Electronic Supplementary Material (ESI) for RSC Advances.

Synthesis of Indeno-[1,2-b]-quinoline-9,11(6H,10H)-dione and 7,7-Dimethyl-10-aryl-7,8-dihydro-5H-indeno[1,2-b]quinoline-9,11(6H,10H)-dione derivatives in presence of heterogeneous Cu/Zeolite-Y as a catalyst

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Index:

A plausible mechanism for the synthesis 7,7-dimethyl-10-aryl-7,8-dihydro-5H-indeno[1,2-b]quinoline-9,11(6H,10H)-dione derivatives

Copies of FT-IR, ^{1}H NMR, ^{13}C NMR, and, Mass spectra.

Table S1 Comparison of the catalytic efficiency of Cu/zeolite-Y with previously reported catalysts for the synthesis of indenoquinoline derivatives via multi-component reactions

Material methods

All chemicals were purchased and used further purification, unless otherwise noted. All products were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR spectra and mass spectrometry.

X-ray diffraction (XRD) patterns of the prepared catalysts were retrieved using PANanalytical X'pert Pro dual goniometer diffractometer working under 40 kV and 30 mA with Cu Kα radiation in 2θ range of 10-90^{o}. Collection of the data was carried out using a flat holder in Bragg–Brentano geometry with 1 slit at the source and receiving sides each. An X'celerator solid-state detector was employed with a scan speed of 0.02^{o}min^{-1}.

X-Ray photoelectron spectroscopy (XPS) data were collected on a VG Scientific ESCA-3000 spectrometer using a non-monochromatised Mg Kα radiation (1253.6 eV) at a pressure of about 1× 10^{-9} Torr (pass energy of 50 eV, electron takeoff angle 55) and overall resolution ~0.7 eV determined from the full width at half maximum of the 4f $_{7/2}$ core level of the gold surface. The error in the binding energy values was within 0.1 eV. The binding energy values were charge-corrected to the C1s signal (285.0 eV).

HR-TEM images of the catalyst were obtained using transmission electron microscope model, JEOL 1200 EX. For the analysis, a small amount of the solid sample was sonicated in 2-propanol for 10-15 min. A drop of the formed suspension was deposited on a Cu grid, coated with a carbon layer and the grid was then dried at room temperature before analysis. Morphology of catalysts was studied by scanning electron microscopy (SEM) as well as EDX analysis was performed on LEO−LEICA STEREOSCAN 440 for the presence of Cu loading. Surface area and BJH pore size distribution was calculated in Quantachrome NovaWin ©1994-2012, Quantachrome Instruments v11.02.

General procedure for the synthesis of 5H-Indeno[1,2-b]quinoline-9, 11(6H, 10H)-dione derivatives by Cu/Zeolite-Y as the heterogeneous catalyst

A solution of an aromatic aldehyde (1 mmol), dimedone (1 mmol), 1.3-indandione (1 mmol), aniline derivative (1 mmol), and Cu/Zeolite-Y (0.012 g) was stirred in ethanol (5 ml) under refluxing conditions for an appropriate time. After completion of the reaction, which was monitored by TLC (Petroleum ether: Ethyl acetate), the catalyst was filtered off, and the solvent was evaporated under reduced pressure. The resulting crude product was purified by recrystallization by methanol.

General procedure for the synthesis of 7,7-dimethyl-10-aryl-7,8-dihydro-5H-indeno[1,2-b]quinoline-9,11(6H,10H)-diones derivatives by Cu/Zeolite-Y as the heterogeneous catalyst

A solution of an aromatic aldehyde (1 mmol), dimedone (1 mmol), 1, 3-indandione (1 mmol), ammonium acetate (1 mmol), and Cu/Zeolite-Y (0.012 g) was stirred in ethanol (5 ml) under refluxing conditions for an appropriate time. After completion of the reaction, which was monitored by TLC (Petroleum ether: Ethyl acetate), the catalyst was filtered off, and the solvent was evaporated under reduced pressure. The resulting crude product was purified by recrystallization by methanol.

Spectral data of representative compound:

7,7-dimethyl-10-(3-nitrophenyl)-5-(p-tolyl)-7,8-dihydro-5H-indeno[1,2-b]quinoline-9,11(6H,10H)-dione (5a).

Red Solid, M.P.: 242-244 °C [242-244 °C]; FT-IR (KBr, ν): 3738, 2952, 1685, 1635, 1592, 1511, 1456, 1351, 1223, 1180, 1101, 1055, 1013, 977, 940, 887, 829, 754, 692, 626 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): 0.80 (s, 3H, -CH_3) , 0.94 (s, 3H, -CH_3), 2.01-2.08 (q, 2H, -CH_2), 2.25-2.42 (dd, 2H, - CH_2), 2.5 (s, 3H, -CH_3), 4.98 (s, 1H, -CH), 7.01-7.05 (t, 1H, ArH), 7.18-7.24 (m, 3H, ArH), 7.50-7.58 (m, 4H, ArH), 7.65-7.67 (dd, 2H, ArH), 8.13-8.15 (dd, 2H, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz): 20.9, 26.1, 29.1, 31.8, 33.8, 49.3, 110.2, 113.7, 120.9, 123.3, 129.1, 129.9, 131.9, 132.7, 135.3, 136.5, 140.2, 145.9, 151.8,152.8, 154.8, 190.7, 195.3 ppm

10-(4-chlorophenyl)-7,7-dimethyl-5-(p-tolyl)-7,8-dihydro-5H-indeno[1,2-b]quinoline-9,11(6H,10H)-dione (5b).

Red Solid, M.P.: 293-294 °C [291-293 °C]; FT-IR (KBr, ν): 3741, 2932, 1682, 1630, 1558, 1512, 1392, 1361, 1252, 1221, 1167, 1098, 1013, 974, 935, 885, 840, 760, 733, 696, 637, 587 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): 0.89 (s, 3H, -CH_3) , 1.00 (s, 3H, -CH_3), 2.03-2.07 (q, 2H, -CH_2), 2.15-2.27 (q, 2H, -CH_2), 2.56 (s, 3H, -CH_3), 5.07 (s, 1H, -CH), 6.85-6.89 (t, 1H, ArH), 7.05-7.09 (m,

3H, ArH), 7.21-7.26 (m, 4H, ArH), 7.28-7.36 (dd, 2H, ArH), 7.37-7.41 (dd, 2H, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz): 21.5, 26.8, 29.7, 32.3, 33.2, 41.0, 50.1, 112.5, 115.5, 120.7, 121.3, 128.4, 129.3, 131.4, 132.0, 135.9, 137.2, 140.6, 144.0, 150.8,154.4, 191.9, 196.0 ppm

GC-MS: m/z = 479 (M-H)

7,7-dimethyl-10-(4-nitrophenyl)-5-(p-tolyl)-7,8-dihydro-5H-indeno[1,2-b]quinoline-9,11(6H,10H)-dione (5c).

Red Solid, M.P.: 290-292 °C [290-292 °C]; FT-IR (KBr, ν): 3740, 2950, 1702, 1633, 1522, 1460, 1352, 1254, 1178, 1098, 1054, 1014, 942, 887, 828, 754, 707, 626 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): 0.80 (s, 3H, -CH_3) , 0.94 (s, 3H, -CH_3), 2.00-2.07 (q, 2H, -CH_2), 2.25-2.42 (dd, 2H, -CH_2), 2.5 (s, 3H, -CH_3), 4.98 (s, 1H, -CH), 7.01-7.05 (t, 1H, ArH), 7.18-7.24 (m, 3H, ArH), 7.50 (m, 3H, ArH), 7.55 (m, 1H, ArH), 7.65-7.67 (dd, 2H, ArH), 8.13-8.15 (dd, 2H, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz): 20.9, 26.1, 29.1, 31.8, 33.8, 49.3, 110.2, 113.7, 120.9, 123.4, 129.1, 129.9, 131.9, 132.7, 135.3, 136.5, 140.2, 145.9, 151.8,152.8, 154.8 190.7, 195.3 ppm; GC-MS: m/z = 490 (M-H)

10-(4-methoxyphenyl)-7,7-dimethyl-5-(p-tolyl)-7,8-dihydro-5H-indeno[1,2-b]quinoline-9,11(6H,10H)-dione (5d).

Red Solid, M.P.: 248-250 °C [250-251 °C]; FT-IR (KBr, ν): 3741, 2954, 2928, 1686, 1642, 1557, 1506, 1455, 1392, 1362, 1252, 1167, 1096, 1032, 973, 931, 885, 830, 759, 704 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): 0.80 (s, 3H, -CH_3) , 0.93 (s, 3H, -CH_3), 1.96-2.05 (q, 2H, -CH_2), 2.23-2.42 (dd, 2H, -CH_2), 2.5 (s, 3H, -CH_3), 3.7 (s, 3H, -OCH_3), 4.80 (s, 1H, -CH), 6.80-6.84 (dd, 2H, ArH), 6.98-7.02 (t, 2H, ArH), 7.15-7.20 (m, 2H, ArH), 7.22-7.28 (m, 2H, ArH), 7.46-7.48 (dd, 2H, ArH), 7.53-7.55 (dd, 2H, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz): 20.9, 25.9, 29.3, 31.7, 32.2, 49.5, 54.9, 111.8, 113.5, 114.8, 120.5, 120.7, 128.6, 129.6, 131.7, 132.9, 135.5, 136.8, 137.9, 140.0, 150.6, 154.1, 157.6, 191.0, 195.3 ppm

10-(4-bromophenyl)-7,7-dimethyl-5-(p-tolyl)-7,8-dihydro-5H-indeno[1,2-b]quinoline-9,11(6H,10H)-dione (5e).

Red Solid, M.P.: 228-229 °C [229-230 °C]; FT-IR (KBr, ν): 3742, 2956, 2932, 1690, 1640, 1575, 1556, 1512, 1434, 1393, 1363, 1253, 1220, 1189, 1098, 1054, 1012, 972, 933, 886, 839, 788, 761, 726, 694, 679, 636, 584 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): 0.80 (s, 3H, -CH_3) , 0.93 (s, 3H, -CH_3), 1.97-2.07 (q, 2H, -CH_2), 2.24-2.41 (dd, 2H, -CH_2), 2.5 (s, 3H, -CH_3), 4.83 (s, 1H, -CH), 7.00-7.04 (t, 1H, ArH), 7.17-7.24 (m, 4H, ArH), 7.31-7.34 (dd, 3H, ArH), 7.43-7.49 (m, 4H, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz): 20.8,

26.0, 29.2, 31.8, 32.9, 49.3, 110.9, 114.2, 119.2, 120.7, 120.8 129.8, 130.0, 130.9, 131.8, 132.8, 135.3, 136.7, 140.1, 144.9, 151.2, 154.5, 195.3 ppm

10-(4-Fluorophenyl)-7,8-dihydro-7,7-dimethyl-5-(p-tolyl)-5H-indeno[1,2-b]quinoline-9,11-(6H,10H)-dione (5f).

Red Solid, M.P.: 224-226 °C [225-227 °C]; ^{1}H NMR (DMSO-d_6, 400 MHz): 0.89 (s, 3H, -CH_3) , 1.0 (s, 3H, -CH_3), 2.03-2.07 (q, 2H, -CH_2), 2.15-2.28 (m, 2H, -CH_2), 2.5 (s, 3H, -CH_3), 5.1 (s, 1H, -CH), 6.85-6.97 (m, 1H, ArH), 7.07-7.11 (m, 2H, ArH), 7.26-7.31 (m, 2H, ArH), 7.31-7.39 (m, 3H, ArH), 7.39-7.42 (m, 4H, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz): 21.5, 26.8, 29.7, 32.2, 32.9, 41.0, 50.1, 112.9, 114.9, 115.1, 115.8, 120.7, 121.3, 129.3, 129.4, 131.3, 133.5, 136.0, 137.2, 140.5, 141.2, 141.3, 150.6, 154.2, 162.6, 192.0, 196.0 ppm

10-(3,4-dihydroxyphenyl)-7,7-dimethyl-5-(p-tolyl)-7,8-dihydro-5H-indeno[1,2-b]quinoline-9,11(6H,10H)-dione(5g)

Red Solid, M.P.: 283-284 °C [-];^{1}H NMR (DMSO-d_6, 400 MHz): 0.78 (s, 3H, -CH_3), 0.90 (d, 3H, -CH_3), 1.91-2.21 (m, 4H, 2-CH_2), 2.45-2.47 (m, 4H, -CH_2), 2.5 (s, 3H, -CH_3), 4.71 (s, 1H, -OH), 6.57-6.58 (m, 2H, ArH), 6.78-6.82 (dd, 2H, ArH), 6.97-7.01 (m, 1H, ArH), 7.10-7.12 (m, 1H, ArH), 7.26-7.31 (m, 4H, ArH), 7.66-7.67 (dd, 2H, ArH), 8.0 (s, 1H, -OH), 8.24 (s, 1H, -OH); ^{13}C NMR (DMSO-d_6, 100 MHz): 26.2, 31.4, 34.5, 36.9, 37.2, 54.9, 117.7, 120.1, 120.2, 120.6, 123.7, 125.5, 133.9, 135.6, 136.3, 138.2, 140.5, 142.1, 145.2, 148.3, 149.4, 155.2, 159.0, 196.7, 200.8 ppm

7,7-Dimethyl-10-(4-nitrophenyl)-7,8-dihydro-5H-indeno[1,2-b]quinoline-9,11(6H,10H)-dione (6a)

Red Solid, M.P.: 215-216 °C [215-217 °C]; FT-IR (KBr, ν): 3740, 3074, 1711, 1610, 1576, 1529, 1347, 1309, 1258, 1172, 1092, 1005, 883, 820, 752, 712, 672, 629 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): 0.86 (s, 3H, -CH_3), 1.08 (s, 3H, -CH_3), 1.98-2.46 (m, 2H, -CH_2), 2.60-2.70 (q, 2H, -CH_2), 4.88 (s, 1H, -CH), 7.25-7.27 (d, 1H, ArH), 7.33-7.37 (t, 1H, ArH), 7.42-7.50 (m, 1H, ArH), 7.50-7.55 (m, 1H, ArH), 7.59-7.63 (m, 1H, ArH), 7.70-7.72 (m, 1H, ArH), 7.93-8.01 (m, 2H, ArH), 10.57 (s, 1H, -NH); ^{13}C NMR (DMSO-d_6, 100 MHz): 26.3, 26.7, 28.6, 29.0, 32.1, 33.4, 34.0, 50.0, 50.1, 108.8, 110.5, 112.2, 119.4, 120.7, 121.0, 121.9, 129.1, 129.5, 130.3, 132.0, 132.7, 134.4, 135.9, 147.5, 148.0, 149.1, 150.0, 151.0, 154.0 ppm; GC-MS: m/z = 400 (M-H)

7,7-Dimethyl-10-(4-bromophenyl)-7,8-dihydro-5H-indeno[1,2-b]quinoline-9,11(6H,10H)-dione (6b)

Red Solid, M.P.: 316-318 °C [316-318 °C]; ^{1}H NMR (DMSO-d_6, 400 MHz): 0.97 (s, 3H, -CH_3), 1.04 (s, 3H, -CH_3), 2.04-2.18 (q, 2H, -CH_2), 2.7 (m, 2H, -CH_2), 4.7 (s, 1H, -CH), 7.11-7.28 (m, 6H, ArH), 7.42-7.44 (d, 1H, ArH), 7.77-7.83 (d, 1H, ArH), 10.11 (s, 1H, -NH); ^{13}C NMR (DMSO-d_6, 100 MHz): 27.5, 29.1, 32.5, 33.8, 40.8, 50.8, 110.3, 113.5, 119.2, 119.5, 120.8, 130.0, 131.0, 131.7, 133.4, 136.6, 145.4, 150.6, 154.2, 191.8, 195.5 ppm.

7,7-Dimethyl-10-(4-chlorophenyl)-7,8-dihydro-5H-indeno[1,2-b]quinoline-9,11(6H,10H)-dione (6c)

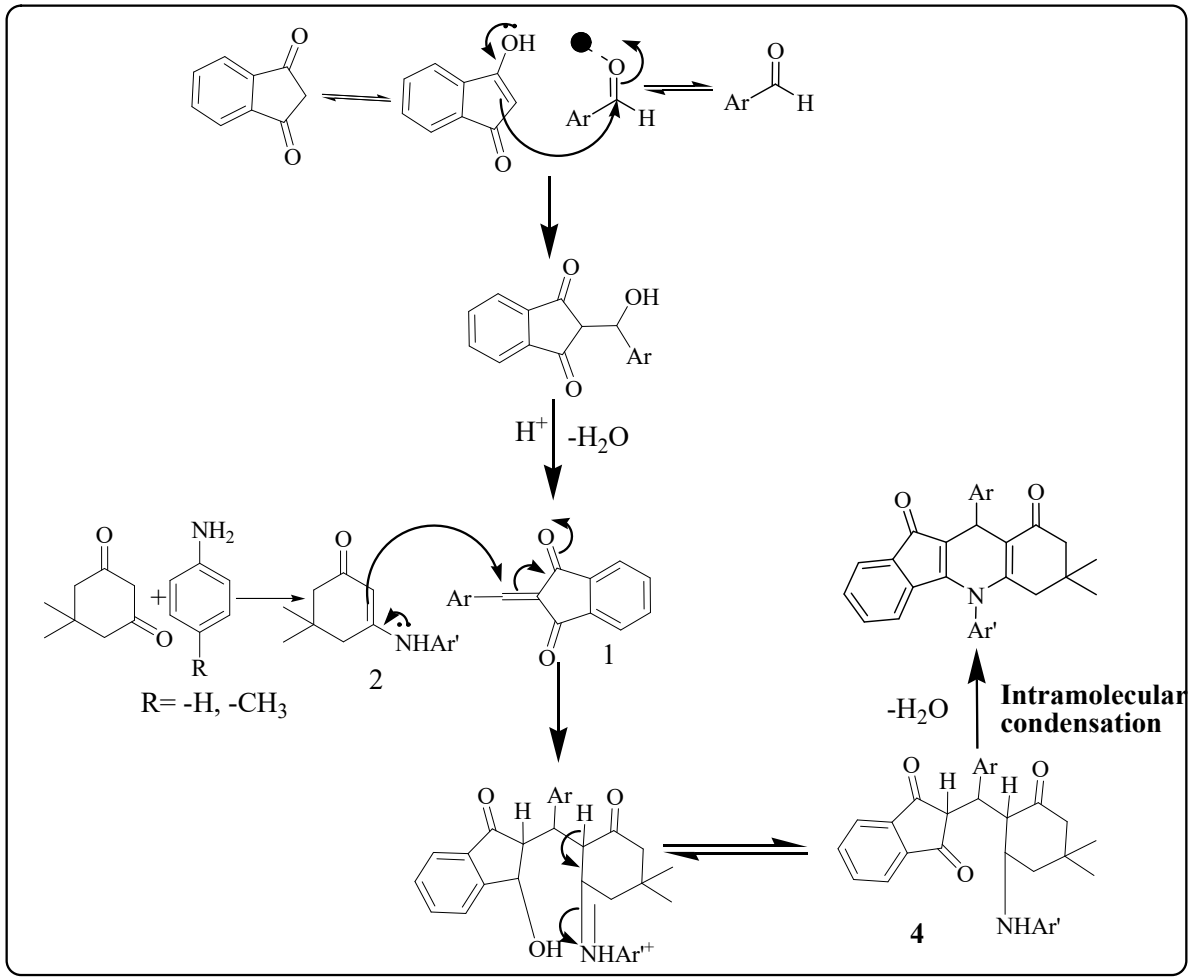
Red Solid, M.P.: 310-311 °C [312-313 °C]; ^{1}H NMR (DMSO-d_6, 400 MHz): 0.84 (s, 2H, -CH_3), 1.03 (s, 1H), 1.94-2.10 (m, 2H, -CH_2), 2.14-2.49 (m, 2H, -CH_2), 4.72-4.79 (s, 1H, -CH), 7.02-7.18 (m, 7H, ArH), 7.24-7.27 (t, 1H, ArH), 7.41-7.43 (d, 1H, ArH), 10.1 (s, 1H, -NH) ppm; GC-MS: m/z = 389 (M-H)

7,7-Dimethyl-10-(4-methoxyphenyl)-7,8-dihydro-5H-indeno[1,2-b]quinoline-9,11(6H,10H)-dione (6d)

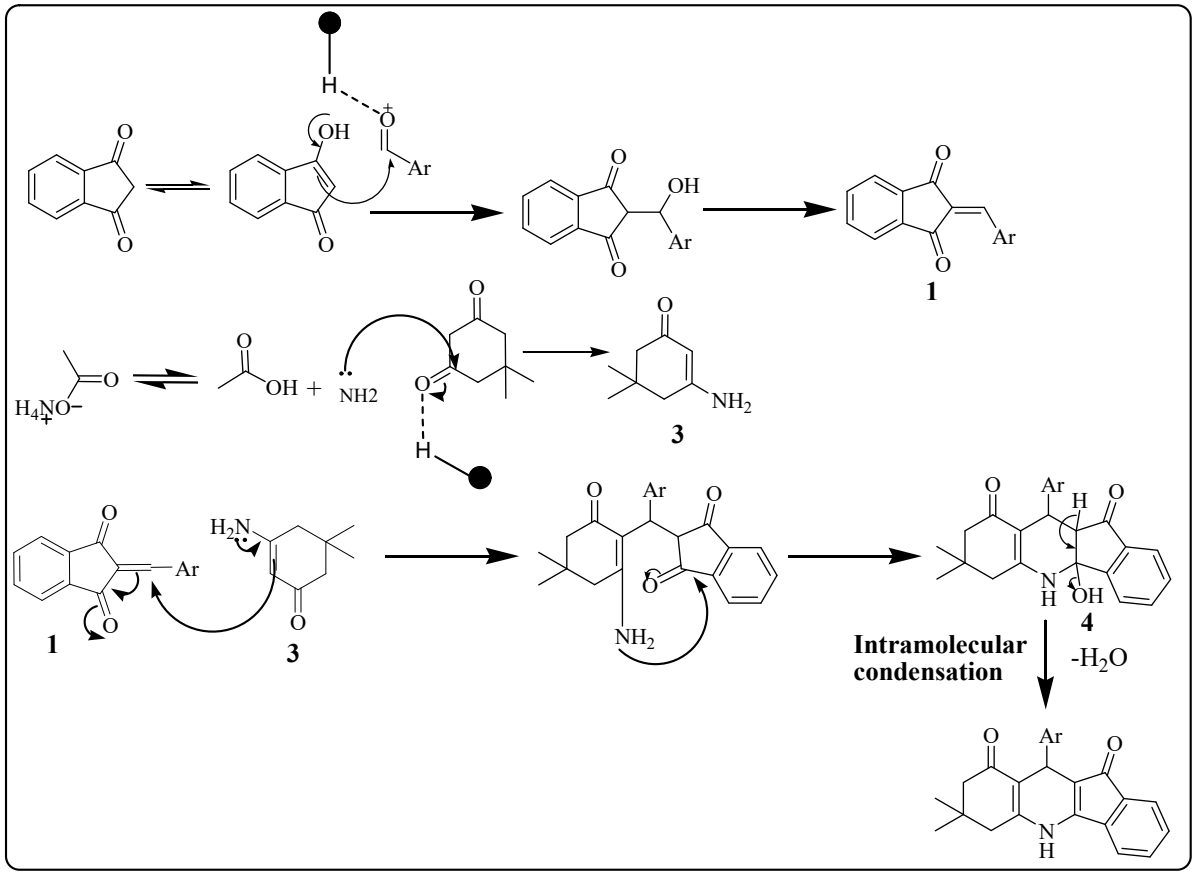
Red Solid, M.P.: 301-302 °C [300-301 °C]; GC-MS: m/z = 385 (M-H)

Plausible reaction mechanism

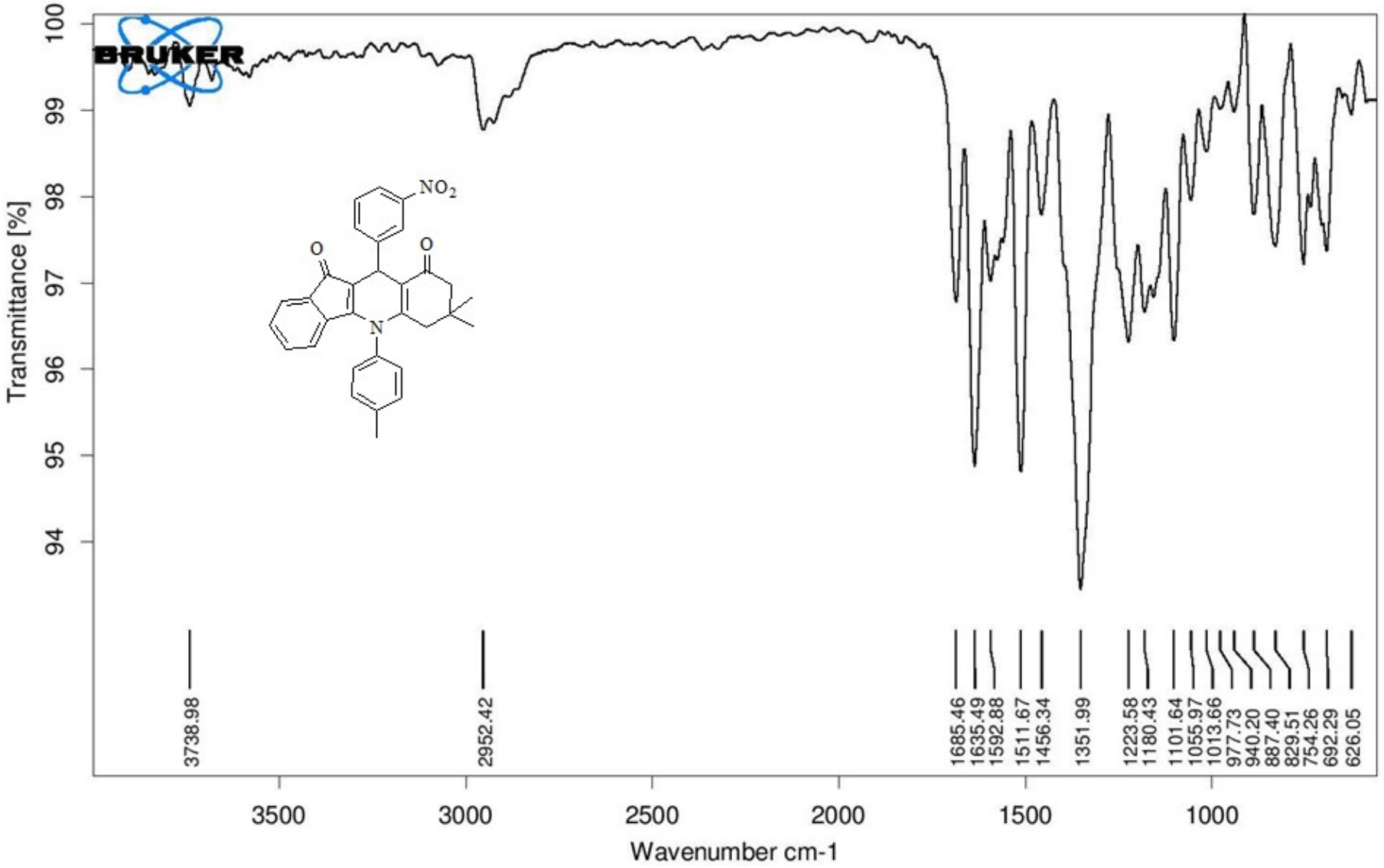
For the synthesis of Indeno-[1,2-b]-quinoline-9,11-(6H, 10H)-dione derivatives, we have used heterogeneous Cu/Zeolite-Y catalyst which was crucial role for the reaction. It acts as acidic nature. Support zeolite-Y shows BrØnsted acidic nature and CuO shows lewis acid in nature. Primarily, reaction of enol form of 1,3-indandione and substituted aromatic aldehyde forms aldol product which on dehydration forms olefinic intermediate (1). In second part, dimedone reacts with p-toluidine forms intermediate (2) or reaction of dimedone with ammonium acetate gives intermediate (3). After that the intermediates (1, 2) or (1, 3) reacts with each other followed by intramolecular dehydration reaction takes place and final product of reaction obtained.



Scheme 3 Plausible mechanism for the heterogeneous Cu/Zeolite-Y catalyzed formation of Indeno-[1,2-b]-quinoline-9,11-(6H, 10H)-dione derivatives



Scheme 4 Plausible mechanism for the heterogeneous Cu/Zeolite-Y catalyzed formation of 7,7-dimethyl-10-aryl-7, 8-dihydro-5H-indeno-[1,2-b]-quinoline-9,11(6H,10H)-diones derivatives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1013.66
977.73
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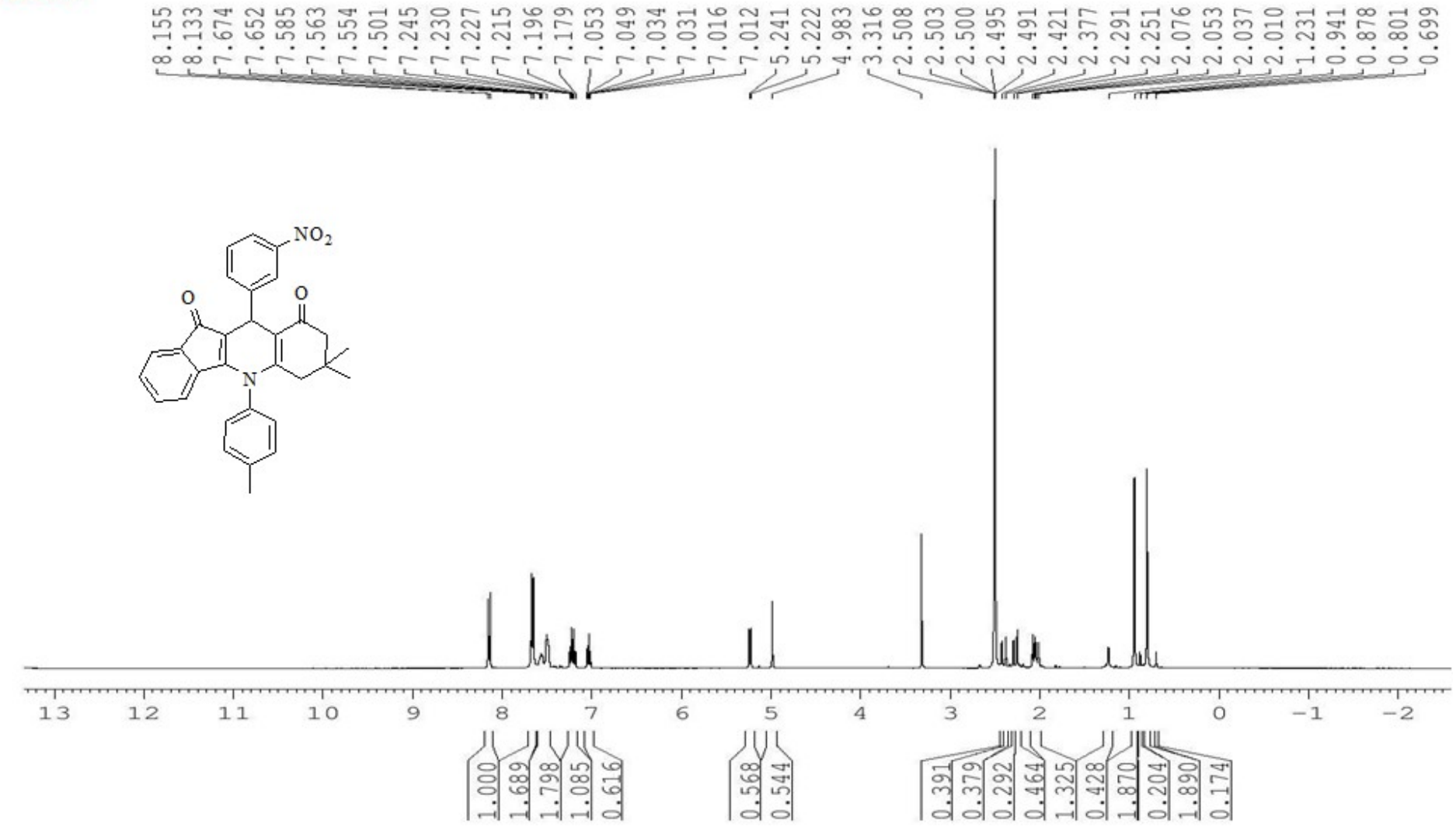
Wavenumber cm-1

FT-IR (5a)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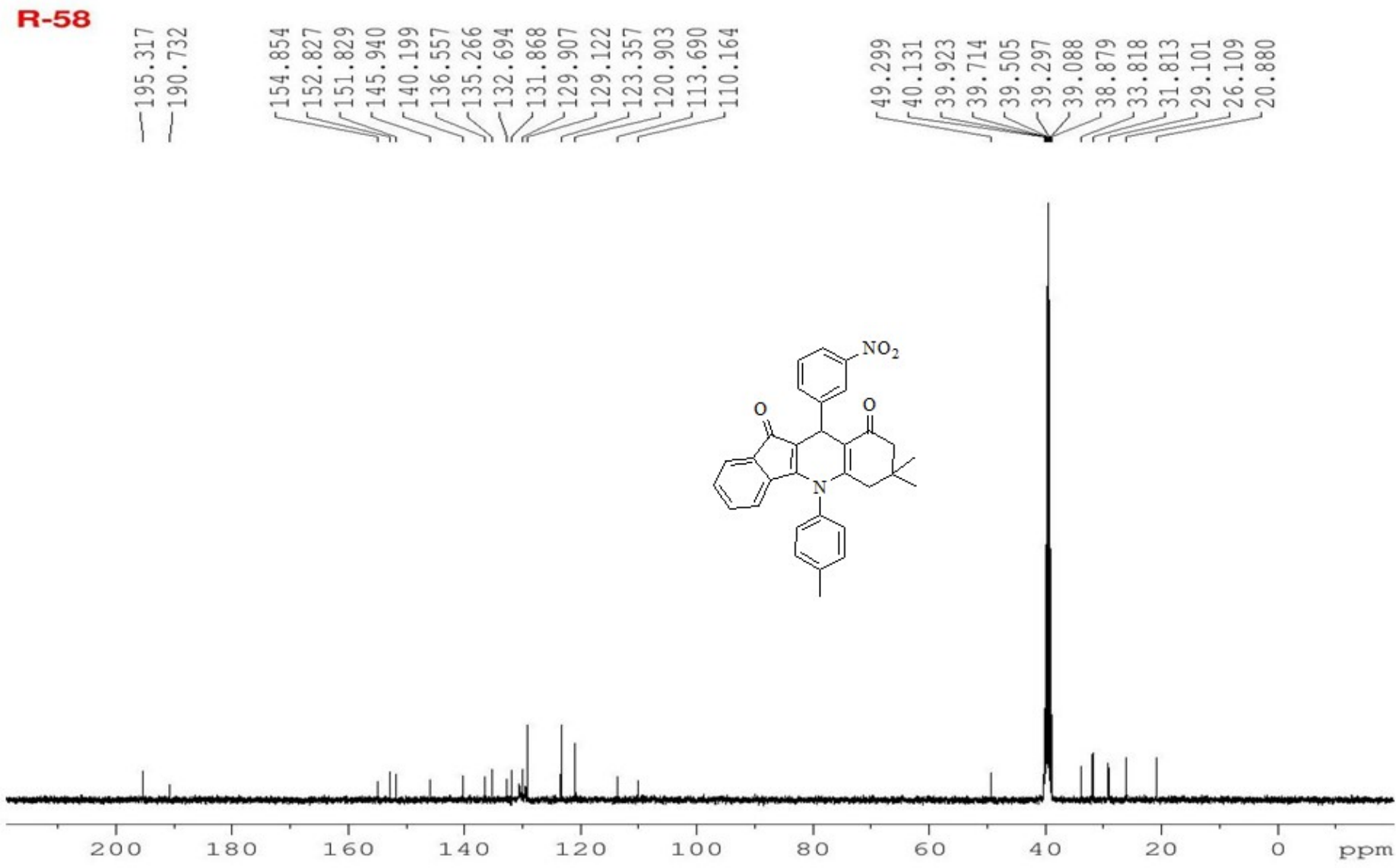
^{1}H NMR (5a)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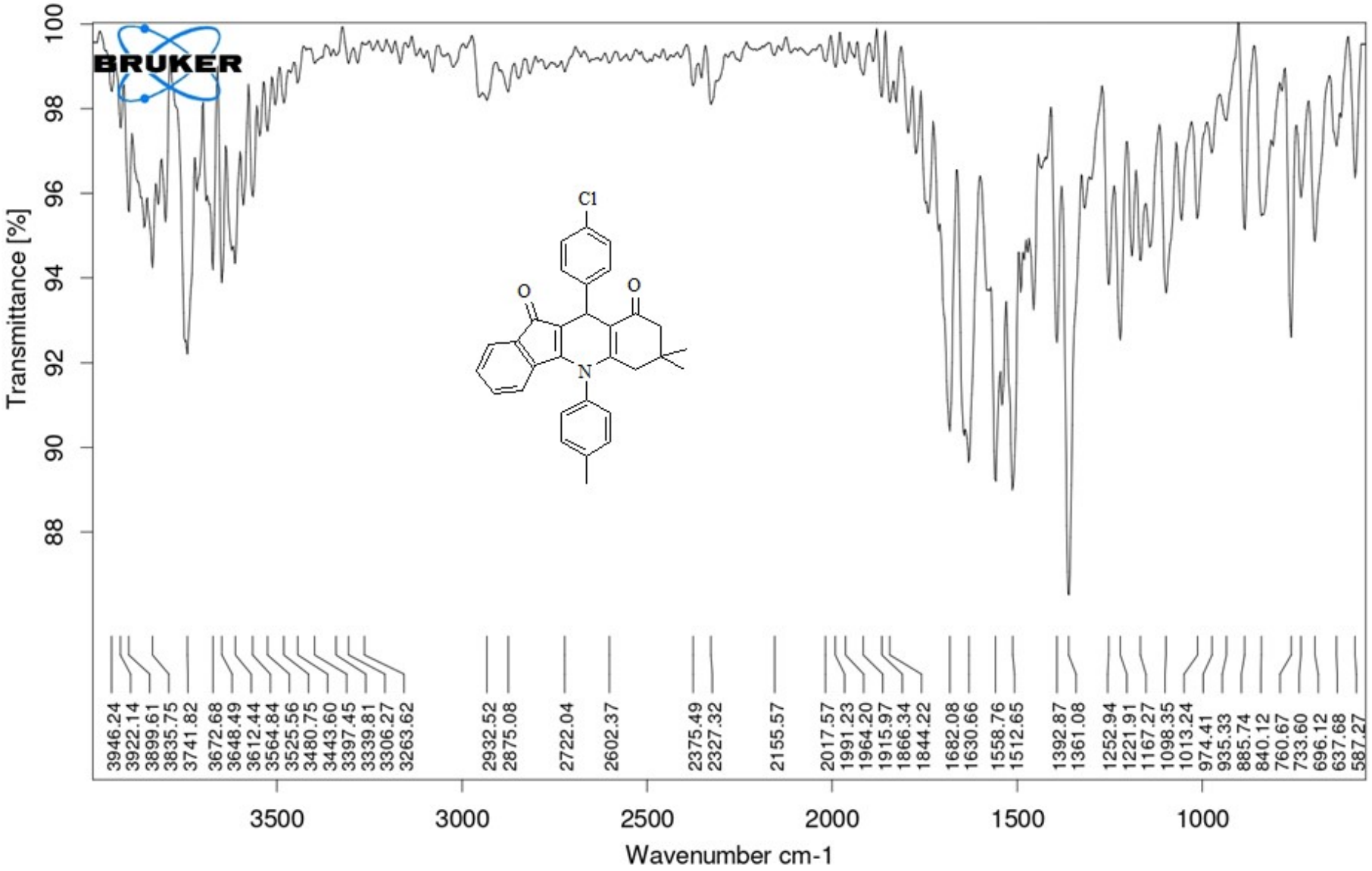
^{13}C NMR (5a)


BRUKER
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1167.27
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935.33
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1500
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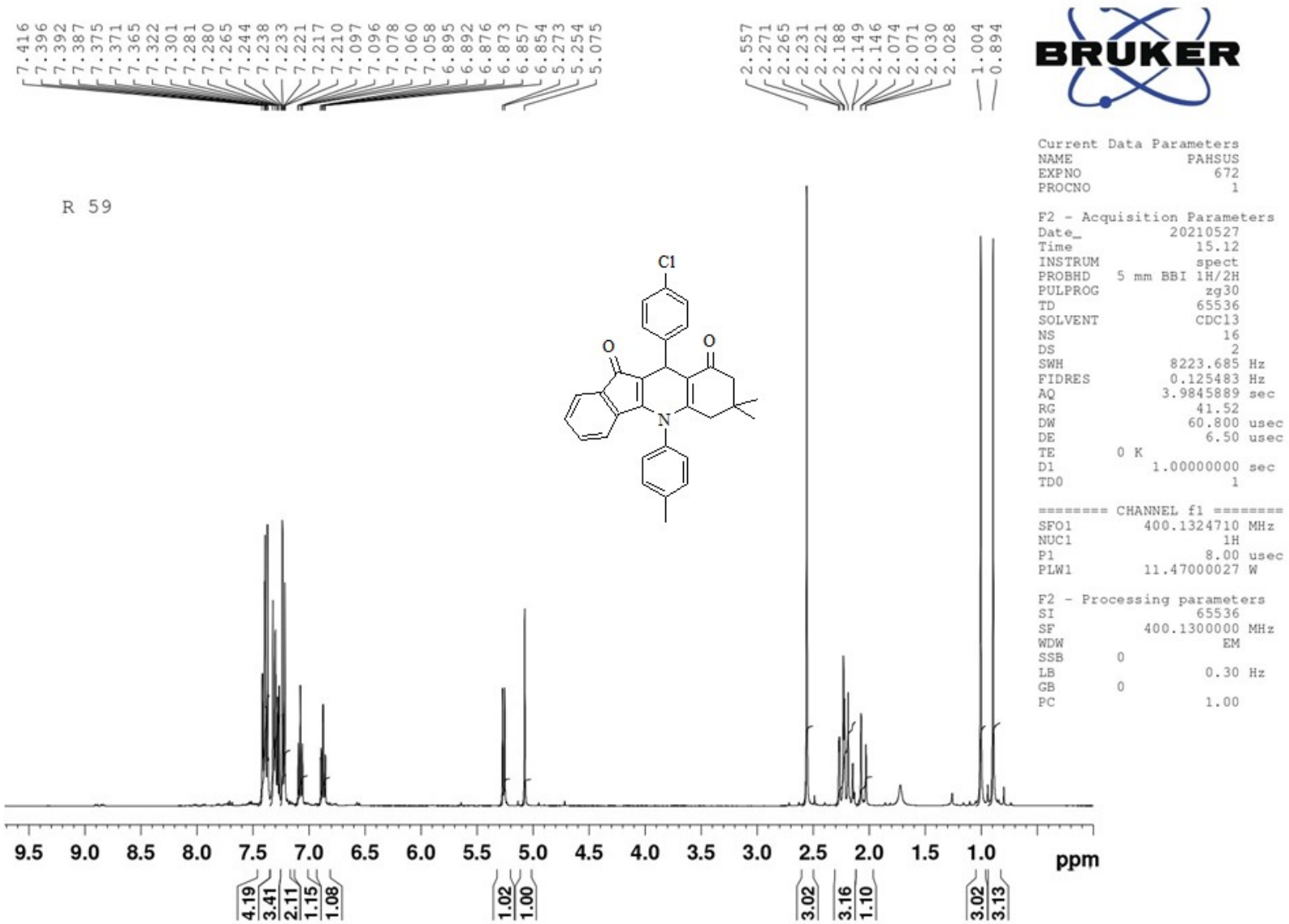
Wavenumber cm-1

FT-IR (5b)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6.873
6.857
6.854
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2.557
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R 59
Cl
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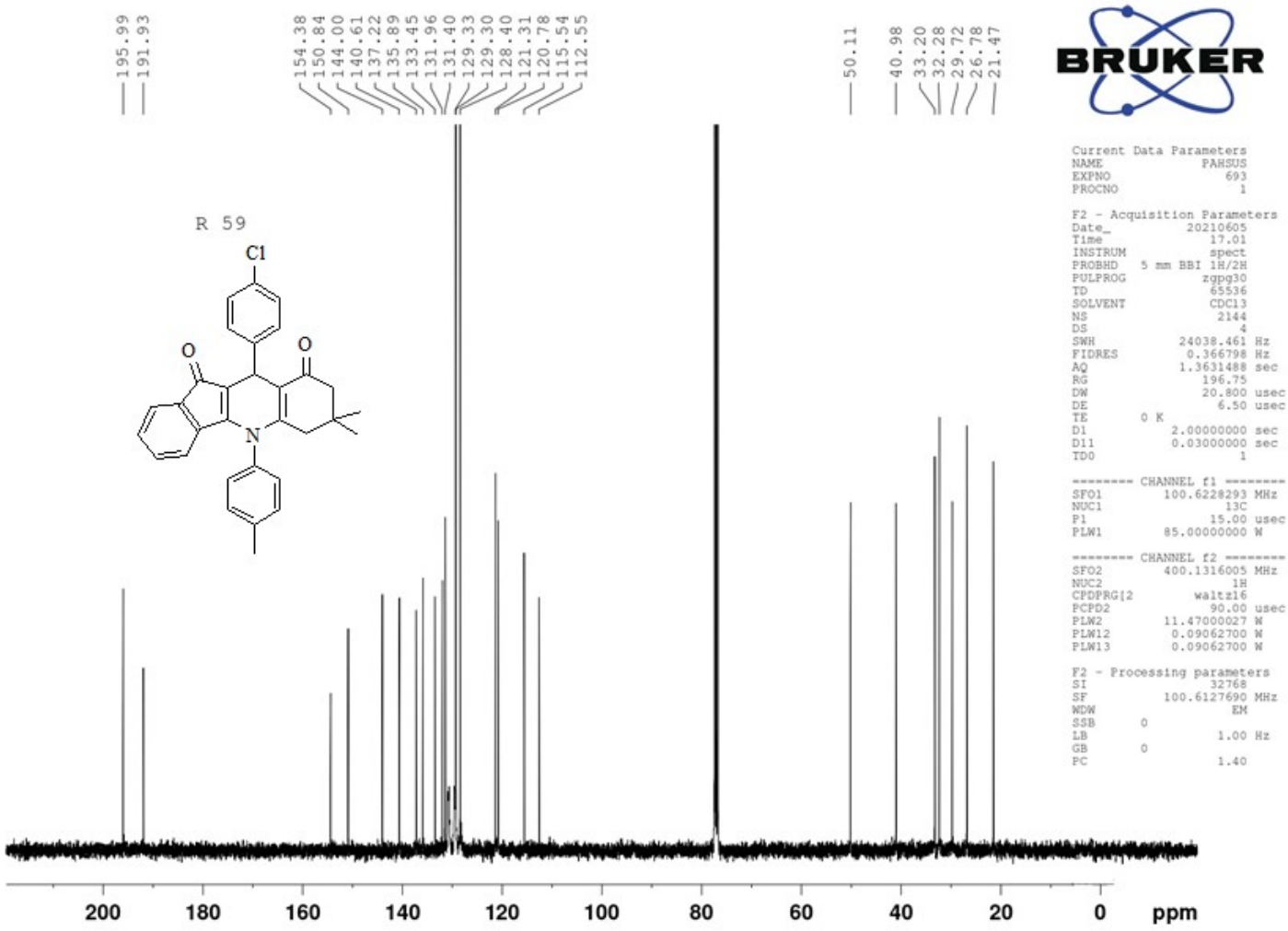
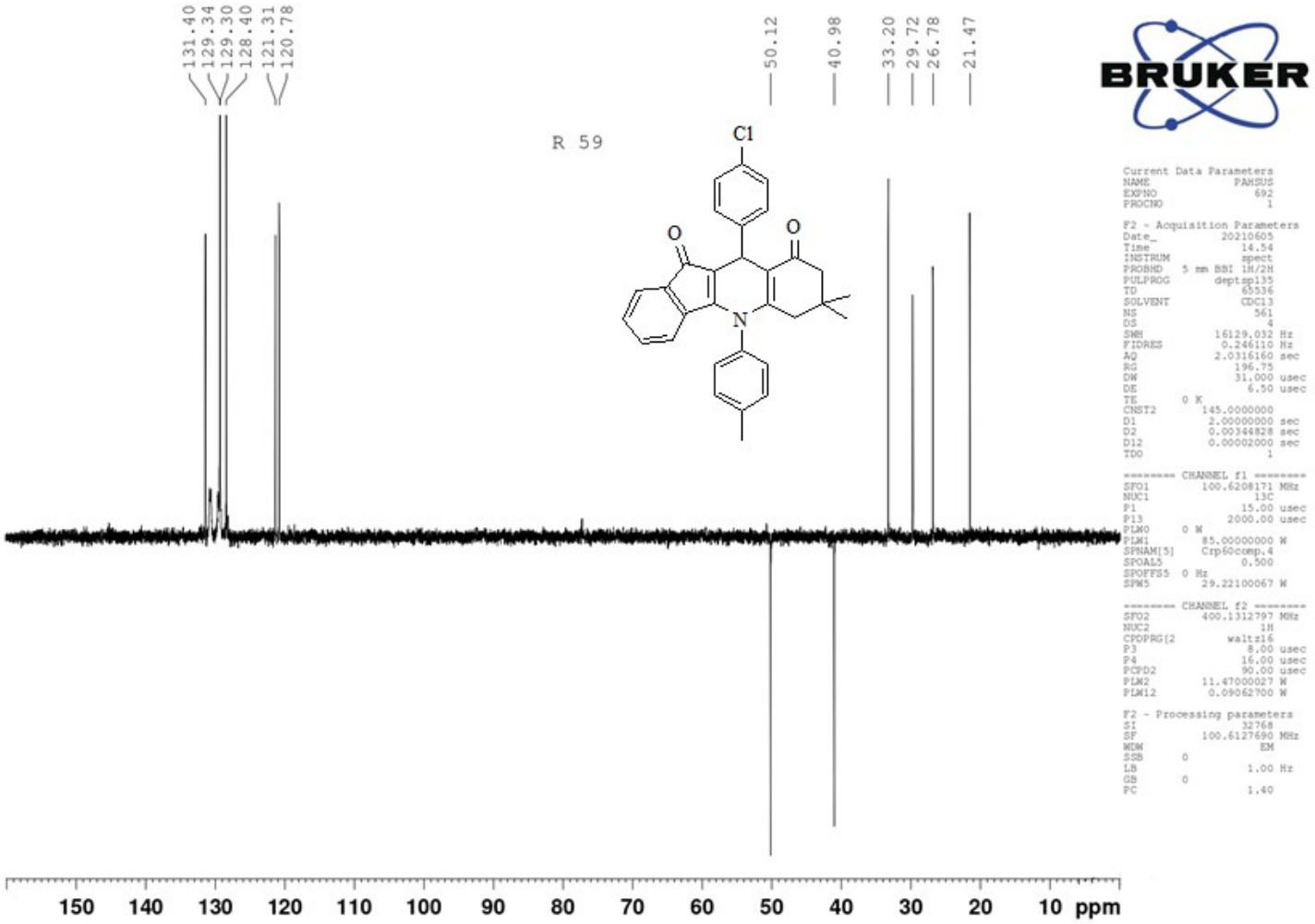
O
N
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm
4.19
3.41
2.11
1.15
1.08
1.02
1.00
3.02
3.16
1.10
3.02
3.13
Current Data Parameters
NAME PAHSUS
EXPNO 672
PROCNO 1
F2 - Acquisition Parameters
Date_ 20210527
Time 15.12
INSTRUM spect
PROBHD 5 mm BBI 1H/2H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9845889 sec
RG 41.52
DW 60.800 usec
DE 6.50 usec
TE 0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 8.00 usec
PLW1 11.47000027 W
F2 - Processing parameters
SI 65536
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

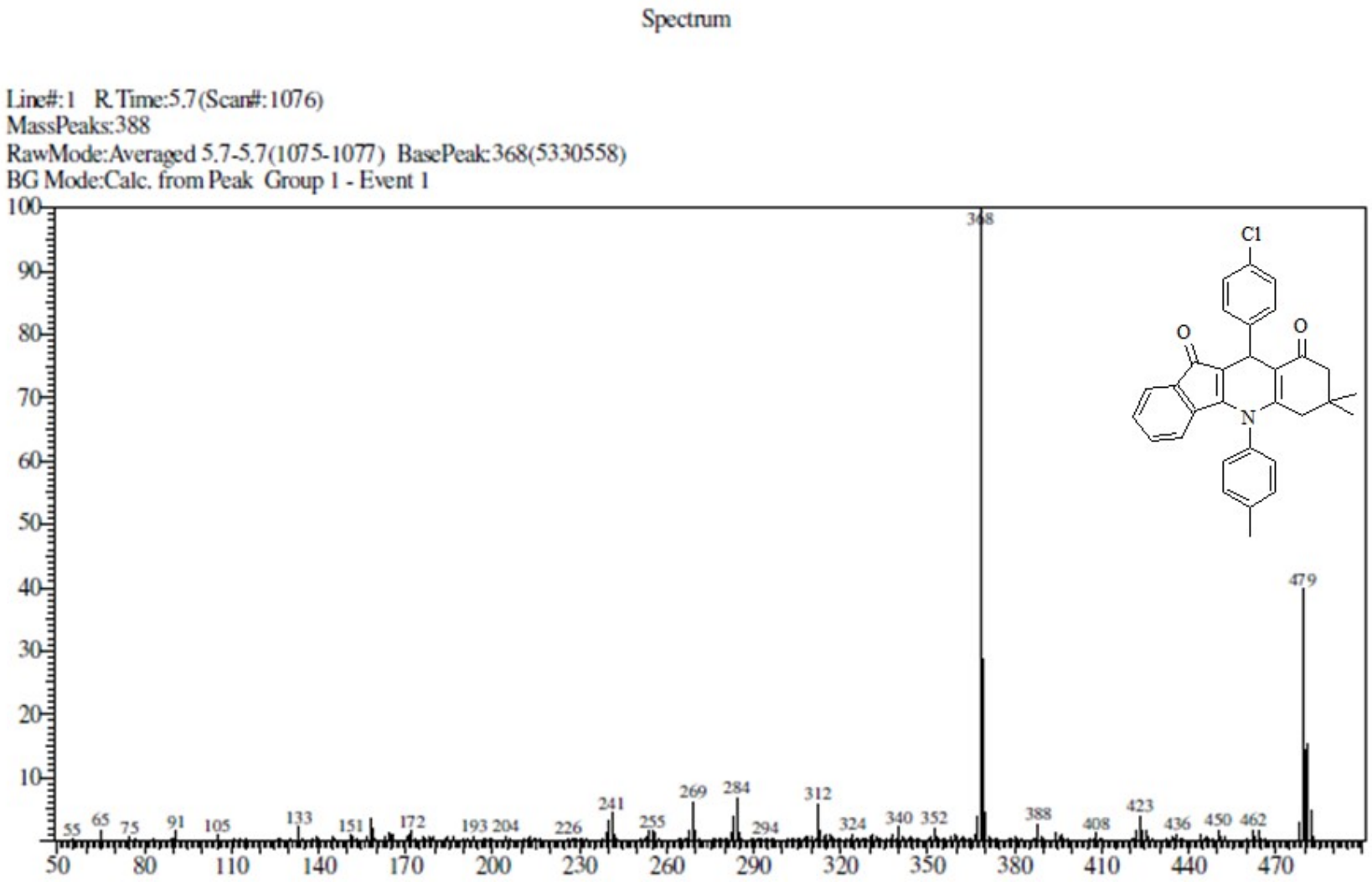
^{1}H NMR (5b)


195.99
191.93
154.38
150.84
144.00
140.61
137.22
135.89
133.45
131.96
131.40
129.33
129.30
128.40
121.31
120.78
115.54
112.55
50.11
40.98
33.20
32.28
29.72
26.78
21.47
R 59
Cl
O
O
N
200
180
160
140
120
100
80
60
40
20
0
ppm
Current Data Parameters
NAME PAHSUS
EXPNO 693
PROCNO 1
F2 - Acquisition Parameters
Date_ 20210605
Time 17.01
INSTRUM spect
PROBHD 5 mm BBI 1H/2H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2144
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 196.75
DW 20.800 usec
DE 6.50 usec
TE 0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 15.00 usec
PLW1 85.00000000 W
======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 11.47000027 W
PLW12 0.09062700 W
PLW13 0.09062700 W
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

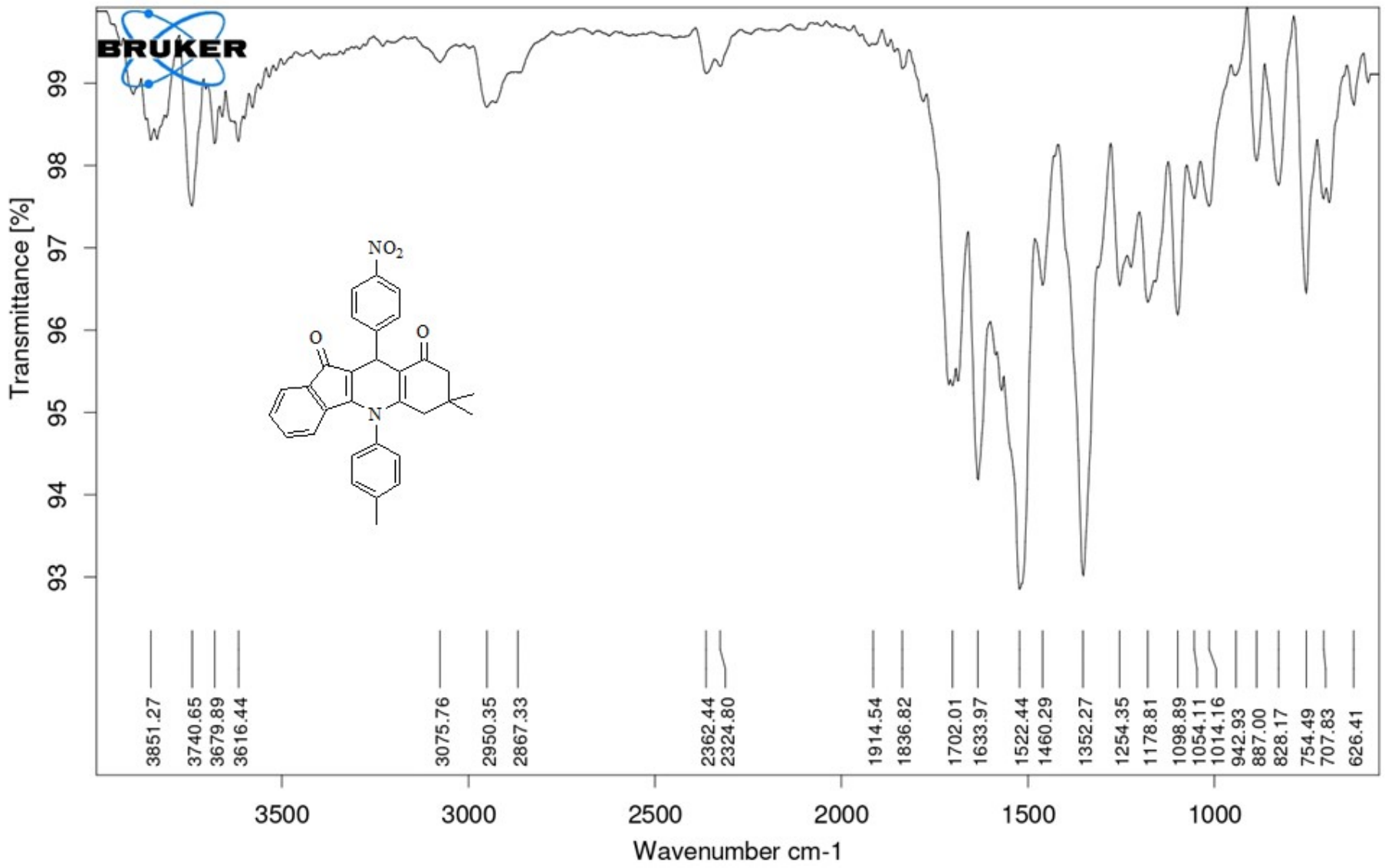
^{13}C NMR (5b)



DEPT 13C NMR (5b)

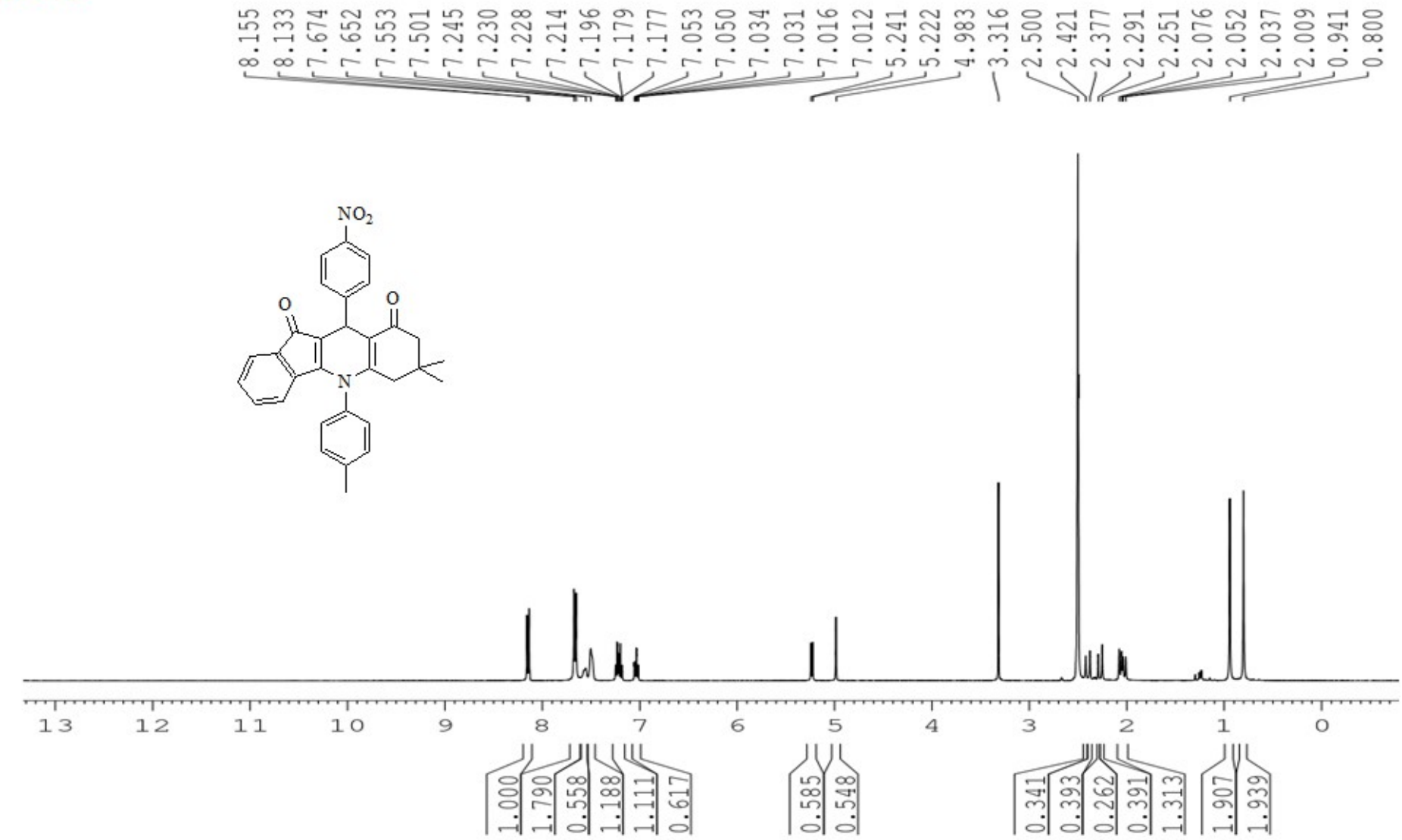

Spectrum
Line#:1 R.Time:5.7(Scan#:1076)
MassPeaks:388
RawMode:Averaged 5.7-5.7(1075-1077) BasePeak:368(5330558)
BG Mode:Calc. from Peak Group 1 - Event 1
100
90
80
70
60
50
40
30
20
10
50
80
110
140
170
200
230
260
290
320
350
380
410
440
470
55
65
75
91
105
133
151
172
193
204
226
241
255
269
284
294
312
324
340
352
368
388
408
423
436
450
462
479
Cl
O
O
N

GC-MS MS (5b)

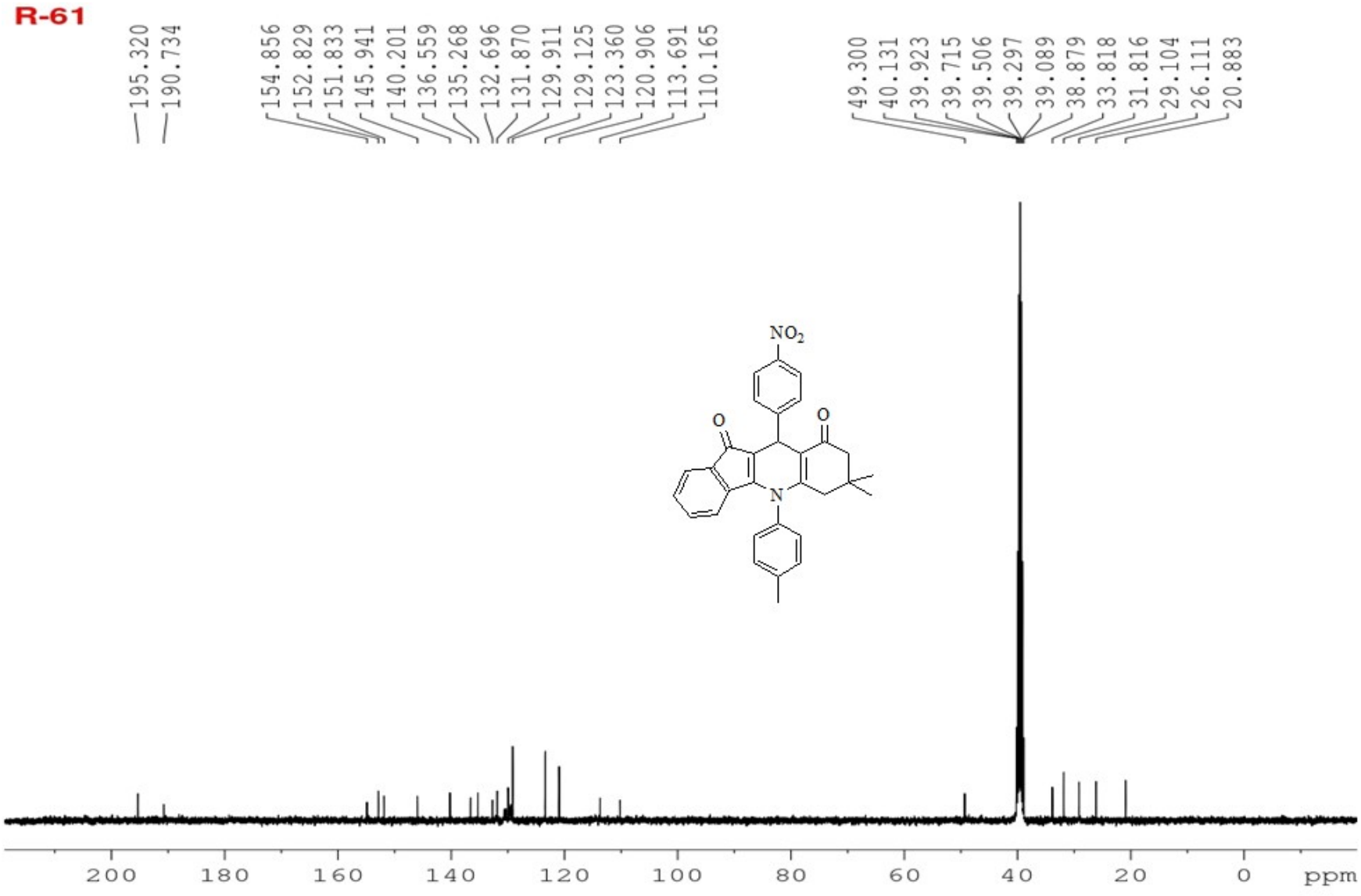

BRUKER
Transmittance [%]
99
98
97
96
95
94
93
NO2
O
O
N
3851.27
3740.65
3679.89
3616.44
3075.76
2950.35
2867.33
2362.44
2324.80
1914.54
1836.82
1702.01
1633.97
1522.44
1460.29
1352.27
1254.35
1178.81
1098.89
1054.11
1014.16
942.93
887.00
828.17
754.49
707.83
626.41
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

FT-IR (5c)

R-61


8.155
8.133
7.674
7.652
7.553
7.501
7.245
7.230
7.228
7.214
7.196
7.179
7.177
7.053
7.050
7.034
7.031
7.016
7.012
5.241
5.222
4.983
3.316
2.500
2.421
2.377
2.291
2.251
2.076
2.052
2.037
2.009
0.941
0.800
NO2
O
O
N
13
12
11
10
9
8
7
6
5
4
3
2
1
0
1.000
1.790
0.558
1.188
1.111
0.617
0.585
0.548
0.341
0.393
0.262
0.391
1.313
1.907
1.939

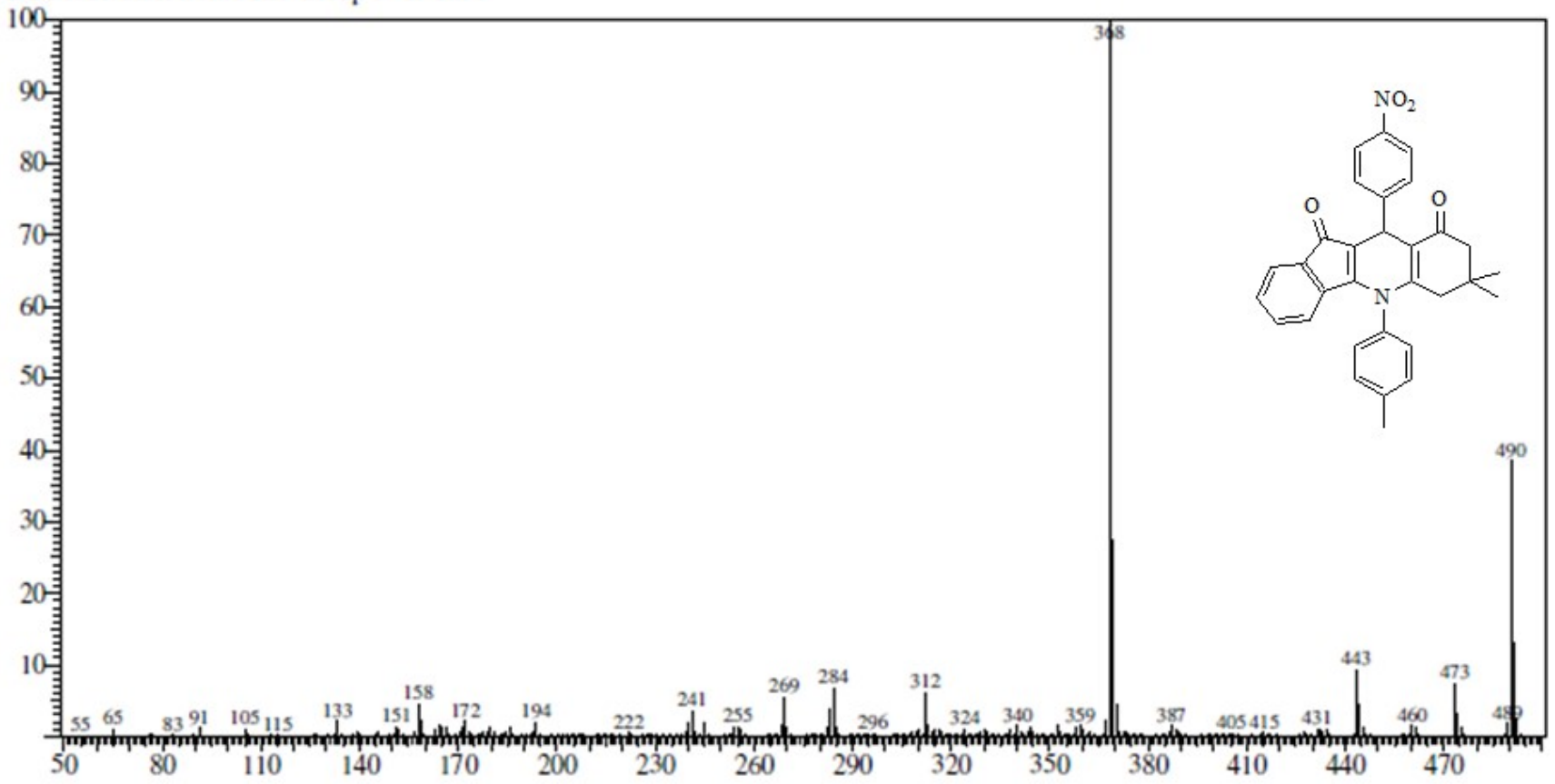
^{1}H NMR (5c)


R-61
195.320
190.734
154.856
152.829
151.833
145.941
140.201
136.559
135.268
132.696
131.870
129.911
129.125
123.360
120.906
113.691
110.165
49.300
40.131
39.923
39.715
39.506
39.297
39.089
38.879
33.818
31.816
29.104
26.111
20.883
NO2
O
O
N
200
180
160
140
120
100
80
60
40
20
0
ppm

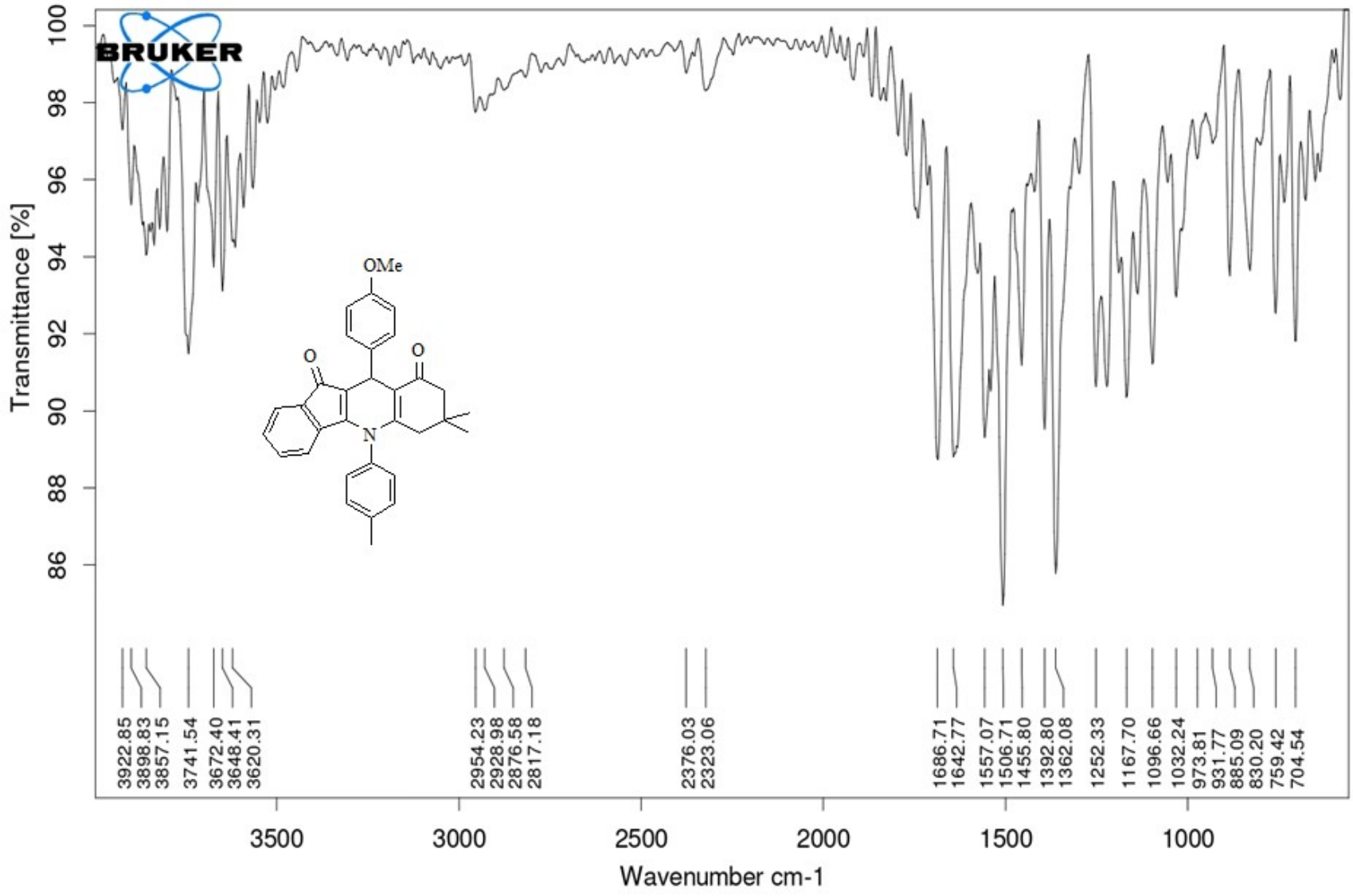
^{13}C NMR (5c)

Spectrum

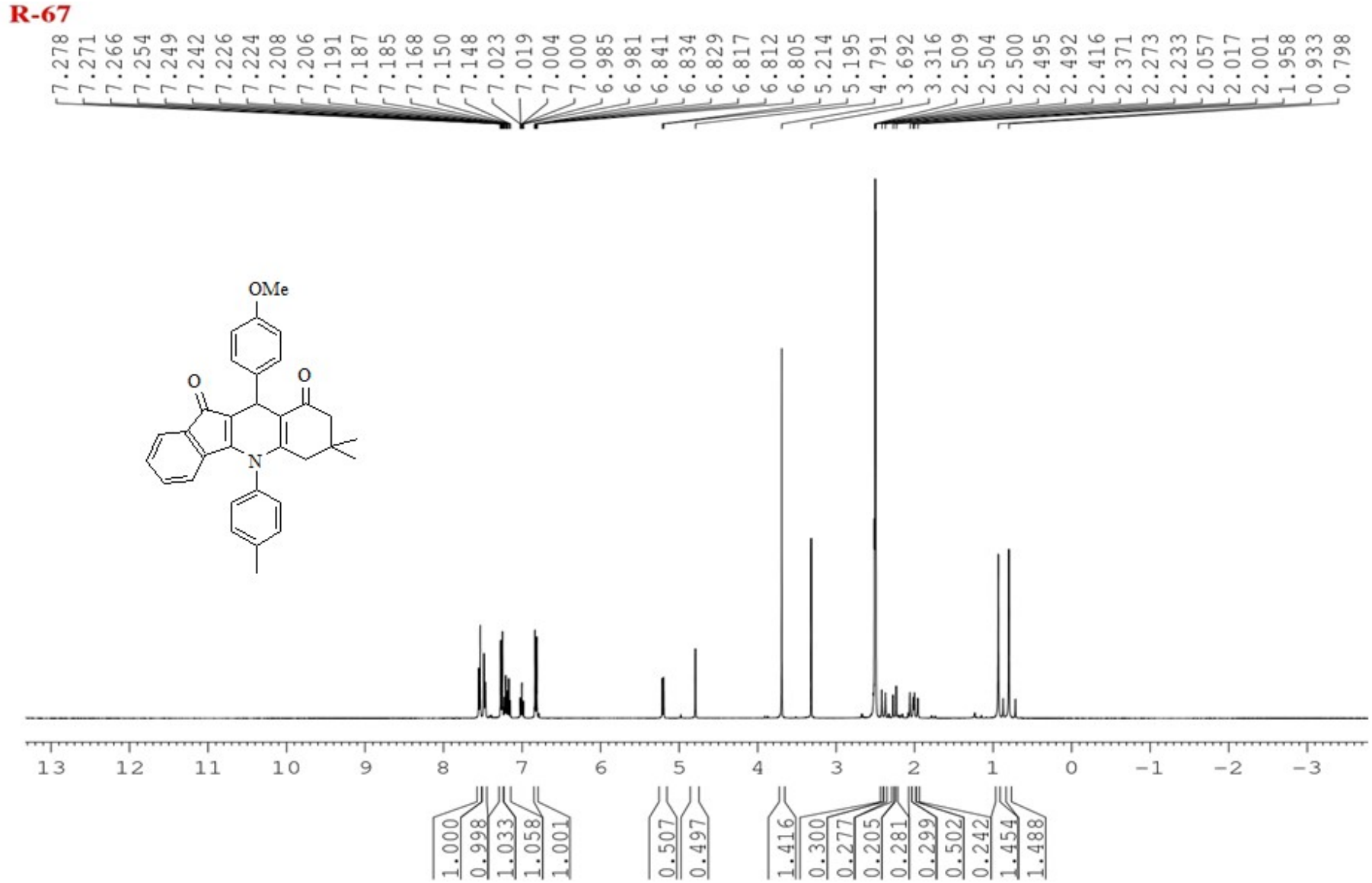
Line#:1 R.Time:5.7(Scan#:1090)
MassPeaks:602
RawMode:Averaged 5.7-5.8(1089-1091) BasePeak:368(3777280)
BG Mode:Calc. from Peak Group 1 - Event 1



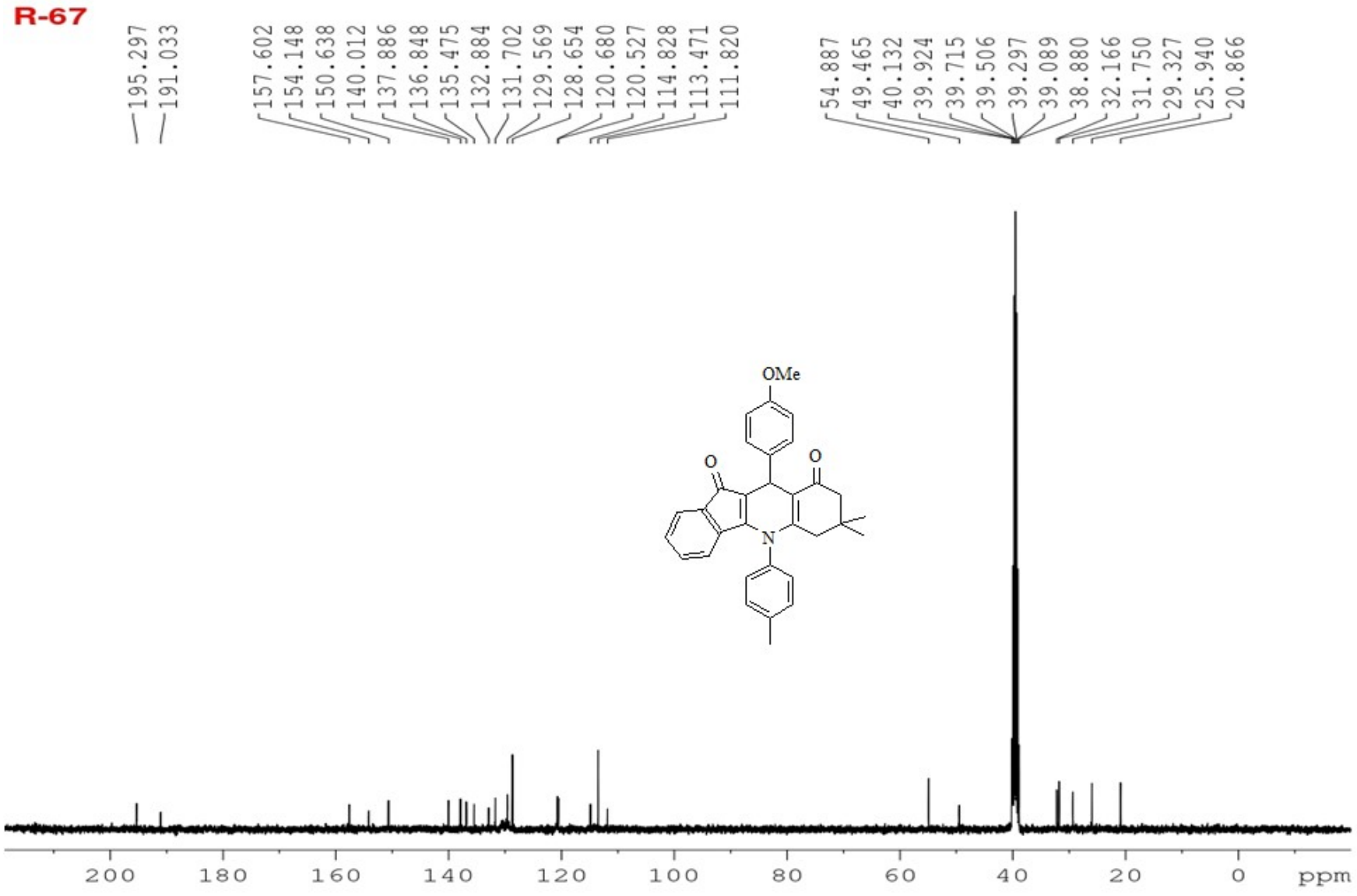
GC-MS MS (5c)


BRUKER
Transmittance [%]
100
98
96
94
92
90
88
86
OMe
O
O
N
3922.85
3898.83
3857.15
3741.54
3672.40
3648.41
3620.31
2954.23
2928.98
2876.58
2817.18
2376.03
2323.06
1686.71
1642.77
1557.07
1506.71
1455.80
1392.80
1362.08
1252.33
1167.70
1096.66
1032.24
973.81
931.77
885.09
830.20
759.42
704.54
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

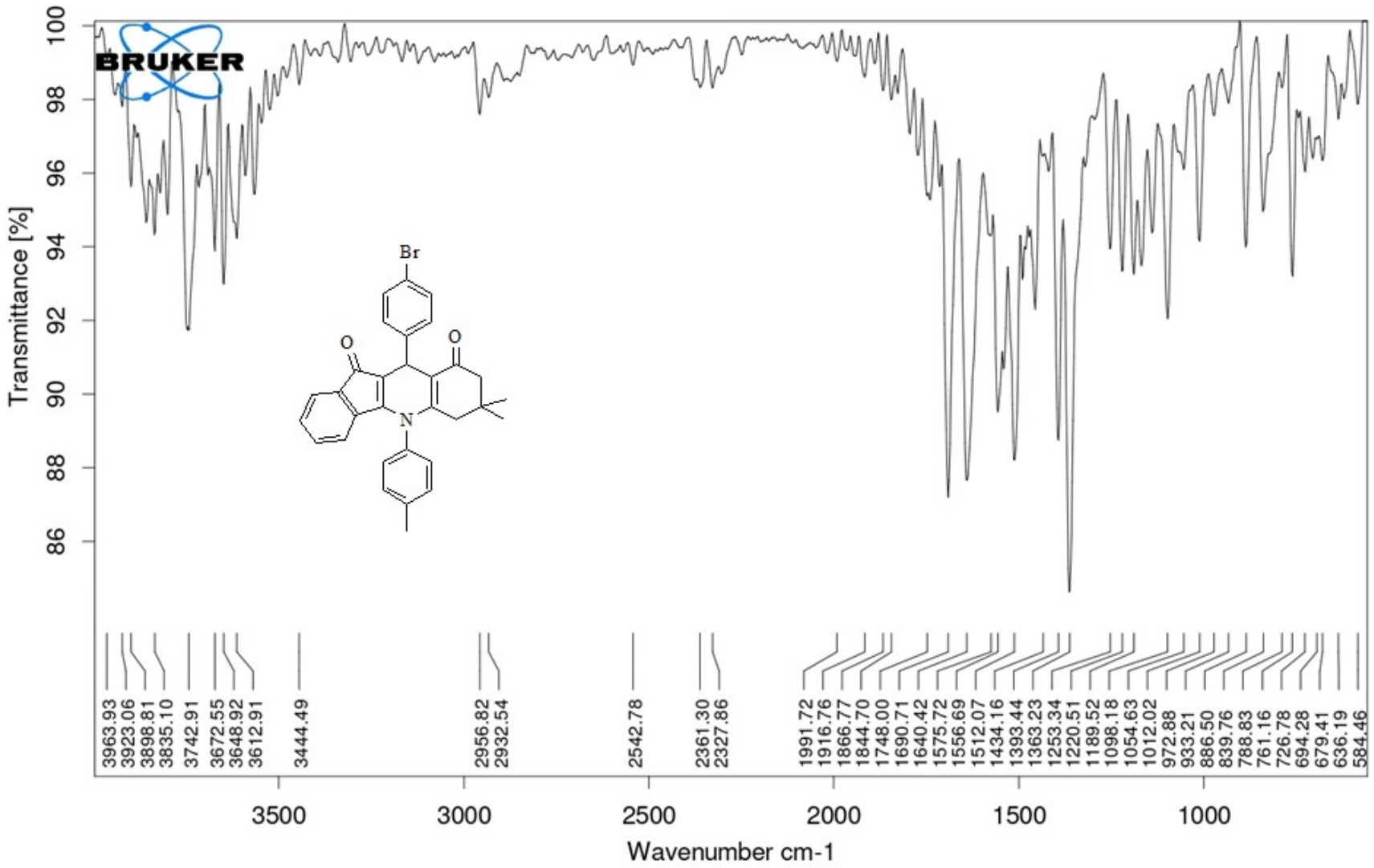
FT-IR (5d)


R-67
7.278
7.271
7.266
7.254
7.249
7.242
7.226
7.224
7.208
7.206
7.191
7.187
7.185
7.168
7.150
7.148
7.023
7.019
7.004
7.000
6.985
6.981
6.841
6.834
6.829
6.817
6.812
6.805
5.214
5.195
4.791
3.692
3.316
2.509
2.504
2.500
2.495
2.492
2.416
2.371
2.273
2.233
2.057
2.017
2.001
1.958
0.933
0.798
OMe
O
O
N
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
1.000
0.998
1.033
1.058
1.001
0.507
0.497
1.416
0.300
0.277
0.205
0.281
0.299
0.502
0.242
1.454
1.488

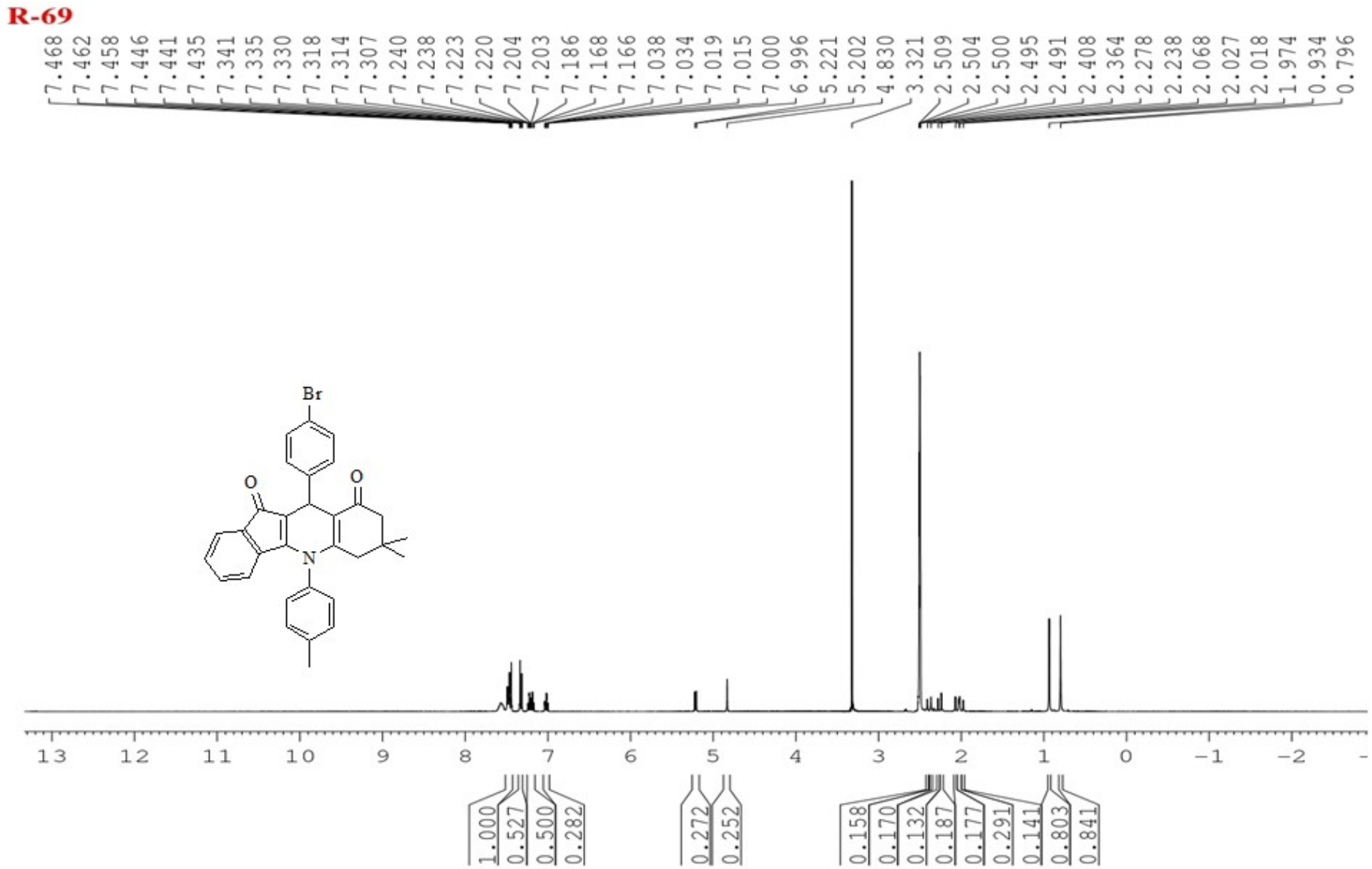
^{1}H NMR (5d)


R-67
195.297
191.033
157.602
154.148
150.638
140.012
137.886
136.848
135.475
132.884
131.702
129.569
128.654
120.680
120.527
114.828
113.471
111.820
54.887
49.465
40.132
39.924
39.715
39.506
39.297
39.089
38.880
32.166
31.750
29.327
25.940
20.866
OMe
O
O
N
200
180
160
140
120
100
80
60
40
20
0
ppm

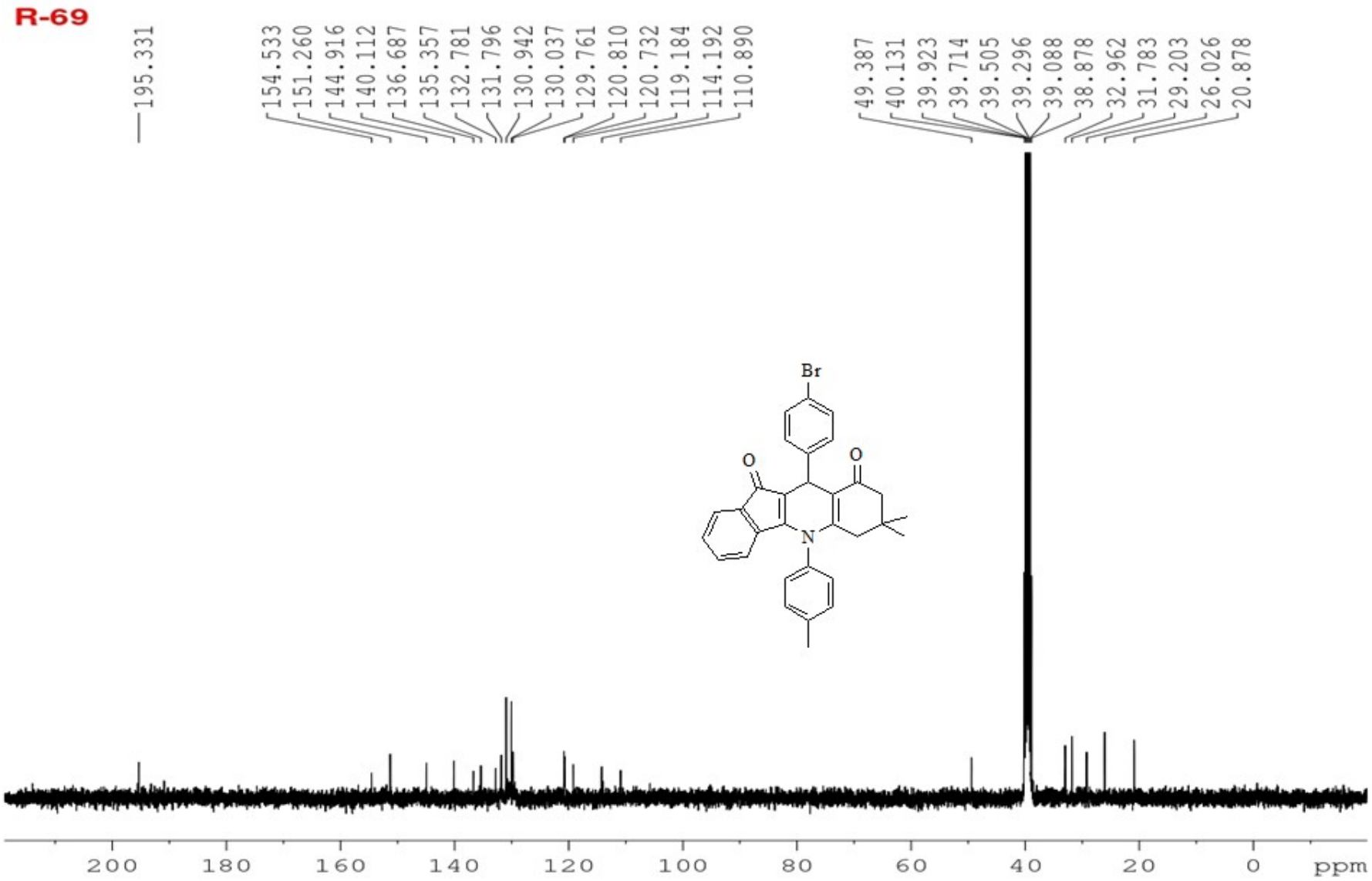
^{13}C NMR (5d)


BRUKER
Transmittance [%]
100
98
96
94
92
90
88
86
Br
O
O
N
3963.93
3923.06
3898.81
3835.10
3742.91
3672.55
3648.92
3612.91
3444.49
2956.82
2932.54
2542.78
2361.30
2327.86
1991.72
1916.76
1866.77
1844.70
1748.00
1690.71
1640.42
1575.72
1556.69
1512.07
1434.16
1393.44
1363.23
1253.34
1220.51
1189.52
1098.18
1054.63
1012.02
972.88
933.21
886.50
839.76
788.83
761.16
726.78
694.28
679.41
636.19
584.46
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

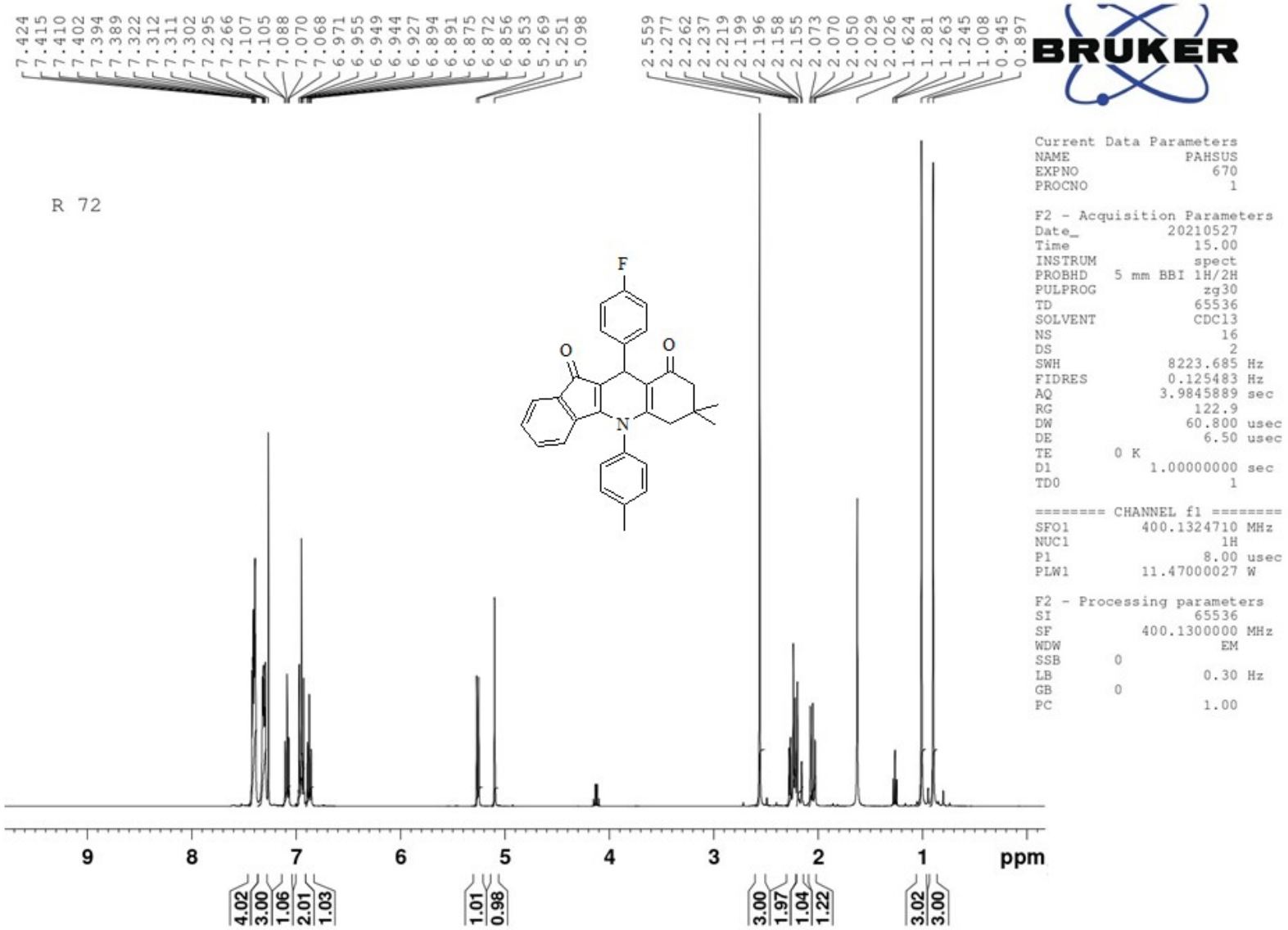
FT-IR (5e)


R-69
7.468
7.462
7.458
7.446
7.441
7.435
7.341
7.335
7.330
7.318
7.314
7.307
7.240
7.238
7.223
7.220
7.204
7.203
7.186
7.168
7.166
7.038
7.034
7.019
7.015
7.000
6.996
5.221
5.202
4.830
3.321
2.509
2.504
2.500
2.495
2.491
2.408
2.364
2.278
2.238
2.068
2.027
2.018
1.974
0.934
0.796
Br
O
O
N
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
1.000
0.527
0.500
0.282
0.272
0.252
0.158
0.170
0.132
0.187
0.177
0.291
0.141
0.803
0.841

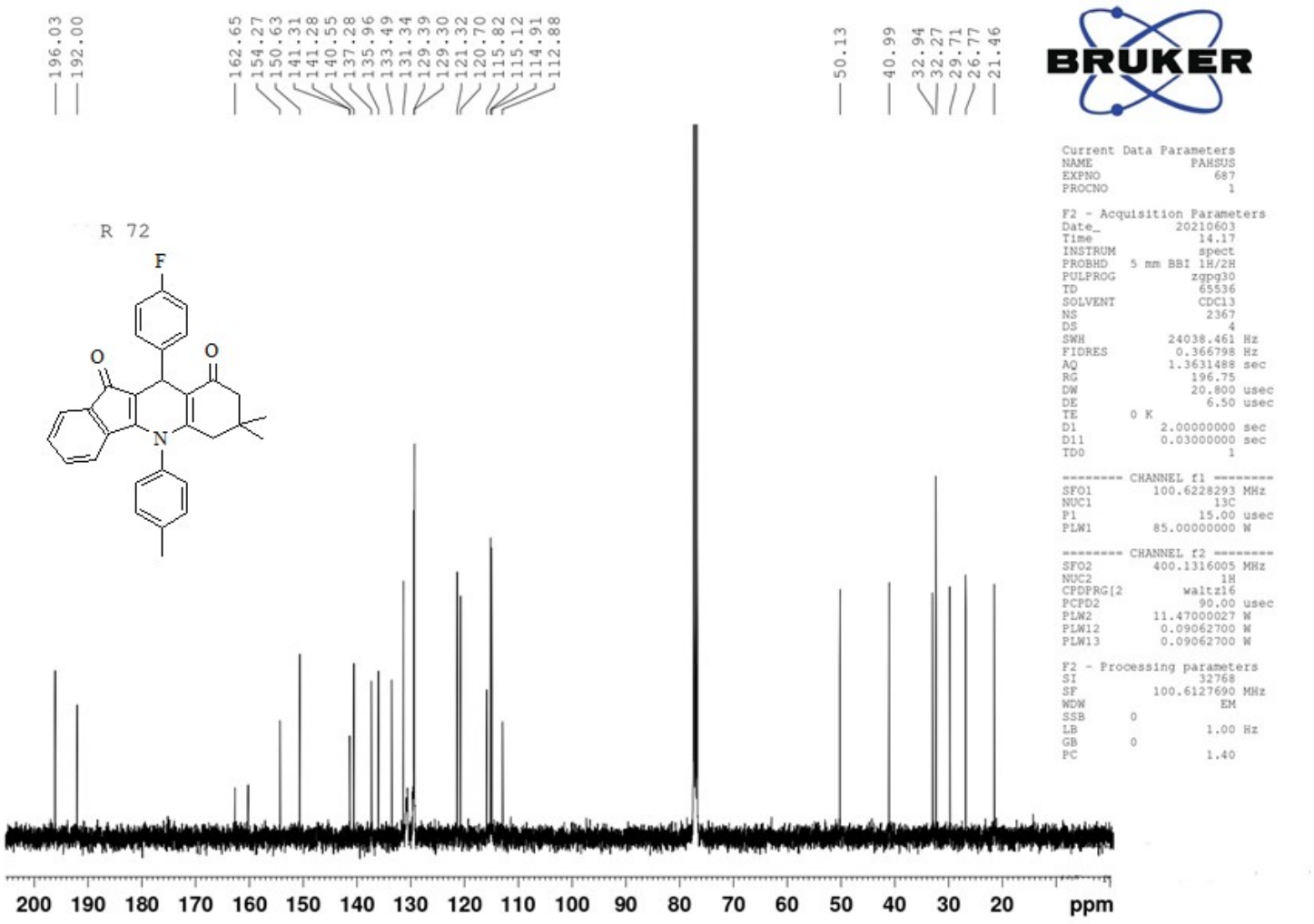
^{1}H NMR (5e)


R-69
195.331
154.533
151.260
144.916
140.112
136.687
135.357
132.781
131.796
130.942
130.037
129.761
120.810
120.732
119.184
114.192
110.890
49.387
40.131
39.923
39.714
39.505
39.296
39.088
38.878
32.962
31.783
29.203
26.026
20.878
Br
O
O
N
200
180
160
140
120
100
80
60
40
20
0
ppm

^{13}C NMR (5e)


7.424
7.415
7.410
7.402
7.394
7.389
7.322
7.312
7.311
7.302
7.295
7.266
7.107
7.105
7.088
7.070
7.068
6.971
6.955
6.949
6.944
6.927
6.894
6.891
6.875
6.872
6.856
6.853
5.269
5.251
5.098
2.559
2.277
2.262
2.237
2.219
2.199
2.196
2.158
2.155
2.073
2.070
2.050
2.029
2.026
1.624
1.281
1.263
1.245
1.008
0.945
0.897
BRUKER
R 72
F
O
O
N
Current Data Parameters
NAME PAHSUS
EXPNO 670
PROCNO 1
F2 - Acquisition Parameters
Date_ 20210527
Time 15.00
INSTRUM spect
PROBHD 5 mm BBI 1H/2H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9845889 sec
RG 122.9
DW 60.800 usec
DE 6.50 usec
TE 0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 8.00 usec
PLW1 11.47000027 W
F2 - Processing parameters
SI 65536
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
4.02
3.00
1.06
2.01
1.03
1.01
0.98
3.00
1.97
1.04
1.22
3.02
3.00

^{1}H NMR (5f)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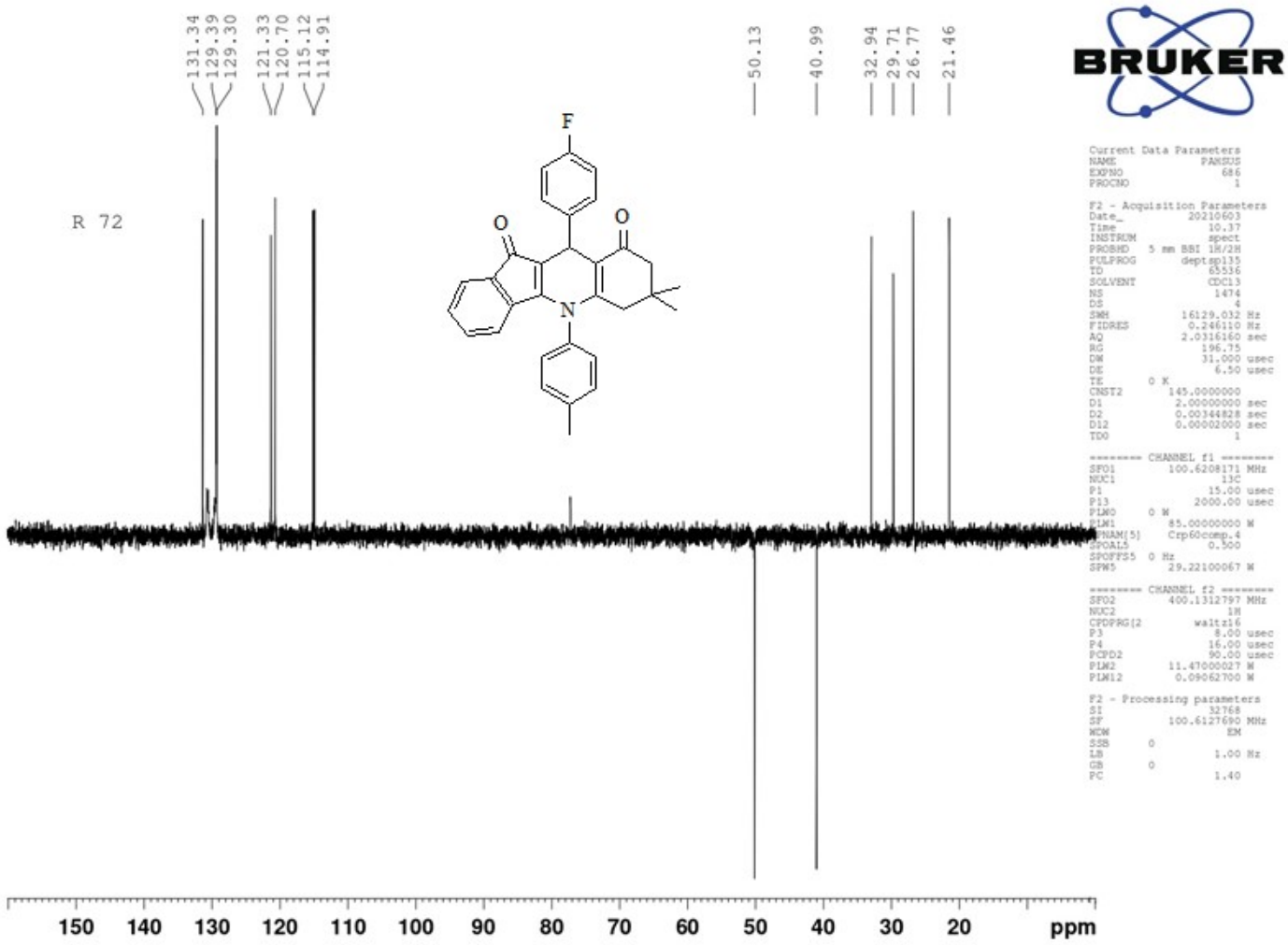
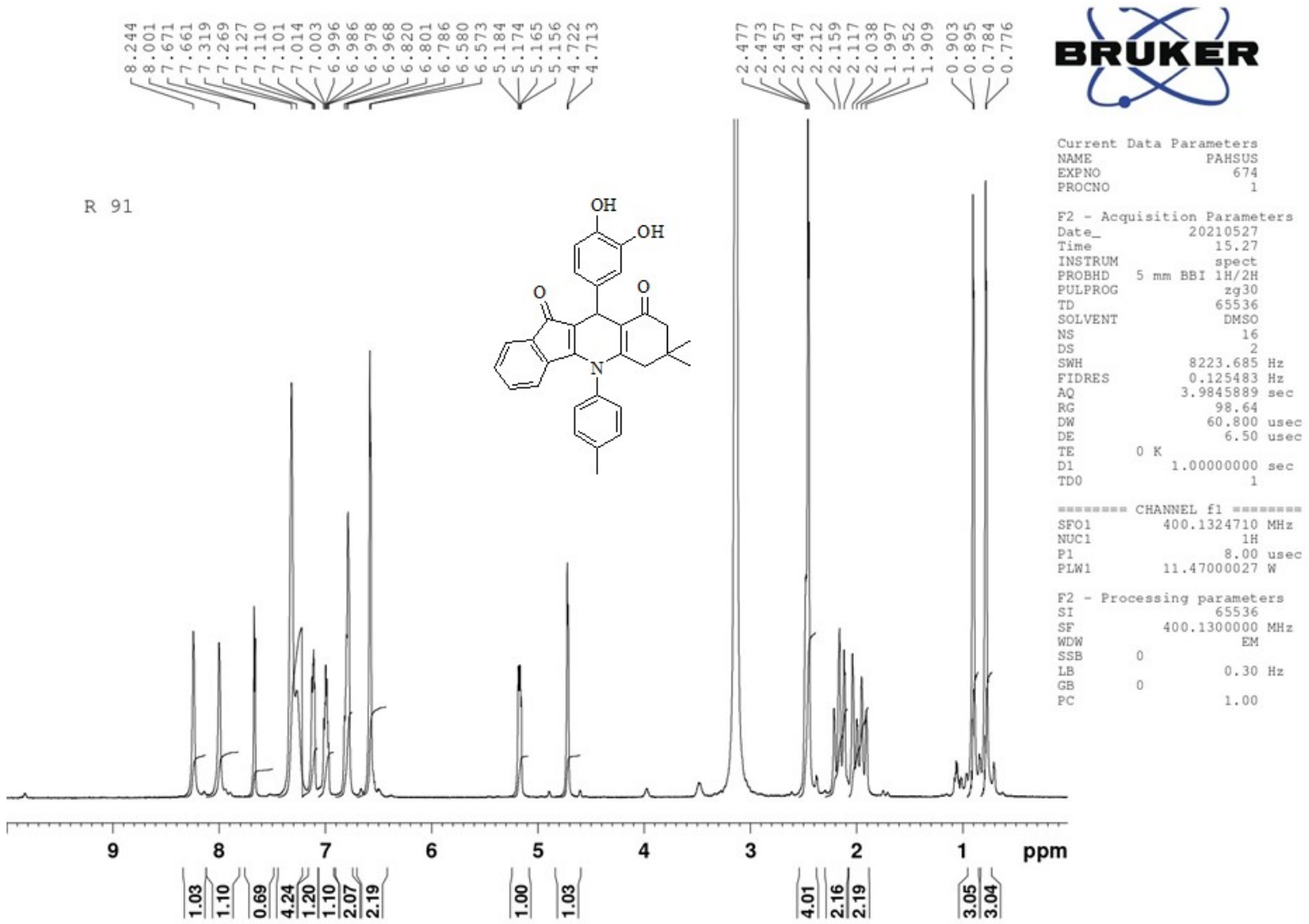
192.00
162.65
154.27
150.63
141.31
141.28
140.55
137.28
135.96
133.49
131.34
129.39
129.30
121.32
120.70
115.82
115.12
114.91
112.88
50.13
40.99
32.94
32.27
29.71
26.77
21.46
BRUKER
R 72
F
O
O
N
Current Data Parameters
NAME PAHSUS
EXPNO 687
PROCNO 1
F2 - Acquisition Parameters
Date_ 20210603
Time 14.17
INSTRUM spect
PROBHD 5 mm BBI 1H/2H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2367
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 196.75
DW 20.800 usec
DE 6.50 usec
TE 0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 15.00 usec
PLW1 85.00000000 W
======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 11.47000027 W
PLW12 0.09062700 W
PLW13 0.09062700 W
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

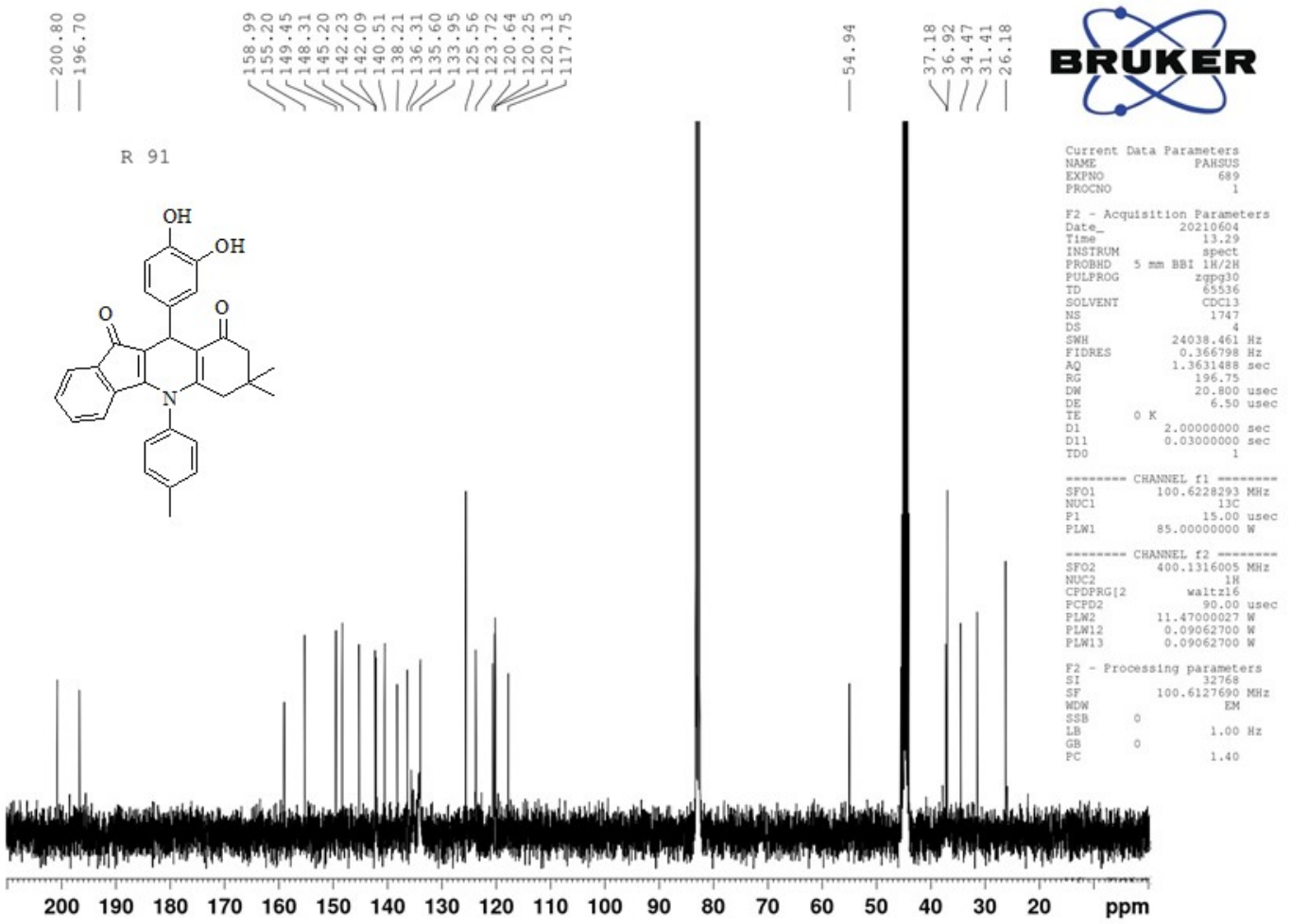
^{13}C NMR (5f)



DEPT ^{13}C NMR (5f)


8.244
8.001
7.671
7.661
7.319
7.269
7.127
7.110
7.101
7.014
7.003
6.996
6.986
6.978
6.968
6.820
6.801
6.786
6.580
6.573
5.184
5.174
5.165
5.156
4.722
4.713
2.477
2.473
2.457
2.447
2.212
2.159
2.117
2.038
1.997
1.952
1.909
0.903
0.895
0.784
0.776
R 91
OH
OH
O
O
N
9
8
7
6
5
4
3
2
1
ppm
1.03
1.10
0.69
4.24
1.20
1.10
2.07
2.19
1.00
1.03
4.01
2.16
2.19
3.05
3.04
BRUKER
Current Data Parameters
NAME PAHSUS
EXPNO 674
PROCNO 1
F2 - Acquisition Parameters
Date_ 20210527
Time 15.27
INSTRUM spect
PROBHD 5 mm BBI 1H/2H
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9845889 sec
RG 98.64
DW 60.800 usec
DE 6.50 usec
TE 0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 8.00 usec
PLW1 11.47000027 W
F2 - Processing parameters
SI 65536
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR (5g)


200.80
196.70
158.99
155.20
149.45
148.31
145.20
142.23
142.09
140.51
138.21
136.31
135.60
133.95
125.56
123.72
120.64
120.25
120.13
117.75
54.94
37.18
36.92
34.47
31.41
26.18
BRUKER
R 91
OH
OH
O
O
N
Current Data Parameters
NAME PAHSUS
EXPNO 689
PROCNO 1
F2 - Acquisition Parameters
Date_ 20210604
Time 13.29
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PROBHD 5 mm BBI 1H/2H
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 1747
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 196.75
DW 20.800 usec
DE 6.50 usec
TE 0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 15.00 usec
PLW1 85.00000000 W
======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 11.47000027 W
PLW12 0.09062700 W
PLW13 0.09062700 W
F2 - Processing parameters
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SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
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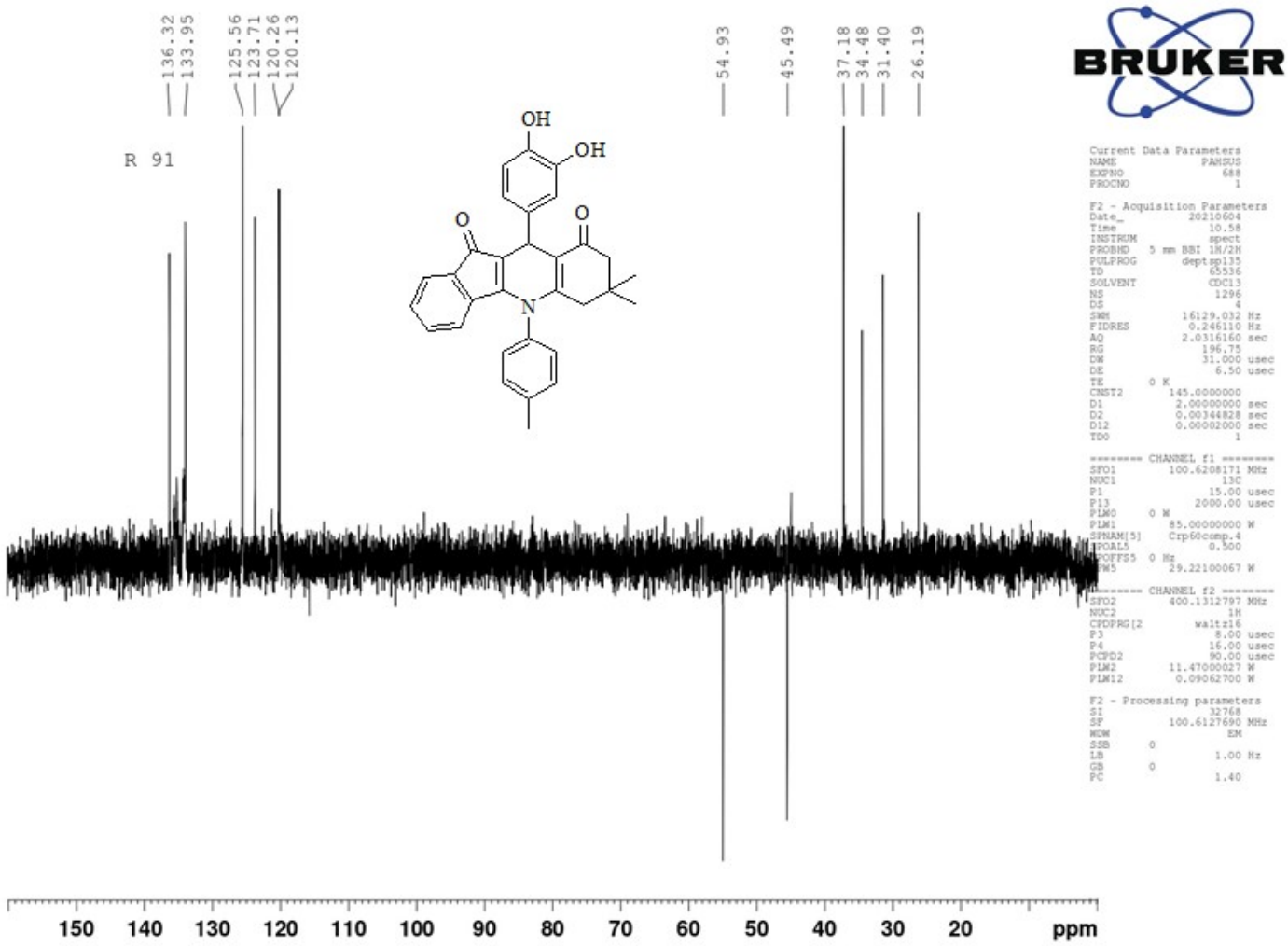
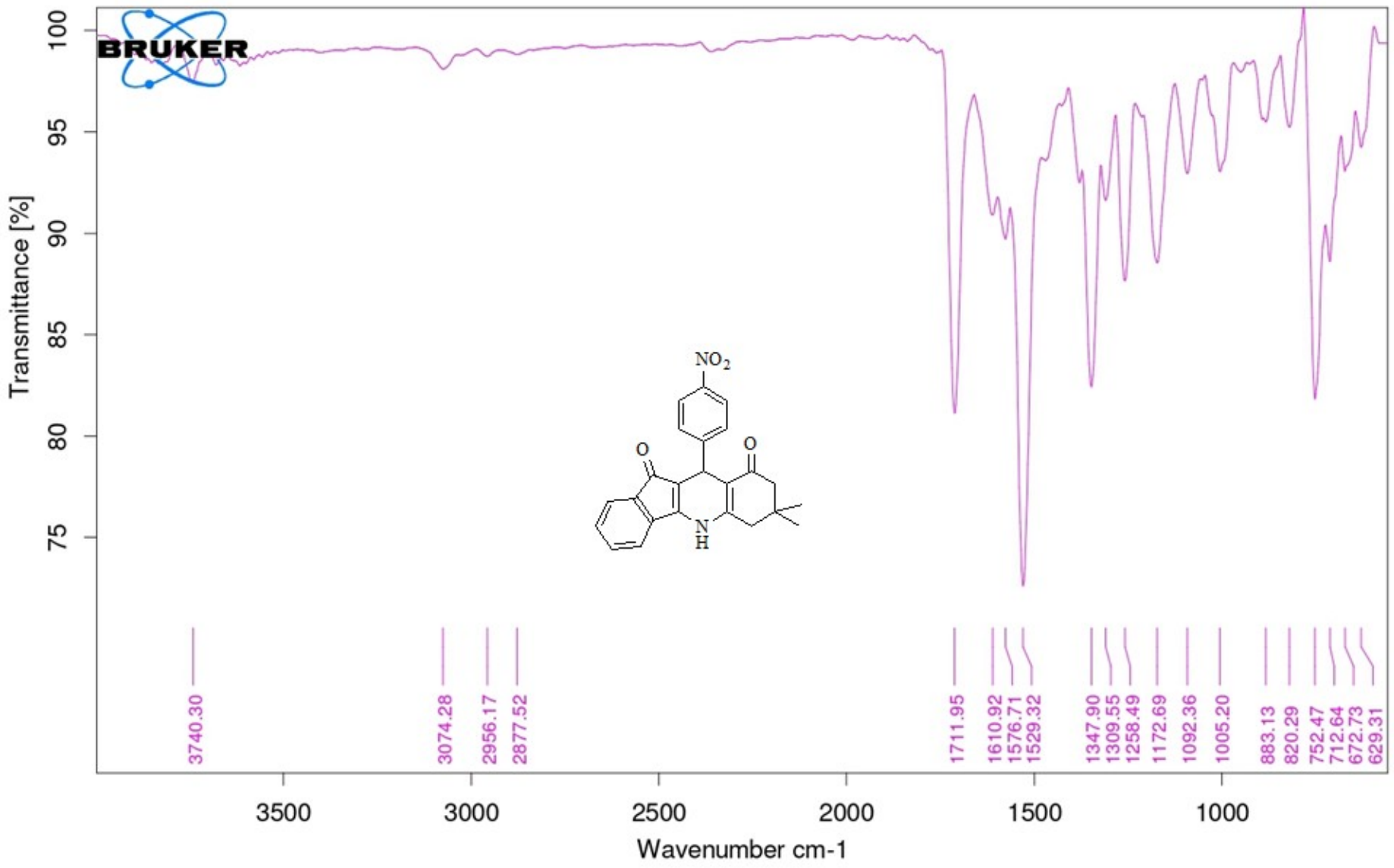
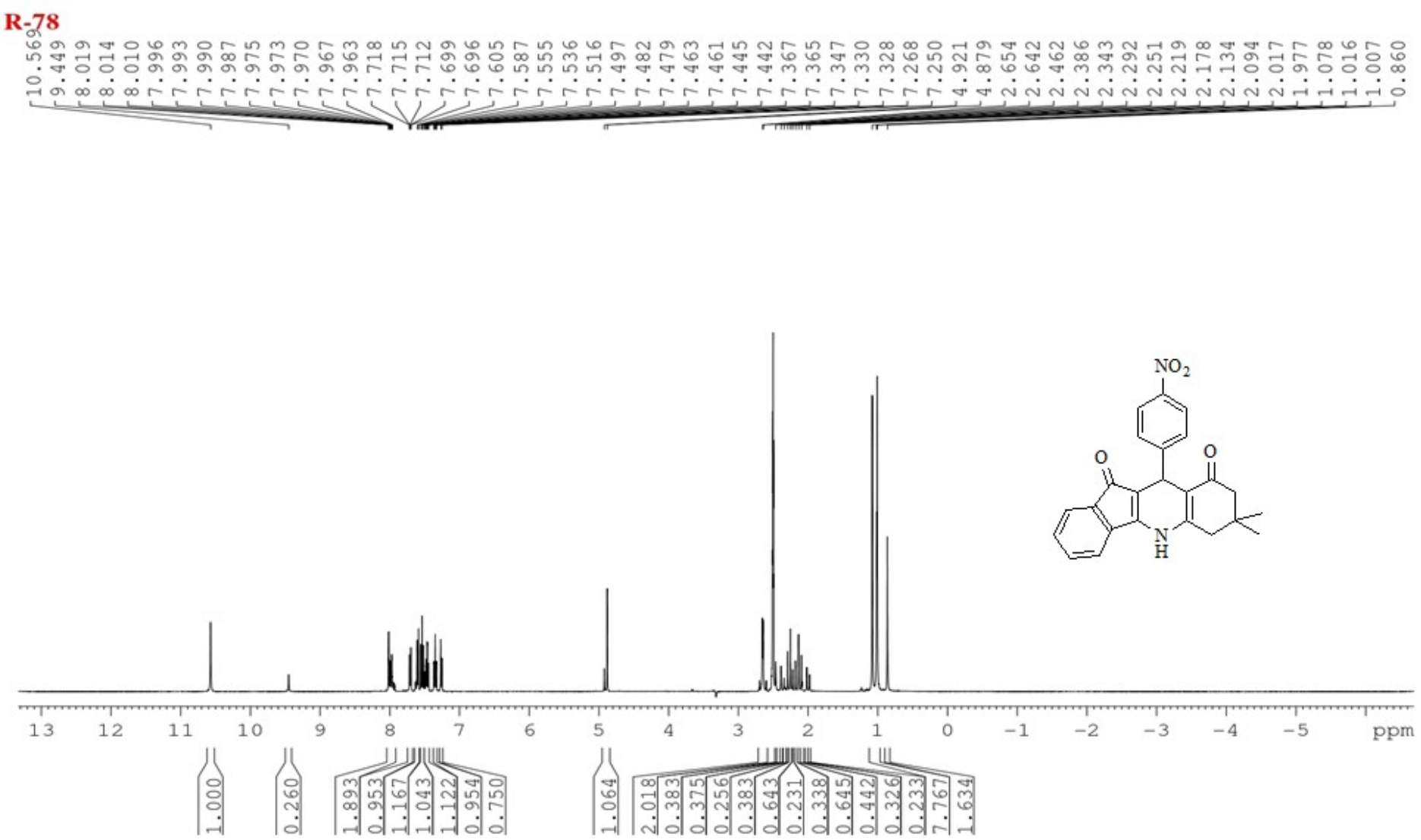
^{13}C NMR (5g)



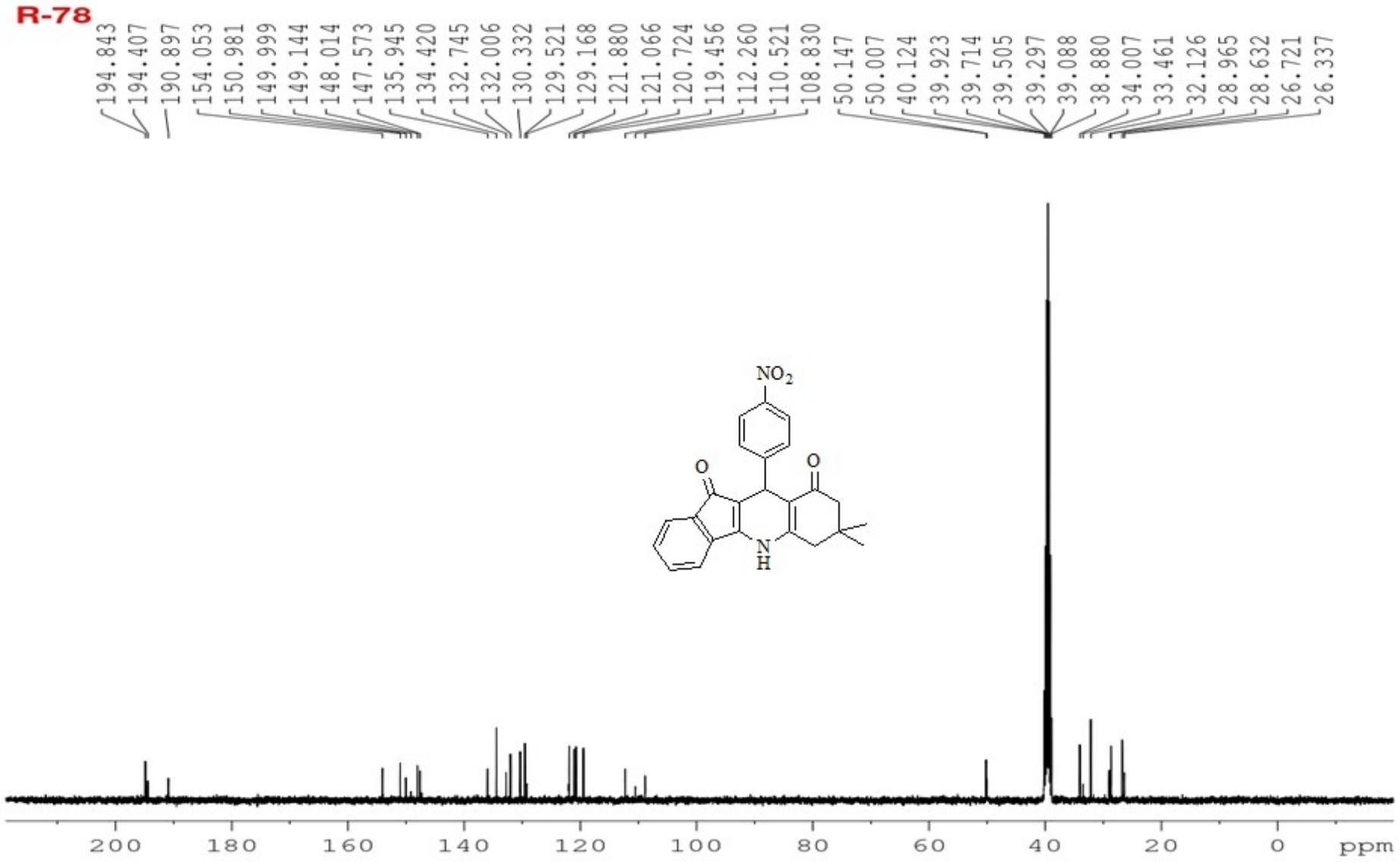
DEPT ^{13}C NMR (5g)


BRUKER
Transmittance [%]
100
95
90
85
80
75
3740.30
3074.28
2956.17
2877.52
1711.95
1610.92
1576.71
1529.32
1347.90
1309.55
1258.49
1172.69
1092.36
1005.20
883.13
820.29
752.47
712.64
672.73
629.31
3500
3000
2500
2000
1500
1000
Wavenumber cm-1
NO2
O
O
N
H

FT-IR (7a)

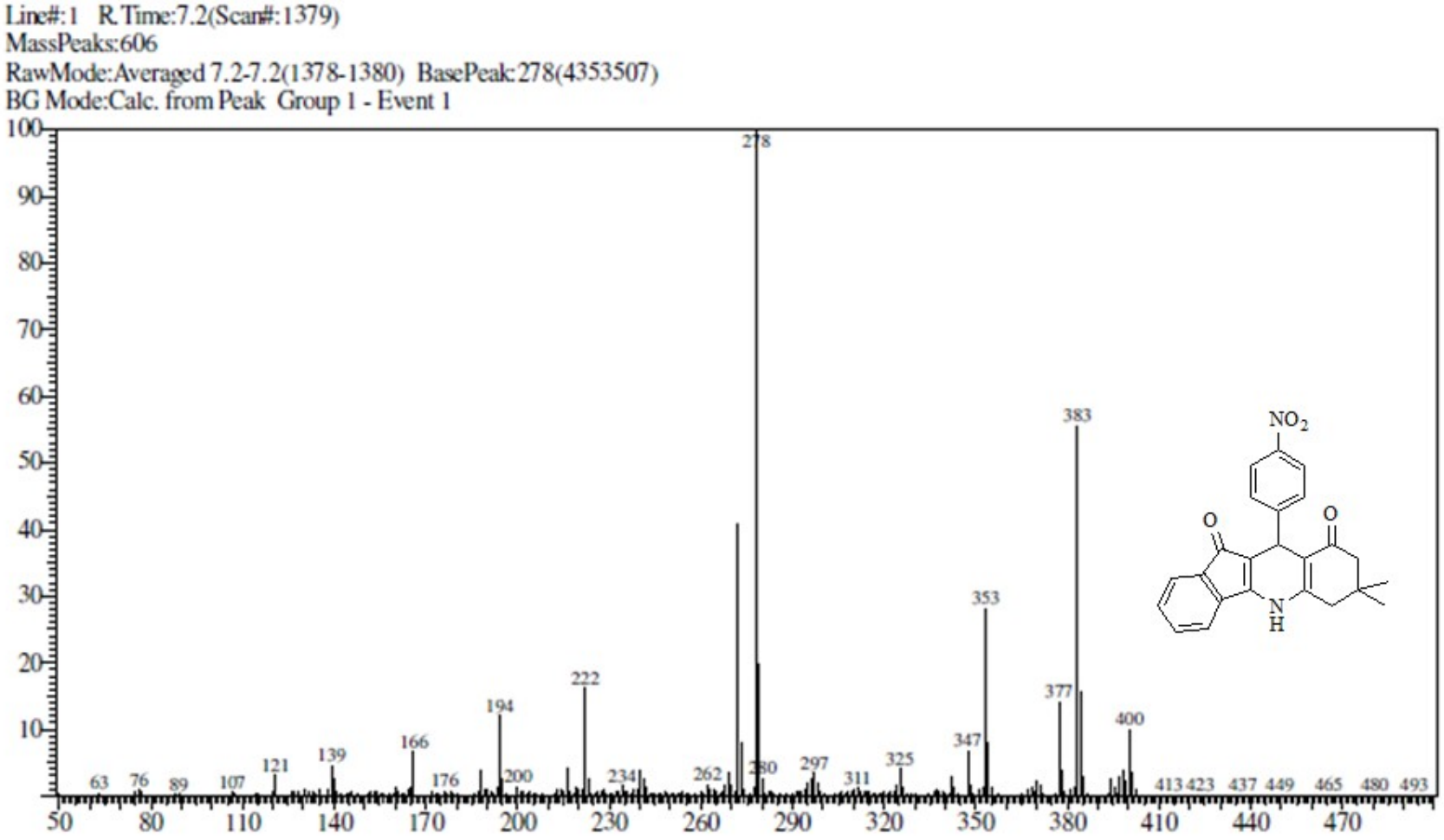

R-78
10.569
9.449
8.019
8.014
8.010
7.996
7.993
7.990
7.987
7.975
7.973
7.970
7.967
7.963
7.718
7.715
7.712
7.699
7.696
7.605
7.587
7.555
7.536
7.516
7.497
7.482
7.479
7.463
7.461
7.445
7.442
7.367
7.365
7.347
7.330
7.328
7.268
7.250
4.921
4.879
2.654
2.642
2.462
2.386
2.343
2.292
2.251
2.219
2.178
2.134
2.094
2.017
1.977
1.078
1.016
1.007
0.860
NO2
O
O
N
H
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
ppm
1.000
0.260
1.893
0.953
1.167
1.043
1.122
0.954
0.750
1.064
2.018
0.383
0.375
0.256
0.383
0.643
0.231
0.338
0.645
0.442
0.326
0.233
7.767
1.634

^{1}H NMR (7a)

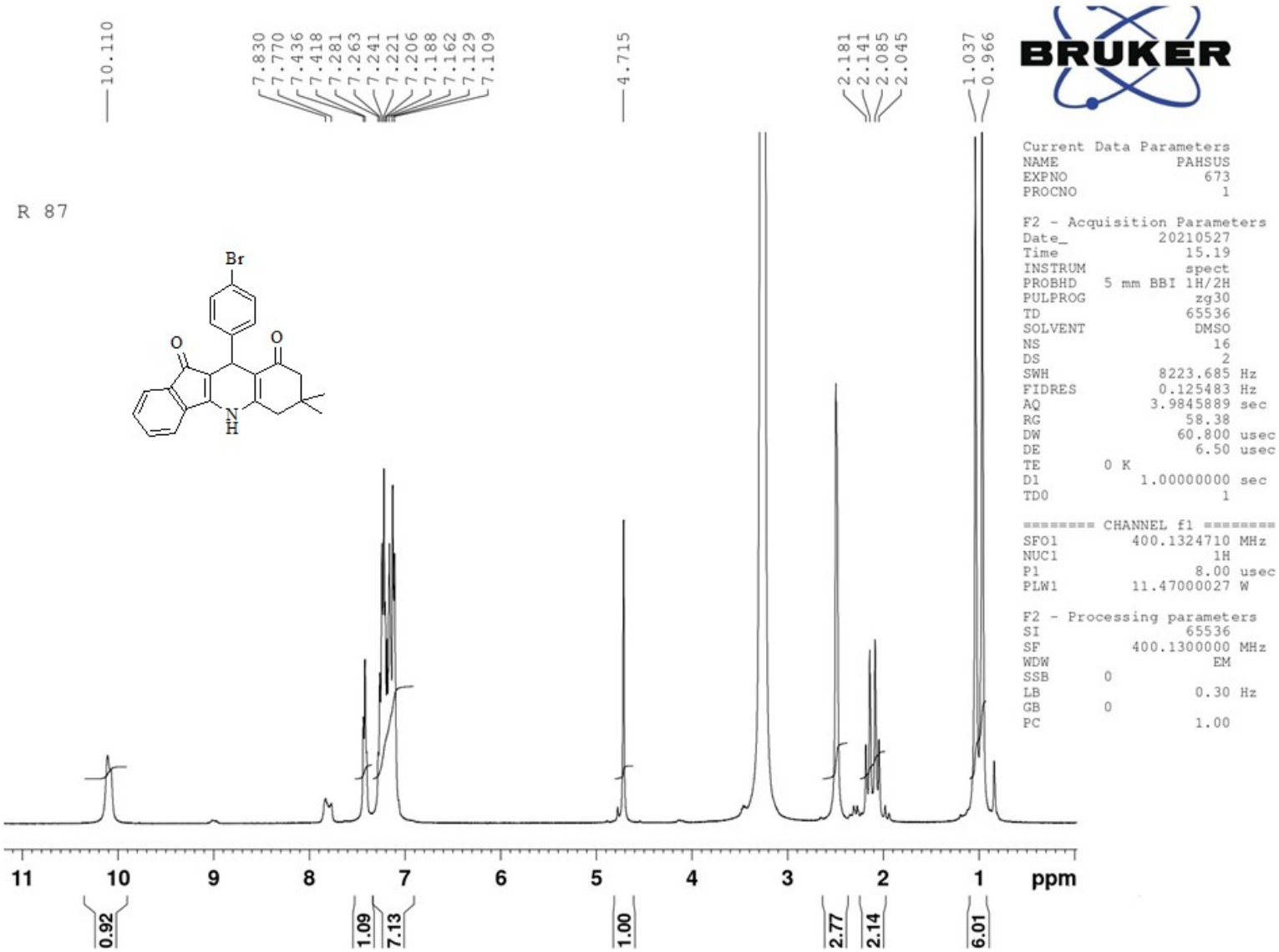

R-78
194.843
194.407
190.897
154.053
150.981
149.999
149.144
148.014
147.573
135.945
134.420
132.745
132.006
130.332
129.521
129.168
121.880
121.066
120.724
119.456
112.260
110.521
108.830
50.147
50.007
40.124
39.923
39.714
39.505
39.297
39.088
38.880
34.007
33.461
32.126
28.965
28.632
26.721
26.337
NO2
O
O
N
H
200
180
160
140
120
100
80
60
40
20
0
ppm

^{13}C NMR (7a)

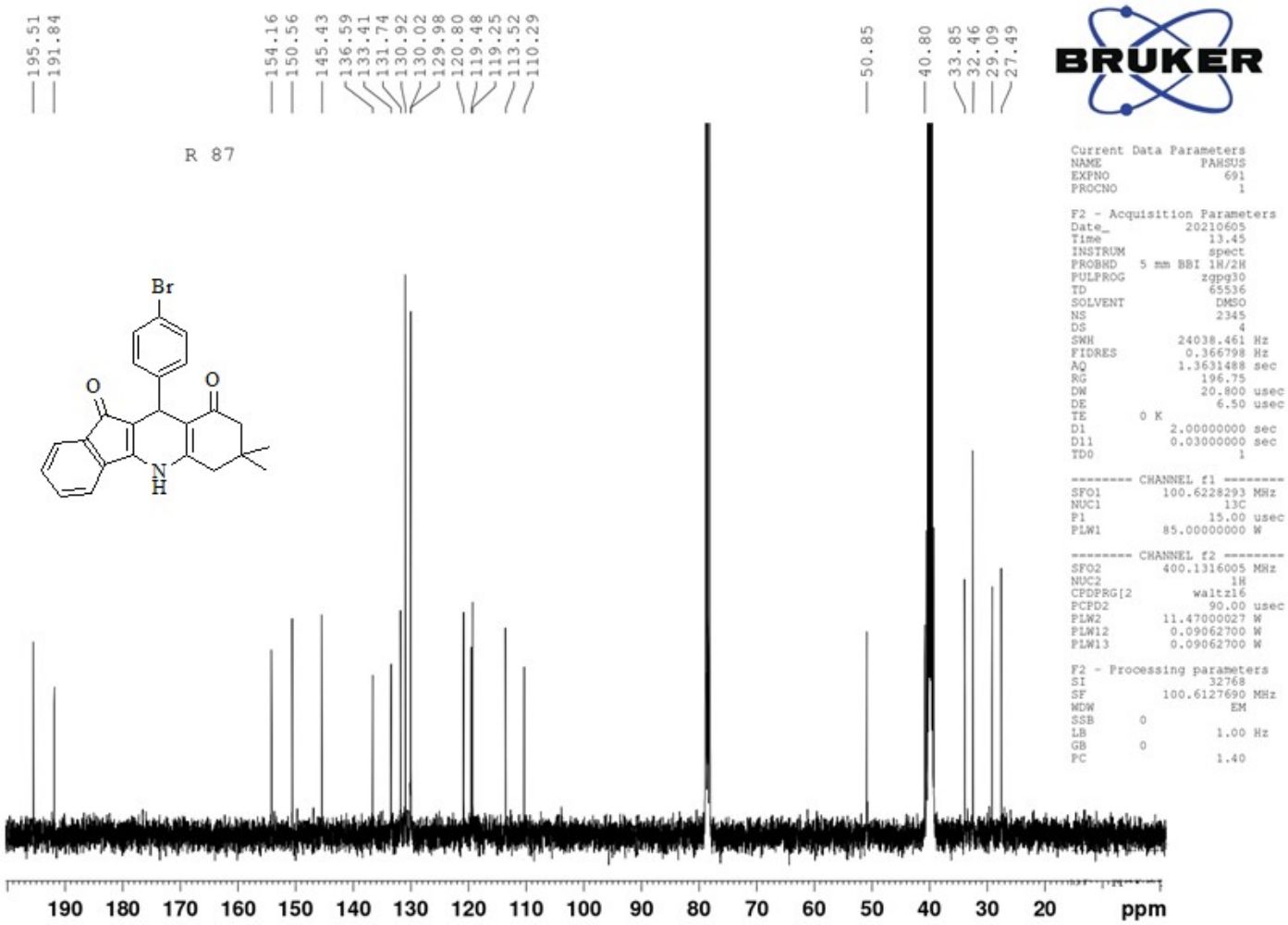
Spectrum



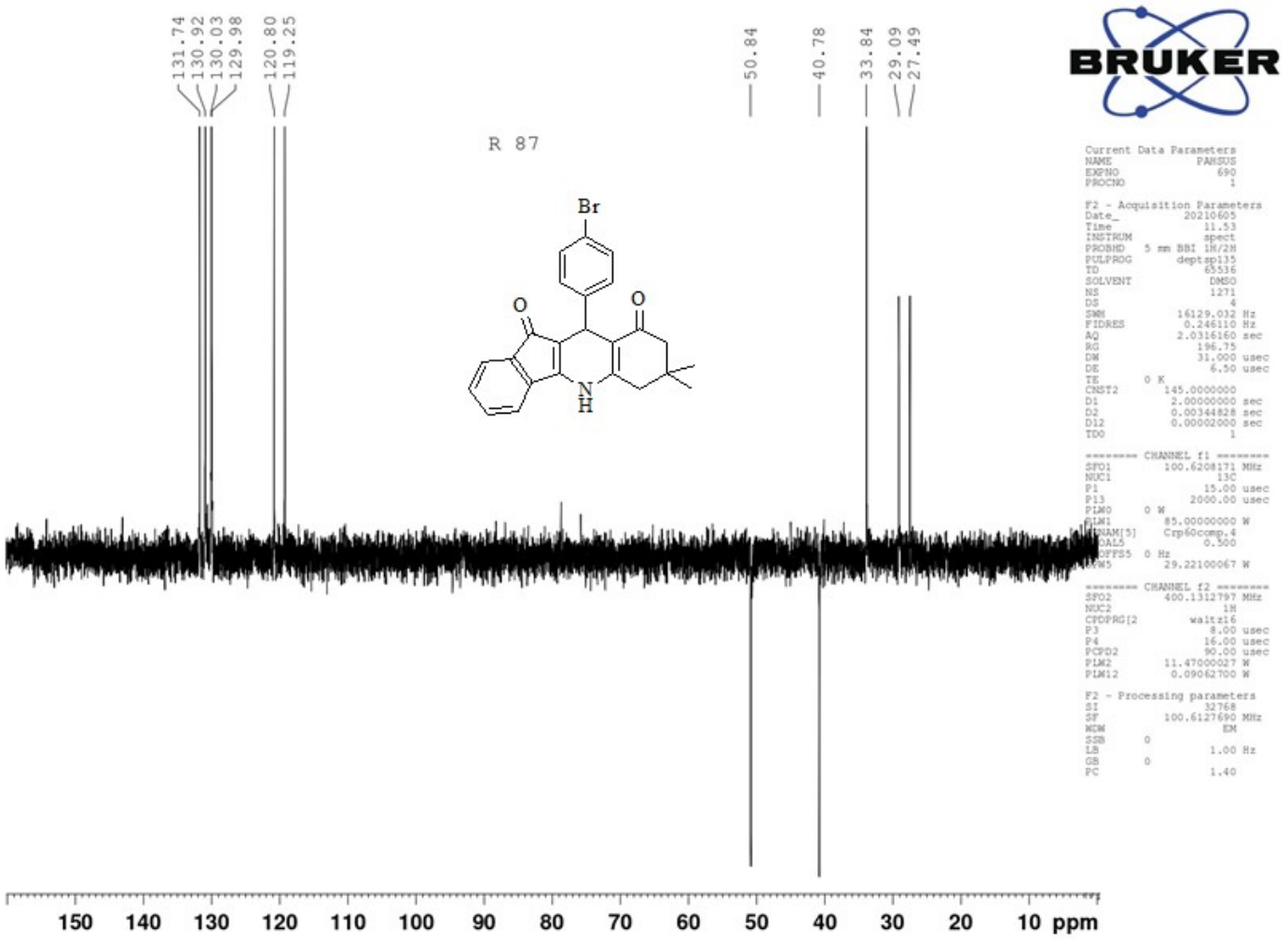
GC-MS MS (7a)


10.110
7.830
7.770
7.436
7.418
7.281
7.263
7.241
7.221
7.206
7.188
7.162
7.129
7.109
4.715
2.181
2.141
2.085
2.045
1.037
0.966
BRUKER
R 87
Br
O
O
N
H
Current Data Parameters
NAME PAHSUS
EXPNO 673
PROCNO 1
F2 - Acquisition Parameters
Date_ 20210527
Time 15.19
INSTRUM spect
PROBHD 5 mm BBI 1H/2H
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9845889 sec
RG 58.38
DW 60.800 usec
DE 6.50 usec
TE 0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 8.00 usec
PLW1 11.47000027 W
F2 - Processing parameters
SI 65536
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
11
10
9
8
7
6
5
4
3
2
1
ppm
0.92
1.09
7.13
1.00
2.77
2.14
6.01

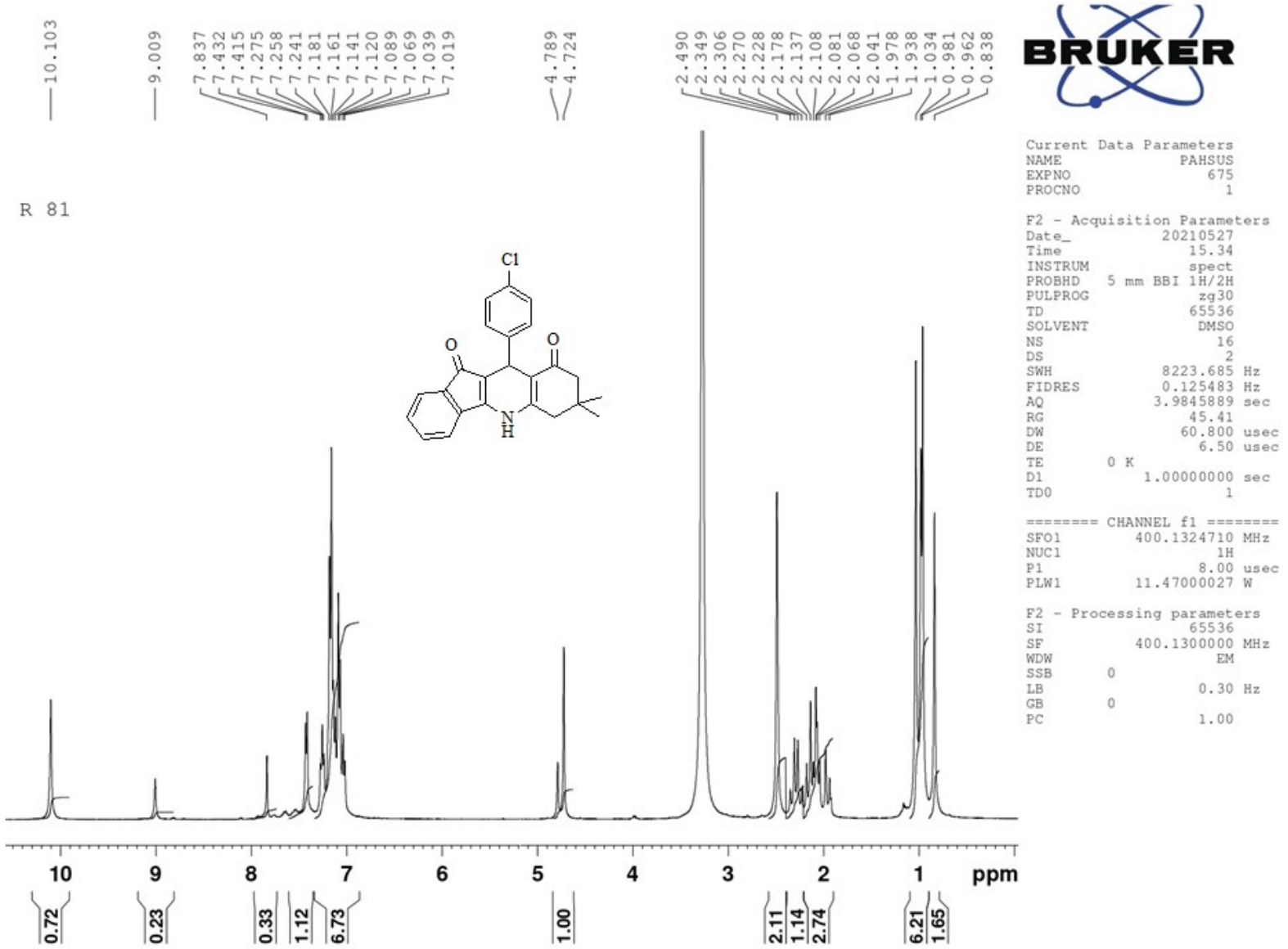
^{1}H NMR (7b)


195.51
191.84
154.16
150.56
145.43
136.59
133.41
131.74
130.92
130.02
129.98
120.80
119.48
119.25
113.52
110.29
50.85
40.80
33.85
32.46
29.09
27.49
R 87
Br
O
O
N
H
BRUKER
Current Data Parameters
NAME PAHSUS
EXPNO 691
PROCNO 1
F2 - Acquisition Parameters
Date_ 20210605
Time 13.45
INSTRUM spect
PROBHD 5 mm BBI 1H/2H
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 2345
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 196.75
DW 20.800 usec
DE 6.50 usec
TE 0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
-------- CHANNEL f1 --------
SFO1 100.6228293 MHz
NUC1 13C
P1 15.00 usec
PLW1 85.00000000 W
-------- CHANNEL f2 --------
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 11.47000027 W
PLW12 0.09062700 W
PLW13 0.09062700 W
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

^{13}C NMR (7b)



DEPT 13C NMR (7b)

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Current Data Parameters
NAME                  PAHSUS
EXPNO                    675
PROCNO                     1

F2 - Acquisition Parameters
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Time                   15.34
INSTRUM                spect
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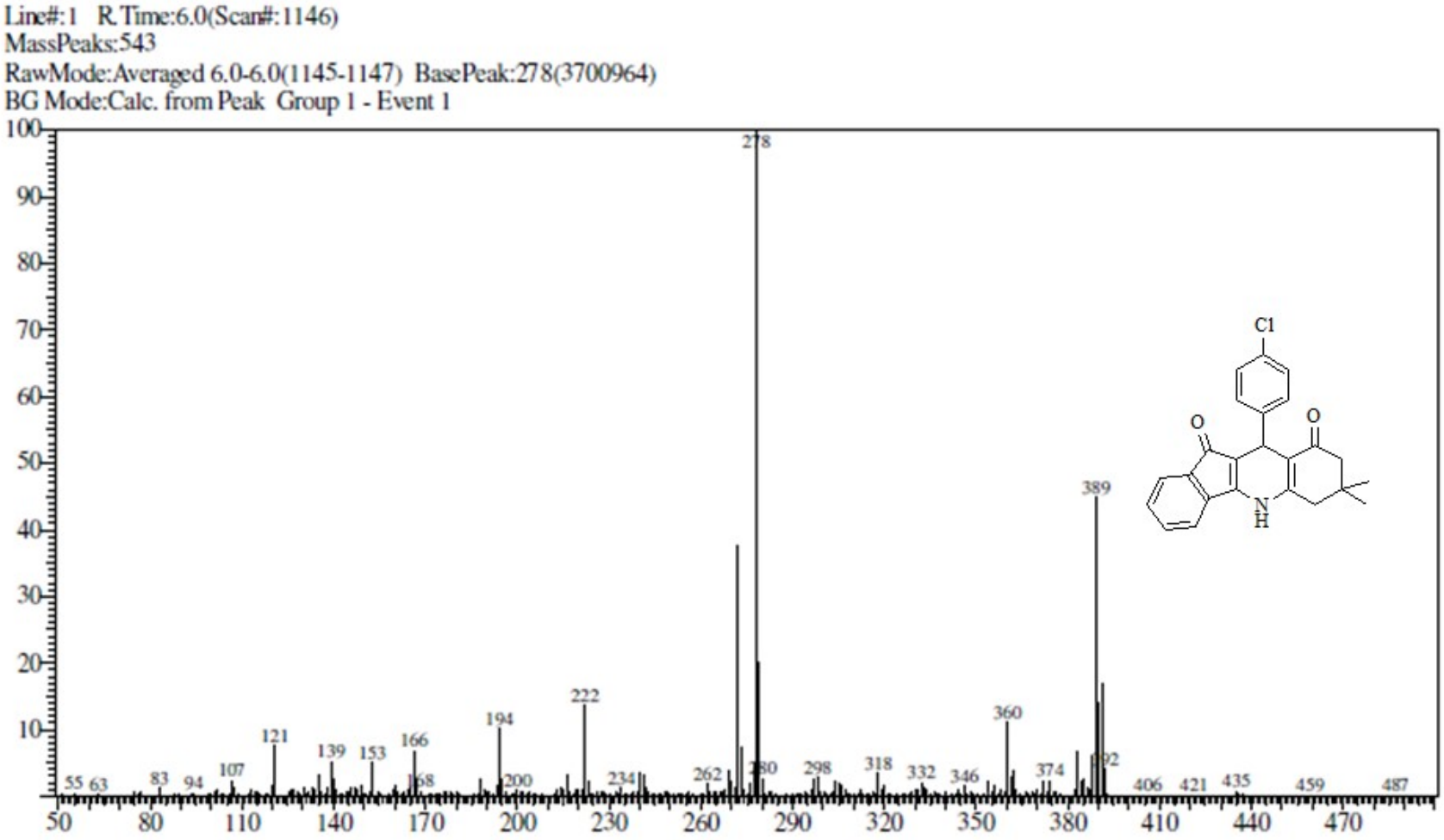
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9845889 sec
RG                     45.41
DW                  60.800 usec
DE                   6.50 usec
TE         0 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                      1H
P1                     8.00 usec
PLW1           11.47000027 W

F2 - Processing parameters
SI                    65536
SF             400.1300000 MHz
WDW                      EM
SSB        0
LB                     0.30 Hz
GB         0
PC                     1.00
```

^{1}H NMR (7c)

Spectrum



GC-MS MS (7c)

Table S1 Comparison of the catalytic efficiency of Cu/zeolite-Y with previously reported catalysts for the synthesis of indenoquinoline derivatives via multi-component reactions

Entry	Catalyst	Reactions condition	Time (Min)	Yield (%)	Literature
1	p-TSA	Solvent free, Gridding/ R.T.	10	86	[10]
2	$H_{14}[NaP_5W_{30}O_{110}]$	Solvent free/ 120 °C, 0.03 g of catalyst	150	70	[12]
3	Melamine trisulfonic acid (MTSA)	EtOH/reflux, 50 mg	270	83	[23]
4	CH_3CO_2H	120 °C/ MWI	4	91	[39]
5	Tribromomelamine (TBM)	EtOH/reflux, 10 mol% of catalyst	60	92	[44]
6	SA	EtOH/reflux, 10 mol% of catalyst	90	61	[44]
7	$ZrOCl_2$	EtOH/reflux, 10 mol% of catalyst	120	52	[44]
8	p-TSA	EtOH/reflux, 10 mol% of	90	73	[44]

		catalyst			
9	$In(OTf)_3$	DMF/100 °C, 0.05 mmol of catalyst	120	76	[42]
10	$[bmim^+][BF^-_4]$	10 mL/90 °C	240	94	[40]
11	Cu/Zeolite-Y	EtOH/reflux, 0.015 g of catalyst	180	95	This work