Advanced Synthesis & Catalysis

Supporting Information

Supporting information

Novel Pd/C-Diphenylsulfide Complex for Chemoselective Hydrogenation: Preparation, Characterization, and Application

Akinori Mori,[1] Tomoteru Mizusaki,[1] Masami Kawase,[1] Tomohiro Maegawa,[1]
*Yasunari Monguchi,[1] Shinobu Takao,[2] Yukio Takagi[2] and Hironao Sajiki[1],**

[1] Laboratory of Medicinal Chemistry, Gifu Pharmaceutical University
5-6-1 Mitahora-higashi, Gifu 502-8585, Japan
[2] N. E. Chemcat Corporation
678 Ipponmatsu, Numazu, Shizuoka 410-0314, Japan

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General experimental.

10% Pd/C was purchased from N. E. Chemcat (Lot. 21A-050759). All reagents were purchased from commercial sources and used without further purification. Flash column chromatography was performed with silica gel Merck 60 (230-400 mesh ASTM), or Kanto Chemical Co., Inc. 60N (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.

Synthesis of benzyl ester

To a solution of a carboxylic acid (10.0 mmol), EDC•HCl (2.30 g, 12.0 mmol), and DMAP (122 mg, 1.00 mmol) in CH_2Cl_2 (15 mL) was added benzyl alcohol (1.04 g, 10.0 mmol). After a certain reaction time, chloroform (50 mL) and water (50 mL) were added and layers were separated. The aqueous layer was extracted with chloroform (50 mL) and the combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the corresponding benzyl ester.

Benzyl 4-vinylbenzoate[1] (Substrate for Table 1, Entry 12)

Obtained by a 20 h reaction of 4-vinylbenzoic acid (740 mg, 5.00 mmol), EDC•HCl (1.15 g, 6.00 mmol), DMAP (61.1 mg, 500 μmol), and benzyl alcohol (540 mg, 5.00 mmol) in 71 % yield (845 mg) as a colorless oil after flash column chromatography on silica gel (*n*-hexane/Et_2O = 2/1), according to the general procedure for the synthesis of benzyl ester. The ^{1}H NMR spectrum of the product was identical with that in the literature.[1]

Benzyl 4-nitrobenzoate[2] (Substrate for Table 1, Entry 19)

Obtained by a 20 h reaction of 4-nitrobenzoic acid (835 mg, 5.00 mmol), EDC•HCl (1.15 g, 6.00 mmol), DMAP (61.1 mg, 500 μmol), and benzyl alcohol (540 mg, 5.00 mmol) in 67 % yield (859 mg) as a colorless oil after a flash column chromatography on silica gel (*n*-hexane/AcOEt = 10/1), according to the general procedure for the synthesis of benzyl ester. The ^{1}H NMR spectrum of the product was identical with that in the literature.[2]

Synthesis of *N*-Cbz protected amine

To a solution of an amine (5.00 mmol) in THF was added *N*-(benzyloxycarbonyloxy)succinimide (1.45 g, 6.00 mmol). After a certain reaction time, AcOEt (150 mL) and water (100 mL) were added and the layers were separated. The organic layer was washed successively with water (100 mL) and brine (100 mL), dried over $MgSO_4$, and concentrated under reduced pressure. If necessary, the residue was purified by flash column chromatography on silica gel to afford the corresponding *N*-Cbz protected amine.

Benzyl *N*,*N*-diallylcarbamate[1] (Substrate for Table 1, Entry 13)

Obtained by a 24 h reaction of diallylamine (485 mg, 5.00 mmol) and *N*-(benzyloxycarbonyloxy)succinimide (1.50 g, 6.00 mmol) in 95% yield (1.10 g) as colorless oil after a flash column chromatography on silica gel (*n*-hexane/Et_2O = 10/1), according to the general procedure for the synthesis of *N*-Cbz protected amine. The ^{1}H NMR spectrum of the product was identical with that in the literature.[1]

Benzyl 4-ethynylphenylcarbamate[1] (Substrate for Table 1, Entry 14)

Obtained by a 48 h reaction of 4-ethynylaniline (585 mg, 5.00 mmol) and *N*-(benzyloxycarbonyloxy)succinimide (1.50 g, 6.00 mmol) in 85% yield (1.05 g) as a colorless solid after a flash column chromatography on silica gel (*n*-hexane/AcOEt = 6/1), according to the general procedure for the synthesis of the *N*-Cbz protected amine. The ^{1}H NMR spectrum of the product was identical with that in the literature.[1]

Benzyl *N*-allyl-*N*-phenylcarbamate[1] (Substrate for Table 1, Entry 15)

Obtained by a 24 h reaction of ethyl *N*-allylaniline (665 mg, 5.00 mmol) and *N*-(benzyloxycarbonyloxy)succinimide (1.50 g, 6.00 mmol) in 85% yield (1.13 g) as colorless solid after a flash column chromatography on silica gel (*n*-hexane), according to the general procedure for the synthesis of *N*-Cbz protected amine. The ^{1}H NMR spectrum of the product was identical with that in the literature.[1]

Ethyl 4-*N*-(benzyloxycarbonylamino)cinnamate[1] (Substrate for Table 1, Entry 16)

Obtained by a 24 h reaction of ethyl 4-aminocinnamate (911 mg, 5.00 mmol) and *N*-(benzyloxycarbonyloxy)succinimide (1.50 g, 6.00 mmol) in 86% yield (1.34 g) as colorless solid after a flash column chromatography on silica gel (*n*-hexane/Et_2O = 10/1), according to the general procedure for the synthesis of *N*-Cbz protected amine. The ^1H NMR spectrum of the product was identical with that in the literature.[1]

Synthesis of aryl azides

To a solution of aniline analog (5.00 mmol) and conc. aqueous hydrochloric acid (11.3 mL) in water (20 mL) was added dropwise a solution of sodium nitrite (362 mg, 5.20 mmol) in water (12.5 mL) at 0–5 °C and the mixture was stirred at the same temperature for 1 h. The mixture was filtered and the filtrate was added to a solution of sodium azide (325 g, 12.5 mmol) in water (12.5 mL). After 6 h, the precipitate was corrected on a Kiriyama funnel and dried under reduced pressure to afford the corresponding aryl azide.

5-Azido-1,2,3-trimethoxybenzene[3] (Substrate for Table 1, Entry 22)

Obtain from 3,4,5-trimethoxyaniline (916 mg, 5.00 mmol), sodium nitrite (362 mg, 5.20 mmol) and sodium azide (325 mg, 12.5 mmol) in 95% yield (1.10 g) as a pale yellow solid according to the general procedure for the synthesis of aryl azides. The ^1H NMR spectrum of the product was identical with that in the literature.[3]

4-Azidobenzophenone (Substrate for Table 1, Entry 23)

Obtain from 4-amino benzophenone (985 mg, 5.00 mmol), sodium nitrite (362 mg, 5.20 mmol) and sodium azide (325 mg, 12.5 mmol) in 80% yield (892 mg) as a pale yellow solid according to the general procedure for the synthesis of arylazides. ^1H NMR ($CDCl_3$) δ 7.84 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 7.2 Hz, 2H), 7.59 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.2 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 195.0, 144.2, 137.4, 133.9, 132.2, 131.9, 129.7, 128.2, 118.6; MS (EI) m/z 223 (M^+, 25%), 195 (100), 167 (50), 140 (10), 105 (100), 91 (10), 77 (60), 63 (10), 51(15); HRMS (EI) Calcd for $C_{13}H_9N_3O$ (M^+) 223.07457. Found 223.07508.; Anal. Calcd for $C_{13}H_9N_3O$: C, 69.95; H, 4.06; N, 18.82. Found: C, 70.04; H, 4.24; N, 18.76.

4-Azidocinnamic acid (Substrate for Table 1, Entry 24)

Obtain from 4-amino cinnamic acid (985 mg, 5.00 mmol), sodium nitrite (362 mg, 5.20 mmol) and sodium azide (325 mg, 12.5 mmol) in 80% yield (892 mg) as a pale yellow solid according to the general procedure for the synthesis of aryl azides. ^{1}H NMR ($CDCl_3$) δ 7.73 (d, J = 15.9 Hz, 2H), 7.55 (d, J = 8.7 Hz, 2H), 7.06 (d, J = 8.7 Hz, 2H), 6.40 (d, J = 15.9 Hz, 2H). ^{13}C NMR (CD_3OD) δ 170.3, 145.1, 143.4, 132.8, 130.9, 120.6, 119.0; MS (EI) m/z 189 (M^+, 50%), 161 (100), 143 (70), 115 (45), 104 (10), 89 (30), 63 (20), 51 (10); HRMS (EI) Calcd for $C_9H_7N_3O_2$ (M^+) 189.0538. Found 189.0545.; Anal. Calcd for $C_9H_7N_3O_2$: C, 56.54; H, 4.74; N, 21.98. Found: C, 57.06; H, 4.04; N, 22.13.

Typical Procedure for the Chemoselective Hydrogenation of Olefin, Acetylene, Aromatic Nitro, and Aromatic Azide Moieties using Pd/C[Ph_2S]

After two vacuum/H_2 cycles to replace the air inside the reaction vessel with hydrogen, the mixture of the substrate (5.00 mmol), Pd/C[Ph_2S] (10 wt % of the substrate) in MeOH (1 mL) was vigorously stirred at room temperature (*ca.* 20 °C) under ordinary hydrogen pressure (balloon) for 24 h. The reaction mixture was filtered using a membrane filter (Millipore, Millex®-LH, 0.45 μm) and the filtrate was concentrated *in vacuo* to provide the product.

1,3-Diphenyl-1-propanone[1] (Product in Table 1, Entry 1)

Obtained from chalcone (104 mg, 0.500 mmol) and Pd/C[Ph_2S] (10.5 mg, 10 wt % of substrate) in 98% yield (103 mg) as a colorless solid according to the typical procedure. The ^{1}H NMR spectrum of the product was identical with that in the literature.[1]

4-Hydroxy-3-propylacetophenone[1] (Product in Table 1, Entry 2)

Obtained from 3-allyl-4-hydroxyacetophenone (88.1 mg, 0.500 mmol) and Pd/C[Ph_2S] (8.8 mg, 10 wt % of substrate) in 88% yield (78.3 mg) as a colorless solid according to the typical procedure. The ^{1}H NMR spectrum of the product was identical with that in the literature.[1]

1-(2-Hydroxyphenyl)-3-phenylpropan-1-one[4] (Product in Table 1, Entry 3)

Obtained from 2'-hydroxychalcone (112 mg, 0.500 mmol) and Pd/C[Ph_2S] (11.2 mg, 10 wt % of substrate) in 97% yield (109 mg) as a pale yellow solid according to the typical procedure. The ^{1}H NMR spectrum of the product was identical with that in the literature.[4]

4-Chloroethylbenzene[1] (Product in Table 1, Entry 6)

Obtained from 4-chlorostyrene (69.3 mg, 0.500 mmol), Pd/C[Ph_2S] (6.9 mg, 10 wt % of substrate) and CD_3OD (1 mL) in 100% conversion yield (^{1}H NMR yield) according to the typical procedure. The ^{1}H NMR spectrum of the product was identical with that in the literature.[1]

3-(4-Chlorophenyl)propanamide[1] (Product in Table 1, Entry 7)

Obtained from 4-chlorocinnamamide (90.8 mg, 0.500 mmol) and Pd/C[Ph_2S] (9.1 mg, 10 wt % of **7a**) in 100% yield (91.5 mg) as a colorless solid according to the typical procedure. The ^{1}H NMR spectrum of the product was identical with that in the literature.[1]

4’-Chloro-3-phenylpropiophenone[1] (Product in Table 1, Entry 8)

Obtained from 4'-chlorochalcone (122 mg, 0.500 mmol) and Pd/C[Ph_2S] (12.2 mg, 10 wt % of substrate) in 99% yield (120 mg) as a colorless oil according to the typical procedure. The ^{1}H NMR spectrum of the product was identical with that in the literature.[1]

Benzyl isobutyrate[1] (Product in Table 1, Entry 9)

Obtained from benzyl methacrylate (88.1 mg, 0.500 mmol), Pd/C[Ph_2S] (8.8 mg, 10 wt % of substrate) and CD_3OD (1 mL) in 100% conversion yield (^{1}H NMR yield) according to the typical procedure. The ^{1}H NMR spectrum of the product was identical with that in the literature.[1]

Benzyl propionate[1] (Product in Table 1, Entry 10)

Obtained from benzyl acrylate (81.1 mg, 0.500 mmol), Pd/C[Ph_2S] (8.1 mg, 10 wt % of substrate) and CD_3OD (1 mL) in 100% conversion yield (^{1}H NMR yield) according to the typical procedure. The ^{1}H NMR spectrum of the product was identical with that in the literature.[1]

Benzyl 3-phenylpropionate[1] (Product in Table 1, Entry 11)

Obtained from benzyl cinnamate (119 mg, 0.500 mmol) and Pd/C[Ph_2S] (11.9 mg, 10 wt % of substrate) in 99% yield (119 mg) as a colorless oil according to the typical procedure. The ^{1}H NMR spectrum of the product was identical with that in the literature.[1]

Benzyl 4-ethylbenzoate[1] (Product in Table 1, Entry 12)

Obtained from benzyl 4-vinylbenzoate (119 mg, 0.500 mmol) and Pd/C[Ph_2S] (11.9 mg, 10 wt % of substrate) in 99% yield (119 mg) as a pale yellow oil according to the typical procedure. The ^{1}H NMR spectrum of the product was identical with that in the literature.[1]

Benzyl *N,N*-dipropylcarbamate[1] (Product in Table 1, Entry 13)

Obtained from benzyl *N*,*N*-diallylcarbamate (116 mg, 0.500 mmol) and Pd/C[Ph_2S] (11.6 mg, 10 wt % of substrate) in 98% yield (115 mg) as a colorless oil according to the typical procedure. The ^{1}H NMR spectrum of the product was identical with that in the literature.[1]

Benzyl *N*-(4-ethylphenyl)carbamate[1] (Product in Table 1, Entry 14)

Obtained from benzyl 4-ethynylphenylcarbamate (253 mg, 0.500 mmol) and Pd/C[Ph_2S] (25.3 mg, 10 wt % of substrate) in 94% yield (240 mg) as a colorless solid according to the typical procedure. The ^{1}H NMR spectrum of the product was identical with that in the literature.[1]

Benzyl *N*-phenyl-*N*-propylcarbamate[1] (Product in Table 1, Entry 15)

Obtained from benzyl *N*-allyl-*N*-phenylcarbamate (134 mg, 0.500 mmol) and Pd/C[Ph_2S] (13.4 mg, 10 wt % of the substrate) in 80% yield (108 mg) as a colorless oil according to the typical procedure. The ^{1}H NMR spectrum of the product was identical with that in the literature.[1]

Ethyl 4-(benzyloxycarbonylamino)phenylpropanoate[1] (Product in Table 1, Entry 16)

Obtained from ethyl 4-*N*-(benzyloxycarbonylamino)cinnamate (163 mg, 0.500 mmol) and Pd/C[Ph_2S] (16.3 mg, 10 wt % of substrate) in 91% yield (150 mg) as a pale yellow oil according to the typical procedure. ^{1}H NMR ($CDCl_3$) δ 7.41−7.04 (m, 9H), 5.15 (s, 2H), 4.09 (q, *J* = 7.0 Hz, 2H), 2.87 (t, *J* = 7.9 Hz, 2H), 2.56 (t, *J* = 7.9 Hz, 2H), 1.20 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 172.9, 136.1, 136.0, 135.7, 128.8, 128.5, 128.3, 128.2, 118.9, 66.9, 60.4, 50.7, 35.9, 30.2, 21.0, 14.1; MS (EI) m/z 327 (M^+, 30%), 283 (10), 240 (10), 219 (30), 196 (35), 174 (10), 145 (60), 132 (50), 108 (20), 91 (100), 77 (20), 65 (10), 44 (10); HRMS (EI) Calcd for $C_{19}H_{21}NO_4$ (M^+) 327.1471. Found 327.1476.

4'-Aminoacetophenone (Product in Table 1, Entry 17)

Obtained from 4'-nitroacetophenone (83 mg, 0.500 mmol) and Pd/C[Ph_2S] (8.3 mg, 10 wt % of substrate) in 99% yield (67 mg) as a pale yellow oil according to the typical procedure. The ^{1}H NMR spectrum of the product was identical with that of the commercial authentic sample from Tokyo Chemical Industry Co., Ltd.

4-Aminochlorobenzene[2] (Product in Table 1, Entry 18)

Obtained from 1-chloro-4-nitrobenzene (79 mg, 0.500 mmol) and Pd/C[Ph_2S] (7.9 mg, 10 wt % of substrate) in 91% yield (58 mg) as a colorless solid according to the typical procedure. The ^{1}H NMR spectrum of the product was identical with that in the literature.[2]

Benzyl 4-aminobenzoate (Product in Table 1, Entry 19)

Obtained from benzyl 4-nitrobenzoate (129 mg, 0.500 mmol) and Pd/C[Ph_2S] (12.9 mg, 10 wt % of substrate) in 97% yield (110 mg) as a pale yellow solid according to the typical procedure. ^{1}H NMR ($CDCl_3$) δ 7.88 (d, *J* = 8.7 Hz, 2H), 7.42−7.32 (m, 5 H), 6.62 (d, *J* = 8.7 Hz, 1H), 5.31 (s, 2H), 4.05 (br, 2H). ^{13}C NMR ($CDCl_3$) δ 166.5, 151.0, 136.5 131.7, 128.4, 128.0, 119.5, 113.7, 111.0, 66.0; MS (EI) m/z 227 (M^+, 55%), 182 (10), 134 (10), 120 (100), 91 (50), 65 (20), 44 (10); HRMS (EI) Calcd for $C_{14}H_{13}NO_2$ (M^+) 227.09463. Found

227.09413.; Anal Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.82; H, 5.90; N, 5.98.

3-(4-aminophenyl)-1-phenylpropan-1-one (Product in Table 1, Entry 20)

Obtained from 4'-nitrochalcone (113 mg, 0.500 mmol) and Pd/C[Ph_2S] (11.3 mg, 10 wt % of substrate) in 91% yield (102 mg) as a pale yellow oil according to the typical procedure. ^{1}H NMR ($CDCl_3$) δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.64 (d, *J* = 8.2 Hz, 2H), 3.58 (br, 2H), 3.24 (t, *J* = 7.7 Hz, 2H), 2.96 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 199.6, 144.5, 137.0, 132.9, 131.2, 129.2, 128.5, 128.0, 115.3, 40.9, 29.4; MS (EI) m/z 225 (M^+, 50%), 120 (10), 106 (100), 77 (25), 44 (15); HRMS (EI) Calcd for $C_{15}H_{15}NO$ (M^+) 225.1154. Found 225.1161.; Anal Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.96; H, 6.76; N, 6.20.

4-Aminobenzoic acid (Product in Table 1, Entry 21)

Obtained from 4-azidobenzoic acid (82 mg, 0.500 mmol) and Pd/C[Ph_2S] (8.2 mg, 10 wt % of substrate) in 91% yield (62 mg) as a colorless solid according to the typical procedure. The ^{1}H NMR spectrum of the product was identical with that of the commercial authentic sample from Tokyo Chemical Industry Co., Ltd.

3,4,5-Trimethoxyaniline (Product in Table 1, Entry 22)

Obtained from 5-azido-1,2,3-trimethoxybenzene (104 mg, 0.500 mmol) and Pd/C[Ph_2S] (10.4 mg, 10 wt % of substrate) in 91% yield (83 mg) as a pale yellow solid according to the typical procedure. The ^{1}H NMR spectrum of the product was identical with that of the commercial authentic sample from Tokyo Chemical Industry Co., Ltd.

4-Aminobenzophenone (Product in Table 1, Entry 23)

Obtained from 4-azidobenzophenone (111 mg, 0.500 mmol) and Pd/C[Ph_2S] (11.1 mg, 10 wt % of substrate) in 99% yield (97 mg) as a pale yellow solid according to the typical procedure. The ^{1}H NMR spectrum of the product was identical with that of the commercial authentic sample from Tokyo Chemical Industry Co., Ltd.

3-(4-Aminophenyl)propanoic acid (Product in Table 1, Entry 24)

Obtained from 4-azidocinnamic acid (95 mg, 0.500 mmol) and Pd/C[Ph_2S] (9.5 mg, 10 wt % of **24a**) in 95% yield (78 mg) as a pale yellow oil according to the typical procedure. The ^1H NMR spectrum of the product was identical with that in the literature.[5]

Reuse test of Pd/C[Ph_2S]

A suspension of benzyl cinnamate (953 mg, 4.00 mmol) and Pd/C[Ph_2S] (95.3 mg) in MeOH (8 mL) was stirred under H_2 atmosphere (balloon). After 24 h, the mixture was passed through a filter paper [Kiriyama, No. 5C (1 μm), diameter = 8 mm] and the filter was washed with Et_2O (10 mL × 3). The combined filtrates were concentrated in vacuo to give benzyl 3-phenylpropionate (945 mg, 99%). The collected Pd/C[Ph_2S] on the filter paper was dried in a desiccator under vacuum for 24 h, weighed (94.3 mg, 99% recovery), and used for the 2nd run.

The reuse test was carried out using benzyl cinnamate (953 mg, 4.00 mmol) and recovered Pd/C[Ph_2S] in the same manner as described for the 1st run.

The reuse tests were repeated until the 5th run.

		1st	2nd	3rd	4th	5th
Recovered	(mg)	94.3	92.4	89.6	90.0	90.4
Pd/C[Ph_2S]	(%)	99	98	97	100	100

Assay of Residual Palladium and Sulfur in the Reaction Mixture

A suspension of benzyl cinnamate (2.38 g, 10 mmol) and Pd/C[Ph_2S] (238 mg) in MeOH (10 mL) was stirred under H_2 atmosphere (balloon). After 24 h, the mixture was passed through a filter paper [Kiriyama, No. 5C (1 μm), diameter = 60 mm] and the filter was washed with MeOH (10 mL × 3). The collected Pd/C[Ph_2S] on the filter paper was dried in a desiccator under vacuum for 24 h and weighed (226 mg, 95%). The 2nd run was carried out using benzyl cinnamate (953 mg, 4.00 mmol) and recovered Pd/C[Ph_2S] (226 mg) in the same manner as described for the 1st run. After filtration of the catalyst, the filtrate was diluted with MeOH to

50 mL of total volume and the residual palladium and sulfur were assayed using an ICP Atomic Emission Spectrometer (Shimadzu ICP-8001, Shimadzu, Japan).

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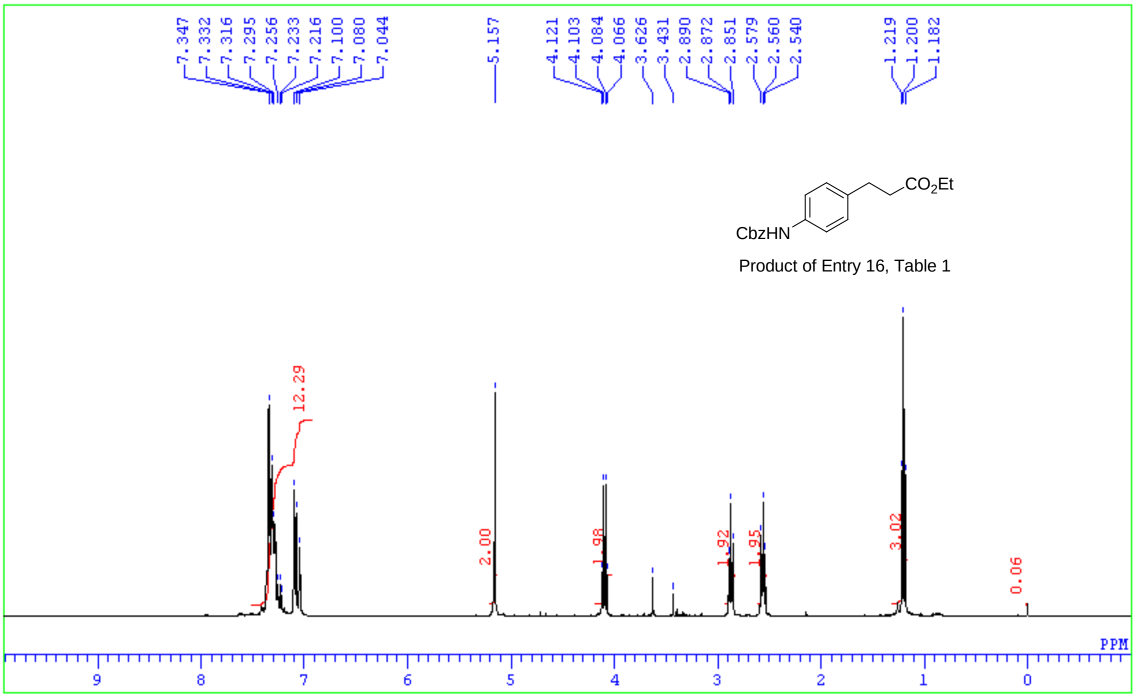
^{1}H NMR and ^{13}C NMR spectra of new compounds



Product of Entry 16, Table 1

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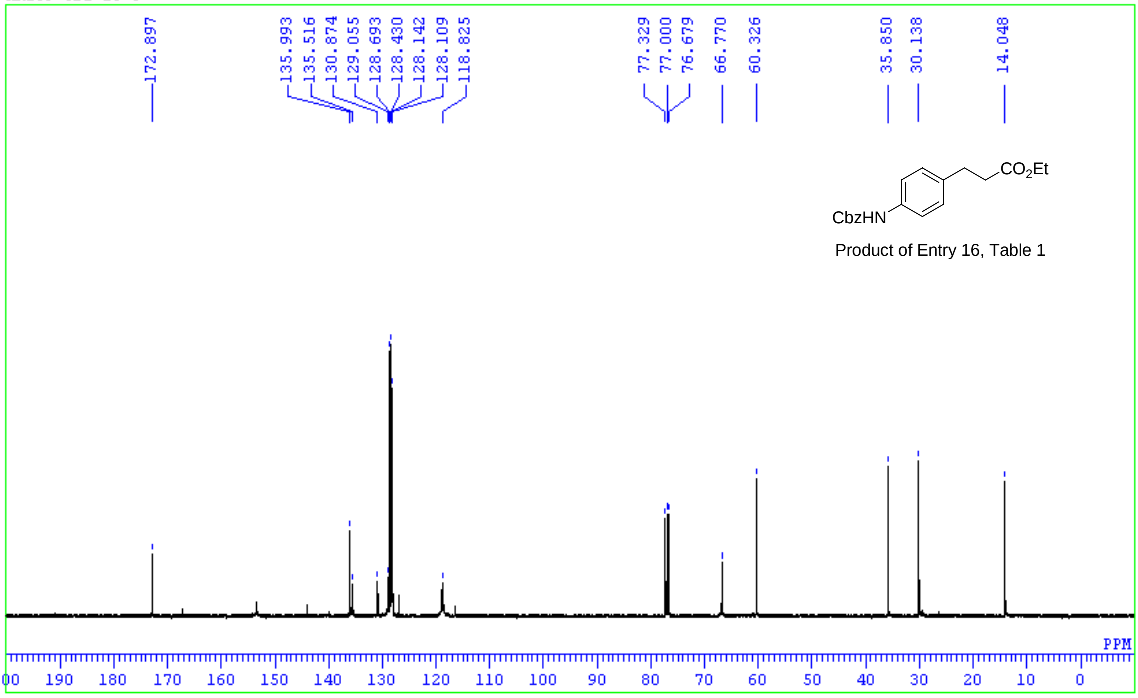
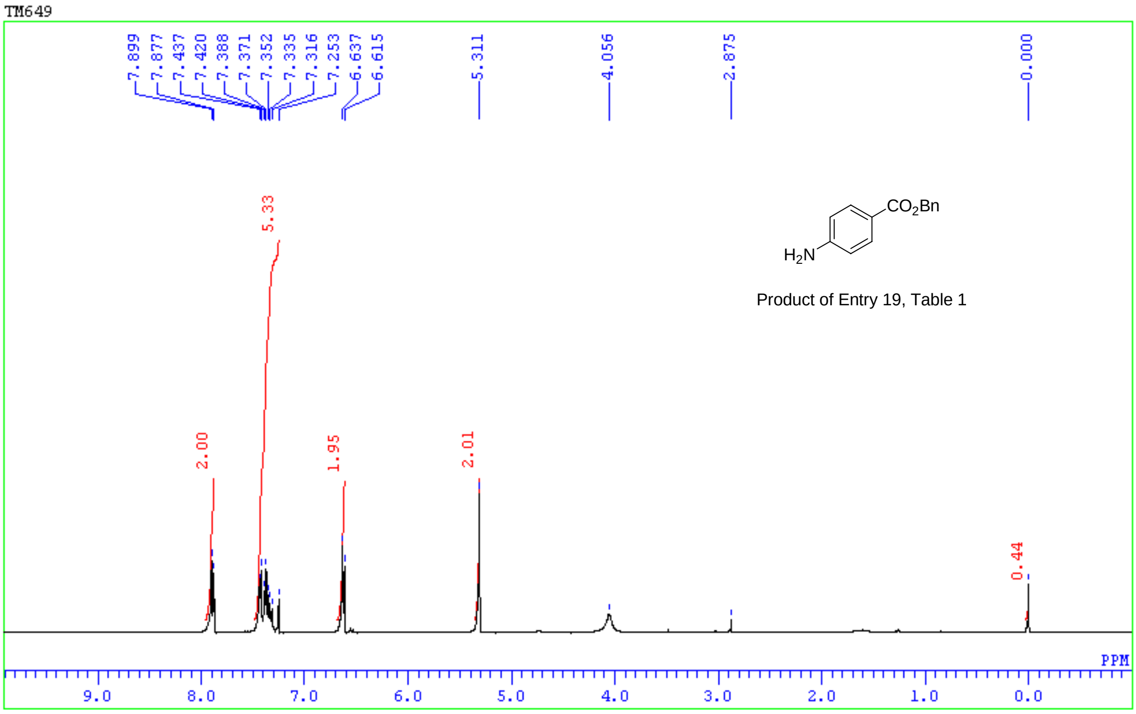


Product of Entry 16, Table 1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0.000
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2.00
1.95
2.01
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CO2Bn
H2N
Product of Entry 19, Table 1
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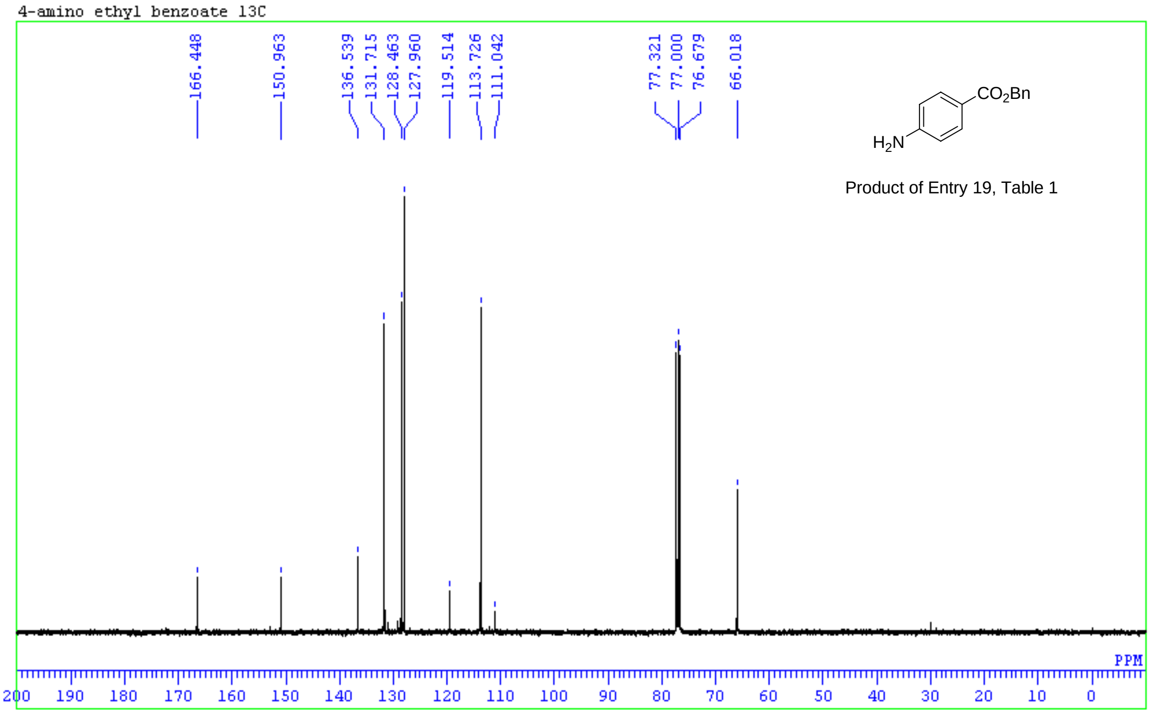
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H2N
Product of Entry 19, Table 1
PPM
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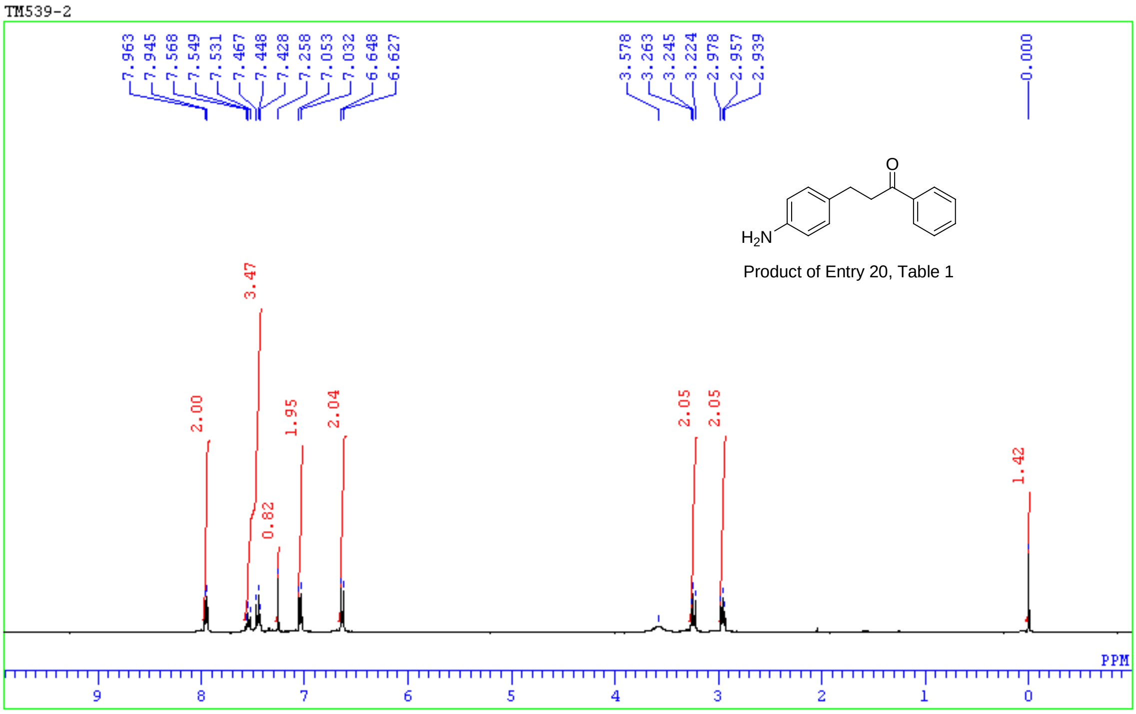
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3.263
3.245
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O
H2N
Product of Entry 20, Table 1
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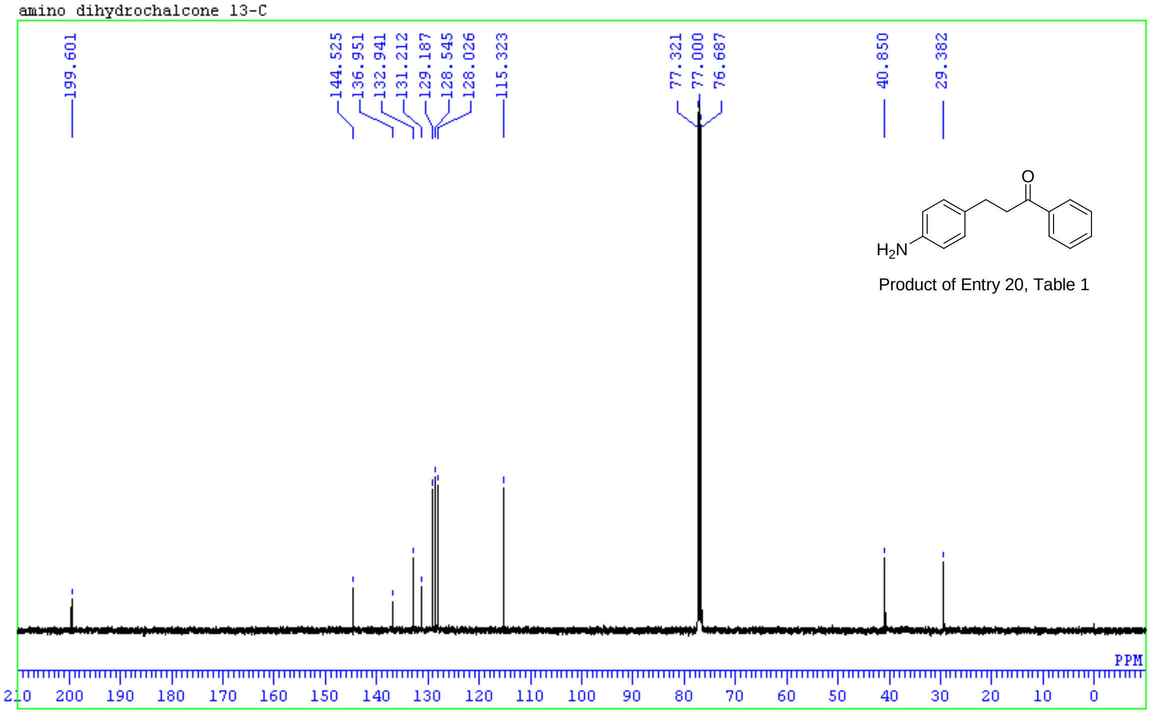
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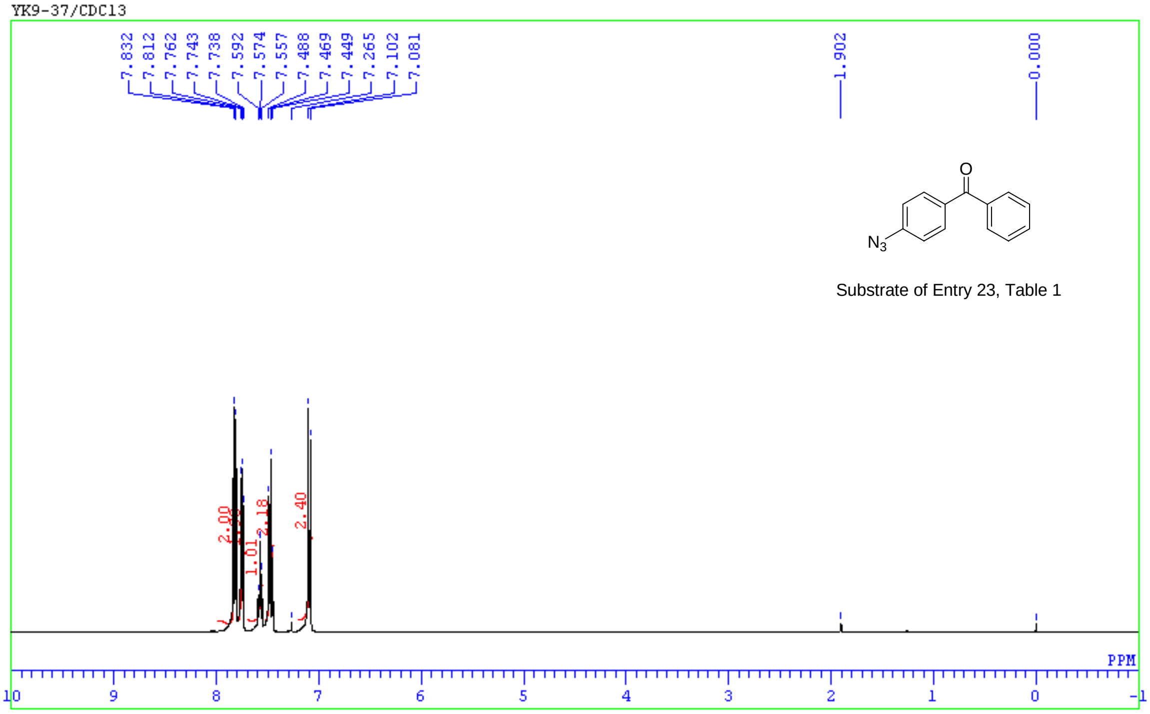
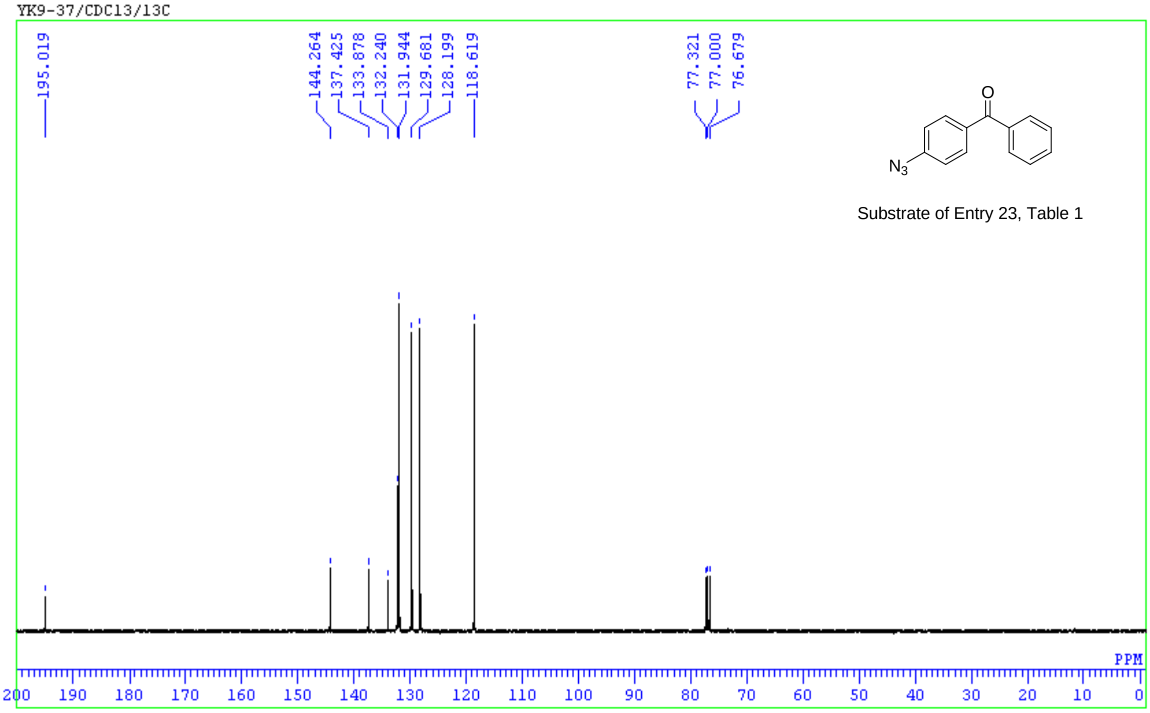
Product of Entry 20, Table 1
PPM
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


YK9-37/CDCl3
7.832
7.812
7.762
7.743
7.738
7.592
7.574
7.557
7.488
7.469
7.449
7.265
7.102
7.081
1.902
0.000
O
N3
Substrate of Entry 23, Table 1
2.00
1.01
2.18
2.40
PPM
10
9
8
7
6
5
4
3
2
1
0
-1


YK9-37/CDCl3/13C
195.019
144.264
137.425
133.878
132.240
131.944
129.681
128.199
118.619
77.321
77.000
76.679
O
N3
Substrate of Entry 23, Table 1
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0