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Selective Hofmann alkylation of aromatic-aliphatic diamines in the presence of carbon dioxide

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1. General information

All starting reagents were purchased from commercial suppliers and used without further purification. MeCN, DMF and DMA were purified by standard techniques and stored over molecular sieves 3 Å. Carbon dioxide >99.99% purity was used. NMR spectra were recorded on a Bruker Avance-400 or an Agilent 400-MR spectrometers (400 and 100 MHz for ^{1}H and ^{13}C, respectively) at room temperature; chemical shifts δ are given in ppm and were measured with reference to the solvent: 1.93 ppm and 1.3 ppm (CD_3CN), 2.49 ppm and 39.5 ppm (DMSO-d_6), When necessary, the assignment of signals in the NMR spectra was carried out using 2D techniques.

The elemental analyses were performed on a "vario MICRO cube" CHN automated analyzer (for salts **6** and **7**) and by Pregl-Dumas-Korshun technique (for salts **4**, **5** and **8** with high iodine content).

Reactions at high pressures were carried out in a diamagnetic steel high-pressure cell with an internal volume of 47 ml. A simplified view of the high-pressure system is presented in Figure S1.

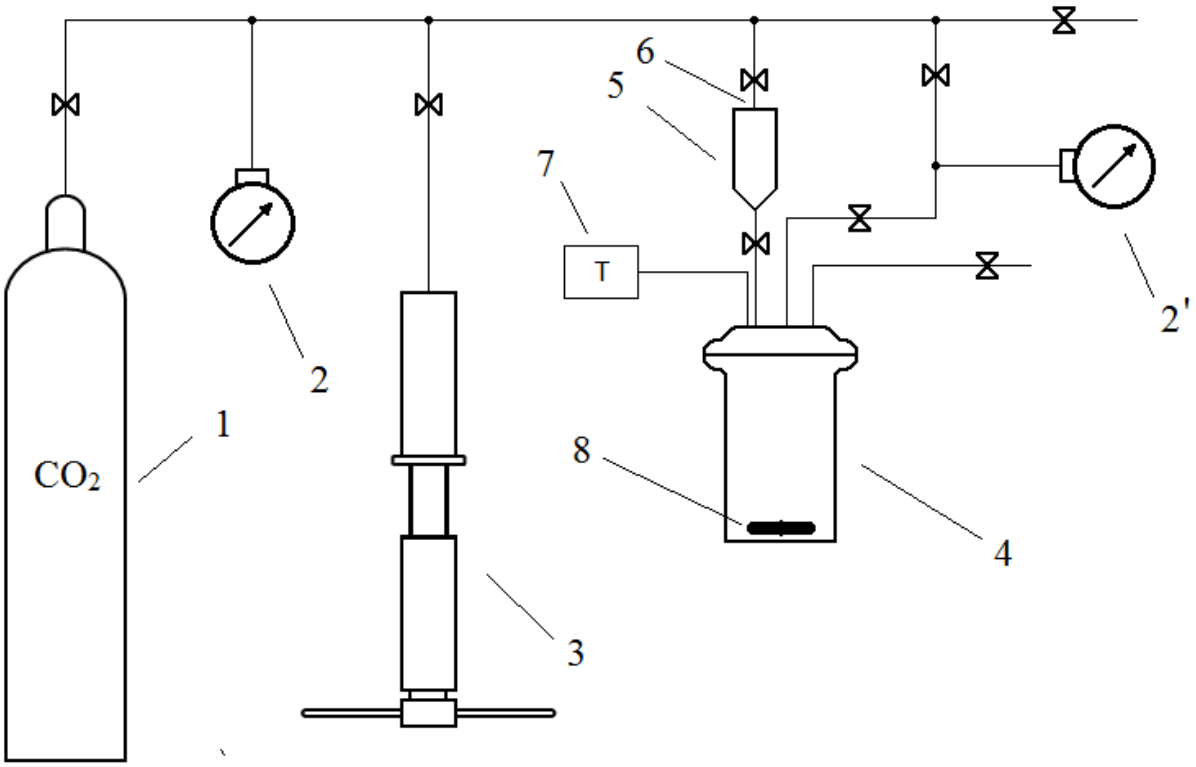


Figure S1. General layout of the high pressure system: **1** – gas cylinder; **2**, **2′** – manometers; **3** – hand screw press; **4** – high-pressure cell assembly; **5** – injector with plug-in connection (**6**); **7** – thermocouple; **8** – magnetic stir bar.

After loading the amine solutions, the high-pressure cell was purged with CO_2 (3 times 5 bar) and the pressure was adjusted to the required value. To carry out the reactions in liquid CO_2, 35 ml of liquid CO_2 was additionally pumped into the high-pressure cell using a hand screw press.

The liquid components were introduced into the high-pressure cell under pressure using an injector. The cell was cooled in an ice bath to ~ 10-15 °C until the pressure dropped to ~ 30-40 bar. The required component was placed via the plug-in connection into the injector body, by means of the top valve the overpressure was created in the injector, and then the bottom valve was opened. Pressure monitoring in the system was carried out via internal (**2′**) and external (**2**) manometers. The temperature in the high-pressure cell was monitored with a thermocouple (**7**). The reaction mixture was stirred with a magnetic stirrer. The pressure drop at the end of the reaction was carried out for ~ 30 min.

2. Alkylation of *o*-, *m*- and *p*-toluidines in MeCN, DMF and DMA

General procedure

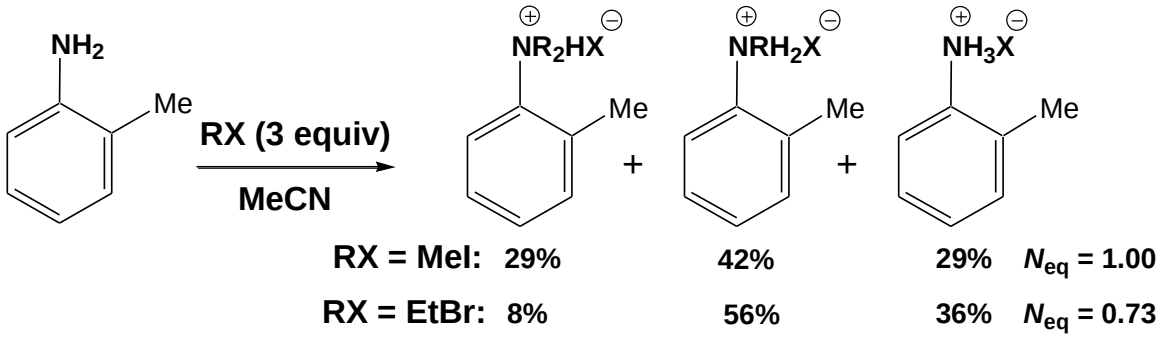
A specified toluidine (100 mg), solvent (0.3 to 1.0 ml) and an alkylating agent (3 or 6 equiv, n RX) were placed in a 4 ml glass vial. The vial was placed in a thermostat and kept at the required temperature for a certain time. For NMR analysis, 0.1 ml of the reaction mixture was dissolved in 0.5 ml of CD_3CN. Completeness of alkylation (the number of RX equivalents reacted with the arylamino group (N_{eq})) was determined from the ratio of the sums of integral intensities (I) based on methyl groups signals: $N_{eq} = \Sigma[I(\mathrm{N}\boldsymbol{Me}_n)]/\Sigma[I(\mathrm{Ar}\boldsymbol{Me})]$ or $N_{eq} = \Sigma[I(\mathrm{N(CH_2}\boldsymbol{Me})_n)]/\Sigma[I(\mathrm{Ar}\boldsymbol{Me})]$ (see Table S1, Figures S2-S13).

Table S1. The number of equivalents of RX (N_{eq}), reacted with *o*-, *m*- and *p*-toluidines in MeCN, DMF and DMA.

Entry	Toluidine	n RX	Solvent	T (°C)	Time (hours)	N_{eq}
1	*o*-[a]	3 MeI	MeCN	60	4	1.00
2	*o*-[a]	3 EtBr	MeCN	60	4	0.73
3	*m*-[a]	3 MeI	MeCN	60	4	1.00
4	*m*-[b]	3 MeI	MeCN	22	24	1.00
5	*m*-[a,c]	3 EtBr	MeCN	60	4	0.98
6	*m*-[b,c]	3 EtBr	MeCN	22	24	0.33
7	*o*-[a]	6 MeI	DMF	50	24	1.67
8	*o*-[a]	6 MeI	DMA	50	24	1.97
9	*m*-[d]	6 MeI	DMF	60	72	2.55
10	*m*-[d]	6 MeI	DMA	60	72	2.92
11	*p*-[d]	6 MeI	DMF	60	72	2.56
12	*p*-[d]	6 MeI	DMA	60	72	3.00

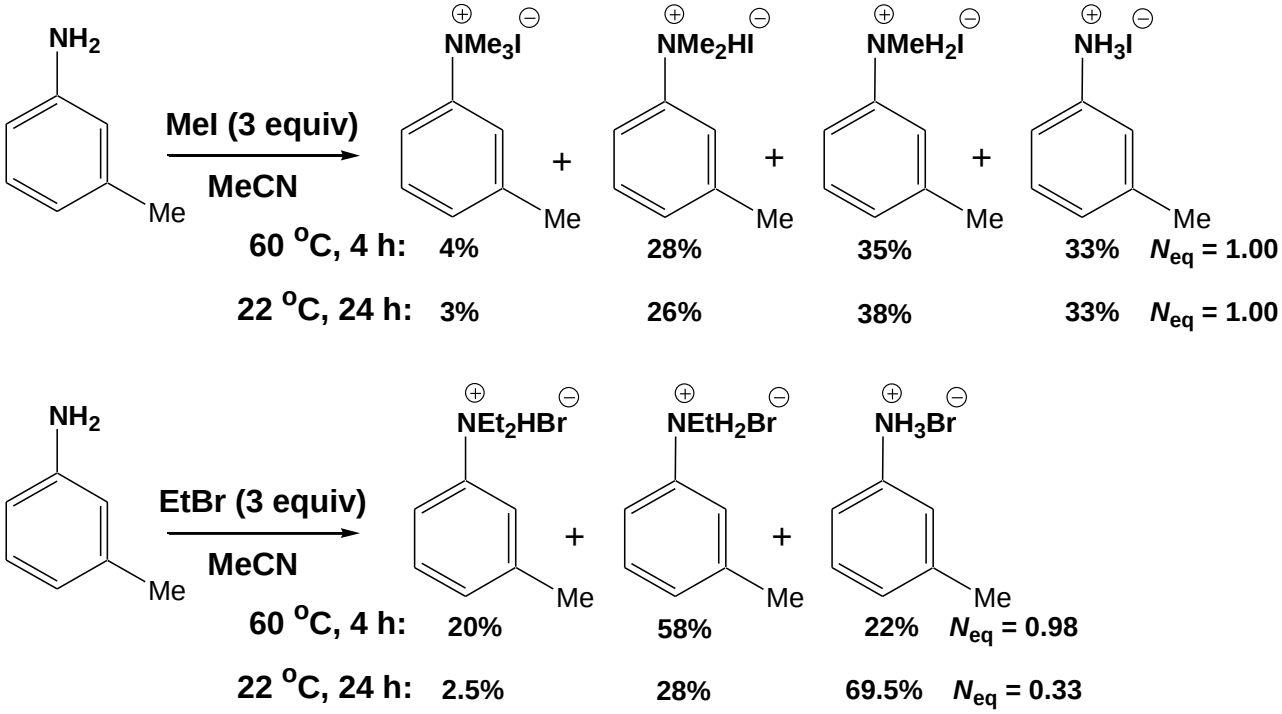
[a] 100 mg of toluidine in 0.3 ml of the solvent.
[b] 100 mg of toluidine in 1.0 ml of the solvent.
[c] The reaction mixture crystallizes on cooling. The solid was dissolved in MeCN, 0.6 ml of the solution was evaporated *in vacuo*, the resulting residue was dissolved in 0.6 ml of CD_3CN.
[d] 100 mg of toluidine in 0.6 ml of the solvent.

Alkylation of *o*-toluidine with an excess of MeI or EtBr in MeCN results in a mixture of three ammonium salts (Scheme S1, Table S1 (entries 1, 2), Figures S2, S3). Quaternary ammonium salt is not formed due to steric hindrances. Methylation proceeds completely (1 equiv of MeI reacts), but only 0.73 equiv of EtBr reacts under the same experimental conditions.



Scheme S1. Alkylation of *o*-toluidine in MeCN (Table S1, entries 1, 2).

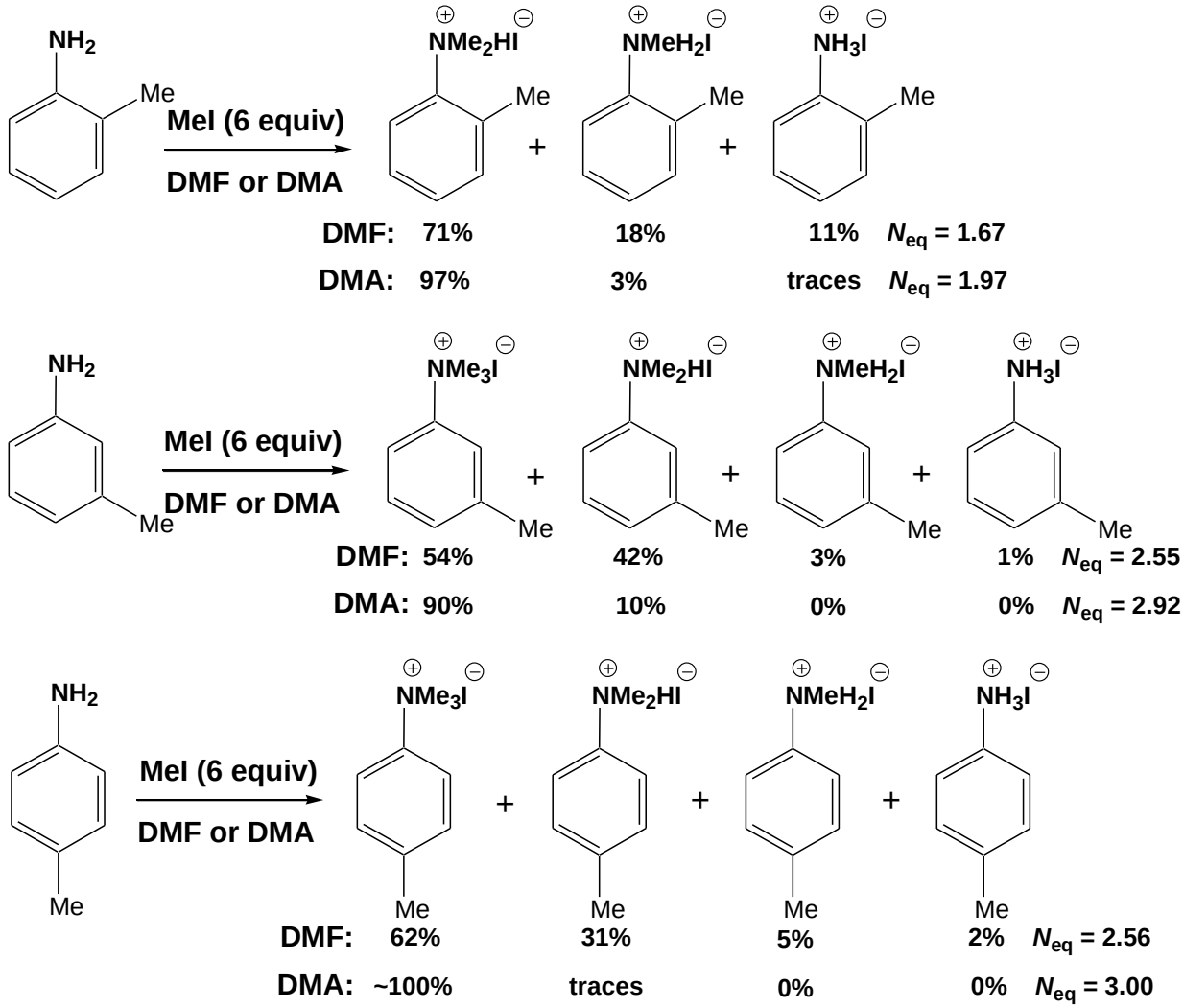
Methylation of *m*-toluidine with an excess of MeI in MeCN at ambient and at an elevated temperature gives a mixture of all four ammonium salts (Scheme S2, Table S1 (entries 3, 4), Figures S4, S5). In both cases the reaction proceeds completely. Sterically hindered and less active EtBr reacts slower and forms only three ammonium salts (Scheme S2, Table S1 (entries 5, 6), Figures S6, S7). Ethylation proceeds almost completely at 60 °C for 4 hours.



Scheme S2. Alkylation of *m*-toluidine in MeCN (Table S1, entries 3-6).

In amide solvents, unlike MeCN, methylation of toluidines occurs with the addition of more than 1 equiv MeI (Scheme S3). In all cases the reaction proceeds faster in DMA compared with DMF. Methylation of *o*-toluidine stops at the stage of formation of dimethylarylammonium iodide (Table S1 (entries 7, 8), Figures S8, S9), it is formed in DMA at 50 °C for 24 hours with almost quantitative yield. At the same time, less sterically hindered *m*-toluidine (Table S1 (entries 9, 10), Figures S10, S11) and *p*-toluidine (Table S1 (entries 11, 12), Figures S12, S13) in this reaction give

quaternary ammonium salts as final products. The reaction rates for *p*-toluidine are slightly higher than for *m*-toluidine, this may be due to the effect of the alkyl substituent occupying *para*-position.



Scheme S3. Methylation of *o*-, *m*- and *p*-toluidines in DMF and DMA (Table S1, entries 7-12).

Table S2. Literature pK_a values of some acids in dilute aqueous solutions and DMSO.

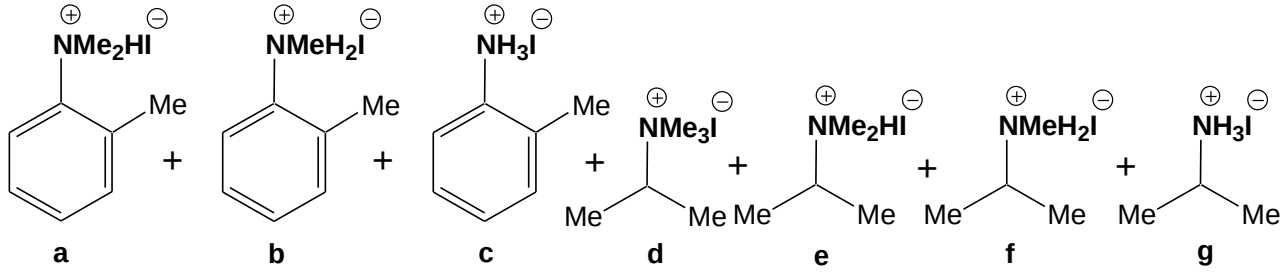
Acid	pK_a (H_2O)	pK_a (DMSO)	Acid	pK_a (H_2O)	pK_a (DMSO)
HBr	-9[a]	0.9[a]	$PhNMe_2H^+$	5.07[b]	2.45[a]
HCl	-8[a]	1.8[a]	$PhCH_2NH_3^+$	9.34[b]	10.16[d]
NH_4^+	9.25[b]	10.5[c]	$EtNH_3^+$	10.65[b]	11.0[c]
$PhNH_3^+$	4.87[b]	3.6[c]	$Et_2NH_2^+$	10.84[b]	10.5[c]
$PhNMeH_2^+$	4.85[b]		Et_3NH^+	10.75[b]	9.0[c]

a) F.G. Bordwell, *Acc. Chem. Res*., 1988, **21**, 456; b) A. K. Covington and W. Davison, in *CRC Handbook of Chemistry and Physics*, 84th edn., ed. D. R. Lide, CRC Press, 2004, pp. 8-46 – 8-56; c) I. M. Kolthoff, M. K. Chantooni, Jr. and S. Bhowmik, *J. Am. Chem. Soc*., 1968, **90**, 23; d) M. R. Crampton and I. A. Robotham, *J. Chem. Res. (S)*, 1997, 22.

3. Alkylation of model mixtures of amines in MeCN

Alkylation of *o*-toluidine – isopropylamine mixture in MeCN in the absence of CO_2

o-Toluidine (107 mg, 1 mmol), Pr^iNH_2 (65 mg, 1.1 mmol, 1.1 equiv, slight excess due to its volatility), CD_3CN (0.4 ml) and MeI (426 mg, 3 mmol, 3 equiv) were mixed and placed in a NMR tube. The NMR spectrum was recorded after 48 hours. The reaction resulted in a mixture of products **a**-**g**. The accuracy of the product signals assignment in ^1H and ^{13}C NMR spectra (Figures S14-S17) was approved by *HMQC* correlation experiment.



^1H NMR (400 MHz, CD_3CN): δ = 1.25 (d, ^3J(H,H) = 6.6 Hz, CH*Me*$_2$ (**e**)), 1.26 (dt (1:1:1), ^3J(H,H) = 6.6 Hz, ^3J(^{1}H,^{14}N) = 1.9 Hz, CH*Me*$_2$ (**d**)), 1.32 (d, ^3J(H,H) = 6.6 Hz, CH*Me*$_2$ (**f**)), 1.35 (d, ^3J(H,H) = 6.6 Hz, CH*Me*$_2$ (**g**)), 2.48 (t, ^3J(HC,NH) = 5.8 Hz, N*Me*H_2^+ (**f**)), 2.49 (s, Ar*Me* (**c**)), 2.52 (s, Ar*Me* (**b**)), 2.60 (s, Ar*Me* (**a**)), 2.64 (d, ^3J(HC,NH) = 5.4 Hz, N*Me*$_2H^+$ (**e**)), 2.92 (s, N*Me*H_2^+ (**b**)), 3.03 (s, N*Me*$_3^+$ (**d**)), 3.21 (s, N*Me*$_2H^+$ (**a**)), 3.45 (br nonet, ^3J(HC,CH) = 6.6 Hz, ^3J(HC,NH) = 6.2 Hz, C*H*Me$_2$ (**f**)), 3.54 (d of septets, ^3J(HC,CH) = 6.6 Hz, ^3J(HC,NH) = 3.2 Hz, C*H*Me$_2$ (**e**)), 3.61 (br decet, ^3J(HC,CH) = 6.6 Hz, ^3J(HC,NH) = 5.8 Hz, C*H*Me$_2$ (**g**)), 3.69 (septet, ^3J(H,H) = 6.6 Hz, C*H*Me$_2$ (**d**)), 7.20-7.77 (set of m, Ar), 7.4, 7.9, 8.8, 9.6, 9.7 (each br, NMe$_n$*H*$_{3-n}^+$); ^{13}C NMR (100 MHz, CD_3CN): δ = 15.9 (CH*Me*$_2$ (**e**)), 16.1 (CH*Me*$_2$ (**d**)), 17.7 (CH*Me*$_2$ (**f**)), 18.1 (Ar*Me* (**b**)), 18.2 (Ar*Me* (**c**)), 19.0 (Ar*Me* (**a**)), 19.6 (CH*Me*$_2$ (**g**)), 29.4 (N*Me*H_2^+ (**f**)), 35.3 (N*Me*H_2^+ (**b**)), 38.7 (N*Me*$_2H^+$ (**e**)), 44.6 (*C*HMe$_2$ (**g**)), 46.7 (N*Me*$_2H^+$ (**a**)), 50.5 (t (1:1:1), ^1J(^{13}C,^{14}N) = 3.9 Hz, N*Me*$_3^+$ (**d**)), 51.2 (*C*HMe$_2$ (**f**)), 57.5 (*C*HMe$_2$ (**e**)), 66.5 (t (1:1:1), ^1J(^{13}C,^{14}N) = 2.0 Hz, *C*HMe$_2$ (**d**)), 120.0, 121.6, 123.1, 126.6, 127.0, 127.4, 127.6, 128.9, 129.2, 129.5, 129.6, 130.9, 131.0, 131.5, 131.8, 131.9, 133.6, 139.7 (Ar).

Alkylation of *o*-toluidine – isopropylamine mixture in MeCN in the presence of CO_2

(**a**) *o*-Toluidine (2.14 g, 20 mmol) was dissolved in MeCN (1.1 ml) in a 50 ml four-necked flask equipped with a magnetic stirrer, thermocouple and capillary for feeding CO_2. The mixture was cooled to -10 °C in an ice/NH_4Cl bath in a slow stream of CO_2. After addition of Pr^iNH_2 (1.3 g, 22 mmol, 1.1 equiv, slight excess due to its volatility), the mixture was cooled to -15 °C, then MeI (8.52 g, 60 mmol, 3 equiv) pre-cooled to -25 °C was added portionwise. The CO_2 supply was stopped after bath temperature reached 0 °C. The reaction mixture was stirred at ambient temperature for 24 hours. A portion of the solution (0.65 ml) was evaporated *in vacuo* at 40 °C, the residue was dissolved in 0.65 ml of CD_3CN for NMR analysis. The main products (~90%) were *o*-Me(C_6H_4)N$Me_2H^+I^-$ (**a**) and *i*Pr$NH_3^+I^-$ (**g**) (Figures S18, S19).

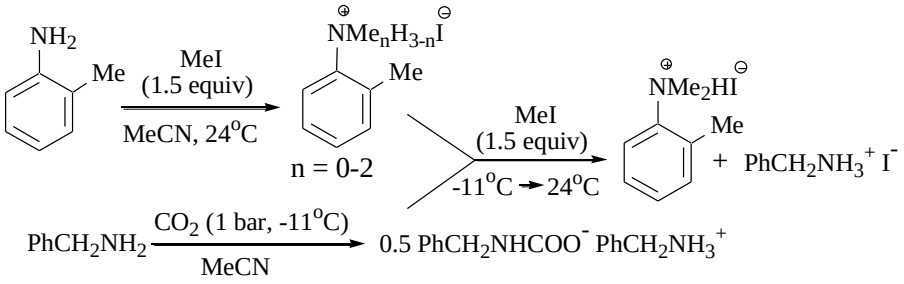
^1H NMR (400 MHz, CD_3CN) (the signals of minor products are omitted): δ = 1.35 (d, ^3J(H,H) = 6.6 Hz, CH*Me*$_2$ (**g**)), 2.59 (s, Ar*Me* (**a**)), 3.22 (s, N*Me*$_2H^+$ (**a**)), 3.60 (br decet,

^3J(HC,CH) = 6.6 Hz, ^3J(HC,NH) = 5.8 Hz, C*H*Me$_2$ (**g**)), 7.29-7.37 (m, H$^{4-6}$(Ar) (**a**)), 7.4 (br, NH_3^+ (**g**)), 7.76 (m, H^3(Ar) (**a**)), 9.6 (br, NMe$_2$*H*$^+$ (**a**)); ^{13}C NMR (100 MHz, CD_3CN): δ = 19.0 (Ar*Me* (**a**)), 19.6 (CH*Me*$_2$ (**g**)), 44.5 (*C*HMe$_2$ (**g**)), 46.8 (N*Me*$_2$H$^+$ (**a**)), 120.1 (C^3(Ar) (**a**)), 127.6, 129.6, 131.9 (C$^{4-6}$(Ar) (**a**)), 129.5 (C^1(Ar) (**a**)), 139.8 (C^2(Ar) (**a**)).

(**b**) In accordance with the general procedure, a solution of *o*-toluidine (0.23 g, 2.15 mmol) and Pr^{i}NH$_2$ (0.14 g, 2.37 mmol, 1.1 equiv, slight excess due to its volatility) in MeCN (0.11 ml) was introduced into the high pressure cell, the pressure of CO_2 was adjusted to 60 bar. After cooling and reducing the pressure, MeI (0.92 g, 6.48 mmol, 3 equiv) was injected. The mixture was stirred 24 hours at ambient temperature. An aliquot (0.2 ml) was dissolved in 0.45 ml of CD_3CN for NMR analysis, the spectrum was almost identical to that presented above for reaction (**a**).

(**c**) The procedure was the same as (**b**), but after adjusting the pressure of CO_2 to 60 bar, ~ 35 ml of liquid CO_2 was added into the cell. The NMR spectral data are almost identical to those presented above for reaction (**a**).

Two-step methylation of the model 1:1 mixture of 2-MeC$_6$H$_4$NH$_2$ + PhCH$_2$NH$_2$ in MeCN in the presence of CO$_2$. A mixture of *o*-toluidine (1.07 g, 10 mmol) and MeI (2.13 g, 15 mmol, 1.5 equiv) was allowed to stand for 24 hours at ambient temperature and then was dissolved in MeCN (4.3 ml). Benzylamine (1.07 g, 10 mmol, 1 equiv) in a 50 ml four-necked flask equipped with a magnetic stirrer, thermocouple and capillary for feeding CO_2 was cooled to -13 °C in an ice/NH_4Cl bath and in a slow CO_2 stream. A solution of the methylated *o*-toluidine was added in several portions while maintaining the temperature below -6 °C, then pre-cooled MeI (2.13 g, 10 mmol, 1.5 equiv) was added, and the CO_2 flow was stopped. The reaction mixture was stirred at ambient temperature for 7 days, and then MeCN (2.5 ml) was added until the precipitate was completely dissolved. An aliquot (0.6 ml) was evaporated *in vacuo* at 40 °C, the residue was dissolved in 0.65 ml of CD_3CN for NMR analysis. The reaction resulted in a 1:1 mixture of 2-Me(C_6H_4)NMe$_2$H$^+$I$^-$ and PhCH$_2$NH$_3^+$I$^-$ (Figures S20, S21).



^{1}H NMR (400 MHz, CD_3CN): δ = 2.62 (s, 3 H, *Me*ArNMe$_2$H$^+$), 3.17 (s, 6 H, MeArN*Me*$_2$H$^+$), 4.19 (s, 2 H, PhC*H*$_2$NH$_3^+$), 7.32-7.42 (set of m, 6 H, *m*-Ph, *p*-Ph, H$^{4-6}$(Ar)), 7.58 (m, 2 H, *o*-Ph), 7.70 (m, 1 H, H^3(Ar)), 7.8 (very br, MeArNMe$_2$*H*$^+$, PhCH$_2$N*H*$_3^+$); ^{13}C NMR (100 MHz, CD_3CN): δ = 19.6 (*Me*ArNMe$_2$H$^+$), 43.2 (PhC*H*$_2$NH$_3^+$), 47.1 (MeArN*Me*$_2$H$^+$), 120.7 (C^3(Ar)), 128.3, 129.93, 132.7 (C$^{4-6}$(Ar)), 128.9 (*m*-Ph), 129.3 (*p*-Ph), 129.89 (*o*-Ph), 130.7 (C^1(Ar)), 132.3 (*i*-Ph), 141.5 (C^2(Ar)).

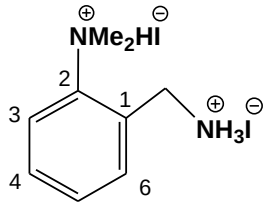
4. Alkylation of diamines

General procedure. All reactions in the presence of CO_2 were carried out in a high-pressure cell in accordance with the general procedure. For NMR analysis 0.1 ml of the reaction mixture was dissolved in 0.5 ml of CD_3CN or DMSO-d_6. Isolation of ammonium salts **5-8** from the reaction mixtures was carried out by precipitation with a fivefold excess (by volume) of MeCN. The resulting suspension was centrifuged, the precipitate was washed with an equal volume of MeCN followed by centrifugation and separation of the liquid by decantation. The procedure was repeated until the supernatant became colorless. The resulting white or beige powder was dried *in vacuo*.

Methylation of 2-$H_2NC_6H_4)H_2NH_2$ (1)

Methylation of 2-$H_2N(C_6H_4)CH_2NH_2$ (1) in the absence of CO_2. Iodomethane (870 mg, 6.13 mmol, 5 equiv) was added in two portions to a solution of **1** (150 mg, 1.23 mmol) in 0.6 ml of MeCN in a 15 ml flask. The mixture was left at room temperature overnight and, then MeCN (1.5 ml) was added until the precipitate was completely dissolved. An aliquot (0.5 ml) was evaporated *in vacuo* to a viscous oil and dissolved in CD_3CN (0.6 ml) for NMR analysis. The reaction resulted in a mixture of 12 products (Figure S22).

Methylation of 2-$H_2N(C_6H_4)CH_2NH_2$ (1) in the presence of CO_2.



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(**a**) A solution of diamine **1** (100 mg, 0.82 mmol) in DMF (0.7 ml) was introduced into the high pressure cell, the pressure of CO_2 was adjusted to 60 bar. After cooling the cell, MeI (700 mg, 4.93 mmol, 6 equiv) was injected and the was stirred for 72 hours at 24 °C. After releasing the CO_2 pressure and adding additional 3 equiv MeI to compensate for its loss upon a pressure relief, stirring at 24 °C was continued for 72 hours. The main product was 2-$HMe_2N^+C_6H_4CH_2NH_3^+$ $2I^-$ (**4**) (94%, brown oil, Figures S23, S24). Besides alkylation by-products, dimethylammonium iodide (~2%) was found in the reaction mixture. Its presence could be due to the hydrolysis of DMF in acid medium by traces of water, or the transformylation reactions of DMF with alkylammonium salts [M. A. Kraus, *Synthesis* **1973**, 361–362.].

(**b**) A solution of diamine **1** (100 mg, 0.82 mmol) in 0.5 ml of DMA was introduced into the high pressure cell, the pressure of CO_2 was adjusted to 10 bar. After cooling the cell, MeI (700 mg,

4.93 mmol, 6 equiv) was injected, and the reaction mixture was stirred 72 hours at 24 °C. The main product (90%) in the reaction mixture (brown oil and solid) was compound **4**. The NMR spectral data are almost identical (with the exception of DMA signals instead of DMF) to those presented below for reaction (**a**).

(**c**) A solution of diamine **1** (100 mg, 0.82 mmol) in 0.3 ml of DMA was introduced into the high pressure cell, the pressure of CO_2 was adjusted to 60 bar. After cooling the cell, MeI (700 mg, 4.93 mmol, 6 equiv) was injected and the reaction mixture was stirred 72 hours at 40 °C. The main product (90%) in the reaction mixture (brown oil and solid) was compound **4**. The NMR spectral data are almost identical (with the exception of DMA signals instead of DMF) to those presented below for reaction (**a**).

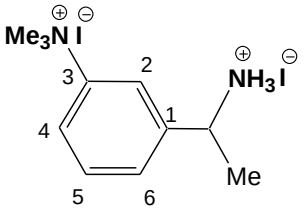
(**d**) A solution of diamine **1** (100 mg, 0.82 mmol) in 0.5 ml of DMA was introduced into the high pressure cell, the pressure of CO_2 was adjusted to 60 bar and ~ 35 ml of liquid CO_2 was added. After cooling the cell, MeI (700 mg, 4.93 mmol, 6 equiv) was injected and the reaction mixture was stirred 144 hours at 24 °C. The main product (80%) in the reaction mixture (brown oil and solid) was compound **4**.

Isolation of salt **4**. The reaction mixture resulted from procedure (**c**) (100 mg, 0.82 mmol of **1**) was dissolved in 5-fold excess of MeCN (3.5 ml), 1.4 ml (one third) of the solution was evaporated *in vacuo*. After the residue was re-dissolved in 2 ml of MeCN, followed by crystallization, the precipitated light yellow powder was separated, washed twice with 0.7 ml of MeCN and dried *in vacuo*. Yield: 46 mg (0.11 mmol) (42%). Light yellow powder (Figures S25, S26).

***N*-[2-(Ammoniomethyl)phenyl]-*N*,*N*-dimethylammonium diiodide** (**4**). Crude material (reaction (**a**)). ^{1}H NMR (400 MHz, CD_3CN): δ = 3.30 (s, 6 H, ArN*Me*$_2$H$^+$), 4.61 (s, 2 H, C*H*$_2$NH$_3^+$), 7.49 (t, ^3J(H,H) = 7.6 Hz, 1 H, H$^{4 \text{ or } 5}$(Ar)), 7.56 (t, ^3J(H,H) = 7.9 Hz, 1 H, H$^{5 \text{ or } 4}$(Ar)), 7.88 (d, ^3J(H,H) = 7.6 Hz, 1 H, H$^{3 \text{ or } 6}$(Ar)), 7.96 (d, ^3J(H,H) = 8.2 Hz, 1 H, H$^{6 \text{ or } 3}$(Ar)), 8.47 (br, 3 H, CH$_2$N*H*$_3^+$); ^{13}C NMR (100 MHz, CD_3CN): δ = 38.1 (CH$_2$NH$_3^+$), 47.3 (ArN*Me*$_2$H$^+$), 121.2, 124.8, 130.7, 131.9 (C$^{3\text{-}6}$(Ar)), 129.5 (C^1(Ar)), 140.9 (C^2(Ar)). Purified material. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 2.89 (br s, 6 H, ArN*Me*$_2$H$^+$), 4.17 (q, ^3J(HC,NH) = 5.6 Hz, 2 H, C*H*$_2$NH$_3^+$), 7.34 (br t, 1 H, H^5(Ar)), 7.49 (t, ^3J(H,H) = 7.6 Hz, 1 H, H^4(Ar)), 7.51 (d, ^3J(H,H) = 7.6 Hz, 1 H, H^6(Ar)), 7.55 (br, 1 H, H^3(Ar)), 8.12 (br, 3 H, CH$_2$N*H*$_3^+$); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ = 38.1 (CH$_2$NH$_3^+$), 45.8 (ArN*Me*$_2$H$^+$), 120.6 (C^4(Ar)), 126.4, 130.3 (each br, C^{3,5}(Ar)), 127.6 (C^1(Ar)), 130.1 (C^6(Ar)), C^2(Ar) is not observable (very br); elemental analysis calcd (%) for $C_9H_{16}I_2N_2$: C 26.62, H 3.97, N 6.90; found: C 26.53, H 3.91, N 6.93.

Alkylation of 3-$H_2NC_6H_4CH(Me)NH_2$ (2)

Methylation of 2

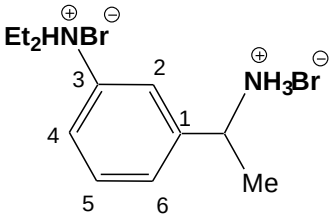


5

A solution of diamine **2** (70 mg, 0.51 mmol) in DMA (0.3 ml) was introduced into the high pressure cell, the pressure of CO_2 was adjusted to 60 bar. After cooling the cell, MeI (440 mg, 3.10 mmol, 6 equiv) was injected, and the mixture was stirred 48 hours at 37 °C. The main product (92%) in the reaction mixture (brown oil) was salt **5** (Figures S27, S28). The isolation of **5** from the reaction mixture resulting from 70 mg (0.51 mmol) of **2** in 0.3 ml of DMA was carried out in accordance with the general procedure (page S8). Yield: 92 mg (0.21 mmol) (41%). Beige powder (Figures S29, S30).

***N*-[3-(1-Ammonioethyl)phenyl]-*N*,*N*,*N*-trimethylammonium diiodide** (**5**). Crude material. ^{1}H NMR (400 MHz, CD_3CN): δ = 1.78 (d, ^3J(H,H) = 6.8 Hz, 3 H, CH(*Me*)NH_3^+), 3.82 (s, 9 H, ArN*Me*$_3^+$), 4.83 (br septet, ^3J(HC,CH) ~ ^3J(HC,NH), 1 H, C*H*(Me)NH_3^+), 7.67 (t, ^3J(H,H) = 8.1 Hz, 1 H, H^5(Ar)), 7.80 (d, ^3J(H,H) = 7.7 Hz, 1 H, $H^{6\text{ or }4}$(Ar)), 8.03 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 2.8 Hz, 1 H, $H^{4\text{ or }6}$(Ar)), 8.44 (br s, 1 H, H^2(Ar)), 8.78 (br, 3 H, CH(Me)N*H*$_3^+$); ^{13}C NMR (100 MHz, CD_3CN): δ = 20.2 (CH(*Me*)NH_3^+), 50.9 (*C*H(Me)NH_3^+), 57.3 (ArN*Me*$_3^+$), 120.5, 120.7 ($C^{2,4}$(Ar)), 129.3, 130.7 ($C^{5,6}$(Ar)), 140.7 (C^1(Ar)), 147.0 (C^3(Ar)). Purified material. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.53 (d, ^3J(H,H) = 6.8 Hz, 3 H, CH(*Me*)NH_3^+), 3.62 (s, 9 H, ArN*Me*$_3^+$), 4.55 (br m, 1 H, C*H*(Me)NH_3^+), 7.67 (d, ^3J(H,H) = 7.8 Hz, 1 H, $H^{4\text{ or }6}$ (Ar)), 7.72 (t, ^3J(H,H) = 7.9 Hz, 1 H, H^5(Ar)), 7.97 (dd, ^3J(H,H) = 8.2 Hz, ^4J(H,H) = 2.8 Hz, 1 H, $H^{6\text{ or }4}$(Ar)), 8.08 (br s, 1 H, H^2(Ar)), 8.29 (br, 3 H, CH(Me)N*H*$_3^+$); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.5 (CH(*Me*)NH_3^+), 49.7 (*C*H(Me)NH_3^+), 56.5 (ArN*Me*$_3^+$), 119.5, 120.5 ($C^{2,4}$(Ar)), 128.1, 130.6 ($C^{5,6}$(Ar)), 141.2 (C^1(Ar)), 147.3 (C^3(Ar)); elemental analysis calcd (%) for $C_{11}H_{20}I_2N_2$: C 30.44, H 4.64, N 6.45; found: C 30.31, H 4.58, N 6.36.

Ethylation of diamine 2



6

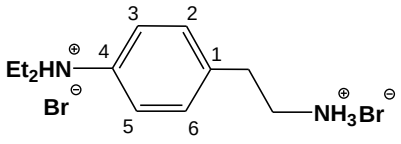
A solution of diamine **2** (100 mg, 0.73 mmol) in DMA (0.3 ml) was introduced into the high pressure cell, the pressure of CO_2 was adjusted to 60 bar. After cooling the cell, EtBr (480 mg, 4.41 mmol, 6 equiv) was injected, and the reaction mixture was stirred 144 hours at 37 °C. The main product (90%) in the reaction mixture (brown oil and solid) was salt **6** (Figure S31). The

isolation of **6** from the reaction mixture resulting from 100 mg (0.73 mmol) of **2** in 0.3 ml of DMA was carried out in accordance with the general procedure (page S8). Yield: 170 mg (0.48 mmol) (66%). Light yellow powder. The product is contaminated with ~4 mol% 3-$EtH_2N^+C_6H_4CH(Me)NH_3^+$ $2Br^-$ (Figures S32, S33).

***N*-[3-(1-Ammonioethyl)phenyl]-*N*,*N*-diethylammonium dibromide** (**6**). Crude material. ^{1}H NMR (400 MHz, CD_3CN): δ = 1.13 (t, ^3J(H,H) = 7.2 Hz, 6 H, $ArN(CH_2C\mathit{H}_3)_2H^+$), 1.74 (d, ^3J(H,H) = 6.9 Hz, 3 H, $CH(\mathit{Me})NH_3^+$), 3.61 (m, *ABX*$_3$-spin system, 4 H, $ArN(C\mathit{H}_2CH_3)_2H^+$), 4.63 (br, 1 H, $C\mathit{H}(Me)NH_3^+$), 7.59 (t, ^3J(H,H) = 7.9 Hz, 1 H, H^5(Ar)), 7.70 (d, ^3J(H,H) = 7.8 Hz, 1 H, $H^{4\text{ or }6}$ (Ar)), 7.89 (d, ^3J(H,H) = 8.0 Hz, 1 H, $H^{6\text{ or }4}$ (Ar)), 8.28 (s, 1 H, H^2(Ar)), 8.49 (br, 3 H, $CH(Me)N\mathit{H}_3^+$), 12.2 (br, 1 H, $ArN(CH_2CH_3)_2\mathit{H}^+$). Purified material. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.02 (t, ^3J(H,H) = 6.9 Hz, 6 H, $ArN(CH_2C\mathit{H}_3)_2H^+$), 1.54 (d, ^3J(H,H) = 6.6 Hz, 3 H, $CH(\mathit{Me})NH_3^+$), 3.59 (br, 4 H, $ArN(C\mathit{H}_2CH_3)_2H^+$), 4.49 (br, 1 H, $C\mathit{H}(Me)NH_3^+$), 7.36-7.80 (set of br m, 3 H, $H^{4\text{-}6}$ (Ar)), 7.95 (br, 1 H, H^2(Ar)), 8.48 (br, 3 H, $CH(Me)N\mathit{H}_3^+$), 11.7 (br, 1 H, $ArN(CH_2CH_3)_2\mathit{H}^+$); ^{13}C NMR (100 MHz, DMSO-d_6): δ=10.3 ($ArN(CH_2\mathit{C}H_3)_2H^+$), 20.3 ($CH(\mathit{Me})NH_3^+$), 49.7 ($\mathit{C}H(Me)NH_3^+$), 52.5 (br, $ArN(\mathit{C}H_2CH_3)_2H^+$), 121.4, 123.4 (each br, $C^{2,4}$(Ar)), 128.3 (br, C^6(Ar)), 130.3 (C^5(Ar)), 137.7 (br, C^3(Ar)), 141.4 (C^1(Ar)). Methylene protons of ethyl groups give the *ABX*$_3$-spin system in ^{1}H NMR spectrum of salt **6** in CD_3CN due to the presence of a chiral center in the molecule. Elemental analysis calcd (%) for $C_{12}H_{22}Br_2N_2$: C 40.70, H 6.26, N 7.91; found: C 40.57, H 6.32, N 7.93.

Alkylation of 4-$H_2NC_6H_4CH_2CH_2NH_2$ (3)

Ethylation of 3



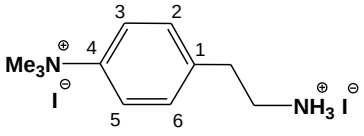
7

A solution of diamine **3** (100 mg, 0.73 mmol) in DMA (0.3 ml) was introduced into the high pressure cell, the pressure of CO_2 was adjusted to 60 bar. After cooling the cell, EtBr (320 mg, 2.94 mmol, 4 equiv) was injected, and the mixture was stirred at 55 °C for 72 hours. The main product (93%) (brown oil and solid) was salt **7**. The isolation of **7** from the reaction mixture resulting from 100 mg (0.73 mmol) of **3** in 0.3 ml of DMA was carried out in accordance with the general procedure (page S8). Yield: 217 mg (0.61 mmol) (84%). White powder (Figures S39, S40).

***N*-[4-(2-Ammonioethyl)phenyl]-*N*,*N*-diethylammonium dibromide** (**7**). Crude material. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.99 (t, ^3J(H,H) = 7.0 Hz, 6 H, $ArN(CH_2C\mathit{H}_3)_2H^+$), 3.00 (br m, 2 H, $ArC\mathit{H}_2$), 3.08 (br m, 2 H, $C\mathit{H}_2NH_3^+$), 3.59 (q, ^3J(H,H) = 7.0 Hz, 4 H, $ArN(C\mathit{H}_2CH_3)_2H^+$), 7.50 (d, ^3J(H,H) = 8.0 Hz, 2 H, $H^{2,6}$), 7.81 (d, ^3J(H,H) = 8.0 Hz, 2 H, $H^{3,5}$), 8.16 (br, 3 H, $CH_2N\mathit{H}_3^+$), 11.8 (br, 1 H, $ArN(CH_2CH_3)_2\mathit{H}^+$); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 9.9 ($ArN(CH_2\mathit{C}H_3)_2H^+$), 32.1 ($ArCH_2$), 39.5 ($CH_2NH_3^+$), 52.7 ($ArN(\mathit{C}H_2CH_3)_2H^+$), 123.1 ($C^{3,5}$), 130.5 ($C^{2,6}$), 136.1 ($C^4$), 139.4 ($C^1$).

Purified material. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 1.01 (t, ^3J(H,H) = 7.0 Hz, 6 H, ArN(CH$_2$C*H*$_3$)$_2$H$^+$), 2.94 (br m, 2 H, ArC*H*$_2$), 3.08 (br m, 2 H, C*H*$_2$NH$_3^+$), 3.57 (br m (overlaps with the signal of H$_2$O), 4 H, ArN(C*H*$_2$CH$_3$)$_2$H$^+$), 7.50 (br m, 2 H, H^{2,6}), 7.72 (br m, 2 H, H^{3,5}), 7.94 (br, 3 H, CH$_2$N*H*$_3^+$), 11.5 (br, 1 H, ArN(CH$_2$CH$_3$)$_2$*H*$^+$); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ = 10.0 (ArN(CH$_2$*C*H$_3$)$_2$H$^+$), 32.3 (Ar*C*H$_2$), 39.5 (overlaps with the signal of the solvent, CH$_2$NH$_3^+$), 52.7 (ArN(*C*H$_2$CH$_3$)$_2$H$^+$), 122.9 (C^{3,5}), 130.5 (C^{2,6}), 136.0 (C^4), 139.3 (C^1). The accuracy of the product signals assignment in ^{1}H and ^{13}C NMR spectra was approved by *DEPT*, *COSY* and *HMQC* experiments (Figures S34-S38). Elemental analysis calcd (%) for C$_{12}$H$_{22}$Br$_2$N$_2$: C 40.70, H 6.26, N 7.91; found: C 40.54, H 6.17, N 7.89.

Methylation of 3



8

A solution of diamine **3** (100 mg, 0.73 mmol) in DMA (0.3 ml) was introduced into the high pressure cell, the pressure of CO$_2$ was adjusted to 60 bar. After cooling the cell, MeI (625 mg, 4.40 mmol, 6 equiv) was injected, and the reaction mixture was stirred at 52 °C for 55 hours. The main product (96%) in the reaction mixture (brown oil) was salt **8** (Figures S41-S43). The isolation of **8** from the reaction mixture resulting from 100 mg (0.73 mmol) of **3** in 0.3 ml of DMA was carried out in accordance with the general procedure (page S8). Yield: 101 mg (0.23 mmol) (32%). Light yellow powder (Figures S44, S45).

***N*-[4-(2-Ammonioethyl)phenyl]-*N*,*N*,*N*-trimethylammonium diiodide** (**8**). Crude material. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 2.92 (m (overlaps with the signal of DMA), 2 H, ArC*H*$_2$), 3.10 (br m, 2 H, C*H*$_2$NH$_3^+$), 3.62 (s, 9 H, ArN*Me*$_3^+$), 7.52 (d, ^3J(H,H) = 8.7 Hz, 2 H, H^{2,6}), 7.82 (br, 3 H, CH$_2$N*H*$_3^+$), 7.94 (d, ^3J(H,H) = 8.7 Hz, 2 H, H^{3,5}); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ = 32.1 (Ar*C*H$_2$), 39.5 (CH$_2$NH$_3^+$), 56.5 (ArN*Me*$_3^+$), 120.6 (C^{3,5}), 130.2 (C^{2,6}), 139.4 (C^1), 145.9 (C^4).

Purified material. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 2.91 (m, 2 H, ArC*H*$_2$), 3.08 (br m, 2 H, C*H*$_2$NH$_3^+$), 3.58 (s, 9 H, ArN*Me*$_3^+$), 7.51 (d, ^3J(H,H) = 8.8 Hz, 2 H, H^{2,6}), 7.78 (br, 3 H, CH$_2$N*H*$_3^+$), 7.91 (d, ^3J(H,H) = 8.8 Hz, 2 H, H^{3,5}); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ = 32.1 (Ar*C*H$_2$), 39.4 (CH$_2$NH$_3^+$), 56.4 (ArN*Me*$_3^+$), 120.6 (C^{3,5}), 130.2 (C^{2,6}), 139.5 (C^1), 145.9 (C^4); elemental analysis calcd (%) for C$_{11}$H$_{20}$I$_2$N$_2$: C 30.44, H 4.64, N 6.45; found: C 30.31, H 4.58, N 6.48.

It should be noted that trimethylammonium salts **5** and **8** in DMSO-d$_6$ give narrow signals in ^{1}H and ^{13}C NMR spectra. At the same time, the signals corresponding to atoms in the nearest environment of the nitrogen atom of the arylammonium group, as well as those in *ortho*- and *para*-positions with respect to it, in dialkylammonium salts **4**, **6** and **7**, are significantly broadened. This broadening is particularly pronounced for salt **6**. Apparently, this is due to the proton exchange between the dialkylarylammonium group and the solvent. The transfer of a proton to a DMSO molecule should be most effective for the least basic nitrogen atom in the *meta*-derivative **6**. This is

in good agreement with the higher methylation rate of **2** compared to **3**. An increase in the concentration of samples leads to a narrowing of the signals of ammonium salts and a simultaneous broadening of the signals of the solvent in ^{1}H and ^{13}C NMR spectra. This fact is also consistent with a proton exchange between ammonium salts and DMSO.

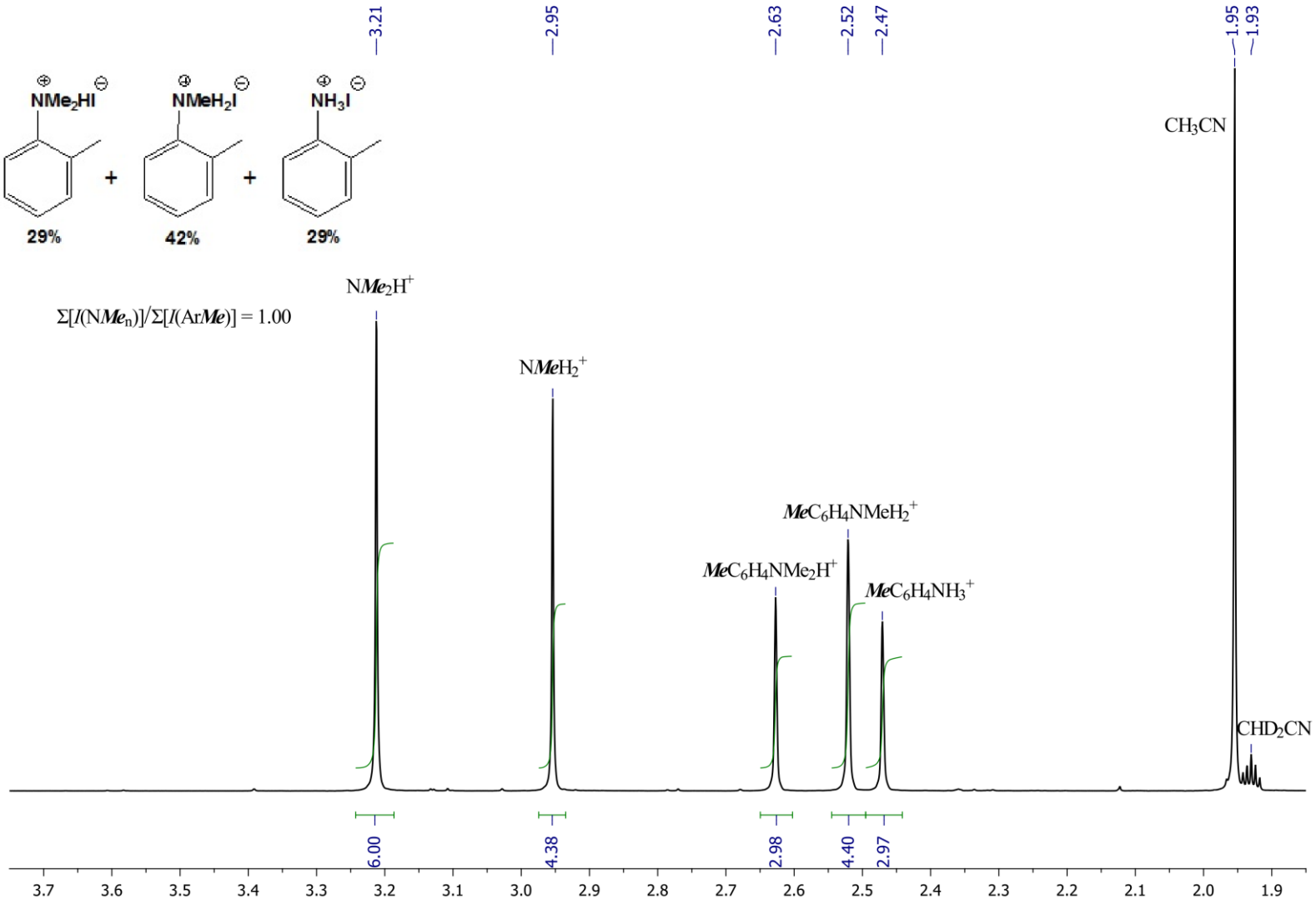


Figure S2. ^{1}H NMR spectrum (aliphatic region) of the reaction mixture 2-Me(C_6H_4)NH_2 + MeI (1 : 3 in MeCN, 60 °C, 4 hours) in CD_3CN.

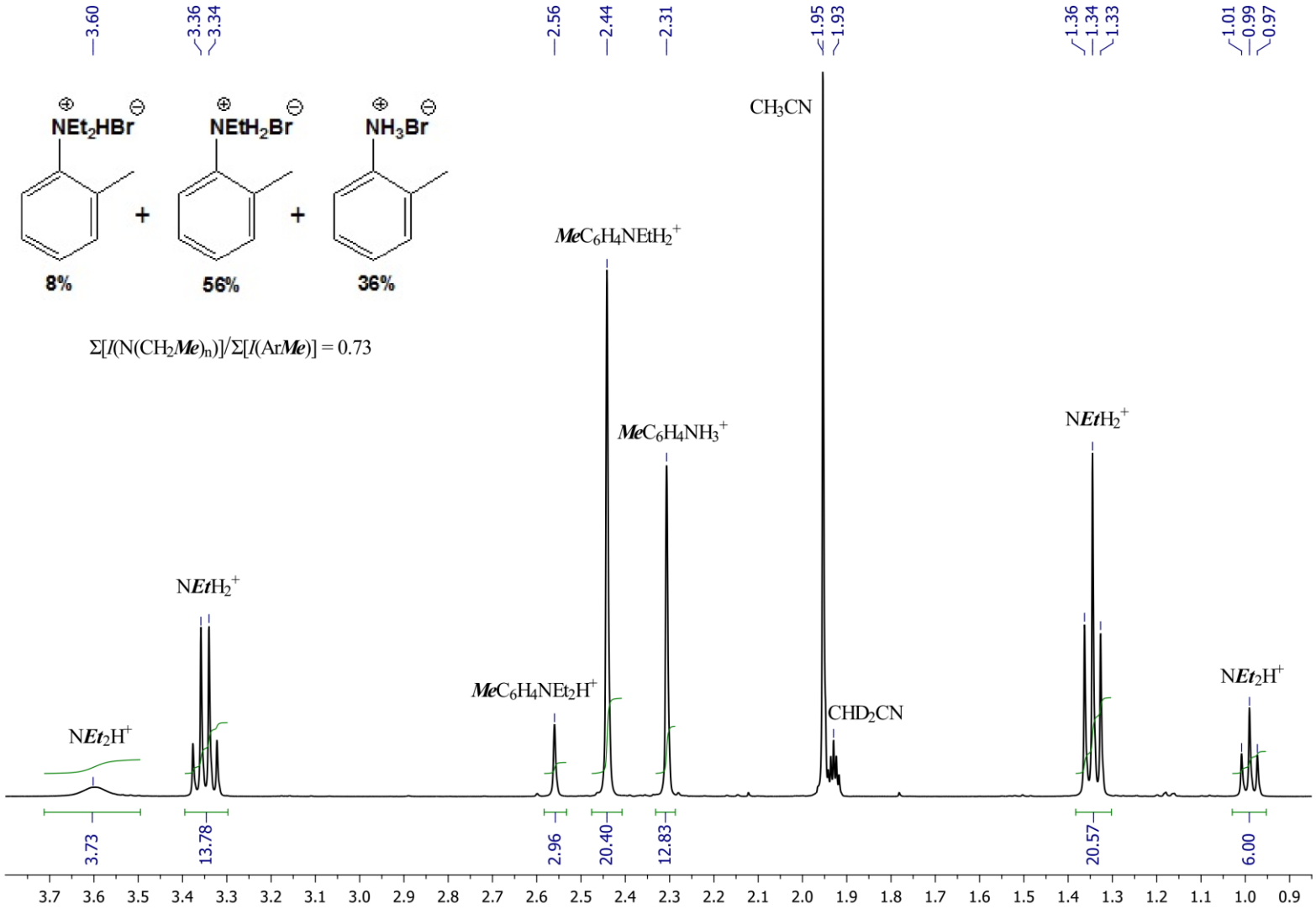


Figure S3. ^{1}H NMR spectrum (aliphatic region) of the reaction mixture 2-Me$C_6H_4NH_2$ + EtBr (1 : 3 in MeCN, 60 °C, 4 hours) in CD_3CN.

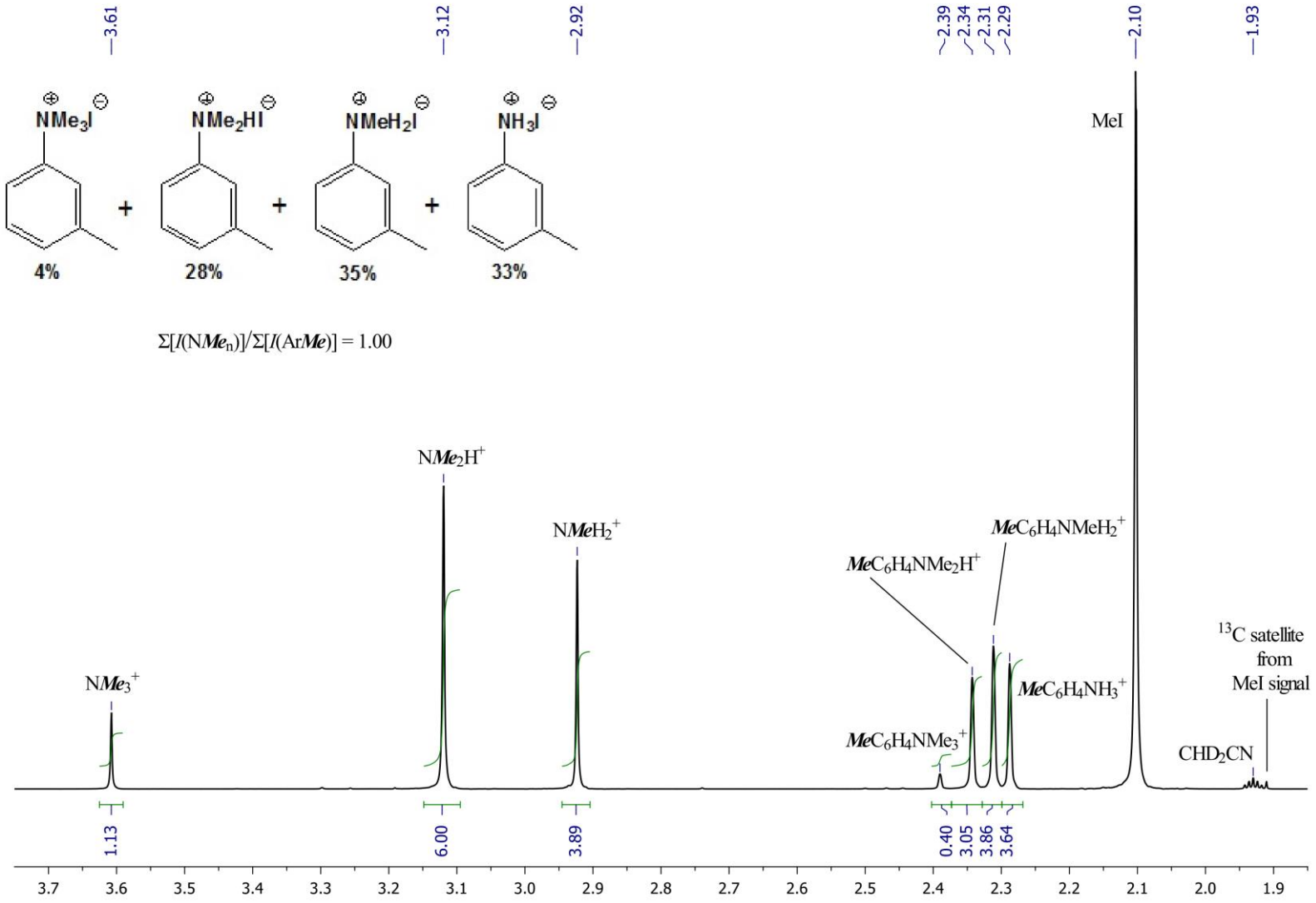


Figure S4. ^{1}H NMR spectrum (aliphatic region) of the reaction mixture 3-Me$C_6H_4NH_2$ + MeI (1 : 3 in MeCN, 60 °C, 4 hours) in CD_3CN.

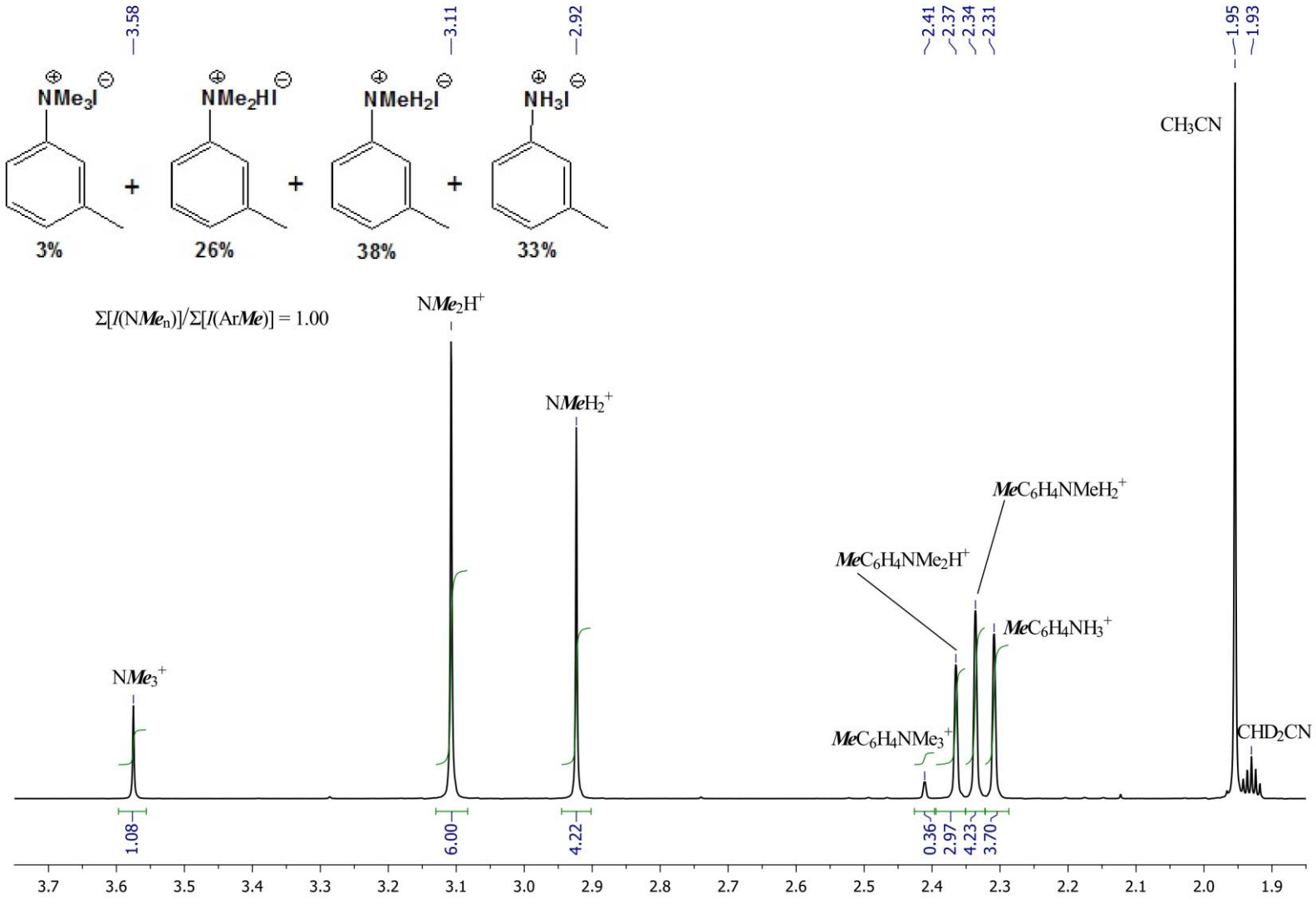


Figure S5. ^{1}H NMR spectrum (aliphatic region) of the reaction mixture 3-Me$C_6H_4NH_2$ + MeI (1 : 3 in MeCN, 22 °C, 24 hours) in CD_3CN.

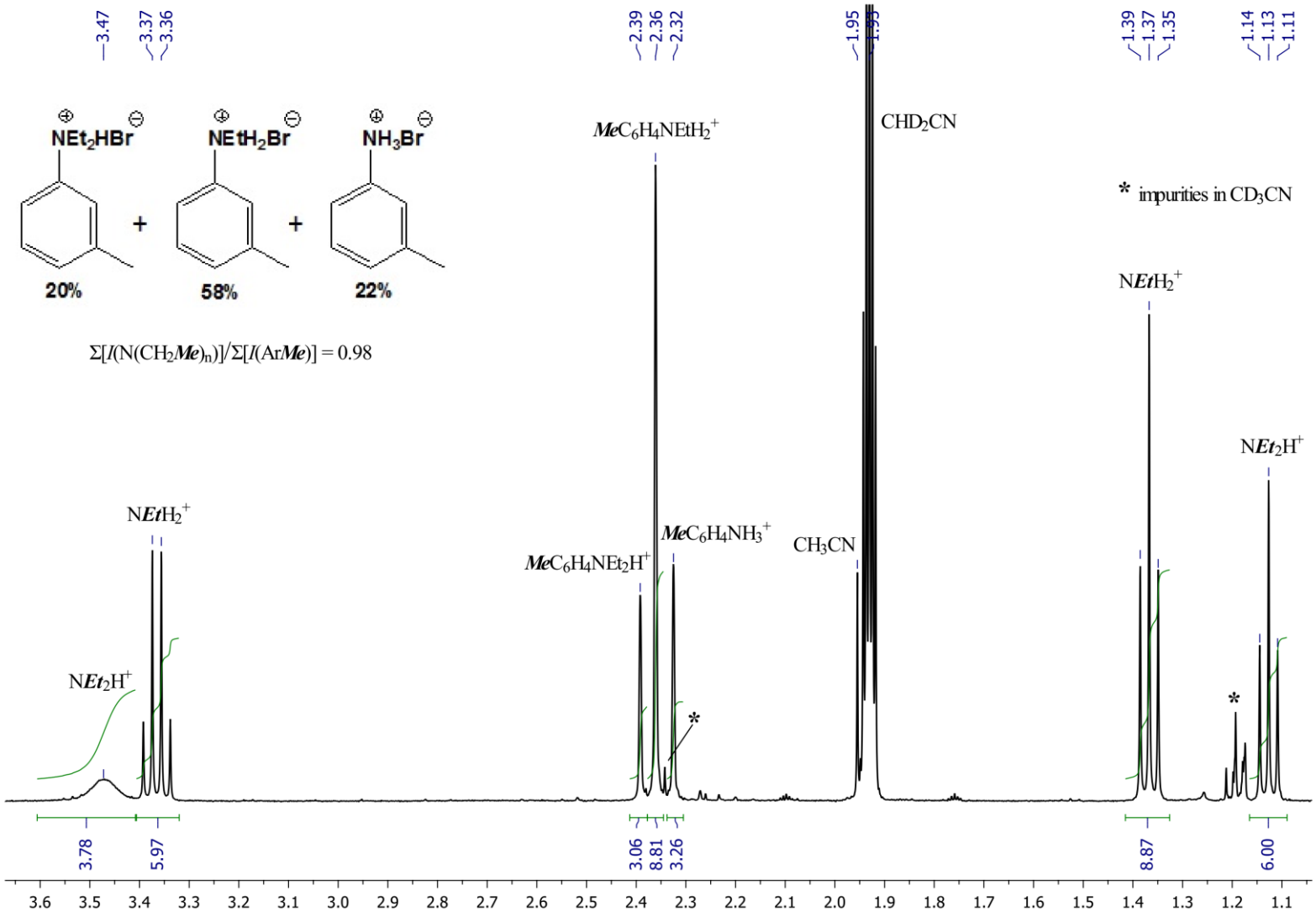


Figure S6. ^{1}H NMR spectrum (aliphatic region) of the reaction mixture 3-Me$C_6H_4NH_2$ + EtBr (1 : 3 in MeCN, 60 °C, 4 hours) in CD_3CN.

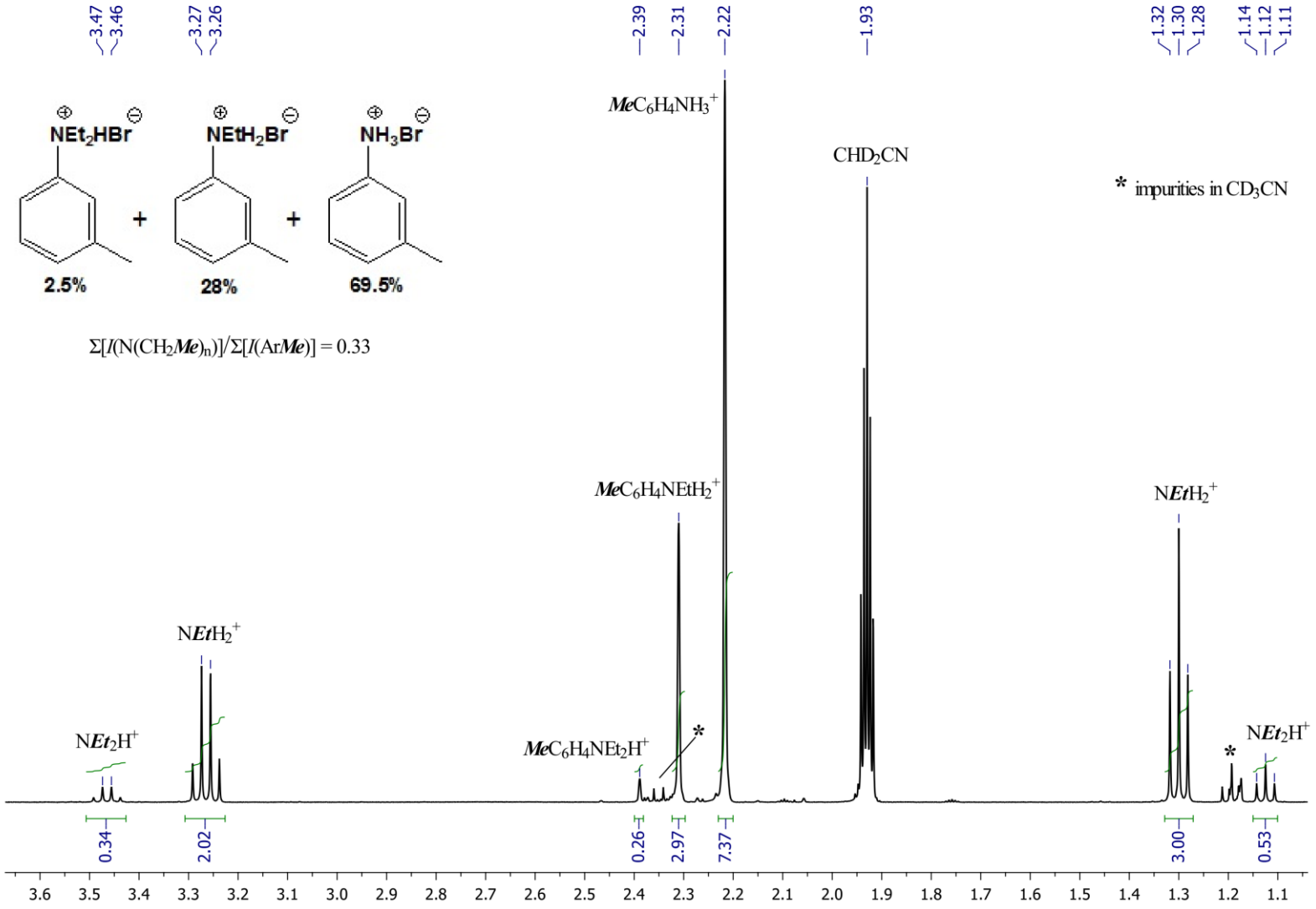


Figure S7. ^{1}H NMR spectrum (aliphatic region) of the reaction mixture 3-Me$C_6H_4NH_2$ + EtBr (1 : 3 in MeCN, 22 °C, 24 hours) in CD_3CN.

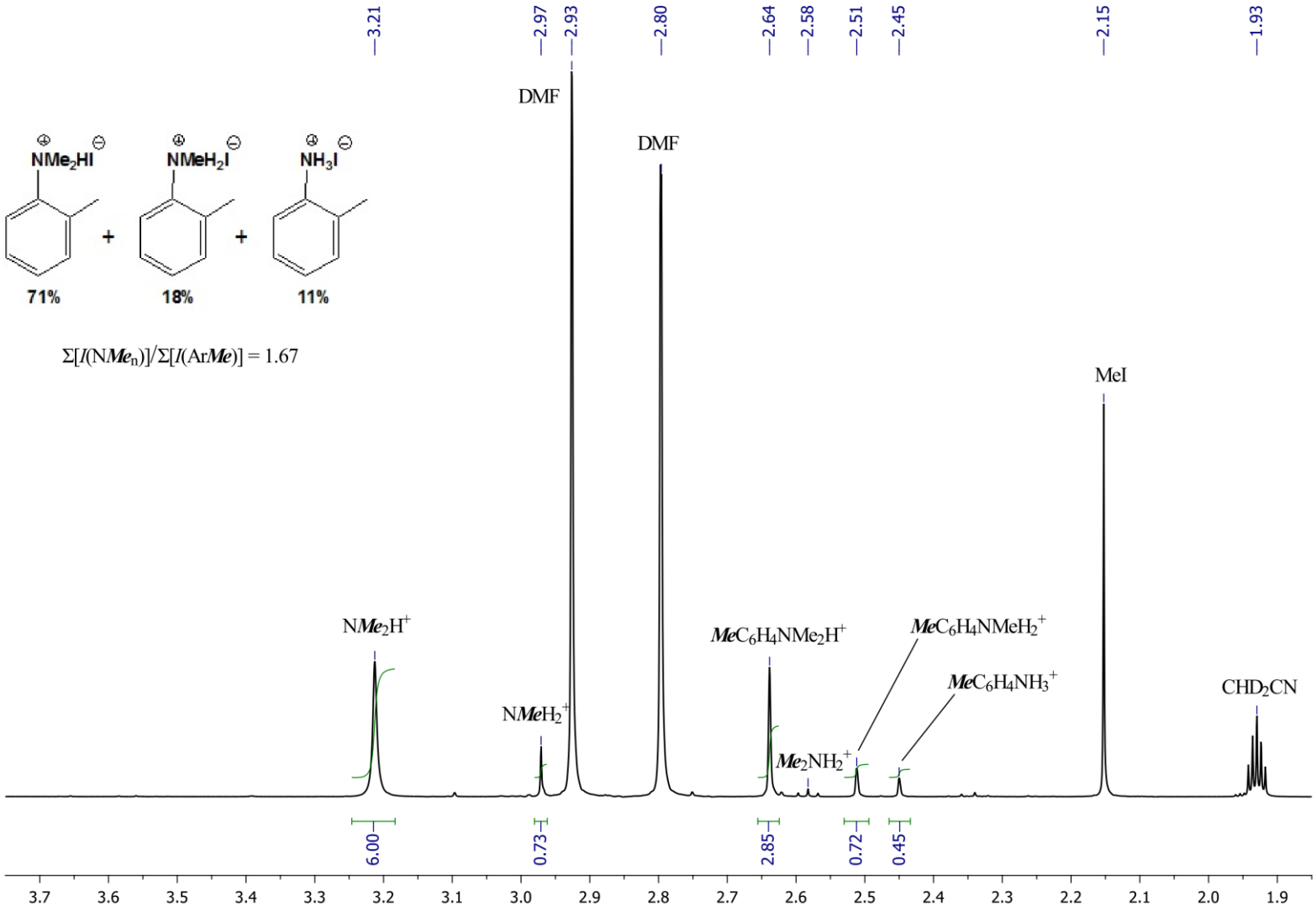


Figure S8. ^{1}H NMR spectrum (aliphatic region) of the reaction mixture 2-Me$C_6H_4NH_2$ + MeI (1 : 6 in DMF, 50 °C, 24 hours) in CD_3CN.

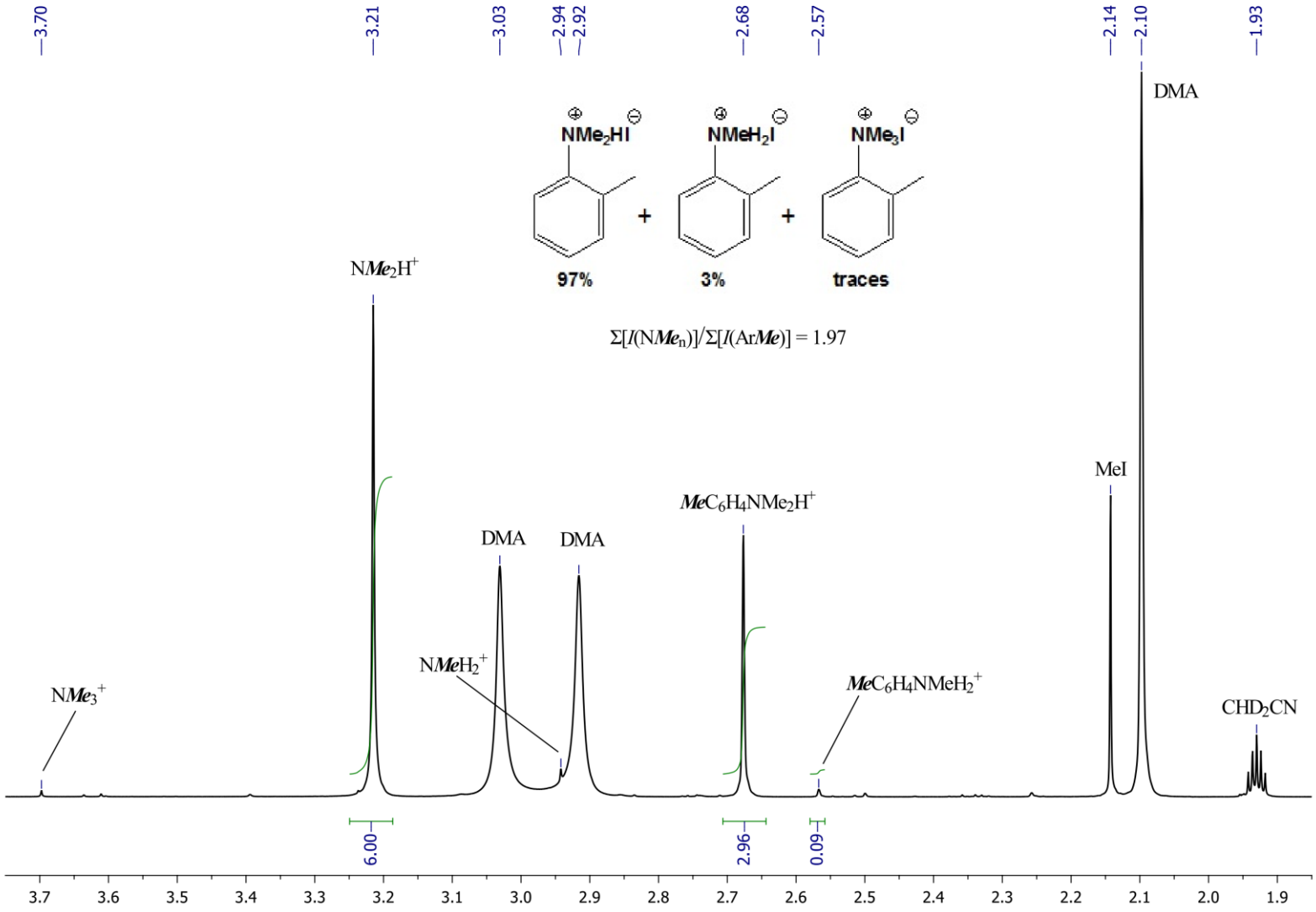


Figure S9. ^{1}H NMR spectrum (aliphatic region) of the reaction mixture 2-Me$C_6H_4NH_2$ + MeI (1 : 6 in DMA, 50 °C, 24 hours) in CD_3CN.

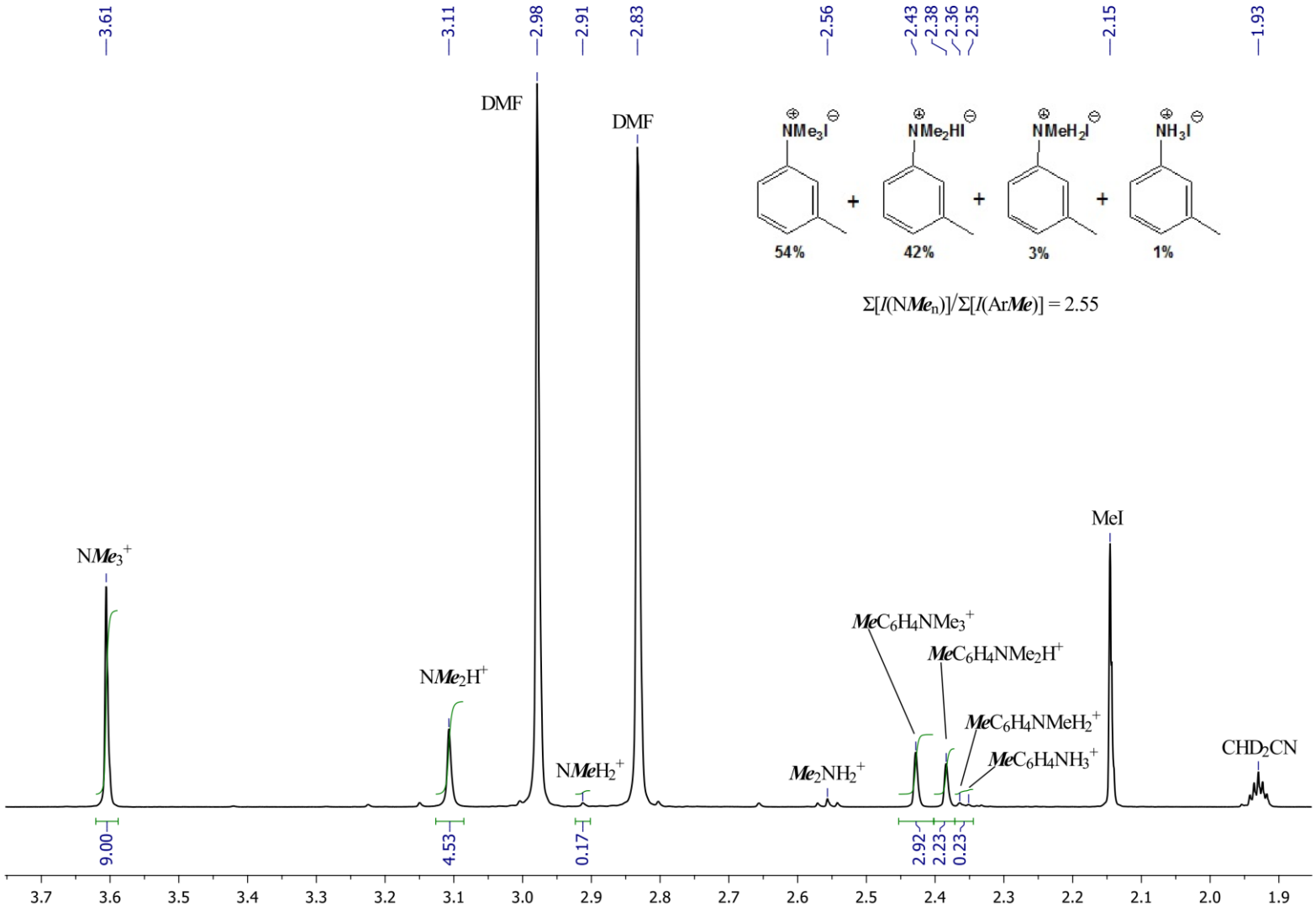


Figure S10. ^{1}H NMR spectrum (aliphatic region) of the reaction mixture 3-$MeC_6H_4NH_2$ + MeI (1 : 6 in DMF, 60 °C, 72 hours) in CD_3CN.

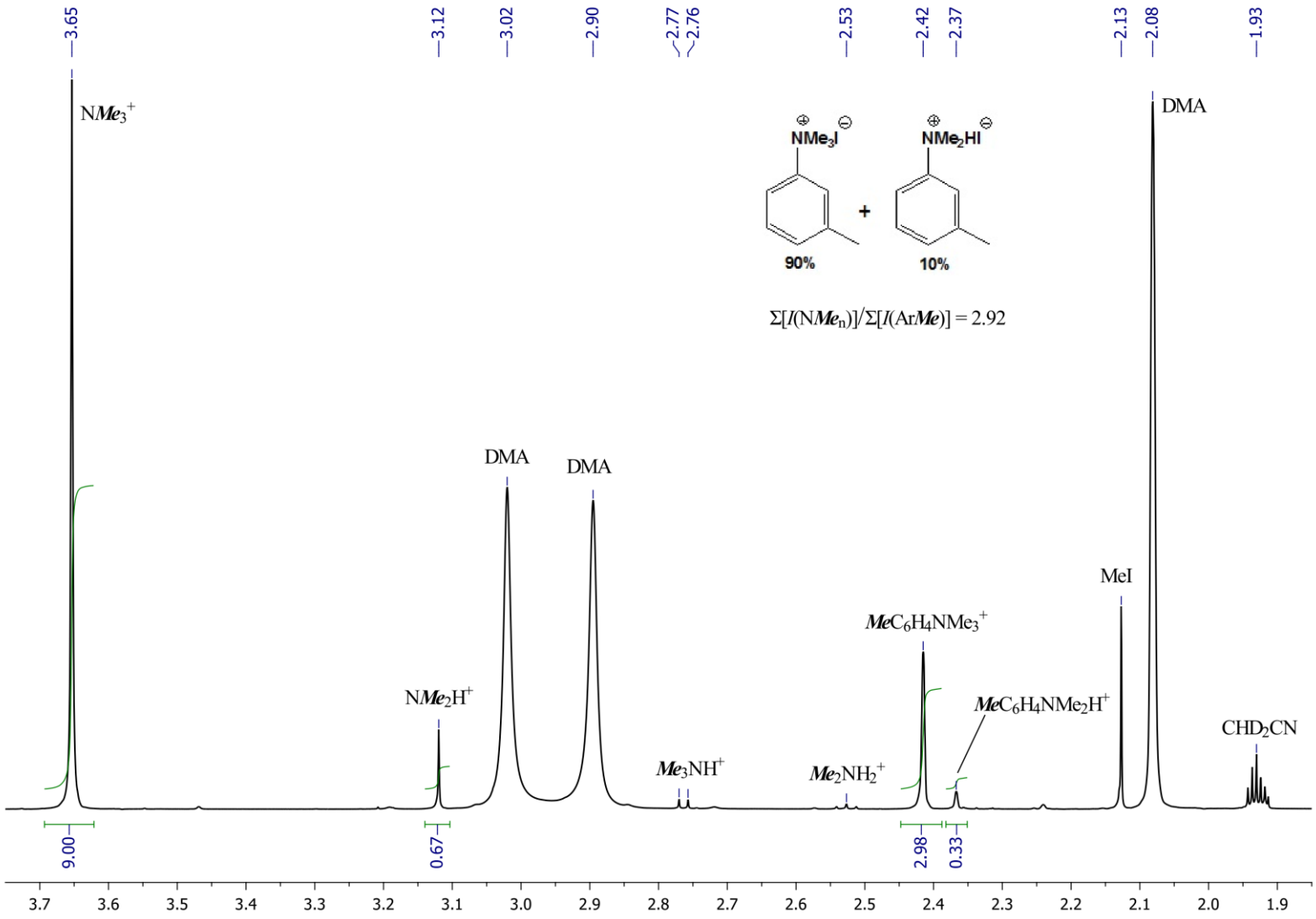


Figure S11. ^{1}H NMR spectrum (aliphatic region) of the reaction mixture 3-$MeC_6H_4NH_2$ + MeI (1 : 6 in DMA, 60 °C, 72 hours) in CD_3CN.

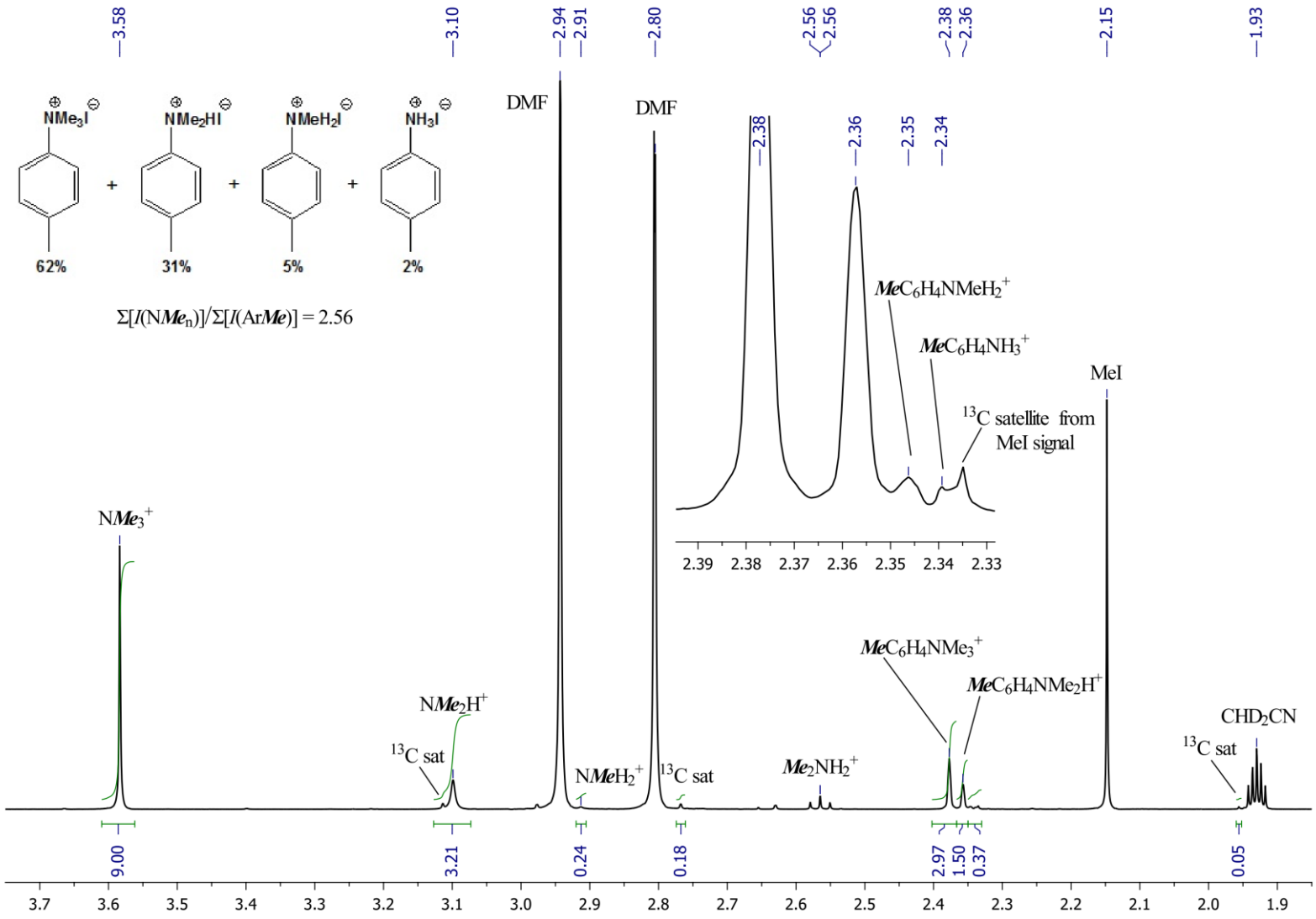


Figure S12. ^{1}H NMR spectrum (aliphatic region) of the reaction mixture 4-Me$C_6H_4NH_2$ + MeI (1 : 6 in DMF, 60 °C, 72 hours) in CD_3CN.

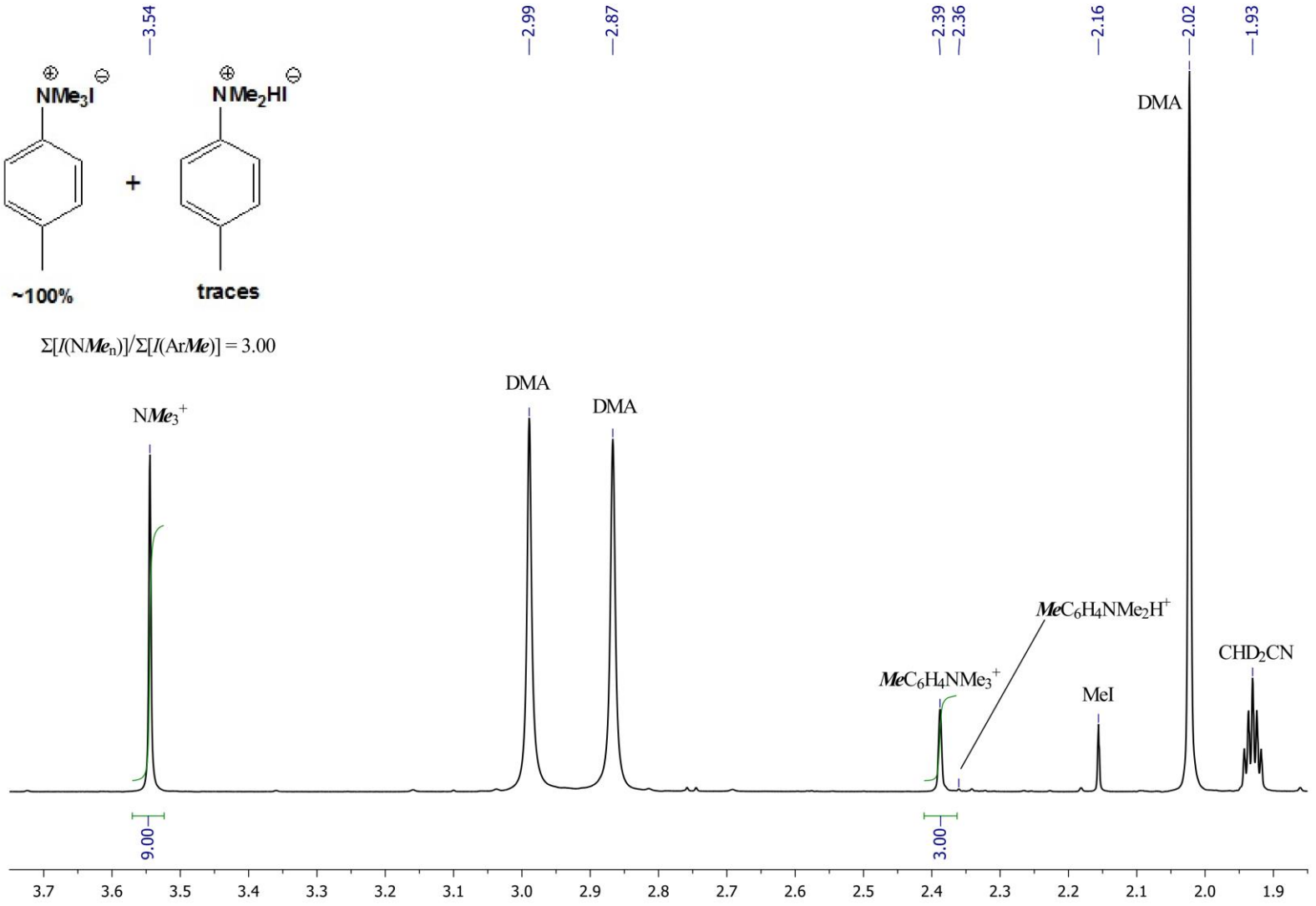


Figure S13. ^{1}H NMR spectrum (aliphatic region) of the reaction mixture 4-Me$C_6H_4NH_2$ + MeI (1 : 6 in DMA, 60 °C, 72 hours) in CD_3CN.

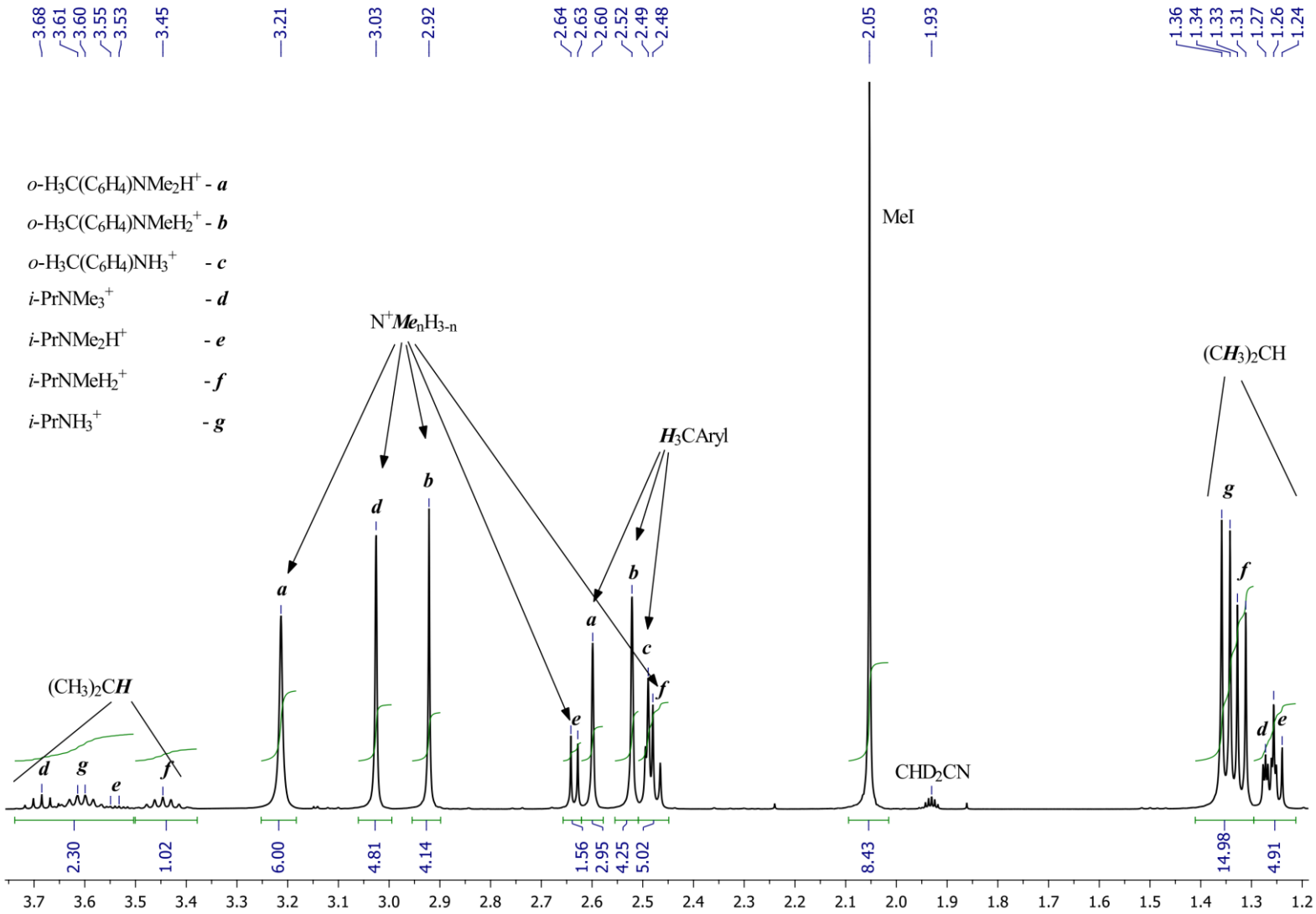


Figure S14. ^{1}H NMR spectrum (aliphatic region) of the model reaction mixture 2-Me$C_6H_4NH_2$ + *i*-PrNH_2 + MeI (1 : 1.1 : 3) in CD_3CN (in the tube for NMR).

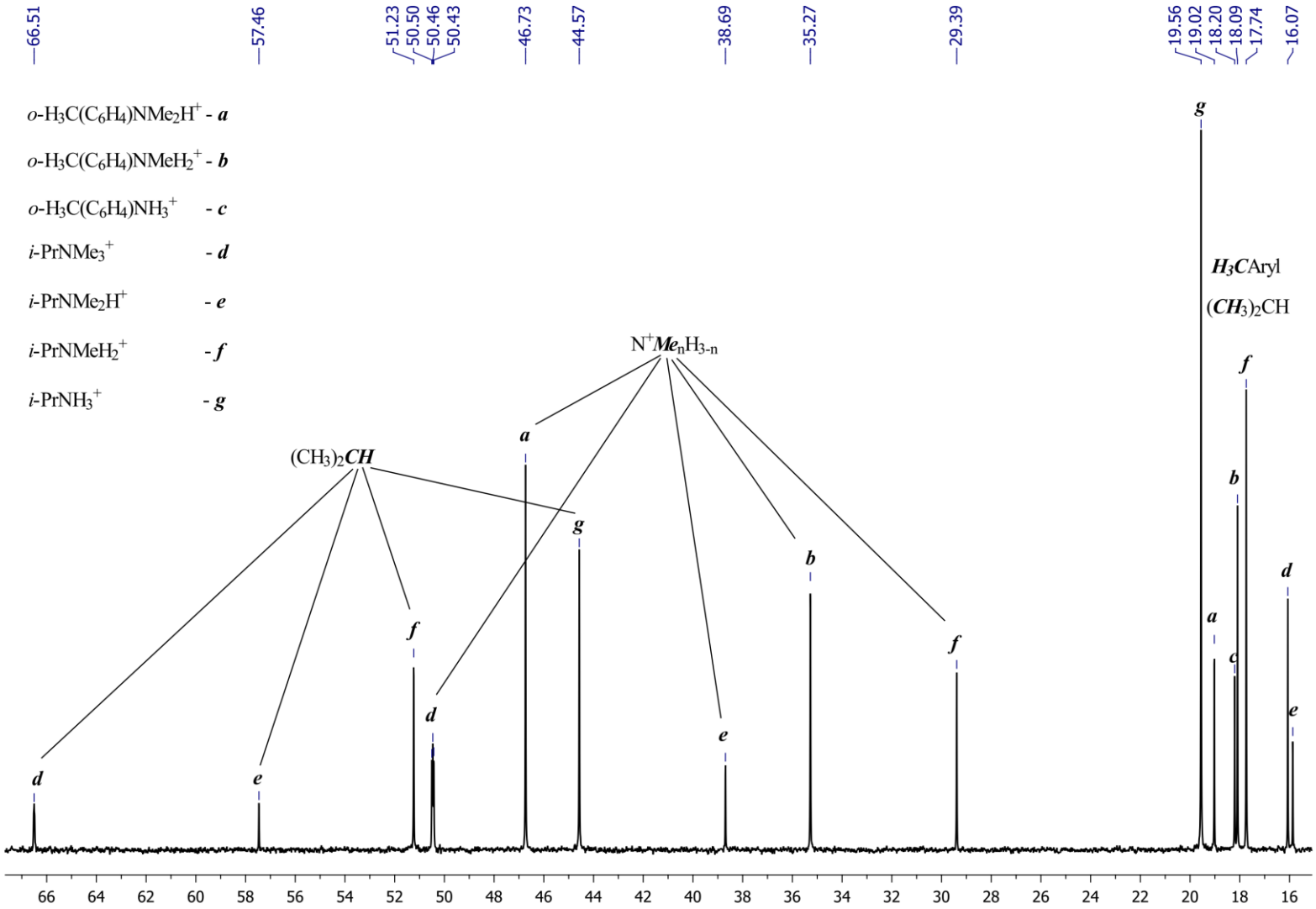


Figure S15. ^{13}C NMR spectrum (aliphatic region) of the model reaction mixture 2-Me$C_6H_4NH_2$ + *i*-PrNH_2 + MeI (1 : 1.1 : 3) in CD_3CN (in the tube for NMR).

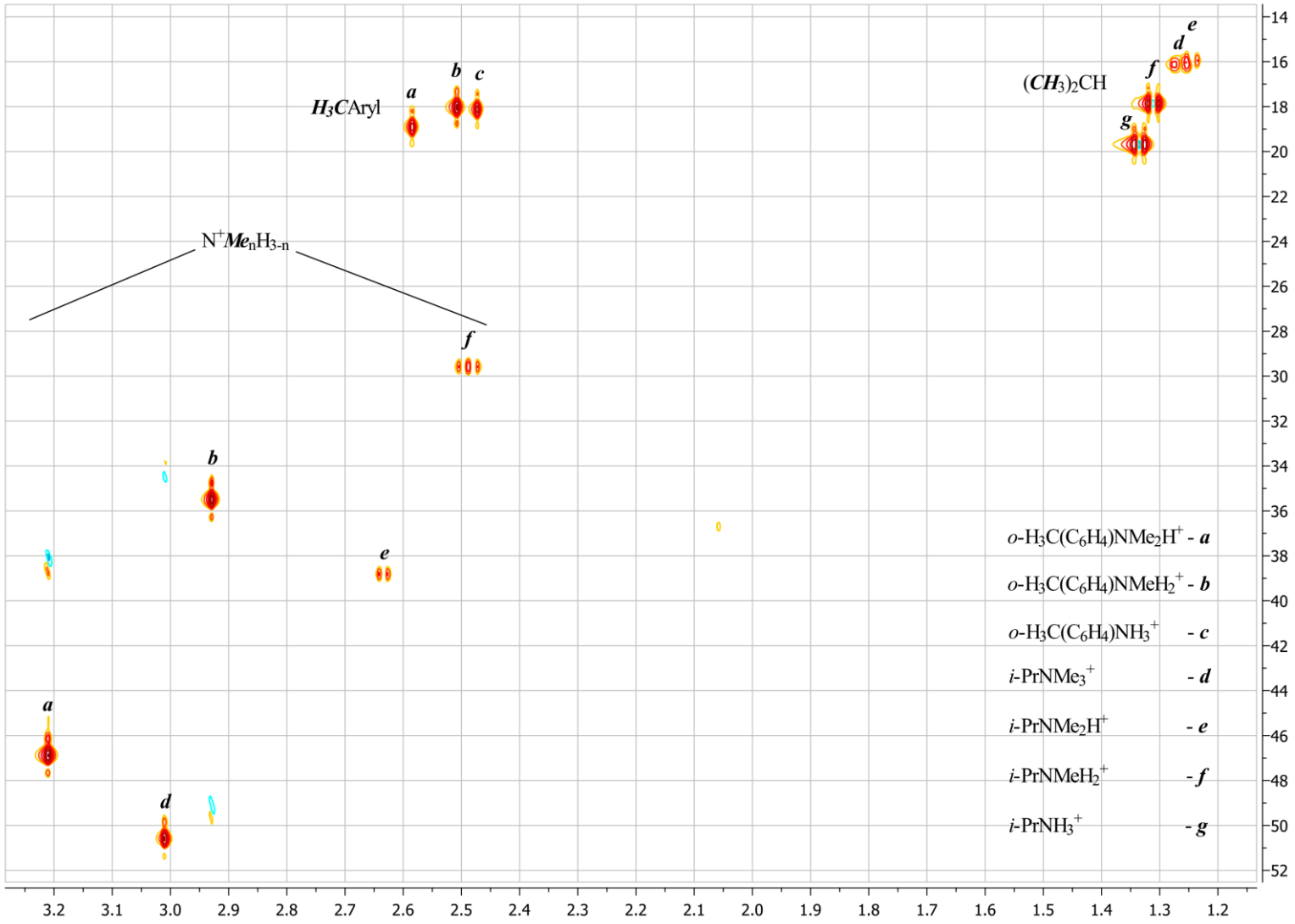


Figure S16. HMQC spectrum (methyl protons region) of the model reaction mixture 2-$MeC_6H_4NH_2$ + *i*-$PrNH_2$ + MeI (1 : 1.1 : 3) in CD_3CN (in the tube for NMR).

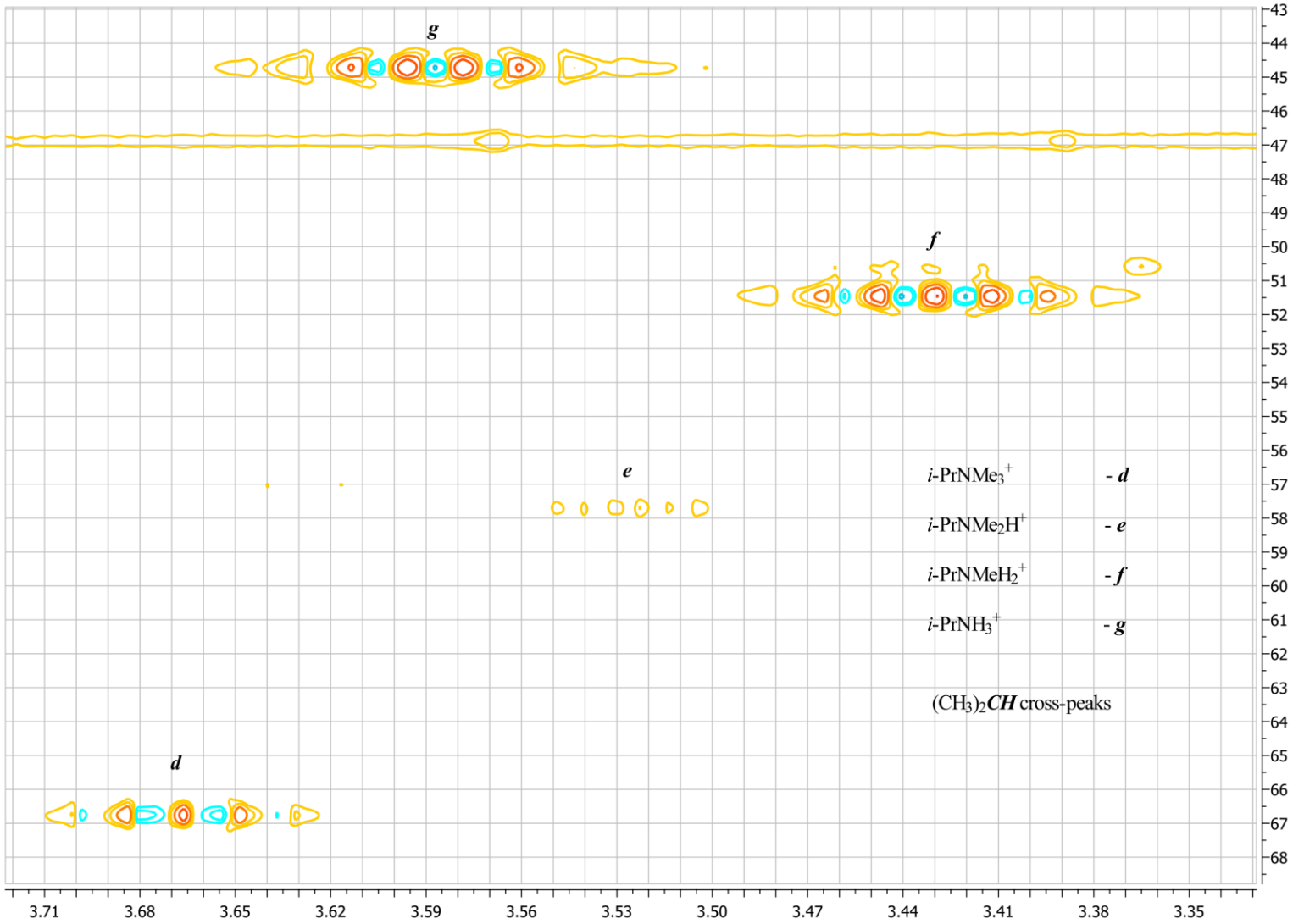


Figure S17. HMQC spectrum (C***H***Me$_2$ protons region) of the model reaction mixture 2-MeC$_6$H$_4$NH$_2$ + *i*-PrNH$_2$ + MeI (1 : 1.1 : 3) in CD$_3$CN (in the tube for NMR).

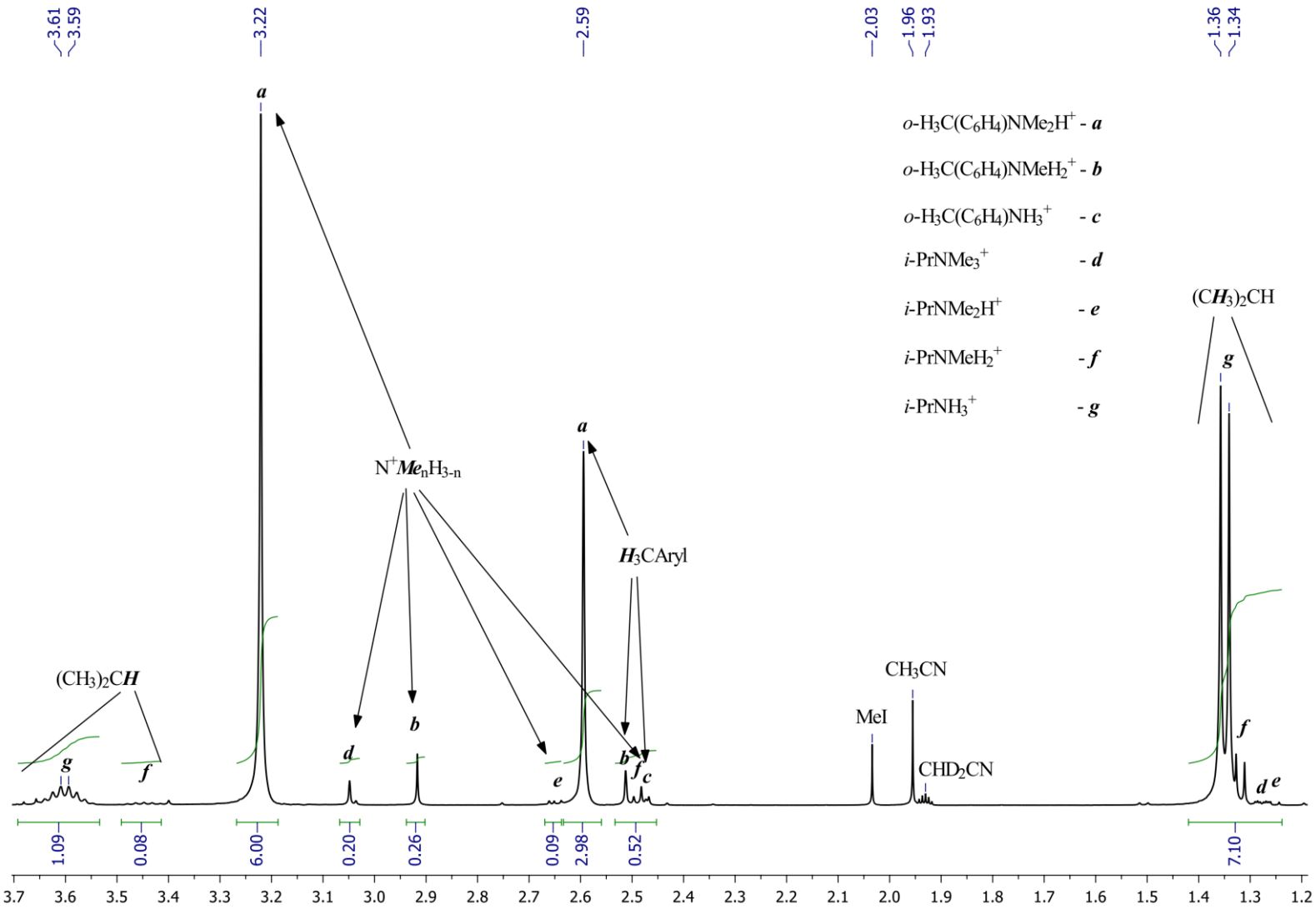


Figure S18. ^{1}H NMR spectrum (CD_3CN, aliphatic region) of the model reaction mixture 2-$MeC_6H_4NH_2$ + *i*-$PrNH_2$ + MeI (1 : 1.1 : 3) in MeCN ($p(CO_2)$ = 1 bar, t °C: -15 °C → 24 °C).

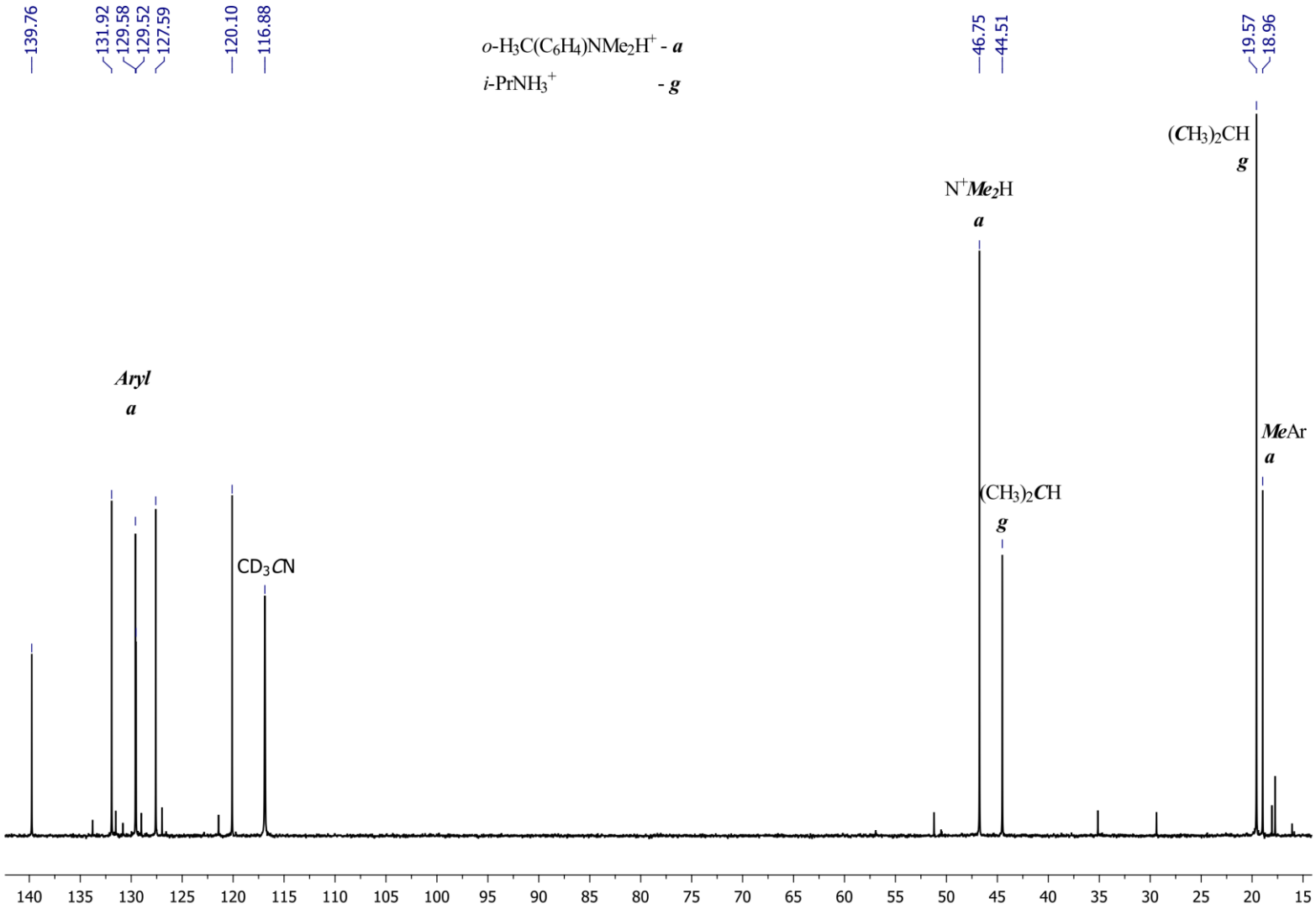


Figure S19. ^{13}C NMR spectrum (CD_3CN) of the model reaction mixture 2-$MeC_6H_4NH_2$ + *i*-$PrNH_2$ + MeI (1 : 1.1 : 3) in MeCN ($p(CO_2)$ = 1 bar, t °C: -15 °C → 24 °C).

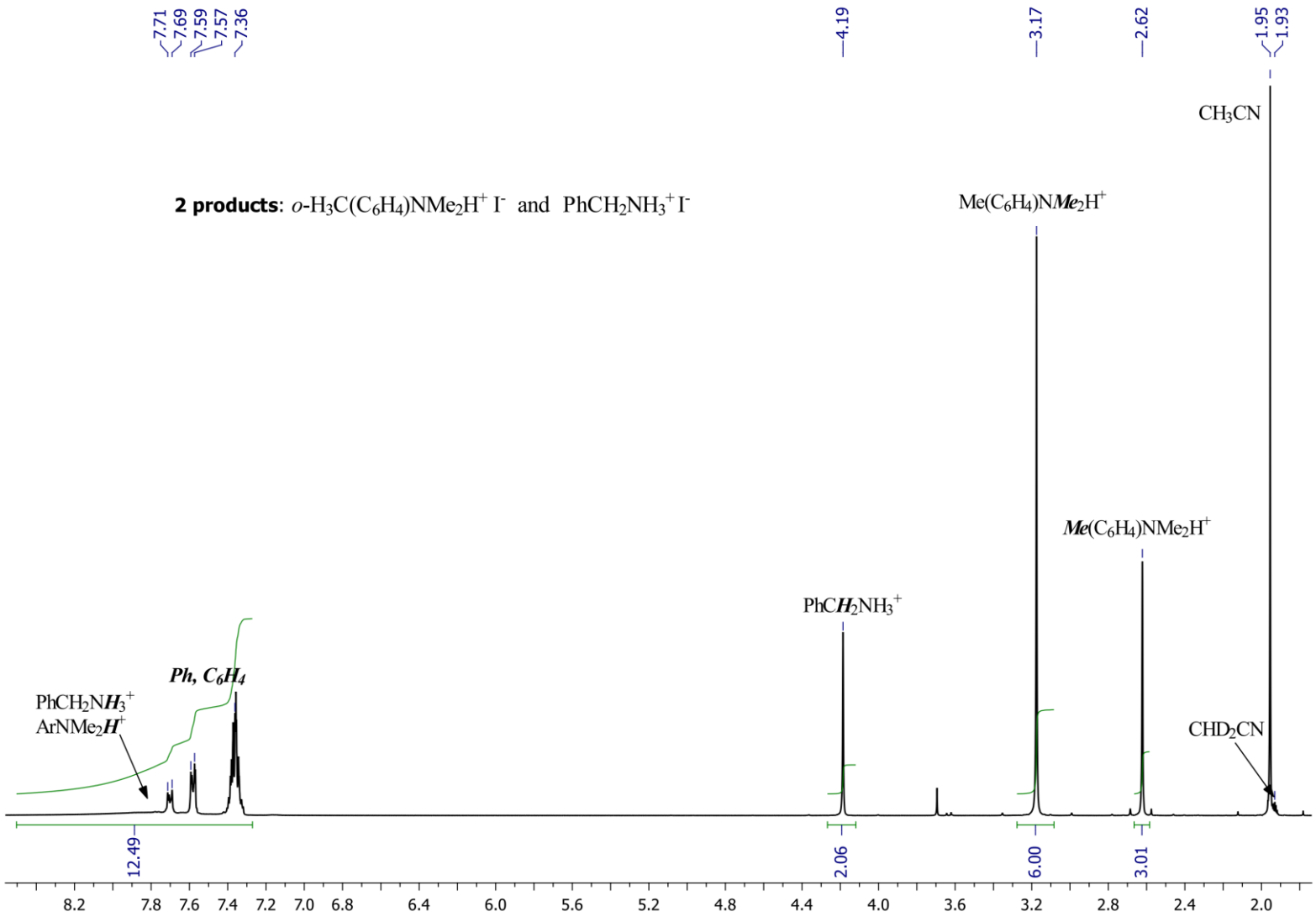


Figure S20. ^{1}H NMR spectrum (CD_3CN) of the two-step methylation reaction [2-$MeC_6H_4NH_2$ + MeI (1 : 1.5) in MeCN (24 °C)] + [$PhCH_2NH_2$ + CO_2 (1 bar, -11 °C)] + MeI (1.5 equiv) products.

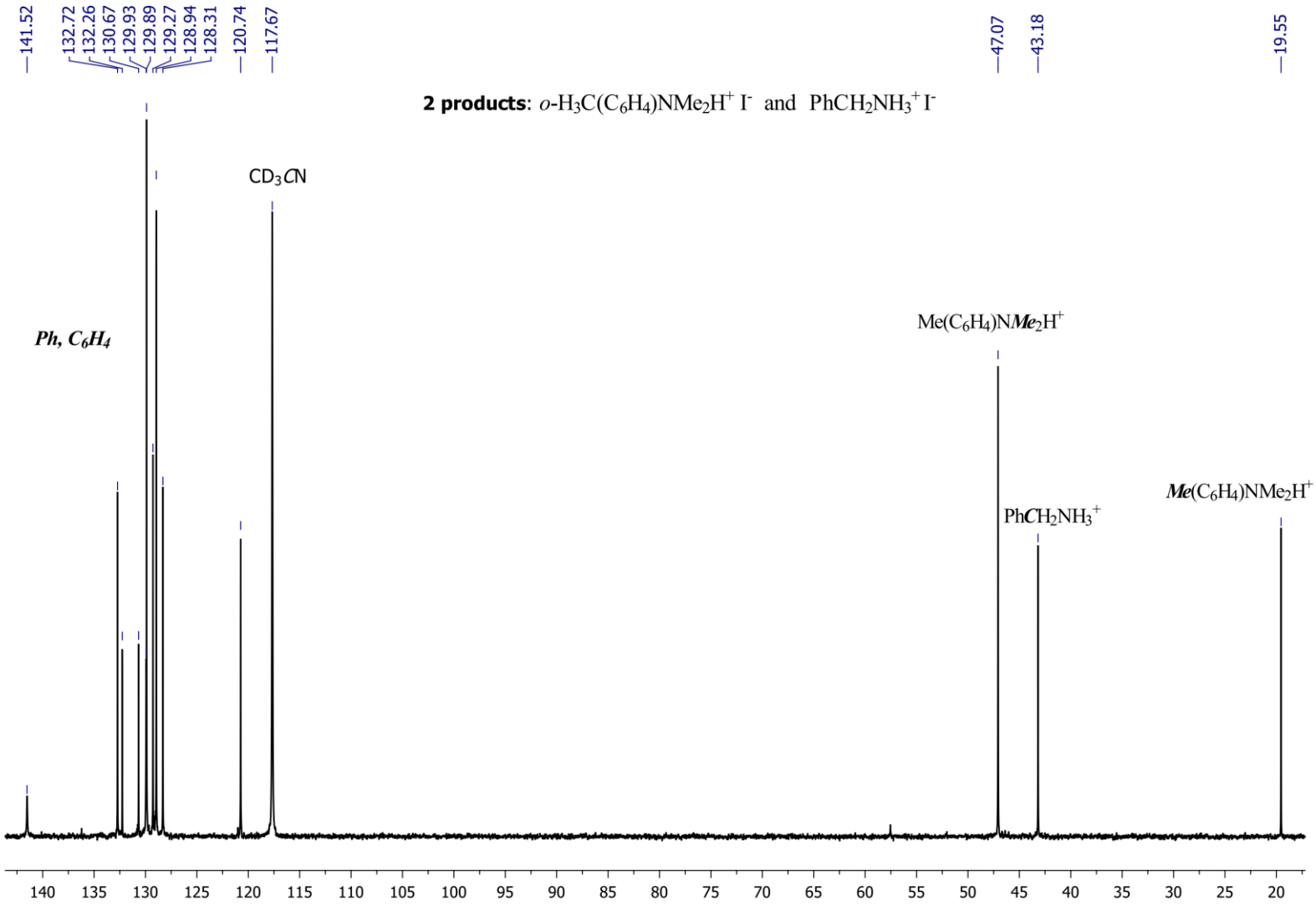


Figure S21. ^{13}C NMR spectrum (CD_3CN) of the two-step methylation reaction [2-$MeC_6H_4NH_2$ + MeI (1 : 1.5) in MeCN (24 °C)] + [$PhCH_2NH_2$ + CO_2 (1 bar, -11 °C)] + MeI (1.5 equiv) products.

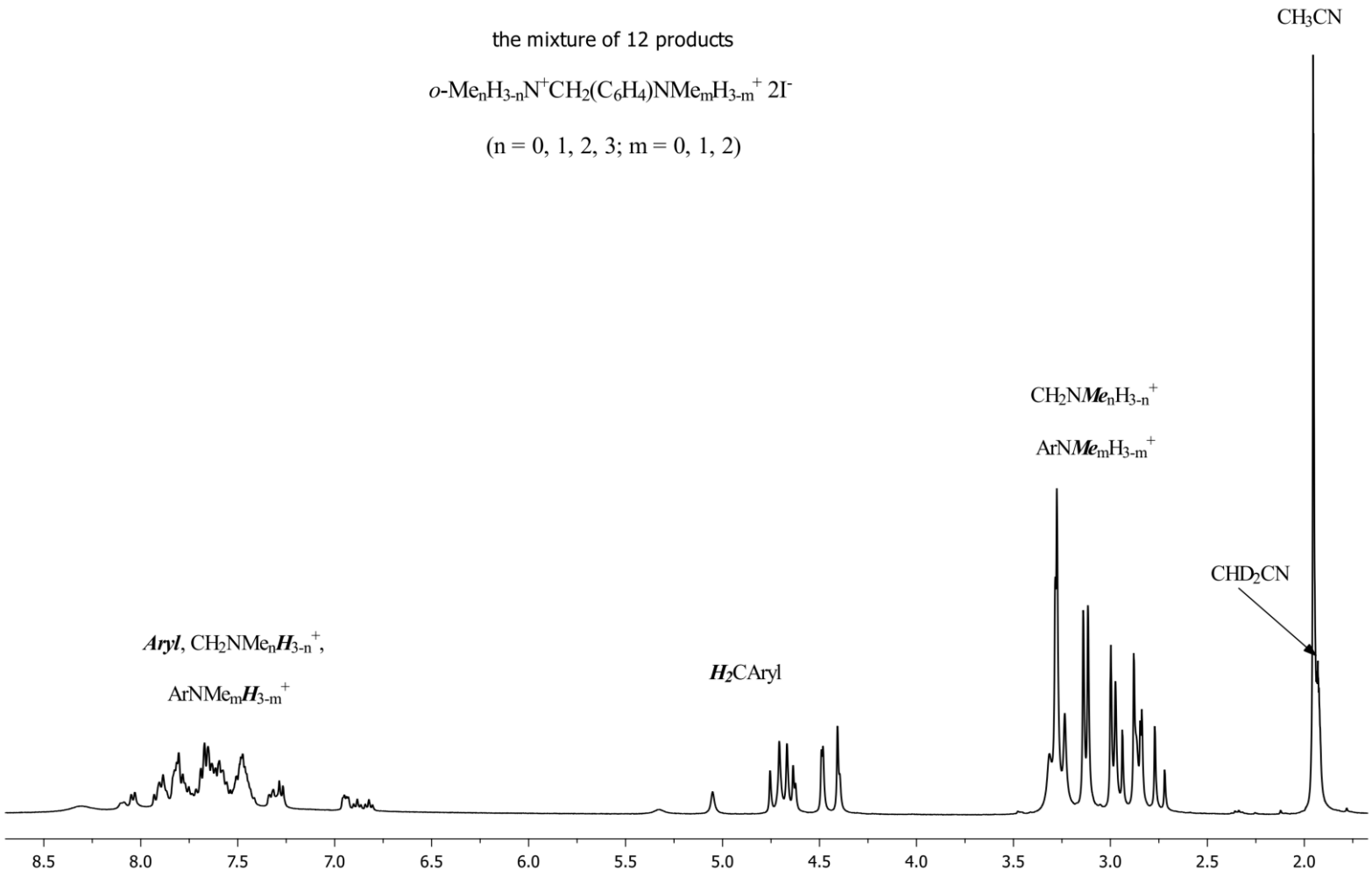


Figure S22. ^{1}H NMR spectrum (CD_3CN) of the reaction 2-$H_2NC_6H_4CH_2NH_2$ + MeI (1 : 3) in MeCN (24 °C) products.

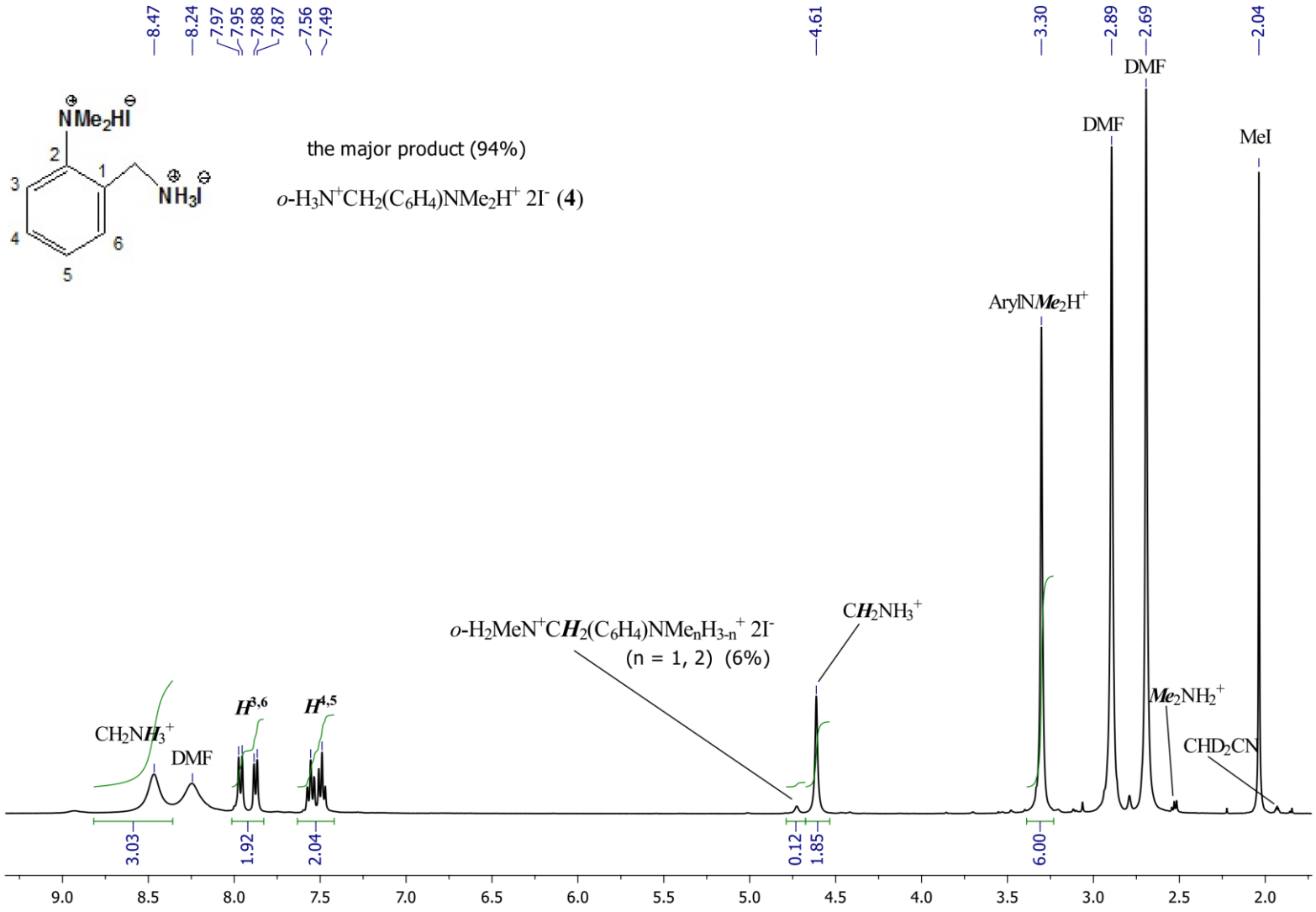


Figure S23. ^{1}H NMR spectrum (CD_3CN) of the reaction mixture 2-$H_2NC_6H_4CH_2NH_2$ + MeI (1 : 6) in DMF ($p(CO_2)$ = 60 bar, 24 °C, 144 hours).

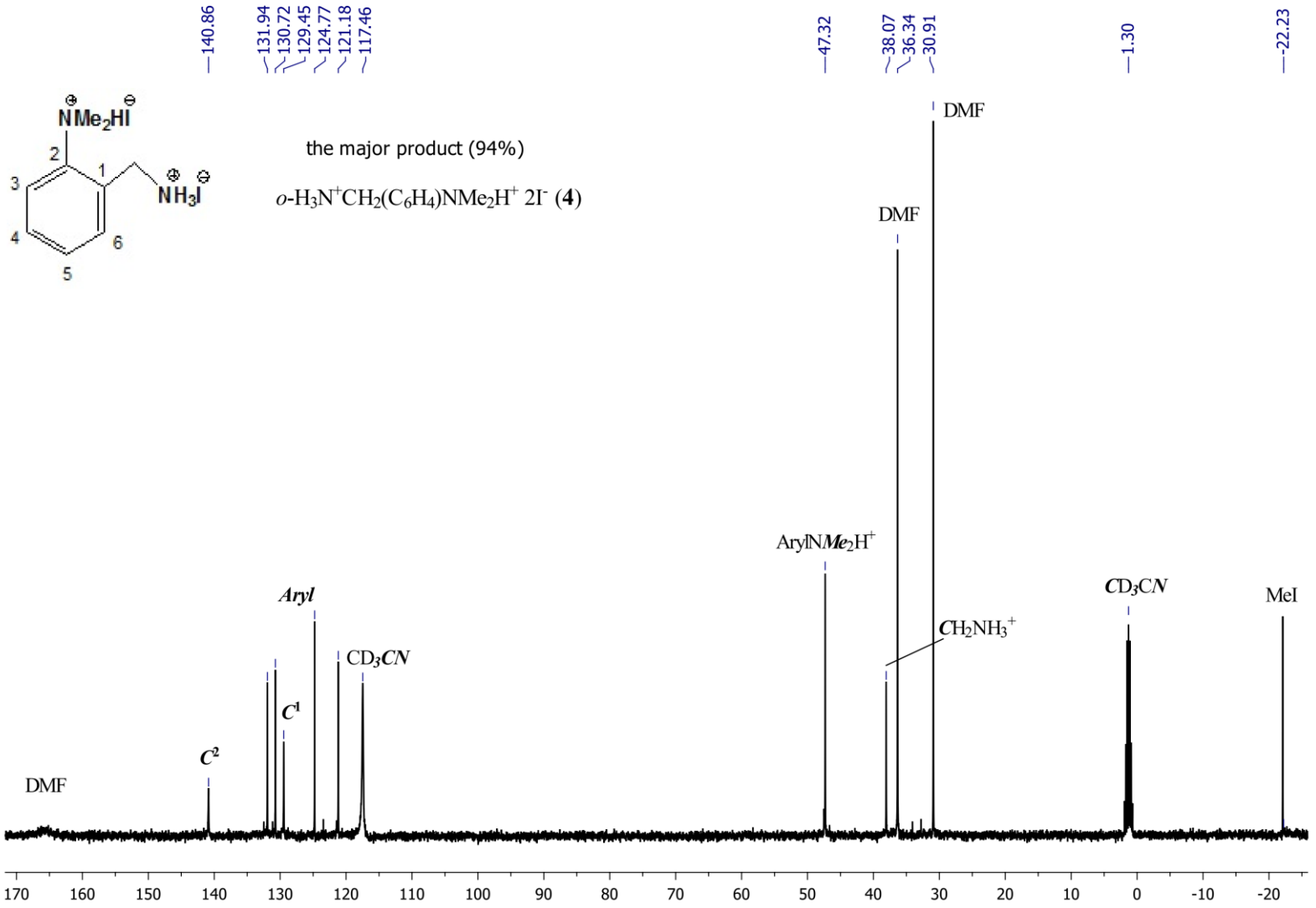


Figure S24. ^{13}C NMR spectrum (CD_3CN) of the reaction mixture 2-$H_2NC_6H_4CH_2NH_2$ + MeI (1 : 6) in DMF ($p(CO_2)$ = 60 bar, 24 °C, 144 hours).

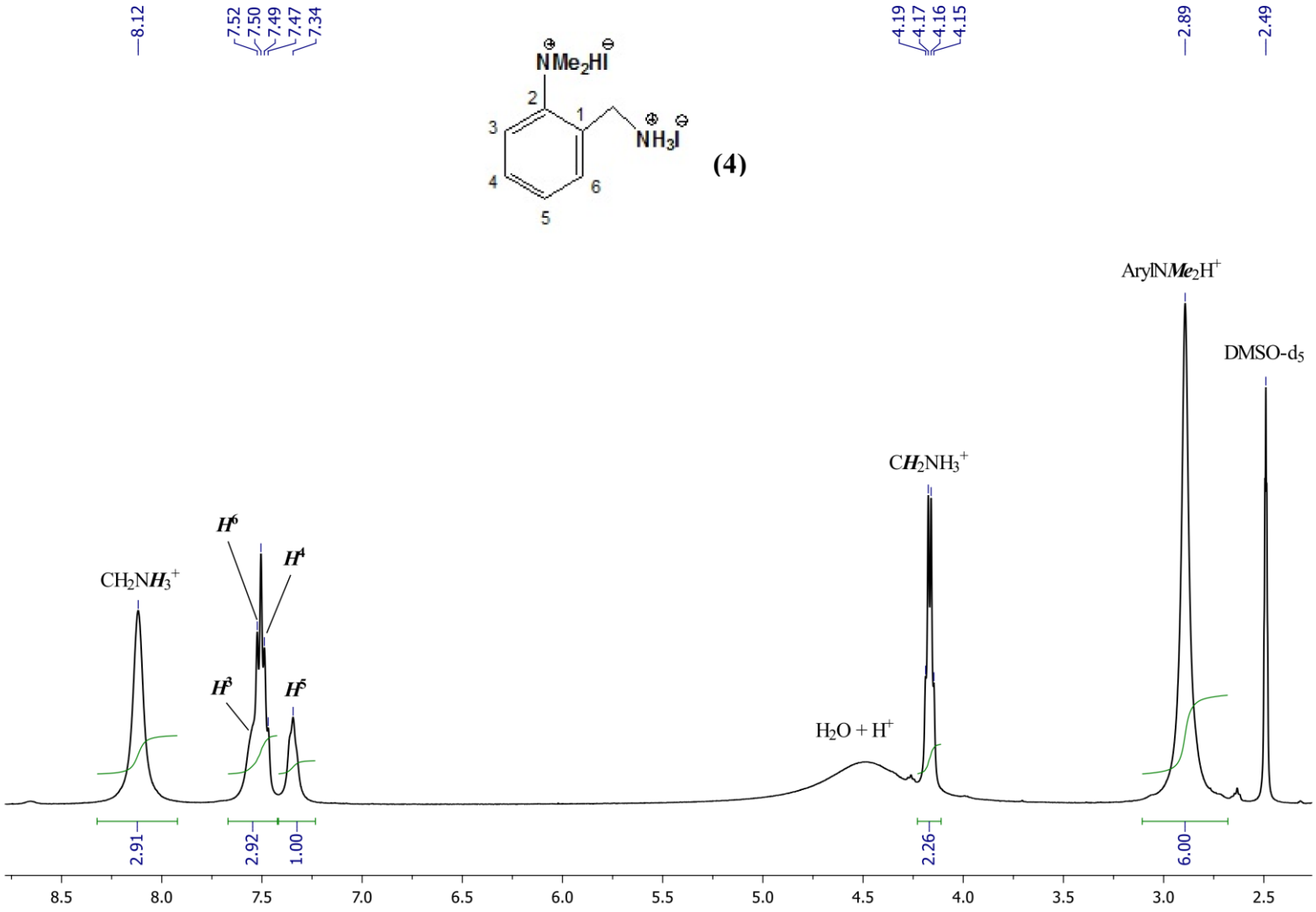


Figure S25. ^{1}H NMR spectrum (DMSO-d$_6$) of isolated 2-HMe$_2$N$^+$C$_6$H$_4$CH$_2$NH$_3^+$ 2I$^-$ (**4**).

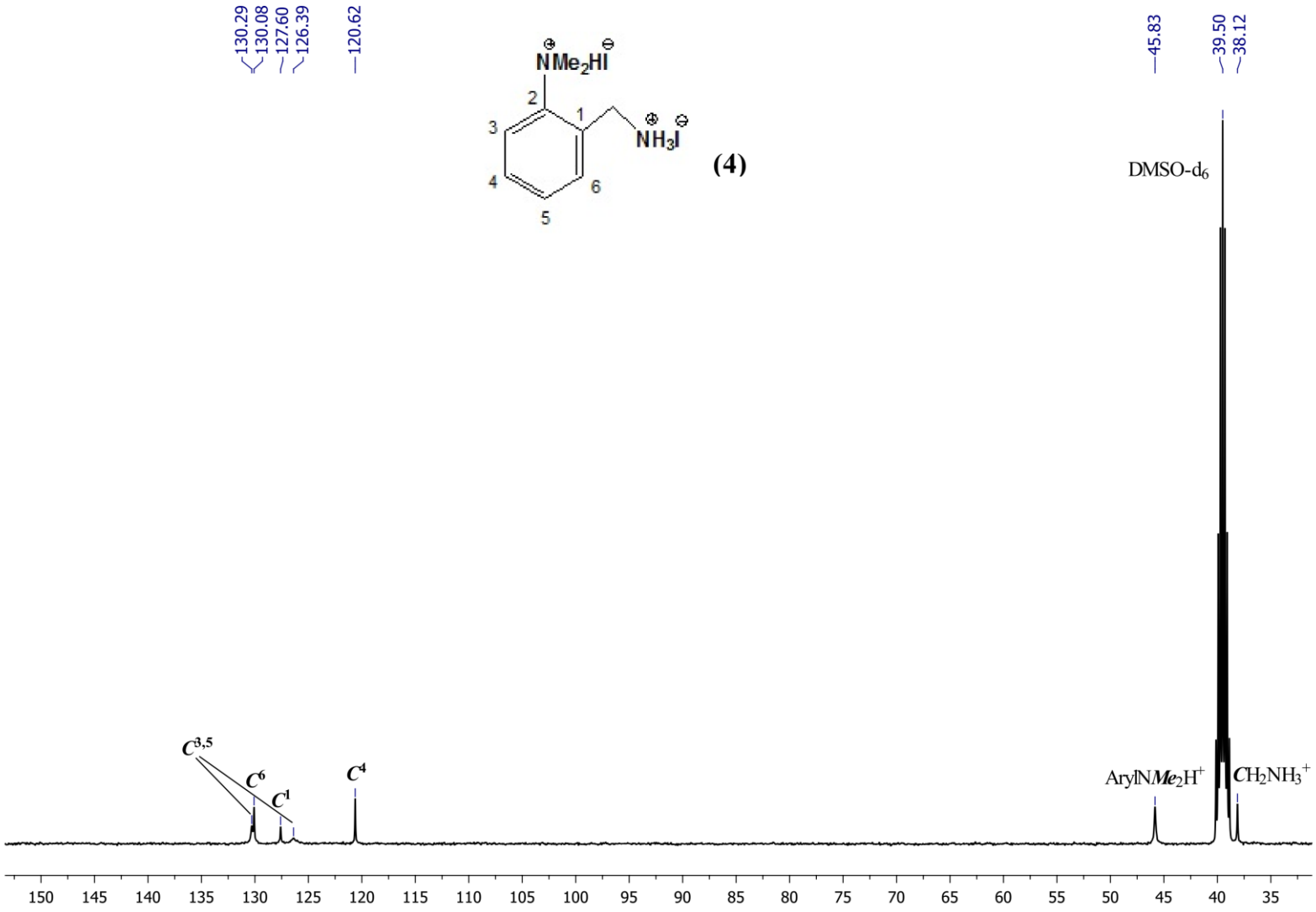


Figure S26. ^{13}C NMR spectrum (DMSO-d_6) of isolated 2-$HMe_2N^+C_6H_4CH_2NH_3^+$ $2I^-$ (**4**).

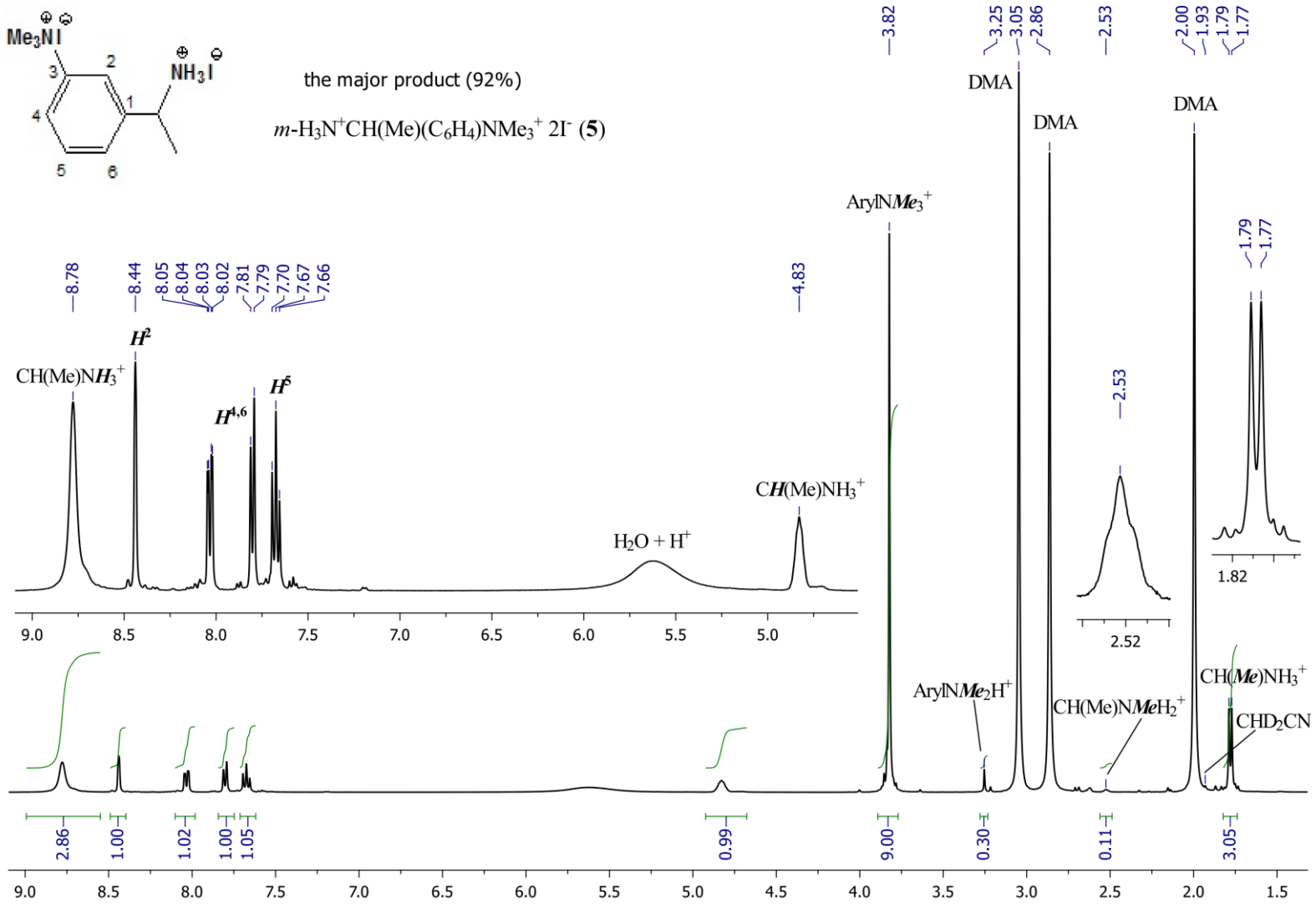


Figure S27. ^{1}H NMR spectrum (CD_3CN) of the reaction mixture 3-$H_2NC_6H_4CH(Me)NH_2$ + MeI (1 : 6) in DMA ($p(CO_2)$ = 60 bar, 37 °C, 48 hours).

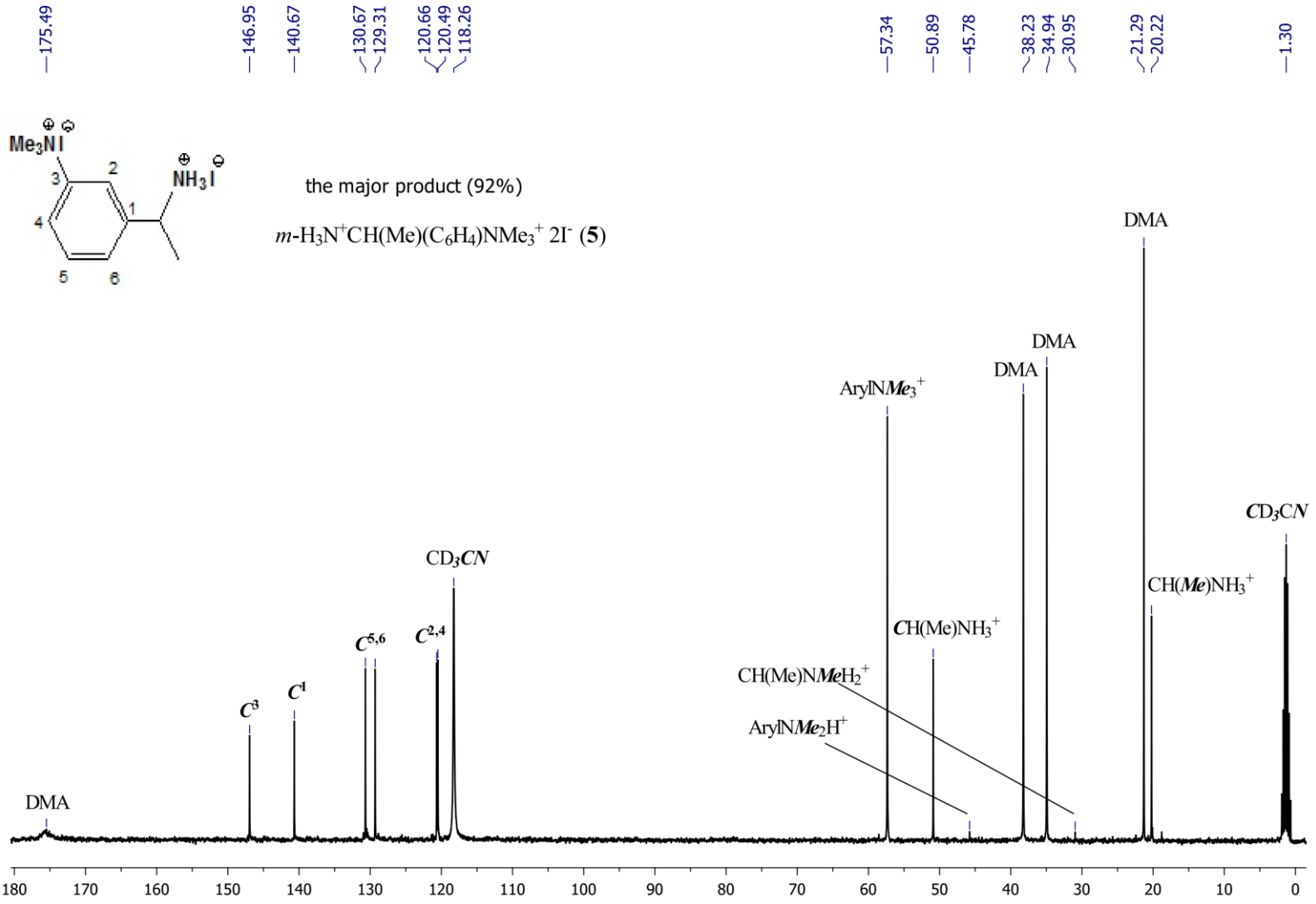


Figure S28. ^{13}C NMR spectrum (CD_3CN) of the reaction mixture 3-$H_2NC_6H_4CH(Me)NH_2$ + MeI (1 : 6) in DMA ($p(CO_2)$ = 60 bar, 37 °C, 48 hours).

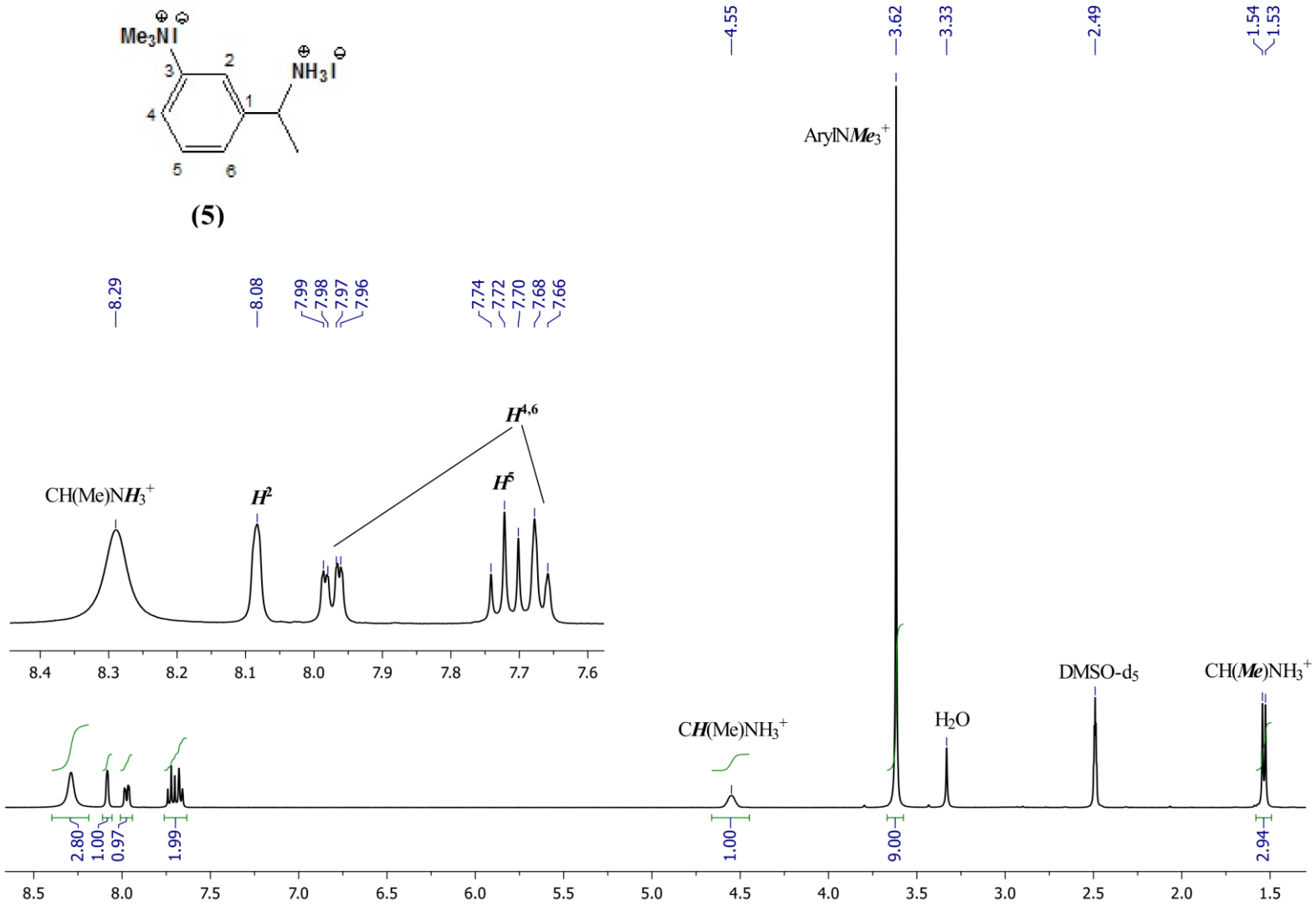


Figure S29. ^{1}H NMR spectrum (DMSO-d$_6$) of isolated 3-Me$_3$N$^+$C$_6$H$_4$CH(Me)NH$_3^+$ 2I$^-$ (**5**).

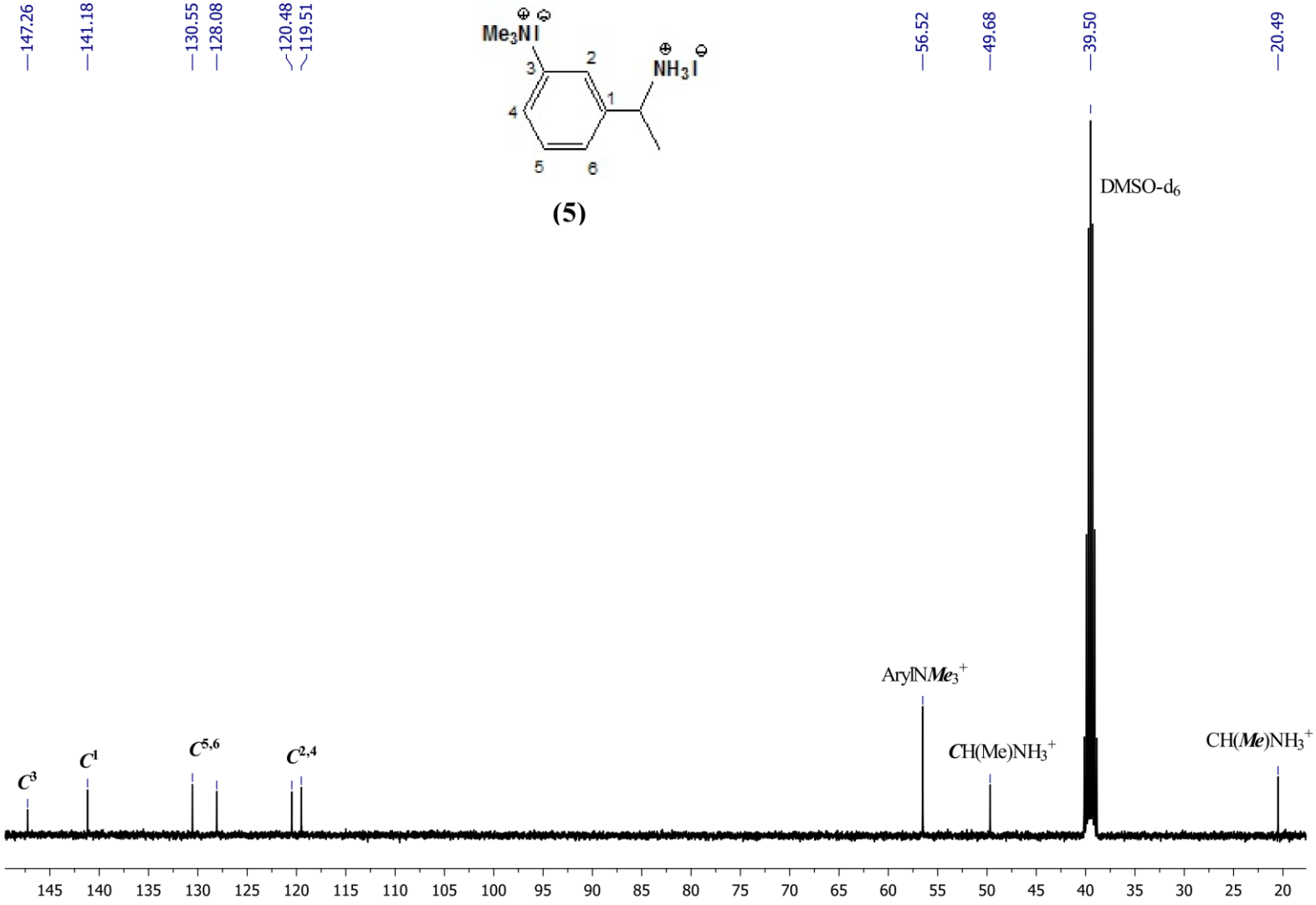


Figure S30. ^{13}C NMR spectrum (DMSO-d$_6$) of isolated 3-Me$_3$N$^+$C$_6$H$_4$CH(Me)NH$_3^+$ 2I$^-$ (**5**).

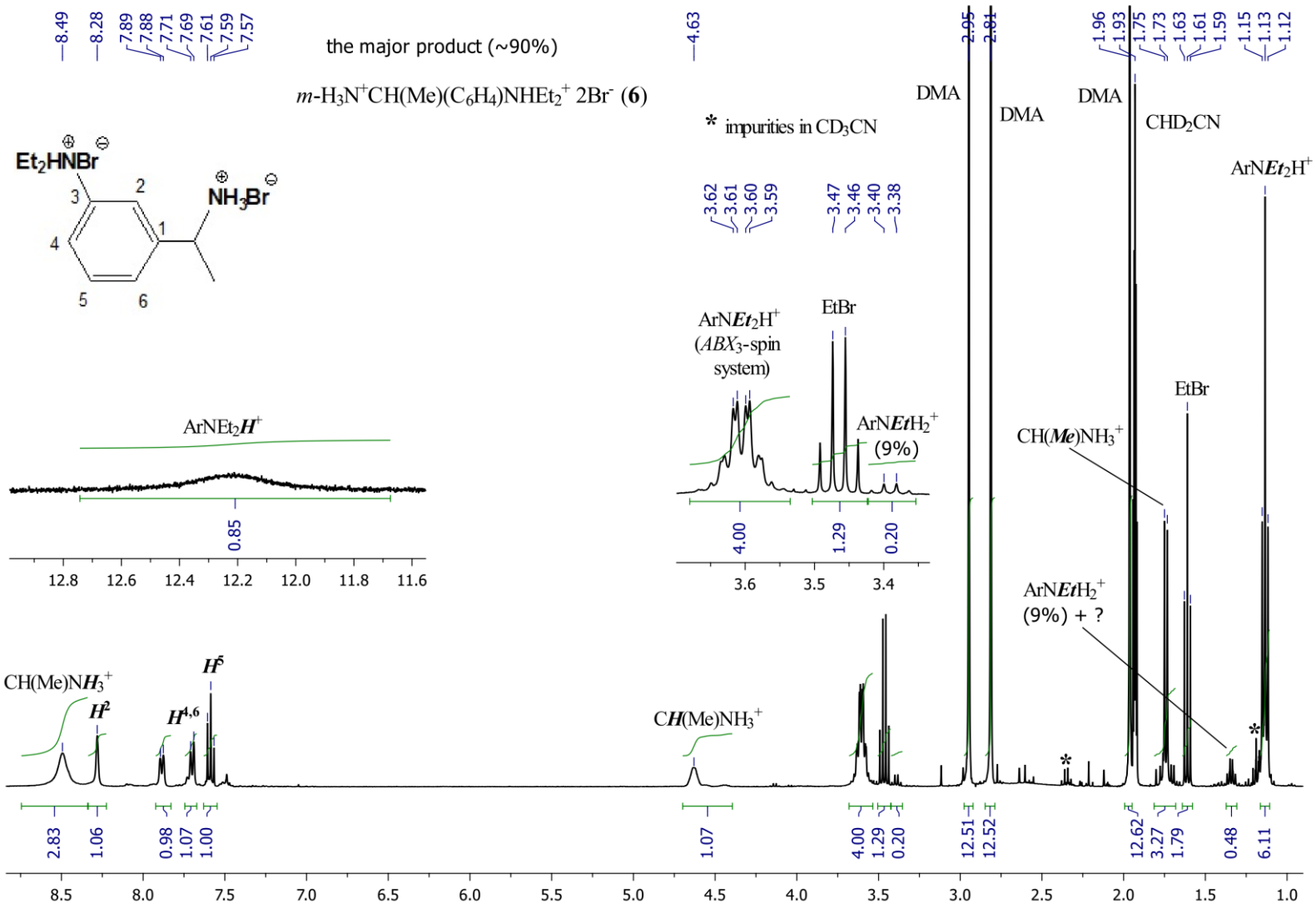


Figure S31. ^{1}H NMR spectrum (CD_3CN) of the reaction mixture 3-$H_2NC_6H_4CH(Me)NH_2$ + EtBr (1 : 6) in DMA ($p(CO_2)$ = 60 bar, 37 °C, 144 hours).

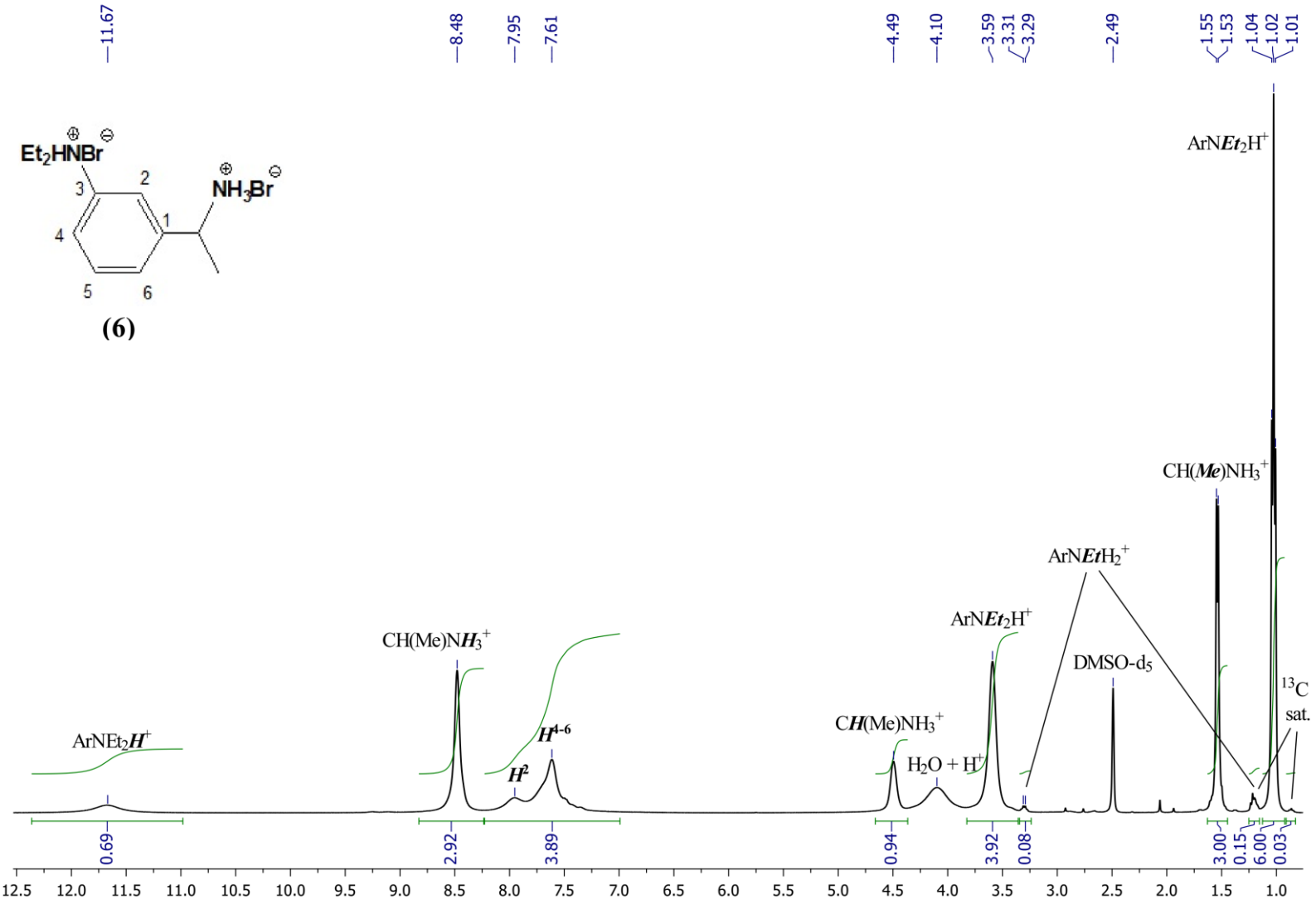


Figure S32. ^{1}H NMR spectrum (DMSO-d$_6$) of isolated 3-Et$_2$HN$^+$C$_6$H$_4$CH(Me)NH$_3^+$ 2Br$^-$ (**6**) (the product is contaminated with 3-EtH$_2$N$^+$C$_6$H$_4$CH(Me)NH$_3^+$ 2Br$^-$ (~4% mol)).

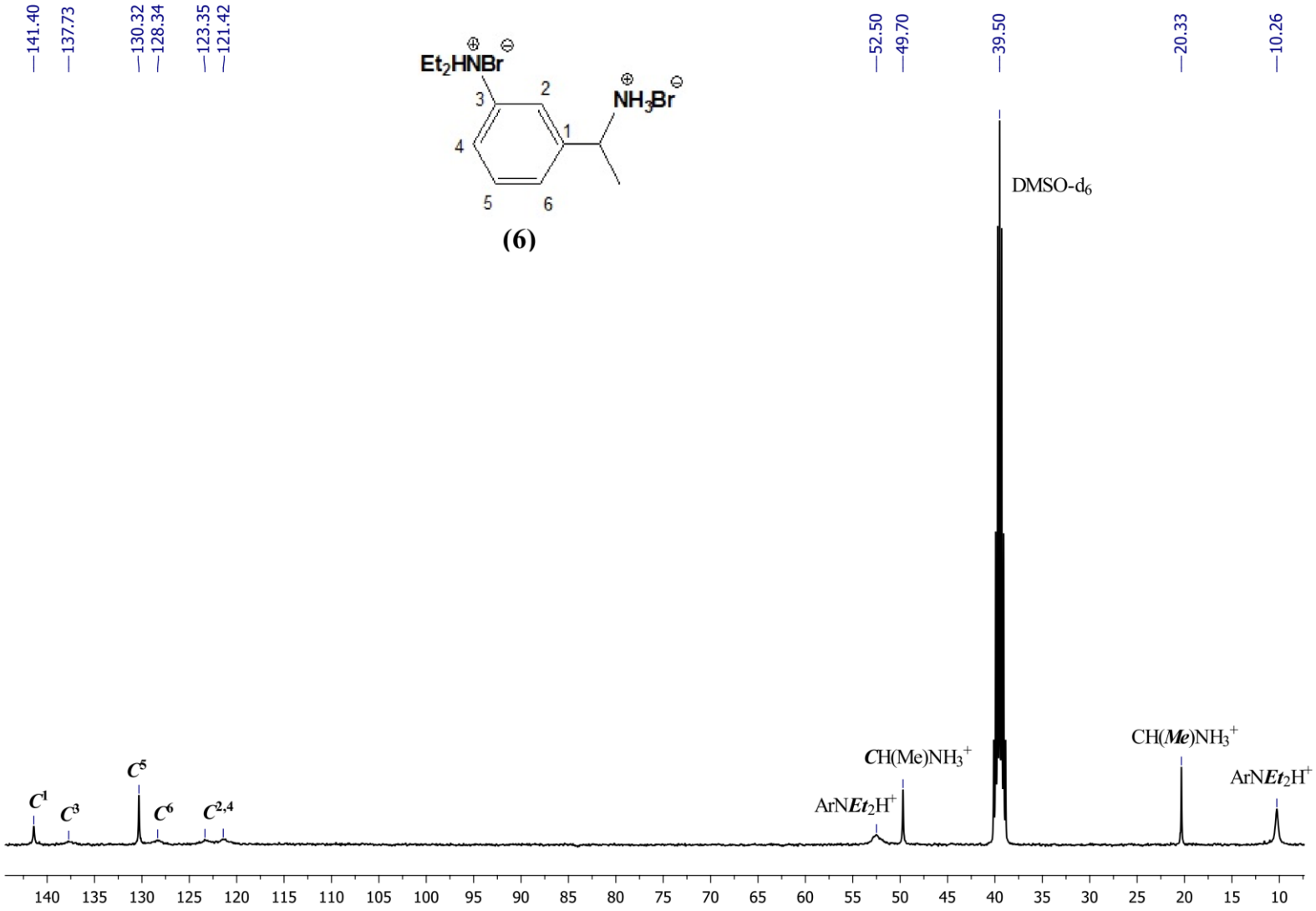


Figure S33. ^{13}C NMR spectrum (DMSO-d$_6$) of isolated 3-Et$_2$HN$^+$C$_6$H$_4$CH(Me)NH$_3^+$ 2Br$^-$ (**6**).

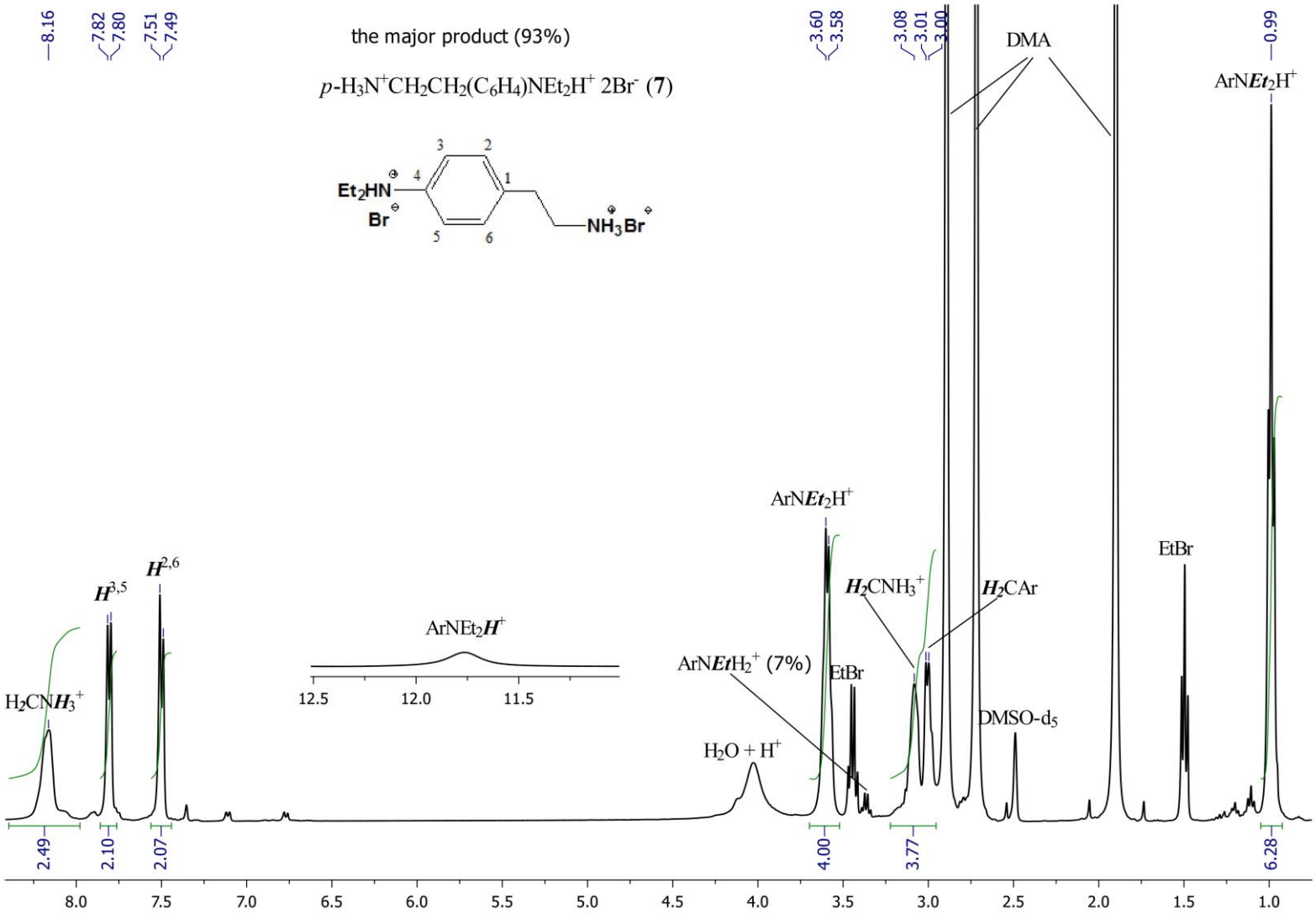


Figure S34. ^{1}H NMR spectrum (DMSO-d$_6$) of the reaction mixture 4-$H_2NC_6H_4CH_2CH_2NH_2$ + EtBr (1 : 4) in DMA ($p(CO_2)$ = 60 bar, 65 °C, 72 hours).

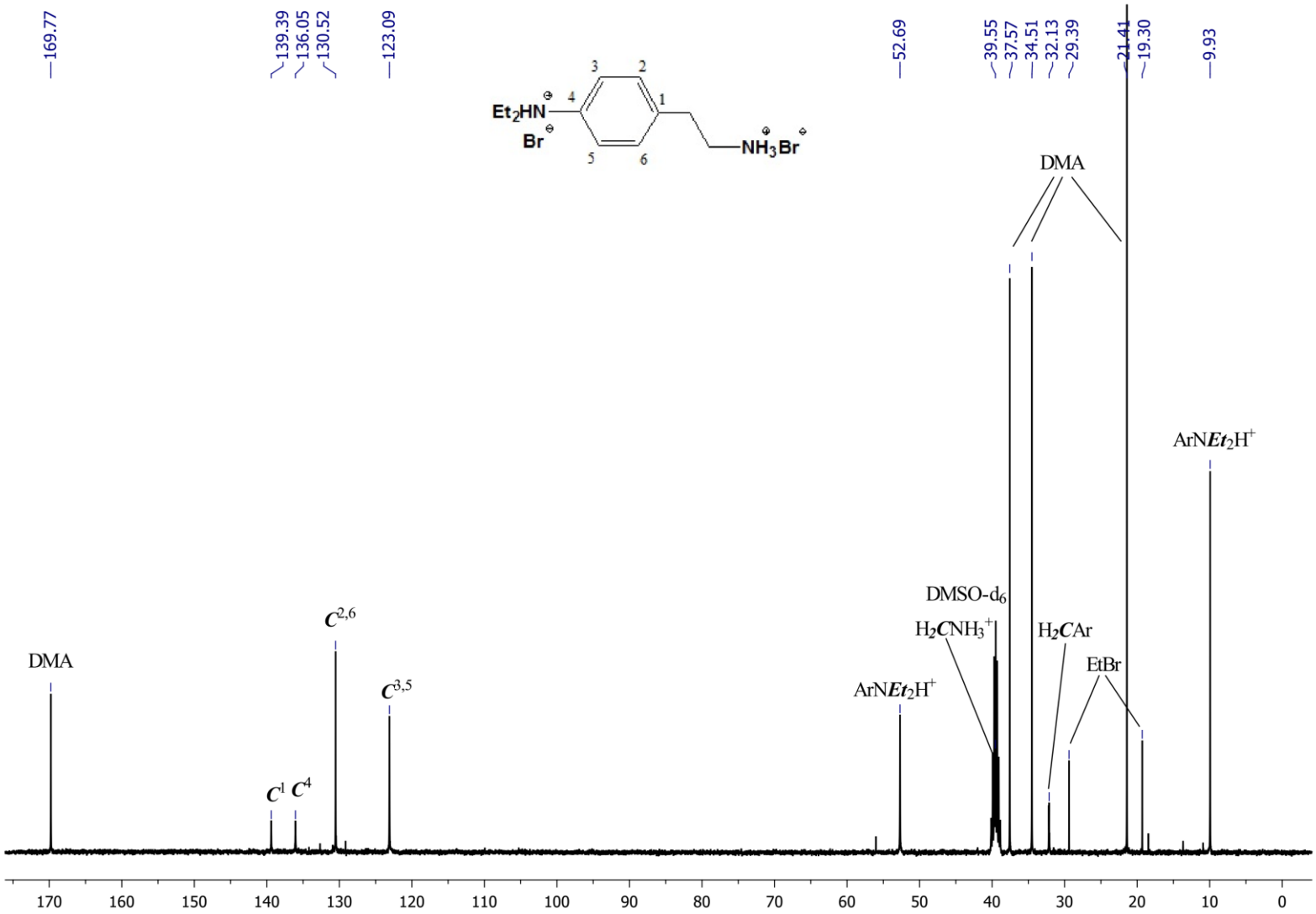


Figure S35. ^{13}C NMR spectrum (DMSO-d_6) of the reaction mixture 4-$H_2NC_6H_4CH_2CH_2NH_2$ + EtBr (1 : 4) in DMA ($p(CO_2)$ = 60 bar, 65 °C, 72 hours).

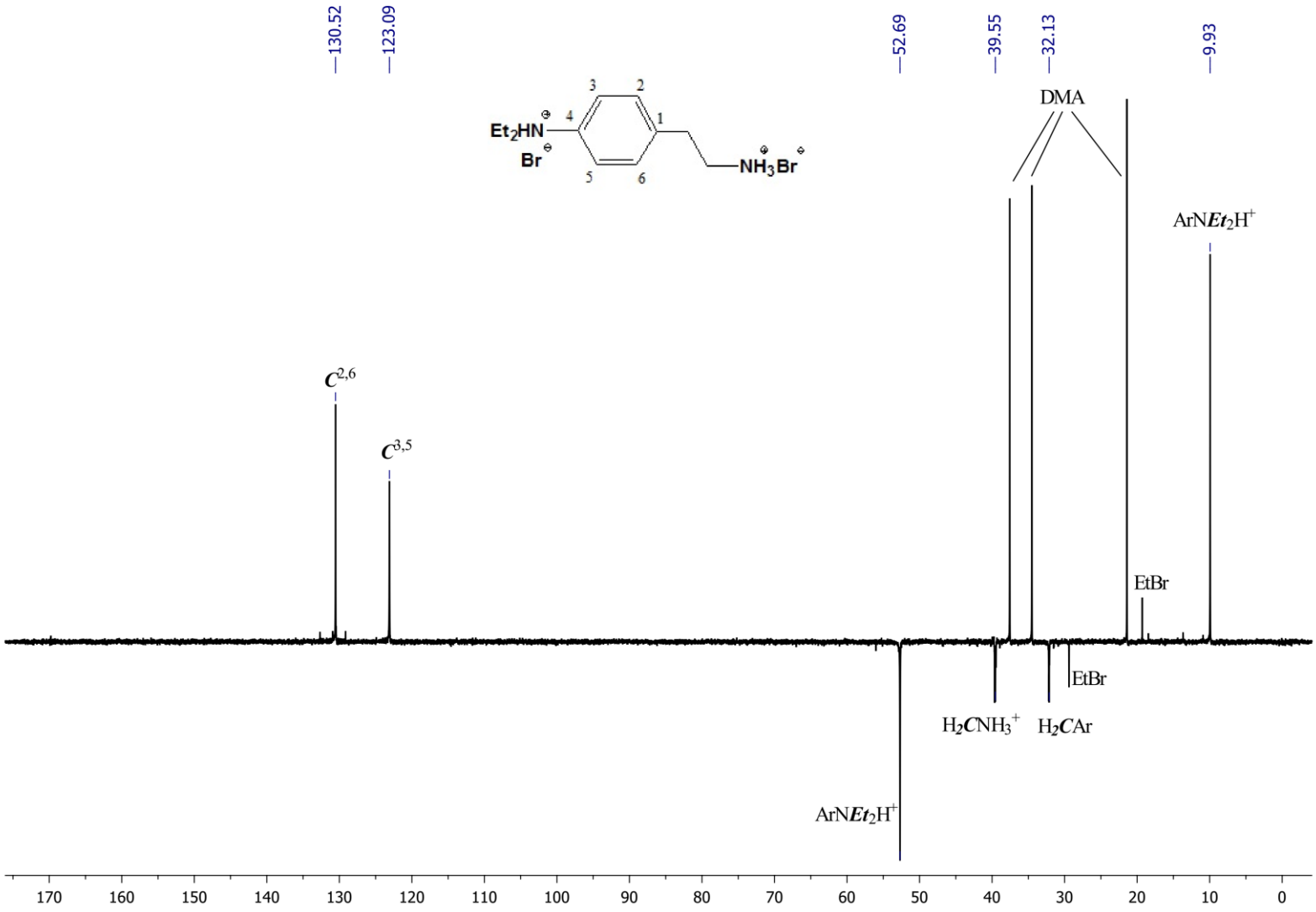


Figure S36. DEPT spectrum (DMSO-d_6) of the reaction mixture 4-$H_2NC_6H_4CH_2CH_2NH_2$ + EtBr (1 : 4) in DMA ($p(CO_2)$ = 60 bar, 65 °C, 72 hours).

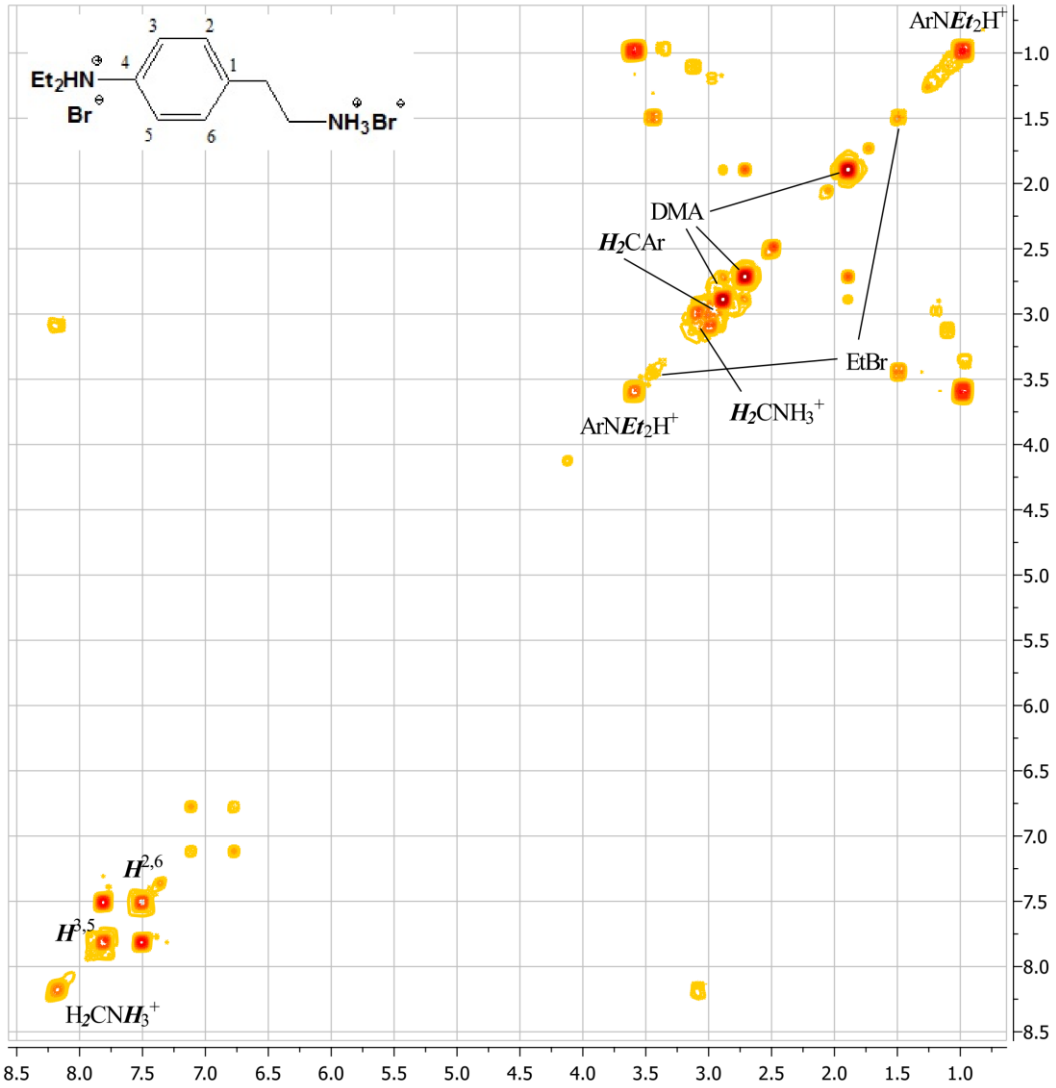


Figure S37. COSY spectrum (DMSO-d_6) of the reaction mixture 4-$H_2NC_6H_4CH_2CH_2NH_2$ + EtBr (1 : 4) in DMA ($p(CO_2)$ = 60 bar, 65 °C, 72 hours).

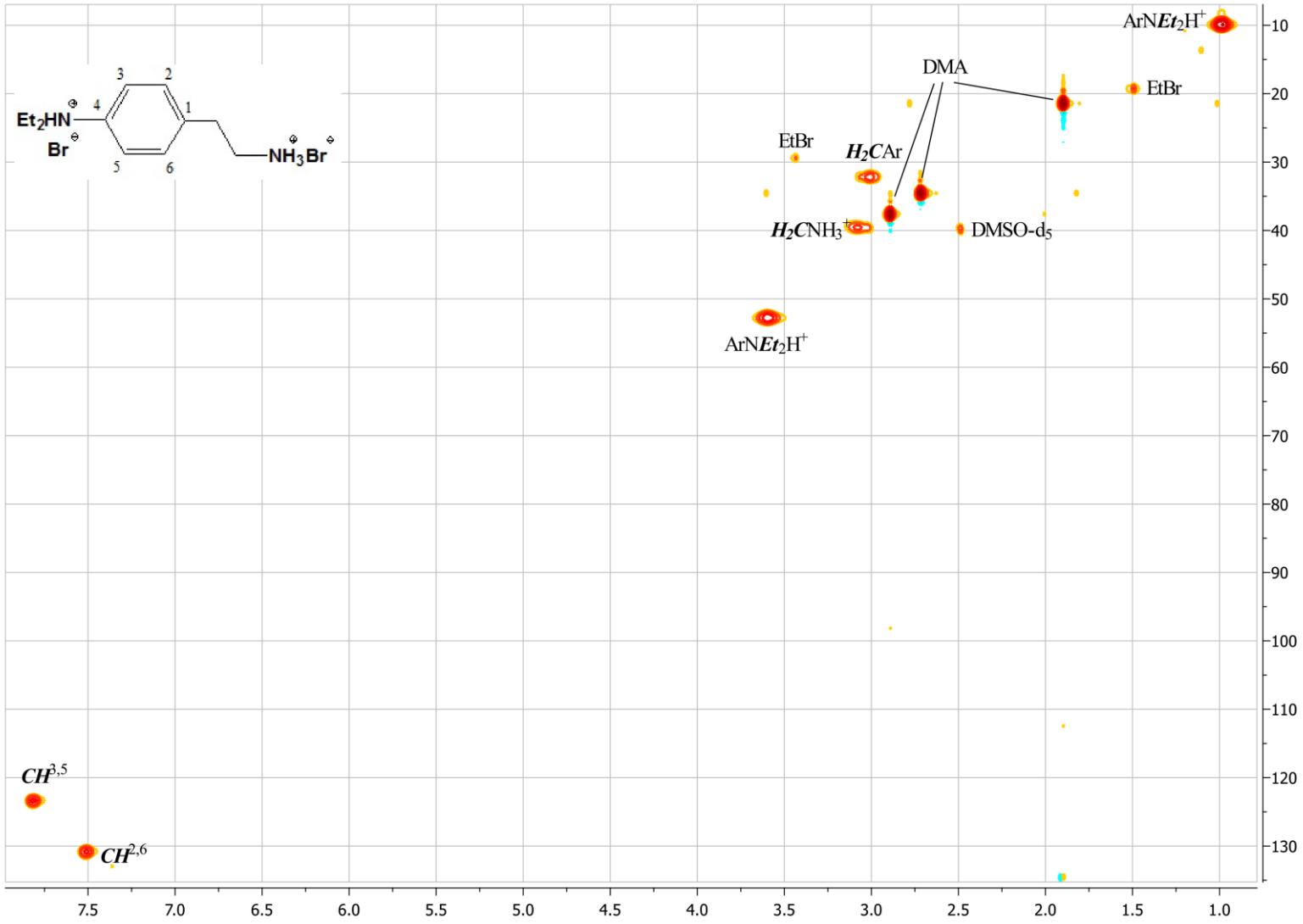


Figure S38. HMQC spectrum (DMSO-d_6) of the reaction mixture 4-$H_2NC_6H_4CH_2CH_2NH_2$ + EtBr (1 : 4) in DMA ($p(CO_2)$ = 60 bar, 65 °C, 72 hours).

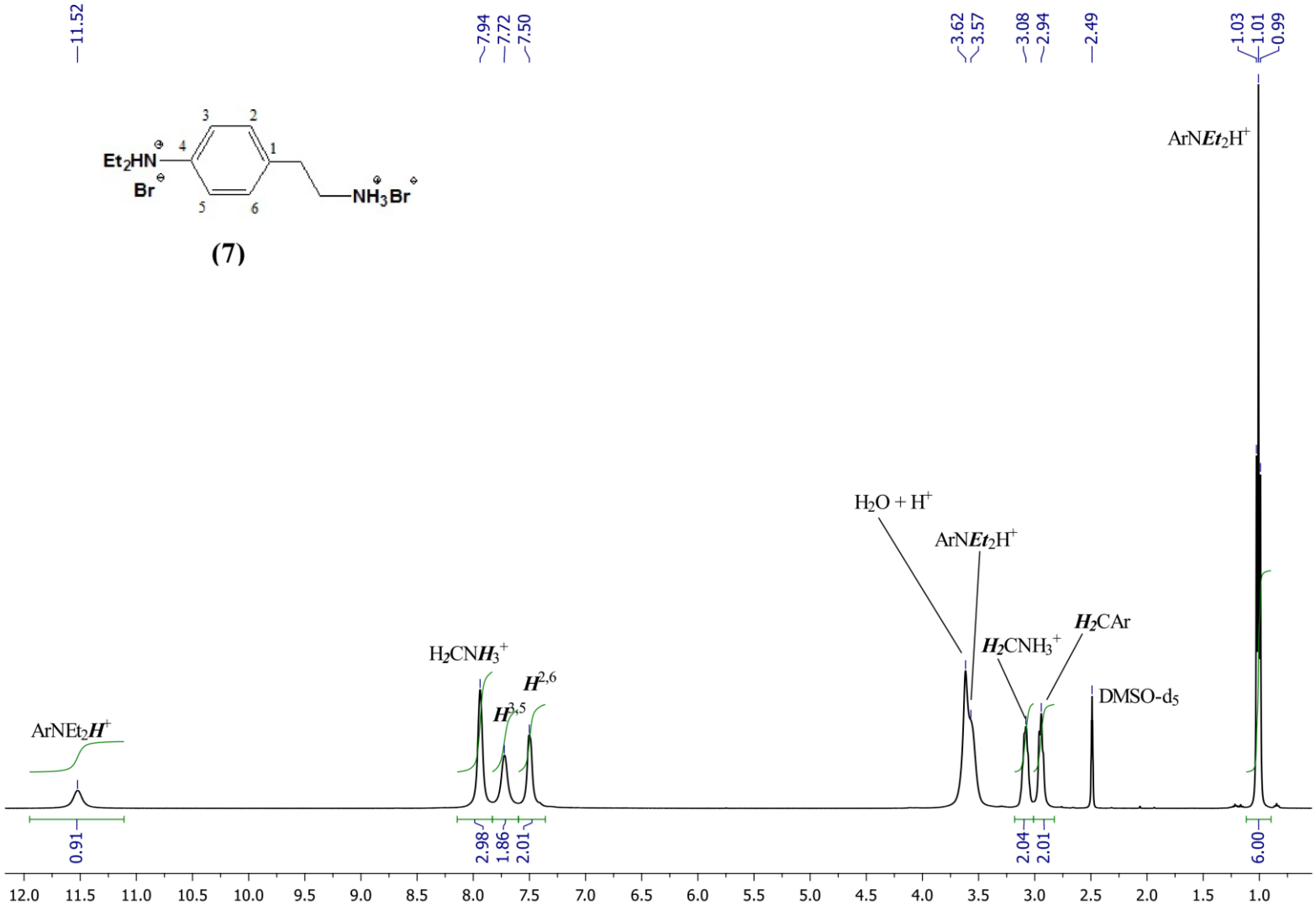


Figure S39. ^{1}H NMR spectrum (DMSO-d$_6$) of isolated 4-Et$_2$HN$^+$C$_6$H$_4$CH$_2$CH$_2$NH$_3^+$ 2 Br$^-$ (**7**).

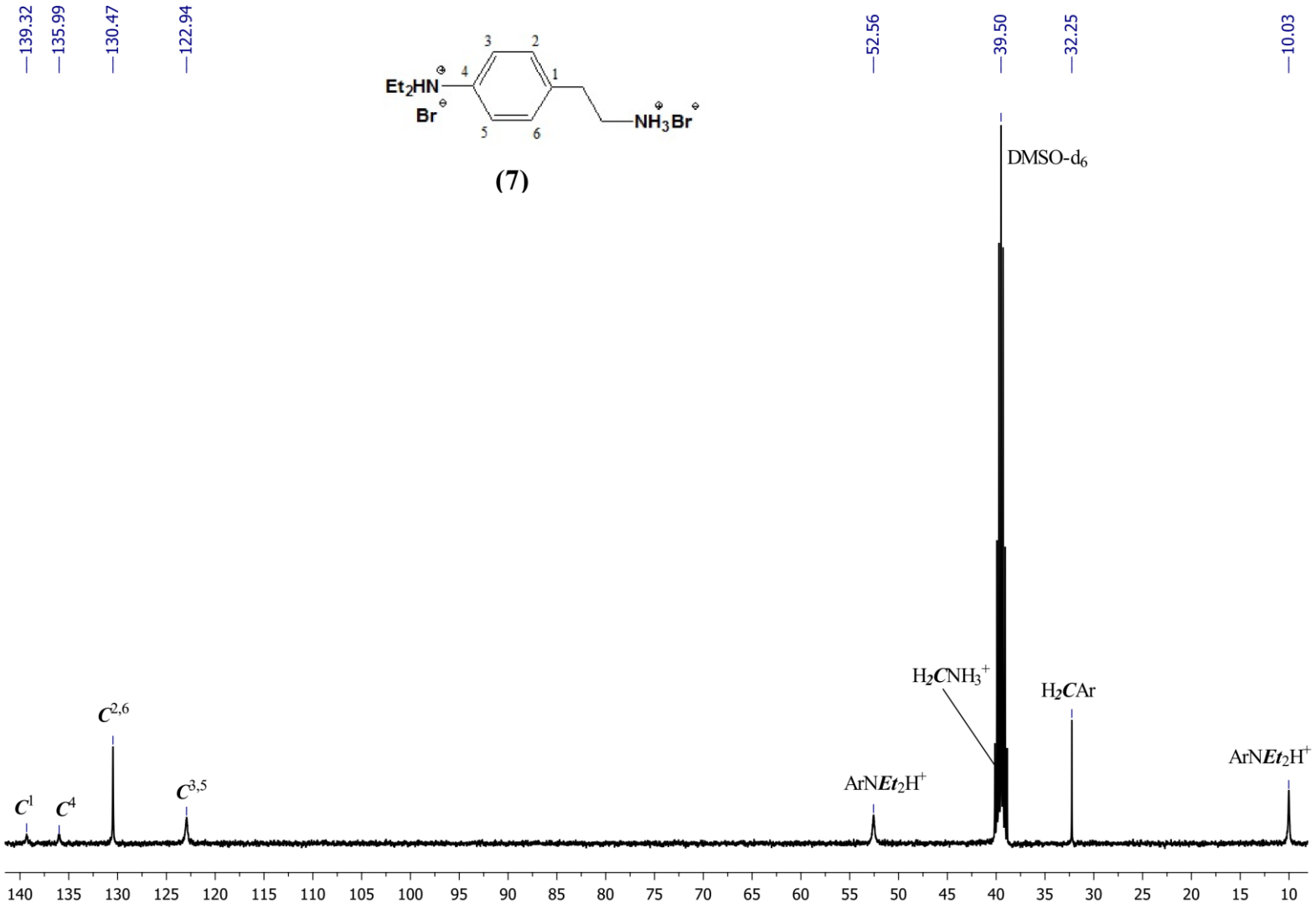


Figure S40. ^{13}C NMR spectrum (DMSO-d$_6$) of isolated 4-$Et_2HN^+C_6H_4CH_2CH_2NH_3^+$ 2 Br^- (**7**).

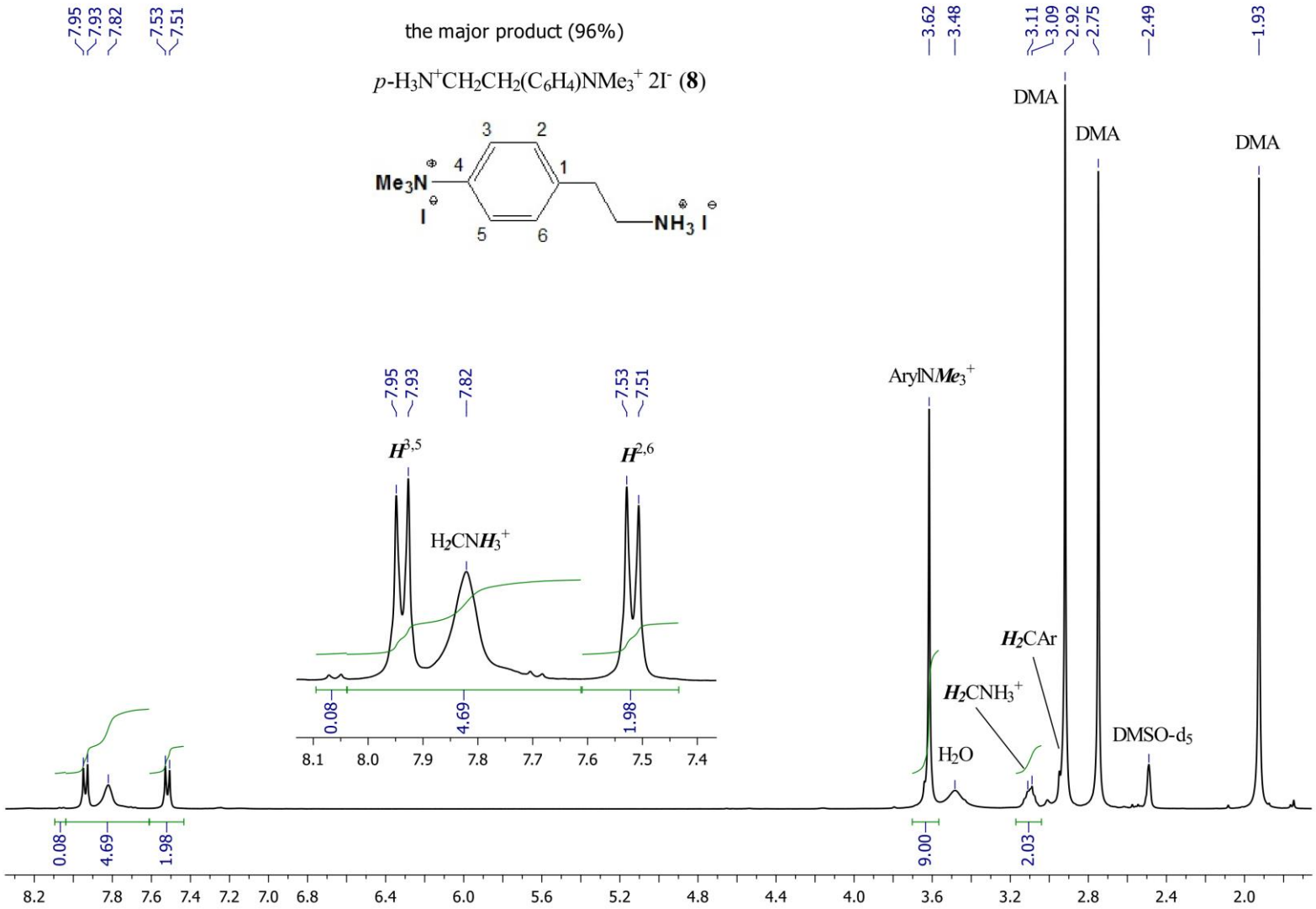


Figure S41. ^{1}H NMR spectrum (DMSO-d$_6$) of the reaction mixture 4-$H_2NC_6H_4CH_2CH_2NH_2$ + MeI (1 : 6) in DMA ($p(CO_2)$ = 60 bar, 52 °C, 55 hours).

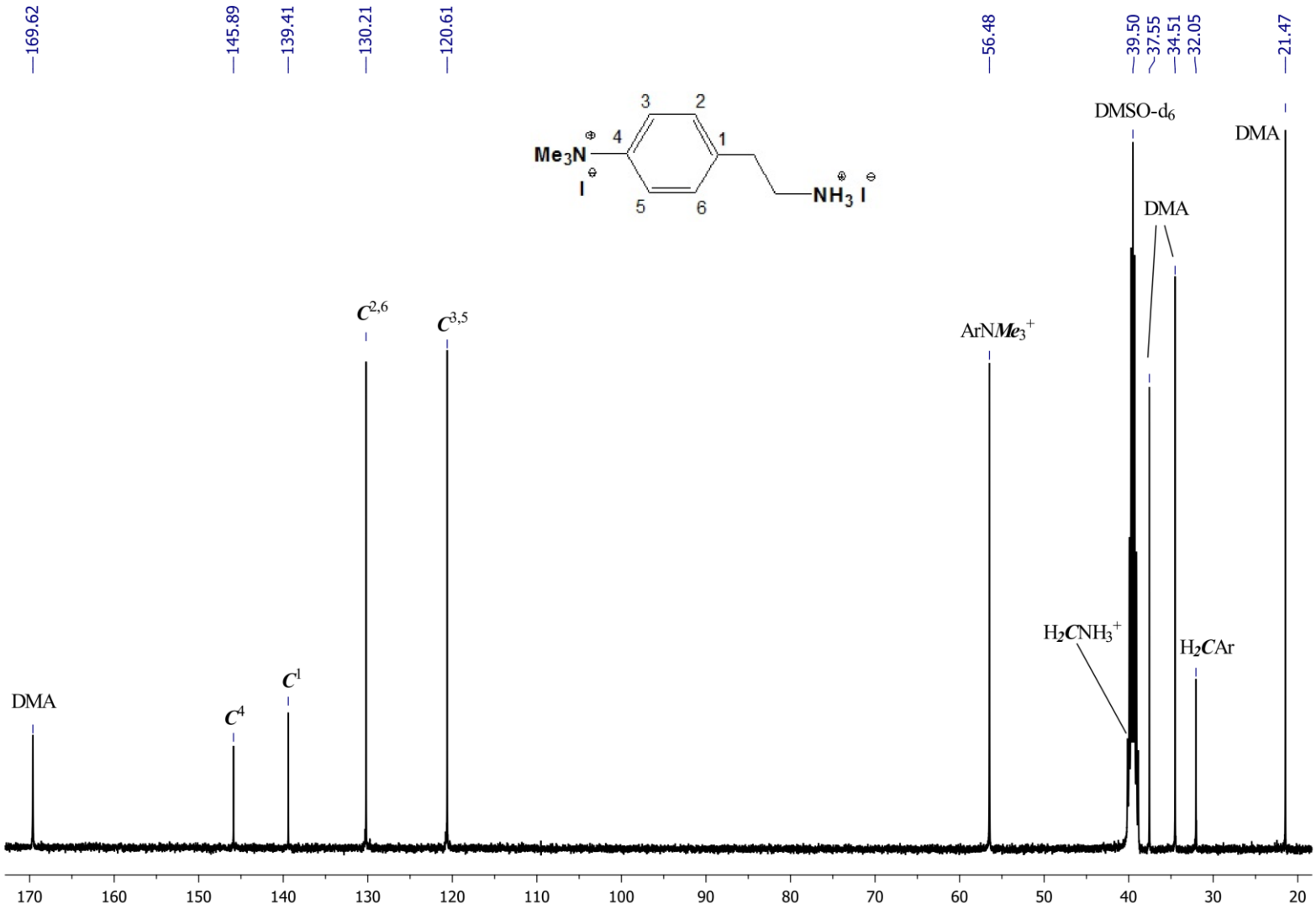


Figure S42. ^{13}C NMR spectrum (DMSO-d_6) of the reaction mixture 4-$H_2NC_6H_4CH_2CH_2NH_2$ + MeI (1 : 6) in DMA ($p(CO_2)$ = 60 bar, 52 °C, 55 hours).

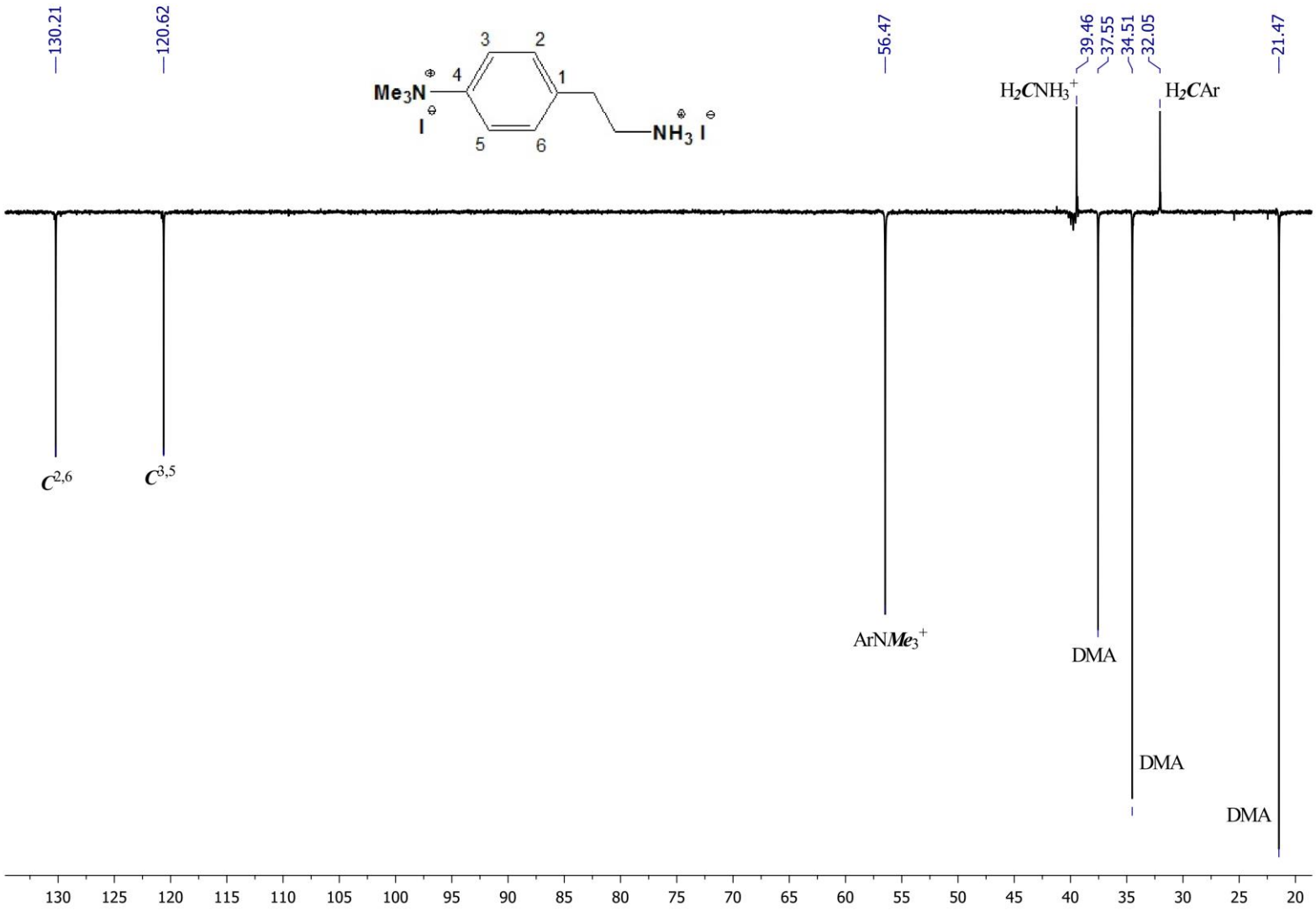


Figure S43. DEPT spectrum (DMSO-d_6) of the reaction mixture 4-$H_2NC_6H_4CH_2CH_2NH_2$ + MeI (1 : 6) in DMA ($p(CO_2)$ = 60 bar, 52 °C, 55 hours).

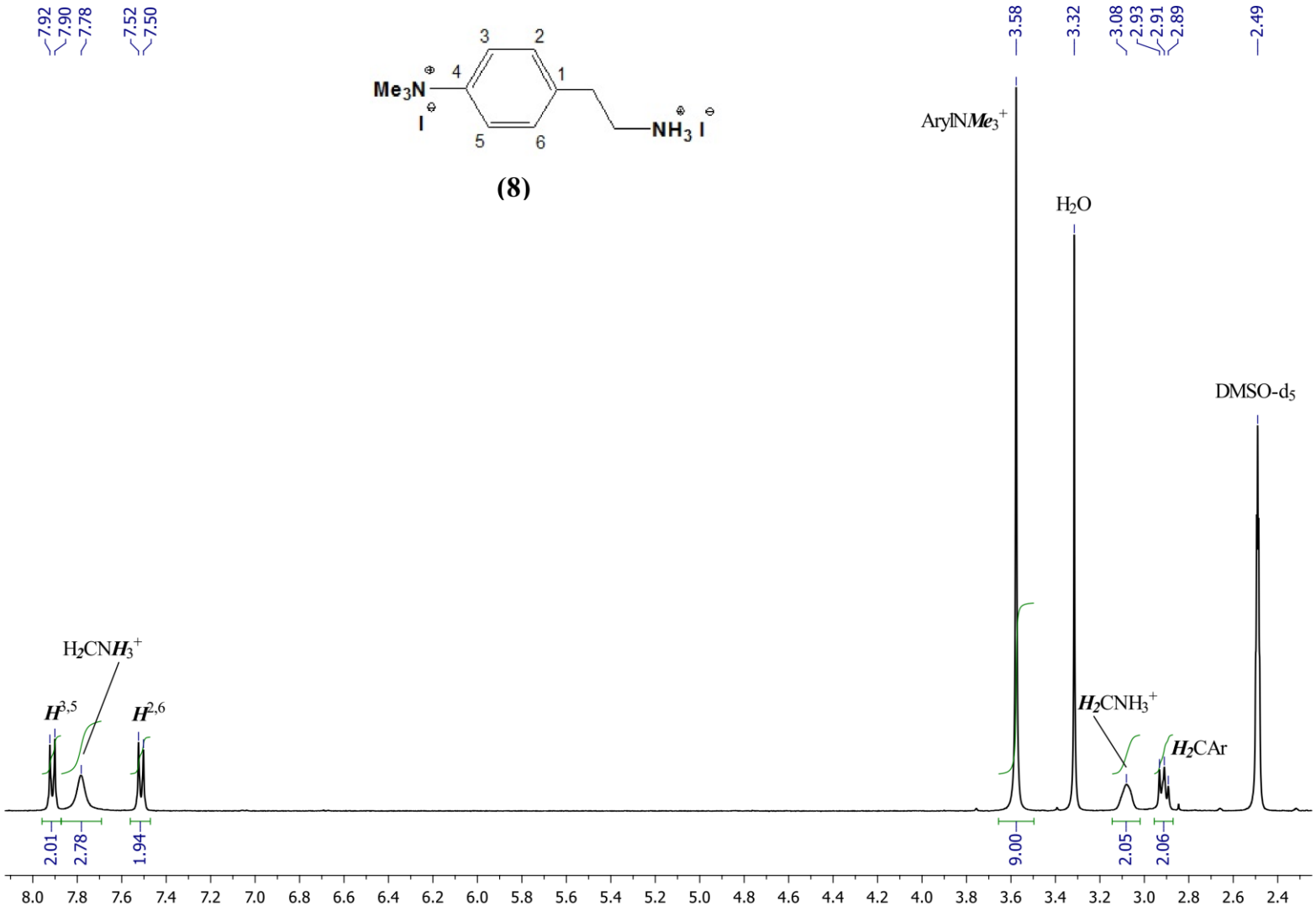


Figure S44. ^{1}H NMR spectrum (DMSO-d$_6$) of isolated 4-Me$_3$N$^+$C$_6$H$_4$CH$_2$CH$_2$NH$_3^+$ 2 I$^-$ (**8**).

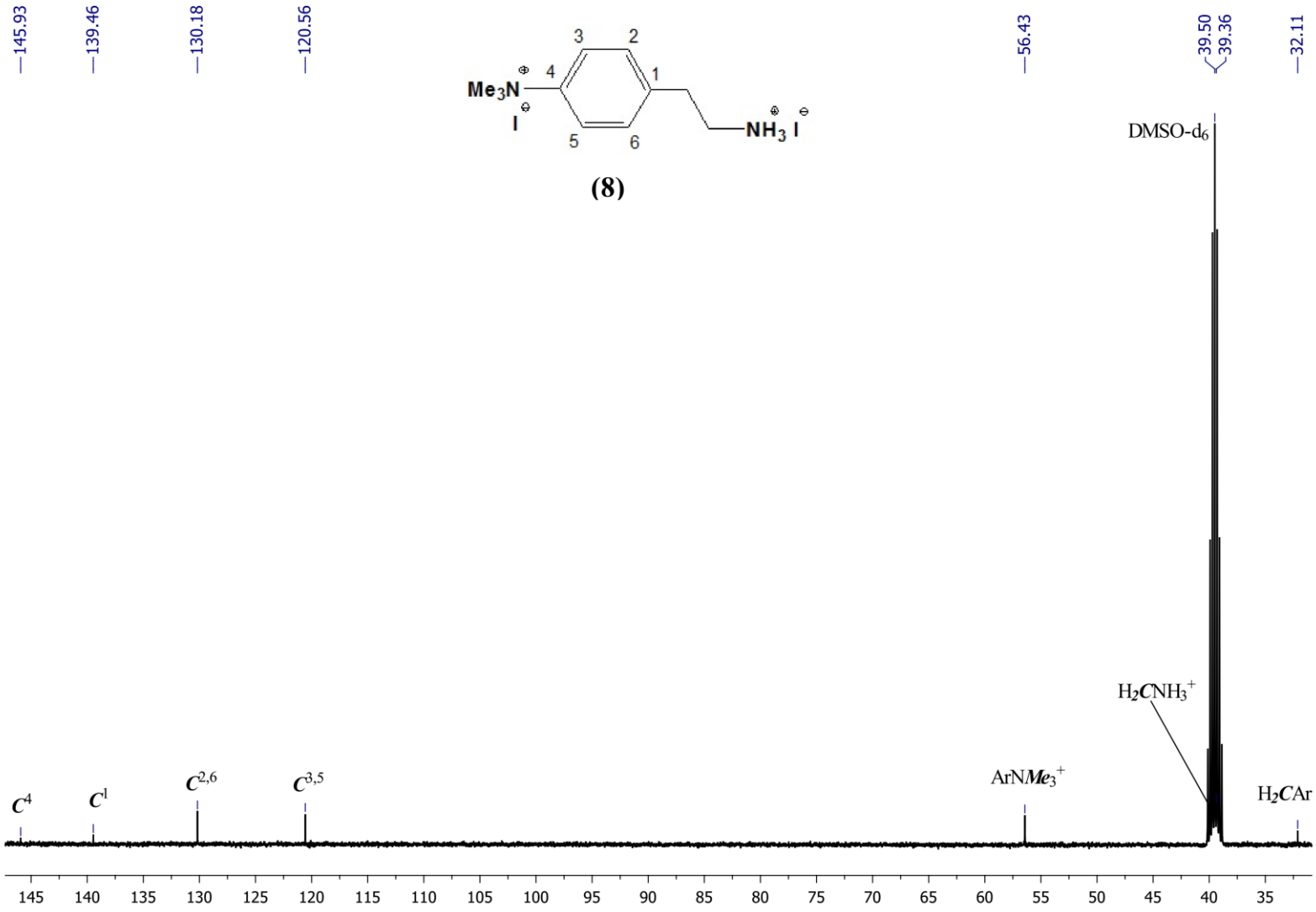


Figure S45. ^{13}C NMR spectrum (DMSO-d$_6$) of isolated 4-$Me_3N^+C_6H_4CH_2CH_2NH_3^+$ 2 I^- (**8**).