SUPPORTING INFORMATION

Fluorene Complexes of Group 9 metals: Fluorene Effect and Application for Reductive Amination

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1. Details of X-ray diffraction experiments.

X-ray diffraction data from single crystals of [**1**]$(SbF_6)_2$ and [**2b**]$(SbF_6)_2$ were collected at 120 K with Bruker APEX2 DUO CCD diffractometer, using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, ω-scans). The structures were solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. Positions of hydrogen atoms were calculated, and they were refined in the isotropic approximation within the riding model. Crystal data and structure refinement parameters are given in Table S1. All calculations were performed using OLEX2 software [Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. &Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.]. CCDC 1916687 and 1916688 contain the supplementary crystallographic information for [**1**]$(SbF_6)_2$ and [**2b**]$(SbF_6)_2$, respectively.

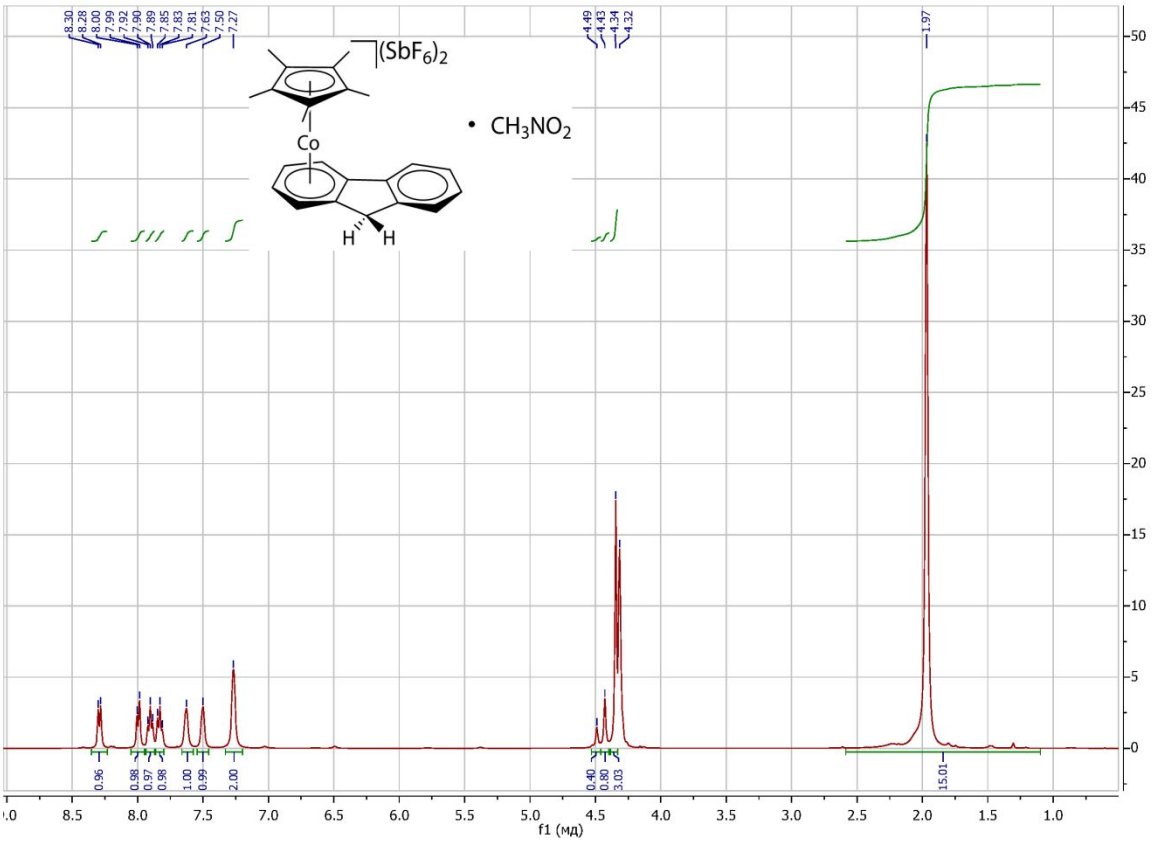
Table S1. Crystal data and structure refinement parameters for [**1**]$(SbF_6)_2$ and [**2b**]$(SbF_6)_2$.

	[**1**]$(SbF_6)_2$	[**2b**]$(SbF_6)_2$
Empirical formula	$C_{23}H_{25}Co$, $(SbF_6)_2$, CH_3NO_2	$C_{18}H_{15}Ir$, $(SbF_6)_2$, CH_3NO_2
Formula weight	892.93	956.08
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Z	4	4
a, Å	17.5223(11)	16.3474(10)
b, Å	11.6815(7)	10.9178(7)
c, Å	19.8490(14)	19.2764(13)
β, °	133.6844(10)	134.6379(10)
V, Å^3	2938.1(3)	2448.1(3)
D_{calc} (g cm^{-1})	2.019	2.594
Linear absorption, μ (cm^{-1})	24.84	77.24
F(000)	1726	1759
$2\theta_{max}$, °	54	58
Reflections measured	39592	31459
Independentreflections	6410	6497
Observed reflections [$I > 2\sigma(I)$]	4942	5305
Parameters	385	366

R1	0.0621	0.0333
wR2	0.1916	0.0745
GOF	1.065	1.044
$\Delta\rho_{max}$/ $\Delta\rho_{min}$ (e Å^{-3})	2.067/–1.450	1.642/–1.508

2. ^{1}H NMR and ^{13}C NMR spectra of the fluorene complexes.

Figure S1. ^{1}H and ^{13}C NMR spectra of [Cp*Co(η^{6}-fluorene)](SbF$_6$)$_2$ ([**1**](SbF$_6$)$_2$) in CD_3NO_2.



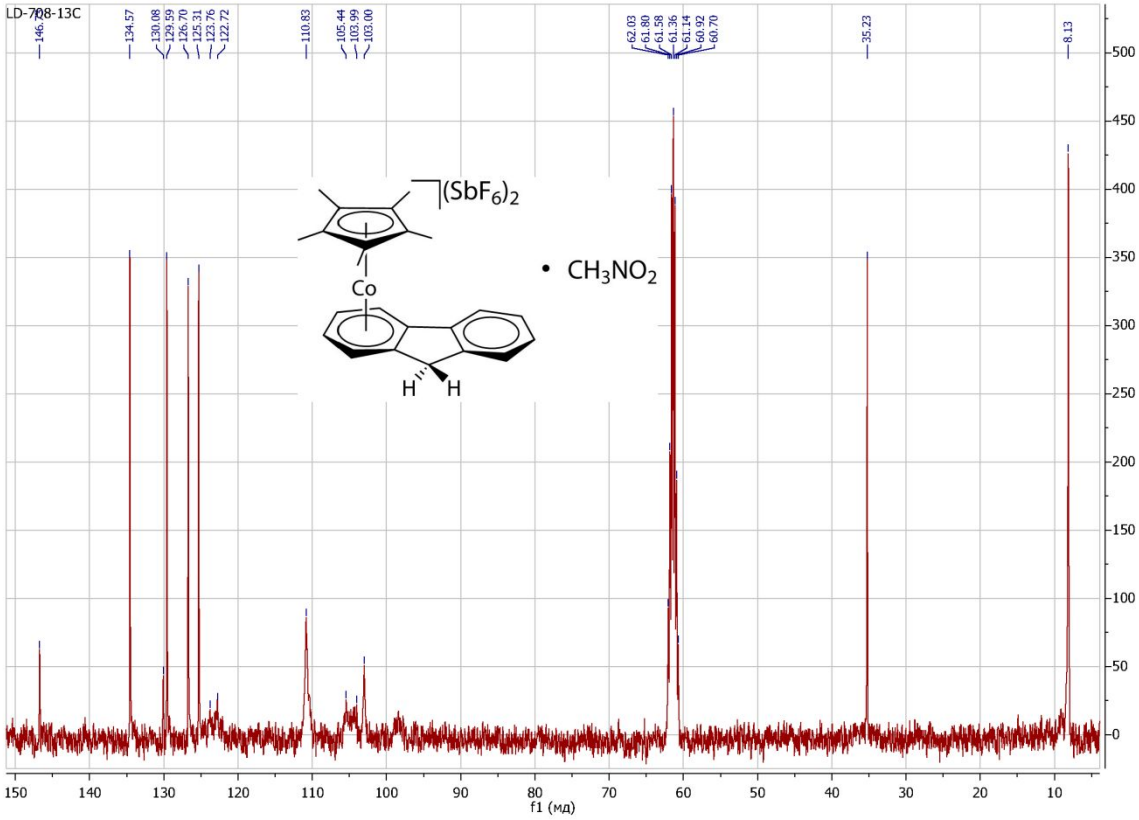
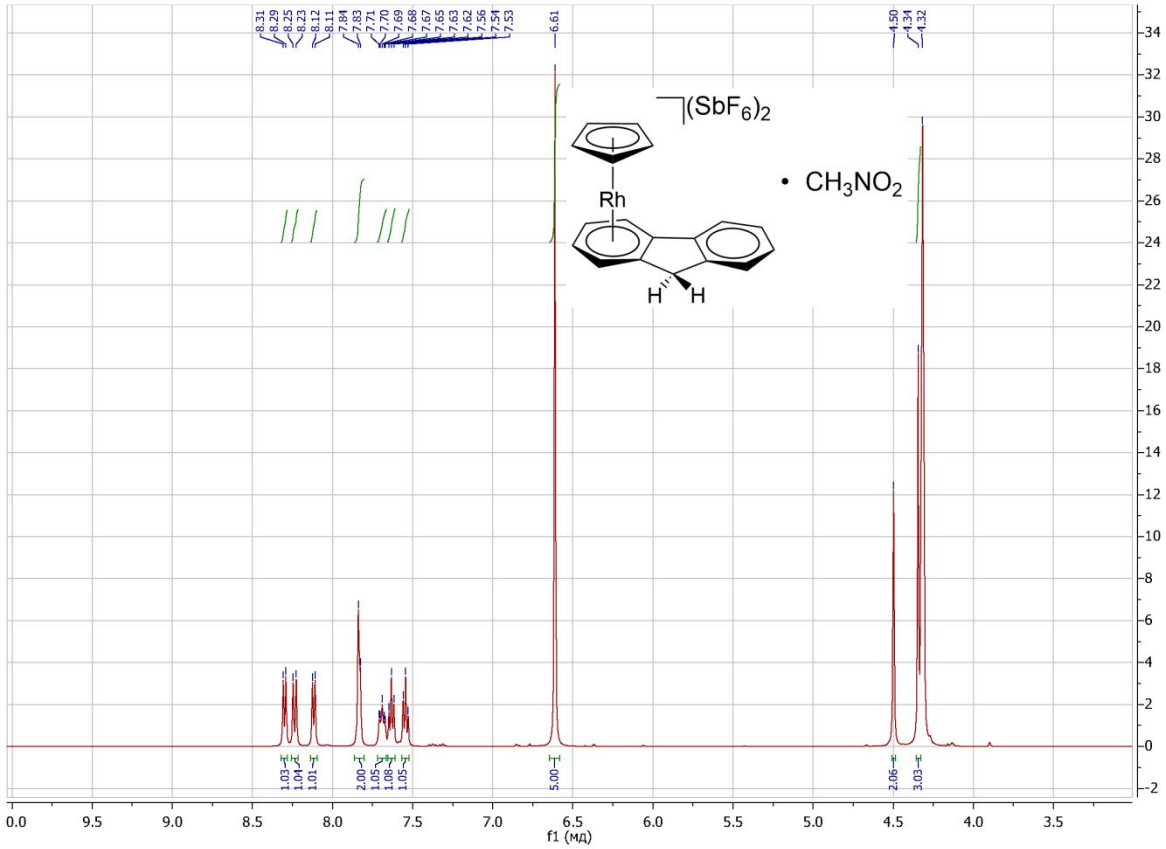


Figure S2. ^{1}H and ^{13}C NMR spectra of [CpRh(η^6-fluorene)]$(SbF_6)_2$ ([**2a**]$(SbF_6)_2$) in CD_3NO_2.



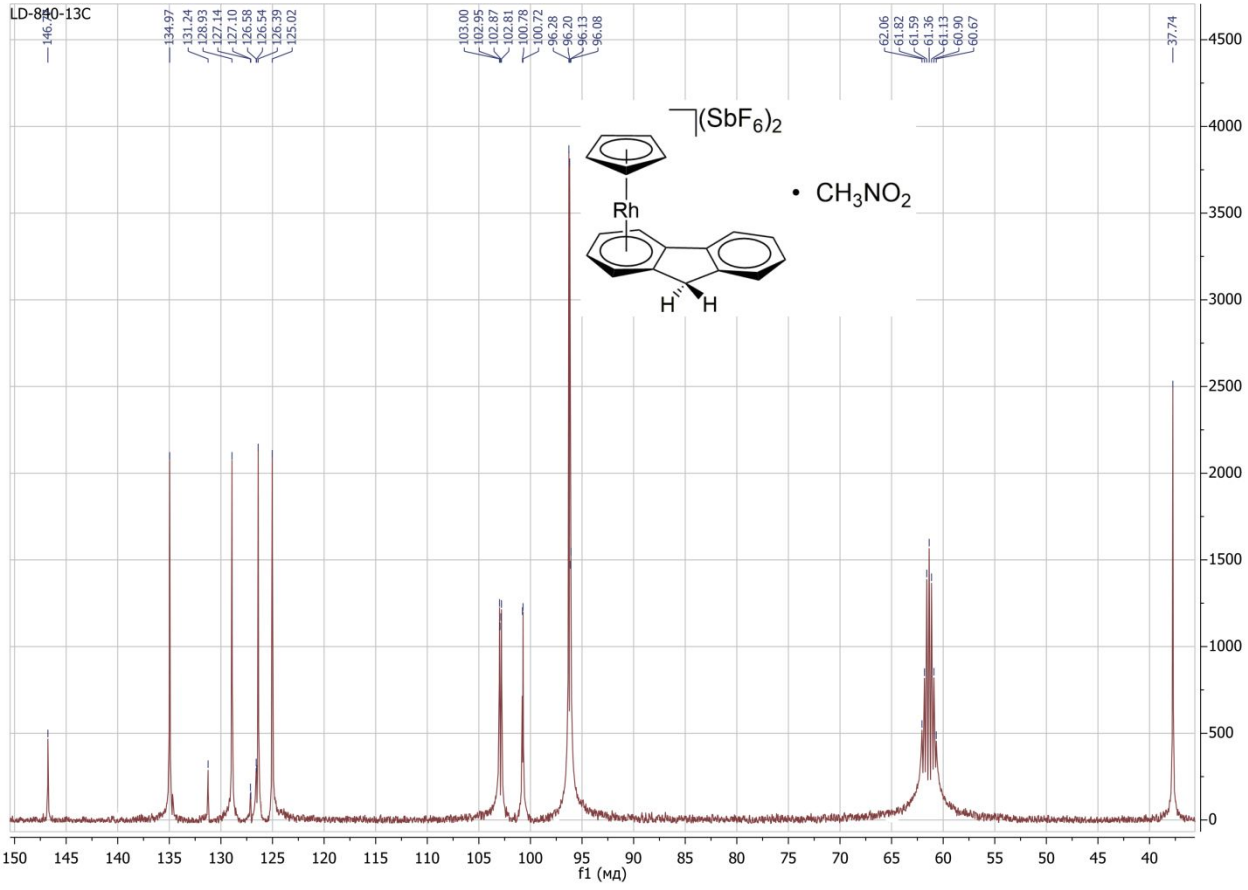
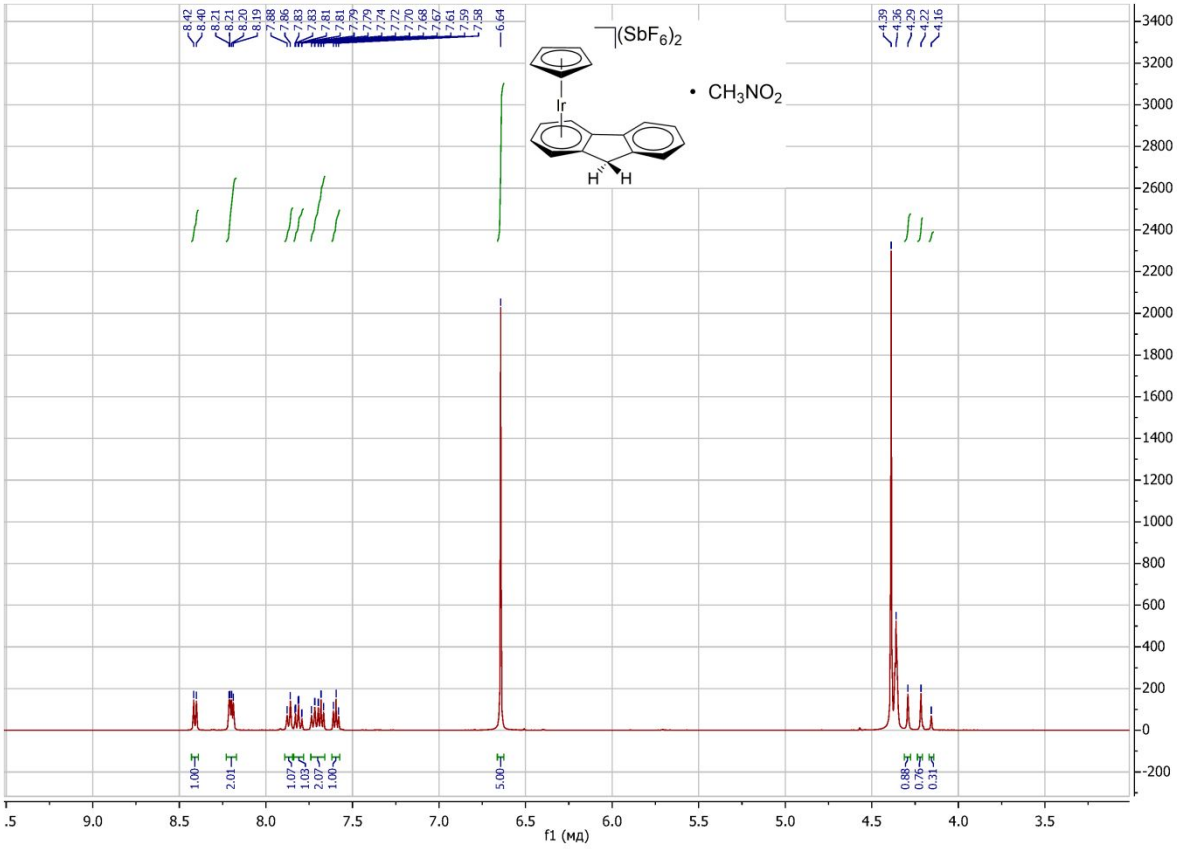


Figure S3. ^{1}H and ^{13}C NMR spectra of [CpIr(η^{6}-fluorene)](SbF$_6$)$_2$ ([**2b**](SbF$_6$)$_2$) in CD_3NO_2.



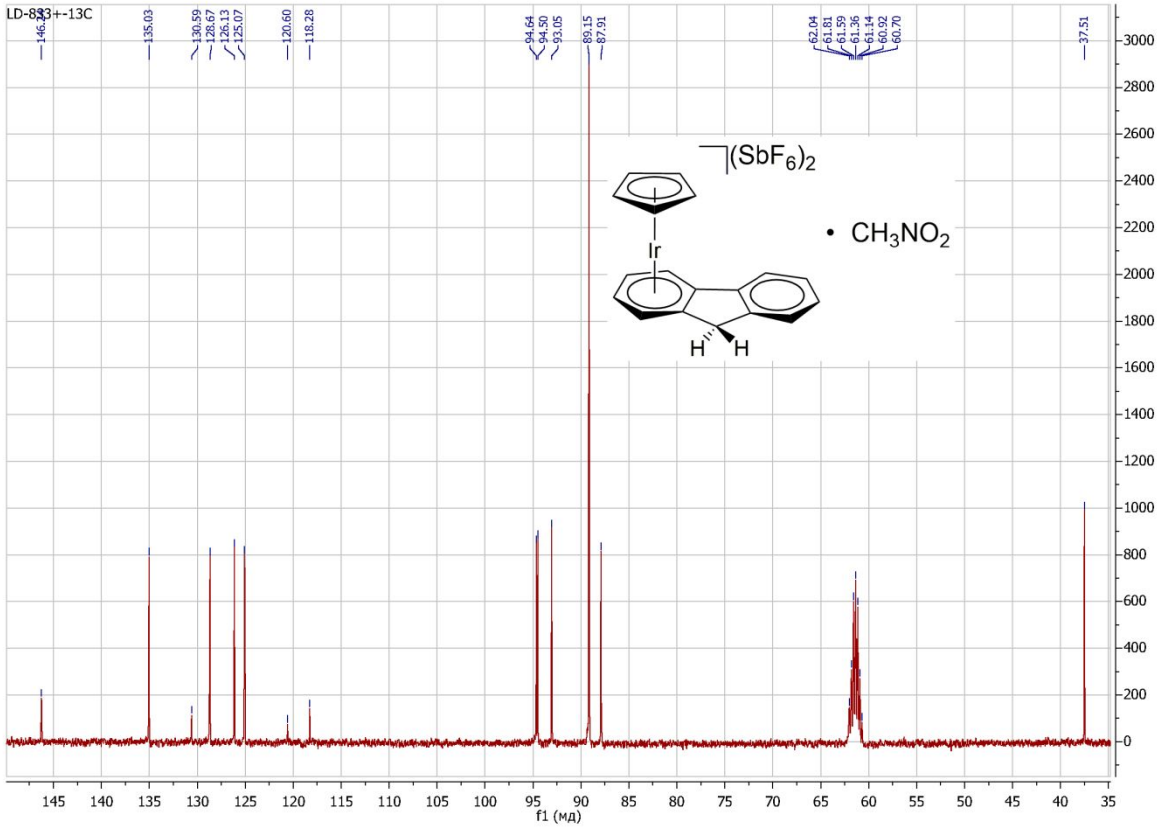
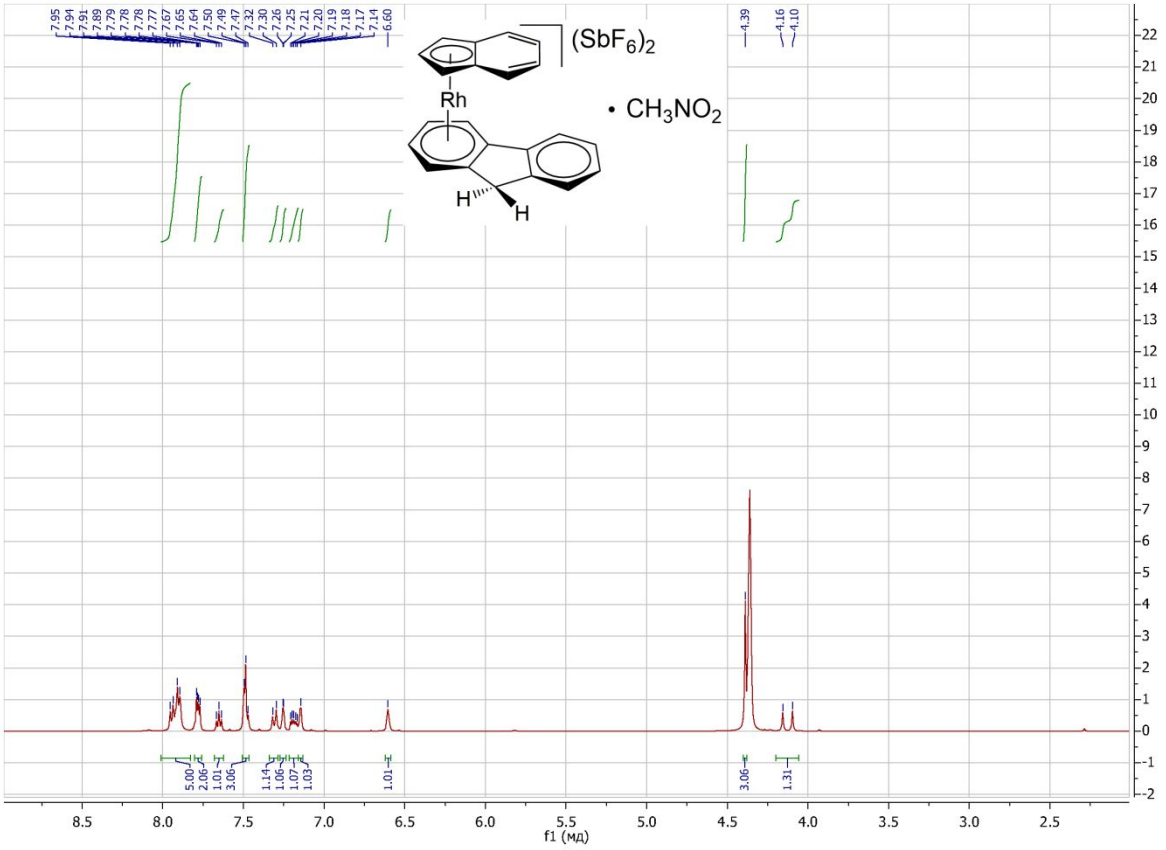


Figure S4. ^{1}H and ^{13}C NMR spectra of [(η^5-indenyl)Rh(η^6-fluorene)]$(SbF_6)_2$ ([**3a**]$(SbF_6)_2$) in CD_3NO_2.



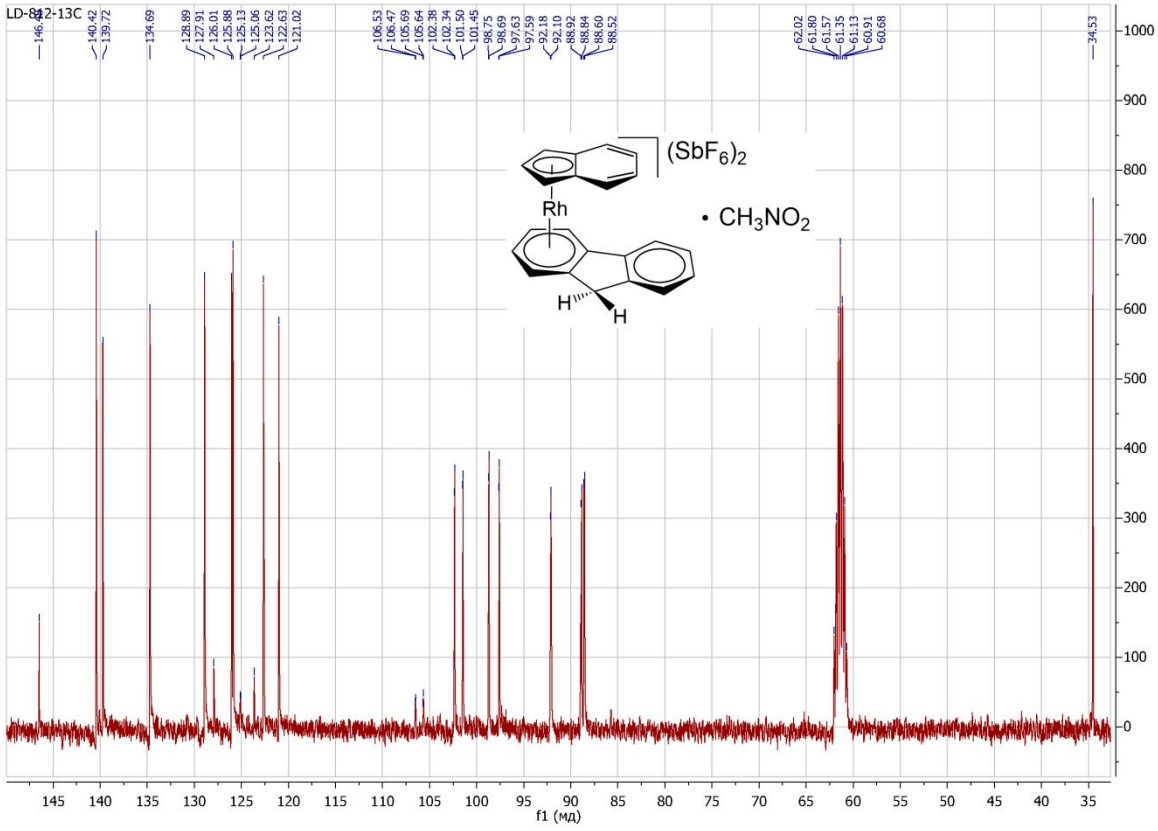
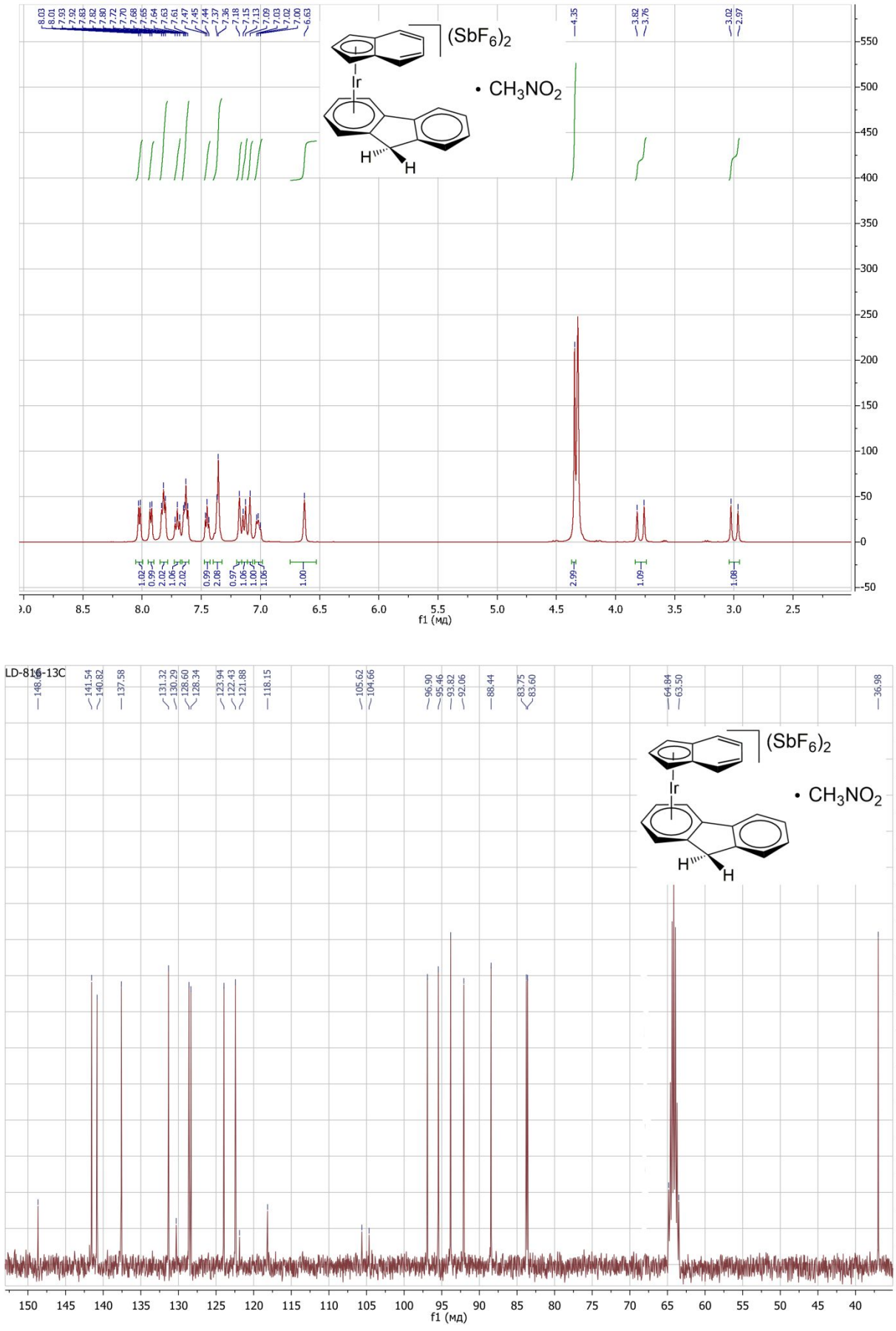
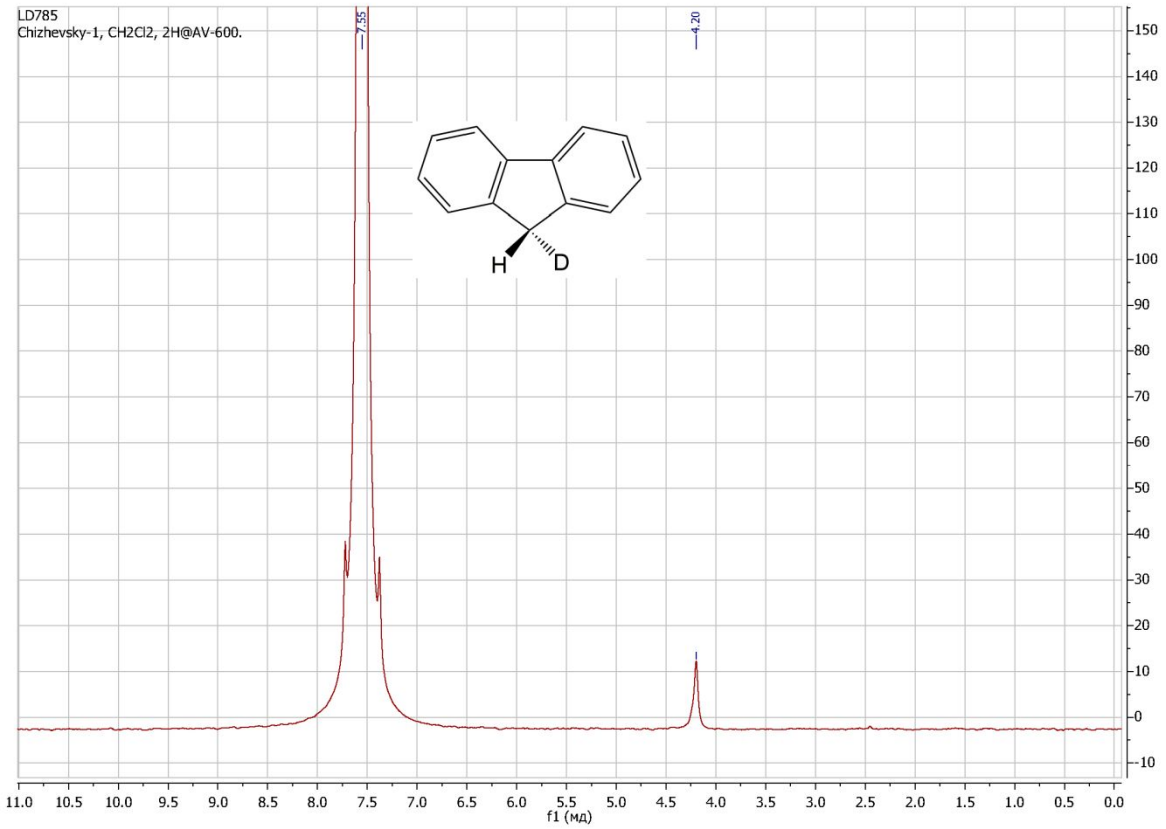


Figure S5. ^{1}H and ^{13}C NMR spectra of [(η^5-indenyl)Ir(η^6-fluorene)]$(SbF_6)_2$ ([**3b**]$(SbF_6)_2$) in CD_3NO_2.



3. ^{2}D NMR spectrum of 9-D-fluorene.

Figure S6. ^{2}D NMR spectrum of 9-D-fluorene in $CDCl_3$.



4. Reductive amination (experimental details and characterization of products)

Figure S7. Reductive amination with carbon monoxide as a reducing agent

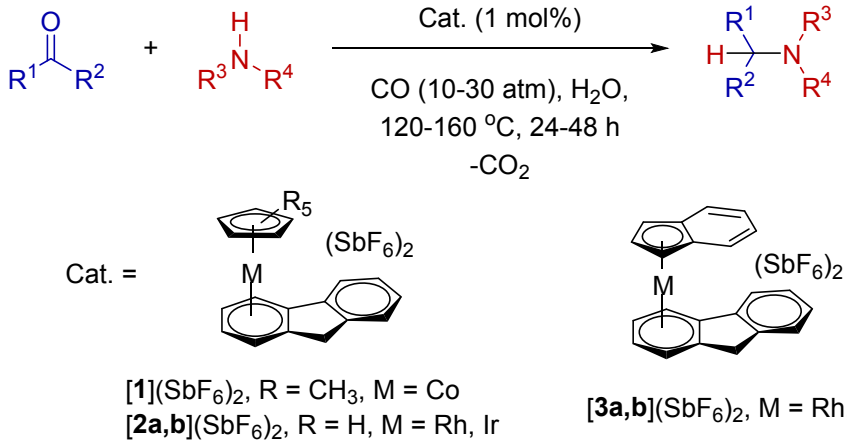
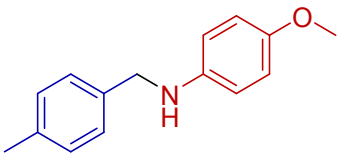


Table S2. Screening of fluorene catalysts

Catalyst	Temperature, °C	Yield of amine (**4**),[b] %	Yield of Schiff base(**5**),[b]%
[**1**](SbF$_6$)$_2$[c]	120	7	78
[**1**](SbF$_6$)$_2$[c]	160	12	79
[**2a**](SbF$_6$)$_2$[c]	120	29	63
[**2a**](SbF$_6$)$_2$[c]	160	55	33
[**3a**](SbF$_6$)$_2$[d]	160	35	38
[**2b**](SbF$_6$)$_2$[c]	120	32	57
[**2b**](SbF$_6$)$_2$[c]	160	88	3
[**3b**](SbF$_6$)$_2$[d]	160	77	15

[a] 22.7 – 27.0 mg (0.18 – 0.22 mmol) *p*-anisidine, 14.5 – 17.3 µL (0.12 – 0.15 mmol) *p*-tolylaldehyde, 1 mol % of catalyst, 133 – 158 µL of water; [b] Yields were determined by ^{1}H NMR with mesitylene as internal standard; [c]catalysts were stored at -20 °C in plastic vessels; [d]catalysts were freshly prepared.

4-methoxy-*N*-(4-methylbenzyl)aniline (4)

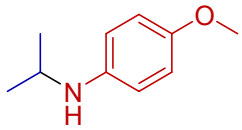


Iridium catalyst [**2b**](SbF$_6$)$_2$ (2.1 mg, 1 mol %, 2.33 µmol), *p*-anisidine (42.3 mg, 150 mol%, 0.35 mmol) and *p*-tolylaldehyde (27.6 µL, 100 mol %, 0.24 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 252 µL of water was added and the autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm CO. The reactor was placed into an oil bath preheated to 160 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (4×1 mL); the product was extracted with dichloromethane (2×1 mL), the combined organic layers were dried with sodium sulfate and filtered through a silica gel pad, solvent was removed on a rotary evaporator. 89% yield by ^{1}H NMR with mesitylene as internal standard. The residue was purified by preparative thin-layer chromatography (eluent: hexane : ethyl acetate = 5 : 1; R_f = 0.53) to afford 46 mg (87%) of the product as a yellowish solid. Melting point 67-69 °C is in agreement with the literature data (68-69 °C).[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, *J* 7.6 Hz, 2H), 7.16 (d, *J* 7.6 Hz, 2H), 6.79 (d, *J* 8.5 Hz, 2H), 6.61 (d, *J* 8.5 Hz, 2H), 4.24 (s, 2H), 3.75 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 142.5, 136.9, 136.6, 129.4, 127.7, 115.0, 114.2, 55.9, 49.1, 21.2
NMR data are in agreement with the literature data.[2]

_N_-isopropyl-4-methoxyaniline (6)



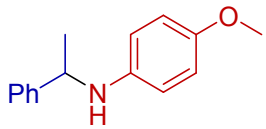
Iridium catalyst [**2b**]$(SbF_6)_2$ (3.8 mg, 1 mol %, 4.21 μmol), *p*-anisidine (51.9 mg, 100 mol%, 0.421 mmol) and acetone (62 μL, 200 mol %, 0.842 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 455 μL of water was added and the autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm CO. The reactor was placed into an oil bath preheated to 160 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (4×1 mL); the product was extracted with dichloromethane (2×1 mL), the combined organic layers were dried with sodium sulfate and filtered through a silica gel pad, solvent was removed on a rotary evaporator. 82% yield by ^{1}H NMR with mesitylene as internal standard. The residue was purified by preparative thin-layer chromatography (eluent: hexane : ethyl acetate = 3 : 1; R_f = 0.62) to afford 54.2 mg (78%) of the product as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.79 (d, *J* 8.7 Hz, 2H), 6.58 (d, *J* 8.7 Hz, 2H), 3.75 (s, 3H), 3.56 (sept, *J* 6.1 Hz, 1H), 3.13-3.05 (br s, 1H), 1.20 (d, *J* 6.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 141.8, 115.1, 115.0, 55.9, 45.4, 23.2.

NMR data are in agreement with the literature data.[2]

4-methoxy-_N_-(1-phenylethyl)aniline (7)



Iridium catalyst [**2b**]$(SbF_6)_2$ (3.51 mg, 1 mol %, 3.92 μmol), *p*-anisidine (72.5 mg, 150mol%, 0.588mmol) and acetophenone (45.7 μL, 100 mol %, 0.392mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 424 μL of water was added and the autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm CO. The reactor was placed into an oil bath preheated to 160 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (4×1 mL); the product was extracted with dichloromethane (2×1 mL), the combined organic layers were dried with sodium sulfate and filtered through a silica gel pad, solvent was removed on a rotary evaporator.
Six equal experiments were conducted to check reproducibility (TableS3).
According to Table S3 yields of **7** determined by ^{1}H NMR with mesitylene as internal standard varied from 37 to 76%.

Table S3. Reproducibility of preparation of **7**

Entry	Yield of **7**, [a] %
1	62
2	76
3	61
4	37
5	44
6	76

[a] Yields were determined by ^{1}H NMR.

The pure product was isolated in low yield by preparative thin-layer chromatography (eluent: hexane : ethyl acetate = 5 : 1; R_f = 0.5) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.30 (m, 4H), 7.22 (t, *J* 7.1 Hz, 1H), 6.69 (d, *J* 8.9 Hz, 2H), 6.47 (d, *J* 8.9 Hz, 2H), 4.41 (q, *J* 6.7 Hz, 1H), 3.69 (s, 3H), 1.50 (d, *J* 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 145.2, 141.0, 128.7, 127.0, 126.1, 115.1, 114.8, 55.8, 54.8, 25.0.

NMR data are in agreement with the literature data.[3]

Table S4. Investigation of pressure influence

Pressure, atm	Yield of **7**, [a] %
10	43
30	60
50	54

[a] Yields were determined by ^{1}H NMR; Loading catalyst - 1 mol %; ratio of carbonyl compound : amine = 1 : 1.5 equivalents; temperature - 160 °C, reaction time – 24

Table S5. Investigation of temperature influence

Temperature, °C	Pressure, atm	Yield of **7**, [a] %
160	30	60
180	30	61
160	50	54
180	50	51

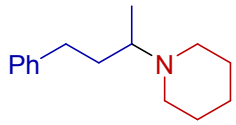
[a] Yields were determined by ^{1}H NMR; Loading catalyst - 1 mol %; ratio of carbonyl compound : amine = 1 : 1.5 equivalents; reaction time - 24 h;

Table S6. Investigation of time influence

Time, h	Yield of **7**, [a] %
24	60
48	59

[a] Yields were determined by ^{1}H NMR; Loading catalyst - 1 mol %; ratio of carbonyl compound : amine = 1 : 1.5 equivalents; temperature - 160 °C, pressure (CO) - 30 atm

1-(4-phenylbutal-2-yl)piperidine (8)



Iridium catalyst [**2b**]$(SbF_6)_2$ (3.1 mg, 1 mol %, 3.43 μmol), piperidine (50.8 μL, 150mol%, 0.515mmol) and benzylacetone (51.4 μL, 100 mol %, 0.343mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 371 μL of water was added and the autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 10 atm CO. The reactor was

placed into an oil bath preheated to 160°C. After 48 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (4×1 mL); the product was extracted with dichloromethane (2×1 mL), the combined organic layers were dried with sodium sulfate and filtered through a silica gel pad, solvent was removed on a rotary evaporator.
Four equal experiments were conducted to check reproducibility (Table S7).
According to Table S7 yields of **8** determined by ^{1}H NMR with mesitylene as internal standard varied from 63 to 88%.

Table S7. Reproducibility of preparation of **8**

Entry	Yield of **8**, [a] %
1	88
2	83
3	63
4	63

[a] Yields were determined by ^{1}H NMR.

The pure product was isolated in low yield by preparative thin-layer chromatography (eluent: hexane : iso-propanol = 10 : 1, R_f = 0.3) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2H), 7.21-7.16 (m, 3H), 2.71-2.56 (m, 3H), 2.50-2.48 (m, 2H), 2.42-2.40 (m, 2H), 1.92-1.83 (m, 1H), 1.60-1.56 (m, 5H), 1.45-1.41 (m, 2H), 1.01 (d, *J* 6.5 Hz, 3H).

^{13}C (101 MHz, $CDCl_3$) δ 143.0, 128.6, 128.4, 125.7, 59.1, 49.4, 35.6, 33.4, 26.6, 25.1, 13.9.

Table S8. Investigation of pressure influence

Pressure, atm	Yield of **8**, [a] %
10	61
30	61
50	73

[a] Yields were determined by ^{1}H NMR; Loading catalyst - 1 mol %; ratio of carbonyl compound : amine = 1 : 1.5 equivalents; temperature - 160 °C, reaction time - 24 h

Table S9. Investigation of temperature influence

Temperature, °C	Pressure, atm	Yield of **8**, [a] %
160	30	61
180	30	63
160	50	73
180	50	70

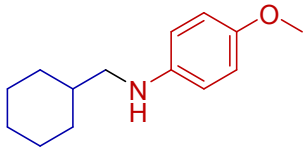
[a] Yields were determined by ^{1}H NMR; Loading catalyst - 1 mol %; ratio of carbonyl compound : amine = 1 : 1.5 equivalents; reaction time - 24 h

Table S10. Investigation of time influence

Pressure, atm	Time, h	Yield of **8**, [a] %
10	24	61
10	48	92
30	24	61
30	48	63

[a] Yields were determined by ^{1}H NMR; Loading catalyst - 1 mol %; ratio of carbonyl compound : amine = 1 : 1.5 equivalents; temperature - 160 °C, reaction time - 24 h

***N*-(cyclohexylmethyl)-4-methoxyaniline (9)**



Iridium catalyst [**2b**]$(SbF_6)_2$ (3.43 mg, 1 mol %, 3.83 μmol), *p*-anisidine (70.8 mg, 150 mol%, 0.575 mmol) and cyclohexanecaroxaldehyde (46.4 μL, 100 mol %, 0.383 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 414 μL of water was added and the autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm CO. The reactor was placed into an oil bath preheated to 160 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (4×1 mL); the product was extracted with dichloromethane (2×1 mL), the combined organic layers were dried with sodium sulfate and filtered through a silica gel pad, solvent was removed on a rotary evaporator.
Two equal experiments were conducted to check reproducibility (Table S11).
According to Table S11 yields of **9** determined by ^{1}H NMR with mesitylene as internal standard varied from 60 to 63%.

Table S11. Reproducibility of preparation of **9**

Entry	Yield of **9**,[a] %
1	63
2	60

[a] Yields were determined by ^{1}H NMR.

The pure product was isolated in low yield by preparative thin-layer chromatography(eluent: toluene : hexane : ethyl acetate : triethylamine = 4 : 16 : 4: 0.1; R_f = 0.62) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (d, *J* 8.8 Hz, 2H), 6.57 (d, *J* 8.8 Hz, 2H), 3.75 (s, 3H), 3.48-3.09 (br s, 1H), 2.91 (d, *J* 6.6 Hz, 2H), 1.82 (d, *J* 12.5 Hz, 2H), 1.76-1.67 (m, 3H), 1.60-1.52 (m, 1H), 1.31-1.17 (m, 3H), 1.02-0.97 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 143.1, 115.0, 114.0, 56.0, 51.8, 37.7, 31.5, 26.7, 26.1.

NMR data are in agreement with the literature data.[4]

Table S12. Investigation of pressure influence

Pressure (CO), atm	Yield of **9**,[a] %
5	60
10	67
30	60
50	43

[a] Yields were determined by ^{1}H NMR; Loading catalyst - 1 mol %; ratio of carbonyl compound : amine = 1 : 1.5 equivalents; temperature - 160 °C, reaction time - 24 h

Table S13. Investigation of temperature influence

Temperature, °C	Pressure, atm	Yield of **9**,[a] %
160	30	60
180	30	50
160	50	43
180	50	55
140	10	35

160	10	67

[a] Yields were determined by ^{1}H NMR; Loading catalyst - 1 mol %; ratio of carbonyl compound : amine = 1 : 1.5 equivalents; reaction time - 24 h

Table S14. Investigation of time influence

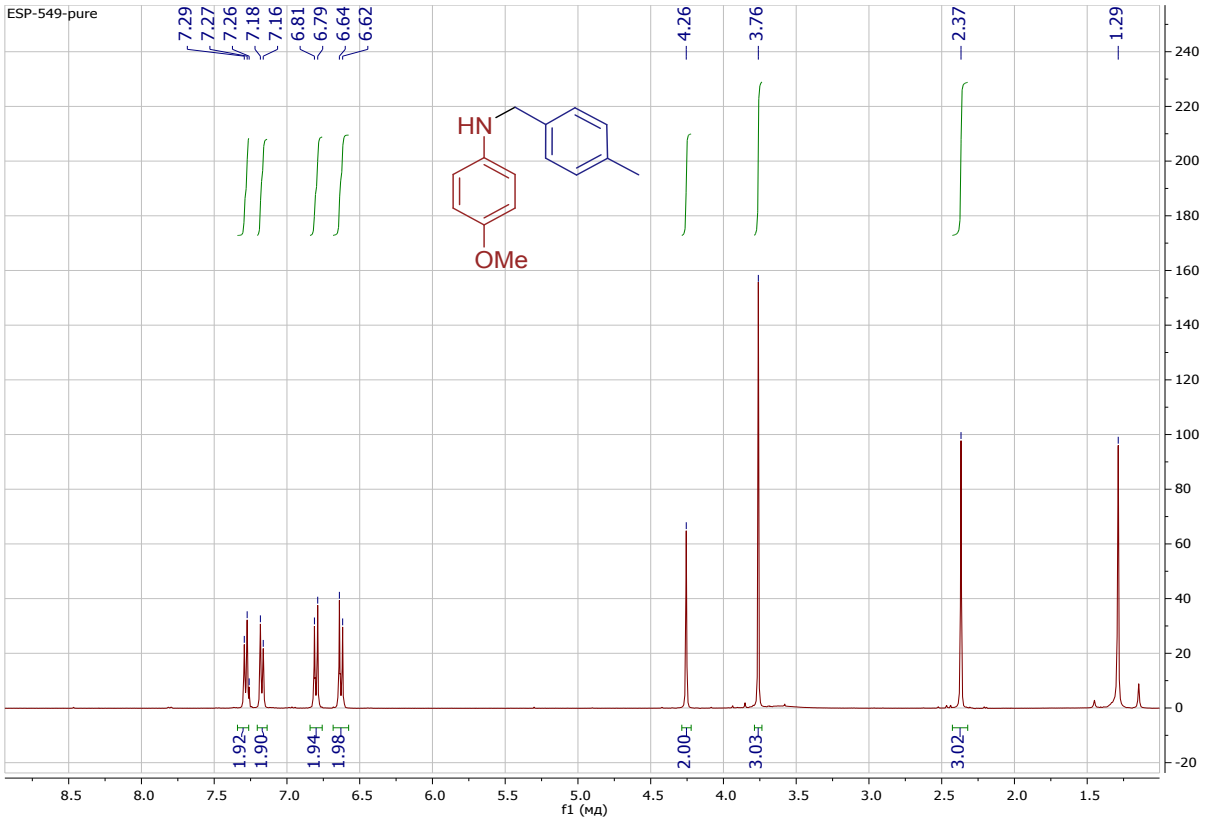
Pressure, atm	Time, h	Yield of **9**,[a] %
5	24	60
5	48	35
10	24	67
10	48	49
30	24	60
30	48	39

[a] Yields were determined by ^{1}H NMR; Loading catalyst - 1 mol %; ratio of carbonyl compound : amine = 1 : 1.5 equivalents; temperature - 160 °C

[1] P. S. Reddy, S. Kanjilal, S. Sunitha, R. B. N. Prasad, Tetrahedron Lett. 48 (2007) 8807.
[2] P. N. Kolesnikov, N. Z. Yagafarov, D. L. Usanov, V. I. Maleev, D. Chusov, Org. Lett. 17 (2015), 173.
[3] S. A. Runikhina, M. A. Arsenov, V. B. Kharitonov, E. R. Sovdagarova, O. Chusova, Y. V. Nelyubina, G. L. Denisov, D. L. Usanov, D. Chusov, D. A. Loginov, J. Organomet. Chem. 867 (2018) 106-112.
[4] (a) D. Chusov, B. List, Angew. Chem. Int. Ed. 53 (2014) 5199-5201; (b) O. S. Nayal, M. S. Thakur, V. Bhatt, M. Kumar, N. Kumar, B. Singh, U. Sharma, Chem. Commun., 52 (2016) 9648-9651.
[5] Podyacheva, E.; Afanasyev, O. I.; Tsygankov, A. A.; Makarova, M.; Chusov, D. Hitchhiker's Guide to Reductive Amination. *Synthesis*, **2019**, DOI: 10.1055/s-0037-1611788.

5. ^{1}H NMR and ^{13}C NMR spectra of the products of reductive amination

Figure S8. ^{1}H and ^{13}C NMR spectra of 4-methoxy-*N*-(4-methylbenzyl)aniline (**4**)



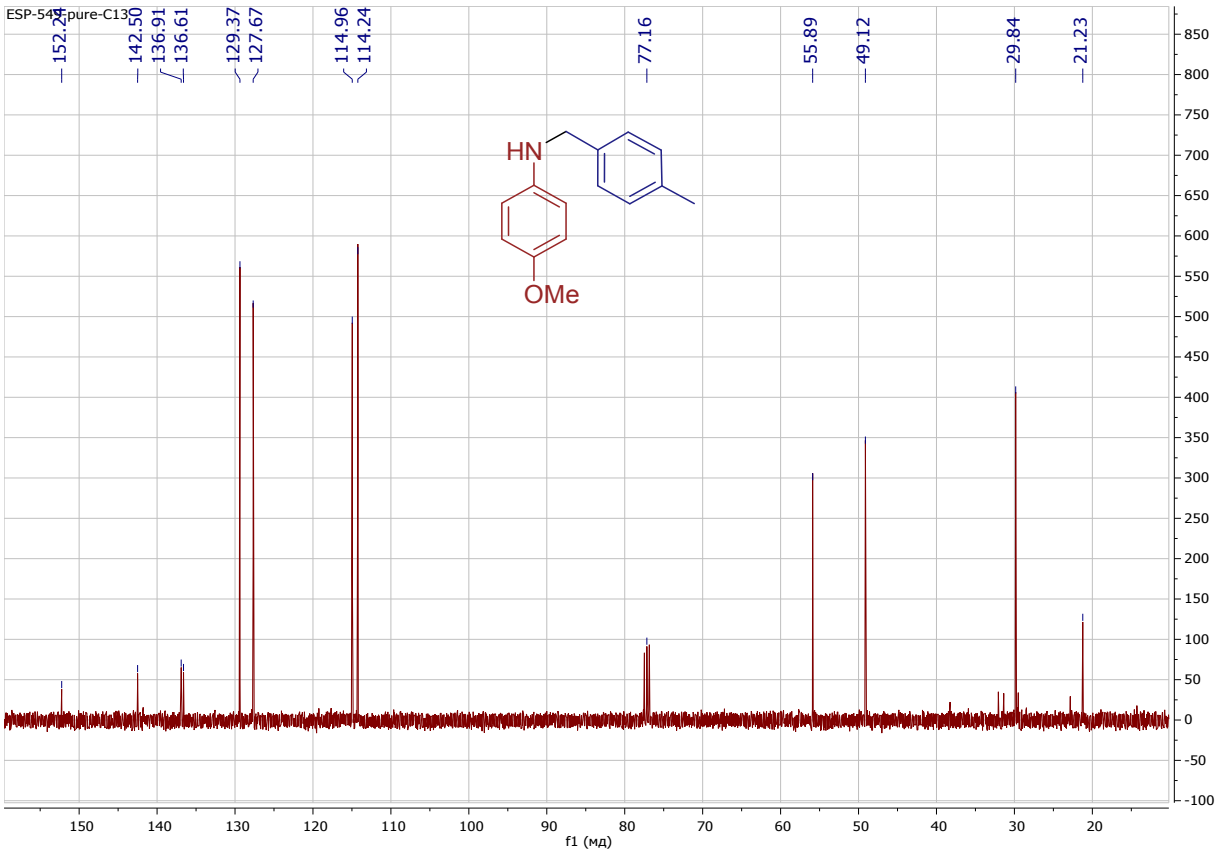
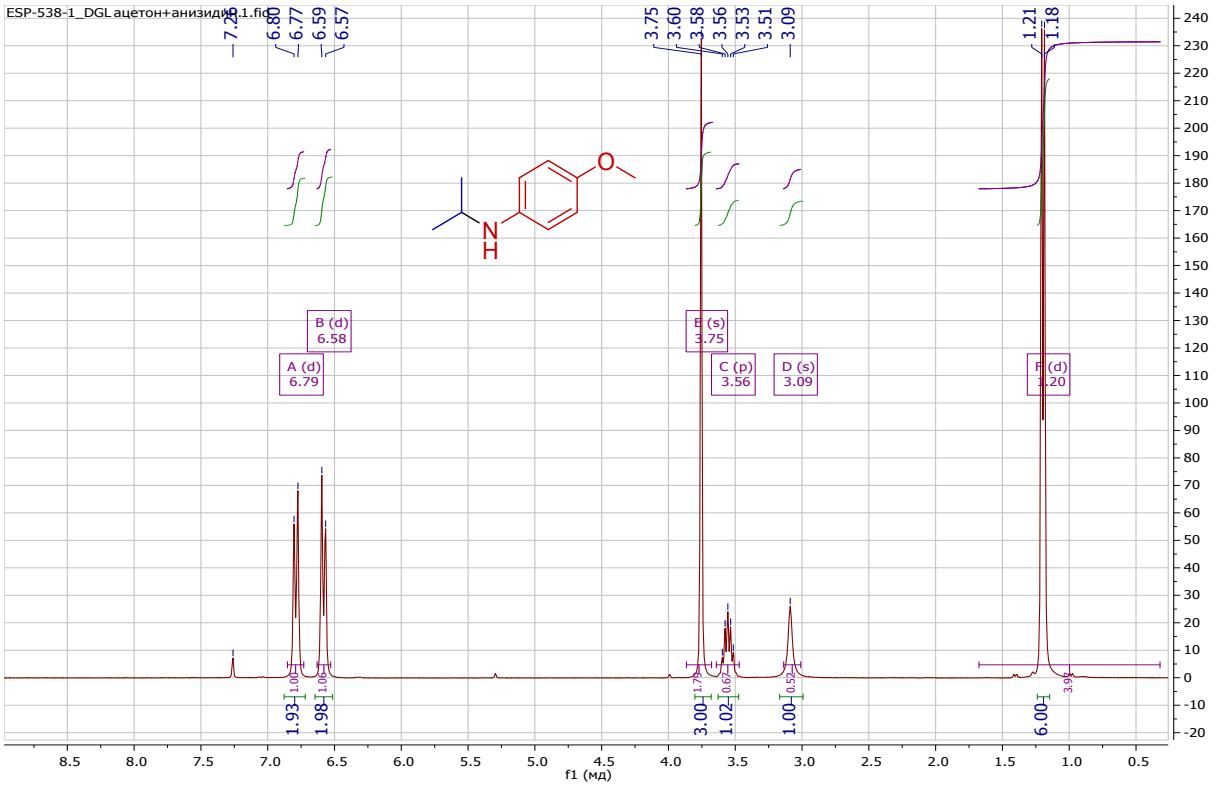


Figure S9. ^{1}H and ^{13}C NMR spectra of *N*-isopropyl-4-methoxyaniline (**6**)



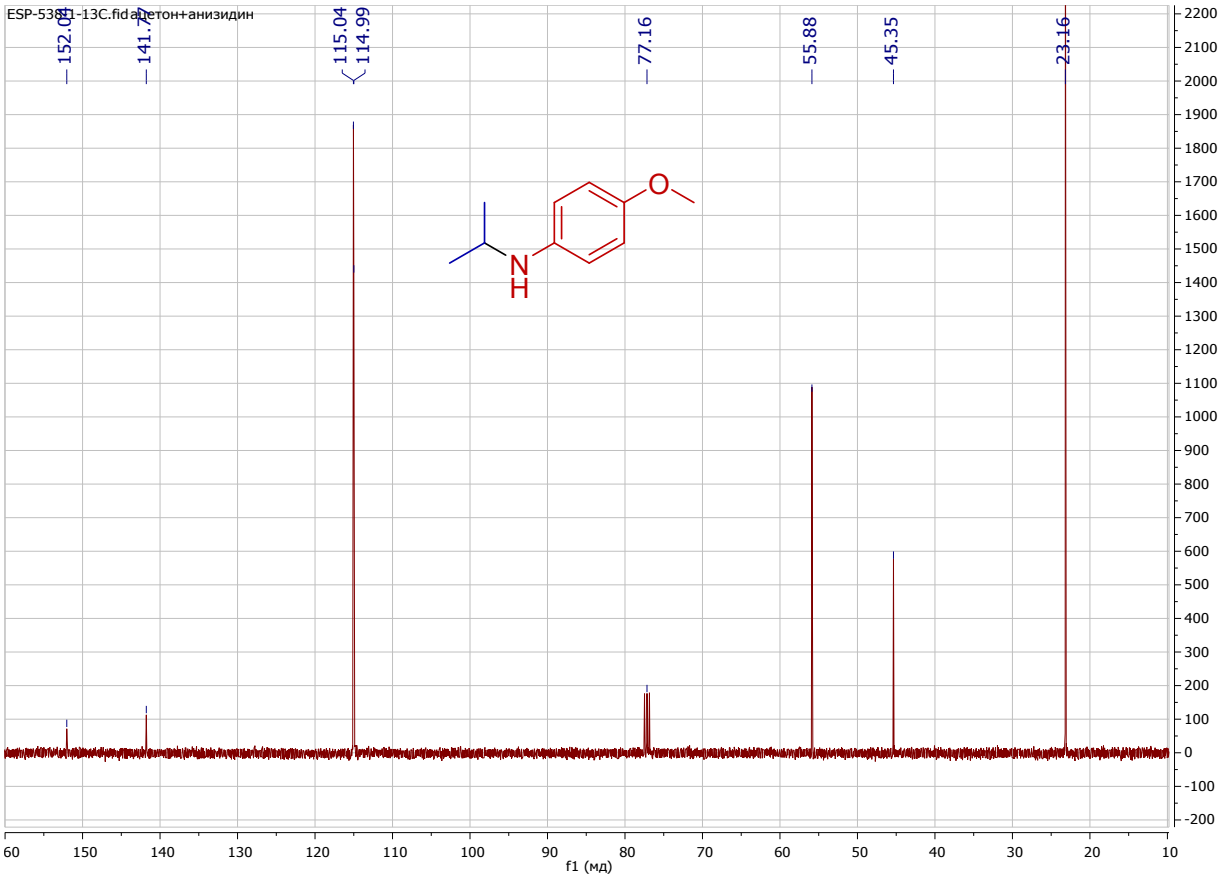
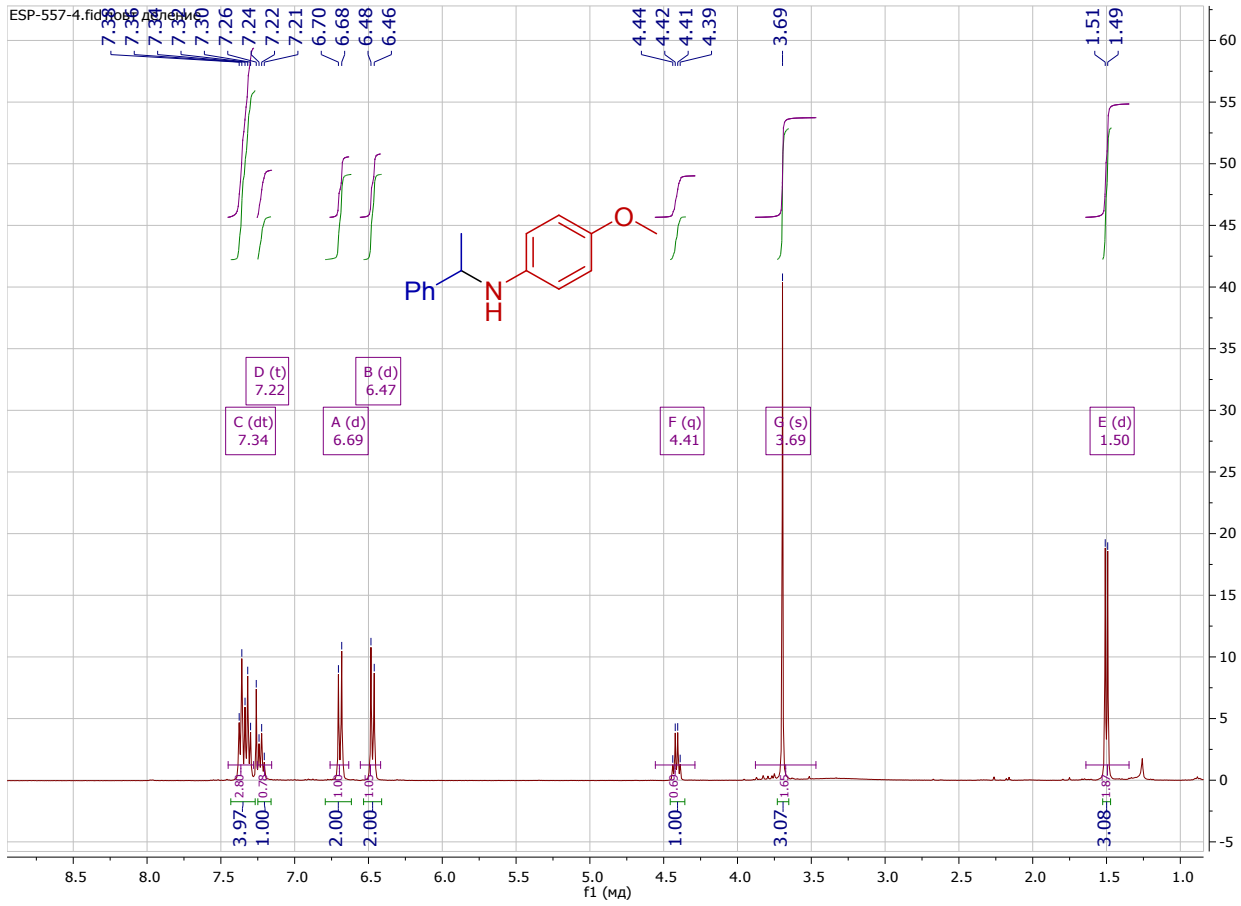


Figure S10. ^{1}H and ^{13}C NMR spectra of 4-methoxy-*N*-(1-phenylethyl)aniline (**7**)



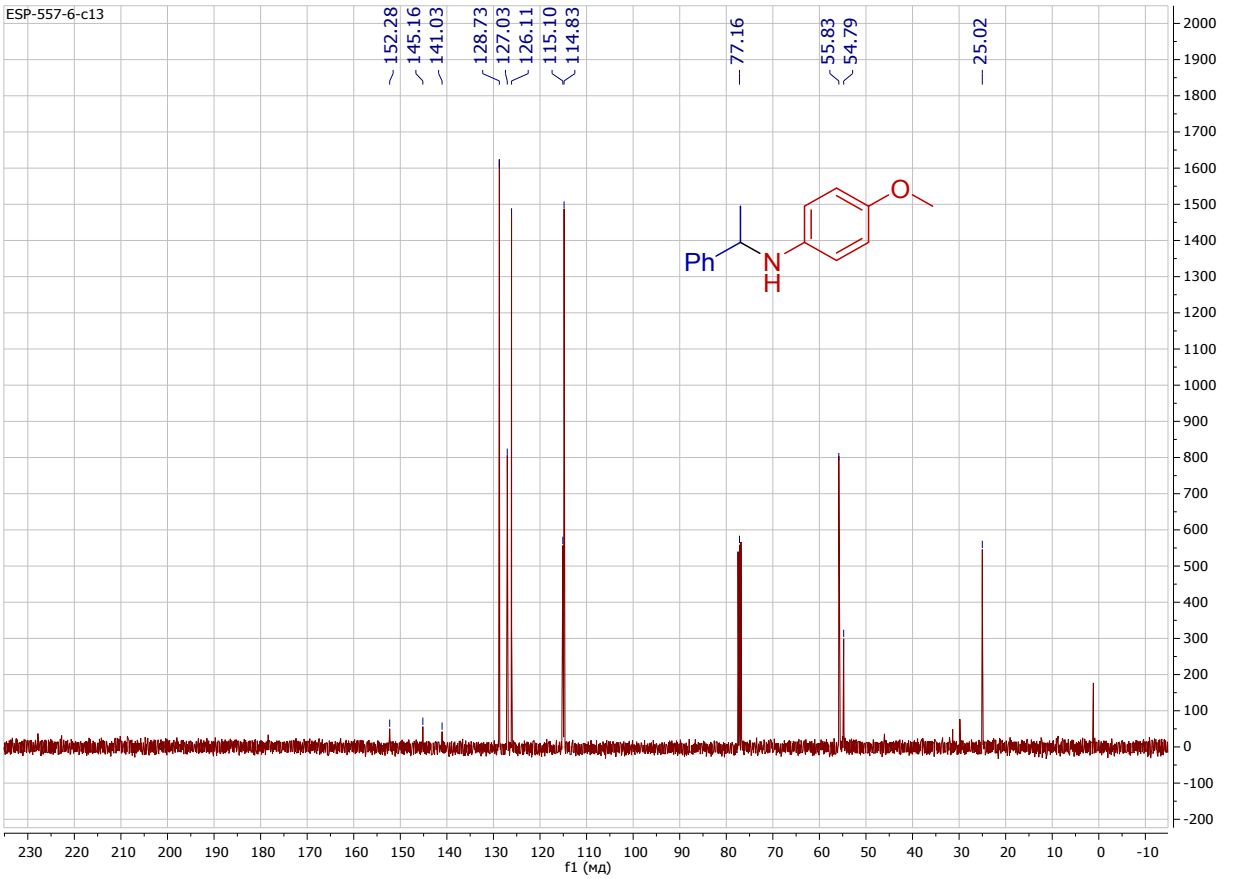
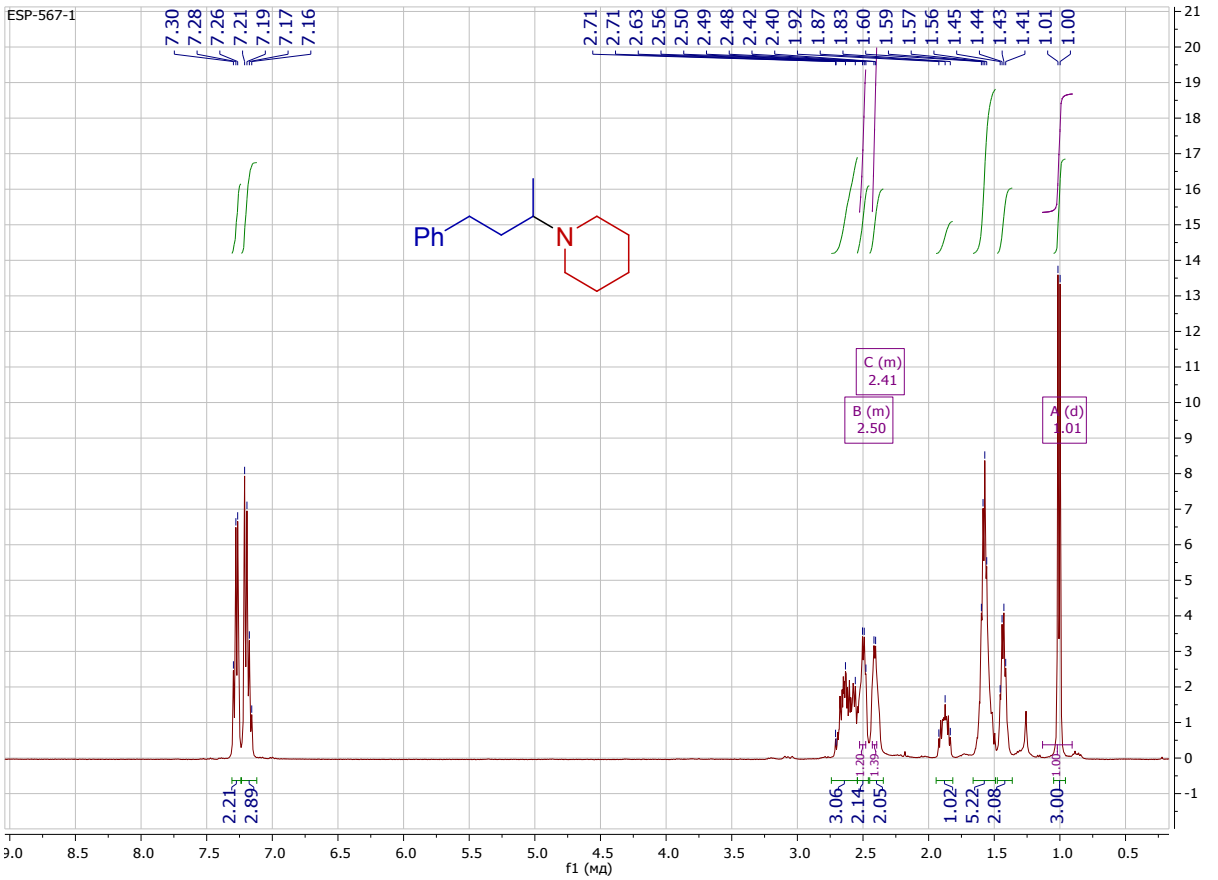


Figure S11. ^{1}H and ^{13}C NMR spectra of 1-(4-phenylbutal-2-yl)piperidine (**8**)



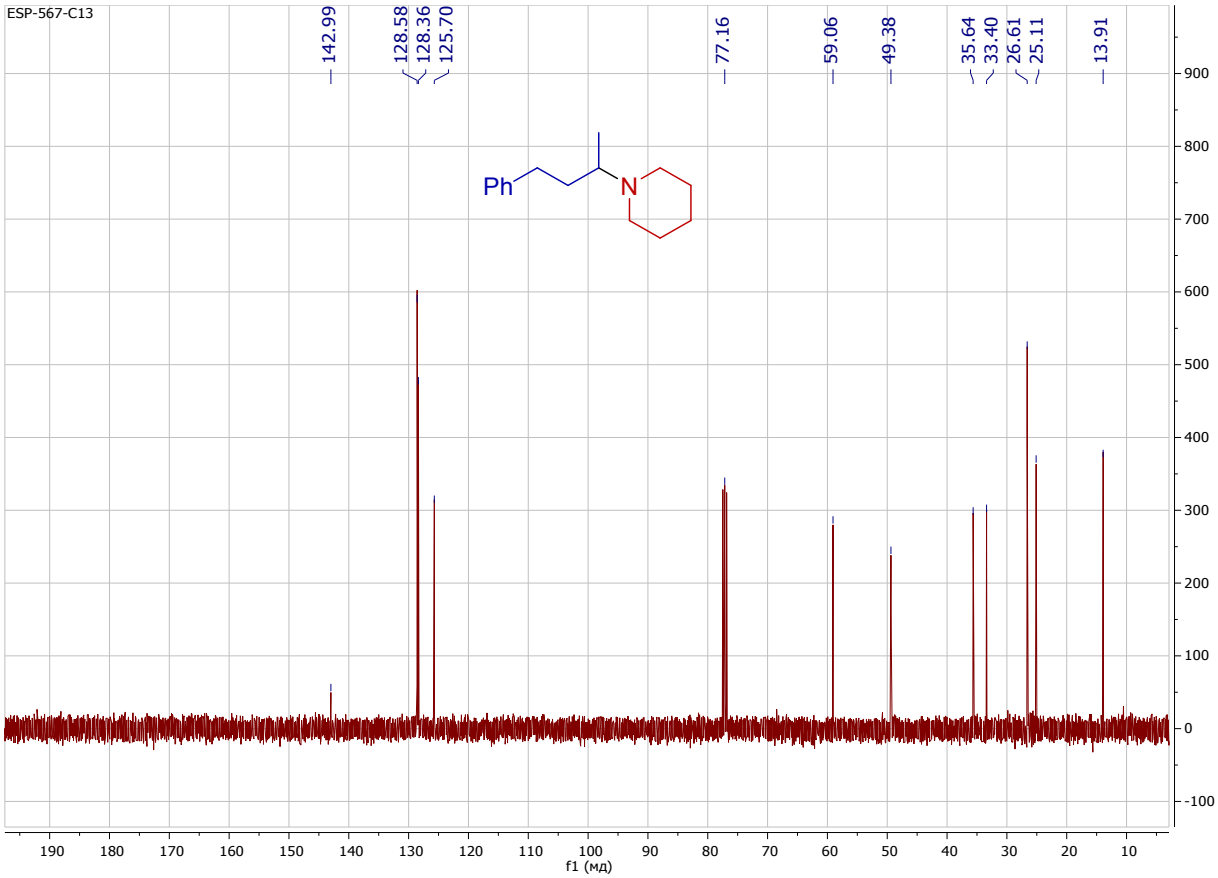


Figure S12. ^{1}H and ^{13}C NMR spectra of *N*-(cyclohexylmethyl)-4-methoxyaniline (**9**)