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Electronic supplementary information (ESI)

Synthesis and antitumor activity of novel 2-substituted indoline imidazolium salt derivatives

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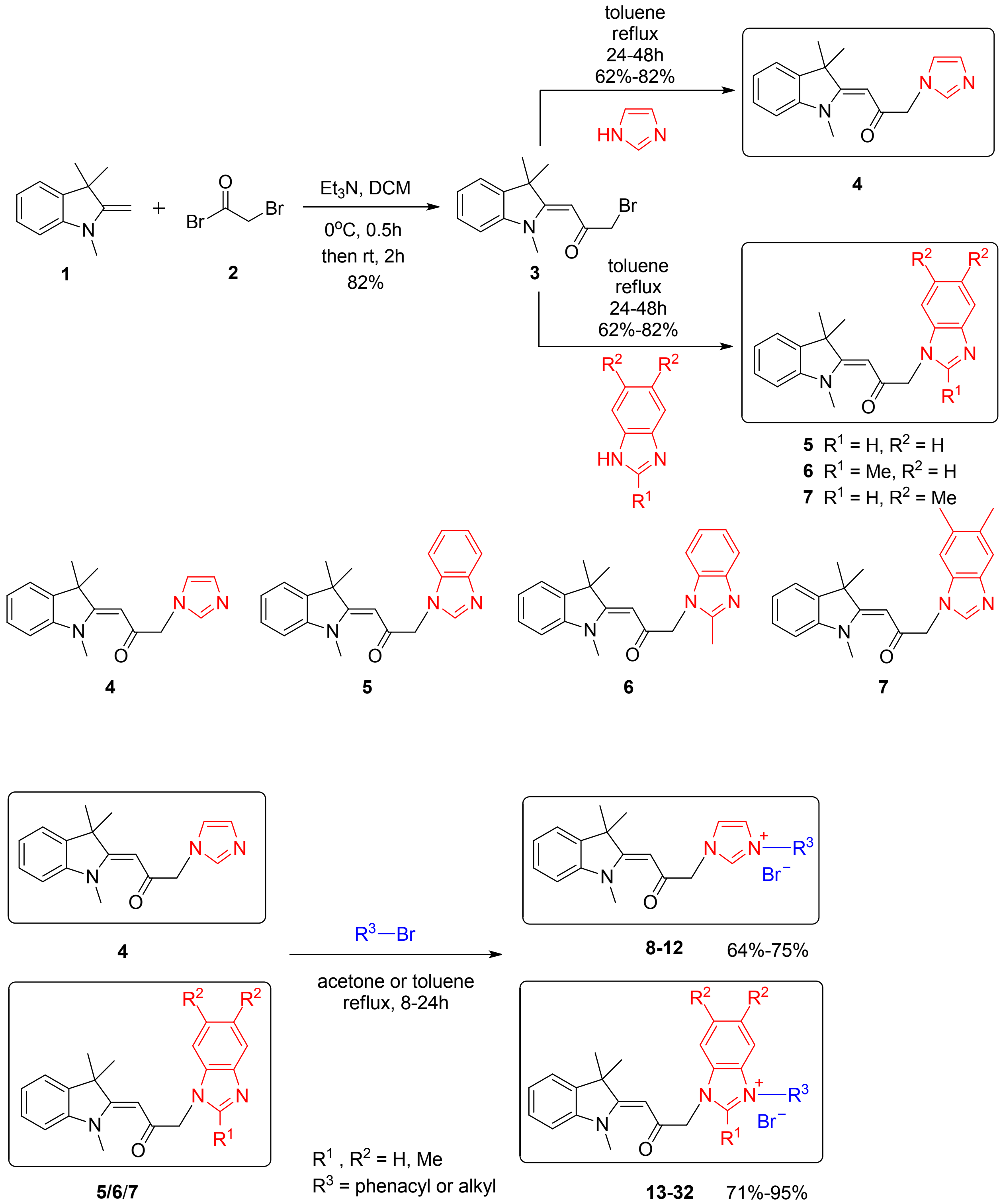
1. General Experimental

Melting points were obtained on a XT-4 melting-point apparatus and were uncorrected. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a BrukerAvance 300 spectrometer at 300 MHz. Carbon-13 nuclear magnetic resonance (^{13}C-NMR) was recorded on BrukerAvance 300 spectrometer at 75 MHz. Chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane (TMS) for all recorded NMR spectra. Low-resolution Mass spectra were recorded on a VG Auto Spec-3000 magnetic sector MS spectrometer. High Resolution Mass spectra were taken on AB QSTAR Pulsar mass spectrometer.

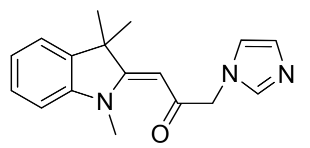
Silica gel (200–300 mesh) for column chromatography and silica GF_{254} for TLC were produced by Qingdao Marine Chemical Company (China). All air- or moisture-sensitive reactions were conducted under an argon atmosphere. Starting materials and reagents used in reactions were obtained commercially from Acros, Aldrich, Fluka and were used without purification, unless otherwise indicated.

2. Experimental Procedures and Analytical Data



Synthesis of hybrid compounds **4-32**.

Entry	Compound No.	imidazole ring	R^3	molecular formula	mp (°C)	Yields (%)
1	**4**	imidazole	–	$C_{17}H_{19}N_3O$	134-136	62
2	**5**	benzimidazole	–	$C_{21}H_{21}N_3O$	192-193	82
3	**6**	2-methyl-benzimidazole	–	$C_{22}H_{23}N_3O$	142-144	80
4	**7**	5,6-dimethyl-benzimidazole	–	$C_{23}H_{25}N_3O$	151-153	66
5	**8**	imidazole	2-bromobenzyl	$C_{24}H_{25}Br_2N_3O$	193-194	65
6	**9**	imidazole	phenacyl	$C_{25}H_{26}BrN_3O_2$	282-284	77
7	**10**	imidazole	4-bromophenacyl	$C_{25}H_{25}Br_2N_3O_2$	163-164	67
8	**11**	imidazole	4-methoxyphenacyl	$C_{26}H_{28}BrN_3O_3$	241-243	75
9	**12**	imidazole	naphthylacyl	$C_{29}H_{28}BrN_3O_2$	155-156	73
10	**13**	benzimidazole	4-methylbenzyl	$C_{29}H_{30}BrN_3O$	264-265	91
11	**14**	benzimidazole	2-bromobenzyl	$C_{28}H_{27}Br_2N_3O$	275-277	84
12	**15**	benzimidazole	2-naphthylmethyl	$C_{32}H_{30}BrN_3O$	247-248	85
13	**16**	benzimidazole	phenacyl	$C_{29}H_{28}BrN_3O_2$	282-284	77
14	**17**	benzimidazole	4-bromophenacyl	$C_{29}H_{27}Br_2N_3O_2$	299-301	88
15	**18**	benzimidazole	naphthylacyl	$C_{33}H_{30}BrN_3O_2$	177-180	80
16	**19**	2-methyl-benzimidazole	4-methylbenzyl	$C_{30}H_{32}BrN_3O$	304-305	94
17	**20**	2-methyl-benzimidazole	2-bromobenzyl	$C_{29}H_{29}Br_2N_3O$	260-263	81
18	**21**	2-methyl-benzimidazole	2-naphthylmethyl	$C_{33}H_{32}BrN_3O$	279-281	91
19	**22**	2-methyl-benzimidazole	phenacyl	$C_{30}H_{30}BrN_3O_2$	257-260	85
20	**23**	2-methyl-benzimidazole	4-bromophenacyl	$C_{30}H_{29}Br_2N_3O$	242-245	89
21	**24**	2-methyl-benzimidazole	4-methoxyphenacyl	$C_{31}H_{32}BrN_3O_3$	264-266	90
22	**25**	2-methyl-benzimidazole	naphthylacyl	$C_{34}H_{32}BrN_3O_2$	255-257	92
23	**26**	5,6-dimethyl-benzimidazole	4-methylbenzyl	$C_{31}H_{34}BrN_3O$	211-214	91
24	**27**	5,6-dimethyl-benzimidazole	2-bromobenzyl	$C_{30}H_{31}Br_2N_3O$	281-284	88
25	**28**	5,6-dimethyl-benzimidazole	2-naphthylmethyl	$C_{34}H_{34}BrN_3O$	228-230	92
26	**29**	5,6-dimethyl-benzimidazole	phenacyl	$C_{31}H_{32}BrN_3O_2$	239-242	80
27	**30**	5,6-dimethyl-benzimidazole	4-bromophenacyl	$C_{31}H_{31}Br_2N_3O_2$	201-202	95
28	**31**	5,6-dimethyl-benzimidazole	4-methoxyphenacyl	$C_{32}H_{34}BrN_3O_3$	183-185	71
29	**32**	5,6-dimethyl-benzimidazole	naphthylacyl	$C_{35}H_{34}BrN_3O_2$	193-195	82



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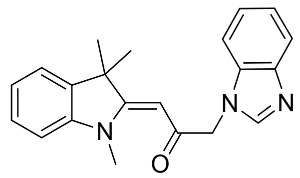

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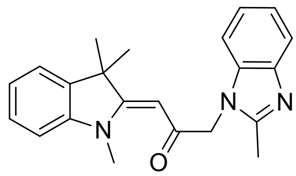

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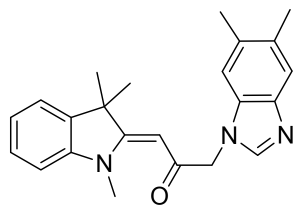

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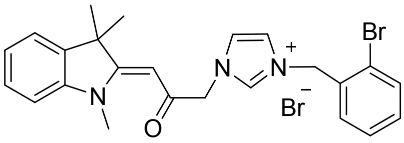

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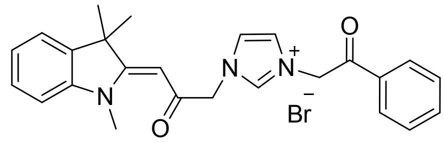

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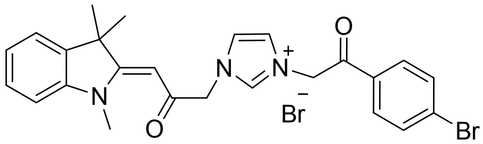

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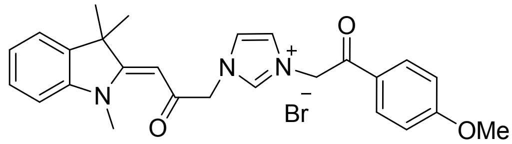

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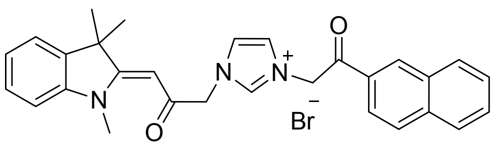

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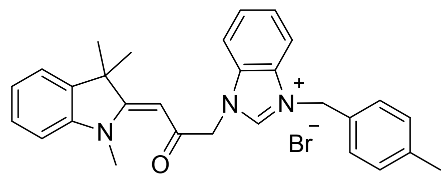

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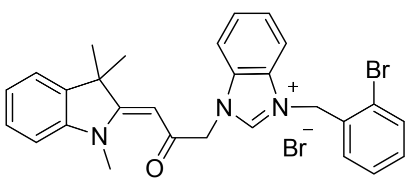

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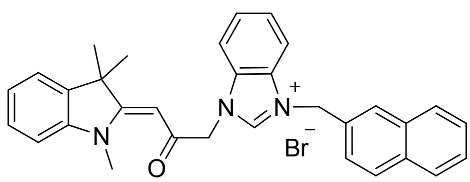

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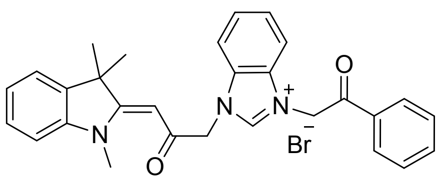

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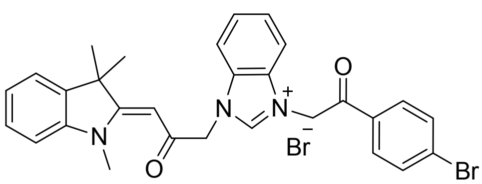

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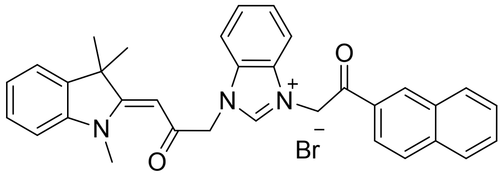

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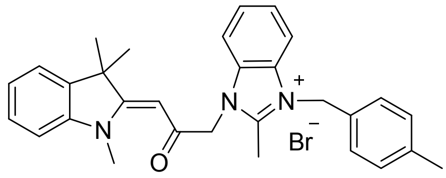

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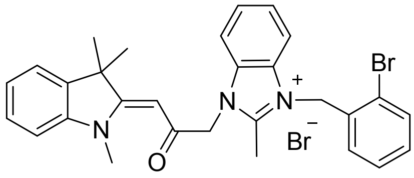

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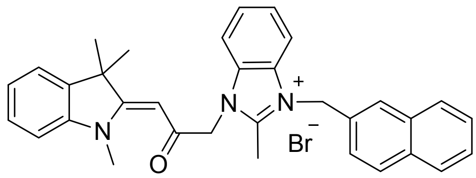

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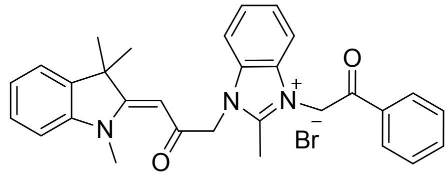

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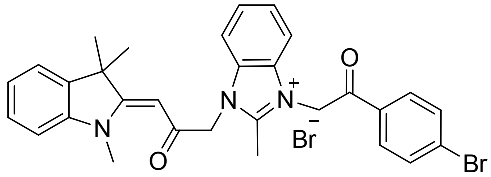

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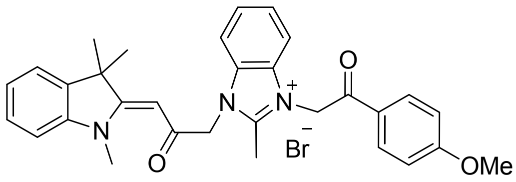

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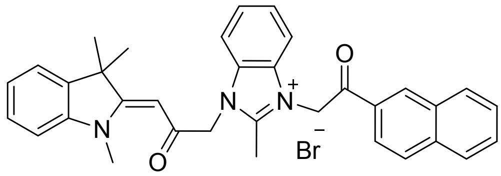

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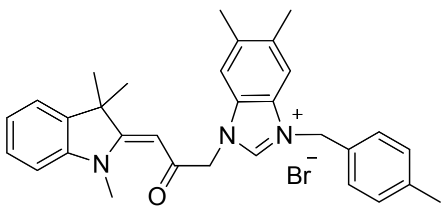

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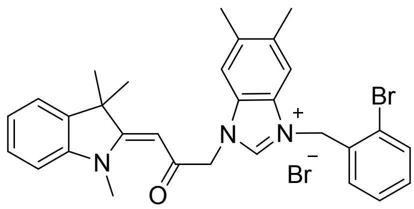

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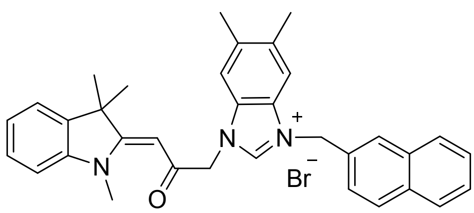

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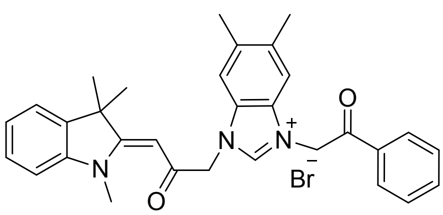

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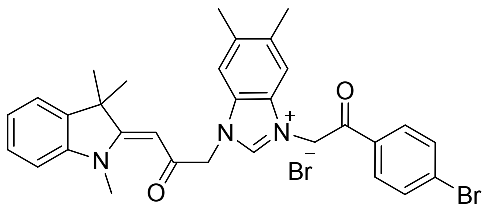

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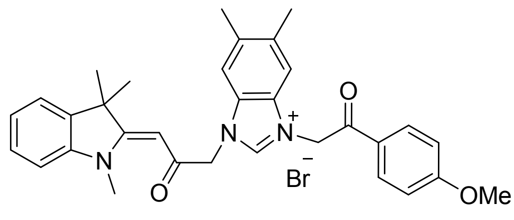

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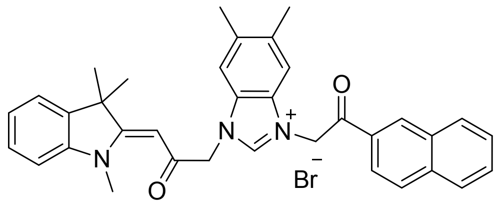
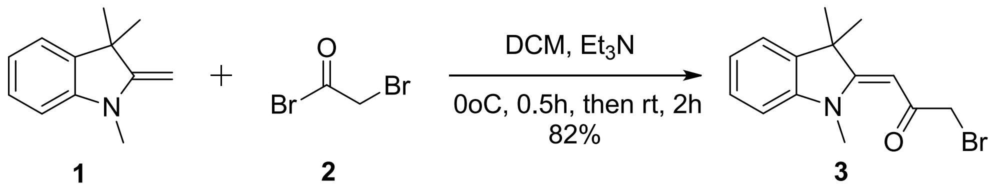
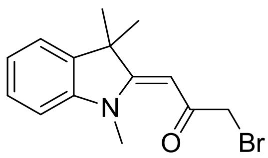


32 (82%)

2.1 Synthesis of compound 3



To a stirred solution of 1,3,3-trimethyl-2-methyleneindoline **1**(8.66g, 50 mmol)and triethylamine (6.57 g, 65 mmol) in dichloromethane (300 mL) at0 °C was added bromoacetyl bromide(12.11 g, 60 mmol) in small portions over a period of 30 minutes, and then at ambient temperature for 2 h. Reaction progress was monitored by TLC.A small amount of water was added and the mixture was stirred for 15 min. The aqueous phase was washed with CH_2Cl_2(4×50 mL).Thecombined organic phases was dried over Na_2SO_4andconcentrated. The residue was purified bycolumn chromatography on silica gel (petroleum ether :EtOAc : Et_3N = 30/1/0.1 as eluant) affordingthe title compound **3** (11.47g, 82%) as a red solid.

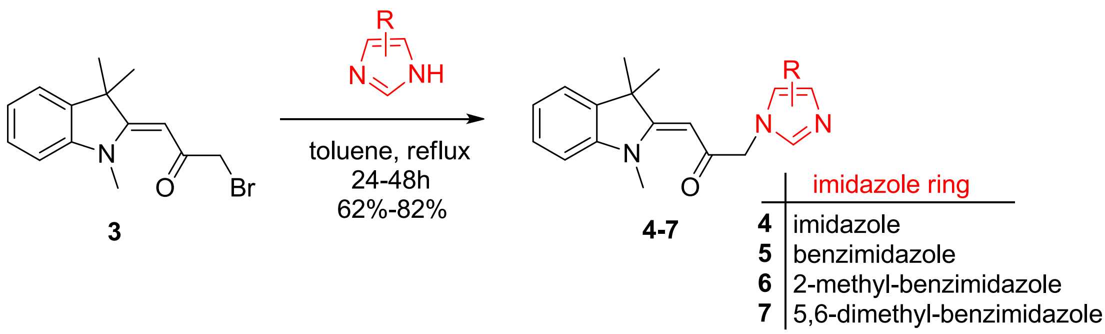


3

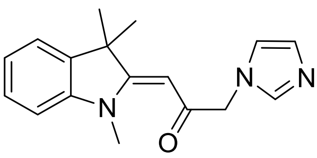
1-bromo-3-(1,3,3-trimethylindolin-2-ylidene)propan-2-one

Yield 82%.Red solid.^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.16-7.26 (2H, m), 7.02 (1H, t, J=7.2 Hz), 6.79 (1H, d, J=7.8 Hz), 5.49 (1H, s), 3.92 (2H, s), 3.27 (3H, s), 1.67 (6H, s).^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.26, 173.58, 143.45, 140.05, 127.65, 122.86, 121.94, 108.14, 89.93, 48.61, 37.13, 30.43, 23.27.

2.2 Synthesis of hybrid compounds 4-7



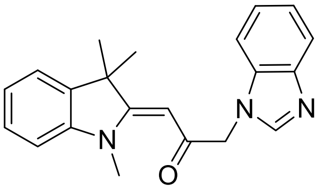
A mixture of compound **3** (2 mmol)and imidazole or substituted imidazole (6mmol) and K_2CO_3 (3 mmol) was stirred in tuloene (20 ml) at reflux for 24–48 h (monitored by TLC). After cooling to room temperature, the solvent was concentrated, and the residue was diluted with EtOAc (20 mL). The organic layer was washed with water (20 mL) and brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography (silica gel, petroleum ether :EtOAc: Et_3N = 1:1:0.1) to afford **4-7** in 62-82% yieldas yellow powder.



4

1-(1*H*-imidazol-1-yl)-3-(1,3,3-trimethylindolin-2-ylidene) propan-2-one

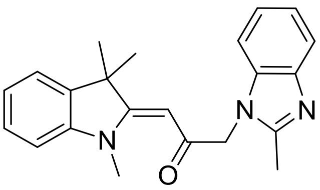
Yield 62%.Yellow solid, Mp134-136°C. IR ν_{max} (cm^{-1}): 3436, 2955, 1651, 1544, 1488, 1365, 1129, 1071, 941, 742.^1H NMR (300 MHz, $CDCl_3$): δ = 7.51 (1H, s), 7.21-7.16 (2H, m), 7.14 (1H, s), 7.02 (1H, d, J= 7.5 Hz), 6.96 (1H, s), 6.76 (1H, d, J=7.8 Hz), 4.91 (1H, s), 4.65 (2H, s), 3.06 (3H, s), 1.69 (6H, s).^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.24, 174.02, 143.09, 140.16, 138.22, 129.64, 127.65, 123.03, 121.97, 120.26, 108.15, 88.21, 56.21, 48.78, 29.66, 22.91.HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{20}N_3O^+$ $[M+1]^+$, 282.1606, found, 282.1600.



1-(1*H*-benzo[*d*]imidazol-1-yl)-3-(1,3,3-trimethylindolin-2-ylidene)propan-2-one

5

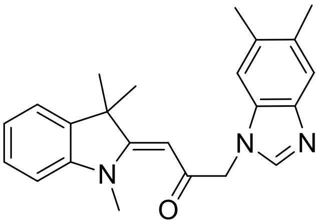
Yield 82%.Yellow solid, Mp 192-193°C.IR ν_{max} (cm^{-1}): 3439, 2913, 2351, 1679, 1539, 1486, 1360, 1119, 934, 750. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (1H, s), 7.89-7.87 (1H ,m), 7.44-7.41 (1H, m), 7.35-7.32 (2H, m), 7.26-7.20 (2H, m), 7.06 (1H, t, J= 7.2 Hz), 6.77 (1H, d, J= 7.5 Hz), 5.02 (1H, s), 4.93 (2H, s), 3.00 (3H, s), 1.75 (6H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.79, 173.99, 143.91, 143.05, 140.14, 134.39, 127.65, 123.19, 123.05, 122.26, 121.98, 120.49, 109.94, 108.15, 88.32, 54.26, 48.82, 29.61, 27.0, 22.91. HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{22}N_3O^+$ $[M+1]^+$ 332.1763, found 332.1753.



1-(2-methyl-1*H*-benzo[*d*]imidazol-1-yl)-3-(1,3,3-trimethylindolin-2-ylidene)propan-2-one

6

Yield 80%.Yellow solid. Mp 151-153°C. IR ν_{max} (cm^{-1}): 3459, 2925, 1651, 1539, 1464, 1366, 1129, 937, 744. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72 (1H, t, J= 3.6 Hz), 7.27-7.21 (m, 3H), 7.16 (2H, d, J= 8.1 Hz), 7.01 (1H, t, J= 7.2 Hz), 6.71 (1H, d, J= 7.8 Hz), 4.87 (1H, s), 4.77 (2H, s), 2.89 (3H, s), 2.58 (3H, s), 1.70 (6H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.12, 173.94, 152.27, 143.04, 142.78, 140.10, 135.69, 127.63, 123.00, 122.28, 122.01, 121.95, 119.23, 109.21, 108.12, 88.08, 53.15, 48.76, 29.53, 22.95, 14.04. HRMS (ESI-TOF) *m/z* Calcd for $C_{22}H_{24}N_3O^+$ $[M+1]^+$ 346.1919. found 346.1911.

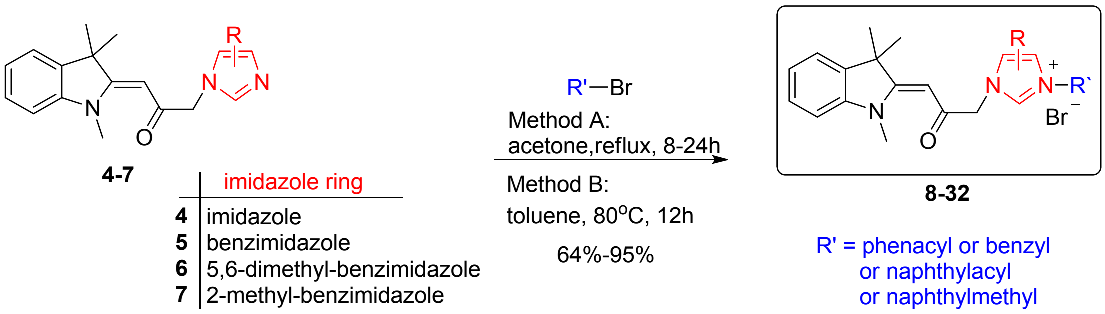


1-(5,6-dimethyl-1*H*-benzo[*d*]imidazol-1-yl)-3-(1,3,3-trimethylindolin-2-ylidene)propan-2-one

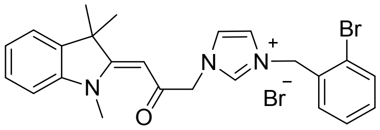
7

Yield 66%.Yellow solid. Mp 142-144°C. IR ν_{max} (cm^{-1}): 3457, 2921, 1659, 1542, 1490, 1364, 1126, 940, 839, 745. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (1H, s), 7.57 (1H, s), 7.14 (3H, t, J= 7.8 Hz), 7.00 (1H, t, J= 7.5 Hz), 6.72 (1H, d, J= 7.8 Hz), 4.94 (1H, s), 4.81 (2H, s), 2.94 (3H, s), 2.35 (6H, d, J= 1.5 Hz), 1.70 (6H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.39, 173.94, 143.07, 142.38, 140.19, 132.93, 132.42, 131.17, 127.64, 123.00, 121.98, 120.43, 110.10, 108.12, 88.33, 54.40, 48.80, 29.62, 22.96, 20.64, 20.32. HRMS (ESI-TOF) *m/z* Calcd for $C_{23}H_{26}N_3O^+$ $[M+1]^+$ 360.2076. found 360.2068.

2.3 Synthesis of compounds 8-32



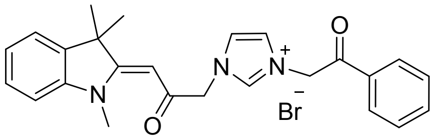
A mixture of substituted imidazole**4-7**(0.25 mmol) and phenacylbromides or phenacyl or benzyl or naphthylacyl or naphthylmethyl (0.75 mmol) was stirred in acetone (10 ml) at reflux 8-24h or toluene (10 ml) at 80°C for12 h. An insoluble substance was formed. After completion of the reaction as indicated by TLC, the precipitate was filteredand washed with toluene (3 × 10 ml), then dried to afford imidazolium salts**8-32**in 64–95% yields.



3-(2-bromobenzyl)-1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl) -1*H*-imidazol-3-ium bromide

8

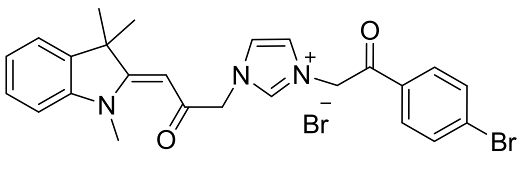
Yield 65%.White solid, Mp 193-194°C.IR ν_{max} (cm^{-1}): 3427, 2968, 1649, 1545, 1479, 1366, 1132, 936, 749.^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.27 (1H, s), 7.81-7.73 (3H, m), 7.48 (1H, d, J= 6.6 Hz), 7.40 (2H, d, J= 7.2 Hz), 7.31 (1H, d, J= 6.6 Hz), 7.23 (1H, d, J= 6.9 Hz), 7.09 (1H, d, J= 7.2 Hz), 7.03 (1H, d, J= 6.9 Hz), 5.62 (2H, s), 5.49 (1H, s), 5.28 (2H, s), 3.30 (3H, s), 1.61 (6H, s).^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 183.69, 172.36, 142.93, 139.23, 137.74, 133.66, 133.10, 130.98, 130.59, 128.47, 127.64, 124.21, 123.03, 122.58, 122.04, 121.68, 108.86, 88.80, 57.20, 52.15, 47.89, 29.80, 22.49.HRMS (ESI-TOF) *m/z* Calcd for $C_{24}H_{25}BrN_3O^+$ [M–Br]$^+$ 450.1175, found 450.1171.



3-(2-oxo-2-phenylethyl)-1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)-1*H*-imidazol-3-ium bromide

9

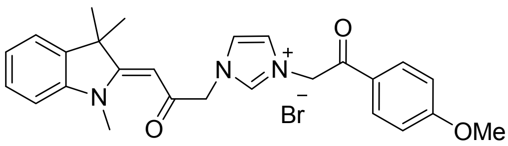
Yield 64%.White solid, Mp 237-238°C.IR v_{max} (cm^{-1}): 3437, 1697, 1646, 1532, 1372, 1131, 931, 753, 622. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 9.09 (1H, s), 8.08 (2H, d, J= 7.5 Hz), 7.81-7.76 (3H, m), 7.67 (2H, t, J= 7.5 Hz), 7.33 (1H, d, J=7.8 Hz), 7.26 (1H, t, J=7.5 Hz), 7.11 (1H, d, J= 7.8 Hz), 7.04 (1H, t, J= 7.5 Hz), 6.16 (2H, s), 5.51 (1H, s), 5.35 (2H, s), 3.32 (3H, s), 1.64 (6H, s).^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 191.34, 183.77, 172.41, 142.96, 139.27, 138.36, 134.43, 133.72, 129.04, 128.08, 127.66, 123.45, 123.32, 122.61, 121.71, 108.88, 88.78, 57.16, 55.40, 47.93, 29.77, 22.50.HRMS (ESI-TOF) *m/z* Calcd for $C_{25}H_{26}N_3O_2^+$ [M–Br]$^+$, 400.2019, found 400.2019.



3-(2-(4-bromophenyl)-2-oxoethyl)-1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)-1*H*-imidazol-3-ium bromide

10

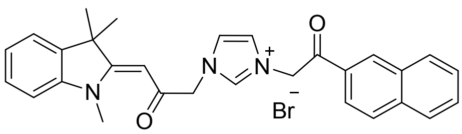
Yield 67%.Red solid, Mp 163-164°C.IR v_{max} (cm^{-1}): 3538, 3440, 3067, 2930, 1697, 1541, 1473, 1368, 1232, 1130, 1072, 935, 808, 743.^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.64 (1H, s), 7.92 (2H, d, J= 8.1 Hz), 7.66 (1H, s), 7.58-7.52 (3H, m), 7.19 (1H, t, J= 7.5 Hz), 7.12 (1H, d, J= 6.9 Hz), 7.00 (1H, t, J= 7.2 Hz), 6.79 (1H, d, J= 7.8 Hz), 6.31 (2H, s), 5.37 (1H, s), 5.27 (2H, s), 3.24 (3H, s), 1.60 (6H, s).^{13}C NMR (75 MHz, CDCl$_3$): δ = 190.16, 182.60, 174.46, 142.98, 139.99, 138.26, 132.50, 130.29, 130.04, 127.79, 123.51, 123.33, 123.18, 121.91, 108.60, 89.23, 57.75, 55.92, 48.86, 46.26, 30.37, 22.79.HRMS (ESI-TOF) *m/z* Calcd for $C_{25}H_{25}BrN_3O_2^+$ [M–Br]$^+$478.1124, found 478.1122.



11

3-(2-(4-methoxyphenyl)-2-oxoethyl)-1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)-1*H*-imidazol-3-ium bromide

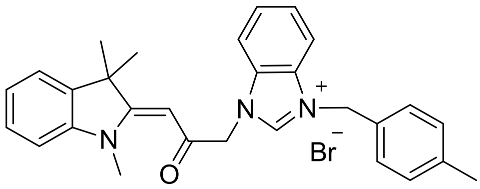
Yield 75%.White solid, Mp 241-243°C.IR ν_{max} (cm^{-1}): 3434, 3068, 2943, 2350, 1682, 1600, 1538, 1474, 1372, 1243, 1144, 1022, 940, 824, 739.^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 9.05 (1H, s), 8.05 (2H, d, J= 8.7 Hz), 7.73 (2H, d, J= 6.9 Hz), 7.33 (1H, d, J= 7.2 Hz), 7.25 (1H, t, J= 7.8 Hz), 7.16 (2H, d, J= 8.7 Hz), 7.09 (1H, d, J= 7.8 Hz), 7.03 (1H, d, J= 7.5 Hz), 6.05 (2H, s), 5.48 (1H, s), 5.31 (2H, s), 3.89 (3H, s), 3.31 (3H,s), 1.63 (6H, s).^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 189.73, 183.93, 172.46, 164.16, 143.08, 138.46, 130.67, 127.82, 126.60, 123.47, 122.76, 121.88, 114.43, 109.04, 88.90, 57.25, 55.85, 55.15, 48.05, 29.89, 22.56.HRMS (ESI-TOF) *m/z* Calcd for $C_{26}H_{28}N_3O_3^+$ [M–Br]$^+$430.2125, found 430.2125.



12

3-(2-(naphthalen-2-yl)-2-oxoethyl)-1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)-1*H*-imidazol-3-ium bromide

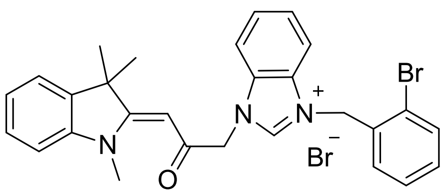
Yield 73%. White solid, Mp 155-156°C.IR ν_{max} (cm^{-1}): 3432, 3048, 2959, 1691, 1631, 1540, 1474, 1369, 1131, 932, 753.^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 9.13 (1H, s), 8.84 (1H, s), 8.21 (1H, d, J= 7.8 Hz), 8.14 (1H, d, J= 8.7 Hz), 8.07 (2H, t, J= 5.7 Hz), 7.79 (2H, s), 7.75-7.676 (2H, m), 7.33 (1H, d, J= 7.2 Hz), 7.25 (1H, t, J= 7.5 Hz), 7.10 (1H, d, J= 7.8 Hz), 7.04 (1H, t, J= 7.5 Hz), 6.27 (2H, s), 5.01 (1H, s), 5.36 (2H, s), 3.32 (3H, s), 1.65 (6H, s).^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 191.25, 183.79, 172.44, 142.98, 139.28, 138.43, 135.49, 132.00, 131.04, 130.40, 129.62, 129.28, 128.74, 127.84, 127.68, 127.36, 123.52, 123.38, 123.16, 122.63, 121.73, 108.89, 88.79, 57.18, 55.44, 47.95, 29.78, 22.52.HRMS (ESI-TOF) *m/z* Calcd for $C_{29}H_{28}N_3O_2^+$ $[M-Br]^+$ 450.2176, found 450.2172.



13

3-(4-methylbenzyl)-1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)-1*H*-benzo[*d*]imidazol-3-ium bromide

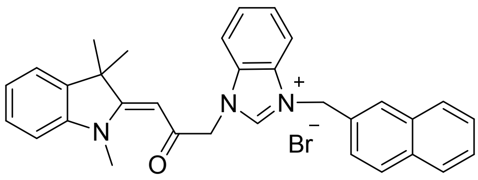
Yield 91%.White solid. Mp 264-265°C. IR ν_{max} (cm^{-1}): 3436, 2959, 1652, 1544, 1481, 1368, 1131, 934, 755. ^1H NMR (300 MHz, DMSO-d_6):δ = 9.92 (1H, s), 8.00-7.95 (2H, m), 7.66 (2H, s), 7.44 (2H, d, J= 6.9 Hz), 7.30 (2H, d, J= 6.9 Hz), 7.23 (2H, d, J= 7.2 Hz), 7.11 (1H, d, J= 7.2 Hz), 7.04 (1H, d, J= 6.6 Hz), 5.83 (2H, s), 5.68 (1H, s), 5.60 (2H, s), 3.35 (3H, s), 2.29 (3H, s), 1.58 (6H, s). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 183.42, 172.65, 143.42, 142.95, 139.30, 138.21, 131.91, 130.98, 130.42, 129.54, 128.27, 127.71, 126.73, 126.52, 122.71, 121.74, 113.88, 113.65, 108.98, 89.12, 54.73, 49.66, 47.98, 29.87, 22.48, 20.67. HRMS (ESI-TOF) *m/z* Calcd for $C_{29}H_{30}N_3O^+$ $[M-Br]^+$ 436.2383. found 436.2384.



14

3-(2-bromobenzyl)-1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)-1*H*-benzo[*d*]imidazol-3-ium bromide

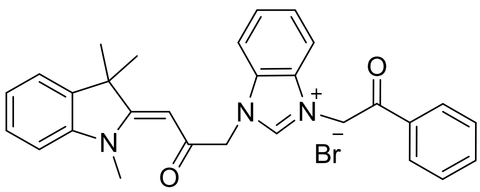
Yield 84%.White solid, Mp 275-277°C. IR ν_{max} (cm^{-1}): 3435, 2921, 1714, 1640, 1537, 1481, 1366, 1129, 934, 749.^1H NMR (300 MHz, DMSO-d_6): δ = 9.86 (1H, s), 8.03-7.95 (2H, m), 7.77 (1H, d, J= 7.5 Hz), 7.68 (2H, t, J= 3.9 Hz), 7.49-7.37 (3H, m), 7.31 (1H, d, J= 7.2 Hz), 7.25 (1H, t, J= 7.8 Hz), 7.11 (1H, d, J= 7.8 Hz), 7.03 (1H, t, J= 7.2 Hz), 5.96 (2H, s), 5.70 (1H, s), 5.65 (2H, s), 3.35 (3H, s), 1.58 (6H, s).^{13}C NMR (75 MHz, DMSO-d_6): δ = 183.34, 172.59, 144.02, 142.94, 139.28, 133.32, 132.65, 131.84, 131.02, 130.61, 128.44, 127.69, 126.83, 126.72, 123.12, 122.67, 121.71, 113.75, 108.96, 89.15, 54.85, 50.38, 47.96, 29.89, 22.45.HRMS (ESI-TOF) *m/z* Calcd for $C_{28}H_{27}BrN_3O^+$ [M-Br]$^+$ 500.1332, found 500.1335.



15

3-(naphthalen-2-ylmethyl)-
1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)-
1*H*-benzo[*d*]imidazol-3-ium bromide

Yield 85%.White solid, Mp 247-248°C. IR v_{max} (cm^{-1}): 3430, 2959, 1638, 1540, 1477, 1367, 1132, 934, 752.^{1}H NMR (300 MHz, DMSO-d_6): δ = 10.03 (1H, s), 8.13 (1H, s), 8.07 (1H, d, J= 8.7 Hz), 8.00-7.92 (4H, m), 7.64 (3H, d), 7.56 (2H, t, J= 4.5 Hz), 7.31 (1H, d, J= 7.2 Hz), 7.25 (1H, t, J= 7.5 Hz), 7.11 (1H, d, J=7.8 Hz), 7.03 (1H, t, J= 7.5 Hz), 6.07 (2H, s), 5.72 (1H, s), 5.65 (2H, s), 3.36 (3H, s), 1.60 (6H, s). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 183.42, 172.66, 143.74, 142.94, 139.30, 132.70, 131.95, 131.47, 130.55, 128.80, 127.81, 127.67, 127.46, 126.73, 126.58, 125.56, 122.70, 121.73, 113.87, 113.70, 108.98, 89.17, 54.81, 50.02, 47.99, 29.90, 22.48. HRMS (ESI-TOF) *m/z* Calcd for $C_{32}H_{30}N_3O^+$ [M-Br]$^+$ 472.2383. found 472.2484.

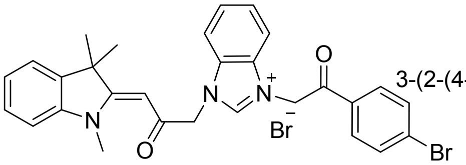


16

3-(2-oxo-2-phenylethyl)-1-(2-oxo-
3-(1,3,3-trimethylindolin-2-ylidene)propyl)-
1*H*-benzo[*d*]imidazol-3-ium bromide

Yield 77%.Yellow solid, Mp 282-284°C.IR v_{max} (cm^{-1}): 3424, 3037, 2914, 1700, 1541, 1472, 1367, 1227, 1133, 933, 752.^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ = 10.01 (1H, s), 8.08 (2H, d, J= 7.2 Hz), 7.84-7.78 (2H, m), 7.66 (1H, t, J= 7.2 Hz), 7.59-7.50 (4H, m), 7.17 (1H, t, J= 7.5 Hz), 7.11 (1H, d, J= 7.2 Hz), 6.97 (1H, t, J= 7.5 Hz), 6.84 (1H, d, J= 7.8 Hz), 6.42 (2H, s), 5.51 (3H, s), 3.02 (3H, s), 1.58 (6H, s).^{13}C NMR (75

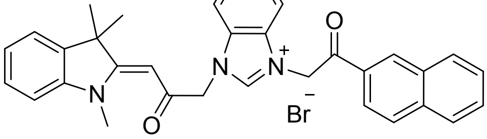
MHz, $CDCl_3$ + DMSO-d_6): δ = 189.70, 181.49, 173.51, 143.62, 142.32, 139.13, 134.18, 133.17, 131.30, 131.07, 128.54, 128.00, 127.21, 126.45, 122.64, 121.19, 113.15, 112.91, 108.09, 88.33, 54.60, 52.79, 48.11, 29.66, 22.09.HRMS (ESI-TOF) *m/z* Calcd for $C_{29}H_{28}N_3O_2^+$ $[M-Br]^+$ 450.2176, found 450.2179.



3-(2-(4-bromophenyl)-2-oxoethyl)-1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)-1*H*-benzo[*d*]imidazol-3-ium bromide

17

Yield 88%.White solid, Mp 299-301°C. IR ν_{max} (cm^{-1}): 3434, 2973, 1698, 1544, 1481, 1364, 1225, 1131, 933, 748.^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.74 (1H, s), 8.09 (3H, d, J= 8.1 Hz), 8.02 (1H, d, J= 7.2 Hz), 7.91 (2H, d, J= 8.1 Hz), 7.69 (2H, t, J= 3.9 Hz), 7.31 (1H, d, J= 7.2 Hz), 7.25 (1H, t, J= 7.8 Hz), 7.12 (1H, d, J= 7.8 Hz), 7.03 (1H, t, J= 6.9 Hz), 6.52 (2H, s), 5.73 (2H, s), 5.71 (1H, s), 3.37 (3H, s), 1.60 (6H, s).^{13}C NMR (75 MHz, DMSO-d_6): δ = 190.63, 183.33, 172.63, 144.31, 142.93, 139.29, 132.86, 132.08, 131.54, 131.33, 130.34, 128.61, 127.68, 126.56, 122.68, 121.70, 113.95, 113.53, 108.95, 89.16, 54.77, 53.30, 47.97, 29.87, 22.47. HRMS (ESI-TOF) *m/z* Calcd for $C_{29}H_{27}BrN_3O_2^+$ $[M-Br]^+$ 528,1281, found 528.1282.

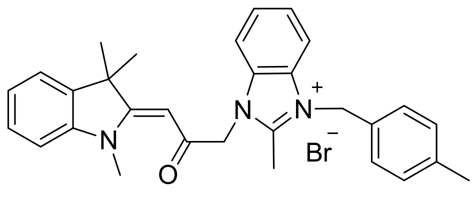


3-(2-(naphthalen-2-yl)-2-oxoethyl)-1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)-1*H*-benzo[*d*]imidazol-3-ium bromide

18

Yield 80%.Yellow solid, Mp 177-180°C. IR ν_{max} (cm^{-1}): 3425, 3027, 2927, 1690, 1628, 1540, 1477, 1368, 1185, 1131, 935, 749. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.79 (1H, s), 8.97 (1H, s), 8.25 (1H, d, J = 7.8 Hz), 8.18-8.08 (4H, m), 8.03 (1H, d, J= 7.2 Hz), 7.79-7.69 (4H, m), 7.32 (1H, d, J= 7.2 Hz), 7.26 (1H, t, J= 7.8 Hz), 7.12 (1H, d, J= 7.8 Hz), 7.04 (1H, t, J= 7.2 Hz), 6.67 (2H, s), 5.74 (2H, s), 5.71 (1H, s), 3.36 (3H, s), 1.62

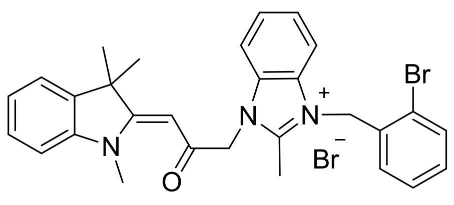
(6H, s).[13]C NMR (75 MHz, DMSO-d$_6$): δ = 191.16, 183.38, 172.67, 144.46, 142.96, 139.32, 135.55, 132.02, 131.64, 131.41, 131.12, 130.86, 129.67, 129.33, 128.68, 127.87, 127.70, 127.38, 126.63, 123.35, 122.71, 121.74, 113.95, 113.57, 108.98, 89.16, 54.80, 53.34, 48.01, 29.88, 22.49. HRMS (ESI-TOF) *m/z* Calcd for $C_{33}H_{30}N_3O_2^+$ $[M-Br]^+$ 500.2332, found 500.2333.



(*Z*)-2-methyl-3-(4-methylbenzyl)-1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)-1*H*-benzo[*d*]imidazol-3-ium bromide

19

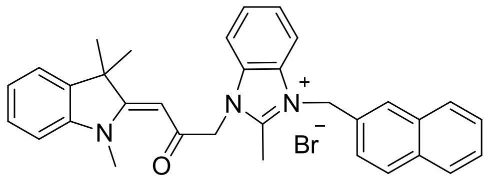
Yield 94%.White solid, Mp 304-305°C. IR ν_{max} (cm^{-1}): 3434, 3021, 2921, 1650, 1536, 1473, 1367, 1131, 933, 760. [1]H NMR (300 MHz, DMSO-d$_6$): δ = 7.99 (2H, s), 7.63 (2H, s), 7.31-7.19 (6H, m), 7.11 (1H, d, J= 7.5 Hz), 7.03 (1H, t, J= 7.2 Hz), 5.85 (2H, s), 5.70 (1H, s), 5.63 (2H, s), 3.36 (3H, s), 2.88 (3H, s), 2.28 (3H, s), 1.59 (6H, s). [13]C NMR (75 MHz, DMSO-d$_6$): δ = 183.41, 172.72, 152.91, 142.97, 139.34, 137.87, 131.58, 131.19, 130.69, 129.59, 127.77, 127.28, 126.28, 122.78, 121.79, 113.29, 112.89, 109.04, 89.32, 53.55, 48.02, 29.90, 22.52, 20.66, 10.94. HRMS (ESI-TOF) *m/z* Calcd for $C_{30}H_{32}N_3O^+$ $[M-Br]^+$ 450.2539, found 450.2540.



3-(2-bromobenzyl)-2-methyl-1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)-1*H*-benzo[*d*]imidazol-3-ium bromide

20

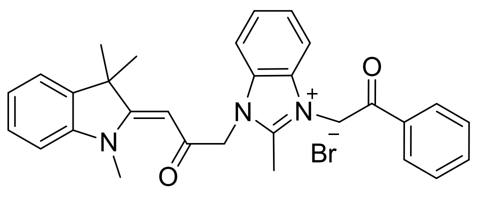
Yield 81%.Yellow solid, Mp 260-263°C. IR ν_{max} (cm^{-1}): 3429, 2927, 1646, 1543, 1474, 1368, 1135, 937, 758. [1]H NMR (300 MHz, DMSO-d$_6$): δ = 8.05 (1H, d, J= 7.2 Hz), 7.79 (2H, d, J= 6.3 Hz), 7.61 (2H, t, J= 9 Hz), 7.33-7.23 (4H, m), 7.12 (1H, d, J= 7.2 Hz), 7.04 (1H, d, J= 6.6 Hz), 6.89 (1H, s), 5.93 (2H, s), 5.74 (1H, s), 5.71 (2H, s), 3.38 (3H, s), 2.83 (3H, s), 1.58 (6H, s). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 183.41, 172.73, 153.78, 143.03, 139.37, 133.40, 132.97, 131.70, 130.75, 130.47, 128.48, 127.86, 126.51, 122.85, 122.00, 113.17, 109.14, 89.47, 48.82, 48.09, 30.00, 22.51, 11.10. HRMS (ESI-TOF) *m/z* Calcd for $C_{29}H_{29}BrN_3O^+$ [M-Br]$^+$ 514.1488, found 514.1489.



21

2-methyl-3-(naphthalen-2-ylmethyl)-1
-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)
-1*H*-benzo[*d*]imidazol-3-ium bromide

Yield 91%.White solid. Mp 279-281°C, IR ν_{max} (cm^{-1}): 3432, 2928, 2352, 1644, 1539, 1474, 1370, 1133, 936, 751. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 7.99-7.86 (6H, m) 7.62-7.47 (5H, m), 7.31 (1H, d, J= 7.2 Hz), 7.25 (1H, t, J= 7.5 Hz), 7.12 (1H, d, J= 7.8 Hz), 7.03 (1H, t, J= 6.9 Hz), 6.09 (2H, s), 5.72 (1H, s), 5.69 (2H, s), 3.37 (3H, s), 2.93 (3H, s), 1.58 (6H, s). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 183.44, 172.76, 153.37, 142.99, 139.36, 132.79, 132.56, 131,78, 130.84, 128.88, 127.78, 126.78, 126.66, 126.44, 125.81, 124,92, 122.82, 121.83, 113.31, 112.99, 109.08, 89.35, 53.65, 48.31, 48.08, 29.94, 22.51, 11.06. HRMS (ESI-TOF) *m/z* Calcd for $C_{33}H_{32}N_3O^+$ [M-Br]$^+$ 486.2539, found 486.2535.

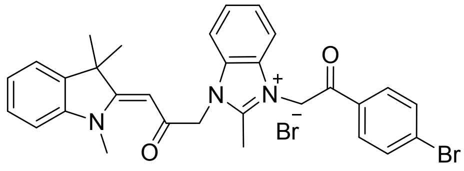


22

2-methyl-3-(2-oxo-2-phenylethyl)-1-
(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)-
1*H*-benzo[*d*]imidazol-3-ium bromide

Yield 85%.White solid, Mp 257-260°C. IR ν_{max} (cm^{-1}): 3440, 3027, 2888, 1694, 1648, 1536, 1478, 1367, 1228, 1130, 935, 753. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 8.17 (2H, d, J= 6.9 Hz), 8.02 (2H, t, J= 7.5 Hz), 7.80 (1H, d, J= 6.9 Hz), 7.71-7.63 (4H, m), 7.32 (1H, d, J= 6.9 Hz), 7.26 (1H, t, J= 7.5 Hz), 7.12 (1H, d, J= 8.1 Hz), 7.05 (1H, d, J= 6.9

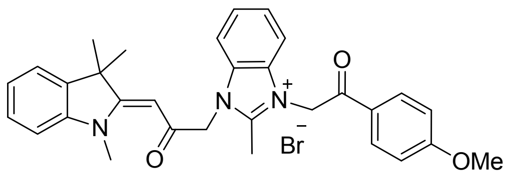
Hz), 6.52 (2H, s), 5.69 (3H, s), 3.36 (3H, s), 2.78 (3H, s), 1.59 (6H, s). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 191.18, 183.40, 172.79, 154.05, 139.41, 134.81, 133.83, 131.39, 129.104, 128.81, 127.88, 126.45, 122.89, 121.92, 113.30, 112.87, 109.16, 89.31, 53.60, 52.03, 48.14, 29.96, 22.55, 10.69. HRMS (ESI-TOF) *m/z* Calcd for $C_{30}H_{30}N_3O_2^+$ [M-Br]$^+$ 464.2332, found 464.2331.



3-(2-(4-bromophenyl)-2-oxoethyl)-2-methyl-1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)-1*H*-benzo[*d*]imidazol-3-ium bromide

23

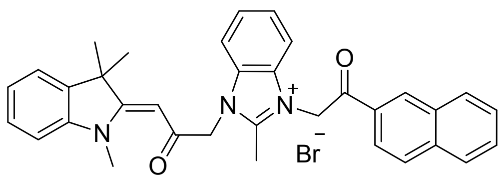
Yield 89%.White solid, Mp 242-245°C.IR ν_{max} (cm^{-1}): 3431, 3015, 1659, 1535, 1477, 1368, 1131, 935, 753. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 8.10 (2H, d, J= 8.1 Hz), 8.02 (2H, t, J= 8.1 Hz), 7.92 (2H, d, J= 8.1 Hz), 7.63 (2H, s), 7.31 (1H, d, J= 7.2 Hz), 7.24 (1H, d, J= 7.5 Hz), 7.12 (1H, d, J= 7.8 Hz), 7.03 (1H, t, J= 7.2 Hz), 6.51 (2H, s), 5.69 (3H, s), 3.36 (3H, s), 2.79 (3H, s), 1.59 (6H, s). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 190.44, 183.27, 172.72, 152.94, 142.95, 139.33, 132.85, 132.01, 131.25, 130.63, 128.75, 127.73, 126.19, 122.76, 121.76, 113.22, 112.77, 109.01, 89.23, 53.53, 51.97, 48.02, 29.86, 22.50, 10.62. HRMS (ESI-TOF) *m/z* Calcd for $C_{30}H_{29}BrN_3O_2^+$ [M-Br]$^+$ 542.1437, found 542.1436.



3-(2-(4-methoxyphenyl)-2-oxoethyl)-2-methyl-1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)-1*H*-benzo[*d*]imidazol-3-ium bromide

24

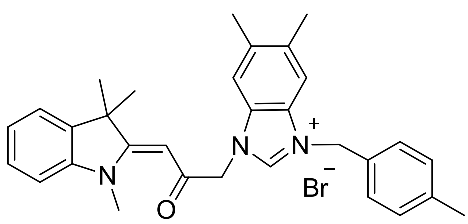
Yield 90%.White solid, Mp 264-266°C. IR ν_{max} (cm^{-1}): 3428, 2923, 2352, 1687, 1604, 1536, 1477, 1365, 1240, 1130, 935, 824, 758. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 8.14 (2H, d, J= 8.7 Hz), 8.03-7.99 (2H, m), 7.67-7.59 (2H, m), 7.32 (1H, d, J= 7.2 Hz), 7.28-7.19 (3H, m), 7.12 (1H, d, J= 7.8 Hz), 7.04 (1H, t, J= 7.5 Hz), 6.47 (2H, s), 5.68 (3H, s), 3.92 (3H, s), 3.36 (3H, s), 2.77 (3H, s), 1.59 (6H, s). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 189.18, 183.28, 172.69, 164.29, 153.88, 142.94, 139.31, 131.28, 131.10, 127.70, 126.61, 126.26, 126.16, 122.73, 121.74, 114.23, 113.08, 112.75, 108.99, 89.20, 55.82, 53.48, 51.50, 48.00, 29.82, 22.48, 10.58. HRMS (ESI-TOF) *m/z* Calcd for $C_{31}H_{32}N_3O_3^+$ [M-Br]$^+$ 494.2438, found 454.2441.



2-methyl-3-(2-(naphthalen-2-yl)-2-oxoethyl)
-1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)
-1*H*-benzo[*d*]imidazol-3-ium bromide

25

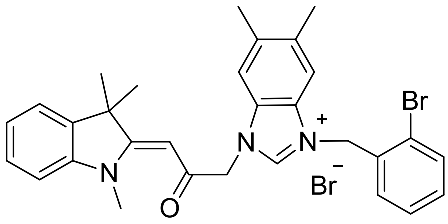
Yield 92%. White solid, Mp 255-257°C. IR ν_{max} (cm^{-1}): 3427, 2920, 1693, 1537, 1476, 1366, 1130, 935, 756. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 9.01 (1H, s), 8.24 (1H, d, J= 6.9 Hz), 8.18-8.03 (4H, m), 7.77-7.64 (4H, m), 7.33 (1H, d, J= 6.9 Hz), 7.26 (1H, t, J= 7.5 Hz), 7.13 (1H, d, J= 7.5 Hz), 7.04 (1H, t, J= 6.9 Hz), 6.69 (2H, s), 5.73 (3H, s), 3.38 (3H, s), 2.84 (3H, s), 1.60 (6H, s). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 191.08, 183.42, 172.73, 154.07, 143.05, 139.38, 135.68, 132.03, 131.40, 129.77, 129.51, 128.68, 128.00, 127.53, 126.31, 123.61, 122.84, 121.89, 113.29, 112.90, 109.13, 89.37, 53.62, 52.10, 48.11, 29.96, 22.54, 10.76. HRMS (ESI-TOF) *m/z* Calcd for $C_{34}H_{32}N_3O_2^+$ [M-Br]$^+$ 514.2489, found 514.2489.



5,6-dimethyl-3-(4-methylbenzyl)-1
-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)
-1*H*-benzo[*d*]imidazol-3-ium bromide

26

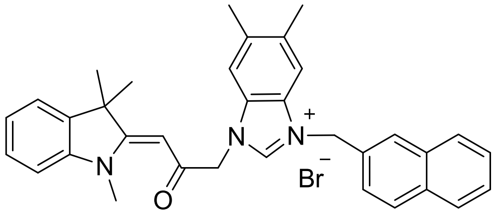
Yield 91%. White solid. Mp 211-214°C. IR ν_{max} (cm^{-1}): 3436, 2932, 1645, 1543, 1484, 1369, 1130, 931, 750. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 9.78 (1H, s), 7.80 (1H, s), 7.75 (1H, s), 7.41 (2H, d, J= 7.1 Hz), 7.30 (1H, d, J= 6.9 Hz), 7.24 (3H, s), 7.11 (1H, d, J= 7.8 Hz), 7.03 (1H, t, J= 7.2 Hz), 5.76 (2H, s), 5.67 (1H, s), 5.32 (2H, s), 3.37 (3H, s), 2.36 (6H, s), 2.28 (3H, s), 1.58 (6H, s). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 183.53, 172.59, 142.98, 142.25, 139.32, 138.12, 136.48, 136.28, 131.21, 130.40, 129.53, 128.95, 128.11, 127.72, 122.70, 121.75, 113.25, 113.08, 108.98, 89.15, 54.63, 49.45, 47.98, 29.89, 22.51, 20.69, 19.97. HRMS (ESI-TOF) *m/z* Calcd for $C_{31}H_{34}N_3O^+$ [M-Br]$^+$ 464.2696, found 464.2699.



27

3-(2-bromobenzyl)-5,6-dimethyl-1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)-1*H*-benzo[*d*]imidazol-3-ium bromide

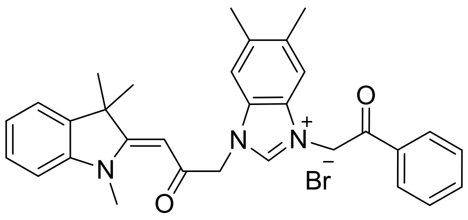
Yield 88%. White solid. Mp 281-284°C. IR ν_{max} (cm^{-1}): 3429, 2924, 1649, 1543, 1450, 1368, 1192, 1131, 931, 747. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 9.63 (1H, s), 7.77 (3H, d, J= 4.2 Hz), 7.48-7.36 (2H, m), 7.31 (1H, d, J= 7.2 Hz), 7.24 (1H, d, J= 7.8 Hz), 7.11 (1H, d, J= 7.8 Hz), 7.03 (1H, t, J= 7.2 Hz), 5.87 (2H, s), 5.65 (1H, s), 5.54 (2H, s), 3.34 (3H, s), 2.38 (6H, s), 1.58 (6H, s). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 183.42, 172.55, 142.96, 142.80, 139.29, 136.62, 136.50, 133.29, 132.89, 130.91, 130.34, 130.15, 129.23, 128.44, 127.70, 122.94, 122.68, 121.72, 113.14, 108.95, 89.07, 54.70, 50.18, 47.97, 29.85, 22.48, 19.96. HRMS (ESI-TOF) *m/z* Calcd for $C_{30}H_{31}BrN_3O^+$ [M-Br]$^+$ 528.1645, found 528.1646.



28

5,6-dimethyl-3-(naphthalen-2-ylmethyl)-1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)-1*H*-benzo[*d*]imidazol-3-ium bromide

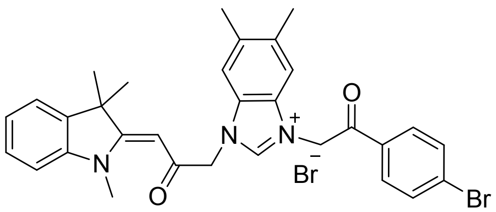
White solid. Yield 92%. Mp 228-230°C. IR ν_{max} (cm^{-1}): 3432, 2928, 2352, 1643, 1541, 1480, 1370, 1130, 932, 752. [1]H NMR (300 MHz, DMSO-d_6): δ = 9.79 (1H, s), 8.05 (1H, s), 8.00-7.89 (3H, m), 7.86 (1H, s), 7.77 (1H, s), 7.61-7.55 (3H, m), 7.32 (1H, d, J= 7.2 Hz), 7.26 (1H, d, J= 8.4 Hz), 7.11 (1H, d, J= 7.8 Hz), 7.04 (1H, d, J= 7.2 Hz), 5.98 (2H, s), 5.65 (1H, s), 5.53 (2H, s), 3.33 (3H, s), 2.36 (6H, s), 1.60 (6H, s). [13]C NMR (75 MHz, DMSO-d_6): δ = 183.49, 142.95, 132.70, 131.69, 130.45, 129.10, 128.78, 127.67, 127.10, 126.72, 125.42, 122.70, 121.74, 113.19, 89.04, 54.63, 49.78, 47.98, 29.83, 22.47, 19.95. HRMS (ESI-TOF) *m/z* Calcd for $C_{34}H_{34}N_3O^+$ $[M\text{-}Br]^+$ 500.2696, found 500.2698.



29

5,6-dimethyl-3-(2-oxo-2-phenylethyl)-1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)-1*H*-benzo[*d*]imidazol-3-ium bromide

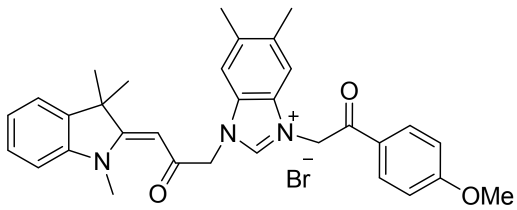
Yield 80%.Yellow solid. Mp 239-242°C. IR ν_{max} (cm^{-1}): 3434, 2956, 1699, 1634, 1534, 1482, 1371, 1228, 1134, 932, 754. [1]H NMR (300 MHz, DMSO-d_6): δ = 9.54 (1H, s), 8.15 (2H, d, J= 7.2 Hz), 7.88 (1H, s), 7.79 (2H, s), 7.68 (2H, t, J= 7.2 Hz), 7.32 (1H, d, J= 7.2 Hz), 7.26 (1H, t, J= 7.5 Hz), 7.12 (1H, d, J= 7.5 Hz), 7.03 (1H, t, J= 7.2 Hz), 6.44 (2H, s), 5.67 (1H, s), 5.63 (2H, s), 3.35 (3H, s), 2.39 (6H, d, J= 8.7 Hz), 1.60 (6H, s). [13]C NMR (75 MHz, DMSO-d_6): δ = 191.27, 183.49, 172.58, 143.20, 142.99, 139.32, 136.32, 134.53, 133.82, 130.10, 129.89, 129.04, 128.39, 127.72, 122.71, 121.76, 113.39, 112.93, 108.98, 89.12, 54.63, 53.17, 48.00, 29.87, 22.50, 19.99. HRMS (ESI-TOF) *m/z* Calcd for $C_{31}H_{32}N_3O_2^+$ $[M\text{-}Br]^+$ 478.2489, found 478.2486.



30

3-(2-(4-bromophenyl)-2-oxoethyl)-5,6-dimethyl-1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)-1*H*-benzo[*d*]imidazol-3-ium bromide

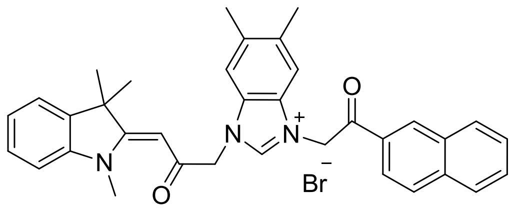
Yield 95%. Yellow solid. Mp 201-202°C. IR v_{max} (cm^{-1}): 3427, 2959, 2354, 1697, 1540, 1480, 1372, 1226, 1132, 1073, 933, 821, 751. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 9.52 (1H, s), 8.07 (2H, d, J= 7.2 Hz), 7.92 (2H, s), 7.88 (1H, d, J= 5.1 Hz), 7.78 (1H, s), 7.31 (1H, d, J= 6.6 Hz), 7.24 (1H, d, J= 6.6 Hz), 7.11 (1H, d, J= 7.2 Hz), 7.04 (1H, d, J= 7.2 Hz), 6.441 (2H, s), 5.65 (1H, s), 5.61 (2H, s), 3.35 (3H, s), 2.39 (6H, d, J= 7.5 Hz), 1.60 (6H, s). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 190.66, 183.46, 172.61, 143.17, 142.98, 139.32, 136.34, 132.89, 132.12, 130.34, 130.06, 129.88, 128.64, 127.73, 122.72, 121.76, 113.39, 112.92, 108.98, 89.11, 54.63, 53.14, 48.00, 29.86, 22.50, 19.93. HRMS (ESI-TOF) *m/z* Calcd for $C_{31}H_{31}BrN_3O_2^+$ [M-Br]$^+$ 556.1594, found 556.1592.



31

3-(2-(4-methoxyphenyl)-2-oxoethyl)-5,6-dimethyl-1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)-1*H*-benzo[*d*]imidazol-3-ium bromide

Yield 71%.Yellow solid. Mp 183-185°C. IR v_{max} (cm^{-1}): 3427, 2957, 1682, 1601, 1539, 1481, 1369, 1241, 1177, 1130, 1016, 932, 836, 752. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 9.53 (1H, s), 8.12 (2H, d, J= 8.4 Hz), 7.84 (1H, s), 7.78 (1H, s), 7.33-7.18 (4H, m), 7.11 (1H, d, J= 7.5 Hz), 7.03 (1H, t, J= 7.2 Hz), 6.37 (2H, s), 5.65 (1H, s), 5.61 (2H, s), 3.91 (3H, s), 3.35 (3H, s), 2.39 (6H, d, J= 8.1 Hz), 1.60 (6H, s). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 189.46, 183.48, 164.19, 143.24, 136.30, 130.83, 130.11, 129.88, 126.65, 122.72, 121.75, 114.31, 113.32, 112.91, 108.89, 89.09, 55.80, 54.16, 52.72, 48.00, 29.86, 22.50, 19.98. HRMS (ESI-TOF) *m/z* Calcd for $C_{32}H_{34}N_3O_3^+$ [M-Br]$^+$ 508.2594, found 508.2594.



32

5,6-dimethyl-3-(2-(naphthalen-2-yl)-2-oxoethyl)-1-(2-oxo-3-(1,3,3-trimethylindolin-2-ylidene)propyl)-1*H*-benzo[*d*]imidazol-3-ium bromide

Yield 82%.Red solid. Mp 193-195°C.IR v_{max} (cm^{-1}): 3415, 2957, 1688, 1540, 1475, 1369, 1186, 1130, 932, 752. ^1H NMR (300 MHz, DMSO-d_6): δ = 9.61 (1H, s), 8.95 (1H, s), 8.24 (1H, d, J= 7.8 Hz), 8.16 (1H, d, J= 8.7 Hz), 8.09 (2H, d, J= 8.1 Hz), 7.93 (1H, s), 7.80 (1H, s), 7.74 (2H, t, J= 7.8 Hz), 7.32 (1H, d, J= 7.2 Hz), 7.26 (1H, t, J= 7.5 Hz), 7.12 (1H, d, J= 7.8 Hz), 7.04 (1H, t, J= 7.2 Hz), 6.58 (2H, s), 5.68 (1H, s), 5.65 (2H, s), 3.37 (3H, s), 2.39 (6H, d, J= 9.9 Hz), 1.62 (6H, s). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 191.15, 183.48, 172.57, 143.24, 142.96, 139.30, 136.31, 135.53, 132.01, 131.11, 130.79, 130.11, 129.90, 129.65, 129.30, 128.65, 127.86, 127.70, 127.36, 123.33, 122.68, 121.72, 113.37, 112.94, 108.95, 89.12, 54.64, 53.19, 47.98, 29.85, 22.49, 19.96, 19.89. HRMS (ESI-TOF) *m/z* Calcd for $C_{35}H_{34}N_3O_2^+$ $[M-Br]^+$ 528.2645, found 528.2644.

3. X-ray crystal structure of compound 24

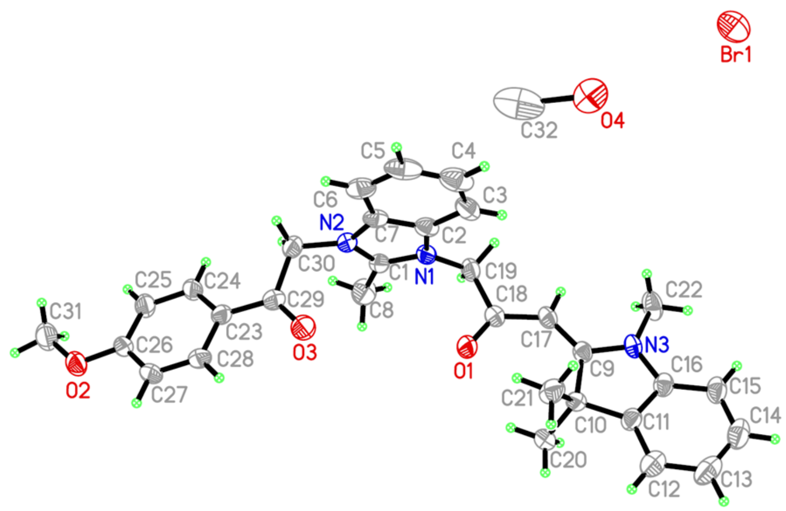


Fig. 1 X-ray crystal structure of compound **24**.

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_diffrn_reflns_av_sigmaI/netI        0.0888
_diffrn_reflns_limit_h_min            -19
_diffrn_reflns_limit_h_max             19
_diffrn_reflns_limit_k_min            -17
_diffrn_reflns_limit_k_max             12
_diffrn_reflns_limit_l_min            -15
_diffrn_reflns_limit_l_max             14
_diffrn_reflns_theta_min              1.90
_diffrn_reflns_theta_max              25.00
_reflns_number_total                  5093
_reflns_number_gt                     2544
_reflns_threshold_expression          >2sigma(I)

_computing_data_collection            'Bruker SMART'
_computing_cell_refinement            'Bruker SMART'
_computing_data_reduction             'Bruker SAINT'
_computing_structure_solution         'SHELXS-97 (Sheldrick, 1990)'
_computing_structure_refinement       'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics         'Bruker SHELXTL'
_computing_publication_material       'Bruker SHELXTL'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
```

_refine_ls_structure_factor_coef Fsqd

_refine_ls_matrix_type full

_refine_ls_weighting_scheme calc

_refine_ls_weighting_details

'calc w=1/[\s^2^(Fo^2^)+(0.0943P)^2^+0.0000P] where P=(Fo^2^+2Fc^2^)/3'

_atom_sites_solution_primary direct

_atom_sites_solution_secondary difmap

_atom_sites_solution_hydrogens geom

_refine_ls_hydrogen_treatment mixed

_refine_ls_extinction_method none

_refine_ls_extinction_coef ?

_refine_ls_number_reflns 5093

_refine_ls_number_parameters 361

_refine_ls_number_restraints 0

_refine_ls_R_factor_all 0.1348

_refine_ls_R_factor_gt 0.0570

_refine_ls_wR_factor_ref 0.1858

_refine_ls_wR_factor_gt 0.1446

_refine_ls_goodness_of_fit_ref 0.968

_refine_ls_restrained_S_all 0.968

_refine_ls_shift/su_max 0.002

_refine_ls_shift/su_mean 0.000

loop_

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_atom_site_type_symbol

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_atom_site_fract_y

_atom_site_fract_z

_atom_site_U_iso_or_equiv

_atom_site_adp_type

_atom_site_occupancy

_atom_site_symmetry_multiplicity

_atom_site_calc_flag

_atom_site_refinement_flags

_atom_site_disorder_assembly

_atom_site_disorder_group

O1 O 0.1041(2) -0.9806(3) 0.1029(3) 0.0704(10) Uani 1 1 d . . .

O2 O 0.1911(2) -0.6137(3) -0.0755(4) 0.0888(13) Uani 1 1 d . . .

O3 O 0.1997(2) -0.3165(2) -0.0665(4) 0.0862(13) Uani 1 1 d . . .

N1 N 0.3517(2) -0.5492(3) 0.0282(3) 0.0517(10) Uani 1 1 d . . .

N2 N 0.3535(2) -0.4024(3) 0.0351(3) 0.0518(10) Uani 1 1 d . . .

N3 N 0.2337(3) -0.0270(3) -0.1113(3) 0.0522(10) Uani 1 1 d . . .

C1 C 0.1530(4) -1.0349(4) 0.1999(5) 0.091(2) Uani 1 1 d . . .

H1A H 0.1194 -1.0866 0.2029 0.136 Uiso 1 1 calc R . .

H1B H 0.1660 -1.0005 0.2684 0.136 Uiso 1 1 calc R . .

H1C H 0.2060 -1.0538 0.1930 0.136 Uiso 1 1 calc R . .

C2 C 0.1405(3) -0.9042(3) 0.0843(4) 0.0531(13) Uani 1 1 d . . .

C3 C 0.0920(3) -0.8559(4) -0.0116(4) 0.0576(14) Uani 1 1 d . . .

H3A H 0.0373 -0.8763 -0.0581 0.069 Uiso 1 1 calc R . .

C4 C 0.1238(3) -0.7787(4) -0.0387(4) 0.0555(13) Uani 1 1 d . . .

H4A H 0.0898 -0.7463 -0.1026 0.067 Uiso 1 1 calc R . .

C5 C 0.2070(3) -0.7471(3) 0.0280(4) 0.0509(13) Uani 1 1 d . . .

C6 C 0.2539(3) -0.7961(3) 0.1255(5) 0.0641(15) Uani 1 1 d . . .

H6A H 0.3086 -0.7764 0.1728 0.077 Uiso 1 1 calc R . .

C7 C 0.2206(3) -0.8732(4) 0.1531(4) 0.0671(15) Uani 1 1 d . . .

H7A H 0.2527 -0.9045 0.2190 0.081 Uiso 1 1 calc R . .

C8 C 0.2387(3) -0.6643(4) -0.0037(4) 0.0580(14) Uani 1 1 d . . .

C9 C 0.3351(3) -0.6409(4) 0.0505(5) 0.0634(15) Uani 1 1 d . . .

H9A H 0.3550 -0.6501 0.1322 0.076 Uiso 1 1 calc R . .

H9B H 0.3677 -0.6807 0.0208 0.076 Uiso 1 1 calc R . .

C10 C 0.3820(3) -0.5192(4) -0.0546(4) 0.0549(14) Uani 1 1 d . . .

C11 C 0.4110(3) -0.5660(4) -0.1300(5) 0.0704(16) Uani 1 1 d . . .

H11A H 0.4128 -0.6283 -0.1327 0.084 Uiso 1 1 calc R . .

C12 C 0.4371(4) -0.5106(7) -0.2005(5) 0.088(2) Uani 1 1 d . . .

H12A H 0.4575 -0.5371 -0.2523 0.105 Uiso 1 1 calc R . .

C13 C 0.4339(4) -0.4167(6) -0.1967(6) 0.091(2) Uani 1 1 d . . .

H13A H 0.4503 -0.3833 -0.2475 0.110 Uiso 1 1 calc R . .

C14 C 0.4078(3) -0.3737(5) -0.1219(5) 0.0697(16) Uani 1 1 d . . .

H14A H 0.4072 -0.3115 -0.1182 0.084 Uiso 1 1 calc R . .

C15 C 0.3818(3) -0.4261(4) -0.0507(4) 0.0535(13) Uani 1 1 d . . .

C16 C 0.3345(3) -0.4769(4) 0.0791(4) 0.0511(13) Uani 1 1 d . . .

C17 C 0.2986(4) -0.4801(4) 0.1698(5) 0.0816(18) Uani 1 1 d . . .

H17A H 0.2919 -0.4202 0.1930 0.122 Uiso 1 1 calc R . .

H17B H 0.3375 -0.5128 0.2340 0.122 Uiso 1 1 calc R . .

H17C H 0.2432 -0.5094 0.1414 0.122 Uiso 1 1 calc R . .

C18 C 0.3452(3) -0.3106(3) 0.0670(5) 0.0610(14) Uani 1 1 d . . .

H18A H 0.3954 -0.2764 0.0691 0.073 Uiso 1 1 calc R . .

H18B H 0.3430 -0.3094 0.1425 0.073 Uiso 1 1 calc R . .

C19 C 0.2623(3) -0.2677(4) -0.0189(5) 0.0614(14) Uani 1 1 d . . .

C20 C 0.2708(3) -0.1737(3) -0.0334(5) 0.0602(14) Uani 1 1 d . . .

H20A H 0.3230 -0.1484 0.0140 0.072 Uiso 1 1 calc R . .

C21 C 0.2130(3) -0.1153(3) -0.1070(4) 0.0488(12) Uani 1 1 d . . .

C22 C 0.1211(3) -0.1307(3) -0.1932(4) 0.0537(13) Uani 1 1 d . . .

C23 C 0.0598(3) -0.1578(4) -0.1343(5) 0.0733(17) Uani 1 1 d . . .

H23A H 0.0624 -0.1139 -0.0775 0.110 Uiso 1 1 calc R . .

H23B H 0.0769 -0.2152 -0.0985 0.110 Uiso 1 1 calc R . .

H23C H 0.0016 -0.1613 -0.1896 0.110 Uiso 1 1 calc R . .

C24 C 0.1199(4) -0.1985(4) -0.2844(5) 0.0728(17) Uani 1 1 d . . .

H24A H 0.1592 -0.1794 -0.3196 0.109 Uiso 1 1 calc R . .

H24B H 0.0623 -0.2025 -0.3411 0.109 Uiso 1 1 calc R . .

H24C H 0.1375 -0.2561 -0.2498 0.109 Uiso 1 1 calc R . .

C25 C 0.0989(3) -0.0386(3) -0.2451(4) 0.0556(13) Uani 1 1 d . . .

C26 C 0.0233(4) -0.0070(4) -0.3304(5) 0.0841(19) Uani 1 1 d . . .

H26A H -0.0246 -0.0170 -0.3055 0.101 Uiso 1 1 calc R . .

H26B H 0.0126 -0.0435 -0.3978 0.101 Uiso 1 1 calc R . .

C27 C 0.0212(5) 0.0831(5) -0.3628(6) 0.091(2) Uani 1 1 d . . .

H27A H -0.0291 0.1059 -0.4180 0.109 Uiso 1 1 calc R . .

C28 C 0.0911(5) 0.1386(5) -0.3151(6) 0.0834(19) Uani 1 1 d . . .

H28A H 0.0881 0.1976 -0.3400 0.100 Uiso 1 1 calc R . .

C29 C 0.1665(4) 0.1079(4) -0.2300(5) 0.0681(15) Uani 1 1 d . . .

H29A H 0.2145 0.1450 -0.1977 0.082 Uiso 1 1 calc R . .

C30 C 0.1673(3) 0.0199(4) -0.1954(4) 0.0546(13) Uani 1 1 d . . .

C31 C 0.3150(4) 0.0131(4) -0.0360(5) 0.0785(17) Uani 1 1 d . . .

H31A H 0.3501 -0.0317 0.0149 0.118 Uiso 1 1 calc R . .

H31B H 0.3029 0.0604 0.0075 0.118 Uiso 1 1 calc R . .

H31C H 0.3456 0.0372 -0.0808 0.118 Uiso 1 1 calc R . .

Br1 Br 0.55540(4) -0.18346(4) 0.12110(5) 0.0810(3) Uani 1 1 d . . .

O4 O 0.4836(6) -0.3259(6) 0.3256(7) 0.091(3) Uani 0.50 1 d P . .

C32 C 0.4681(9) -0.4226(15) 0.3777(13) 0.132(7) Uani 0.50 1 d P . .

loop_

_atom_site_aniso_label

_atom_site_aniso_U_11

_atom_site_aniso_U_22

_atom_site_aniso_U_33

_atom_site_aniso_U_23

_atom_site_aniso_U_13

_atom_site_aniso_U_12

O1 0.063(2) 0.058(3) 0.077(3) 0.000(2) 0.010(2) -0.014(2)

O2 0.061(2) 0.081(3) 0.102(3) 0.036(3) 0.004(2) 0.000(2)

O3 0.052(2) 0.047(2) 0.135(4) 0.010(2) 0.005(2) -0.008(2)

N1 0.042(2) 0.047(3) 0.063(3) 0.005(2) 0.016(2) 0.001(2)

N2 0.043(2) 0.056(3) 0.054(3) 0.008(2) 0.014(2) -0.002(2)

N3 0.062(3) 0.037(3) 0.058(3) -0.004(2) 0.022(2) -0.013(2)

C1 0.086(4) 0.067(4) 0.098(5) 0.013(4) 0.010(4) -0.013(4)

C2 0.046(3) 0.046(3) 0.064(3) -0.006(3) 0.016(3) -0.004(3)

C3 0.042(3) 0.064(4) 0.058(3) -0.006(3) 0.008(3) -0.011(3)

C4 0.045(3) 0.063(4) 0.052(3) 0.003(3) 0.011(2) 0.006(3)

C5 0.043(3) 0.048(3) 0.055(3) 0.000(3) 0.010(2) 0.006(3)

C6 0.044(3) 0.053(4) 0.074(4) 0.007(3) -0.003(3) -0.006(3)

C7 0.057(3) 0.053(4) 0.070(4) 0.010(3) 0.000(3) -0.007(3)

C8 0.050(3) 0.058(4) 0.060(3) 0.004(3) 0.014(3) 0.004(3)

C9 0.056(3) 0.048(4) 0.075(4) 0.010(3) 0.011(3) 0.007(3)

C10 0.035(3) 0.076(4) 0.048(3) 0.004(3) 0.008(2) 0.005(3)

C11 0.046(3) 0.095(5) 0.060(4) -0.014(3) 0.007(3) 0.006(3)

C12 0.045(3) 0.166(8) 0.049(4) -0.016(5) 0.013(3) 0.002(5)

C13 0.058(4) 0.143(8) 0.067(5) 0.023(5) 0.016(3) -0.005(5)

C14 0.055(3) 0.088(5) 0.063(4) 0.016(4) 0.019(3) -0.011(3)

C15 0.038(3) 0.074(4) 0.044(3) 0.011(3) 0.011(2) 0.001(3)

C16 0.046(3) 0.052(4) 0.058(3) 0.007(3) 0.022(2) 0.003(3)

C17 0.099(4) 0.082(5) 0.083(4) 0.014(4) 0.056(4) 0.006(4)

C18 0.059(3) 0.045(4) 0.072(4) 0.004(3) 0.016(3) -0.011(3)

C19 0.052(3) 0.048(4) 0.080(4) 0.002(3) 0.020(3) -0.005(3)

C20 0.053(3) 0.044(3) 0.075(4) -0.004(3) 0.014(3) -0.016(3)

C21 0.053(3) 0.044(3) 0.053(3) -0.006(3) 0.024(3) -0.004(3)

C22 0.043(3) 0.044(3) 0.072(3) -0.003(3) 0.019(3) -0.002(2)

C23 0.052(3) 0.065(4) 0.106(5) 0.013(3) 0.033(3) -0.004(3)

C24 0.068(4) 0.058(4) 0.082(4) -0.018(3) 0.015(3) 0.006(3)

C25 0.060(3) 0.047(3) 0.063(3) 0.005(3) 0.027(3) 0.012(3)

C26 0.090(5) 0.089(5) 0.080(4) 0.007(4) 0.039(4) 0.024(4)

C27 0.106(5) 0.085(6) 0.084(5) 0.030(4) 0.037(4) 0.041(5)

C28 0.119(6) 0.056(4) 0.097(5) 0.014(4) 0.064(5) 0.017(5)

C29 0.092(4) 0.044(4) 0.086(4) 0.004(3) 0.053(4) 0.005(3)

C30 0.070(4) 0.045(3) 0.056(3) -0.003(3) 0.031(3) 0.001(3)

C31 0.092(4) 0.056(4) 0.075(4) -0.008(3) 0.017(3) -0.030(3)

Br1 0.0686(4) 0.0851(5) 0.0862(5) -0.0078(4) 0.0253(3) -0.0177(3)

O4 0.098(6) 0.093(7) 0.071(5) -0.020(5) 0.018(5) -0.003(5)

C32 0.086(10) 0.22(2) 0.096(11) -0.051(12) 0.040(9) -0.016(12)

_geom_special_details

All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.

loop_

_geom_bond_atom_site_label_1

_geom_bond_atom_site_label_2

_geom_bond_distance

_geom_bond_site_symmetry_2

_geom_bond_publ_flag

O1 C2 1.353(6) . ?

O1 C1 1.441(6) . ?

O2 C8 1.218(6) . ?

O3 C19 1.228(6) . ?

N1 C16 1.341(6) . ?

N1 C10 1.395(6) . ?

N1 C9 1.444(6) . ?

N2 C16 1.333(6) . ?

N2 C15 1.380(6) . ?

N2 C18 1.448(6) . ?

N3 C21 1.367(6) . ?

N3 C30 1.400(6) . ?

N3 C31 1.460(6) . ?

C1 H1A 0.9600 . ?

C1 H1B 0.9600 . ?

C1 H1C 0.9600 . ?

C2 C7 1.369(6) . ?

C2 C3 1.382(7) . ?

C3 C4 1.363(7) . ?

C3 H3A 0.9300 . ?

C4 C5 1.404(6) . ?

C4 H4A 0.9300 . ?

C5 C6 1.395(6) . ?

C5 C8 1.457(7) . ?

C6 C7 1.376(7) . ?

C6 H6A 0.9300 . ?

C7 H7A 0.9300 . ?

C8 C9 1.528(7) . ?

C9 H9A 0.9700 . ?

C9 H9B 0.9700 . ?

C10 C15 1.389(7) . ?

C10 C11 1.404(7) . ?

C11 C12 1.399(9) . ?

C11 H11A 0.9300 . ?

C12 C13 1.403(9) . ?

C12 H12A 0.9300 . ?

C13 C14 1.342(9) . ?

C13 H13A 0.9300 . ?

C14 C15 1.378(7) . ?

C14 H14A 0.9300 . ?

C16 C17 1.477(6) . ?

C17 H17A 0.9600 . ?

C17 H17B 0.9600 . ?

C17 H17C 0.9600 . ?

C18 C19 1.539(7) . ?

C18 H18A 0.9700 . ?

C18 H18B 0.9700 . ?

C19 C20 1.427(7) . ?

C20 C21 1.371(6) . ?

C20 H20A 0.9300 . ?

C21 C22 1.526(6) . ?

C22 C25 1.508(7) . ?

C22 C23 1.523(7) . ?

C22 C24 1.529(7) . ?

C23 H23A 0.9600 . ?

C23 H23B 0.9600 . ?

C23 H23C 0.9600 . ?

C24 H24A 0.9600 . ?

C24 H24B 0.9600 . ?

C24 H24C 0.9600 . ?

C25 C30 1.384(7) . ?

C25 C26 1.396(7) . ?

C26 C27 1.402(8) . ?

C26 H26A 0.9700 . ?

C26 H26B 0.9700 . ?

C27 C28 1.369(9) . ?

C27 H27A 0.9300 . ?

C28 C29 1.389(8) . ?

C28 H28A 0.9300 . ?

C29 C30 1.383(7) . ?

C29 H29A 0.9300 . ?

C31 H31A 0.9600 . ?

C31 H31B 0.9600 . ?

C31 H31C 0.9600 . ?

O4 C32 1.65(2) . ?

loop_

_geom_angle_atom_site_label_1

_geom_angle_atom_site_label_2

_geom_angle_atom_site_label_3

_geom_angle

_geom_angle_site_symmetry_1

_geom_angle_site_symmetry_3

_geom_angle_publ_flag

C2 O1 C1 118.3(4) . . ?

C16 N1 C10 107.7(4) . . ?

C16 N1 C9 125.3(4) . . ?

C10 N1 C9 126.9(5) . . ?

C16 N2 C15 108.5(4) . . ?

C16 N2 C18 127.6(4) . . ?

C15 N2 C18 123.9(4) . . ?

C21 N3 C30 111.9(4) . . ?

C21 N3 C31 123.7(4) . . ?

C30 N3 C31 124.4(4) . . ?

O1 C1 H1A 109.5 . . ?

O1 C1 H1B 109.5 . . ?

H1A C1 H1B 109.5 . . ?

O1 C1 H1C 109.5 . . ?

H1A C1 H1C 109.5 . . ?

H1B C1 H1C 109.5 . . ?

O1 C2 C7 124.5(5) . . ?

O1 C2 C3 116.1(4) . . ?

C7 C2 C3 119.4(5) . . ?

C4 C3 C2 120.5(4) . . ?

C4 C3 H3A 119.8 . . ?

C2 C3 H3A 119.8 . . ?

C3 C4 C5 121.3(5) . . ?

C3 C4 H4A 119.4 . . ?

C5 C4 H4A 119.4 . . ?

C6 C5 C4 117.0(5) . . ?

C6 C5 C8 123.3(4) . . ?

C4 C5 C8 119.7(4) . . ?

C7 C6 C5 121.2(5) . . ?

C7 C6 H6A 119.4 . . ?

C5 C6 H6A 119.4 . . ?

C2 C7 C6 120.6(5) . . ?

C2 C7 H7A 119.7 . . ?

C6 C7 H7A 119.7 . . ?

O2 C8 C5 122.0(5) . . ?

O2 C8 C9 118.2(5) . . ?

C5 C8 C9 119.8(5) . . ?

N1 C9 C8 112.0(4) . . ?

N1 C9 H9A 109.2 . . ?

C8 C9 H9A 109.2 . . ?

N1 C9 H9B 109.2 . . ?

C8 C9 H9B 109.2 . . ?

H9A C9 H9B 107.9 . . ?

C15 C10 N1 106.7(4) . . ?

C15 C10 C11 121.9(5) . . ?

N1 C10 C11 131.4(6) . . ?

C12 C11 C10 113.9(6) . . ?

C12 C11 H11A 123.1 . . ?

C10 C11 H11A 123.1 . . ?

C11 C12 C13 122.9(6) . . ?

C11 C12 H12A 118.5 . . ?

C13 C12 H12A 118.5 . . ?

C14 C13 C12 121.8(7) . . ?

C14 C13 H13A 119.1 . . ?

C12 C13 H13A 119.1 . . ?

C13 C14 C15 116.9(7) . . ?

C13 C14 H14A 121.6 . . ?

C15 C14 H14A 121.6 . . ?

C14 C15 N2 130.5(6) . . ?

C14 C15 C10 122.5(6) . . ?

N2 C15 C10 107.0(4) . . ?

N2 C16 N1 110.1(4) . . ?

N2 C16 C17 125.3(5) . . ?

N1 C16 C17 124.5(5) . . ?

C16 C17 H17A 109.5 . . ?

C16 C17 H17B 109.5 . . ?

H17A C17 H17B 109.5 . . ?

C16 C17 H17C 109.5 . . ?

H17A C17 H17C 109.5 . . ?

H17B C17 H17C 109.5 . . ?

N2 C18 C19 110.5(4) . . ?

N2 C18 H18A 109.5 . . ?

C19 C18 H18A 109.5 . . ?

N2 C18 H18B 109.5 . . ?

C19 C18 H18B 109.5 . . ?

H18A C18 H18B 108.1 . . ?

O3 C19 C20 128.7(5) . . ?

O3 C19 C18 118.0(5) . . ?

C20 C19 C18 113.3(4) . . ?

C21 C20 C19 129.3(5) . . ?

C21 C20 H20A 115.3 . . ?

C19 C20 H20A 115.3 . . ?

N3 C21 C20 121.1(4) . . ?

N3 C21 C22 108.4(4) . . ?

C20 C21 C22 130.5(5) . . ?

C25 C22 C23 110.8(4) . . ?

C25 C22 C21 101.0(4) . . ?

C23 C22 C21 111.3(4) . . ?

C25 C22 C24 110.0(4) . . ?

C23 C22 C24 111.7(4) . . ?

C21 C22 C24 111.5(4) . . ?

C22 C23 H23A 109.5 . . ?

C22 C23 H23B 109.5 . . ?

H23A C23 H23B 109.5 . . ?

C22 C23 H23C 109.5 . . ?

H23A C23 H23C 109.5 . . ?

H23B C23 H23C 109.5 . . ?

C22 C24 H24A 109.5 . . ?

C22 C24 H24B 109.5 . . ?

H24A C24 H24B 109.5 . . ?

C22 C24 H24C 109.5 . . ?

H24A C24 H24C 109.5 . . ?

H24B C24 H24C 109.5 . . ?

C30 C25 C26 119.1(5) . . ?

C30 C25 C22 110.5(4) . . ?

C26 C25 C22 130.3(5) . . ?

C25 C26 C27 117.8(6) . . ?

C25 C26 H26A 107.9 . . ?

C27 C26 H26A 107.9 . . ?

C25 C26 H26B 107.9 . . ?

C27 C26 H26B 107.9 . . ?

H26A C26 H26B 107.2 . . ?

C28 C27 C26 121.8(6) . . ?

C28 C27 H27A 119.1 . . ?

C26 C27 H27A 119.1 . . ?

C27 C28 C29 120.9(6) . . ?

C27 C28 H28A 119.6 . . ?

C29 C28 H28A 119.6 . . ?

C30 C29 C28 117.2(6) . . ?

C30 C29 H29A 121.4 . . ?

C28 C29 H29A 121.4 . . ?

C25 C30 C29 123.1(5) . . ?

C25 C30 N3 108.1(4) . . ?

C29 C30 N3 128.8(5) . . ?

N3 C31 H31A 109.5 . . ?

N3 C31 H31B 109.5 . . ?

H31A C31 H31B 109.5 . . ?

N3 C31 H31C 109.5 . . ?

H31A C31 H31C 109.5 . . ?

H31B C31 H31C 109.5 . . ?

_diffrn_measured_fraction_theta_max 0.995

_diffrn_reflns_theta_full 25.00

_diffrn_measured_fraction_theta_full 0.995

_refine_diff_density_max 0.403

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_refine_diff_density_rms 0.061

4. Biological Assay Procedures and Results

4.1 Cytotoxicity assay

The assay was in five kinds of cell lines (HL-60, SMMC-7721, A549, MCF-7 and SW480). Cells were cultured at 37 ^{o}C under a humidified atmosphere of 5% CO_2 in RPMI 1640 medium supplemented with 10% fetal serum and dispersed in replicate 96-well plates. Compounds were then added. After 48 h exposure to the compounds, cells viability were determined by the [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-tetrazoliumbromide] (MTT) cytotoxicity assay by measuring the absorbance at 570 nm with a microplate spectrophotometer. Each test was performed in triplicate.

4.2 Cytotoxic activities of hybrid compounds8–21 invitro[b] (IC_{50}, μM[a])

Compound	HL-60	SMMC-7721	A-549	MCF-7	SW480
DDP	1	6.33	7.25	15.93	13.57
8	0.69	5.45	3	6.33	11.71
9			—		
10	2.2	8.42	15.48	10.45	18.48
11			—		
12	0.73	2.45	8.37	3.37	9.29
13	0.7	1.98	2.93	2.96	4.54
14	0.39	1.1	1.21	3.96	2.54
15	0.47	1.1	1.4	1.91	2.23
16	2.03	10.26	16.95	23.76	15.64
17	1.48	5.8	8.41	3.76	4.47
18	0.67	2.13	2.85	4.47	2.85
19	0.24	1.09	0.77	2.03	4.95
20	0.29	1.29	0.96	1.68	1.86
21	0.4	0.87	1.02	1.92	2.04
22	1.86	4.46	10.64	8.04	5.49
23	0.69	3.01	8.25	1.95	4.19
24	0.43	1.03	2.78	2.17	1.71
25	0.24	1.09	0.98	1.13	1.18
26	0.41	0.75	0.64	2.06	2.02
27	0.6	1.27	0.89	1.38	2.04
28	0.69	1.21	1.21	1.2	2.34
29	0.64	2.45	3.74	2.36	3.84
30	0.94	2.44	4.28	2.42	2.74
31	0.38	1.88	1.67	2.5	3.46
32	0.47	1.11	1.82	1.83	2.33

[a] Cytotoxicity as IC_{50} for each cell line, is the concentration of compound which reduced by 50% the optical density of treated cells with respect to untreated cells using the MTT assay.

[b] Data represent the mean values of three independent determinations.

5. Cell apoptosis and cell cycle analysis

5.1 Cell apoptosis analysis

Cell apoptosis was analyzed using the Annexin V-FITC/PI Apoptosis kit (BD Biosciences, Franklin Lakes, NJ) according to the manufacturer's protocols. Cells were seeded in 6-well plates at a density of 1.2×10^6 cells/well. After 48 h of compound treatment at the indicated concentrations, cells were collected and then washed twice with cold PBS, and then resuspended in a binding buffer containing Annexin V-FITC and propidium iodine (PI). After incubation for 15 min at room temperature in the dark, the fluorescent intensity was measured using a FACSCalibur flow cytometer (BD Biosciences, Franklin Lakes, NJ).

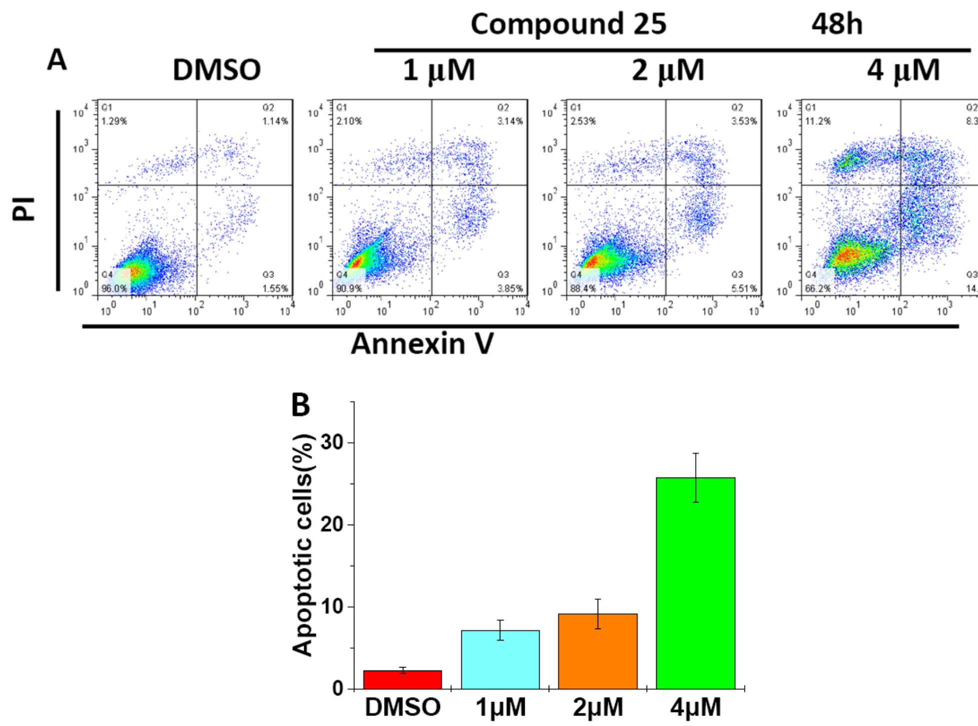
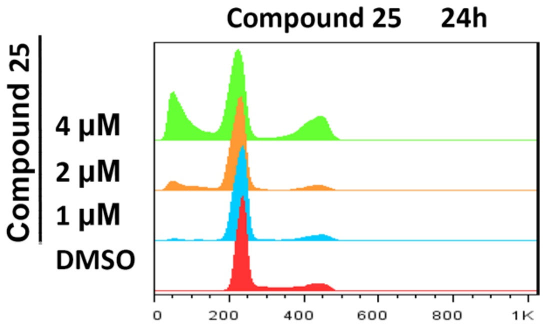


Fig. 1 Compound **25** caused significant apoptosis of SMMC-7721 cells. (A) Cells were treated with 4, 8 and 16 μM compound **25** for 48 h. Cell apoptosis was determined by Annexin V-FITC/PI double-staining assay. (B) The quantification of cell apoptosis. Data represents the mean ± S.D. of three independent experiments.

5.2 Cell cycle analysis

To analyze the DNA content by flow cytometry, cells were collected and washed twice with PBS. Cells were fixed with 70% ethanol overnight. Fixed cells were washed with PBS, and then stained with a 50 μg/ml propidium iodide (PI) solution containing 50 μg/ml RNase A for 30 min at room temperature. Fluorescence intensity was analyzed by FACSCalibur flow cytometer (BD Biosciences, San Jose, CA, USA). The percentages of the cells distributed in different phases of the cell cycle were determined using ModFIT LT 2.0.

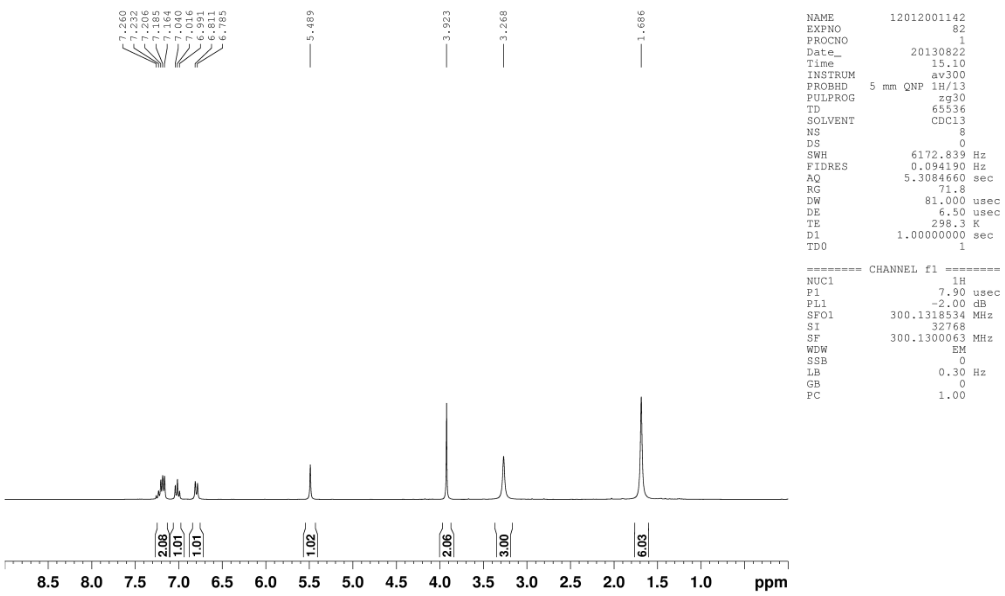


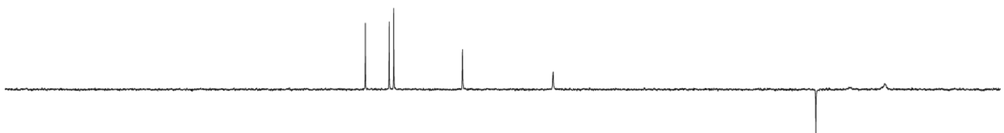
Treatment	Cells (%)		
	G0/G1	S	G2/M
DMSO	72.56±3.29	14.32±3.68	15.21±2.57
Compound **25** (1 μM)	76.21±1.35	2.32±0.24	8.43±0.85
Compound **25** (2 μM)	82.59±3.75	1.64±0.19	7.98±1.24
Compound **25** (4 μM)	60.15±4.29	1.18±0.31	11.08±1.23

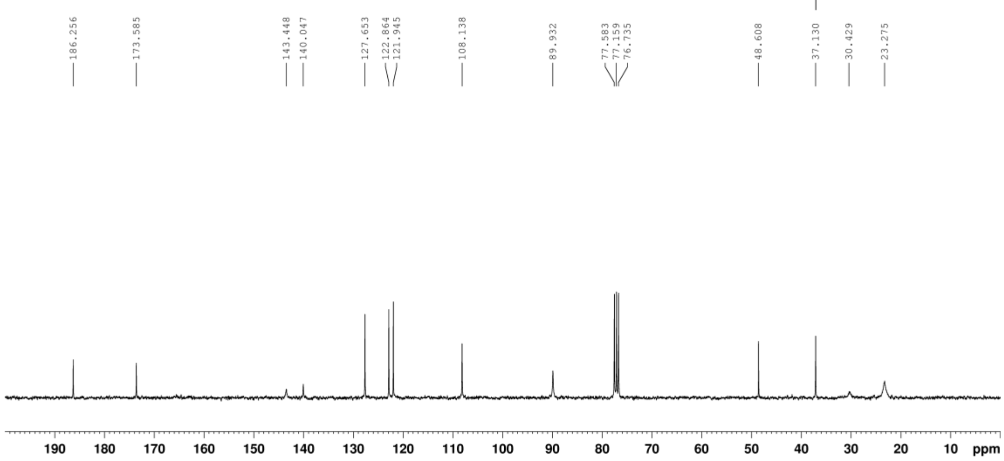
Fig. 2 Compound **25** induces S phase arrest in SMMC-7721 cells. (A) Cells were treated with 1, 2 and 4 μM of compound **25** for 24 h. Cell cycle was determined by PI staining and cell cytometry. (B) The percentages of cells in different phases were quantified. At least three independent experiments were performed and data of one representative experiment is shown.

6. ^{1}H-NMR and ^{13}C-NMR Spectral of New Compounds

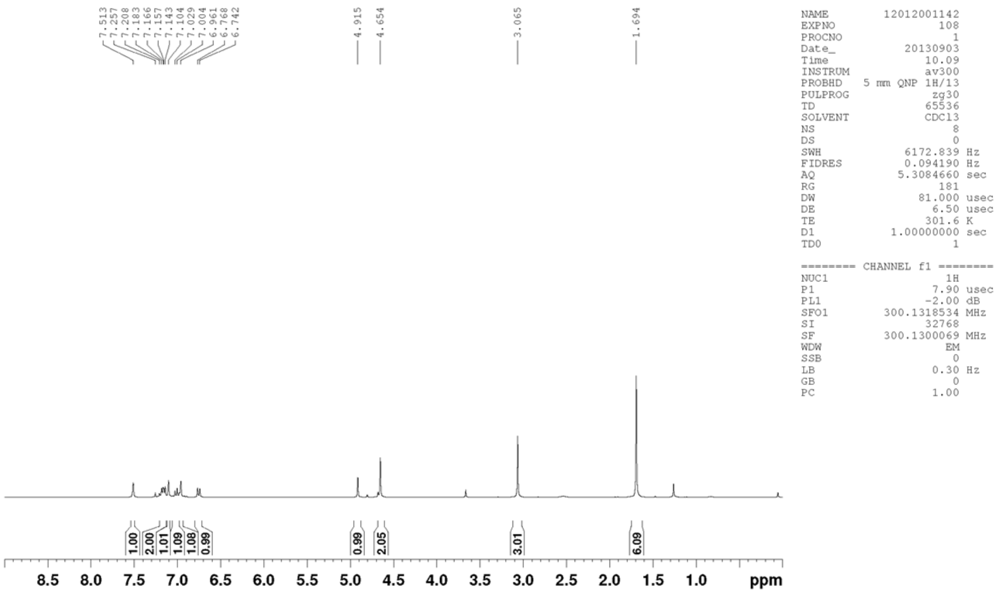
Compounds **3**

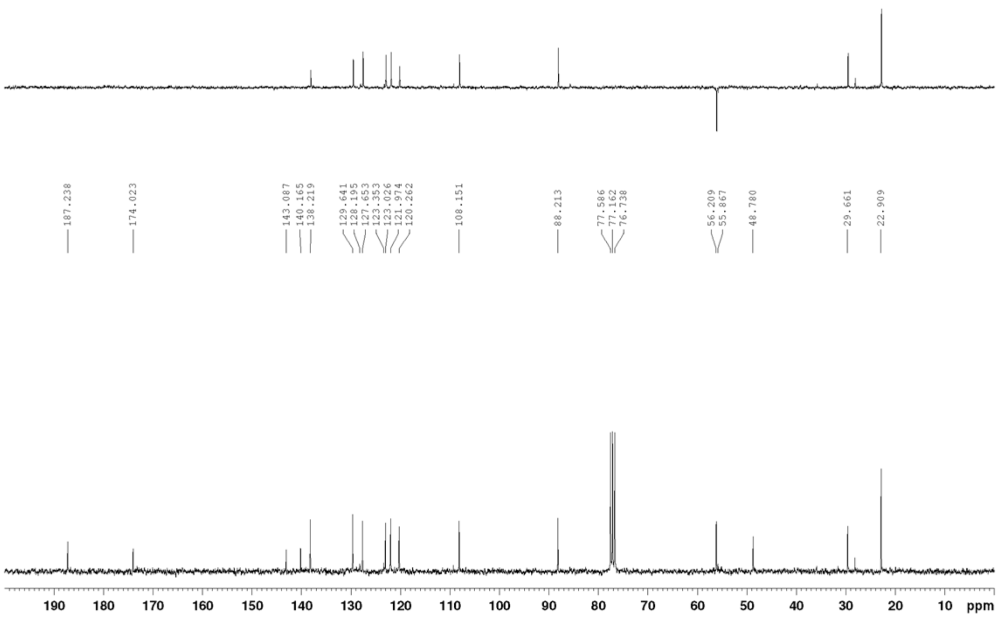

7.260
7.232
7.206
7.185
7.164
7.040
7.016
6.991
6.811
6.785
5.489
3.923
3.268
1.686
NAME 12012001142
EXPNO 82
PROCNO 1
Date_ 20130822
Time 15.10
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 71.8
DW 81.000 usec
DE 6.50 usec
TE 298.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300063 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.08
1.01
1.01
1.02
2.06
3.00
6.03
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
ppm



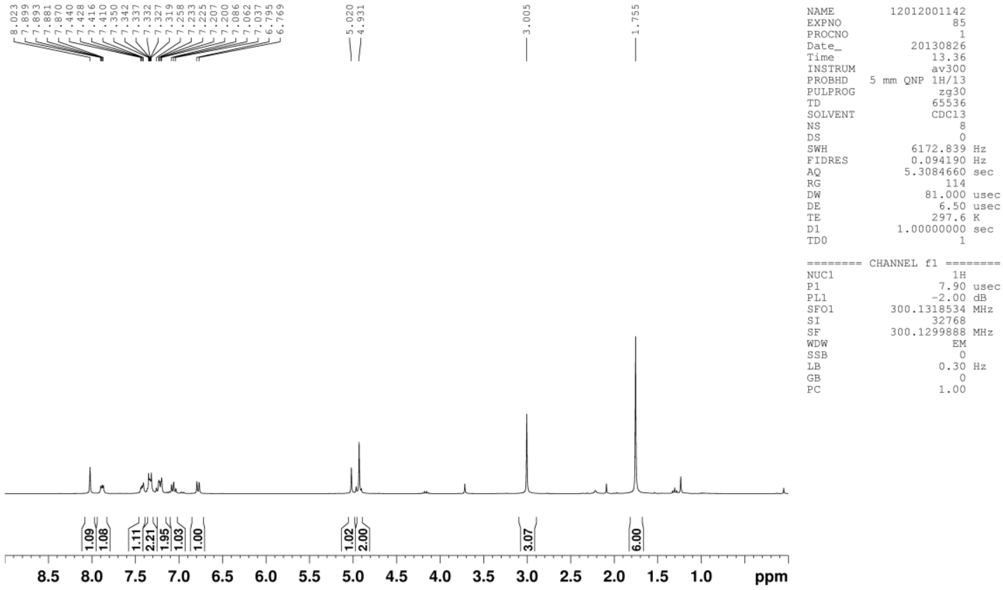

186.256
173.585
143.448
140.047
127.653
122.864
121.945
108.138
89.932
77.583
77.159
76.735
48.608
37.130
30.429
23.275
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

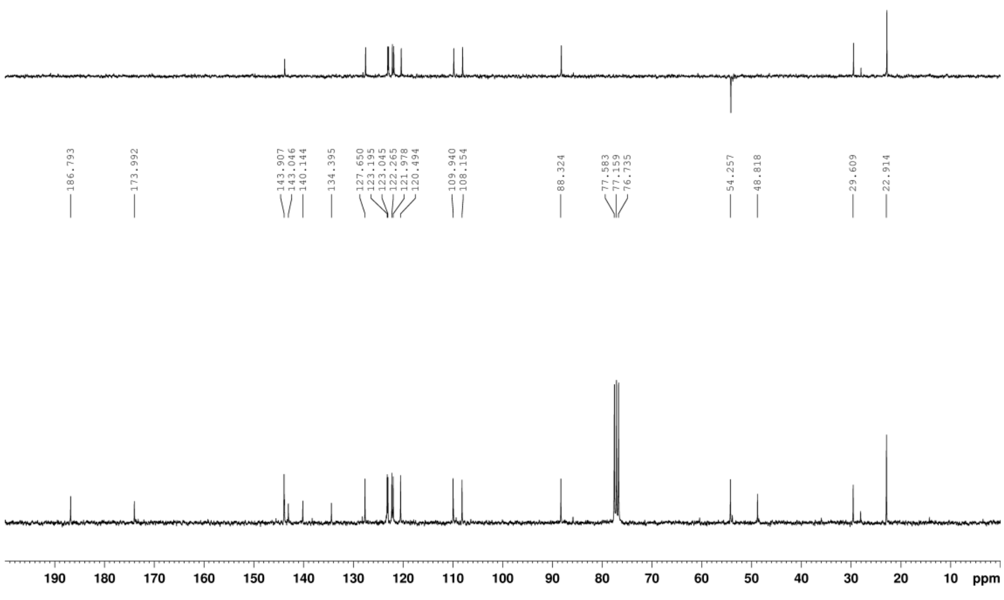
Compound **4**



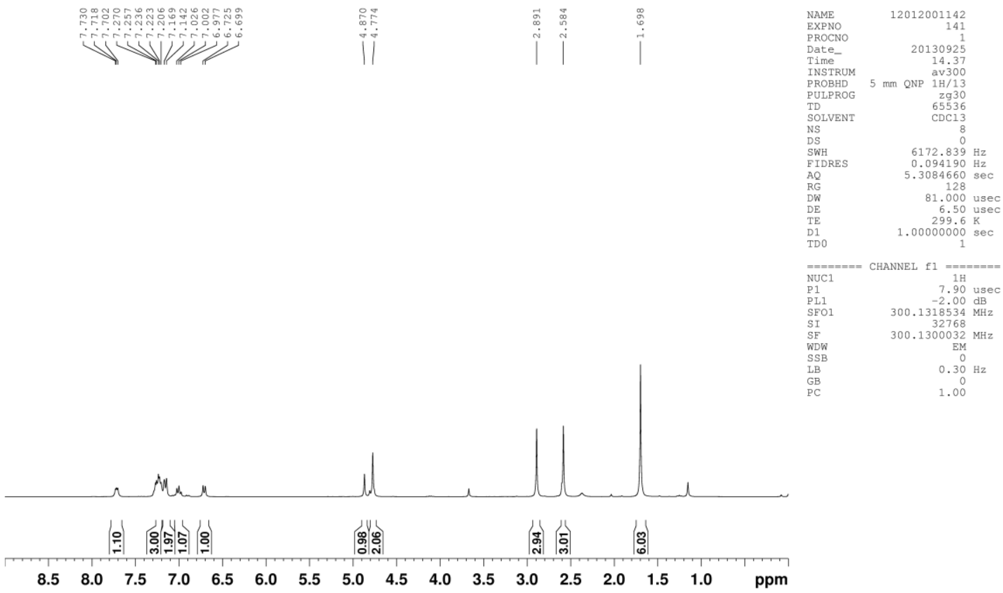


Compound **5**





Compound **6**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7.702
7.270
7.257
7.236
7.223
7.206
7.169
7.142
7.026
7.002
6.977
6.725
6.699
4.870
4.774
2.891
2.584
1.698
1.10
3.00
1.97
1.07
1.00
0.98
2.06
2.94
3.01
6.03
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 ppm
NAME 12012001142
EXPNO 141
PROCNO 1
Date_ 20130925
Time 14.37
INSTRUM av300
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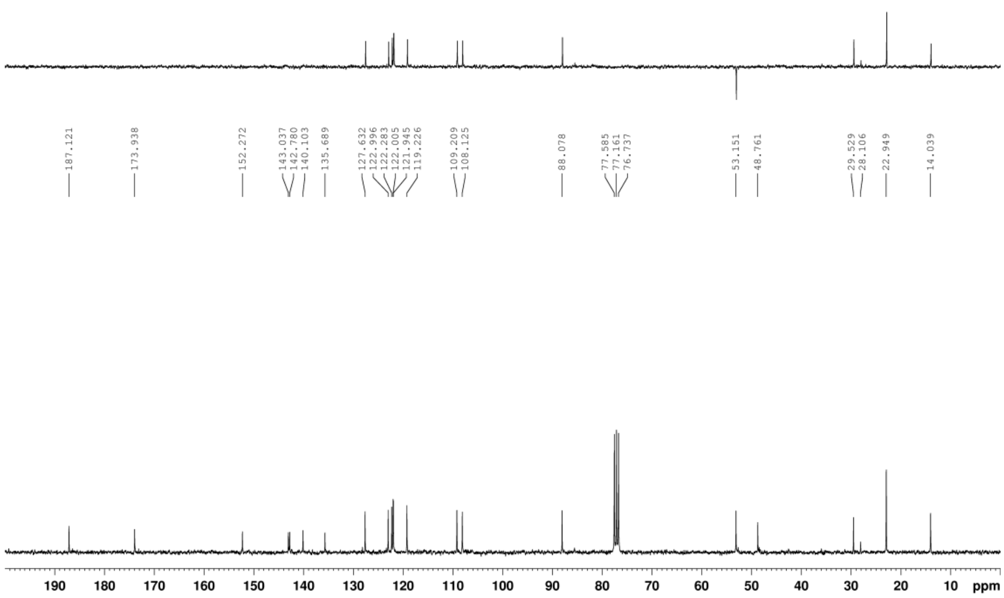
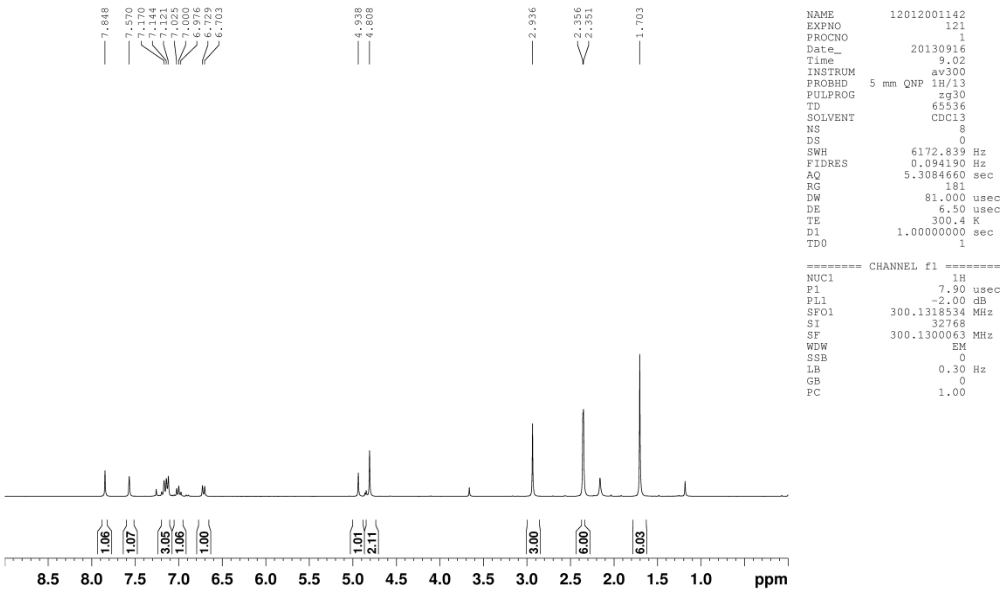
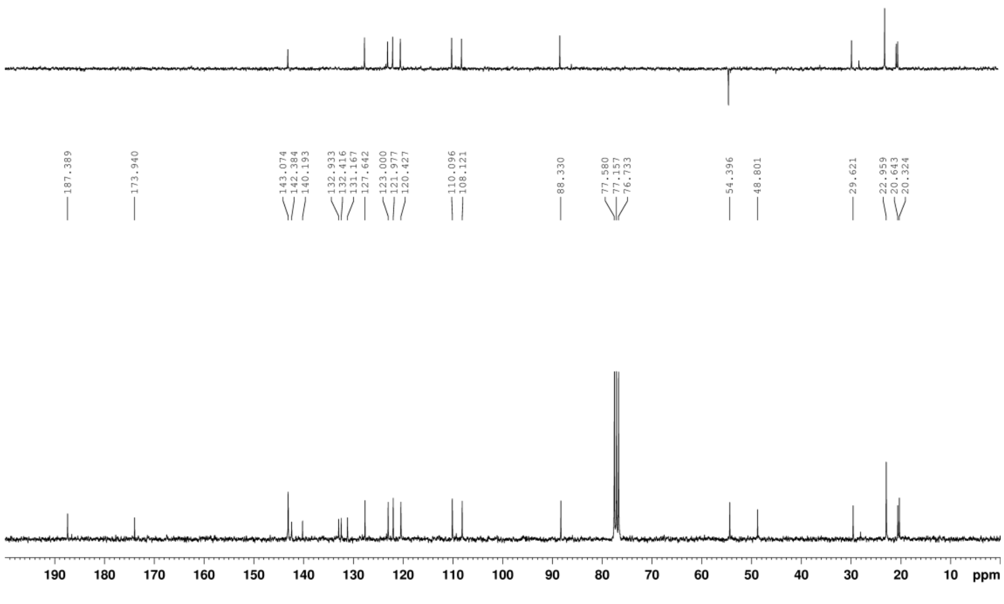
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 128
DW 81.000 usec
DE 6.50 usec
TE 299.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


187.121
173.938
152.272
143.037
142.780
140.103
135.689
127.632
122.996
122.283
122.005
121.945
119.226
109.209
108.125
88.078
77.585
77.161
76.737
53.151
48.761
29.529
28.106
22.949
14.039
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Compound **7**


7.848
7.570
7.170
7.144
7.121
7.025
7.000
6.976
6.729
6.703
4.938
4.808
2.936
2.356
2.351
1.703
NAME 12012001142
EXPNO 121
PROCNO 1
Date_ 20130916
Time 9.02
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 181
DW 81.000 usec
DE 6.50 usec
TE 300.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300063 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.06
1.07
3.05
1.06
1.00
1.01
2.11
3.00
6.00
6.03
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 ppm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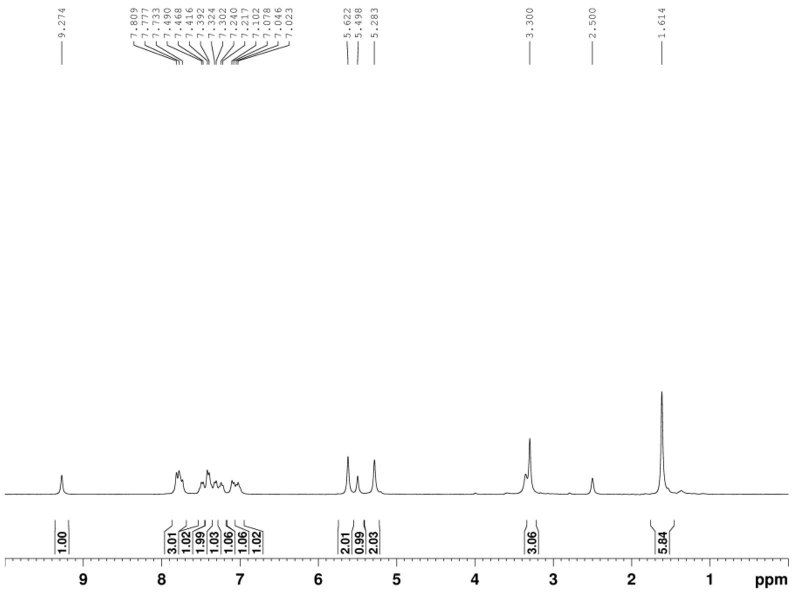
142.384
140.193
132.933
132.416
131.167
127.642
123.000
121.977
120.427
110.096
108.121
88.330
77.580
77.157
76.733
54.396
48.801
29.621
22.959
20.643
20.324
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Compound **8**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PROCNO 1
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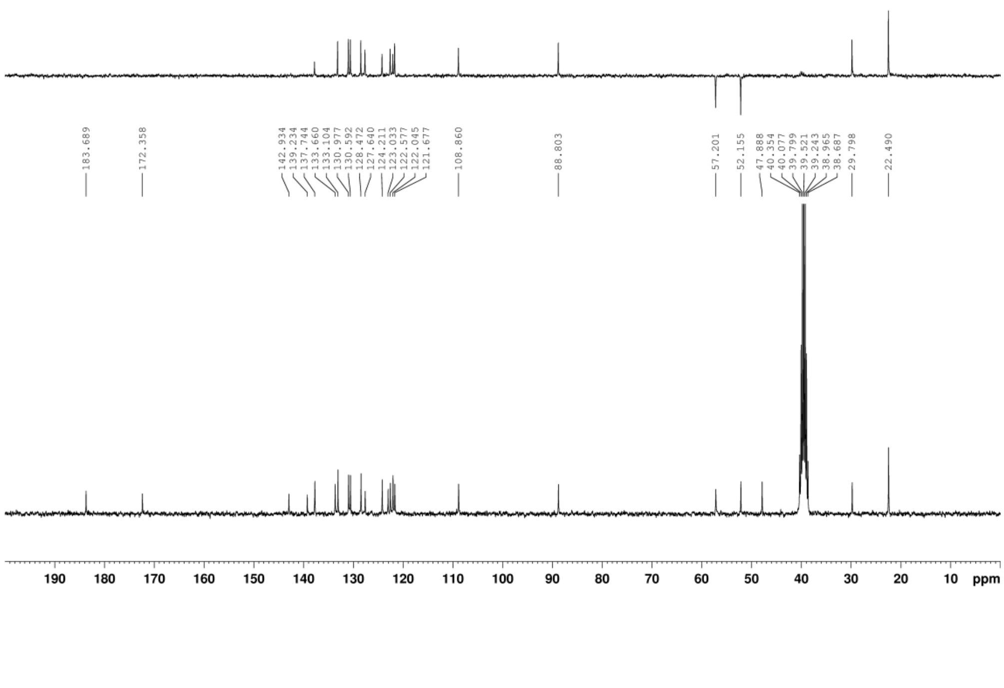
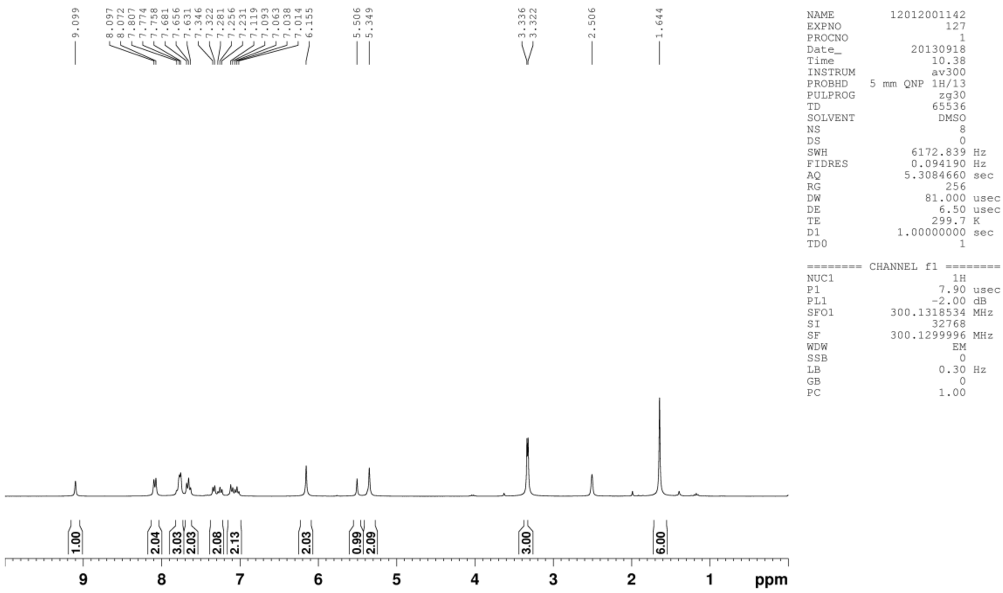
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 181
DW 81.000 usec
DE 6.50 usec
TE 299.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300017 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm


ppm

Compound **9**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8.072
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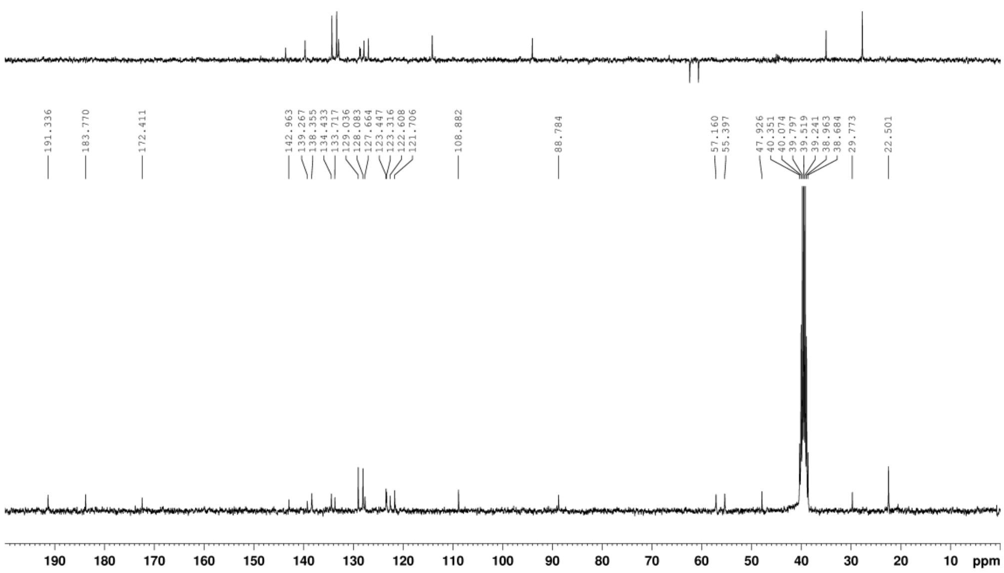
7.774
7.758
7.681
7.656
7.631
7.346
7.322
7.281
7.256
7.231
7.119
7.093
7.063
7.038
7.014
6.155
5.506
5.349
3.336
3.322
2.506
1.644
1.00
2.04
3.03
2.03
2.08
2.13
2.03
0.99
2.09
3.00
6.00
9 8 7 6 5 4 3 2 1 ppm
NAME 12012001142
EXPNO 127
PROCNO 1
Date_ 20130918
Time 10.38
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 256
DW 81.000 usec
DE 6.50 usec
TE 299.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1299996 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00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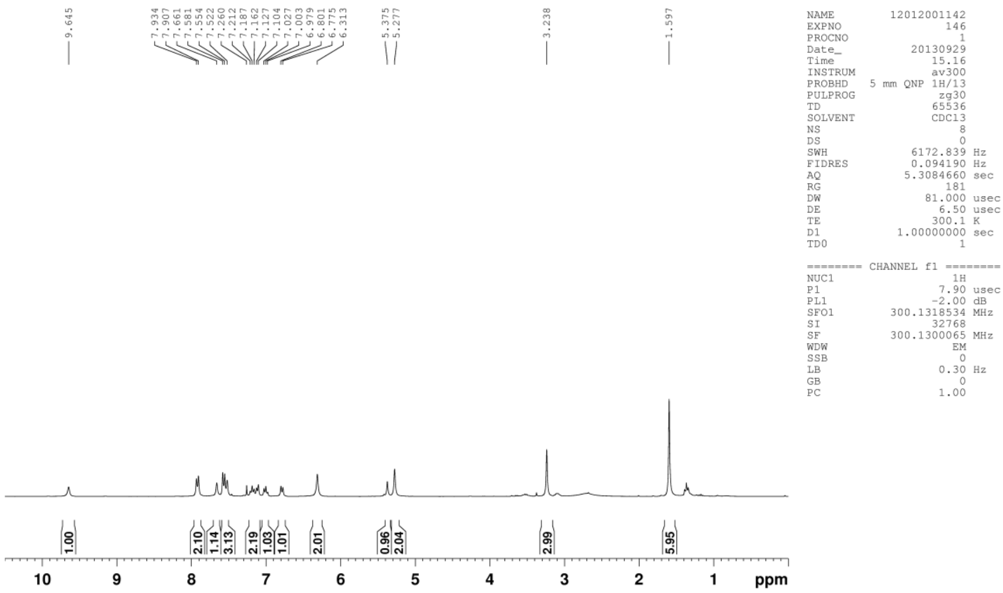
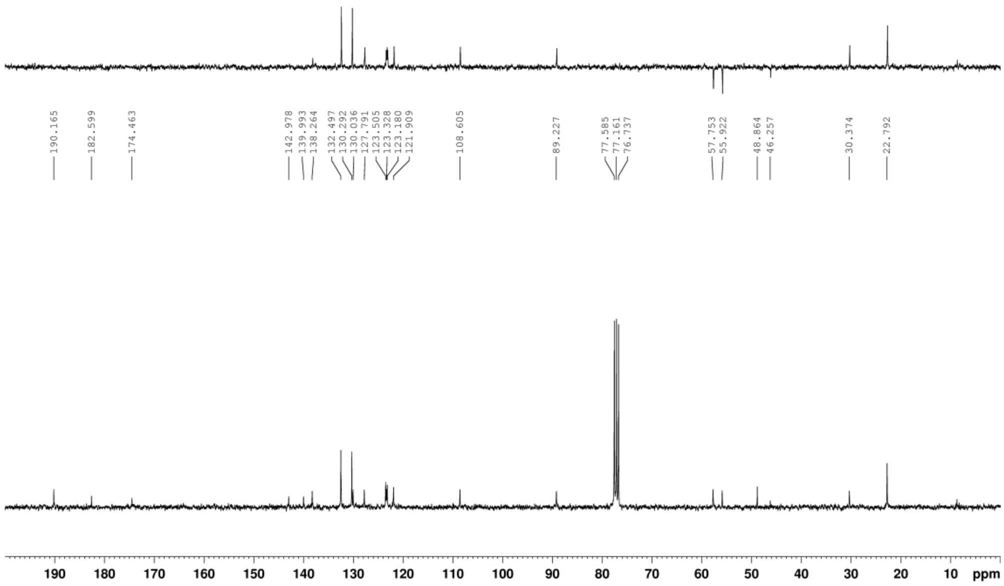
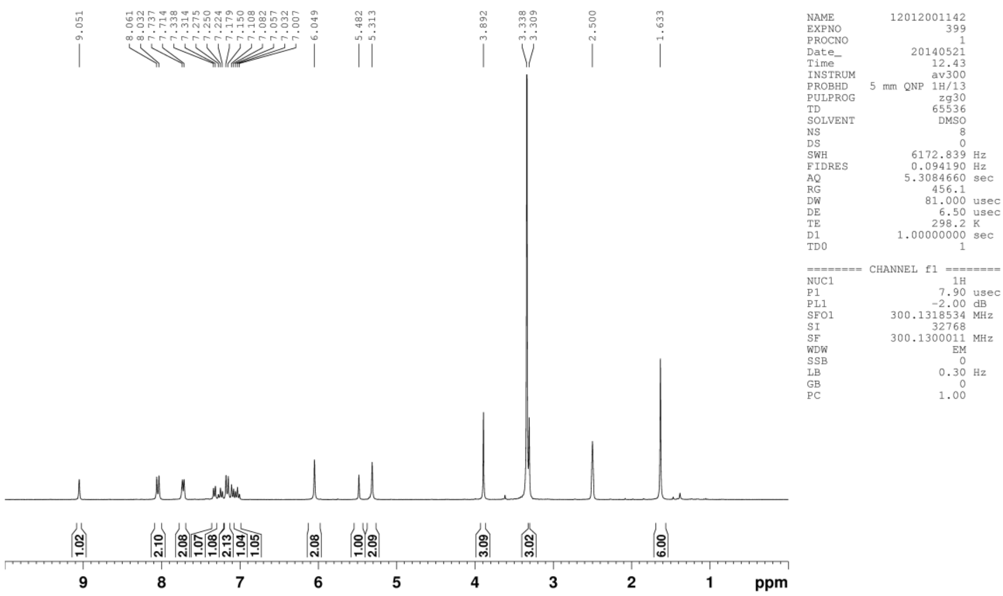
142.963
139.267
138.355
134.433
133.717
129.036
128.083
127.664
123.447
123.316
122.608
121.706
108.882
88.784
57.160
55.397
47.926
40.351
40.074
39.797
39.519
39.241
38.963
38.684
29.773
22.501
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

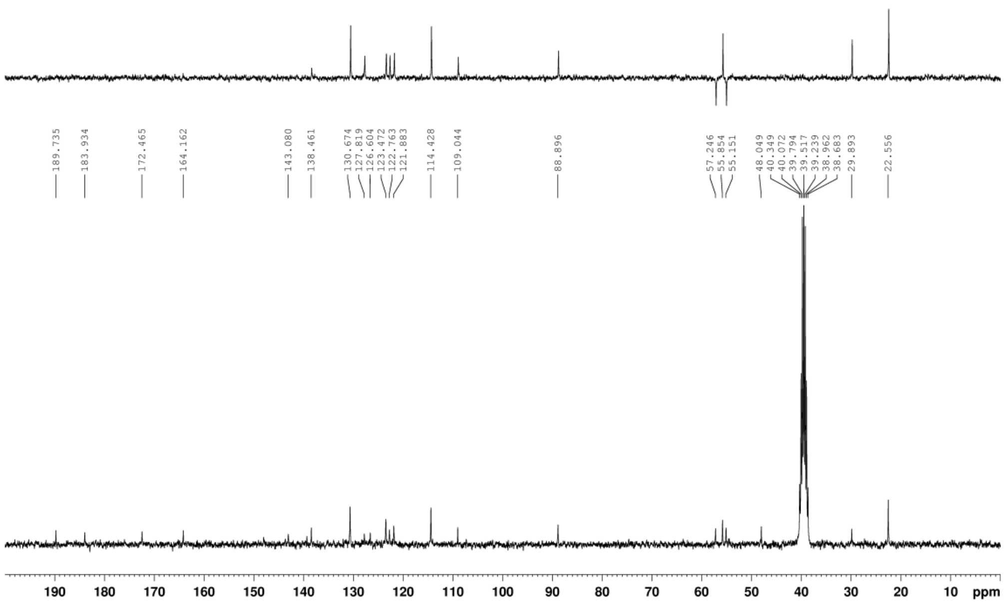
Compound **10**


9.645
7.934 7.907 7.661 7.581 7.554 7.522 7.260 7.212 7.187 7.162 7.127 7.104 7.027 7.003 6.979 6.801 6.775 6.313
5.375 5.277
3.238
1.597
1.00 2.10 1.14 3.13 2.19 1.03 1.01 2.01 0.96 2.04 2.99 5.95
10 9 8 7 6 5 4 3 2 1 ppm
NAME 12012001142
EXPNO 146
PROCNO 1
Date_ 20130929
Time 15.16
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 181
DW 81.000 usec
DE 6.50 usec
TE 300.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300065 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

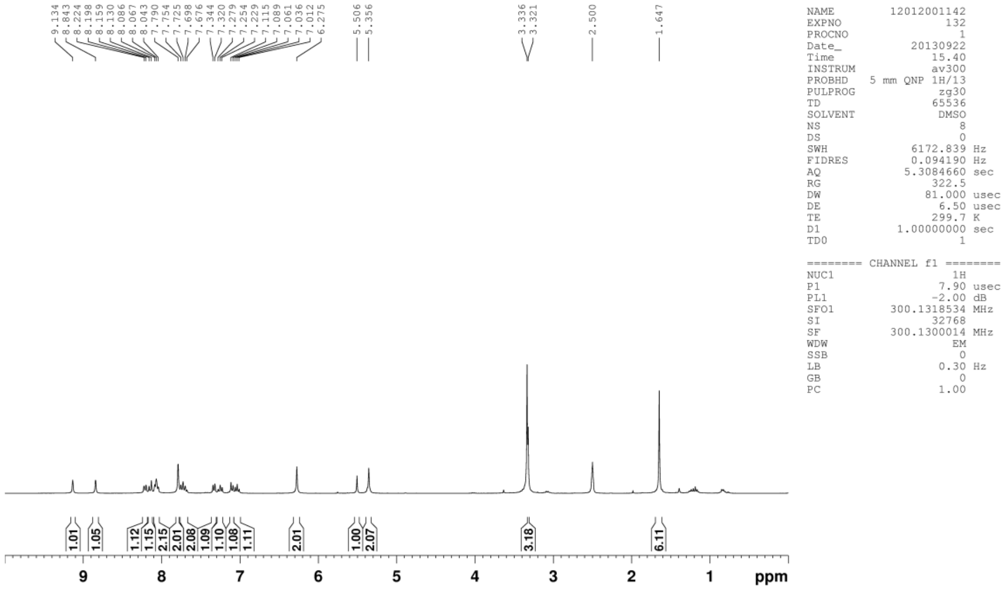

190.165
182.599
174.463
142.978 139.993 138.264
132.497 130.292 130.036 127.791 123.505 123.328 123.180 121.909
108.605
89.227
77.585 77.161 76.737
57.753 55.922
48.864 46.257
30.374
22.792
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

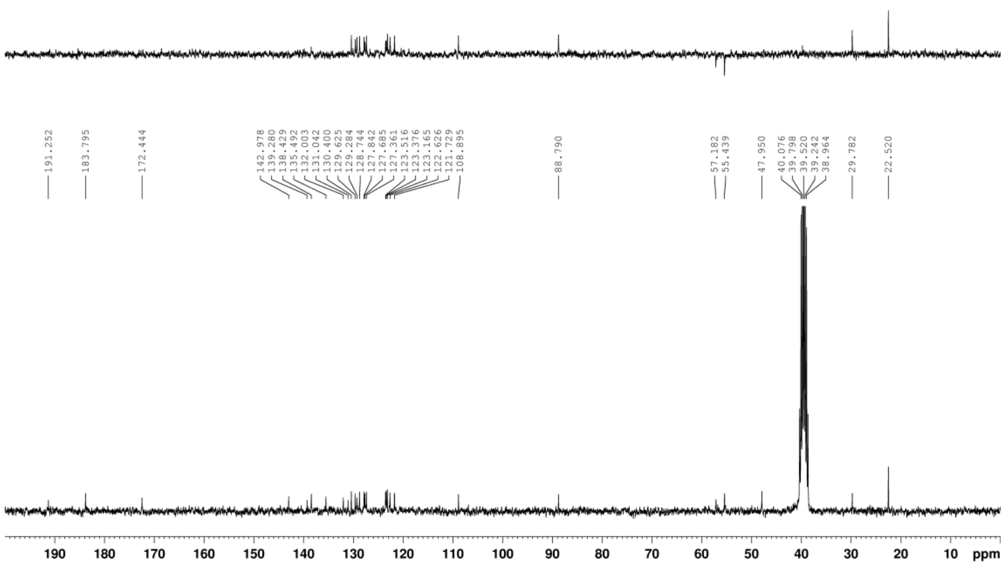
Compound **11**



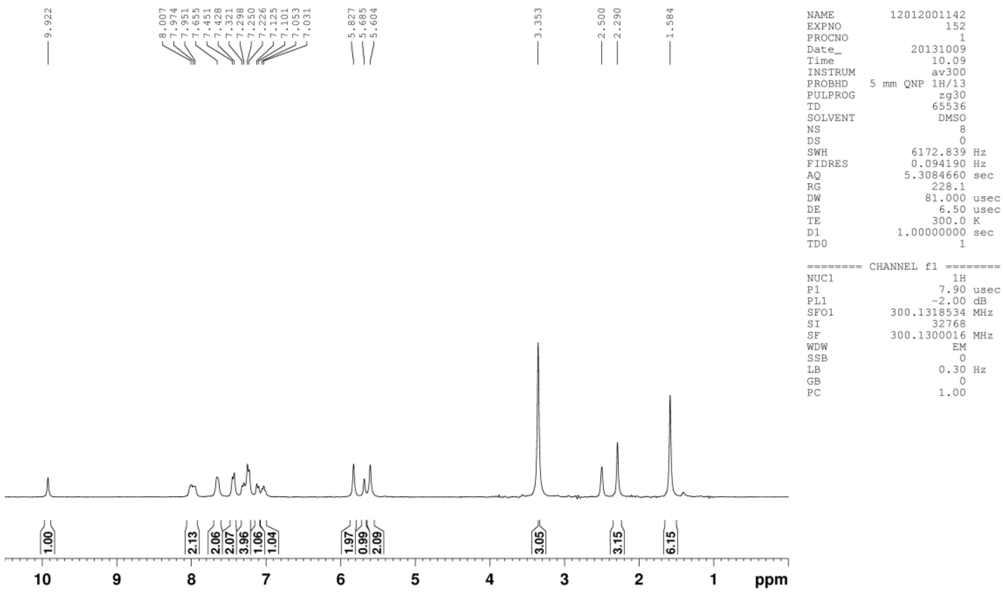


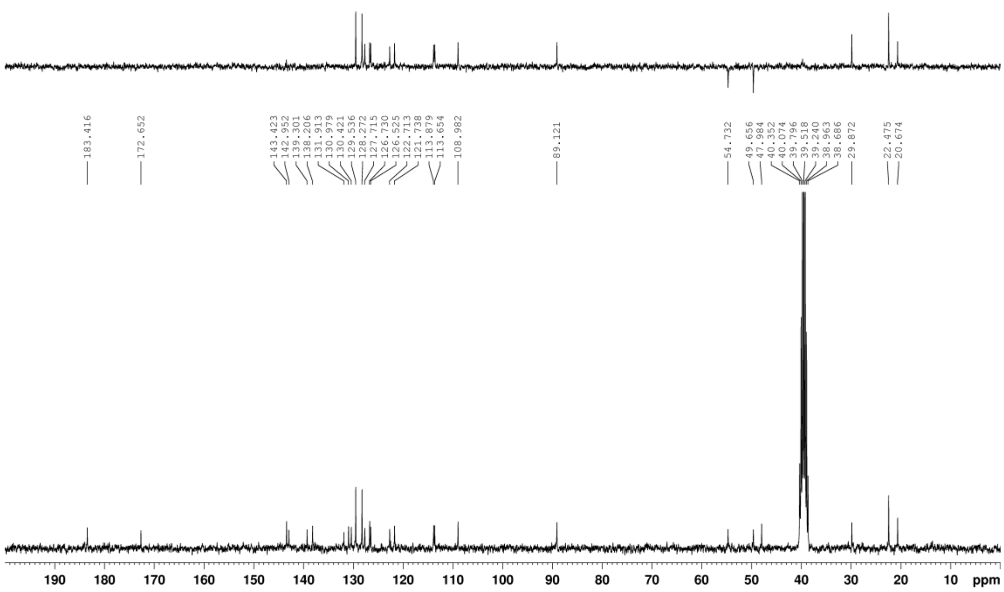
Compound **12**



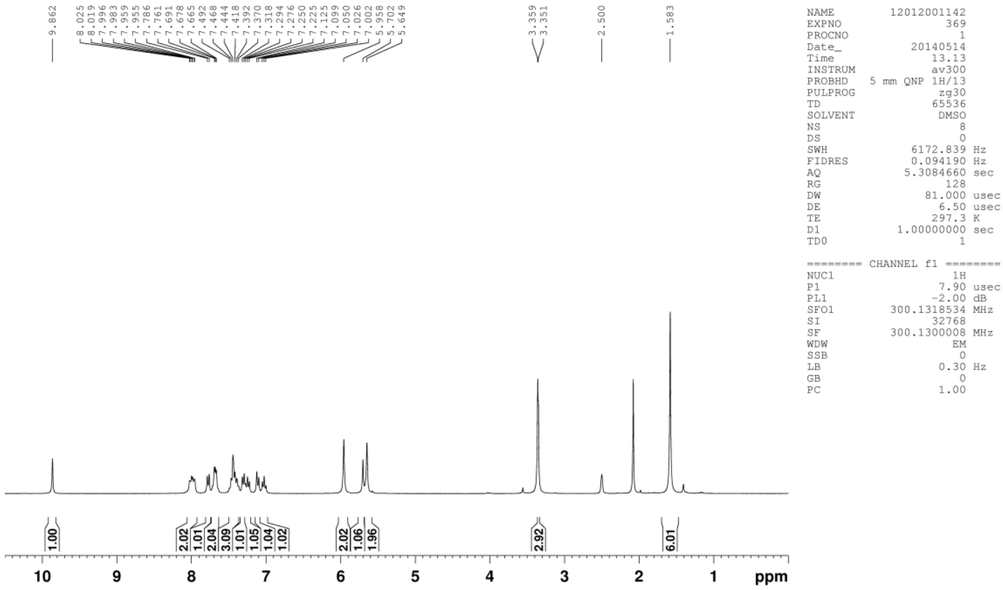


Compound **13**





Compound **14**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PROCNO 1
Date_ 20140514
Time 13.13
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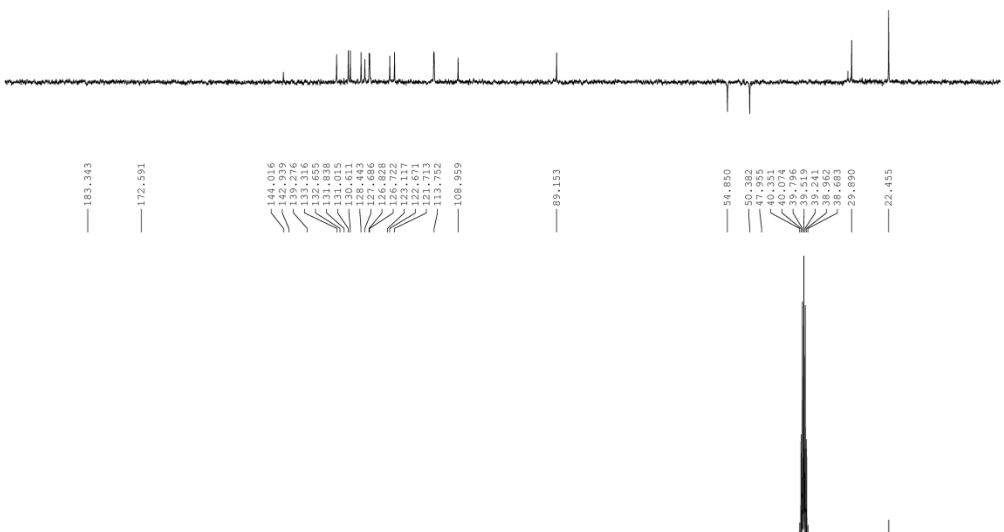
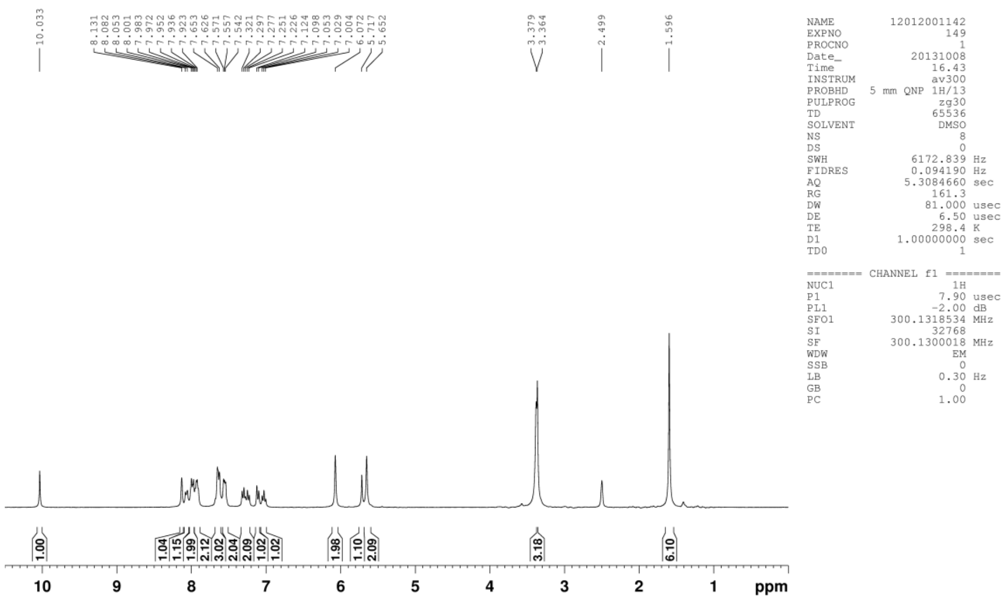
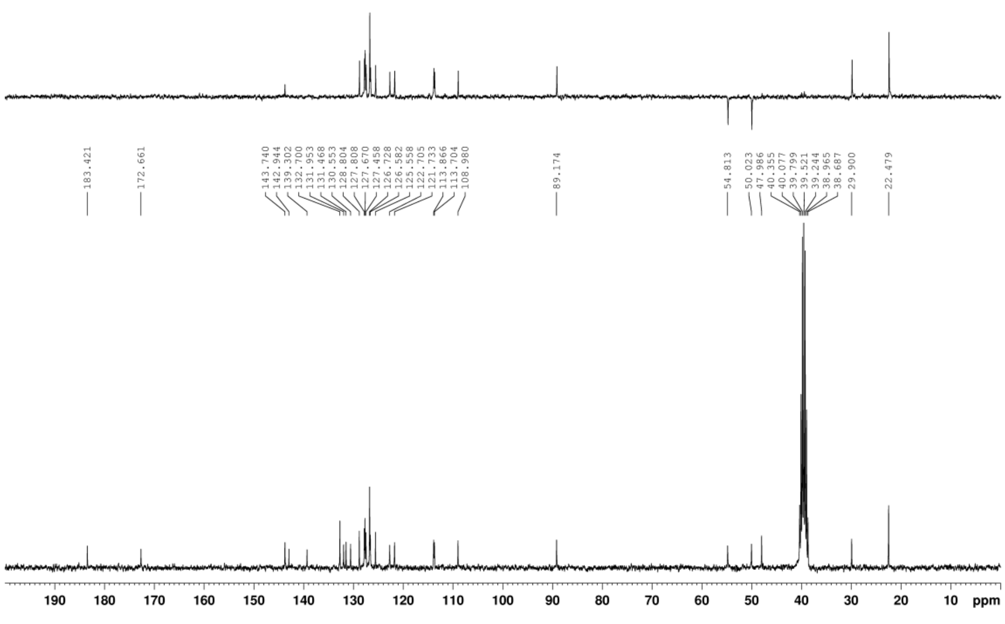
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 128
DW 81.000 usec
DE 6.50 usec
TE 297.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300008 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm

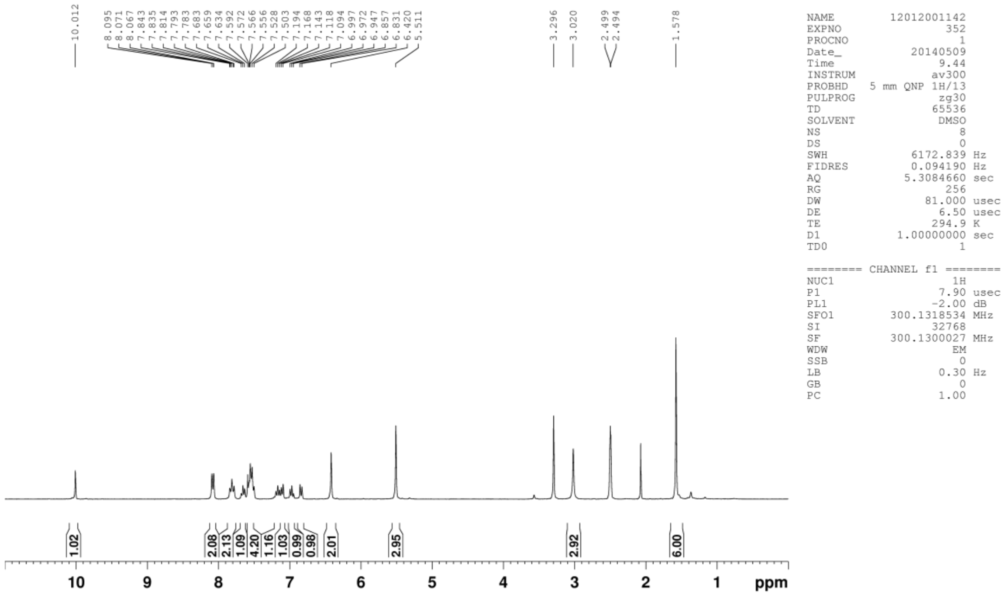

ppm

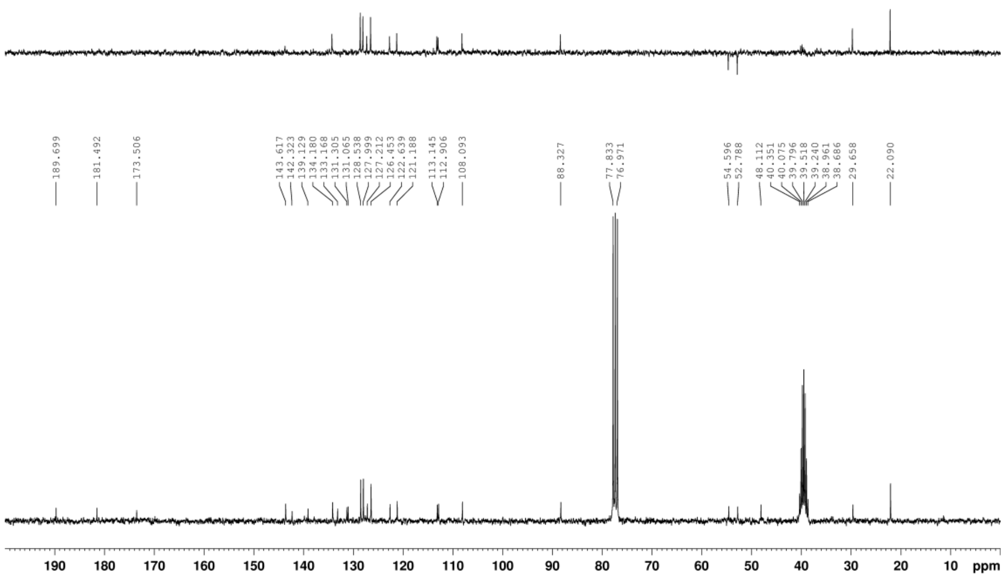
Compound **15**



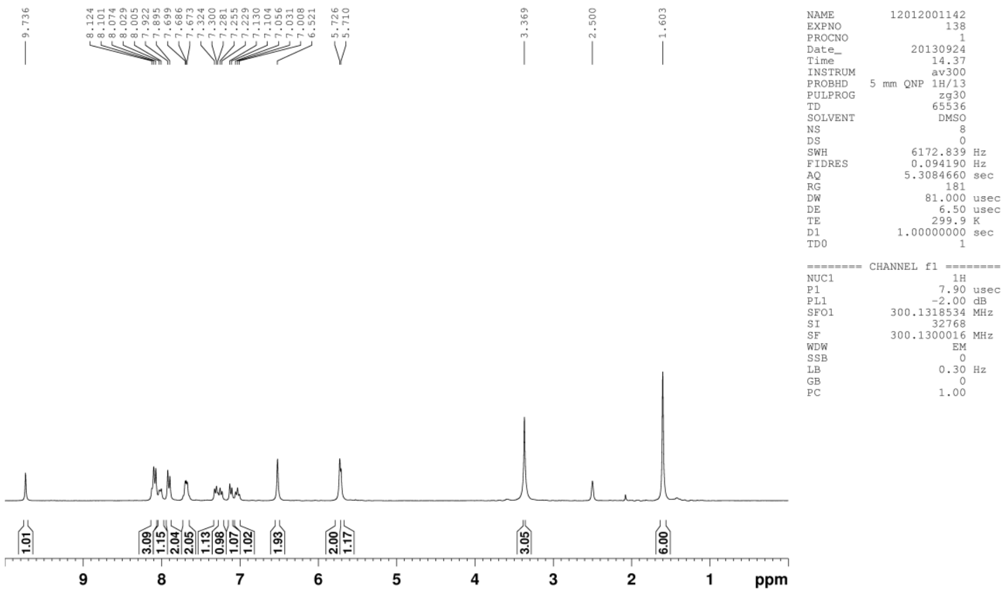


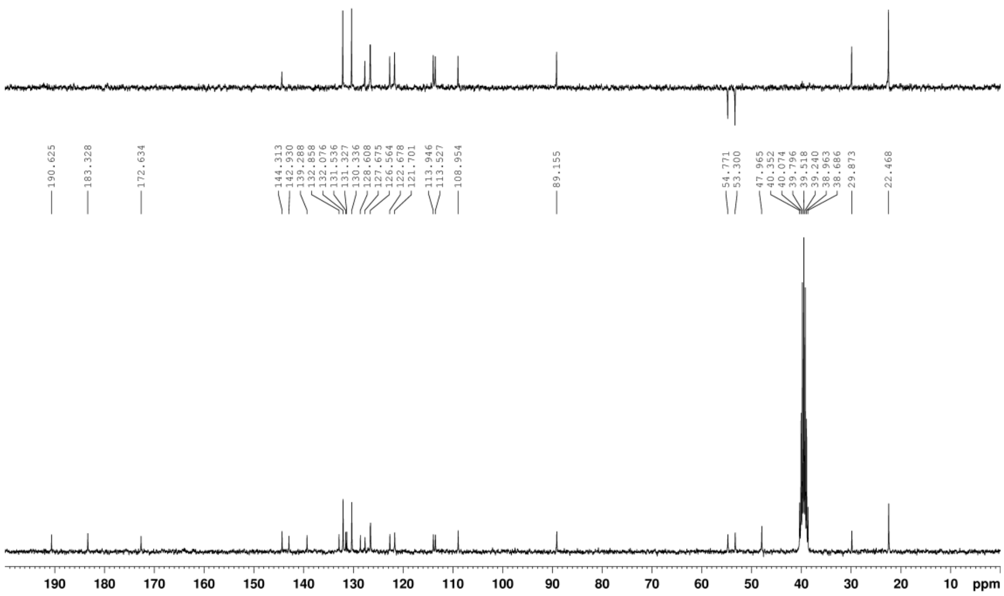
Compound **16**


10.012
8.095 8.071 8.067 7.843 7.835 7.814 7.793 7.783 7.683 7.659 7.634 7.592 7.572 7.566 7.556 7.528 7.503 7.194 7.168 7.143 7.118 7.094 6.997 6.972 6.947 6.857 6.831 6.420 5.511
3.296
3.020
2.499 2.494
1.578
NAME 12012001142
EXPNO 352
PROCNO 1
Date_ 20140509
Time 9.44
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 256
DW 81.000 usec
DE 6.50 usec
TE 294.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300027 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.02 2.08 2.13 1.09 4.20 1.16 1.03 0.99 0.98 2.01 2.95 2.92 6.00
10 9 8 7 6 5 4 3 2 1 ppm

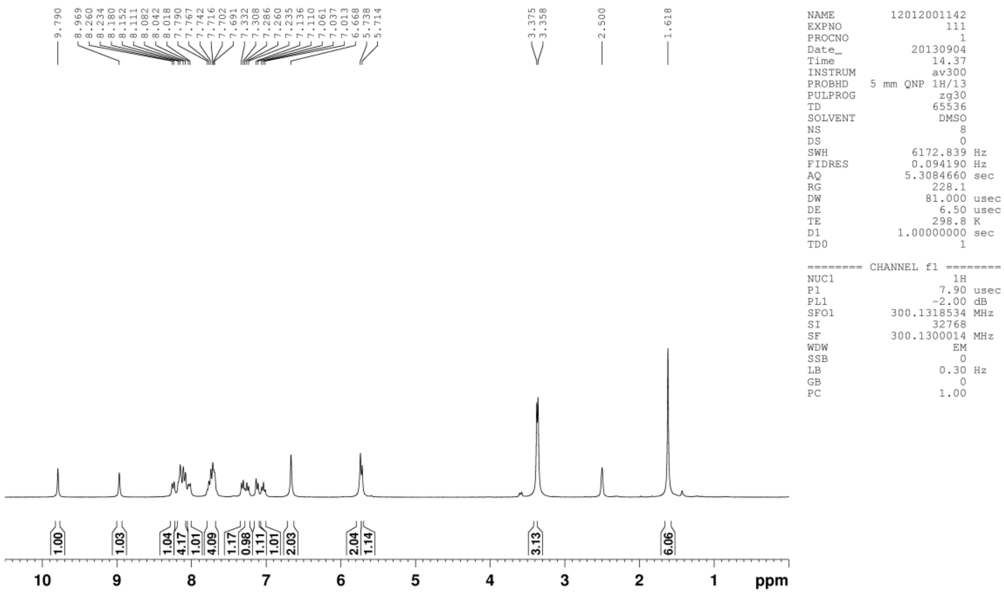

189.699
181.492
173.506
143.617 142.323 139.129 134.180 133.468 131.305 131.065 128.538 127.999 127.212 126.453 122.639 121.188
113.145 112.906
108.093
88.327
77.833 76.971
54.596 52.788
48.112 40.351 40.075 39.796 39.518 39.240 38.961 38.686
29.658
22.090
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

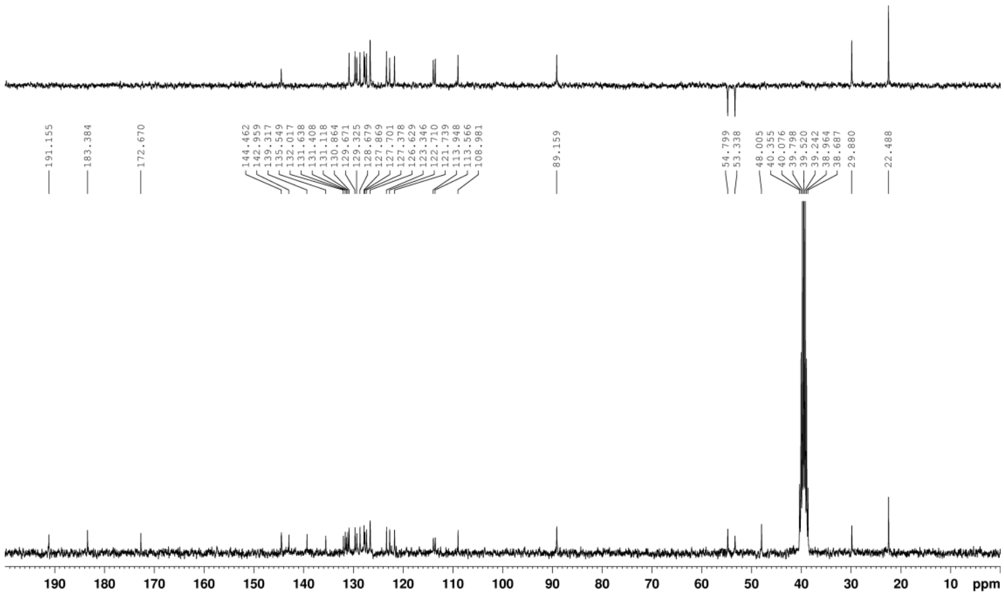
Compound **17**


NAME 12012001142
EXPNO 138
PROCNO 1
Date_ 20130924
Time 14.37
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 181
DW 81.000 usec
DE 6.50 usec
TE 299.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300016 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm

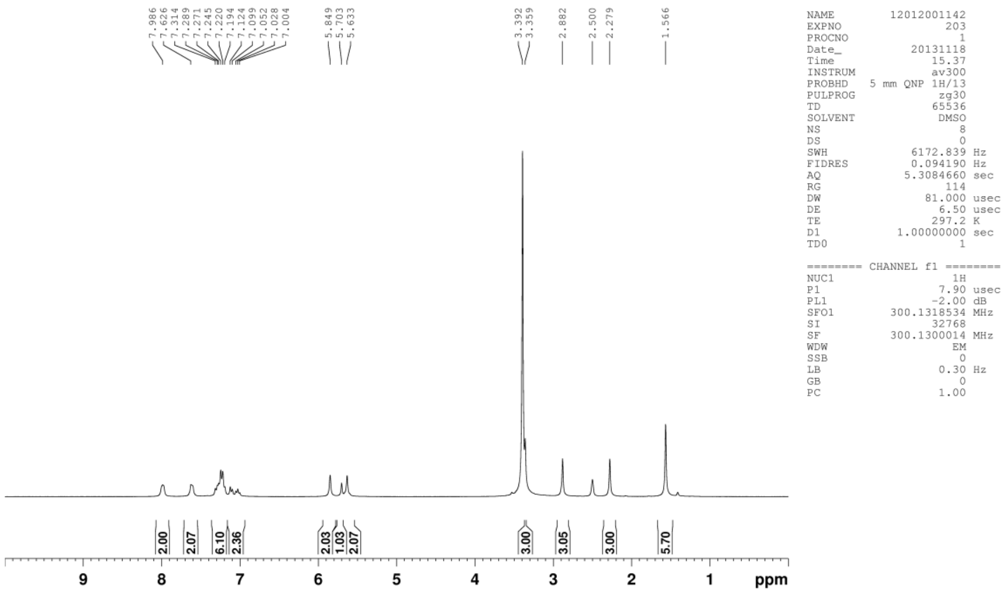

ppm

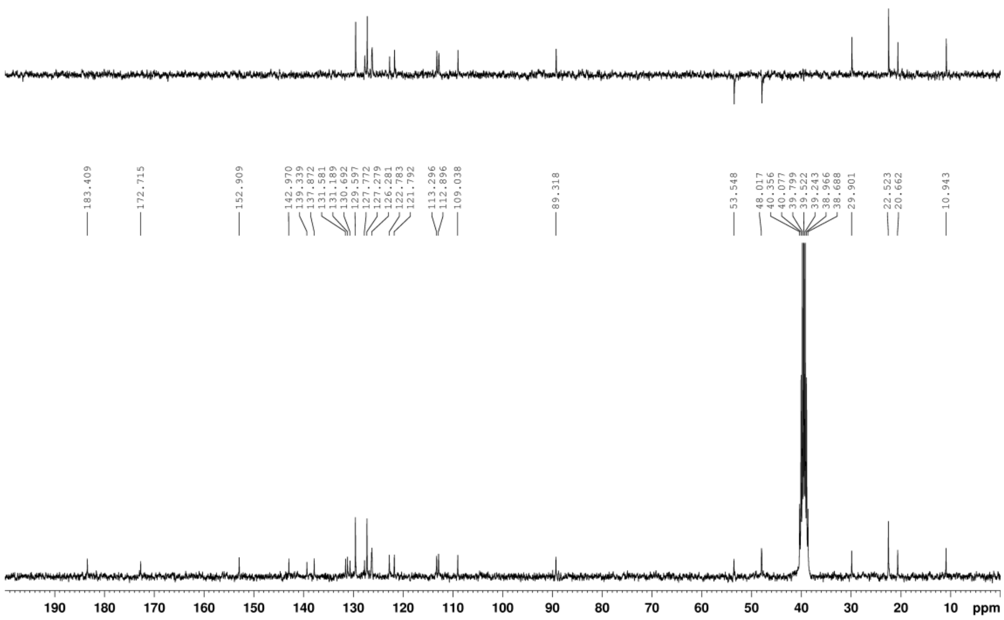
Compound **18**


9.790
8.969
8.260
8.234
8.180
8.152
8.111
8.082
8.042
8.018
7.790
7.767
7.742
7.716
7.702
7.691
7.332
7.308
7.286
7.260
7.235
7.136
7.110
7.061
7.037
7.013
6.668
5.738
5.714
3.375
3.358
2.500
1.618
NAME 12012001142
EXPNO 111
PROCNO 1
Date_ 20130904
Time 14.37
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 228.1
DW 81.000 usec
DE 6.50 usec
TE 298.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300014 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.00
1.03
1.04
4.17
1.01
4.09
1.17
0.98
1.11
1.01
2.03
2.04
1.14
3.13
6.06
10 9 8 7 6 5 4 3 2 1 ppm

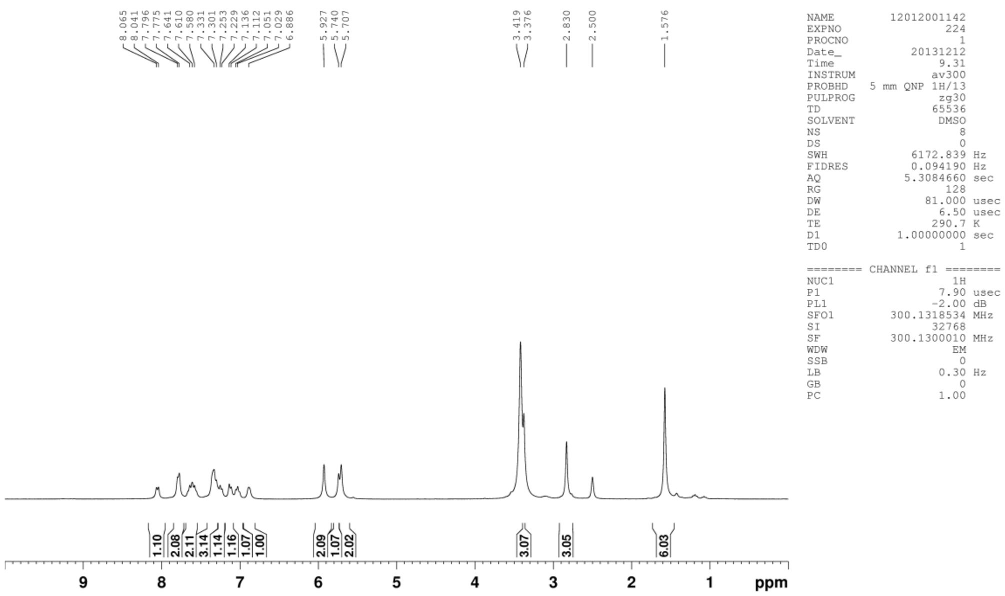

191.155
183.384
172.670
144.462
142.959
139.317
135.549
132.017
131.638
131.408
131.118
130.864
129.671
129.325
128.679
127.869
127.701
127.378
126.629
123.346
122.710
121.739
113.948
113.566
108.981
89.159
54.799
53.338
48.005
40.355
40.076
39.798
39.520
39.242
38.964
38.687
29.880
22.488
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

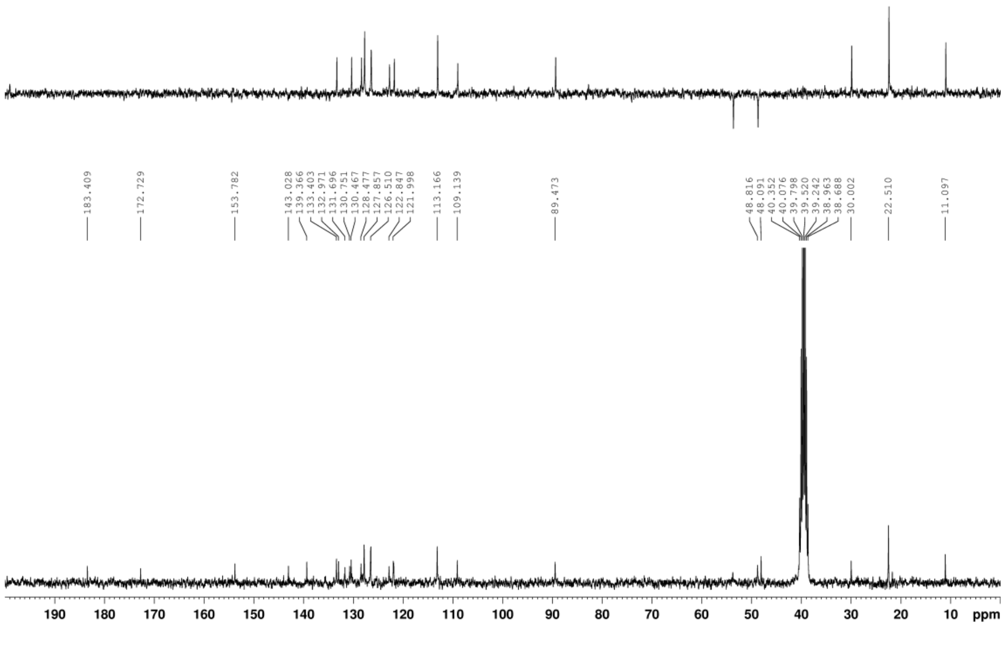
Compound **19**


7.986
7.626
7.314
7.289
7.271
7.245
7.220
7.194
7.124
7.099
7.052
7.028
7.004
5.849
5.703
5.633
3.392
3.359
2.882
2.500
2.279
1.566
NAME 12012001142
EXPNO 203
PROCNO 1
Date_ 20131118
Time 15.37
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 114
DW 81.000 usec
DE 6.50 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300014 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.00
2.07
6.10
2.36
2.03
1.03
2.07
3.00
3.05
3.00
5.70
9
8
7
6
5
4
3
2
1
ppm

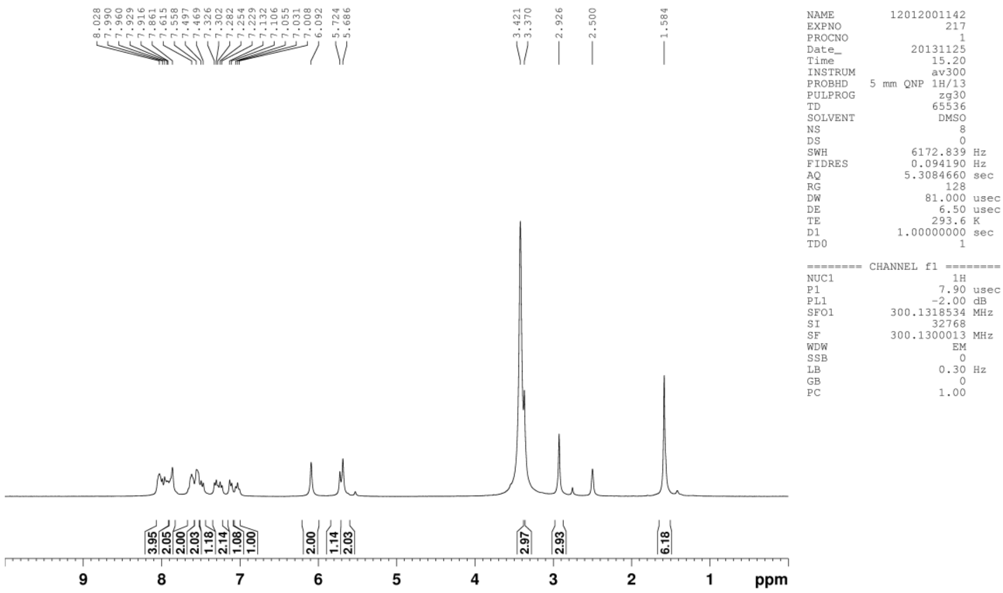

183.409
172.715
152.909
142.970
139.339
137.872
131.581
131.189
130.692
129.597
127.772
127.279
126.281
122.783
121.792
113.296
112.896
109.038
89.318
53.548
48.017
40.356
40.077
39.799
39.522
39.243
38.966
38.688
29.901
22.523
20.662
10.943
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

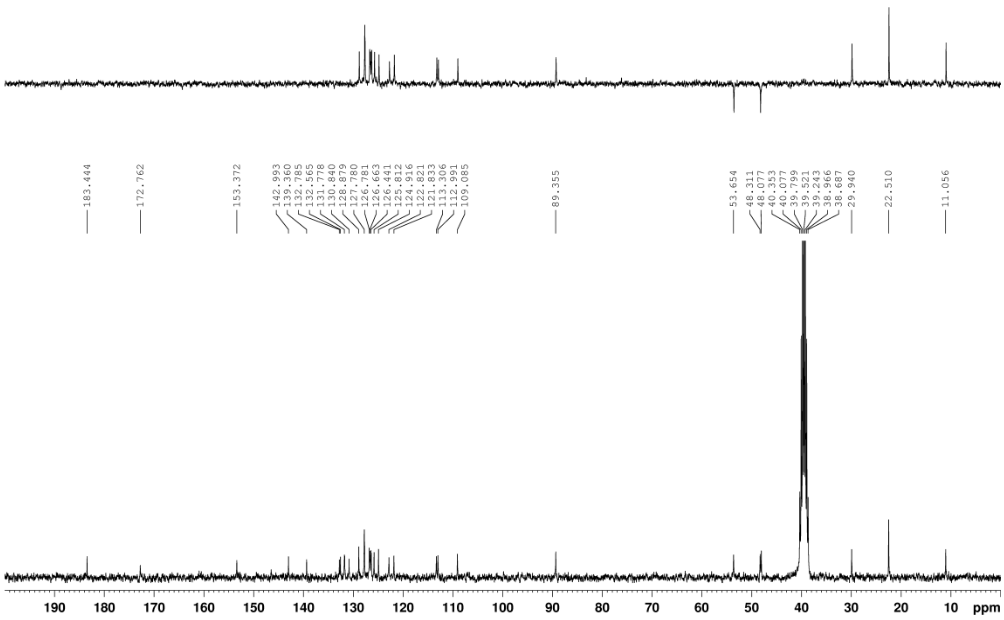
Compound **20**


8.065
8.041
7.796
7.775
7.641
7.610
7.580
7.331
7.301
7.253
7.229
7.136
7.112
7.051
7.029
6.886
5.927
5.740
5.707
3.419
3.376
2.830
2.500
1.576
1.10
2.08
2.11
3.14
1.14
1.16
1.07
1.00
2.09
1.07
2.02
3.07
3.05
6.03
9 8 7 6 5 4 3 2 1 ppm
NAME 12012001142
EXPNO 224
PROCNO 1
Date_ 20131212
Time 9.31
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 128
DW 81.000 usec
DE 6.50 usec
TE 290.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300010 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

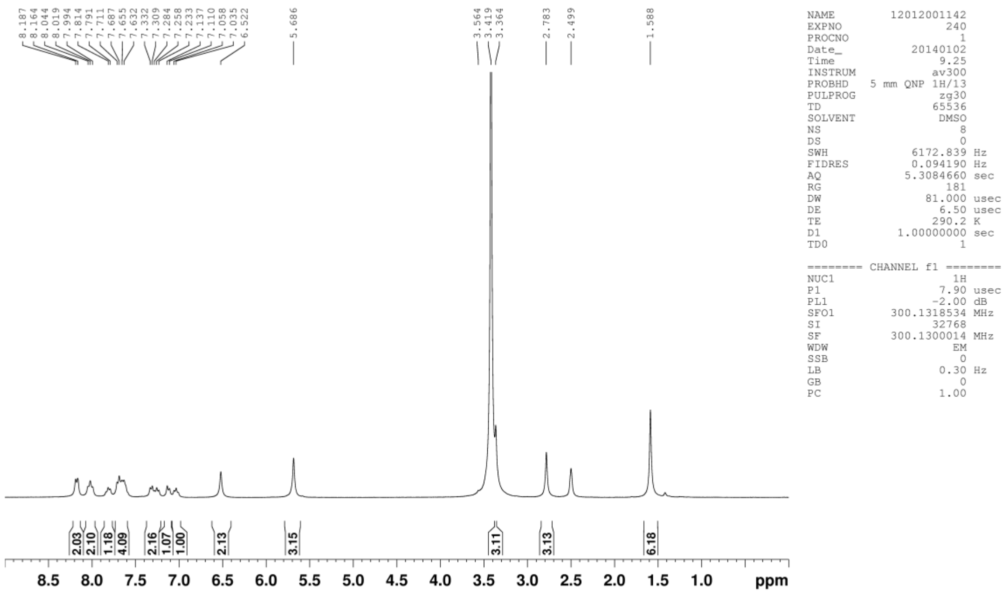

183.409
172.729
153.782
143.028
139.366
133.403
132.971
131.696
130.751
130.467
128.477
127.857
126.510
122.847
121.998
113.166
109.139
89.473
48.816
48.091
40.352
40.076
39.798
39.520
39.242
38.963
38.688
30.002
22.510
11.097
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

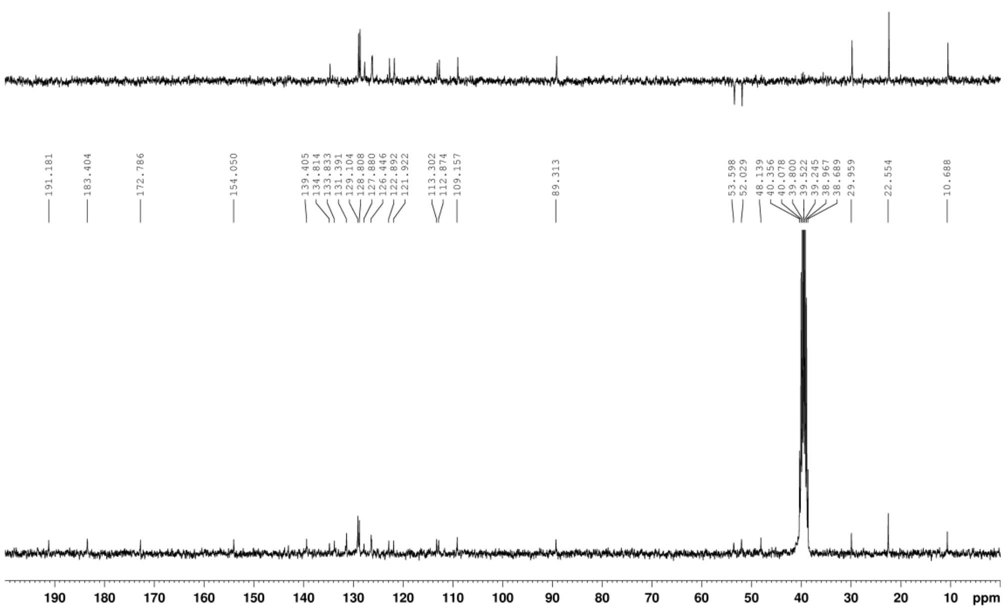
Compound **21**


8.028 7.990 7.960 7.929 7.916 7.861 7.615 7.558 7.497 7.469 7.326 7.302 7.282 7.254 7.229 7.132 7.106 7.055 7.031 7.008 6.092 5.724 5.686
3.421 3.370 2.926 2.500 1.584
3.95 2.05 2.00 2.03 1.18 2.14 1.08 1.00 2.00 1.14 2.03 2.97 2.93 6.18
9 8 7 6 5 4 3 2 1 ppm
NAME 12012001142
EXPNO 217
PROCNO 1
Date_ 20131125
Time 15.20
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 128
DW 81.000 usec
DE 6.50 usec
TE 293.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300013 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

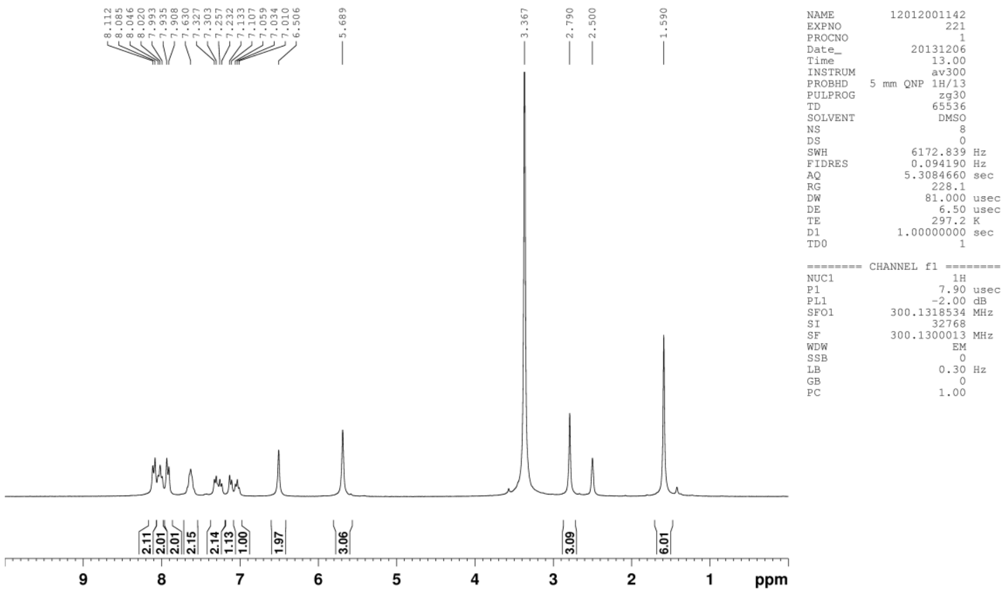

183.444 172.762 153.372 142.993 139.360 132.785 132.565 131.778 130.840 128.879 127.780 126.781 126.663 126.441 125.812 124.916 122.821 121.833 113.306 112.991 109.085 89.355 53.654 48.311 48.077 40.353 40.077 39.799 39.521 39.243 38.966 38.687 29.940 22.510 11.056
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

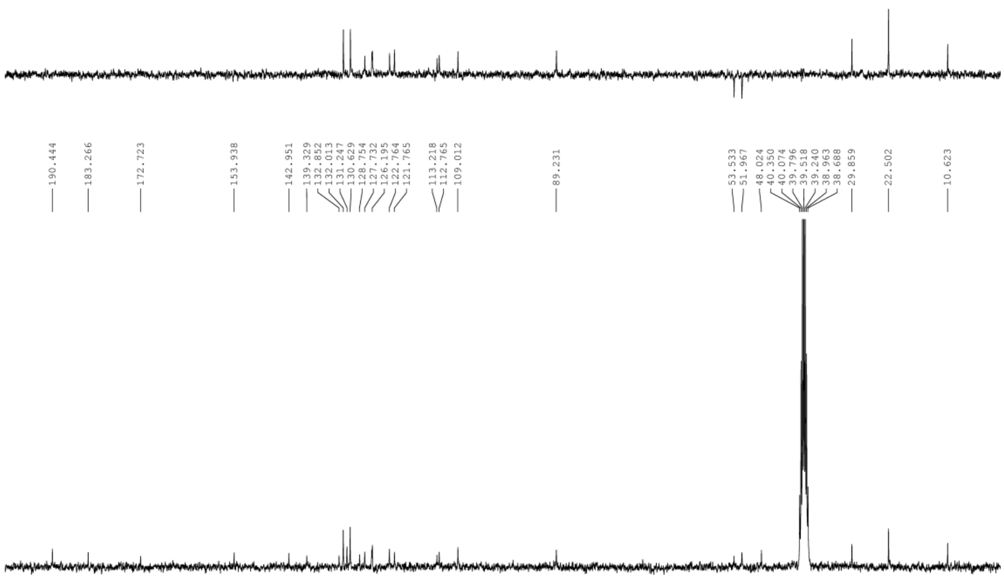
Compound **22**


NAME 12012001142
EXPNO 240
PROCNO 1
Date_ 20140102
Time 9.25
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 181
DW 81.000 usec
DE 6.50 usec
TE 290.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300014 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm

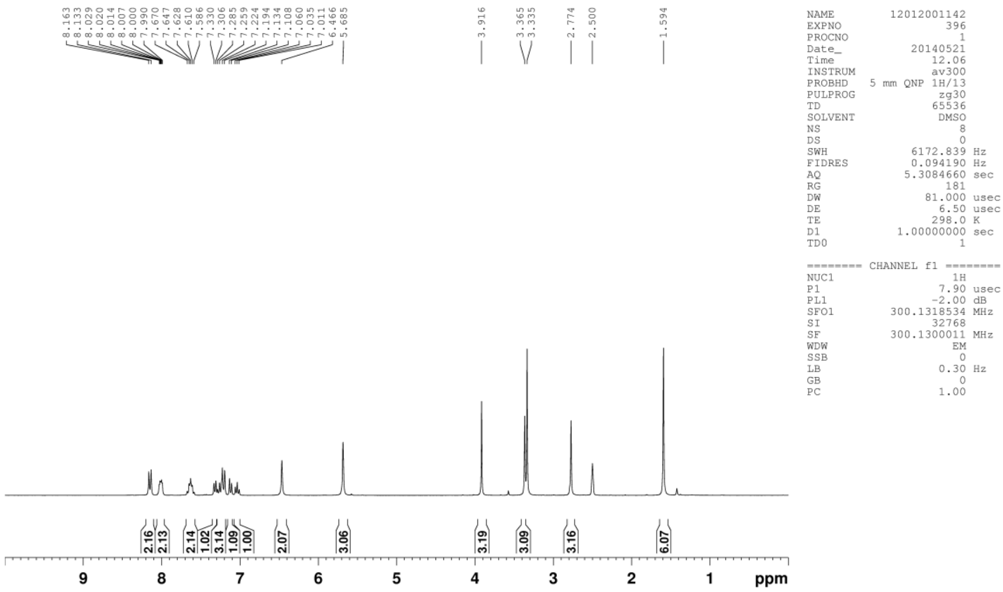

ppm

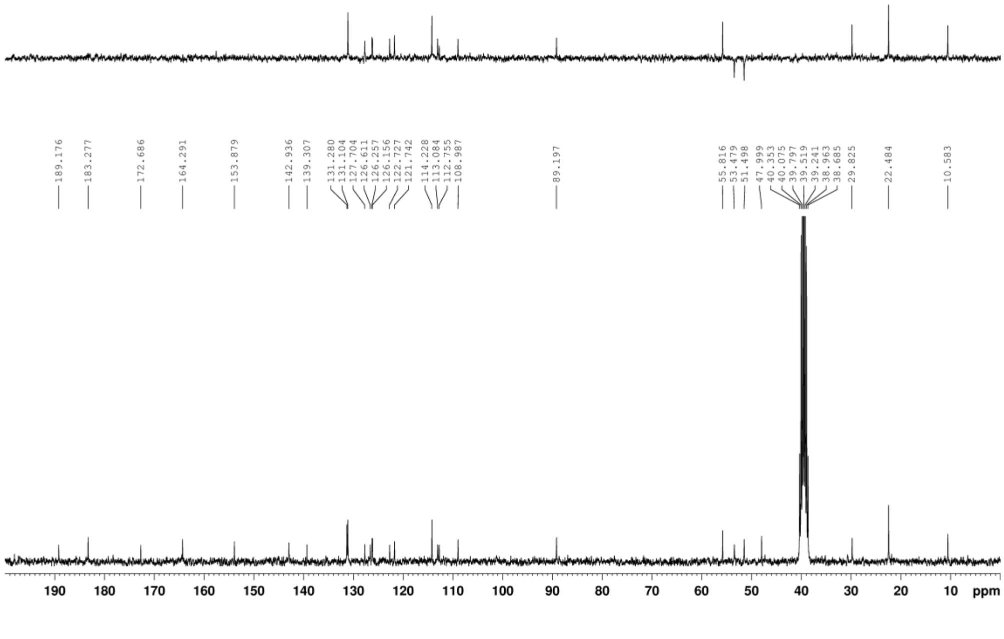
Compound **23**


8.112
8.085
8.046
8.020
7.993
7.935
7.908
7.630
7.327
7.303
7.257
7.232
7.133
7.107
7.059
7.034
7.010
6.506
5.689
3.367
2.790
2.500
1.590
2.11
2.01
2.01
2.15
2.14
1.13
1.00
1.97
3.06
3.09
6.01
9
8
7
6
5
4
3
2
1
ppm
NAME 12012001142
EXPNO 221
PROCNO 1
Date_ 20131206
Time 13.00
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 228.1
DW 81.000 usec
DE 6.50 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300013 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

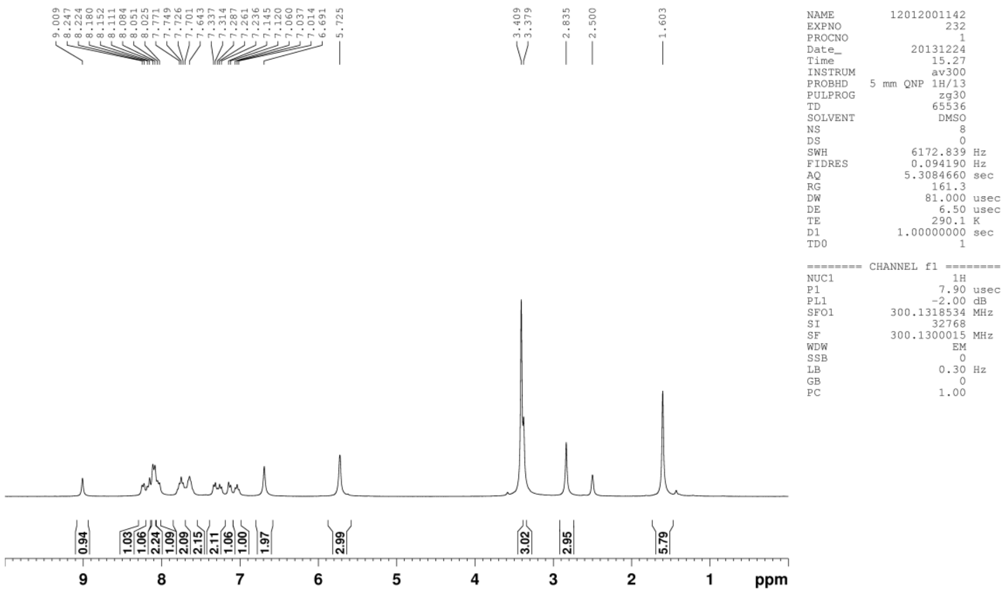

190.444
183.266
172.723
153.938
142.951
139.329
132.852
132.013
131.247
130.629
128.754
127.732
126.195
122.764
121.765
113.218
112.765
109.012
89.231
53.533
51.967
48.024
40.350
40.074
39.796
39.518
39.240
38.963
38.688
29.859
22.502
10.623
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

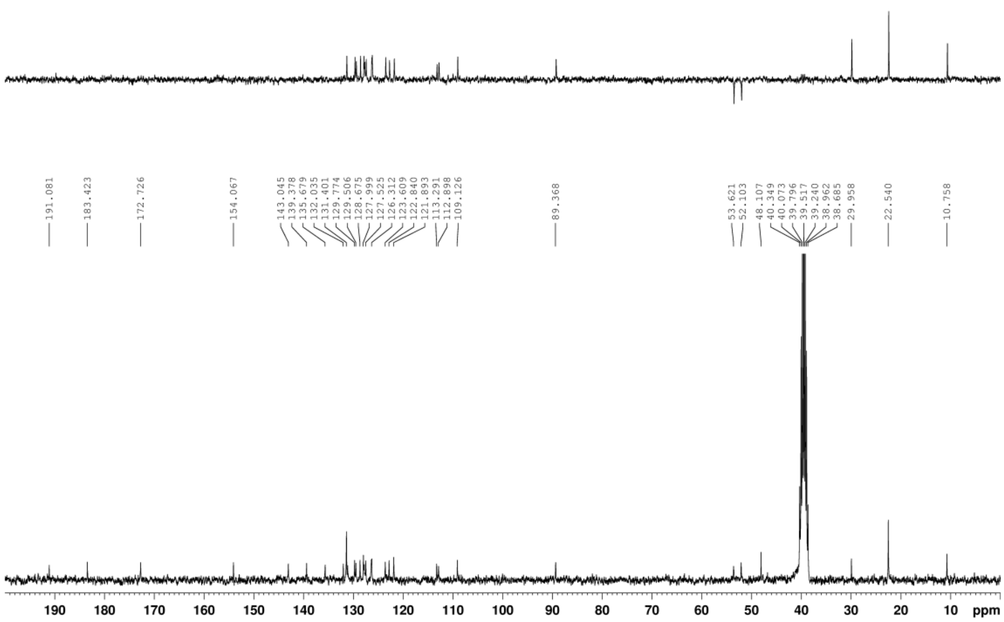
Compound **24**



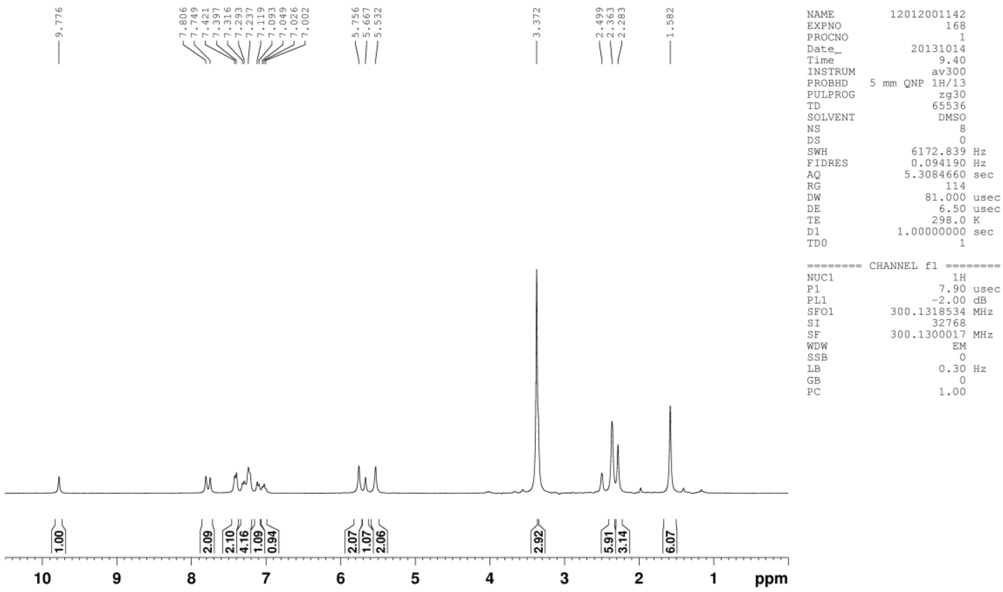


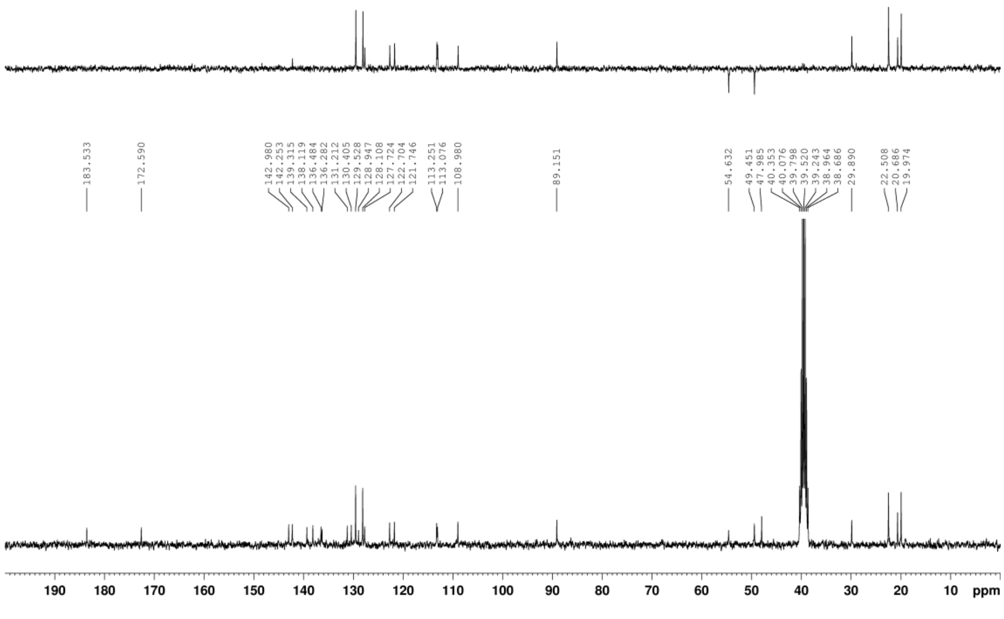
Compound **25**


9.009
8.247
8.224
8.180
8.152
8.111
8.084
8.051
8.025
7.771
7.749
7.726
7.701
7.643
7.337
7.314
7.287
7.261
7.236
7.145
7.120
7.060
7.037
7.014
6.691
5.725
3.409
3.379
2.835
2.500
1.603
NAME 12012001142
EXPNO 232
PROCNO 1
Date_ 20131224
Time 15.27
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 161.3
DW 81.000 usec
DE 6.50 usec
TE 290.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300015 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.94
1.03
1.06
2.24
1.09
2.09
2.15
2.11
1.06
1.00
1.97
2.99
3.02
2.95
5.79
9 8 7 6 5 4 3 2 1 ppm

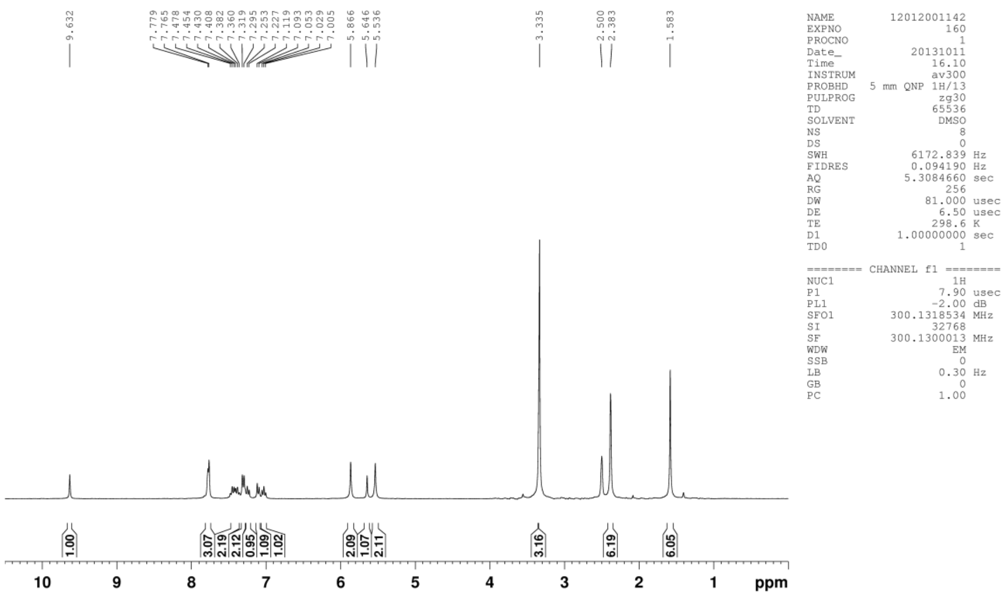

191.081
183.423
172.726
154.067
143.045
139.378
135.679
132.035
131.401
129.774
129.506
128.675
127.999
127.525
126.312
123.609
122.840
121.893
113.291
112.898
109.126
89.368
53.621
52.103
48.107
40.349
40.073
39.796
39.517
39.240
38.962
38.685
29.958
22.540
10.758
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

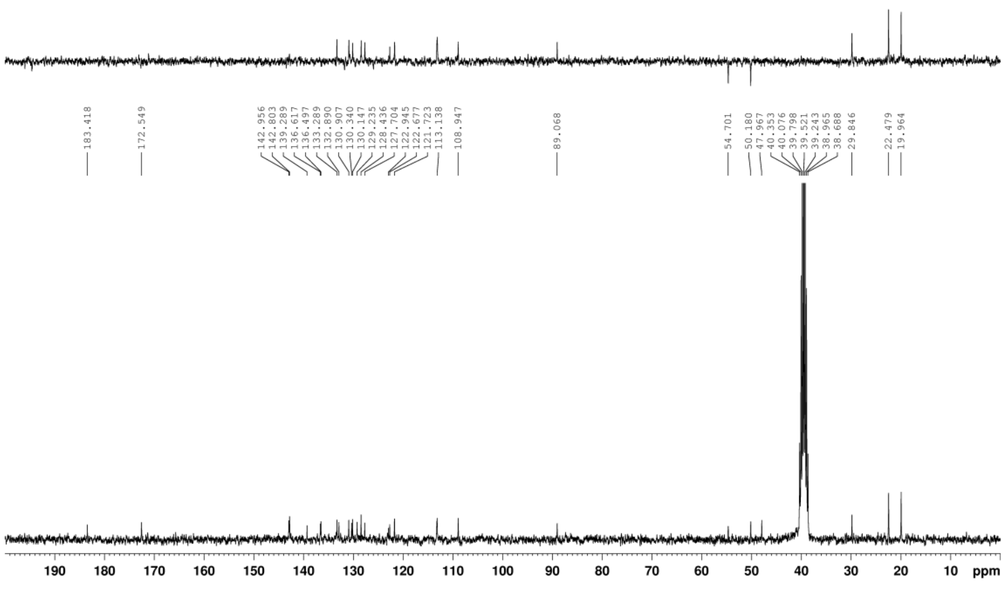
Compound **26**



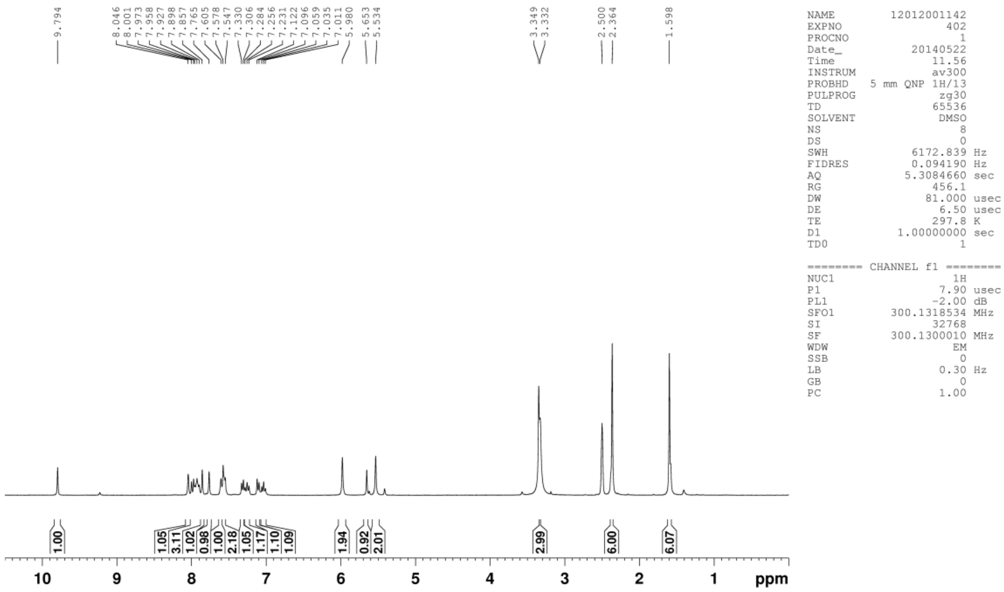


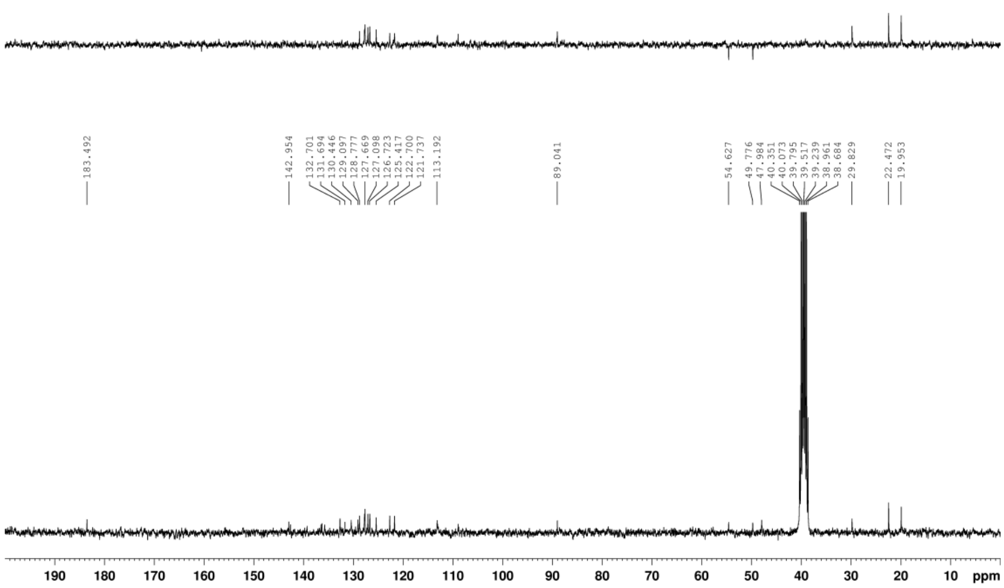
Compound **27**


NAME 12012001142
EXPNO 160
PROCNO 1
Date_ 20131011
Time 16.10
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 256
DW 81.000 usec
DE 6.50 usec
TE 298.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300013 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm

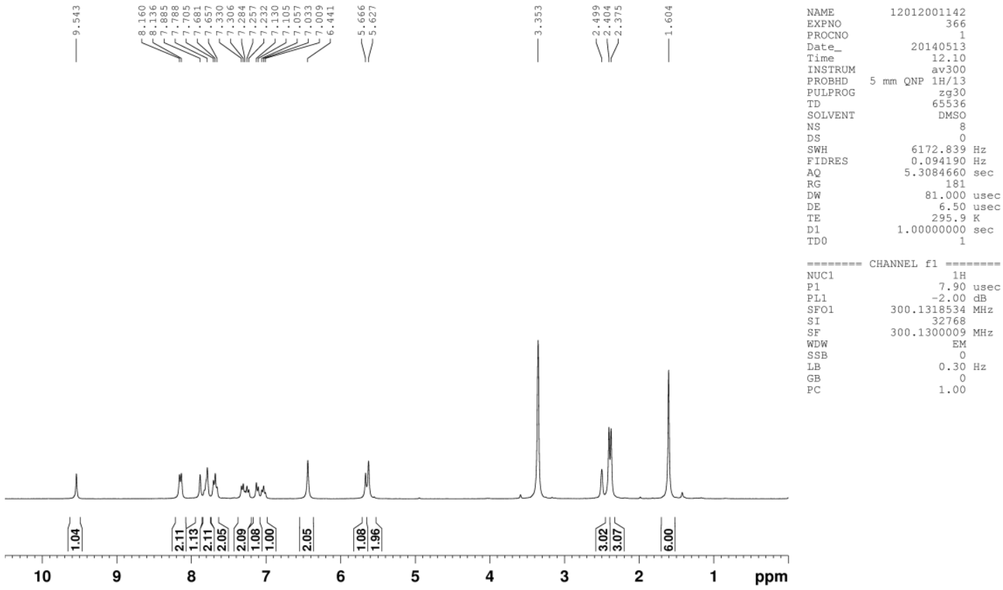

ppm

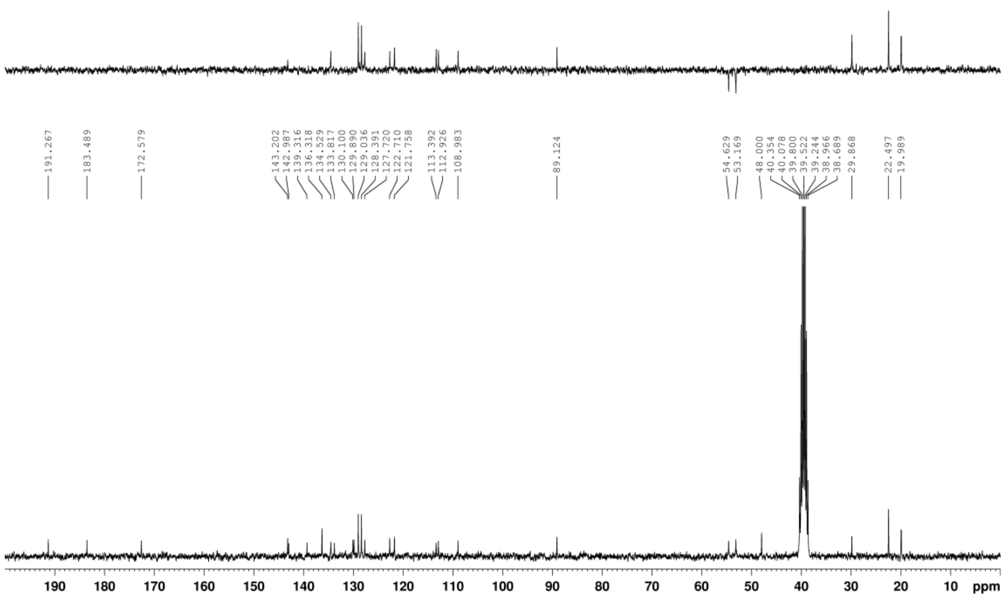
Compound **28**



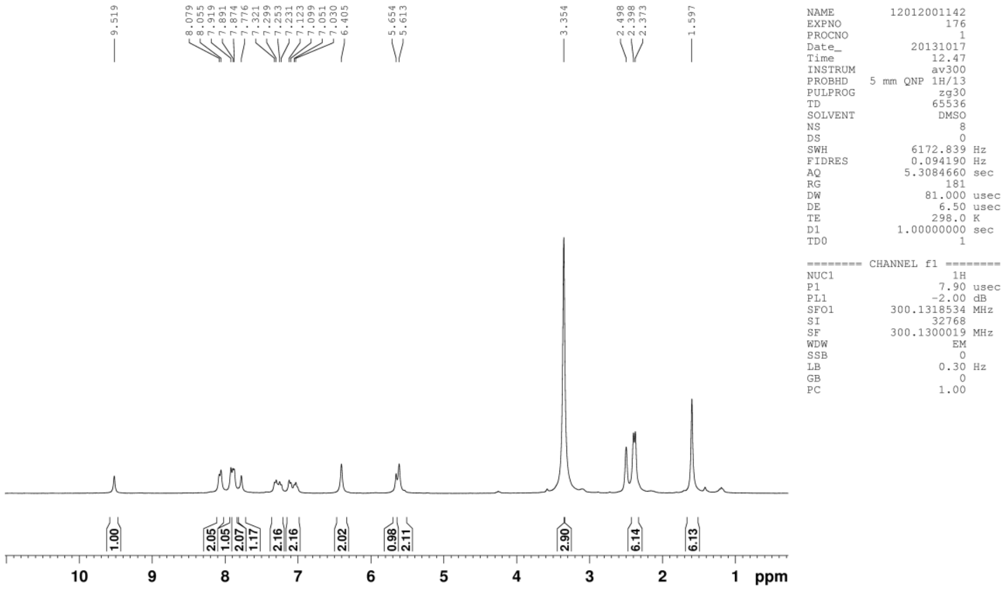


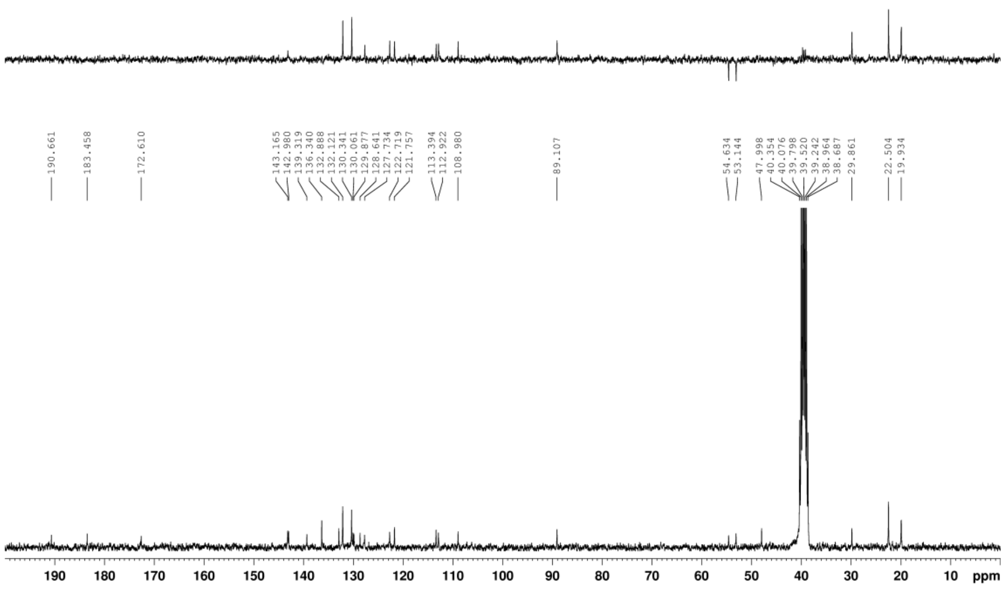
Compound **29**


NAME 12012001142
EXPNO 366
PROCNO 1
Date_ 20140513
Time 12.10
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 181
DW 81.000 usec
DE 6.50 usec
TE 295.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300009 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

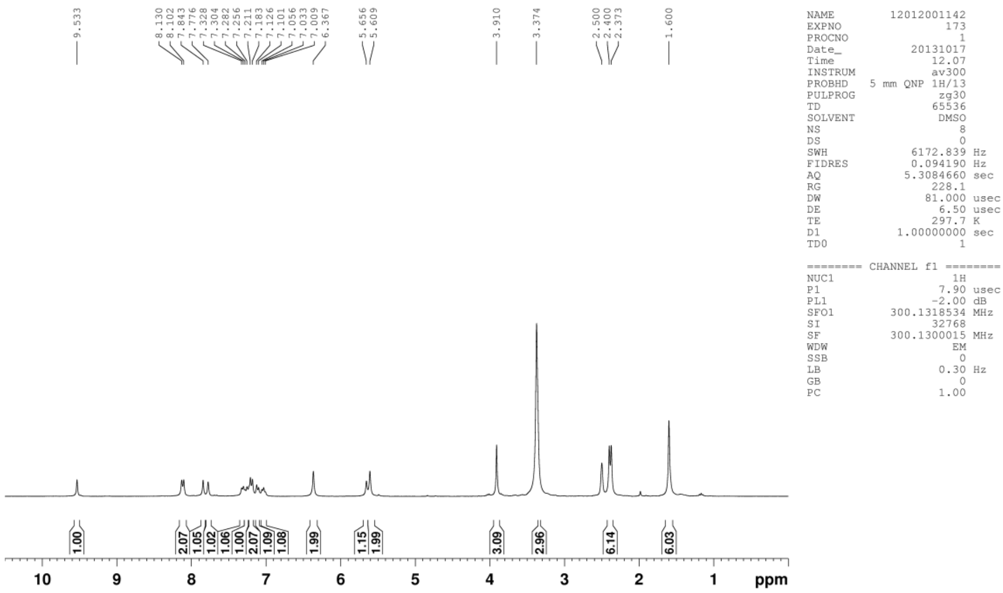


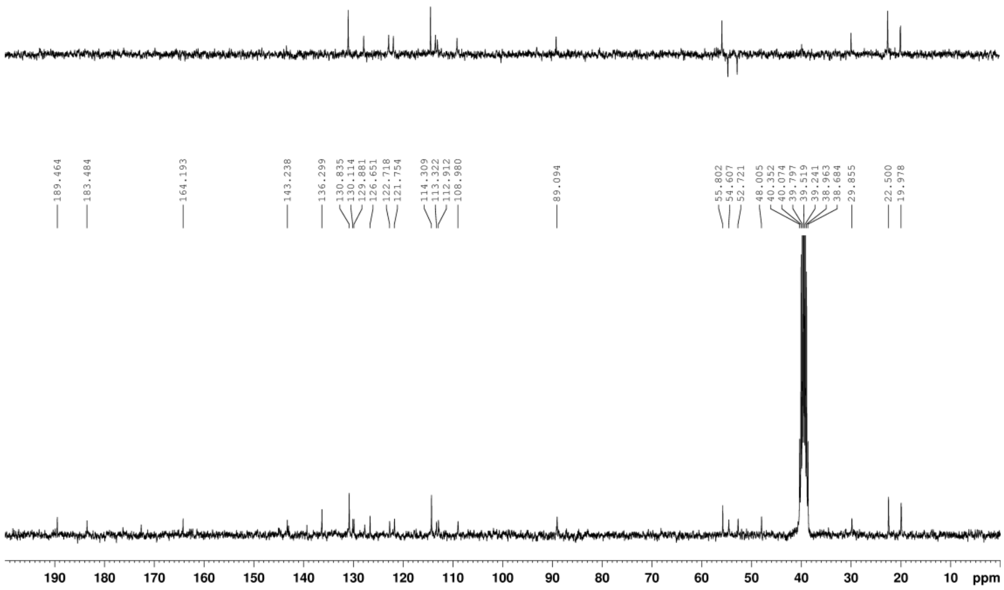
Compound **30**


NAME 12012001142
EXPNO 176
PROCNO 1
Date_ 20131017
Time 12.47
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 181
DW 81.000 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300019 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm

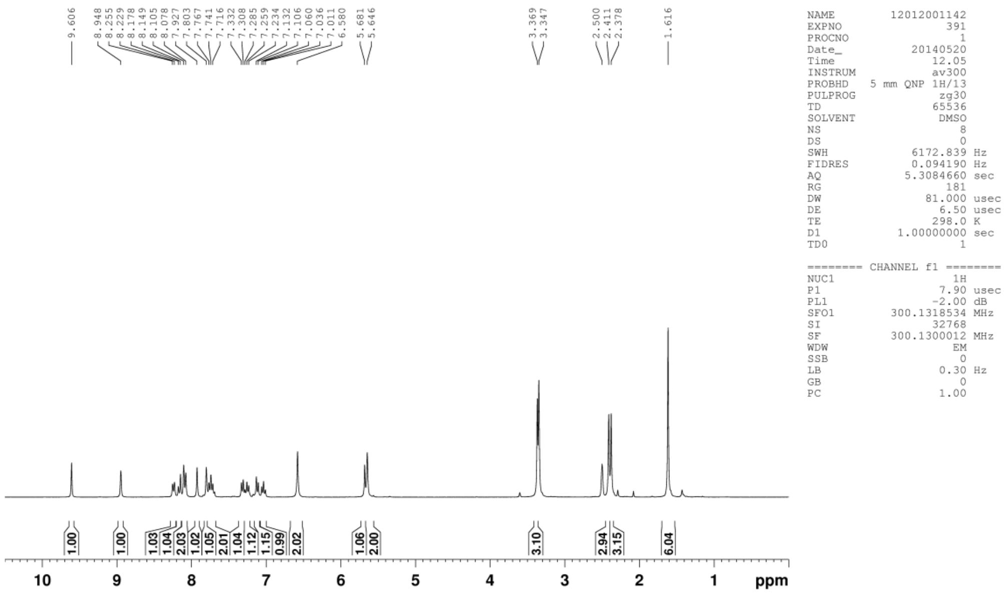

ppm

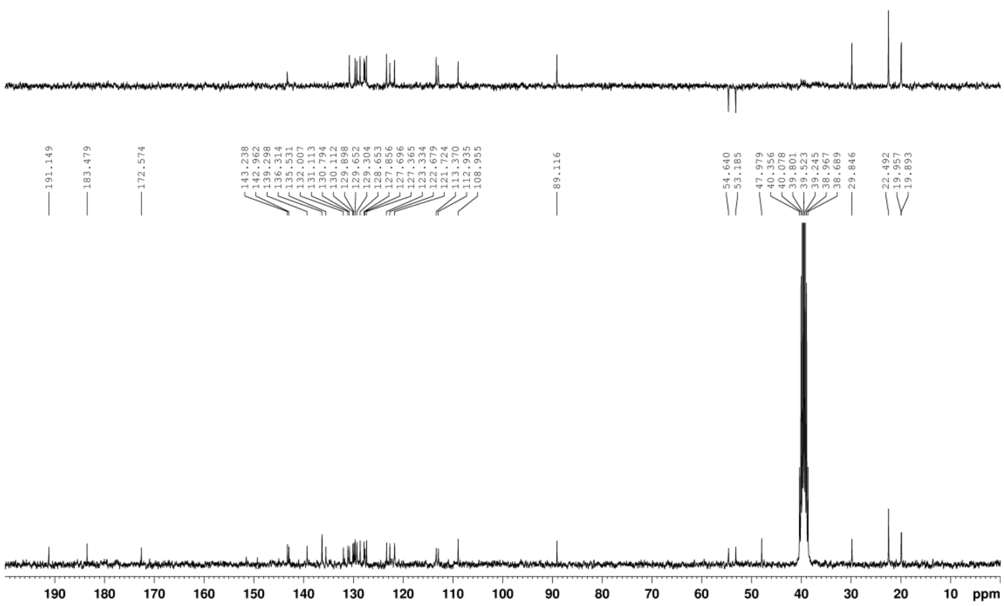
Compound **31**


9.533
8.130 8.102 7.843 7.776 7.328 7.304 7.282 7.256 7.211 7.183 7.126 7.101 7.056 7.033 7.009 6.367
5.656 5.609
3.910
3.374
2.500 2.400 2.373
1.600
1.00 2.07 1.05 1.02 1.06 1.00 2.07 1.09 1.08 1.99 1.15 1.99 3.09 2.96 6.14 6.03
10 9 8 7 6 5 4 3 2 1 ppm
NAME 12012001142
EXPNO 173
PROCNO 1
Date_ 20131017
Time 12.07
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 228.1
DW 81.000 usec
DE 6.50 usec
TE 297.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300015 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


189.464
183.484
164.193
143.238
136.299 130.835 130.114 129.881 126.651 122.718 121.754
114.309 113.322 112.912 108.980
89.094
55.802 54.607 52.721 48.005 40.352 40.074 39.797 39.519 39.241 38.963 38.684 29.855
22.500 19.978
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Compound **32**


9.606
8.948
8.255
8.229
8.178
8.149
8.105
8.078
7.927
7.803
7.767
7.741
7.716
7.332
7.308
7.285
7.259
7.234
7.132
7.106
7.060
7.036
7.011
6.580
5.681
5.646
3.369
3.347
2.500
2.411
2.378
1.616
1.00
1.00
1.03
1.04
2.03
1.02
1.05
2.01
1.04
1.12
1.15
0.99
2.02
1.06
2.00
3.10
2.94
3.15
6.04
10 9 8 7 6 5 4 3 2 1 ppm
NAME 12012001142
EXPNO 391
PROCNO 1
Date_ 20140520
Time 12.05
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 181
DW 81.000 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300012 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


191.149
183.479
172.574
143.238
142.962
139.298
136.314
135.531
132.007
131.113
130.794
130.112
129.898
129.652
129.304
128.653
127.856
127.696
127.365
123.334
122.679
121.724
113.370
112.935
108.955
89.116
54.640
53.185
47.979
40.356
40.078
39.801
39.523
39.245
38.967
38.689
29.846
22.492
19.957
19.893
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm