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Alkyl formates as reagents for reductive amination of carbonyl compounds

Oleg I. Afanasyev, Ilia Cherkashchenko, Anton Kuznetsov, Fedor Kliuev, Sergey Semenov, Olga Chusova, Gleb Denisov and Denis Chusov

1. General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification, THF was distilled over sodium/benzophenone. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-300, AV-400 and Varian Inova-400 spectrometers at ambient temperature. Chemical shifts δ are reported in ppm using the solvent resonance signal as an internal standard. NMR yields were calculated with mesitylene as an internal standard (unless otherwise noted). The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; coupling constants are given in Hertz (Hz).

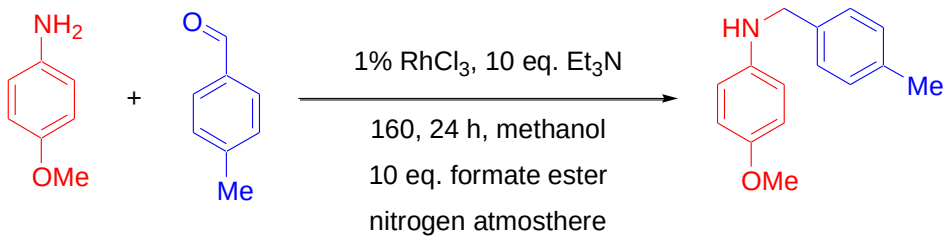
Analytical gas chromatography (GC) was performed using a Chromatec Crystal 5000.2 Gas Chromatograph fitted with a flame ionization detector (He carrier gas, 37 mL min^{-1}). Injections were made on a Chromatec CR-5 (30 meter) capillary column. The injector temperature was 250 °C, the detector temperature was 260 °C, with a split ratio of 23:1. Retention times (t_R) and integrated ratios were obtained using Chromatec Analytic Software.

General procedure for the reductive amination

A 10 ml stainless steel autoclave was charged with 1 mol% of the catalyst, 1500 mol% of the dry sodium acetate, 100 mol% of the amine, the corresponding solvent, 100 mol% of the carbonyl compound, 1000 mol% of methyl formate and magnetic stirring bar. The autoclave was sealed, flushed two times with 10 atm of N_2, and then placed into a preheated oil bath at 160°C. After the specified time, the reactor was cooled to room temperature and depressurized. The reaction mixture was diluted in CH_2Cl_2, dried with Na_2SO_4, and the solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel.

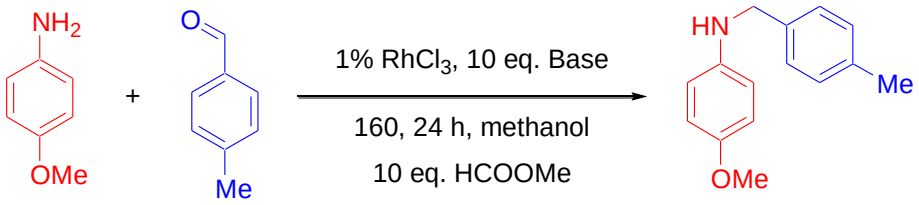
2. Optimization of the reaction conditions

Table S1. Formate structure influence



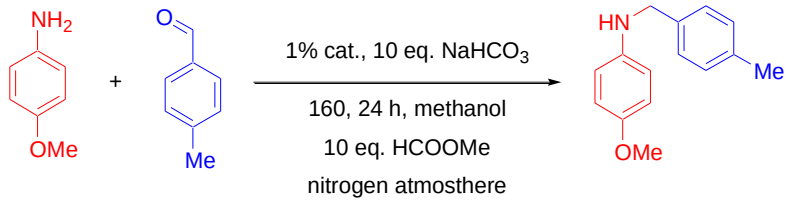
Entry	Formate	GC yield, %
1	methyl formate	31%
2	isobutyl formate	17%
3	benzyl formate	29%

Table S2. Base influence



Entry	Base	GC yield, %
1	$NaHCO_3$	49%
2	K_2CO_3	2%
3	CsOH	traces
4	Et_3N	31%
5	NaH_2PO_4	traces
6	Na_2HPO_4	13%
7	K_3PO_4	none
8	NaOAc	53%
9	NaOAc (dry)	57%
10	$Na_2B_4O_7*10H_2O$	10%

Table S3. Catalyst influence



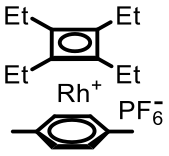
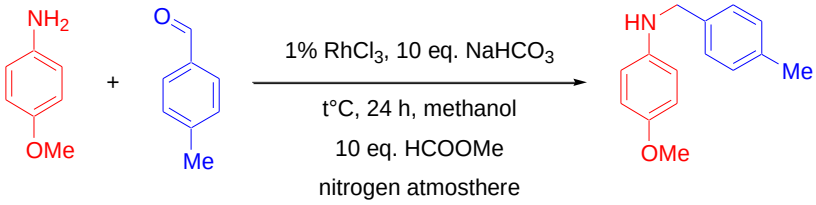
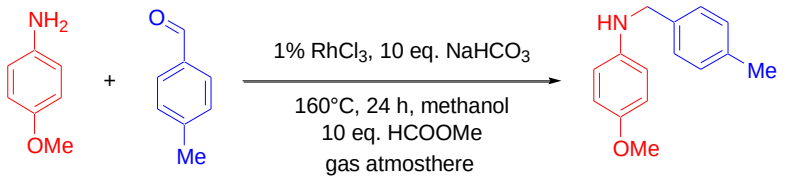
Entry	Catalyst	GC yield, %
1	$RhCl_3$	49%
2	$RuCl_3$	30%
3	$Rh(OAc)_2$	32%
4		37%

Table S4. Temperature influence



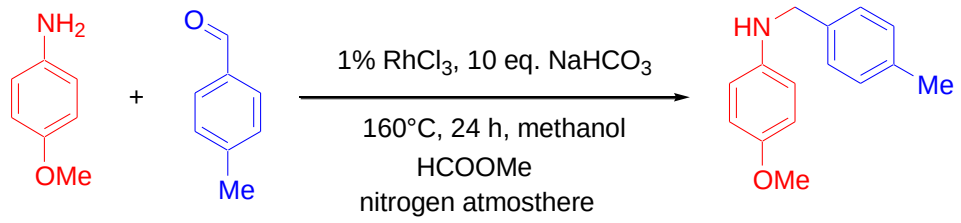
Entry	Temperature	GC yield, %
1	100 °C	Traces
2	120 °C	10%
3	140 °C	26%
4	160 °C	49%
5	180 °C	27%

Table S5. Reaction atmosphere influence



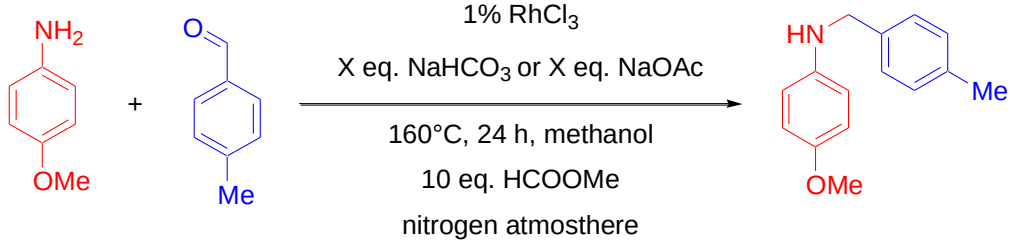
Entry	Headspace fill gas	GC yield, %
1	Ar	36%
2	Air	41%
3	N_2	49%

Table S6. Quantity of methyl formate optimization



Entry[a]	Equivalents of HCOOMe	GC yield, %
1	2.5	41%
2	5	44%
3	10	49%
4	20	34%
5	40	27%

Table S7. Quantity of base optimization

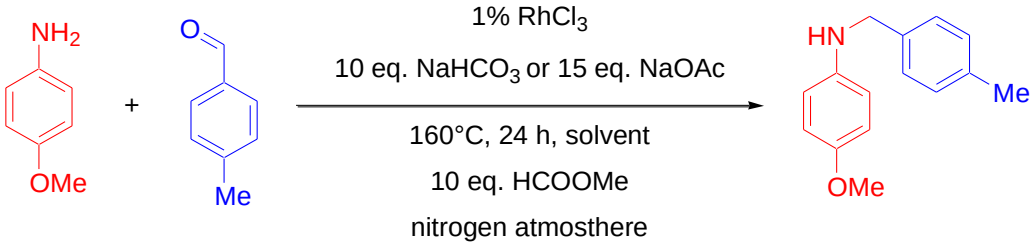


Entry	Number of equivalents	GC yield, %
1[a]	1	10%
2[a]	2.5	14%
3[a]	5	27%
4[a]	10	49%
5[a]	20	22%
6[b]	5	27%
7[b]	10	57%
8[b]	15	62%
9[b]	20	43%

[a] $NaHCO_3$ was used as a base.

[b] NaOAc (dry) was used as a base.

Table S8. Solvent screening



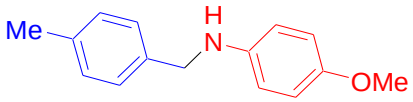
Entry	Solvent	Yelid%
1 [a]	MeOH	49%
2 [a]	THF	18%
3 [a]	H_2O	17%
4 [a]	EtOH	30%
5 [a]	Et_2O	20%
6 [a]	MeCN	21%
7 [a]	Neat	15%
8 [a]	MeOH/H_2O (1/1)	42%
9 [a]	EtOH/H_2O (1/1)	41%
10 [a]	iPrOH/H_2O (1/1)	39%
11 [b]	MeOH/H_2O (1/1)	67%
12 [b]	EtOH/H_2O (1/1)	42%
13 [b]	iPrOH/H_2O (1/1)	3%

[a] $NaHCO_3$ was used as a base.

[b] NaOAc (dry) was used as a base.

3. Spectroscopic and analytical data for isolated compounds

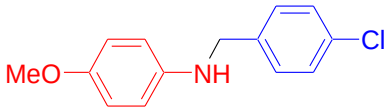
4-Methoxy-*N*-(4-methylbenzyl)aniline (3a)



A 10 ml stainless steel autoclave was charged with $RhCl_3 \cdot 4H_2O$ (2.0 mg; 7.1 µmol; 1 mol%), dry sodium acetate (874 mg; 10.7 mmol; 1500 mol%), *p*-anisidine (105.1 mg; 853 µmol; 120 mol%), HPLC grade water (1 ml) and methanol (1 ml), 4-methylbenzaldehyde (84.5 µL; 711 µmol, 100 mol%), methyl formate (436 µL; 711 mmol; 1000 mol%) and magnetic stirrer. The autoclave was sealed, flushed two times with 10 atm of N_2, and then placed into a preheated oil bath. After 24 h at 160 °C in the oil bath, the reactor was cooled to room temperature and depressurized. The reaction mixture was diluted in DCM, dried with Na_2SO_4, and solvents were removed under reduced pressure. 67% yield by NMR. The product was isolated by column chromatography, eluent: hexane/ethyl acetate 7/1 (Rf = 0.4). Isolated as a yellowish oil, 89 mg (55%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.80 (d, *J* = 8.9 Hz, 2H), 6.63 (d, *J* = 8.9 Hz, 2H), 4.26 (s, 2H), 3.76 (s, 3H), 2.37 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.25, 142.63, 136.89, 136.71, 129.37, 127.66, 115.00, 114.20, 55.92, 49.11, 21.22.
NMR spectra are in agreement with the literature data.[1]

***N*-(4-Chlorobenzyl)-4-methoxyaniline (3b)**



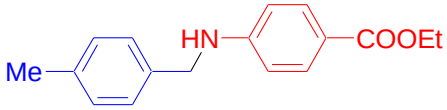
A 10 ml stainless steel autoclave was charged with $RhCl_3 \cdot 4H_2O$ (2.0 mg; 7.1 µmol; 1 mol%), dry sodium acetate (874 mg; 10.7 mmol; 1500 mol%), *p*-anisidine (87.6 mg; 711 µmol; 100 mol%), HPLC grade water (1 ml) and methanol (1 ml), 4-chlorobenzaldehyde (99.9 mg; 711 µmol, 100 mol%), methyl formate (436 µL; 711 mmol; 1000 mol%) and magnetic stirrer. The autoclave was sealed, flushed two times with 10 atm of N_2, and then placed into a preheated oil bath. After 24 h at 160 °C in the oil bath, the reactor was cooled to room temperature and depressurized. The reaction mixture was diluted in DCM, dried with Na_2SO_4, and solvents were removed under reduced pressure. 54% yield by NMR. The product was isolated by column chromatography, eluent: hexane/ethyl acetate 5/1 (Rf = 0.6). Isolated as a yellowish solid 79 mg (45%). Melting point is 74-75°C (Lit. mp 75-76)[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 4H), 6.79 (d, *J* = 8.9 Hz, 2H), 6.60 (d, *J* = 8.9 Hz, 2H), 4.27 (s, 2H), 3.75 (s, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.51, 141.84, 138.15, 132.89, 128.90, 128.78, 114.98, 114.44, 55.84, 48.70.
NMR spectra are in agreement with the literature data.2

[1] Kolesnikov, P.N.; Yagafarov, N. Z.; Usanov, D. L.; Maleev, V. I.; Chusov, D. Org. Lett. 2015, **17,** 173.

[2] Lei, Q.; Wei, Y.; Talwar, D.; Wang, C.; Xue, D. and Xiao, J. Chem. Eur. J., 2013, **19**, 4021

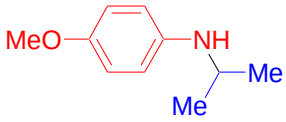
Ethyl 4-((4-methylbenzyl)amino)benzoate (3c)



A 10 ml stainless steel autoclave was charged with $RhCl_3 \cdot 4H_2O$ (2.0 mg; 7.1 µmol; 1 mol%), dry sodium acetate (874 mg; 10.7 mmol; 1500 mol%), benzocaine (117.4 mg; 711 µmol; 100 mol%), HPLC grade water (1 ml) and methanol (1 ml), 4-methylbenzaldehyde (84.5 µL; 711 µmol, 100 mol%), methyl formate (436 µL; 711 mmol; 1000 mol%) and magnetic stirrer. The autoclave was sealed, flushed two times with 10 atm of N_2, and then placed into a preheated oil bath. After 24 h at 160 °C in the oil bath, the reactor was cooled to room temperature and depressurized. The reaction mixture was diluted in DCM, dried with Na_2SO_4, and solvents were removed under reduced pressure. 66% yield by NMR. The product was isolated by column chromatography, eluent: hexane/ethyl acetate 10/1 (Rf = 0.2). Isolated as a yellowish solid, 105 mg (55%). Melting point is 89-90°C (Lit. mp 91-92)[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.58 (d, *J* = 8.7 Hz, 2H), 4.33 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.96, 151.83, 137.28, 135.42, 131.58, 129.52, 127.51, 118.95, 111.68, 60.29, 47.51, 21.21, 14.56.
NMR spectra are in agreement with the literature data.3

***N*-Isopropyl-4-methoxyaniline (3d)**



A 10 ml stainless steel autoclave was charged with $RhCl_3 \cdot 4H_2O$ (2.0 mg; 7.1 µmol; 1 mol%), dry sodium acetate (874 mg; 10.7 mmol; 1500 mol%), *p*-anisidine (87.6 mg; 711 µmol; 100 mol%), HPLC grade water (1 ml) and methanol (1 ml), acetone (790 µL; 10.7 mmol, 1500 mol%), methyl formate (436 µL; 711 mmol; 1000 mol%) and magnetic stirrer. The autoclave was sealed, flushed two times with 10 atm of N_2, and then placed into a preheated oil bath. After 24 h at 160 °C in the oil bath, the reactor was cooled to room temperature and depressurized. The reaction mixture was diluted in DCM, dried with Na_2SO_4, and solvents were removed under reduced pressure. 62% yield by NMR. The product was isolated by column chromatography, eluent: hexane/ethyl acetate 10/1 (Rf = 0.4). Isolated as a yellowish oil, 47 mg (40%).

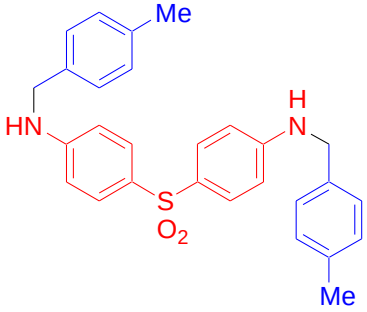
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (d, *J* = 8.9 Hz, 2H), 6.57 (d, *J* = 8.9 Hz, 2H), 3.75 (s, 3H), 3.55 (sept., *J* = 6.2 Hz, 1H), 1.19 (d, *J* = 6.2 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.99, 141.86, 114.99, 55.89, 45.30, 23.19.
NMR spectra are in agreement with the literature data.1

Byproduct **3'd** was also isolated by column chromatography, eluent: hexane/ethyl acetate 10/1 (Rf = 0.5). Isolated as a yellowish oil, 11 mg

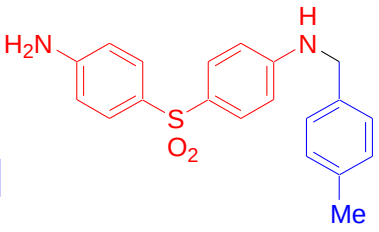
[3] Moskovets, A. P.; Usanov, D. L.; Afanasyev, O. I.; Fastovskiy, V. A.; Molotkov, A. P.; Muratov, K. M.; Denisov, G. L.; Zlotskii, S. S.; Smol'yakov, A. F.; Loginov, D. A., Chusov, D. Org. Biomol. Chem., 2017, **15**, 6384

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 – 6.77 (m, 4H), 3.89 (sept., *J* = 6.6 Hz, 1H), 3.76 (s, 3H), 2.66 (s, 3H), 1.12 (d, *J* = 6.6 Hz, 6H).
NMR spectrum is in agreement with the literature data.[4]

4,4'-Sulfonylbis(*N*-(4-methylbenzyl)aniline) (5b) and 4-(4-aminophenylsulfonyl)-*N*-(4-methylbenzyl)aniline (5a)



5b

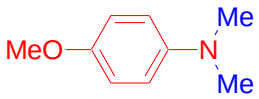


5a

A 10 ml stainless steel autoclave was charged with $RhCl_3 \cdot 4H_2O$ (2.0 mg; 7.1 µmol; 2 mol%), dry sodium acetate (874 mg; 10.7 mmol; 3000 mol%), 4,4'-sulfonyldianiline (88.3 mg; 355 µmol; 100 mol%), HPLC grade water (1 ml) and methanol (1 ml), 4-methylbenzaldehyde (92.2 µL; 711 µmol, 220 mol%), methyl formate (436 µL; 711 mmol; 1000 mol%) and magnetic stirrer. The autoclave was sealed, flushed two times with 10 atm of N_2, and then placed into a preheated oil bath. After 24 h at 160 °C in the oil bath, the reactor was cooled to room temperature and depressurized. The reaction mixture was diluted in DCM, dried with Na_2SO_4, and solvents were removed under reduced pressure. Reaction mixture was separated by column chromatography: 30 mg of **5a** (Rf 0.4 in hexane:ethyl acetate 1:1) and 45 mg of **5b** (Rf 0.1 in hexane:ethyl acetate 1:1) were isolated.

5b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.6 Hz, 4H), 7.19 (d, *J* = 7.9 Hz, 4H), 7.14 (d, *J* = 7.9 Hz, 4H), 6.59 (d, *J* = 8.6 Hz, 4H), 4.29 (s, 4H), 2.33 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.77, 137.50, 134.73, 130.13, 129.62, 129.28, 127.62, 112.39, 47.79, 21.26.
5a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (app. dd, *J* = 8.7 Hz, 4H, two interfering dublets), 7.19 (d, *J* = 8.0 Hz, 4H), 7.14 (d, *J* = 8.0 Hz, 4H), 6.62 (d, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 4.29 (s, 2H), 2.34 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.43, 150.44, 137.48, 135.00, 131.50, 129.93, 129.61, 129.33, 129.31, 127.48, 114.26, 112.12, 47.51, 21.24.

4-Methoxy-*N*,*N*-dimethylaniline (6a)



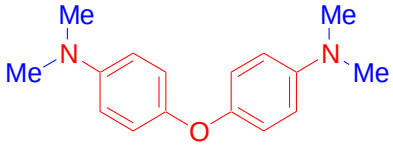
A 10 ml stainless steel autoclave was charged with $RhCl_3 \cdot 4H_2O$ (2.0 mg; 7.1 µmol; 1 mol%), dry sodium acetate (874 mg; 10.7 mmol; 1500 mol%), *p*-anisidine (87.6 mg; 711 µmol; 100 mol%), methanol (1 ml), formaldehyde solution in water (612 mL of 38% solution; 711 µmol, 1200 mol%), methyl formate (436 µL; 711 mmol; 1000 mol%) and magnetic stirrer. The autoclave was sealed, flushed two times with 10 atm of N_2, and then placed into a preheated oil bath. After 24 h at 160 °C in the oil bath, the reactor was cooled to room temperature and depressurized. The reaction mixture was diluted in DCM, dried with Na_2SO_4, and solvents were

[4] Lundgren, R. J.; Sappong-Kumankumah, A.; Stradiotto, M. Chem. – A Eur. J. 2010, **16** (6), 1983

removed under reduced pressure. 73% yield by NMR. The product was isolated by column chromatography, eluent: hexane/ethyl acetate 10/1 (Rf = 0.2). Isolated as a yellowish oil, 43 mg (40%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (d, *J* = 9.2 Hz, 2H), 6.81 (d, *J* = 9.2 Hz, 2H), 3.77 (s, 3H), 2.88 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.48, 145.39, 115.39, 114.76, 55.87, 42.22.
NMR spectra are in agreement with the literature data.[5]

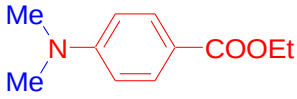
4,4'-Oxybis(N,N-dimethylaniline) (8a)



A 10 ml stainless steel autoclave was charged with $RhCl_3 \cdot 4H_2O$ (2.0 mg; 7.1 µmol; 2 mol%), dry sodium acetate (874 mg; 10.7 mmol; 3000 mol%), *4,4'*-oxydianiline (71.8 mg; 355 µmol; 100 mol%), methanol (1 ml), formaldehyde solution in water (511 mL of 38% solution; 711 µmol, 2000 mol%), methyl formate (436 µL; 711 mmol; 1000 mol%) and magnetic stirrer. The autoclave was sealed, flushed two times with 10 atm of N_2, and then placed into a preheated oil bath. After 24 h at 160 °C in the oil bath, the reactor was cooled to room temperature and depressurized. The reaction mixture was diluted in DCM, dried with Na_2SO_4, and solvents were removed under reduced pressure. 76% yield by NMR. The product was isolated by column chromatography, eluent: hexane/ethyl acetate 3/1 (Rf = 0.5). Isolated as a yellowish oil, 60 mg (66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (d, *J* = 9.1 Hz, 2H), 6.75 (d, *J* = 9.1 Hz, 2H), 2.92 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.80, 146.85, 119.35, 114.38, 41.60

Ethyl 4-(dimethylamino)benzoate (6b)



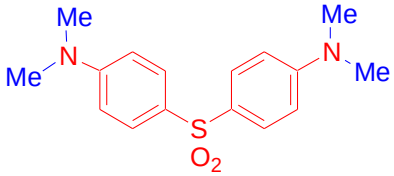
A 10 ml stainless steel autoclave was charged with $RhCl_3 \cdot 4H_2O$ (2.0 mg; 7.1 µmol; 1 mol%), dry sodium acetate (874 mg; 10.7 mmol; 1500 mol%), benzocaine (117.4 mg; 711 µmol; 100 mol%), methanol (1 ml), formaldehyde solution in water (612 mL of 38% solution; 711 µmol, 1200 mol%), methyl formate (436 µL; 711 mmol; 1000 mol%) and magnetic stirrer. The autoclave was sealed, flushed two times with 10 atm of N_2, and then placed into a preheated oil bath. After 24 h at 160 °C in the oil bath, the reactor was cooled to room temperature and depressurized. The reaction mixture was diluted in DCM, dried with Na_2SO_4, and solvents were removed under reduced pressure. 85% yield by NMR. The product was isolated by column chromatography, eluent: hexane/ethyl acetate 10/1 (Rf = 0.2). Isolated as a white solid, 92 mg (67%). Melting point is 61-62°C (Lit. mp 61.4-62.3)[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 9.0 Hz, 2H), 6.64 (d, *J* = 9.0 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.02 (s, 6H), 1.36 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.11, 153.24, 131.27, 117.04, 110.82, 60.21, 40.18, 14.57.
NMR spectra are in agreement with the literature data.6

[5] Hodges, J. A.; Raines, R. T. Org. Lett. 2006, **8** (21), 4695

[6] Popp, T. A.; Bracher, F. Synthesis (Stuttg). 2015, **47** (21), 3333.

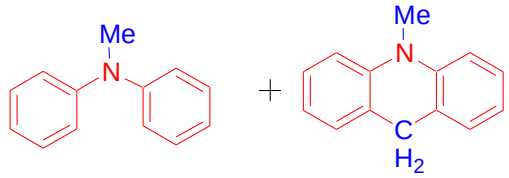
4,4'-Sulfonylbis(*N*,*N*-dimethylaniline) (8b)



A 10 ml stainless steel autoclave was charged with $RhCl_3 \cdot 4H_2O$ (2.0 mg; 7.1 µmol; 2 mol%), dry sodium acetate (874 mg; 10.5 mmol; 3000 mol%), 4,4'-sulfonyldianiline (88.3 mg; 355 µmol; 100 mol%), methanol (1 ml), formaldehyde solution in water (511 mL of 38% solution; 711 µmol, 2000 mol%), methyl formate (436 µL; 711 mmol; 1000 mol%) and magnetic stirrer. The autoclave was sealed, flushed two times with 10 atm of N_2, and then placed into a preheated oil bath. After 24 h at 160 °C in the oil bath, the reactor was cooled to room temperature and depressurized. The reaction mixture was diluted in DCM, dried with Na_2SO_4, and solvents were removed under reduced pressure. 99% yield by NMR, no isolation required.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.6 Hz, 4H), 6.61 (d, *J* = 8.6 Hz, 4H), 2.98 (s, 12H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.71, 128.81, 111.13, 40.18.

***N*-Methyl-*N*-phenylaniline (10) and 10-methyl-9,10-dihydroacridine (10')**



10 **10'**

A 10 ml stainless steel autoclave was charged with $RhCl_3 \cdot 4H_2O$ (2.0 mg; 7.1 µmol; 1 mol%), dry sodium acetate (874 mg; 10.7 mmol; 1500 mol%), diphenylamine (120.3 mg; 711 µmol; 100 mol%), methanol (1 ml), formaldehyde solution in water (612 mL of 38% solution; 711 µmol, 1200 mol%), methyl formate (436 µL; 711 mmol; 1000 mol%) and magnetic stirrer. The autoclave was sealed, flushed two times with 10 atm of N_2, and then placed into a preheated oil bath. After 24 h at 160 °C in the oil bath, the reactor was cooled to room temperature and depressurized. The reaction mixture was diluted in DCM, dried with Na_2SO_4, and solvents were removed under reduced pressure. 32% of **10a** and 30% of **10b** were detected by NMR. Product **10a** was isolated by column chromatography, eluent: hexane/ethyl acetate 10/1 (Rf = 0.8). Isolated as a yellowish oil, 39 mg (30%).

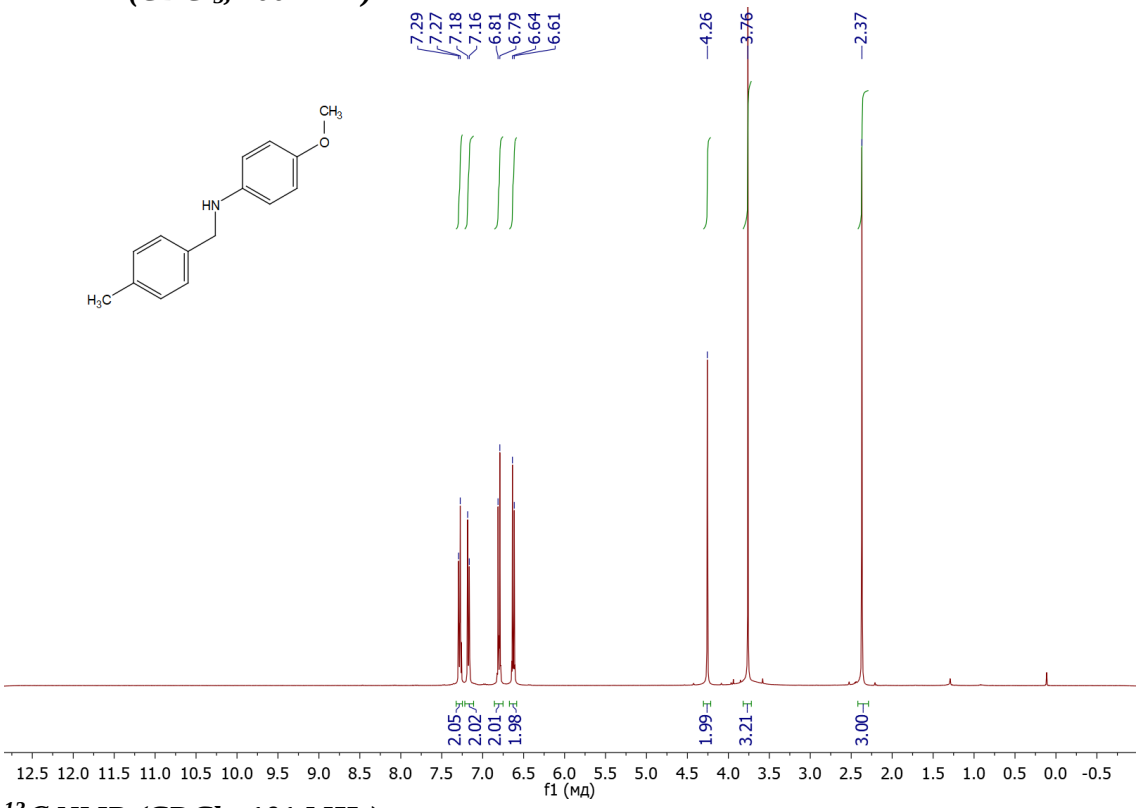
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.09 – 7.02 (m, 2H), 7.02 – 6.94 (m, 1H), 3.34 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.01, 129.32, 121.53, 120.59, 40.47.
NMR spectra are in agreement with the literature data.[7]

[7] Bhojgude, S. S.; Kaicharla, T.; Biju, A. T. Org. Lett. 2013, **15** (21), 5452

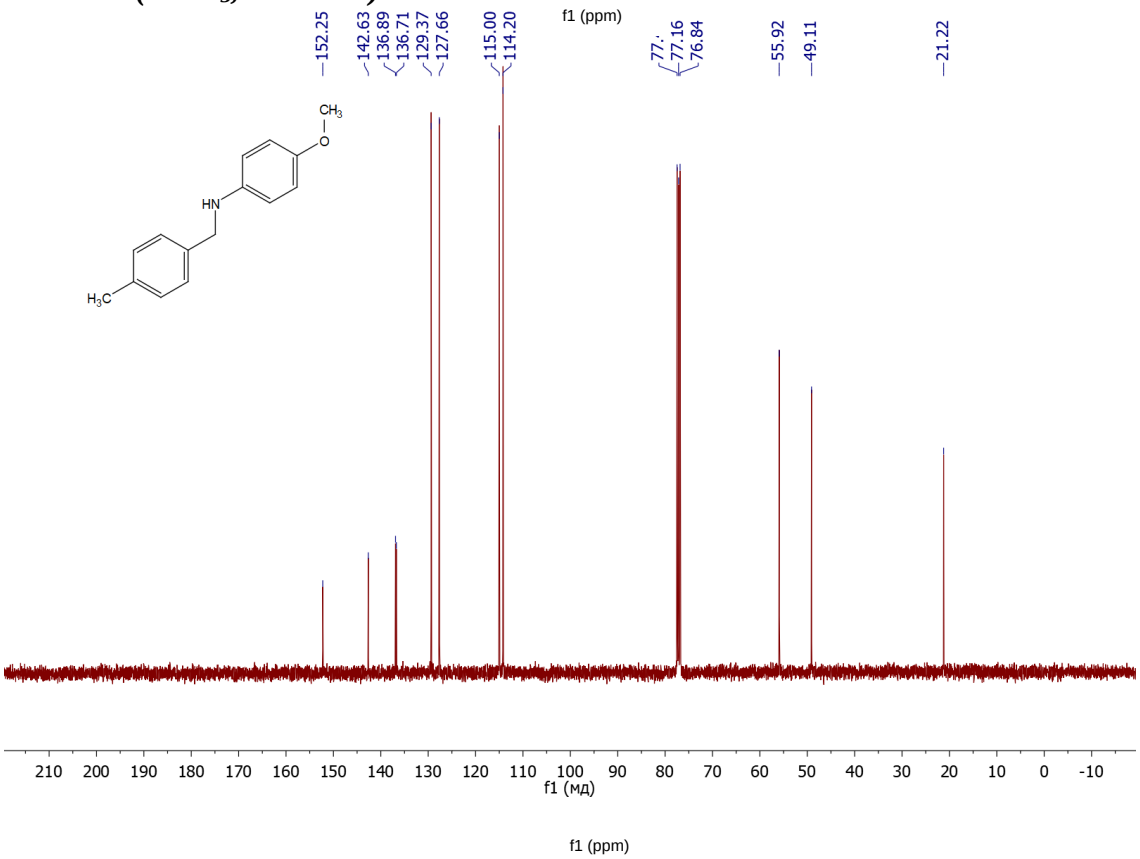
4. Copies of NMR spectra

4-Methoxy-*N*-(4-methoxybenzyl)aniline (3a)

^{1}H NMR ($CDCl_3$, 400 MHz)



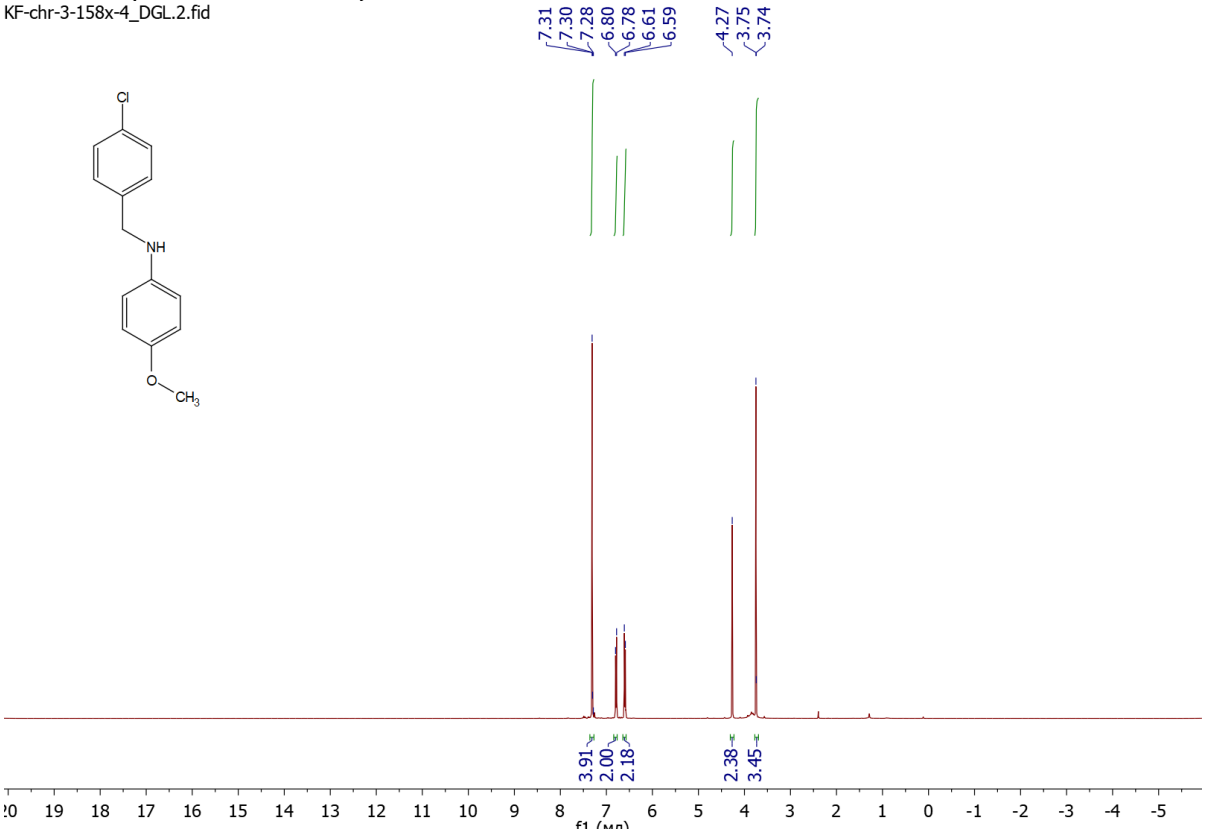
^{13}C NMR ($CDCl_3$, 101 MHz)



N-(4-Chlorobenzyl)-4-methoxyaniline (3b)

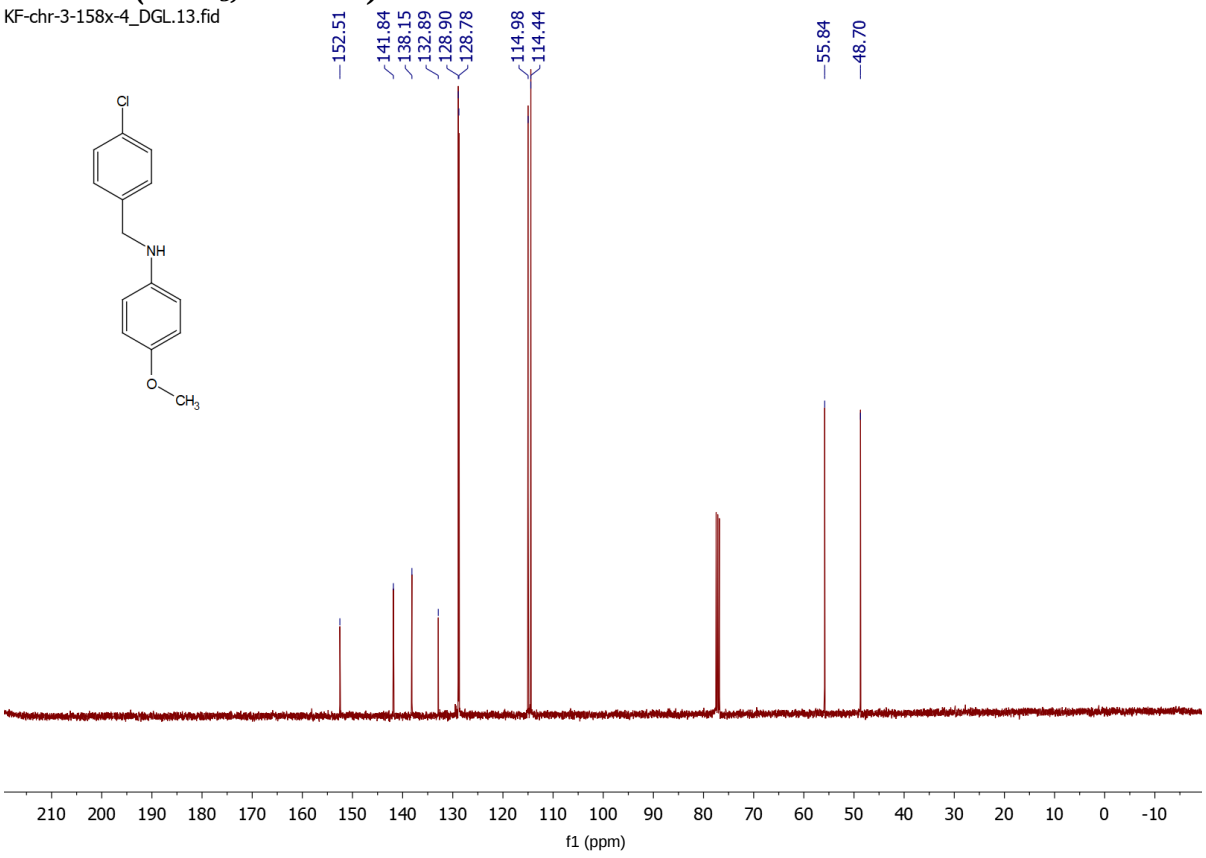
^{1}H NMR ($CDCl_3$, 400 MHz)

KF-chr-3-158x-4_DGL.2.fid



^{13}C NMR ($CDCl_3$, 101 MHz)

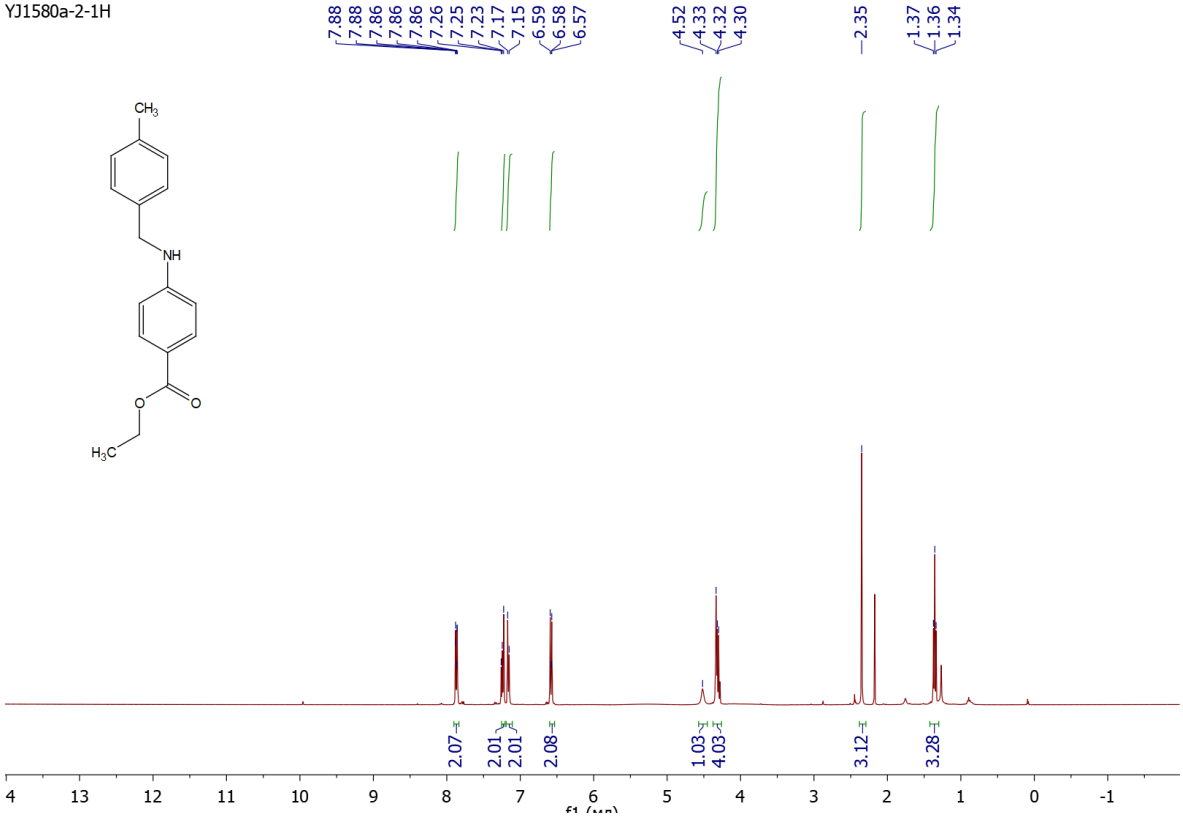
KF-chr-3-158x-4_DGL.13.fid



Ethyl 4-((4-methylbenzyl)amino)benzoate (3c)

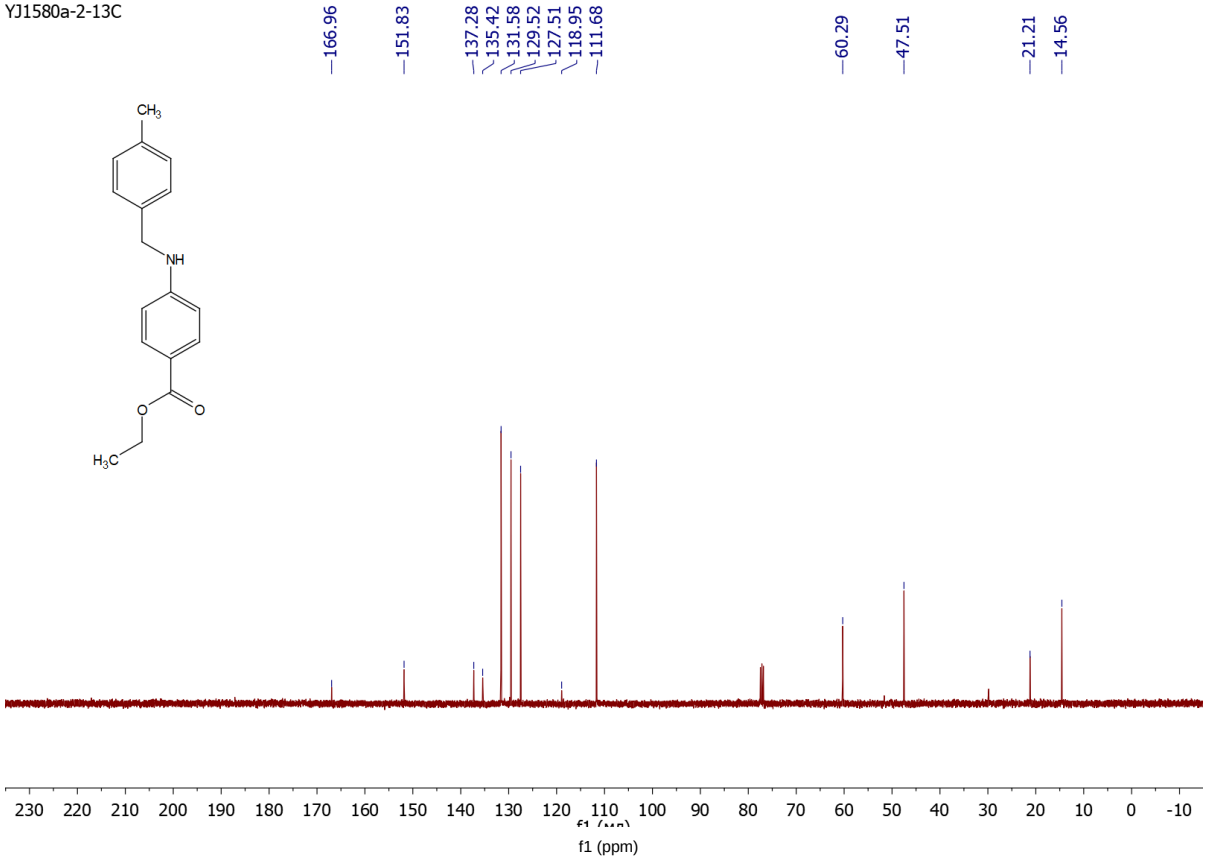
^{1}H NMR ($CDCl_3$, 400 MHz)

YJ1580a-2-1H



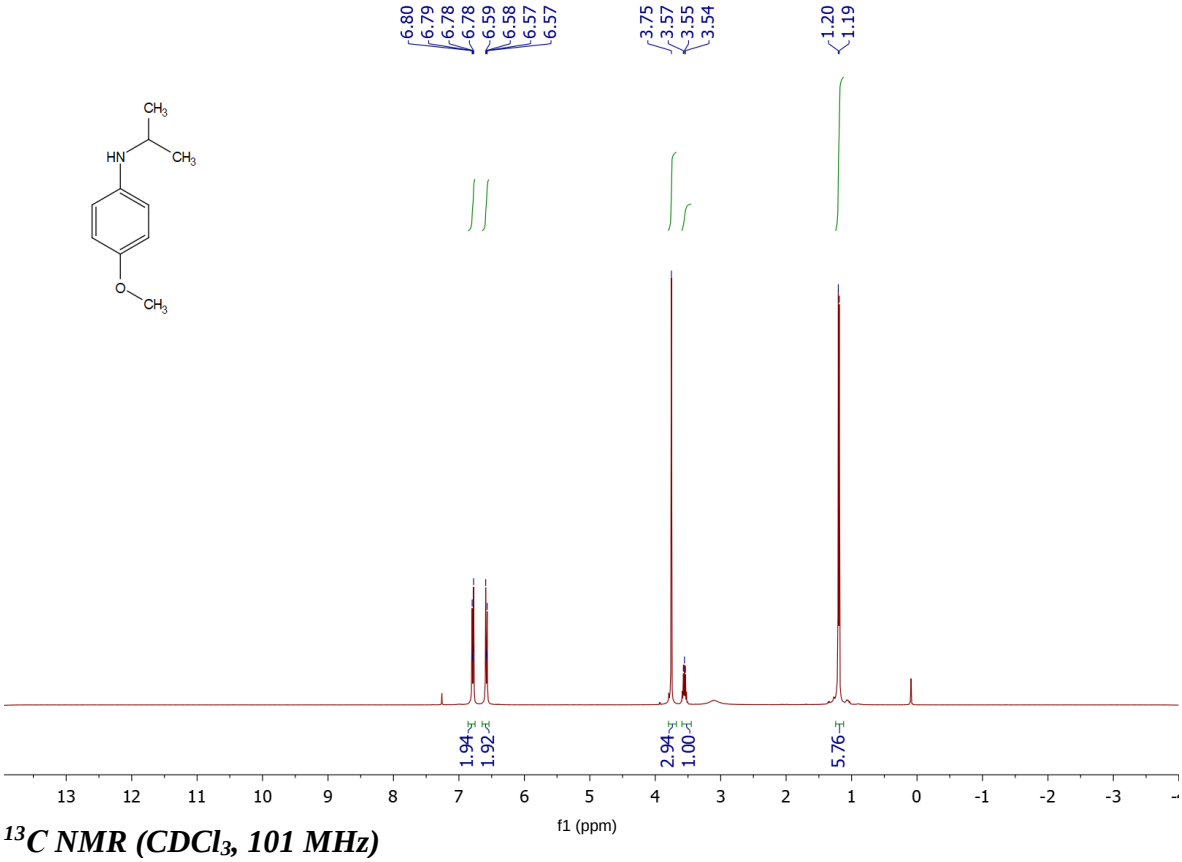
^{13}C NMR ($CDCl_3$, 101 MHz)

YJ1580a-2-13C

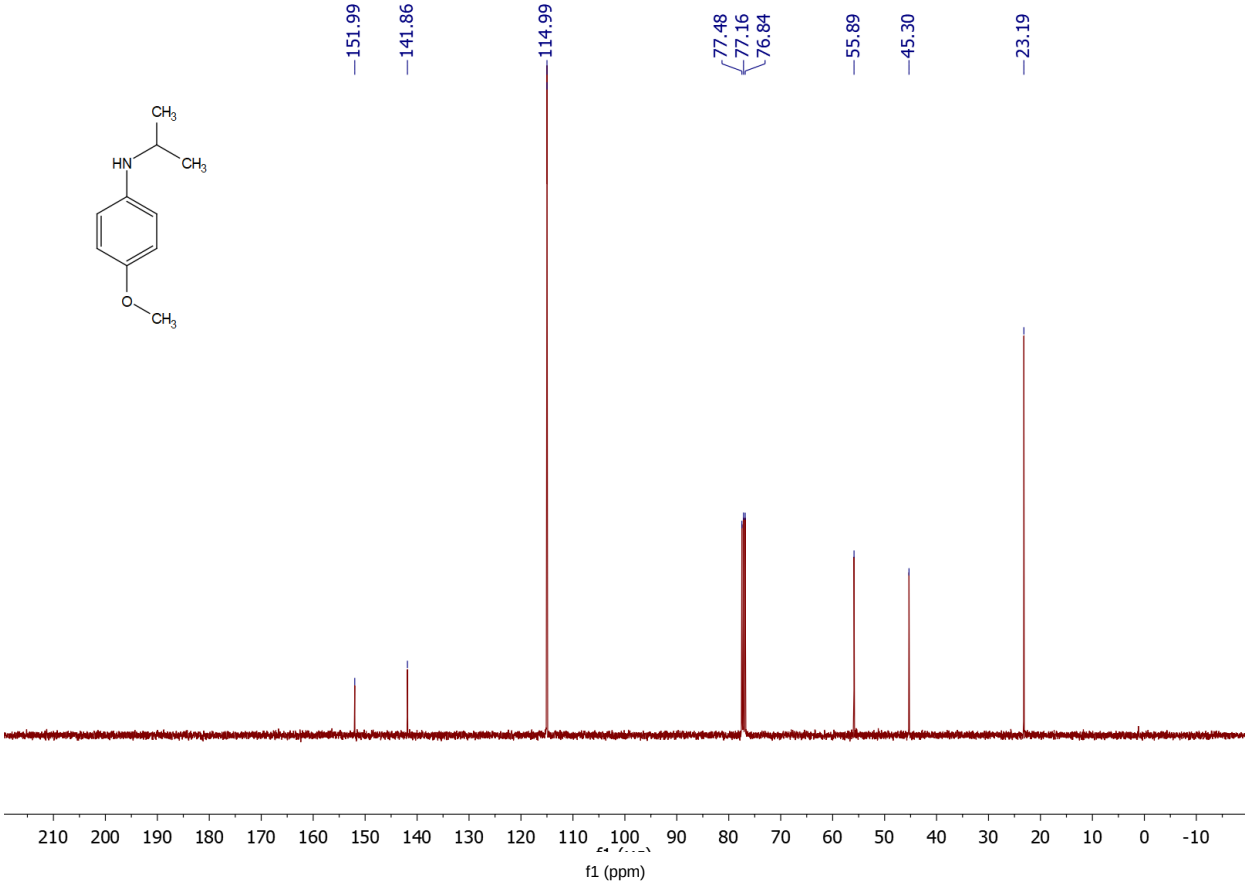


***N*-Isopropyl-4-methoxyaniline (3d)**

^{1}H NMR ($CDCl_3$, 400 MHz)

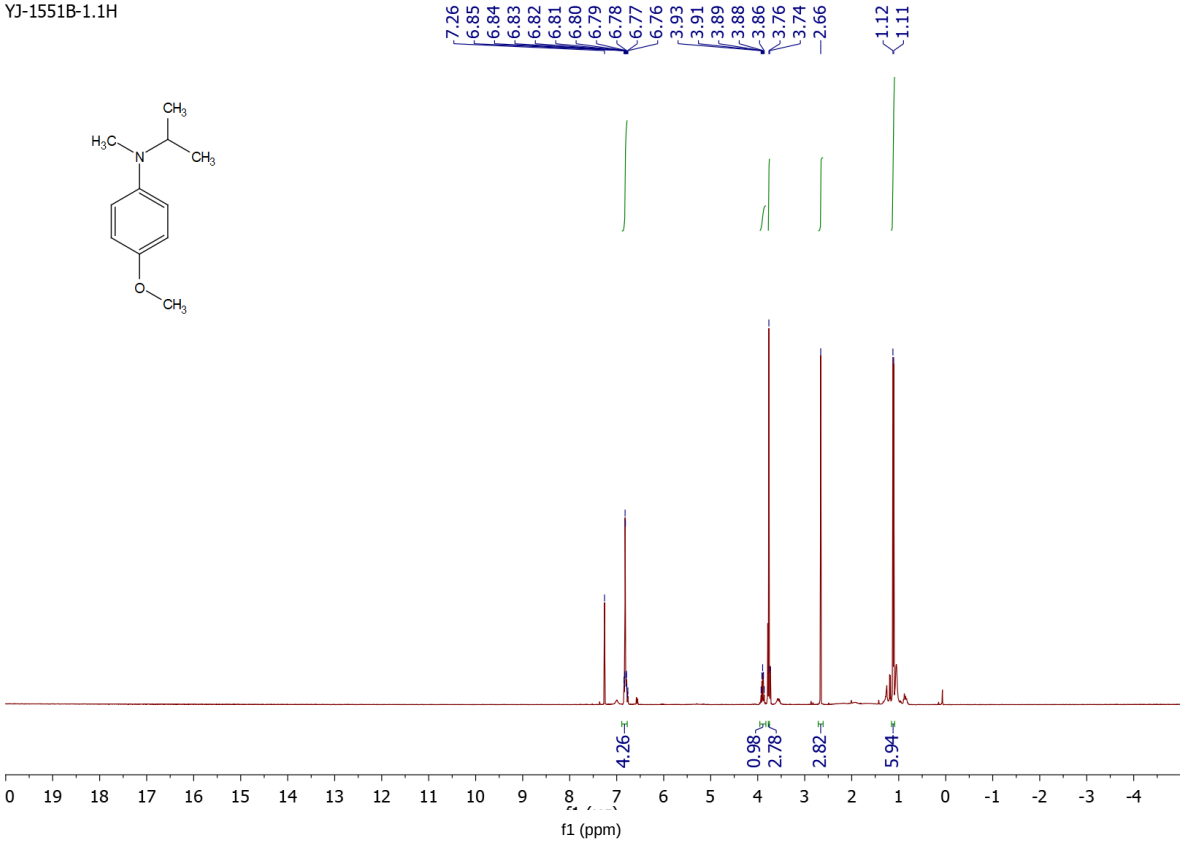


^{13}C NMR ($CDCl_3$, 101 MHz)



_N_-Isopropyl-_N_-methyl-4-methoxyaniline (3'd)

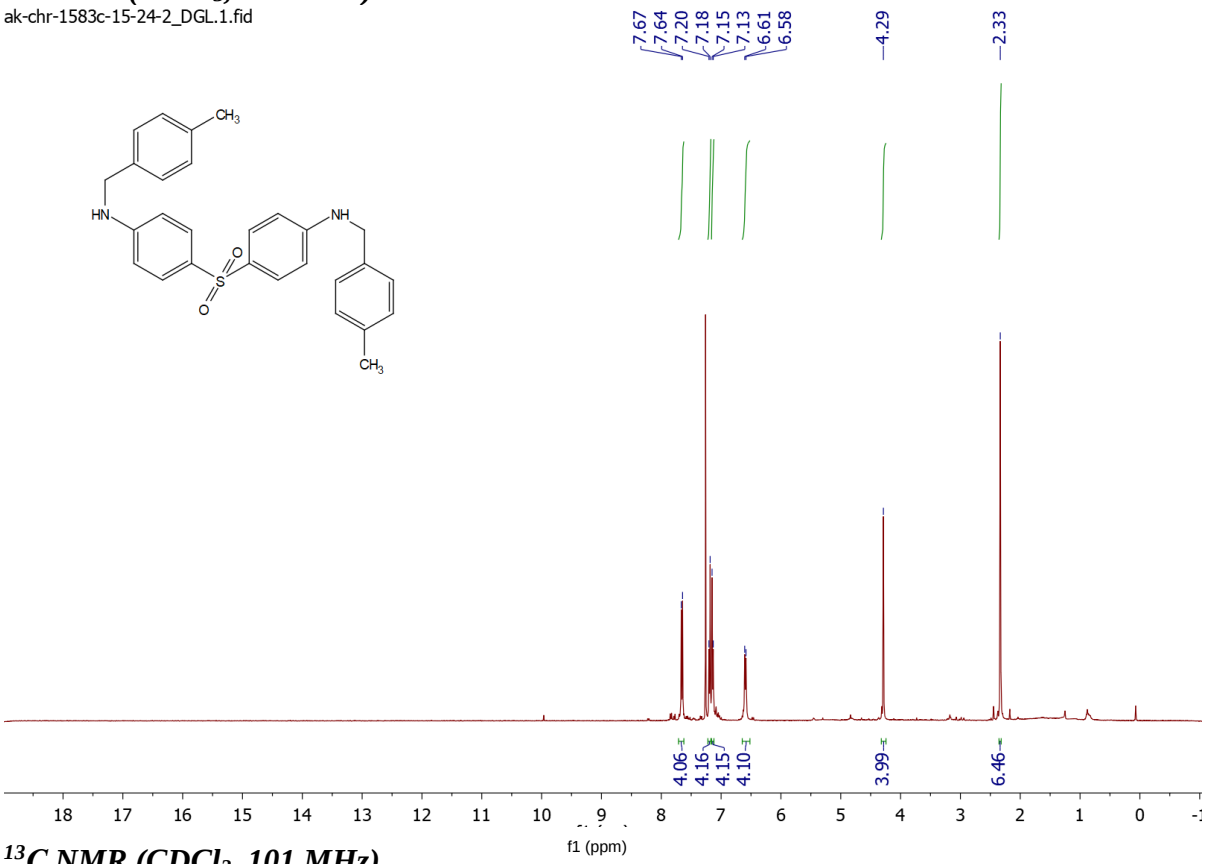
^{1}H NMR ($CDCl_3$, 400 MHz)



4,4'-Sulfonylbis(*N*-(4-methylbenzyl)aniline) (5b)

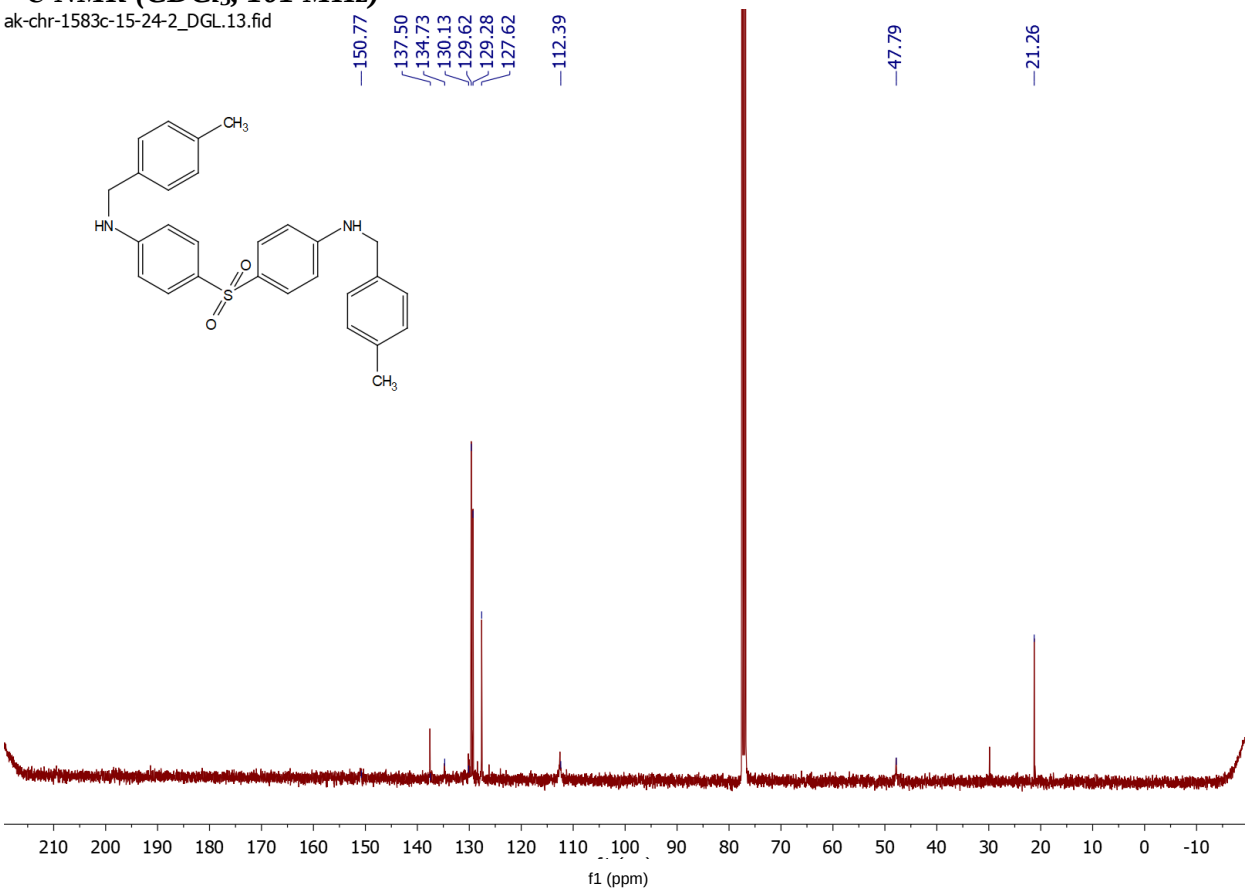
^{1}H NMR ($CDCl_3$, 400 MHz)

ak-chr-1583c-15-24-2_DGL.1.fid



^{13}C NMR ($CDCl_3$, 101 MHz)

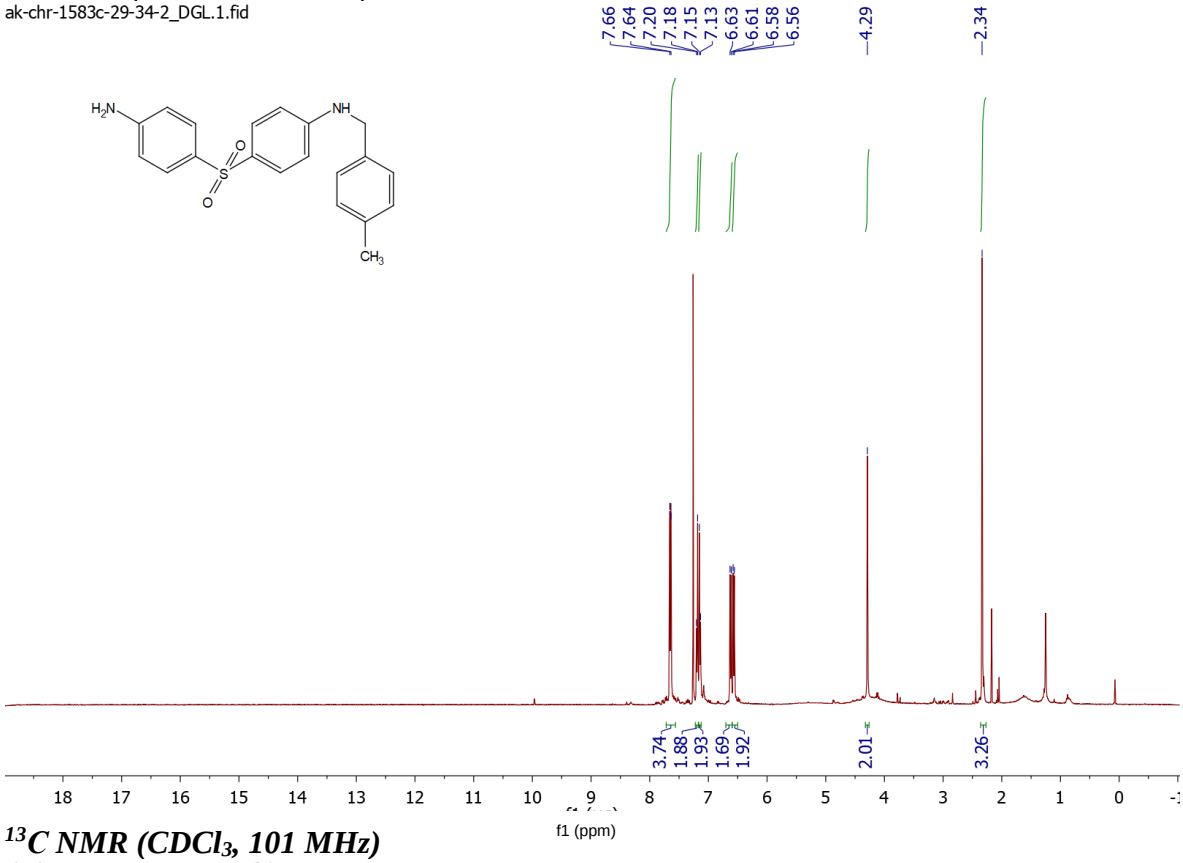
ak-chr-1583c-15-24-2_DGL.13.fid



4-(4-Aminophenylsulfonyl)-*N*-(4-methylbenzyl)aniline (5a)

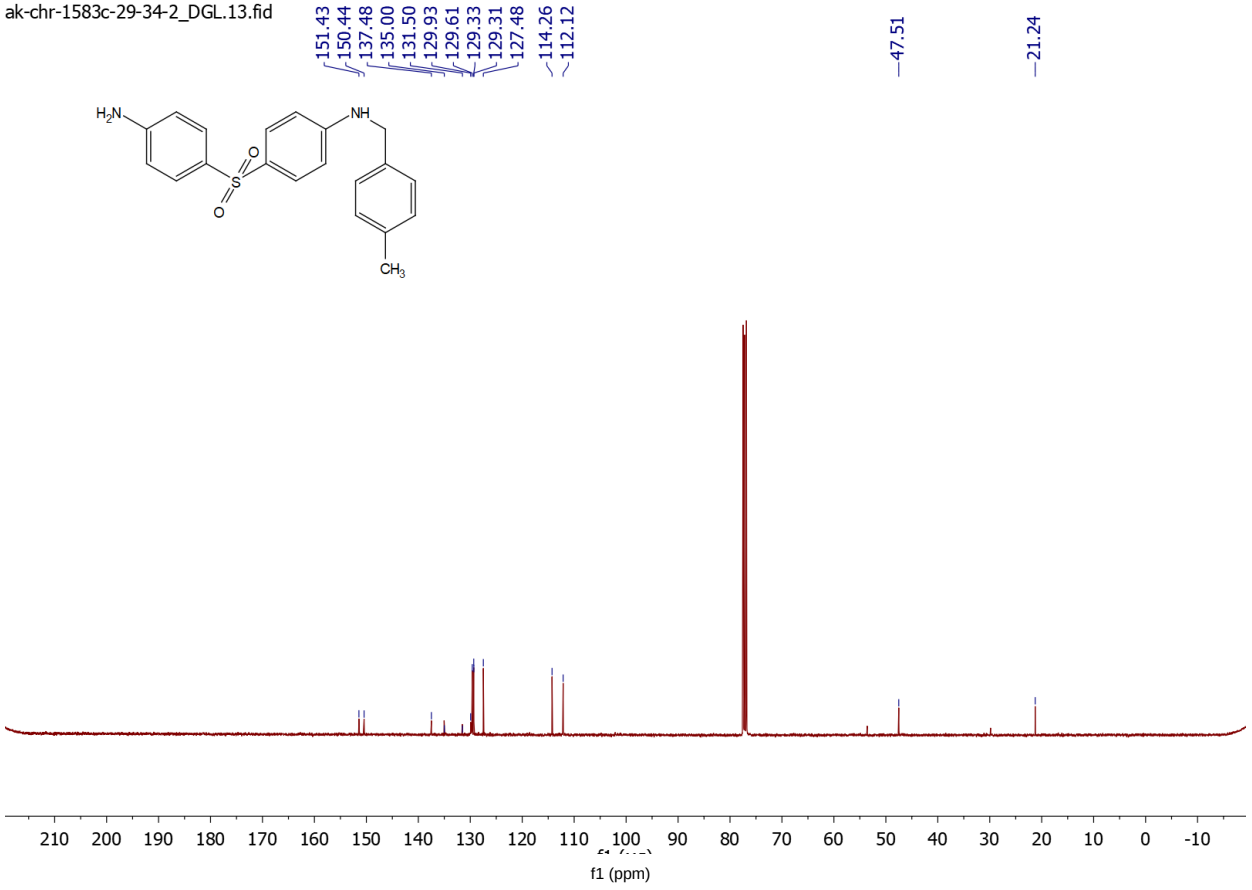
^{1}H NMR ($CDCl_3$, 400 MHz)

ak-chr-1583c-29-34-2_DGL.1.fid



^{13}C NMR ($CDCl_3$, 101 MHz)

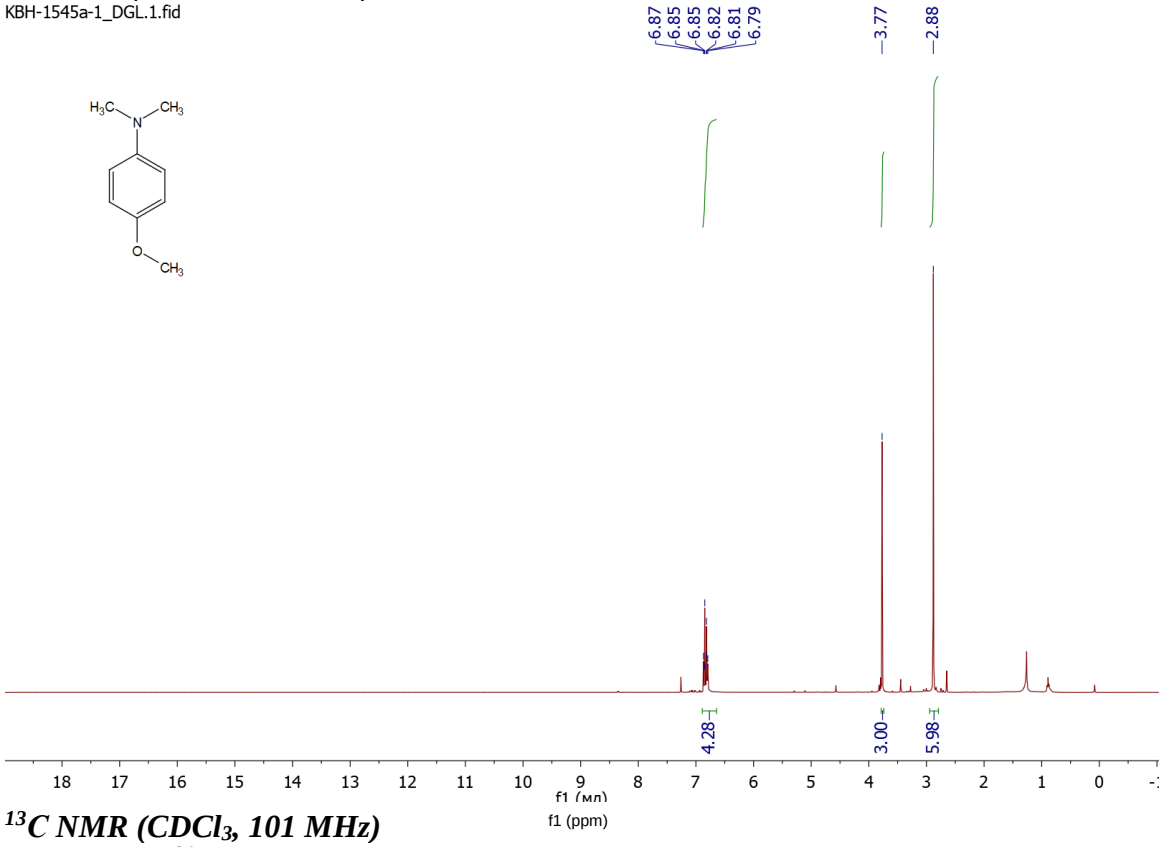
ak-chr-1583c-29-34-2_DGL.13.fid



4-Methoxy-*N*,*N*-dimethylaniline (6a)

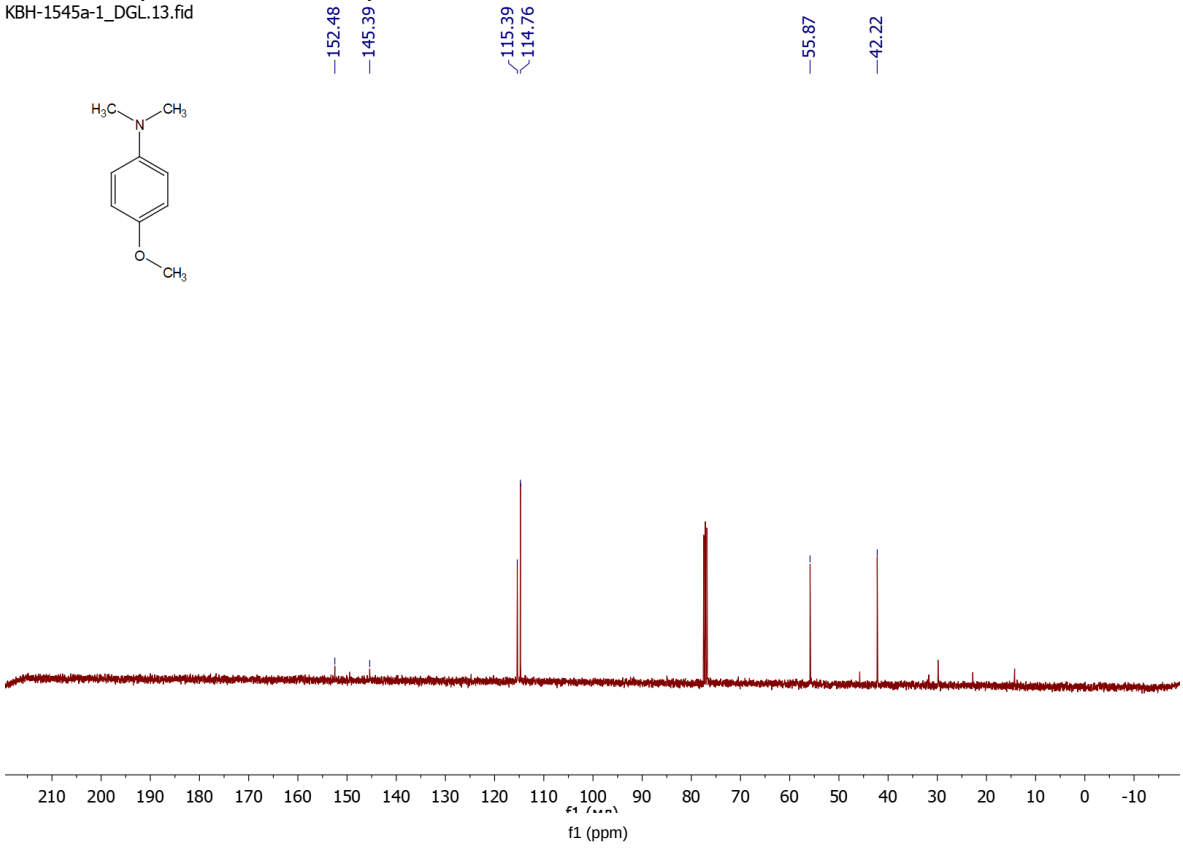
^{1}H NMR ($CDCl_3$, 400 MHz)

KBH-1545a-1_DGL.1.fid



^{13}C NMR ($CDCl_3$, 101 MHz)

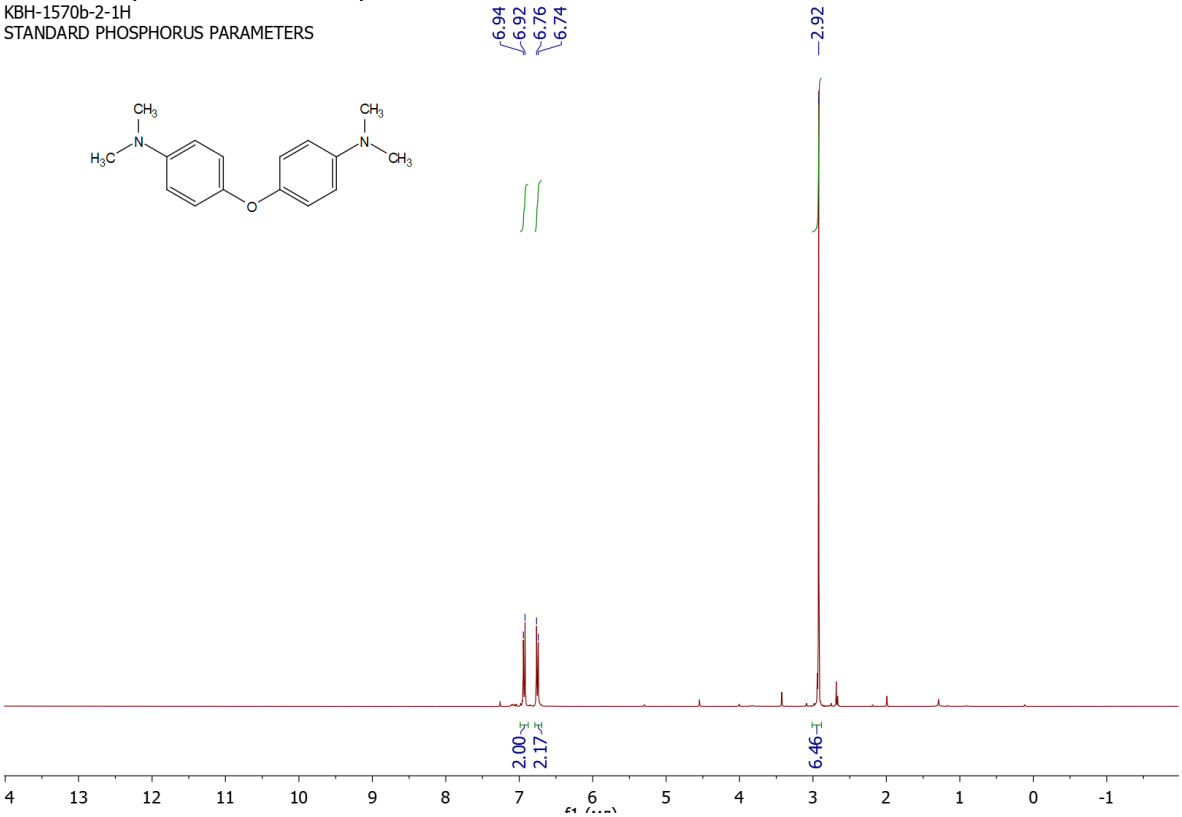
KBH-1545a-1_DGL.13.fid



4,4'-Oxybis(*N*,*N*-dimethylaniline) (8a)

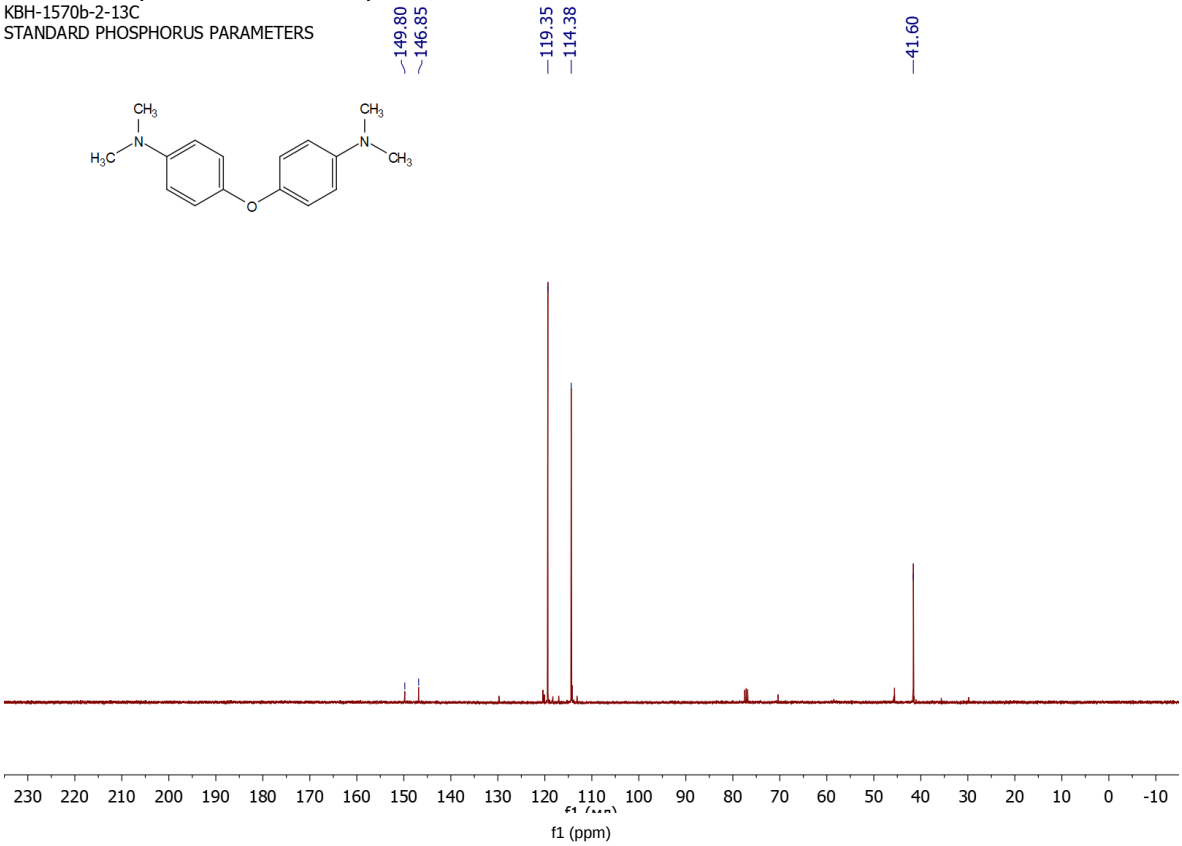
^{1}H NMR ($CDCl_3$, 400 MHz)

KBH-1570b-2-1H
STANDARD PHOSPHORUS PARAMETERS



^{13}C NMR ($CDCl_3$, 101 MHz)

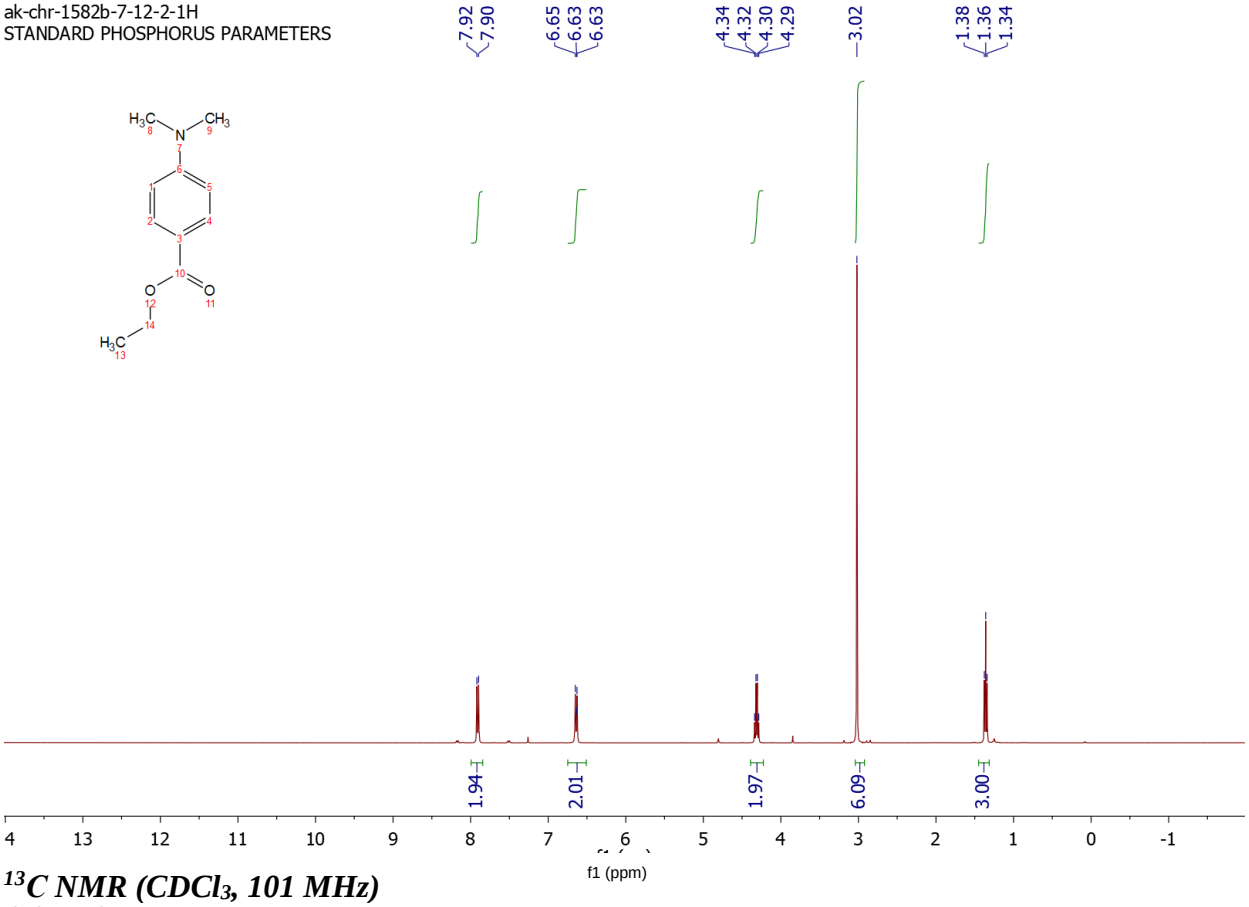
KBH-1570b-2-13C
STANDARD PHOSPHORUS PARAMETERS



Ethyl 4-(dimethylamino)benzoate (6b)

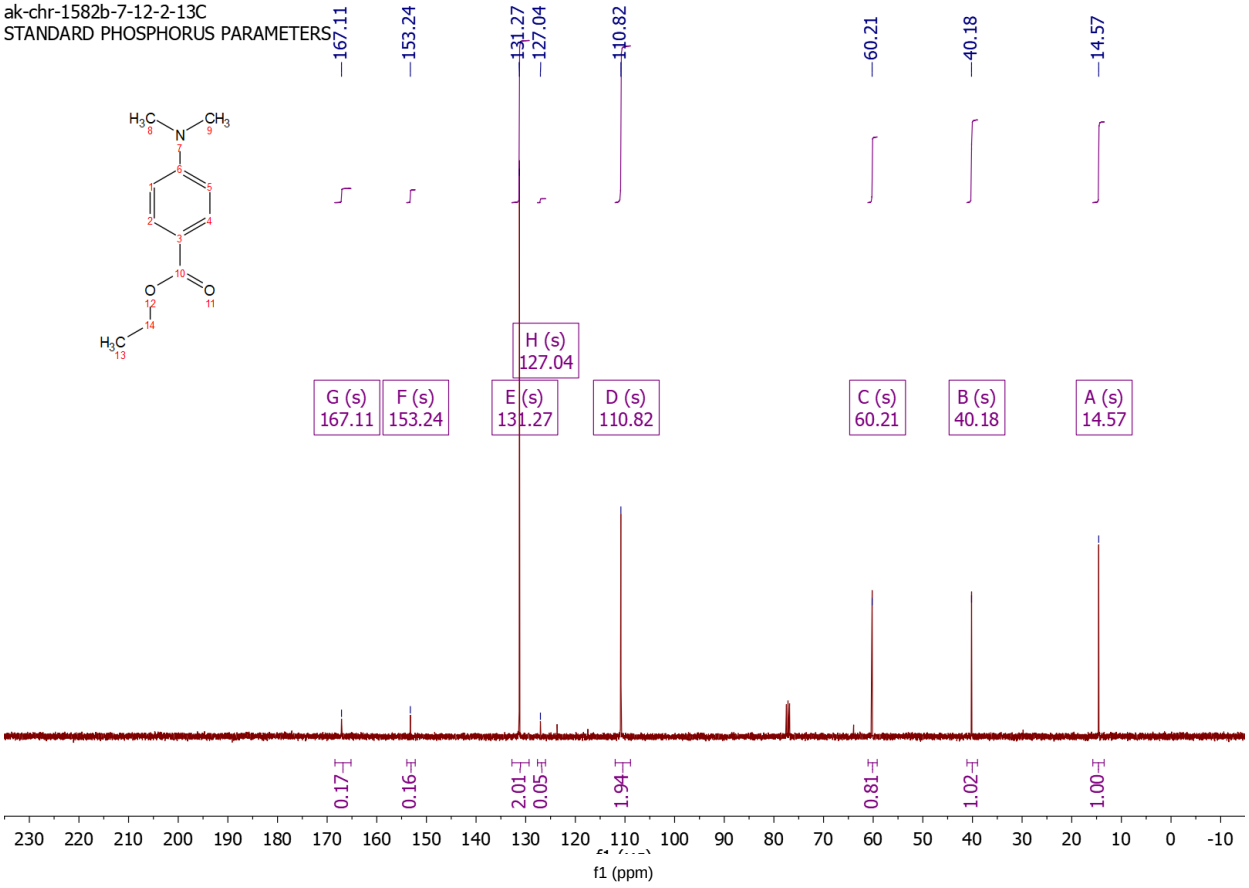
^{1}H NMR ($CDCl_3$, 400 MHz)

ak-chr-1582b-7-12-2-1H
STANDARD PHOSPHORUS PARAMETERS



^{13}C NMR ($CDCl_3$, 101 MHz)

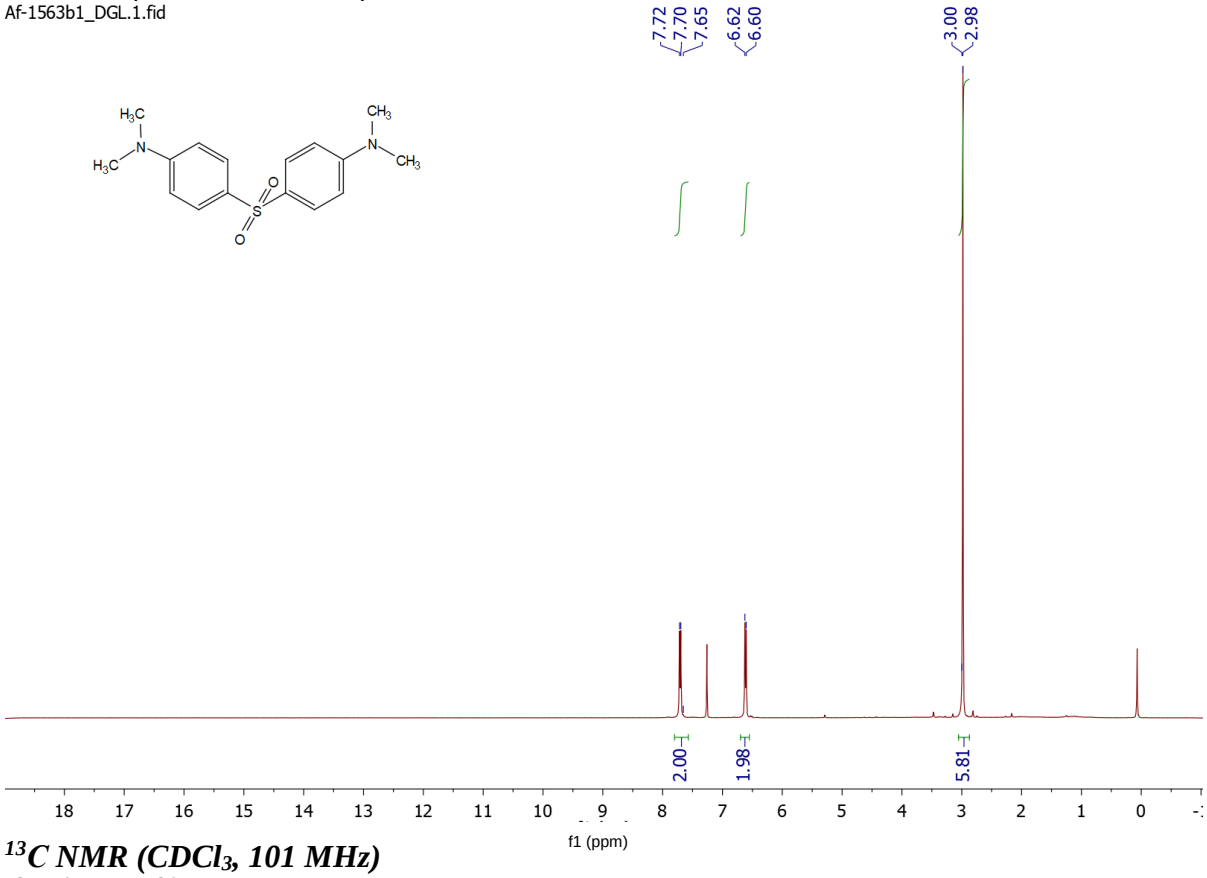
ak-chr-1582b-7-12-2-13C
STANDARD PHOSPHORUS PARAMETERS



4,4'-Sulfonylbis(*N*,*N*-dimethylaniline) (8b)

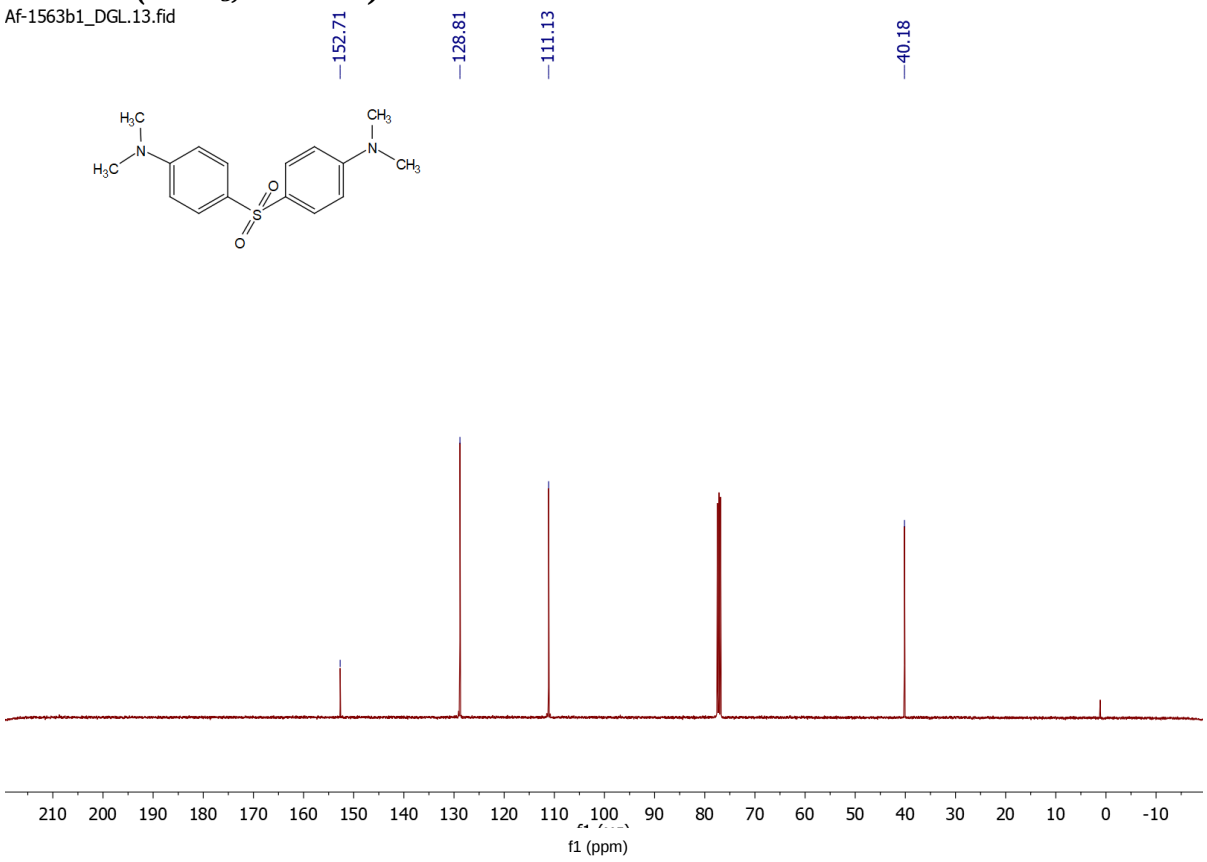
^{1}H NMR ($CDCl_3$, 400 MHz)

Af-1563b1_DGL.1.fid



^{13}C NMR ($CDCl_3$, 101 MHz)

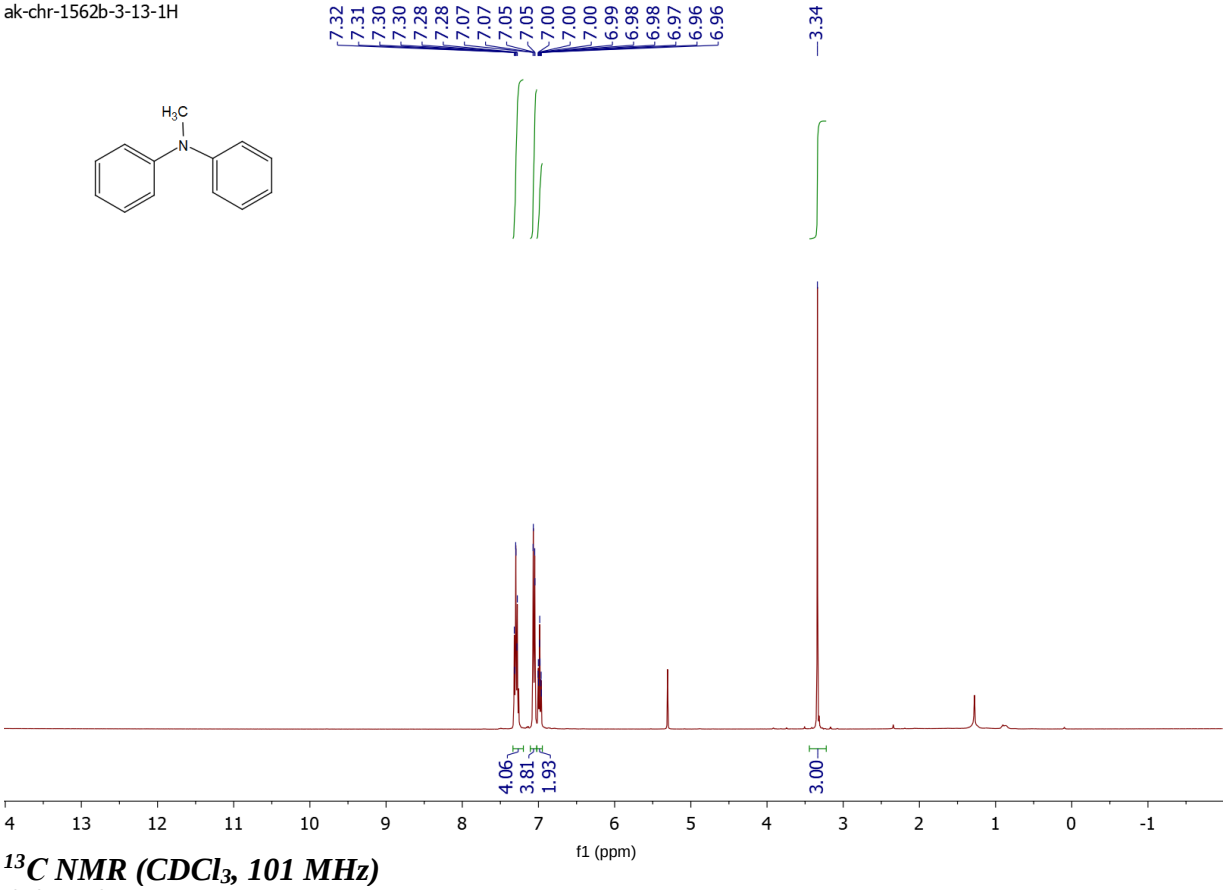
Af-1563b1_DGL.13.fid



N-Methyl-*N*-phenylaniline (10)

^{1}H NMR ($CDCl_3$, 400 MHz)

ak-chr-1562b-3-13-1H



^{13}C NMR ($CDCl_3$, 101 MHz)

ak-chr-1562b-3-13-13C