$FeCl_3$-Catalyzed AB_2 Three-component [3 + 3] Annulation: An Efficient Access to Functionalized Indolo[3,2-*b*]carbazoles

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Supporting Information

Table of Contents

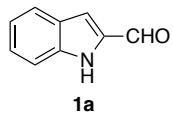
1. General Information

All chemicals were purchased from various commercial suppliers including Alfa Aesar, Sigma-Aldrich, Merck, SRL, SDFine, CDH and used without any further purification. All the reactions were carried out in oven dried glassware. The reactions were monitored by thin layer chromatography using Merck silica gel 60F254 and visualized by UV detection or using molecular iodine or *p*-anisaldehyde stain. Silica gel (230-400 mesh) was used for flash column chromatography. Melting points were recorded on a melting point apparatus in capillaries and are uncorrected. ^{1}H and ^{13}C{^{1} H}-NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 at room temperature on a Brucker AC-400 spectrometer operating at 400 MHz for ^{1}H and 101 MHz for ^{13}C{^{1}H}. Chemical shifts (δ) are expressed in ppm using TMS as an internal standard and coupling constants (*J*) are given in Hz. Infrared (IR) spectra were recorded on Perkin-Elmer FTIR spectrophotometer. Elemental analyses were determined at the CAI de Microanálisis Elemental, Universidad Complutense, by using a Leco 932 CHNS combustion microanalyzer.

2. Synthesis of 1*H*-Indole-2-carbaldehyde Derivatives 1a-c

Compounds **1a-c** were synthesized using the literature procedure in a 13 mmol scale.[1]

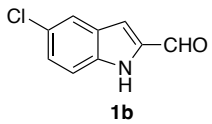
1*H*-Indole-2-carbaldehyde (1a): [1]



1a

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as white solid; mp: 143-145 °C; yield: 57% (0.843 g).

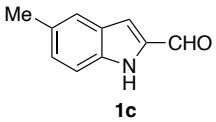
5-Chloro-1*H*-indole-2-carbaldehyde (1b):[1]



1b

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as white solid; mp: 198-200 °C; yield: 69% (1.264 g).

5-Methyl-1*H*-indole-2-carbaldehyde (1c):[2]



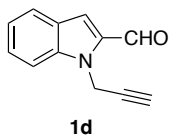
1c

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as white solid; mp: 157-159 °C; yield: 67% (1.087 g).

3. General Procedure for the Synthesis of *N*-Substituted 1*H*-Indole-2-carbaldehydes 1d-f

Compounds **1d-f** were synthesized using the literature procedure in a 7 mmol scale.[2]

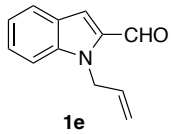
1-(Prop-2-yn-1-yl)-1*H*-indole-2-carbaldehyde (1d):[2]



1d

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as white solid; mp: 133-135 °C; yield: 84% (1.060 g).

1-Allyl-1*H*-indole-2-carbaldehyde (1e):[2]



1e

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as colourless solid; mp: 39-41 °C; yield: 76% (0.969 g).

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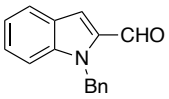
[1] Liu, Y.; Luo, G.; Yang, X.; Jiang, S.; Xue, W.; Chi, Y. R.; Jin, Z. *Angew. Chem., Int. Ed.* **2020**, *59*, 442–448.

[2] Wang, L.-X.; Qiu, B.; An, X.-D.; Dong, P.-Z.; Liu, R.-B.; Xiao, J. *Green Chem*. **2021**, *23*, 8181–8186.

1-Benzyl-1*H*-indole-2-carbaldehyde (1f):[2]



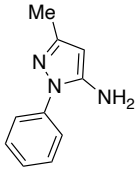
1f

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as yellow solid; mp: 71-73 °C; yield: 91% (1.475 g).

4. General Procedure for the Synthesis of 3-Methyl-1-aryl-1*H*-pyrazol-5-amines 2

Compounds **2** were synthesized using the literature procedure in a 29 mmol scale.[3]

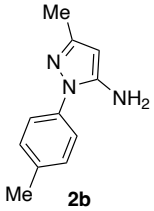
3-Methyl-1-phenyl-1*H*-pyrazol-5-amine (2a):[4]



2a

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 70:30, v/v) afforded the title compound as white solid; mp: 107-109 °C; yield: 95% (3.949 g).

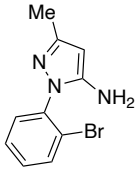
3-Methyl-1-(*p*-tolyl)-1*H*-pyrazol-5-amine (2b):[4]



2b

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 70:30, v/v) afforded the title compound as white solid; mp: 121-123 °C; yield: 88% (3.954 g).

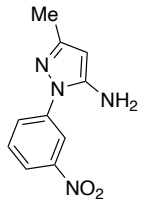
1-(2-Bromophenyl)-3-methyl-1*H*-pyrazol-5-amine (2c):



2c

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 70:30, v/v) afforded the title compound as colorless viscous liquid; yield: 73% (4.417 g); IR (neat): 3414.2, 1617.7, 1520.8, 1076.1. cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, J = 8.0, 1.1 Hz, 1H), 7.40-7.32 (m, 2H), 7.25-7.28 (m, 1H), 5.37 (s, 1H), 3.51 (s, 2H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 146.4, 137.5, 133.5, 130.7, 130.5, 128.6, 122.4, 90.1, 14.0; Anal Calcd for $C_{10}H_{10}BrN_3$: Calcd: C, 47.64; H, 4.00; N, 16.67. Found: C, 46.85; H, 4.03; N, 16.69.

3-Methyl-1-(3-nitrophenyl)-1*H*-pyrazol-5-amine (2d): [4]



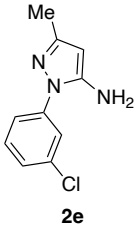
2d

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 70:30, v/v) afforded the title compound as yellow solid; mp: 105-107 °C; yield: 76% (3.980 g).

[3] Marinozzi, M.; Marcelli, G.; Carotti, A.; Natalini, B. *RSC Adv.* **2014**, *4*, 7019–7023

[4] Muthukrishnan, I.; Vachan, B. S.; Karuppasamy, M.; Eniyaval, A.; Maheswari, C. U.; Nagarajan, S.; Menéndez, J. C.; Sridharan, V. *Org. Biomol. Chem.* **2019,** *17,* 6872–6879.

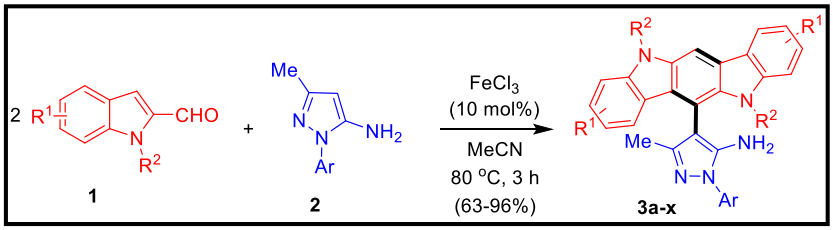
1-(3-Chlorophenyl)-3-methyl-1*H*-pyrazol-5-amine (2e): [4]



2e

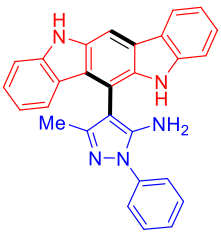
Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 70:30, v/v) afforded the title compound as white solid; mp: 137-139 °C; yield: 72% (3.588 g).

5. General Procedure for the Synthesis of Indolo[3,2-*b*]carbazoles 3



To a stirred solution of aldehyde **1** (1 mmol, 2.0 equiv) and 3-methyl-1-aryl-1*H*-pyrazol-5-amine **2** (0.5 mmol, 1.0 equiv) in MeCN (3 mL) was added $FeCl_3$ (10 mol%). The resulting mixture was stirred at 80 °C for 3 h and after completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature and diluted with water. The aqueous suspension was extracted with DCM (2 x 20 mL), washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography using petroleum ether-ethyl acetate mixture as eluent (90:10 to 85:15, v/v) to obtain compounds **3a-x**.

4-(5,11-Dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1-phenyl-1*H*-pyrazol-5-amine (3a):

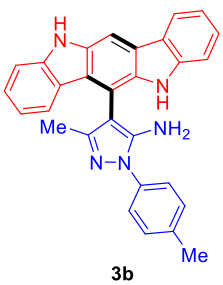


3a

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as off-white solid; mp: 317-319 °C; yield: 0.198 g, 93% (1.945 g, 91%)[#]; IR (neat): 3397.3, 2923.3, 1729.3, 1618.8, 1527.2, 1453.8, 1348.3, 1283.2, 1059.8. cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 11.14 (s, 1H), 10.60 (s, 1H), 8.23 (d, *J* = 7.7 Hz, 1H), 8.14 (s, 1H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 6.9 Hz, 3H), 7.48 (t, *J* = 7.9 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 3H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 4.83 (s, 2H), 1.96 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ* 147.9, 145.0, 141.7, 140.2, 135.9, 135.4, 129.6, 126.3, 125.7, 125.5, 123.4, 123.3, 123.1, 122.7, 122.0, 121.5, 120.6, 118.0, 117.5, 111.4, 110.6, 107.9, 100.1, 99.3, 13.5; Anal Calcd for $C_{28}H_{21}N_5$: Calcd: C, 78.67; H, 4.95; N, 16.38. Found: C, 78.55; H, 5.01; N, 16.44. *One aromatic carbon is merged with others.

[#]Yield obtained from 10 mmol scale reaction.

4-(5,11-Dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1-(*p*-tolyl)-1*H*-pyrazol-5-amine (3b):

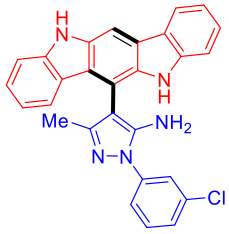


3b

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as pale yellow solid; mp: 290-292 °C; yield: 0.194 g, 88%; IR (neat): 3398.3.7, 2922.2, 1617.8, 1595.2, 1528.5, 1453.9, 1349.6, 1294.5. cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 11.13 (s, 1H), 10.60 (s, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 8.14 (s, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 8.5 Hz, 2H), 7.39-7.30 (m, 4H), 7.13 (t, *J* = 7.3 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 4.76 (s, 2H), 2.40 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ* 147.6, 144.9, 141.7, 137.7, 135.9,

135.6, 135.5, 130.0, 125.7, 125.4, 123.4, 123.3, 123.1, 122.7, 122.0, 121.9, 120.6, 118.0 117.5, 111.4, 110.6, 108.0, 100.0, 99.1, 21.1, 13.5; Anal Calcd for $C_{29}H_{23}N_5$: Calcd: C, 78.89; H, 5.25; N, 15.86. Found: C, 78.68; H, 5.21; N, 15.79. *One aromatic carbon is merged with others.

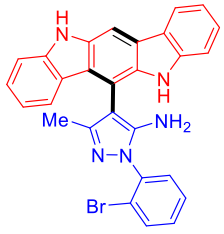
1-(3-Chlorophenyl)-4-(5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1*H*-pyrazol-5-amine (3c):



3c

Purification by flash column chromatography on silica gel eluting with petroleum ether–ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as off-white solid; mp: 298-300 °C; yield: 0.164 g, 71%; IR (neat): 3414.2, 2922.0, 1745.3, 1596.3, 1520.8, 1453.7, 1319.5, 1259.8, 1099.7. cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 11.15 (s, 1H), 10.61 (s, 1H), 8.23 (d, J = 7.5 Hz, 1H), 8.15 (s, 1H), 7.95 (s, 1H), 7.87 (d, J = 7.7 Hz, 1H), 7.60-7.53 (m, 2H), 7.50-7.45 (m, 2H), 7.41-7.31 (m, 3H), 7.14 (t, J = 7.3 Hz, 1H), 7.00 (t, J = 7.3 Hz, 1H), 5.02 (s, 2H), 1.95 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ* 148.8, 145.5, 141.7, 141.5, 135.9, 135.5, 133.8, 131.2, 125.8, 125.7, 125.5, 123.3, 123.2, 122.7, 122.2, 122.0, 121.7, 121.1, 120.6, 118.0, 111.3, 110.6, 107.5, 100.2, 99.9, 13.5; Anal Calcd for $C_{28}H_{20}ClN_5$: Calcd: C, 72.80; H, 4.36; N, 15.16. Found: C, 72.58; H, 4.27; N, 15.10. *Two aromatic carbon are merged with others.

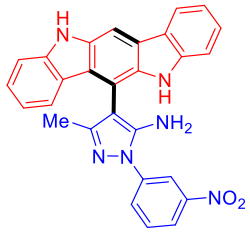
1-(2-Bromophenyl)-4-(5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1*H*-pyrazol-5-amine (3d):



3d

Purification by flash column chromatography on silica gel eluting with petroleum ether–ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as off-white solid; mp: 230-232 °C; yield: 0.222 g, 88%; IR (neat): 3345.1, 2907.0, 1625.7, 1520.8, 1461.1, 1379.1, 1312.0, 1265.7, 1085.3. cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 11.11 (s, 1H), 10.48 (s, 1H), 8.23 (d, J = 7.0 Hz, 1H), 8.13 (s, 1H), 7.91 (d, J = 7.4 Hz, 1H), 7.83 (d, J = 7.1 Hz, 1H), 7.74-7.61 (m, 2H), 7.56-7.44 (m, 3H), 7.41-7.31 (m, 2H), 7.14 (t, J = 7.1 Hz, 1H), 6.9 (t, J = 7.0 Hz, 1H), 4.64 (s, 2H), 1.96 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.7, 146.0, 141.7, 141.6, 138.4, 135.9, 135.4, 133.9, 131.2, 131.1, 129.1, 125.7, 125.4, 123.4, 123.3, 122.7, 122.6, 122.5, 122.2, 120.6, 118.0, 117.9, 111.4, 110.4, 108.3, 99.8, 96.8, 13.6; Anal Calcd for $C_{28}H_{20}BrN_5$: Calcd: C, 66.41; H, 3.98; N, 13.83 Found: C, 66.14; H, 3.96; N, 13.77.

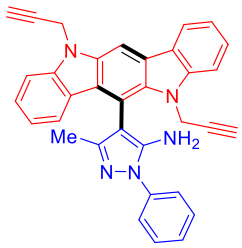
4-(5,11-Dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1-(3-nitrophenyl)-1*H*-pyrazol-5-amine (3e):



3e

Purification by flash column chromatography on silica gel eluting with petroleum ether–ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as yellow solid; mp: 240-242 °C; yield: 0.215 g, 91%; IR (neat): 3399.4, 3324.7, 1617.8, 1583.4, 1528.3, 1453.8, 1349.4, 1263.4, 1095.4. cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 11.16 (s, 1H), 10.65 (s, 1H), 8.73 (t, J = 2.0 Hz, 1H), 8.37 (dd, J = 8.1, 1.2 Hz, 1H), 8.24 (d, J = 7.7 Hz, 1H), 8.21-8.14 (m, 2H), 7.84 (t, J = 8.2 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.38-7.32 (m, 2H), 7.14 (t, J = 7.2 Hz, 1H), 7.01 (t, J = 7.3 Hz, 1H), 5.22 (s, 2H), 1.97 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ* 149.5, 148.7, 145.9, 141.7, 141.1, 135.9, 135.5, 131.1, 128.5, 125.8, 125.5, 123.3, 123.2, 122.8, 122.1, 121.7, 120.7, 120.4, 118.1, 116.9, 111.3, 110.7, 107.3, 100.3, 100.1, 13.5; Anal Calcd for $C_{28}H_{20}N_6O_2$: Calcd: C, 71.18; H, 4.27; N, 17.79; Found: C, 71.02; H, 4.19; N, 17.85. *Two aromatic carbon are merged with others.

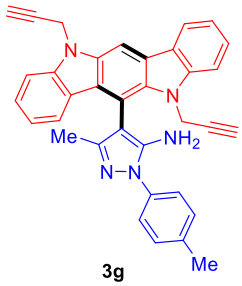
4-(5,11-Di(prop-2-yn-1-yl)-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1-phenyl-1*H*-pyrazol-5-amine (3f):



3f

Purification by flash column chromatography on silica gel eluting with petroleum ether–ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as off-white solid; mp: 245-247 °C; yield: 0.224 g, 89%; IR (neat): 3280.1, 2922.2, 2847.7, 1729.5, 1595.3, 1513.3, 1453.7, 1319.5, 1177.8, 1043.7. cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.7 Hz, 1H), 8.19 (s, 1H), 7.82 (d, *J* = 7.7 Hz, 2H), 7.60-7.46 (m, 7H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.1 Hz, 1H), 7.16-7.10 (m, 1H), 5.22 (d, *J* = 2.2 Hz, 2H), 5.13 (dd, *J* = 18.3, 2.2 Hz, 1H), 5.06 (dd, *J* = 18.3, 2.2 Hz, 1H), 3.70 (s, 2H), 2.34 (t, *J* = 2.1 Hz, 1H), 2.17 (s, 3H), 2.10 (t, *J* = 2.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 143.6, 142.5, 141.1, 139.0, 135.8, 134.7, 129.6, 127.3, 126.4, 125.9, 124.4, 124.0, 123.7, 123.6, 123.5, 122.0, 120.1, 119.6, 119.5, 109.3, 108.2, 108.0, 99.5, 99.0, 79.4, 78.1, 72.3, 71.5, 33.7, 32.6, 13.0.; Anal Calcd for $C_{34}H_{25}N_5$: Calcd: C, 81.09; H, 5.00; N, 13.91. Found: C, 80.88; H, 5.06; N, 13.83.

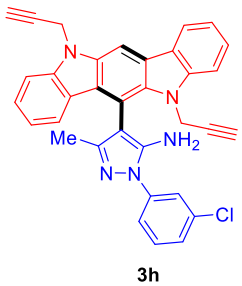
4-(5,11-Di(prop-2-yn-1-yl)-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1-(*p*-tolyl)-1*H*-pyrazol-5-amine (3g):



3g

Purification by flash column chromatography on silica gel eluting with petroleum ether–ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as pale yellow solid; mp: 260-262 °C; yield: 0.219 g, 85%; IR (neat): 3396.3, 2834.2, 1723.8, 1618.8, 1527.2, 1453.3, 1349.2, 1186.4, 1117.9. cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.7 Hz, 1H), 8.19 (s, 1H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.58-7.47 (m, 5H), 7.38-7.26 (m, 3H), 7.17-7.10 (m, 1H), 5.22 (d, *J* = 2.2 Hz, 2H), 5.13 (dd, *J* = 18.3, 2.2 Hz, 1H), 5.06 (dd, *J* = 18.3, 2.2 Hz, 1H), 3.67 (s, 2H), 2.46 (s, 3H), 2.34 (t, *J* = 2.2 Hz, 1H), 2.16 (s, 3H), 2.10 (t, *J* = 2.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 143.6, 142.4, 141.1, 137.3, 136.4, 135.8, 134.6, 130.2, 126.4, 125.9, 124.4, 123.9, 123.7, 123.6, 123.5, 122.0, 120.2, 119.6, 119.4, 109.3, 108.1, 99.2, 98.9, 79.4, 78.1, 77.3, 72.2, 71.5, 33.7, 32.6, 21.2, 13.0; Anal Calcd for $C_{35}H_{27}N_5$: Calcd: C, 81.21; H, 5.26; N, 13.53. Found: C, 80.94; H, 5.18; N, 13.56.

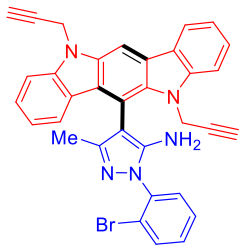
1-(3-Chlorophenyl)-4-(5,11-di(prop-2-yn-1-yl)-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1*H*-pyrazol-5-amine (3h):



3h

Purification by flash column chromatography on silica gel eluting with petroleum ether–ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as off-white solid; mp: 228-230 °C; yield: 0.185 g, 69%; IR (neat): 3380.1, 2923.2, 1730.5, 1633.5 1585.3, 1512.3, 1452.7, 1318.5, 1175.8, 1033.7. cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.7 Hz, 1H), 8.20 (s, 1H), 7.92 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.60-7.43 (m, 6H), 7.39-7.33 (m, 2H), 7.14 (dt, *J* = 8.0, 2.3 Hz, 1H), 5.21 (d, *J* = 2.2 Hz, 2H), 5.09 (dd, *J* = 18.3, 2.2 Hz, 1H), 5.02 (dd, *J* = 18.3, 2.2 Hz, 1H), 3.70 (s, 2H), 2.34 (s, 1H), 2.16 (s, 3H), 2.10 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 143.7, 142.5, 141.1, 140.2, 135.8, 135.3, 134.6, 130.6, 127.1, 126.5, 125.9, 124.5, 123.6, 123.5, 123.4, 121.9, 121.1, 120.2, 119.7, 119.5, 109.3, 108.3, 107.5, 100.3, 99.2, 79.4, 78.1, 77.3, 72.4, 71.6, 33.8, 32.6, 13.0; Anal Calcd for $C_{34}H_{24}ClN_5$: Calcd: C, 75.90; H, 4.50; N, 13.02. Found: C, 75.62; H, 4.58; N, 12.97.

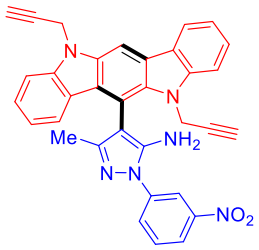
1-(2-Bromophenyl)-4-(5,11-di(prop-2-yn-1-yl)-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1*H*-pyrazol-5-amine (3i):



3i

Purification by flash column chromatography on silica gel eluting with petroleum ether–ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as off-white solid; mp: 190-192 °C; yield: 0.195 g, 67%; IR (neat): 3470.1, 2913.2, 2817.2, 1729.1, 1592.3, 1511.1, 1432.2, 1218.5, 1175.4, 1013.7. cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.7 Hz, 1H), 8.19 (s, 1H), 7.82 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.61-7.47 (m, 6H), 7.41 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.36-7.32 (m, 1H), 7.16-7.12 (m, 1H), 5.26-5.13 (m, 4H), 3.53 (s, 2H), 2.34 (t, *J* = 2.3 Hz, 1H), 2.16 (s, 3H), 2.11 (t, *J* = 2.2 Hz, 1H ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 144.5, 142.4, 141.1, 137.6, 135.8, 134.6, 133.7, 131.0, 130.7, 128.7, 126.3, 125.9, 124.4, 123.7, 123.6, 123.5, 122.5, 120.2, 119.6, 119.3, 109.3, 108.2, 107.9, 99.0, 98.8, 79.5, 78.1, 77.3, 72.3, 71.7, 33.7, 32.6, 13.1; Anal Calcd for $C_{34}H_{24}BrN_5$: Calcd: C, 70.11; H, 4.15; N, 12.02. Found: C, 69.88; H, 4.11; N, 11.95.

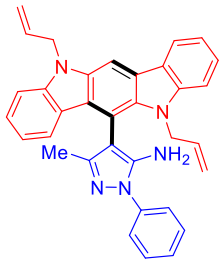
4-(5,11-Di(prop-2-yn-1-yl)-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1-(3-nitrophenyl)-1*H*-pyrazol-5-amine (3j):



3j

Purification by flash column chromatography on silica gel eluting with petroleum ether–ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as off-white solid; mp: 192-194 °C; yield: 0.194 g, 71%; IR (neat): 3482.2, 2870.6, 1739.6, 1567.7, 1520.8, 1455.9, 1274.7, 1177.8, 10.26.9 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.28 (d, *J* = 7.7 Hz, 2H), 8.24-8.2180 (m, 2H), 7.74 (t, *J* = 8.1 Hz, 1H), 7.62-7.47 (m, 4H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.15-7.120 (m, 1H), 5.23 (d, *J* = 2.0 Hz, 2H), 5.08 (dd, *J* = 18.3, 2.0 Hz, 1H), 5.00 (dd, *J* = 18.3, 2.0 Hz, 1H), 3.72 (s, 2H), 2.35 (s, 1H), 2.18 (s, 3H), 2.16 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 148.9, 143.8, 142.5, 141.1, 140.4, 135.8, 134.6, 130.5, 128.4, 126.6, 126.0, 124.5, 123.5, 123.4, 121.7, 121.2, 120.2, 119.8, 119.5, 117.5, 109.3, 108.3, 107.0, 101.8, 99.4, 79.4, 78.0, 77.2, 72.4, 71.7, 33.9, 32.6, 13.1;.Anal Calcd for $C_{34}H_{24}N_6O_2$: Calcd: C, 74.44; H, 4.41; N, 15.32. Found: C, 74.17; H, 4.38; N, 15.36.

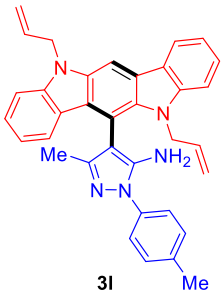
4-(5,11-Diallyl-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1-phenyl-1*H*-pyrazol-5-amine (3k):



3k

Purification by flash column chromatography on silica gel eluting with petroleum ether–ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as off-white solid; mp: 108-110 °C; yield: 0.162 g, 64%; IR (neat): 3442.2, 2760.6, 1728.3, 1512.3, 1452.7, 1321.5, 1293.8, 1191.3, 1078.9. cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.5 Hz, 1H), 8.11 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 2H), 7.55-7.36 (m, 6H), 7.34-7.30 (m, 1H), 7.09 (t, *J* = 7.0 Hz, 1H), 6.19-6.12 (m, 1H), 5.96-5.78 (m, 1H), 5.29-5.24. (m, 2H), 5.09 (s, 2H), 5.03-5.00 (m, 3H), 4.78 (d, *J* = 18.0 Hz, 1H), 3.64 (s, 2H), 2.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 143.4, 142.7, 141.7, 139.0, 136.1, 134.9, 133.6, 132.6, 129.6, 127.2, 126.1, 125.6, 124.0, 123.6, 123.4, 123.3, 122.9, 121.8, 119.9, 118.8, 116.9, 115.6, 109.1, 108.2, 107.4, 100.4, 98.8, 77.3, 46.4, 45.6, 13.0; Anal Calcd for $C_{34}H_{29}N_5$: Calcd: C, 80.45; H, 5.76; N, 13.80. Found: C, 80.36; H, 5.71; N, 13.74.

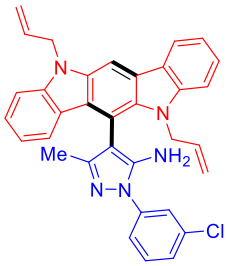
4-(5,11-Diallyl-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1-(*p*-tolyl)-1*H*-pyrazol-5-amine (3l):



3l

Purification by flash column chromatography on silica gel eluting with petroleum ether–ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as pale yellow solid; mp: 136-138 °C; yield: 0.175 g, 67%; IR (neat): 3442.2, 2770.6, 1763.8, 165.3, 1513.3, 1453.7, 1319.5, 1185.3, 1025.9 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.7 Hz, 1H), 8.10 (s, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.48-7.35 (m, 6H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.19-6.10 (m, 1H), 5.96-5.78 (m, 1H), 5.28-5.26 (m, 2H), 5.09 (d, *J* = 7.1 Hz, 2H), 5.06-4.89 (m, 3H), 4.78 (d, *J* = 18.0 Hz, 1H), 3.59 (s, 2H), 2.47 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 143.3, 142.7, 141.7, 137.2, 136.5, 136.1, 134.9, 133.6, 132.6, 130.2, 126.1, 125.6, 123.9, 123.7, 123.4, 123.3, 122.9, 121.9, 119.9, 118.7, 116.9, 115.6, 109.1, 108.2, 107.5, 100.0, 98.7, 77.2, 46.4, 45.6, 21.2, 13.0; Anal Calcd for $C_{35}H_{31}N_5$: Calcd: C, 80.58; H, 5.99; N, 13.43. Found: C, 80.34; H, 6.02; N, 13.39.

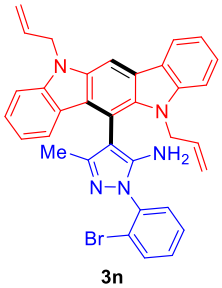
1-(3-Chlorophenyl)-4-(5,11-diallyl-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1*H*-pyrazol-5-amine (3m):



3m

Purification by flash column chromatography on silica gel eluting with petroleum ether–ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as off-white solid; mp: 108-110 °C; yield: 0.187 g, 69%; IR (neat): 3342.2, 2460.6, 1763.4, 1645.9, 1518.3, 1457.7, 1329.5, 1193.3, 1067.8 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.6 Hz, 1H), 8.11 (s, 1H), 7.89 (t, *J* = 2.0 Hz, 1H), 7.72 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.48-7.36 (m, 6H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.11-7.06 (m, 1H), 6.19-6.10 (m, 1H), 5.93-5.78 (m, 1H), 5.28-5.20 (m, 2H), 5.12-5.08 (m, 2H), 5.04-4.99 (m, 1H), 4.98-4.87 (m, 2H), 3.64 (s, 2H), 2.11 (s, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$): ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 143.4, 142.7, 141.7, 140.2, 136.1, 135.4, 134.8, 133.5, 132.5, 130.6, 127.0, 126.2, 125.7, 124.0, 123.3, 123.3, 123.2, 122.9, 121.7, 120.9, 120.0, 118.8, 116.9, 115.6, 109.1, 108.3, 106.8, 101.1, 98.9, 77.2, 46.4, 45.6, 13.0; Anal Calcd for $C_{34}H_{28}ClN_5$: Calcd: C, 75.33; H, 5.21; N, 12.92. Found: C, 75.09; H, 5.15; N, 12.99.

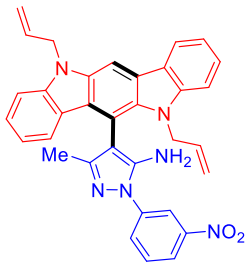
1-(2-Bromophenyl)-4-(5,11-diallyl-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1*H*-pyrazol-5-amine (3n):



3n

Purification by flash column chromatography on silica gel eluting with petroleum ether–ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as off-white solid; mp: 75-77 °C; yield: 0.225 g, 77%; IR (neat): 3332.2, 2740.6, 1763.7, 1645.5, 1516.3, 1459.7, 1323.5, 1265.7, 1181.3. cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.7 Hz, 1H), 8.10 (s, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 7.1 Hz, 1H), 7.57-7.52 (m, 2H), 7.44-7.38 (m, 3H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.19-6.10 (m, 1H), 5.94-5.86 (m, 1H), 5.28-5.21 (m, 2H), 5.09-5.08 (m, 2H), 5.04-5.01 (m, 2H), 4.82 (d, *J* = 17.2 Hz, 1H), 3.78-3.60 (m, 4H), 3.48 (s, 2H), 2.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 144.3, 142.7, 141.7, 137.7, 136.1, 133.8, 133.7, 132.6, 130.9, 130.8, 130.6, 128.7, 126.0, 125.6, 123.9, 123.5, 123.3, 122.9, 122.2, 119.9, 118.7, 118.6, 116.9, 115.6, 109.2, 108.1, 107.3, 98.8, 77.2, 70.5, 46.3, 45.6, 13.1; Anal Calcd for $C_{34}H_{28}BrN_5$: Calcd: C, 69.62; H, 4.81; N, 11.94. Found: C, 69.35; H, 4.72; N, 11.91.

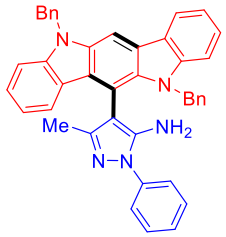
4-(5,11-Diallyl-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1-(3-nitrophenyl)-1*H*-pyrazol-5-amine (3o):



3o

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as yellow solid; mp: 108-110 °C; yield: 0.245 g, 89%; IR (neat): 3399.3, 3324.8, 2767.8, 1723.4, 1610.2, 1528.1,1238.9, 1185.3, 1080.9. cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.78 (t, *J* = 2.0 Hz, 1H), 8.26 (d, *J* = 7.8 Hz, 2H), 8.23 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.13 (s, 1H), 7.74 (t, *J* = 8.2 Hz, 1H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.48-7.53 (m, 2H), 7.41-7.35 (m, 2H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.08 (dt, *J* = 7.8, 1.5 Hz, 1H), 6.20-6.10 (m, 1H), 5.91-5.79 (m, 1H), 5.33-5.21 (m, 2H), 5.10 (d, *J* = 6.9 Hz, 2H), 5.06-5.01 (m, 1H), 5.01-4.86 (m, 2H), 4.76 (dd, *J* = 17.2, 1.0 Hz, 1H), 3.64 (s, 2H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 149.0, 143.2, 142.7, 141.7, 140.4, 136.1, 134.8, 133.5, 132.5, 130.5, 128.1, 126.3, 125.7, 124.1, 123.2, 123.1, 122.9, 121.5, 121.0, 120.0, 118.9, 118.8, 117.3, 117.0, 115.6, 109.1, 108.3, 106.3, 102.5, 99.2, 46.4, 45.6, 13.1; Anal Calcd for $C_{34}H_{28}N_6O_2$: Calcd: C, 73.90; H, 5.11; N, 15.21. Found: C, 72.82; H, 5.13; N, 15.09.

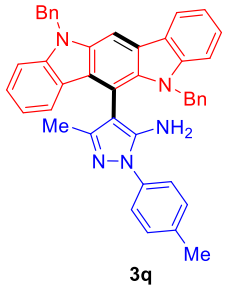
4-(5,11-Dibenzyl-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1-phenyl-1*H*-pyrazol-5-amine (3p):



3p

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as off-white solid; mp: 92-94 °C; yield: 0.209 g, 69%; IR (neat): 3026.6, 2922.2, 2789.8, 1765.7, 1595.3, 1505.8, 1453.7, 1276.9, 1185.4. cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.7 Hz, 1H), 8.14 (s, 1H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.43-7.35 (m, 6H), 7.34-7.30 (m, 5H), 7.07-7.01 (m, 4H), 6.74 (d, *J* = 7.0 Hz, 2H), 5.70 (s, 2H), 5.58 (s, 2H), 2.92 (s, 2H), 1.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 143.7, 143.2, 142.0, 138.9, 137.5, 136.5, 134.6, 129.5, 128.9, 128.4, 127.5, 126.9, 126.8, 126.5, 126.4, 125.8, 125.4, 124.1, 123.6, 123.3, 123.2, 122.6, 121.9, 120.1, 119.0, 118.9, 108.7, 108.3, 107.5, 100.4, 98.9, 77.3, 47.4, 46.9, 12.8; Anal Calcd for $C_{42}H_{33}N_5$: Calcd: C, 83.00; H, 5.47; N, 11.52. Found: C, 82.91; H, 5.45; N, 11.59.

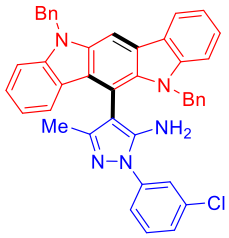
4-(5,11-Dibenzyl-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1-(*p*-tolyl)-1*H*-pyrazol-5-amine (3q):



3q

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as off-white solid; mp: 70-72 °C; yield: 0.226 g, 73%; IR (neat): 2922.2, 2755.1, 1610.2, 1575.8, 1513.3, 1453.7, 1319.5, 1117.8, 1051.1. cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.7 Hz, 1H), 8.13 (s, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.42-7.32 (m, 4H), 7.37-7.30 (m, 8H), 7.06 (t, *J* = 7.3 Hz, 4H), 6.73 (d, *J* = 7.0 Hz, 2H), 5.69 (s, 2H), 5.58 (s, 2H), 2.91 (s, 2H), 2.47 (s, 3H), 1.97 (s, 3H; ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 143.6, 143.1, 143.0, 138.8, 137.5, 136.9, 136.5, 136.3, 134.6, 130.0, 128.9, 128.4, 127.5, 126.8, 126.5, 126.3, 125.7, 125.4, 124.0, 123.6, 123.4, 123.3, 122.6, 121.9, 120.1, 118.9, 108.7, 108.2, 107.7, 100.0, 98.8, 77.3, 47.3, 46.8, 21.2, 12.7; Anal Calcd for $C_{43}H_{35}N_5$: Calcd: C, 83.06; H, 5.67; N, 11.26 . Found: C, 82.89; H, 5.61; N, 11.21.

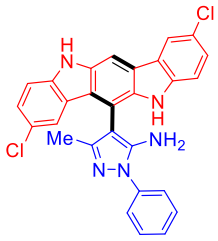
1-(3-Chlorophenyl)-4-(5,11-dibenzyl-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1*H*-pyrazol-5-amine (3r):



3r

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as off-white solid; mp: 102-104 °C; yield: 0.215 g, 67%; IR (neat): 2921.2, 1612.2, 1589.6, 1512.3, 1452.7, 1319.4, 1118.2, 1051.3. cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.7 Hz, 1H), 8.14 (s, 1H), 7.71 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.53-7.45 (m, 2H), 7.43-7.39 (m, 3H), 7.39-7.30 (m, 8H), 7.09-7.02 (m, 4H), 6.74 (d, *J* = 7.2 Hz, 2H), 5.70 (s, 2H), 5.60-5.49 (m, 2H), 2.86 (s, 2H), 2.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 143.7, 143.2, 142.0, 140.1, 138.8, 137.4, 136.5, 135.1, 134.6, 130.4, 128.9, 128.5, 127.5, 126.9, 126.7, 126.5, 126.4, 125.8, 125.3, 124.1, 123.6, 123.2, 123.0, 122.6, 121.8, 120.7, 120.1, 119.0, 108.7, 108.3, 107.0, 101.2, 99.1, 77.2, 47.5, 46.9, 12.8; Anal Calcd for $C_{42}H_{32}ClN_5$: Calcd: C, 78.55; H, 5.02; N, 10.91 Found: C, 78.41; H, 4.92; N, 10.88.

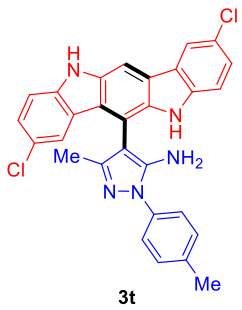
4-(2,8-Dichloro-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1-phenyl-1*H*-pyrazol-5-amine (3s):



3s

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as pale yellow solid; mp: 186-188 °C; yield: 0.188 g, 76%; IR (neat): 3398.1, 1765.6, 1575.3, 1527.3, 1468.3, 1271.2, 1128.9, 1023.4. cm^{-1}; ^1H NMR (400 MHz, DMSO) δ 11.39 (s, 1H), 10.85 (s, 1H), 8.37 (s, 1H), 8.24 (s, 1H), 7.83 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 2H), 7.48-7.50 (m, 3H), 7.38 (t, *J* = 7.4 Hz, 3H), 4.98 (s, 2H), 1.96 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 147.8, 145.3, 140.3, 140.2, 140.0, 136.6, 136.2, 129.7, 126.5, 125.7, 125.3, 124.5, 124.3, 123.2, 122.5, 122.4, 122.1, 121.8, 121.3, 120.4, 112.8, 112.0, 108.5, 100.9, 98.2, 13.4; Anal Calcd for $C_{28}H_{19}Cl_2N_5$: Calcd: C, 67.75; H, 3.86; N, 14.11. Found: C, 67.48; H, 4.82; N, 14.20.

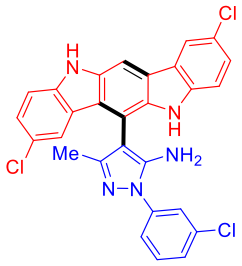
4-(2,8-Dichloro-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1-(*p*-tolyl)-1*H*-pyrazol-5-amine (3t):



3t

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as pale yellow; mp: above 360 °C; yield: 0.199 g, 78%; IR (neat): 3399.3, 1587.8, 1520.8, 1453.3, 1387.4, 1282.2, 1023.5. cm^{-1}; ^1H NMR (400 MHz, DMSO) δ 11.42 (s, 1H), 10.87 (s, 1H), 8.37 (s, 1H), 8.24 (s, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.49 (dd, *J* = 8.2, 2.7 Hz, 3H), 7.38-7.36 (m, 4H), 4.95 (s, 2H), 2.40 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 147.4, 145.2, 140.3, 140.2, 137.5, 136.5, 136.1, 135.9, 130.1, 125.7, 125.3, 124.5, 124.3, 123.2, 122.5, 122.3, 122.0, 121.7, 121.4, 120.4, 112.8, 112.0, 108.6, 100.8, 97.9, 21.1, 13.4; Anal Calcd for $C_{29}H_{21}Cl_2N_5$: Calcd: C, 68.24; H, 4.15; N, 13.72. Found: C, 67.96; H, 4.13; N, 13.64.

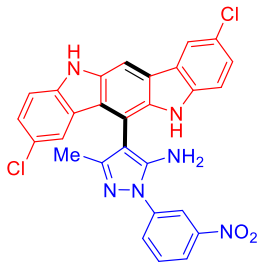
1-(3-Chlorophenyl)-4-(2,8-dichloro-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1*H*-pyrazol-5-amine (3u):



3u

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as pale yellow solid; mp: 202-204 °C; yield: 0.167 g, 63%; IR (neat): 3399.3, 1587.8, 1520.8, 1453.3, 1367.7, 1282.2, 1023.4 cm^{-1}; ^1H NMR (400 MHz, DMSO) δ 11.44 (s, 1H), 10.88 (s, 1H), 8.38 (d, *J* = 1.8 Hz, 1H), 8.26 (s, 1H), 7.91 (t, *J* = 1.8 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.59 (t, *J* = 8.1 Hz, 1H), 7.53-7.46 (m, 3H), 7.45-7.35 (m, 3H), 5.22 (s, 2H), 1.95 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 148.7, 145.8, 141.4, 140.3, 140.2, 136.5, 136.1, 133.9, 131.4, 126.1, 125.8, 125.4, 124.5, 124.2, 122.5, 122.4, 122.3, 121.7, 121.3, 121.2, 121.1 120.5, 112.7, 112.1, 108.1, 101.0, 98.7, 14.5; Anal Calcd for $C_{28}H_{18}Cl_3N_5$: Calcd: C, 63.35; H, 3.42; N, 13.19. Found: C, 63.03; H, 3.38; N, 13.26.

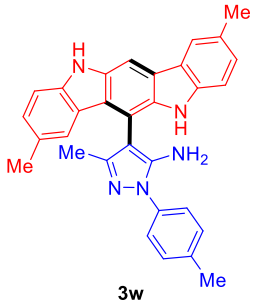
4-(2,8-Dichloro-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1-(3-nitrophenyl)-1*H*-pyrazol-5-amine (3v):



3v

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as yellow solid; mp: >360 °C; yield: 0.192 g, 71%; IR (neat): 3399.3, 3324.8, 1617.7, 1528.2, 1453.7, 1349.3, 1245.5, 1067.7. cm^{-1}; ^1H NMR (400 MHz, DMSO) δ 11.38 (s, 1H), 10.84 (s, 1H), 8.64 (t, *J* = 2.2 Hz, 1H), 8.33 (d, *J* = 2.1 Hz, 1H), 8.32 (dd, *J* = 8.1, 2.0, Hz, 1H), 8.21 (s, 1H), 8.15 (dd, *J* = 8.3, 2.2, Hz, 1H), 7.81 (t, *J* = 8.2 Hz, 1H), 7.45-7.42 (m, 3H), 7.36-7.31 (m, 2H), 5.32 (s, 2H), 1.91 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 148.7, 145.8, 141.5, 140.4, 140.3, 136.6, 136.2, 134.0, 131.4, 126.1, 125.8, 125.4, 124.6, 124.3, 122.6, 122.5, 122.4, 122.1, 121.8, 121.4, 121.3, 120.5, 112.8, 112.1, 108.2, 101.1, 98.8, 13.5; Anal Calcd for $C_{28}H_{18}Cl_2N_6O_2$: Calcd: C, 62.12; H, 3.35; N, 15.52. Found: C, 61.92; H, 3.39; N, 15.61.

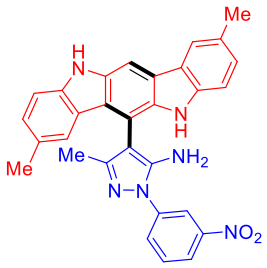
4-(2,8-Dimethyl-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1-(*p*-tolyl)-1*H*-pyrazol-5-amine (3w):



3w

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as yelow solid; mp: 227-229 °C; yield: 0.221 g, 94%; IR (neat): 3336.2, 2922.4, 1759.0, 1770.1, 1519.2, 1483.3, 1369.2, 1293.4, 1079.8. cm^{-1}; ^1H NMR (400 MHz, DMSO) δ 10.98 (s, 1H), 10.45 (s, 1H), 8.03-8.11 (m, 2H), 7.71 (d, *J* = 7.1 Hz, 2H), 7.53-7.24 (m, 5H), 7.23-7.02 (m, 2H), 4.86 (s, 2H), 2.51 (s, 3H), 2.41 (s, 3H), 2.36 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 147.5, 145.2, 140.0, 136.1, 136.0, 135.6, 130.2, 130.1, 127.0, 126.7, 126.6, 126.4, 126.0, 123.5, 123.4, 122.5, 121.9, 121.8, 120.5, 120.4, 111.1, 110.4, 110.3, 100.0, 99.2, 22.0, 21.7, 21.1, 13.4; Anal Calcd for $C_{31}H_{27}N_5$: Calcd: C, 79.29; H, 5.80; N, 14.91. Found: C, 78.98; H, 5.83; N, 14.95.

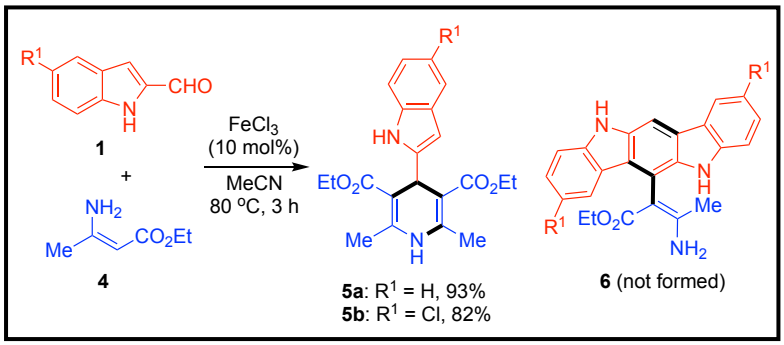
4-(2,8-Dimethyl-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-3-methyl-1-(3-nitrophenyl)-1*H*-pyrazol-5-amine (3x):



3x

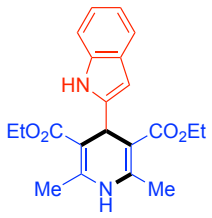
Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as yellow solid; mp: above 360 °C; yield: 0.240 g, 96%; IR (neat): 3397.4, 2896.5, 1759.3, 1770.4, 1535.9, 1482.8, 1385.6, 1294.5, 1246.3. cm^{-1}; ^1H NMR (400 MHz, DMSO) δ 10.99 (s, 1H), 10.47 (s, 1H), 8.73 (s, 1H), 8.35 (d, *J* = 7.1 Hz, 1H), 8.19 (d, *J* = 7.2 Hz, 1H), 8.05-8.10 (m, 2H), 7.85 (s, 1H), 7.37 (s, 3H), 7.18 (s, 2H), 5.20 (s, 2H), 2.51 (s, 3H), 2.36 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 149.5, 148.7, 145.9, 141.2, 140.0, 136.1, 135.7, 131.1, 128.6, 127.0, 126.7, 126.5, 126.1, 123.4, 123.3, 122.5, 121.9, 121.8, 120.4, 116.9, 111.1, 110.3, 107.1, 100.2, 100.1, 60.2, 22.0, 21.7, 21.3, 13.5; Anal Calcd for $C_{30}H_{24}N_6O_2$: Calcd: C, 71.99; H, 4.83; N, 16.79. Found: C, 71.73; H, 4.81; N, 16.87.

6. General Procedure for the Synthesis of Compounds 5a and 5b.



To a stirred solution of compound **1** (1.0 mmol, 1.0 equiv) and ethyl (*Z*)-3-aminobut-2-enoate **4** (2.0 equiv) in MeCN (6 mL) were added and $FeCl_3$ (10 mol%). The resulting mixture was stirred at 80 °C for 3 h and after completion of the reaction, as monitored by TLC, the mixture was diluted with water, the aqueous suspension was extracted with DCM (2 x 30 mL), washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography using petroleum ether-ethyl acetate mixture as eluent (90:10 to 85:15, v/v) to obtain compound **5**.

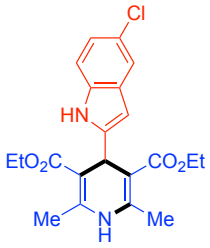
Diethyl 4-(1*H*-indol-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5a):



5a

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as off-white solid; mp: 175-177 °C; yield: 0.342 g, 93%; IR (neat): 3396.7, 3344.6, 2933.1, 1456.3, 1368.5, 1322.3, 1291.5, 1125.5, 1018.4 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.18 (s, 1H), 8.94 (s, 1H), 7.35 (t, *J* = 7.3 Hz, 2H), 6.96 (t, *J* = 7.3 Hz, 1H), 6.89 (t, *J* = 7.3 Hz, 1H), 5.96 (s, 1H), 5.13 (s, 1H), 4.08 (q, *J* = 7.0 Hz, 4H), 2.30 (s, 6H), 1.18 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.5, 146.5, 145.4, 136.3, 128.5, 120.3, 119.6, 118.9, 111.8, 100.2, 97.9, 59.7, 33.2, 18.9, 14.8; Anal Calcd for $C_{21}H_{24}N_2O_4$: Calcd: C, 68.46; H, 6.57; N, 7.60. Found: C, 68.19; H, 6.52; N, 7.55.

Diethyl 4-(5-chloro-1*H*-indol-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5b):



5b

Purification by flash column chromatography on silica gel eluting with petroleum ether−ethyl acetate mixture (90:10 to 85:15, v/v) afforded the title compound as off-white solid; mp: 173-175 °C; yield: 0.330 g, 82%; IR (neat): 3396.7, 3332.1, 2988.0, 1737.9, 1651.2, 1368.5, 1308.7, 1129.3, 1099.4, 1017.5 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.40 (s, 1H), 8.94 (s, 1H), 7.40 (d, J = 1.8 Hz, 1H), 7.33 (d, J = 8.6 Hz, 1H), 6.95 (dd, J = 8.6, 2.0 Hz, 1H), 5.97 (s, 1H), 5.11 (s, 1H), 4.08 (q, J = 7.0 Hz, 4H), 2.29 (s, 6H), 1.16 (t, J = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.4, 147.3, 146.6, 134.7, 129.7, 123.5, 120.2, 118.8, 113.2, 100.0, 97.8, 59.7, 33.4, 18.9, 14.7; Anal Calcd for $C_{21}H_{23}ClN_2O_4$: Calcd: C, 62.61; H, 5.75; N, 6.95. Found: C, 62.42; H, 5.71; N, 6.84.

7. X-Ray crystallography data of compounds 3f

Compound **3f** was dissolved by heating in minimum amount of acetonitrile and kept undisturbed for two days to obtain the crystals. The mother liquor was removed by filtration and the crystals were taken out carefully using micro spatula for characterization.

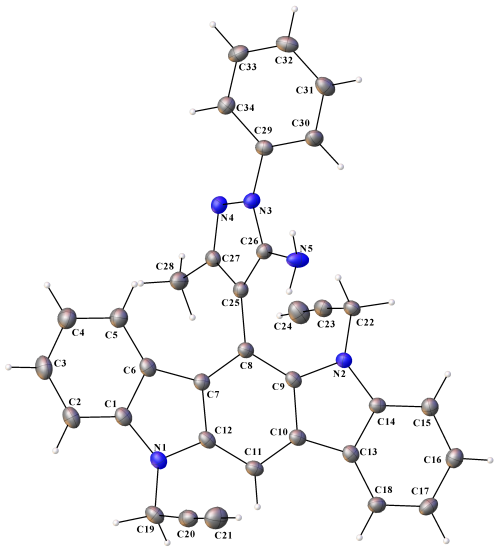


Figure S1. ORTEP representation of compound **3f** displaying thermal ellipsoid at 50% probability (CCDC: 2289177).

The crystal was kept at 100.15 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the olex2.refine [3] refinement package using Gauss-Newton minimization.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.
3. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.

Table S1. Crystal data and structure refinement for compound 3f.

Identification code	**3f**	
Empirical formula	$C_{34}H_{25}N_5$	
Formula weight	503.59	
Temperature	110.00 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 7.6326(4) Å	α = 90°.
	b = 16.0132(9) Å	β = 107.461(2)°.
	c = 10.7244(6) Å	γ = 90°.
Volume	1250.36(12) $Å^3$	
Z	2	

Density (calculated)	1.338 Mg/m^3
Absorption coefficient	0.630 mm^{-1}
F(000)	528
Crystal size	0.046 x 0.037 x 0.032 mm^3
Theta range for data collection	4.322 to 70.247°.
Index ranges	-9<=h<=9, -19<=k<=19, -13<=l<=13
Reflections collected	4718
Independent reflections	4718 [R(int) = 0.0924]
Completeness to theta = 67.679°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.753 and 0.623
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4718 / 1 / 355
Goodness-of-fit on F^2	1.076
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.1043
R indices (all data)	R1 = 0.0422, wR2 = 0.1045
Absolute structure parameter	-0.1(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.340 and -0.295 $e.Å^{-3}$

8. Absorption and Emission Spectra of Compound 3a

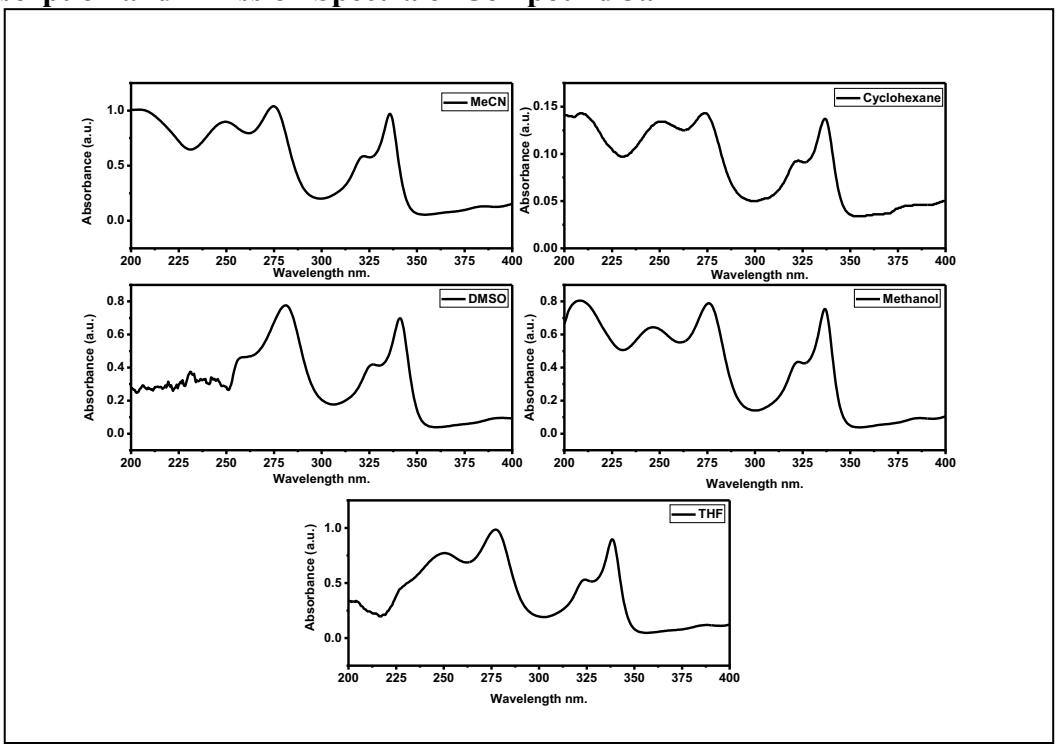


Figure S2. Absorption spectra of compound **3a** in different solvents

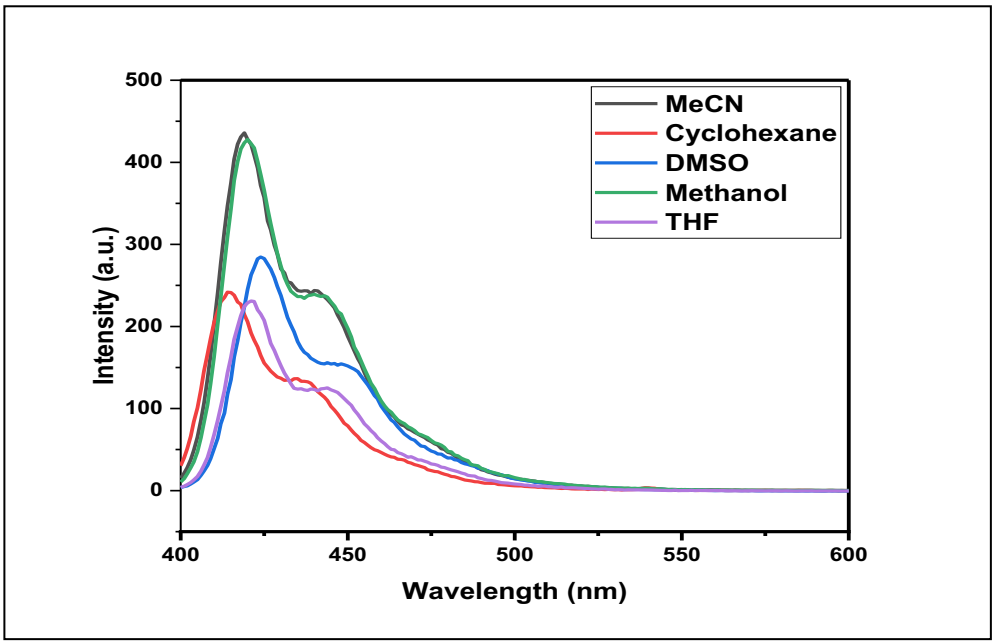


Figure S3. Emission spectra of compound **3a** in different solvents (Excitation wavelength 270 nm)

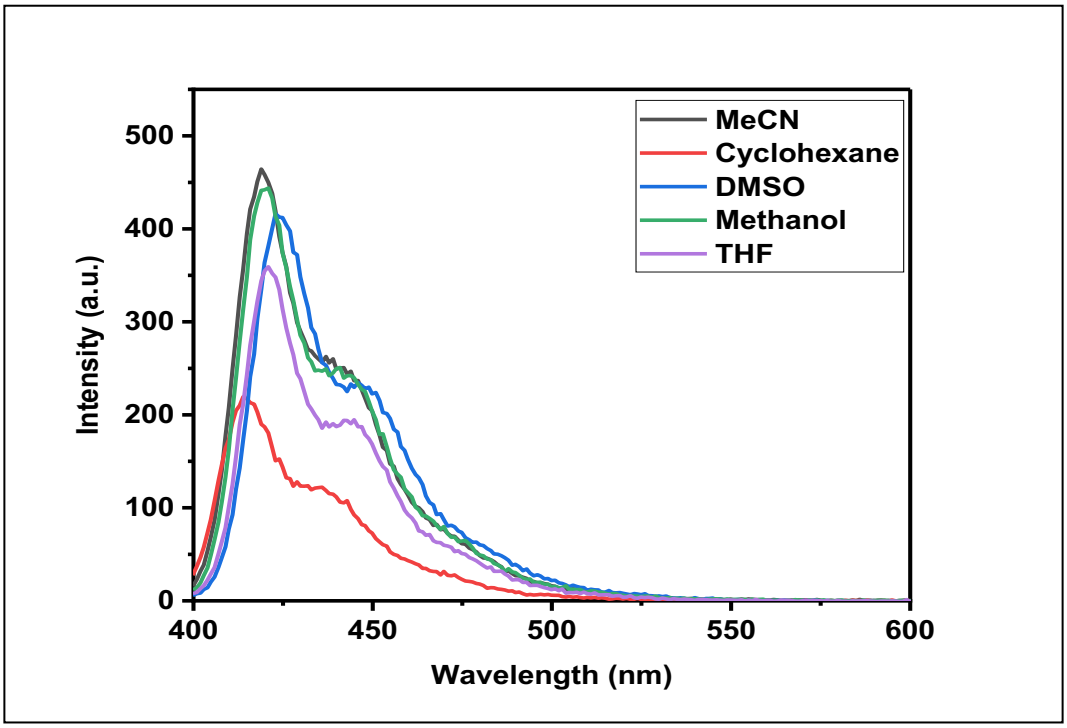
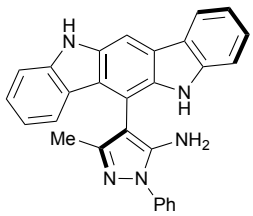
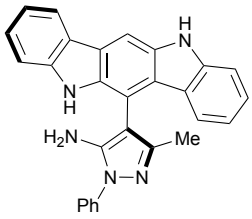


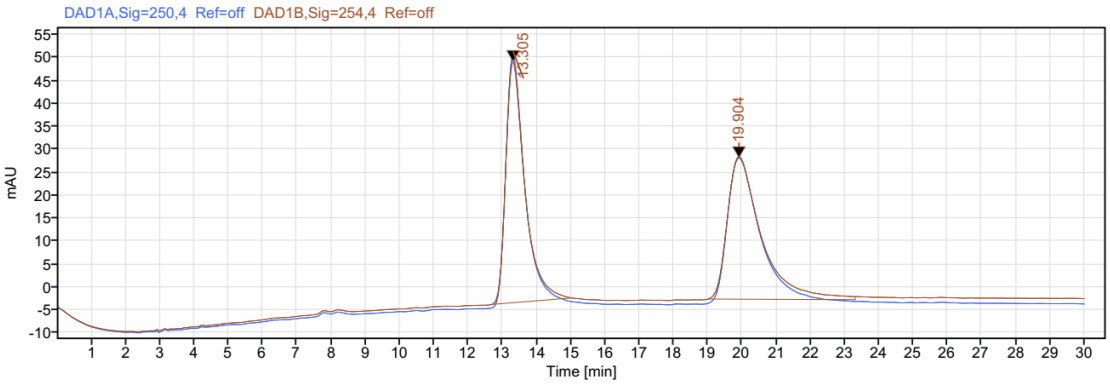
Figure S4. Emission spectra of compound **3a** in different solvents (Excitation wavelength 330 nm)

9. HPLC Resolution of Compound 3a

Column: Daicel Chiralpak IB column
Solvent System: Hexane: EtOAc (80:20)
Flow Rate: 1 mL/min.







Signal: DAD1B,Sig=254,4 Ref=off

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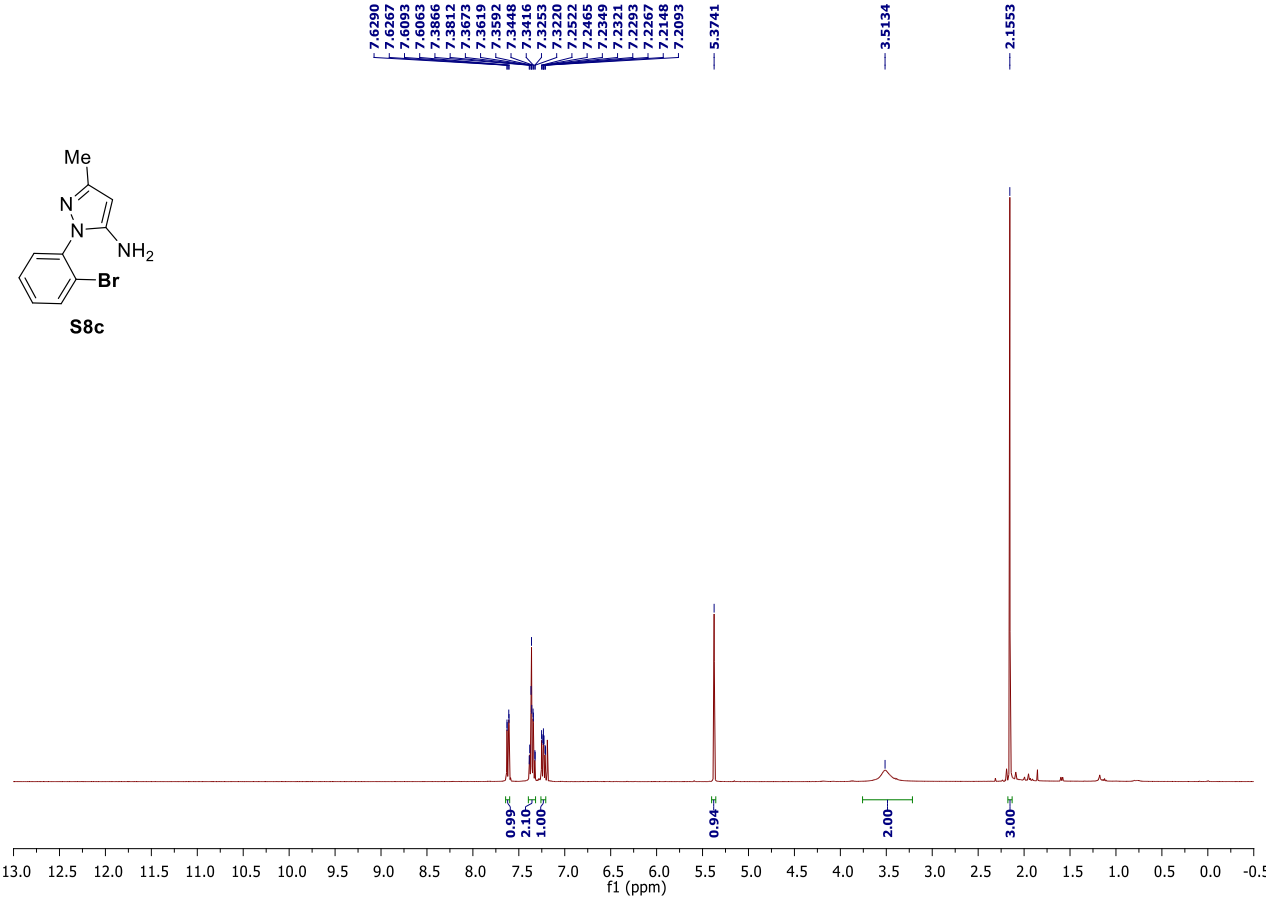
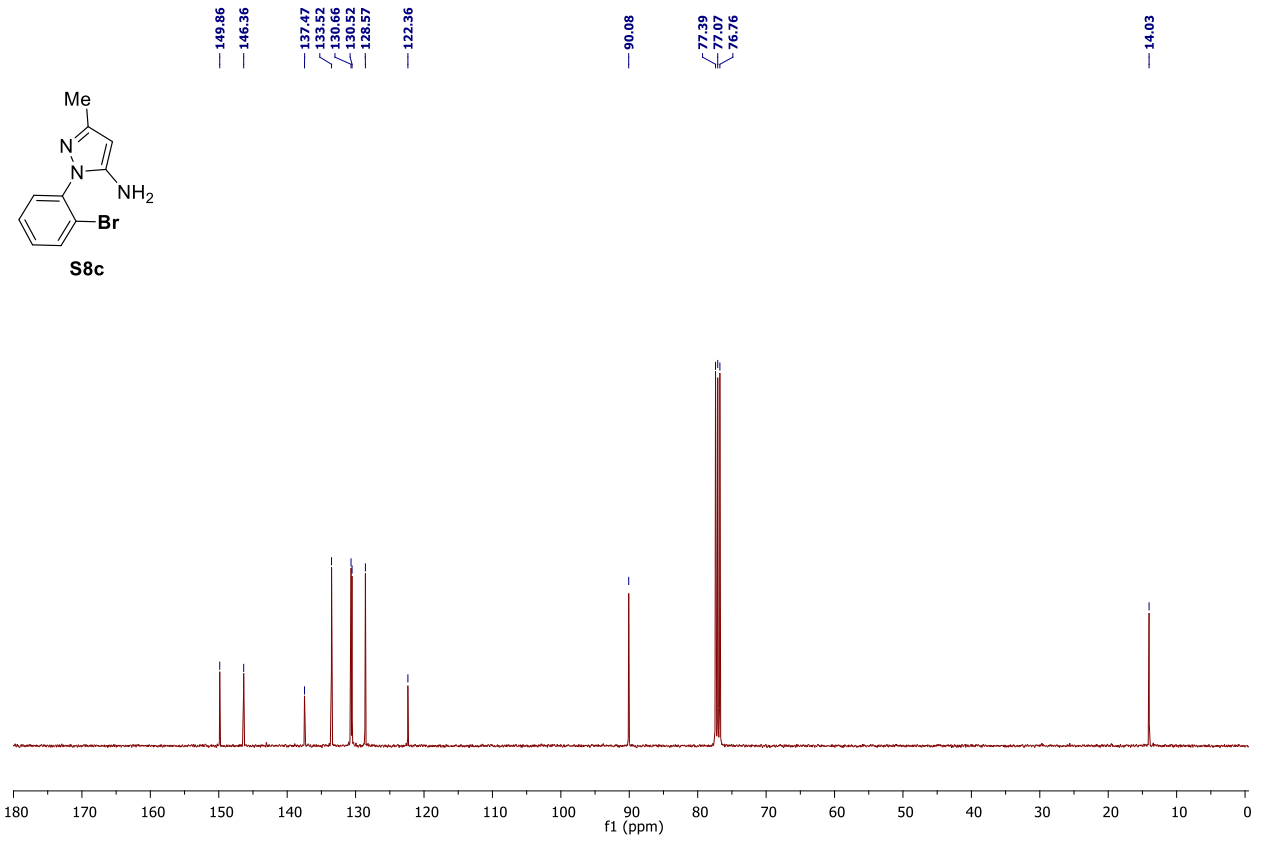
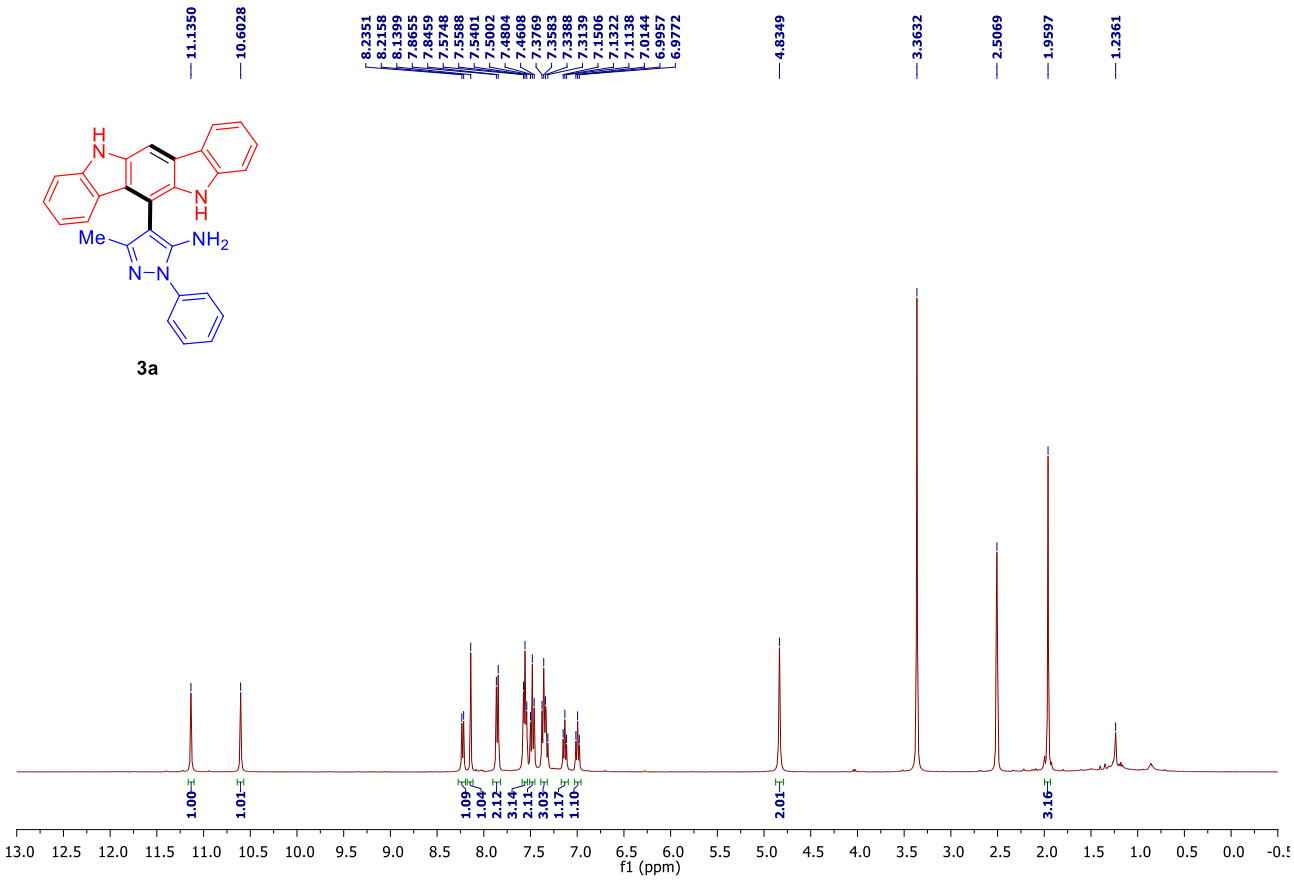
13.305	2.33	2030.60	52.53	48.80
19.904	4.30	2130.19	30.78	51.20
	Sum	**4160.79**		

10. Copies of ^{1}H and ^{13}C NMR Spectra



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8.2158
8.1399
7.8655
7.8459
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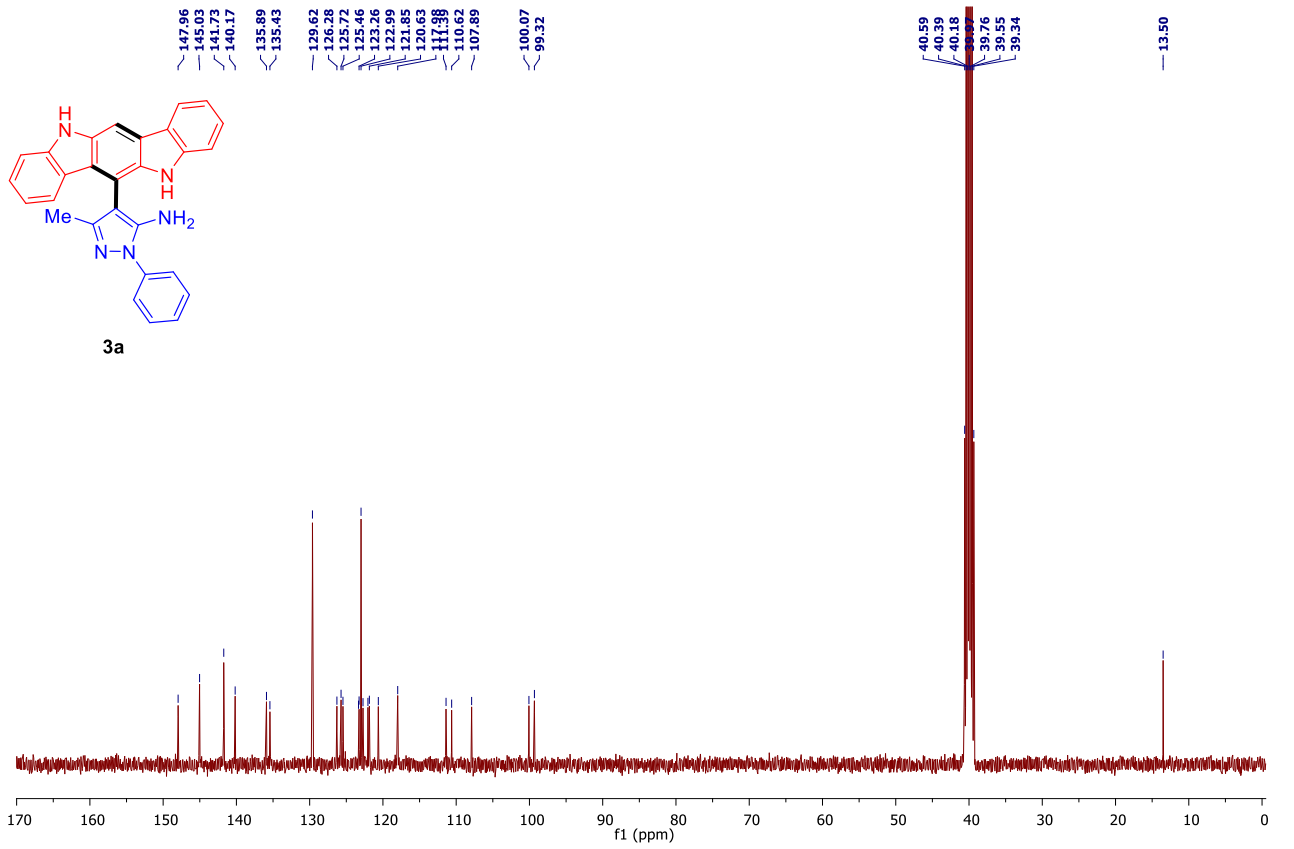
7.5588
7.5401
7.5002
7.4804
7.4608
7.3769
7.3583
7.3388
7.3139
7.1506
7.1322
7.1138
7.0144
6.9957
6.9772
4.8349
3.3632
2.5069
1.9597
1.2361
1.00
1.01
1.09
1.04
2.12
3.14
2.11
3.03
1.17
1.10
2.01
3.16
f1 (ppm)

3a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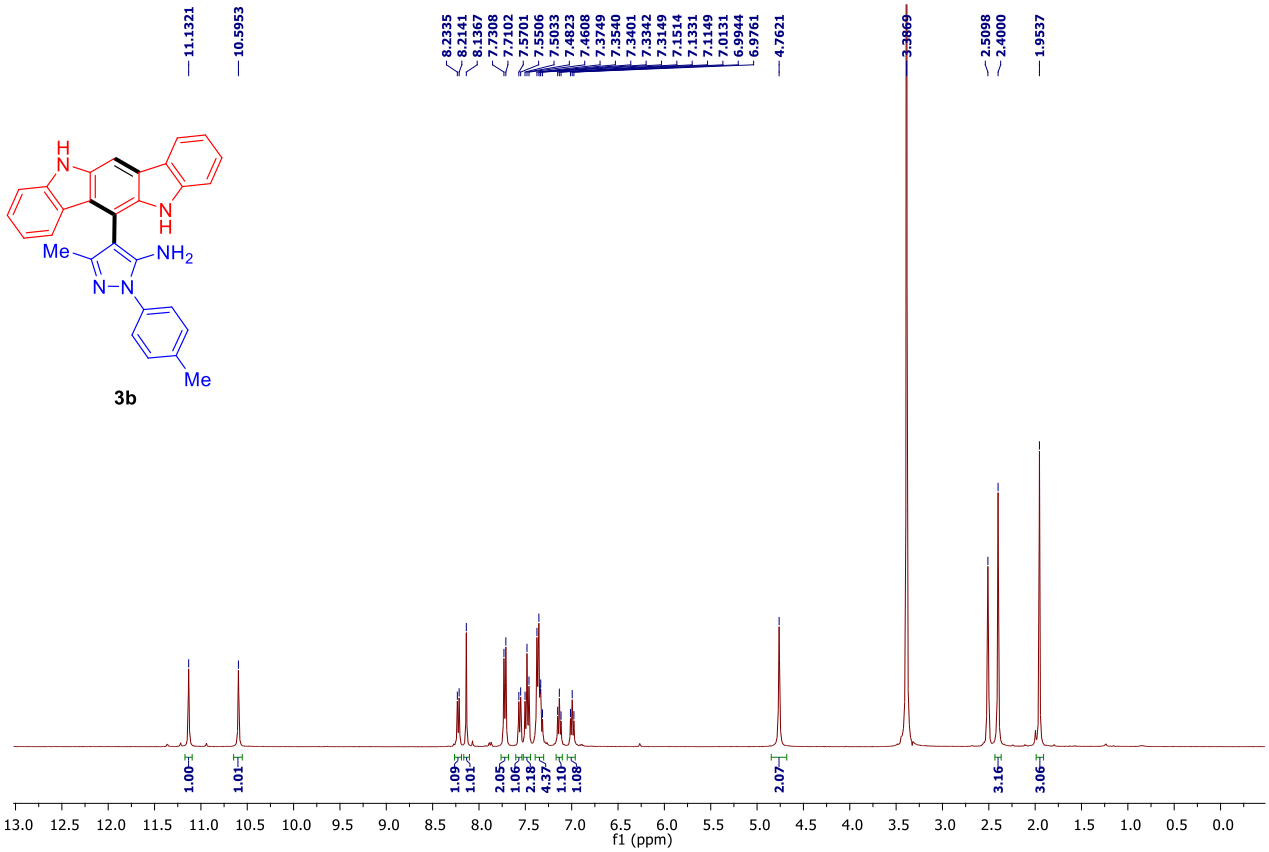
145.03
141.73
140.17
135.89
135.43
129.62
126.28
125.72
125.46
123.26
122.99
121.85
120.63
110.62
107.89
100.07
99.32
40.59
40.39
40.18
39.97
39.76
39.55
39.34
13.50
f1 (ppm)

3a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8.2335
8.2141
8.1367
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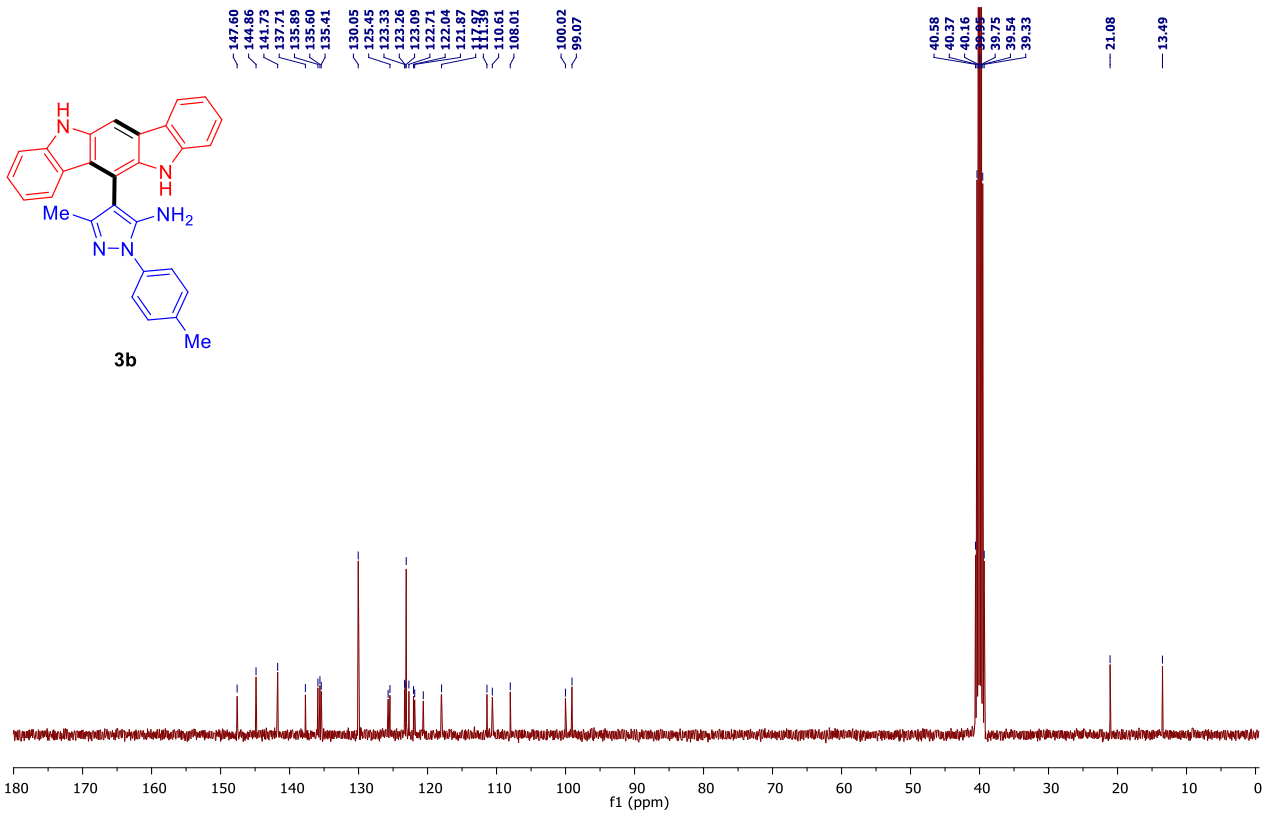
7.7102
7.5701
7.5506
7.5033
7.4823
7.4608
7.3749
7.3540
7.3401
7.3342
7.3149
7.1514
7.1331
7.1149
7.0131
6.9944
6.9761
4.7621
3.3869
2.5098
2.4000
1.9537
1.00
1.01
1.09
1.01
2.05
1.06
2.18
4.37
1.10
1.08
2.07
3.16
3.06
f1 (ppm)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135.60
135.41
130.05
125.45
123.33
123.26
123.09
122.71
122.04
121.87
110.61
108.01
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40.37
40.16
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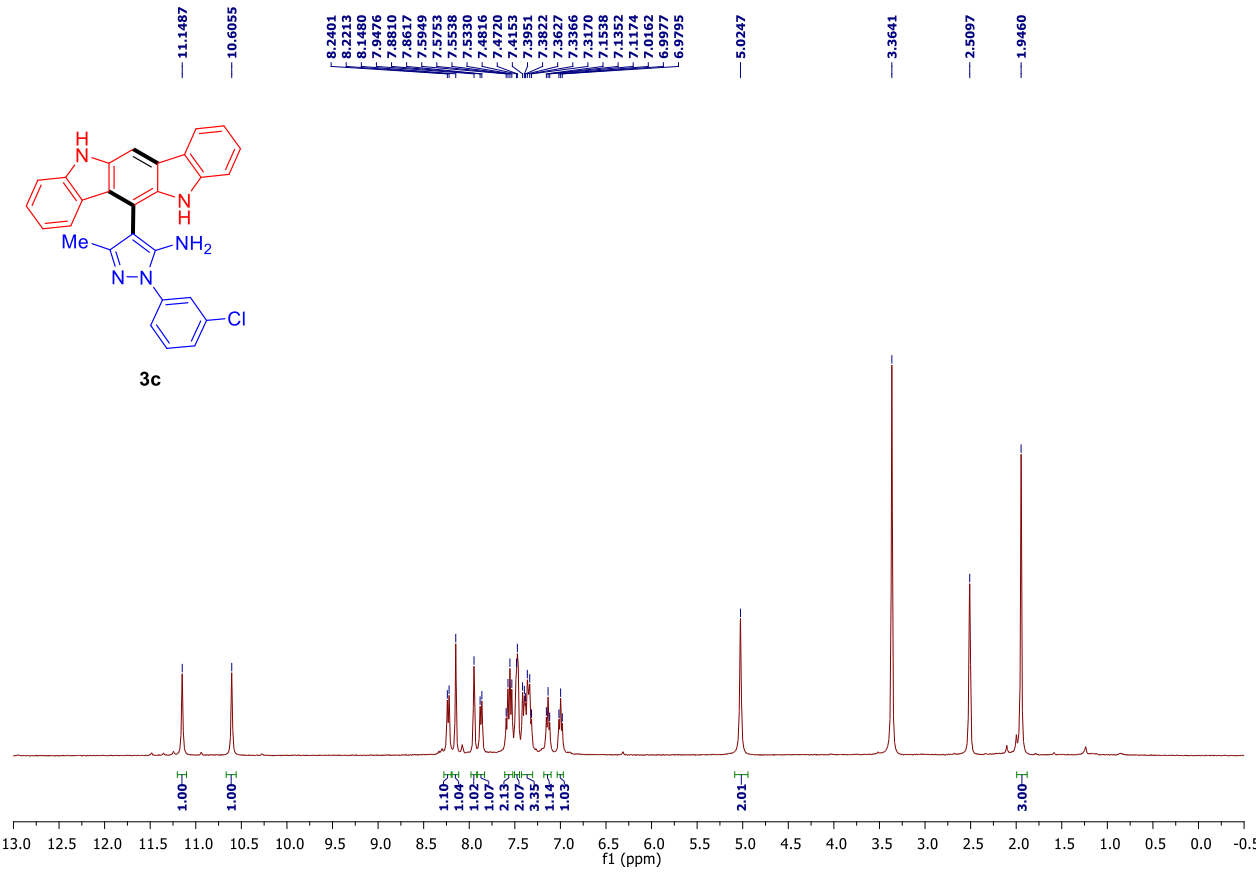
39.33
21.08
13.49
f1 (ppm)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7.5949
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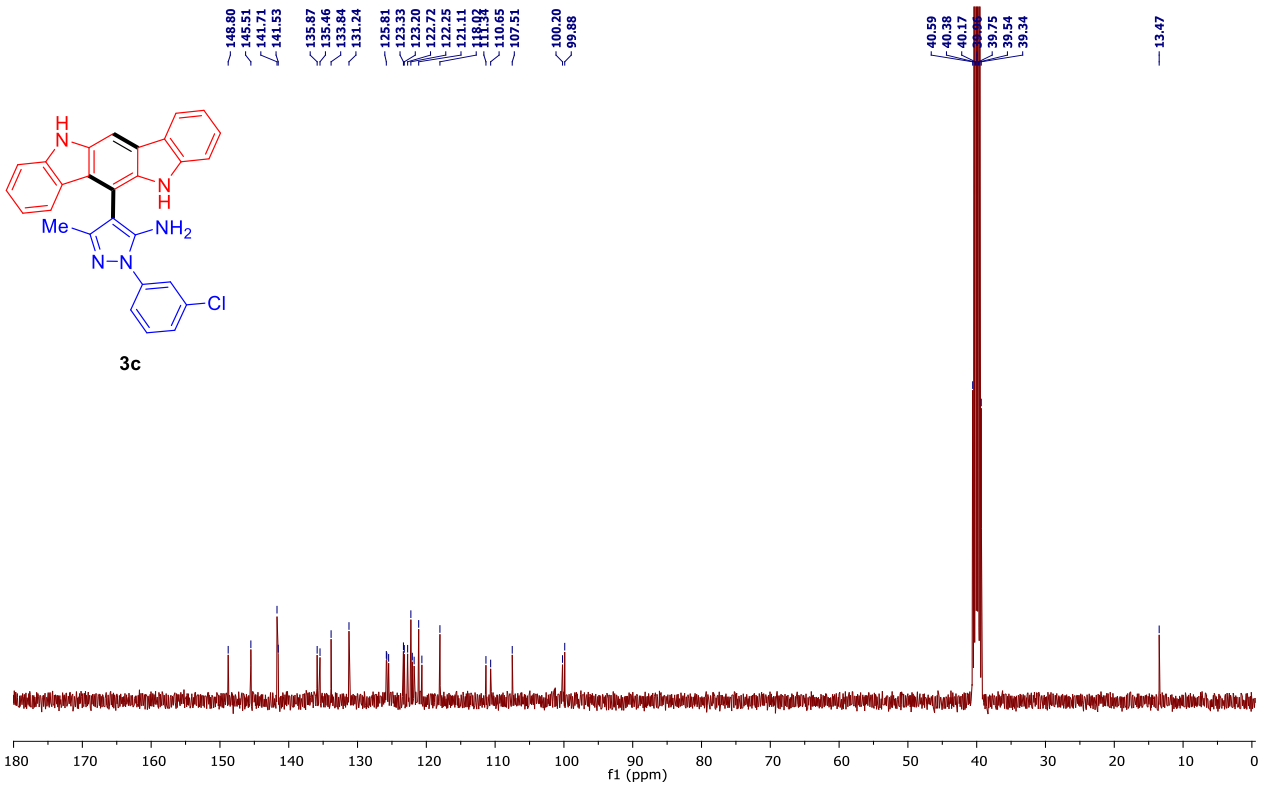
7.5538
7.5330
7.4816
7.4720
7.4153
7.3951
7.3822
7.3627
7.3366
7.3170
7.1538
7.1352
7.1174
7.0162
6.9977
6.9795
5.0247
3.3641
2.5097
1.9460
1.00
1.00
1.10
1.04
1.02
1.07
2.13
2.07
3.35
1.14
1.03
2.01
3.00
f1 (ppm)

H
N
N
H
Me
NH2
N–N
Cl

3c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122.25
121.11
118.02
111.34
110.65
107.51
100.20
99.88
40.59
40.38
40.17
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13.47
f1 (ppm)

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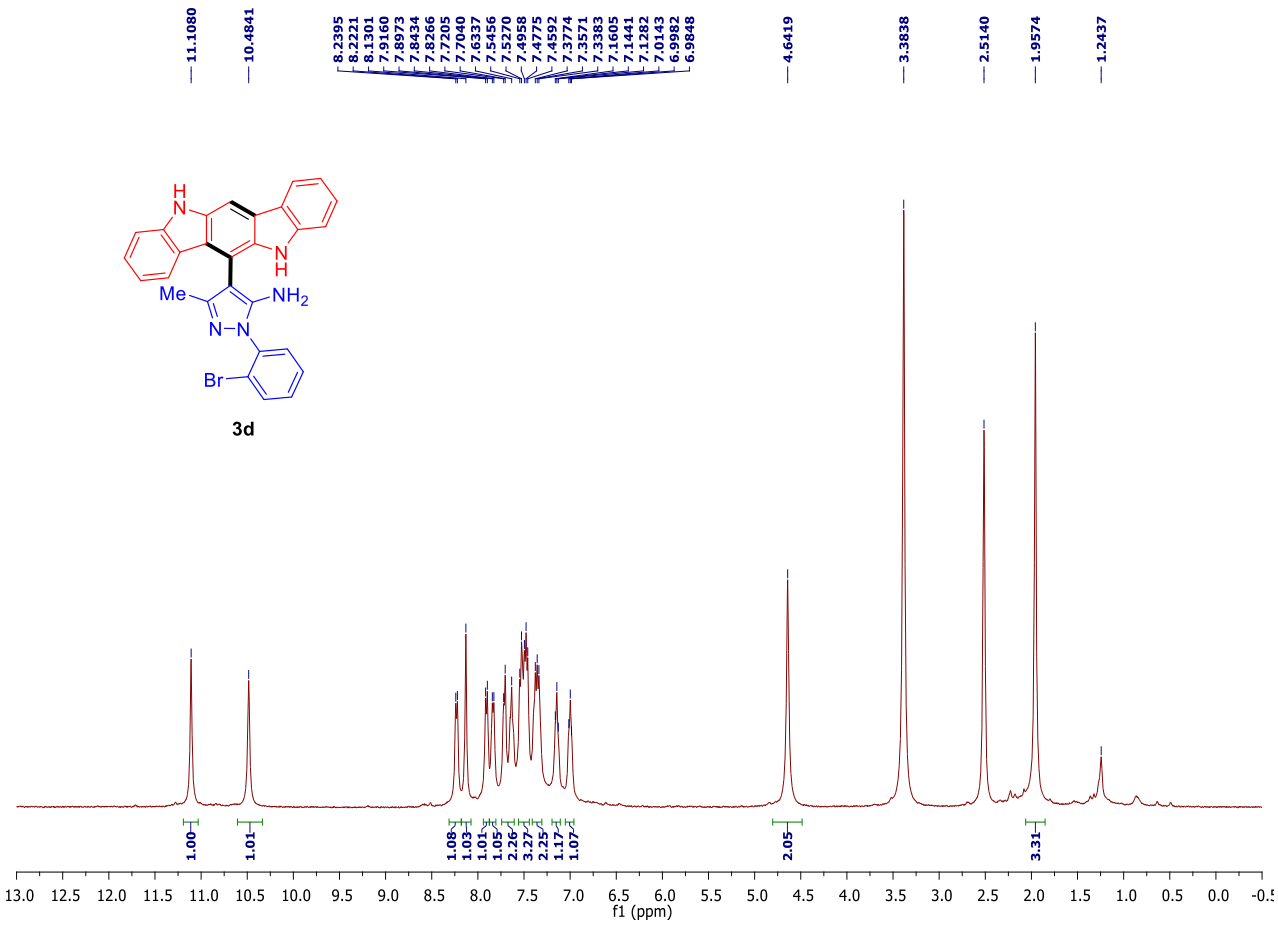
N
H
Me
NH2
N–N
Cl

3c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7.6337
7.5456
7.5270
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7.4775
7.4592
7.3774
7.3571
7.3383
7.1605
7.1441
7.1282
7.0143
6.9982
6.9848
4.6419
3.3838
2.5140
1.9574
1.2437
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2.26
3.27
2.25
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1.07
2.05
3.31
f1 (ppm)

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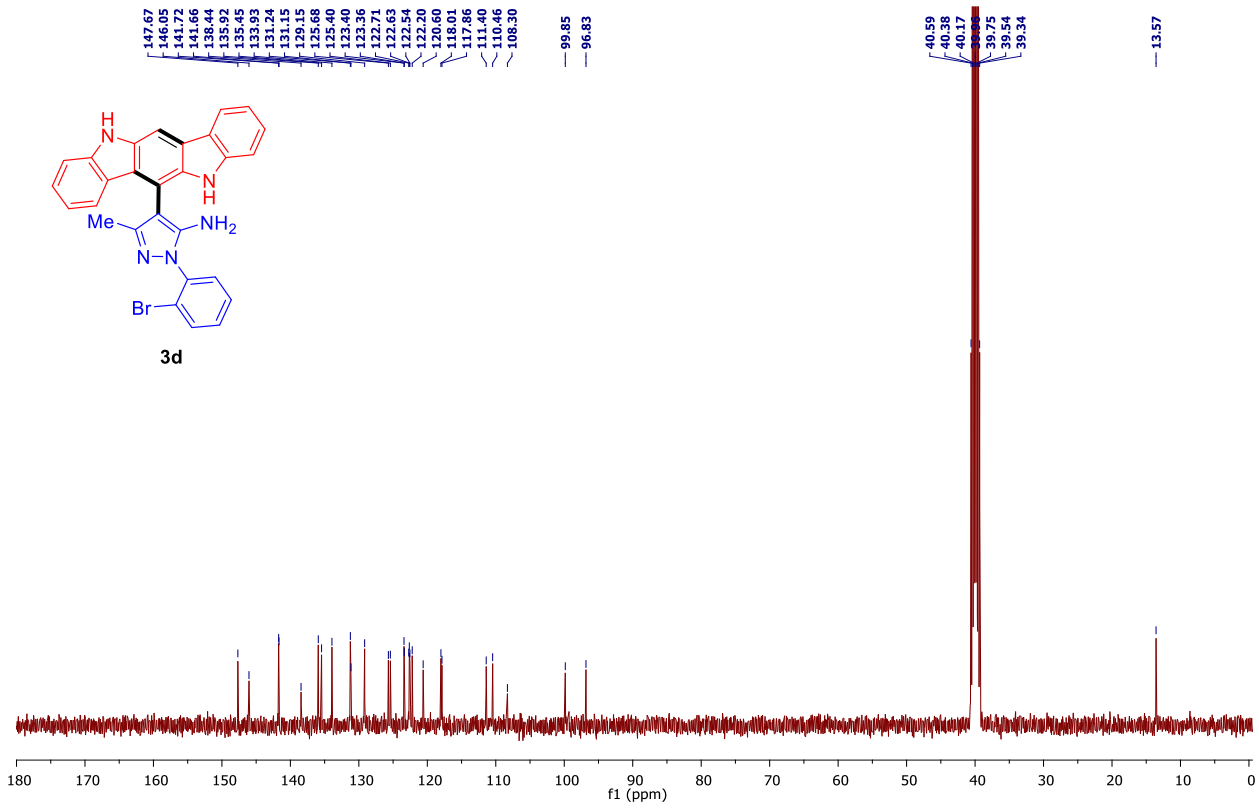
N
H
Me
NH2
N–N
Br

3d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133.93
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129.15
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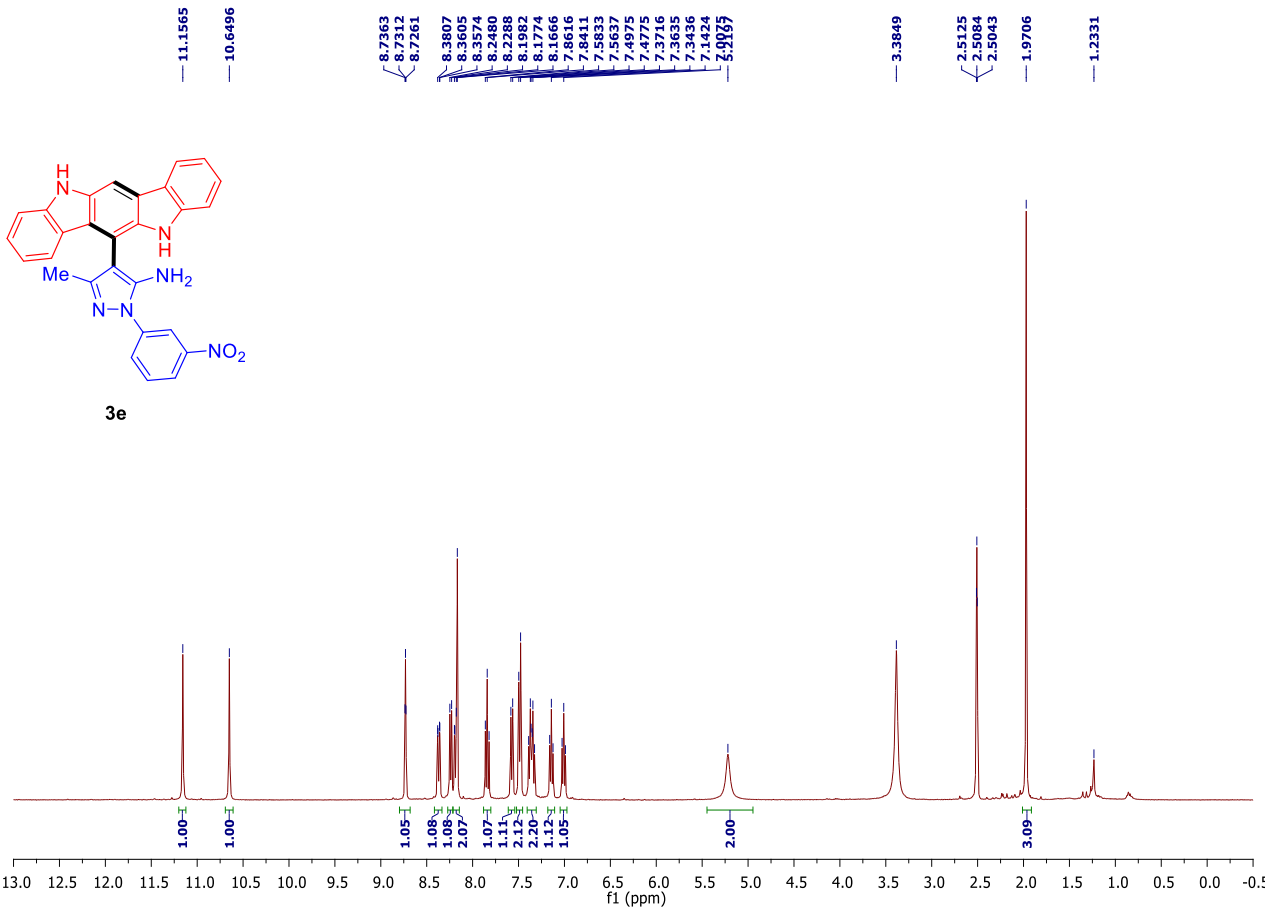
125.40
123.40
123.36
122.71
122.63
122.54
122.20
120.60
118.01
117.86
111.40
110.46
108.30
99.85
96.83
40.59
40.38
40.17
39.96
39.75
39.54
39.34
13.57
f1 (ppm)

H
N
N
H
Me
NH2
N–N
Br

3d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8.2288
8.1982
8.1774
8.1666
7.8616
7.8411
7.5833
7.5637
7.4975
7.4775
7.3716
7.3635
7.3436
7.1424
3.3849
2.5125
2.5084
2.5043
1.9706
1.2331
1.00
1.00
1.05
1.08
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2.07
1.07
1.11
2.12
2.20
1.12
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2.00
3.09
f1 (ppm)

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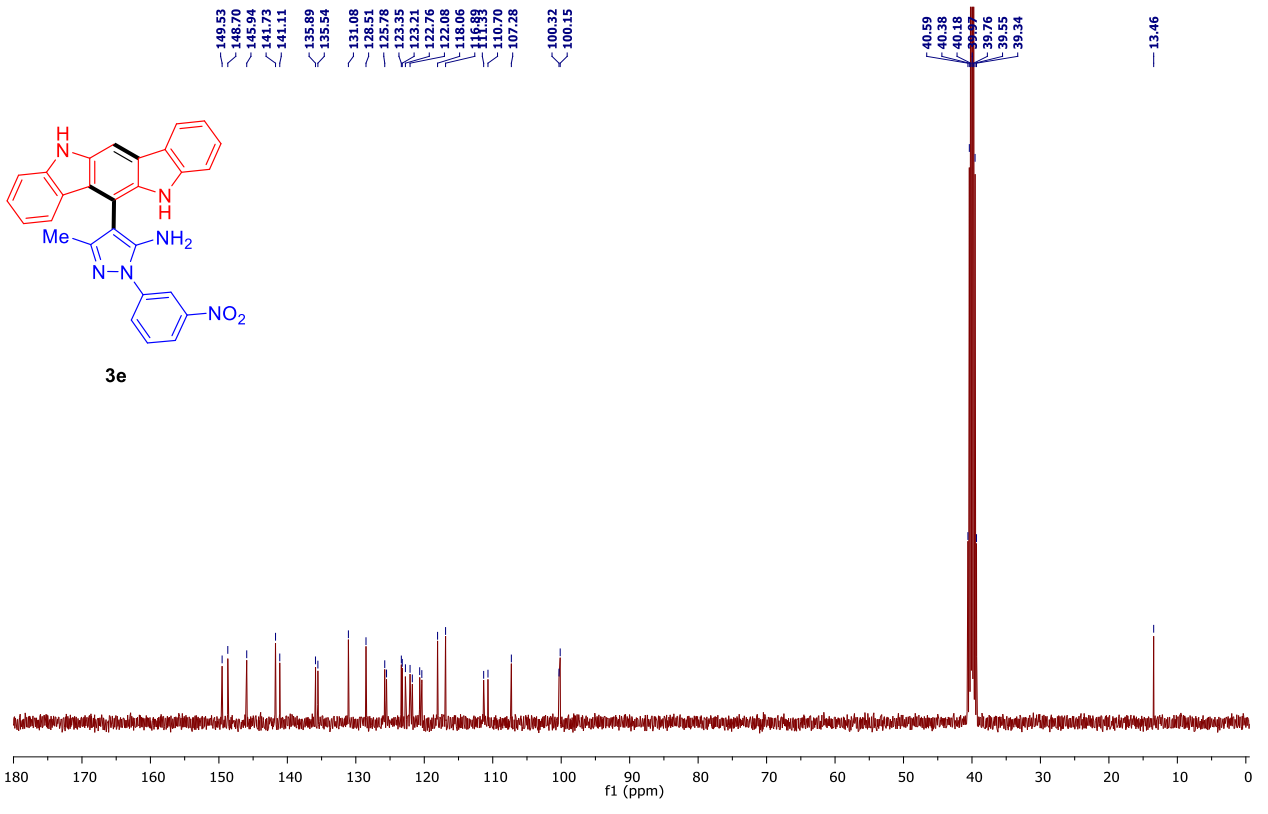
N
H
Me
NH2
N–N
NO2

3e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123.21
122.76
122.08
118.06
111.33
110.70
107.28
100.32
100.15
40.59
40.38
40.18
39.76
39.55
39.34
13.46
f1 (ppm)

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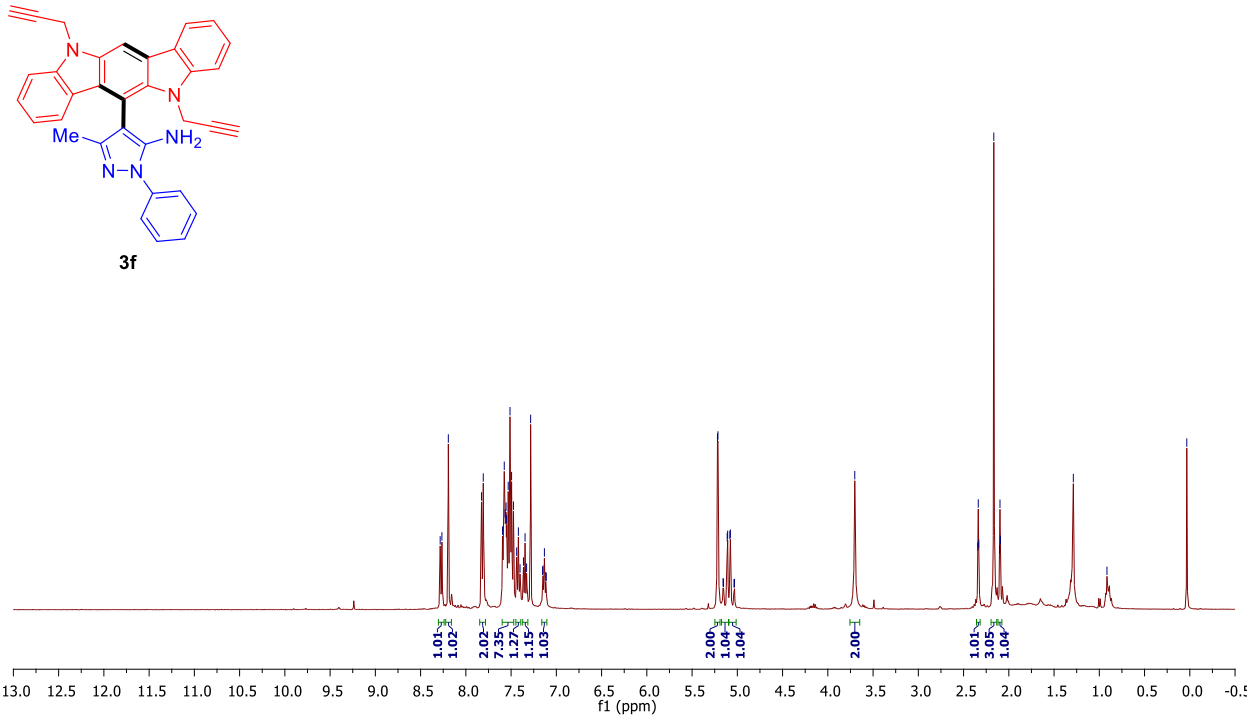
N
N
H
Me
NH2
N–N
NO2

3e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7.5120
7.4945
7.4739
5.2140
5.1580
5.1524
5.1122
5.1067
5.0823
5.0769
5.0367
5.0312
3.7022
2.3429
2.3375
2.3323
2.1658
2.1027
2.0976
2.0925
1.2870
0.9154
0.0332
Me
NH2
N–N
3f
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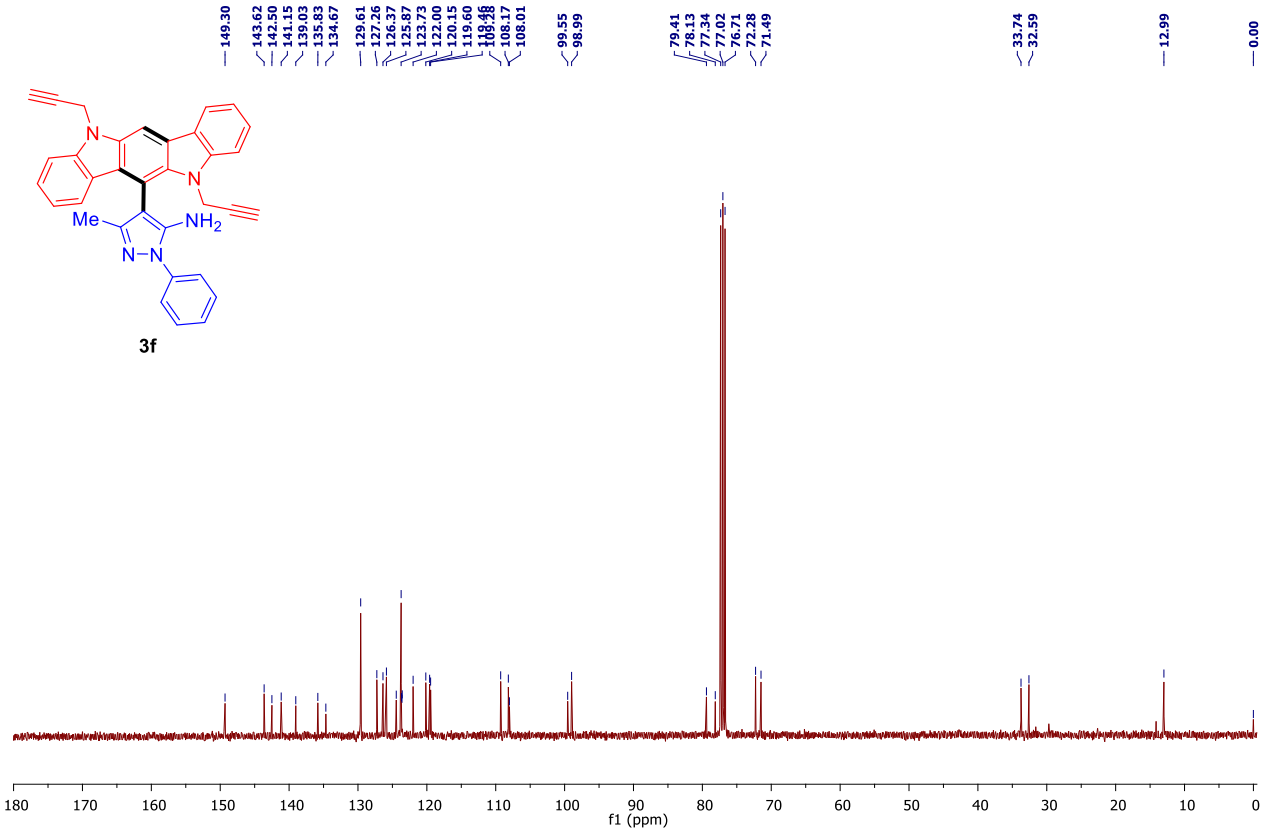
1.02
2.02
7.35
1.27
1.15
1.03
2.00
1.04
1.04
2.00
1.01
3.05
1.04
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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134.67
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126.37
125.87
123.73
122.00
120.15
119.60
108.17
108.01
99.55
98.99
79.41
78.13
77.34
77.02
76.71
72.28
71.49
33.74
32.59
12.99
0.00
Me
NH2
N–N
3f
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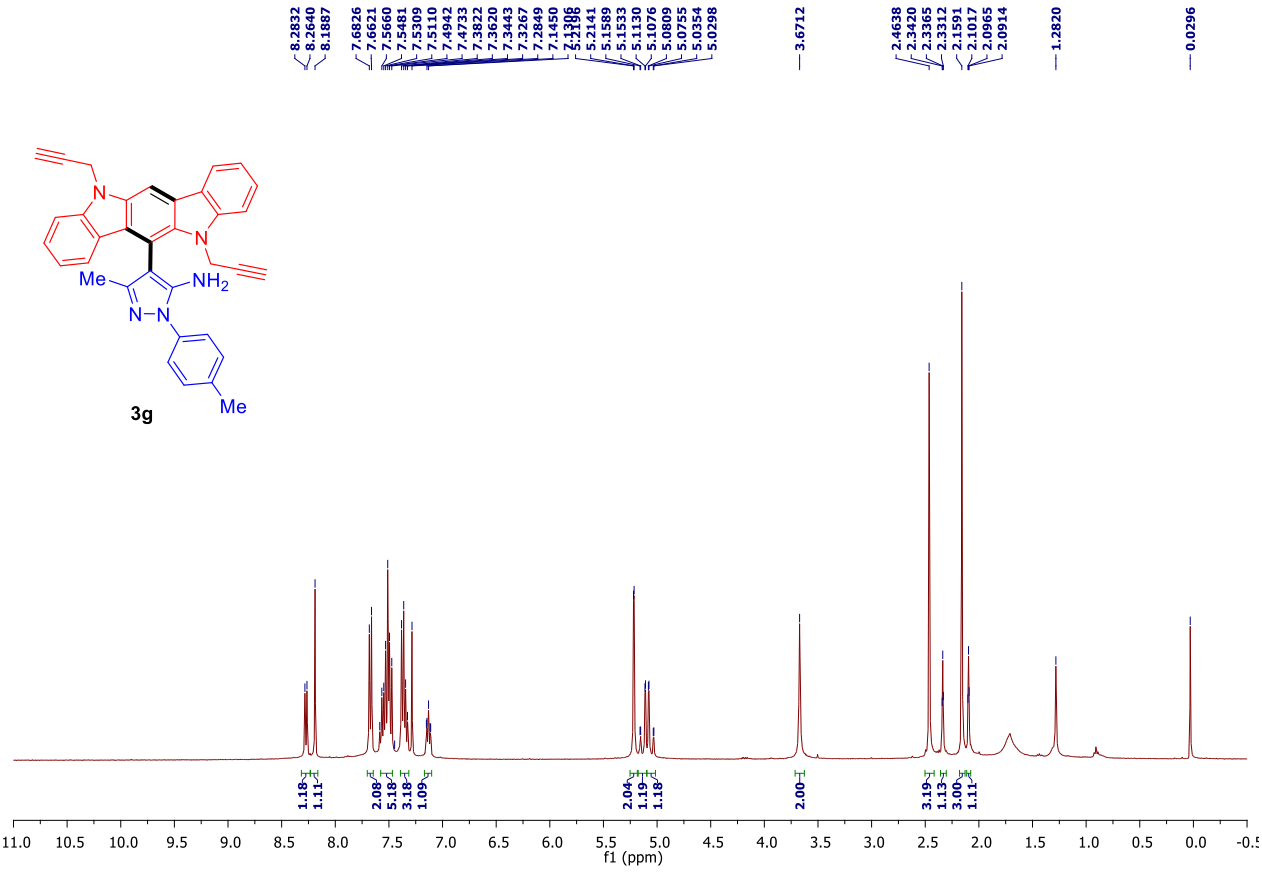
f1 (ppm)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7.4733
7.3822
7.3620
7.3443
7.3267
7.2849
7.1450
5.2141
5.1589
5.1533
5.1130
5.1076
5.0809
5.0755
5.0354
5.0298
3.6712
2.4638
2.3420
2.3365
2.3312
2.1591
2.1017
2.0965
2.0914
1.2820
0.0296
Me
NH2
N–N
Me
3g
1.18
1.11
2.08
5.18
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1.09
2.04
1.19
1.18
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3.19
1.13
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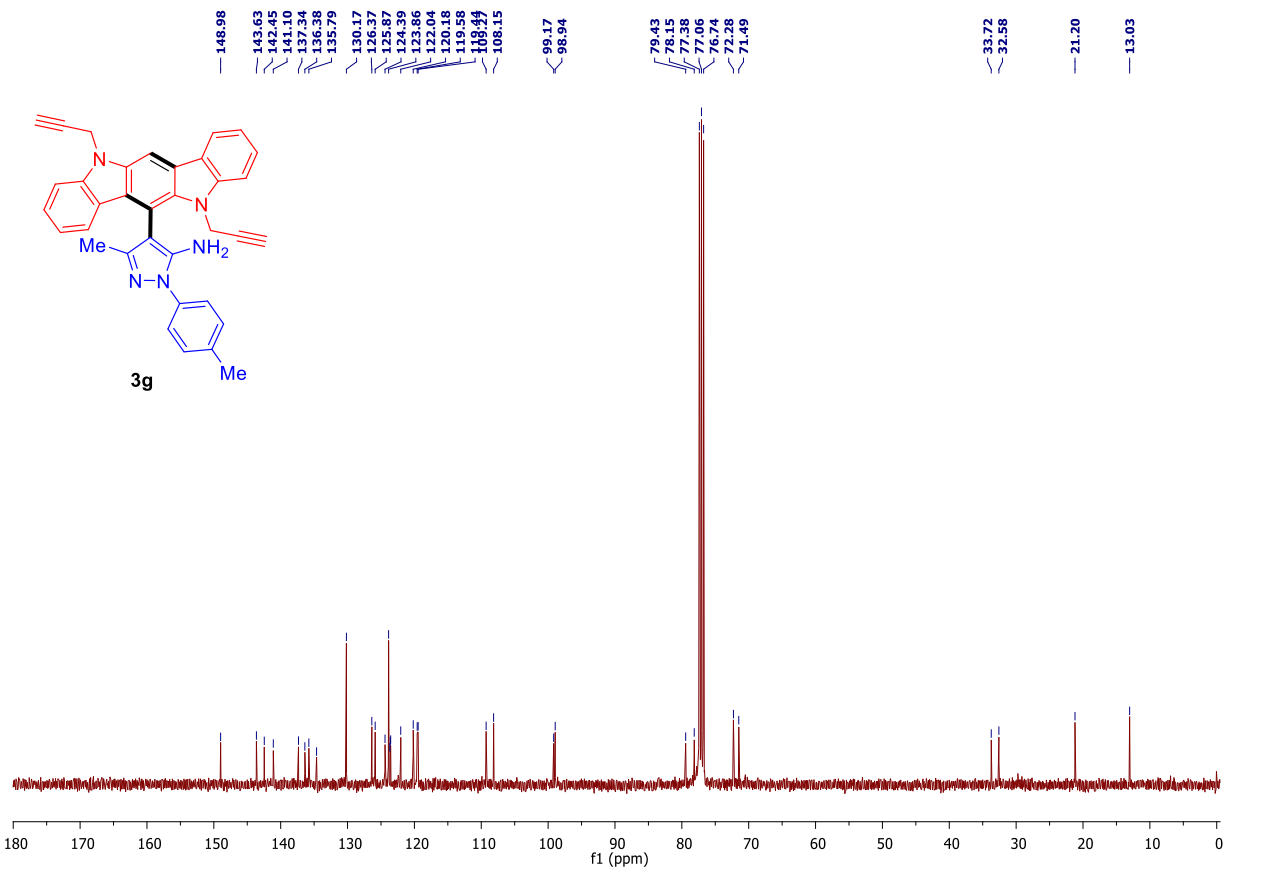
1.11
f1 (ppm)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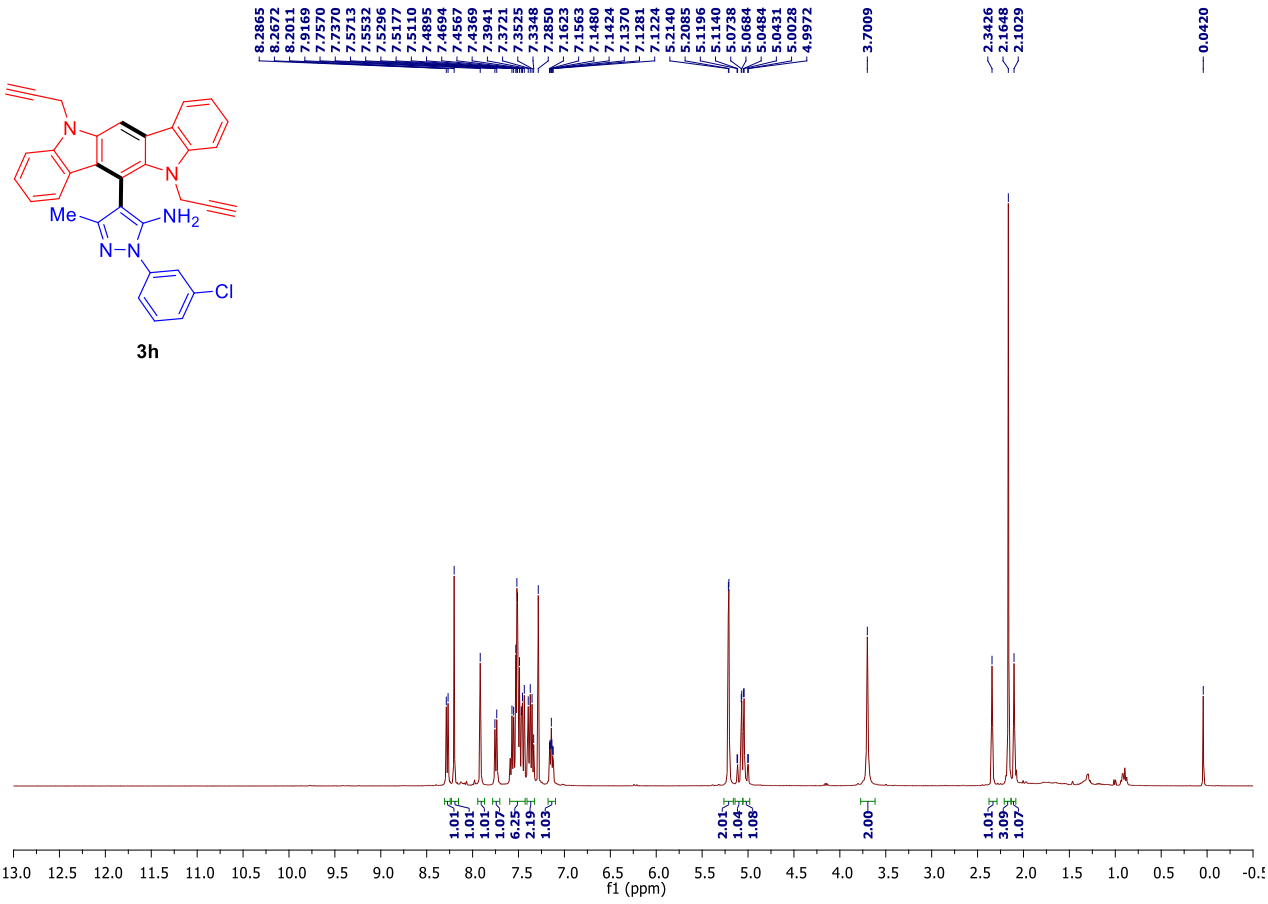
122.04
120.18
119.58
108.15
99.17
98.94
79.43
78.15
77.38
77.06
76.74
72.28
71.49
33.72
32.58
21.20
13.03
Me
NH2
N–N
Me
3g
f1 (ppm)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7.5110
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7.4694
7.4567
7.4369
7.3941
7.3721
7.3525
7.3348
7.2850
7.1623
7.1563
7.1480
7.1424
7.1370
7.1281
7.1224
5.2140
5.2085
5.1196
5.1140
5.0738
5.0684
5.0484
5.0431
5.0028
4.9972
3.7009
2.3426
2.1648
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0.0420
1.01
1.01
1.01
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1.01
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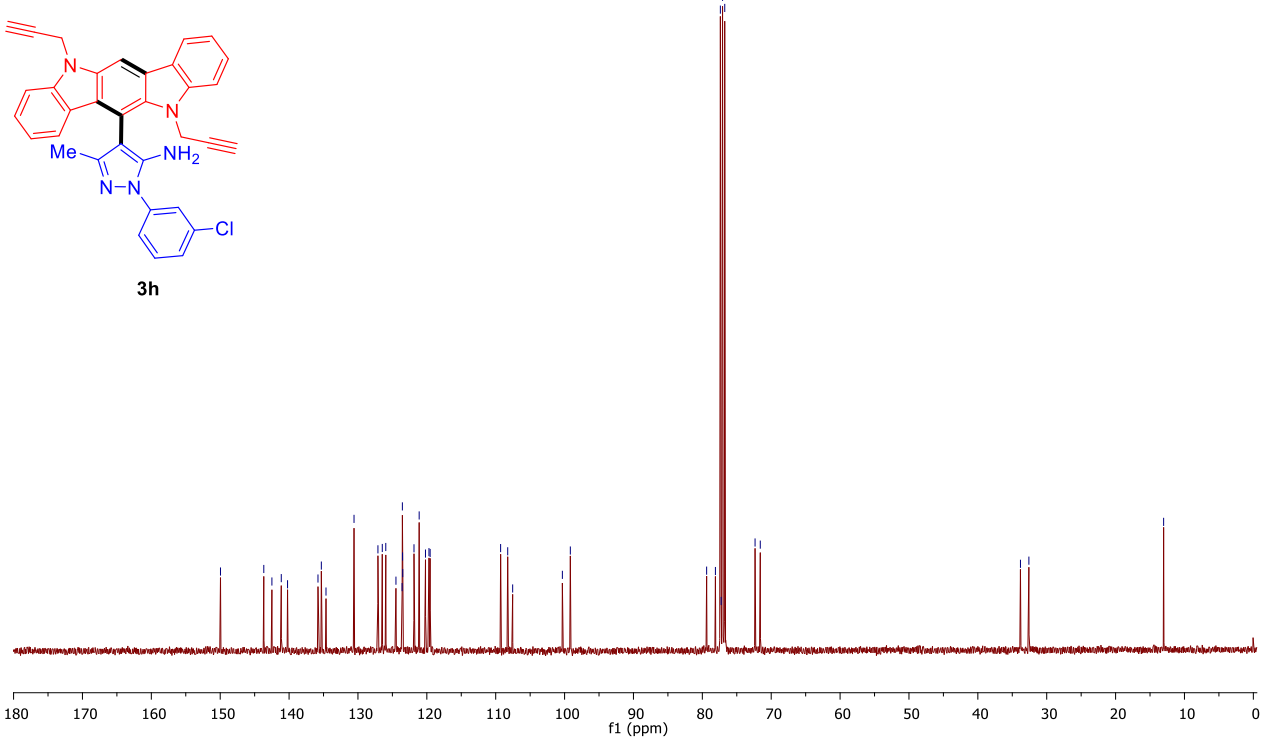
1.07
f1 (ppm)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123.53
123.50
121.86
121.11
120.20
119.69
108.26
107.54
100.32
99.17
79.38
78.10
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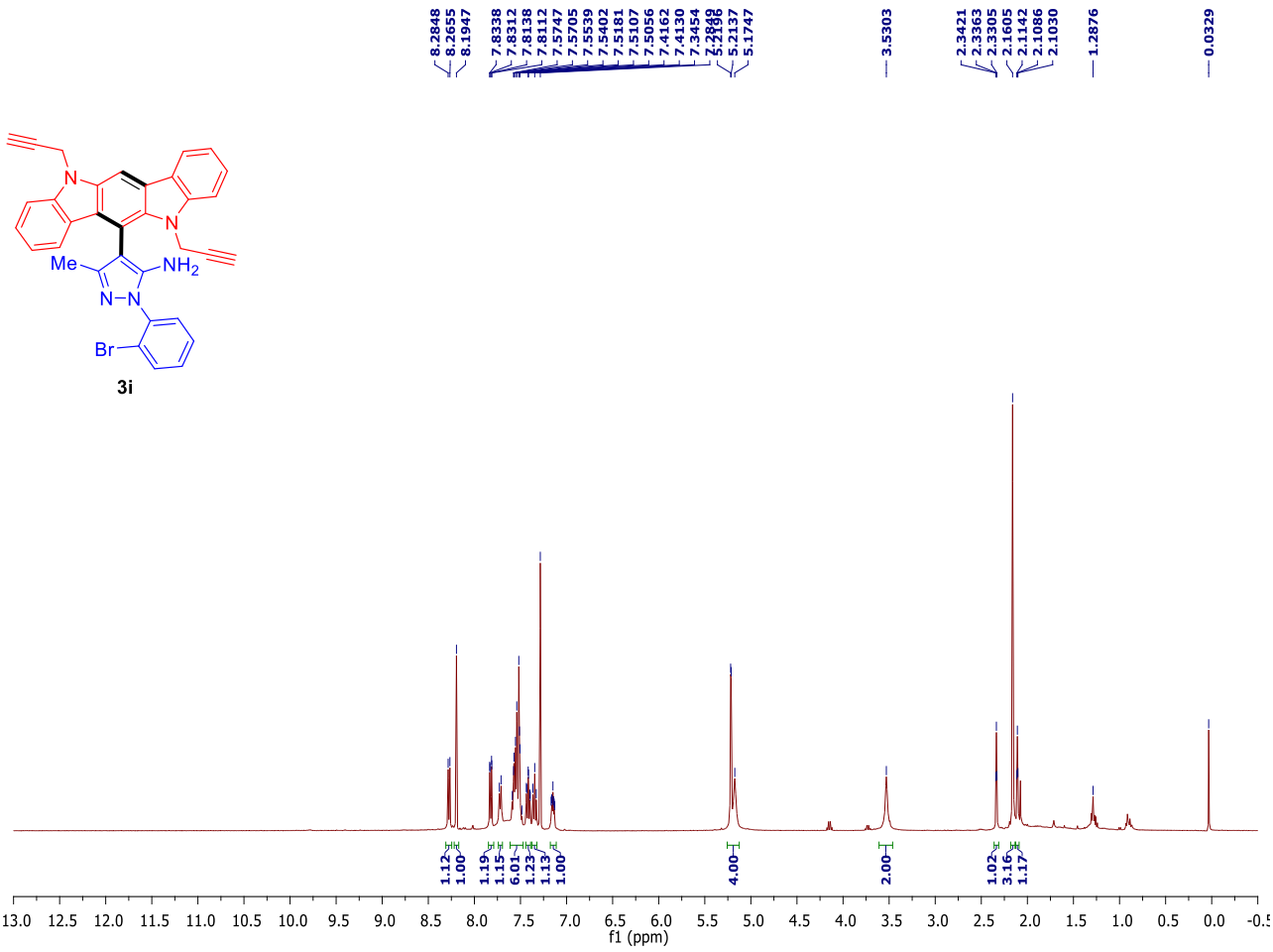
77.06
76.75
72.34
71.59
33.81
32.59
13.03
f1 (ppm)

3h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7.5181
7.5107
7.5056
7.4162
7.4130
7.3454
5.2137
5.1747
3.5303
2.3421
2.3363
2.3305
2.1605
2.1142
2.1086
2.1030
1.2876
0.0329
Me
NH2
N–N
Br
3i
1.12
1.00
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1.23
1.13
1.00
4.00
2.00
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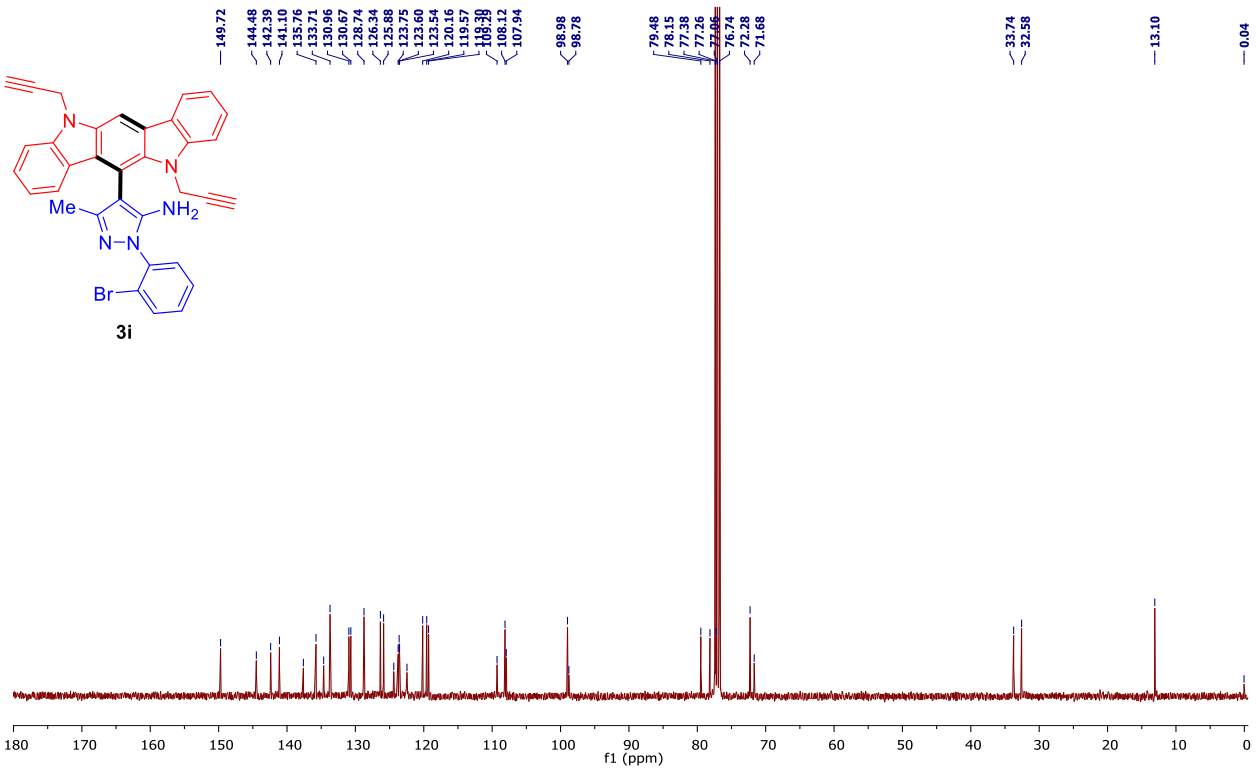
1.17
f1 (ppm)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123.54
120.16
119.57
108.12
107.94
98.98
98.78
79.48
78.15
77.38
77.26
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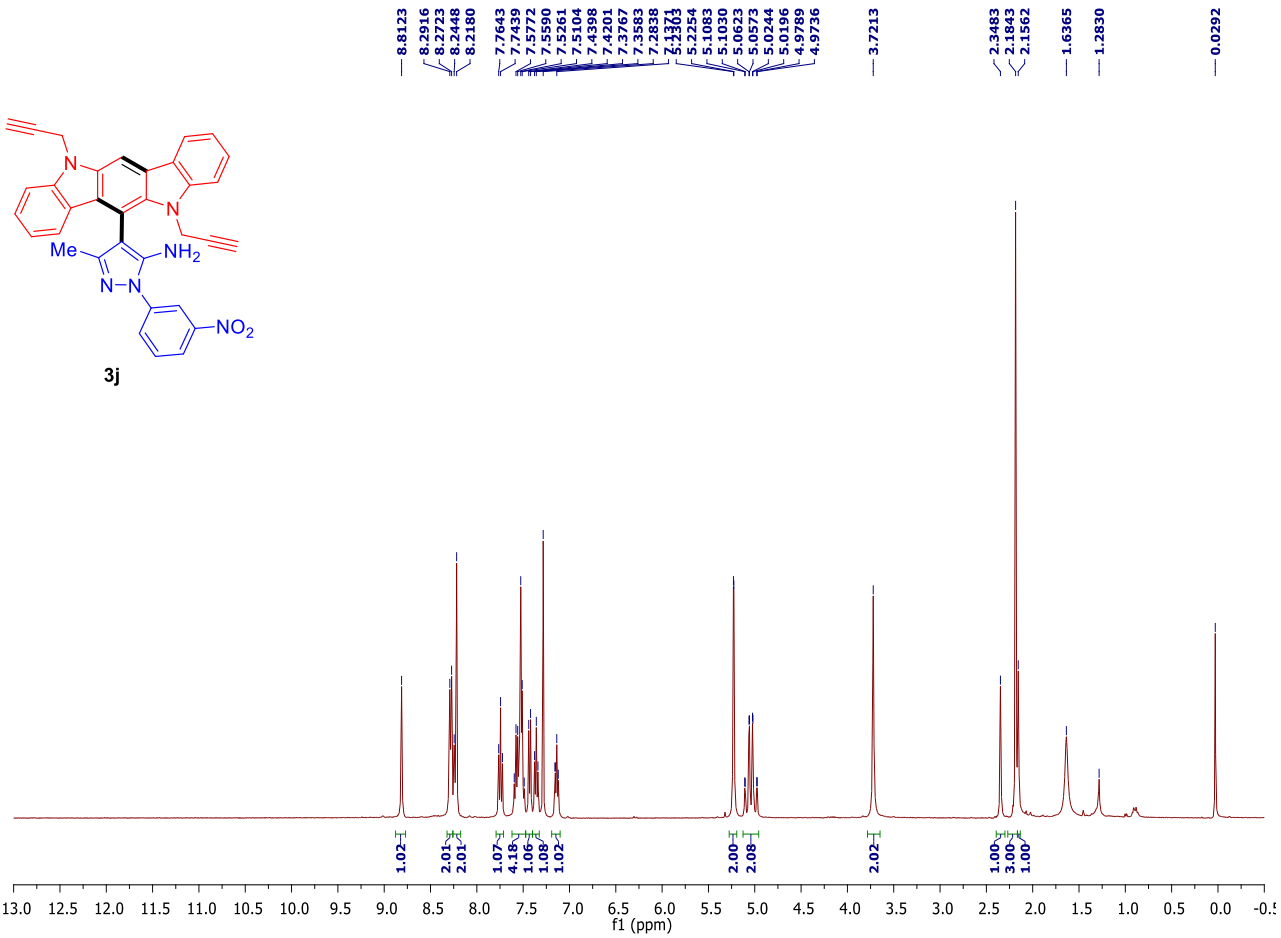
33.74
32.58
13.10
0.04
Me
NH2
N–N
Br
3i
f1 (ppm)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1.2830
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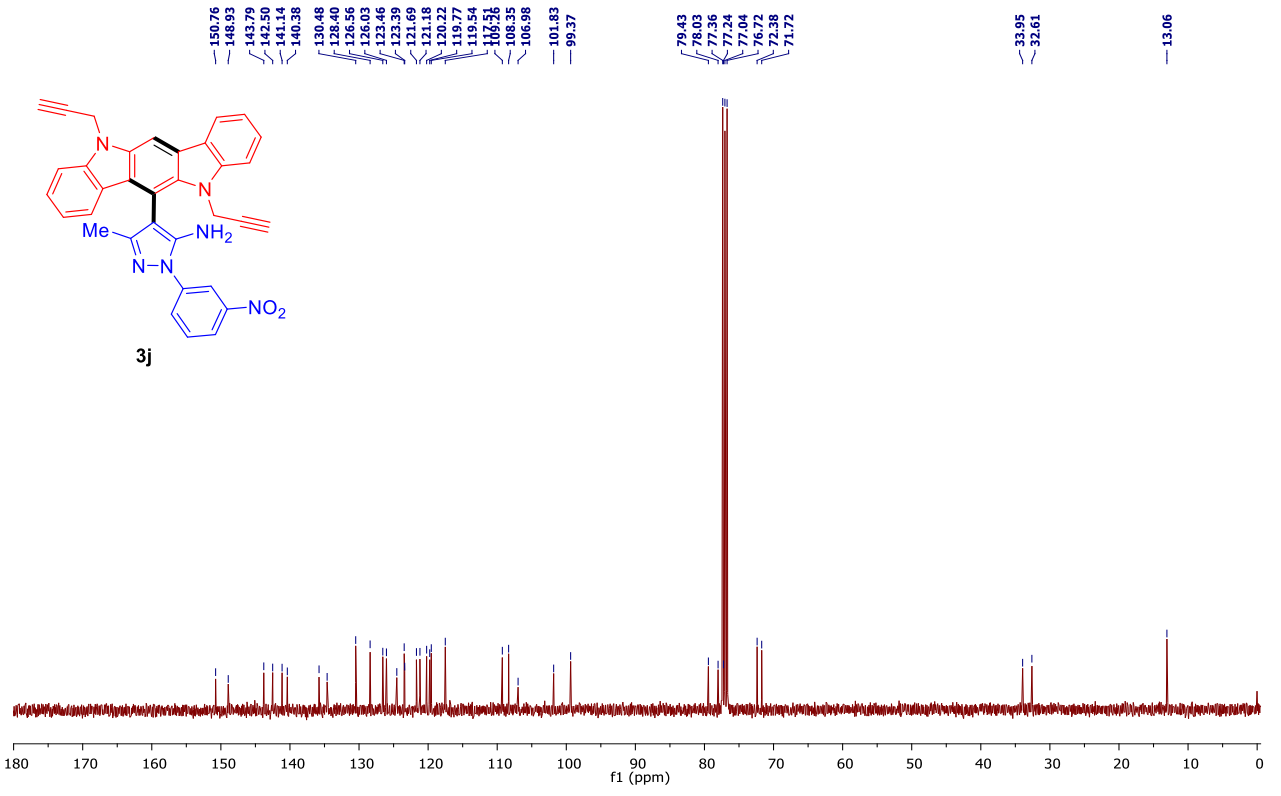
Me
NH2
N-N
NO2
3j
1.02
2.01
2.01
1.07
4.18
1.06
1.08
1.02
2.00
2.08
2.02
1.00
3.00
1.00
f1 (ppm)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126.56
126.03
123.46
123.39
121.69
121.18
120.22
119.77
119.54
108.35
106.98
101.83
99.37
79.43
78.03
77.36
77.24
77.04
76.72
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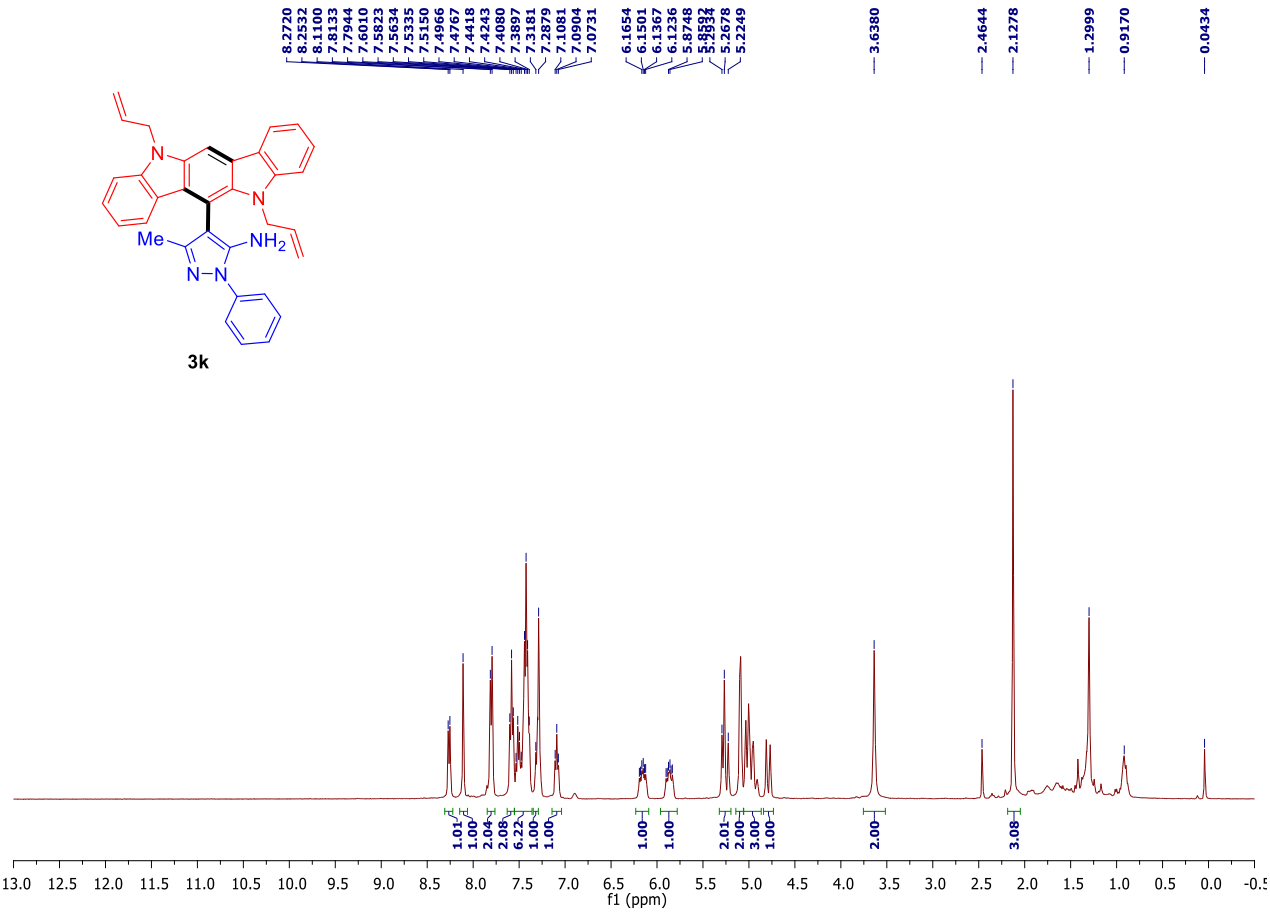
71.72
33.95
32.61
13.06
Me
NH2
N-N
NO2
3j
f1 (ppm)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7.6010
7.5823
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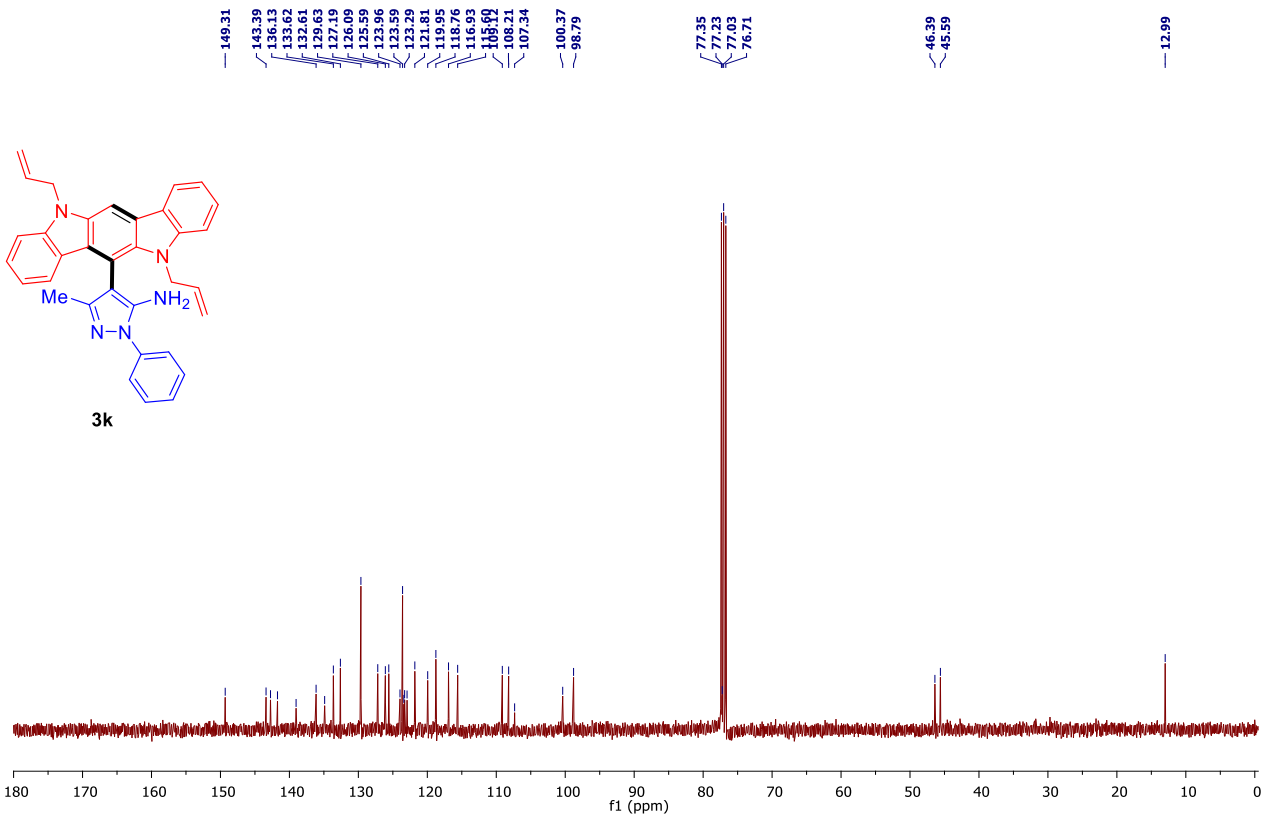
7.5150
7.4966
7.4767
7.4418
7.4243
7.4080
7.3897
7.3181
7.2879
7.1081
7.0904
7.0731
6.1654
6.1501
6.1367
6.1236
5.8748
5.2678
5.2249
3.6380
2.4644
2.1278
1.2999
0.9170
0.0434
Me
NH2
N–N
3k
1.01
1.00
2.04
2.08
6.22
1.00
1.00
1.00
1.00
2.01
2.00
3.00
1.00
2.00
3.08
f1 (ppm)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126.09
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119.95
118.76
116.93
108.21
107.34
100.37
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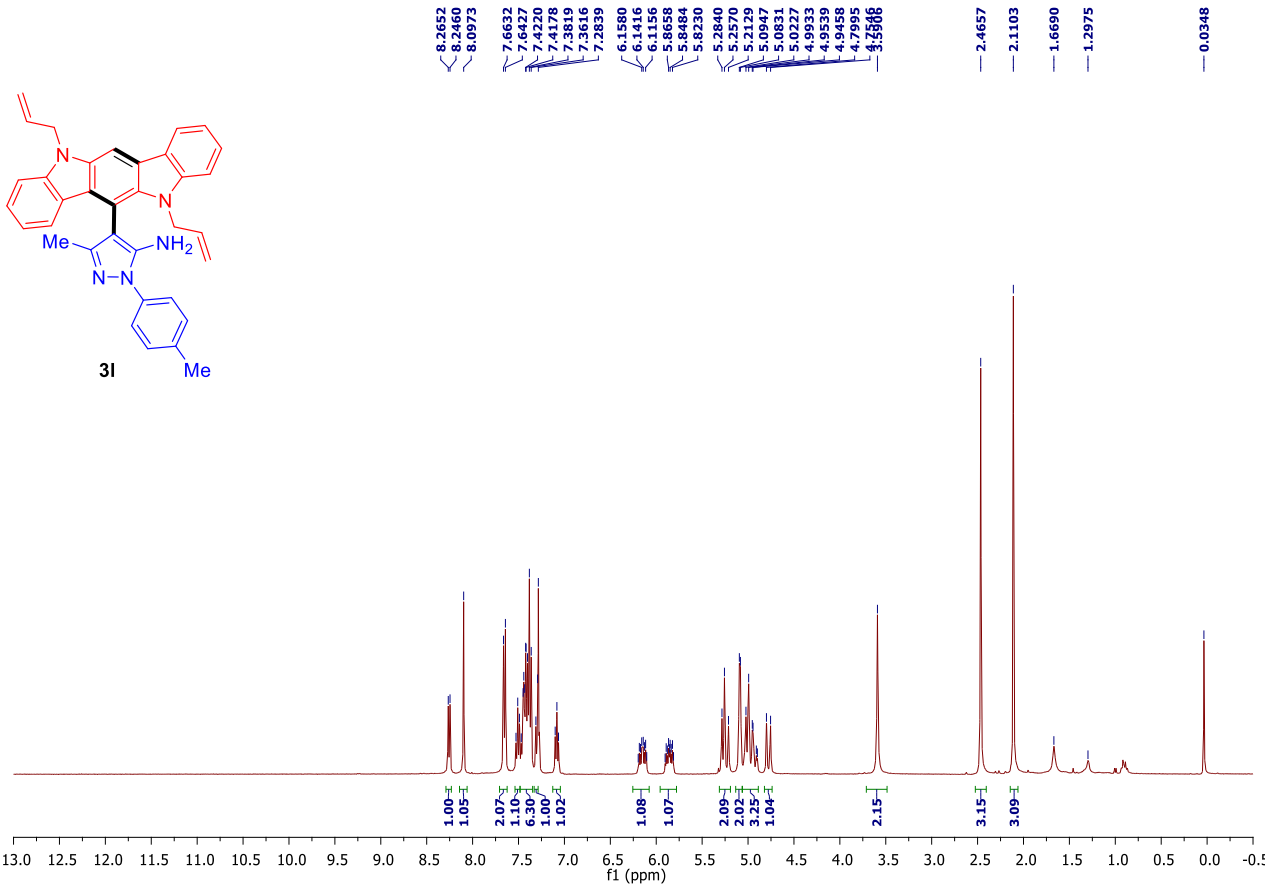
77.03
76.71
46.39
45.59
12.99
Me
NH2
N–N
3k
f1 (ppm)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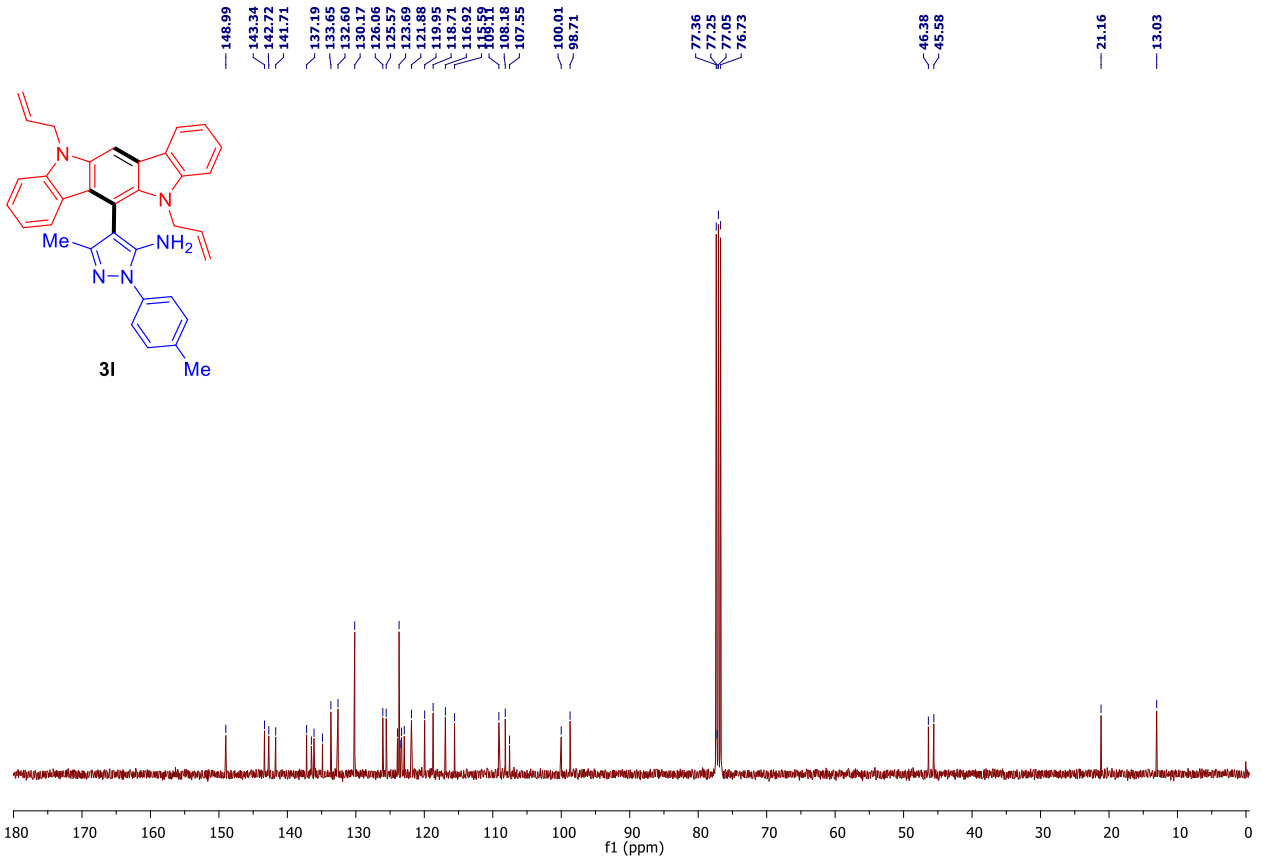
6.1580
6.1416
6.1156
5.8658
5.8484
5.8230
5.2840
5.2570
5.2129
5.0947
5.0831
5.0227
4.9933
4.9539
4.9458
4.7995
4.7546
4.7506
2.4657
2.1103
1.6690
1.2975
0.0348
Me
NH2
N–N
3l
Me
1.00
1.05
2.07
1.10
6.30
1.00
1.02
1.08
1.07
2.09
2.02
3.25
1.04
2.15
3.15
3.09
f1 (ppm)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123.69
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118.71
116.92
108.18
107.55
100.01
98.71
77.36
77.25
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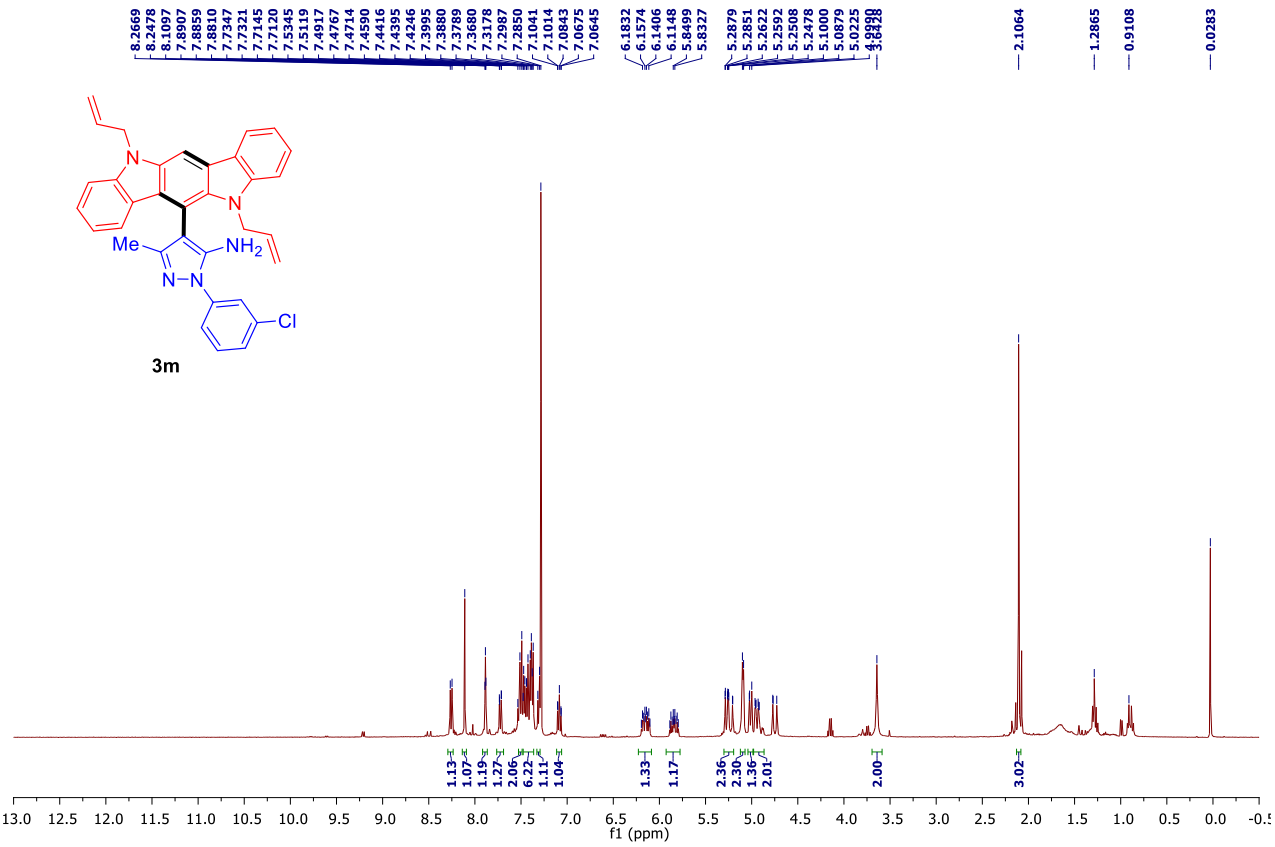
76.73
46.38
45.58
21.16
13.03
Me
NH2
N–N
3l
Me
f1 (ppm)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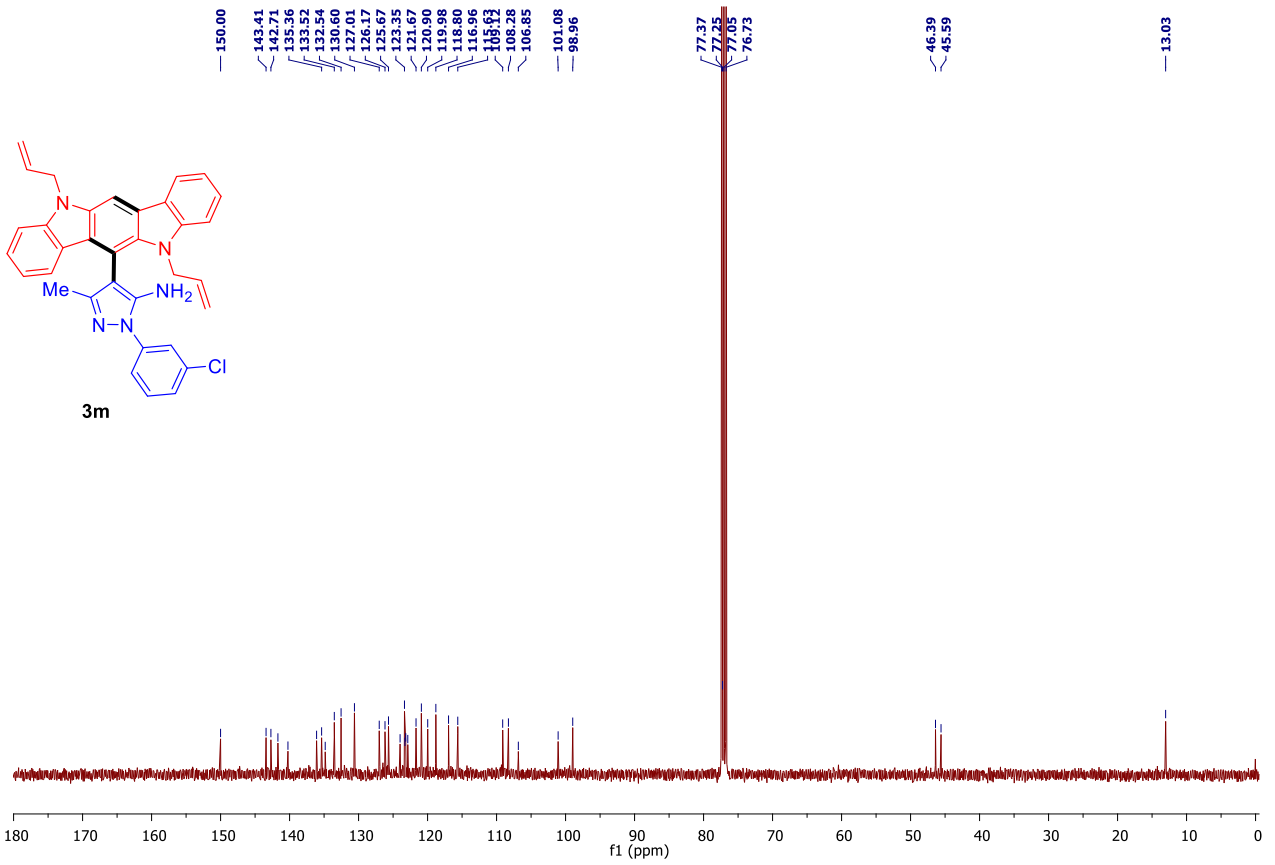
7.7120
7.5345
7.5119
7.4917
7.4767
7.4714
7.4590
7.4416
7.4395
7.4246
7.3995
7.3880
7.3789
7.3680
7.3178
7.2987
7.2850
7.1041
7.1014
7.0843
7.0675
7.0645
6.1832
6.1574
6.1406
6.1148
5.8499
5.8327
5.2879
5.2851
5.2622
5.2592
5.2508
5.2478
5.1000
5.0879
5.0225
4.9990
3.8428
2.1064
1.2865
0.9108
0.0283
Me
NH2
N–N
Cl
3m
1.13
1.07
1.19
1.27
2.06
6.22
1.11
1.04
1.33
1.17
2.36
2.30
1.36
2.01
2.00
3.02
f1 (ppm)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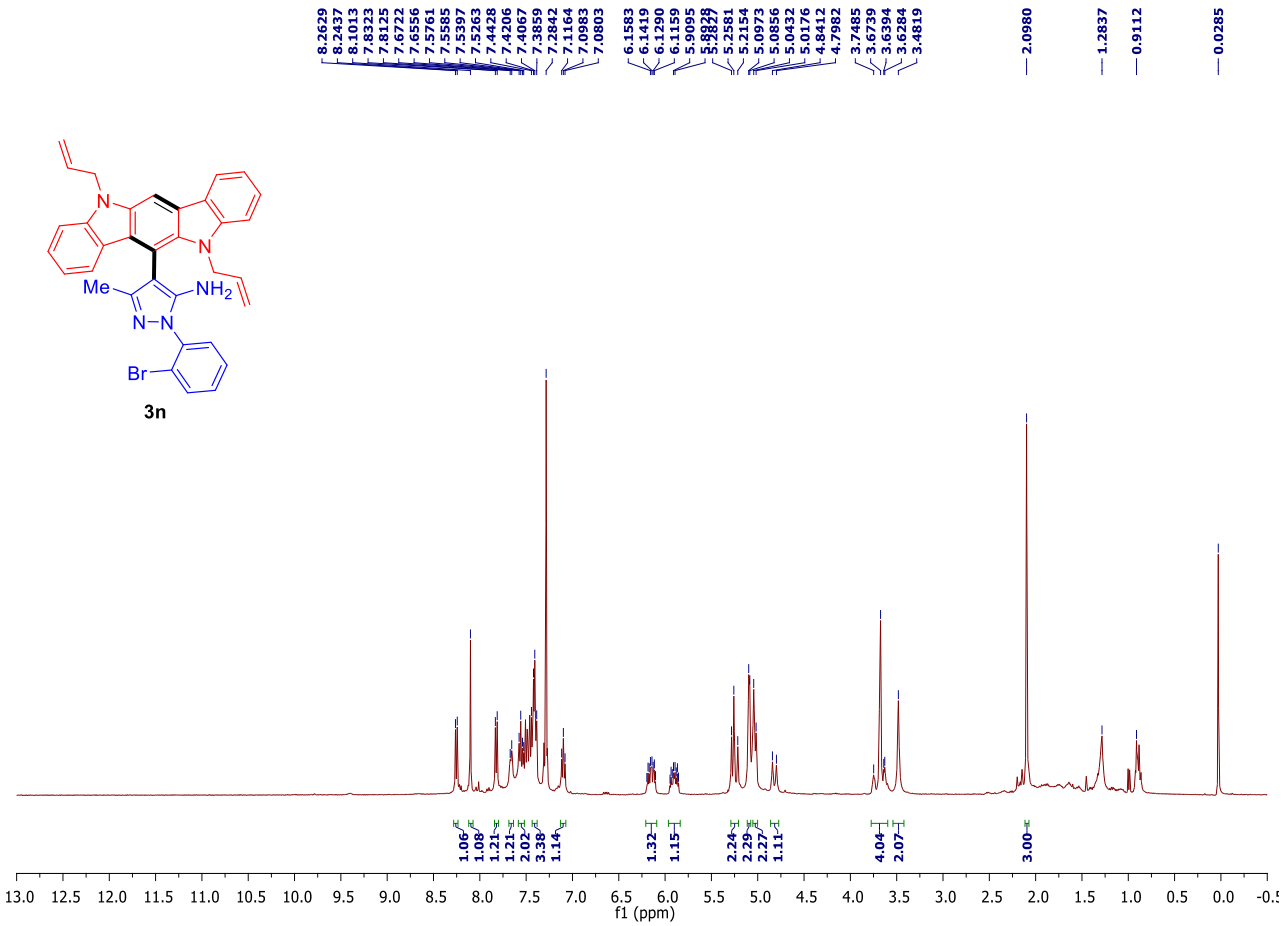
132.54
130.60
127.01
126.17
125.67
123.35
121.67
120.90
119.98
118.80
116.96
108.28
106.85
101.08
98.96
77.37
77.25
77.05
76.73
46.39
45.59
13.03
Me
NH2
N–N
Cl
3m
f1 (ppm)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7.8125
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7.6556
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7.5585
7.5397
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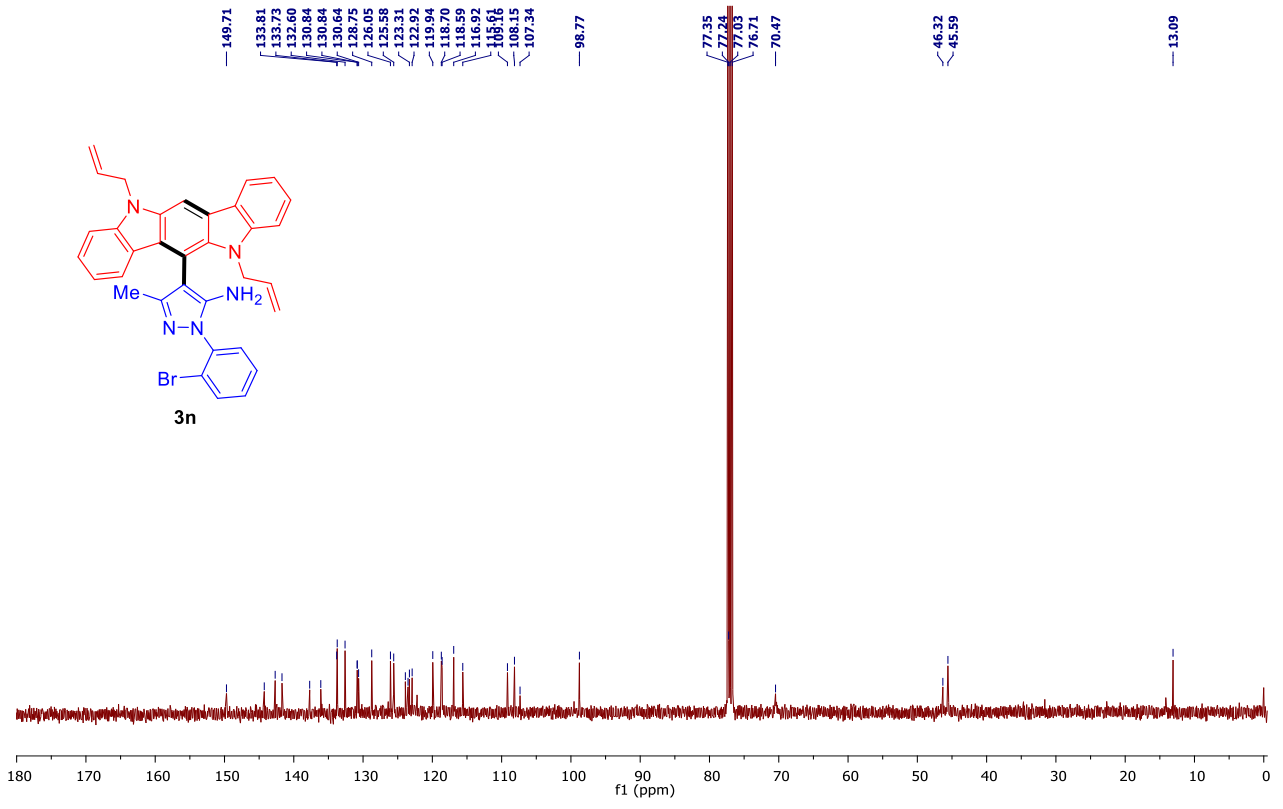
7.4428
7.4206
7.4067
7.3859
7.2842
7.1164
7.0983
7.0803
6.1583
6.1419
6.1290
6.1159
5.9095
5.8928
5.8827
5.2581
5.2154
5.0973
5.0856
5.0432
5.0176
4.8412
4.7982
3.7485
3.6739
3.6394
3.6284
3.4819
2.0980
1.2837
0.9112
0.0285
Me
NH2
N–N
Br
3n
1.06
1.08
1.21
1.21
2.02
3.38
1.14
1.32
1.15
2.24
2.29
2.27
1.11
4.04
2.07
3.00
f1 (ppm)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130.84
130.64
128.75
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125.58
123.31
122.92
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111.61
109.16
108.15
107.34
98.77
77.35
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77.03
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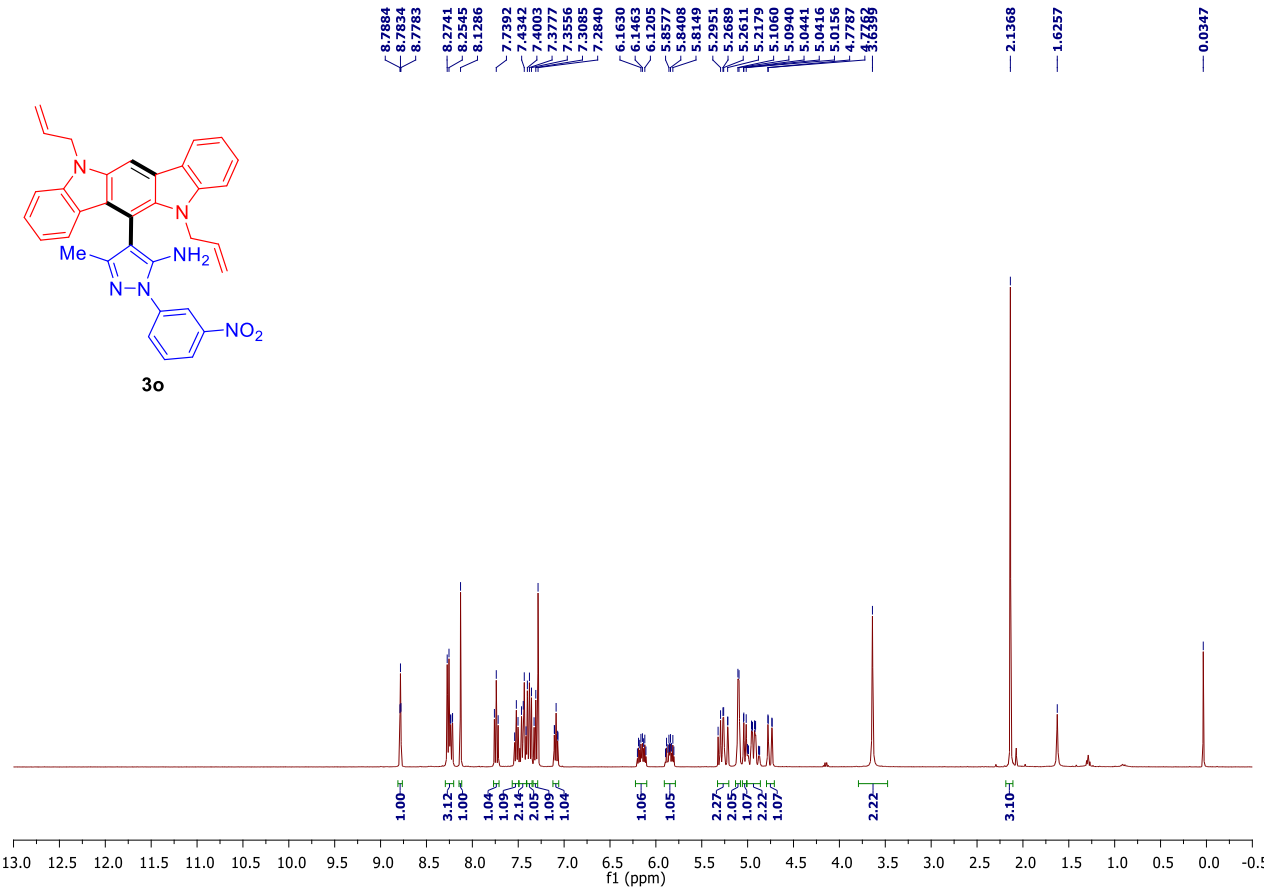
70.47
46.32
45.59
13.09
Me
NH2
N–N
Br
3n
f1 (ppm)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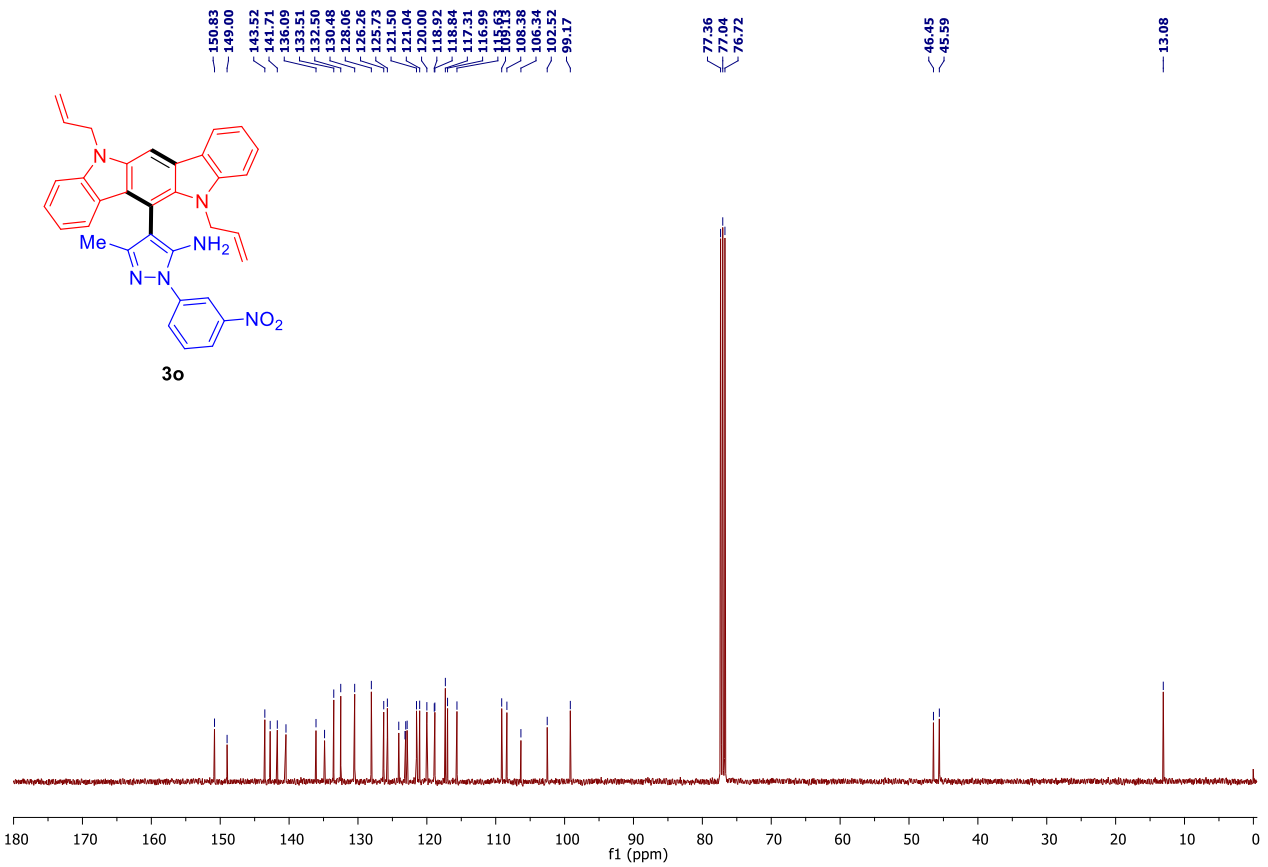
7.3777
7.3556
7.3085
7.2840
6.1630
6.1463
6.1205
5.8577
5.8408
5.8149
5.2951
5.2689
5.2611
5.2179
5.1060
5.0940
5.0441
5.0156
4.7787
2.1368
1.6257
0.0347
1.00
3.12
1.00
1.04
1.09
2.14
2.05
1.09
1.04
1.06
1.05
2.27
2.05
1.07
2.22
1.07
2.22
3.10
f1 (ppm)

Me
NH2
N–N
NO2

3o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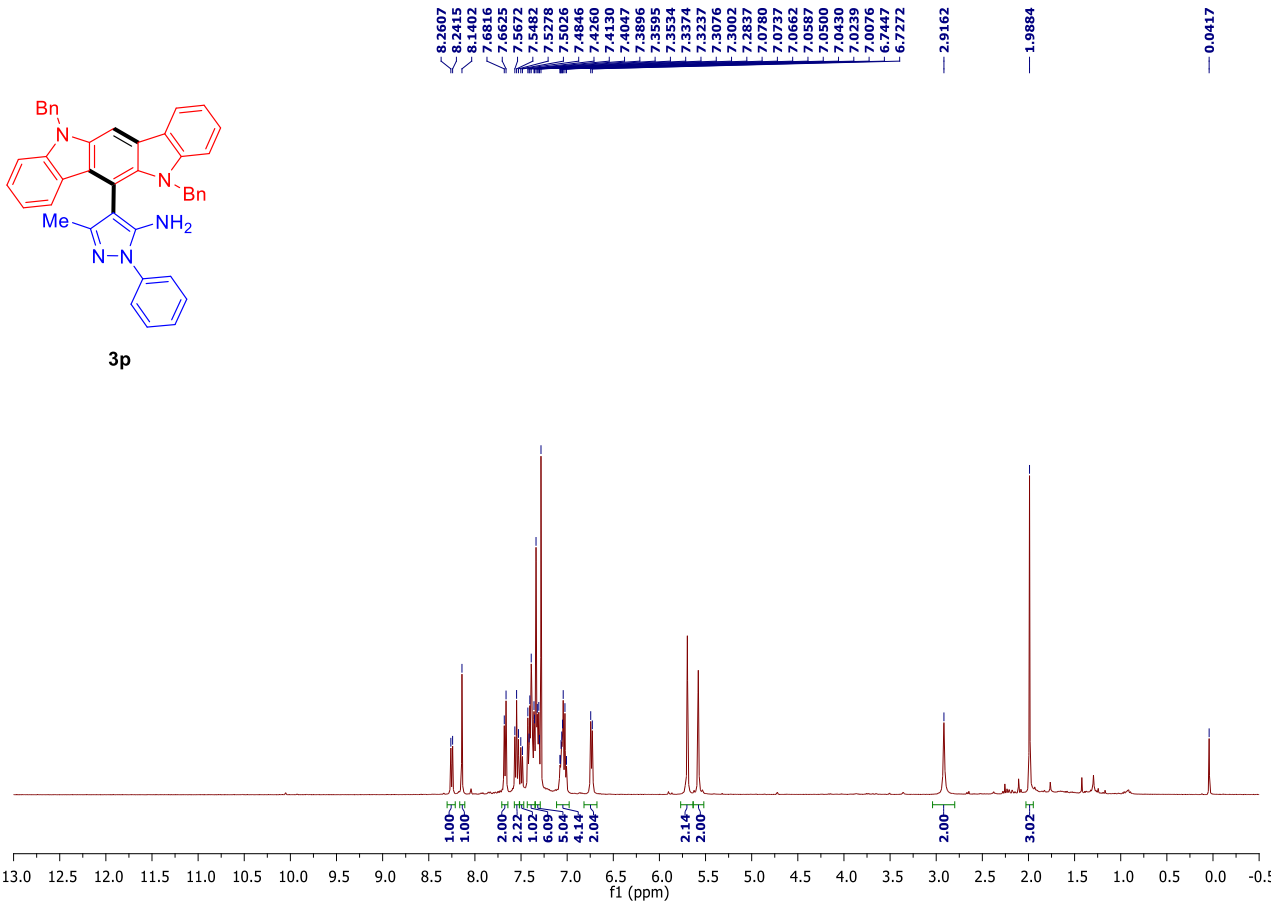
136.09
133.51
132.50
130.48
128.06
126.26
125.73
121.50
121.04
120.00
118.92
118.84
117.31
116.99
108.38
106.34
102.52
99.17
77.36
77.04
76.72
46.45
45.59
13.08
f1 (ppm)

Me
NH2
N–N
NO2

3o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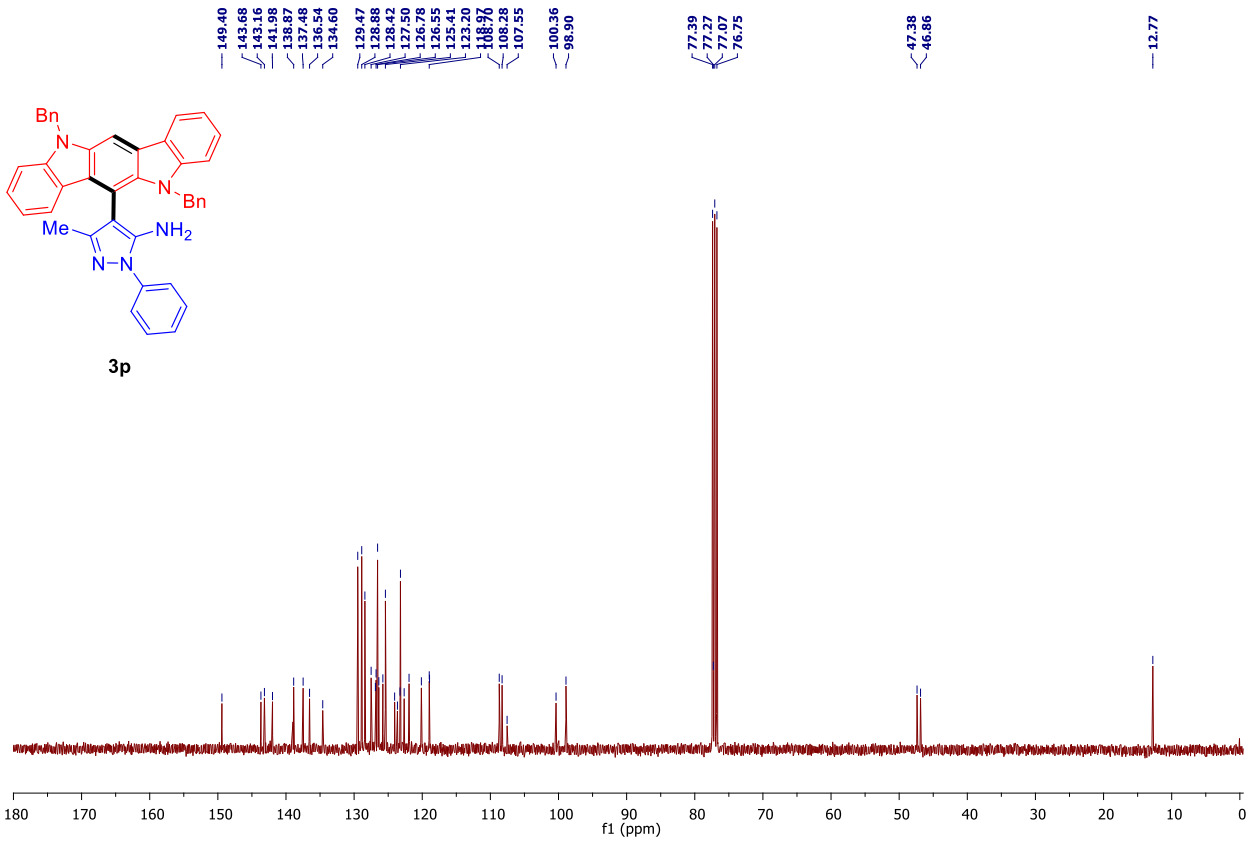
7.5482
7.5278
7.5026
7.4846
7.4260
7.4130
7.4047
7.3896
7.3595
7.3534
7.3374
7.3237
7.3076
7.3002
7.2837
7.0780
7.0737
7.0662
7.0587
7.0500
7.0430
7.0239
7.0076
6.7447
6.7272
2.9162
1.9984
0.0417
Bn
N
N
Bn
Me
NH2
N–N
1.00
1.00
2.00
2.22
1.02
6.09
5.04
4.14
2.04
2.14
2.00
2.00
3.02
13.0 12.5 12.0 11.5 11.0 10.5 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)

3p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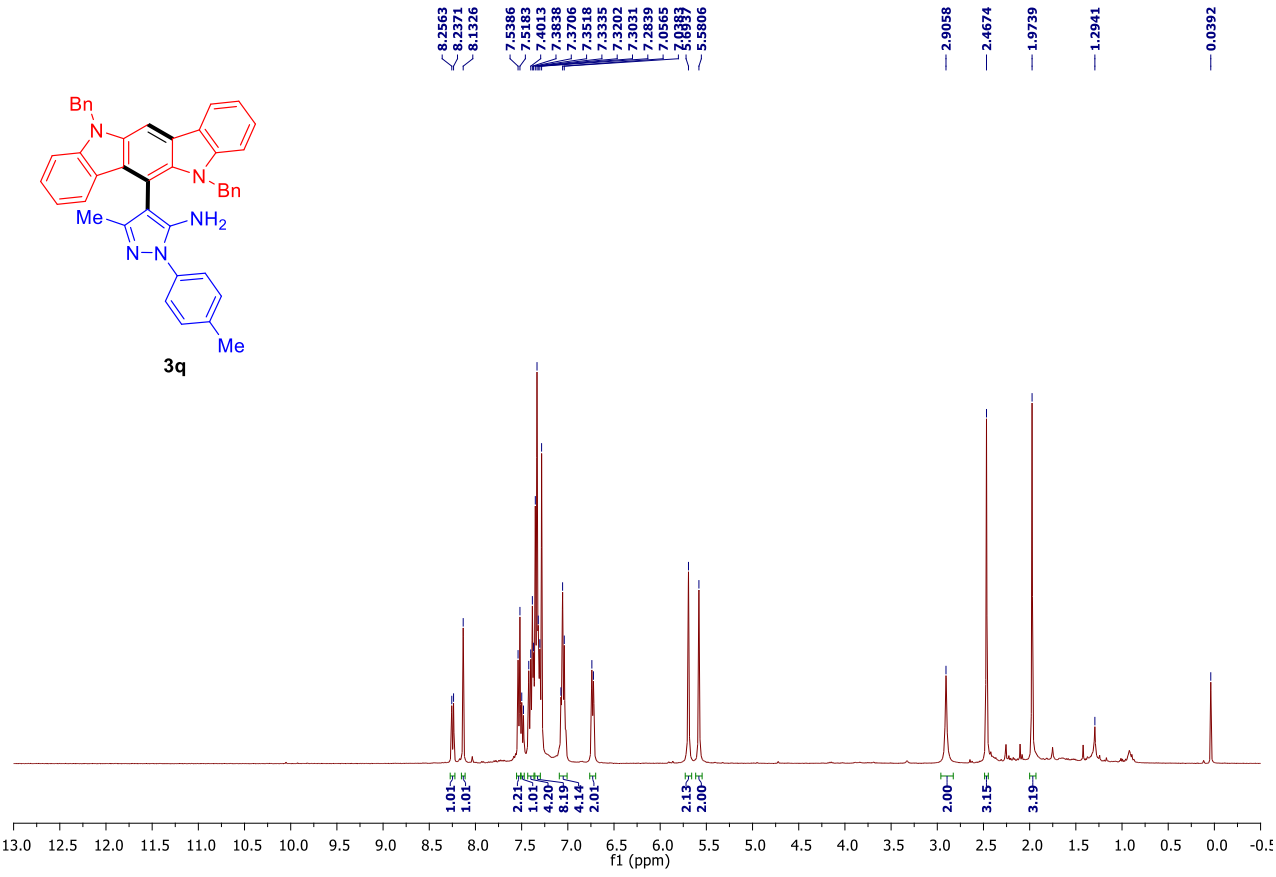
137.48
136.54
134.60
129.47
128.88
128.42
127.50
126.78
126.55
125.41
123.20
118.97
118.76
108.28
107.55
100.36
98.90
77.39
77.27
77.07
76.75
47.38
46.86
12.77
Bn
N
N
Bn
Me
NH2
N–N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3p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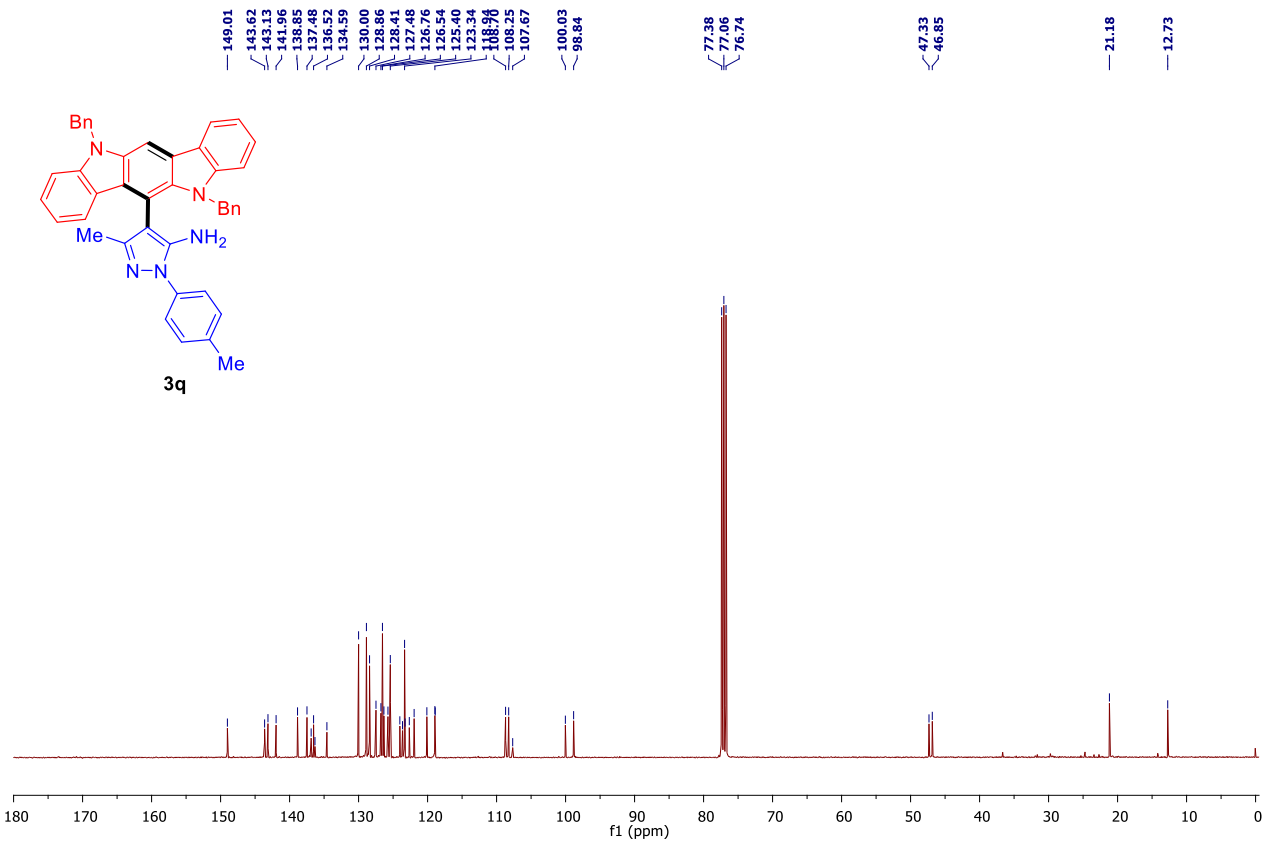
7.3838
7.3706
7.3518
7.3335
7.3202
7.3031
7.2839
7.0565
5.5806
2.9058
2.4674
1.9739
1.2941
0.0392
Bn
N
N
Bn
Me
NH2
N–N
Me
3q
1.01
1.01
2.21
1.01
4.20
8.19
4.14
2.01
2.13
2.00
2.00
3.15
3.19
f1 (ppm)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136.52
134.59
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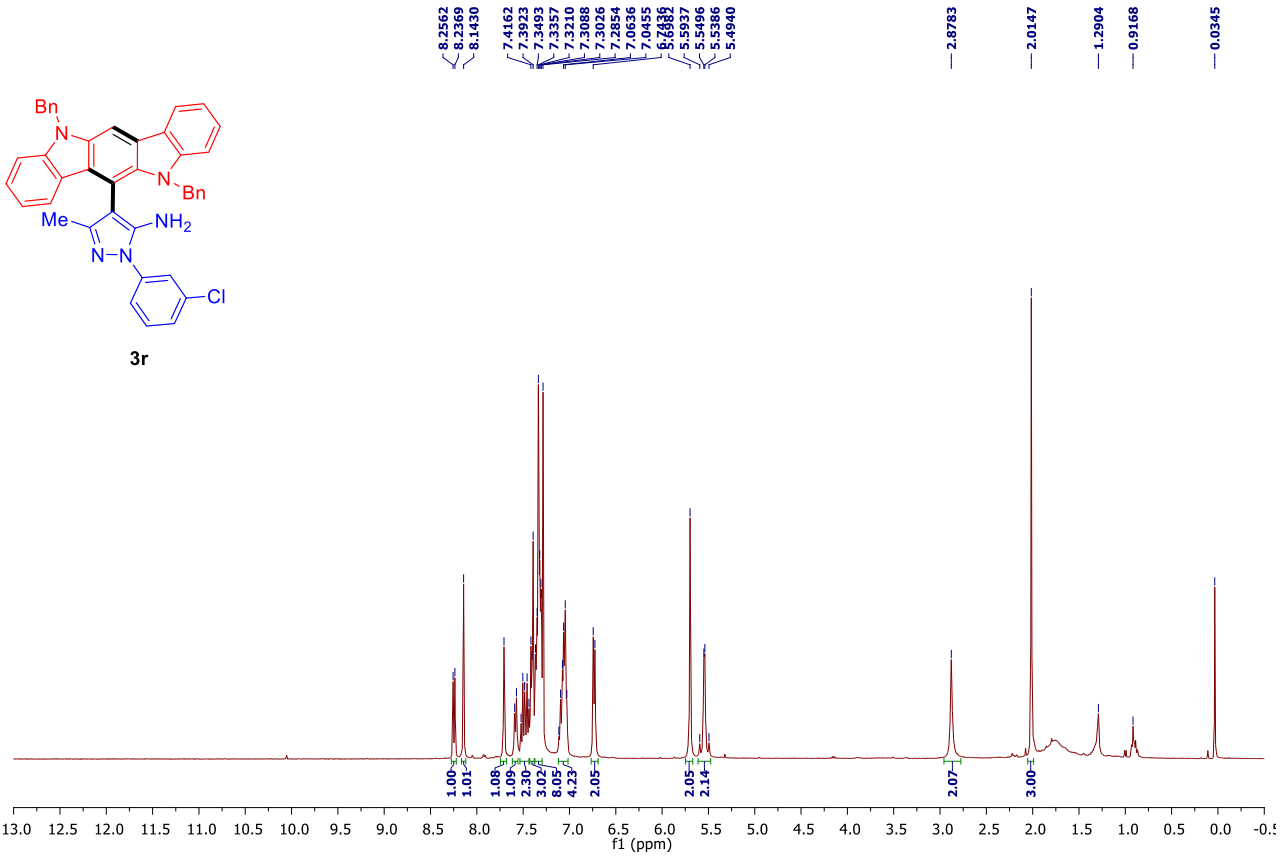
128.86
128.41
127.48
126.76
126.54
125.40
123.34
108.25
107.67
100.03
98.84
77.38
77.06
76.74
47.33
46.85
21.18
12.73
Bn
N
N
Bn
Me
NH2
N–N
Me
3q
f1 (ppm)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7.3088
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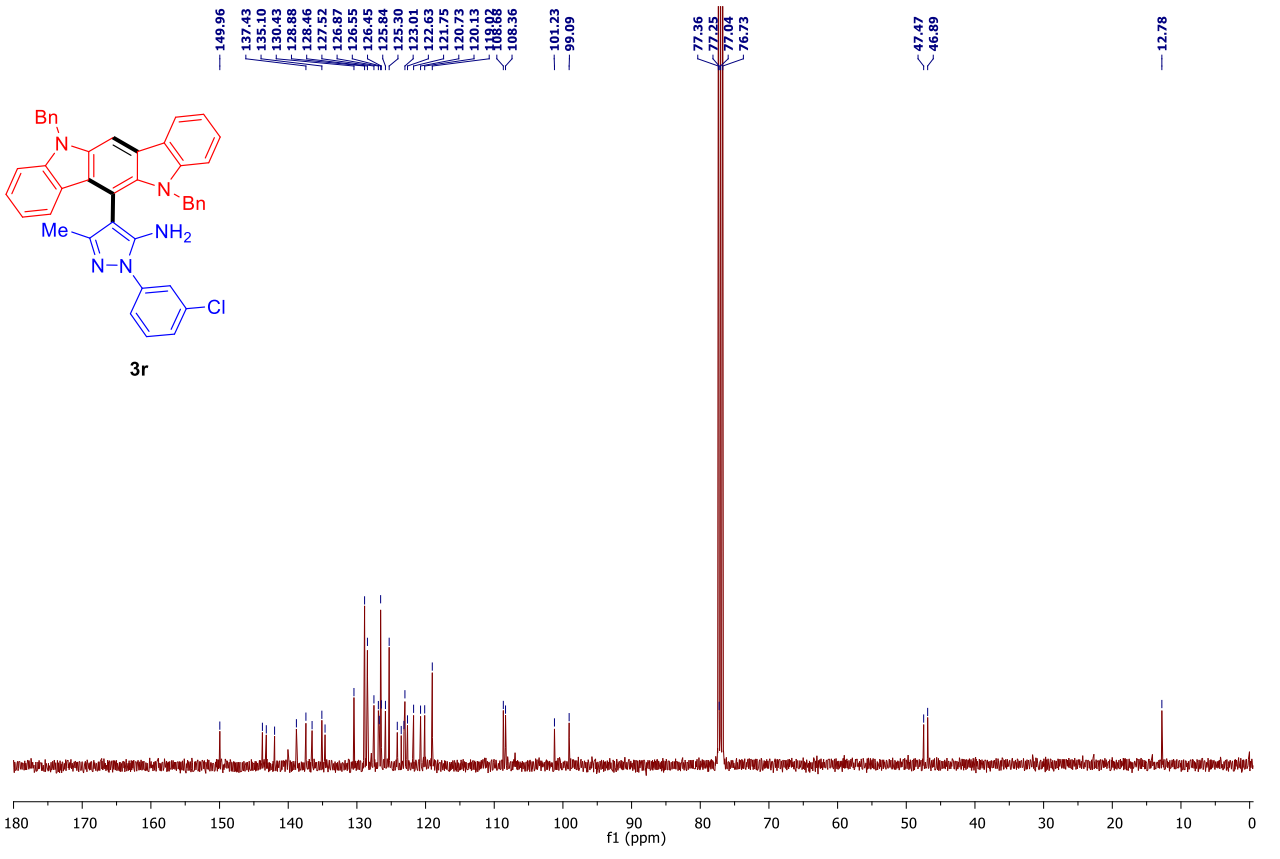
7.0636
7.0455
6.7436
6.6982
5.5937
5.5496
5.5386
5.4940
2.8783
2.0147
1.2904
0.9168
0.0345
Bn
N
N
Bn
Me
NH2
N–N
Cl
1.00
1.01
1.08
1.09
2.30
3.02
8.05
4.23
2.05
2.05
2.14
2.07
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3r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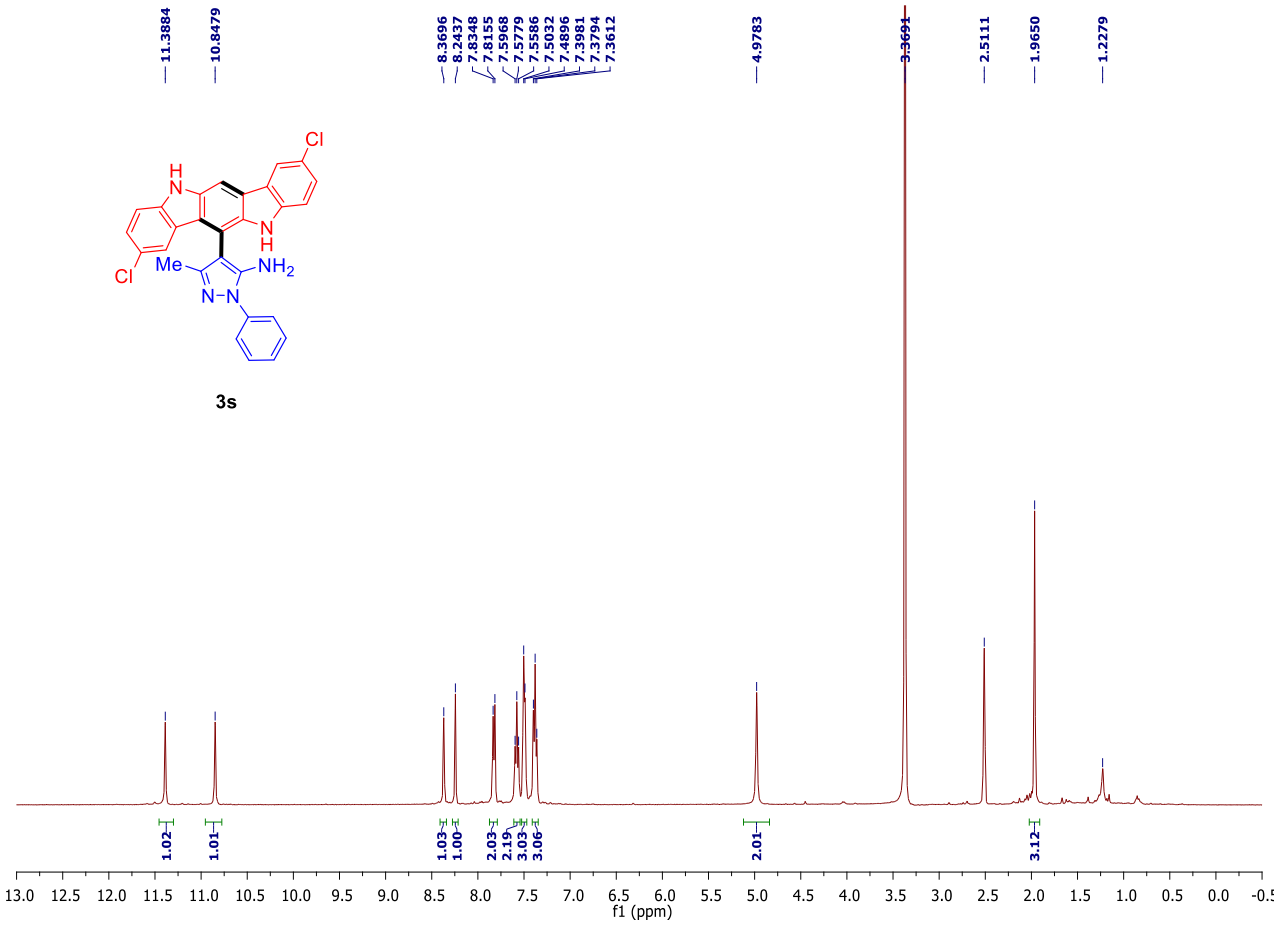
128.46
127.52
126.87
126.55
126.45
125.84
125.30
123.01
122.63
121.75
120.73
120.13
118.02
108.88
108.36
101.23
99.09
77.36
77.25
77.04
76.73
47.47
46.89
12.78
Bn
N
N
Bn
Me
NH2
N–N
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3r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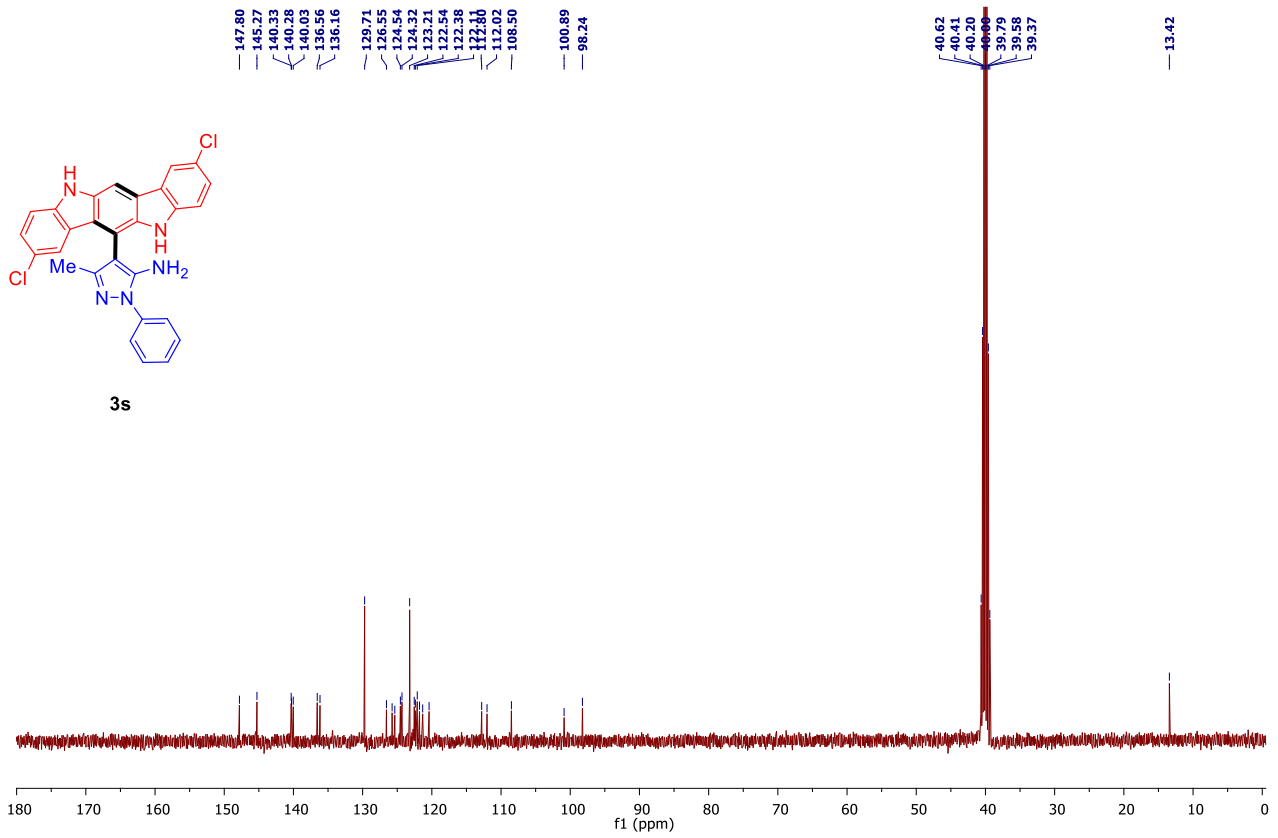
7.3981
7.3794
7.3612
4.9783
3.3691
2.5111
1.9650
1.2279
1.02
1.01
1.03
1.00
2.03
2.19
3.03
3.06
2.01
3.12
f1 (ppm)

3s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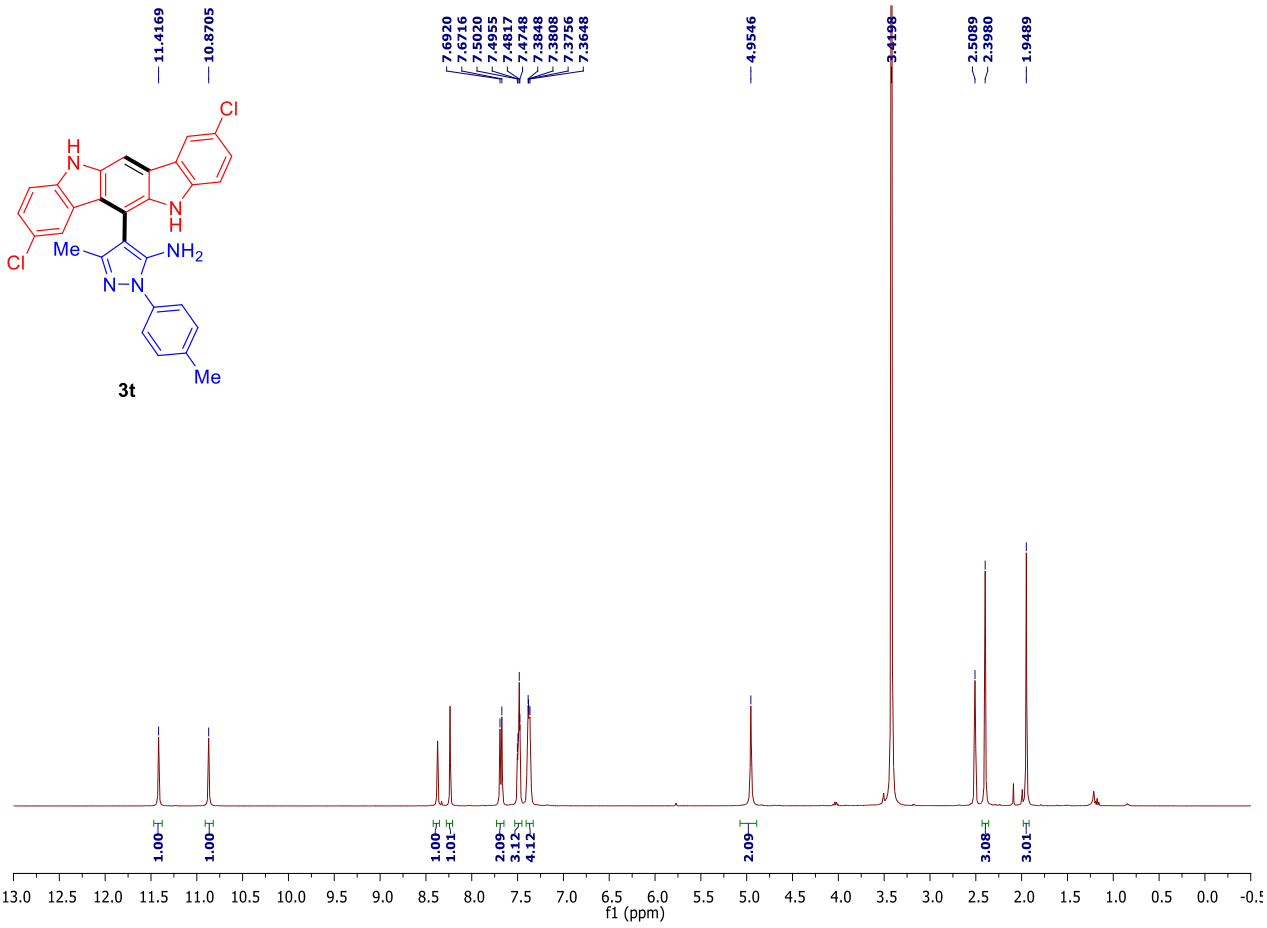
140.28
140.03
136.56
136.16
129.71
126.55
124.54
124.32
123.21
122.54
122.38
112.02
108.50
100.89
98.24
40.62
40.41
40.20
39.79
39.58
39.37
13.42
f1 (ppm)

3s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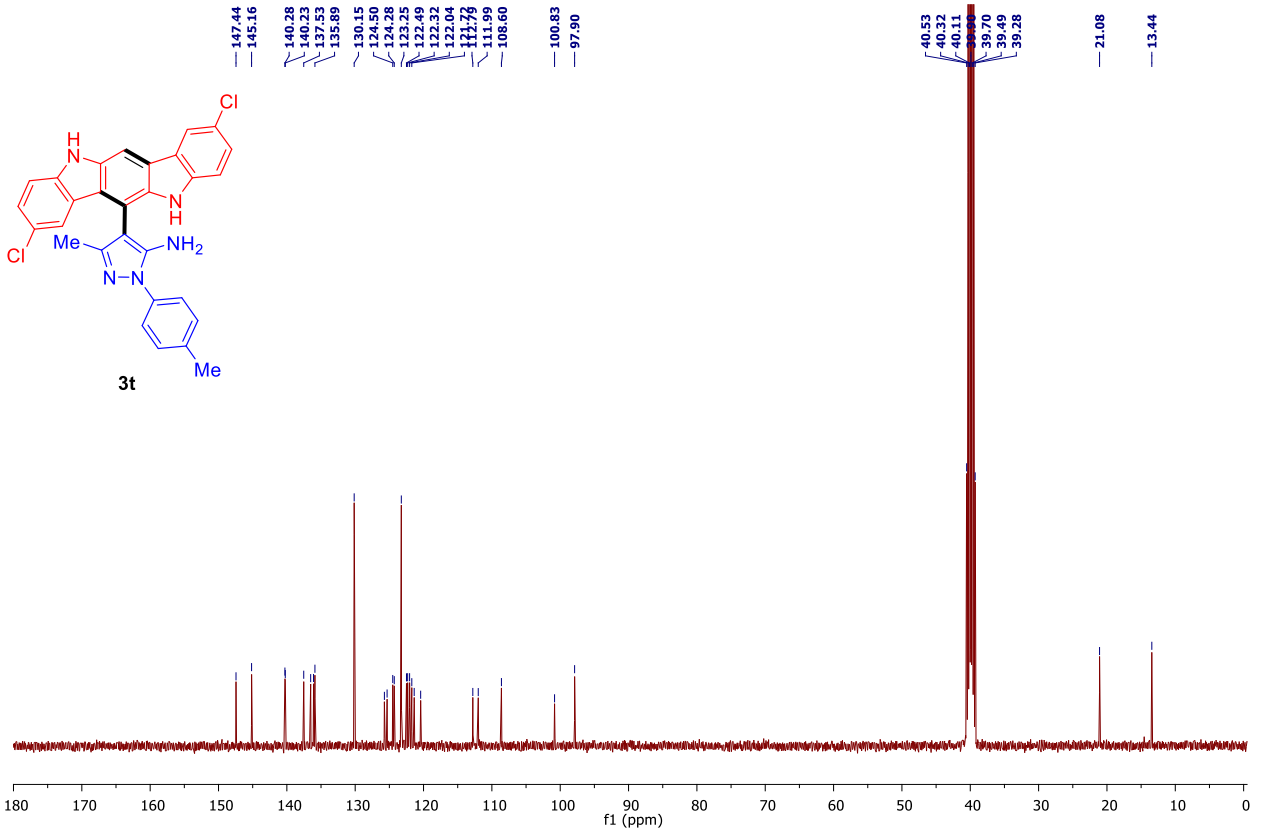
7.4955
7.4817
7.4748
7.3848
7.3808
7.3756
7.3648
4.9546
3.4498
2.5089
2.3980
1.9489
Cl
H
N
N
H
Cl
Me
NH2
N–N
Me
3t
1.00
1.00
1.00
1.01
2.09
3.12
4.12
2.09
3.08
3.01
f1 (ppm)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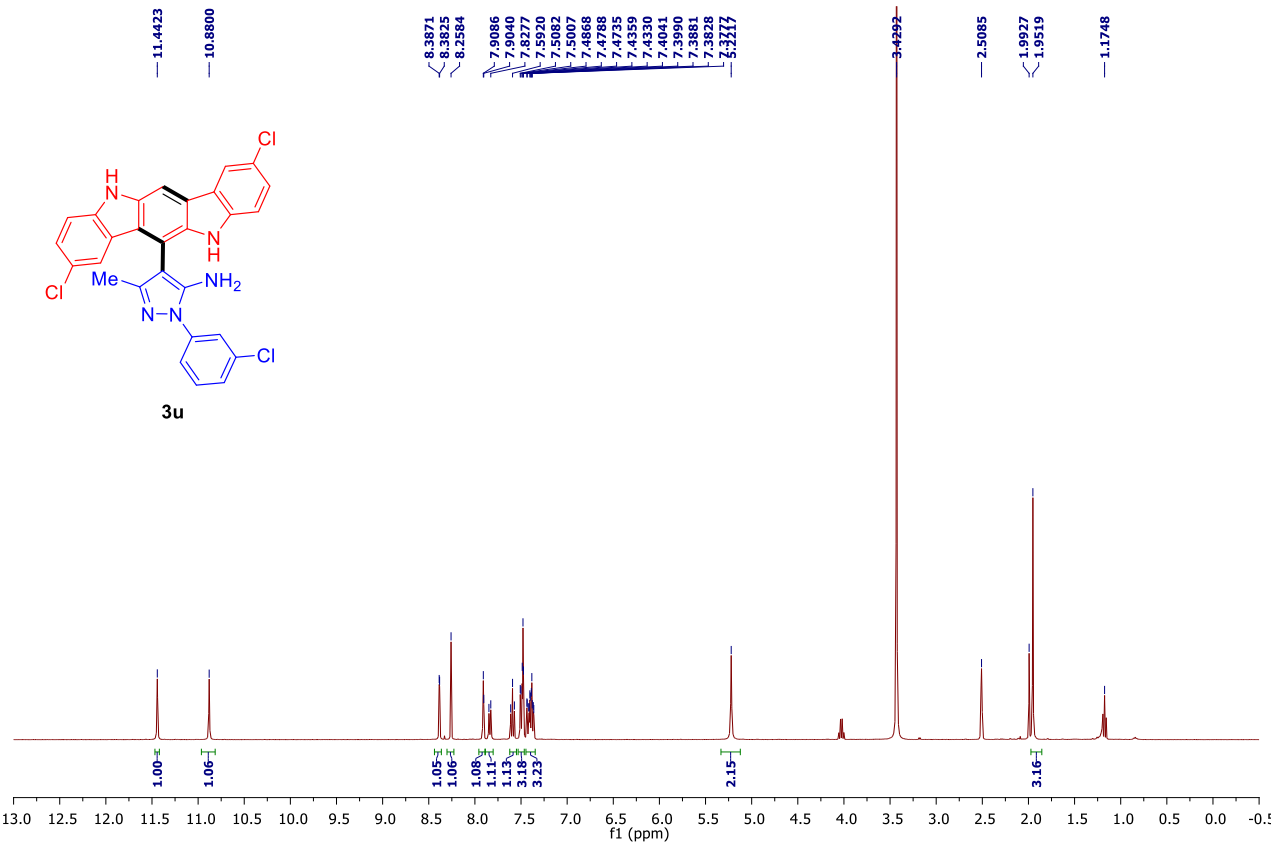
124.50
124.28
123.25
122.49
122.32
122.04
111.99
108.60
100.83
97.90
40.53
40.32
40.11
39.70
39.49
39.28
21.08
13.44
Cl
H
N
N
H
Cl
Me
NH2
N–N
Me
3t
f1 (ppm)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8.2584
7.9086
7.9040
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7.5920
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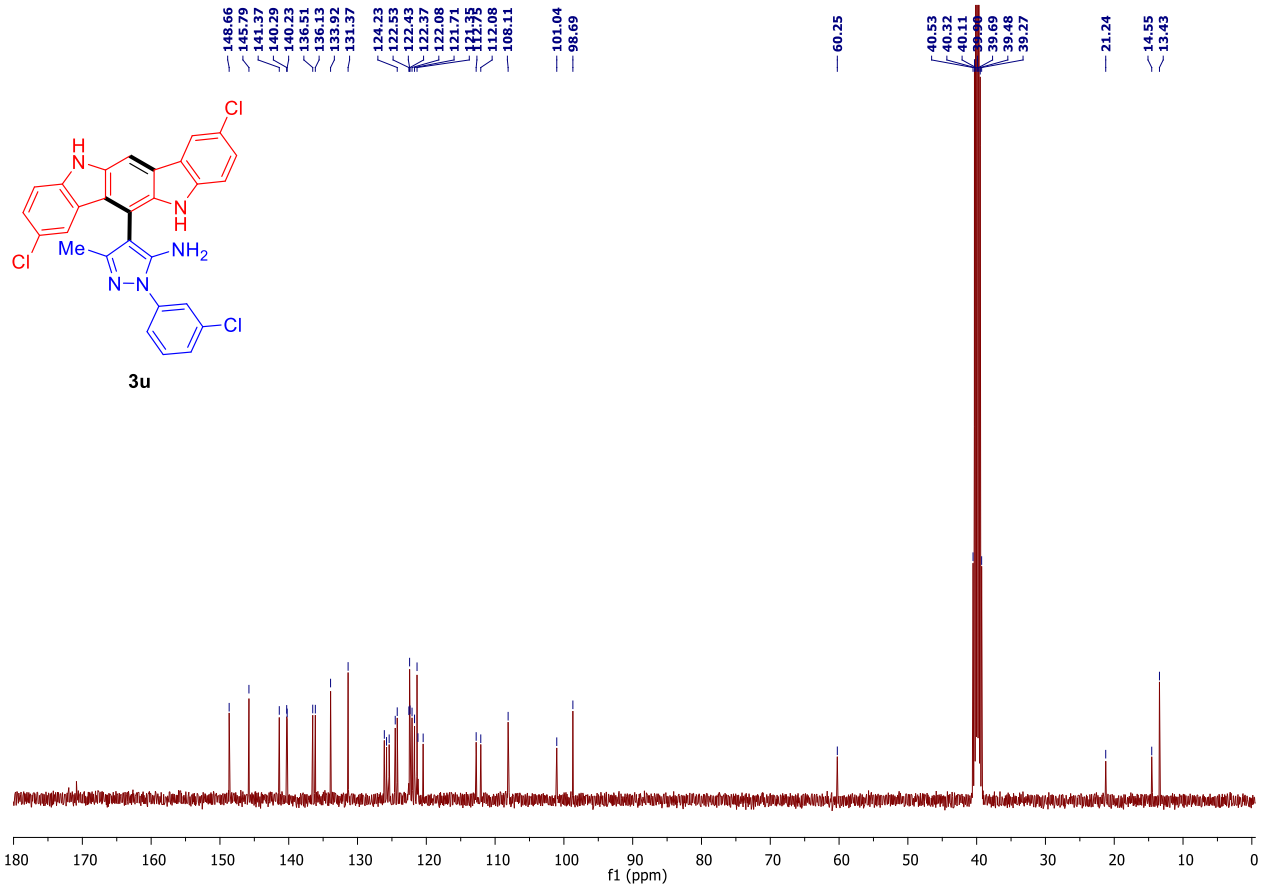
7.5007
7.4868
7.4788
7.4735
7.4359
7.4330
7.4041
7.3990
7.3881
7.3828
3.4292
2.5085
1.9927
1.9519
1.1748
1.00
1.06
1.05
1.06
1.08
1.11
1.13
3.18
3.23
2.15
3.16
f1 (ppm)

3u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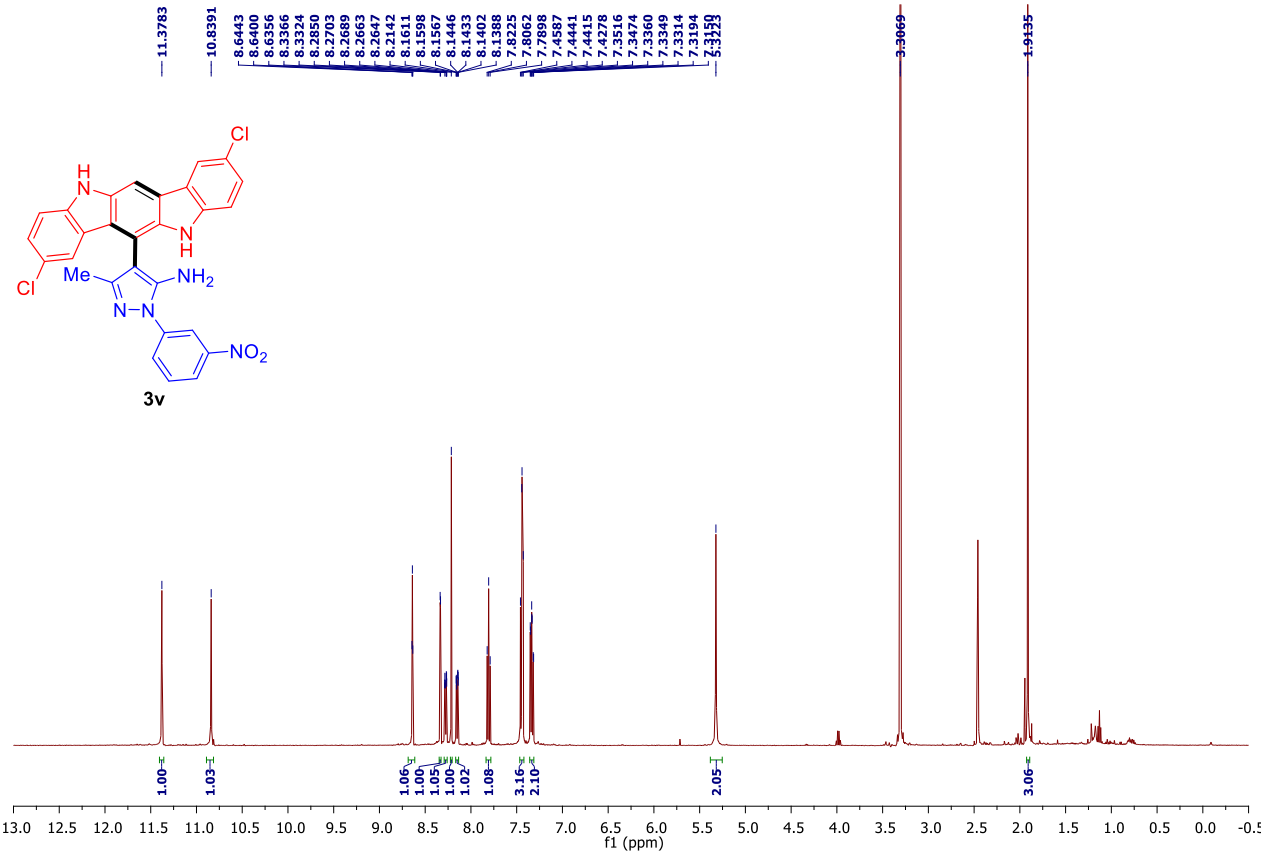
145.79
141.37
140.29
140.23
136.51
136.13
133.92
131.37
124.23
122.53
122.43
122.37
122.08
121.71
112.08
108.11
101.04
98.69
60.25
40.53
40.32
40.11
39.90
39.69
39.48
39.27
21.24
14.55
13.43
f1 (ppm)

3u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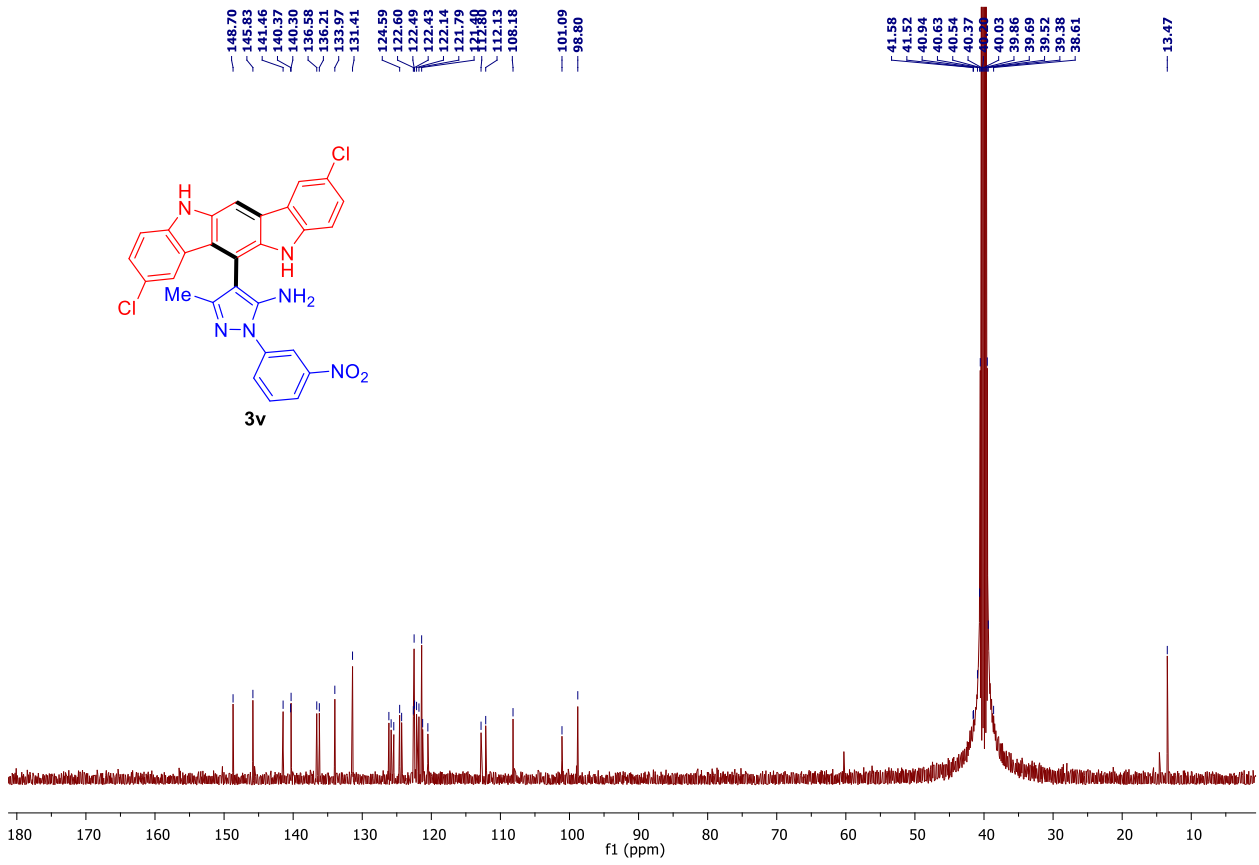
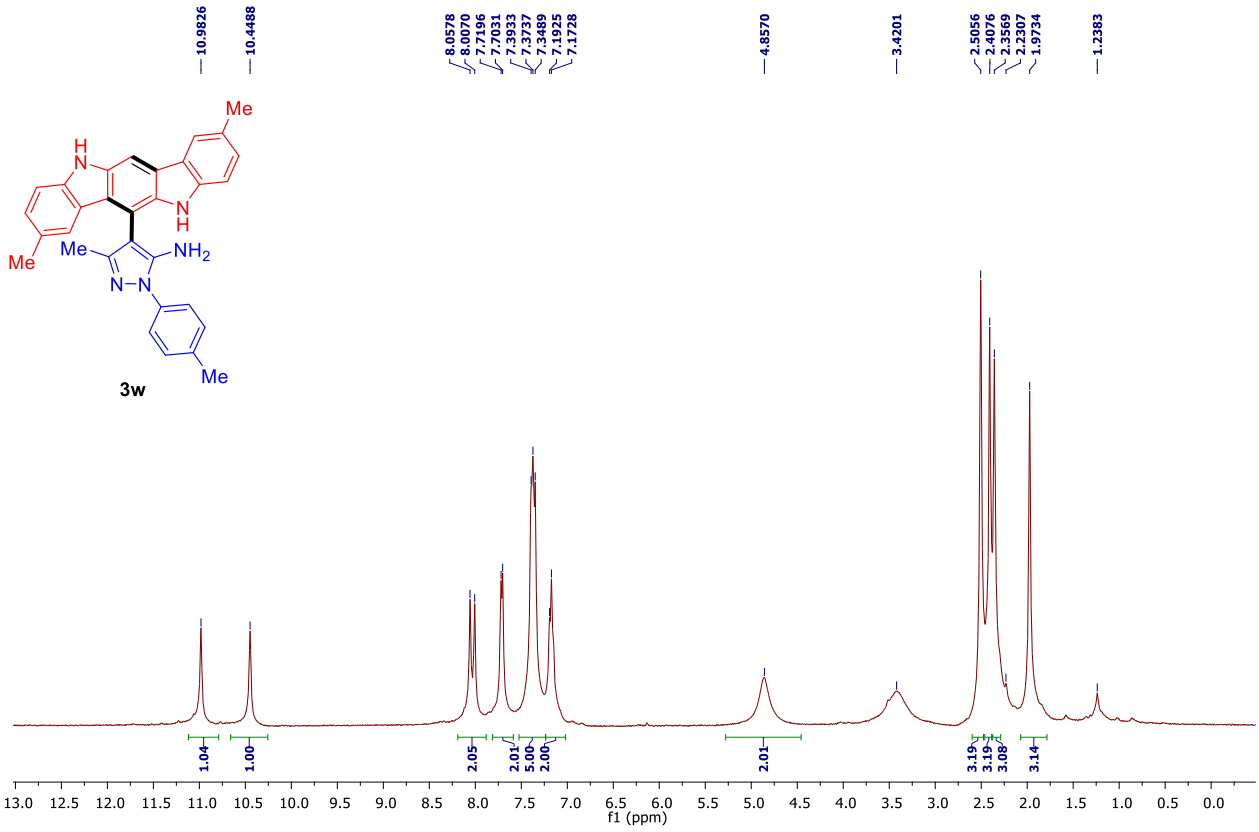
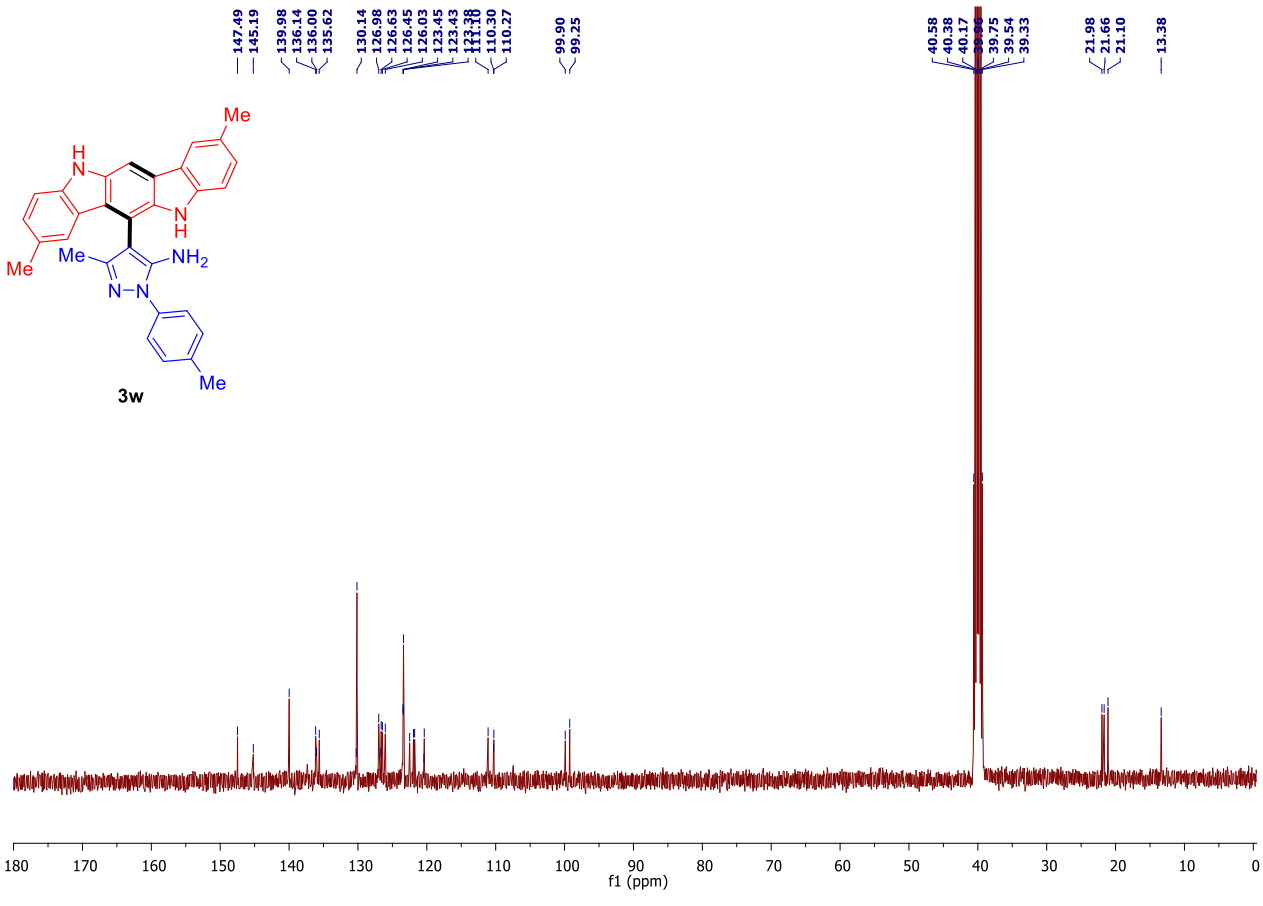
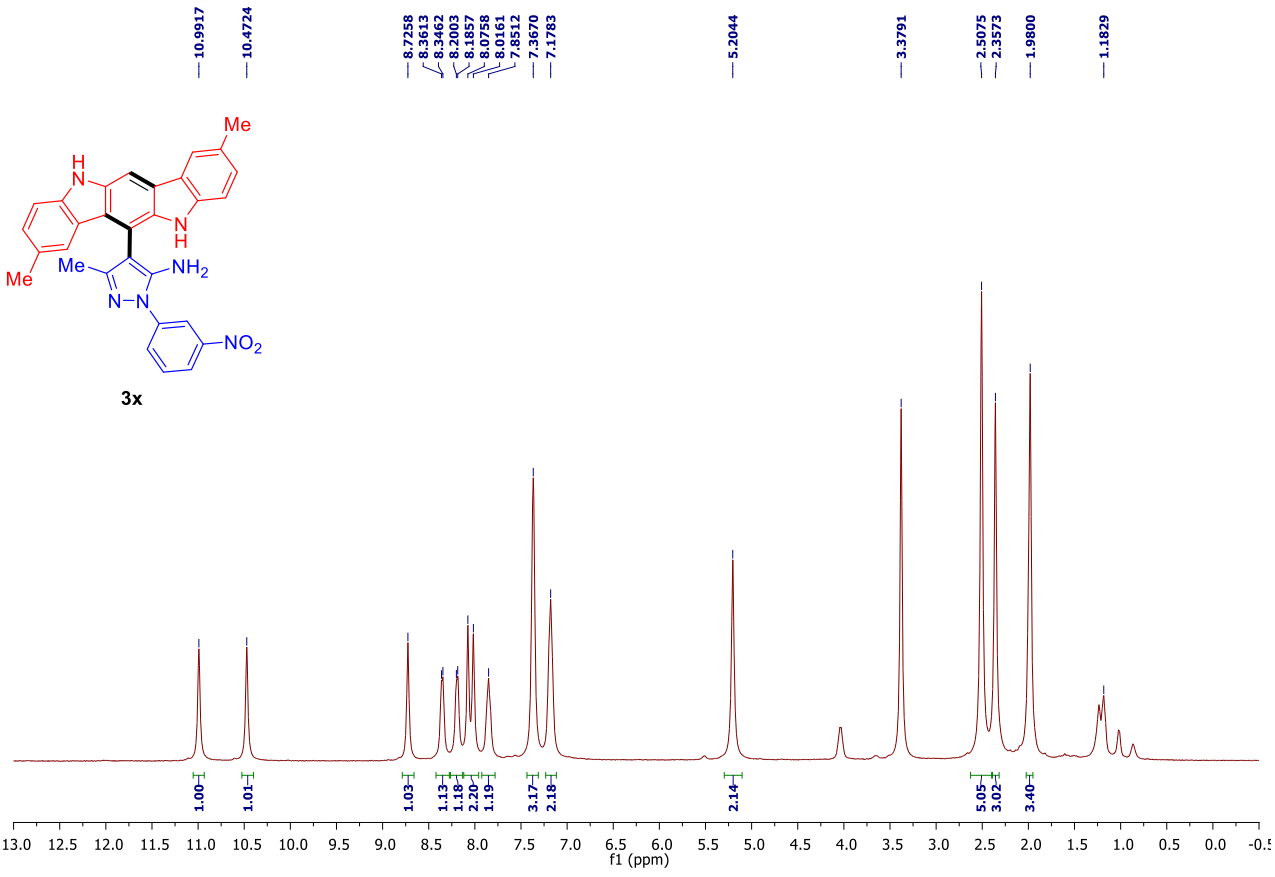
10.8391
8.6443
8.6400
8.6356
8.3366
8.3324
8.2850
8.2703
8.2689
8.2663
8.2647
8.2142
8.1611
8.1598
8.1567
8.1446
8.1433
8.1402
8.1388
7.8225
7.8062
7.7898
7.4587
7.4441
7.4415
7.4278
7.3516
7.3474
7.3360
7.3349
7.3314
7.3194
3.3069
1.9135
1.00
1.03
1.06
1.00
1.05
1.00
1.02
1.08
3.16
2.10
2.05
3.06
f1 (ppm)
3v

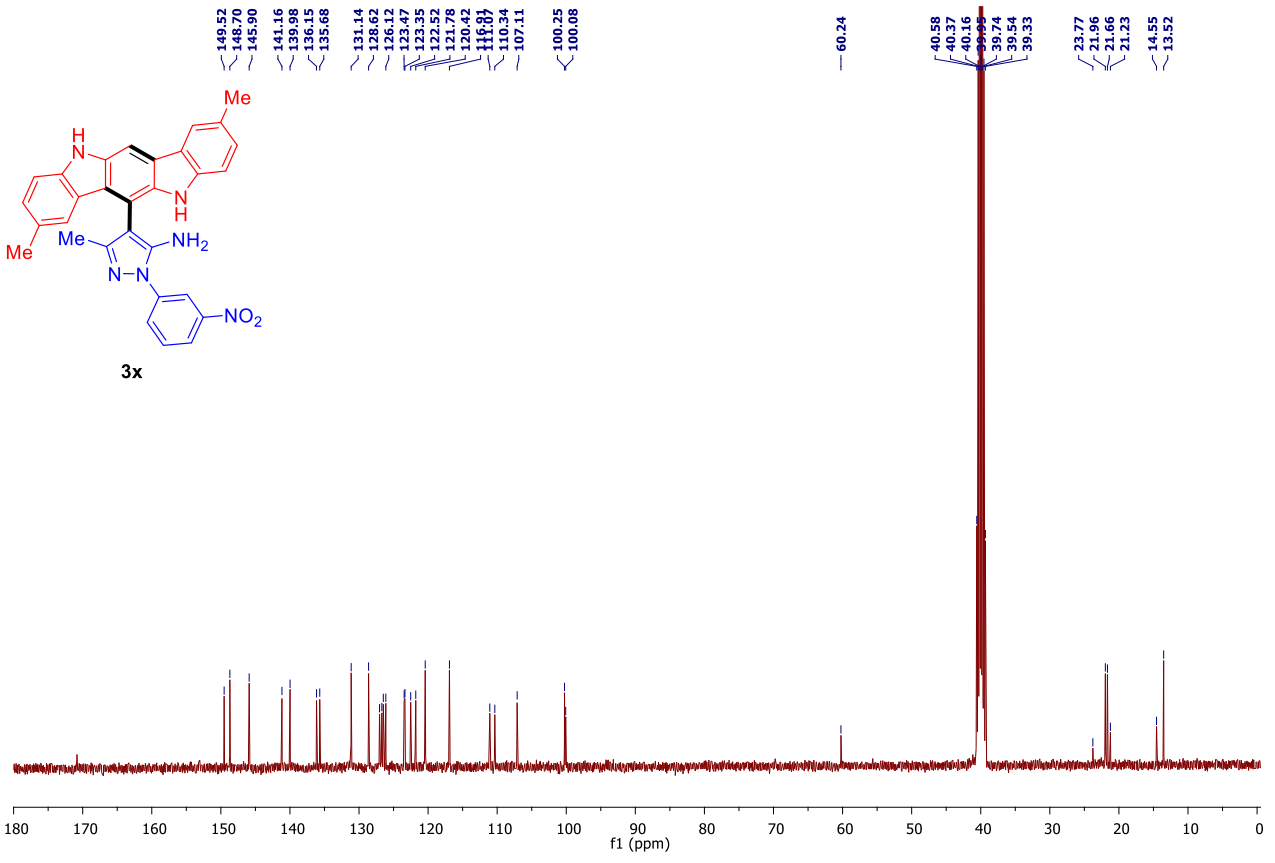

148.70
145.83
141.46
140.37
140.30
136.58
136.21
133.97
131.41
124.59
122.60
122.49
122.43
122.14
121.79
112.13
108.18
101.09
98.80
41.58
41.52
40.94
40.63
40.54
40.37
40.03
39.86
39.69
39.52
39.38
38.61
13.47
f1 (ppm)
3v


10.9826
10.4488
8.0578
8.0070
7.7196
7.7031
7.3933
7.3737
7.3489
7.1925
7.1728
4.8570
3.4201
2.5056
2.4076
2.3569
2.2307
1.9734
1.2383
Me
H
N
N
H
Me
Me
NH2
N–N
Me
3w
1.04
1.00
2.05
2.01
5.00
2.00
2.01
3.19
3.19
3.08
3.14
13.0 12.5 12.0 11.5 11.0 10.5 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)

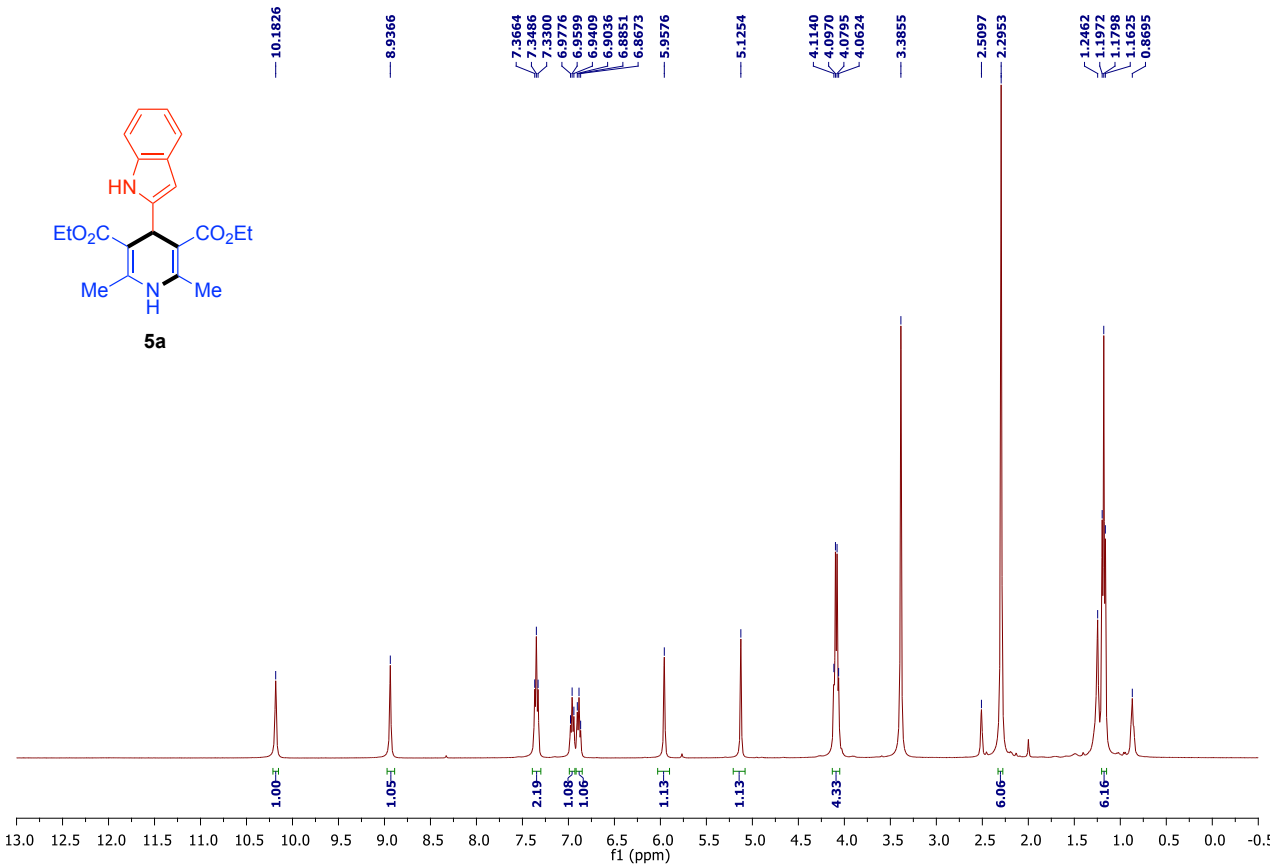

147.49
145.19
139.98
136.14
136.00
135.62
130.14
126.98
126.63
126.45
126.03
123.45
123.43
111.38
110.30
110.27
99.90
99.25
40.58
40.38
40.17
39.75
39.54
39.33
21.98
21.66
21.10
13.38
Me
H
N
N
H
Me
Me
NH2
N–N
Me
3w
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10.9917
10.4724
8.7258
8.3613
8.3462
8.2003
8.1857
8.0758
8.0161
7.8512
7.3670
7.1783
5.2044
3.3791
2.5075
2.3573
1.9800
1.1829
1.00
1.01
1.03
1.13
1.18
2.20
1.19
3.17
2.18
2.14
5.05
3.02
3.40
f1 (ppm)

3x


149.52
148.70
145.90
141.16
139.98
136.15
135.68
131.14
128.62
126.12
123.47
123.35
122.52
121.78
120.42
110.34
107.11
100.25
100.08
60.24
40.58
40.37
40.16
39.74
39.54
39.33
23.77
21.96
21.66
21.23
14.55
13.52
f1 (ppm)

3x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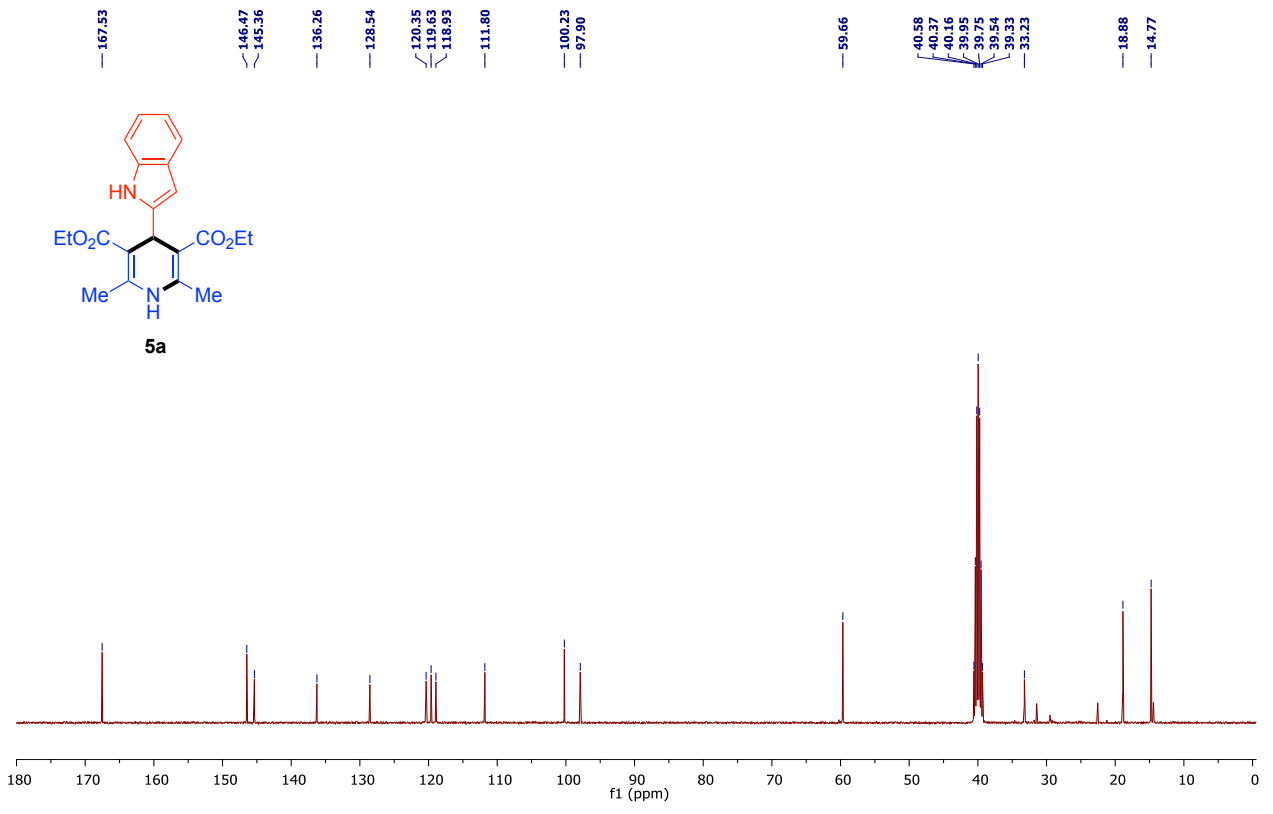
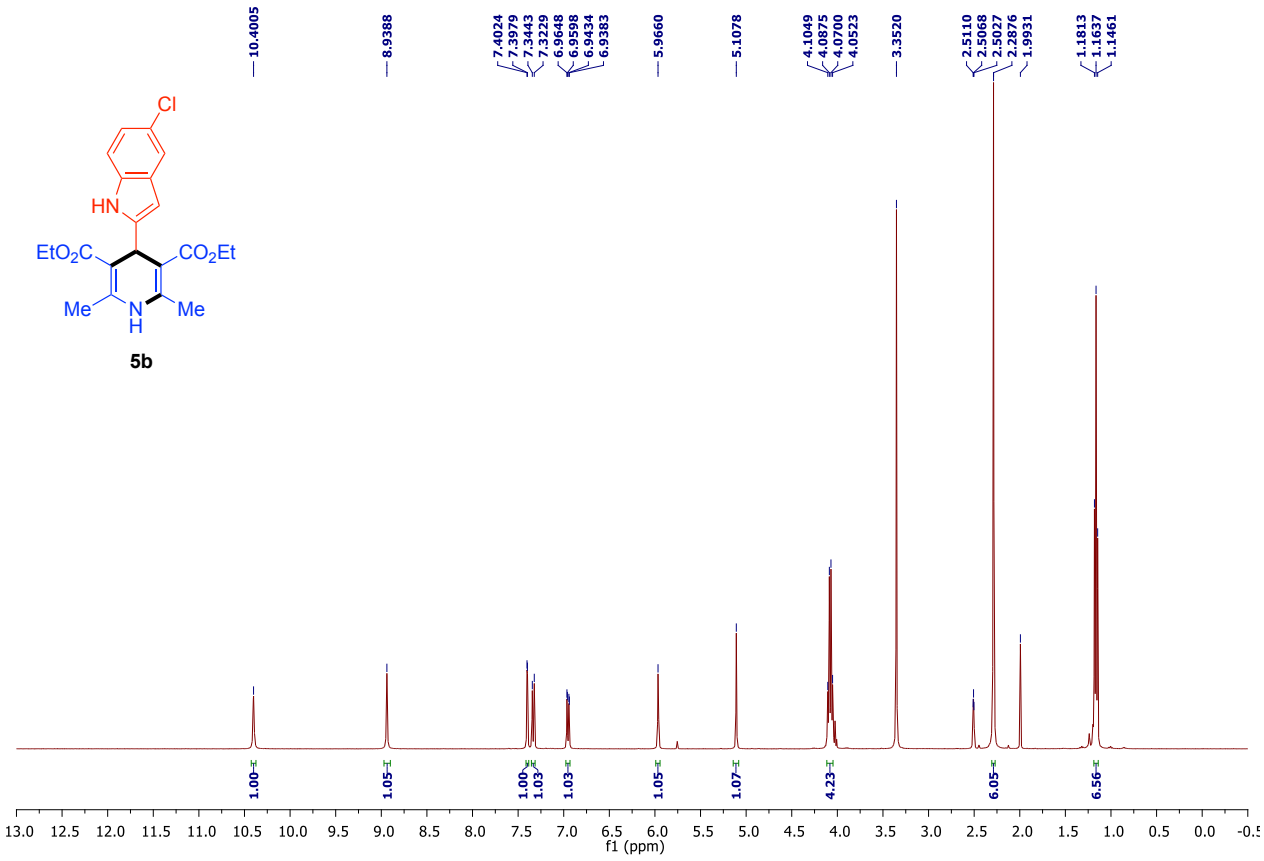
8.9366
7.3664
7.3486
7.3300
6.9776
6.9599
6.9409
6.9036
6.8851
6.8673
5.9576
5.1254
4.1140
4.0970
4.0795
4.0624
3.3855
2.5097
2.2953
1.2462
1.1972
1.1798
1.1625
0.8695
HN
EtO2C
CO2Et
Me
N
H
Me
5a
1.00
1.05
2.19
1.08
1.06
1.13
1.13
4.33
6.06
6.16
f1 (ppm)


167.53
146.47
145.36
136.26
128.54
120.35
119.63
118.93
111.80
100.23
97.90
59.66
40.58
40.37
40.16
39.95
39.75
39.54
39.33
33.23
18.88
14.77
HN
EtO2C
CO2Et
Me
N
H
Me
5a
f1 (ppm)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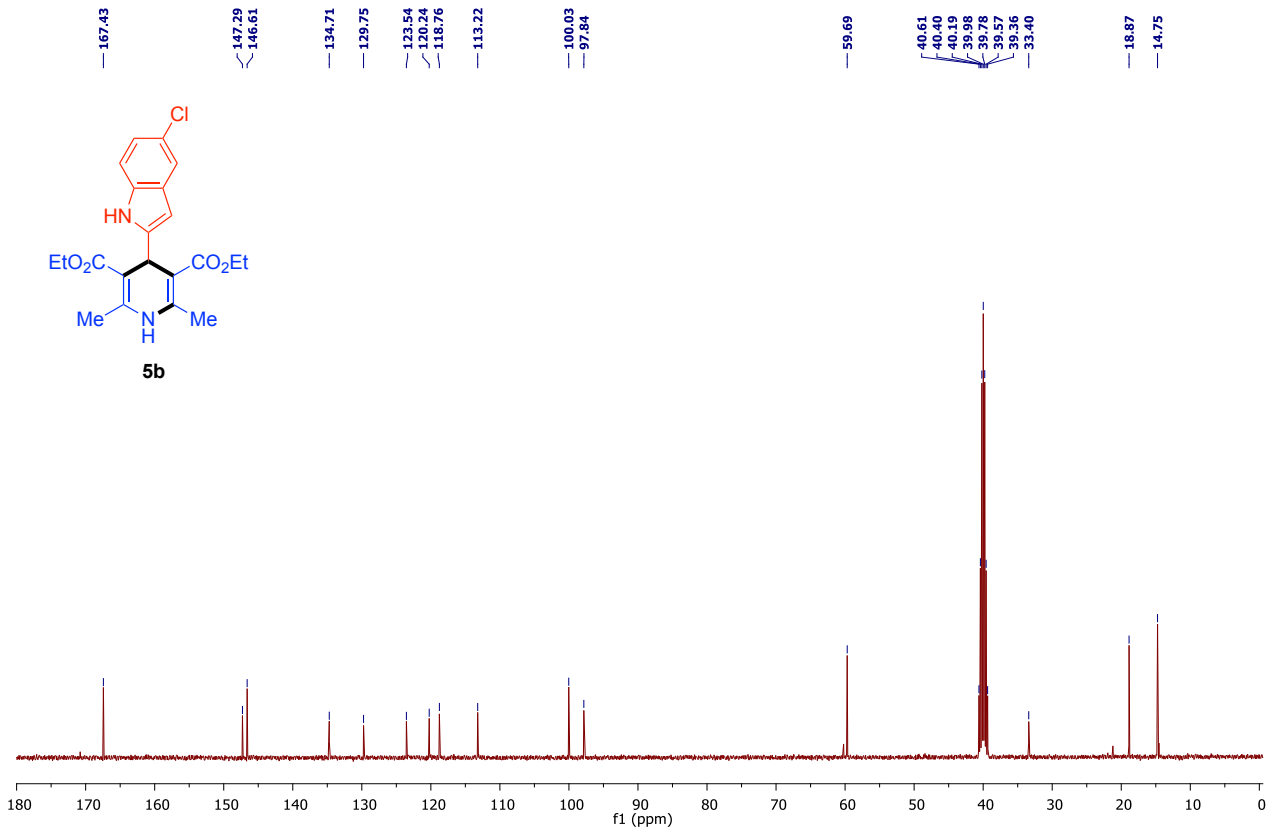
7.4024
7.3979
7.3443
7.3229
6.9648
6.9598
6.9434
6.9383
5.9660
5.1078
4.1049
4.0875
4.0700
4.0523
3.3520
2.5110
2.5068
2.5027
2.2876
1.9931
1.1813
1.1637
1.1461
Cl
HN
EtO2C
CO2Et
Me
N
H
Me
5b
1.00
1.05
1.00
1.03
1.03
1.05
1.07
4.23
6.05
6.56
f1 (ppm)


167.43
147.29
146.61
134.71
129.75
123.54
120.24
118.76
113.22
100.03
97.84
59.69
40.61
40.40
40.19
39.98
39.78
39.57
39.36
33.40
18.87
14.75
Cl
HN
EtO2C
CO2Et
Me
N
H
Me
5b
f1 (ppm)