Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Vicinal Bis(trifluoroacetimidoyl chloride)s: Novel Building Blocks for the Synthesis of Benzo-fused Eight-membered Rings via [2+2+2] Cycloadditions

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Supporting Information

General Information

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. Solvents were purified before used by standard procedures. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a 400 MHz or 300 MHz NMR spectrometer. ^{1}H NMR chemical shifts were determined relative to internal TMS at δ 0.0. ^{13}C NMR chemical shifts were determined relative to internal TMS at δ 0.0. For the isolated compounds, ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ at δ 0.0. Melting points were measured on a Melt-Temp apparatus and were uncorrected. IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Mass spectra and elemental analyses were recorded in this institute. TLC analysis was performed on silica gel plates, column chromatography over silica gel (mesh 300-400) and petroleum ether and ethyl acetate combination was used as the eluent.

Synthesis of Vicinal Bis(trifluoroacetimidoyl chloride)s 2

Optimization synthesis of 2a

A 25-mL flask was added Ph_3P, Et_3N, CCl_4 (10 mL), and trifluoroacetic acid (TFA). After the solution was stirred for 10 minutes in ice-water bath, *o*-phenylenediamine (**1a**, 5 mmol) was added. Then the mixture was heated at 60 ^{o}C for 3 hours under stirring. The reaction was treated with petroleum ether (100 mL) and filtered. Residual solid was washed with petroleum ether several times. The filtrate was concentrated under reduced pressure. The residue was purified by chromatography on silica gel (petroleum ether) to afford vicinal bis(trifluoroacetimidoyl chloride) **2a** as transparent oil.

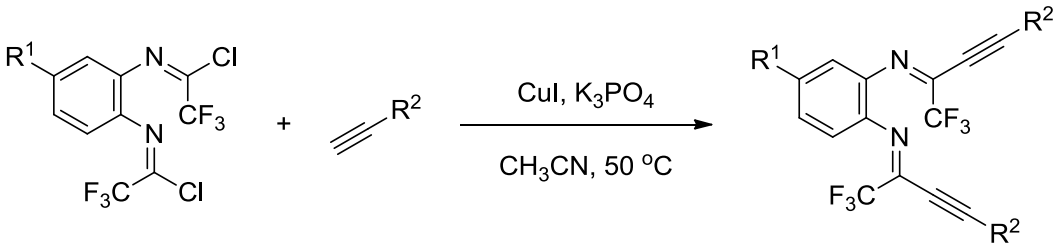
General procedure for synthesis of 4

A 25-mL flask was added Ph_3P (22.9 mmol), Et_3N (11.5 mmol), CCl_4 (10 mL), and TFA (10.4 mmol). After the solution was stirred for 10 minutes in ice-water bath, *o*-phenylenediamines (**1**, 5 mmol) was added. Then the mixture was heated at 60 ^{o}C for 3 hours under stirring. The reaction was treated with petroleum ether (100 mL) and filtered. Residual solid was washed with petroleum ether several times. The filtrate was concentrated under reduced pressure. The residue was purified by chromatography on silica gel (petroleum ether) to afford vicinal bis(trifluoroacetimidoyl chloride) **2**.

Synthesis of Vicinal Bisalkynylimines 3

Vicinal bisalkynylimines **3** were synthesis according to literature.[2] Vicinal bis(trifluoroacetimidoyl chloride)s **2** (2 mmol), alkynes (2.6 equiv), K_3PO_4 (2.4 equiv), and CuI (1 equiv) in CH_3CN (2 mL) were stirred at 50 ^{o}C under nitrogen. After the reaction was over detected by TLC, solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel (ethyl acetate and petroleum ether) to afford **3**. The results are shown in Table S1.

Table S1. The synthesis of **3**.[a]



2 **3**

Entry	**2**	R^2	Yield/%[b]
1	**2a**	Ph	**3a**/84
2	**2a**	*o*-ClC_6H_4	**3b**/89
3	**2a**	*p*-BrC_6H_4	**3c**/80
4	**2a**	*m*-$OMeC_6H_4$	**3d**/74
5	**2a**	2-naphthyl	**3e**/76
6	**2a**	2-thienyl	**3f**/63
7	**2a**	*n*-Bu	**3g**/68
8	**2b**	Ph	**3h**/95
9	**2d**	Ph	**3i**/82

[a] **2**/ alkyne / CuI / K_3PO_4 =1/2.6/1/2.4, CH_3CN (0.2 M).

[b] Isolated yield.

Synthesis of 1,4-diazocines 4

Optimization of [2+2+2] cycloaddition of 3a with 3-hexyne to give 4a

Vicinal bisalkynylimine **3a**, 3-hexyne and catalyst in solvent (2 mL) were stirred at certain reaction temperature under nitrogen. After the reaction was over detected by TLC, water (10 mL) was added, the resulting mixture was extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. The volatile compounds were removed under reduced pressure and the residue was purified by chromatography on silica gel (eluent: ethyl acetate/ petroleum ether=1:15) to afford **4a** as a white solid.

General procedure for synthesis of 4

Vicinal bisalkynylimines **3** (0.2 mmol), alkynes (3 equiv) and $[RhCl(PPh_3)_3]$ (5 mol%) in NMP (2 mL) were stirred at 120°C under nitrogen. After the reaction was over detected by TLC, water (10 mL) was added, the resulting mixture was extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. The volatile compounds were removed under reduced pressure and the residue was purified by chromatography on silica gel (ethyl acetate and petroleum ether) to afford **4**.

X-Ray of 4a

(5*E*,11*E*)-8,9-diethyl-7,10-diphenyl-6,11-bis(trifluoromethyl)dibenzo[*b*,*f*][1,4]diazocine (**4a**)

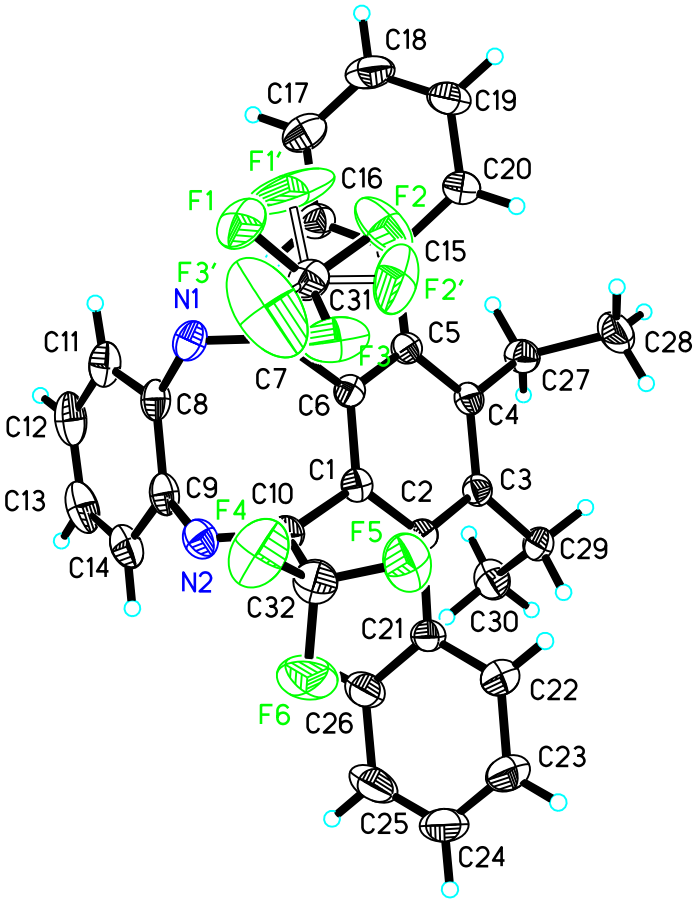


Table S4. Crystallographic Data of Compound **4a**

Compound reference	cd212508
Chemical formula	$C_{32}H_{24}F_6N_2$
Formula Mass	550.53
Crystal system	Triclinic
a/Å	10.4678(10)
b/Å	11.7231(11)
c/Å	11.8283(12)
α/°	69.655(2)
β/°	86.031(2)
γ/°	80.188(2)
Unit cell volume/Å^3	1341.0(2)
Temperature/K	293(2)
Space group	$P1^-$

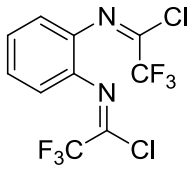
No. of formula units per unit cell, Z	2
No. of reflections measured	7200
No. of independent reflections	5136
R_{int}	0.0150
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1349
Final R_1 values (all data)	0.0588
Final $wR(F^2)$ values (all data)	0.1455
CCDC number	946290

References

1 Tamura, K. Mizukami, H. Maeda, K. Watanabe, H. Uneyama, K. *J. Org. Chem.* **1993**, *58*, 32.
2 S. Li, J. T. Zhu, H. B. Xie, Z. X. Chen, Y. M. Wu, *J. Fluorine Chem.* **2011**, *132*, 196.

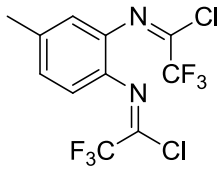
Characterization Data for the Substrates and Products

N',*N*''-(1,2-phenylene)bis(2,2,2-trifluoroacetimidoyl chloride) (2a)



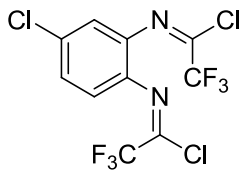
Light yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40–7.37 (m, 2H), 7.21–7.18 (m, 2H); ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.25 (s); ^{13}C NMR (126 MHz, $CDCl_3$): δ 135.01 (q, *J* = 43.5 Hz), 134.62, 127.80, 120.41, 116.55 (q, *J* = 277.5 Hz); IR (neat, cm^{-1}): 3074, 1700, 1482, 1299, 1207, 1163, 953, 936, 758, 732, 713; MS (EI): *m/z* (relative intensity) 336 (38) [M^+], 301 (45), 113 (31), 102 (33), 75 (59); HRMS Calcd. For $C_{10}H_4N_2F_6Cl_2$: 335.9656; Found: 335.9656.

N',*N*''-(4-methyl-1,2-phenylene)bis(2,2,2-trifluoroacetimidoyl chloride) (2b)



Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16–7.15 (m, 2H), 6.95 (s, 1H), 2.40 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -71.74 (s), -71.84 (s); ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.75, 135.52, 134.93 (q, *J* = 43.5 Hz), 133.55 (q, *J* = 43.5 Hz), 131.27, 128.23, 120.66, 120.46, 116.60 (q, *J* = 277.3 Hz), 116.54 (q, *J* = 277.5 Hz), 21.17; IR (neat, cm^{-1}): 2928, 1693, 1299, 1283, 1216, 1162, 954, 812, 760, 716; MS (EI): *m/z* (relative intensity) 350 (49) [M^+], 315 (52), 127 (32), 125 (100), 116 (30); HRMS Calcd. For $C_{11}H_6N_2F_6Cl_2$: 349.9812; Found: 349.9812.

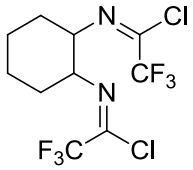
N',*N*''-(4-chloro-1,2-phenylene)bis(2,2,2-trifluoroacetimidoyl chloride) (2d)



Light yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.31 (m, 1H), 7.20-7.17 (m, 2H); ^{19}F NMR (282 MHz, $CDCl_3$): δ -71.87 (s), -71.93 (s); ^{13}C NMR (126 MHz, $CDCl_3$): δ136.70 (q, *J* = 43.8 Hz), 135.49 (q, *J* = 43.6 Hz), 136.11, 133.64, 132.58, 127.66, 121.67, 120.50, 116.49 (q, *J* = 277.6 Hz), 116.43 (q, *J* = 277.7 Hz); IR (neat, cm^{-1}): 1703, 1476, 1299, 1226, 1207, 1165, 954,

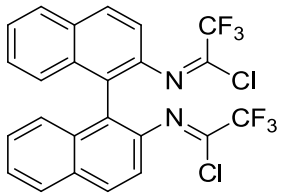
899, 823, 717; MS (EI): *m/z* (relative intensity) 370 (15) [M^+], 147 (29), 109 (31), 85 (26), 69 (100); HRMS Calcd. For $C_{10}H_3N_2F_6Cl_3$: 369.9266; Found: 369.9266.

_N'_,_N''_-(cyclohexane-1,2-diyl)bis(2,2,2-trifluoroacetimidoyl chloride) (2e)



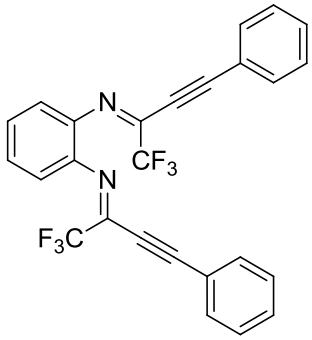
Transparent liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.05 (m, 2H), 1.89–1.80 (m, 4H), 1.76–1.47 (m, 4H); ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.28 (s); ^{13}C NMR (101 MHz, $CDCl_3$): δ 131.01 (q, *J* = 43.1 Hz), 116.29 (q, *J* = 276.8 Hz), 62.83, 27.90, 21.94; IR (neat, cm^{-1}): 2946, 2867, 1707, 1449, 1285, 1213, 1176, 1000, 946, 929, 910, 729; MS (EI): *m/z* (relative intensity) 342 (5) [M^+], 307 (89), 176 (82), 148 (33), 81 (100). HRMS Calcd. For $C_{10}H_{10}N_2F_6Cl_2$: 342.0125; Found: 342.0125.

_N'_,_N''_-([1,1'-binaphthalene]-2,2'-diyl)bis(2,2,2-trifluoroacetimidoyl chloride) (2f)



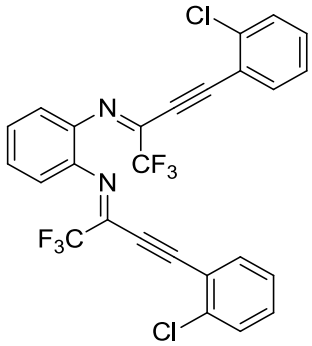
White solid, m. p.:115-117°C.^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (dd, *J* = 24.5, 8.5 Hz, 4H), 7.20–7.47 (m, 2H), 7.36–7.21 (m, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -71.81 (s); ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.29, 132.66, 132.05, 129.55, 128.20, 127.14, 126.23, 126.02, 124.59, 118.02; IR(neat, cm^{-1}): 1688, 1283, 1213, 1163, 938, 815, 748, 702, 408; MS (EI): *m/z*(relative intensity) 512(100) [M^+], 441 (48), 277 (58), 250 (44), 138 (41); HRMS Calcd. For $C_{24}H_{12}N_2F_6Cl_2$: 512.0282; Found. 512.0282.

N^1,N^2-bis(1,1,1-trifluoro-4-phenylbut-3-yn-2-ylidene)benzene-1,2-diamine (3a)



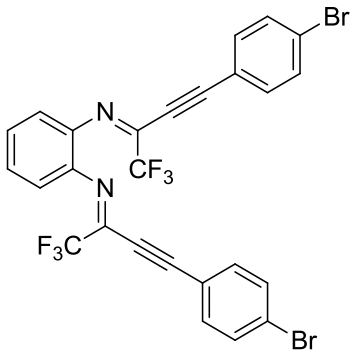
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (s, 4H), 7.32–7.26 (m, 2H), 7.26–7.20 (m, 4H), 7.17-7.12 (m, 4H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -71.88 (s); ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.87 (q, *J* = 38.7 Hz), 139.58, 132.70, 130.75, 128.43, 127.15, 120.53, 119.68, 118.52 (q, *J* = 277.6 Hz), 100.62, 79.45; IR (neat, cm^{-1}): 2205, 1620, 1349, 1260, 1222, 1193, 1146, 1064, 755, 686; MS (EI): *m/z* (relative intensity) 468 (5) [M^+], 399 (73), 165 (25), 127 (16), 84 (77); HRMS Calcd. For $C_{26}H_{14}F_6N_2$: 468.1061; Found: 468.1061.

N^1,N^2-bis(4-(2-chlorophenyl)-1,1,1-trifluorobut-3-yn-2-ylidene)benzene-1,2-diamine (3b)



Orange solid, m. p.:73-74 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45–7.31 (m, 4H), 7.25–7.17 (m, 6H), 7.03 (m, 3H); ^{19}F NMR (282 MHz, $CDCl_3$): δ -71.71 (s); ^{13}C NMR (101 MHz, $CDCl_3$): δ141.59 (q, *J* = 39.1 Hz), 139.51, 137.39, 134.40, 131.63, 129.36, 127.42, 126.39, 120.52, 120.02, 118.46 (q, *J* = 277.7 Hz), 96.54, 83.54; IR (neat, cm^{-1}): 2359, 2341, 2197, 1268, 1224, 1194, 1148, 1075, 1050, 754; MS (EI): *m/z* (relative intensity) 526 (4) [M^+], 383 (59), 286 (100), 176 (37), 161(37); HRMS Calcd. For $C_{26}H_{12}Cl_2F_6N_2$: 536.0282; Found: 536.0282.

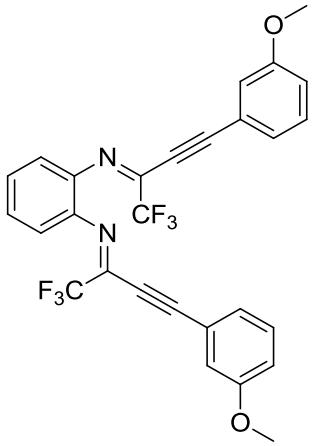
N^1,N^2-bis(4-(4-bromophenyl)-1,1,1-trifluorobut-3-yn-2-ylidene)benzene-1,2-diamine (3c)



Orange solid, m. p.:73-74 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ7.38–7.35 (m, 2H), 7.33–7.29 (m, 6H), 7.08–6.99 (m, 4H); ^{19}F NMR (282 MHz, $CDCl_3$): δ -71.84 (s); ^{13}C NMR (101 MHz, $CDCl_3$): δ141.80 (q, *J* = 39.2 Hz), 139.37, 133.77, 131.88, 127.21, 125.73, 120.49, 118.48, 118.34 (q, *J* = 277.4 Hz), 99.07, 80.29; IR (neat, cm^{-1}): 2196, 1261, 1223, 1197, 1150, 1060,

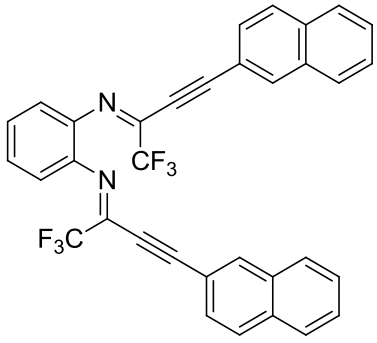
1009, 845, 825, 759; MS (EI): *m/z* (relative intensity) 626 (5) [M^+], 557 (78), 201 (56), 176 (95), 126 (100); HRMS Calcd. For $C_{26}H_{12}F_6N_2Br_2$: 623.9271; Found: 623.9271.

N^1,N^2-bis(1,1,1-trifluoro-4-(3-methoxyphenyl)but-3-yn-2-ylidene)benzene-1,2-diamine (3d)



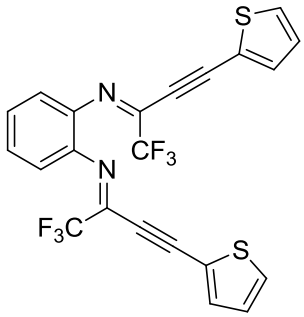
Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (s, 4H), 7.09–7.00 (m, 2H), 6.82 (ddd, *J* = 5.5, 4.2, 2.0 Hz, 4H), 6.71 (dd, *J* = 2.2, 1.4 Hz, 2H), 3.67 (s, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -71.47 (s); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.20, 141.83 (q, *J* = 38.9 Hz), 139.55, 129.49, 127.08, 125.22, 120.61, 120.54, 118.46 (q, *J* = 277.5 Hz), 117.24, 100.55, 79.12, 55.21; IR (neat, cm^{-1}): 3270, 2198, 1718, 1574, 1541, 1287, 1206, 1153, 1063, 757; MS (EI): *m/z* (relative intensity) 528 (19) [M^+], 459 (100), 421 (26), 169 (24), 114 (21); HRMS Calcd. For $C_{28}H_{18}F_6N_2O_2$: 528.1272; Found: 528.1272.

N^1,N^2-bis(1,1,1-trifluoro-4-(naphthalen-2-yl)but-3-yn-2-ylidene)benzene-1,2-diamine (3e)



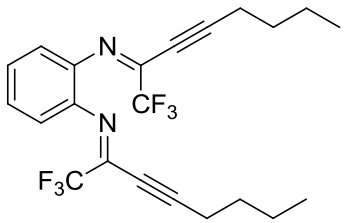
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (s, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.45–7.34 (m, 10H), 7.30–7.22 (m, 2H), 7.11 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -71.37 (s. 6F); ^{13}C NMR (126 MHz, $CDCl_3$): δ142.14 (q, *J* = 38.6 Hz), 139.60, 133.72, 133.56, 132.20, 128.08, 127.92, 127.81, 127.74, 127.57, 127.05, 126.70, 120.61, 118.47 (q, *J* = 279.9 Hz), 116.72, 100.96, 79.75; IR (neat, cm^{-1}): 2930, 2883, 1666, 1461, 1505, 1427, 1406, 1303, 1275, 764, 749; MS (EI): *m/z* (relative intensity) 568 (6) [M^+], 434 (100), 365 (37), 268 (34), 129 (40); HRMS Calcd. For $C_{34}H_{18}F_6N_2$: 568.1374; Found: 568.1374.

N^1,N^2-bis(1,1,1-trifluoro-4-(thiophen-2-yl)but-3-yn-2-ylidene)benzene-1,2-diamine （3f）



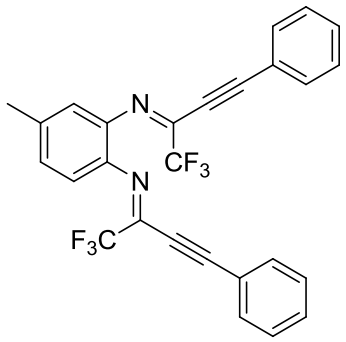
Brown oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.37–7.36 (m, 6H), 7.21–7.20 (m, 2H), 6.94–6.85 (m, 2H); ^{19}F NMR (282 MHz, $CDCl_3$): δ -71.14 (s); ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.22 (q, *J* = 39.0 Hz), 139.50, 136.18, 131.49, 127.48, 127.18 , 120.53, 119.43, 118.37 (q, *J* = 277.6 Hz), 94.28, 83.93; IR (neat, cm^{-1}): 3109, 2926, 2845, 2190, 1615, 1328, 1203, 1183, 1027, 751; MS (ESI): *m/z* 481.2 (M + Na^+); HRMS (ESI), calcd. for $C_{22}H_{10}N_2F_6NaS_2$: 503.00802; Found: 503.00818.

N^1,N^2-bis(1,1,1-trifluorooct-3-yn-2-ylidene)benzene-1,2-diamine (3g)



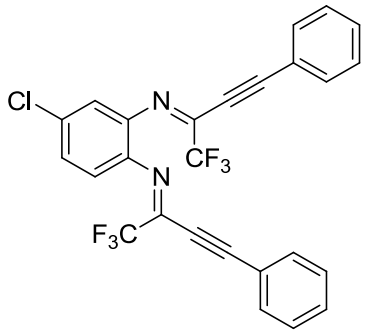
Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.20 (m, 4H), 2.32 (t, *J* = 7.0 Hz, 4H), 1.50–1.42 (m, 4H), 1.37–1.19 (m, 4H), 0.85 (t, *J* = 7.3 Hz, 6H); ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.41 (s); ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.41 (q, *J* = 38.5 Hz), 139.20, 126.71, 120.28, 118.33 (q, *J* = 277.4 Hz), 103.92, 71.77, 29.42, 21.69, 19.16, 13.36; IR (neat, cm^{-1}): 2962, 2936, 2875, 2215, 1628, 1342, 1319, 1199, 1146, 760; MS (EI): *m/z* (relative intensity) 428 (11) [M^+], 372 (79), 337 (48), 145 (77), 69 (100); HRMS Calcd. For $C_{22}H_{22}F_6N_2$:428.1687; Found: 428.1687.

4-methyl-N^1,N^2-bis(1,1,1-trifluoro-4-phenylbut-3-yn-2-ylidene)benzene-1,2-diamine (3h)



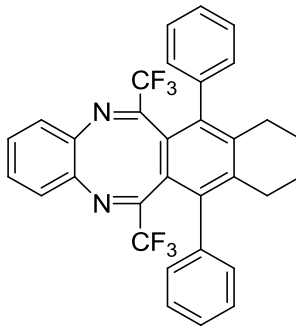
Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.23 (m, 7H), 7.22–7.09 (m, 6H), 2.43 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -71.36 (s), -71.49 (s); ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.82 (q, *J* = 38.8 Hz), 140.40 (q, *J* = 38.7 Hz), 140.27, 137.83, 136.52, 132.69, 132.65, 130.61, 128.43, 128.40, 127.63, 121.13, 120.43, 119.93, 119.83, 118.63 (q, *J* = 277.4 Hz), 118.49 (q, *J* = 277.3 Hz), 100.26, 100.13, 79.75, 79.63, 21.28; IR (neat, cm^{-1}): 2925, 2207, 1618, 1262, 1204, 1192, 1147, 1064, 756, 686. MS (EI): *m/z* (relative intensity) 482 (11) [M^+], 413 (100), 189 (30), 172 (32), 89 (30); HRMS Calcd. For $C_{27}H_{16}F_6N_2$: 482.1218; Found: 482.1218.

(*N*^{1},*N*^{2})-4-chloro-*N*^{1},*N*^{2}-bis(1,1,1-trifluoro-4-phenylbut-3-yn-2-ylidene)benzene-1,2-diamine (3i)



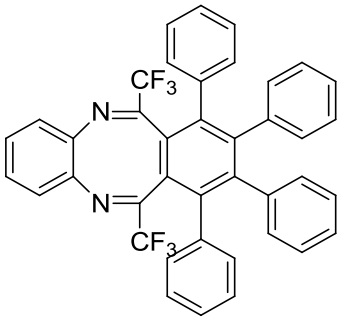
Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (s, 1H), 7.36–7.27 (m, 8H), 7.22–7.17 (m, 4H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -71.47 (s), -71.52 (s); ^{13}C NMR (126 MHz, $CDCl_3$): δ 142.75 (q, *J* = 39.4 Hz), 142.16 (q, *J* = 39.0 Hz), 140.46, 138.03, 132.85, 132.72, 132.43, 130.99, 130.90, 128.50, 128.47, 126.94, 118.35 (q, *J* = 277.6 Hz), 118.28 (q, *J* = 277.5 Hz), 101.79, 101.21, 79.29, 79.17; IR (neat, cm^{-1}): 3068, 2207, 1622, 1267, 1222, 1193, 1149, 1065, 756, 686; MS (ESI): *m/z* 503.4 (M + H^+). HRMS (ESI) Calcd. For $C_{26}H_{14}ClF_6N_2$: 503.07649; Found; 503.07442.

(5*E*,11*E*)-8,9-diethyl-7,10-diphenyl-6,11-bis(trifluoromethyl)dibenzo[*b*,*f*][1,4]diazocine (4a)



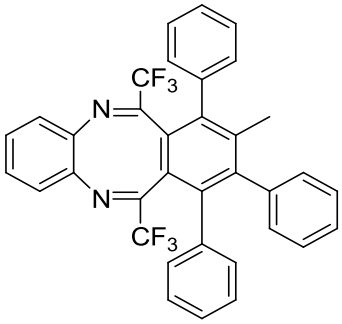
White solid, m. p.:196-197 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45–7.44(m, 8H), 7.27 (dd, *J* = 5.8, 3.5 Hz, 2H), 7.11 (dd, *J* = 5.7, 3.5 Hz, 2H), 6.90 (s, 2H), 2.72–2.20 (m, 4H), 0.91 (t, *J* = 7.4 Hz, 6H); ^{19}F NMR (282 MHz, $CDCl_3$): δ -67.41 (s). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.57 (q, *J* = 36.3 Hz), 144.22, 139.29, 137.78, 137.10, 130.11, 129.20, 128.91, 128.49, 128.31, 128.06, 125.99, 120.03, 118.13 (q, *J* = 279.8 Hz), 23.07, 15.11; IR (neat, cm^{-1}): 2972, 1659, 1287, 1233, 1191, 1165, 1142, 1009, 757, 720, 702; MS (EI): *m/z* (relative intensity) 550 (14) [M^{+}], 481 (100), 381 (9), 191 (12), 184 (12); HRMS Calcd. For $C_{32}H_{24}N_2F_6$: 550.1844; Found: 550.1844.

(5*E*,11*E*)-7,8,9,10-tetraphenyl-6,11-bis(trifluoromethyl)dibenzo[*b*,*f*][1,4]diazocine (4b)



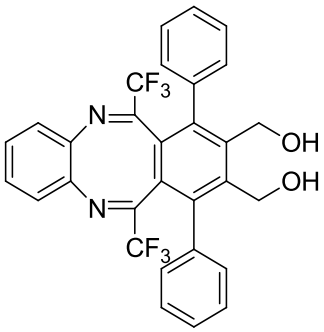
White solid, m. p.:253-254 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (dd, *J* = 5.9, 3.4 Hz, 2H), 7.30–7.12 (m, 8H), 7.09–6.99 (m, 6H), 6.90 (d, *J* = 7.2 Hz, 2H), 6.82 (t, *J* = 7.5 Hz, 2H), 6.66 (t, *J* = 7.5 Hz, 2H), 6.31 (d, *J* = 7.7 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -67.00 (s); ^{13}C NMR (101 MHz, $CDCl_3$): δ162.97 (q, *J* = 36.2 Hz), 144.62, 139.16, 137.77, 137.66, 136.50, 131.51, 131.27, 131.27, 130.08, 129.60, 129.16, 127.98, 127.61, 127.53, 127.06, 126.47, 126.34, 126.32, 120.41, 118.20 (q, *J* = 280.2 Hz); IR (neat, cm^{-1}): 1290, 1193, 1167, 1144, 1088, 985, 757, 719, 707, 697. MS (EI): *m/z* (relative intensity) 656 (19) [M^{+}], 577 (100), 508 (30), 246 (41), 215 (21). HRMS Calcd. For $C_{40}H_{24}N_2F_6$: 646.1844; Found: 646.1844.

(5*E*,11*E*)-8-methyl-7,9,10-triphenyl-6,11-bis(trifluoromethyl)dibenzo[*b*,*f*][1,4]diazocine (4c)



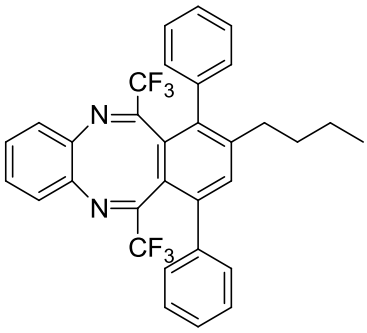
White solid, m. p.: 282-283 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54–7.40 (m, 4H), 7.41–7.07 (m, 9H), 7.07–6.85 (m, 4H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.43 (d, *J* = 7.6 Hz, 1H), 1.81 (s, 3H); ^{19}F NMR (282 MHz, $CDCl_3$): δ -67.44 (s), -67.69 (s); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.33 (q, *J* = 36.0 Hz), 163.29 (q, *J* = 35.9 Hz), 144.90, 139.48, 138.70, 138.69, 138.50, 137.88, 137.09, 136.80, 131.09, 130.59, 130.31, 130.04, 129.19, 129.15, 128.66, 128.39, 128.33, 128.03, 127.80, 127.70, 127.61, 127.60, 126.97, 126.23, 126.21, 120.23, 120.15, 118.19 (q, *J* = 280.2 Hz), 19.72; IR (neat, cm^{-1}): 1289, 1262, 1232, 1193, 1146, 1039, 1021, 985, 758, 700; MS (EI): *m/z* (relative intensity) 584 (17) [M^{+}], 515 (100), 445 (15), 223 (12), 215 (23); HRMS Calcd. For $C_{35}H_{22}N_2F_6$: 548.1687; Found: 584.1687.

((5*E*,11*E*)-7,10-diphenyl-6,11-bis(trifluoromethyl)dibenzo[*b*,*f*][1,4]diazocine-8,9-diyl)dimethanol (4d)



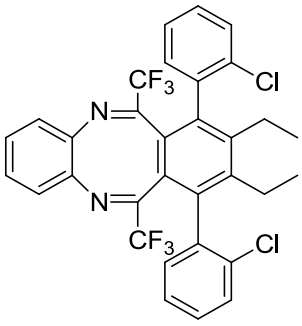
White solid, m. p.: ＞300^{o}C; ^{1}H NMR (300 MHz, DMSO): δ 7.53 (s, 8H), 7.36 (d, *J* = 9.3 Hz, 4H), 6.89 (d, *J* = 6.8 Hz, 2H), 5.10 (s, 2H), 4.39 (dd, *J* = 93.6, 11.4 Hz, 4H); ^{19}F NMR (282 MHz, DMSO): δ -66.63 (s); ^{13}C NMR (101 MHz, DMSO): δ 162.83 (q, *J* = 35.5 Hz), 142.97, 140.21, 137.23, 135.92, 130.81, 130.05, 129.35, 129.29, 129.10, 128.59, 127.48, 120.28, 118.29 (q, *J* = 280.1 Hz), 57.71; IR (neat, cm^{-1}): 1287, 1193, 1145, 1024, 1009, 760, 720, 702, 684, 637, 613. MS (EI): *m/z* (relative intensity) 554 (53) [M^{+}], 485 (85), 369 (100), 190 (78), 135 (70). HRMS Calcd. For $C_{30}H_{20}N_2F_6O_2$: 554.1429; Found: 554.1429.

(5*E*,11*E*)-8-butyl-7,10-diphenyl-6,11-bis(trifluoromethyl)dibenzo[*b*,*f*][1,4]diazocine (4f)



White solid, m. p.: 156-159°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.42 (m, 6H), 7.41–7.36 (m, 2H), 7.33–7.19 (m, 5H), 7.19–7.06 (m, 1H), 6.90–6.88 (m, 1H), 2.55–2.28 (m, 2H), 1.51–1.21 (m, 2H), 1.24–1.05 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -66.85 (s), -66.86 (s), -67.97 (s), -67.98 (s); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.50 (q, *J* = 36.5 Hz), 163.14 (q, *J* = 36.1 Hz), 144.83, 139.68, 138.51, 137.99, 137.63, 135.98, 133.24, 131.60, 130.25, 129.16, 128.72, 128.70, 128.59, 128.53, 128.36, 128.18, 126.80, 126.28, 126.19, 120.07, 32.97, 118.41 (q, *J* = 280.0 Hz), 118.08 (q, *J* = 280.2 Hz), 32.72, 22.56, 13.64; IR (neat, cm^{-1}): 2955, 2922, 1662, 1287, 1232, 1193, 1153, 1115, 1033, 1022, 758, 701; MS (EI): *m/z* (relative intensity): 550 (9) [M^+], 481 (100), 369 (29), 184 (17), 41 (12); HRMS Calcd. For $C_{32}H_{24}N_2F_6$: 550.1844; Found: 550.1844.

(5*E*,11*E*)-2-chloro-8,9-diethyl-7,10-diphenyl-6,11-bis(trifluoromethyl)dibenzo[*b*,*f*][1,4]diazocine



4h-2

(4h-1)

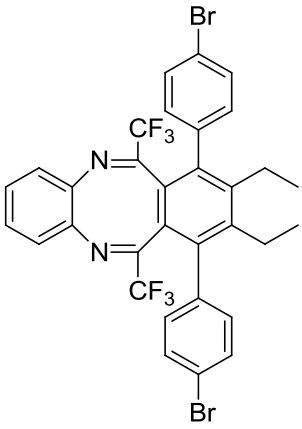
White solid, m. p.: 228-230 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 7.7 Hz, 2H), 7.37 (dt, *J* = 20.4, 7.6 Hz, 4H), 7.26 (s, 2H), 7.09 (dd, *J* = 5.7, 3.1 Hz, 2H), 6.92 (d, *J* = 7.3 Hz, 2H), 2.52 (tdd, *J* = 21.6, 14.3, 7.5 Hz, 4H), 0.78 (t, *J* = 7.4 Hz, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -67.37 (s); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.96 (q, *J* = 37.0 Hz), 145.03, 137.39, 136.54, 135.81, 134.54, 131.20, 130.26, 130.19, 129.39, 126.60, 126.07, 119.84, 118.07 (q, *J* = 280.0 Hz), 23.37,

14.37; IR (neat, cm^{-1}): 2978, 2923, 1292, 1265, 1233, 1196, 1147, 1058, 1009, 757; MS (EI): *m/z* (relative intensity) 618 (12) [M^+], 551 (65), 549 (100), 307 (82), 176 (82); HRMS Calcd. For $C_{32}H_{22}N_2F_6Cl_2$: 618.1064; Found: 618.1064.

(4h-2)

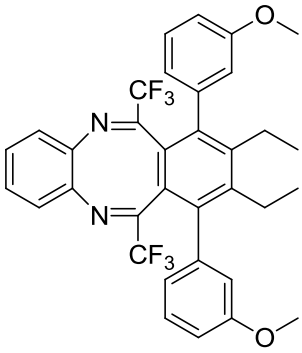
White solid, m. p.:212-214 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.52 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.49–7.32 (m, 6H), 7.23–7.18 (m, 1H), 7.16–7.11 (m, 2H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.99 (dd, *J* = 7.4, 1.7 Hz, 1H), 2.63 (dq, *J* = 14.8, 7.4 Hz, 1H), 2.47 (dq, *J* = 14.9, 7.5 Hz, 2H), 2.07 (dq, *J* = 14.9, 7.5 Hz, 1H), 0.99 (t, *J* = 7.5 Hz, 3H), 0.66 (t, *J* = 7.5 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -65.51 (s), -65.51 (s), -67.70 (s), -67.70 (s); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.16 (q, *J* = 36.1 Hz), 161.23 (q, *J* = 36.3 Hz), 145.40, 144.68, 137.11, 136.77, 136.44, 136.37, 135.69, 135.24, 134.43, 134.11, 133.92, 132.73, 132.71, 130.28, 130.20, 130.07, 129.47, 129.40, 129.05, 127.70, 126.65, 126.23, 125.97, 125.32, 123.30, 119.59, 118.21 (q, *J* = 278.4 Hz), 118.13 (q, *J* = 279.8 Hz), 23.45, 23.26, 15.08, 14.41; IR (neat, cm^{-1}): 2973, 2926, 1659, 1473, 1291, 1192, 1150, 1008, 785; MS (EI): *m/z* (relative intensity) 618 (12) [M^+], 550 (25), 549 (100), 380 (16), 190 (42). HRMS Calcd. For $C_{32}H_{22}N_2F_6Cl_2$: 618.1064; Found: 618.1064; Anal. Calcd. For $C_{32}H_{22}N_2F_6Cl_2$: C, 62.05; H, 3.58; N, 4.52; Found. C, 62.05; H, 3.58; N, 4.52.

(5*E*,11*E*)-7,10-bis(4-bromophenyl)-8,9-diethyl-6,11-bis(trifluoromethyl)dibenzo[*b*,*f*][1,4]diazocine (4i)



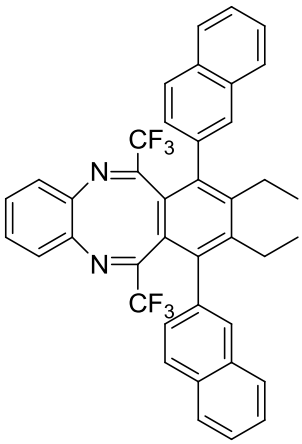
White solid, m. p.: 221-222 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (dd, *J* = 11.8, 8.2 Hz, 4H), 7.38–7.22 (m, 4H), 7.07 (dd, *J* = 5.7, 3.4 Hz, 2H), 6.73 (dd, *J* = 8.0, 1.7 Hz, 2H), 2.72–2.22 (m, 4H), 0.90 (t, *J* = 7.4 Hz, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -68.83 (s); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.02 (q, *J* = 36.7 Hz), 144.34, 138.34, 137.53, 135.83, 131.66, 131.45, 130.72, 128.95, 126.22, 123.01, 120.00, 118.05 (q, *J* = 280.0 Hz), 23.07, 15.09; IR (neat, cm^{-1}): 1491, 1286, 1233, 1192, 1163, 1147, 1070, 1010, 765, 750; MS (ESI): *m/z* 709.1 (M + H^+); HRMS (ESI) Calcd. For $C_{32}H_{23}N_2F_6Br_2$: 707.0127; Found: 707.01267; Anal. Calcd. For $C_{32}H_{22}N_2F_6Br_2$: C, 54.26; H, 3.13; N, 3.95; Found: C, 53.89; H, 3.10; N, 3.71.

(5*E*,11*E*)-8,9-diethyl-7,10-bis(3-methoxyphenyl)-6,11-bis(trifluoromethyl)dibenzo[*b*,*f*][1,4]diazocine (4j)



White solid, m. p.:148-150 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45–7.31 (m, 2H), 7.26 (s, 2H), 7.18–7.04 (m, 4H), 7.04–6.91 (m, 2H), 6.59–6.03 (m, 2H), 3.87 (s, 6H), 2.80–2.18 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -66.90 (s), -66.92 (s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.49 (q, *J* = 36.3 Hz), 163.39 (q, *J* = 36.4 Hz), 159.41, 159.11, 144.12, 144.09, 144.03, 144.00, 138.97, 138.96, 138.95, 138.94, 138.24, 137.67, 137.64, 129.31, 129.06, 128.70, 128.68, 128.67, 128.64, 125.95, 125.92, 125.88, 122.51, 121.59, 121.58, 120.03, 120.01, 119.95, 119.93, 118.10 (q, *J* = 280.0 Hz), 118.08 (q, *J* = 280.0 Hz), 116.19, 116.17, 115.53, 114.43, 114.39, 112.52, 112.51, 55.36, 55.31, 23.07, 15.28, 15.27; IR (neat, cm^{-1}): 2973, 1578, 1471, 1431, 1225, 1148, 1012, 777, 770, 700; MS (ESI): *m/z* 611.4 (M + H^{+}); HRMS (ESI) Calcd. For $C_{34}H_{29}N_2O_2F_6$: 611.2125; Found: 611.21277.

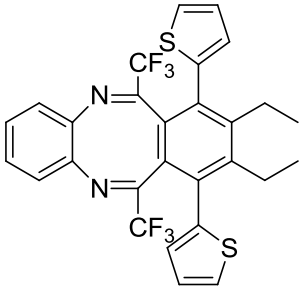
(5*E*,11*E*)-8,9-diethyl-7,10-di(naphthalen-2-yl)-6,11-bis(trifluoromethyl)dibenzo[*b*,*f*][1,4]diazocine (4k)



White solid, m. p.:265-267 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97–7.86 (m, 6H), 7.58 (s, 4H), 7.48–7.10 (m, 6H), 7.01 (d, *J* = 8.6 Hz, 2H), 2.78–2.29 (m, 4H), 0.94 (t, *J* = 6.9 Hz, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -66.87 (s), -66.95 (s), -66.98 (s), -67.08 (s); ^{13}C NMR (126 MHz,

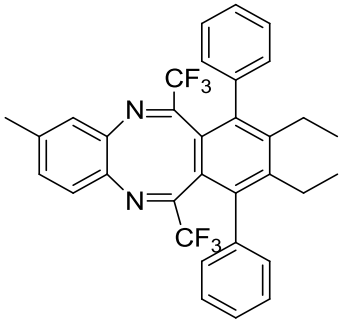
$CDCl_3$): δ 163.48 (q, *J* = 35.0 Hz), 163.45 (q, *J* = 36.2 Hz), 163.43 (q, *J* = 36.1 Hz), 144.53, 144.47, 144.44, 144.37, 139.30 (d, *J* = 25.7 Hz), 139.20, 137.97, 137.93, 137.76, 137.72, 134.96, 134.06, 134.04, 132.97, 132.93, 132.77, 129.33, 129.27, 129.13, 129.00, 128.82, 128.74, 128.34, 128.15, 128.13, 127.96, 127.86, 127.85, 127.80, 127.70, 127.69, 127.66, 126.81, 126.76, 126.74, 126.70, 126.69, 126.64, 126.62, 126.16, 126.09, 126.08, 126.01, 120.31, 120.26, 120.20, 120.15, 118.08 (q, *J* = 280.1 Hz), 118.05 (q, *J* = 280.2 Hz), 23.13, 15.12; IR (neat, cm^{-1}): 3054, 2973, 2926, 2854, 1721, 1286, 1266, 1228, 1147, 1010, 743. MS (ESI): *m/z* 651.5 ($M + Na^+$); HRMS (ESI) Calcd. For $C_{40}H_{28}F_6N_2Na$: 673.20400; Found: 673.20489.

(5*E*,11*E*)-8,9-diethyl-7,10-di(thiophen-2-yl)-6,11-bis(trifluoromethyl)dibenzo[*b*,*f*][1,4]diazocine (4l)



White solid, m. p.:245-246 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 4.7 Hz, 2H), 7.30–7.16 (m, 2H), 7.13 (dd, *J* = 8.7, 3.9 Hz, 4H), 6.98 (s, 2H), 2.58 (dtd, *J* = 35.2, 14.0, 6.5 Hz, 4H), 1.01 (t, *J* = 7.4 Hz, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -67.13 (s); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.73 (q, *J* = 35.8 Hz), 146.32, 137.33, 136.33, 132.70, 130.38, 129.32, 127.36, 126.96, 125.89, 120.20, 118.14 (q, *J* = 279.9 Hz), 23.51, 15.64. IR (neat, cm^{-1}): 2973, 1660, 1269, 1257, 1191, 1163, 1139, 1083, 1002, 701; MS (EI): *m/z* (relative intensity): 562 (22) [M^+], 495 (14), 493 (100), 129 (8), 43 (18); HRMS Calcd. For $C_{28}H_{20}N_2F_6S_2$:562.0972; Found: 562.0972.

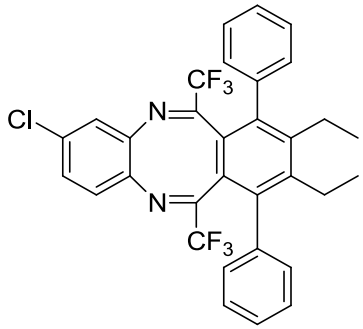
(5*E*,11*E*)-8,9-diethyl-2-methyl-7,10-diphenyl-6,11-bis(trifluoromethyl)dibenzo[*b*,*f*][1,4]diazocine ()



White solid, m. p.: 200-201 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53–7.35 (m, 8H), 7.04 (dd, *J* = 21.1, 8.1 Hz, 2H), 6.95–6.84 (m, 3H), 2.61 (dq, *J* = 14.3, 7.2 Hz, 2H), 2.47 – 2.29 (m, 5H), 0.93

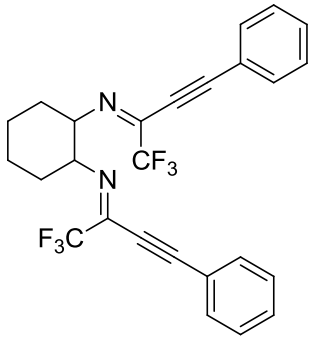
(td, *J* = 7.4, 4.9 Hz, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -66.98 (s), -67.02 (s); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.27 (q, *J* = 36.2 Hz), 163.18 (q, *J* = 35.2 Hz), 144.12, 144.06, 139.31, 139.24, 137.58, 137.13, 135.96, 135.27, 130.15, 130.12, 129.26, 129.23, 129.01, 128.98, 128.45, 128.30, 128.29, 128.05, 128.01, 126.88, 120.33, 120.08, 118.17 (q, *J* = 279.9 Hz), 118.15 (q, *J* = 280.0 Hz), 23.09, 23.07, 21.20, 15.16, 15.12; IR (KBr, cm^{-1}): 2981, 1661, 1290, 1218, 1164, 1145, 1067, 1010, 723, 702; MS (EI): *m/z* (relative intensity): 564 (16) [M$^+$], 495 (100), 395 (9), 198 (10), 191 (9); HRMS Calcd. For $C_{33}H_{26}N_2F_6$: 564.2000; Found: 564.2000.

(5*E*,11*E*)-2-chloro-8,9-diethyl-7,10-diphenyl-6,11-bis(trifluoromethyl)dibenzo[*b*,*f*][1,4]diazocine



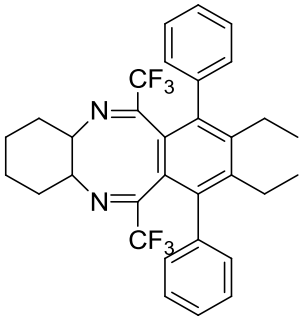
White solid, m. p.: 196-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (ddd, *J* = 16.2, 6.9, 4.6 Hz, 8H), 7.25 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.11 (d, *J* = 2.0 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 6.85 (dd, *J* = 18.6, 5.7 Hz, 2H), 2.69–2.33 (m, 4H), 0.93 (dt, *J* = 11.2, 7.5 Hz, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -67.09 (s); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.46 (q, *J* = 36.7 Hz), 164.17 (q, *J* = 36.5 Hz), 144.52, 144.48, 139.35, 139.33, 138.78, 136.84, 136.81, 136.34, 131.33, 130.04, 128.99, 128.98, 128.59, 128.56, 128.44, 128.29, 128.12, 126.16, 121.37, 119.97, 117.95 (q, *J* = 280.0 Hz), 117.91 (q, *J* = 280.1 Hz), 23.11, 23.06, 15.13, 15.04; IR (neat, cm^{-1}):3059, 2970, 2929, 1659, 1649, 1288, 1193, 1165, 1148, 1010, 149; MS (ESI): *m/z* 585.5 (M + H$^+$); HRMS (ESI) Calcd. For $C_{32}H_{25}ClN_2F_6$: 585.14988; Found: 585.15267.

***N*^{1},*N*^{2}-bis(1,1,1-trifluoro-4-phenylbut-3-yn-2-ylidene)cyclohexane-1,2-diamine (5)**



White solid, m. p.:68-69^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.48 (m, 4H), 7.45–7.42 (m, 2H), 7.37–7.33 (m, 4H), 4.26–4.25 (m, 2H), 2.12–1.96 (m, 4H), 1.76–1.72 (m, 2H), 1.59–1.56 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -71.62 (s); ^{13}C NMR (126 MHz, $CDCl_3$): δ 140.78 (q, *J* = 38.0 Hz), 132.41, 130.50, 128.61, 120.16, 118.36 (q, *J* = 277.2 Hz), 99.38, 65.79, 29.49, 22.35; IR (neat, cm^{-1}): 2934, 2210, 1347, 1248, 1203, 1118, 1065, 756, 686; MS (ESI): *m/z* 475 (M + H^{+}); HRMS (ESI) Calcd. For $C_{26}H_{21}N_2F_6$: 475.16006; Found: 475.16034.

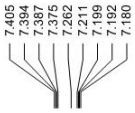
(5*E*,11*E*)-8,9-diethyl-7,10-diphenyl-6,11-bis(trifluoromethyl)-1,2,3,4,4a,12a-hexahydrodibenzo[*b*,*f*][1,4]diazocine (6)

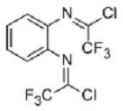


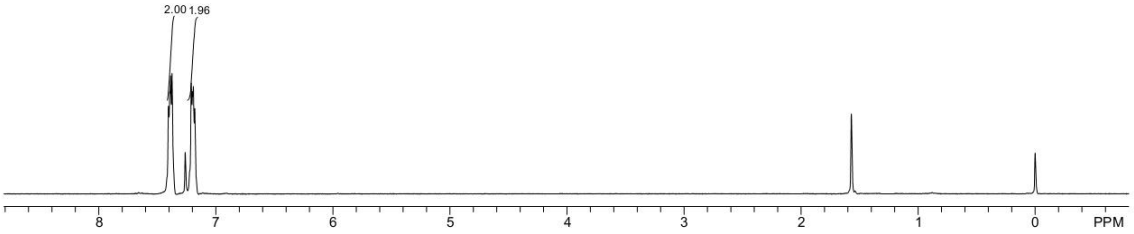
White solid, m. p.: 168-170^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (m, 8H), 6.83 (d, *J* = 6.6 Hz, 2H), 4.05 (s, 2H), 2.91–2.35 (m, 4H), 2.04–1.73 (m, 6H), 1.58–1.55 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 6H); ^{19}F NMR (282 MHz, $CDCl_3$): δ -67.66 (s); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.20 (q, *J* = 33.5 Hz), 163.20 (q, *J* = 33.5 Hz), 144.04, 143.97, 139.24, 139.17, 137.51, 137.05, 135.90, 135.19, 130.10, 130.09, 130.07, 130.06, 130.04, 129.19, 129.16, 128.92, 128.89, 128.39, 128.26, 128.23, 128.00, 127.96, 126.83, 120.28, 120.04, 118.09 (q, *J* = 280.0 Hz), 118.06 (q, *J* = 279.9 Hz), 23.05, 23.03, 21.20, 15.15, 15.10; IR (neat, cm^{-1}): 2936, 1281, 1193, 1144, 1118, 1098, 1002, 748, 726, 702; MS (EI): *m/z* (relative intensity): 556 (0.7) [M^{+}], 487 (14), 461 (7), 96 (100), 41 (4); HRMS Calcd. For $C_{32}H_{30}N_2F_6$: 556.2313; Found: 556.2313.

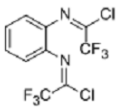
NMR Spectra for the Substrates and Product

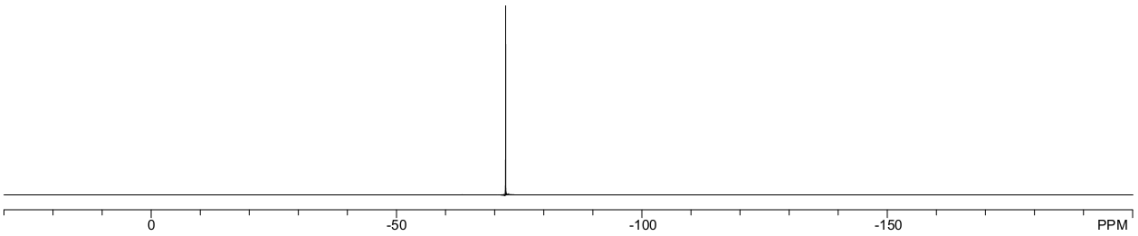
2a

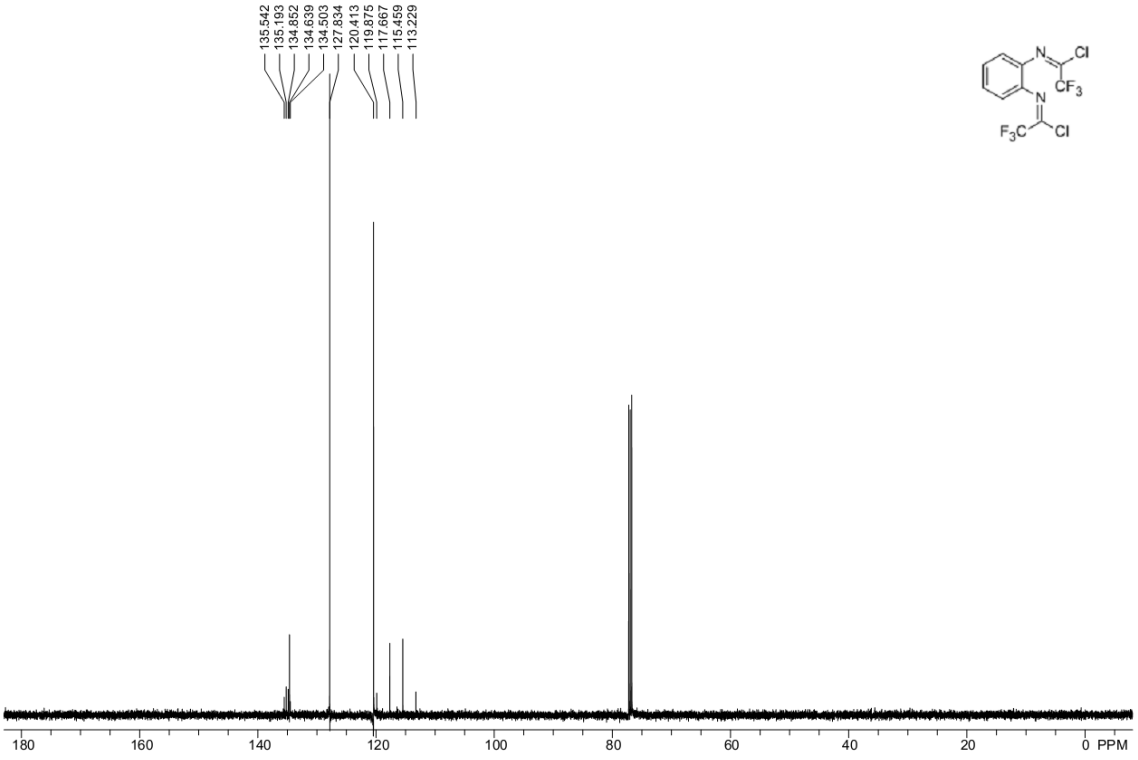












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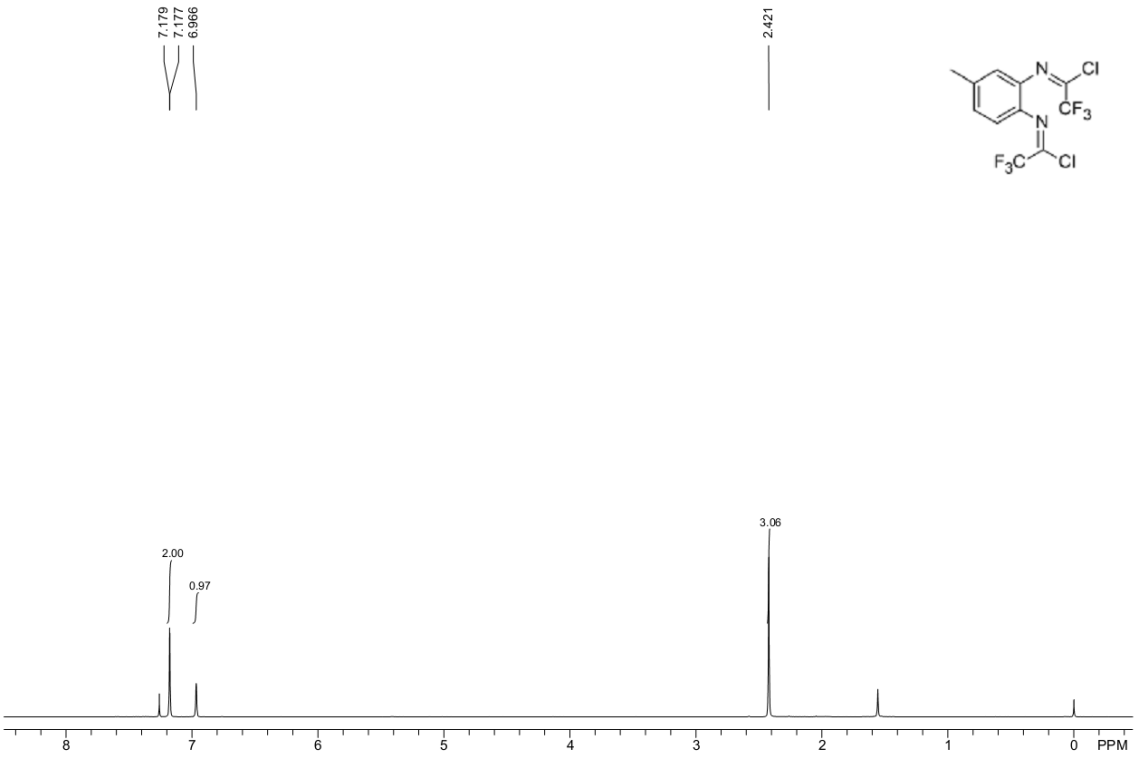
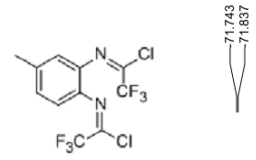
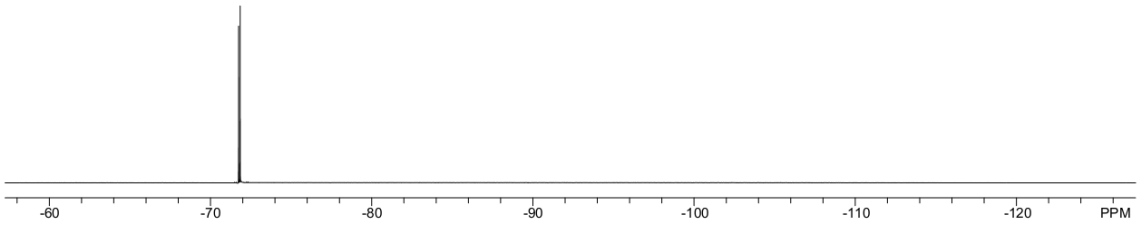
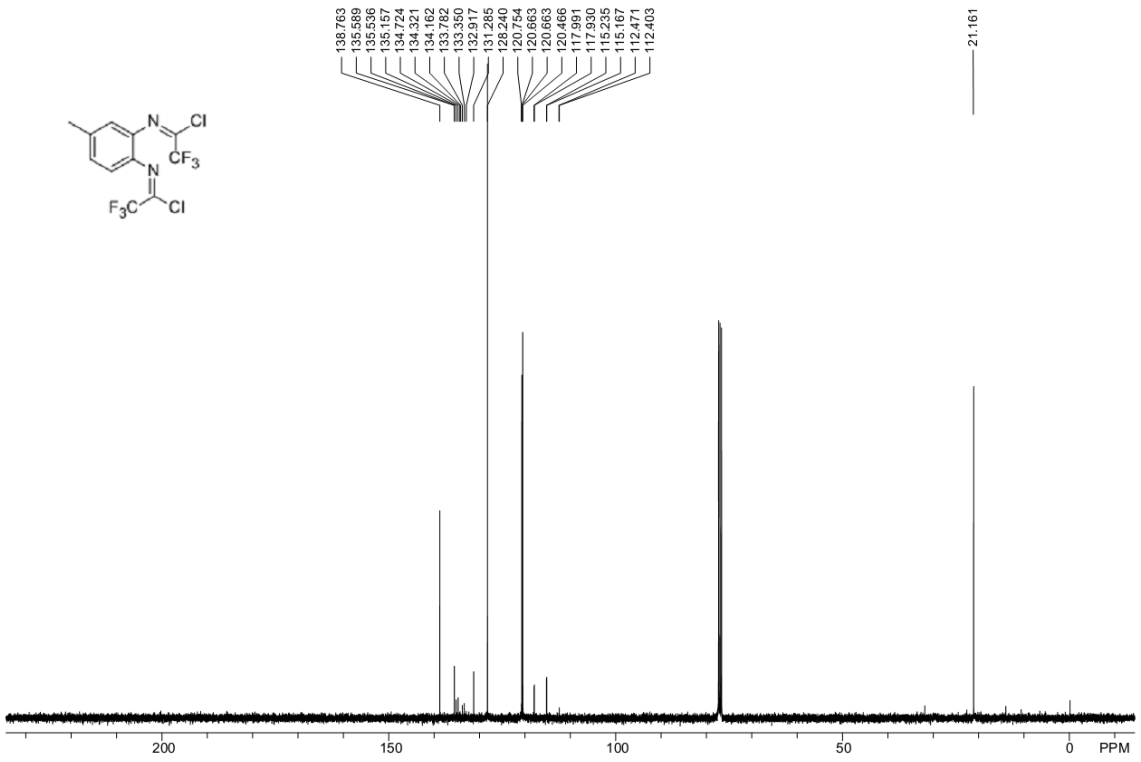
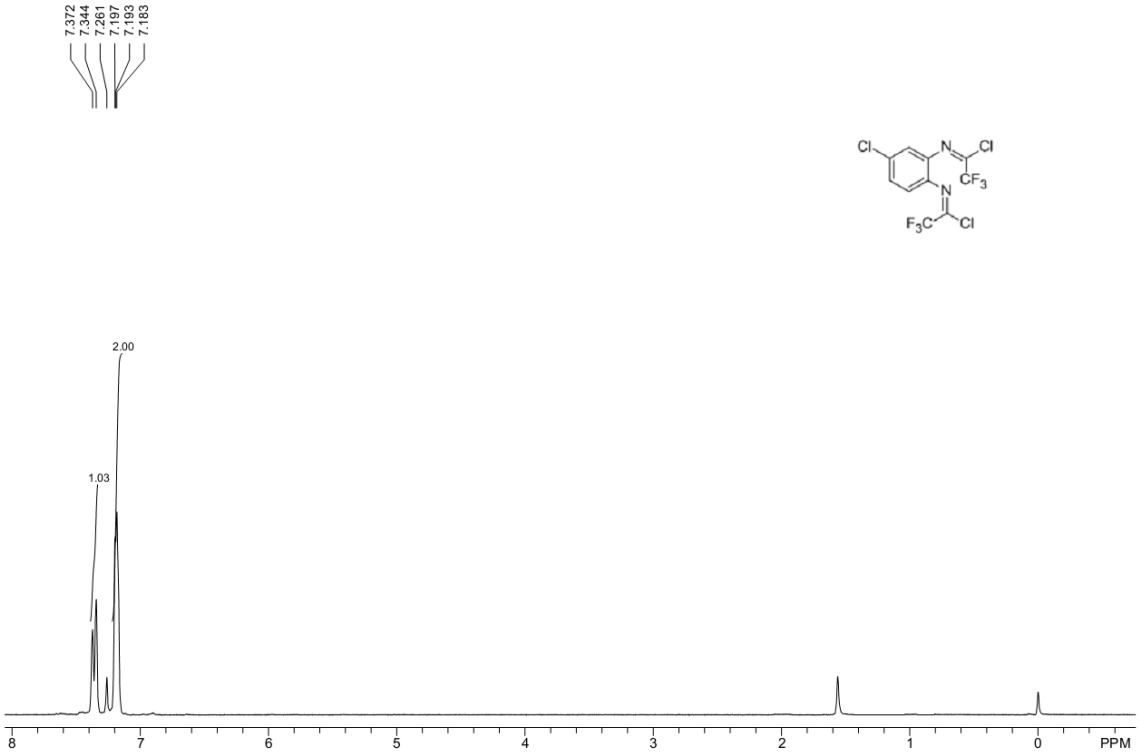


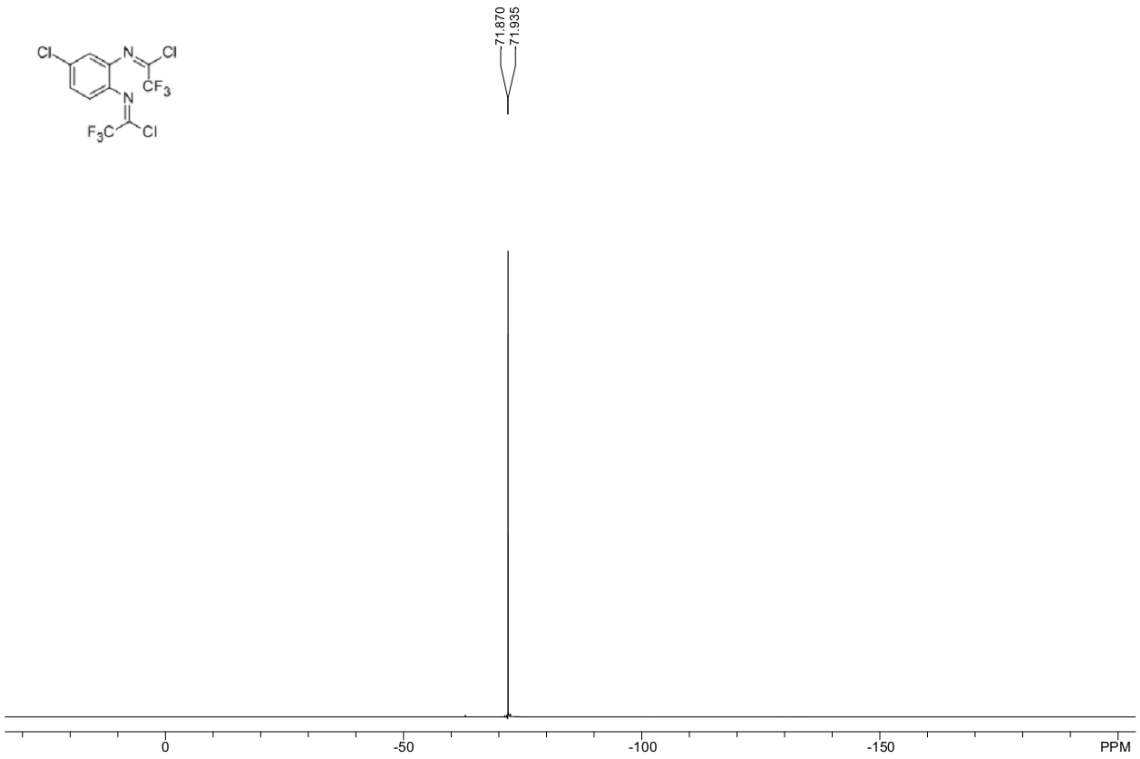


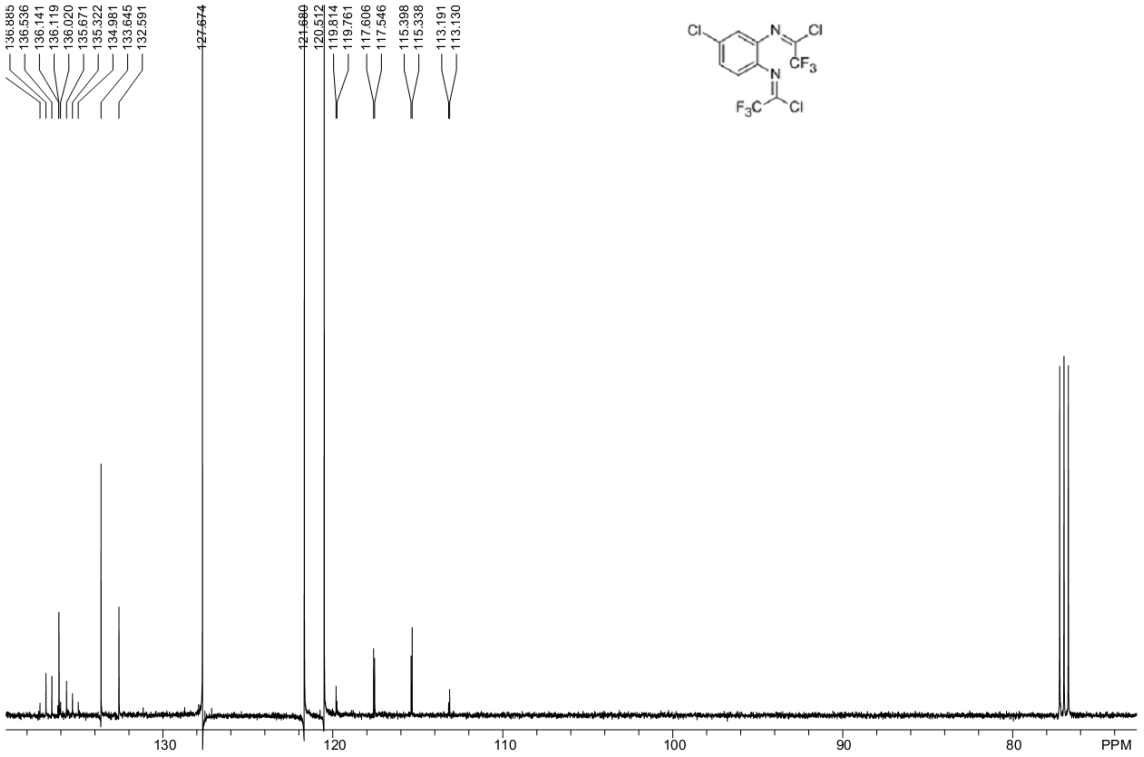




2d



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117.606
117.546
115.398
115.338
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Cl
CF3
N
F3C
Cl
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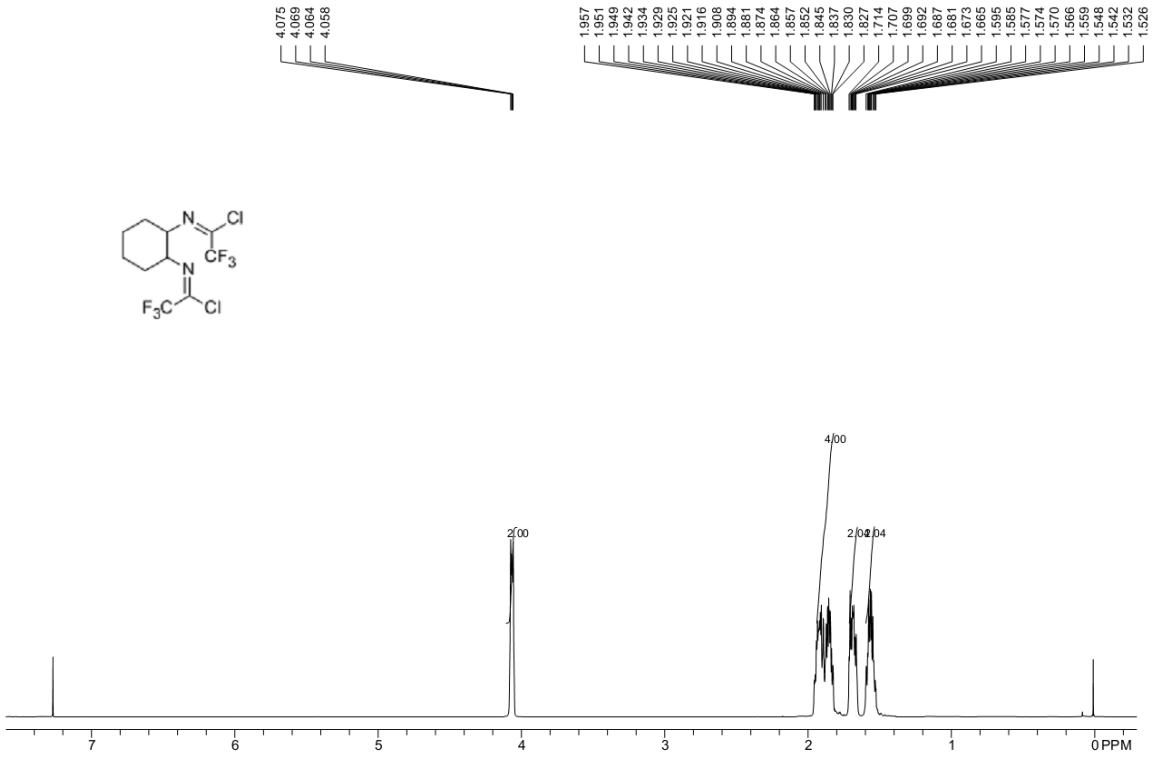
120
110
100
90
80
PPM

2e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1.852
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1.837
1.830
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1.692
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1.542
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Cl
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6
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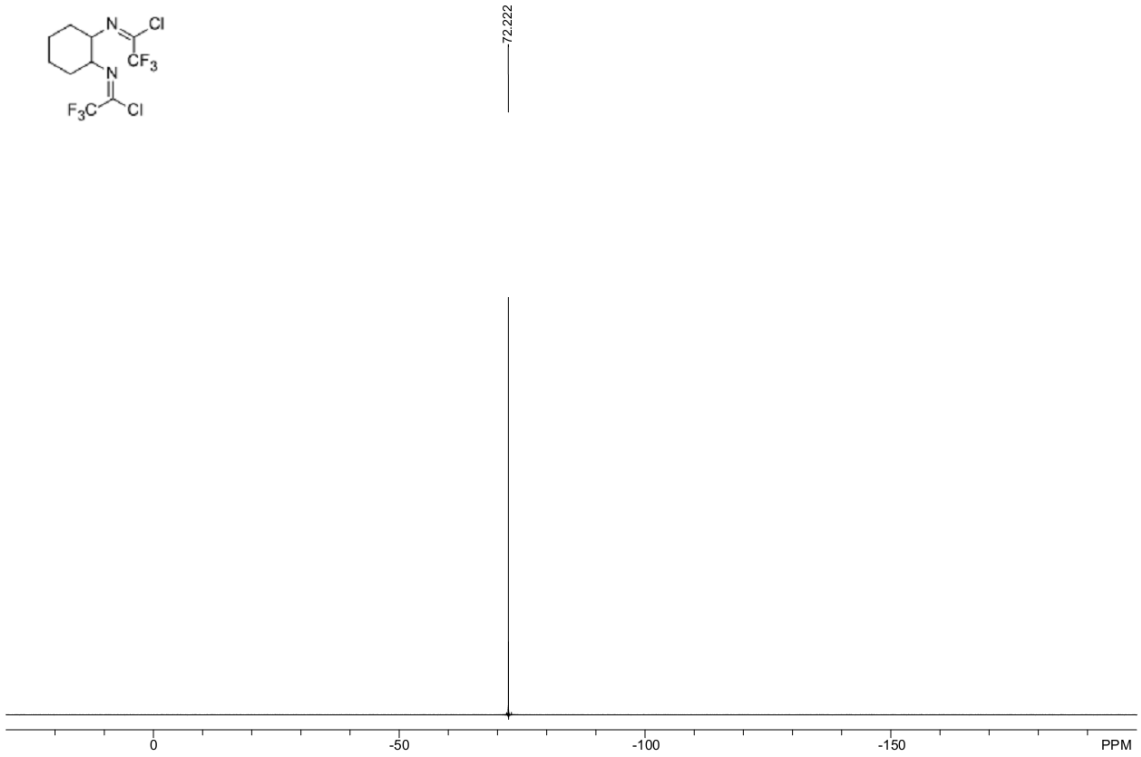

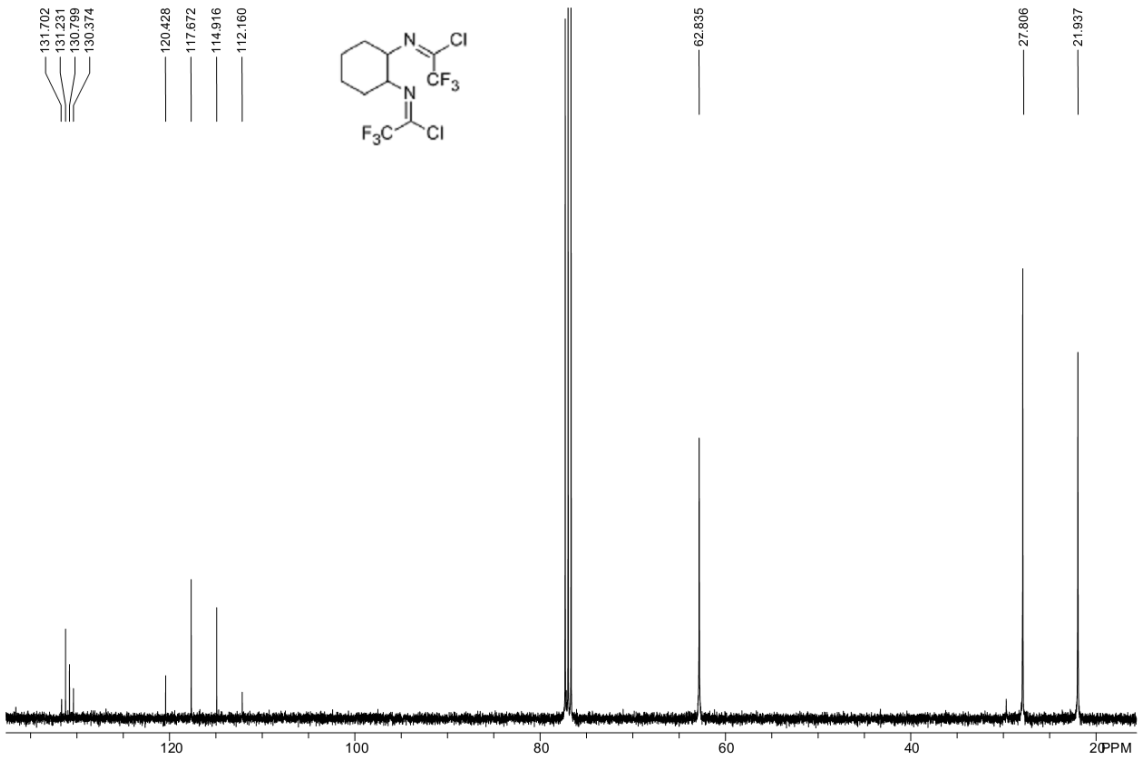

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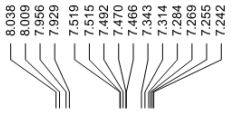
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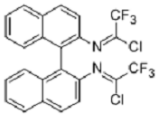
7.242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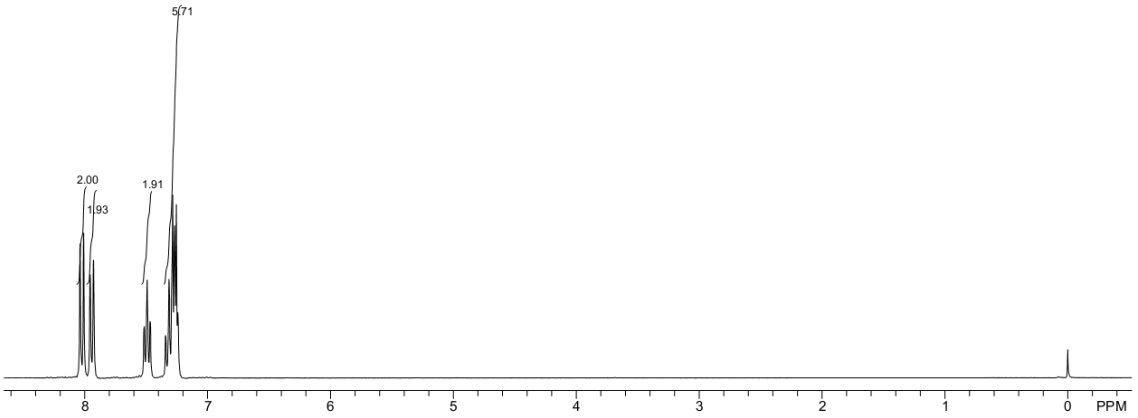
CF3
Cl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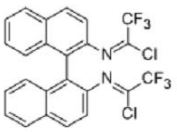
4
3
2
1
0
PPM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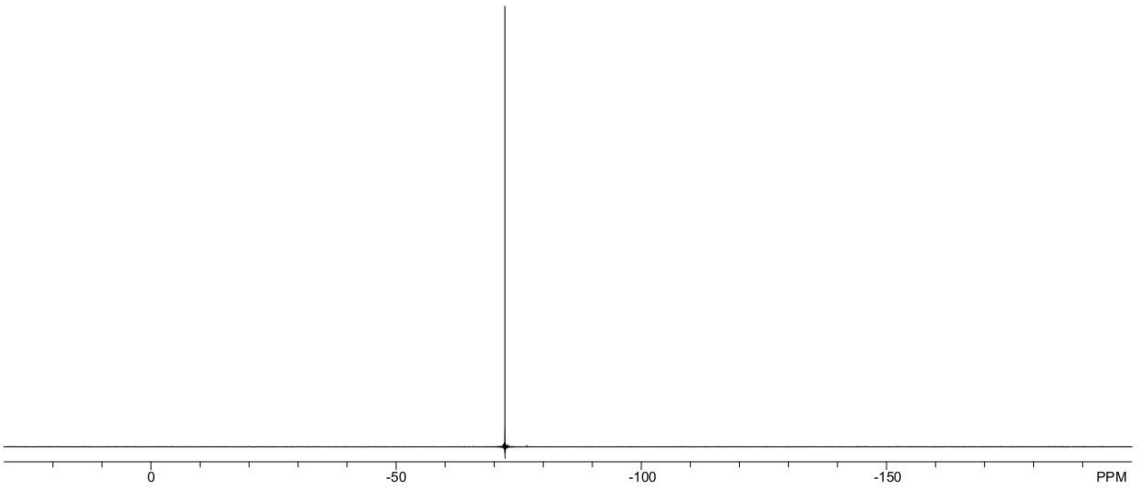
Cl
N
N
CF3
Cl


72.179


0
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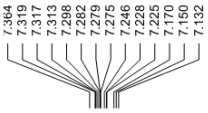
PPM

3a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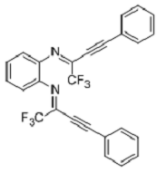
7.132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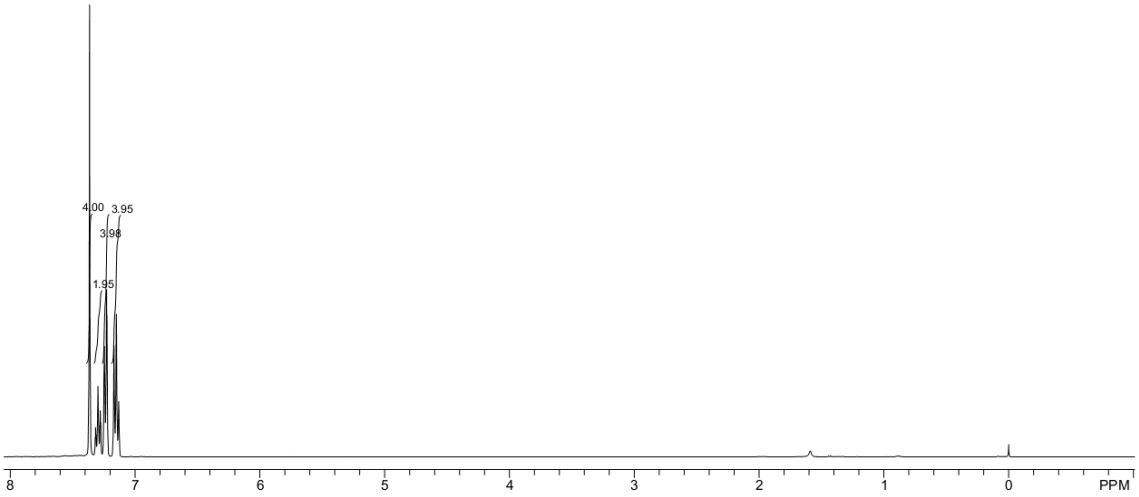
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5
4
3
2
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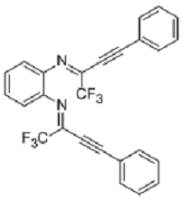
0
PPM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F3C

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-100
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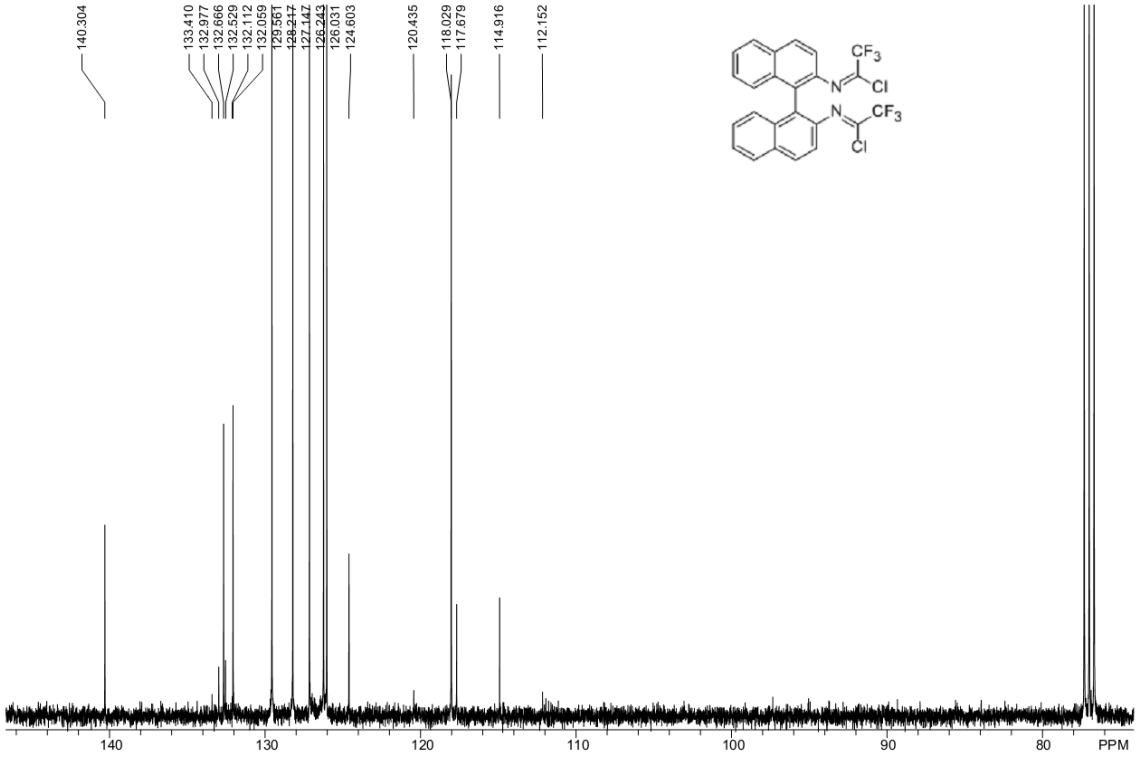
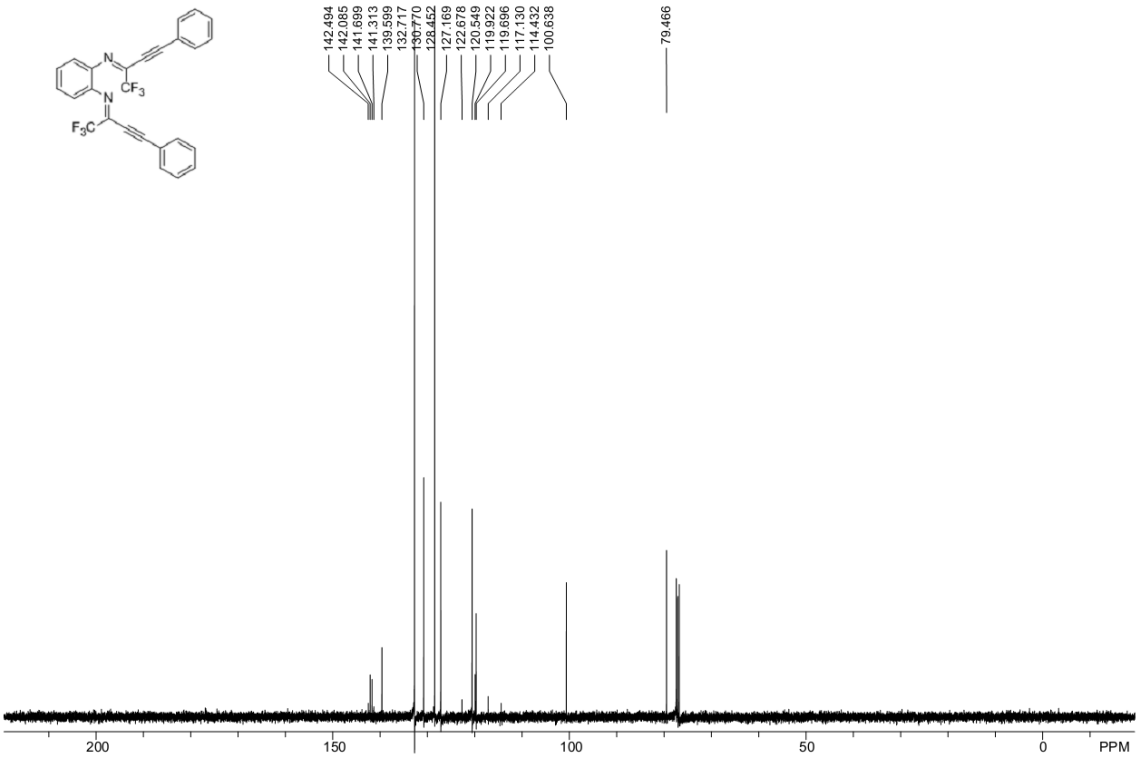
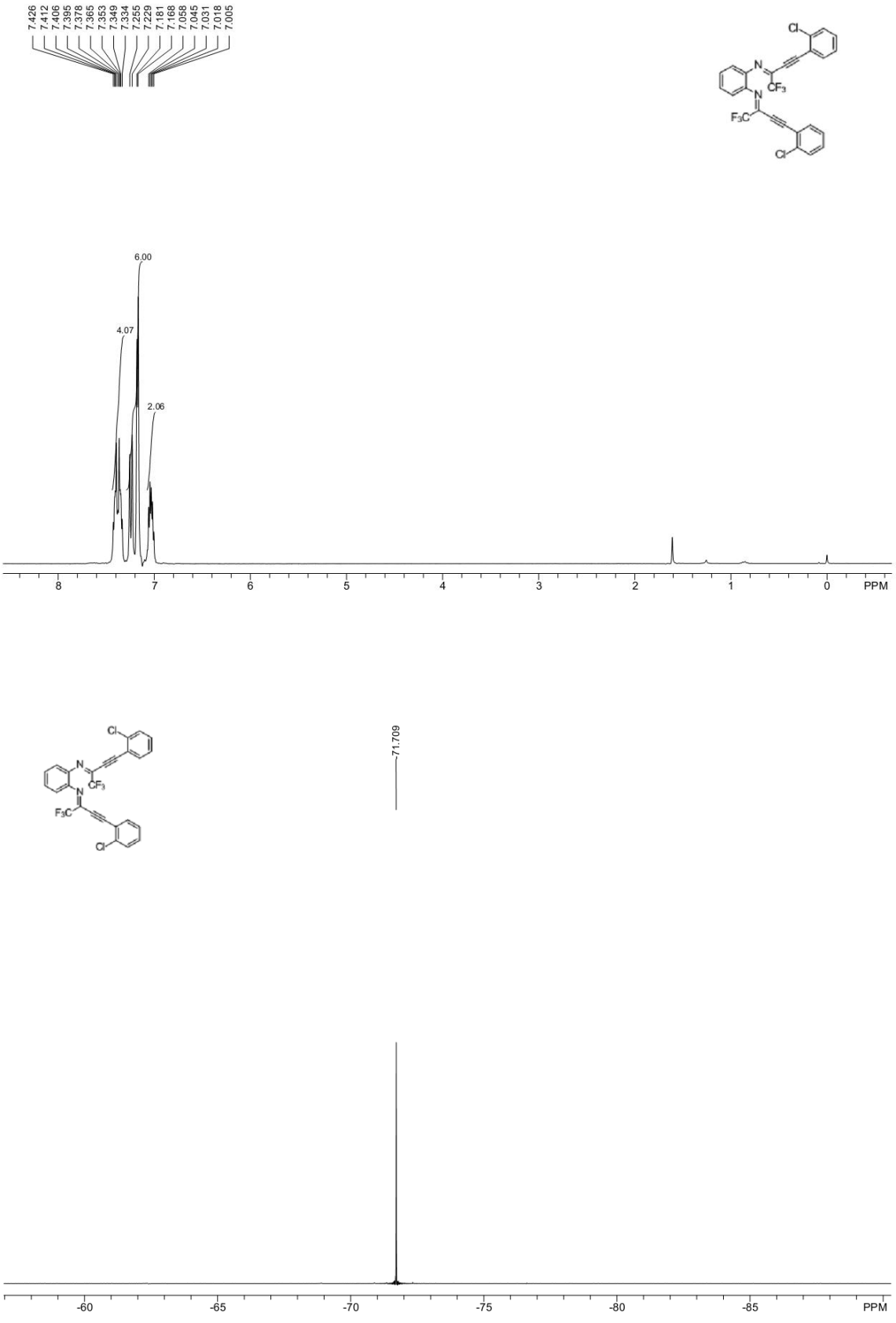
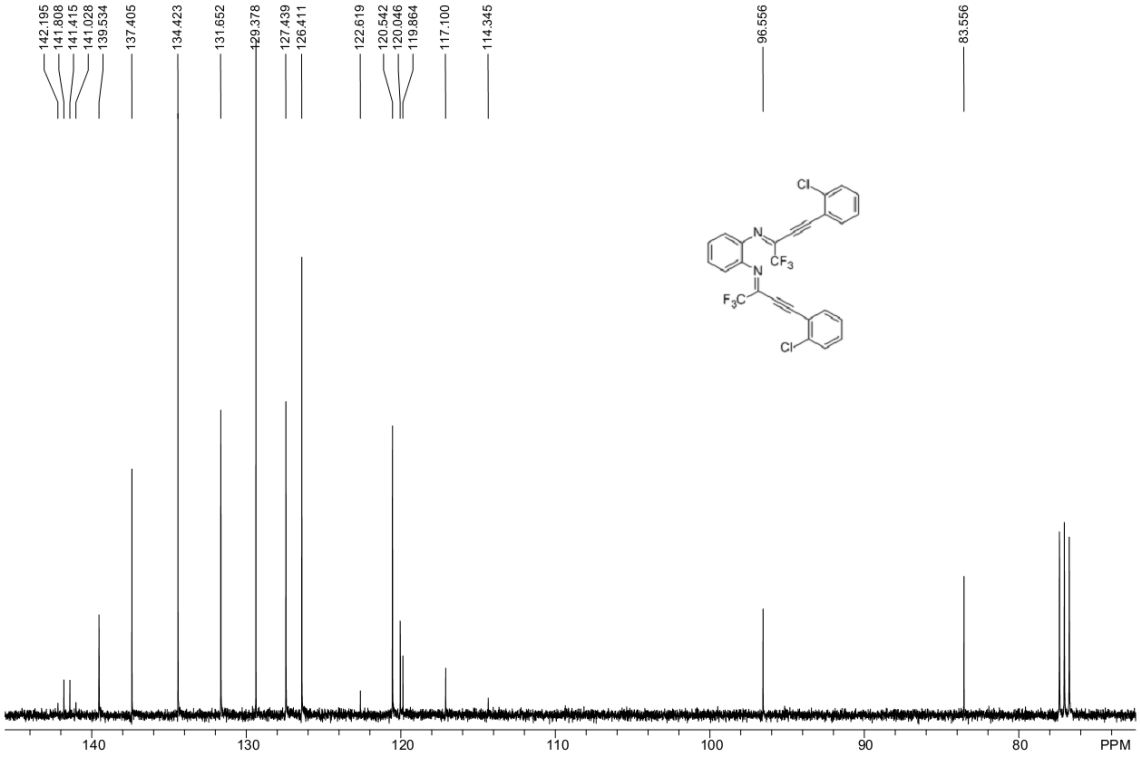
PPM



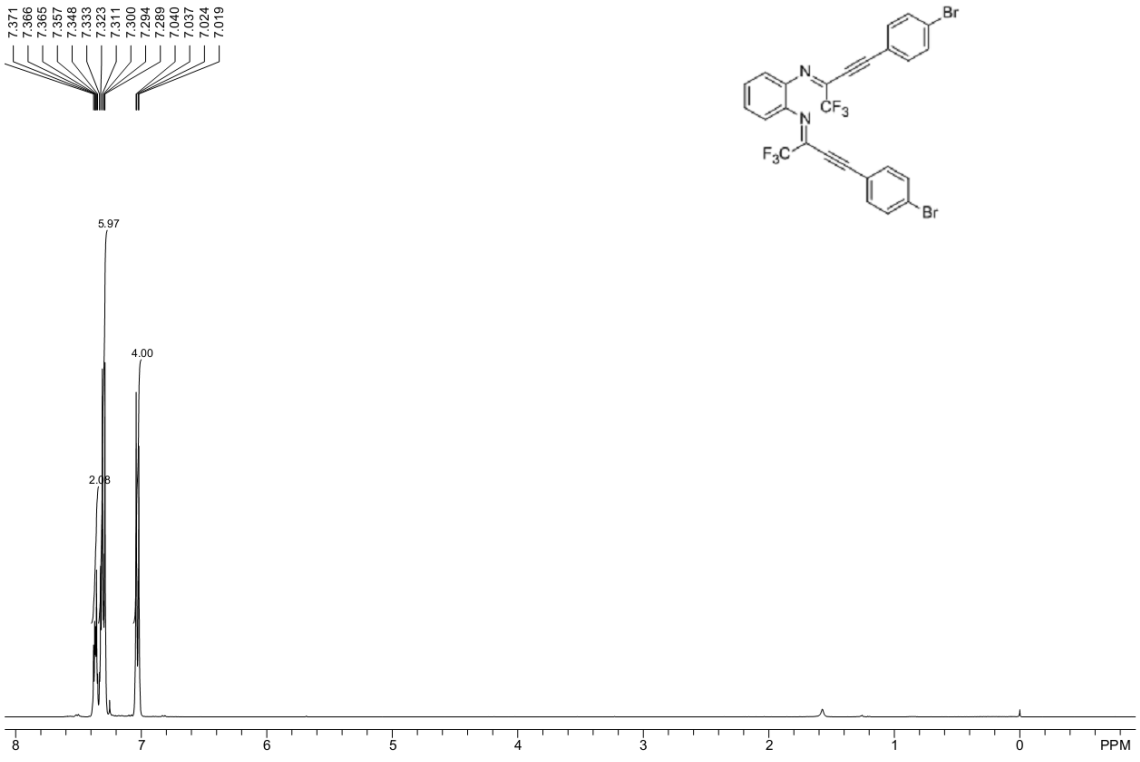


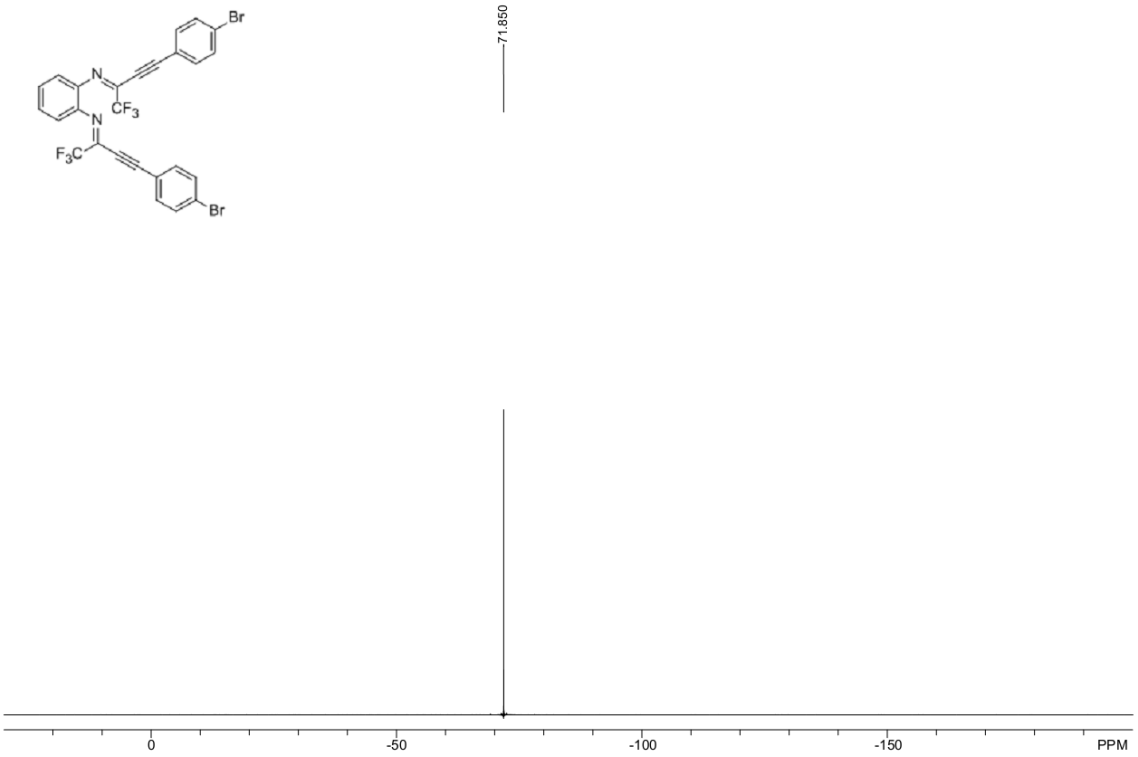
3b

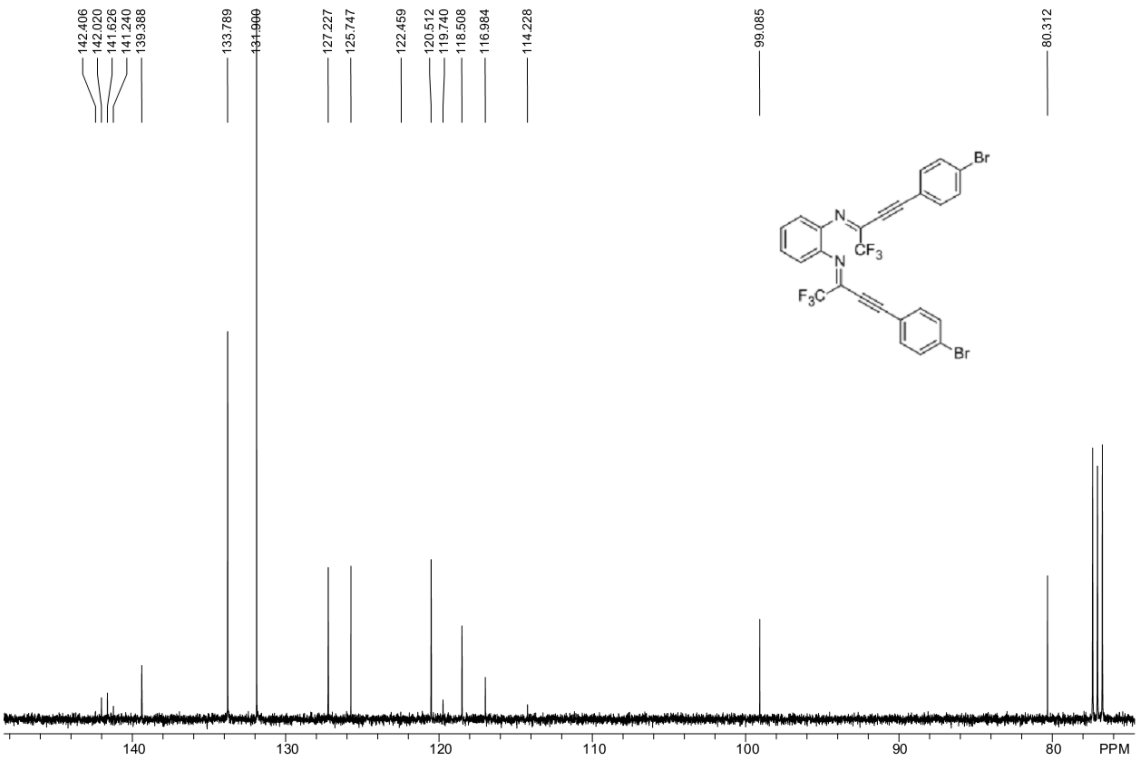




3c







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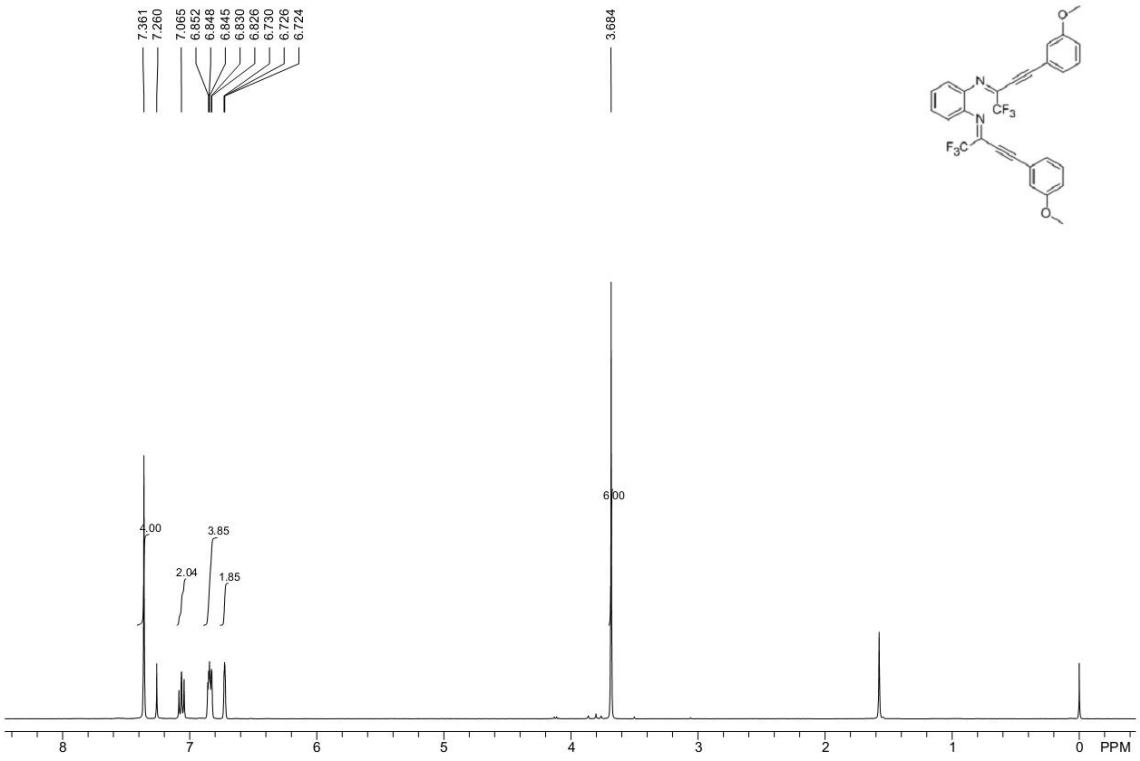

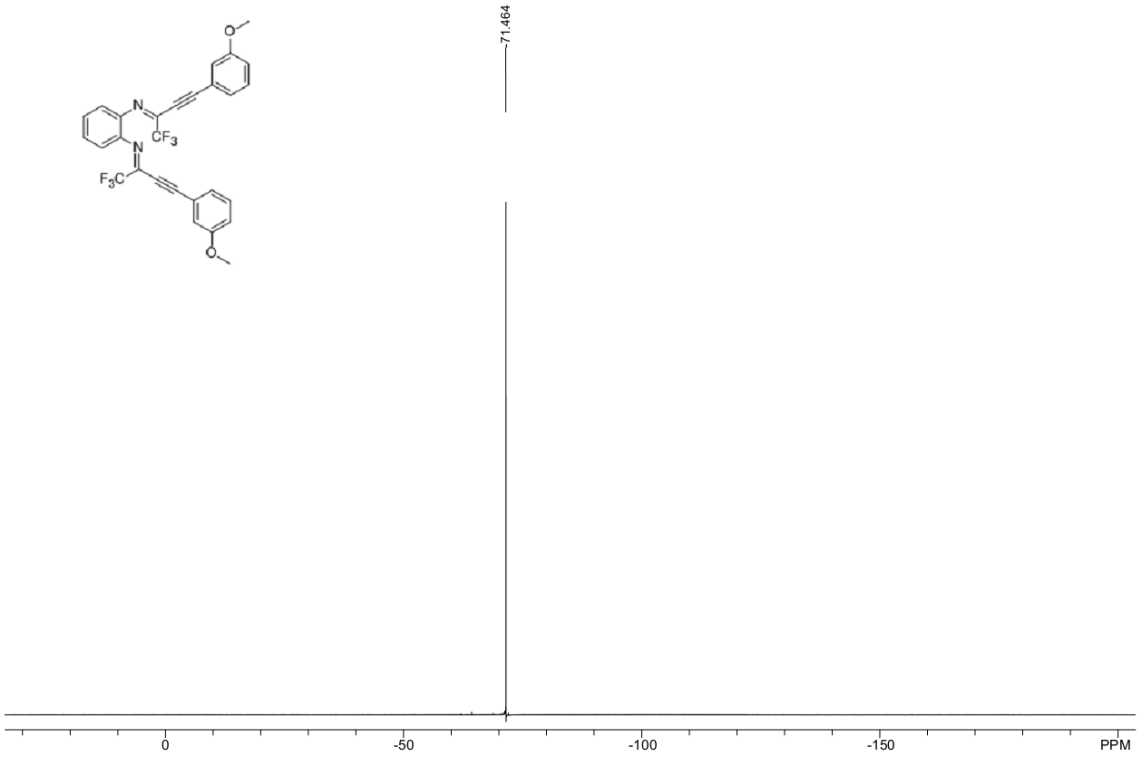

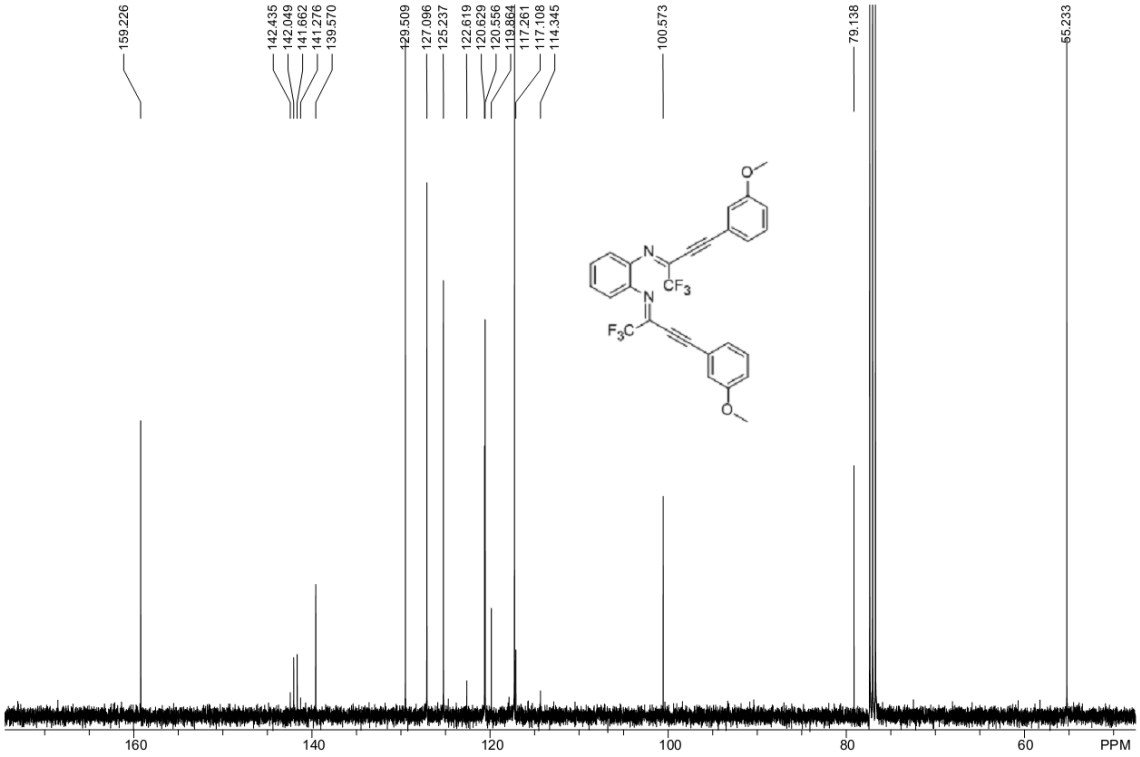
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100.573
79.138
55.233
O
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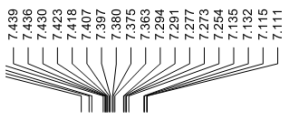
CF3
N
F3C
O
160
140
120
100
80
60
PPM

3e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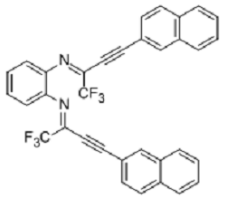
7.132
7.115
7.111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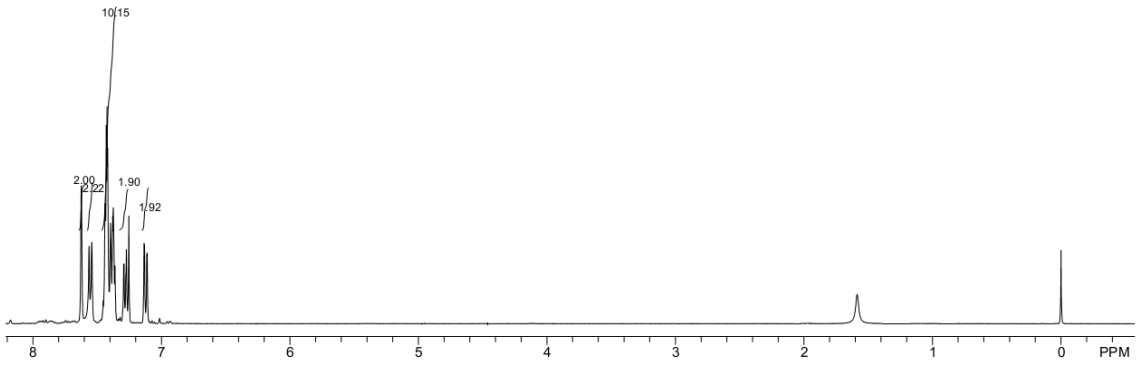
F3C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1.92
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5
4
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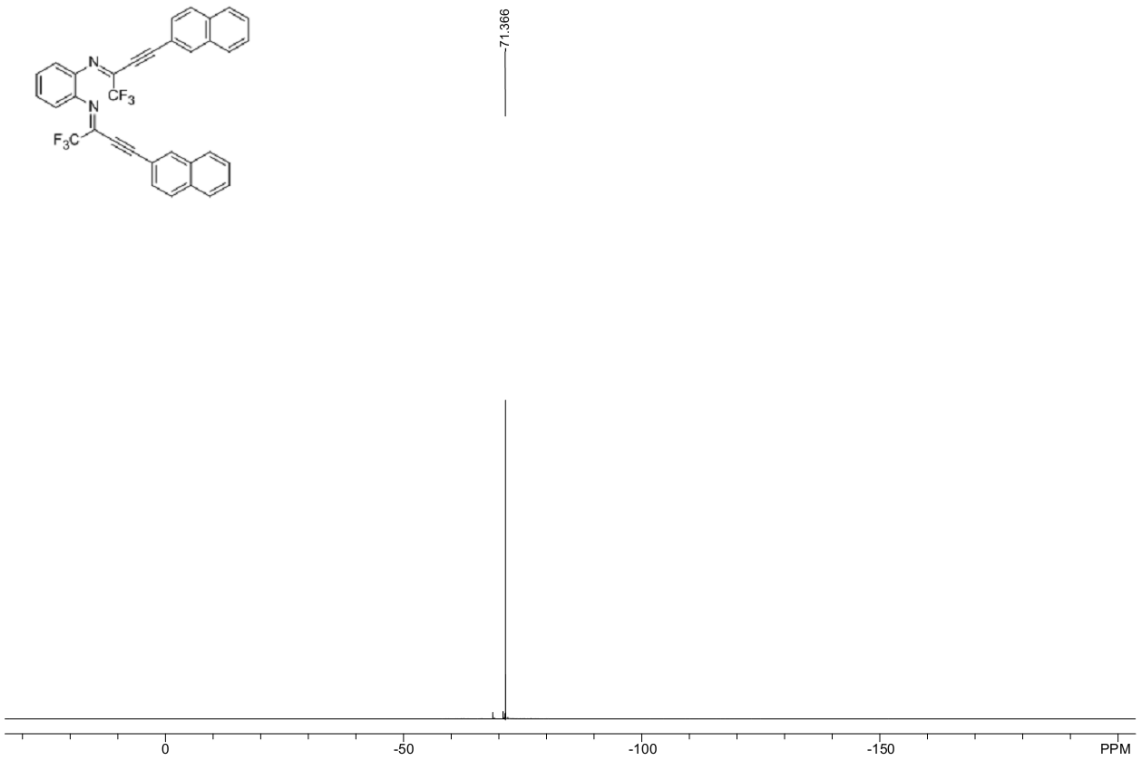
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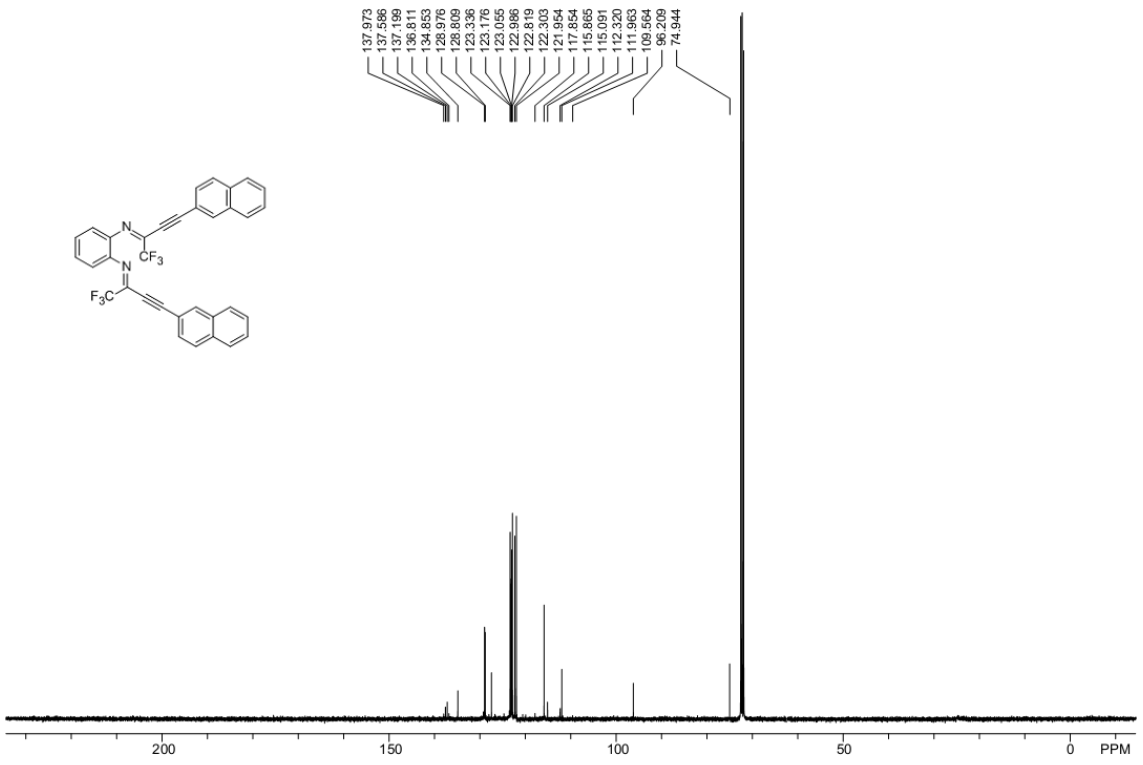
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121.954
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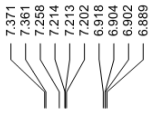
3f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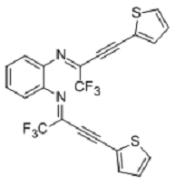
6.902
6.889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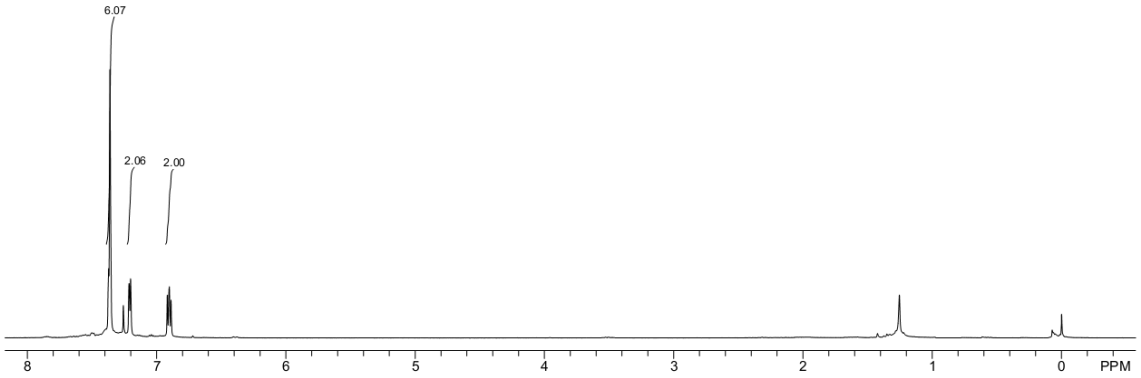
CF3
N
F3C
S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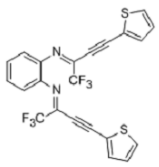
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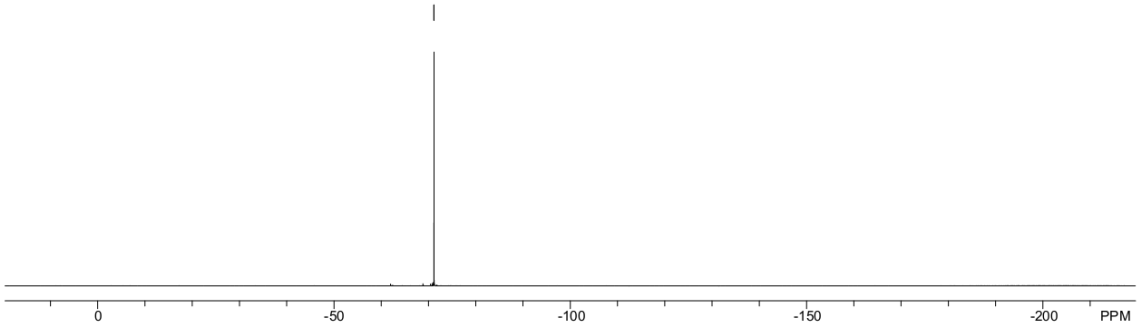
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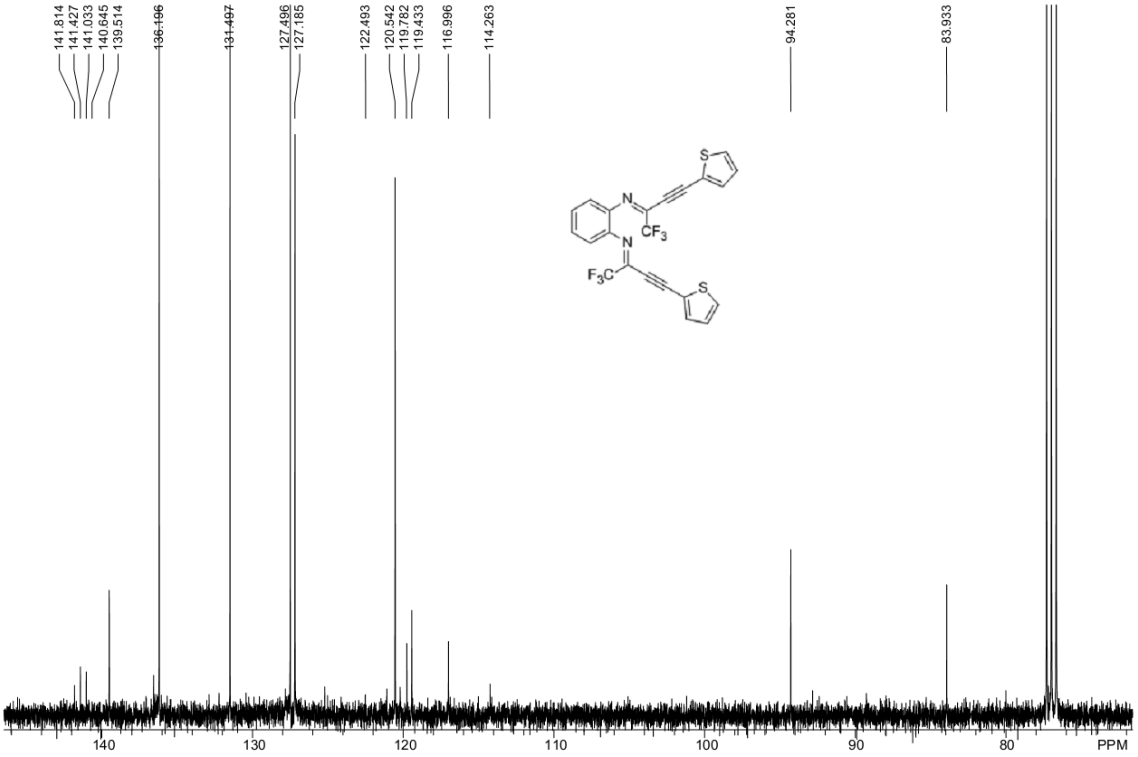
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116.996
114.263
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F3C
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90
80
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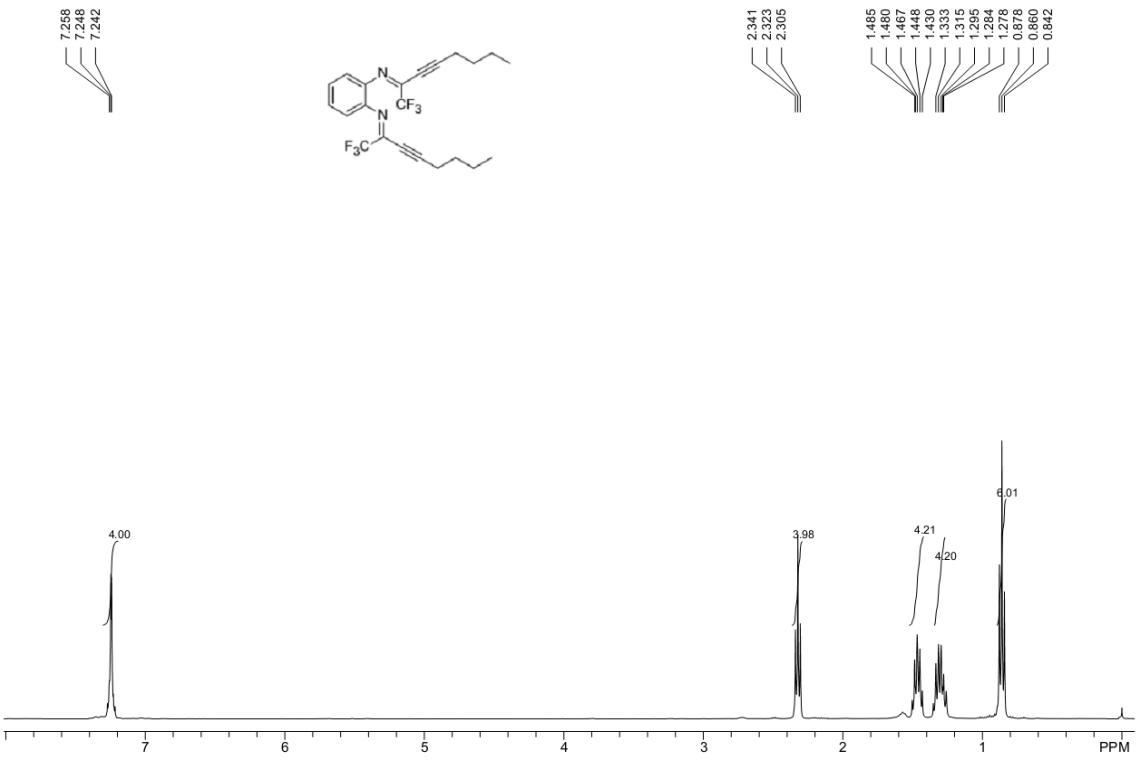
3g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F3C
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1.480
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1.448
1.430
1.333
1.315
1.295
1.284
1.278
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3
2
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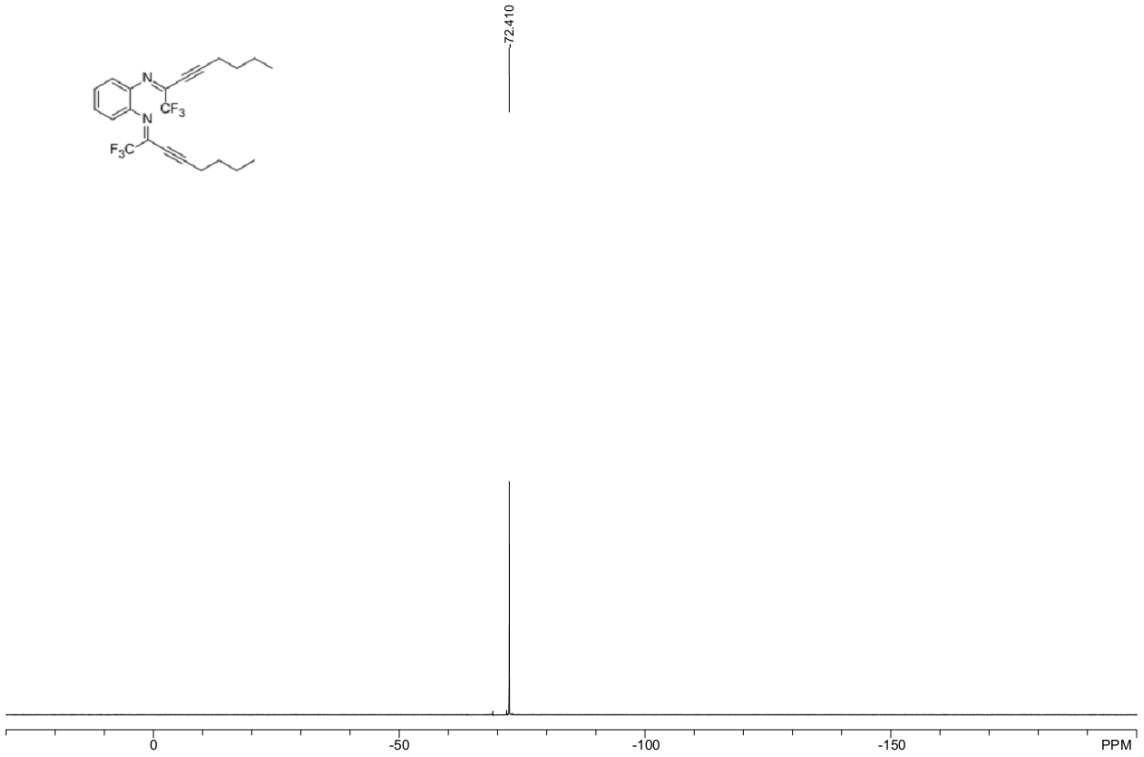
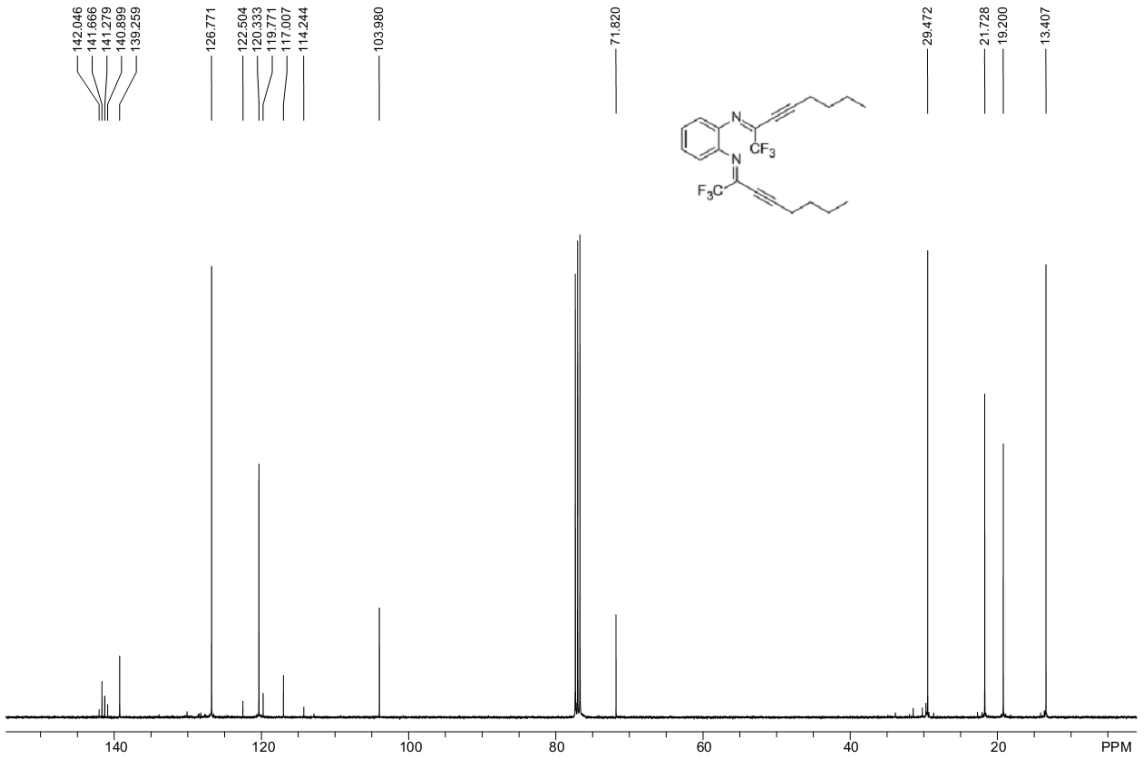
PPM





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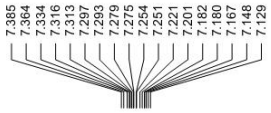
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7.297
7.293
7.279
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7.251
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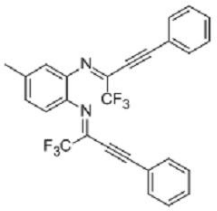
7.201
7.182
7.180
7.167
7.148
7.129


2.442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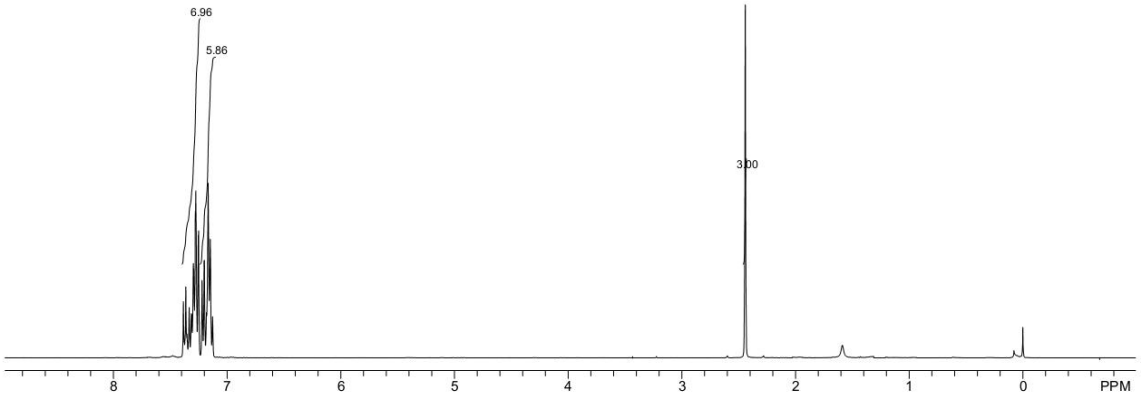
F3C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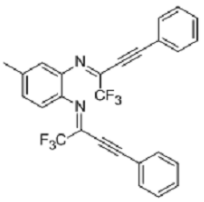
71.486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CF3
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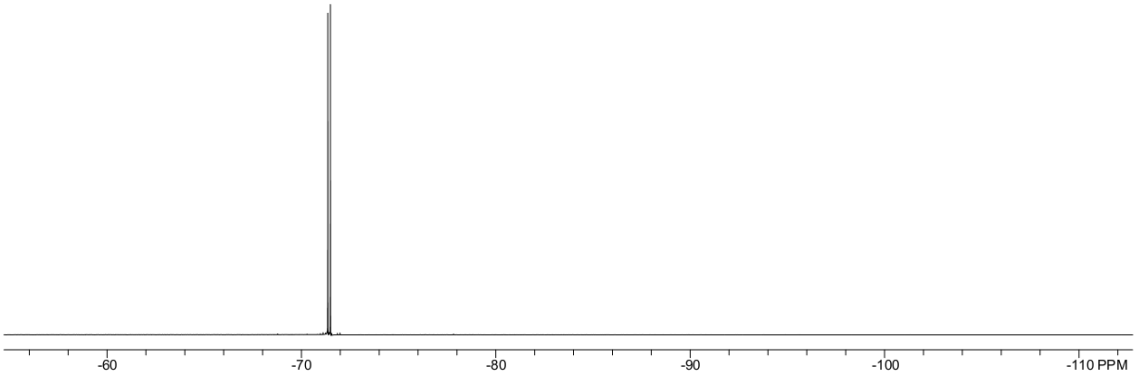
F3C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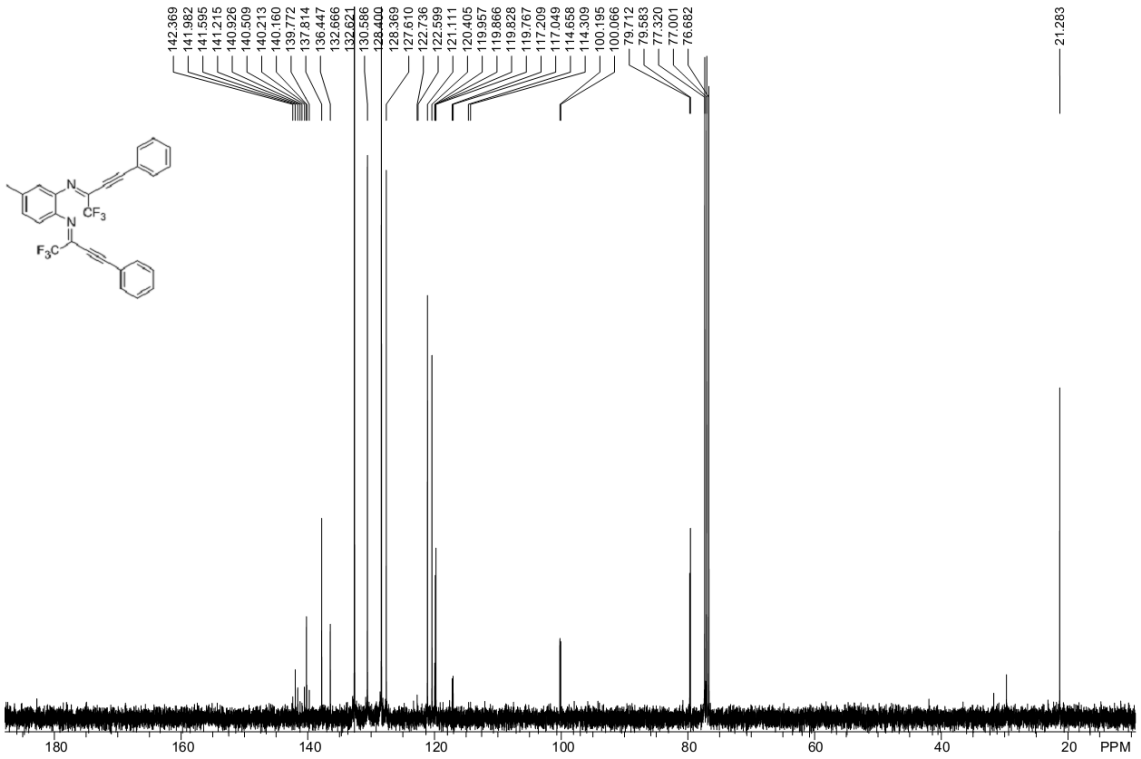
-100
-110 PPM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140.213
140.160
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132.666
132.621
130.586
128.400
128.369
127.610
122.736
122.599
121.111
120.405
119.957
119.866
119.828
119.767
117.209
117.049
114.658
114.309
100.195
100.066
79.712
79.583
77.320
77.001
76.682
21.283
180
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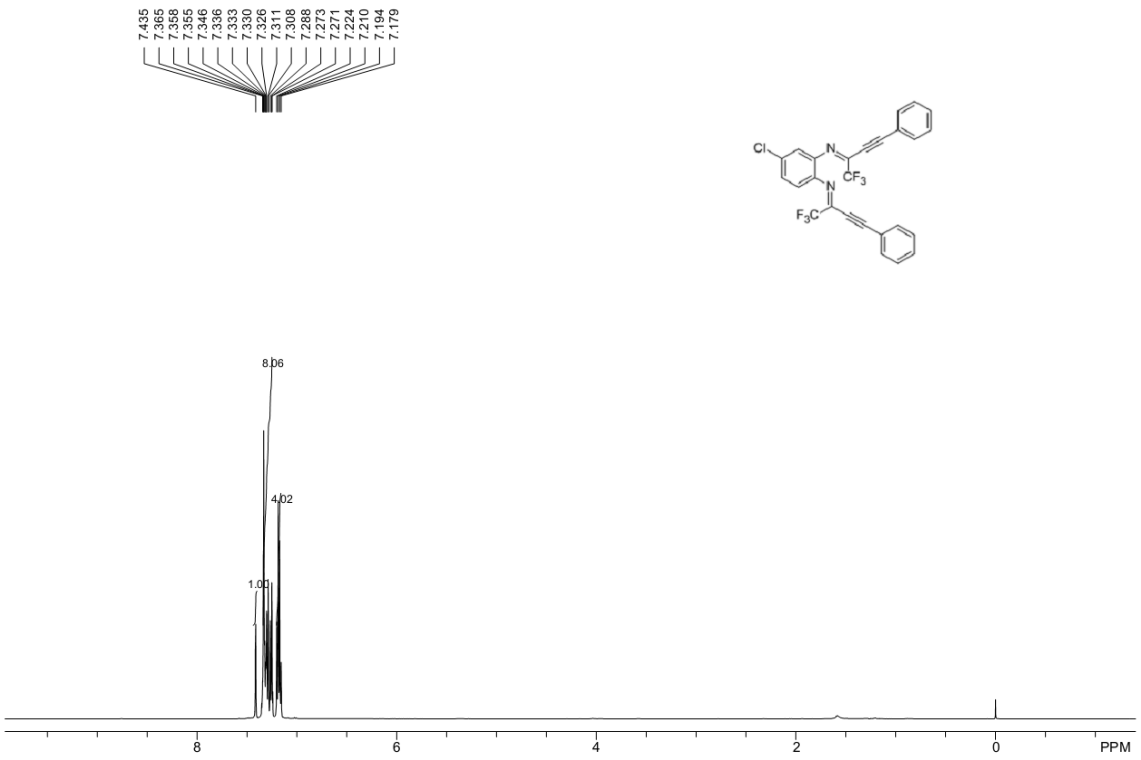
140
120
100
80
60
40
20
PPM

3i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7.333
7.330
7.326
7.311
7.308
7.288
7.273
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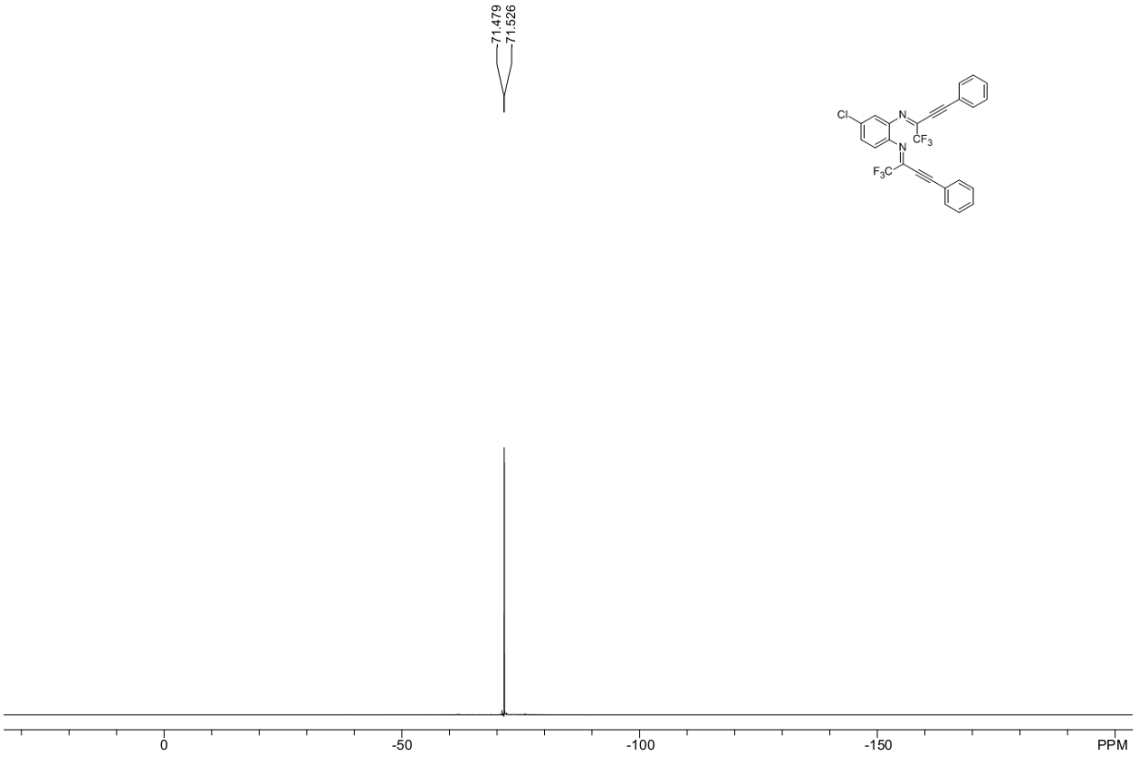
4.02
1.00
8
6
4
2
0
PPM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F3C
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-100
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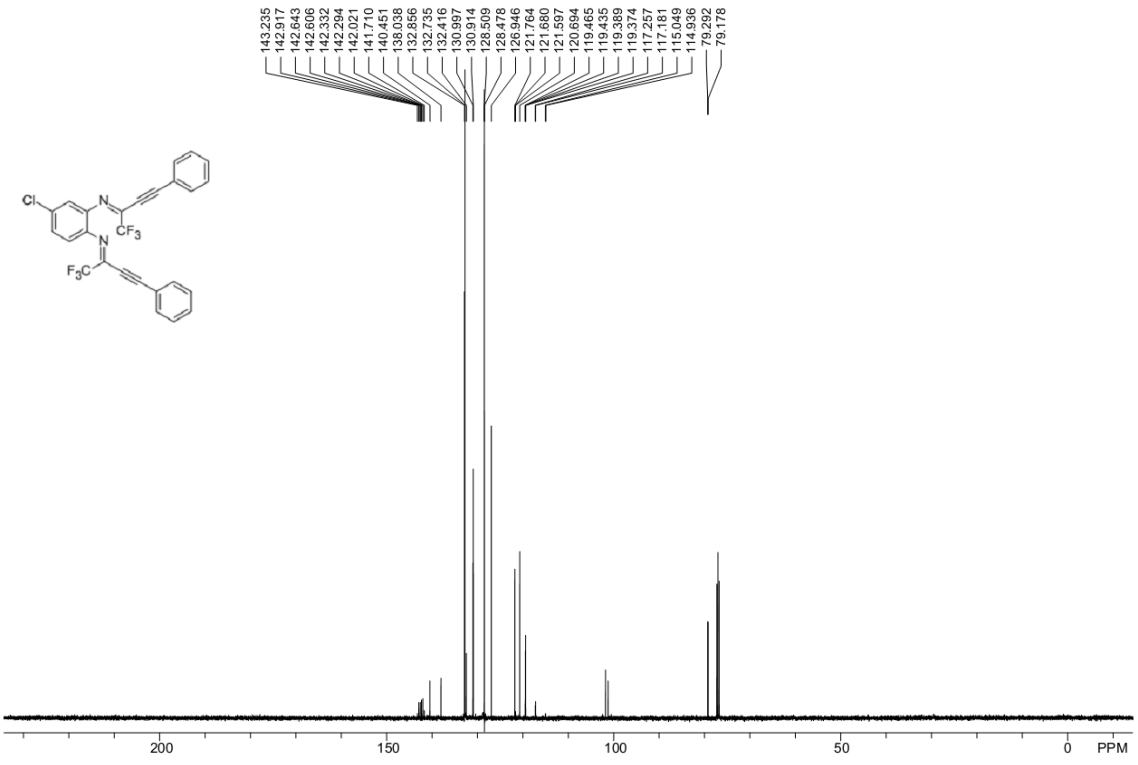
PPM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142.332
142.294
142.021
141.710
140.451
138.038
132.856
132.735
132.416
130.997
130.914
128.509
128.478
126.946
121.764
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121.597
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119.465
119.435
119.389
119.374
117.257
117.181
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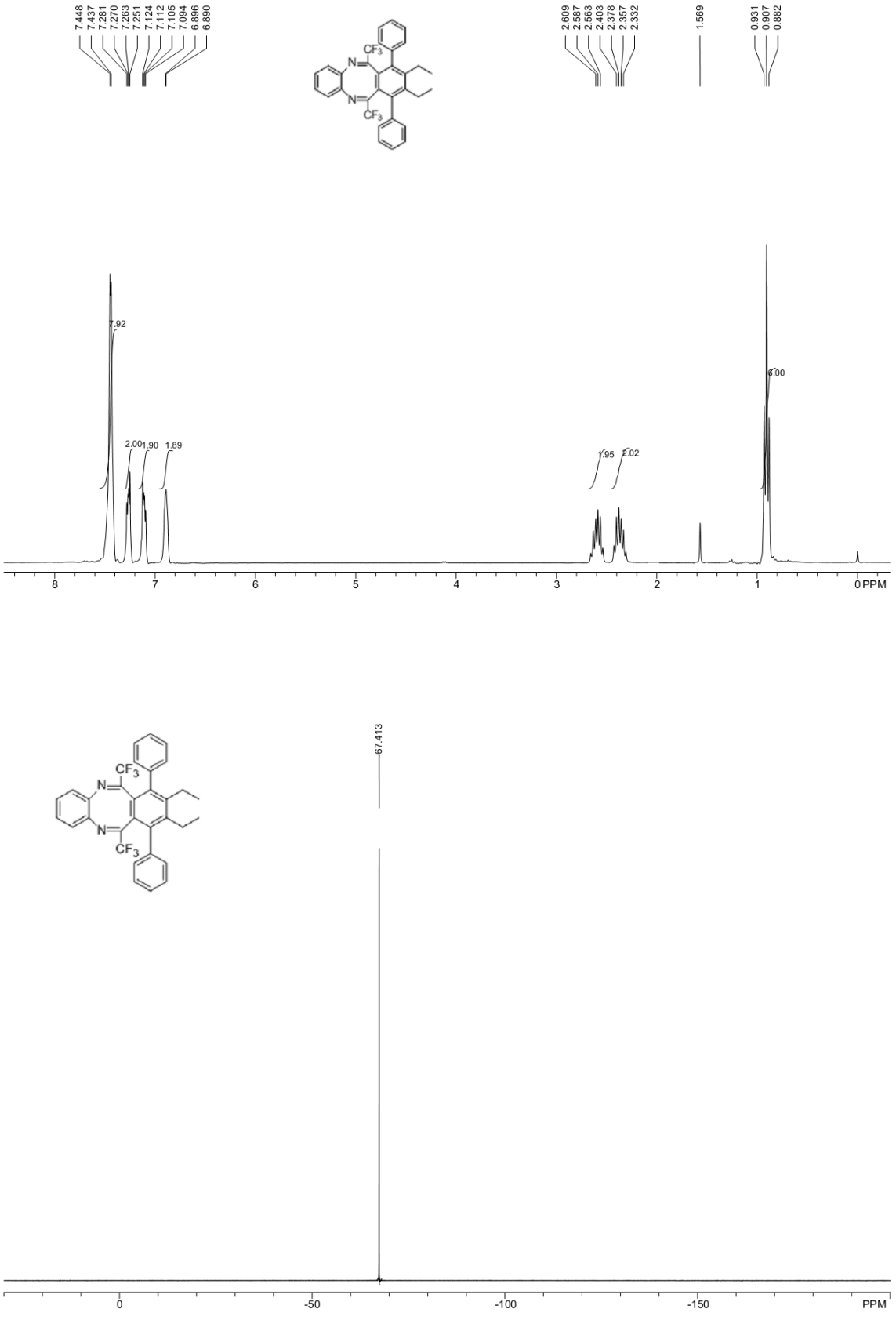
79.292
79.178
Cl
N
CF3
N
F3C
200
150
100
50
0
PPM

4a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7.251
7.124
7.112
7.105
7.094
6.896
6.890
2.609
2.587
2.563
2.403
2.378
2.357
2.332
1.569
0.931
0.907
0.882
CF3
N
CF3
7.92
2.00
1.90
1.89
1.95
2.02
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8
7
6
5
4
3
2
1
0 PPM
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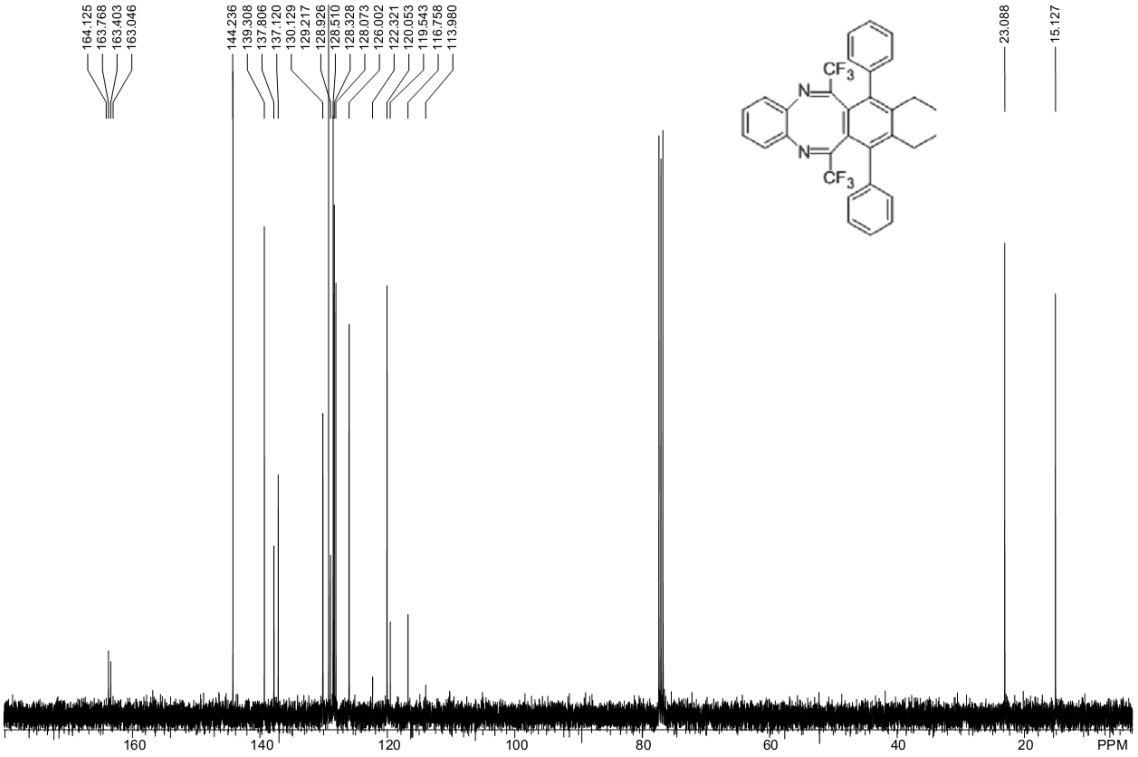
-100
-150
PPM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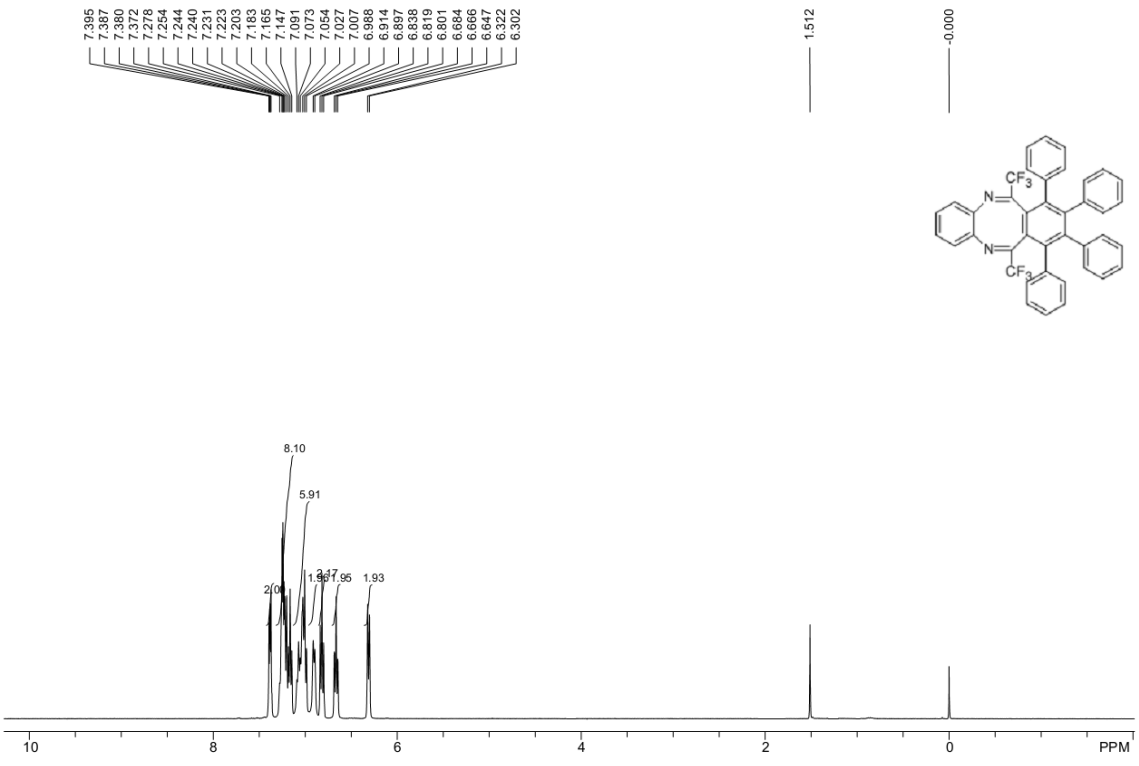
40
20
PPM

4b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7.223
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7.165
7.147
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7.073
7.054
7.027
7.007
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6.897
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6.819
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6.302
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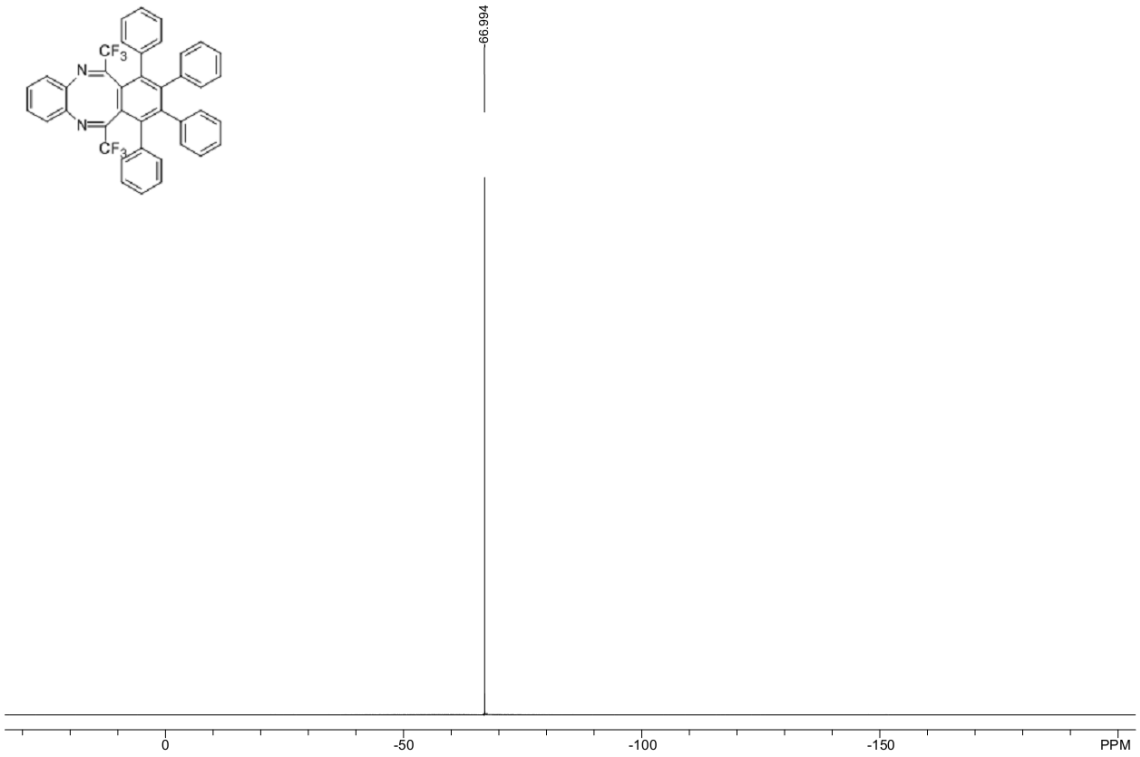
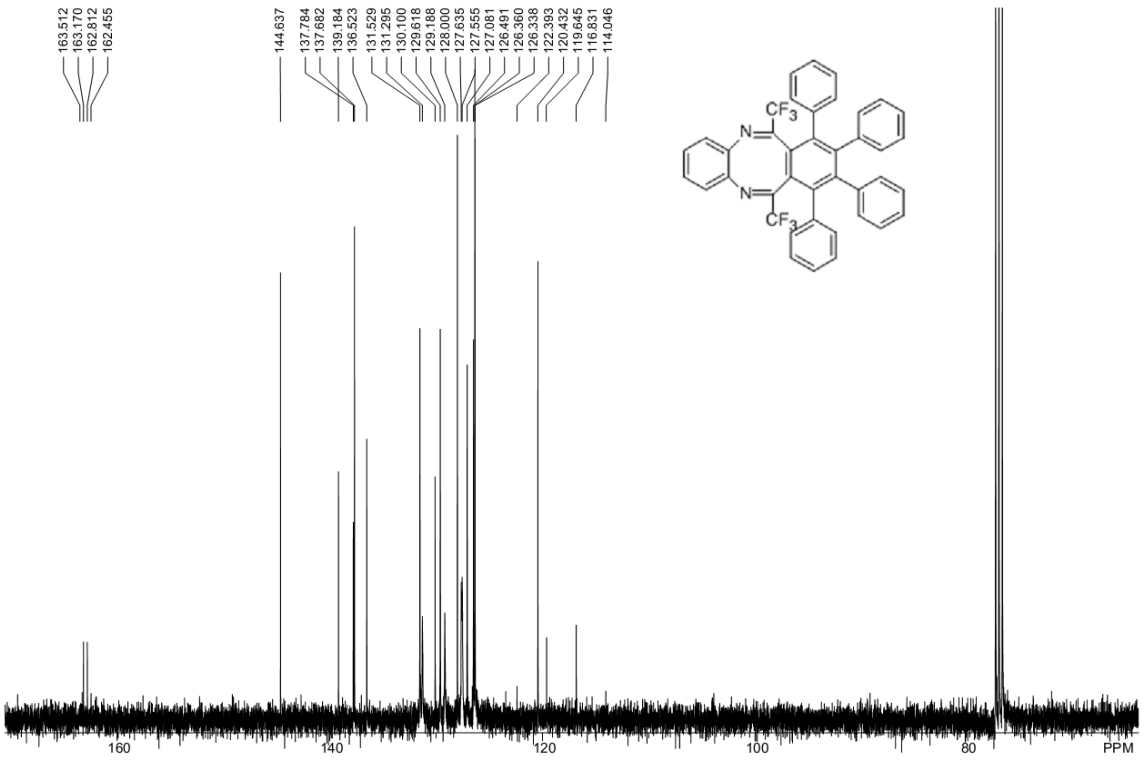
PPM





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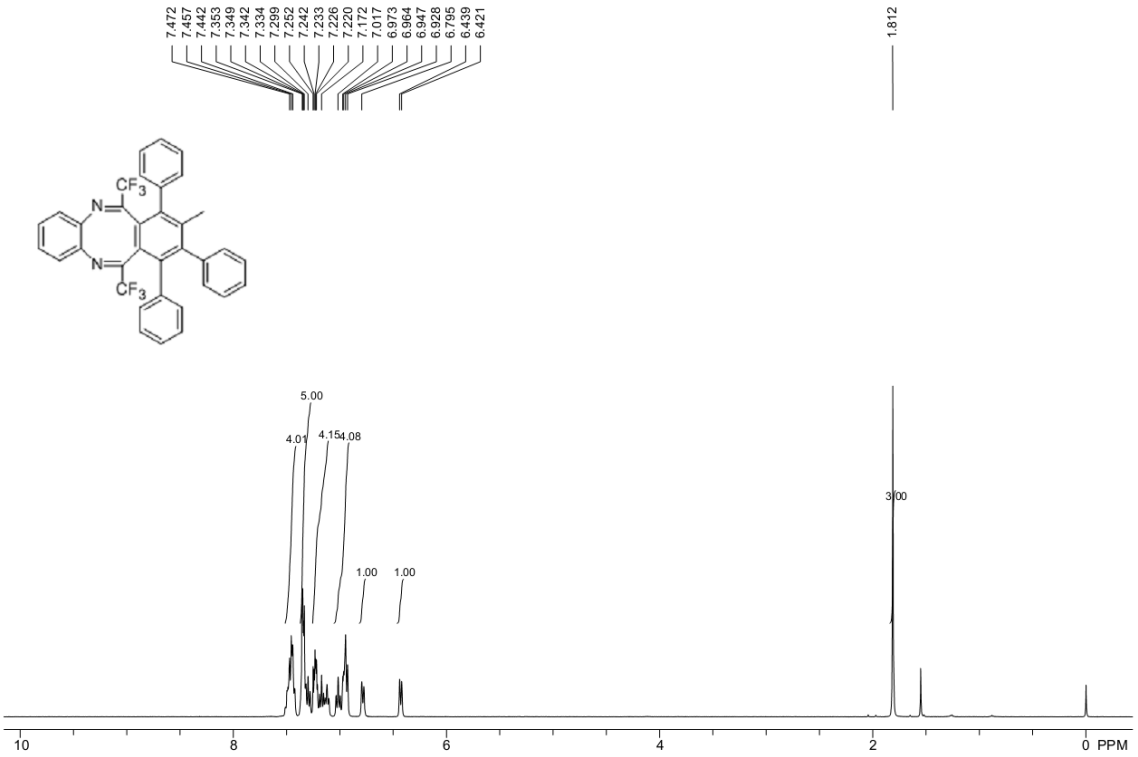

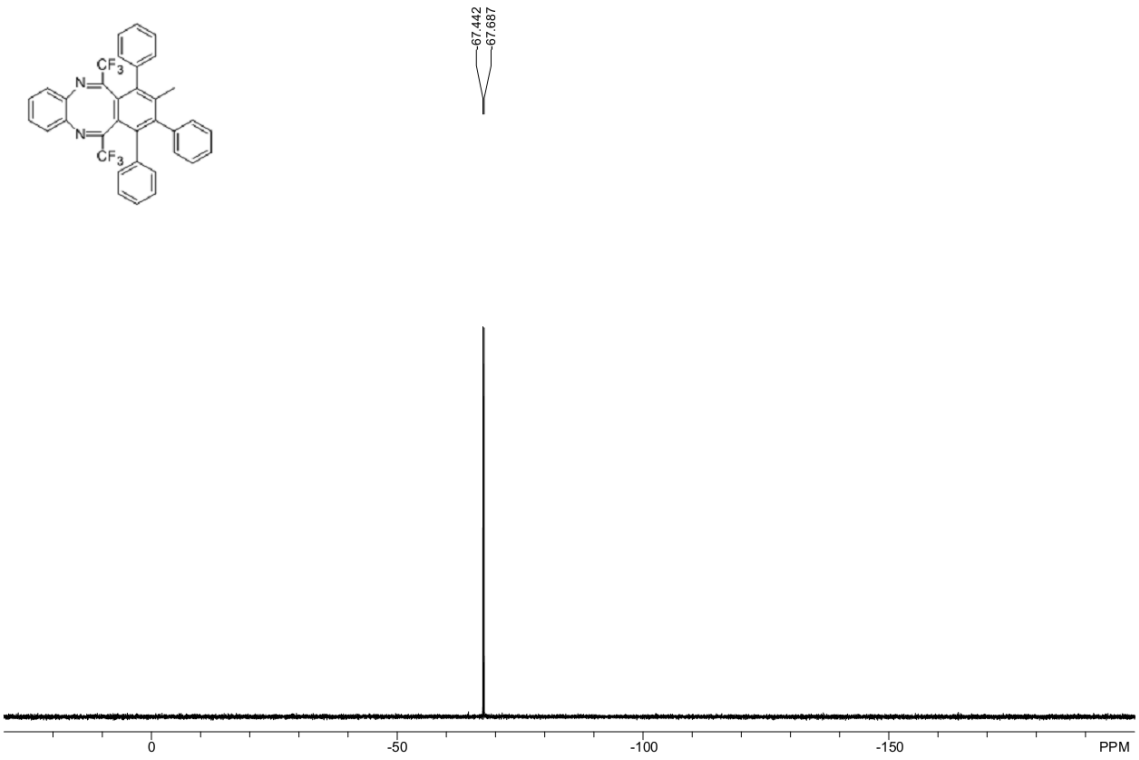

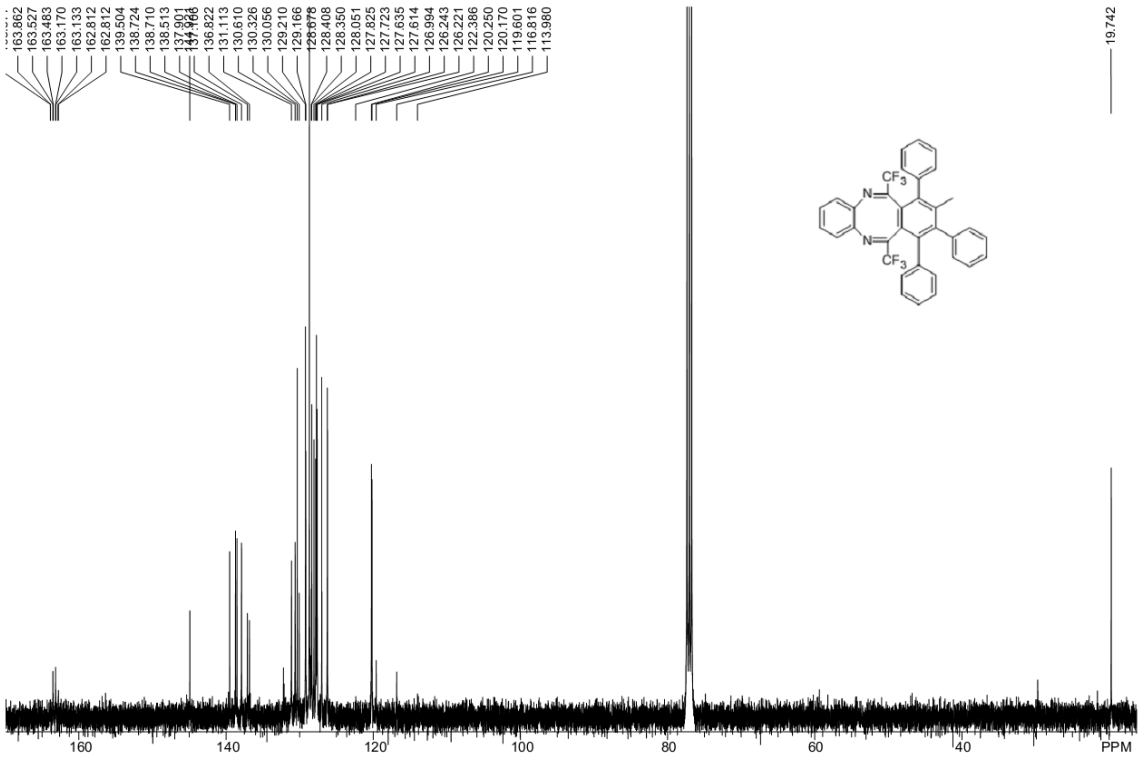
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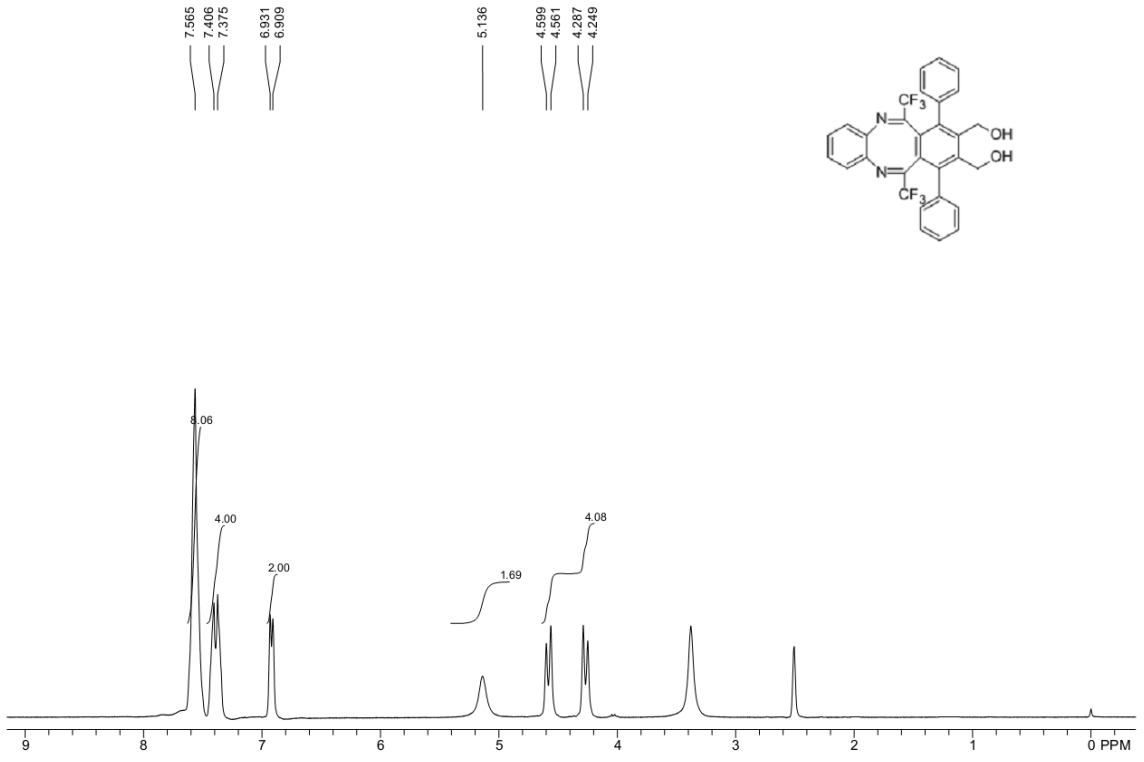
PPM

4d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4.561
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4.249
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N
CF3
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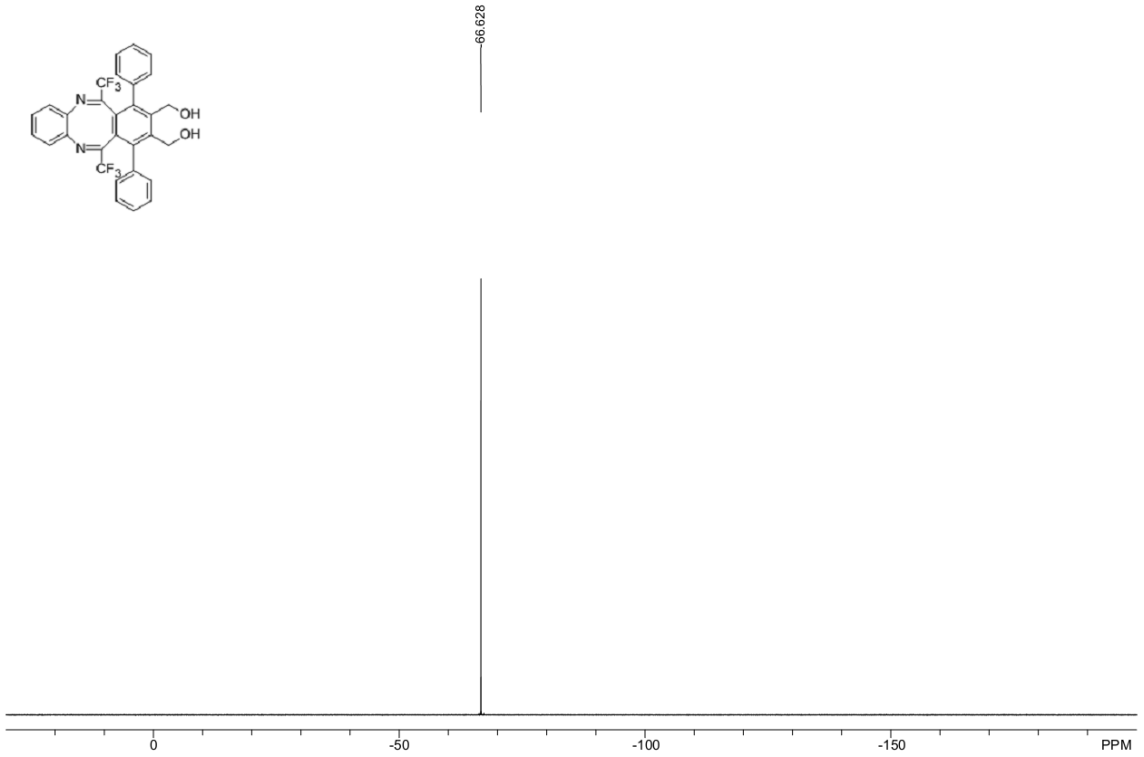
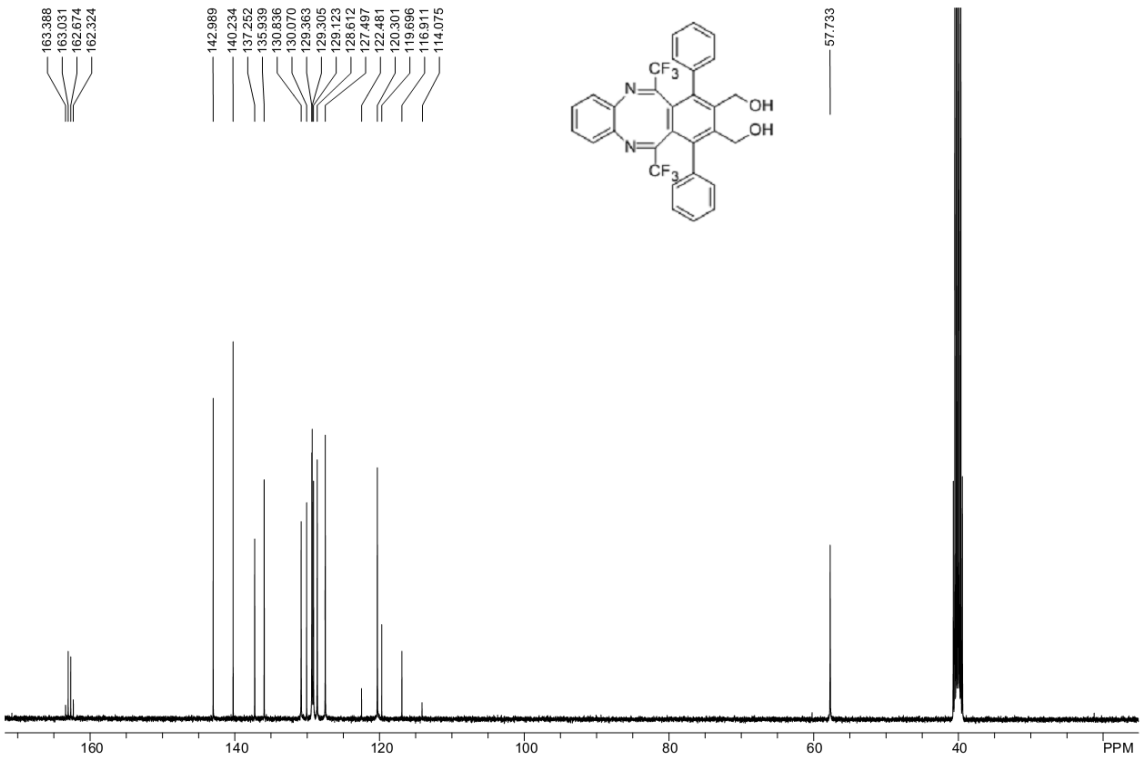
0 PPM





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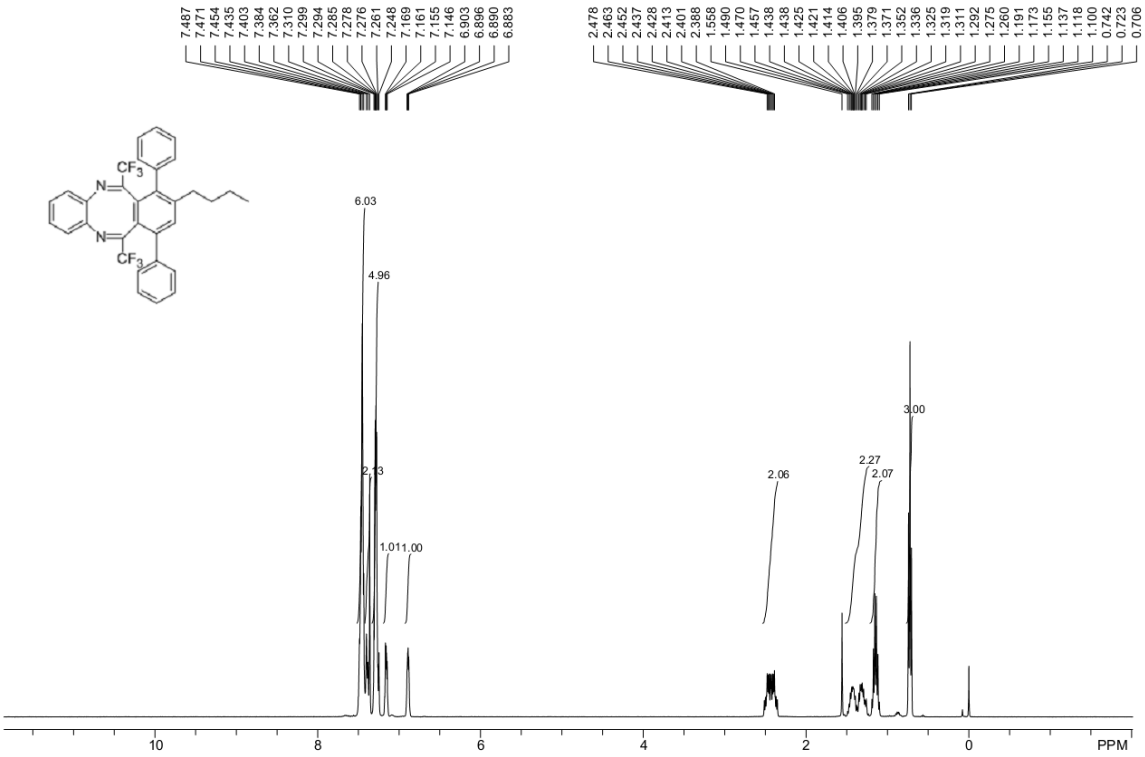
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7.248
7.169
7.161
7.155
7.146
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6.896
6.890
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1.173
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0.706
CF3
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N
CF3
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10
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4
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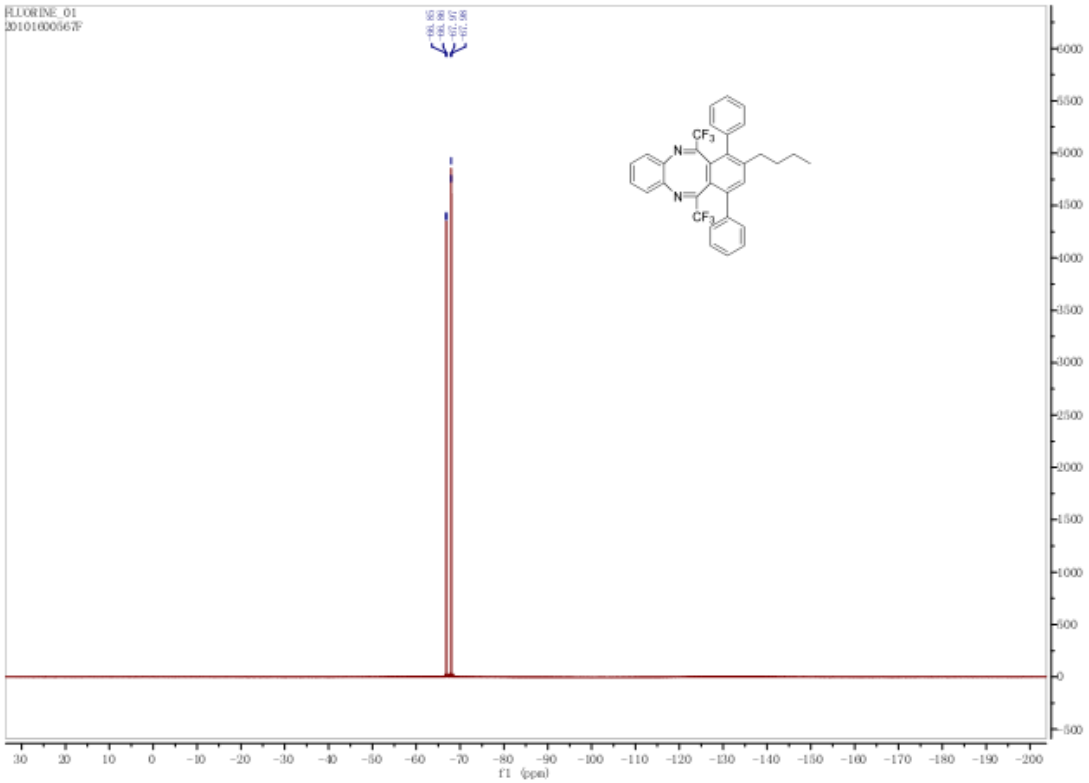
0
PPM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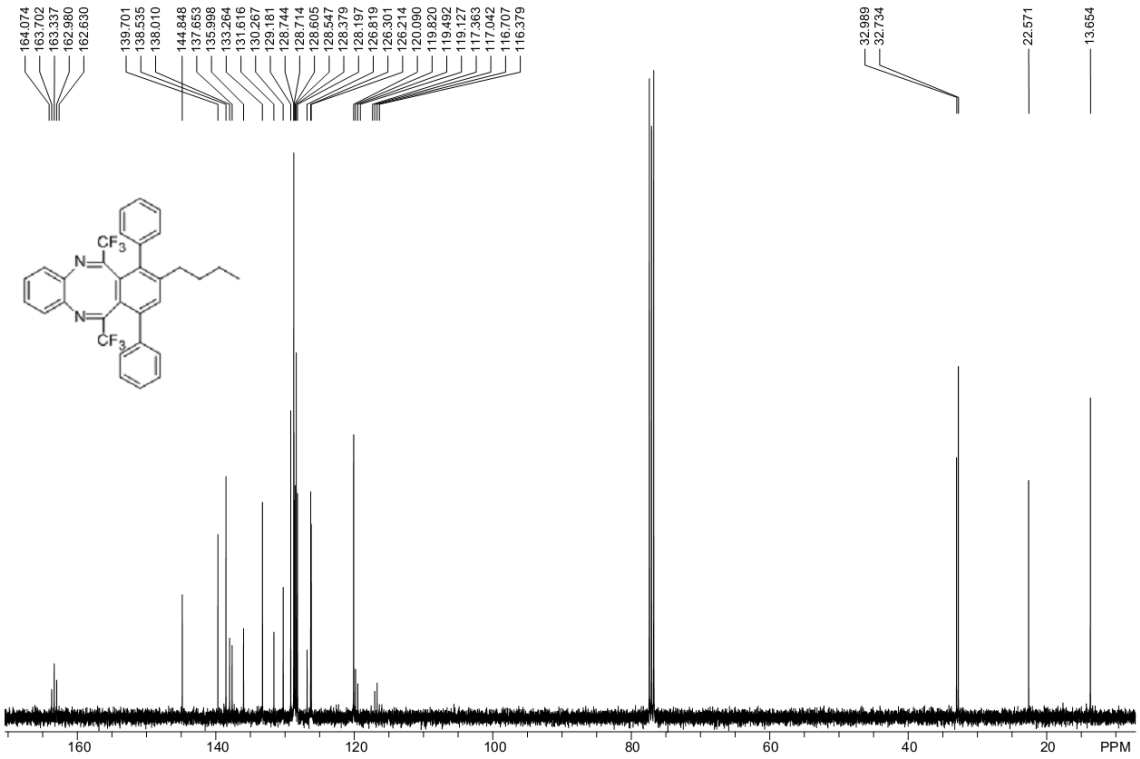
CF3
f1 (ppm)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126.301
126.214
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116.707
116.379
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32.734
22.571
13.654
CF3
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N
CF3
160
140
120
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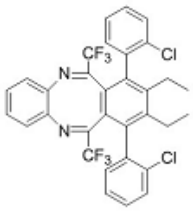
60
40
20
PPM

4h-1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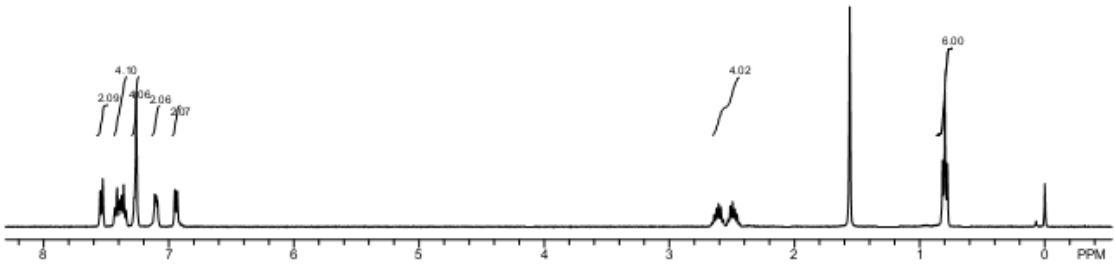
Cl
N
N
CF3
Cl

4h-1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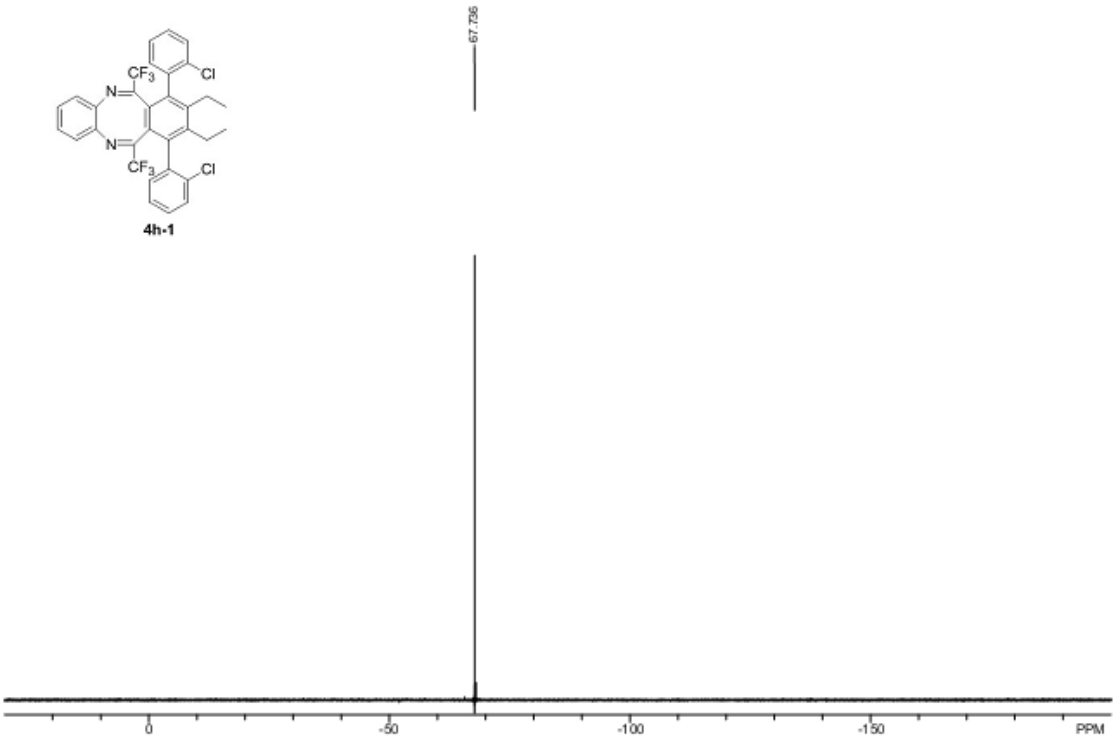
4.06
2.06
2.07
4.02
6.00
8
7
6
5
4
3
2
1
0
PPM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-100
-150
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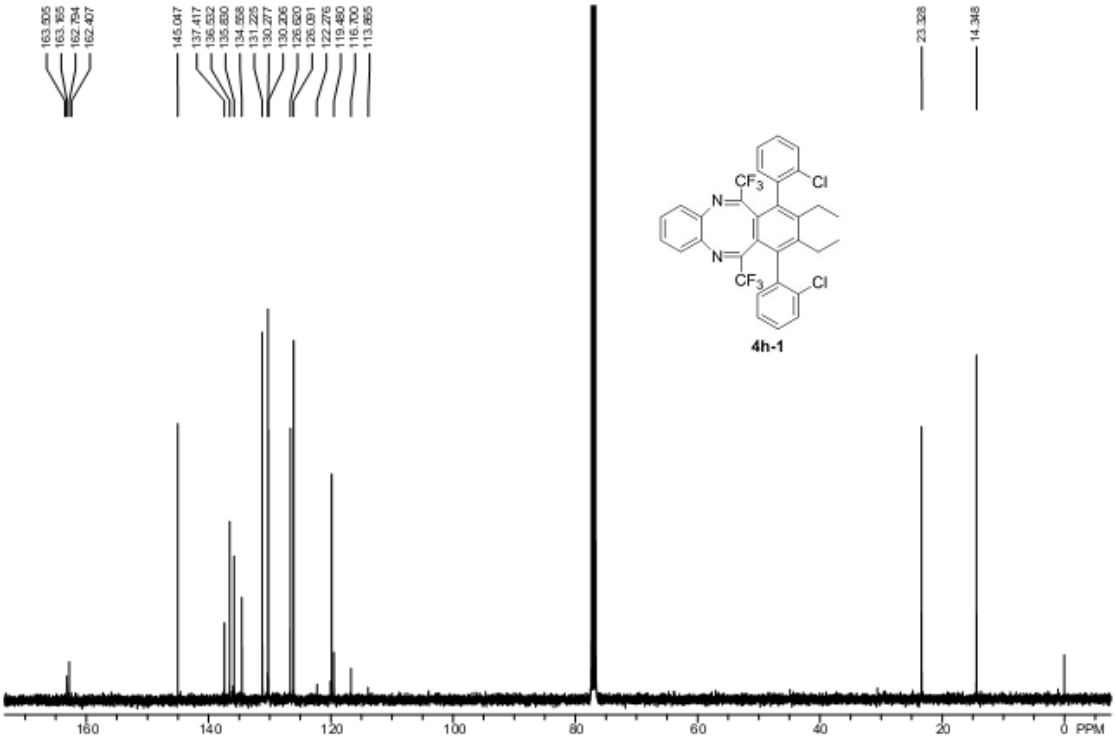
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162.407
145.047
137.417
136.532
135.830
134.568
131.225
130.277
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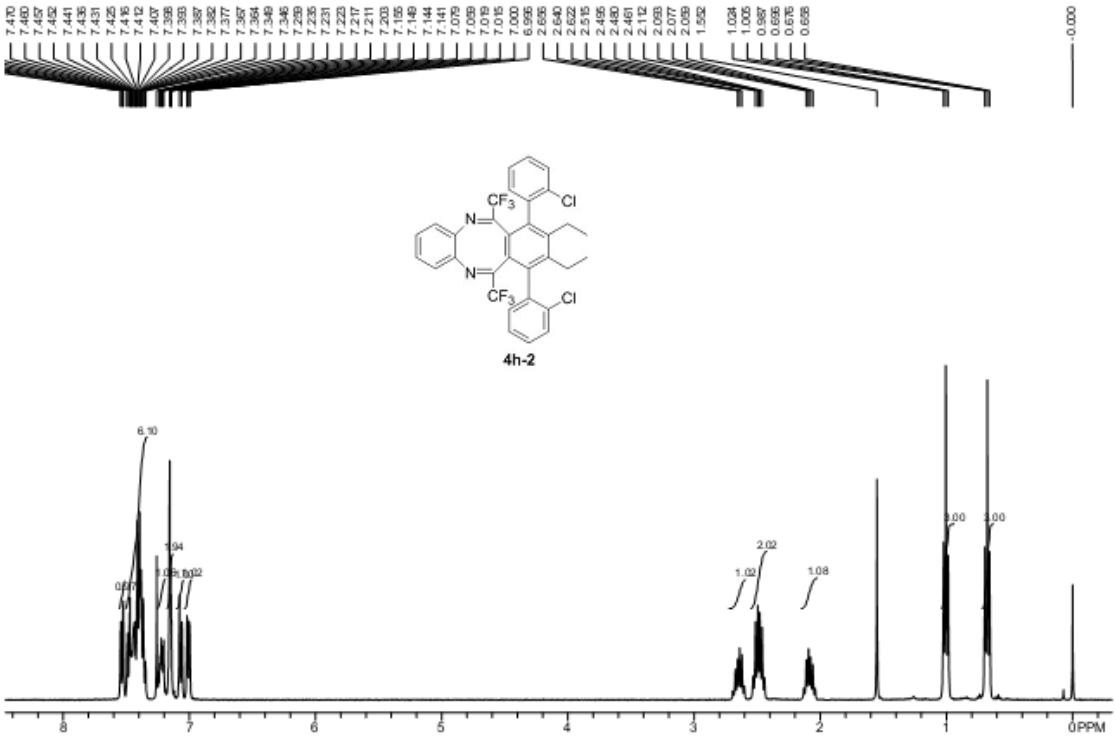
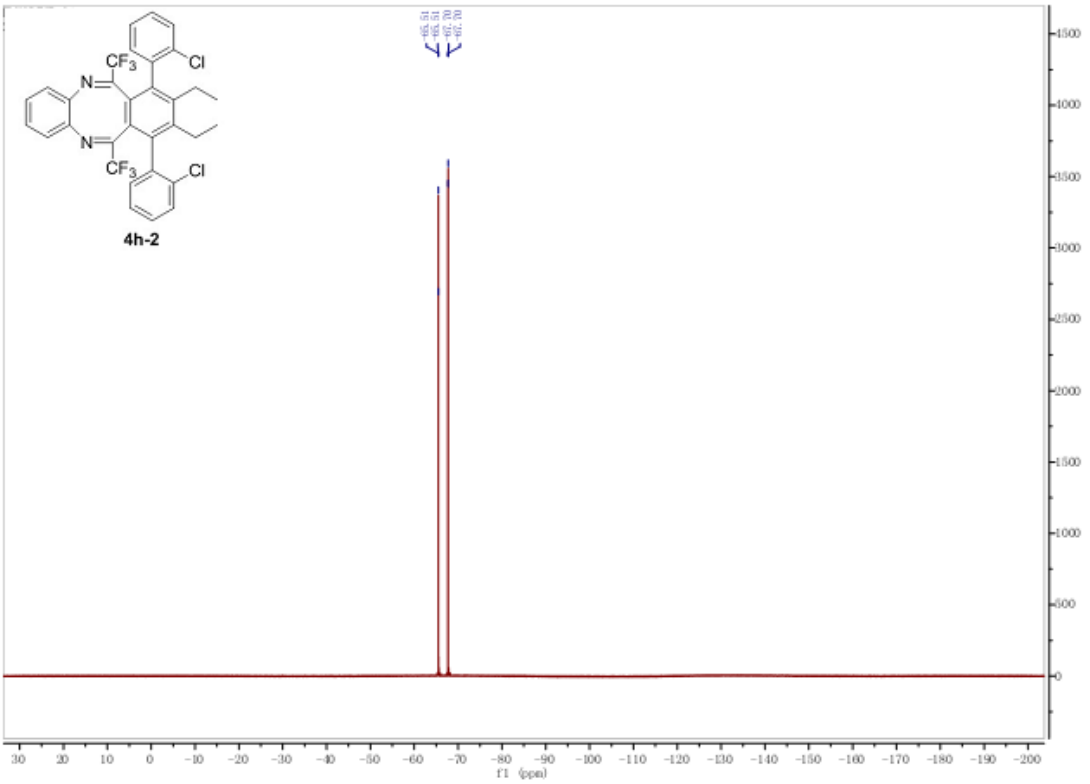
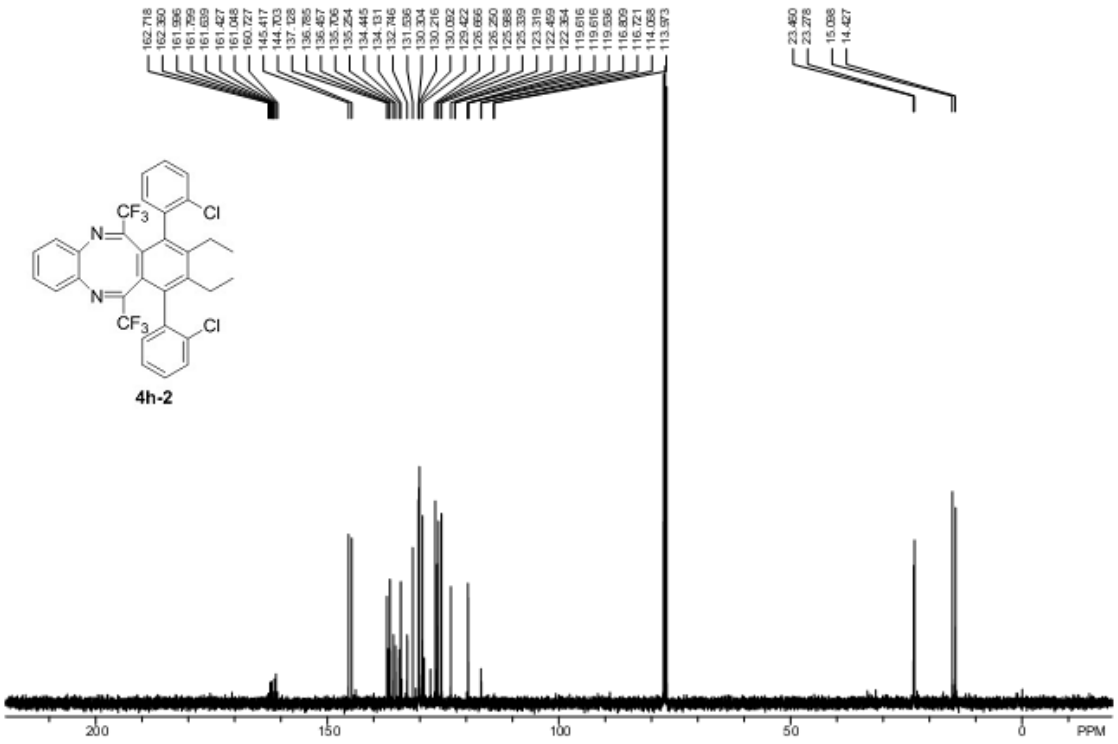
126.820
126.091
122.276
119.460
116.700
113.865
23.328
14.348
4h-1
160
140
120
100
80
60
40
20
0 PPM

4h-2



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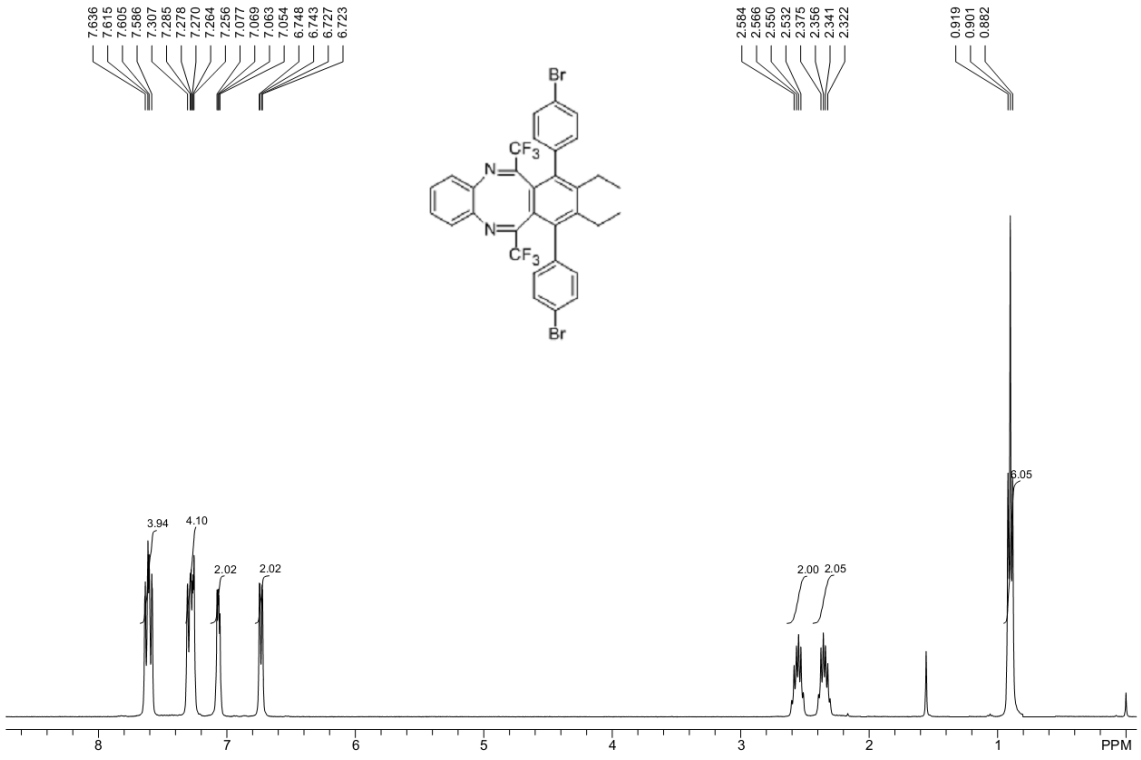
161.639
161.427
161.048
160.727
145.417
144.703
137.128
136.785
136.457
135.706
135.254
134.445
134.131
132.746
131.536
130.304
130.216
130.092
129.422
126.666
126.260
125.988
125.339
123.319
122.459
122.354
119.616
119.616
119.596
116.809
116.721
114.068
113.973
23.490
23.278
15.098
14.427
CF3
Cl
N
N
CF3
Cl
4h-2
200
150
100
50
0
PPM

4i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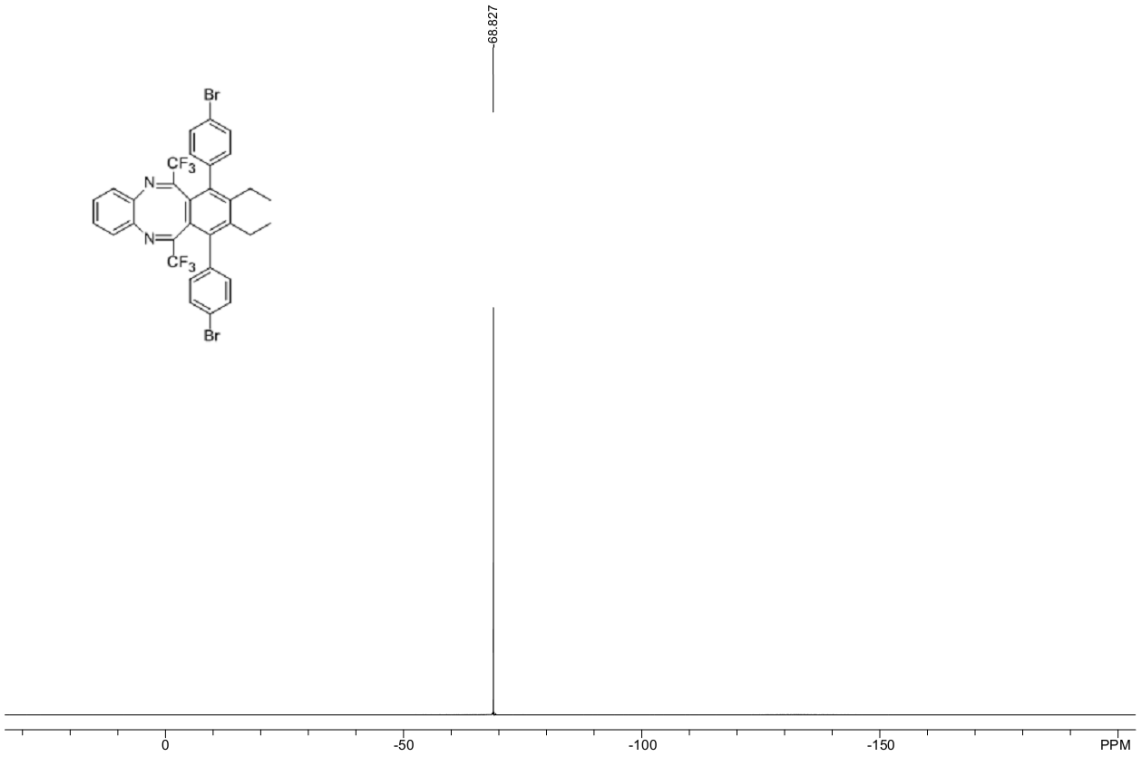
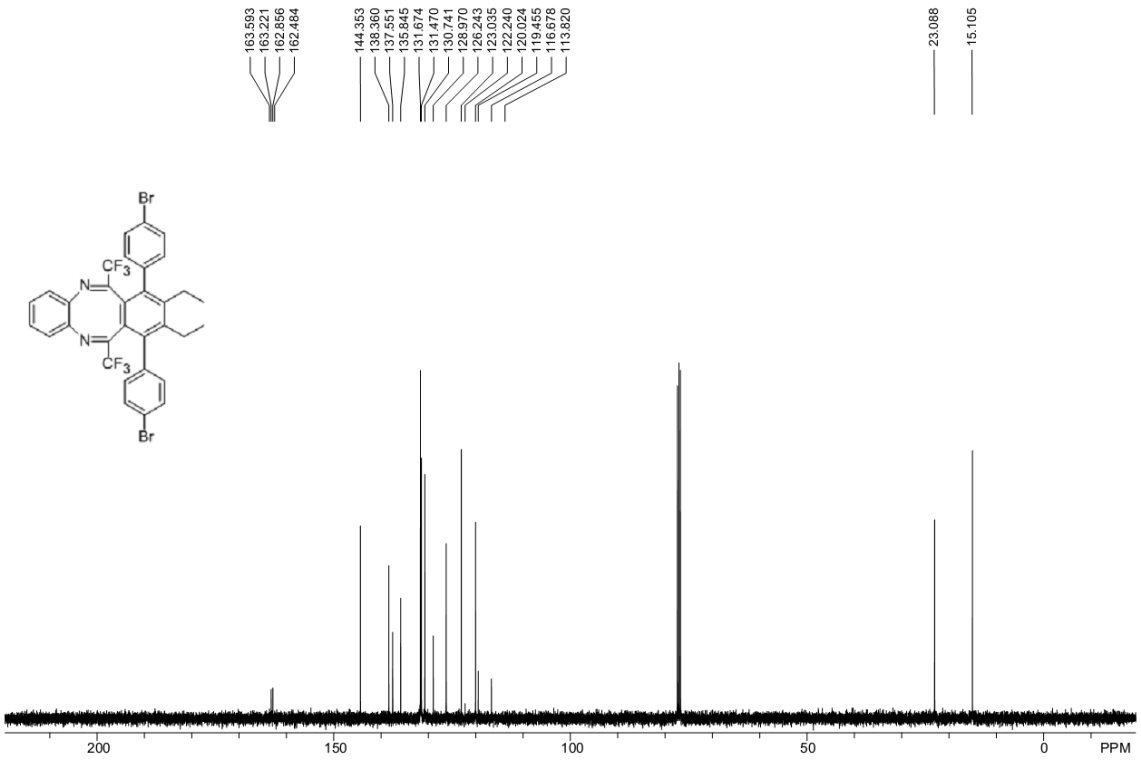
7.615
7.605
7.586
7.307
7.285
7.278
7.270
7.264
7.256
7.077
7.069
7.063
7.054
6.748
6.743
6.727
6.723
2.584
2.566
2.550
2.532
2.375
2.356
2.341
2.322
0.919
0.901
0.882
Br
CF3
N
N
CF3
Br
3.94
4.10
2.02
2.02
2.00
2.05
6.05
8
7
6
5
4
3
2
1
PPM





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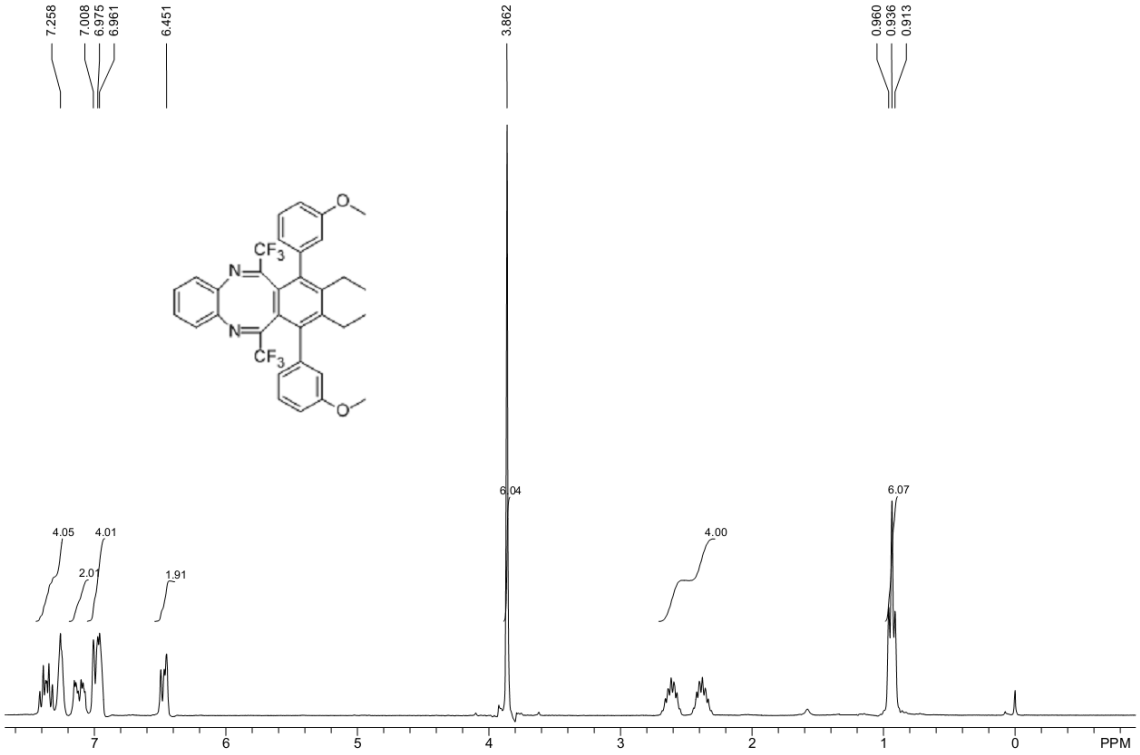

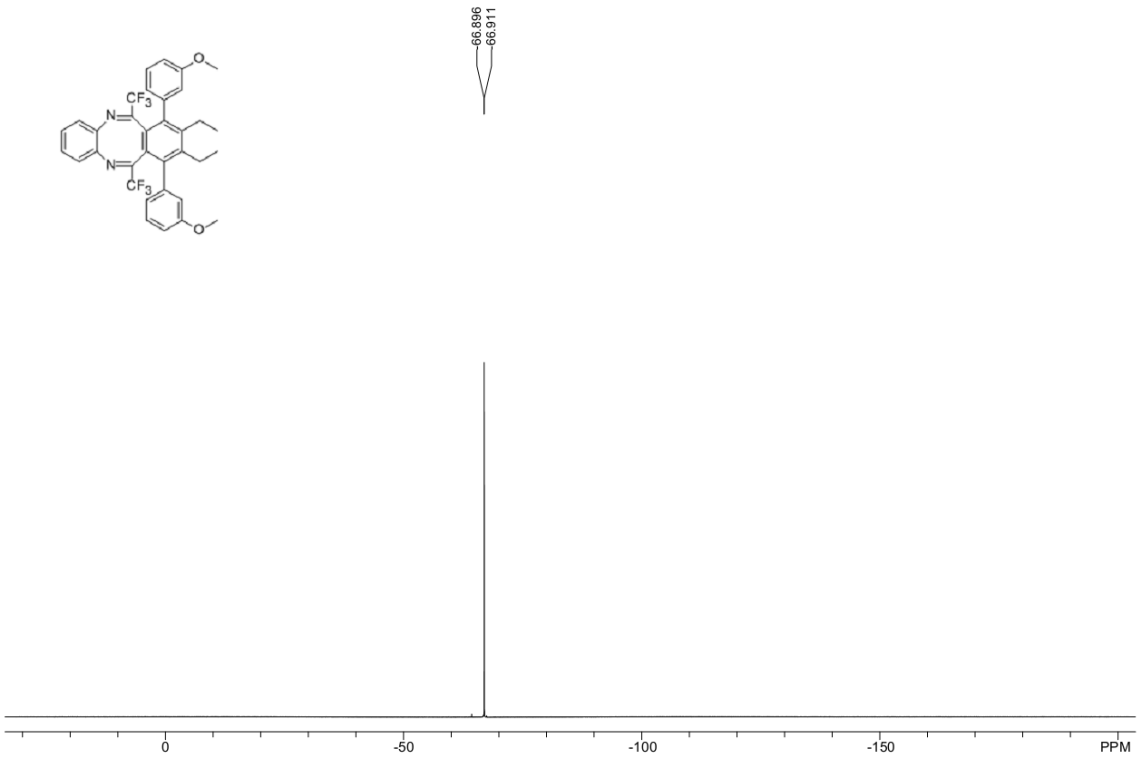

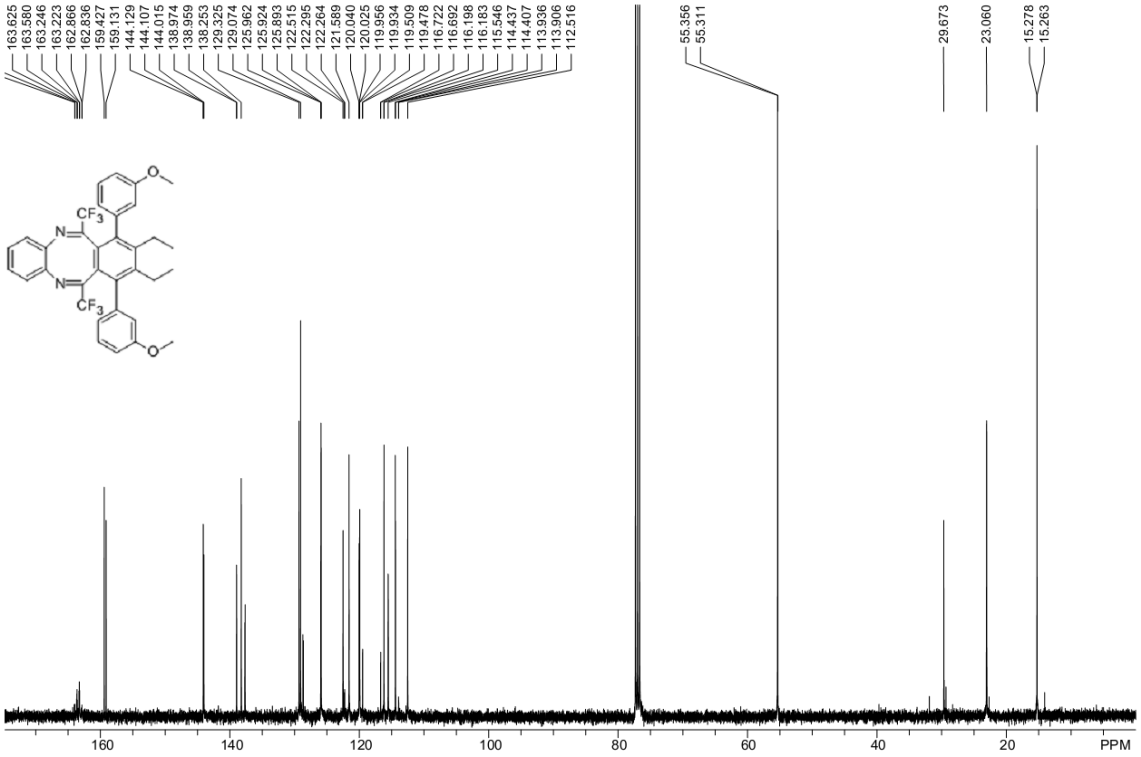
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162.836
159.427
159.131
144.129
144.107
144.015
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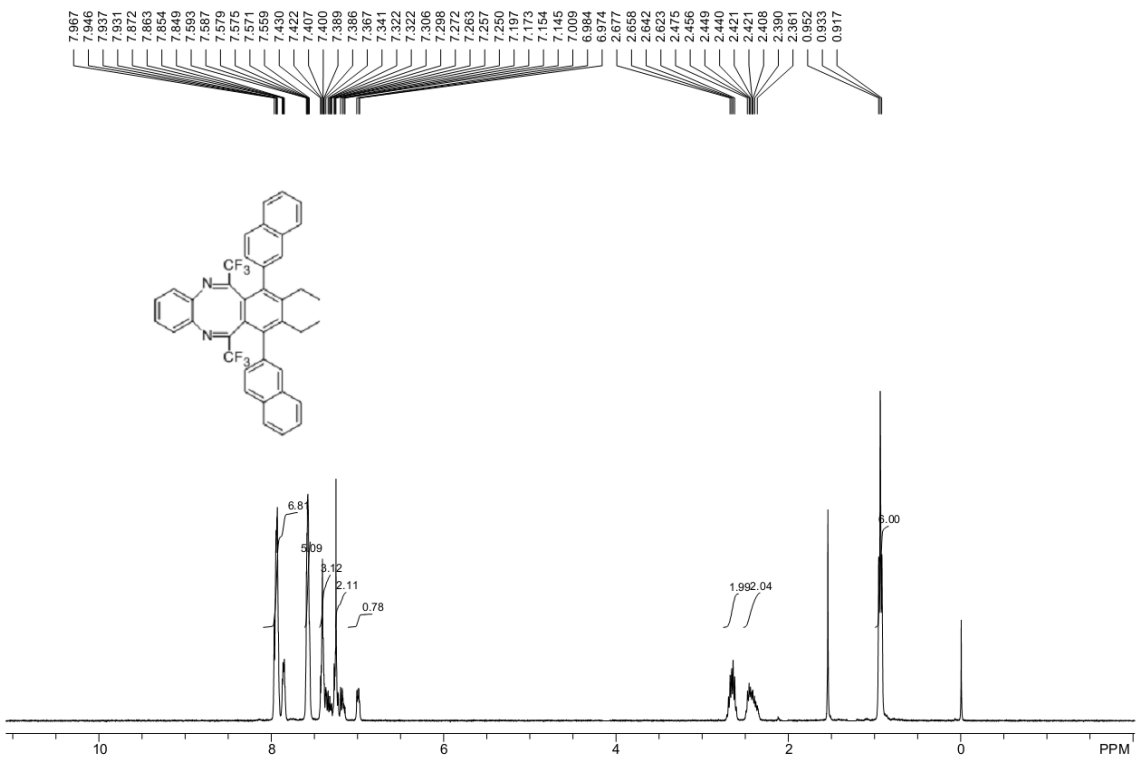
138.959
138.253
129.325
129.074
125.962
125.924
125.893
122.515
122.295
122.264
121.589
120.040
120.025
119.956
119.934
119.509
119.478
116.722
116.692
116.198
116.183
115.546
114.437
114.407
113.936
113.906
112.516
55.356
55.311
29.673
23.060
15.278
15.263
CF3
CF3
160
140
120
100
80
60
40
20
PPM

4k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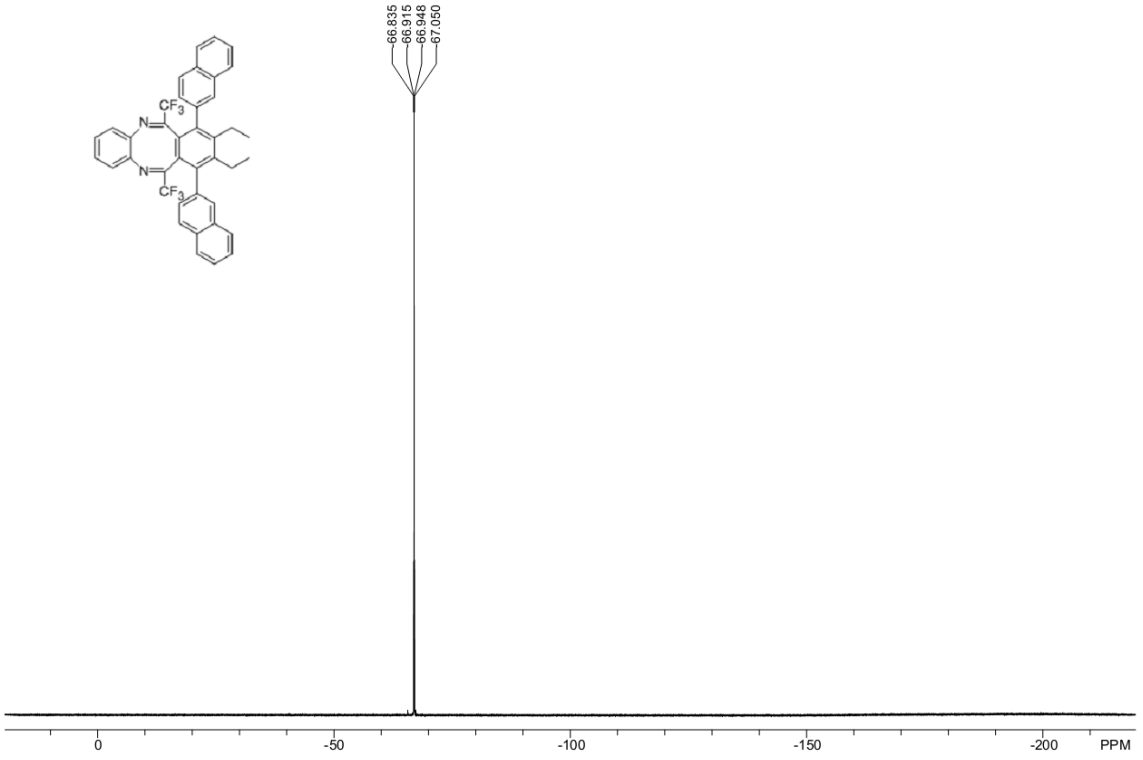
7.937
7.931
7.872
7.863
7.854
7.849
7.593
7.587
7.579
7.575
7.571
7.559
7.430
7.422
7.407
7.400
7.389
7.386
7.367
7.341
7.322
7.322
7.306
7.298
7.272
7.263
7.257
7.250
7.197
7.173
7.154
7.145
7.009
6.984
6.974
2.677
2.658
2.642
2.623
2.475
2.456
2.449
2.440
2.421
2.421
2.408
2.390
2.361
0.952
0.933
0.917
CF3
CF3
6.81
5.09
3.12
2.11
0.78
1.99
2.04
6.00
10
8
6
4
2
0
PPM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-66.948
-67.050
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N
CF3
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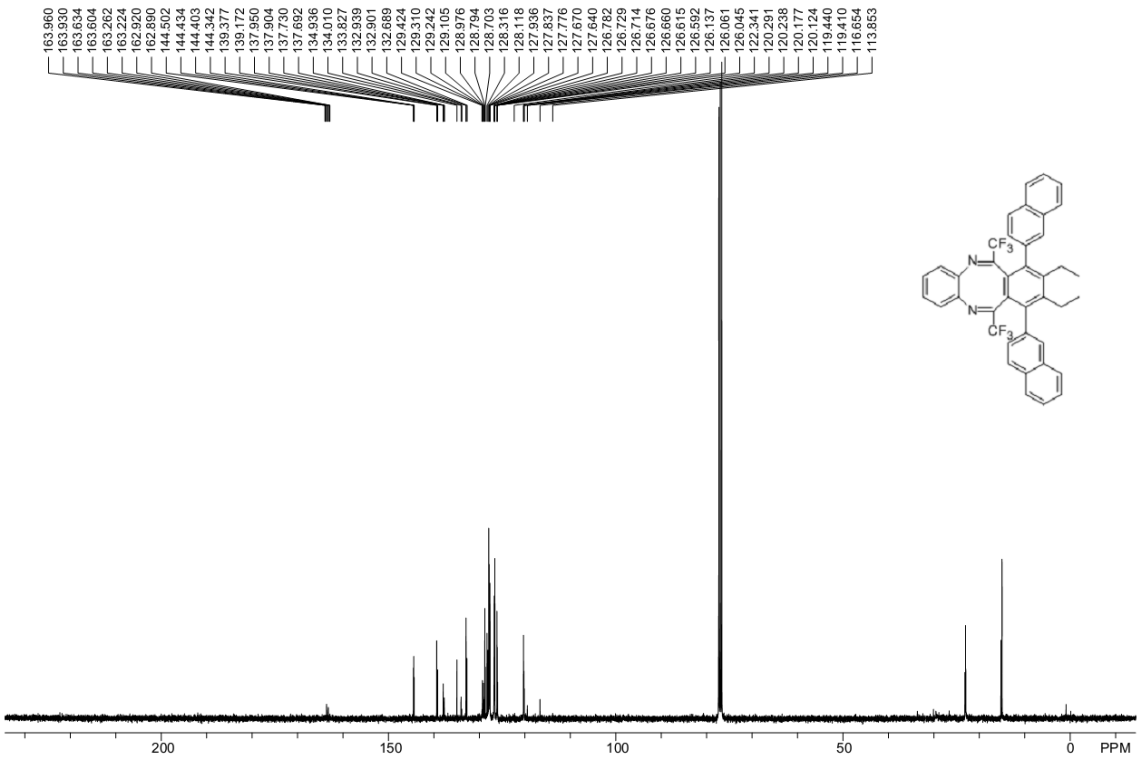
-100
-150
-200
PPM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144.403
144.342
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139.172
137.950
137.904
137.730
137.692
134.936
134.010
133.827
132.939
132.901
132.689
129.424
129.310
129.242
129.105
128.976
128.794
128.703
128.316
128.118
127.936
127.837
127.776
127.670
127.640
126.782
126.729
126.714
126.676
126.660
126.615
126.592
126.137
126.061
126.045
122.341
120.291
120.238
120.177
120.124
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116.654
113.853
CF3
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N
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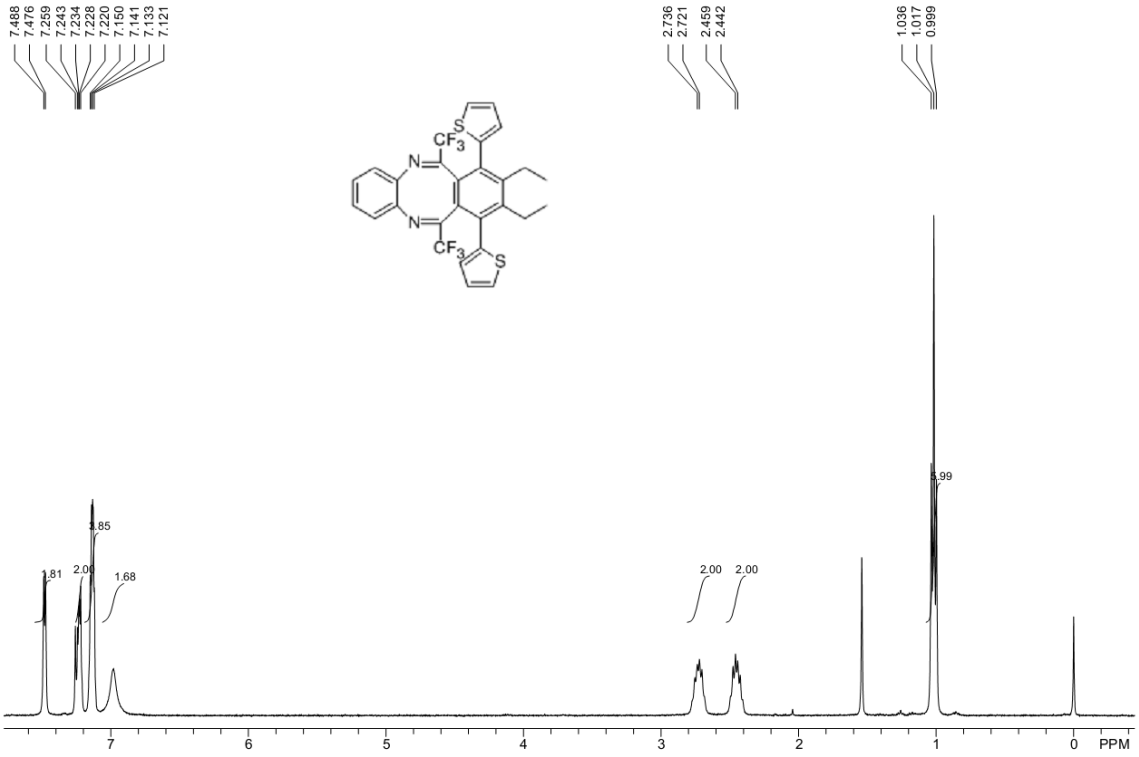
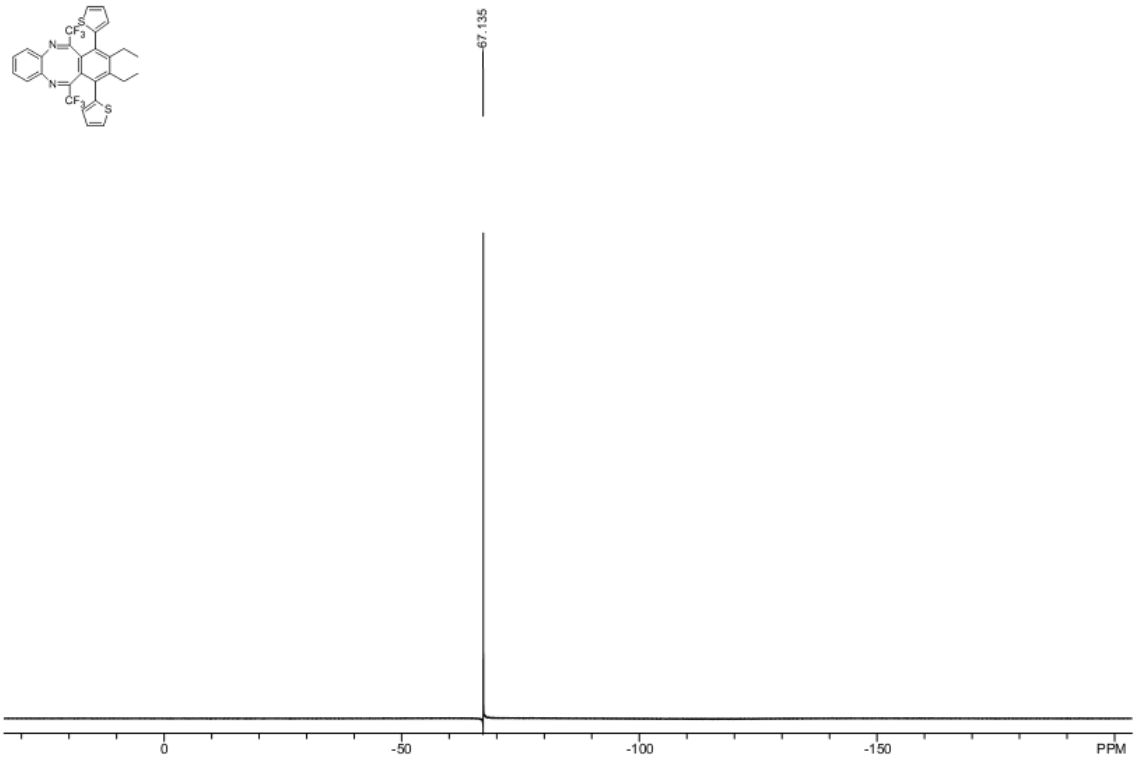
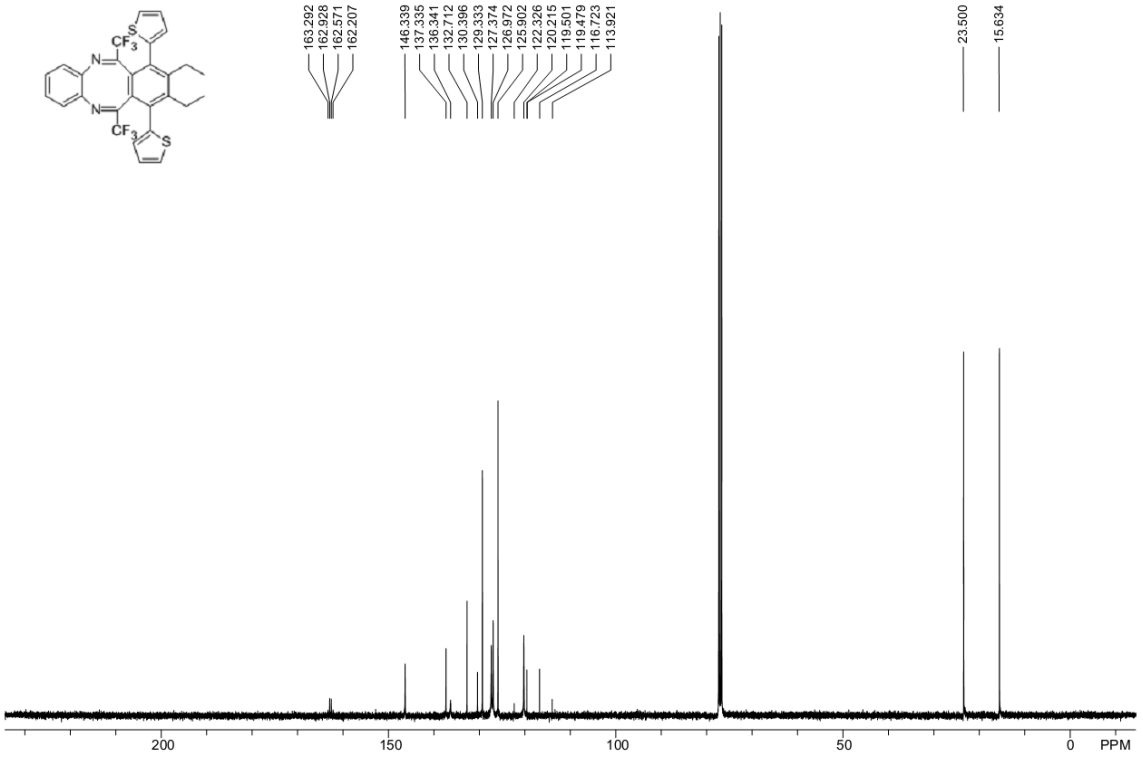
200
150
100
50
0
PPM

4l



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129.333
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125.902
122.326
120.215
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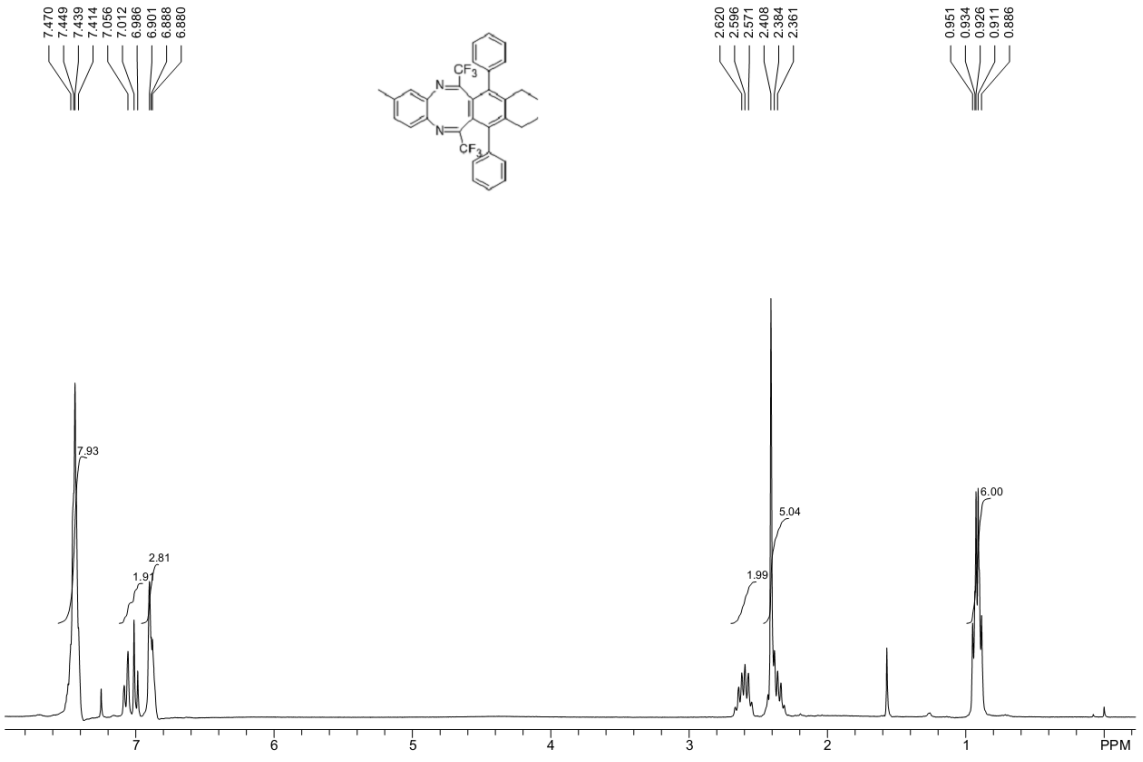
119.479
116.723
113.921
23.500
15.634
200
150
100
50
0
PPM

4n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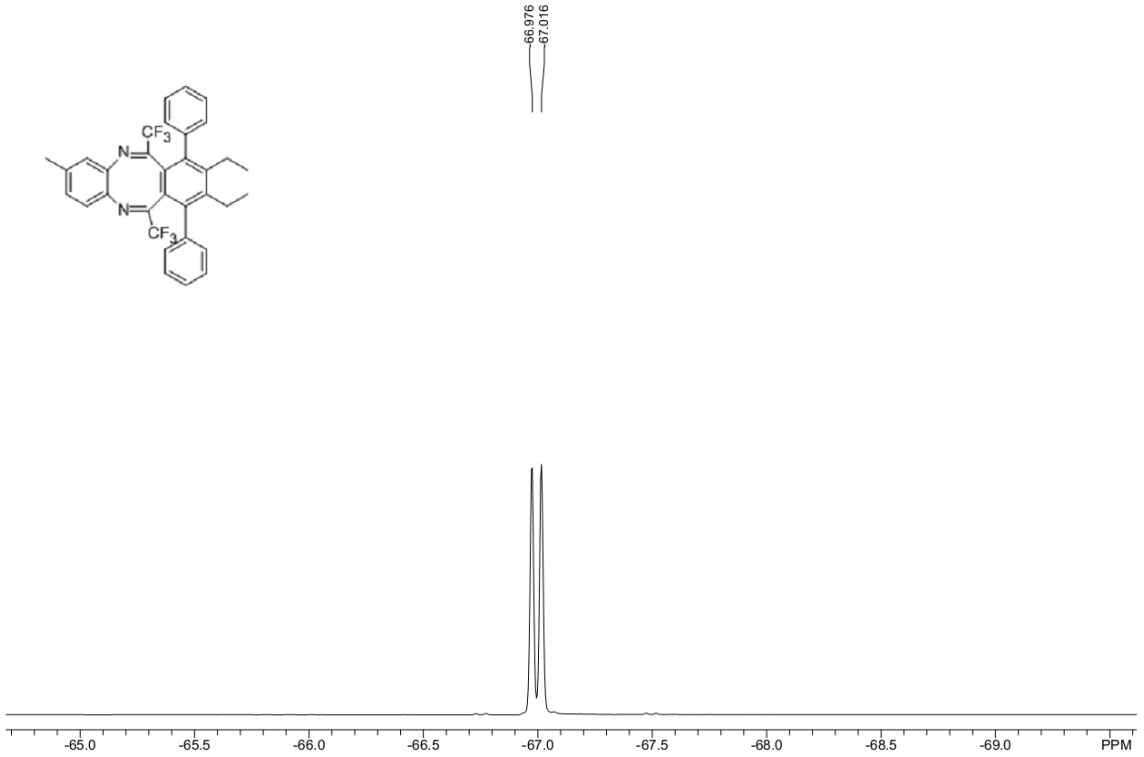
7.439
7.414
7.056
7.012
6.986
6.901
6.888
6.880
2.620
2.596
2.571
2.408
2.384
2.361
0.951
0.934
0.926
0.911
0.886
7.93
2.81
1.91
1.99
5.04
6.00
7
6
5
4
3
2
1
PPM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CF3
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-68.5
-69.0
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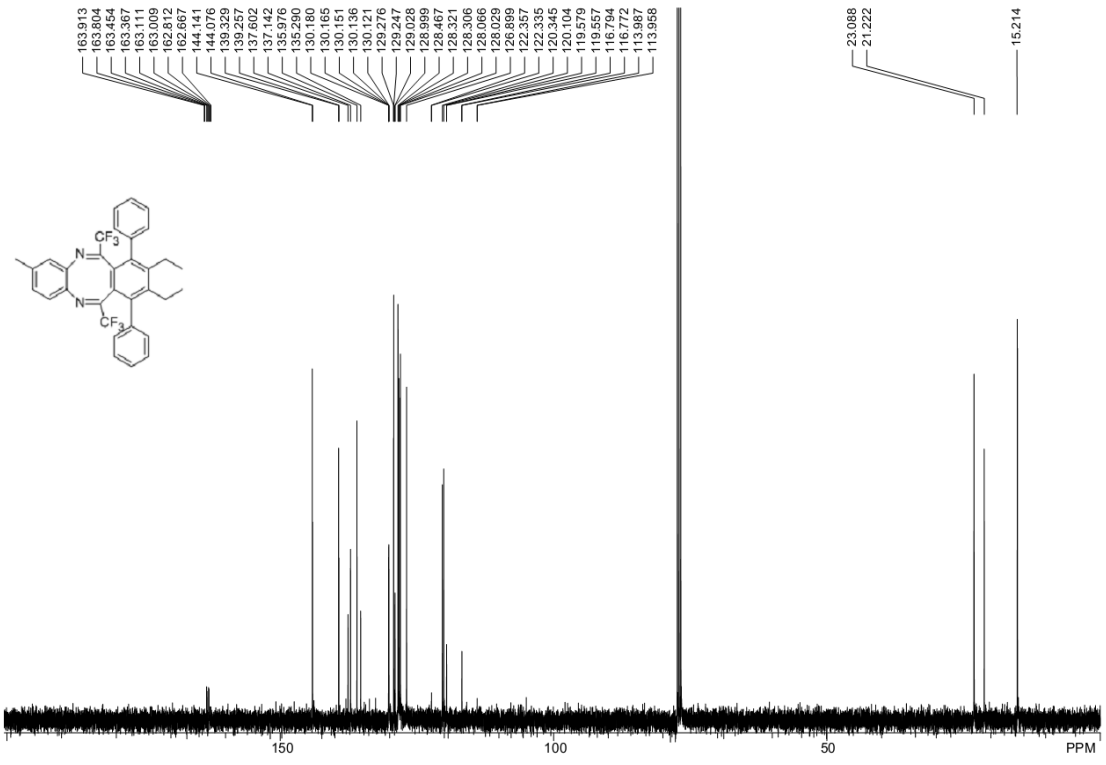
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137.142
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135.290
130.180
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122.335
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113.958
23.088
21.222
15.214
CF3
N
N
CF3
150
100
50
PPM

4o