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Stereoselective synthesis of spirocyclic nitronates by $SnCl_4$-promoted reaction of nitroalkenes with C-2 substituted 4-methylidene-1,3-dioxolane

Andrey A. Mikhaylov, Petr A. Zhmurov, Anastasia S. Naumova, Yulia A. Khoroshutina, Alexey Yu. Sukhorukov and Sema L. Ioffe

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General experimental

All reactions were performed in oven-dried (150 °C) glassware under argon. The following solvents and reagents were distilled from indicated drying agents: CH_2Cl_2 (CaH_2); DMSO (CaH_2, *in vacuo*). NMR spectra were recorded on a Bruker AM-300 (^{1}H: 300.13 MHz, ^{13}C: 75.47 MHz, AMX-400 (^{1}H: 400.13 MHz, ^{13}C: 100.61 MHz) or AV 600 (^{1}H: 600.13 MHz) instruments and referenced to residual solvent peak. Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. The ratios of stereoisomers were derived from the relative integral intensities of the characteristic signals in the ^{1}H NMR spectra. Key NOESY interactions are shown on figure with red and blue arrows.

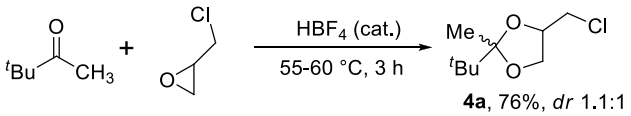
Elemental analyses were performed by the Analytical Laboratory of the Institute of Organic Chemistry. High Resolution Mass Spectra were recorded on a Bruker MicroTOFF spectrometer. Melting points were determined on Kofler melting point apparatus and are uncorrected.

Analytical thin-layer chromatography was performed on Merck silica gel plates with QF-254 indicator. Visualization of TLC plates was accomplished with UV light and/or anisaldehyde/H_2SO_4. All solvents for chromatography and extractions were technical grade and distilled from the indicated drying agents: pentane, hexane, ethyl acetate (K_2CO_3). Column chromatography was performed using 230–400-mesh Merck silica gel or Brockmann Type III Al_2O_3.

Commercial reagents: epichlorohydrine, *tert*-butyl methyl ketone, aqueous HBF_4 solution, 48% (Aldrich), NaH (Alfa Aesar). The following reagents were prepared according to literature procedures: (*E*)-β-nitrostyrene,[1] (*E*)-β-methyl-β-nitrostyrene,[2] (*E*)-2-nitrovinyl benzoate.[3]

Synthesis of 2-*tert*-butyl-2-methyl-4-methylene-1,3-dioxolane

2-tert-butyl-4-chloromethyl-2-methyl-1,3-dioxolane 4a.[4]



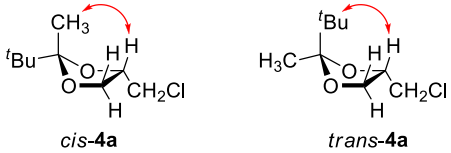
tert-Butyl methyl ketone (25.0 ml, 20.0 g, 200 mmol) and $HBF_{4(aq)}$ (100 mg, cat.) were placed in 50 mL two-bottomed round flask equipped with condenser and dropping funnel with epichlorohydrine (7.2 ml, 9.3 g, 100 mmol). The latter was added dropwise to a vigorously stirred solution for 15 min. The temperature of the reaction mixture rose appreciably. The reaction mixture was stirred for extra 20 min and then was gently heated to 55-60 °C (*caution! exotermic reaction!*) and kept at this temperature for 3 h. After that excess of *tert*-butyl methyl ketone is distilled out at atmosphere pressure (bp 103-110 °C) and the residue was vacuum distilled from the same flask to give 14.7 g (76 mmol, 76%, 1:1.1 mixture of isomers) of target dioxolane **4a** as a colorless liquid.

Colorless liquid, bp 98-99 °C/22 Torr, 1:1.1 mixture of *trans*- and *cis*- isomers

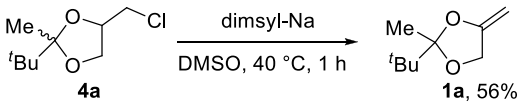
^{1}H NMR (600.13 MHz, CD_2Cl_2, 299 K): *trans*-**4a**: δ = 0.96 [s, 9H, $C(CH_3)_3$], 1.31 [s, 3H, CH_3], 3.57 [dd, ^2J = 11.1, ^3J = 6.8 Hz, 1H, CH_2Cl], 3.70 [dd, ^2J = 11.1, ^3J = 4.4 Hz, 1H, CH_2Cl], 3.82 [t, $^3J \approx {}^2J$ = 7.9 Hz, 1H, CH_2O], 4.22 [dd, ^2J = 8.1, ^3J = 6.1 Hz, 1H, CH_2O), 4.25 [dtd, ^3J = 7.7, $^3J \approx {}^3J$ = 6.5, ^3J = 4.4 Hz, 1H, CH]; *cis*-**4a**: δ = 0.98 [s, 9H, $C(CH_3)_3$], 1.27 [s, 3H, CH_3], 3.54 [dd, ^2J = 10.9, ^3J = 7.1 Hz, 1H, CH_2Cl], 3.65 [dd, ^2J = 10.9, ^3J = 5.2 Hz, 1H, CH_2Cl], 3.75 [dd, ^2J = 8.3, ^3J = 6.0 Hz, 1H, CH_2O], 4.17 [dd, ^2J = 8.3, ^3J = 6.6 Hz, 1H, CH_2O], 4.38 [tt, $^3J \approx {}^3J$ = 6.2, $^3J \approx {}^3J$ = 6.0 Hz, 1H, CH].

^{13}C NMR (75.47 MHz, CD_2Cl_2, 301 K): *trans*-**4a**: δ = 20.4 (CH_3), 24.9 ($C(\underline{CH_3})_3$), 38.0 ($\underline{C}(CH_3)_3$), 44.8 (CH_2Cl), 68.6 (CH_2O), 76.4 (OCH), 115.3 (OCO); *cis*-**4a**: δ = 18.3 (CH_3), 25.0 ($C(\underline{CH_3})_3$), 39.3 ($\underline{C}(CH_3)_3$), 44.6 (CH_2Cl), 68.1 (CH_2O), 75.0 (OCH), 115.7 (OCO).

Key NOESY interactions:



2-*tert*-Butyl-2-methyl-4-methylidene-1,3-dioxolane 1a.



NaH (2.30 g, 60% suspension in mineral oil, 57.5 mmol) was added to DMSO (30 ml) under atmosphere of dry argon and the reaction mixture stirred at 70 °C for 1.5 h to give clear solution of dimsyl-Na in DMSO. Reaction mixture was allowed to cool to 40 °C and chloride **4a** (9.63 g, 50.0 mmol) was added dropwise for 20 min to the reaction mixture at this temperature to give a brown solution. Reaction mixture was stirred at 40 °C for 1 extra hour and was poured into H_2O (100 ml)/Et_2O (40 ml) mixture. Organic layer was separated and the aqueous layer was back-extracted with Et_2O (2×40 ml). Combined organic layers were washed with brine (2×50 ml), dried over Na_2SO_4 and evaporated *in vacuo*. The residue was vacuum distilled over KOH pellets to give 4.37 g (28.0 mmol, 56%) of vinyl ether **1a** as a colorless liquid.

Colorless liquid, bp 68-70 °C/33 torr.

Storred at −30 °C over KOH pellets. Oxidises upon storage, can be easily purified by eluatuon through a short pad of Al_2O_3 with hexane. R_f 0.71 (hexane, Al_2O_3, $KMnO_4$ visualisation).

^{1}H NMR (400.13 MHz, $(CD_3)_2CO$, 305 K): δ = 0.98 [s, 9H, $C(CH_3)_3$], 1.31 [s, 3H, CH_3], 3.79 [q, $^2J \approx {}^4J \approx {}^4J$ = 1.8 Hz, 1H, =C$\underline{H}_A$H$_B$], 4.17 [q, $^2J \approx {}^4J \approx {}^4J$ = 2.0 Hz, 1H, =CH$_A\underline{H}_B$], 4.48 [dt, ^2J = 12.3, $^4J \approx {}^4J$ = 1.7 Hz, 1H, OC$\underline{H}_C$H$_D$], 4.53 [dt, ^2J = 12.3, $^4J \approx {}^4J$ = 2.0 Hz, 1H, OCH$_C\underline{H}_D$].

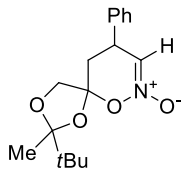
^{13}C NMR (100.61 MHz, $(CD_3)_2CO$, 305 K): δ = 19.1 (CH_3), 25.1 (C($\underline{CH_3}$)$_3$), 39.5 ($\underline{C}(CH_3)_3$), 67.7 (CH_2), 76.8 (=CH_2), 117.9 (OCO), 158.0 (C=).

[4+2]-Cycloaddition with nitroalkenes

$SnCl_4$ (260 μl, 573 mg, 2.2 mmol) was added simultaneously to a stirred solution of nitroalkene **3a-c** (2.0 mmol) in CH_2Cl_2 (8 ml) at –78 °C. The reaction mixture was stirred for 15 min and then solution of methylidenedioxalane **1a** (354 mg, 2.2 mmol) in CH_2Cl_2 (2.0 ml) was added dropwise. The reaction mixture was stirred for 2 h and poured into a mixture of EtOAc (20 ml) and saturated aqueous solution of $NaHCO_3$ (15 ml). The aqueous phase was back-extracted with EtOAc (2 × 10 ml), combined organic layers were washed with water (20 ml), brine (30 ml) and dried over Na_2SO_4. The solvents were removed in vacuum and the residue was subjected to column chromatography (silica gel, EtOAc/hexane 1/3 → 1/2 → 1/1) to give nitronate **2a,b** or nitrodiene **5**.

2-*tert*-Butyl-2-methyl-9-phenyl-1,3,6-trioxa-7-azaspiro[4.5]dec-7-ene 7-oxide 2a

Yield 324 mg (1.1 mmol, 53%), 3.0 : 1 mixture of diastereomers, white flakes, mp = 150-153 °C (Et_2O), R_f = 0.49 (SiO_2, EtOAc/hexane, 1/1).

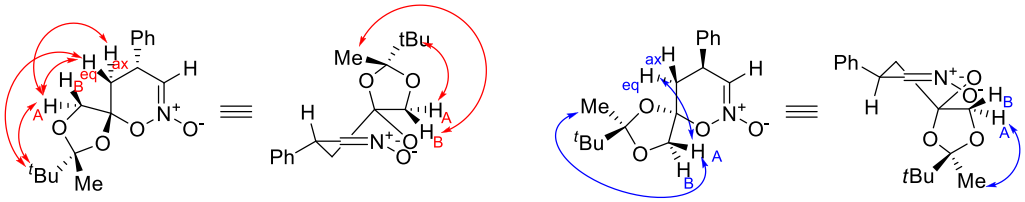


^{1}H NMR (400.13 MHz, $CDCl_3$, 305 K): ***rel-2S,5S,9R isomer*** *(major)*: δ = 1.14 [s, 9H, $C(CH_3)_3$], 1.70 [s, 3H, CH_3], 2.15 [t, $^{2}J \approx {}^{3}J$ = 12.4 Hz, 1H, $C\underline{H}_{Ax}H_{Eq}$], 2.36 [dd, ^{2}J = 12.8, ^{3}J = 6.7 Hz, 1H, $CH_{Ax}\underline{H}_{Eq}$], 4.03 [d, ^{2}J = 9.5 Hz, 1H, $OC\underline{H}_{A}H_{B}$], 4.15 [ddd, ^{2}J = 11.9, ^{3}J = 6.7, ^{3}J = 3.1 Hz, 1H, $C\underline{H}$Ph], 4.35 [d, ^{2}J = 9.5 Hz, 1H, $OCH_{A}\underline{H}_{B}$], 6.42 [d, ^{3}J = 3.1 Hz, 1H, CH=N], 7.24-7.41 [m, 5H, Ph]; ***rel-2S,5R,9S isomer*** *(minor)*: δ = 1.21 [s, 9H, $C(CH_3)_3$], 1.48 [s, 3H, CH_3], 2.20 [t, $^{2}J \approx {}^{3}J$ = 12.4 Hz, 1H, $C\underline{H}_{Ax}H_{Eq}$], 2.25 [dd, ^{2}J = 12.8, ^{3}J = 7.3 Hz, 1H, $CH_{Ax}\underline{H}_{Eq}$], 4.07 [d, ^{2}J = 9.8 Hz, 1H, $OC\underline{H}_{A}H_{B}$], 4.19 [ddd, ^{2}J = 11.2, ^{3}J = 7.3, ^{3}J = 3.1 Hz, 1H, $C\underline{H}$Ph], 4.38 [d, ^{2}J = 9.8 Hz, 1H, $OCH_{A}\underline{H}_{B}$], 6.40 [d, ^{3}J = 3.1 Hz, 1H, CH=N], 7.24-7.41 [m, 5H, Ph].

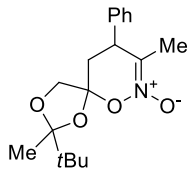
^{13}C NMR (100.61 MHz, $CDCl_3$, 305 K): ***rel-2S,5S,9R isomer*** *(major)*: δ = 20.5 (CH_3), 25.1 ($C(\underline{C}H_3)_3$), 34.4 and 38.1 (CH and CH_2), 39.0 ($\underline{C}(CH_3)_3$), 74.0 (OCH_2), 108.9 and 119.7 (2×OCO), 113.4 (CH=N), 127.4 and 129.2 ($CH_{o\text{Ph}}$ and $CH_{m\text{Ph}}$), 128.0 ($CH_{p\text{Ph}}$), 139.2 (C_iPh); ***rel-2S,5R,9S isomer*** *(minor)*: δ = 19.3 (CH_3), 25.4 ($C(\underline{C}H_3)_3$), 35.4 and 37.9 (CH and CH_2), 38.1 ($\underline{C}(CH_3)_3$), 73.1 (OCH_2), 107.7 and 119.7 (2×OCO), 113.1 (CH=N), 127.5 and 129.1 ($CH_{o\text{Ph}}$ and $CH_{m\text{Ph}}$), 127.9 ($CH_{p\text{Ph}}$), 139.3 (C_iPh).

HRMS (ESI) calcd for $C_{17}H_{23}NNaO_4$ [M+Na^+] 328.1519; found 328.1518.

Key NOESY interactions:



***rel*-(2*RS*,5S,9R)-2-*tert*-Butyl-2,8-dimethyl-9-phenyl-1,3,6-trioxa-7-azaspiro[4.5]dec-7-ene 7-oxide 2b**



Yield 295 mg (0.9 mmol, 46%), 4.1 : 1 mixture of diastereomers, white flakes, mp = 150-153 °C (Et_2O) R_f = 0.53 (SiO_2, EtOAc/hexane, 1/1).

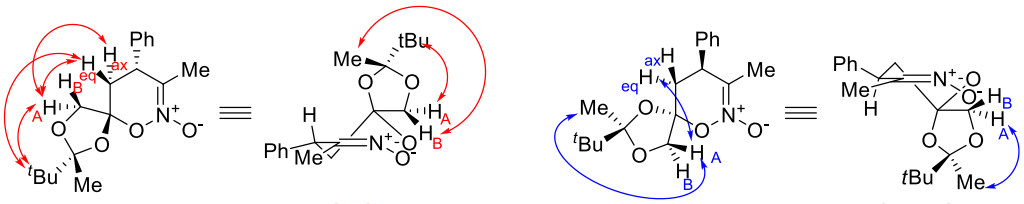
^{1}H NMR (300.13 MHz, $CDCl_3$, 305 K): ***rel-2S,5S,9R isomer*** *(major)*: δ = 1.00 [s, 9H, $C(CH_3)_3$], 1.58 [s, 3H, CH_3], 1.86 [d, ^{4}J = 1.8 Hz, 3H, CH_3], 2.13 [dd, ^{2}J = 13.2, ^{3}J = 11.4 Hz, 1H, $C\underline{H}_{Ax}H_{Eq}$], 2.27 [dd, ^{2}J = 13.2, ^{3}J = 7.5 Hz, 1H, $CH_{Ax}\underline{H}_{Eq}$], 3.88 [d, ^{2}J = 9.5 Hz, 1H, $OC\underline{H}_{A}H_{B}$], 3.92 [ddd, ^{2}J = 11.4, ^{3}J = 7.5, ^{2}J = 1.8 Hz, 1H, $C\underline{H}$Ph], 4.25 [d, ^{2}J = 9.5 Hz, 1H, $OCH_{A}\underline{H}_{B}$], 7.13-7.41 [m, 5H, Ph]; ***rel-2S,5R,9S isomer*** *(minor)*: δ = 1.07 [s, 9H, $C(CH_3)_3$], 1.34

[s, 3H, CH_3], 1.85 [d, ^4J = 1.5 Hz, 3H, CH_3], 2.14-2.27 [m, 2H, $CH_{Ax}H_{Eq}$], 3.90-4.02 [m, 2H, OCH_AH_B and CHPh], 4.27 [d, ^2J = 10.0 Hz, 1H, OCH_AH_B], 7.13-7.41 [m, 5H, Ph].

^{13}C NMR (100.61 MHz, $CDCl_3$, 305 K): ***rel-2S,5S,9R isomer*** *(major)*: δ = 17.1 (CH_3C=N), 20.5 (CH_3), 24.9 ($C(CH_3)_3$), 36.4 (CH_2), 39.0 ($C(CH_3)_3$), 42.3 (CH), 74.3 (OCH_2), 108.3, 119.6 and 122.2 (2×OCO and C=N), 128.4 and 129.8 ($CH_{o\text{Ph}}$, $CH_{m\text{Ph}}$ and $CH_{p\text{Ph}}$, overlap), 140.4 (C_iPh); ***rel-2S,5R,9S isomer*** *(minor)*: δ (selected sygnals) = 17.1 (CH_3C=N), 19.1 (CH_3), 25.3 ($C(CH_3)_3$), 37.7 (CH_2), 38.1 ($C(CH_3)_3$), 42.3 (CH), 73.2 (OCH_2), 107.2 (OCO), 140.6 ($C_{i\text{Ph}}$).

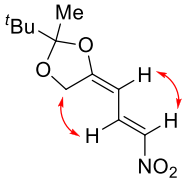
HRMS (ESI) calcd for $C_{18}H_{26}NO_4$ [M+H$^+$] 320.1856; found 320.1856.

Key NOESY interactions:



(*E*)-2-*tert*-Butyl-2-methyl-4-((*E*)-3-nitroallylidene)-1,3-dioxolane 5

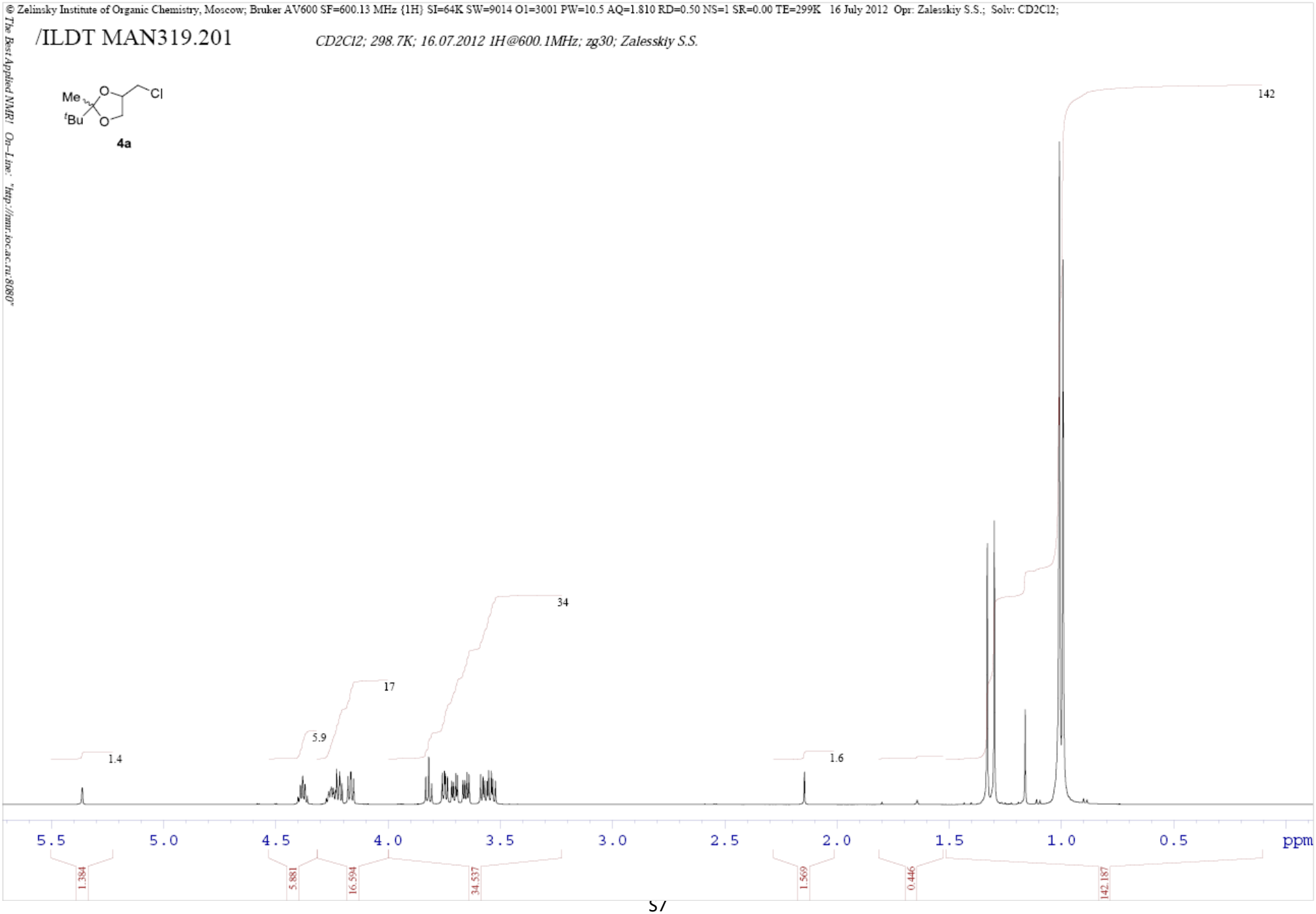
Yield 245 mg (1.1 mmol, 54%), yellow needles, mp = 118-124 °C (^{i}PrOH), R_f = 0.67 (EtOAc/hexane, 1/1).



^{1}H NMR (300.13 MHz, $CDCl_3$, 298 K): δ = 1.02 [s, 9H, $C(CH_3)_3$], 1.43 [s, 3H, CH_3], 4.88 [dd, ^2J = 14.2, ^4J = 1.2 Hz, 1H, OCH_AH_B], 4.99 [d, ^2J = 14.2, ^4J = 1.1 Hz, Hz, 1H, OCH_AH_B], 5.66 [dt, ^3J = 13.2, $^4J \approx {}^4J$ = 1.2 Hz, 1H, =CH], 7.02 [d, ^3J = 12.8 Hz, 1H, $=CHNO_2$], 7.53 [t, $^3J \approx {}^3J$ = 12.8 Hz, 1H, =CH].

^{13}C NMR (75.47 MHz, $CDCl_3$, 299 K): δ = 19.1 (CH_3), 24.7 ($C(CH_3)_3$), 39.0 ($C(CH_3)_3$), 67.6 (OCH_2), 91.0 (=CH), 121.9 (OCO), 133.3 and 136.6 (2×=CH), 166.3 (C=).

HRMS (ESI) calcd for $C_{11}H_{17}NNaO_4$ [M+Na$^+$] 250.1050; found 250.1046.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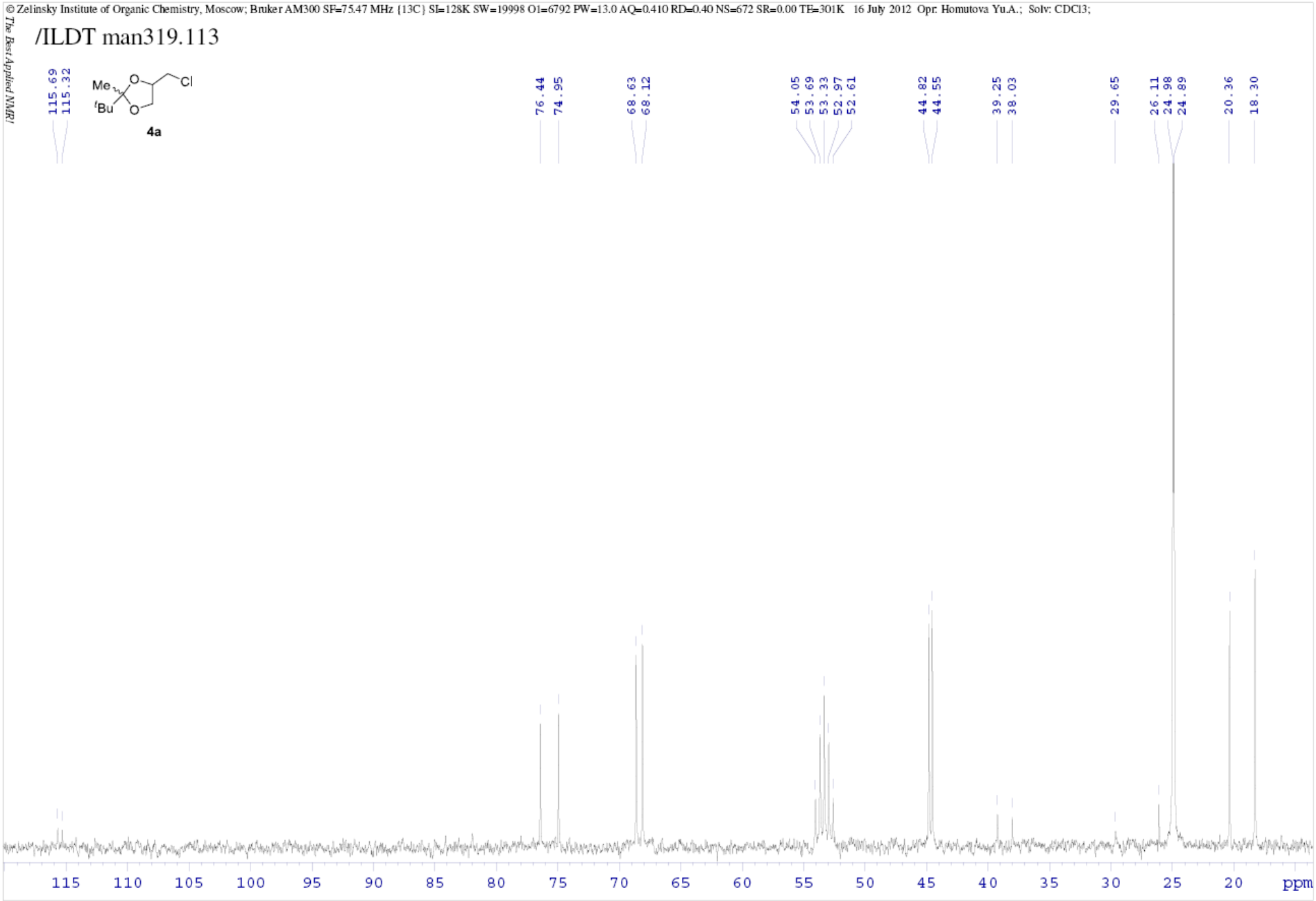
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The Best Applied NMR!
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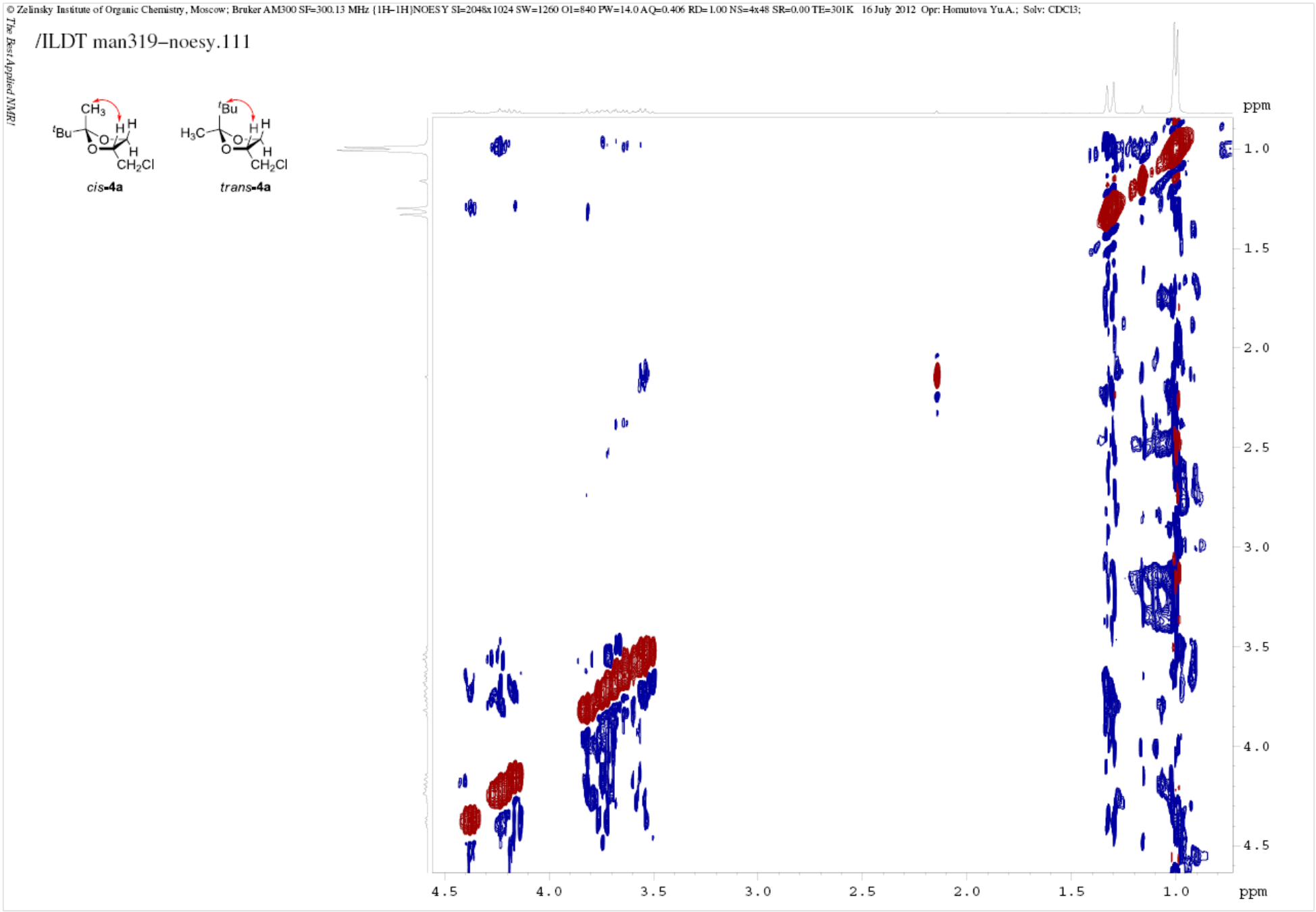
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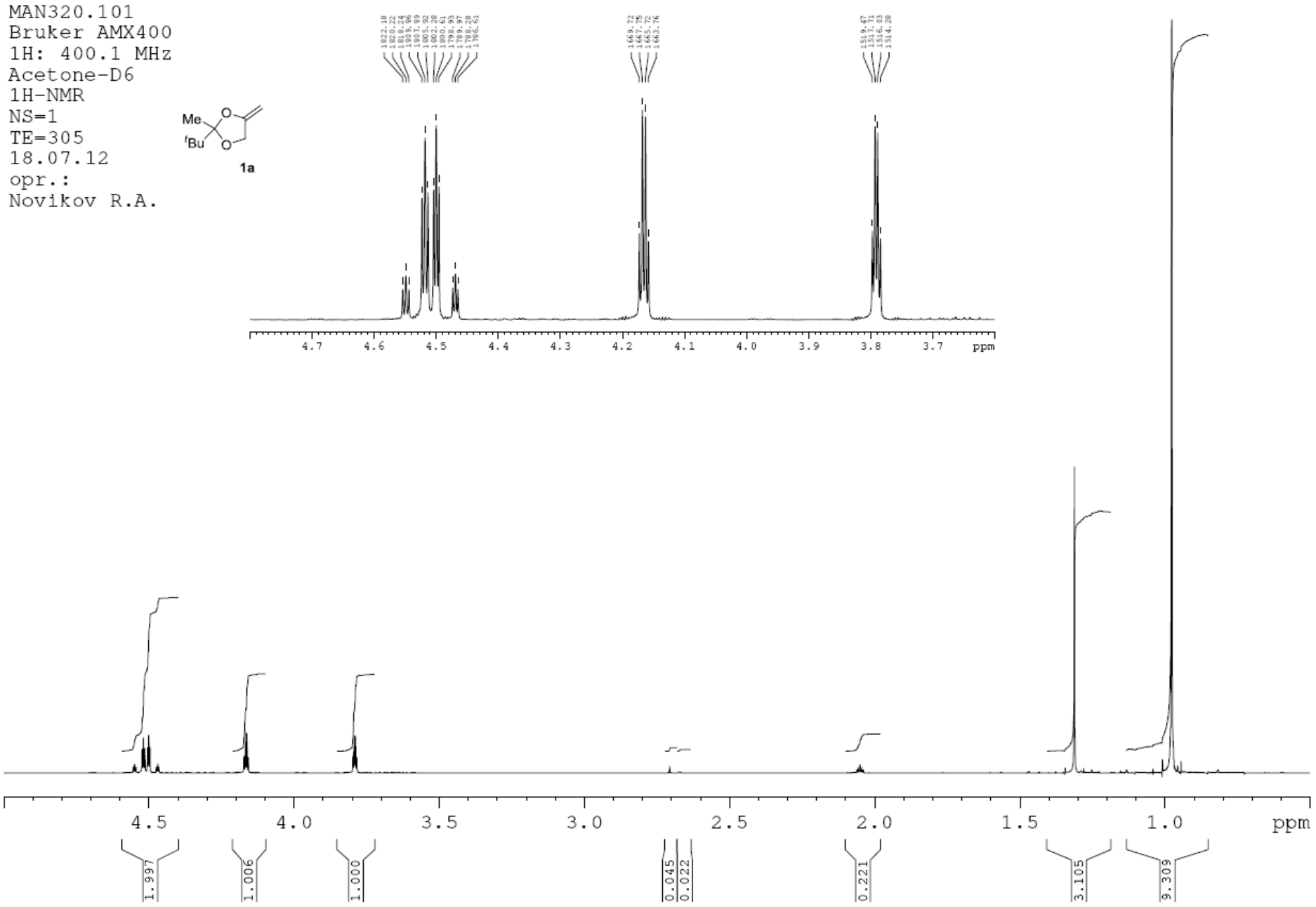
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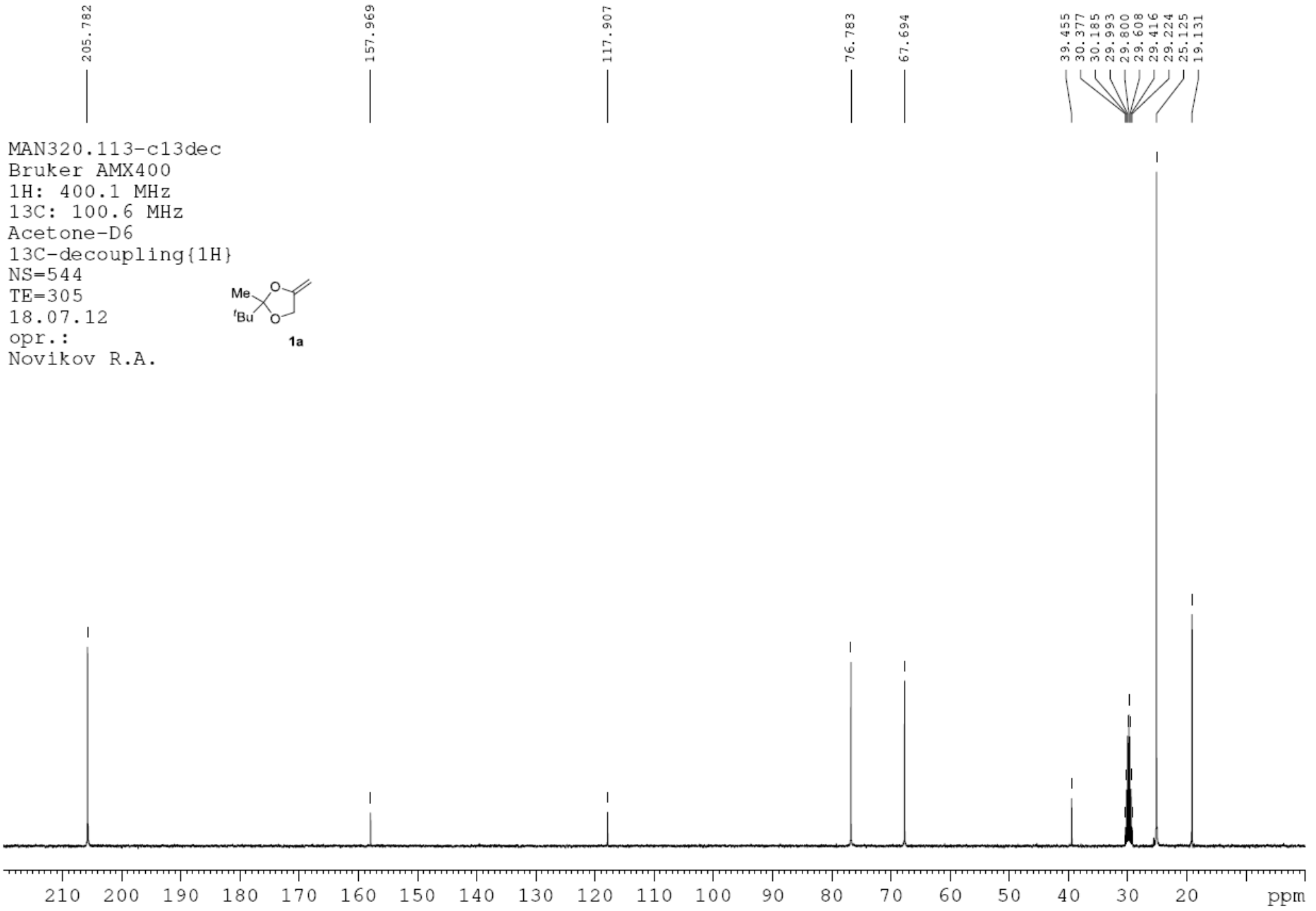
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The Best Applied NMR!

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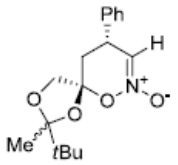
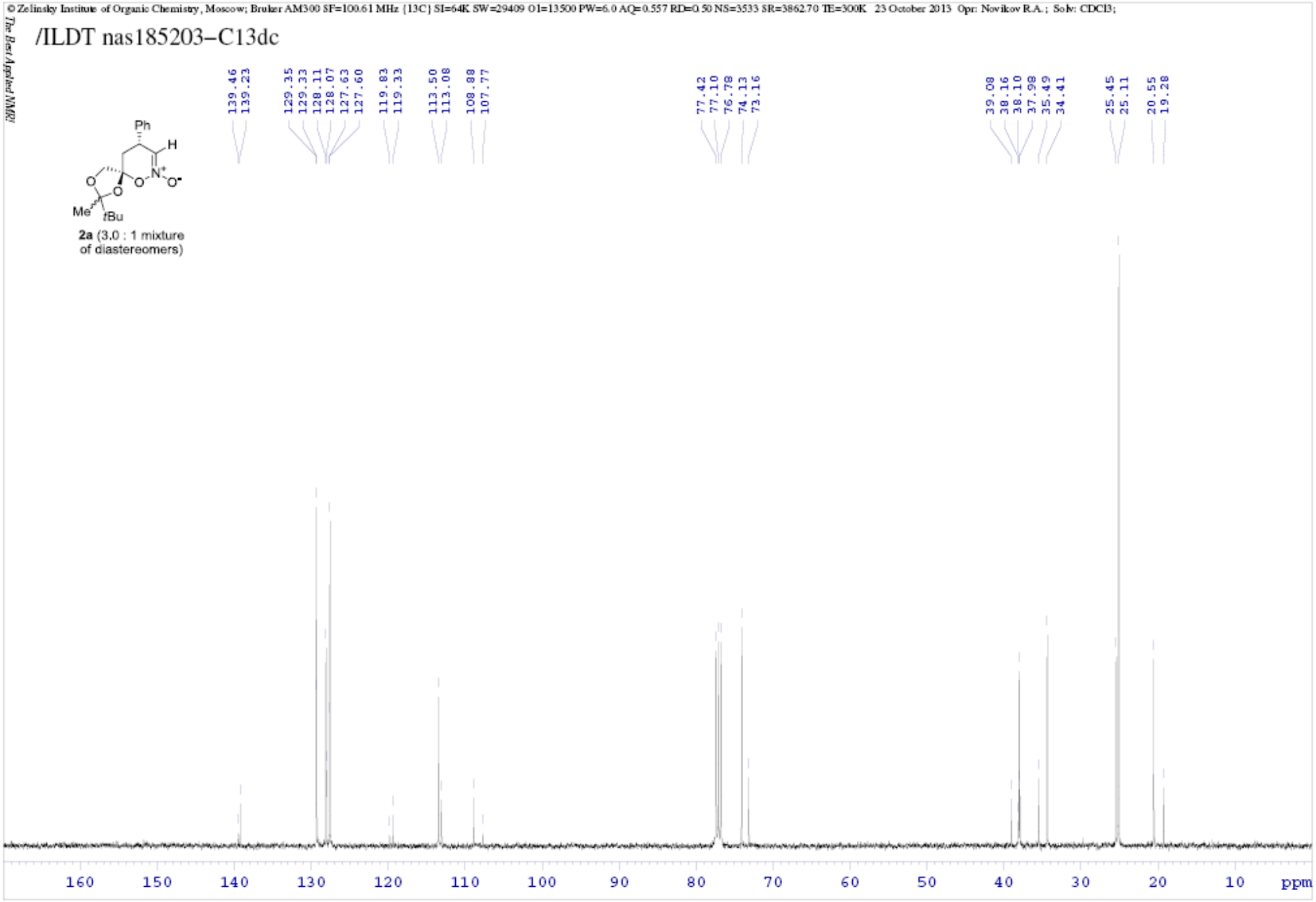
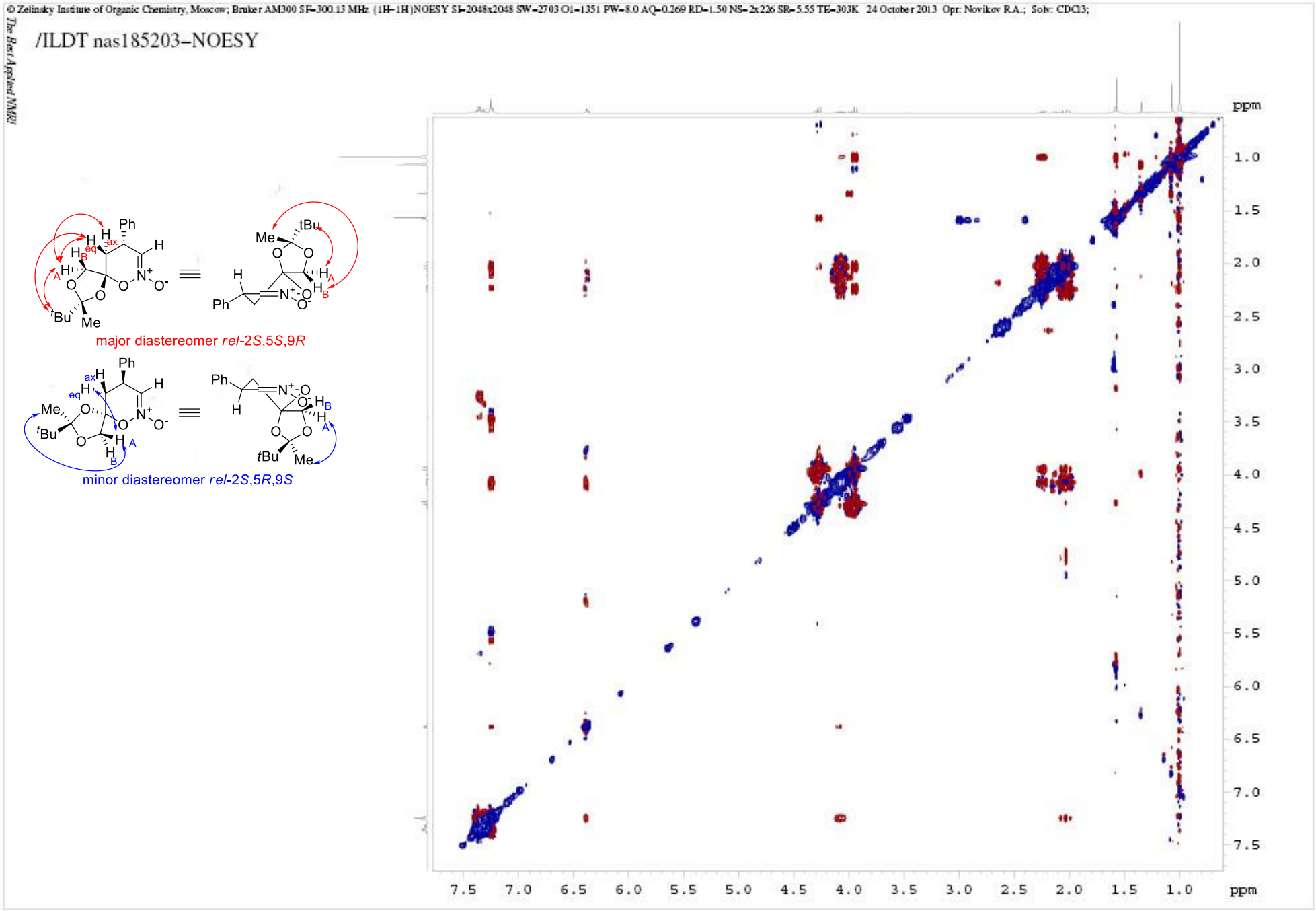
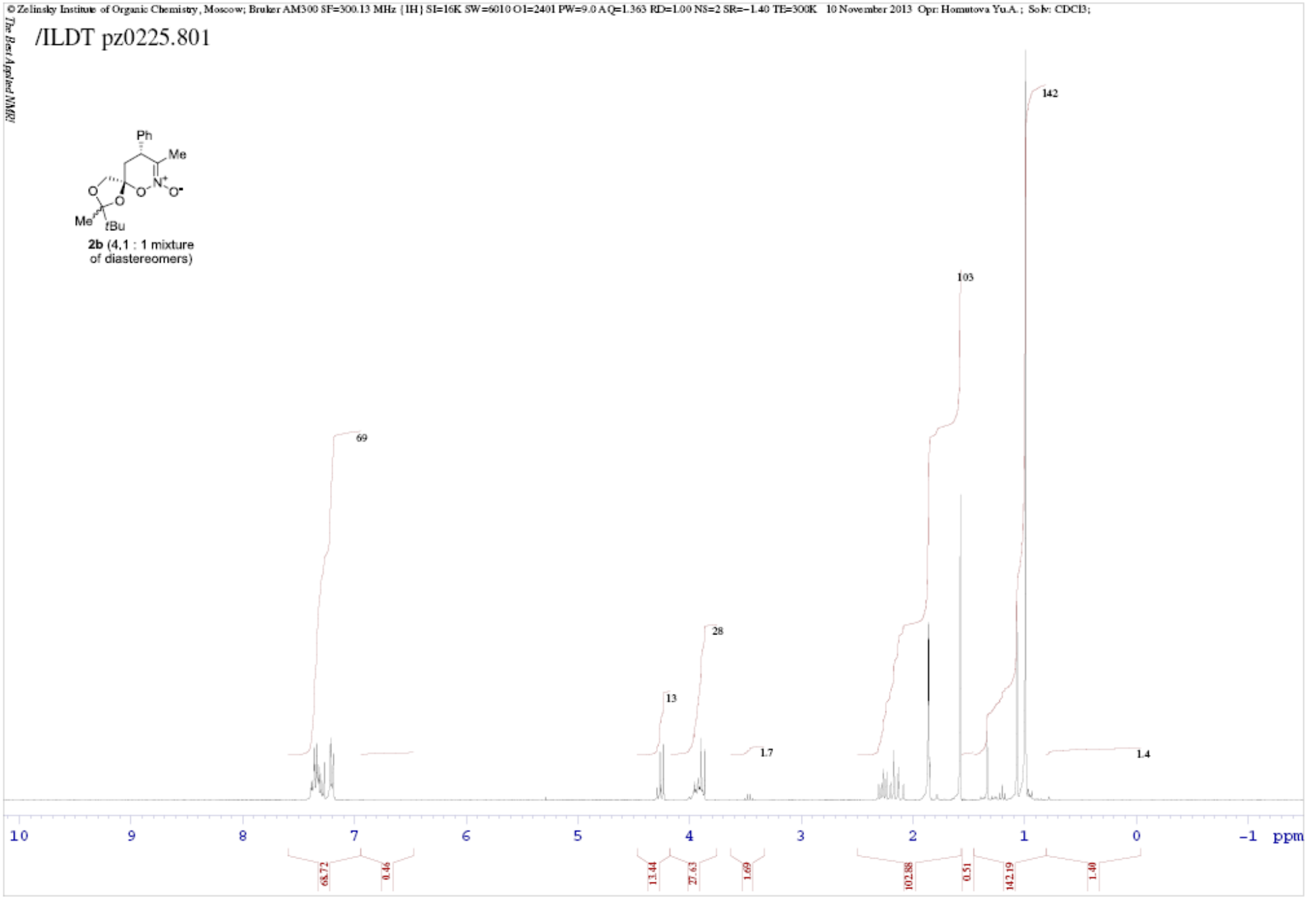
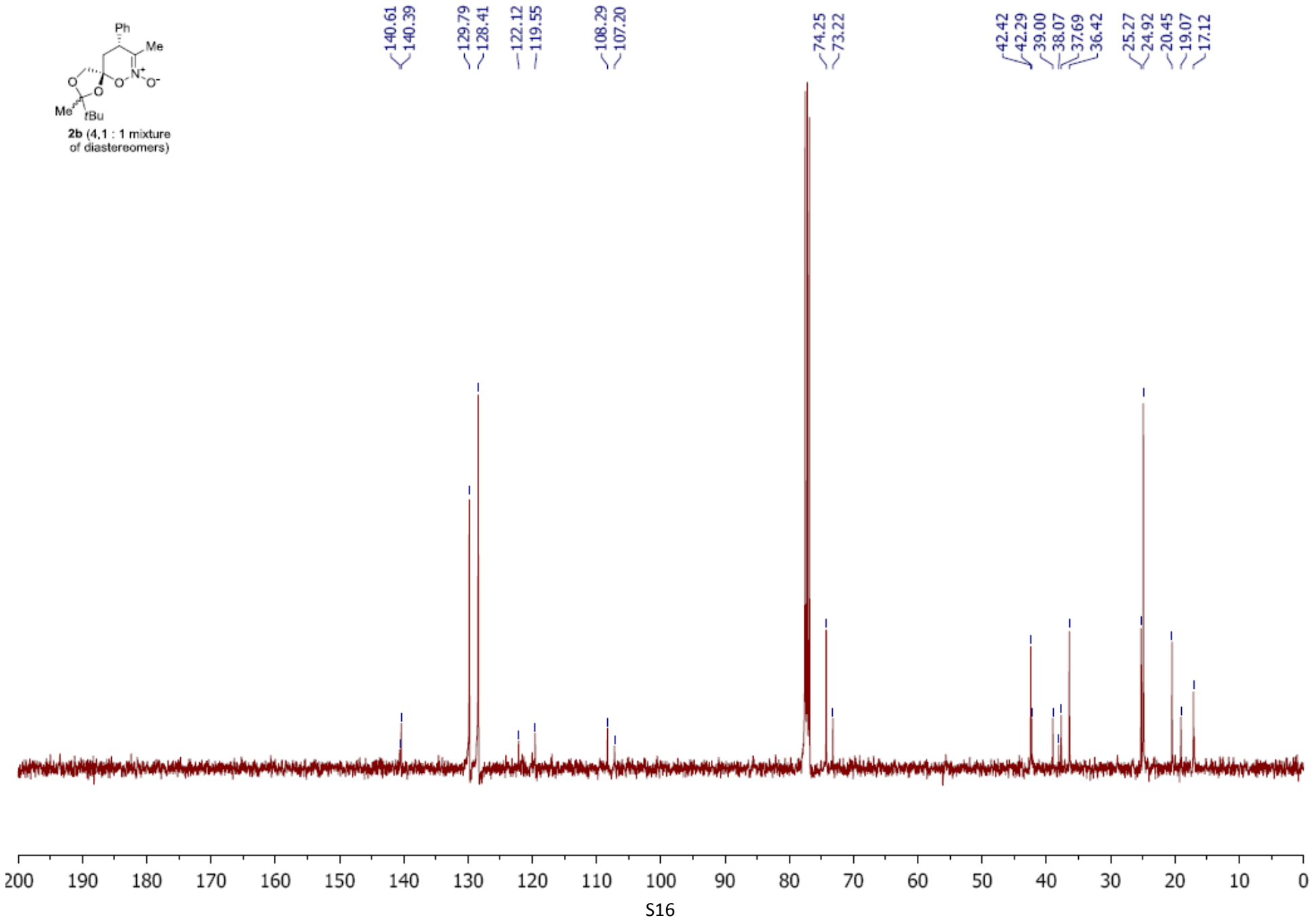


2a (3.0 : 1 mixture of diastereomers)


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=100.61 MHz {13C} SI=64K SW=29409 O1=13500 PW=6.0 AQ=0.557 RD=0.50 NS=3533 SR=3862.70 TE=300K 23 October 2013 Opr: Novikov R.A.; Solv: CDCl3;
The Best Applied NMR!
/ILDT nas185203–C13dc
139.46
139.23
129.35
129.33
128.11
128.07
127.63
127.60
119.83
119.33
113.50
113.08
108.88
107.77
77.42
77.10
76.78
74.13
73.16
39.08
38.16
38.10
37.98
35.49
34.41
25.45
25.11
20.55
19.28
Ph
H
N+
O-
O
O
O
Me
tBu
2a (3,0 : 1 mixture of diastereomers)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.13 MHz (1H-1H)NOESY SI=2048x2048 SW=2703 O1=1351 PW=8.0 AQ=0.269 RD=1.50 NS=2x226 SB=5.55 TE=303K 24 October 2013 Opr: Novikov R.A.; Solv: CDCl3;
The Best Applied NMR!
/ILDT nas185203–NOESY
major diastereomer rel-2S,5S,9R
minor diastereomer rel-2S,5R,9S
ppm
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.13 MHz {1H} SI=16K SW=6010 O1=2401 PW=9.0 AQ=1.363 RD=1.00 NS=2 SR=-1.40 TE=300K 10 November 2013 Opr: Homutova Yu.A.; Solv: CDCl3;
The Best Aspired NMR!
/ILDT pz0225.801
Ph
Me
N+
O-
O
O
O
Me
tBu
2b (4.1 : 1 mixture of diastereomers)
142
103
69
28
13
1.7
1.4
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
68.72
0.46
13.44
27.63
1.69
102.88
0.51
142.19
1.40


Ph
Me
N+
O-
O
O
O
Me
tBu
2b (4.1 : 1 mixture of diastereomers)
140.61
140.39
129.79
128.41
122.12
119.55
108.29
107.20
74.25
73.22
42.42
42.29
39.00
38.07
37.69
36.42
25.27
24.92
20.45
19.07
17.12
200
190
180
170
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130
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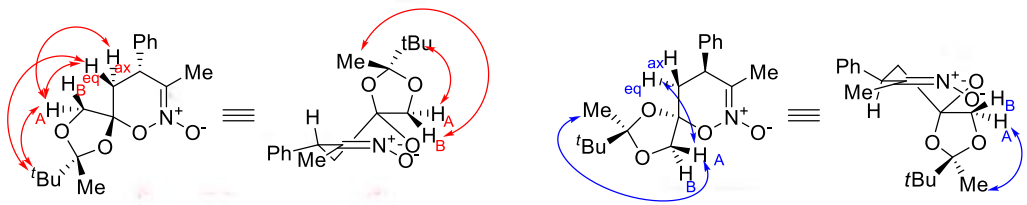
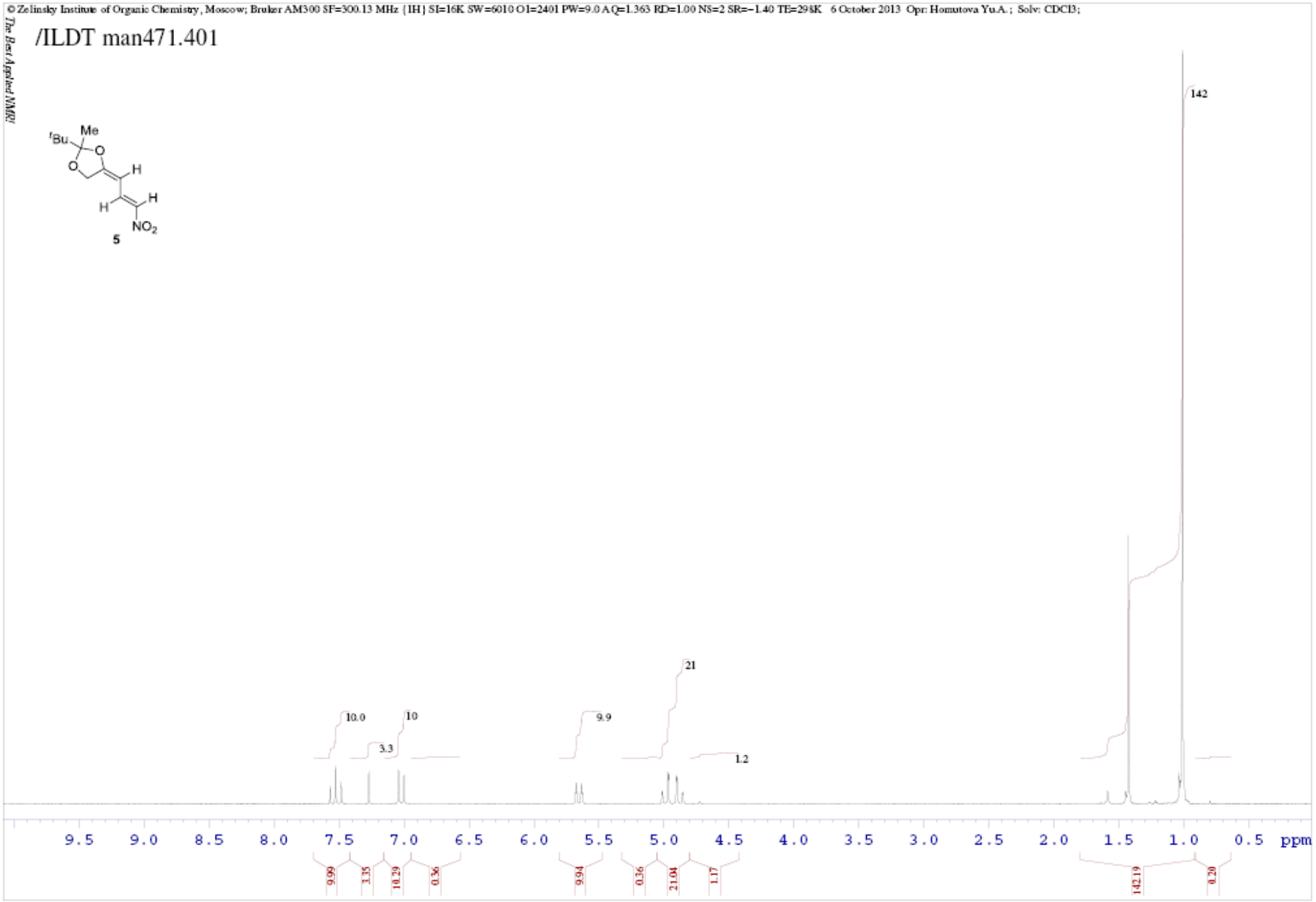
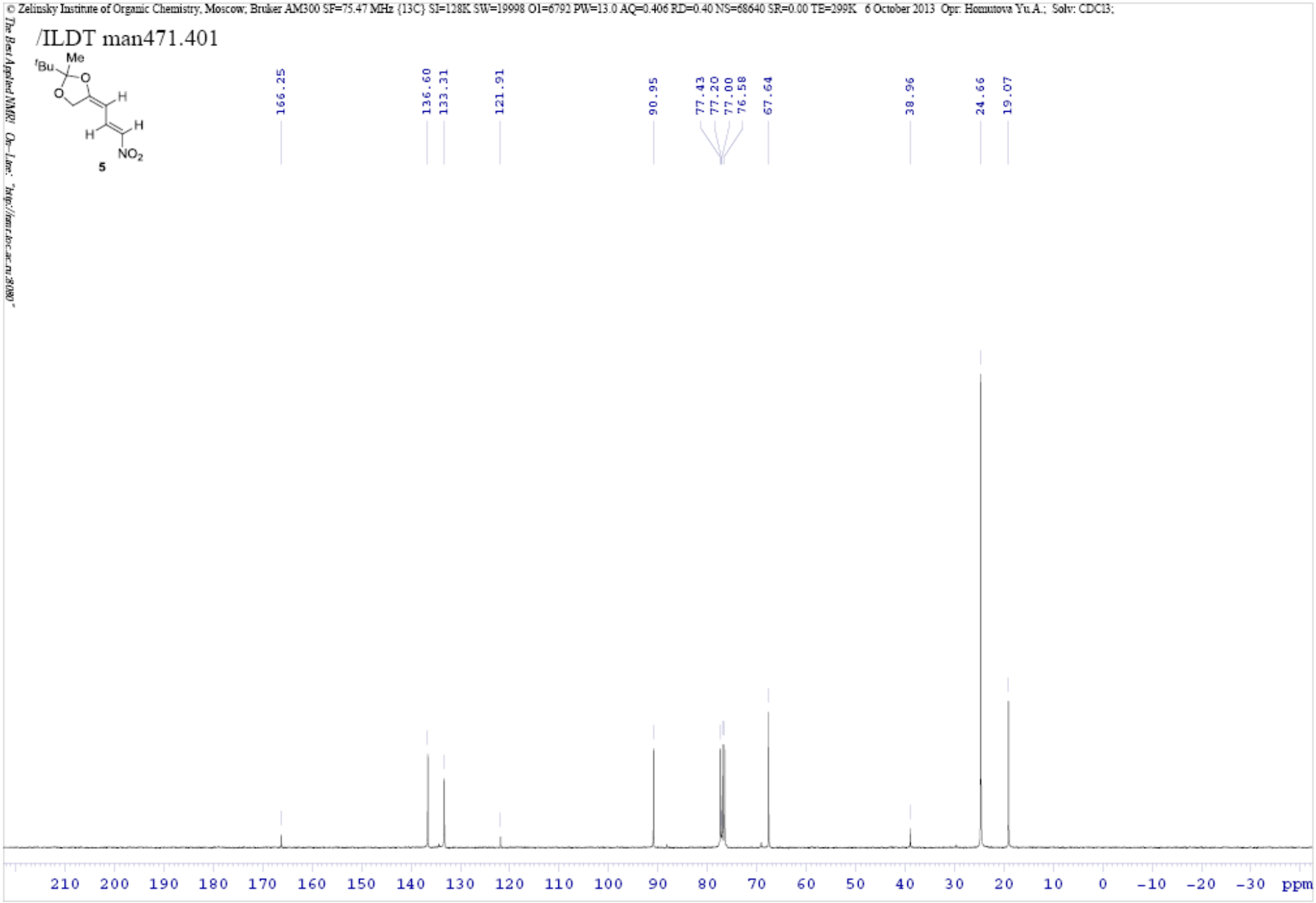
90
80
70
60
50
40
30
20
10
0

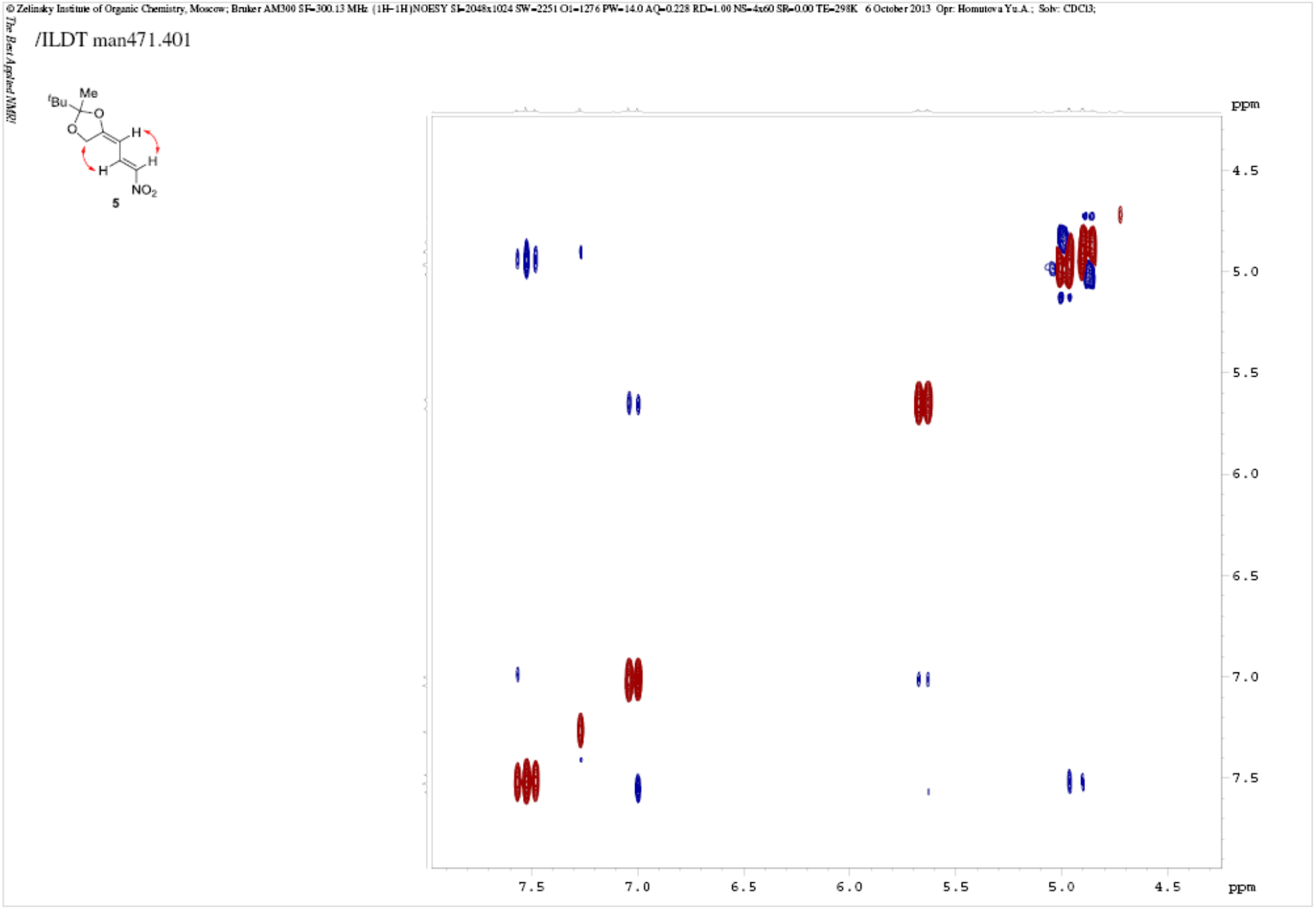


major diastereomer *rel*-2*S*,5*S*,9*R*

minor diastereomer *rel*-2*S*,5*R*,9*S*


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.13 MHz {1H} SI=16K SW=6010 O1=2401 PW=9.0 AQ=1.363 RD=1.00 NS=2 SR=-1.40 TE=298K 6 October 2013 Opr: Homutova Yu.A.; Solv: CDCl3;
The Best Applied NMR!
/ILDT man471.401
tBu
Me
O
O
H
H
H
NO2
5
142
21
10.0
10
3.3
9.9
1.2
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
9.99
3.35
10.29
0.36
9.94
0.36
21.04
1.17
142.19
0.20


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=75.47 MHz {13C} SI=128K SW=19998 O1=6792 PW=13.0 AQ=0.406 RD=0.40 NS=68640 SR=0.00 TE=299K 6 October 2013 Opr: Homutova Yu.A.; Solv: CDCl3;
The Best Applied NMR! On-Line: "http://nmr.ioc.ac.ru:8080"
/ILDT man471.401
Me
tBu
O
O
H
H
H
NO2
5
166.25
136.60
133.31
121.91
90.95
77.43
77.20
77.00
76.58
67.64
38.96
24.66
19.07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.13 MHz (1H-1H)NOESY SI=2048x1024 SW=2251 O1=1276 PW=14.0 AQ=0.228 RD=1.00 NS=4x60 SR=0.00 TE=298K 6 October 2013 Opr: Homutova Yu.A.; Solv: CDCl3;
The Best Applied NMR!
/ILDT man471.401
Me
tBu
O
O
H
H
H
NO2
5
ppm
4.5
5.0
5.5
6.0
6.5
7.0
7.5
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5

References

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