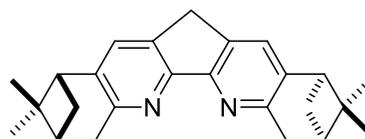


Electronic supplementary materials *Mendeleev Commun.*, 2017, **27**, 128–130

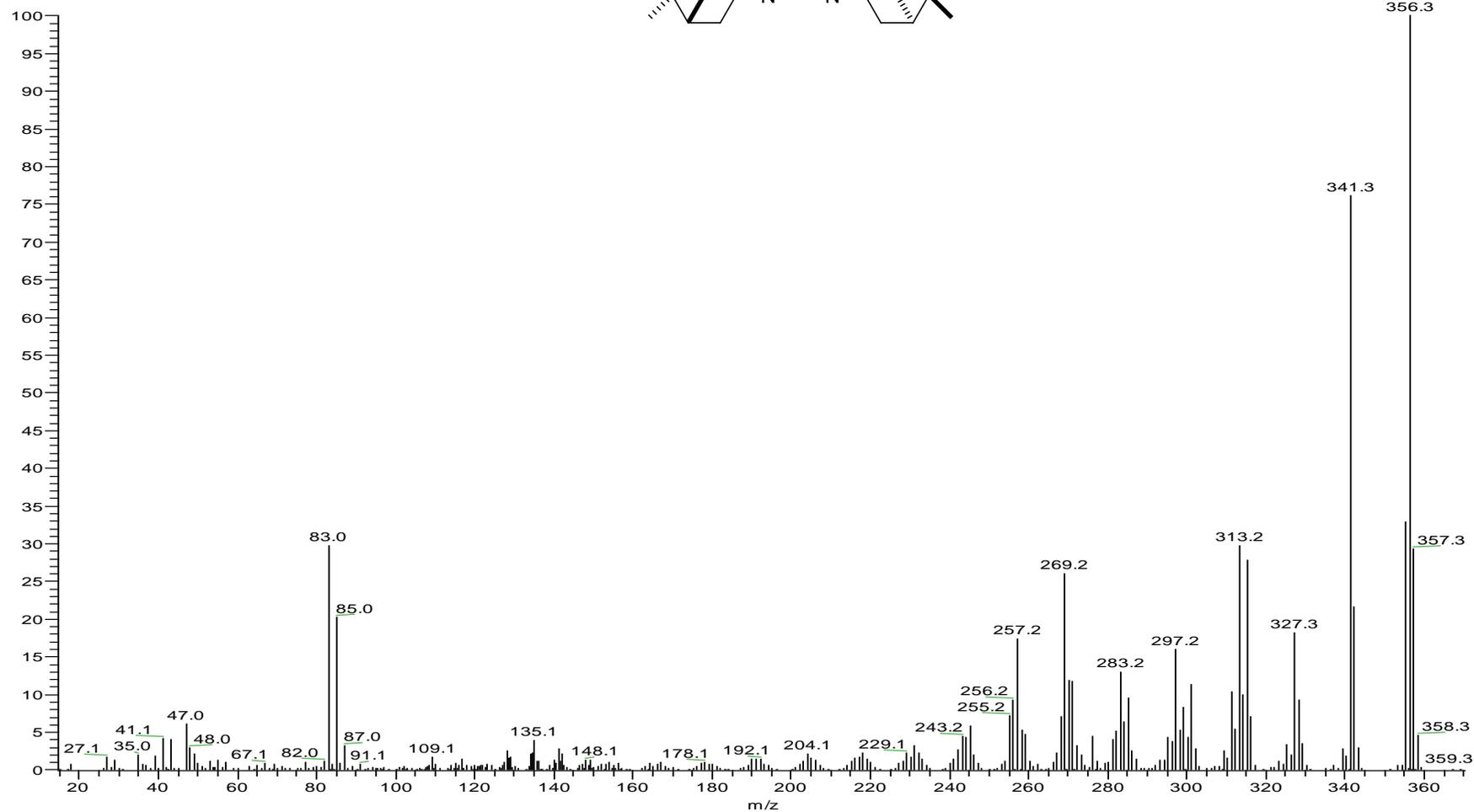
Syntheses of chiral nopinane-annulated pyridines of C_2 and D_2 -symmetry: X-ray structures of the fused derivatives of 4,5-diazafluorene, 4,5-diaza-9*H*-fluoren-9-one, and 9,9'-bi-4,5-diazafluorenylidene

Eugene S. Vasilyev, Irina Yu. Bagryanskaya and Alexey V. Tkachev

(1*R*,3*R*,8*R*,10*R*)-2,2,9,9-tetramethyl-2,3,4,7,8,9,10,12-octahydro-1*H*-1,3:8,10-dimethanocyclopenta[1,2-*b*:5,4-*b'*]diquinoline

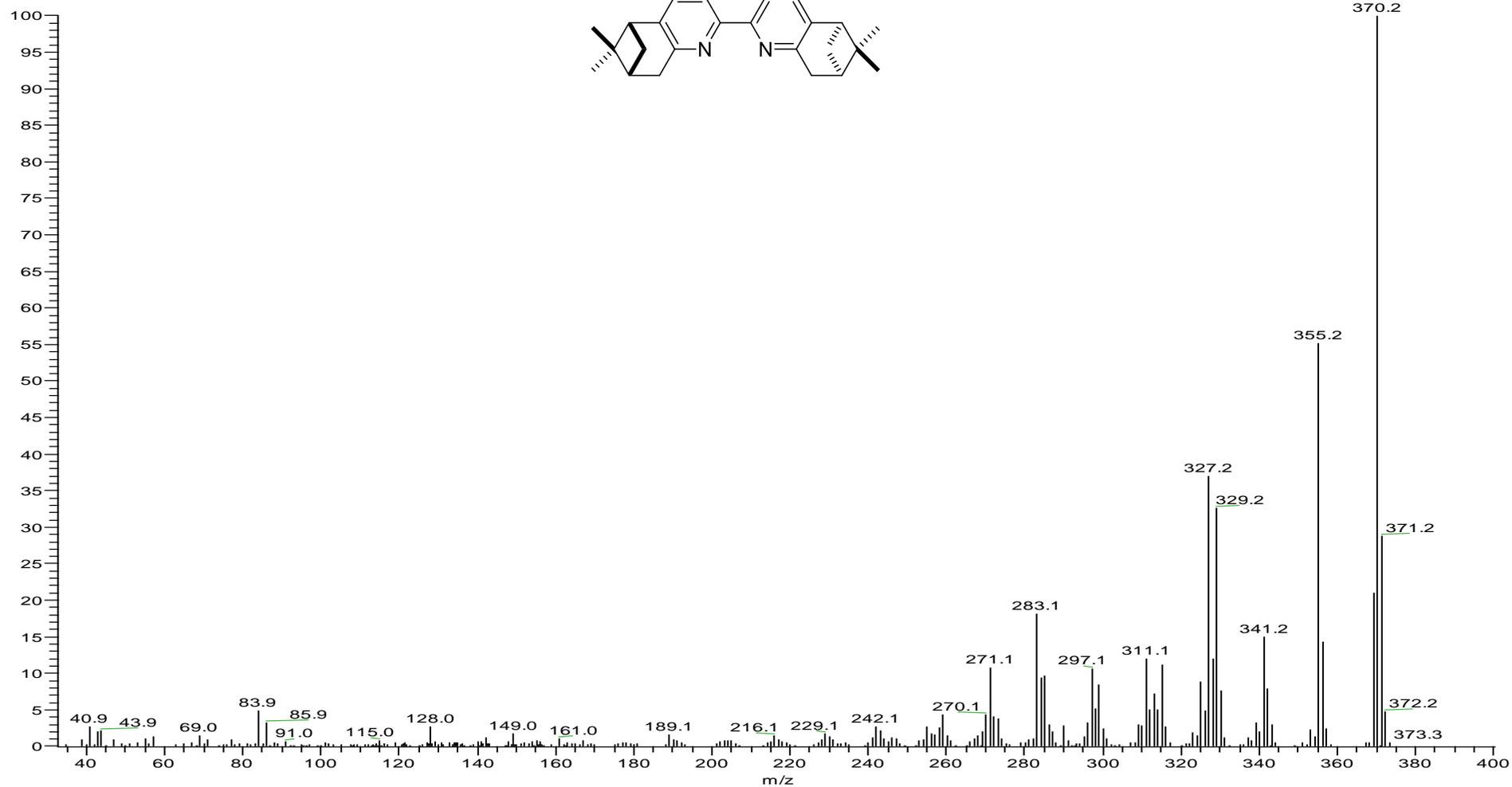
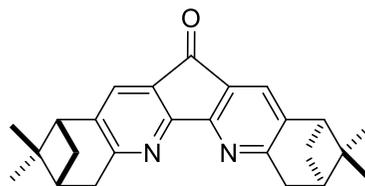


ESV0212-1 #2 RT: 0.08 AV: 1 NL: 6.33E6
T: + c EI Full ms [14.50-370.50]



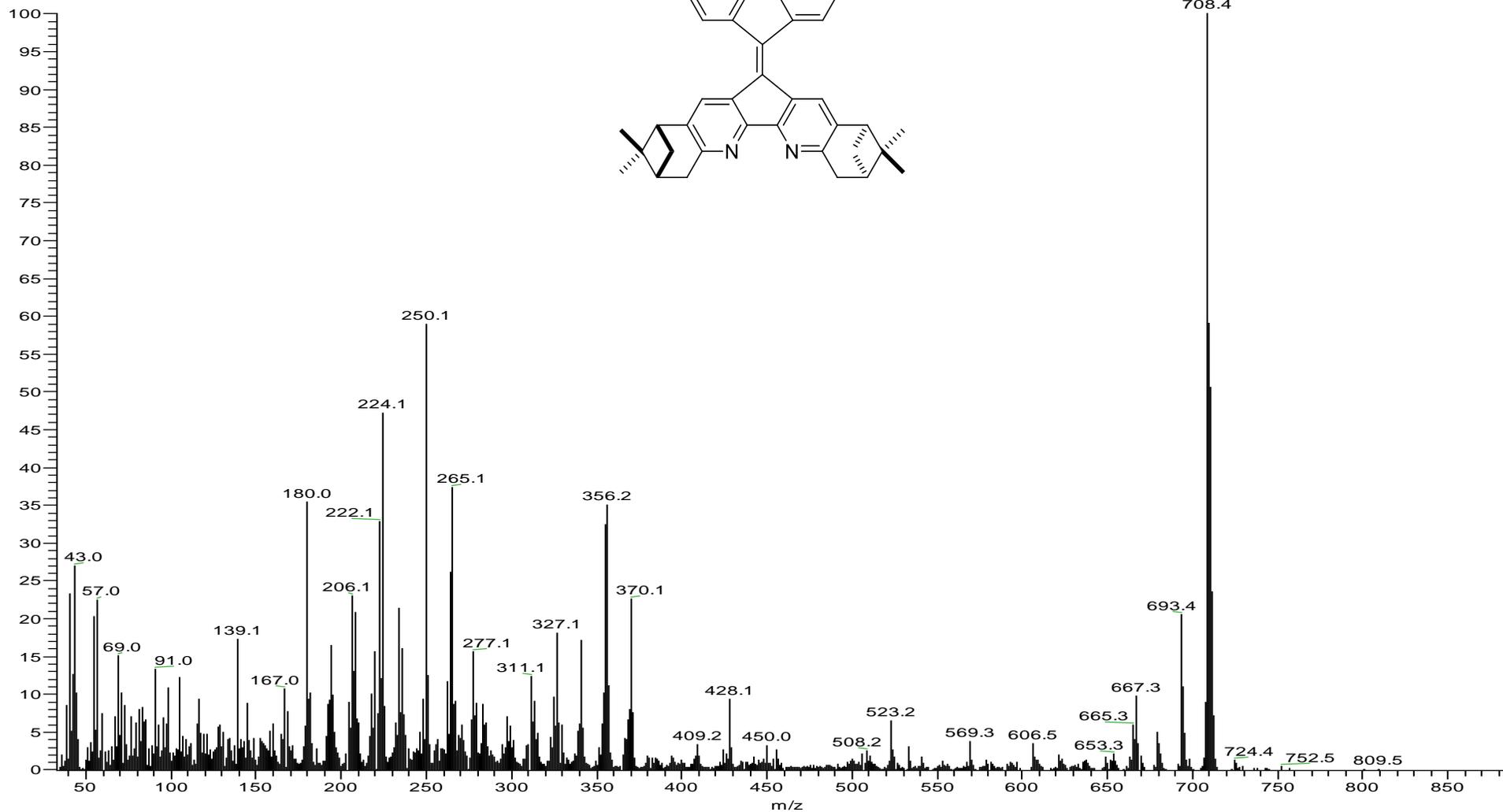
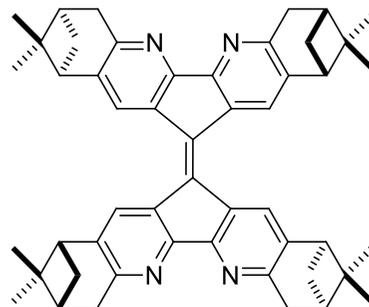
(1R,3R,8R,10R)-2,2,9,9-tetramethyl-3,4,7,8,9,10-hexahydro-1H-1,3:8,10-dimethanocyclopenta[1,2-b:5,4-b']diquinolin-12(2H)-one

ESV0307-2 #13 RT: 0.71 AV: 1 NL: 3.32E6
T: + c EI Full ms [32.50-400.50]

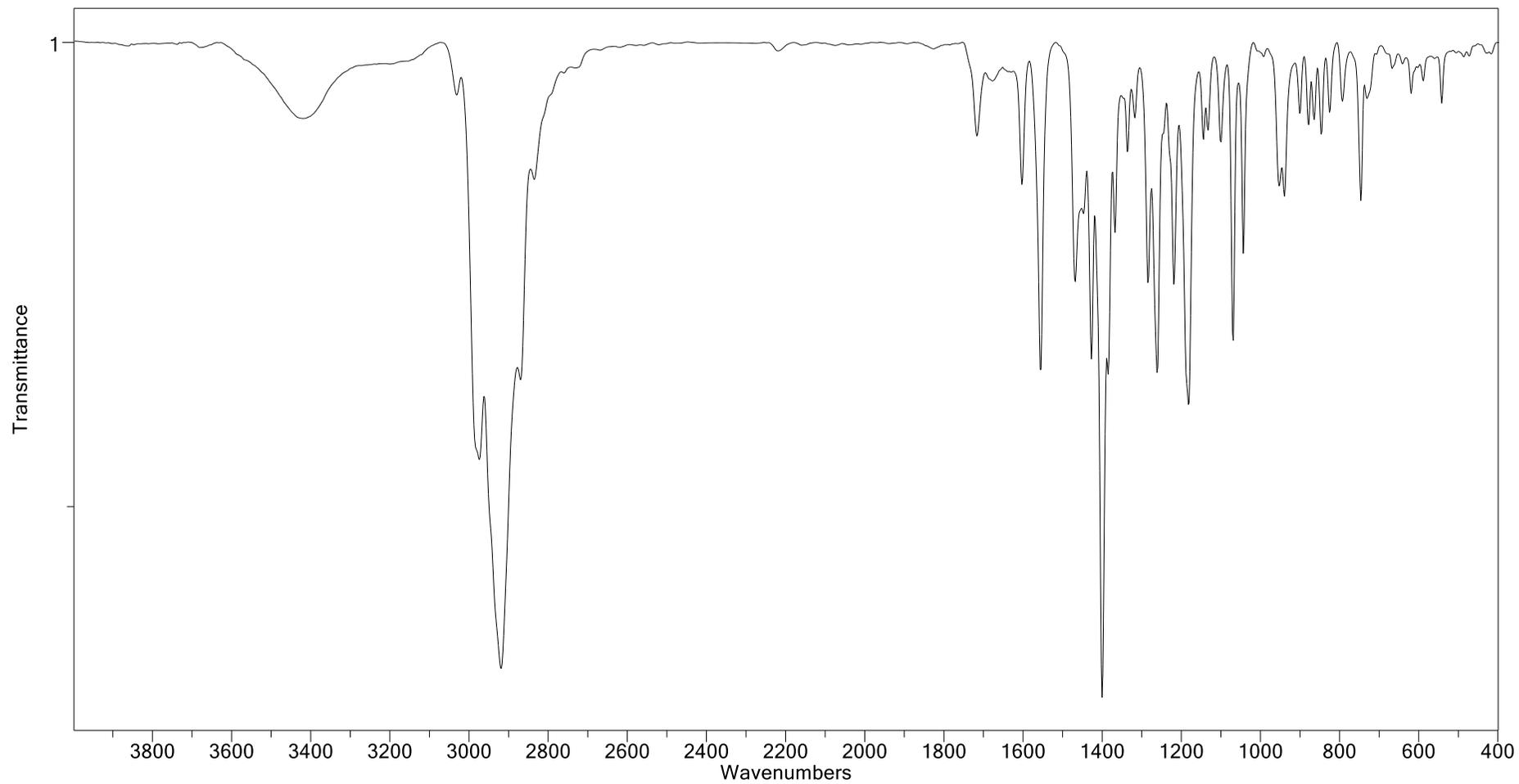
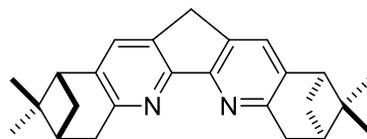


(1*R*,3*R*,8*R*,10*R*,1'*R*,3'*R*,8'*R*,10'*R*)-2,2,2',2',9,9,9',9'-octamethyl-1,1',2,2',3,3',4,4',7,7',8,8',9,9',10,10'-hexadecahydro-1,3:1',3':8,10:8',10'-tetramethano-12,12'-bi(cyclopenta[1,2-*b*:5,4-*b'*]diquinolinylidene)

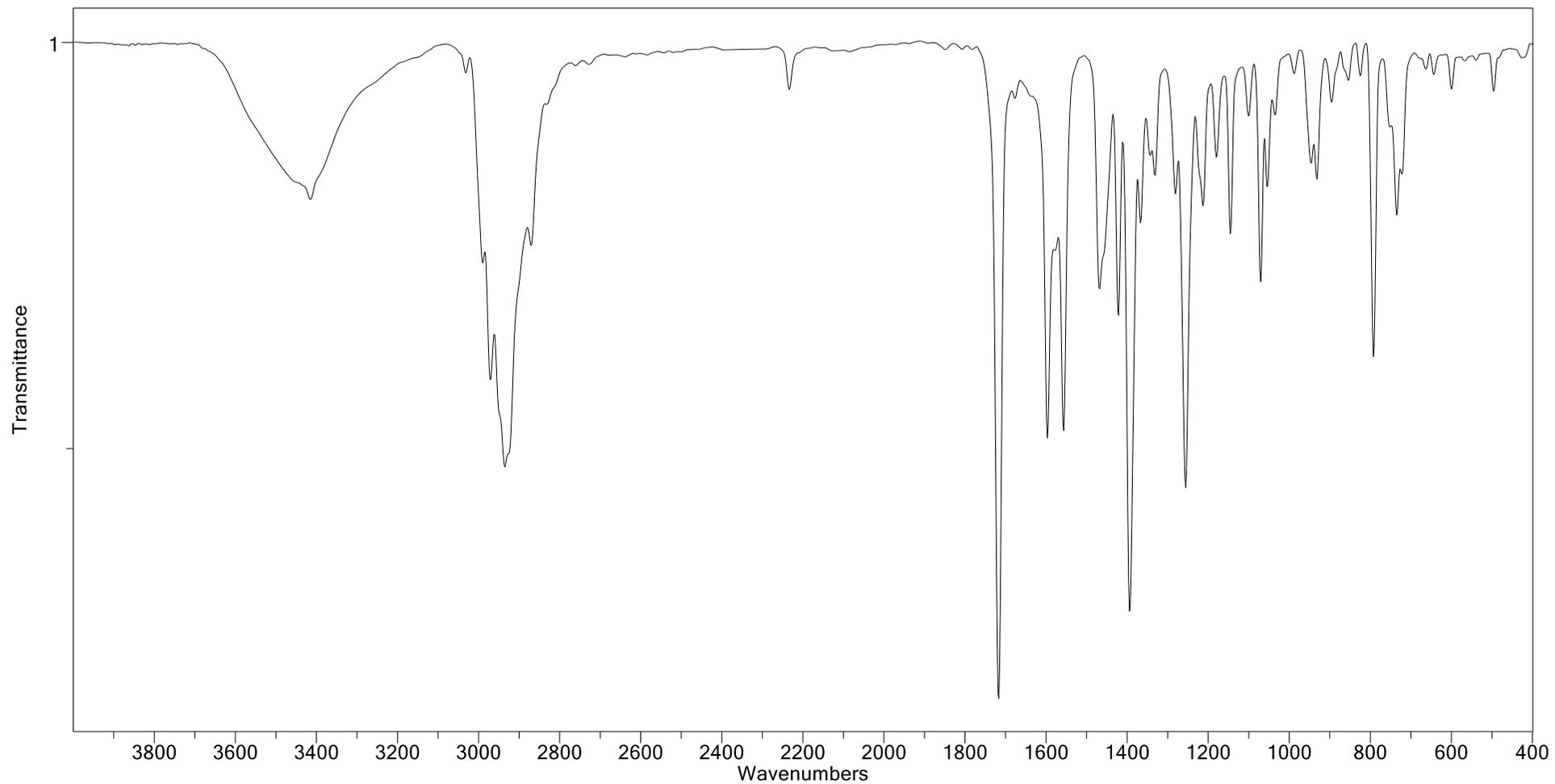
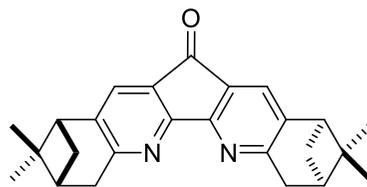
ESV0308-3 #51 RT: 3.82 AV: 1 NL: 2.62E6
T: + c EI Full ms [32.50-900.50]



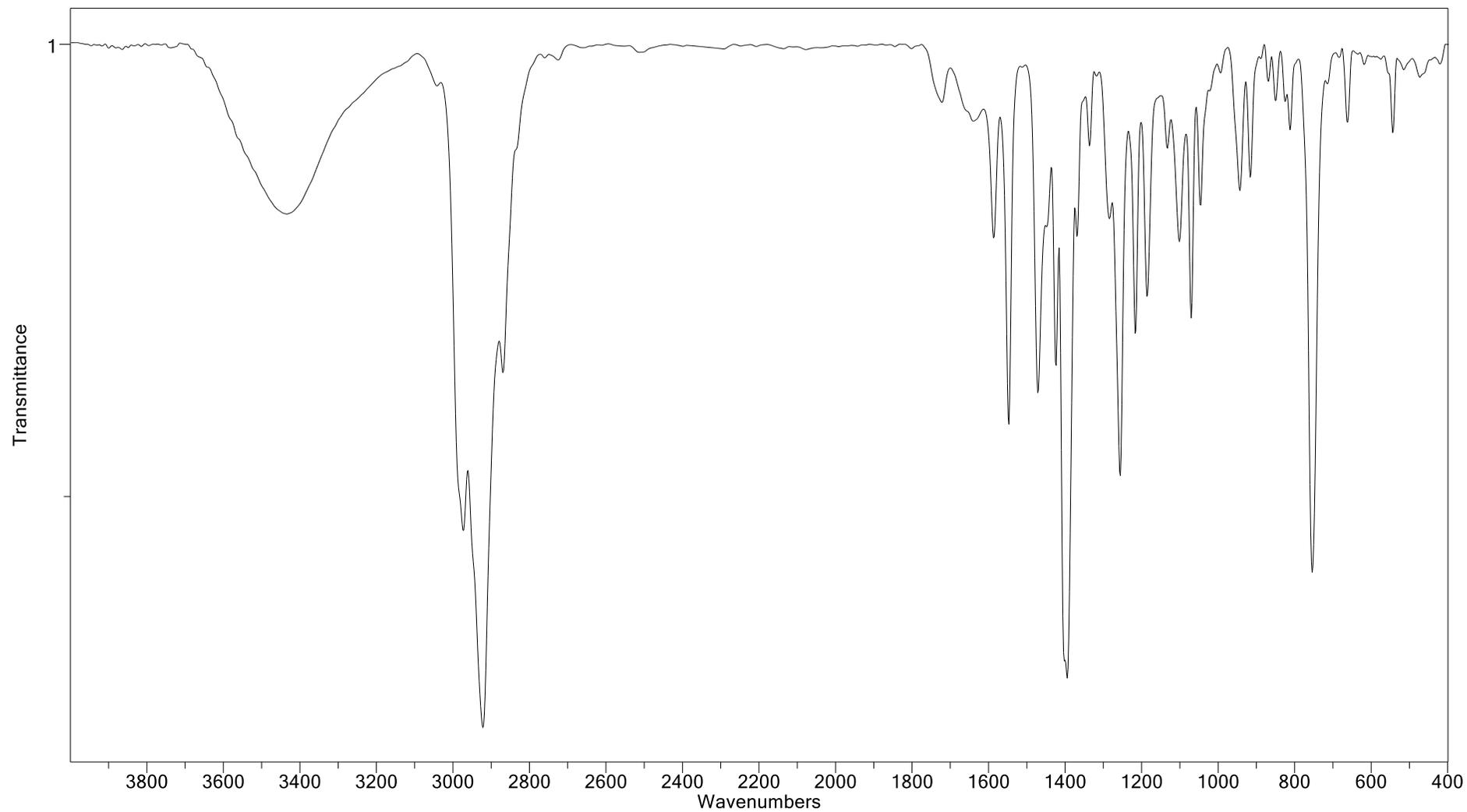
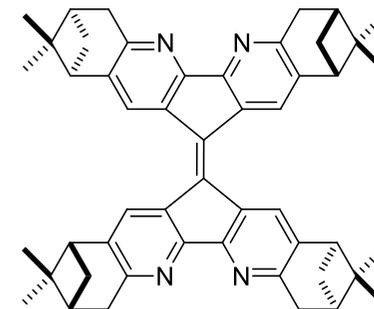
(1*R*,3*R*,8*R*,10*R*)-2,2,9,9-tetramethyl-2,3,4,7,8,9,10,12-octahydro-1*H*-1,3:8,10-dimethanocyclopenta[1,2-*b*:5,4-*b'*]diquinoline



(1*R*,3*R*,8*R*,10*R*)-2,2,9,9-tetramethyl-3,4,7,8,9,10-hexahydro-1*H*-1,3:8,10-dimethanocyclopenta[1,2-*b*:5,4-*b'*]diquinolin-12(2*H*)-one



**(1*R*,3*R*,8*R*,10*R*,1'*R*,3'*R*,8'*R*,10'*R*)-2,2,2',2',9,9,9',9'-
octamethyl-1,1',2,2',3,3',4,4',7,7',8,8',9,9',10,10'-
hexadecahydro-1,3:1',3':8,10:8',10'-tetramethano-12,12'-
bi(cyclopenta[1,2-*b*:5,4-*b'*]diquinolinylidene)**



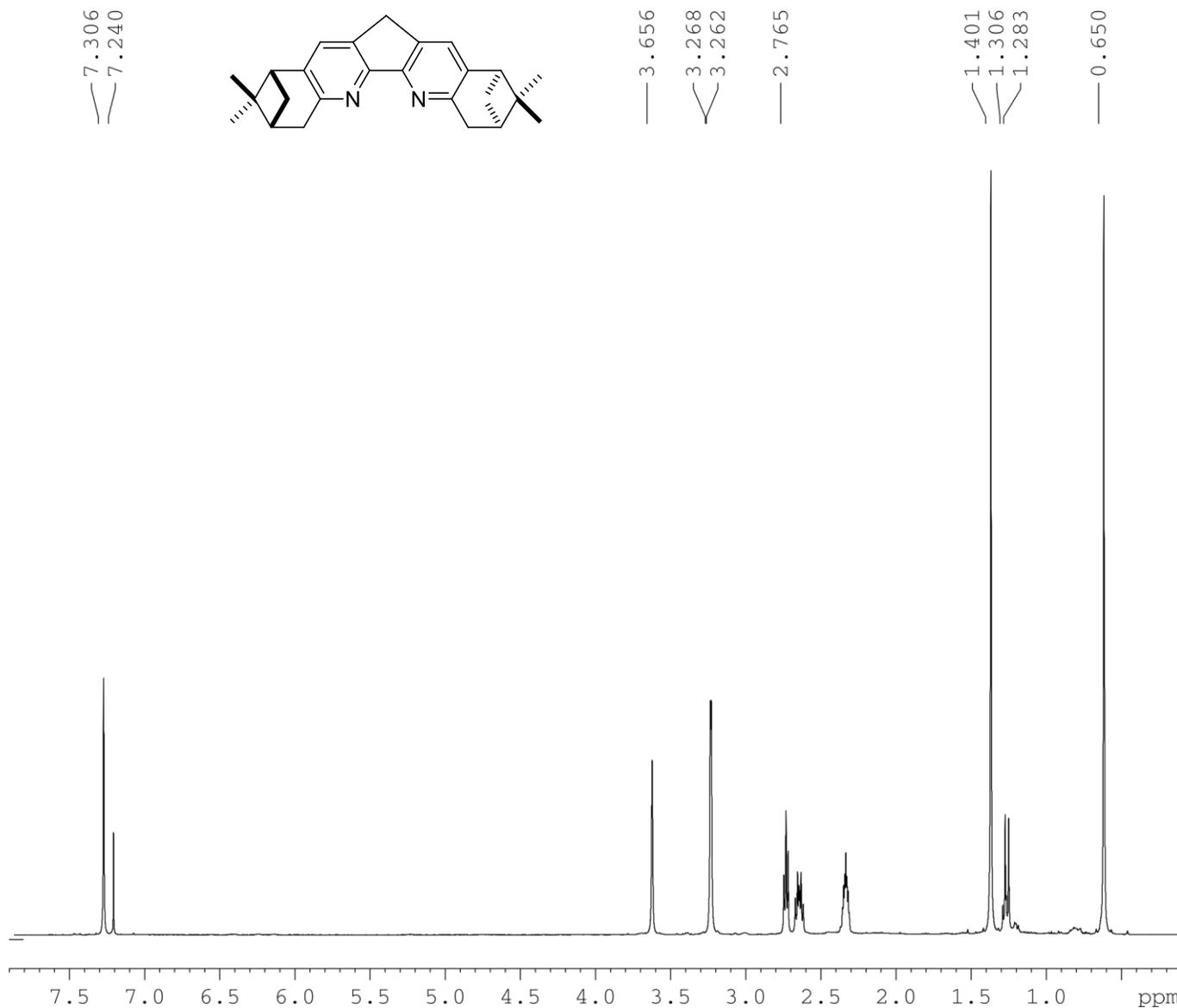
(1R,3R,8R,10R)-2,2,9,9-tetramethyl-2,3,4,7,8,9,10,12-octahydro-1H-1,3:8,10-dimethanocyclopenta[1,2-b:5,4-b']diquinoline

Current Data Parameters
NAME tka-dtc0212-1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20131112
Time 9.24
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32000
SOLVENT CDCl3
NS 64
DS 2
SWH 8802.817 Hz
FIDRES 0.275088 Hz
AQ 1.8176500 sec
RG 203
DW 56.800 usec
DE 6.50 usec
TE 293.3 K
D1 5.00000000 sec
TD0 11111

==== CHANNEL f1 =====
NUC1 1H
P1 13.70 usec
PL1 0 dB
PL1W 9.52005005 W
SFO1 400.1340013 MHz

F2 - Processing parameters
SI 262144
SF 400.1300177 MHz
WDW EM
SSB 0
LB 0.50 Hz
GB 0
PC 1.00



(1R,3R,8R,10R)-2,2,9,9-tetramethyl-3,4,7,8,9,10-hexahydro-1H-1,3,8,10-dimethanocyclopenta[1,2-b:5,4-b']diquinolin-12(2H)-one

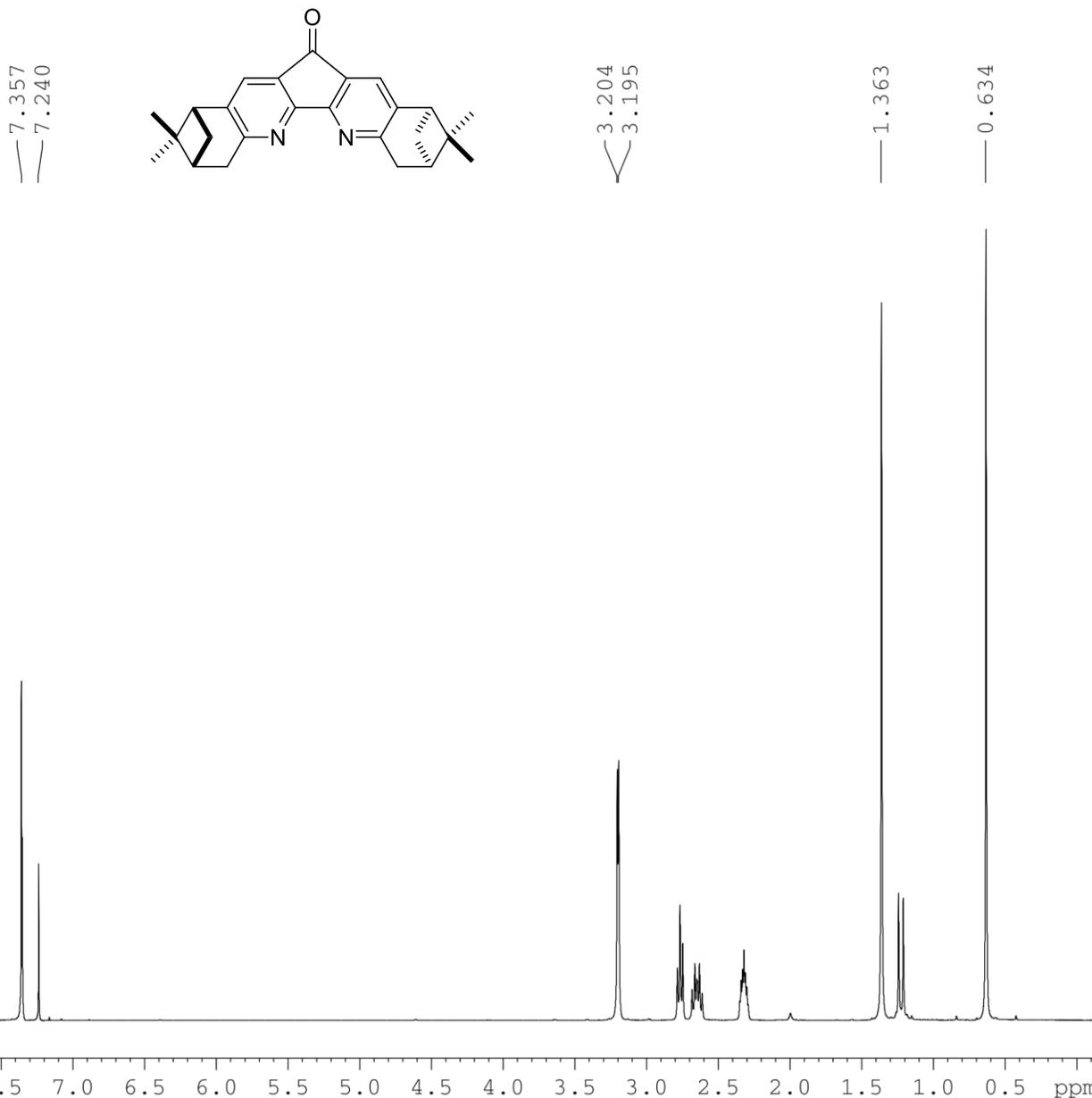
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NAME tka-esv0307-2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

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Time 8.13
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6613.757 Hz
FIDRES 0.201836 Hz
AQ 2.4773109 sec
RG 45.3
DW 75.600 usec
DE 6.00 usec
TE 300.0 K
D1 5.00000000 sec
TD0 111111

==== CHANNEL f1 =====
NUC1 1H
P1 14.90 usec
PL1 0 dB
PL1W 9.79635715 W
SFO1 300.1328512 MHz

F2 - Processing parameters
SI 131072
SF 300.1300126 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00



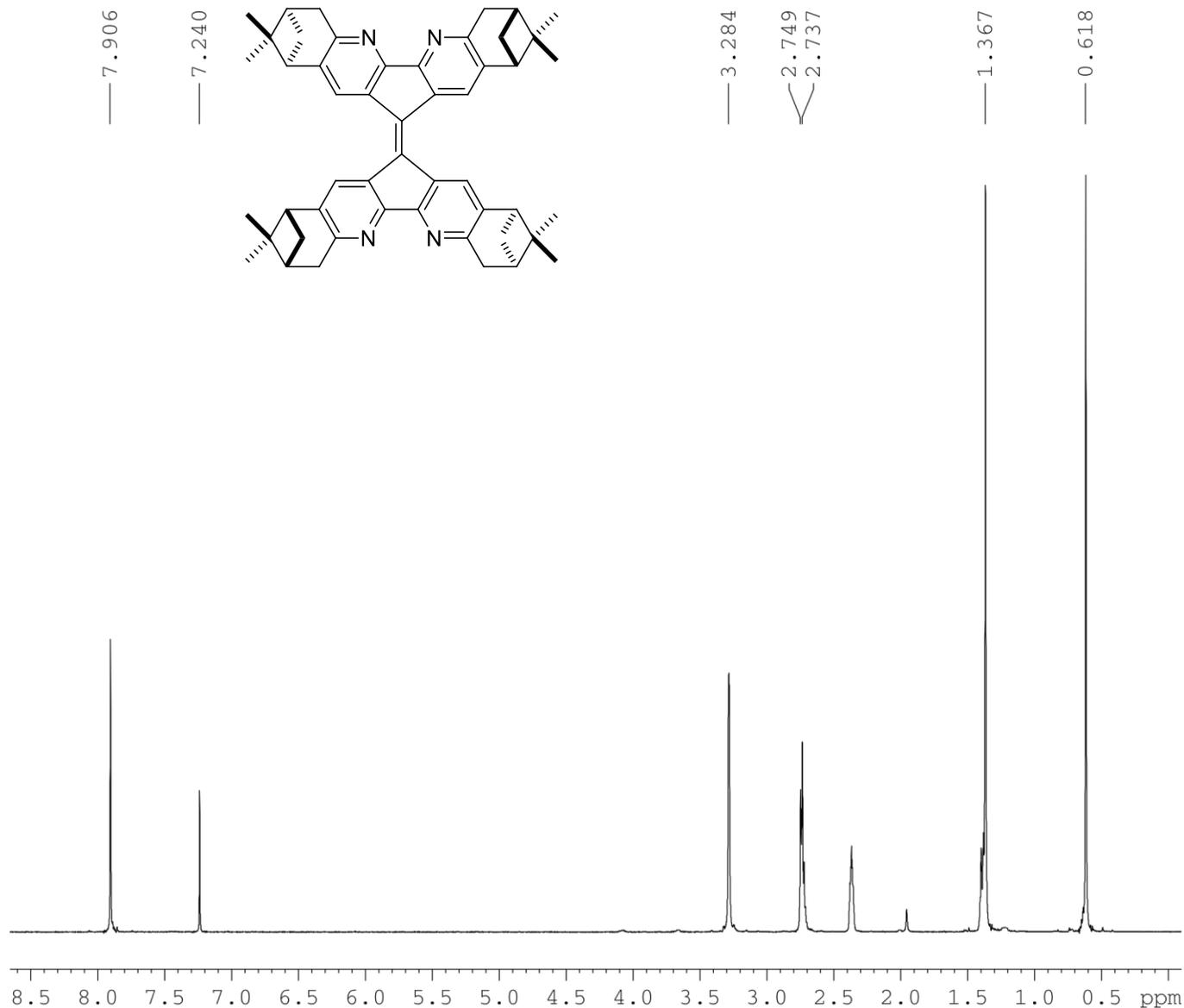
(1*R*,3*R*,8*R*,10*R*,1'*R*,3'*R*,8'*R*,10'*R*)-2,2,2',2',9,9,9',9'-octamethyl-1,1',2,2',3,3',4,4',7,7',8,8',9,9',10,10'-hexadecahydro-1,3:1',3':8,10:8',10'-tetramethano-12,12'-bi(cyclopenta[1,2-*b*:5,4-*b'*]diquinolinylidene)

Current Data Parameters
NAME tka-esvo308-2-1
EXPNO 1
PROCNO 1

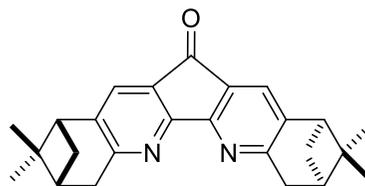
F2 - Acquisition Parameters
Date_ 20160411
Time 16.33
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 3
DS 2
SWH 10964.912 Hz
FIDRES 0.167311 Hz
AQ 2.9884915 sec
RG 128
DW 45.600 usec
DE 6.00 usec
TE 293.7 K
D1 5.00000000 sec
TD0 11111

==== CHANNEL f1 =====
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
SFO1 500.1347512 MHz

F2 - Processing parameters
SI 131072
SF 500.1300242 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00



(1R,3R,8R,10R)-2,2,9,9-tetramethyl-3,4,7,8,9,10-hexahydro-1H-1,3,8,10-dimethanocyclopenta[1,2-b:5,4-b']diquinolin-12(2H)-one



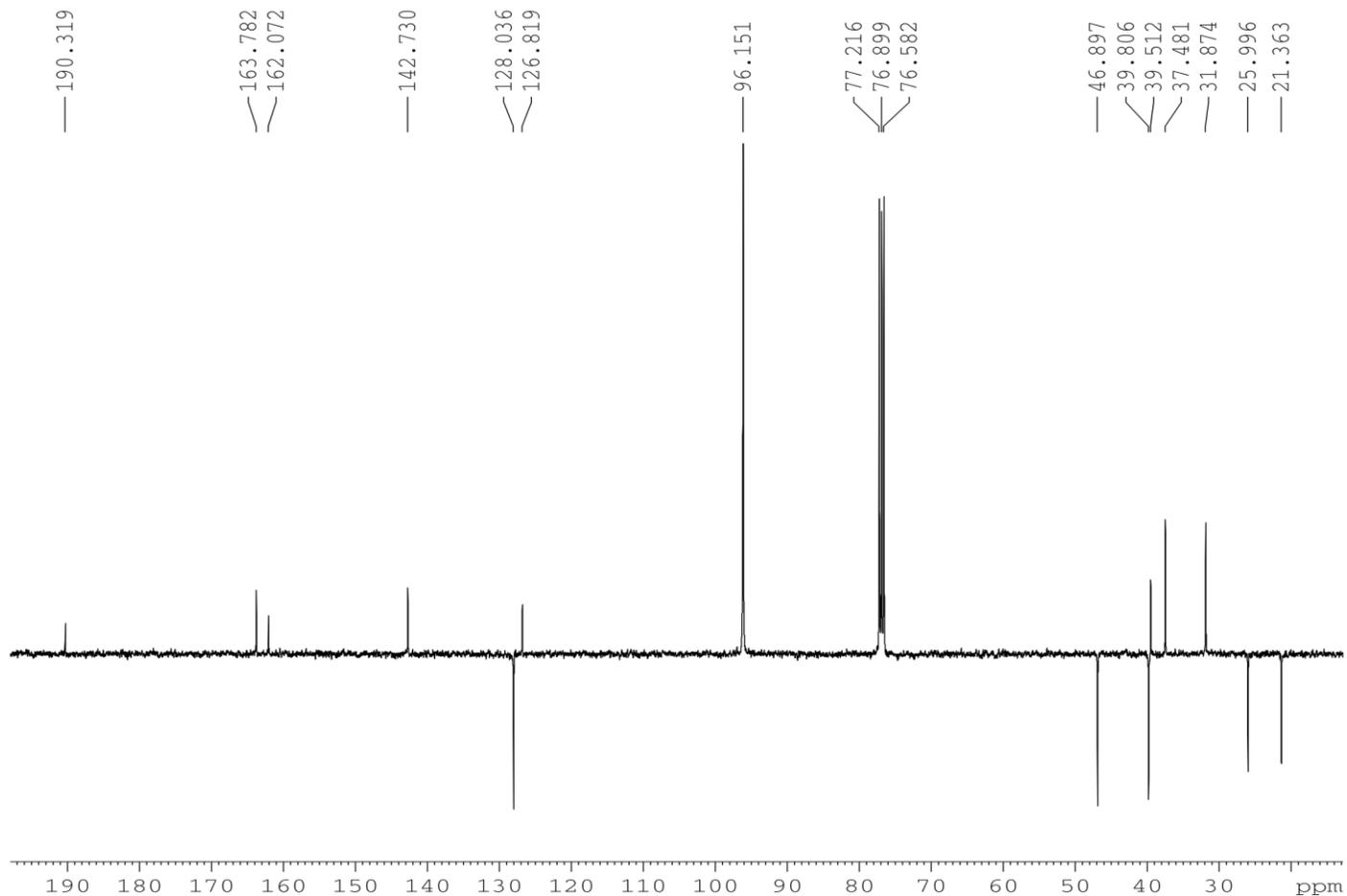
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Current Data Parameters
 NAME tka-esv-0310-1p
 EXPNO 137
 PROCNO 1

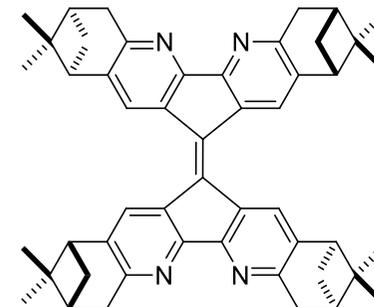
F2 - Acquisition Parameters
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 Time 17.50
 INSTRUM spect
 PROBHD 5 mm QNP 1H/13
 PULPROG jmod
 TD 65536
 SOLVENT CDC13
 NS 8144
 DS 2
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 203
 DW 20.800 usec
 DE 6.50 usec
 TE 294.6 K
 CNST2 145.0000000
 CNST11 1.0000000
 D1 5.0000000 sec
 D20 0.00689655 sec
 TD0 11111

==== CHANNEL f1 =====
 NUC1 13C
 P1 9.60 usec
 P2 19.20 usec
 PL1 0 dB
 PL1W 36.42235184 W
 SFO1 100.6243395 MHz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 86.00 usec
 PL2 0 dB
 PL12 16.00 dB
 PL2W 9.52005005 W
 PL12W 0.23913284 W



(1*R*,3*R*,8*R*,10*R*,1'*R*,3'*R*,8'*R*,10'*R*)-2,2,2',2',9,9,9',9'-octamethyl-1,1',2,2',3,3',4,4',7,7',8,8',9,9',10,10'-hexadecahydro-1,3:1',3':8,10:8',10'-tetramethano-12,12'-bi(cyclopenta[1,2-*b*:5,4-*b'*]diquinolinylidene)



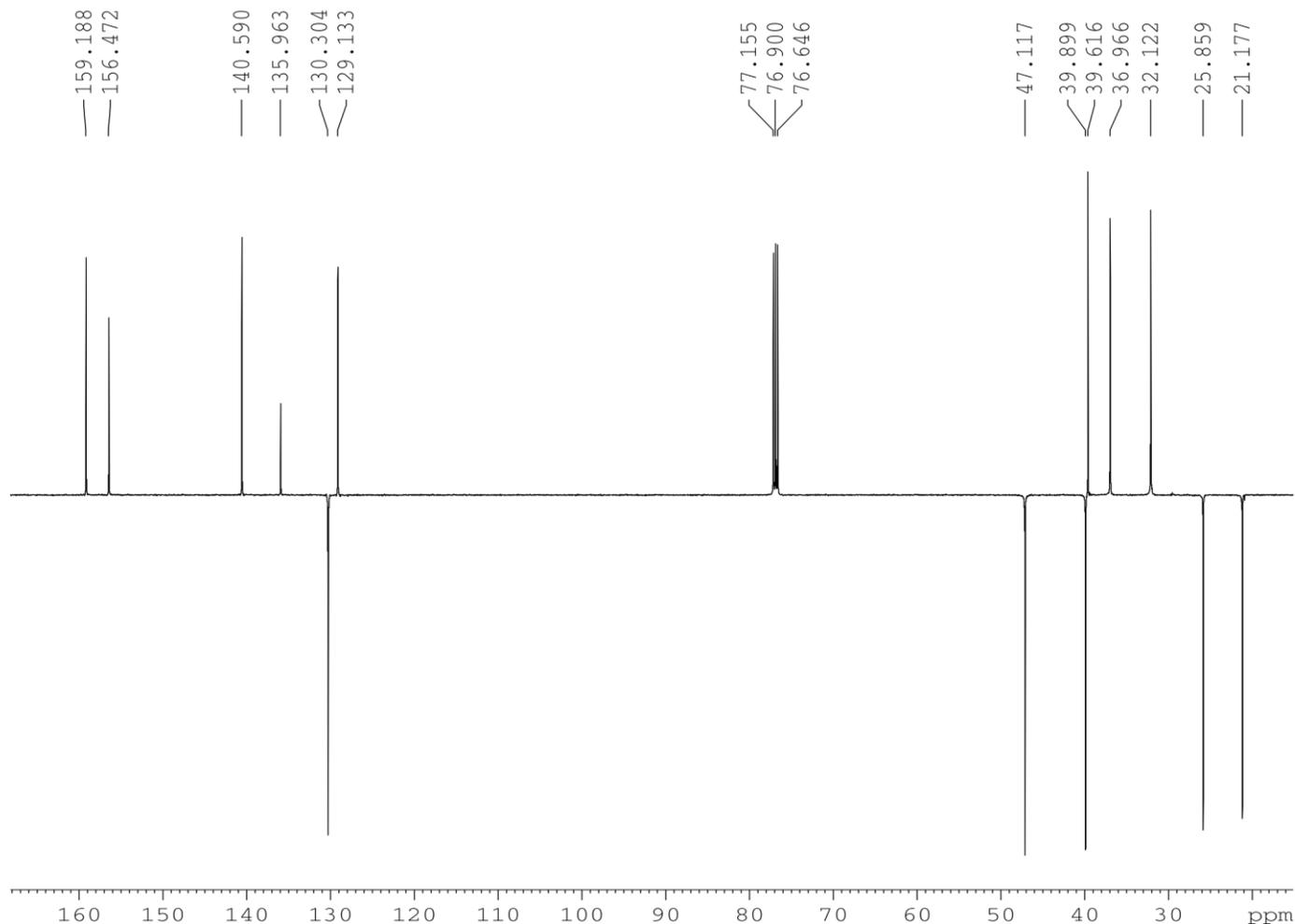
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Current Data Parameters
 NAME tka-esvo308-2-1
 EXPNO 137
 PROCNO 1

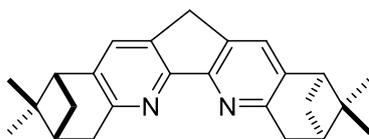
F2 - Acquisition Parameters
 Date_ 20160411
 Time 16.37
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG jmod
 TD 65536
 SOLVENT DMSO
 NS 10512
 DS 4
 SWH 30303.031 Hz
 FIDRES 0.462388 Hz
 AQ 1.0813940 sec
 RG 4096
 DW 16.500 usec
 DE 6.00 usec
 TE 294.4 K
 CNST2 145.0000000
 CNST11 1.0000000
 D1 4.00000000 sec
 d20 0.00689655 sec
 DELTA 0.00001184 sec
 TD0 11111

==== CHANNEL f1 =====
 NUC1 13C
 P1 9.30 usec
 p2 18.60 usec
 PL1 5.00 dB
 SFO1 125.7720754 MHz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 76.50 usec
 PL2 -3.00 dB
 PL12 13.00 dB
 SFO2 500.1320005 MHz



(1*R*,3*R*,8*R*,10*R*)-2,2,9,9-tetramethyl-2,3,4,7,8,9,10,12-octahydro-1*H*-1,3:8,10-dimethanocyclopenta[1,2-*b*:5,4-*b'*]diquinoline



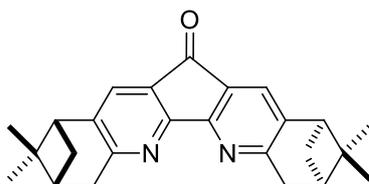
IR (1:150 w/w in KBr, $\nu_{\max}/\text{cm}^{-1}$): 2974, 2918, 1556, 1400, 1261, 1182, 1068.

NMR ^1H (400 MHz, $\text{CCl}_4\text{-CDCl}_3$ 1:1 v/v): δ = 0.65 (s, 6 H, H-8), 1.29 (d, J = 9.5 Hz, 2 H, *pro-R*-H-7), 1.40 (s, 6 H, H-9), 2.37 (ddt, J = 5.8, 5.3 and 3.0 Hz, 2 H, H-5), 2.68 (ddd, J = 9.5, 5.8 and 5.8 Hz, 2 H, *pro-S*-H-7), 2.77 (dd, J = 5.8 and 5.3 Hz, 2 H, H-1), 3.26 (d, J = 3.0 Hz, 4 H, H-4), 3.66 (s, 2 H, H-14) 7.31 (s, 2 H, H-10).

NMR ^{13}C (100 MHz, $\text{CCl}_4\text{-CDCl}_3$ 1:1 v/v): δ = 21.37 (C-8), 26.21 (C-9), 31.76 (C-7), 32.22 (C-14), 36.62 (C-4), 39.58 (C-6), 40.18 (C-5), 47.18 (C-1), 129.80 (C-10), 133.91 (C-11), 140.29 (C-2), 156.60 (C-12), 156.74 (C-3).

MS, m/z (EI, 70 eV, %): 356 (100), 341 (76), 327 (18), 313 (30), 297 (16), 269 (26), 257 (17).

(1*R*,3*R*,8*R*,10*R*)-2,2,9,9-tetramethyl-3,4,7,8,9,10-hexahydro-1*H*-1,3:8,10-dimethanocyclopenta[1,2-*b*:5,4-*b'*]diquinolin-12(2*H*)-one



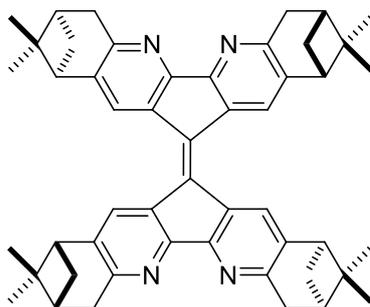
IR (1:150 w/w in KBr, $\nu_{\max}/\text{cm}^{-1}$): 2935, 2870, 1716, 1596, 1556, 1394, 1255, 792.

NMR ^1H (400 MHz, $\text{CCl}_4\text{-CDCl}_3$ 1:1 v/v): δ = 0.63 (s, 6 H, H-8), 1.23 (d, J = 9.6 Hz, 2 H, *pro-R*-H-7), 1.36 (s, 6 H, H-9), 2.32 (ddt, J = 5.9, 5.4 and 2.9 Hz, 2 H, H-5), 2.64 (ddd, J = 9.8, 5.9 and 5.9 Hz, 2 H, *pro-S*-H-7), 2.77 (dd, J = 5.9 and 5.4 Hz, 2 H, H-1), 3.24 (d, J = 2.9 Hz, 4 H, H-4), 7.36 (s, 2 H, H-10).

NMR ^{13}C (100 MHz, $\text{CCl}_4\text{-CDCl}_3$ 1:1 v/v): δ = 21.36 (C-8), 26.00 (C-9), 31.87 (C-7), 37.48 (C-4), 39.51 (C-6), 39.81 (C-5), 46.90 (C-1), 126.82 (C-11), 128.04 (C-10), 142.73 (C-2), 162.07 (C-12), 163.78 (C-3), 190.32 (C-14).

MS, m/z (EI, 70 eV, %): 370 (100), 355 (55), 341 (15), 329 (33), 327 (37), 311 (12), 297 (11), 283 (18), 271 (11).

(1*R*,3*R*,8*R*,10*R*,1'*R*,3'*R*,8'*R*,10'*R*)-2,2,2',2',9,9,9',9'-octamethyl-1,1',2,2',3,3',4,4',7,7',8,8',9,9',10,10'-hexadecahydro-1,3:1',3':8,10:8',10'-tetramethano-12,12'-bi(cyclopenta[1,2-*b*:5,4-*b'*]diquinolinylidene)



IR (1:150 w/w in KBr, $\nu_{\max}/\text{cm}^{-1}$): 2972, 2922, 1547, 1470, 1394, 1255, 1070.

^1H NMR (500 MHz, CDCl_3): δ = 0.62 (*s*, 12 H, H-8), 1.37 (*s*, 12 H, H-9), 1.39 (*m*, 4 H, *pro-R*-H-7), 2.37 (*m*, 4 H, H-5), 2.73 (*m*, 4 H, *pro-S*-H-7), 2.74 (*m*, 4 H, H-1), 3.28 (*m*, 4 H, H-4a), 3.29 (*m*, 4 H, H-4b), 7.91 (*s*, 4 H, H-10). Spin-spin couplings calculated from the second-order spectrum: $J(\text{H-1}, \text{H-5}) = 5.4$ Hz, $J(\text{H-1}, \textit{pro-S}\text{-H-7}) = 5.2$ Hz, $J(\text{H-4a}, \text{H-4b}) = -18.1$ Hz, $J(\text{H-4a}, \text{H-5}) = 2.7$ Hz, $J(\text{H-4b}, \text{H-5}) = 3.1$ Hz, $J(\text{H-5}, \textit{pro-S}\text{-H-7}) = 6.6$ Hz, $J(\text{H-7-S}, \textit{pro-R}\text{-H-7}) = -9.2$ Hz.

^{13}C NMR (125 MHz, CDCl_3): δ = 21.18 (C-8), 25.86 (C-9), 32.12 (C-7), 36.96 (C-4), 39.61 (C-6), 39.90 (C-5), 47.12 (C-1), 129.13 (C-11), 130.30 (C-10), 135.96 (C-14), 140.59 (C-2), 156.47 (C-12), 159.19 (C-3).

MS, m/z (EI, 70 eV, %): 708 (100), 693 (21), 370 (23), 356 (35), 265 (37), 250 (59), 224 (47), 222 (33), 180 (35).