Electronic Supplementary Information (ESI)

Preparation of carbon-based AuAg alloy nanoparticles by using the heterometallic [Au_4Ag_4] cluster for efficient oxidative coupling of anilines†

Bin-Bin Gao,[a] Min Zhang,[a] Xu-Ran Chen,[a] Da-Liang Zhu,[a] Hong Yu,*[a] Wen-Hua Zhang*[a] and Jian-Ping Lang*[ab]

[a] *College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China*

[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P. R. China*

Contents

Table S1 Crystal data and structure refinement parameters for **1** and **2**·7CH_3CN.

Compound	**1**	**2**·7CH_3CN
formula	$C_{26}H_{27}AuF_6N_2P_2S$	$C_{126}H_{138}Ag_4Au_4F_{48}N_{19}P_{12}S_4$
fw	772.46	4549.77
cryst. syst.	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a/Å	8.6627(6)	18.0668(8)
b/Å	10.6870(8)	18.0736(6)
c/Å	15.6440(7)	26.7497(8)
α/deg	86.714(5)	104.108(3)
β/deg	87.918(4)	95.390(3)
γ/deg	75.153(6)	99.338(3)
V/Å^3	1397.29(16)	8277.2(5)
D_c/(g cm^{-3})	1.836	1.826
Z	2	2
μ(Mo–Kα)/mm^{-1}	5.513	4.264
F(000)	752	4414
total reflns	14375	86420
unique reflns	7230	29113
no. of observations	6355	19097
no. of param	343	1970
R_{int}	0.0302	0.1207
R_1[a]	0.0340	0.0987
wR_2[b]	0.0743	0.2427
GOF[c]	1.048	1.057

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$. [c] GOF = $\{\Sigma w((F_o^2-F_c^2)^2)/(n-p)\}^{1/2}$, where n = number of reflections and p = total number of parameters refined.

Table S2 Selected bond distances (Å) and angles (°) for compound **1**.

Au(1)-P(1)	2.2540(10)	N(1)-C(4)	1.485(6)
Au(1)-S(1)	2.2890(11)	N(1)-C(8)	1.497(6)
P(1)-C(10)	1.807(4)	N(1)-C(9)	1.498(6)
P(1)-C(21)	1.815(4)	N(1)-C(7)	1.505(6)
P(1)-C(15)	1.820(4)	N(2)-C(10)	1.360(6)
S(1)-C(1)	1.757(5)	N(2)-C(14)	1.374(9)
P(1)-Au(1)-S(1)	175.17(4)	C(4)-N(1)-C(9)	111.5(4)
C(10)-P(1)-C(21)	105.13(19)	C(8)-N(1)-C(9)	108.9(4)
C(10)-P(1)-C(15)	105.54(18)	C(4)-N(1)-C(7)	112.7(4)
C(21)-P(1)-C(15)	106.82(18)	C(8)-N(1)-C(7)	106.8(4)
C(10)-P(1)-Au(1)	113.88(14)	C(9)-N(1)-C(7)	107.5(5)
C(21)-P(1)-Au(1)	116.68(13)	C(10)-N(2)-C(14)	116.6(5)
C(15)-P(1)-Au(1)	108.05(13)	C(6)-C(1)-S(1)	124.0(3)
C(1)-S(1)-Au(1)	102.76(13)	C(2)-C(1)-S(1)	119.2(3)
C(4)-N(1)-C(8)	109.3(3)		

Table S3 Selected bond distances (Å) and angles (°) for compound **2**.

Au(1)-P(3)	2.259(4)	Ag(5)-S(2)	2.487(4)
Au(1)-S(3)	2.325(4)	Ag(5)-N(11)	2.502(15)
Au(1)-Au(4)	2.9835(8)	Ag(5)-S(3)	2.647(4)
Au(1)-Ag(8)	3.0711(13)	Ag(6)-N(10)	2.296(19)
Au(2)-P(2)	2.258(4)	Ag(6)-N(4)	2.366(16)
Au(2)-S(2)	2.320(4)	Ag(6)-S(3)	2.544(4)
Au(2)-Ag(7)	3.0163(14)	Ag(6)-S(1)	2.646(4)
Au(2)-Au(3)	3.1950(8)	Ag(7)-N(2)	2.309(14)
Au(3)-P(1)	2.266(4)	Ag(7)-S(1)	2.485(4)
Au(3)-S(1)	2.328(4)	Ag(7)-N(12)	2.543(15)
Au(3)-Ag(5)	3.0567(14)	Ag(7)-S(4)	2.569(4)
Au(4)-P(4)	2.281(4)	Ag(8)-N(3)	2.340(13)
Au(4)-S(4)	2.337(4)	Ag(8)-N(9)	2.384(18)
Au(4)-Ag(6)	3.1203(14)	Ag(8)-S(4)	2.575(4)
Ag(5)-N(1)	2.299(13)	Ag(8)-S(2)	2.614(4)
P(3)-Au(1)-S(3)	169.18(14)	N(4)-Ag(6)-S(1)	103.5(4)
P(3)-Au(1)-Au(4)	98.44(10)	S(3)-Ag(6)-S(1)	91.51(12)
S(3)-Au(1)-Au(4)	90.07(10)	N(10)-Ag(6)-Au(4)	152.2(6)
P(3)-Au(1)-Ag(8)	75.75(11)	N(4)-Ag(6)-Au(4)	74.3(4)
S(3)-Au(1)-Ag(8)	111.94(10)	S(3)-Ag(6)-Au(4)	83.19(9)
Au(4)-Au(1)-Ag(8)	84.46(3)	S(1)-Ag(6)-Au(4)	93.43(9)
P(2)-Au(2)-S(2)	171.01(13)	N(2)-Ag(7)-S(1))	133.9(3)

P(2)-Au(2)-Ag(7)	80.51(10)	N(2)-Ag(7)-N(12)	91.1(5)
S(2)-Au(2)-Ag(7)	106.32(10)	S(1)-Ag(7)-N(12)	99.4(3)
P(2)-Au(2)-Au(3)	103.36(10)	N(2)-Ag(7)-S(4)	114.9(3)
S(2)-Au(2)-Au(3)	83.56(9)	S(1)-Ag(7)-S(4)	108.07(13)
Ag(7)-Au(2)-Au(3)	82.68(3)	N(12)-Ag(7)-S(4)	97.7(4)
P(1)-Au(3)-S(1)	171.93(14)	N(2)-Ag(7)-Au(2)	84.1(4)
P(1)-Au(3)-Ag(5)	78.24(11)	S(1)-Ag(7)-Au(2)	80.87(9)
S(1)-Au(3)-Ag(5)	107.58(10)	N(12)-Ag(7)-Au(2)	173.4(4)
P(1)-Au(3)-Au(2)	107.47(10)	S(4)-Ag(7)-Au(2)	88.45(9)
S(1)-Au(3)-Au(2)	79.43(9)	N(3)-Ag(8)-N(9)	87.7(6)
Ag(5)-Au(3)-Au(2)	79.60(3)	N(3)-Ag(8)-S(4)	145.2(3)
P(4)-Au(4)-S(4)	173.10(15)	N(9)-Ag(8)-S(4)	108.8(5)
P(4)-Au(4)-Au(1)	103.95(11)	N(3)-Ag(8)-S(2)	111.6(3)
S(4)-Au(4)-Au(1)	82.96(9)	N(9)-Ag(8)-S(2)	105.9(6)
P(4)-Au(4)-Ag(6)	74.42(12)	S(4)-Ag(8)-S(2)	93.58(12)
S(4)-Au(4)-Ag(6)	107.33(9)	N(3)-Ag(8)-Au(1)	77.8(3)
Au(1)-Au(4)-Ag(6)	79.06(3)	N(9)-Ag(8)-Au(1)	160.0(5)
N(1)-Ag(5)-S(2)	145.3(4)	S(4)-Ag(8)-Au(1)	77.55(9)
N(1)-Ag(5)-N(11)	92.8(5)	S(2)-Ag(8)-Au(1)	92.34(9)
S(2)-Ag(5)-N(11)	98.0(4)	Au(3)-S(1)-Ag(7)	117.01(14)
N(1)-Ag(5)-S(3)	103.2(4)	Au(3)-S(1)-Ag(6)	109.42(14)
S(2)-Ag(5)-S(3)	107.07(13)	Ag(7)-S(1)-Ag(6)	107.82(15)
N(11)-Ag(5)-S(3)	100.6(4)	Au(2)-S(2)-Ag(5)	112.76(14)
N(1)-Ag(5)-Au(3)	83.6(3)	Au(2)-S(2)-Ag(8)	112.58(15)
S(2)-Ag(5)-Au(3)	83.96(9)	Ag(5)-S(2)-Ag(8)	108.77(15)
N(11)-Ag(5)-Au(3)	175.9(4)	Au(1)-S(3)-Ag(6)	105.82(16)
S(3)-Ag(5)-Au(3)	82.20(9)	Au(1)-S(3)-Ag(5)	95.60(13)
N(10)-Ag(6)-N(4)	83.4(7)	Ag(6)-S(3)-Ag(5)	129.93(16)
N(10)-Ag(6)-S(3)	113.0(5)	Au(4)-S(4)-Ag(7)	98.11(13)
N(4)-Ag(6)-S(3)	153.5(4)	Au(4)-S(4)-Ag(8)	111.81(15)
N(10)-Ag(6)-S(1)	108.0(6)	Ag(7)-S(4)-Ag(8)	125.64(16)

Table S4 Average crystallite size calculated for each NPs synthesized at different temperature by using Scherrer formula on the most dominating (111) diffraction peak.

Nanoalloys	d-values of different (*hkl*) planes					Average Crystallite size (nm)
	<111>	<200>	<220>	<311>	<222>	
AuAg/C-450	2.3817	2.0591	1.4511	1.2359	1.1823	7.4
AuAg/C-500	2.3817	2.0591	1.4511	1.2359	1.1825	8.6
AuAg/C-550	2.3816	2.0591	1.4504	1.2357	1.1827	6.5
AuAg/C-600	2.3817	2.0600	1.4508	1.2357	1.1820	6.2

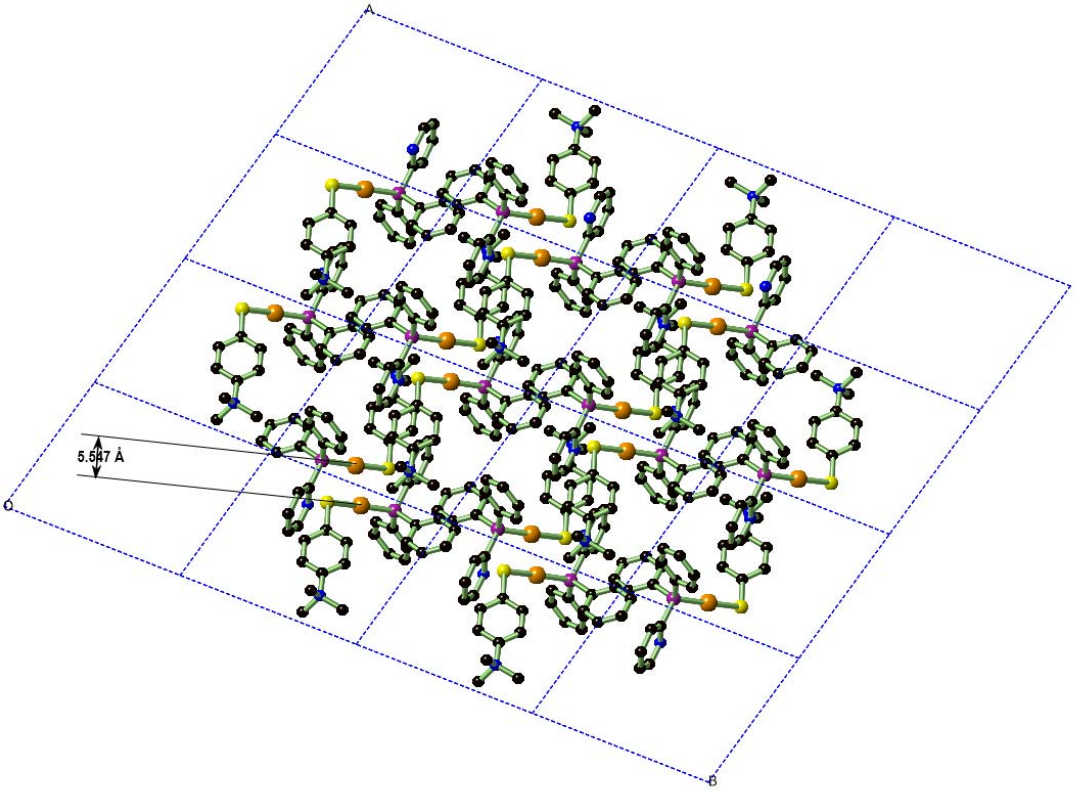


Fig. S1 Crystal packing diagram of compound **1** with PF_6^- anion and H atoms omitted and the shortest bond contact of Au(I)···Au(I) (5.547 Å). Color codes: Au (orange), S (yellow), P (purple), N (blue), C (black).

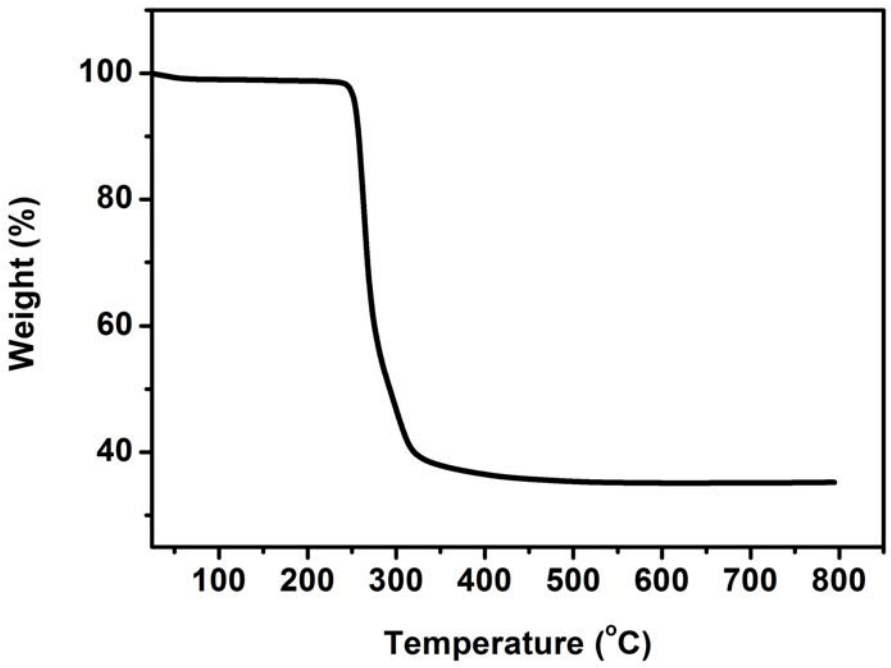


Fig. S2 TGA curve of compound **2**.

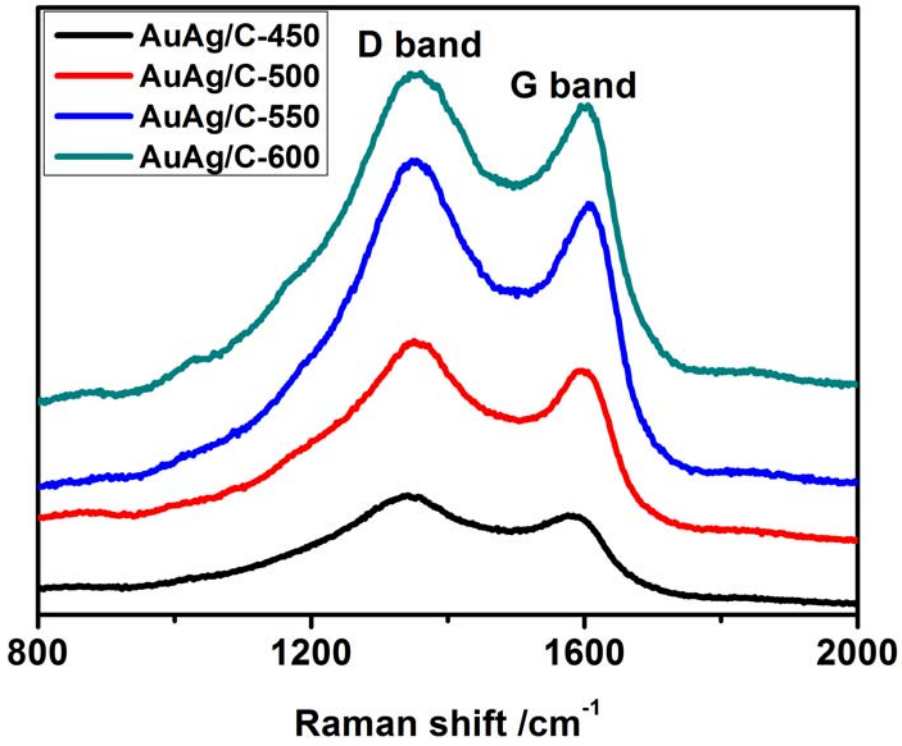


Fig. S3 Raman spectra of AuAg/C-450, AuAg/C-500, AuAg/C-550, and AuAg/C-600.

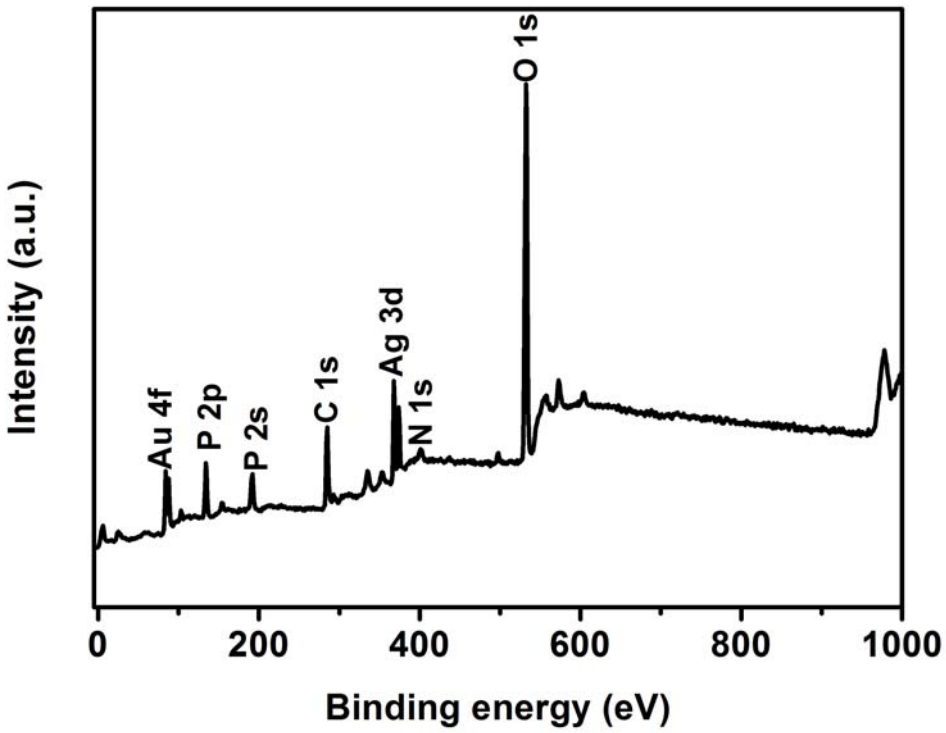


Fig. S4 XPS spectrum of AuAg/C-450.

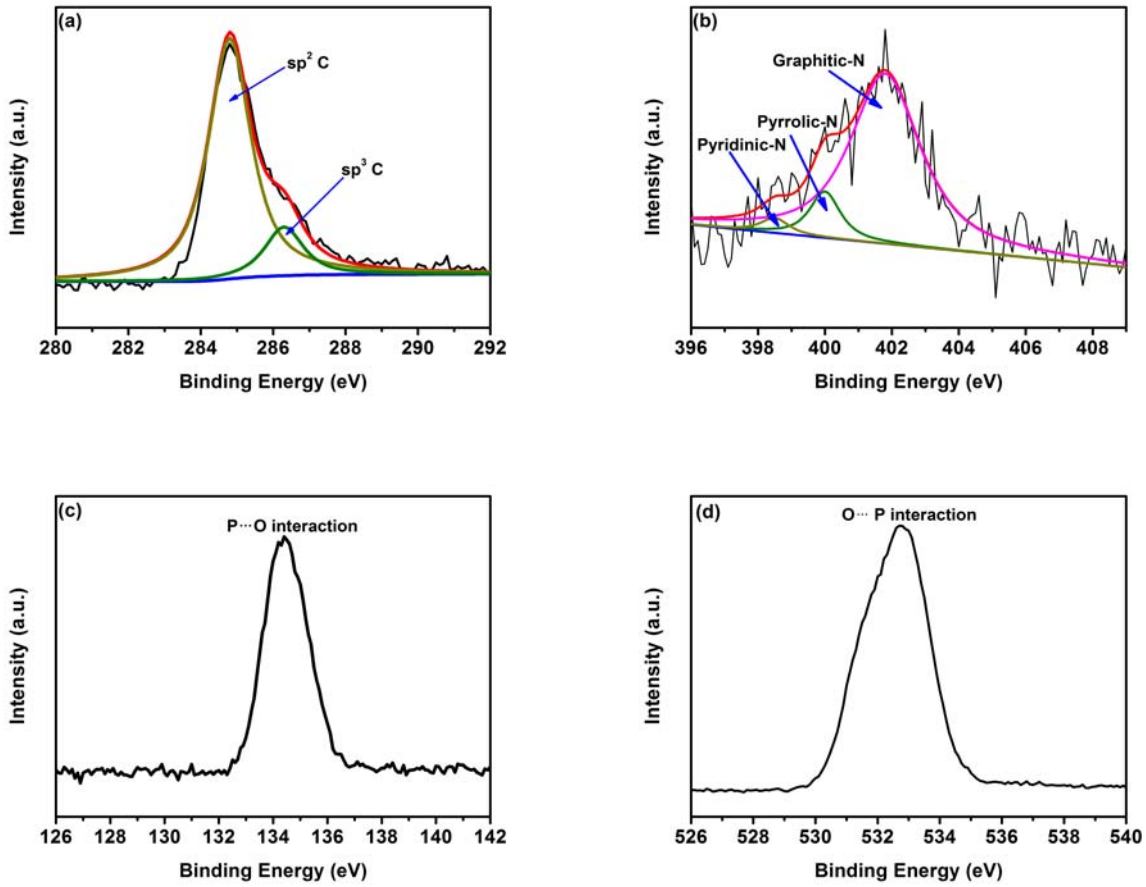


Fig. S5 High resolution XPS spectra of C 1s (a), N 1s (b), P 2p (c) and O 1s (d) of AuAg/C-450.

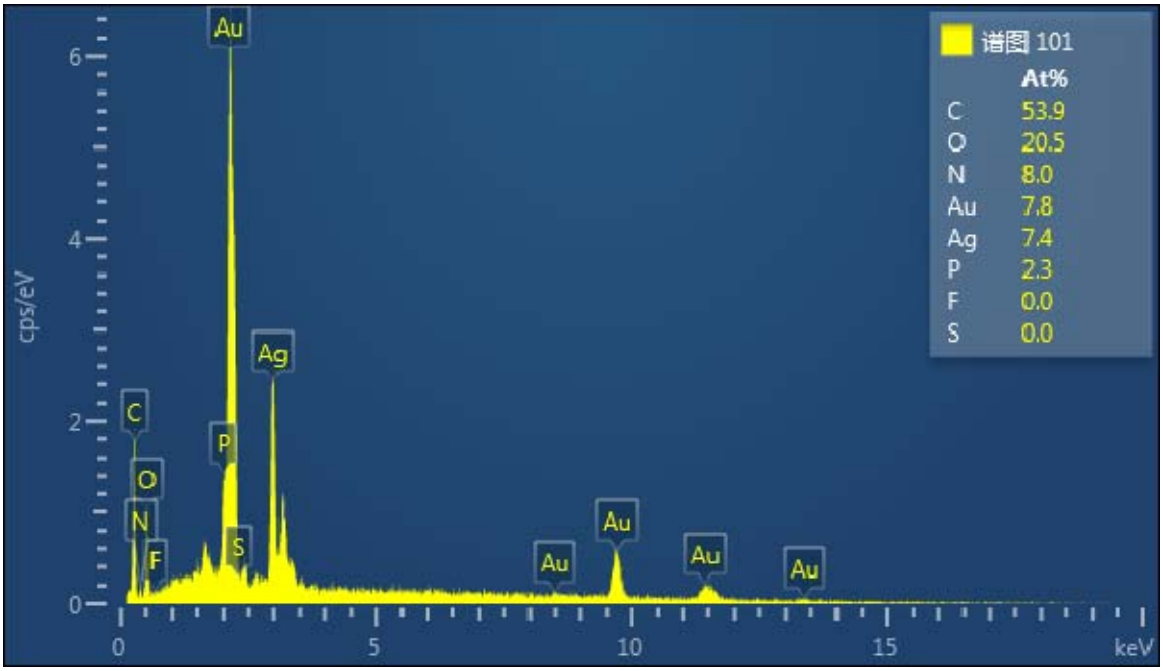


Fig. S6 The EDX spectrum of AuAg/C-450.

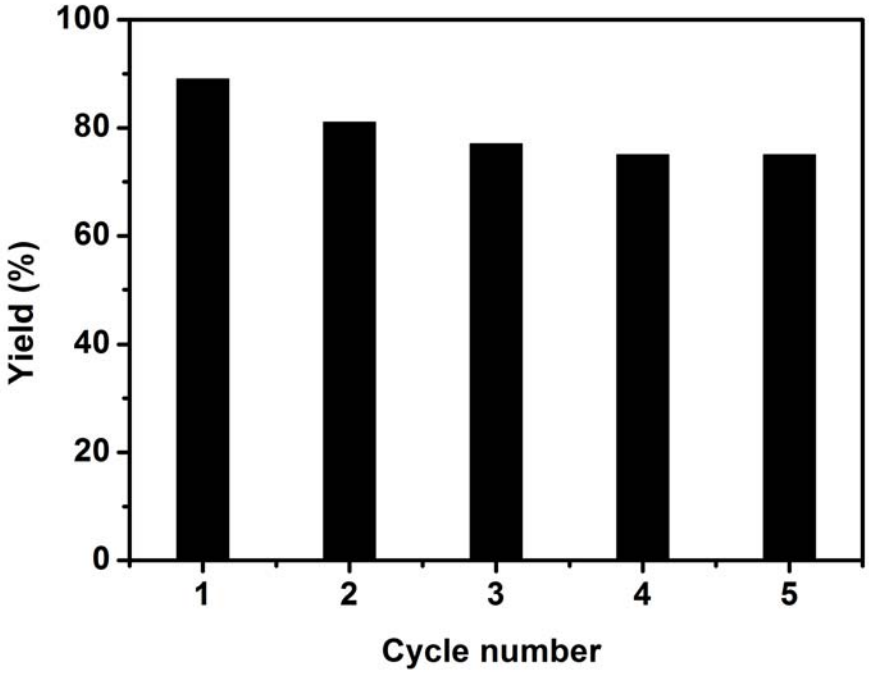


Fig. S7 The reusability of AuAg/C-450 as a catalyst for aerobic oxidative coupling of anilines.

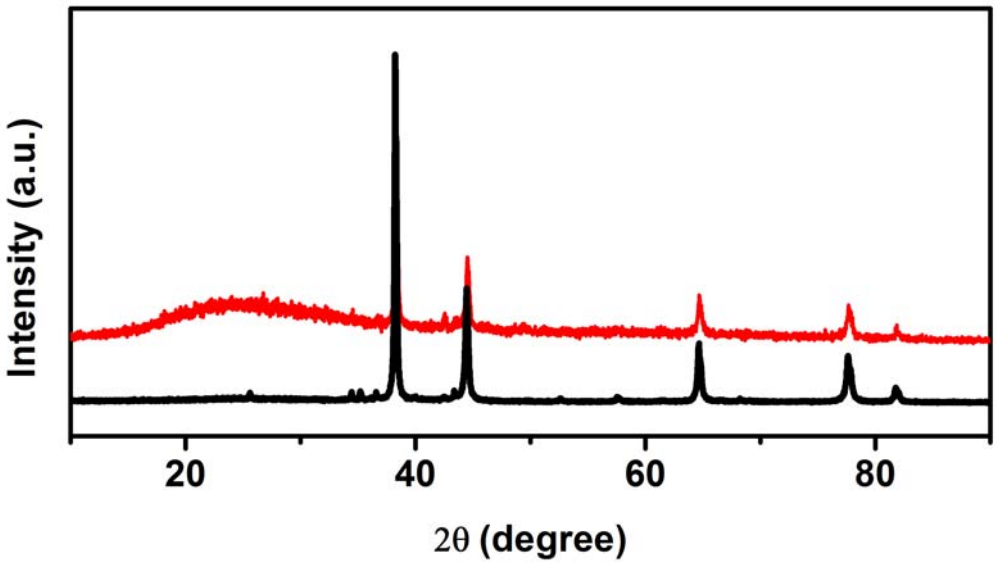


Fig. S8 The PXRD patterns of pure AuAg/C-450 (black line) and the recycled catalyst sample (red line).

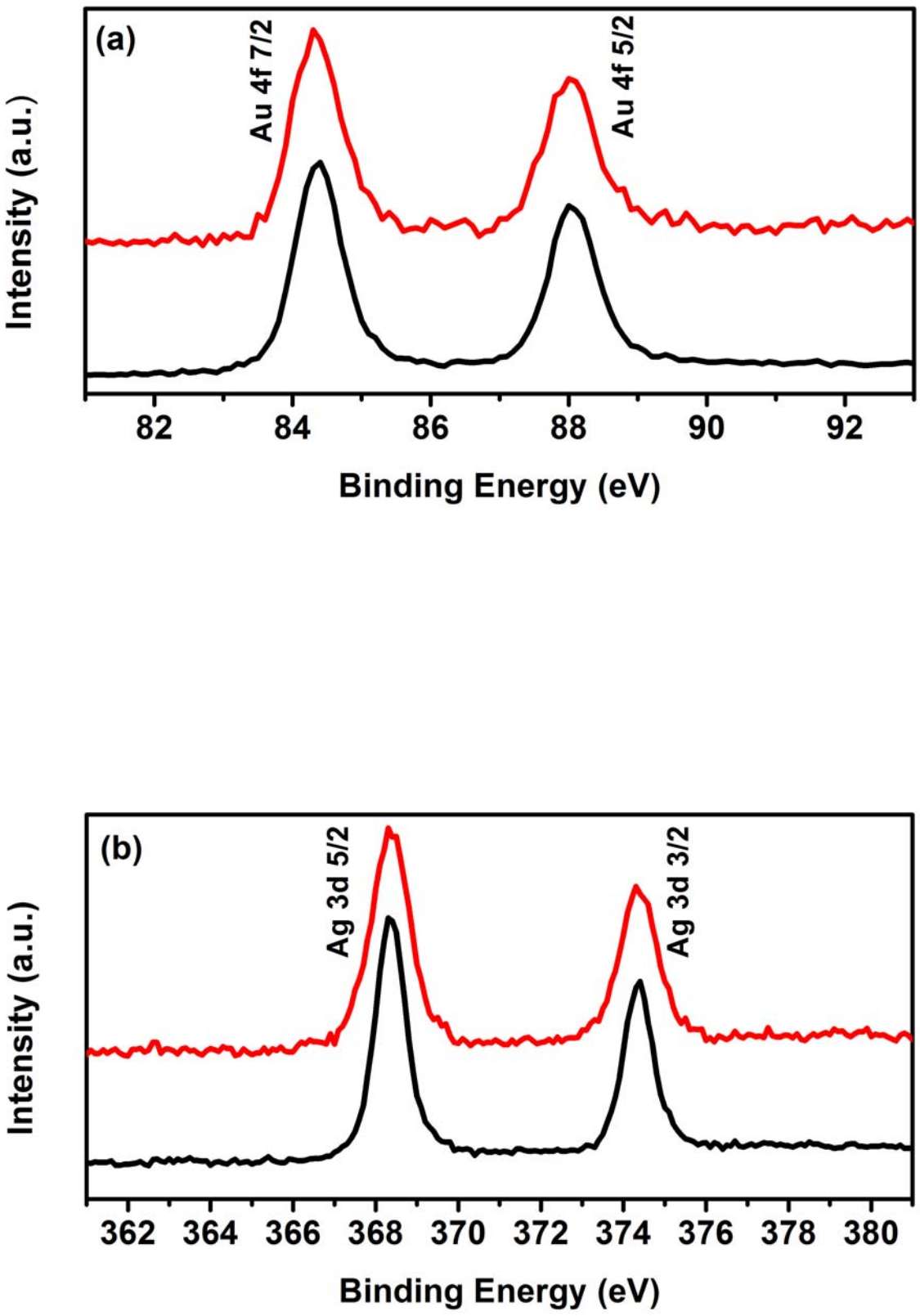
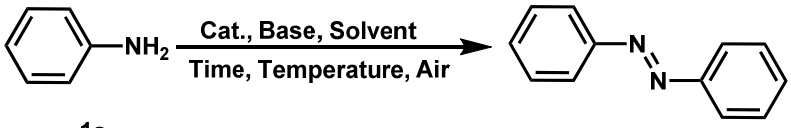


Fig. S9 (a) Au XPS spectrum of catalyst: pure AuAg/C-450 (black line) and the recycled catalyst sample (red line); (b) Ag XPS spectrum of catalyst: pure AuAg/C-450 (black line) and the recycled catalyst sample (red line)

Table S5 Optimizing conditions for oxidative dehydrogenative coupling of anilines.



1a 2a

Entry[a]	Catalyst	Base	Solvent	Time (h)	Yield (%)[b]
1	AuAg/C-450	KOH	DMSO	24	89
2	AuAg/C-500	KOH	DMSO	24	75
3	AuAg/C-550	KOH	DMSO	24	73
4	AuAg/C-600	KOH	DMSO	24	59
5	AuAg/C-450	NaOH	DMSO	24	58
6	AuAg/C-450	K_2CO_3	DMSO	24	Trace
7	AuAg/C-450	Na_2CO_3	DMSO	24	Trace
8	AuAg/C-450	$CsCO_3$	DMSO	24	Trace
9	AuAg/C-450	Et_3N	DMSO	24	Trace
10	AuAg/C-450	KOH	1,4-dioxane	24	20
11	AuAg/C-450	KOH	DMF	24	12
12	AuAg/C-450	KOH	CH_3CN	24	Trace
13	AuAg/C-450	KOH	Toluene	24	22
14	AuAg/C-450	KOH	H_2O	24	Trace
15	AuAg/C-450	KOH	DMSO	4	31
16	AuAg/C-450	KOH	DMSO	8	52
17	AuAg/C-450	KOH	DMSO	16	67
18	AuAg/C-450	KOH	DMSO	32	92
[c]19	AuAg/C-450	KOH	DMSO	24	25
[c]20	AuAg/C-450	KOH	DMSO	32	31
[d]21	AuAg/C-450	KOH	DMSO	24	90
[e]22	AuAg/C-450	KOH	DMSO	24	87
[f]23	AuAg/C-450	KOH	DMSO	8	70
[f]24	AuAg/C-450	KOH	DMSO	24	92
[g]25	AuAg/C-450	KOH	DMSO	24	Trace

[a]Reaction conditions: **1a** (2 mmol), cat. (5 mg), base (1 mmol), solvent (3 mL), air (1 atm), 60 °C. [b]GC yields. [c]Room temperature. [d]Cat. (10 mg). [e]Cat. (2 mg). [f]O_2. [g]N_2.

^{1}H NMR and ^{13}C NMR data of the oxidative dehydrogenative coupling products

(*E*)-1,2-Diphenyldiazene. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.94 (d, J = 7.6 Hz, 4H), 7.59 − 7.45 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 152.8, 131.1, 129.2, 123.0. HRMS *m/z* calcd for $C_{12}H_{10}N_2$ $[M + H]^+$ 183.0922, found 183.0921.

(*E*)-1,2-Bis(4-tert-butylphenyl)diazene. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.85 (d, J = 8.4 Hz, 4H), 7.53 (d, J = 8.4 Hz, 4H), 1.38 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 154.4, 150.9,

126.1, 122.6, 35.13 (s), 31.44 (s). HRMS *m/z* calcd for $C_{20}H_{26}N_2$ $[M + H]^+$ 295.2174, found 295.2173.

(*E*)-1,2-Bis(4-methoxyphenyl)diazene. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.92 (d, *J* = 8.7 Hz, 4H), 7.01 (d, *J* = 8.6 Hz, 4H), 3.89 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 162.0, 146.8, 124.7, 114.4, 55.7. HRMS *m/z* calcd for $C_{14}H_{14}N_2O_2$ $[M + H]^+$ 243.1133, found 243.1135.

(*E*)-1,2-Bis(4-chlorophenyl)diazene. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.86 (d, *J* = 8.6 Hz, 4H), 7.49 (d, *J* = 8.6 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 150.9, 137.4, 129.6, 124.3. HRMS *m/z* calcd for $C_{12}H_8Cl_2N_2$ $[M + H]^+$ 251.0143, found 251.0140.

(*E*)-1,2-Bis(4-bromophenyl)diazene. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.79 (d, *J* = 8.6 Hz, 4H), 7.65 (d, *J* = 8.6 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 151.3, 132.6, 125.9, 124.6. HRMS *m/z* calcd for $C_{12}H_8Br_2N_2$ $[M + H]^+$ 338.9132, found 338.9142.

(*E*)-1,2-Bis(3-methoxyphenyl)diazene. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.57 (d, *J* = 7.7 Hz, 2H), 7.51 – 7.38 (m, 4H), 7.05 (d, *J* = 9.8 Hz, 2H), 3.91 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 160.5, 154.0, 129.9, 118.0, 117.3, 105.9, 55.6. HRMS *m/z* calcd for $C_{14}H_{14}N_2O_2$ $[M + H]^+$ 243.1133, found 243.1141.

(*E*)-1,2-Bis(2-methoxyphenyl)diazene. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.64 (d, *J* = 7.9 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 2H), 4.02 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 157.0, 143.1, 132.3, 120.9, 117.6, 112.7, 56.4. HRMS *m/z* calcd for $C_{14}H_{14}N_2O_2$ $[M + H]^+$ 243.1133, found 243.1128.

(*E*)-1,2-Bis(3-bromophenyl)diazene. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.04 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 153.3, 134.2, 130.6, 124.9, 123.4, 123.3. HRMS *m/z* calcd for $C_{12}H_8Br_2N_2$ $[M + H]^+$ 338.9132, found 338.9135.

(*E*)-1,2-Bis(1-naphthyl)diazene. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.06 (d, *J* = 8.4 Hz, 2H), 8.08 – 7.91 (m, 6H), 7.73 – 7.57 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 148.4, 134.5, 131.7, 131.6, 128.1, 127.1, 126.6, 125.8, 123.8, 112.4. HRMS *m/z* calcd for $C_{20}H_{14}N_2$ $[M + H]^+$ 283.1235, found 283.1239.

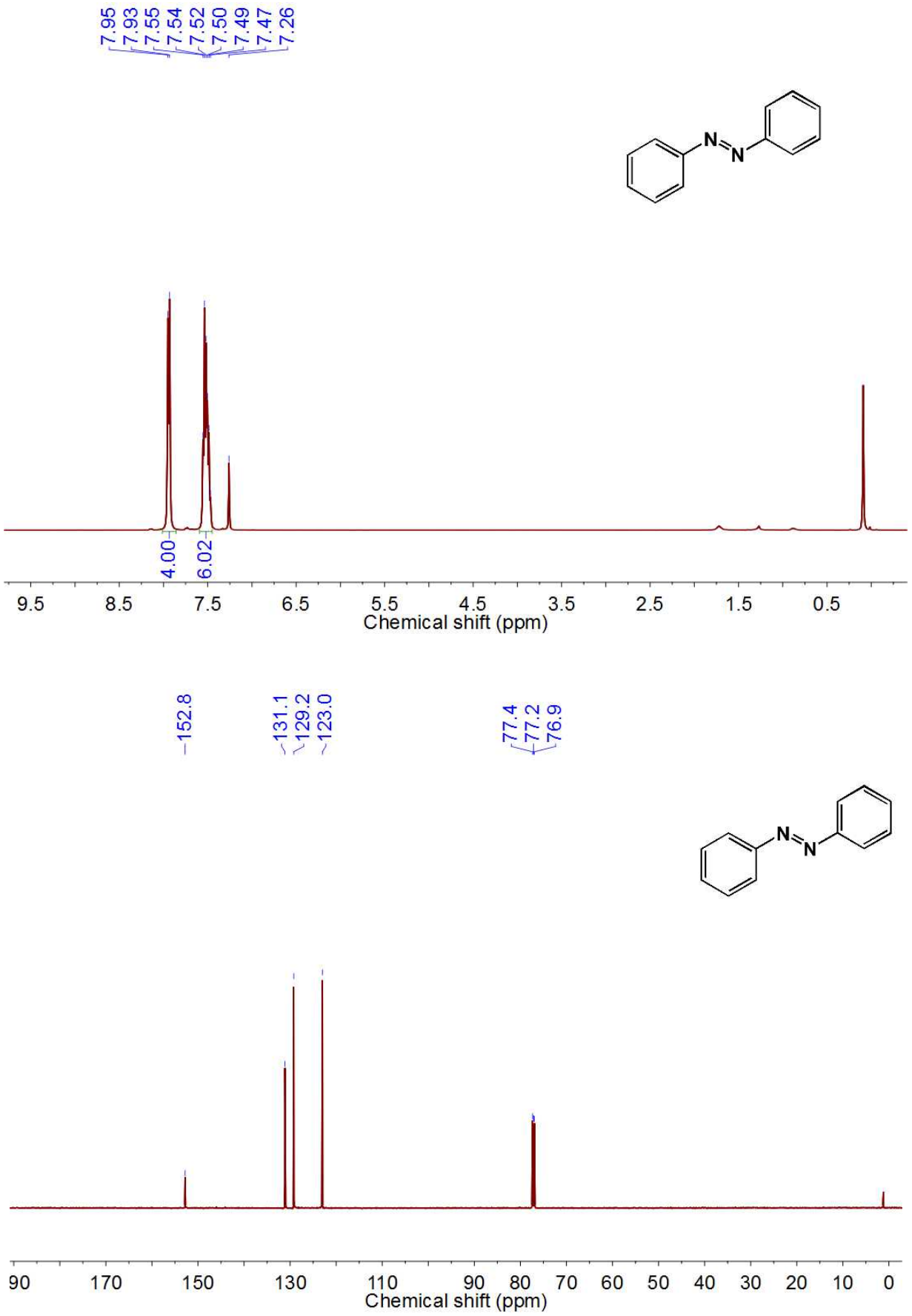


Fig. S10 The ^{1}H (top) and ^{13}C (below) NMR spectra for (*E*)-1,2-Diphenyldiazene in $CDCl_3$.

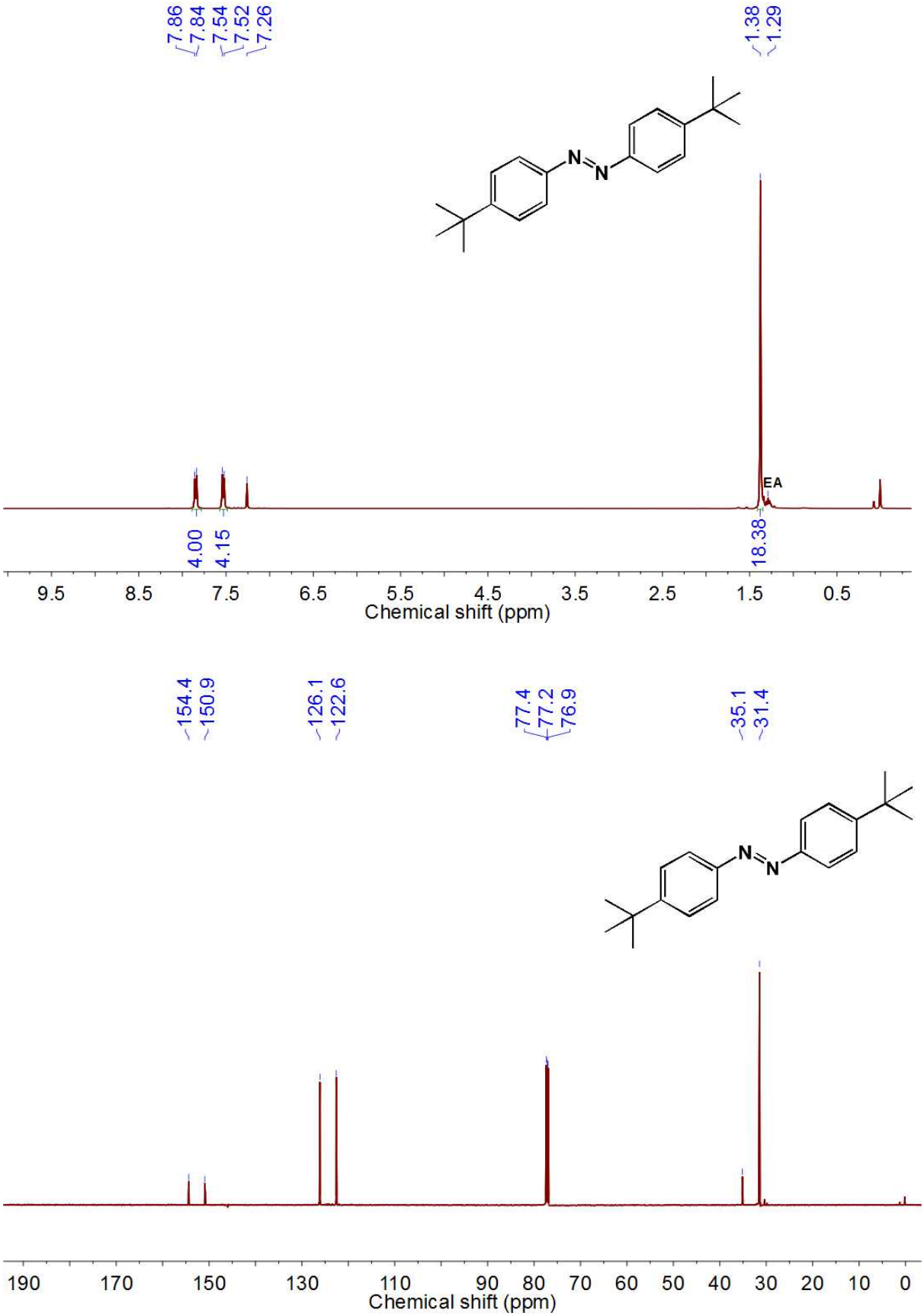


Fig. S11 The ^{1}H (top) and ^{13}C (below) NMR spectra for (*E*)-1,2-Bis(4-tert-butylphenyl)diazene in $CDCl_3$.

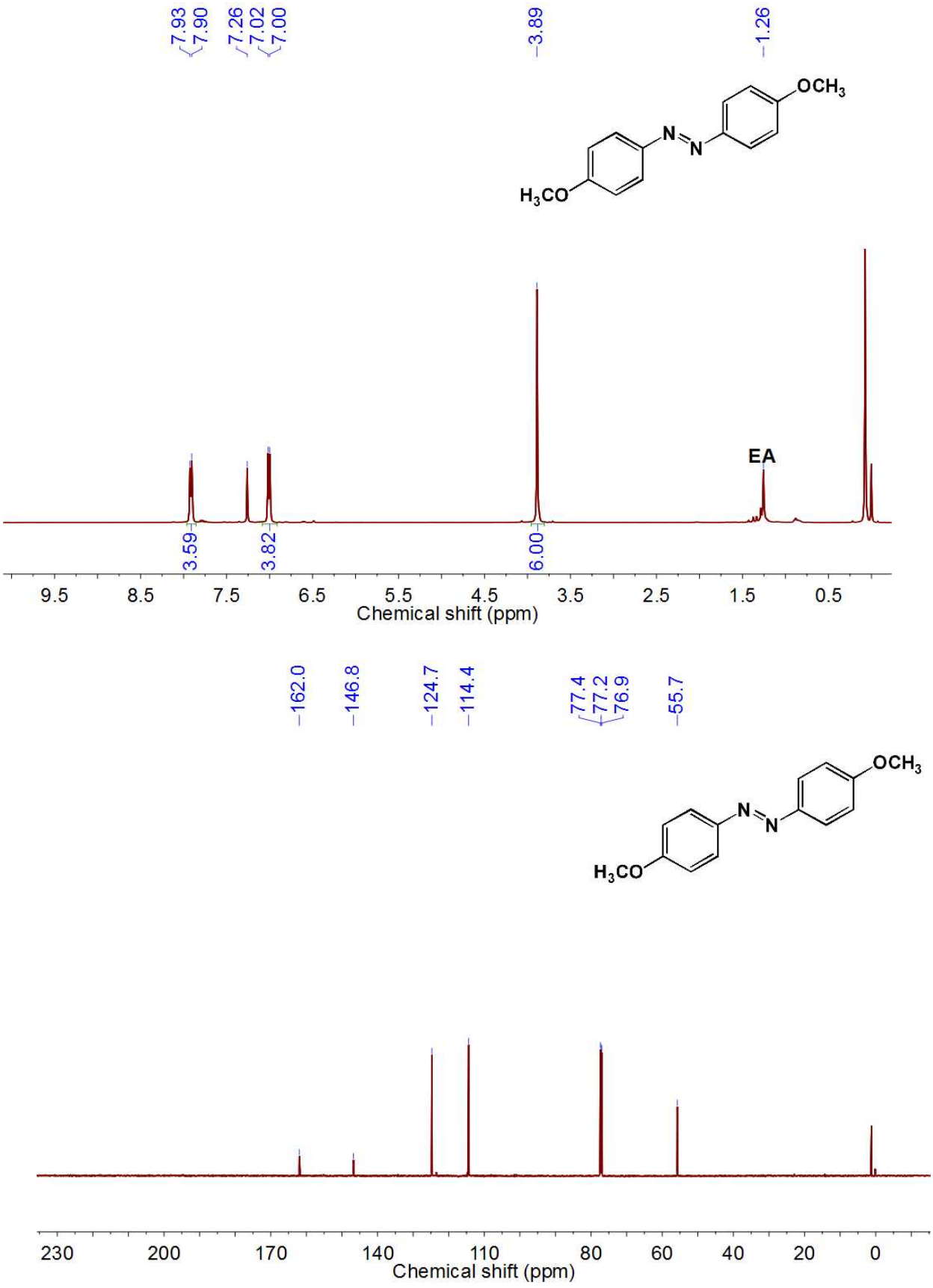


Fig. S12 The ^{1}H (top) and ^{13}C (below) NMR spectra for (*E*)-1,2-Bis(4-methoxyphenyl)diazene in $CDCl_3$.

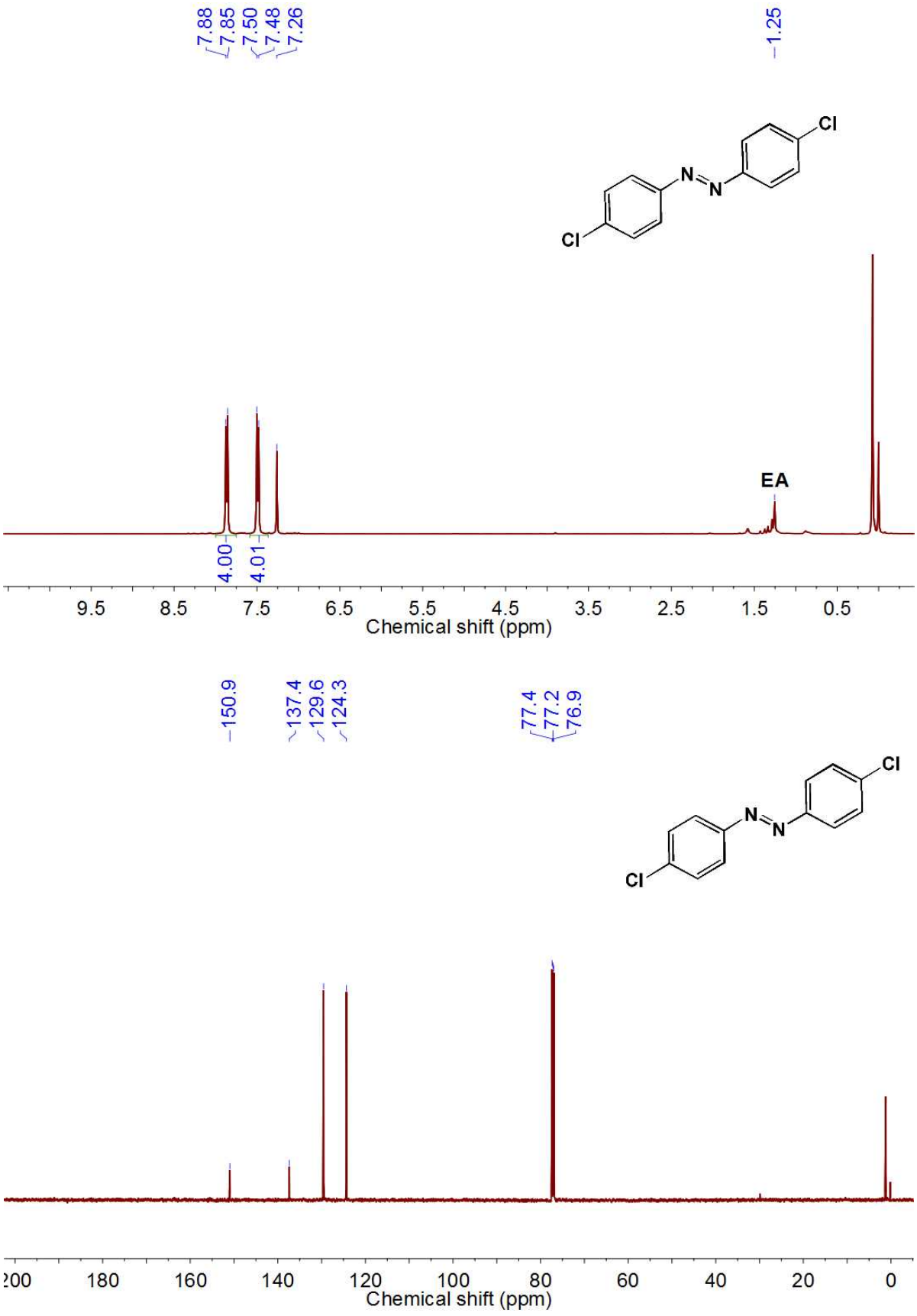


Fig. S13 The ^{1}H (top) and ^{13}C (below) NMR spectra for (*E*)-1,2-Bis(4-chlorophenyl)diazene in $CDCl_3$.

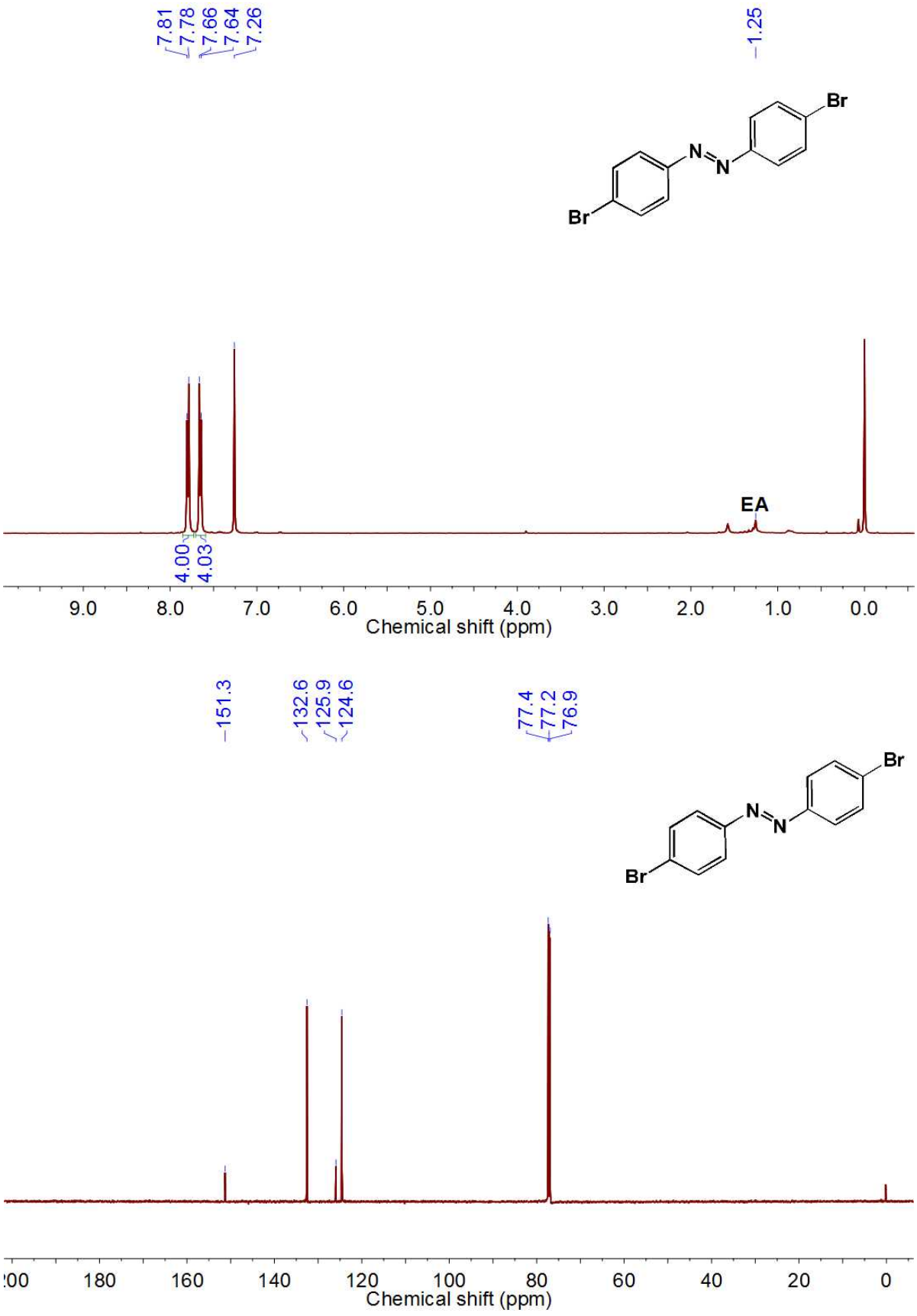


Fig. S14 The ^{1}H (top) and ^{13}C (below) NMR spectra for (*E*)-1,2-Bis(4-bromophenyl)diazene in $CDCl_3$.

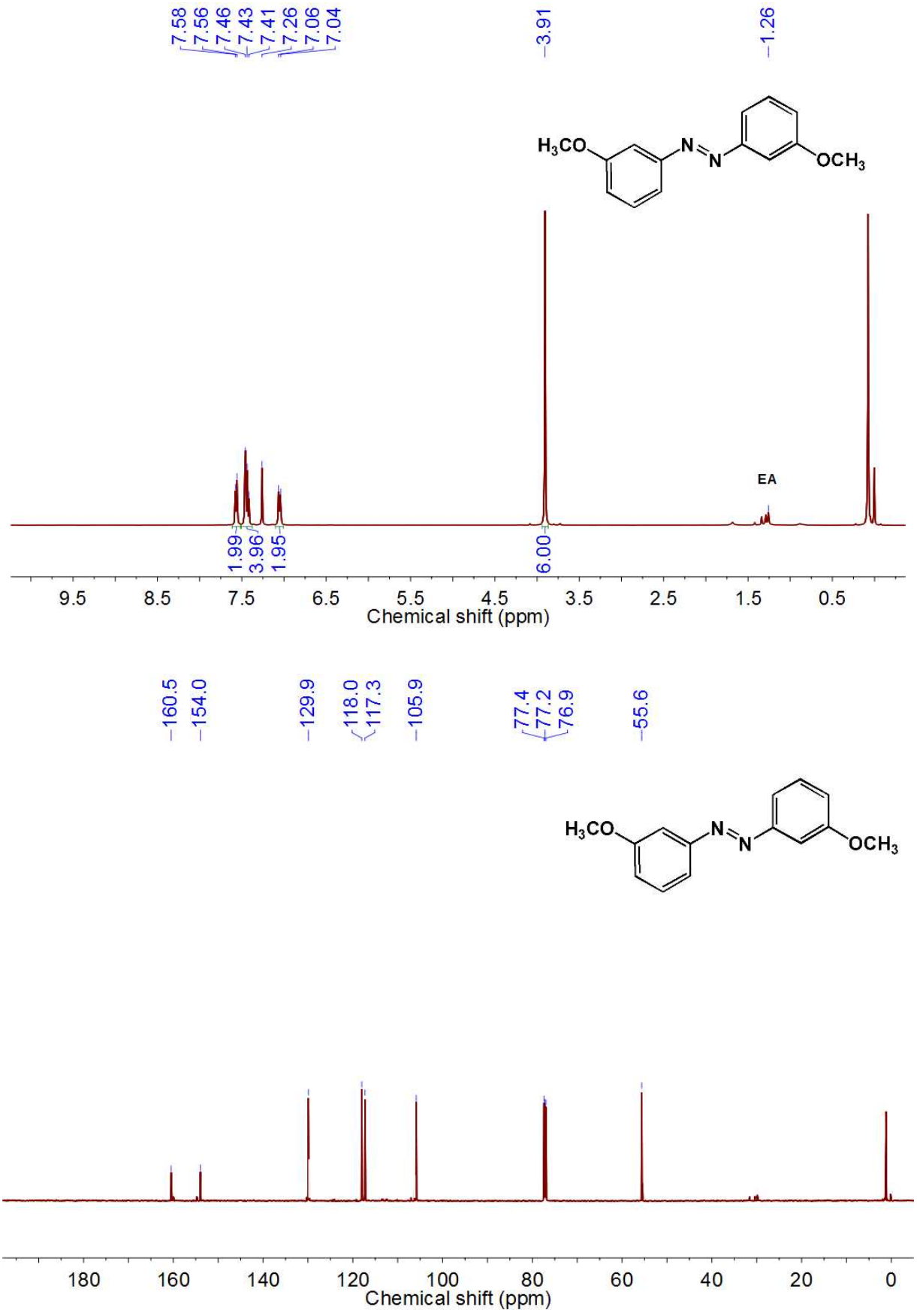


Fig. S15 The ^{1}H (top) and ^{13}C (below) NMR spectra for (*E*)-1,2-Bis(3-methoxyphenyl)diazene in $CDCl_3$.

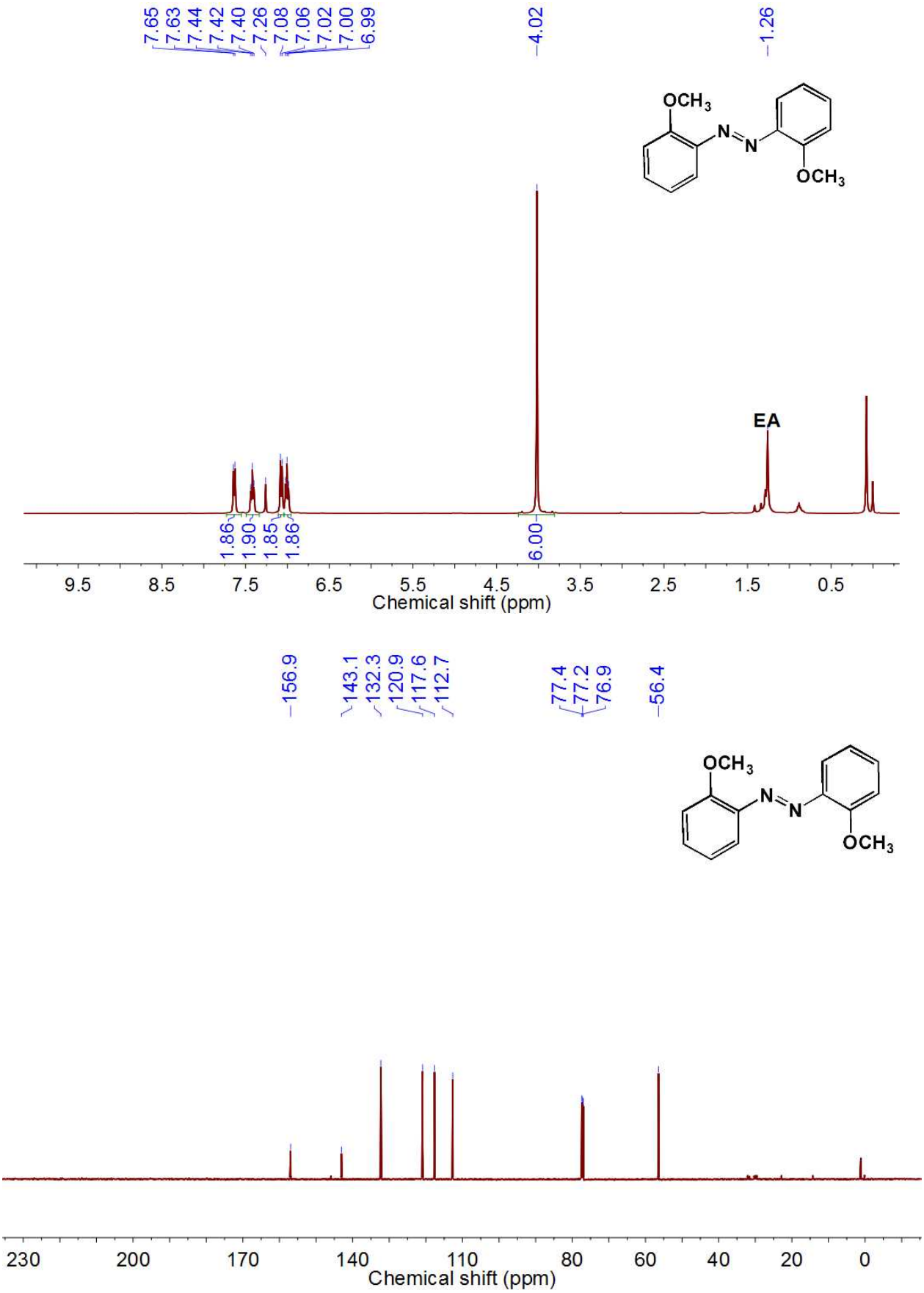


Fig. S16 The ^{1}H (top) and ^{13}C (below) NMR spectra for (*E*)-1,2-Bis(2-methoxyphenyl)diazene in $CDCl_3$.

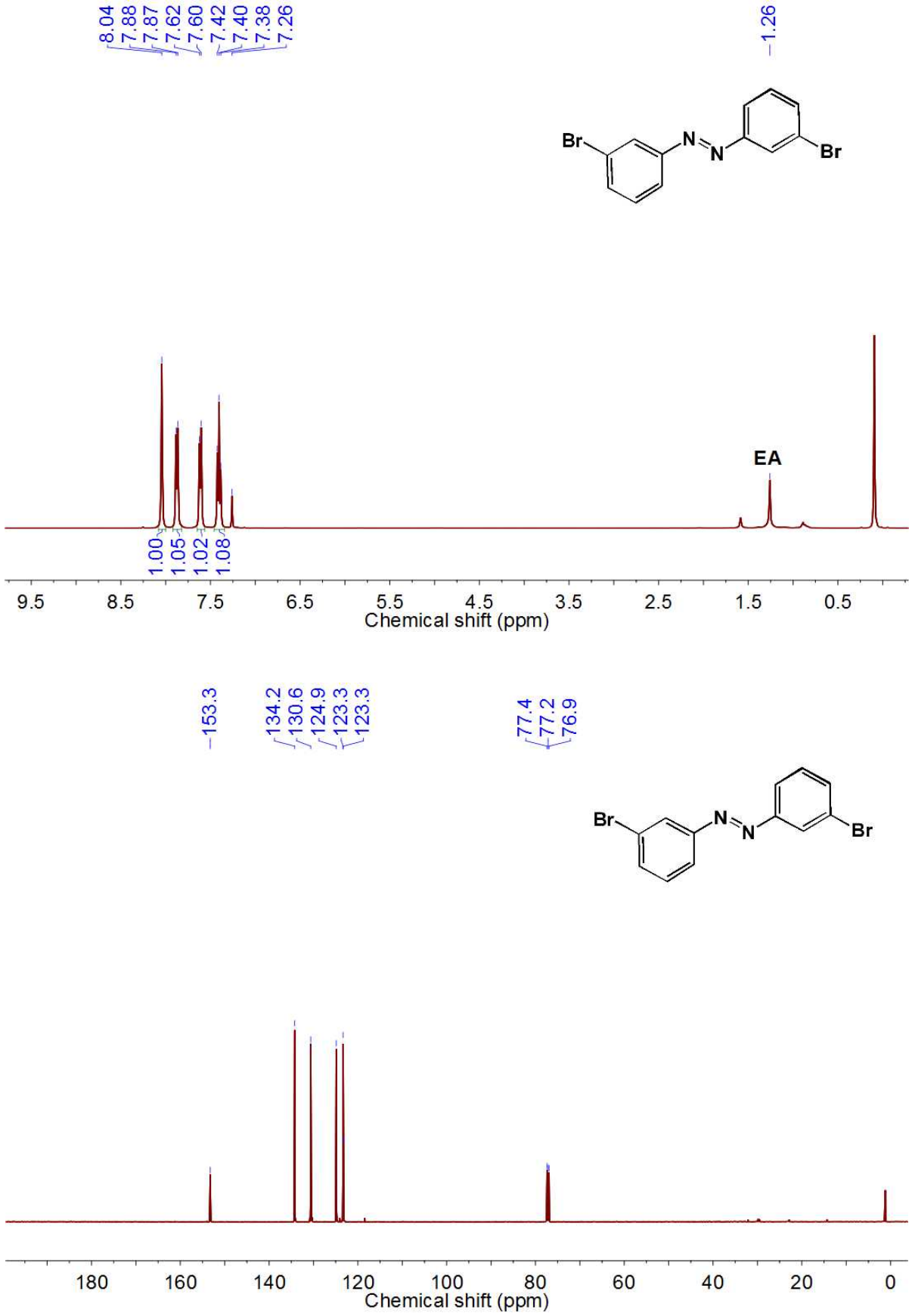


Fig. S17 The ^{1}H (top) and ^{13}C (below) NMR spectra for (*E*)-1,2-Bis(3-bromophenyl)diazene in $CDCl_3$.

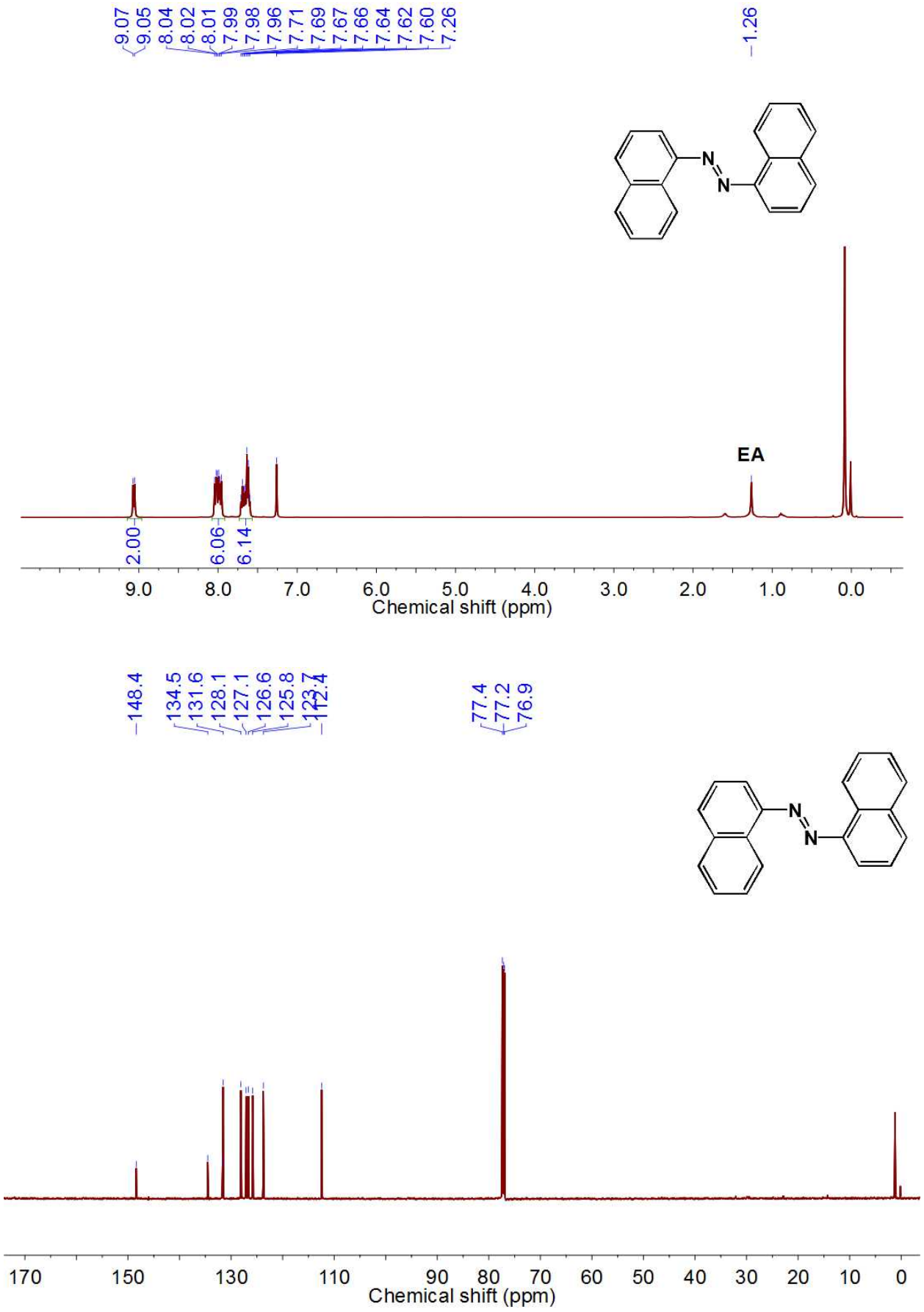


Fig. S18 The ^{1}H (top) and ^{13}C (below) NMR spectra for (*E*)-1,2-(1-naphthyl)diazene in $CDCl_3$.

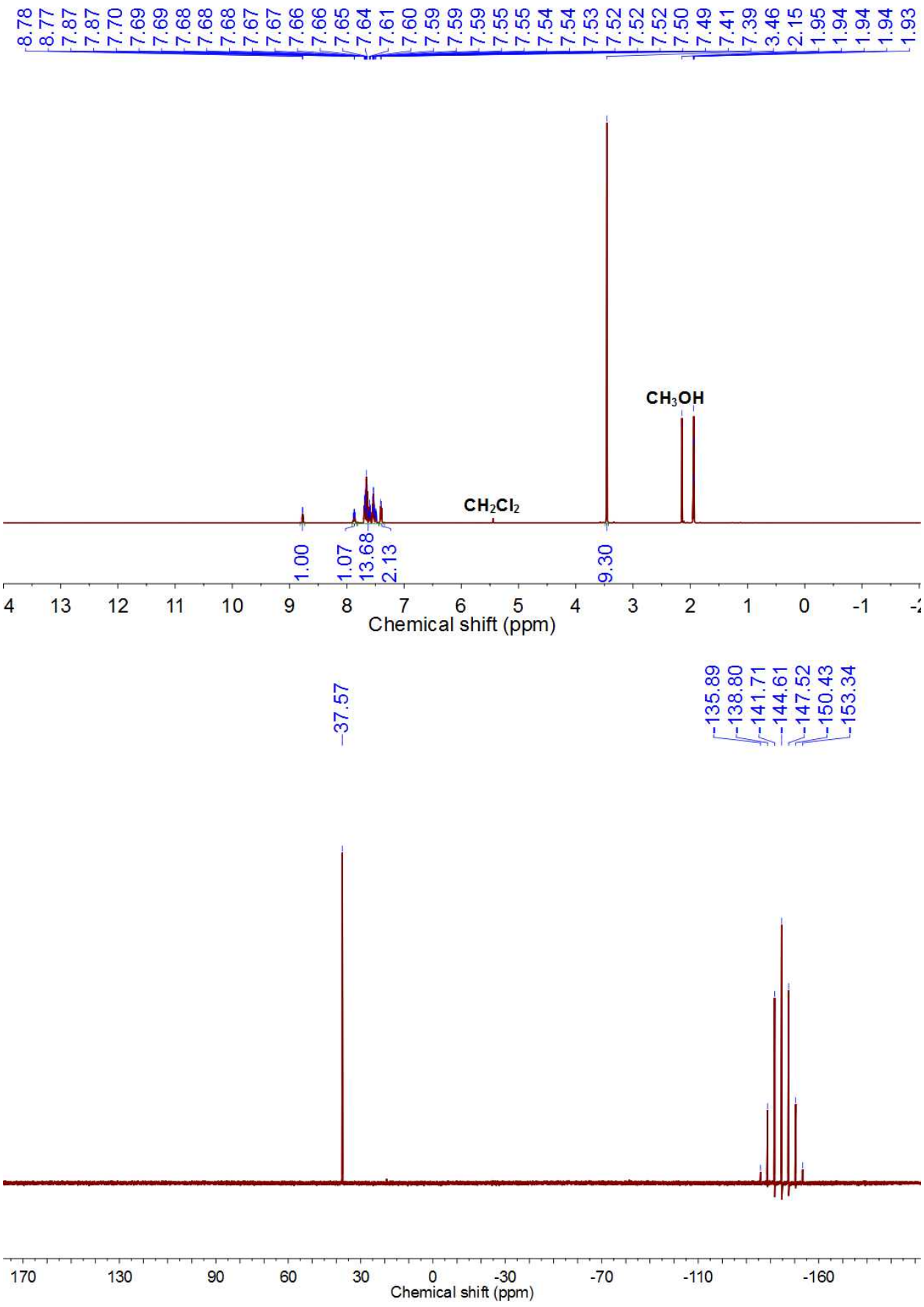


Fig. S19 The ^{1}H (top) and ^{31}P (below) NMR spectra of compound **1**.

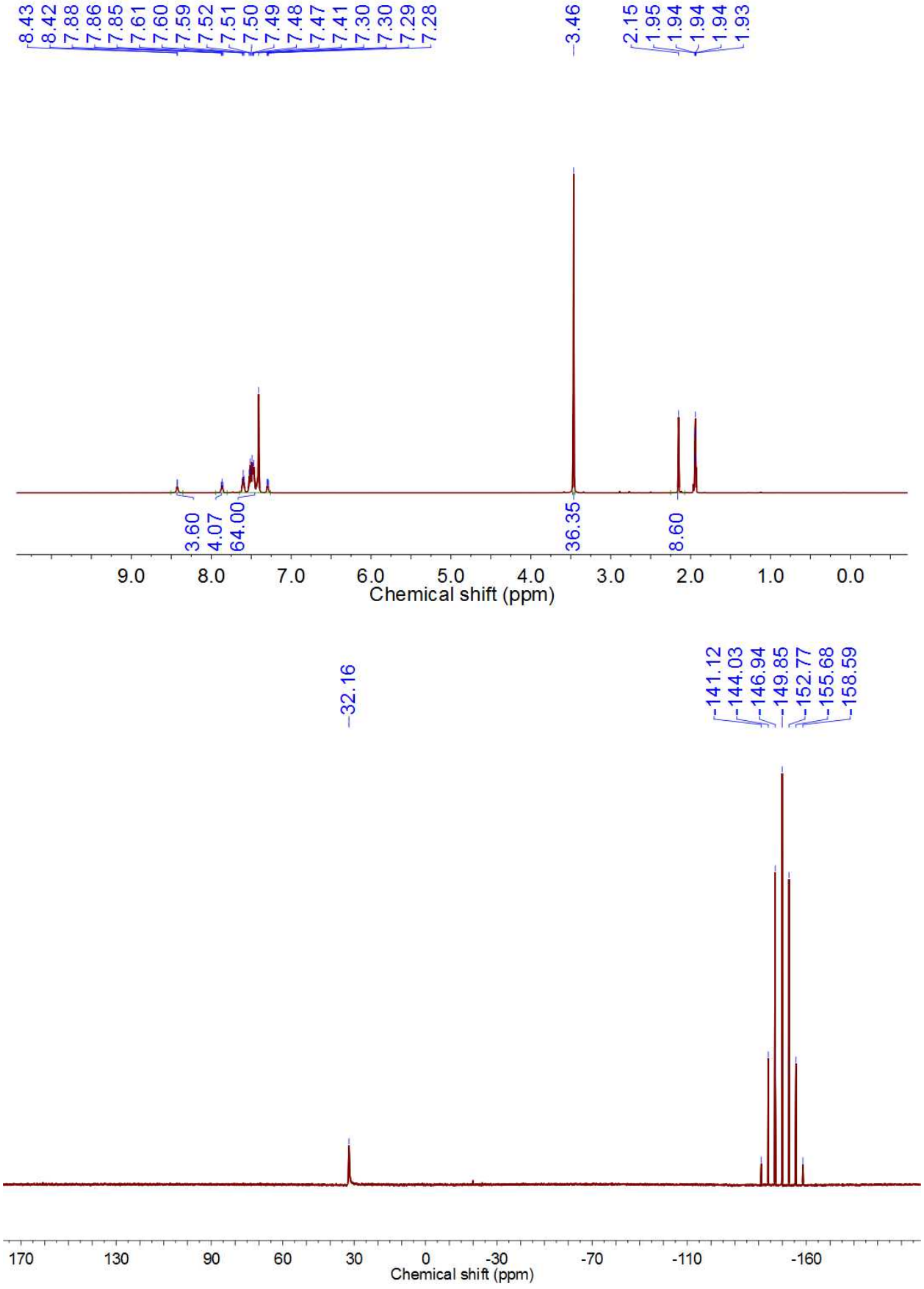
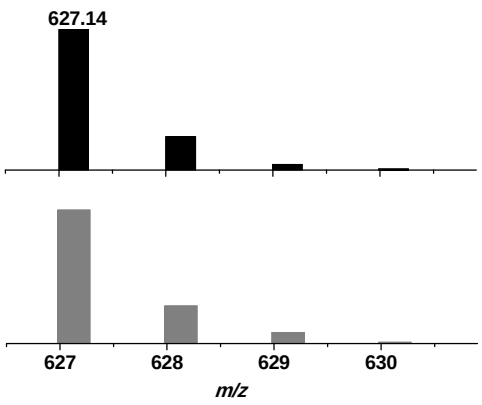
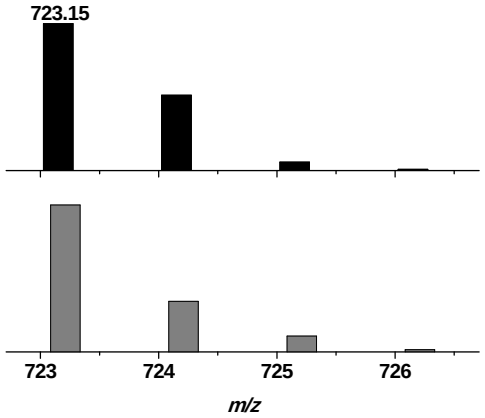


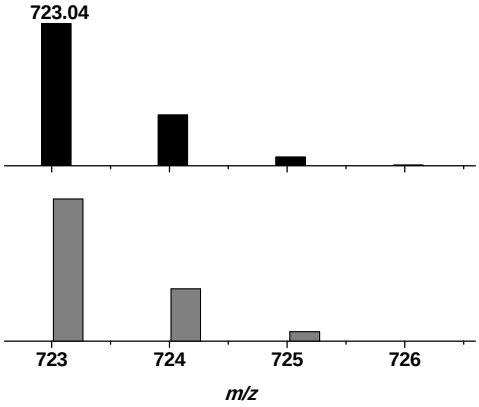
Fig. S20 The ^{1}H (top) and ^{31}P (below) NMR spectra of compound **2**.



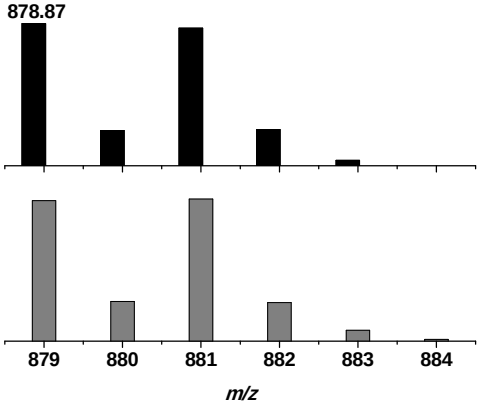
1a



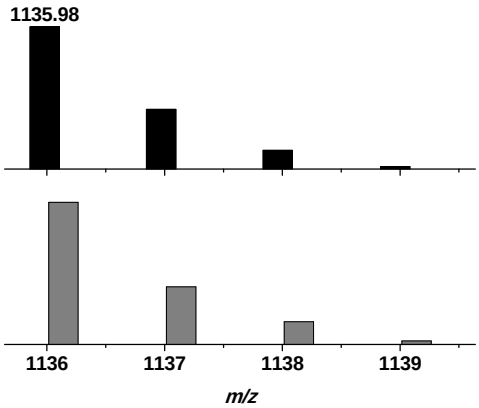
1b



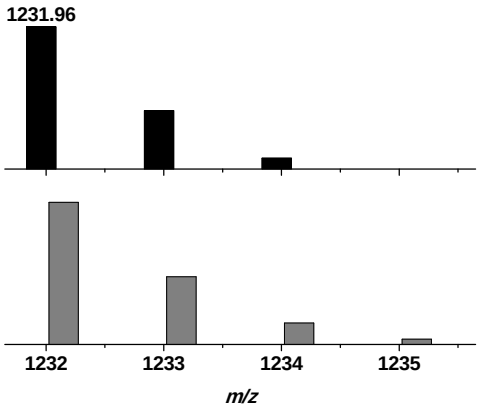
2a



2b



2c



(2d)

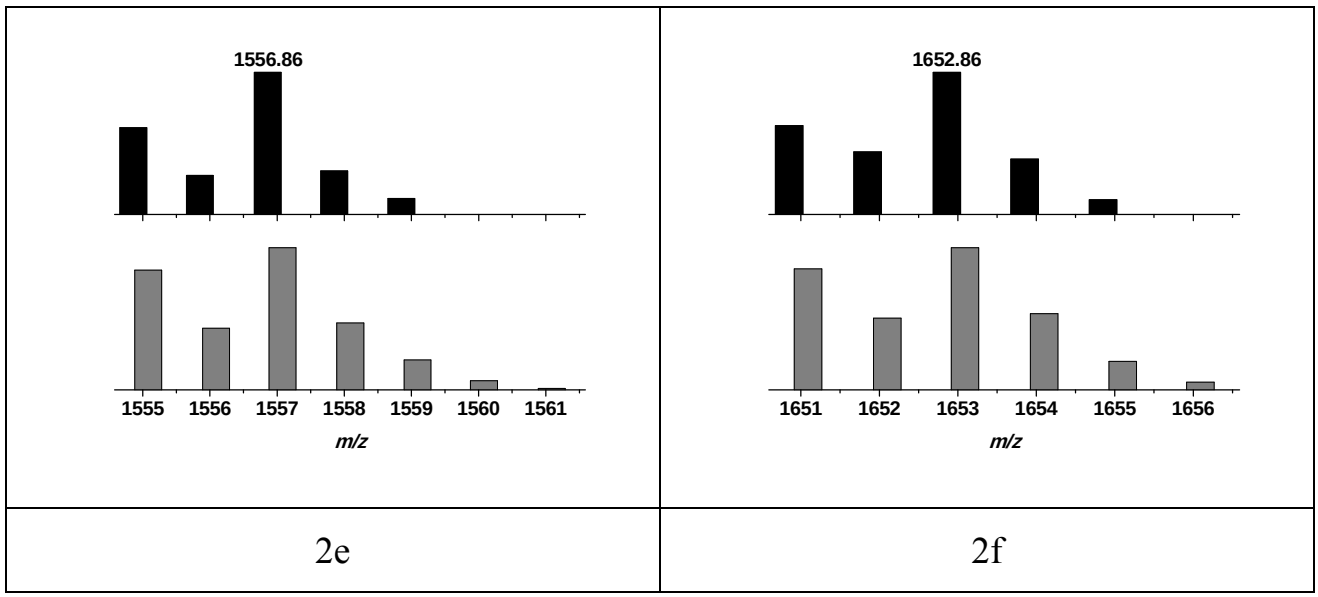


Fig. S21 The positive-ion ESI mass spectrum (black) and the calculated isotope pattern (gray) of $[Au(Dppy)(Tab)]^+$ cation of **1** (1a). The positive-ion ESI mass spectrum (black) and the calculated isotope pattern (gray) of $[Au(Dppy)(Tab)(CH_3OH)_3]^+$ cation of **1** (1b). The positive-ion ESI mass spectrum (black) and the calculated isotope pattern (gray) of $[Au(Dppy)_2]^+$ cation of **2** (2a). The positive-ion ESI mass spectrum (black) and the calculated isotope pattern (gray) of $[AuAg(Dppy)(Tab)(PF_6)]^+$ cation of **2** (2b). The positive-ion ESI mass spectrum (black) and the calculated isotope pattern (gray) of $[Au_2(Dppy)(Tab)_2(PF_6)]^+$ cation of **2** (2c). The positive-ion ESI mass spectrum (black) and the calculated isotope pattern (gray) of $[Au_2(Dppy)_2(Tab)(PF_6)]^+$ cation of **2** (2d). The positive-ion ESI mass spectrum (black) and the calculated isotope pattern (gray) of $[Au_2Ag(Dppy)(Tab)_3(PF_6)_2]^+$ cation of **2** (2e). The positive-ion ESI mass spectrum (black) and the calculated isotope pattern (gray) of $[Au_2Ag(Dppy)_2(Tab)_2(PF_6)_2]^+$ cation of **2** (2f).