Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information (ESI) for

Supported gold–palladium alloy nanoparticles catalyzed tandem oxidation routes to *N*-substituted anilines from non-aromatic compounds

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Full experimental details

Instrumental and reagents: GC analyses were performed on Shimadzu GC-2014 with a FID detector equipped with a InertCap5 and TC-1 capillary column. GC-MS spectra were recorded on Shimadzu GCMS-QP2010 equipped with a InertCap5 capillary column at an ionization voltage of 70 eV. Liquid-state ^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-ECA 500. ^{1}H and ^{13}C NMR were measured at 500 and 125 MHz, respectively, with TMS as an internal standard ($\delta = 0$ ppm). ICP-AES analyses were performed on Shimadzu ICPS-8100. TEM measurements were performed on JEOL JEM-2010HC. HAADF-STEM and EDS images were obtained using a JEOL-ARM 200F instrument operating at 200 kV. TEM and STEM samples were prepared by placing a drop of the suspension on carbon-coated Cu grids and dried in air. Al_2O_3 (160 m^{2} g^{-1}, Cat. No. KHS-24, Sumitomo Chemical), TiO_2 (316 m^{2} g^{-1}, Cat. No. ST-01, Ishihara Sangyo Kaisya) were commercially available. Solvents and substrates (except for **10**) were obtained from Kanto Chemical, TCI, Wako, or Aldrich (reagent grade). Substrates **1b**–**1k** were mixtures of *cis* and *trans* isomers, and the *cis*/*trans* ratios were determined by ^{1}H NMR analyses; **1b** (*cis*:*trans* = 58:42), **1c** (*cis*:*trans* = 74:26), **1d** (*cis*:*trans* = 30:70), **1e** (*cis*:*trans* = 59:41), **1f** (*cis*:*trans* = 49:51), **1g** (*cis*:*trans* = 51:49), **1h** (*cis*:*trans* = 38:62), **1i** (*cis*:*trans* = 38:62), **1j** (*cis*:*trans* = 52:48), and **1k** (*cis*:*trans* = 46:54). Substrate **10** was synthesized by the reaction of cyclohexanone with isopropylamine (see: Y. Mao, E. Lobkovsky, D. B. Collum, *J. Org. Chem.* **2005**, 70, 2335.).

Preparation of catalysts: An aqueous solution of $HAuCl_4 \cdot 4H_2O$ and K_2PdCl_4 (6.67 mM and 1.67 mM, 60 mL) containing Al_2O_3 (2.0 g) was vigorously stirred at room temperature for 15 min. Then, the pH of the solution was adjusted to 10.0 by using an aqueous solution of NaOH (1.0 M). Then, the resulting slurry was further stirred for 24 h at room temperature, giving 2.0 g of the hydroxide precursor. By the reduction of the precursor with H_2 (1 atm) at 150 °C for 30 min, the supported gold–palladium bimetallic nanoparticles catalyst, Au–Pd/Al_2O_3, was obtained. The contents of gold and palladium in Au–Pd/Al_2O_3 were 0.137 mmol g^{-1} and 0.042 mmol g^{-1} (Au/Pd = 3.3), respectively (determined by ICP-AES). HAADF-STEM and EDS mapping analyses indicated that alloyed gold–palladium bimetallic nanoparticles were formed on the Al_2O_3 support (Fig. S1). It was confirmed by the TEM analysis that the average particle size of gold–palladium alloy nanoparticles was 1.7 nm (standard deviation: 0.4 nm, Fig. S2). The size distribution were determined using 200 particles.

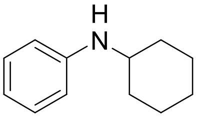
The supported gold catalyst Au/Al_2O_3 (Au: 0.158 mmol g^{-1}, average size: 3.2 nm) and palladium catalyst Pd/Al_2O_3 (Pd: 0.237 mmol g^{-1}, average size: 2.2 nm) were prepared by the same manner as that for Au–Pd/Al_2O_3. Other Au–Pd/Al_2O_3 catalysts with different Au/Pd molar ratios, *e.g.*, Au/Pd = 7.8 (Au: 0.180 mmol g^{-1}, Pd: 0.023 mmol g^{-1}), 0.64 (Au: 0.070 mmol g^{-1}, Pd: 0.109 mmol g^{-1}), and 0.16 (Au: 0.025 mmol g^{-1}, Pd: 0.155 mmol g^{-1}), and Au–Pd/TiO_2 (Au/Pd = 0.59, Au: 0.070 mmol g^{-1}, Pd: 0.118 mmol g^{-1}) were also prepared by the same manner.

Catalytic reaction: The catalytic reaction was typically carried out according to the following procedure. Into a Pyrex glass reactor (volume: ca. 20 mL) were successively placed Au–Pd/Al_2O_3 (Au: 1.15 mol%, Pd: 0.35 mol%), cyclohexylamine (**1**, 1.0 mmol), *n*-hexadecane (0.1 mmol, internal standard), mesitylene (2 mL), and a Teflon-coated magnetic stir bar, and then the mixture was stirred at 130 °C under open air (1 atm). The conversions and product yields were determined by GC analysis using *n*-hexadecane as an internal standard.

As for isolation of products, an internal standard was not added. After the reaction, the catalyst was removed by simple filtration (>90 % catalyst recovery), and then the filtrate was concentrated by evaporation of mesitylene. The crude product was subjected to column chromatography on silica gel (typically using hexane/diethyl ether as an eluent), giving the pure *N*-cyclohexylaniline. The products were identified by GC-MS and NMR (^{1}H and ^{13}C) analyses (see below). Compounds **2b**–**2k** were the mixtures of *cis* and *trans* isomers, and the *cis*/*trans* ratios were determined by GC and/or ^{1}H NMR analyses.

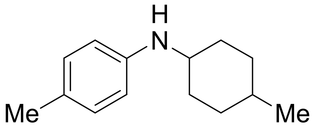
The retrieved Au–Pd/Al_2O_3 catalyst after the reaction was washed with chloroform and methanol, and calcined at 300 °C in air (1 atm) for 2 h. Then, the catalyst was treated at 150 °C in H_2 (1 atm) for 30 min before being used for the reuse experiment.

Spectral data of *N*-substituted anilines



2a

***N*-Cyclohexylaniline (2a):** colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C,TMS): δ = 7.16–7.11 (m, 2H), 6.64 (tt, J = 7.5 and 1.0 Hz, 1H), 6.56 (m, 2H), 3.47 (brs, 1H), 3.26–3.20 (m, 1H), 2.05–2.02 (m, 2H), 1.77–1.72 (m, 2H), 1.66–1.61 (m, 1H), 1.39–1.31 (m, 2H), 1.26–1.08 (m, 3H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 25 °C,TMS): δ = 147.7, 129.5, 117.1, 113.4, 51.9, 33.8, 26.2, 25.3; MS (70 eV, EI): *m/z* (%): 175 (37) [M^+], 176 (5), 146 (5), 133 (13), 132 (100), 119 (13), 118 (15), 117 (9), 106 (8), 93 (11), 91 (5), 77 (9).

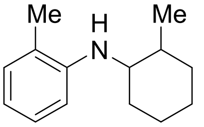


2b

4-Methyl-*N*-(4-methylcyclohexyl)benzenamine (2b, *cis*:*trans* = 39:61): colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): δ = 6.97–6.94 (m, 2H), 6.54–6.49 (m, 2H), 3.38 (brs, 1H), 3.52–3.49 (m, 1H for *cis*-isomer), 3.16–3.10 (m, 1H for *trans*-isomer), 2.22 (s, 3H), 2.10–0.90 (m, 12H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 25 °C, TMS): δ = 145.5, 145.4, 130.0, 129.8, 126.4, 126.2, 113.8, 113.7, 52.7, 48.7, 34.4, 33.9, 32.7, 31.2, 30.1, 29.6, 22.6, 21.7, 20.7; MS (70 eV, EI): *m/z* (%): 203 (26) [M^+], 147 (12), 146 (100), 133 (9), 132 (9), 131 (11), 130 (5), 120 (5), 118 (5), 107 (8), 106 (9), 91 (8), 55 (5).

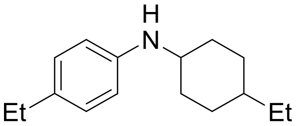
2c

3-Methyl-*N*-(3-methylcyclohexyl)benzenamine (2c, *cis*:*trans* = 80:20): colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.05–7.01 (m, 1H), 6.47 (m, 1H), 6.40–6.37 (m, 2H), 3.66–3.63 (m, 1H for *trans*-isomer), 3.41 (brs, 1H), 3.24–3.18 (m, 1H for *cis*-isomer), 2.25 (t, J = 18 Hz, 3H), 2.10–0.67 (m, 12H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 25 °C, TMS): δ = 147.7, 139.2, 129.4, 118.1, 117.9, 114.2, 114.1, 110.6, 110.4, 52.3, 47.7, 42.8, 39.1, 34.9, 34.3, 33.7, 32.3, 30.7, 27.4, 25.3, 22.8, 22.0, 21.9, 20.8; MS (70 eV, EI): *m/z* (%): 203 (57) [M^+], 204 (9), 188 (6), 161 (13), 160 (100), 147 (11), 146 (83), 145 (9), 144 (7), 134 (5), 133 (26), 132 (23), 131 (15), 130 (10), 120 (19), 118 (16), 117 (8), 108 (5), 107 (36), 106 (11), 91 (19), 79 (5), 77 (7), 65 (9), 55 (11).



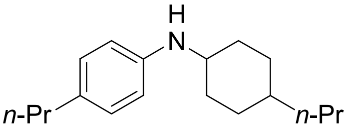
2d

2-Methyl-*N*-(2-methylcyclohexyl)benzenamine (2d, *cis*:*trans* = 16:84): pale yellow oil; ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.09–7.02 (m, 2H), 6.62–6.56 (m, 2H), 3.58–3.56 (brs, 1H for *cis*-isomer), 3.28 (brs, 1H), 2.96–2.91 (m, 1H for *trans*-isomer), 2.20–0.91 (m, 15H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 25 °C, TMS): δ = 146.3, 145.8, 130.5, 127.39, 127.35, 121.8, 121.6, 116.2, 116.1, 110.3, 110.0, 58.2, 53.1, 41.2, 39.4, 35.1, 34.0, 33.6, 30.7, 29.1, 26.2, 25.8, 23.5, 23.1, 19.9, 17.9, 17.8; MS (70 eV, EI): *m/z* (%): 203 (38) [M^+], 204 (6), 161 (5), 160 (31), 147 (13), 146 (100), 144 (5), 133 (9), 132 (5), 131 (12), 130 (8), 120 (15), 119 (5), 118 (42), 117 (6), 107 (10), 106 (8), 91 (14), 77 (5), 65 (7), 55 (8).



2e

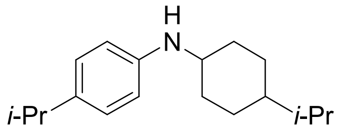
4-Ethyl-*N*-(4-ethylcyclohexyl)benzenamine (2e, *cis*:*trans* = 52:48): colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): δ = 6.99–6.97 (m, 2H), 6.55–6.51 (m, 2H), 3.53–3.50 (m, 1H for *cis*-isomer), 3.41 (brs, 1H), 3.16–3.11 (m, 1H for *trans*-isomer), 2.52 (q, J = 7.5 Hz, 2H), 2.12–0.86 (m, 17H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 25 °C, TMS): δ = 145.74, 145.65, 133.0, 132.9, 128.8, 113.6, 113.5, 53.0, 49.0, 39.3, 38.1, 33.9, 32.0, 29.9, 29.7, 28.6, 28.2, 27.8, 16.3, 11.9; MS (70 eV, EI): *m/z* (%): 231 (32) [M^+], 232 (6), 161 (13), 160 (100), 147 (10), 134 (5), 132 (18), 131 (9), 130 (9), 106 (14), 105 (6), 77 (5), 55 (5).



2f

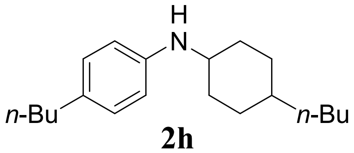
4-Propyl-*N*-(4-propylcyclohexyl)benzenamine (2f, *cis*:*trans* = 40:60): colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): δ = 6.96–6.94 (m, 2H), 6.53–6.49 (m, 2H), 3.52–3.49 (m, 1H for *cis*-isomer), 3.41 (brs, 1H), 3.16–3.10 (m, 1H for *trans*-isomer), 2.45 (t, J = 7.5 Hz, 2H), 2.11–0.87 (m, 21H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 25 °C, TMS): δ = 145.7, 145.6, 131.4, 131.2, 129.4, 113.52, 113.45, 53.0, 49.0, 39.6, 38.3, 37.5, 37.3, 36.0, 34.0, 32.4, 29.7, 28.1, 25.2, 20.5, 20.4, 14.7, 14.1; MS (70 eV, EI): *m/z*

(%): 259 (41) [M^+], 260 (8), 231 (7), 230 (39), 175 (14), 174 (100), 161 (8), 148 (6), 144 (5), 132 (29), 131 (6), 130 (10), 106 (38), 105 (9), 91 (5), 81 (5), 79 (5), 55 (9).



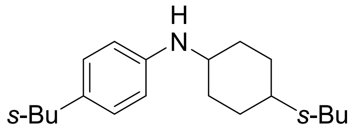
2g

4-(1-Methylethyl)-*N*-[4-(1-methylethyl)cyclohexyl]benzenamine (2g, *cis*:*trans* = 37:63): pale yellow oil; ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.02–7.00 (m, 2H), 6.55–6.50 (m, 2H), 3.57–3.55 (m, 1H for *cis*-isomer), 3.44 (brs, 1H), 3.14–3.09 (m, 1H, *trans*-isomer), 2.82–2.74 (sept, J = 7 Hz, 1H), 2.14–1.01 (m, 16H); 0.87 (d, J = 7.0 Hz, 6H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 25 °C, TMS): δ = 145.83, 145.75, 137.6, 137.4, 127.4, 113.4, 113.3, 52.9, 48.3, 43.9, 43.5, 34.2, 33.4, 32.9, 32.1, 30.2, 29.0, 24.8, 24.6, 20.3, 20.2; MS (70 eV, EI): *m/z* (%): 259 (48) [M^+], 260 (10), 245 (9), 244 (45), 175 (13), 174 (100), 161 (11), 148 (7), 146 (23), 135 (6), 133 (5), 132 (31), 131 (7), 130 (12), 120 (35), 119 (7), 118 (6), 117 (6), 91 (10), 81 (7), 79 (5), 77 (6), 69 (5), 67 (5), 55 (8),



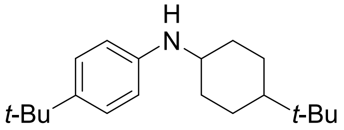
2h

4-Butyl-*N*-(4-butylcyclohexyl)benzenamine (2h, *cis*:*trans* = 32:68): pale yellow oil; ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): δ = 6.96–6.94 (m, 2H), 6.53–6.49 (m, 2H), 3.51–3.49 (m, 1H for *cis*-isomer), 3.35 (brs, 1H), 3.16–3.10 (m, 1H for *trans*-isomer), 2.47 (t, J = 7.8 Hz, 2H), 2.37–0.88 (m, 25H), ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 25 °C, TMS): δ = 145.7, 145.6, 131.6, 131.4, 129.4, 113.55, 113.47, 53.0, 49.0, 41.1, 37.6, 37.0, 36.32, 36.27, 35.7, 35.5, 35.0, 34.3, 34.0, 33.1, 32.4, 29.83, 29.75, 29.67, 29.64, 28.2, 23.29, 23.26, 22.6, 14.42, 14.36, 14.3; MS (70 eV, EI): *m/z* (%): 287 (55) [M^+], 288 (12), 245 (9), 244 (47), 189 (15), 188 (100), 175 (8), 162 (5), 144 (5), 132 (27), 131 (5), 130 (9), 106 (40), 105 (8), 91 (5), 81 (6), 67 (5), 55 (9).



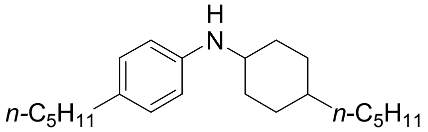
2i

4-(1-Methylpropyl)-*N*-[4-(1-methylpropyl)cyclohexyl]benzenamine (2i, *cis*:*trans* = 27:73): pale yellow oil; ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): δ = 6.97–6.94 (m, 2H), 6.54–6.51 (m, 2H), 3.59–3.57 (m, 1H for *cis*-isomer), 3.40 (brs, 1H), 3.14–3.09 (m, 1H, for *trans*-isomer), 2.49–0.79 (m, 27H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 145.84, 145.77, 136.4, 136.3, 128.0, 113.4, 113.3, 53.1, 48.2, 42.1, 41.8, 41.0, 39.6, 39.0, 34.4, 34.2, 31.7, 30.4, 30.3, 29.7, 27.7, 27.1, 26.9, 25.3, 23.7, 22.3, 16.13, 16.06, 12.6, 12.2, 12.0; MS (70 eV, EI): *m/z* (%): 287 (35) [M^+], 288 (8), 272 (7), 259 (20), 258 (100), 188 (21), 146 (10), 132 (11), 120 (28), 57 (5), 55 (6).



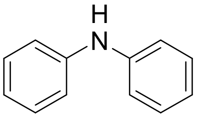
2j

4-(1,1-Dimethylethyl)-*N*-[4-(1,1-dimethylethyl)cyclohexyl]benzenamine (2j, *cis*:*trans* = 30:70): colorless oil; ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.19–7.15 (m, 2H), 6.56–6.51 (m, 2H), 3.63–3.60 (m, 1H for *cis*-isomer), 3.49 (brs, 1H), 3.14–3.08 (m, 1H for *trans*-isomer), 2.17–0.86 (m, 27H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 145.5, 145.4, 139.8, 139.6, 126.3, 113.1, 113.0, 52.9, 48.3, 48.2, 48.0, 47.2, 34.5, 34.1, 32.8, 32.7, 31.9, 30.8, 28.0, 27.8, 26.7, 21.9; MS (70 eV, EI): *m/z* (%): 287 (48) [M^+], 288 (10), 273 (21), 272 (100), 189 (6), 188 (39), 160 (13), 134 (23), 132 (15), 106 (8), 81 (5), 57 (17), 55 (5).



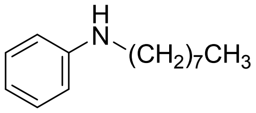
2k

4-Pentyl-*N*-(4-pentylcyclohexyl)benzenamine (2k, *cis*:*trans* = 39:61): pale yellow oil; ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.96–6.94 (m, 2H), 6.54–6.49 (m, 2H), 3.53–3.50 (m, 1H for *cis*-isomer), 3.41 (brs, 1H), 3.16–3.10 (m, 1H, *trans*-isomer), 2.47 (t, J = 7.8 Hz, 2H), 2.12–0.86 (m, 29H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 145.7, 145.6, 131.7, 131.5, 129.4, 113.6, 113.5, 53.0, 49.1, 37.6, 37.3, 36.3, 35.7, 35.3, 34.0, 32.52, 32.45, 31.9, 29.8, 28.2, 27.13, 27.09, 23.0, 22.9, 14.43, 14.40; MS (70 eV, EI): *m/z* (%): 315 (62) [M^+], 316 (15), 259 (12), 258 (59), 203 (15), 202 (100), 189 (7), 176 (5), 144 (6), 132 (29), 130 (10), 106 (49), 105 (9), 81 (8), 67 (6), 55 (12).



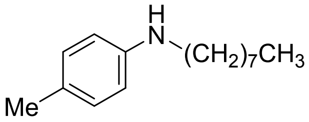
3a

Diphenylamine (3a): MS (70 eV, EI): *m/z* (%): 169 (100) [M^+], 170 (13), 168 (52), 167 (26), 84 (11), 77 (8), 66 (7), 65 (6), 51 (11).



8aa

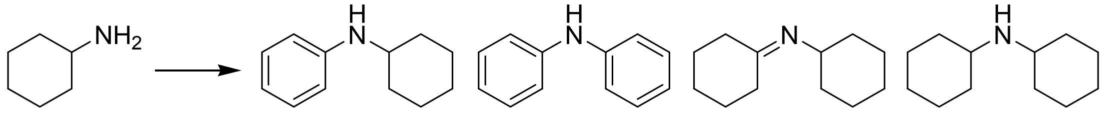
***N*-Octylbenzenamine (8aa):** MS (70 eV, EI): *m/z* (%): 205 (13) [M^+], 107 (8), 196 (100), 77 (8).



8ba

4-Methyl-*N*-octylbenzenamine (8ba): MS (70 eV, EI): *m/z* (%): 219 (18) [M^+], 121 (10), 120 (100), 91 (7).

Table S1 Tandem oxidation of cyclohexylamine (**1a**) to *N*-cyclohexylaniline (**2a**) using various catalysts[a]

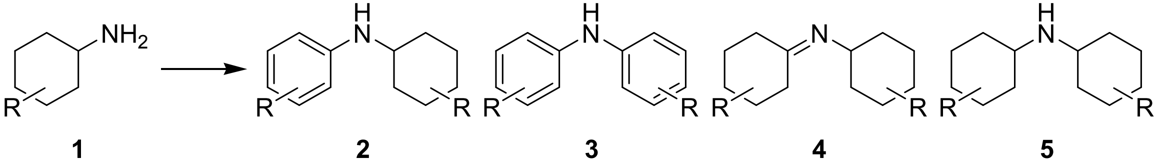


1a **2a** **3a** **4a** **5a**

Entry	Catalyst	Au/Pd molar ratio	Conv. of **1a** (%)	Yield (%)			
				2a	**3a**	**4a**	**5a**
1	**Au–Pd/Al_2O_3**	**3.3**	**>99**	**95**	**<1**	**<1**	**<1**
2	Au/Al_2O_3	–	42	<1	<1	18	<1
3	Pd/Al_2O_3	–	34	<1	<1	<1	<1
4[b]	Au/Al_2O_3 + Pd/Al_2O_3	3.3	76	3	<1	12	<1
5	Au–Pd/TiO_2	0.59	>99	62	3	<1	4
6	Au–Pd/Al_2O_3	7.8	81	40	<1	6	5
7	Au–Pd/Al_2O_3	0.64	96	68	<1	<1	<1
8	Au–Pd/Al_2O_3	0.16	93	60	4	<1	5
9[c]	Al_2O_3	–	<1	<1	<1	<1	<1
10	None	–	<1	<1	<1	<1	<1

[a] Reaction conditions: **1a** (1.0 mmol), catalyst (Au: 1.15 mol%, Pd: 0.35 mol% for entiries 1–4; total metal (Au + Pd): 1.5 mol % for entries 5–11), mesitylene (2 mL), 130 °C, open air (1 atm), 3 h. Conversions and yields were determined by GC analysis using *n*-hexadecane as an internal standard. [b] Physical mixture of Au/Al_2O_3 and Pd/Al_2O_3. [c] Al_2O_3 83.9 mg.

Table S2 Scope of substrates (details for Fig. 2)[a]



Entry	Substrate (**1**)	*cis*/*trans* ratio of **1**	Time (h)	Conv. of **1** (%)[b]	Yield (%)[b] **2**	**3**	**4**	**5**	Isolated yield of **2** (%)[c]	*cis*/*trans* ratio of **2**
1	R = H (**1a**)	—	3	>99	95	<1	<1	<1	88	—
2	= 4-Me (**1b**)	58:42	2.5	>99	82	<1	<1	<1	73	39:61
3	= 3-Me (**1c**)	74:26	2.5	>99	91	<1	<1	<1	81	80:20
4	= 2-Me (**1d**)	30:70	5	>99	53	<1	<1	<1	40	16:84
5	= 4-Et (**1e**)	59:41	2	>99	78	<1	2	<1	64	52:48
6	= 4-*n*-Pr (**1f**)	49:51	3	>99	76	<1	2	<1	74	40:60
7	= 4-*i*-Pr (**1g**)	51:49	3	>99	83	5	<1	<1	74	37:63
8	= 4-*n*-Bu (**1h**)	38:62	3	>99	71	<1	2	<1	72	32:68
9	= 4-*sec*-Bu (**1i**)	38:62	3	>99	78	2	2	<1	82	27:73
10	= 4-*tert*-Bu (**1j**)	52:48	2	>99	78	10	<1	<1	65	30:70
11[d]	= 4-*n*-C_5H_{11} (**1k**)	46:54	4	>99	60	4	<1	2	65	39:61

[a] Reaction conditions: **1** (1.0 mmol), Au–Pd/Al_2O_3 (Au: 1.15 mol%, Pd: 0.35 mol%), mesitylene (2 mL), 130 °C, open air (1 atm). [b] Conversions and yields were determined by GC analysis using *n*-hexadecane as an internal standard. [c] Isolated yields of **2**. [d] Au: 2.3 mol%, Pd: 0.7 mol%.

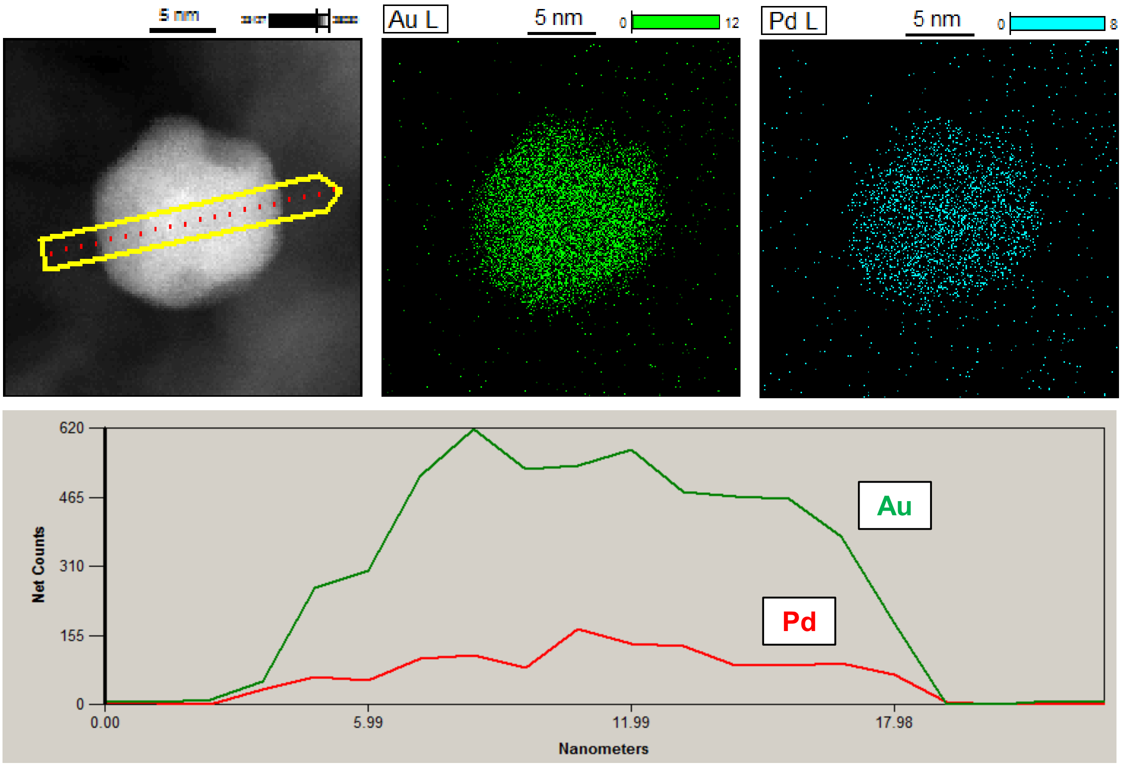


Fig. S1 HAADF-STEM and EDS images of Au–Pd/Al_2O_3 (Au/Pd = 3.3).

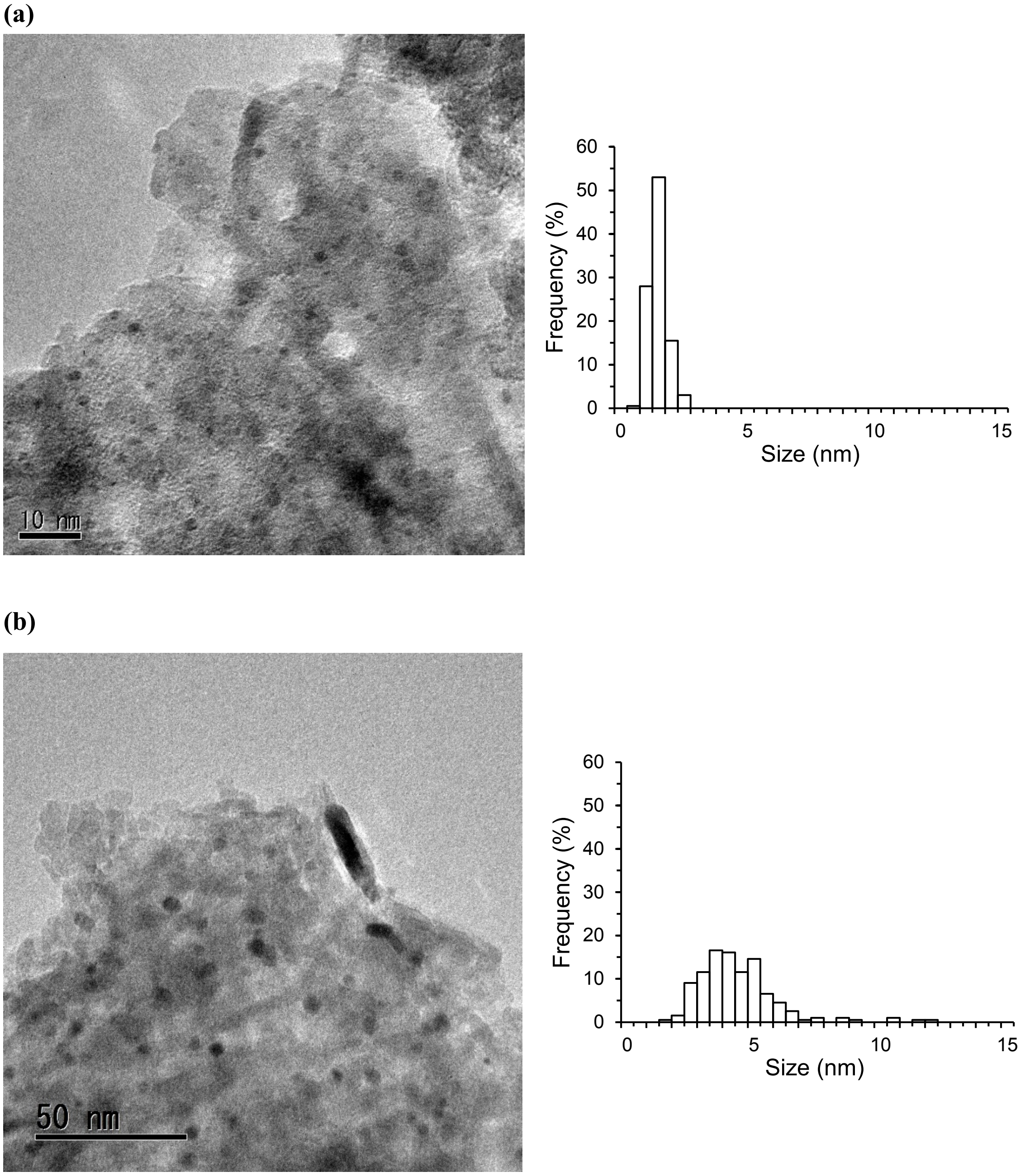


Fig. S2 TEM images and Au–Pd bimetallic nanoparticle size distribution of (a) fresh Au–Pd/Al_2O_3 (average: 1.7 nm, σ: 0.4 nm) and (b) Au–Pd/Al_2O_3 after the fifth reuse experiment (average: 4.6 nm, σ: 1.6 nm). The size distribution were determined using 200 particles.

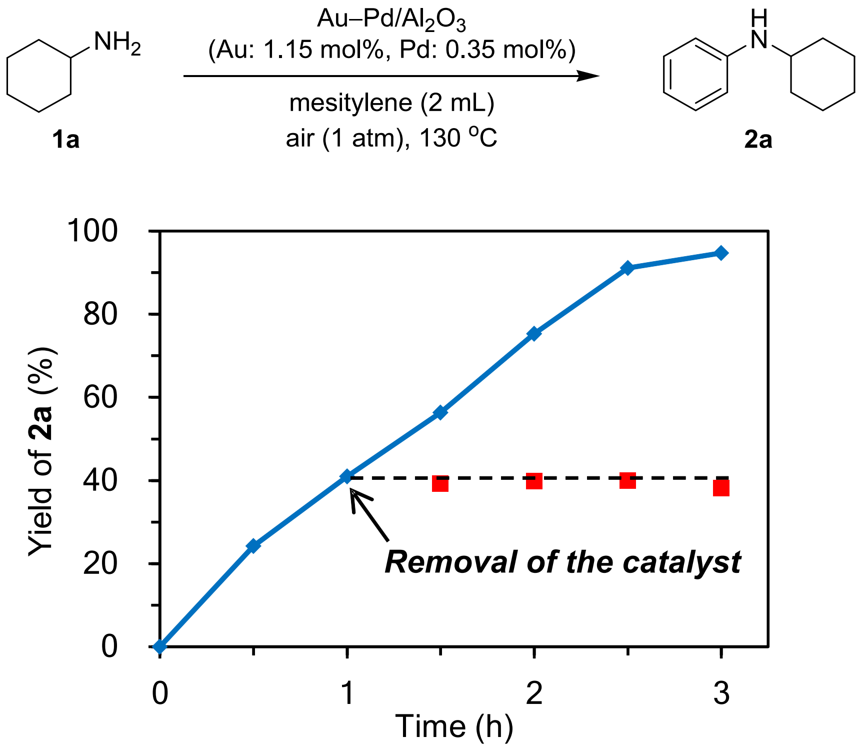


Fig. S3 The effect of removal of the Au–Pd/Al_2O_3 catalyst (verification of heterogeneous catalysis). The reaction conditions were the same as those described in Table S1. GC yields are shown here.

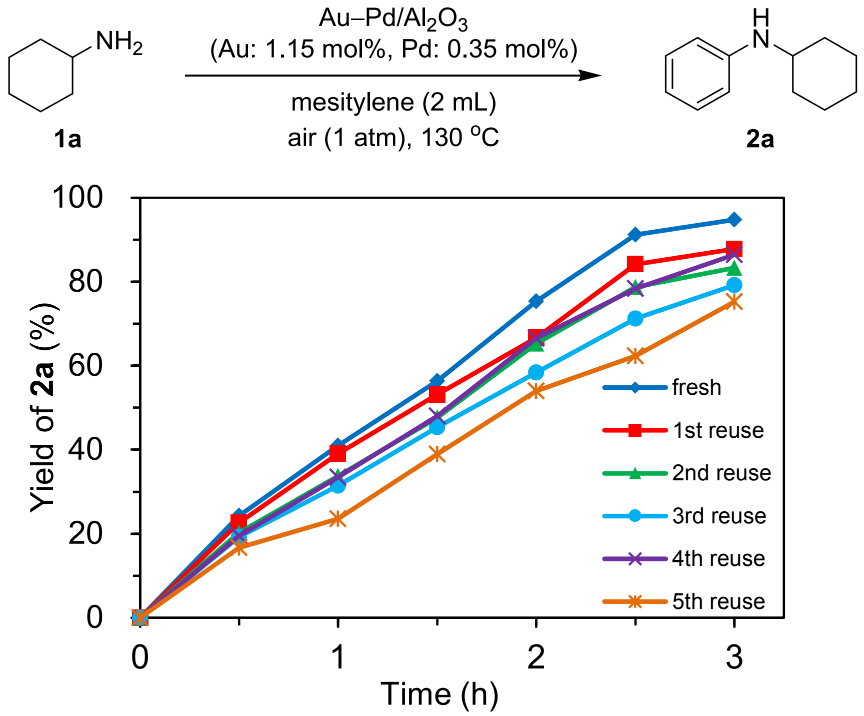


Fig. S4 The reaction profiles for the catalyst reuse experiments. The reaction conditions were the same as those described in Table S1. GC yields are shown here. Final yields (3 h): Fresh (95 %), 1st reuse (88 %), 2nd reuse (83 %), 3rd reuse (79 %), 4th reuse (86 %), 5th reuse (75 %).

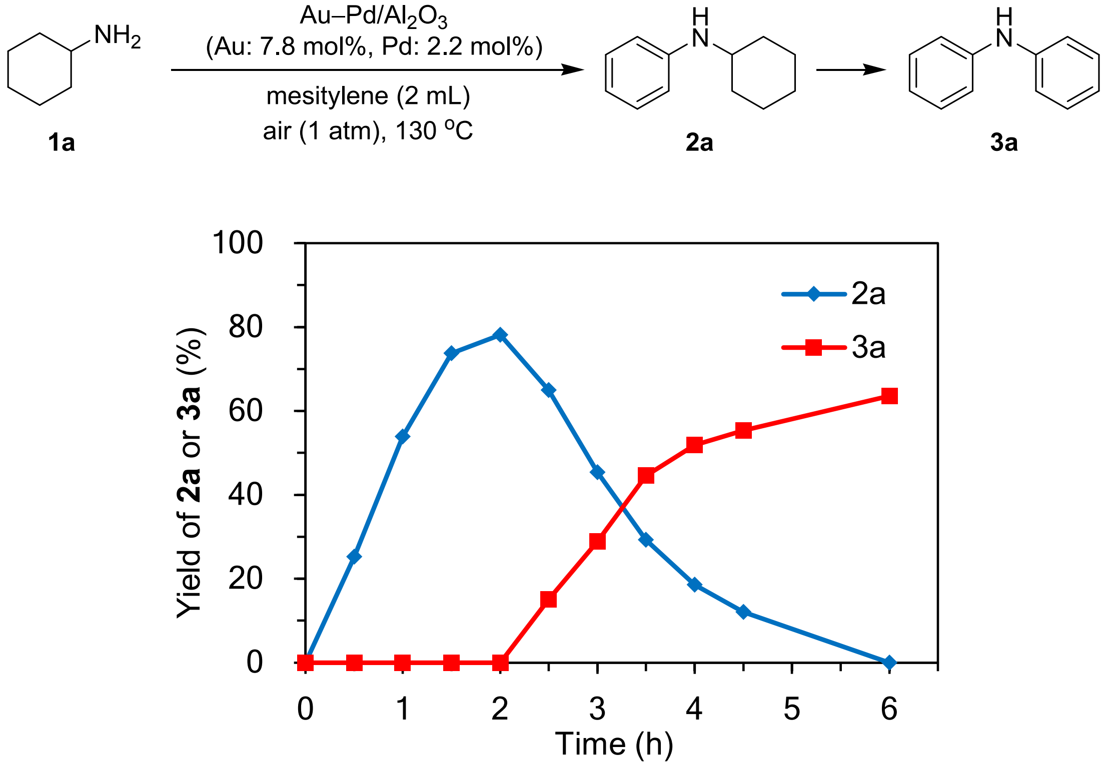


Fig. S5 The reaction profile for the tandem oxidation reaction of cyclohexylamine (**1a**) to diphenylamine (**3a**) using Au–Pd/Al_2O_3. Reaction conditions: **1a** (0.5 mmol), Au–Pd/Al_2O_3 (Au: 7.8 mol%, Pd: 2.2 mol%), mesitylene (2 mL), 130 °C, open air (1 atm). Yields were determined by GC analysis using *n*-hexadecane as an internal standard.

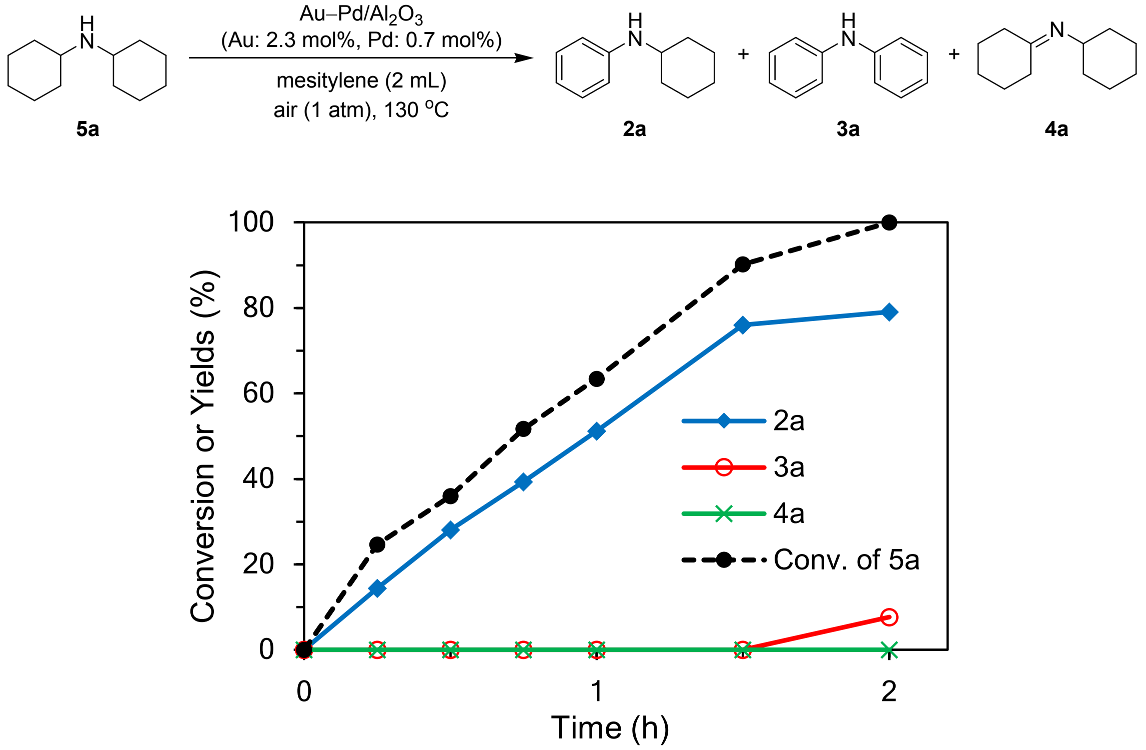
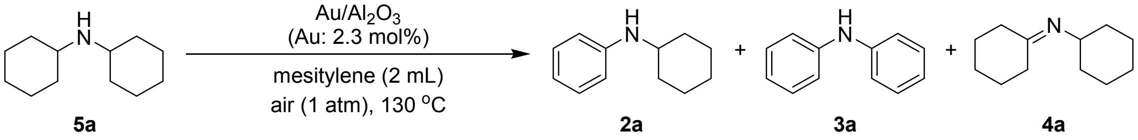


Fig. S6 The reaction profile for the tandem oxidation of dicyclohexylamine (**5a**) using Au–Pd/Al$_2$O$_3$. Reaction conditions: **5a** (0.5 mmol), Au–Pd/Al$_2$O$_3$ (Au: 2.3 mol%, Pd: 0.7 mol%), mesitylene (2 mL), 130 °C, open air (1 atm). Yields were determined by GC analysis using *n*-hexadecane as an internal standard.



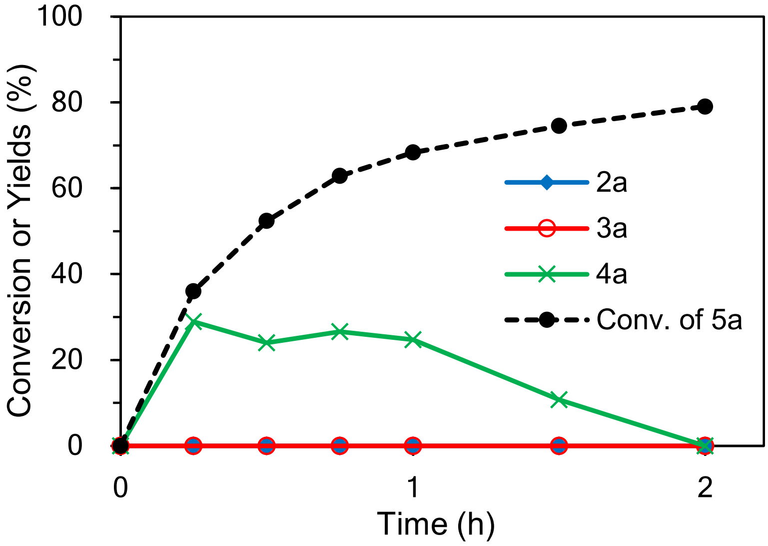


Fig. S7 The reaction profile for the tandem oxidation of dicyclohexylamine (**5a**) using Au/Al$_2$O$_3$. Reaction conditions: **5a** (0.5 mmol), Au/Al$_2$O$_3$ (Au: 2.3 mol%), mesitylene (2 mL), 130 °C, open air (1 atm). Yields were determined by GC analysis using *n*-hexadecane as an internal standard.

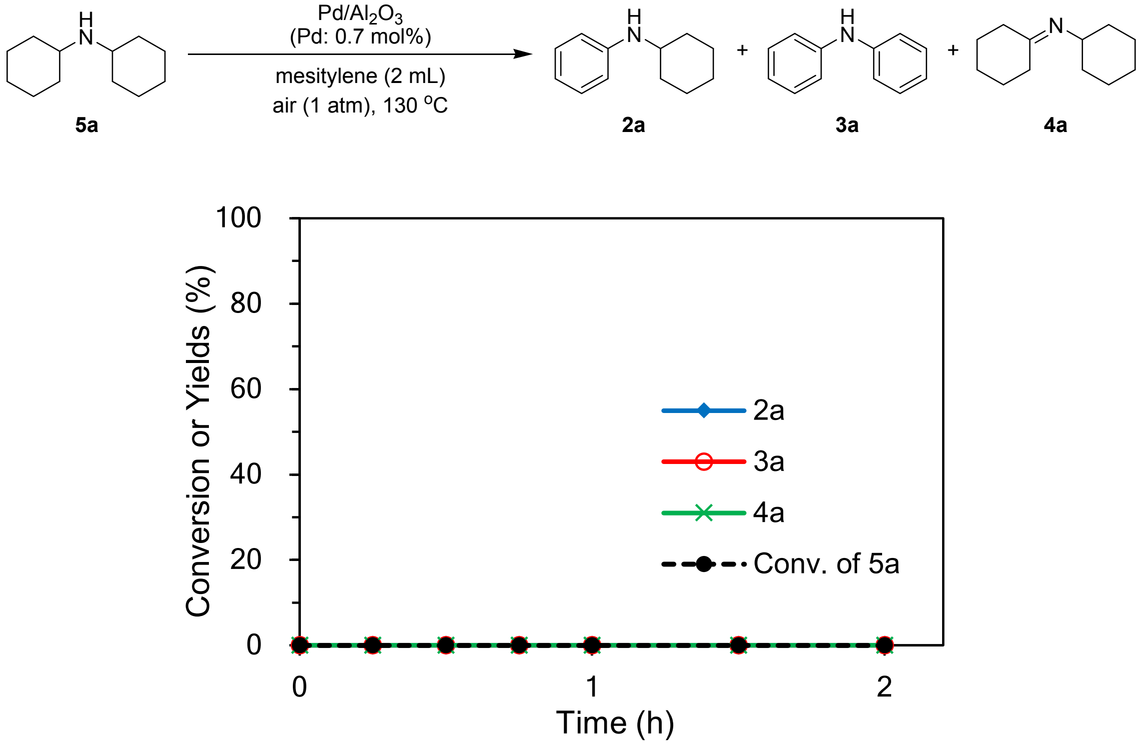


Fig. S8 The reaction profile for the tandem oxidation of dicyclohexylamine (**5a**) using Pd/Al_2O_3. Reaction conditions: **5a** (0.5 mmol), Pd/Al_2O_3 (Pd: 0.7 mol%), mesitylene (2 mL), 130 °C, air (1 atm). Yields were determined by GC analysis using *n*-hexadecane as an internal standard.

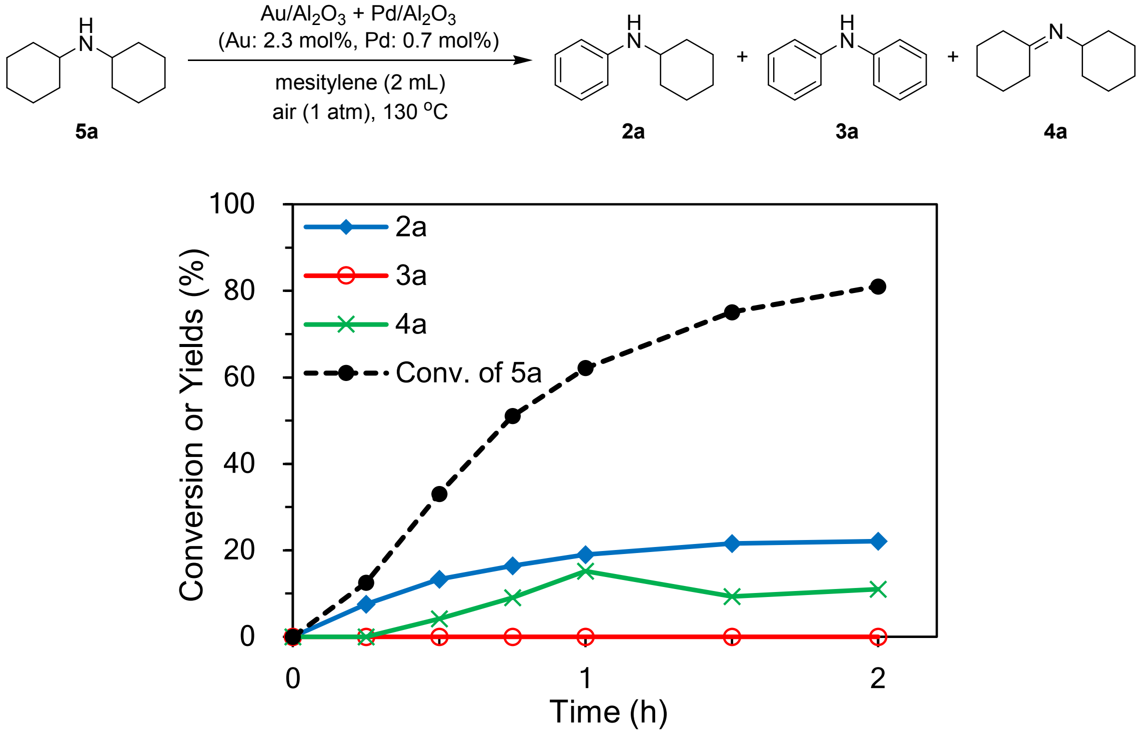
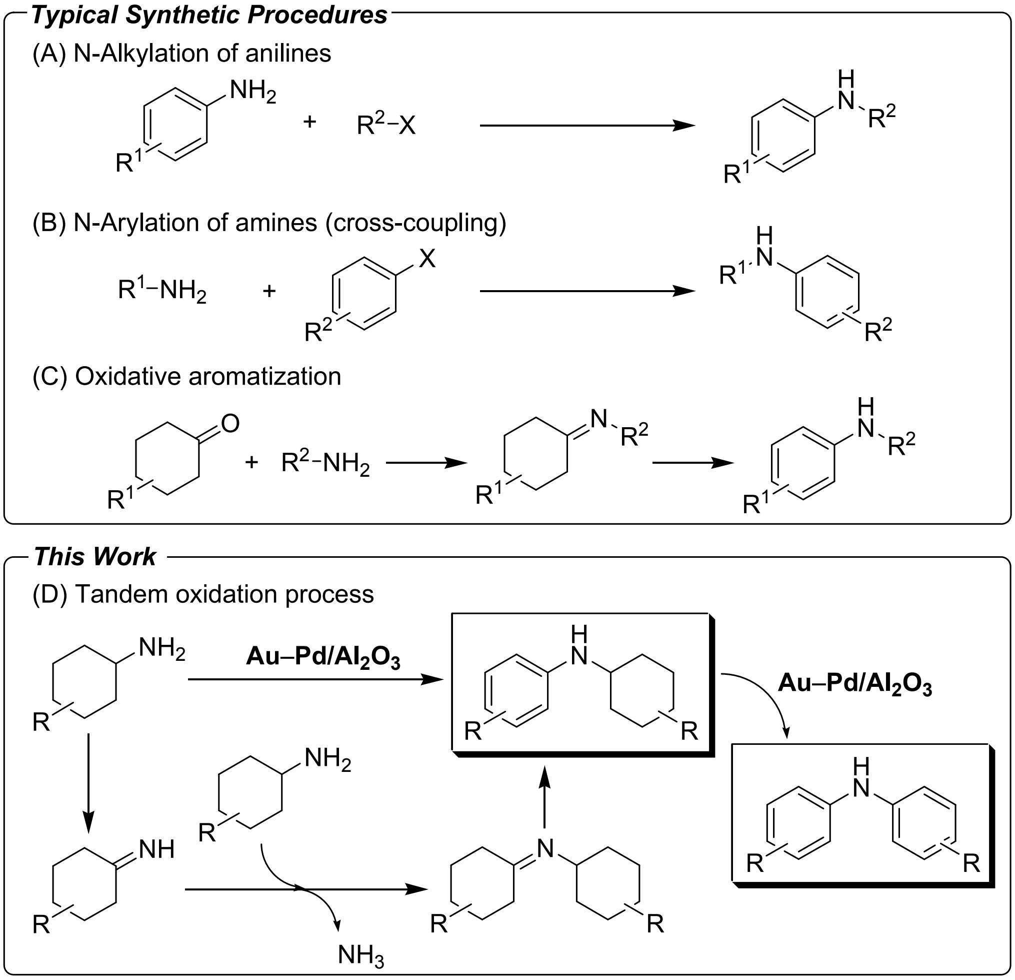
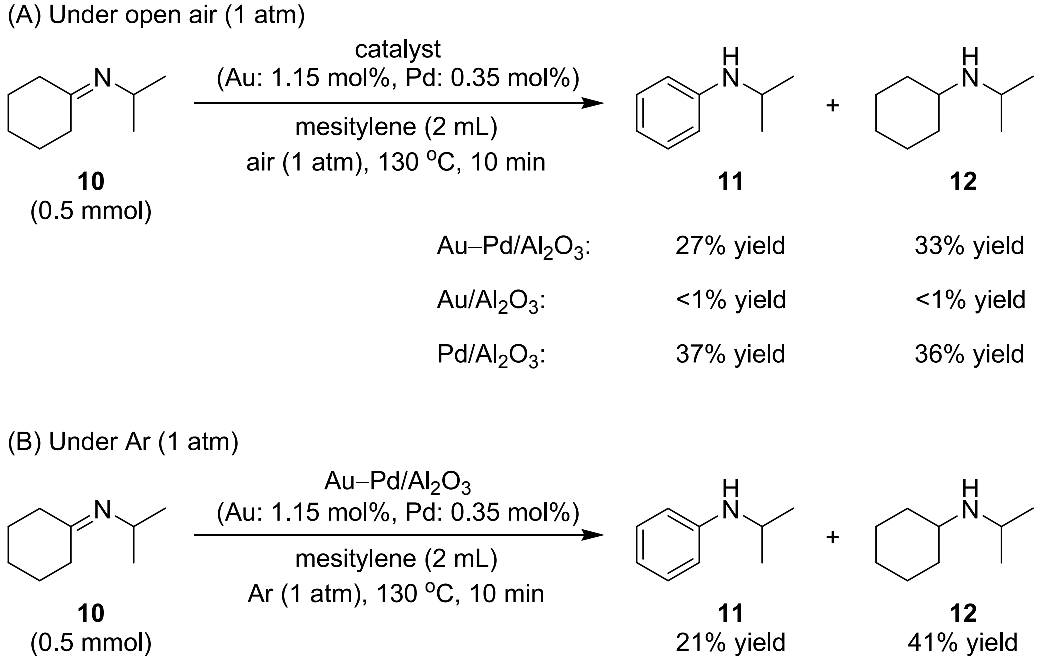


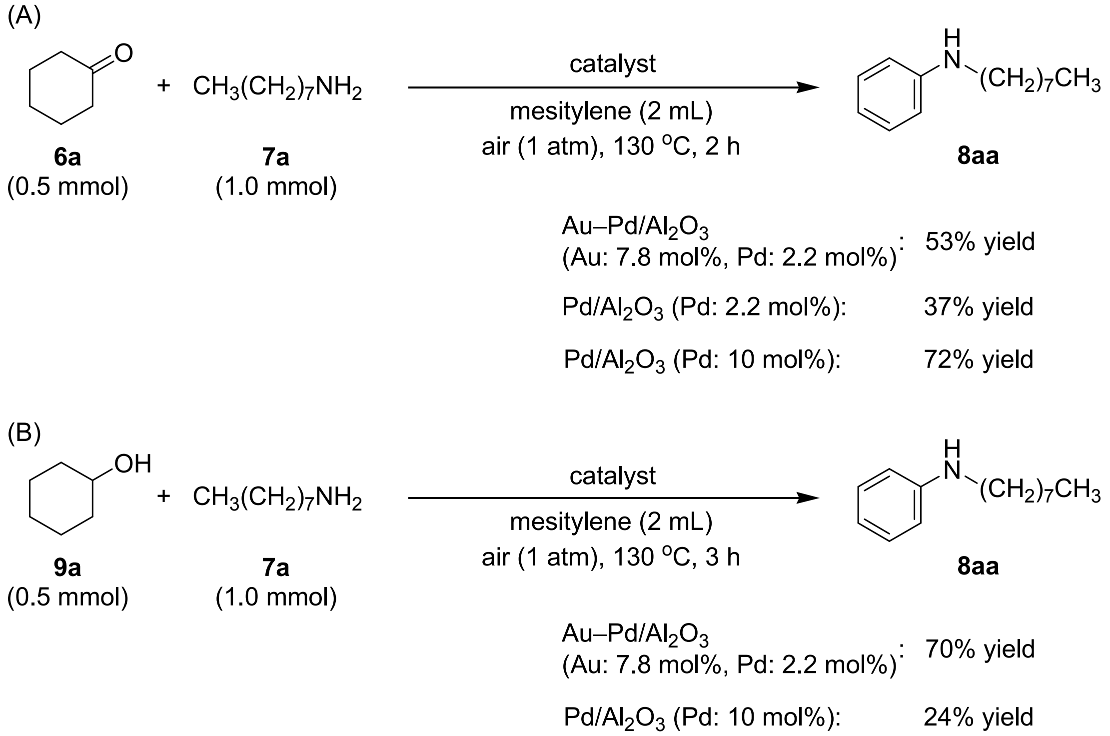
Fig. S9 The reaction profile for the tandem oxidation of dicyclohexylamine (**5a**) using the physical mixture of Au/Al_2O_3 and Pd/Al_2O_3. Reaction conditions: **5a** (0.5 mmol), Au/Al_2O_3 + Pd/Al_2O_3 (physical mixture; Au: 2.3 mol%, Pd: 0.7 mol%), mesitylene (2 mL), 130 °C, open air (1 atm). Yields were determined by GC analysis using *n*-hexadecane as an internal standard.



Scheme S1 Synthetic procedures for *N*-substituted anilines.

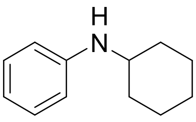


Scheme S2. Aromatization of *N*-cyclohexylideneisopropylamine (**10**) to *N*-isopropylaniline (**11**) under open air (1 atm) or Ar (1 atm). Reaction conditions: **10** (0.5 mmol), catalyst (Au: 1.15 mol%, Pd: 0.35 mol%), mesitylene (2 mL), 130 °C, air (1 atm), 10 min. Yields (based on **10**) were determined by GC analysis using *n*-hexadecane as an internal standard.

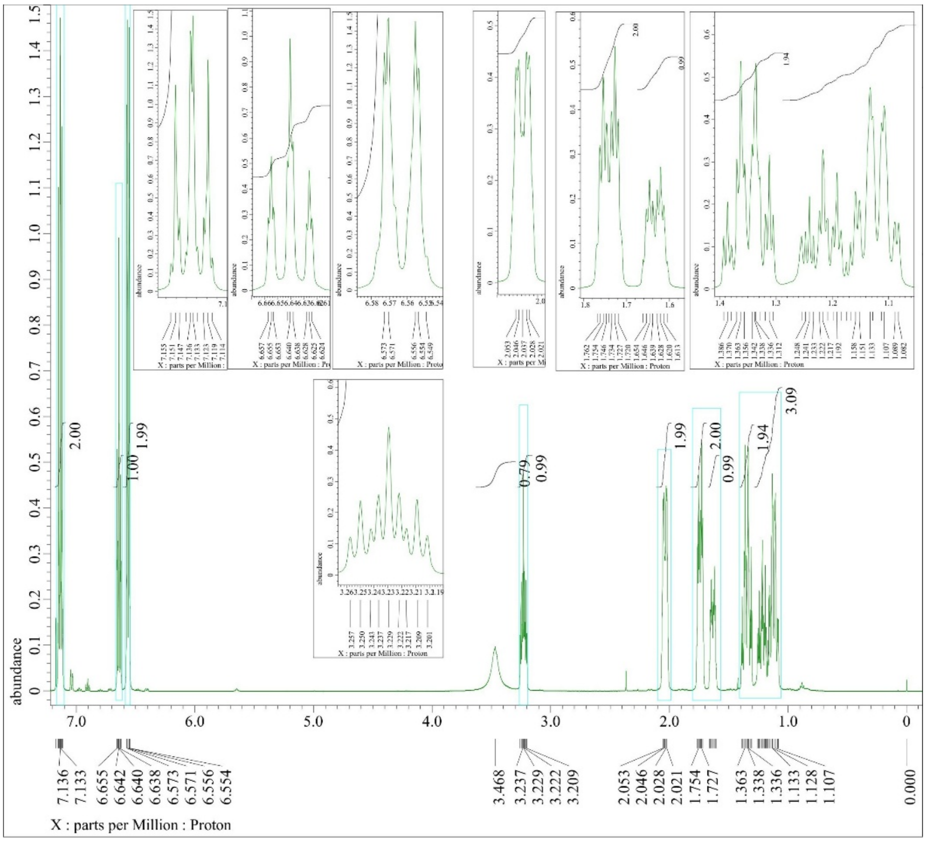


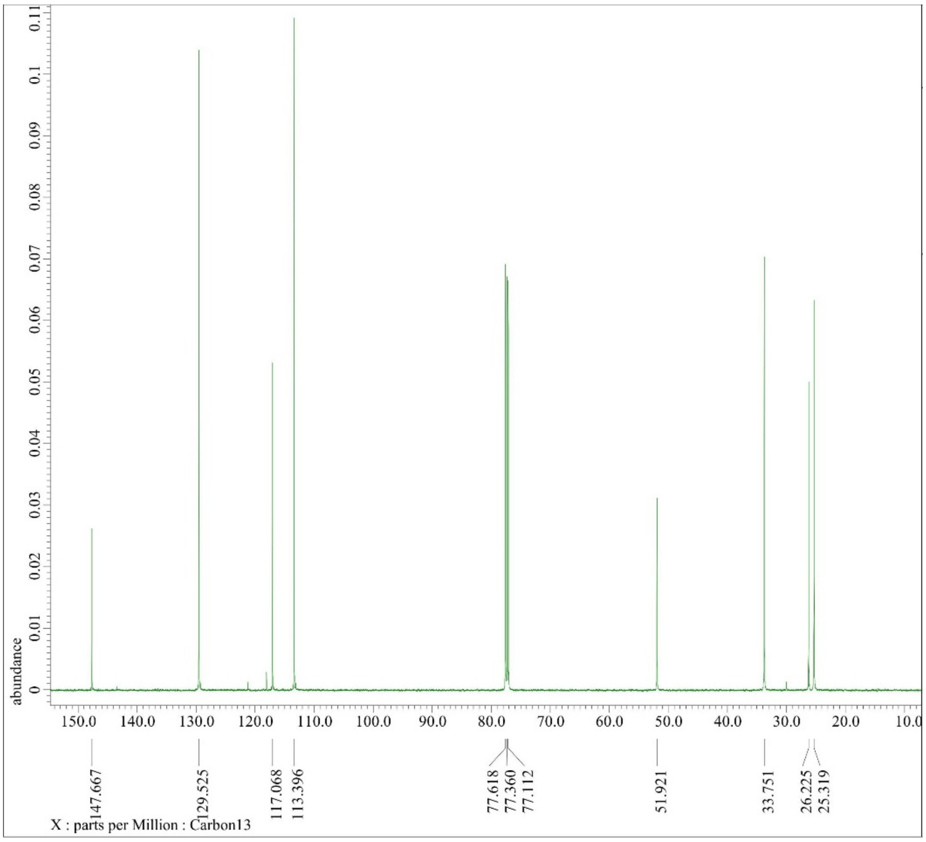
Scheme S3. Tandem oxidations of cyclohexanone (**6a**) or cyclohexanol (**9a**) with *N*-octylamine (**7a**). Reaction conditions (A): **6a** (mmol), **7a** (mmol), catalyst, mesitylene (2 mL), 130 °C, open air (1 atm), 2 h. Reaction conditions (B): **9a** (mmol), **7a** (mmol), catalyst (total metal: 10 mol%), mesitylene (2 mL), 130 °C, open air (1 atm), 3 h. Yields (based on **6a** or **9a**) were determined by GC analysis using dodecane as an internal standard.

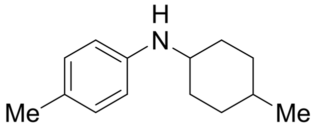
NMR Spectra



2a

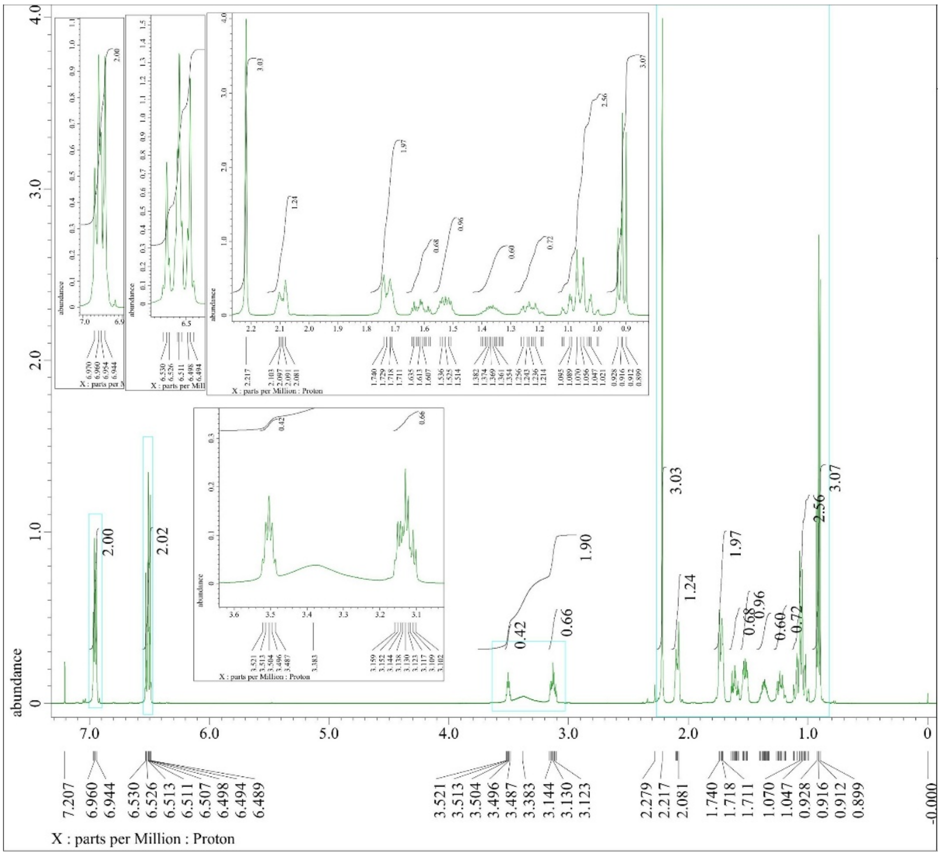






H
N
Me
Me

2b



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1.97
0.68
0.96
0.60
0.72
2.56
3.07
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.207
6.960
6.944
6.530
6.526
6.513
6.511
6.507
6.498
6.494
6.489
3.521
3.513
3.504
3.496
3.487
3.383
3.144
3.130
3.123
2.279
2.217
2.081
1.740
1.718
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1.070
1.047
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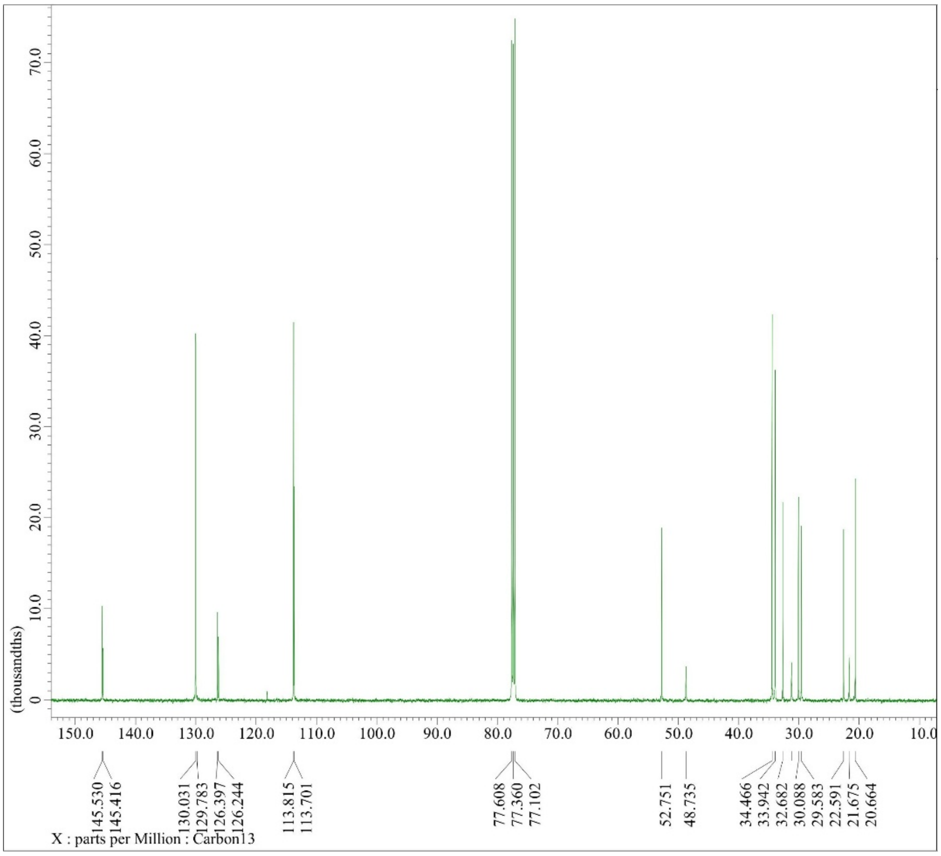
0.916
0.912
0.899
-0.000
X : parts per Million : Proton



(thousandths)
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120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
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145.416
130.031
129.783
126.397
126.244
113.815
113.701
77.608
77.360
77.102
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30.088
29.583
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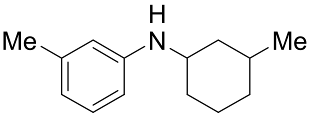
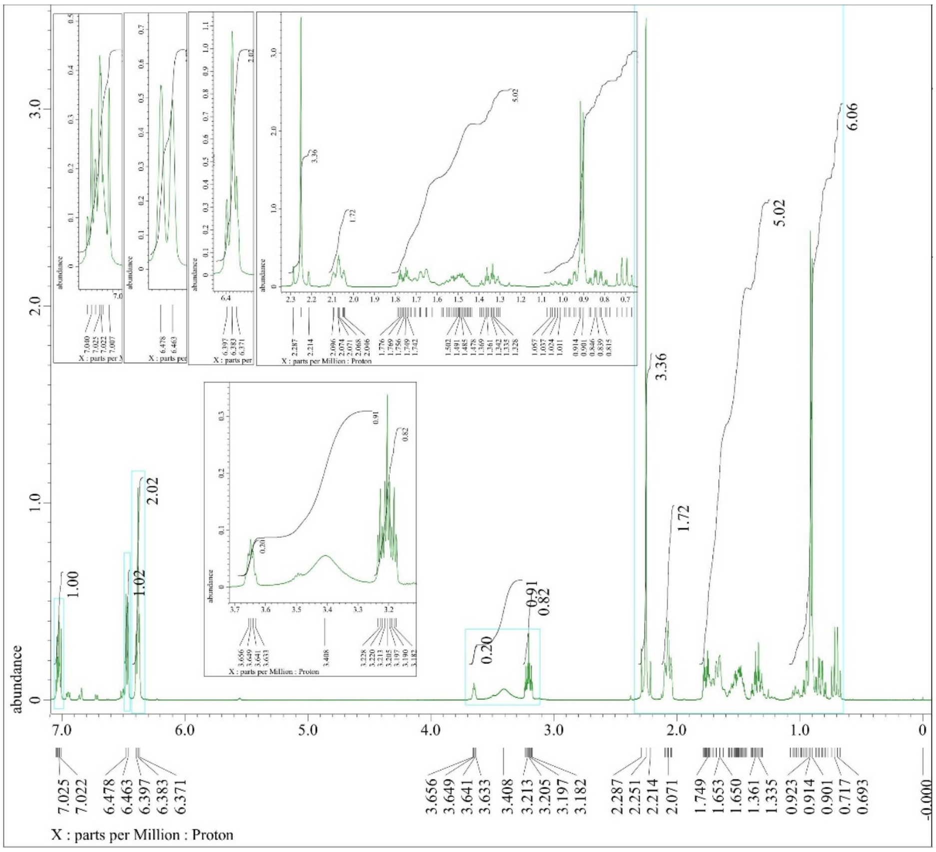
20.664
X : parts per Million : Carbon13


H
N
Me
Me

2c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6.06
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7.022
6.478
6.463
6.397
6.383
6.371
3.656
3.649
3.641
3.633
3.408
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3.205
3.197
3.182
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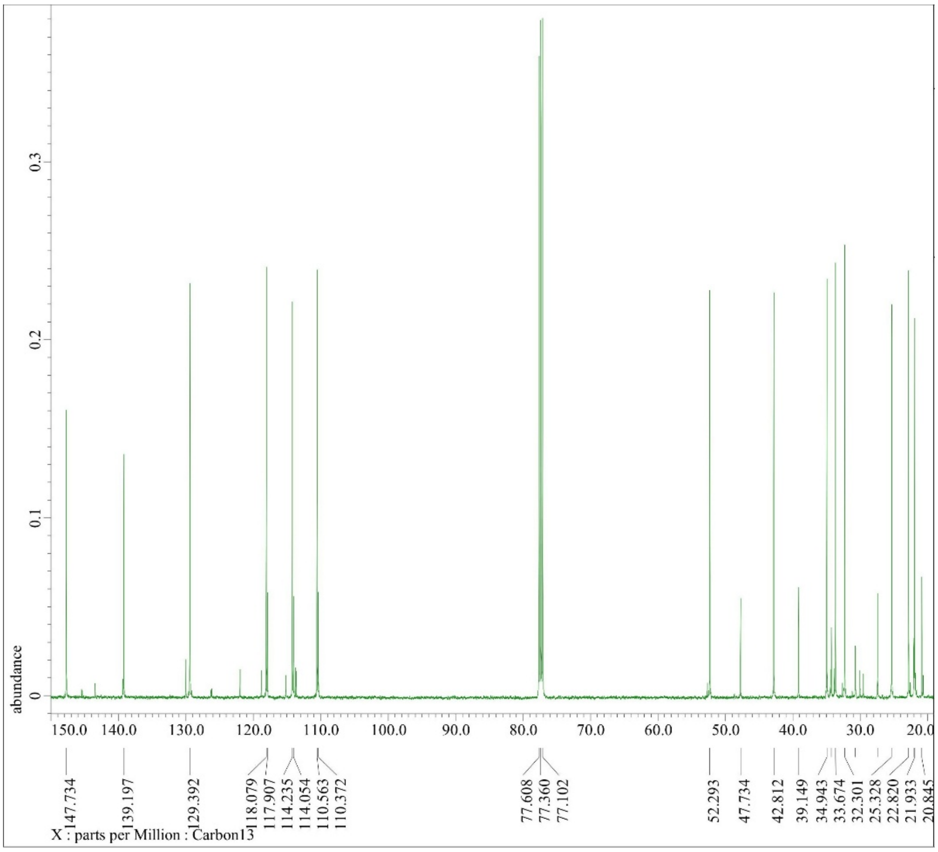
X : parts per Million : Proton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77.102
52.293
47.734
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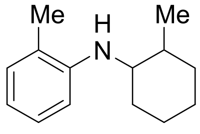
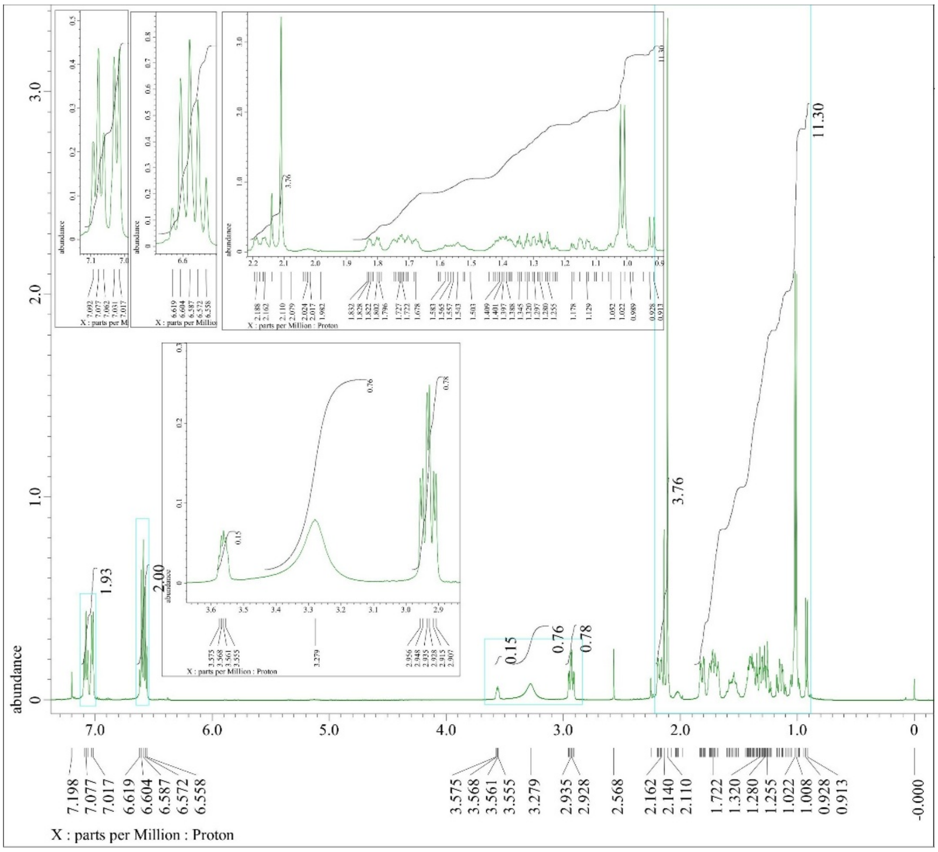
X : parts per Million : Carbon13


Me
H
N
Me

2d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6.0
5.0
4.0
3.0
2.0
1.0
0
7.198
7.077
7.017
6.619
6.604
6.587
6.572
6.558
3.575
3.568
3.561
3.555
3.279
2.935
2.928
2.568
2.162
2.140
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1.255
1.022
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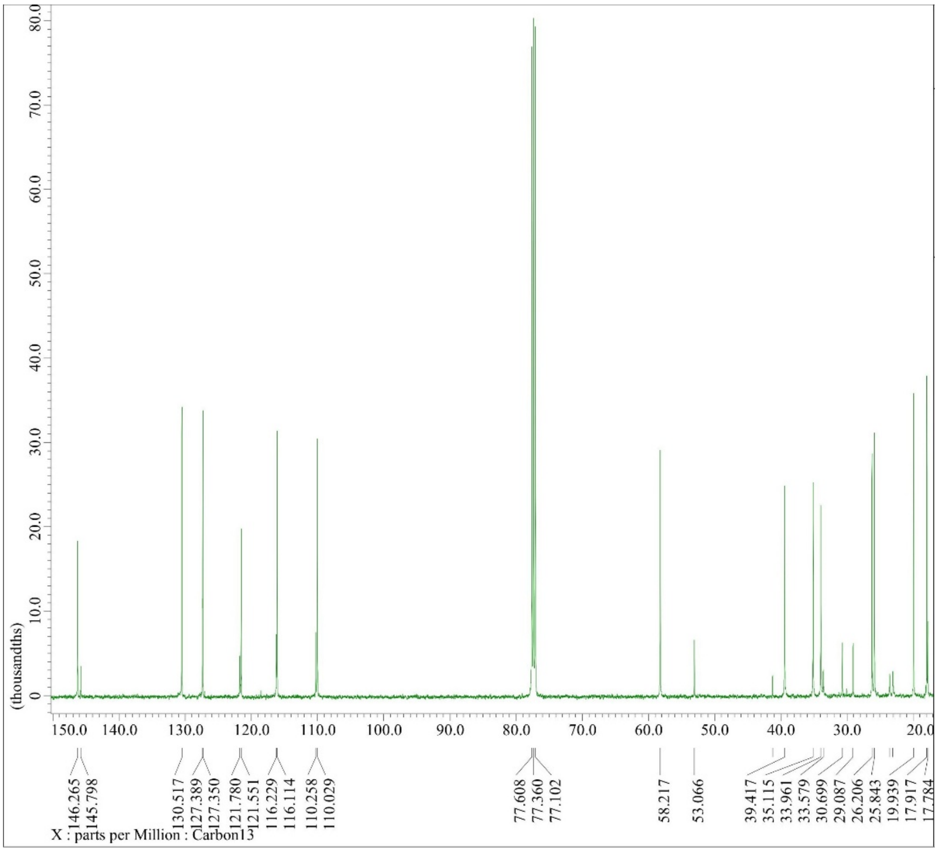
0.913
-0.000
X : parts per Million : Proton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120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
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130.517
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127.350
121.780
121.551
116.229
116.114
110.258
110.029
77.608
77.360
77.102
58.217
53.066
39.417
35.115
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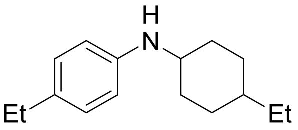
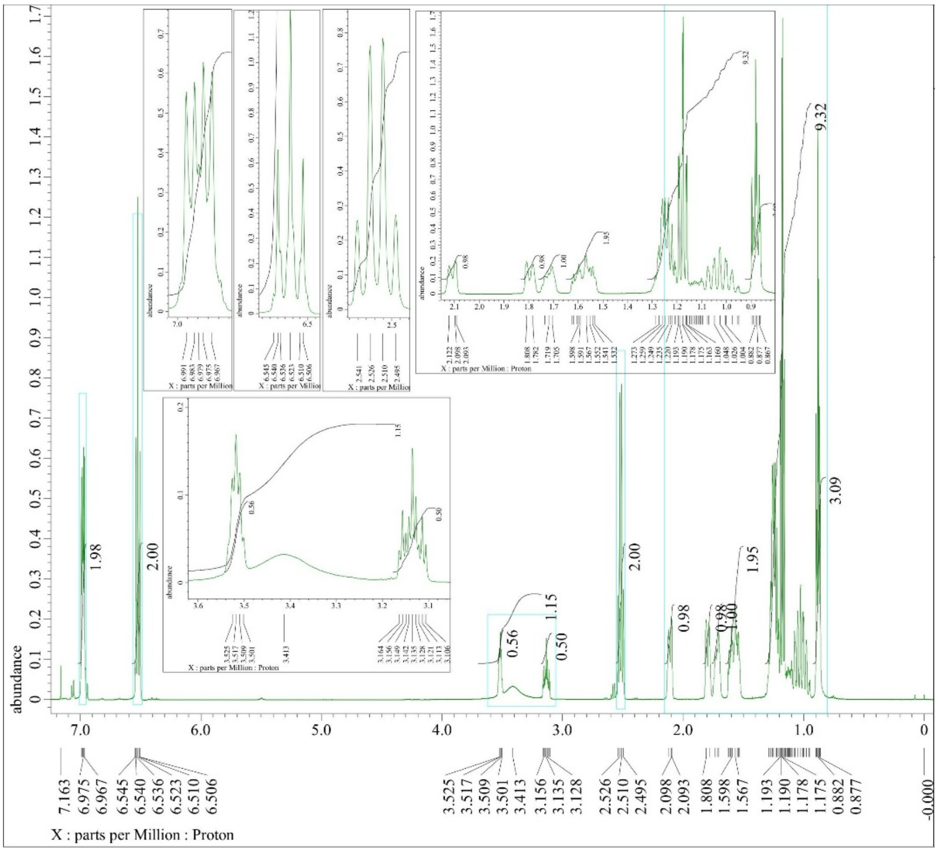
X : parts per Million : Carbon13


H
N
Et
Et

2e


abundance
X : parts per Million : Proton
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0.50
2.00
0.98
0.98
1.00
1.95
9.32
3.09
7.163
6.975
6.967
6.545
6.540
6.536
6.523
6.510
6.506
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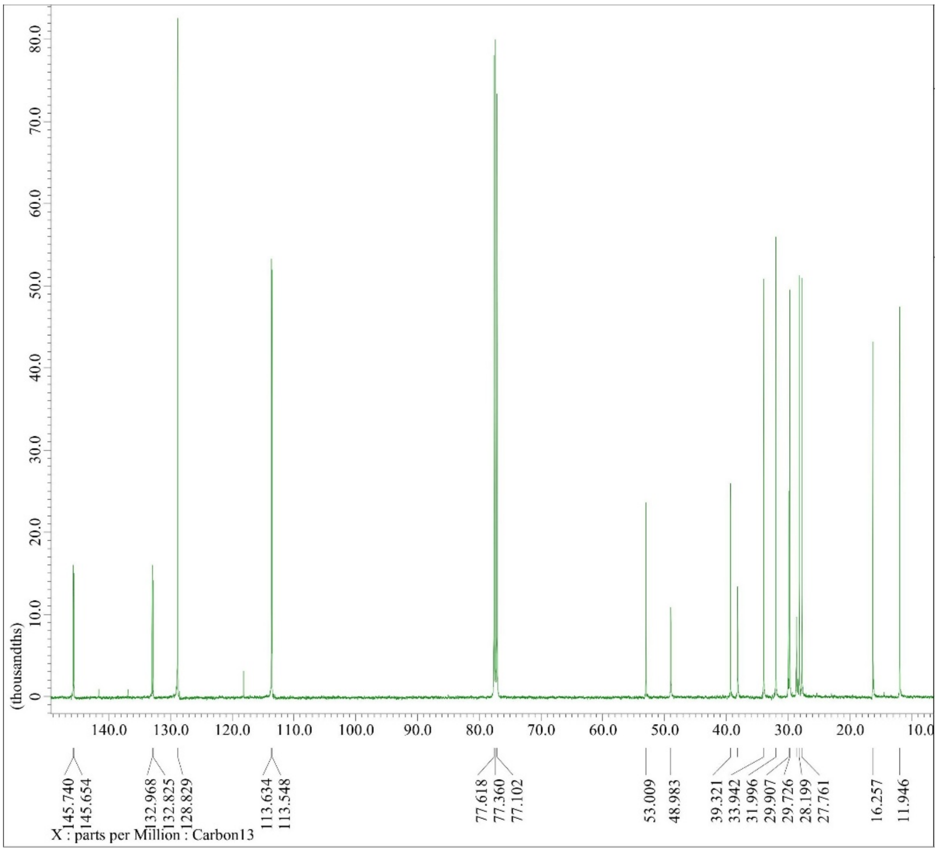
(thousandths)
X : parts per Million : Carbon13
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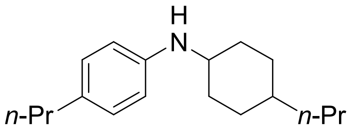
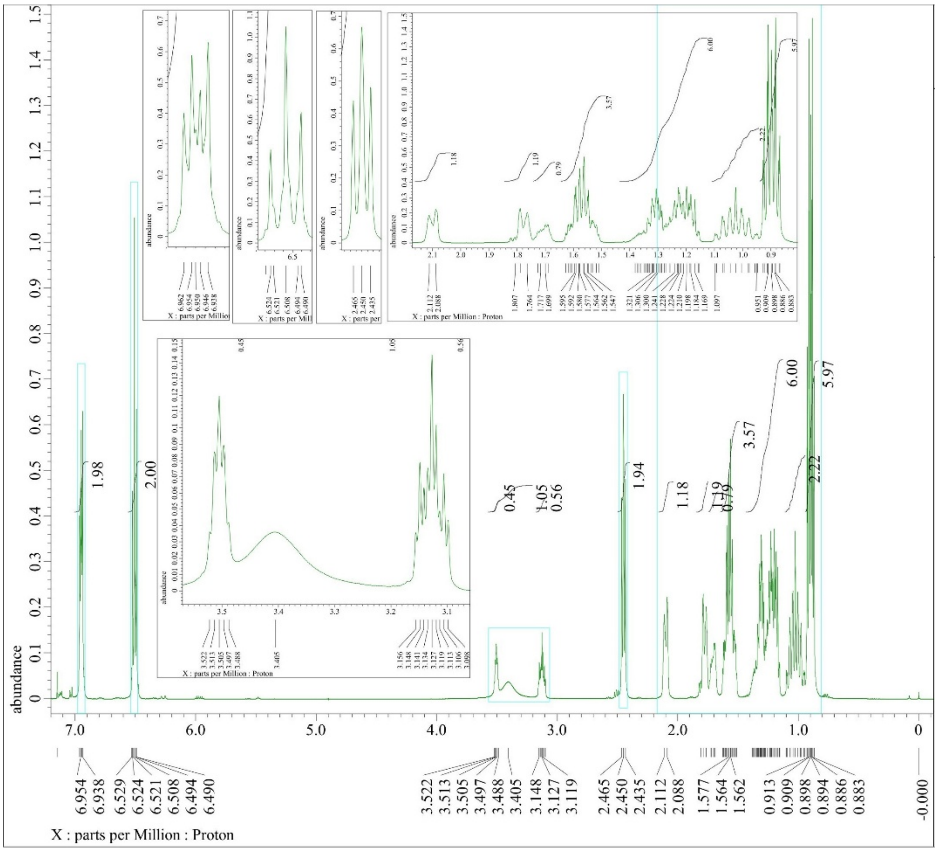
11.946


H
N
n-Pr
n-Pr

2f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3.57
6.00
2.22
5.97
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
6.954
6.938
6.529
6.524
6.521
6.508
6.494
6.490
3.522
3.513
3.505
3.497
3.488
3.405
3.148
3.127
3.119
2.465
2.450
2.435
2.112
2.088
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0.898
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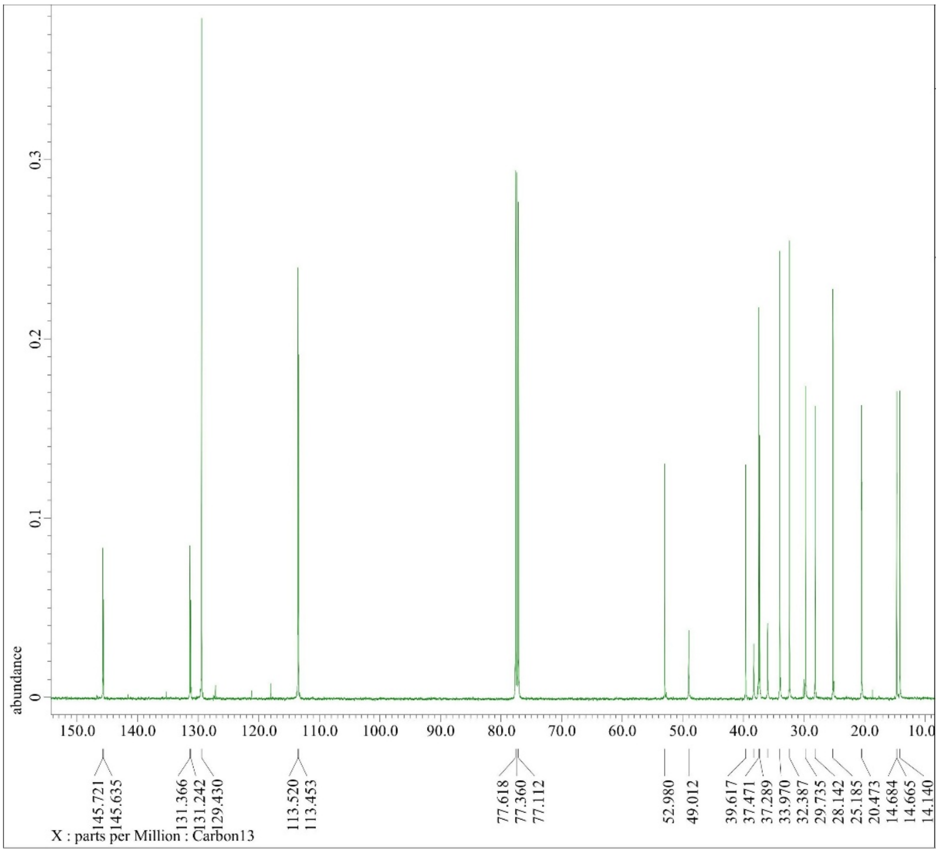
X : parts per Million : Proton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120.0
110.0
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60.0
50.0
40.0
30.0
20.0
10.0
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145.635
131.366
131.242
129.430
113.520
113.453
77.618
77.360
77.112
52.980
49.012
39.617
37.471
37.289
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29.735
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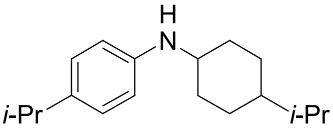
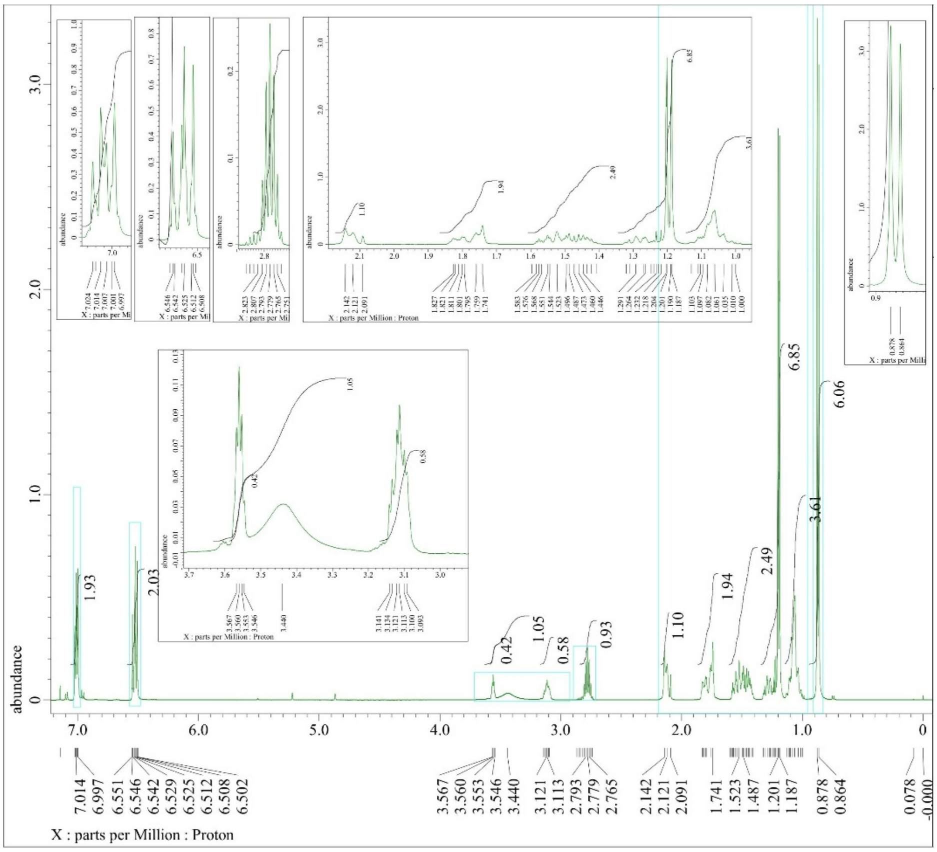
14.140
X : parts per Million : Carbon13


H
N
i-Pr
i-Pr

2g


abundance
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3.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.93
2.03
0.42
1.05
0.58
0.93
1.10
1.94
2.49
6.85
3.61
6.06
7.014
6.997
6.551
6.546
6.542
6.529
6.525
6.512
6.508
6.502
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3.560
3.553
3.546
3.440
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3.113
2.793
2.779
2.765
2.142
2.121
2.091
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1.201
1.187
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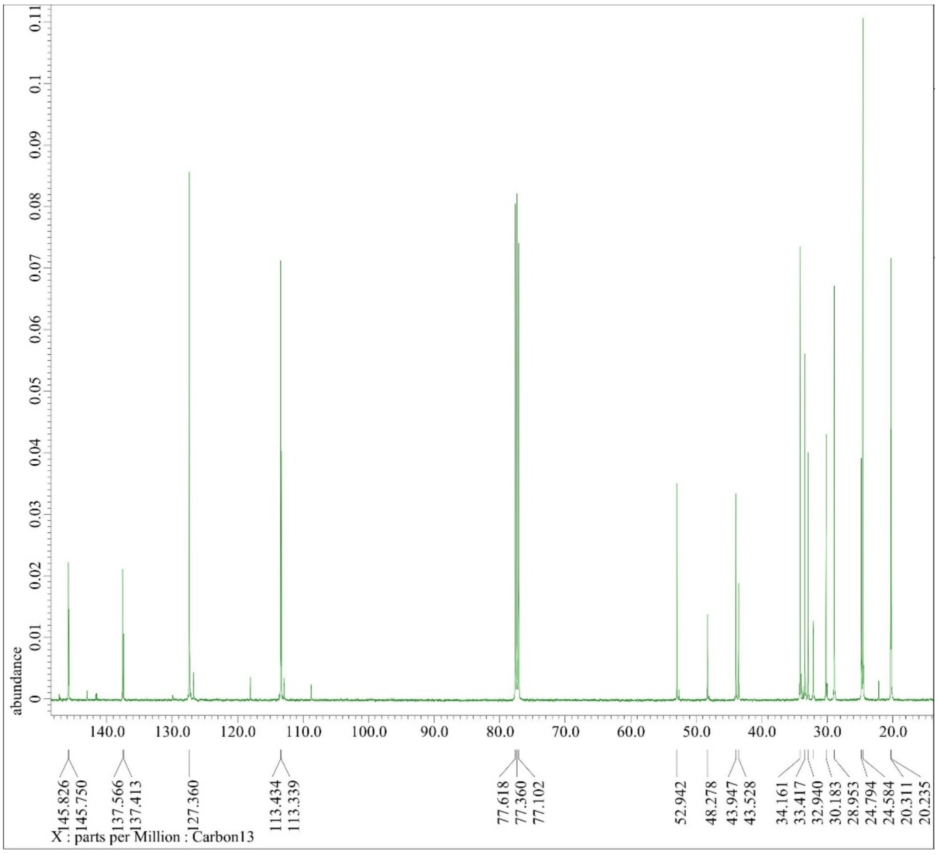
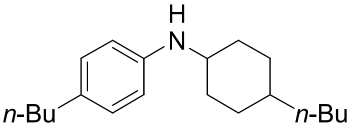
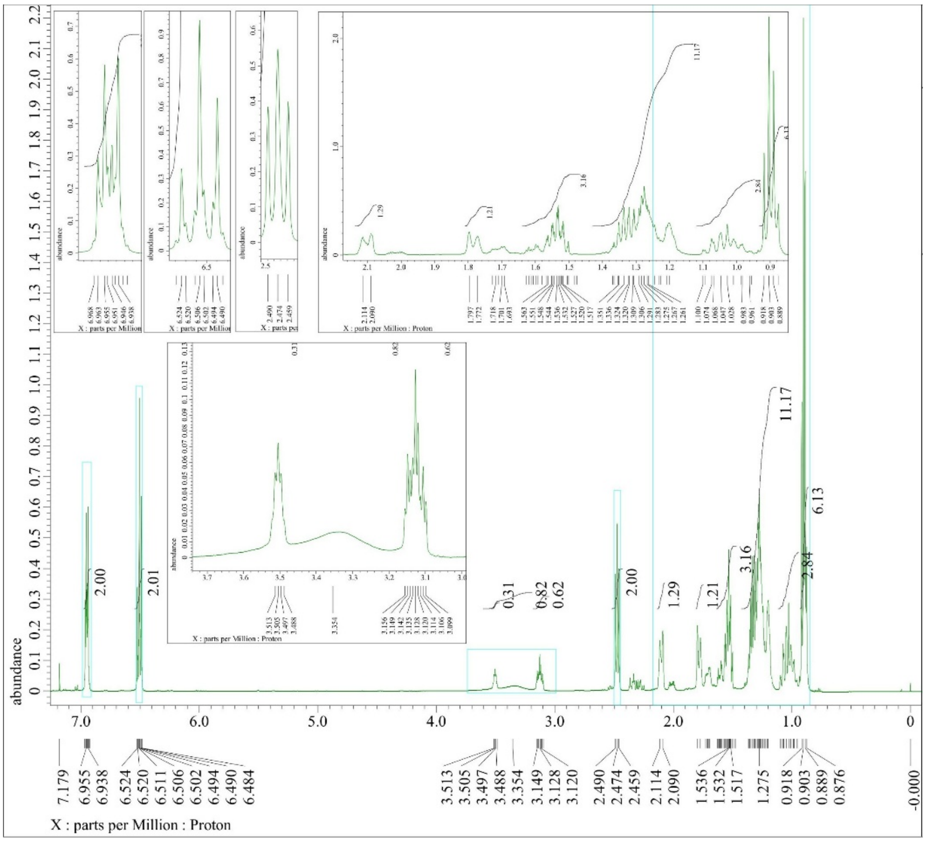
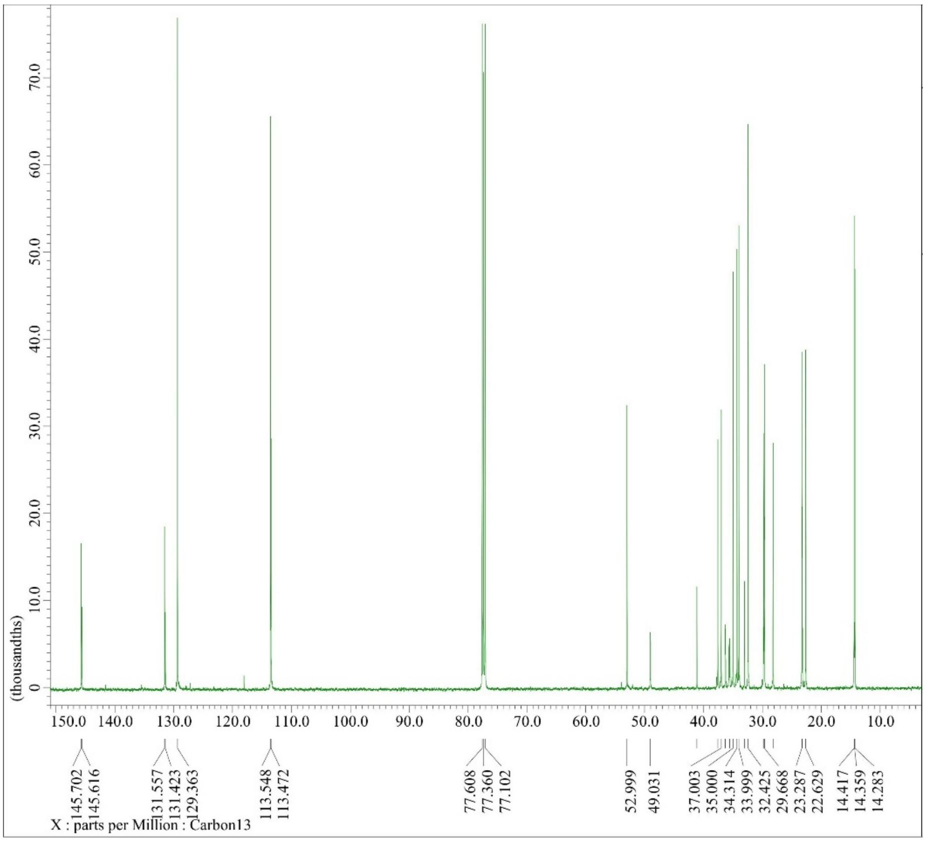
0.864
0.078
-0.000
X : parts per Million : Proton

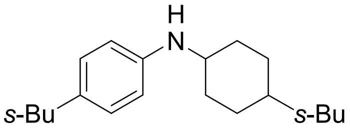

abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
145.826
145.750
137.566
137.413
127.360
113.434
113.339
77.618
77.360
77.102
52.942
48.278
43.947
43.528
34.161
33.417
32.940
30.183
28.953
24.794
24.584
20.311
20.235
X : parts per Million : Carbon13


H
N
n-Bu
n-Bu

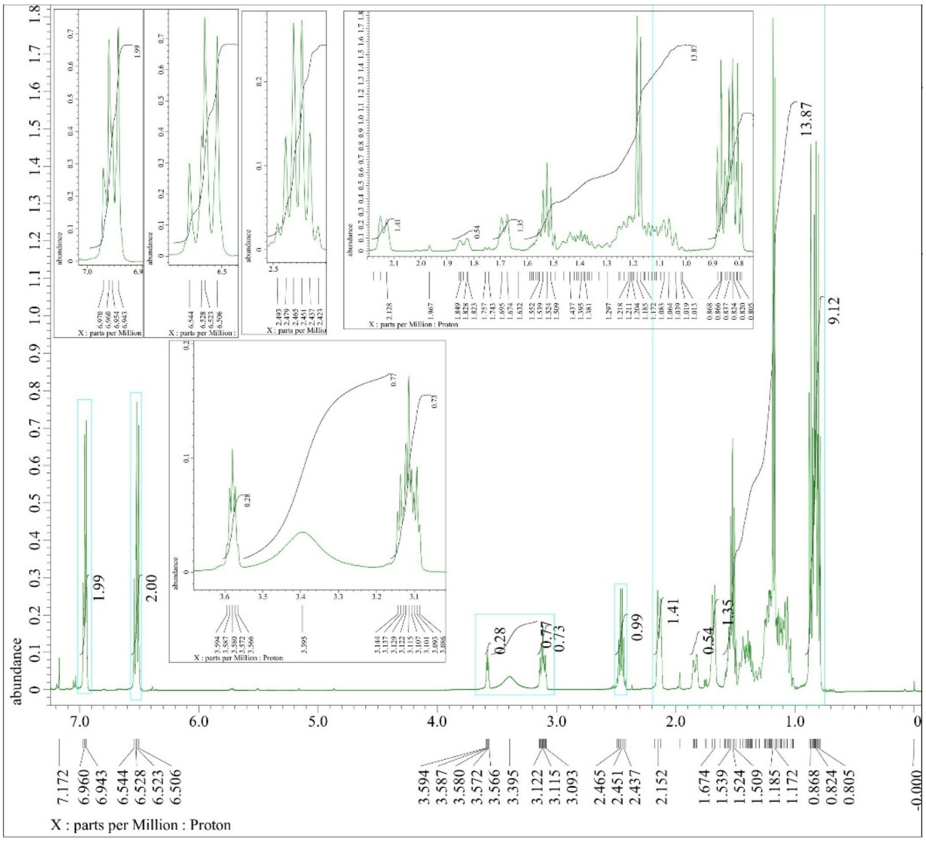
2h

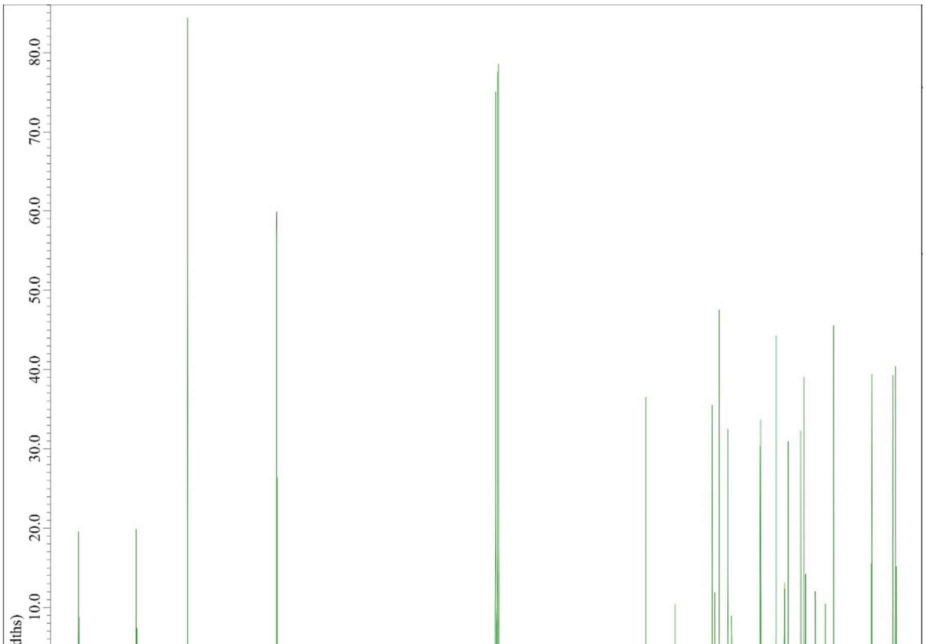

abundance
2.00
2.01
0.31
0.82
0.62
2.00
1.29
1.21
3.16
11.17
2.84
6.13
7.179
6.955
6.938
6.524
6.520
6.511
6.506
6.502
6.494
6.490
6.484
3.513
3.505
3.497
3.488
3.354
3.149
3.128
3.120
2.490
2.474
2.459
2.114
2.090
1.536
1.532
1.517
1.275
0.918
0.903
0.889
0.876
-0.000
X : parts per Million : Proton

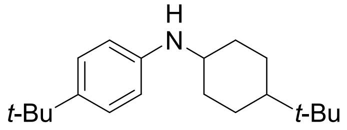

(thousandths)
145.702
145.616
131.557
131.423
129.363
113.548
113.472
77.608
77.360
77.102
52.999
49.031
37.003
35.000
34.314
33.999
32.425
29.668
23.287
22.629
14.417
14.359
14.283
X : parts per Million : Carbon13


H
N
s-Bu
s-Bu

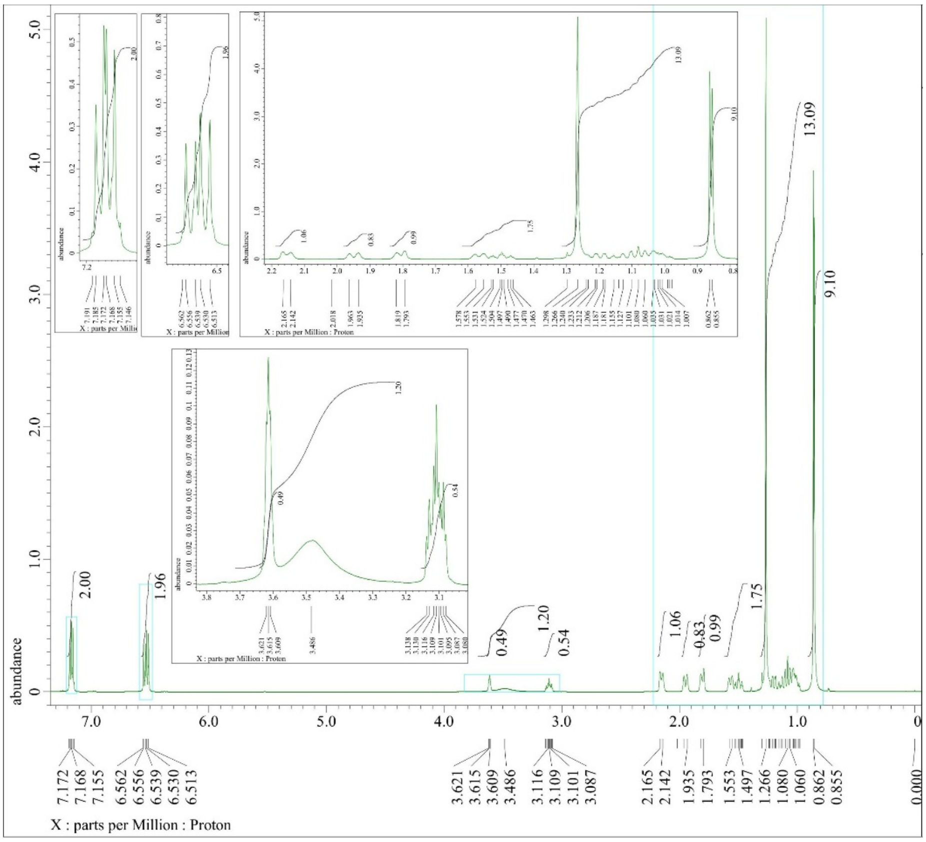
2i

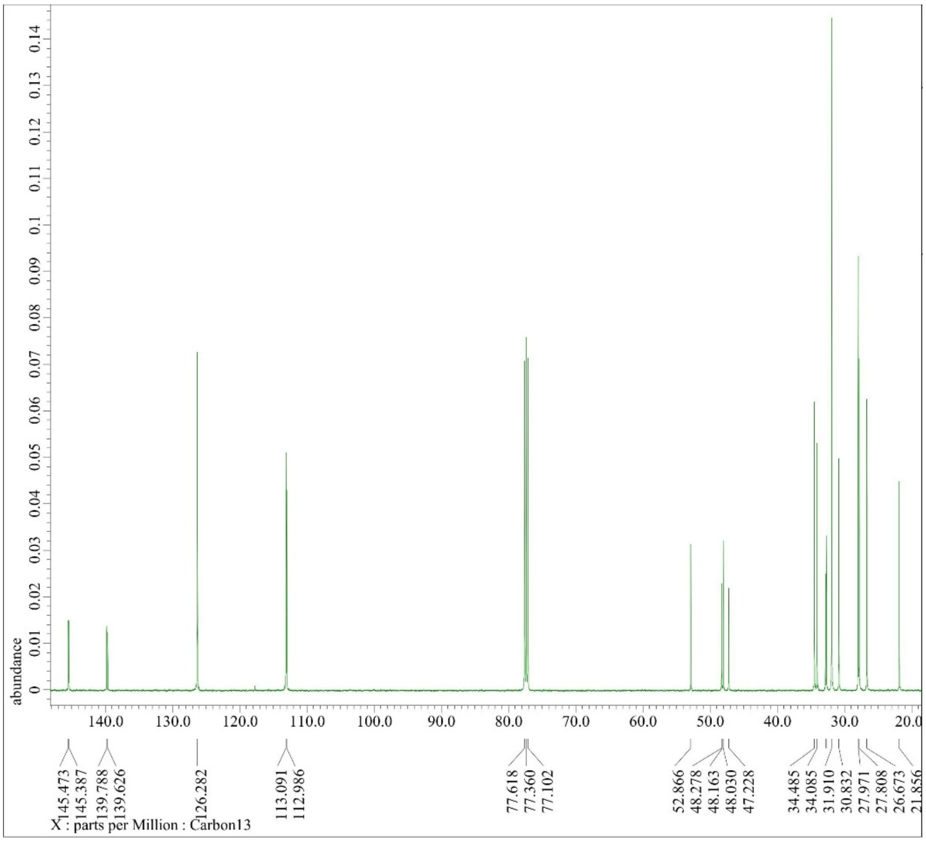

abundance
1.99
2.00
0.28
0.77
0.73
0.99
1.41
0.54
1.35
13.87
9.12
7.172
6.960
6.943
6.544
6.528
6.523
6.506
3.594
3.587
3.580
3.572
3.566
3.395
3.122
3.115
3.093
2.465
2.451
2.437
2.152
1.674
1.539
1.524
1.509
1.185
1.172
0.868
0.824
0.805
-0.000
X : parts per Million : Proton

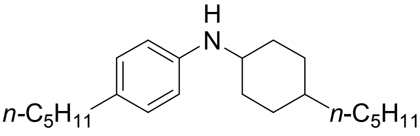

(thousandths)
145.836
145.769
136.393
136.250
127.999
113.424
113.339
77.608
77.360
77.102
53.066
48.249
42.173
41.009
34.247
31.710
29.735
27.684
27.131
22.305
16.057
12.614
12.232
X : parts per Million : Carbon13


H
N
t-Bu
t-Bu

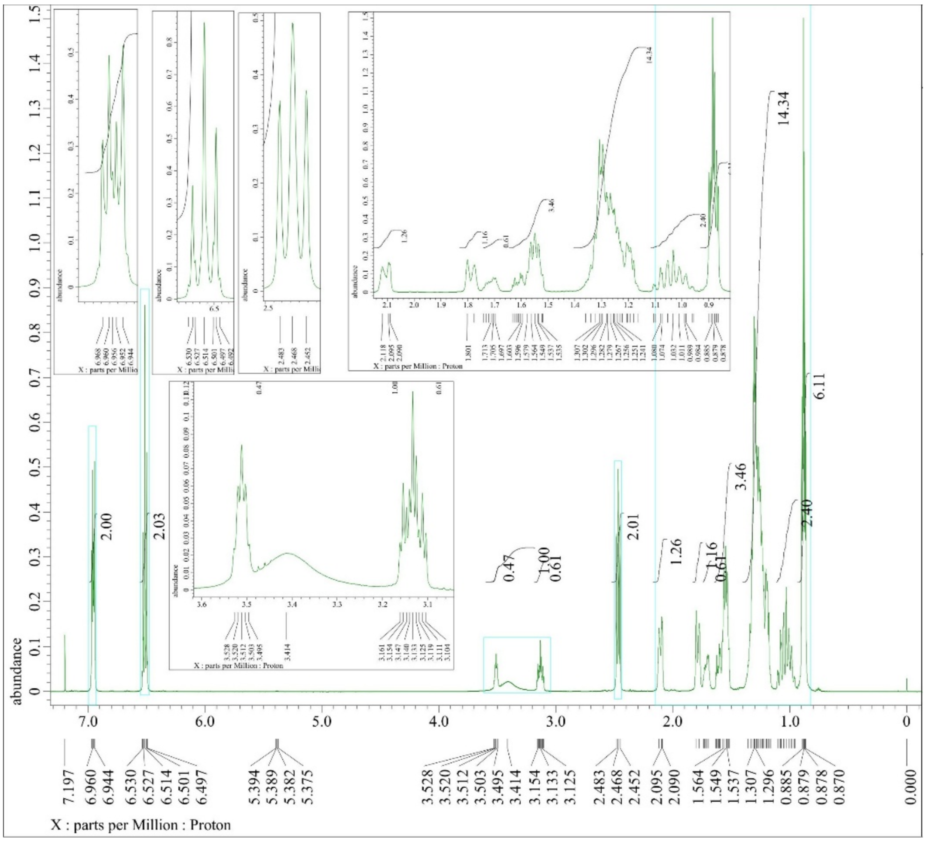
2j

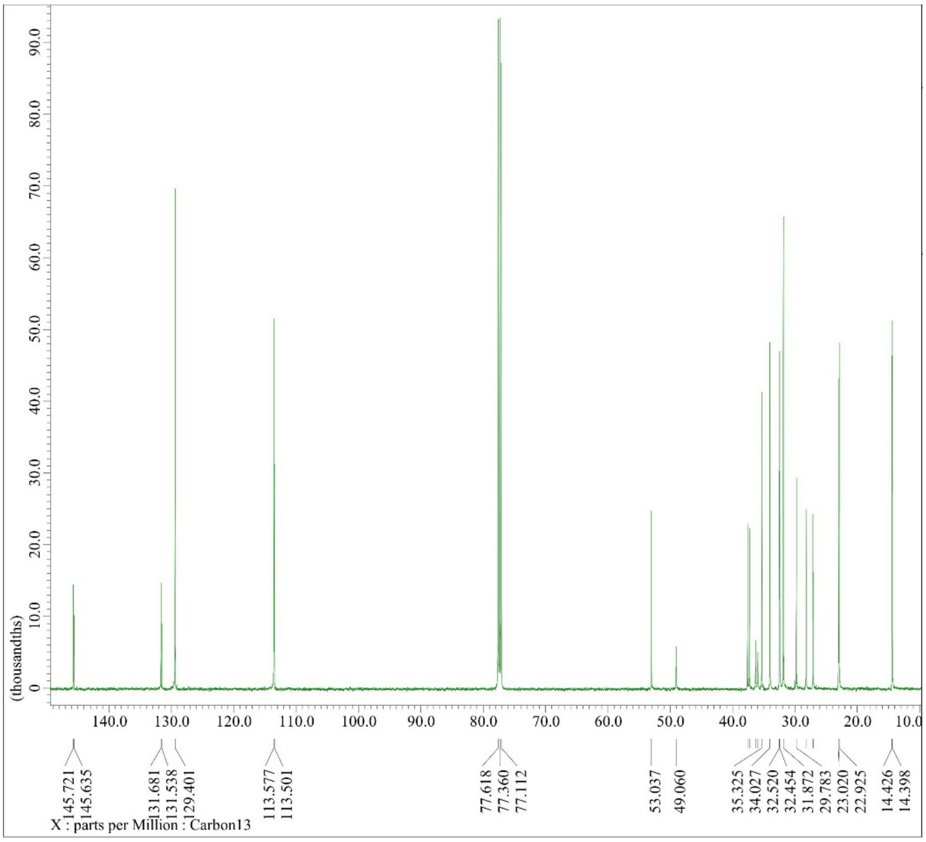

abundance
5.0
4.0
3.0
2.0
1.0
0
2.00
1.96
0.49
1.20
0.54
1.06
0.83
0.99
1.75
13.09
9.10
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.172
7.168
7.155
6.562
6.556
6.539
6.530
6.513
3.621
3.615
3.609
3.486
3.116
3.109
3.101
3.087
2.165
2.142
1.935
1.793
1.553
1.497
1.266
1.080
1.060
0.862
0.855
0.000
X : parts per Million : Proton


abundance
0.14
0.13
0.12
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
145.473
145.387
139.788
139.626
126.282
113.091
112.986
77.618
77.360
77.102
52.866
48.278
48.163
48.030
47.228
34.485
34.085
31.910
30.832
27.971
27.808
26.673
21.856
X : parts per Million : Carbon13


H
N
n-C5H11
n-C5H11

2k


abundance
2.00
2.03
0.47
1.00
0.61
2.01
1.26
1.16
0.61
3.46
14.34
2.40
6.11
7.197
6.960
6.944
6.530
6.527
6.514
6.501
6.497
5.394
5.389
5.382
5.375
3.528
3.520
3.512
3.503
3.495
3.414
3.154
3.133
3.125
2.483
2.468
2.452
2.095
2.090
1.564
1.549
1.537
1.307
1.296
0.885
0.879
0.878
0.870
0.000
X : parts per Million : Proton


(thousandths)
145.721
145.635
131.681
131.538
129.401
113.577
113.501
77.618
77.360
77.112
53.037
49.060
35.325
34.027
32.520
32.454
31.872
29.783
23.020
22.925
14.426
14.398
X : parts per Million : Carbon13