CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Partial Hydrogenation of Alkynes to *cis*-Olefins Using Novel Pd(0)-Polyethyleneimine Catalyst

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Contents

General experimental. $Pd(OAc)_2$ was purchased from Kishida (catalog No. 000-59012). Polyethyleneimine (average M_w ~25,000 by LS) was purchased from Aldrich (catalog No. 408727). MeOH and cyclohexane for HPLC, dehydrated AcOEt were purchased from Wako Pure Chemical Industries, Ltd., dehydrated dioxane was purchased from Kanto Chemical Co., and The were used without purification. CH_2Cl_2 were distilled from calcium hydride. All other reagents were purchased from commercially sources and used without further purification. Flash column chromatography was performed using Silica Gel 60 N (Kanto Chemical Co., Inc., 63-210 μm spherical, neutral). ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL AL 400 spectrometer or JEOL EX 400 spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). Chemical shifts (δ) are expressed in ppm and are internally referenced (0.00 ppm for TMS for $CDCl_3$ for ^{1}H NMR and 77.0 ppm for $CDCl_3$ for ^{13}C NMR). EI and FAB mass spectra were taken on a JEOL JMS-SX102A instrument.

Preparation of 5% Pd(0)-PEI catalyst (Scheme 1). Polyethyleneimine (2.11 g) was put in a 200 mL-round-bottom flask and deaerated for 48 h *in vacuo*. MeOH (100 mL, HPLC grade) was added and the resulting solution was pourded into $Pd(OAc)_2$ (225 mg, 1.00 mmol), which was placed in a 200 mL round bottom flask under an argon atmosphere, in one portion. After $Pd(OAc)_2$ was completely solved (about 10.0 min), the air inside the flask was replaced with H_2 (balloon) by three vacuum/H_2 cycles. The resulting solution was stirred at rt for 24 h and concentrated *in vacuo* to give 5% Pd(0)-PEI catalyst (2.58 g) as a black gummy solid.

Solvent effect of partial hydrogenation of diphenylacetylene using 5% Pd(0)-PEI catalyst (Table 1). In a test tube were placed diphenylacetylene (178 mg, 1.00 mmol), 5% Pd(0)-PEI (17.8 mg, 10 wt % of diphenylacetylene), a stir bar, and solvent given in Table 1. The air inside the test tube was replaced with H_2 by three vacuum/H_2 (balloon) cycles, and the mixture was vigorously stirred at ambient temperature. After 24 h, the reaction mixture was partitioned between Et_2O (10 mL) and H_2O (10 mL) and the organic layer was washed with brine (10 mL), dried ($MgSO_4$), and filtered, and concentrated *in vacuo* to afford the residue which could include **1a**–**4a**. The product ratio was determined by the comparison of the integration of the following three peaks at 6.60 ppm (olefin protonss of **2a**), 7.12 ppm (olefin protonss of **3a**) and 2.92 ppm (methylene protonss of **4a**) in ^{1}H NMR spectrum. The structures of all compounds, **1a**, **2a**, **3a,** and **4a**, were assigned on the basis of ^{1}H NMR of authentic commercial samples.

Typical procedure for Pd(0)-PEI-catalyzed partial hydrogenation of *di*-substituted alkynes (Table 2). In a test tube were placed substrate (1.00 mmol), 5% Pd(0)-PEI (10 wt % of substrate), a stir bar, and the mixed-solvent of MeOH (1 mL) and dioxane (1 mL). The air inside the test tube was replaced with H_2 (balloon) by three vacuum/H_2 cycles, and the mixture was vigorously stirred at ambient temperature. After 24 h, the reaction mixture was partitioned between Et_2O (10 mL) and H_2O (10 mL) and the organic layer was washed with brine (10 mL), dried ($MgSO_4$), and filtered, and concentrated *in vacuo* to afford the residue which could include **1**, **2**, **3**, and **4**. The ratio of **1**, **2**, **3**, and **4** was determined by ^{1}H NMR analysis.

***cis*-Cinnamic Acid and *trans*-Cinnamic Acid (Entry 1).**

Obtained from phenylpropynoic acid (146 mg, 1.00 mmol), 5% Pd(0)-PEI (14.6 mg, 10 wt % of phenylpropionic acid) and K_2CO_3 (138 mg, 1.00 mmol) according to the typical procedure. The ratio of *cis*- to *trans*-cinnamic acids was determined based on the integration of the following ^{1}H NMR signals at 5.95 ppm (olefin protons of *cis*-cinnamic acid) and 6.43 ppm (olefin protons of *trans*-cinnamic acid) to be 96 : 4. The chemical shifts of *cis*-isomer and *trans*-isomer were confirmed by those of the literature[1] and commercial authentic sample, respectively.

Ethyl *cis*-Cinnamate and Ethyl 3-Phenylpropionate (Entry 2).

Obtained from ethyl phenylpropiolate (174 mg, 1.00 mmol), 5% Pd(0)-PEI (17.4 mg, 10 wt % of ethyl phenylpropiolate) according to the typical procedure. The ratio of ethyl *cis*-cinnamate and ethyl 3-phenylpropionate was determined based on the integration of the following ^{1}H NMR signals at 5.93 ppm (olefin protons of ethyl *cis*-cinnamate) and 2.60 ppm (methylene protons of ethyl 3-phenylpropionate) to be 94 : 6. The chemical shifts of ethyl *cis*-cinnamate and ethyl 3-phenylpropionate were confirmed by those of the literature[2] and commercial authentic sample, respectively.

***cis*-4-Phenyl-3-buten-2-one and *trans*-4-Phenyl-3-buten-2-one and Benzylacetone (Entry 3).**

Obtained from 4-phenyl-3-butyn-2-one (144 mg, 1.00 mmol), 5% Pd(0)-PEI (14.4 mg, 10 wt % of 4-phenyl-3-butyn-2-one) according to the typical procedure. The ratio of *cis*-4-phenyl-3-buten-2-one and *trans*-4-phenyl-3-buten-2-one and benzylacetone was determined based on the integration of the following ^{1}H NMR signals at 6.18 ppm (olefin protons of *cis*-4-phenyl-3-buten-2-one), 6.72 ppm (olefin protons of *trans*-4-phenyl-3-buten-2-one) and 2.76 ppm (methylene protons of benzylacetone) to be 36 : 58 : 6. The chemical shifts of *cis*-isomer and *trans*-isomer, benzylacetone were confirmed by those of the literature[3] and commercial authentic sample, respectively.

***cis*-6-Dodecene (Entry 4).**

Obtained from 6-dodecyne (166 mg, 1.00 mmol), 5% Pd(0)-PEI (16 mg, 10 wt % of 6-dodecyne) according to the typical procedure. ^{1}H NMR spectrum of the residue was identical with that of *cis*-dodecene in the literature.[4]

***cis*-3-Octen-1-ol (Entry 5).**

Obtained from 3-octyn-1-ol (126 mg, 1.00 mmol), 5% Pd(0)-PEI (12.6 mg, 10 wt % of 3-octyn-1-ol) according to the typical procedure. ^{1}H NMR spectrum of the residue was identical with that of commercial authentic sample.

***cis*-2,5-Dimethyl-3-hexene-2,5-diol (Entry 6).**

Obtained from 2,5-dimethyl-3-hexyne-2,5-diol (142 mg, 1.00 mmol), 5% Pd(0)-PEI (14.2 mg, 10 wt % of 2,5-dimethyl-3-hexyne-2,5-diol) according to the typical procedure. ^{1}H NMR spectra showed that other products were not included in the residue. ^{1}H NMR ($CDCl_3$) δ 5.32 (2H, s), 4.23 (2H, s*), 1.37 (12H, s). ^{13}C NMR ($CDCl_3$) δ: 135.4, 71.0, 31.5. MS (EI) m/z 129 (M^{+}-CH_3, 21%), 111 (100%), 43 (49%); HRMS (EI) Calcd for $C_7H_{13}O_2$ (M^{+}-CH_3)129.0916. Found 129.0922.

Typical procedure for Pd(0)-PEI-catalyzed partial hydrogenation of *mono*-substituted alkynes (Table 3). In a test tube were placed substrate (1.00 mmol), 5% Pd(0)-PEI (10 wt % of substrate), a stir bar, and solvent given in Table 3. The air inside the test tube was replaced with H_2 (balloon) by three vacuum/H_2 cycles, and the mixture was vigorously stirred at ambient temperature. After 24 h, the reaction mixture was partitioned between Et_2O (10 mL) and H_2O (10 mL) and the organic layer was washed with brine (10 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo* to afford the residue which could include **5**, **6**, and **7**. The ratio of **5**, **6**, and **7** was determined by ^{1}H NMR analysis.

4-Ethynylaniline and 4-Vinylaniline and 4-Ethylaniline (Entry 1).

Obtained from 4-ethynylaniline (117 mg, 1.00 mmol), 5% Pd(0)-PEI (11.7 mg, 10 wt % of 4-ethynylaniline) according to the typical procedure. The ratio of 4-ethynylaniline and 4-vinylaniline and 4-ethylaniline was determined based on the integration of the following ^{1}H NMR signals at 2.95 ppm (alkyne protons of 4-ethynylaniline), 5.03 ppm (olefin protons of 4-vinylaniline) and 1.17 ppm (methyl protons of 4-ethylaniline) to be 11 : 85 : 4. The chemical shifts of these compounds were confirmed by those of commercial authentic sample.

***N*-Benzyloxycarbonyl-4-vinylaniline and *N*-Benzyloxycarbonyl-4-ethylaniline (Entry 2).**

Obtained from *N*-benzyloxycarbonyl-4-ethynylaniline (126 mg, 0.5 mmol), 5% Pd(0)-PEI (12.6 mg, 10 wt % of *N*-benzyloxycarbonyl-4-ethynylaniline) according to the typical procedure. The ratio of *N*-benzyloxycarbonyl-4-vinylaniline and *N*-benzyloxycarbonyl-4-ethylaniline was determined based on integration of the following ^{1}H NMR signals at 5.68 ppm (olefin protons of *N*-benzyloxycarbonyl-4-vinylaniline) and 1.21 ppm (methyl protons of *N*-benzyloxycarbonyl-4-ethylaniline) to be 93 : 7. These chemical shifts were confirmed by those of the literature[5].

1-Dodecene and 1-dodecane (Entry 3).

Obtained from 1-dodecyne (166 mg, 1.00 mmol), 5% Pd(0)-PEI (16.6 mg, 10 wt % of 1-dodecyne) according to the typical procedure. The ratio of 1-dodecene and 1-dodecane was determined based on integration of the following ^{1}H NMR signals 4.94 ppm (olefin protons of 1-dodecene) and 0.88 ppm (methyl protons of 1-dodecane) to be 83 : 17. These chemical shifts were confirmed by those of commercial authentic sample.

Allylphenylsulfide and Phenylpropylsulfide (Entry 4).

Obtained from phenylpropargylsulfide (148 mg, 1.00 mmol), 5% Pd(0)-PEI (14.8 mg, 10 wt % of phenylpropargylsulfide) according to the typical procedure. The ratio of allylphenylsulfide and phenylpropylsulfide was determined based on integration of the following ^{1}H NMR signals 5.09 ppm (olefin protons of allylphenylsulfide) and 1.02 ppm (methyl protons of phenylpropylsulfide) to be 98 : 2. These chemical shifts were confirmed by those of commercial authentic sample.

Benzylheptenoate (Entry 5).

Obtained from benzylheptynoate (108 mg, 0.5 mmol), 5% Pd(0)-PEI (10.8 mg, 10 wt % of benzylheptynoate) according to the typical procedure. ^{1}H NMR spectra showed that other products were not included in the residue. ^{1}H NMR (CDCl$_3$) δ 7.39-7.30 (5H, m), 5.83-5.73 (1H, m), 5.12 (2H, s), 4.98 (2H, m), 2.37 (2H, t, *J* = 7.7 Hz), 2.06 (2H, m), 1.67 (2H, m), 1.46-1.38 (2H, m). MS (EI) m/z 218 (M^+, 2%), 91 (100%); HRMS (EI) Calcd for $C_{14}H_{18}O_2$ (M^+) 218.1307. Found 218.1295.

4-(Benzyloxy)butene and Benzyl butyl ether (Entry 6).

Obtained from 4-(benzyloxy)butyne (80.0 mg, 1.00 mmol), 5% Pd(0)-PEI (8.00 mg, 10 wt % of 4-(benzyloxy)butyne) according to the typical procedure. The ratio of 4-(benzyloxy)butene and benzyl butyl ether was determined based on the integration of the following ^{1}H NMR signals 5.08 ppm (olefin protons of 4-(benzyloxy)butene) and 3.48 ppm (methylene protons of benzyl butyl ether) to be 96 : 4. These chemical shifts of 4-(benzyloxy)butene and benzyl butyl ether were confirmed by those of the literature[6] and commercial authentic sample, respectively.

(17α, 20E)-19-Norpregna-1, 3, 5(10), 20-tetraene-3, 7-diol (Entry 7).

Obtained from ethynylestradiol (296 mg, 1.00 mmol), 5% Pd(0)-PEI (29.6 mg, 10 wt % of ethynylestradiol) and K_2CO_3 (138 mg, 1.00 mmol) according to the typical procedure. ^1H NMR spectrum of the residue was identical with that in the literature.[7]

9-Vinyl-9-fluorenol and 9-Ethyl-9-fluorenol (Entry 8).

Obtained from 9-ethynyl-9-fluorenol (206 mg, 1.00 mmol), 5% Pd(0)-PEI (20.6 mg, 10 wt % of 9-ethynyl-9-fluorenol) according to the typical procedure. The ratio of 9-vinyl-9-fluorenol and 9-ethyl-9-fluorenol was determined based on the integration of the following ^1H NMR signals 5.22 ppm (olefin protons of 9-vinyl-9-fluorenol) and 0.55 ppm (methyl protons of 9-ethyl-9-fluorenol) to be 88 : 12. The chemical shifts of 9-vinyl-9-fluorenol and 9-ethyl-9-fluorenol were confirmed by those of the literature 8 and literature 9, respectively.

Allylbenzoate and Propylbenzoate (Entry 9).

Obtained from propargylbenzoate (160 mg, 1.00 mmol), 5% Pd(0)-PEI (16.0 mg, 10 wt % of propargylbenzoate) according to the typical procedure. The ratio of allylbenzoate and propargylbenzoate was determined based on the integration of the following ^1H NMR signals 5.38 ppm (olefin protons of allylbenzoate) and 1.02 ppm (methyl protons of propargylbenzoate) to be 83 : 17. The chemical shifts of allylbenzoate and propargylbenzoate were confirmed by those of the literature[10] and commercial authentic sample, respectively.

2-*tert*-Butyldimethylsilyloxy-2-phenyl-3-butene (Entry 10).

Obtained from 2-*tert*-butyldimethylsilyloxy-2-phenyl-3-butyne (130 mg, 0.5 mmol), 5% Pd(0)-PEI (13.0 mg, 10 wt % of 2-*tert*-butyldimethylsilyloxy-2-phenyl-3-butyne) according to the typical procedure. ^1H NMR spectra showed that other products were not included in the residue. ^1H NMR ($CDCl_3$) δ 7.44 - 7.20 (5H, m), 5.99 (1H, dd, J = 17.2, 10.5 Hz), 5.27 (1H, dd, J = 17.2, 1.0 Hz), 5.09 (1H, dd, J = 10.5, 1.0 Hz), 1.65 (3H, s), 0.95 (9H, s), 0.05 (3H, s), 0.00 (3H, s); MS (EI) m/z 247 (M^+-CH_3, 6%), 205 (98%), 131 (20%), 91 (11%), 75 (100%), 44 (14%); HRMS (EI) Calcd for $C_{15}H_{23}OSi$ (M^+-CH_3) 247.1518. Found 247.1509.

2-Phenyl-3-buten-2-ol and 2-phenyl-2-butanol (Entry 11).

Obtained from 2-phenyl-3-butyn-2-ol (146 mg, 1.00 mmol), 5% Pd(0)-PEI (14.6 mg, 10 wt % of 2-phenyl-3-butyn-2-ol) according to the typical procedure. The ratio of 2-phenyl-3-buten-2-ol and 2-phenyl-2-butanol was determined based on the integration of the following ^1H NMR signals 6.17 ppm (olefin protons of 2-phenyl-3-buten-2-ol) and 0.80 ppm (methyl protons of 2-phenyl-2-butanol) to be 88 : 12. The chemical shifts of 2-phenyl-3-buten-2-ol and 2-phenyl-2-butanol were confirmed by those of the literature[11] and commercial authentic sample, respectively.

Synthesis of the substrate (Table 3, Entries 2, 5, 6, and 10).

N-Benzyloxycarbonyl-4-ethynylaniline (Table 3, Entry 2)[5]

To a solution of 4-ethynylaniline (586 mg, 5.00 mmol) in THF (10.0 mL) was added *N*-(benzyloxycarbonyloxy)succinimide (1.50 g, 6.00 mmol). After 16 h, the mixture was extracted with AcOEt (150 mL) and H_2O (100 mL). The organic layer was washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (*n*-hexane/Et_2O, 10/1) in 93% (1.17 g) as a pale brownish yellow solid. The ^1H NMR data was identical with that of the literature.[5]

Benzylheptynoate (Table 3, Entry 5)[12]

To a solution of 6-heptynoic acid (1.26 g, 10.0 mmol), EDC· HCl (1.92 g, 10.0 mmol), and DMAP (122 mg, 1.00 mmol) in CH_2Cl_2 (20.0 mL) was added benzyl alcohol (1.08 g, 10.0 mmol). After 44 h, the mixture was extracted with AcOEt (150 mL) and H_2O (100 mL). The organic layer was washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (*n*-hexane/Et_2O, 20/1) in 84% (1.82 g) as a pale yellow oil. The ^1H NMR data was identical with that of the literature.[12]

4-(Benzyloxy)butyne (Table 3, Entry 6)[13]

To a suspension of NaH (60% W/W in mineral oil, 300 mg, 7.50 mmol) in THF (5.00 mL) and DMF (4.00 mL) was added THF solution (5.00 mL) of 3-butyn-1-ol (351 mg, 5.00 mmol) at 0 °C. After 30 min, the resulting solution was stirred at rt for 1 h, benzyl bromide (1.31 g, 7.50 mmol) was added dropwise, and the mixture was stirred at 0 °C for 30 min and at rt for 16 h. The mixture was extracted with Et_2O (150 mL) and H_2O (100 mL). The organic layer was washed with brine (100 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (*n*-hexane/Et_2O, 20/1) in 96% (766 mg) as a pale yellow oil. The ^1H NMR data was identical with that of the literature.[13]

2-*tert*-Butyldimethylsilyloxy-2-phenyl-3-butyne (Table 3, Entry 10)

To a solution of 2-phenyl-3-butyn-2-ol (731 mg, 5.00 mmol), 2,6-lutidine (1.07 g, 10.0 mmol) in CH_2Cl_2 (5.00 mL) was added dropwise *tert*-butyldimethylsilyl trifluoromethanesulfonate (1.98 g, 7.5 mmol) at 0 °C under argon atmosphere and the mixture was stirred at rt. After 30 min, the mixture was extracted with Et_2O (150 mL) and H_2O (100 mL). The organic layer was washed with brine (100 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (*n*-hexane) in 95% (1.24 g) as a colorless oil. ^1H NMR

($CDCl_3$) δ 7.44 - 7.20 (5H, m), 5.99 (1H, dd, *J* = 17.2, 10.5 Hz), 5.27 (1H, dd, *J* = 17.2, 1.0 Hz), 5.09 (1H, dd, *J* = 10.5, 1.0 Hz), 1.65 (3H, s), 0.95 (9H, s), 0.05 (3H, s), 0.00 (3H, s); MS (EI) m/z 247 (M^+-CH_3, 6%), 205 (98%), 131 (20%), 91 (11%), 75 (100%), 44 (14%); HRMS (EI) Calcd for $C_{15}H_{23}OSi$ (M^+-CH_3) 247.1518. Found 247.1509.

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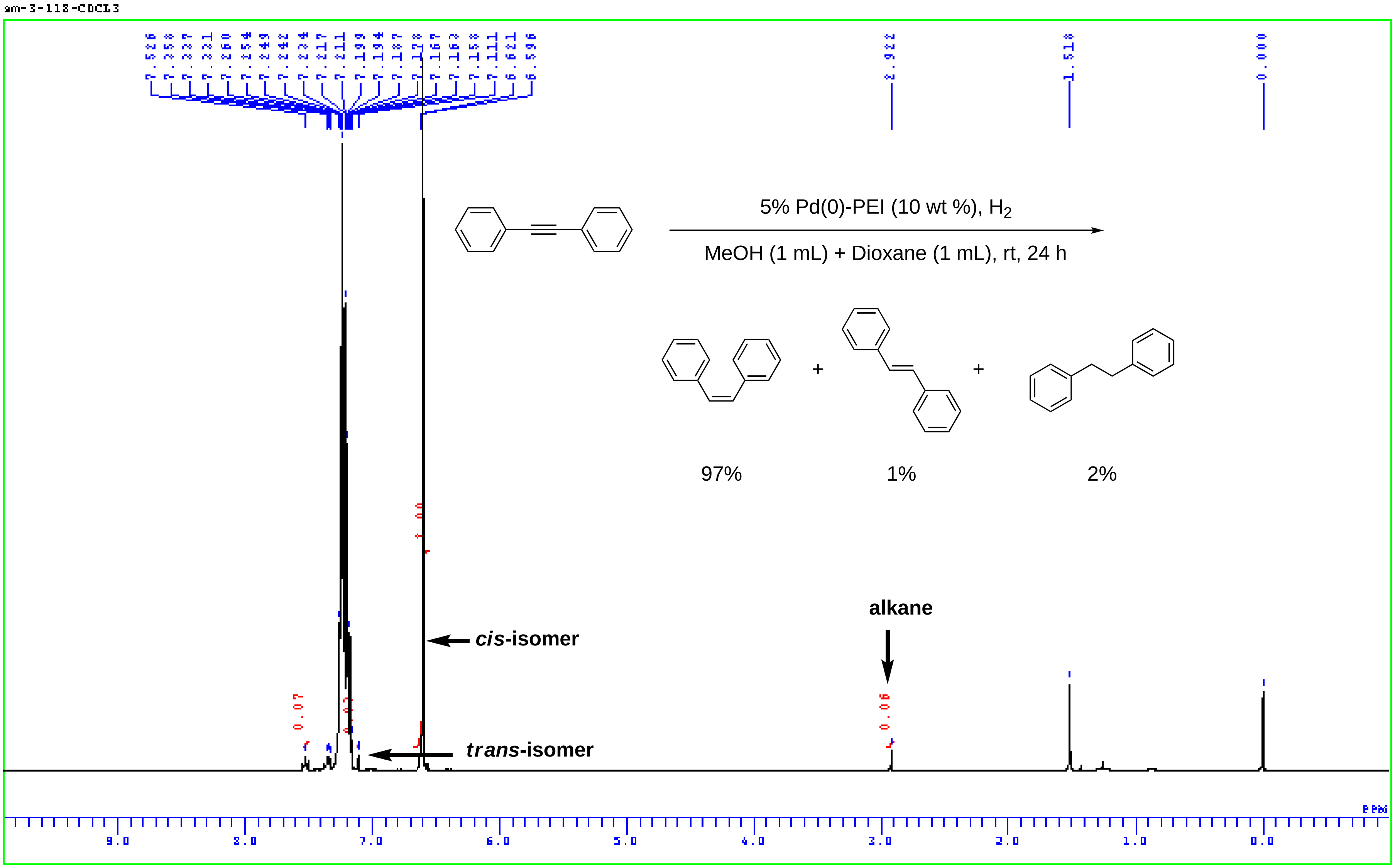
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MeOH (1 mL) + Dioxane (1 mL), rt, 24 h
+
+
97%
1%
2%
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trans-isomer
0.07
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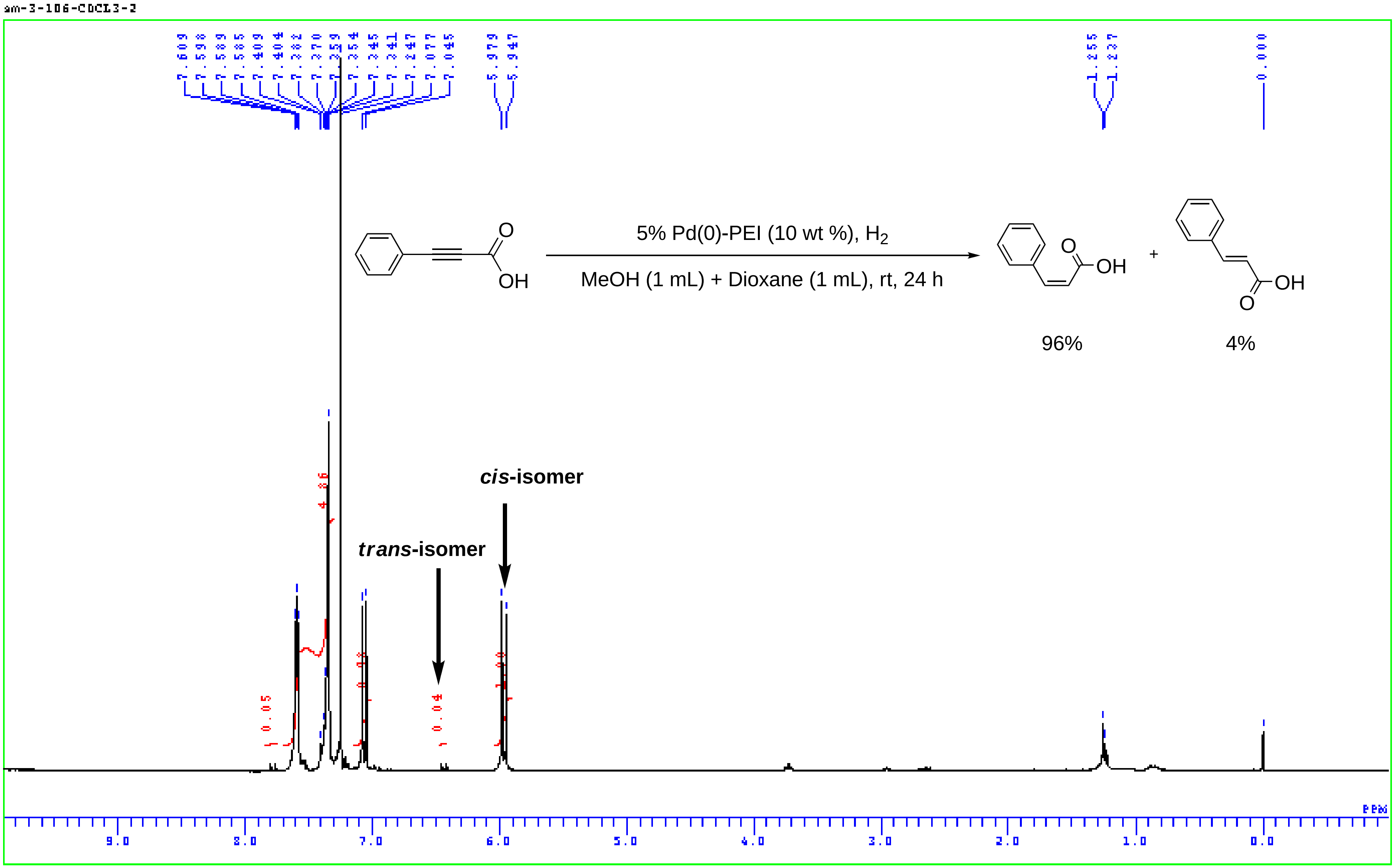
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+
OH
O
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4%
cis-isomer
trans-isomer
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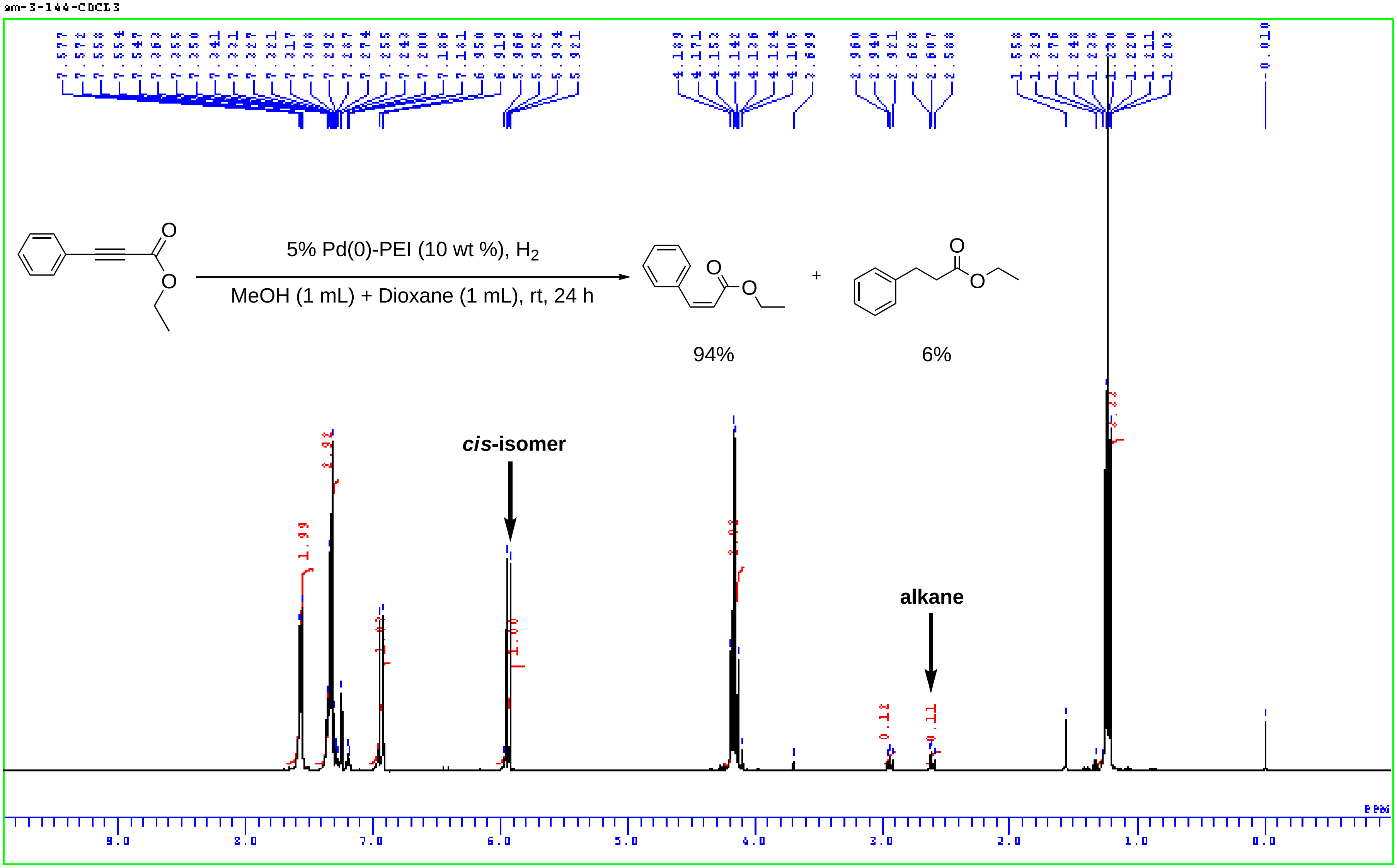
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O
+
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O
94%
6%
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1.00
2.08
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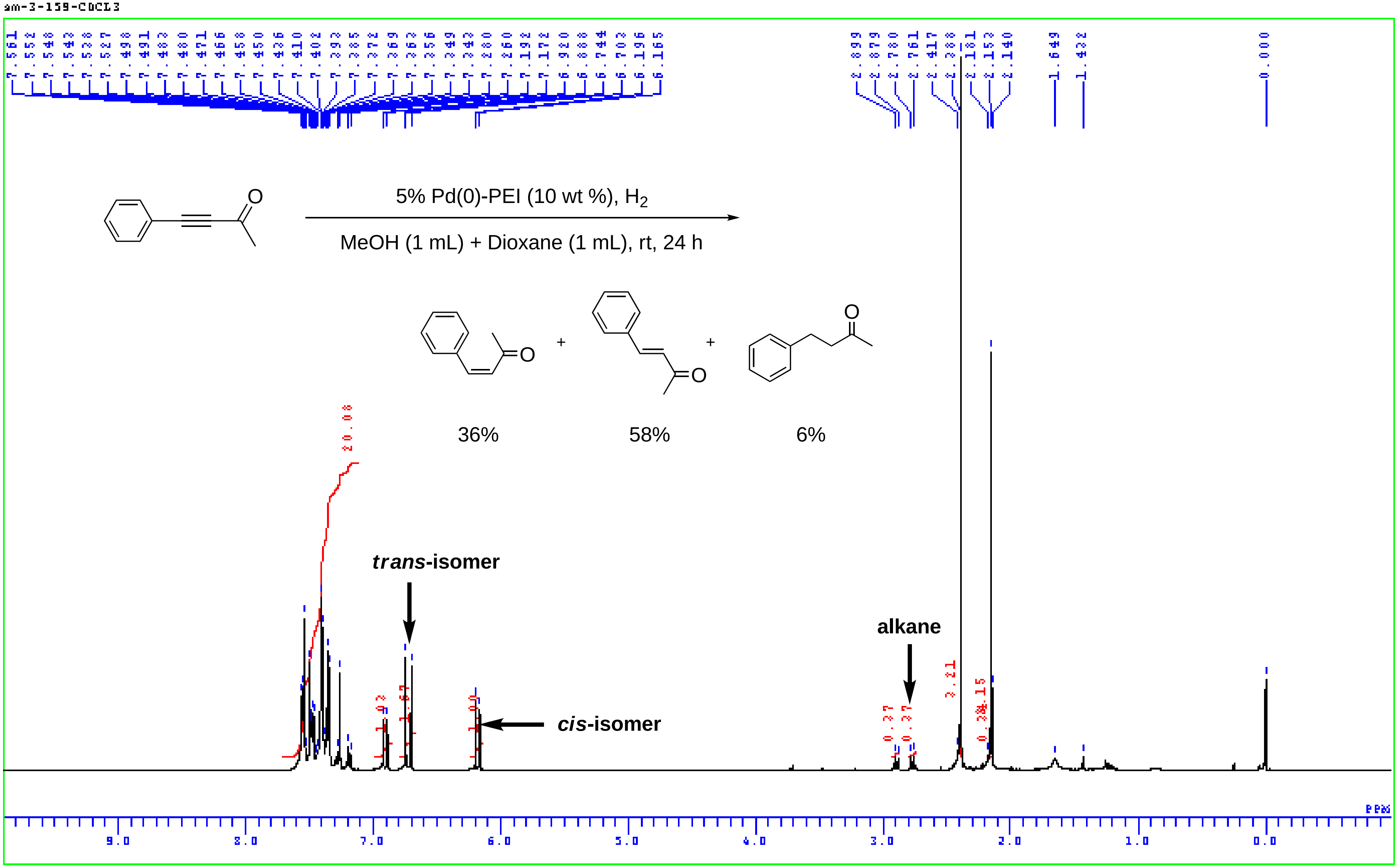
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+
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6%
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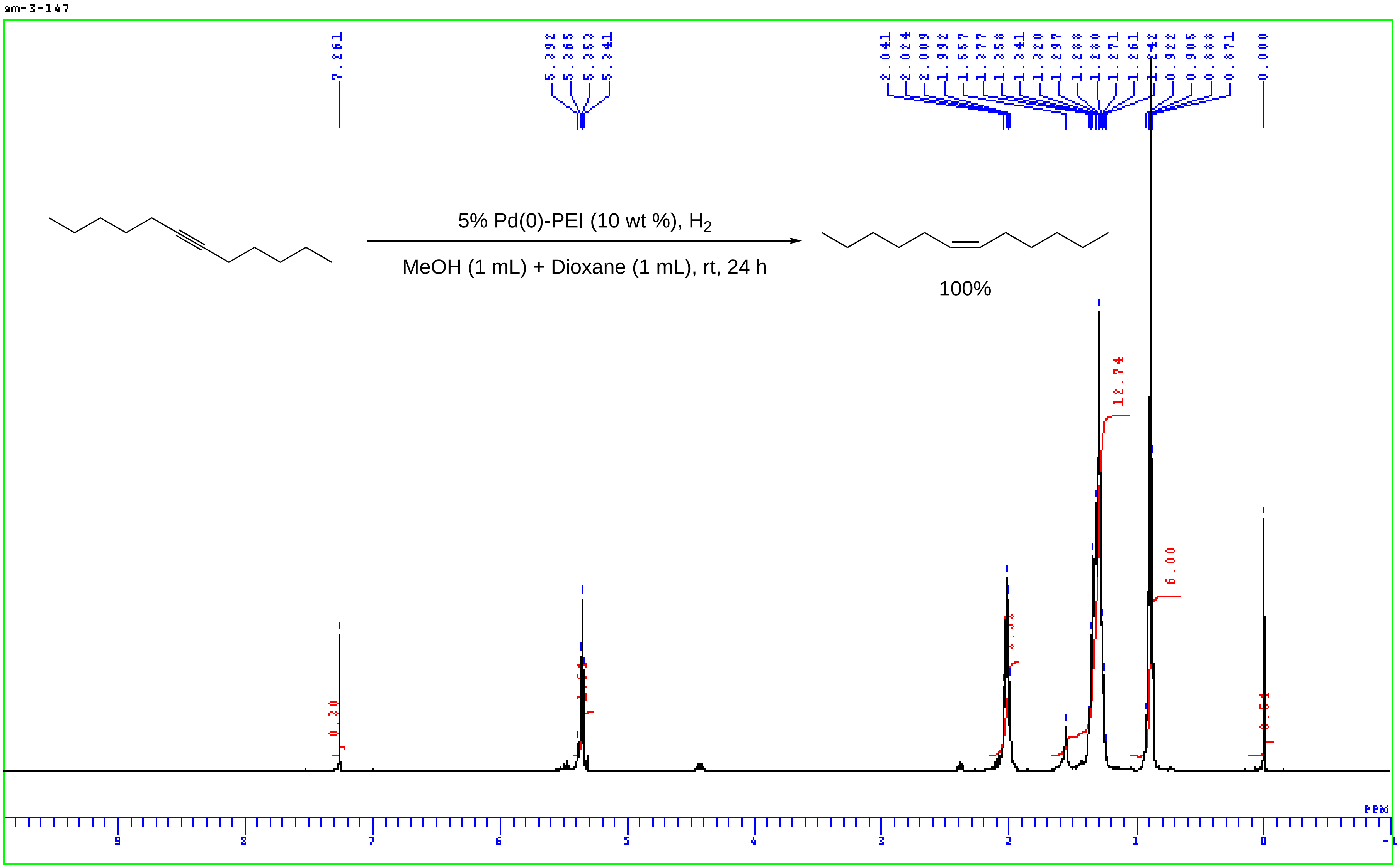am-3-147
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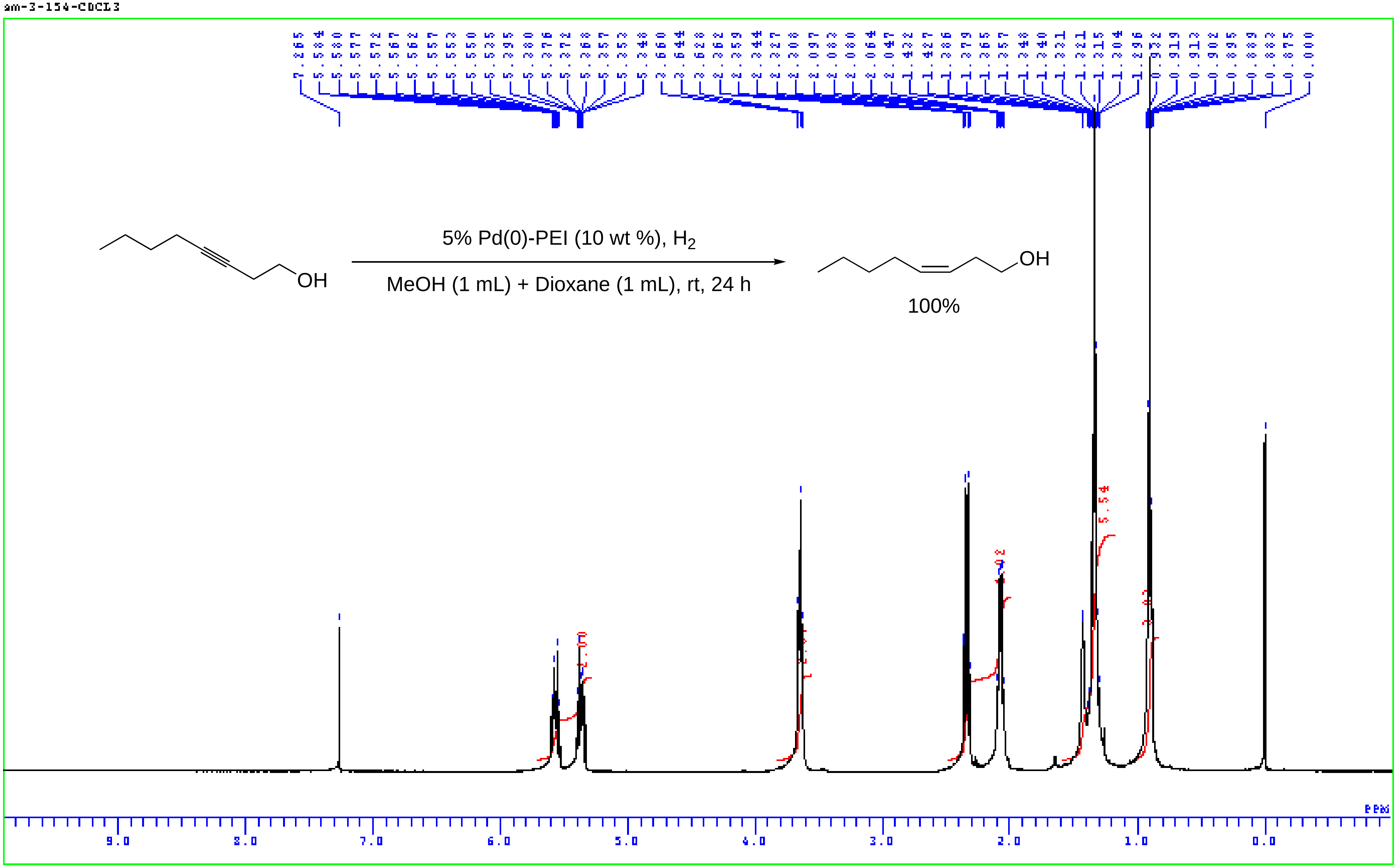
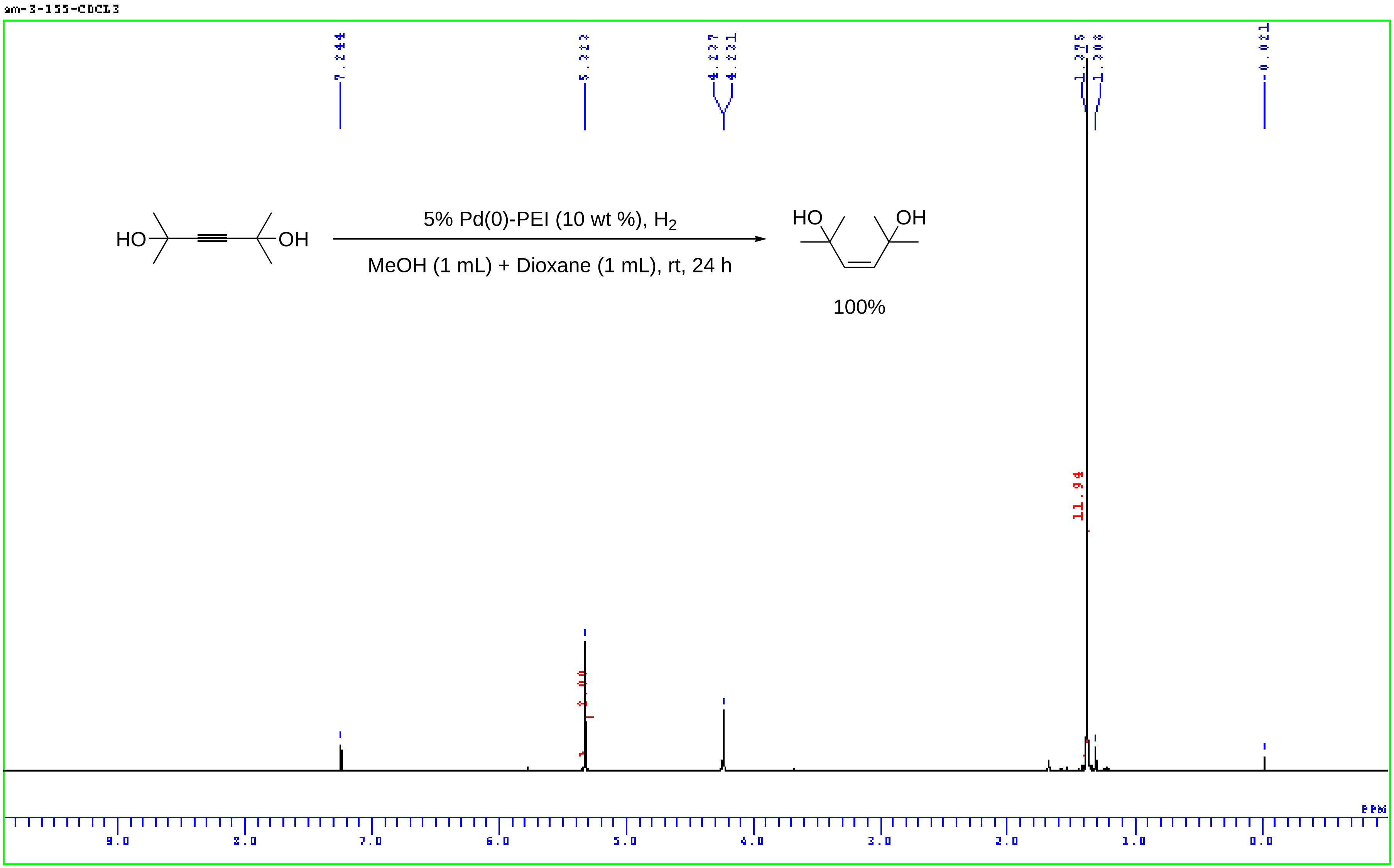
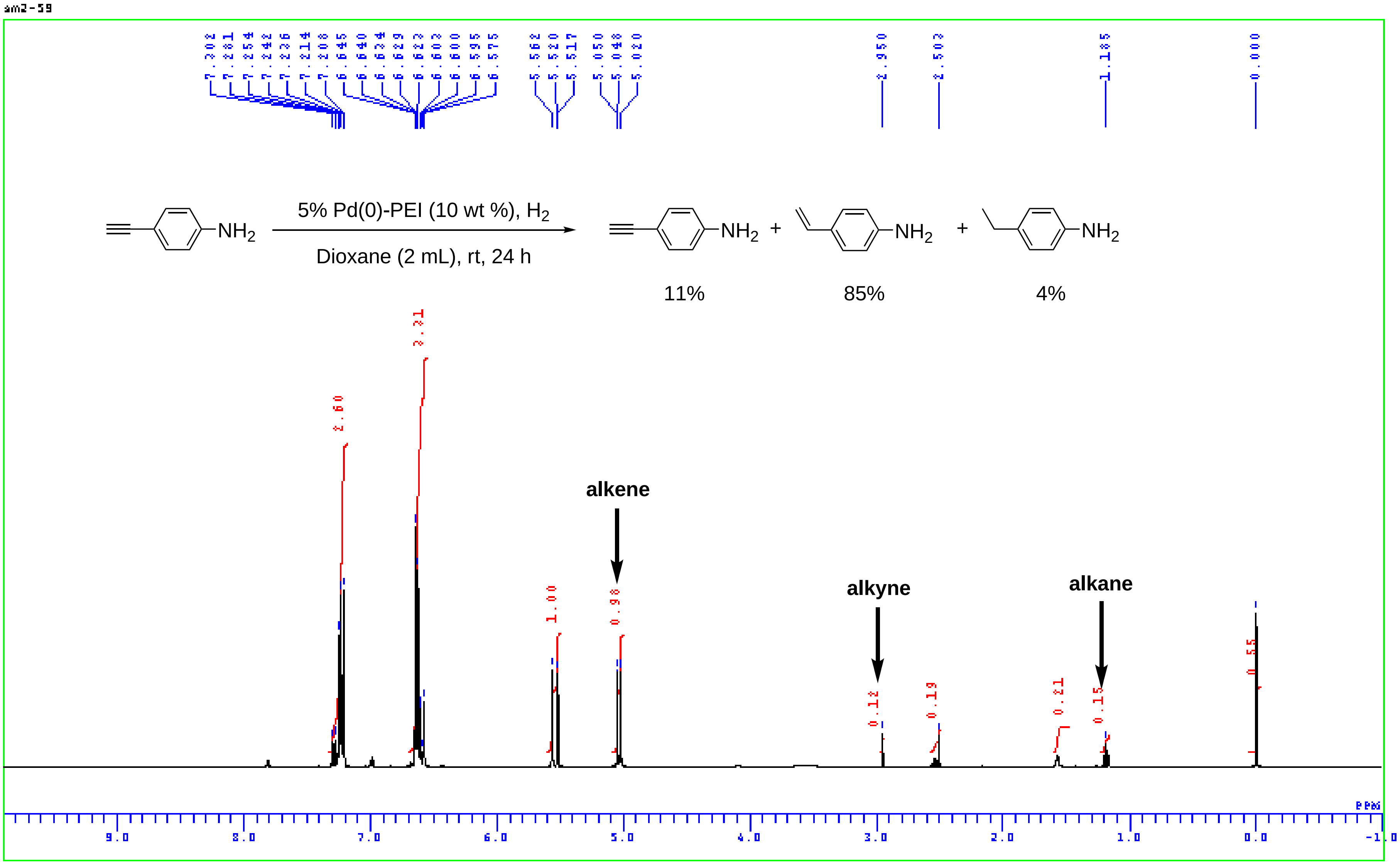
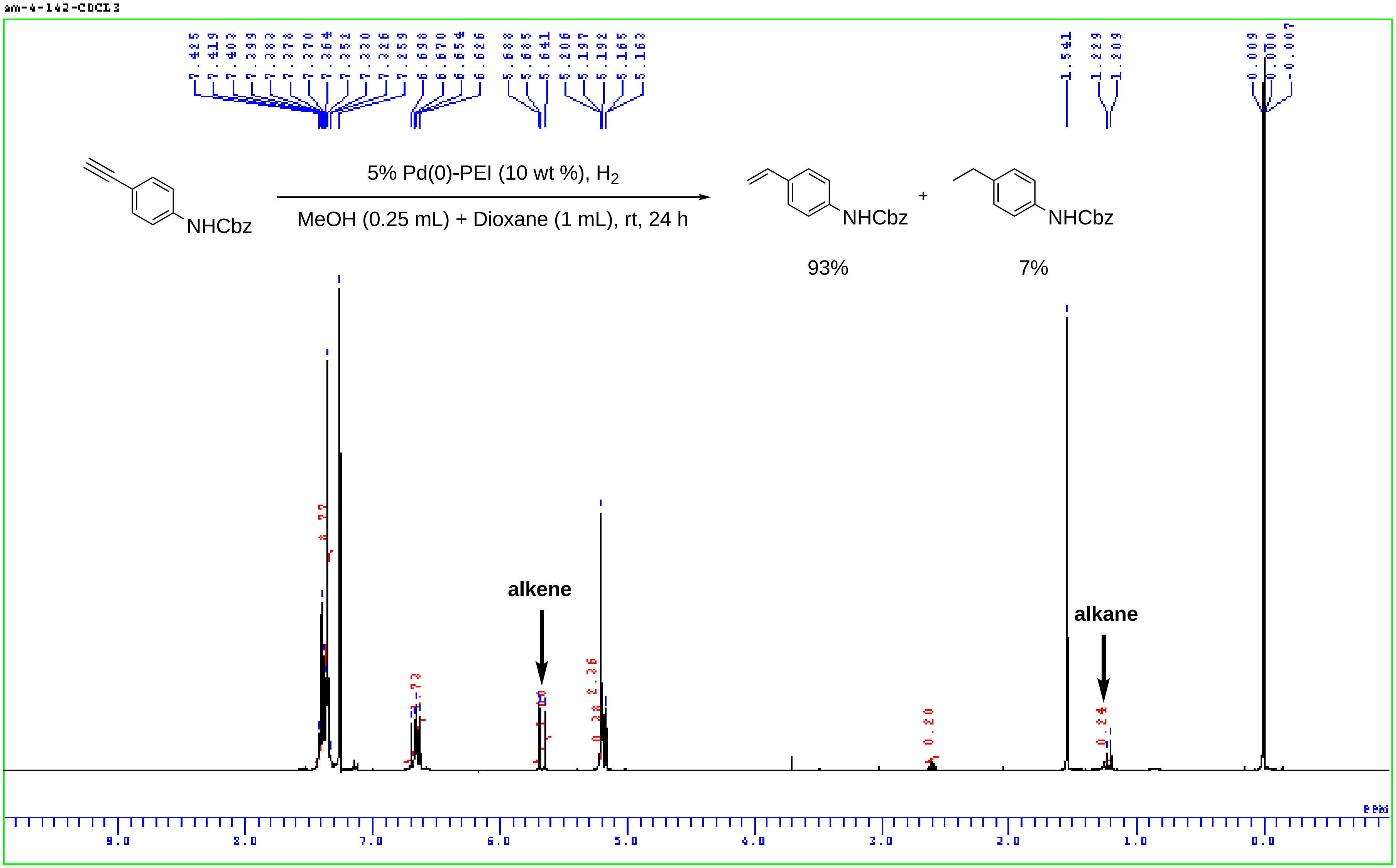
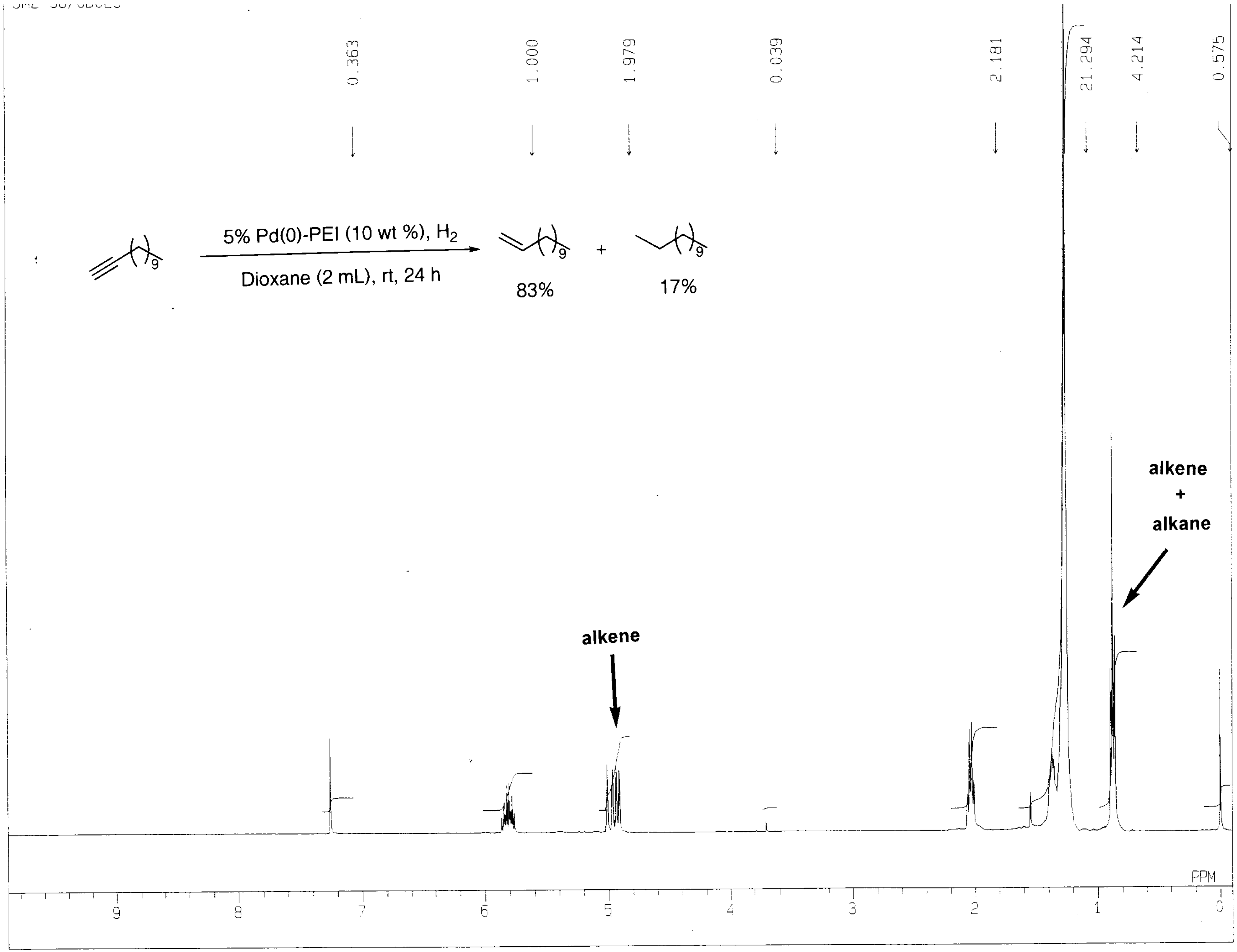
1.297
1.288
1.280
1.271
1.261
1.242
0.922
0.905
0.888
0.871
0.000
5% Pd(0)-PEI (10 wt %), H_2
MeOH (1 mL) + Dioxane (1 mL), rt, 24 h
100%
0.20
12.74
6.00
0.51
9
8
7
6
5
4
3
2
1
0
-1
PPM

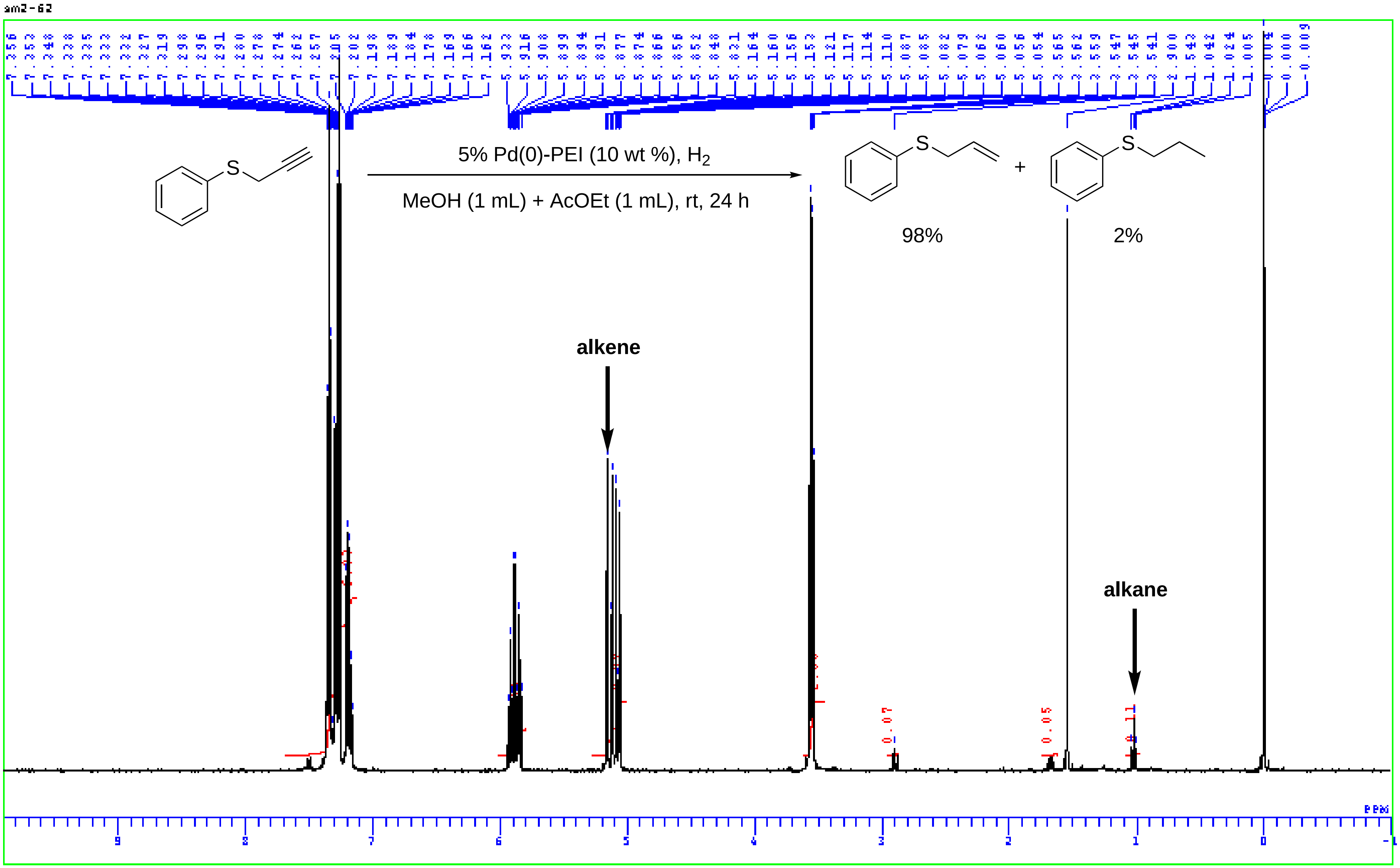

am-3-154-CDCL3
5% Pd(0)-PEI (10 wt %), H_2
MeOH (1 mL) + Dioxane (1 mL), rt, 24 h
OH
OH
100%
7.265 5.584 5.580 5.577 5.572 5.567 5.562 5.557 5.553 5.550 5.535 5.395 5.380 5.376 5.372 5.368 5.357 5.353 5.348 3.660 3.644 3.628 2.362 2.359 2.344 2.327 2.308 2.097 2.083 2.080 2.064 2.047 1.432 1.427 1.386 1.379 1.365 1.357 1.348 1.340 1.331 1.321 1.315 1.304 1.296 0.932 0.919 0.913 0.902 0.895 0.889 0.882 0.875 0.000
1.00
5.54
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

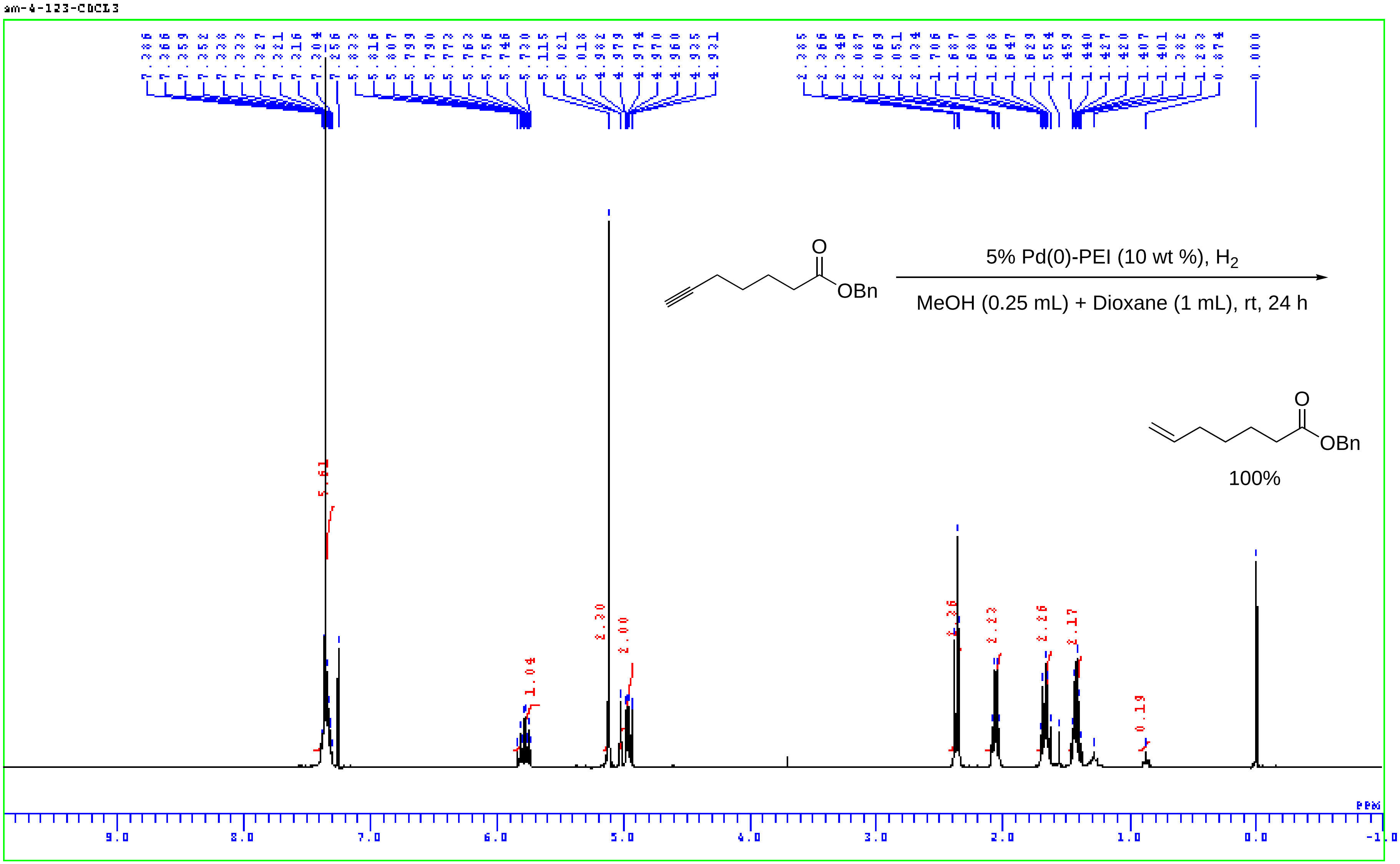

am-3-155-CDCL3
HO
OH
5% Pd(0)-PEI (10 wt %), H_2
MeOH (1 mL) + Dioxane (1 mL), rt, 24 h
HO
OH
100%
7.244
5.323
4.237
4.231
1.375
1.308
0.021
2.00
11.94
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

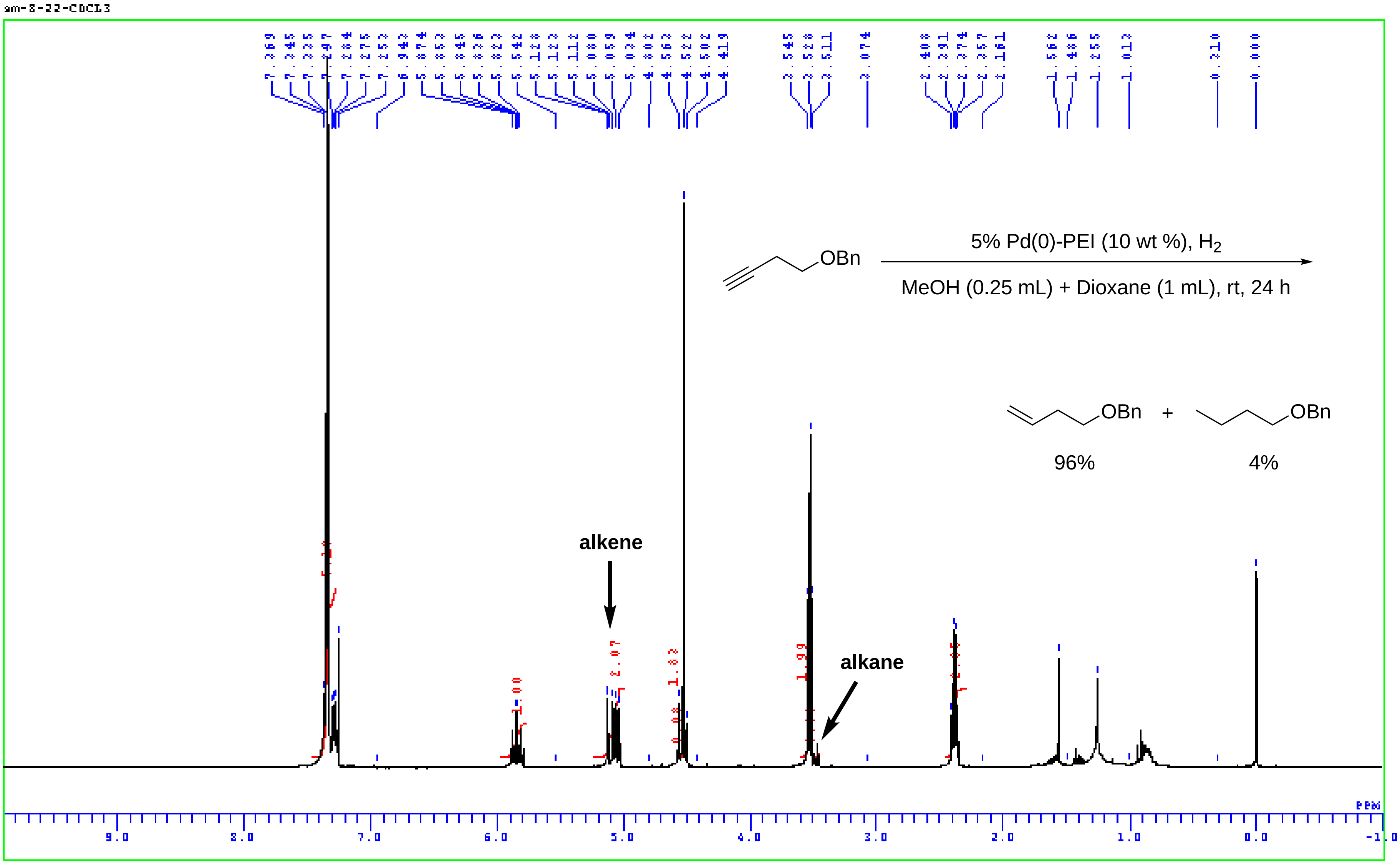

am2-59
7.302
7.281
7.254
7.242
7.236
7.214
7.208
6.645
6.640
6.634
6.629
6.623
6.603
6.600
6.595
6.575
5.562
5.520
5.517
5.050
5.048
5.020
2.950
2.503
1.185
0.000
NH2
5% Pd(0)-PEI (10 wt %), H2
Dioxane (2 mL), rt, 24 h
NH2
+
NH2
+
NH2
11%
85%
4%
alkene
alkyne
alkane
2.60
3.31
1.00
0.98
0.12
0.19
0.21
0.15
0.55
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0

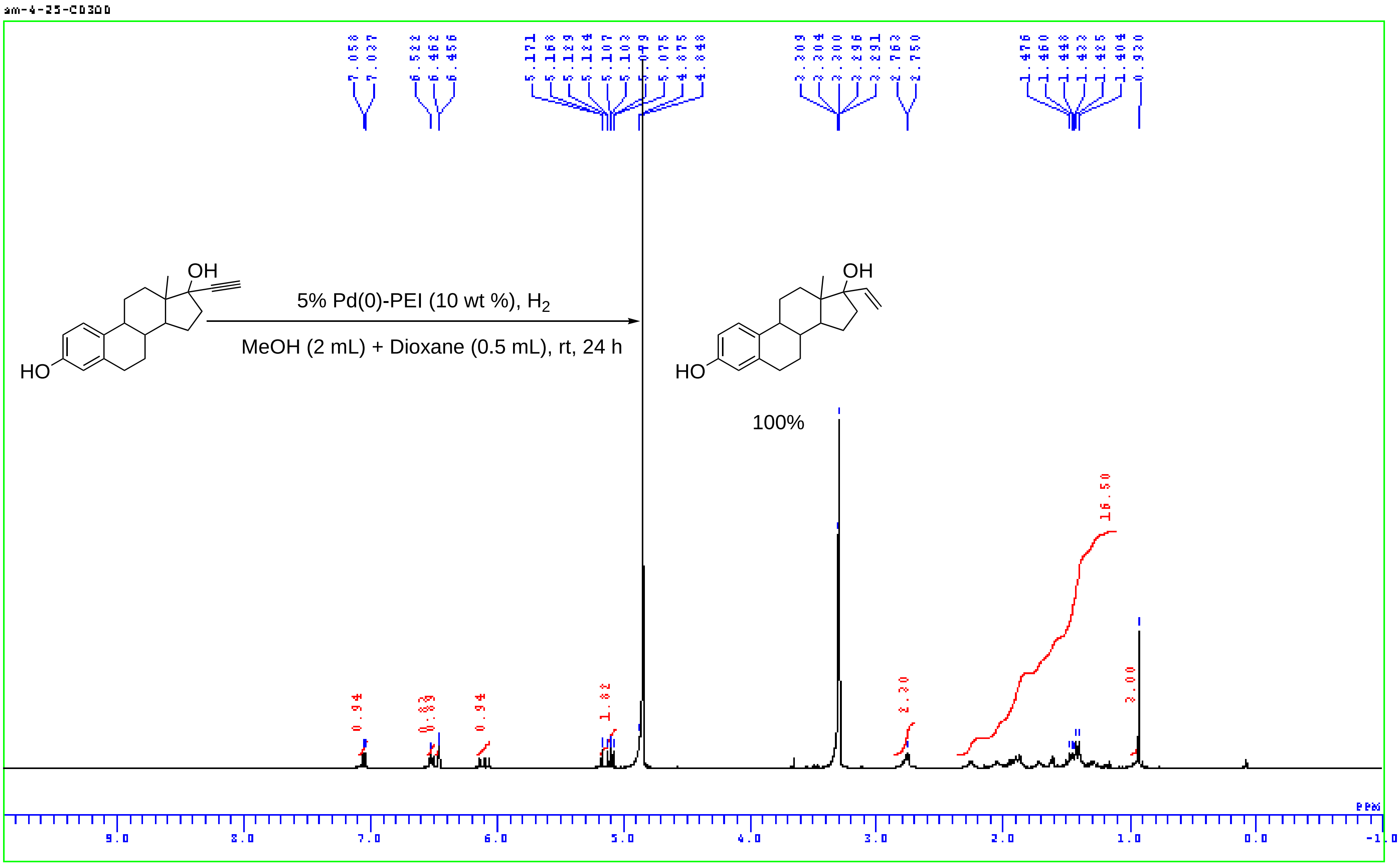

am-4-142-CDCL3
7.425
7.419
7.403
7.399
7.383
7.378
7.370
7.364
7.352
7.330
7.326
7.259
6.698
6.670
6.654
6.626
5.688
5.685
5.641
5.206
5.197
5.192
5.165
5.163
1.541
1.229
1.209
0.009
0.000
-0.007
NHCbz
5% Pd(0)-PEI (10 wt %), H_2
MeOH (0.25 mL) + Dioxane (1 mL), rt, 24 h
NHCbz
+
NHCbz
93%
7%
alkene
alkane
8.72
1.73
2.36
0.20
0.24
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

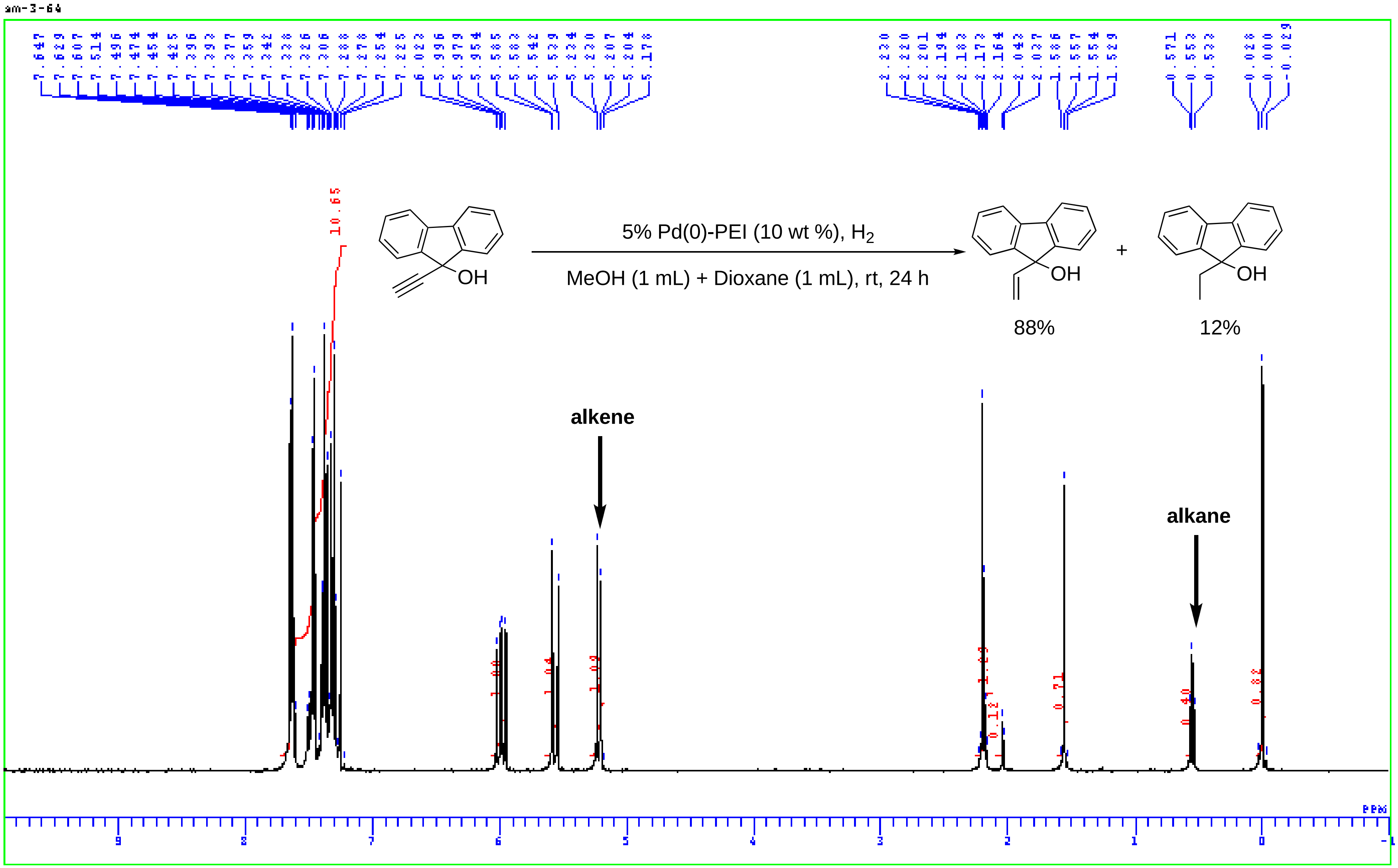

0.363
1.000
1.979
0.039
2.181
21.294
4.214
0.575
5% Pd(0)-PEI (10 wt %), H$_2$
Dioxane (2 mL), rt, 24 h
9
+
83%
17%
alkene
alkene
+
alkane
PPM
9
8
7
6
5
4
3
2
1
0

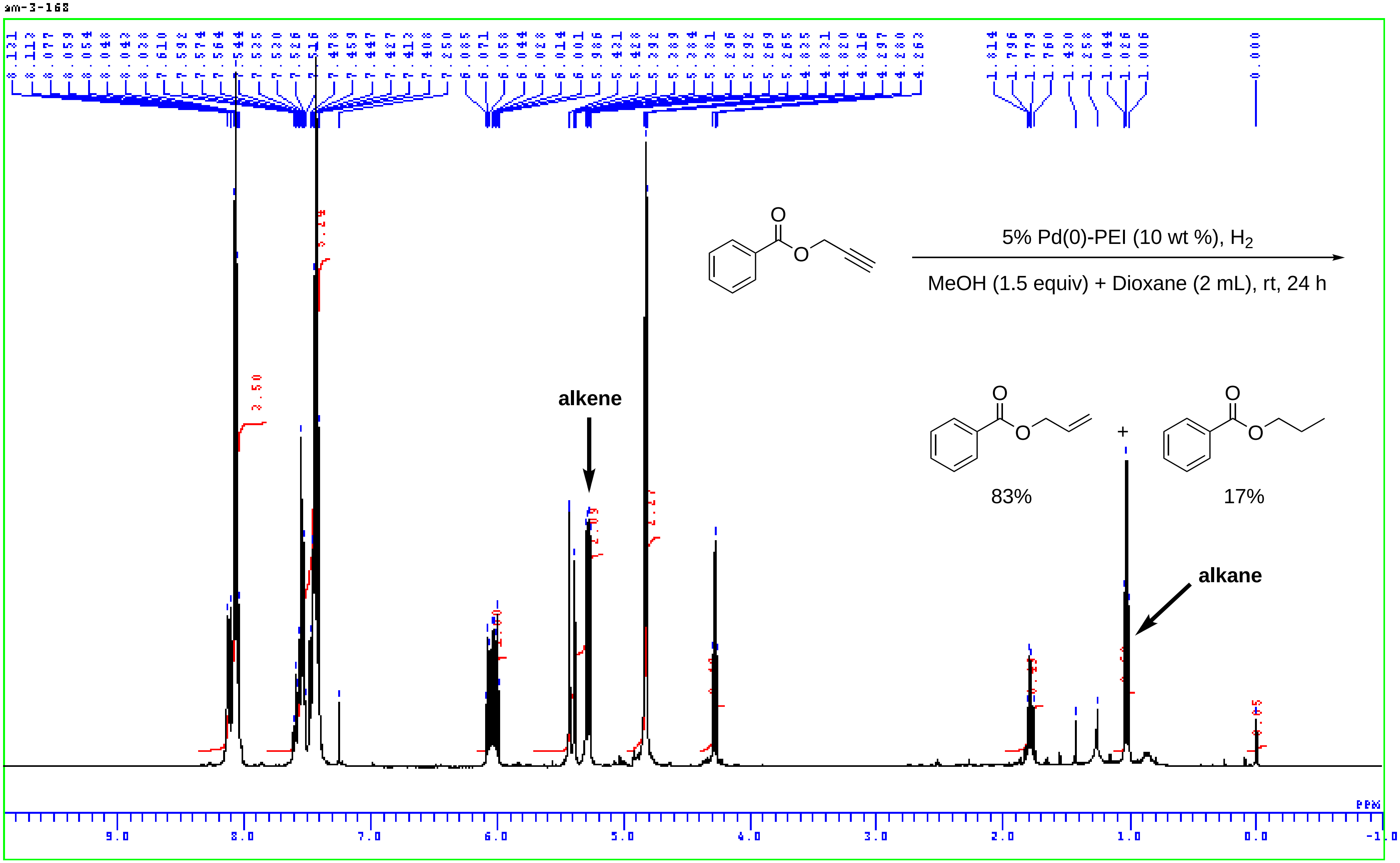

am2-62
7.356
7.353
7.348
7.338
7.335
7.333
7.332
7.327
7.319
7.298
7.296
7.291
7.280
7.278
7.274
7.262
7.257
7.205
7.202
7.198
7.189
7.184
7.178
7.169
7.166
7.162
5.933
5.916
5.908
5.899
5.894
5.891
5.877
5.874
5.866
5.856
5.852
5.848
5.831
5.164
5.160
5.156
5.153
5.121
5.117
5.114
5.110
5.087
5.085
5.082
5.079
5.062
5.060
5.056
5.054
3.565
3.562
3.559
3.547
3.545
3.541
2.900
1.543
1.042
1.024
1.005
0.004
0.000
-0.009
S
5% Pd(0)-PEI (10 wt %), H$_2$
MeOH (1 mL) + AcOEt (1 mL), rt, 24 h
S
+
S
98%
2%
alkene
alkane
0.07
0.05
0.11
ppm
9
8
7
6
5
4
3
2
1
0
-1

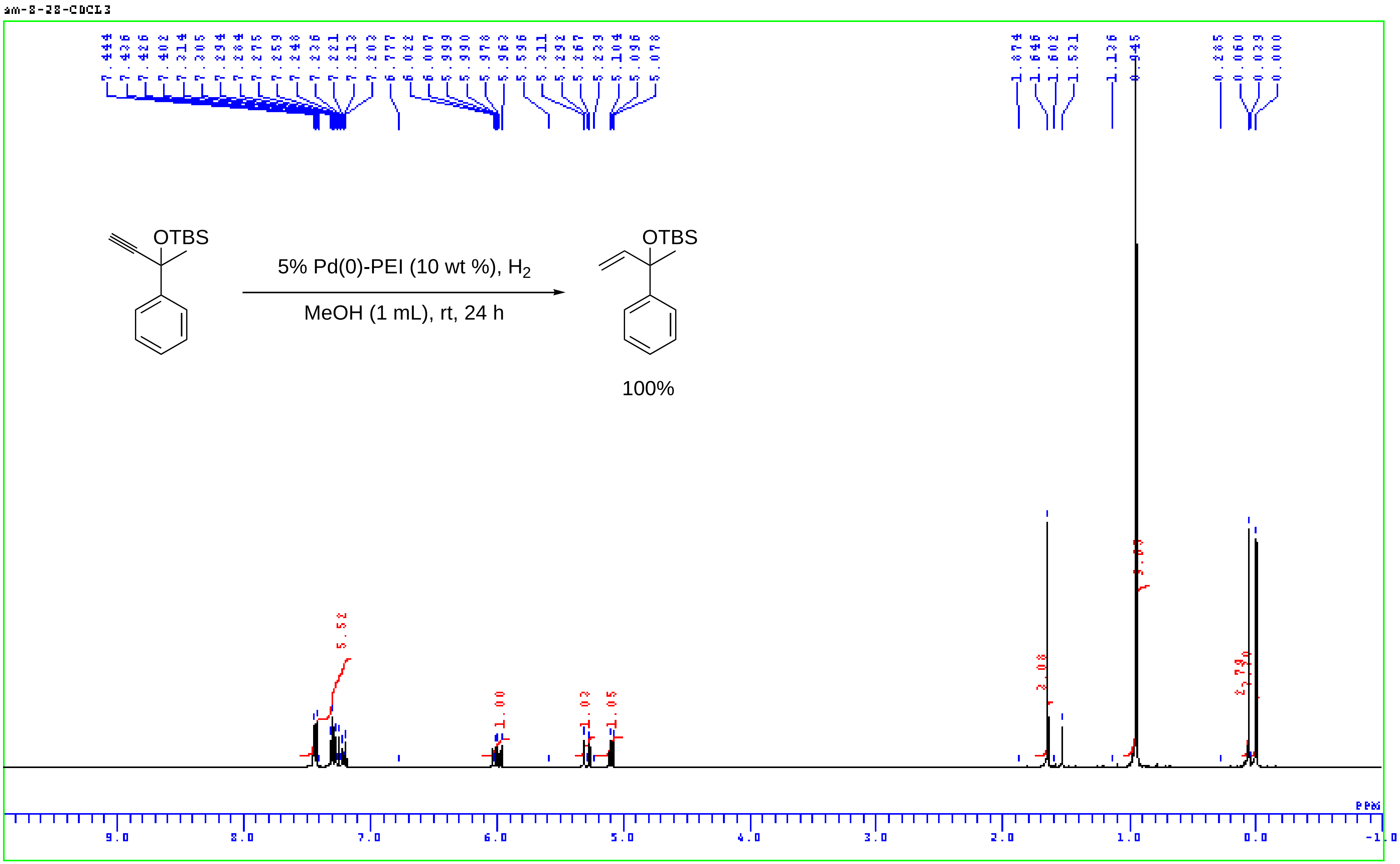

am-4-123-CDCL3
7.386
7.366
7.359
7.352
7.338
7.332
7.327
7.321
7.316
7.304
7.256
5.833
5.816
5.807
5.799
5.790
5.773
5.763
5.756
5.746
5.730
5.115
5.021
5.018
4.982
4.979
4.974
4.970
4.960
4.935
4.921
2.385
2.366
2.346
2.087
2.069
2.051
2.034
1.706
1.687
1.680
1.666
1.647
1.629
1.554
1.459
1.440
1.427
1.420
1.407
1.401
1.382
1.283
0.874
0.000
O
OBn
5% Pd(0)-PEI (10 wt %), H2
MeOH (0.25 mL) + Dioxane (1 mL), rt, 24 h
O
OBn
100%
5.61
1.04
2.30
2.00
2.26
2.23
2.26
2.17
0.19
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0

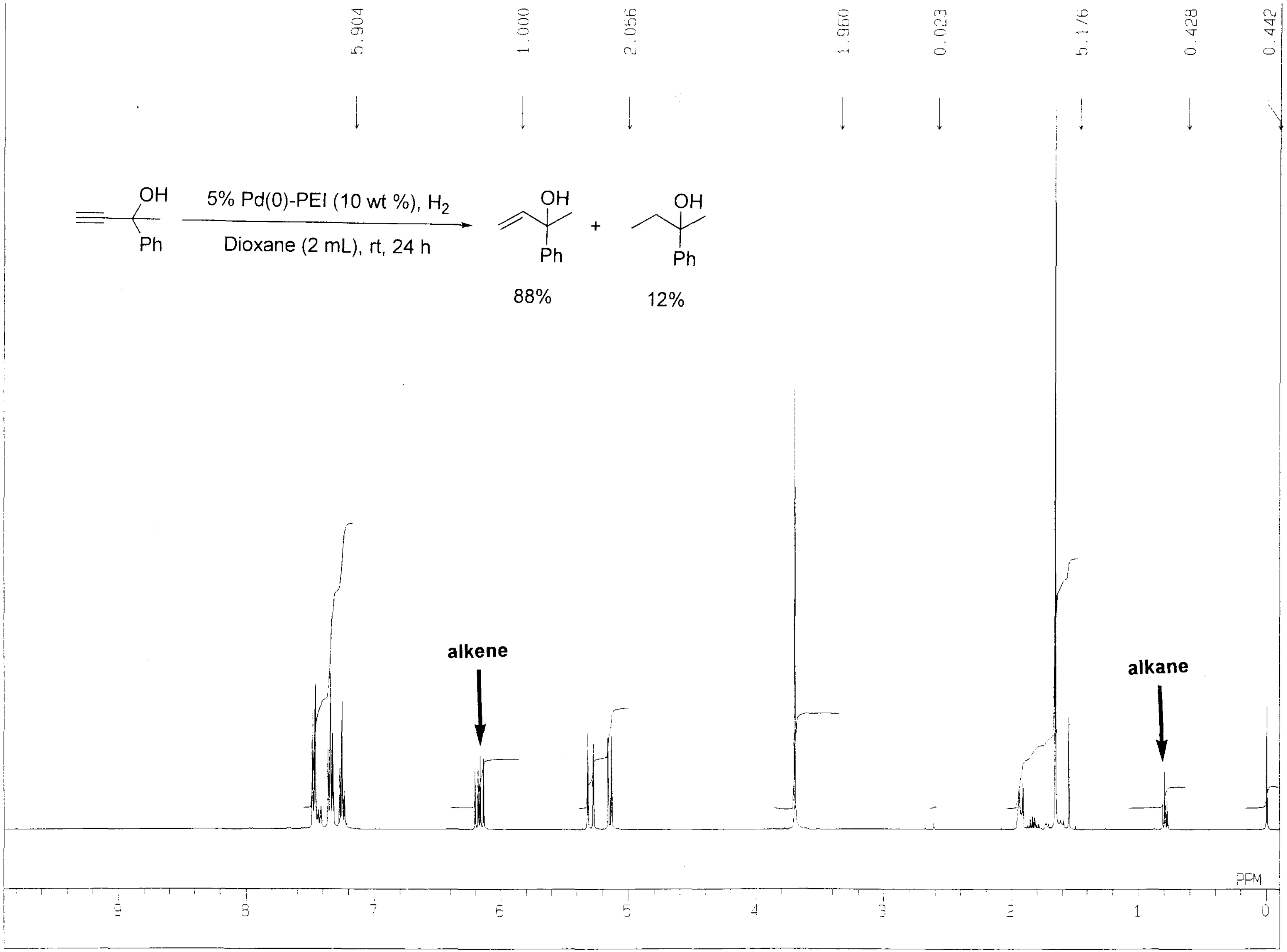

am-8-22-CDCL3
7.369
7.345
7.335
7.297
7.284
7.275
7.253
6.943
5.874
5.853
5.845
5.836
5.823
5.542
5.128
5.123
5.112
5.080
5.059
5.034
4.802
4.563
4.522
4.502
4.419
3.545
3.528
3.511
3.074
2.408
2.391
2.374
2.357
2.161
1.562
1.486
1.255
1.013
0.310
0.000
OBn
5% Pd(0)-PEI (10 wt %), H2
MeOH (0.25 mL) + Dioxane (1 mL), rt, 24 h
OBn
+
OBn
96%
4%
alkene
alkane
1.00
2.07
1.83
0.08
1.99
2.05
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0


am-4-25-CD3OD
7.058
7.037
6.522
6.462
6.456
5.171
5.168
5.129
5.124
5.107
5.103
5.079
5.075
4.875
4.848
3.309
3.304
3.300
3.296
3.291
2.763
2.750
1.476
1.460
1.448
1.433
1.425
1.404
0.930
OH
HO
5% Pd(0)-PEI (10 wt %), H_2
MeOH (2 mL) + Dioxane (0.5 mL), rt, 24 h
100%
0.94
0.83
0.89
0.94
1.82
2.30
16.50
3.00
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0


am-3-64
7.647
7.629
7.607
7.514
7.496
7.474
7.454
7.425
7.396
7.393
7.377
7.359
7.342
7.338
7.326
7.306
7.288
7.278
7.254
7.225
6.023
5.996
5.979
5.954
5.585
5.583
5.542
5.539
5.234
5.230
5.207
5.204
5.178
2.230
2.220
2.201
2.194
2.183
2.173
2.164
2.043
2.037
1.586
1.557
1.554
1.529
0.571
0.553
0.533
0.028
0.000
-0.029
10.65
OH
5% Pd(0)-PEI (10 wt %), H_2
MeOH (1 mL) + Dioxane (1 mL), rt, 24 h
OH
+
OH
88%
12%
alkene
alkane
1.00
1.04
1.03
1.03
0.12
0.71
0.40
0.82
ppm
9
8
7
6
5
4
3
2
1
0
-1


am-3-168
8.131
8.113
8.077
8.059
8.054
8.048
8.043
8.038
7.610
7.592
7.574
7.564
7.544
7.535
7.530
7.526
7.516
7.478
7.459
7.447
7.427
7.413
7.408
7.250
6.085
6.071
6.058
6.044
6.028
6.014
6.001
5.986
5.421
5.428
5.392
5.389
5.384
5.381
5.296
5.292
5.269
5.265
4.835
4.821
4.820
4.816
4.297
4.280
4.263
1.814
1.796
1.779
1.760
1.430
1.258
1.044
1.026
1.006
0.000
3.50
5.24
alkene
alkane
O
O
5% Pd(0)-PEI (10 wt %), H$_2$
MeOH (1.5 equiv) + Dioxane (2 mL), rt, 24 h
+
83%
17%
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0

am-8-28-CDCL3
7.444
7.436
7.426
7.402
7.314
7.305
7.294
7.284
7.275
7.259
7.248
7.236
7.221
7.213
7.203
6.777
6.022
6.007
5.999
5.990
5.978
5.963
5.596
5.311
5.292
5.267
5.239
5.104
5.096
5.078
1.874
1.646
1.602
1.531
1.136
0.945
0.285
0.060
0.039
0.000
OTBS
5% Pd(0)-PEI (10 wt %), H2
MeOH (1 mL), rt, 24 h
OTBS
100%
5.52
1.00
1.03
1.05
3.08
9.07
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0


5.904
1.000
2.056
1.960
0.023
5.176
0.428
0.442
OH
Ph
5% Pd(0)-PEI (10 wt %), H2
Dioxane (2 mL), rt, 24 h
OH
Ph
+
OH
Ph
88%
12%
alkene
alkane
PPM
9
8
7
6
5
4
3
2
1
0