75 (m, 2H, C***H*****$_2$**CCH) 1.49 (s, 9H, tBu) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.85 (C_q), 138.46 (C_q), 128.51 (C_{Ar}), 127.68 (C_{Ar}), 127.18 (C_{Ar}), 83.68 (***C***CH), 79.82 (O***C***Me_3), 68.72 (C***C***H), 50.90 and 50.07 (***C***H_2Ph), 45.81 and 45.56 (NCH_2***C***H_2), 28.45 (tBu), 26.94 (***C***H_2CCH), 15.99 (NCH_2***C***H_2) ppm. IR : νmax = 3305, 2972, 2927, 1687, 1413, 1365, 1242, 1158, 1119, 698, 631 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{12}H_{16}N$ [M(-Boc)H]$^{+}$: 174.1283; found : 174.1280.

5-(1-benzylpyrrolidin-2-yl)-1H-tetrazole 37



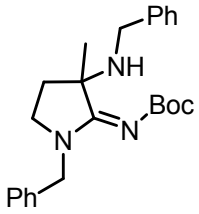
Treatment D, Yield: 80 mg, 35%. White solid, Mp : 131-133°C (degradatoin), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.17 (bs, 1H, N***H***), 7.42-7.30 (m, 5H, Ph), 4.81 (t, J=8.4 Hz, 1H C***H***Tet), 4.25 (d, J=13.5 Hz, 2H, C***H*****$_2$**Ph), 4.16 (m, 1H, NC***H***H), 4.06 (d, J=13.5 Hz, 2H, C***H*****$_2$**Ph), 3.16 (q, J=9.3 Hz, 1H, NCH***H***), 2.59-2.48 (m, 1H, C***H***HCHTet), 2.39-2.22 (m, 2H, NCH_2C***H***H and CH***H***CHTet), 2.17-2.01 (m, 1H, NCH_2CH***H***) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.43 (C_q), 131.30 (C_{Ar}), 129.68 (C_{Ar}), 129.11 (C_{Ar}), 60.05 (***C***HTet), 54.80 (***C***H_2Ph), 52.01 (N ***C***H_2), 30.44 (***C***H_2CHTet), 21.17 (NCH_2***C***H_2) ppm. IR : νmax = 2964, 2439, 1449, 1040, 1017, 741, 695 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{12}H_{16}N_5$ [MH]$^{+}$: 230.1406; found : 230.1404.

1-(2-(1H-tetrazol-5-yl)piperidin-1-yl)ethanone 39



Treatment C, Yield: 80%. White sticky solid, Rf : 0.15 (PE/EtOAc/MeOH/AcOH 30/70/1/1), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.17 (d, J=5.1 Hz, 1H, C***H***Tet, *majo*), 5.41 (d, J=5.1 Hz, 1H, C***H***Tet, *mino*), 4.66 (d, J=12.6 Hz, 1H, NC***H*****$_2$**, *mino*), 3.75 (d, J=13.5 Hz, 1H, NC***H*****$_2$**, *majo*), 3.25 (dt, J=13.5 Hz and 2.4 Hz, 1H, NC***H*****$_2$**, *majo*), 2.86 (d, J=13.2 Hz, 1H, C***H*****$_2$**CHTet, *mino*), 2.44 (m, 1H, NC***H*****$_2$**, *mino*), 2.37 (d, J=14.1 Hz, 1H, C***H*****$_2$**CHTet, *majo*), 2.27-1.45 (m, 8H, C***H*****$_3$** and C***H*****$_2$**C***H*****$_2$**C***H*****$_2$**CHTet) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.68 and 171.13 (C_q), 156.60 and 156.18 (C_q), 50.73 and 43.78 (***C***HTet), 43.72 and 39.02 (N***C***H_2), 28.33 and 27.29 (***C***H_2CHTet), 25.30 and 24.66 (***C***H_2***C***$H_2$$CH_2$CHTet), 21.58 and 21.51 (***C***H_3), 19.57 and 19.49 (***C***H_2***C***$H_2$$CH_2$CHTet) ppm. IR : νmax = 2932, 2857, 2720, 1595, 1421, 1264, 1236, 1033, 987 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_8H_{14}N_5O$ $[MH]^+$: 196.1198; found : 196.1194.

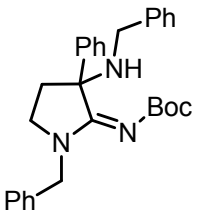
(*E*)-*tert*-butyl (1-benzyl-3-(benzylamino)-3-methylpyrrolidin-2-ylidene)carbamate 43



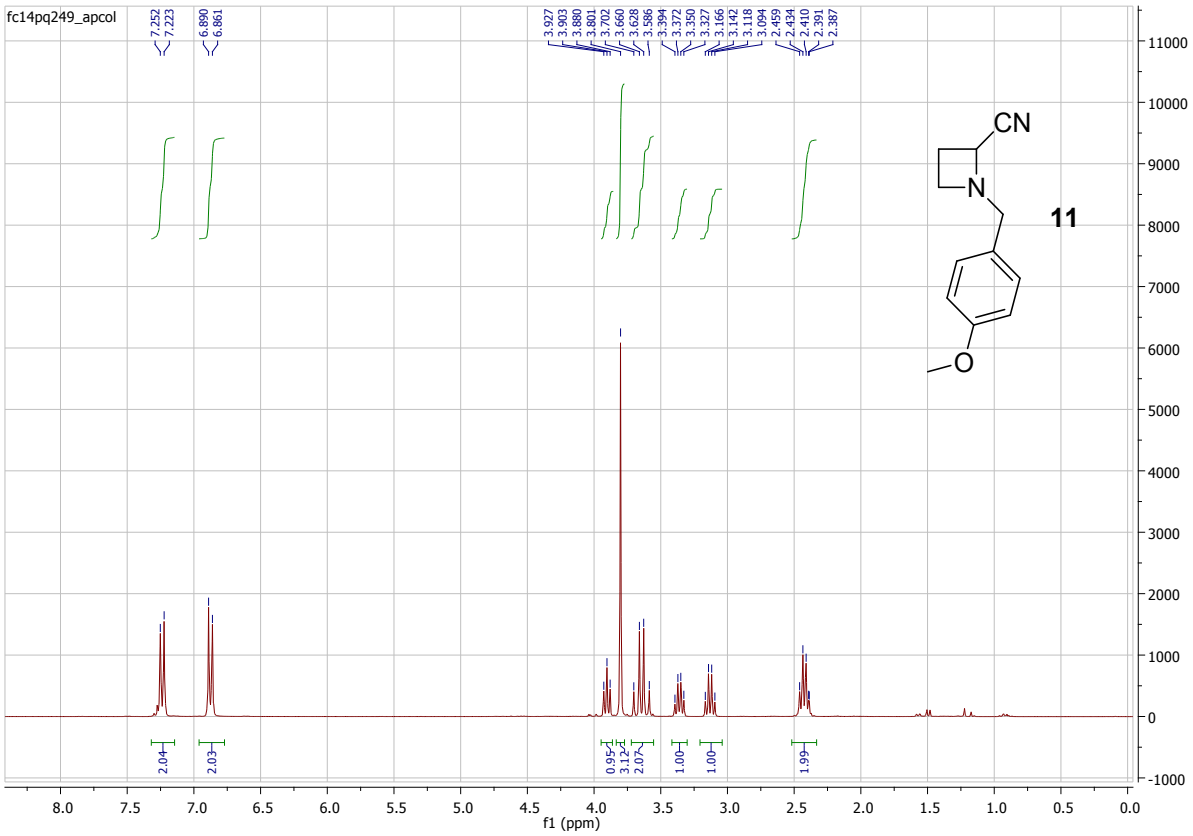
Treatment A, Yield: 79 mg, 20%. Colorless oil, Rf : 0.24 (PE/EtOAc 80/20), ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43-7.20 (m, 10H, Ph), 4.64 (two d, 2H, J=14.4 Hz, NC***H*****$_2$**Ph), 3.75 (s, 2H, NHC***H*****$_2$**Ph), 3.30-3.15 (m, 2H, NC***H*****$_2$**CH_2), 2.40-2.25 (m, 1H, NCH_2C***H***H), 1.90-1.77 (m, 1H, NCH_2CH***H***), 1.63 (s, 3H, C***Me***), 1.49 (s, 9H, N***Boc***) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.48 (N-***C***=N), 161.72 (C_q), 140.13 (C_q) 135.89 (C_q), 128.76 (C_{Ar}), 128.36 (C_{Ar}), 128.23 (C_{Ar}), 128.03 (C_{Ar}), 127.75 (C_{Ar}), 126.94 (C_{Ar}), 79.26 (C_q), 65.58 (C_q), 49.20 (N***C***H_2Ph), 47.65 (NH***C***H_2Ph), 45.56 (N***C***$H_2$$CH_2$), 32.65 ($NCH_2$***C***$H_2$), 28.20 (N***Boc***), 24.11 (C***Me***) ppm. IR : νmax = 2980, 2930, 2866, 1564, 1599, 1494,

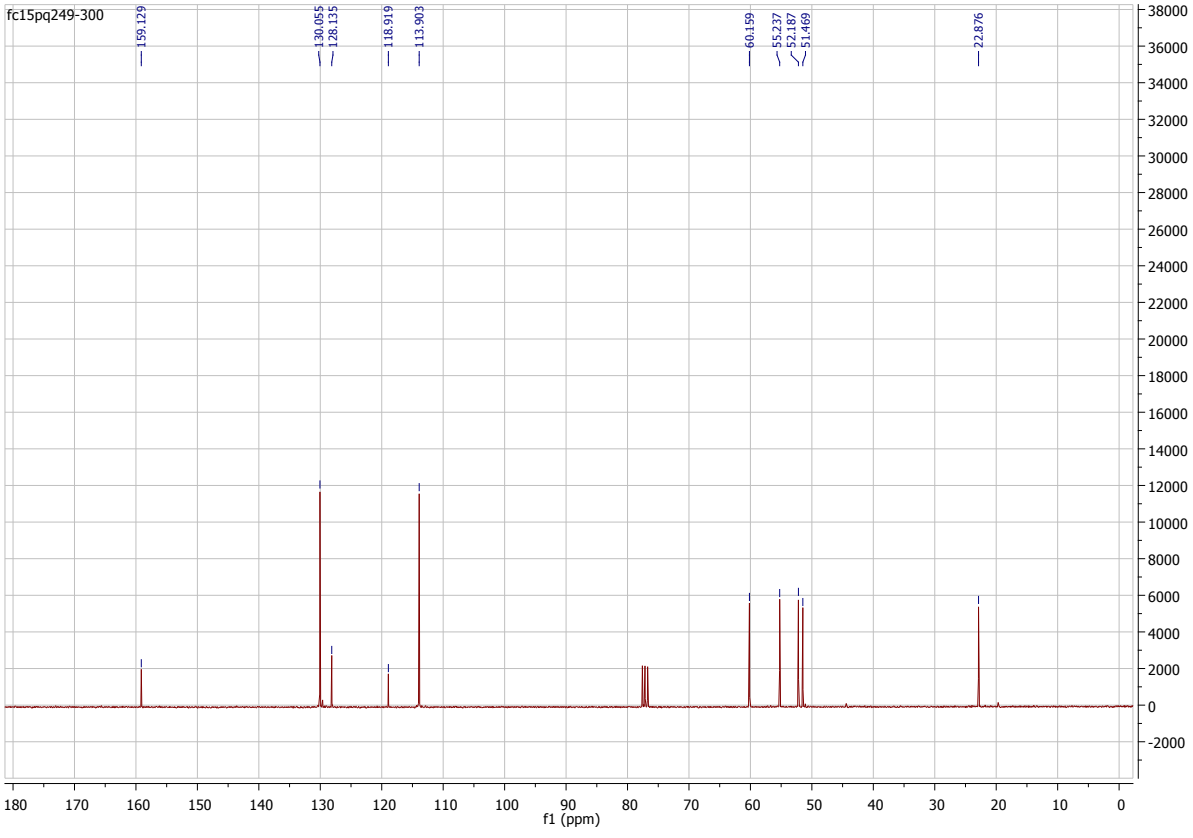
1452, 1364, 1244, 1146, 1121, 733, 698 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{24}H_{32}N_3O_2$ $[MH]^+$: 394.2495; found : 394.2467.

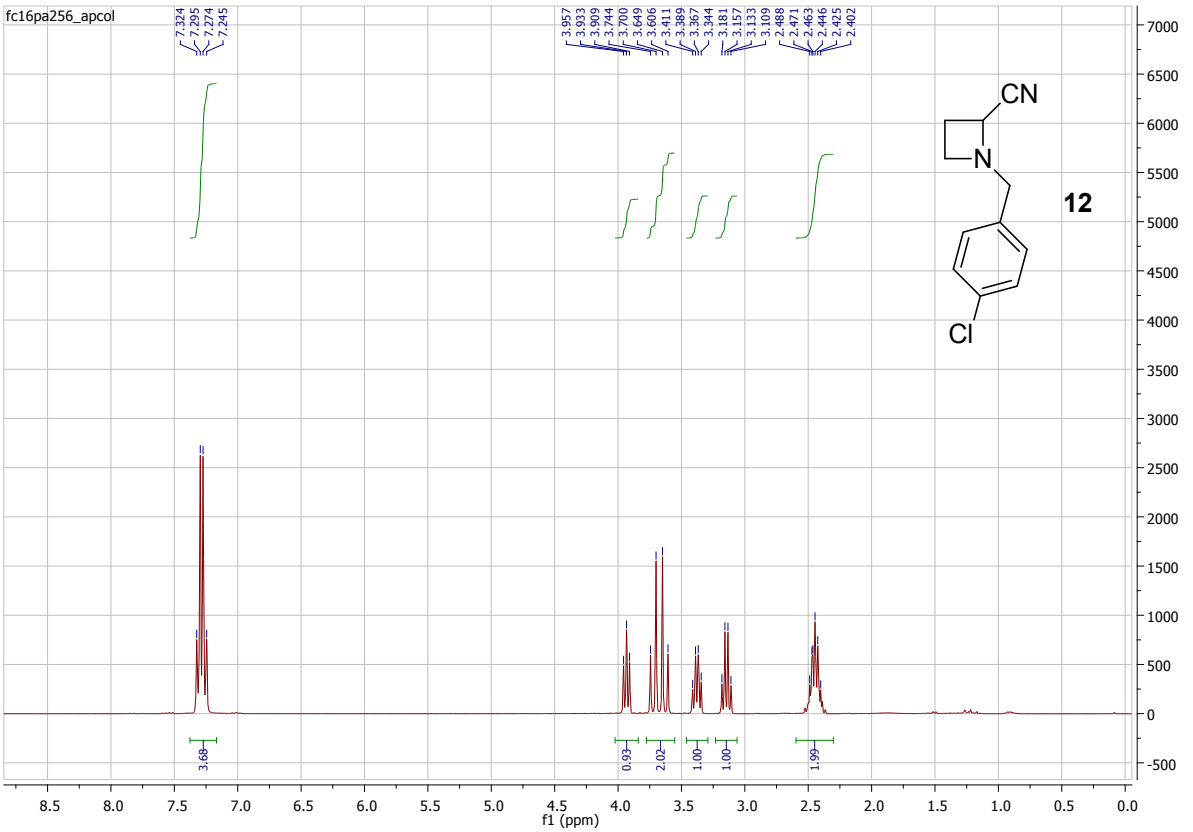
(*E*)-*tert*-butyl (1-benzyl-3-(benzylamino)-3-phenylpyrrolidin-2-ylidene)carbamate 44

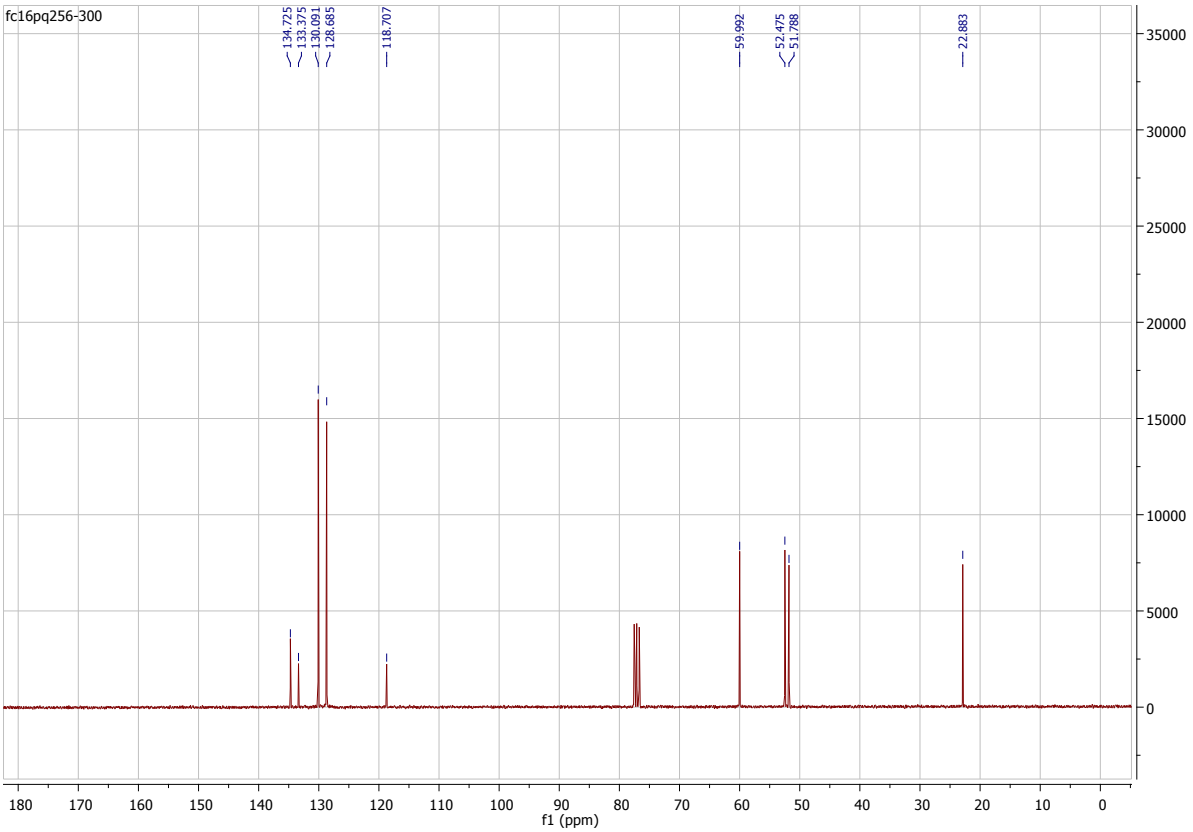


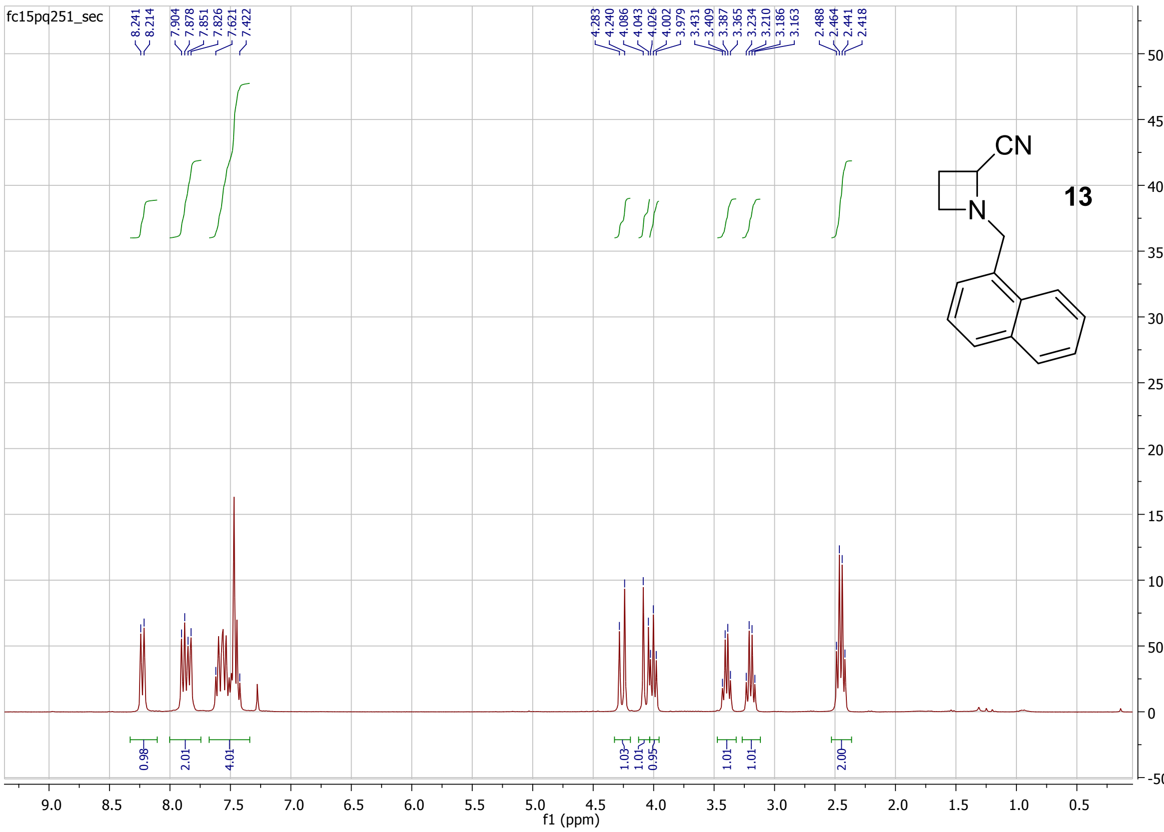
Treatment A, Yield: 60 mg, 13%. Colorless oil, Rf : 0.42 (PE/EtOAc 85/15), ^1H NMR (300 MHz, $CDCl_3$): δ = 7.55 (d, 2H, J=7.2 Hz, Ph), 7.48-7.20 (m, 13H, Ph), 5.04 and 4.55 (two d, 2H, J=14.4 Hz, NC***H*****$_2$**Ph), 3.86 (s, 2H, NHC***H*****$_2$**Ph), 3.39-3.21 (m, 2H, NC***H*****$_2$**CH_2), 2.56-2.39 (m, 1H, NCH_2C***H***H), 2.25-2.10 (m, 1H, NCH_2CH***H***), 1.13 (s, 9H, N***Boc***) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.51 (N-***C***=N), 161.37 (C_q), 144.22 (C_q), 136.06 (C_q), 128.82 (C_{Ar}), 128.78 (C_{Ar}), 128.32 (C_{Ar}), 128.25 (C_{Ar}), 128.02 (C_{Ar}), 127.93 (C_{Ar}), 127.12 (C_{Ar}), 126.89 (C_{Ar}), 126.00 (C_{Ar}), 79.03 (C_q), 71.91 (C_q), 49.34 (N***C***H_2Ph), 47.70 (NH***C***H_2Ph), 46.48 (N***C***H_2CH_2), 35.88 (NCH_2***C***H_2), 27.70 (N***Boc***) ppm. IR : νmax = 2975, 1657, 1597, 1496, 1453, 1243, 1133, 732, 697 cm^{-1}. HRMS (TOF MSES positive mode) *m/z* calcd. for $C_{29}H_{34}N_3O_2$ $[MH]^+$: 456.2651; found : 456.2646.

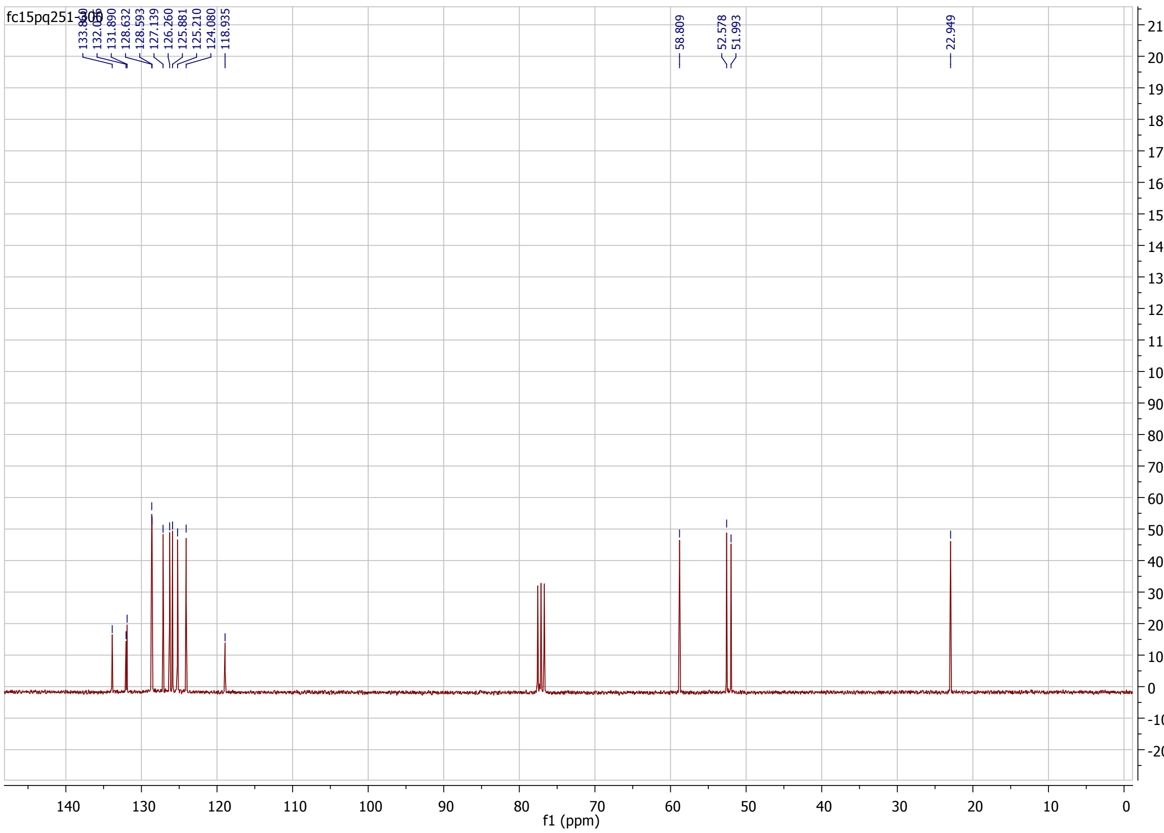

fc14pq249_apcol
7.252
7.223
6.890
6.861
3.927
3.903
3.880
3.801
3.702
3.660
3.628
3.586
3.394
3.372
3.350
3.327
3.166
3.142
3.118
3.094
2.459
2.434
2.410
2.391
2.387
CN
N
O
11
2.04
2.03
0.95
3.12
2.07
1.00
1.00
1.99
f1 (ppm)

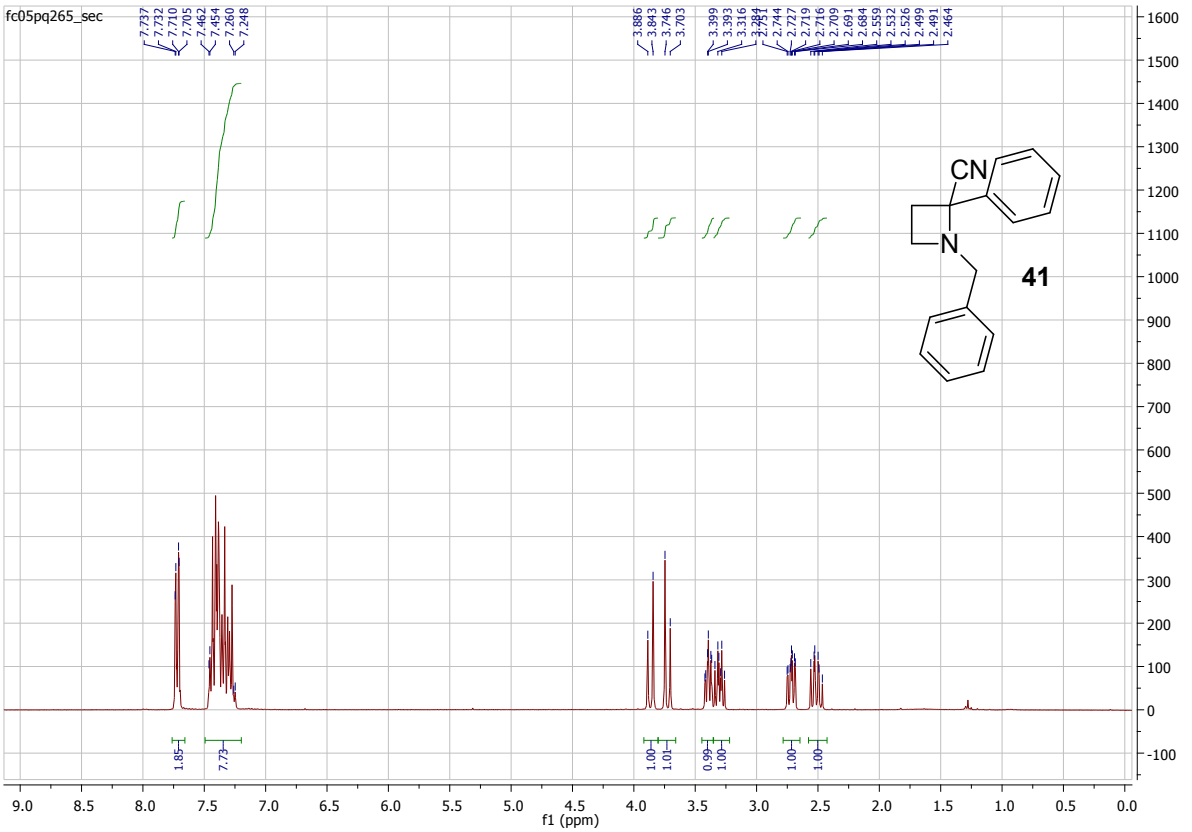

fc15pq249-300
159.129
130.055
128.135
118.919
113.903
60.159
55.237
52.187
51.469
22.876
f1 (ppm)

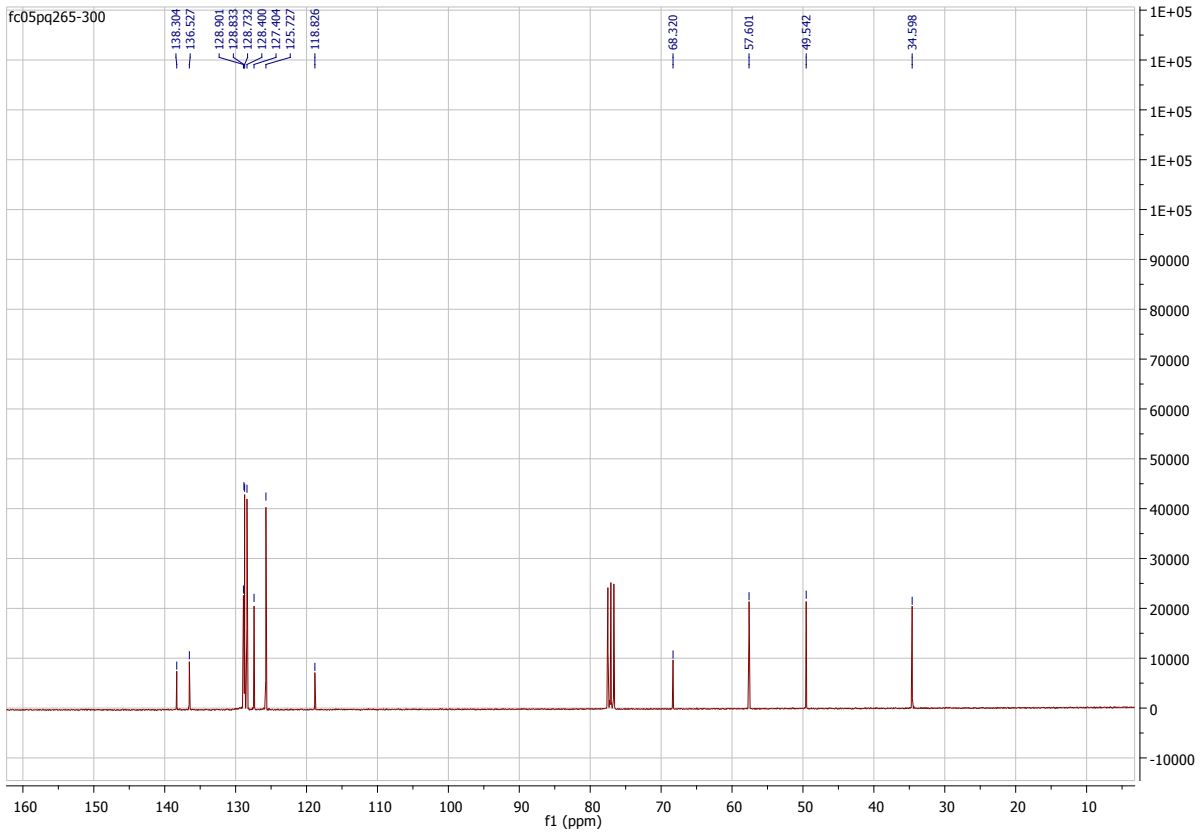

fc16pa256_apcol
7.324
7.295
7.274
7.245
3.957
3.933
3.909
3.744
3.700
3.649
3.606
3.411
3.389
3.367
3.344
3.181
3.157
3.133
3.109
2.488
2.471
2.463
2.446
2.425
2.402
CN
N
Cl
12
3.68
0.93
2.02
1.00
1.00
1.99
f1 (ppm)

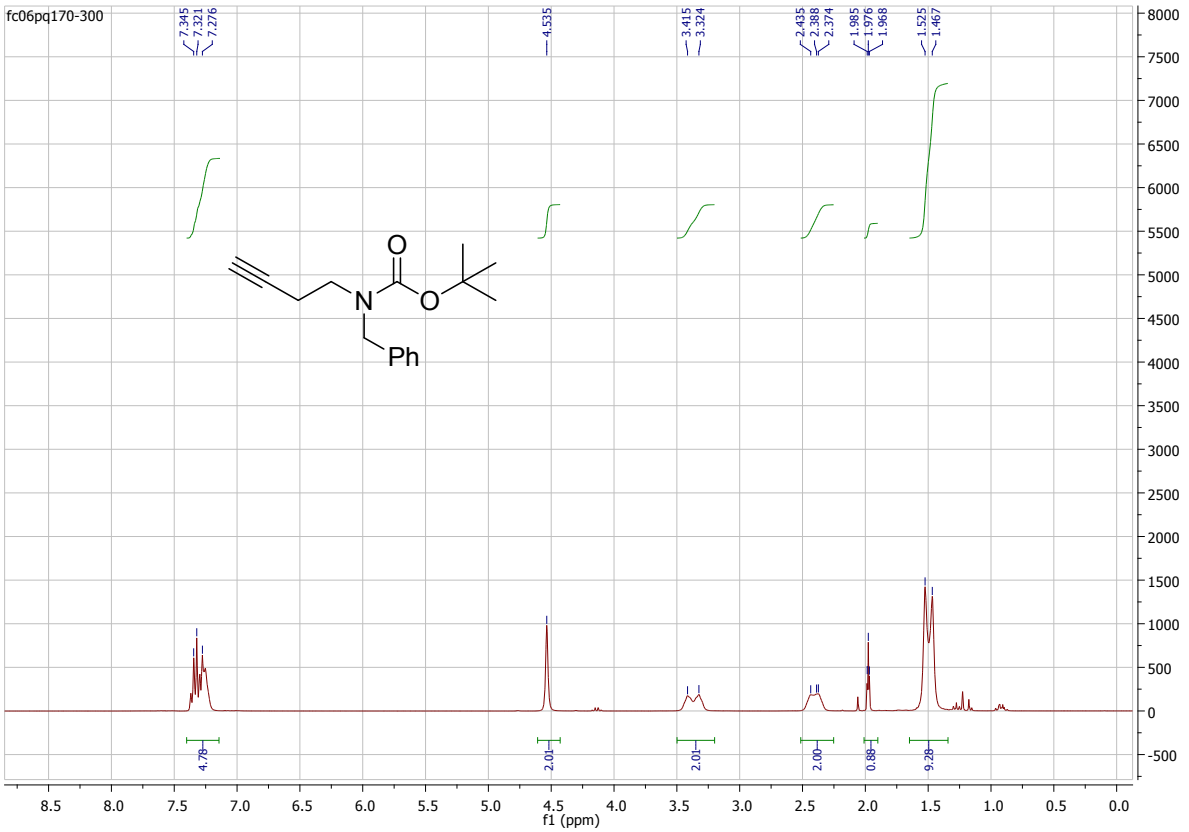

fc16pq256-300
134.725
133.375
130.091
128.685
118.707
59.992
52.475
51.788
22.883
f1 (ppm)

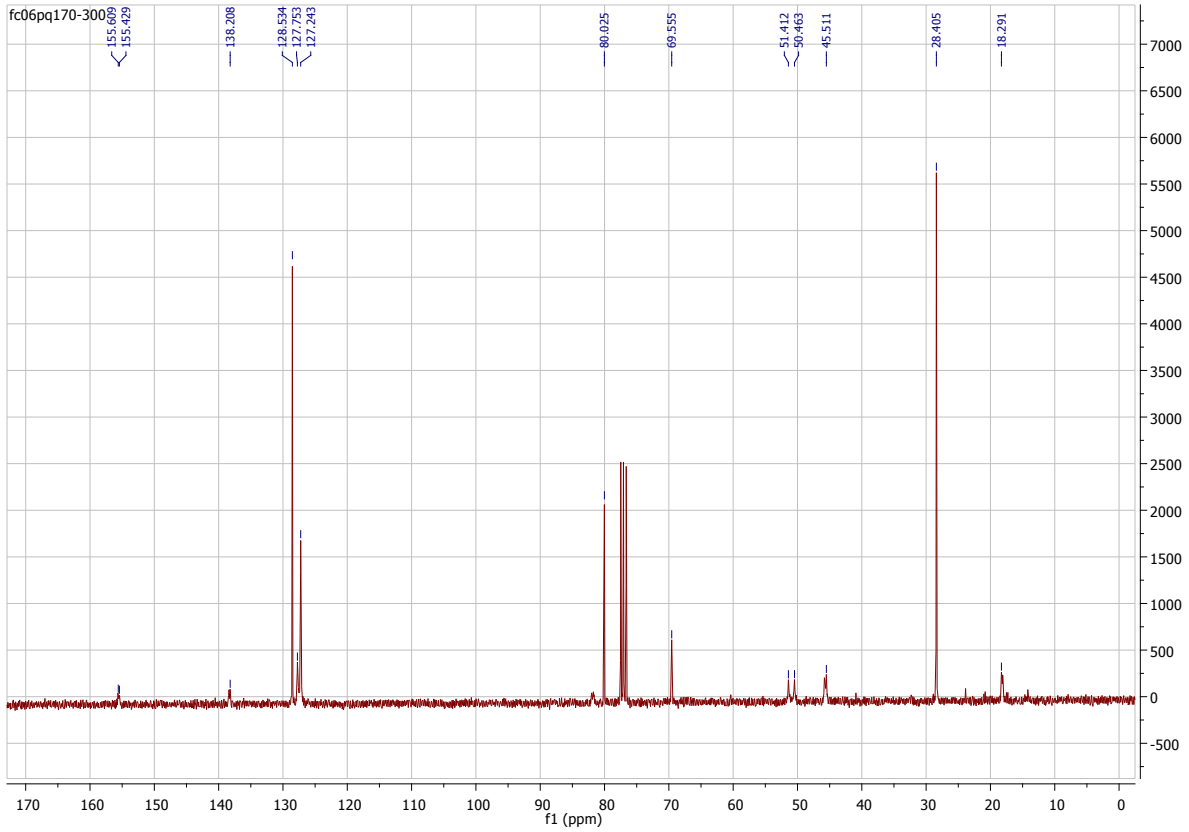

fc15pq251_sec
8.241
8.214
7.904
7.878
7.851
7.826
7.621
7.422
4.283
4.240
4.086
4.043
4.026
4.002
3.979
3.431
3.409
3.387
3.365
3.234
3.210
3.186
3.163
2.488
2.464
2.441
2.418
CN
N
13
0.98
2.01
4.01
1.03
1.01
0.95
1.01
1.01
2.00
f1 (ppm)

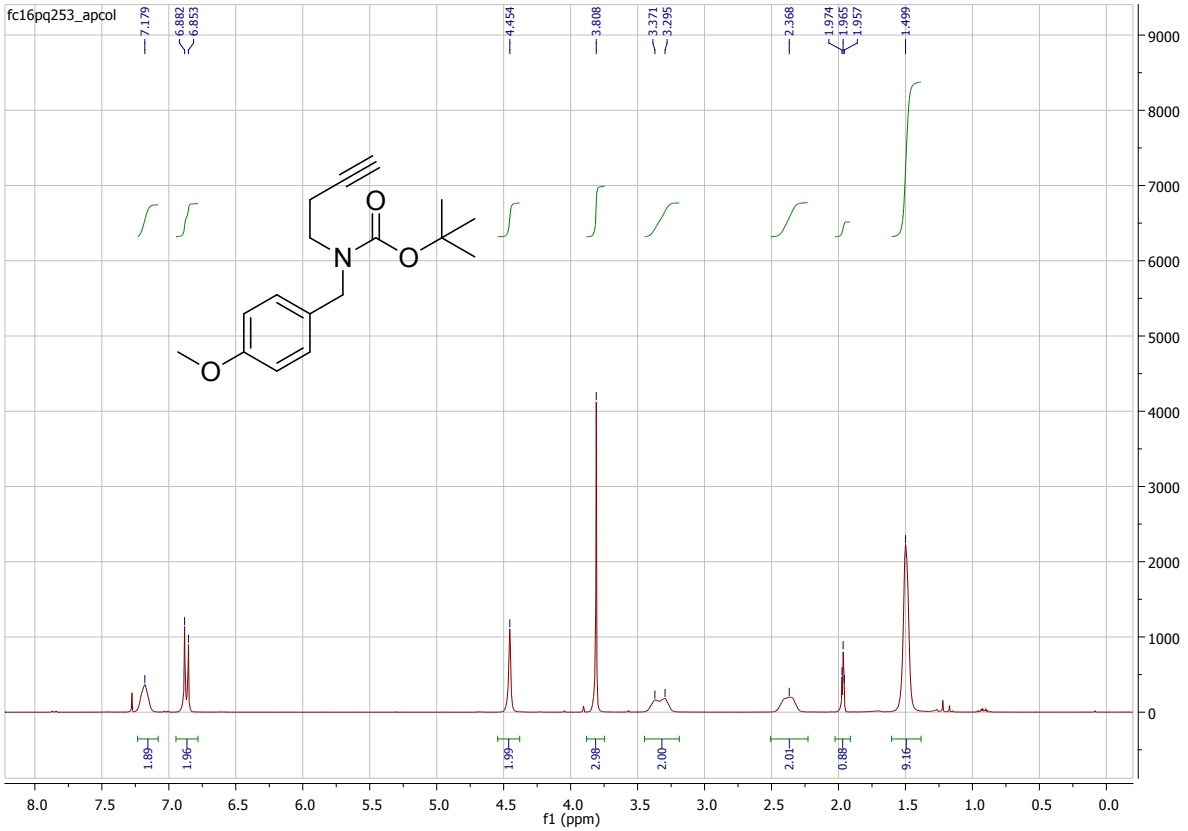

131.890
128.632
128.593
127.139
126.260
125.881
125.210
124.080
118.935
58.809
52.578
51.993
22.949
f1 (ppm)

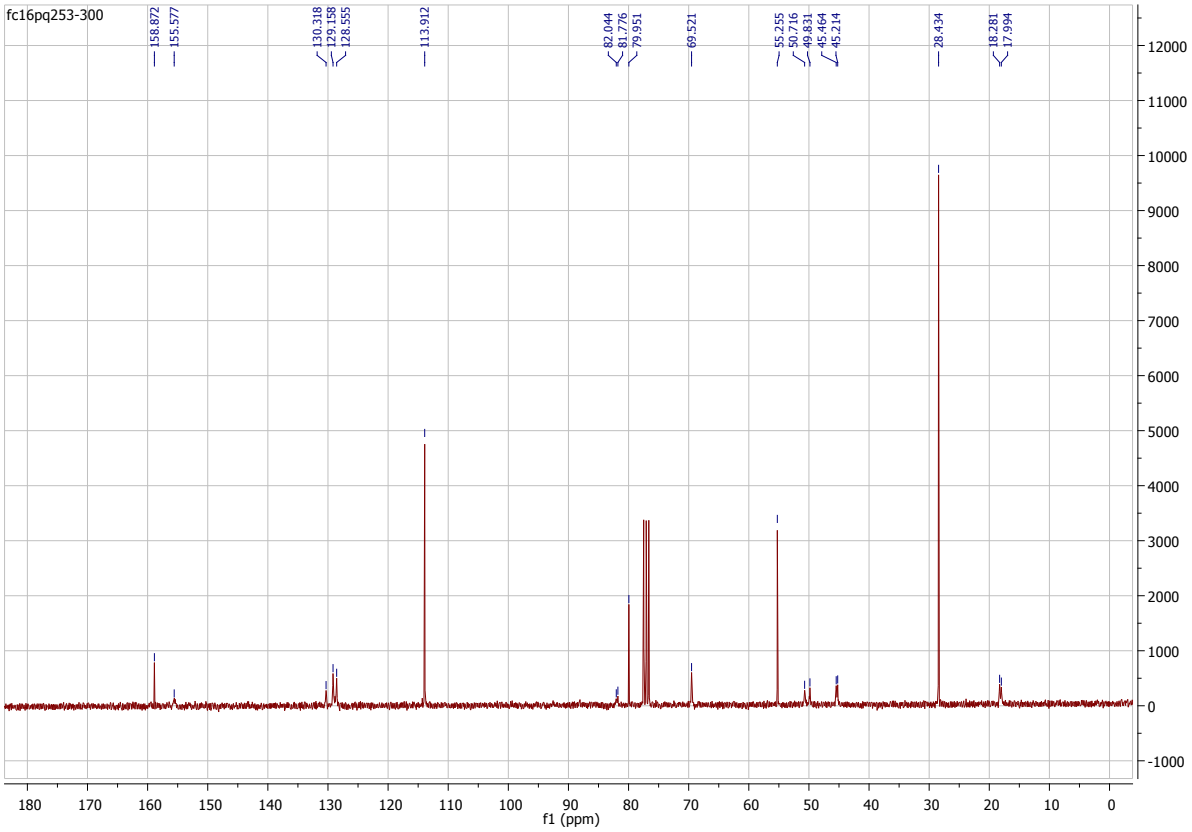

fc05pq265_sec
7.737
7.732
7.710
7.705
7.462
7.454
7.260
7.248
3.886
3.843
3.746
3.703
3.399
3.393
3.316
3.284
2.751
2.744
2.727
2.719
2.716
2.709
2.691
2.684
2.559
2.532
2.526
2.499
2.491
2.464
CN
N
41
1.85
7.73
1.00
1.01
0.99
1.00
1.00
1.00
f1 (ppm)

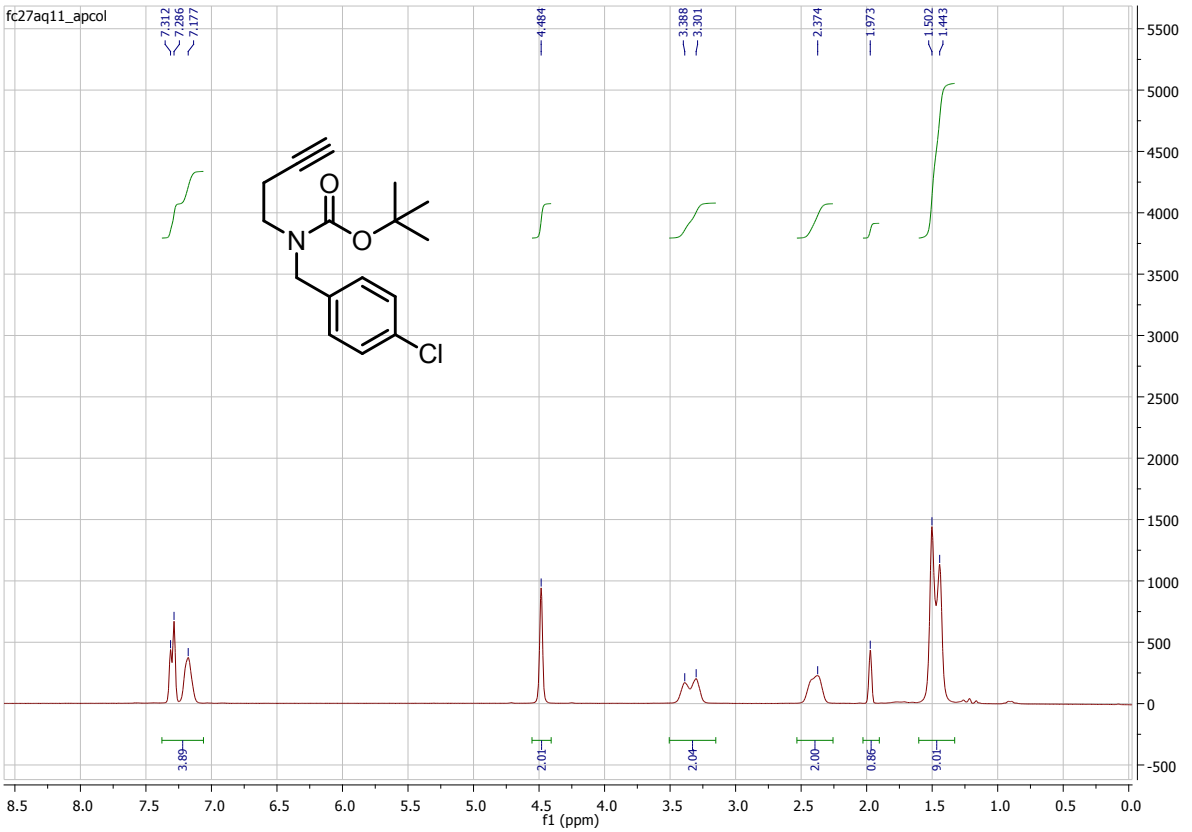

fc05pq265-300
138.304
136.527
128.901
128.833
128.732
128.400
127.404
125.727
118.826
68.320
57.601
49.542
34.598
f1 (ppm)

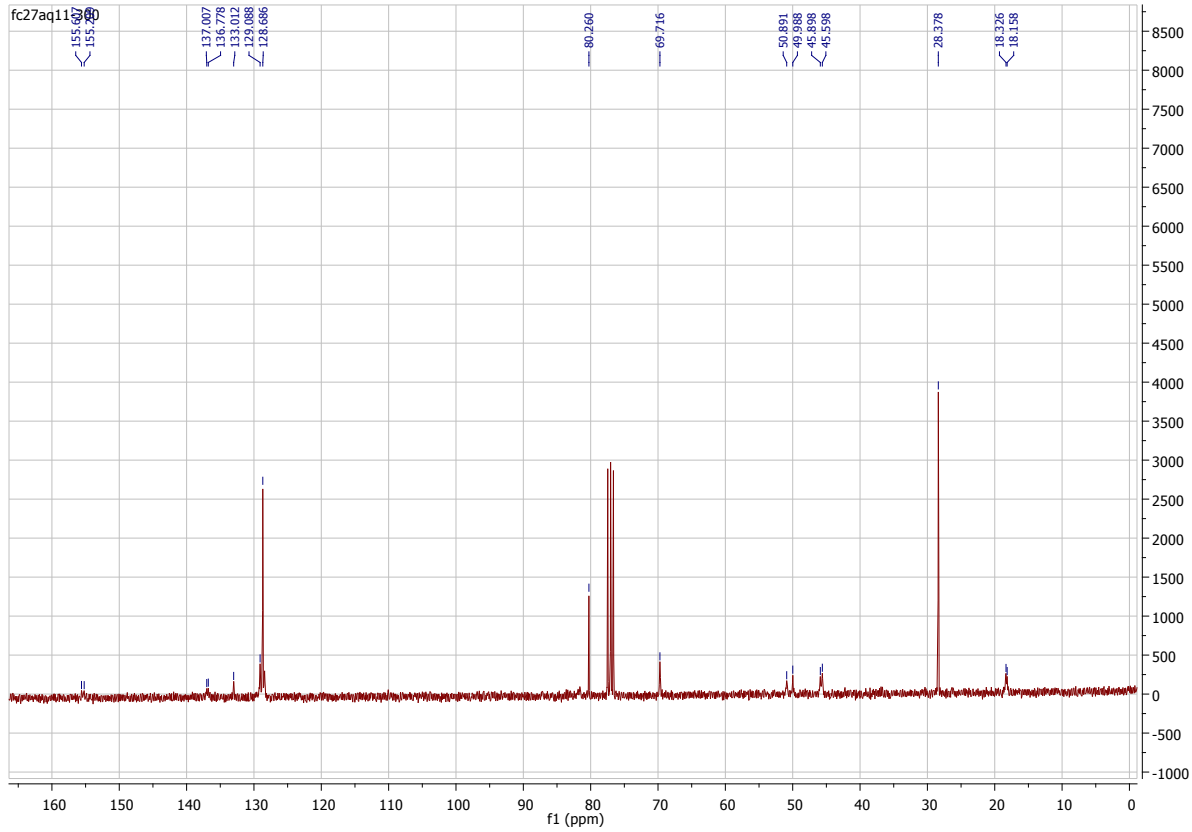

fc06pq170-300
7.345
7.321
7.276
4.535
3.415
3.324
2.435
2.388
2.374
1.985
1.976
1.968
1.525
1.467
O
N
O
Ph
4.78
2.01
2.01
2.00
0.88
9.28
f1 (ppm)


fc06pq170-300
155.609
155.429
138.208
128.534
127.753
127.243
80.025
69.555
51.412
50.463
45.511
28.405
18.291
f1 (ppm)


fc16pq253_apcol
7.179
6.882
6.853
4.454
3.808
3.371
3.295
2.368
1.974
1.965
1.957
1.499
1.89
1.96
1.99
2.98
2.00
2.01
0.88
9.16
f1 (ppm)


fc16pq253-300
158.872
155.577
130.318
129.158
128.555
113.912
82.044
81.776
79.951
69.521
55.255
50.716
49.831
45.464
45.214
28.434
18.281
17.994
f1 (ppm)


fc27aq11_apcol
7.312
7.286
7.177
4.484
3.388
3.301
2.374
1.973
1.502
1.443
O
N
O
Cl
3.89
2.01
2.04
2.00
0.86
9.01
f1 (ppm)


fc27aq11_apcol
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155.280
137.007
136.778
133.012
129.088
128.686
80.260
69.716
50.891
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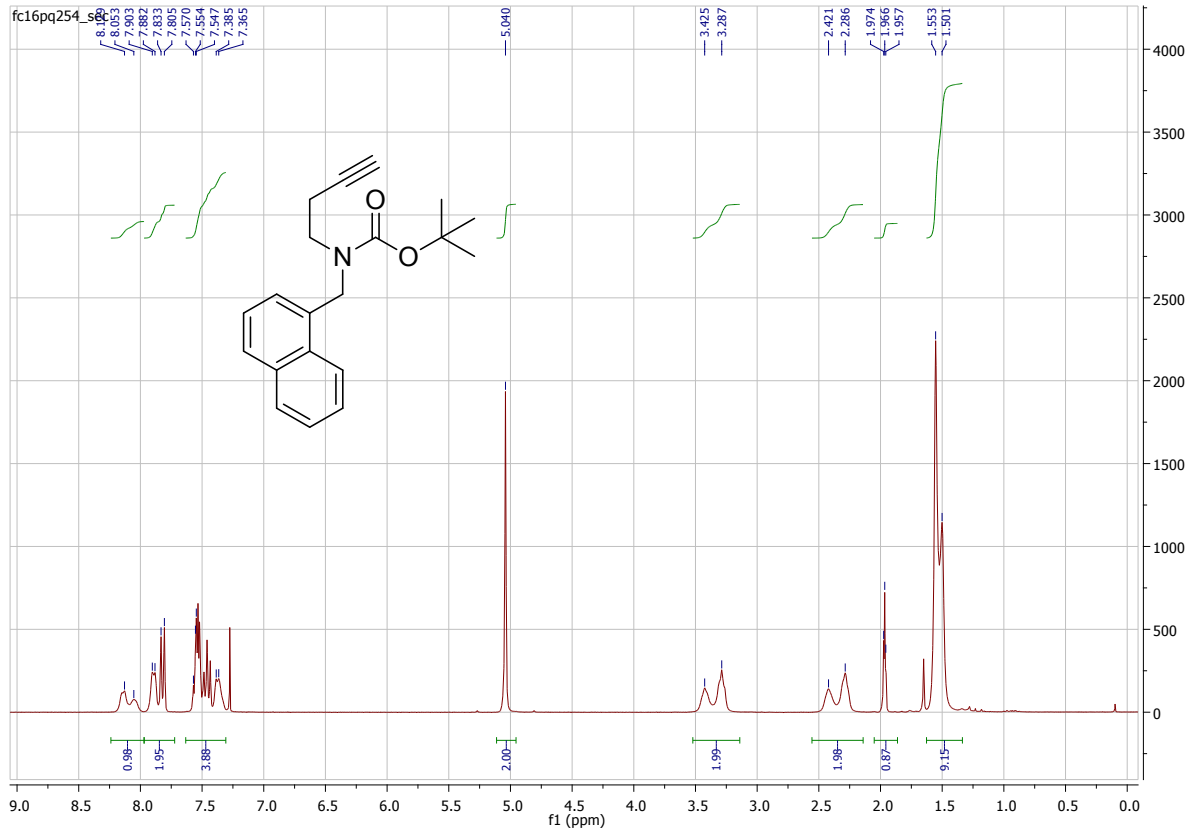
45.898
45.598
28.378
18.326
18.158
f1 (ppm)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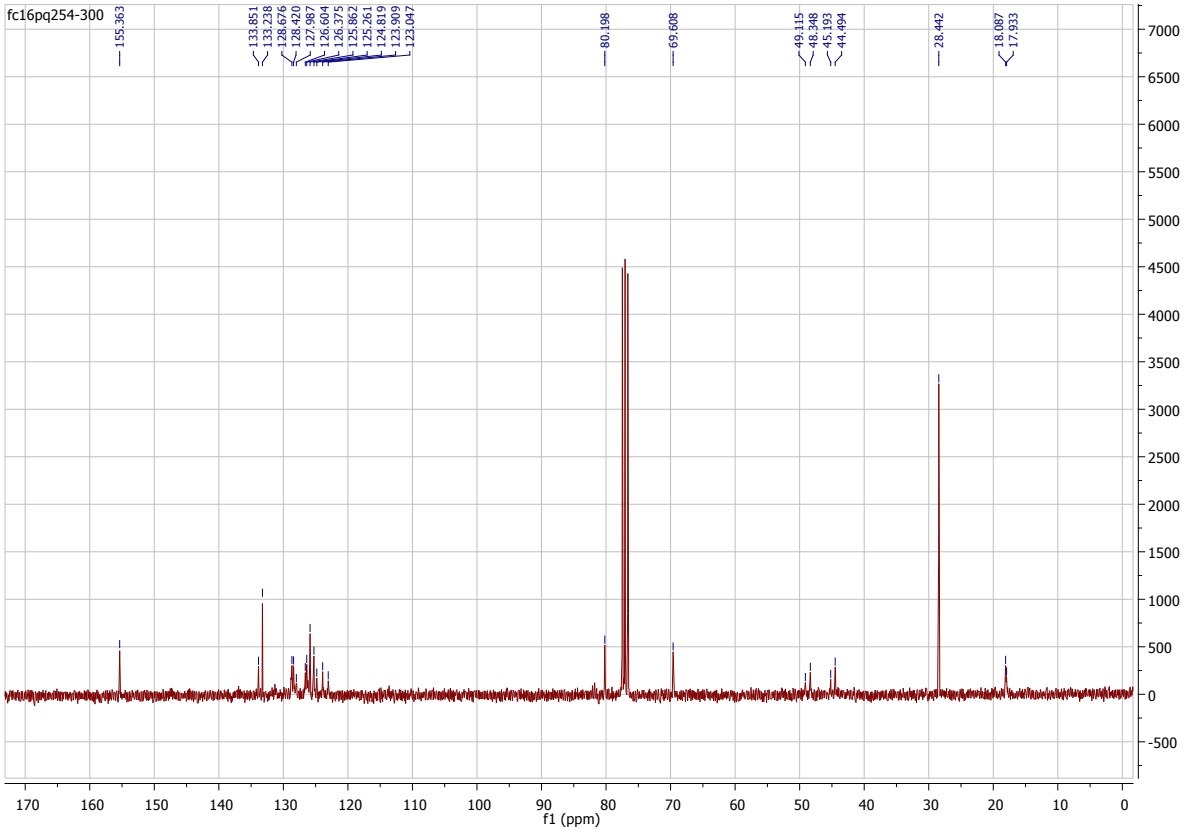
8.053
7.903
7.882
7.833
7.805
7.570
7.554
7.547
7.385
7.365
5.040
3.425
3.287
2.421
2.286
1.974
1.966
1.957
1.553
1.501
O
N
O
0.98
1.95
3.88
2.00
1.99
1.98
0.87
9.15
f1 (ppm)


fc16pq254-300
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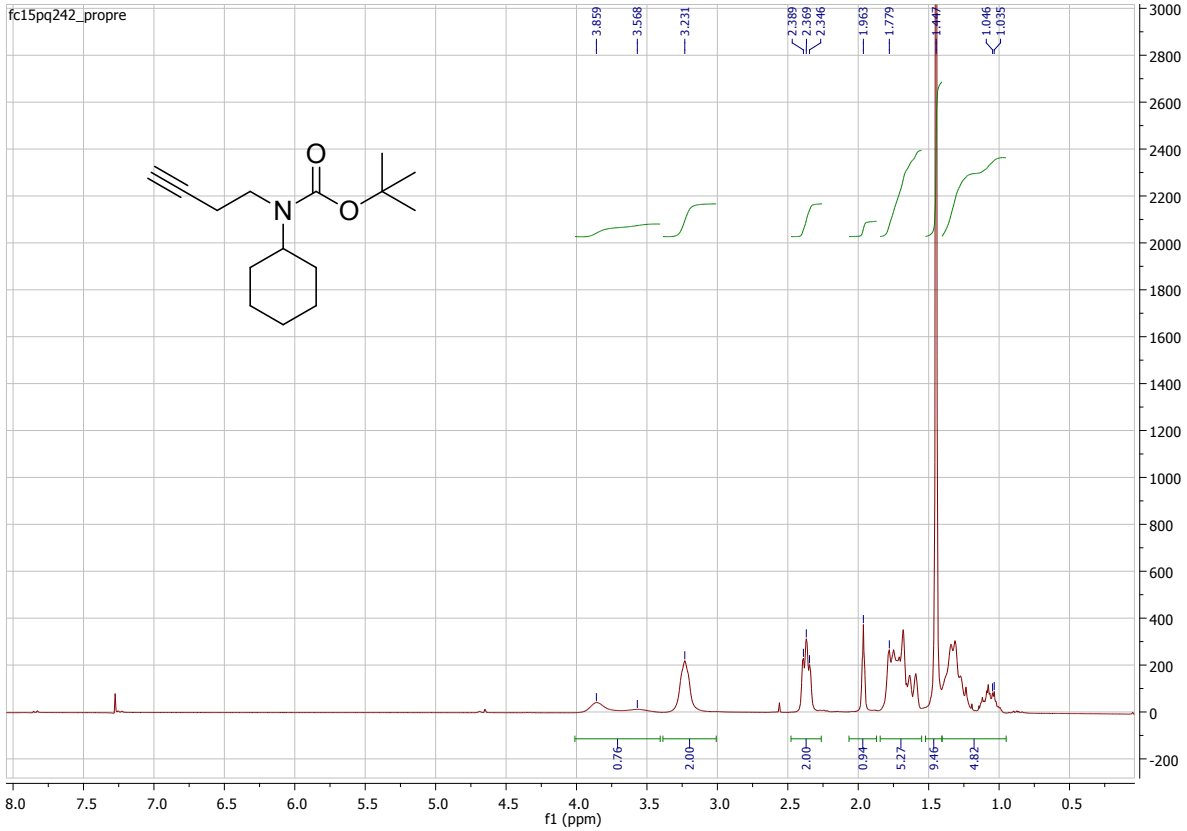
133.851
133.238
128.676
128.420
127.987
126.604
126.375
125.862
125.261
124.819
123.909
123.047
80.198
69.608
49.115
48.348
45.193
44.494
28.442
18.087
17.933
f1 (ppm)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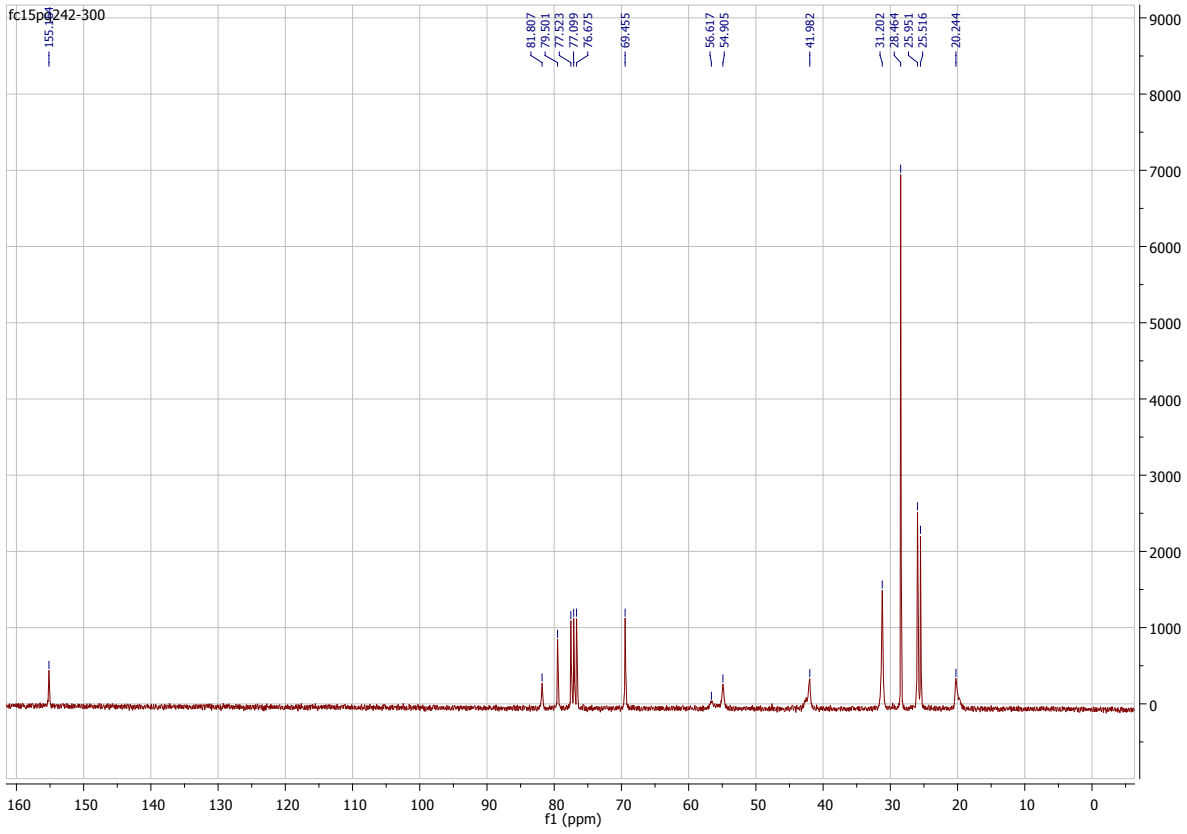
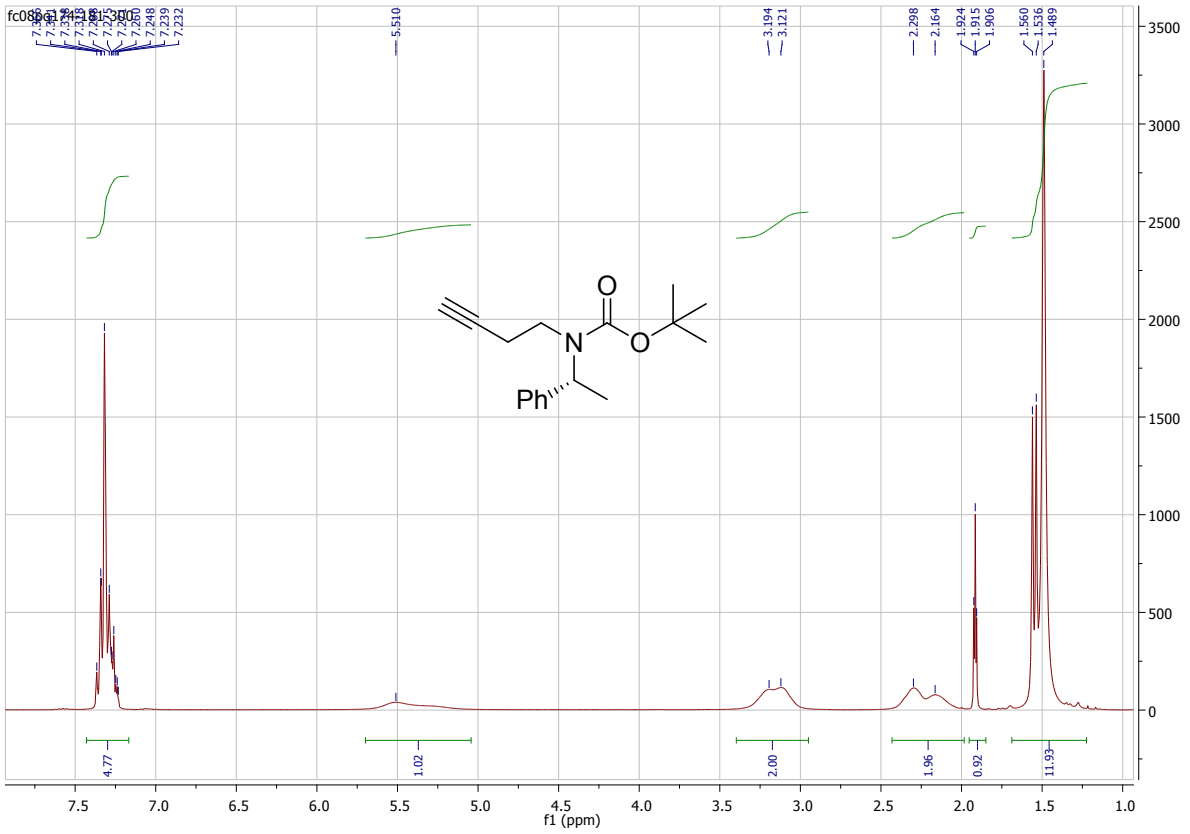
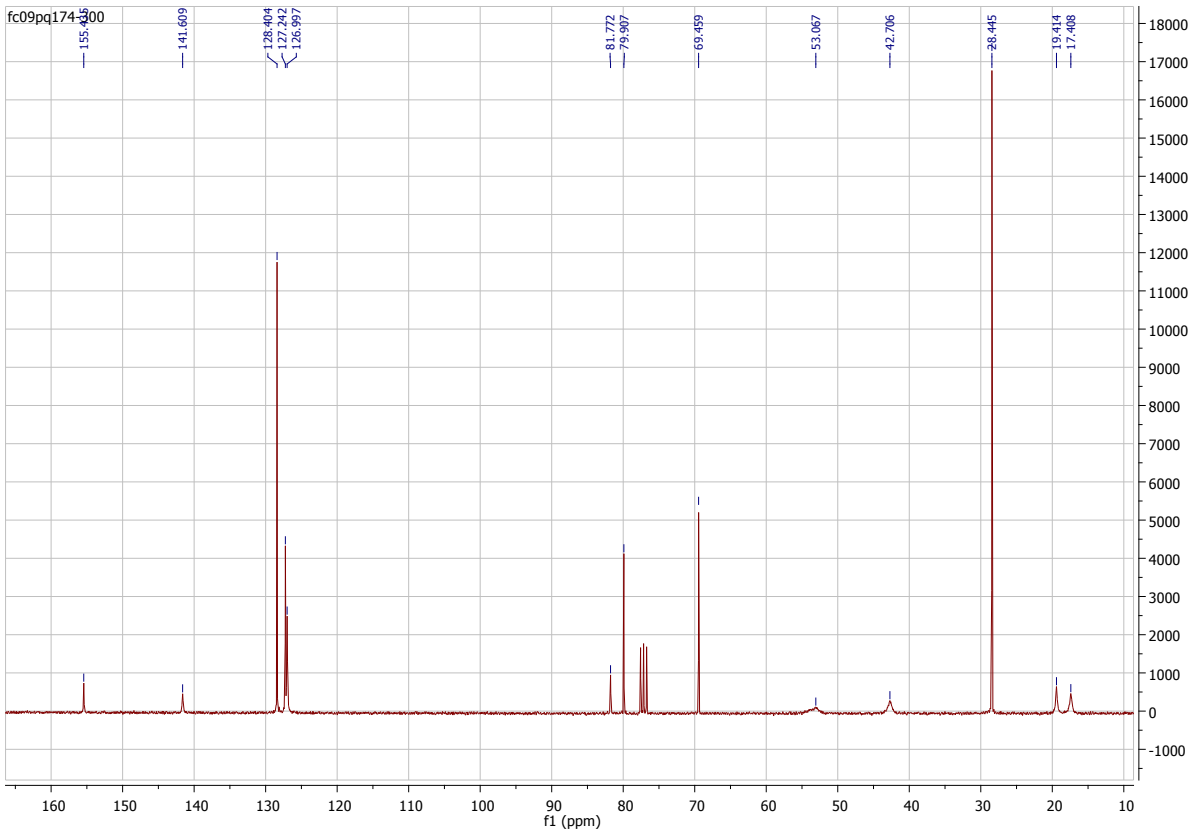
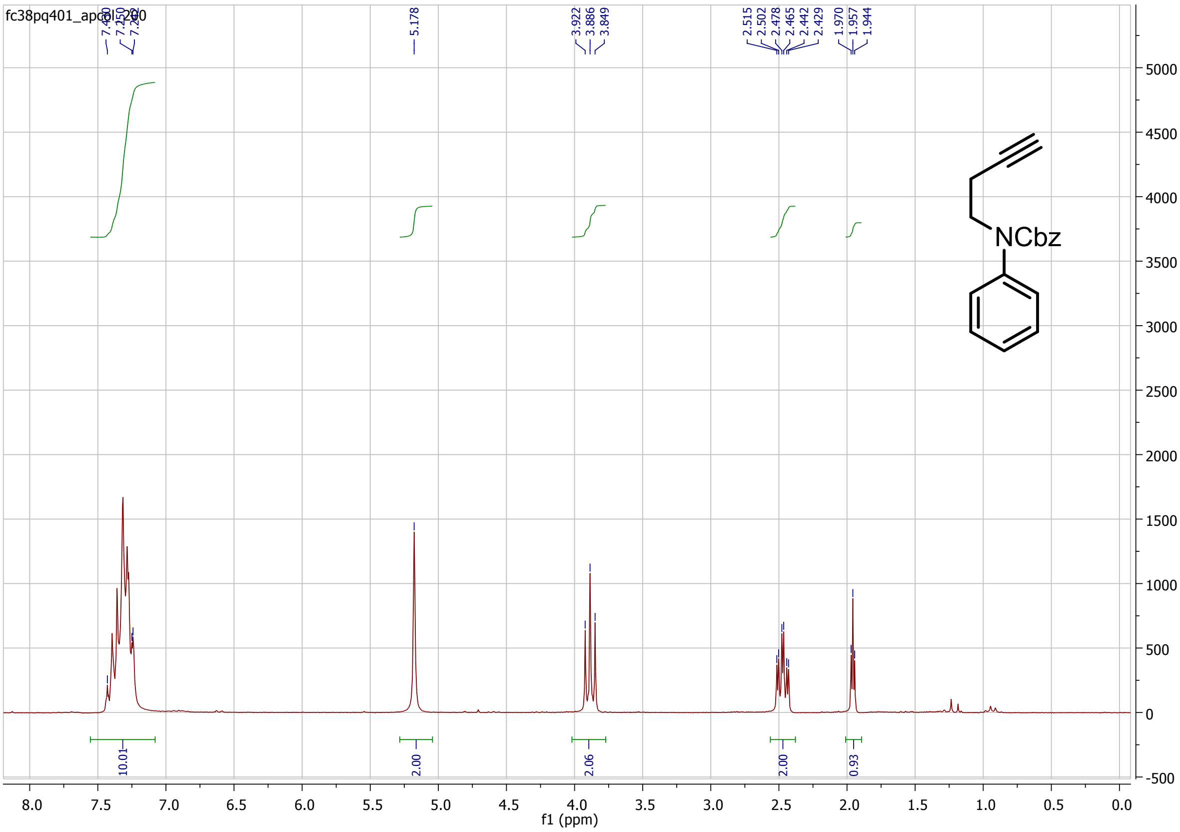
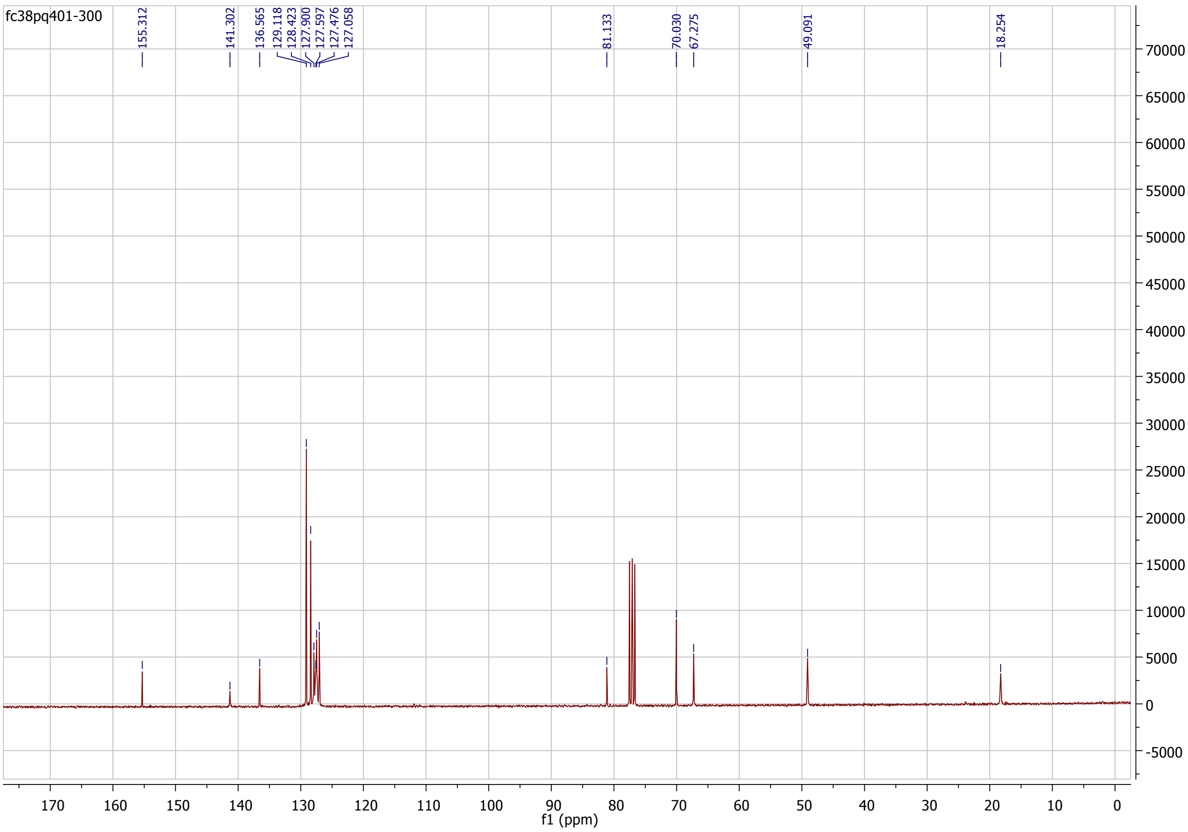
3.859
3.568
3.231
2.389
2.369
2.346
1.963
1.779
1.447
1.046
1.035
O
N
O
0.76
2.00
2.00
0.94
5.27
9.46
4.82
f1 (ppm)

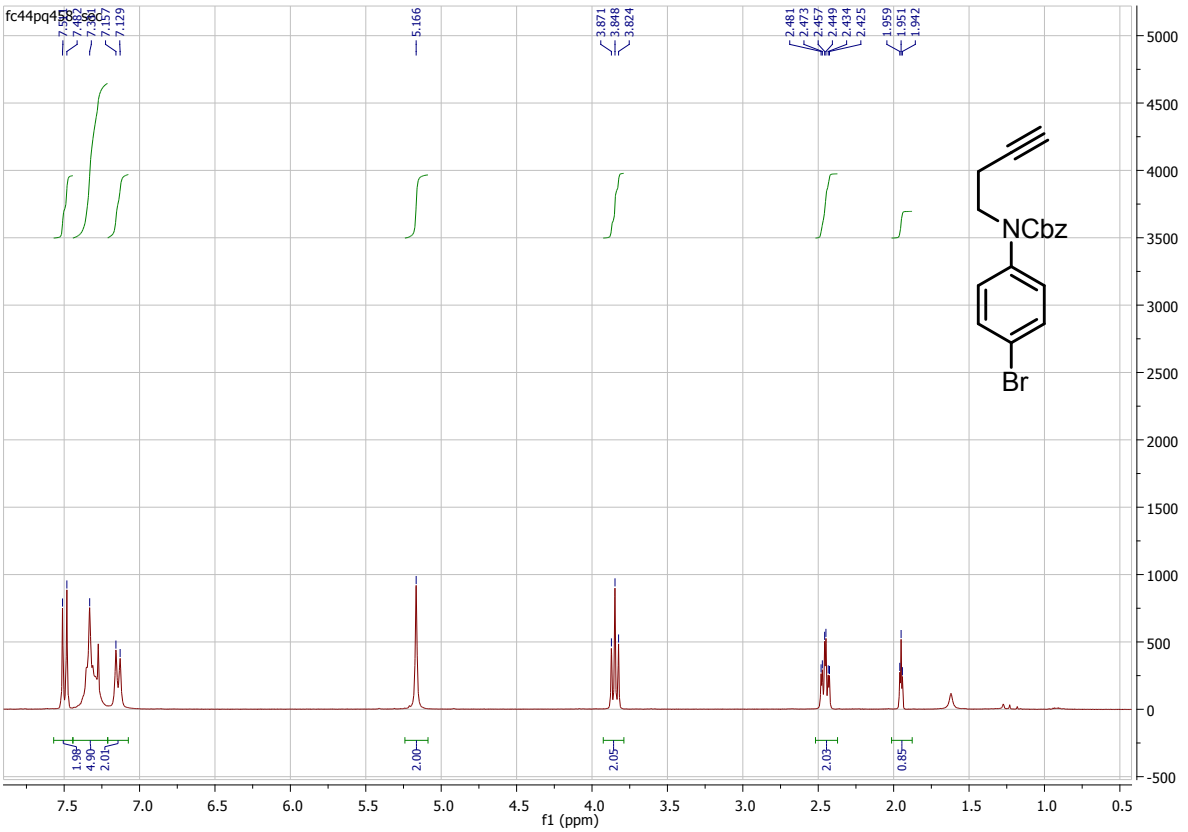

fc15pq242-300
155.143
81.807
79.501
77.523
77.099
76.675
69.455
56.617
54.905
41.982
31.202
28.464
25.951
25.516
20.244
f1 (ppm)

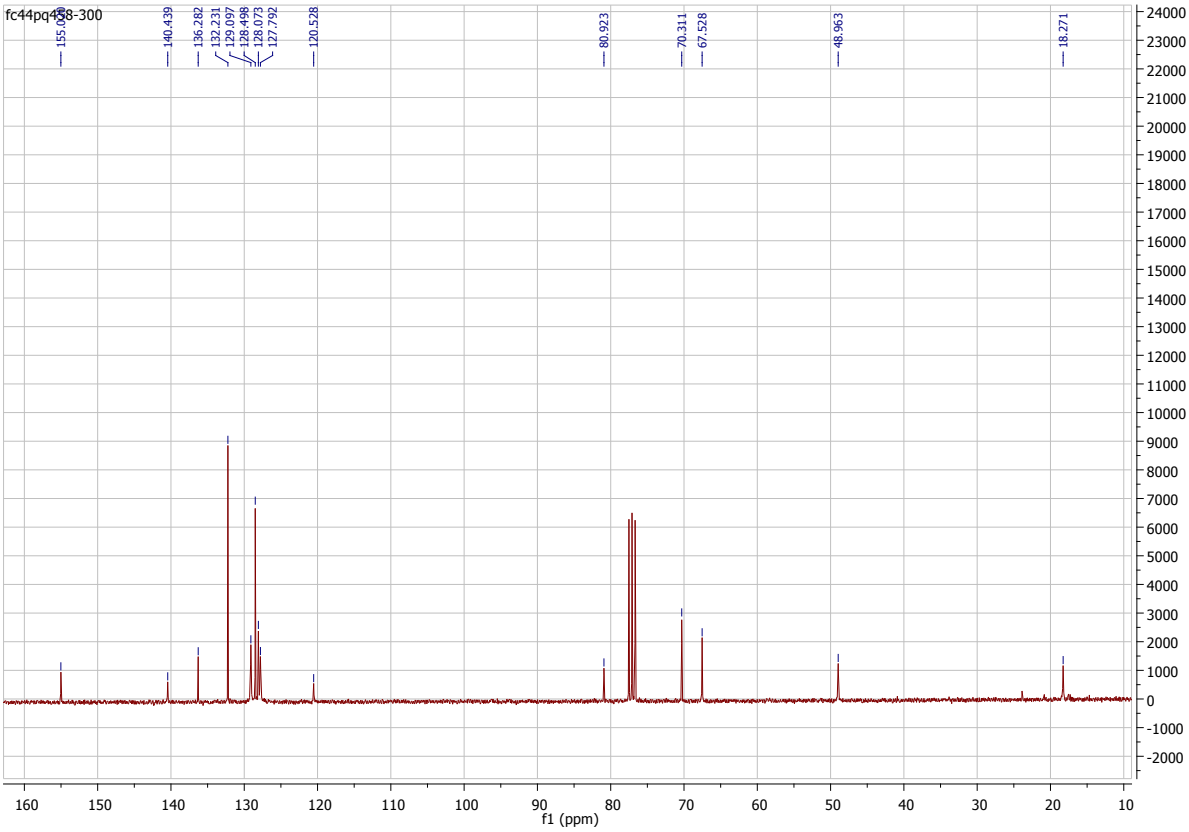

7.248
7.239
7.232
5.510
3.194
3.121
2.298
2.164
1.924
1.915
1.906
1.560
1.536
1.489
O
N
O
Ph
4.77
1.02
2.00
1.96
0.92
11.93
f1 (ppm)

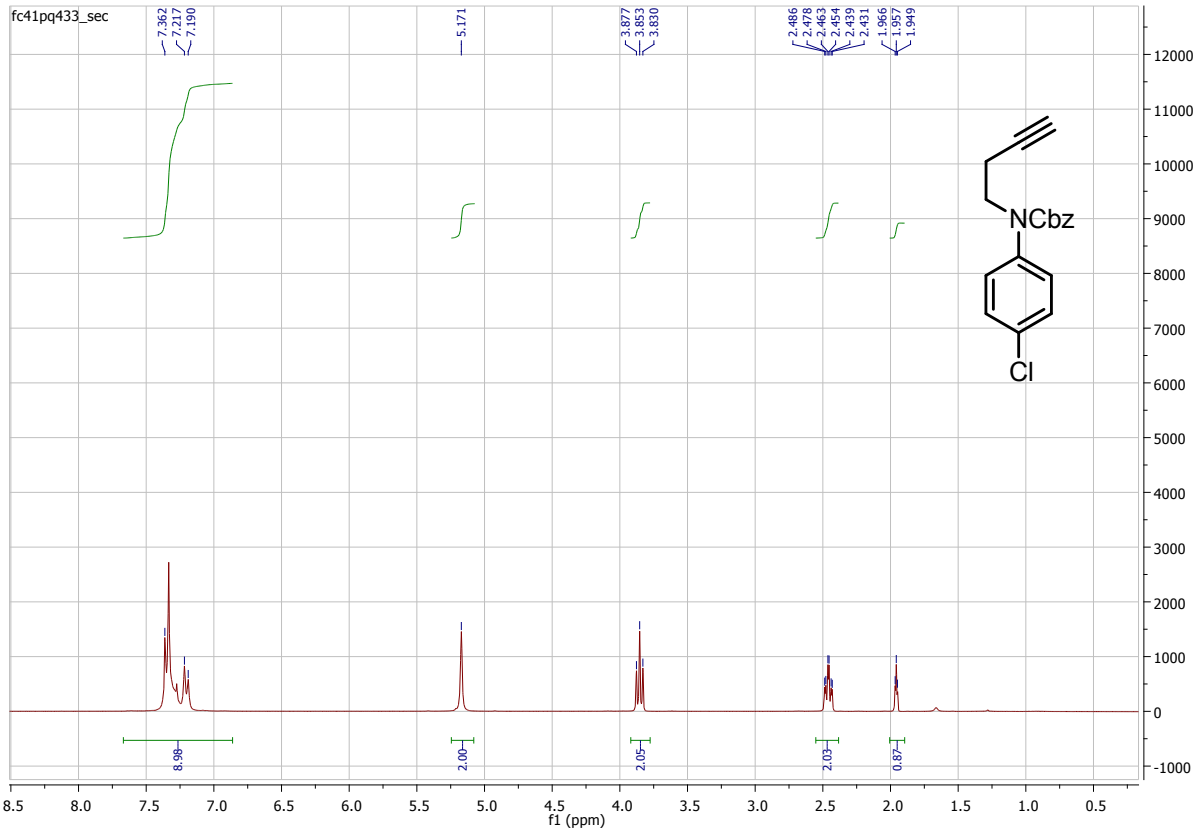

155.465
141.609
128.404
127.242
126.997
81.772
79.907
69.459
53.067
42.706
28.445
19.414
17.408
f1 (ppm)

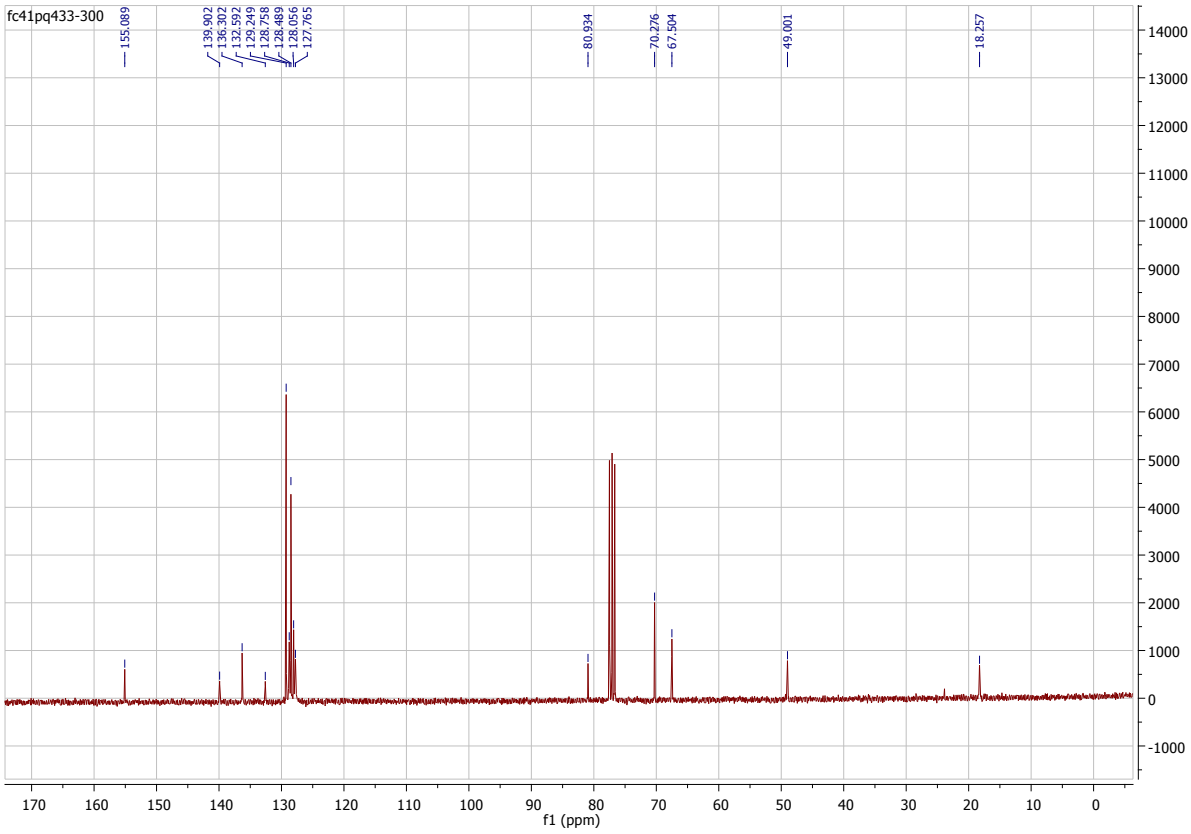

fc38pq401_apcol-200
NCbz
f1 (ppm)

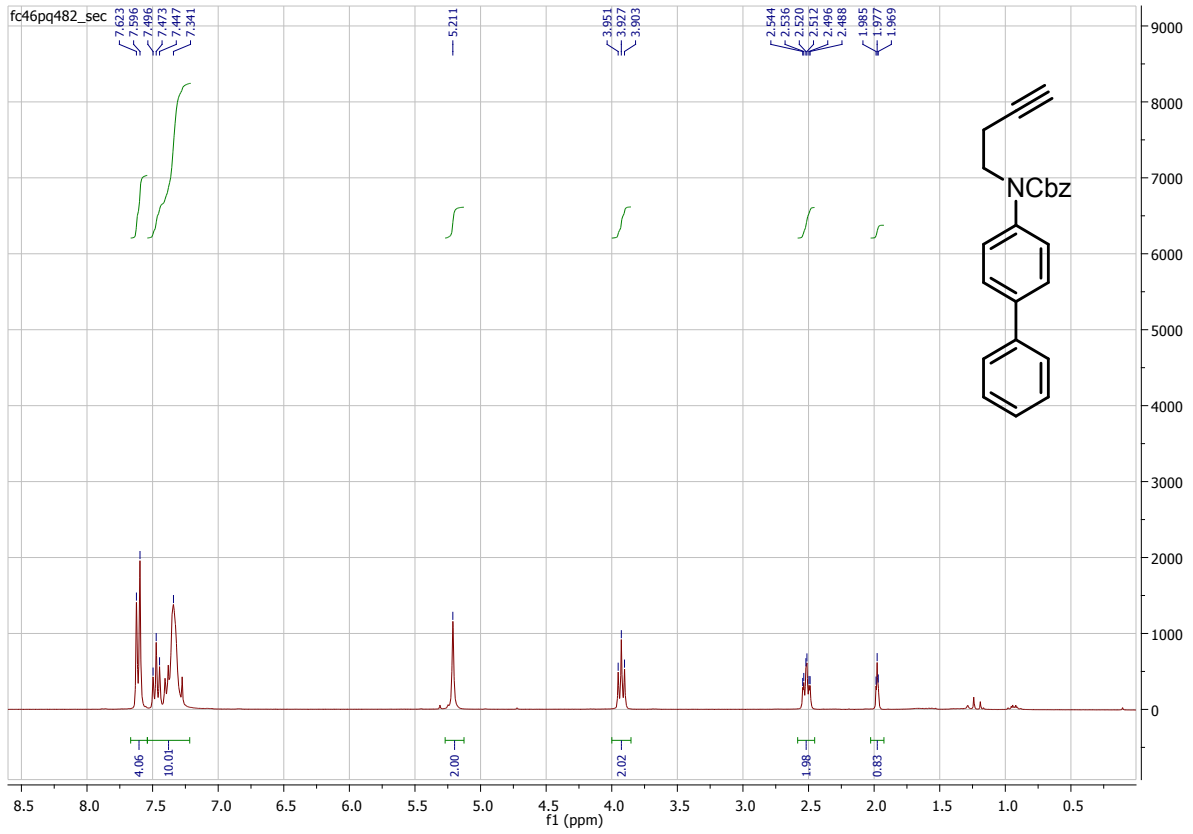

fc38pq401-300
155.312
141.302
136.565
129.118
128.423
127.900
127.597
127.476
127.058
81.133
70.030
67.275
49.091
18.254
f1 (ppm)

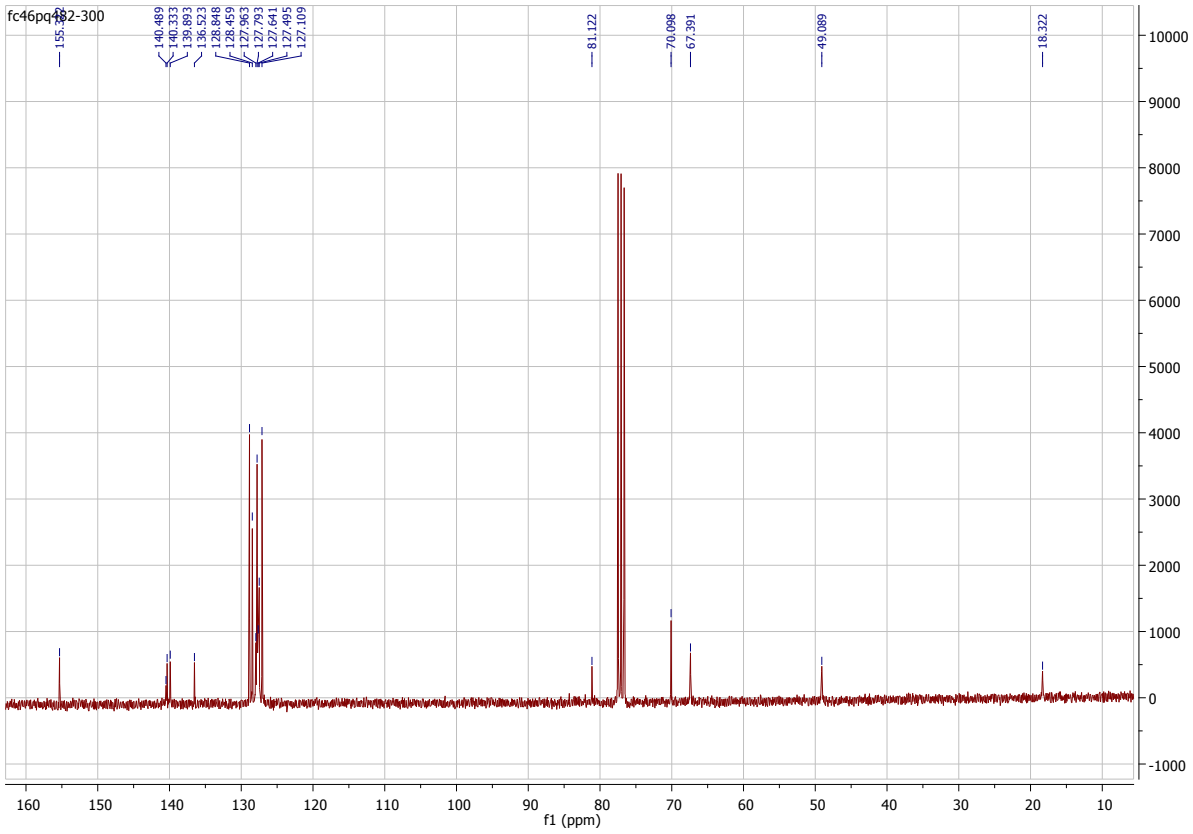

fc44pq458-sc
7.592
7.482
7.360
7.157
7.129
5.166
3.871
3.848
3.824
2.481
2.473
2.457
2.449
2.434
2.425
1.959
1.951
1.942
1.98
4.90
2.01
2.00
2.05
2.03
0.85
NCbz
Br
f1 (ppm)

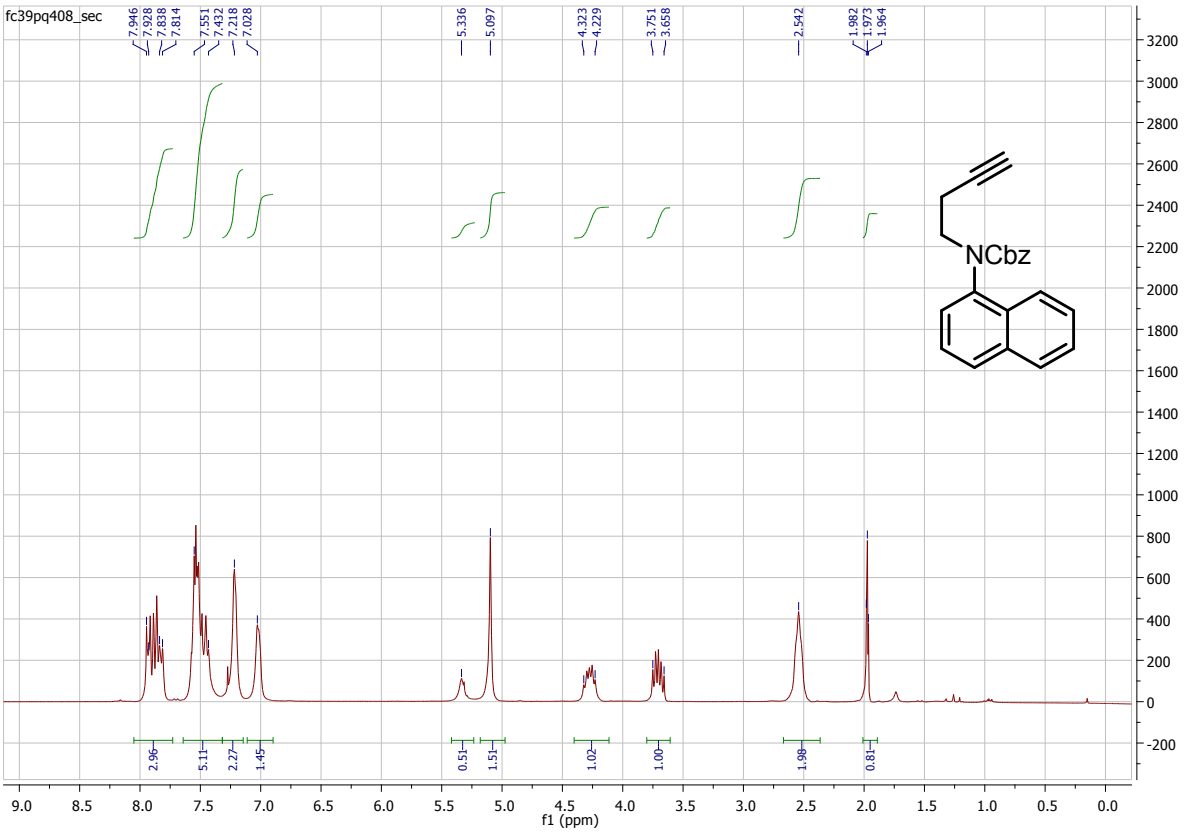

fc44pq458-300
155.458
140.439
136.282
132.231
129.097
128.498
128.073
127.792
120.528
80.923
70.311
67.528
48.963
18.271
f1 (ppm)

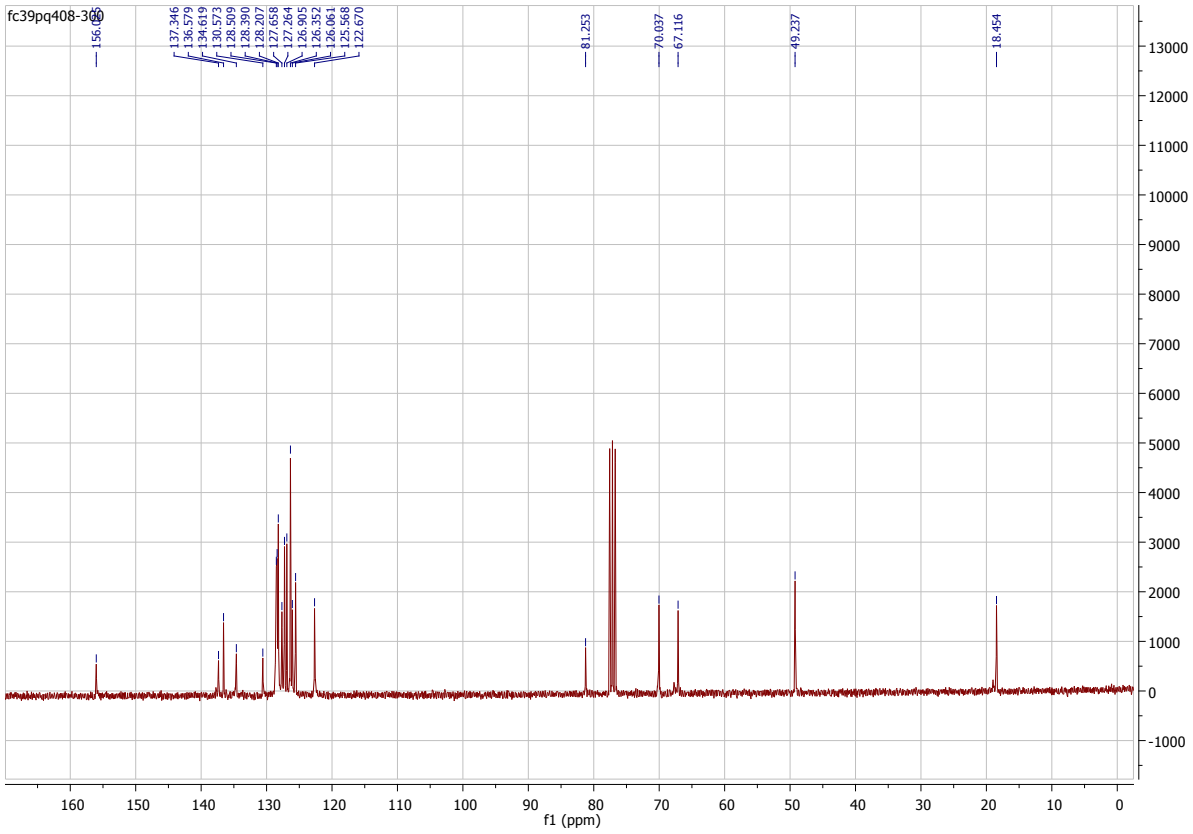

fc41pq433_sec
7.362
7.217
7.190
5.171
3.877
3.853
3.830
2.486
2.478
2.463
2.454
2.439
2.431
1.966
1.957
1.949
NCbz
Cl
8.99
2.00
2.05
2.03
0.87
f1 (ppm)

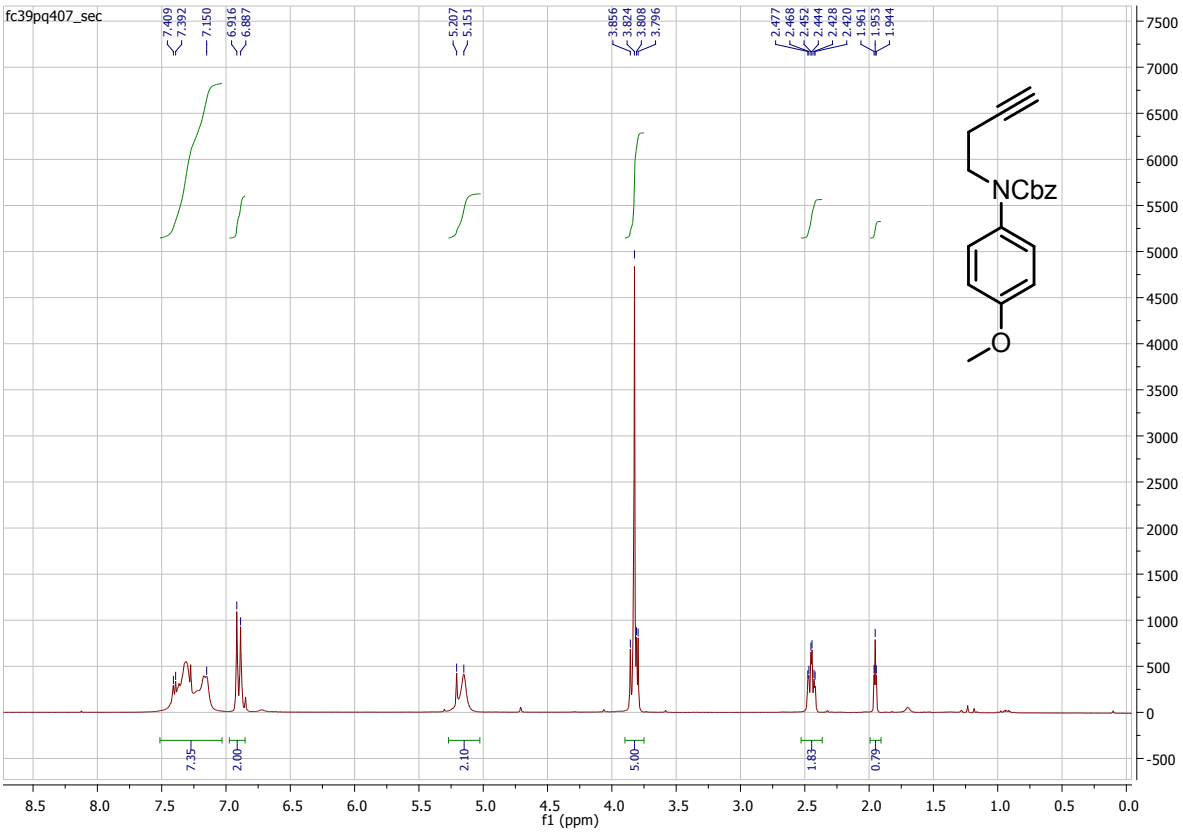

fc41pq433-300
155.089
139.902
136.302
132.592
129.249
128.758
128.489
128.056
127.765
80.934
70.276
67.504
49.001
18.257
f1 (ppm)

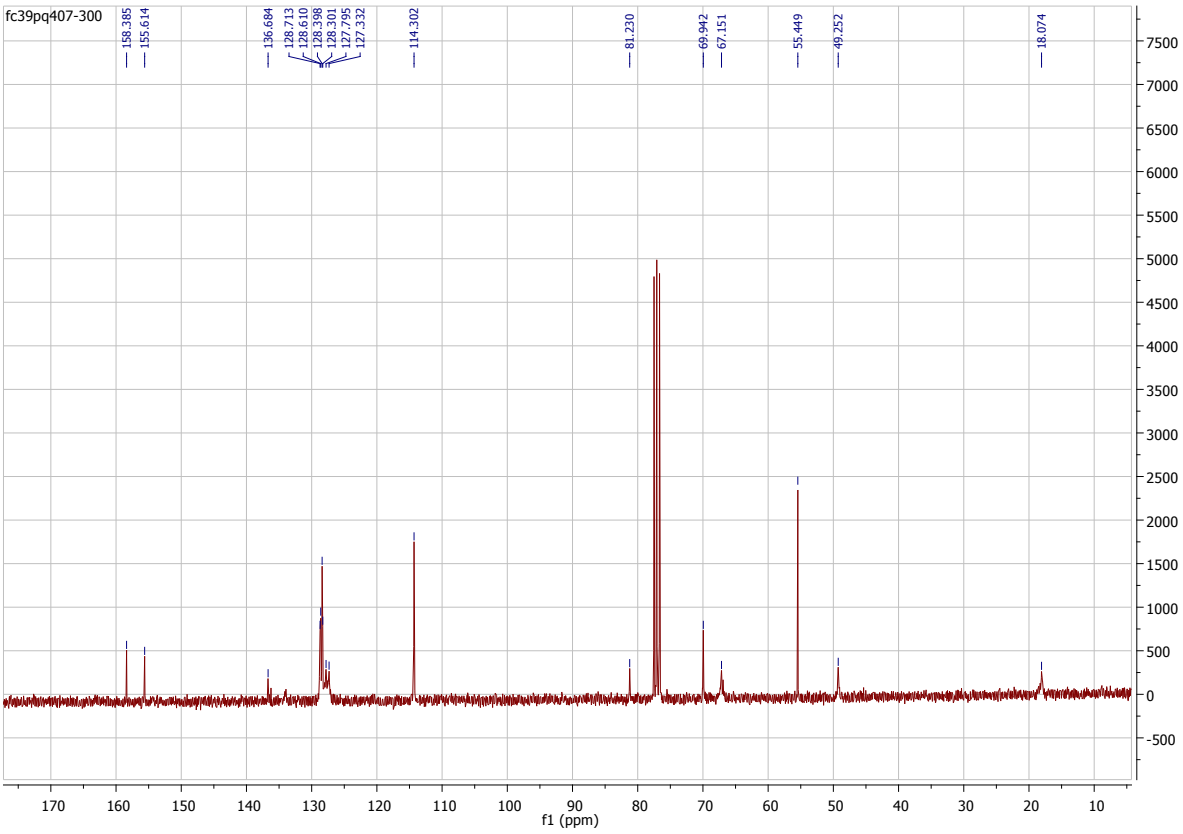

fc46pq482_sec
7.623
7.596
7.496
7.473
7.447
7.341
5.211
3.951
3.927
3.903
2.544
2.536
2.520
2.512
2.496
2.488
1.985
1.977
1.969
NCbz
4.06
10.01
2.00
2.02
1.98
0.83
f1 (ppm)

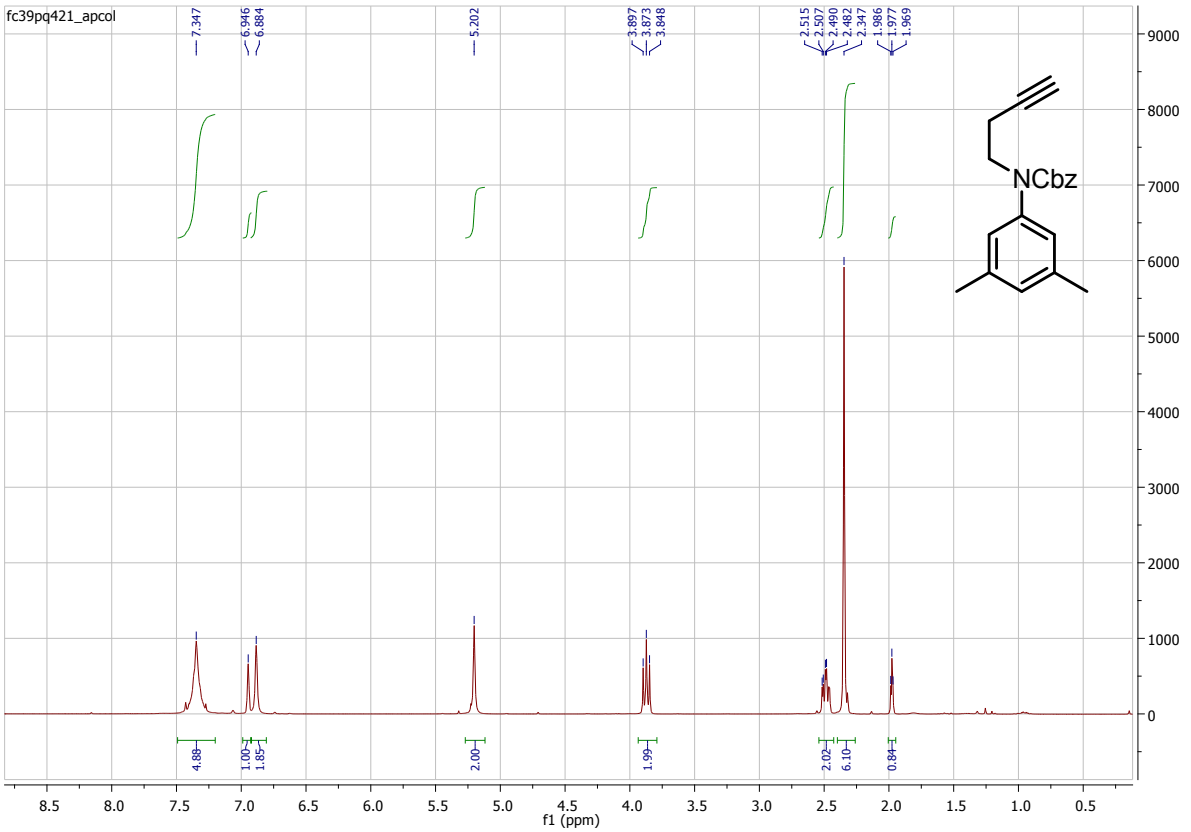

fc46pq482-300
155.
140.489
140.333
139.893
136.523
128.848
128.459
127.963
127.793
127.641
127.495
127.109
81.122
70.098
67.391
49.089
18.322
f1 (ppm)

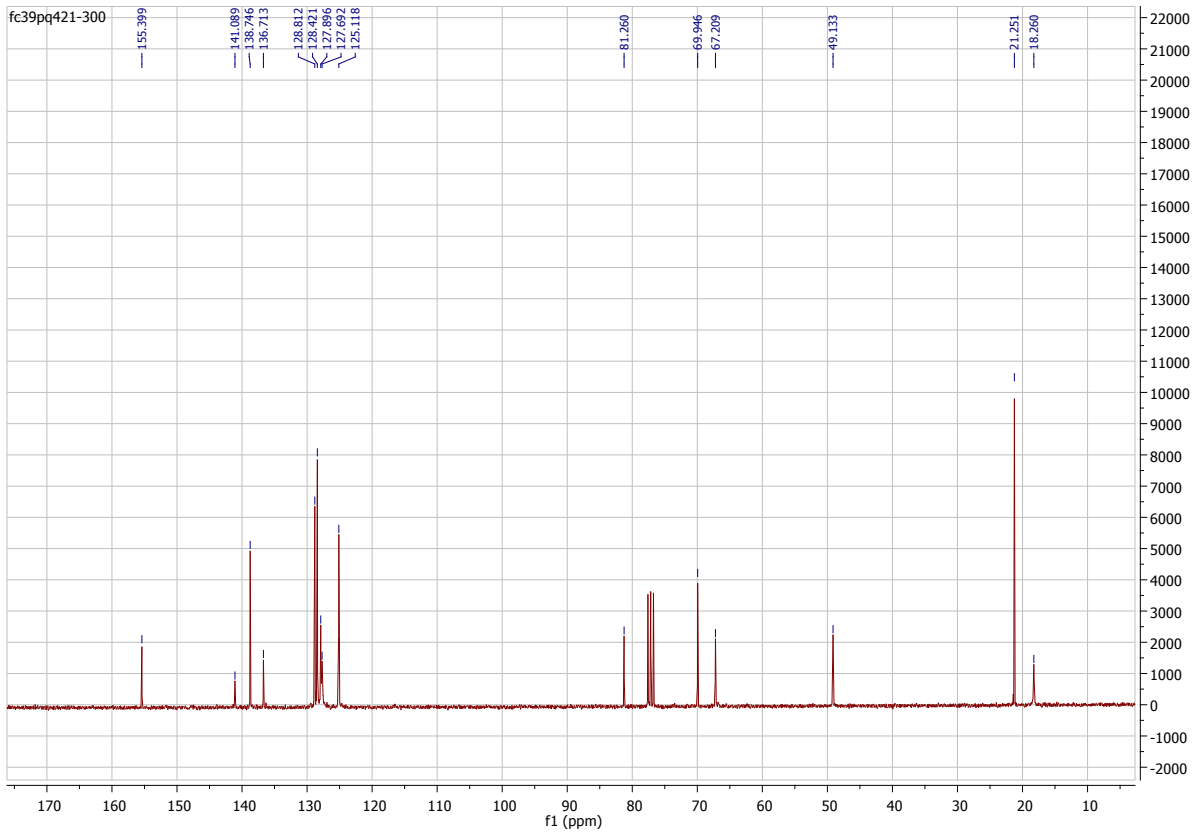

fc39pq408_sec
7.946
7.928
7.838
7.814
7.551
7.432
7.218
7.028
5.336
5.097
4.323
4.229
3.751
3.658
2.542
1.982
1.973
1.964
NCbz
2.96
5.11
2.27
1.45
0.51
1.51
1.02
1.00
1.98
0.81
f1 (ppm)

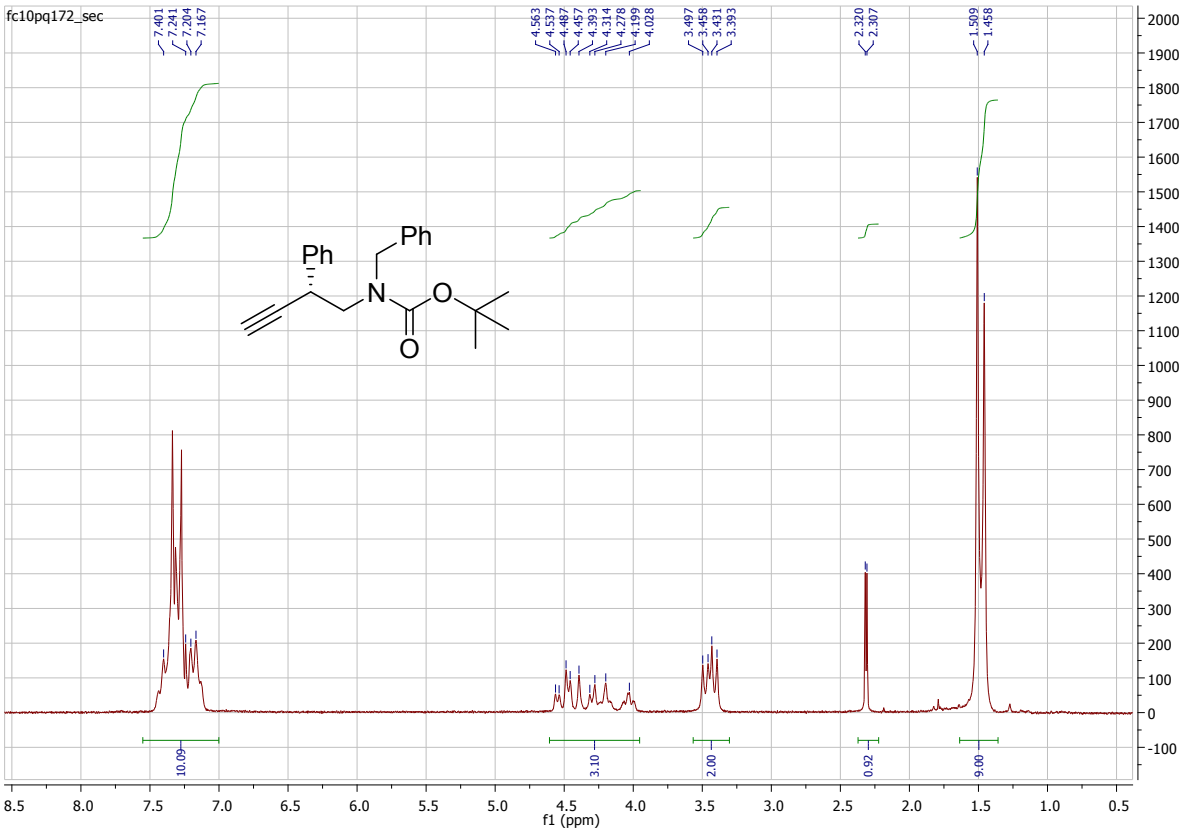

fc39pq408-300
156.066
137.346
136.579
134.619
130.573
128.509
128.390
128.207
127.658
127.264
126.905
126.352
126.061
125.568
122.670
81.253
70.037
67.116
49.237
18.454
f1 (ppm)

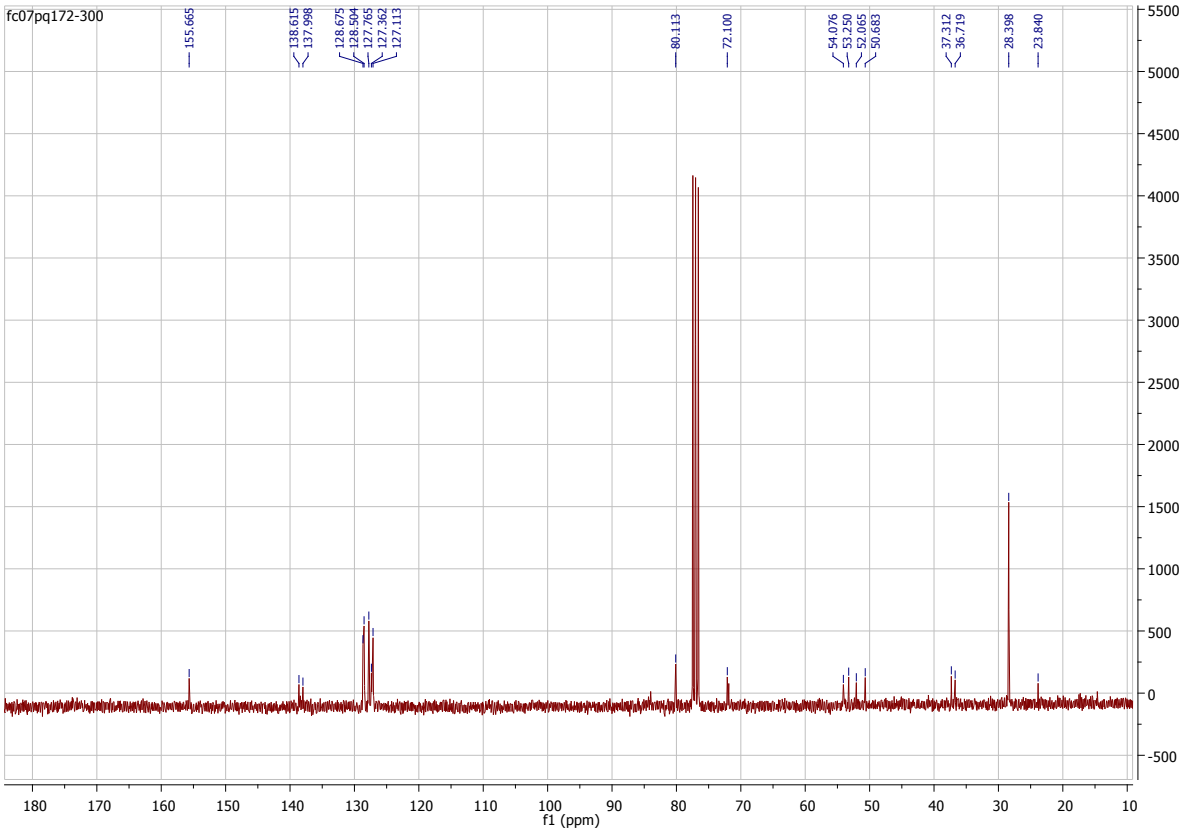

fc39pq407_sec
7.409
7.392
7.150
6.916
6.887
5.207
5.151
3.856
3.824
3.808
3.796
2.477
2.468
2.452
2.444
2.428
2.420
1.961
1.953
1.944
NCbz
O
7.35
2.00
2.10
5.00
1.83
0.79
f1 (ppm)

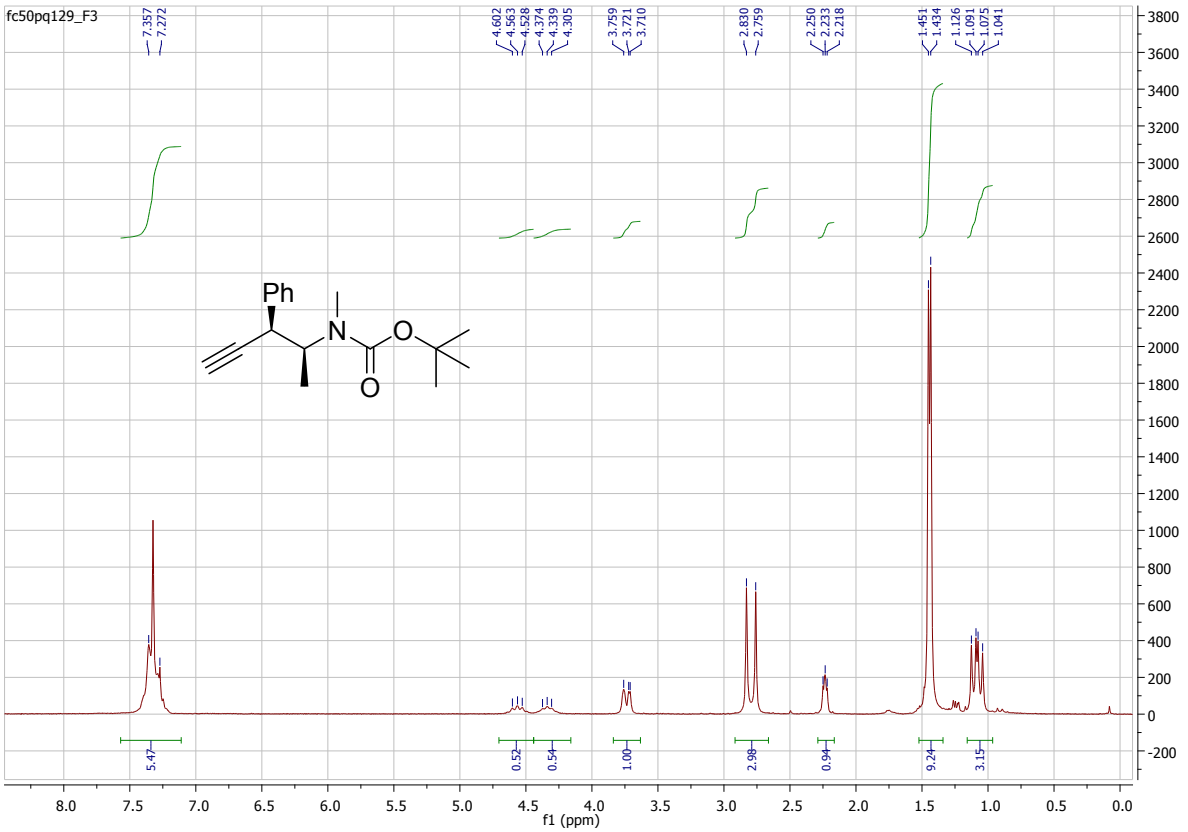

fc39pq407-300
158.385
155.614
136.684
128.713
128.610
128.398
128.301
127.795
127.332
114.302
81.230
69.942
67.151
55.449
49.252
18.074
f1 (ppm)

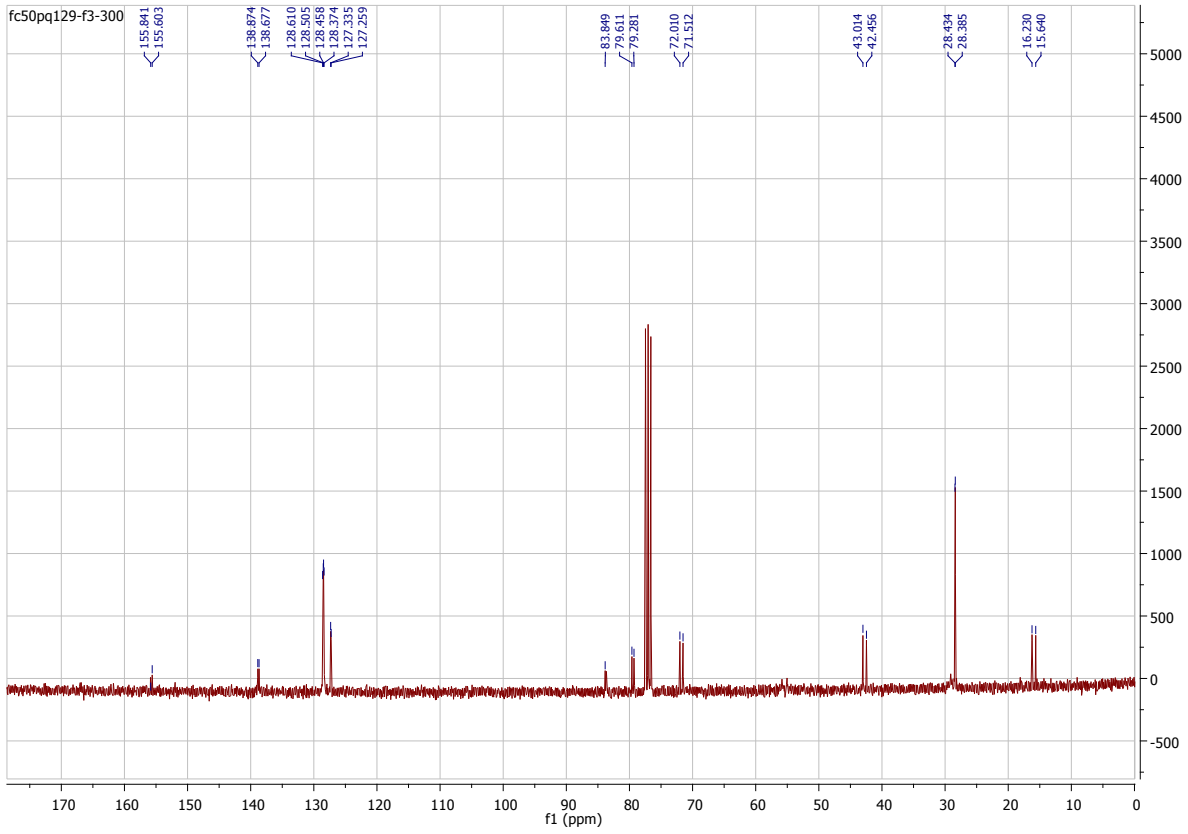

fc39pq421_apcol
7.347
6.946
6.884
5.202
3.897
3.873
3.848
2.515
2.507
2.490
2.482
2.347
1.986
1.977
1.969
NCbz
4.88
1.00
1.85
2.00
1.99
2.02
6.10
0.84
f1 (ppm)

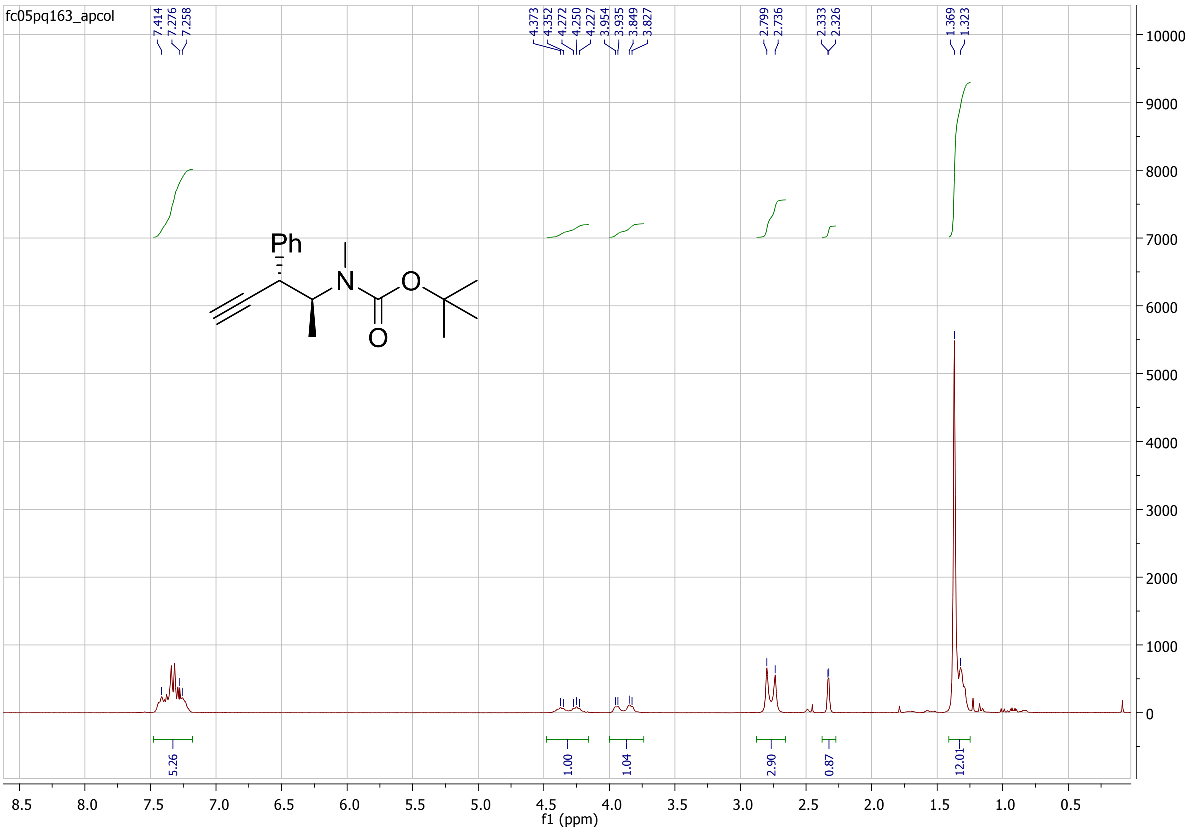

fc39pq421-300
155.399
141.089
138.746
136.713
128.812
128.421
127.896
127.692
125.118
81.260
69.946
67.209
49.133
21.251
18.260
f1 (ppm)

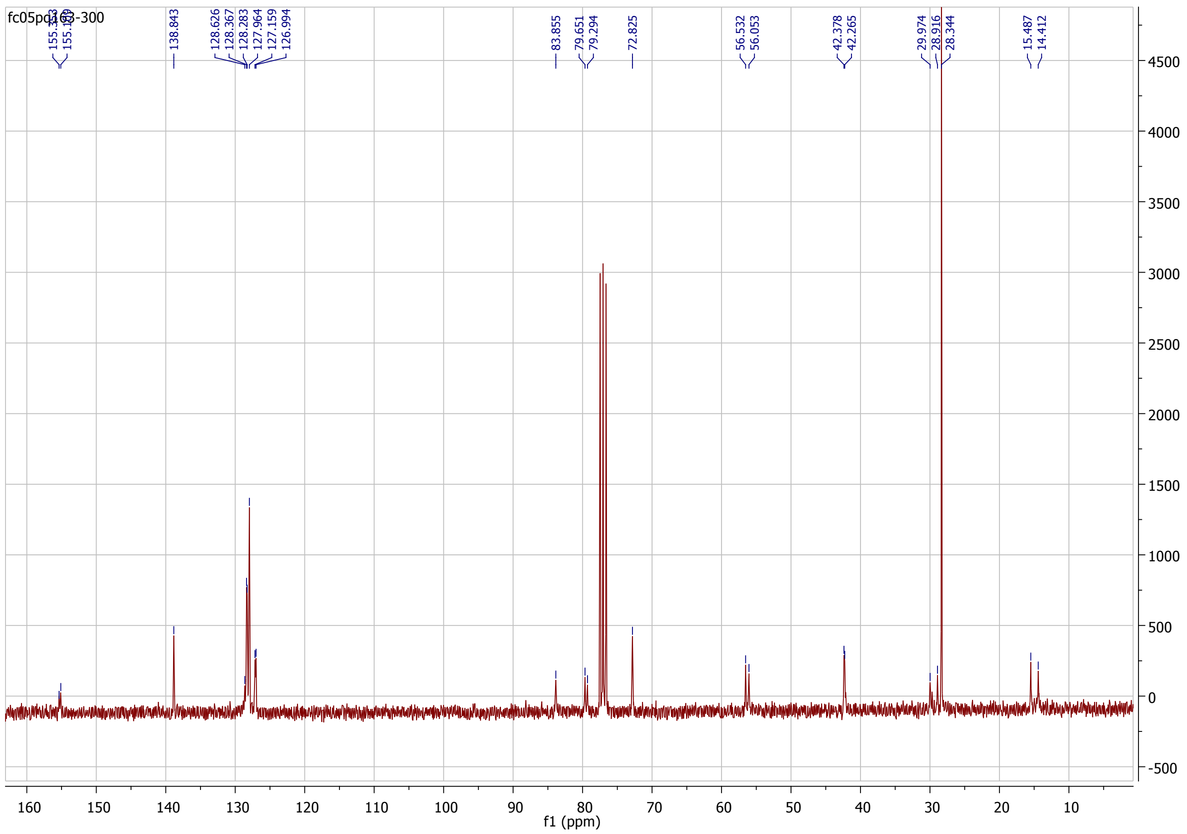

fc10pq172_sec
7.401
7.241
7.204
7.167
4.563
4.537
4.487
4.457
4.393
4.314
4.278
4.199
4.028
3.497
3.458
3.431
3.393
2.320
2.307
1.509
1.458
Ph
Ph
N
O
O
10.09
3.10
2.00
0.92
9.00
f1 (ppm)

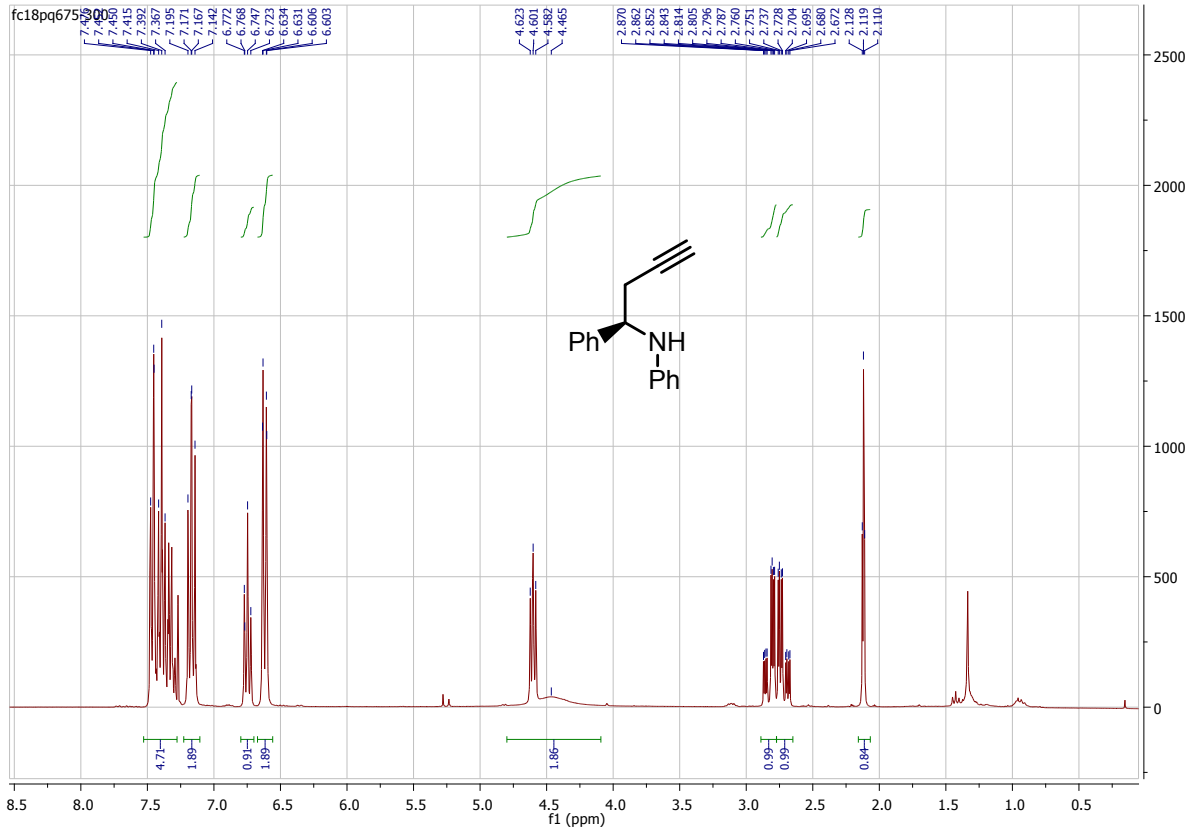

fc07pq172-300
155.665
138.615
137.998
128.675
128.504
127.765
127.362
127.113
80.113
72.100
54.076
53.250
52.065
50.683
37.312
36.719
28.398
23.840
f1 (ppm)

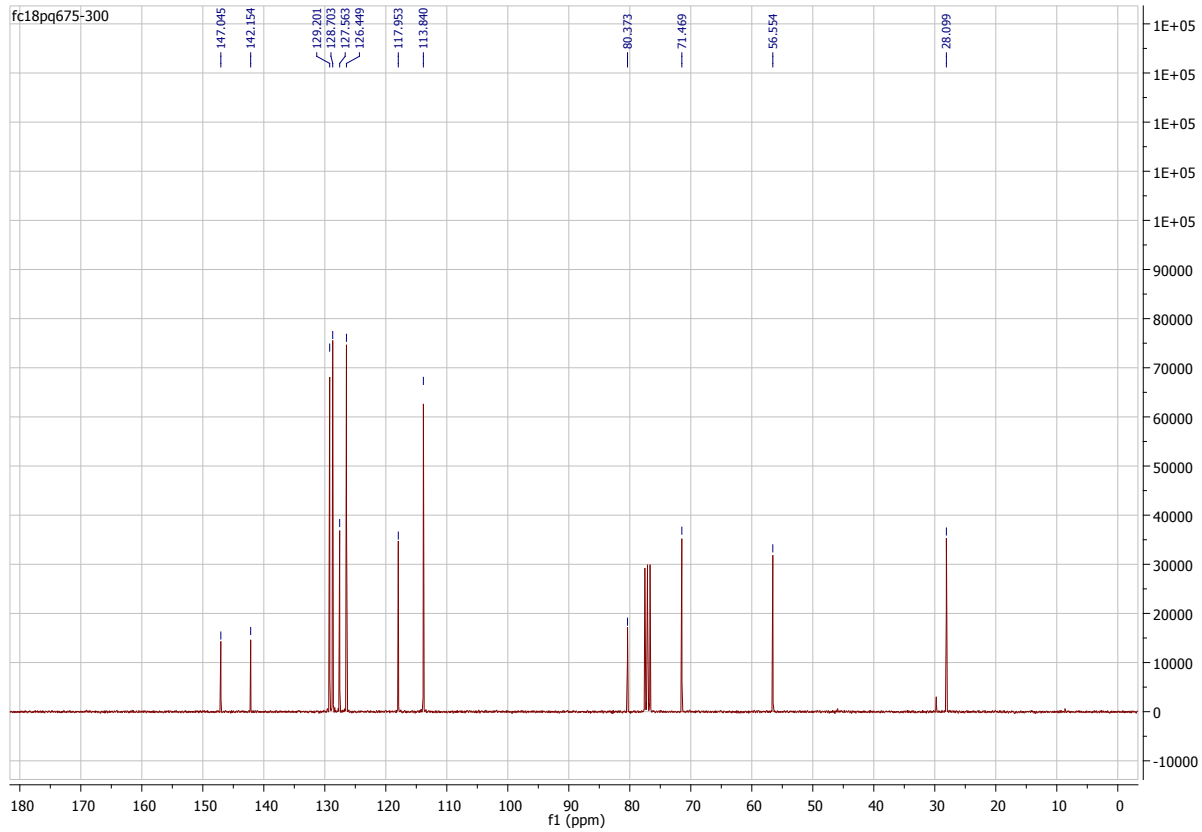

fc50pq129_F3
7.357
7.272
4.602
4.563
4.528
4.374
4.339
4.305
3.759
3.721
3.710
2.830
2.759
2.250
2.233
2.218
1.451
1.434
1.126
1.091
1.075
1.041
Ph
N
O
O
5.47
0.52
0.54
1.00
2.98
0.94
9.24
3.15
f1 (ppm)

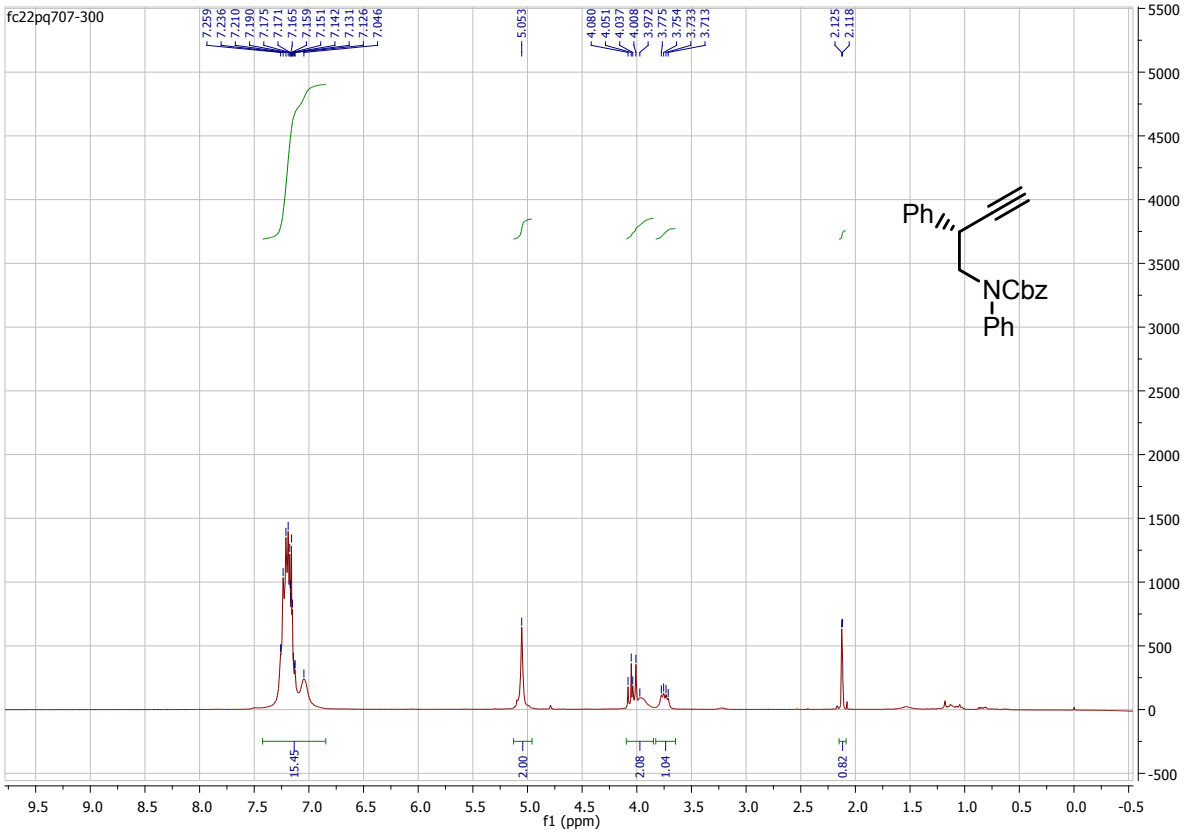

fc50pq129-f3-300
155.841
155.603
138.874
138.677
128.610
128.505
128.458
128.374
127.335
127.259
83.849
79.611
79.281
72.010
71.512
43.014
42.456
28.434
28.385
16.230
15.640
f1 (ppm)

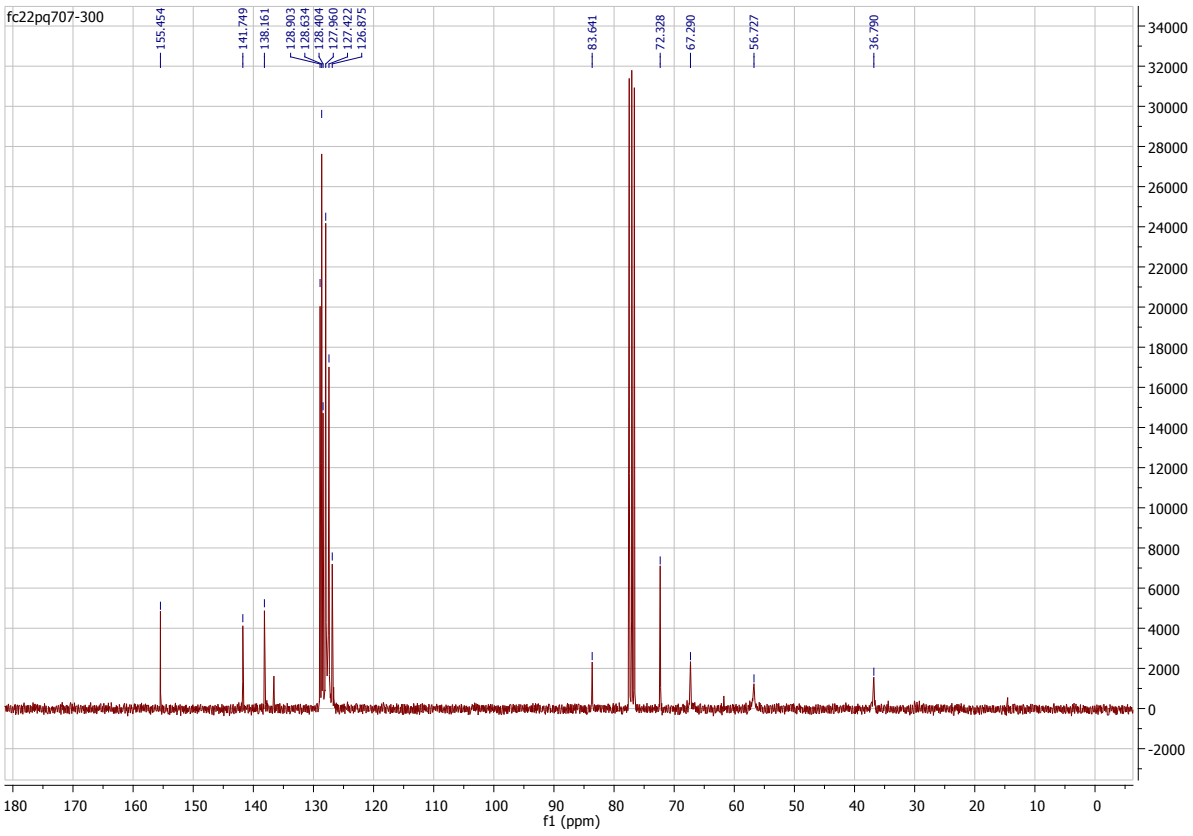

fc05pq163_apcol
7.414
7.276
7.258
4.373
4.352
4.272
4.250
4.227
3.954
3.935
3.849
3.827
2.799
2.736
2.333
2.326
1.369
1.323
Ph
N
O
O
5.26
1.00
1.04
2.90
0.87
12.01
f1 (ppm)

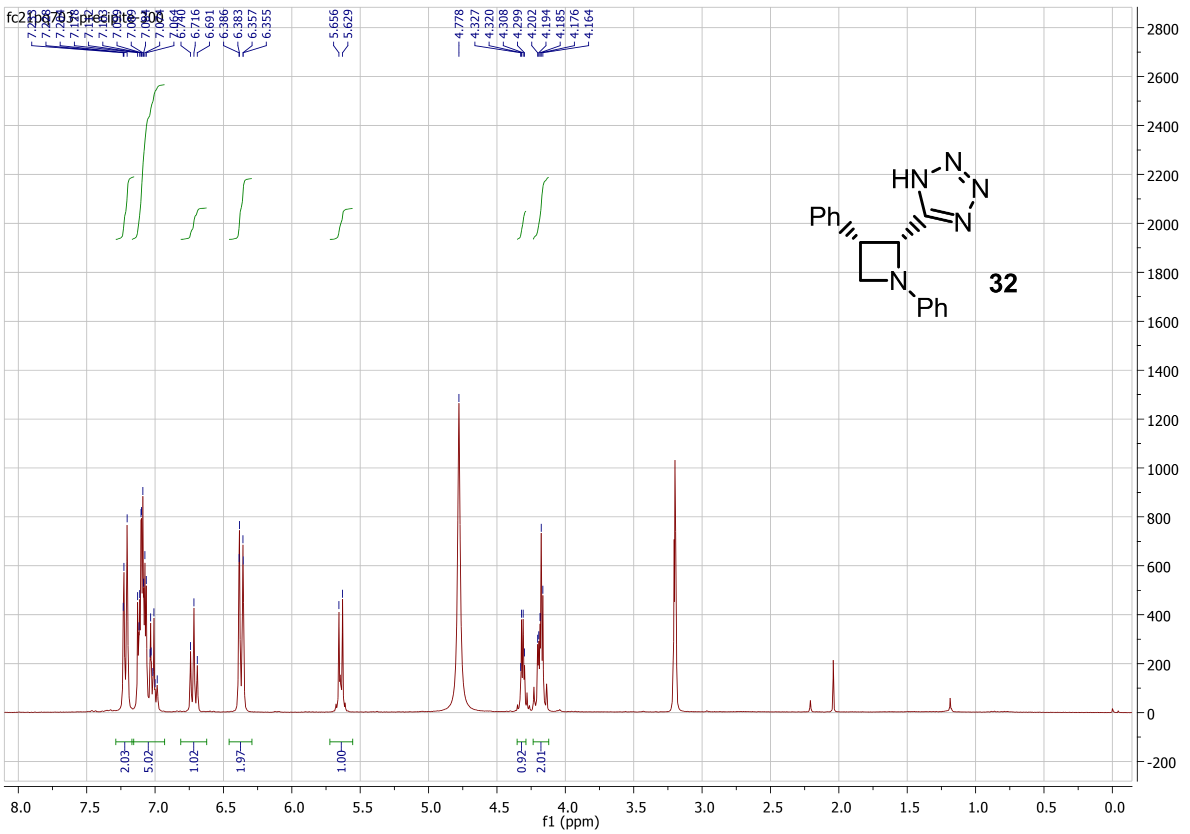

138.843
128.626
128.367
128.283
127.964
127.159
126.994
83.855
79.651
79.294
72.825
56.532
56.053
42.378
42.265
29.974
28.916
28.344
15.487
14.412
f1 (ppm)

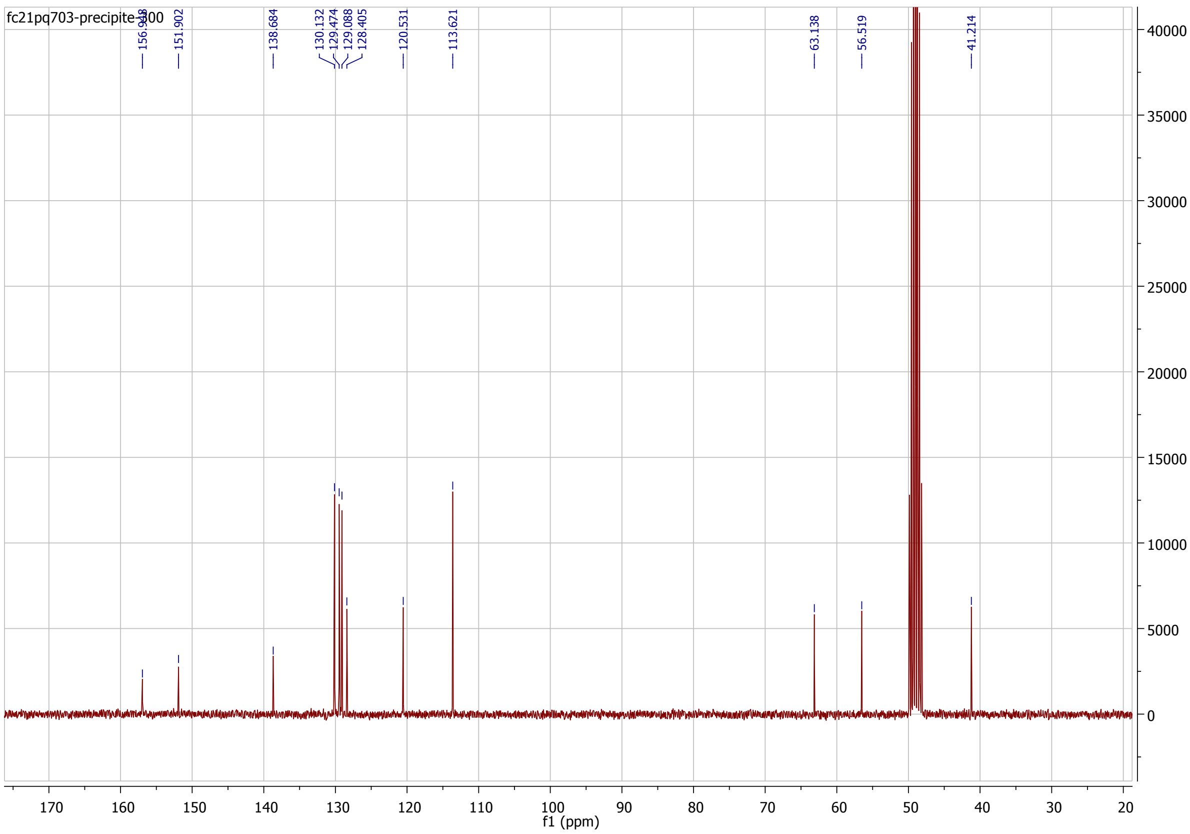

fc18pq675-300
Ph
NH
Ph
f1 (ppm)

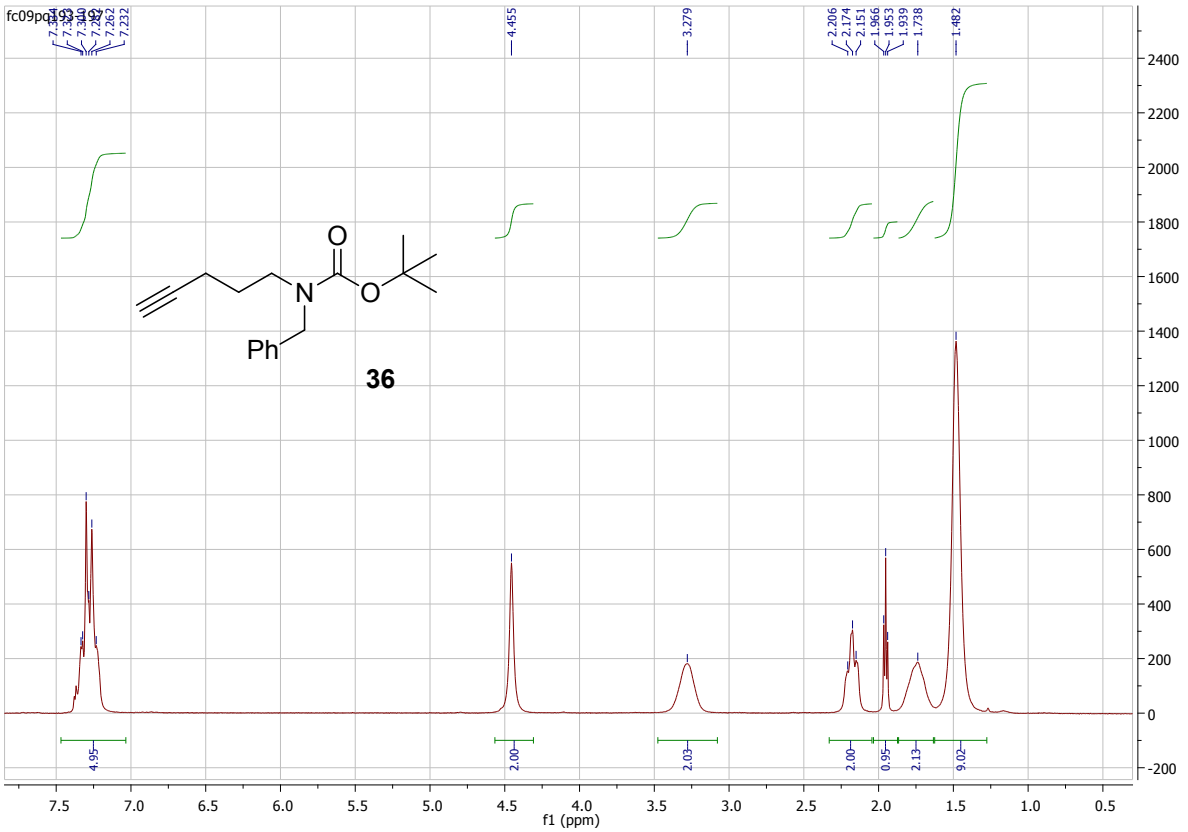

fc18pq675-300
f1 (ppm)

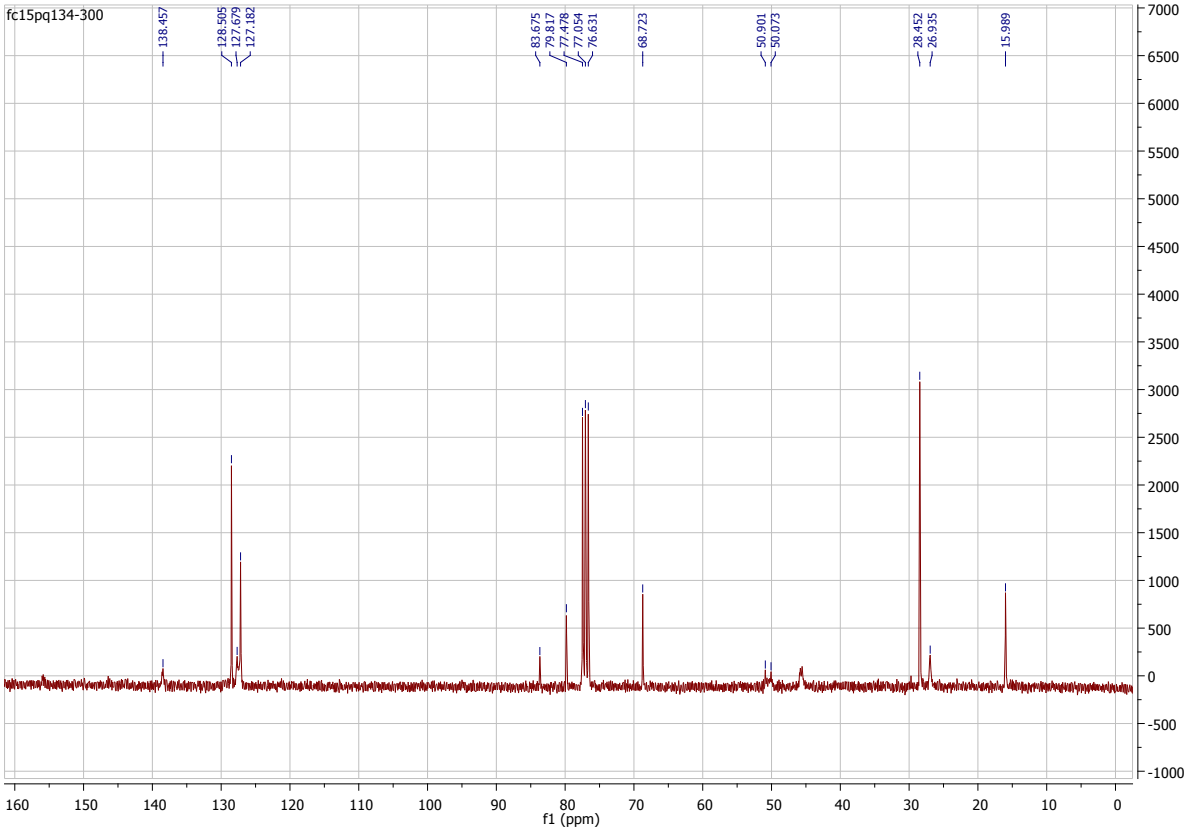

fc22pq707-300
7.259
7.236
7.210
7.190
7.175
7.171
7.165
7.159
7.151
7.142
7.131
7.126
7.046
5.053
4.080
4.051
4.037
4.008
3.972
3.775
3.754
3.733
3.713
2.125
2.118
Ph
NCbz
Ph
15.45
2.00
2.08
1.04
0.82
f1 (ppm)

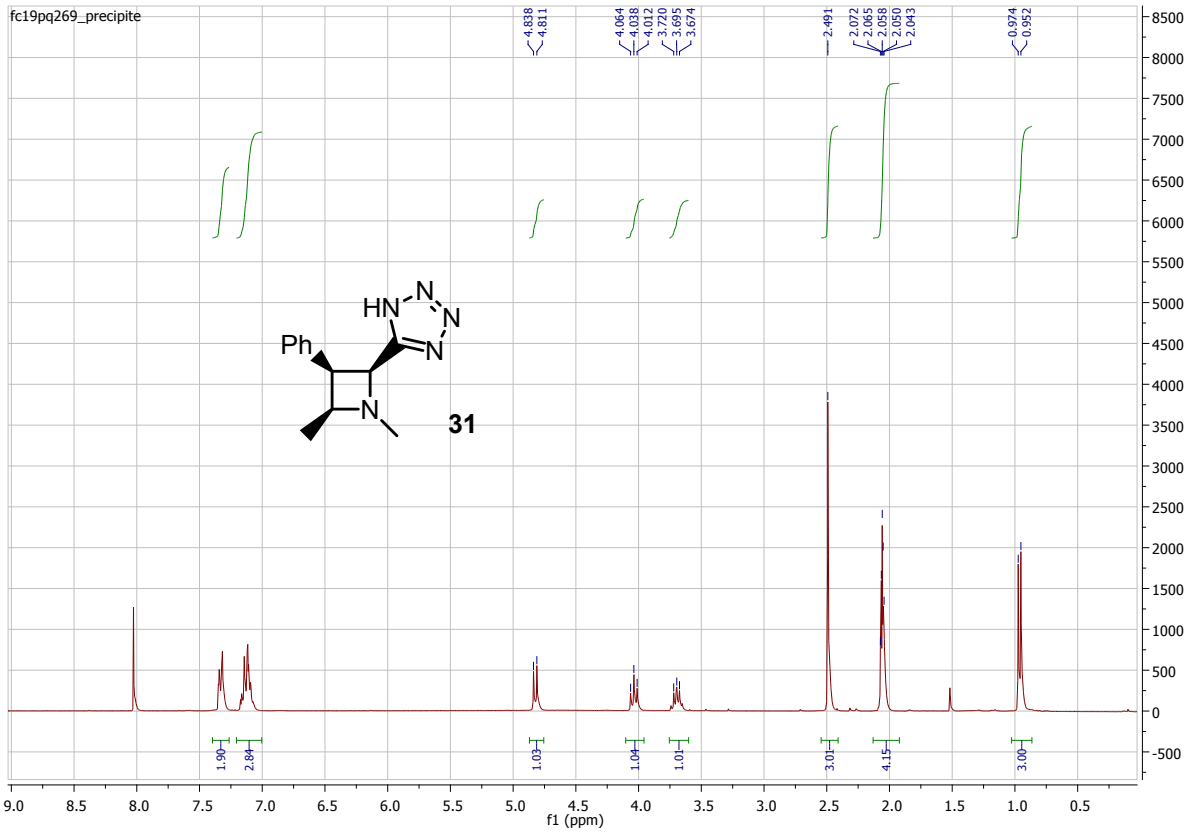

fc22pq707-300
155.454
141.749
138.161
128.903
128.634
128.404
127.960
127.422
126.875
83.641
72.328
67.290
56.727
36.790
f1 (ppm)

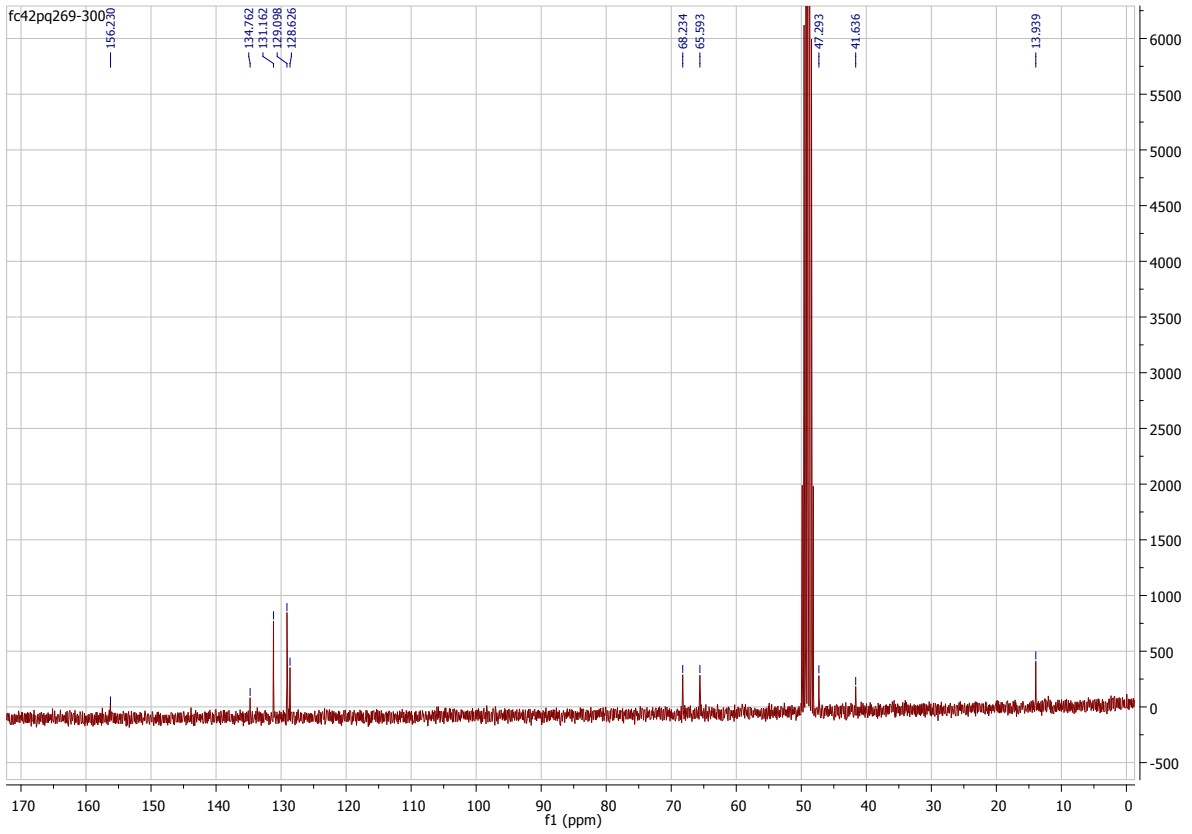

fc21pq703-precipite-300
6.716
6.691
6.386
6.383
6.357
6.355
5.656
5.629
4.778
4.327
4.320
4.308
4.299
4.202
4.194
4.185
4.176
4.164
2.03
5.02
1.02
1.97
1.00
0.92
2.01
HN
N
N
N
Ph
N
Ph
32
f1 (ppm)

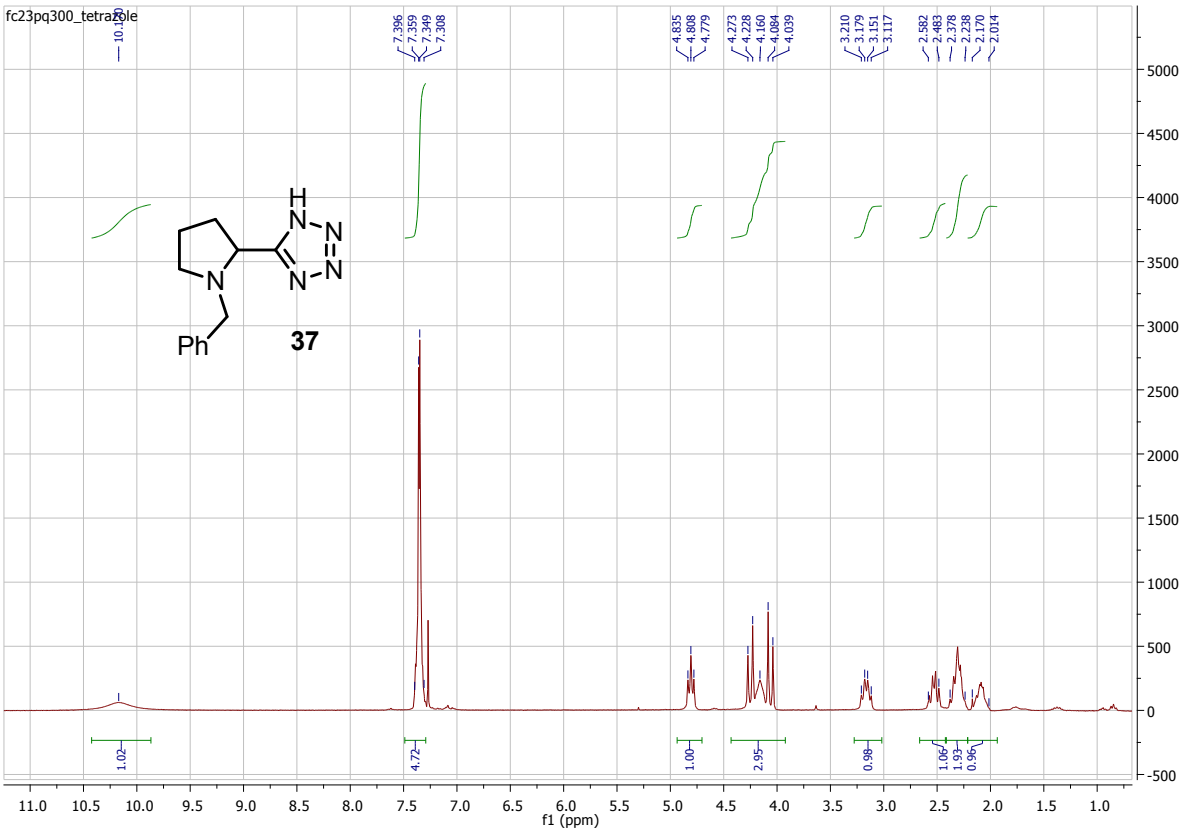

fc21pq703-precipite-300
151.902
138.684
130.132
129.474
129.088
128.405
120.531
113.621
63.138
56.519
41.214
f1 (ppm)


fc09pq193-02
4.455
3.279
2.206
2.174
2.151
1.966
1.953
1.939
1.738
1.482
O
N
O
Ph
36
4.95
2.00
2.03
2.00
0.95
2.13
9.02
f1 (ppm)

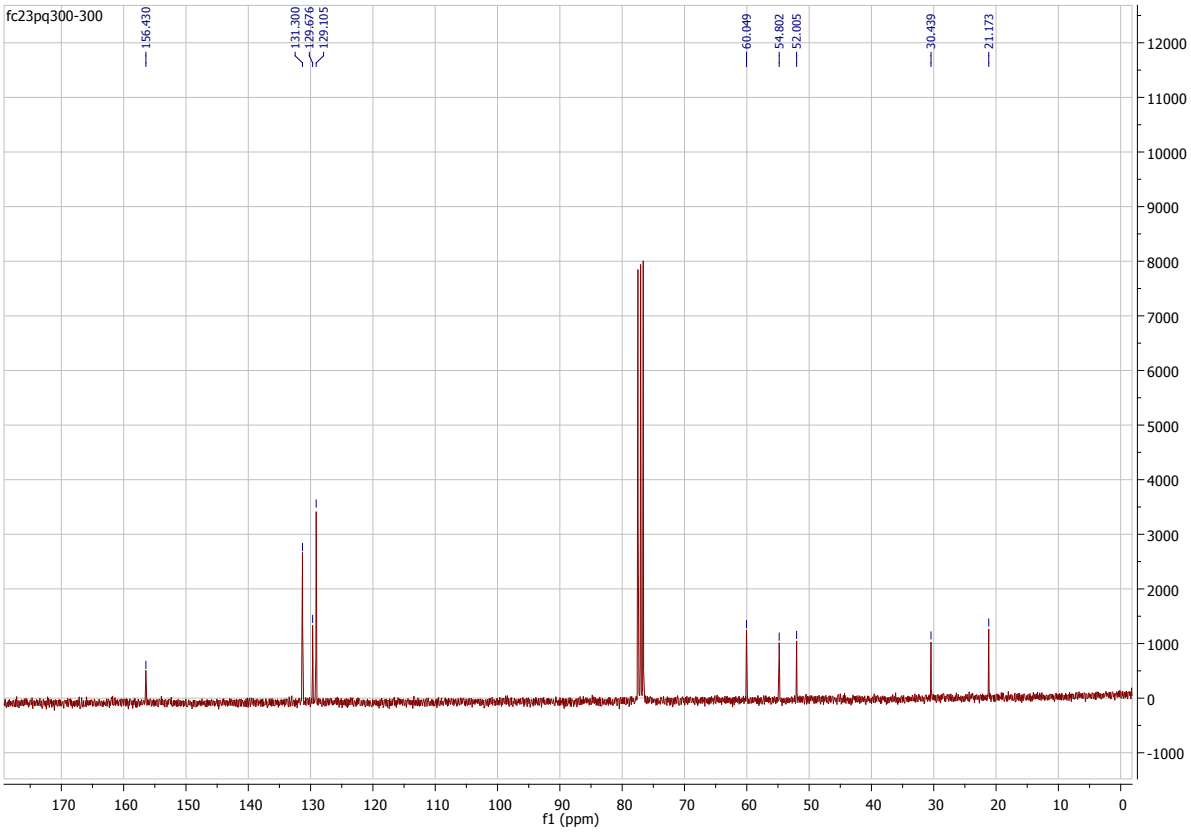

fc15pq134-300
138.457
128.505
127.679
127.182
83.675
79.417
77.478
77.054
76.631
68.723
50.901
50.073
28.452
26.935
15.989
f1 (ppm)

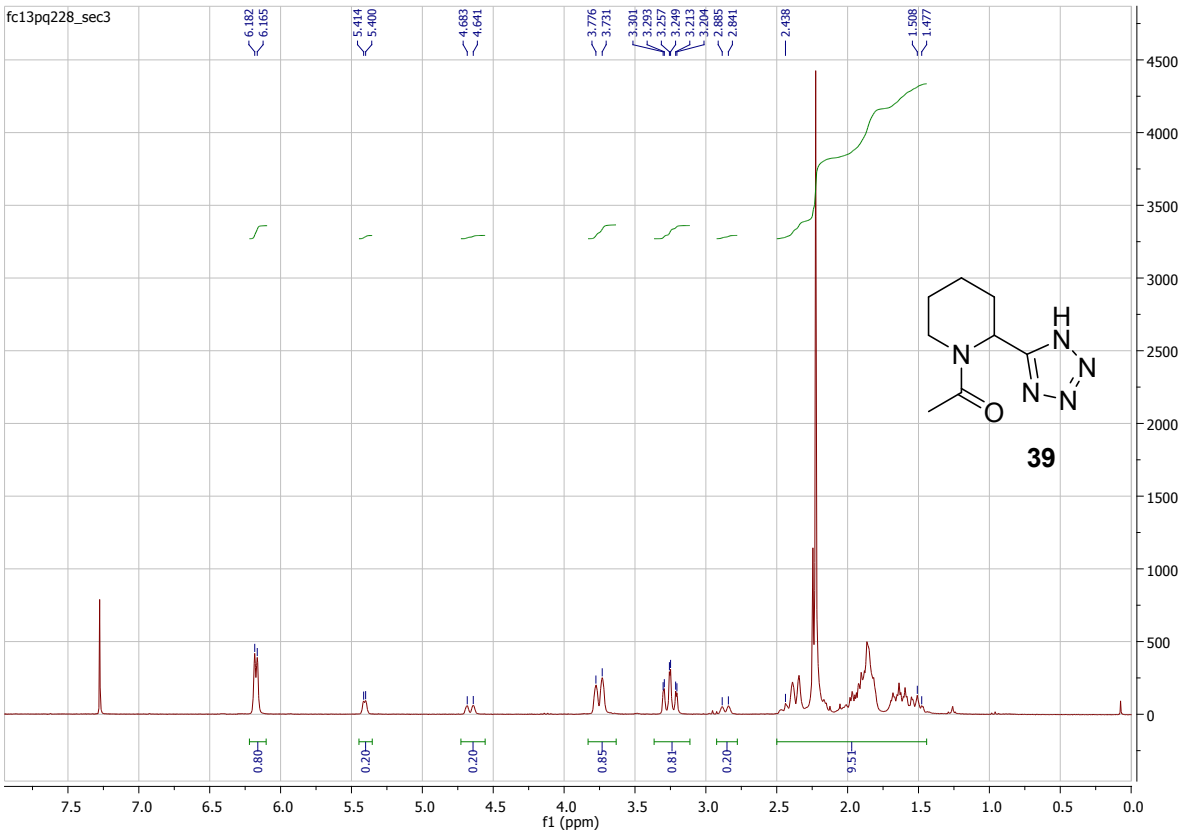

fc19pq269_precipite
4.838
4.811
4.064
4.038
4.012
3.720
3.695
3.674
2.491
2.072
2.065
2.058
2.050
2.043
0.974
0.952
HN
N
N
N
Ph
N
31
1.90
2.84
1.03
1.04
1.01
3.01
4.15
3.00
f1 (ppm)

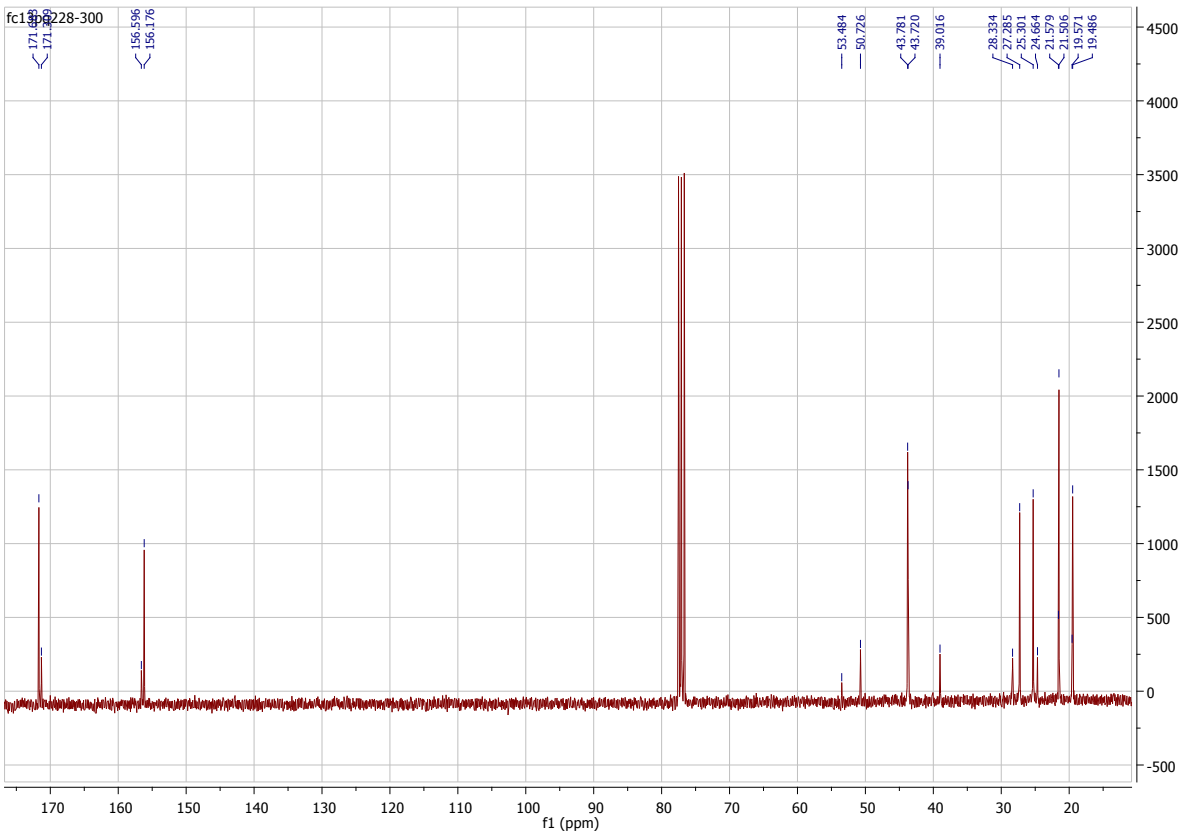

fc42pq269-300
156.230
134.762
131.162
129.098
128.626
68.234
65.593
47.293
41.636
13.939
f1 (ppm)

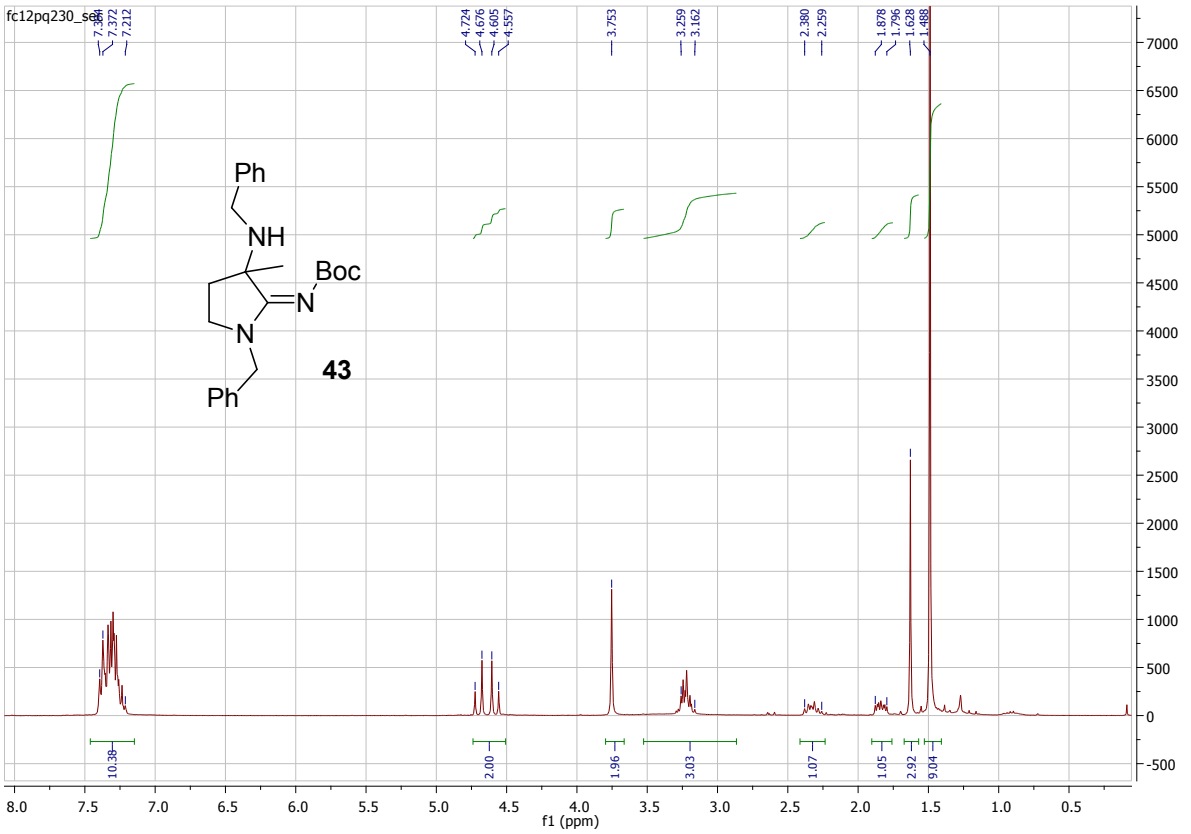

fc23pq300_tetrazole
10.182
7.396
7.359
7.349
7.308
4.835
4.808
4.779
4.273
4.228
4.160
4.084
4.039
3.210
3.179
3.151
3.117
2.582
2.483
2.378
2.238
2.170
2.014
1.02
4.72
1.00
2.95
0.98
1.06
1.93
0.96
f1 (ppm)

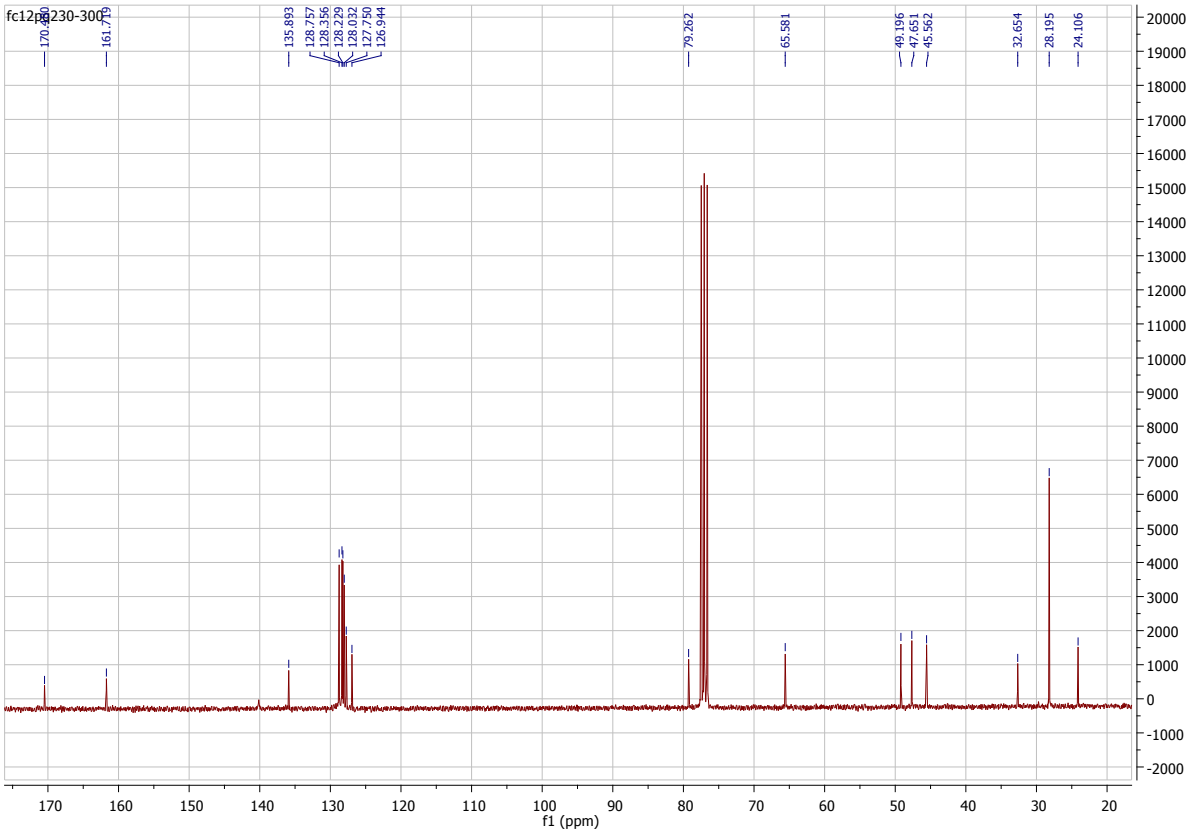
37

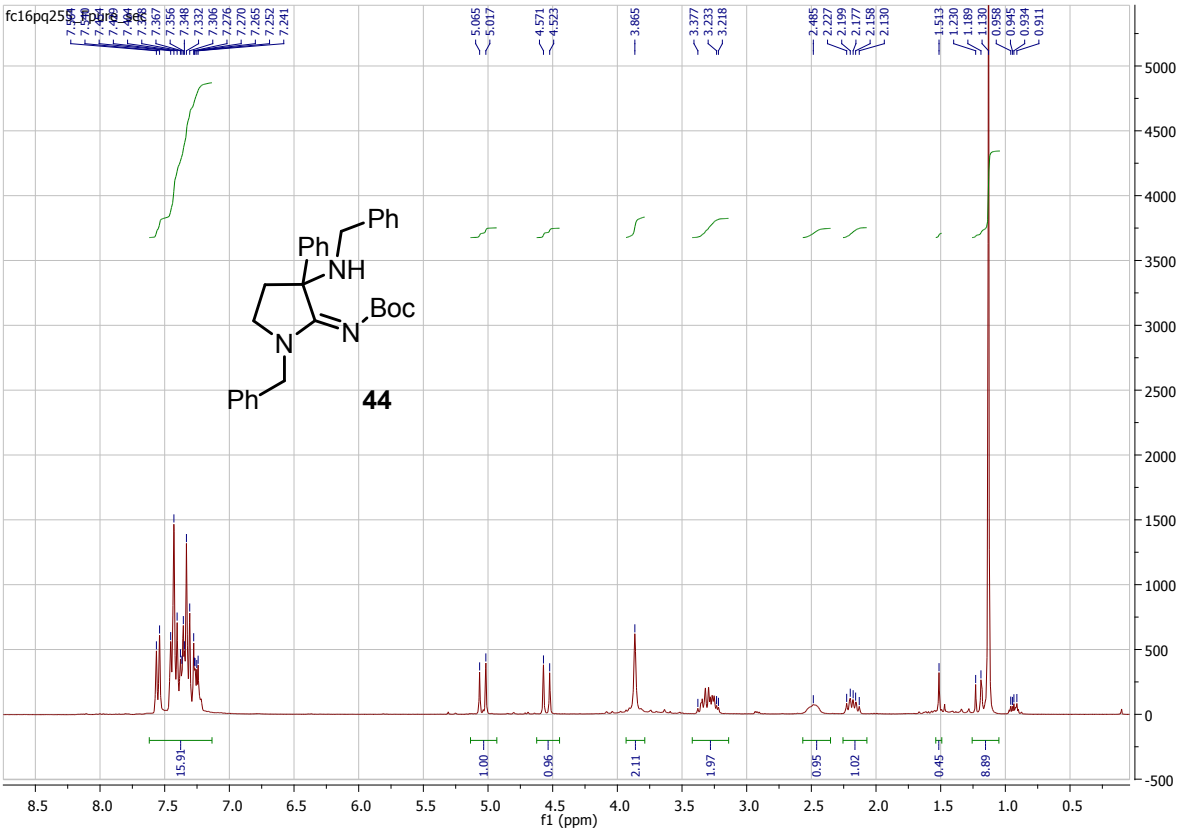

fc23pq300-300
156.430
131.300
129.676
129.105
60.049
54.802
52.005
30.439
21.173
f1 (ppm)

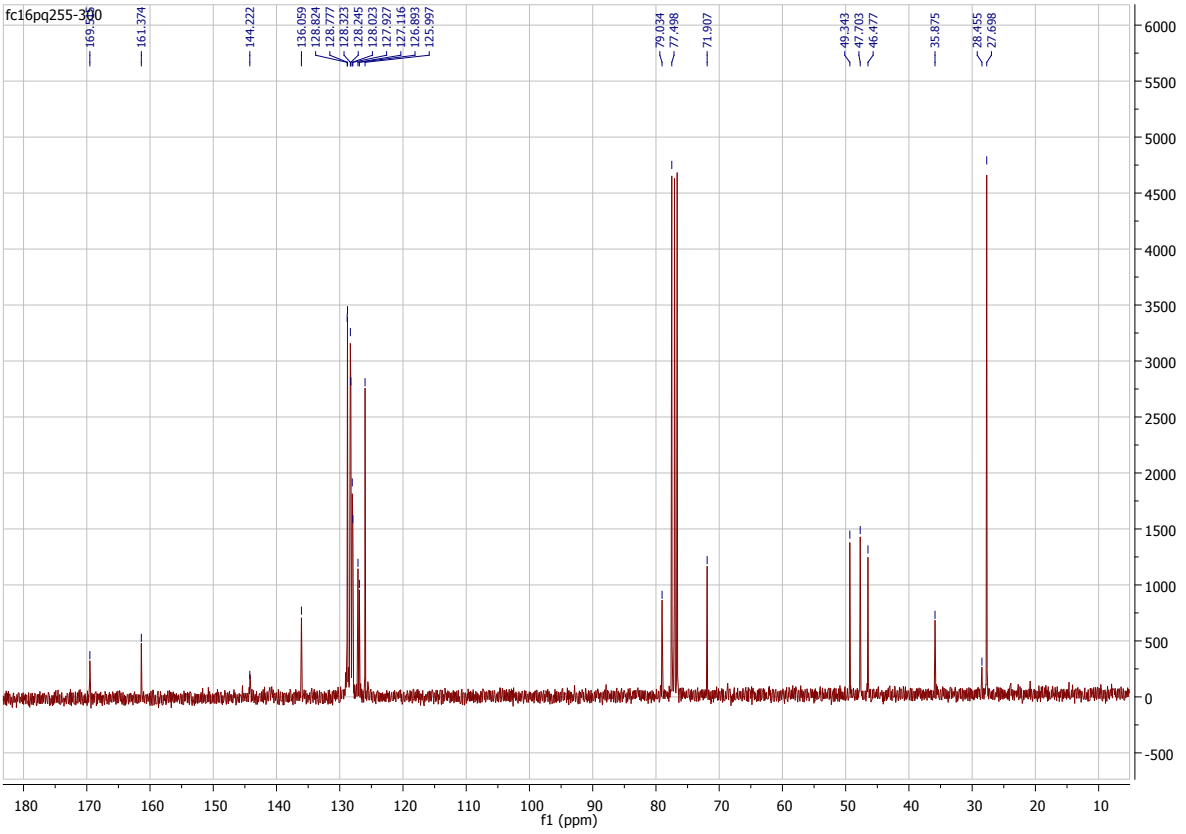

fc13pq228_sec3
6.182
6.165
5.414
5.400
4.683
4.641
3.776
3.731
3.301
3.293
3.257
3.249
3.213
3.204
2.885
2.841
2.438
1.508
1.477
0.80
0.20
0.20
0.85
0.81
0.20
9.51
f1 (ppm)
39


fc13pq228-300
171.439
171.298
156.596
156.176
53.484
50.726
43.781
43.720
39.016
28.334
27.285
25.301
24.664
21.579
21.506
19.571
19.486
f1 (ppm)

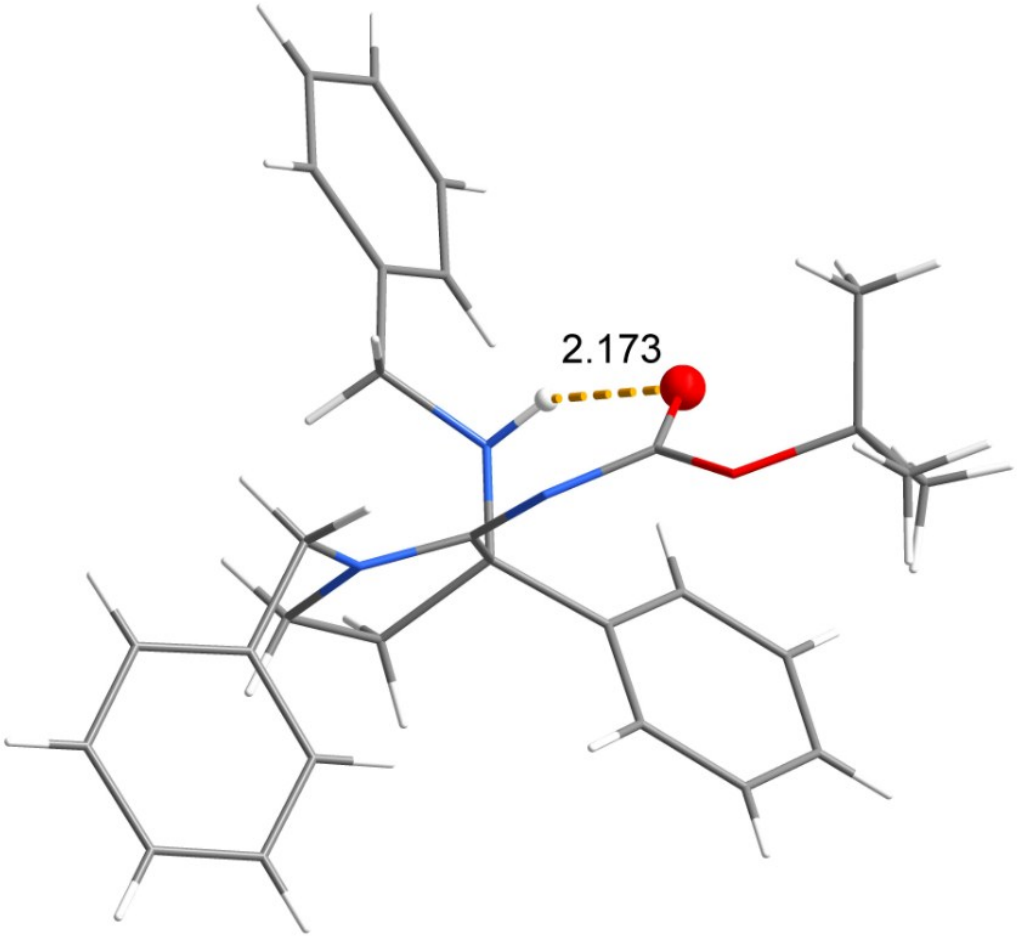

fc12pq230_sen
7.380
7.372
7.212
4.724
4.676
4.605
4.557
3.753
3.259
3.162
2.380
2.259
1.878
1.796
1.628
1.488
Ph
NH
Boc
N
N
Ph
43
10.39
2.00
1.96
3.03
1.07
1.05
2.92
9.04
f1 (ppm)


fc12pq230-300
170.480
161.779
135.893
128.757
128.356
128.229
128.032
127.750
126.944
79.262
65.581
49.196
47.651
45.562
32.654
28.195
24.106
f1 (ppm)


Ph
Ph
NH
Boc
N
N
Ph
44
f1 (ppm)


f1 (ppm)

X-Ray data for 44 (R = Ph)



structure report

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Computing details

Data collection: Bruker *APEX2*; cell refinement: Bruker *SAINT*; data reduction: Bruker *SAINT*; program(s) used to solve
structure: *SHELXS97* (Sheldrick 2008); program(s) used to refine structure: *SHELXL2014*/7 (Sheldrick, 2014); molecular
graphics: Bruker *SHELXTL*; software used to prepare material for publication: Bruker *SHELXTL*.

Crystal data

$C_{29}H_{33}N_3O_2$
M_r = 455.58
Triclinic, *P*1
a = 9.6437 (4) Å
b = 11.6855 (5) Å
c = 12.1217 (6) Å
α= 87.115 (2)°
β= 71.784 (2)°
γ= 82.973 (2)°
V = 1287.70 (10) Å^3
Z = 2
F(000) = 488
D_x = 1.175 Mg m^{-3}
Mo *Kα*radiation, *λ*= 0.71073 Å
Cell parameters from 9883 reflections
θ= 2.4–29.5°
μ= 0.07 mm^{-1}
T = 295 K
Parallelepiped, yellow
0.20 × 0.18 × 0.12 mm

Data collection

Bruker D8 VENTURE
diffractometer
Radiation source: microsource
*φ*and *ω*scans
Absorption correction: multi-scan
SADABS (Sheldrick, V2014/5)
73096 measured reflections
7537 independent reflections
5739 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 30.1°, θ_{min} = 2.4°
h = −13→13
k = −16→16
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.196
S = 1.11
7537 reflections
314 parameters
0 restraints
Hydrogen site location: mixed

structure report

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H atoms treated by a mixture of independent and
constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1056P)^2 + 0.1933P]$
where $P = (F_o^2 + 2F_c$

$_2$)/3
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.52$ e Å^{-3}
Special details
Geometry
All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s
are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell
parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for
estimating e.s.d.'s involving l.s. planes.
Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.41122 (13)	0.34910 (10)	0.40396 (10)	0.0381 (3)
C2	0.31439 (13)	0.38554 (11)	0.32486 (11)	0.0407 (3)
C3	0.16637 (15)	0.34362 (15)	0.39756 (13)	0.0524 (3)
H3A	0.0850	0.3988	0.3920	0.063*
H3B	0.1555	0.2699	0.3697	0.063*
C4	0.16865 (15)	0.33209 (15)	0.52272 (13)	0.0536 (3)
H4A	0.1147	0.3988	0.5677	0.064*
H4B	0.1272	0.2631	0.5597	0.064*
N5	0.32434 (12)	0.32477 (11)	0.51041 (10)	0.0459 (3)
N6	0.55271 (11)	0.34025 (10)	0.38207 (9)	0.0414 (2)
C7	0.64330 (13)	0.37782 (11)	0.27905 (11)	0.0383 (3)
O8	0.62203 (11)	0.46338 (9)	0.22241 (9)	0.0490 (2)
O9	0.77092 (10)	0.30824 (8)	0.25201 (8)	0.0448 (2)
C10	0.89435 (14)	0.33215 (13)	0.14989 (12)	0.0468 (3)
C11	0.8527 (2)	0.32246 (17)	0.04039 (14)	0.0626 (4)
H11A	0.8111	0.2515	0.0426	0.094*
H11B	0.9388	0.3235	−0.0261	0.094*
H11C	0.7820	0.3862	0.0354	0.094*
C12	0.94355 (19)	0.44812 (16)	0.16088 (18)	0.0638 (4)
H12A	0.8757	0.5085	0.1442	0.096*
H12B	1.0397	0.4530	0.1069	0.096*
H12C	0.9464	0.4564	0.2385	0.096*
C13	1.01292 (18)	0.23620 (17)	0.15813 (18)	0.0660 (4)
H13A	1.0281	0.2385	0.2325	0.099*
H13B	1.1029	0.2467	0.0979	0.099*
H13C	0.9825	0.1629	0.1492	0.099*
C14	0.37319 (14)	0.32660 (12)	0.20746 (12)	0.0431 (3)
C15	0.37698 (17)	0.38567 (14)	0.10490 (13)	0.0508 (3)
H15	0.3459	0.4643	0.1066	0.061*
C16	0.4268 (2)	0.32880 (18)	−0.00060 (14)	0.0655 (4)
H16	0.4291	0.3696	−0.0689	0.079*
C17	0.4723 (2)	0.2135 (2)	−0.00450 (17)	0.0731 (5)
H17	0.5061	0.1758	−0.0753	0.088*
C18	0.4680 (3)	0.15322 (18)	0.09658 (19)	0.0759 (5)
H18	0.4981	0.0744	0.0942	0.091*
C19	0.4190 (2)	0.20931 (14)	0.20210 (16)	0.0613 (4)
H19	0.4168	0.1678	0.2700	0.074*
N20	0.30014 (14)	0.51071 (10)	0.30681 (10)	0.0460 (3)

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C21	0.24164 (17)	0.58292 (13)	0.40806 (13)	0.0503 (3)
H21A	0.3109	0.5760	0.4520	0.060*
H21B	0.1508	0.5565	0.4574	0.060*
C22	0.21288 (15)	0.70742 (13)	0.37532 (14)	0.0500 (3)
C23	0.2053 (2)	0.79168 (17)	0.4532 (2)	0.0754 (6)
H23	0.2222	0.7713	0.5234	0.090*
C24	0.1726 (4)	0.9061 (2)	0.4273 (3)	0.1095 (10)
H24	0.1671	0.9625	0.4804	0.131*
C25	0.1481 (4)	0.9371 (2)	0.3240 (3)	0.1084 (9)
H25	0.1301	1.0147	0.3058	0.130*
C26	0.1502 (3)	0.8541 (2)	0.2474 (2)	0.0942 (8)

H26 0.1289 0.8746 0.1788 0.113*
C27 0.1843 (2) 0.73953 (17) 0.27313 (16) 0.0701 (5)
H27 0.1880 0.6832 0.2204 0.084*
C28 0.37620 (18) 0.30302 (14) 0.61099 (12) 0.0498 (3)
H28A 0.3374 0.3668 0.6642 0.060*
H28B 0.4825 0.2992 0.5859 0.060*
C29 0.33092 (14) 0.19285 (11) 0.67374 (11) 0.0417 (3)
C30 0.3544 (3) 0.09033 (16) 0.61479 (18) 0.0737 (5)
H30 0.3958 0.0897 0.5344 0.088*
C31 0.3171 (3) −0.01030 (17) 0.6738 (3) 0.0931 (8)
H31 0.3324 −0.0785 0.6331 0.112*
C32 0.2583 (3) −0.01094 (19) 0.7904 (3) 0.0902 (8)
H32 0.2353 −0.0798 0.8300 0.108*
C33 0.2326 (3) 0.0891 (2) 0.8504 (2) 0.0907 (7)
H33 0.1909 0.0886 0.9308 0.109*
C34 0.2685 (2) 0.19152 (15) 0.79165 (14) 0.0623 (4)
H34 0.2500 0.2597 0.8327 0.075*
H20 0.391 (2) 0.5305 (15) 0.2730 (16) 0.052 (4)*

Atomic displacement parameters (Å²)

U_{11} U_{22} U_{33} U_{12} U_{13} U_{23}

C1 0.0373 (6) 0.0397 (6) 0.0370 (6) −0.0047 (4) −0.0117 (4) 0.0044 (4)
C2 0.0356 (6) 0.0468 (6) 0.0398 (6) −0.0023 (5) −0.0132 (5) 0.0047 (5)
C3 0.0376 (6) 0.0685 (9) 0.0516 (8) −0.0093 (6) −0.0144 (6) 0.0073 (7)
C4 0.0384 (7) 0.0698 (9) 0.0480 (7) −0.0082 (6) −0.0076 (5) 0.0097 (6)
N5 0.0397 (6) 0.0595 (7) 0.0377 (5) −0.0098 (5) −0.0106 (4) 0.0097 (5)
N6 0.0359 (5) 0.0513 (6) 0.0366 (5) −0.0050 (4) −0.0114 (4) 0.0059 (4)
C7 0.0360 (6) 0.0416 (6) 0.0384 (6) −0.0062 (4) −0.0129 (4) 0.0026 (5)
O8 0.0437 (5) 0.0478 (5) 0.0520 (5) −0.0034 (4) −0.0126 (4) 0.0123 (4)
O9 0.0355 (4) 0.0489 (5) 0.0451 (5) −0.0026 (4) −0.0078 (4) 0.0094 (4)
C10 0.0361 (6) 0.0521 (7) 0.0477 (7) −0.0089 (5) −0.0056 (5) 0.0027 (6)
C11 0.0663 (10) 0.0731 (11) 0.0456 (8) −0.0157 (8) −0.0105 (7) 0.0010 (7)
C12 0.0509 (8) 0.0633 (10) 0.0757 (11) −0.0206 (7) −0.0127 (7) 0.0008 (8)
C13 0.0399 (7) 0.0684 (10) 0.0825 (12) 0.0010 (7) −0.0107 (7) −0.0031 (9)
C14 0.0393 (6) 0.0490 (7) 0.0436 (7) −0.0035 (5) −0.0175 (5) 0.0009 (5)
C15 0.0537 (8) 0.0572 (8) 0.0437 (7) −0.0104 (6) −0.0174 (6) 0.0049 (6)
C16 0.0740 (11) 0.0823 (12) 0.0427 (8) −0.0208 (9) −0.0176 (7) 0.0003 (7)
C17 0.0751 (12) 0.0895 (14) 0.0577 (10) −0.0044 (10) −0.0231 (8) −0.0232 (9)
C18 0.0921 (14) 0.0622 (10) 0.0807 (13) 0.0119 (9) −0.0413 (11) −0.0228 (9)
C19 0.0787 (11) 0.0509 (8) 0.0603 (9) 0.0036 (7) −0.0339 (8) −0.0030 (7)

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N20 0.0443 (6) 0.0461 (6) 0.0427 (6) 0.0036 (5) −0.0103 (5) 0.0031 (5)
C21 0.0494 (7) 0.0531 (8) 0.0461 (7) 0.0024 (6) −0.0148 (6) 0.0001 (6)
C22 0.0387 (6) 0.0524 (8) 0.0558 (8) 0.0061 (5) −0.0140 (6) −0.0018 (6)
C23 0.0874 (13) 0.0637 (10) 0.0860 (13) 0.0141 (9) −0.0488 (11) −0.0152 (9)
C24 0.149 (3) 0.0615 (12) 0.141 (2) 0.0261 (14) −0.088 (2) −0.0281 (14)
C25 0.143 (3) 0.0562 (12) 0.131 (2) 0.0239 (13) −0.063 (2) 0.0002 (13)
C26 0.130 (2) 0.0696 (13) 0.0805 (14) 0.0239 (13) −0.0428 (14) 0.0074 (11)
C27 0.0893 (13) 0.0607 (10) 0.0574 (10) 0.0124 (9) −0.0261 (9) −0.0017 (8)
C28 0.0586 (8) 0.0565 (8) 0.0376 (6) −0.0182 (6) −0.0166 (6) 0.0080 (5)
C29 0.0438 (6) 0.0447 (6) 0.0379 (6) −0.0038 (5) −0.0149 (5) 0.0007 (5)
C30 0.1078 (16) 0.0539 (9) 0.0598 (10) 0.0015 (9) −0.0285 (10) −0.0121 (8)
C31 0.134 (2) 0.0445 (9) 0.123 (2) −0.0050 (11) −0.0730 (18) −0.0032 (11)
C32 0.1019 (17) 0.0637 (12) 0.124 (2) −0.0325 (11) −0.0604 (15) 0.0417 (13)
C33 0.1089 (18) 0.0922 (16) 0.0622 (12) −0.0228 (13) −0.0149 (11) 0.0346 (11)
C34 0.0824 (11) 0.0581 (9) 0.0407 (7) −0.0072 (8) −0.0118 (7) 0.0041 (6)

Geometric parameters (Å, º)

C1—N6 1.2980 (16) C17—C18 1.374 (3)
C1—N5 1.3391 (16) C17—H17 0.9300
C1—C2 1.5473 (17) C18—C19 1.386 (3)
C2—N20 1.4641 (17) C18—H18 0.9300
C2—C14 1.5231 (19) C19—H19 0.9300
C2—C3 1.5477 (19) N20—C21 1.4462 (19)
C3—C4 1.523 (2) N20—H20 0.899 (19)
C3—H3A 0.9700 C21—C22 1.504 (2)
C3—H3B 0.9700 C21—H21A 0.9700

C4—N5 1.4538 (18) C21—H21B 0.9700
C4—H4A 0.9700 C22—C27 1.376 (2)
C4—H4B 0.9700 C22—C23 1.378 (2)
N5—C28 1.4561 (17) C23—C24 1.379 (3)
N6—C7 1.3682 (16) C23—H23 0.9300
C7—O8 1.2173 (16) C24—C25 1.369 (4)
C7—O9 1.3465 (15) C24—H24 0.9300
O9—C10 1.4672 (16) C25—C26 1.371 (4)
C10—C12 1.515 (2) C25—H25 0.9300
C10—C11 1.515 (2) C26—C27 1.383 (3)
C10—C13 1.523 (2) C26—H26 0.9300
C11—H11A 0.9600 C27—H27 0.9300
C11—H11B 0.9600 C28—C29 1.5025 (19)
C11—H11C 0.9600 C28—H28A 0.9700
C12—H12A 0.9600 C28—H28B 0.9700
C12—H12B 0.9600 C29—C34 1.367 (2)
C12—H12C 0.9600 C29—C30 1.384 (2)
C13—H13A 0.9600 C30—C31 1.372 (3)
C13—H13B 0.9600 C30—H30 0.9300
C13—H13C 0.9600 C31—C32 1.349 (4)
C14—C15 1.384 (2) C31—H31 0.9300
C14—C19 1.386 (2) C32—C33 1.363 (4)
C15—C16 1.390 (2) C32—H32 0.9300
C15—H15 0.9300 C33—C34 1.386 (3)
C16—C17 1.363 (3) C33—H33 0.9300

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C16—H16 0.9300 C34—H34 0.9300
N6—C1—N5 120.27 (11) C15—C16—H16 119.8
N6—C1—C2 130.83 (11) C16—C17—C18 119.74 (16)
N5—C1—C2 108.90 (10) C16—C17—H17 120.1
N20—C2—C14 109.27 (10) C18—C17—H17 120.1
N20—C2—C1 111.13 (11) C17—C18—C19 120.29 (18)
C14—C2—C1 112.40 (10) C17—C18—H18 119.9
N20—C2—C3 111.50 (11) C19—C18—H18 119.9
C14—C2—C3 110.98 (11) C18—C19—C14 120.67 (16)
C1—C2—C3 101.42 (10) C18—C19—H19 119.7
C4—C3—C2 106.75 (11) C14—C19—H19 119.7
C4—C3—H3A 110.4 C21—N20—C2 118.03 (11)
C2—C3—H3A 110.4 C21—N20—H20 104.4 (11)
C4—C3—H3B 110.4 C2—N20—H20 107.1 (11)
C2—C3—H3B 110.4 N20—C21—C22 111.71 (12)
H3A—C3—H3B 108.6 N20—C21—H21A 109.3
N5—C4—C3 103.01 (11) C22—C21—H21A 109.3
N5—C4—H4A 111.2 N20—C21—H21B 109.3
C3—C4—H4A 111.2 C22—C21—H21B 109.3
N5—C4—H4B 111.2 H21A—C21—H21B 107.9
C3—C4—H4B 111.2 C27—C22—C23 118.78 (16)
H4A—C4—H4B 109.1 C27—C22—C21 121.96 (15)
C1—N5—C4 115.18 (11) C23—C22—C21 119.11 (15)
C1—N5—C28 123.76 (11) C22—C23—C24 120.2 (2)
C4—N5—C28 120.81 (11) C22—C23—H23 119.9
C1—N6—C7 121.79 (11) C24—C23—H23 119.9
O8—C7—O9 123.35 (11) C25—C24—C23 120.5 (2)
O8—C7—N6 128.09 (12) C25—C24—H24 119.8
O9—C7—N6 108.37 (10) C23—C24—H24 119.8
C7—O9—C10 120.92 (10) C24—C25—C26 120.1 (2)
O9—C10—C12 110.43 (12) C24—C25—H25 120.0
O9—C10—C11 109.81 (11) C26—C25—H25 120.0
C12—C10—C11 113.05 (14) C25—C26—C27 119.3 (2)
O9—C10—C13 102.03 (12) C25—C26—H26 120.4
C12—C10—C13 109.69 (13) C27—C26—H26 120.4
C11—C10—C13 111.29 (14) C22—C27—C26 121.17 (19)
C10—C11—H11A 109.5 C22—C27—H27 119.4
C10—C11—H11B 109.5 C26—C27—H27 119.4
H11A—C11—H11B 109.5 N5—C28—C29 112.43 (11)

C10—C11—H11C 109.5 N5—C28—H28A 109.1
H11A—C11—H11C 109.5 C29—C28—H28A 109.1
H11B—C11—H11C 109.5 N5—C28—H28B 109.1
C10—C12—H12A 109.5 C29—C28—H28B 109.1
C10—C12—H12B 109.5 H28A—C28—H28B 107.8
H12A—C12—H12B 109.5 C34—C29—C30 118.45 (15)
C10—C12—H12C 109.5 C34—C29—C28 120.24 (13)
H12A—C12—H12C 109.5 C30—C29—C28 121.29 (14)
H12B—C12—H12C 109.5 C31—C30—C29 120.6 (2)
C10—C13—H13A 109.5 C31—C30—H30 119.7
C10—C13—H13B 109.5 C29—C30—H30 119.7
H13A—C13—H13B 109.5 C32—C31—C30 120.4 (2)

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C10—C13—H13C 109.5 C32—C31—H31 119.8
H13A—C13—H13C 109.5 C30—C31—H31 119.8
H13B—C13—H13C 109.5 C31—C32—C33 120.19 (19)
C15—C14—C19 118.22 (14) C31—C32—H32 119.9
C15—C14—C2 121.98 (13) C33—C32—H32 119.9
C19—C14—C2 119.74 (13) C32—C33—C34 119.9 (2)
C14—C15—C16 120.72 (16) C32—C33—H33 120.0
C14—C15—H15 119.6 C34—C33—H33 120.0
C16—C15—H15 119.6 C29—C34—C33 120.41 (18)
C17—C16—C15 120.35 (17) C29—C34—H34 119.8
C17—C16—H16 119.8 C33—C34—H34 119.8

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: pq255_a

```
Bond precision:  C-C = 0.0026 A          Wavelength=0.71073

Cell:          a=9.6437(4)       b=11.6855(5)     c=12.1217(6)
               alpha=87.115(2)   beta=71.784(2)   gamma=82.973(2)
Temperature:   295 K
```

	Calculated	Reported
Volume	1287.70(10)	1287.70(10)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C29 H33 N3 O2	?
Sum formula	C29 H33 N3 O2	C29 H33 N3 O2
Mr	455.58	455.58
Dx,g cm-3	1.175	1.175
Z	2	2
Mu (mm-1)	0.074	0.074
F000	488.0	488.0
F000'	488.19	
h,k,lmax	13,16,17	13,16,17
Nref	7556	7537
Tmin,Tmax	0.985,0.991	0.701,0.746
Tmin'	0.985	

```
Correction method= # Reported T Limits: Tmin=0.701 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.997          Theta(max)= 30.069

R(reflections)= 0.0511( 5739)     wR2(reflections)= 0.1960( 7537)

S = 1.106                  Npar= 314
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT241_ALERT_2_C	High	'MainMol' Ueq as Compared to Neighbors of	C24 Check
PLAT242_ALERT_2_C	Low	'MainMol' Ueq as Compared to Neighbors of	C29 Check

Alert level G

PLAT072_ALERT_2_G	SHELXL First Parameter in WGHT Unusually Large		0.11 Report
PLAT154_ALERT_1_G	The s.u.'s on the Cell Angles are Equal ..(Note)		0.002 Degree
PLAT793_ALERT_4_G	The Model has Chirality at C2	(Centro SPGR)	S Verify

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
3 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 19/11/2015; check.def file version of 17/11/2015

Datablock pq255_a - ellipsoid plot