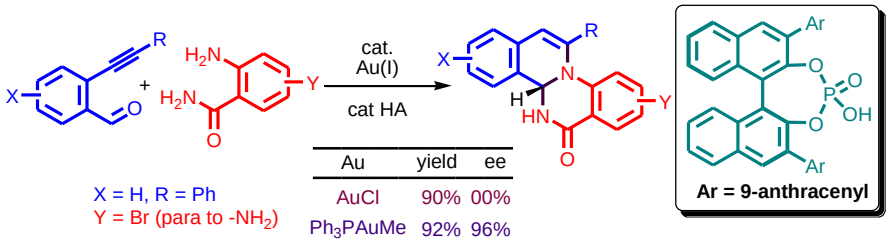
Tuning the Reactivity of Au-Complexes in Au(I)/Chiral Brønsted Acid Cooperative Catalytic System: An Approach to Optically Active Fused 1,2-Dihydroisoquinolines

Nitin T. Patil, Anil Kumar Mutyala, Ashok Konala, Ramesh Babu Tella*



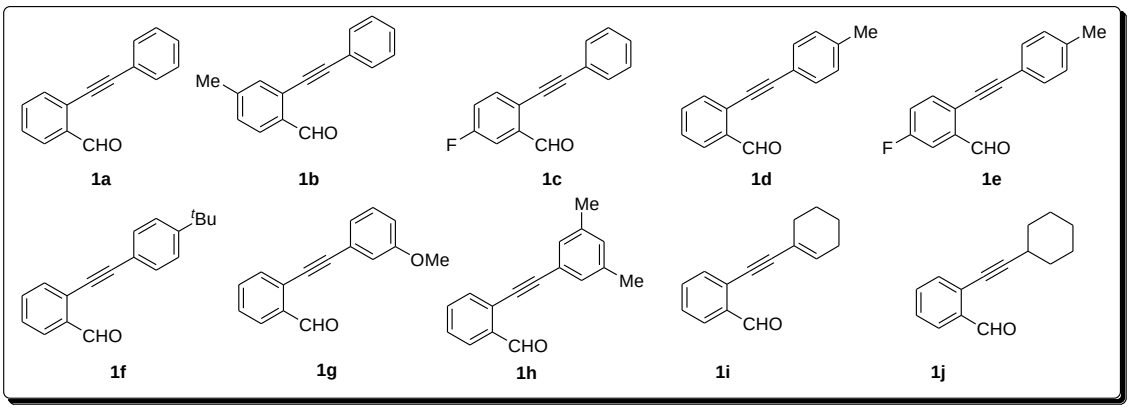
1. General Information

All reactions were carried out in oven or flame dried vials with magnetic stirring under nitrogen atmosphere. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccators. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining $KMnO_4$ and charring on a hot plate. Solvents were removed under reduced pressure in a water bath at 35 °C. Silica gel finer than 200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in hexane and equilibrated with the appropriate solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with an air pump.

Melting points are uncorrected. IR spectra were recorded as neat liquids or KBr pellets and absorptions are reported in cm^{-1}. ^1H NMR spectra were recorded on 300, 400 and 500 MHz spectrometers in appropriate solvents using TMS as internal standard or the solvent signals as secondary standards and the chemical shifts were shown in δ scales. Multiplicities of NMR signals were designated as s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), pent (pentet), m (multiplet) etc. ^{13}C NMR spectra were recorded on 75, 100 MHz spectrometers. High-resolution mass spectra were obtained by using ESI-QTOF mass spectrometry. The enantiomeric ratios (e.r.) were determined by HPLC analysis employing a Chiralcel OD-H column. Optical rotations were measured on a JASCO digital polarimeter.

2. Synthesis and Characterization of Starting Materials

2.1 Preparation of 2-Alkynylbenzaldehydes



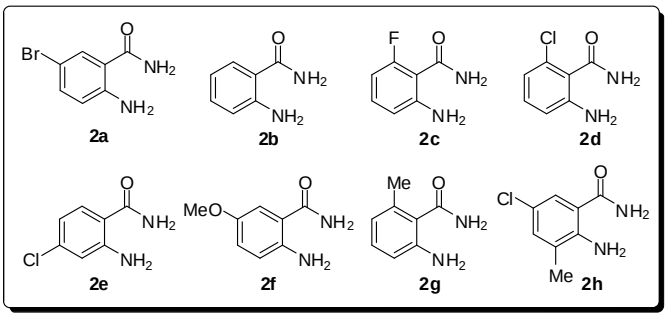
The substrates **1a**,[1] **1b**,[2] **1c**,[3] **1d**,[4] **1f**,[5] **1g**,[6] **1i**[7] and **1j**[7] were prepared according to literature known procedures. 2-alkynylbenzaldehydes **1e** and **1h** were unknown and prepared by Sonogashira reaction as described below.

Preparation of 5-fluoro-2-(p-tolylethynyl)benzaldehyde (1e): To a 25 mL round bottom flask a solution of 2-bromo-5-fluorobenzaldehyde (1.0 g, 4.98 mmol) in Et_3N (6 mL) was taken and purged with dry nitrogen for 25 minutes. To the above flask a solution of 1-ethynyl-4-methylbenzene (0.773 g, 6.66 mmol) in Et_3N (6 mL) was added drop wise. Catalysts $PdCl_2(PPh_3)_2$ (0.128 g, 0.28 mmol) and CuI (0.031 g, 0.17 mmol) were introduced into the flask under nitrogen atmosphere at room temperature. The reaction mixture was warmed to 65 °C and stirred for 10 h. The reaction mixture was cooled to room temperature and filtered through a short SiO_2 pad and the filtrate was concentrated. The residue was purified by column chromatography by using hexane/ethylacetate (98/02) as eluent to afford **1e**. 79% (932 mg) yield; brown solid; mp 82–84 °C; R_f = 0.36 (hexane/EtOAc = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.55 (d, *J* = 3.2 Hz, 1H), 7.62-7.57 (m, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.29-7.22 (m, 1H), 7.15 (d, *J* = 7.7 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.5, 163.9, 160.5, 139.4, 137.6, 137.5, 135.1, 135.0, 131.5, 129.3, 123.3, 123.2, 121.4, 121.1, 119.0, 113.7, 113.4, 96.3, 83.2, 21.5; IR (KBr): ν_{max} 3027, 2922, 2852, 1692, 1601, 1508, 1260, 1140, 815, 732, 525 cm^{-1}; HRMS calcd for $C_{16}H_{12}FO$ (M^++H) 239.0872, found 239.0887.

2-((3,5-dimethylphenyl)ethynyl)benzaldehyde (1h): The compound **1h** was prepared following the procedure for the preparation of **1e**; 75% (870 mg) yield; pale yellow solid; mp 95–97 °C; R_f = 0.41 (hexane/EtOAc = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.62 (s, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.60-7.52 (m, 2H), 7.42 (t, *J* = 6.8 Hz, 1H), 7.16 (s, 2H), 6.98 (s, 1H), 2.33 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.7, 138.1, 135.7, 133.7, 133.1, 131.0, 129.3, 128.4, 127.1, 121.9, 96.8, 84.2, 21.0; IR (KBr): ν_{max} 2914, 2837, 2750, 1693, 1597, 1476, 1263, 1188, 1086, 845, 768, 684, 640 cm^{-1}; HRMS calcd for $C_{17}H_{14}ONa$ (M^++Na) 257.0942 found 257.0943.

2.2 Preparation of 2-Aminobenzamides

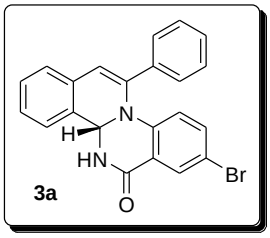
1 S. Takao, K. Yoshinori, M. Norio, H. Kazuhiko, Y. Hiroshi, *Heterocycles* 1986, **24**, 2411-2314.
2 Y. Reiko, H. Kana, T. Rie, M. Yoshihisa, M. Hideki, Y. Kazuo, I. Minoru, T. Yoshiji, *J. Org. Chem*. 2008, **73**, 5135 - 5138.
3 S. Obika, H. Kono, Y. Yasui, R. Yanada, Y. Takemoto, *J. Org. Chem*. 2007, **72**, 4462-4468.
4 G. B. Bajracharya, I. Nakamura, Y. Yamamoto, *J. Org. Chem*. 2005, **70**, 892-897.
5 K. K. Wang, H.-R. Zhang, J. L. Petersen, *J. Org. Chem.* 1999**, 64**, 1650-1656.
6 N. T. Patil, A. Konala, V. Singh, V. V. N. Reddy, *Eur. J. Org. Chem*. 2009, 5178-5184.
7 K. R. Roesch, R. C. Larock, *J. Org. Chem.* 2002**, 67**, 86-94.



All substrates **2a**,[8] **2b**,[9] **2c**,[10] **2d**,[10] **2e**,[11] **2f**,[12] **2g**[10] and **2h**[13] were prepared according to literature known procedures.

3. General Procedure and Characterization Data of Compounds

A dichloroethane (2 mL) solution of 2-alkynyl benzaldehydes **1** (0.2424 mmol), 2-aminobenzamides **2** (0.2424 mmol) and 50 mg 4Å molecular sieves were taken in 2.5 mL screw capped vial under nitrogen atmosphere and cooled to –5 °C. Catalysts 5 mol% **4c** and 2 mol% PPh_3AuMe were introduced to the reaction mixture under nitrogen atmosphere at –5 °C. The resulting solution was stirred for 32 h at –5 °C after reaction mixture was warm to room temperature and stirred for 24 h. The crude reaction mixture was filtered through a short pad of active neutral Al_2O_3 with dichloromethane as an eluent and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (active neutral Al_2O_3) using CH_2Cl_2/MeOH (98/02) as eluent to obtain **3**.



(*S*)-8-bromo-4b,5-dihydro-12-phenylisoquinolino[2,1-a]quinazolin-6-one (3a):[14] 92% (90 mg) yield; yellow solid; mp 259–269 °C; R_f = 0.41, (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.21 (d, *J* = 5.1 Hz, 1H), 7.82-7.76 (m, 3H), 7.47-7.28 (m, 7H), 7.12 (s, 1H), 7.11 (dd, *J* = 8.2, 2.5 Hz, 1H),

8 M. Tobe, Y. Isobe, H. Tomizawa, T. Nagasaki, H. Takahashi, T. Fukazawa, H. Hayashi, *Bioorg. Med. Chem.* 2003, **11**, 383-391.
9 A. D. Roy, A. Subramanian, R. Roy, *J. Org. Chem*. 2006, **71**, 382-385.
10 X. Cheng, S. Vellalath, R. Goddard, B. List, *J. Am. Chem. Soc.* 2008, **130**, 15786-15787.
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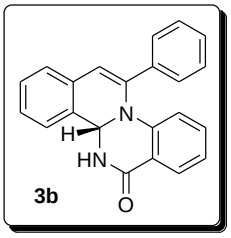
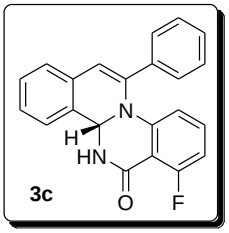
12 M.-J. Hour, L.-J. Huang, X.-Y. Kuo, K. Bastow, Y. Nakanishi, E. Hamel, K. -H. Lee, *J. Med. Chem.* 2000, **43**, 4479-4487.
13 N. T. Patil, R. D. Kavthe, V. S. Raut, V. S. Shinde, B. Sridhar, *J. Org. Chem*. 2010, **75**, 1277-1280.
14 N. T. Patil, A. K. Mutyala, P. G. V. V. Lakshmi, P. V. K. Raju, B. Sridhar, *Eur. J. Org. Chem.* 2010, 1999-2007.

6.05 (d, *J* = 8.7 Hz, 1H), 5.69 (d, *J* = 4.9 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.5, 143.1, 141.3, 135.4, 134.3, 131.9, 131.3, 129.3, 129.2, 128.3, 128.2, 125.7, 123.3, 118.7, 116.9, 111.3, 67.1; IR (KBr): ν_{max} 3520, 3167, 3051, 2920, 1684, 1597, 1473, 1364, 1025, 814, 758, 698 cm^{-1}; HRMS calcd for $C_{22}H_{16}BrN_2O$ (M^++H) 403.0446, found 403.0438; 98:02 e.r.; HPLC conditions: OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{major} = 13.60, t_{minor} = 29.86; $[\alpha]_D^{29.8}$ = –147.5 (c = 0.07, $CHCl_3$).

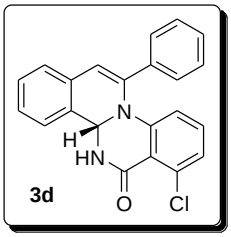


(*S*)-4b,5-dihydro-12-phenylisoquinolino[2,1-a]quinazolin-6-one (3b):[14] 82% (64.5 mg) yield; yellow solid; mp 192–194 °C; R_f = 0.38 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.76 (s, 1H), 7.78-7.75 (m, 3H), 7.39-7.22 (m, 7H), 6.98-6.93 (m, 2H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.13 (d, *J* = 8.4 Hz, 1H), 5.73 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.8, 143.9, 141.9, 134.8, 132.9, 132.1, 129.1, 128.9, 128.7, 128.2, 128.1, 127.3, 126.7, 126.5, 125.8, 125.6, 123.4, 122.3, 119.7, 116.5, 67.2; IR (KBr): ν_{max} 3498, 3164, 2987, 1710, 1622, 1432, 1082, 752, 685, 672 cm^{-1}; HRMS calcd for $C_{22}H_{17}N_2O$ (M^+ + H) 325.1340, found 325.1331; 94:06 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 15.32, t_{major} = 23.67; $[\alpha]_D^{29.1}$ = –80.1(c = 0.7, $CHCl_3$).

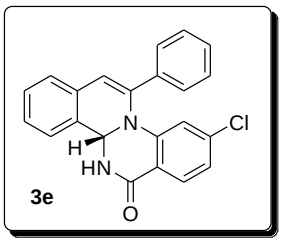


(*S*)-7-fluoro-4b,5-dihydro-12-phenylisoquinolino[2,1-a]quinazolin-6-one (3c):[14] 76% (63 mg) yield; white solid; mp 231–233 °C; R_f = 0.40 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (s, 2H), 7.39-7.16 (m, 8H), 6.90-6.83 (m, 1H), 6.83 (s, 1H), 6.46 (t, *J* = 8.7 Hz, 1H), 5.98 (d, *J* = 8.3 Hz, 1H), 5.83 (d, *J* = 4.5 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 163.1, 159.7, 158.9, 146.0, 141.7, 138.3, 136.4, 134.6, 133.7, 131.9, 129.1, 128.8, 128.7, 128.3, 128.1, 127.3, 127.0, 126.5, 125.7, 123.4, 118.5, 116.9, 112.8, 111.5, 108.3, 101.6, 67.0; IR (KBr): ν_{max} 3187, 3071, 2929, 1669, 1613, 1468, 1359, 1113, 804, 755, 691, 470 cm^{-1}; HRMS calcd for $C_{22}H_{16}N_2OF$ (M^++H) 343.1246, found 343.1244; 90:10 e.r.;

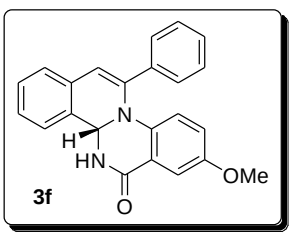
HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 16.85, t_{major} = 26.09; $[\alpha]_D^{29.8}$ = –125.2 (c = 0.07, $CHCl_3$).



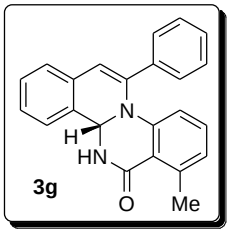
(*S*)-7-chloro-4b,5-dihydro-12-phenylisoquinolino[2,1-a]quinazolin-6-one (3d): 59% (51 mg) yield; mp 213–216 °C; R_f = 0.39 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.15 (d, *J* = 5.9 Hz, 1H), 7.87-7.67 (m, 2H), 7.47-7.35 (m, 8H), 7.0 (t, *J* = 8.3 Hz, 1H), 6.84 (d, *J* = 7.4 Hz, 1H), 6.15 (d, *J* = 8.3 Hz, 1H), 5.7 (S, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 159.6, 146.5, 141.7, 134.5, 133.4, 132.4, 131.9, 129.0, 128.4, 128.1, 123.5, 66.6; IR (KBr): 3286, 3186, 3066, 2927, 2851, 1675, 1597, 1472, 1318, 1172, 816, 754, 542; HRMS calcd for $C_{22}H_{16}N_2OCl$ (M^++H) 359.0951, found 359.0956; 81:19 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 16.54, t_{major} = 26.36; $[\alpha]_D^{32.7}$ = –51.6 (c = 0.5, $CHCl_3$).



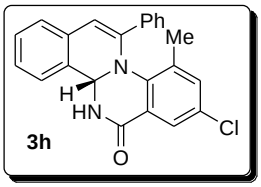
(*S*)-9-chloro-4b,5-dihydro-12-phenylisoquinolino[2,1-a]quinazolin-6-one (3e):[14] 64% (53 mg) yield; yellow solid; mp 197–199 °C; R_f = 0.41 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.15 (s, 1H), 7.82 (d, *J* = 6.8 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.49-7.34 (m, 8H), 6.78 (t, *J* = 8.8 Hz, 1H), 6.05 (s, 1H), 5.73 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.4, 145.6, 141.7, 137.9, 134.7, 132.3, 129.8, 129.7, 128.9, 128.8, 126.4, 126.1, 123.8, 120.3, 117.9, 117.2, 116.2, 67.8; IR (KBr): ν_{max} 3369, 3164, 3056, 2923, 1668, 1614, 1456, 1324, 1133, 1032, 767 cm^{-1}; HRMS calcd for $C_{22}H_{16}N_2OCl$ (M^++H) 359.0951, found 359.0939; 97:03 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 17.33, t_{major} = 31.60; $[\alpha]_D^{28.4}$ = –104.6 (c = 0.5, $CHCl_3$).



(*S*)-4b,5-dihydro-8-methoxy-12-phenylisoquinolino[2,1-a]quinazolin-6-one (3f): 71% (60 mg) yield; white solid; mp 216–218 °C; R_f = 0.33 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (d, *J* = 7.7 Hz, 1H), 7.64 (bs, 1H), 7.42-7.40 (m, 1H), 7.45-7.16 (m, 7H), 7.02 (t, *J* = 8.3 Hz, 1H), 6.89-6.78 (m, 3H), 6.24 (d, *J* = 8.3 Hz, 1H), 5.94 (d, *J* = 4.0 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.8, 153.1, 142.0, 137.4, 135.0, 132.0, 129.0, 128.2, 127.8, 126.0, 125.3, 123.7, 119.6, 110.8, 67.2, 55.2; IR (KBr): ν_{max} 3429, 3060, 2933, 1669, 1609, 1516, 1486, 1349, 1286, 1156, 1029, 823, 768, 700, 641, 555 cm^{-1}; HRMS calcd for $C_{23}H_{19}N_2O_2$ (M^++H) 355.1446, found .355.1445; 95:05 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 15.42, t_{major} = 25.18; $[\alpha]_D^{28.4}$ = –117.8 (c = 0.5, $CHCl_3$).

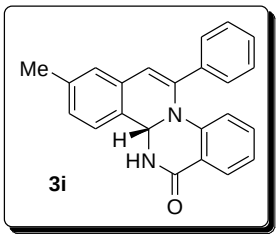


(*S*)-4b,5-dihydro-7-methyl-12-phenylisoquinolino[2,1-a]quinazolin-6-one (3g): 65% (53 mg) yield; white solid; mp 217–219 °C; R_f = 0.38 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 8.74 (d, *J* = 5.3 Hz, 1H), 7.74-7.61 (m, 2H), 7.36-7.16 (m, 8H), 6.76 (t, *J* = 7.9 Hz, 1H), 6.50 (d, *J* = 7.2 Hz, 1H), 5.98 (d, *J* = 8.1 Hz, 1H), 5.57 (s, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ 163.2, 145.3, 142.8, 140.7, 135.6, 132.5, 131.5, 130.5, 129.2, 128.5, 128.0, 126.4, 125.7, 124.3, 67.3, 22.2; IR (KBr): ν_{max} 3439, 3200, 3064, 2924, 1732, 1668, 1599, 1467, 1247, 1039, 759, 693, 533 cm^{-1}; HRMS calcd for $C_{23}H_{19}N_2O$ (M^++H) 339.1497, found 339.1508; 93:07 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 14.52, t_{major} = 18.46; $[\alpha]_D^{29.8}$ = –88.47 (c = 0.5, $CHCl_3$).

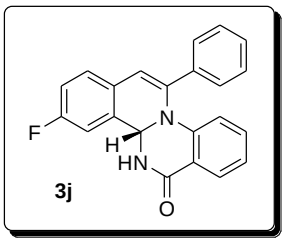


(*S*)-8-chloro-4b,5-dihydro-10-methyl-12-phenylisoquinolino[2,1-a]quinazolin-6-one (3h): 36% (33 mg) yield; yellow solid; mp 194–196 °C; R_f = 0.38 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (d, *J* = 2.0 Hz, 1H), 7.35-7.32 (m, 1H), 7.21-7.09 (m, 6H), 7.00 (d, *J* = 2.0 Hz, 1H), 6.90 (d, *J* = 7.0 Hz, 2H), 6.40 (s, 1H) 6.13 (d, *J* = 2.0 Hz, 1H), 5.77 (s, 1H), 1.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.7, 141.8, 140.9, 136.2, 135.3, 134.0, 132.5, 131.5, 130.0, 128.6, 128.1, 127.6, 126.6, 125.7, 124.8, 124.1, 105.3, 68.2, 17.7; IR (KBr): ν_{max} 3368, 3058, 2922, 1669, 1602, 1454, 1315, 1130, 1033,

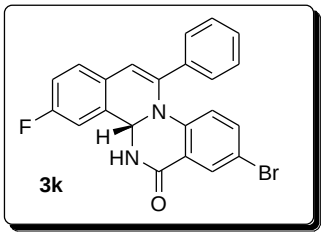
880, 760, 693, 512 cm^{-1}; HRMS calcd for $C_{23}H_{18}N_2OCl$ (M^++H) 373.1107, found 373.1112; 81:19 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 12.67, t_{major} = 11.04; $[\alpha]_D^{32.6}$= –35.1(c = 0.5, $CHCl_3$).



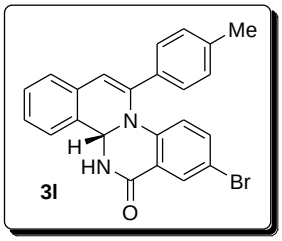
(*S*)-4b,5-dihydro-2-methyl-12-phenylisoquinolino[2,1-a]quinazolin-6-one (3i): 74% (61 mg) yield; white solid; mp 232–234 °C; R_f= 0.39 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.4 Hz, 1H), 7.64-7.51 (m, 2H), 7.39-7.19 (m, 4H), 7.04-6.75 (m, 5H), 6.66 (s, 1H), 6.16 (d, *J* = 8.3 Hz, 1H), 5.85 (d, *J* = 3.8 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.6, 143.9, 141.8, 137.4, 134.9, 132.7, 131.9, 129.0, 128.4, 127.1, 126.1, 125.6, 123.3, 119.6, 116.4, 67.1, 20.6; IR (KBr): ν_{max} 3396, 3191, 3060, 2922, 1673, 1602, 1511, 1339, 1077, 1027, 757, 699, 535 cm^{-1}; HRMS calcd for $C_{23}H_{19}N_2O$ (M^++H) 339.1497, found 339.1492; 90:10 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 12.90, t_{major} = 18.24; $[\alpha]_D^{29.1}$ = –90.8 (c = 0.5, $CHCl_3$).



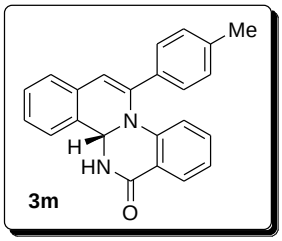
(*S*)-3-fluoro-4b,5-dihydro-12-phenylisoquinolino[2,1-a]quinazolin-6-one (3j): 86% (71 mg) yield; white solid; mp 156–158 °C; R_f= 0.39 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.28 (bs, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 6.6 Hz, 2H), 7.40-7.34 (m, 3H), 7.23-7.18 (m, 2H), 7.03-6.95 (m, 2H), 6.95 (s, 1H), 6.82 (t, *J* = 7.6 Hz, 1H), 6.18 (d, *J* = 8.3 Hz, 1H), 5.87 (d, *J* = 4.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.2, 161.3, 141.8, 135.0, 133.4, 129.2, 129.1, 128.4, 128.1, 127.1, 126.2, 120.6, 117.5, 115.6, 114.8, 111.8, 111.5, 67.8; IR (KBr): ν_{max} 3430, 3190, 3067, 2924, 1672, 1604, 1492, 1358, 1265, 1188, 1028, 950, 837, 754, 693 cm^{-1}; HRMS calcd for $C_{22}H_{16}FN_2O$ (M^++H) 343.1246, found 343.1240; 99:01 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 13.03, t_{major} =15.52; $[\alpha]_D^{29.1}$ = –162.0 (c = 0.5, $CHCl_3$).



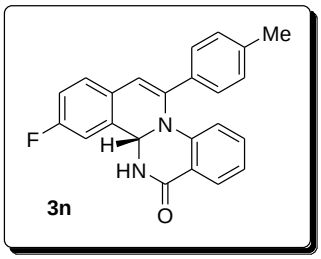
(*S*)-8-bromo-3-fluoro-4b,5-dihydro-12-phenylisoquinolino[2,1-a]quinazolin-6-one (3k): 89% (91mg) yield; pale yellow solid; mp 175–177 °C; R_f = 0.42 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 (d, *J* = 2.5 Hz, 1H), 7.75-7.67 (m, 3H), 7.45-7.38 (m, 3H), 7.27-6.98 (m, 5H), 6.11 (d, *J* = 8.69 Hz, 1H), 5.85 (d, *J* = 4.9 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 160.3, 143.0, 140.7, 135.5, 134.2, 129.4, 129.2, 128.4, 128.0, 125.6, 118.6, 115.4, 115.1, 111.5, 111.0, 110.7, 66.7; IR (KBr): ν_{max} 3341, 3170, 2921, 1682, 1598, 1479, 1363, 1271, 1185, 821, 759, 697 cm^{-1}; HRMS calcd for $C_{22}H_{15}BrN_2OF$ (M^++H) 421.0351, found 421.0350; 99:01 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 11.84, t_{major} = 15.72; $[\alpha]_D^{29.8}$ = –172.4 (c = 0.07, $CHCl_3$).



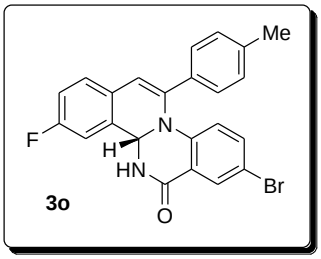
(*S*)-8-bromo-4b,5-dihydro-12-p-tolylisoquinolino[2,1-a]quinazolin-6-one (3l): 93% (94 mg yield; yellow solid; mp 240–242 °C; R_f = 0.43 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (d, *J* = 2.2 Hz, 1H), 7.60-7.44 (m, 3H), 7.33-7.19 (m, 5H), 7.07 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.87 (s, 1H), 6.09 (d, *J* = 8.9 Hz, 1H), 5.88 (d, *J* = 4.5 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 162.8, 143.0, 141.9, 139.5, 135.8, 132.2, 131.8, 130.5, 129.8, 128.7, 128.0, 127.0, 126.2, 125.4, 123.5, 119.6, 68.1, 21.3; IR (KBr): ν_{max} 3369, 3167, 3047, 2917, 1679, 1600, 1474, 1352, 1185, 810, 748 cm^{-1}; HRMS calcd for $C_{23}H_{18}BrN_2O$ (M^++H) 417.0603, found 417.0609; 98:02 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 12.23, t_{major} = 21.95; $[\alpha]_D^{29.1}$ = –124.1 (c = 0.5, $CHCl_3$).



(*S*)-4b,5-dihydro-12-p-tolylisoquinolino[2,1-a]quinazolin-6-one (3m): 84% (69 mg) yield; white solid; mp 256–258 °C; R_f = 0.40, (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.1 Hz, 1H), 7.54-7.44 (m, 3H), 7.27-7.26 (m, 3H), 7.18-7.14 (m, 3H), 6.98 (t, *J* = 7.1 Hz, 1H), 6.81 (t, *J* = 7.1 Hz, 1H), 6.73 (s, 1H), 6.19 (d, *J* = 8.1 Hz, 1H), 5.91 (d, *J* = 4.1 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.9, 144.0, 142.1, 139.2, 133.5, 133.2, 132.4, 130.0, 129.7, 128.6, 128.0, 127.8, 127.1, 126.5, 125.2, 123.7, 122.1, 120.6, 118.2, 117.3, 68.1, 21.4; IR (KBr): ν_{max} 3426, 3187, 3046, 2917, 1670, 1604, 1484, 1404, 1362, 1336, 1045, 816, 753 cm^{-1}; HRMS calcd for $C_{23}H_{19}N_2O$ (M^++H), 339.1497 found 339.1484; 97:03 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 14.04, t_{major} = 19.48; $[\alpha]_D^{29.1}$ = –150.7 (c = 1.9, $CHCl_3$).

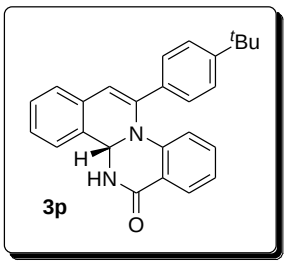


(*S*)-3-fluoro-4b,5-dihydro-12-p-tolylisoquinolino[2,1-a]quinazolin-6-one (3n): 93% (81mg) white solid; mp 273–275 °C; R_f = 0.39, (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (d, *J* = 6.8 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.20-7.16 (m, 4H), 7.01-6.94 (m, 2H), 6.86 (s, 1H), 6.79 (t, *J* = 7.8 Hz, 1H), 6.21 (d, *J* = 8.8 Hz, 1H), 5.82 (d, *J* = 4.9 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 163.5, 161.6, 160.2, 143.8, 138.7, 132.9, 131.9, 129.6, 128.9, 128.7, 128.6, 127.5, 127.4, 127.2, 125.5, 124.6, 119.7, 116.3, 115.1, 114.8, 110.9, 110.6, 66.8, 20.7; IR (KBr): ν_{max} 3391, 3187, 3043, 2923, 1668, 1604, 1481, 1357, 1265, 1181, 1042, 827, 752, 553 cm^{-1}; HRMS calcd for $C_{23}H_{18}N_2OF$ (M^++H) 357.1403, found 357.1420; 99:01 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 12.31, t_{major} = 13.32; $[\alpha]_D^{29.1}$ = –179 (c = 0.5, $CHCl_3$).

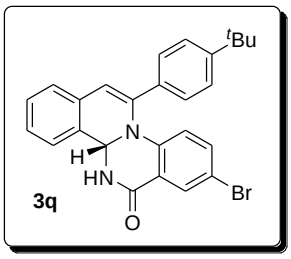


(*S*)-8-bromo-3-fluoro-4b,5-dihydro-12-p-tolylisoquinolino[2,1-a]quinazolin-6-one (3o): 95% (100 mg**)** yellow solid; mp 256–258 °C; R_f = 0.42 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.41 (bs, 1H), 7.96 (d, *J* = 2.3 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.23-7.16 (m, 4H), 7.08 (dd, *J* = 9.1, 2.3 Hz, 1H), 7.00 (td, *J* = 8.3, 2.3 Hz, 1H), 6.93 (s, 1H), 6.09 (d, *J* = 9.1 Hz, 1H), 5.82 (d, *J* = 5.3 Hz, 1H),

2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.5, 162.7, 143.1, 139.6, 136.1, 131.6, 130.6, 130.3, 129.9, 128.4, 127.0, 126.0, 119.2, 115.7, 115.4, 114.4, 112.9, 111.6, 111.3, 67.7, 21.3; IR (KBr): ν_{max} 3423, 3066, 2921, 1678, 1596, 1485, 1348, 1267, 1182, 1267, 816 cm^{-1}; HRMS calcd for $C_{23}H_{17}Br\ FN_2O$ (M^++H) 435.0508, found 435.0330; 97:03 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 11.02, t_{major} = 12.42; $[\alpha]_D^{32.8}$ = -136.5 (c = 0.5, $CHCl_3$).

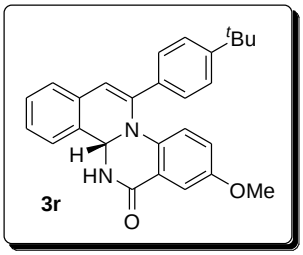


(*S*)-12-(4-tert-butylphenyl)-4b,5-dihydroisoquinolino[2,1-a]quinazolin-6-one (3p): 86% (79 mg) yield; white solid; mp 256–258 °C; R_f = 0.45 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.15 (d, *J* = 4.9 Hz, 1H), 7.82 (d, *J* = 8.9 Hz, 2H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 8.9 Hz, 2H), 7.45-7.40 (m, 5H), 7.15 (t, *J* = 6.9 Hz, 1H), 6.85 (t, *J* = 6.9 Hz, 1H), 6.23 (d, *J* = 7.9 Hz, 1H), 5.75 (d, *J* = 4.9 Hz, 1H), 1.39 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.8, 151.7, 144.0, 141.9, 132.9, 132.1, 132.0, 128.1, 127.8, 127.2, 125.9, 125.4, 123.3, 119.6, 116.3, 115.9, 67.2, 34.4, 30.9; IR (KBr): ν_{max} 3384, 3195, 2959, 1663, 1602, 1474, 1355, 1160, 1120, 831, 753, 534 cm^{-1}; HRMS calcd for $C_{26}H_{24}N_2ONa$ (M^++Na) 403.1786, found 403.1769; 93:07 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} =12.74, t_{major} = 22.99; $[\alpha]_D^{29.8}$ = –152.6 (c = 0.07, $CHCl_3$).

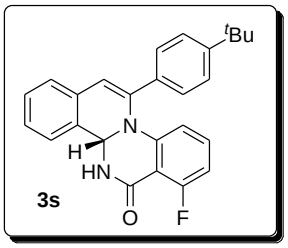


(*S*)-12-(4-tert-butylphenyl)-8-bromo-4b,5-dihydroisoquinolino[2,1-a]quinazolin-6-one (3q): 91% (101 mg) yield; white solid; mp 196–198 °C; R_f = 0.47, (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.92 (bs, 1H), 8.02 (s, 1H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.55-7.41 (m, 3H), 7.39-7.28 (m, 3H), 7.08 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.01 (s, 1H), 6.15 (d, *J* = 8.7 Hz, 1H), 5.92 (d, *J* = 4.3 Hz, 1H), 1.37 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.2, 152.7, 143.2, 141.8, 135.9, 132.8, 132.2, 131.7, 130.4, 128.6, 128.1, 125.9, 125.4, 123.5, 119.3, 115.4, 112.7, 68.1, 34.7, 31.2 ; IR (KBr): ν_{max} 3394, 3191, 3071, 2964, 1667, 1600, 1478, 1355, 1264, 1189, 1126, 1022, 834, 753, 530 cm^{-1}; HRMS calcd for $C_{26}H_{24}BrN_2O$

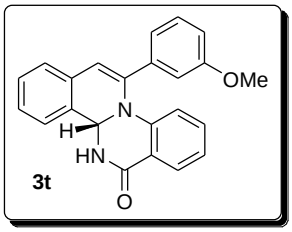
(M^++H) 459.1071, found 459.1068; 97:03 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 11.54, t_{major} = 34.25; $[\alpha]_D^{28.4}$ = –145.8 (c = 0.07, $CHCl_3$).



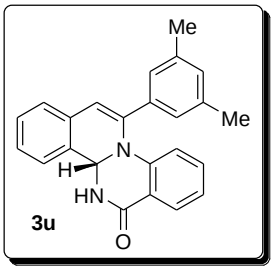
(*S*)-12-(4-tert-butylphenyl)-4b,5-dihydro-8-methoxyisoquinolino[2,1-a]quinazolin-6-one (3r): 81% (80.5mg) yield; white solid; mp 214–216 °C; R_f = 0.41 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43-7.16 (m, 9H), 7.15 (d, *J* = 6.9 Hz, 1H), 6.61 (dd, *J* = 9.1, 3.0 Hz, 1H), 6.46 (s, 1H), 6.20 (d, *J* = 9.1 Hz, 1H), 5.98 (s, 1H), 3.74 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.7, 152.9, 151.6, 142.1, 137.6, 132.2, 128.1, 127.6, 125.8, 125.6, 125.3, 123.5, 119.7, 110.7, 67.2, 55.2, 34.4, 30.9; IR (KBr): ν_{max} 3376, 3211, 3066, 2961, 1673, 1492, 1328, 1269, 1217, 1164, 1044, 835, 757, 541 cm^{-1}; HRMS calcd for $C_{27}H_{25}N_2O_2$ (M^--H) 409.1226, found 409.1215; 90:10 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 12.50, t_{major} = 22.38; $[\alpha]_D^{29.8}$ = –124.2 (c = 0.07, $CHCl_3$).



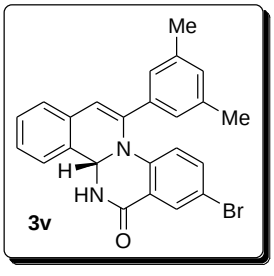
(*S*)-12-(4-tert-butylphenyl)-7-fluoro-4b,5-dihydroisoquinolino[2,1-a]quinazolin-6-one (3s): 91% (88 mg); white solid; mp 230–232 °C; R_f = 0.46, (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.6 Hz, 2H), 7.48-7.40 (m, 4H), 7.33-7.30 (m, 2H), 7.26-7.19 (m, 1H), 6.99-6.91 (m, 1H), 6.83 (s, 1H), 6.53 (t, *J* = 9.1 Hz, 1H), 6.08 (d, *J* = 8.3 Hz, 1H), 5.84 (d, *J* = 4.5 Hz, 1H), 1.39 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 163.6, 160.2, 159.5, 152.4, 146.8, 142.4, 134.3, 134.2, 132.6, 132.3, 128.8, 128.6, 126.4, 126.2, 125.9, 123.9, 113.2, 108.7, 108.4, 67.6, 34.9, 31.5; IR (KBr): ν_{max} 3406, 3096, 2964, 1668, 1616, 1475, 1324, 1120, 1077, 834, 802, 752, 573 cm^{-1}; HRMS calcd for $C_{26}H_{24}FN_2O$ (M^++H) 399.1872, found 399.1860; 98:02 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 14.66, t_{major} = 27.77; $[\alpha]_D^{29.8}$ =–183.6 (c = 0.07, $CHCl_3$).



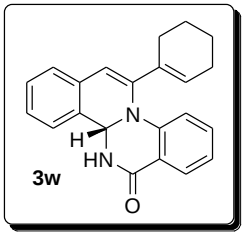
(*S*)-4b,5-dihydro-12-(3-methoxyphenyl)isoquinolino[2,1-a]quinazolin-6-one (3t): 78% (67 mg) yield; white solid; mp 171–173 °C; R_f = 0.32 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (bs, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 5.7 Hz, 1H), 7.30-7.16 (m, 6H), 7.01 (t, *J* = 8.3 Hz, 1H), 6.88-6.79 (m, 3H), 6.22 (d, *J* = 8.3 Hz, 1H), 5.95 (d, *J* = 4.9 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.1, 160.1, 142.2, 136.8, 133.5, 133.2, 132.2, 130.6, 130.0, 128.6, 128.1, 125.4, 123.9, 120.7, 119.0, 118.1, 117.7, 114.8, 111.9, 68.1, 55.4; IR (KBr): ν_{max} 3391, 3185, 3050, 2922, 1679, 1602, 1483, 1263, 1135, 1042, 750, 695 cm^{-1}; HRMS calcd for $C_{23}H_{19}N_2O_2$ (M^++H) 355.1446, found 355.1435; 94:06 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 16.75, t_{major} = 26.59; $[\alpha]_D^{29.8}$ = –117.3 (c = 0.07, $CHCl_3$).



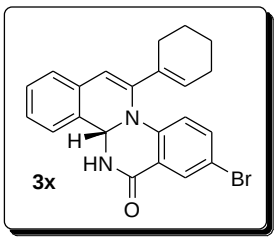
(*S*)-4b,5-dihydro-12-(3,5-dimethylphenyl)isoquinolino[2,1-a]quinazolin-6-one (3u): 91% (80 mg) yield; white solid; mp 264–266 °C; R_f = 0.41 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.35 (d, *J* = 4.7 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 2H), 7.68 (m, 2H), 7.60-7.47 (m, 4H), 7.32-7.21 (m, 2H), 7.02-6.93 (m, 1H), 6.43 (t, *J* = 8.3 Hz, 1H), 5.91 (d, *J* = 4.7 Hz, 1H), 2.54 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.7, 144.0, 142.2, 138.1, 135.0, 134.1, 132.8, 132.1, 130.7, 128.1, 127.8, 127.1, 125.4, 123.3, 119.5, 116.3, 67.2, 20.9; IR (KBr): ν_{max} 3347, 3180, 3040, 2918, 1668, 1602, 1484, 1333, 1224, 842, 754, 536 cm^{-1}; HRMS calcd for $C_{24}H_{20}N_2ONa$ (M^++Na) 375.1473, found 375.1478; 95:05 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 12.39, t_{major} = 17.15; $[\alpha]_D^{28.4}$= –141.3 (c = 0.07, $CHCl_3$).



(*S*)-8-bromo-4b,5-dihydro-12-(3,5-dimethylphenyl)isoquinolino[2,1-a]quinazolin-6-one (3v): 92% (94 mg) yield; pale yellow solid; mp 254–256 °C; R_f = 0.36 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.56 (d, *J* = 4.9 Hz, 1H), 8.06 (d, *J* = 2.1 Hz, 1H), 7.73 (s, 2H), 7.65-7.59 (m, 5H), 7.50 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.34 (s, 1H), 6.39 (d, *J* = 8.8 Hz, 1H), 5.99 (d, *J* = 4.9 Hz, 1H), 2.63 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 160.4, 143.1, 141.6, 138.0, 135.1, 134.3, 131.8, 130.6, 129.2, 128.0, 127.8, 125.3, 123.2, 118.4, 111.1, 67.1, 20.8; IR (KBr): ν_{max} 3397, 3166, 3055, 2914, 1668, 1600, 1477, 1353, 1184, 839, 751, 534 cm^{-1}; HRMS calcd for $C_{24}H_{19}N_2ONaBr$ (M^++Na) 453.0578, found 453.0583; 98:02 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 10.89, t_{major} = 18.80; $[\alpha]_D^{28.4}$= –101.3 (c = 0.5, $CHCl_3$).

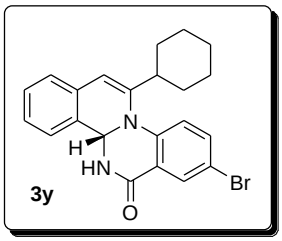


(*S*)-12-cyclohexenyl-4b,5-dihydroisoquinolino[2,1-a]quinazolin-6-one (3w): 84% (67 mg) yield; light yellow solid; mp 213–216 °C; R_f = 0.36 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.3 Hz, 1H), 7.58 (s, 1H), 7.40 (t, *J* = 4.5 HZ, 1H), 7.26-7.12 (m, 4H), 6.81 (t, *J* = 7.6 HZ, 1H), 6.56 (s, 1H), 6.48-6.45 (m, 2H), 5.66 (d, *J* = 4.5 HZ, 1H), 2.46-2.17 (m, 3H), 1.82-1.64 (m, 5H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.9, 144.8, 143.8, 134.4, 132.8, 132.1, 130.9, 128.8, 127.9, 127.6, 126.8, 125.7, 123.3, 119.3, 117.9, 116.1, 114.6, 66.9, 25.3, 24.1, 22.1, 21.6; IR (KBr): ν_{max} 3188, 3071, 2931, 2862, 1665, 1602, 1477, 1358, 1036, 752, 529; HRMS calcd for $C_{24}H_{21}N_2O$ (M^++H) 329.1653, found 329.1654; 94:06 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 298 nm; t_{minor} = 11.46, t_{major} = 18.44; $[\alpha]_D^{20.2}$ = –349.1 (c = 0.33, $CHCl_3$).

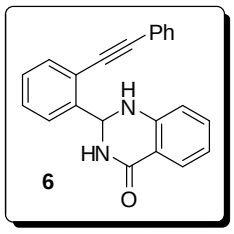


(*S*)-8-bromo-12-cyclohexenyl-4b,5-dihydroisoquinolino[2,1-a]quinazolin-6-one (3x): 90% (91 mg) yield; white solid; mp 219–222 °C; R_f = 0.38 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (d, *J* = 2.3 Hz, 1H), 7.70 (s, 1H), 7.37 (t, *J* = 4.5 Hz, 1H), 7.26-7.21 (m, 3H), 7.15-7.12 (m, 1H), 6.58 (s, 1H), 6.43 (s, 1H), 6.32 (d, *J* = 8.3 Hz, 1H), 5.63 (d, *J* = 4.5 Hz, 1H), 2.47-2.16 (m, 3H), 1.85-1.65 (m, 5H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.2, 144.7, 143.7, 136.0, 134.8, 132.5, 131.1, 129.6, 129.5,

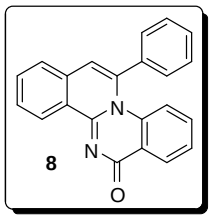
128.7, 128.4, 126.5, 123.9, 120.1, 119.1, 115.6, 111.5, 67.4, 25.9, 24.6, 22.6, 22.1; IR (KBr): ν_{max} 3480, 3170, 3041, 2924, 1667, 1602, 1475, 1355, 1240, 1006, 806, 752, 528; HRMS calcd for $C_{29}H_{20}BrN_2O$ (M^++H) 407.0758, found 407.0750; 97:03 e.r.; HPLC conditions: OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 298 nm; t_{minor} = 10.24, t_{major} = 21.46; $[\alpha]_D^{28.4}$ = –272.6 (c = 0.33, $CHCl_3$).



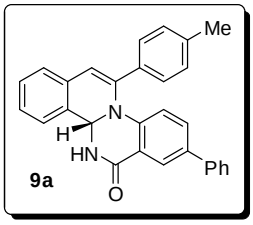
(*S*)-8-bromo-12-cyclohexyl-4b,5-dihydroisoquinolino[2,1-a]quinazolin-6-one (3y): 84% (83 mg) yield; white solid; mp 250–252 °C; R_f = 0.37 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44 (d, *J* = 2.08 Hz, 1H), 8.09 (d, *J* = 7.7 Hz, 1H), 7.75 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.63-7.58 (m, 1H), 7.52-7.48 (m, 3H), 7.18-7.21 (m, 2H), 5.44 (d, *J* = 6.4 Hz, 1H), 2.17-2.09 (m, 1H), 1.77-1.50 (m, 5H), 1.35-0.91 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.4, 144.9, 137.0, 136.6, 133.0, 132.2, 131.7, 129.3, 124.8, 122.5, 120.9, 118.9, 116.4, 62.0, 40.5, 34.1, 33.5, 33.1; IR (KBr): ν_{max} 3371, 3183, 3065, 2929, 2849, 1681, 1606, 1468, 1357, 1197, 1016, 841, 752, 606, 554 cm^{-1}; HRMS calcd for $C_{22}H_{21}N_2ONaBr$ (M^++Na) 431.0734, found 431.0752; 90:10 e.r.; HPLC conditions: OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 10.3, t_{major} = 14.39; $[\alpha]_D^{32.6}$ = –87.24 (c = 0.5, $CHCl_3$).



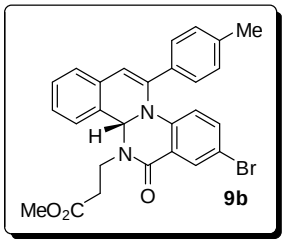
2-(2-(phenylethynyl)phenyl)-2,3-dihydroquinazolin-4(1H)-one (6): 94% (74 mg) yield; yellow solid; mp 86–89 °C; R_f = 0.37 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.75-7.72 (m, 1H), 7.58-7.55 (m, 1H), 7.51-7.47 (m, 2H), 7.39-7.26 (m, 6H), 6.84 (t, *J* = 8.1 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 6.49-6.47 (m, 2H), 4.82 (bs, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.3, 146.9, 140.8, 134.1, 131.6, 129.2, 129.1, 129.0, 128.6, 126.6, 122.3, 121.6, 119.4, 115.3, 114.7, 95.4, 85.7, 65.9; IR (KBr): ν_{max} 3451, 3121, 2942, 1658, 1612, 1489, 1377, 1155, 754, 691, 539; HRMS calcd for $C_{22}H_{16}N_2ONa$ (M^++Na) 347.1160, found 347.1177.



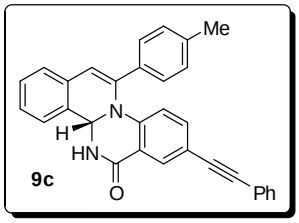
12-phenyl-6H-isoquinolino[2,1-a]quinazolin-6-one (8): 20% (16 mg) yield; yellow solid; mp 122-126 °C; R_f = 0.37 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.96 (d, *J* = 7.9, Hz, 1H), 8.30 (d, *J* = 7.6, Hz, 1H), 7.75-7.58 (m, 3H), 7.40-7.37 (m, 6H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.03 (s, 1H), 6.92 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1, 138.5, 137.0, 133.5, 130.6, 129.4, 129.1, 128.8, 128.2, 127.7, 127.2, 126.8, 126.4, 126.0, 122.1, 117.8; IR (KBr): ν_{max} 3057, 2923, 2853, 1652, 1628, 1597, 1516, 1448, 1339, 1132, 1025, 760, 702; HRMS calcd for $C_{22}H_{15}N_2O$ (M^++H) 323.1184, found 323.1176.



(*S*)-8-phenyl-12-p-tolyl-4bH-isoquinolino[2,1-a]quinazolin-6(5H)-one (**9a**): To a 25 mL round bottom flask a solution of **3l** (0.050 g, 0.1179 mmol) in DMF and water 2 mL (5:1) was added K_2CO_3 (0.041 g, 0.2947 mmol) and purged with nitrogen for 30 minutes. To the above flask benzene boronic acid (0.028 g, 0.2358 mmol) and $PdCl_2(PPh_3)_2$ (0.008 g, 0.01179 mmol) were introduced under nitrogen atmosphere at room temperature. The reaction mixture was warmed to 80 °C and stirred for 2 h. The reaction mixture was cooled to room temperature and filtered through a short SiO_2 pad and the filterate was extracted with DCM followed by water workup to remove DMF . The residue was purified by column chromatography by using hexane/ethyl acetate (70/30) as eluent to afford **9a** (0.047 g, 95%) as a pure product. yellow solid; mp 254-256°C; R_f = 0.34 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.17 (s, 1H), 7.93 (s, 1H), 7.72 (d, *J* = 6.9 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 3H), 7.27- 7.37 (m, 10H), 6.19 (d, *J* = 7.9 Hz, 1H), 5.70 (m, 1H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.7, 143.3, 141.8, 138.9, 132.2, 132.1, 131.9, 131.5, 131.4, 131.2, 129.8, 128.8, 128.7, 128.3, 127.9, 126.9, 125.9, 125.7, 125.6, 124.9, 123.3, 117.1, 67.2, 20.9.; IR (KBr): ν_{max} 3417, 3189, 3053, 2920, 1673, 1606, 1478, 1356, 1262, 1184, 1114, 816, 751, 695, 604, 515, 455, 405 cm^{-1}; HRMS calcd for $C_{29}H_{23}N_2O$ (M^+ + H) 415.1810, found 415.1816; 97:03 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 286 nm; t_{minor} = 15.90, t_{major} = 25.68; $[\alpha]_D^{29.1}$ = –34.0 (c = 0.5, $CHCl_3$).

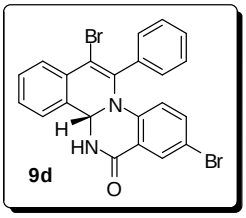


(*R*)-methyl 3-(8-bromo-6-oxo-12-p-tolyl-4bH-isoquinolino[2,1-a]quinazolin-5(6H)-yl)propanoate (9b): To a solution of **3l** (0.050 g, 0.1179 mmol) in DMF (2 mL) were added methyl acrylate (0.012 g, 0.1415 mmol) and K_2CO_3 (0.040 g, 0.2947 mmol). After the reaction mixture was stirred for 1h at room temperature, the reaction mixture was extracted with DCM followed by water workup to remove DMF. the organic layer was washed with brine, dried and concentrated in vacuo. The residue was purified by column chromatography by using CH_2Cl_2/MeOH (98/02) as eluent to afford **9c** (0.046 g, 91%) as a pure product. white solid; mp 108-110°C; R_f = 0.38 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00-7.96 (m, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.28- 7.22 (m, 5H), 7.11-7.01 (m, 3H), 6.03 (d, *J* = 9.0 Hz, 1H), 5.84 (s, 1H), 4.68-4.60 (m, 1H), 3.68 (s, 3H), 3.43-3.33 (m, 1H), 3.08-2.97 (m, 1H), 2.87-2.78 (m, 1H), 2.40 (s, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.1, 161.3, 142.9, 142.5, 139.7, 135.6, 132.7, 131.8, 131.7, 130.5, 129.9, 128.5, 128.1, 125.9, 125.8, 122.9, 119.4, 118.4, 115.9, 112.6, 73.7, 51.9, 43.0, 33.3, 21.3. ; IR (KBr): ν_{max} 3451, 3022, 2922, 1735, 1658, 1600, 1474, 1435, 1368, 1312, 1208, 1132, 1027, 899, 818, 753, 583, 529, 455 cm^{-1}; HRMS calcd for $C_{27}H_{24}BrN_2O_3$ (M^+ + H) 503.0970, found 503.0982; 97:03 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 309 nm; t_{minor} = 17.73, t_{major} = 14.57; $[\alpha]_D^{29.1}$ = –145.8 (c = 0.5, $CHCl_3$).



(*S*)-8-(phenylethynyl)-12-p-tolyl-4bH-isoquinolino[2,1-a]quinazolin-6(5H)-one (9c): To a 25 mL round bottom flask a solution of **3l** (0.050 g, 0.1179 mmol) in DCE (2 mL) was added Et_3N (0.047 g, 0.4716 mmol) and purged with nitrogen for 30 minutes. To the above flask a solution of Phenyl acetylene (0.018 g, 0.1697 mmol) was added. Catalysts $PdCl_2(PPh_3)_2$ (0.004 g, 0.00589 mmol) and CuI (0.001 g, 0.00354 mmol) were introduced into the flask under nitrogen atmosphere at room temperature. The reaction mixture was warmed to 70 °C and stirred for 12 h. The reaction mixture was cooled to room temperature and filtered through a short SiO_2 pad and the filtrate was concentrated. The residue was purified by column chromatography by using CH_2Cl_2/MeOH (98/02) as eluent to afford **9b** (0.044 g, 84%) as a pure product. yellow solid; mp 186-188°C; R_f = 0.35 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300

MHz, $CDCl_3$): δ 8.56 (1H, s), 7.95 (d, *J* = 3.0 Hz, 1H), 7.68-7.44 (m, 7H), 7.31-7.18 (m, 6H), 7.05 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.89 (s, 1H), 6.08 (d, *J* = 8.3 Hz, 1H), 5.88 (d, *J* = 4.5 Hz, 1H), 2.40 (s, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.9, 143.1, 141.8, 139.5, 135.8, 132.1, 131.9, 131.3, 130.5, 129.8, 128.6, 128.5, 128.4, 128.2, 128.0, 126.2, 125.4, 123.6, 119.5, 114.8, 112.8, 68.1, 21.3.; IR (KBr): ν_{max} 3174, 3051, 2922, 2856, 1677, 1600, 1470, 1351, 1275, 1179, 1116, 1025, 893, 810, 750, 711, 531, 446 cm^{-1}; HRMS calcd for $C_{31}H_{23}N_2O$ (M^+ + H) 439.1810, found 439.1816; 97:03 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 313 nm; t_{minor} = 15.39, t_{major} = 24.18; $[\alpha]_D^{29.1}$ = – 93.9 (c = 0.5, $CHCl_3$).

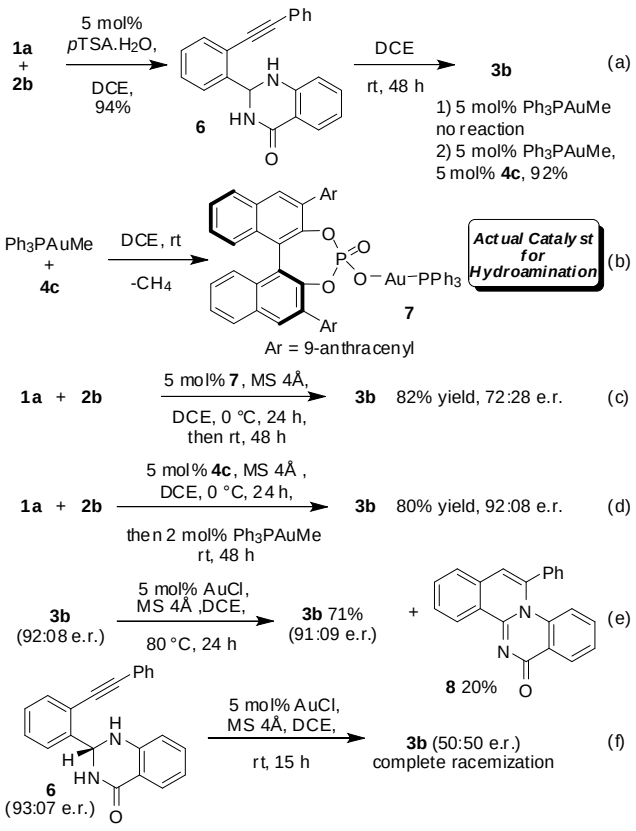


(***S*)-8,13-dibromo-12-phenyl-4bH-isoquinolino[2,1-a]quinazolin-6(5H)-one (9d)**: To a solution of **3a** (0.050 g, 0.1219 mmol) in DCE (2 ml) were successively added $^{i}Pr_2NH$ (0.025 g, 0.2438 mmol) and NBS (0.033 g, 0.1828 mmol) at 0º C. After the reaction mixture was stirred for 1 h at room temperature, the reaction was quenched by addition of saturated solution of $NaHCO_3$ at 0º C. The crude reaction mixture was extracted with EtOAc and the combined organic extracts were washed with brine, dried and concentrated in vacuo. The residue was purified by column chromatography by using CH_2Cl_2/MeOH (98/02) as eluent to afford **9d** (0.045 g, 76%) as a pure product. solid; mp 178-180°C; R_f = 0.36 (CH_2Cl_2/MeOH = 98/02); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (t, *J* = 2.3 Hz, 1H), 7.73-7.55 (m, 3H), 7.50-7.31 (m, 6H), 7.10 (dd, *J* = 9.1, 2.3 Hz, 1H), 6.8 (s, 1H), 6.22 (d, *J* = 9.1 Hz, 1H), 6.10 (d, *J* = 3.0 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 162.8, 142.9, 141.8, 135.9, 134.6, 131.9, 130,6, 129.3, 129.1, 128.7, 128.2, 126.3, 125.5, 123.6, 119.6, 115.4, 113.1, 68.0; IR (KBr): 3297, 2924, 2854, 1726, 1685, 1595, 1465, 1363, 1278, 1196, 1174, 1127, 1073, 885, 813, 758, 667, 577, 543, 499, 417 ν_{max} cm^{-1}; HRMS calcd for $C_{22}H_{15}Br_2N_2O$ (M^+ + H) 325.1340, found 325.1344; 96:04 e.r.; HPLC conditions**:** OD-H, n-hexane/2-propanol = 80/20, flow rate 0.5 mL/min; λ = 307 nm; t_{minor} = 13.49, t_{major} = 20.24; $[\alpha]_D^{29.1}$ = + 16.3 (c = 0.5, $CHCl_3$).

4. Mechanistic Studies

To gain insight into the mechanism we synthesized aminal **6**, by the *p*-TSA catalyzed reaction of **1a** with **2b**, in 94% yield (Scheme 2a). The intramolecular hydroamination was then studied using 5 mol% Ph_3PAuMe in DCE at rt. However, product **3b** was detected only in trace amount though reaction mixture was stirred for 24 h. Very interestingly, the addition of 5 mol% **4c** in the same reaction mixture gave **3b** in 92% yield. These results unambiguously suggests that gold phosphate **7** was the actual hydroamination catalyst (Scheme 2b).[4f] The existence of gold phosphate **7** was further confirmed by ^{31}P NMR analysis studies.[13] It also possible that the gold phosphate **7**, generated in situ, might be responsible for the enantioselective condensation. To ascertain the above possibility, the reaction was conducted between **1a** and **2b** in the presence of pre-generated gold phosphate. However, under the standard condition **3b** was obtained only with moderate e.r. (Scheme 2c). On the other hand, **3b** was obtained with excellent e.r. when the reaction was conducted in sequential manner (Scheme 2d). This led us to conclude that the condensation process is catalyzed by only **4c** and not by the chiral gold phosphate **7**. In short, the overall reaction presumably proceeds via the formation of chiral aminals, by the reaction between **1a** and **2b** under the catalysis of **4c**, which after intramolecular hydroamination catalyzed by gold phosphate **7** afforded fused 1,2-dihydroisoquinolines. The compound **3b** (92:08 e.r.) was subjected to the AuCl catalysis under the standard conditions under prolonged heating at elevated temperature no significant racemisation took place and the **3b** was isolated in 91:09 e.r. along with the dehydrogenation product **8** in 20% yield (Scheme 2e). These results clearly indicate high configurational stability of the fused 1,2-dihydroisoquinolines synthesized in this studies. On the other hand, optically active aminal **6** (93:07 e.r.) when subjected to AuCl catalysis, a complete racemisation occurred in just 15 hours.

Scheme 2. Control experiments.



. To definitely demonstrate the role of **7** as the actual gold catalyst the experiment between **1a** and **2b** using **7** (2 mol%) and **4c** (3 mol%) was performed under the standard reaction conditions. An exactly identical results to that described in Scheme **2d** were obtained indicating the clear role of **7**. The gold phosphate **7** is fully characterized and spectral images of ^{1}H NMR, ^{13}C NMR and ^{31}P NMR are provided in section **6** and **8** of this ESI.[15]

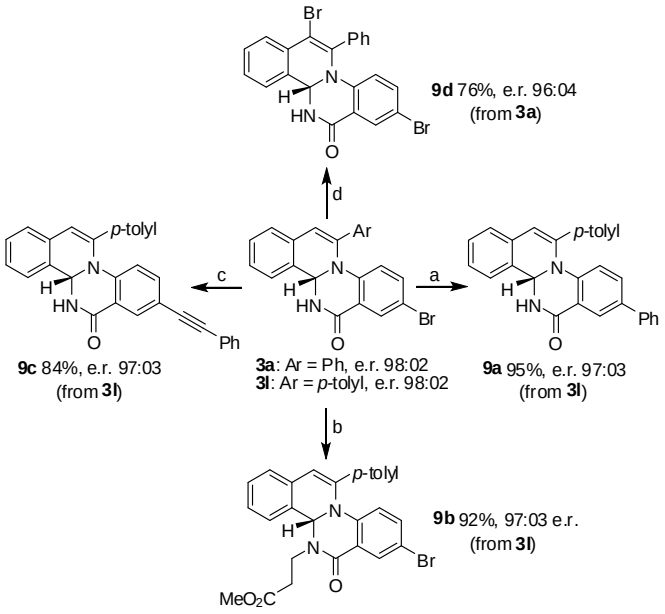
Characterization data for gold phosphate 7:

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (s, 2H), 7.96-7.93 (m, 8H), 7.74 (t, *J* = 7.9 Hz, 4H), 7.60 (t, *J* = 7.9 Hz, 2H), 7.54 (t, *J* = 7.9 Hz, 3H), 7.74 (t, *J* = 6.9 Hz, 5H), 7.27-7.38 (m, 10H), 7.10 (t, *J* = 6.9 Hz, 2H), 6.89-7.03 (m, 7H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.2 (d, *J* = 9.9 Hz), 134.1(d, *J* = 13.6 Hz), 133.5, 132.9, 132.8, 131.7, 131.6, 131.4, 131.2, 131.0, 130.9, 130.5, 128.9, 128.8, 128.2 (d, *J* = 20.1 Hz), 127.5 (d, *J* = 13.6 Hz), 126.9 (d, *J* = 11.8 Hz), 126.4, 125.7, 124.9, 124.7, 123.1; ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.9, 27.9. HRMS calcd for $C_{66}H_{44}AuO_4P_2$ [M^+ + H] 1158.9592 found 1158.9574.

[15] Such type of gold(I) phosphate complexes has recently been reported, see: M. Raducan, M. Moreno, C. Bour, A. M. Echavarren *Chem. Commun*. **2012**, *48*, 52-54.

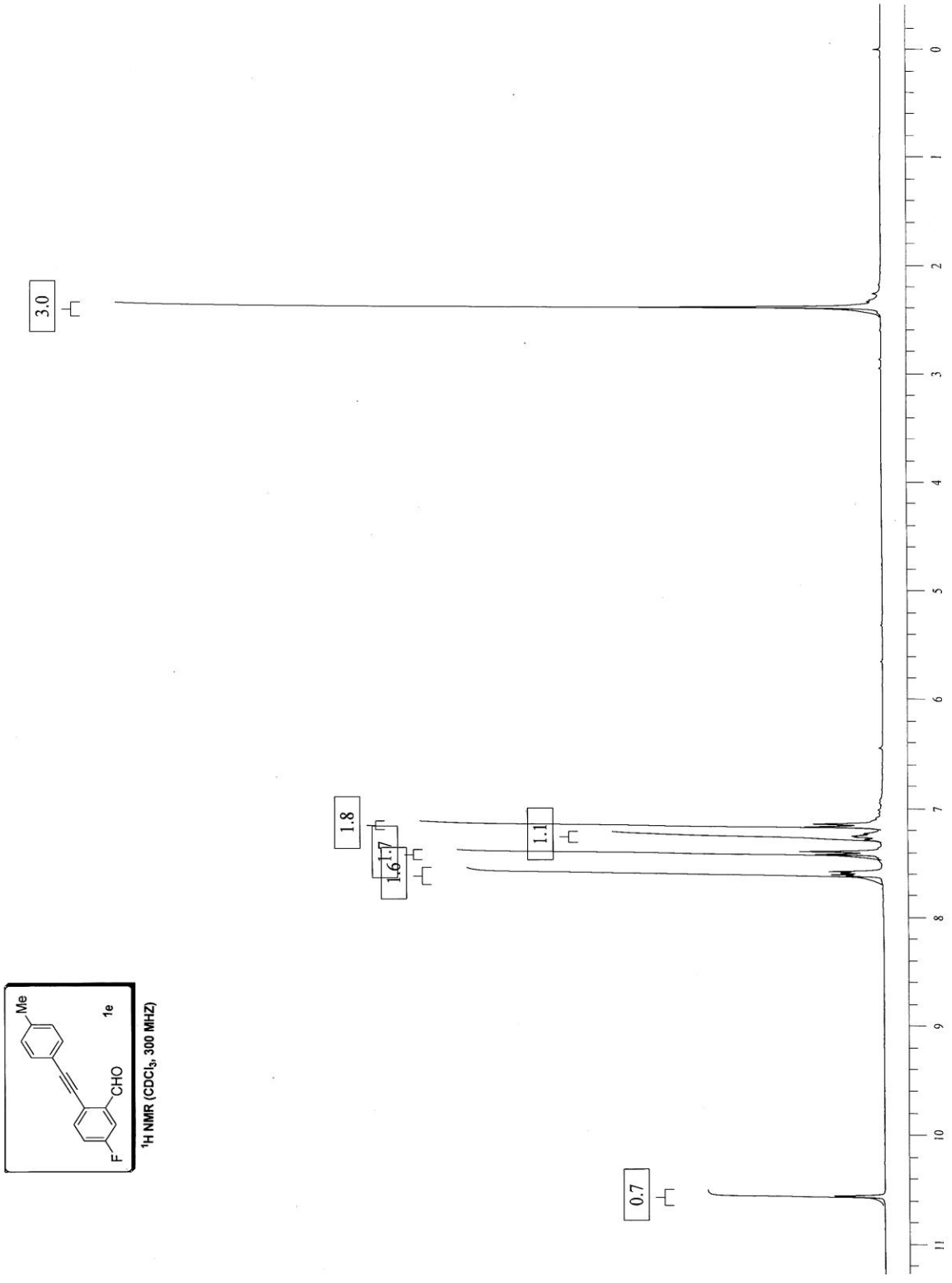
5. Diversification of Products

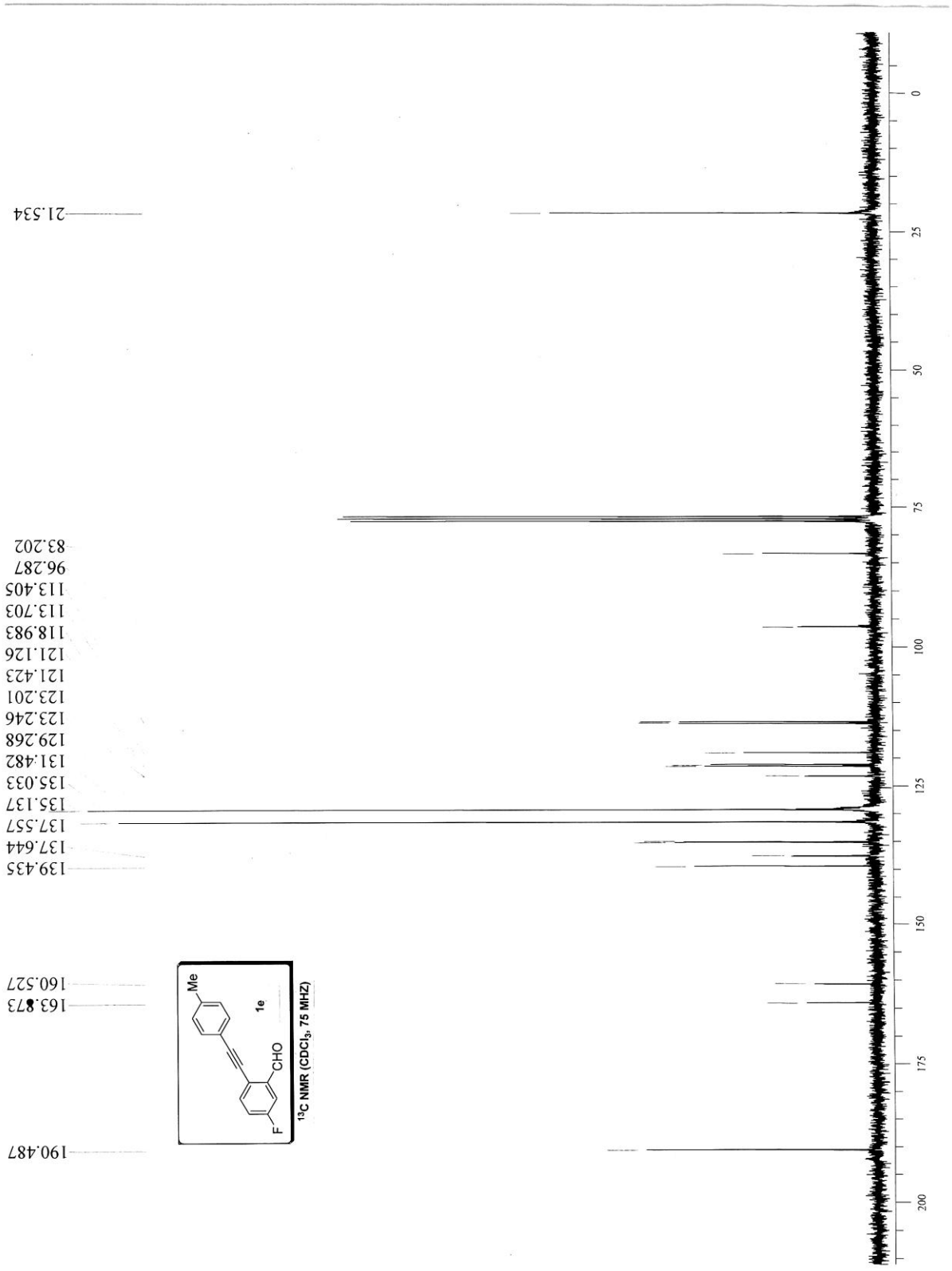
As can be judged from following scheme that various metal-catalyzed or electrophile-induced reactions can be performed for diversification of the fused-quinolines without disturbing the enantioselectivity of the products.

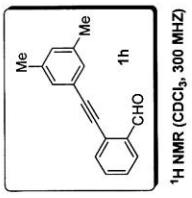


Reaction Conditions: a) $PhB(OH)_2$, K_2CO_3, $PdCl_2(PPh_3)_2$, DMF:H_2O, 75° C, 2 h. b) methyl acrylate, K_2CO_3, DMF, rt, 2 h. c) phenyl acetylene, $PdCl_2(PPh_3)_2$, CuI, Et_3N, DCE, 70° C, 6 h. d) NBS, $^iPr_2NH$, DCE, 0 °C to rt, 2 h.

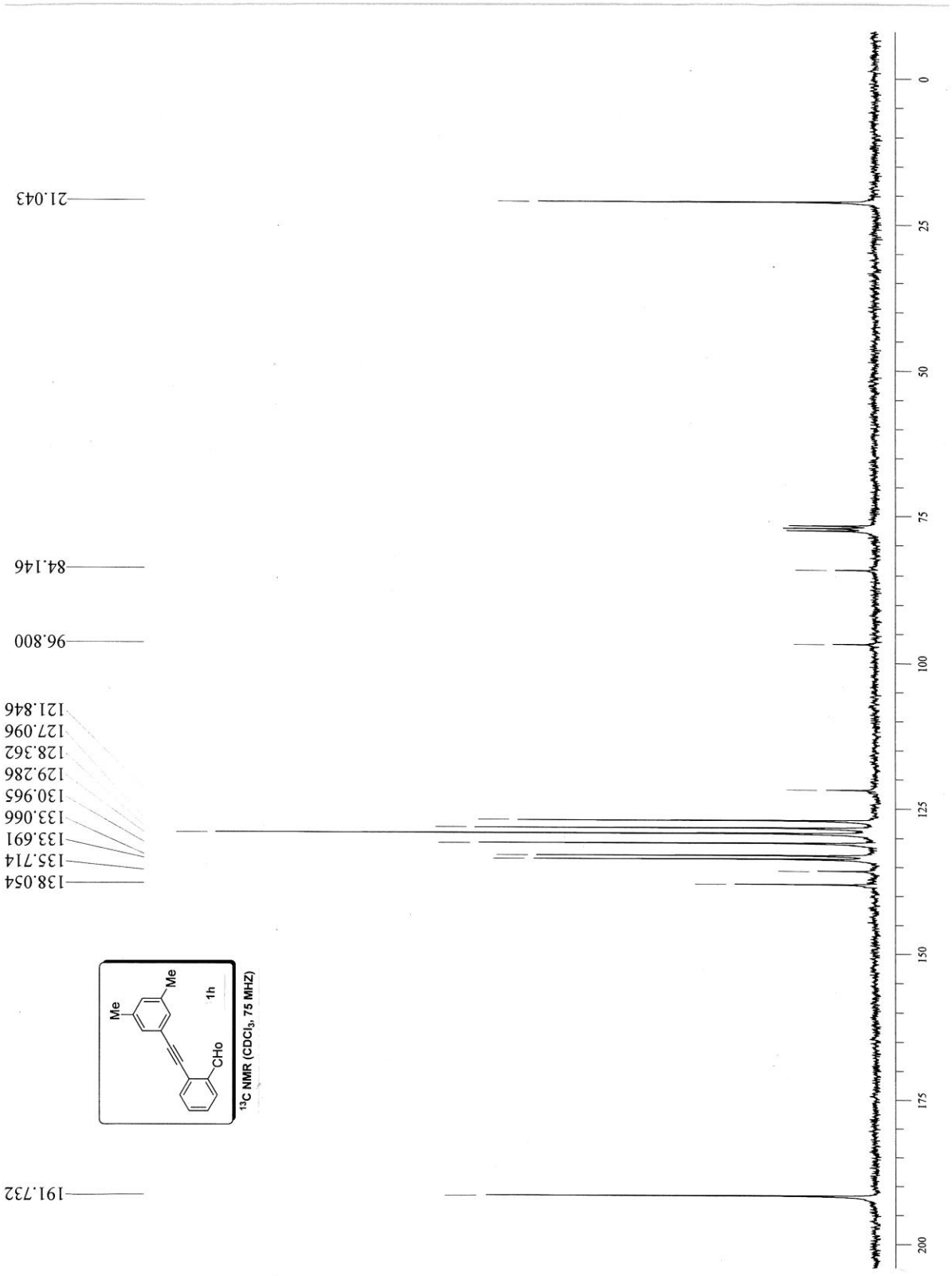
6. ^{1}H NMR and ^{13}C NMR Spectra of Compounds

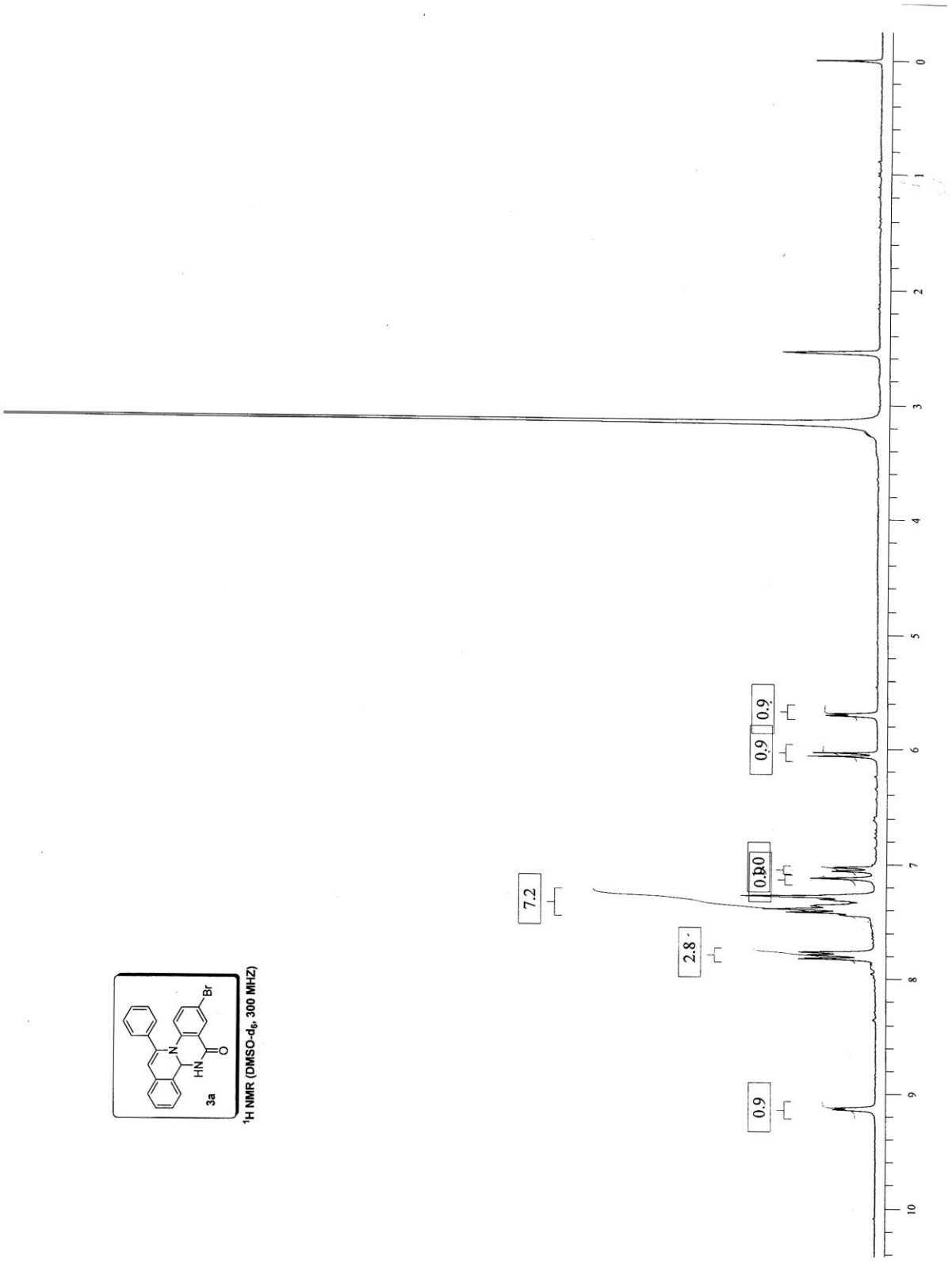


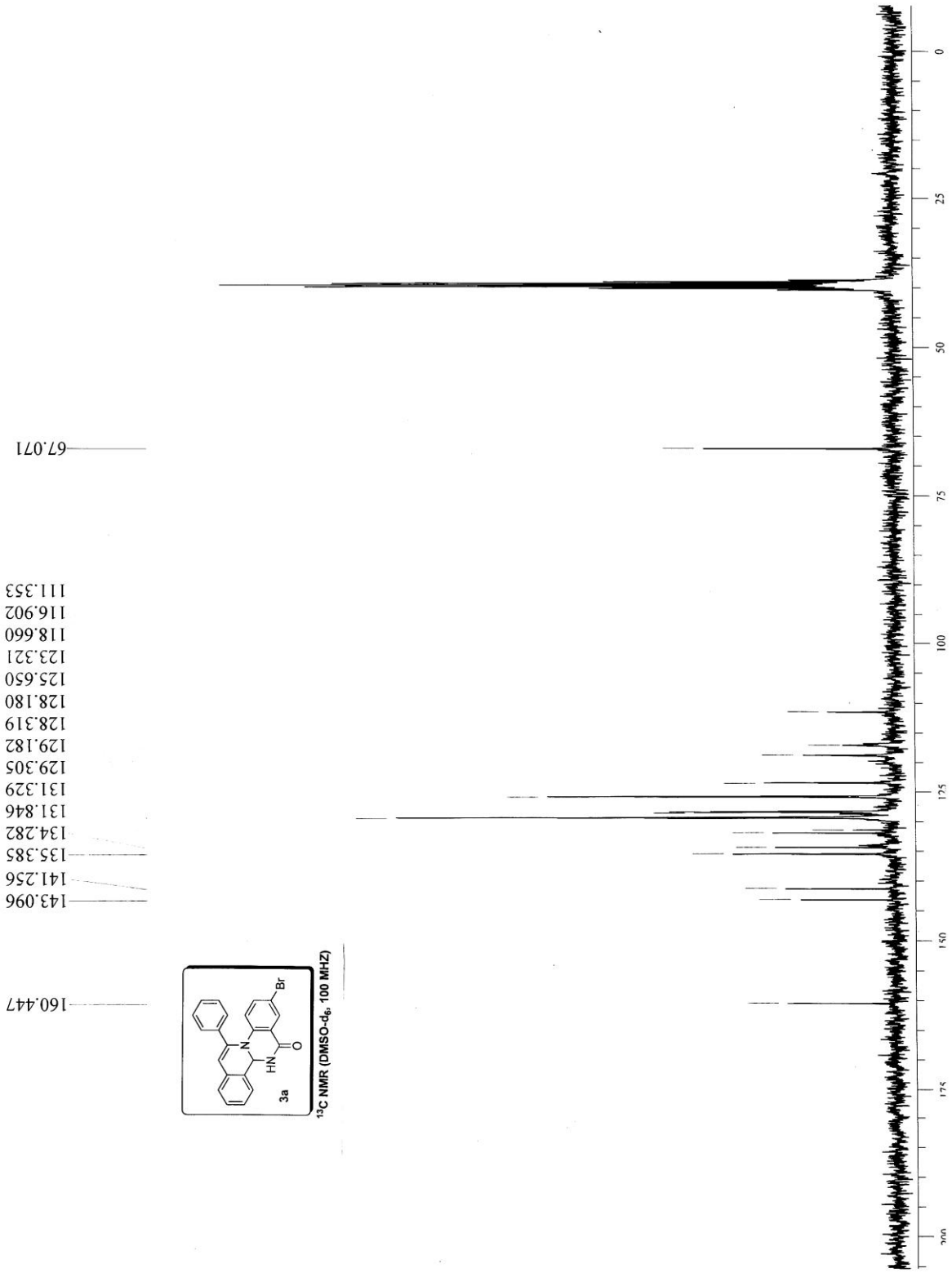

21.534
83.202
96.287
113.405
113.703
118.983
121.126
121.423
123.201
123.246
129.268
131.482
135.033
135.137
137.557
137.644
139.435
160.527
163.873
190.487
Me
1e
CHO
F
^{13}C NMR (CDCl$_3$, 75 MHz)
0
25
50
75
100
125
150
175
200

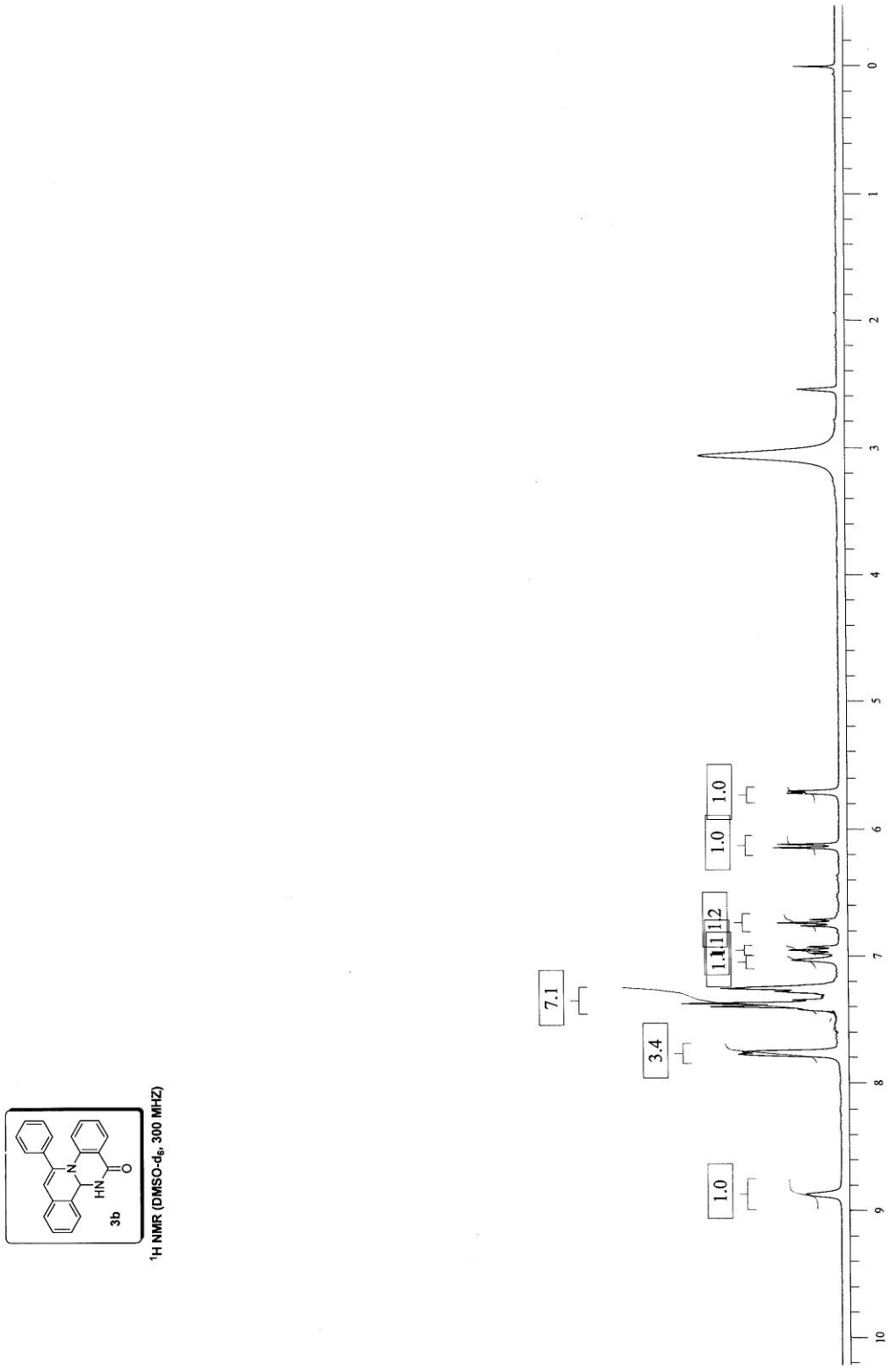


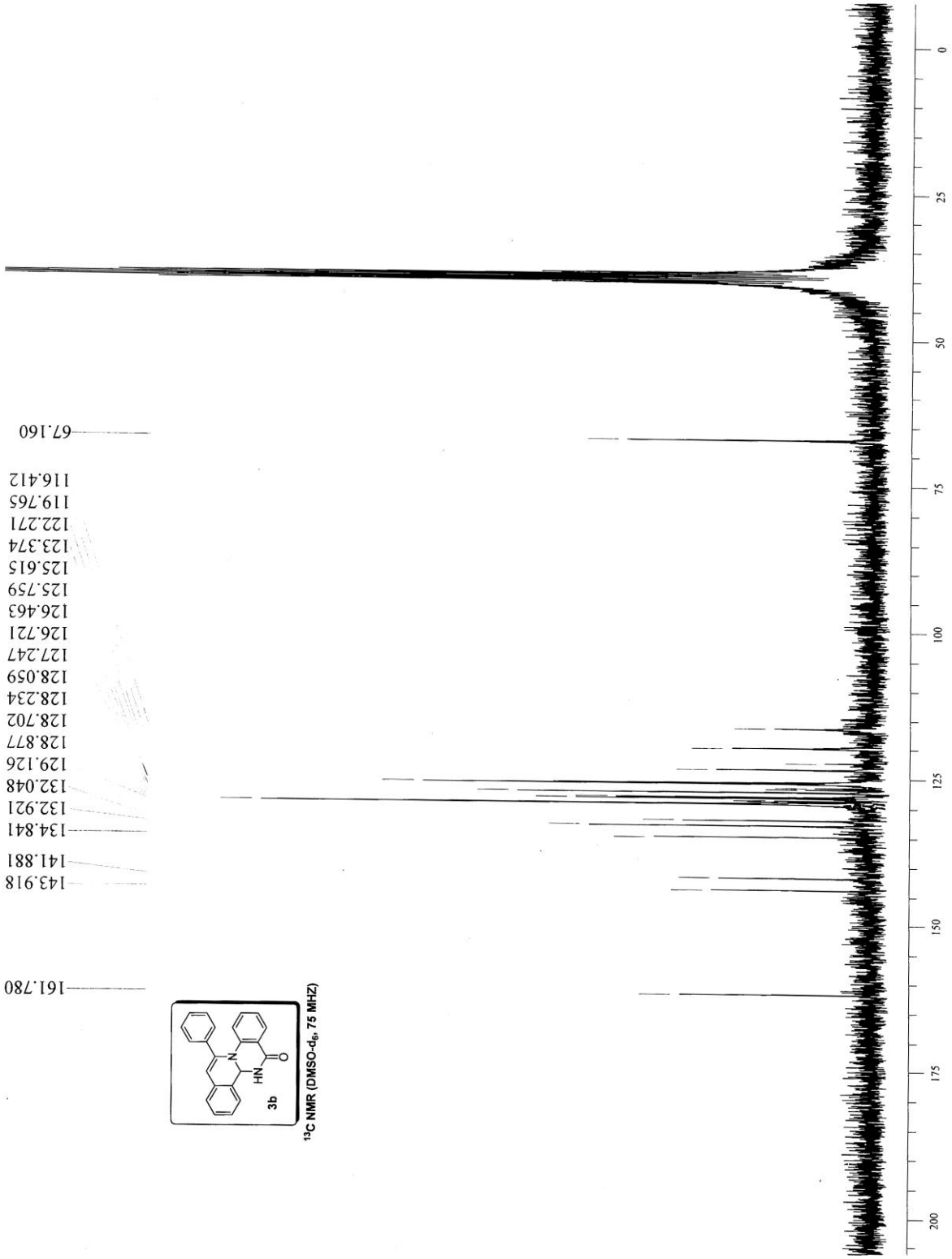
^{1}H NMR ($CDCl_3$, 300 MHZ)

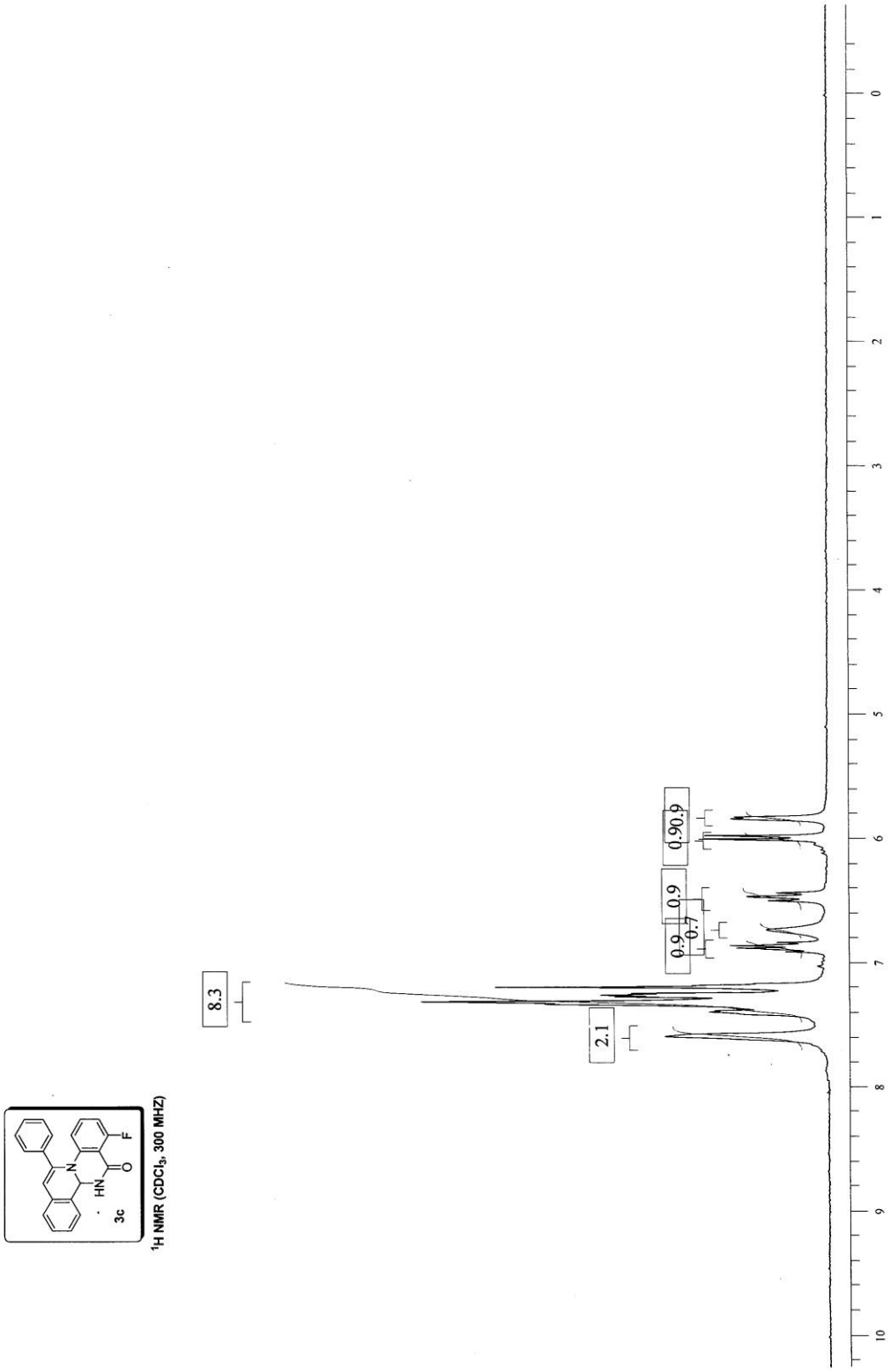

21.043
84.146
96.800
121.846
127.096
128.362
129.286
130.965
133.066
133.691
135.714
138.054
191.732
Me
Me
1h
CHo
^{13}C NMR (CDCl$_3$, 75 MHZ)
0
25
50
75
100
125
150
175
200

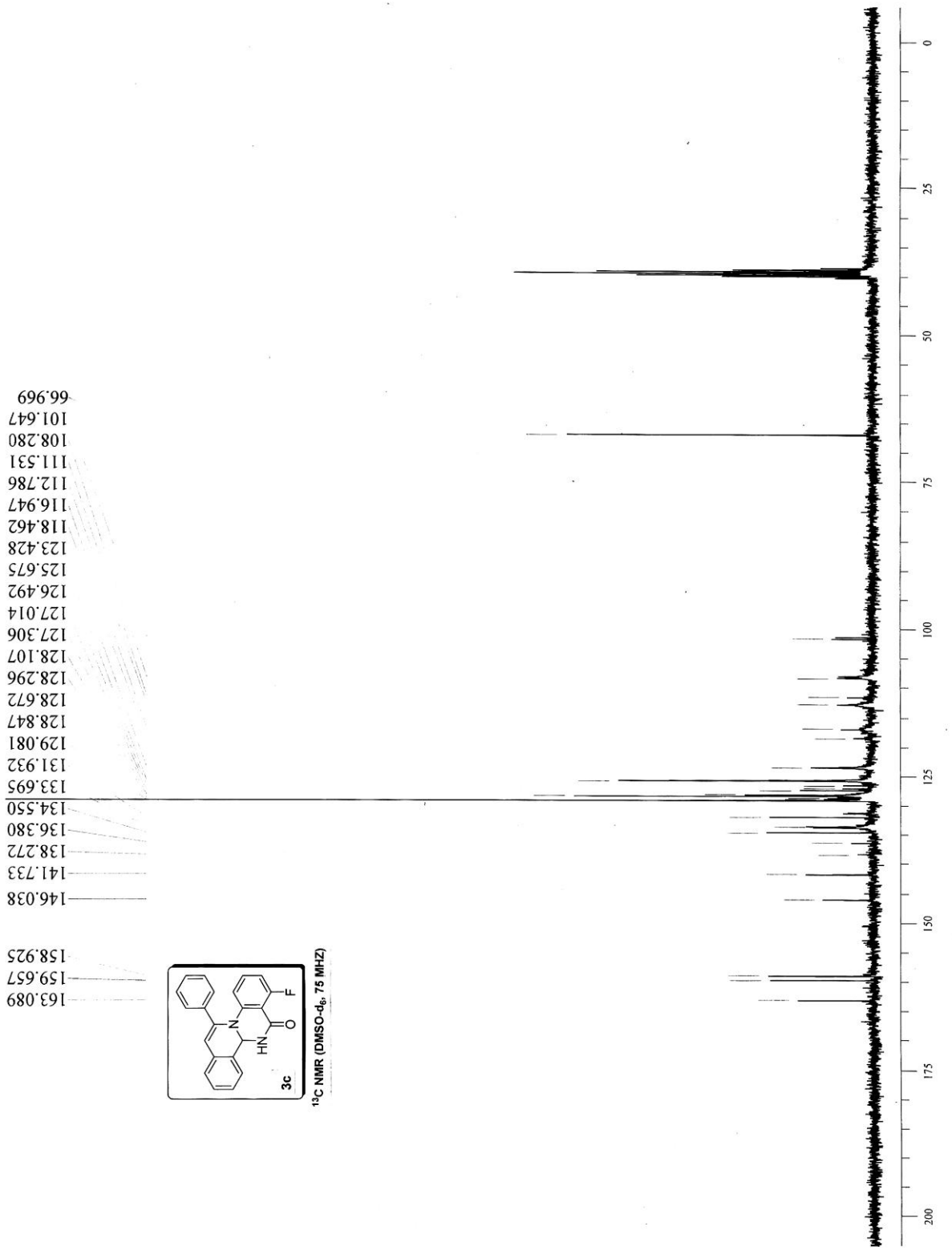

Br
N
HN
O
3a
^{1}H NMR (DMSO-d_6, 300 MHZ)
0.9
2.8
7.2
0.9
0.9
0
1
2
3
4
5
6
7
8
9
10

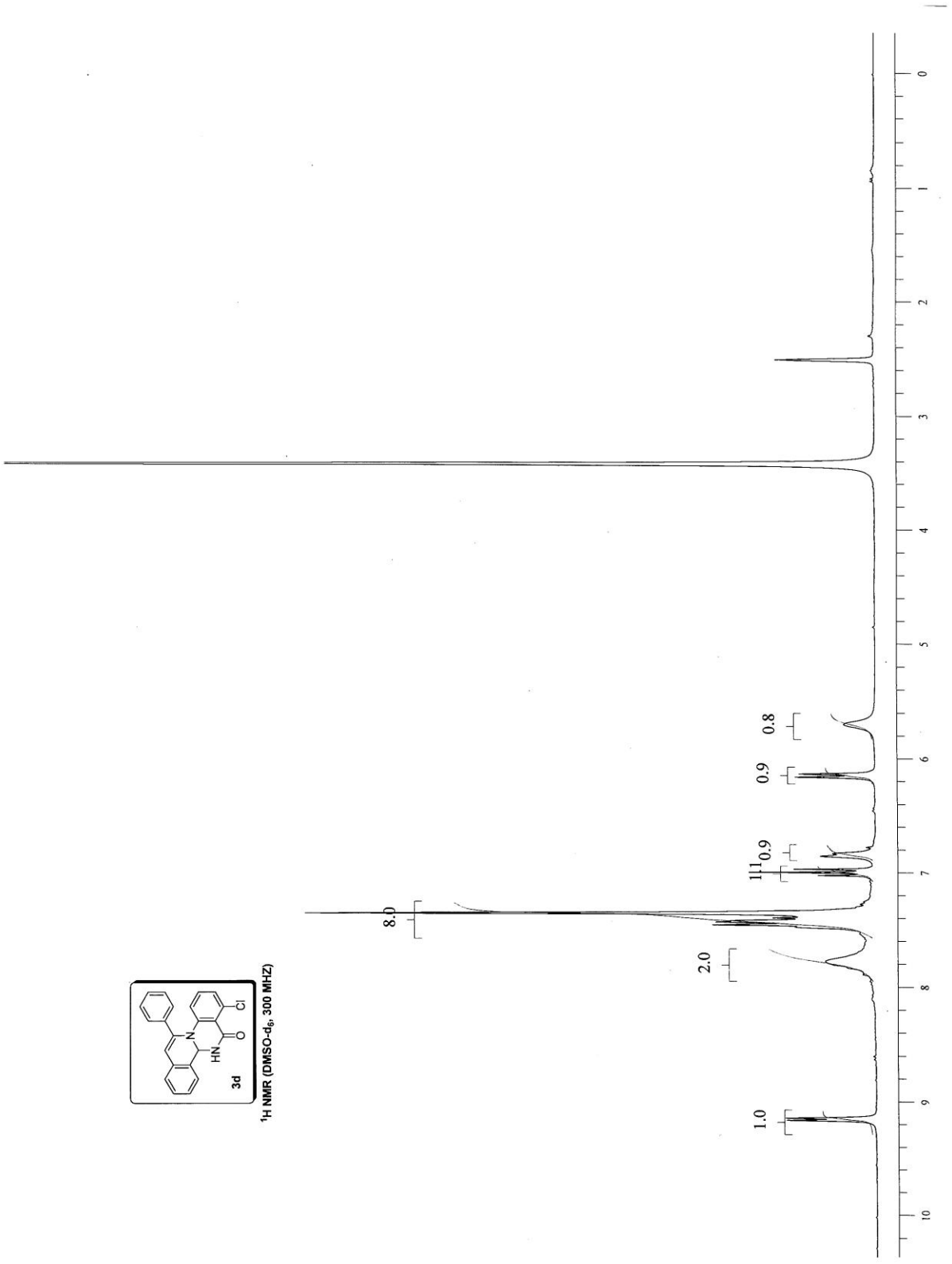

67.071
111.353
116.902
118.660
123.321
125.650
128.180
128.319
129.182
129.305
131.329
131.846
134.282
135.385
141.256
143.096
160.447
^{13}C NMR (DMSO-d_6, 100 MHZ)
Br
N
HN
O
3a

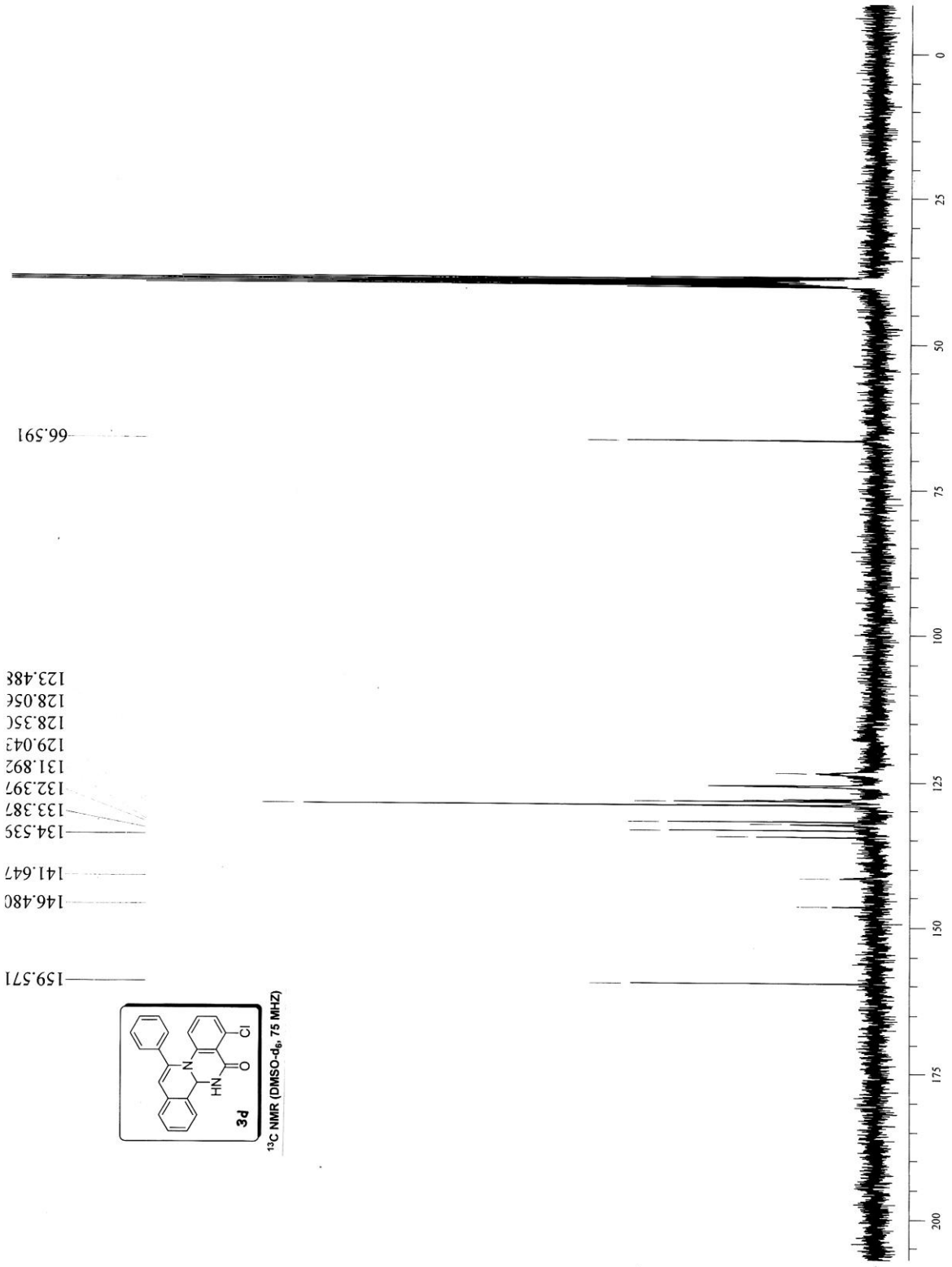

3b
^{1}H NMR (DMSO-d_6, 300 MHZ)
7.1
3.4
1.0
1.0
1.0
1.1
1.1
1.2
0
1
2
3
4
5
6
7
8
9
10

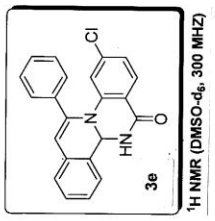

67.160
116.412
119.765
122.271
123.374
125.615
125.759
126.463
126.721
127.247
128.059
128.234
128.702
128.877
129.126
132.048
132.921
134.841
141.881
143.918
161.780
HN
O
3b
^{13}C NMR (DMSO-d_6, 75 MHZ)
0
25
50
75
100
125
150
175
200


F
O
HN
N
3c
^{1}H NMR (CDCl$_3$, 300 MHZ)
8.3
2.1
0.9
0.9
0.7
0.9
0.9
0
1
2
3
4
5
6
7
8
9
10

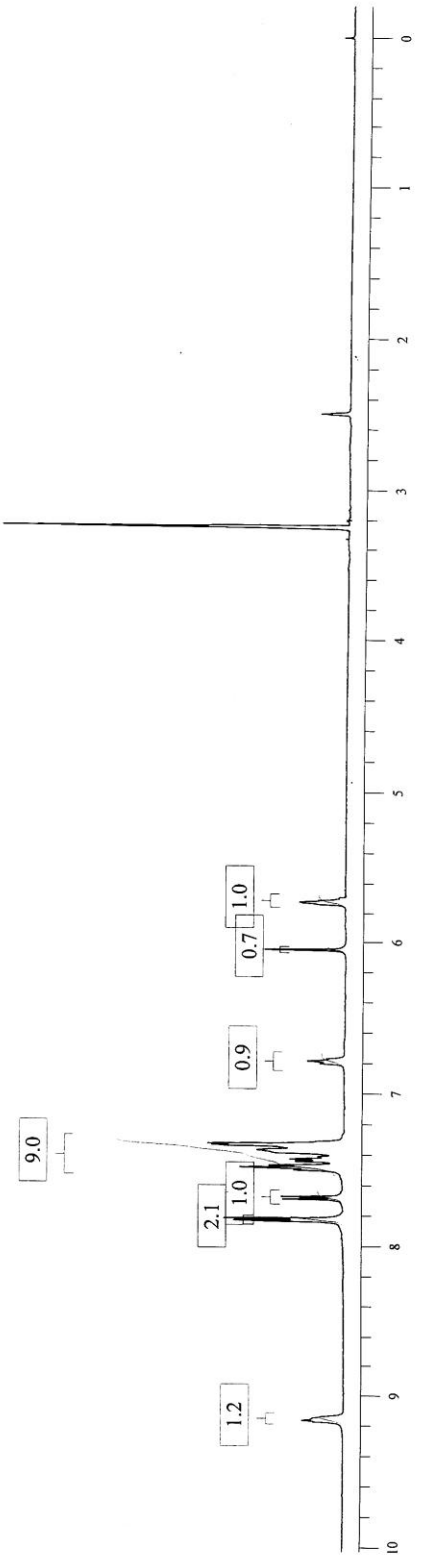

66.969
101.647
108.280
111.531
112.786
116.947
118.462
123.428
125.675
126.492
127.014
127.306
128.107
128.296
128.672
128.847
129.081
131.932
133.695
134.550
136.380
138.272
141.733
146.038
158.925
159.657
163.089
HN
N
O
F
3c
^{13}C NMR (DMSO-d_6, 75 MHZ)
0
25
50
75
100
125
150
175
200

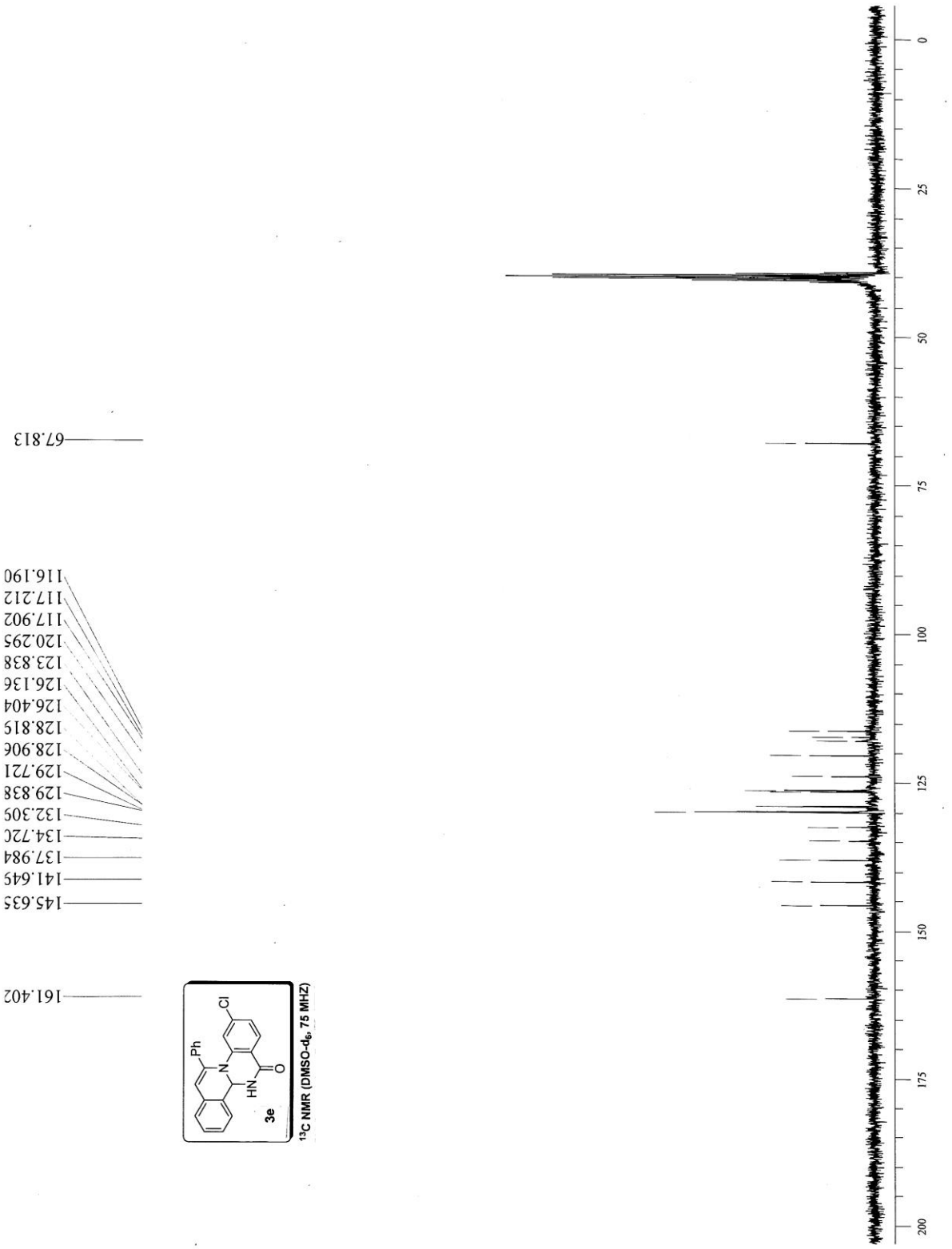

3d
^{1}H NMR (DMSO-d_6, 300 MHZ)
Cl
O
HN
N
8.0
2.0
1.0
0.8
0.9
0.9
1
1
0
1
2
3
4
5
6
7
8
9
10

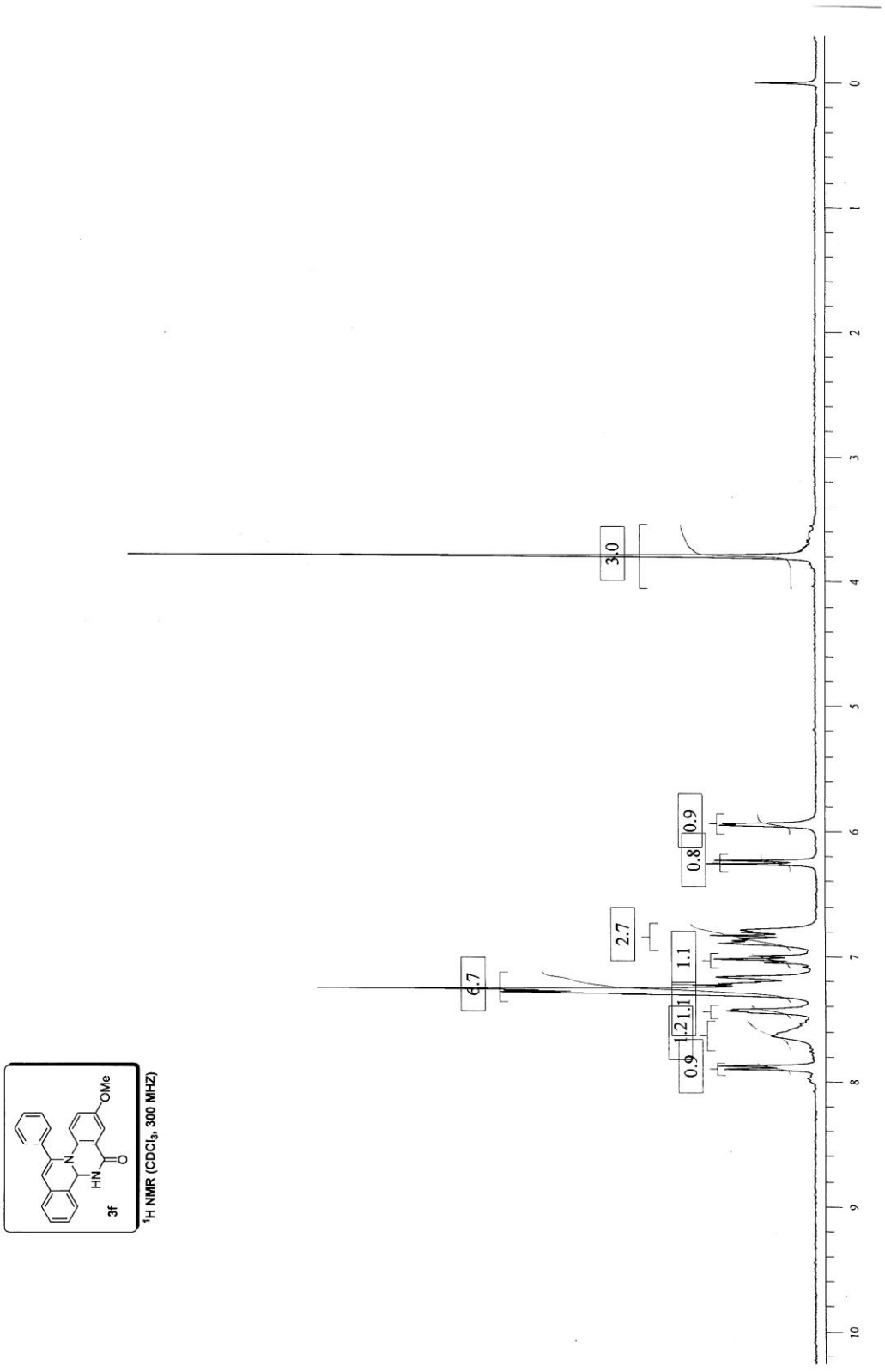

66.591
123.488
128.056
128.356
129.043
131.892
132.397
133.387
134.539
141.647
146.480
159.571
Cl
O
HN
N
3d
^{13}C NMR (DMSO-d_6, 75 MHZ)
0
25
50
75
100
125
150
175
200

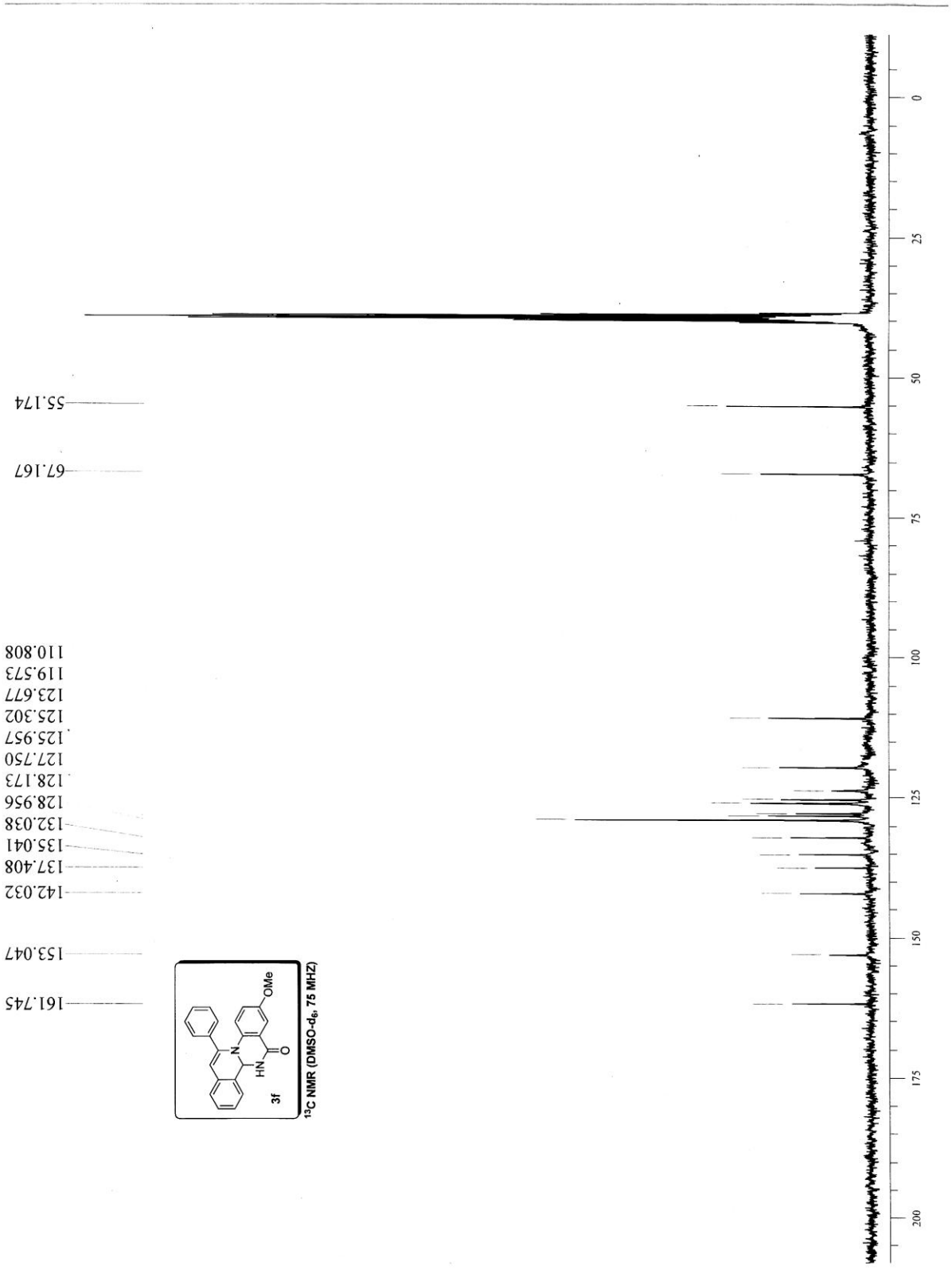


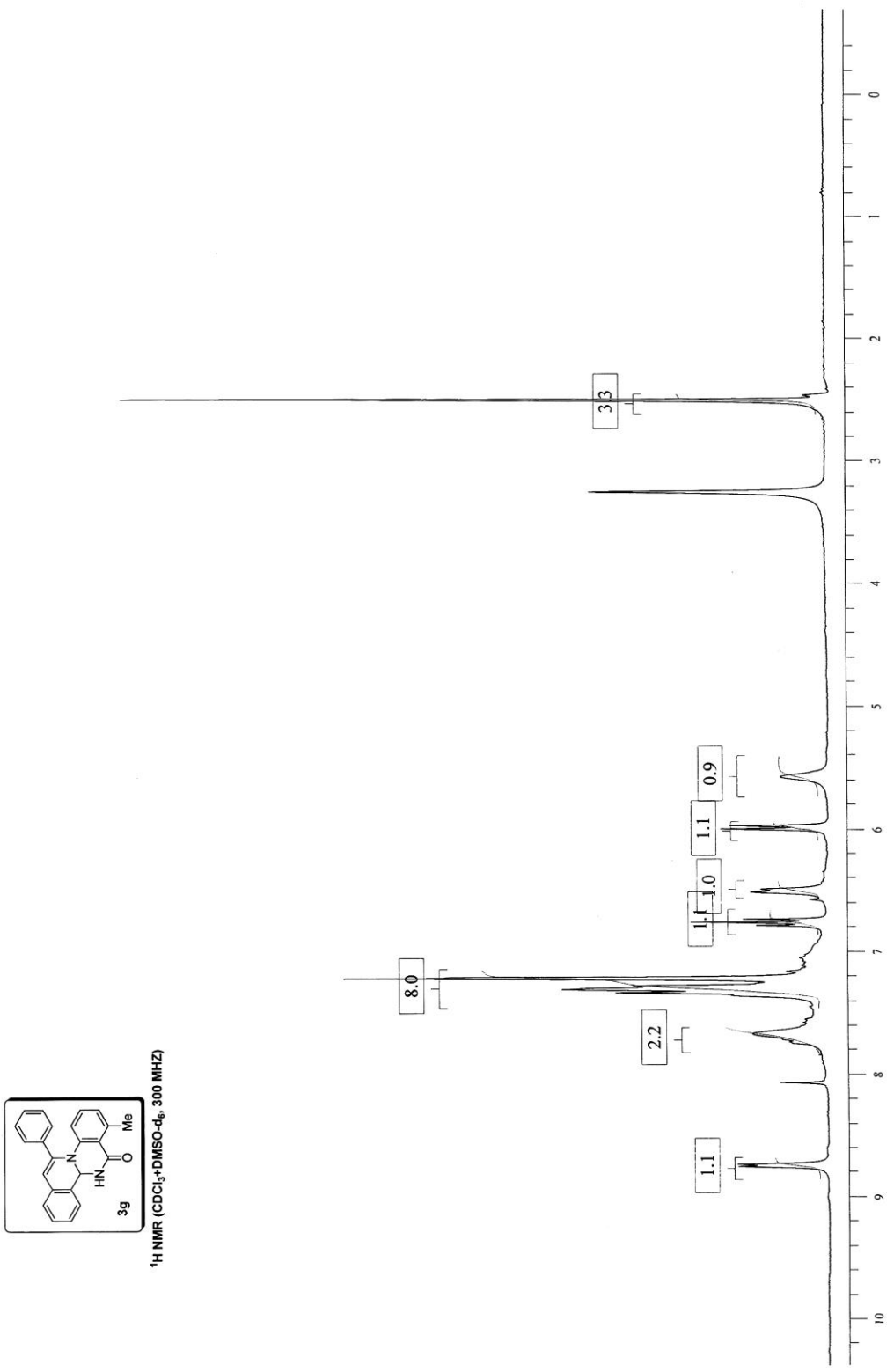
^{1}H NMR (DMSO-d_6, 300 MHZ)

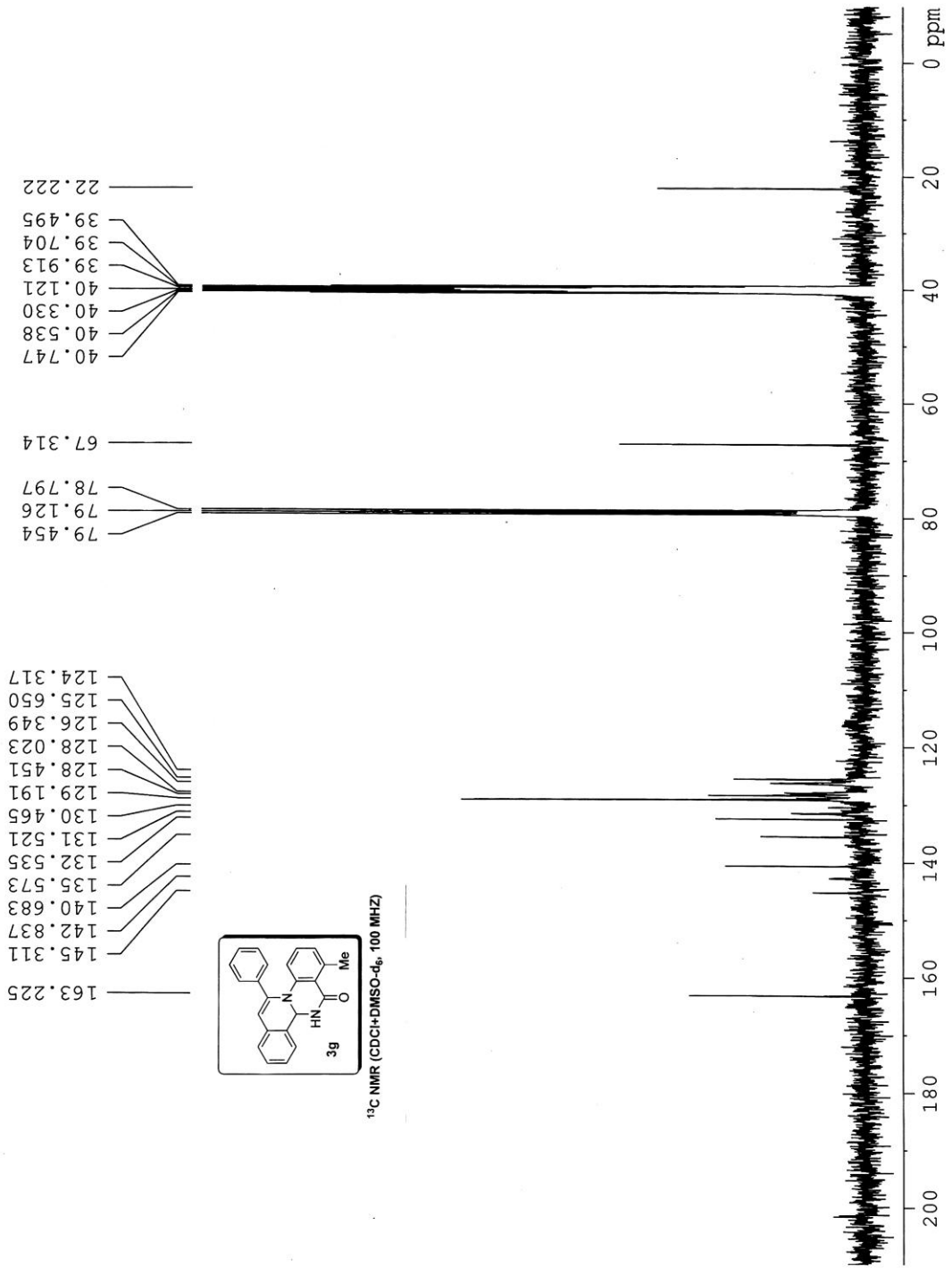


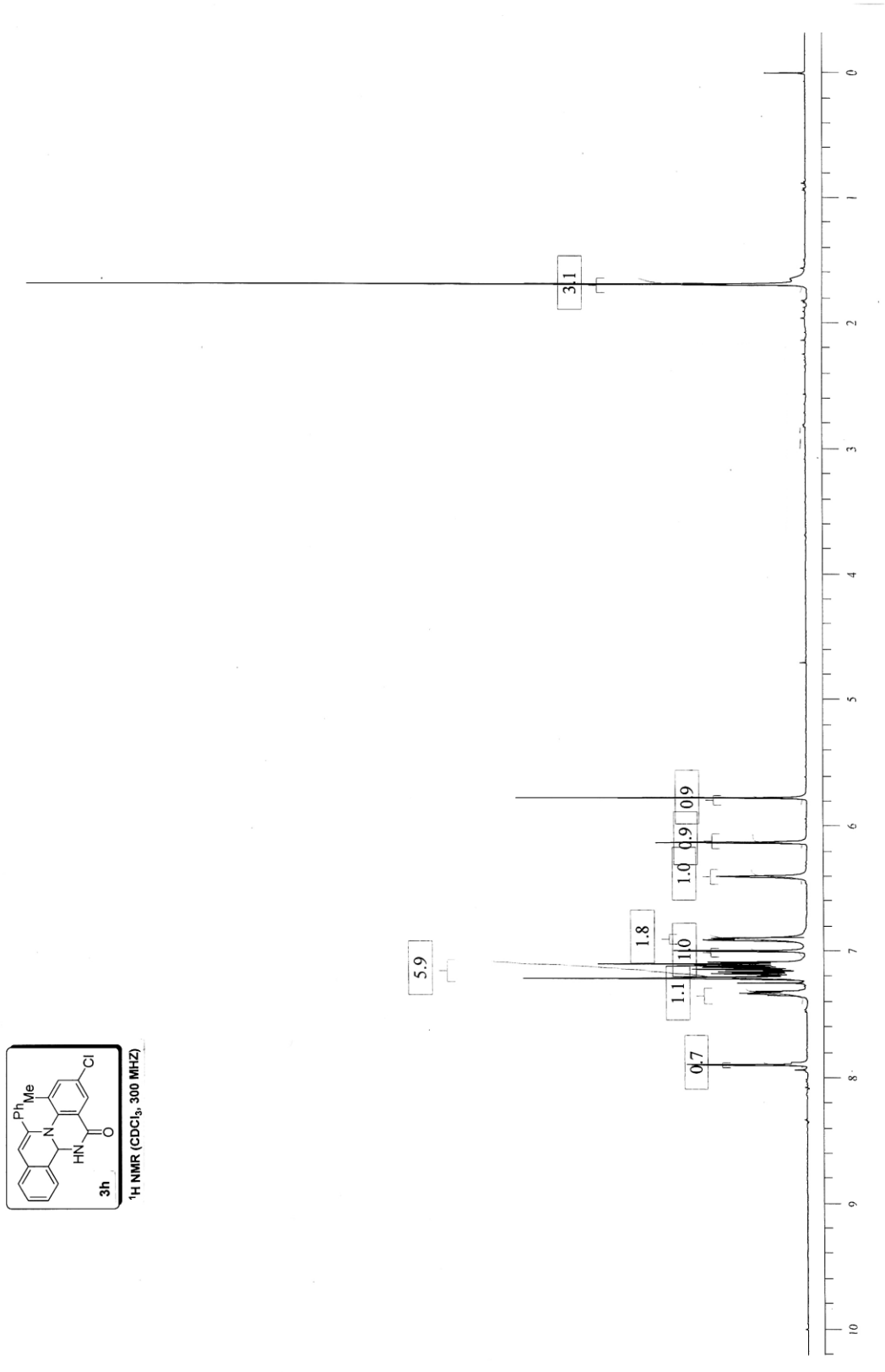

67.813
116.190
117.212
117.902
120.295
123.838
126.136
126.404
128.819
128.906
129.721
129.838
132.305
134.720
137.984
141.649
145.635
161.402
Cl
Ph
N
HN
O
3e
^{13}C NMR (DMSO-d_6, 75 MHZ)
0
25
50
75
100
125
150
175
200

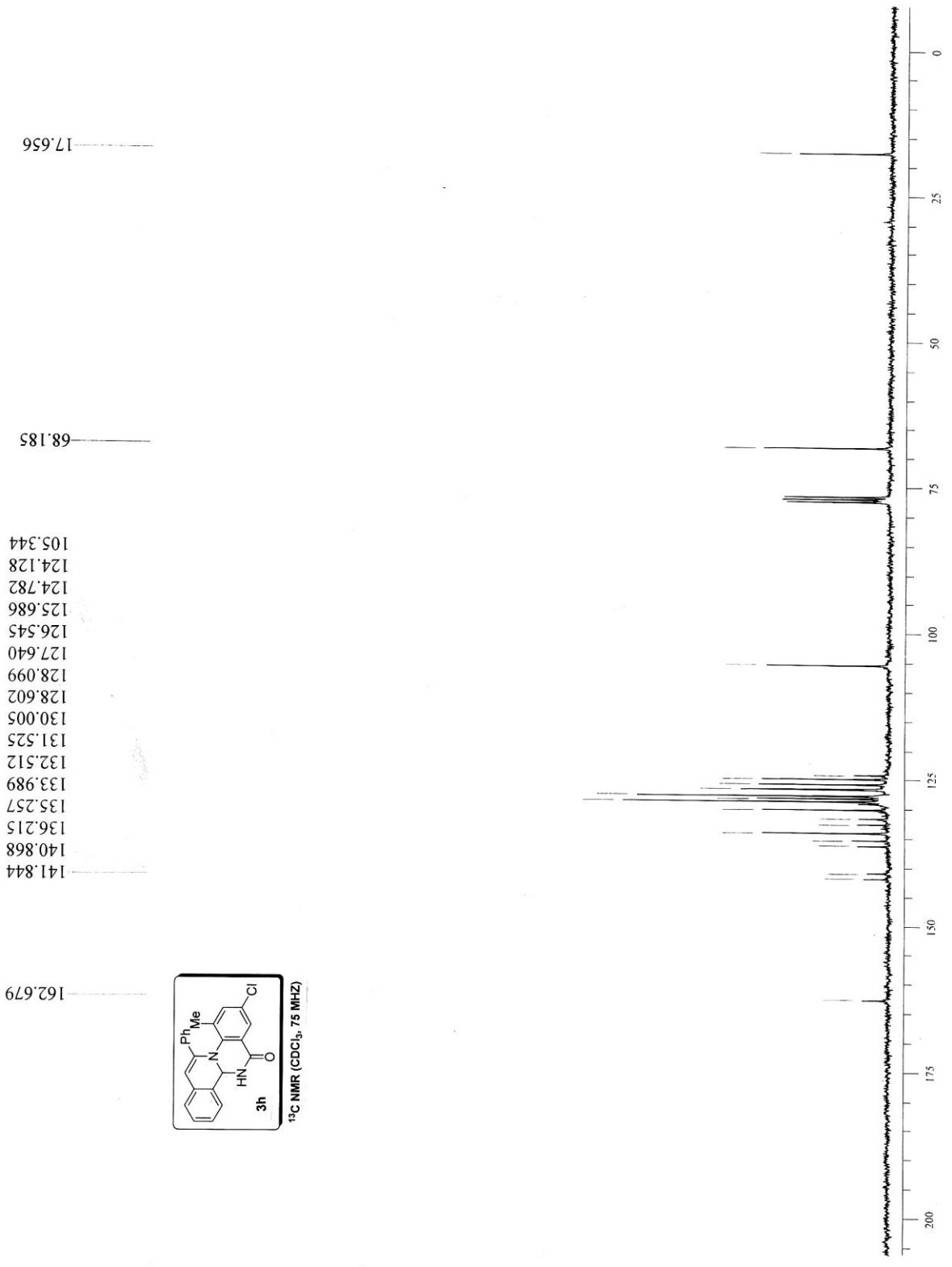

OMe
HN
O
3f
^{1}H NMR ($CDCl_3$, 300 MHZ)
3.0
0.8
0.9
2.7
6.7
1.1
1.2
1.1
0.9

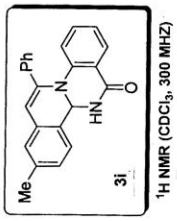

55.174
67.167
110.808
119.573
123.677
125.302
125.957
127.750
128.173
128.956
132.038
135.041
137.408
142.032
153.047
161.745
OMe
N
HN
O
3f
^{13}C NMR (DMSO-d_6, 75 MHZ)
0
25
50
75
100
125
150
175
200


Me
N
HN
O
3g
^{1}H NMR (CDCl$_3$+DMSO-d$_6$, 300 MHZ)
3.3
0.9
1.1
1.0
1.1
8.0
2.2
1.1

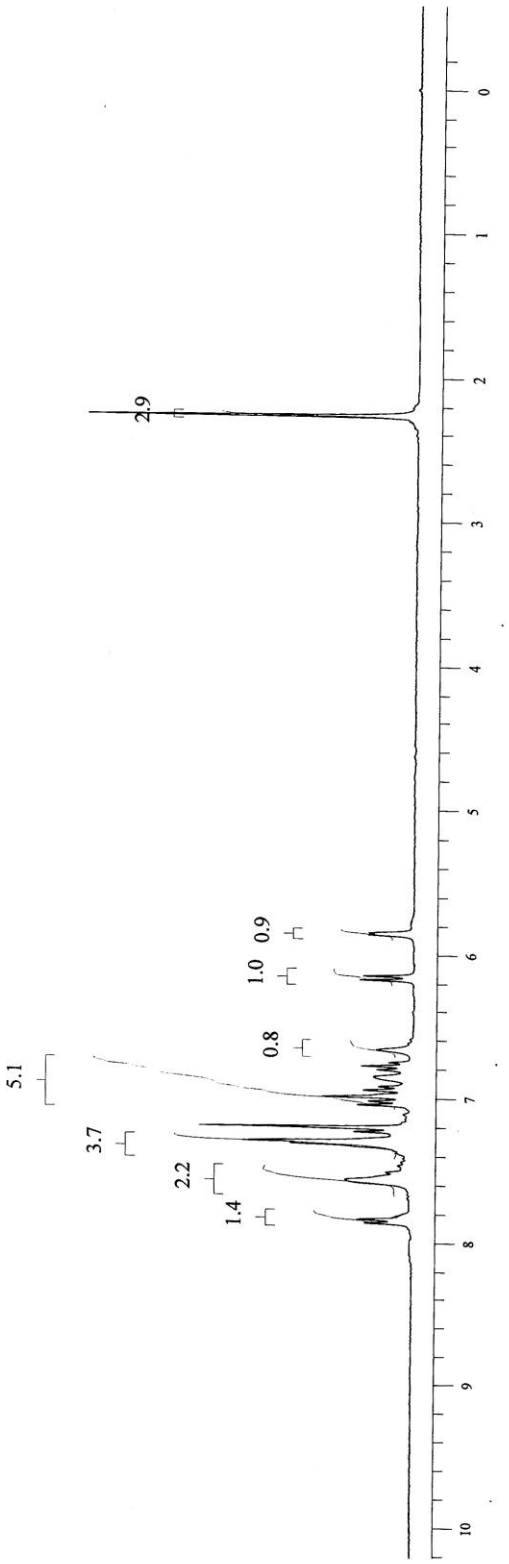

22.222
39.495
39.704
39.913
40.121
40.330
40.538
40.747
67.314
78.797
79.126
79.454
124.317
125.650
126.349
128.023
128.451
129.191
130.465
131.521
132.535
135.573
140.683
142.837
145.311
163.225
^{13}C NMR (CDCl+DMSO-d_6, 100 MHZ)
3g
Me
O
HN
N
0 ppm
20
40
60
80
100
120
140
160
180
200

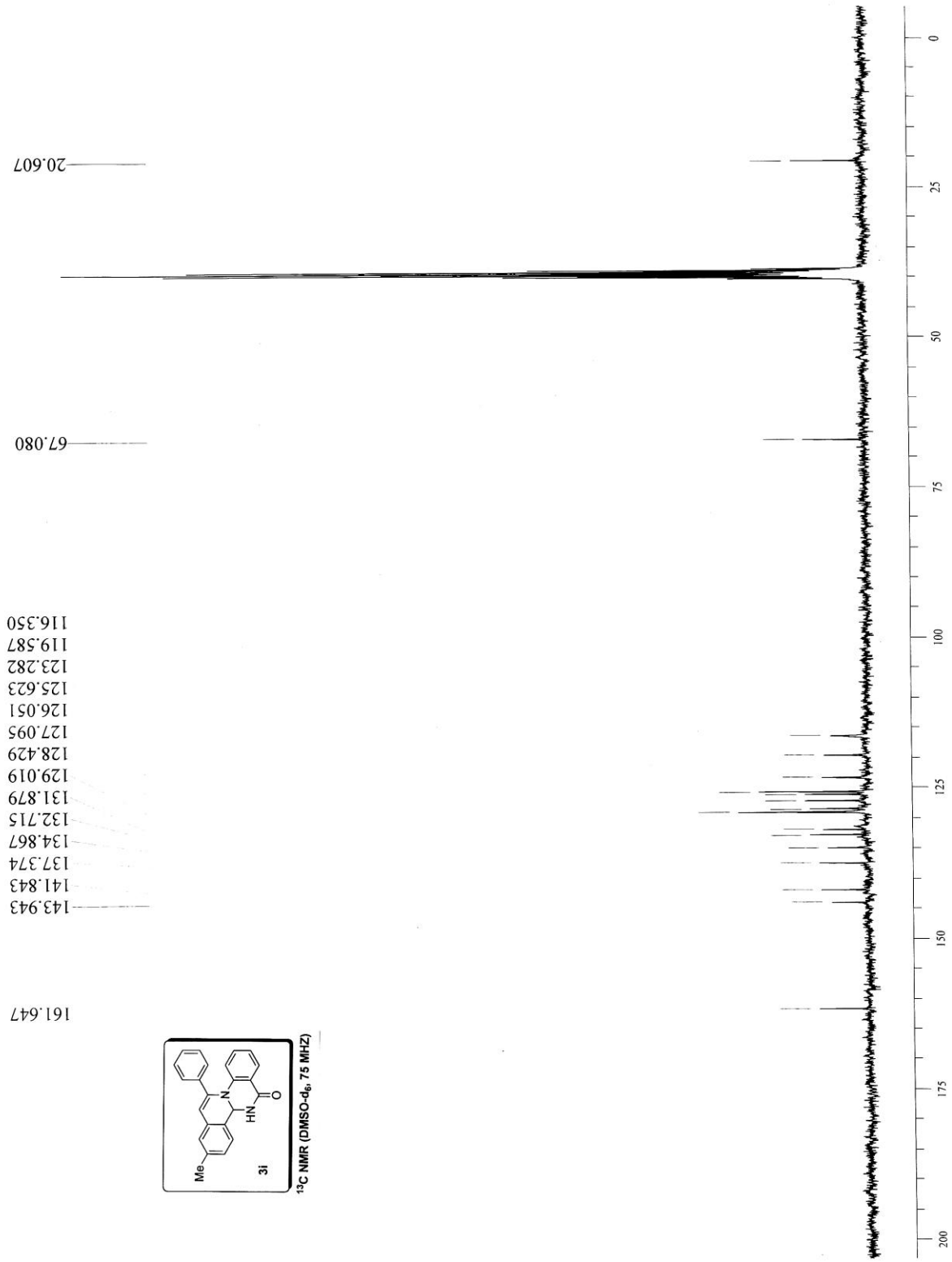

Ph
Me
Cl
N
HN
O
3h
^{1}H NMR (CDCl$_3$, 300 MHZ)
3.1
5.9
1.8
1.6
1.1
1.0
0.9
0.9
0.7

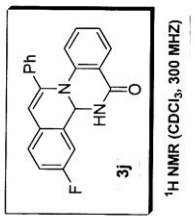




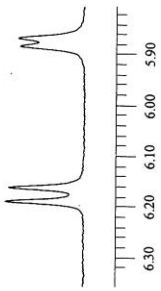
^{1}H NMR ($CDCl_3$, 300 MHZ)

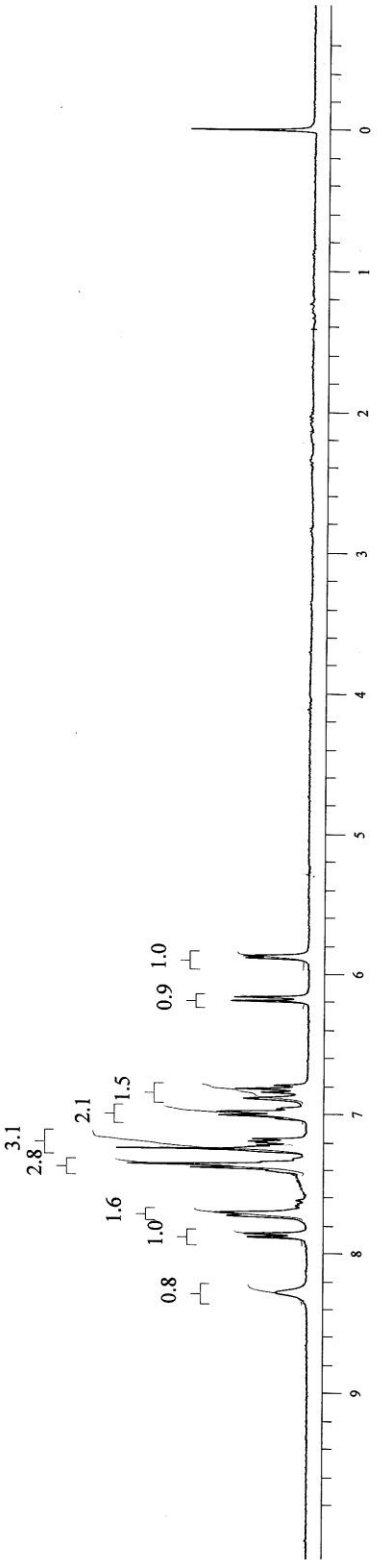


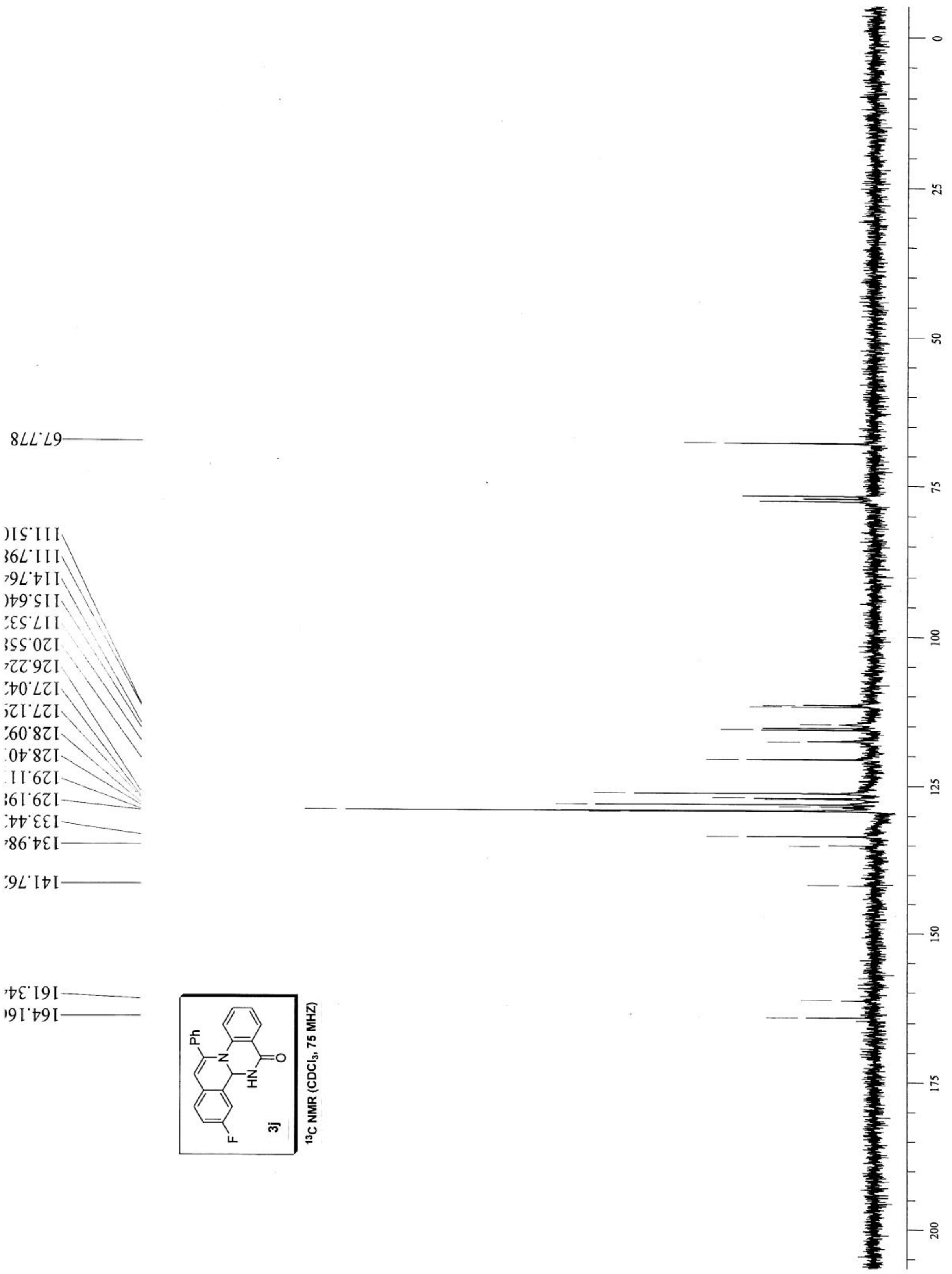

20.607
67.080
116.350
119.587
123.282
125.623
126.051
127.095
128.429
129.019
131.879
132.715
134.867
137.374
141.843
143.943
161.647
0
25
50
75
100
125
150
175
200
Me
HN
O
N
3i
^{13}C NMR (DMSO-d_6, 75 MHZ)

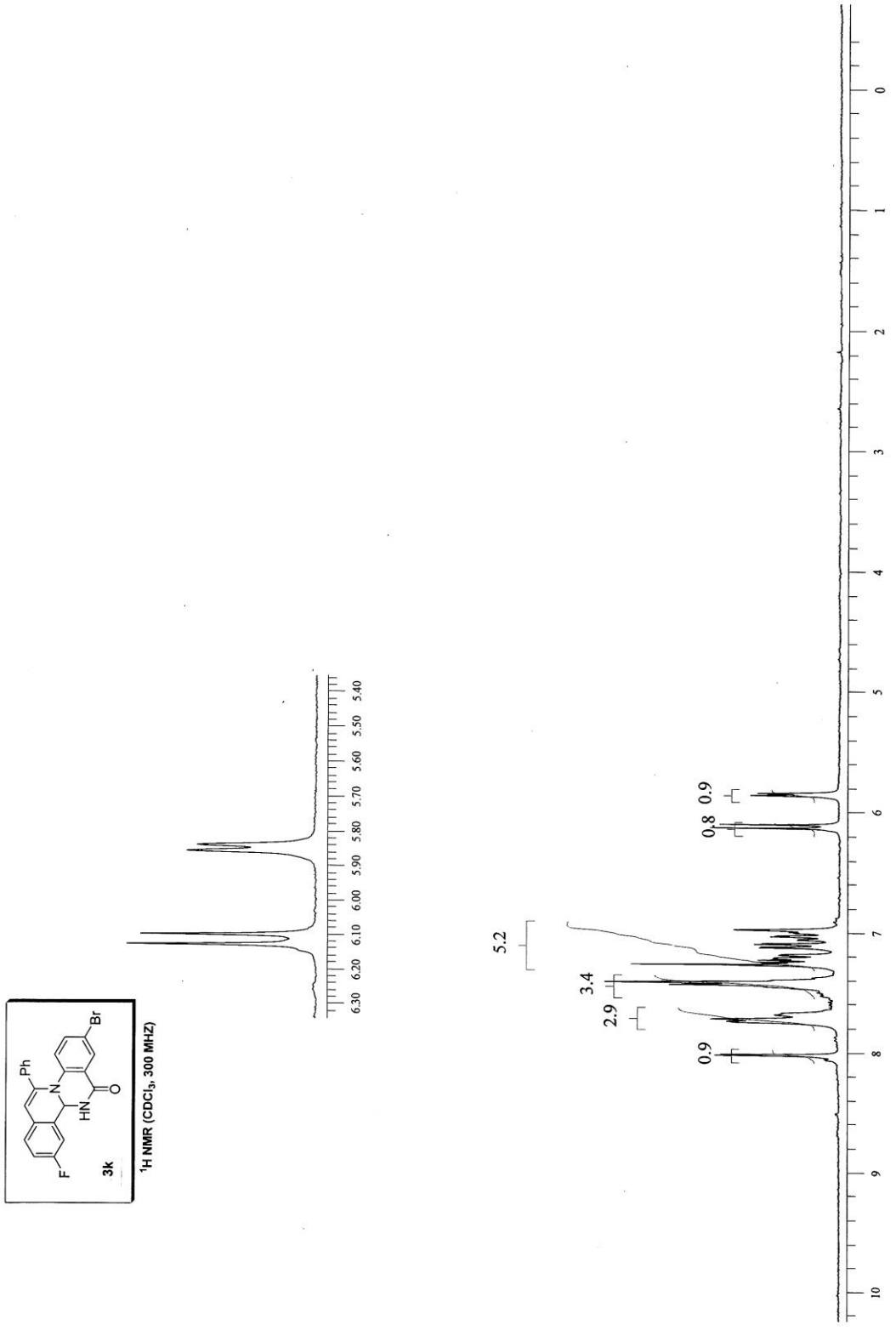


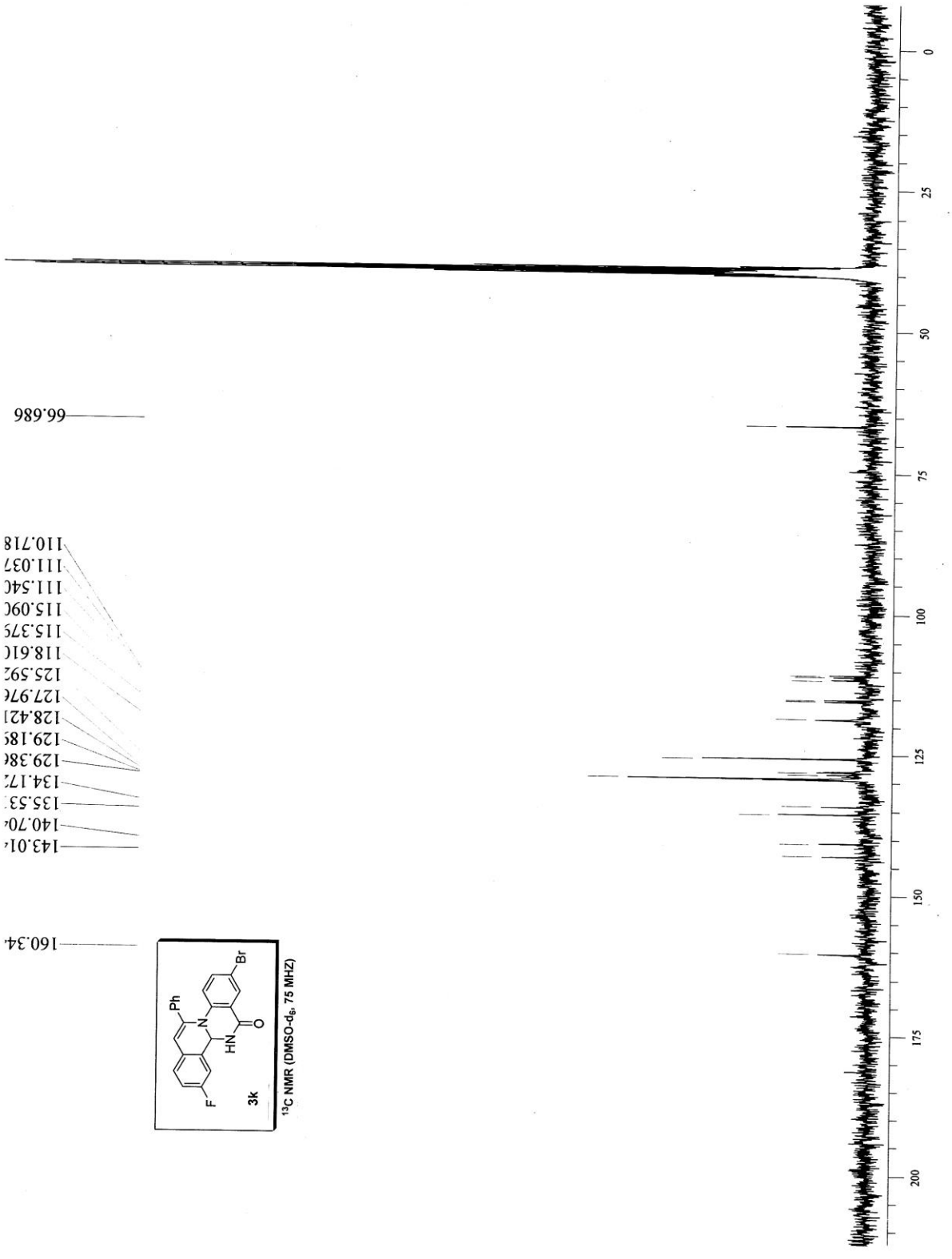
^{1}H NMR ($CDCl_3$, 300 MHZ)

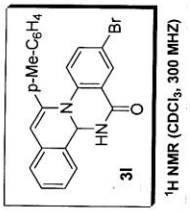




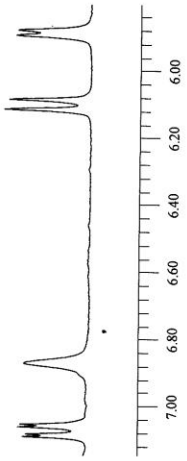

67.778
111.51
111.79
114.76
115.64
117.53
120.55
126.22
127.04
127.12
128.09
128.40
129.11
129.19
133.44
134.98
141.76
161.34
164.16
Ph
N
HN
O
F
3j
13C NMR (CDCl3, 75 MHZ)
0
25
50
75
100
125
150
175
200

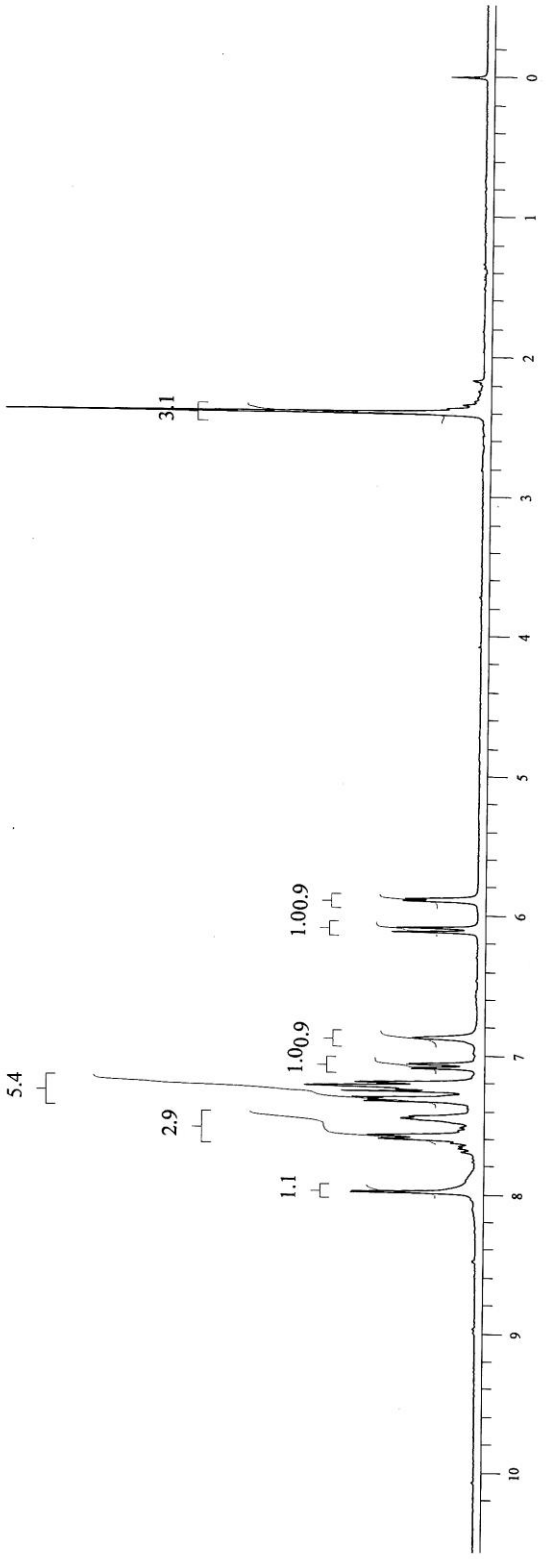

Ph
Br
N
HN
O
F
3k
^{1}H NMR ($CDCl_3$, 300 MHZ)
6.30 6.20 6.10 6.00 5.90 5.80 5.70 5.60 5.50 5.40
5.2
3.4
2.9
0.9
0.8
0.9
10 9 8 7 6 5 4 3 2 1 0

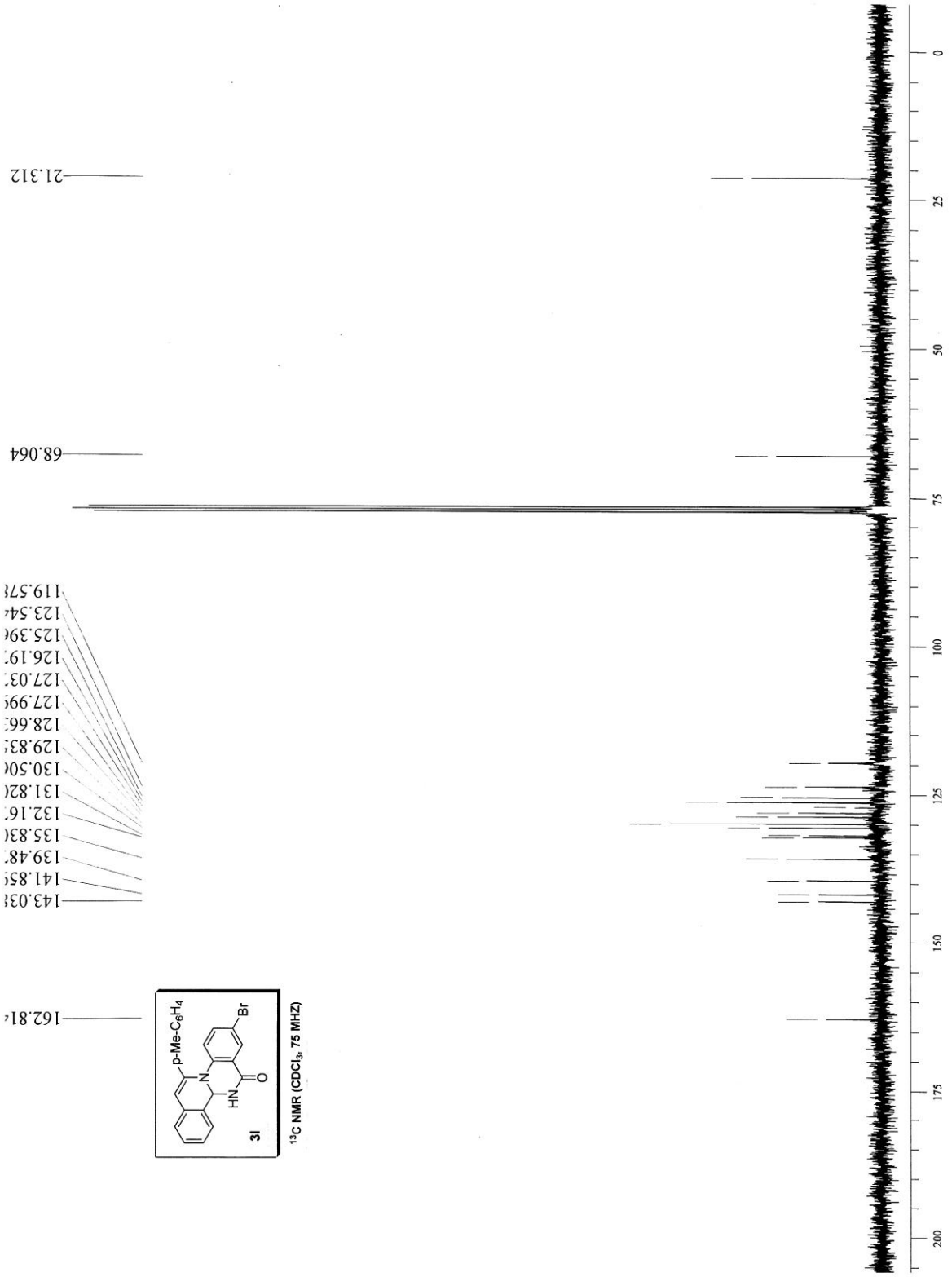

66.686
110.718
111.037
111.540
115.090
115.375
118.610
125.592
127.976
128.421
129.189
129.386
134.172
135.532
140.706
143.014
160.344
Br
Ph
N
HN
O
F
3k
^{13}C NMR (DMSO-d_6, 75 MHZ)
0
25
50
75
100
125
150
175
200

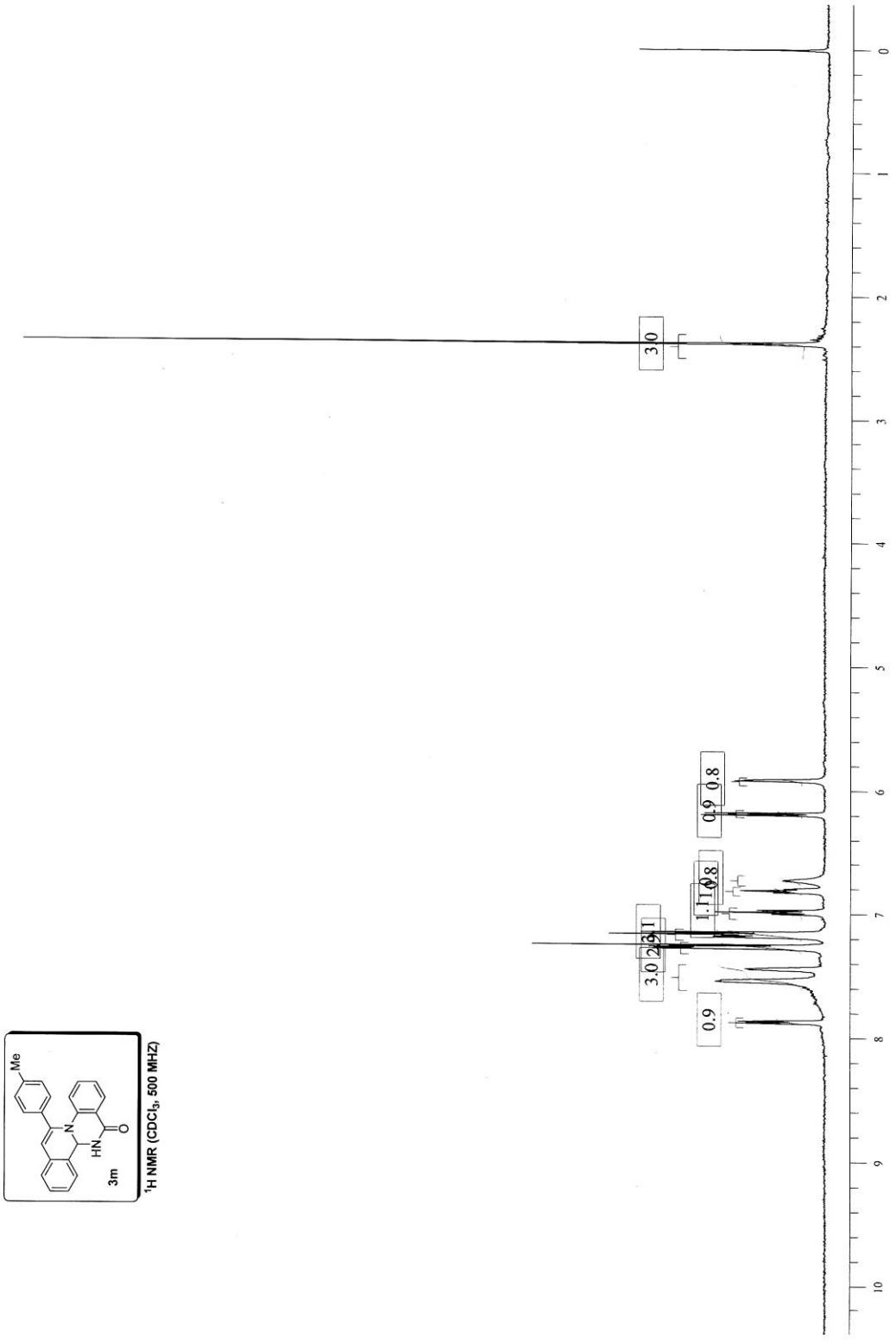


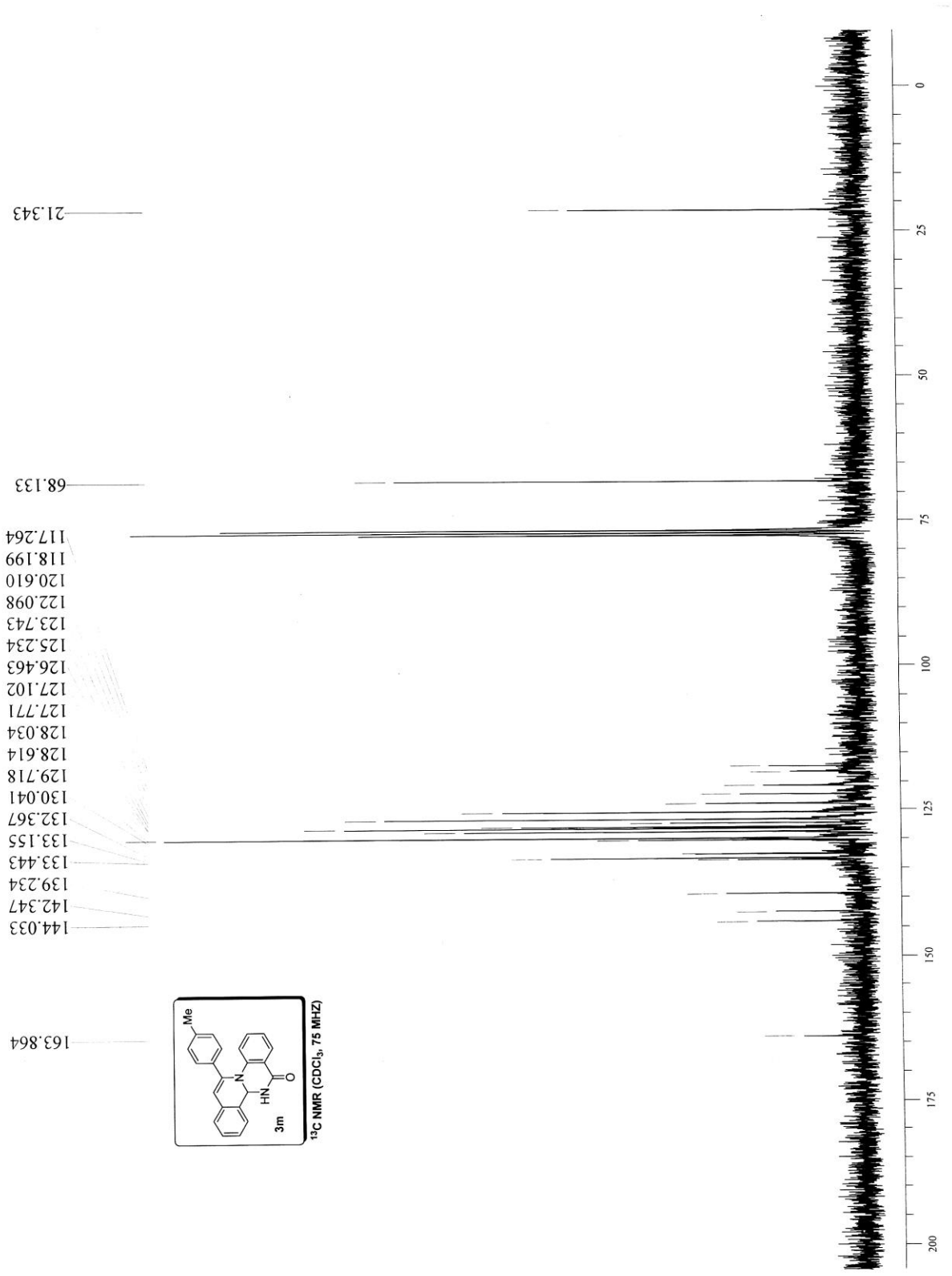
^{1}H NMR (CDCl$_3$, 300 MHZ)

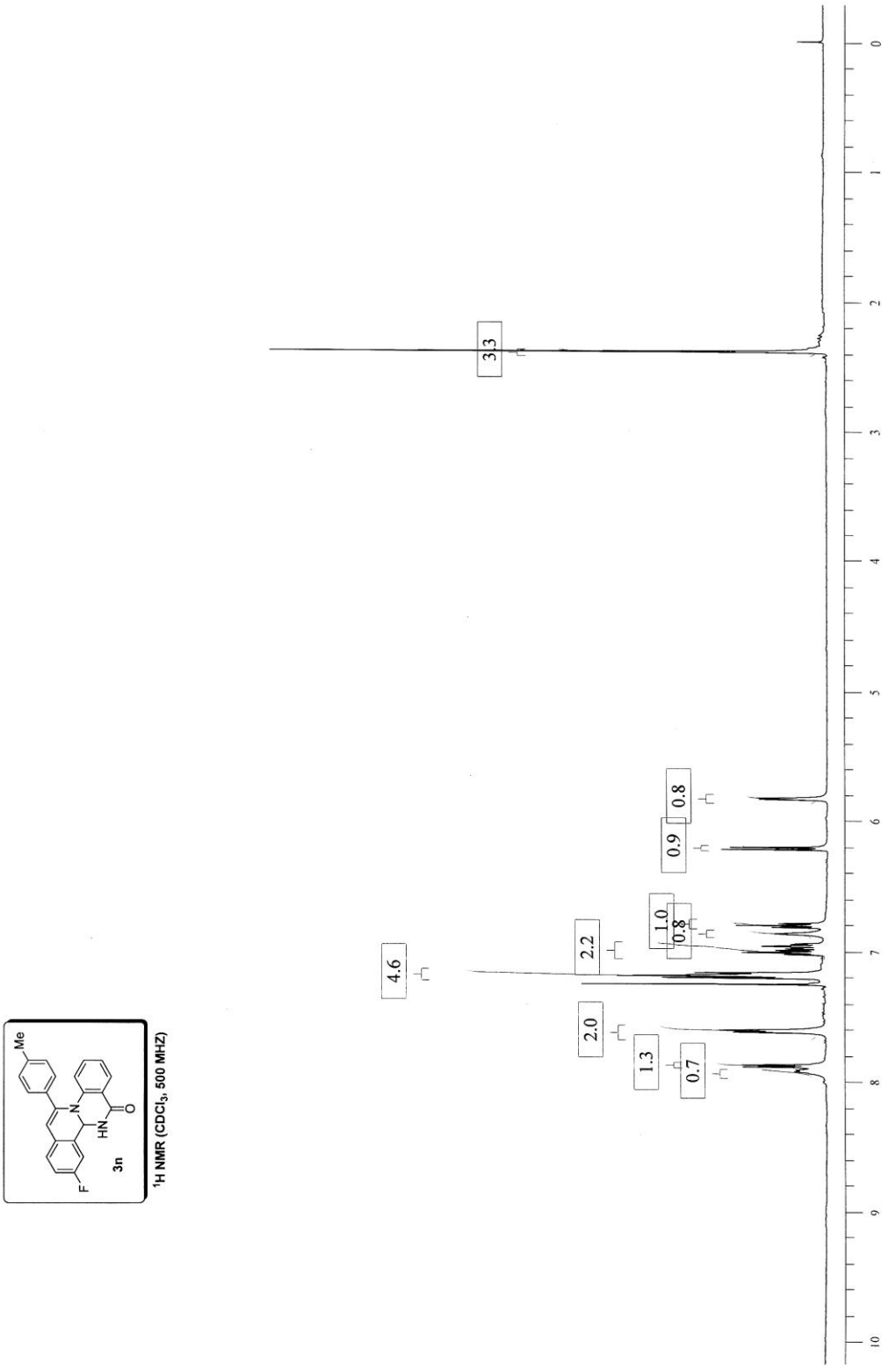


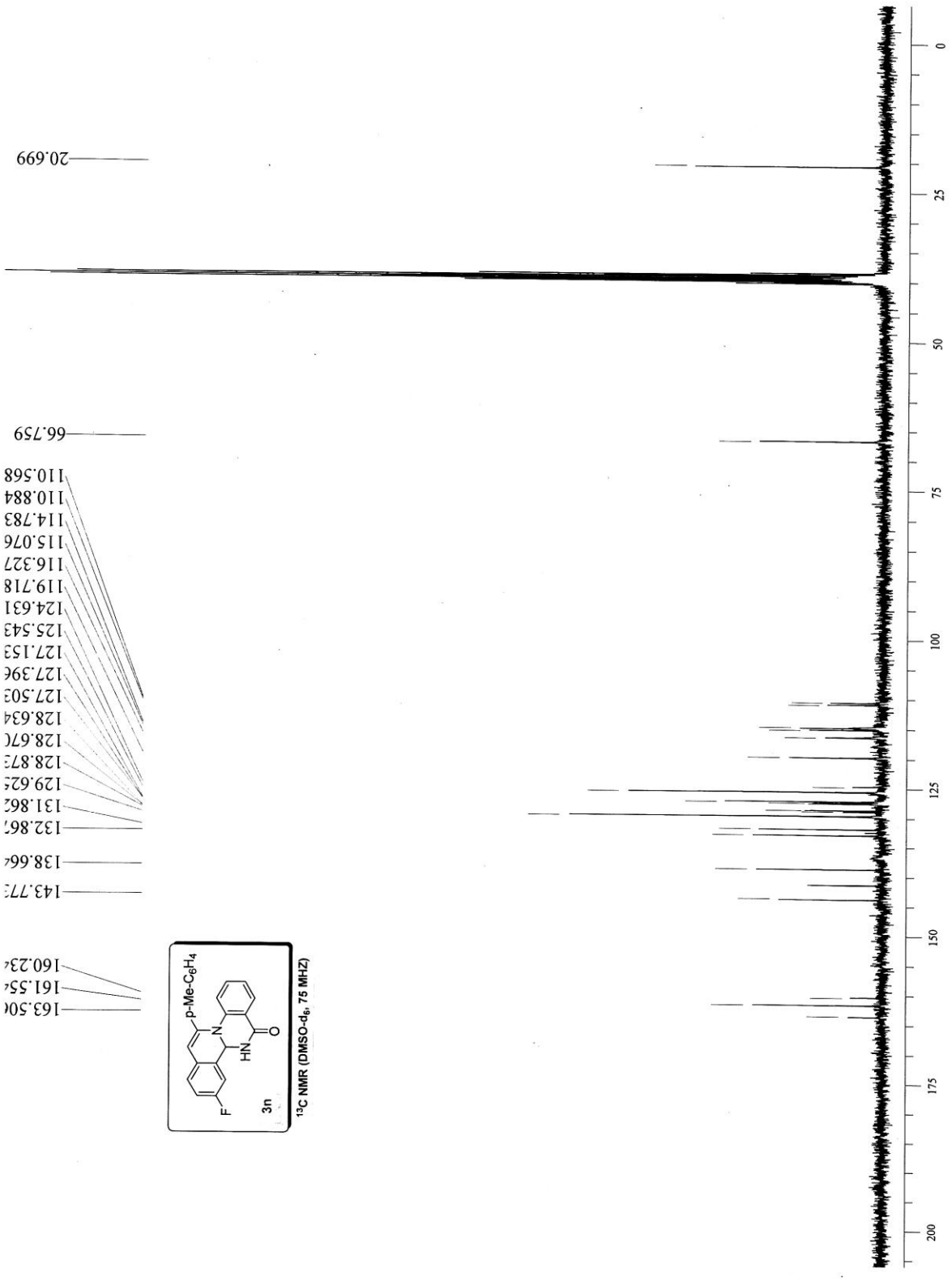


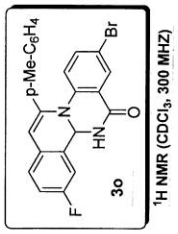

21.312
68.064
119.578
123.544
125.396
126.197
127.037
127.999
128.663
129.833
130.506
131.820
132.167
135.830
139.487
141.859
143.033
162.817
p-Me-C6H4
Br
N
HN
O
3l
13C NMR (CDCl3, 75 MHZ)
0
25
50
75
100
125
150
175
200


Me
N
HN
O
3m
^{1}H NMR ($CDCl_3$, 500 MHZ)
3.0
0.9
0.8
1.1
1.0
0.8
3.0
2.8
1.1
0.9
0
1
2
3
4
5
6
7
8
9
10

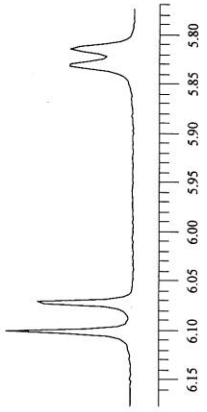

21.343
68.133
117.264
118.199
120.610
122.098
123.743
125.234
126.463
127.102
127.771
128.034
128.614
129.718
130.041
132.367
133.155
133.443
139.234
142.347
144.033
163.864
Me
N
HN
O
3m
^{13}C NMR ($CDCl_3$, 75 MHZ)
0
25
50
75
100
125
150
175
200

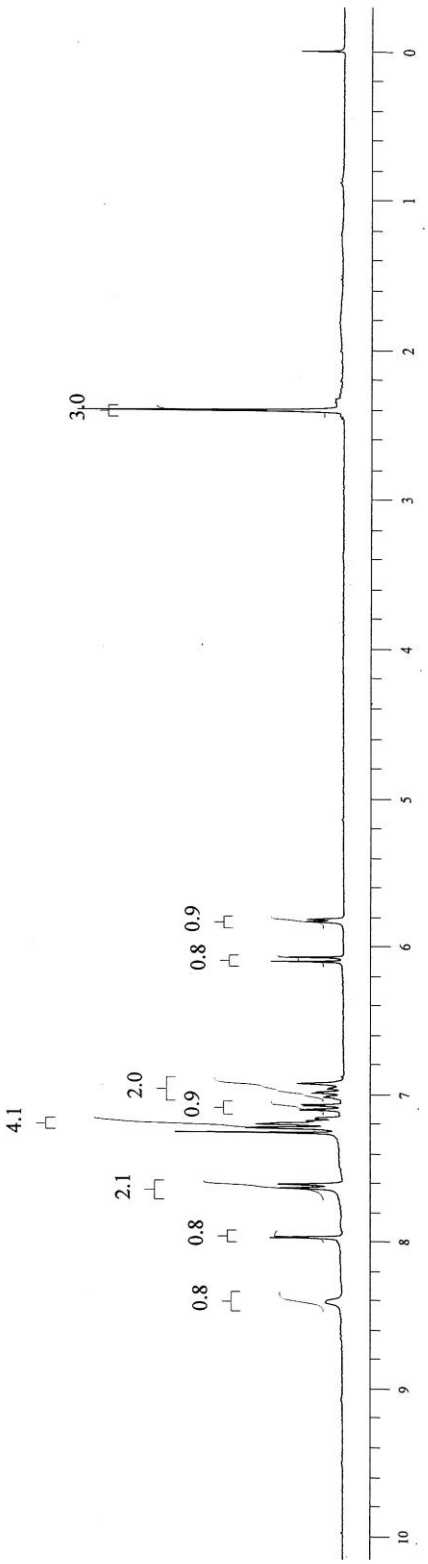

Me
N
HN
O
F
3n
^{1}H NMR ($CDCl_3$, 500 MHZ)
3.3
4.6
2.2
2.0
1.3
0.7
1.0
0.8
0.9
0.8


20.699
66.759
110.568
110.884
114.783
115.076
116.327
119.718
124.631
125.543
127.153
127.396
127.503
128.634
128.670
128.873
129.625
131.862
132.867
138.664
143.773
160.234
161.554
163.506
p-Me-C6H4
HN
O
F
3n
13C NMR (DMSO-d6, 75 MHZ)
0
25
50
75
100
125
150
175
200

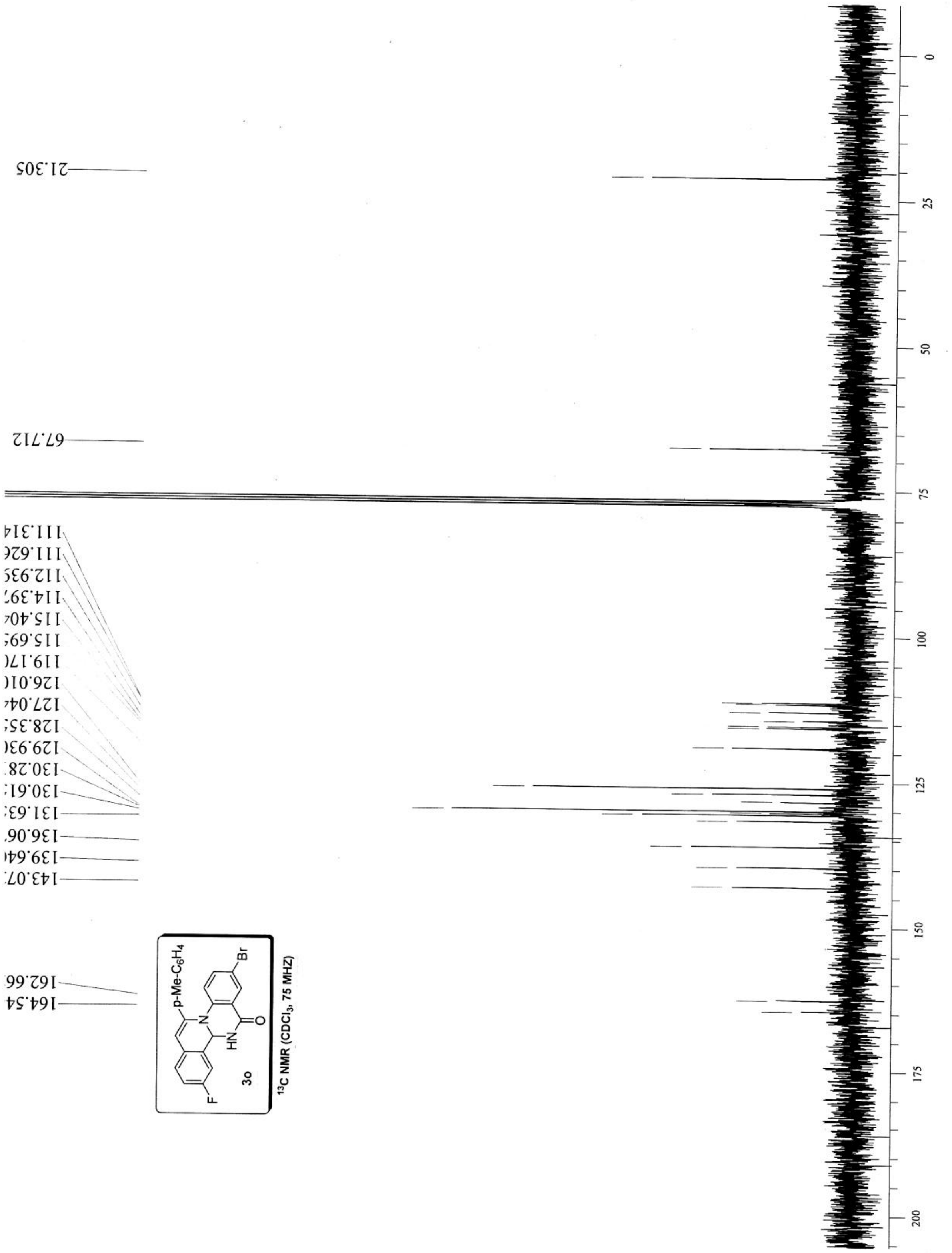


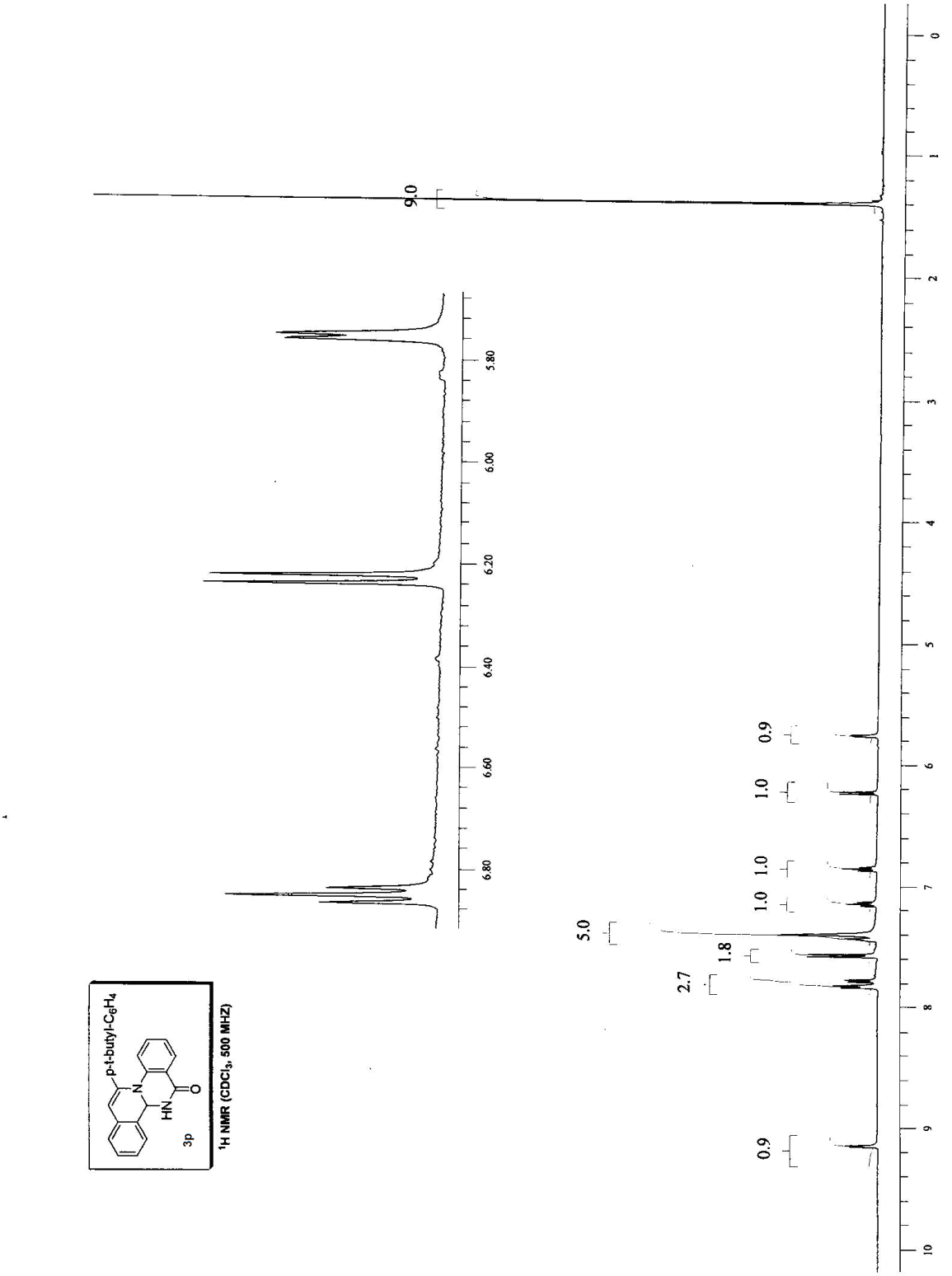
^{1}H NMR ($CDCl_3$, 300 MHZ)

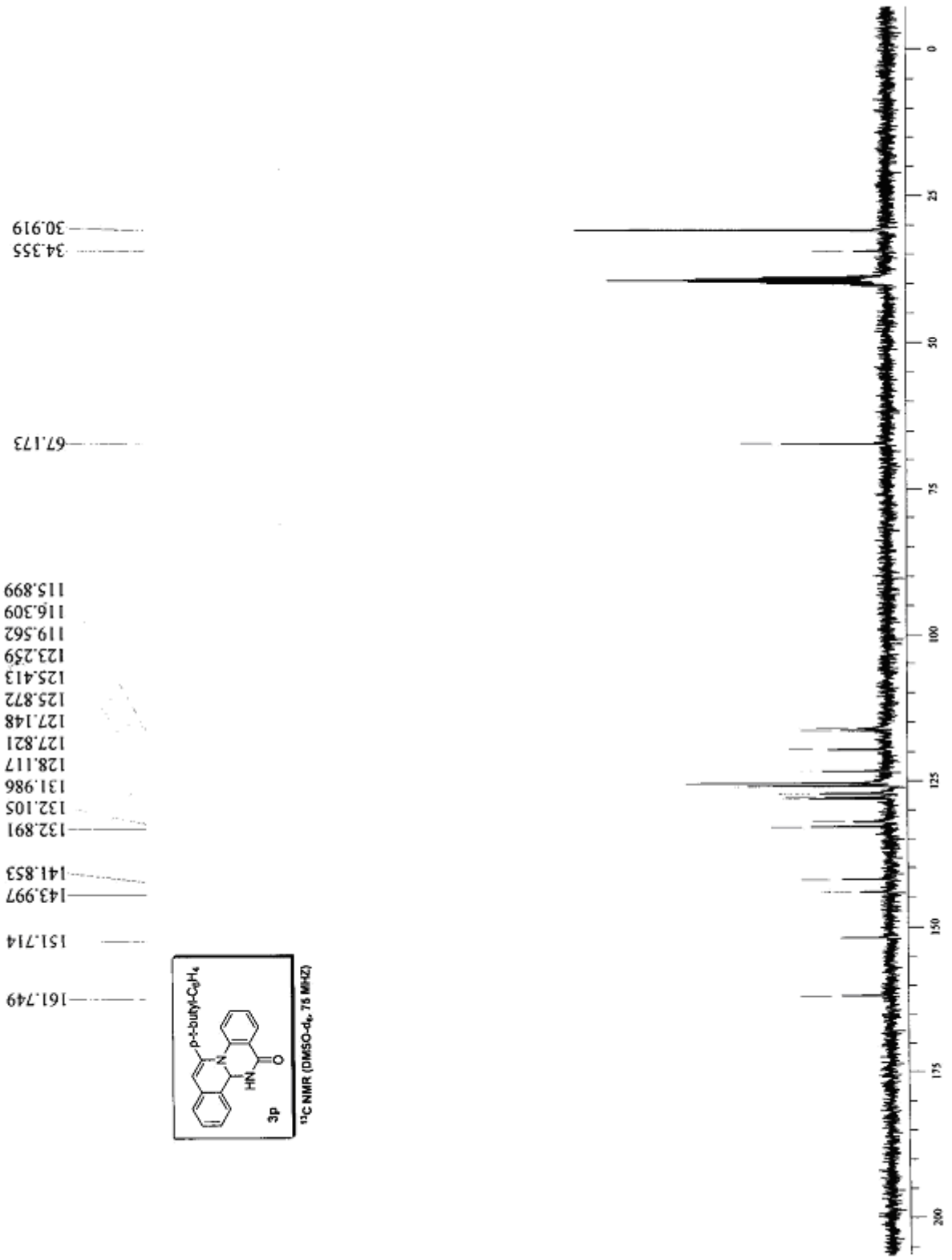


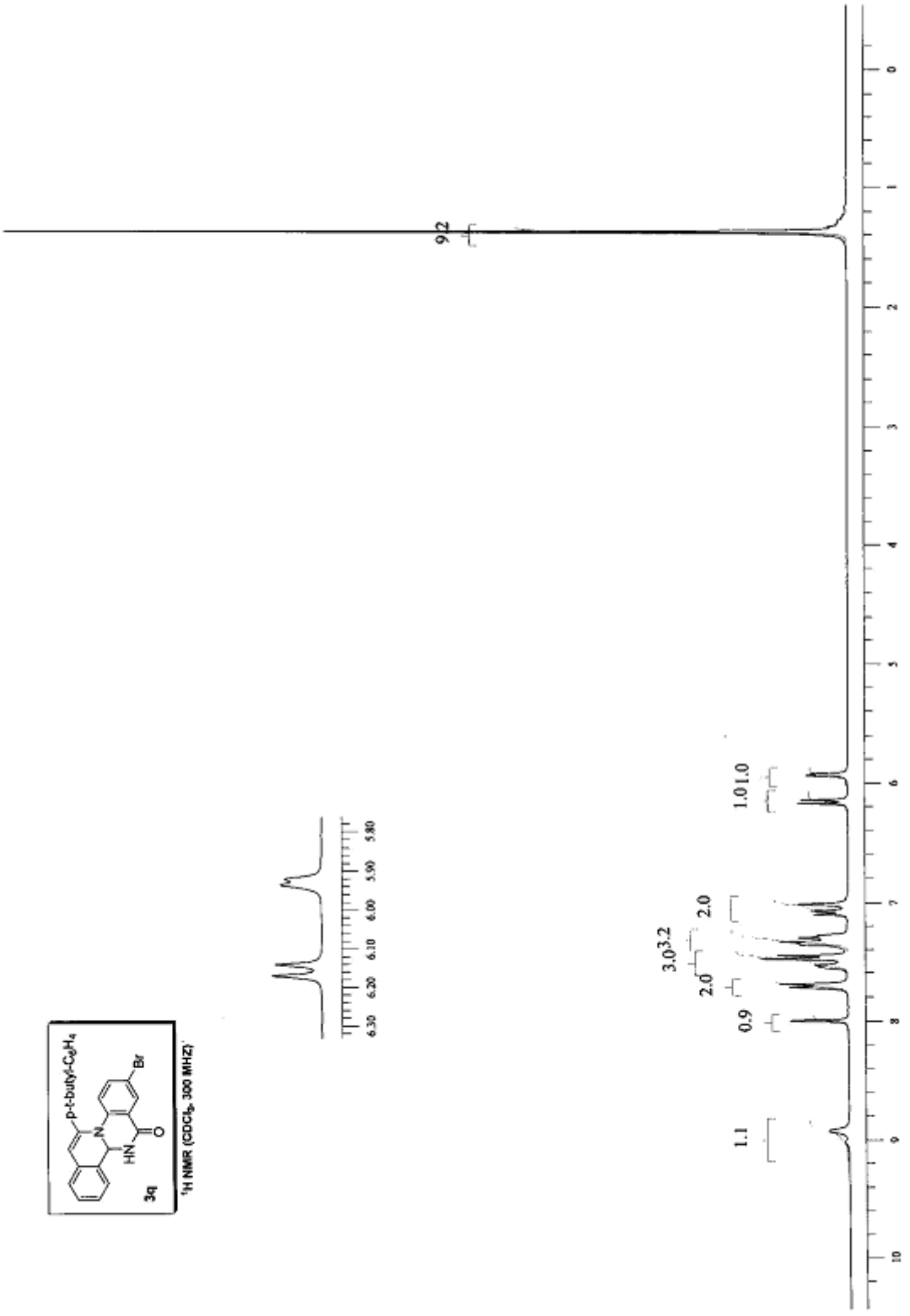


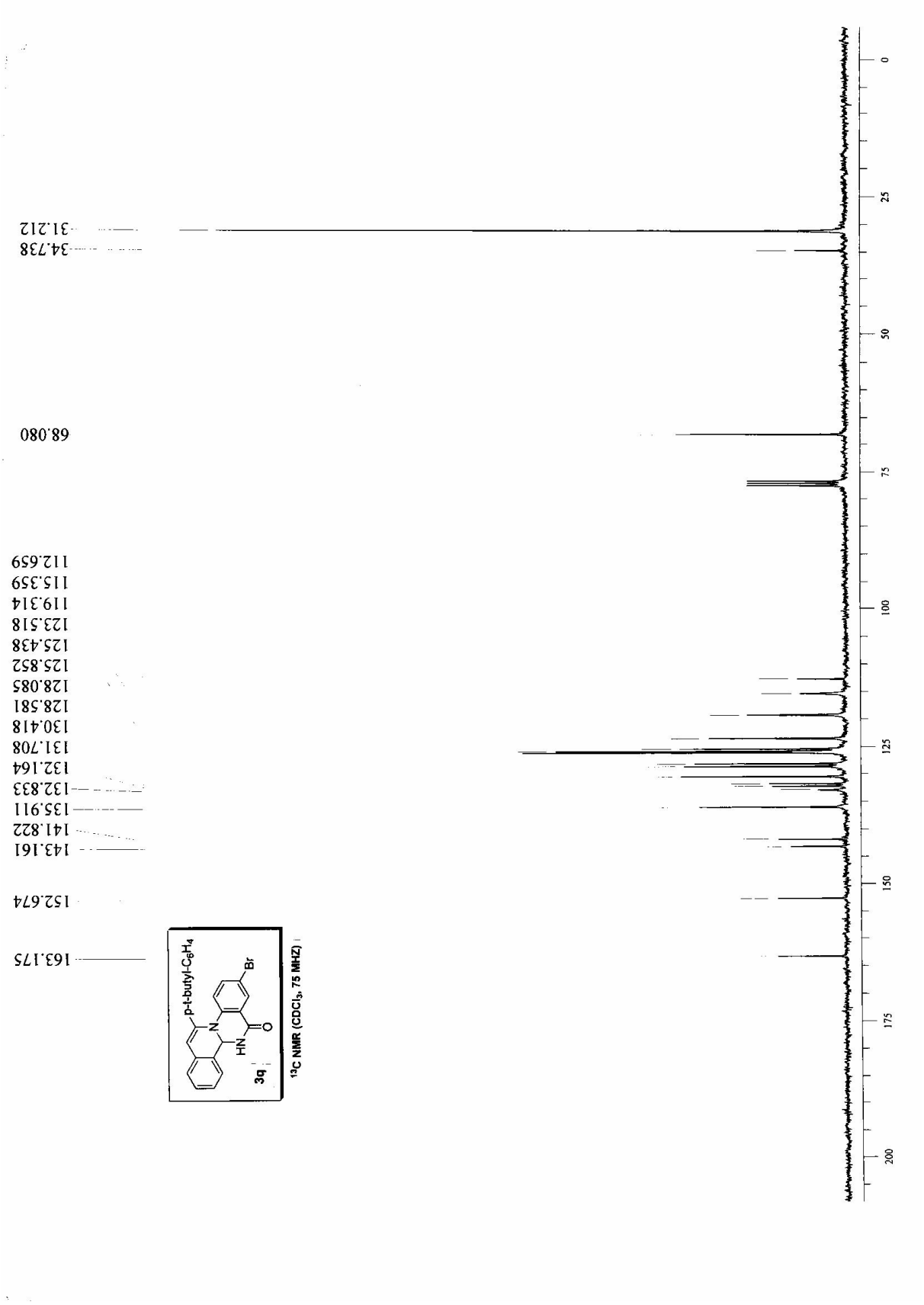
Electronic Supplementary Material (ESI) for Chemical Communications

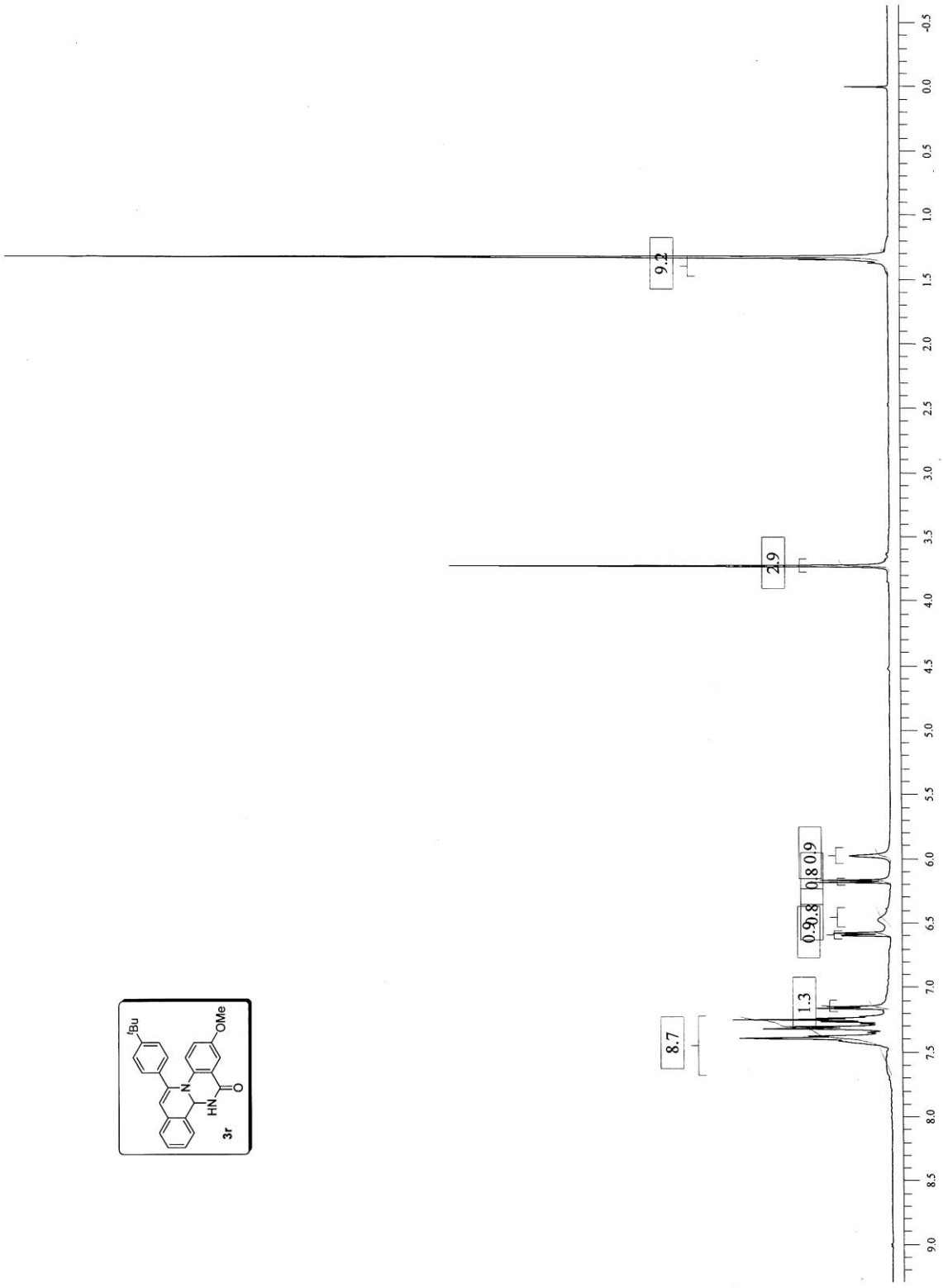


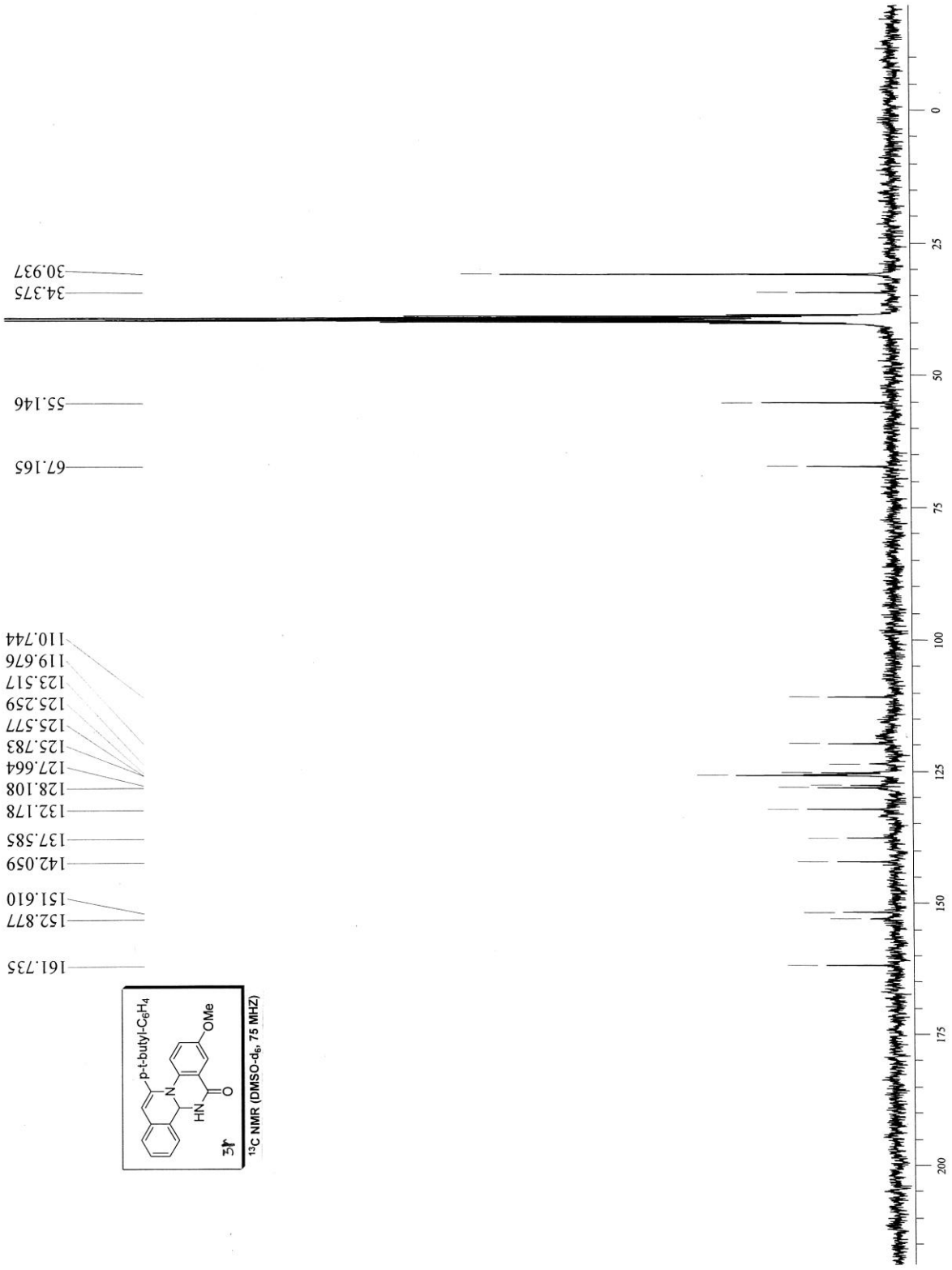

p-t-butyl-C6H4
N
HN
O
3p
1H NMR (CDCl3, 500 MHz)
9.0
5.0
2.7
1.8
1.0
1.0
1.0
0.9
0.9
5.80
6.00
6.20
6.40
6.60
6.80
0
1
2
3
4
5
6
7
8
9
10

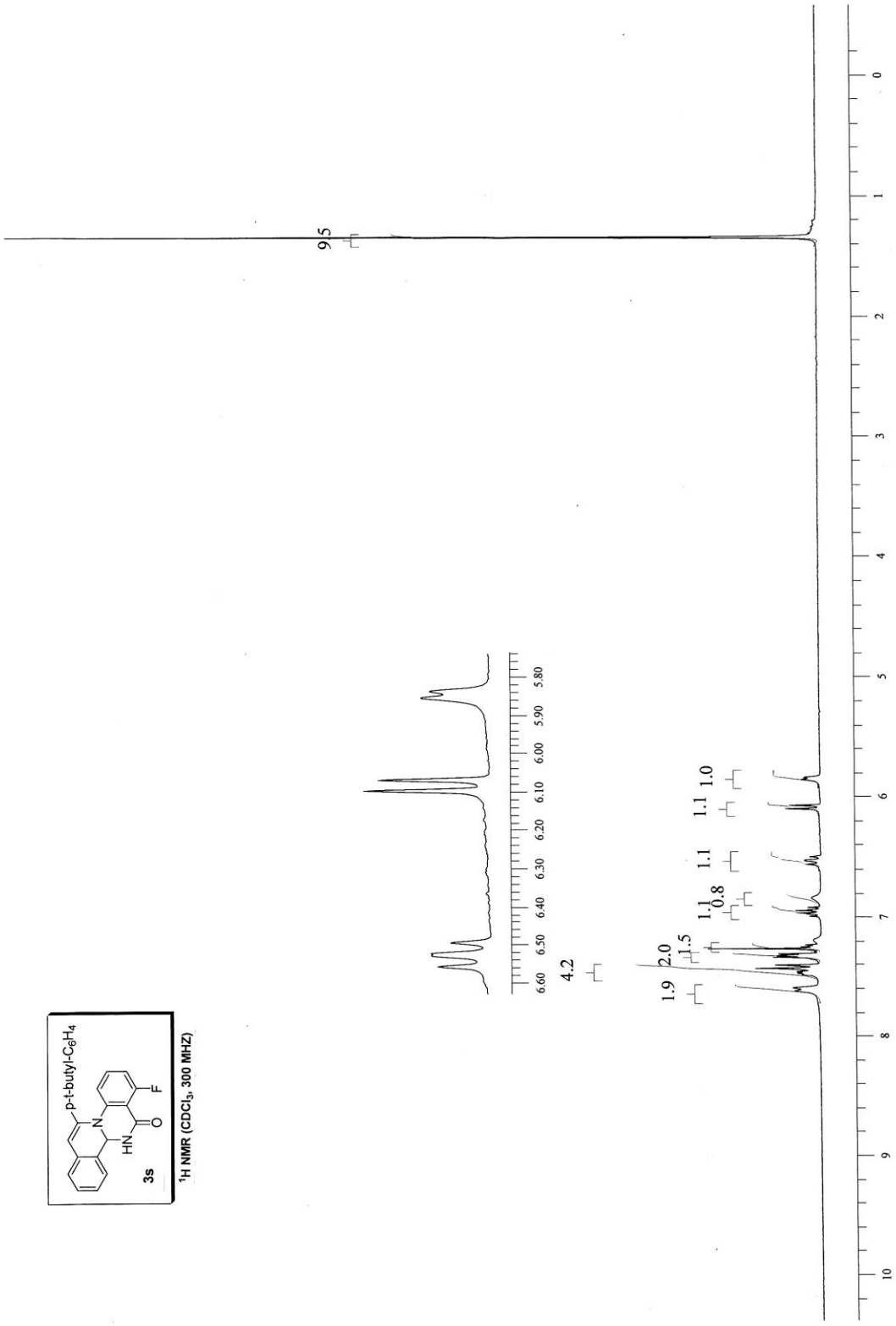

30.919
34.355
67.173
115.899
116.309
119.562
123.259
125.413
125.872
127.148
127.821
128.117
131.986
132.105
132.891
141.853
143.997
151.714
161.749
p-t-butyl-C6H4
HN
O
3p
13C NMR (DMSO-d6, 76 MHZ)
0
25
50
75
100
125
150
175
200

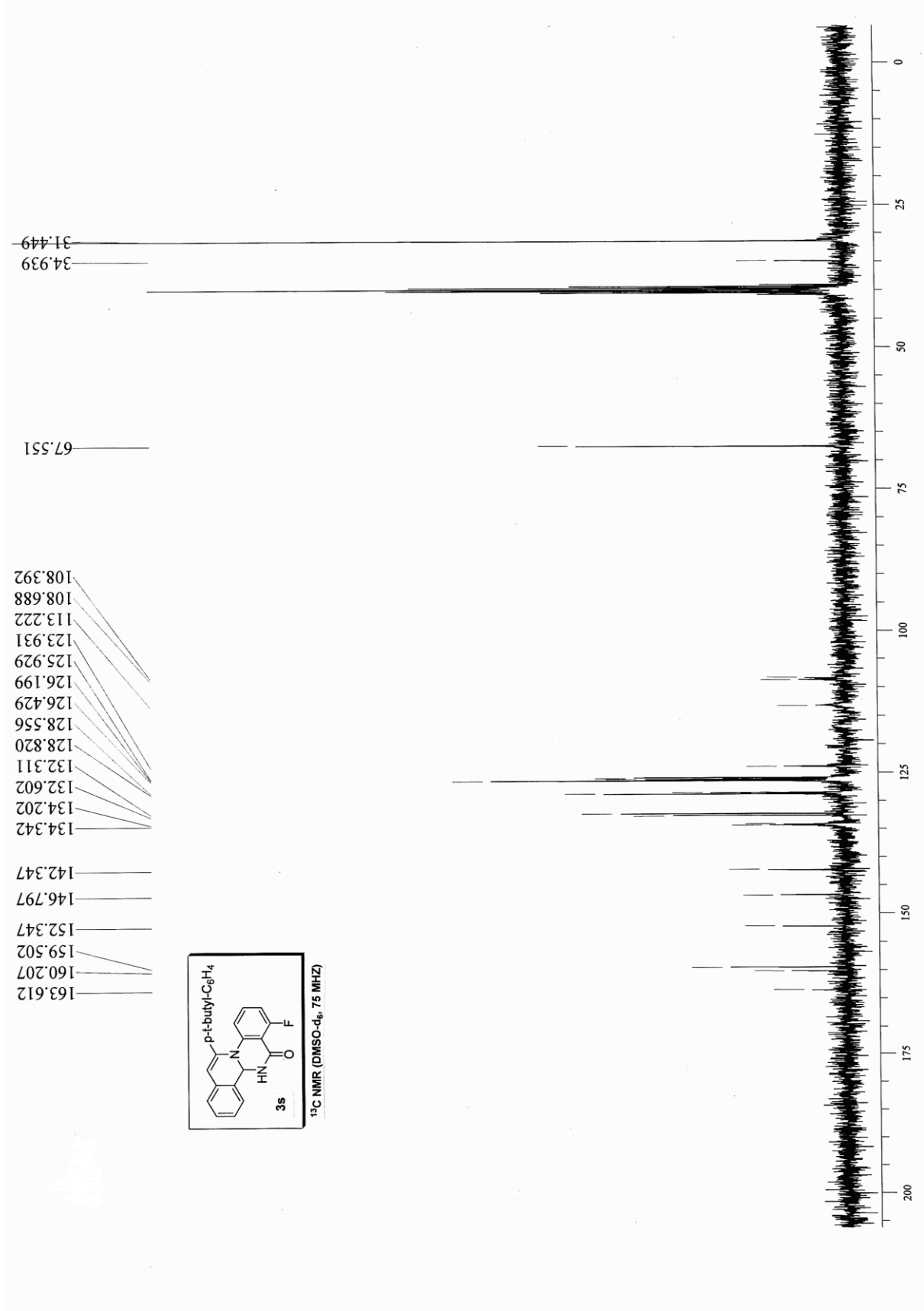

p-t-butyl-C6H4
Br
N
HN
O
3q
¹H NMR (CDCl3, 300 MHZ)
9.2
1.1
0.9
2.0
3.0
3.2
2.0
1.0
1.0
6.30
6.20
6.10
6.00
5.90
5.80

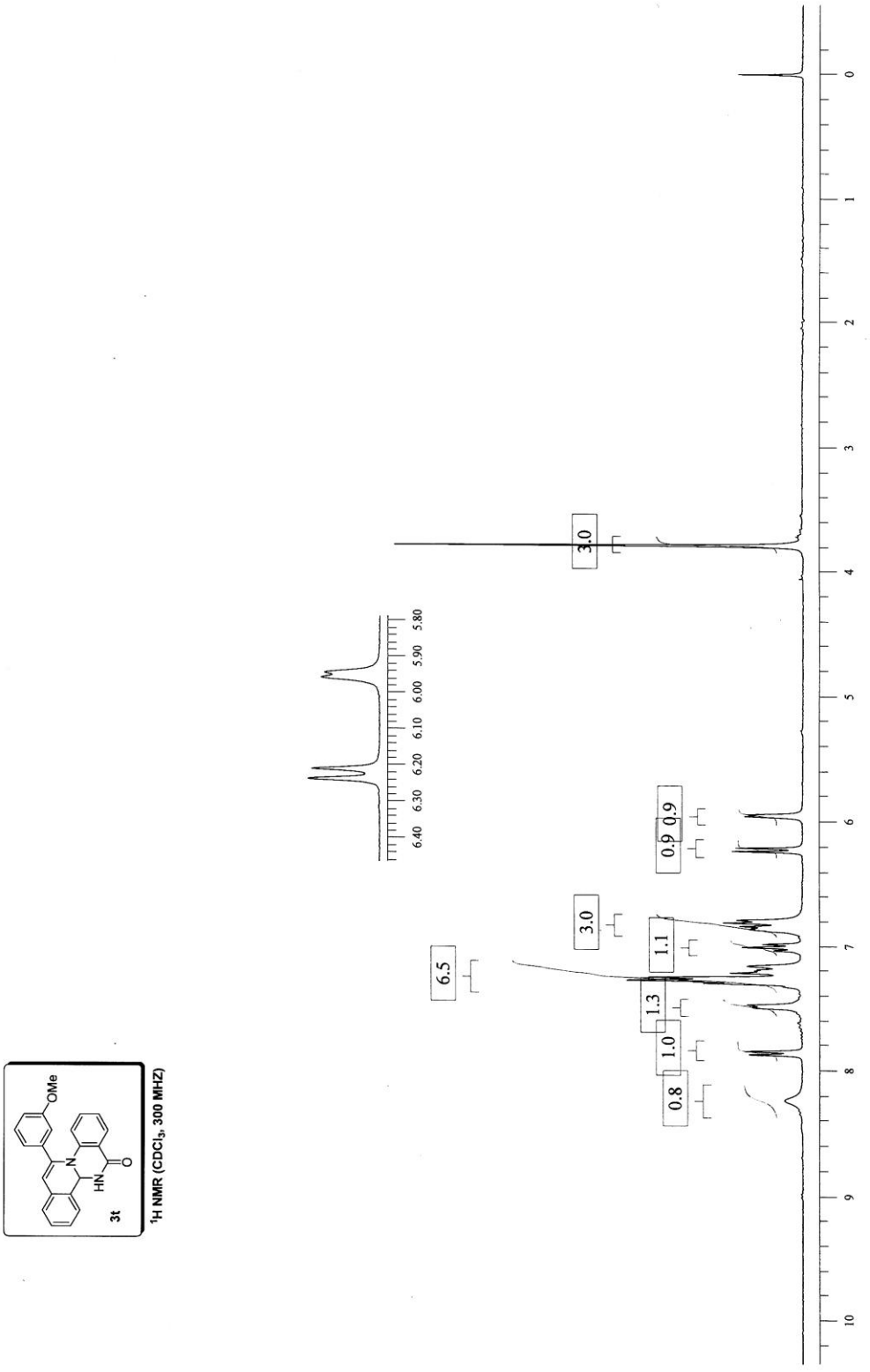


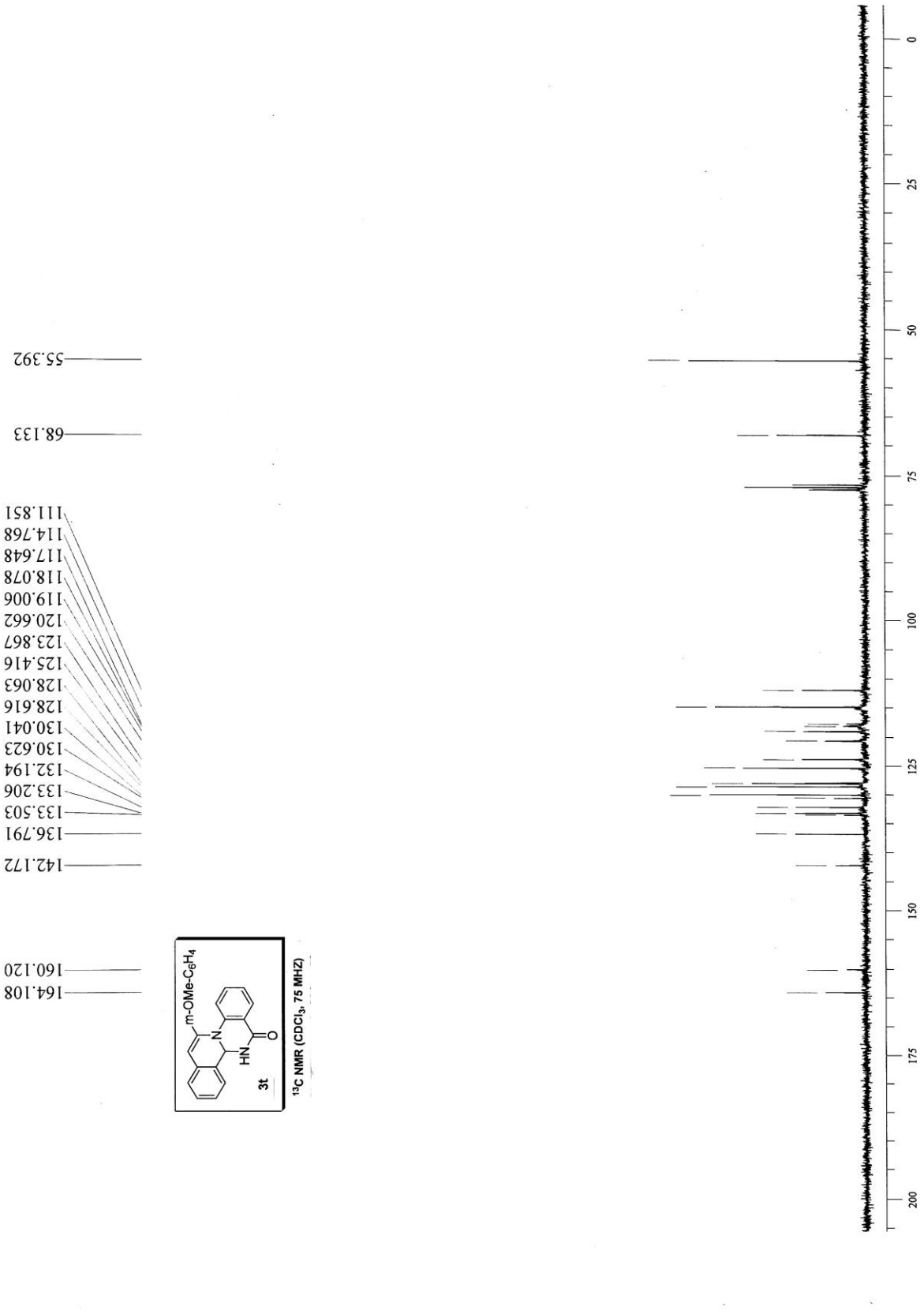

9.2
2.9
0.9
0.8
0.8
0.9
1.3
8.7
tBu
OMe
N
HN
O
3r

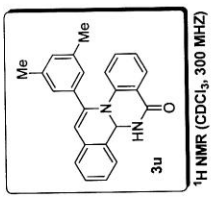

30.937
34.375
55.146
67.165
110.744
119.676
123.517
125.259
125.577
125.783
127.664
128.108
132.178
137.585
142.059
151.610
152.877
161.735
p-t-butyl-C6H4
OMe
N
HN
O
3f
13C NMR (DMSO-d6, 75 MHZ)
0
25
50
75
100
125
150
175
200


p-t-butyl-C6H4
N
HN
O
F
3s
1H NMR (CDCl3, 300 MHZ)
9.5
4.2
2.0
1.9
1.5
1.1
0.8
1.1
1.1
1.0
6.60
6.50
6.40
6.30
6.20
6.10
6.00
5.90
5.80
0
1
2
3
4
5
6
7
8
9
10

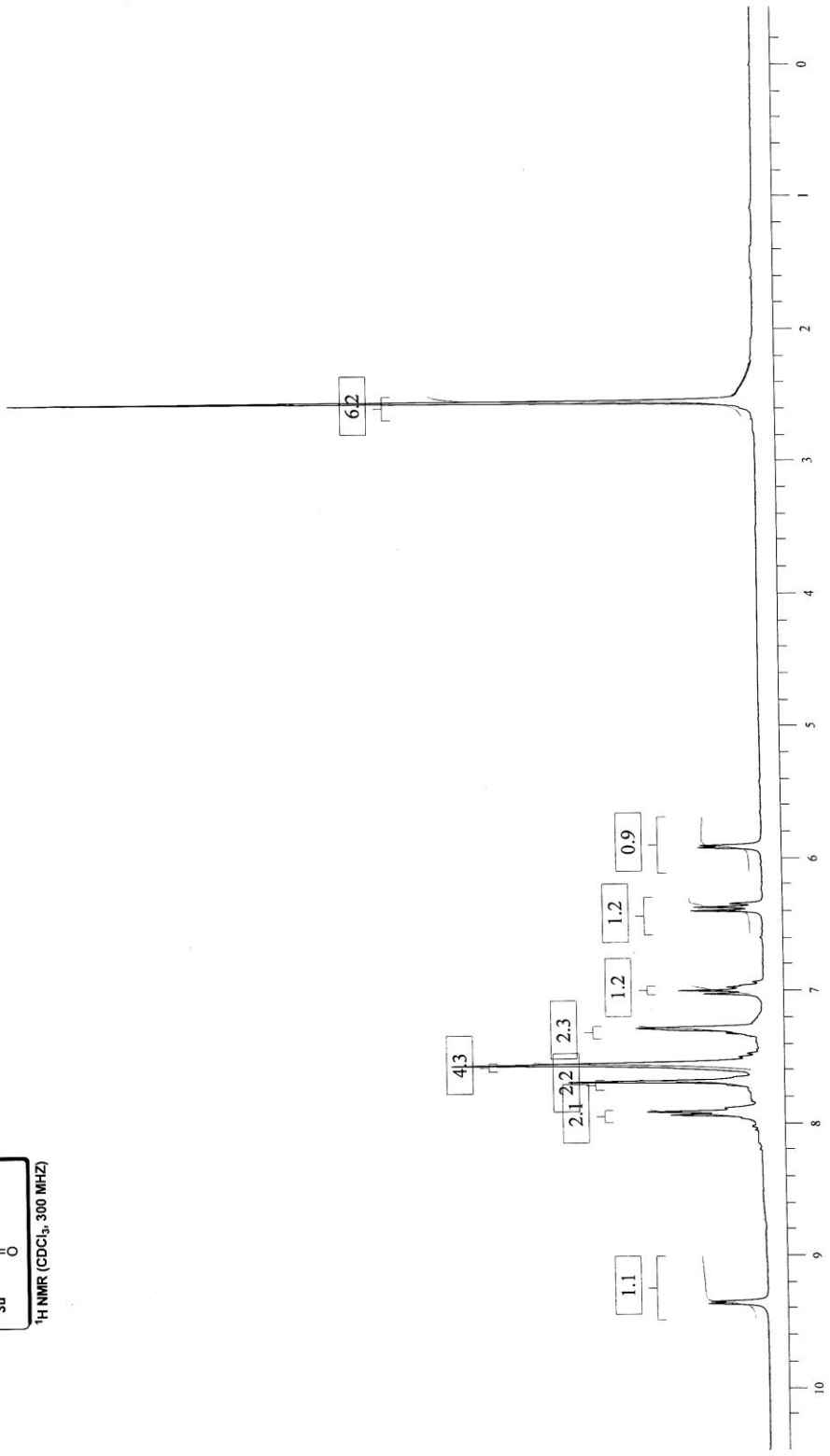

31.449
34.939
67.551
108.392
108.688
113.222
123.931
125.929
126.199
126.429
128.556
128.820
132.311
132.602
134.202
134.342
142.347
146.797
152.347
159.502
160.207
163.612
p-t-butyl-C6H4
F
O
HN
N
3s
13C NMR (DMSO-d6, 75 MHZ)
0
25
50
75
100
125
150
175
200

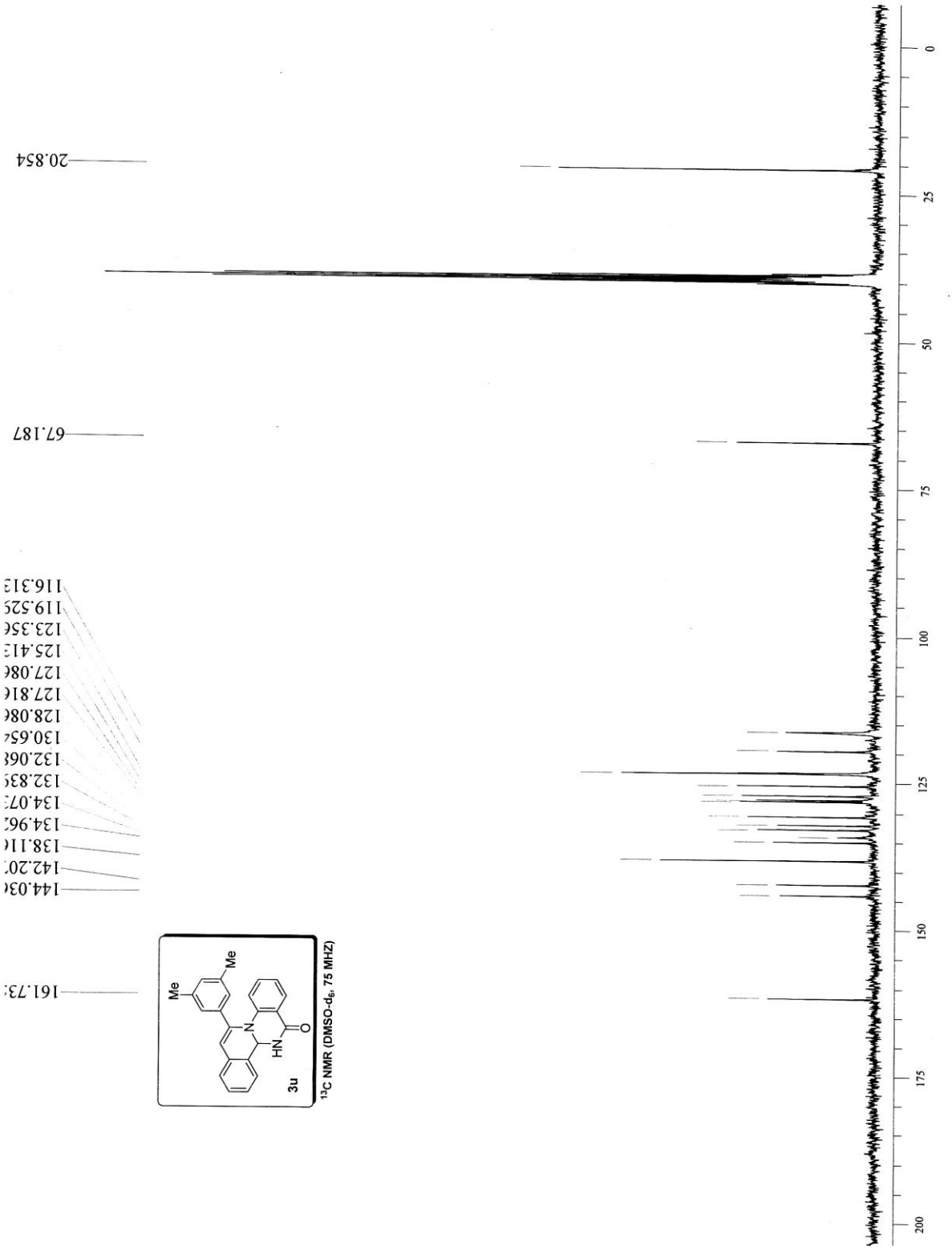

OMe
N
HN
O
3t
^{1}H NMR (CDCl$_3$, 300 MHZ)
3.0
6.5
3.0
1.1
1.3
1.0
0.8
0.9
0.9
6.40
6.30
6.20
6.10
6.00
5.90
5.80
0
1
2
3
4
5
6
7
8
9
10

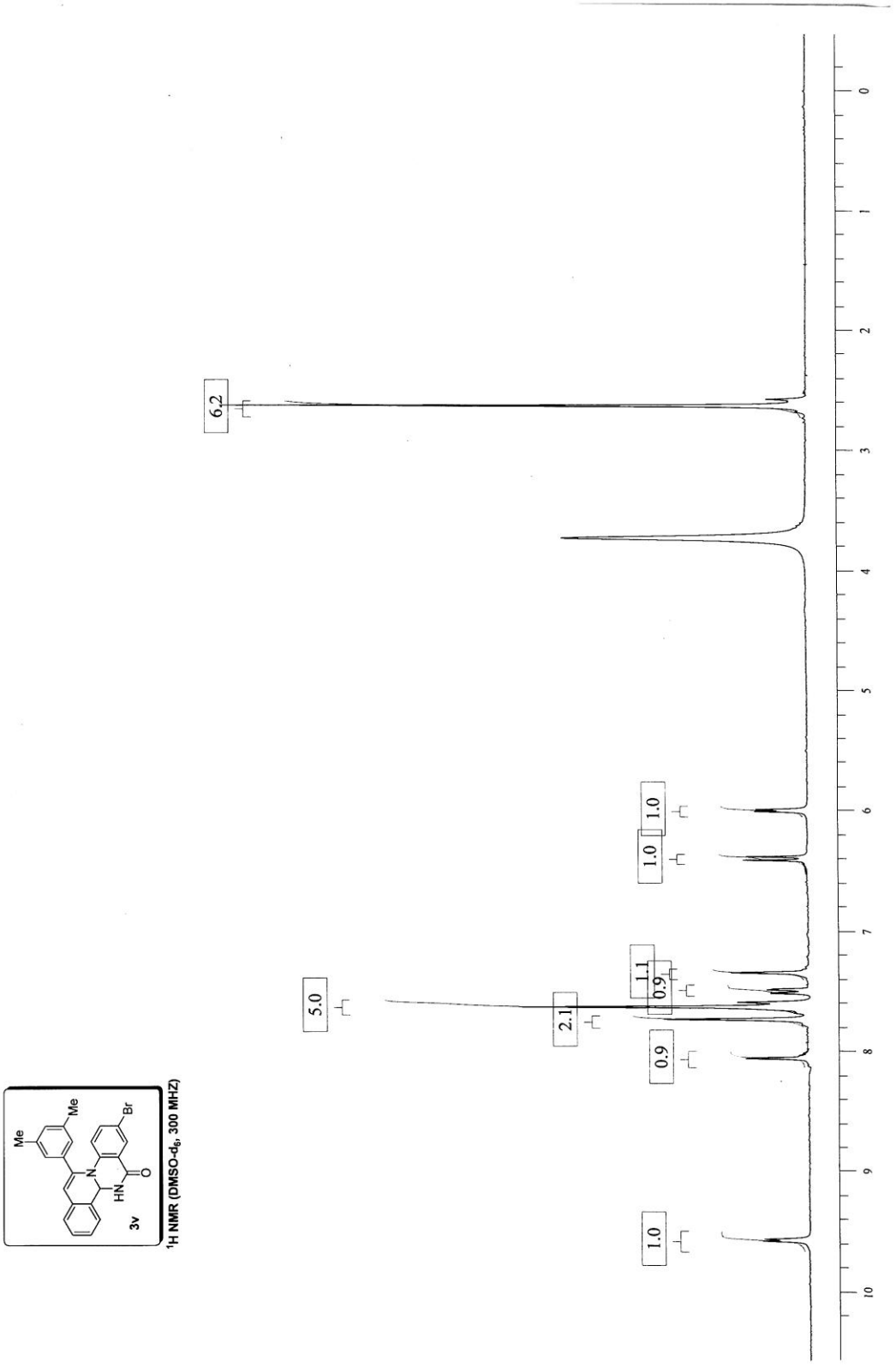

55.392
68.133
111.851
114.768
117.648
118.078
119.006
120.662
123.867
125.416
128.063
128.616
130.041
130.623
132.194
133.206
133.503
136.791
142.172
160.120
164.108
m-OMe-C6H4
N
HN
O
3t
13C NMR (CDCl3, 75 MHZ)
0
25
50
75
100
125
150
175
200

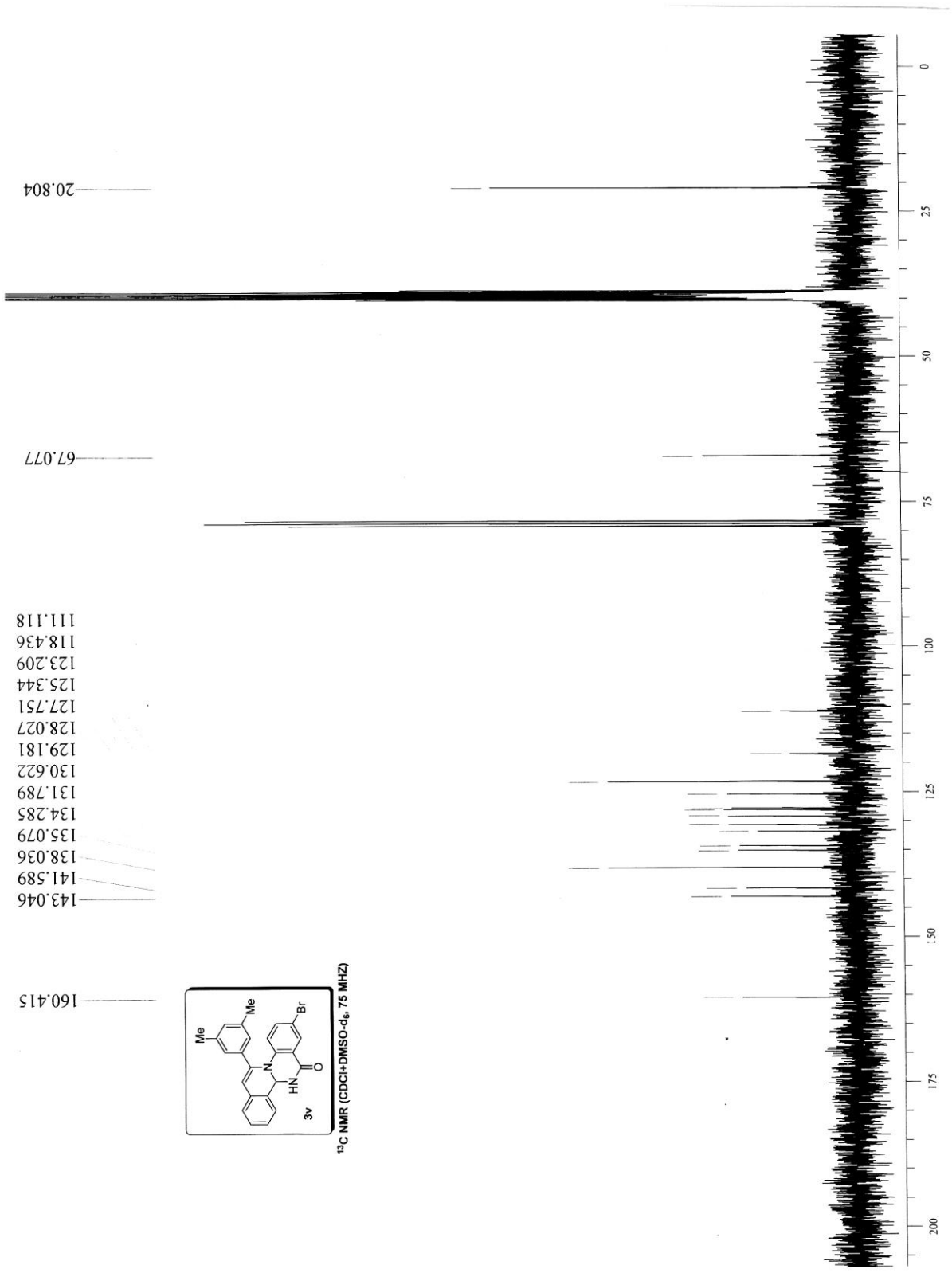


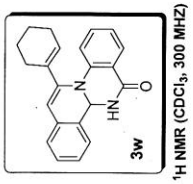
^{1}H NMR ($CDCl_3$, 300 MHZ)



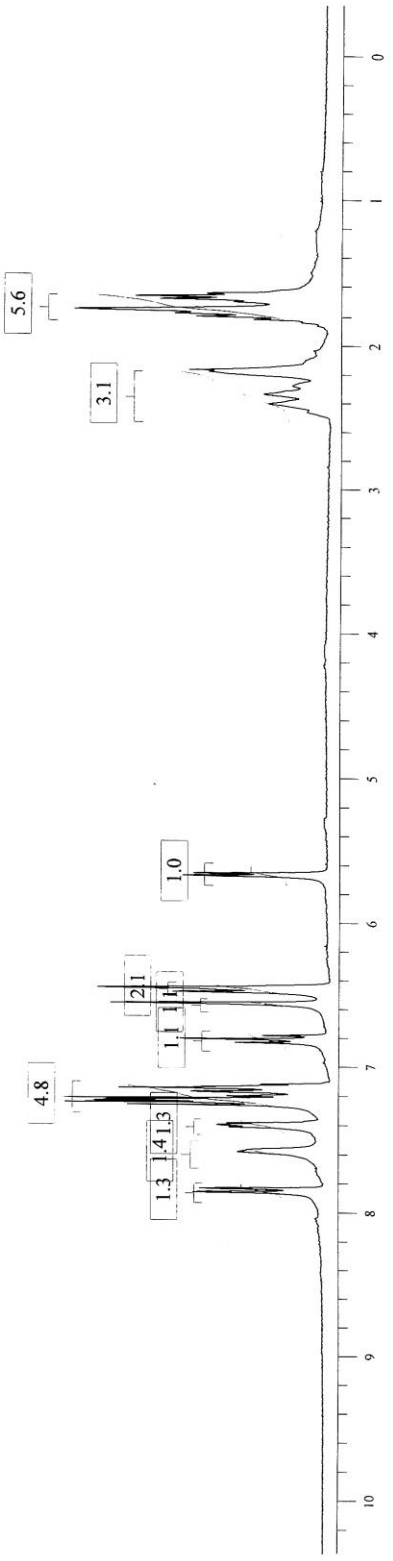

20.854
67.187
116.313
119.529
123.356
125.413
127.086
127.816
128.086
130.657
132.068
132.839
134.073
134.962
138.116
142.207
144.036
161.733
Me
Me
N
HN
O
3u
^{13}C NMR (DMSO-d_6, 75 MHZ)
0
25
50
75
100
125
150
175
200

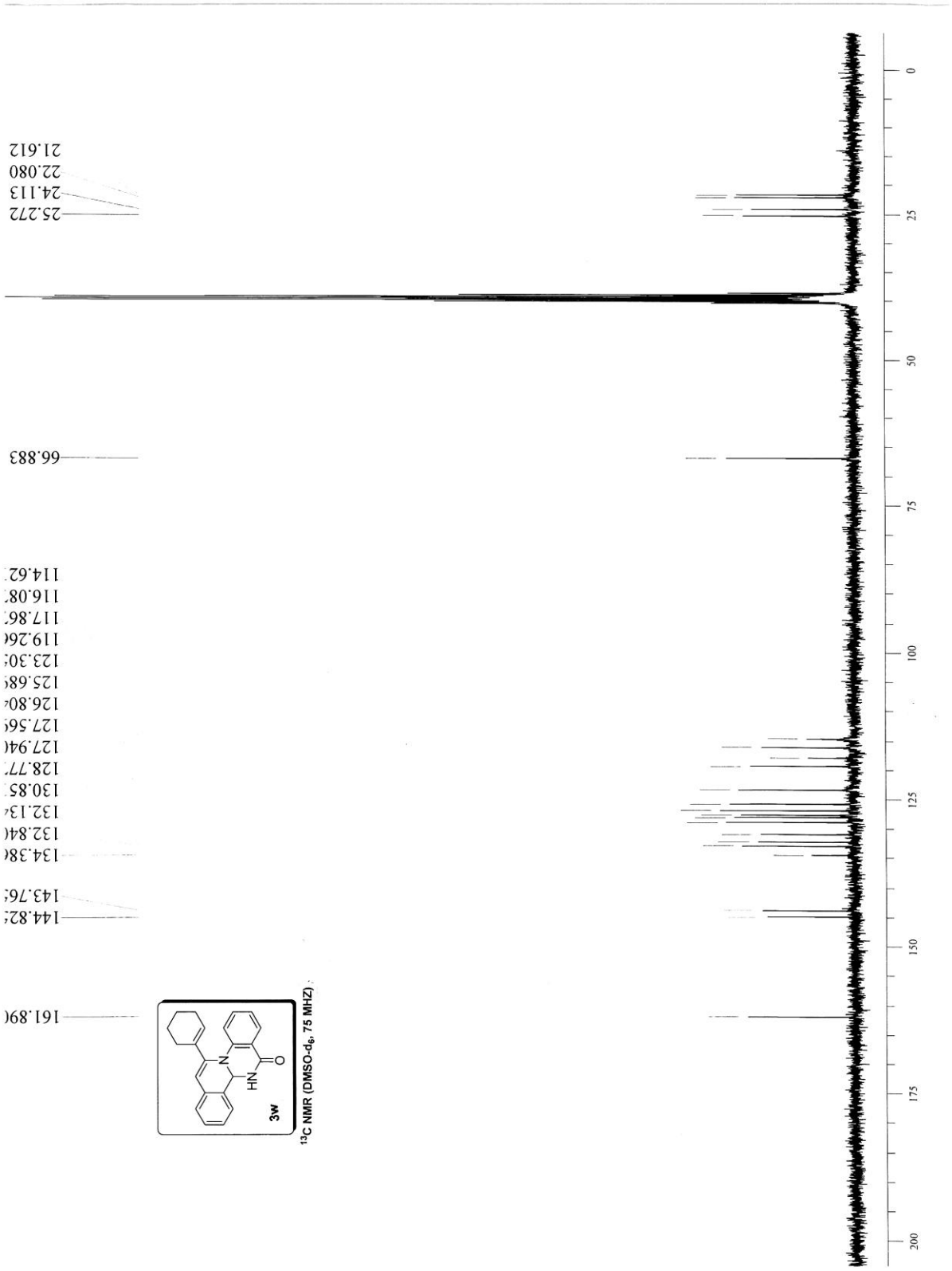

Me
Me
Br
N
HN
O
3v
^{1}H NMR (DMSO-d_6, 300 MHZ)
6.2
5.0
2.1
1.1
0.9
1.0
1.0
1.0
0.9
1.0

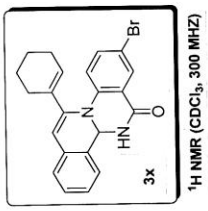

20.804
67.077
111.118
118.436
123.209
125.344
127.751
128.027
129.181
130.622
131.789
134.285
135.079
138.036
141.589
143.046
160.415
Me
Me
Br
N
HN
O
3v
^{13}C NMR (CDCl+DMSO-d_6, 75 MHZ)
0
25
50
75
100
125
150
175
200



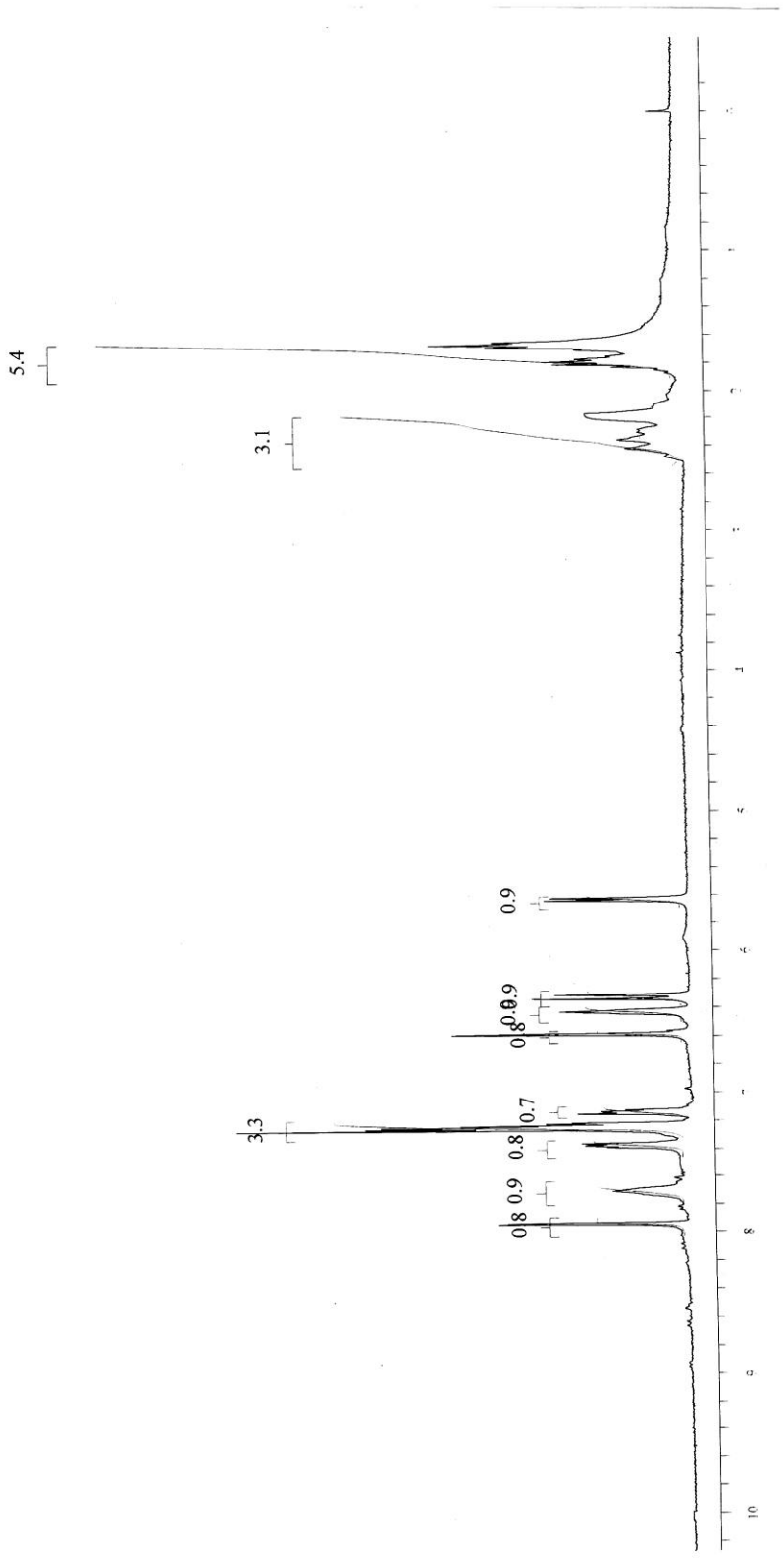
^{1}H NMR ($CDCl_3$, 300 MHZ)

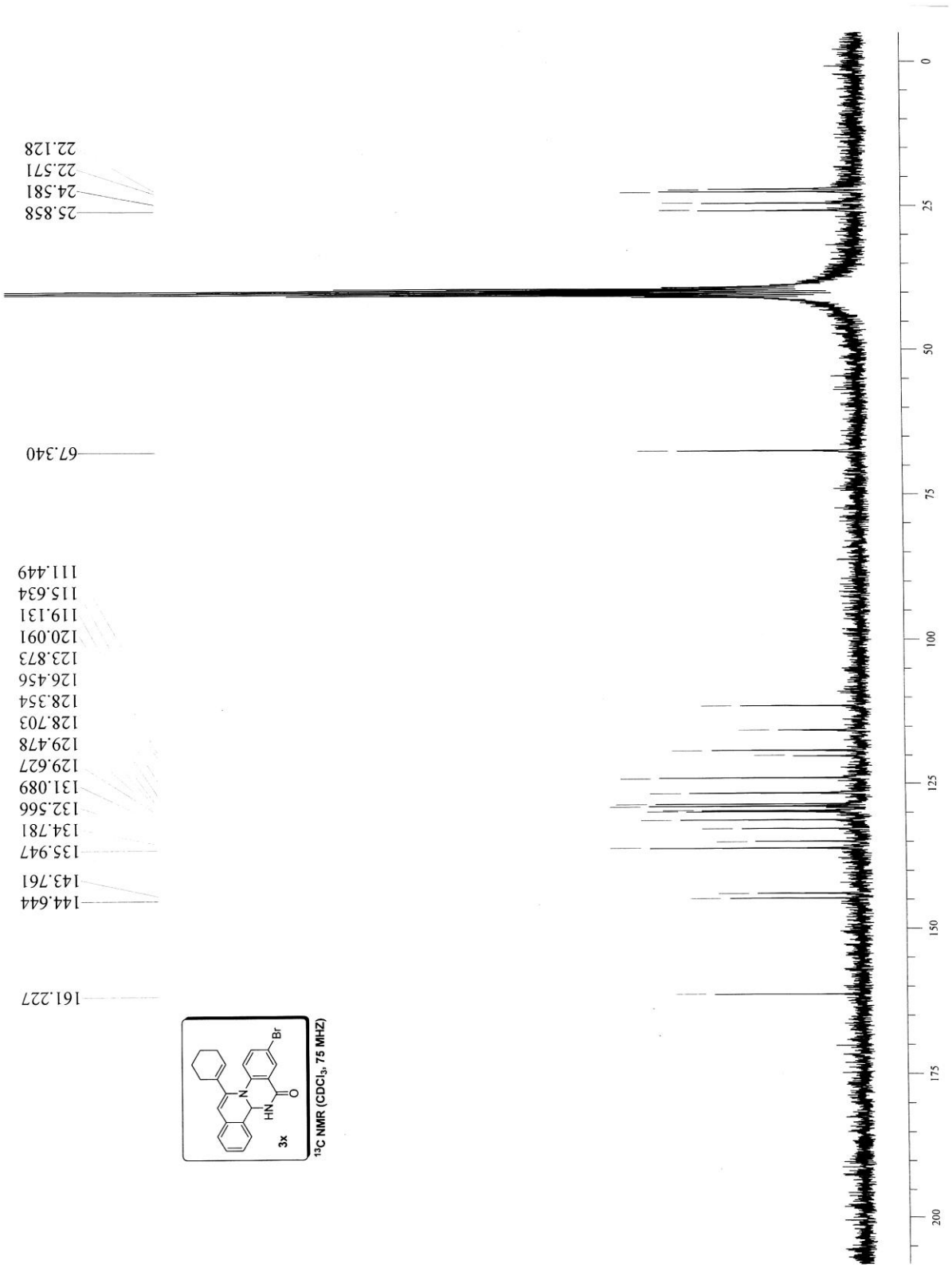


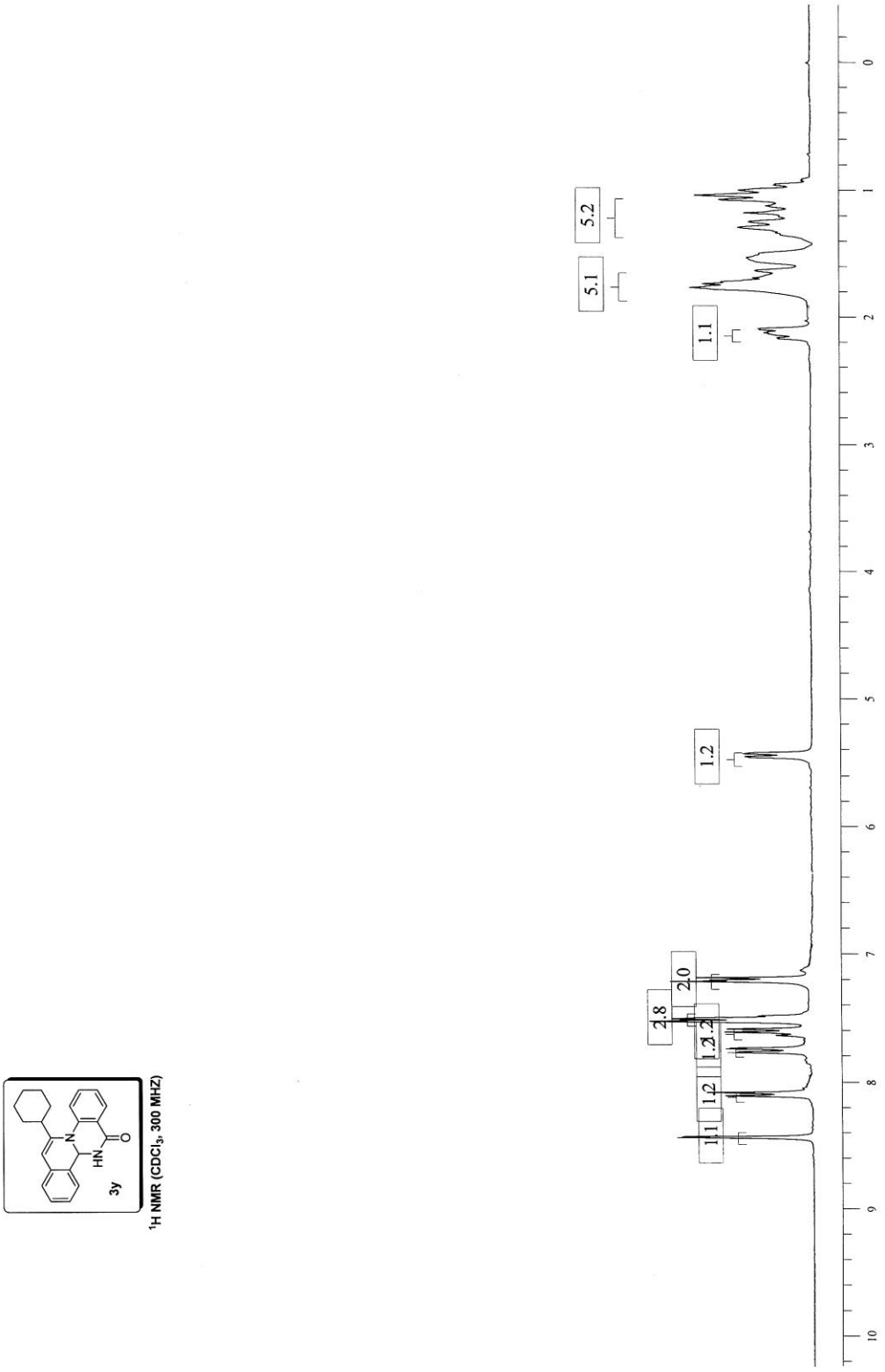

21.612
22.080
24.113
25.272
66.883
114.62
116.08
117.86
119.26
123.30
125.68
126.80
127.56
127.94
128.77
130.85
132.13
132.84
134.38
143.76
144.82
161.89
0
25
50
75
100
125
150
175
200
3w
^{13}C NMR (DMSO-d_6, 75 MHZ)



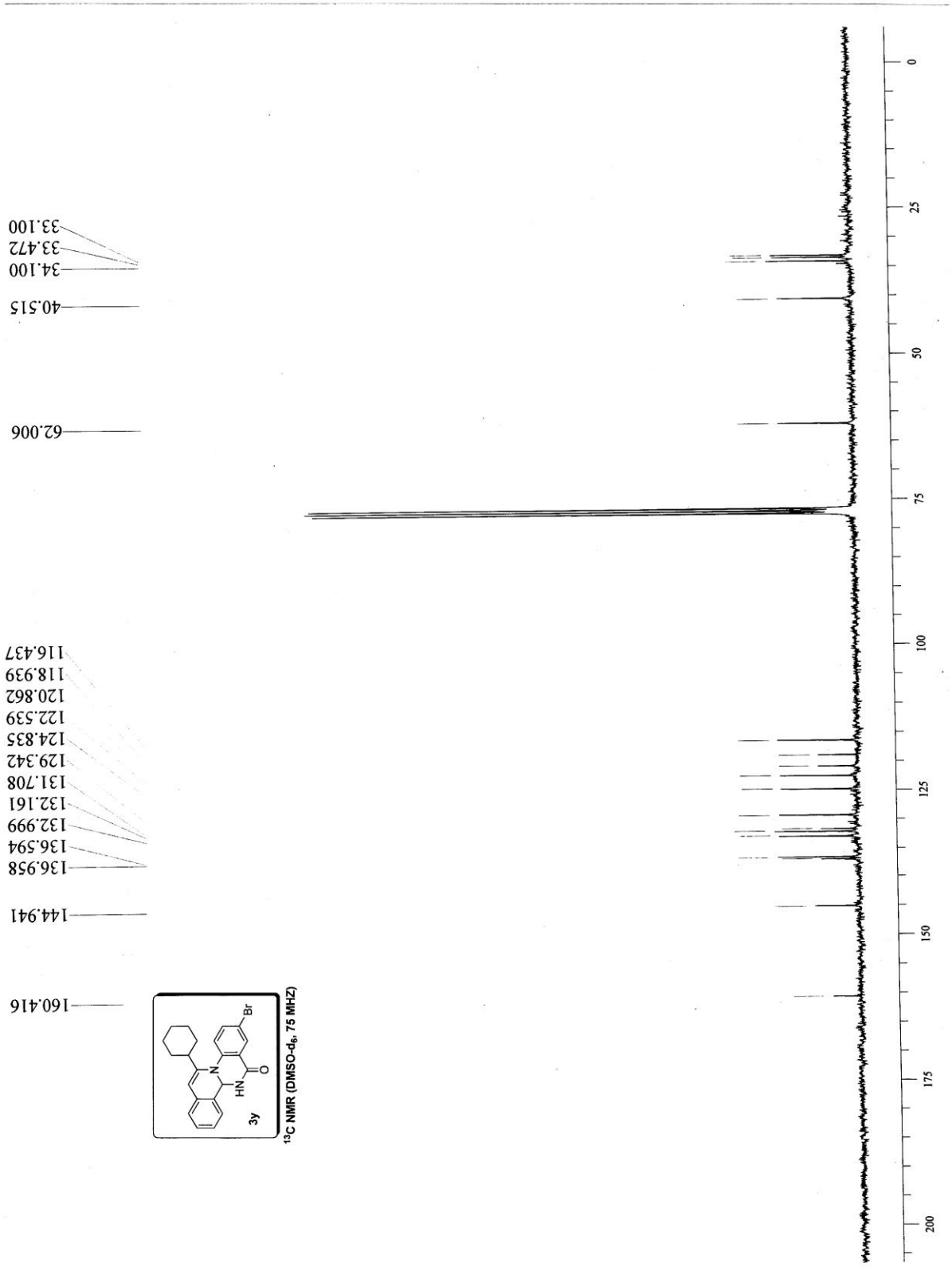
^{1}H NMR ($CDCl_3$, 300 MHZ)

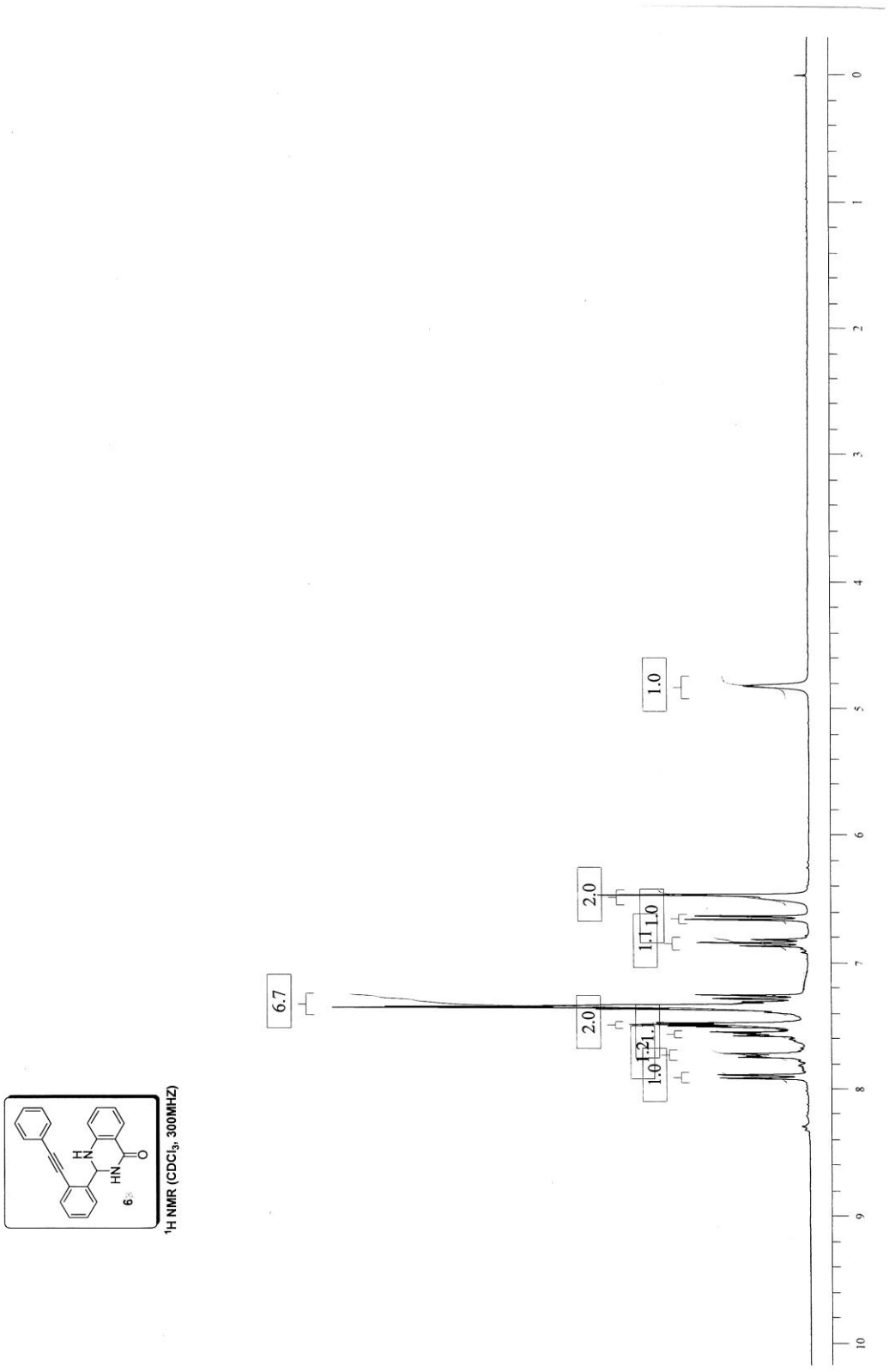




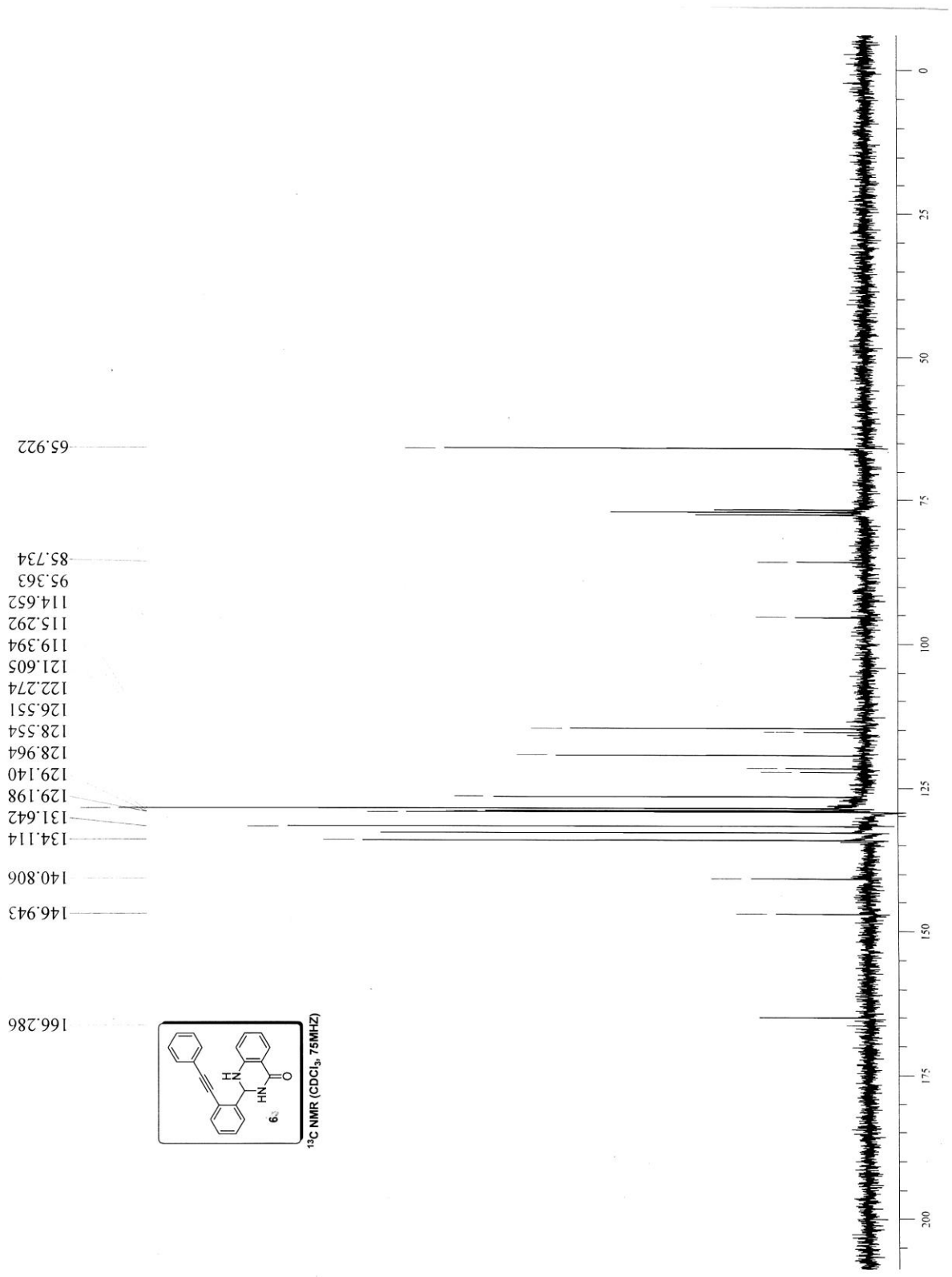


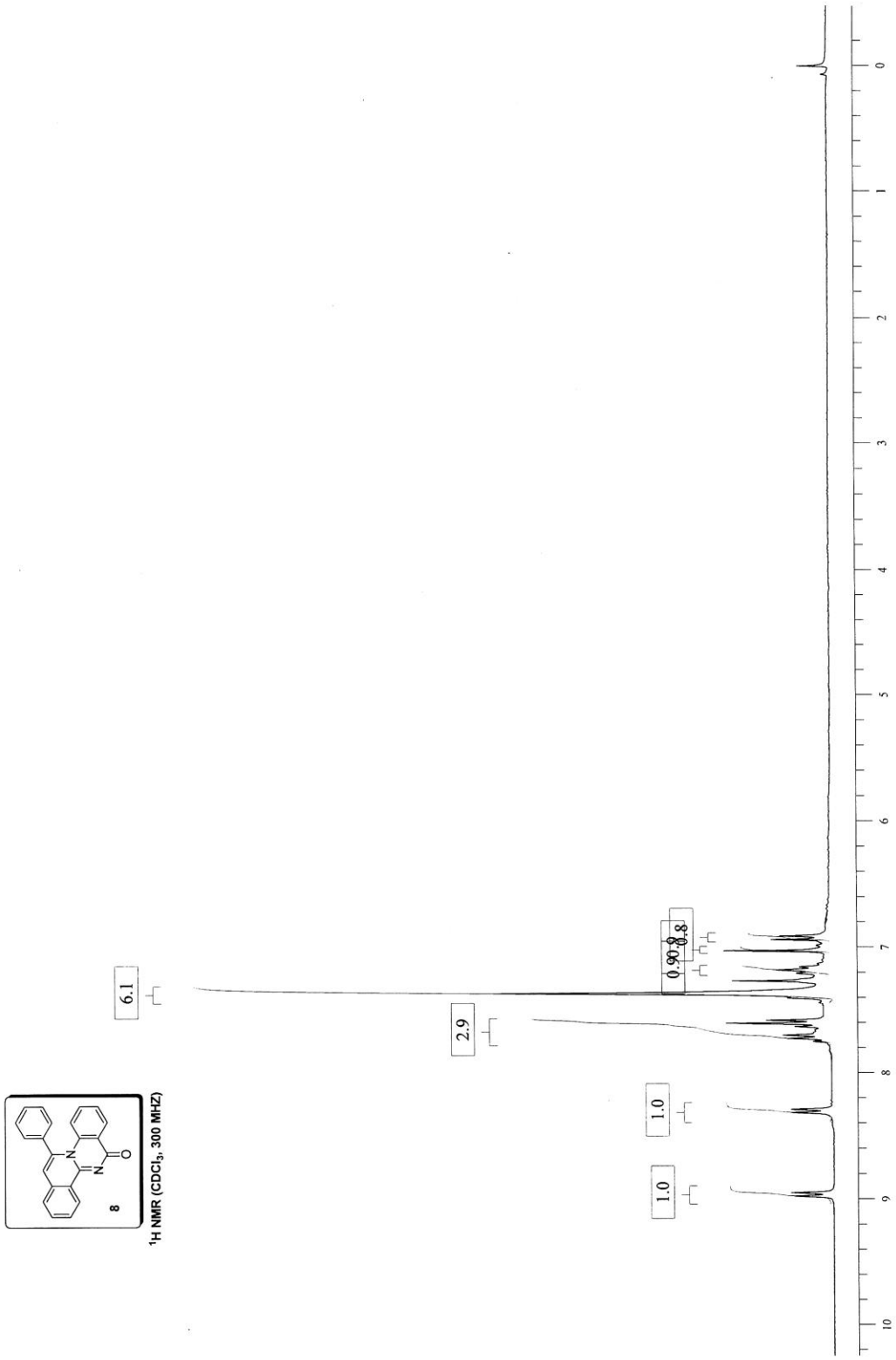
^{1}H NMR ($CDCl_3$, 300 MHZ)

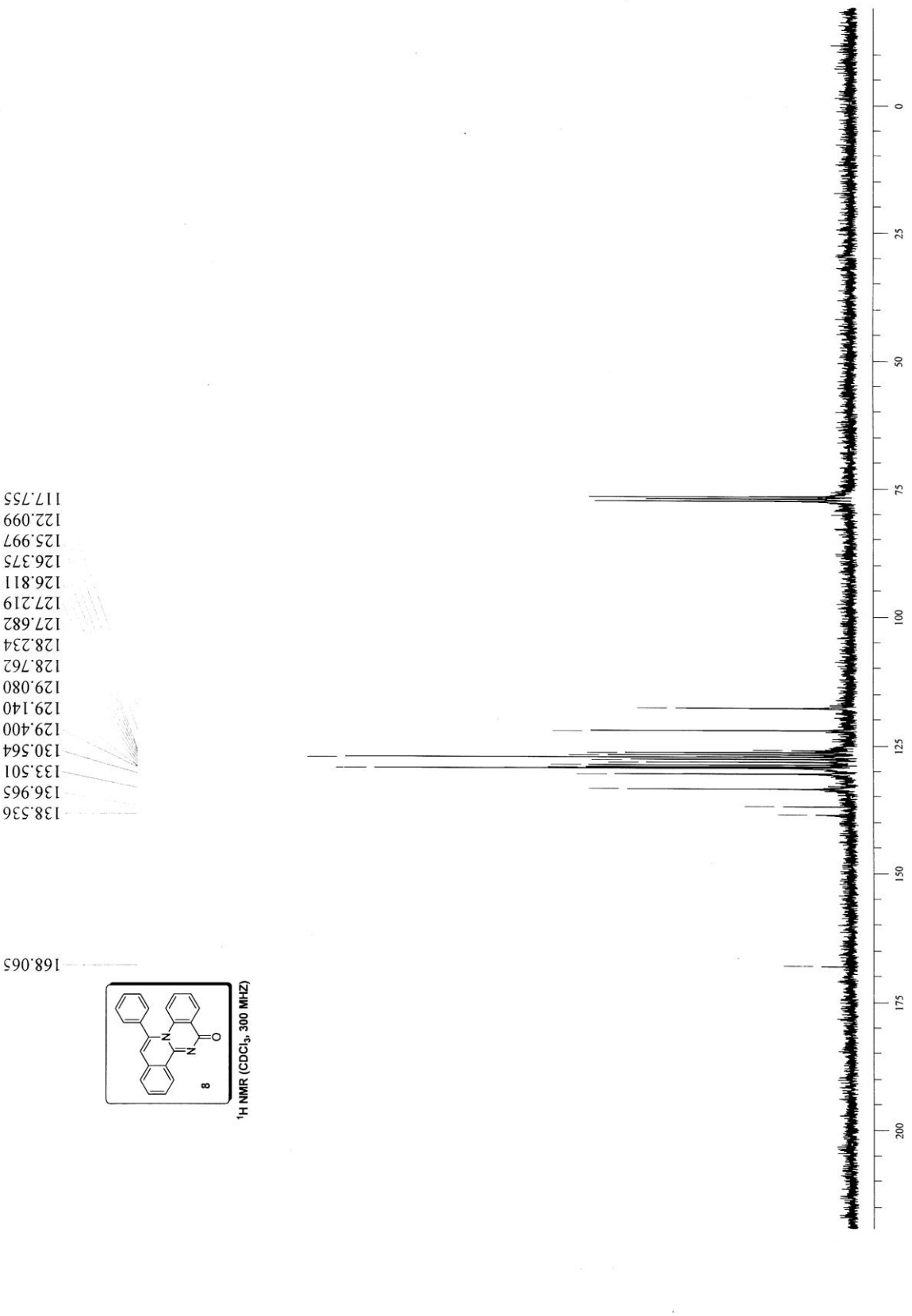

33.100
33.472
34.100
40.515
62.006
116.437
118.939
120.862
122.539
124.835
129.342
131.708
132.161
132.999
136.594
136.958
144.941
160.416
^{13}C NMR (DMSO-d_6, 75 MHZ)
3y
Br
N
HN
O
0
25
50
75
100
125
150
175
200

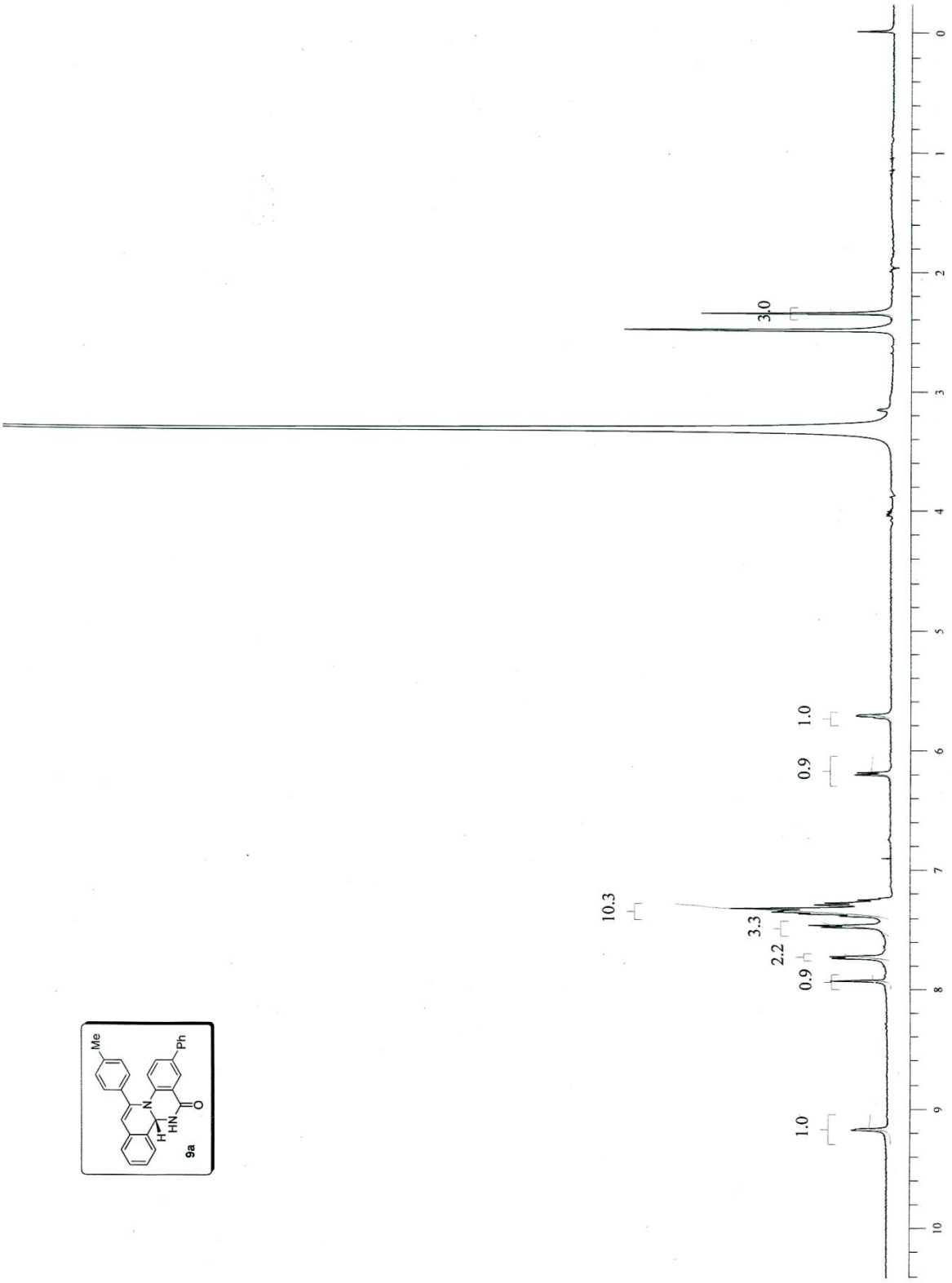


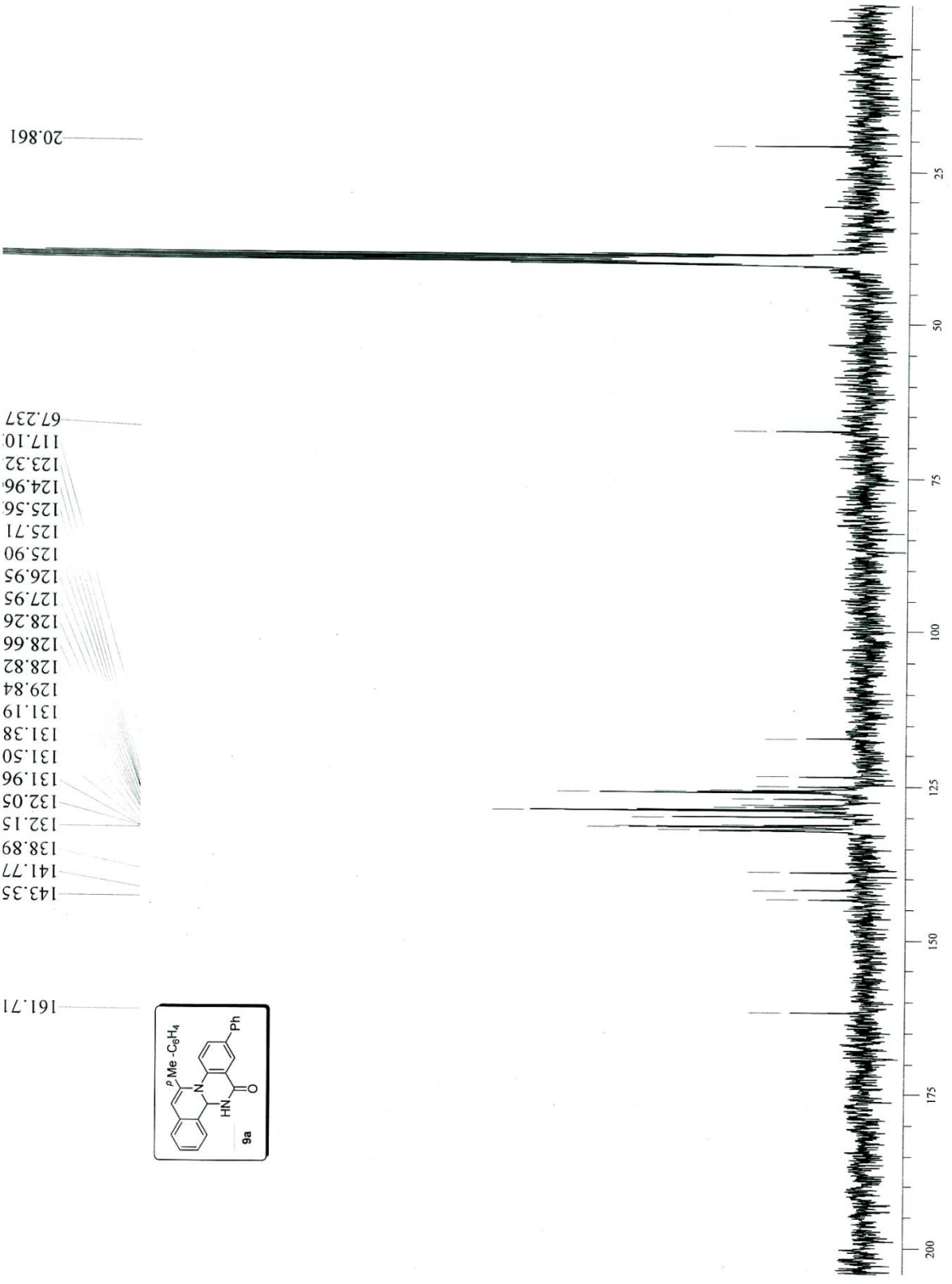
^{1}H NMR ($CDCl_3$, 300MHz)

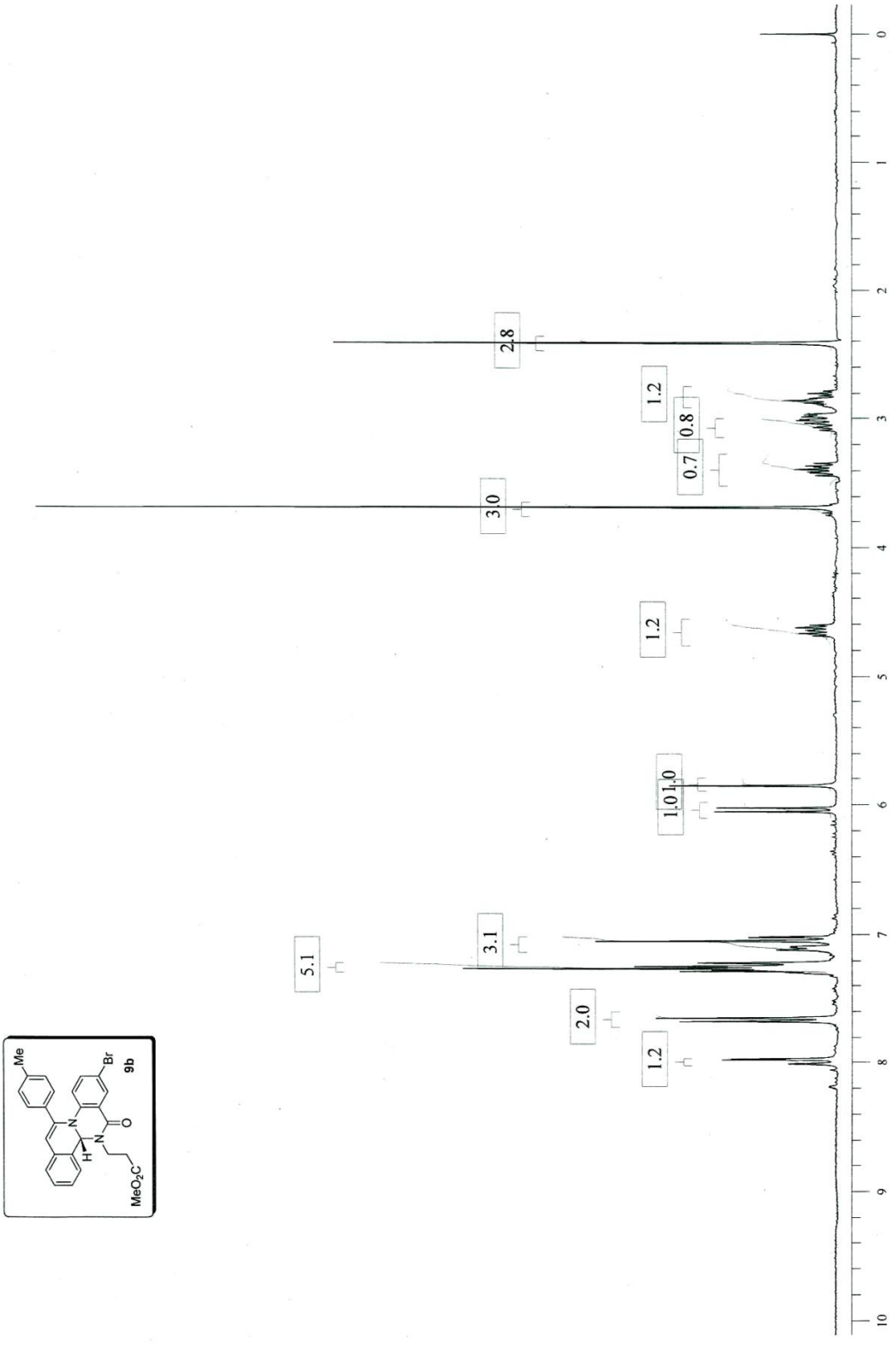

65.922
85.734
95.363
114.652
115.292
119.394
121.605
122.274
126.551
128.554
128.964
129.140
129.198
131.642
134.114
140.806
146.943
166.286
0
25
50
75
100
125
150
175
200
HN
NH
O
6g
^{13}C NMR (CDCl$_3$, 75MHz)

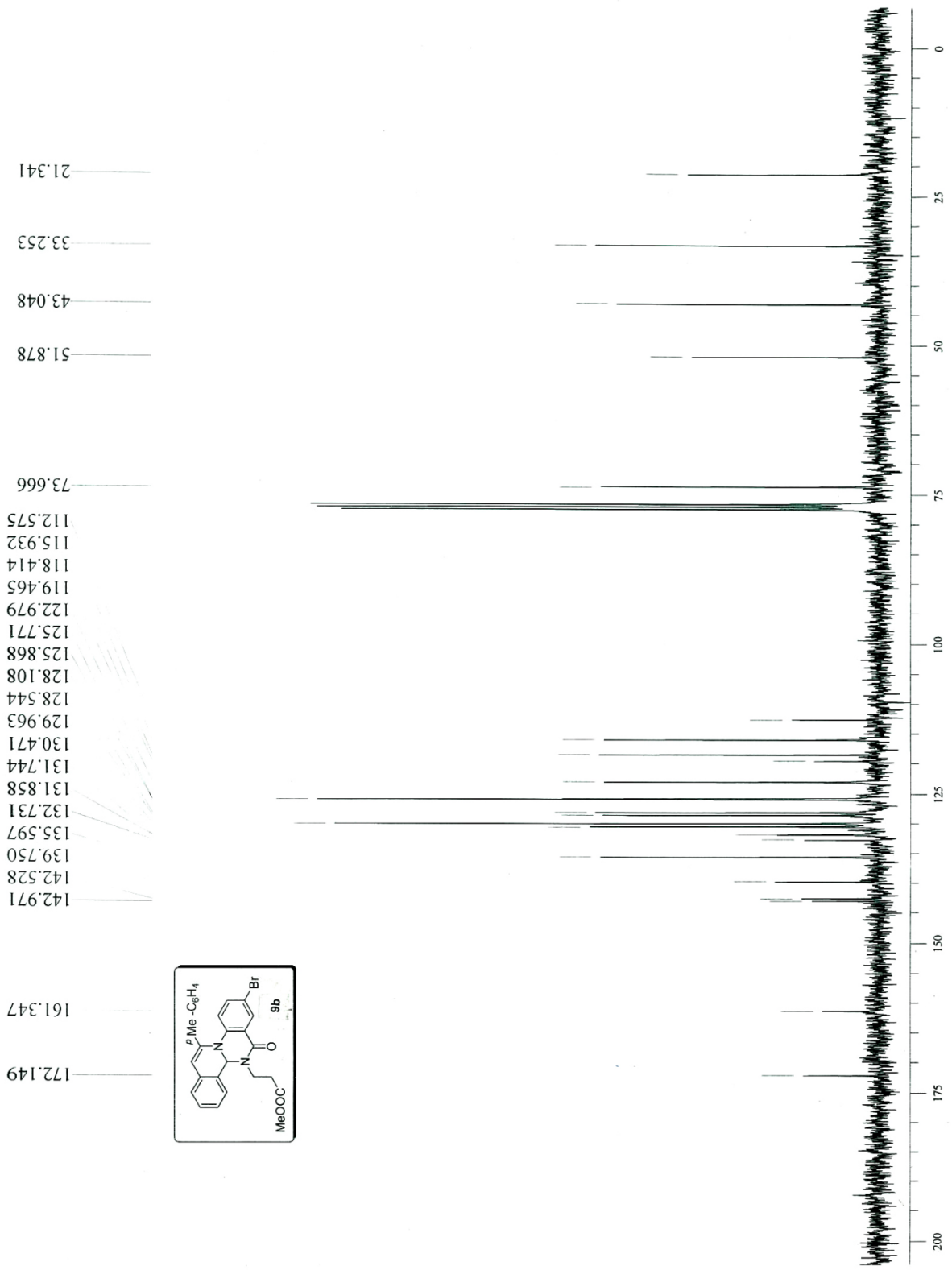

8
^{1}H NMR (CDCl$_3$, 300 MHZ)
6.1
2.9
1.0
1.0
0.9
0.8

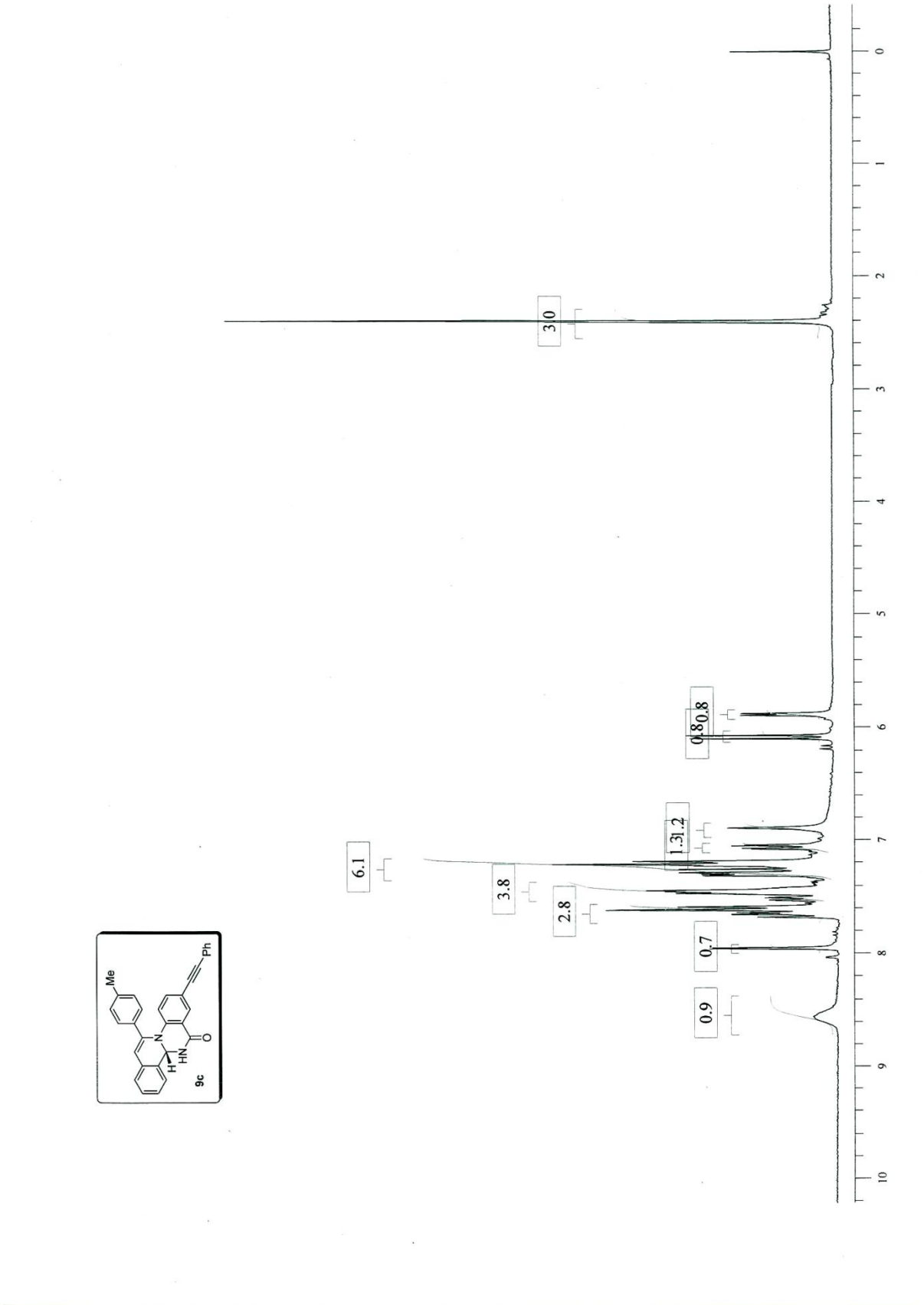

168.065
138.536
136.965
133.501
130.564
129.400
129.140
129.080
128.762
128.234
127.682
127.219
126.811
126.375
125.997
122.099
117.755
0
25
50
75
100
125
150
175
200
8
^{1}H NMR (CDCl$_3$, 300 MHZ)

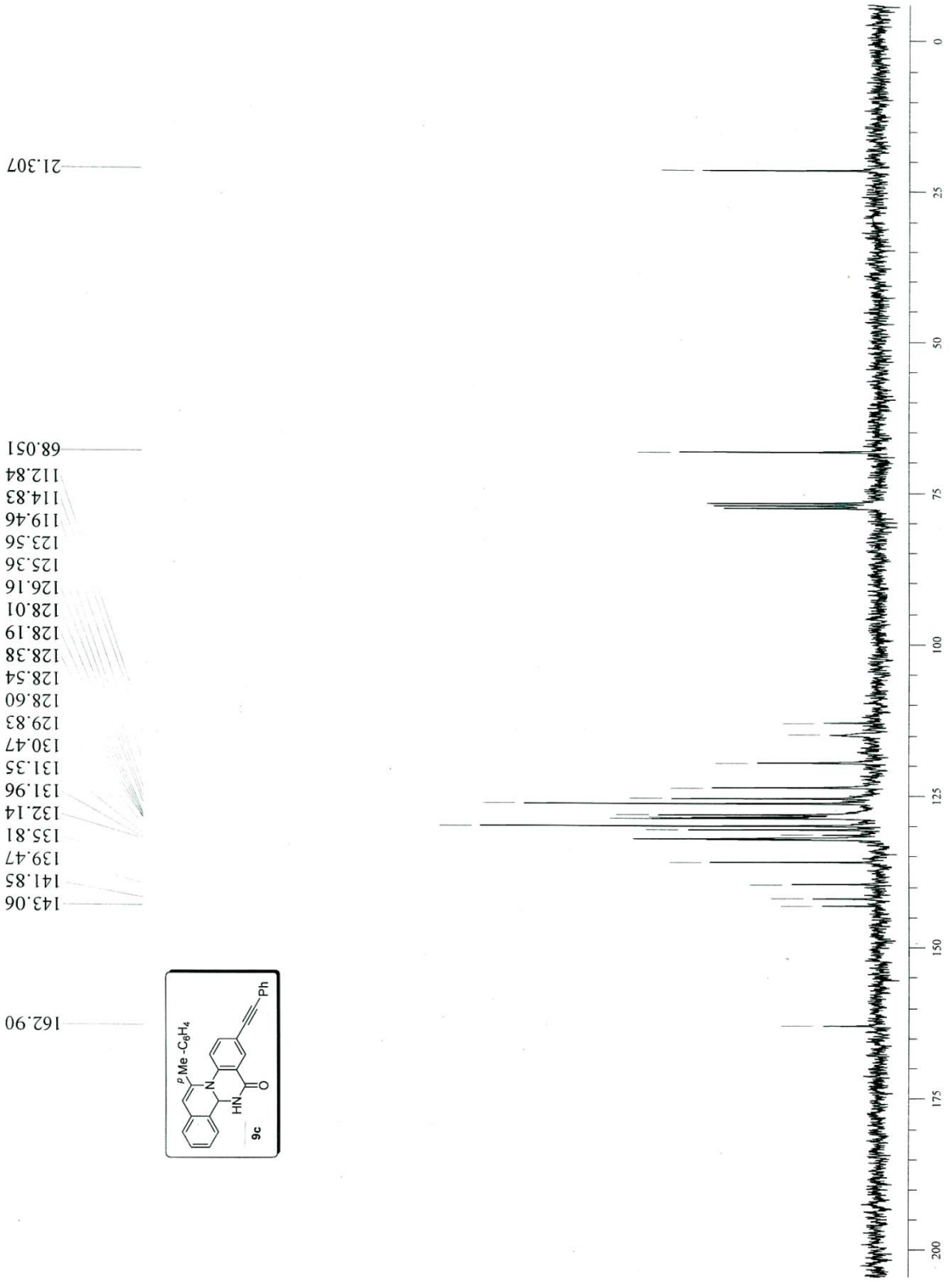

Me
Ph
N
HN
H
O
9a
3.0
1.0
0.9
10.3
3.3
2.2
0.9
1.0

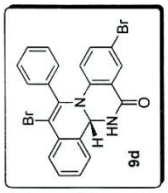

20.861
67.237
117.10
123.32
124.96
125.56
125.71
125.90
126.95
127.95
128.26
128.66
128.82
129.84
131.19
131.38
131.50
131.96
132.05
132.15
138.89
141.77
143.35
161.71
Ph
p Me -C6H4
N
HN
O
9a
25
50
75
100
125
150
175
200

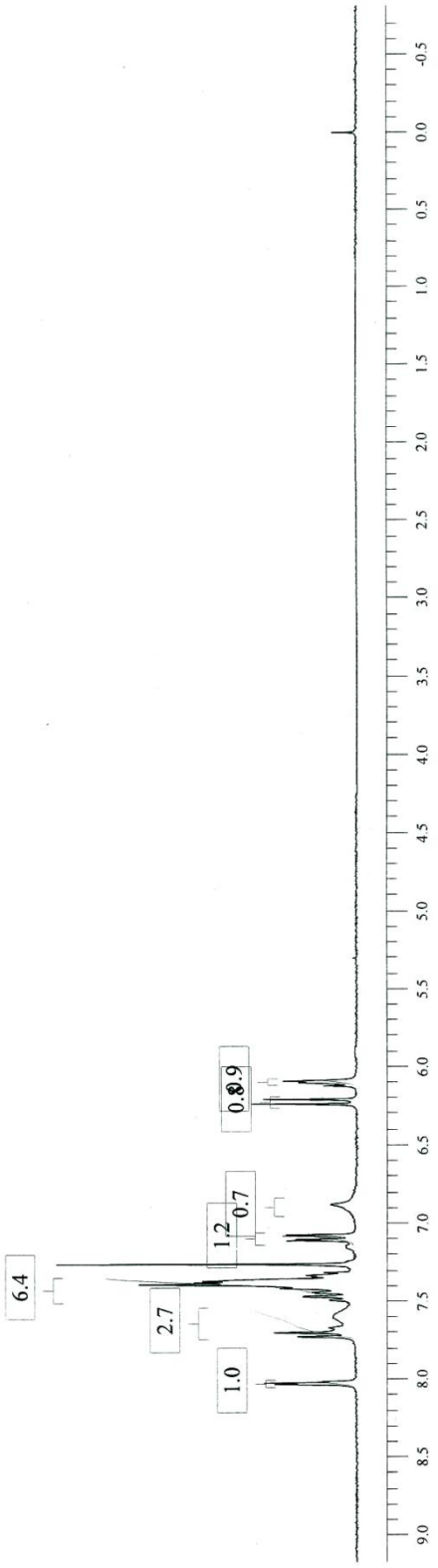

Me
Br
9b
O
N
N
H
MeO2C
5.1
3.1
2.0
1.2
3.0
1.2
1.0
1.0
1.2
0.7
0.8
2.8

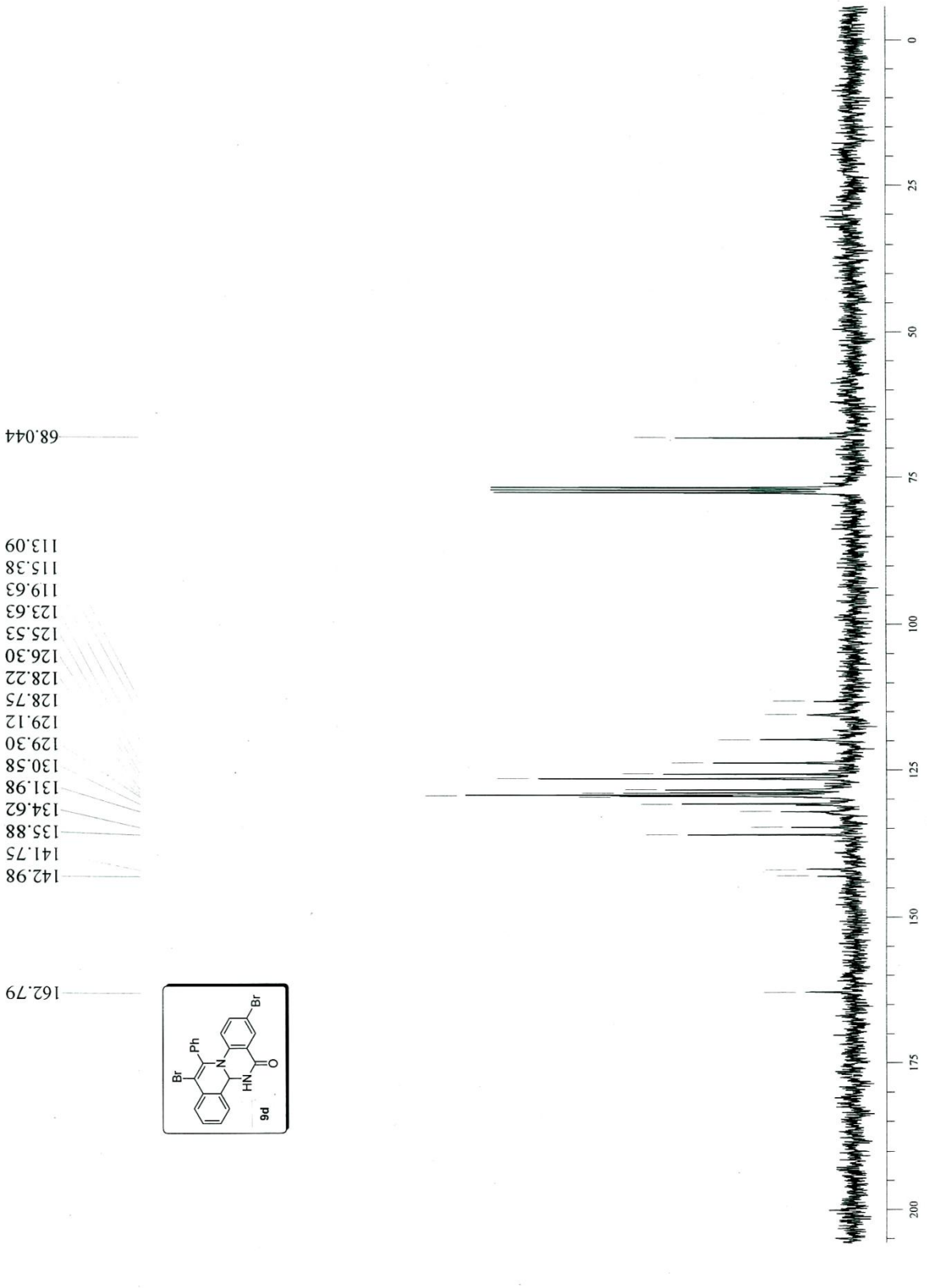

21.341
33.253
43.048
51.878
73.666
112.575
115.932
118.414
119.465
122.979
125.771
125.868
128.108
128.544
129.963
130.471
131.744
131.858
132.731
135.597
139.750
142.528
142.971
161.347
172.149
Br
9b
MeOOC
0
25
50
75
100
125
150
175
200

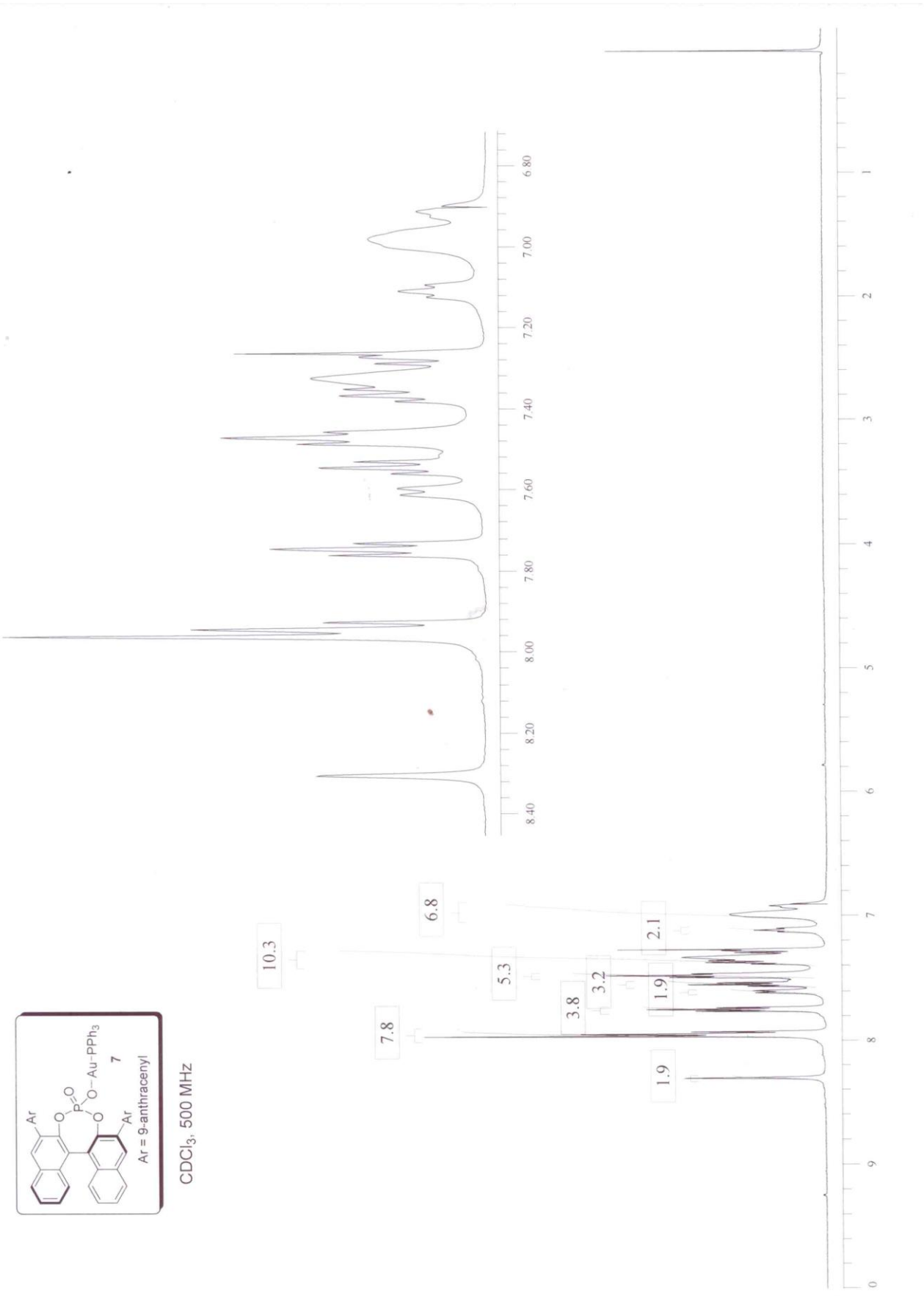

Me
Ph
N
HN
H
O
9c
6.1
3.8
2.8
1.3
1.2
0.8
0.8
0.7
0.9
3.0
0
1
2
3
4
5
6
7
8
9
10

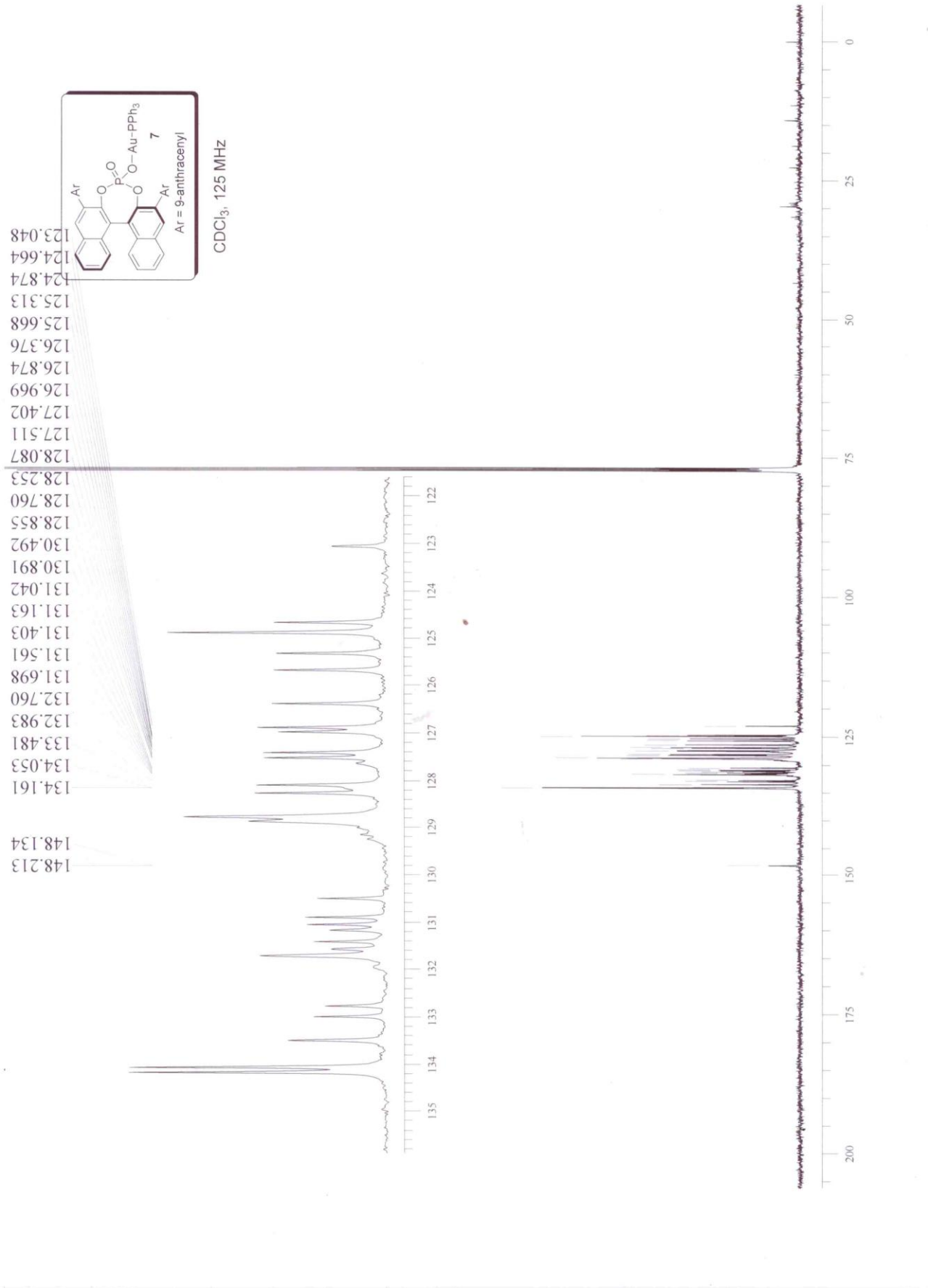

21.307
68.051
112.84
114.83
119.46
123.56
125.36
126.16
128.01
128.19
128.38
128.54
128.60
129.83
130.47
131.35
131.96
132.14
135.81
139.47
141.85
143.06
162.90
Ph
^{p}Me-C$_6$H$_4$
N
HN
O
9c
0
25
50
75
100
125
150
175
200


Br
Br
N
O
HN
H
9d

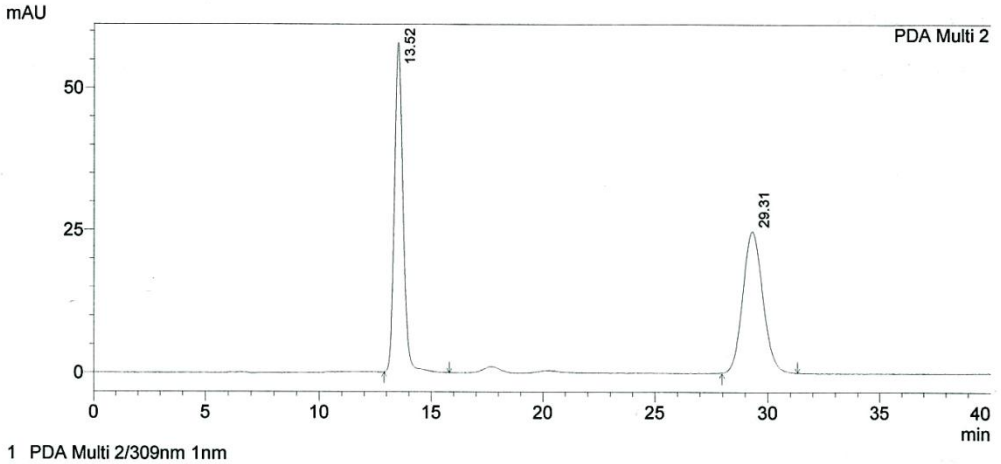

6.4
2.7
1.0
1.2
0.7
0.9
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


68.044
113.09
115.38
119.63
123.63
125.53
126.30
128.22
128.75
129.12
129.30
130.58
131.98
134.62
135.88
141.75
142.98
162.79
Br
Ph
N
HN
O
Br
9d
0
25
50
75
100
125
150
175
200


Ar
O
O
P
O
O–Au–PPh3
Ar
Ar = 9-anthracenyl
7
CDCl3, 500 MHz
10.3
6.8
7.8
5.3
3.8
3.2
2.1
1.9
1.9
8.40
8.20
8.00
7.80
7.60
7.40
7.20
7.00
6.80
0
1
2
3
4
5
6
7
8
9


CDCl3, 125 MHz
Ar = 9-anthracenyl
7
O–Au–PPh3
Ar
123.048
124.664
124.874
125.313
125.668
126.376
126.874
126.969
127.402
127.511
128.087
128.253
128.760
128.855
130.492
130.891
131.042
131.163
131.403
131.561
131.698
132.760
132.983
133.481
134.053
134.161
148.134
148.213

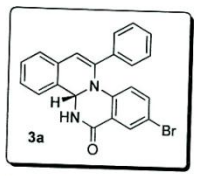
7. HPLC Chromatograms

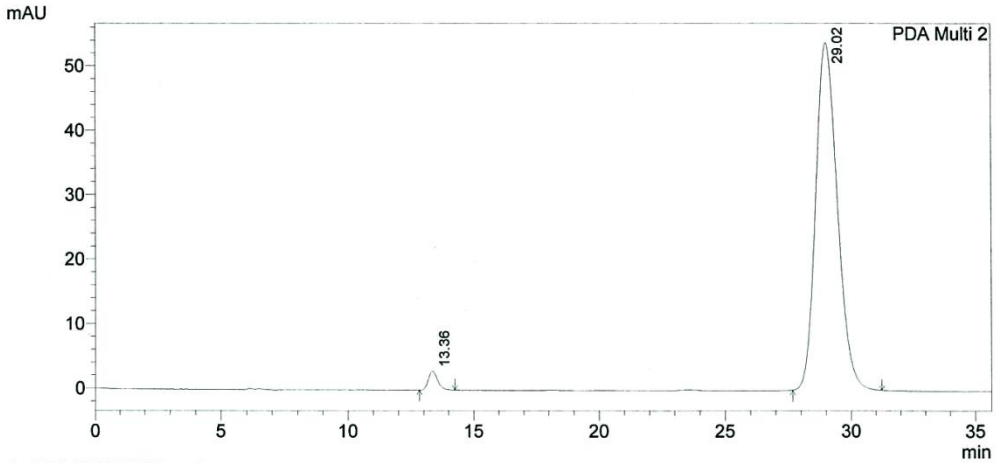


1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

Peak#	Ret. Time	Area	Area %
1	13.52	1564339	50.34
2	29.31	1542926	49.66
Total		3107265	100.00

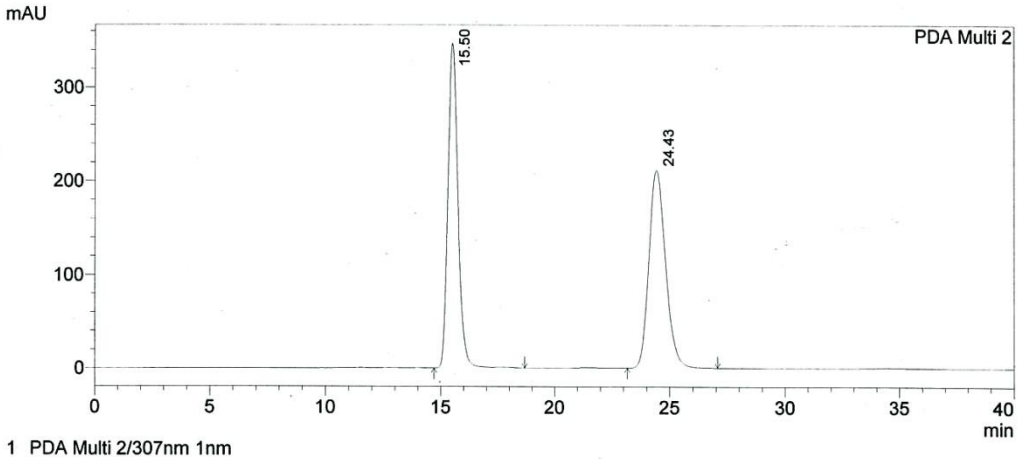




1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

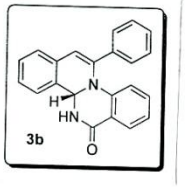
Peak#	Ret. Time	Area	Area %
1	13.36	76084	2.30
2	29.02	3237416	97.70
Total		3313501	100.00

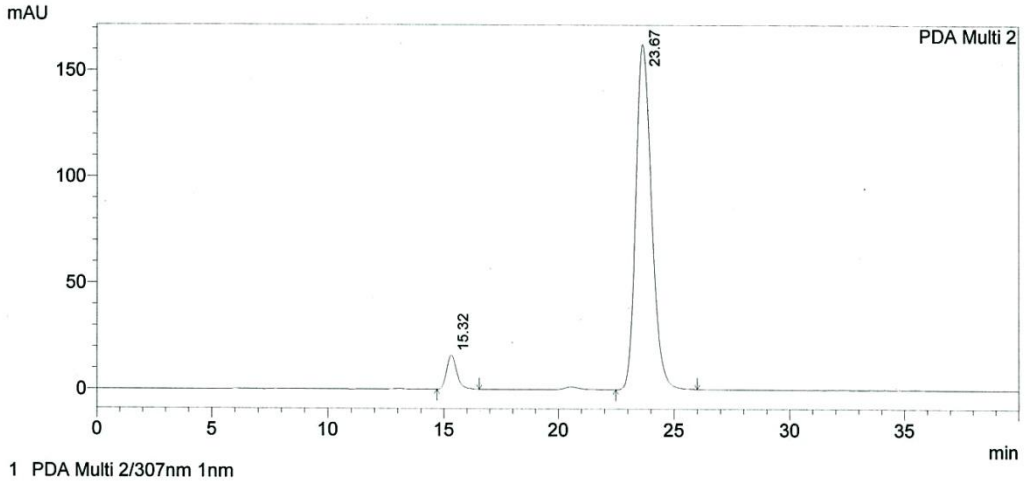


1 PDA Multi 2/307nm 1nm

PDA Ch2 307nm 1nm

Peak#	Ret. Time	Area	Area %
1	15.50	10608239	49.92
2	24.43	10641443	50.08
Total		21249682	100.00

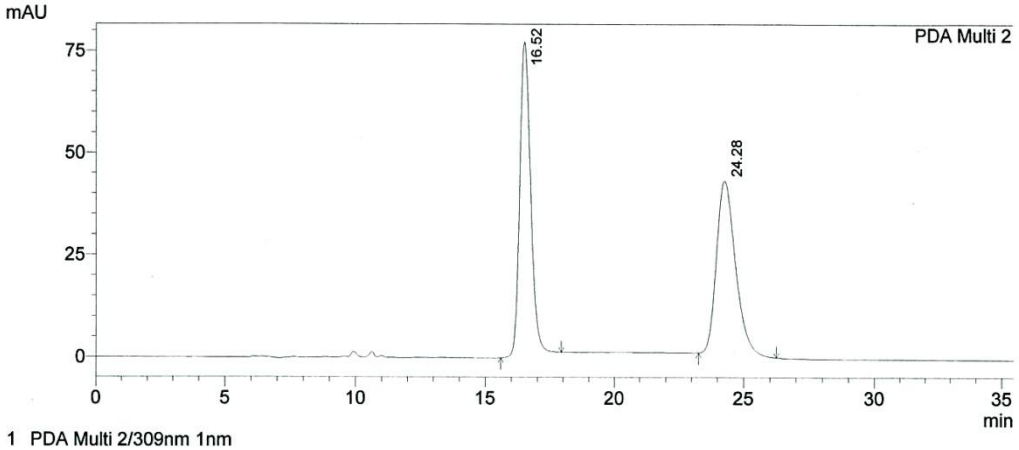




1 PDA Multi 2/307nm 1nm

PDA Ch2 307nm 1nm

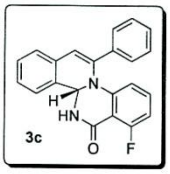
Peak#	Ret. Time	Area	Area %
1	15.32	490324	5.97
2	23.67	7716187	94.03
Total		8206511	100.00

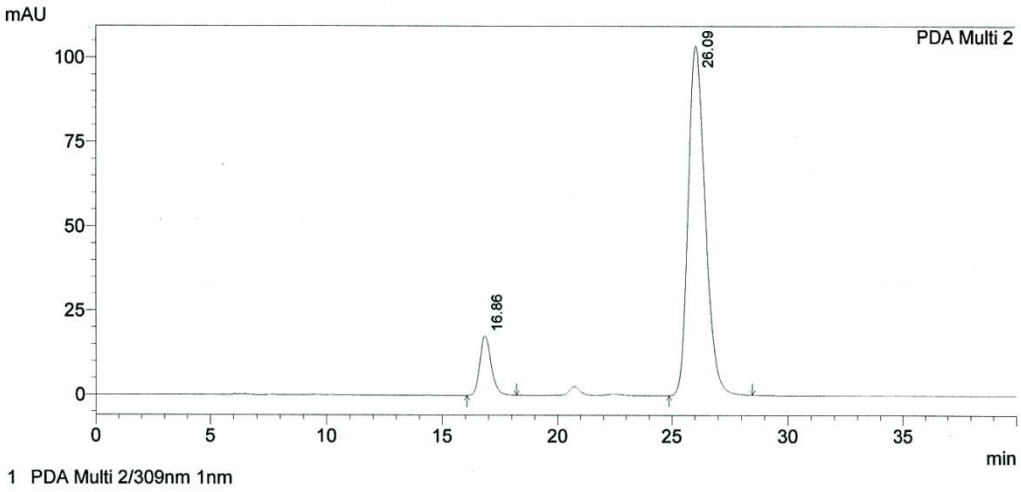


1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

Peak#	Ret. Time	Area	Area %
1	16.52	2245789	50.86
2	24.28	2169719	49.14
Total		4415508	100.00

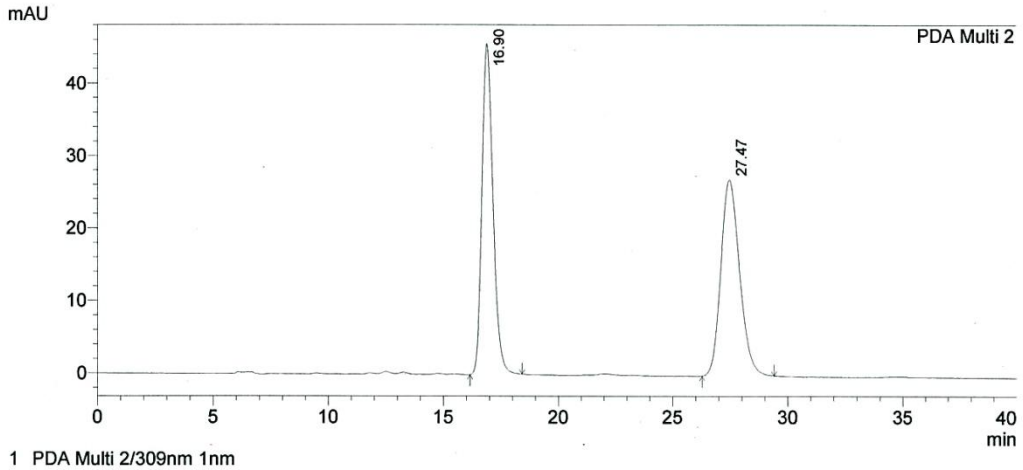




1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

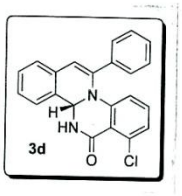
Peak#	Ret. Time	Area	Area %
1	16.86	602399	10.16
2	26.09	5323924	89.84
Total		5926322	100.00

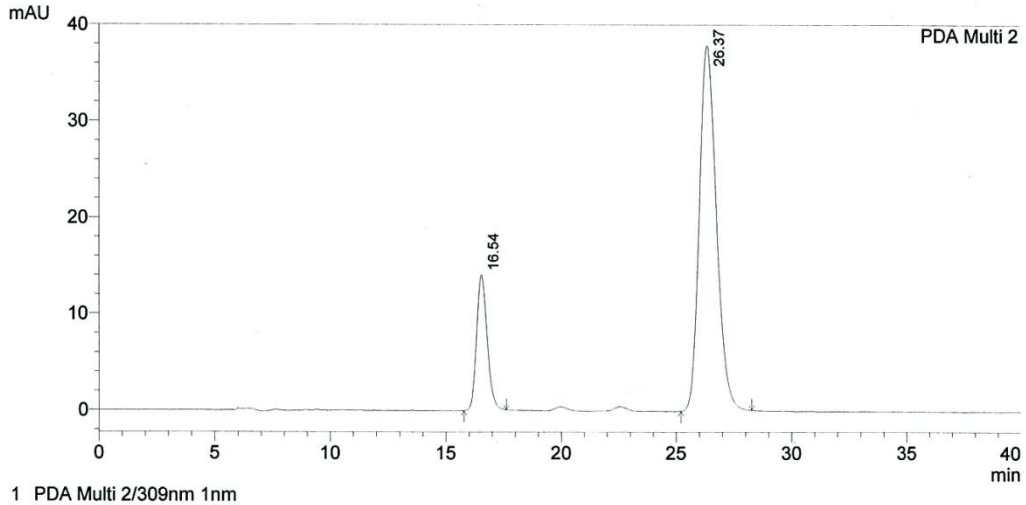


1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

Peak#	Ret. Time	Area	Area %
1	16.90	1531365	50.01
2	27.47	1530467	49.99
Total		3061832	100.00

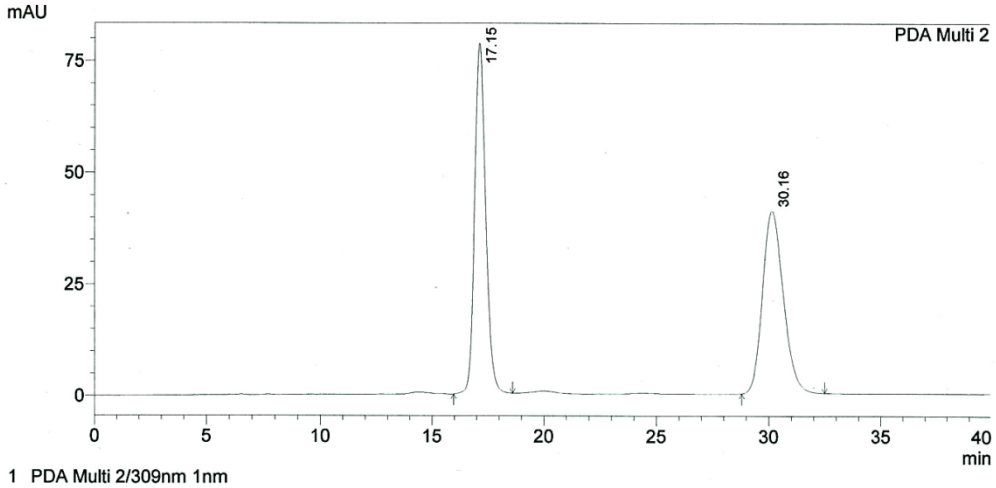




1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

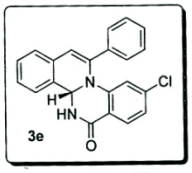
Peak#	Ret. Time	Area	Area %
1	16.54	448202	18.67
2	26.37	1951825	81.33
Total		2400027	100.00

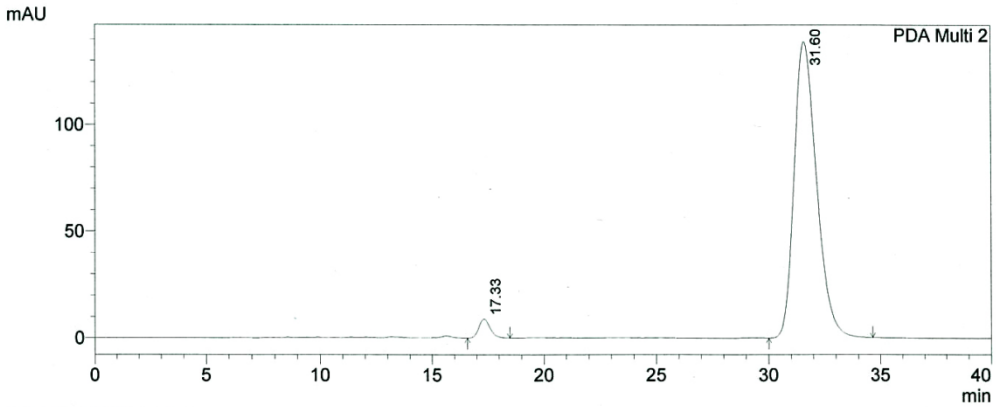


1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

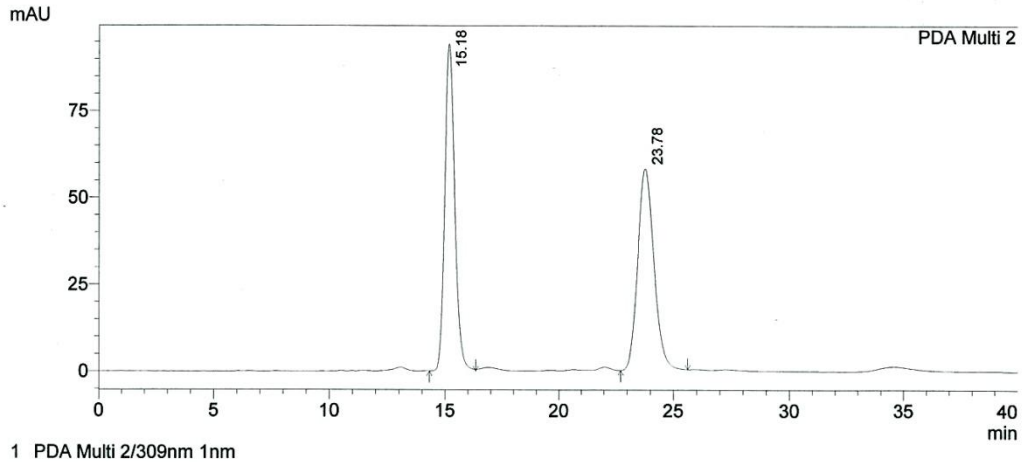
Peak#	Ret. Time	Area	Area %
1	17.15	2707213	50.60
2	30.16	2642672	49.40
Total		5349884	100.00





PDA Ch2 309nm 1nm

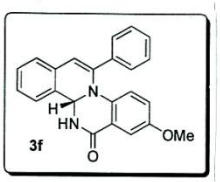
Peak#	Ret. Time	Area	Area %
1	17.33	311789	3.11
2	31.60	9703854	96.89
Total		10015643	100.00

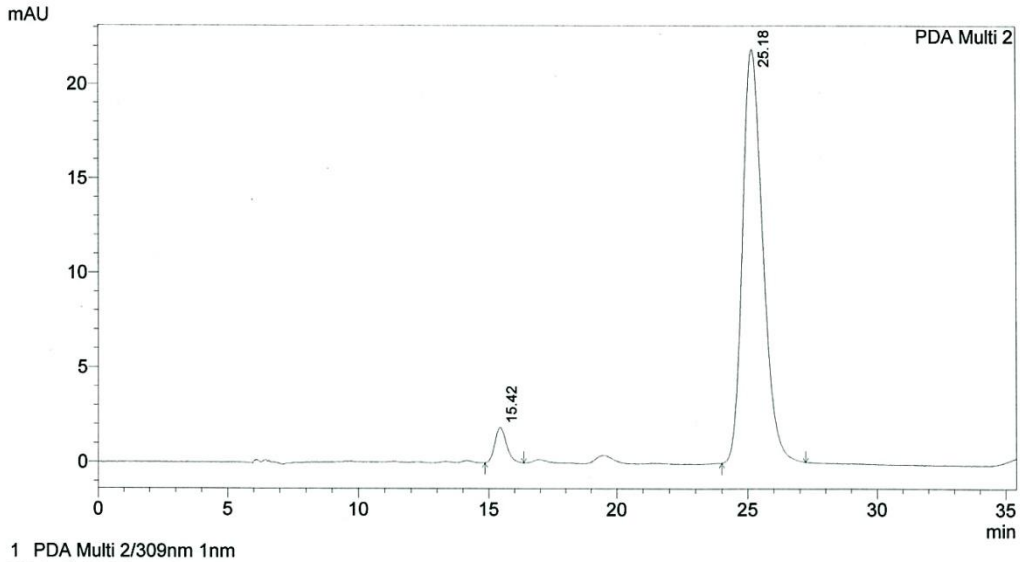


1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

Peak#	Ret. Time	Area	Area %
1	15.18	2850817	50.32
2	23.78	2814876	49.68
Total		5665693	100.00

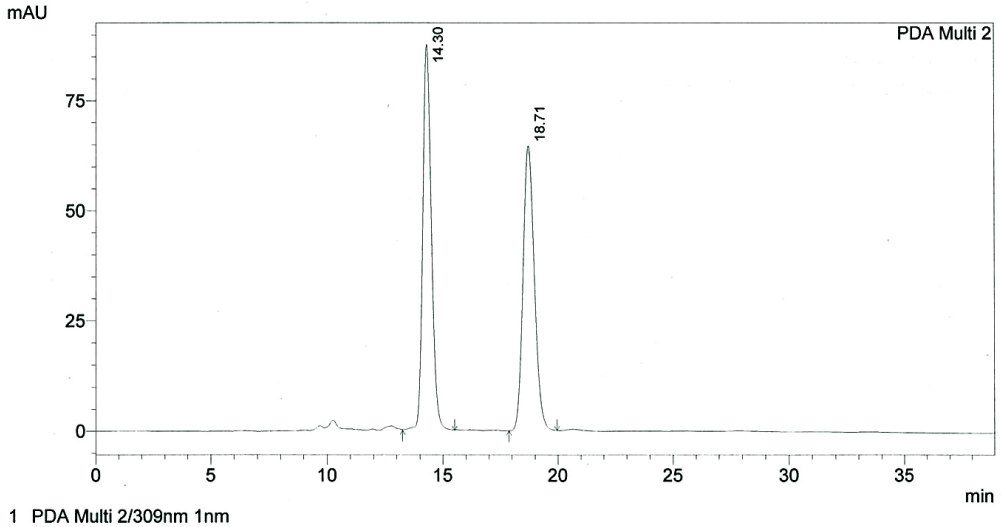




1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

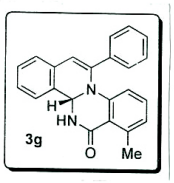
Peak#	Ret. Time	Area	Area %
1	15.42	58527	4.73
2	25.18	1178301	95.27
Total		1236827	100.00

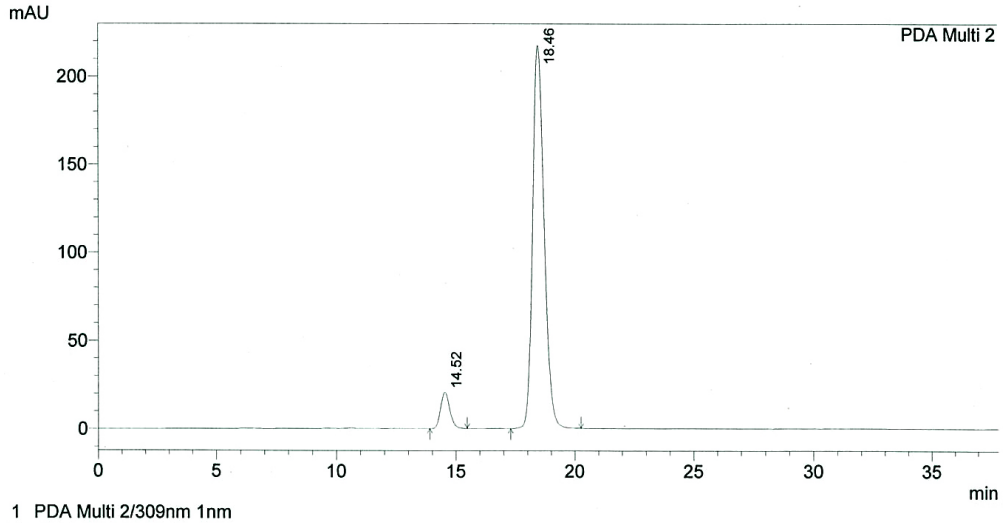


1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

Peak#	Ret. Time	Area	Area %
1	14.30	2279942	50.80
2	18.71	2207767	49.20
Total		4487708	100.00

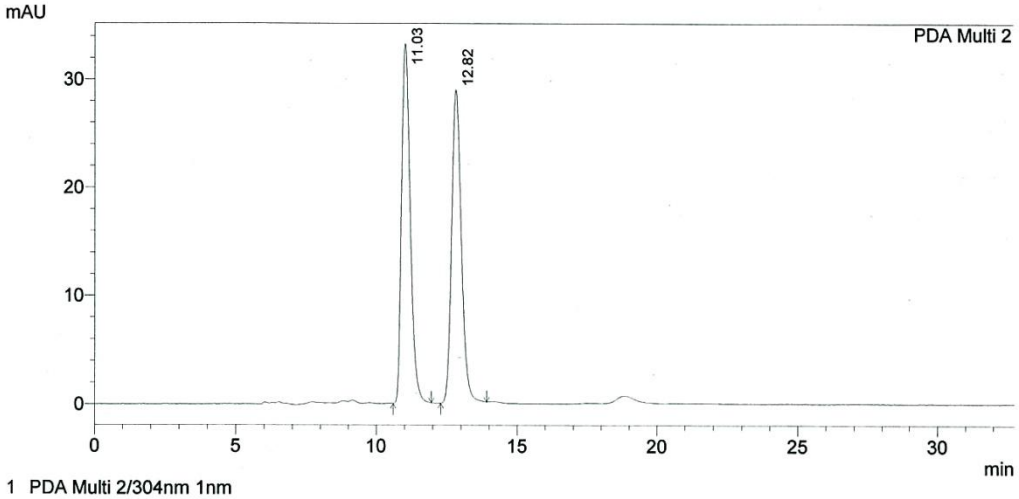




1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

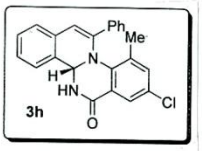
Peak#	Ret. Time	Area	Area %
1	14.52	549553	7.00
2	18.46	7300753	93.00
Total		7850306	100.00

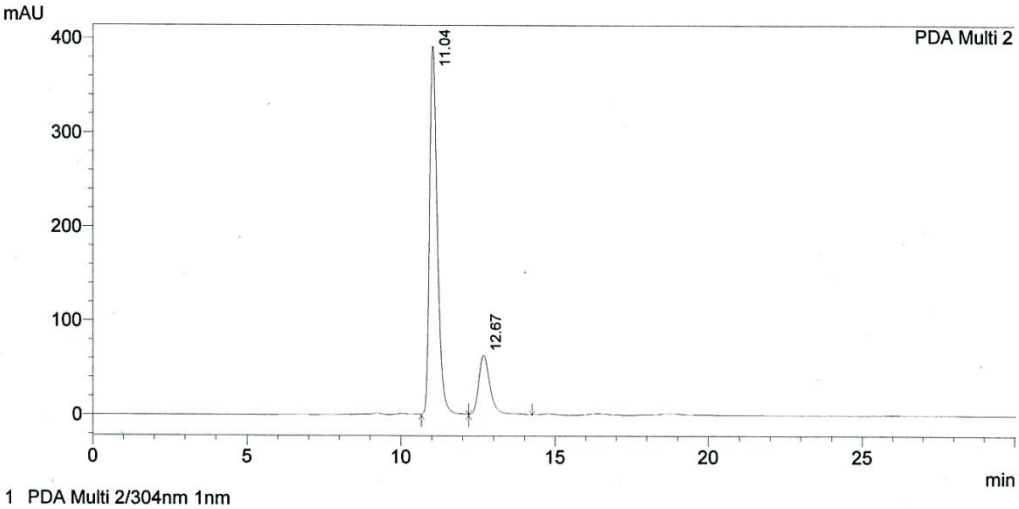


1 PDA Multi 2/304nm 1nm

PDA Ch2 304nm 1nm

Peak#	Ret. Time	Area	Area %
1	11.03	712417	50.77
2	12.82	690695	49.23
Total		1403112	100.00

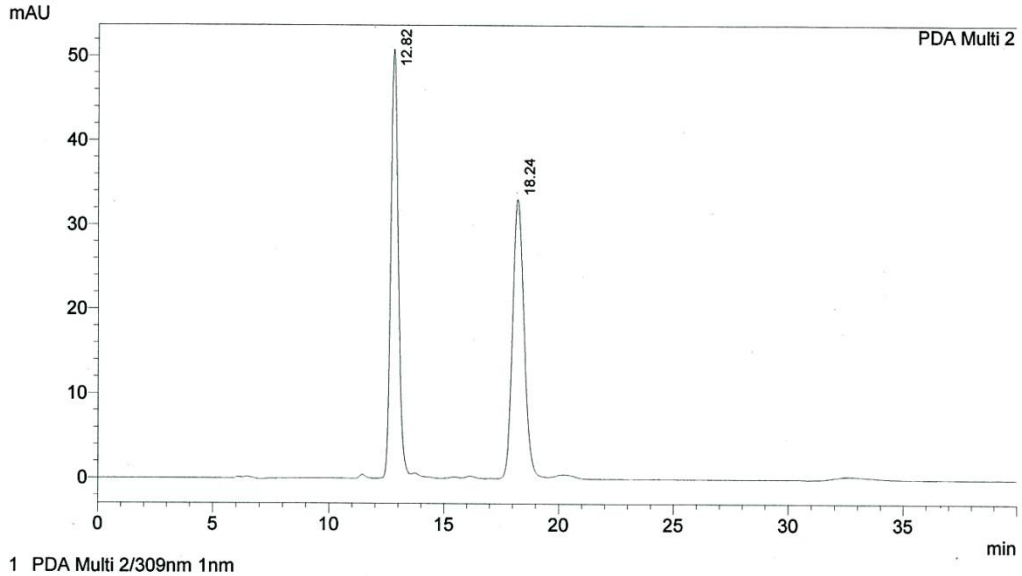




1 PDA Multi 2/304nm 1nm

PDA Ch2 304nm 1nm

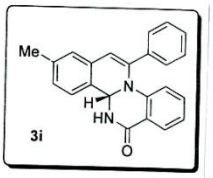
Peak#	Ret. Time	Area	Area %
1	11.04	6889742	80.55
2	12.67	1663202	19.45
Total		8552943	100.00

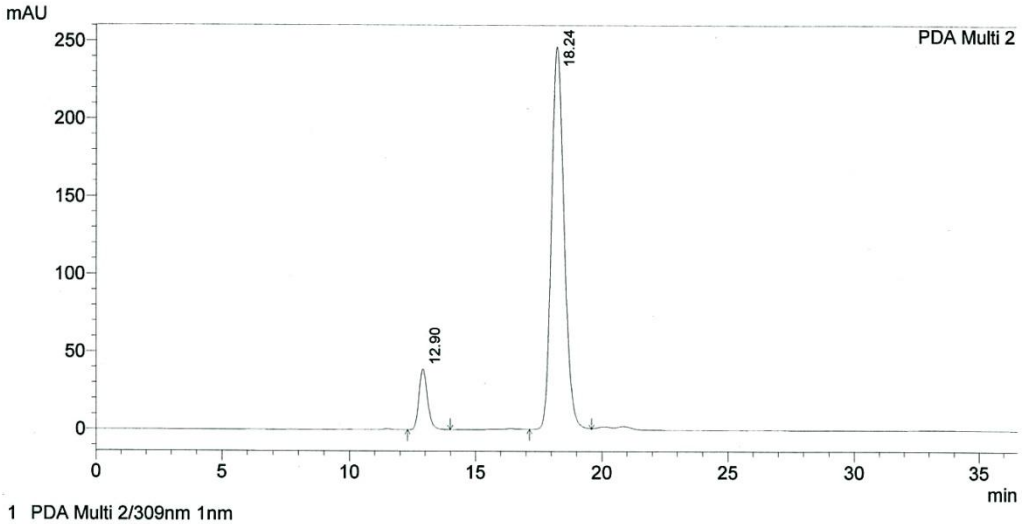


1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

Peak#	Ret. Time	Area	Area %
1	12.82	1151507	50.26
2	18.24	1139547	49.74
Total		2291054	100.00

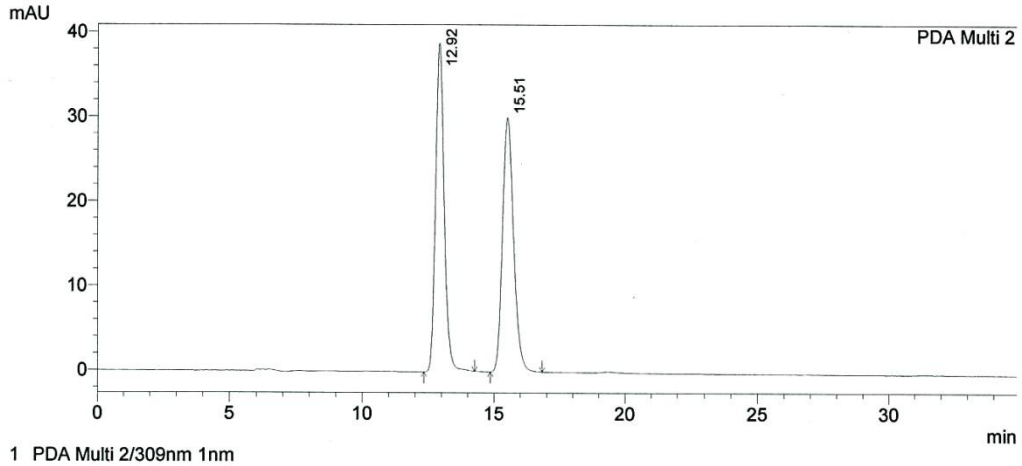




1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

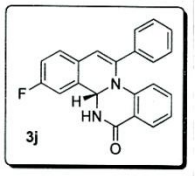
Peak#	Ret. Time	Area	Area %
1	12.90	921594	9.67
2	18.24	8612892	90.33
Total		9534486	100.00

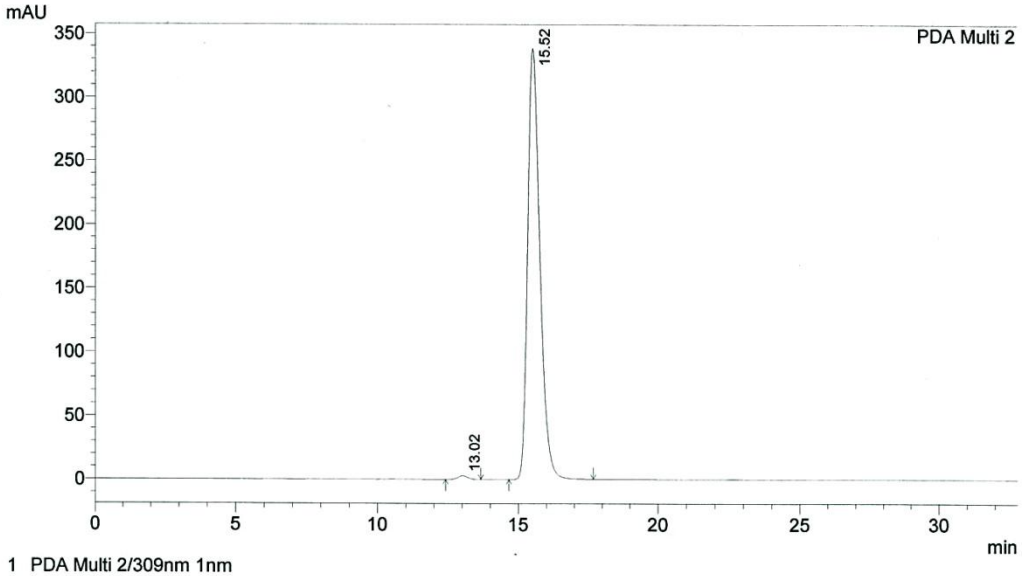


1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

Peak#	Ret. Time	Area	Area %
1	12.92	891184	50.19
2	15.51	884392	49.81
Total		1775576	100.00

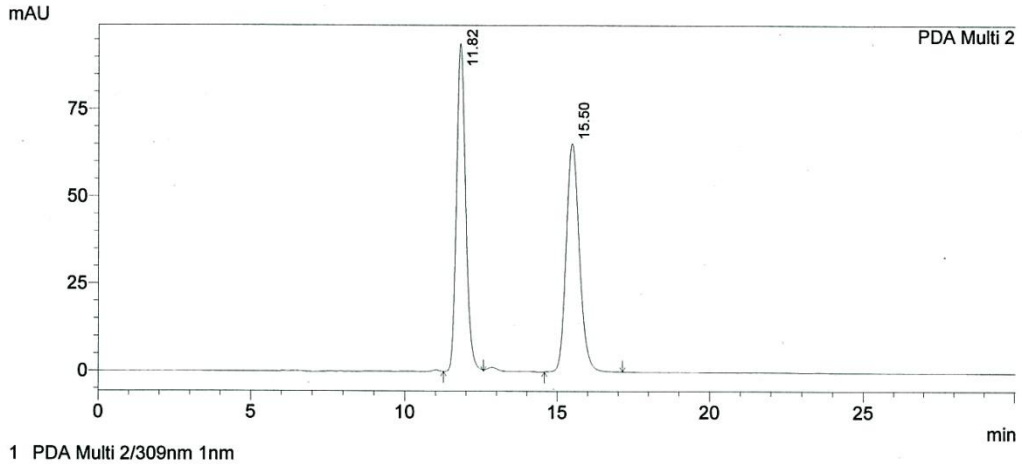




1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

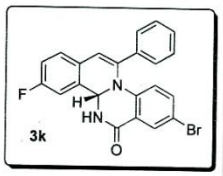
Peak#	Ret. Time	Area	Area %
1	13.02	73778	0.71
2	15.52	10248585	99.29
Total		10322364	100.00

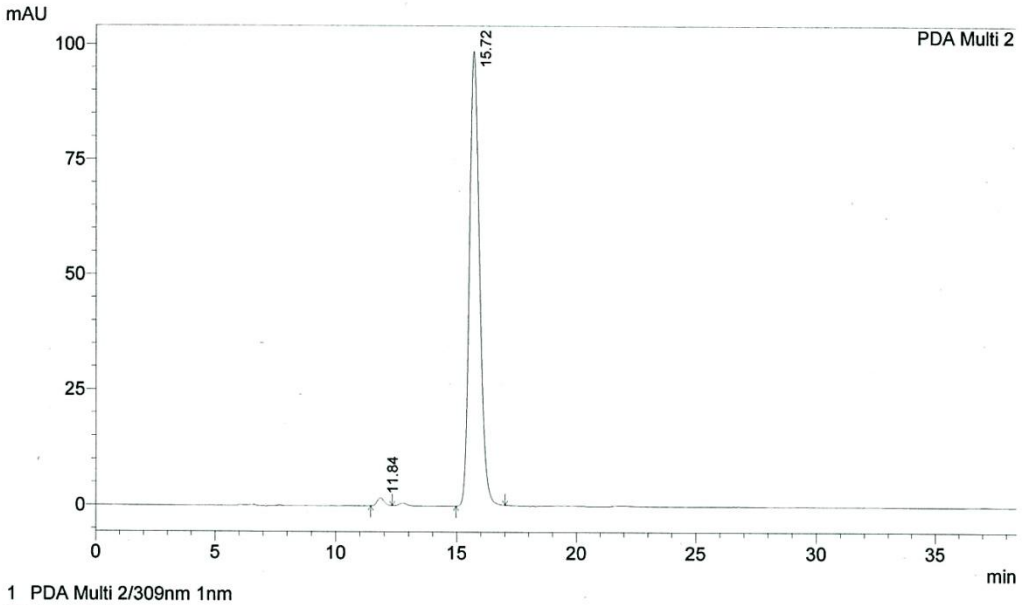


1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

Peak#	Ret. Time	Area	Area %
1	11.82	1969985	49.92
2	15.50	1976520	50.08
Total		3946505	100.00

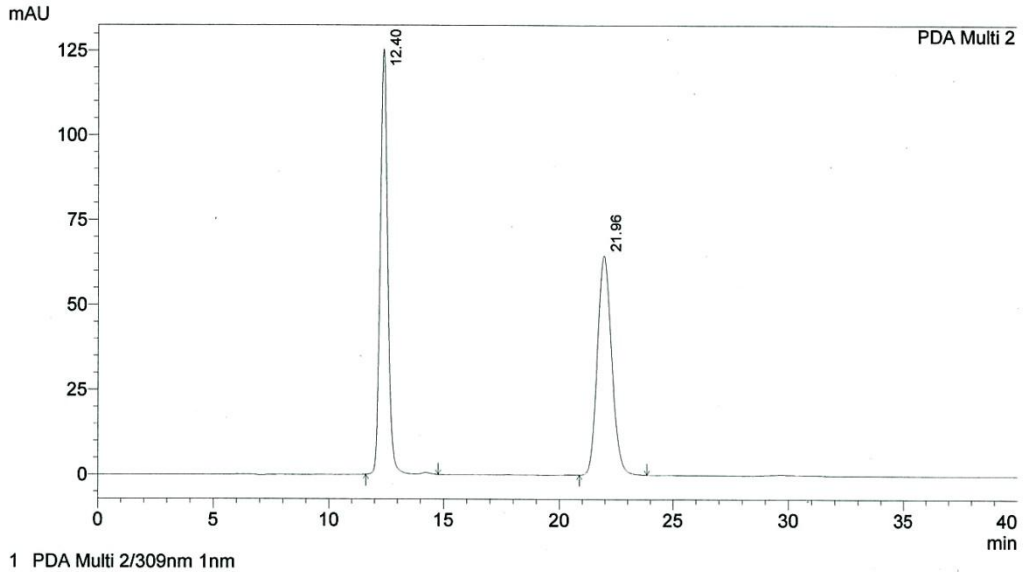




1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

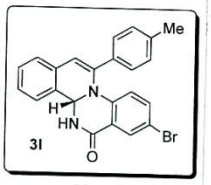
Peak#	Ret. Time	Area	Area %
1	11.84	35434	1.22
2	15.72	2879033	98.78
Total		2914467	100.00

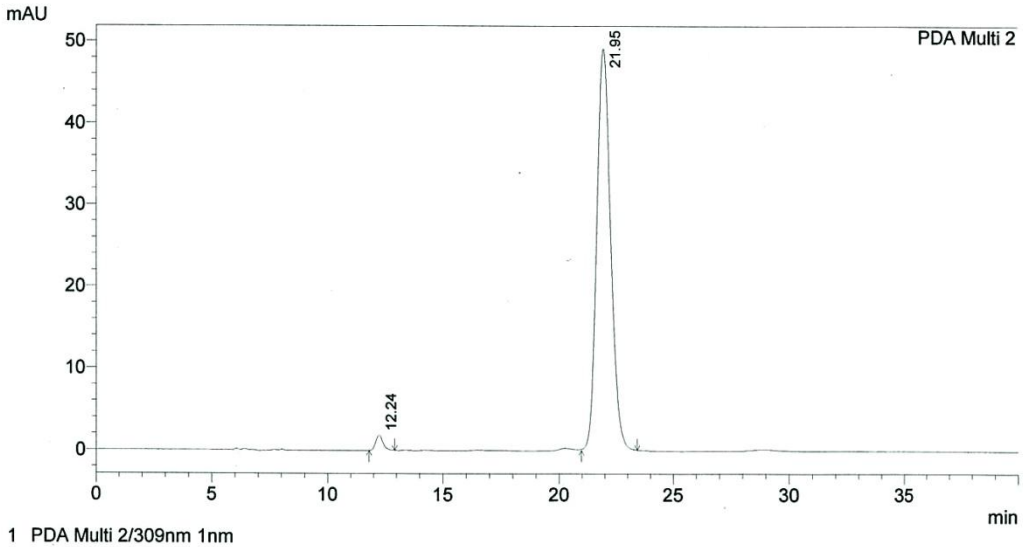


1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

Peak#	Ret. Time	Area	Area %
1	12.40	2864775	50.35
2	21.96	2824923	49.65
Total		5689697	100.00

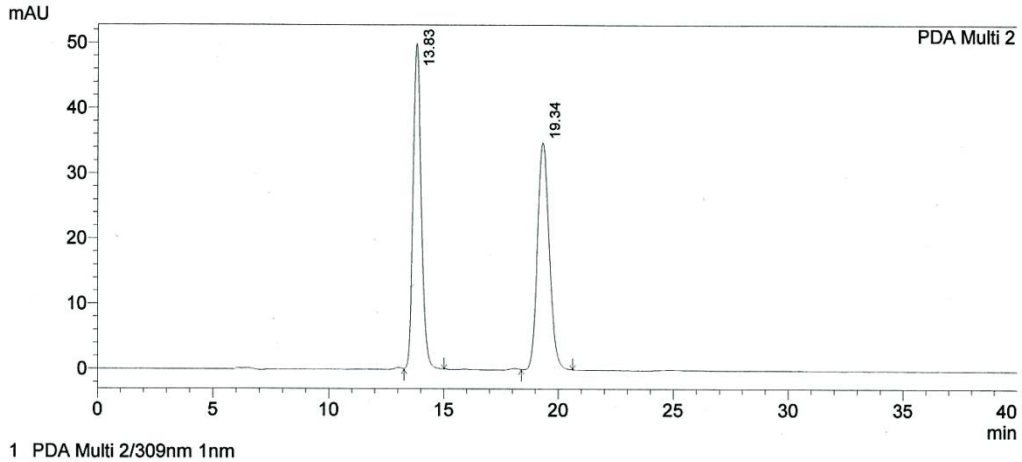




1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

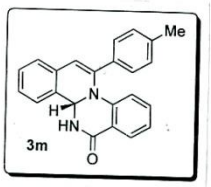
Peak#	Ret. Time	Area	Area %
1	12.24	41134	1.94
2	21.95	2078887	98.06
Total		2120022	100.00

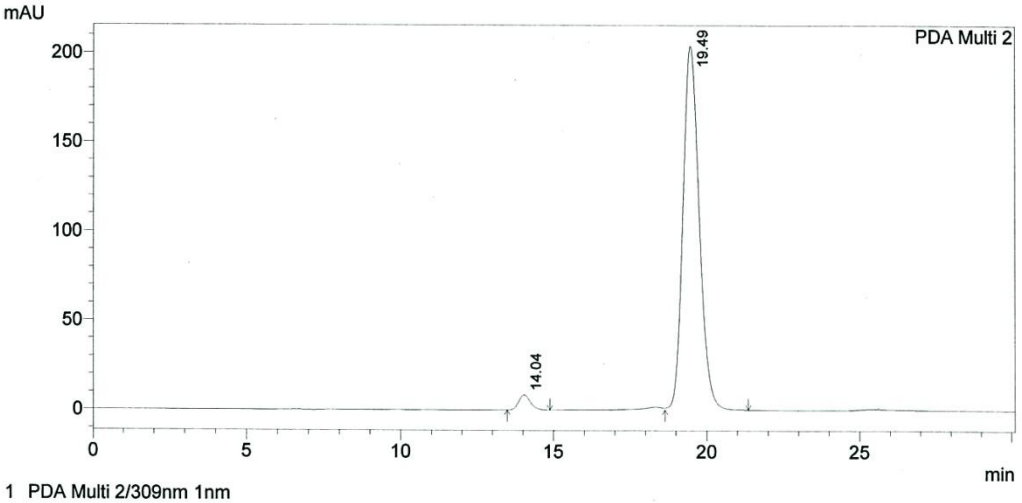


1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

Peak#	Ret. Time	Area	Area %
1	13.83	1240745	50.02
2	19.34	1239957	49.98
Total		2480702	100.00

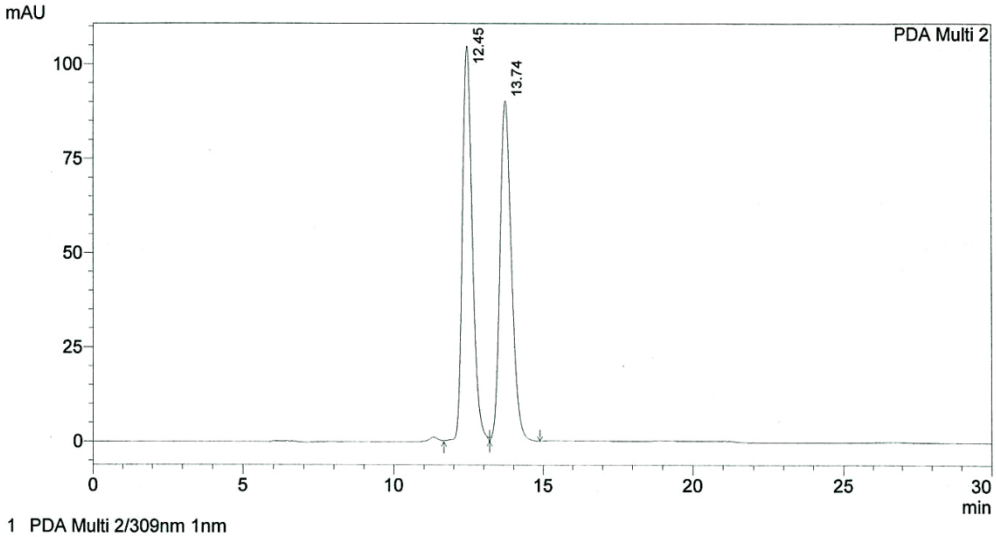




1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

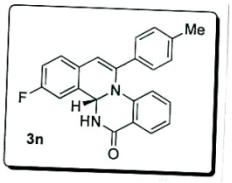
Peak#	Ret. Time	Area	Area %
1	14.04	224538	2.90
2	19.49	7514846	97.10
Total		7739385	100.00

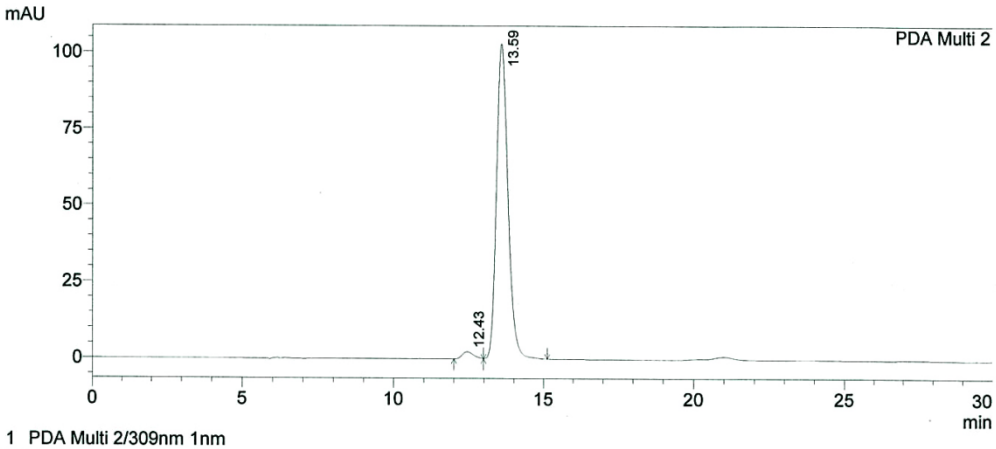


1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

Peak#	Ret. Time	Area	Area %
1	12.45	2420855	49.97
2	13.74	2423992	50.03
Total		4844846	100.00

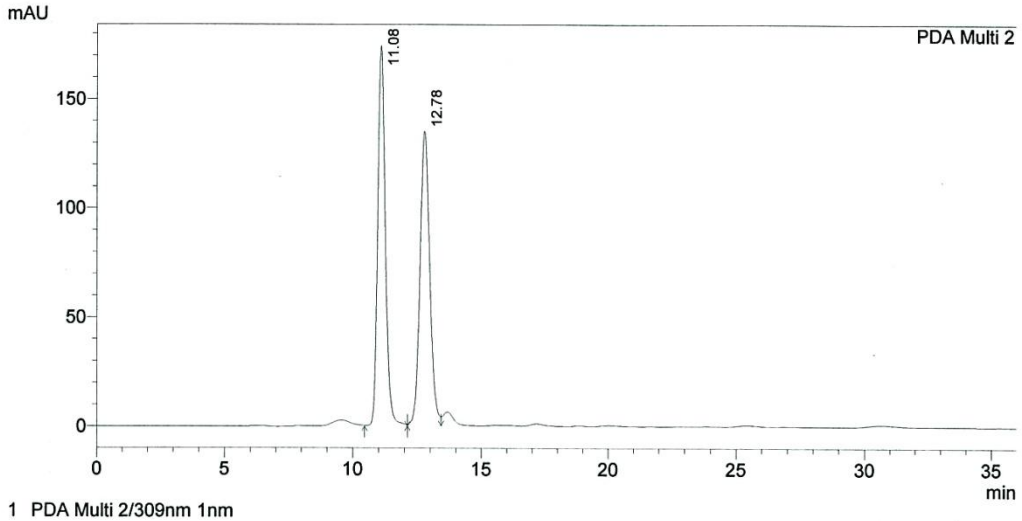




1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

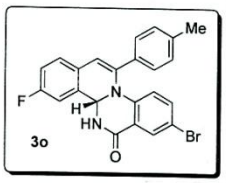
Peak#	Ret. Time	Area	Area %
1	12.43	61659	2.19
2	13.59	2757290	97.81
Total		2818949	100.00

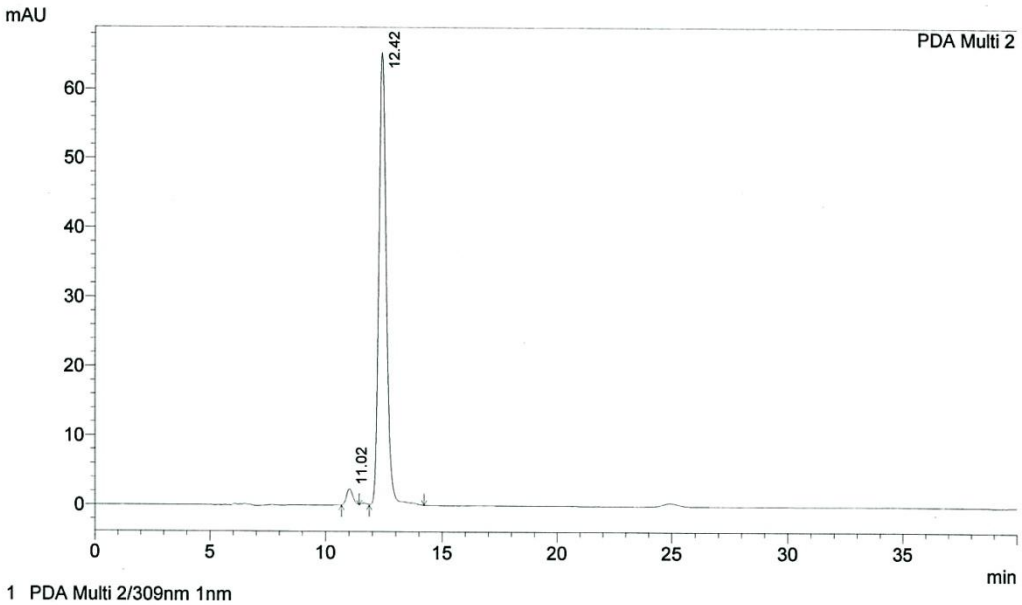


1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

Peak#	Ret. Time	Area	Area %
1	11.08	3588905	49.96
2	12.78	3593993	50.04
Total		7182898	100.00

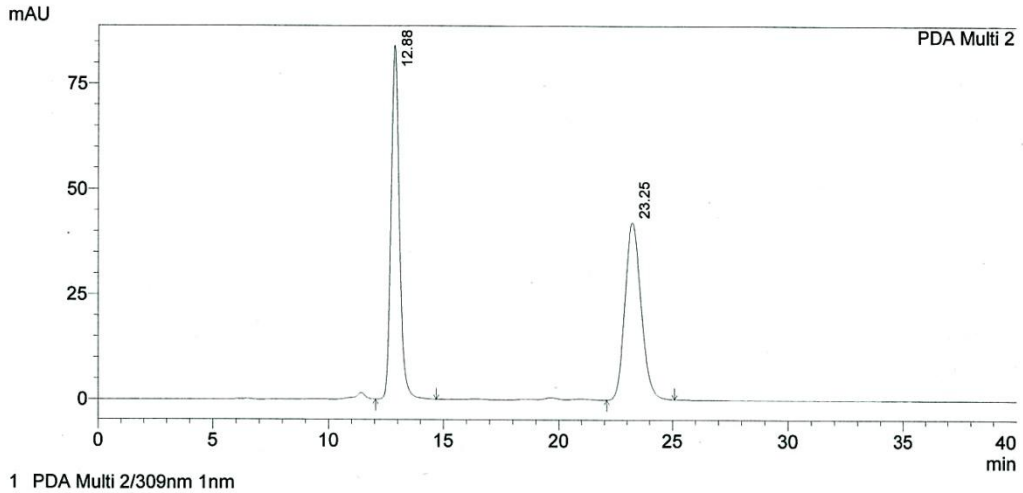




1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

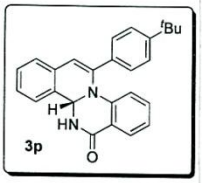
Peak#	Ret. Time	Area	Area %
1	11.02	46102	3.04
2	12.42	1470369	96.96
Total		1516470	100.00

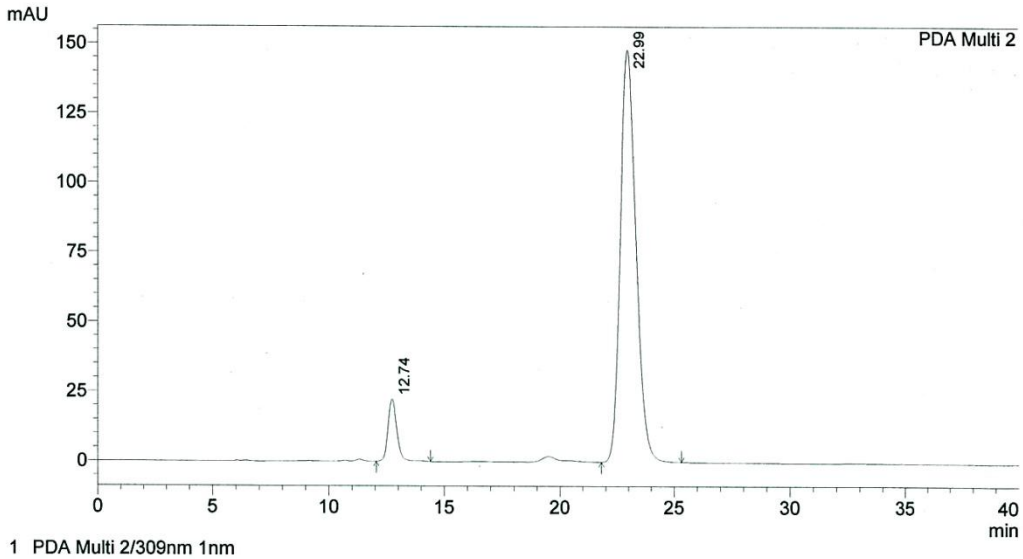


1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

Peak#	Ret. Time	Area	Area %
1	12.88	2144359	50.60
2	23.25	2093158	49.40
Total		4237517	100.00

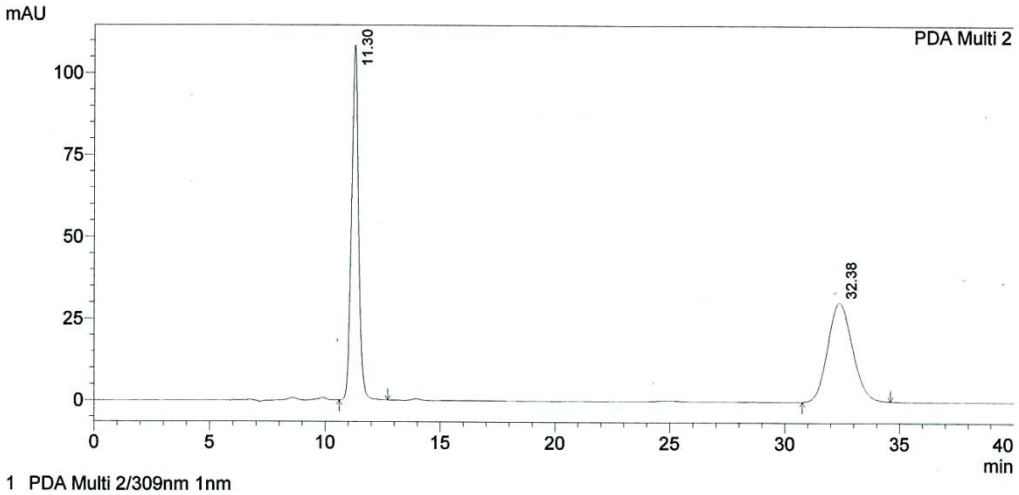




1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

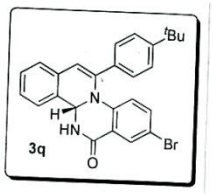
Peak#	Ret. Time	Area	Area %
1	12.74	595559	7.73
2	22.99	7104121	92.27
Total		7699679	100.00

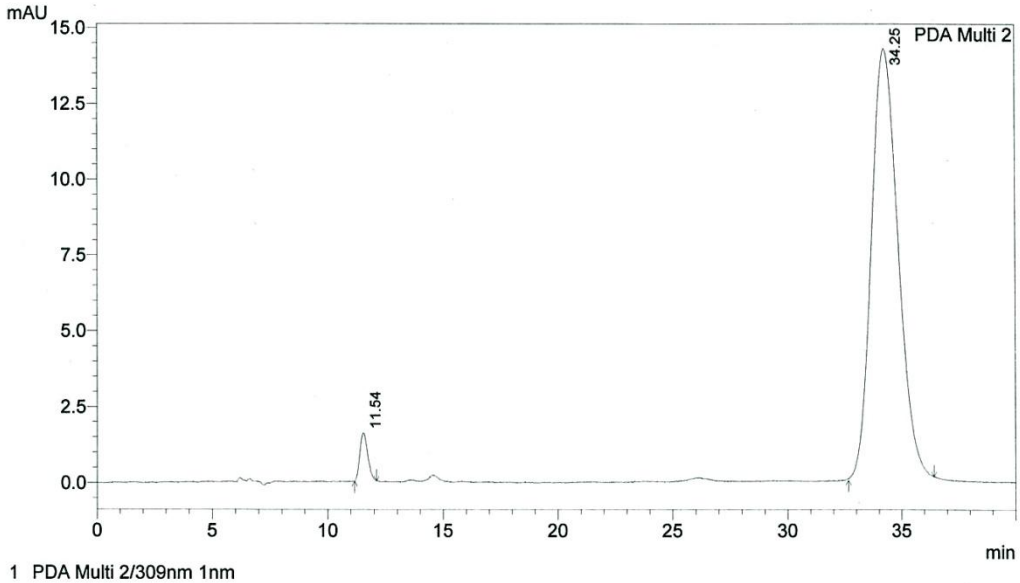


1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

Peak#	Ret. Time	Area	Area %
1	11.30	2295585	50.28
2	32.38	2269579	49.72
Total		4565163	100.00

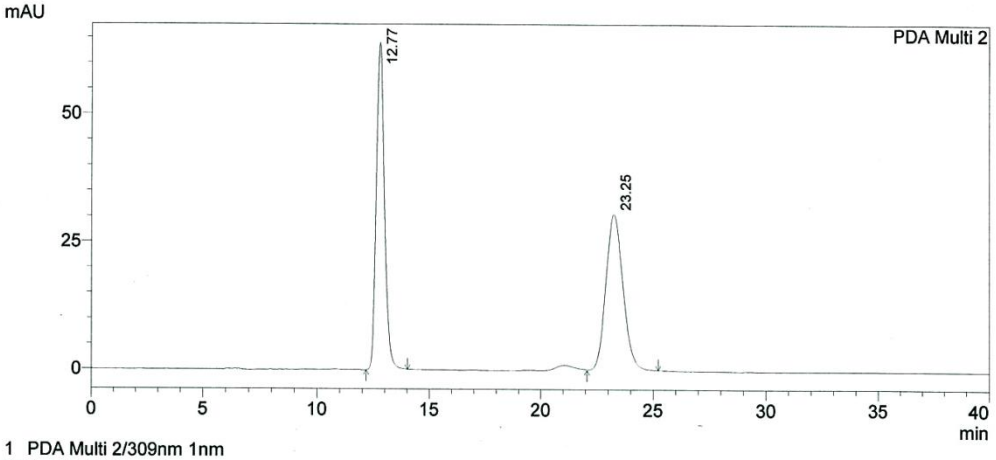




1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

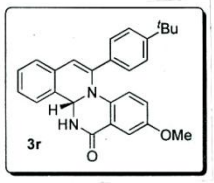
Peak#	Ret. Time	Area	Area %
1	11.54	37603	3.15
2	34.25	1155517	96.85
Total		1193120	100.00

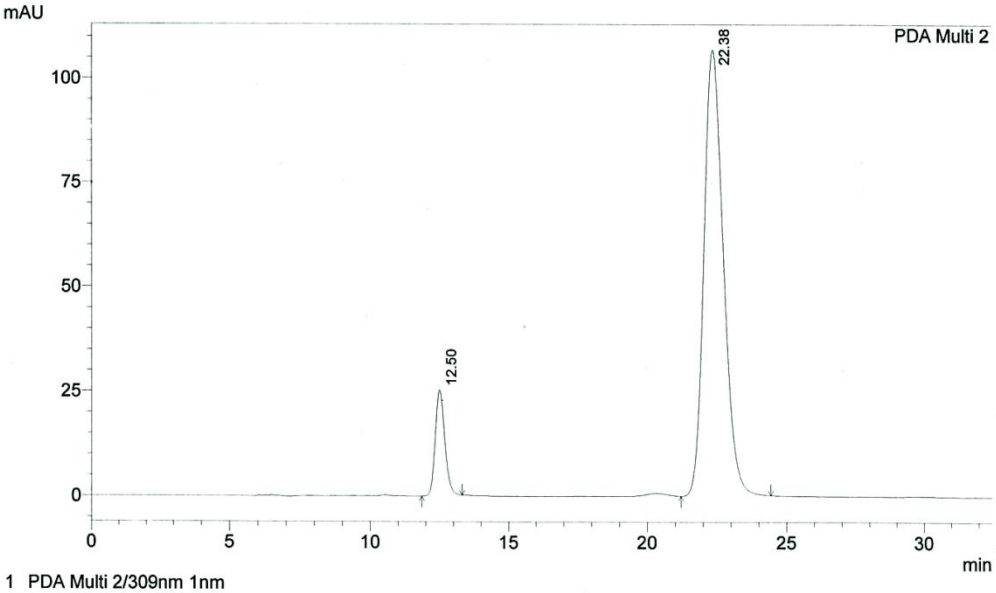


1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

Peak#	Ret. Time	Area	Area %
1	12.77	1630403	50.17
2	23.25	1619623	49.83
Total		3250026	100.00

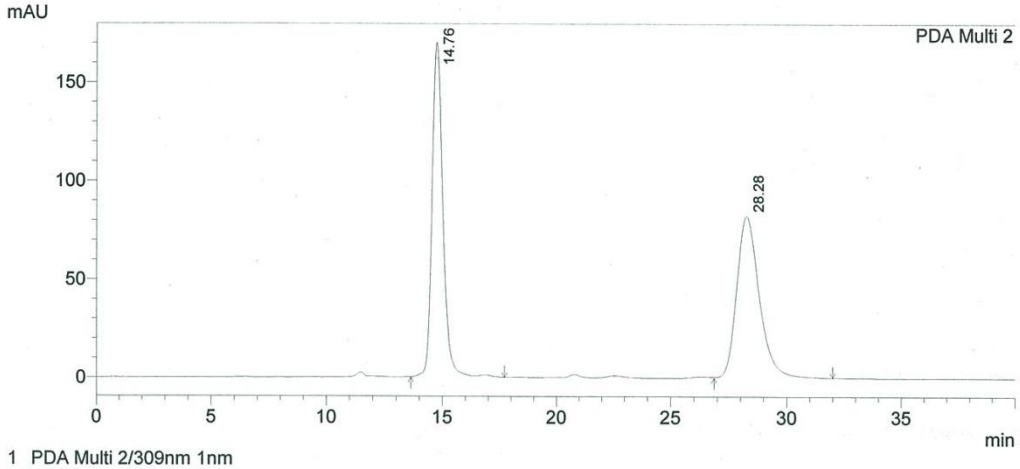




1 PDA Multi 2/309nm 1nm

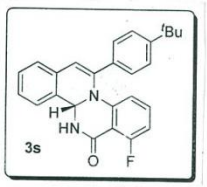
PDA Ch2 309nm 1nm

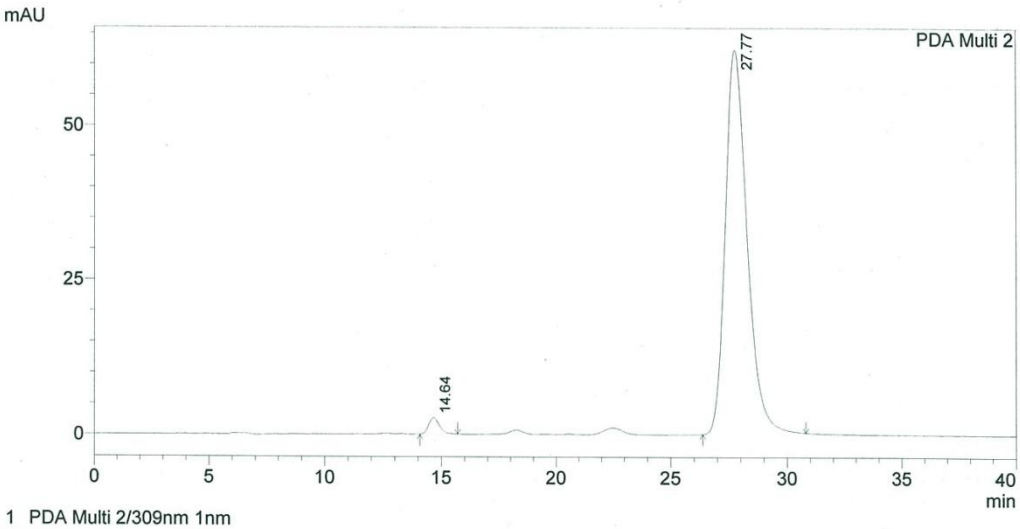
Peak#	Ret. Time	Area	Area %
1	12.50	601841	10.42
2	22.38	5172305	89.58
Total		5774146	100.00



1 PDA Multi 2/309nm 1nm
PDA Ch2 309nm 1nm

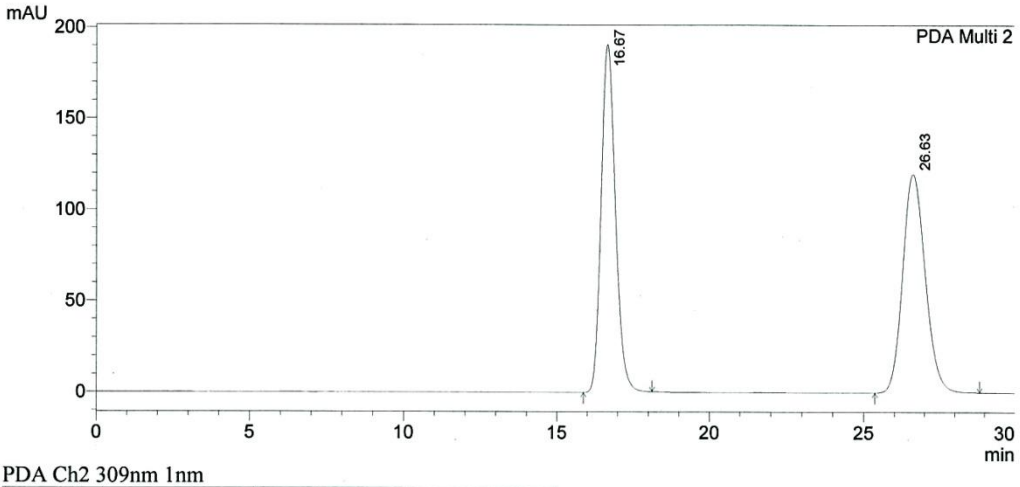
Peak#	Ret. Time	Area	Area %
1	14.76	5592906	50.01
2	28.28	5589738	49.99
Total		11182644	100.00





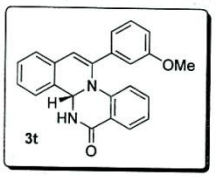
1 PDA Multi 2/309nm 1nm
PDA Ch2 309nm 1nm

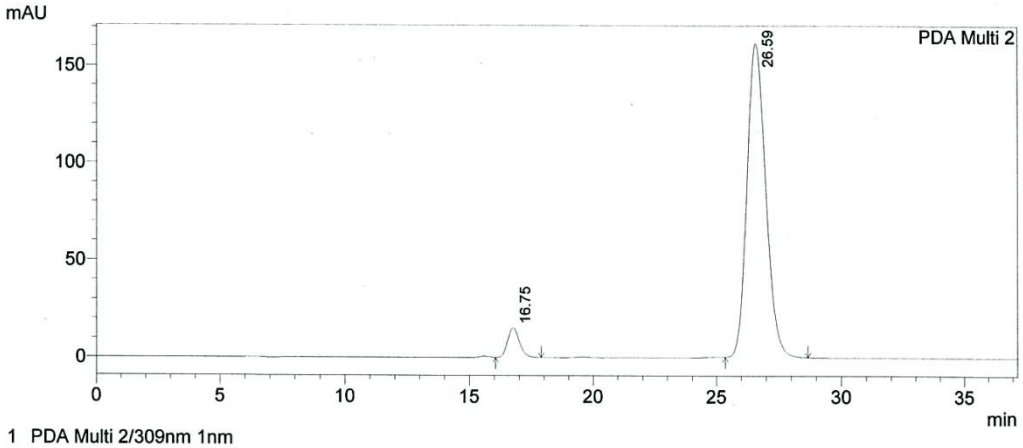
Peak#	Ret. Time	Area	Area %
1	14.64	86146	2.08
2	27.77	4055385	97.92
Total		4141531	100.00



PDA Ch2 309nm 1nm

Peak#	Ret. Time	Area	Area %
1	16.67	6229702	49.92
2	26.63	6250507	50.08
Total		12480209	100.00

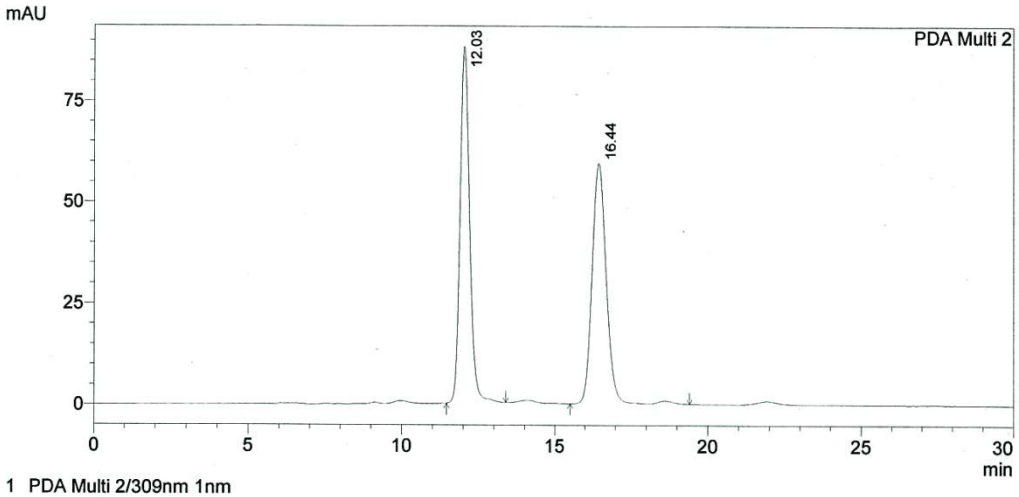




1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

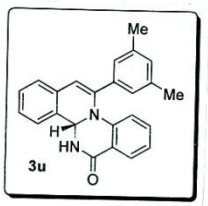
Peak#	Ret. Time	Area	Area %
1	16.75	508668	5.70
2	26.59	8410588	94.30
Total		8919257	100.00

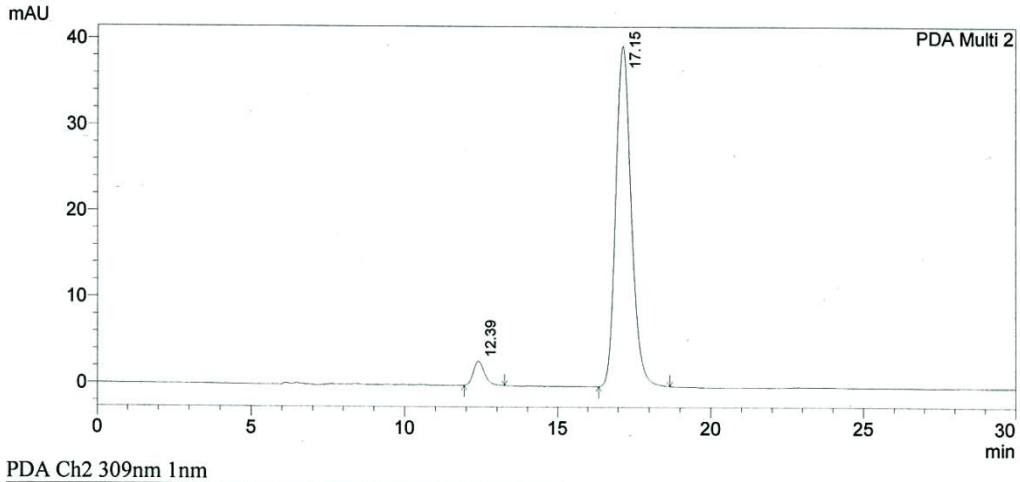


1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

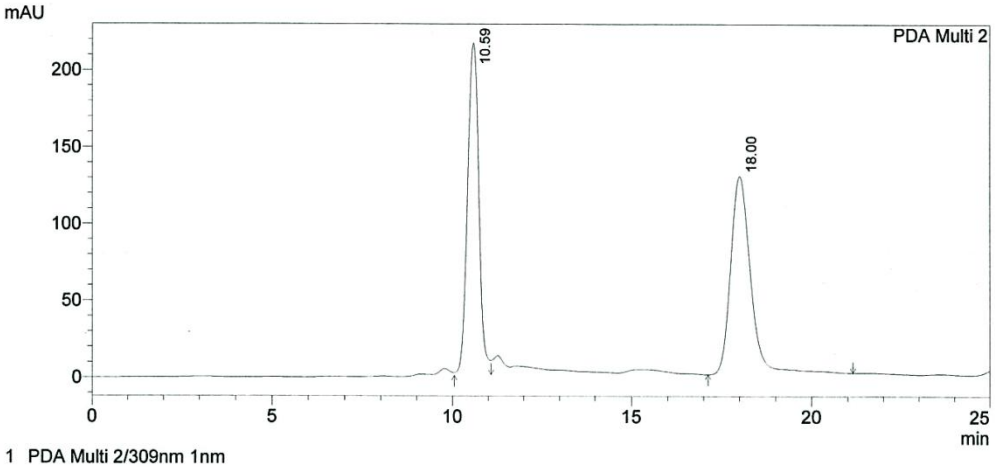
Peak#	Ret. Time	Area	Area %
1	12.03	1906063	49.90
2	16.44	1913464	50.10
Total		3819527	100.00





PDA Ch2 309nm 1nm

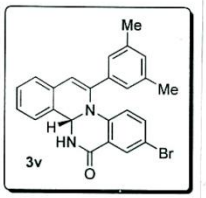
Peak#	Ret. Time	Area	Area %
1	12.39	70677	4.89
2	17.15	1374845	95.11
Total		1445522	100.00

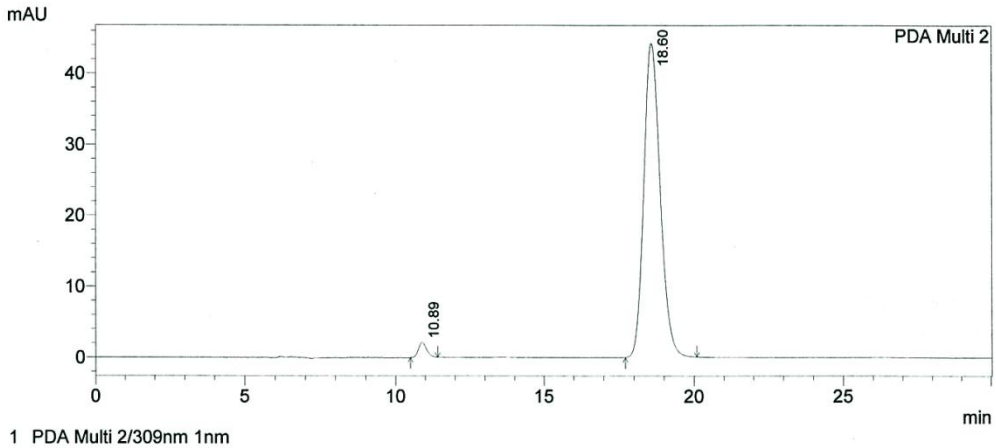


1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

Peak#	Ret. Time	Area	Area %
1	10.59	4849405	49.16
2	18.00	5014980	50.84
Total		9864385	100.00

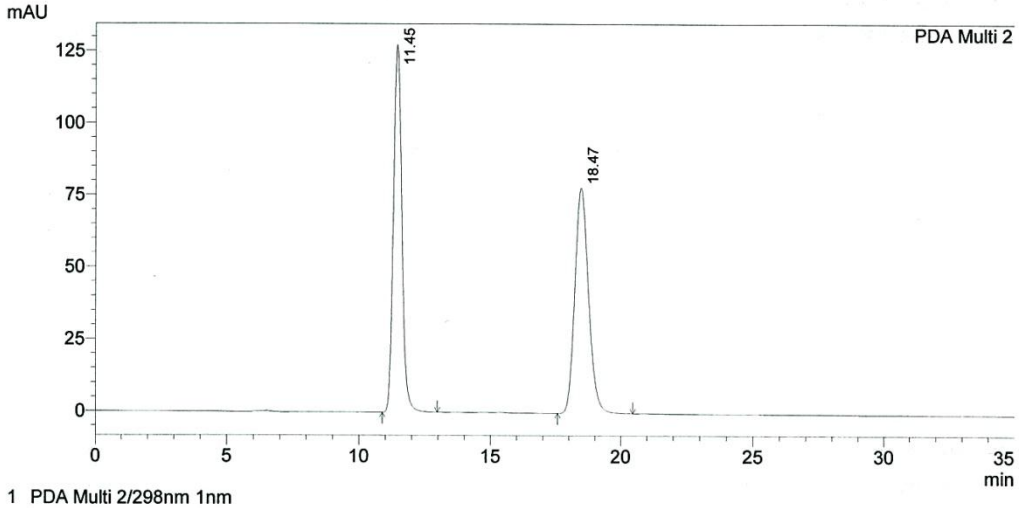




1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

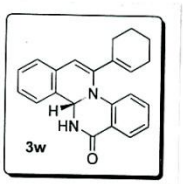
Peak#	Ret. Time	Area	Area %
1	10.89	40655	2.35
2	18.60	1690200	97.65
Total		1730856	100.00

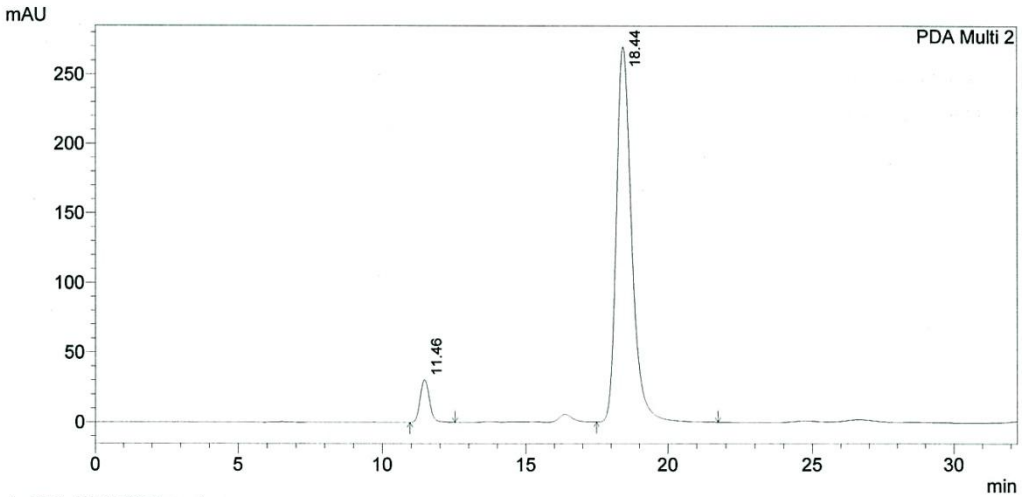


1 PDA Multi 2/298nm 1nm

PDA Ch2 298nm 1nm

Peak#	Ret. Time	Area	Area %
1	11.45	2838736	49.75
2	18.47	2867311	50.25
Total		5706047	100.00

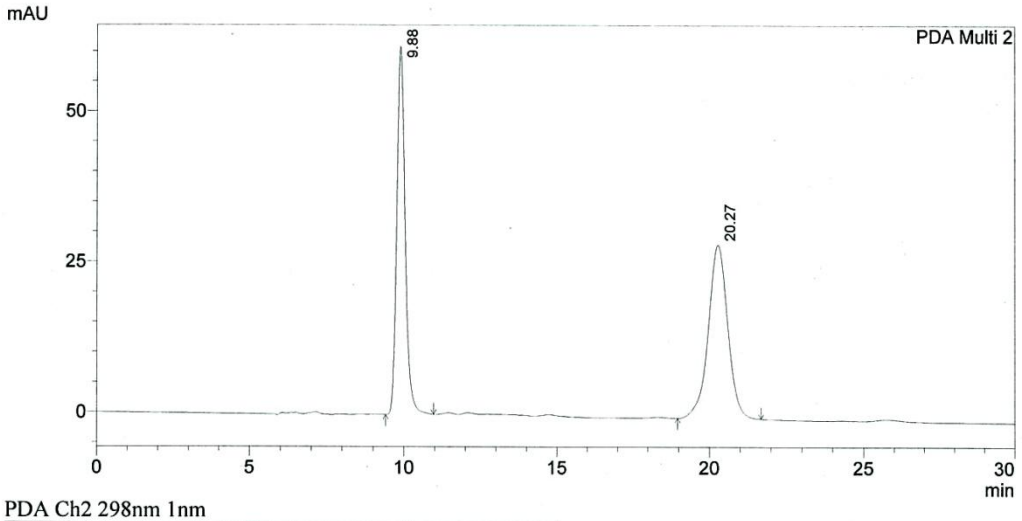




1 PDA Multi 2/298nm 1nm

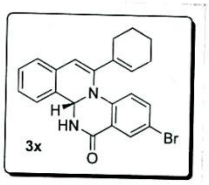
PDA Ch2 298nm 1nm

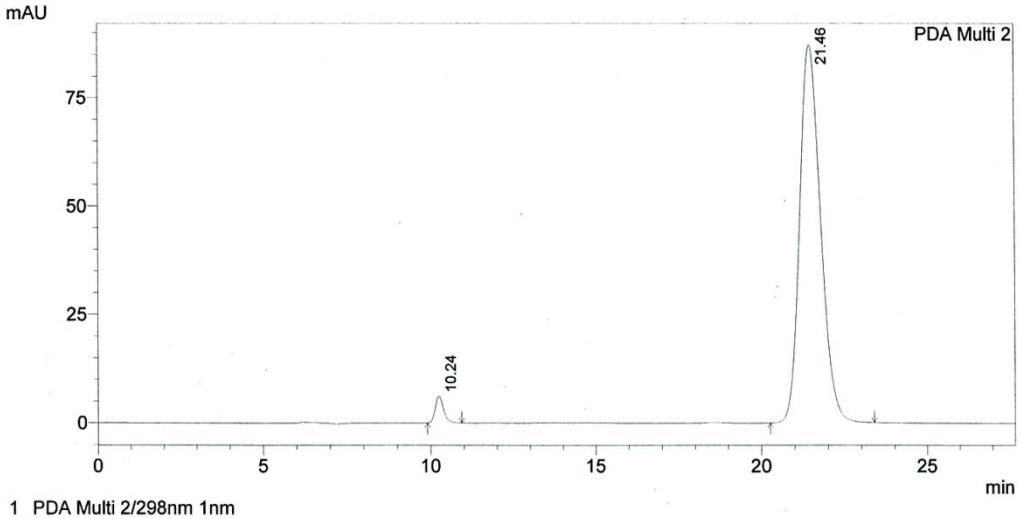
Peak#	Ret. Time	Area	Area %
1	11.46	683130	6.29
2	18.44	10177757	93.71
Total		10860887	100.00



PDA Ch2 298nm 1nm

Peak#	Ret. Time	Area	Area %
1	9.88	1158953	47.64
2	20.27	1273591	52.36
Total		2432543	100.00

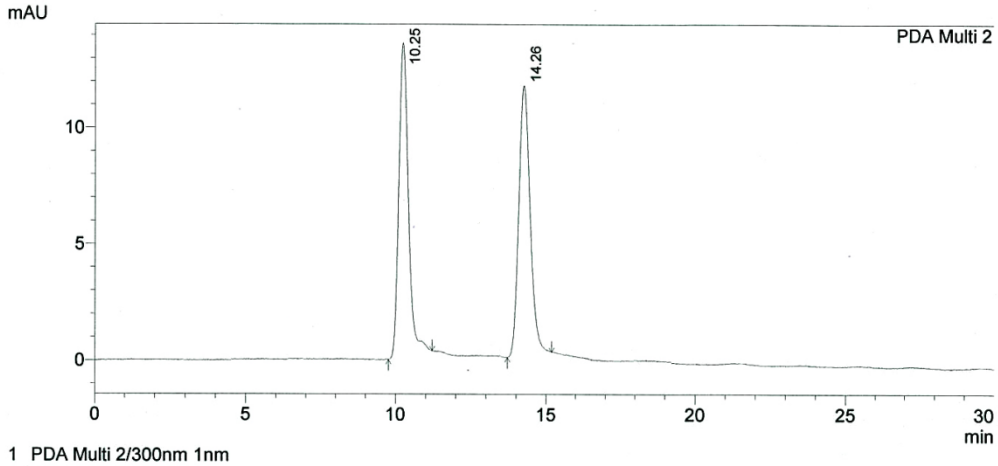




1 PDA Multi 2/298nm 1nm

PDA Ch2 298nm 1nm

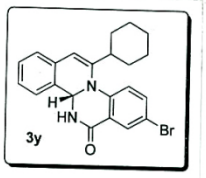
Peak#	Ret. Time	Area	Area %
1	10.24	107040	2.73
2	21.46	3810076	97.27
Total		3917116	100.00

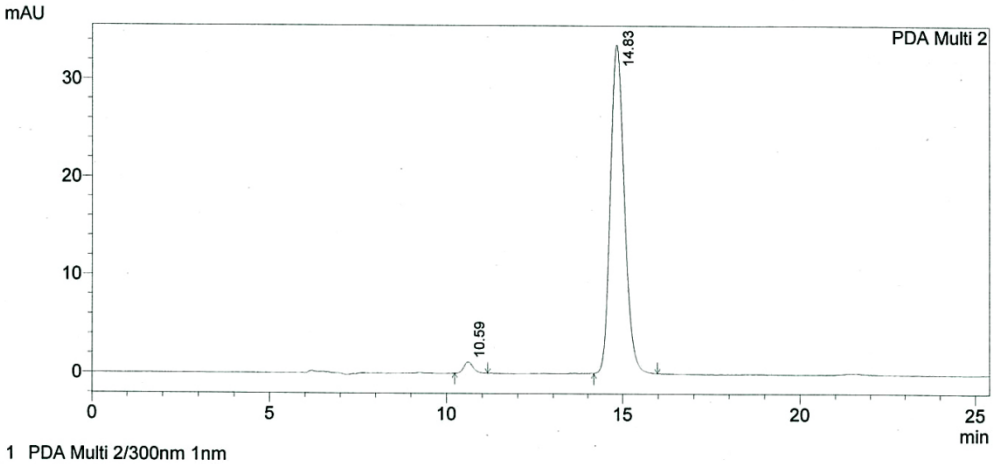


1 PDA Multi 2/300nm 1nm

PDA Ch2 300nm 1nm

Peak#	Ret. Time	Area	Area %
1	10.25	299132	49.50
2	14.26	305194	50.50
Total		604326	100.00

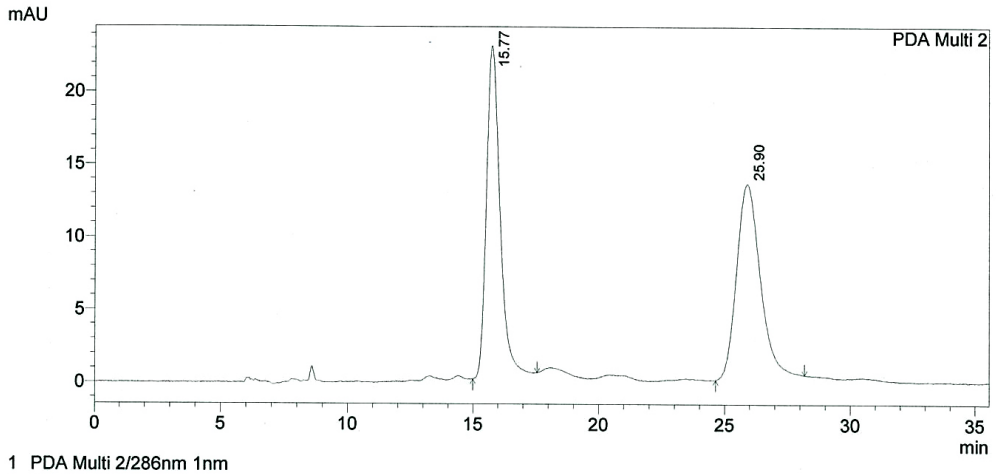




1 PDA Multi 2/300nm 1nm

PDA Ch2 300nm 1nm

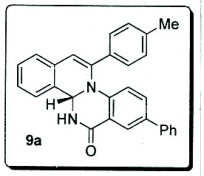
Peak#	Ret. Time	Area	Area %
1	10.59	21115	2.21
2	14.83	934167	97.79
Total		955282	100.00

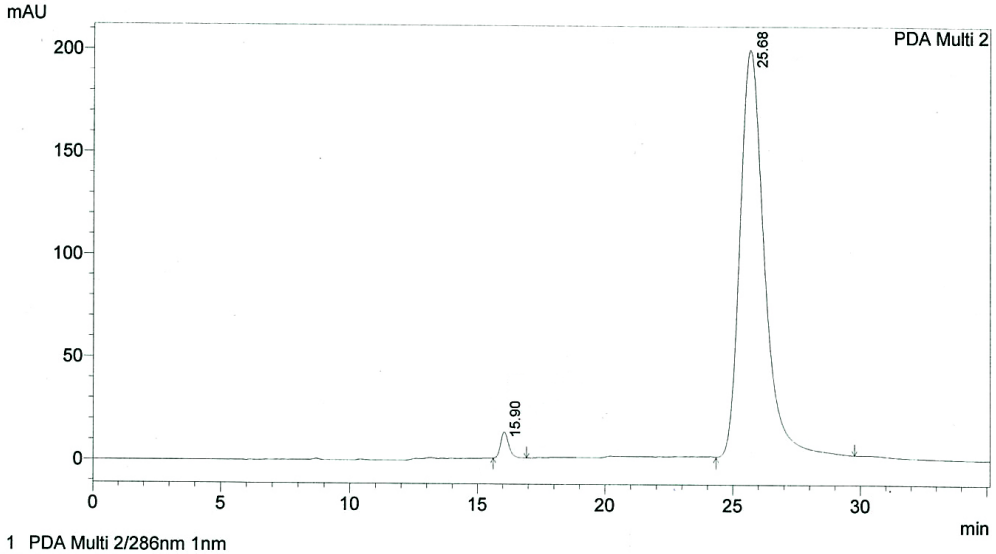


1 PDA Multi 2/286nm 1nm

PDA Ch2 286nm 1nm

Peak#	Ret. Time	Area	Area %
1	15.77	861504	49.61
2	25.90	874882	50.39
Total		1736385	100.00

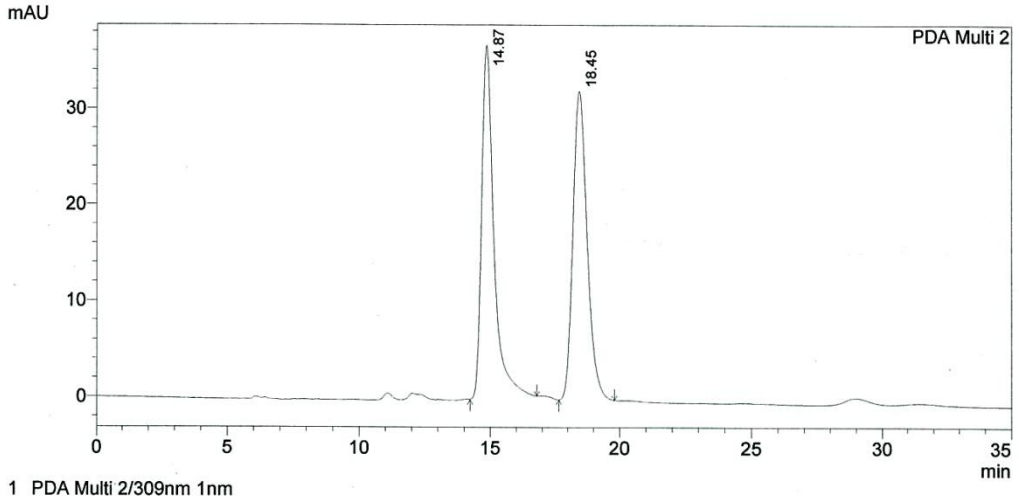




1 PDA Multi 2/286nm 1nm

PDA Ch2 286nm 1nm

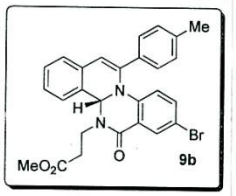
Peak#	Ret. Time	Area	Area %
1	15.90	457393	3.22
2	25.68	13756152	96.78
Total		14213545	100.00

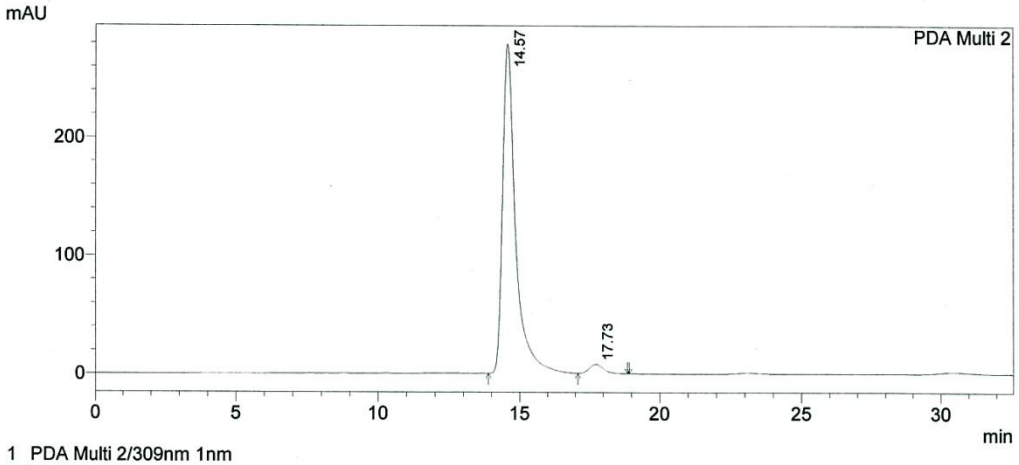


1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

Peak#	Ret. Time	Area	Area %
1	14.87	1207794	49.48
2	18.45	1232982	50.52
Total		2440776	100.00

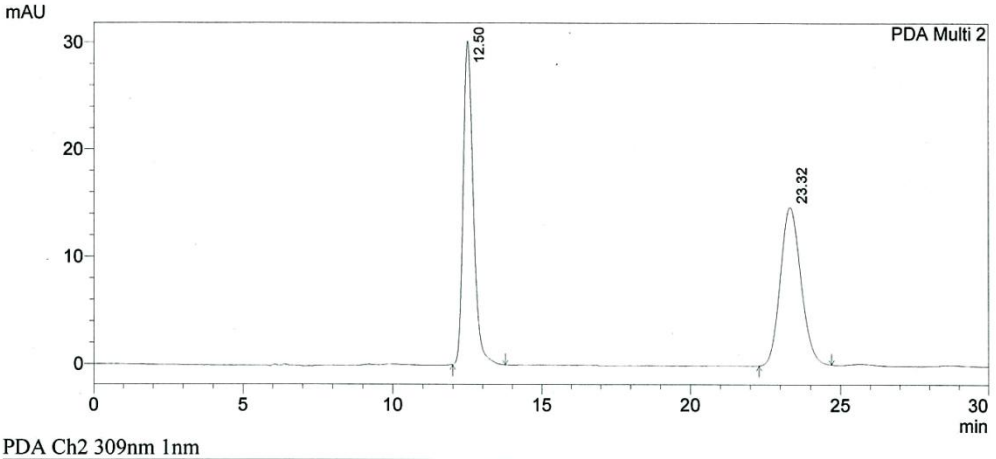




1 PDA Multi 2/309nm 1nm

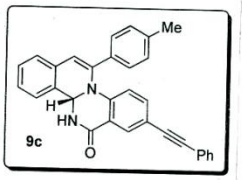
PDA Ch2 309nm 1nm

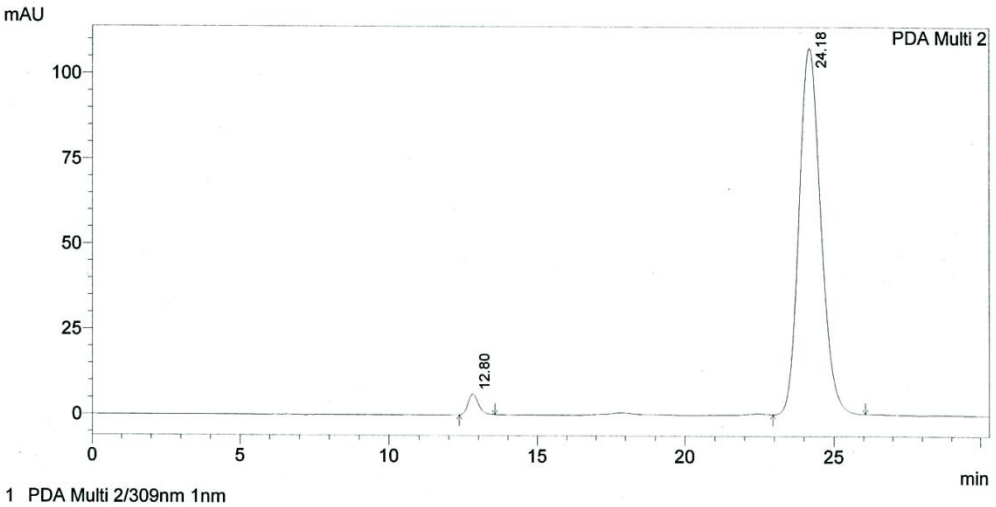
Peak#	Ret. Time	Area	Area %
1	14.57	9007430	97.17
2	17.73	262462	2.83
Total		9269893	100.00



PDA Ch2 309nm 1nm

Peak#	Ret. Time	Area	Area %
1	12.50	716155	50.55
2	23.32	700585	49.45
Total		1416740	100.00

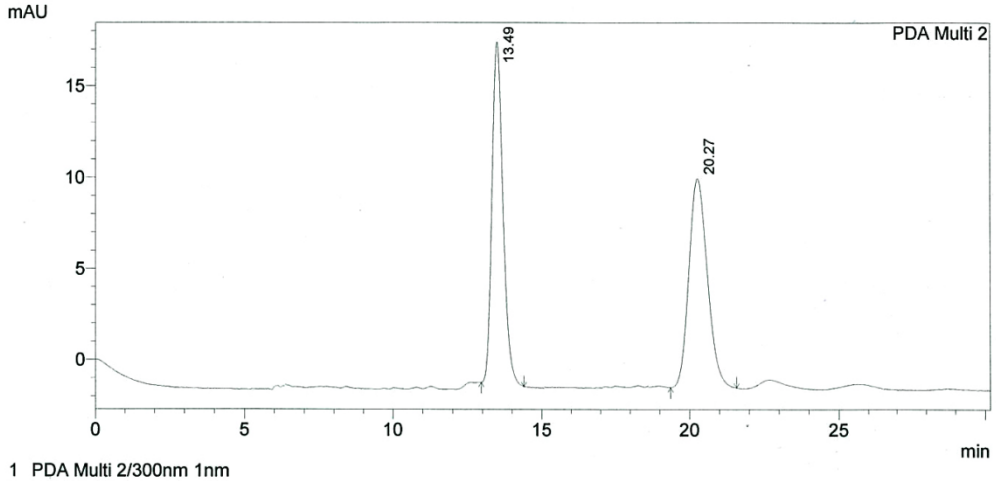




1 PDA Multi 2/309nm 1nm

PDA Ch2 309nm 1nm

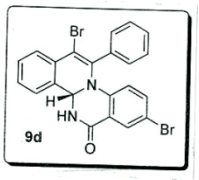
Peak#	Ret. Time	Area	Area %
1	12.80	147649	2.64
2	24.18	5437179	97.36
Total		5584829	100.00

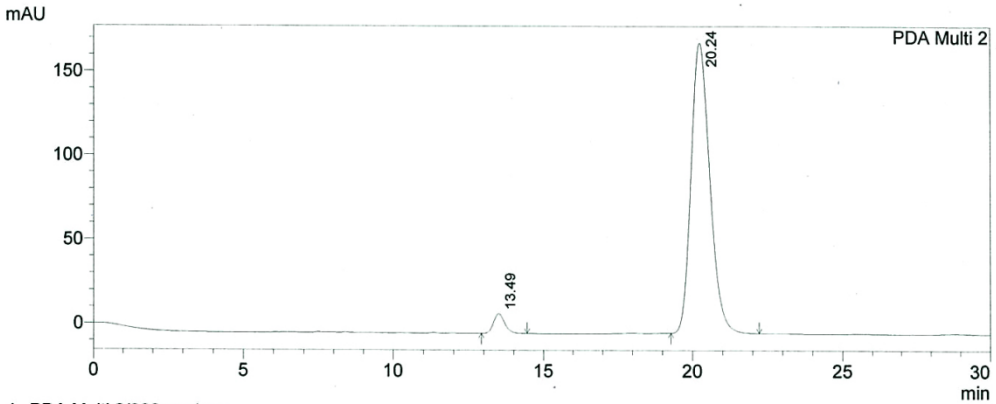


1 PDA Multi 2/300nm 1nm

PDA Ch2 300nm 1nm

Peak#	Ret. Time	Area	Area %
1	13.49	484000	49.42
2	20.27	495439	50.58
Total		979438	100.00





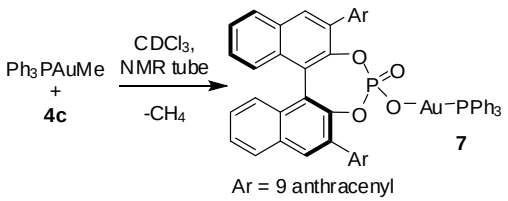
1 PDA Multi 2/300nm 1nm

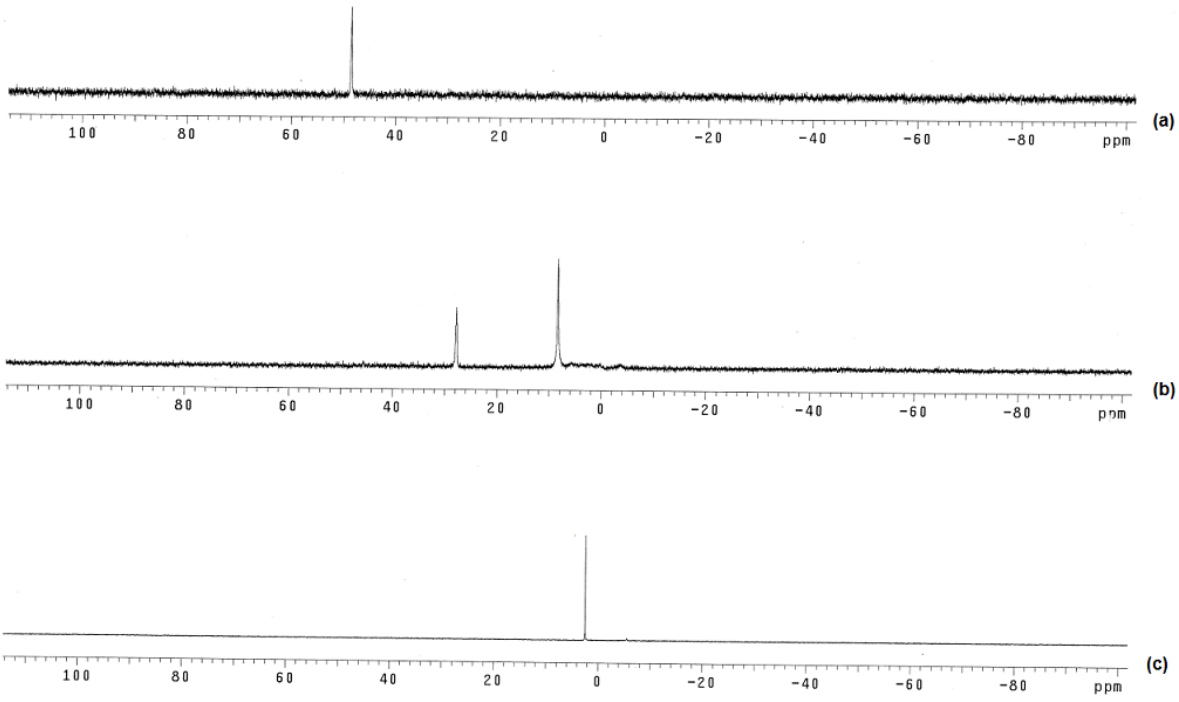
PDA Ch2 300nm 1nm

Peak#	Ret. Time	Area	Area %
1	13.49	304397	3.92
2	20.24	7470002	96.08
Total		7774400	100.00

8. ^{31}P NMR Studies

To a $CDCl_3$ solution of phosphoric acid **4c** (7.4 mg, 0.0105 mmol) in NMR tube, PPh_3AuMe (5 mg, 0.0105 mmol) was added and kept under sonication for five minutes. Then ^{31}P NMR recorded on 400 MHz spectrometer.





a) PPh_3AuMe in $CDCl_3$

b) Equimolar mixture of PPh_3AuMe and **4c** in $CDCl_3$

c) Phosphoric acid **4c** in $CDCl_3$