Electronic supplementary materials *Mendeleev Commun.*, 2025, **35**, 27–30

Highly regioselective synthesis and structure of 1-substituted 3a,6,6a-triphenylglycolurils

Vladimir V. Baranov, Maria M. Antonova, Svetlana A. Aksenova, Natalya G. Kolotyrkina and Angelina N. Kravchenko

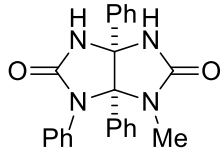
General

All reagents were purchased from Acros and used without treatment, unless otherwise indicated. ^{1}H and ^{13}C NMR were recorded at 23 to 29 °C using Bruker AM300 (^{1}H, 300.13 MHz; ^{13}C, 75.5 MHz) and Bruker DRX500 (^{13}C, 125.76 MHz).Chemical shifts are reported in the δ scale relative to Me_4Si as internal standard. High resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF II instrument using the electrospray ionization method (ESI). Melting points were determined in a SMP10 instrument (Stuart).

Synthesis of 1-substituted 3a,6,6a-triphenyltetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-diones 1a-e; General procedure

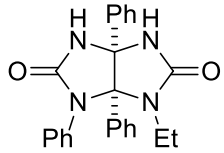
A mixture of imidazolone **3a-d** or imidazooxazole **4a** (2 mmol) and 1-phenylurea **2a** (0.272 g, 2 mmol), MeCN (20 mL) and HCl (35% aq., 0.2 mL) was refluxed for 20 min with stirring. The reaction mixture was evaporated to dryness. The resulting solid was washed with $CHCl_3$ (4 mL), H_2O (5 mL) and recrystallized from MeCN.

(3a*R**,6a*S**)-1-Methyl-3a,6,6a-triphenyltetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione 1a



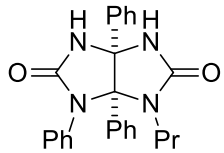
Yield 83% (0.637 g);mp 345 – 347°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ2.20 (s, 3H, Me); 6.94 – 7.36 (m, 15H, Ph); 8.39 (s, 1H, NH); 8.45 (s, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ28.61 (Me); 80.10, 89.74((Ph)-C-C-(Ph)); 126.62, 127.33, 127.39, 127.42, 128.09, 128.19, 128.45, 128.86 (Ph); 134.53, 137.06, 137.61 (C(Ph)); 158.73, 159.62 (C=O).HRMS, m/z, found: 385.1664 $[M+H]^+$ (calcd for$C_{23}H_{20}N_4O_2$+H 385.1659).

(3a*R**,6a*S**)-1-Ethyl-3a,6,6a-triphenyltetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione 1b



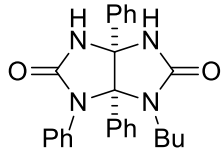
Yield 80% (0.637 g);mp 313 – 315°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ0.71 (t,3H, *J* = 6.9 Hz, Me); 2.43 – 2.49 (m, 1H, CH_2); 2.70 – 2.82 (m, 1H, CH_2); 6.99 – 7.24 (m, 13H, Ph); 7.30 (t, 2H, *J*=7.5 Hz, Ph); 8.29 (s, 1H, NH); 8.41 (s, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ14.73(Me); 39.25 (CH_2);81.19, 92.11((Ph)-C-C-(Ph)); 127.17, 127.60, 128.29, 128.46, 129.05, 129.21, 129.51, 129.79 (Ph); 136.03, 138.07, 138.54 (C(Ph)); 159.43, 160.85 (C=O).HRMS, m/z, found: 399.1811 $[M+H]^+$ (calcd for$C_{24}H_{22}N_4O_2$+H 399.1816).

(3a*R,6a*S**)-1,3a,6a-Triphenyl-6-propyltetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione 1c**



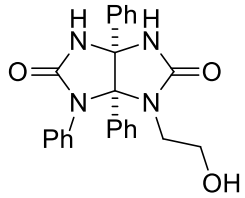
Yield 82% (0.676 g);mp 220 – 222°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ0.40 (t,3H, *J*=7.0 Hz, Me); 0.69 – 0.89 (m, 1H, CH_2); 1.39 – 1.57 (m, 1H, CH_2); 2.29 – 2.42 (m, 1H, CH_2); 2.70 – 2.85 (m, 1H, CH_2); 6.94 – 7.23 (m, 13H, Ph); 7.28 (t, 2H, *J*=7.3 Hz, Ph); 8.29 (s, 1H, NH); 8.48 (s, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ11.28 (Me); 21.47, 45.52 (CH_2);80.19, 90.94((Ph)-C-C-(Ph)); 125.90, 126.14, 127.41, 127.55, 128.10, 128.21, 128.30, 128.57, 128.77 (Ph); 135.03, 137.28, 137.66 (C(Ph)); 158.38, 159.91 (C=O).HRMS, m/z, found: 413.1965 $[M+H]^+$ (calcd for$C_{25}H_{24}N_4O_2$+H 413.1972).

(3a*R,6a*S**)-1-Butyl-3a,6,6a-triphenyltetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione 1d**

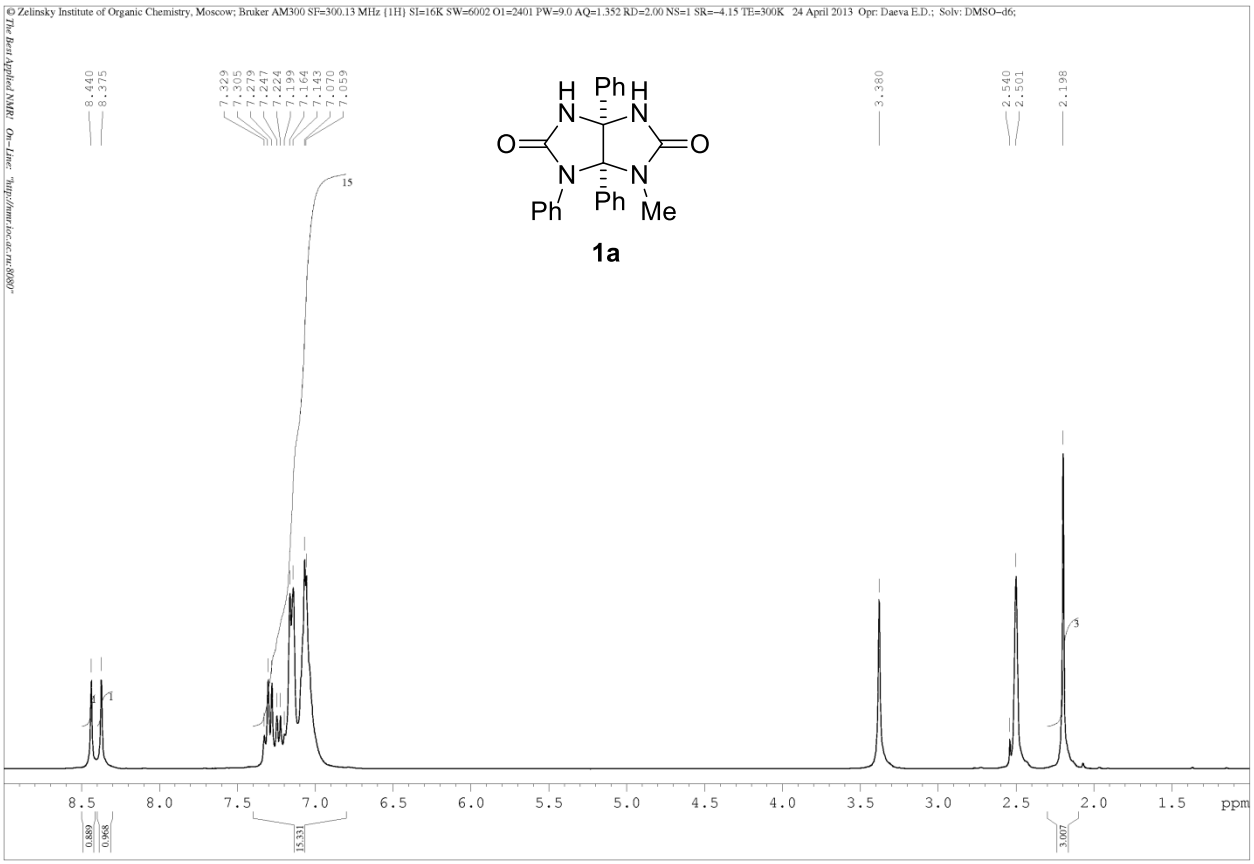


Yield 74% (0.630 g);mp 268 – 270°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ0.55 (t,3H, *J*=6.7 Hz, Me); 0.51 – 0.79 (m,2H, CH_2); 0.80 – 0.95 (m, 1H, CH_2); 1.39 – 1.55 (m, 1H, CH_2); 2.30 – 2.43 (m, 1H, CH_2); 2.78 – 2.93 (m, 1H, CH_2); 6.94 – 7.23 (m, 13H, Ph); 7.28 (t,2H, *J*=7.3 Hz, Ph); 8.28 (s, 1H, NH); 8.48 (s, 1H, NH). ^{13}C NMR (125 MHz, DMSO-d_6): δ13.41 (Me); 19.82, 30.19, 43.69 (CH_2);80.14, 90.98((Ph)-C-C-(Ph)); 125.81, 126.08, 127.38, 127.51, 128.08, 128.18, 128.26, 128.54, 128.73 (Ph); 135.07, 137.27, 137.69 (C(Ph)); 158.32, 159.86 (C=O).HRMS, m/z, found: 427.2128 $[M+H]^+$ (calcd for $C_{26}H_{26}N_4O_2$+H 427.2129).

(3a*R,6a*S**)-1-(2-Hydroxyethyl)-3a,6,6a-triphenyltetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione 1e**



Yield 75% (0.621 g);mp 292 – 294°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ2.39– 2.49 (m, 1H, CH_2); 2.59– 2.71 (m, 1H, CH_2); 3.00– 3.13 (m, 1H, CH_2); 3.36– 3.47 (m, 1H, CH_2); 4.53 (t,1H, *J* = 5.5 Hz, OH); 6.98– 7.27 (m, 13H, 3Ph); 7.32 (t,2H, *J* = 7.5 Hz, Ph); 8.43 (s, 1H, NH); 8.46 (s, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ46.02, 58.87(CH_2); 80.63, 90.72((Ph)-C-C-(Ph)); 126.62, 127.09, 127.38, 127.59, 128.09, 128.35, 128.64, 129.01 (Ph); 134.71, 136.89, 137.42 (C(Ph)); 159.65, 160.47 (C=O).HRMS, m/z, found: 415.1762 $[M+H]^+$ (calcd for $C_{24}H_{22}N_4O_3$+H 415.1765).


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.13 MHz {1H} SI=16K SW=6002 O1=2401 PW=9.0 AQ=1.352 RD=2.00 NS=1 SR=-4.15 TE=300K 24 April 2013 Opr: Daeva E.D.; Solv: DMSO-d6;
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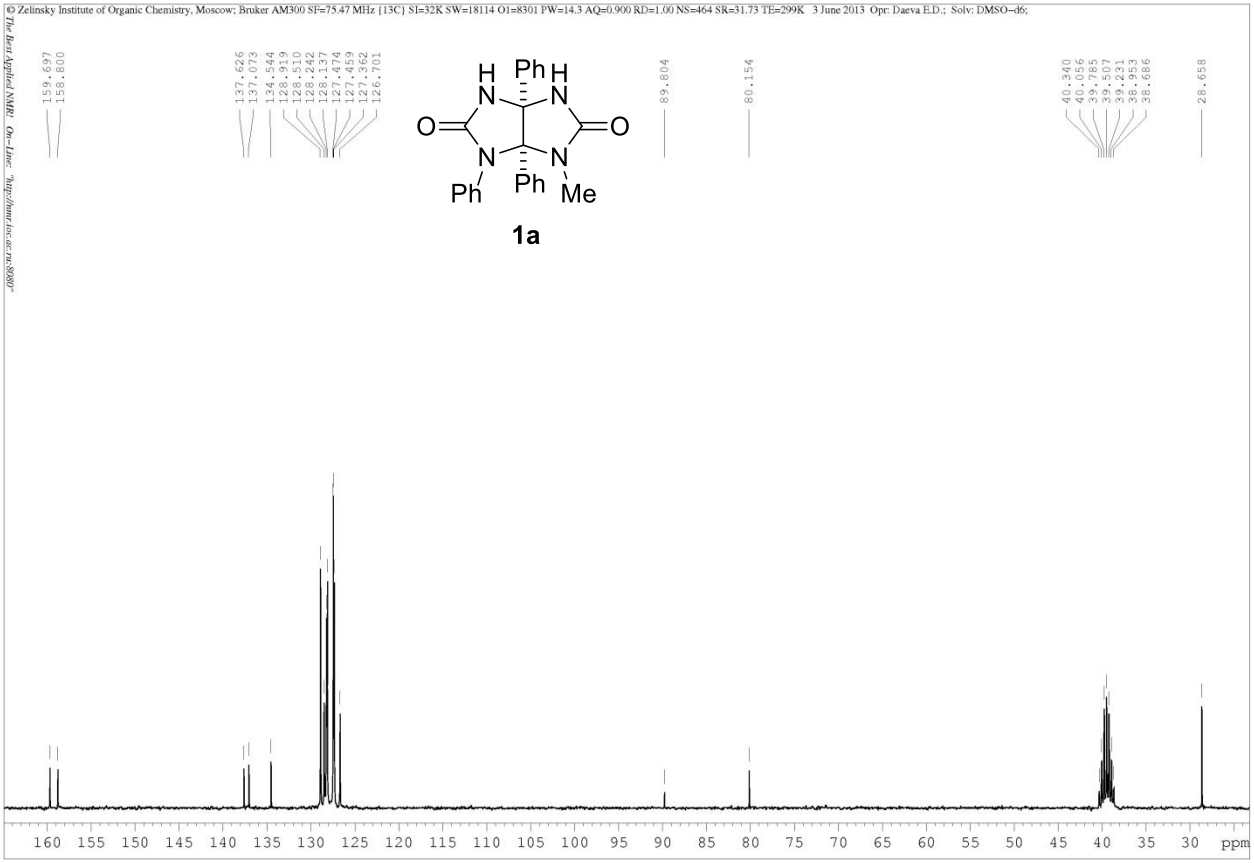
7.305
7.279
7.247
7.224
7.199
7.164
7.143
7.070
7.059
3.380
2.540
2.501
2.198
15
3
1
0.889
0.968
15.331
3.007
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

1a


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=75.47 MHz {13C} SI=32K SW=18114 O1=8301 PW=14.3 AQ=0.900 RD=1.00 NS=464 SR=31.73 TE=299K 3 June 2013 Opr: Daeva E.D.; Solv: DMSO-d6;
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128.242
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127.459
127.362
126.701
89.804
80.154
40.340
40.056
39.765
39.517
39.271
39.023
38.953
38.686
28.658
160
155
150
145
140
135
130
125
120
115
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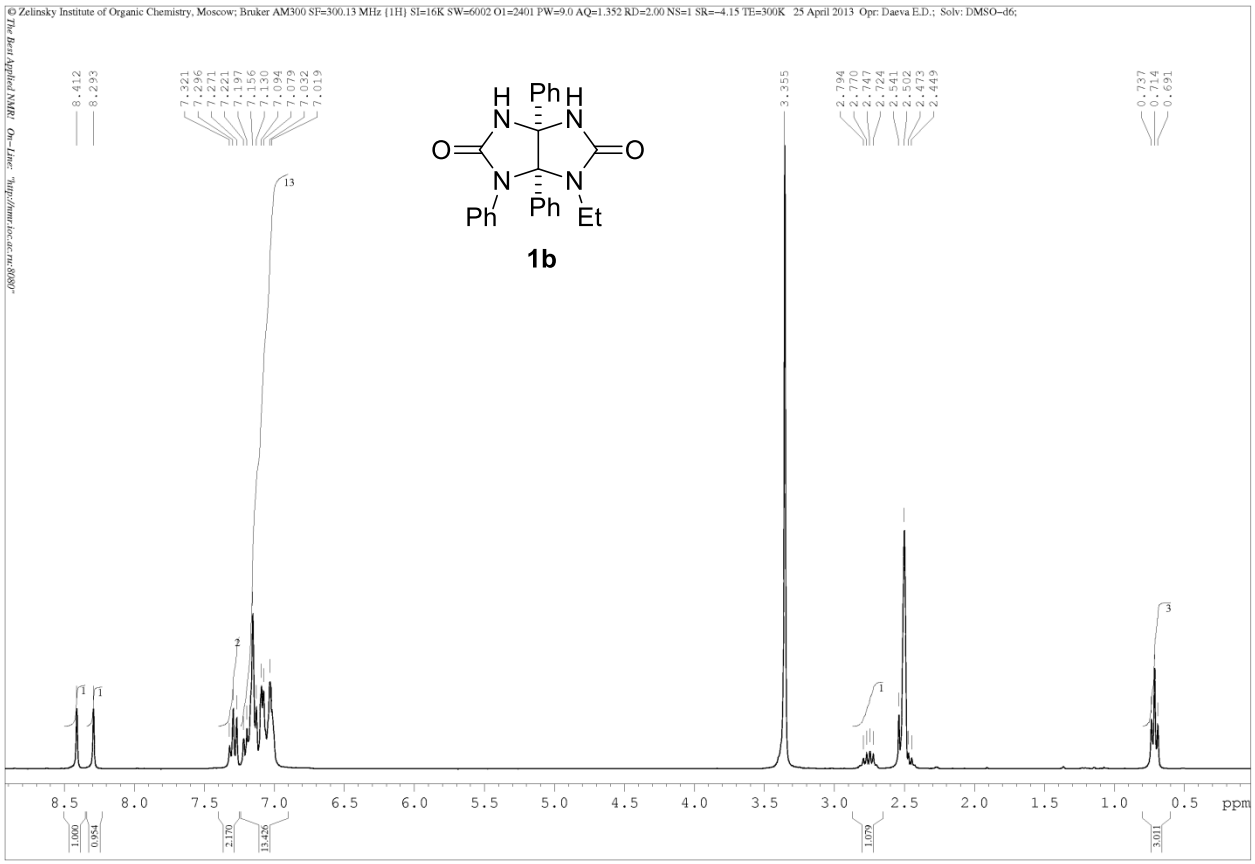
30
ppm

1a


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.13 MHz {1H} SI=16K SW=6002 O1=2401 PW=9.0 AQ=1.352 RD=2.00 NS=1 SR=-4.15 TE=300K 25 April 2013 Opr: Daeva E.D.; Solv: DMSO-d6;
© The Best Applied NMR: On-Line: "http://nmr.ioc.ac.ru:8080/"
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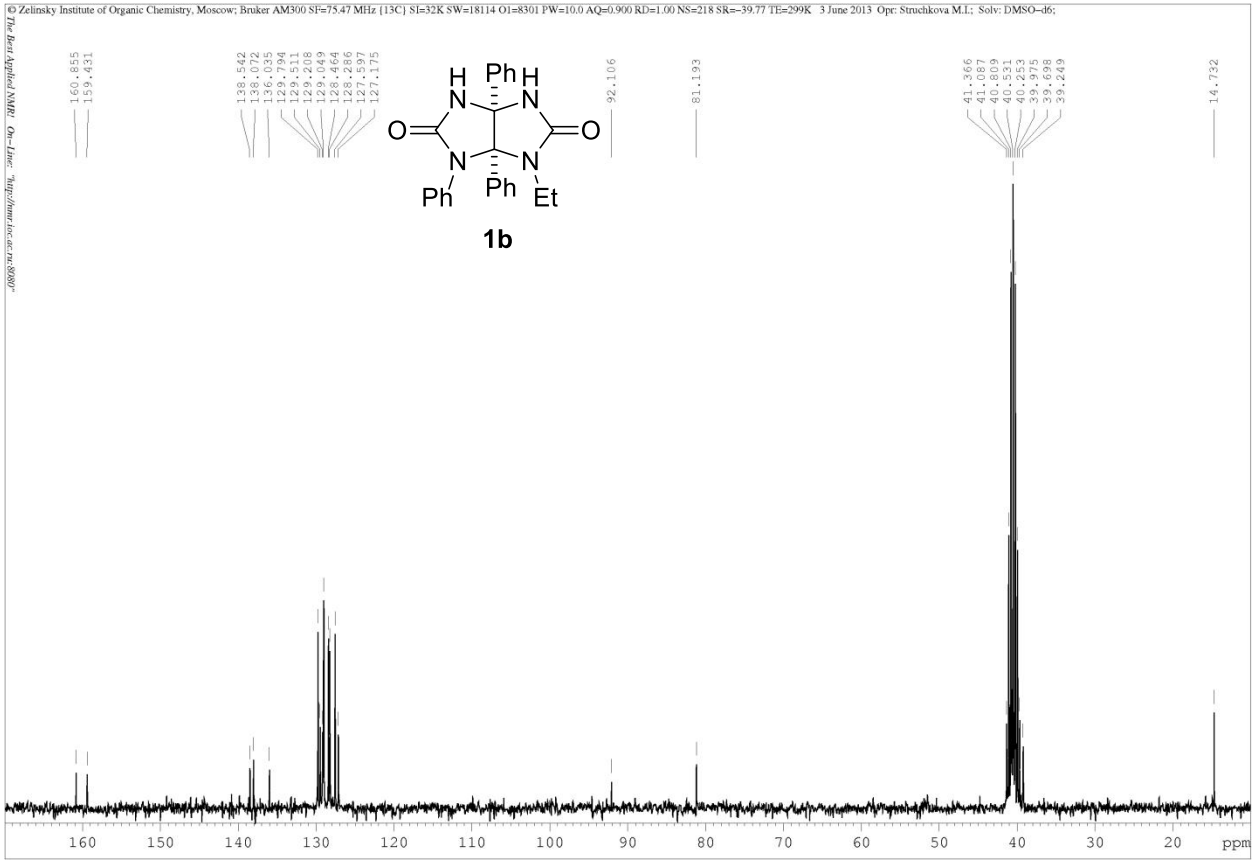
8.293
7.321
7.296
7.271
7.221
7.197
7.156
7.130
7.094
7.079
7.032
7.019
3.355
2.794
2.770
2.747
2.724
2.541
2.502
2.473
2.449
0.737
0.714
0.691
1.000
0.954
2.170
13.426
1.079
3.011
ppm
1b


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=75.47 MHz {13C} SI=32K SW=18114 O1=8301 PW=10.0 AQ=0.900 RD=1.00 NS=218 SR=-39.77 TE=299K 3 June 2013 Opr: Struchkova M.I.; Solv: DMSO-d6;
© The Best Applied NMR: On-Line: "http://nmr.ioc.ac.ru:8080/"
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138.072
136.035
129.754
129.711
129.208
129.049
128.464
128.286
127.597
127.175
92.106
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41.087
40.809
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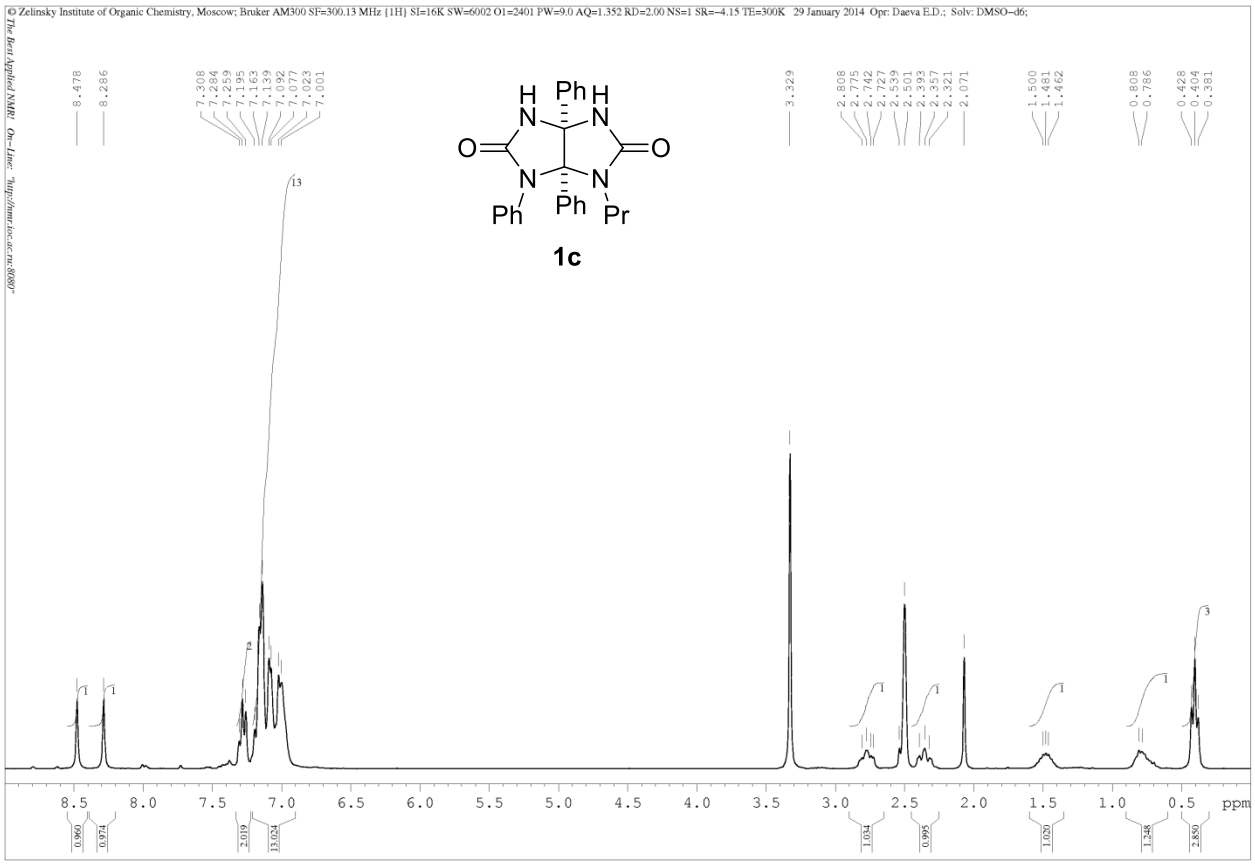
ppm
1b


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SI=300.13 MHz {1H} SI=16K SW=6002 O1=2401 PW=9.0 AQ=1.352 RD=2.00 NS=1 SR=-4.15 TE=300K 29 January 2014 Opr: Daeva E.D.; Solv: DMSO-d6;
The Best Applied NMR: On-Line: "http://nmr.ioc.ac.ru:8080/"
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7.092
7.077
7.023
7.001
3.329
2.808
2.775
2.742
2.727
2.539
2.501
2.393
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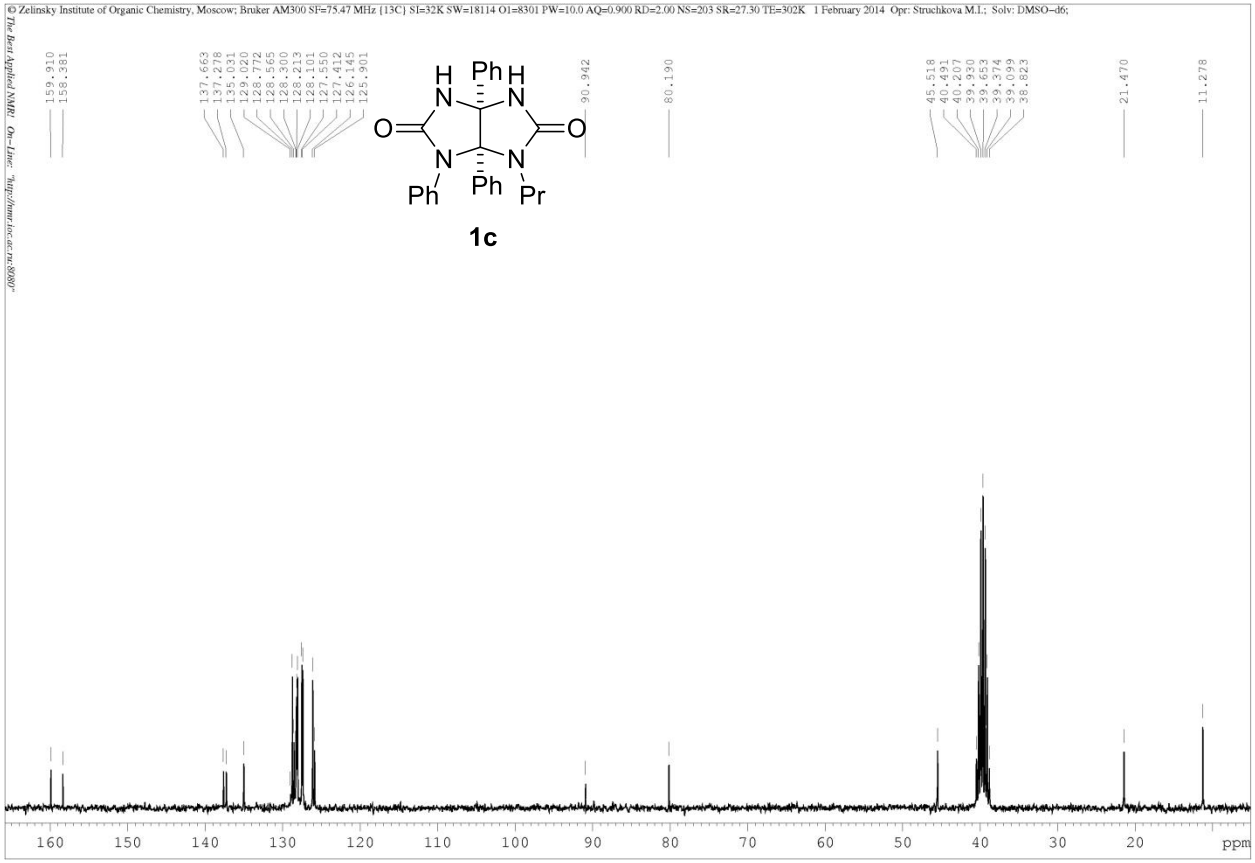
© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SI=75.47 MHz {13C} SI=32K SW=18114 O1=8301 PW=10.0 AQ=0.900 RD=2.00 NS=203 SR=27.30 TE=302K 1 February 2014 Opr: Struchkova M.I.; Solv: DMSO-d6;
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128.213
128.101
127.550
127.422
126.465
125.901
90.942
80.190
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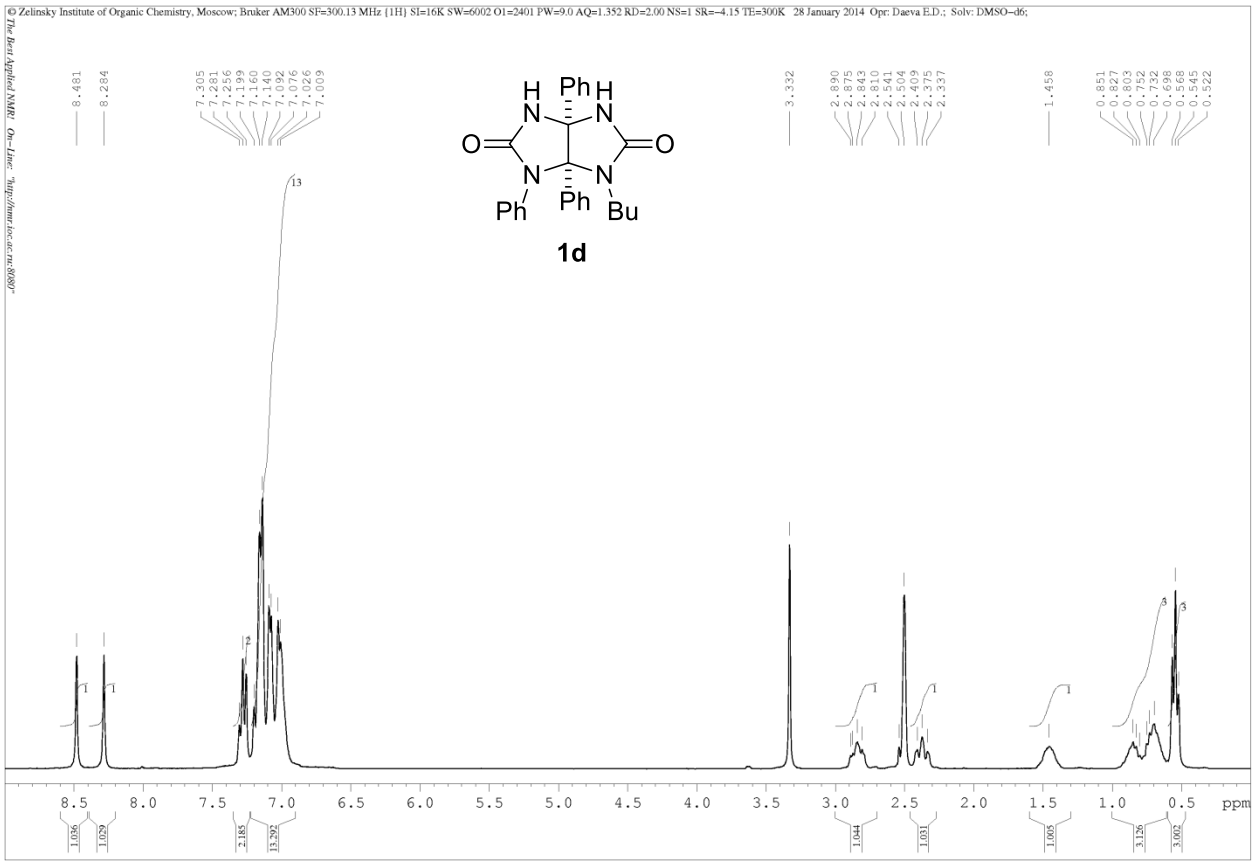
1c
ppm


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.13 MHz {1H} SI=16K SW=6002 O1=2401 PW=9.0 AQ=1.352 RD=2.00 NS=1 SR=-4.15 TE=300K 28 January 2014 Opr: Daeva E.D.; Solv: DMSO-d6;
The Best Applied NMR! On-Line: "http://nmr.ioc.ac.ru:8080/"
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7.199
7.160
7.140
7.092
7.076
7.026
7.009
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2.890
2.875
2.843
2.810
2.541
2.504
2.409
2.375
2.337
1.458
0.851
0.827
0.803
0.752
0.732
0.698
0.568
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1.005
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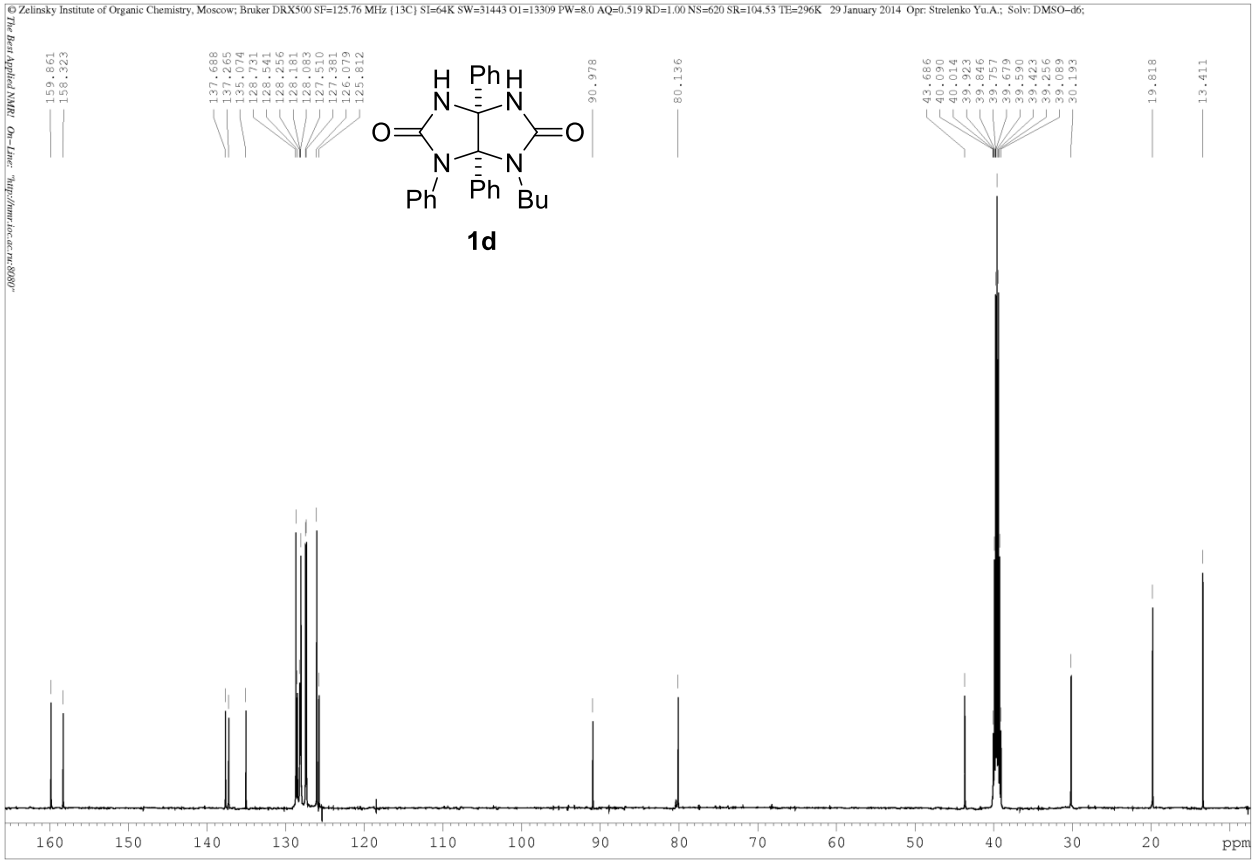
3.002
ppm

1d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125.812
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80.136
43.686
40.090
40.024
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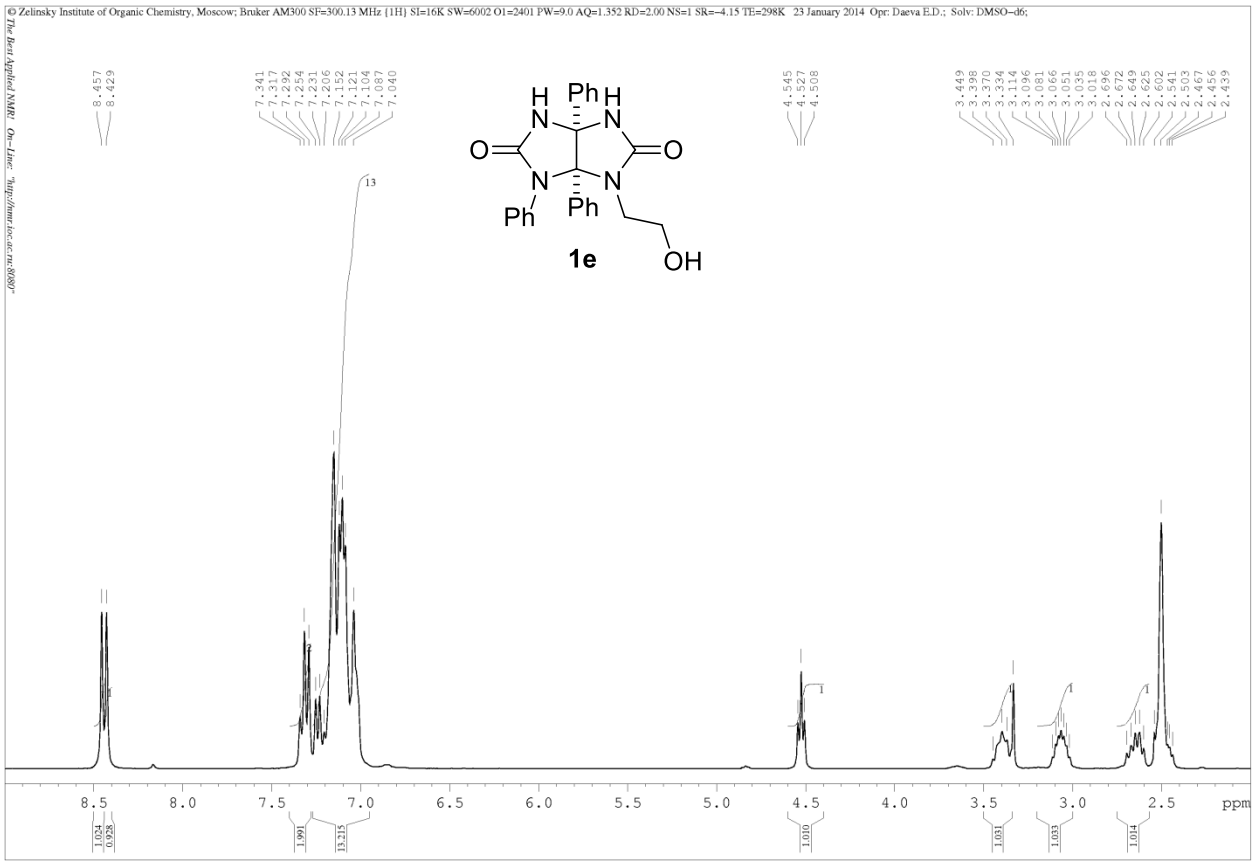
1d


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.13 MHz {1H} SI=16K SW=6002 O1=2401 PW=9.0 AQ=1.352 RD=2.00 NS=1 SR=-4.15 TE=298K 23 January 2014 Opr: Daeva E.D.; Solv: DMSO-d6;
The Best Applied NMR: On-Line: "http://nmr.ioc.ac.ru:8080/"
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7.152
7.121
7.104
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3.018
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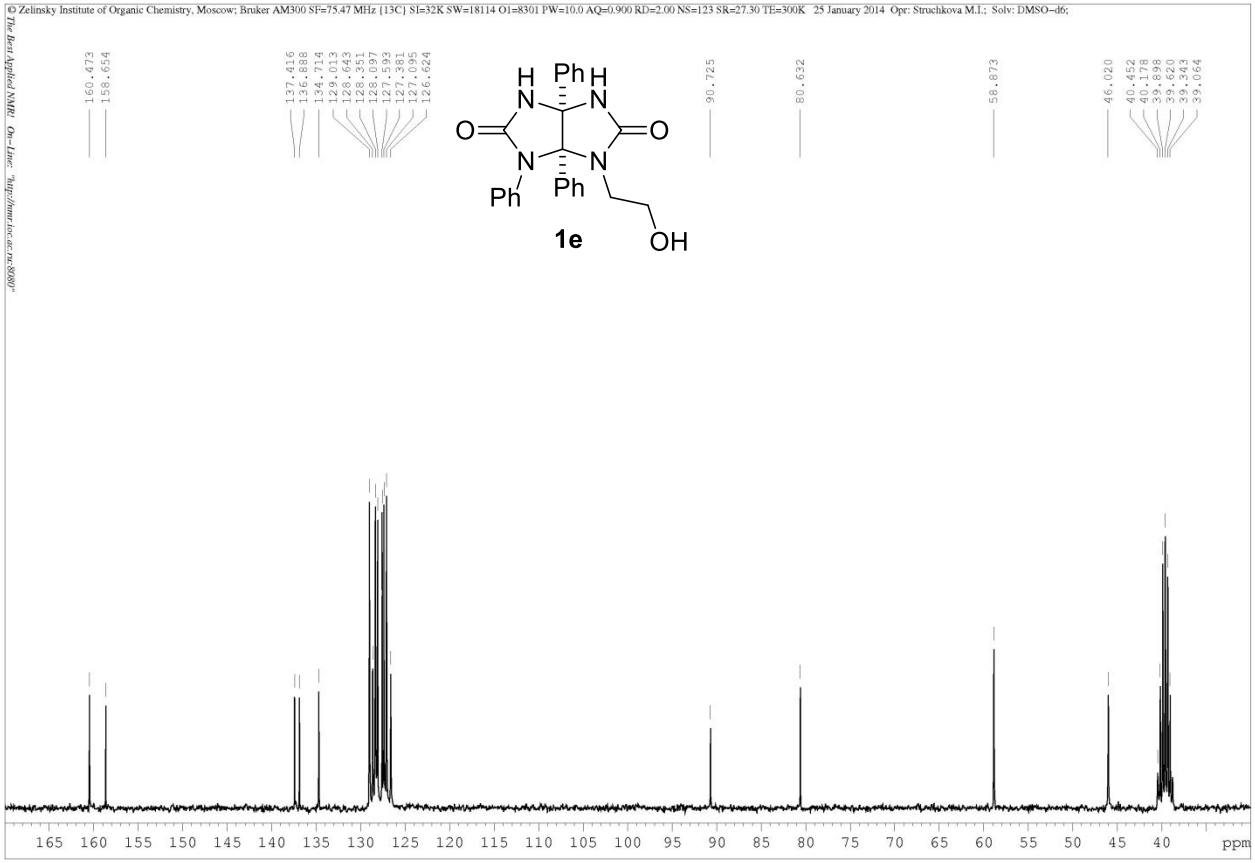
© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=75.47 MHz {13C} SI=32K SW=18114 O1=8301 PW=10.0 AQ=0.900 RD=2.00 NS=123 SR=27.30 TE=300K 25 January 2014 Opr: Struchkova M.I.; Solv: DMSO-d6;
The Best Applied NMR: On-Line: "http://nmr.ioc.ac.ru:8080/"
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127.593
127.381
127.095
126.624
90.725
80.632
58.873
46.020
40.452
40.178
39.898
39.620
39.343
39.064
1e
OH
ppm

Table S1. Crystal data and structure refinement parameters for **1a**, **1b**, **1d** and **1e**.

	1a	**1b**	**1d**	**1e**
Empirical formula	$C_{23}H_{20}N_4O_2$	$C_{24}H_{22}N_4O_2$	$C_{26}H_{26}N_4O_2$	$C_{24}H_{22}N_4O_3$
Formula weight	384.43	398.45	426.51	414.45
T, K	120	120	120	120
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
Z	4	4	4	4
a, Å	7.4907(8)	11.9188(9)	14.8551(12)	8.8829(3)
b, Å	14.4336(14)	8.6408(6)	8.0851(7)	13.3240(4)
c, Å	18.5675(19)	21.0884(15)	18.4823(16)	17.6994(6)
α, °	90	90	90	90
β, °	90	96.378(2)	99.081(2)	90
γ, °	90	90	90	90
V, Å^3	2007.5(4)	2158.4(3)	2192.0(3)	2094.83(12)
D_{calc} (g cm^{-1})	1.272	1.226	1.292	1.314
Linear absorption, μ (cm^{-1})	0.84	0.8	0.84	0.89
F(000)	808	840	904	872
$2\theta_{max}$, °	58	58	58	58
Reflections measured	11786	17292	17599	17434
Independent reflections	5322	5736	5813	5569
Observed reflections [$I > 2\sigma(I)$]	4750	3978	4057	5253
Parameters	263	272	301	280
R1	0.0403	0.0501	0.0560	0.0322
wR2	0.0992	0.1286	0.1536	0.0824
GOF	1.034	1.017	1.009	1.025
$\Delta\rho_{max}$/ $\Delta\rho_{min}$ (e Å^{-3})	0.206/-0.207	0.322/-0.259	0.592/-0.329	0.276/-0.195
CCDC	2363535	2363536	2363537	2363538