Photochemical Synthesis of Carbazoles Using a $[Fe(phen)_3](NTf_2)_2/O_2$ Catalyst System: Catalysis Towards Sustainability.

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SUPPORTING INFORMATION

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GENERAL

All reactions that were carried out under anhydrous conditions were performed under an inert argon or nitrogen atmosphere in glassware that had previously been dried overnight at 120°C or had been flame dried and cooled under a stream of argon or nitrogen.[1] All chemical products were obtained from Sigma-Aldrich Chemical Company or Strem Chemicals and were reagent quality. The following products were prepared according to their respective literature procedures: 4-methoxy-*N*,*N*-diphenylaniline,[2] 4-methyl-*N*,*N*-diphenylaniline,[2] 4-methoxy-*N*-(4-methoxyphenyl)-*N*-phenylaniline,[3] 3,5-dimethoxy-*N*,*N*-diphenylaniline,[3] Tris-(4-methoxyphenyl)amine,[2] *N*,*N*-diphenylpyrimidin-5-amine,[2] 4-fluoro-*N*,*N*-diphenylaniline,[3] 4-chloro-*N*,*N*-diphenylaniline,[3] 2,4,6-Trimethyl-*N*,*N*-diphenylaniline,[2] *N*-(4-methylphenyl)-*N*-methylaniline,[2] *N*-ethyl-*N*-phenylaniline,[2] 1-phenyl-1,2,3,4-tetrahydroquinoline,[2] *N*-(2,5-Xylyl)-*p*-anisidine.[4] Technical solvents were obtained from VWR International Co. Anhydrous solvents (CH_2Cl_2, Et_2O, THF, DMF, Toluene, and n-hexane) were dried and deoxygenated using a GlassContour system (Irvine, CA). Isolated yields reflect the mass obtained following flash column silica gel chromatography. Organic compounds were purified using the method reported by W. C. Still[5] and using silica gel obtained from Silicycle Chemical division (40-63 nm; 230-240 mesh). Analytical thin-layer chromatography (TLC) was performed on glass-backed silica gel 60 coated with a fluorescence indicator (Silicycle Chemical division, 0.25 mm, F_{254}.). Visualization of TLC plate was performed by UV (254 nm), $KMnO_4$ or *p*-anisaldehyde stains. All mixed solvent eluents are reported as v/v solutions. Concentration refers to removal of volatiles at low pressure on a rotary evaporator. All reported compounds were homogeneous by thin layer chromatography (TLC) and by ^{1}H NMR. NMR spectra were taken in deuterated $CDCl_3$ using Bruker AV-300 and AV-400 instruments unless otherwise noted. Signals due to the solvent served as the internal standard ($CHCl_3$: δ 7.27 for ^{1}H, δ 77.0 for ^{13}C). The ^{1}H NMR chemical shifts and coupling constants were determined assuming first-order behavior. Multiplicity is indicated by one or more of the following: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad); the list of couplings constants (*J*) corresponds to the order of the multiplicity assignment. The ^{1}H NMR assignments were made based on chemical shift and multiplicity. The ^{13}C NMR assignments were made on the basis of chemical shift and multiplicity. High resolution mass spectroscopy (HRMS) was done by the Centre régional de spectrométrie de masse at the Département de Chimie, Université de Montréal from an Agilent LC-MSD TOF system using ESI mode of ionization unless otherwise noted. All photochemical experiments using visible light were carried out using common household energy saving lightbulbs. Typically, the experiments conducted utilized "Blue Planet Energy Saving Lightbulbs" (23W, Model number: 052-5510-2, Bulb type: Bare Spiral, Base Type: E26/24 (Medium), Technology: CFL, Light Output: 1600 Lumens).

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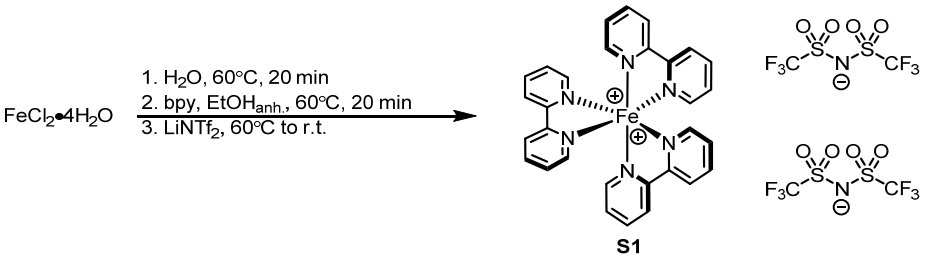
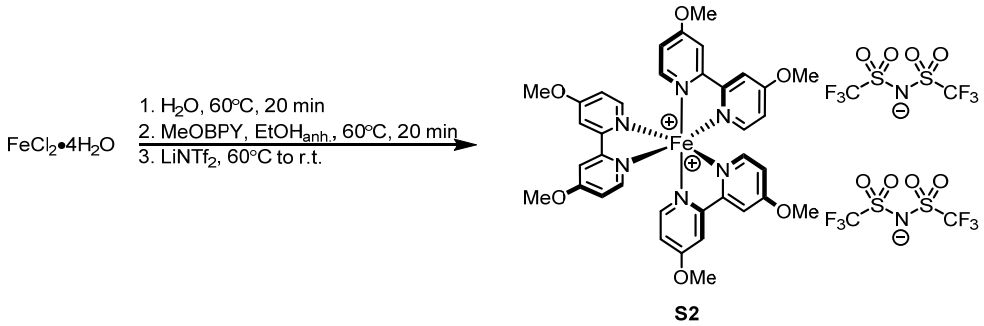
[1] Shriver, D. F.; Drezdon, M. A. in *The Manipulation of Air-Sensitive Compounds*; Wiley-VCH: New York, 1986.
[2] Hernandez-Perez, A. C.; Collins, S. K. *Angew. Chem., Int. Ed.* **2013**, *52*, 12696.
[3] Hernandez-Perez, A. C.; Caron, A.; Collins, S. K. *Chem. Eur. J.* **2015**, *21*, 16673
[4] Wolfe, J. P.; Tomori, H.; Sadighi, J. P.; Yin, J.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65,* 1158
[5] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

SYNTHESIS OF PHOTOSENSITIZERS

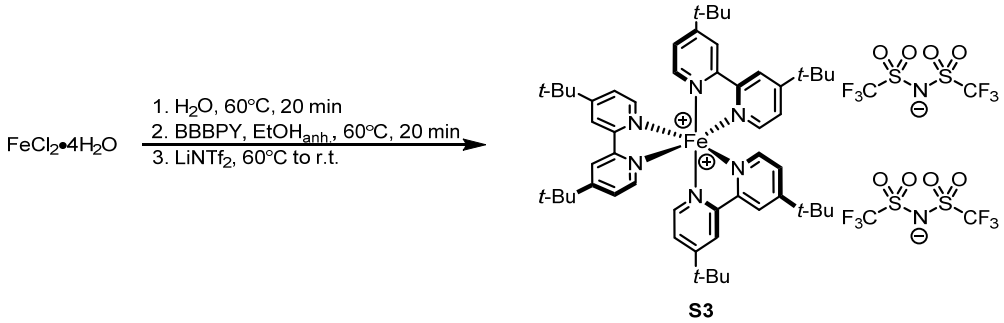


Tris(2,2'-bipyridyl)iron(II)bis(bis(trifluoromethane)sulfonimide) (S1): In a round bottom flask equipped with a stir bar was charged with iron(II) chloride tetrahydrate (298 mg, 1.50 mmol, 1.0 equiv.) and distilled water (30.0 mL, 0.05 M). The reaction mixture was placed in a pre-heated oil bath at 60°C during 20 minutes. Then, to the reaction mixture was added a solution of 2,2'-bipyridyl (714 mg, 4.57 mmol, 3.05 equiv) in anhydrous EtOH (45.7 mL, 0.10 M). The reaction mixture temperature was maintained at 60°C during another 20 minutes. $LiNTf_2$ (1289 mg, 4.49 mmol, 3.0 equiv) was added in one portion and the heating was stopped. The reaction mixture was left to cool at room temperature (without removing the oil bath). The reaction mixture was filtered with a Buchner funnel with a fritted disk and the precipitate was washed with Et_2O. The red precipitate was dried under vacuum overnight to afford the desired product as a red powder (1.14 g, 70 %). ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ ppm 8.85 (d, J = 7.7 Hz, 6H), 8.28 (t, J = 7.2 Hz, 6H), 7.74 (d, J = 4.6 Hz, 6H), 7.59 (d, J = 5.9 Hz, 6H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ ppm 161.30, 156.18, 140.79, 129.58, 125.98; ^{19}F NMR (282 MHz, $(CD_3)_2CO$) δ ppm -81.27 (s, 3F); HRMS (ESI) m/z calculated for $C_{30}H_{24}[^{56}Fe]N_6$ $[M]^{2+}$, 262.0700; found: 262.0697. ; HRMS (ESI) m/z calculated for $C_2F_6N_1O_4S_2$ $[M]^-$, 279.9178; found: 279.9177.



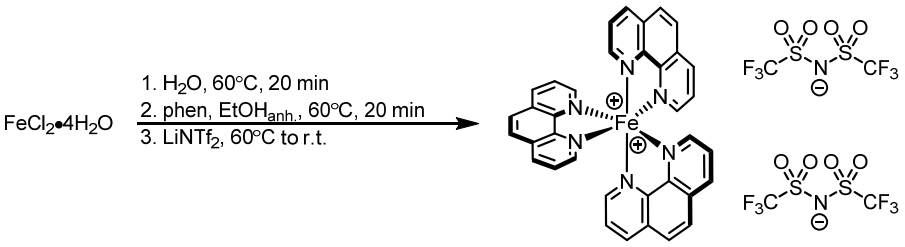
Tris(4,4'dimethoxy-2,2'-bipyridyl)iron(II)bis(bis(trifluoromethane)sulfonimide) (S2): In a round bottom flask equipped with a stir bar was charged with iron(II) chloride tetrahydrate (302 mg, 1.52 mmol, 1.0 equiv.) and distilled water (30.4 mL, 0.05 M). The reaction mixture was placed in a pre-heated oil bath at 60°C during 20 minutes. Then, to the reaction mixture was added a solution of 4,4'-dimethoxy-2,2'-bipyridyl (1002 mg, 4.64 mmol, 3.05 equiv) in anhydrous EtOH (46.4 mL, 0.10 M). The reaction mixture

temperature was maintained at 60°C during another 20 minutes. $LiNTf_2$ (1309 mg, 4.56 mmol, 3.0 equiv) was added in one portion and the heating was stopped. The reaction mixture was left to cool at room temperature (without removing the oil bath). The reaction mixture was filtered with a Buchner funnel with a fritted disk and the precipitate was washed with Et_2O. The red precipitate was dried under vacuum overnight to afford the desired product as a dark purple powder (1.55 g, 81 %). ^1H NMR (300 MHz, $(CD_3)_2CO$) δ ppm 8.42 (s, 6H), 7.50 (d, J = 6.0 Hz, 6H), 7.16 (d, J = 6.0 Hz, 6H), 4.06 (s, 18H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ ppm 169.98, 162.40, 156.59, 116.05, 112.88, 58.19; ^{19}F NMR (282 MHz, $(CD_3)_2CO$) δ ppm -81.31 (s, 3F); HRMS (ESI) m/z calculated for $C_{36}H_{36}[^{56}Fe]N_6O_6$ $[M]^{+2}$, 352.1017; found: 352.1022. ; HRMS (ESI) m/z calculated for $C_2F_6N_1O_4S_2$ $[M]^-$, 279.9178; found: 279.9184.



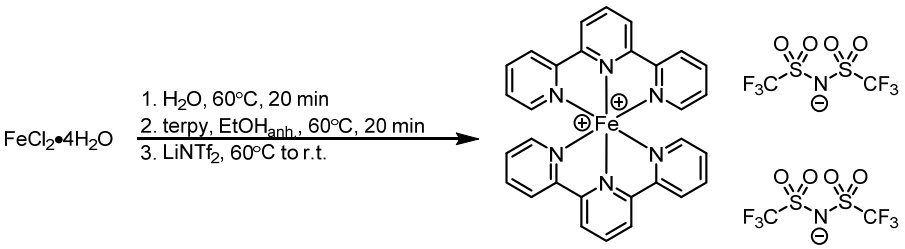
S3

Tris(4,4'-di-*tert*-butyl-2,2'-bipyridyl)iron(II)bis(bis(trifluoromethane)sulfonimide) (S3): In a round bottom flask equipped with a stir bar was charged with iron(II) chloride tetrahydrate (252 mg, 1.27 mmol, 1.0 equiv.) and distilled water (25.4 mL, 0.05 M). The reaction mixture was placed in a pre-heated oil bath at 60°C during 20 minutes. Then, to the reaction mixture was added a solution of 4,4'-di-*tert*-butyl-2,2'-bipyridyl (1038 mg, 3.87 mmol, 3.05 equiv) in anhydrous EtOH (38.7 mL, 0.10 M). The reaction mixture temperature was maintained at 60°C during another 20 minutes. $LiNTf_2$ (1094 mg, 3.81 mmol, 3.0 equiv) was added in one portion and the heating was stopped. The reaction mixture was left to cool at room temperature (without removing the oil bath). The reaction mixture was filtered with a Buchner funnel with a fritted disk and the precipitate was washed with Et_2O. The red precipitate was dried under vacuum overnight to afford the desired product as a red powder (1.34 g, 74 %). ^1H NMR (300 MHz, $(CD_3)_2CO$) δ ppm 8.91 (s, 6H), 7.53 (d, J = 15.0 Hz, 12H), 1.41 (s, 54H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ ppm 156.27, 161.21, 155.69, 126.83, 123.37, 37.14, 31.57; ^{19}F NMR (282 MHz, $(CD_3)_2CO$) δ ppm -81.21 (s, 3F); HRMS (ESI) m/z calculated for $C_{54}H_{72}[^{56}Fe]N_6$ $[M]^{+2}$, 430.2578; found: 430.2596. ; HRMS (ESI) m/z calculated for $C_2F_6N_1O_4S_2$ $[M]^-$, 279.9178; found: 279.9170.



3

Tris(1,10-phenanthroline)iron(II) bis(bis(trifluoromethane)sulfonimide) (3): In a round bottom flask equipped with a stir bar was charged iron(II) chloride tetrahydrate (334 mg, 1.68 mmol, 1.0 equiv.) and distilled water (33.6 mL, 0.05 M). The reaction mixture was placed in a pre-heated oil bath at 60°C for 20 minutes. Then, to the reaction mixture was added a solution of 1,10-phenanthroline (924 mg, 5.13 mmol, 3.05 equiv) in anhydrous EtOH (51.3 mL, 0.10 M). The reaction mixture temperature was maintained at 60°C for another 20 minutes. $LiNTf_2$ (1447 mg, 5.04 mmol, 3.0 equiv) was added in one portion and the heating was stopped. The reaction mixture was left to cool at room temperature (without removing the oil bath). The reaction mixture was filtered on a Buchner funnel with a fritted disk and the precipitate was washed with Et_2O. The red precipitate was dried under vacuum overnight to afford the desired product **3** as a red powder (1.34 g, 69%). ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ ppm 8.84-8.82 (d, J = 7.8 Hz, 6H), 8.43 (s, 6H), 8.05 (d, J = 4.2 Hz, 6H), 7.80 (t, J = 5.4 Hz, 6H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ ppm 158.18, 151.78, 139.41, 132.48, 130.09, 128.07; ^{19}F NMR (282 MHz, $(CD_3)_2CO$) δ ppm -81.03 (s, 3F); HRMS (ESI) m/z calculated for $C_{36}H_{24}FeN_6$ $[M]^{+2}$, 298.0700; found: 298.0697. HRMS (ESI) m/z calculated for $C_2F_6N_1O_4S_2$ $[M]^-$, 279.9178; found: 279.9189.

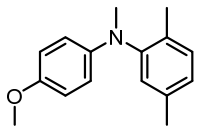


S4

Bis(2,2':6',2''-terpyridyl)iron(II)bis(bis(trifluoromethane)sulfonimide) (S4): In a round bottom flask equipped with a stir bar was charged with iron(II) chloride tetrahydrate (199 mg, 1.00 mmol, 1.0 equiv.) and distilled water (20.0 mL, 0.05 M). The reaction mixture was placed in a pre-heated oil bath at 60°C during 20 minutes. Then, to the reaction mixture was added a solution of 2,2':6',2"-terpyridyl (707 mg, 3.03 mmol, 3.03 equiv) in anhydrous EtOH (30.3 mL, 0.10 M). The reaction mixture temperature was maintained at 60°C during another 20 minutes. $LiNTf_2$ (862 mg, 3.00 mmol, 3.0 equiv) was added in one portion and the heating was stopped. The reaction mixture was left to cool at room temperature (without removing the oil bath). The reaction mixture was

filtered with a Buchner funnel with a fritted disk and the precipitate was washed with Et_2O. The purple precipitate was dried under vacuum overnight to afford the desired product as a purple powder (1.14 g, 70 %). ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ ppm 9.25 (d, *J* = 8.1 Hz, 4H), 8.87 (t, *J* = 8.1 Hz, 2H), 8.79 (d, *J* = 7.8 Hz, 4H), 8.03 (td, *J* = 7.8, 1.2 Hz, 4H), 7.43 (d, *J* = 5.6 Hz, 4H), 7.24 (td, *J* = 6.6, 1.2 Hz, 4H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ ppm 161.47, 159.08, 154.17, 139.93, 139.33, 128.60, 124.88, 124.86; ^{19}F NMR (282 MHz, $(CD_3)_2CO$) δ ppm -81.30 (s, 3F); HRMS (ESI) m/z calculated for $C_{30}H_{22}[^{56}Fe]N_6$ $[M]^{2+}$, 261.0631; found: 261.0622. ; HRMS (ESI) m/z calculated for $C_2F_6N_1O_4S_2$ $[M]^-$, 279.9187; found: 279.9178.

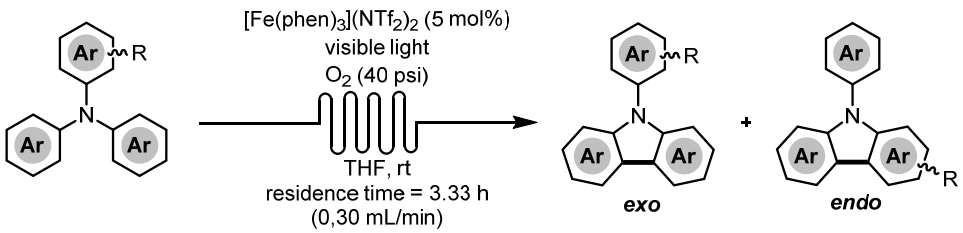
SYNTHESIS OF PRECUSOR



16

N-(4-methoxyphenyl)-N,2,5-trimethylaniline (16): A solution of *N*-(2,5-xylyl)-*p*-anisidine (1.00 g, 4.4 mmol, 1 eq.) and NaH (352 mg, 2 eq.) in anhydrous DMF (1 M) was stirred at room temperature for 1 hour. Iodomethane (0.41 mL, 1.5 eq.) was then added to the solution and the mixture was heated at 70 °C of 16 hours. The solution was cooled down to room temperature and was diluted with EtOAc/H_2O. The organic phase was washed with water (3x). The combined organic phases were washed with brine (1x) and dried with anhydrous sodium sulfate. The resulting suspension was filtered. The filtrate was concentrated under vacuum to provide a crude reaction mixture, which was purified by column chromatography on silica-gel (100 % hexanes to 5 % diethyl ether in hexanes) to afford the desired product as a colorless oil (273 mg, 26 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.14 (d, *J* = 7.6 Hz, 1H), 6.96 (m, 2H), 6.78 (d, *J* = 9.3 Hz, 2H), 6.53 (d, *J* = 9.1 Hz, 2H), 3.76 (s, 3H), 3.18 (s, 3H), 2.30 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 151.74, 147.54, 144.08, 136.98, 132.99, 131.04, 127.87, 126.46, 114.81 (2C), 114.53 (2C), 55.76, 39.74, 20.88, 17.53; HRMS (ESI) m/z calculated for $C_{16}H_{19}NO$ $[M+H]^+$, 242.1547; found: 242.1539.

SYNTHESIS OF CARBAZOLES



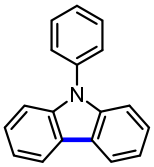
General Procedure for Visible Light Mediated Synthesis of carbazole under continuous-flow using $[Fe(phen)_3](NTf_2)_2$ catalyst procedure (A): A solution of $[Fe(phen)_3](NTf_2)_2$ **3** (9.3 mg, 0.01 mmol, 5 mol %), triarylamine (0.16 mmol, 1 equiv.) and tetrahydrofuran (32 mL, 5 mM) was prepared and injected via a VapourTec R2+ pumping module. The solution was first pumped through a 15 mL gas-liquid reactor connected to an oxygen supply (40 psi), and then through five PFA coiled reactors (13 mL volume), each having a compact fluorescent lamp (energy saving lightbulb, 23W) located in its center. A 8 bar back pressure regulator was connected at the end of the line. The reaction mixture was pumped at a flow rate of 0.325 mL/min for an "oxygenation" time of 0.77 h and an "irradiation" time of 3.33 h. Following elution through the flow reactor, the crude reaction mixture was quenched by the addition of silica gel. The resulting slurry was concentrated under reduced pressure and purified by column chromatography to afford the desired product.

Figure S1. Continuous-flow reactor set-up used for the visible light mediated synthesis of carbazoles. (left: VapourTec module connected to five PFA coils; right: disposition of CFL inside PFA coils)

Figure S2. Continuous-flow reactor. (left: VapourTec PFA coil (10mL, 1mm I.D.) ; right: homemade PFA coil (12mL, 1mm I.D.)

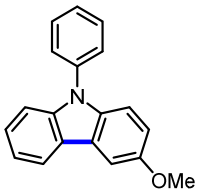
General Procedure for Large-Scale Visible Light Mediated Synthesis of carbazole under continuous-flow using [Fe(phen)$_3$](NTf$_2$)$_2$ catalyst procedure (B): A solution of [Fe(phen)$_3$](NTf$_2$)$_2$ **3** (243 mg, 0.21 mmol, 5 mol %), triarylamine (4.1 mmol, 1 equiv.) and tetrahydrofuran (820 mL, 5 mM) was prepared and injected via a VapourTec R2+ pumping module. The solution was first pumped through a 15 mL gas-liquid reactor connected to an oxygen supply (100 psi), then through a T-shaped split in which each reaction mixture stream was pumped through four PFA coiled reactors (13 mL volume), each having a compact fluorescent lamp (energy saving lightbulb, 23W) located in its center. Following elution from the coiled reactors, the streams were recombined via a T-shaped junction equipped with two 8 bar back pressures regulators in series. The reaction mixture was pumped at a flow rate of 0.65 mL/min for an "oxygenation" time of 0.38 h and an "irradiation" time of 2.67 h. Following elution through the flow reactor, the crude reaction mixture was quenched by the addition of silica gel. The resulting slurry was concentrated under reduced pressure and purified by column chromatography to afford the desired product.

Figure S3. Continuous-flow reactor numbering-up set-up used for the visible light mediated synthesis of carbazoles.



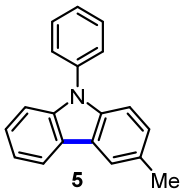
2

9-Phenylcarbazole (2): Following the general procedure **A** using continuous-flow with amine **1** (39 mg, 0.16 mmol, 1.0 equiv.), the crude reaction mixture was purified by silica gel column chromatography (100 % hexanes) to afford the desired product **2** as a white solid (35.4 mg, 91 %). Following the general procedure **B** using continuous-flow with amine **1** (1.006 g, 4.1 mmol, 1.0 equiv.), the crude reaction mixture was purified by silica gel column chromatography (100 % hexanes) to afford the desired product **2** as a white solid (897.9 mg, 90 %). The NMR data obtained for carbazole **2** were in agreement with that found in the literature. [6]



4

3-Methoxy-9-phenylcarbazole (4): Following the general procedure **A** using continuous-flow with 4-methoxy-*N*,*N*-diphenylaniline (51 mg, 0.16 mmol, 1.0 equiv.), the crude reaction mixture was purified by silica gel column chromatography (100 % hexanes to 5 % diethyl ether/hexanes) to afford the desired carbazole **4** as colorless oil (37.2 mg, 85 %) in a 11:89 ratio for the "endo" product 3-methoxy-9-phenylcarbazole. The NMR data obtained for carbazole **4** were in agreement with that found in the literature.[7]

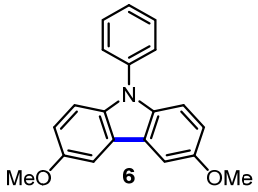


5

3-Methyl-9-phenylcarbazole (5): Following the general procedure **A** using continuous-flow with 4-methyl-*N*,*N*-diphenylaniline (41.5 mg, 0.16 mmol, 1.0 equiv.), the crude reaction mixture was purified by silica gel column chromatography (100 % hexanes to 5 % diethyl ether/hexanes) to afford the desired carbazole **5** as a colorless oil (33.4 mg, 81

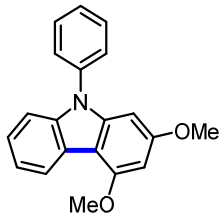
[6] Zhou, Y.; Verdake, J. G. *Adv. Synth. Catal.* **2010**, *352*, 616.
[7] Guerra, W. D.; Rossi, R. A.; Pierini, A. B.; Barolo, S. M. *Org. Lett.* **2015**, 80, 928-941.

%) in a 33:67 ratio for the "endo" product 3-methyl-9-phenylcarbazole. The NMR data obtained for carbazole **5** were in agreement with that found in the literature.[8]



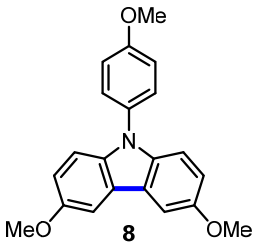
6

3,6-Dimethoxy-9-phenylcarbazole (6): Following the general procedure **A** using continuous-flow with 4-methoxy-*N*-(4-methoxyphenyl)-*N*-phenylaniline (48.9 mg, 0.16 mmol, 1.0 equiv.), the crude reaction mixture was purified by silica gel column chromatography (5 % ethyl acetate/hexanes) to afford the desired carbazole **6** as a yellow oil (24.3 mg, 50 %) in a 50:50 ratio. The NMR data obtained for carbazole **6** were in agreement with that found in the literature.[9]



7

2,4-Dimethoxy-9-phenylcarbazole (7): Following the general procedure **A** using continuous-flow with 3,5-dimethoxy-*N*,*N*-diphenylaniline (48.9 mg, 0.16 mmol, 1.0 equiv.), the crude reaction mixture was purified by silica gel column chromatography (5 % to 15 % diethyl ether/hexanes) to afford the desired carbazole **7** as a colorless oil (26.7 mg, 55 %) in a 33:67 ratio for the "endo" product 2,4-dimethoxy-9-phenylcarbazole. The NMR data obtained for carbazole **7** were in agreement with that found in the literature.[5]

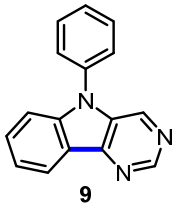


8

3,6-Dimethoxy-9-(4-methoxyphenyl)carbazole (8): Following the general procedure **A** using continuous-flow with tris-(4-methoxyphenyl)amine (53.7 mg, 0.16 mmol, 1.0 equiv.), the crude reaction mixture was purified by silica gel column chromatography (5 % to 20 % diethyl ether/hexanes) to afford the desired carbazole **8** as pale yellow oil (33.6 mg, 63 %). The NMR data obtained for carbazole **8** were in agreement with that

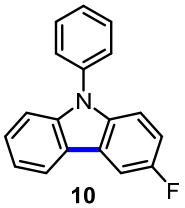
[8] Yoo, W. J.; Tsukamoto, T.; Kobayashi, S. *J. Org. Chem.* **2015**, 17, 3640-3642.
[9] Jones, A. W.; Louillat-Habermeyer, M.-L.; Patureau, F. W. *Adv. Synth. Catal.* **2015**, *357*, 945.

found in the literature.[10]



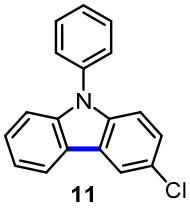
9

5-Phenylpyrimido[5,4-b]indole (9): Following the representative procedure **A** using continuous-flow with *N*,*N*-diphenylpyrimidin-5-amine (40 mg, 0.16 mmol, 1.0 equiv.), the crude reaction mixture was purified by silica gel column chromatography (30 % ethyl acetate/hexanes to 100 % ethyl acetate) to afford the desired carbazole **9** as an off-white solid (36.0 mg, 91 %). The NMR data obtained for carbazole **9** were in agreement with that found in the literature.[2]



10

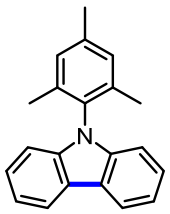
3-fluoro-9-phenylcarbazole (10): Following the general procedure **A** using continuous-flow with 4-fluoro-*N*,*N*-diphenylaniline (42.1 mg, 0.16 mmol, 1.0 equiv.), the crude reaction mixture was purified by silica gel column chromatography (100 % hexanes) to afford the desired carbazole **10** as a colorless oil (31.8 mg, 76 %) in a 7:93 ratio for the "endo" product 3-fluoro-9-phenylcarbazole. The NMR data obtained for carbazole **10** were in agreement with that found in the literature.[3]



11

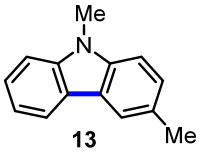
3-chloro-9-phenylcarbazole (11): Following the representative procedure **A** using continuous-flow with 4-chloro-*N*,*N*-diphenylaniline (44.8 mg, 0.16 mmol, 1.0 equiv.), the crude reaction mixture was purified by silica gel column chromatography (100 % hexanes) to afford the desired carbazole **11** as an colorless oil (38.7 mg, 87 %) in a 5:95 ratio for the "endo" product 3-chloro-9-phenylcarbazole. The NMR data obtained for carbazole **11** were in agreement with that found in the literature.[3]

[10] Nozaki, K,; Takahashi, K.; Nakano, K.; Hiyama, T.; Tang, H.-Z.; Fujiki, M.; Yamaguchi, S.; Tamao, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 4051.



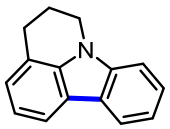
12

9-Mesitylcarbazole (12): Following the representative procedure **A** using continuous-flow with 2,4,6-Trimethyl-*N*,*N*-diphenylaniline (46.0 mg, 0.16 mmol, 1.0 equiv.), the crude reaction mixture was purified by silica gel column chromatography (100 % hexanes to 5 % diethyl ether/hexanes) to afford the desired carbazole **10** as an off-white solid (35.2 mg, 77 %). The NMR data obtained for carbazole **10** were in agreement with that found in the literature.[2]



13

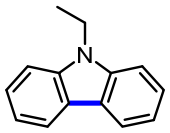
3,9-Dimethylcarbazole (13): Following the general procedure **A** using continuous-flow with *N*-(4-methylphenyl)-*N*-methylaniline (31.6 mg, 0.16 mmol, 1.0 equiv.), the crude reaction mixture was purified by silica gel column chromatography (100 % hexanes to 5 % diethyl ether/hexanes) to afford the desired alkyl carbazole **11** as a white solid (25.0 mg, 80 %). The NMR data obtained for carbazole **11** were in agreement with that found in the literature.[11]



14

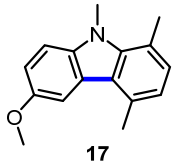
5,6-Dihydro-4H-pyrido[3,2,1-jk]carbazole (14): Following the general procedure **A** using continuous-flow with 1-phenyl-1,2,3,4-tetrahydroquinoline (33.6 mg, 0.16 mmol, 1.0 equiv.), the crude reaction mixture was purified by silica gel column chromatography (100 % hexanes to 5 % diethyl ether/hexanes) to afford the desired carbazole **14** as an off-white solid (22.2 mg, 67%). The NMR data obtained for carbazole **14** were in agreement with that found in the literature.[12]

[11] Han, X.; Lu, X. *Org. Lett.* **2009**, *11*, 2381.
[12] Markgraf, J. H.; Finkelstein, M.; Cort, J. R. *Tetrahedron* **1996**, *52*, 461.



15

9-Ethyl-carbazole (15): Following the general procedure **A** using continuous-flow with *N*-ethyl-*N*-phenylaniline (31.6 mg, 0.16 mmol, 1.0 equiv.), the crude reaction mixture was purified by silica gel column chromatography (100 % hexanes to 5 % diethyl ether/hexanes) to afford the desired carbazole **15** as a white solid (25.0 mg, 80 %). The NMR data obtained for carbazole **15** were in agreement with that found in the literature.[13]



17

6-Methoxy-1,4,9-trimethylcarbazole (17): Following the general procedure **B** using continuous-flow with amine **S5** (268 mg, 1.0 mmol, 1.0 equiv.), the crude reaction mixture was purified by silica gel column chromatography (5% diethyl ether/hexanes) to afford the desired product **17** as a white solid (129 mg, 54 %).^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.73 (d, *J* = 2.5 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.14 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.07 (d, *J* = 7.3 Hz, 1H), 6.87 (d, *J* = 7.3 Hz, 1H), 4.09 (s, 3H), 3.96 (s, 3H), 2.86 (s, 3H), 2.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 153.30, 140.32, 136.92, 131.15, 128.53, 123.88, 121.72, 120.19, 117.75, 113.17, 108.71, 106.48, 56.23, 32.40, 20.78, 20.32; HRMS (ESI) m/z calculated for $C_{16}H_{17}NO$ $[M+H]^+$, 240.1372; found: 240.1383.

[13] Lin, J.; Chen, J.; Su, W. *Adv. Synth. Catal.* **2013**, *355*, 41.

UV-VIS SPECTRA

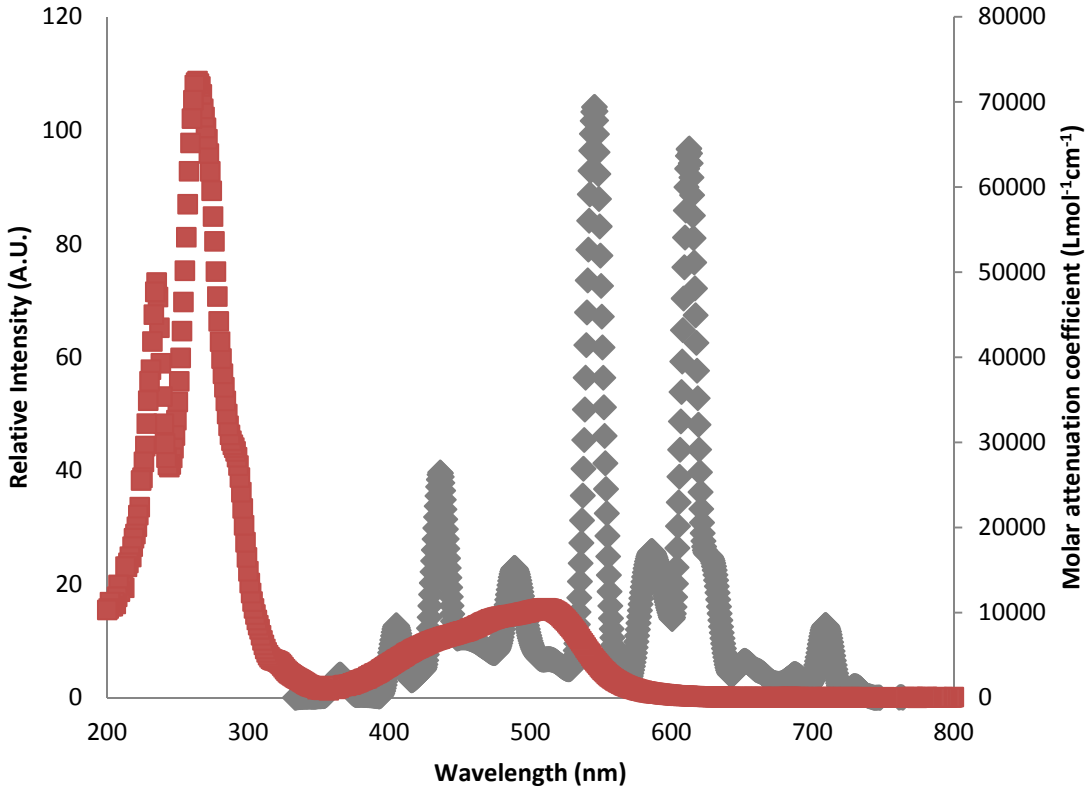
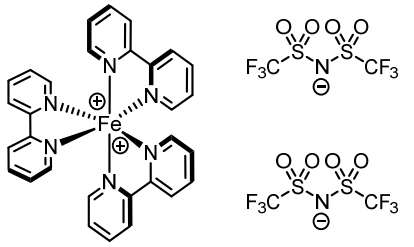
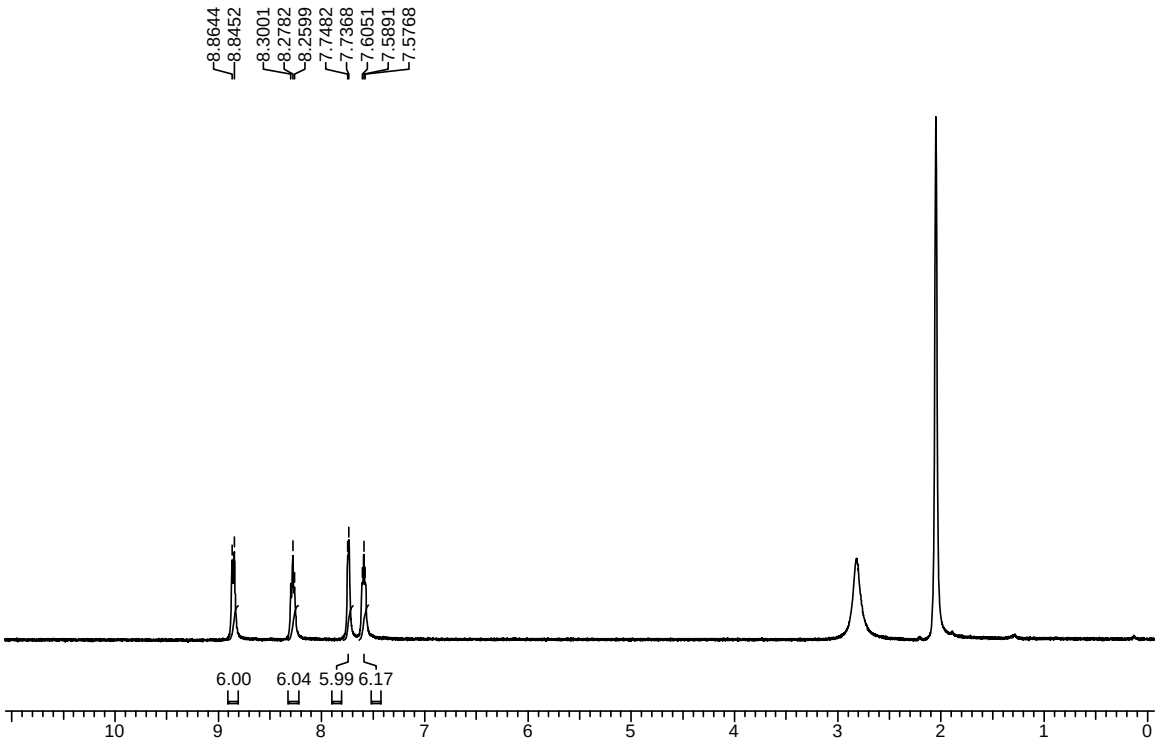


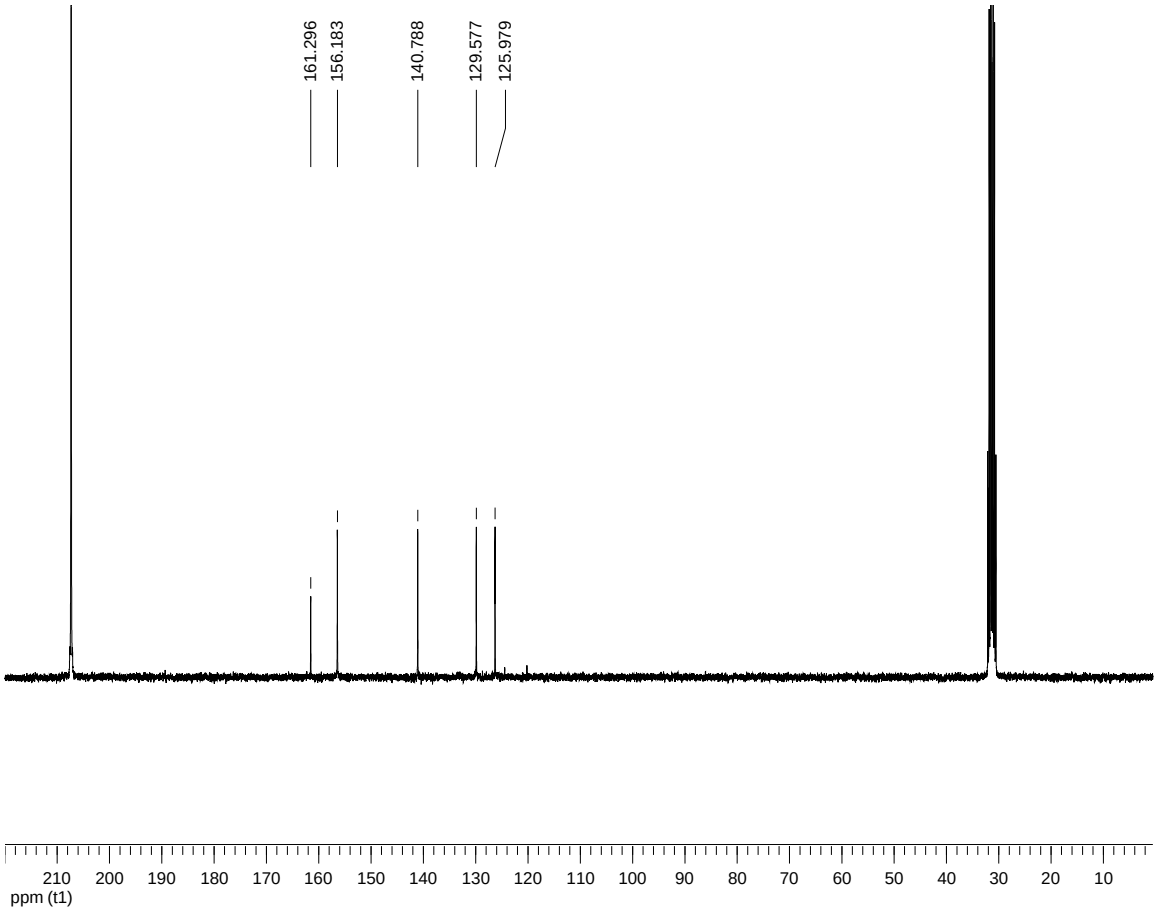
Figure S3. Absorption spectra of **3** $[Fe(phen)_3](NTf_2)_2$ 5 $x10^{-5}$ M (red) and emission spectra for CFL blub light (grey).

NMR SPECTRAL DATA



S1

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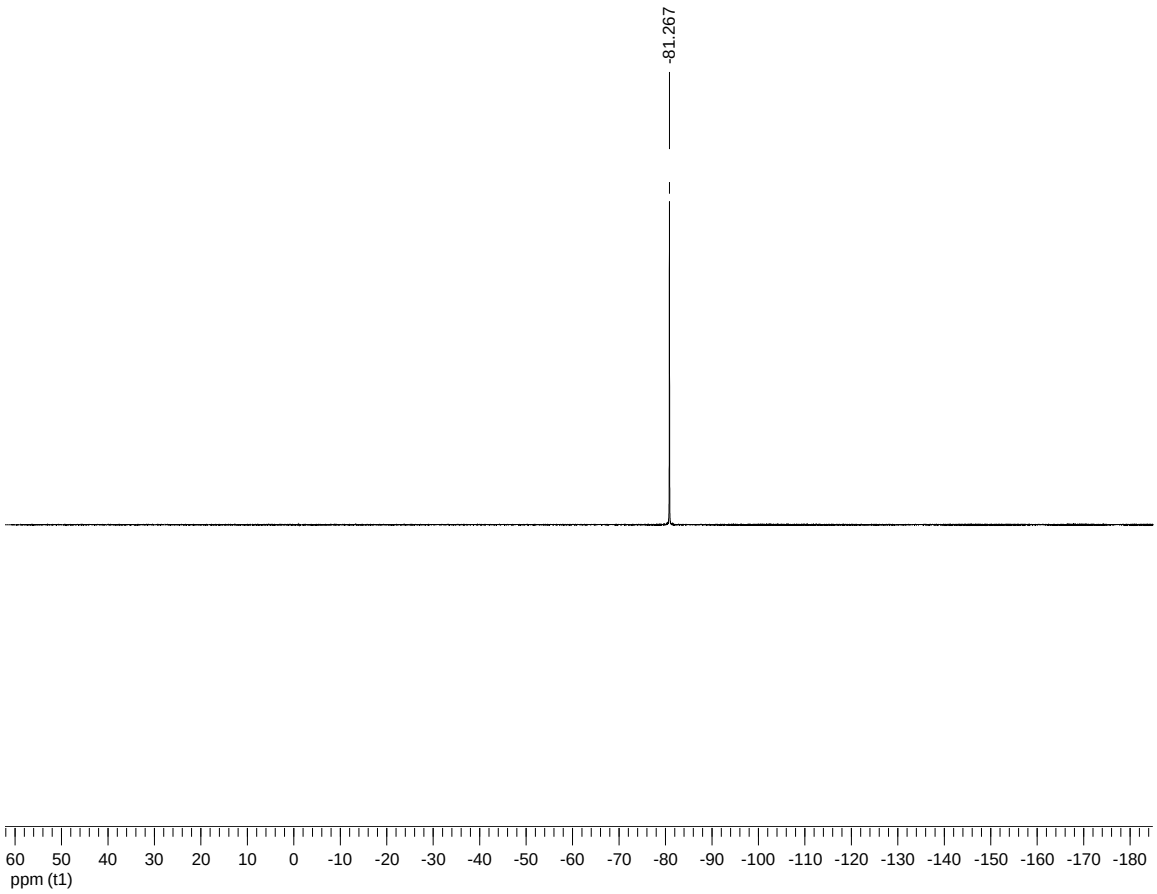
-81.267
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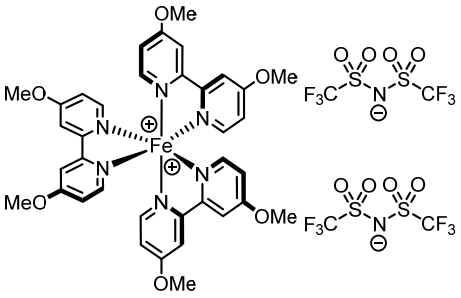
ppm (t1)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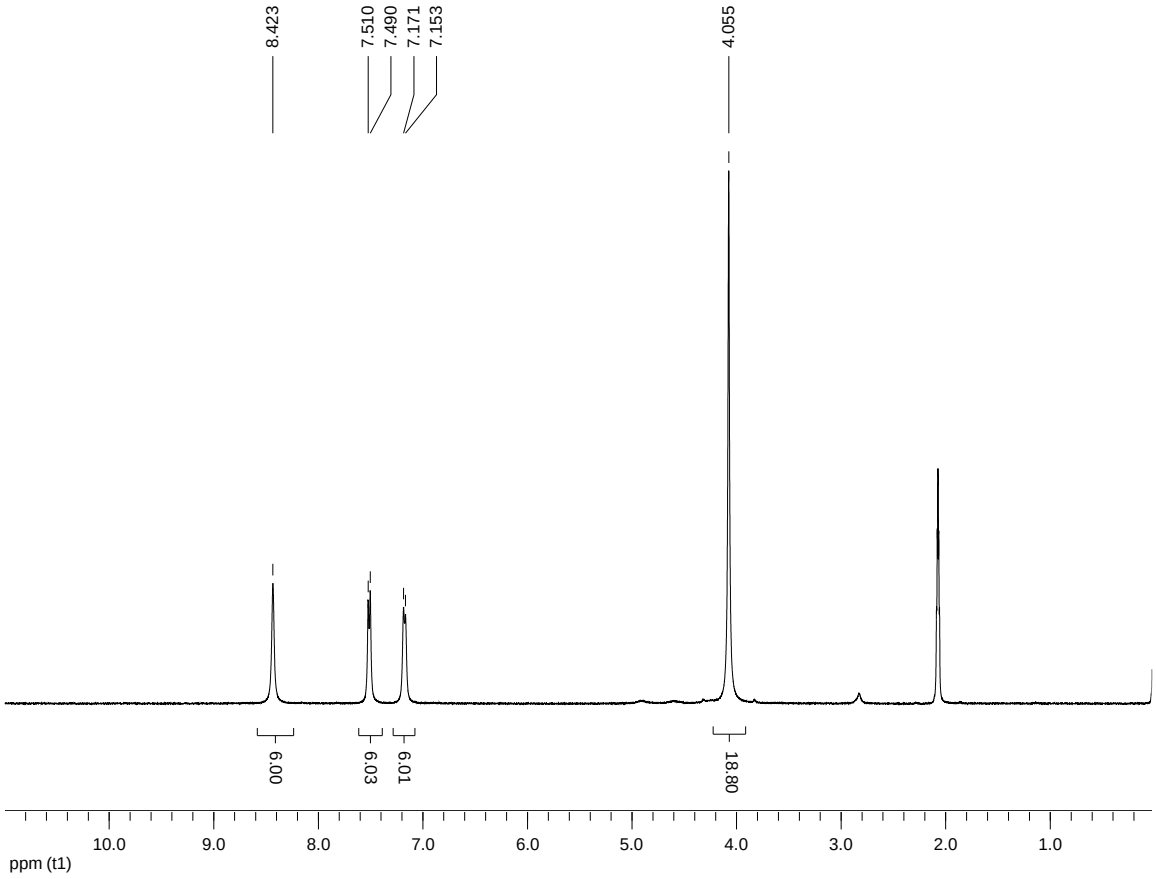
N
Fe
F3C
S
O
N
CF3

S2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7.490
7.171
7.153
4.055
6.00
6.03
6.01
18.80
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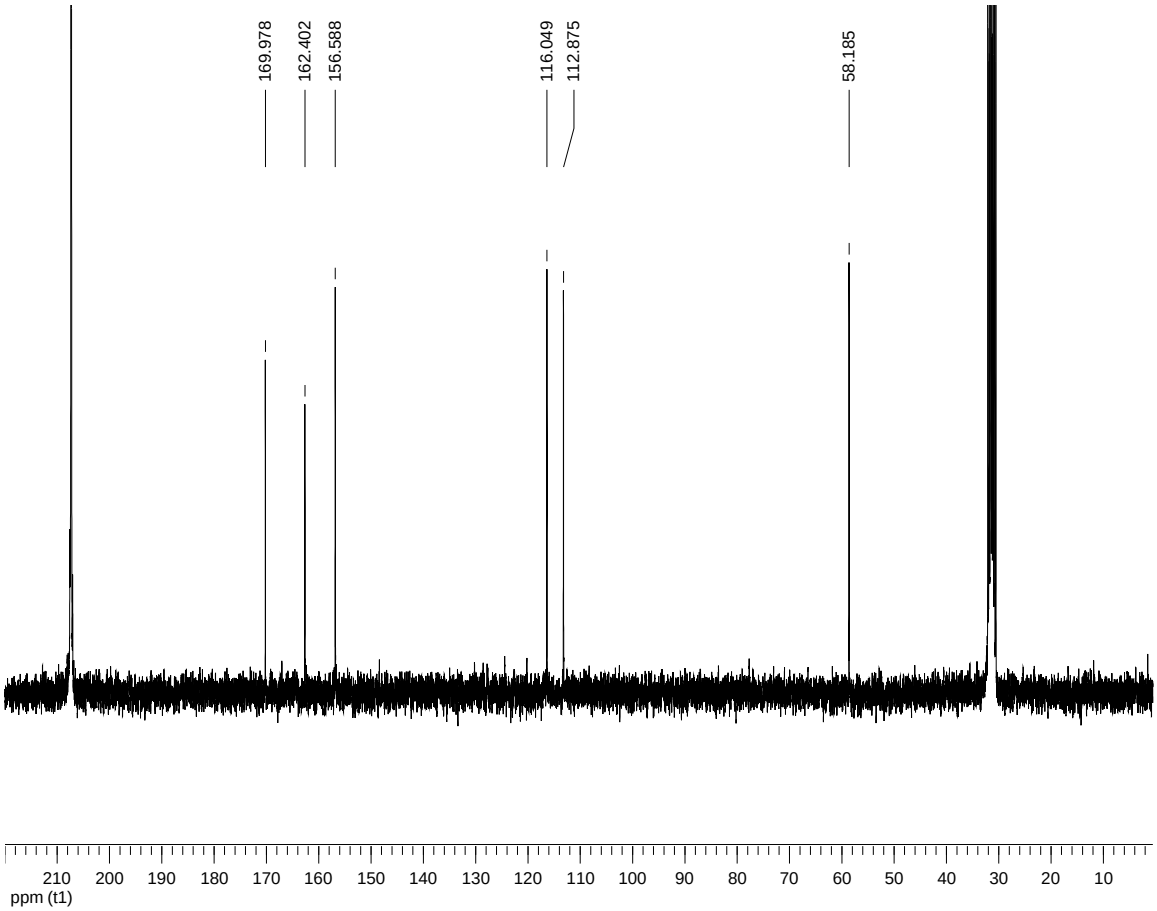
4.0
3.0
2.0
1.0
ppm (t1)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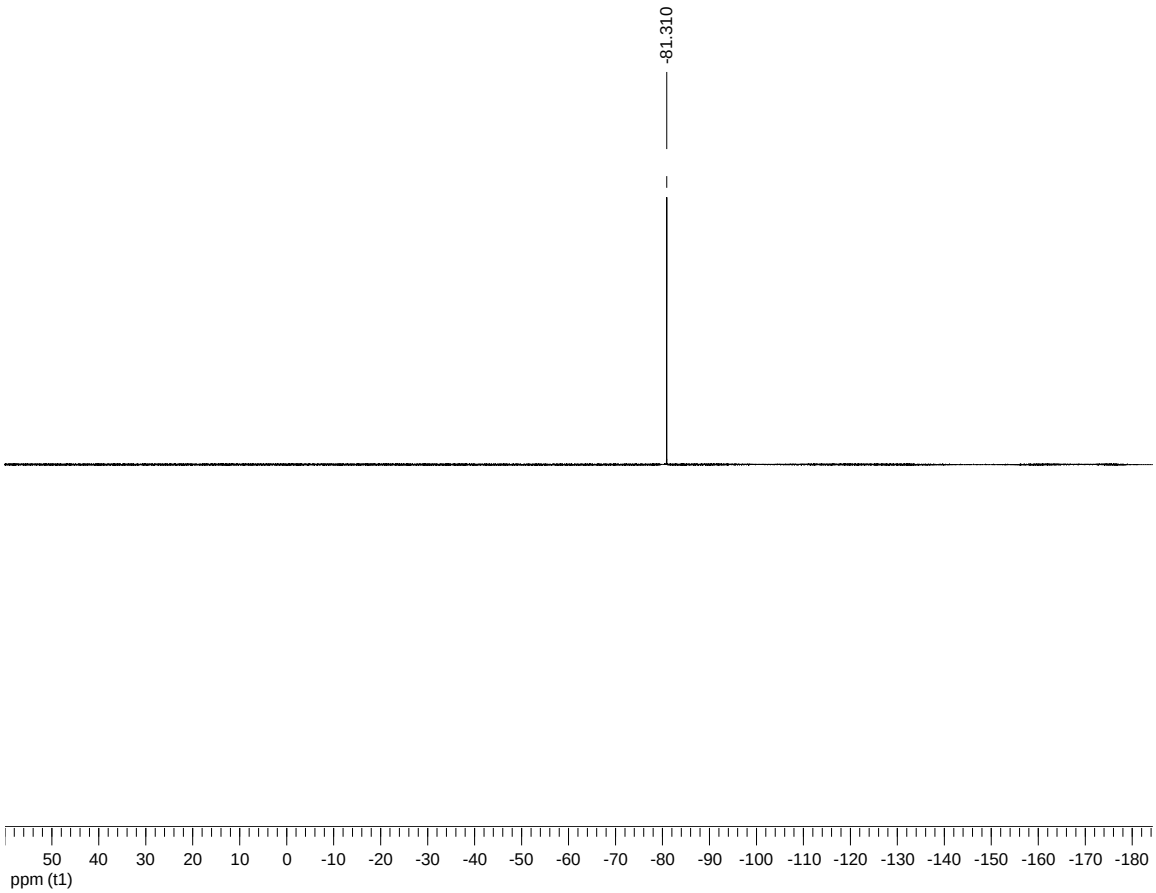
ppm (t1)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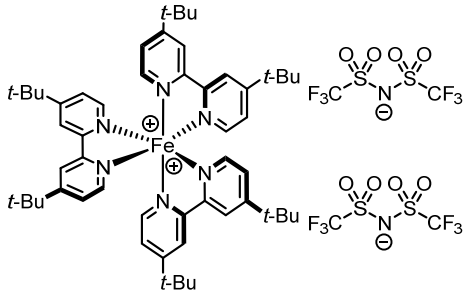
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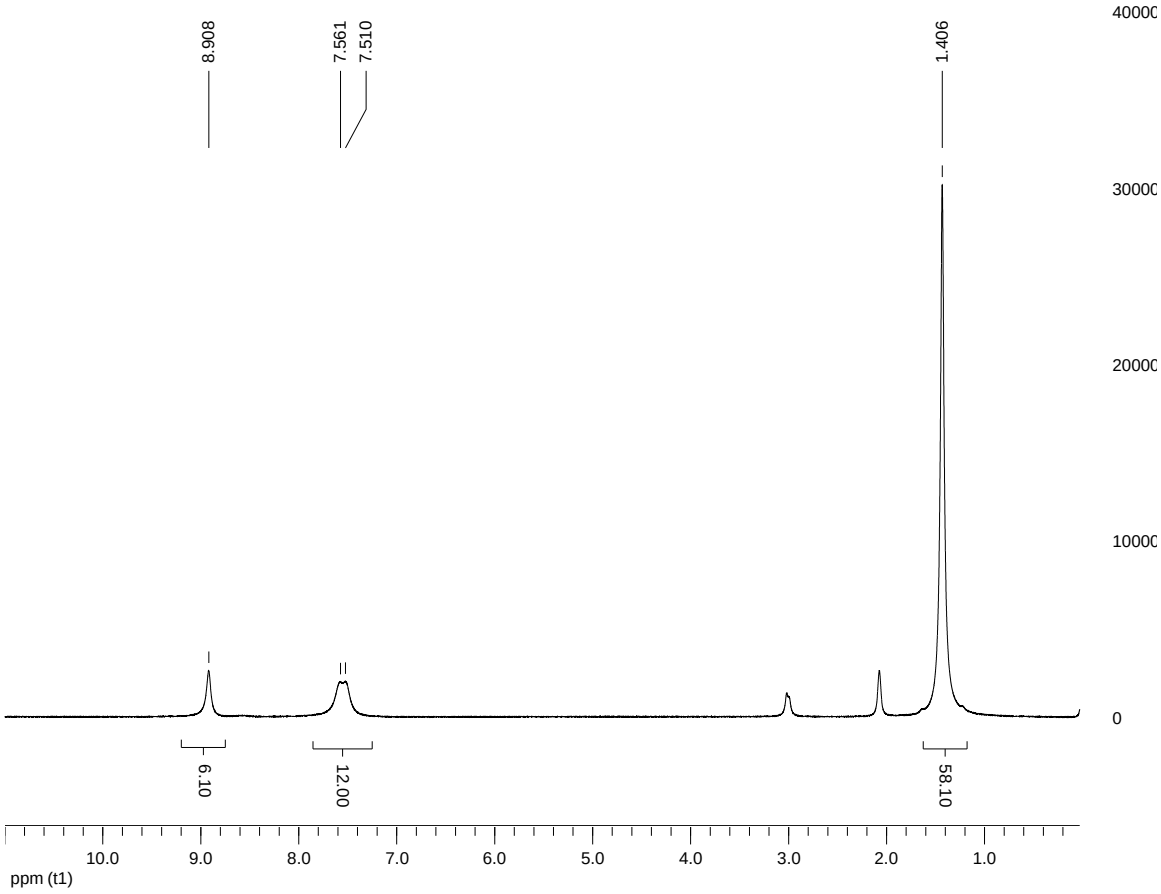
t-Bu
t-Bu
t-Bu
t-Bu
Fe
F3C
CF3
F3C
CF3

S3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1.406
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10.0
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8.0
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1.0
ppm (t1)
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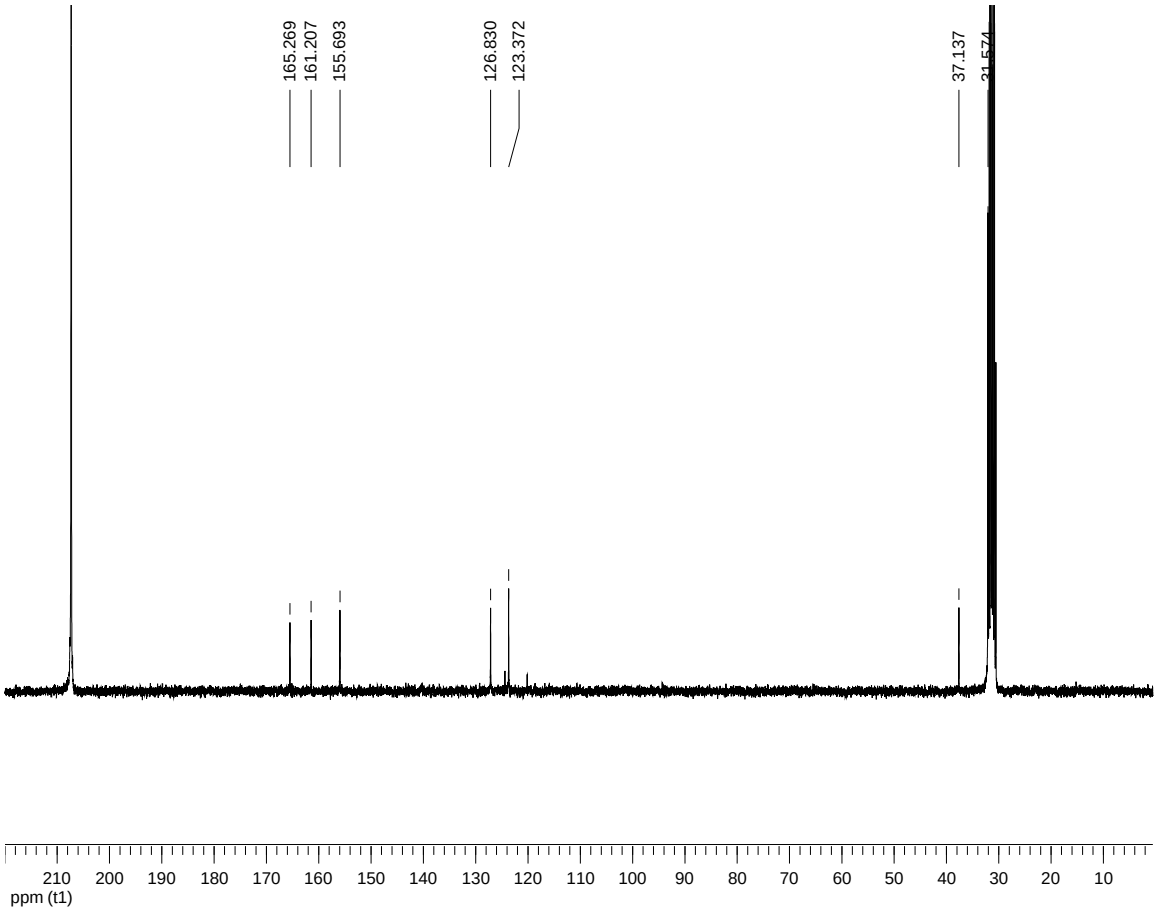
20000
10000
0


165.269
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123.372
37.137
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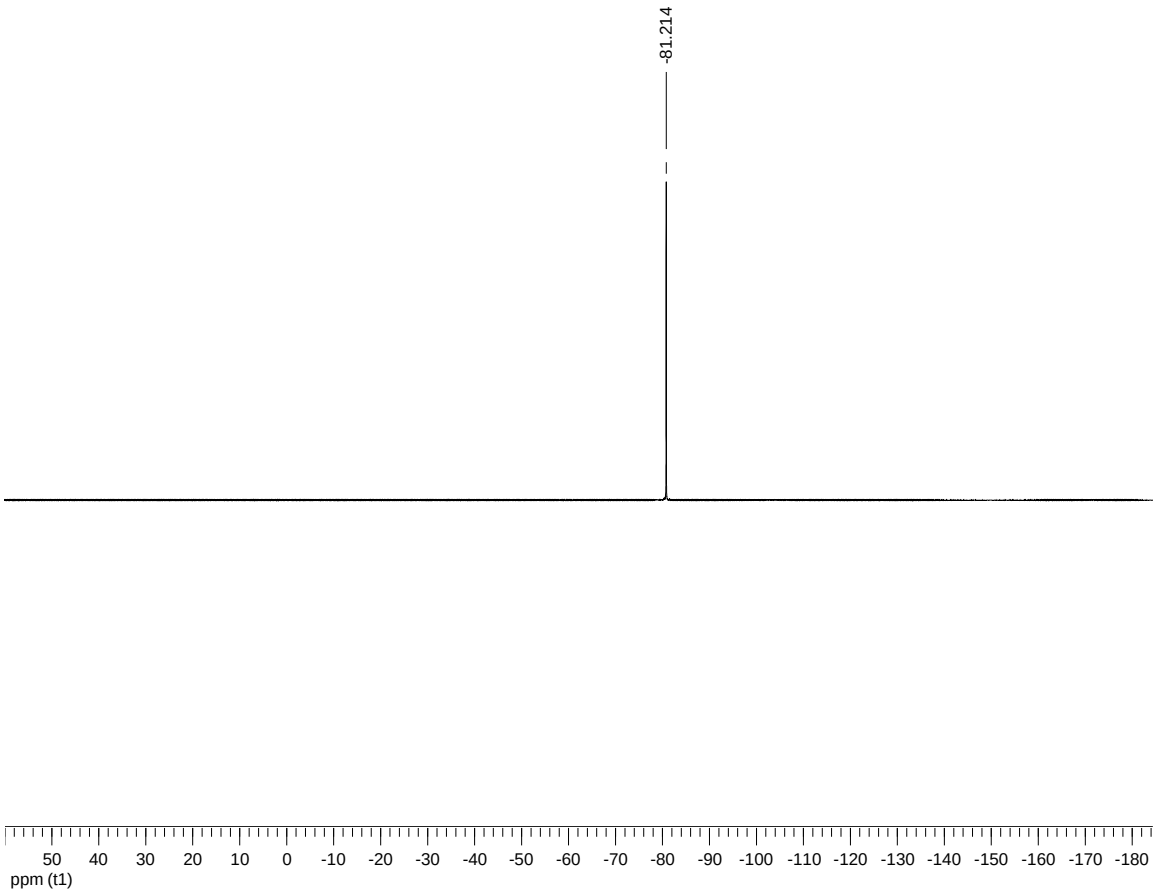
ppm (t1)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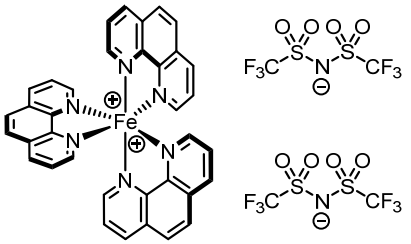
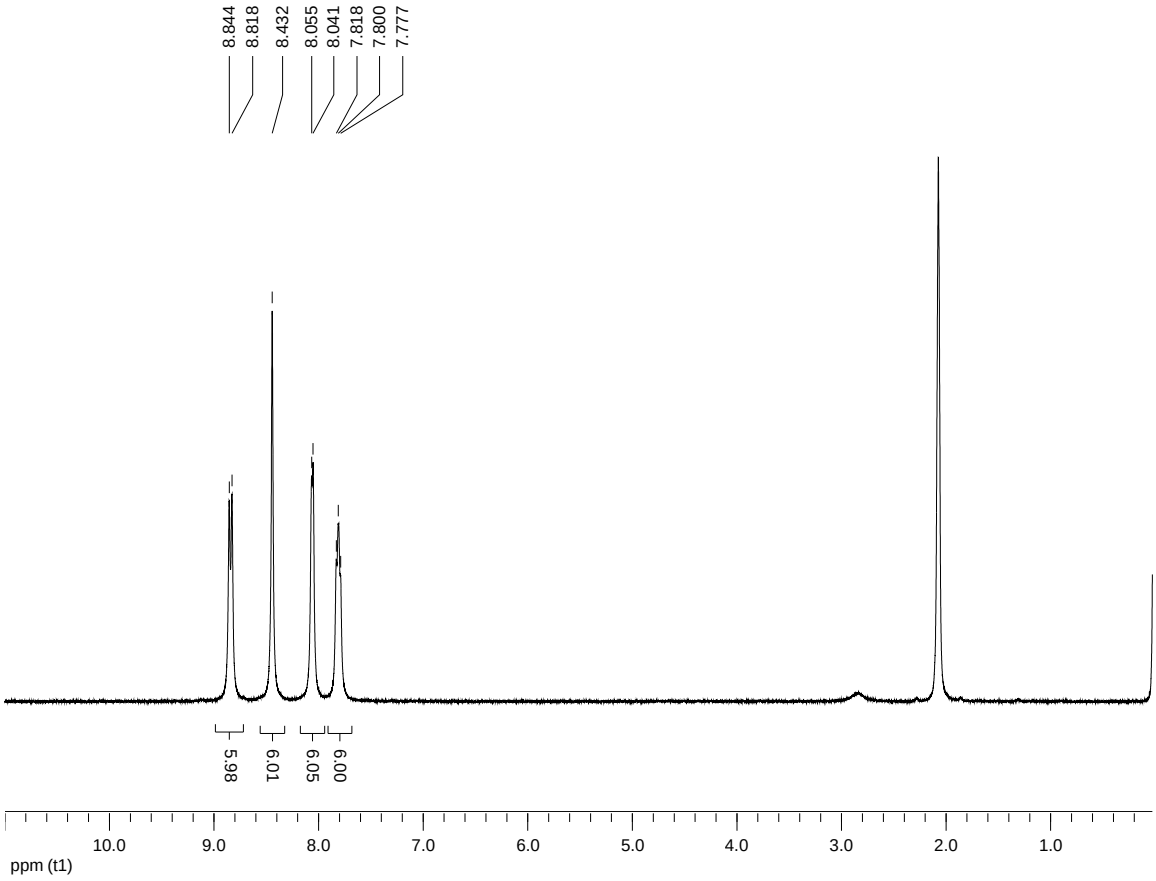


3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8.041
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7.777
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6.05
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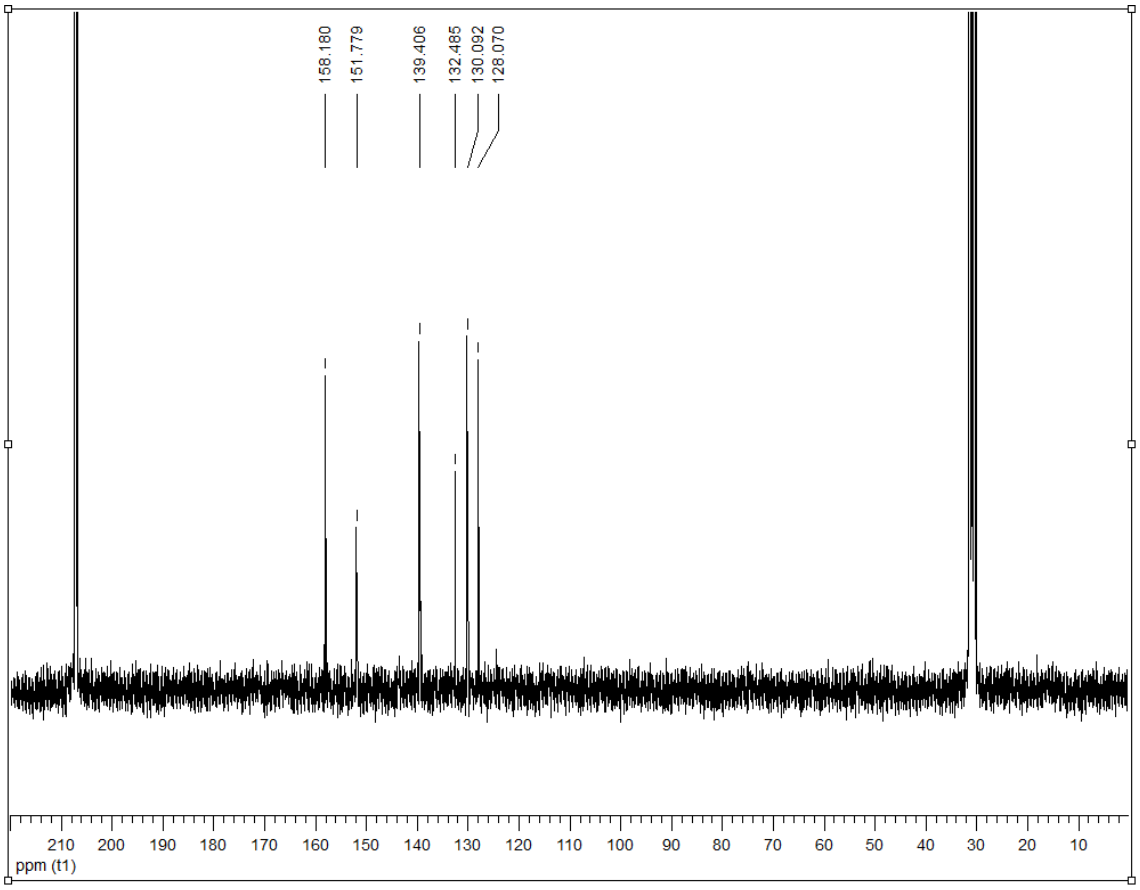
3.0
2.0
1.0
ppm (t1)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128.070
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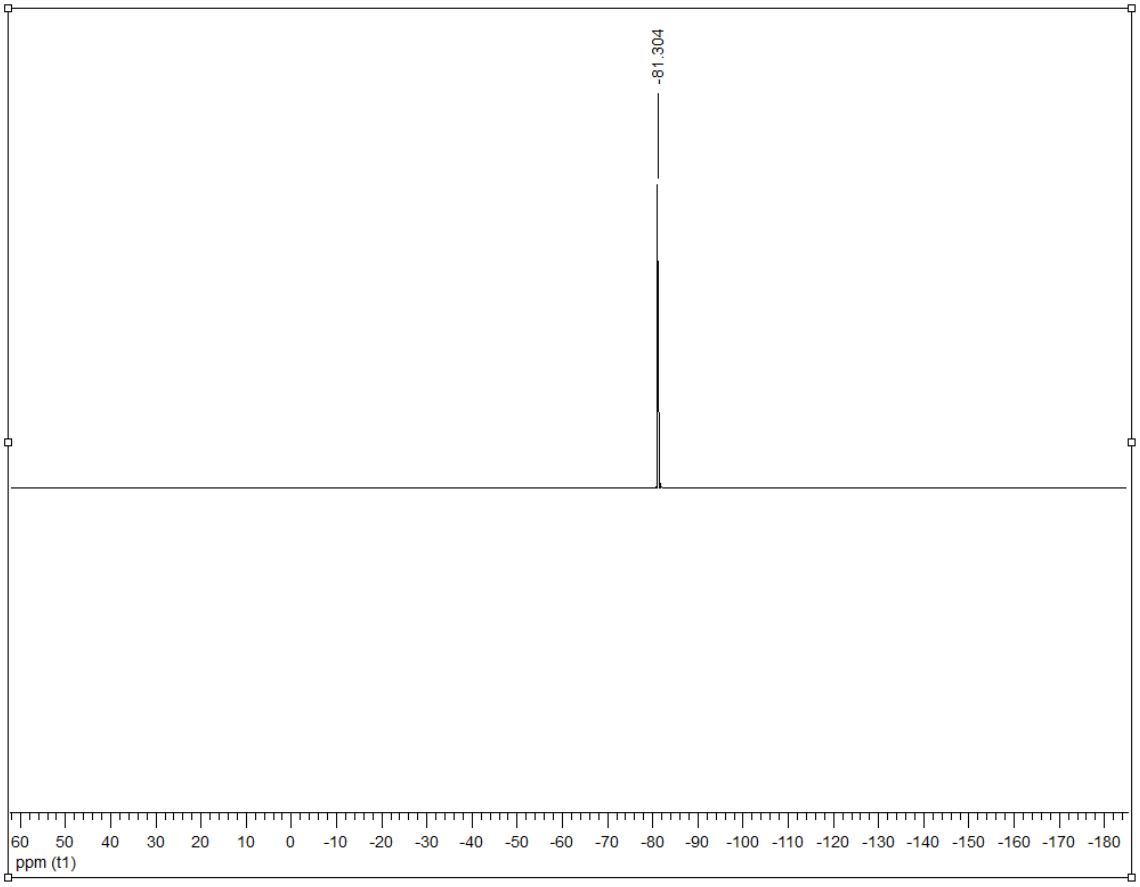
ppm (t1)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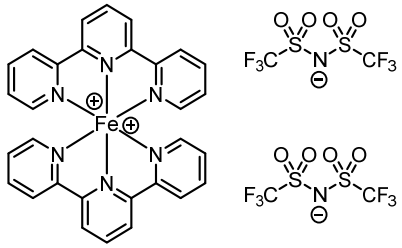
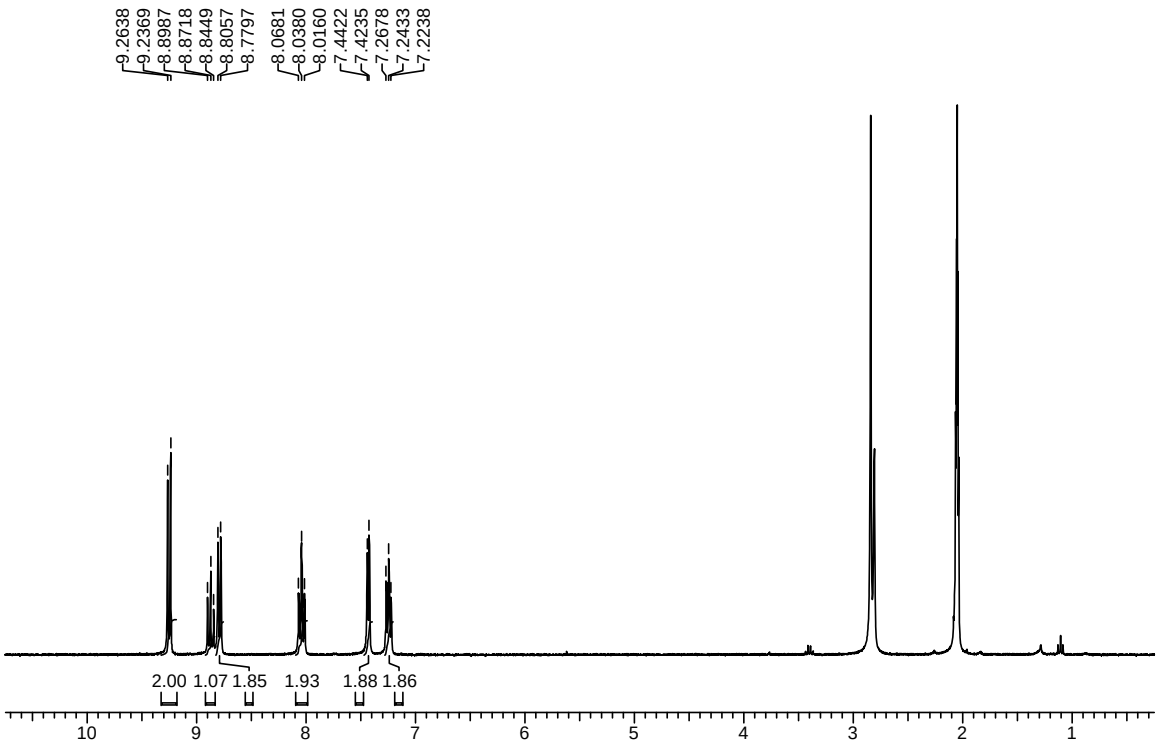
ppm (t1)



S4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8.8057
8.7797
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7.2678
7.2433
7.2238
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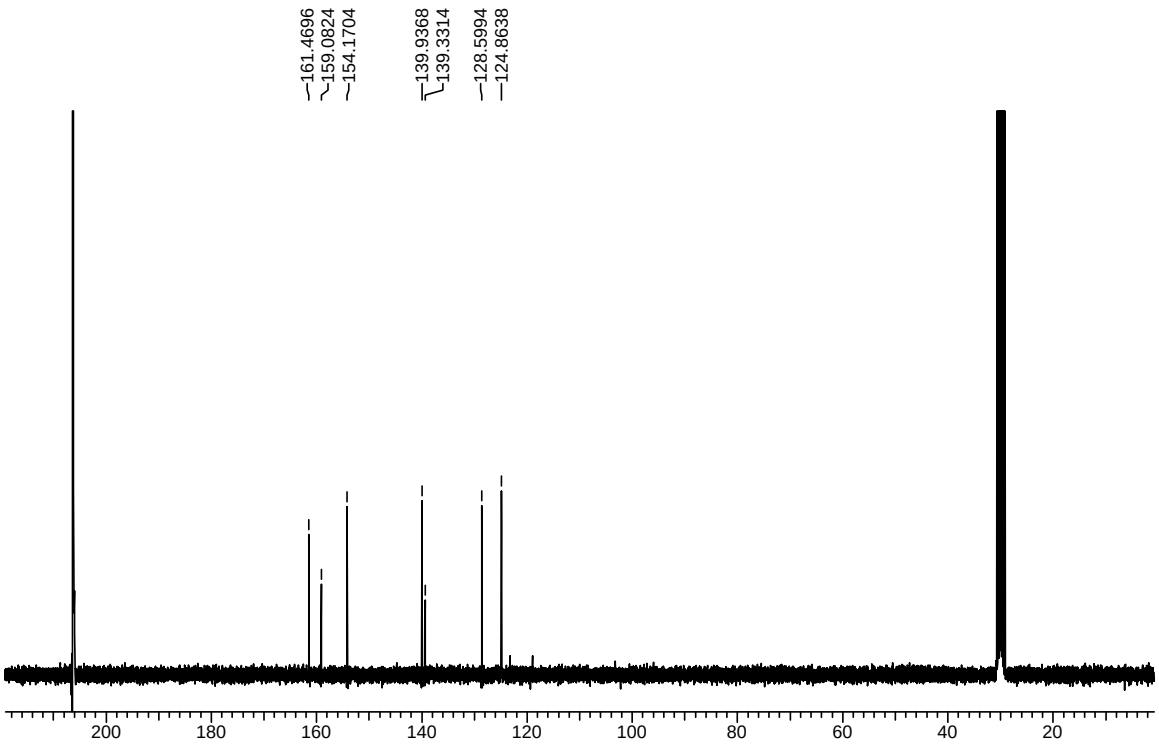
10 9 8 7 6 5 4 3 2 1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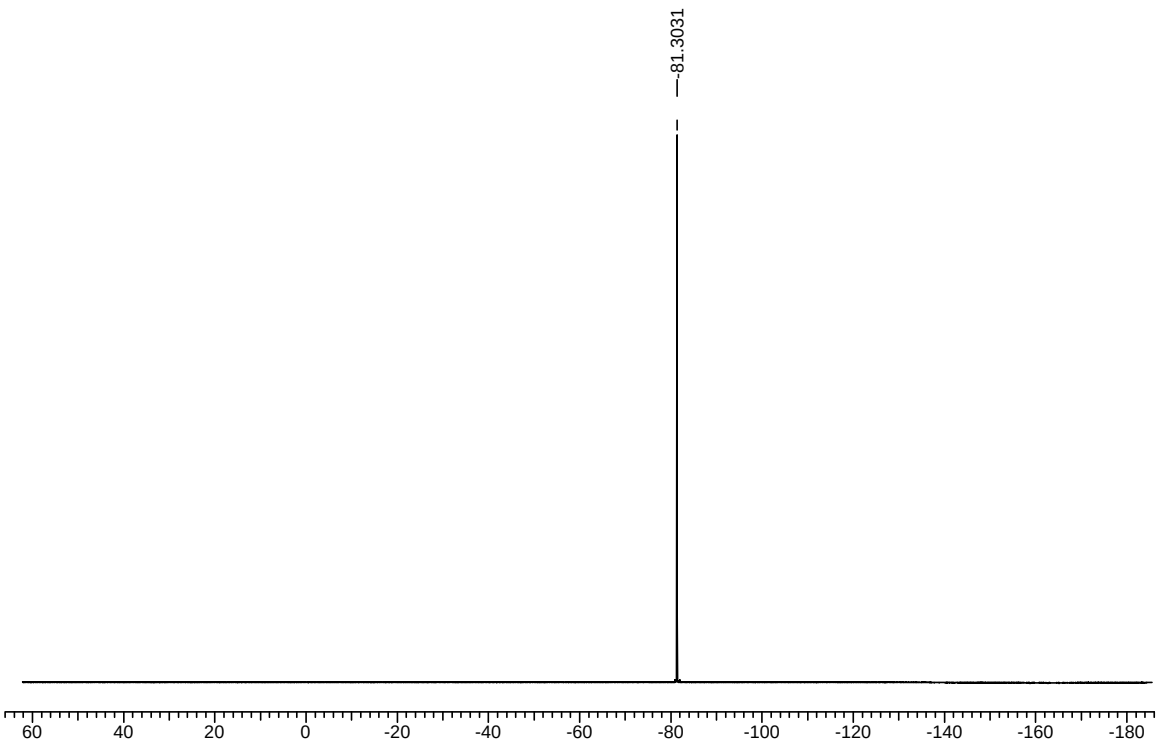
60
40
20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-160
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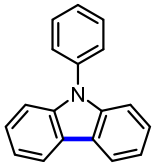

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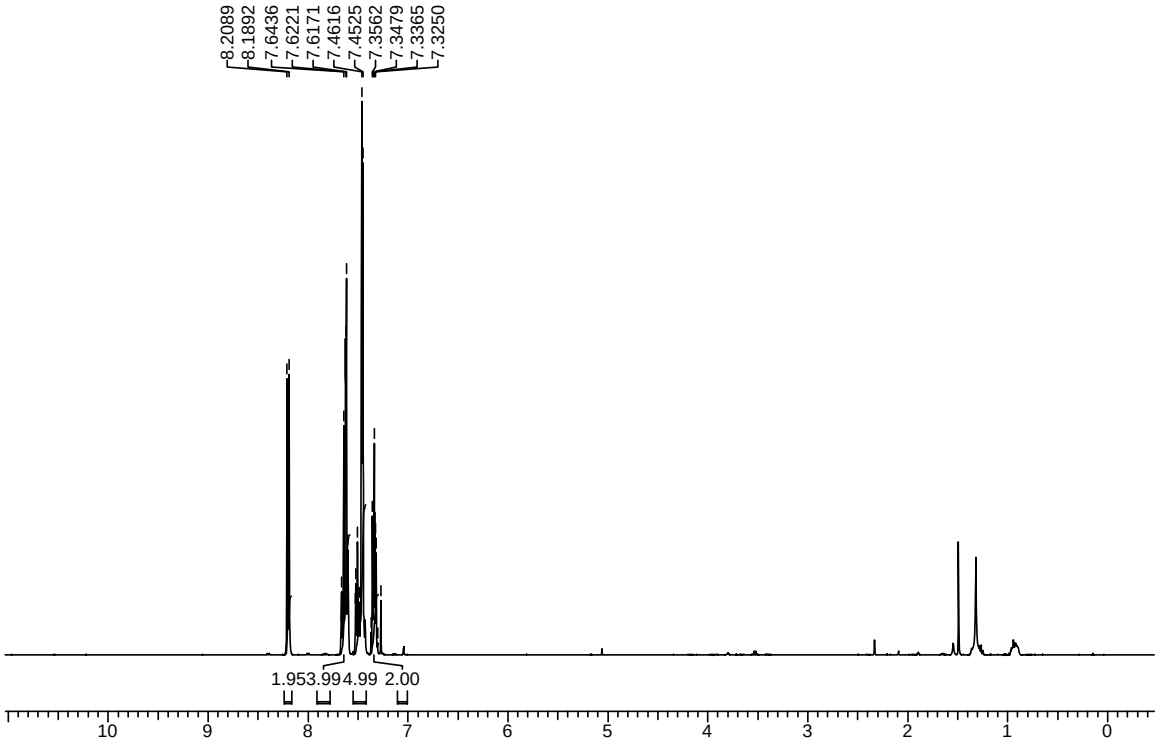
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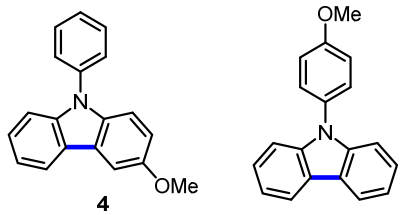
9
8
7
6
5
4
3
2
1
0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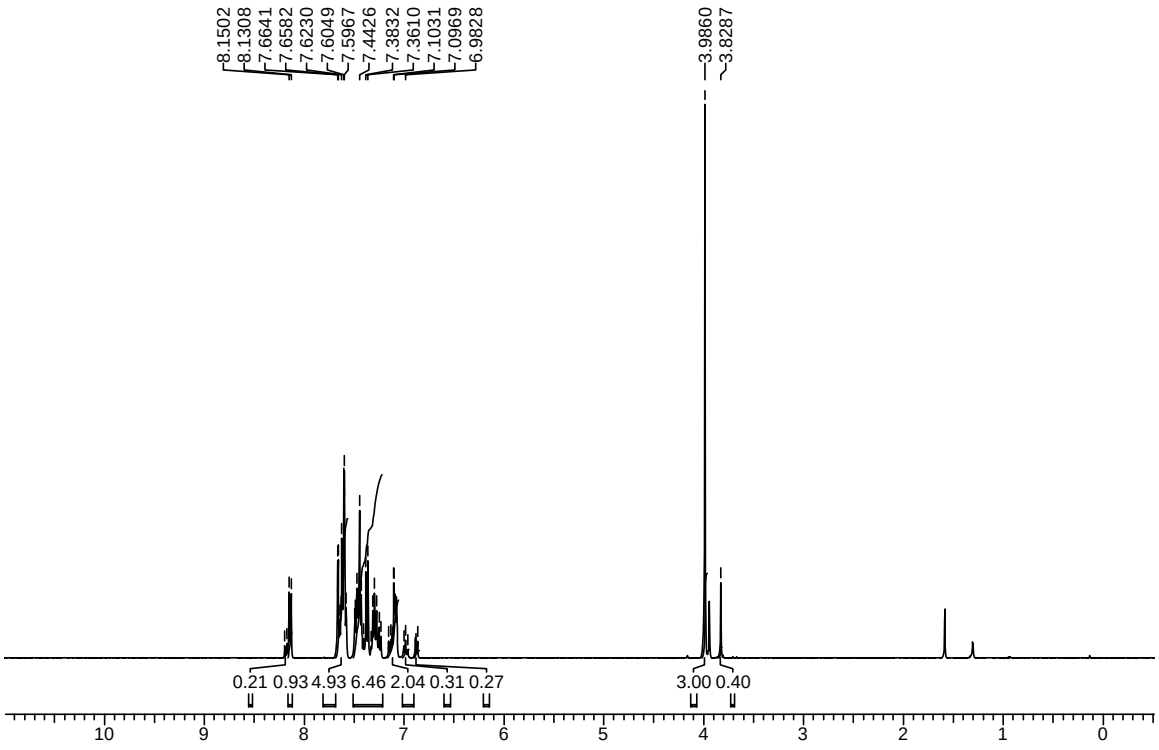
N
OMe

4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7.0969
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0.21 0.93 4.93 6.46 2.04 0.31 0.27
3.00 0.40
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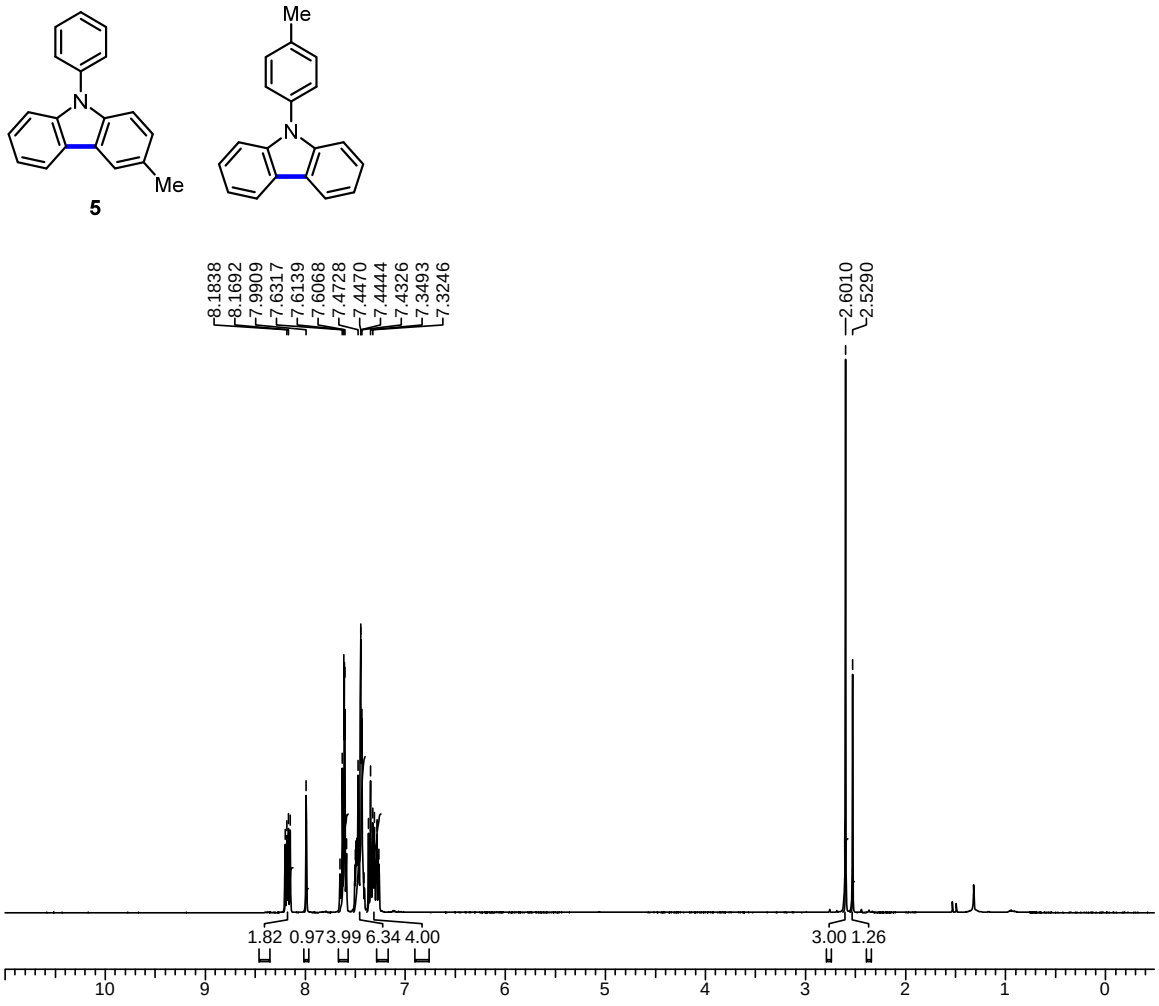
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Me
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7.4444
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7.3246
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2.5290
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7
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2
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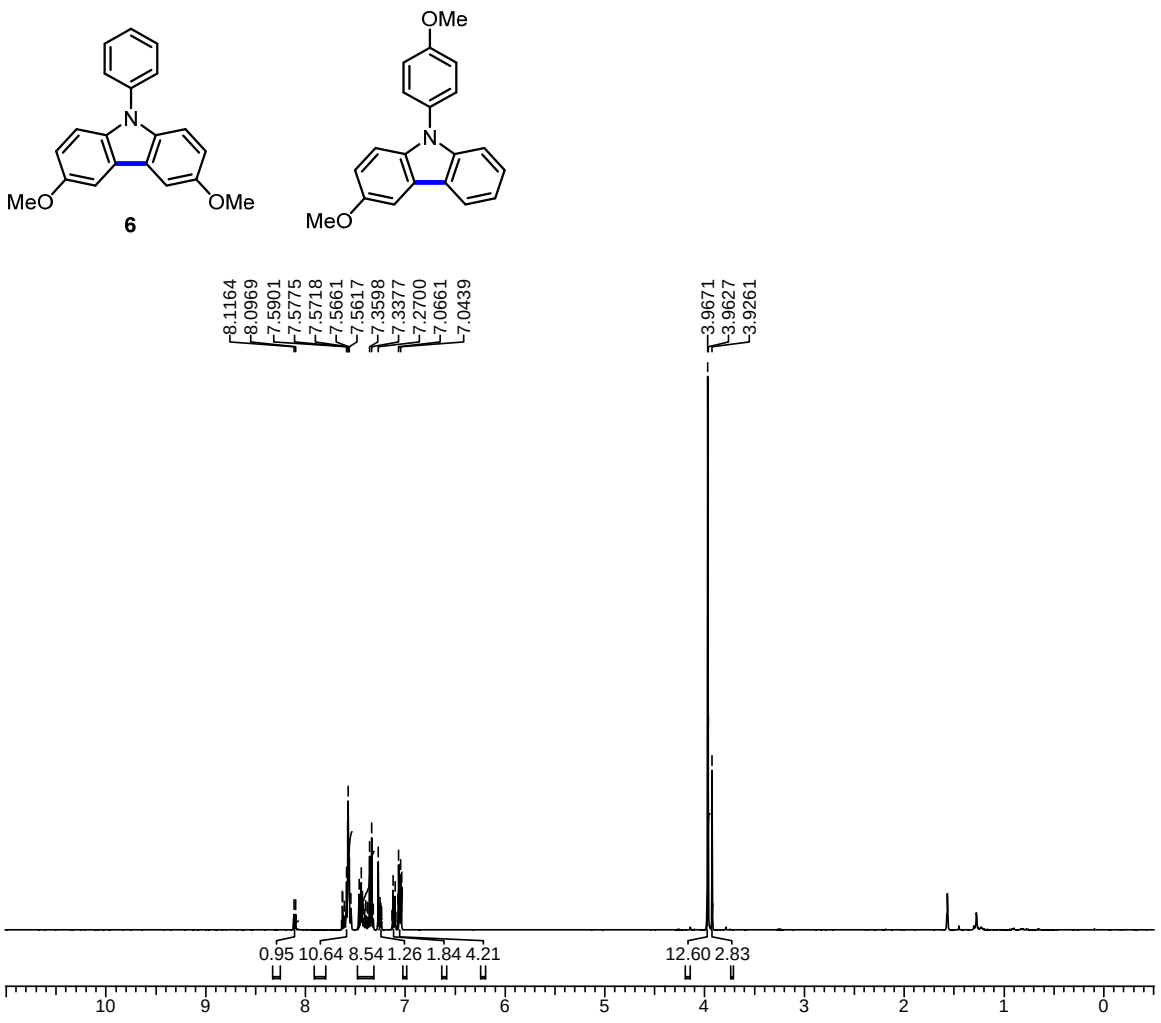
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7.3598
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7.0661
7.0439
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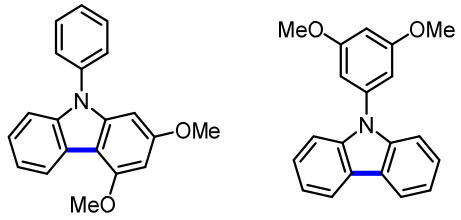
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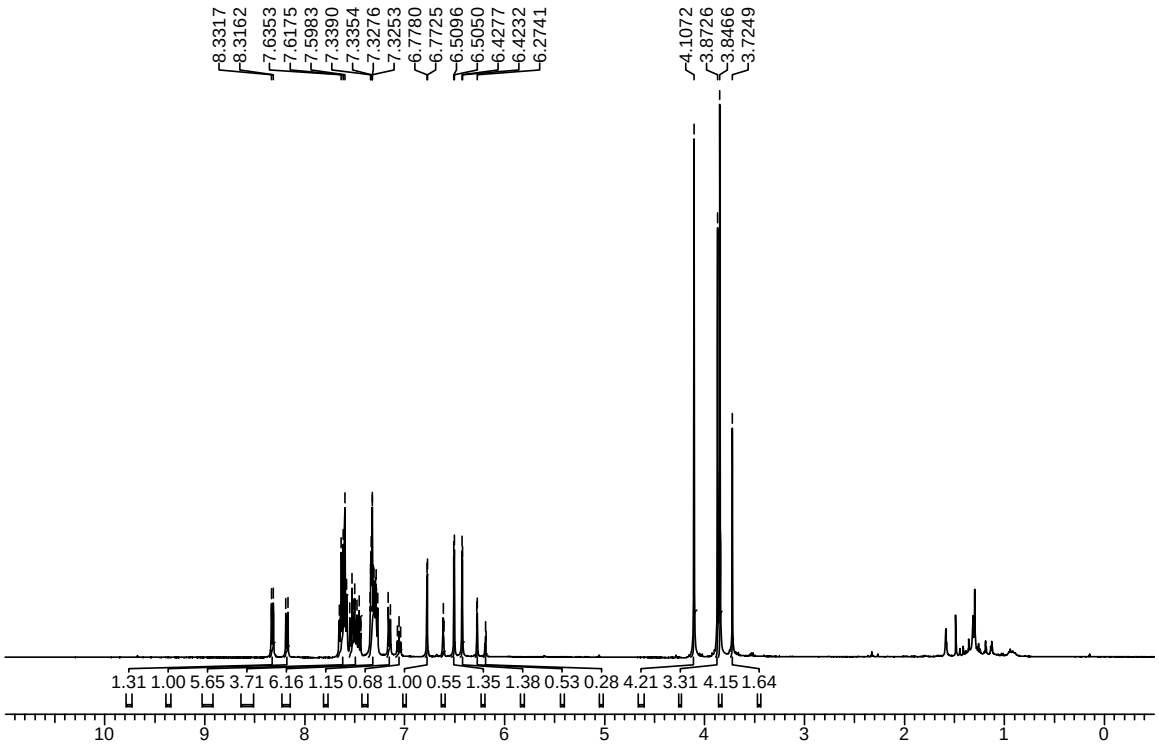
MeO
MeO
OMe
N

7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3.7249
1.31 1.00 5.65 3.71 6.16 1.15 0.68 1.00 0.55 1.35 1.38 0.53 0.28 4.21 3.31 4.15 1.64
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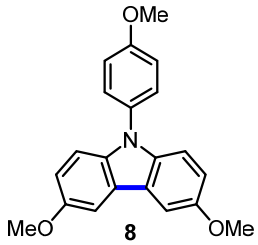
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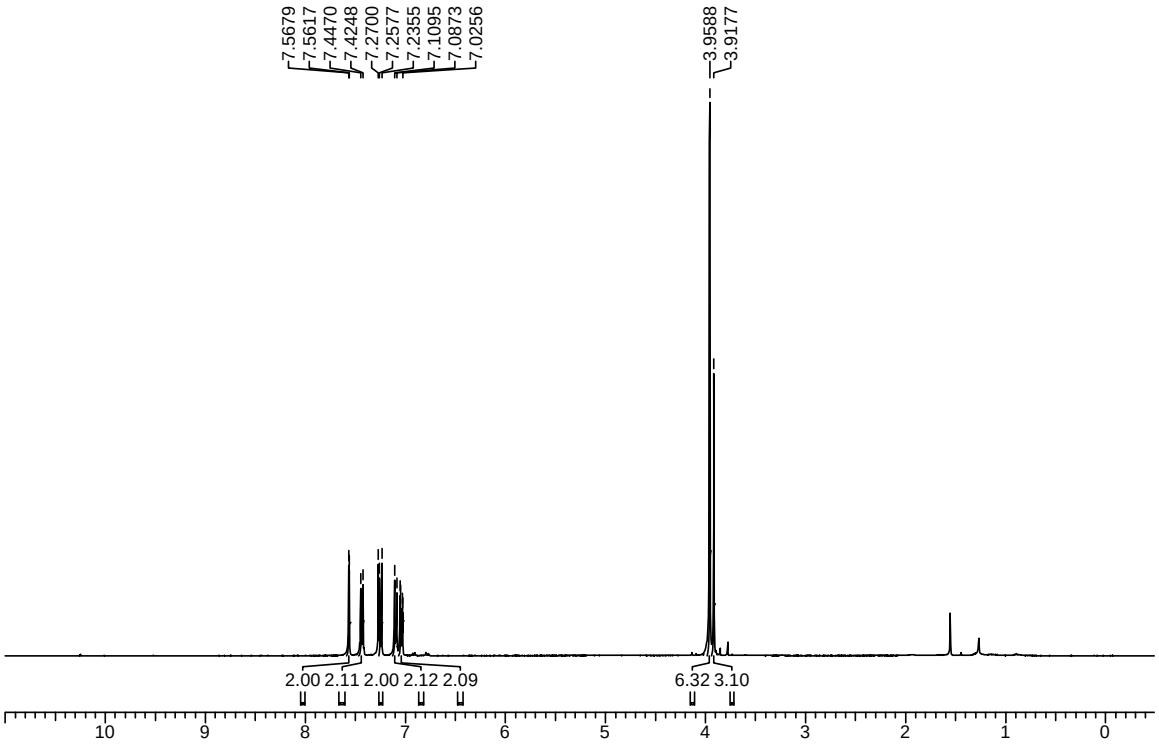
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6.32 3.10
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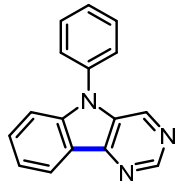

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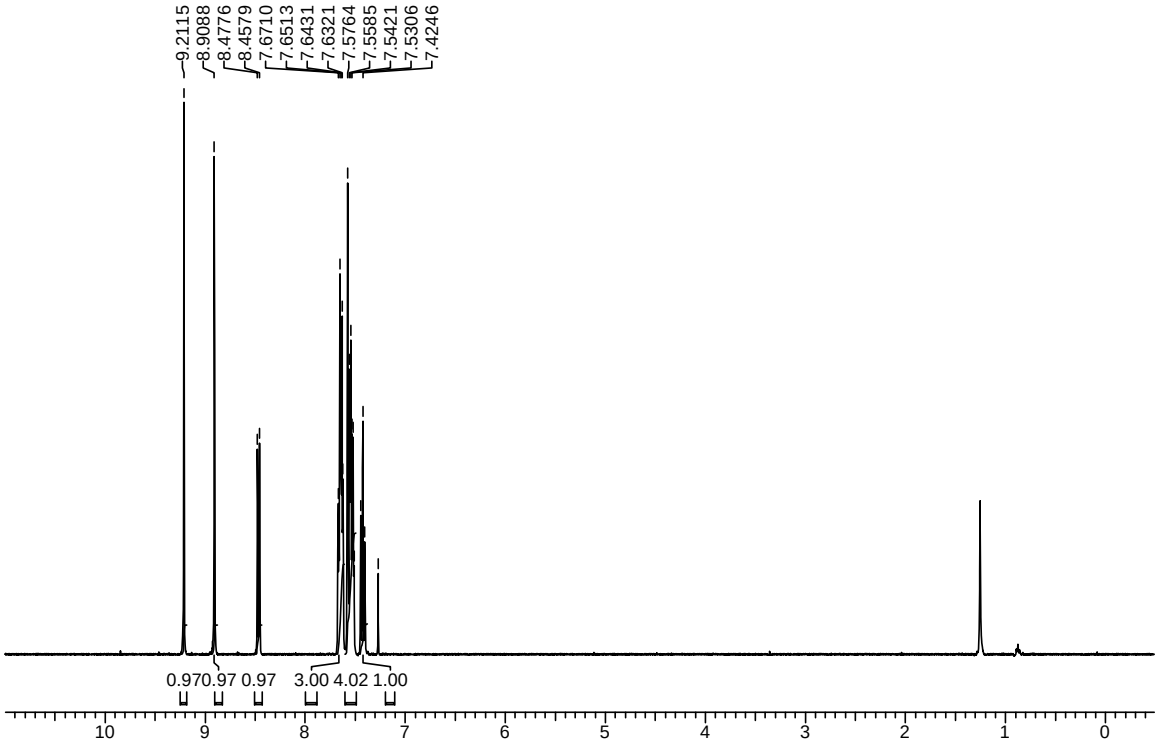
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7.5421
7.5306
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0.97 0.97 0.97 3.00 4.02 1.00
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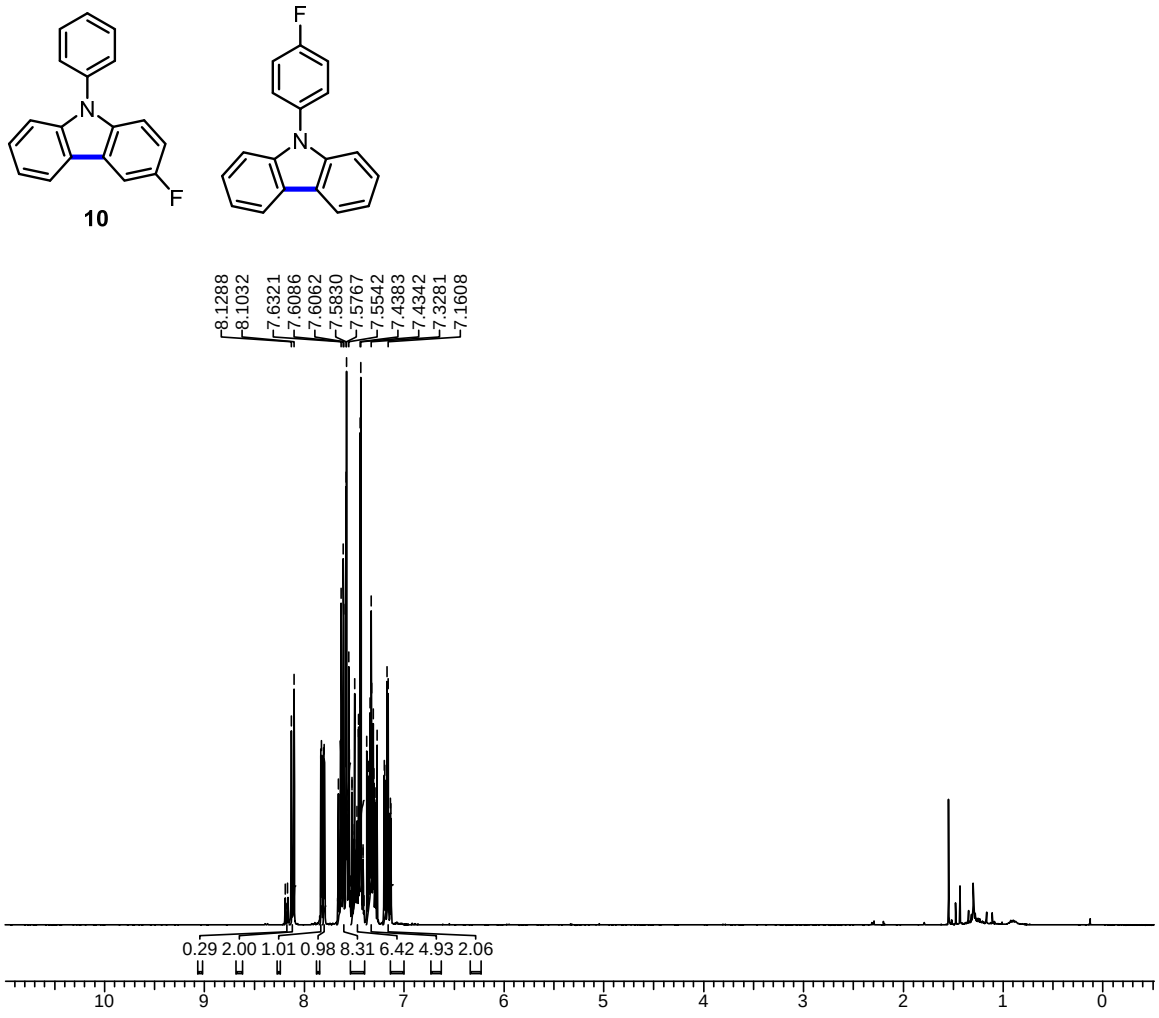
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F
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7.4342
7.3281
7.1608
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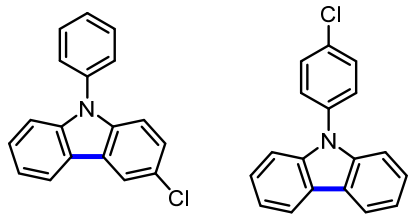
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Cl
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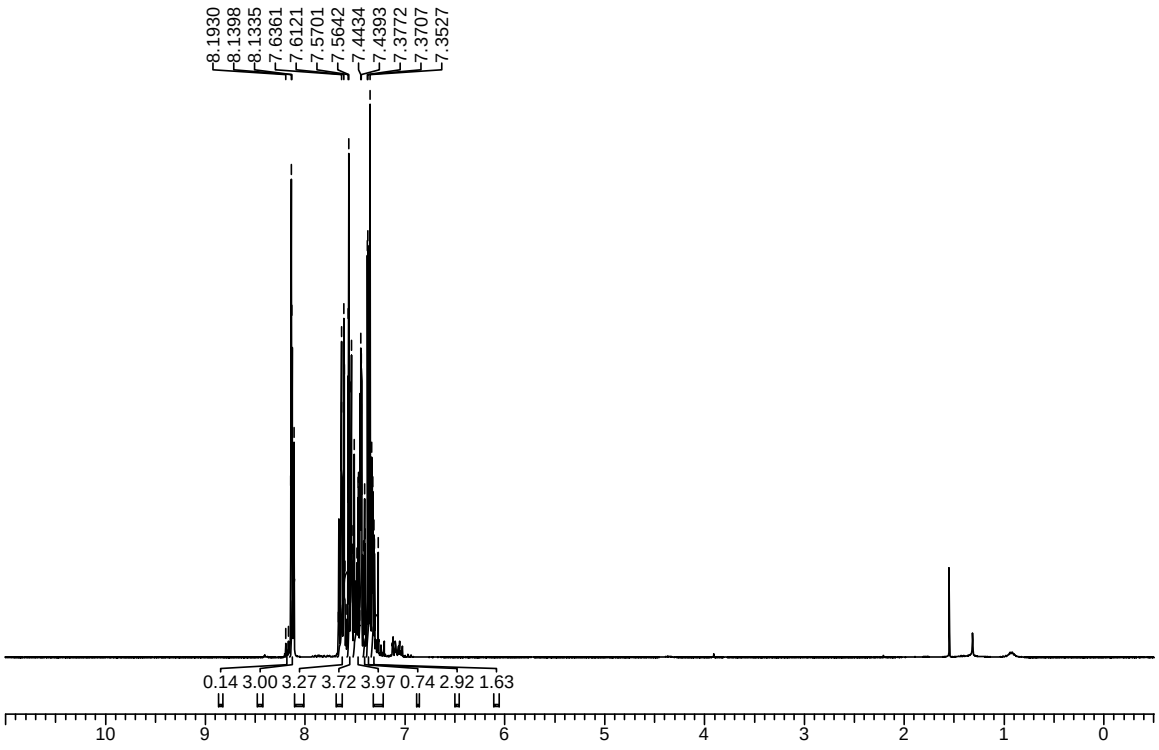
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7.3527
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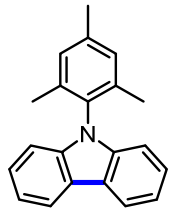

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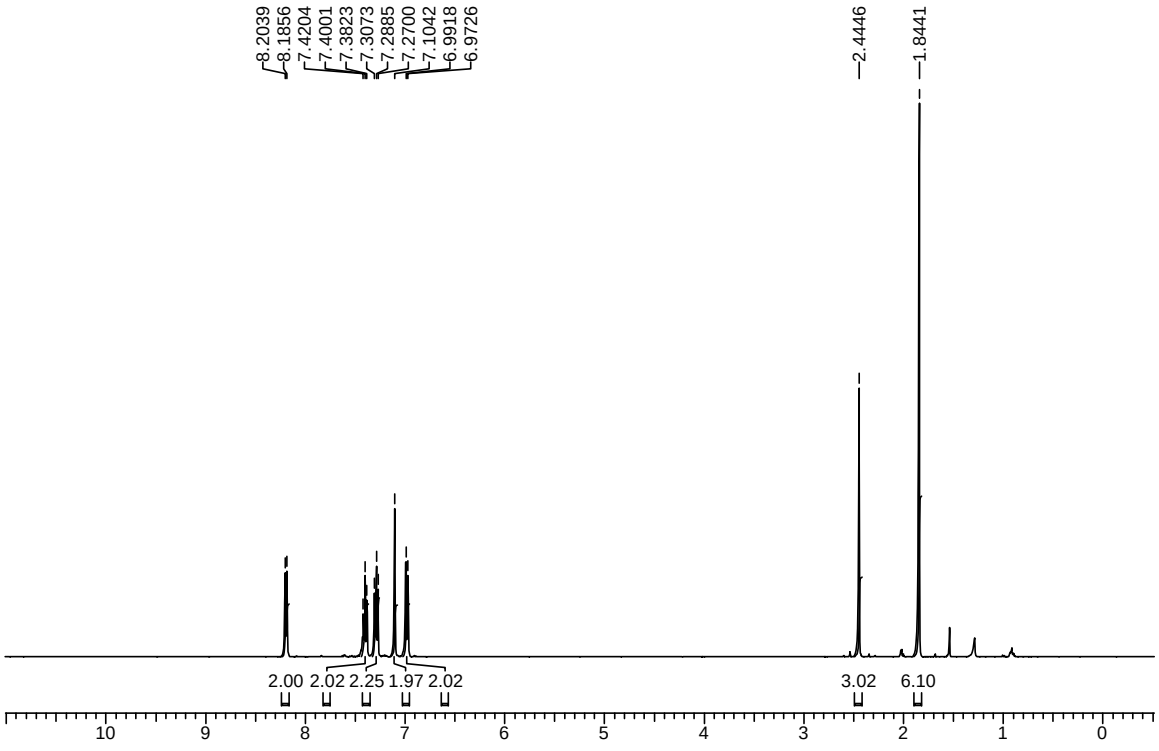
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1.8441
2.00 2.02 2.25 1.97 2.02
3.02 6.10
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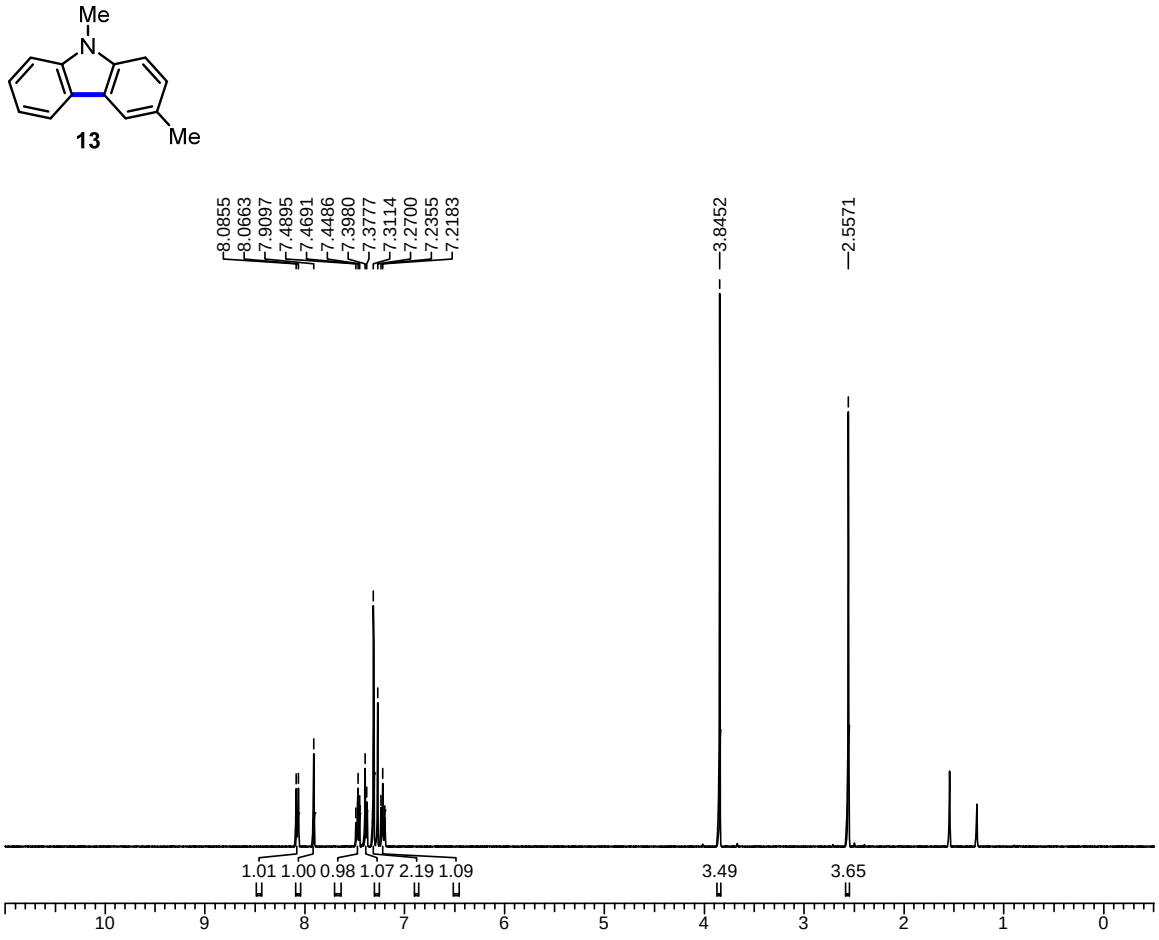
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7.2700
7.2355
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3.49
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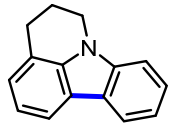

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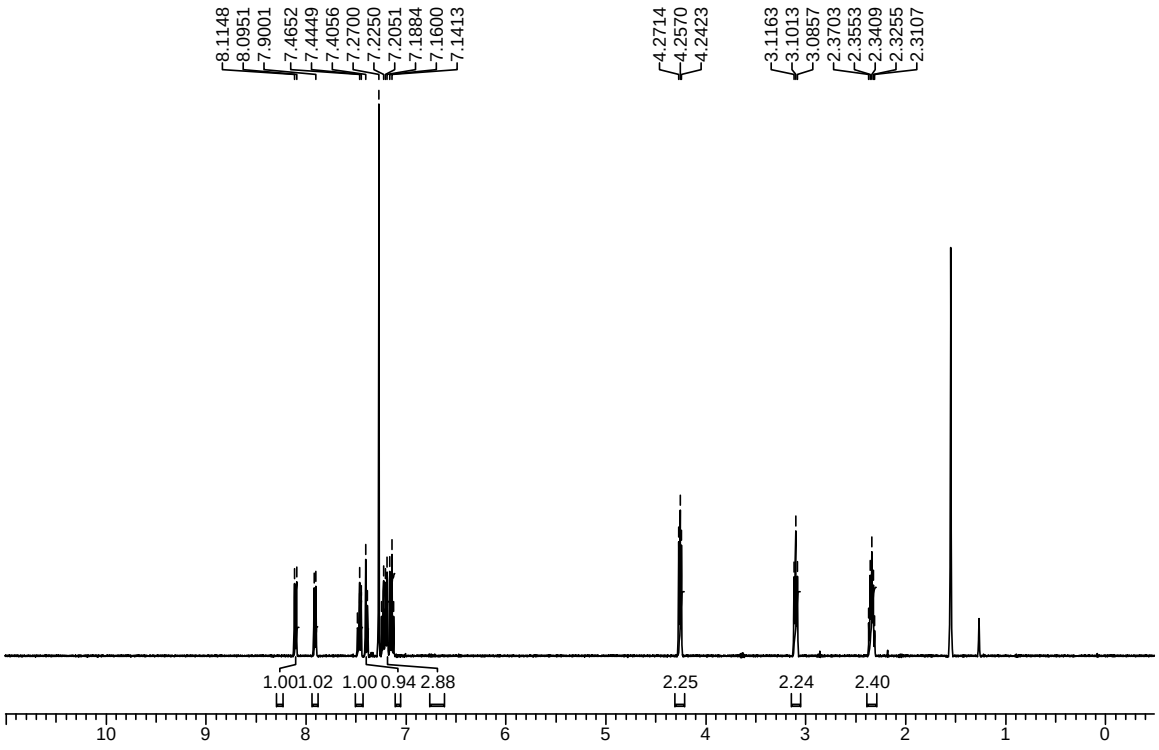
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4.2423
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3.0857
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2.3553
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2.3255
2.3107
1.00 1.02 1.00 0.94 2.88
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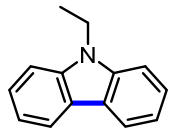

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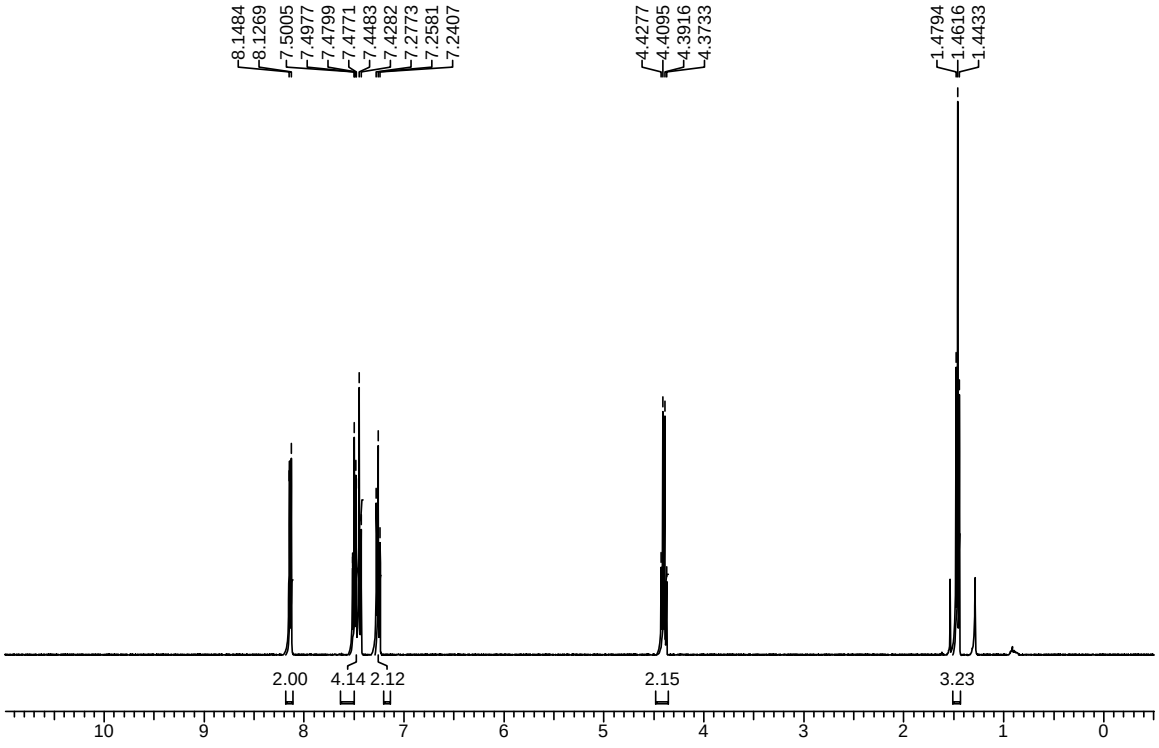
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4.3916
4.3733
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1.4433
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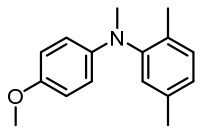

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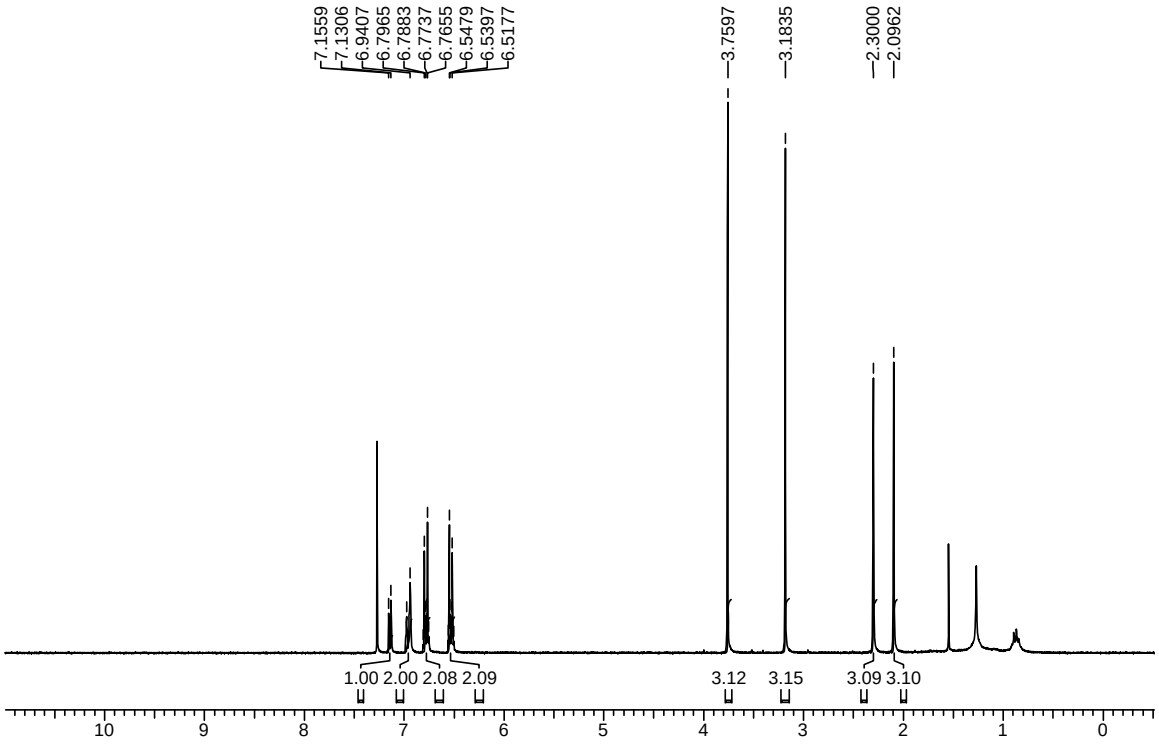
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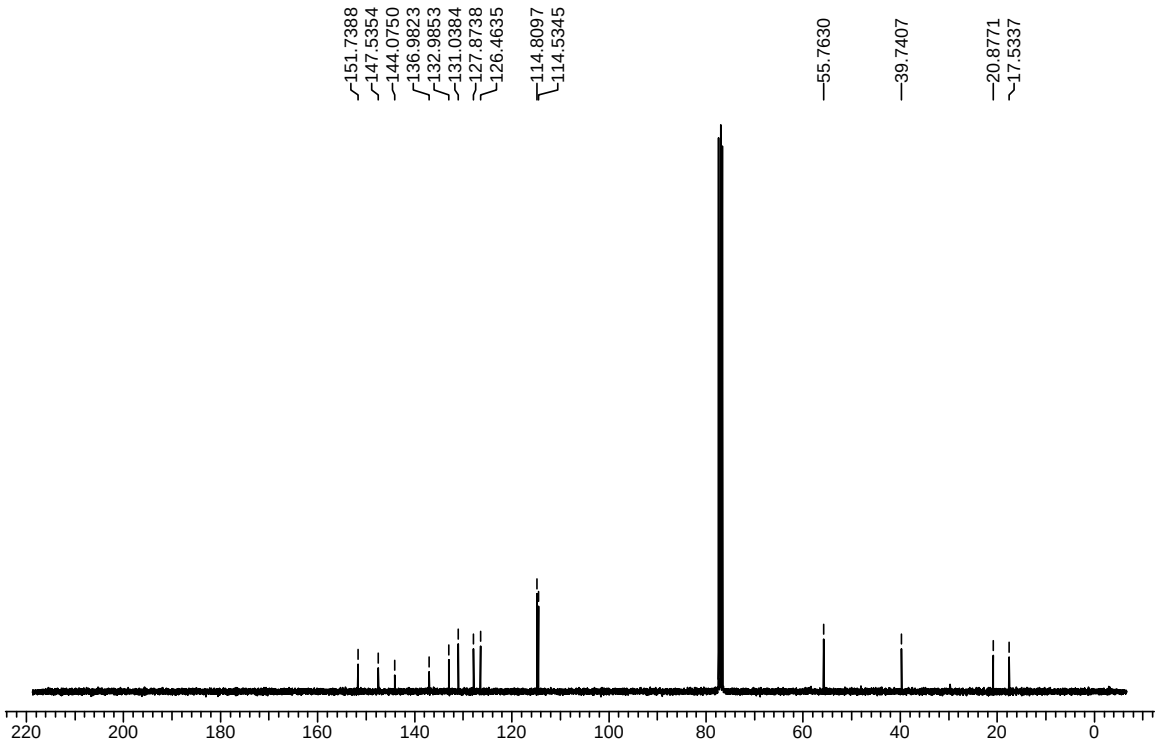
1.00 2.00 2.08 2.09
3.12 3.15 3.09 3.10
10 9 8 7 6 5 4 3 2 1 0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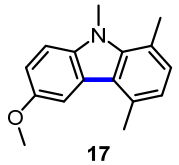

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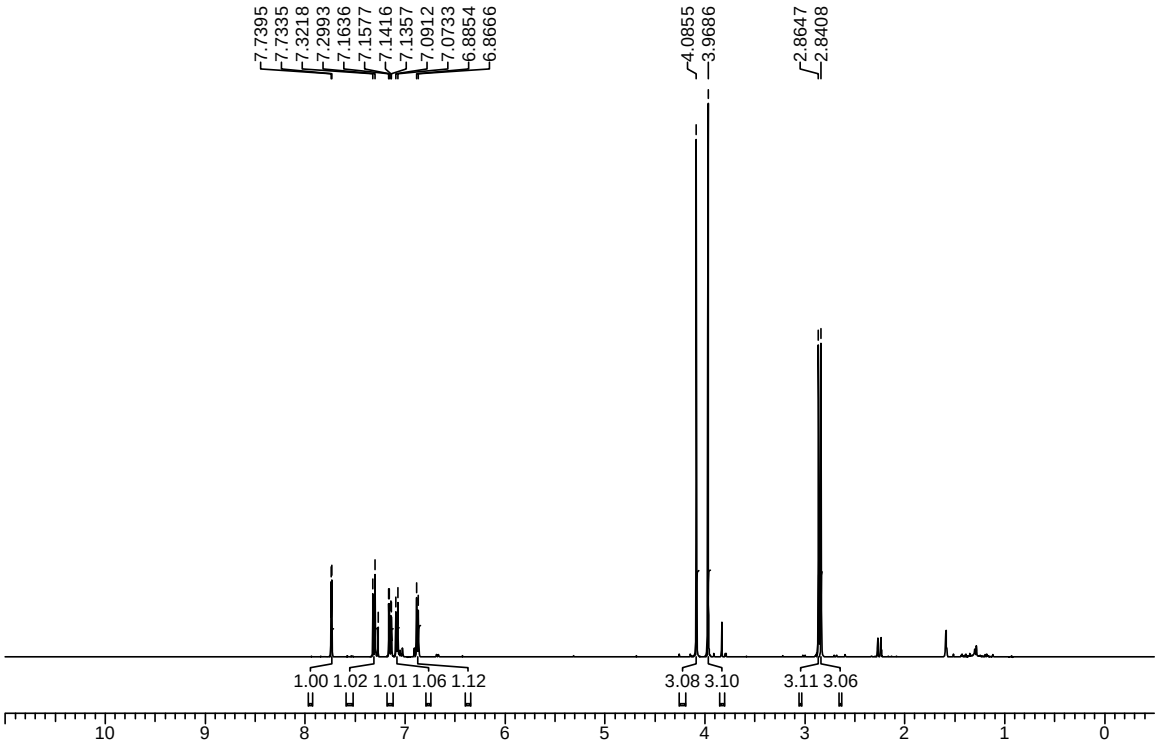
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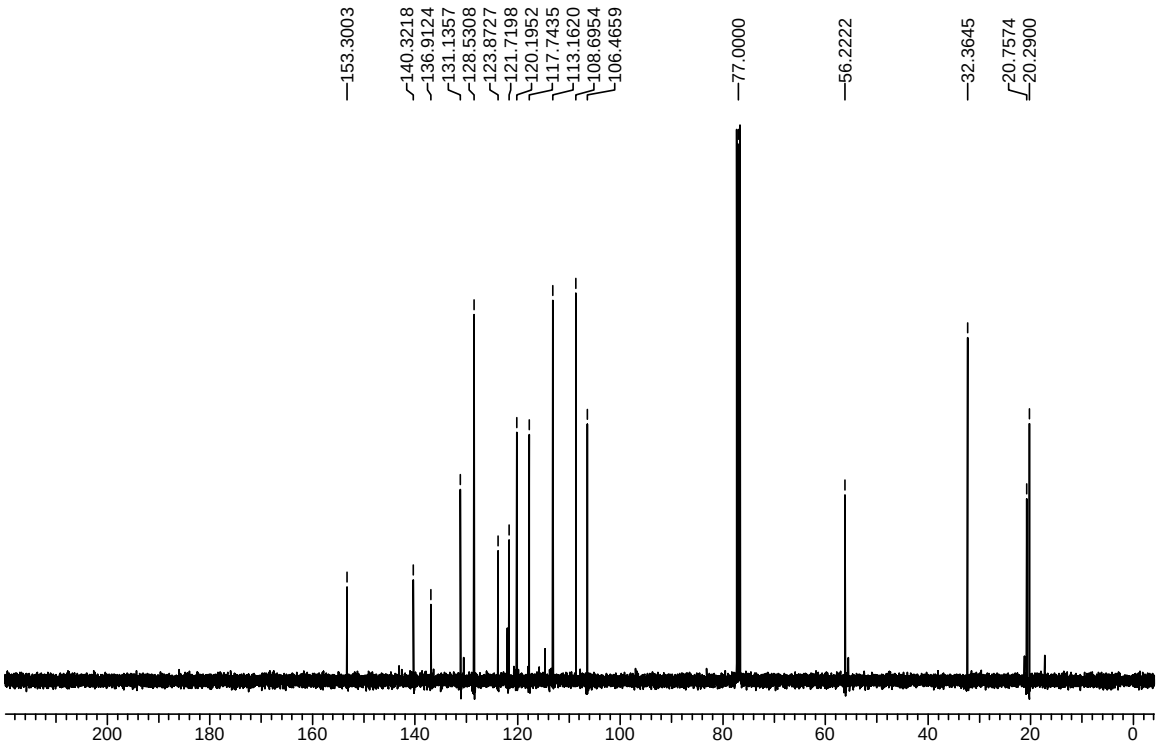
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