ANEXOS

ANEXO I. *El compuesto (S_{Rh},R_C)-[(η^5-C_5Me_5)Rh{(R)-profos}(H)]SbF_6 (**7**).*

Las figuras A y B recogen los espectros de RMN de $^{31}P\{^1H\}$ y de ^1H, en CD_2Cl_2, respectivamente, donde se muestra la presencia del compuesto (S_{Rh},R_C)-[(□□-C_5Me_5)Rh{(*R*)-profos}(H)][SbF_6]. El espectro de $^{31}P\{^1H\}$ muestra dos dobletes de dobletes centrados en 81.74 (*J*(Rh,P) = 135.1 Hz, *J*(P,P) = 23.7 Hz) y 58.88 ppm (*J*(Rh,P) = 139.8 Hz).

En el espectro de RMN de ^1H se observan tres señales a 2.58 (dpt, *J* = 53.7, 13.00 Hz), 2.49 (m) y 1.90 (m) que los espectros COSY (Figura C) y NOESY (Figuras D y E) nos permiten atribuir a los hidrógenos H_{21}, H_{11} y H_{22}, respectivamente, del metalaciclo. El grupo C_5Me_5 aparece como un singlete a 1.46 ppm y el grupo metilo del ligando profos como un doblete de dobletes a 1.12 ppm (*J* = 12.7, 6.5 Hz).

El NOE entre el Hidruro y el H_{11} nos permite asignar la configuración *S* al átomo de rodio (Figura F).

El espectro correlación $^{31}P\{^1H\}$-^1H (Figura G), nos indica que la resonancia a 81.74 ppm es la correspondiente al átomo de fósforo P^1 unido al carbono asimétrico, ya que muestra correlación con el grupo Me del ligando profos. Además, el espectro correlación $^{31}P\{^1H\}$-^1H (Figura G) identifica las resonancias 7.43, 7.60, 7.16 y 7.73 ppm correspondientes a los protones -*orto* de los grupos fenilo Ph_1, Ph_2, Ph_3 y Ph_4 respectivamente.

Finalmente, los NOE entre el Me del ligando profos, y de los hidrógenos H_{21}, H_{11} y H_{22}, con los protones -*orto* de los grupos fenilo Ph_1, Ph_2, Ph_3 y Ph_4 (Figura H) (especialmente los NOE entre Me y Ph_1 y entre H_{22} y Ph_2), así como la ausencia de NOE entre el hidruro y H_{21} (Figuras F y E) nos indican que la conformación del ligando difosfano es λ.

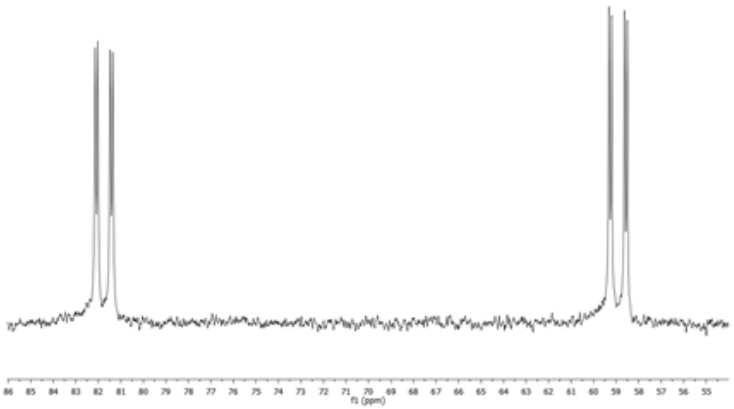


Figura A. Espectro de RMN de $^{31}P\{^1H\}$ del complejo **7** a - 70 °C.

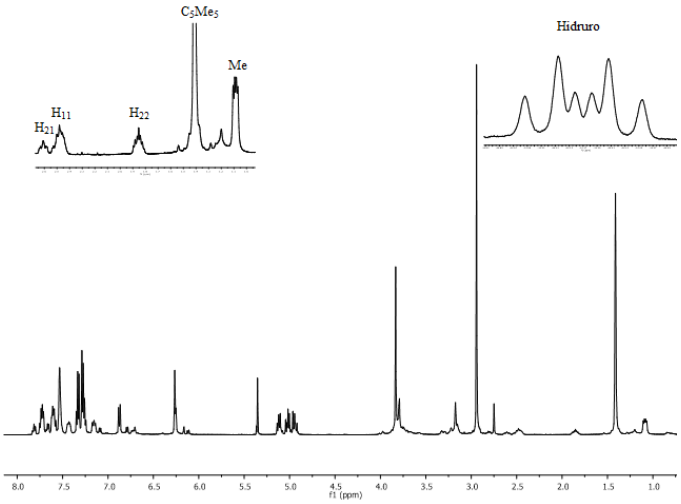


Figura B. Espectro de RMN de ^{1}H del complejo **7** a - 70 °C.

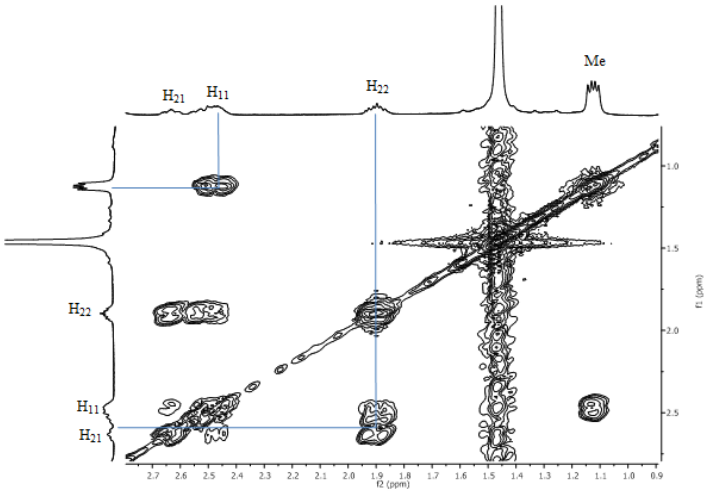


Figura C. Fragmento del espectro ^{1}H-^{1}H COSY del complejo **7** a - 70 °C.

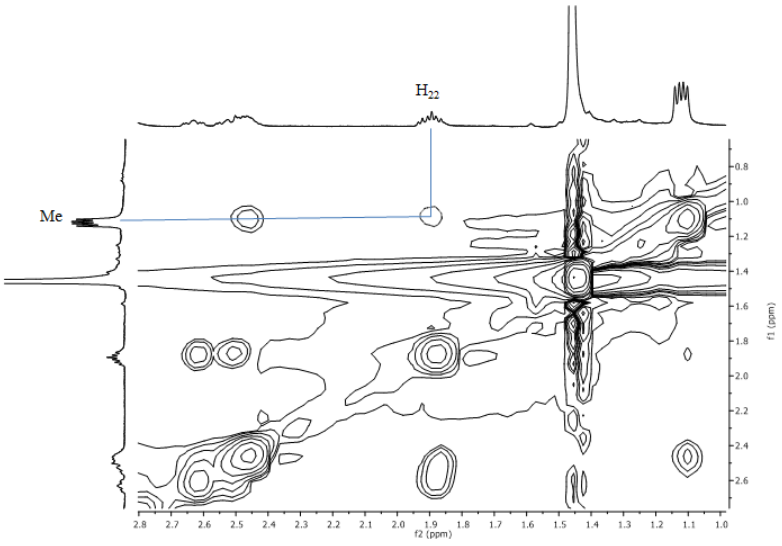
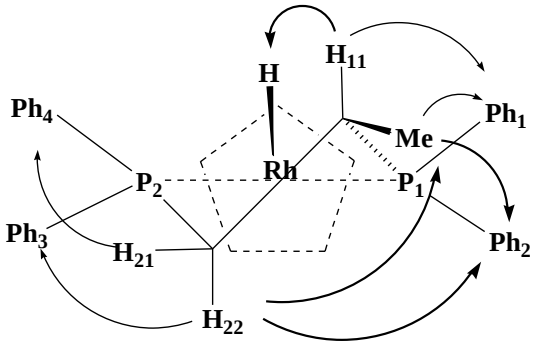


Figura D Fragmento del espectro NOESY del complejo **7** a - 70 °C.



S_{Rh}, λ

Figura E. Diagrama de efectos NOE de **7**.

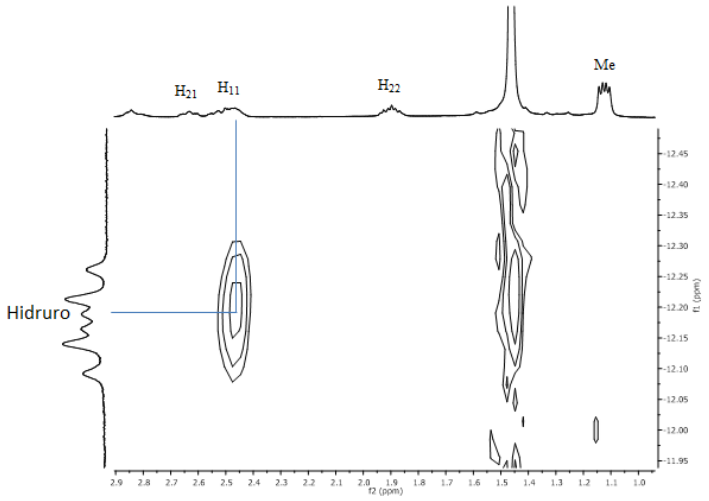


Figura F. Fragmento del espectro NOESY del complejo **7** a - 70 °C.

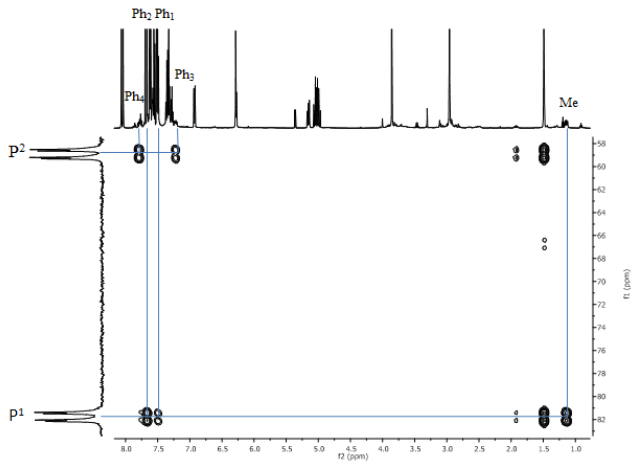


Figura G. Espectro de heterocorrelación ^{1}H- ^{31}P{^{1}H} del complejo **7** a - 70 °C.

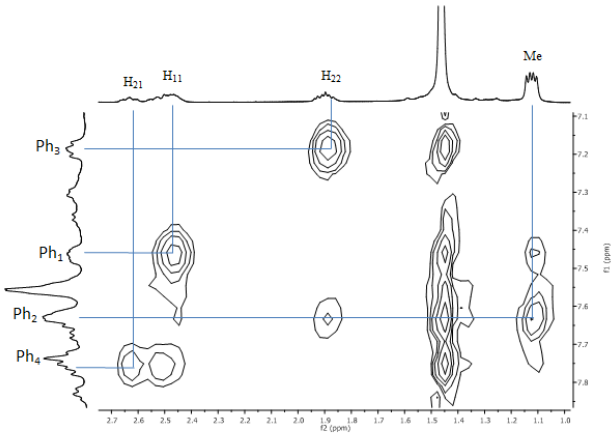
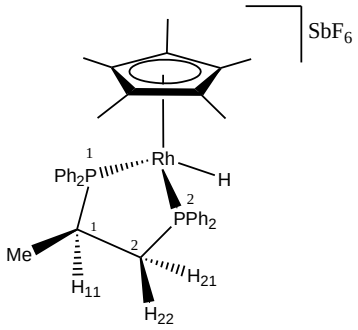


Figura H. Fragmento del espectro NOESY del complejo **7** a - 70 °C.

Caracterización de (S_{Rh},R_C)-[(η^5–C_5Me_5)Rh{(R)-profos}(H)][SbF_6] (7)



^{1}H-NMR (500.10 MHz, CD_2Cl_2, 253 K): δ = 7.9-7.0 (m, 20H, H_{Ar}, *o*-Ph_1= 7.43, *o*-Ph_2= 7.60, *o*-Ph_3= 7.16, *o*-Ph_4= 7.73), 2.58 (dpt, *J* = 53.7, 13.00 Hz, 1H, H_{21}), 2.49 (m, 1H, H_{11}), 1.90 (m, 1H, H_{22}), 1.46 (s, 15H, C_5Me_5), 1.12 (dd, *J* = 12.7, 6.5 Hz, 3H, Me), -12.28 ppm (m, 1H, H).

^{31}P{^{1}H} NMR (202.46 MHz, CD_2Cl_2, 253 K): δ = 81.74 (dd, *J*(Rh,P) = 135.1 Hz, *J*(P,P) = 23.7 Hz, P^1), 58.88 ppm (dd, *J*(Rh,P) = 139.8 Hz, P^2).

^{13}C-RMN (125.77 MHz, 253 K): δ = 136.95-122.28 (Ph), 101.98 (C_5Me_5), 38.29 (dd, *J* = 40.0, 14.0 Hz, C_4), 15.31 (m, Me), 9.78 ppm (C_5Me_5).

ANEXO II. *Síntesis precursores catalíticos.*

Síntesis del precursor catalítico de iridio de estequiometría (S_{Ir},R_C)-[(η^5-C_5Me_5)Ir{(R)-profos}(H_2O)][SbF_6]$_2$.

En atmósfera de argón, a una suspensión de [{(η^5–C_5Me_5)IrCl}$_2$(μ-Cl)$_2$] (0.400 mmol) en acetona (20 mL) se le añaden 1.600 mmol de $AgSbF_6$. La suspensión resultante se mantiene en agitación durante 4 horas y se filtra a través de una cánula metálica con un filtro de papel adecuado.[1]El filtrado se concentra hasta un volumen de unos 5 mL y se enfría hasta -50ºC en un baño de isopropanol. A esta temperatura y bajo atmósfera de argón, se añade (*R*)-profos (0.800 mmol) y se agita durante 30 minutos. Por adición de *n*-hexano (20 mL) se forma un sólido aceitoso amarillento que se disgrega, obteniendo un sólido por agitación en un baño de ultrasonidos. La disolución sobrenadante se decanta, el sólido se lava con *n*-hexano (3 × 20 mL) y se seca a vacío. A continuación el sólido se recristaliza tres veces, a -50ºC en CH_2Cl_2/*n*-hexano, obteniendo un sólido amarillo (472.7 mg obtenidos, 60.2% Rdto.).

Síntesis de los precursores catalíticos de rodio de estequiometría [(η^5 C_5Me_5)Rh(dppe)(H_2O)][SbF_6]$_2$.

La obtención del precatalizador aquiral se llevó a cabo utilizando la misma metodología mostrada en la síntesis anterior, pero utilizando dppe en lugar de (R)-profos.

Se obtienen 723.5 mg (77.8% Rdto.).

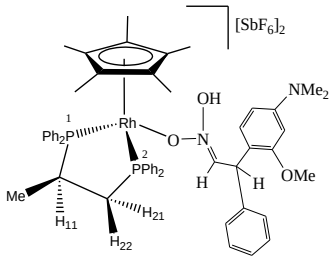
[1] Filter Papers. 542 (Hardened Ashless, Cat No 1542 110) de la empresa Whatman ®.

ANEXO III. *Caracterización de compuestos.*

*Caracterización compuesto aci-nitro (**5**)*

Mayoritario

(S_{Rh}, $R_{C(profos)}$, R or $S_{C(aci-nitro)}$)-[(η^5–C_5Me_5)Rh{(R)-profos}(aci-nitro)][SbF_6]$_2$



^{1}H-NMR (500.10 MHz, CD_2Cl_2, 253 K): δ = 10.0 (br, OH), 3.32 (m, 1H, H_{11}), 2.96 (m, 1H, H_{12}), 2.21 (m, 1H, H_{22}), 1.21 (s, 15H, C_5Me_5), 1.21 (3H, Me).

^{31}P{^{1}H} NMR (202.46 MHz, CD_2Cl_2, 253 K): δ = 76.39 (dd, *J*(Rh,P) = 129.8 Hz, *J*(P,P) = 41.4 Hz, P^1), 58.88 ppm (dd, *J*(Rh,P) = 130.2 Hz, P^2).

^{13}C-RMN (125.77 MHz, 253 K): δ = 8.77 ppm (C_5Me_5).

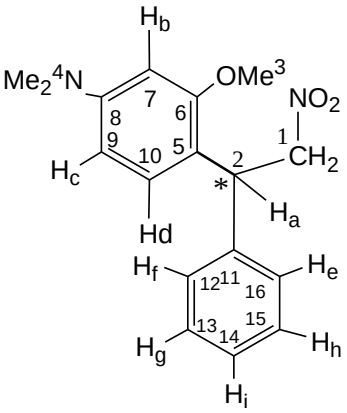
Minoritario

[(η^5–C_5Me_5)Rh{(R)-profos}(aci-nitro)][SbF_6]$_2$

^{31}P{^{1}H} NMR (202.46 MHz, CD_2Cl_2, 253 K): δ = 76.90 (br), 74.77 (br), 60.64 (br), 58.16 (br), 49.90 (br), 46.91 ppm (br).

^{13}C-RMN (125.77 MHz, 253 K): δ = 9,09, 8.63, 8.38 ppm (C_5Me_5).

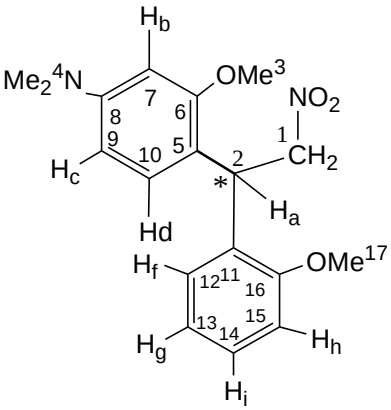
Caracterización de 3-metoxi-N,N-dimetil-4-(2-nitro-1-feniletil)anilina (6a)



[1]H-RMN (300.13 MHz, $CDCl_3$): δ = 7.27-7.14 (m, 5H, Ph), 6.78 (d, *J* = 9.4 Hz, H_c), 6.20 (s, 1H, H_b), 6.17 (m, 1H, H_d), 5.06 (dd, *J* = 8.3, 6.1 Hz, H_a), 4.82-4.93 (m, 2H, CH_2), 3.73 (s, 3H, OMe), 2.84 ppm (s, 6H, NMe_2). *[13]C-RMN (100.61 MHz): δ* = 157.74 (s, C^6), 150.98 (s, C^8), 139.65 (s, C^{11}), 129.08, (s, C^9), 128.63, (s, 2C, C^{13}, C^{17}), 127.74 (s, 2C, C^{12}, C^{16}), 127.00 (s, C^{14}), 115.80 (s, C^5)104.82 (s, C^{10}), 96.39 (s, C^7), 78.19 (s, C^1), 55.33 (s, C^3), 42.95 (s, C^2), 40.75 ppm (s, 2C, C^4).

Determinación del ee: Chiralpak IB (95:5 *n*-hexano/2-propanol, 0.5 mL/min); t_r = 21.3 min (mayor.) y t_r = 28.2 min (minor.).

Caracterización de 3-metoxi-N,N-dimetil-4-(2-nitro-1-o-metoxifeniletil)anilina (6b)

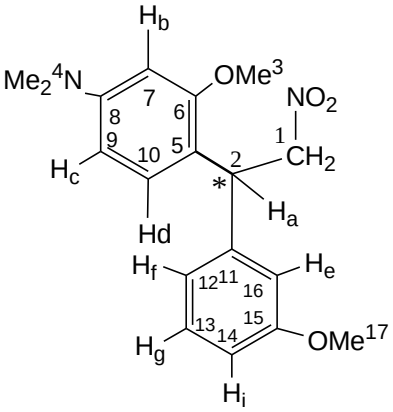


[1]H-RMN (300.13 MHz, $CDCl_3$): δ = 7.11 (m, 2H, Ph), 6.88 (d, *J* = 9.3 Hz, H_c), 6.80 (m, 2H, Ph), 6.18 (s, 1H, H_b), 6.16 (m, 1H, H_d), 5.35 (dd, *J* = 8.00, 8.00 Hz, H_a), 4.91 (m, 2H, CH_2), 3.75 (s, 3H, OMe), 3.74 (s, 3H, OMe), 2.86 ppm (s, 6H, NMe_2). *[13]C-RMN (100.61 MHz): δ* = 158.16, (s, C^6), 157.24 (s, C^{16}), 151.16 (s, C^8), 129.51 (s, C^9), 128.98 (s, C^{12}), 128.20 (s, C^{13}) 120.69 (s, C^{14}), 127.67 (s, C^{11}) 115.23 (s, C^5), 111.12 (s, C^{15}), 104.60 (s, C^{10}), 96,42 (s, C^7), 77.24 (s, 2C, C^1), 55.51(s, C^{17}), 55.36 (s, C^3), 40.62(s, C^2), 38.14 ppm (s, 2C, C^4).

Determinación del ee: Chiralpak IB (95:5 *n*-hexano/2-propanol, 0.5 mL/min); t_r = 18.7 min (mino.) y t_r = 19.3 min (mayor.).

HRMS (ESI): *m/z* = 331.1645 (calc. 331.1652 $[C_{18}H_{23}N_2O_4]^+$).

Caracterización de 3-metoxi-N,N-dimetil-4-(2-nitro-1-m-metoxifeniletil)anilina (6c)

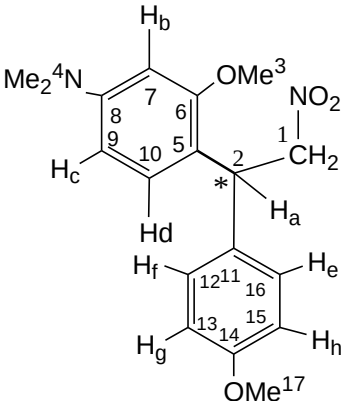


^{1}H-RMN (300.13 MHz, $CDCl_3$): δ = 6.66-6.81 (m, 4H, Ph), 6.68 (dd, 1H, *J* = 8.2, 2.5 Hz, H_c), 6.16 (s, 1H, H_b), 6.15 (m, 1H, H_d), 5.04 (dd, *J* = 9.2, 6.9 Hz, H_a), 4.87 (m, 2H, CH_2), 3.75 (s, 3H, OMe^3), 3.69 (s, 3H, OMe^{17}), 2.85 ppm (s, 6H, NMe_2). *^{13}C-RMN (100.61 MHz): δ* = 159.77, (s, C^{15}), 157.69, (s, C^6), 151.29 (s, C^8), 129.05 (s, C^9), 141.34, (s, C^{11}) 129.57 (s, C^{13}), 129.02 (s, C^{12}) 120.14 (s, C^{14}), 114.06 (s, C^{16}), 112.15 (s, C^9), 104.68 (s, C^{10}), 96.20 (s, C^7), 78.22 (s, C, C^1), 55.30 (s, C^3), 55.15 (s, C^{17}), 42.88 ppm (s, C^2), 40.57 ppm (s, 2C, C^4).

Determinación del ee: Chiralpak IB (95:5 *n*-hexano/2-propanol, 0.5 mL/min); t_r = 26.3 min (mayor.) y t_r = 42.6 min (minor.).

HRMS (ESI): *m/z* = 331.1637 (calc. 331.1652 $[C_{18}H_{23}N_2O_4]^+$).

Caracterización de 3-metoxi-N,N-dimetil-4-(2-nitro-1-p-metoxifeniletil)anilina (6d)

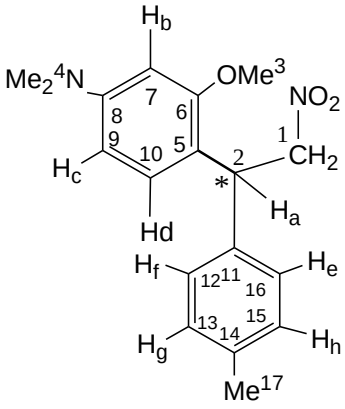


^{1}H-RMN (300.13 MHz, $CDCl_3$): δ = 7.11 (m, 2H, Ph), 6.79 (d, *J* = 8.4 Hz, H_c), 6.75 (m, 2H, Ph), 6.21 (sa, 1H, H_b), 6.18 (m, 1H, H_d), 5.03 (dd, *J* = 9.4, 6.7 Hz, H_a), 4.91 (m, 2H, CH_2), 3.75 (s, 3H, OMe^3), 3.69 (s, 3H, OMe^{17}), 2.86 ppm (s, 6H, NMe_2). *^{13}C-RMN (100.61 MHz): δ* = 158.55 (s, C^{14}), 157.74 (s, C^6), 150.73 (s, C^8), 131.66 (s, C^{11}), 129.05 (s, C^9), 128.93 (s, 2C, C^{12}, C^{16}), 115.23 (s, C^5), 114.05 (s, 2C, C^{13}, C^{15}), 105.00 (s, C^{10}), 96.61 (s, C^7), 78.46 (s, C, C^1), 55.36 (s, C^3), 55.23 (s, C^{17}), 42.33 (s, 2C, C^4), 40.89 ppm (s, C^2).

Determinación del ee: Chiralpak IB (95:5 *n*-hexano/2-propanol, 0.5 mL/min); t_r = 28.2 min (mayor.) y t_r = 38.6 min (minor.).

HRMS (ESI): *m/z* = 331.1648 (calc. 331.1652 $[C_{18}H_{23}N_2O_4]^+$).

Caracterización de 3-metoxi-N,N-dimetil-4-(2-nitro-1-p-metilfeniletil)anilina (6e)

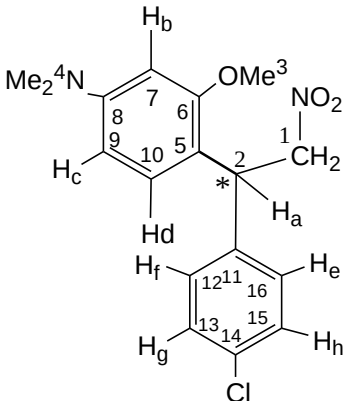


[1]H-RMN (300.13 MHz, $CDCl_3$): δ = 7.05 (m, 4H, Ph), 6.79 (d, *J* = 8.2 Hz, H_c), 6.19 (s, 1H, H_b), 6.17 (m, 1H, H_d), 5.03 (dd, *J* = 9.3, 6.9 Hz, H_a), 4.81-4.92 (m, 2H, CH_2), 3.75 (s, 3H, OMe), (s, 6H, NMe_2) 2.22 2.85 ppm (s, 3H, Me). *[13]C-RMN (100.61 MHz):* δ = 157.71 (s, C^6), 151.21 (s, C^8), 136.59 (s, C^{11}), 129.33 (s, 2C, C^{13}, C^{15}), 129.03, (s, C^9), 127.76, (s, 2C, C^{12}, C^{16}), 127.74 (s, 2C, C^{12}, C^{16}), 127.00 (s, C^{14}), 116.16 (s, C^5), 104.85 (s, C^{10}), 96.51 (s, C^7), 78.35 (s, C^1), 55.33 (s, C^3), 42.60 (s, C^2), 40.77 (s, 2C, C^4), 21.02 ppm (s, C^{17}).

Determinación del ee: Chiralpak IB (95:5 *n*-hexano/2-propanol, 0.5 mL/min); t_r = 19.0 min (mayor.) y t_r = 24.1 min (minor).

HRMS (ESI): *m/z* = 315.1695 (calc. 331.1703 $[C_{18}H_{23}N_2O_3]^+$).

Caracterización de 3-metoxi-N,N-dimetil-4-(2-nitro-1-p-clorofeniletil)anilina (6f)

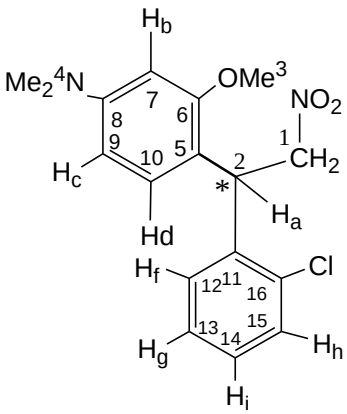


[1]H-RMN (300.13 MHz, $CDCl_3$): δ = 7.15 (dd, *J* = 17.1, 5.3 Hz, 4H, Ph), 6.78 (d, *J* = 8.2, Hz, H_c), 6.21(s, 1H, H_b), 6.18 (m, 1H, H_d), 5.06 (dd, *J* = 9,4, 6.6 Hz, H_c), 4.85 (m, 2H, CH_2), 3.74 (s, 3H, OMe), 2.87 ppm (s, 6H, NMe_2). *[13]C-RMN (100.61 MHz):* δ = 157.67, (s, C^6), 151.01 (s, C^8), 138.28 (s, C^5), 132.82 (s, C^{11}), 129.23 (s, 2C, C^{12}, C^{16}), 128.90 (s, C^9), 129.50 (s, C^{14}), 128.78 (s, 2C, C^{13}, C^{15}), 104.88 (s, C^{10}), 96.51 (s, C^7), 78.05 (s, C^1), 55.31(s, C^3), 42.56 (s, 2C, C^4), 40.77 ppm (s, C^2).

Determinación del ee: Chiralpak IB (95:5 *n*-hexano/2-propanol, 0.5 mL/min); t_r = 26.7 min (mayor.) y t_r = 34.1 min (minor.).

HRMS (ESI): *m/z* = 335.1155 (calc. 335.1157 $[C_{17}H_{20}ClN_2O_3]^+$).

Caracterización de 3-metoxi-N,N-dimetil-4-(2-nitro-1-o-clorofeniletil)anilina (6g)



[1]H-RMN (300.13 MHz, $CDCl_3$): δ = 7.38-7.10 (m, 4H, Ph), 6.76 (d, J = 8.4 Hz, H_c), 6.21 (s, 1H, H_b), 6.17 (m, 1H, H_d), 5.51 (t, J = 8.1 Hz, H_a), 4.86-4.88 (m, 2H, CH_2), 3.76 (s, 3H, OMe), 2.86 ppm (s, 6H, NMe_2). *[13]C-RMN (100.61 MHz):* δ = 158.18 (s, C^6), 151.25 (s, C^8), 137.06 (s, C^{11}), 134.52 s, C^{16}), 129.32, (s, C^9), 130,28, 128.56, 128.41, 126.92 (s, 4C, C^{12}, C^{13}, C^{14}, C^{15}), 114.04 (s, C^5), 104.85 (s, C^{10}), 96.60 (s, C^7), 76.72 (s, C^1), 55.41 (s, C^3), 40.85 (s, 2C, C^4), 40.06 ppm (s, C^2).

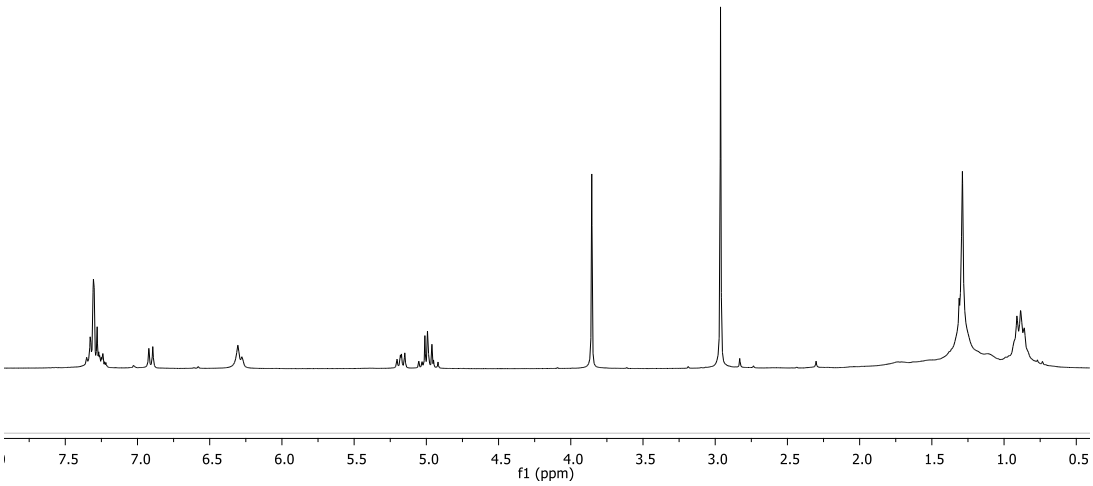
Determinación del ee: Chiralpak IB (95:5 *n*-hexano/2-propanol, 0.5 mL/min); t_r = 20.5 min (mayor.) y t_r = 25.0 min (minor.).

HRMS (ESI): *m/z* = 335.1160 (calc. 335.1157 $[C_{17}H_{20}ClN_2O_3]^+$).

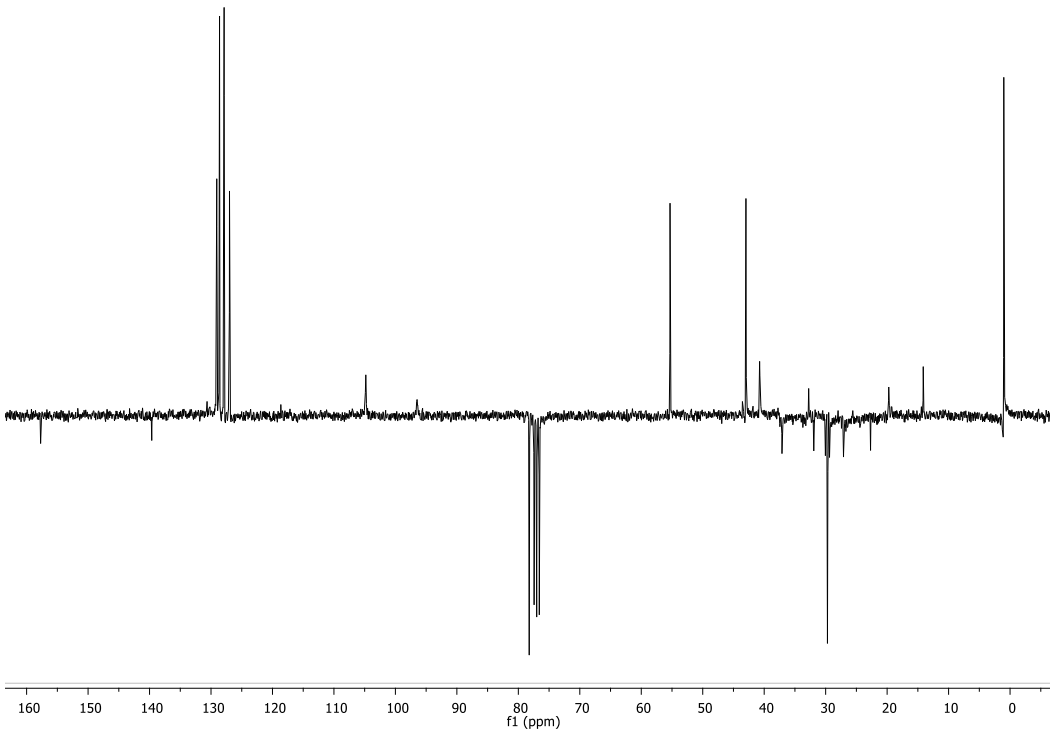
ANEXO IV. *Espectros.*

Espectros de 3-metoxi-N,N-dimetil-4-(2-nitro-1-feniletil)anilina (6a)

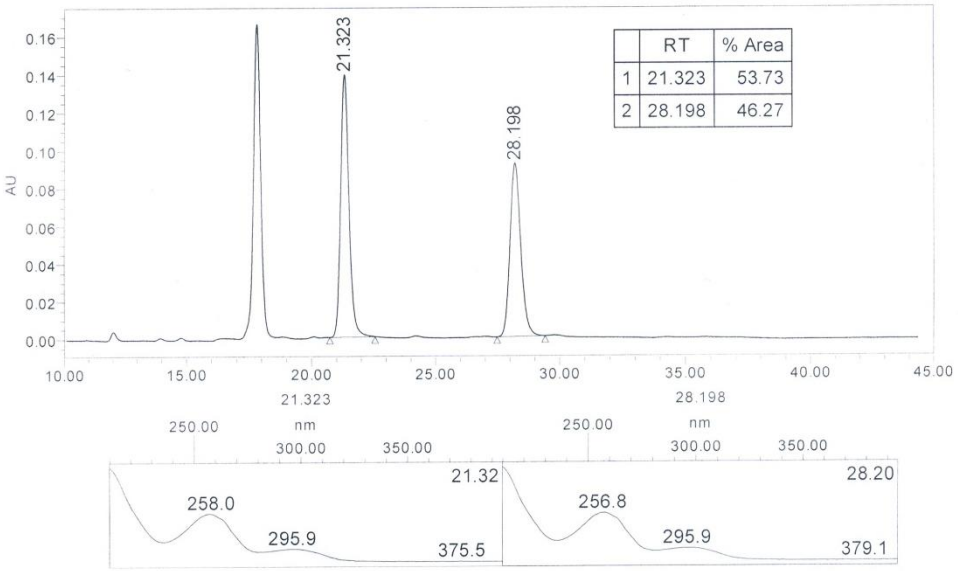
Espectro de RMN de ^{1}H



Espectro de RMN de APT $^{13}C\{^{1}H\}$

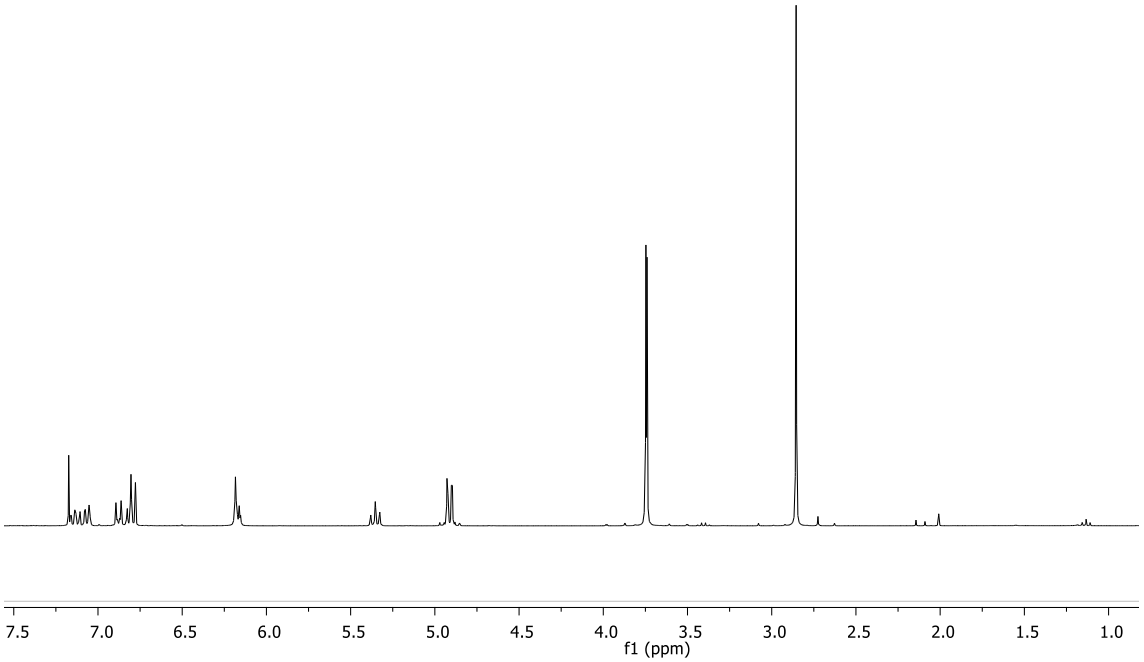


Cromatograma HPLC y Espectro UV

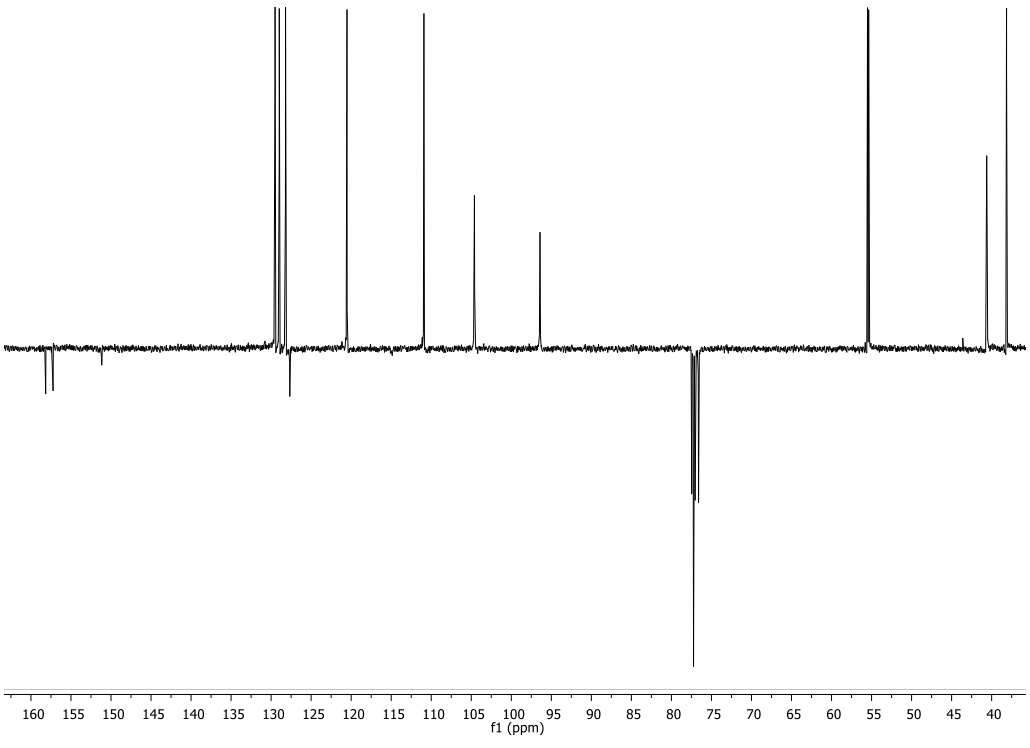


Espectros de 3-metoxi-N,N-dimetil-4-(2-nitro-1-o-metoxifeniletil)anilina (6b)

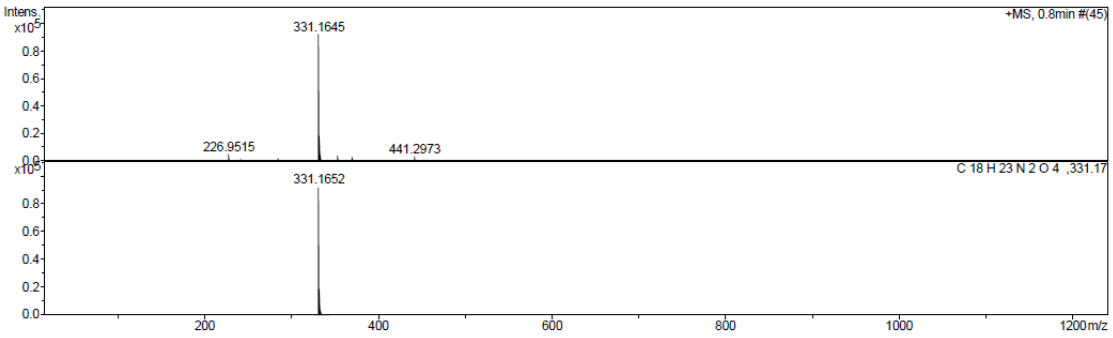
Espectro de RMN de ^{1}H



Espectro de RMN de APT $^{13}C\{^{1}H\}$

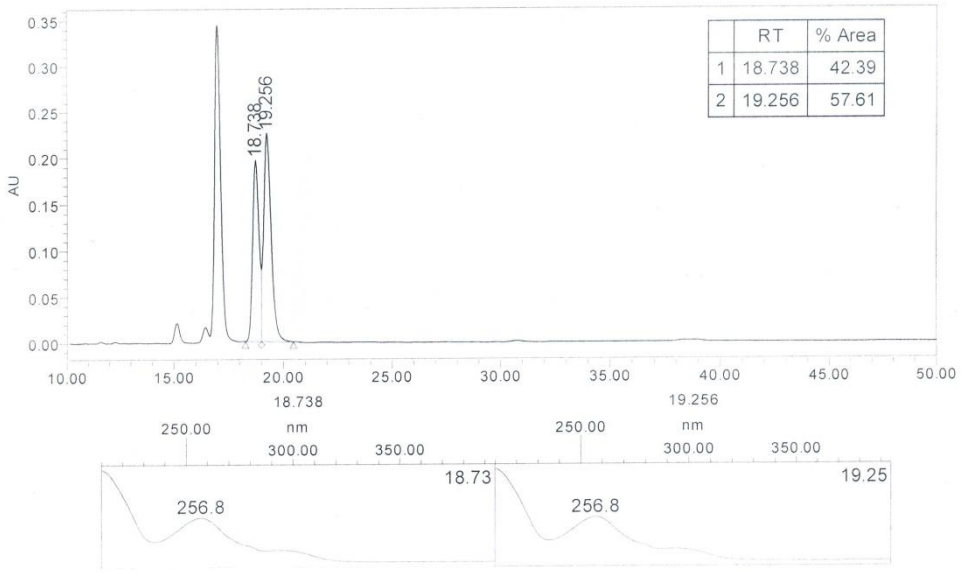


Espectro de masas HRMS (ESI)



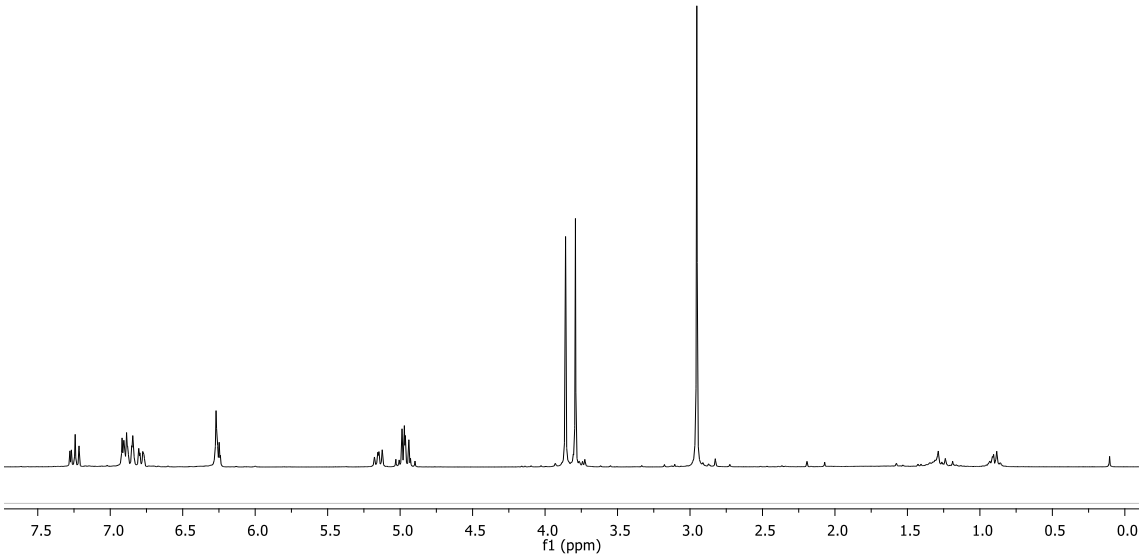
Meas. m/z	#	Formula	m/z	err [mDa]	err [ppm]	mSigma
331.1645	1	C 18 H 23 N 2 O 4	331.1652	0.8	2.4	6.6

Cromatograma HPLC y Espectro UV

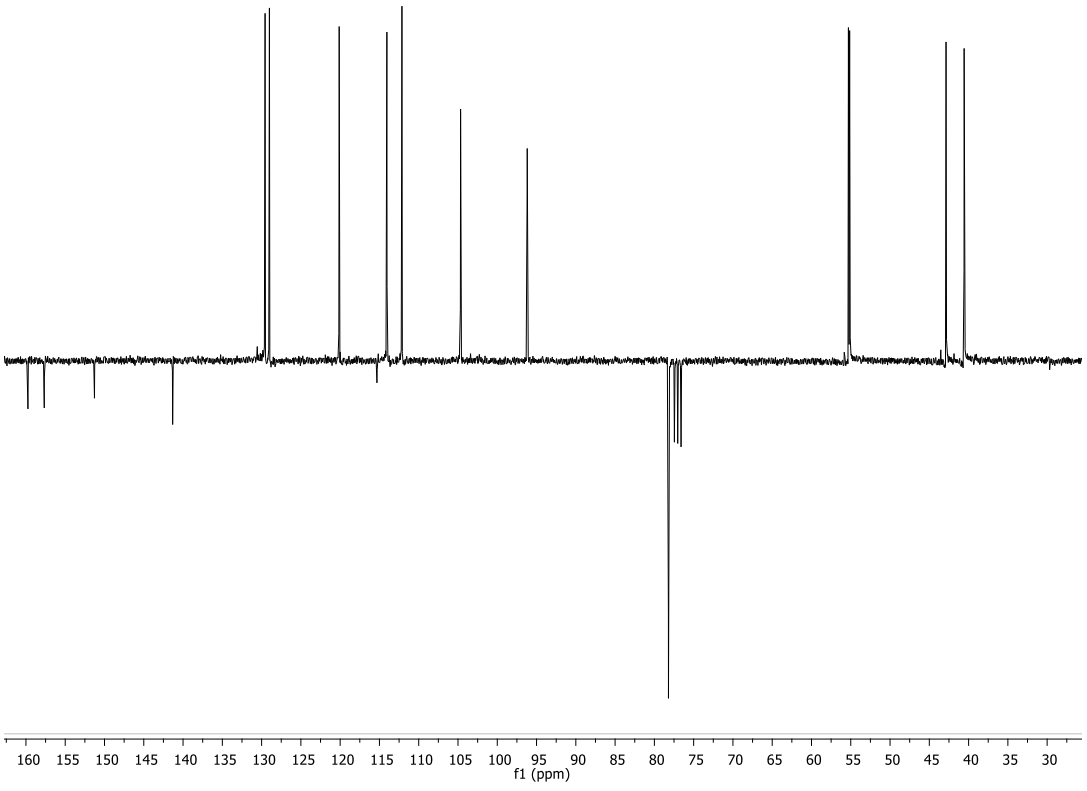


Espectros de 3-metoxi-N,N-dimetil-4-(2-nitro-1-m-metoxifeniletil)anilina (6c)

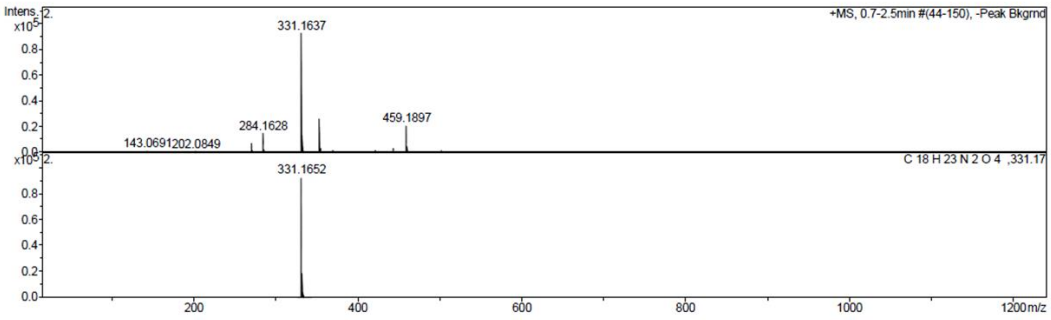
Espectro de RMN de ^{1}H



Espectro de RMN de APT $^{13}C\{^{1}H\}$

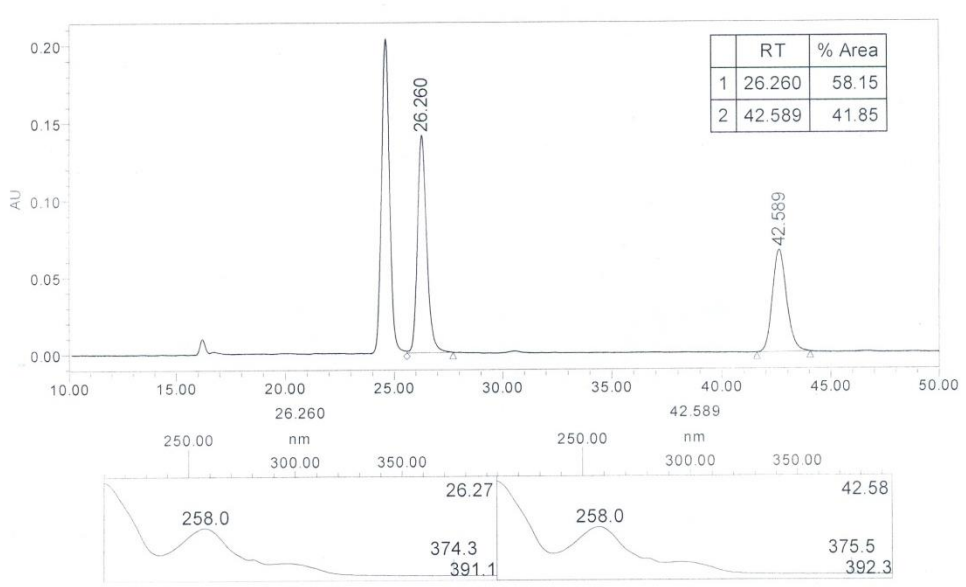


Espectro de masas HRMS (ESI)



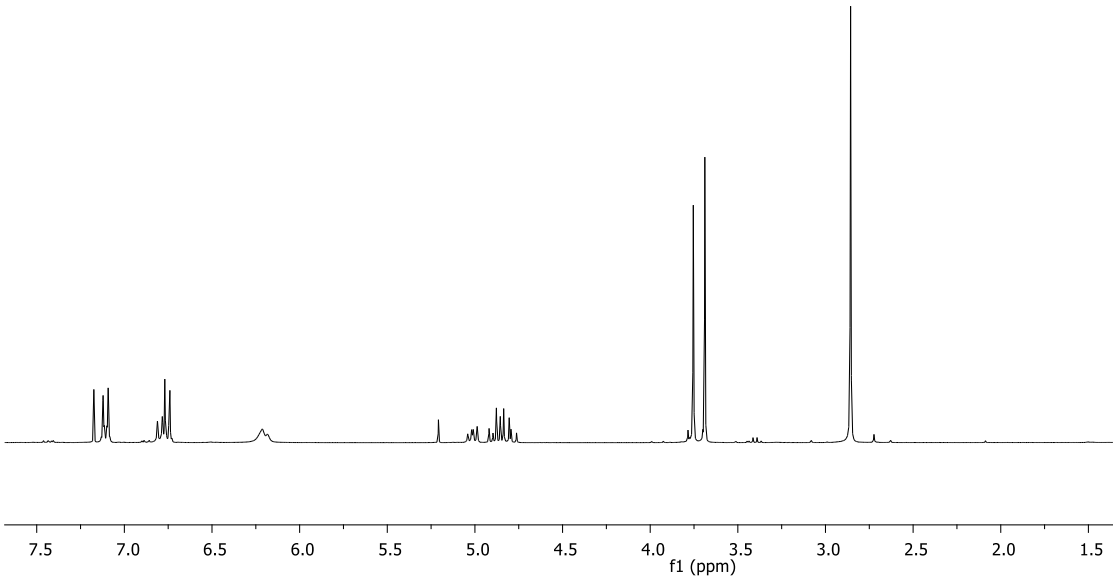
Meas. m/z	#	Formula	m/z	err [mDa]	err [ppm]	mSigma
331.1637	1	C 18 H 23 N 2 O 4	331.1652	1.5	4.6	33.8

Cromatograma HPLC y Espectro UV

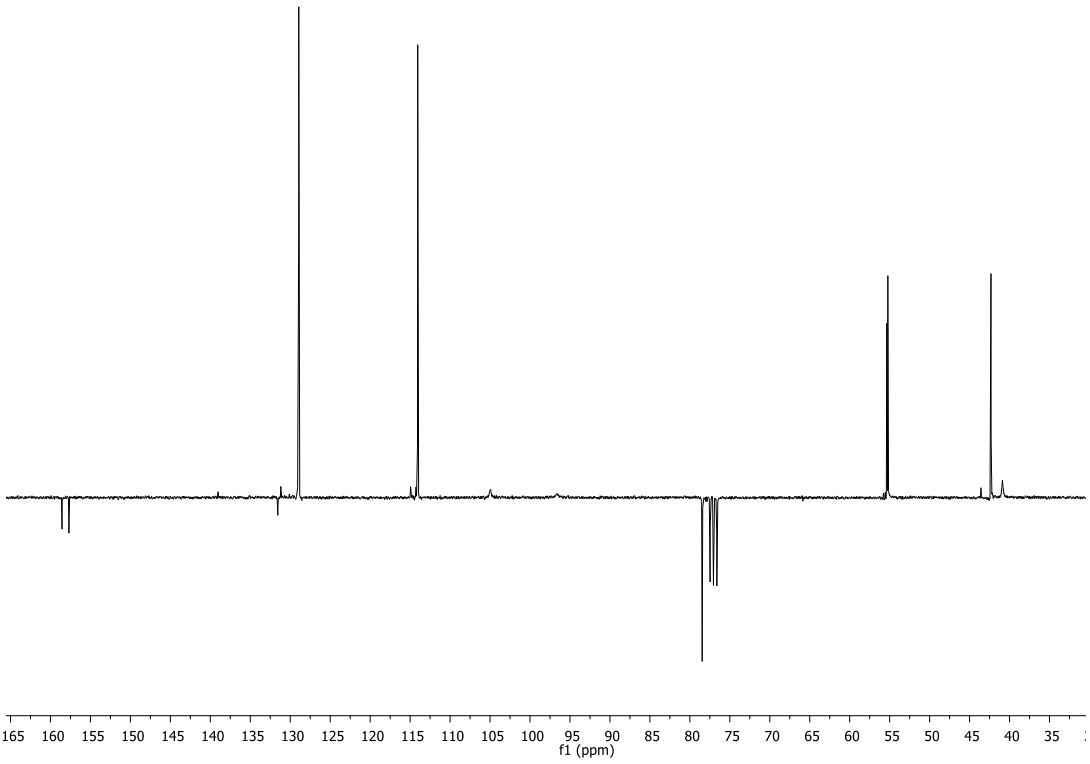


Espectros de 3-metoxi-N,N-dimetil-4-(2-nitro-1-p-metoxifeniletil)anilina (6d)

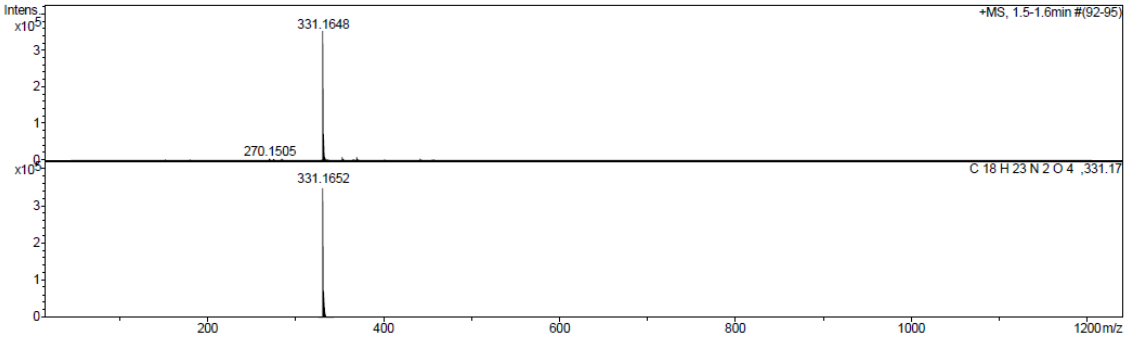
Espectro de RMN de ^{1}H



Espectro de RMN de APT $^{13}C\{^{1}H\}$

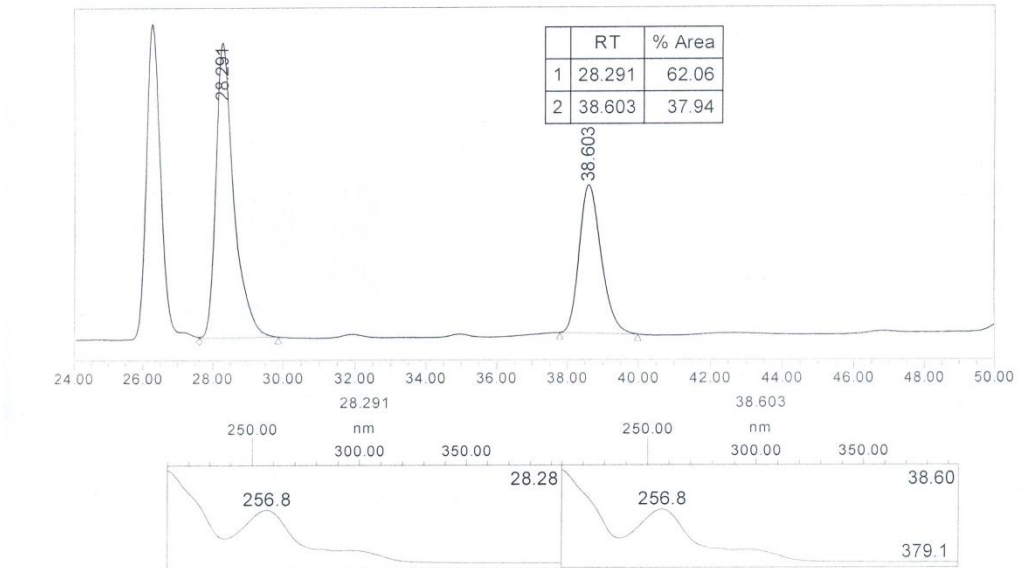


Espectro de masas HRMS (ESI)



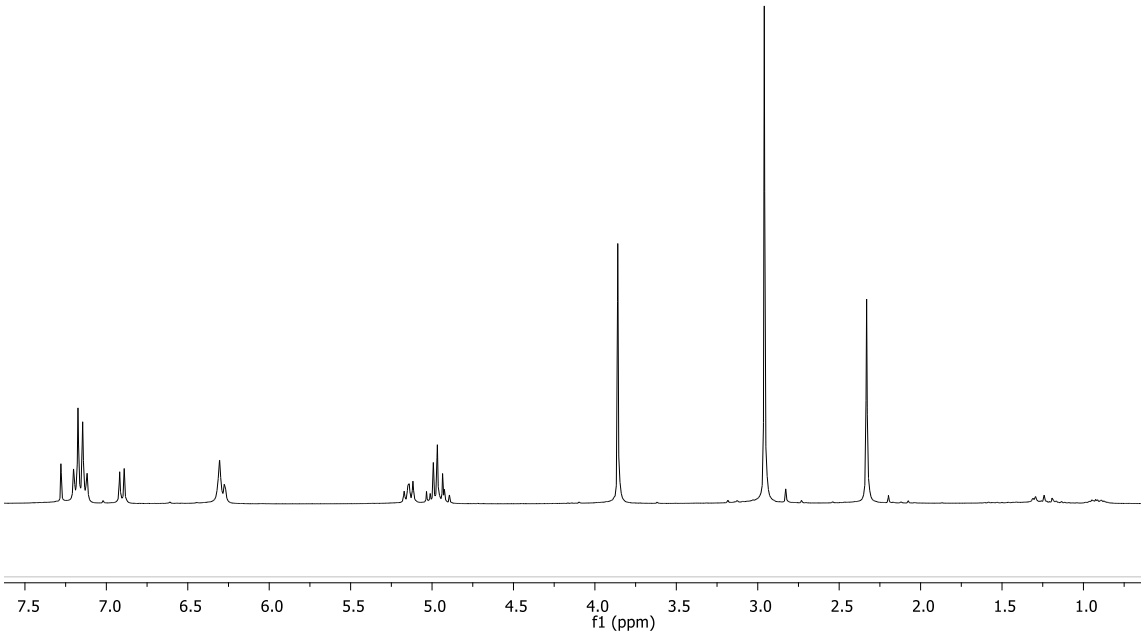
Meas. m/z	#	Formula	m/z	err [mDa]	err [ppm]	mSigma
331.1648	1	C 18 H 23 N 2 O 4	331.1652	0.4	1.2	12.0

Cromatograma HPLC y Espectro UV

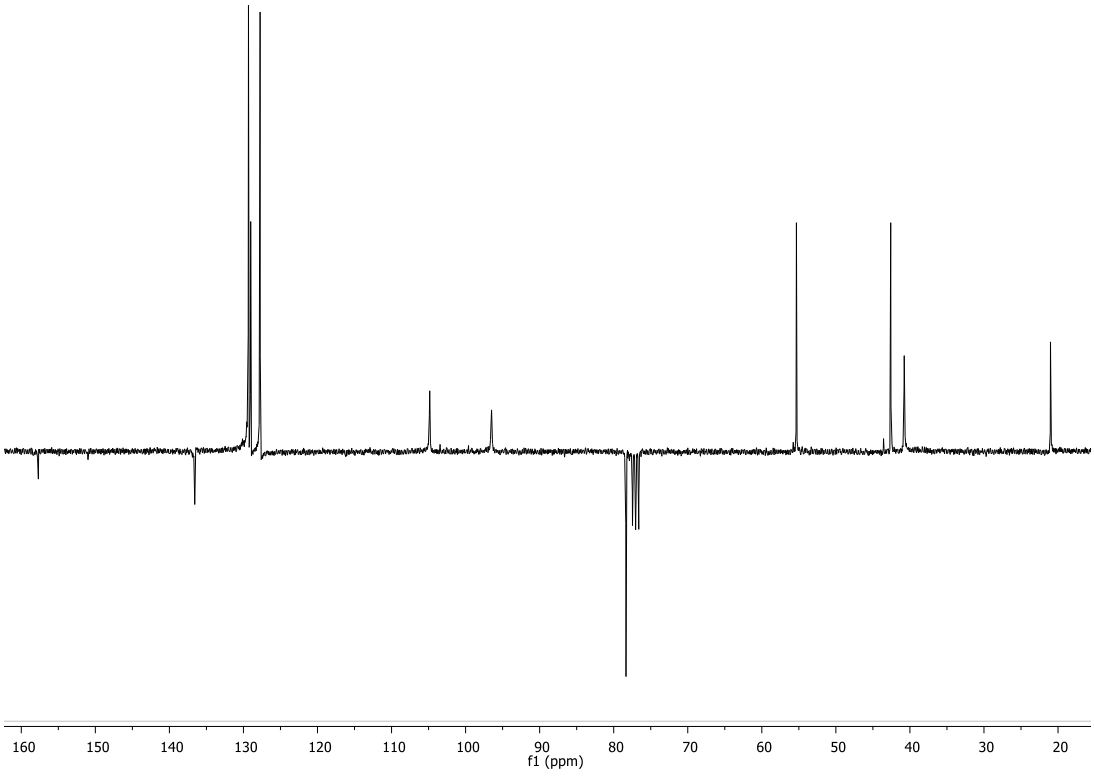


Espectros de 3-metoxi-N,N-dimetil-4-(2-nitro-1-p-metilfeniletil)anilina (6e)

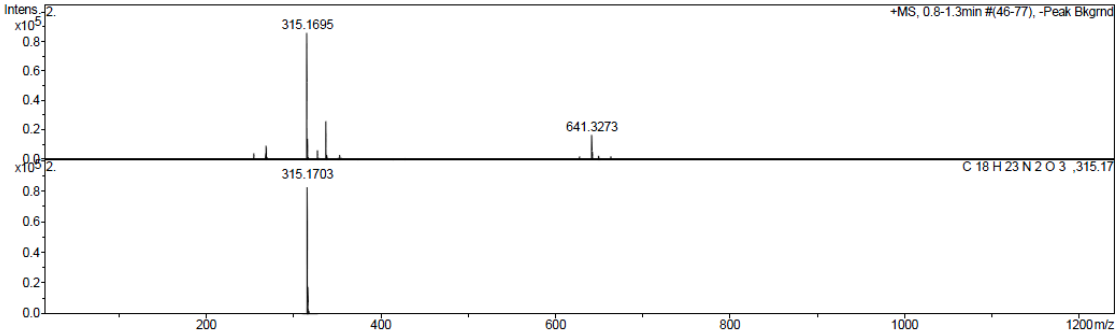
Espectro de RMN de ^{1}H



Espectro de RMN de APT $^{13}C\{^{1}H\}$

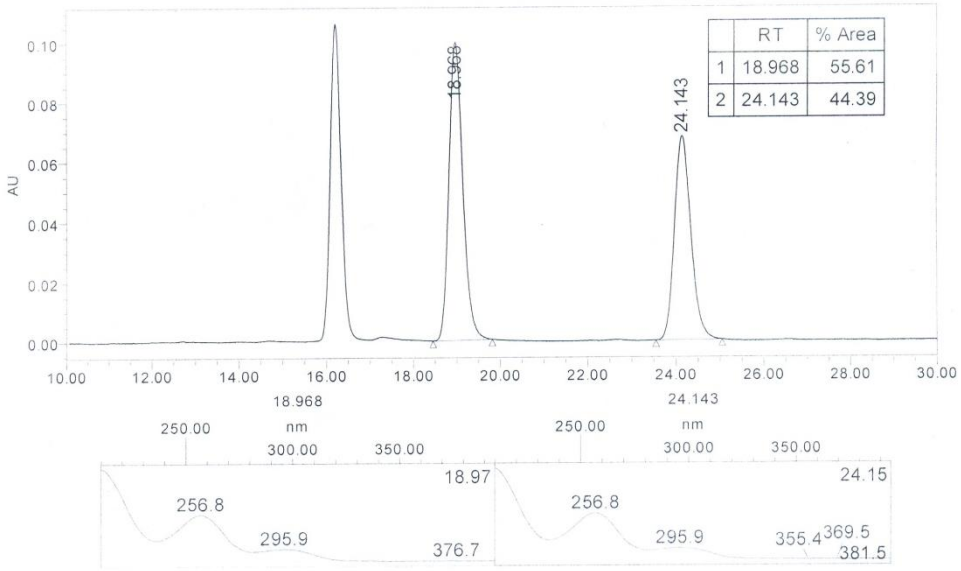


Espectro de masas HRMS (ESI)



Meas. m/z	#	Formula	m/z	err [mDa]	err [ppm]	mSigma
315.1695	1	C 18 H 23 N 2 O 3	315.1703	0.9	2.7	21.6

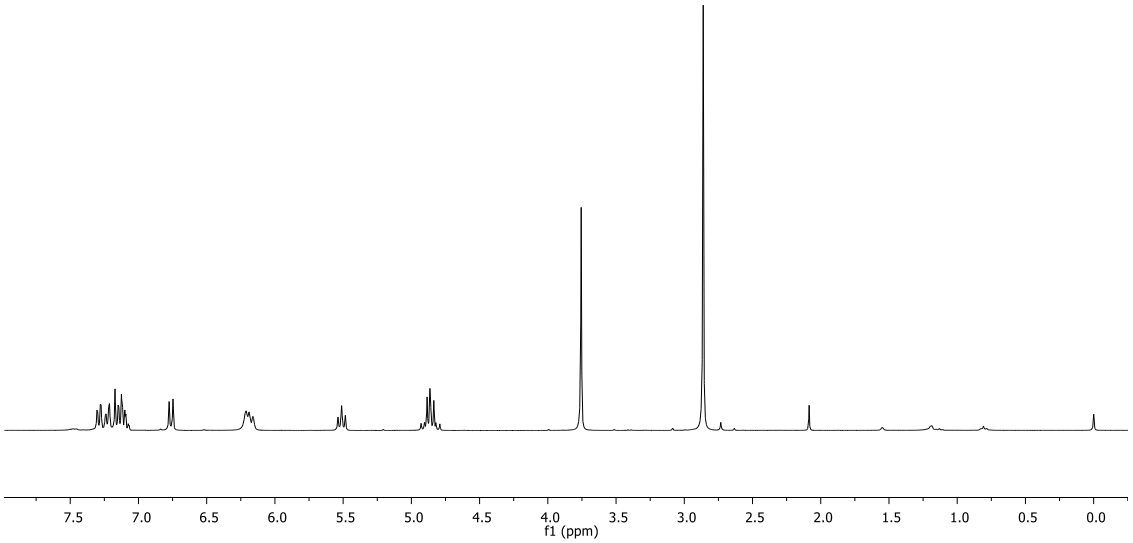
Cromatograma HPLC y Espectro UV



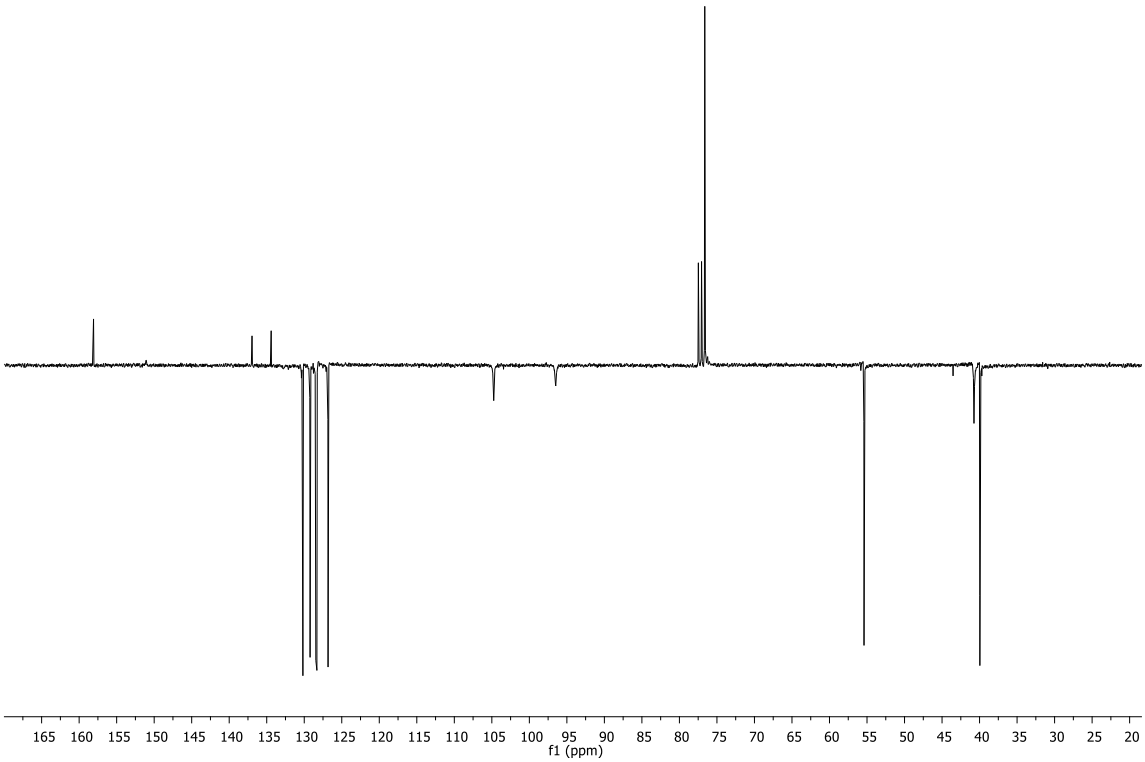
	RT	% Area
1	18.968	55.61
2	24.143	44.39

Espectros de 3-metoxi-N,N-dimetil-4-(2-nitro-1-o-clorofeniletil)anilina (6f)

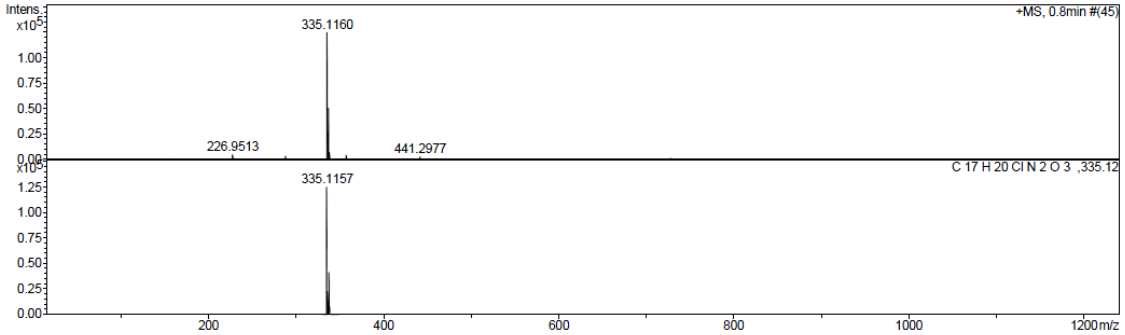
Espectro de RMN de ^{1}H



Espectro de RMN de APT $^{13}C\{^{1}H\}$

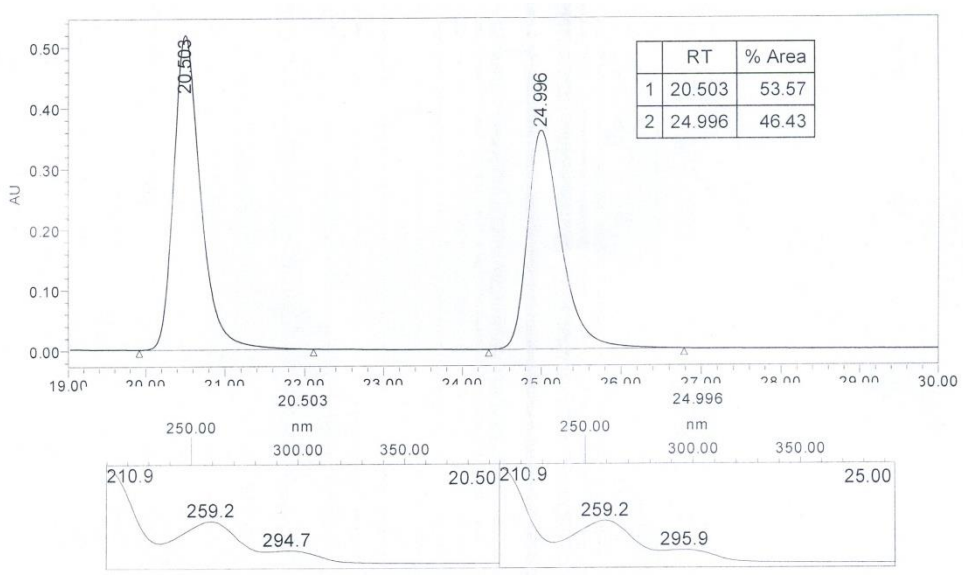


Espectro de masas HRMS (ESI)



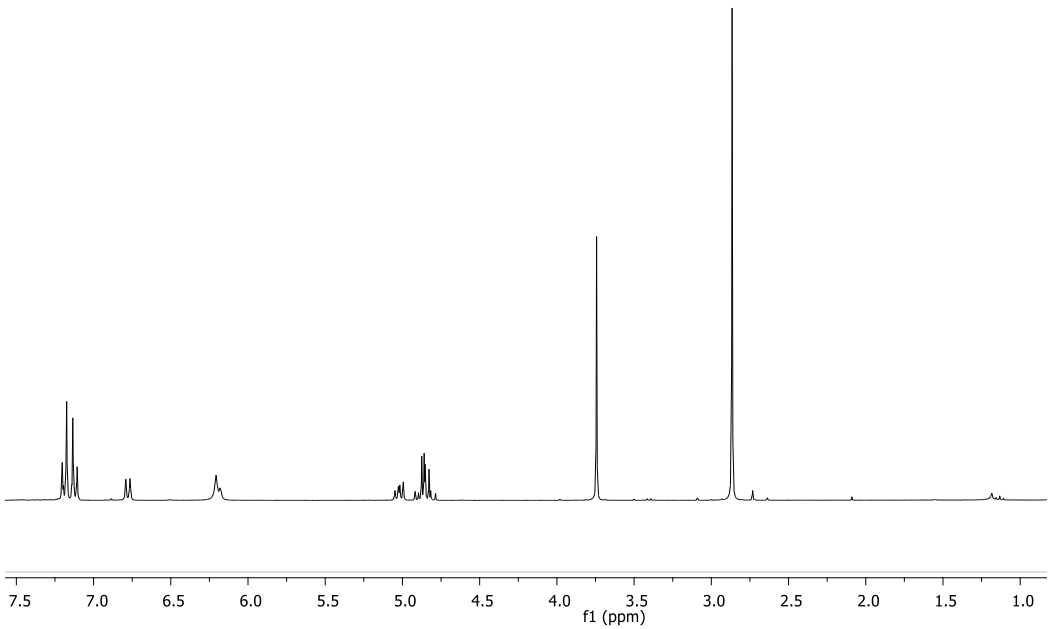
Meas. m/z	#	Formula	m/z	err [mDa]	err [ppm]	mSigma
335.1160	1	C 17 H 20 Cl N 2 O 3	335.1157	-0.3	-0.8	29.9

Cromatograma HPLC y Espectro UV

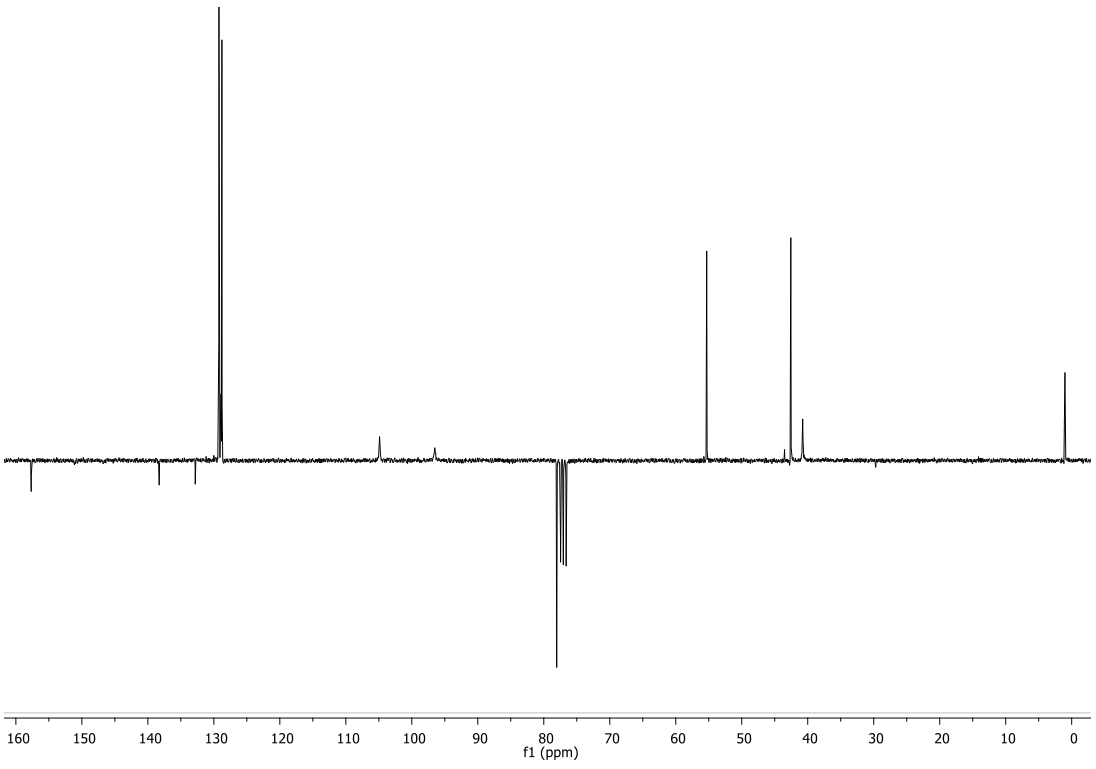


Espectros de de 3-metoxi-N,N-dimetil-4-(2-nitro-1-p-clorofeniletil)anilina (6g)

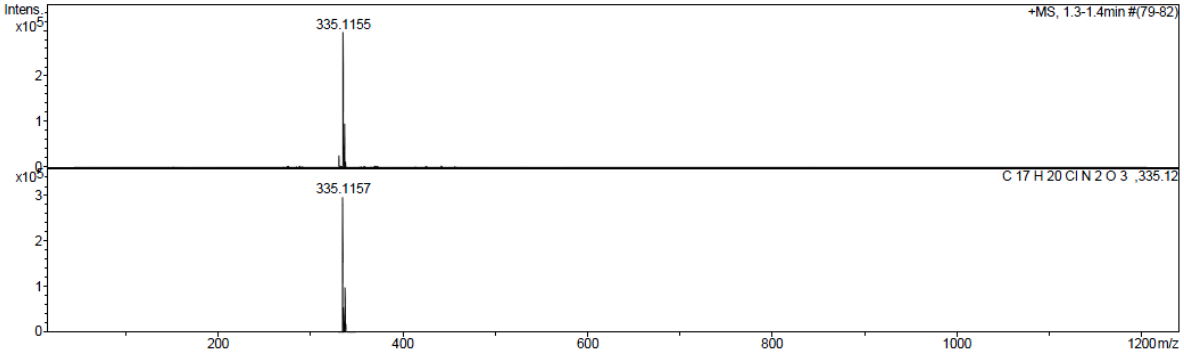
Espectro de RMN de ^{1}H



Espectro de RMN de APT $^{13}C\{^{1}H\}$



Espectro de masas HRMS (ESI)



Meas. m/z	#	Formula	m/z	err [mDa]	err [ppm]	mSigma
335.1155	1	C 17 H 20 Cl N 2 O 3	335.1157	0.2	0.7	19.8

Cromatograma HPLC y Espectro UV