Rhodium-Catalyzed Pyridannulation of Indoles With Diazoenals: A Direct Approach to Pyrido[1,2-a]indoles

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1. General Methods:

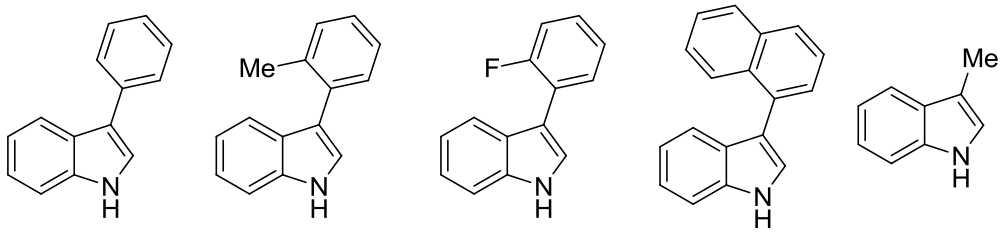
All the reactions were performed in an oven-dried glassware under argon atmosphere. Solvents were dried using standard methods. Toluene, dichloromethane and dichloroethane were distilled over calcium hydride. Unless otherwise stated, all the commercial reagents were used as received. Progress of the reaction was monitored by thin layer chromatography (Merck Silica gel 60 F-254, 0.25 nm, precoated plates on alumina). Column chromatographic purifications were performed on Merck silica gel (100-200 mesh). Melting points were recorded on a digital melting point apparatus and are uncorrected.

Spectroscopic characterizations were carried out at the Central Instrumentation Facility (CIF), Indian Institute of Science Education and Research (IISER) Bhopal. ^{1}H-NMR spectra were recorded on Bruker Avance III FT-NMR spectrometers at 400 MHz, 500 MHz or 700 MHz and ^{13}C-NMR spectra were recorded at 101 MHz, 126 MHz or 176 MHz. ^{1}H-NMR chemical shifts are reported in ppm relative to the TMS (δ=0) or $CDCl_3$ signal (δ= 7.26) and are abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). ^{13}C-NMR chemical shifts are reported in ppm relative to the residual $CDCl_3$ signal (δ= 77.16). IR spectra were recorded on a Perkin Elmer FT-IR spectrometer. HRMS data was obtained on a Bruker microTOF-QII or Agilent 5975C high resolution mass spectrometers.

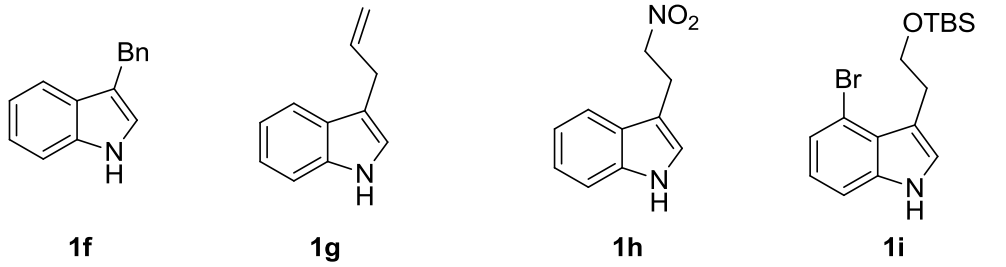
2. Preparation of starting Materials:

a) 3-Substituted indoles 1a-m

Indoles **1a-d** and **1f-m** were prepared according to the literature Procedures.[1-5] Indole **1e** was obtained from the Sigma-Aldrich.

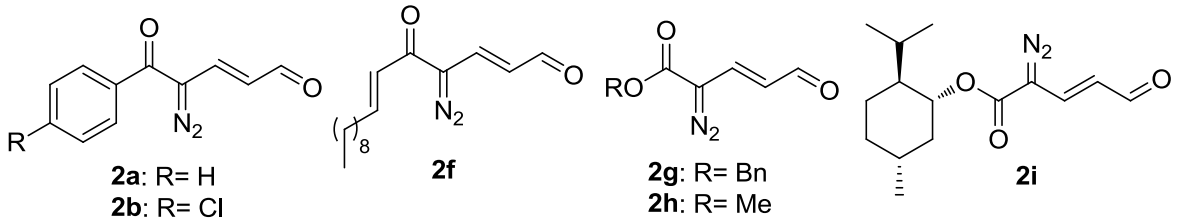


1a **1b** **1c** **1d** **1e**



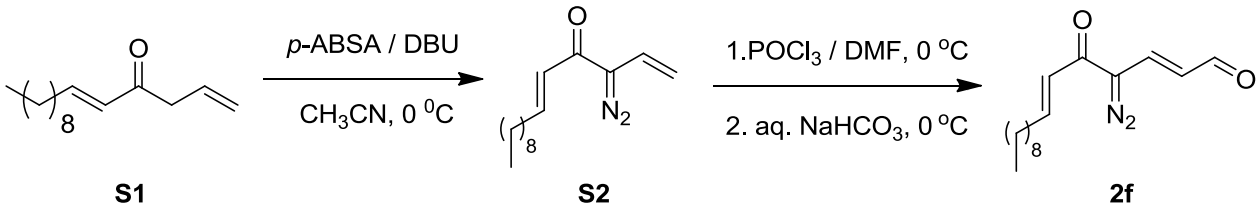
b) Diazoenals 2a-i

The known diazoenals **2a-e**, **2g-i** and the new diazoenal **2f** were prepared according to our reported procedures.[6]



2a: R= H
2b: R= Cl
2c: R= F
2d: R= Me
2e: R= OMe

Preparation of diazoenal 2f:



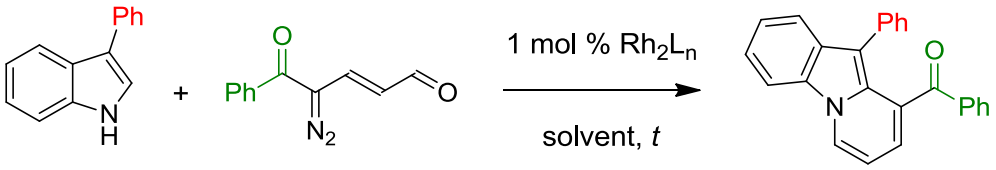
S1 **S2** **2f**

(E)-3-diazopentadeca-1,5-dien-4-one (S2): Prepared according to the literature procedure.[6a] Obtained as an yellow liquid. Yield = 71%; ^{1}H NMR (700 MHz, $CDCl_3$) δ = 6.96 – 6.89 (m, 1H), 6.36 – 6.29 (m, 1H), 6.24 (dd, *J* = 15.0, 1.3 Hz, 1H), 5.15 (dd, *J* = 10.8, 2.7 Hz, 1H), 4.83 (dd, *J* = 17.3, 2.8 Hz, 1H), 2.19 –

2.13 (m, 2H), 1.42 – 1.36 (m, 2H), 1.30 – 1.12 (m, 12H), 0.84 – 0.75 (m, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ = 181.8, 147.8, 123.3, 120.4, 108.7, 73.1, 32.6, 32.0, 29.6, 29.5, 29.4, 29.3, 28.3, 22.8, 14.2; IR (neat): 2223, 1672, 1605, 1467, 1253, 1126, 1010, 910 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{15}H_{24}N_2O$ $(M+H)^+$ 249.1961, found 249.1971.

(2E,6E)-4-diazo-5-oxohexadeca-2,6-dienal (2f): Prepared according to the literature procedure.[6a] Obtained as an yellow solid; R_f = 0.4 (ethyl acetate/hexane : 30/70); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (d, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 15.7 Hz, 1H), 7.15 – 7.04 (m, 1H), 6.34 (d, *J* = 15.0 Hz, 1H), 5.94 (dd, *J* = 15.6, 7.5 Hz, 1H), 2.32 – 2.21 (m, 2H), 1.52 – 1.41 (m, 2H), 1.35 – 1.16 (m, 12H), 0.86 (t, *J* = 6.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 179.8, 150.5, 138.5, 122.6, 122.3, 75.1, 32.7, 31.9, 29.5, 29.4, 29.3, 29.2, 28.1, 22.7, 14.1; IR (neat): 2223, 1672, 1605, 1467, 1253, 1126, 1010, 910 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{16}H_{24}N_2O_2$ $(M+H)^+$ 277.1911, found 277.1917.

3. Optimization of pyridannulation:

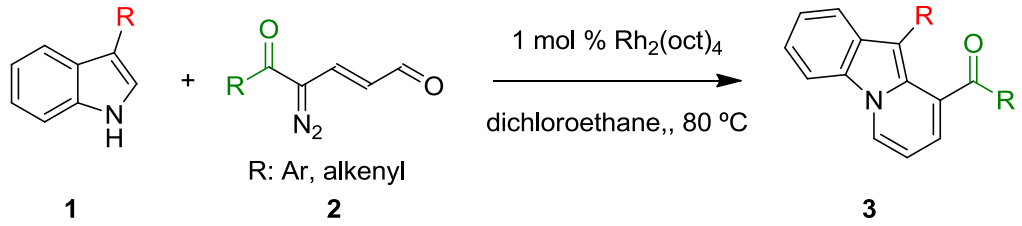


1a **2a** **3a**

entry	Rh_2L_n	solvent	*t* (°C)	yield (%)
1	$Rh_2(oct)_4$	dichloromethane	25	47
2	$Rh_2(oct)_4$	chloroform	60	62
3	**$Rh_2(oct)_4$**	**dichloroethane**	**80**	**73**
4	$Rh_2(oct)_4$	trifluorotoluene	100	63
5	$Rh_2(oct)_4$	toluene	80	65
6	$Rh_2(OAc)_4$	dichloroethane	80	68
7	$Rh_2(TFA)_4$	dichloroethane	80	41
8	$Rh_2(esp)_2$	dichloroethane	80	68
9	Rh_2(*R*-DOSP)$_4$	dichloroethane	80	70
10	Rh_2(*R*-PTAD)$_4$	dichloroethane	80	67

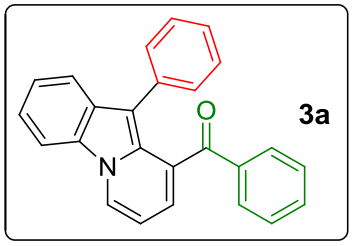
Procedure for the optimization reactions: A 10 ml round-bottom flask was charged with Rh_2L_n (0.001 mmol), 3-phenylindole **1a** (0.1 mmol) and 1 ml of solvent and stirred at the appropriate temperature. To the contents was added a 0.1 M solution of the enaldiazo ketone **2a** (0.15 mmol) in the same solvent via a syringe pump, with a flow rate of 1 ml/h. The reaction was continued at the same temperature for additional 5 h. The solvent was evaporated under reduced pressure and the crude material was purified by a silica gel flash column chromatography using ethyl acetate-petroleum ether as the eluent to furnish pyrido[1,2-a]indole **3a** as a red color semisolid.

4. Pyridannulation with keto diazoenals:



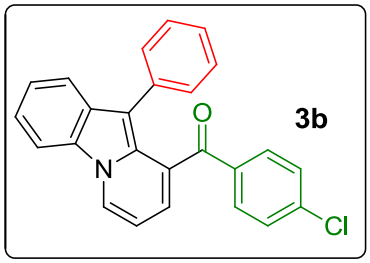
1 **2** **3**

General procedure-1: A 10 ml round-bottom flask was charged with $Rh_2(oct)_4$ (0.002 mmol), 3-substituted indole **1** (0.2 mmol) and 2 ml of dichloroethane and stirred at 80 ^oC. To the contents was added a 0.1 M solution of the enaldiazo ketone **2** (0.3 mmol) in dichloroethane via a syringe pump with a flow rate of 1 ml/h. The reaction was continued at the same temperature for additional 5 h. The solvent was evaporated under reduced pressure and the crude material was purified by a silica gel flash column chromatography using ethyl acetate-petroleum ether as the eluent to furnish pyrido[1,2-a]indole **3**.

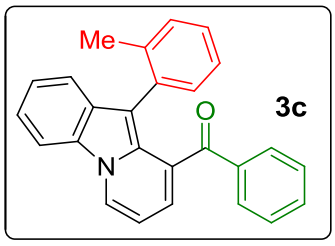


Phenyl (10-phenylpyrido[1,2-a]indol-9-yl)methanone (3a): Prepared by following general procedure-1. Obtained as a red liquid. Yield = 73%; R_f = 0.5 (Ethyl Acetate/Hexane : 20/80); ^1H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 6.5 Hz, 1H), 7.93 – 7.89 (m, 1H), 7.66 – 7.63 (m, 1H), 7.34 – 7.30 (m, 2H), 7.27 – 7.23 (m, 3H), 7.08 – 7.02 (m, 6H), 6.99 – 6.96 (m, 2H), 6.57 (t, *J* = 6.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.2, 137.0, 134.7, 132.6, 131.4, 130.3, 130.2,

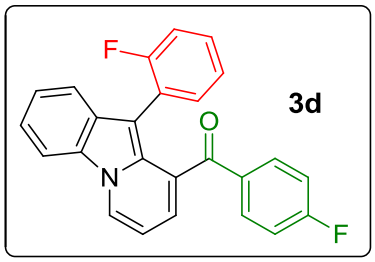
129.3, 129.2, 129.0, 128.4, 128.0, 126.7, 126.3, 125.7, 123.8, 121.2, 119.6, 110.3, 108.9, 107.1; IR (neat): 1661, 1602, 1543, 1447, 1258, 960 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{25}H_{18}NO$ $(M+H)^+$ 348.1383, found 348.1397.



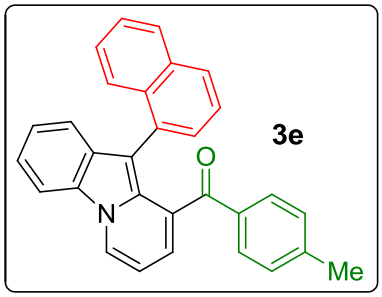
(4-chlorophenyl)(10-phenyl pyrido[1,2-a]indol-9-yl)methanone (3b): Prepared by following general procedure-1. Obtained as a red solid. Yield = 78%; m. p.=131-132 °C; R_f = 0.5 (Ethyl Acetate/Hexane : 20/80); ^1H NMR (500 MHz, $CDCl_3$) δ = 8.43 (d, *J* = 6.4 Hz, 1H), 7.92 – 7.84 (m, 1H), 7.64 – 7.61 (m, 1H), 7.34 – 7.29 (m, 2H), 7.14 – 7.10 (m, 2H), 7.09 – 7.03 (m, 4H), 6.99 – 6.94 (m, 4H), 6.55 (t, *J* = 6.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.2, 138.8, 135.4, 134.7, 130.9, 130.5, 130.3, 130.1, 129.4, 128.9, 128.5, 128.2, 127.0, 126.4, 126.0, 124.0, 121.4, 119.6, 110.4, 108.9, 107.2; IR (neat): 1661, 1649, 1588, 1456, 1343, 1245, 1091, 961 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{25}H_{17}ClNO$ $(M+H)^+$ 382.0993, found 382.1002.



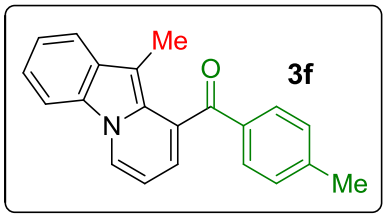
Phenyl (10-(o-tolyl)pyrido[1,2-a]indol-9-yl)methanone (3c): Prepared by following general procedure-1. Obtained as a red solid. Yield = 73%; m. p.= 74-75 °C; R_f = 0.5 (Ethyl Acetate/Hexane : 20/80); ^1H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 7.0 Hz, 1H), 7.97 (d, *J* = 7.2 Hz, 1H), 7.42 – 7.24 (m, 6H), 7.13 (t, *J* = 7.6 Hz, 2H), 7.05 (t, *J* = 6.2 Hz, 2H), 6.95 – 6.89 (m, 3H), 6.60 (t, *J* = 6.8 Hz, 1H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2, 138.0, 137.3, 133.4, 132.6, 132.1, 131.7, 130.3, 130.0, 129.2, 129.1, 128.7, 128.0, 127.2, 126.5, 125.6, 124.7, 123.5, 121.0, 120.2, 110.3, 107.8, 106.9, 20.4; IR (neat): 1661, 1650, 1600, 1526, 1456, 1278, 1175, 1013, 960 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{26}H_{20}NO$ $(M+H)^+$ 362.1539, found 362.1513.



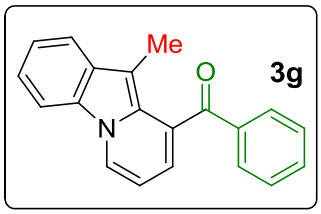
(4-fluorophenyl)(10-(2-fluorophenyl)pyrido[1,2-a]indol-9-yl)methanone (3d): Prepared by following general procedure-1. Obtained as a red solid. Yield = 75%; m. p. = 170-171 °C; R_f = 0.35 (Ethyl Acetate/Hexane : 10/90); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 6.9 Hz, 1H), 7.98 – 7.94 (m, 1H), 7.64 (d, *J* = 5.1 Hz, 1H), 7.48 (dd, *J* = 8.2 Hz, 5.7 Hz, 2H), 7.41 – 7.39 (m, 2H), 7.25 – 7.10 (m, 3H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.86 (t, *J* = 8.5 Hz, 2H), 6.80 (t, *J* = 9.0 Hz, 1H), 6.64 (t, *J* = 6.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6 (s), 165.5 (d, *J* = 254.5 Hz), 160.4 (d, *J* = 245.6 Hz), 133.4 (d, *J* = 2.9 Hz), 132.2 (d, *J* = 3.5 Hz), 131.8 (d, *J* = 9.4 Hz), 130.7 (s), 130.6 (s), 129.4 (s), 129.0 (s), 128.5 (d, *J* = 8.0 Hz), 127.0 (s), 126.7 (s), 124.0 (s), 123.9 (d, *J* = 3.4 Hz), 122.5 (d, *J* = 16.1 Hz), 121.4 (s), 119.8 (s), 115.3 (d, *J* = 22.3 Hz), 115.1 (d, *J* = 22 Hz), 110.3 (s), 107.0 (s), 101.6 (s); IR (Neat): 1663, 1632, 1507, 1464 1258, 960 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{25}H_{16}F_2NO$ $(M+H)^+$ 384.1194, found 384.1195.



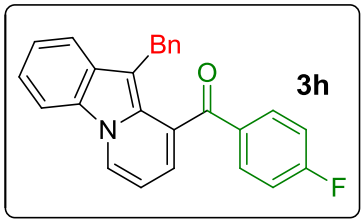
(10-(naphthalen-1-yl)pyrido[1,2-a]indol-9-yl)(p-tolyl)methanone (3e): Prepared by following general procedure-1. Obtained as a red liquid. Yield = 71%; R_f = 0.5 (Ethyl Acetate/Hexane : 20/80); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 6.9 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 5.6 Hz, 2H), 7.34 – 7.13 (m, 7H), 7.05 – 7.00 (m, 2H), 6.82 (d, *J* = 7.8 Hz, 2H), 6.56 (t, *J* = 6.7 Hz, 1H), 6.38 (d, *J* = 7.7 Hz, 2H), 1.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.1, 142.6, 133.9, 133.86, 132.4, 132.2, 132.1, 131.8, 129.7, 129.3, 129.2, 128.3, 128.2, 128.0, 127.8, 127.1, 126.5, 125.5, 125.2, 125.0, 123.6, 121.1, 120.5, 110.4, 107.3, 106.3, 21.4; IR (neat): 1660, 1651, 1605, 1526, 1464, 1279, 1177, 960 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{30}H_{22}NO$ $(M+H)^+$ 412.1696, found 412.1654.



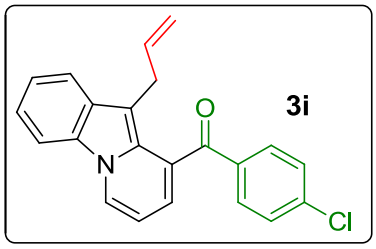
(10-methylpyrido[1,2-a]indol-9-yl)(p-tolyl)methanone (3f): Prepared by following general procedure-1. Obtained as a red viscous liquid. Yield = 68%; R_f = 0.3 (Ethyl Acetate/Hexane : 10/90); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 7.1 Hz, 0.8 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.35 – 7.32 (m, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 6.92 (dd, *J* = 6.5 Hz, 0.8 Hz, 1H), 6.44 (t, *J* = 6.8 Hz, 1H), 2.43 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.8, 144.6, 135.1, 131.2, 130.5, 130.1, 129.6, 129.5, 129.0, 126.6, 124.1, 123.0, 120.6, 119.1, 110.1, 105.6, 101.1, 21.9, 10.3; IR (neat): 1661, 1649, 1605, 1456, 1271, 1179, 1020, 955 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{21}H_{18}NO$ $(M+H)^+$ 300.1383, found 300.1378.



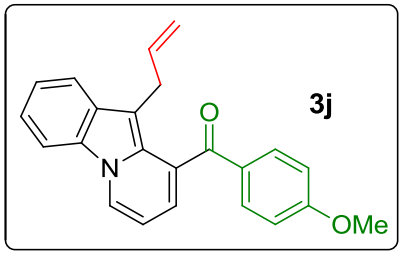
(10-methyl pyrido[1,2-a]indol-9-yl)(phenyl)methanone (3g): Prepared by following general procedure-1. Obtained as a red solid. Yield = 69%; m. p. = 126-127 °C; R_f = 0.3 (Ethyl Acetate/Hexane : 10/90); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 7.1 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.36 (dd, *J* = 11.2, 4.0 Hz, 1H), 6.97 (d, *J* = 6.5 Hz, 1H), 6.45 (t, *J* = 6.8 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.0, 137.7, 133.5, 130.9, 130.4, 130.1, 129.5, 129.0, 128.7, 126.9, 124.7, 123.0, 120.7, 119.1, 110.1, 105.5, 101.2, 10.3; IR (neat): 1661, 1643, 1596, 1465, 1272, 1080, 955 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{20}H_{16}NO$ $(M+H)^+$ 286.1226, found 286.1248.



(10-benzylpyrido[1,2-a]indol-9-yl)(4-fluorophenyl)methanone (3h): Prepared by following general procedure-1. Obtained as a red liquid. Yield = 67%; R_f = 0.5 (Ethyl Acetate/Hexane : 20/80); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 6.6 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.44 – 7.34 (m, 2H), 6.96 (t, *J* = 8.6 Hz, 2H), 6.92 – 6.81 (m, 6H), 6.47 (t, *J* = 6.8 Hz, 1H), 4.20 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.9 (s), 165.8 (d, *J* = 255 Hz), 141.1 (s), 133.5 (d, *J* = 2.9 Hz), 132.9 (d, *J* = 9.5 Hz), 130.5 (d, *J* = 21.4 Hz), 129.6 (s), 129.2 (s), 128.6 (s), 128.0 (s), 127.1 (s), 125.6 (s), 125.3 (s), 123.5 (s), 121.0 (s), 119.4 (s), 115.5 (d, *J* = 22.0 Hz), 110.2 (s), 105.6 (s), 104.9 (s), 30.5 (s); IR (neat): 1660, 1651, 1608, 1451, 1262, 1145, 1068, 950 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{26}H_{19}FNO$ $(M+H)^+$ 380.1445, found 380.1479.

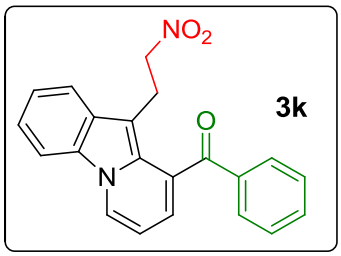


(10-allyl pyrido[1,2-a]indol-9-yl)(4-chlorophenyl)methanone (3i): Prepared by following general procedure-1. Obtained as a red solid. Yield = 61%; m. p. = 124-125 °C; R_f = 0.5 (Ethyl Acetate/Hexane : 20/80); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.0 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.32 (m, 3H), 7.28 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 6.5 Hz, 1H), 6.39 (t, *J* = 6.8 Hz, 1H), 5.67 – 5.59 (m, 1H), 4.72 – 4.64 (m, 2H), 3.48 (d, *J* = 5.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.3, 139.9, 136.6, 135.9, 131.9, 130.3, 129.8, 129.3, 129.25, 129.0, 127.3, 125.8, 123.3, 121.0, 119.4, 115.1, 110.2, 105.5, 103.7, 29.1; IR (neat): 1660, 1645, 1586, 1465, 1268, 1091 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{22}H_{17}ClNO$ $(M+H)^+$ 346.0993, found 346.0986.

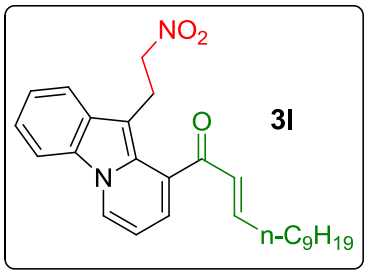


(10-allyl pyrido[1,2-a]indol-9-yl)(4-methoxyphenyl)methanone (3j): Prepared by following general procedure-1. Obtained as a red viscous liquid. Yield = 58%; R_f = 0.3 (Ethyl

Acetate/Hexane : 20/80); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 6.6 Hz, 1H), 7.93 (d, *J* = 8.9 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.1 Hz, 1H), 7.35 (t, *J* = 7.1 Hz, 1H), 7.96 – 6.90 (m, 3H), 6.47 (t, *J* = 6.8 Hz, 1H), 5.78 – 5.67 (m, 1H), 4.86 – 4.74 (m, 2H), 3.88 (s, 3H), 3.55 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.7, 136.9, 132.9, 131.1, 130.4, 129.7, 129.6, 129.3, 126.5, 124.3, 123.1, 120.7, 119.4, 114.8, 113.9, 110.2, 105.7, 103.3, 55.7, 29.2; IR (neat): 1654, 1634, 1520, 1462, 1266, 1020 cm^{-1}.

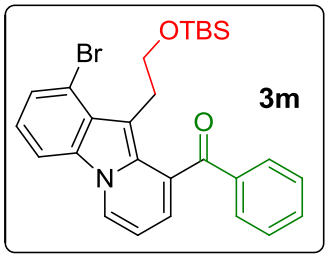


(10-(2-nitroethyl)pyrido[1,2-a]indol-9-yl)(phenyl)methanone (3k): Prepared by following general procedure-1. Obtained as a red solid. Yield = 72%; m. p. = 164-165 °C; R_f = 0.4 (Ethyl Acetate/Hexane : 20/80); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.0 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 6.6 Hz, 1H), 6.45 (t, *J* = 6.8 Hz, 1H), 4.47 (t, *J* = 7.5 Hz, 2H), 3.49 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.0, 137.3, 133.9, 130.6, 130.3, 129.8, 129.5, 129.3, 128.9, 127.5, 127.4, 124.0, 121.4, 118.4, 110.5, 106.0, 99.5, 74.7, 23.7; IR (neat): 1661, 1650, 1550, 1465, 1270, 1151, 1015 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{21}H_{17}N_2O_3$ $(M+H)^+$ 345.1234, found 345.1238.

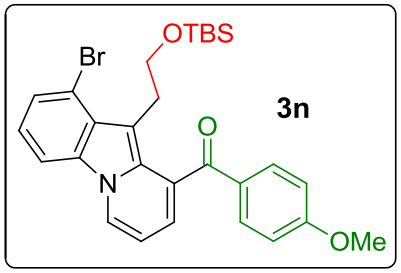


(*E*)-1-(10-(2-nitroethyl)pyrido[1,2-a]indol-9-yl)dodec-2-en-1-one (3l): Prepared by following general procedure-1. Obtained as a red viscous liquid. Yield = 66%; m. p.=201-202 °C; R_f = 0.41 (Ethyl Acetate/Hexane : 20/80); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.1 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.29 – 7.25 (m, 1H), 7.07 (dd, *J* = 6.6, 0.9 Hz, 1H), 6.91 (dt, *J* = 15.7, 6.9 Hz, 1H), 6.53 (dt, *J* = 15.7, 1.4 Hz, 1H), 6.42 – 6.39 (m, 1H), 4.60 – 4.55 (m, 2H), 3.57 – 3.54 (m, 2H), 2.28 – 2.23 (m, 2H), 1.44 – 1.41 (m, 2H), 1.29 –

1.14 (m, 12H), 0.80 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.2, 153.3, 130.5, 129.8, 129.5, 129.2, 127.4, 126.2, 123.9, 121.3, 118.4, 110.7, 110.3, 105.9, 99.6, 75.0, 33.0, 32.0, 29.6, 29.5, 29.4, 28.2, 23.8, 22.8, 14.2; IR (neat): 1669, 1649, 1616, 1551, 1465, 1379, 1120, 1016, 995 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{26}H_{33}N_2O_3$ $(M+H)^+$ 421.2486, found 421.2494.

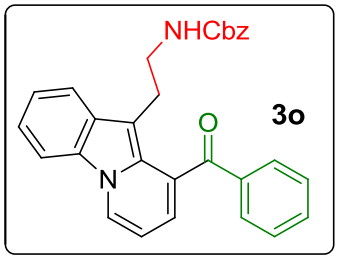


(1-bromo-10-(2-((tert-butyldimethylsilyl)oxy)ethyl)pyrido[1,2-a]indol-9-yl)(phenyl)methanone (3m): Prepared by following general procedure-1. Obtained as a red viscous liquid. Yield = 71%; R_f = 0.5 (Ethyl Acetate/Hexane : 20/80); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 7.1, 1.0 Hz, 1H), 8.06 (d, *J* = 1.6 Hz, 1H), 7.99 – 7.97 (m, 2H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.54 – 7.50 (m, 2H), 7.43 (dd, *J* = 8.7, 1.8 Hz, 1H), 6.98 (dd, *J* = 6.6, 1.0 Hz, 1H), 6.53 (t, *J* = 6.8 Hz, 1H), 3.57 (t, *J* = 7.1 Hz, 2H), 2.98 (t, *J* = 7.1 Hz, 2H), 0.79 (s, 9H), -0.15 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.6, 137.2, 133.9, 131.9, 130.7, 130.6, 130.5, 128.9, 127.7, 126.7, 125.3, 123.7, 122.6, 116.7, 111.4, 106.2, 103.1, 63.3, 28.6, 26.1, 18.4, -5.4; IR (neat): 1662, 1599, 1466, 1270, 1095, 936 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{27}H_{31}BrNO_2Si$ $(M+H)^+$ 508.1302, found 508.1304.

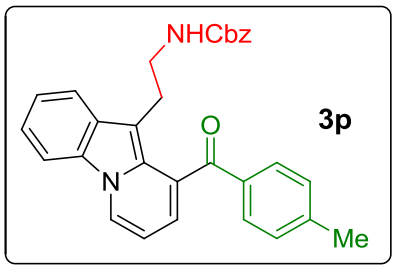


(1-bromo-10-(2-((tert-butyldimethylsilyl)oxy)ethyl)pyrido[1,2-a]indol-9-yl)(4-methoxyphenyl) methanone (3n): Prepared by following general procedure-1. Obtained as a red viscous liquid. Yield = 69%; R_f = 0.3 (Ethyl Acetate/Hexane : 20/80); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.1 Hz, 1H), 8.01 (d, *J* = 1.8 Hz, 1H), 7.94 – 7.92 (m, 2H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.38 (dd, *J* = 8.7, 1.7 Hz, 1H), 6.96 – 6.94 (m, 2H), 6.90 (d, *J* = 6.5 Hz, 1H), 6.50 (t, *J* = 6.8 Hz, 1H), 3.88 (s, 3H), 3.53 (t, *J* = 7.2 Hz, 2H), 2.92 (t, *J* = 7.2 Hz, 2H), 0.77 (s, 9H), -0.16 (s, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 193.5, 164.3, 132.9, 131.8, 131.1, 130.7, 130.1, 127.7,

126.2, 124.1, 123.5, 122.5, 116.6, 114.1, 111.4, 106.4, 102.7, 63.4, 55.7, 28.5, 26.1, 18.4, -5.4; IR (neat): 1660, 1650, 1599, 1466, 1260, 1168, 1029, 935 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{28}H_{33}BrNO_3Si$ $(M+H)^+$ 538.1408, found 538.1426.

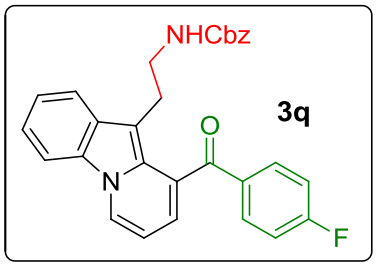


benzyl (2-(9-benzoylpyrido[1,2-a]indol-10-yl)ethyl)carbamate (3o): Prepared by following general procedure-1. Obtained as a red solid. Yield = 72%; m. p. = 105-106 °C; R_f = 0.3 (Ethyl Acetate/Hexane : 20/80); ^1H NMR (500 MHz, $CDCl_3$) δ 8.43 (d, *J* = 7.0 Hz, 1H), 7.95 (d, *J* = 7.4 Hz, 2H), 7.89 (t, *J* = 6.8 Hz, 2H); 7.62 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.39 – 7.28 (m, 6H), 6.95 (d, *J* = 6.5 Hz, 1H), 6.46 (t, *J* = 6.8 Hz, 1H), 5.04 (s, 3H), 3.39 – 3.33 (m, 2H), 3.03 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.4, 156.5, 137.5, 136.9, 133.8, 130.5, 130.2, 129.9, 129.8, 129.3, 128.8, 128.6, 128.14, 128.1, 127.2, 126.1, 123.6, 121.1, 119.4, 110.2, 105.5, 102.9, 66.5, 41.3, 25.3; IR (neat): 3365, 1715, 1661, 1650, 1596, 1455, 1208, 1130, 910 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{29}H_{25}N_2O_3$ $(M+H)^+$ 449.1726, found 449.1704.

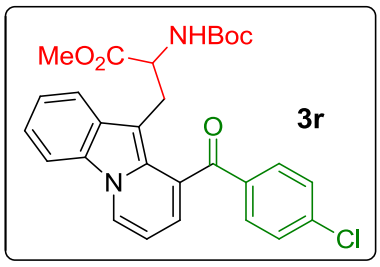


benzyl(2-(9-(4-methylbenzoyl)pyrido[1,2-a]indol-10-yl)ethyl)carbamate (3p): Prepared by following general procedure-1. Obtained as a red viscous liquid. Yield = 74%; R_f = 0.34 (Ethyl Acetate/Hexane : 20/80); ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.0 Hz, 1H), 7.85 (dd, *J* = 13.5, 8.2 Hz, 4H), 7.43 – 7.24 (m, 9H), 6.90 (d, *J* = 6.4 Hz, 1H), 6.44 (t, *J* = 6.8 Hz, 1H), 5.05 (br s, 1H), 5.02 (s, 2H), 3.37 – 3.29 (m, 2H), 3.00 (t, *J* = 6.9 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2, 156.6, 144.9, 136.9, 134.9, 130.6, 130.4, 129.9, 129.6, 129.2, 128.5, 128.1, 128.0, 126.9, 125.4, 123.5, 121.0, 119.4, 110.2, 105.6, 102.7, 66.5, 41.4, 25.2, 21.9; IR

(neat): 3331, 1715, 1661, 1641, 1572, 1456, 1245, 1137, 911 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{30}H_{26}N_2NaO_3$ $(M+Na)^+$ 485.1836, found 485.1865.



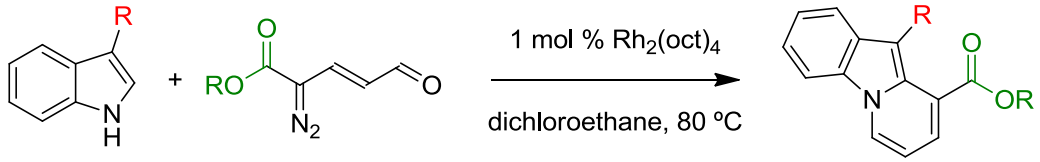
benzyl(2-(9-(4-fluorobenzoyl)pyrido[1,2-a]indol-10-yl)ethyl)carbamate (3q): Prepared by following general procedure-1. Obtained as a red viscous liquid. Yield = 70%; R_f = 0.3 (Ethyl Acetate/Hexane : 20/80); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 6.9 Hz, 1H), 7.96 (dd, *J* = 8.2, 5.6 Hz, 2H), 7.88 (d, *J* = 8.6 Hz, 2H), 7.44 – 7.25 (m, 7H), 7.14 (t, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 6.3 Hz, 1H), 6.45 (t, *J* = 6.8 Hz, 1H), 5.02 (s, 3H), 3.37 (dd, *J* = 12.7, 6.4 Hz, 2H), 3.01 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8 (s), 166.2 (d, *J* = 256 Hz), 156.5 (s), 136.9 (s), 133.8 (d, *J* = 2.8 Hz), 133.2 (d, *J* = 9.5 Hz), 129.9 (s), 129.6 (s), 129.3 (s), 128.6 (s), 128.14 (s), 128.1 (s), 127.3 (s), 125.9 (s), 123.6 (s), 121.2 (s), 119.4 (s), 116.1 (d, *J* = 22.0 Hz), 110.2 (s), 105.5 (s), 102.9 (s), 66.5 (s), 41.4 (s), 25.2 (s); IR (neat): 3369, 1715, 1660, 1640, 1586, 1456, 1247, 1131, 929 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{29}H_{24}FN_2O_3$ $(M+H)^+$ 467.1726, found 467.1749.



Methyl 2-((tert-butoxycarbonyl)amino)-3-(9-(4-chlorobenzoyl)pyrido[1,2-a]indol-10-yl)propanoate (3r): Prepared by following general procedure-1. Obtained as a red solid. Yield = 66%; m. p. = 87 ^{0}C; R_f = 0.4 (Ethyl Acetate/Hexane : 30/70); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 6.9 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.35 (m, 3H), 7.33 – 7.26 (m, 1H), 6.93 (d, *J* = 6.6 Hz, 1H), 6.39 (t, *J* = 6.8 Hz, 1H), 5.45 (d, *J* = 8.0 Hz, 1H), 4.45 – 4.38 (m, 1H), 3.52 (s, 3H), 3.34 (dd, *J* = 14.8, 5.1 Hz, 1H), 3.18 (dd, *J* = 14.8, 9.2 Hz, 1H), 1.17 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.8, 173.3, 155.6, 140.1, 136.0, 132.1,

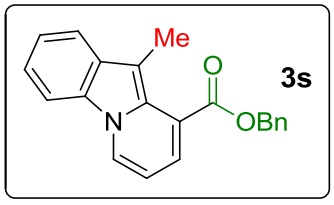
130.1, 130.0, 129.4, 129.3, 129.1, 128.2, 127.9, 123.8, 121.4, 119.3, 110.2, 105.4, 101.3, 79.5, 54.5, 52.3, 28.3, 27.8; IR (neat): 3375, 1744, 1715, 1650, 1586, 1269, 1173, 1015 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{28}H_{28}ClN_2O_5$ $(M+H)^+$ 507.1681 found 507.1699.

5. Pyridannulation with ester diazoenals:

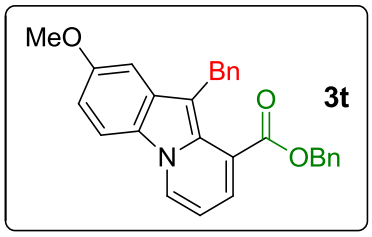


1 **2** **3**

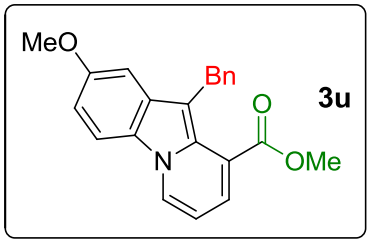
General procedure-2: A 10 ml round-bottom flask was charged with $Rh_2(oct)_4$ (0.002 mmol), 3-substituted indole **1** (0.2 mmol) and 2 ml of dichloroethane and stirred at 80 ^oC. To the contents was added a 0.1 M solution of the enaldiazo ester **2** (0.4 mmol) in dichloroethane via a syringe pump with a flow rate of 1 ml/h. The reaction was continued at the same temperature for additional 5 h. The solvent was evaporated under reduced pressure and the crude material was purified by a silica gel flash column chromatography using ethyl acetate-petroleum ether as the eluent to furnish pyrido[1,2-a]indole **3**.



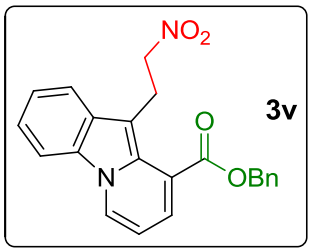
Benzyl-10-methylpyrido[1,2-a]indole-9-carboxylate (3s): Prepared by following general procedure-2. Obtained as a red liquid. Yield = 69%; R_f = 0.5 (Ethyl Acetate/Hexane : 20/80); ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.0 Hz, 1H), 7.73 (t, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 6.8 Hz, 2H), 7.36 – 7.22 (m, 6H), 6.28 (t, *J* = 6.8 Hz, 1H), 5.35 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 135.9, 130.6, 128.9, 128.8, 128.7, 128.6, 128.5, 128.1, 127.0, 123.3, 123.1, 120.7, 119.2, 110.0, 105.1, 101.6, 67.2, 10.7; IR (neat): 1715, 1609, 1526, 1465, 1360, 1183, 1025, 910 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{21}H_{18}NO_2$ $(M+H)^+$ 316.1332, found 316.1326.



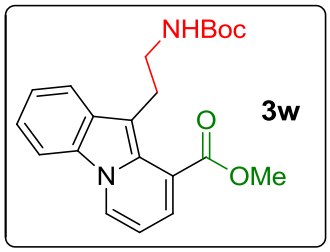
Benzyl-10-benzyl-2-methoxy pyrido[1,2-a]indole-9-carboxylate (3t): Prepared by following general procedure-2. Obtained as a red solid. Yield = 73%; m. p. = 82-83 °C; R_f = 0.4 (Ethyl Acetate/Hexane : 20/80); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 6.9, 0.7 Hz, 1H); 7.69 (d, *J* = 9.0 Hz, 1H), 7.31 (dd, *J* = 6.8, 0.9 Hz, 1H), 7.27 – 7.19 (m, 5H), 7.12 – 7.09 (m, 2H), 7.06 – 7.02 (m, 3H), 6.98 (d, *J* = 2.3 Hz, 1H), 6.90 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.34 (t, *J* = 6.9 Hz, 1H), 5.07 (s, 2H), 4.43 (s, 2H), 3.77 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 156.9, 142.0, 135.7, 131.4, 129.8, 128.7, 128.6, 128.43, 128.4, 128.3, 127.9, 127.0, 125.6, 124.4, 122.8, 112.0, 111.1, 105.3, 104.1, 99.5, 67.1, 55.8, 30.8; IR (neat): 1715, 1609, 1525, 1456, 1260, 1140, 1040, 919 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{28}H_{24}NO_3$ $(M+H)^+$ 422.1751, found 422.1777.



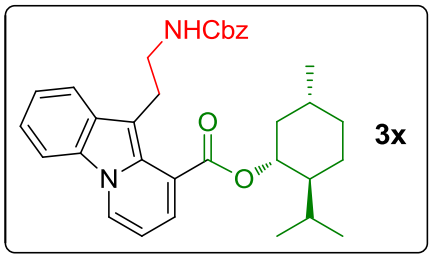
Methyl 10-benzyl-2-methoxy pyrido[1,2-a]indole-9-carboxylate (3u): Prepared by following general procedure-2. Obtained as a red liquid. Yield = 60%; R_f = 0.4 (Ethyl Acetate/Hexane : 20/80); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.29 (dd, *J* = 6.7, 1.1 Hz, 1H), 7.15 – 7.11 (m, 2H), 7.08 – 7.03 (m, 2H), 6.98 (d, *J* = 2.3 Hz, 1H), 6.91 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.37 (t, *J* = 6.9 Hz, 1H), 4.40 (s, 2H), 3.77 (s, 3H), 3.59 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 167.3, 156.9, 141.9, 131.4, 129.9, 128.3, 128.27, 127.9, 126.8, 125.6, 124.4, 122.9, 112.1, 111.2, 105.4, 103.8, 99.4, 55.8, 52.3, 30.8; IR (neat): 1715, 1610, 1588, 1474, 1276, 1160, 1034, cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{22}H_{20}NO_3$ $(M+H)^+$ 346.1438, found 346.1446.



benzyl 10-(2-nitroethyl)pyrido[1,2-a]indole-9-carboxylate (3v): Prepared by following general procedure-2. Obtained as a red solid. Yield = 70%; m. p. = 122-123 °C; R_f = 0.45 (Ethyl Acetate/Hexane : 20/80); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 7.0, 1.1 Hz, 1H), 7.71 (t, *J* = 8.6 Hz, 2H), 7.51 (dd, *J* = 6.8, 1.1 Hz, 1H), 7.40 (dd, *J* = 7.8, 1.0 Hz, 2H), 7.37– 7.24 (series of m, 5H), 6.33 (t, *J* = 6.9 Hz, 1H), 5.33 (s, 2H), 4.59 (dd, *J* = 8.2, 7.1 Hz, 2H), 3.75 – 3.71 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 135.7, 129.8, 129.6, 129.13, 129.1, 128.9, 128.71, 128.7, 128.6, 124.1, 122.1, 121.4, 118.4, 110.3, 105.8, 99.7, 75.8, 67.4, 24.0; IR (neat): 1715, 1605, 1549, 1443, 1380, 1261, 1086, 940 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{22}H_{19}N_2O_4$ $(M+H)^+$ 375.1339, found 375.1357.

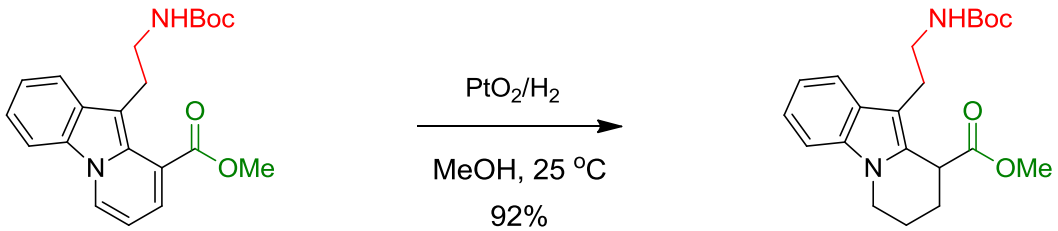


Methyl-10-(2-((tert-butoxycarbonyl)amino)ethyl)pyrido[1,2-a]indole-9-carboxylate (3w): Prepared by following general procedure-2. Obtained as a red solid; Yield = 71%; m. p. = 187-188 °C; R_f = 0.35 (Ethyl Acetate/Hexane : 20/80); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 7.0, 0.7 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.36 – 7.33 (m, 1H), 6.41 (t, *J* = 6.9 Hz, 1H), 4.83 (br s, 1H), 3.98 (s, 3H), 3.47 (dd, *J* = 12.5, 6.1 Hz, 2H), 3.30 (t, *J* = 7.0 Hz, 2H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 156.2, 130.4, 129.1, 128.9, 128.3, 127.8, 123.5, 122.8, 121.0, 119.5, 110.0, 105.3, 103.3, 78.9, 52.6, 41.7, 28.6, 25.6; IR (neat): 3387, 1715, 1666, 1526, 1465, 1270, 1179, 1085 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{21}H_{25}N_2O_4$ $(M+H)^+$ 369.1809, found 369.1795.



(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 10-(2-(((benzyloxy)carbonyl)amino)ethyl)pyrido[1,2-a]indole-9-carboxylate (3x): Prepared by following general procedure-1. Obtained as a red viscous liquid; Yield = 62%; R_f = 0.4 (Ethyl Acetate/Hexane : 20/80); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.41 (d, *J* = 7.0 Hz, 2H), 7.37 – 7.28 (m, 6H), 6.41 (t, *J* = 6.9 Hz, 1H), 5.34 (br s, 1H), 5.08 (s, 2H), 5.05 – 4.98 (m, 1H), 3.63 – 3.57 (m, 2H), 3.40 – 3.30 (m, 2H), 2.22 – 2.16 (m, 1H), 2.08 – 2.00 (m, 1H), 1.76 (d, *J* = 11.4 Hz, 2H), 1.64 – 1.50 (m, 2H), 1.22 – 1.13 (m, 2H), 0.98 (d, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 7.2 Hz, 3H), 0.96 – 0.90 (m, 1H), 0.87 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 156.7, 136.99, 130.25, 129.1, 128.52, 128.1, 128.0, 127.3, 123.6, 123.4, 121.0, 119.4, 110.0, 105.4, 103.0, 75.4, 66.4, 47.3, 42.1, 41.0, 34.4, 31.6, 26.5, 25.1, 23.4, 22.2, 21.0, 16.3; IR (neat): 3370, 1729, 1715, 1696, 1455, 1262, 1035 cm^{-1}; LRMS (ESI) *m/z* calc. for $C_{33}H_{39}N_2O_5$ $(M+H_3O)^+$ 545, found 545.

6. Synthesis of the tetrahydropyrido[1,2-a]indole 4:



3w **4**

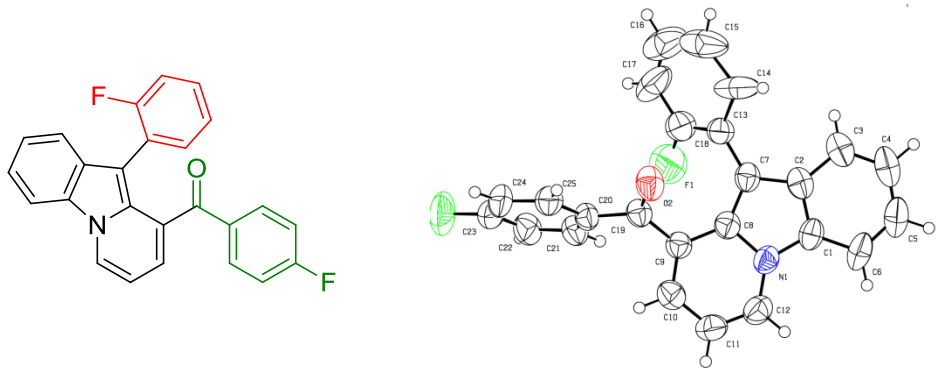
A 10 ml round bottom flask was charged with the pyrido[1,2-a]indole **3w** (50 mg, 0.136 mmol), 5 ml of anhydrous methanol and PtO_2 (3 mg). The reaction vessel was thoroughly flushed with argon followed by hydrogen. The reaction mixture was stirred under hydrogen atmosphere (hydrogen balloon) at room temperature. After 3 h, the reaction mixture was filtered through a celite pad and the solvent was evaporated under reduced pressure. Purification of the crude

material on a silica gel flash column chromatography using ethyl acetate/petroleum ether (20:80) as the eluent furnished the tetrahydropyrido[1,2-a]indole **4** as a colorless liquid (47 mg). Yield = 92%; R_f = 0.35 (Ethyl Acetate/Hexane : 30/70); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.51 (d, *J*=7.8 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 1H), 7.14 – 7.10 (m, 1H), 7.06 – 7.02 (m, 1H), 4.59 (br s, 1H), 4.18 (ddd, *J*=11.4, 5.4, 3.4 Hz, 1H), 4.06 – 4.02 (m, 1H), 3.81 – 3.72 (m, 1H), 3.65 (s, 3H), 3.41 – 3.34 (m, 1H), 3.32 –3.23 (m, 1H), 2.96 – 2.85 (m, 1H), 2.78 – 2.71 (m, 1H), 2.36 – 2.29 (m, 1H), 2.25 – 2.12 (m, 1H), 2.02 – 1.86 (m, 2H), 1.36 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 173.6, 156.1, 136.5, 130.0, 127.8, 121.4, 119.7, 118.8, 109.1, 79.1, 52.6, 42.2, 40.7, 38.8, 28.6, 25.0, 24.8, 20.2; IR (neat): 3427, 1734, 1715, 1630, 1568, 1470, 1212, 1119, 1005 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{21}H_{28}N_2O_4$ $(M+H)^+$ 373.2122, found 373.2158.

7. References:

1. Y. Jia, J. Zhu, *J. Org. Chem.* **2006**, *71*, 7826.
2. M. Kimura, M. Futamata, R. Mukai, Y. Tamaru, *J. Am. Chem. Soc*. **2005**, 127, 4592.
3. L. Han, C. Liu, W. Zhang, X.-X. Shia, S.-L. You, *Chem. Commun*. **2014**, *50*, 1231.
4. S. Cai, S. Zhang, Y. Zhao, D. Z. Wang, *Org. Lett*. **2013**, *15*, 2660.
5. (a) K. S. Feldman, P. Ngernmeesri, *Org. Lett*. **2010**, *12*, 4502.; (b) P. R.-S. Svetlana, A. Savina, G. A. Acosta, F. Albericio, M. Álvarez, *Eur. J. Org. Chem.* **2012**, 67.
6. (a) S. G. Dawande, V. Kanchupalli, J. Kalepu, H. Chennamsetti, B. S. Lad, S. Katukojvala, *Angew. Chem. Int. Ed.* **2014**, *53*, 4076; (b) K. S. Rathore, B. S. Lad, H. Chennamsetti, S. Katukojvala, *Chem. Commun*. under revision, manuscript ID: CC-COM-12-2015-010637.

8. X-ray Crystallographic Data of 3d:

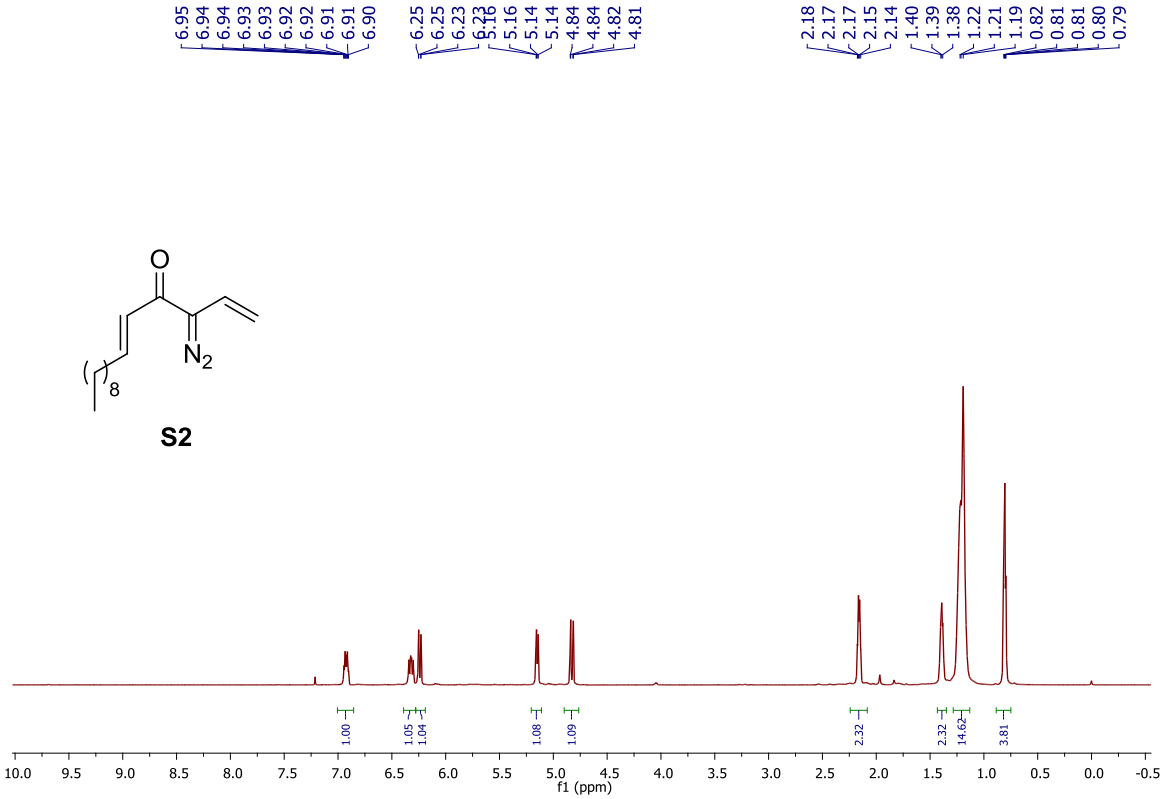


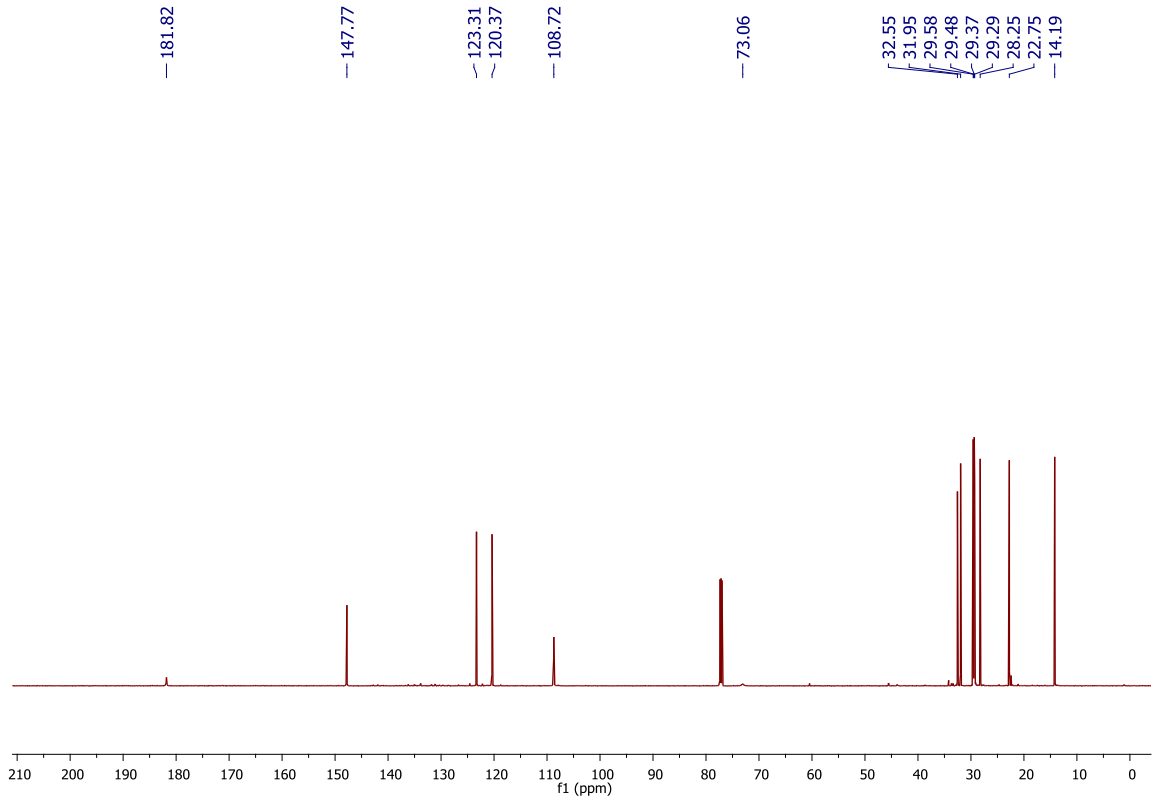
Ortep diagram of **3d**

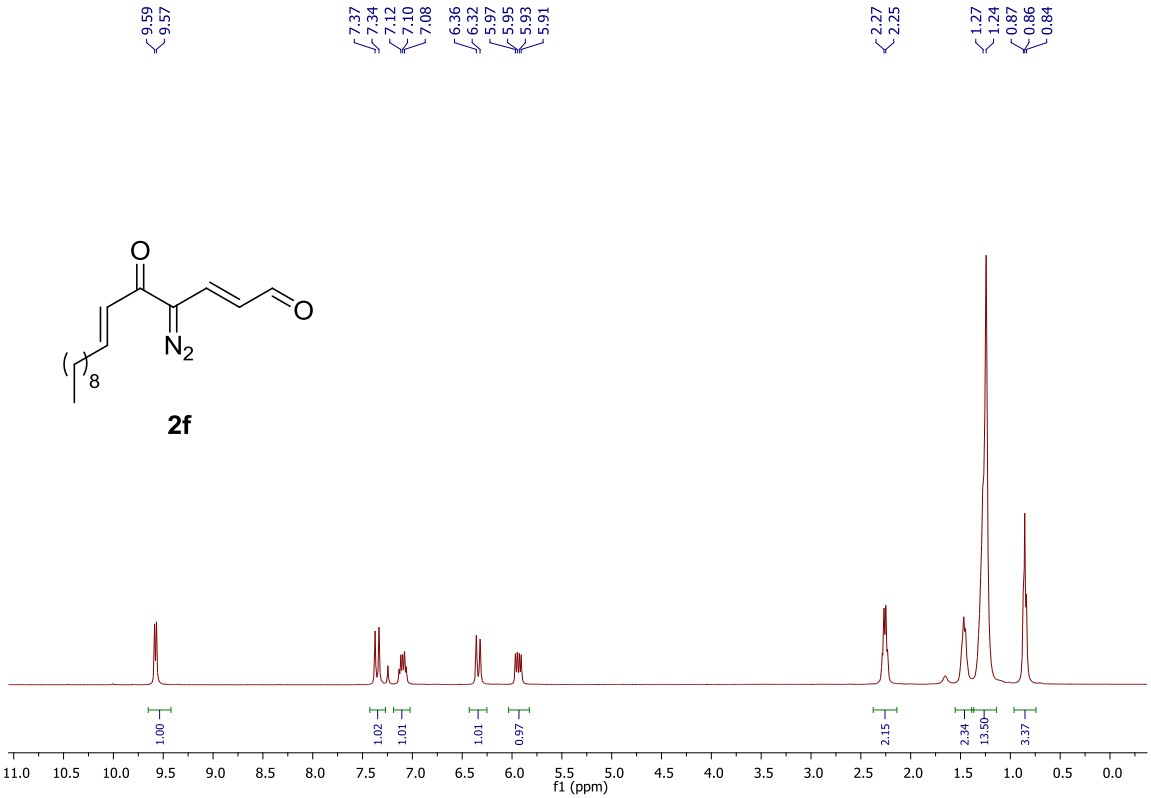
DATA	**Pyrido[1,2,a]indole 3d**
Formula	$C_{25}H_{15}F_2N_1O_1$
Formula Weight	383.38
CCDC No.	1453038
Wavelength (Å)	0.71073
Crystal System	Monoclinic
Space Group	$P2_1$
a (Å)	9.3775(7)
b (Å)	11.0241(8)
c (Å)	9.5231(6)
α (˚)	90
β (˚)	110.422(4)
γ (˚)	90
Volume	922.61(11)
Z	2
Density (g/cm^3)	1.380
μ (mm^{-1})	0.098
F (000)	396
θ (min, max)	2.28, 22.97
Treatment of Hydrogen	Fixed

$h_{min,max}/k_{min,max}/l_{min,max}$	-10, 7/ 0, 12/0, 12
No. of ref.	1237
No. unique ref./ obs. ref.	1237/1149
No. of parameters	232
R_obs, R_all,	0.0855, 0.0808
wR_2_obs, wR_2_all	0.2380, 0.2307
$\Delta\rho_{min,max}(eÅ^{-3})$	-0.323, 0.813
G. o. F	1.064

9. NMR spectra:



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9.57
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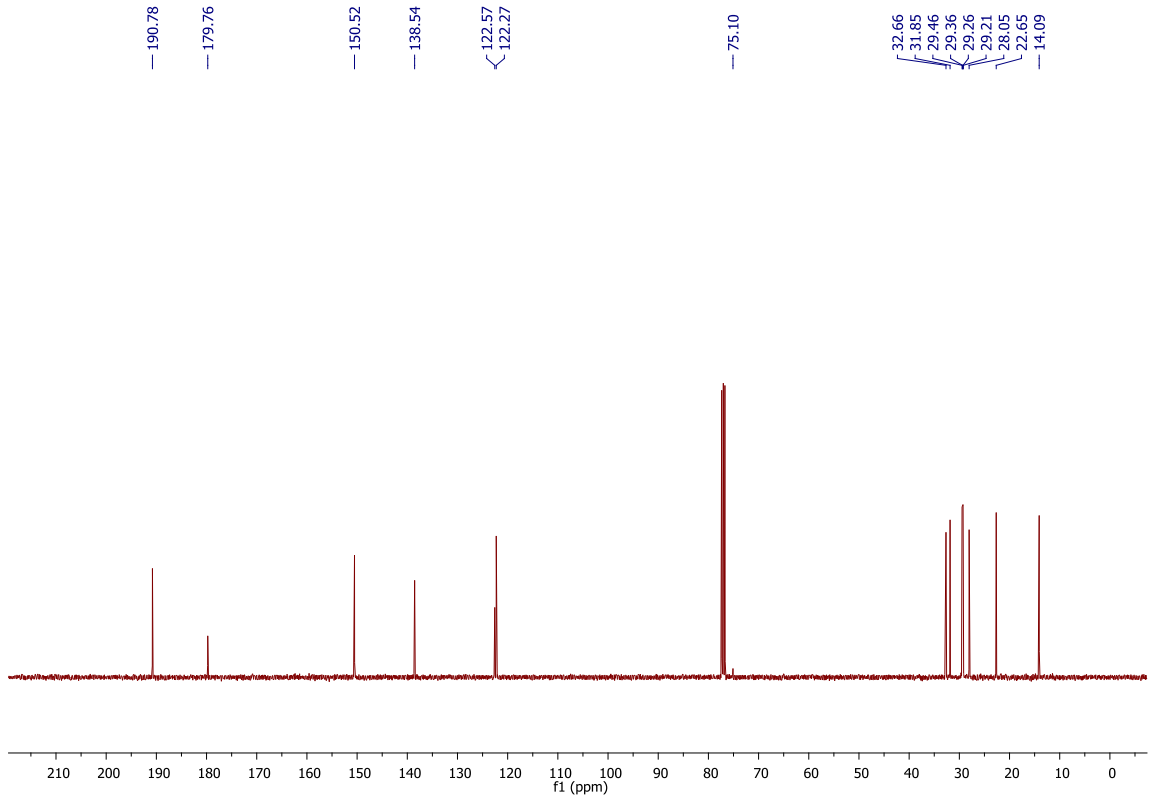
7.34
7.12
7.10
7.08
6.36
6.32
5.97
5.95
5.93
5.91
2.27
2.25
1.27
1.24
0.87
0.86
0.84
O
O
N2
8
1.00
1.02
1.01
1.01
0.97
2.15
2.34
13.50
3.37
f1 (ppm)

2f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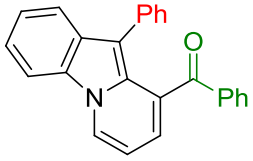
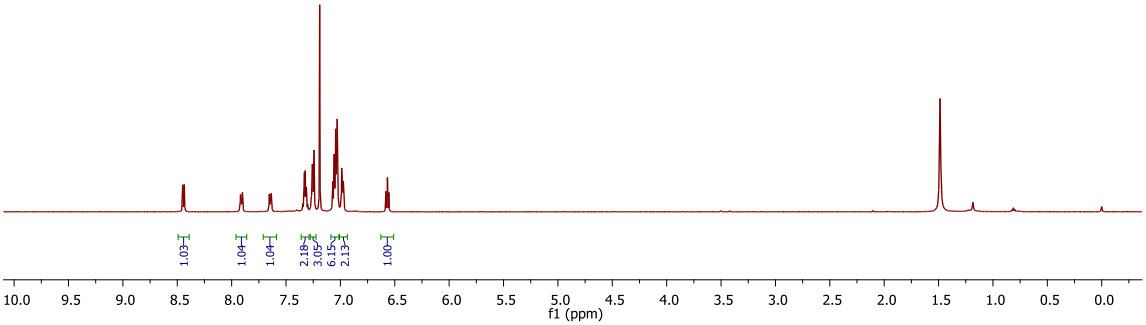
179.76
150.52
138.54
122.57
122.27
75.10
32.66
31.85
29.46
29.36
29.26
29.21
28.05
22.65
14.09
f1 (ppm)


8.45
8.44
7.26
7.26
7.24
7.06
7.04
7.03
7.03
6.58
6.57
6.55


Ph
O
N
Ph

3a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1.04
1.04
2.18
3.05
6.15
2.13
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


195.19
137.03
134.72
132.57
131.40
130.30
130.23
129.30
129.22
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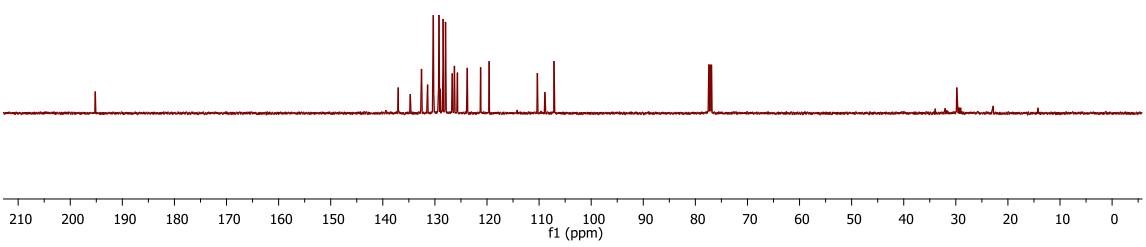
107.14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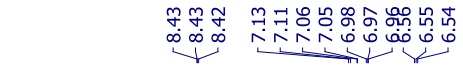
f1 (ppm)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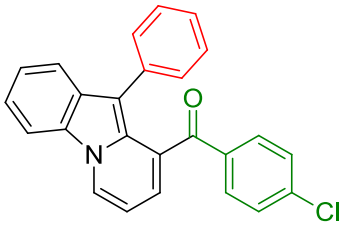
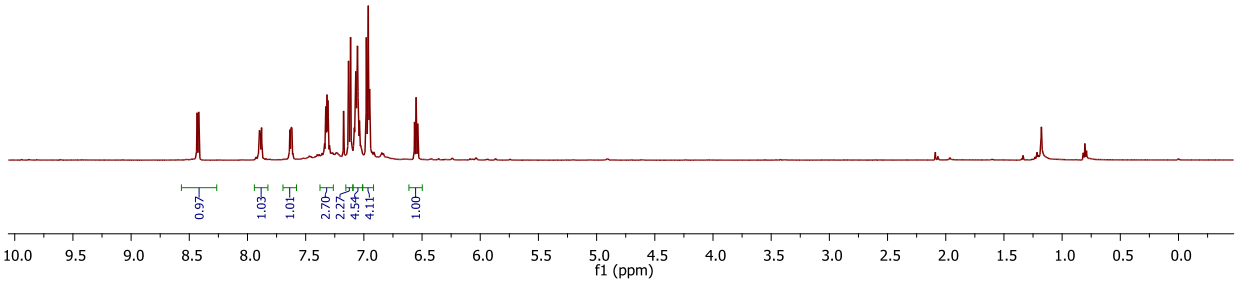
6.55
6.54


O
N
Cl

3b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1.03
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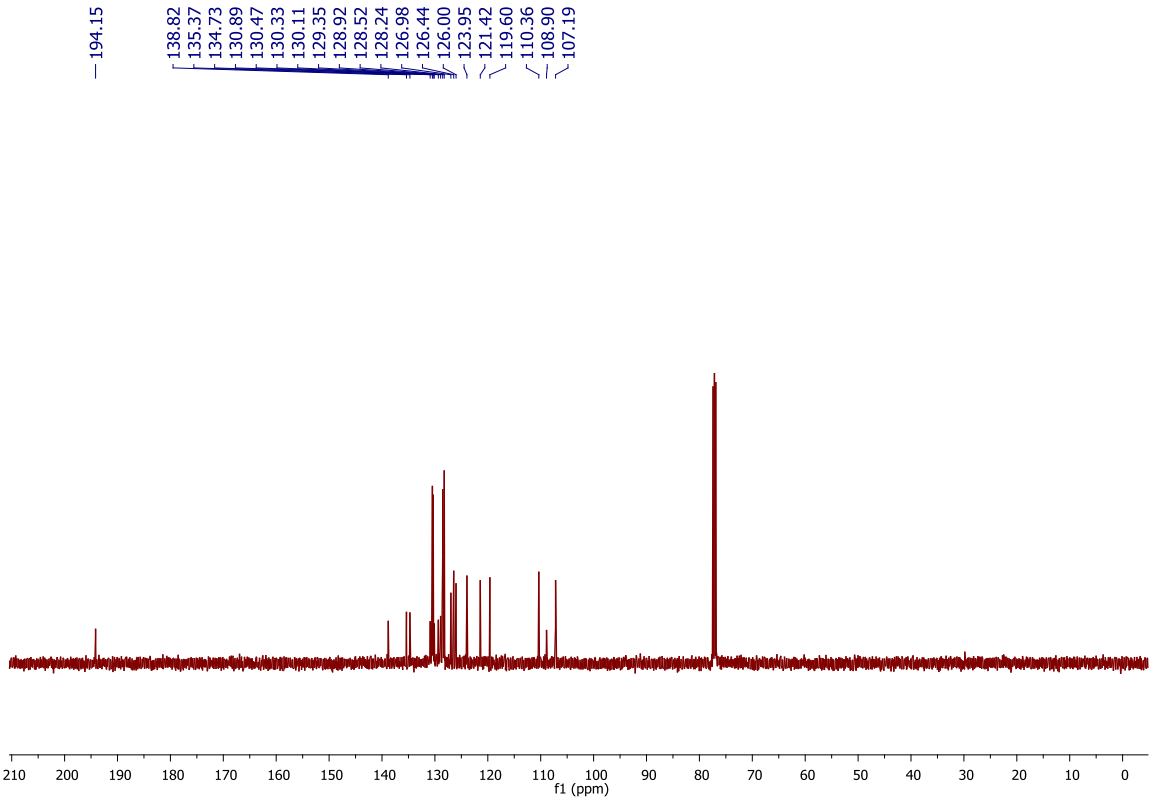
4.54
4.11
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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130.11
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128.92
128.52
128.24
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126.44
126.00
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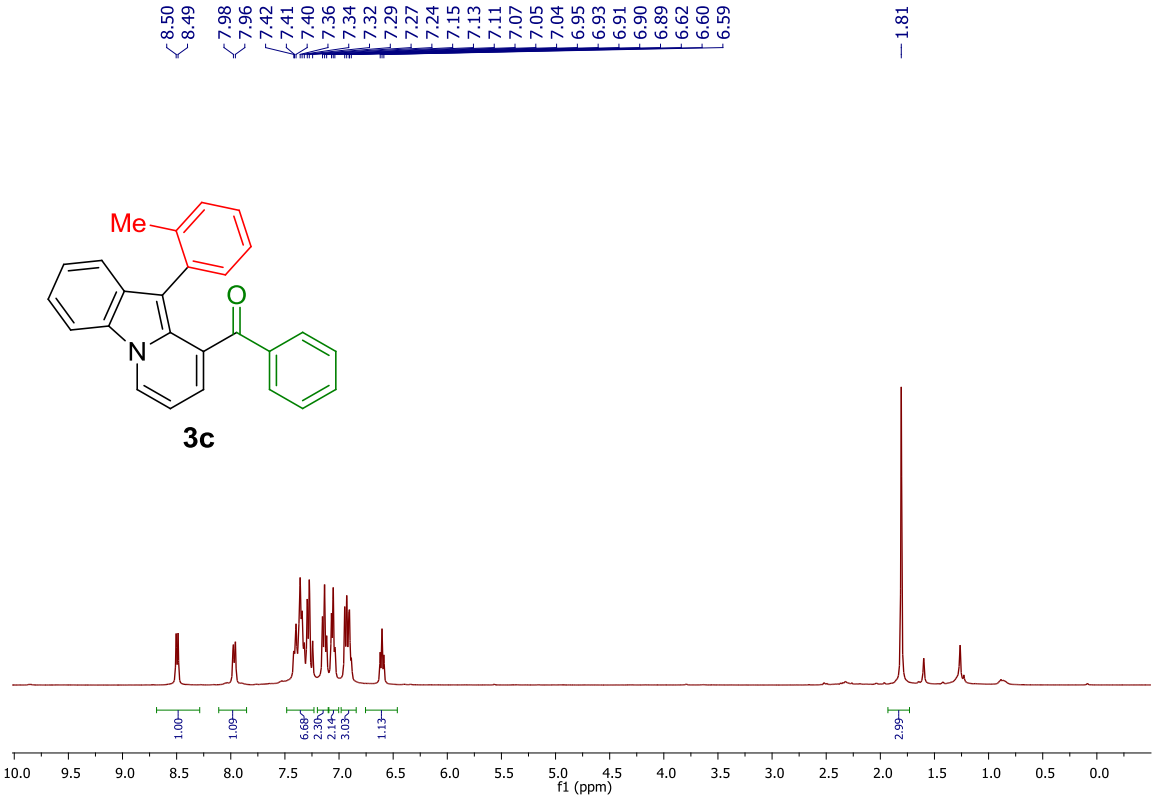
121.42
119.60
110.36
108.90
107.19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.15
7.13
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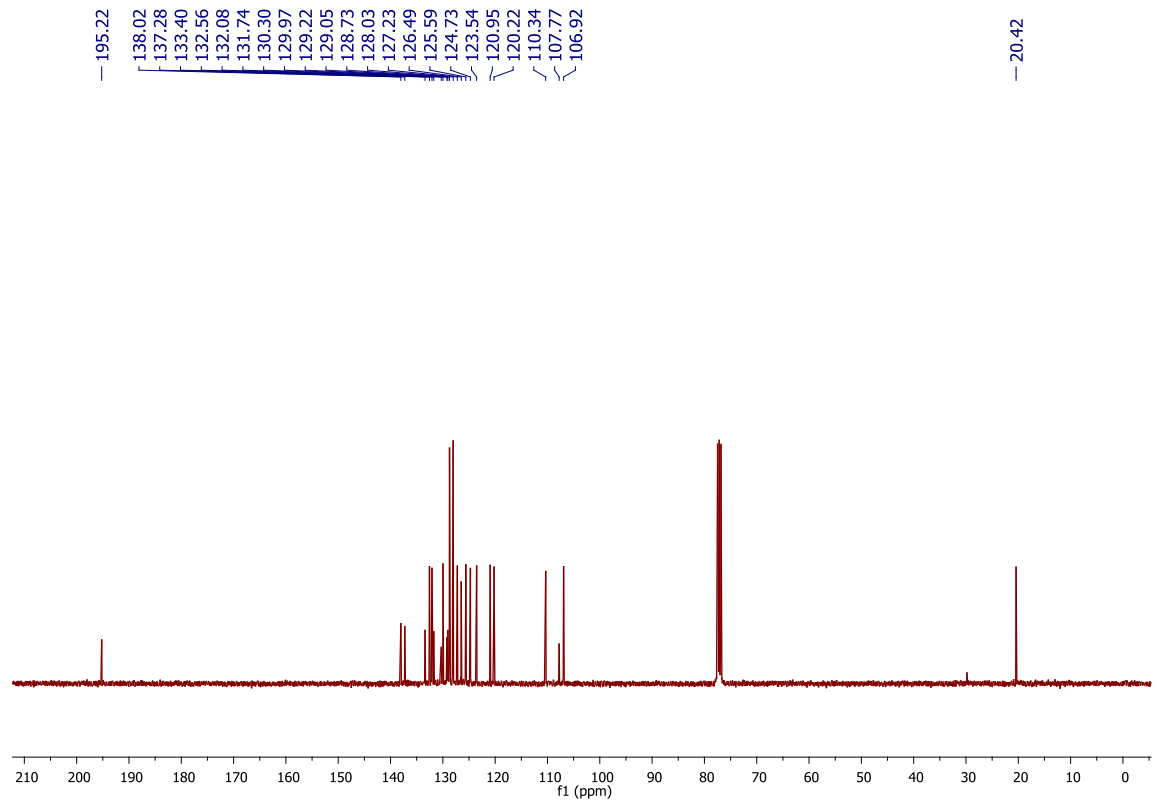
O
N
3c
1.00
1.09
6.68
2.30
2.14
3.03
1.13
2.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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107.77
106.92
20.42
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.54
8.53
7.97
7.96
7.95
7.64
7.63
7.50
7.49
7.48
7.47
7.41
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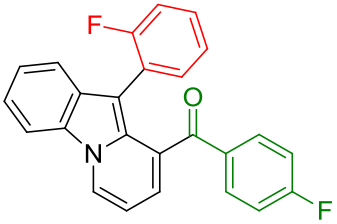
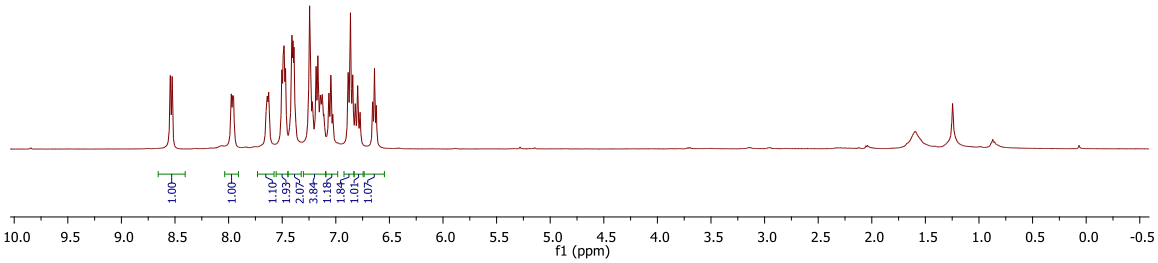
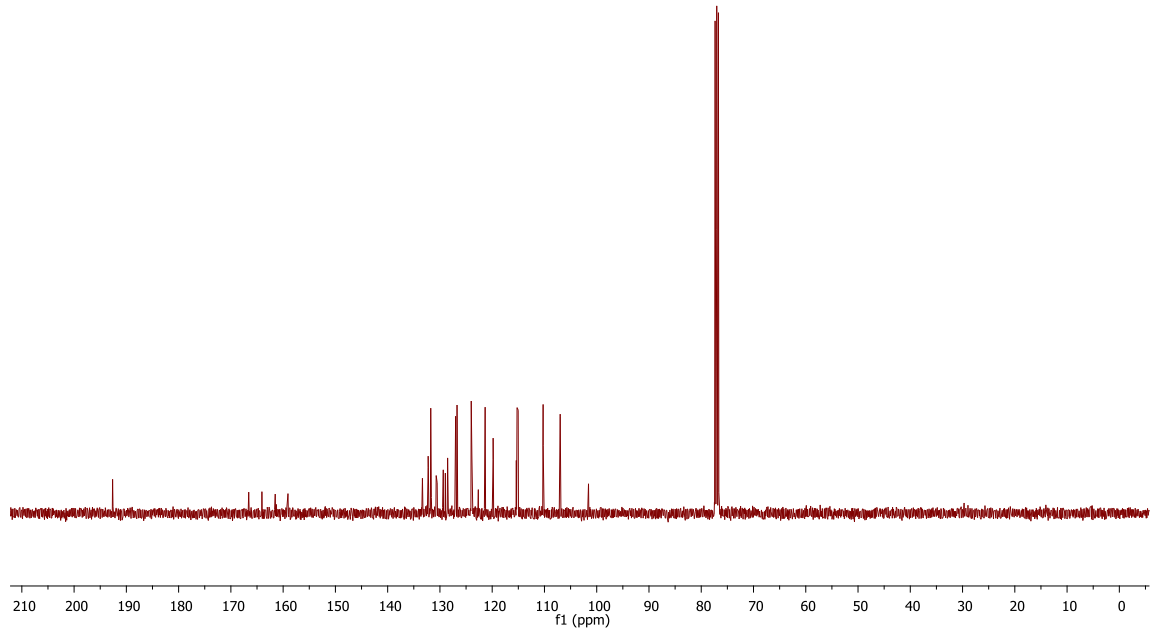
6.64
6.62


F
O
N
F

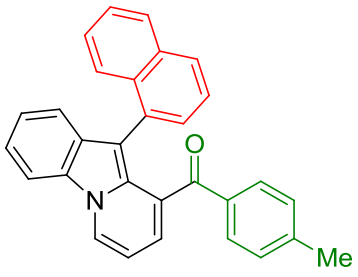
3d


1.00
1.00
1.10
1.93
2.07
3.84
1.18
1.84
1.01
1.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

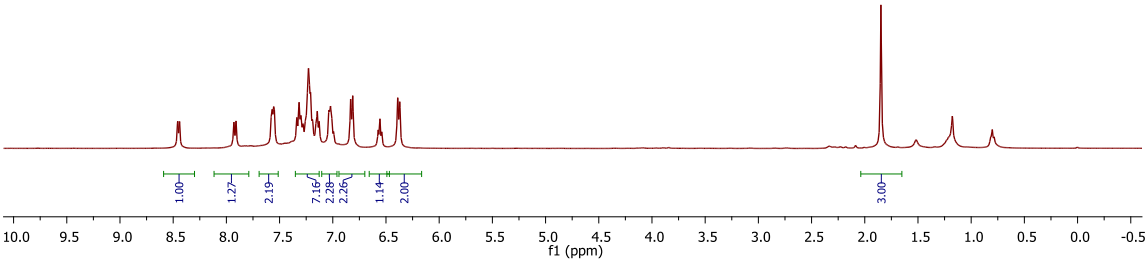

192.63
166.59
164.06
161.51
159.07
132.25
132.21
131.76
131.66
129.36
128.53
128.45
127.00
126.73
124.01
123.91
123.88
121.35
119.82
115.38
115.24
115.16
115.03
110.25
106.99
106.97

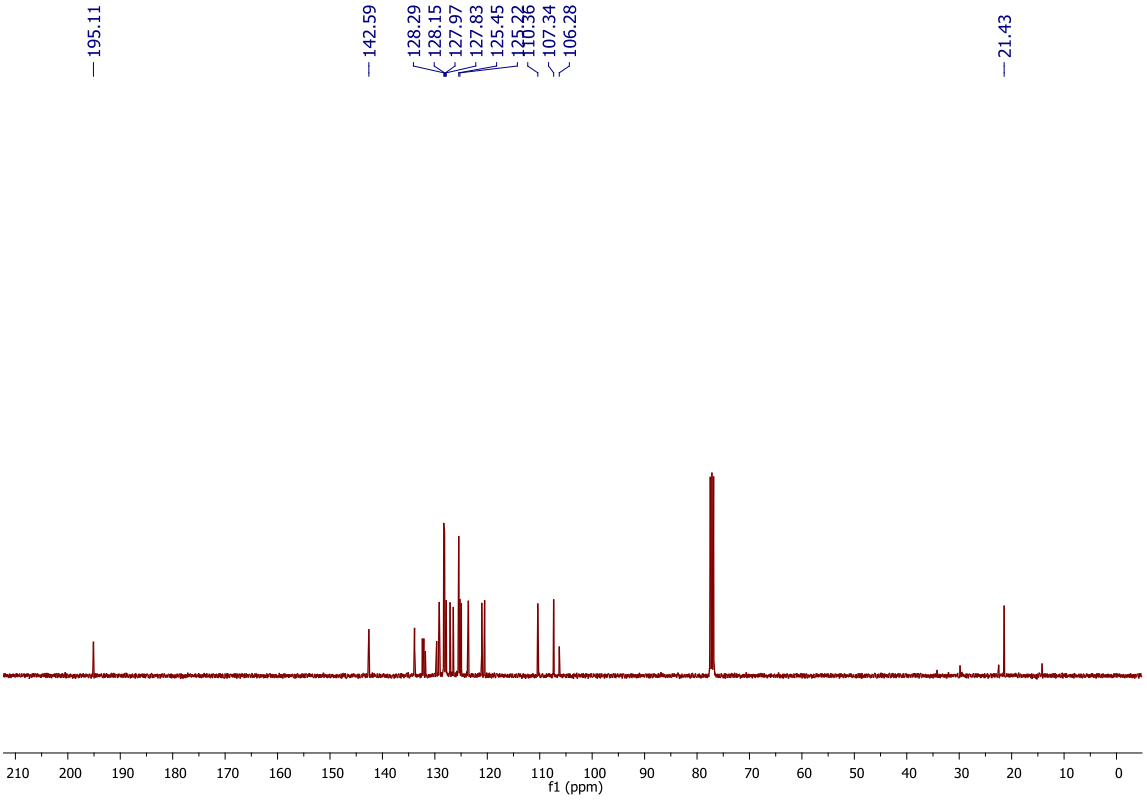

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

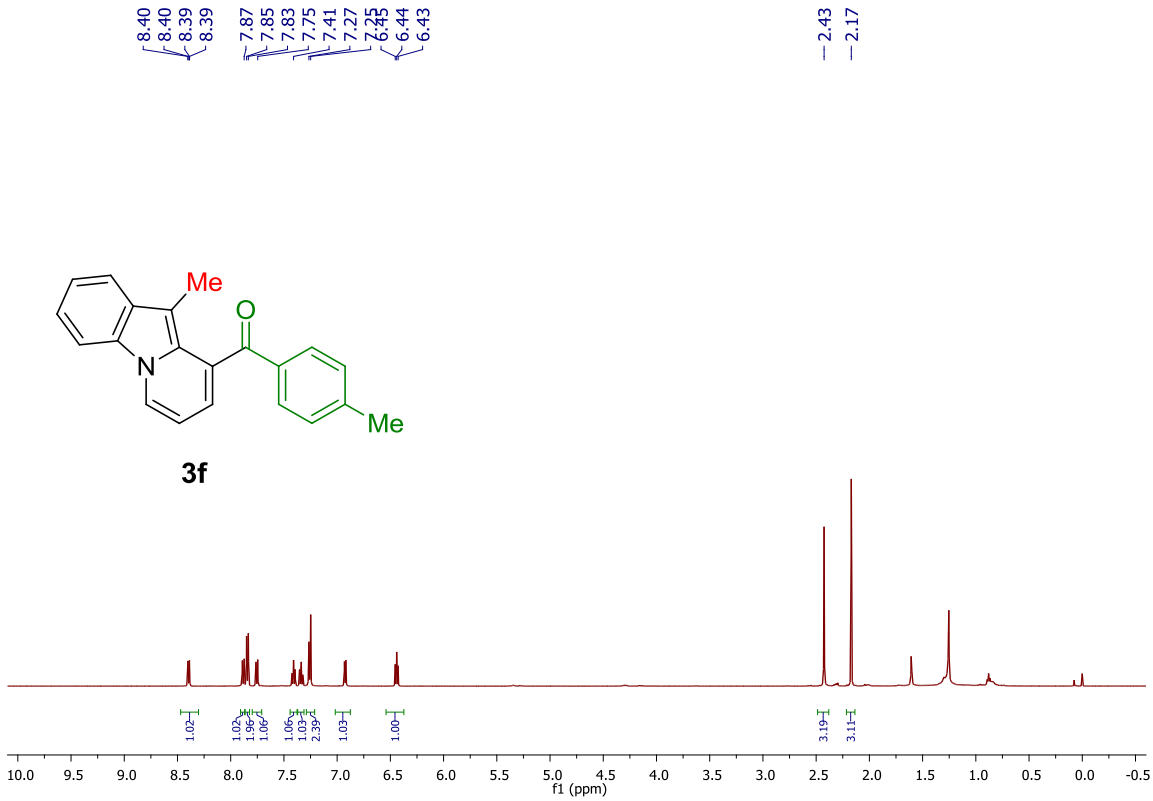

8.46
8.44
7.93
7.91
7.57
7.56
7.34
7.32
7.30
7.28
7.25
7.23
7.21
7.19
7.16
7.15
7.13
7.04
7.02
6.99
6.83
6.81
6.57
6.56
6.54
6.39
6.37
1.85

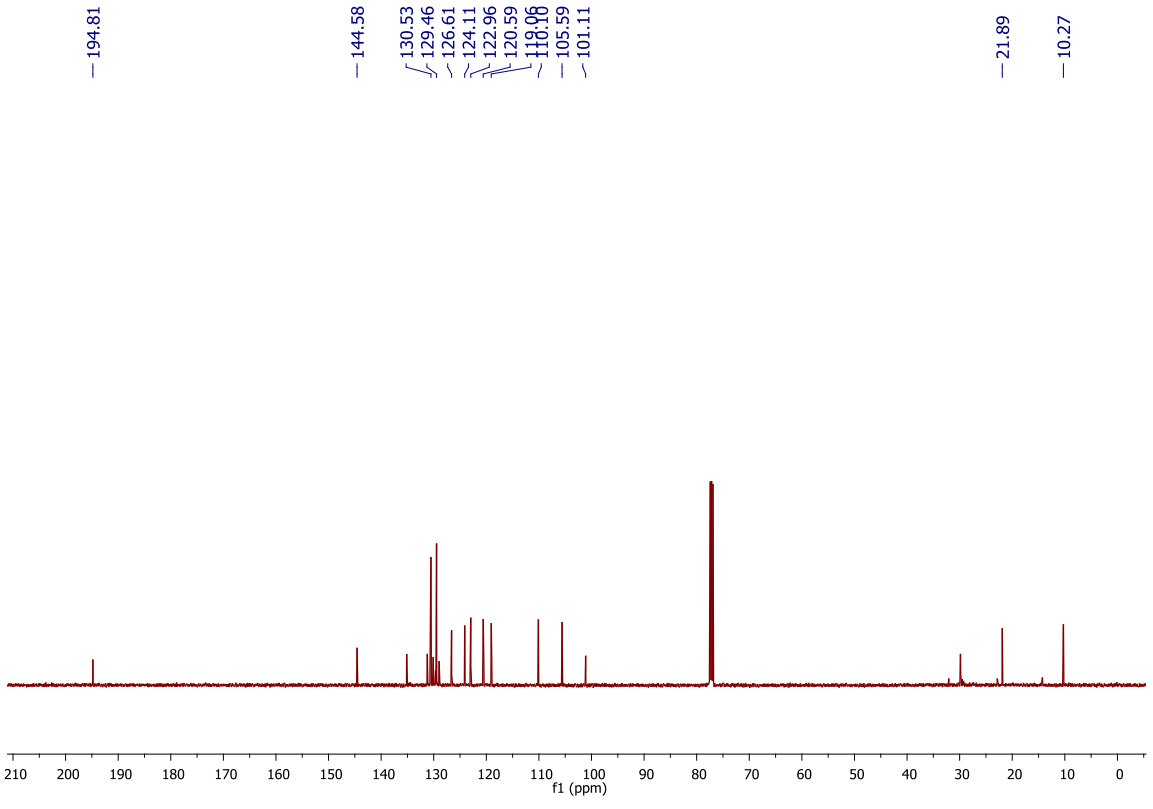

O
N
Me

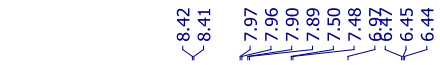
3e

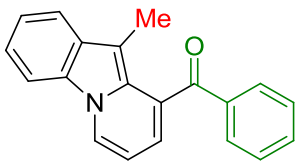

1.00
1.27
2.19
7.16
2.28
2.26
1.14
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


195.11
142.59
128.29
128.15
127.97
127.83
125.45
110.36
107.34
106.28
21.43
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

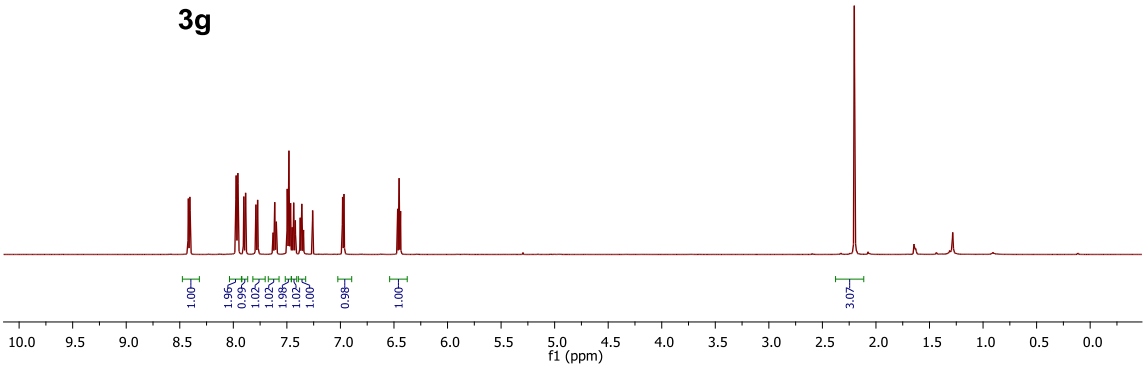

8.40
8.40
8.39
8.39
7.87
7.85
7.83
7.75
7.41
7.27
7.25
6.45
6.44
6.43
2.43
2.17
Me
O
N
Me
3f
1.02
1.02
1.96
1.06
1.06
1.03
2.39
1.03
1.00
3.19
3.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

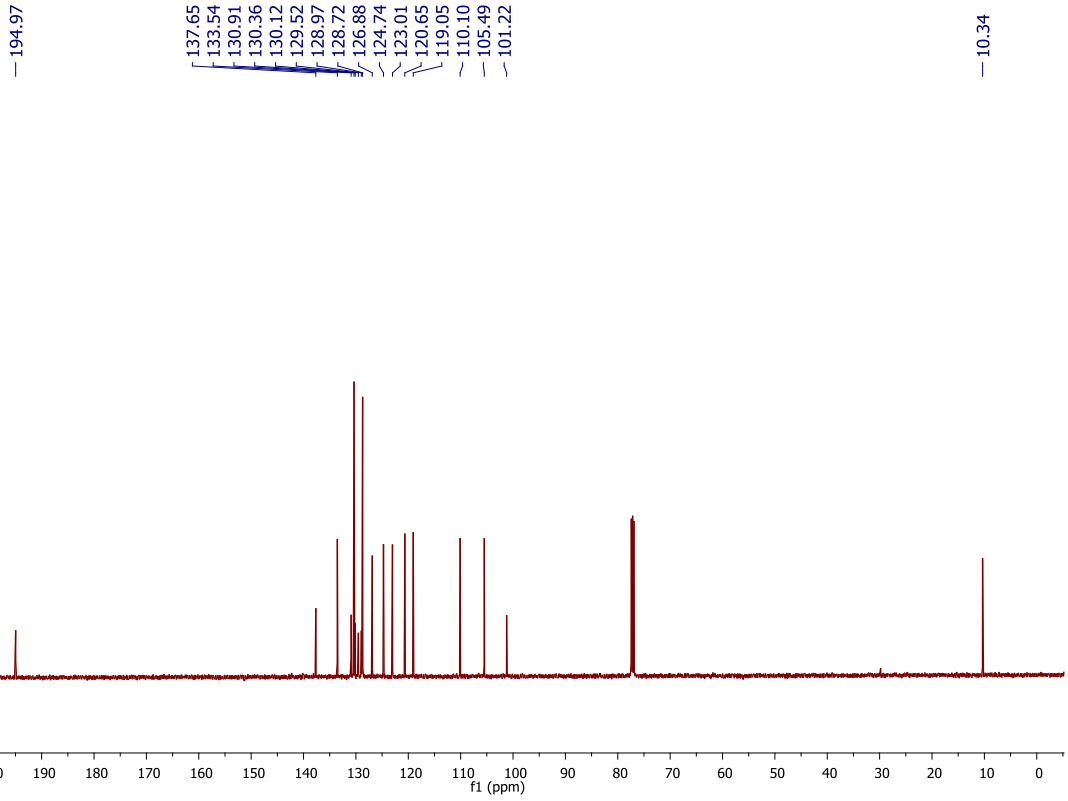

194.81
144.58
130.53
129.46
126.61
124.11
122.96
120.59
119.06
110.10
105.59
101.11
21.89
10.27
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

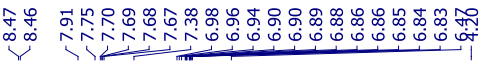

8.42
8.41
7.97
7.96
7.90
7.89
7.50
7.48
6.47
6.45
6.44
2.20

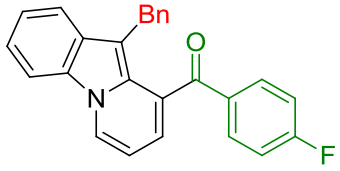

Me
O
N

3g

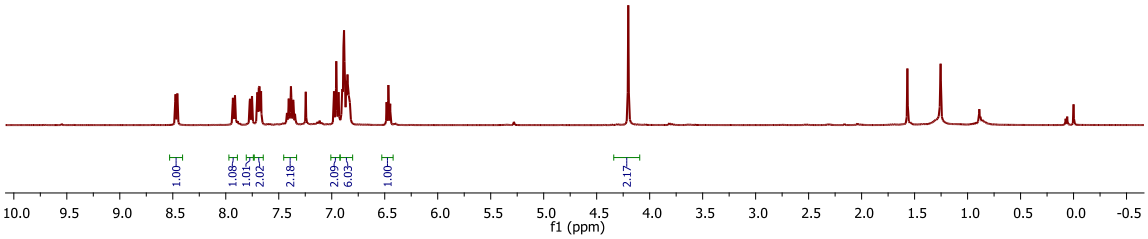

1.00
1.96
0.99
1.02
1.02
1.98
1.02
1.00
0.98
1.00
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


194.97
137.65
133.54
130.91
130.36
130.12
129.52
128.97
128.72
126.88
124.74
123.01
120.65
119.05
110.10
105.49
101.22
10.34
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.47
8.46
7.91
7.75
7.70
7.69
7.68
7.67
7.38
6.98
6.96
6.94
6.90
6.90
6.89
6.88
6.86
6.86
6.85
6.84
6.83
6.47
4.20


Bn
O
N
F

3h


1.00
1.09
1.01
2.02
2.18
2.09
6.03
1.00
2.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


192.88
167.10
164.56
141.07
133.54
133.51
132.96
132.87
130.57
130.36
129.58
129.21
128.60
127.98
127.09
125.58
125.30
123.48
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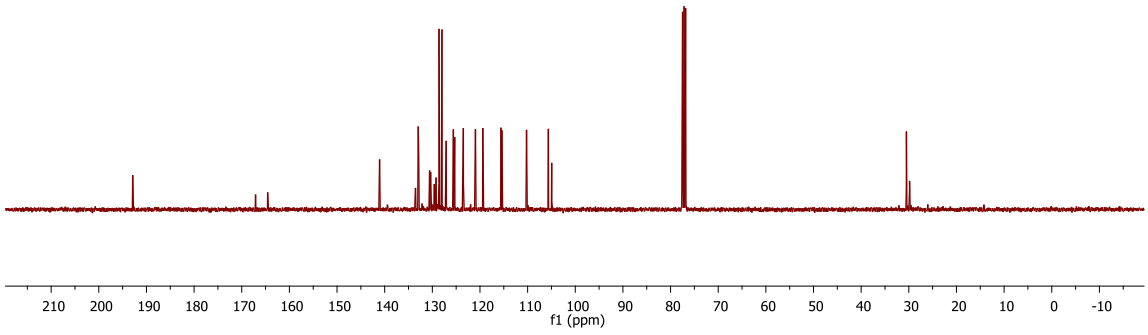
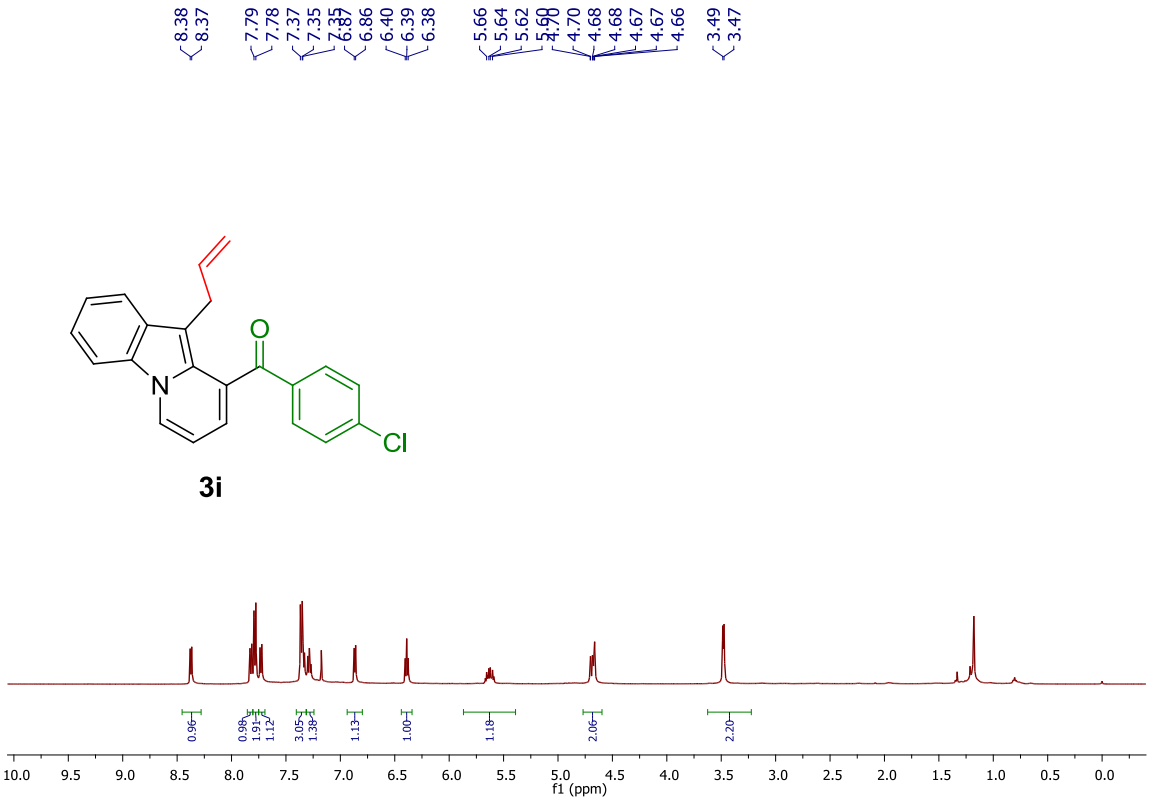
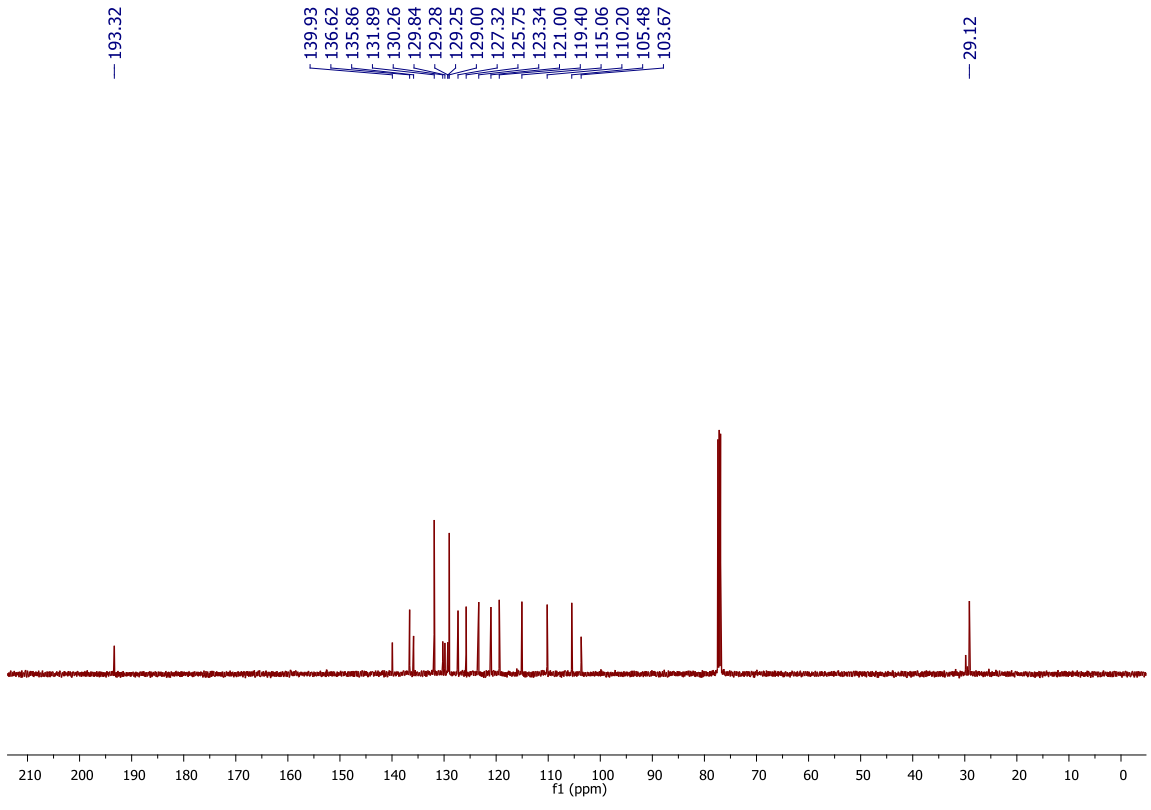
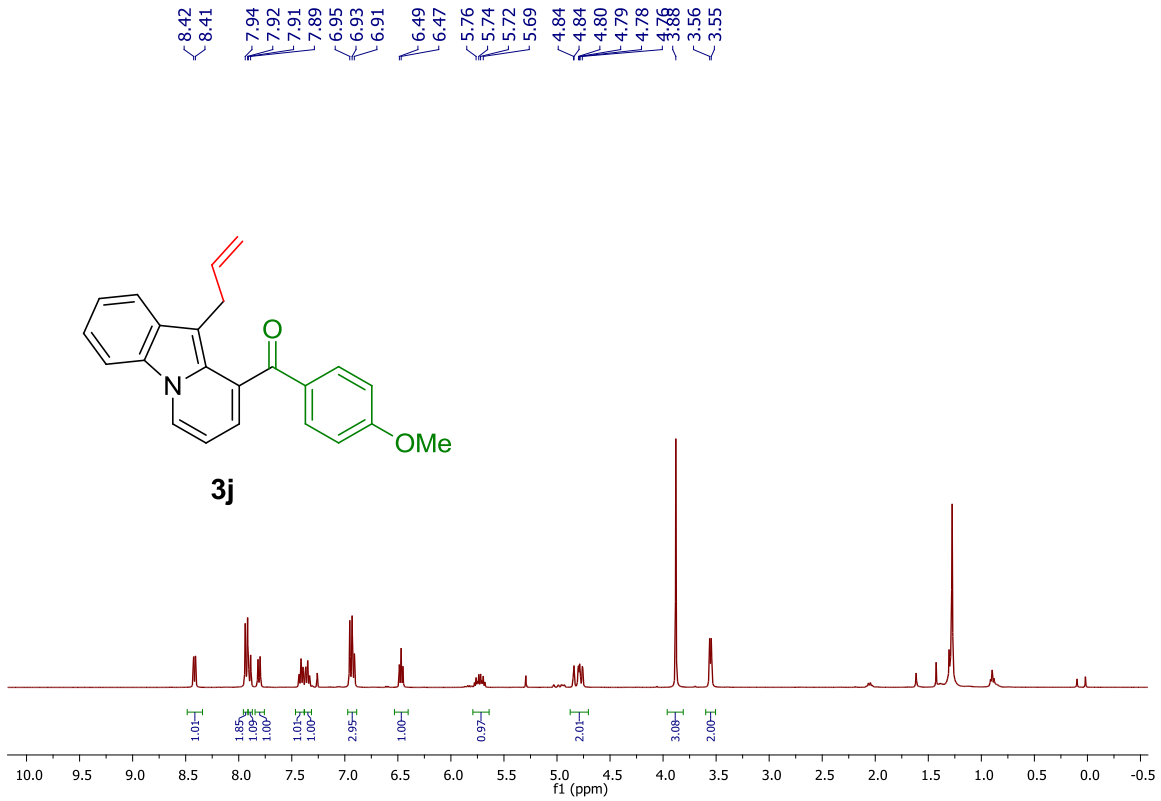
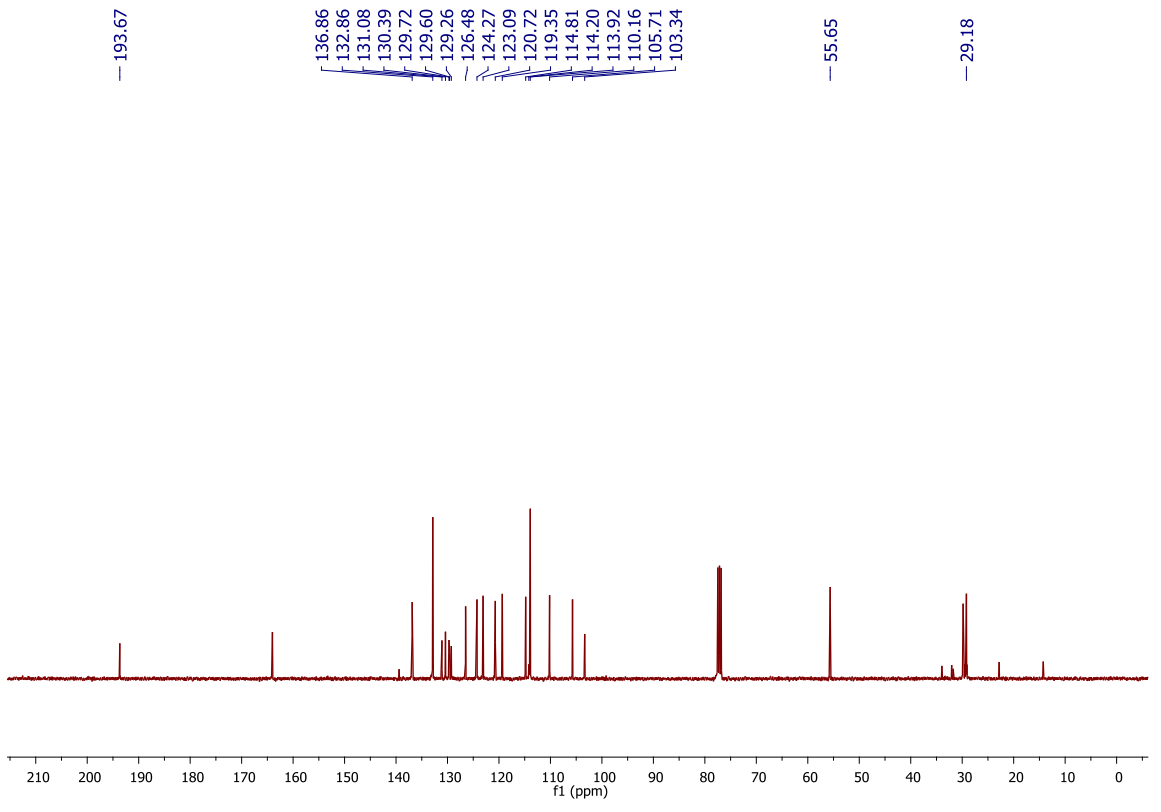
119.40
115.60
115.38
110.22
105.65
104.94
30.50

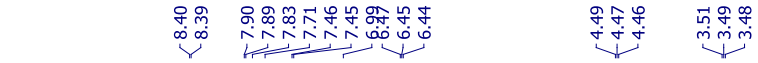

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

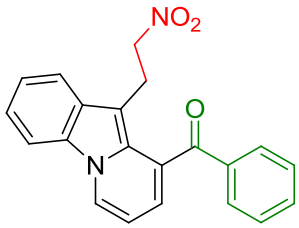

8.38
8.37
7.79
7.78
7.37
7.35
6.87
6.86
6.40
6.39
6.38
5.66
5.64
5.62
5.60
4.70
4.68
4.67
4.67
4.66
3.49
3.47
O
N
Cl
3i
0.96
0.98
1.91
1.12
3.05
1.38
1.13
1.00
1.18
2.06
2.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


193.32
139.93
136.62
135.86
131.89
130.26
129.84
129.28
129.25
129.00
127.32
125.75
123.34
121.00
119.40
115.06
110.20
105.48
103.67
29.12
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

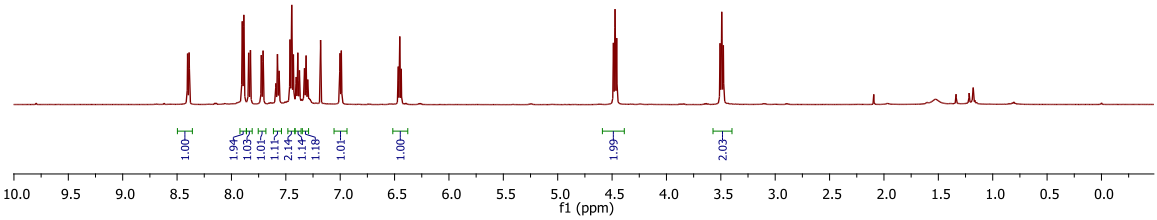

8.42
8.41
7.94
7.92
7.91
7.89
6.95
6.93
6.91
6.49
6.47
5.76
5.74
5.72
5.69
4.84
4.84
4.80
4.79
4.78
4.76
3.88
3.56
3.55
O
N
OMe
3j
1.01
1.85
1.00
1.00
1.01
1.00
2.95
1.00
0.97
2.01
3.08
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

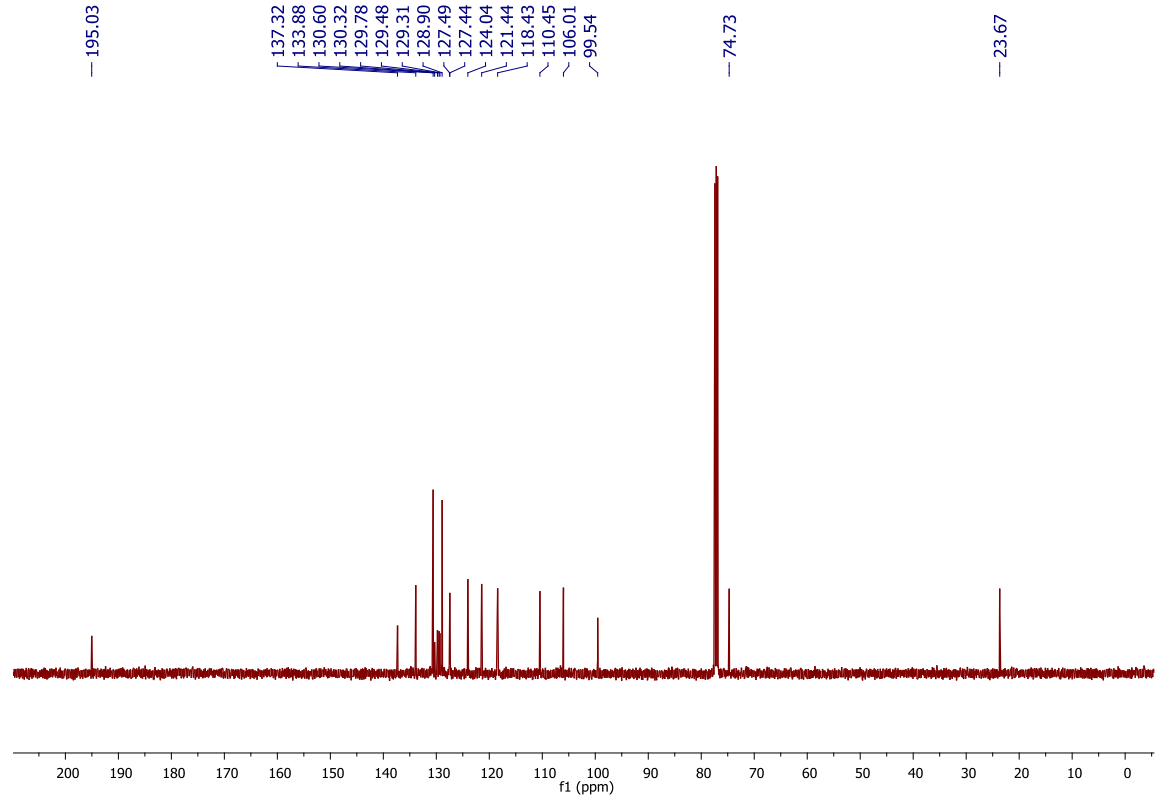

193.67
136.86
132.86
131.08
130.39
129.72
129.60
129.26
126.48
124.27
123.09
120.72
119.35
114.81
114.20
113.92
110.16
105.71
103.34
55.65
29.18
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.40
8.39
7.90
7.89
7.83
7.71
7.46
7.45
6.45
6.44
4.49
4.47
4.46
3.51
3.49
3.48

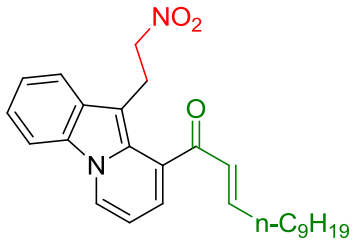

NO2
O
N

3k

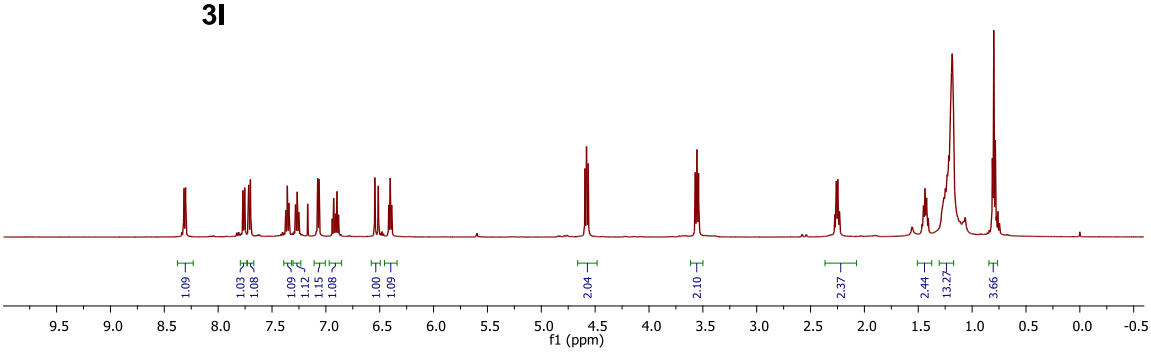

1.00
1.94
1.03
1.01
1.11
2.14
1.14
1.18
1.01
1.00
1.99
2.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


195.03
137.32
133.88
130.60
130.32
129.78
129.48
129.31
128.90
127.49
127.44
124.04
121.44
118.43
110.45
106.01
99.54
74.73
23.67
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

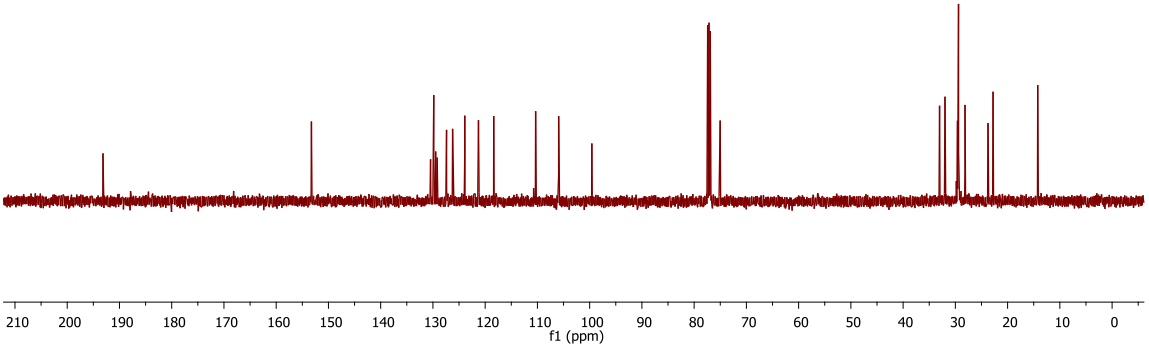

8.32
8.30
7.77
7.75
7.72
7.70
7.37
7.37
7.36
7.34
7.34
7.28
7.28
7.27
7.25
7.08
7.08
7.06
7.06
6.93
6.91
6.90
6.55
6.54
6.54
6.52
6.51
6.51
6.42
6.40
6.39
6.39
4.59
4.58
4.56
3.57
3.56
3.55
3.55
3.54
2.27
2.26
2.25
2.23
2.23
1.45
1.44
1.42
1.22
1.19
1.17
0.81
0.80
0.78

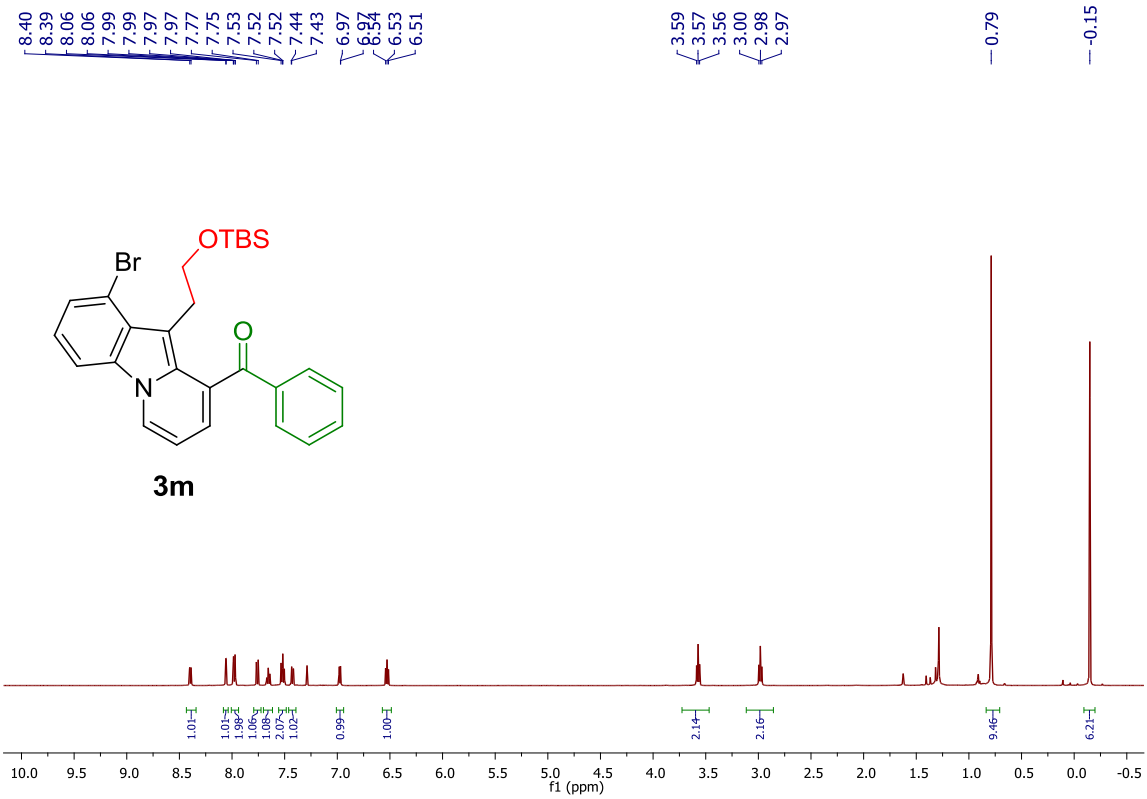

NO2
O
N
n-C9H19

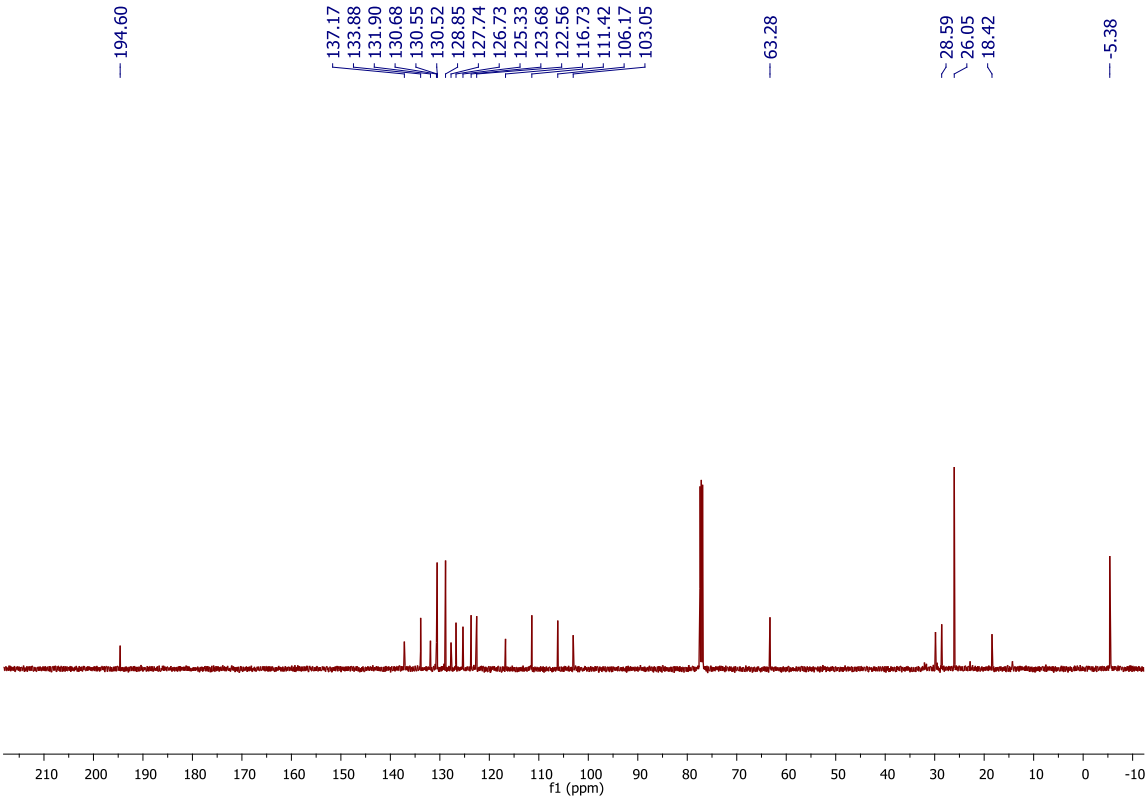
3l

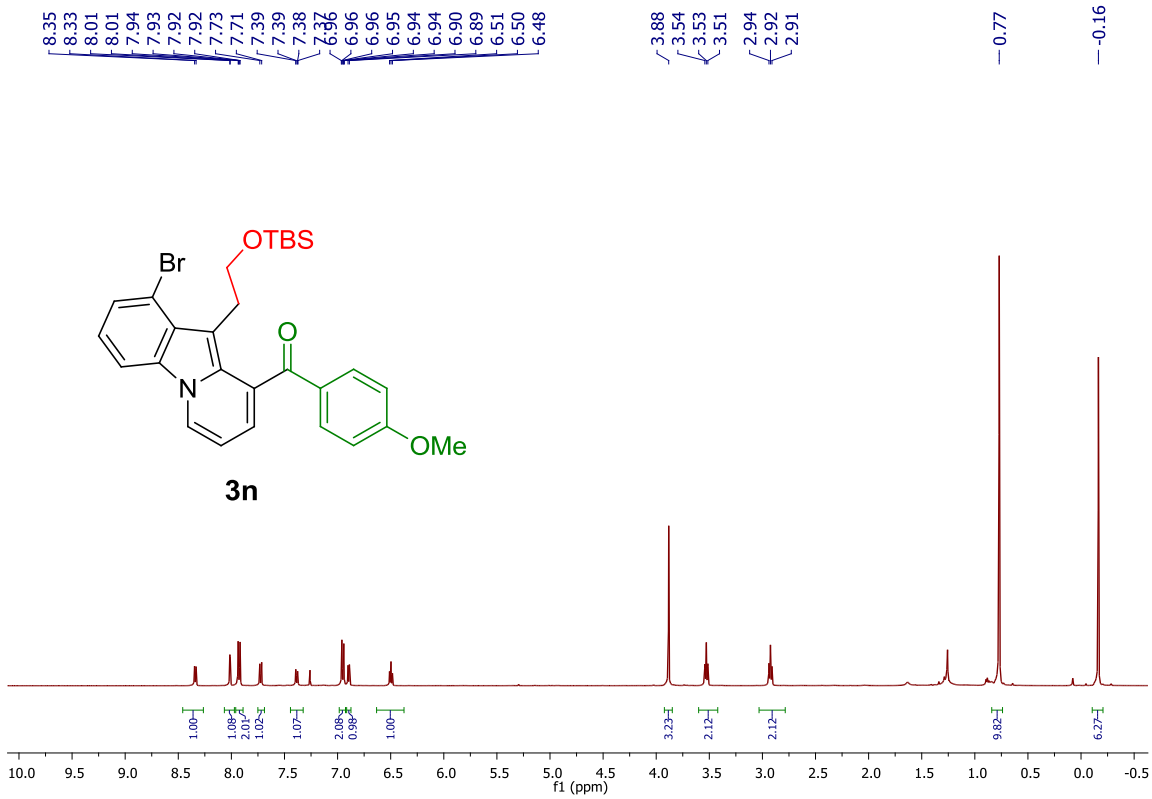

1.09
1.03
1.08
1.09
1.12
1.15
1.08
1.00
1.09
2.04
2.10
2.37
2.44
13.27
3.66
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

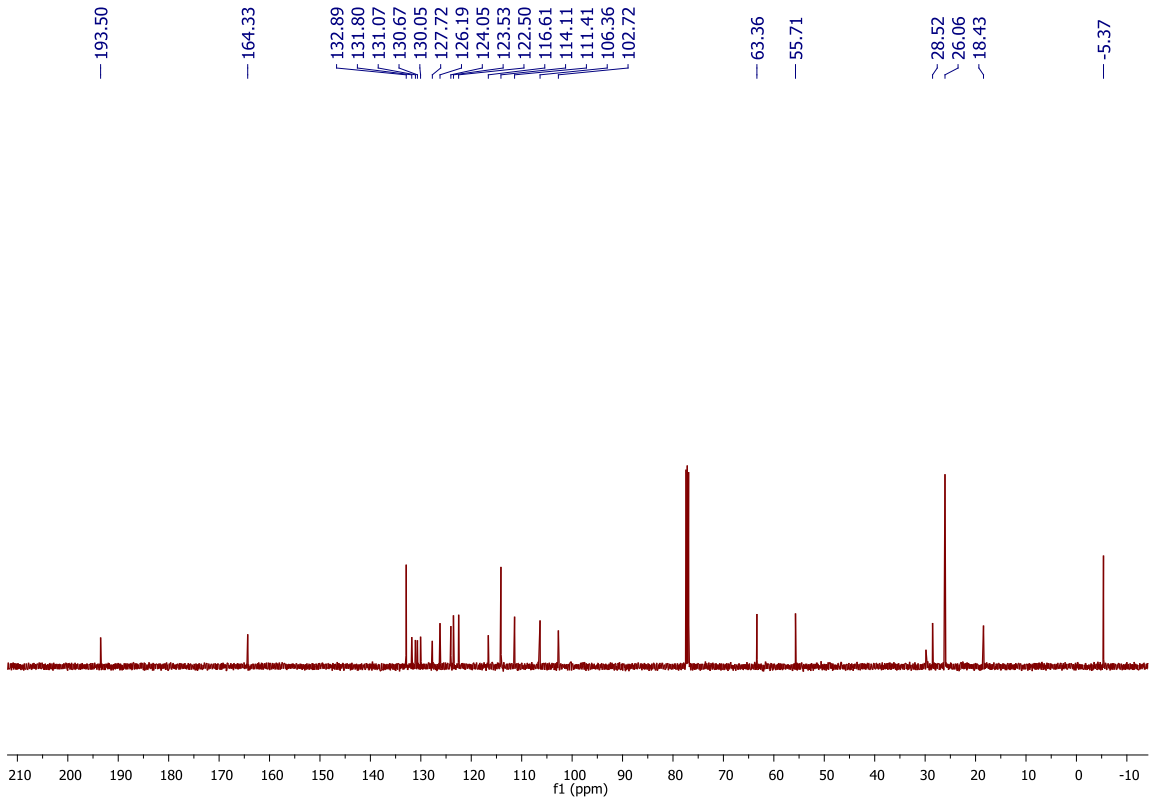

193.15
153.26
130.45
129.84
129.48
129.19
127.39
126.23
123.90
121.28
118.36
110.73
110.34
105.93
99.58
75.01
33.03
31.98
29.59
29.49
29.40
28.15
23.75
22.79
14.24


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

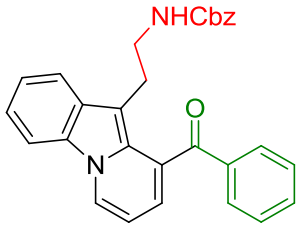

8.40
8.39
8.06
8.06
7.99
7.99
7.97
7.97
7.77
7.75
7.53
7.52
7.52
7.44
7.43
6.97
6.94
6.53
6.51
3.59
3.57
3.56
3.00
2.98
2.97
0.79
-0.15
OTBS
Br
O
N
3m
1.01
1.01
1.98
1.06
1.08
2.07
1.02
0.99
1.00
2.14
2.16
9.46
6.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


194.60
137.17
133.88
131.90
130.68
130.55
130.52
128.85
127.74
126.73
125.33
123.68
122.56
116.73
111.42
106.17
103.05
63.28
28.59
26.05
18.42
-5.38
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

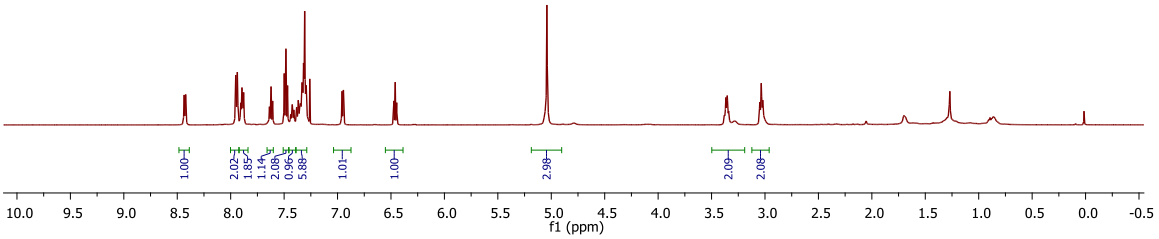

8.35
8.33
8.01
8.01
7.94
7.93
7.92
7.92
7.73
7.71
7.39
7.39
7.38
7.37
6.96
6.96
6.96
6.95
6.94
6.94
6.90
6.89
6.51
6.50
6.48
3.88
3.54
3.53
3.51
2.94
2.92
2.91
0.77
-0.16
OTBS
Br
O
N
OMe
3n
1.00
1.08
2.01
1.02
1.07
2.08
0.98
1.00
3.23
2.12
2.12
9.82
6.27
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


193.50
164.33
132.89
131.80
131.07
130.67
130.05
127.72
126.19
124.05
123.53
122.50
116.61
114.11
111.41
106.36
102.72
63.36
55.71
28.52
26.06
18.43
-5.37
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

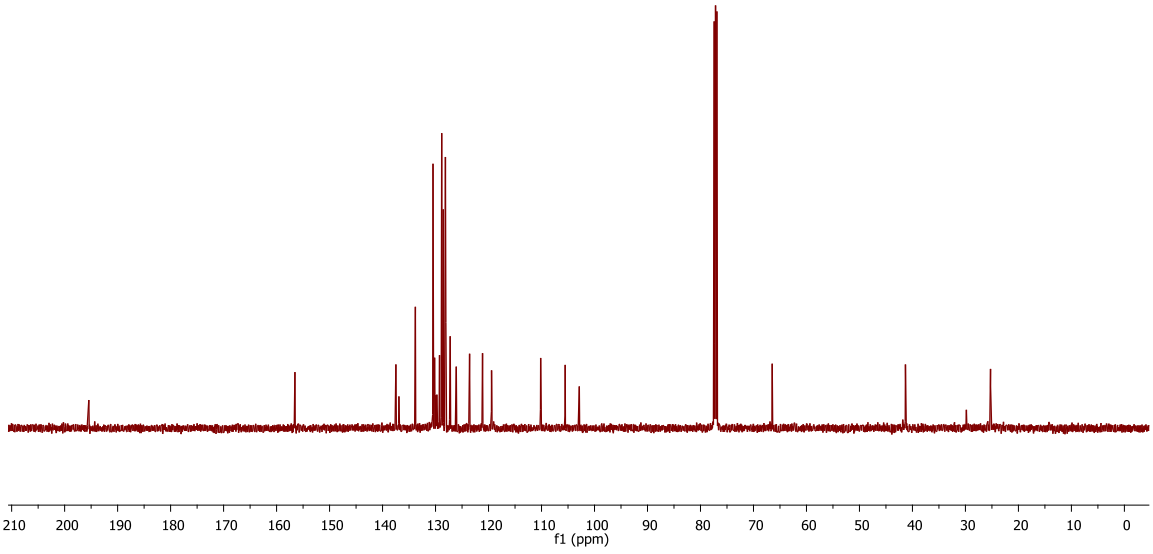

8.44
8.42
7.95
7.94
7.50
7.48
7.32
7.31
7.29
6.47
6.46
6.45
5.04
3.38
3.37
3.35
3.34
3.05
3.03
3.02


NHCbz
O
N

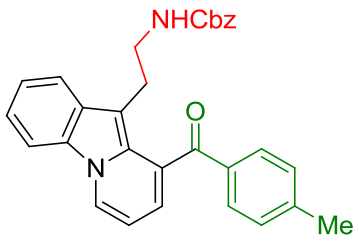
3o


1.00
2.02
1.85
1.14
2.08
0.96
5.88
1.01
1.00
2.98
2.09
2.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

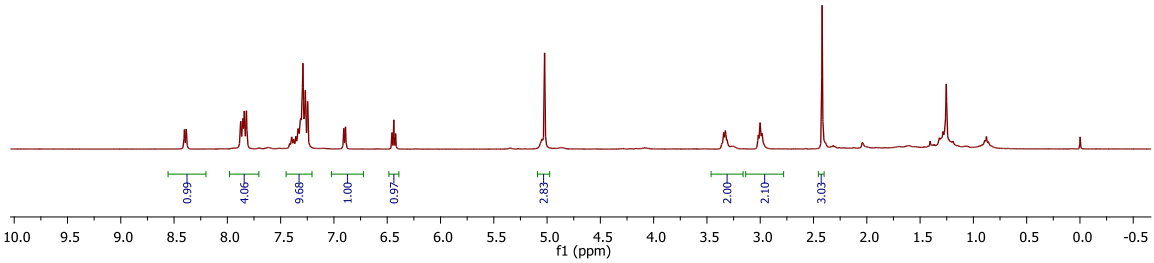

195.43
156.54
133.80
130.48
129.25
128.84
128.55
128.14
128.05
127.23
123.57
121.13
110.16
105.53
102.87
66.46
41.32
25.26


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

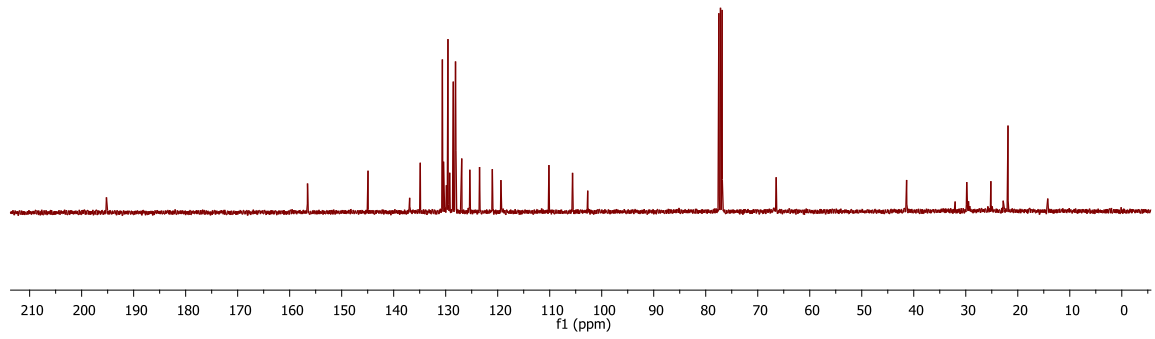

8.40
8.39
7.84
7.82
7.31
7.29
7.27
7.25
6.46
6.44
6.42
5.05
5.02
3.36
3.34
3.33
3.31
3.02
3.00
2.98
2.42

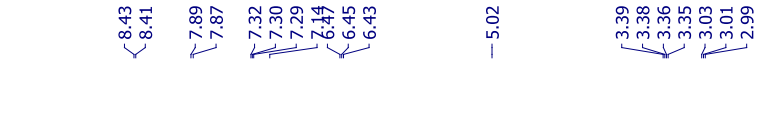

NHCbz
O
N
Me

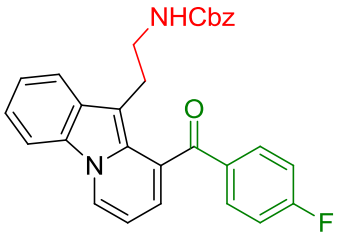
3p


0.99
4.06
9.68
1.00
0.97
2.83
2.00
2.10
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

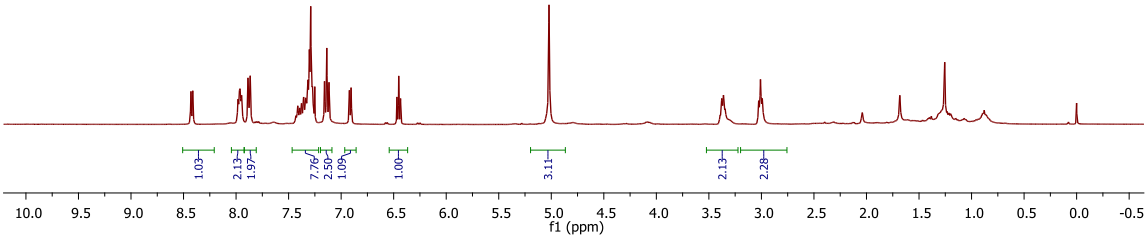

195.23
156.57
134.89
130.64
130.42
129.56
128.53
128.11
128.03
126.92
123.49
121.03
110.15
105.61
102.69
66.45
41.38
25.17
21.88


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

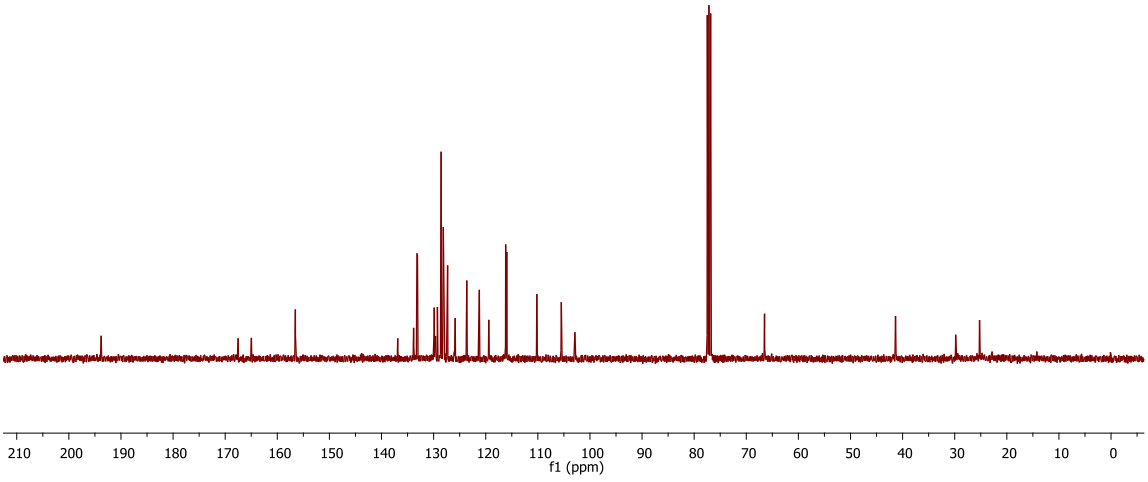

8.43
8.41
7.89
7.87
7.32
7.30
7.29
7.14
6.47
6.45
6.43
5.02
3.39
3.38
3.36
3.35
3.03
3.01
2.99

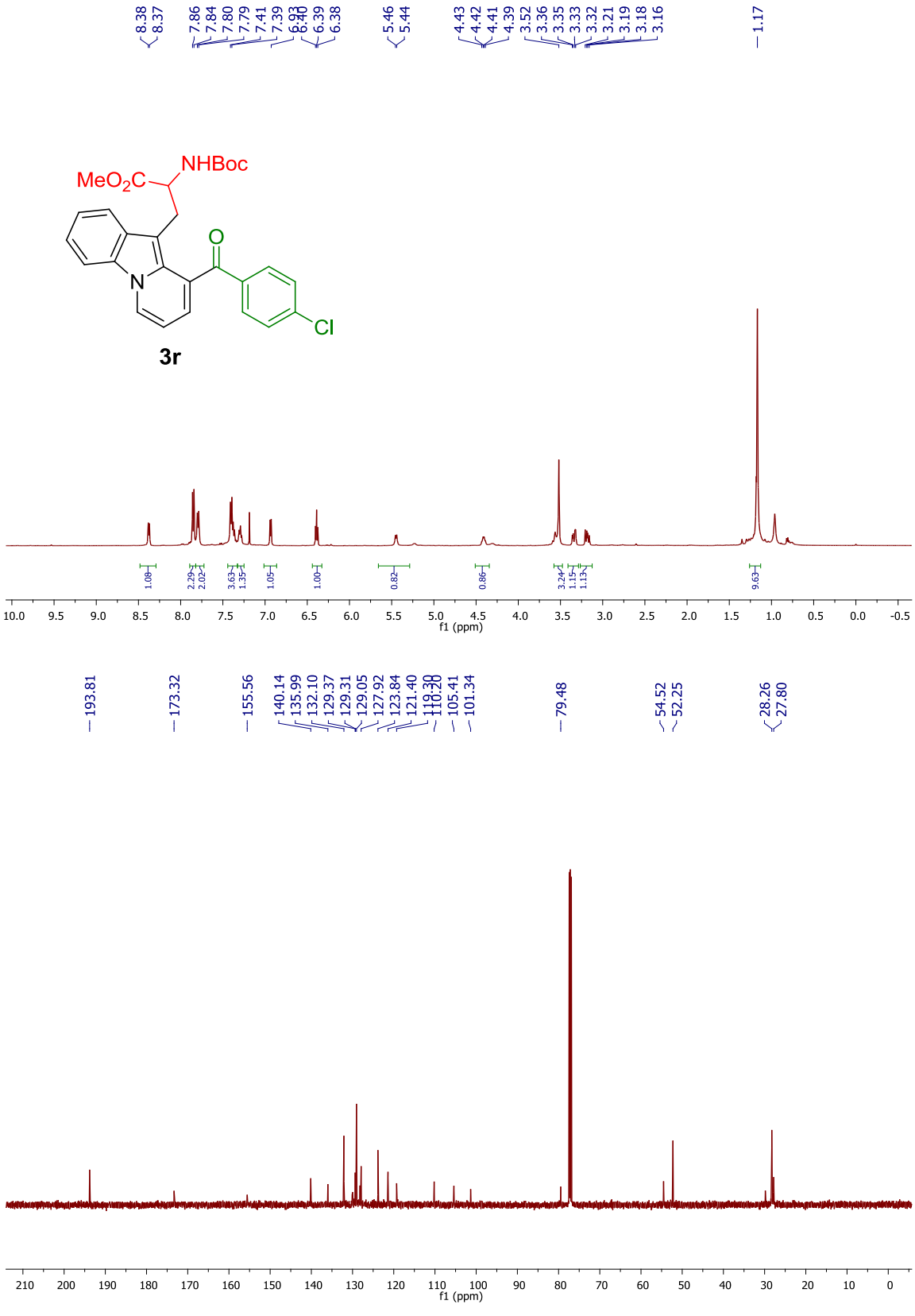

NHCbz
O
N
F

3q

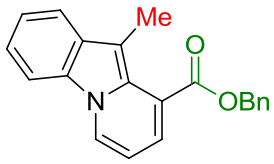

1.03
2.13
1.97
7.76
2.50
1.09
1.00
3.11
2.13
2.28
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


193.80
167.51
164.97
156.53
136.89
133.84
133.81
133.19
133.10
129.89
129.63
129.27
128.56
128.14
128.07
127.32
125.87
123.64
121.23
119.41
116.17
115.96
110.19
105.49
102.89
66.50
41.36
25.23

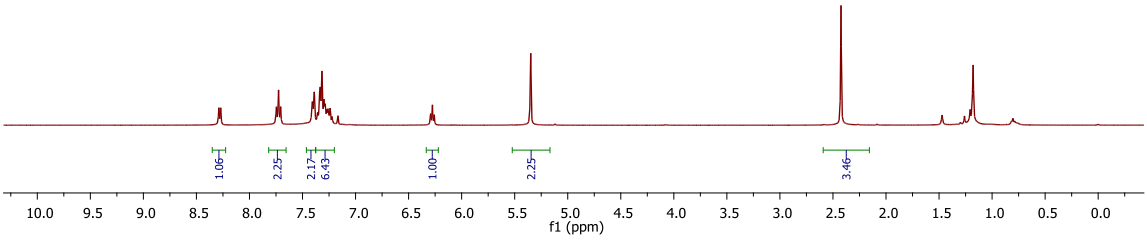

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.38
8.37
7.86
7.84
7.80
7.79
7.41
7.39
6.40
6.39
6.38
5.46
5.44
4.43
4.42
4.41
4.39
3.52
3.36
3.35
3.33
3.32
3.21
3.19
3.18
3.16
1.17
NHBoc
MeO2C
O
N
Cl
3r
1.00
2.29
2.02
3.63
1.35
1.05
1.00
0.82
0.86
3.24
1.15
1.13
9.63
f1 (ppm)
193.81
173.32
155.56
140.14
135.99
132.10
129.37
129.31
129.05
127.92
123.84
121.40
110.30
110.20
105.41
101.34
79.48
54.52
52.25
28.26
27.80
f1 (ppm)

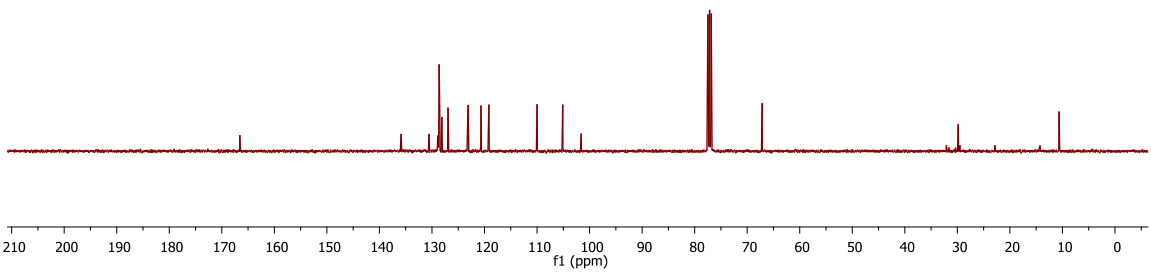

8.29
8.27
7.73
7.41
7.39
7.34
7.33
7.32
7.30
6.28
6.26
5.35
2.42

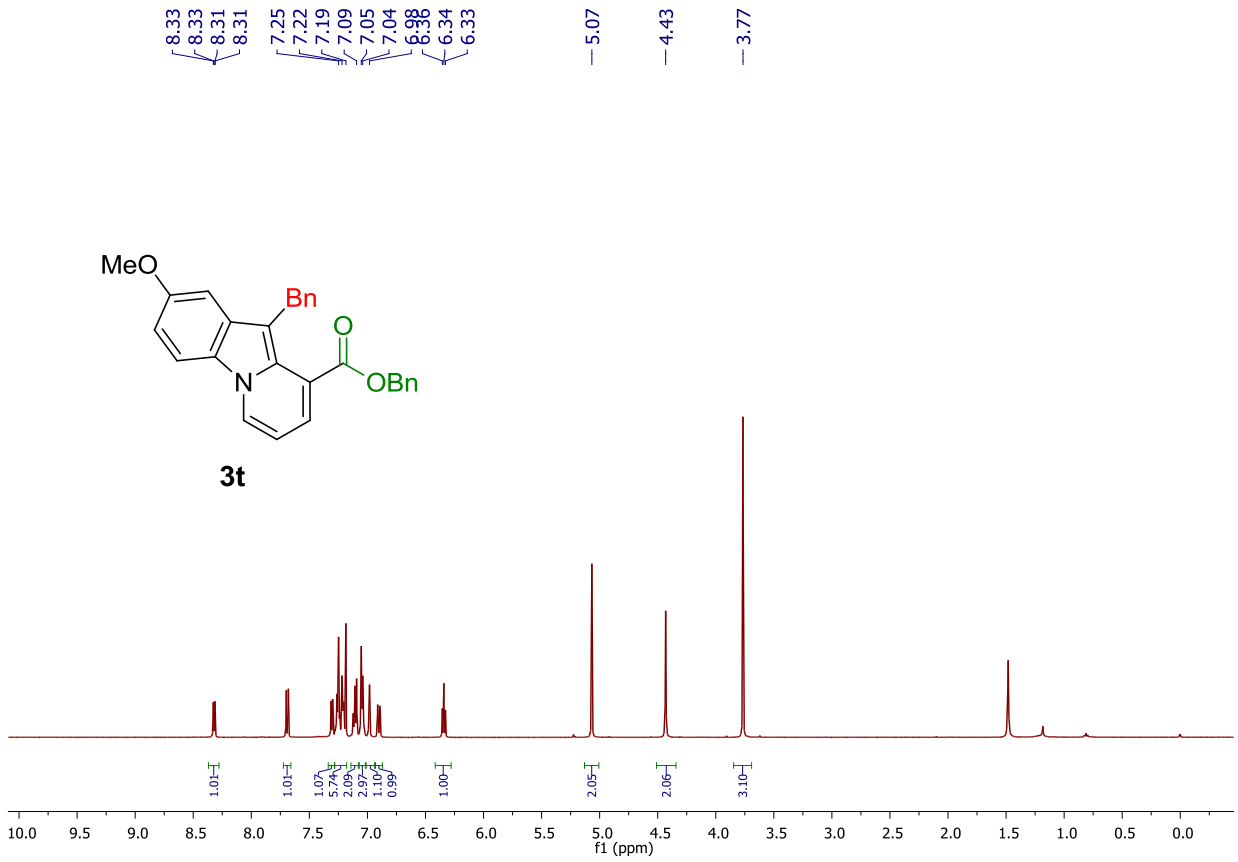

Me
O
N
OBn

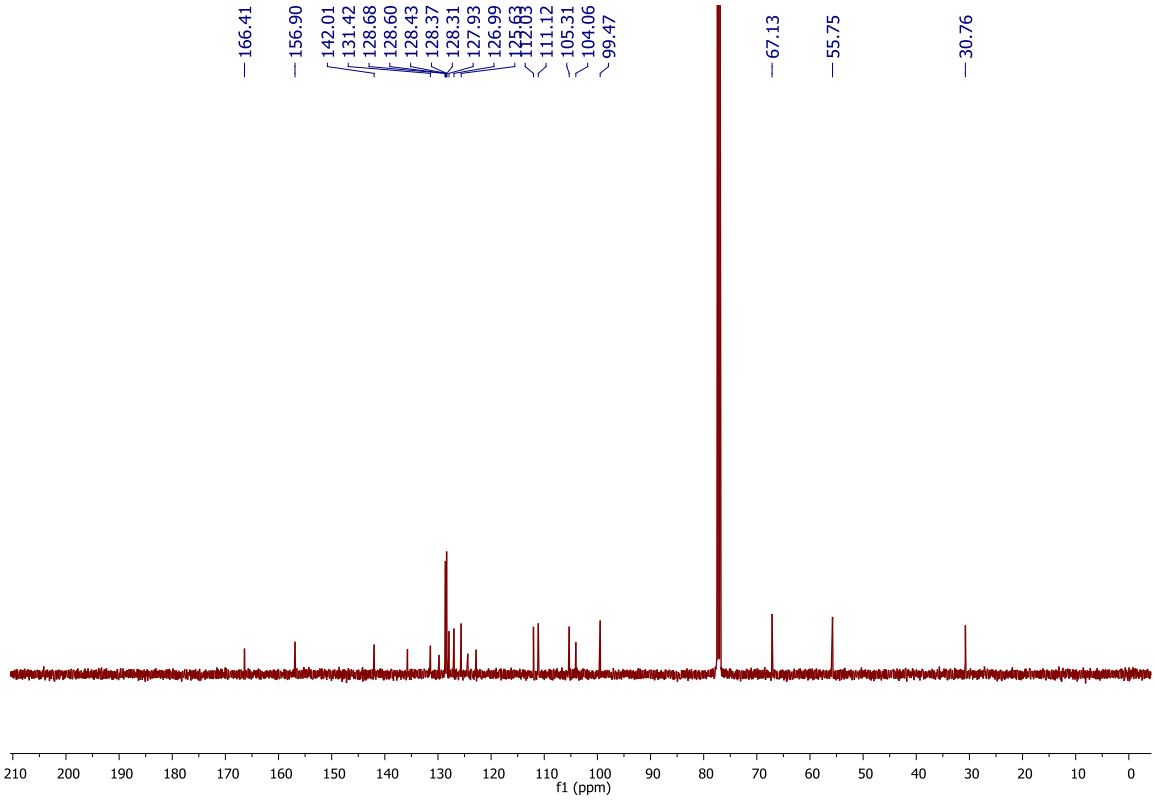
3s


1.06
2.25
2.17
6.43
1.00
2.25
3.46
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

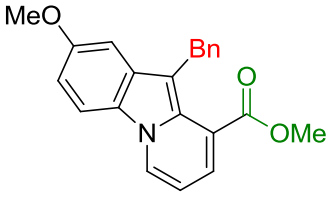

166.58
135.87
130.55
128.89
128.79
128.66
128.64
128.54
128.11
126.95
123.26
123.12
120.67
119.16
109.99
105.11
101.59
67.16
10.66


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

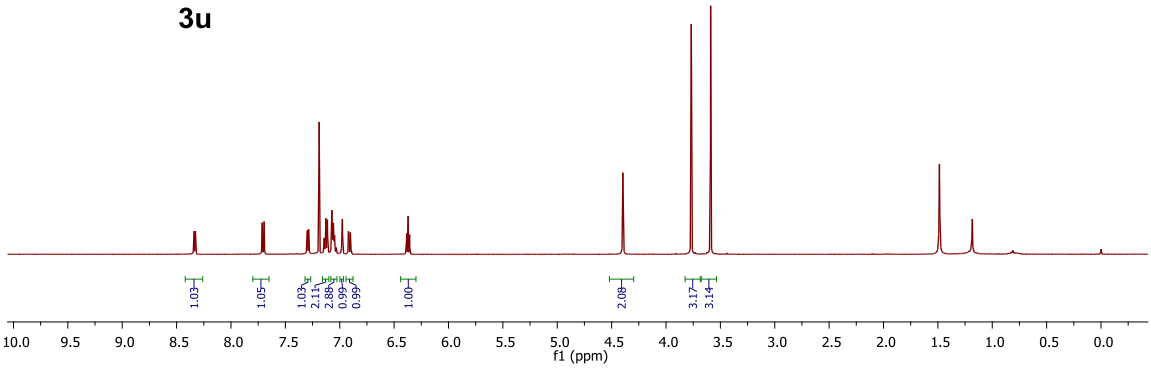

8.33
8.33
8.31
8.31
7.25
7.22
7.19
7.09
7.05
7.04
6.34
6.33
5.07
4.43
3.77
MeO
Bn
O
OBn
N
3t
1.01
1.01
1.07
5.74
2.09
2.97
1.10
0.99
1.00
2.05
2.06
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

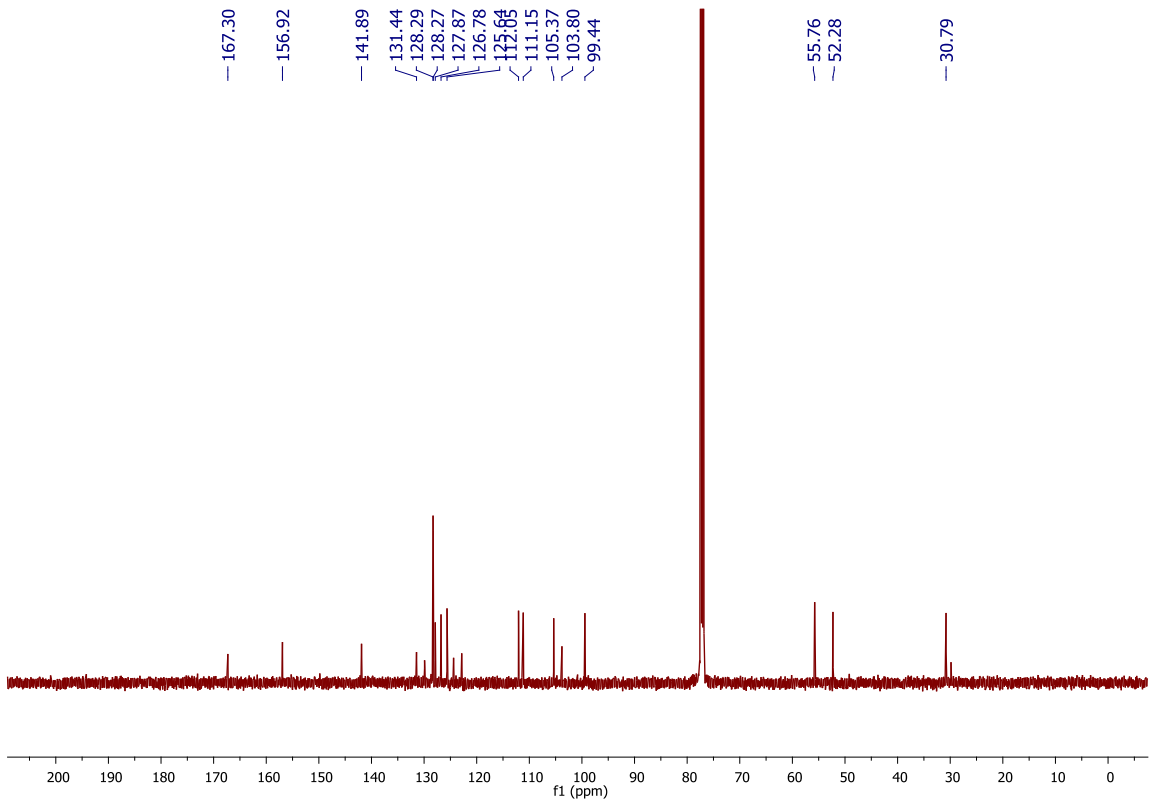

166.41
156.90
142.01
131.42
128.68
128.60
128.43
128.37
128.31
127.93
126.99
125.63
112.03
111.12
105.31
104.06
99.47
67.13
55.75
30.76
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.34
8.34
8.33
8.33
7.71
7.69
7.19
7.13
7.07
6.38
6.37
6.36
4.40
3.77
3.59


MeO
Bn
O
N
OMe

3u


1.03
1.05
1.03
2.11
2.88
0.99
0.99
1.00
2.08
3.17
3.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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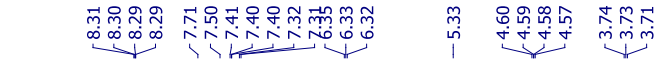
156.92
141.89
131.44
128.29
128.27
127.87
126.78
125.64
112.05
111.15
105.37
103.80
99.44
55.76
52.28
30.79
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.31
8.30
8.29
8.29
7.71
7.50
7.41
7.40
7.40
7.32
7.31
6.33
6.32
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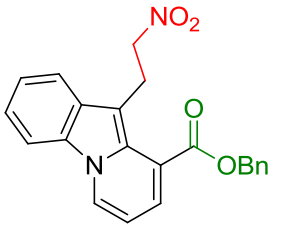
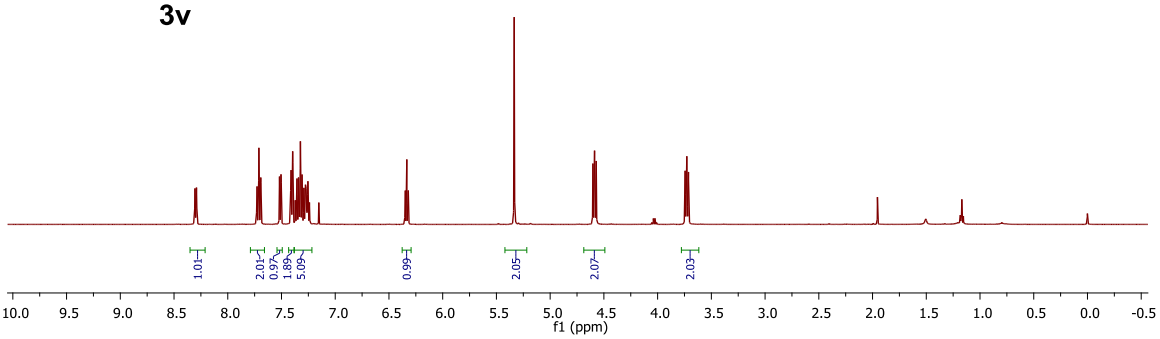
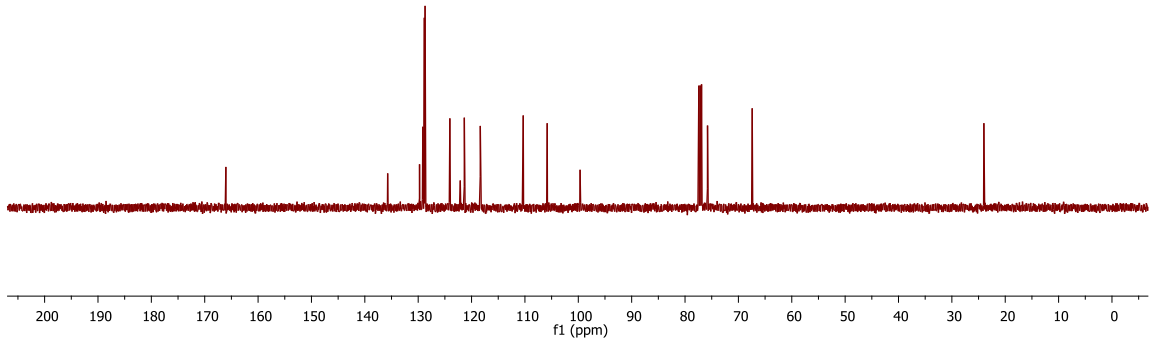
4.59
4.58
4.57
3.74
3.73
3.71

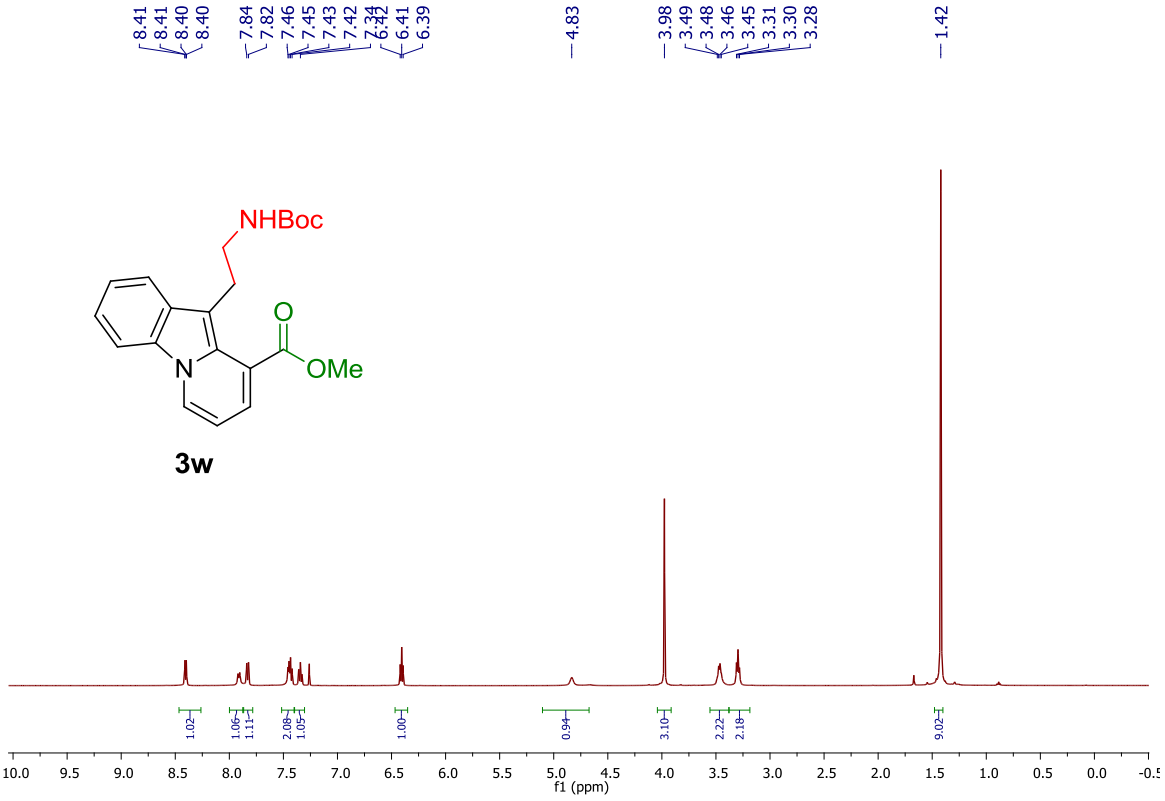

NO2
O
OBn
N

3v

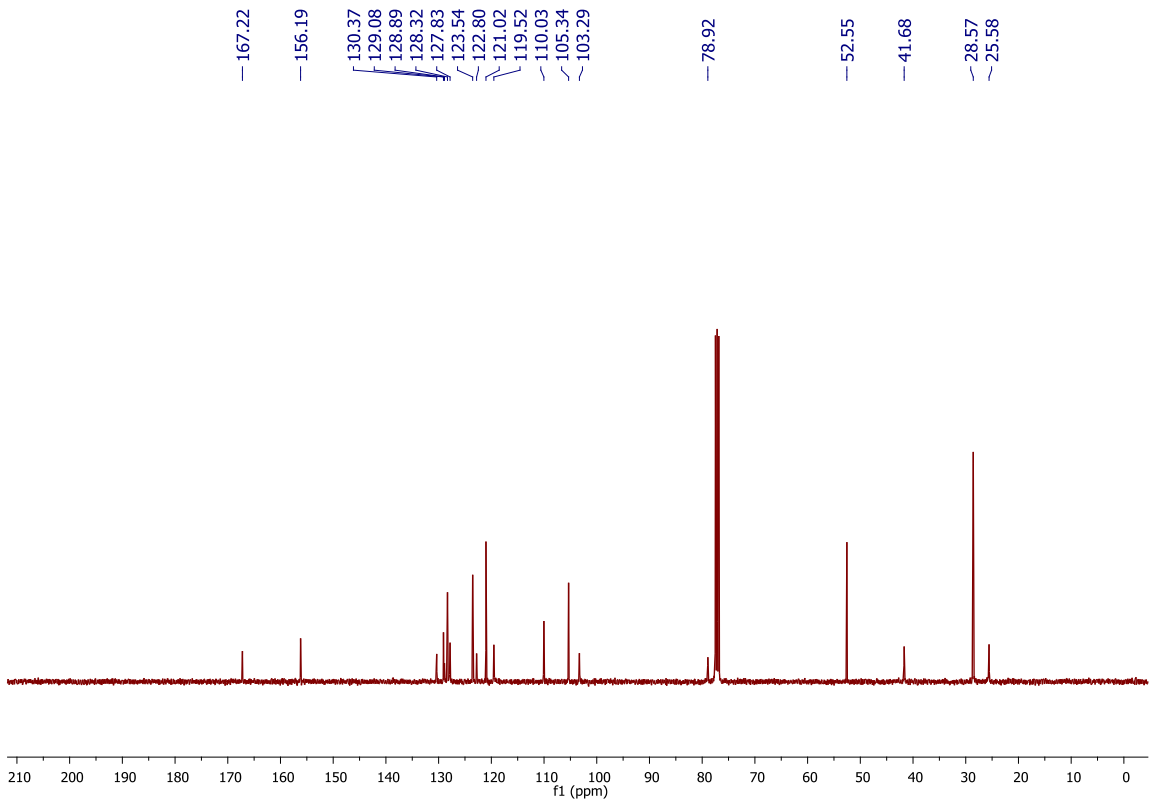

1.01
2.01
0.97
1.89
5.09
0.99
2.05
2.07
2.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


166.04
135.72
129.75
129.58
129.13
129.07
128.85
128.71
128.67
128.62
124.06
122.12
121.35
118.36
110.31
105.82
99.66
75.78
67.41
24.00

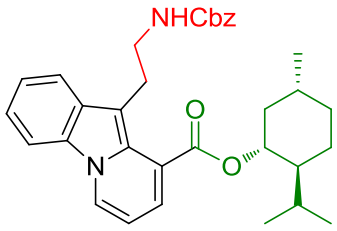

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.41
8.41
8.40
8.40
7.84
7.82
7.46
7.45
7.43
7.42
6.41
6.39
4.83
3.98
3.49
3.48
3.46
3.45
3.31
3.30
3.28
1.42
NHBoc
O
OMe
N
1.02
1.06
1.11
2.08
1.05
1.00
0.94
3.10
2.22
2.18
9.02
f1 (ppm)

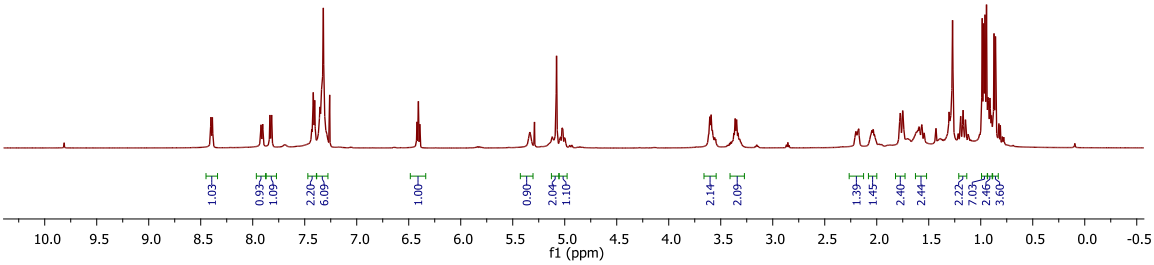
3w

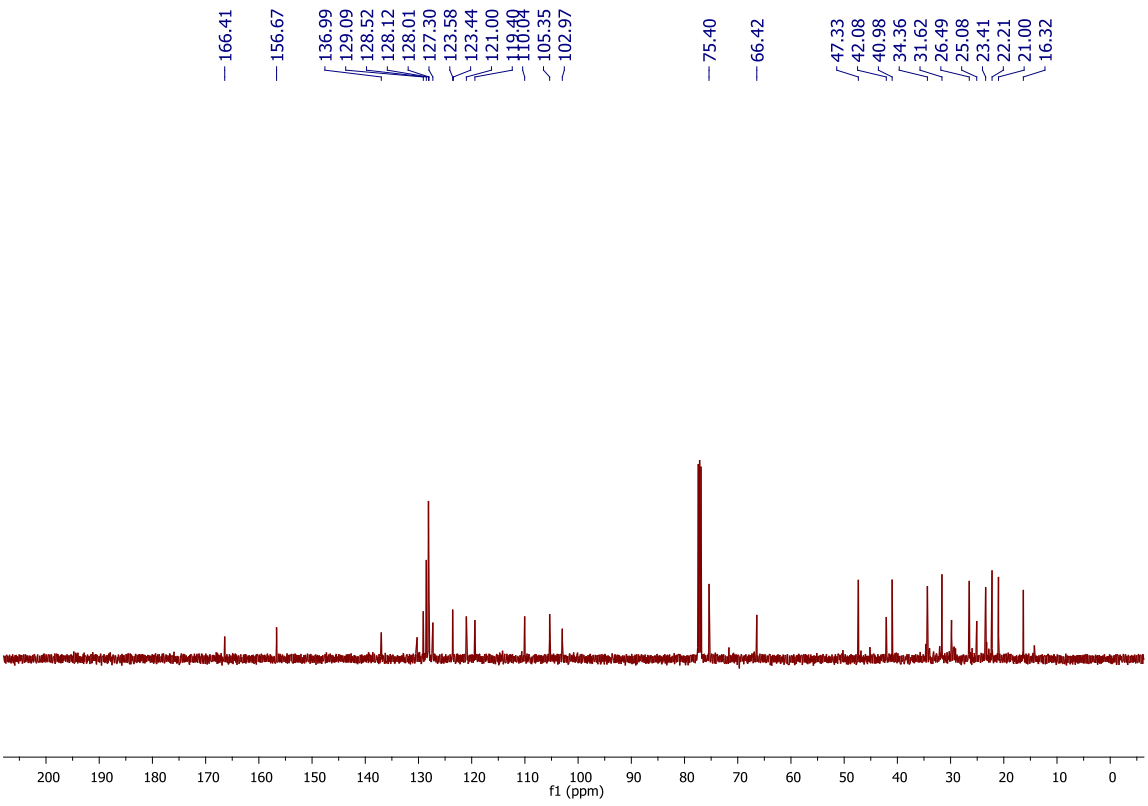

167.22
156.19
130.37
129.08
128.89
128.32
127.83
123.54
122.80
121.02
119.52
110.03
105.34
103.29
78.92
52.55
41.68
28.57
25.58
f1 (ppm)


8.40
8.39
7.92
7.90
7.83
7.82
7.42
7.40
7.35
7.34
7.32
6.42
6.41
6.39
5.34
5.08
5.03
5.02
3.60
3.59
3.58
3.37
3.36
3.35
3.33
2.20
2.18
2.17
2.05
2.05
2.03
1.77
1.75
1.62
1.61
1.60
1.60
1.59
1.57
1.54
1.22
1.19
1.17
1.15
0.99
0.97
0.96
0.94
0.93
0.93
0.91
0.90
0.87
0.86


NHCbz
O
O
N

3x


1.03
0.93
1.09
2.20
6.09
1.00
0.90
2.04
1.10
2.14
2.09
1.39
1.45
2.40
2.44
2.22
7.03
2.46
3.60
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


166.41
156.67
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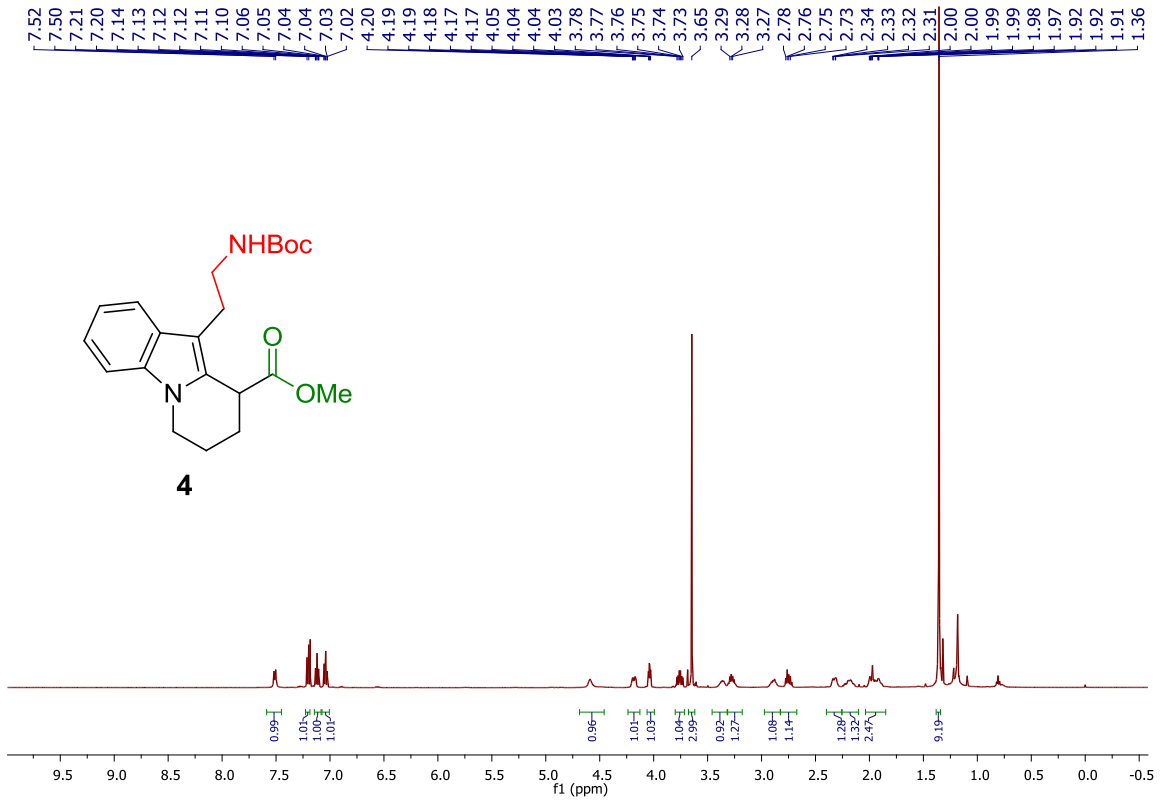
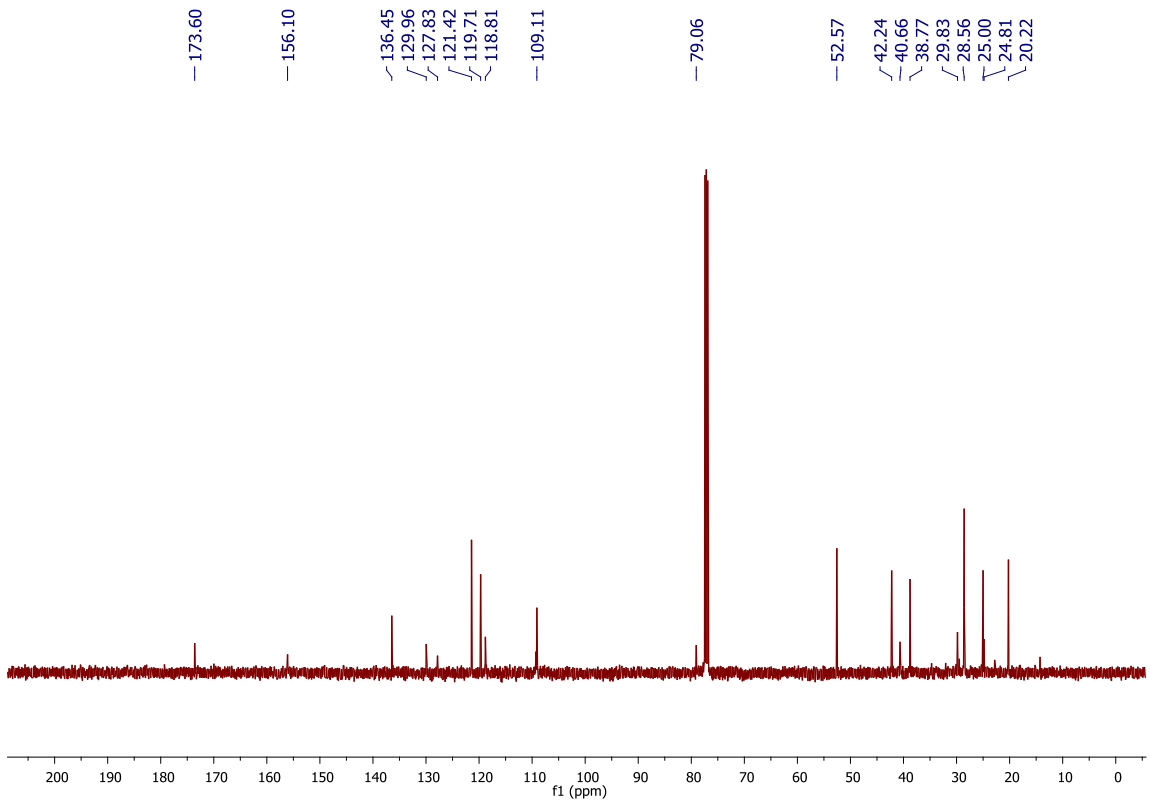
129.09
128.52
128.12
128.01
127.30
123.58
123.44
121.00
119.40
110.04
105.35
102.97
75.40
66.42
47.33
42.08
40.98
34.36
31.62
26.49
25.08
23.41
22.21
21.00
16.32
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


NHBoc
O
OMe
N
4
f1 (ppm)


173.60
156.10
136.45
129.96
127.83
121.42
119.71
118.81
109.11
79.06
52.57
42.24
40.66
38.77
29.83
28.56
25.00
24.81
20.22
f1 (ppm)