

Synthesis of Imines from Amines in Aliphatic Alcohols on Pd/ZrO₂ Catalyst at Ambient Conditions

Wenjing Cui,^a Bao Zhaorigetu,^{*a} Meilin Jia,^a and Wulan Ao,^a Huaiyong Zhu^b

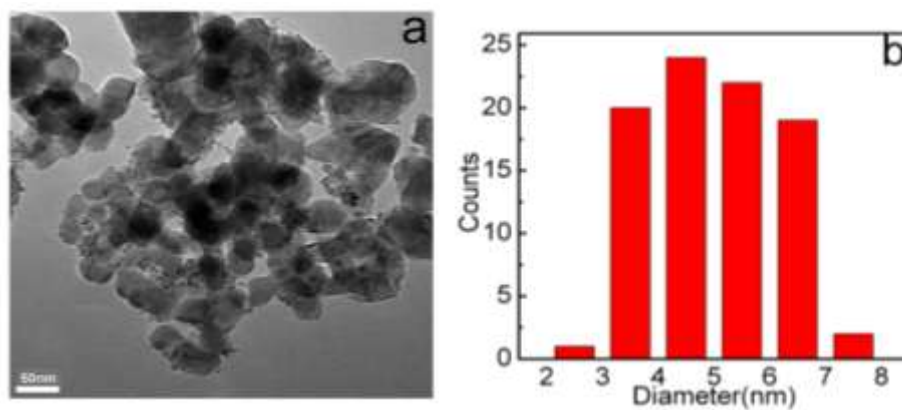


Figure S1. (a) TEM images and (b) size distribution of the 1% wtPd/ZrO₂ catalysts.

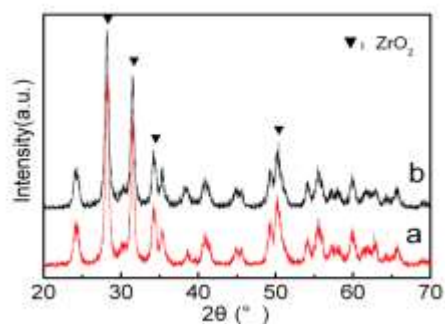


Figure S2. XRD pattern of (a) 1 wt% Pd/ZrO₂ catalysts and (b) ZrO₂

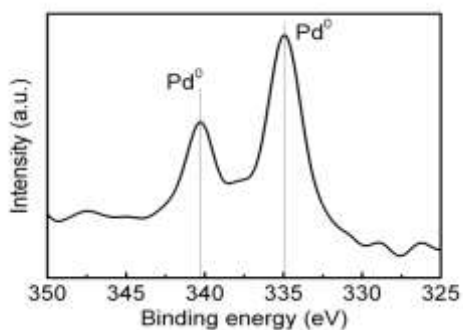


Figure S3. X-ray photoelectron spectrum (XPS) of Pd 3d in 1 wt% Pd/ZrO₂

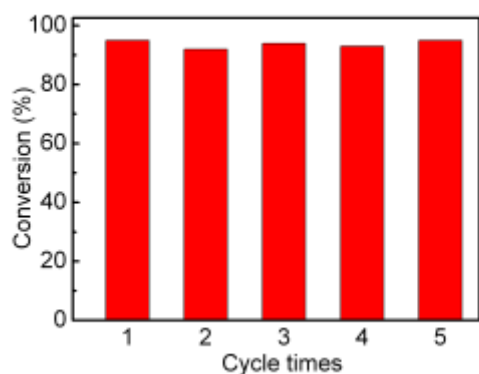


Figure S4. Recyclability tests of Pd/ZrO₂ for the synthesis of imine from benzylamine and ethanol

Table S1 The reaction of benzylamine with aliphatic alcohols on different catalysts^a

Entry	Aliphatic Alcohol	Yield (%) ^b		
		3 wt% Au/ZrO ₂	3 wt% Pd/ZrO ₂	3 wt% Au-Pd/ZrO ₂
1	CH ₃ OH(2b)	0	88	84
2	2a	34	97	94
3	CH ₃ (CH ₂) ₂ OH(2c)	34	84	64
4	CH ₃ (CH ₂) ₃ OH(2d)	46	83	83
5	CH ₃ (CH ₂) ₄ OH(2e)	51	96	84
6	CH ₃ (CH ₂) ₅ OH(2f)	39	86	74
7	(2g)	25	77	86
8	(2h)	44	74	83
9	(2i)	33	10	59(76) ^c
10	(2j)	30	12	97
11	(2k)	33	3	97
12	(2l)	0	0	0

^a Reaction conditions: 1 (1 mmol), 2 (10 mL), catalyst (10 mg), KOH (0.1 mmol), air atmosphere, 30°C, 6h;
^b determined by GC; ^c reaction time 12 h.

Experimental

General. The mixture of amine **1a** (1 mmol), alcohol **2a** (10 mL), 1 wt% Pd/ZrO₂ (10 mg) and KOH (0.1 mmol) was sealed under air in a 25 mL tube, stirred at 30 °C for 6 h. During the reactions 0.1 mL specimens were periodically sampled, filtered and analyzed by GC (Shimadzu GC-2014) with a capillary column of Rtx-5 (30 m length, 0.25 mm internal diameter, 0.25 μm film thickness), temperature of column ranged from 100 to 220 °C (6 °C/min), and injector temperature was 260 °C and flame ionization detector was used for product analysis. All synthetic compounds are known, and they were identified by comparison with authentic samples. Selected products were purified by column chromatography on alumina gel (V petroleum ether: V ethyl acetate: V triethylamine was 100: 10: 1), and were analyzed by ¹H NMR. We compared their ¹H NMR spectra with the reported literature. GC-MS (Thermo DSQ II) with a HP-5 column was also used to identify the products.

Characterization of products and Reference

N-ethylidenebenzylamine

Product **3aa** (CAS registry No: 34233-75-5) ¹H NMR (500 MHz, MeOD) δ 7.74 (t, *J* = 5.2 Hz, 1H), 7.39–7.31 (m, 5H), 4.54 (s, 2H), 1.86 (dt, 3H) ppm. This compound was known: F. Texier-Boullet, *Synthesis*, 1985, 679–681.

N-propylidenebenzylamine

Product **3ac** (CAS registry No: 63459-05-2): ¹H NMR (500 MHz, MeOD) δ 7.82 (t, *J* = 5.2 Hz, 1H), 7.39–7.19 (m, 5H), 4.53 (s, 2H), 2.33–2.18 (m, 2H), 1.69–1.53 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H) ppm. This compound was known: V. Coeffard, C. Thobie-Gautier, I. Beaudet, *Eur. J. Org. Chem.*, 2008, 383–391.

N-butylidenebenzylamine

Product **3ad** (CAS registry No: 56249-61-7)

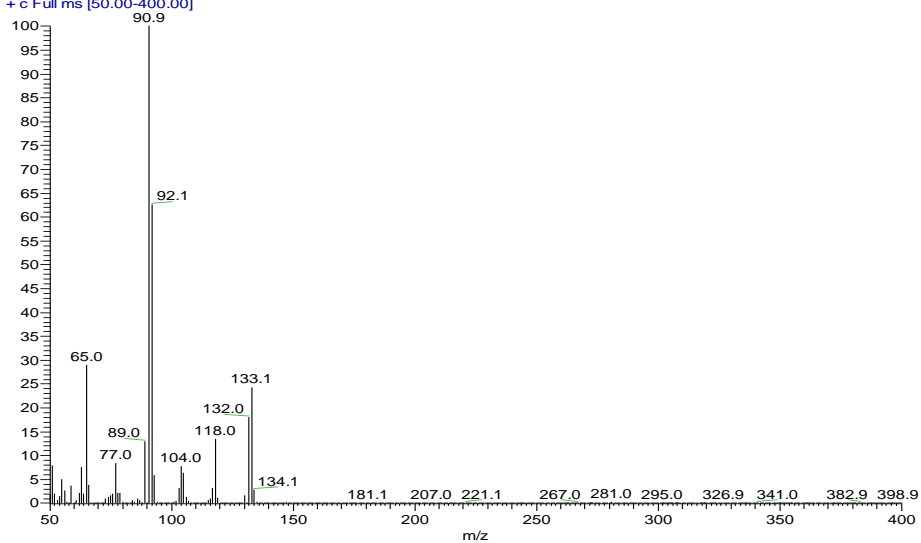
¹H NMR (500 MHz, MeOD) δ 7.94 (t, 1H), 7.50–7.35 (m, 5H), 4.54(s, 2H), 2.57 (td, *J* = 7.0, 1.2

Hz, 2H), 1.71 (dt, $J = 14.5, 7.2$ Hz, 2H), 0.95 (t, $J = 7.4$ Hz, 3H). This compound was known: P. K. Khatri, S. L. Jain, L. N. Sivakumar K, Org. Biomol. Chem., 2011, 9, 3370–3374.

Results of GC-MS:

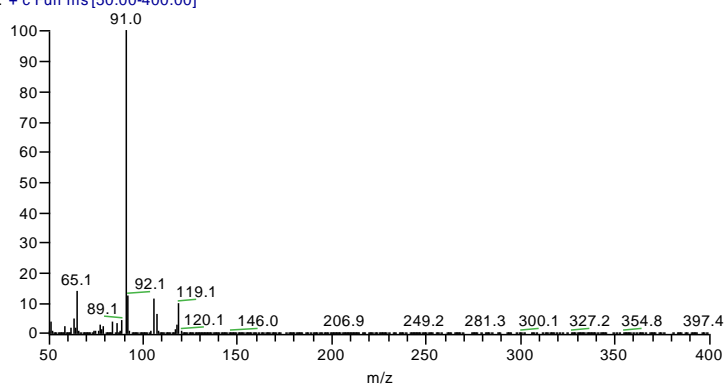
3aa

D #312-405 RT: 4.32-4.71 AV: 94 NL: 5.53E8
T: + c Full ms [50.00-400.00]



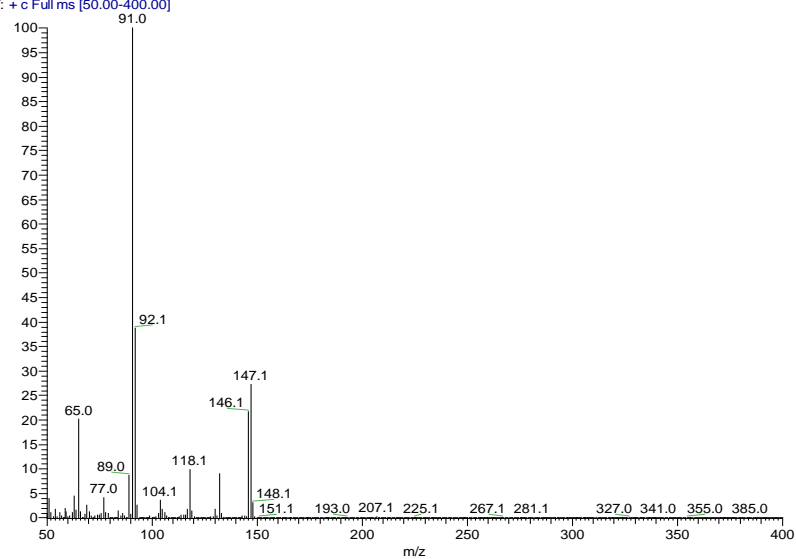
3ab

A #200 RT: 3.84 AV: 1 NL: 8.22E⁻
T: + c Full ms [50.00-400.00]



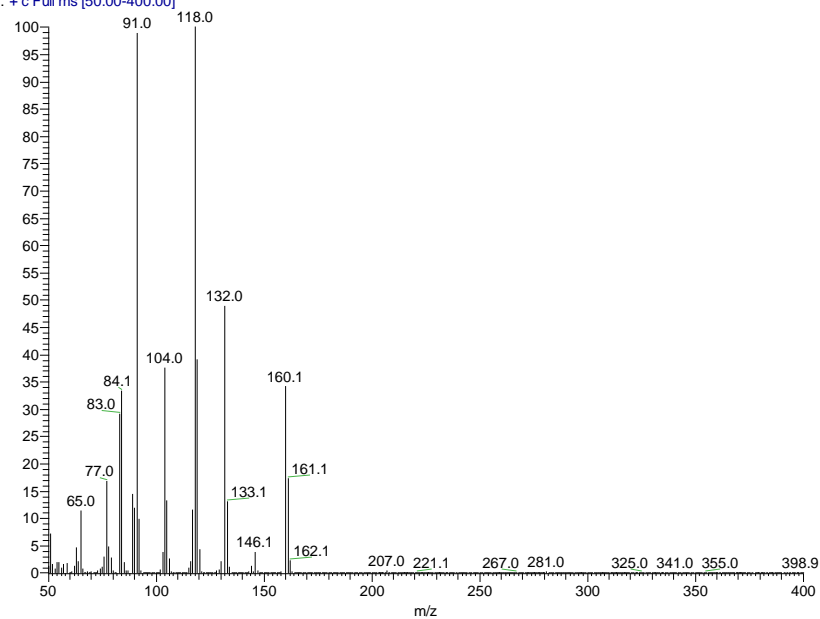
3ac

A #449-561 RT: 4.90-5.38 AV: 113 NL: 2.61E8
T: + c Full ms [50.00-400.00]



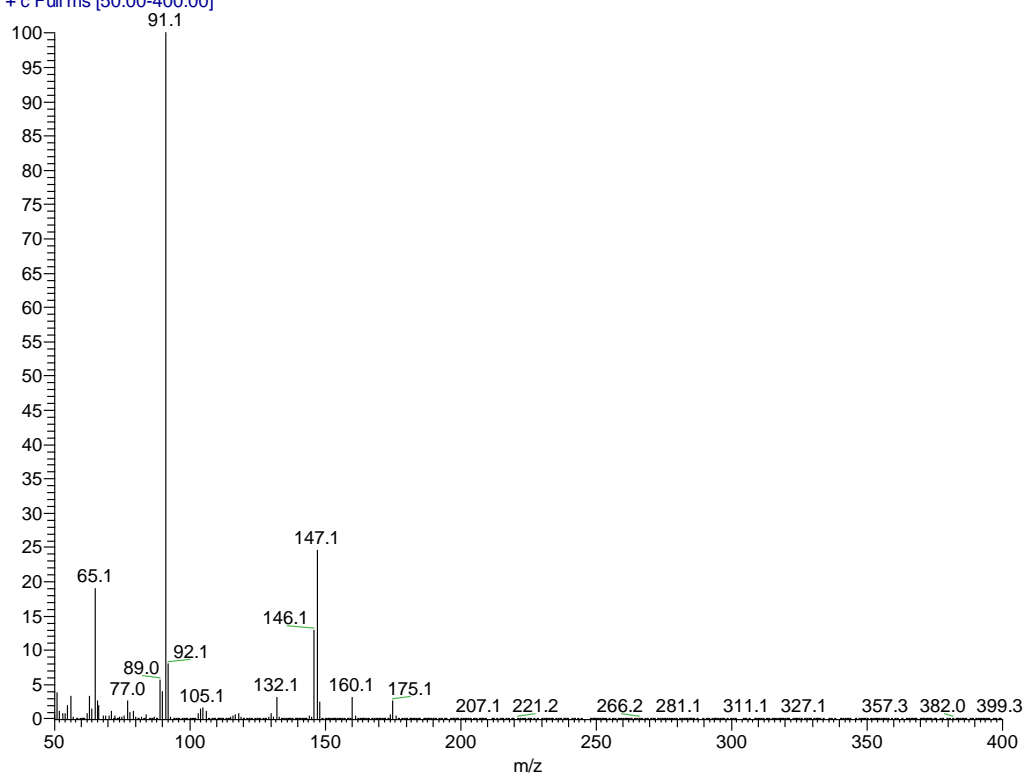
3ad

F #748 RT: 6.17 AV: 1 NL: 1.02E9
T: + c Full ms [50.00-400.00]



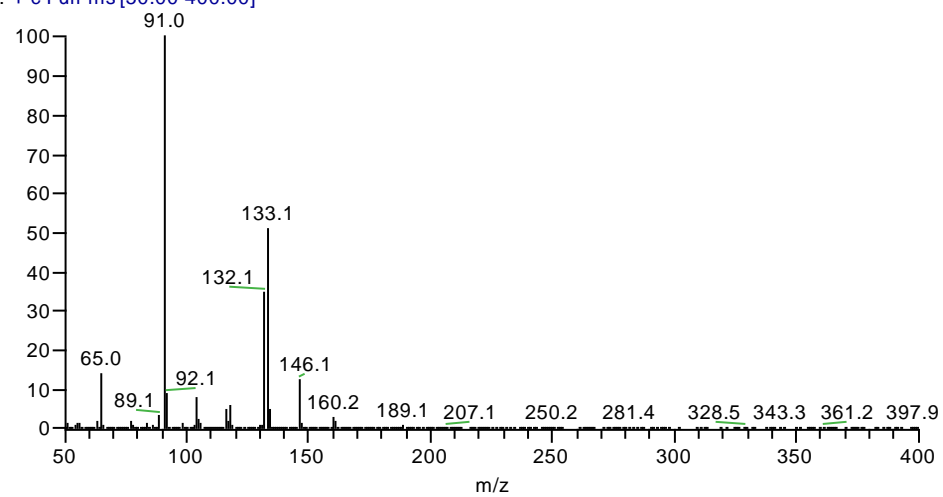
3ae

O #962 RT: 7.08 AV: 1 NL: 2.27E8
T: + c Full ms [50.00-400.00]



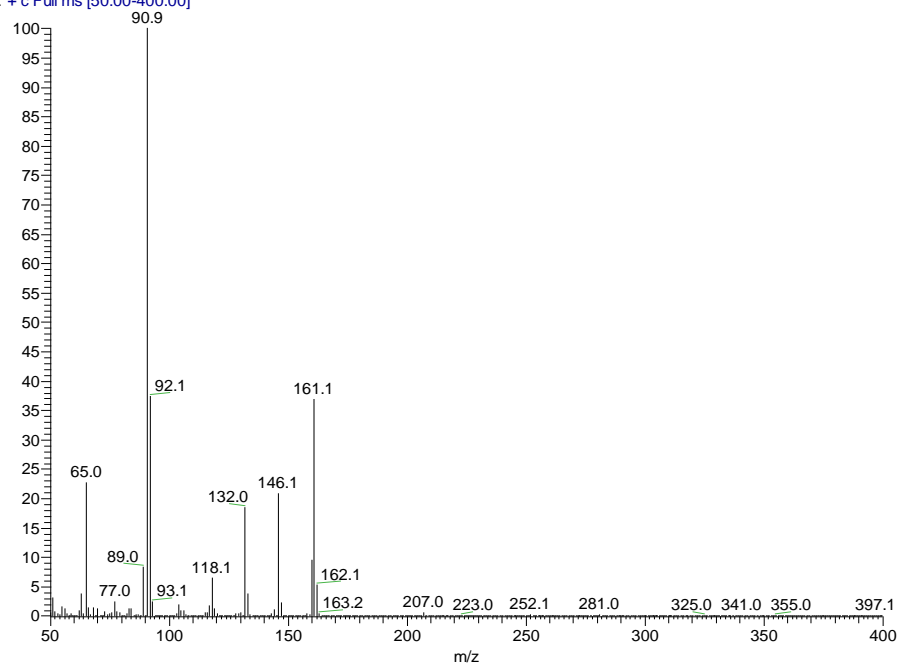
3af

I #1324 RT: 8.61 AV: 1 NL: 3.26E⁻
T: + c Full ms [50.00-400.00]



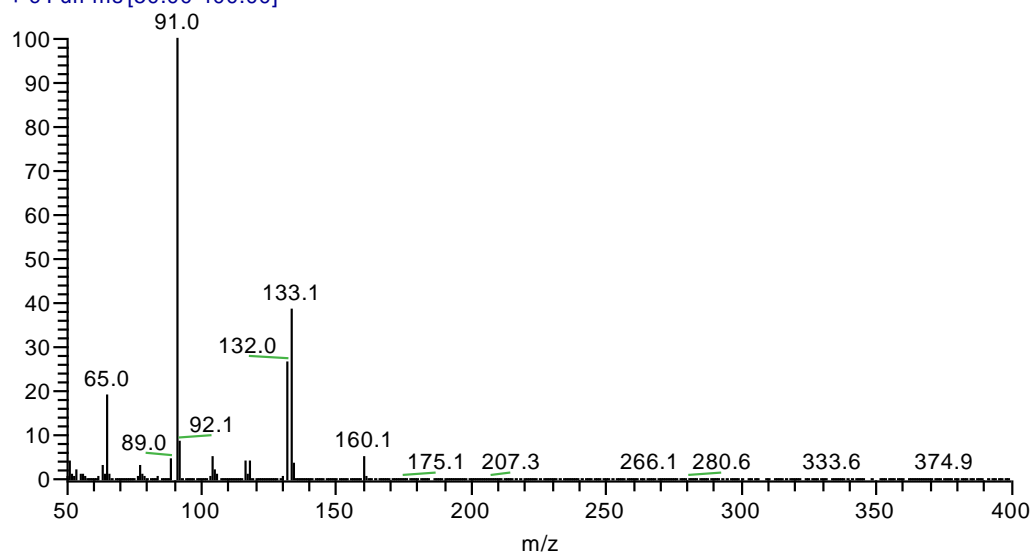
3ag

C #580-629 RT: 5.46-5.66 AV: 50 NL: 9.79E8
T: + c Full ms [50.00-400.00]



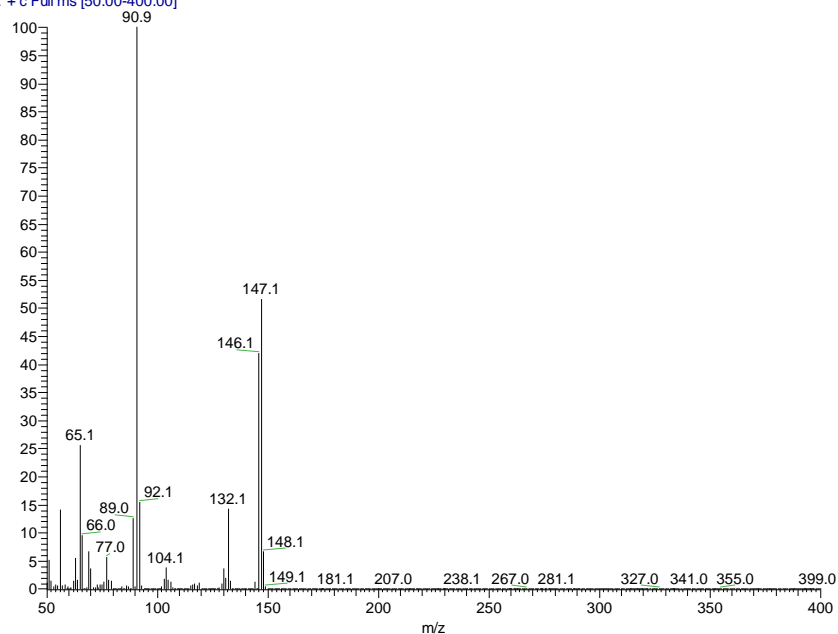
3ah

14 #818 RT: 6.47 AV: 1 NL: 1.80E^8
T: + c Full ms [50.00-400.00]



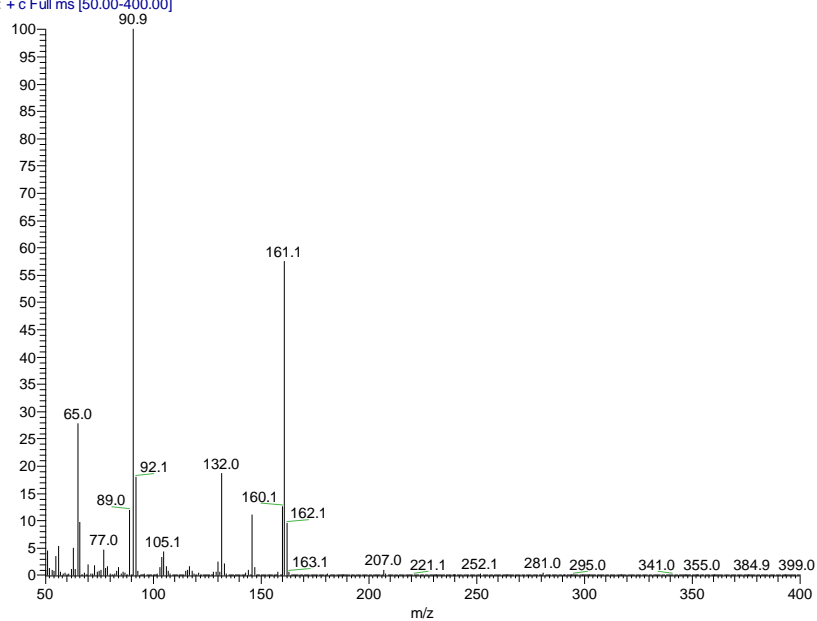
3ai

E #554-616 RT: 5.35-5.61 AV: 63 NL: 4.01E8
T: + c Full ms [50.00-400.00]



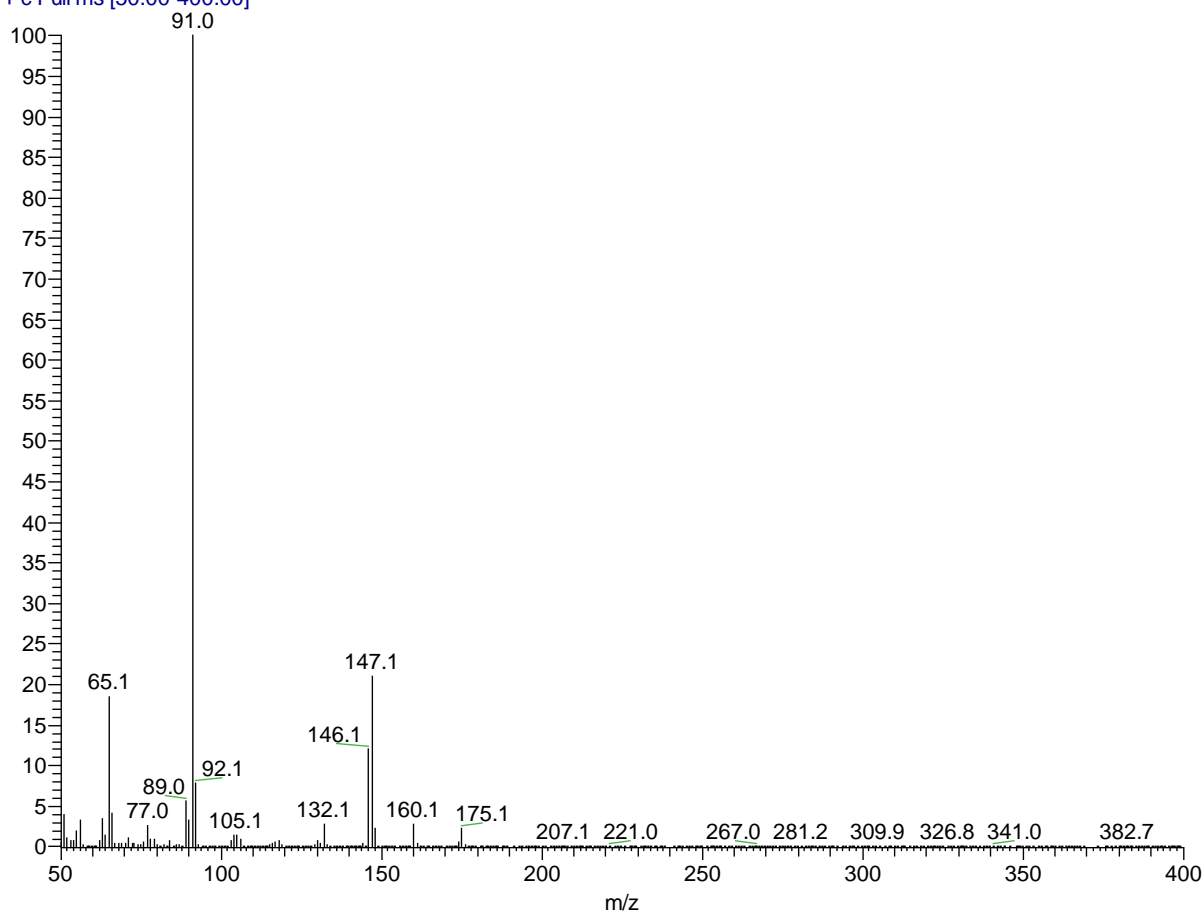
3aj

B #672-858 RT: 5.85-6.64 AV: 187 NL: 2.34E8
T: + c Full ms [50.00-400.00]



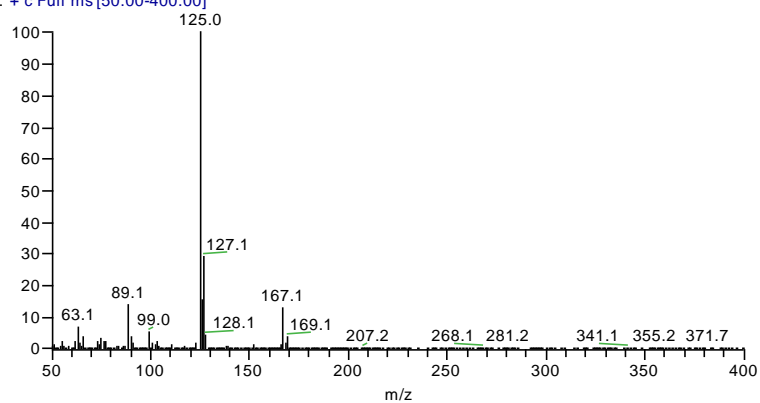
3ak

C #961 RT: 7.07 AV: 1 NL: 8.28E7
T: + c Full ms [50.00-400.00]



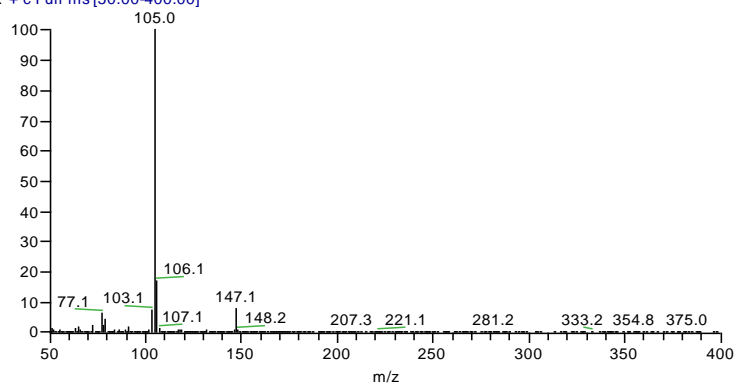
3ba

W #706 RT: 5.99 AV: 1 NL: 2.34E7
T: + c Full ms [50.00-400.00]



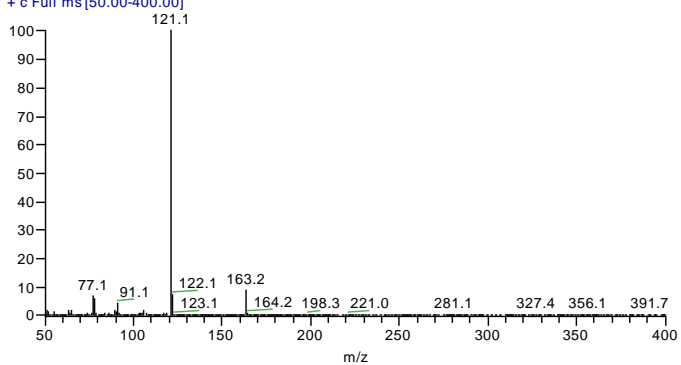
3ca

10 #520 RT: 5.20 AV: 1 NL: 1.65F⁺
T: + c Full ms [50.00-400.00]



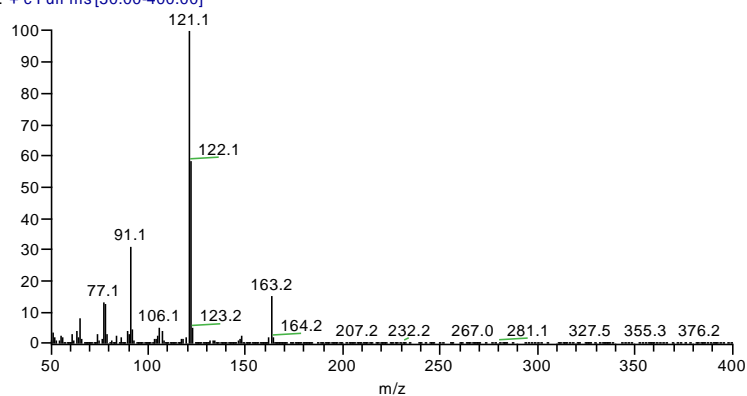
3da

V #869 RT: 6.68 AV: 1 NL: 7.30E⁻
T: + c Full ms [50.00-400.00]



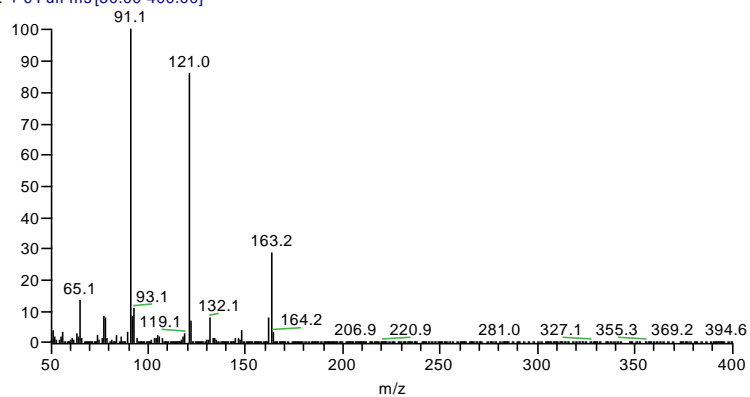
3ea

X #837 RT: 6.54 AV: 1 NL: 3.03E⁻
T: + c Full ms [50.00-400.00]



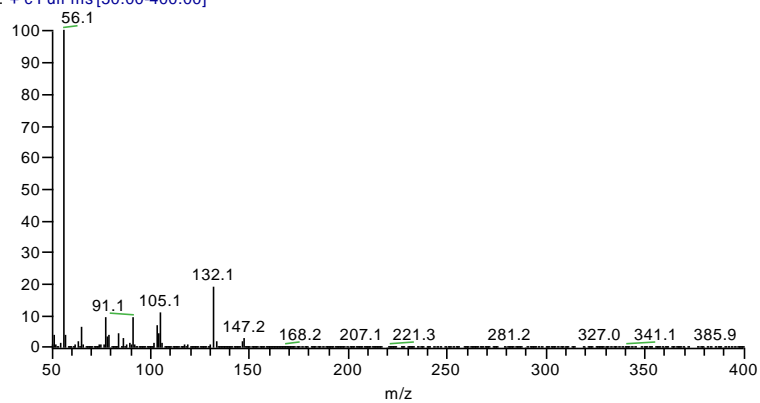
3fa

9 #765 RT: 6.24 AV: 1 NL: 4.80E⁻
T: + c Full ms[50.00-400.00]



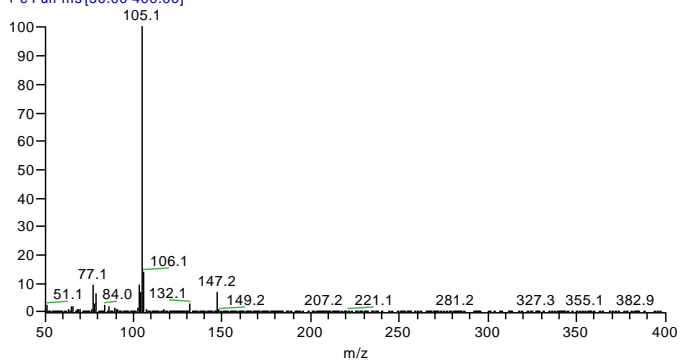
3ga

T #433 RT: 4.83 AV: 1 NL: 4.35E⁻
T: + c Full ms[50.00-400.00]



3ha

Y #347 RT: 4.47 AV: 1 NL: 6.08E⁻
T: + c Full ms[50.00-400.00]



3ia

U #2188 RT: 12.28 AV: 1 NL: 1.2⁺
T: + c Full ms [50.00-400.00]

