Supporting Information

Product Selective Reaction Controlled by the Combination of a Palladium Nanoparticles, Continuous Microwave Irradiation, and a Co-existing Solid; Ligand-Free Buchwald–Hartwig Amination vs Aryne Amination

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Abstract: We have developed a continuous microwave irradiation-assisted Buchwald–Hartwig amination using our original Pd nanoparticle catalyst with copper plate as a co-existing metal solid. In this methodology, a microwave-controlled product selectivity was achieved between Buchwald–Hartwig amination and aryne amination performed under strongly basic conditions and a high reaction temperature, because a polar chemical species such as Ar–Pd–halogen might be activated selectively by microwave radiation. Moreover, our catalyst could be used repeatedly over 10 times, and the amount of Pd leaching could be suppressed to a low level.

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General Consideration

^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-AL-400 (400 MHz) with tetramethylsilane as an internal standard. ICP-S spectra were obtained on an AGLIRNT ICP-MS 7500 CS. HPLC was carried out using a Mightysil RP-18 GP 150-4.6 (3 μm, KANTO CHEMICAL CO., INC.; column), and HPLC spectra were by JASCO PU-986 Plus (pump), JASCO MD-2010 Plus (detector), JASCO LC-NET II/ADC (system controller) and GL Science CO 705 (column oven). Chemistation (TOKYO RIKAKIKAI CO., LTD, PPS-CTRL) was used for heating reactions. Microwave heating reactions were carried out using a single mode microwave generator (Anton Paar, Monowave 300) or semiconductor microwave generator (TOKYO RIKAKIKAI CO., LTD, GPS-1000C). Au (mesh) was purchased from Sanwa Metal CO. LTD. Column chromatography was carried out with silica gel (Kanto Chemical Co. Inc., Silica Gel 60 N, spherical neutral) unless otherwise stated.
Unless otherwise indicated, all reactions were carried out with magnetic stirring and under argon atmosphere. Reactions were monitored by thin layer chromatography.

Experimental Procedures

Preparation of SGlPd

A 10 × 10 mm^2 sample of glass was placed in piranha solution for 15 min and then rinsed in succession with H_2O (2 mL × 6) and EtOH (2 mL × 6). The sample was placed in a flask and dried for 10 min under reduced pressure. The resulting sulfur-modified glass [S-Gl] was placed in a solution of $Pd(OAc)_2$ (5.3 mg, 0.024 mmol) in *p*-xylene (3.0 mL) and stirred at 100 ℃ for 12 h under N_2 atmosphere. Then the plate was rinsed with *p*-xylene (2 mL × 6) and dried under vacuum. The obtained plate was placed in *p*-xylene (3 mL) and heated at 135 ℃ for 12 h two times. The plate was rinsed with *p*-xylene (2 mL × 6) and dried under vacuum for 10 min to give SGlPd (Pd: 56.3 ± 4.1 μg).

SGlPd-catalysed ligand-free Buchwald-Hartwig amination of aryl bromide under conventional heating (Table 1)

A mixture of 4-bromoanisole (**1a**) (50.5 mg, 0.27 mmol) or 2-bromonaphthalene (**1b**) (55.9 mg, 0.27 mmol) or 3-bromopyridine (**1c**) (42.7 mg, 0.27 mmol) or 3-bromoquinoline (**1d**) (56.2 mg, 0.27 mmol), morpholine (**2a**) (28.2 mg, 0.32 mmol), KO*t*Bu (42.4 mg, 0.38 mmol) and SGlPd (10 × 10 mm^2, Pd: 56.3 ± 4.1 μg) in *p*-xylene (2.0 mL) was heated at 130 ℃ for 24 h. After the reaction mixture was cooled to room temperature, the SGlPd plate was removed from the reaction mixture and rinsed several times with EtOH. Then sat. NH_4Cl aq. (4.0 mL) was added and extracted with AcOEt. The organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography (hexane : AcOEt = 5 : 1) to provide the desired compounds, *N*-(4-anisyl)morpholine (**3aa**, 48%, 25.0 mg), as a white solid, *N*-(2-naphtyl)morpholine (**3ba**, 76%, 43.8 mg), as a slight brown solid, *N*-(3-pyridyl)morpholine (**3ca**, 59%, 26.2 mg), as a brown oil, *N*-(3-quinolyl)morpholine (**3da**, 30%, 17.4 mg), as a yellow solid and the biproducts *N*-(3-anisyl)morpholine[1] (**3aa'**, 41%, 21.4 mg), as a colorless oil, *N*-(1-naphtyl)morpholine[2] (**3ba'**, 22%, 12.7 mg), as a white solid, *N*-(4-pyridyl)morpholine[3] (**3ca'**, 39%, 17.3 mg) as a colorless solid, *N*-(4-quinolyl)morpholine[3] (**3da'**, 19%, 11.0 mg) as a yellow solid.

Researching the effect of the co-existing metal in the SGlPd-catalyzed Buchwald-Hartwig amination of 4-bromoanisole under continuous microwave irradiation (Table 2, entry 15)

A mixture of 4-bromoanisole (**1a**) (31.8 mg, 0.17 mmol), morpholine (**2a**) (29.6 mg, 0.34 mmol), KO*t*Bu (43.9 mg, 0.39 mmol), SGlPd (10 × 10 mm^2, Pd: 56.3 ± 4.1 μg) and Cu plate (10 × 12 × 0.5 mm^3) in *p*-xylene (2.0 mL) was heated and irradiated with a semi-conductor type microwave machine at 100 W and 90 ℃ for 2 h. After the reaction mixture was cooled to room temperature, the SGlPd plate was removed from the reaction mixture and rinsed several times with EtOH. Then, the reaction mixture was heated and irradiated microwave at 100 W and 90 ℃ for 30 h. After the reaction mixture was cooled to room temperature, Cu plate was rinsed with EtOH then sat. NH_4Cl aq. (4.0 mL) was added and extracted with AcOEt. The organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography (hexane : AcOEt = 5 : 1) to provide the title compound, *N*-(4-anisyl)morpholine (**3aa**, 90%, 29.6 mg), as a white solid.

Recycling experiment of SGlPd-catalysed ligand-free Buchwald-Hartwig amination of 4-bromoanisole (Table 3, run 1)

A mixture of 4-bromoanisole (**1a**) (31.8 mg, 0.17 mmol), morpholine (**2a**) (29.6 mg, 0.34 mmol), KO*t*Bu (43.9 mg, 0.39 mmol), SGlPd (10 × 10 mm^2, Pd: 56.3 ± 4.1 μg) and Cu plate (10 × 12 × 0.5 mm^3) in *p*-xylene (2.0 mL) was heated and irradiated with a semi-conductor type microwave machine at 100 W and 90 ℃ for 2 h. After the reaction mixture was cooled to room temperature, the SGlPd plate was removed from the reaction mixture and rinsed several times with EtOH. Then, the reaction mixture was heated and irradiated microwave at 100 W and 90 ℃ for 30 h. After the reaction mixture was cooled to room temperature, Cu plate was rinsed with EtOH. Then the yield was measured using HPLC (conditions: Mightysil-RP18 (150 mm, ø 4.6 mm, 3 μm, Kanto Chemical Co. Inc.), MeCN : H_2O = 70 : 30, 0.80 mL min-1, 25 ℃, tR 11.2 min).

ICP-mass analysis

The whole reaction mixture or the SGlPd substrate was treated with concentrated nitric acid, and the Pd species in this mixture was examined by ICP-mass. For ICP-mass analysis, an Agilent 7700x (Agilent Technologies, Santa Clara, CA, USA) was used. The analysis conditions were the followings. RF power was set at 1550 W, Ar and He were used as carrier and collision gas, respectively. Flow rate of carrier gas was 1.05 L/min. Target isotope was ^{108}Pd. Three data points were monitored in unit mass. Dwell time was 0.1 second for

each data point. Measurements were repeated three times. Pd standard solution was obtained from Kanto Chemical. Calibration curve were prepared from 1.0 - 100 mg/L.

The SGIPd-catalysed Buchwald-Hartwig amination of 4-chloroanisole under continuous microwave irradiation (Table 6, entry 5)

A mixture of 4-chloroanisole (**4a**) (24.2 mg, 0.17 mmol), KO*t*Bu (43.9 mg, 0.39 mmol), SGIPd (10 × 10 mm^2, Pd: 56.3 ± 4.1 μg) and Cu plate (10 × 12 × 0.5 mm^3) in *p*-xylene (2.0 mL) was heated and irradiated with a semi-conductor type microwave machine at 100 W and 90 ℃ for 2 h. After the reaction mixture was cooled to room temperature, the SGIPd plate was removed from the reaction mixture and rinsed several times with EtOH. Then, morpholine (**2a**) (29.6 mg, 0.34 mmol) was added into the reaction mixture and heated and irradiated microwave at 100 W and 120 ℃ for 30 h. After the reaction mixture was cooled to room temperature, the Cu plate was rinsed with EtOH then sat. NH_4Cl (4.0 mL) was added, and extracted with AcOEt. The organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography (hexane : AcOEt = 5 : 1) to provide the title compound, *N*-(4-anisyl)morpholine (**3aa**, 81%, 26.6 mg), as a white solid.

XPS analysis for Pd NPs on SGFIPd (Figure S1)

X-ray photoelectron spectroscopy (XPS) analyses were operated with an X-ray photoelectron spectrometer (JEOL JPS-9010MC) using a monochromated A1 Kα X-ray source (hu 1486.6 eV) operated at 12 kV and 25 mA under a base pressure of ~10^{-7} Pa.

The C1s peak was used as a reference for binding energy calibration (284.6 eV).

X-ray diffraction for Pd NPs on SGFIPd (XRD, Figure S2)

X-ray diffraction (XRD) analysis was performed with an X-ray diffractometer (Rigaku, SmartLab) using Cu Kα radiation in the 2θ range from 0 ° to 90 °.

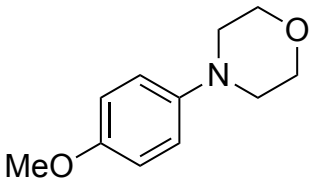
TEM-STEM analysis for Pd NPs on SGFIPd (Figure S3)

The TEM and STEM images were obtained with a JEOL JEM-ARM200F instrument at an accelerating voltage of 200 kV.

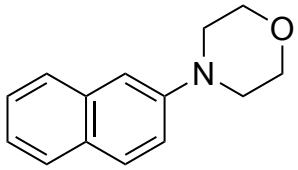
Preparation of the TEM sample

The nanoparticle solution was diluted with methanol and added dropwise onto the TEM grid (Cu).

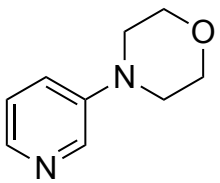
Experimental Data



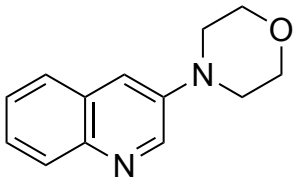
***N*-(4-anisyl)morpholine** (**3aa**).[4], Mp. 72.0–73.5 °C (lit.[5] 73.0–74.0 °C), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.89–6.85 (m, 4H), 3.88 (t, *J* = 8.7 Hz, 4H), 3.78 (s, 3H); 3.07 (t, *J* = 7.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.1, 145.4, 118.9, 114.3, 67.0, 55.8, 51.0.



***N*-(2-naphtyl)morpholine** (**3ba**).[4], Mp. 89.0–90.5 °C (lit.[6] 90.0 °C), slightly brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76–7.70 (m, 3H), 7.42 (ddd, *J* = 8.0, 7.0 and 1.0 Hz, 1H), 7.33–7.28 (m, 3H), 3.93 (t, *J* = 4.6 Hz, 4H), 3.28 (t, *J* = 4.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.5, 128.8, 128.7, 127.4, 126.8, 126.4, 123.6, 118.9, 110.1 (d), 66.9, 49.8.



***N*-(3-pyridyl)morpholine** (**3ca**).[1], brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31 (s, 1H), 8.13 (s, 1H), 7.21–7.19 (m, 2H), 3.89–3.87 (m, 4H), 3.21–3.18 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.9, 140.7, 137.9, 123.6, 122.3, 66.6, 48.5.



***N*-(3-quinolyl)morpholine** (**3da**).[2], Mp. 84.5–85.5 °C (lit.[2] 84.0–86.0 °C), yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.80 (d, J = 2.8 Hz, 1H), 8.03 (d, 8.0 Hza, 1H), 7.71 (dd, 8.0 and 1.5 Hz, 1H), 7.57–7.47 (m, 2H), 7.38 (d, *J* = 2.8 Hz, 1H), 3.95 (t, J = 4.8 Hz, 4H), 3.30 (t, *J* = 4.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.7, 143.6, 142.2, 128.8, 128.3, 127.3, 127.0, 126.6, 117.4, 66.6, 49.3.

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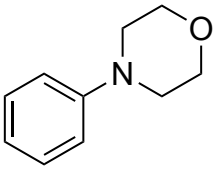
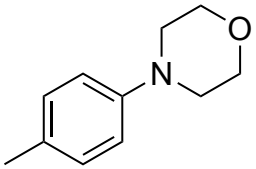
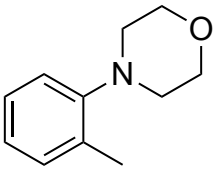


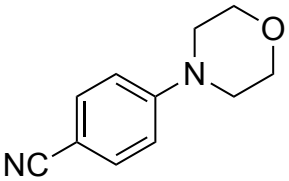
***N*-phenylmorpholine** (**3ea**).[4], Mp. 52.0–53.5 °C (lit.[7] 51.0–54.0 °C), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32–7.27 (m, 2H), 6.95–6.88 (m, 3H), 3.88 (t, J = 4.8 Hz, 4H), 3.17 (t, *J* = 4.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.2, 129.2, 120.1, 115.7, 66.9, 49.4.



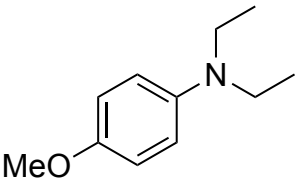
***N*-(4-tolyl)morpholine** (**3fa**).[8], Mp. 49.5–51.0 °C (lit.[6] 51.0 °C), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.09 (d, J = 8.2 Hz, 2H), 6.84 (d, J = 8.2 Hz, 2H), 3.86 (t, *J* = 4.8 Hz, 4H) 3.10 (t, *J* = 4.8 Hz, 4H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.1, 129.7, 129.6, 116.0, 67.0, 49.9, 20.4.



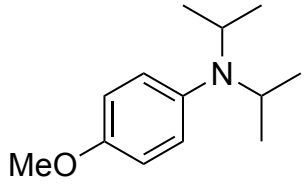
***N*-(2-tolyl)morpholine** (**3ga**).[1], brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.15–7.08 (m, 2H), 6.95–6.90 (m, 2H), 3.77 (t, J = 4.6 Hz, 4H), 2.83 (t, *J* = 4.6 Hz, 4H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.2, 132.5, 131.1, 126.6, 123.3, 118.9, 67.4, 52.2, 17.8.



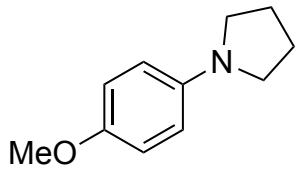
***N*-(4-cyano)morpholine** (**3ha**).[1], Mp. 77.5–79.0 °C (lit.[9] 77.0–78.0 °C), pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54–7.52 (m, 2H), 6.91–6.88 (m, 2H), 3.87 (t, *J* = 5.0 Hz, 4H), 3.29 (t, *J* = 5.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.3, 133.5, 119.8, 114.2, 101.4, 66.4, 47.4.



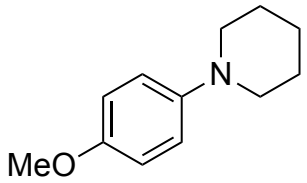
***N*,*N*-diethyl-4-anisidine** (**3ab**).[10], pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.84–6.82 (m, 2H), 6.72 (d, J = 8.7 Hz, 2H), 3.76 (s, 3H), 3.26 (q, *J* = 7.0 Hz, 4H), 1.11 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.4, 142.7, 115.2, 114.7, 55.7, 45.3, 12.4.



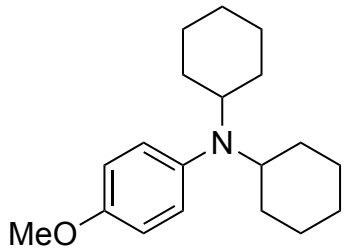
***N*,*N*-diisopropyl-4-anisidine** (**3ac**).[11], pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.97 (d, *J* = 7.3 Hz, 2H), 6.80 (d, *J* = 7.3 Hz, 2H), 3.79 (s, 3H), 3.54 (br, 2H), 1.03–0.98 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.3, 140.4, 127.5, 113.3, 55.4, 48.5, 21.2.



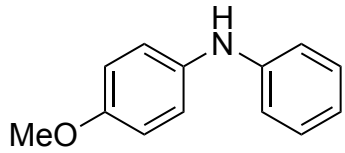
***N*-(4-anisyl)pyrrolidine** (**3ad**).[8], Mp. 42.5–44.5 °C (lit.[5] 44.0–45.0 °C), brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.85 (d, *J* = 8.7 Hz, 2H), 6.54 (d, *J* = 8.7 Hz, 4H), 3.76 (s, 3H), 3.23 (t, *J* = 6.2 Hz, 4H), 1.99 (t, *J* = 6.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.7, 143.2, 115.0, 112.6, 56.0, 48.2, 25.4.



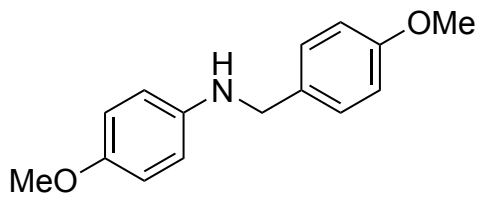
***N*-(4-anisyl)piperidine** (**3ae**).[12], pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.93 (d, *J* = 8.7 Hz, 2H), 6.85–6.82 (m, 2H), 3.77 (s, 3H), 3.03 (t, *J* = 5.3 Hz, 4H), 1.76–1.70 (m, 4H), 1.57–1.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.6, 146.7, 118.8, 114.3, 55.5, 52.4, 25.9, 24.1.



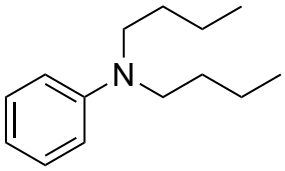
***N*,*N*-dicyclohexyl-4-anisidine** (**3af**).[13], colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.98 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H), 3.10 (tt, *J* = 10.8 and 3.3 Hz, 2H), 1.79 (d, *J* = 12.8 Hz, 4H), 1.72 (dt, *J* = 12.7 and 3.3 Hz, 4H), 1.56 (dt, *J* = 12.8 and 3.2 Hz, 2H), 1.30–0.98 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.0, 141.2, 115.0, 114.9, 55.8, 53.0, 33.5, 25.9, 25.0.



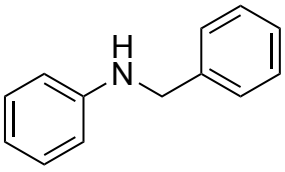
***N*-phenyl-4-anisidine** (**3ag**).[4], Mp. 104–106 °C (lit.[5] 105.0–106.0 °C), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40–7.28 (m, 2H), 7.22–7.12 (m, 2H), 7.10–6.84 (m, 5H), 5.20 (br, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.2, 145.1, 135.7, 129.3, 122.2, 119.5, 115.6, 114.6, 55.7.



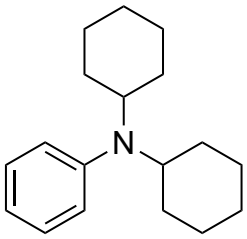
***N*-(4-methoxybenzyl)-4-anisidine** (**3ah**).[8], Mp. 91.5–93.0 °C (lit.[14] 92.0–94.0 °C), pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.80–6.73 (m, 4H), 4.22 (s, 2H), 3.78 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.8, 152.5, 141.6, 131.1, 129.0, 122.1, 114.8, 113.9, 55.7, 55.0, 49.0.



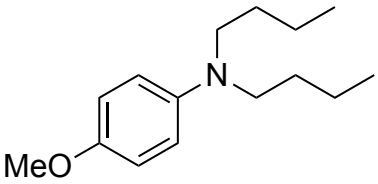
***N*,*N*-dibutylaniline** (**3ei**).[15], colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (m, 2H), 6.71–6.66 (m, 3H), 3.31 (t, *J* = 7.8 Hz, 4H), 1.66–1.59 (m, 4H), 1.41 (td, *J* = 15.1 and 7.5 Hz, 4H), 1.01 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.1, 129.1, 115.0, 111.6, 50.7, 29.4, 20.3, 14.0.



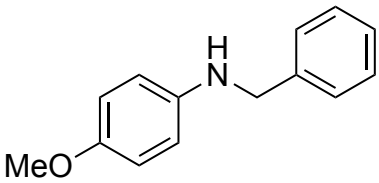
***N*-benzylaniline** (**3ej**).[4], pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39–7.27 (m, 5H), 7.21 (m, 2H), 6.79 (dd, *J* =14.9 and 7.4 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 2H) 4.34 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.4, 138.9, 129.3, 128.6, 127.6, 127.3, 118.1, 113.4, 48.7.



***N*,*N*-dicyclohexylaniline** (**3ef**).[16], colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18 (dd, *J* = 7.8 and 3.9 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.80 (dd, *J* = 7.8 and 3.9 Hz, 1H), 3.24 (tt, *J* = 11.4 and 3.3 Hz, 2H), 1.81–1.76 (m, 8H), 1.65–1.47 (m, 6H), 1.37–1.26 (m, 4H), 1.11 (tdd, 16.8, 8.5 and 4.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.7, 128.2, 120.9, 118.9, 57.5, 32.0, 26.3, 26.0.



***N*,*N*-dibutyl-4-anisidine** (**3ai**).[17], colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.82 (d, *J* = 8.2 Hz, 2H), 6.65 (d, *J* = 7.8 Hz, 2H), 3.76 (s, 3H), 3.17 (t, *J* = 7.1 Hz, 4H), 158–1.51 (m, 4H), 1.37–1.26 (m, 4H), 0.92 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.9, 143.3, 114.8, 114.3, 55.8, 51.8, 29.4, 20.4, 14.0.



***N*-benzyl-4-anilsidine** (**3aj**).[8], Mp. 50.0–51.0 °C (lit.[5] 49.0–50.0 °C), brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40–7.26 (m, 5H), 6.82–6.76 (m, 2H), 6.64–6.60 (m, 2H), 4.30 (s, 2H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.2, 142.3, 139.6, 128.6, 127.5, 127.1, 114.8, 114.1, 55.8, 49.2.

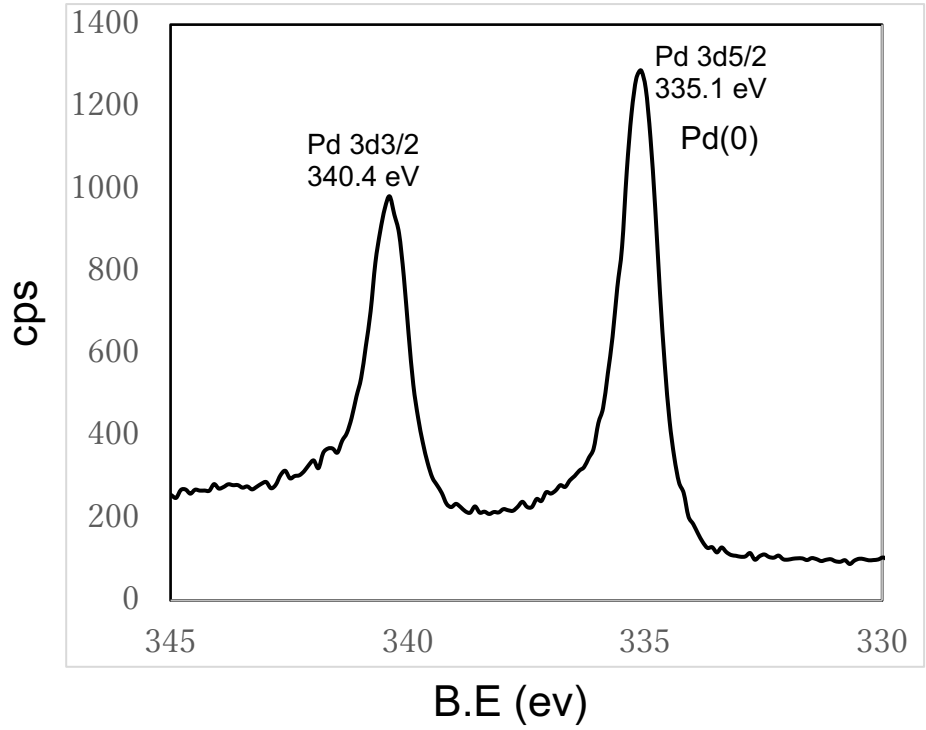


Figure S1. XPS analysis of Pd NPs on SGlPd (eching rate_10s 500W).
A peak at 335.1 eV indicates that the Pd NPs on SGlPd is 0 valences, based on the previous report.[18]

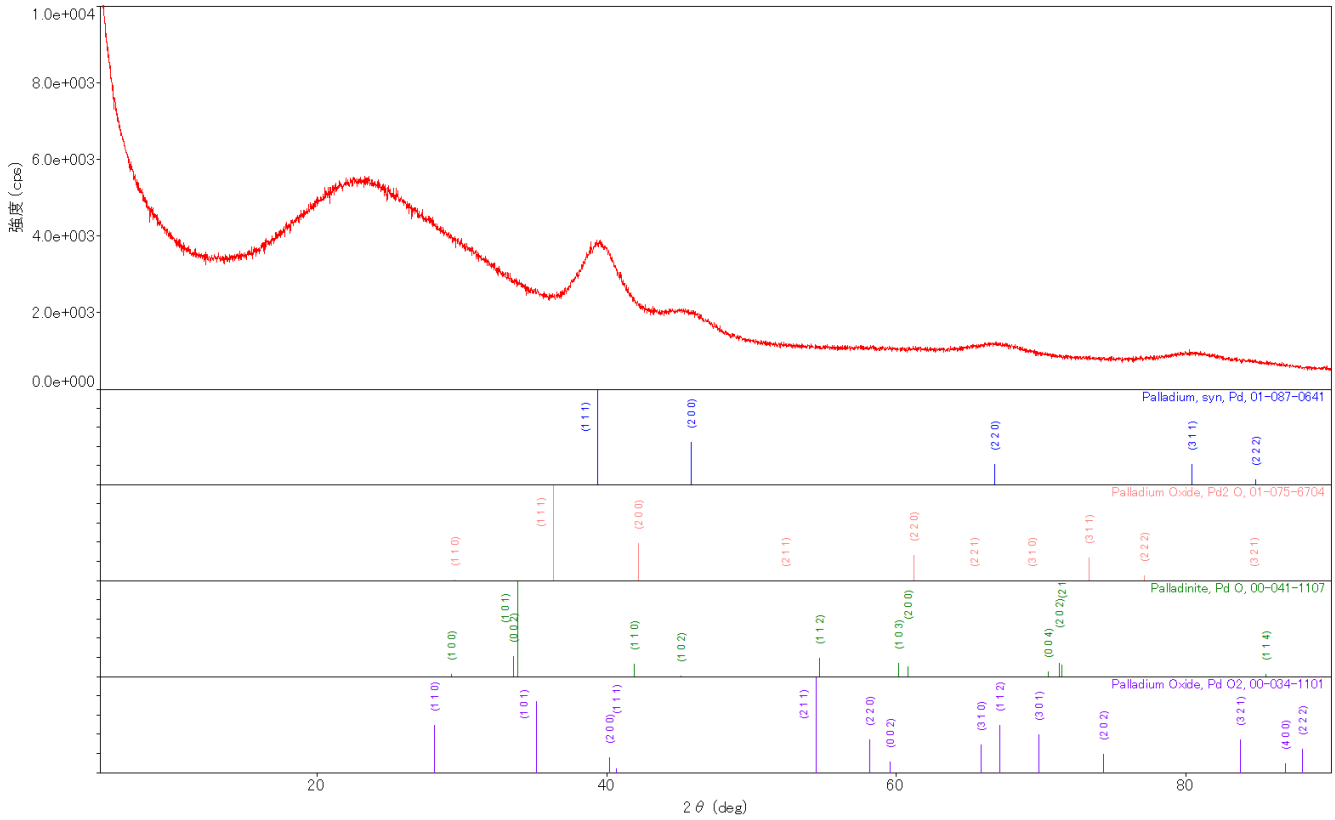


Figure S2. Powder XRD spectra of Pd NPs on SGlPd.
Red line means spectra of SGlPd. Peaks of the red lines almost match blue peaks of Pd(0) between other standard samples. This result support that the Pd(0) is immobilized on SGlPd.

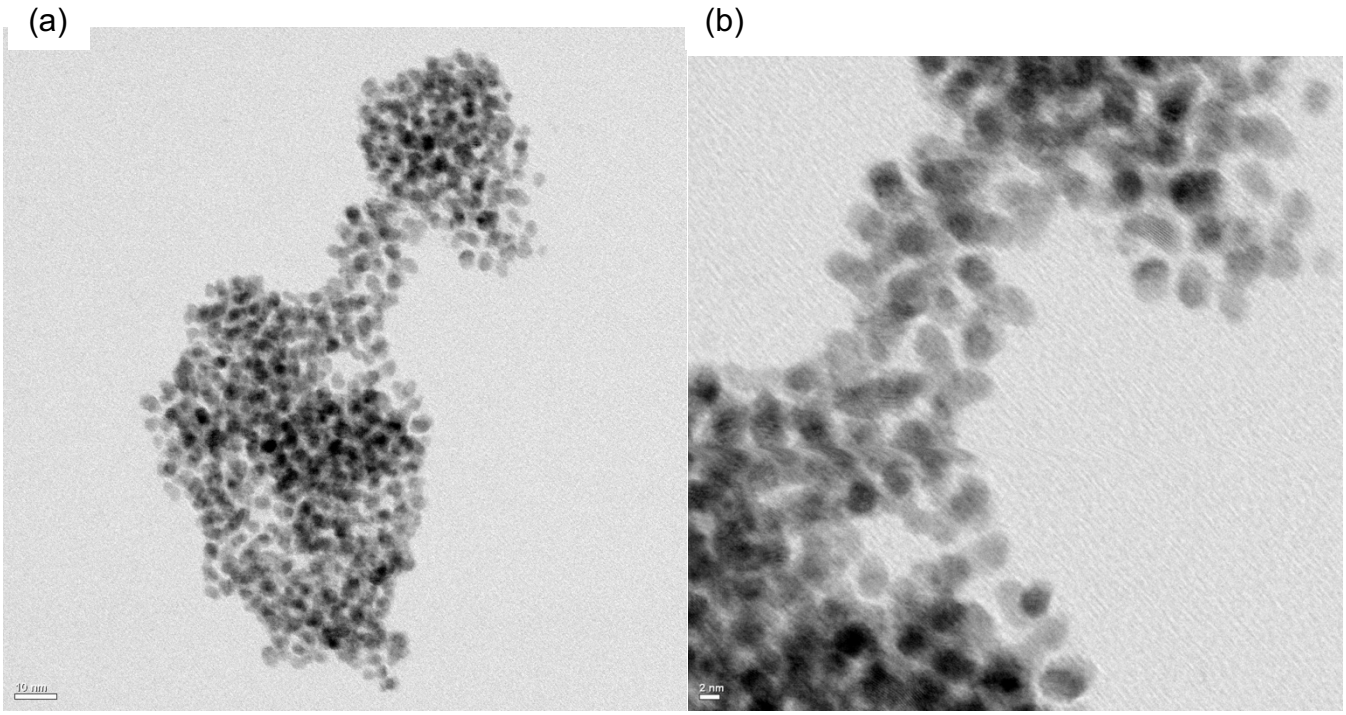
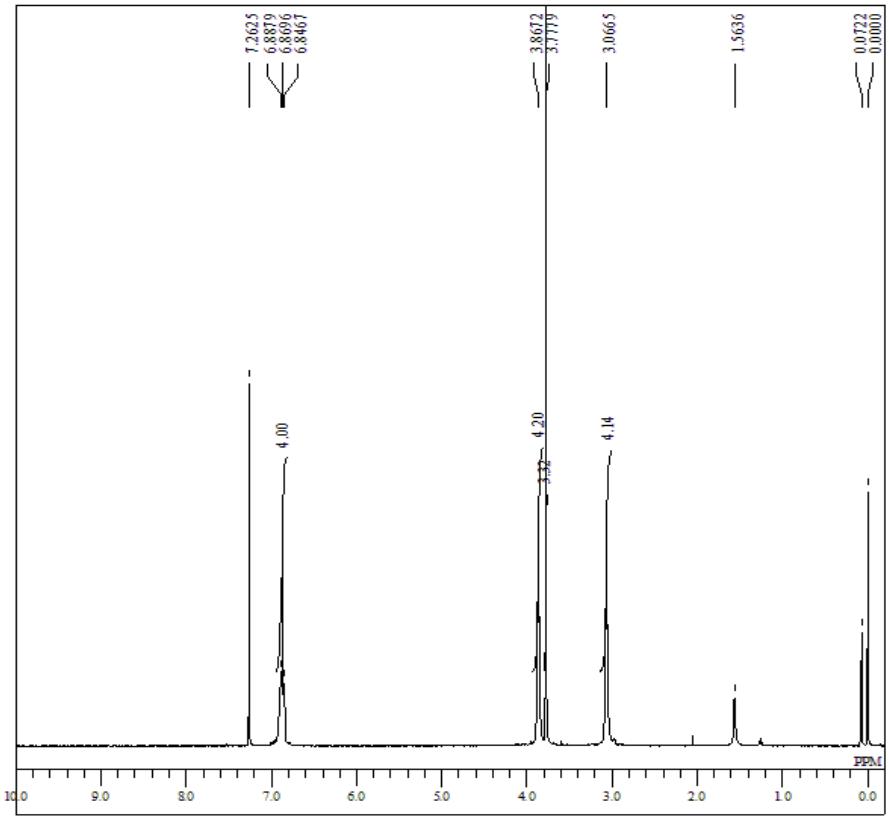


Figure S3. HR TEM images of Pd NPs on SGlPd : (a) 10 nm scale, (b) 2 nm scale. Average diameter of Pd NP is 5.17 nm.

single_pulse



DFILE N-(4-anisyl)morphorine-3aa_product_yam
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DATIM 2021-01-31 18:41:17
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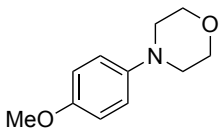
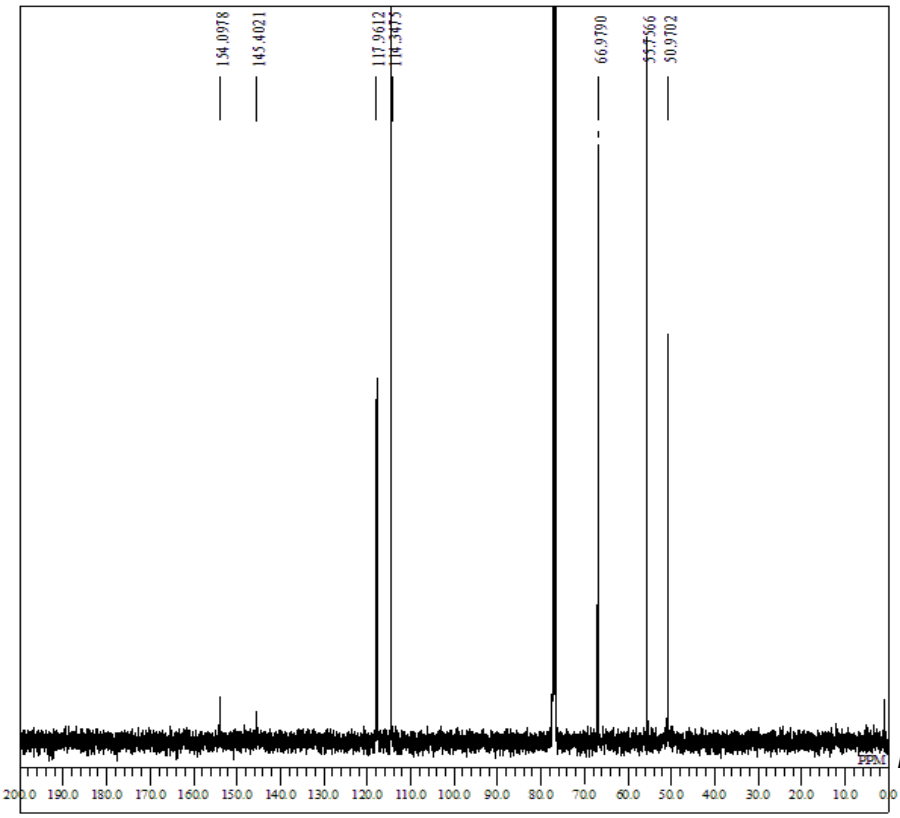
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 20.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50

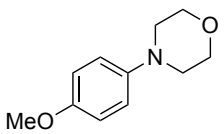


***N*-(4-anisyl)morphorine (3aa)**

single pulse decoupled gated NOE

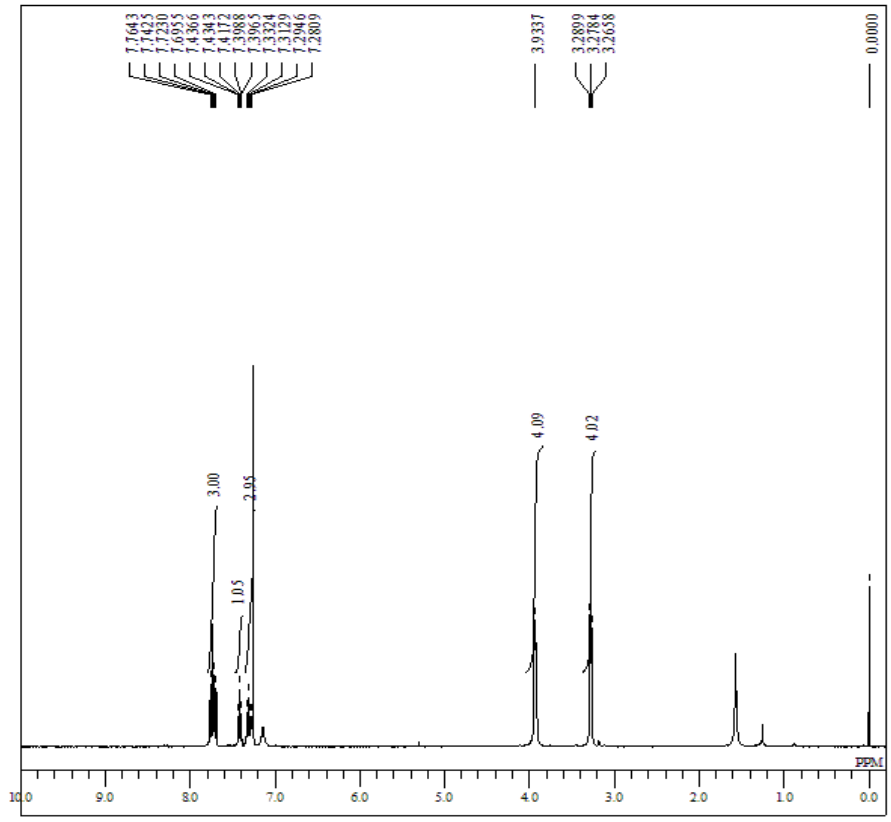


DFILE N-(4-anisyl)morphorine_yamada_Carbon-
COMNT single pulse decoupled gated NOE
DATIM 2021-04-21 05:05:19
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1024
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 20.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50



***N*-(4-anisyl)morphorine (3aa)**

single_pulse

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EXMOD   proton.jxp
OBFRQ     399.78 MHz
OBSET       4.19 KHz
OBFIN       7.29 Hz
POINT      13107
FREQU    6002.40 Hz
SCANS         8
ACQTM     2.1837 sec
PD        5.0000 sec
PW1         6.40 usec
IRNUC   1H
CTEMP      19.7 c
SLVNT   CDCL3
EXREF      0.00 ppm
BF         0.12 Hz
RGAIN        50
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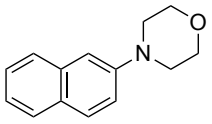
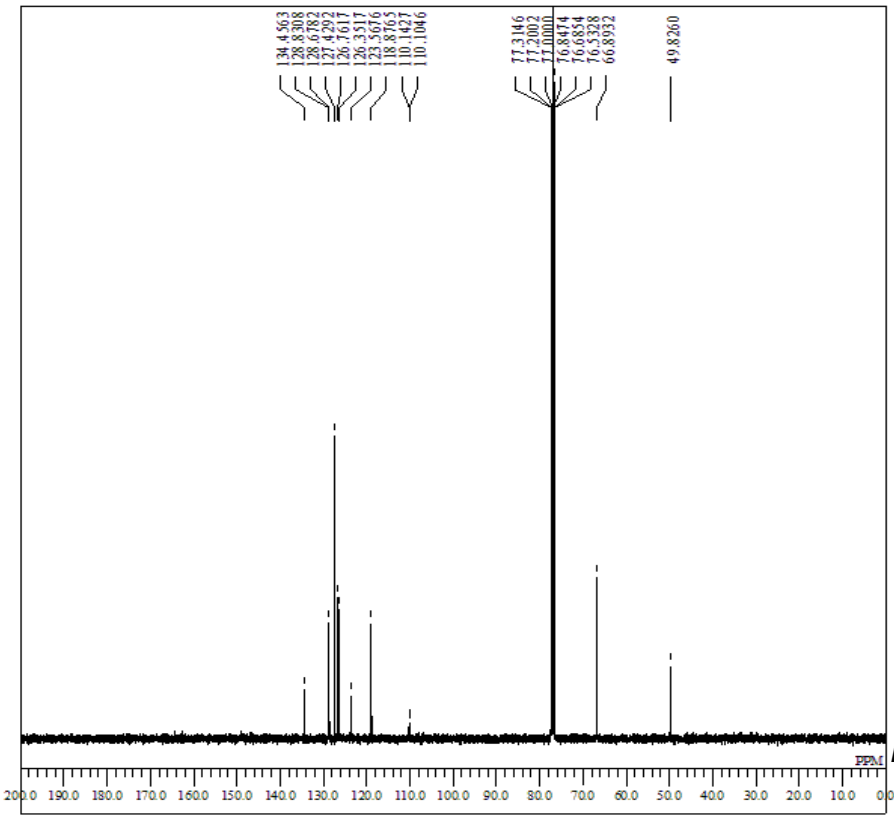


***N*-(2-naphtyl)morphorine (3ba)**

single pulse decoupled gated NOE

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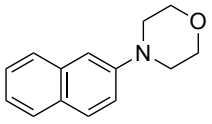
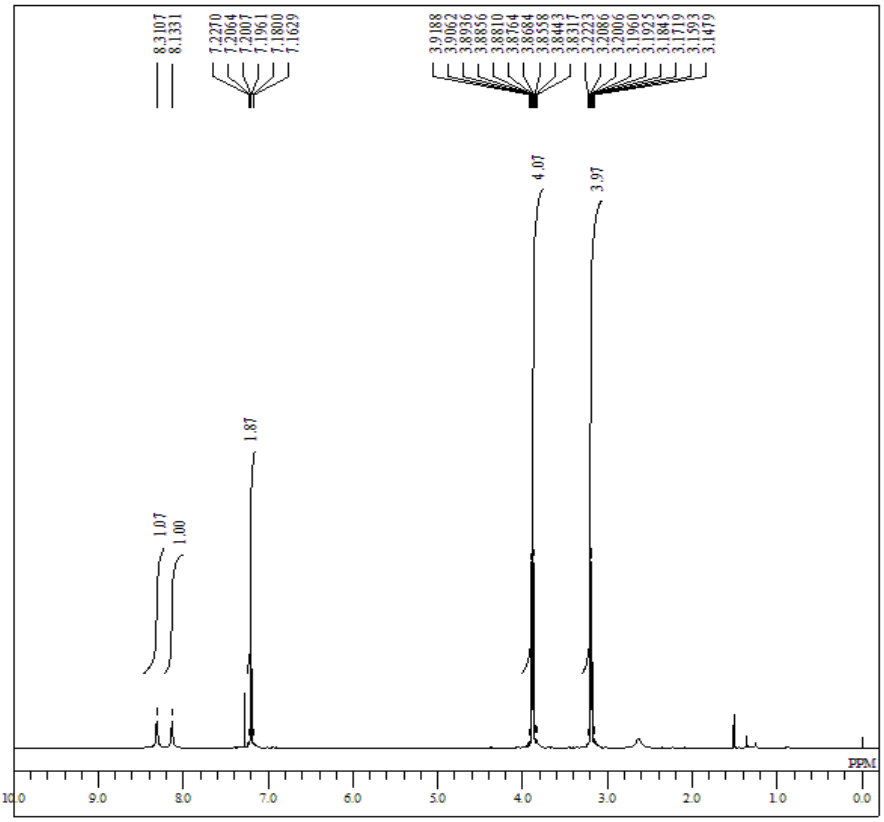
DFILE   N-(2-naphtyl)morpholine_yamada_Carbor
COMNT   single pulse decoupled gated NOE
DATIM   2021-04-22 04:05:24
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ     100.53 MHz
OBSET       5.35 KHz
OBFIN       5.86 Hz
POINT      26214
FREQU    25125.63 Hz
SCANS       1024
ACQTM     1.0433 sec
PD        2.0000 sec
PW1         2.87 usec
IRNUC   1H
CTEMP      19.9 c
SLVNT   CDCL3
EXREF     77.00 ppm
BF         0.12 Hz
RGAIN        50
```



***N*-(2-naphtyl)morpholine (3ba)**

single_pulse

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COMNT   single_pulse
DATIM   2021-04-13 23:50:58
OBNUC   1H
EXMOD   proton.jxp
OBFRQ     399.78 MHz
OBSET       4.19 KHz
OBFIN       7.29 Hz
POINT      13107
FREQU    6002.40 Hz
SCANS          8
ACQTM     2.1837 sec
PD        5.0000 sec
PW1          6.40 usec
IRNUC   1H
CTEMP      19.9 c
SLVNT   CDCL3
EXREF      0.00 ppm
BF         0.12 Hz
RGAIN        40
```
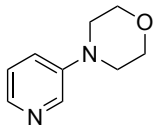
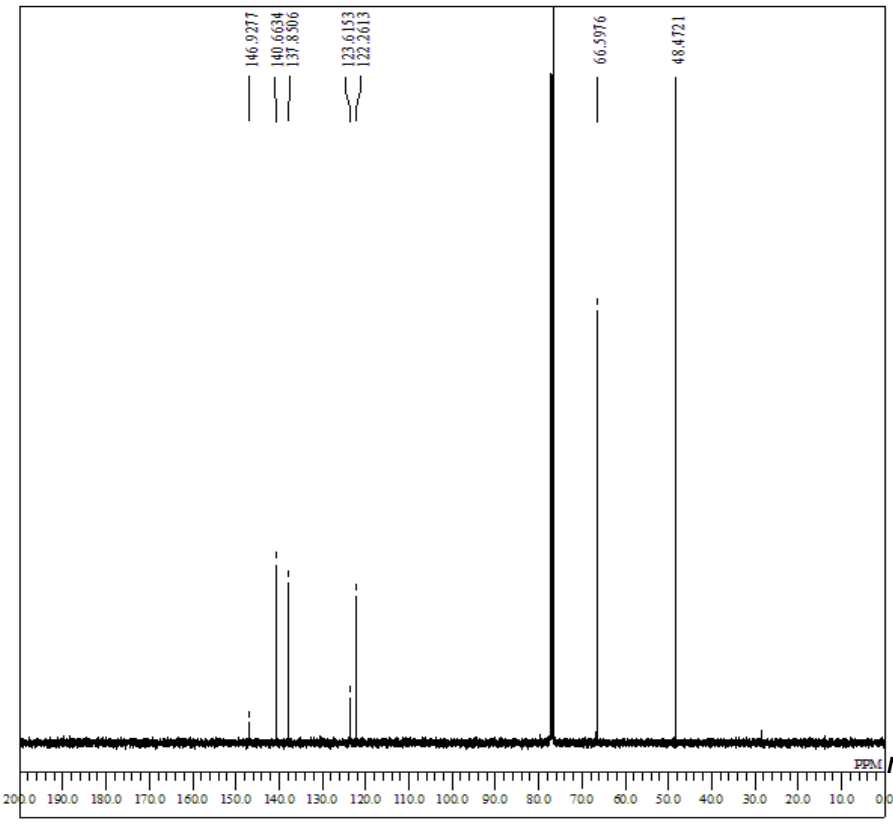



***N*-(3-pyridyl)morphorine (3ca)**

single pulse decoupled gated NOE

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DFILE   N-(3-pyridyl)morphorine_yamada_Carbon
COMNT   single pulse decoupled gated NOE
DATIM   2021-04-14 07:55:22
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ     100.53 MHz
OBSET       5.35 KHz
OBFIN       5.86 Hz
POINT      26214
FREQU    25125.63 Hz
SCANS       1024
ACQTM     1.0433 sec
PD        2.0000 sec
PW1          2.87 usec
IRNUC   1H
CTEMP      20.0 c
SLVNT   CDCL3
EXREF      77.00 ppm
BF         0.12 Hz
RGAIN        50
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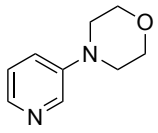
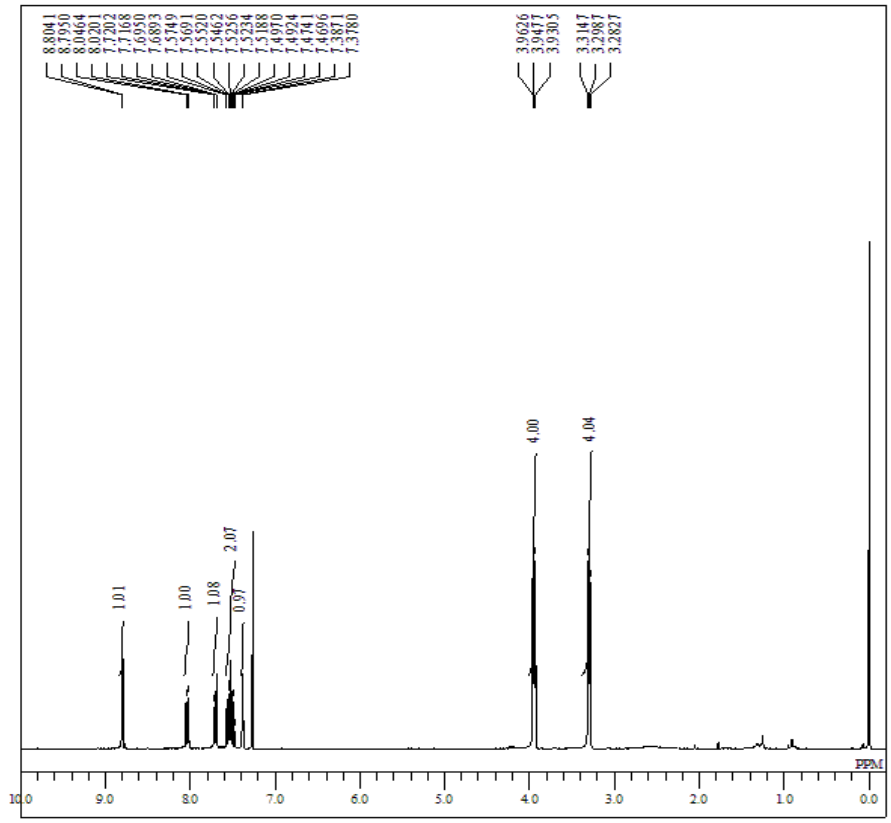


***N*-(3-pyridyl)morphorine (3ca)**

single_pulse



DFILE N-(3-quinolyl)morphorine_yamada_Protor
COMNT single_pulse
DATIM 2020-11-25 16:15:40
OBNUC 1H
EXMOD proton.jxp
OBFRQ 300.53 MHz
OBSET 1.15 KHz
OBFIN 8.57 Hz
POINT 13107
FREQU 4508.57 Hz
SCANS 8
ACQTM 2.9072 sec
PD 5.0000 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 17.3 c
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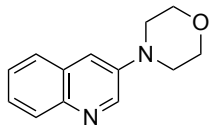
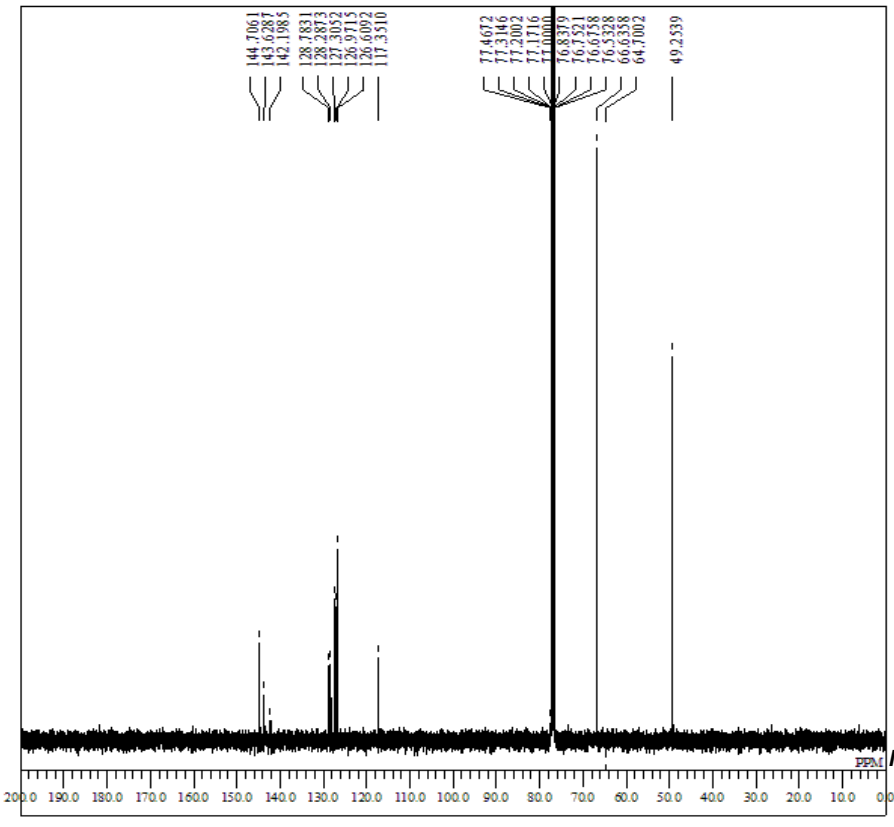
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 44

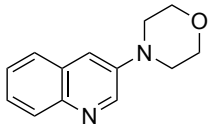


***N*-(3-quinolyl)morphorine (3da)**

single pulse decoupled gated NOE

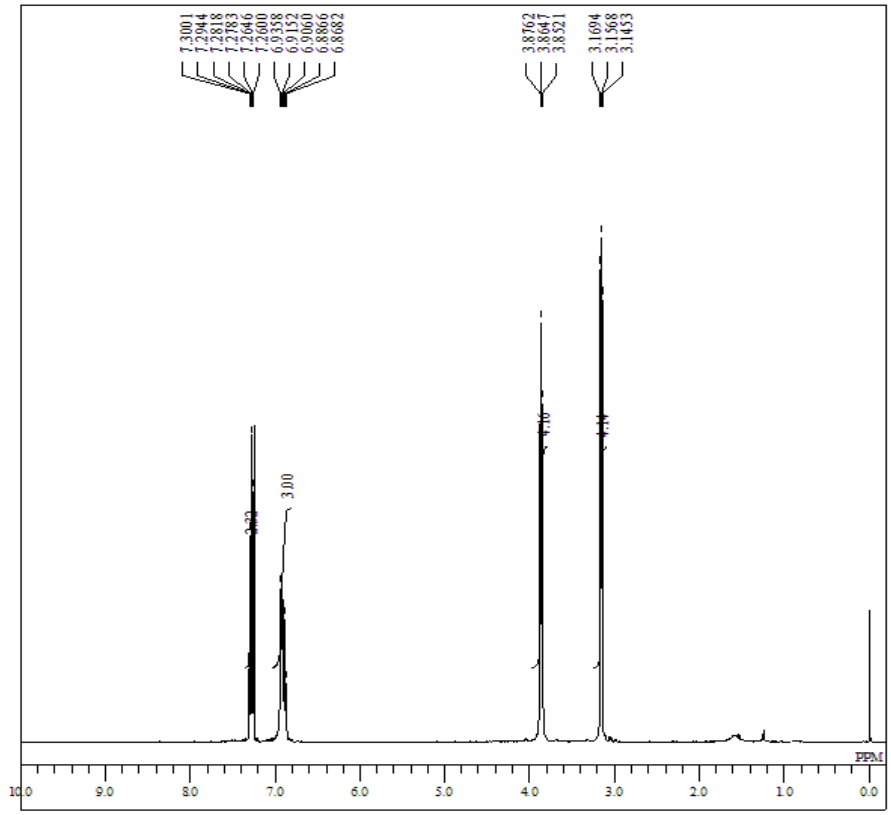


DFILE N-(3-quinolyl)morphorine_yamada_Carbo
COMNT single pulse decoupled gated NOE
DATIM 2021-04-22 05:04:37
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1024
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50



***N*-(3-quinolyl)morphorine (3da)**

single_pulse



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DATIM 2021-04-01 00:29:17
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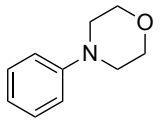
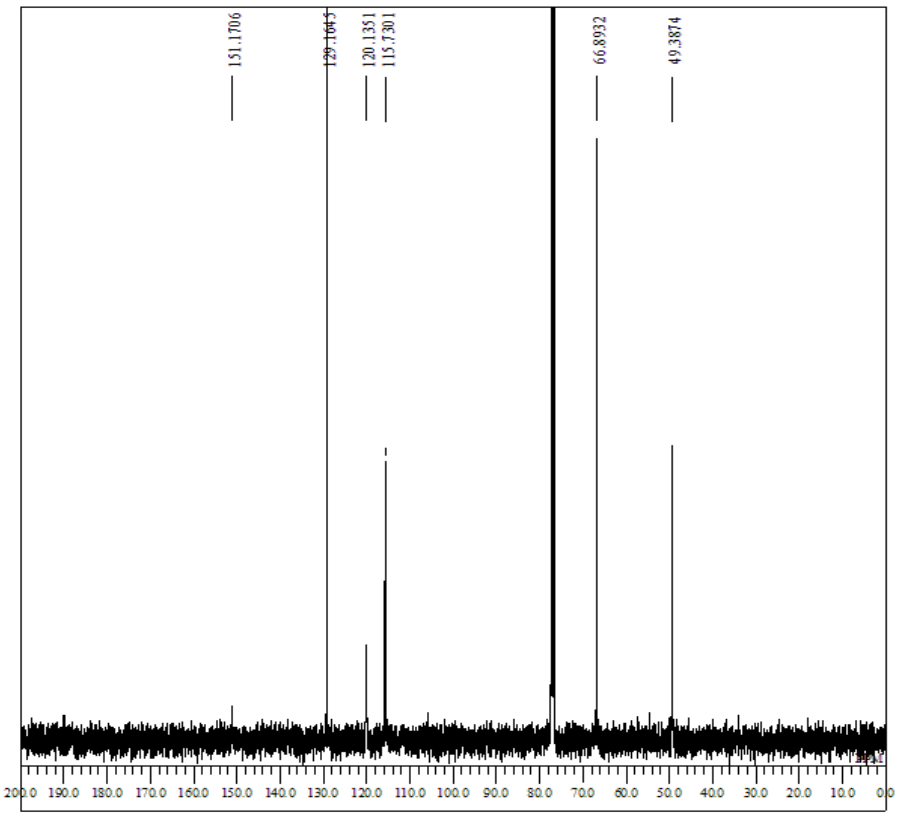
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 19.8 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 44

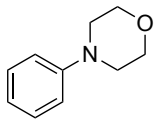


***N*-phenylmorphorine (3ea)**

single pulse decoupled gated NOE

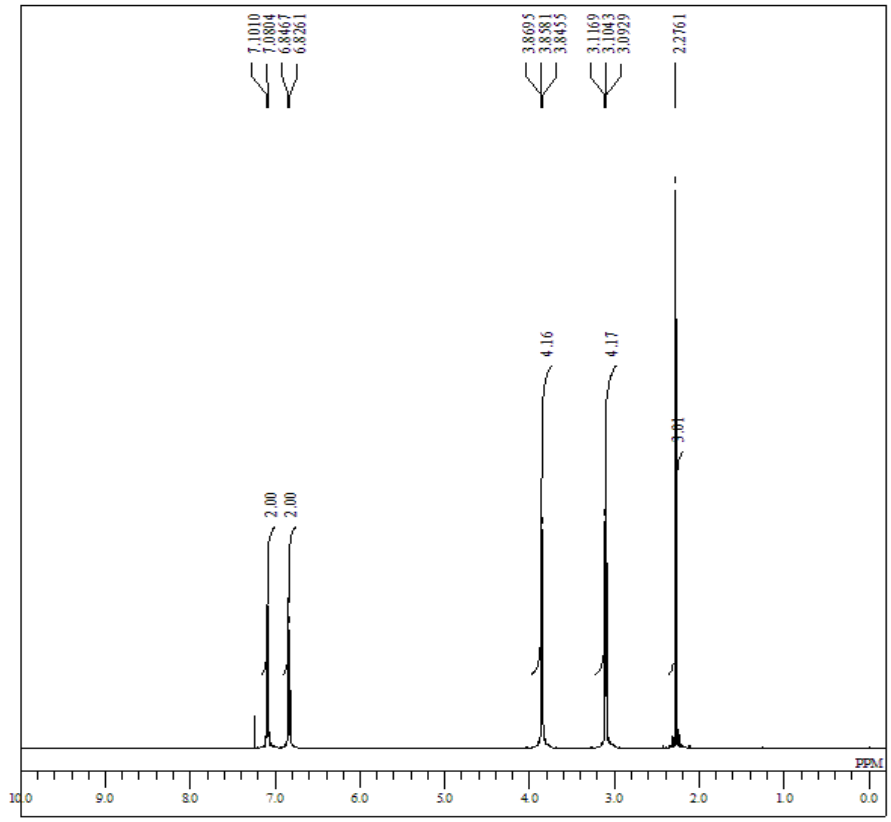


DFILE N-phenylmorphorine_yamada_Carbon-1-1
COMNT single pulse decoupled gated NOE
DATIM 2021-04-01 02:30:28
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1024
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 20.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50



***N*-phenylmorphorine (3ea)**

single_pulse

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OBNUC   1H
EXMOD   proton.jxp
OBFRQ     399.78 MHz
OBSET       4.19 KHz
OBFIN       7.29 Hz
POINT      13107
FREQU    6002.40 Hz
SCANS         8
ACQTM     2.1837 sec
PD        5.0000 sec
PW1       6.40 usec
IRNUC   1H
CTEMP      19.7 c
SLVNT   CDCL3
EXREF      0.00 ppm
BF         0.12 Hz
RGAIN        34
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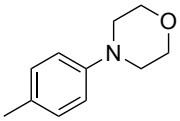
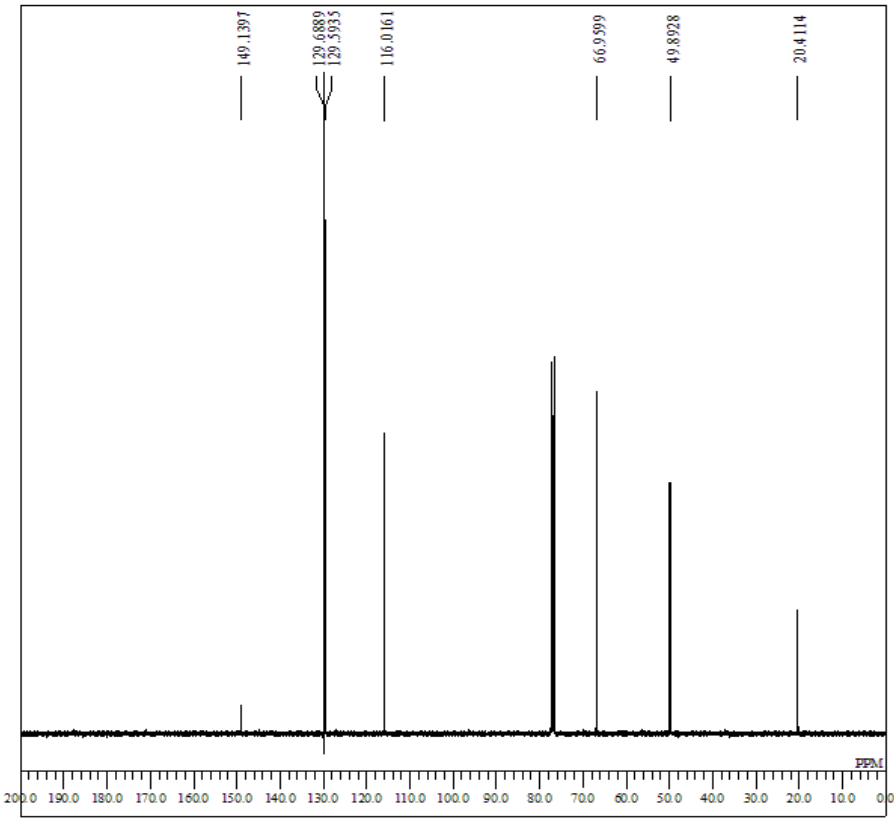


***N*-(4-tolyl)morphorine (3fa)**

single pulse decoupled gated NOE

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COMNT   single pulse decoupled gated NOE
DATIM   2021-04-21 17:39:60
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ     100.53 MHz
OBSET       5.35 KHz
OBFIN       5.86 Hz
POINT      26214
FREQU    25125.63 Hz
SCANS       1024
ACQTM     1.0433 sec
PD        2.0000 sec
PW1       2.87 usec
IRNUC   1H
CTEMP      20.2 c
SLVNT   CDCL3
EXREF      77.00 ppm
BF         0.12 Hz
RGAIN        50
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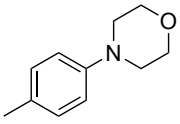
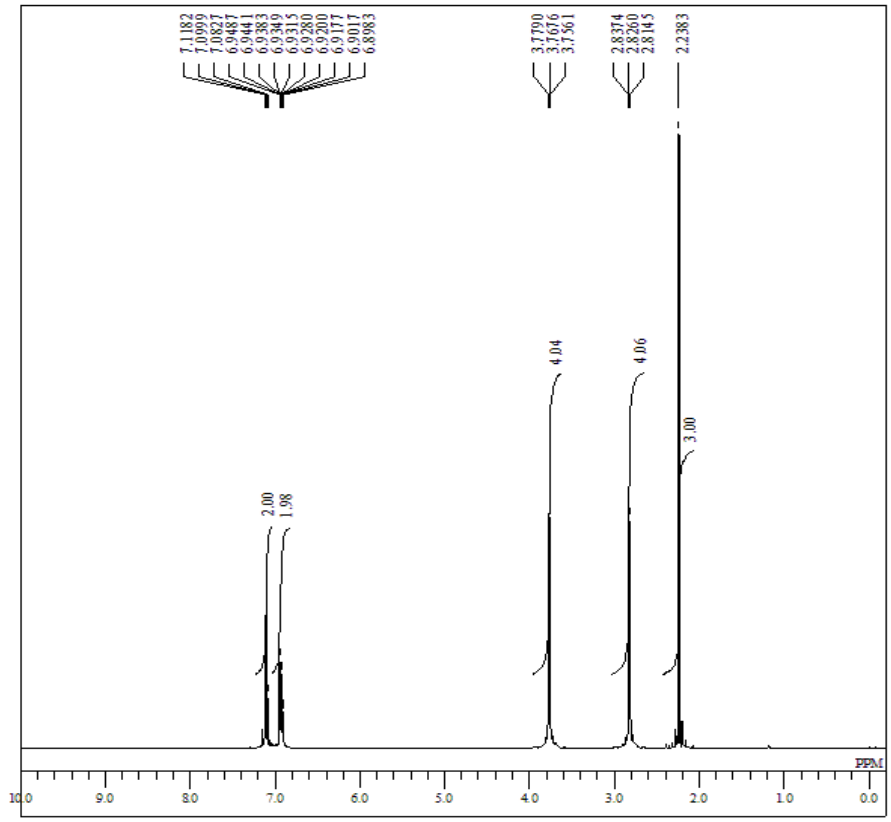
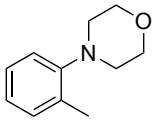


***N*-(4-tolyl)morphorine (3fa)**

single_pulse

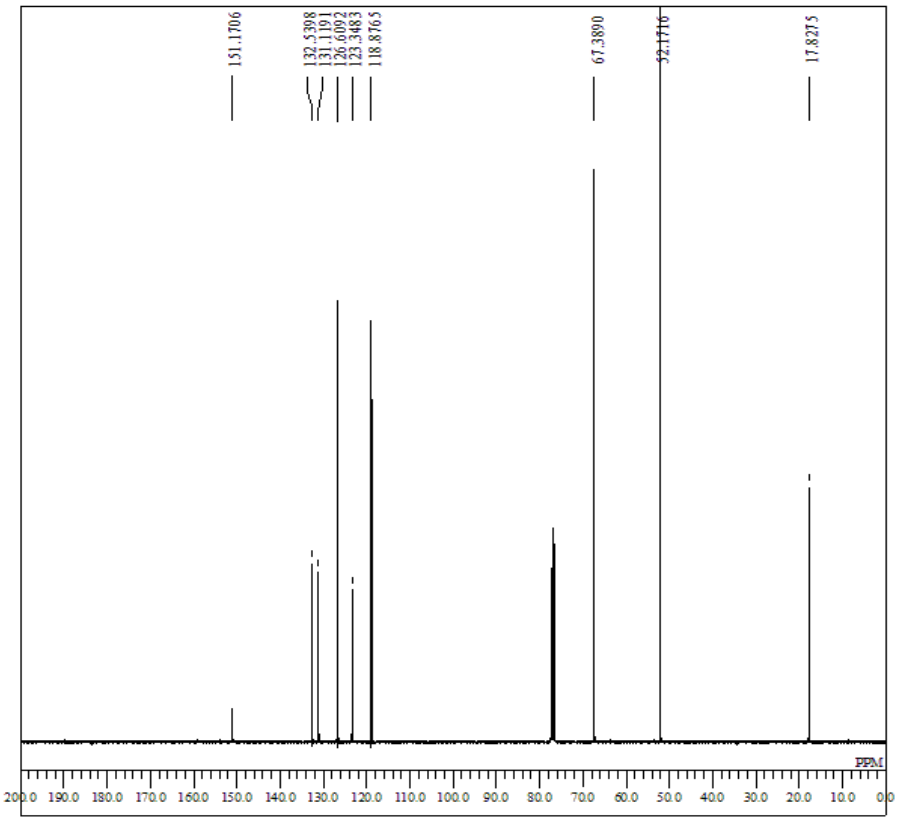


DFILE N-(2-tolyl)morpholine_yamada_Proton-1-
COMNT single_pulse
DATIM 2021-04-22 20:50:45
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 28

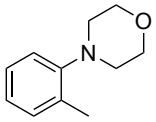


***N*-(2-tolyl)morphorine (3ga)**

single pulse decoupled gated NOE

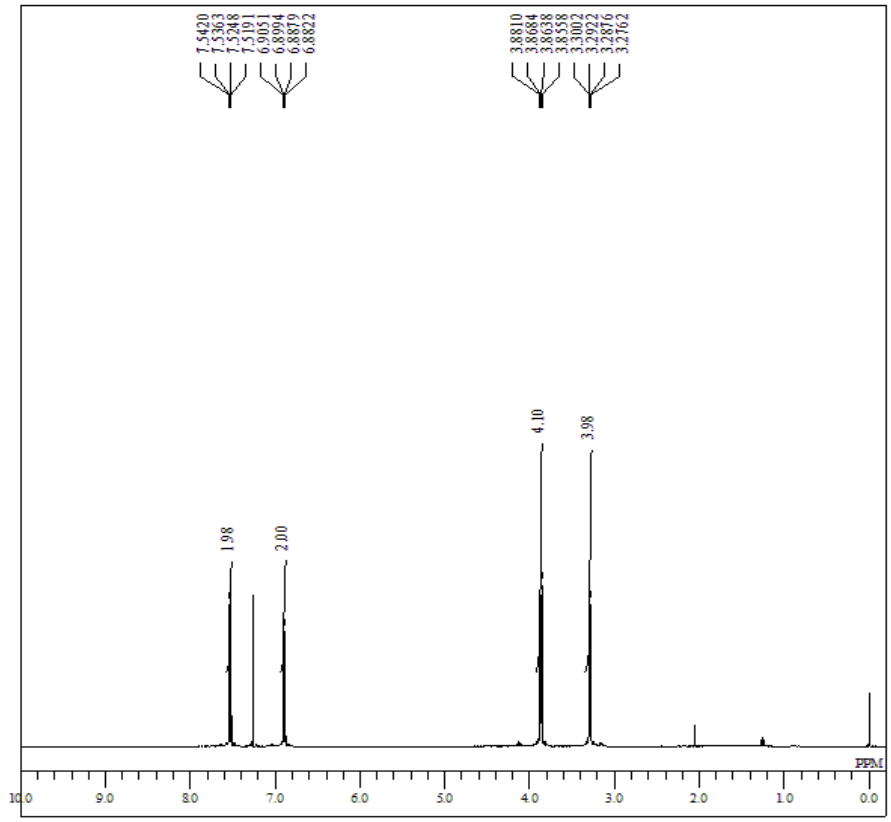


DFILE N-(2-tolyl)morpholine_yamada_Carbon-1-
COMNT single pulse decoupled gated NOE
DATIM 2021-04-22 20:52:10
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1024
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50

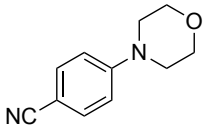


***N*-(2-tolyl)morphorine (3ga)**

single_pulse

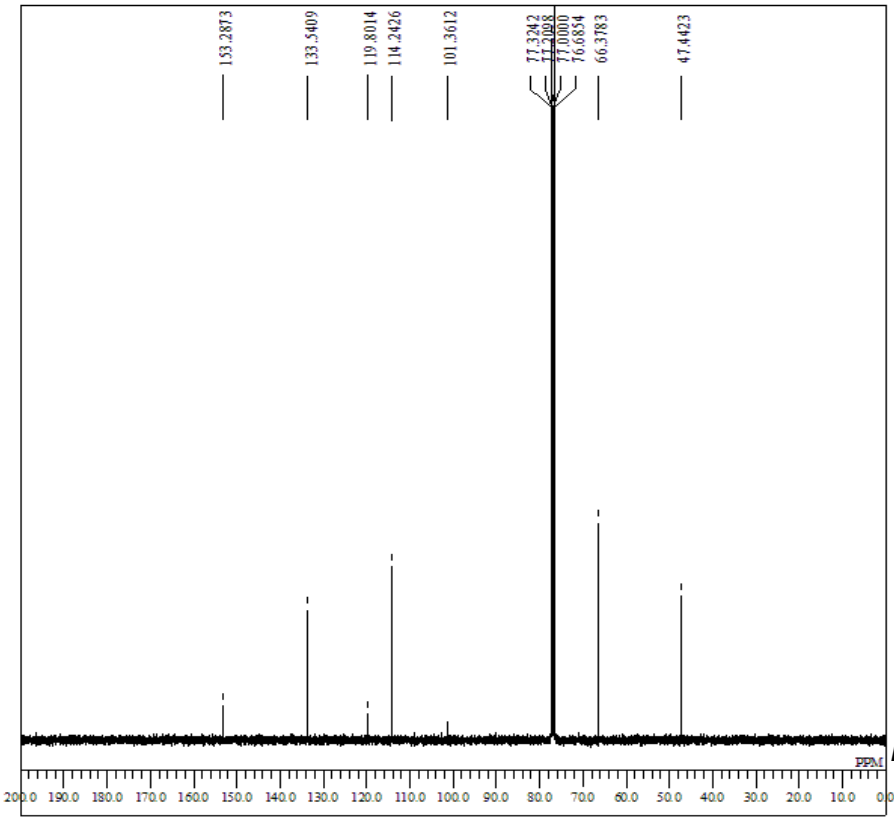


DFILE 4-cyanomorphorine_yamada_Proton-1-1.a
COMNT single_pulse
DATIM 2021-04-13 13:45:24
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 19.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 48

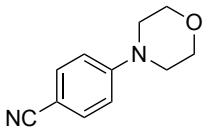


***N*-(4-cyano)morphorine (3ha)**

single pulse decoupled gated NOE

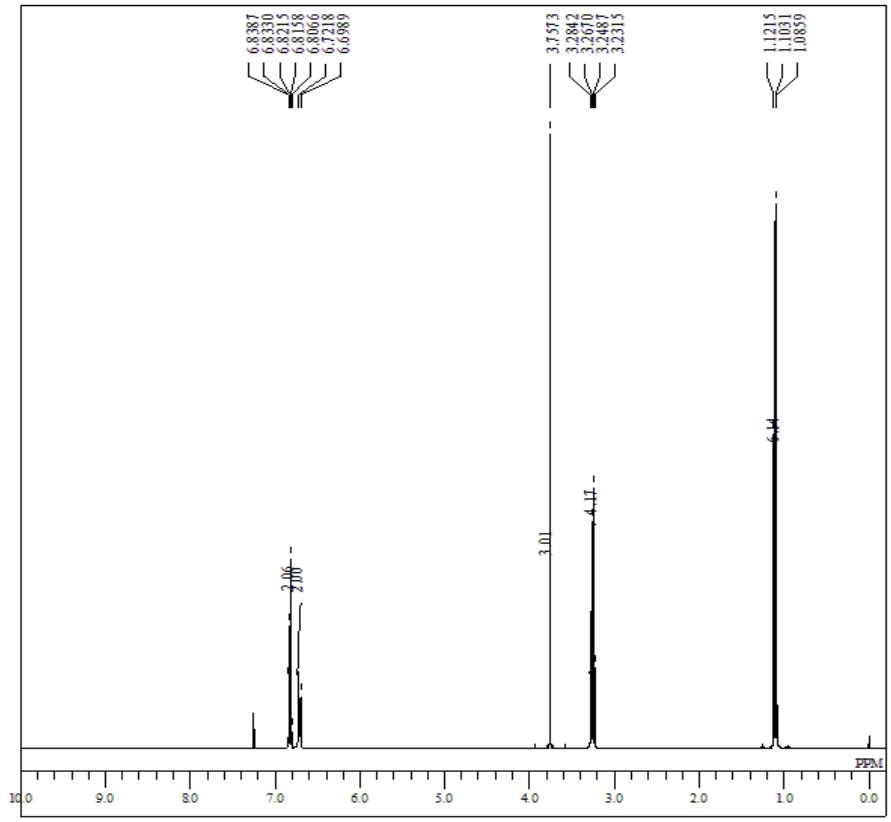


DFILE 4-cyanophenylmorphorine_yamada_Carbo
COMNT single pulse decoupled gatedNOE
DATIM 2021-04-13 13:58:04
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1024
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50

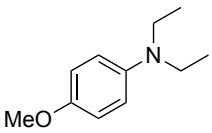


***N*-(4-cyano)morphorine (3ha)**

single_pulse

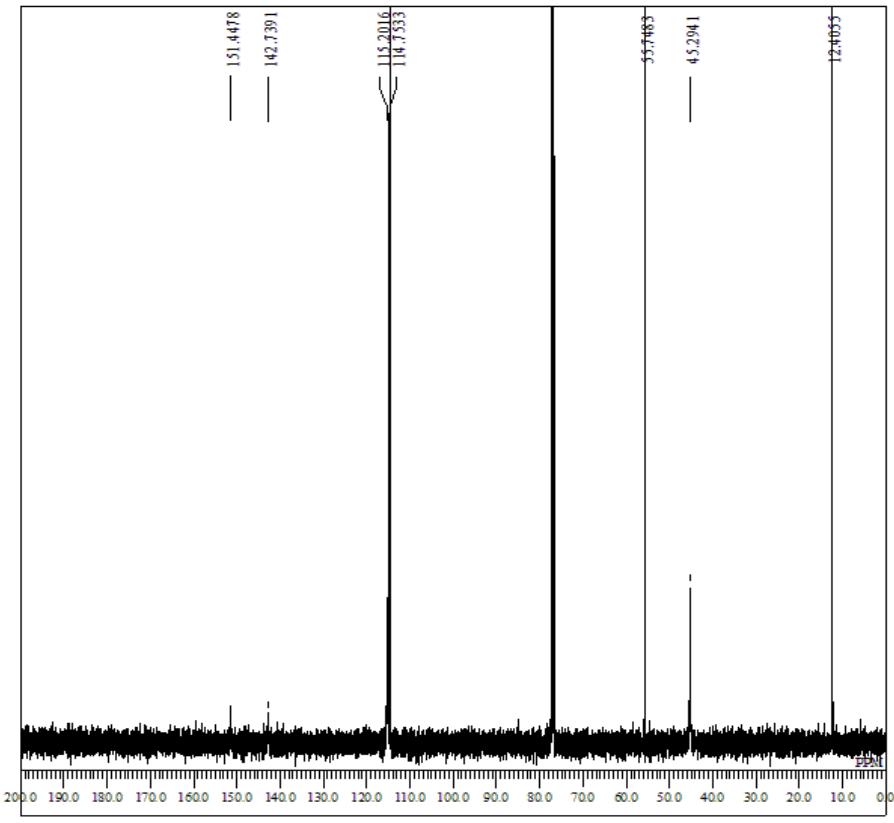


DFILE NN-diethyl-4-anisidine_product_yamada_
COMNT single_pulse
DATIM 2021-01-22 10:12:10
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 20.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 34

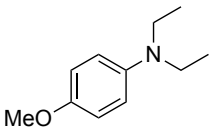


***N,N*-diethyl-4-anisidine (3ab)**

single pulse decoupled gated NOE

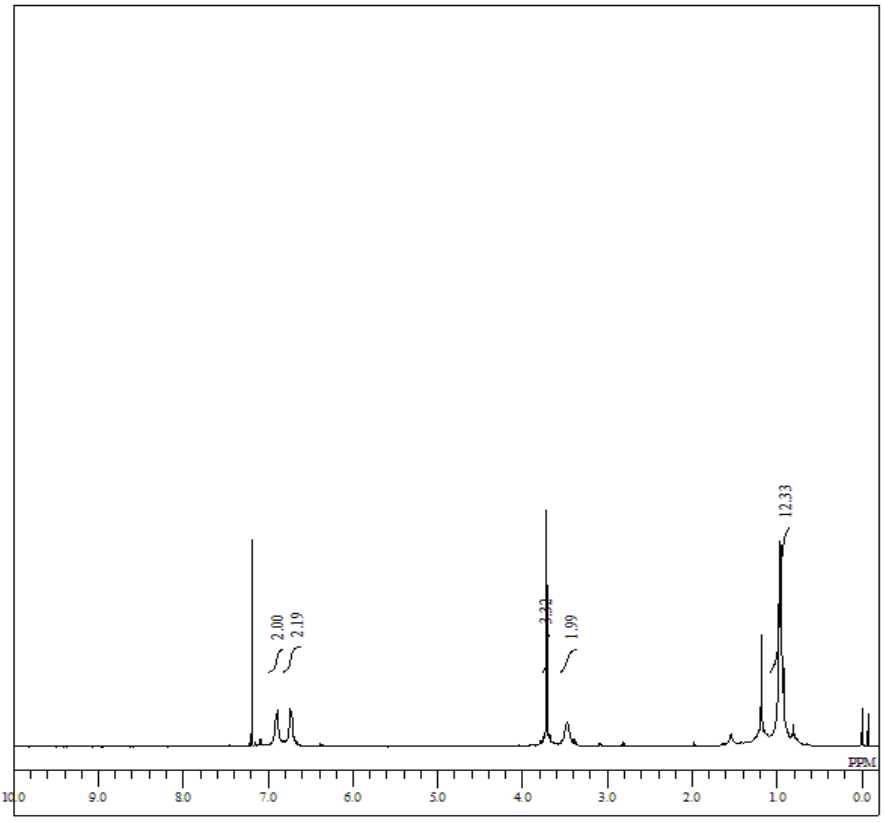


DFILE NN-diethyl-4-anisidine_yamada_Carbon-
COMNT single pulse decoupled gated NOE
DATIM 2021-04-28 02:13:50
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.54 Hz
SCANS 1024
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.27 usec
IRNUC 1H
CTEMP 17.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50

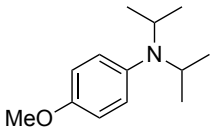


***N,N*-diethyl-4-anisidine (3ab)**

single_pulse

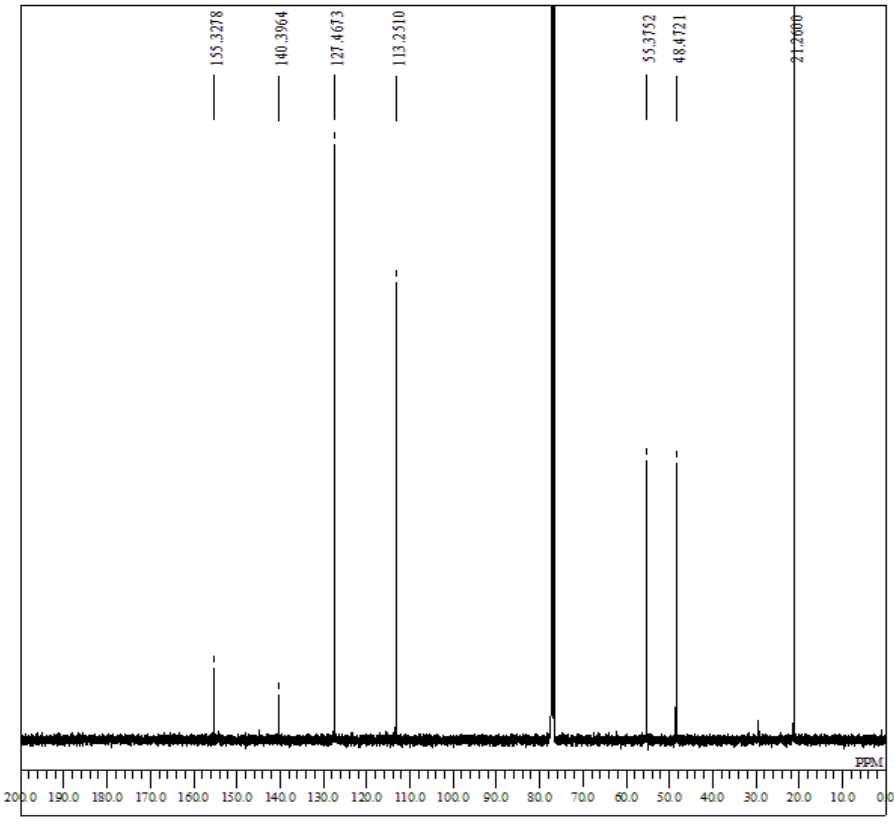



```
DFILE    NN-diisopropyl-4-anisidine_yamada_Prot
COMNT    single_pulse
DATIM    2021-04-14 22:52:07
OBNUC    1H
EXMOD    proton.jxp
OBFRQ      399.78 MHz
OBSET        4.19 KHz
OBFIN        7.29 Hz
POINT       13107
FREQU     6002.40 Hz
SCANS           8
ACQTM      2.1837 sec
PD         5.0000 sec
PW1           6.40 usec
IRNUC    1H
CTEMP       19.8 c
SLVNT    CDCL3
EXREF       0.00 ppm
BF           0.12 Hz
RGAIN          44
```

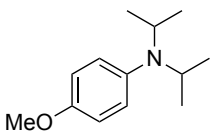


***N,N*-diisopropyl-4-anisidine (3ac)**

single pulse decoupled gated NOE

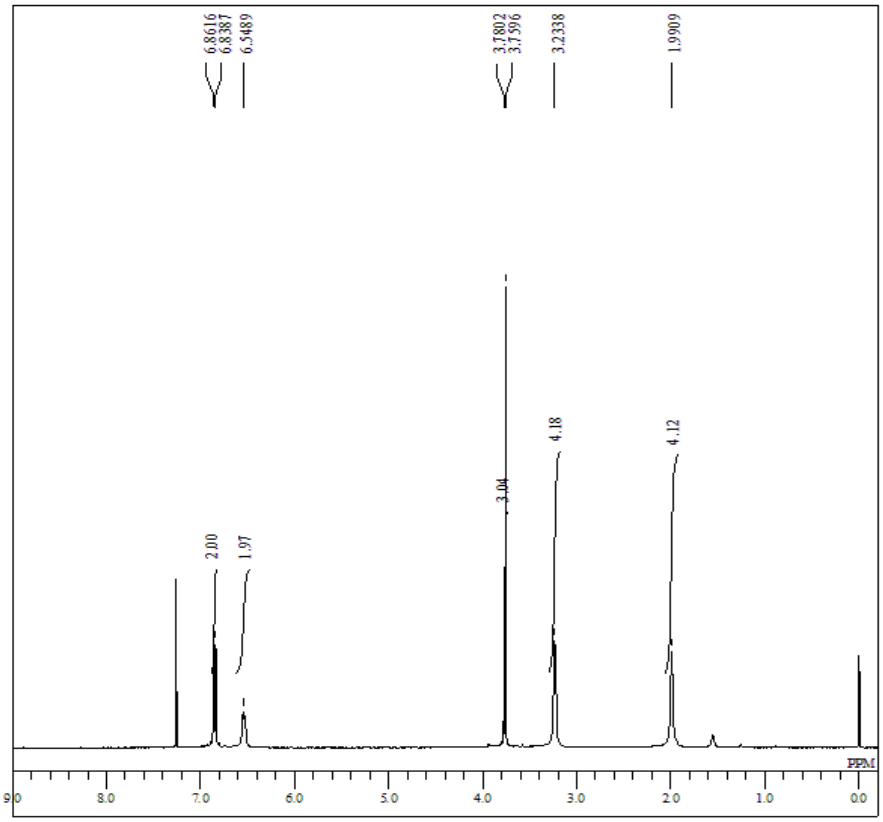



```
DFILE    NN-diisopropyl-4-anisidine_yamada_Carl
COMNT    single pulse decoupled gated NOE
DATIM    2021-05-10 00:49:04
OBNUC    13C
EXMOD    carbon.jxp
OBFRQ      100.53 MHz
OBSET        5.35 KHz
OBFIN        5.86 Hz
POINT       26214
FREQU     25125.63 Hz
SCANS        2048
ACQTM      1.0433 sec
PD         2.0000 sec
PW1           2.87 usec
IRNUC    1H
CTEMP       20.2 c
SLVNT    CDCL3
EXREF       77.00 ppm
BF           0.12 Hz
RGAIN          50
```

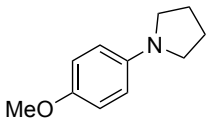


***N,N*-diisopropyl-4-anisidine (3ac)**

single_pulse

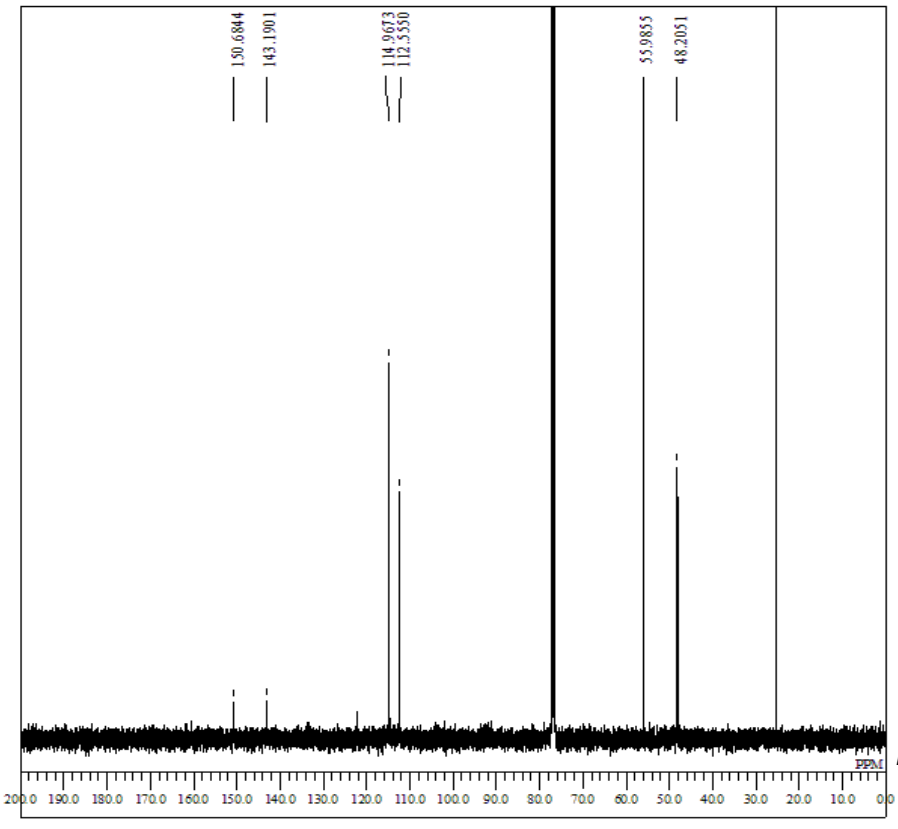


DFILE N-(4-anisyl)pyrrolidine_product_yamada_
COMNT single_pulse
DATIM 2021-01-19 00:18:21
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 20.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50

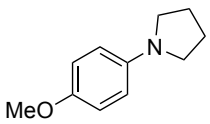


***N*-(4-anisyl)pyrrolidine (3ad)**

single pulse decoupled gated NOE

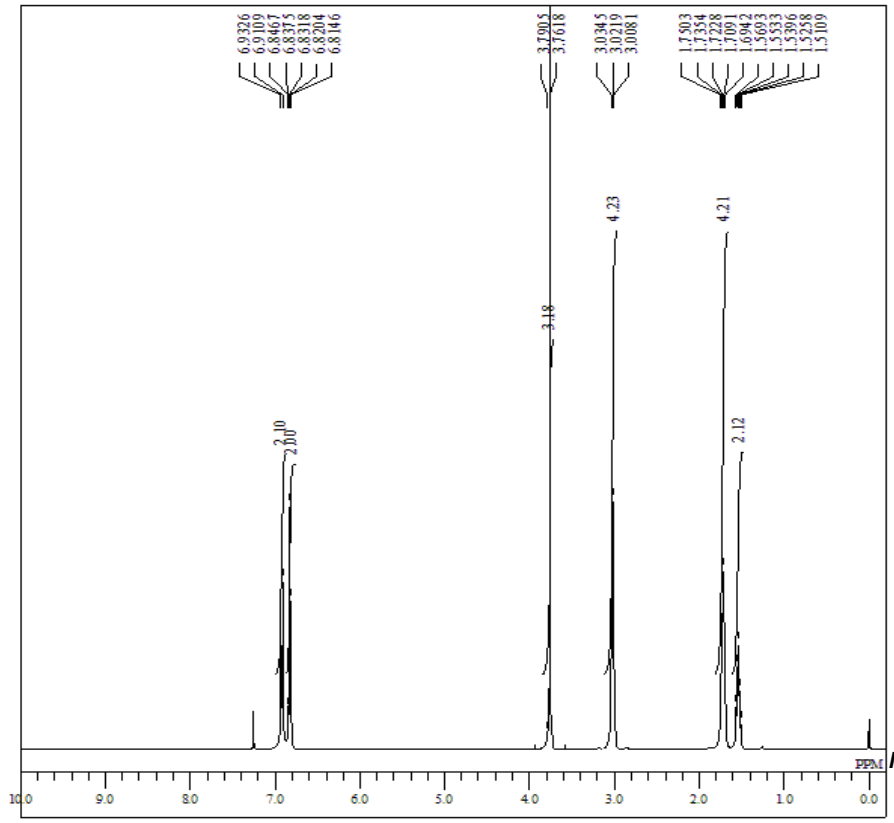


DFILE N-(4-anisyl)pyrrolidine_yamada_Carbon-1-
COMNT single pulse decoupled gated NOE
DATIM 2021-05-01 11:24:25
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1024
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 20.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50

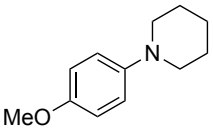


***N*-(4-anisyl)pyrrolidine (3ad)**

single_pulse

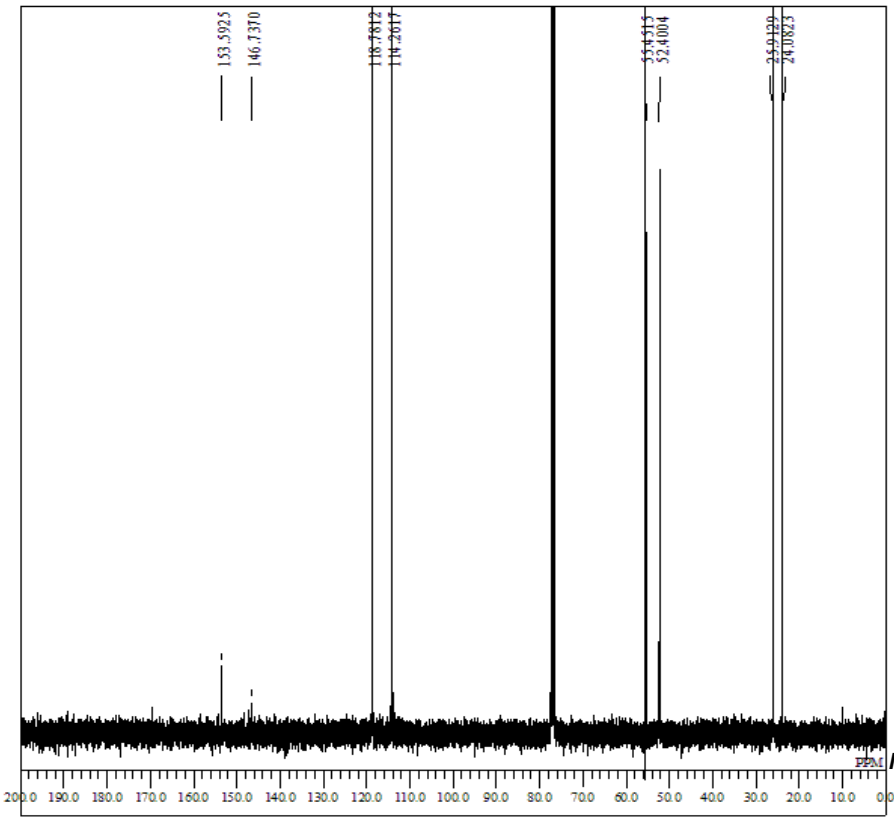


DFILE N-(4-anisyl)piperidine_yamada_Proton-1-
COMNT single_pulse
DATIM 2021-01-29 16:34:46
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 20.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 34

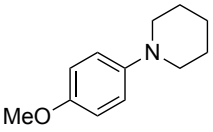


***N*-(4-anisyl)piperidine (3ae)**

single pulse decoupled gated NOE

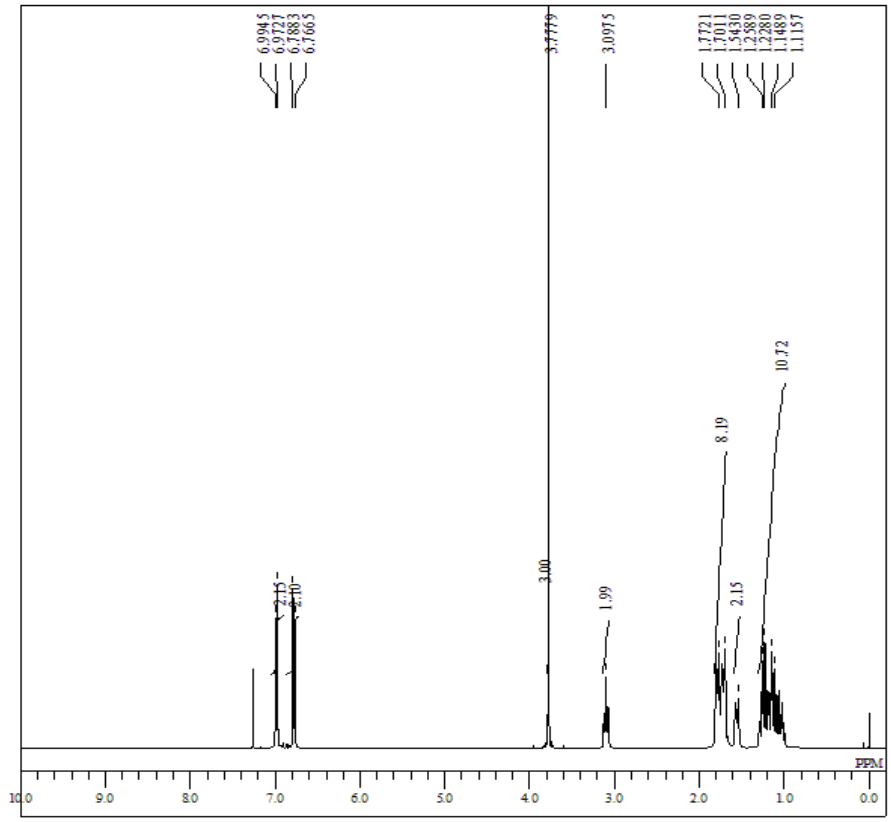


DFILE N-(4-anisyl)piperidine_yamada_Carbon-1-
COMNT single pulse decoupled gated NOE
DATIM 2021-04-22 13:42:12
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1024
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 20.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50

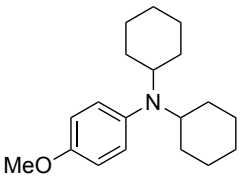


***N*-(4-anisyl)piperidine (3ae)**

single_pulse

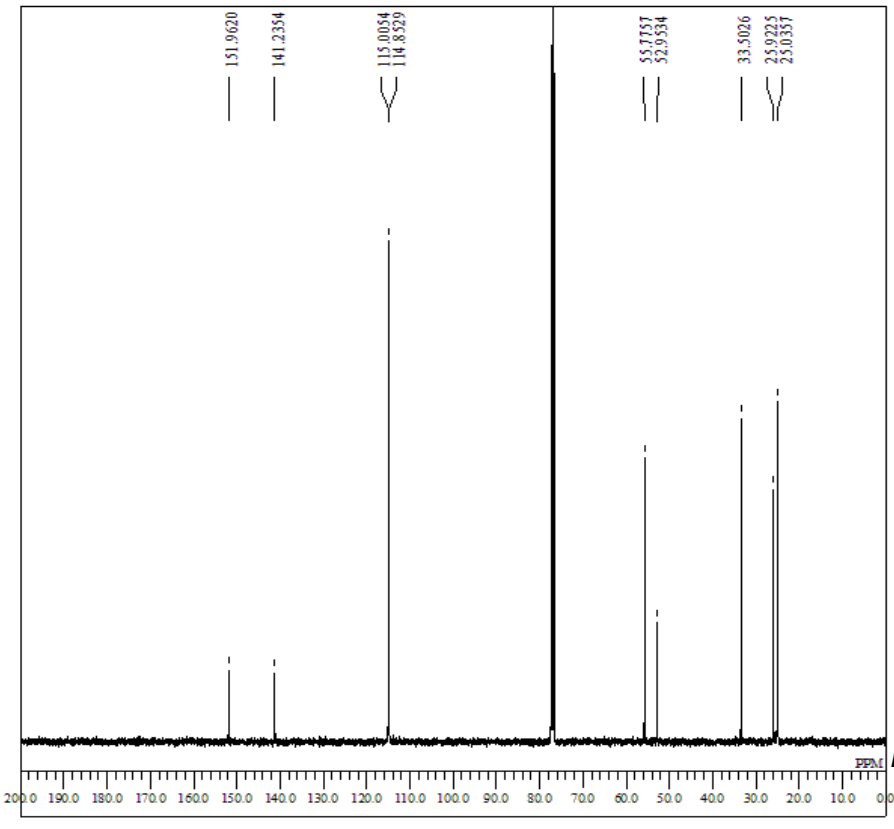


DFILE NN-dicyclohexyl-4-anisidine_yamada_Pr
COMNT single_pulse
DATIM 2021-01-19 23:37:37
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 36

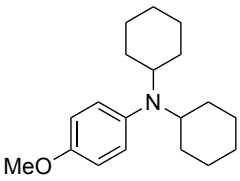


***N,N*-dicyclohexyl-4-anisidine (3af)**

single pulse decoupled gated NOE

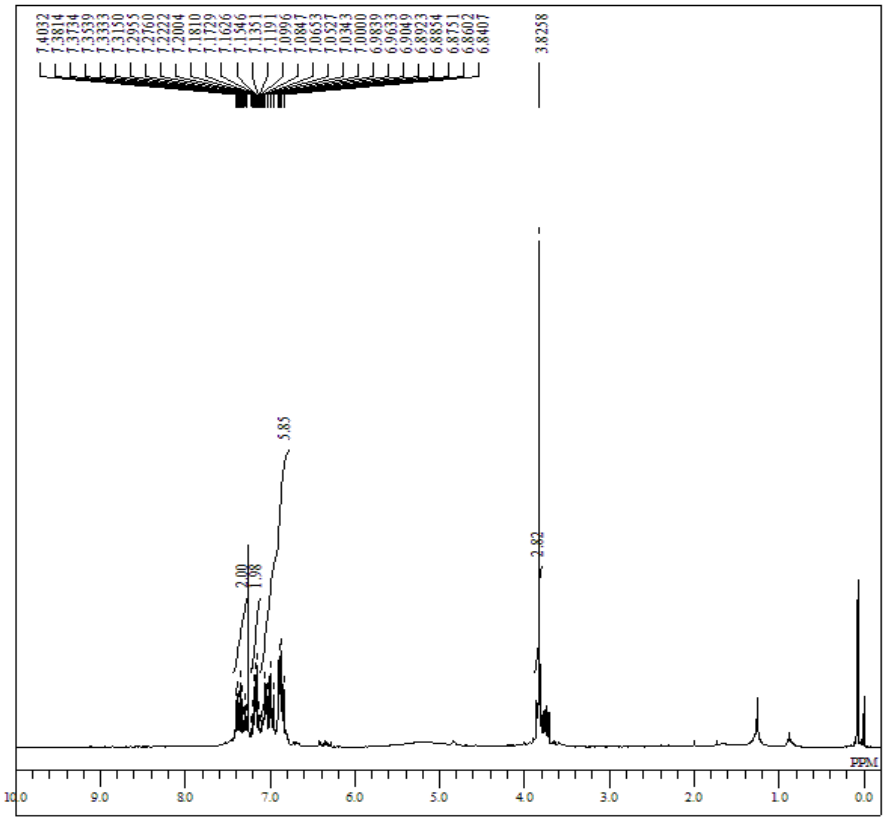


DFILE NN-dicyclohexyl-4-anisidine_yamada_Ca
COMNT single pulse decoupled gated NOE
DATIM 2021-04-09 21:56:44
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1024
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 20.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50

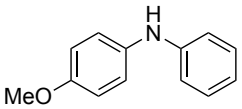


***N,N*-dicyclohexyl-4-anisidine (3af)**

single_pulse

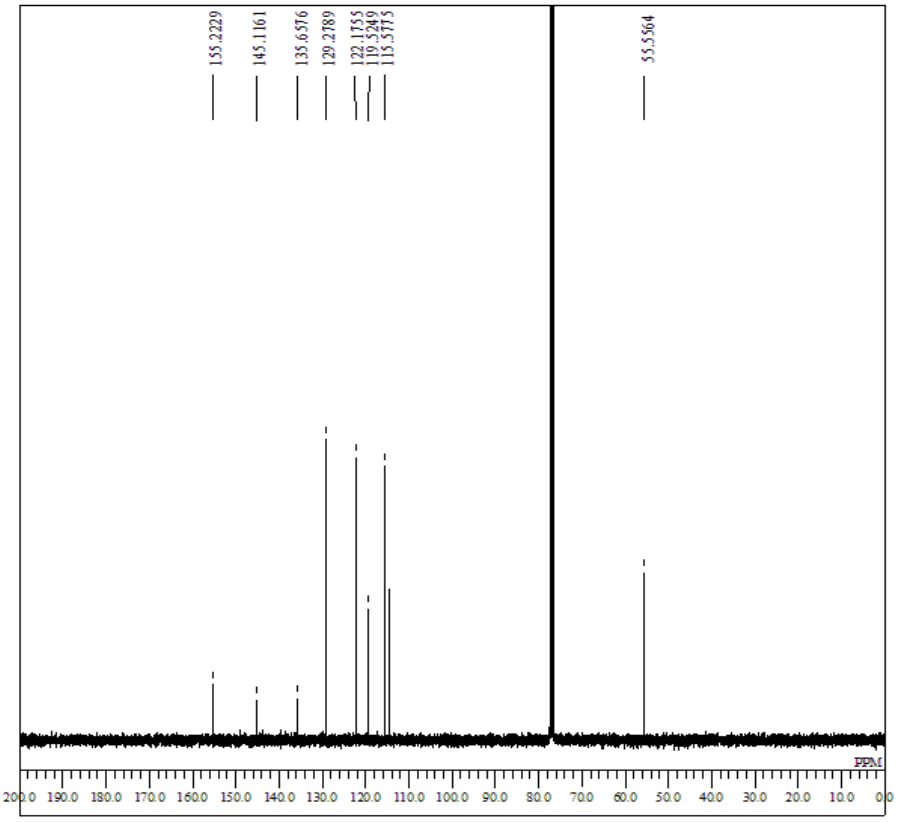


DFILE N-phenyl-4-anisidine_yamada_Proton-1-1.
COMNT single_pulse
DATIM 2021-04-11 19:29:32
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 19.6 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 1.20 Hz
RGAIN 46

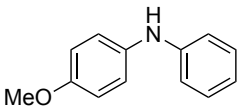


***N*-phenyl-4-anisidine (3ag)**

single pulse decoupled gated NOE

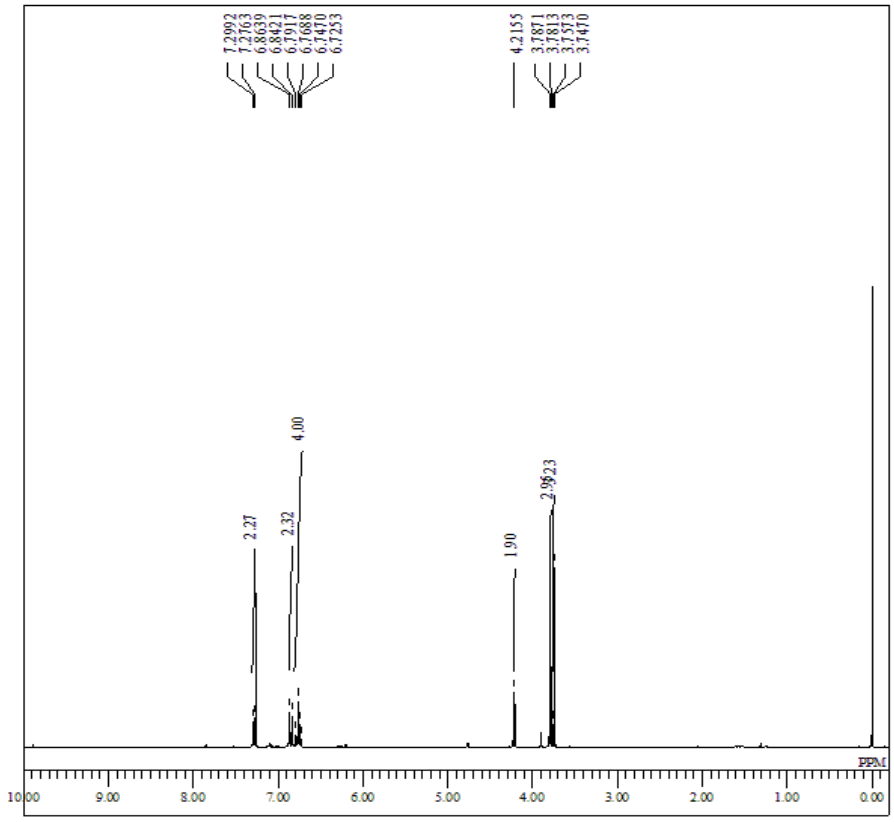


DFILE N-(4-anisyl)aniline_yamada_Carbon-1-1.a
COMNT single pulse decoupled gated NOE
DATIM 2021-05-09 17:24:15
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1024
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50

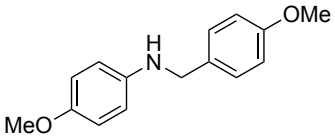


***N*-phenyl-4-anisidine (3ag)**

single_pulse

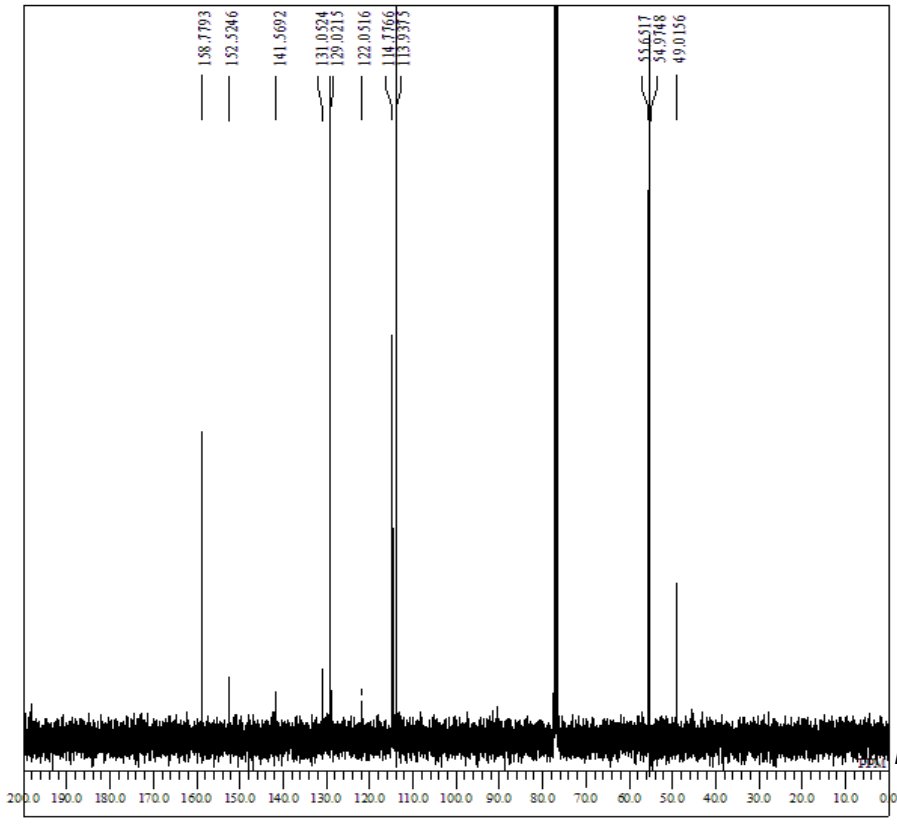



```
DFILE   N-(4-methoxybenzyl)-4-anisidine_yamada
COMNT   single_pulse
DATIM   2021-01-08 14:12:00
OBNUC   1H
EXMOD   proton.jxp
OBFRQ     399.78 MHz
OBSET       4.19 KHz
OBFIN       7.29 Hz
POINT      13107
FREQU    6002.40 Hz
SCANS         8
ACQTM     2.1837 sec
PD        5.0000 sec
PW1         6.40 usec
IRNUC   1H
CTEMP      20.3 c
SLVNT   CDCL3
EXREF      0.00 ppm
BF         0.12 Hz
RGAIN        50
```

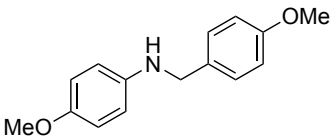


***N*-(4-methoxybenzyl)-4-anisidine (3ah)**

single pulse decoupled gated NOE

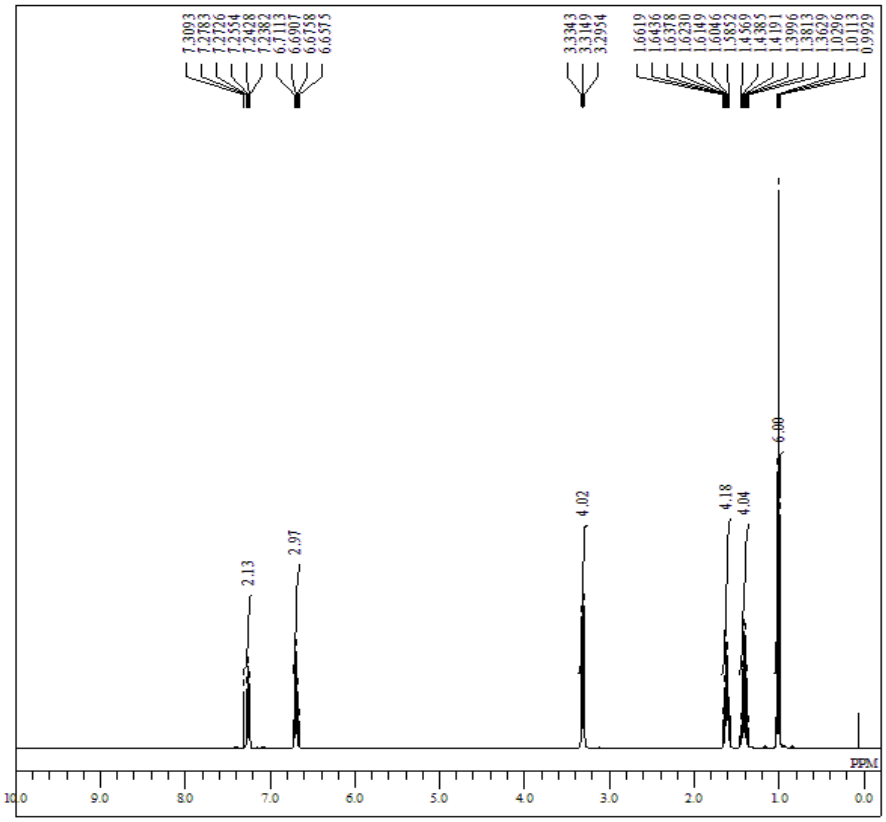



```
DFILE   N-(4-methoxybenzyl)-4-anisidine_yamada
COMNT   single pulse decoupled gated NOE
DATIM   2021-04-23 05:03:57
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ     100.53 MHz
OBSET       5.35 KHz
OBFIN       5.86 Hz
POINT      26214
FREQU    25125.63 Hz
SCANS       1024
ACQTM     1.0433 sec
PD        2.0000 sec
PW1         2.87 usec
IRNUC   1H
CTEMP      20.0 c
SLVNT   CDCL3
EXREF     77.00 ppm
BF         0.12 Hz
RGAIN        50
```

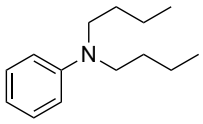


***N*-(4-methoxybenzyl)-4-anisidine (3ah)**

single_pulse

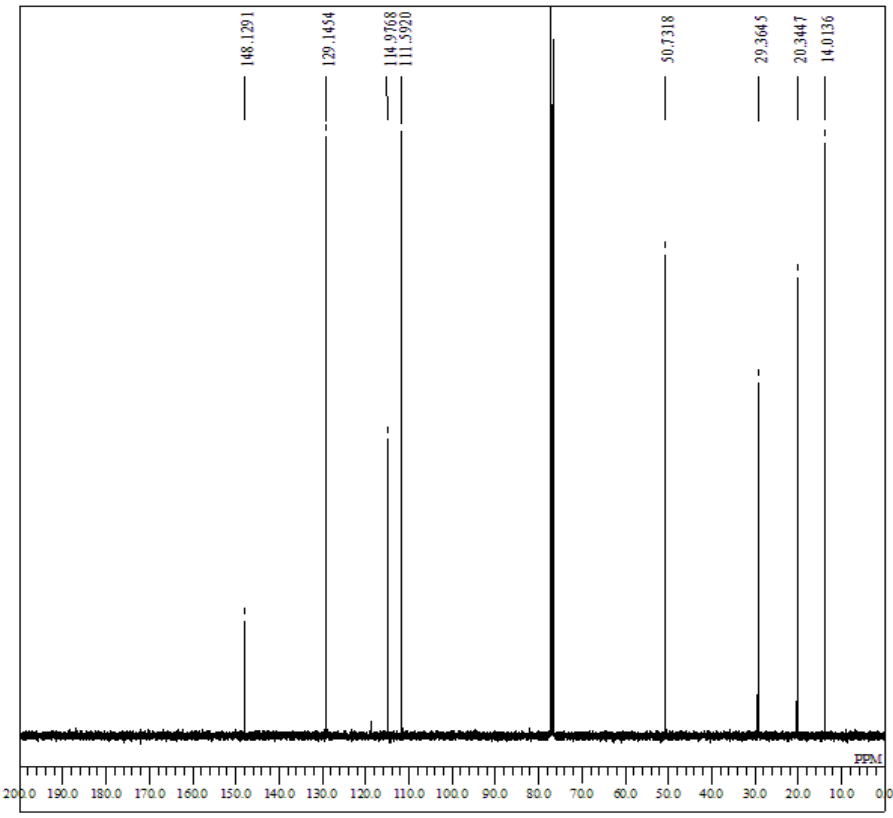


DFILE NN-dibutylaniline_yamada_Proton-1-1.al
COMNT single_pulse
DATIM 2021-04-01 00:22:52
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 19.8 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 36

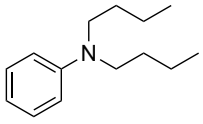


***N,N*-dibutylaniline (3ei)**

single pulse decoupled gated NOE

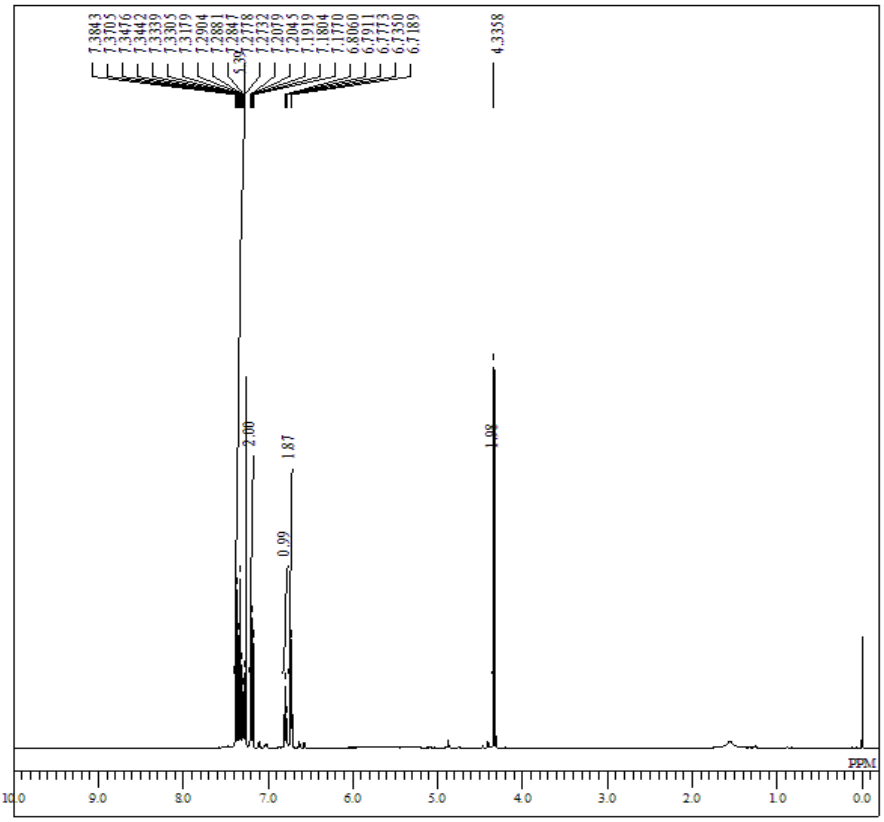


DFILE NN-dibutylaniline_yamada_Carbon-1-1.a
COMNT single pulse decoupled gated NOE
DATIM 2021-04-01 01:32:42
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1024
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 20.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50

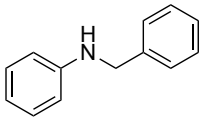


***N,N*-dibutylaniline (3ei)**

single_pulse

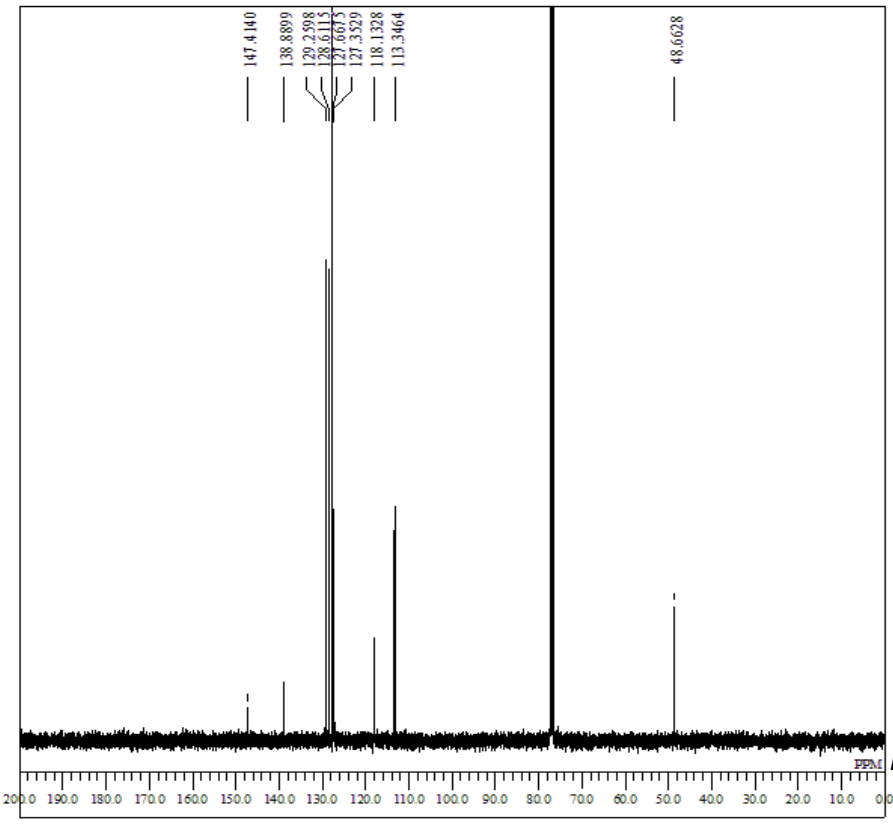


DFILE N-benzylaniline_yamada_Proton-1-1.als
COMNT single_pulse
DATIM 2021-03-23 22:56:34
OBNUC 1H
EXMOD proton.jxp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.51 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 18.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50

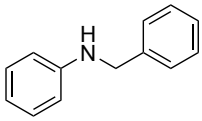


***N*-benzylaniline (3ej)**

single pulse decoupled gated NOE

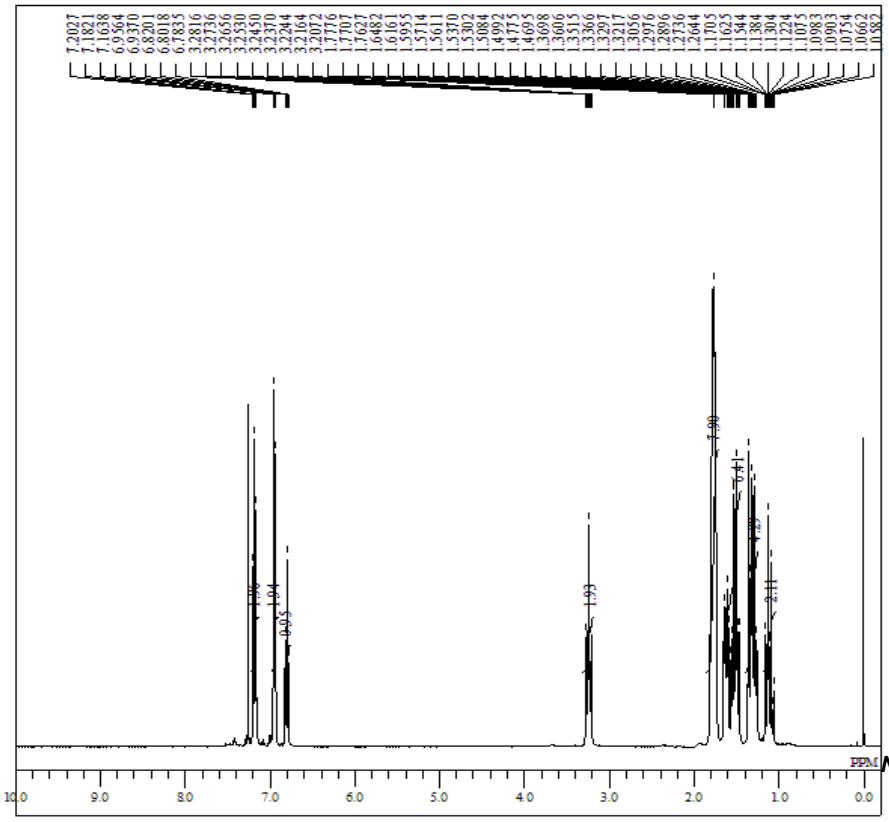


DFILE N-benzylaniline_yamada_Carbon-1-2.als
COMNT single pulse decoupled gated NOE
DATIM 2021-04-21 07:05:11
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1024
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 20.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50

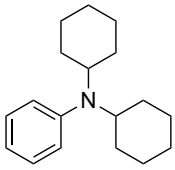


***N*-benzylaniline (3ej)**

single_pulse

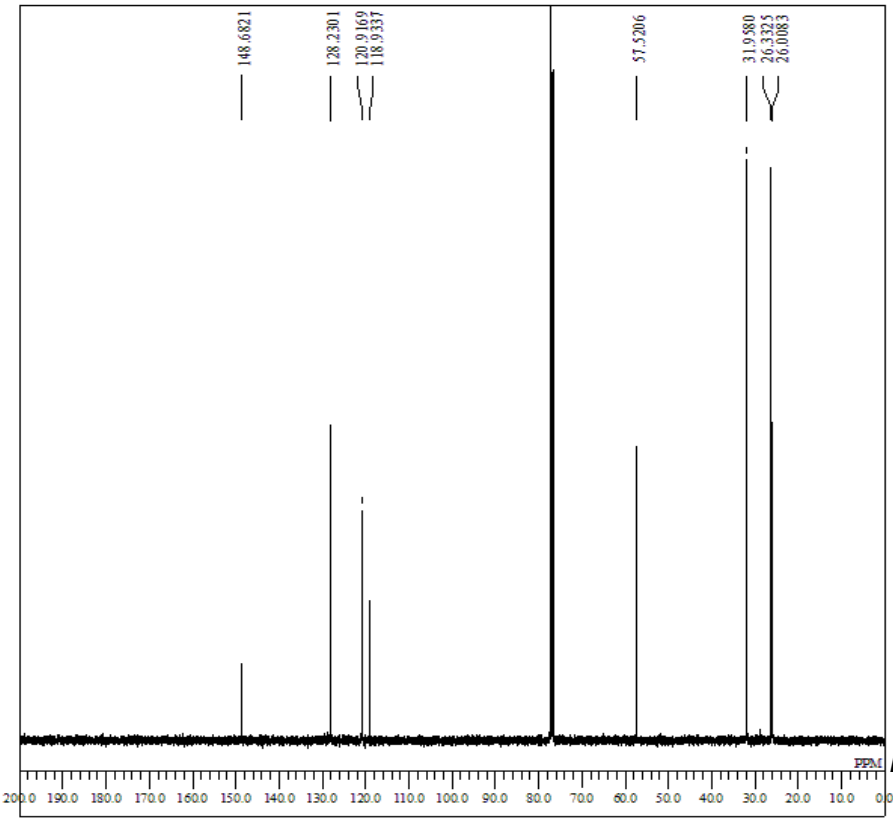


DFILE NN-dicyclohexylaniline_yamada_Proton-
COMNT single_pulse
DATIM 2021-04-01 00:15:55
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 19.7 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 36

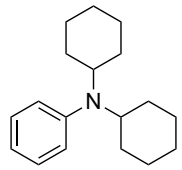


***N,N*-dicyclohexylaniline (3ef)**

single pulse decoupled gated NOE

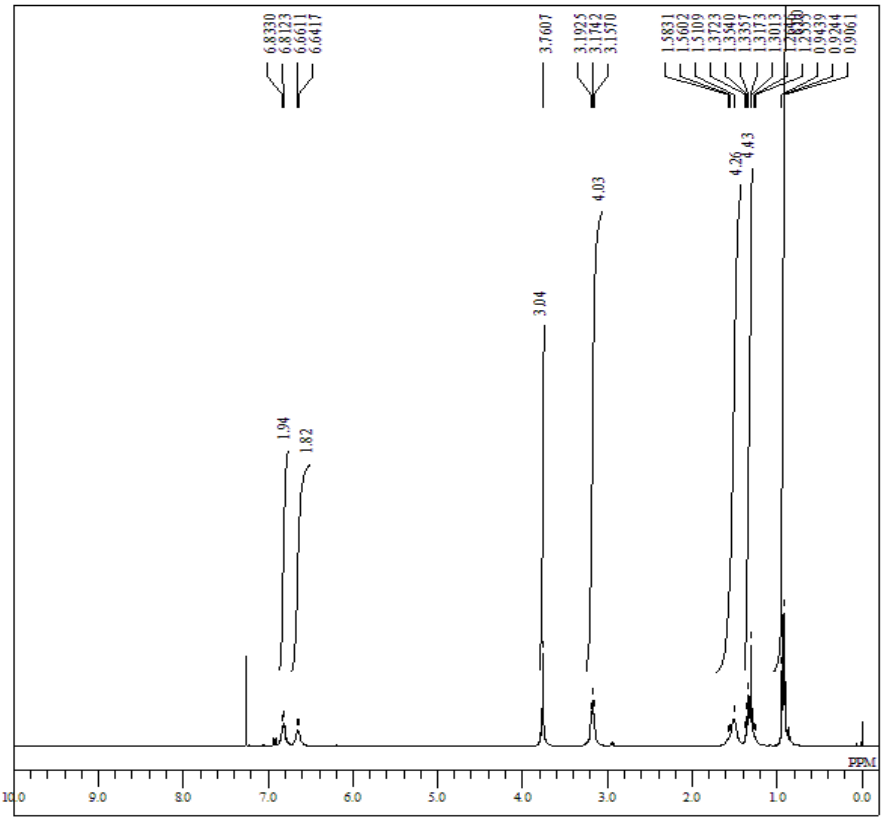


DFILE NN-dicyclohexylaniline_yamada_Carbon-
COMNT single pulse decoupled gated NOE
DATIM 2021-04-23 06:03:58
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1024
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 20.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50

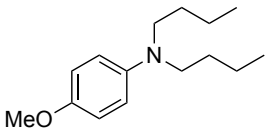


***N,N*-dicyclohexylaniline (3ef)**

single_pulse

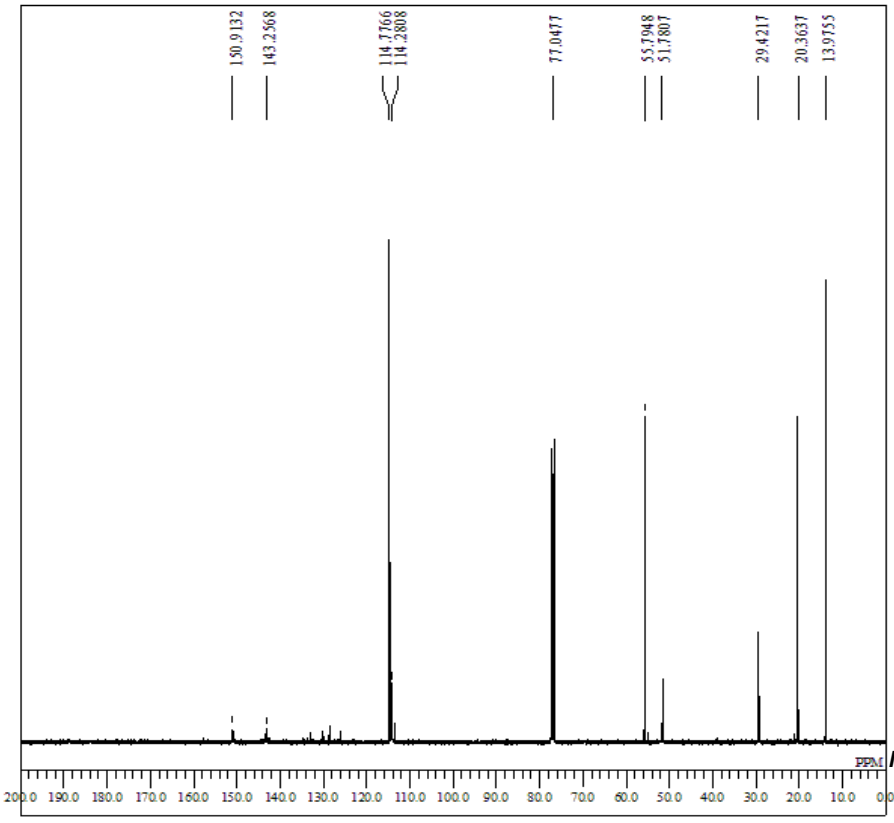


DFILE N-anisyl-dibutylamine_yamada_Proton-1-
COMNT single_pulse
DATIM 2021-04-16 22:37:25
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 19.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 42

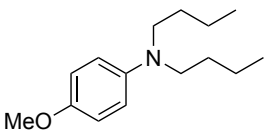


***N,N*-dibutyl-4-anisidine (3ai)**

single pulse decoupled gated NOE

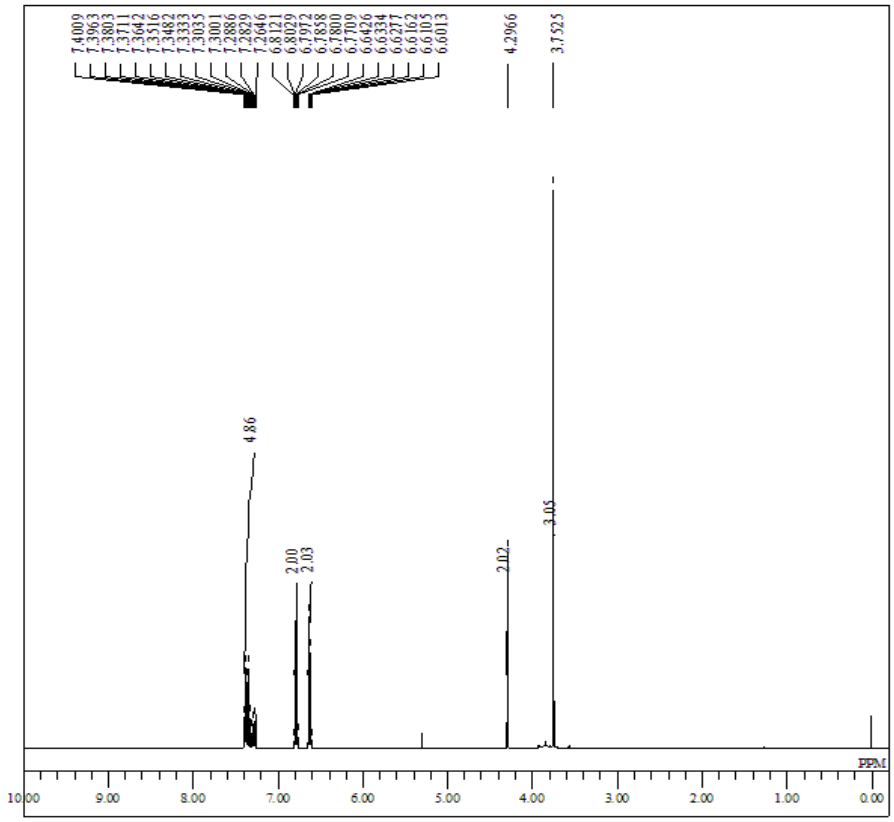


DFILE NN-dibutyl-4-anisidine_yamada_Carbon-
COMNT single pulse decoupled gated NOE
DATIM 2021-04-23 18:04:08
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1024
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 20.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50

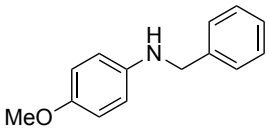


***N,N*-dibutyl-4-anisidine (3ai)**

single_pulse

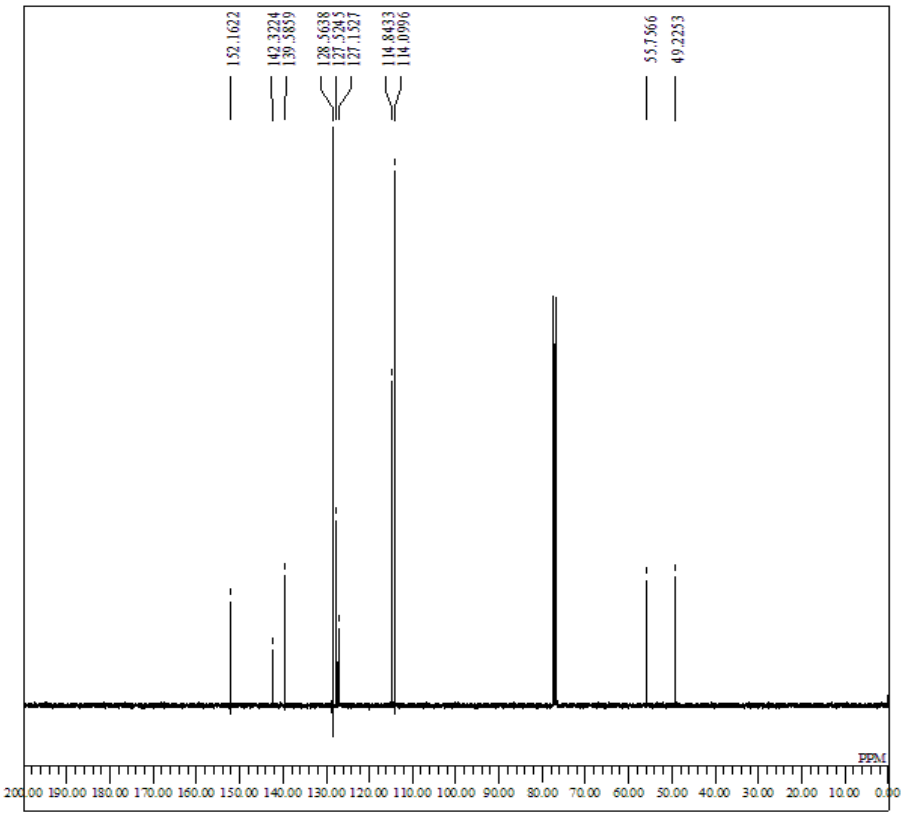


DFILE N-benzyl-4-anisidine_product_yamada_Pr
COMNT single_pulse
DATIM 2021-01-09 22:05:30
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 20.4 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 38

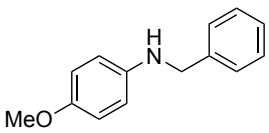


***N*-benzyl-4-anilsidine (3aj)**

single pulse decoupled gated NOE



DFILE N-benzyl-4-anisidine_product_yamada_Ca
COMNT single pulse decoupled gated NOE
DATIM 2021-01-09 22:17:11
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 1024
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50



***N*-benzyl-4-anilsidine (3aj)**

References

[1] E. O. Bortnikov, S. N. Semenov, *J. Org. Chem.* **2021**, *86*, 782-793.
[2] C. A. Malapit, M. Borrell, M. W. Milbauer, C. E. Brigham, M. S. Sanford, *J. Am. Chem. Soc.* **2020**, *142*, 5918-5923.
[3] M. Balkenhohl, B. Heinz, T. Abegg, P. Knochel, *Org. Lett.* **2018**, *20*, 8057-8060.
[4] A. Bismuto, T. Delcaillan, P. Müller, B. Morandi, *ACS Catal.* **2020**, *10*, 4630-4639.
[5] X. Zhu, L. Su, L. Huang, G. Chen, J. Wang, H. Song, Y. Wan, *Eur. J. Org. Chem*. **2009**, 635–642.
[6] L. H. Cretcher, W. H. Pittenger, *J. Am. Chem. Soc.* **1925**, *47*, 163–166.
[7] D. Jiang, H. Fu, Y. Jiang, Y. Zhao, *J. Org. Chem*. **2007**, *72*, 672–674.
[8] W. Liu, J. Xu, X. Chen, F. Zhang, Z. Xu, D. Wang, Y. He, X. Xia, X. Zang, Y. Liang, *Org. Lett.* **2020**, *22*, 7486-7490.
[9] J.-H. Huang, L.-M. Yang, *Org. Lett*. **2011**, *13*, 3750–3753.
[10] Y. Xu, Z. Zhang, C. Qiu, S. Chen, X. Ling, C. Su, *ChemSusChem.* **2020**, *14*, 582-589.
[11] N. Z. Yagafanov, P. N. Kolesnikov, D. L. Usanov, V. V. Novikov, Y. V. Nelyubina, D. Chusov, *Chem. Commun.* **2016**, *52*, 1397-1400.
[12] J. Tappen, I. Rodstein, K. McGuire, A. Großjohann, J. Löffler, T. Scherpf, V. Gessner, *Chem. Eur. J.* **2020**, *26*, 4281-4288.
[13] D. C. SamblanetJoseph, A. R. Schmidt, *J. Organomet. Chem.* **2012**, *720*, 7-18.
[14] Y.-B. Huang, C. Cai, *J. Chem. Res.* **2009**, 686-688.
[15] J. Kim, S. Kim, G. Choi, G. S. Lee, D. Kim, J. Choi, H. Ihee, S. H. Hong, *Chem. Sci.* **2021**, *12*, 1915-1923.
[16] L. Shi, M. Wang, C.-A. Fan, F.-M. Zhang, Y.-Q. Tu, *Org. Lett.* **2003**, *5*, 3515-3517.
[17] T. J. Barker, E. R. Jarvo, *J. Am. Chem. Soc.* **2009** *131*, 15598-15599.
[18] A. R. Phani, S. Manorama, *J. Phys. Chem. Solids* **2000**, *61*, 985-993.