Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

A Ru-Catalyzed One-pot Synthesis of Homopropargylic Amines from Alkyl Azides under Photolytic Conditions

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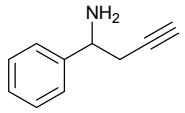
I. General information:

All solvents were dried and distilled according to the standard methods before use. Ruthenium catalysts **1** were synthesized according to the literature procedure.[1] $AgSbF_6$ were purchased from Aldrich Chemicals and stored in a dry-keeper. $Au\{P(C_6F_5)_3\}Cl$ was prepared according to the literature procedures.[2] Syntheses of homopropargylamines and imines were performed in a flame-dried J-young flask under nitrogen atmosphere. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as a visulaizing agent and acidic *p*-anisaldehyde, PMA, ninhydrin and heat as developing agents. Flash chromatography was carried out on Merck 60 silica gel (230-400 mesh). Preparative thin-layer chromatography (PTLC) was carried out using silica gel 60 F_{254} on PLC plate purchased from Merck (1mm x 20 cm x 20 cm). ^1H and ^{13}C NMR spectra were recorded with Bruker (300 MHz and 500 MHz) spectrometer. ^1H NMR spectra were referenced to residual $CDCl_3$ (7.26 ppm) and reported as follows; chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet). Chemical shifts of ^{13}C NMR spectra were measured relative to $CDCl_3$ (77.23 ppm). Mass spectral data were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer. Infrared spectra were recorded on a Shimadzu IR-470 spectrometer.

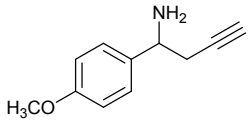
II. General procedure for the homopropargylation



3

The ruthenium catalyst **1** (2.6 mg, 0.0025 mmol) was introduced to a flame-dried J-young flask. The flask was filled with N_2 gas. Then THF (0.5 mL) was added to the J-young flask under N_2 gas flow condition. The solution was stirred at room temperature for 10 min without light to dissolve **1**. Then benzyl azide **2** (33.3 mg, 0.25 mmol) in THF (0.5 mL) and allenylboronic acid pinacol ester (134 μL, 0.75 mmol) were added to the solution under N_2 gas flow condition. The reaction mixture was stirred at 50 ^oC under the 30 W fluoroscent light for 3 h. The reaction was quenched by adding $CHCl_3$ (1 mL). 1N HCl was added to the solution to make pH ~ 1. The solution was washed with Et_2O (3 x 5 mL) and neutralized by 6

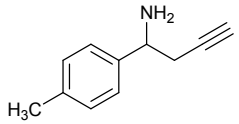
N NaOH. The solution was extracted with Et_2O (5 x 5 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue oil was purified by preparative TLC eluting with hexane: isopropylamine = 95: 5 to give **3** as yellow oil (29.5 mg, 0.21 mmol, 81% yield). R_f = 0.64 (CH_2Cl_2: MeOH = 90:10). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.07 (t, *J* = 2.6 Hz, 1H), 2.37 (br s, 2H), 2.54 (ddd, *J* = 16.6, 7.8, 2.6 Hz, 1H), 2.64 (ddd, *J* = 16.6, 5.3, 2.6 Hz, 1H), 4.20 (dd, *J* = 7.8, 5.3 Hz, 1H), 7.43-7.28 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.5, 54.9, 70.9, 81.6, 126.5, 127.8, 128.8, 143.8; IR: (cm^{-1}) v 3293, 2926, 2855, 1557, 1455, 1384; HRMS(FAB+) calcd for $C_{10}H_{12}N$: 146.0970, found: 146.0970.



15

Using the representative procedure, a mixture of **5** (40.8 mg, 0.25 mmol), ruthenium catalyst **1** (5.1 mg, 0.005 mmol) and allenylboronic acid pinacol ester (134 μL, 0.75 mmol) were reacted at 50 °C under 30W fluoroscent light for 4 h to give **15** as pale yellow oil (30.5 mg, 0.174 mmol, 70% yield). R_f = 0.60 (CH_2Cl_2: MeOH = 90:10).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.70 (br s, 2H), 2.04 (t, *J* = 2.7 Hz, 1H), 2.46 (ddd, *J* = 16.5, 8.1, 2.7 Hz, 1H), 2.56 (ddd, *J* = 16.5, 5.1, 2.7 Hz, 1H), 3.80 (s, 3H), 4.13 (dd, *J* = 8.0, 5.3 Hz, 1H), 6.84-6.92 (m, 2H), 7.27-7.35 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.0, 54.3, 55.5, 70.6, 82.1, 114.0, 127.5, 136.7, 159.1; IR: (cm^{-1}) v 3290, 2925, 2855, 1663, 1611, 1512, 1369, 1302, 1247, 1176, 1109, 1034; HRMS(FAB+) calcd for $C_{11}H_{13}NO$: 176.1075, found: 176.1077.

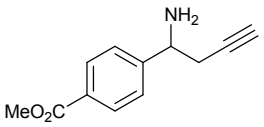


16

Using the representative procedure, a mixture of **6** (36.8 mg, 0.25 mmol), ruthenium catalyst **1** (5.1 mg, 0.005 mmol) and allenylboronic acid pinacol ester (134 μL, 0.75 mmol) were reacted at 50 °C under 30W fluoroscent light for 6 h to give **16** as yellow oil (25.8 mg, 0.163 mmol, 65% yield). R_f = 0.65 (CH_2Cl_2: MeOH = 90:10).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.94 (br s, 2H), 2.04 (t, *J* = 2.6 Hz, 1H), 2.34 (s, 3H), 2.47 (ddd, *J* = 16.6, 8.0, 2.6 Hz, 1H), 2.58 (ddd, *J* = 16.6, 5.1, 2.6 Hz, 1H), 4.13 (dd, *J* = 7.9, 5.1

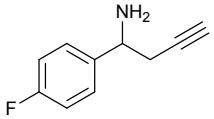
Hz, 1H), 7.15 (d, J = 7.9 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3, 29.9, 54.6, 70.6, 82.0, 126.3, 129.4, 137.3, 141.6; IR: (cm^{-1}) v 3292, 2925, 1515, 1458; HRMS(FAB+) calcd for $C_{11}H_{14}N$: 160.1126, found: 160.1128.



17

Using the representative procedure, a mixture of **7** (47.8 mg, 0.25 mmol), ruthenium catalyst **1** (5.1 mg, 0.005 mmol) and allenylboronic acid pinacol ester (134 μL, 0.75 mmol) were reacted at 50 °C under 30W fluoroscent light for 6 h to give **17** as yellow oil (38.6 mg, 0.190 mmol, 76% yield). R_f = 0.67 (CH_2Cl_2: MeOH = 90:10).

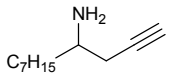
^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.93-1.98 (br s, 2H), 2.04 (t, J = 2.6 Hz, 1H), 2.49 (ddd, J = 16.6, 7.7, 2.6 Hz, 1H), 2.60 (ddd, J = 16.6, 5.2, 2.6 Hz, 1H), 3.90 (s, 3H), 4.22 (dd, J = 7.6, 5.3 Hz, 1H), 7.46 (d, J = 8.2 Hz, 2H), 8.01 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.7, 52.3, 54.7, 71.1, 81.2, 126.6, 129.6, 130.1, 149.5, 167.1; IR: (cm^{-1}) v 3293, 2952, 1721, 1281, 1113; HRMS(FAB+) calcd for $C_{12}H_{14}NO_2$: 204.1025, found: 204.1025.



18

Using the representative procedure, a mixture of **8** (37.8 mg, 0.25 mmol), ruthenium catalyst **1** (7.6 mg, 0.0075 mmol) and allenylboronic acid pinacol ester (134 μL, 0.75 mmol) were reacted at 50 °C under 30W fluoroscent light for 12 h to give **18** as pale yellow oil (27.7 mg, 0.170 mmol, 68% yield). R_f = 0.51 (CH_2Cl_2: MeOH = 90:10).

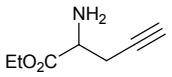
^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.71 (br s, 2H), 2.04 (t, J = 2.7 Hz, 1H), 2.45 (ddd, J = 16.5, 7.8, 2.6 Hz, 1H), 2.55 (ddd, J = 16.5, 5.1, 2.6 Hz, 1H), 4.15 (dd, J = 7.7, 5.3 Hz, 1H), 6.97-7.07 (m, 2H), 7.31-7.40 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.0, 54.2, 70.8, 81.6, 115.4 (d, J = 21.2 Hz), 128.0 (d, J = 8.0 Hz), 140.2 (d, J = 3.1 Hz), 162.3 (d, J = 243.8 Hz); IR: (cm^{-1}) v 3375, 3301, 2930, 1603, 1510, 1420, 1374, 1221, 1157, 1096, 1014; HRMS(FAB+) calcd for $C_{10}H_{10}FN$: 164.0876, found: 164.0872.



19

Using the representative procedure, a mixture of **9** (38.8 mg, 0.25 mmol), ruthenium catalyst **1** (5.1 mg, 0.005 mmol) and allenylboronic acid pinacol ester (134 μL, 0.75 mmol) were reacted at 50 °C under 30W fluoroscent light for 12 h to give **19** as yellow oil (31.7 mg, 0.190 mmol, 76% yield). R_f = 0.47 (CH_2Cl_2: MeOH = 90:10).

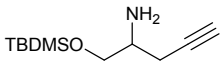
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.7 Hz, 3H), 1.20-1.46 (m, 12H), 1.55 (br s, 2H), 2.00 (t, *J* = 2.6 Hz, 1H), 2.16 (ddd, *J* = 16.6, 7.1, 2.7 Hz, 1H), 2.33 (ddd, *J* = 16.6, 4.7, 2.6 Hz, 1H), 2.88 (dt, *J* = 11.0, 5.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3, 22.9, 26.5, 28.0, 29.5, 29.8, 32.0, 37.2, 50.5, 70.4, 82.2; IR: (cm^{-1}) v 3311, 2927, 2856, 1456, 1377; HRMS(FAB+) calcd for $C_{11}H_{22}N$: 168.1752, found: 168.1755.



20

Using the representative procedure, a mixture of **10** (32.2 mg, 0.25 mmol), ruthenium catalyst **1** (5.1 mg, 0.005 mmol) and allenylboronic acid pinacol ester (134 μL, 0.75 mmol) were reacted at 50 °C under 30W fluoroscent light for 6 h to give **20** as pale yellow oil (21.5 mg, 0.153 mmol, 61% yield). R_f = 0.51 (CH_2Cl_2: MeOH = 90:10).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (t, *J* = 7.1 Hz, 3H), 1.77-1.80 (m, 2H), 2.05 (t, *J* = 2.7 Hz, 1H), 2.63 (dt, *J* = 4.4, 2.7 Hz, 2H), 3.62 (t, *J* = 5.7 Hz, 1H), 4.21 (qd, *J* = 7.1, 2.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4, 25.1, 53.4, 61.6, 71.5, 79.8, 174.0; IR: (cm^{-1}) v 3017, 2921, 2851, 1735, 1384, 1261; HRMS(FAB+) calcd for $C_7H_{12}NO_2$: 142.0868, found: 142.0868.

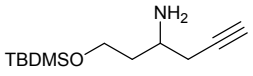


21

Using the representative procedure, a mixture of **11** (50.3 mg, 0.25 mmol), ruthenium catalyst **1** (5.1 mg, 0.005 mmol) and allenylboronic acid pinacol ester (134 μL, 0.75 mmol) were reacted at 50 °C under 30W fluoroscent light for 12 h to give **21** as pale yellow oil (38.2 mg, 0.179 mmol, 71% yield). R_f = 0.42 (CH_2Cl_2: MeOH = 90:10).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.05 (s, 6H), 0.89 (s, 9H), 1.52 (br s, 2H), 1.99 (t, *J* = 3.0

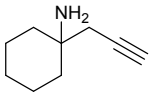
Hz, 1H), 2.29 (ddd, *J* = 16.7, 6.1, 2.7 Hz, 2H), 2.98 (dt, *J* = 12.3, 5.7 Hz, 1H), 3.56 (dd, *J* = 9.6, 5.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = -5.2, 18.4, 24.1, 26.0, 51.9, 66.9, 70,3, 81.8; IR: (cm^{-1}) v 3079, 1579, 1516, 1437, 1294, 1234, 1119, 1036, 945; HRMS(FAB+) calcd for $C_{11}H_{24}NOSi$: 214.1627, found: 214.1629.



22

Using the representative procedure, a mixture of **12** (53.8 mg, 0.25 mmol), ruthenium catalyst **1** (5.1 mg, 0.005 mmol) and allenylboronic acid pinacol ester (134 μL, 0.75 mmol) were reacted at 50 °C under 30W fluoroscent light for 12 h to give **22** as pale yellow oil (42.5 mg, 0.187 mmol, 75% yield). R_f = 0.49 (CH_2Cl_2: MeOH = 90:10).

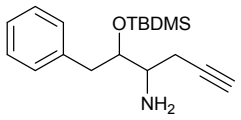
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.08 (s, 6H), 0.91 (s, 9H), 1.57 (br s, 2H), 1.59-1.65 (m, 1H), 1.68-1.81 (m, 1H), 2.04 (t, *J* = 2.7 Hz, 1H), 2.24 (ddd, *J* = 16.5, 6.9, 2.6 Hz, 1H), 2.39 (ddd, *J* = 16.5, 5.0, 2.6 Hz, 1H), 3.12 (ddt, *J* = 7.8, 6.9, 4.8 Hz, 1H), 3.68-3.85 (m, 2H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ = -5.1, 18.5, 26.1, 28.3, 39.6, 48.3, 61.1, 70.4, 82.1; IR: (cm^{-1}) v 3312, 2930, 2858, 1629, 1473, 1386, 1362, 1256, 1091; HRMS(FAB+) calcd for $C_{12}H_{26}NOSi$: 228.1784, found: 228.1784.



23

Using the representative procedure, a mixture of **13** (31.3 mg, 0.25 mmol), ruthenium catalyst **1** (7.6 mg, 0.0075 mmol) and allenylboronic acid pinacol ester (134 μL, 0.75 mmol) were reacted at 50 °C under 30W fluoroscent light for 24 h to give **23** as yellow oil (24.8 mg, 0.181 mmol, 72% yield). R_f = 0.45 (CH_2Cl_2: MeOH = 90:10).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25-1.60 (m, 12H), 2.03 (t, *J* = 2.7 Hz, 1H), 2.26 (d, *J* = 2.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.5, 26.0, 33.3, 38.1, 50.7, 71.1, 81.6; IR: (cm^{-1}) v 3017, 2925, 1384, 1262; HRMS(FAB+) calcd for $C_9H_{16}N$: 138.1283, found: 138.1284.

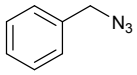


24

Using the representative procedure, a mixture of **14** (72.9 mg, 0.25 mmol), ruthenium catalyst **1** (7.6 mg, 0.0075 mmol) and allenylboronic acid pinacol ester (134 μL, 0.75 mmol) were reacted at 50 ^{o}C under 30W fluoroscent light for 12 h to give **24** as pale yellow oil (64.6 mg, 0.212 mmol, 85% yield). R_f = 0.82 (CH_2Cl_2: MeOH = 90:10).

^{1}H NMR (300 MHz, $CDCl_3$): δ = -0.30 (s, 0.6H), -0.09 (s, 2.4H), -0.02 (s, 0.6H), 0.06 (s, 2.4H), 0.85 (s, 1.8H), 0.89 (s, 7.2H), 1.39-1.46 (m, 2H), 1.98 (t, *J* = 2.6 Hz, 0.8H), 2.03 (t, *J* = 2.7 Hz, 0.2H), 2.19-2.46 (m, 2H), 2.71-2.78 (m, 2H), 2.92-3.00 (m, 1H), 3.92-3.99 (m, 1H), 7.18-7.29 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = -4.8, -4.5, -4.5, -4.4, 18.2, 18.3, 24.8, 25.1, 25.5, 26.1, 26.1, 38.9, 40.6, 52.8, 54.3, 70.2, 70.5, 75.4, 76.4, 82.3, 82.7, 126.5, 126.5, 128.5, 128.6, 129.7, 130.0, 138.6, 138.8; IR: (cm^{-1}) v 3311, 2955, 2929, 2857, 1252, 1084, 810, 777; HRMS(FAB+) calcd for $C_{18}H_{30}NOSi$: 304.2097, found: 304.2099.

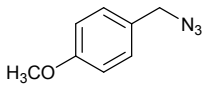
III. Representative Procedure for the Preparation of Azides



2

A solution of benzyl bromide (2.0 g, 11.7 mmol) and sodium azide (2.28 g, 35.1 mmol) in DMF (58.5 mL, 0.2 M) was stirred at 70 ^{o}C for 11 h. The reaction mixture was quenched with water (30 mL). The solution was extracted with EtOAc (5 x 30 mL). The organic layers were combined and washed with brine (3 x 20 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue oil was purified by flash column chromatography on deactivated silica gel eluting with hexane: ether = 90:10 (1.48 g, 11.1 mmol, 95% yield). R_f = 0.68 (hexane: EtOAc = 90:10). The spectral data are in complete agreement with the literature data.[3]

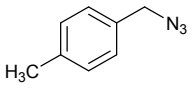
^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.39 (s, 2H), 7.38-7.52 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 54.4, 128.0, 128.0, 128.6, 135.3;



5

Yield: 86 % yield. R_f = 0.33 (Hexane: Ether = 95:5); The spectral data are in complete agreement with the literature data.[4]

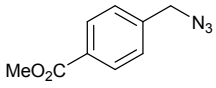
^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.84 (s, 3H), 4.29 (s, 2H), 6.92-6.96 (m, 2H), 7.25-7.30 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 54.6, 55.5, 114.4, 127.6, 129.9, 159.8.



6

Yield: 67 %. R_f = 0.61 (Hexane: Ether = 90: 10); The spectral data are in complete agreement with the literature data.[5]

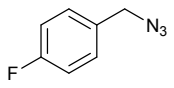
^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 4.29 (s, 2H), 7.14-7.25 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4, 54.8, 128.5, 129.7, 132.5, 138.4.



7

Yield: 89 %. R_f = 0.23 (Hexane: Ether = 90: 10); The spectral data are in complete agreement with the literature data.[6]

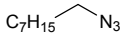
^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.92 (s, 3H), 4.41 (s, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 8.05 (d, *J* = 6.6, 1.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.4, 54.5, 128.1, 130.2, 130.3, 140.6, 166.8.



8

Yield: 91 % yield. R_f = 0.47 (Hexane: Ether= 95:5); The spectral data are in complete agreement with the literature data.[4]

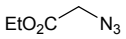
^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.32 (s, 2H), 7.05-7.11 (m, 2H), 7.28-7.32 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 54.3, 116.0 (d, *J* = 21.4 Hz), 130.2 (d, *J* = 8.2 Hz), 131.4 (d, *J* = 3.2 Hz), 162.9 (d, *J* = 245.5 Hz).



9

Yield: 77 % yield. R_f = 0.83 (Hexane: EtOAc= 90: 10); The spectral data are in complete agreement with the literature data.[3]

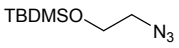
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3H), 1.22-1.41 (m, 10H), 1.52-1.68 (m, 2H), 3.25 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3, 22.8, 26.9, 29.0, 29.3, 29.4, 32.0, 51.7.



10

Yield: 84 % yield. R_f = 0.48 (Hexane: EtOAc= 90: 10); The spectral data are in complete agreement with the literature data.[6]

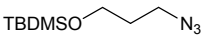
^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (t, *J* = 7.1 Hz, 3H), 3.89 (s, 2H), 4.29 (q, *J* = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3, 50.5, 62.0, 168.5.



11

Yield: 72.6 %. R_f = 0.65 (Hexane: EtOAc = 95:5); The spectral data are in complete agreement with the literature data.[7]

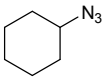
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.09 (s, 6H), 0.91 (s, 9H), 3.26 (t, *J* = 5.1 Hz, 2H), 3.80 (t, *J* = 5.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = -5.2, 18.4, 26.0, 53.4, 62.8.



12

Yield: 57.4 %. R_f = 0.65 (Hexane: EtOAc = 95:5); The spectral data are in complete agreement with the literature data.[8]

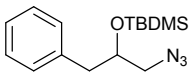
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.09 (s, 6H), 0.89 (s, 9H), 1.77 (dt, *J* = 6.6, 6.0 Hz, 2H), 3.39 (t, *J* = 6.6 Hz, 2H), 3.69 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = -5.2, 18.5, 26.1, 32.0, 48.4, 59.8.



13

Yield = 73%. R_f = 0.81 (hexane: EtOAC = 90: 10). The spectral data are in complete agreement with the literature data.[6]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06-1.40 (m, 5H), 1.42-1.58 (m, 1H), 1.61-1.74 (m, 2H), 1.75-1.97 (m, 2H), 3.20-3.41 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.2, 25.3, 31.6, 59.9.

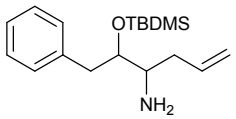


14

Yield: 64%. R_f = 0.76 (hexane: EtOAc = 80: 20). The spectral data are in complete agreement with the literature data.[9]

^{1}H NMR (300 MHz, $CDCl_3$): δ = -0.10 (s, 3H), -0.05 (s, 3H), 0.89 (s, 9H), 2.79 (dd, *J* = 13.7, 6.8 Hz, 1H), 2.85 (dd, *J* = 13.7, 6.8 Hz, 1H), 3.08 (dd, *J* = 12.5, 5.3 Hz, 1H), 3.25 (dd, *J* = 12.5, 4.1 Hz, 1H), 3.98 (tdd, *J* = 6.6, 5.3, 4.1 Hz, 1H), 7.12-7.24 (m, 3H), 7.26-7.37 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = -4.9, -4.7, 18.2, 26.0, 41.8, 56.1, 73.4, 126.7, 128.6, 129.9, 138.0.

IV. Assignment of the stereochemistry of 24



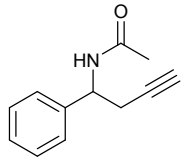
S - 24

To a solution of **24** (10 mg, 0.033 mmol) and quinoline (1 drop in 7 mL of MeOH) in MeOH (0.16 mL) was added Lindlar's catalyst (2 mg, 20 wt%) at room temperature. Then the atmosphere was changed slowly to H_2 gas and was stirred for 1 hour. After the complete conversion, the reaction mixture was filtered over celite and concentrated under reduced pressure. **S-24** was obtained in 81% NMR yield with 79: 21 diastereoselectivity. Syn-product was deteremined as a major diastereomer by comparison ^{1}H-NMR spectra to the literature data.[6]

^{1}H NMR (300 MHz, $CDCl_3$): δ = -0.14 (s, 3H), 0.03 (s, 3H), 0.94 (s, 9H), 1.24-1.38 (m, 2H), 2.04-2.08 (m, 2H), 2.22-2.37 (m, 1H), 2.54-2.66 (m, 1H), 2.67-2.78 (m, 1H), 2.97 (dd, *J* = 13.4. 7.1 Hz, 1H), 3.74-3.89 (m, 1H), 5.00-5.16 (m, 2H), 5.64-5.88 (m, 1H), 7.19-7.30 (m, 3H), 7.31-7.42 (m, 2H).

V. Synthesis of 2,6-dialkyl-4-hydroxy-piperidine 26

Preparation of substrate 25

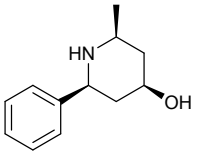


25

To **3** (232 mg, 1.60 mmol) and triethylamine (0.54 mL, 3.20 mmol) in CH_2Cl_2 (8.0 mL, 0.2 M) was added acetyl chloride (0.14 mL, 1.92 mmol) at room temperature. The reaction mixture was stirred at room termperature for 5 h. The reaction was quenched with water (10 mL). The solution was extracted with CH_2Cl_2 (3 x 5 mL). The organic layers were combined, washed with saturated $NaHCO_3$ (10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue oil was purified by flash column chromatography on silica gel eluting with hexane: EtOAc = 93: 7 to give the substrate **25** as a white powder (200 mg, 1.07 mmol, 67% yield). R_f = 0.15 (hexane: EtOAc = 50:50). The spectral data are in complete agreement with the literature data.[10]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.02 (t, *J* = 2.4 Hz, 1H), 2.05 (s, 3H), 2.77 (m, 2H), 5.23 (m, 1H), 6.01 (br s, 1H), 7.26-7.40 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.6, 25.7, 51.1, 71.7, 80.2, 126.8, 128.0, 128.9, 140.5, 169.6.

Gold(I)-catalyzed cycloisomerization-reduction of substrate 25



26

To **25** (37.4 mg, 0.2 mmol) and 4Å MS (200 mg) was added a solution of MsOH (15.6 μL, 0.24 mmol) and $[Au(PPh_3)]^+NTf_2^-$ (7.4 mg, 0.01 mmol) in CH_2Cl_2 (4.0 mL). The reaction mixture was stirred at room temperature for 20 min and cooled to -78 ^{o}C. Catecholborane (1.2 mL, 1.2 mmol) was added dropwise to the reaction mixture. The reaction mixture was slowly warmed to room temperature and stirred for 10 h. The reaction was quenched with MeOH (2 mL) and stirred for 15 min. Saturated sodium tartarate solution (5 mL) was added and then the solution was stirred for 15 min. Brine (40 mL) and saturated NaOH (20 mL) was added. The solution was extracted with CH_2Cl_2 (4 x 20 mL). The organic layers were

combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue oil was purified by preparative TLC eluting with hexane: EtOAc = 20: 80 to give **26** as a white solid (21.8 mg, 0.114 mmol, 57% yield). R_f = 0.11 (hexane: EtOAc = 20: 80). The spectral data are in complete agreement with the literature data.[10]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16 (q, *J* = 11.4 Hz, 1H), 1.17 (d, *J* = 6.3 Hz, 3H), 1.45 (q, *J* = 11.4 Hz, 1H), 1.62 (bs, 2H), 2.01 (m, 1H), 2.11 (m, 1H), 2.86 (m, 1H), 3.69 (dd, *J* = 2.4, 11.4 Hz, 1H), 3.81 (m, 1H), 7.21 – 7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.5, 43.4, 43.4, 50.7, 59.7, 69.7, 126.7, 127.3, 128.5, 143.9.

VI. References:

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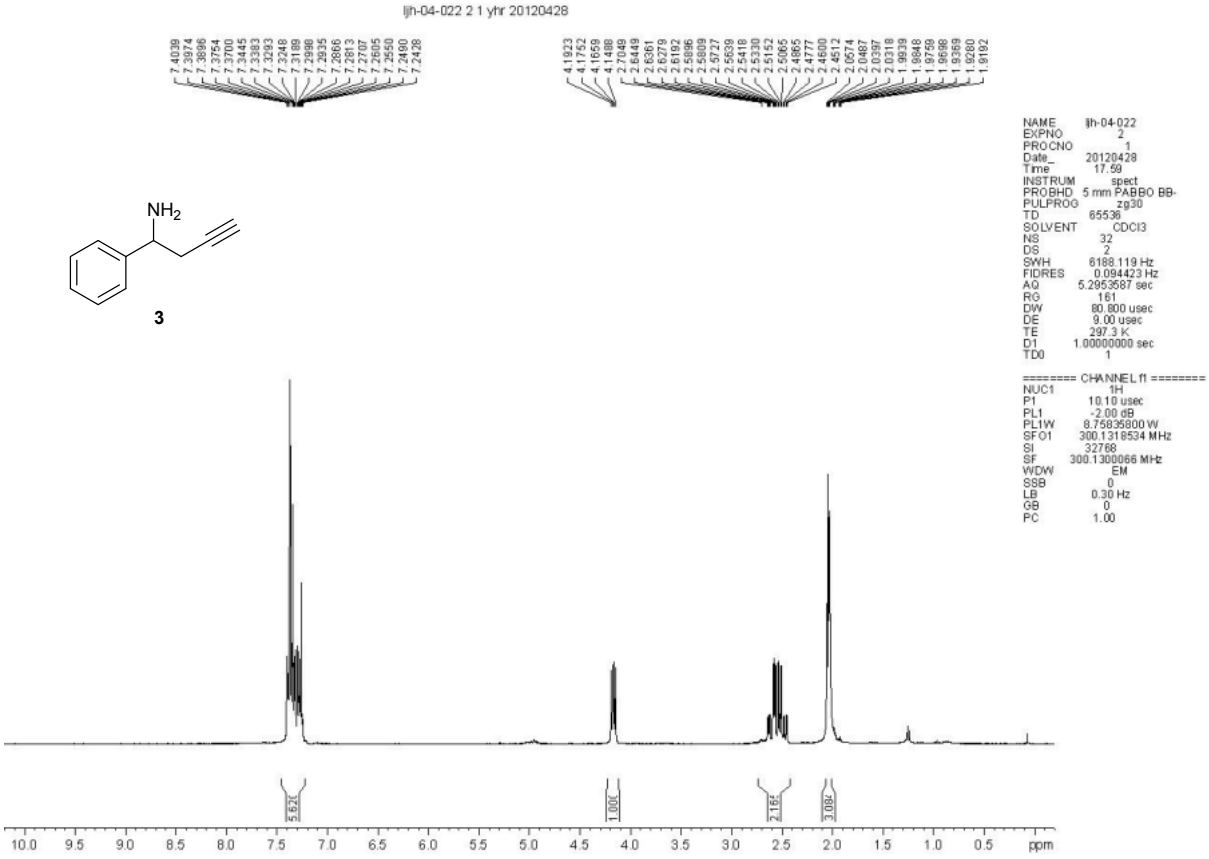
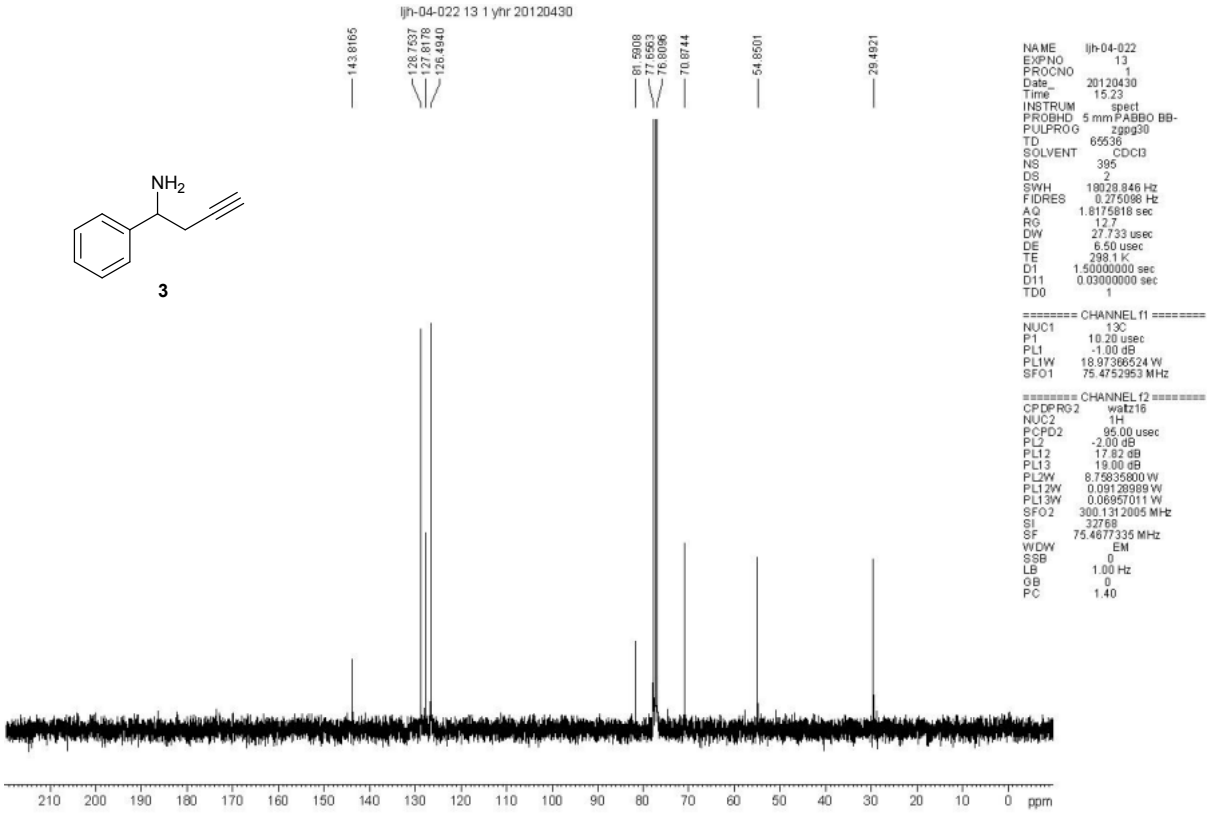
VII. ^{1}H- and ^{13}C-NMR spectra:

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76.8096
70.6744
54.8501
29.4921
NH2
3
NAME ljh-04-022
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PROCNO 1
Date_ 20120430
Time 15.23
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DE 6.50 usec
TE 298.1 K
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D11 0.03000000 sec
TD0 1
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PL1 -1.00 dB
PL1W 18.97366524 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
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NUC2 1H
PCPD2 95.00 usec
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PL12 17.82 dB
PL13 19.00 dB
PL2W 8.75835800 W
PL12W 0.09128989 W
PL13W 0.06957011 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677335 MHz
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SSB 0
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GB 0
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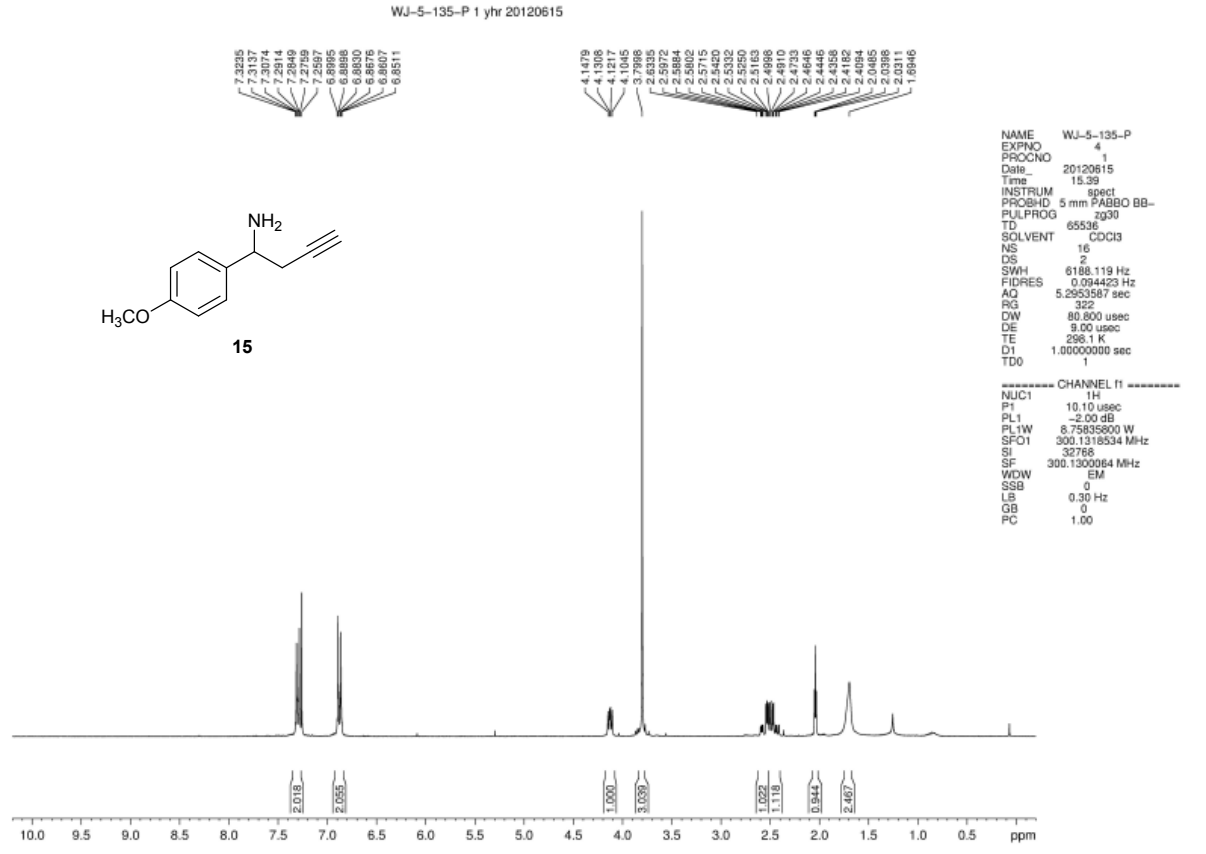
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6.8607
6.8511
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DE 9.00 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
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PL1 -2.00 dB
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SFO1 300.1318534 MHz
SI 32768
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SSB 0
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2.055
1.000
3.039
1.022
1.118
0.944
2.467
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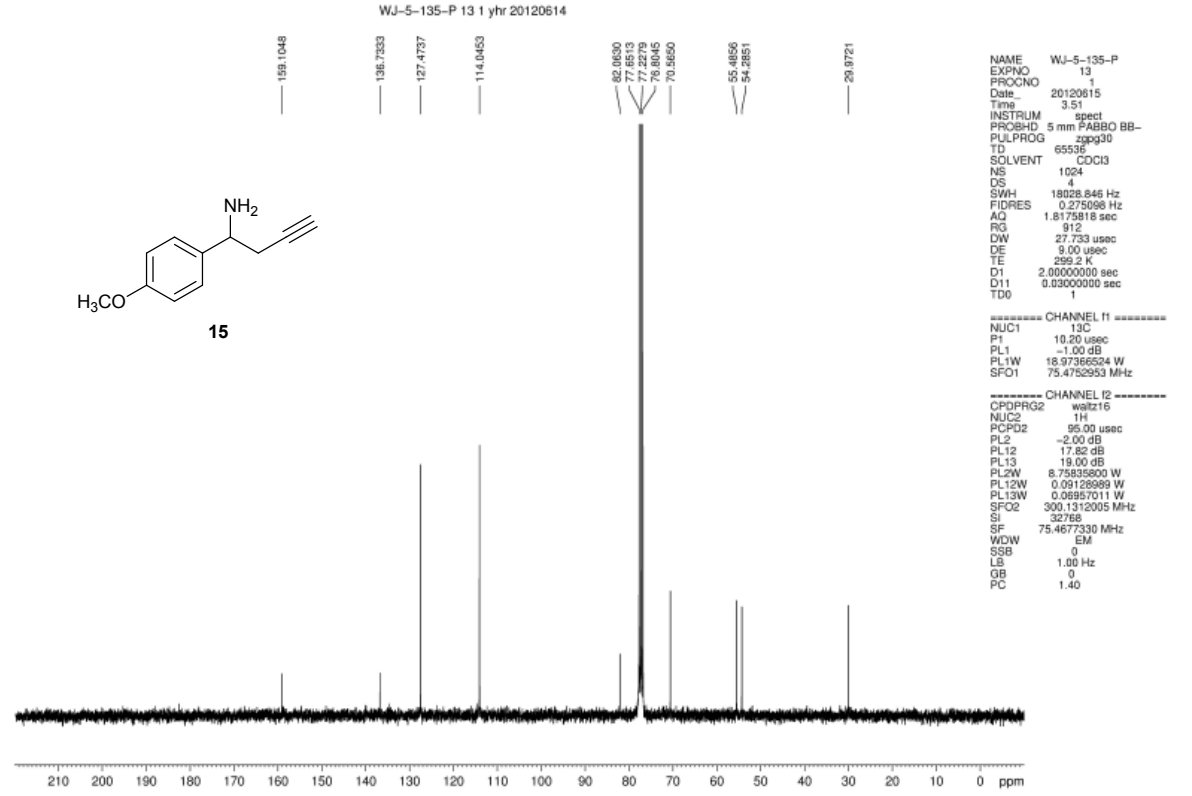
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DE 9.00 usec
TE 299.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
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P1 10.20 usec
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PL1W 18.97366524 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
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PCPD2 95.00 usec
PL2 -2.00 dB
PL12 17.82 dB
PL13 19.00 dB
PL2W 8.75835800 W
PL12W 0.09128989 W
PL13W 0.06957011 W
SFO2 300.1312005 MHz
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SF 75.4677330 MHz
WDW EM
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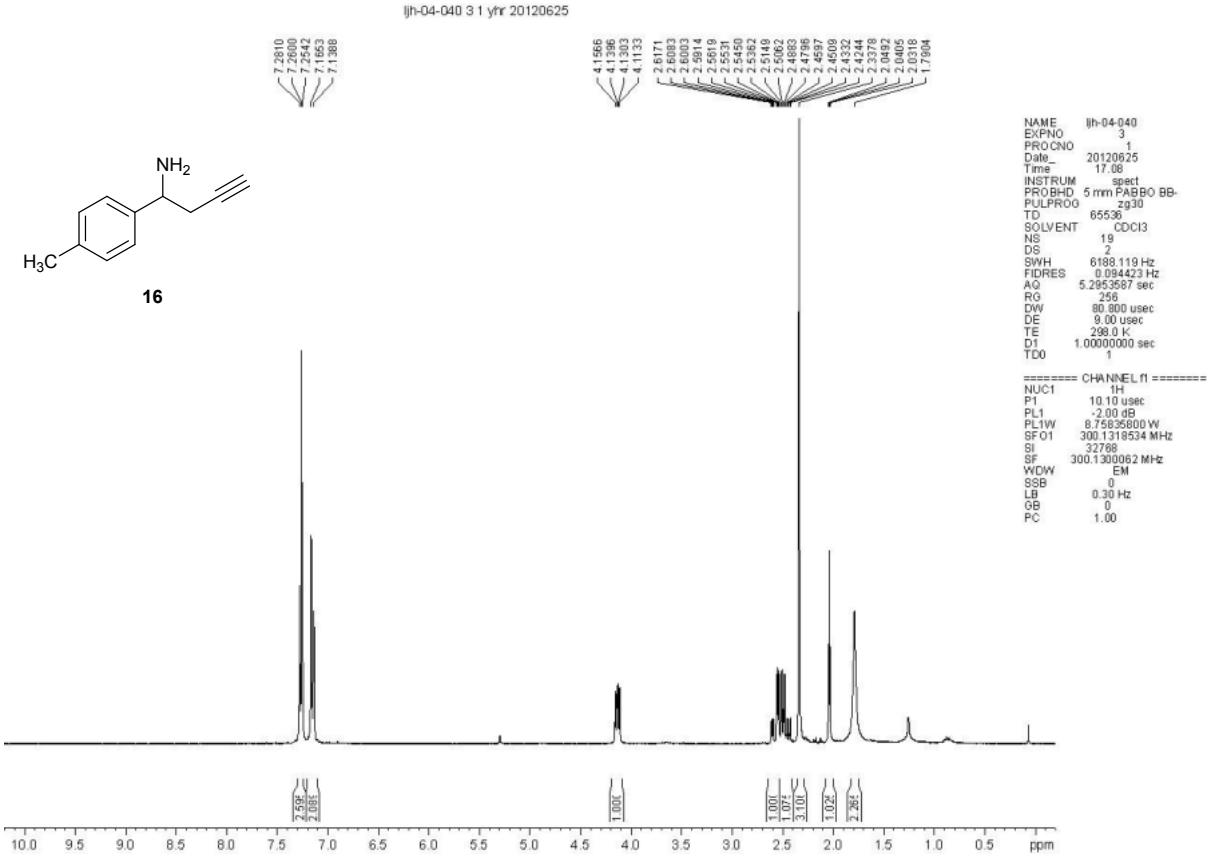
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1.00
1.00
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1.02
2.26
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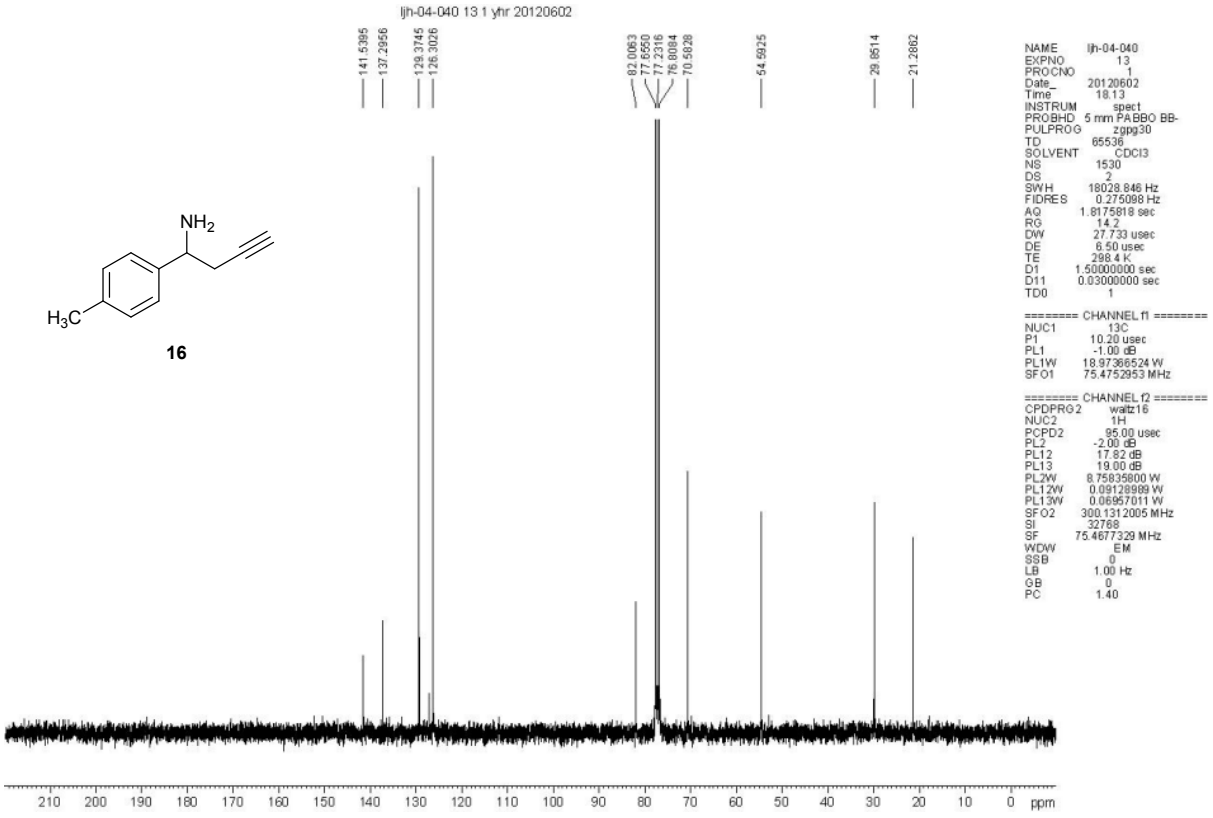
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D1 1.50000000 sec
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PL2 -2.00 dB
PL12 17.82 dB
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PL12W 0.09128989 W
PL13W 0.06957011 W
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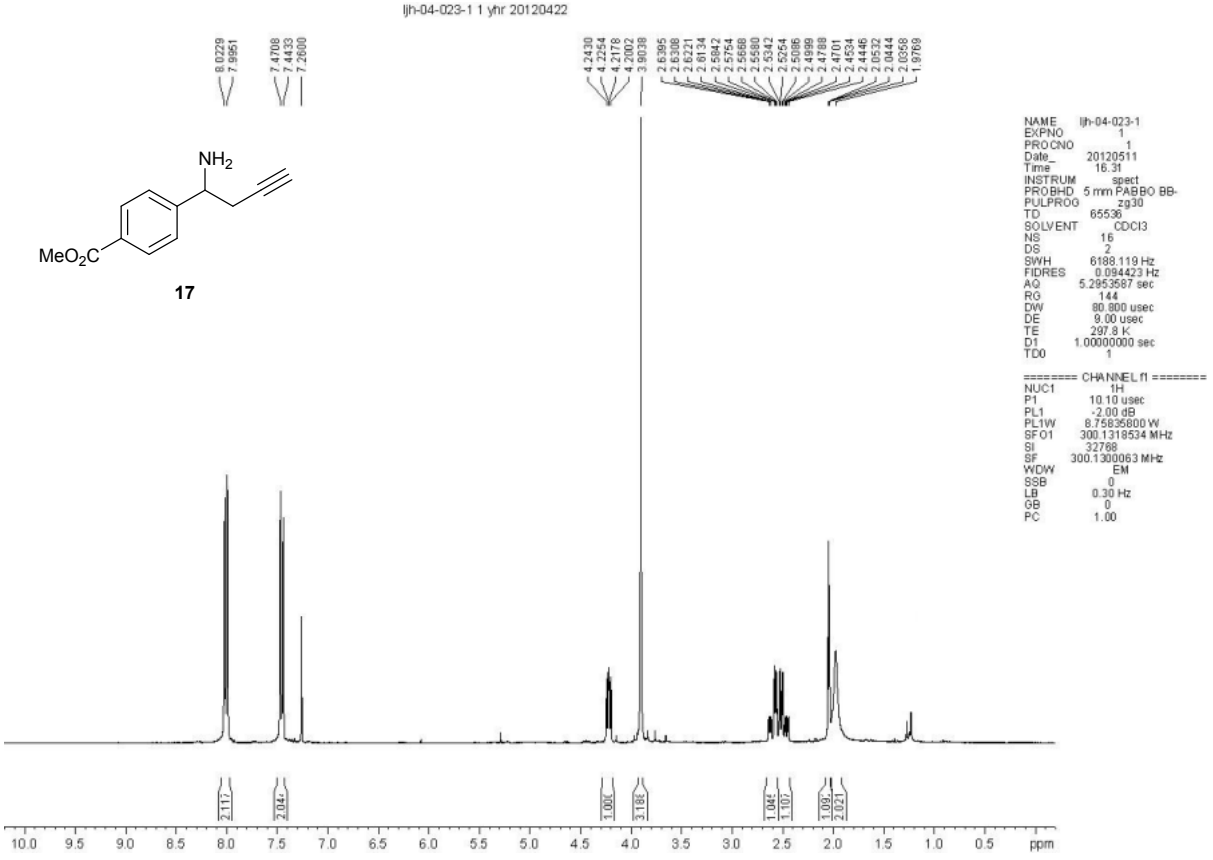
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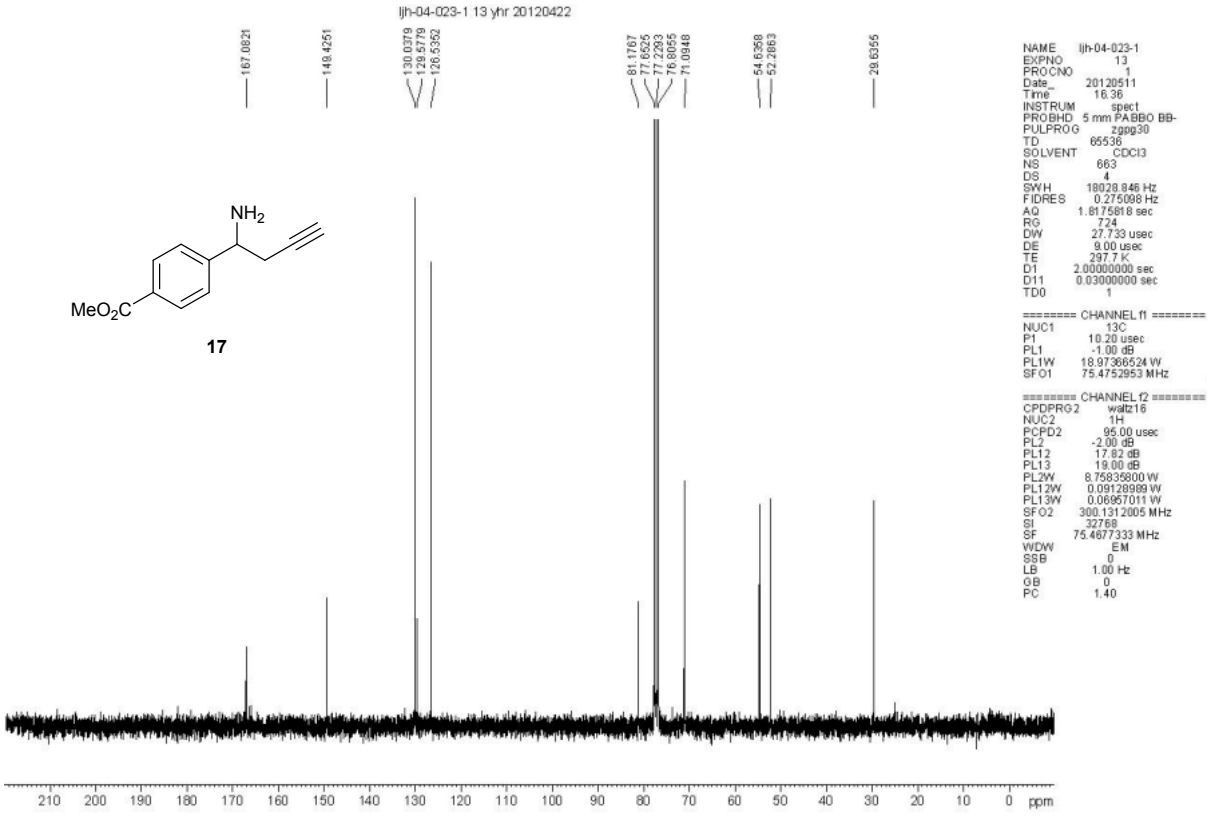
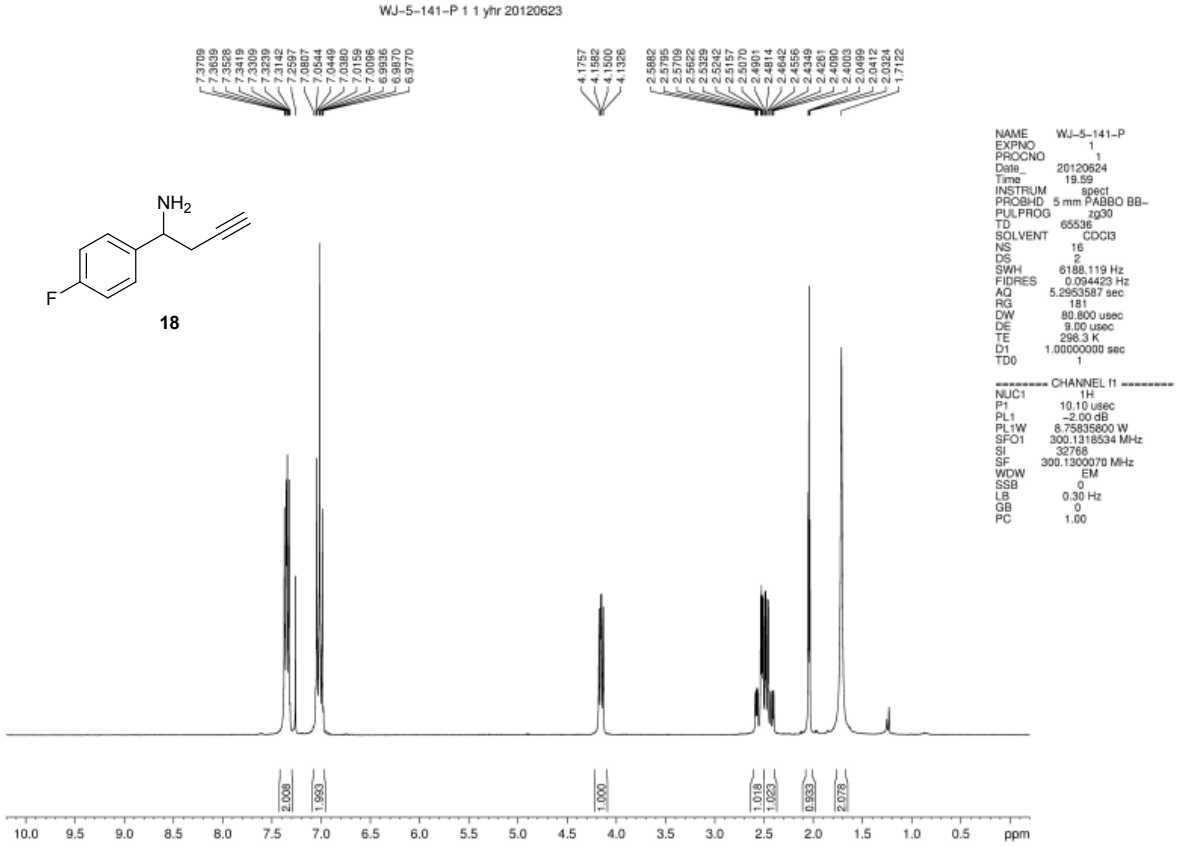
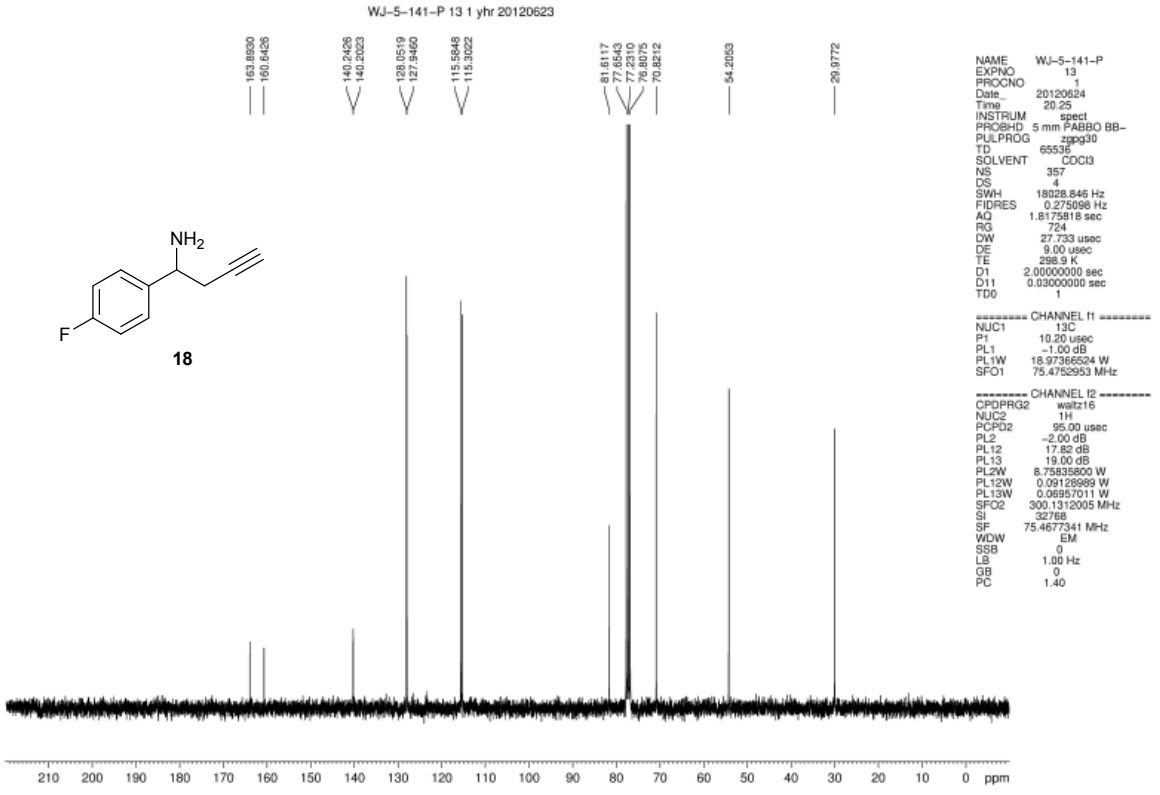
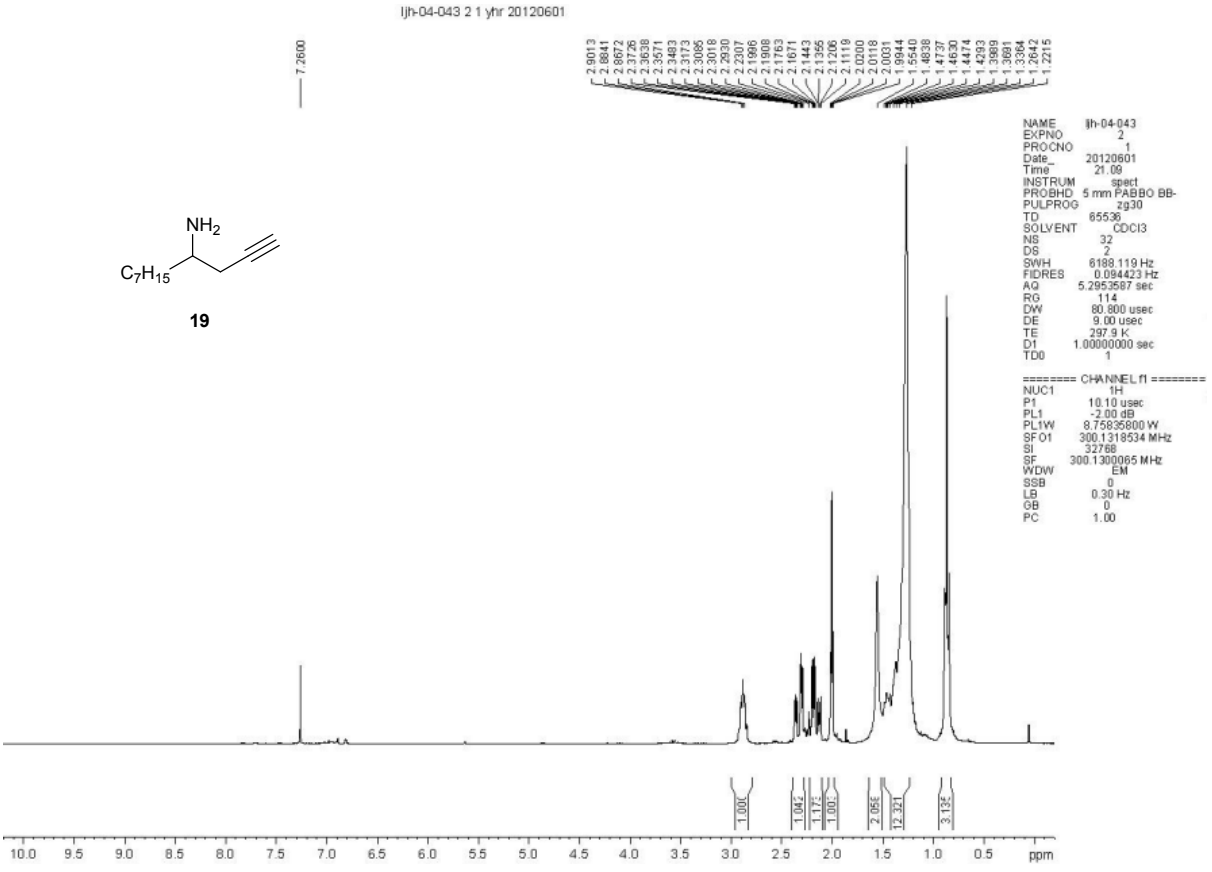
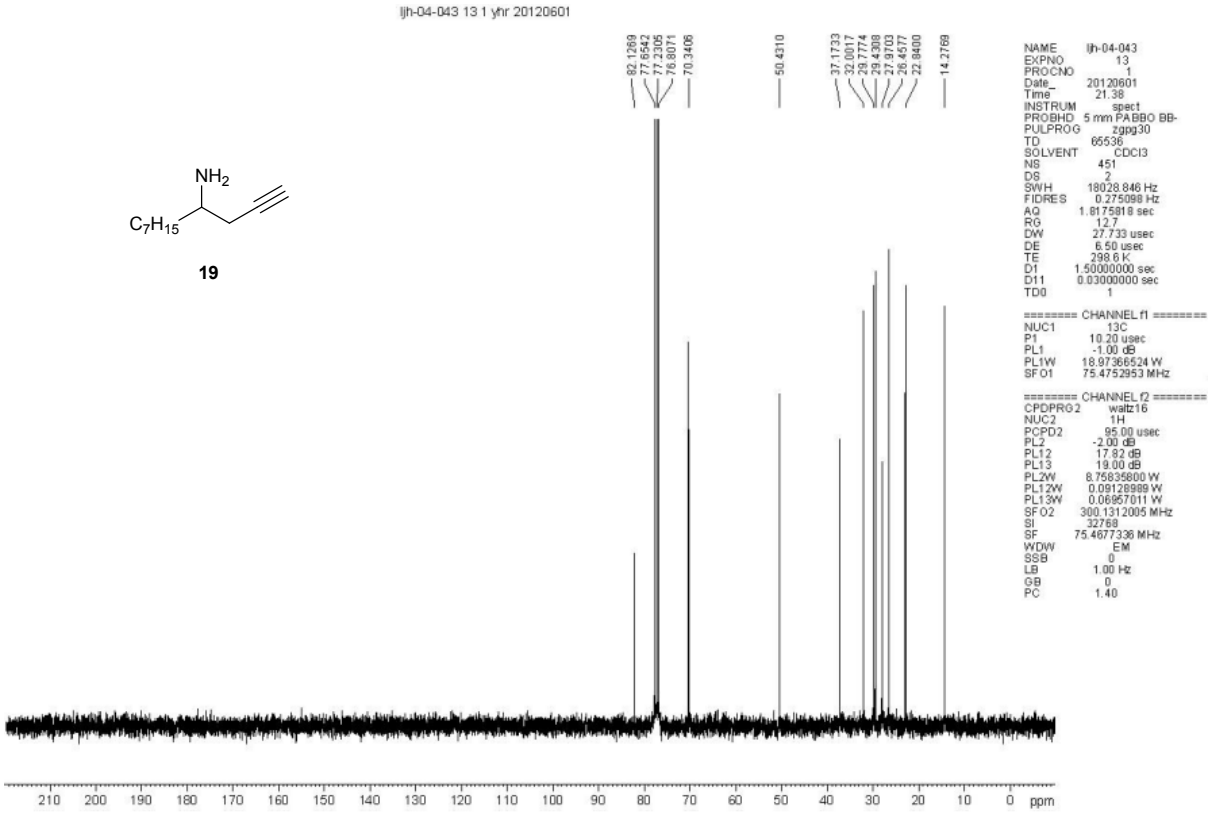
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 144
DW 80.800 usec
DE 9.00 usec
TE 297.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.10 usec
PL1 -2.00 dB
PL1W 8.75835800 W
SFO1 300.1318534 MHz
SI 32768
SF 300.1300063 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
NH2
MeO2C
17
2.117
2.044
1.000
3.188
1.044
1.107
1.095
2.021
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


ljh-04-023-1 13 yhr 20120422
167.0821
149.4251
130.0379
129.5779
126.5362
81.1767
77.6525
77.2293
76.8055
71.0948
54.6358
52.2863
29.6355
NAME ljh-04-023-1
EXPNO 13
PROCNO 1
Date_ 20120511
Time 16.36
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 663
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 724
DW 27.733 usec
DE 9.00 usec
TE 297.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.20 usec
PL1 -1.00 dB
PL1W 18.97366524 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 95.00 usec
PL2 -2.00 dB
PL12 17.82 dB
PL13 19.00 dB
PL2W 8.75835800 W
PL12W 0.09128989 W
PL13W 0.06957011 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677333 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
NH2
MeO2C
17
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


WJ-5-141-P 1 1 yhr 20120623
7.3709
7.3639
7.3526
7.3419
7.3309
7.3239
7.3142
7.2597
7.0807
7.0544
7.0449
7.0380
7.0159
7.0096
6.9935
6.9870
6.9770
4.1757
4.1582
4.1500
4.1326
2.5882
2.5795
2.5709
2.5622
2.5329
2.5242
2.5157
2.5070
2.4901
2.4814
2.4642
2.4556
2.4349
2.4261
2.4090
2.4003
2.0489
2.0412
2.0324
1.7122
NAME WJ-5-141-P
EXPNO 1
PROCNO 1
Date_ 20120624
Time 19.59
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 181
DW 80.800 usec
DE 9.00 usec
TE 298.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.10 usec
PL1 -2.00 dB
PL1W 8.75835800 W
SFO1 300.1318534 MHz
SI 32768
SF 300.1300070 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
NH2
F
18
2.008
1.993
1.000
1.018
1.083
0.933
2.078
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

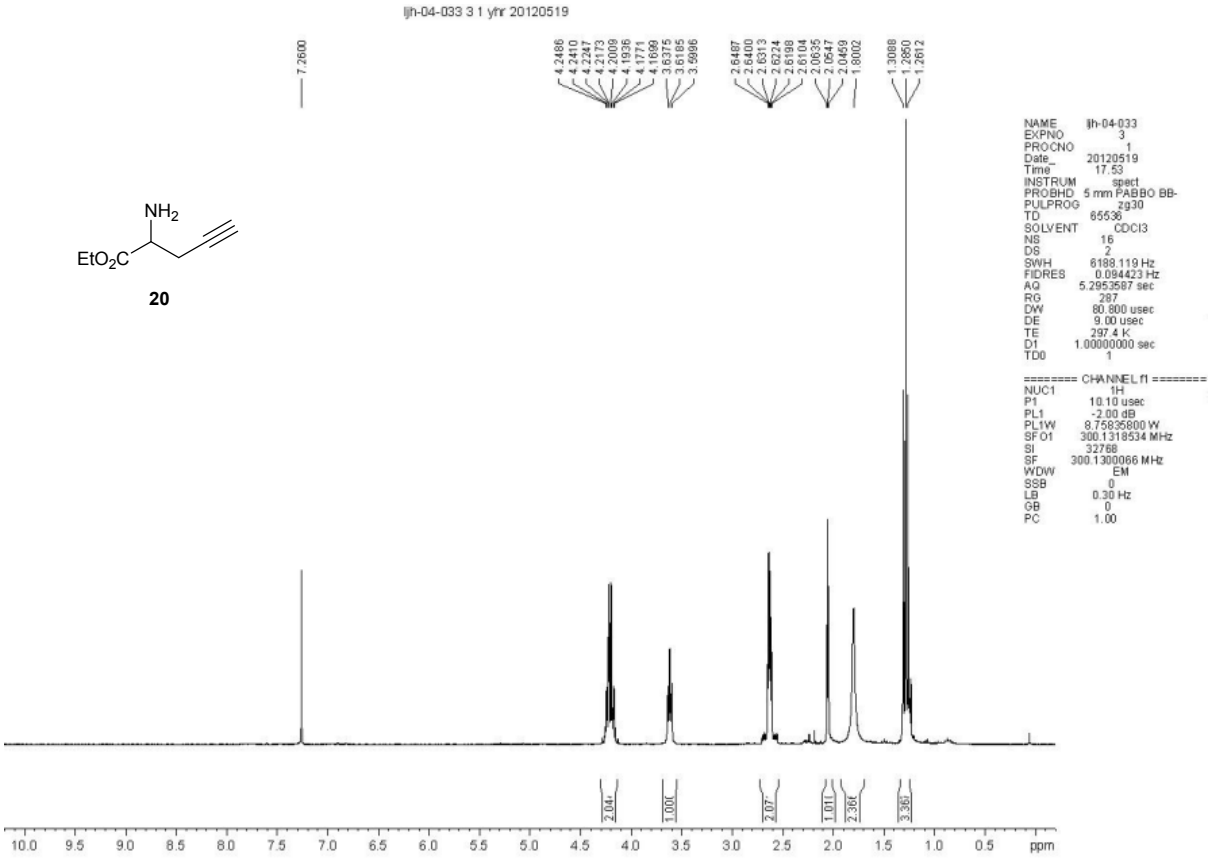

WJ-5-141-P 13 1 yhr 20120623
163.8930
160.6426
140.2426
140.2023
128.0519
127.9460
115.5848
115.3022
81.6117
77.6543
77.2310
76.8075
70.8212
54.2053
29.9772
NAME WJ-5-141-P
EXPNO 13
PROCNO 1
Date_ 20120624
Time 20.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 357
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 724
DW 27.733 usec
DE 9.00 usec
TE 298.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 10.20 usec
PL1 -1.00 dB
PL1W 18.97366524 W
SFO1 75.4752953 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 95.00 usec
PL2 -2.00 dB
PL12 17.82 dB
PL13 19.00 dB
PL2W 8.75835800 W
PL12W 0.09126989 W
PL13W 0.06957011 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677341 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
NH2
F
18
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


ljh-04-043 2 1 yhr 20120601
7.2600
2.9013
2.8841
2.8672
2.3726
2.3638
2.3571
2.3483
2.3173
2.3085
2.3018
2.2930
2.2307
2.1996
2.1908
2.1763
2.1671
2.1443
2.1355
2.1266
2.1119
2.0200
2.0018
2.0031
1.9944
1.5540
1.4838
1.4737
1.4630
1.4474
1.4293
1.3989
1.3691
1.3364
1.2642
1.2215
NAME ljh-04-043
EXPNO 2
PROCNO 1
Date_ 20120601
Time 21.09
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 114
DW 80.800 usec
DE 9.00 usec
TE 297.9 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 10.10 usec
PL1 -2.00 dB
PL1W 8.75835800 W
SFO1 300.1318534 MHz
SI 32768
SF 300.1300065 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
NH2
C7H15
19
1.00
1.04
1.11
1.00
2.05
12.32
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


ljh-04-043 13 1 yhr 20120601
82.1269
77.6542
77.2305
76.8071
70.3406
50.4310
37.1733
32.0017
29.7774
29.4708
27.9700
26.4577
22.8400
14.2769
NAME ljh-04-043
EXPNO 13
PROCNO 1
Date_ 20120601
Time 21.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 451
DS 2
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 12.7
DW 27.733 usec
DE 6.50 usec
TE 298.6 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.20 usec
PL1 -1.00 dB
PL1W 18.97366524 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 95.00 usec
PL2 -2.00 dB
PL12 17.82 dB
PL13 19.00 dB
PL2W 8.75835800 W
PL12W 0.09128989 W
PL13W 0.06957011 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677336 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

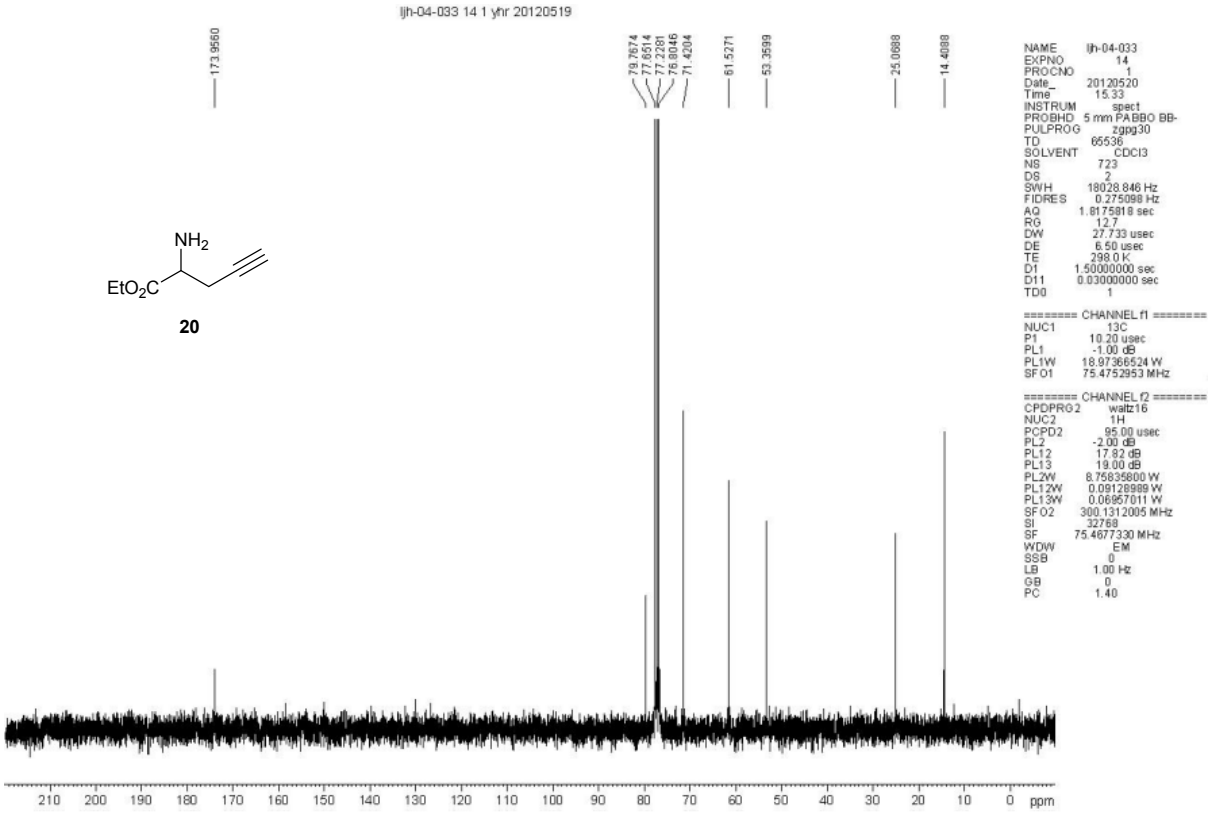
NH2
C7H15

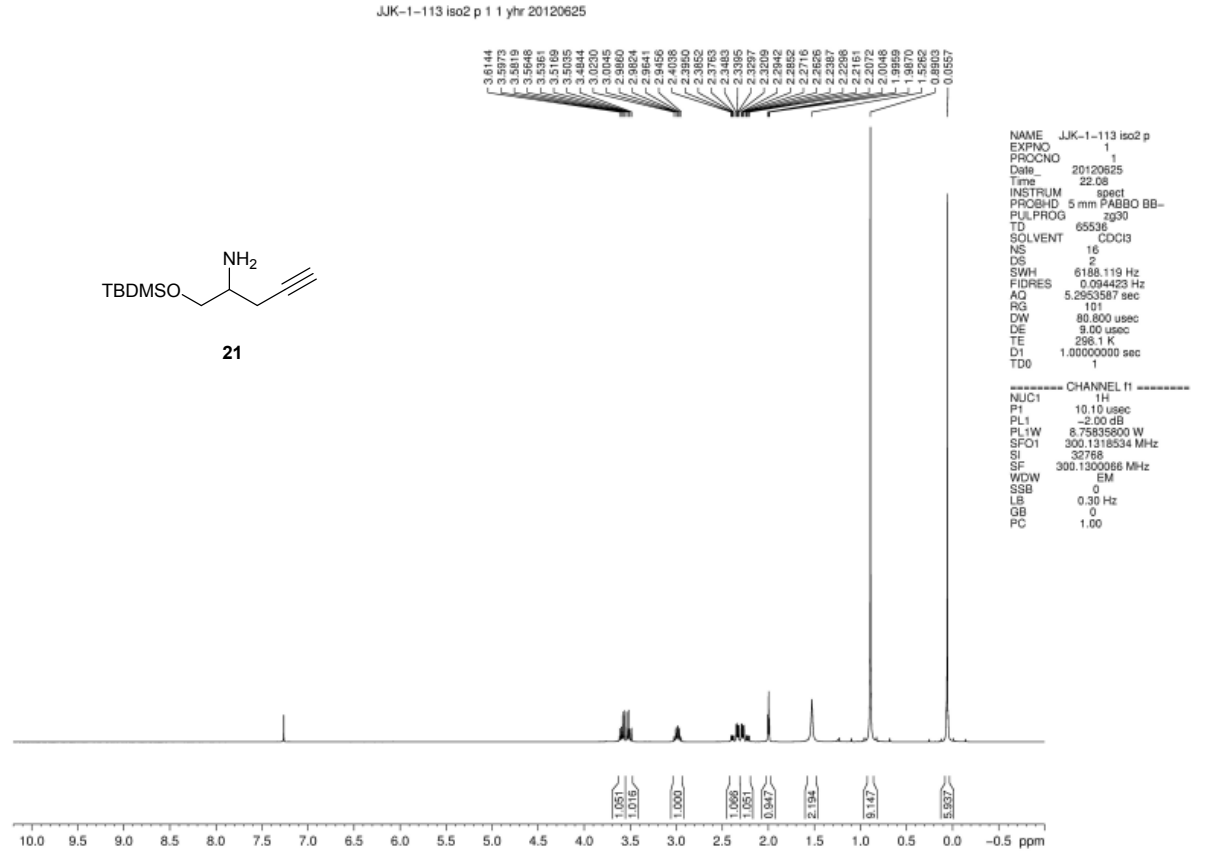
19

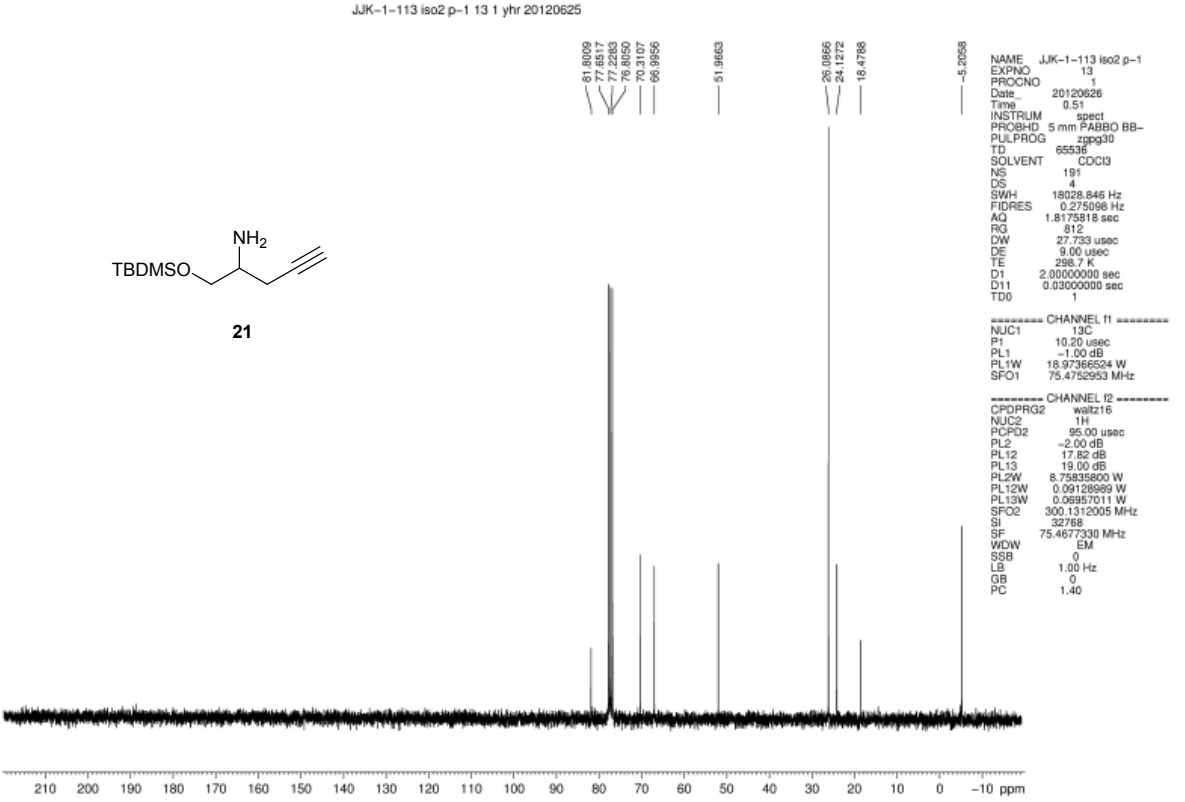

ljh-04-033 3 1 yhr 20120519
7.2600
4.2486
4.2410
4.2247
4.2173
4.2009
4.1936
4.1771
4.1699
3.6375
3.6295
3.5996
2.6497
2.6400
2.6313
2.6224
2.6198
2.6104
2.0635
2.0547
2.0459
1.8002
1.3088
1.2950
1.2612
NAME ljh-04-033
EXPNO 3
PROCNO 1
Date_ 20120519
Time 17.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 287
DW 80.800 usec
DE 9.00 usec
TE 297.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.10 usec
PL1 -2.00 dB
PL1W 8.75835800 W
SFO1 300.1318534 MHz
SI 32768
SF 300.1300066 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.04
1.00
2.07
1.01
2.36
3.36
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

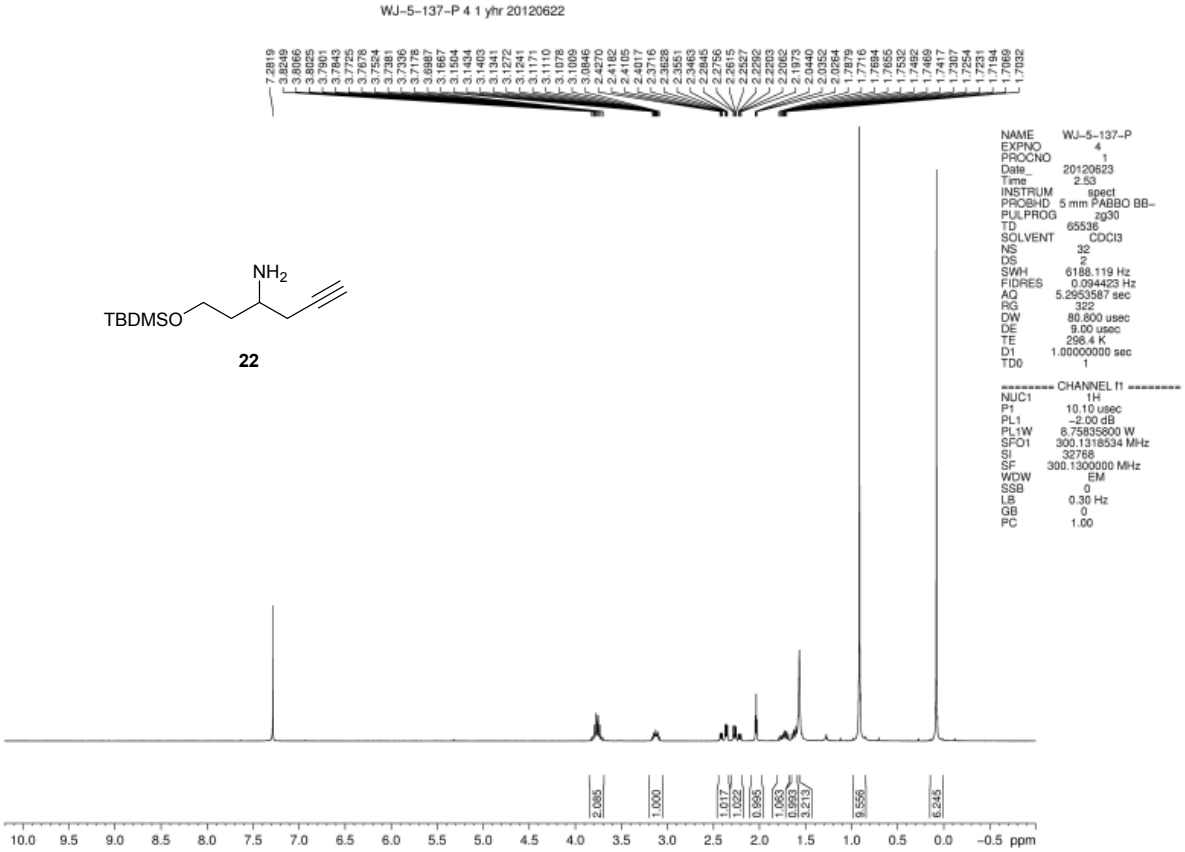
NH2
EtO2C

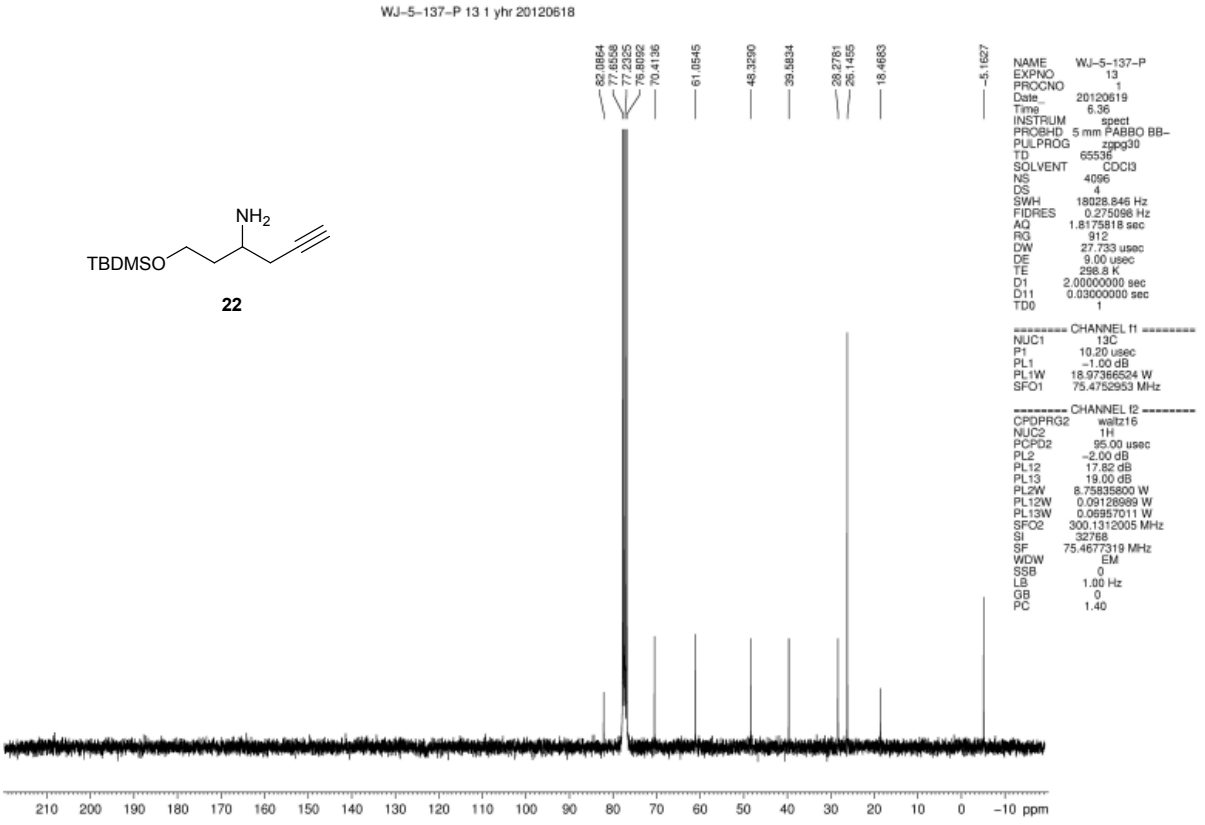
20

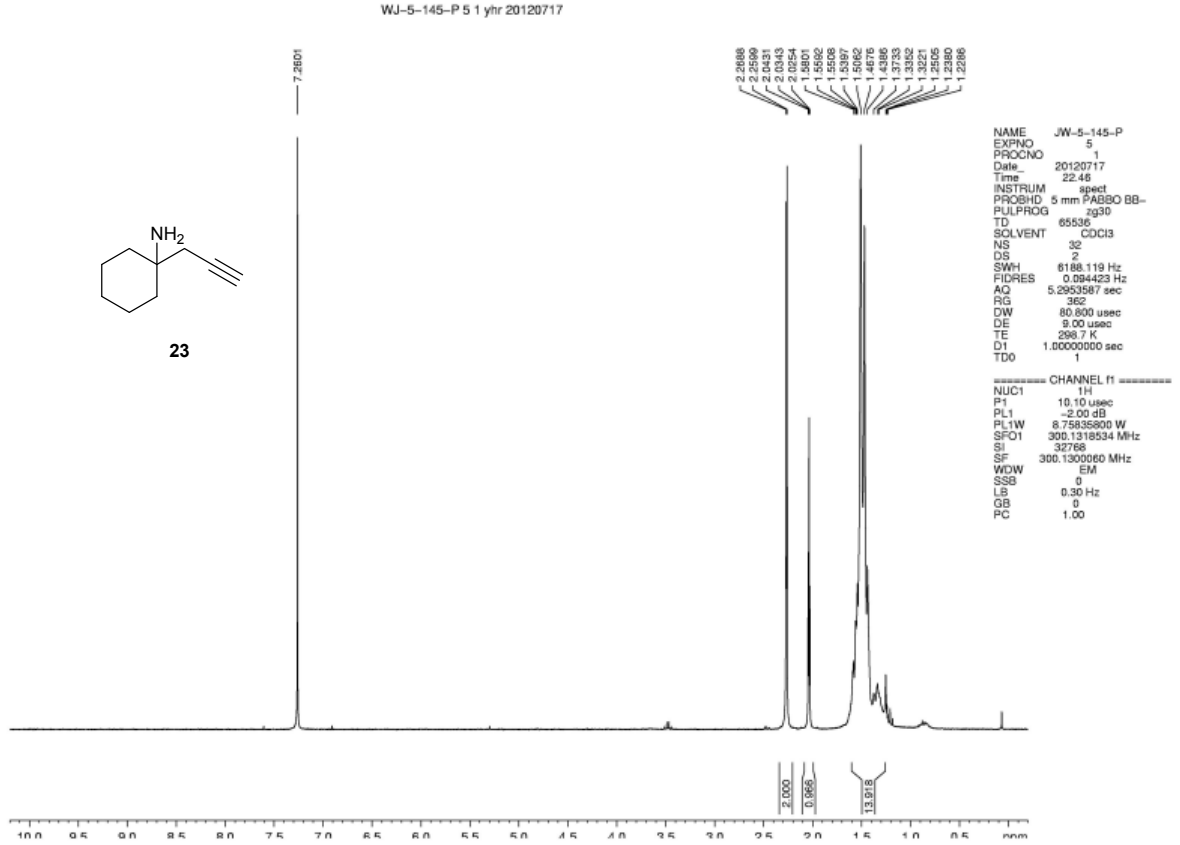

ljh-04-033 14 1 yhr 20120519
173.9560
79.7674
77.6514
77.2281
76.8046
71.4204
61.5271
53.3599
25.0688
14.4088
NAME ljh-04-033
EXPNO 14
PROCNO 1
Date_ 20120520
Time 15.33
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 723
DS 2
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 12.7
DW 27.733 usec
DE 6.50 usec
TE 298.0 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.20 usec
PL1 -1.00 dB
PL1W 18.97366524 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 95.00 usec
PL2 -2.00 dB
PL12 17.82 dB
PL13 19.00 dB
PL2W 8.75835800 W
PL12W 0.09128989 W
PL13W 0.06957011 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677330 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
NH2
EtO2C
20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

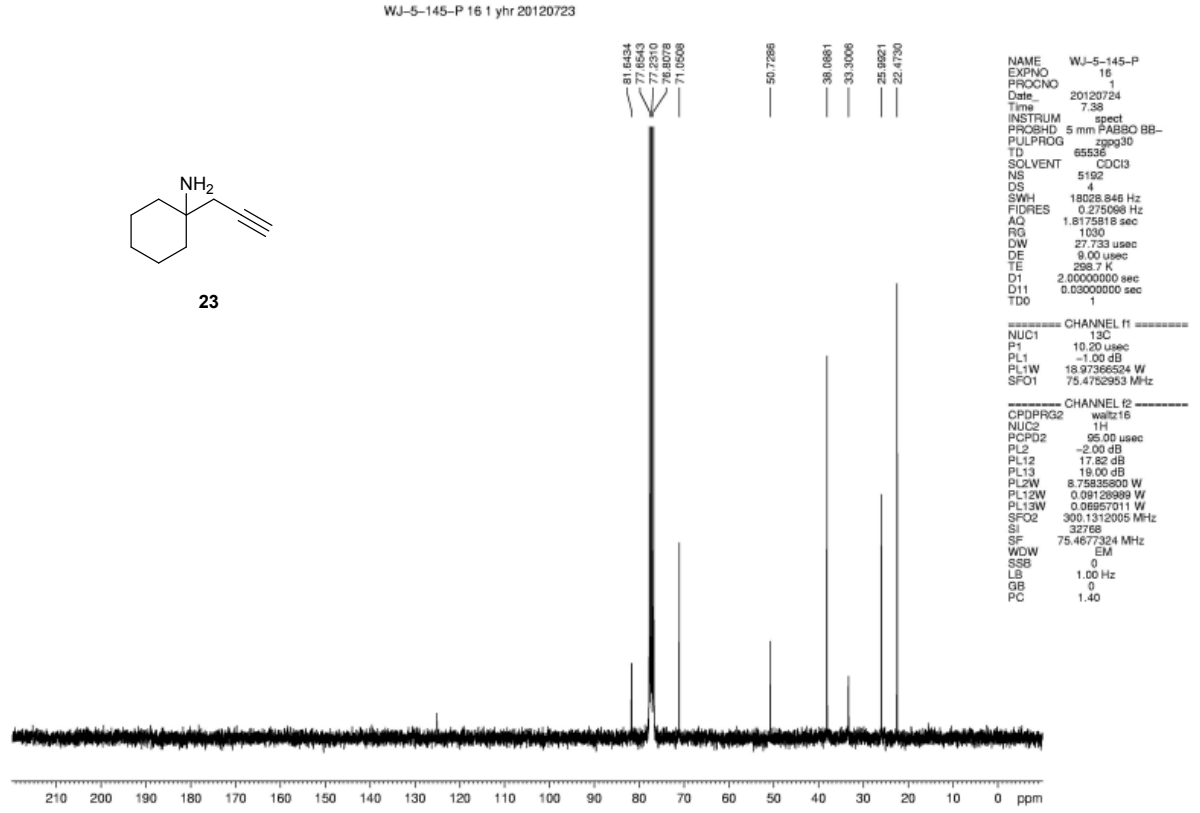

JJK-1-113 iso2 p 1 1 yhr 20120625
3.6144
3.5973
3.5819
3.5648
3.5361
3.5169
3.5035
3.4844
3.0230
3.0045
2.9860
2.9824
2.9641
2.9456
2.4038
2.3950
2.3852
2.3763
2.3483
2.3395
2.3297
2.3209
2.2942
2.2855
2.2716
2.2626
2.2387
2.2296
2.2161
2.2072
2.0048
1.9959
1.9870
1.5262
0.8903
0.0557
NAME JJK-1-113 iso2 p
EXPNO 1
PROCNO 1
Date_ 20120625
Time 22.08
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 101
DW 80.800 usec
DE 9.00 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.10 usec
PL1 -2.00 dB
PL1W 8.75835800 W
SFO1 300.1318534 MHz
SI 32768
SF 300.1300086 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.051
1.016
1.000
1.066
1.051
0.947
2.194
9.147
5.937
NH2
TBDMSO
21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm

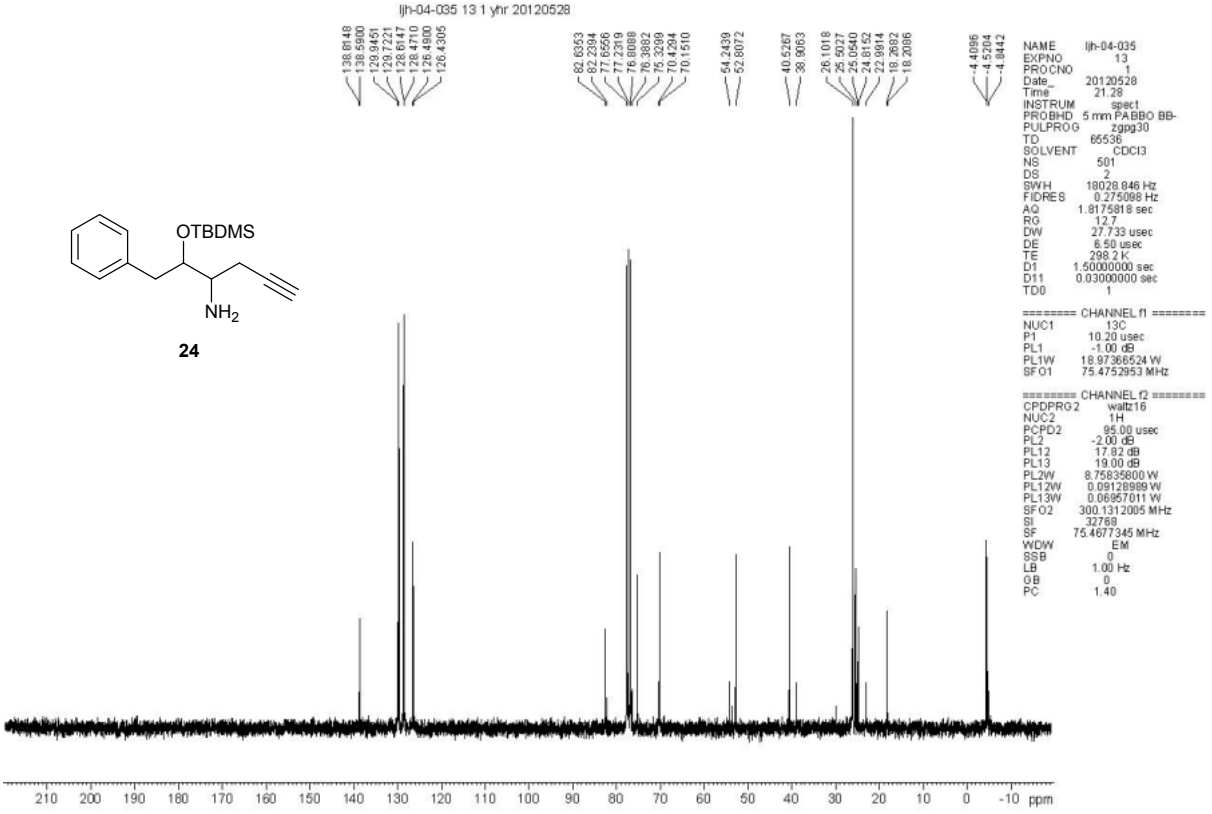

JJK-1-113 iso2 p-1 13 1 yhr 20120625
NH2
TBDMSO
21

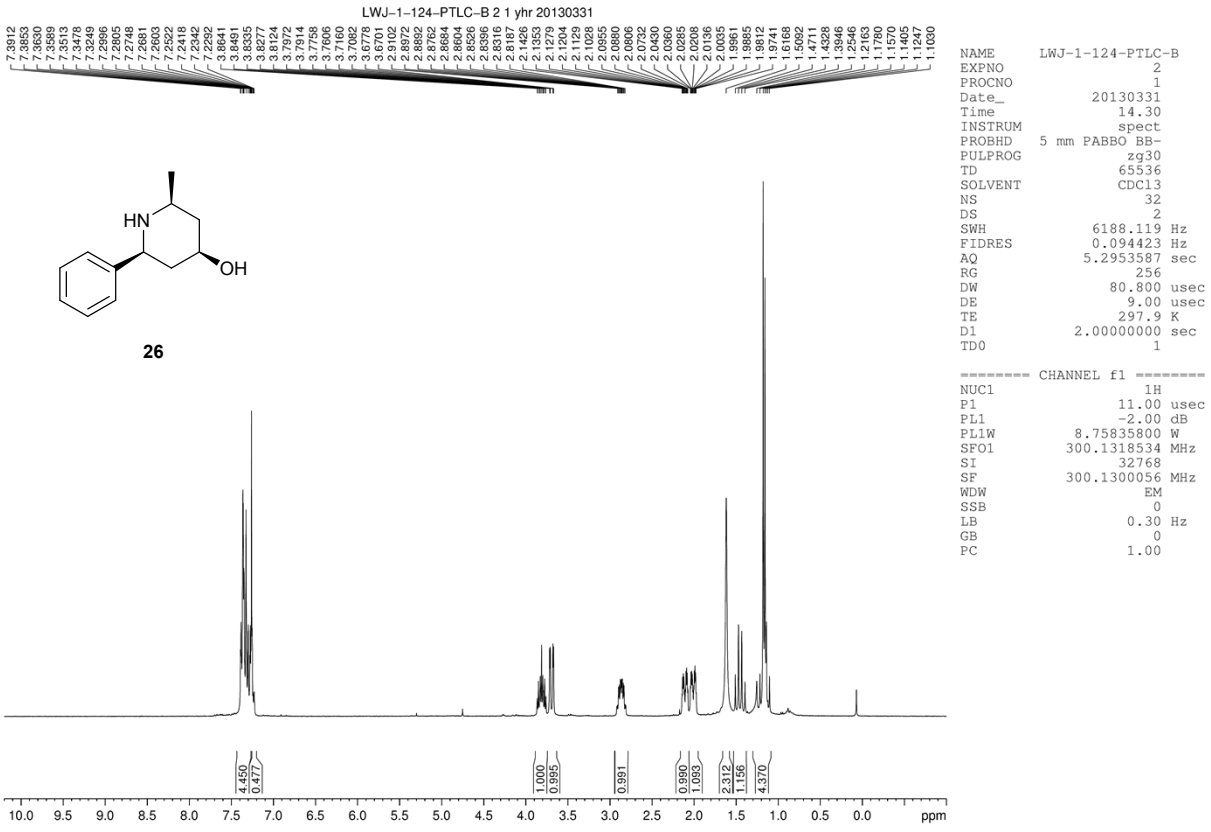

WJ-5-137-P 4 1 yhr 20120622
NH2
TBDMSO
22

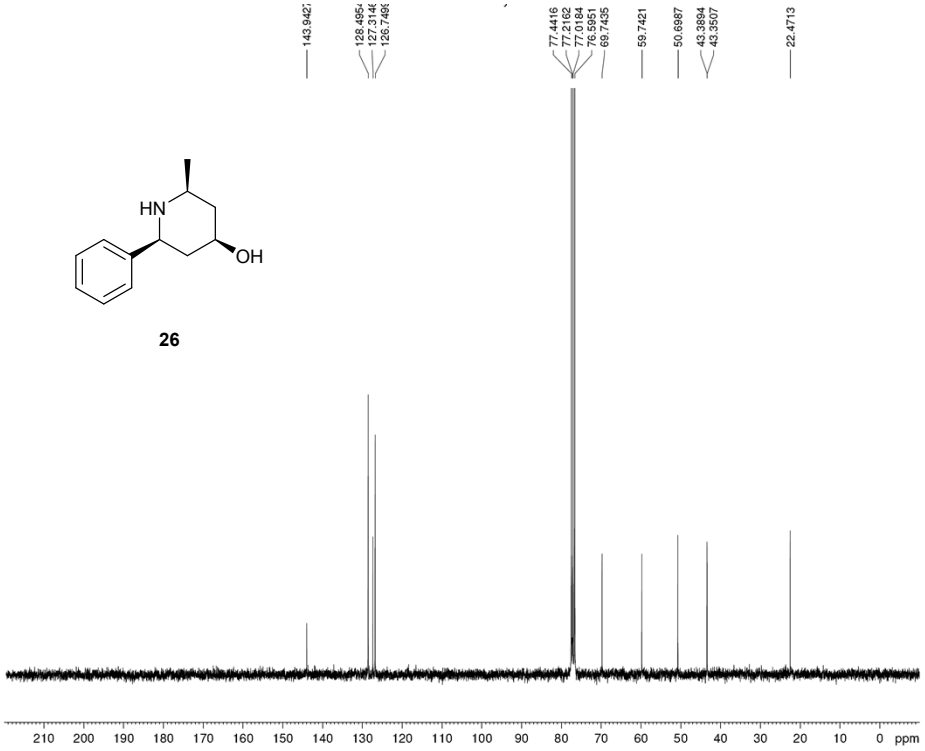

WJ-5-137-P 13 1 yhr 20120618
NH2
TBDMSO
22
82.0864
77.6558
77.2325
76.8092
70.4136
61.0545
45.3290
39.5834
28.2761
26.1455
18.4683
-5.1627
NAME WJ-5-137-P
EXPNO 13
PROCNO 1
Date_ 20120619
Time 6.36
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 4096
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 912
DW 27.733 usec
DE 9.00 usec
TE 298.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 10.20 usec
PL1 -1.00 dB
PL1W 18.97366524 W
SFO1 75.4752953 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 95.00 usec
PL2 -2.00 dB
PL12 17.82 dB
PL13 19.00 dB
PL2W 8.75835800 W
PL12W 0.09128989 W
PL13W 0.06957011 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677319 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm


WJ-5-145-P 5 1 yhr 20120717
NH2
23
7.2601
2.2688
2.2599
2.2431
2.0343
2.0254
1.5801
1.5582
1.5508
1.5397
1.5062
1.4676
1.4386
1.3733
1.3352
1.3221
1.2505
1.2380
1.2266
2.000
0.966
13.918
NAME JW-5-145-P
EXPNO 5
PROCNO 1
Date_ 20120717
Time 22.46
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 362
DW 80.800 usec
DE 9.00 usec
TE 298.7 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 10.10 usec
PL1 -2.00 dB
PL1W 8.75835800 W
SFO1 300.1318534 MHz
SI 32768
SF 300.1300060 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


WJ-5-145-P 16 1 yhr 20120723
81.6434
77.6543
77.2310
76.8078
71.0508
50.7286
38.0661
33.3006
25.9921
22.4730
NH2
23
NAME WJ-5-145-P
EXPNO 16
PROCNO 1
Date_ 20120724
Time 7.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 5192
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 1030
DW 27.733 usec
DE 9.00 usec
TE 298.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.20 usec
PL1 -1.00 dB
PL1W 18.97366524 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 95.00 usec
PL2 -2.00 dB
PL12 17.82 dB
PL13 19.00 dB
PL2W 8.75835800 W
PL12W 0.09128989 W
PL13W 0.06957011 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677324 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
ljh-04-035 1 1 yhr 20120518
OTBDMS
NH2
24
NAME ljh-04-035
EXPNO 1
PROCNO 1
Date_ 20120518
Time 17.00
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 101
DW 80.800 usec
DE 9.00 usec
TE 297.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.10 usec
PL1 -2.00 dB
PL1W 8.75835800 W
SFO1 300.1319534 MHz
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm


ljh-04-035 13 1 yhr 20120528
OTBDMS
NH2
24
NAME ljh-04-035
EXPNO 13
PROCNO 1
Date_ 20120528
Time 21.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 501
DS 2
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 12.7
DW 27.733 usec
DE 6.50 usec
TE 298.2 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.20 usec
PL1 -1.00 dB
PL1W 18.97366524 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 95.00 usec
PL2 -2.00 dB
PL12 17.82 dB
PL13 19.00 dB
PL2W 8.75835800 W
PL12W 0.09126989 W
PL13W 0.06957011 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677345 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


LWJ-1-124-PTLC-B 2 1 yhr 20130331
HN
OH
26
NAME LWJ-1-124-PTLC-B
EXPNO 2
PROCNO 1
Date_ 20130331
Time 14.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 256
DW 80.800 usec
DE 9.00 usec
TE 297.9 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -2.00 dB
PL1W 8.75835800 W
SFO1 300.1318534 MHz
SI 32768
SF 300.1300056 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



26

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NAME      LWJ-1-124-PTLC-B
EXPNO                   13
PROCNO                   1
Date_             20130401
Time                 12.01
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH              18028.846 Hz
FIDRES            0.275098 Hz
AQ                1.8175818 sec
RG                      912
DW                  27.733 usec
DE                   9.00 usec
TE                   298.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    10.20 usec
PL1                   -1.00 dB
PL1W          18.97366524 W
SFO1           75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                    1H
PCPD2                 95.00 usec
PL2                   -2.00 dB
PL12                  16.73 dB
PL13                  19.00 dB
PL2W           8.75835800 W
```