Supporting Information

Palladium(II)-Catalyzed Intramolecular C−H Amination to Carbazole: Crucial Role of Cyclic Diacyl Peroxides

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1. General information

Unless otherwise noted, all experiments were carried out under air atmosphere. Commercially available reagents, starting materials and solvents were used without further purification. All the solvents including *N*,*N*-dimethylformamide (DMF), 1,2-dimethoxyethane (DME), dimethyl sulfoxide (DMSO), 1,2-dichloroethane (DCE), dichloromethane (DCM), acetonitrile (MeCN), toluene (PhMe), tetrahydrofuran (THF), ethyl acetate (EA), petroleum ether (PE) and acetone were used as received without purification. Flash column chromatography was performed using 200-300 mesh silica gel. Schlenk tubes were purchased from Synthware.

All reactions were monitored by TLC and visualized by UV lamp (254 nm). ^{1}H NMR (400 MHz or 600 MHz) and ^{13}C NMR (101 MHz or 150 MHz) spectra were obtained on Bruker 400M or 600M or Zhongke-Niujin (Quantum-I Plus 400M) nuclear magnetic resonance spectrometers. For $CDCl_3$ solutions, the chemical shifts are reported as parts per million (ppm) referenced to residual protium or carbon of the solvents; $CHCl_3$ δ H (7.26 ppm) and $CDCl_3$ δ C (77.16 ppm). For DMSO-d_6 solutions, the chemical shifts are reported as parts per million (ppm) referenced to residual protium or carbon of the solvents; DMSO-d_6 δ H (2.5 ppm) and DMSO-d_6 δ C (39.6 ppm). Coupling constants (*J*) are reported in Hertz (Hz). Data for ^{1}H NMR and ^{13}C NMR spectra are reported as follows: chemical shift (ppm, referenced to protium: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet (quintet), dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration). HRMS (ESI) was recorded using an Agilent 6520 accurate-Mass Q-TOF spectrometer. Yields of kinetic experiments were determined by LC-MS using the Agilent 1260 Infinity II G7129A/ G7115A/ G6125B or GC using Agilent 7890B.

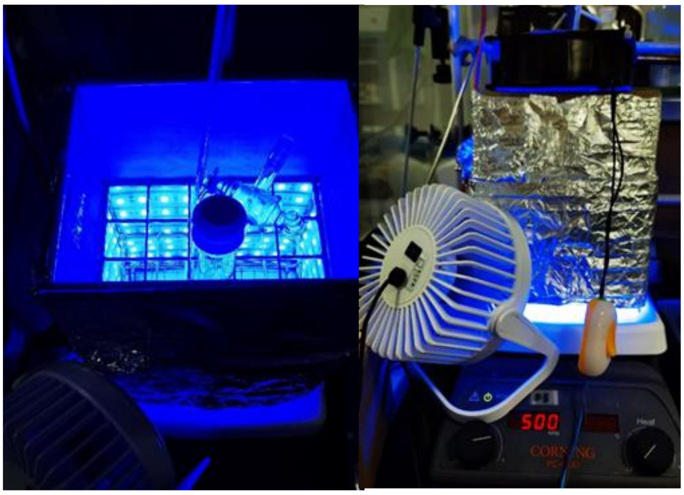
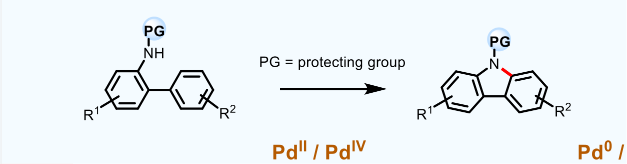


Figure S1. The photoreaction setup using blue LEDs

2. Representative conditions in carbazoles synthesis



	Pd^{II} / Pd^{IV}			Pd^{0} / Pd^{II}	Cu^{II}-catalyzed or Metal-free	Metal-free
Cat	$Pd(OAc)_2$ 5-10 mol%	$Pd(OAc)_2$ 5-10 mol%	$Pd(OAc)_2$ 10 mol% Photocatalyst 1 mol%	$Pd(OAc)_2$ 5 mol%	$Cu(OTf)_2$ 5 mol%	RI 10 mol%
Ox	$PhI(OAc)_2$ 1.2 equiv	Oxone 1.0 equiv	O_2	$Cu(OAc)_2/O_2$ 1.0 equiv	$PhI(OAc)_2$ or $PhI(OTFA)_2$ 1.5 equiv	AcOOH 2.0 equiv
A	AcOH 1.0 equiv	*p*-TsOH 0.5 equiv	—	—	CF_3COOH	—
hν	—	—	blue LEDs	—	—	—
PG	Bn up to 96% yield 29 examples	Ts up to 98% yield 31 examples	Ac, SO_2Ph up to 98% yield 25 examples	Ac up to 98% yield 18 examples	Ac, SO_2Ph up to 98% yield 27 examples	Ac up to 98% yield 18 examples
Solvent & Temp.	Toluene RT	PivOH/DMF(1:3) 25-80 °C	DMSO 80 °C	Toluene 120 °C	DME 25-50 °C	HFIP/DCM(1:1) RT

Figure S2. Various conditions in carbazoles synthesis[1-6]

3. Representative KIE values of electrophilic aromatic mechanism

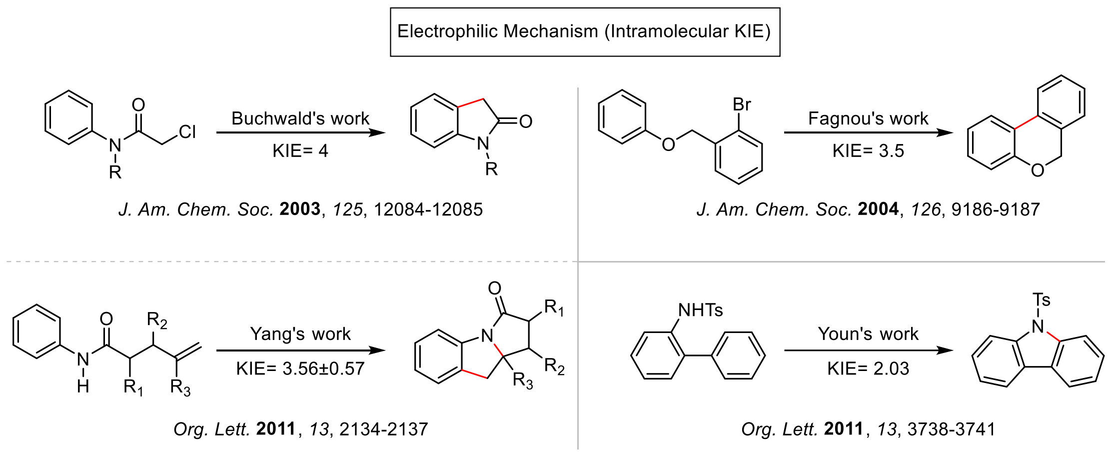


Figure S3. Various intramolecular KIE values in electrophilic aromatic mechanism

4. Possible mechanism

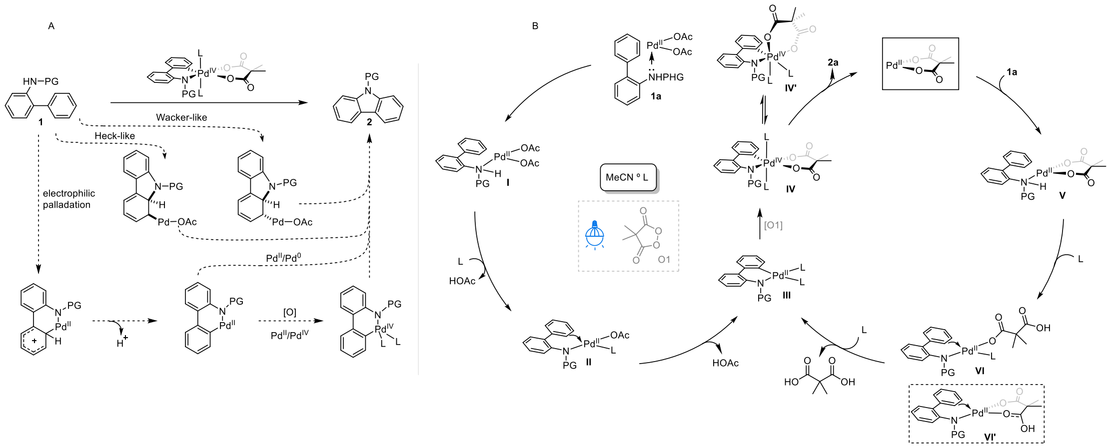
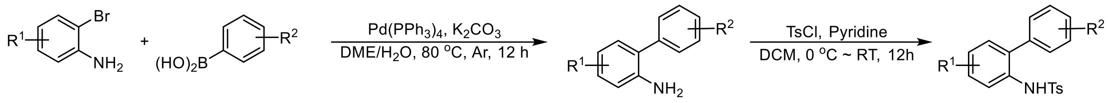


Figure S4. Possible mechanism for C−H bond amination

5. General procedures for the preparation of substrates (1)

5.1 General procedure A

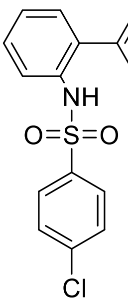


1

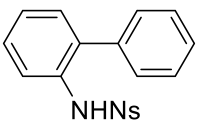
A dry round bottom flask flushed with argon and equipped with a magnetic stirrer bar and a septum was charged with arylboronic acid (1.5 equiv), K_2CO_3 (4.0 equiv), and $Pd(PPh_3)_4$ (10 mol%). A mixture of DME and H_2O (DME : H_2O = 1:1, 0.25 M), 2-Bromoaniline (1.0 equiv) were added, and the resulting mixture was heated to 80 ℃ for 12 hours. The reaction mixture was then poured into water and extracted with CH_2Cl_2 (3-5 times), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the corresponding 2-aminobiphenyl product.

A dry round bottom flask equipped with a magnetic stirrer bar was charged with 2-aminobiphenyl (1.0 equiv), pyridine (0.2 M) in CH_2Cl_2 (0.2 M). 4-toluenesulfonyl chloride (1.1 equiv) was added at 0 ℃. After being stirred at 25 ℃ for 12 h, the reaction mixture was poured into water and extracted with CH_2Cl_2 (3-5 times), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired product **1**.

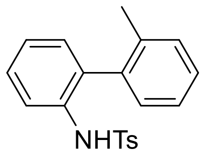
The spectral data of the compounds **1a-1d**, **1g-1n**, **1aa**, **1ab**, **1ad**, **1ae**, **1ag-1ai**, **1ak**, **1al**, **1ao**, **1aq**, **1ba-1be**, **1da**, **1ea**, **1fb**, **1fc** are in accordance with previous reports.[2, 7]



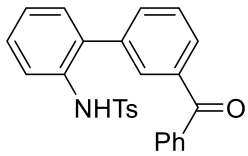
***N*-(4-Chlorobenzenesulfonyl)-2-aminobiphenyl(1e):** white solid; Yield 90%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.70 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.41 – 7.30 (m, 6H), 7.19 (td, *J* = 7.5, 1.2 Hz, 1H), 7.12 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.89 – 6.80 (m, 2H), 6.67 (s, 1H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 139.64, 137.56, 137.22, 134.71, 133.20, 130.50, 129.36, 129.27, 128.90, 128.83, 128.63, 128.29, 125.73, 122.45; **HRMS (ESI)** m/z calcd for $C_{18}H_{14}ClNNaO_2S^+$ $(M+Na)^+$ 366.0326, found 366.0329.



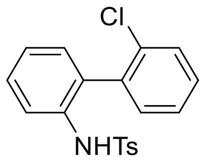
***N*-([1,1'-biphenyl]-2-yl)-4-nitrobenzenesulfonamide(1f):** grey solid; Yield 92%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.21 – 8.13 (m, 2H), 7.71 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.68 – 7.60 (m, 2H), 7.43 – 7.28 (m, 4H), 7.23 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.13 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.82 (dt, *J* = 6.5, 1.5 Hz, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 130.64, 129.37, 129.10, 128.70, 128.46, 126.43, 124.24, 123.12; **HRMS (ESI)** m/z calcd for $C_{18}H_{14}N_2NaO_4S^+$ $(M+Na)^+$ 377.0566, found 377.0568.



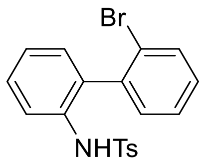
4-methyl-*N*-(2'-methyl-[1,1'-biphenyl]-2-yl)benzenesulfonamide(1ac): white solid; Yield 87%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.81 – 7.59 (m, 2H), 7.54 – 7.48 (m, 2H), 7.33 – 7.27 (m, 1H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.12 (qd, *J* = 7.5, 1.6 Hz, 2H), 7.04 – 6.92 (m, 2H), 6.56 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.25 (s, 1H), 2.40 (s, 3H), 1.84 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 144.06, 136.82, 136.32, 136.08, 134.20, 132.69, 132.42, 130.83, 130.17, 129.70, 128.83, 128.65, 127.39, 126.45, 124.48, 120.00, 21.70, 21.66, 19.61; **HRMS (ESI)** m/z calcd for $C_{20}H_{19}NNaO_2S^+$ $(M+Na)^+$ 360.1029, found 360.1029.



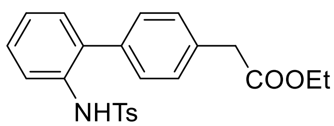
***N*-(3'-benzoyl-[1,1'-biphenyl]-2-yl)-4-methylbenzenesulfonamide(1af):** white solid; Yield 84%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.86 – 7.77 (m, 2H), 7.76 – 7.67 (m, 2H), 7.66 – 7.59 (m, 1H), 7.57 – 7.41 (m, 5H), 7.36 (td, *J* = 8.2, 7.8, 1.9 Hz, 1H), 7.24 – 7.07 (m, 6H), 6.55 (s, 1H), 2.31 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 196.03, 144.25, 138.49, 137.79, 137.21, 136.01, 133.77, 133.46, 132.96, 132.81, 130.51, 130.30, 130.20, 129.77, 129.22, 128.99, 128.65, 127.19, 125.40, 122.23, 21.61; **HRMS (ESI)** m/z calcd for $C_{26}H_{21}NNaO_3S^+$ $(M+Na)^+$ 450.1134, found 450.1133.



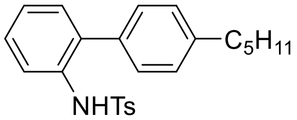
***N*-(2'-chloro-[1,1'-biphenyl]-2-yl)-4-methylbenzenesulfonamide(1aj):** white solid; Yield 90%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.71 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.50 – 7.41 (m, 3H), 7.35 (dtd, *J* = 21.5, 7.8, 1.7 Hz, 2H), 7.16 (dtd, *J* = 8.7, 7.5, 1.3 Hz, 4H), 7.05 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.62 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.29 (s, 1H), 2.39 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 143.94, 136.31, 135.93, 134.04, 133.56, 131.57, 130.58, 130.01, 129.98, 129.70, 129.39, 127.36, 127.29, 125.16, 121.97, 21.69; **HRMS (ESI)** m/z calcd for $C_{19}H_{16}ClNNaO_2S^+$ $(M+Na)^+$ 380.0482, found 380.0486.



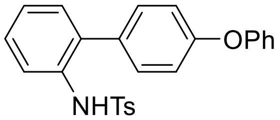
***N*-(2'-bromo-[1,1'-biphenyl]-2-yl)-4-methylbenzenesulfonamide(1am):** white solid; Yield 89%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.67 (ddd, *J* = 26.8, 8.0, 1.3 Hz, 2H), 7.52 – 7.45 (m, 2H), 7.37 (td, *J* = 7.7, 1.7 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.20 – 7.13 (m, 4H), 7.03 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.58 (dd, *J* = 7.3, 2.0 Hz, 1H), 6.24 (s, 1H), 2.40 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 143.99, 137.92, 136.34, 133.87, 133.22, 133.06, 131.48, 130.45, 130.17, 129.73, 129.39, 127.87, 127.44, 124.98, 123.90, 121.57, 21.70; **HRMS (ESI)** m/z calcd for $C_{19}H_{16}BrNNaO_2S^+$ $(M+Na)^+$ 423.9977, found 423.9979.



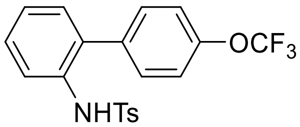
ethyl 2-(2'-((4-methylphenyl)sulfonamido)-[1,1'-biphenyl]-4-yl)acetate(1an): white solid; Yield 85%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.70 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.32 (td, *J* = 8.2, 7.8, 1.8 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.22 – 7.17 (m, 2H), 7.16 – 7.05 (m, 2H), 6.85 – 6.78 (m, 2H), 6.58 (s, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.65 (s, 2H), 2.40 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 171.44, 144.03, 136.25, 136.07, 134.25, 133.89, 133.60, 130.42, 130.10, 129.73, 129.24, 128.79, 127.30, 125.02, 121.43, 61.22, 41.14, 21.70, 14.36; **HRMS (ESI)** m/z calcd for $C_{23}H_{23}NNaO_4S^+$ $(M+Na)^+$ 432.1240, found 432.1244.



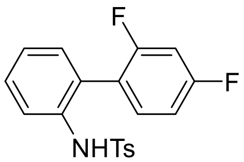
4-methyl-*N*-(4'-pentyl-[1,1'-biphenyl]-2-yl)benzenesulfonamide(1ap): white solid; Yield 88%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.69 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.26 (m, 1H), 7.22 – 7.00 (m, 6H), 6.80 – 6.71 (m, 2H), 6.64 (s, 1H), 2.63 (dd, *J* = 8.8, 6.7 Hz, 2H), 2.40 (s, 3H), 1.86 (s, 1H), 1.72 – 1.62 (m, 2H), 1.37 (ddt, *J* = 7.2, 5.6, 2.8 Hz, 4H), 0.98 – 0.86 (m, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 143.95, 143.12, 136.26, 134.45, 133.94, 130.46, 129.68, 129.34, 129.22, 128.87, 128.56, 127.32, 125.50, 124.91, 121.22, 35.75, 31.69, 31.24, 22.69, 21.70, 14.20; **HRMS (ESI)** m/z calcd for $C_{24}H_{27}NNaO_2S^+$ (M+Na)$^+$ 416.1655, found 416.1656.



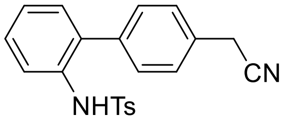
4-methyl-*N*-(4'-phenoxy-[1,1'-biphenyl]-2-yl)benzenesulfonamide(1as): white solid; Yield 87%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.70 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.23 – 7.07 (m, 7H), 6.96 (d, *J* = 7.4 Hz, 2H), 6.82 (d, *J* = 7.4 Hz, 2H), 6.60 (s, 1H), 2.38 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 157.62, 156.51, 144.03, 136.27, 133.93, 133.43, 131.76, 130.53, 130.43, 130.05, 129.70, 128.70, 127.25, 125.03, 124.04, 121.49, 119.61, 118.83, 21.65; **HRMS (ESI)** m/z calcd for $C_{25}H_{21}NNaO_3S^+$ (M+Na)$^+$ 438.1134, found 438.1136.



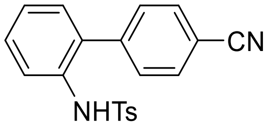
4-methyl-*N*-(4'-(trifluoromethoxy)-[1,1'-biphenyl]-2-yl)benzenesulfonamide(1at): white solid; Yield 80%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.73 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.53 – 7.41 (m, 3H), 7.40 (td, *J* = 7.8, 1.7 Hz, 1H), 7.26 – 7.17 (m, 4H), 7.12 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.50 (s, 1H), 2.45 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 149.06, 144.16, 136.33, 136.11, 133.71, 133.12, 132.71, 130.58, 130.45, 129.78, 129.24, 127.23, 125.47, 128.83 – 122.16 (m), 121.52, 21.68; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -57.72; **HRMS (ESI)** m/z calcd for $C_{20}H_{16}F_3NNaO_3S^+$ (M+Na)$^+$ 430.0695, found 430.0699.



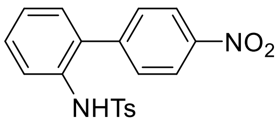
***N*-(2',4'-difluoro-[1,1'-biphenyl]-2-yl)-4-methylbenzenesulfonamide(1au):** white solid; Yield 81%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.66 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.21 (td, *J* = 7.5, 1.3 Hz, 1H), 7.16 – 7.05 (m, 4H), 6.91 – 6.75 (m, 2H), 6.67 (td, *J* = 8.5, 6.4 Hz, 1H), 6.39 (s, 1H), 2.38 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ162.99 (d, *J* = 238.8 Hz), 159.42 (d, *J* = 260.0 Hz), 143.88, 136.30, 134.18, 132.55 – 132.40 (m), 132.38, 131.16, 129.79, 129.64, 128.39, 127.11, 126.93 (d, *J* = 105.7 Hz), 126.01, 124.00, 112.06 (d, J = 21.1 Hz), 104.49 (t, J = 25.7 Hz). 21.65; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -109.00, -109.99; **HRMS (ESI)** m/z calcd for $C_{19}H_{15}F_2NNaO_2S^+$ (M+Na)$^+$ 382.0684, found 382.0689.



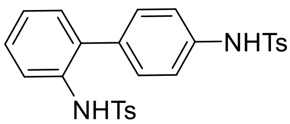
N-(4'-(cyanomethyl)-[1,1'-biphenyl]-2-yl)-4-methylbenzenesulfonamide(1av): white solid; Yield 82%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.68 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.38 – 7.27 (m, 3H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.16 (td, *J* = 7.5, 1.2 Hz, 1H), 7.08 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.92 – 6.86 (m, 2H), 6.52 – 6.48 (m, 1H), 3.80 (s, 2H), 2.41 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 144.16, 137.31, 136.21, 133.29, 130.36, 129.97, 129.83, 129.73, 129.05, 128.68, 127.21, 125.24, 121.87, 117.66, 77.48, 77.16, 76.84, 23.45, 21.66; **HRMS (ESI)** m/z calcd for $C_{21}H_{18}N_2NaO_2S^+$ $(M+Na)^+$ 385.0981, found 385.0987.



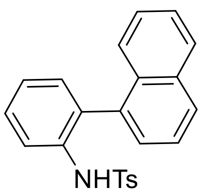
N-(4'-cyano-[1,1'-biphenyl]-2-yl)-4-methylbenzenesulfonamide(1aw): white solid; Yield 72%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.63 – 7.56 (m, 3H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 3H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.3 Hz, 2H), 6.60 (s, 1H), 2.42 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 144.15, 142.47, 136.27, 133.54, 133.29, 132.49, 130.22, 129.93, 129.74, 129.60, 127.08, 125.91, 123.62, 118.48, 111.68, 29.70, 21.62; **HRMS (ESI)** m/z calcd for $C_{20}H_{16}N_2NaO_2S^+$ $(M+Na)^+$ 371.0825, found 371.0825.



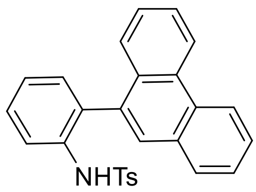
4-methyl-N-(4'-nitro-[1,1'-biphenyl]-2-yl)benzenesulfonamide(1ax): yellow solid; Yield 70%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.16 (d, *J* = 8.8 Hz, 2H), 7.67 – 7.60 (m, 1H), 7.44 (dd, *J* = 26.7, 7.9 Hz, 2H), 7.38 (d, *J* = 1.5 Hz, 1H), 7.28 – 7.18 (m, 3H), 7.11 (ddd, *J* = 14.1, 7.2, 1.7 Hz, 3H), 6.43 (s, 1H), 2.43 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 147.49, 144.47, 144.39, 136.33, 133.44, 133.06, 130.26, 130.20, 129.94, 129.86, 127.20, 126.00, 124.09, 123.59, 77.37, 77.16, 76.95, 21.72; **HRMS (ESI)** m/z calcd for $C_{19}H_{16}N_2NaO_4S^+$ $(M+Na)^+$ 391.0723, found 391.0722.



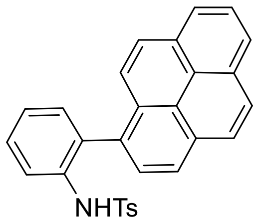
N,N'-([1,1'-biphenyl]-2,4'-diyl)bis(4-methylbenzenesulfonamide)(1ay): white solid; Yield 76%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.78 – 7.72 (m, 2H), 7.65 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.32 (d, *J* = 5.7 Hz, 2H), 7.16 – 7.07 (m, 4H), 7.09 – 6.96 (m, 4H), 6.75 – 6.67 (m, 2H), 6.44 (d, *J* = 2.7 Hz, 1H), 2.40 (d, *J* = 10.9 Hz, 6H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 144.54, 144.11, 136.70, 136.11, 134.02, 133.75, 133.43, 130.33, 130.05, 129.70, 128.93, 127.42, 127.21, 125.26, 122.01, 121.46, 77.48, 77.16, 76.84, 21.74, 21.69; **HRMS (ESI)** m/z calcd for $C_{26}H_{24}N_2NaO_4S_2^+$ $(M+Na)^+$ 515.1070, found 515.1073.



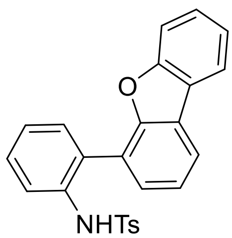
4-methyl-N-(2-(naphthalen-1-yl)phenyl)benzenesulfonamide(1az): white solid; Yield 77%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.92 (t, *J* = 7.1 Hz, 2H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.44 (dt, *J* = 14.9, 7.6 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.9 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.14 (dd, *J* = 20.9, 9.1 Hz, 4H), 6.84 (d, *J* = 6.9 Hz, 1H), 6.27 (s, 1H), 2.41 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 143.82, 136.07, 134.84, 134.26, 133.82, 131.73, 131.71, 131.26, 129.57, 129.06, 129.04, 128.63, 127.48, 127.31, 127.01, 126.42, 125.54, 125.10, 124.84, 121.22, 21.69; **HRMS (ESI)** m/z calcd for $C_{23}H_{19}NNaO_2S^+$ $(M+Na)^+$ 396.1029, found 396.1032.



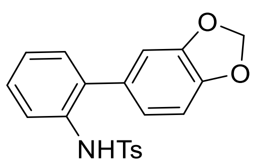
4-methyl-*N*-(2-(phenanthren-9-yl)phenyl)benzenesulfonamide(1aa'): white solid; Yield 78%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.78 (dd, *J* = 12.2, 8.3 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.76 (ddd, *J* = 8.3, 5.3, 3.1 Hz, 1H), 7.72 – 7.64 (m, 3H), 7.55 – 7.46 (m, 1H), 7.46 – 7.38 (m, 1H), 7.32 – 7.24 (m, 3H), 7.26 – 7.17 (m, 2H), 7.08 – 6.97 (m, 3H), 6.31 (s, 1H), 2.44 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.61, 135.90, 134.78, 132.83, 132.01, 131.14, 130.99, 130.57, 130.42, 130.31, 129.40, 129.01, 128.51, 128.14, 127.39, 127.32, 127.12, 127.08, 127.05, 125.80, 125.14, 123.22, 122.71, 121.85, 21.67; **HRMS (ESI)** m/z calcd for $C_{27}H_{21}NNaO_2S^+$ $(M+Na)^+$ 446.1185, found 446.1187.



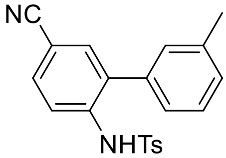
4-methyl-*N*-(2-(pyren-1-yl)phenyl)benzenesulfonamide(1ab'): grey solid; Yield 58%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.31 (d, *J* = 7.6 Hz, 1H), 8.24 – 8.05 (m, 5H), 7.93 (dd, *J* = 10.8, 8.7 Hz, 2H), 7.54 – 7.51 (m, 1H), 7.42 (dd, *J* = 8.4, 2.9 Hz, 2H), 7.32 – 7.30 (m, 4H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.39 (d, *J* = 3.2 Hz, 1H), 2.37 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.86, 136.12, 134.99, 132.27, 131.70, 131.53, 131.44, 131.37, 130.87, 129.53, 129.30, 129.19, 128.60, 128.33, 127.37, 127.35, 127.22, 126.53, 125.87, 125.57, 124.95, 124.62, 124.09, 121.47, 21.64; **HRMS (ESI)** m/z calcd for $C_{29}H_{21}NNaO_2S^+$ $(M+Na)^+$ 470.1185, found 470.1189.



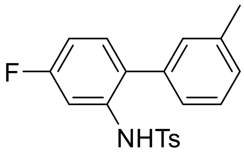
***N*-(2-(dibenzo[b,d]furan-4-yl)phenyl)-4-methylbenzenesulfonamide(1ac'):** white solid; Yield 81%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.02 (d, *J* = 7.7 Hz, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 4.9 Hz, 3H), 7.42 (t, *J* = 6.8 Hz, 1H), 7.34 (d, *J* = 4.0 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.02 (s, 1H), 6.91 (d, *J* = 7.8 Hz, 2H), 6.86 (d, *J* = 7.4 Hz, 1H), 2.21 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 155.83, 152.62, 143.30, 135.77, 133.88, 131.15, 130.60, 129.29, 129.23, 127.97, 127.71, 126.59, 126.34, 125.43, 124.59, 123.89, 123.33, 123.28, 121.75, 120.92, 120.54, 111.94, 21.29; **HRMS (ESI)** m/z calcd for $C_{25}H_{19}NNaO_3S^+$ $(M+Na)^+$ 436.0978, found 436.0981.



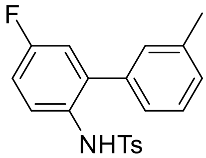
***N*-(2-(benzo[d][1,3]dioxol-5-yl)phenyl)-4-methylbenzenesulfonamide(1ad'):** white solid; Yield 82%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.64 (s, 1H), 6.34 (d, *J* = 7.9 Hz, 1H), 6.19 (s, 1H), 6.00 (s, 2H), 2.39 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 148.17, 147.50, 144.01, 136.07, 133.91, 133.75, 130.76, 130.37, 129.62, 128.56, 127.17, 124.97, 122.20, 121.61, 109.43, 108.72, 101.40, 21.57; **HRMS (ESI)** m/z calcd for $C_{20}H_{17}NNaO_4S^+$ $(M+Na)^+$ 390.0770, found 390.0774.



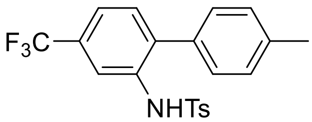
N-(5-cyano-3'-methyl-[1,1'-biphenyl]-2-yl)-4-methylbenzenesulfonamide(1ca): white solid; Yield 73%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.79 (d, *J* = 8.6 Hz, 1H), 7.61 – 7.51 (m, 4H), 7.38 (d, *J* = 2.1 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 15.3 Hz, 2H), 6.81 (s, 1H), 6.75 (dt, *J* = 7.5, 1.7 Hz, 1H), 6.71 – 6.67 (m, 1H), 2.43 (s, 3H), 2.35 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 144.84, 139.65, 138.34, 135.78, 134.81, 134.13, 133.74, 132.55, 130.11, 130.06, 129.65, 129.50, 127.29, 125.84, 119.81, 118.52, 107.78, 21.76, 21.54; **HRMS (ESI)** m/z calcd for $C_{21}H_{18}N_2NaO_2S^+$ (M+Na)$^+$ 385.0981, found 385.0985.



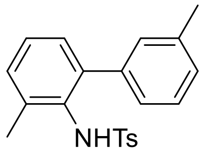
N-(4-fluoro-3'-methyl-[1,1'-biphenyl]-2-yl)-4-methylbenzenesulfonamide(1cb): white solid; Yield 62%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.60 – 7.50 (m, 3H), 7.34 – 7.24 (m, 4H), 7.25 – 7.18 (m, 1H), 7.07 (dd, *J* = 8.5, 6.3 Hz, 1H), 6.86 (td, *J* = 8.2, 2.6 Hz, 1H), 6.71 (dt, *J* = 7.3, 1.7 Hz, 1H), 6.66 – 6.60 (m, 1H), 2.45 (s, 3H), 2.36 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 162.51 (d, *J* = 246.3 Hz), 161.29, 144.31, 139.11, 136.14 (d, *J* = 32.3 Hz), 135.32 (d, *J* = 10.8 Hz), 131.42 (d, *J* = 9.1 Hz), 111.60 (d, *J* = 21.1 Hz), 108.09 (d, *J* = 26.5 Hz), 129.84, 129.26, 127.33, 126.17, 111.60 (d, *J* = 21.1 Hz), 108.09 (d, *J* = 26.5 Hz), 21.72, 21.52; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -111.86; **HRMS (ESI)** m/z calcd for $C_{20}H_{18}FNNaO_2S^+$ (M+Na)$^+$ 378.0934, found 378.0934.



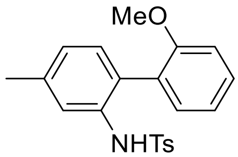
N-(5-fluoro-3'-methyl-[1,1'-biphenyl]-2-yl)-4-methylbenzenesulfonamide(1cc): white solid; Yield 61%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.76 (dd, *J* = 9.0, 5.2 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.29 – 7.17 (m, 5H), 7.09 (ddd, *J* = 9.0, 7.9, 3.0 Hz, 1H), 6.84 (dd, *J* = 8.8, 3.1 Hz, 1H), 6.63 (dt, *J* = 7.3, 1.8 Hz, 1H), 6.51 (q, *J* = 1.4, 1.0 Hz, 1H), 2.46 (s, 3H), 2.33 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 159.95 (d, *J* = 245.9 Hz), 143.98, 139.01, 136.84, 136.25, 135.96, 129.69, 129.34, 129.29, 129.12, 127.29, 125.64, 124.49 (d, *J* = 8.3 Hz), 116.95 (d, *J* = 22.8 Hz), 115.40 (d, *J* = 22.4 Hz), 21.71, 21.52; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -116.98; **HRMS (ESI)** m/z calcd for $C_{20}H_{18}FNNaO_2S^+$ (M+Na)$^+$ 378.0934, found 378.0935.



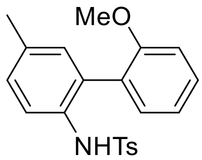
4-methyl-N-(4'-methyl-4-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)benzenesulfonamide(1cd): white solid; Yield 59%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.60 – 7.48 (m, 3H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 6.99 (dt, *J* = 16.1, 8.1 Hz, 4H), 6.40 (s, 1H), 2.41 (d, *J* = 5.3 Hz, 6H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 144.12, 141.38, 139.72, 136.34, 133.28, 131.11 (q, *J* = 32.1 Hz), 130.63, 130.08, 129.76, 129.56, 127.45, 127.19, 126.58, 125.90 (d, *J* = 3.8 Hz), 123.65, 123.50 (q, *J* = 272.3 Hz), 21.68, 21.52. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -62.61; **HRMS (ESI)** m/z calcd for $C_{21}H_{19}F_3NO_2S^+$ (M+H)$^+$ 406.1083, found 406.1083.



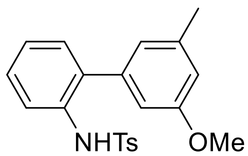
***N*-(3,3'-dimethyl-[1,1'-biphenyl]-2-yl)-4-methylbenzenesulfonamide(1ce) :** white solid; Yield 73%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.28 (dd, *J* = 7.6, 2.2 Hz, 1H), 7.21 (q, *J* = 7.6, 7.0 Hz, 1H), 7.12 – 6.90 (m, 7H), 6.65 – 6.59 (m, 2H), 6.50 (d, *J* = 2.0 Hz, 1H), 2.57 (d, *J* = 18.8 Hz, 3H), 2.40 (d, *J* = 12.6 Hz, 3H), 2.22 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 142.88, 140.57, 138.89, 138.86, 138.24, 136.69, 131.18, 130.97, 129.31, 129.22, 128.40, 128.37, 127.82, 127.50, 127.13, 125.42, 21.69, 21.54, 20.10; **HRMS (ESI)** m/z calcd for $C_{21}H_{21}NNaO_2S^+$ $(M+Na)^+$ 374.1185, found 374.1187.



***N*-(2'-methoxy-4-methyl-[1,1'-biphenyl]-2-yl)-4-methylbenzenesulfonamide(1cf):** white solid; Yield 70%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.52 – 7.48 (m, 1H), 7.32 – 7.19 (m, 1H), 7.17 – 7.10 (m, 2H), 7.07 – 6.98 (m, 2H), 6.98 – 6.80 (m, 4H), 6.75 (td, *J* = 7.5, 1.1 Hz, 1H), 6.39 (dd, *J* = 7.5, 1.8 Hz, 1H), 3.80 (s, 3H), 2.41 (s, 3H), 2.33 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 155.18, 142.99, 138.78, 136.22, 133.96, 131.84, 130.90, 130.57, 129.31, 127.36, 127.03, 126.75, 126.27, 121.34, 111.20, 56.22, 21.58, 21.35; **HRMS (ESI)** m/z calcd for $C_{21}H_{21}NNaO_3S^+$ $(M+Na)^+$ 390.1134, found 390.1135.

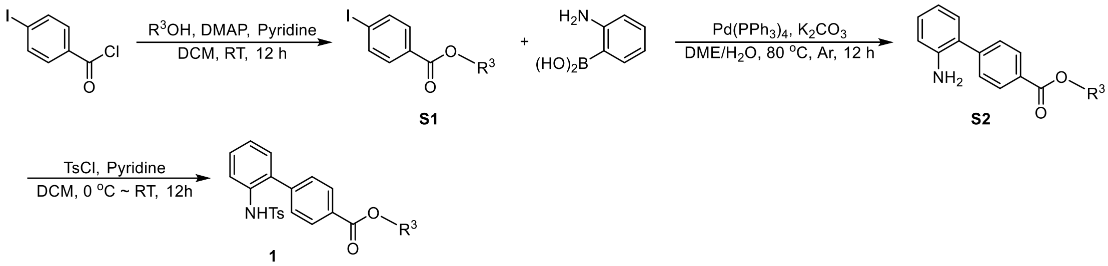


***N*-(2'-methoxy-5-methyl-[1,1'-biphenyl]-2-yl)-4-methylbenzenesulfonamide(1fa):** white solid; Yield 72%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.47 (d, *J* = 8.2 Hz, 1H), 7.23 – 7.15 (m, 1H), 7.13 – 7.00 (m, 3H), 6.91 – 6.80 (m, 4H), 6.78 (d, *J* = 2.4 Hz, 1H), 6.66 (td, *J* = 7.5, 1.2 Hz, 1H), 6.30 (dd, *J* = 7.5, 1.8 Hz, 1H), 3.71 (s, 3H), 2.24 (d, *J* = 5.4 Hz, 6H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 155.07, 142.90, 136.34, 136.21, 133.55, 131.77, 131.71, 131.61, 129.41, 129.36, 129.31, 127.21, 126.75, 125.99, 121.31, 111.14, 56.24, 21.58, 21.08; **HRMS (ESI)** m/z calcd for $C_{21}H_{21}NNaO_3S^+$ $(M+Na)^+$ 390.1134, found 390.1134.



***N*-(3'-methoxy-5'-methyl-[1,1'-biphenyl]-2-yl)-4-methylbenzenesulfonamide(1fe):** white solid; Yield 73%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.74 (dt, *J* = 8.2, 1.5 Hz, 1H), 7.45 (dd, *J* = 8.4, 2.3 Hz, 2H), 7.31 (tt, *J* = 8.1, 2.1 Hz, 1H), 7.22 – 7.01 (m, 4H), 6.72 (dd, *J* = 18.0, 2.0 Hz, 2H), 6.40 – 5.93 (m, 2H), 3.74 (d, *J* = 2.4 Hz, 3H), 2.37 (d, *J* = 2.4 Hz, 3H), 2.28 (d, *J* = 2.4 Hz, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 159.92, 143.73, 140.14, 138.15, 136.00, 134.13, 133.59, 129.96, 129.47, 128.46, 127.04, 124.88, 121.62, 121.50, 114.16, 111.63, 77.48, 77.16, 76.84, 55.11, 21.48, 21.45; **HRMS (ESI)** m/z calcd for $C_{21}H_{21}NNaO_3S^+$ $(M+Na)^+$ 390.1134, found 390.1135.

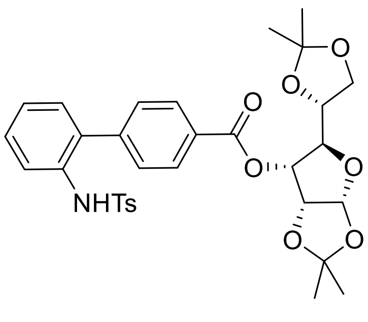
5.2 General procedure B



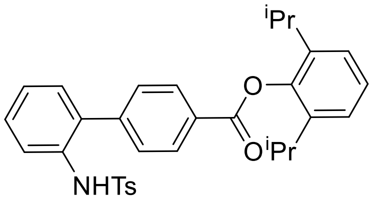
A dry round bottom flask equipped with a magnetic stirrer bar was charged with alcohol (1.0 equiv), pyridine (5 equiv), and DMAP (2 mol%) in CH_2Cl_2 (0.1 M). 4-Iodobenzoyl chloride (1.2 equiv) was added and the resulting mixture stirring at 25 ℃ for 12 h. The reaction mixture was poured into water and extracted with CH_2Cl_2 (3-5 times), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired product **S1**.

A dry round bottom flask flushed with argon and equipped with a magnetic stirrer bar and a septum was charged with arylboronic acid (1.5 equiv), K_2CO_3 (4.0 equiv), and $Pd(PPh_3)_4$ (10 mol%). A mixture of DME and H_2O (DME : H_2O = 1:1, 0.25 M), **S1** (1.0 equiv) were added, and the resulting mixture was heated to 80 ℃ for 12 h. The reaction mixture was poured into water and extracted with CH_2Cl_2 (3-5 times), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired product **S2**.

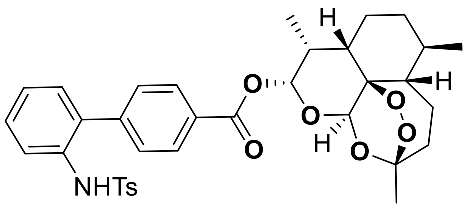
A dry round bottom flask equipped with a magnetic stirrer bar was charged with **S2** (1.0 equiv), DMAP (2 mol%) and pyridine (5.0 equiv) in CH_2Cl_2 (0.2 M). 4-toluenesulfonyl chloride (1.1 equiv) was added at 0 ℃. After being stirred at 25 ℃ for 12 h, the reaction mixture was poured into water and extracted with CH_2Cl_2 (3-5 times), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the corresponding product **1**.



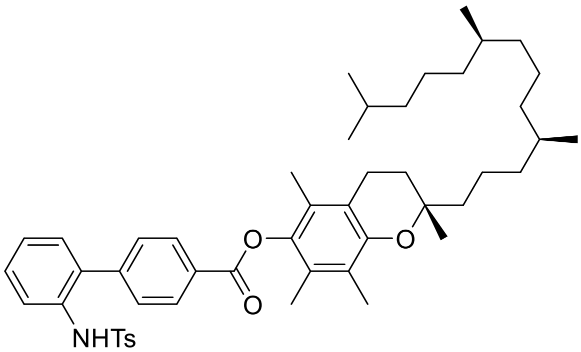
(3aR,5R,6R,6aR)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 2'-((4-methylphenyl)sulfonamido)-[1,1'-biphenyl]-4-carboxylate (1ff): white solid; Yield 63%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.97 – 7.91 (m, 2H), 7.70 – 7.56 (m, 1H), 7.42 (dd, *J* = 8.4, 2.1 Hz, 2H), 7.31 (td, *J* = 7.8, 1.7 Hz, 1H), 7.15 (dt, *J* = 7.5, 2.6 Hz, 2H), 7.07 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.00 – 6.94 (m, 2H), 6.61 (dd, *J* = 10.4, 6.4 Hz, 1H), 5.95 (q, *J* = 3.1, 2.4 Hz, 1H), 5.50 (d, *J* = 3.1 Hz, 1H), 4.63 (t, *J* = 3.4 Hz, 1H), 4.42 – 4.28 (m, 2H), 4.16 – 4.01 (m, 2H), 2.37 (s, 3H), 1.53 (s, 3H), 1.40 (s, 3H), 1.29 (d, *J* = 13.2 Hz, 6H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 164.79, 144.23, 142.81, 136.21, 133.60, 133.20, 130.43, 130.16, 129.80, 129.47, 129.36, 127.55, 127.25, 125.43, 122.22, 112.56, 109.63, 105.27, 83.50, 80.03, 76.84, 72.68, 67.42, 27.02, 26.84, 26.32, 25.40, 21.69; **HRMS (ESI)** m/z calcd for $C_{32}H_{35}KNO_9S^+$ $(M+K)^+$ 648.1664, found 648.1669.



2,6-diisopropylphenyl 2'-((4-methylphenyl)sulfonamido)-[1,1'-biphenyl]-4-carboxylate(1fg): white solid; Yield 70%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.26 – 8.19 (m, 2H), 7.75 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.40 (td, *J* = 7.8, 1.8 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.22 (ddd, *J* = 14.1, 6.7, 2.3 Hz, 4H), 7.15 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.05 (dq, *J* = 8.3, 2.0 Hz, 2H), 6.49 (s, 1H), 3.03 (hept, *J* = 6.9 Hz, 2H), 2.43 (s, 3H), 1.27 (dd, *J* = 6.8, 2.2 Hz, 12H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 164.80, 145.83, 144.34, 142.88, 140.61, 136.21, 133.71, 133.13, 130.96, 130.19, 129.86, 129.56, 129.19, 127.33, 126.89, 125.38, 124.23, 122.05, 27.81, 24.10, 22.86, 21.73; **HRMS (ESI)** m/z calcd for $C_{32}H_{33}KNO_4S^+$ $(M+K)^+$ 566.1762, found 566.1762.



(3*R*,5a*R*,6*S*,8a*R*,9*S*,12*S*,12a*S*)-3,6,9-trimethyldecahydro-12*H*-3,12-epoxy[1,2]dioxepino[4,3-*i*]isochromen-10-yl 2'-((4-methylphenyl)sulfonamido)-[1,1'-biphenyl]-4-carboxylate(1fh): colorless oil; Yield 88%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.00 (dd, *J* = 8.3, 2.2 Hz, 2H), 7.66 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.48 – 7.37 (m, 2H), 7.37 – 7.25 (m, 1H), 7.19 – 7.12 (m, 3H), 7.07 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 2H), 6.68 – 6.63 (m, 1H), 5.99 (d, *J* = 1.5 Hz, 1H), 5.51 (s, 1H), 2.79 – 2.69 (m, 2H), 2.37 (s, 3H), 2.12 – 1.99 (m, 3H), 1.93 – 1.60 (m, 4H), 1.51 – 1.24 (m, 6H), 0.93 (dd, *J* = 9.8, 5.9 Hz, 6H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 164.88, 144.25, 142.54, 136.14, 133.60, 133.47, 130.86, 130.21, 130.05, 129.83, 129.41, 129.08, 127.22, 125.47, 122.53, 104.64, 92.91, 91.79, 80.35, 51.76, 45.45, 37.43, 36.37, 34.24, 32.16, 26.10, 24.72, 22.21, 21.74, 20.39, 12.43; **HRMS (ESI)** m/z calcd for $C_{35}H_{39}KNO_8S^+$ $(M+K)^+$ 672.2028, found 672.2030.

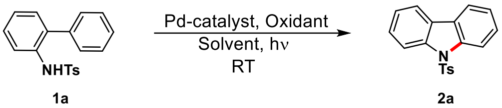


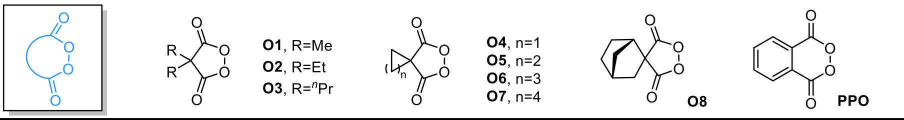
2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl 2'-((4-methylphenyl)sulfonamido)-[1,1'-biphenyl]-4-carboxylate(1fi): colorless oil; Yield 66%; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.25 (d, *J* = 8.3 Hz, 2H), 7.78 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.43 (td, *J* = 7.8, 1.7 Hz, 1H), 7.25 (dd, *J* = 7.7, 6.1 Hz, 3H), 7.19 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.10 – 7.04 (m, 2H), 6.59 (s, 1H), 2.70 (t, *J* = 6.8 Hz, 2H), 2.46 (s, 3H), 2.22 – 2.10 (m, 9H), 1.88 (ddp, *J* = 19.5, 13.4, 6.8, 6.3 Hz, 2H), 1.73 – 1.07 (m, 24H), 0.92 (t, *J* = 6.0 Hz, 12H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 164.74, 149.69, 144.20, 142.67, 140.64, 136.23, 133.63, 133.41, 130.83, 130.17, 129.79, 129.40, 129.38, 129.32, 127.25, 126.92, 125.44, 125.18, 123.33, 122.40, 117.68, 75.24, 39.47, 37.64, 37.55, 37.49, 37.39, 32.87, 32.81, 28.08, 24.92, 24.55, 22.84, 22.75, 21.67, 21.16, 20.76, 19.87, 19.81, 13.23, 12.39, 12.00; **HRMS (ESI)** m/z calcd for $C_{49}H_{65}KNO_5S^+$ $(M+K)^+$ 818.4215, found 818.4213.

6. Synthesis of carbazoles (2)

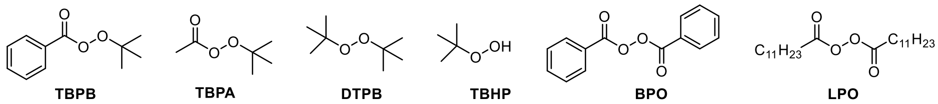
6.1 Reaction optimization

Table S1. Optimization of the Reaction Conditions[a]



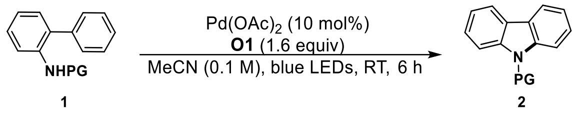


Entry	Pd-Catalyst	Oxidant	Solvent	hν	Yield (%)[b]	Entry	Pd-Catalyst	Oxidant	Solvent	hν	Yield (%)[b]
1	$Pd(OAc)_2$	**O1**	DMSO	-	7	21	$Pd(OAc)_2$	**$PhI(OAc)_2$**	MeCN	Blue LEDs	49
2	$Pd(OAc)_2$	**O1**	DMF	-	11	22	$Pd(OAc)_2$	**TBPB**	MeCN	Blue LEDs	10
3	$Pd(OAc)_2$	**O1**	DCE	-	6	23	$Pd(OAc)_2$	**TBPA**	MeCN	Blue LEDs	<5
4	$Pd(OAc)_2$	**O1**	Toluene	-	6	24	$Pd(OAc)_2$	**DTPB**	MeCN	Blue LEDs	17
5	$Pd(OAc)_2$	**O1**	DCM	-	5	25	$Pd(OAc)_2$	**TBHP**	MeCN	Blue LEDs	<5
6	$Pd(OAc)_2$	**O1**	MeCN	-	70 / 90[c]	26	$Pd(OAc)_2$	**BPO**	MeCN	Blue LEDs	<5
7	$Pd(OAc)_2$	**O1**	MeCN	Blue LEDs	94	27	$Pd(OAc)_2$	**LPO**	MeCN	Blue LEDs	39
8	$Pd(OAc)_2$	**O1**	PhCN	Blue LEDs	80	28	$Pd(TFA)_2$	**O1**	MeCN	Blue LEDs	86
9	$Pd(OAc)_2$	**O1**	$PhCH_2CN$	Blue LEDs	75	29	$PdCl_2$	**O1**	MeCN	Blue LEDs	10
10	$Pd(OAc)_2$	**O2**	MeCN	Blue LEDs	84	30	$Pd(MeCN)_2Cl_2$	**O1**	MeCN	Blue LEDs	12
11	$Pd(OAc)_2$	**O3**	MeCN	Blue LEDs	76	31	$Pd(acac)_2$	**O1**	MeCN	Blue LEDs	69
12	$Pd(OAc)_2$	**O4**	MeCN	Blue LEDs	90	32[d]	$Pd(OAc)_2$	**O1**	MeCN	Blue LEDs	51
13	$Pd(OAc)_2$	**O5**	MeCN	Blue LEDs	88	33[e]	$Pd(OAc)_2$	**O1**	MeCN	Blue LEDs	64
14	$Pd(OAc)_2$	**O6**	MeCN	Blue LEDs	92	34[f]	$Pd(OAc)_2$	**O1**	MeCN	Blue LEDs	90
15	$Pd(OAc)_2$	**O7**	MeCN	Blue LEDs	90	35[g]	$Pd(OAc)_2$	**O1**	MeCN	Blue LEDs	**98**
16	$Pd(OAc)_2$	**O8**	MeCN	Blue LEDs	83	36[h]	$Pd(OAc)_2$	**O1**	MeCN	Blue LEDs	94
17	$Pd(OAc)_2$	**PPO**	MeCN	Blue LEDs	80	37[i]	$Pd(OAc)_2$	**O1**	MeCN	Blue LEDs	86
18	$Pd(OAc)_2$	**NFSI**	MeCN	Blue LEDs	23	38[j]	$Pd(OAc)_2$	**O1**	MeCN	Blue LEDs	81
19	$Pd(OAc)_2$	**H_2O_2**	MeCN	Blue LEDs	<5	39[k]	$Pd(OAc)_2$	**O1**	MeCN	Blue LEDs	95
20	$Pd(OAc)_2$	***m*-CPBA**	MeCN	Blue LEDs	40						



[a]Reaction conditions:**1a** (0.10 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.01 mmol, 10 mol%), oxidant (0.20 mmol, 2.0 equiv) and solvent (1 mL), irradiation with blue LEDs for 6 h at room temperature. [b]Isolated yields. [c]24 h. [d]Oxidant (1 equiv). [e]Oxidant (1.2 equiv). [f]Oxidant (1.4 equiv).[g]Oxidant (1.6 equiv). [h]Oxidant (1.8 equiv). [i]Solvent (0.2 M), **O1** (1.6 equiv). [j]Solvent (0.07 M), **O1** (1.6 equiv). [k]$Pd(OAc)_2$ (5 mol%), **O1** (1.6 equiv), 24 h.

Table S2. Effect of Nitrogen-Protecting Groups on the Carbazole Synthesis[a]

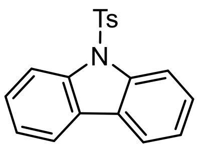


Entry	PG	Product	Yield (%)[b]	Predicted pK_a[c]
1	**Ts**	**2a**	**98**	**17.69**
2	H	**2b**	80	26.03
3	$PhSO_2$	**2c**	94	17.45
4	Ms	**2d**	96	16.86
5	*p*-$ClC_6H_4SO_2$	**2e**	91	16.5
6	Ns	**2f**	72	15.79
7	COOMe	**2g**	56	20.51
8	Ac	**2h**	41	23.17
9	PhCO	**2i**	23	22.21
10	*p*-ClC_6H_4CO	**2j**	20	21.07
11	^{t}BuCO	**2k**	<5	23.87
12	CF_3CO	**2l**	<5	13.91
13	Me	**2m**	<5	25.48
14	Bn	**2n**	<5	24.54

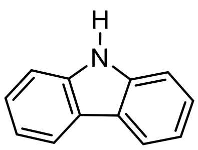
[a]Reaction conditions: **1** (0.1 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.01 mmol 10 mol%), **O1** (0.16 mmol, 1.6 equiv) and solvent (1 mL), irradiation with blue LEDs for 6 h at room temperature. PG = protecting group, Ts = *p*-$MeC_6H_4SO_2$, Ns = *p*-$NO_2C_6H_4SO_2$, Ms = $MeSO_2$. [b]Isolated yield. [c]Predicted pK_a in MeCN.

6.2 General procedure for carbazoles synthesis

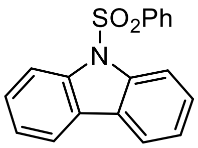
A dry Schlenk tube equipped with a magnetic stirrer bar was charged with substrate **1** (0.10 mmol, 1.0 equiv) and $Pd(OAc)_2$ (0.01 mmol, 10 mol%) in MeCN (1 mL). **O1** (0.16 mmol, 1.6 equiv) was added, and the reaction mixture was stirred at room temperature under irradiation with blue LEDs (20 W) for 6-12 h. The reaction mixture was then purified by flash chromatography on silica gel (PE/EA).



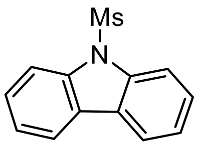
9-Tosyl-9*H*-carbazole (2a): white solid; Yield 98%, 6h; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.37 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 7.89 (d, *J* = 7.7 Hz, 2H; H_{Ar}), 7.71 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 7.50 (t, *J* = 7.8 Hz, 2H; H_{Ar}), 7.36 (t, *J* = 7.5 Hz, 2H; H_{Ar}), 7.05 (d, *J* = 8.3 Hz, 2H; H_{Ar}), 2.21 (s, 3H; CH_3); **^{13}C NMR (150 MHz, $CDCl_3$)** δ144.95 (C_{Ar}), 138.43 (C_{Ar}), 134.98 (C_{Ar}), 129.71 (C_{Ar}), 127.46 (C_{Ar}), 126.52 (C_{Ar}), 126.44 (C_{Ar}), 123.98 (C_{Ar}), 120.09 (C_{Ar}), 115.21 (C_{Ar}), 21.52 (CH_3).



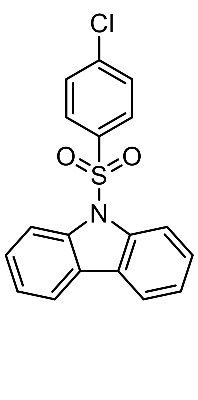
9*H*-carbazole (2b): white solid; Yield 80%, 6h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 7.8 Hz, 2H; H_{Ar}), 8.04 (s, 1H; NH), 7.46 – 7.39 (m, 4H; H_{Ar}), 7.27 – 7.22 (m, 2H; H_{Ar}); **^{13}C NMR (101 MHz, $CDCl_3$)** δ139.62 (C_{Ar}), 125.98 (C_{Ar}), 123.50 (C_{Ar}), 120.47 (C_{Ar}), 119.59 (C_{Ar}), 110.71 (C_{Ar}).



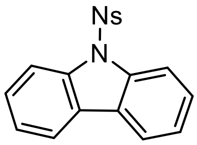
9-(Phenylsulfonyl)-9*H*-carbazole (2c): white solid; Yield 94%, 6h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.35 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 7.90 (d, *J* = 7.6 Hz, 2H; H_{Ar}), 7.83 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 7.50 (t, *J* = 7.6 Hz, 2H; H_{Ar}), 7.43 (t, *J* = 7.6 Hz, 1H; H_{Ar}), 7.37 (t, *J* = 7.6 Hz, 2H; H_{Ar}), 7.30 (t, *J* = 7.6 Hz, 2H; H_{Ar}); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.46 (C_{Ar}), 137.99 (C_{Ar}), 133.88 (C_{Ar}), 129.13 (C_{Ar}), 127.54 (C_{Ar}), 126.53 (C_{Ar}), 126.52 (C_{Ar}), 124.11 (C_{Ar}), 120.15 (C_{Ar}), 115.24 (C_{Ar}).



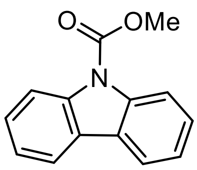
9-(Methylsulfonyl)-9*H*-carbazole (2d): white solid; Yield 96%, 6h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.17 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 8.01 (d, *J* = 7.6 Hz, 2H; H_{Ar}), 7.51 (t, *J* = 7.6 Hz, 2H; H_{Ar}), 7.43 (t, *J* = 7.6 Hz, 2H; H_{Ar}), 2.98 (s, 3H; CH_3); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.45 (C_{Ar}), 127.70 (C_{Ar}), 126.34 (C_{Ar}), 124.23 (C_{Ar}), 120.31 (C_{Ar}), 114.77 (C_{Ar}), 38.75 (CH_3).



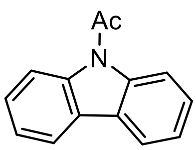
9-((4-chlorophenyl)sulfonyl)-9*H*-carbazole (2e): white solid; Yield 91%, 6h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.30 (dd, J = 8.3, 4.3 Hz, 2H; H_{Ar}), 7.91 (dd, J = 7.9, 3.8 Hz, 2H; H_{Ar}), 7.76 – 7.68 (m, 2H; H_{Ar}), 7.49 (td, J = 7.9, 3.7 Hz, 2H; H_{Ar}), 7.38 (td, J = 7.6, 4.1 Hz, 2H; H_{Ar}), 7.27 (dd, J = 9.0, 4.3 Hz, 2H; H_{Ar}); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.64 (C_{Ar}), 138.34 (C_{Ar}), 136.23 (C_{Ar}), 129.53 (C_{Ar}), 127.98 (C_{Ar}), 127.71 (C_{Ar}), 126.74 (C_{Ar}), 124.44 (C_{Ar}), 120.31 (C_{Ar}), 115.32 (C_{Ar}).



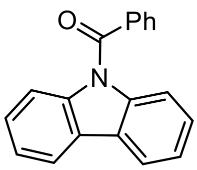
4-(9*H*-carbazol-9-yl)-3-nitrobenzenesulfonic acid (2f): yellow solid; Yield 72%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.31 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 8.11 (d, *J* = 8.9 Hz, 2H; H_{Ar}), 7.98 – 7.92 (m, 2H; H_{Ar}), 7.89 (d, *J* = 7.7 Hz, 2H; H_{Ar}), 7.55 – 7.48 (m, 2H; H_{Ar}), 7.40 (t, *J* = 7.5 Hz, 2H; H_{Ar}); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 150.73 (C_{Ar}), 142.83 (C_{Ar}), 138.07 (C_{Ar}), 127.93 (C_{Ar}), 127.82 (C_{Ar}), 126.90 (C_{Ar}), 124.93 (C_{Ar}), 124.36 (C_{Ar}), 120.46 (C_{Ar}), 115.33 (C_{Ar}); **HRMS (ESI)** m/z calcd for $C_{18}H_{13}N_2O_4S^+$ (M+H)$^+$ 353.0591, found 353.0595.



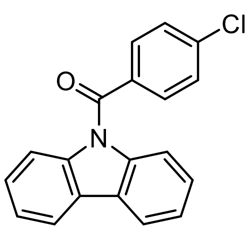
Methyl 9*H*-carbazole-9-carboxylate (g): white solid; Yield 56%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.31 (d, *J* = 8.3 Hz, 2H; H_{Ar}), 7.99 (d, *J* = 7.6 Hz, 2H; H_{Ar}), 7.49 (dd, *J* = 11.5, 4.2 Hz, 2H; H_{Ar}), 7.38 (t, *J* = 7.5 Hz, 2H; H_{Ar}), 4.15 (s, 3H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 153.12 (CO), 138.36 (C_{Ar}), 127.37 (C_{Ar}), 126.09 (C_{Ar}), 123.52 (C_{Ar}), 119.81 (C_{Ar}), 116.39 (C_{Ar}), 53.71 (CH_3); **HRMS (ESI)** m/z calcd for $C_{14}H_{12}NO_2^+$ (M+H)$^+$ 226.0863, found 226.0868.



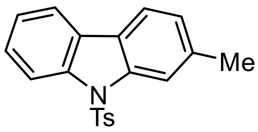
1-(9*H*-carbazol-9-yl)ethan-1-one (2h): white solid; Yield 41%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.23 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 8.01 (d, *J* = 7.6 Hz, 2H; H_{Ar}), 7.49 (t, *J* = 7.6 Hz, 2H; H_{Ar}), 7.40 (t, *J* = 7.6 Hz, 2H; H_{Ar}), 2.90 (s, 3H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 170.23 (C_{Ar}), 138.84 (C_{Ar}), 127.52 (C_{Ar}), 126.61 (C_{Ar}), 123.85 (C_{Ar}), 110.01 (C_{Ar}), 116.43 (C_{Ar}), 27.89 (CH_3).



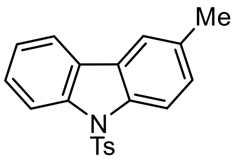
(9*H*-carbazol-9-yl)(phenyl)methanone (2i): white solid; Yield 23%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.02 (dd, J = 6.8, 2.3 Hz, 2H; H_{Ar}), 7.75 – 7.70 (m, 2H; H_{Ar}), 7.69 – 7.63 (m, 1H; H_{Ar}), 7.57 – 7.49 (m, 4H; H_{Ar}), 7.34 (pd, J = 7.3, 1.7 Hz, 4H; H_{Ar}); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 169.81 (CO), 139.31 (C_{Ar}), 135.91 (C_{Ar}), 132.55 (C_{Ar}), 129.22 (C_{Ar}), 129.07 (C_{Ar}), 126.90 (C_{Ar}), 126.19 (C_{Ar}), 123.57 (C_{Ar}), 119.98 (C_{Ar}), 115.96 (C_{Ar}).



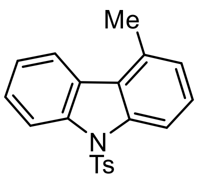
(9*H*-carbazol-9-yl)(4-chlorophenyl)methanone (2j): white solid; Yield 20%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.03 – 8.00 (m, 2H; H_{Ar}), 7.71 – 7.66 (m, 2H; H_{Ar}), 7.55 – 7.48 (m, 4H; H_{Ar}), 7.40 – 7.32 (m, 4H; H_{Ar}); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 168.56 (C_{Ar}), 139.10 (C_{Ar}), 138.94 (C_{Ar}), 134.10 (C_{Ar}), 130.79 (C_{Ar}), 129.40 (C_{Ar}), 126.97 (C_{Ar}), 126.19 (C_{Ar}), 123.73 (C_{Ar}), 120.07 (C_{Ar}), 115.80 (C_{Ar}).



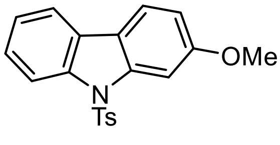
2-Methyl-9-tosyl-9*H*-carbazole (2aa/2ba): white solid; Yield 98% from **1aa**; Yield 93% from **1ba**, 6h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.31 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 8.17 (s, 1H; H_{Ar}), 7.84 (d, *J* = 7.7 Hz, 1H; H_{Ar}), 7.76 (d, *J* = 7.9 Hz, 1H; H_{Ar}), 7.70 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 7.49 – 7.41 (m, 1H; H_{Ar}), 7.37 – 7.30 (m, 1H; H_{Ar}), 7.18 (d, *J* = 7.8 Hz, 1H; H_{Ar}), 7.08 (d, *J* = 8.2 Hz, 2H; H_{Ar}), 2.57 (s, 3H; CH_3), 2.24 (s, 3H; CH_3); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 144.88 (C_{Ar}), 138.87 (C_{Ar}), 138.41 (C_{Ar}), 137.85 (C_{Ar}), 135.14 (C_{Ar}), 129.74 (C_{Ar}), 126.91 (C_{Ar}), 126.58 (C_{Ar}), 126.53 (C_{Ar}), 125.30 (C_{Ar}), 124.08 (C_{Ar}), 123.91 (C_{Ar}), 119.76 (C_{Ar}), 119.71 (C_{Ar}), 115.42 (C_{Ar}), 115.20 (C_{Ar}), 22.40 (CH_3), 21.57 (CH_3); **HRMS (ESI)** m/z calcd for $C_{20}H_{18}NO_2S^+$ $(M+H)^+$ 336.1053, found 336.1055.



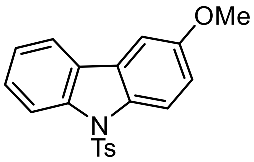
2-Methyl-9-tosyl-9*H*-carbazole (2ab/2bb): white solid; Yield 97% from **1ab**; Yield 97% from **1bb**, 6h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.31 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 8.17 (s, 1H; H_{Ar}), 7.84 (d, *J* = 7.6 Hz, 1H; H_{Ar}), 7.76 (d, *J* = 8.0 Hz, 1H; H_{Ar}), 7.70 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 7.49 – 7.41 (m, 1H; H_{Ar}), 7.37 – 7.30 (m, 1H; H_{Ar}), 7.18 (d, *J* = 7.6 Hz, 1H; H_{Ar}), 7.08 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 2.57 (s, 3H; CH_3), 2.24 (s, 3H; CH_3); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 144.85 (C_{Ar}), 138.75 (C_{Ar}), 136.61 (C_{Ar}), 135.02 (C_{Ar}), 133.74 (C_{Ar}), 129.89 (C_{Ar}), 129.71 (C_{Ar}), 128.70 (C_{Ar}), 127.32 (C_{Ar}), 126.66 (C_{Ar}), 126.57 (C_{Ar}), 123.93 (C_{Ar}), 120.19 (C_{Ar}), 110.00 (C_{Ar}), 115.33 (C_{Ar}), 115.00 (C_{Ar}), 21.60 (CH_3), 21.41 (CH_3); **HRMS (ESI)** m/z calcd for $C_{20}H_{18}NO_2S^+$ $(M+H)^+$ 336.1053, found 336.1055.



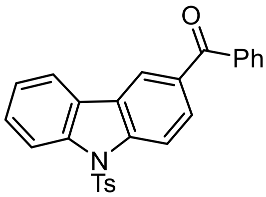
4-Methyl-9-tosyl-9*H*-carbazole (2ac/2bc): white solid; Yield 64% from **1ac**; Yield 39% from **1bc**, 6h; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.41 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 8.24 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 8.03 (d, *J* = 7.8 Hz, 1H; H_{Ar}), 7.69 (d, *J* = 8.3 Hz, 2H; H_{Ar}), 7.50 (t, *J* = 7.8 Hz, 1H; H_{Ar}), 7.38 (td, *J* = 7.8, 3.7 Hz, 2H; H_{Ar}), 7.14 (d, *J* = 7.4 Hz, 1H; H_{Ar}), 7.08 (d, *J* = 8.3 Hz, 2H; H_{Ar}), 2.76 (s, 3H; CH_3), 2.25 (s, 3H; CH_3); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 144.88 (C_{Ar}), 138.66 (C_{Ar}), 138.55 (C_{Ar}), 135.21 (C_{Ar}), 133.30 (C_{Ar}), 129.72 (C_{Ar}), 127.28 (C_{Ar}), 127.06 (C_{Ar}), 126.76 (C_{Ar}), 126.61 (C_{Ar}), 125.85 (C_{Ar}), 124.82 (C_{Ar}), 123.91 (C_{Ar}), 122.67 (C_{Ar}), 115.09 (C_{Ar}), 112.78 (C_{Ar}), 21.57 (CH_3), 21.02 (CH_3); **HRMS (ESI)** m/z calcd for $C_{20}H_{18}NO_2S^+$ $(M+H)^+$ 336.1053, found 336.1056.



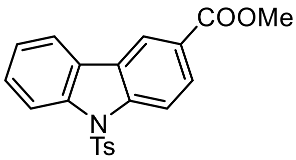
2-Methoxy-9-tosyl-9*H*-carbazole (2ad): yellow solid; Yield 87%, 6h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.28 (d, *J* = 8.3 Hz, 1H; H_{Ar}), 7.90 (d, *J* = 2.2 Hz, 1H; H_{Ar}), 7.79-7.76 (m, 1H; H_{Ar}), 7.75 (d, *J* = 8.5 Hz, 1H; H_{Ar}), 7.69 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 7.40 (td, *J* = 8.4, 7.9, 1.3 Hz 1H; H_{Ar}), 7.31 (td, *J* = 7.6, 0.9 Hz, 1H; H_{Ar}), 7.09 (d, *J* = 8.1 Hz, 2H; H_{Ar}), 6.95 (dd, *J* = 8.5, 2.3 Hz, 1H; H_{Ar}), 3.95 (s, 3H; CH_3), 2.25 (s, 3H; CH_3); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.92 (C_{Ar}), 144.99 (C_{Ar}), 139.86 (C_{Ar}), 138.48 (C_{Ar}), 135.10 (C_{Ar}), 129.77 (C_{Ar}), 126.62 (C_{Ar}), 126.58 (C_{Ar}), 126.14 (C_{Ar}), 124.06 (C_{Ar}), 120.68 (C_{Ar}), 119.93 (C_{Ar}), 119.26 (C_{Ar}), 115.17 (C_{Ar}), 112.21 (C_{Ar}), 100.03 (C_{Ar}), 55.94 (CH_3), 21.59 (CH_3); **HRMS (ESI)** m/z calcd for $C_{20}H_{18}NO_3S^+$ $(M+H)^+$ 352.1002, found 352.1001.



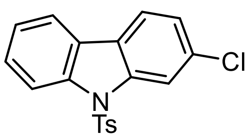
3-Methoxy-9-tosyl-9*H*-carbazole (2ae): red solid; Yield 92%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.31 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 8.23 (d, *J* = 9.2 Hz, 1H; H_{Ar}), 7.84 (d, *J* = 7.7 Hz, 1H; H_{Ar}), 7.64 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 7.51 – 7.44 (m, 1H; H_{Ar}), 7.38 – 7.30 (m, 2H; H_{Ar}), 7.11 – 7.03 (m, 3H; H_{Ar}), 3.89 (s, 3H; CH_3), 2.24 (s, 3H; CH_3); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 156.95 (C_{Ar}), 144.85 (C_{Ar}), 139.18 (C_{Ar}), 134.82 (C_{Ar}), 132.82 (C_{Ar}), 129.70 (C_{Ar}), 127.66 (C_{Ar}), 127.55 (C_{Ar}), 126.70 (C_{Ar}), 126.58 (C_{Ar}), 123.94 (C_{Ar}), 120.06 (C_{Ar}), 116.39 (C_{Ar}), 115.60 (C_{Ar}), 115.42 (C_{Ar}), 103.31 (C_{Ar}), 55.88 (CH_3), 21.62 (CH_3); **HRMS (ESI)** m/z calcd for $C_{20}H_{18}NO_3S^+$ $(M+H)^+$ 352.1002, found 352.1001.



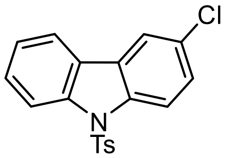
phenyl(9-tosyl-9*H*-carbazol-3-yl)methanone (2af): colorless liquid; Yield 90%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.43 (d, J = 8.8 Hz, 1H; H_{Ar}), 8.40 (d, J = 2.0 Hz, 1H; H_{Ar}), 8.35 (d, J = 8.4 Hz, 1H; H_{Ar}), 7.98 (dd, J = 8.8, 1.8 Hz, 1H; H_{Ar}), 7.96 – 7.90 (m, 1H; H_{Ar}), 7.87 – 7.80 (m, 2H; H_{Ar}), 7.78 – 7.71 (m, 2H; H_{Ar}), 7.66 – 7.58 (m, 1H; H_{Ar}), 7.58 – 7.47 (m, 3H; H_{Ar}), 7.38 (td, J = 7.7, 0.9 Hz, 1H; H_{Ar}), 7.14 (d, J = 8.3 Hz, 2H; H_{Ar}), 2.27 (s, 3H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)**: δ 196.27 (C_{Ar}), 145.47 (C_{Ar}), 140.91 (C_{Ar}), 138.97 (C_{Ar}), 137.93 (C_{Ar}), 134.86 (C_{Ar}), 133.34 (C_{Ar}), 132.51 (C_{Ar}), 130.12 (C_{Ar}), 129.96 (C_{Ar}), 129.64 (C_{Ar}), 128.47 (C_{Ar}), 128.22 (C_{Ar}), 126.61 (C_{Ar}), 126.28 (C_{Ar}), 125.83 (C_{Ar}), 124.36 (C_{Ar}), 122.58 (C_{Ar}), 120.50 (C_{Ar}), 115.17 (C_{Ar}), 114.66 (C_{Ar}), 21.62 (CH_3); **HRMS (ESI)** m/z calcd for $C_{26}H_{20}NO_3S^+$ $(M+H)^+$ 426.1158, found 426.1159.



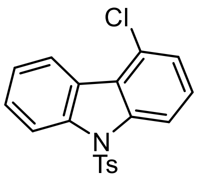
methyl 9-tosyl-9*H*-carbazole-3-carboxylate(2ag): white solid; Yield 84%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)**δ 1 8.61 (d, J = 1.7 Hz, 1H; H_{Ar}), 8.35 (dd, J = 16.1, 8.7 Hz, 2H; H_{Ar}), 8.18 (dt, J = 8.7, 1.5 Hz, 1H; H_{Ar}), 7.97 (d, J = 7.8 Hz, 1H; H_{Ar}), 7.71 (d, J = 8.4 Hz, 2H; H_{Ar}), 7.53 (ddd, J = 8.6, 7.3, 1.3 Hz, 1H; H_{Ar}), 7.40 (t, J = 7.6 Hz, 1H; H_{Ar}), 7.12 (d, J = 8.3 Hz, 2H; H_{Ar}), 3.97 (s, 3H; CH_3), 2.28 (s, 3H; CH_3); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 167.11 (CO), 145.46 (C_{Ar}), 141.28 (C_{Ar}), 138.96 (C_{Ar}), 134.88 (C_{Ar}), 129.97 (C_{Ar}), 128.81 (C_{Ar}), 128.19 (C_{Ar}), 126.64 (C_{Ar}), 126.45 (C_{Ar}), 125.91 (C_{Ar}), 124.43 (C_{Ar}), 122.16 (C_{Ar}), 120.49 (C_{Ar}), 115.25 (C_{Ar}), 114.81 (C_{Ar}), 52.43 (CH_3), 21.69 (CH_3); **HRMS (ESI)** m/z calcd for $C_{21}H_{18}NO_4S^+$ $(M+H)^+$ 380.0951, found 380.0951.



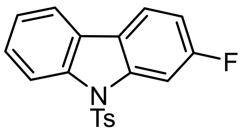
2-Chloro-9-tosyl-9*H*-carbazole (2ah): white solid; Yield 93%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.37 (d, *J* = 1.6 Hz, 1H; H_{Ar}), 8.30 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 7.85 (d, *J* = 7.6 Hz, 1H; H_{Ar}), 7.79 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 7.71 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 7.54 – 7.46 (m, 1H; H_{Ar}), 7.40 – 7.30 (m, 2H; H_{Ar}), 7.12 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 2.27 (s, 3H; CH_3); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 145.35 (C_{Ar}), 138.93 (C_{Ar}), 138.61 (C_{Ar}), 134.82 (C_{Ar}), 133.22 (C_{Ar}), 129.94 (C_{Ar}), 127.77 (C_{Ar}), 126.63 (C_{Ar}), 125.63 (C_{Ar}), 124.98 (C_{Ar}), 124.52 (C_{Ar}), 124.26 (C_{Ar}), 120.85 (C_{Ar}), 120.10 (C_{Ar}), 115.43 (C_{Ar}), 115.21 (C_{Ar}), 21.66 (CH_3); **HRMS (ESI)** m/z calcd for $C_{19}H_{15}ClNO_2S^+$ $(M+H)^+$ 356.0507, found 356.0505.



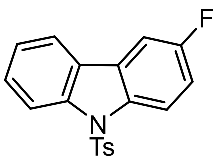
3-Chloro-9-tosyl-9*H*-carbazole (2ai): yellow solid; Yield 97%, 6h; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.32 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 8.26 (d, *J* = 8.9 Hz, 1H; H_{Ar}), 7.86 – 7.82 (m, 2H; H_{Ar}), 7.67 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 7.54 – 7.50 (m, 1H; H_{Ar}), 7.44 (dd, *J* = 8.9, 2.1 Hz, 1H; H_{Ar}), 7.37 (dd, *J* = 11.2, 3.9 Hz, 1H; H_{Ar}), 7.10 (d, *J* = 8.3 Hz, 2H; H_{Ar}), 2.26 (s, 3H; CH$_3$); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 145.27 (C_{Ar}), 138.96 (C_{Ar}), 136.81 (C_{Ar}), 134.75 (C_{Ar}), 129.86 (C_{Ar}), 129.79 (C_{Ar}), 128.24 (C_{Ar}), 127.91 (C_{Ar}), 127.50 (C_{Ar}), 126.57 (C_{Ar}), 125.43 (C_{Ar}), 124.27 (C_{Ar}), 120.31 (C_{Ar}), 110.00 (C_{Ar}), 116.36 (C_{Ar}), 115.39 (C_{Ar}), 21.63 (CH$_3$); **HRMS (ESI)** m/z calcd for $C_{19}H_{15}ClNO_2S^+$ $(M+H)^+$ 356.0507, found 356.0502.



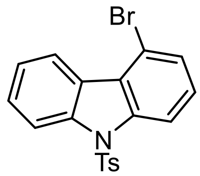
4-Chloro-9-tosyl-9*H*-carbazole (2aj): white solid; Yield 96%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.53 (d, *J* = 7.9 Hz, 1H; H_{Ar}), 8.39 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 8.31 (d, *J* = 8.2 Hz, 1H; H_{Ar}), 7.69 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 7.59 – 7.51 (m, 1H; H_{Ar}), 7.40 (t, *J* = 8.0 Hz, 2H; H_{Ar}), 7.34 (d, *J* = 7.8 Hz, 1H; H_{Ar}), 7.10 (d, *J* = 8.2 Hz, 2H; H_{Ar}), 2.26 (s, 3H; CH$_3$); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 145.31 (C_{Ar}), 139.71 (C_{Ar}), 138.63 (C_{Ar}), 134.89 (C_{Ar}), 129.87 (C_{Ar}), 128.69 (C_{Ar}), 127.99 (C_{Ar}), 127.59 (C_{Ar}), 126.63 (C_{Ar}), 125.34 (C_{Ar}), 125.13 (C_{Ar}), 124.14 (C_{Ar}), 123.72 (C_{Ar}), 123.24 (C_{Ar}), 114.91 (C_{Ar}), 113.56 (C_{Ar}), 21.62 (CH$_3$); **HRMS (ESI)** m/z calcd for $C_{19}H_{15}ClNO_2S^+$ $(M+H)^+$ 356.0507, found 356.0505.



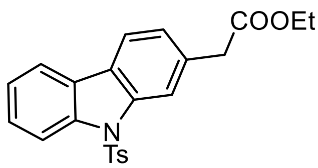
2-Fluoro-9-tosyl-9*H*-carbazole (2ak): white solid; Yield 94%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.31 (d, *J* = 8.3 Hz, 1H; H_{Ar}), 8.08 (dd, *J* = 10.2, 1.9 Hz, 1H; H_{Ar}), 7.82 (dd, *J* = 12.2, 6.6 Hz, 2H; H_{Ar}), 7.71 (d, *J* = 8.2 Hz, 2H; H_{Ar}), 7.47 (t, *J* = 7.8 Hz, 1H; H_{Ar}), 7.35 (t, *J* = 7.5 Hz, 1H; H_{Ar}), 7.09 (dd, *J* = 16.2, 5.1 Hz, 3H; H_{Ar}), 2.26 (s, 3H; CH$_3$); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 162.47 (d, *J* = 244.0 Hz) (C_{Ar}), 145.30 (C_{Ar}), 139.11 (d, *J* = 12.5 Hz) (C_{Ar}), 138.85 (d, *J* = 2.2 Hz) (C_{Ar}), 134.93 (C_{Ar}), 129.89 (C_{Ar}), 127.11 (C_{Ar}), 126.63 (C_{Ar}), 125.84 (C_{Ar}), 124.23 (C_{Ar}), 122.68 (d, J = 1.9 Hz) (C_{Ar}), 120.97 (d, *J* = 10.1 Hz) (C_{Ar}), 119.80 (C_{Ar}), 115.16 (C_{Ar}), 111.97 (d, *J* = 24.0 Hz) (C_{Ar}), 102.93 (d, *J* = 29.1 Hz) (C_{Ar}), 21.60 (CH$_3$); **^{19}F NMR (376 MHz, CDCl$_3$)** δ -36.11 – -36.22 (m, 1F); **HRMS (ESI)** m/z calcd for $C_{19}H_{15}FNO_2S^+$ $(M+H)^+$ 340.0802, found 340.0807.



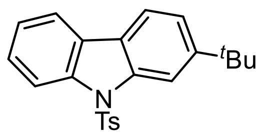
3-Fluoro-9-tosyl-9*H*-carbazole (2al): white solid; Yield 92%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.27 – 8.14 (m, 2H; H_{Ar}), 7.73 (d, *J* = 7.6 Hz, 1H; H_{Ar}), 7.56 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 7.42 (t, *J* = 7.9 Hz, 2H; H_{Ar}), 7.26 (t, *J* = 7.5 Hz, 1H; H_{Ar}), 7.11 (dd, *J* = 12.4, 5.3 Hz, 1H; H_{Ar}), 6.99 (d, *J* = 7.9 Hz, 2H; H_{Ar}), 2.15 (s, 3H; CH$_3$); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 160.05 (d, *J* = 242.1 Hz) (C_{Ar}), 145.15 (C_{Ar}), 139.37 (C_{Ar}), 134.83 (C_{Ar}), 134.65 (d, J = 1.8 Hz) (C_{Ar}), 129.81 (C_{Ar}), 128.15 (C_{Ar}), 127.89 (d, *J* = 9.5 Hz) (C_{Ar}), 126.58 (C_{Ar}), 126.01 (d, *J* = 3.7 Hz) (C_{Ar}), 124.15 (C_{Ar}), 110.35 (C_{Ar}), 116.53 (d, *J* = 8.9 Hz) (C_{Ar}), 115.58 (C_{Ar}), 114.94 (d, *J* = 24.7 Hz) (C_{Ar}), 106.28 (d, *J* = 24.2 Hz) (C_{Ar}), 21.60 (CH$_3$); **^{19}F NMR (376 MHz, CDCl$_3$)** δ -42.55 (td, *J* = 8.6, 4.5 Hz, 1F); **HRMS (ESI)** m/z calcd for $C_{19}H_{15}FNO_2S^+$ $(M+H)^+$ 340.0802, found 340.0800.



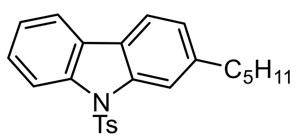
4-bromo-9-tosyl-9*H*-carbazole (2am): colorless liquid; Yield 90%, 6h; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.71 (d, J = 7.9 Hz, 1H; H_{Ar}), 8.39 (t, J = 8.6 Hz, 2H; H_{Ar}), 7.68 (d, J = 8.4 Hz, 2H; H_{Ar}), 7.60 – 7.49 (m, 2H; H_{Ar}), 7.41 (t, J = 7.6 Hz, 1H; H_{Ar}), 7.33 (t, J = 8.1 Hz, 1H; H_{Ar}), 7.10 (d, J = 8.4 Hz, 2H; H_{Ar}), 2.25 (s, 3H; CH_3); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 145.35 (C_{Ar}), 139.71 (C_{Ar}), 138.69 (C_{Ar}), 134.73 (C_{Ar}), 129.87 (C_{Ar}), 128.56 (C_{Ar}), 128.14 (C_{Ar}), 127.79 (C_{Ar}), 126.60 (C_{Ar}), 125.85 (C_{Ar}), 124.99 (C_{Ar}), 123.83 (C_{Ar}), 122.82 (C_{Ar}), 116.42 (C_{Ar}), 114.89 (C_{Ar}), 114.07 (C_{Ar}), 21.63 (CH_3); **HRMS (ESI)** m/z calcd for $C_{19}H_{15}BrNO_2S^+$ $(M+H)^+$ 400.0001, found 400.0000.



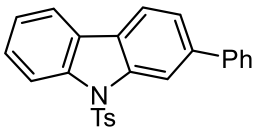
Ethyl 2-(9-tosyl-9*H*-carbazol-2-yl)acetate (2an): yellow solid; Yield 97%, 6h; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.34 – 8.28 (m, 2H; H_{Ar}), 7.86 (d, *J* = 7.7 Hz, 1H; H_{Ar}), 7.83 (d, *J* = 7.9 Hz, 1H; H_{Ar}), 7.71 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 7.50 – 7.44 (m, 1H; H_{Ar}), 7.34 (t, *J* = 7.5 Hz, 1H; H_{Ar}), 7.29 (dd, *J* = 7.9, 0.9 Hz, 1H; H_{Ar}), 7.08 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 4.21 (q, *J* = 7.1 Hz, 2H; CH_2), 3.82 (s, 2H; CH_2), 2.24 (s, 3H; CH_3), 1.30 (t, *J* = 7.1 Hz, 3H; CH_3); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 171.57 (CO), 144.99 (C_{Ar}), 138.68 (C_{Ar}), 138.62 (C_{Ar}), 134.91 (C_{Ar}), 133.75 (C_{Ar}), 129.74 (C_{Ar}), 127.37 (C_{Ar}), 126.61 (C_{Ar}), 126.28 (C_{Ar}), 125.50 (C_{Ar}), 125.34 (C_{Ar}), 124.03 (C_{Ar}), 110.05 (C_{Ar}), 110.02 (C_{Ar}), 116.17 (C_{Ar}), 115.25 (C_{Ar}), 61.09 (CH_2), 41.98 (CH_2), 21.57 (CH_3), 14.33 (CH_3); **HRMS (ESI)** m/z calcd for $C_{23}H_{22}NO_4S^+$ $(M+H)^+$ 408.1264, found 408.1267.



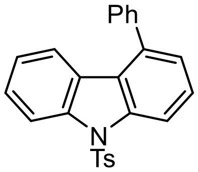
2-(Tert-butyl)-9-tosyl-9*H*-carbazole (2ao): white solid; Yield 96%, 6h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.37 (dd, *J* = 12.0, 4.8 Hz, 2H; H_{Ar}), 7.85 (dd, *J* = 7.6, 0.4 Hz, 1H; H_{Ar}), 7.79 (d, *J* = 8.0 Hz, 1H; H_{Ar}), 7.68 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 7.50 – 7.43 (m, 1H; H_{Ar}), 7.41 (dd, *J* = 8.0, 1.6 Hz, 1H; H_{Ar}), 7.34 (td, *J* = 7.6, 0.8 Hz, 1H; H_{Ar}), 7.07 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 2.24 (s, 3H; CH_3), 1.46 (s, 9H; CH_3); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 151.28 (C_{Ar}), 144.88 (C_{Ar}), 138.82 (C_{Ar}), 138.74 (C_{Ar}), 135.04 (C_{Ar}), 129.67 (C_{Ar}), 126.99 (C_{Ar}), 126.59 (C_{Ar}), 126.56 (C_{Ar}), 124.12 (C_{Ar}), 123.97 (C_{Ar}), 121.60 (C_{Ar}), 119.84 (C_{Ar}), 119.46 (C_{Ar}), 115.35 (C_{Ar}), 112.15 (C_{Ar}), 35.53 (C), 31.81 (CH_3), 21.58 (CH_3) ; **HRMS (ESI)** m/z calcd for $C_{23}H_{24}NO_2S^+$ $(M+H)^+$ 378.1522, found 378.1521.



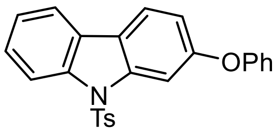
2-Pentyl-9-tosyl-9*H*-carbazole (2ap): white solid; Yield 98%, 6h; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.32 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 8.16 (s, 1H; H_{Ar}), 7.84 (d, *J* = 7.6 Hz, 1H; H_{Ar}), 7.78 (d, *J* = 7.9 Hz, 1H; H_{Ar}), 7.69 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 7.45 (dd, *J* = 11.5, 4.1 Hz, 1H; H_{Ar}), 7.33 (t, *J* = 7.5 Hz, 1H; H_{Ar}), 7.18 (d, *J* = 7.4 Hz, 1H; H_{Ar}), 7.08 (d, *J* = 8.3 Hz, 2H; H_{Ar}), 2.81 (t, *J* = 7.7 Hz, 2H; CH_2), 2.25 (s, 3H; CH_3), 1.77 – 1.68 (m, 2H; CH_2), 1.43 – 1.32 (m, 4H; CH_2), 0.93 (t, *J* = 7.0 Hz, 3H; CH_3); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.87 (C_{Ar}), 143.04 (C_{Ar}), 138.85 (C_{Ar}), 138.57 (C_{Ar}), 135.13 (C_{Ar}), 129.69 (C_{Ar}), 126.93 (C_{Ar}), 126.70 (C_{Ar}), 126.58 (C_{Ar}), 124.77 (C_{Ar}), 124.38 (C_{Ar}), 123.97 (C_{Ar}), 119.77 (C_{Ar}), 119.74 (C_{Ar}), 115.31 (C_{Ar}), 115.01 (C_{Ar}), 36.72 (CH_2), 31.76 (CH_2), 31.53 (CH_2), 22.73 (CH_2), 21.58 (CH_3), 14.22 (CH_3); **HRMS (ESI)** m/z calcd for $C_{24}H_{26}NO_2S^+$ $(M+H)^+$ 392.1679, found 392.1679.



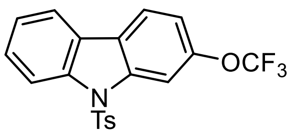
2-Phenyl-9-tosyl-9*H*-carbazole (2aq): yellow solid; Yield 98%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.60 (d, *J* = 1.1 Hz, 1H; H_{Ar}), 8.36 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 7.92 (dd, *J* = 10.0, 8.1 Hz, 2H; H_{Ar}), 7.78 – 7.70 (m, 4H; H_{Ar}), 7.61 (dd, *J* = 8.1, 1.4 Hz, 1H; H_{Ar}), 7.51 (dt, *J* = 8.3, 4.3 Hz, 3H; H_{Ar}), 7.40 (dt, *J* = 18.4, 7.3 Hz, 2H; H_{Ar}), 7.09 (d, *J* = 8.2 Hz, 2H; H_{Ar}), 2.25 (s, 3H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 145.05 (C_{Ar}), 141.26 (C_{Ar}), 139.15 (C_{Ar}), 138.90 (C_{Ar}), 135.09 (C_{Ar}), 129.82 (C_{Ar}), 129.04 (C_{Ar}), 127.67 (C_{Ar}), 127.49 (C_{Ar}), 126.62 (C_{Ar}), 126.27 (C_{Ar}), 125.63 (C_{Ar}), 124.13 (C_{Ar}), 123.47 (C_{Ar}), 120.31 (C_{Ar}), 120.14 (C_{Ar}), 115.31 (C_{Ar}), 113.72 (C_{Ar}), 21.61 (CH_3); **HRMS (ESI)** m/z calcd for $C_{25}H_{20}NO_2S^+$ $(M+H)^+$ 398.1209, found 398.1206.



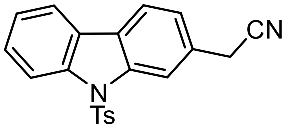
4-phenyl-9-tosyl-9*H*-carbazole (2ar): yellow solid; Yield 72%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.35 – 8.20 (m, 2H; H_{Ar}), 7.71 – 7.56 (m, 2H; H_{Ar}), 7.45 – 7.23 (m, 6H; H_{Ar}), 7.13 (d, *J* = 6.3 Hz, 1H; H_{Ar}), 7.12 – 7.07 (m, 1H; H_{Ar}), 7.02 (dt, *J* = 13.7, 6.7 Hz, 3H; H_{Ar}), 6.94 (dd, *J* = 13.9, 7.0 Hz, 1H; H_{Ar}), 2.16 (d, *J* = 5.9 Hz, 3H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 145.02 (C_{Ar}), 130.36 (C_{Ar}), 138.78 (C_{Ar}), 138.71 (C_{Ar}), 137.76 (C_{Ar}), 135.27 (C_{Ar}), 129.83 (C_{Ar}), 129.18 (C_{Ar}), 128.66 (C_{Ar}), 127.99 (C_{Ar}), 127.18 (C_{Ar}), 126.96 (C_{Ar}), 126.70 (C_{Ar}), 126.19 (C_{Ar}), 125.71 (C_{Ar}), 123.82 (C_{Ar}), 123.46 (C_{Ar}), 122.44 (C_{Ar}), 114.93 (C_{Ar}), 112.8 (C_{Ar}), 21.63 (CH_3); **HRMS (ESI)** m/z calcd for $C_{25}H_{20}NO_2S^+$ $(M+H)^+$ 398.1209, found 398.1205.



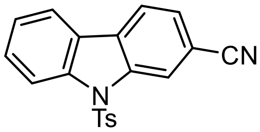
2-Phenoxy-9-tosyl-9*H*-carbazole (2as): yellow solid; Yield 93%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.34 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 8.01 (d, *J* = 1.2 Hz, 1H; H_{Ar}), 7.88 – 7.79 (m, 2H; H_{Ar}), 7.67 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 7.47 (t, *J* = 7.6 Hz, 1H; H_{Ar}), 7.43 – 7.32 (m, 3H; H_{Ar}), 7.16 (t, *J* = 7.6 Hz, 1H; H_{Ar}), 7.11 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 7.05 (d, *J* = 7.6 Hz, 3H; H_{Ar}), 2.28 (s, 3H; CH_3); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 157.73 (C_{Ar}), 156.94 (C_{Ar}), 145.14 (C_{Ar}), 139.37 (C_{Ar}), 138.83 (C_{Ar}), 134.87 (C_{Ar}), 129.95 (C_{Ar}), 129.80 (C_{Ar}), 126.89 (C_{Ar}), 126.69 (C_{Ar}), 126.16 (C_{Ar}), 124.16 (C_{Ar}), 123.54 (C_{Ar}), 122.22 (C_{Ar}), 120.94 (C_{Ar}), 119.68 (C_{Ar}), 118.73 (C_{Ar}), 115.95 (C_{Ar}), 115.18 (C_{Ar}), 106.44 (C_{Ar}), 21.65 (CH_3); **HRMS (ESI)** m/z calcd for $C_{25}H_{20}NO_3S^+$ $(M+H)^+$ 414.1158, found 414.1157.



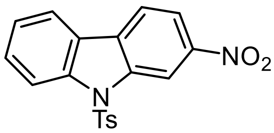
9-Tosyl-2-(trifluoromethoxy)-9*H*-carbazole (2at): yellow solid; Yield 95%, 6h; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.34 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 8.25 (s, 1H; H_{Ar}), 7.87 (d, *J* = 8.3 Hz, 2H; H_{Ar}), 7.70 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 7.52 (t, *J* = 7.8 Hz, 1H; H_{Ar}), 7.38 (t, *J* = 7.5 Hz, 1H; H_{Ar}), 7.24 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 7.12 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 2.27 (s, 3H H; CH_3); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 148.37 (d, J = 1.8 Hz) (C_{Ar}), 145.46 (C_{Ar}), 139.09 (C_{Ar}), 138.65 (C_{Ar}), 134.64 (C_{Ar}), 129.93 (C_{Ar}), 127.87 (C_{Ar}), 126.65 (C_{Ar}), 125.47 (C_{Ar}), 125.14 (C_{Ar}), 124.38 (C_{Ar}), 120.84 (C_{Ar}), 120.73 (q, *J* = 257.2 Hz) (C_{Ar}), 120.22 (C_{Ar}), 117.41 (C_{Ar}), 115.29 (C_{Ar}), 108.93 (C_{Ar}), 21.64 (CH_3); **^{19}F NMR (376 MHz, CDCl$_3$)** δ -57.86 (s, 3F); **HRMS (ESI)** m/z calcd for $C_{20}H_{15}F_3NO_3S^+$ $(M+H)^+$ 406.0719, found 406.0725.



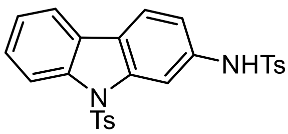
2-(9-Tosyl-9*H*-carbazol-2-yl)acetonitrile (2au): yellow solid; Yield 83%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.35 – 8.24 (m, 2H; H_{Ar}), 7.87 (dd, *J* = 7.6, 4.6 Hz, 2H; H_{Ar}), 7.70 (d, *J* = 8.2 Hz, 2H; H_{Ar}), 7.51 (t, *J* = 7.6 Hz, 1H; H_{Ar}), 7.41 – 7.30 (m, 2H; H_{Ar}), 7.11 (d, *J* = 8.1 Hz, 2H; H_{Ar}), 3.93 (s, 2H; CH_2), 2.26 (s, 3H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 145.30 (C_{Ar}), 138.79 (C_{Ar}), 138.73 (C_{Ar}), 134.88 (C_{Ar}), 129.92 (C_{Ar}), 129.35 (C_{Ar}), 127.91 (C_{Ar}), 126.59 (C_{Ar}), 126.28 (C_{Ar}), 125.72 (C_{Ar}), 124.20 (C_{Ar}), 123.77 (C_{Ar}), 120.76 (C_{Ar}), 120.26 (CN), 118.03 (C_{Ar}), 115.22 (C_{Ar}), 114.82 (C_{Ar}), 24.34 (CH_2), 21.60 (CH_3); **HRMS (ESI)** m/z calcd for $C_{21}H_{17}N_2O_2S^+$ $(M+H)^+$ 361.1005, found 361.1008.



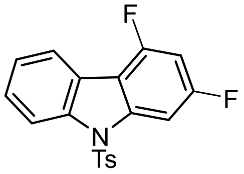
9-Tosyl-9*H*-carbazole-2-carbonitrile (2av): yellow solid; Yield 83%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.66 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 7.98 (dd, *J* = 12.8, 8.0 Hz, 2H; H_{Ar}), 7.72 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 7.61 (dd, *J* = 15.6, 8.0 Hz, 2H; H_{Ar}), 7.43 (t, *J* = 7.6 Hz, 1H; H_{Ar}), 7.16 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 2.30 (s, 3H; CH_3); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 145.78 (C_{Ar}), 139.45 (C_{Ar}), 137.68 (C_{Ar}), 134.64 (C_{Ar}), 130.13 (C_{Ar}), 129.51 (C_{Ar}), 127.36 (C_{Ar}), 126.68 (C_{Ar}), 124.89 (C_{Ar}), 124.60 (C_{Ar}), 121.07 (C_{Ar}), 120.93 (C_{Ar}), 119.46 (CN), 119.17 (C_{Ar}), 115.29 (C_{Ar}), 110.33 (C_{Ar}), 21.72 (CH_3); **HRMS (ESI)** m/z calcd for $C_{20}H_{15}N_2O_2S^+$ $(M+H)^+$ 347.0849, found 347.0851.



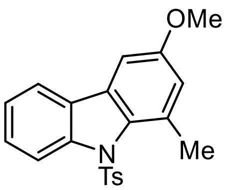
2-Nitro-9-tosyl-9*H*-carbazole (2aw/2be): white solid; Yield 47% from 1ax, 12h; Yield 23% from 1be, 12h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.23 (d, *J* = 2.0 Hz, 1H; H_{Ar}), 8.39 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 8.28 (dd, *J* = 8.4, 2.0 Hz, 1H; H_{Ar}), 8.01 (t, *J* = 8.0 Hz, 2H; H_{Ar}), 7.76 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 7.63 (t, *J* = 8.4 Hz, 1H; H_{Ar}), 7.45 (t, *J* = 7.6 Hz, 1H; H_{Ar}), 7.17 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 2.30 (s, 3H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 158.00 (C_{Ar}), 147.37 (C_{Ar}), 145.82 (C_{Ar}), 136.21 (C_{Ar}), 133.02 (C_{Ar}), 132.92 (C_{Ar}), 130.17 (C_{Ar}), 129.79 (C_{Ar}), 126.80 (C_{Ar}), 124.72 (C_{Ar}), 120.28 (C_{Ar}), 119.36 (C_{Ar}), 116.25 (C_{Ar}), 115.45 (C_{Ar}), 111.28 (C_{Ar}), 111.25 (C_{Ar}), 21.71 (CH_3); **HRMS (ESI)** m/z calcd for $C_{19}H_{15}N_2O_4S^+$ $(M+H)^+$ 367.0704, found 367.0702.



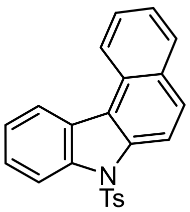
4-Methyl-N-(9-tosyl-9*H*-carbazol-2-yl)benzenesulfonamide (2ax): red solid; Yield 75%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.28 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 8.10 (d, *J* = 1.5 Hz, 1H; H_{Ar}), 7.79 (d, *J* = 7.6 Hz, 1H; H_{Ar}), 7.73 (t, *J* = 8.9 Hz, 3H; H_{Ar}), 7.65 (d, *J* = 8.3 Hz, 2H; H_{Ar}), 7.44 (dd, *J* = 11.5, 4.1 Hz, 1H; H_{Ar}), 7.32 (t, *J* = 7.2 Hz, 1H; H_{Ar}), 7.23 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 7.10 (dd, *J* = 10.8, 4.7 Hz, 4H; H_{Ar}), 2.36 (s, 3H; CH_3), 2.27 (s, 3H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 145.16 (C_{Ar}), 144.13 (C_{Ar}), 138.85 (C_{Ar}), 138.75 (C_{Ar}), 136.18 (C_{Ar}), 136.13 (C_{Ar}), 134.83 (C_{Ar}), 129.88 (C_{Ar}), 129.85 (C_{Ar}), 127.61 (C_{Ar}), 127.32 (C_{Ar}), 126.76 (C_{Ar}), 125.89 (C_{Ar}), 124.17 (C_{Ar}), 123.63 (C_{Ar}), 120.75 (C_{Ar}), 119.86 (C_{Ar}), 117.77 (C_{Ar}), 115.17 (C_{Ar}), 108.04 (C_{Ar}), 21.69 (CH_3), 21.65 (CH_3); **HRMS (ESI)** m/z calcd for $C_{26}H_{23}N_2O_4S_2^+$ $(M+H)^+$ 491.1094, found 491.1098.



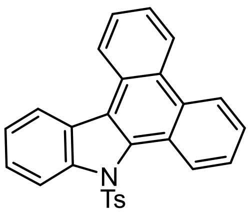
2,4-Difluoro-9-tosyl-9*H*-carbazole (2ay): white solid; Yield 91%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.30 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 8.00 (d, *J* = 7.7 Hz, 1H; H_{Ar}), 7.91 (d, *J* = 9.8 Hz, 1H; H_{Ar}), 7.72 (d, *J* = 8.1 Hz, 2H; H_{Ar}), 7.50 (t, *J* = 7.9 Hz, 1H; H_{Ar}), 7.38 (t, *J* = 7.6 Hz, 1H; H_{Ar}), 7.16 (d, *J* = 8.2 Hz, 2H; H_{Ar}), 6.84 (t, *J* = 9.5 Hz, 1H; H_{Ar}), 2.30 (s, 3H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)** δ163.37 (d, J = 12.0 Hz) (C_{Ar}), 160.93 (d, J = 12.1 Hz) (C_{Ar}), 158.77 (d, J = 14.8 Hz) (C_{Ar}), 156.27 (d, J = 14.8 Hz) (C_{Ar}), 145.63 (C_{Ar}), 140.18 (C_{Ar}), 140.03 (C_{Ar}), 139.92 (C_{Ar}), 138.31 (d, *J* = 2.2 Hz) (C_{Ar}), 134.70 (C_{Ar}), 120.04 (C_{Ar}), 127.38 (C_{Ar}), 126.71 (C_{Ar}), 124.66 (C_{Ar}), 123.19 (C_{Ar}), 122.62 (d, *J* = 4.7 Hz) (C_{Ar}), 114.87 (C_{Ar}), 111.53 (d, J = 19.8 Hz) (C_{Ar}), 100.07 (C_{Ar}), 99.82 (d, *J* = 4.9 Hz) (C_{Ar}), 99.57 (C_{Ar}), 99.16 (d, *J* = 4.4 Hz) (C_{Ar}), 98.87 (d, *J* = 4.3 Hz) (C_{Ar}), 21.70 (CH_3); **^{19}F NMR (376 MHz, CDCl$_3$)** δ -33.47 (td, *J* = 9.6, 6.6 Hz, 1F), -39.75 (dd, *J* = 9.7, 6.7 Hz, 1F); **HRMS (ESI)** m/z calcd for $C_{19}H_{14}F_2NO_2S^+$ $(M+H)^+$ 358.0708, found 358.0702.



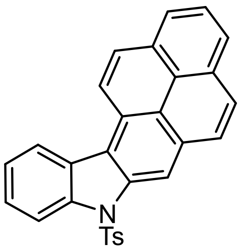
3-methoxy-1-methyl-9-tosyl-9*H*-carbazole (2az): pale yellow solid; Yield 65%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.20 (dd, J = 8.3, 2.5 Hz, 1H; H_{Ar}), 7.61 – 7.54 (m, 1H; H_{Ar}), 7.41 (tdd, J = 8.4, 2.9, 1.4 Hz, 1H; H_{Ar}), 7.33 – 7.25 (m, 1H; H_{Ar}), 7.06 – 7.00 (m, 3H; H_{Ar}), 6.87 (dd, J = 7.9, 2.4 Hz, 3H; H_{Ar}), 3.90 (s, 3H; CH_3), 2.83 (s, 3H; CH_3), 2.22 (s, 3H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)**: δ 157.90 (C_{Ar}), 144.10 (C_{Ar}), 142.43 (C_{Ar}), 134.47 (C_{Ar}), 132.53 (C_{Ar}), 132.47 (C_{Ar}), 132.05 (C_{Ar}), 130.20 (C_{Ar}), 128.69 (C_{Ar}), 127.23 (C_{Ar}), 127.15 (C_{Ar}), 125.52 (C_{Ar}), 119.96 (C_{Ar}), 119.66 (C_{Ar}), 117.63 (C_{Ar}), 101.19 (C_{Ar}), 55.72 (CH_3), 21.88 (CH_3), 21.60 (CH_3); **HRMS (ESI)** m/z calcd for $C_{21}H_{19}NNaO_3S^+$ $(M+Na)^+$ 388.0978, found 388.0975.



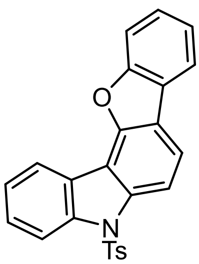
7-Tosyl-7*H*-benzo[*c*]carbazole (2aa'): white solid; Yield 89%, 12h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.71 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 8.61 (d, *J* = 9.2 Hz, 1H; H_{Ar}), 8.53 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 8.47 (d, *J* = 7.6 Hz, 1H; H_{Ar}), 8.00 (d, *J* = 8.0 Hz, 1H; H_{Ar}), 7.95 (d, *J* = 9.2 Hz, 1H; H_{Ar}), 7.69 (d, *J* = 8.0 Hz, 3H; H_{Ar}), 7.52 (dt, *J* = 20.0, 7.6 Hz, 3H; H_{Ar}), 7.05 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 2.21 (s, 3H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 145.07 (C_{Ar}), 138.31 (C_{Ar}), 136.73 (C_{Ar}), 135.17 (C_{Ar}), 131.17 (C_{Ar}), 129.80 (C_{Ar}), 129.26 (C_{Ar}), 128.93 (C_{Ar}), 128.71 (C_{Ar}), 127.43 (C_{Ar}), 127.26 (C_{Ar}), 126.53 (C_{Ar}), 126.30 (C_{Ar}), 125.00 (C_{Ar}), 124.44 (C_{Ar}), 123.66 (C_{Ar}), 122.27 (C_{Ar}), 120.01 (C_{Ar}), 115.58 (C_{Ar}), 115.09 (C_{Ar}), 21.58 (CH_3); **HRMS (ESI)** m/z calcd for $C_{23}H_{18}NO_2S^+$ $(M+H)^+$ 372.1053, found 372.1052.



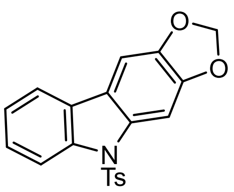
9-Tosyl-9*H*-dibenzo[*a*,*c*]carbazole (2ab'): white solid; Yield 41%, 12h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.97 (d, *J* = 7.6 Hz, 1H; H_{Ar}), 8.82 (d, *J* = 7.6 Hz, 1H; H_{Ar}), 8.75 (d, *J* = 7.6 Hz, 1H; H_{Ar}), 8.56 (d, *J* = 7.6 Hz, 1H; H_{Ar}), 8.42 (d, *J* = 8.0 Hz, 1H; H_{Ar}), 8.18 (d, *J* = 7.6 Hz, 1H; H_{Ar}), 7.78 – 7.67 (m, 4H; H_{Ar}), 7.44 (dt, *J* = 21.6, 7.6 Hz, 2H; H_{Ar}), 6.84 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 6.68 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 2.09 (s, 3H; CH_3); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 144.38 (C_{Ar}), 142.17 (C_{Ar}), 137.01 (C_{Ar}), 131.07 (C_{Ar}), 130.81 (C_{Ar}), 130.77 (C_{Ar}), 130.26 (C_{Ar}), 128.82 (C_{Ar}), 128.57 (C_{Ar}), 127.79 (C_{Ar}), 127.37 (C_{Ar}), 127.20 (C_{Ar}), 127.12 (C_{Ar}), 126.51 (C_{Ar}), 126.25 (C_{Ar}), 126.08 (C_{Ar}), 126.02 (C_{Ar}), 125.79 (C_{Ar}), 124.37 (C_{Ar}), 124.19 (C_{Ar}), 123.83 (C_{Ar}), 122.97 (C_{Ar}), 121.97 (C_{Ar}), 120.08 (C_{Ar}), 21.52 (CH_3); **HRMS (ESI)** m/z calcd for $C_{27}H_{20}NO_2S^+$ $(M+H)^+$ 422.1209, found 422.1210.



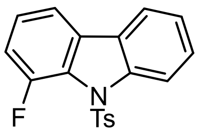
7-Tosyl-7*H*-phenaleno[1,9-*bc*]carbazole (2ac'): yellow solid; Yield 39%, 12h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.27 (s, 1H; H_{Ar}), 9.03 (d, J = 9.2 Hz, 1H; H_{Ar}), 8.75 – 8.68 (m, 1H; H_{Ar}), 8.63 (d, J = 8.1 Hz, 1H; H_{Ar}), 8.36 (d, J = 9.0 Hz, 1H; H_{Ar}), 8.33 – 8.25 (m, 2H; H_{Ar}), 8.17 (d, J = 8.9 Hz, 1H; H_{Ar}), 8.08 (t, J = 7.6 Hz, 1H; H_{Ar}), 7.80 – 7.73 (m, 2H; H_{Ar}), 7.70 – 7.57 (m, 2H; H_{Ar}), 7.06 (d, J = 8.4 Hz, 2H; H_{Ar}), 2.22 (s, 3H; CH_3).; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.11 (C_{Ar}), 139.39 (C_{Ar}), 137.22 (C_{Ar}), 134.92 (C_{Ar}), 132.09 (C_{Ar}), 131.21 (C_{Ar}), 131.02 (C_{Ar}), 130.31 (C_{Ar}), 129.80 (C_{Ar}), 129.11 (C_{Ar}), 128.43 (C_{Ar}), 127.99 (C_{Ar}), 127.42 (C_{Ar}), 127.11 (C_{Ar}), 126.93 (C_{Ar}), 126.59 (C_{Ar}), 126.29 (C_{Ar}), 125.92 (C_{Ar}), 125.85 (C_{Ar}), 125.75 (C_{Ar}), 124.97 (C_{Ar}), 124.58 (C_{Ar}), 123.09 (C_{Ar}), 122.91 (C_{Ar}), 122.41 (C_{Ar}), 115.67 (C_{Ar}), 111.68 (C_{Ar}), 21.59 (CH_3); **HRMS (ESI)** m/z calcd for $C_{29}H_{20}NO_2S$ $(M+H)^+$ 446.1209, found 446.1213.



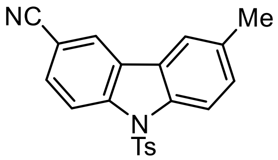
5-Tosyl-5*H*-benzofuro[3,2-*c*]carbazole (2ad'): white solid; Yield 71%, 12h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.40 (dd, *J* = 13.2, 8.4 Hz, 3H; H_{Ar}), 8.02 (dd, *J* = 15.2, 8.0 Hz, 2H; H_{Ar}), 7.70 (dd, *J* = 13.6, 8.4 Hz, 3H; H_{Ar}), 7.56 (t, *J* = 7.6 Hz, 1H; H_{Ar}), 7.48 (dd, *J* = 14.4, 7.2 Hz, 2H; H_{Ar}), 7.39 (t, *J* = 7.2 Hz, 1H; H_{Ar}), 7.08 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 2.24 (s, 3H; CH_3); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 156.69 (C_{Ar}), 150.37 (C_{Ar}), 150.33 (C_{Ar}), 145.17 (C_{Ar}), 138.46 (C_{Ar}), 138.40 (C_{Ar}), 134.90 (C_{Ar}), 129.82 (C_{Ar}), 127.39 (C_{Ar}), 126.67 (C_{Ar}), 126.61 (C_{Ar}), 124.56 (C_{Ar}), 124.25 (C_{Ar}), 123.34 (C_{Ar}), 122.84 (C_{Ar}), 120.48 (C_{Ar}), 120.38 (C_{Ar}), 119.25 (C_{Ar}), 115.34 (C_{Ar}), 112.25 (C_{Ar}), 111.96 (C_{Ar}), 110.43 (C_{Ar}), 21.64 (CH_3); **HRMS (ESI)** m/z calcd for $C_{25}H_{18}NO_3S^+$ $(M+H)^+$ 412.1002, found 412.1004.



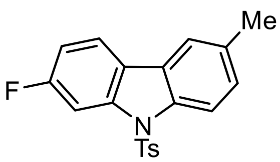
5-Tosyl-5*H*-[1,3]dioxolo[4,5-*b*]carbazole (2ae'): white solid; Yield 47%, 12h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.27 (d, *J* = 8.3 Hz, 1H; H_{Ar}), 7.86 (s, 1H; H_{Ar}), 7.72 (d, *J* = 7.8 Hz, 1H; H_{Ar}), 7.66 (d, *J* = 8.3 Hz, 2H; H_{Ar}), 7.39 (t, *J* = 7.2 Hz, 1H; H_{Ar}), 7.31 (t, *J* = 7.5 Hz, 1H; H_{Ar}), 7.24 (s, 1H; H_{Ar}), 7.10 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 6.06 (s, 2H; CH_2), 2.27 (s, 3H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 148.30 (C_{Ar}), 145.51 (C_{Ar}), 145.00 (C_{Ar}), 138.59 (C_{Ar}), 134.96 (C_{Ar}), 133.55 (C_{Ar}), 129.80 (C_{Ar}), 126.88 (C_{Ar}), 126.65 (C_{Ar}), 126.10 (C_{Ar}), 124.00 (C_{Ar}), 120.46 (C_{Ar}), 119.12 (C_{Ar}), 115.46 (C_{Ar}), 101.84 (C_{Ar}), 99.22 (C_{Ar}), 97.36 (CH_2), 21.66 (CH_3); **HRMS (ESI)** m/z calcd for $C_{20}H_{16}NO_4S^+$ $(M+H)^+$ 366.0795, found 366.0797.



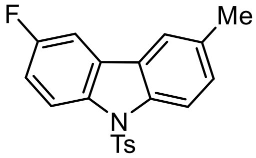
1-Fluoro-9-tosyl-9*H*-carbazole (2bd): yellow solid; Yield 51%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.45 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 7.92 (d, *J* = 7.2 Hz, 1H; H_{Ar}), 7.75 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 7.70 (dd, *J* = 7.6, 0.8 Hz, 1H; H_{Ar}), 7.58 – 7.51 (m, 1H; H_{Ar}), 7.40 (t, *J* = 7.6 Hz, 1H; H_{Ar}), 7.27 (td, *J* = 7.8, 4.0 Hz, 1H; H_{Ar}), 7.21 – 7.09 (m, 3H; H_{Ar}), 2.33 (s, 3H; CH_3); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 150.62 (d, *J* = 252.5 Hz) (C_{Ar}), 145.00 (C_{Ar}), 140.39 (C_{Ar}), 136.11 (C_{Ar}), 130.74 (d, *J* = 3.3 Hz) (C_{Ar}), 129.84 (C_{Ar}), 128.37 (C_{Ar}), 127.27 (C_{Ar}), 127.25 (C_{Ar}), 126.05 (d, *J* = 2.8 Hz) (C_{Ar}), 125.62 (d, *J* = 9.9 Hz) (C_{Ar}), 125.09 (d, *J* = 7.2 Hz) (C_{Ar}), 124.34 (C_{Ar}), 120.29 (C_{Ar}), 116.52 (C_{Ar}), 115.87 (d, *J* = 3.3 Hz) (C_{Ar}), 115.07 (d, *J* = 22.0 Hz) (C_{Ar}), 77.37 (C_{Ar}), 77.16 (C_{Ar}), 76.95 (C_{Ar}), 21.85 (CH_3); **^{19}F NMR (376 MHz, CDCl$_3$)** δ -40.52 (dd, *J* = 12.4, 4.0 Hz, 1F); **HRMS (ESI)** m/z calcd for $C_{19}H_{15}FNO_2S$ $(M+H)^+$ 340.0802, found 340.0801.



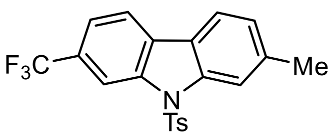
6-Methyl-9-tosyl-9*H*-carbazole-3-carbonitrile (2ca): yellow oil; Yield 66%, 12h; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.79 (d, J = 5.2 Hz, 1H; H_{Ar}), 7.50 (d, J = 8.0 Hz, 1H; H_{Ar}), 7.26 (d, J = 7.7 Hz, 1H; H_{Ar}), 7.14 (d, J = 4.1 Hz, 1H; H_{Ar}), 7.06 (d, J = 7.9 Hz, 1H; H_{Ar}), 6.89 (s, 2H; H_{Ar}), 6.58 (s, 1H; H_{Ar}), 6.42 (s, 2H; H_{Ar}), 1.58 (d, J = 5.5 Hz, 3H; CH_3), 1.38 (d, J = 5.5 Hz, 3H; CH_3).; **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 146.06 (C_{Ar}), 139.90 (C_{Ar}), 136.12 (C_{Ar}), 134.28 (C_{Ar}), 133.53 (C_{Ar}), 130.94 (C_{Ar}), 130.32 (C_{Ar}), 130.18 (C_{Ar}), 126.34 (C_{Ar}), 126.26 (C_{Ar}), 125.48 (C_{Ar}), 124.47 (C_{Ar}), 121.30 (CN), 118.98 (C_{Ar}), 115.48 (C_{Ar}), 114.32 (C_{Ar}), 106.69 (C_{Ar}), 21.07 (CH_3), 20.88 (CH_3); **HRMS (ESI)** m/z calcd for $C_{21}H_{17}N_2O_2S^+$ $(M+H)^+$ 361.1005, found 361.1007.



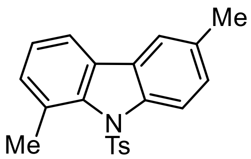
2-Fluoro-6-methyl-9-tosyl-9*H*-carbazole (2cb): yellow solid; Yield 69%, 12h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.16 (d, *J* = 8.5 Hz, 1H; H_{Ar}), 8.04 (dd, *J* = 10.3, 2.3 Hz, 1H; H_{Ar}), 7.77 (dd, *J* = 8.5, 5.4 Hz, 1H; H_{Ar}), 7.71 – 7.67 (m, 2H; H_{Ar}), 7.62 (s, 1H; H_{Ar}), 7.28 (s, 1H; H_{Ar}), 7.08 (ddd, *J* = 11.1, 9.6, 5.2 Hz, 3H; H_{Ar}), 2.47 (s, 3H; CH_3), 2.27 (s, 3H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 162.40 (d, *J* = 243.8 Hz) (C_{Ar}), 145.17 (C_{Ar}), 139.36 (d, *J* = 12.4 Hz) (C_{Ar}), 136.99 (d, J = 2.2 Hz) (C_{Ar}), 134.91 (C_{Ar}), 134.03 (C_{Ar}), 129.87 (C_{Ar}), 128.30 (C_{Ar}), 126.65 (C_{Ar}), 126.02 (C_{Ar}), 122.75 (d, *J* = 1.8 Hz) (C_{Ar}), 120.82 (d, *J* = 10.0 Hz) (C_{Ar}), 119.91 (C_{Ar}), 114.92 (C_{Ar}), 111.89 (d, *J* = 24.0 Hz) (C_{Ar}), 103.00 (d, *J* = 29.1 Hz) (C_{Ar}), 21.64 (CH_3), 21.40 (CH_3); **^{19}F NMR (376 MHz, CDCl$_3$)** δ -42.70 (td, *J* = 8.5, 4.4 Hz, 1F); **HRMS (ESI)** m/z calcd for $C_{20}H_{17}FNO_2S^+$ $(M+H)^+$ 354.0959, found 354.0956.



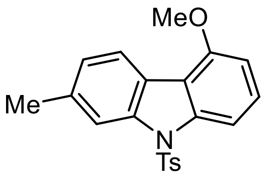
3-Fluoro-6-methyl-9-tosyl-9*H*-carbazole (2cc): yellow solid; Yield 67%, 12h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.26 (dd, *J* = 9.1, 4.4 Hz, 1H; H_{Ar}), 8.18 (d, *J* = 8.5 Hz, 1H; H_{Ar}), 7.62 (dd, *J* = 9.9, 4.5 Hz, 3H; H_{Ar}), 7.48 (dd, *J* = 8.3, 2.6 Hz, 1H; H_{Ar}), 7.32 (d, *J* = 7.7 Hz, 1H; H_{Ar}), 7.17 (td, *J* = 9.0, 2.6 Hz, 1H; H_{Ar}), 7.08 (d, *J* = 8.5 Hz, 2H; H_{Ar}), 2.47 (s, 3H; CH_3), 2.25 (s, 3H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 160.04 (d, *J* = 241.9 Hz) (C_{Ar}), 145.02 (C_{Ar}), 137.52 (C_{Ar}), 134.85 (d, *J* = 12.6 Hz) (C_{Ar}), 133.97 (C_{Ar}), 129.76 (C_{Ar}), 129.40 (C_{Ar}), 127.97 (d, *J* = 9.5 Hz) (C_{Ar}), 126.59 (C_{Ar}), 126.19 (d, *J* = 3.5 Hz) (C_{Ar}), 120.38 (C_{Ar}), 116.58 (d, *J* = 9.0 Hz) (C_{Ar}), 115.34 (C_{Ar}), 114.75 (d, *J* = 24.7 Hz) (C_{Ar}), 106.17 (d, *J* = 24.2 Hz) (C_{Ar}), 21.62 (CH_3), 21.38 (CH_3); **^{19}F NMR (376 MHz, CDCl$_3$)** δ **-**112.50 (s, 1F); **HRMS (ESI)** m/z calcd for $C_{20}H_{17}FNO_2S^+$ $(M+H)^+$ 354.0959, found 354.0958.



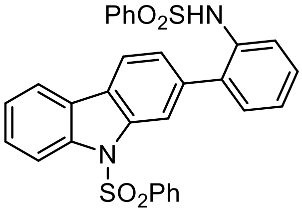
2-Methyl-9-tosyl-7-(trifluoromethyl)-9*H*-carbazole (2cd): white solid; Yield 65%, 12h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.58 (s, 1H), 8.17 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 2.58 (s, 3H), 2.28 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 145.42 (C_{Ar}), 139.80 (C_{Ar}), 139.46 (C_{Ar}), 137.88 (C_{Ar}), 134.91 (C_{Ar}), 129.98 (C_{Ar}), 129.37 (C_{Ar}), 128.97 (C_{Ar}), 128.64 (C_{Ar}), 125.92 (C_{Ar}), 125. (C_{Ar}), 124.76(q, *J* = 272.3 Hz) (C_{Ar}), 122.89 (C_{Ar}), 120.81 (d, *J* = 3.7 Hz) (C_{Ar}), 120.37 (C_{Ar}), 120.08 (C_{Ar}), 115.48 (C_{Ar}), 112.57 (d, *J* = 4.2 Hz) (C_{Ar}), 22.52 (CH_3), 21.65 (CH_3); **^{19}F NMR (376 MHz, CDCl$_3$) δ -**61.17 (s, 3F); **HRMS (ESI)** m/z calcd for $C_{21}H_{17}F_3NO_2S^+$ $(M+H)^+$ 404.0927, found 404.0931.



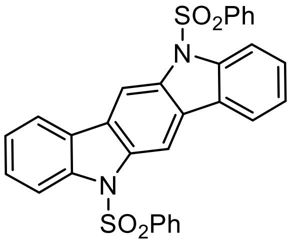
1,6-Dimethyl-9-tosyl-9*H*-carbazole (2ce): white solid; Yield 34%, 12h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.06 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 7.52 – 7.45 (m, 1H; H_{Ar}), 7.40 (s, 1H; H_{Ar}), 7.29 – 7.16 (m, 3H; H_{Ar}), 7.03 (d, *J* = 8.2 Hz, 2H; H_{Ar}), 6.85 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 2.81 (s, 3H; CH_3), 2.41 (s, 3H; CH_3), 2.19 (s, 3H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 144.06 (C_{Ar}), 140.65 (C_{Ar}), 139.56 (C_{Ar}), 135.30 (C_{Ar}), 132.59 (C_{Ar}), 131.26 (C_{Ar}), 131.06 (C_{Ar}), 130.88 (C_{Ar}), 129.99 (C_{Ar}), 128.74 (C_{Ar}), 128.30 (C_{Ar}), 127.08 (C_{Ar}), 125.71 (C_{Ar}), 119.90 (C_{Ar}), 119.37 (C_{Ar}), 117.19 (C_{Ar}), 21.92 (CH_3), 21.60 (CH_3), 21.48 (CH_3); **HRMS (ESI)** m/z calcd for $C_{21}H_{20}NO_2S^+$ $(M+H)^+$ 350.1209, found 350.1210.



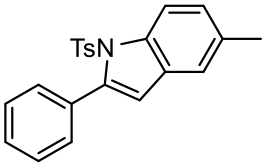
5-Methoxy-2-methyl-9-tosyl-9*H*-carbazole (2cf): white solid; Yield 76%, 12h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.14 (s, 1H; H_{Ar}), 8.07 (d, *J* = 8.0 Hz, 1H; H_{Ar}), 7.92 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 7.69 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 7.36 (t, *J* = 8.4 Hz, 1H; H_{Ar}), 7.17 (d, *J* = 8.0 Hz, 1H; H_{Ar}), 7.08 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 6.80 (d, *J* = 8.0 Hz, 1H; H_{Ar}), 3.99 (s, 3H; CH_3), 2.55 (s, 3H; CH_3), 2.25 (s, 3H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 155.48 (C_{Ar}), 144.82 (C_{Ar}), 139.71 (C_{Ar}), 138.20 (C_{Ar}), 136.76 (C_{Ar}), 135.28 (C_{Ar}), 129.73 (C_{Ar}), 127.57 (C_{Ar}), 126.59 (C_{Ar}), 125.33 (C_{Ar}), 123.42 (C_{Ar}), 122.88 (C_{Ar}), 115.73 (C_{Ar}), 114.87 (C_{Ar}), 107.81 (C_{Ar}), 105.12 (C_{Ar}), 55.62 (CH_3), 22.39 (CH_3), 21.59 (CH_3); **HRMS (ESI)** m/z calcd for $C_{21}H_{20}NO_3S^+$ $(M+H)^+$ 366.1158, found 366.1159.



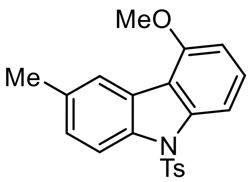
***N*-(2-(9-(phenylsulfonyl)-9*H*-carbazol-2-yl)phenyl)benzenesulfonamide (2da)**: yellow solid; Yield 70%, 6h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.36 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 8.04 (s, 1H; H_{Ar}), 7.94 (d, *J* = 7.7 Hz, 1H; H_{Ar}), 7.85 (dd, *J* = 15.3, 8.0 Hz, 3H; H_{Ar}), 7.70 (d, *J* = 8.1 Hz, 1H; H_{Ar}), 7.57 (dd, *J* = 16.8, 8.2 Hz, 4H; H_{Ar}), 7.50 (t, *J* = 7.2 Hz, 1H; H_{Ar}), 7.40 (dt, *J* = 16.5, 8.1 Hz, 6H; H_{Ar}), 7.25 – 7.16 (m, 2H; H_{Ar}), 6.87 (d, *J* = 7.9 Hz, 1H; H_{Ar}), 6.72 (s, 1H; NH); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 139.00 (C_{Ar}), 138.84 (C_{Ar}), 138.83 (C_{Ar}), 137.80 (C_{Ar}), 136.61 (C_{Ar}), 134.28 (C_{Ar}), 134.05 (C_{Ar}), 133.85 (C_{Ar}), 133.35 (C_{Ar}), 130.82 (C_{Ar}), 129.51 (C_{Ar}), 129.18 (C_{Ar}), 129.09 (C_{Ar}), 128.14 (C_{Ar}), 127.29 (C_{Ar}), 126.56 (C_{Ar}), 126.28 (C_{Ar}), 125.86 (C_{Ar}), 125.27 (C_{Ar}), 124.83 (C_{Ar}), 124.46 (C_{Ar}), 121.56 (C_{Ar}), 120.79 (C_{Ar}), 120.38 (C_{Ar}), 115.74 (C_{Ar}), 115.38 (C_{Ar}); **HRMS (ESI)** m/z calcd for $C_{30}H_{23}N_2O_4S_2^+$ $(M+H)^+$ 539.1094, found 539.1091.



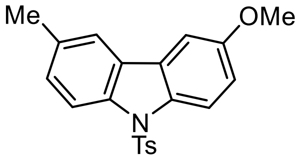
5,11-Bis(phenylsulfonyl)-5,11-dihydroindolo[3,2-*b*]carbazole (2da'): white solid; Yield 80% (with 4.0 equiv **O1**) , 12h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.83 (s, 2H; H_{Ar}), 8.34 (d, *J* = 8.4 Hz, 2H H_{Ar}), 8.10 (d, *J* = 7.7 Hz, 2H H_{Ar}), 7.81 (d, *J* = 8.1 Hz, 4H H_{Ar}), 7.58 – 7.48 (m, 3H H_{Ar}), 7.44 (t, *J* = 7.6 Hz, 5H H_{Ar}), 7.30 (d, *J* = 7.7 Hz, 2H H_{Ar}); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 139.41 (C_{Ar}), 137.75 (C_{Ar}), 135.89 (C_{Ar}), 134.07 (C_{Ar}), 129.25 (C_{Ar}), 128.06 (C_{Ar}), 127.00 (C_{Ar}), 126.82 (C_{Ar}), 126.61 (C_{Ar}), 124.43 (C_{Ar}), 120.54 (C_{Ar}), 115.50 (C_{Ar}), 106.43 (C_{Ar}).



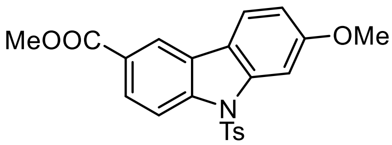
6-Methyl-2-phenyl-1-tosyl-1*H*-indole (2ea): yellow solid; Yield 13%, 12h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.13 (s, 1H; H_{Ar}), 7.50 – 7.44 (m, 2H; H_{Ar}), 7.41 (d, *J* = 5.2 Hz, 3H; H_{Ar}), 7.27 (s, 1H; H_{Ar}), 7.25 (s, 1H; H_{Ar}), 7.22 (s, 1H; H_{Ar}), 7.17 (d, *J* = 8.6 Hz, 1H; H_{Ar}), 7.03 (d, *J* = 8.2 Hz, 2H; H_{Ar}), 6.49 (s, 1H; CH), 2.53 (s, 3H; CH_3), 2.29 (s, 3H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 144.53 (C_{Ar}), 142.39 (C_{Ar}), 136.63 (C_{Ar}), 134.73 (C_{Ar}), 134.12 (C_{Ar}), 132.67 (C_{Ar}), 130.97 (C_{Ar}), 130.41 (C_{Ar}), 129.30 (C_{Ar}), 128.71 (C_{Ar}), 127.62 (C_{Ar}), 126.95 (C_{Ar}), 126.31 (C_{Ar}), 120.77 (C_{Ar}), 116.52 (C_{Ar}), 113.74 (C_{Ar}), 100.11 (CH), 21.67 (CH_3), 21.42 (CH_3); **HRMS (ESI)** m/z calcd for $C_{22}H_{20}NO_2S^+$ $(M+H)^+$ 362.1209, found 362.1209.



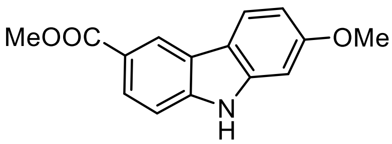
5-methoxy-3-methyl-9-tosyl-9*H*-carbazole (2fa): white solid; Yield 70%, 12h; **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.10 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 7.93-7.90 (m, 1H; H_{Ar}), 7.84 (dd, *J* = 8.4, 0.6 Hz, 1H; H_{Ar}), 7.58 (d, *J* = 8.6 Hz, 2H; H_{Ar}), 7.29 (t, *J* = 8.3 Hz, 1H; H_{Ar}), 7.20 – 7.14 (m, 1H; H_{Ar}), 7.04 – 6.91 (m, 2H; H_{Ar}), 6.71 (d, *J* = 8.2 Hz, 1H; H_{Ar}), 3.91 (s, 3H; CH_3), 2.39 (s, 3H; CH_3), 2.14 (s, 3H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)**: δ 155.72 (C_{Ar}), 144.78 (C_{Ar}), 140.01 (C_{Ar}), 135.88 (C_{Ar}), 135.07 (C_{Ar}), 133.72 (C_{Ar}), 129.67 (C_{Ar}), 127.96 (C_{Ar}), 127.65 (C_{Ar}), 126.58 (C_{Ar}), 125.99 (C_{Ar}), 123.37 (C_{Ar}), 115.62 (C_{Ar}), 114.31 (C_{Ar}), 107.85 (C_{Ar}), 105.09 (C_{Ar}), 55.62 (CH_3), 21.57 (CH_3), 21.45 (CH_3). **HRMS (ESI)** m/z calcd for $C_{21}H_{19}NNaO_3S^+$ $(M+Na)^+$ 388.0978, found 388.0978.



3-Methoxy-6-methyl-9-tosyl-9*H*-carbazole (2fb): white solid; Yield 98%, 12h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.18 (dd, *J* = 12.4, 8.8 Hz, 2H; H_{Ar}), 7.62 (d, *J* = 8.4 Hz, 3H; H_{Ar}), 7.29 (t, *J* = 6.0 Hz, 2H; H_{Ar}), 7.05 (dd, *J* = 8.8, 2.8 Hz, 3H; H_{Ar}), 3.88 (s, 3H; CH_3), 2.47 (s, 3H; CH_3), 2.24 (s, 3H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 156.95 (C_{Ar}), 144.70 (C_{Ar}), 137.37 (C_{Ar}), 134.88 (C_{Ar}), 133.69 (C_{Ar}), 133.15 (C_{Ar}), 129.64 (C_{Ar}), 128.77 (C_{Ar}), 127.76 (C_{Ar}), 126.90 (C_{Ar}), 126.59 (C_{Ar}), 120.14 (C_{Ar}), 116.47 (C_{Ar}), 115.38 (C_{Ar}), 115.25 (C_{Ar}), 103.26 (C_{Ar}), 55.87 (CH_3), 21.60 (CH_3), 21.41 (CH_3); **HRMS (ESI)** m/z calcd for $C_{21}H_{20}NO_3S^+$ $(M+H)^+$ 366.1158, found 365.1159.

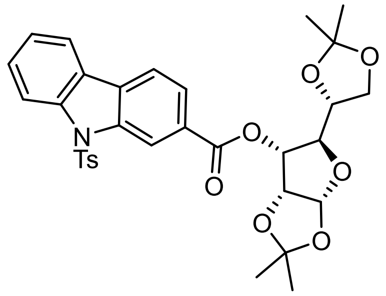


methyl 7-methoxy-9-tosyl-9*H*-carbazole-3-carboxylate (2fc): white solid; Yield 85%, 12h; **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.48 (d, J = 1.7 Hz, 1H; H_{Ar}), 8.30 (d, J = 8.8 Hz, 1H; H_{Ar}), 8.09 (dd, J = 8.7, 1.8 Hz,1H; H_{Ar}), 7.87 (d, J = 2.3 Hz, 1H; H_{Ar}), 7.82 (d, J = 8.6Hz, 1H; H_{Ar}), 7.72 – 7.67 (m, 2H; H_{Ar}), 7.13 (d, J = 7.8 Hz, 2H; H_{Ar}), 6.99 (dd, J = 8.6, 2.3 Hz, 1H; H_{Ar}), 3.95 (d, J = 1.0 Hz, 6H; CH_3), 2.28 (s, 3H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)**: δ 167.19 (C=O), 160.41 (C_{Ar}), 145.45 (C_{Ar}), 141.30 (C_{Ar}), 140.41 (C_{Ar}), 134.94 (C_{Ar}), 129.97 (C_{Ar}), 127.53 (C_{Ar}), 126.63 (C_{Ar}), 126.01 (C_{Ar}), 121.19 (C_{Ar}), 121.09 (C_{Ar}), 119.27 (C_{Ar}), 114.70 (C_{Ar}), 112.63 (C_{Ar}), 99.99 (C_{Ar}). 56.01 (CH_3), 52.34 (CH_3), 21.67 (CH_3); **HRMS (ESI)** m/z calcd for $C_{22}H_{19}NNaO_5S^+$ $(M+Na)^+$ 432.0876, found 432.0879.

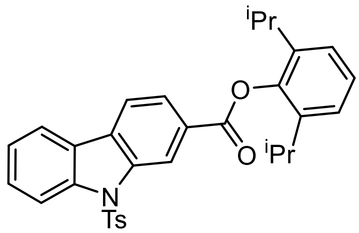


To a solution of **2fc** in THF (0.1 M) was added TBAF (1.0 M solution in THF, 5 equiv) at room temperature. The reaction mixture was refluxed for 3 h. The reaction mixture was poured into water and extracted with CH_2Cl_2 (3-5 times), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (PE/EA).

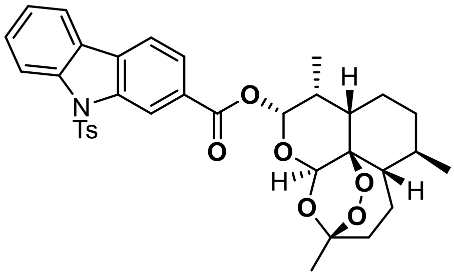
Clausine C (2fd): white solid; Yield 80% in two steps; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.73 (s, 1H; NH), 7.81 (d, J = 1.8 Hz, 1H; H_{Ar}), 7.27 (d, J = 8.6 Hz, 1H; H_{Ar}), 7.08 (dd, J = 8.5, 1.8 Hz, 1H; H_{Ar}), 6.65 (d, J = 8.6 Hz, 1H; H_{Ar}), 6.16 (d, J = 2.3 Hz, 1H; H_{Ar}), 5.98 (dd, J = 8.6, 2.3 Hz, 1H; H_{Ar}), 3.02 (s, 3H; CH_3), 3.00 (s, 3H; CH_3); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 167.17 (C_{Ar}), 159.17 (C_{Ar}), 142.77 (C_{Ar}), 141.93 (C_{Ar}), 125.60 (C_{Ar}), 122.65 (C_{Ar}), 121.65 (C_{Ar}), 121.44 (C_{Ar}), 119.98 (C_{Ar}), 116.13 (C_{Ar}), 110.57 (C_{Ar}), 108.88 (C_{Ar}), 94.93 (C_{Ar}), 55.44(CH_3), 51.85 (CH_3).



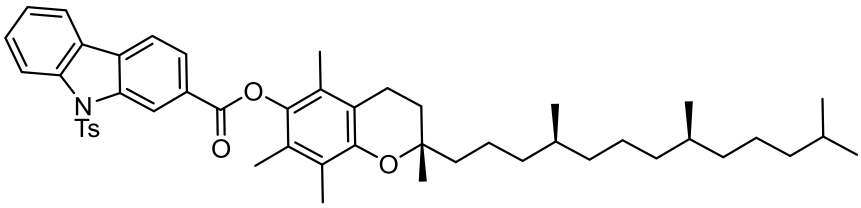
(3aR,5R,6R,6aR)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 9-tosyl-9*H*-carbazole-2-carboxylate (2fe): colorless liquid; Yield 90%, 12h; **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 9.00 (d, *J* = 1.6 Hz, 1H; H_{Ar}), 8.36 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 8.03 (dd, *J* = 8.1, 1.7 Hz, 1H; H_{Ar}), 7.97 (d, *J* = 3.7 Hz, 1H; H_{Ar}), 7.95 (d, *J* = 4.0 Hz, 1H; H_{Ar}), 7.74 – 7.68 (m, 2H; H_{Ar}), 7.58 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H; H_{Ar}), 7.41 (t, *J* = 7.5 Hz, 1H; H_{Ar}), 7.12 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 6.01 (d, *J* = 3.7 Hz, 1H; CH), 5.54 (d, *J* = 3.1 Hz, 1H; CH), 4.74 (d, *J* = 3.7 Hz, 1H; CH), 4.51 (dt, *J* = 7.9, 5.4 Hz, 1H; CH), 4.39 (dd, *J* = 7.9, 3.1 Hz, 1H; CH), 4.17 (dd, *J* = 9.2, 5.5 Hz, 2H; CH_2), 2.27 (s, 3H; CH_3), 1.59 (s, 3H; CH_3), 1.45 (s, 3H; CH_3), 1.35 (s, 3H; CH_3), 1.29 (s, 3H; CH_3).; **^{13}C NMR (101 MHz, CDCl$_3$)**: δ 165.43 (CO), 145.40 (C_{Ar}), 139.79 (C_{Ar}), 138.06 (C_{Ar}), 134.90 (C_{Ar}), 130.67 (C_{Ar}), 129.97 (C_{Ar}), 129.06 (C_{Ar}), 128.38 (C_{Ar}), 126.71 (C_{Ar}), 125.33 (C_{Ar}), 125.25 (C_{Ar}), 124.36 (C_{Ar}), 121.02 (C_{Ar}), 120.02 (C_{Ar}), 116.90 (C_{Ar}), 115.38 (C_{Ar}), 112.52 (C), 109.58 (C), 105.32 (CH), 83.54 (CH), 80.18 (CH), 77.23 (CH), 72.87 (CH), 67.50 (CH_2), 27.03 (CH_3), 26.90 (CH_3), 26.38 (CH_3), 25.37 (CH_3), 21.68 (CH_3); **HRMS (ESI)** m/z calcd for $C_{32}H_{33}NNaO_9S^+$ $(M+Na)^+$ 630.1768, found 630.1763.



2,6-Diisopropylphenyl 9-tosyl-9*H*-carbazole-2-carboxylate (2ff): white solid; Yield 74%, 12h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.23 (s, 1H; H_{Ar}), 8.43 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 8.25 (dd, *J* = 8.1, 1.2 Hz, 1H; H_{Ar}), 8.03 (dd, *J* = 13.7, 7.9 Hz, 2H; H_{Ar}), 7.77 (d, *J* = 8.3 Hz, 2H; H_{Ar}), 7.61 (t, *J* = 7.4 Hz, 1H; H_{Ar}), 7.44 (t, *J* = 7.5 Hz, 1H; H_{Ar}), 7.34 – 7.21 (m, 3H; H_{Ar}), 7.13 (d, *J* = 8.2 Hz, 2H; H_{Ar}), 3.13 – 2.99 (m, 2H; CH), 2.30 (s, 3H; CH_3), 1.30 (s, 2H; CH_3), 1.27 (dd, *J* = 7.9, 4.3 Hz, 10H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 165.23 (CO), 146.19 (C_{Ar}), 145.42 (C_{Ar}), 140.65 (C_{Ar}), 139.91 (C_{Ar}), 138.11 (C_{Ar}), 135.00 (C_{Ar}), 130.81 (C_{Ar}), 129.94 (C_{Ar}), 129.08 (C_{Ar}), 128.25 (C_{Ar}), 126.77 (C_{Ar}), 125.93 (C_{Ar}), 125.41 (C_{Ar}), 124.39 (C_{Ar}), 124.21 (C_{Ar}), 121.04 (C_{Ar}), 120.18 (C_{Ar}), 117.13 (C_{Ar}), 115.41 (C_{Ar}), 114.2 (C_{Ar}), 27.96 (CH), 24.13 (CH_3), 22.77 (CH_3), 21.70 (CH_3); **HRMS (ESI)** m/z calcd for $C_{32}H_{31}NO_4S^+$ $(M+H)^+$ 526.2047, found 526.2045.



(3*R*,5a*S*,6*R*,8a*S*,9*R*,12*R*)-3,6,9-trimethyldecahydro-12*H*-3,12-epoxy[1,2]dioxepino[4,3-*i*]isochromen-10-yl 9-tosyl-9*H*-carbazole-2-carboxylate (2fg): white solid; Yield 90%, 12h; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 9.04 (s, 1H; H_{Ar}), 8.36 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 8.12 (d, *J* = 8.1 Hz, 1H; H_{Ar}), 7.92 (t, *J* = 8.8 Hz, 2H; H_{Ar}), 7.72 (d, *J* = 8.1 Hz, 2H; H_{Ar}), 7.55 (t, *J* = 7.8 Hz, 1H; H_{Ar}), 7.38 (t, *J* = 7.5 Hz, 1H; H_{Ar}), 7.10 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 6.05 (d, *J* = 9.8 Hz, 1H; CH), 5.57 (s, 1H; CH), 2.92 – 2.80 (m, 1H; CH), 2.40 (td, *J* = 14.2, 3.4 Hz, 1H; CH), 2.24 (s, 3H; CH_3), 2.05 (d, *J* = 14.6 Hz, 1H; CH), 1.91 (dd, *J* = 8.9, 4.7 Hz, 1H; CH), 1.84 (d, *J* = 13.1 Hz, 1H; CH_2), 1.79 – 1.68 (m, 2H; CH_2), 1.56 – 1.46 (m, 2H; CH_2), 1.44 (s, 3H; CH_3), 1.41 – 1.30 (m, 2H; CH_2), 1.09 – 1.03 (m, 1H; CH_2), 0.99 (dd, *J* = 11.0, 6.7 Hz, 6H; CH_3); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 165.30 (CO), 145.23 (C_{Ar}), 139.66 (C_{Ar}), 137.92 (C_{Ar}), 134.77 (C_{Ar}), 130.50 (C_{Ar}), 129.88 (C_{Ar}), 128.85 (C_{Ar}), 128.56 (C_{Ar}), 126.68 (C_{Ar}), 125.64 (C_{Ar}), 125.37 (C_{Ar}), 124.24 (C_{Ar}), 120.93 (C_{Ar}), 119.73 (C_{Ar}), 117.14 (C_{Ar}), 115.29 (C_{Ar}), 104.52 (C), 92.91 (CH), 91.74 (CH), 80.31 (C), 51.73 (CH), 45.43 (CH), 37.35 (CH), 36.35 (CH_2), 34.19 (CH), 32.07 (CH_2), 26.09 (CH_3), 24.66 (CH_2), 22.15 (CH_2), 21.59 (CH_3), 20.33 (CH_3), 12.44 (CH_3); **HRMS (ESI)** m/z calcd for $C_{35}H_{37}NNaO_8S^+$ $(M+Na)^+$ 654.2138, found 654.2141.



(*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl 9-tosyl-9*H*-carbazole-2-carboxylate (2fh): white solid; Yield 63%, 12h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.21 (d, *J* = 0.8 Hz, 1H; H_{Ar}), 8.42 (d, *J* = 8.4 Hz, 1H; H_{Ar}), 8.25 (dd, *J* = 8.0, 1.3 Hz, 1H; H_{Ar}), 8.01 (t, *J* = 8.4 Hz, 2H; H_{Ar}), 7.77 (d, *J* = 8.4 Hz, 2H; H_{Ar}), 7.64 – 7.56 (m, 1H; H_{Ar}), 7.43 (t, *J* = 7.8 Hz, 1H; H_{Ar}), 7.13 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 2.66 (t, *J* = 6.4 Hz, 2H; CH_2), 2.29 (s, 3H; CH_3), 2.17 (s, 3H; CH_3), 2.14 (s, 3H; CH_3), 2.09 (s, 3H; CH_3), 1.85 (m, 2H; CH_2), 1.69 – 1.57 (m, 2H; CH_2), 1.56 – 1.48 (m, 2H; CH_2), 1.47 – 1.36 (m, 4H; CH_2), 1.29 (s, 10H; CH_2), 1.19 – 1.07 (m, 6H; CH, CH_3), 0.90 – 0.85 (m, 12H; CH_3); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 165.21 (CO), 149.69 (C_{Ar}), 145.35 (C_{Ar}), 140.92 (C_{Ar}), 139.89 (C_{Ar}), 138.09 (C_{Ar}), 135.00 (C_{Ar}), 130.64 (C_{Ar}), 129.92 (C_{Ar}), 128.97 (C_{Ar}), 128.53 (C_{Ar}), 127.06 (C_{Ar}), 126.79 (C_{Ar}), 125.83 (C_{Ar}), 125.46 (C_{Ar}), 125.31 (C_{Ar}), 124.33 (C_{Ar}), 123.35 (C_{Ar}), 120.99 (C_{Ar}), 120.06 (C_{Ar}), 117.70 (C_{Ar}), 117.14 (C_{Ar}), 115.41 (C_{Ar}), 75.27 (C), 39.53 (CH_2), 37.74 (CH_2), 37.63 (CH_2), 37.55 (CH_2), 37.45 (CH_2), 32.94 (CH), 32.88 (CH), 28.13 (CH_2), 24.95 (CH_2), 24.61 (CH_3), 22.87 (CH_3), 22.78 (CH_3), 21.67 (CH_3), 20.83 (CH_2), 19.91 (CH_2), 19.86 (CH_3), 19.85 (CH_3), 13.29 (CH_3), 12.45 (CH_3), 12.03 (CH_3); **HRMS (ESI)** m/z calcd for $C_{49}H_{64}NO_5S^+$ $(M+H)^+$ 778.4500, found 778.4504.

7. Gram-scale synthesis of *N*-Ts-Carbazole (2a)

A dry round bottom flask equipped with a magnetic stirrer bar was charged with **1a** (1.29 g, 4.00 mmol, 1.0 equiv) and $Pd(OAc)_2$ (0.40 mmol, 10 mol%) in MeCN (40 mL). **O1** (6.4 mmol, 1.6 equiv) was added, and the reaction mixture was stirred at room temperature under irradiation with blue LEDs (20 W). The reaction mixture was then purified by flash chromatography on silica gel (PE/EA). Yield 95%, 12h.

8. Optical and photoperties

8.1 Photographs of 2a, 2i, 2j Powders.

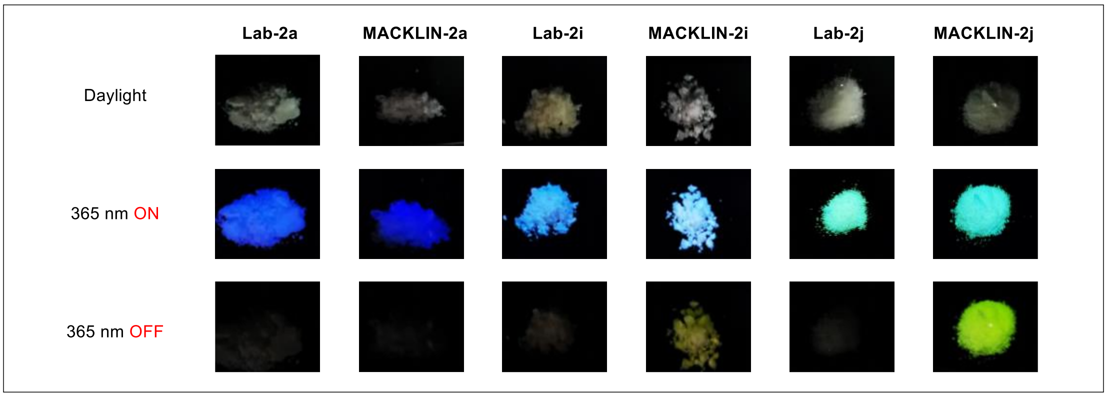


Figure S5. Photographs of **2a**, **2i**, **2j** powders in daylight and under 365 nm irradiation ON/OFF

8.2 UV-Vis and fluorescence spectra.

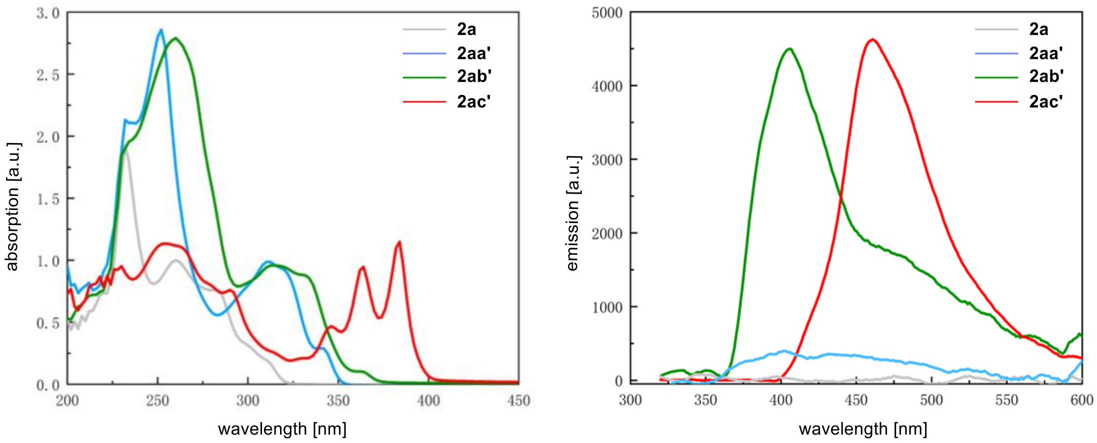


Figure S6. Absorption and emission spectra of selected compounds in CH_2Cl_2

8.3 Photophysical data

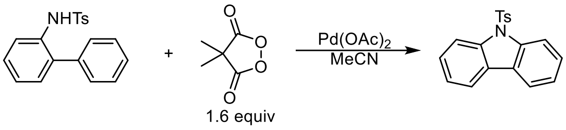
Table S3. Photophysical Data of Representative Carbazoles

Compound	$\lambda_{max, abs}$ ^{a}	$\lambda_{max, em}$ ^{b}	Stokes Shift (cm^{-1})	$\lambda_{onset, abs}$	$E_{g(opt)}$ (eV)^{c}
2a	232 nm	-	-	255 nm	4.86
2aa’	252 nm	-	-	288 nm	4.31
2ab’	260 nm	403 nm	13648	303 nm	4.09
2ac’	384 nm	461 nm	4350	402 nm	3.09

^{a}Maximum of the longest absorption wavalength. ^{b}Maximum of the shortest emission wavelength. ^{c}Optical gap estimated from $\lambda_{onset, abs}$: $E_{g(opt)} = 1239.8/\lambda_{onset, abs}$.

9. Green chemistry metrics analysis

Table S4. *E*-Factor, AE, RME, PMI, CE and Atom Efficiency for Carbazoles Synthesis (This work).



323.41	130.10	321.39
32.3 mg	20.8 mg	31.5 mg

Total amount of reactants: 32.3 mg + 20.8 mg = 53.1 mg
Amount of final product: 31.5 mg
Amount of waste: 53.1 mg - 31.5 mg = 21.6 mg
E-Factor = Amount of waste/Amount of final product = 21.6/31.5 = 0.69

Molecular weight of product: 321.39
Sum of molecular weight of reagent: 323.41 + 130.10 × 1.6 = 531.57
Atom economy = Molecular weight of product/Sum of molecular weight of reagent = 321.39/531.57 = 60.5%

Mass of product: 31.5 mg
Total Mass of reagent: 32.3 mg + 20.8 mg = 53.1 mg
RME = Mass of product/Total Mass of reagent = 31.5/53.1 = 59.3%

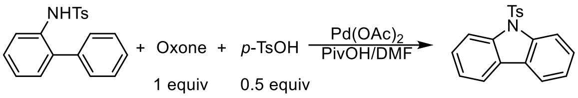
Total Mass in process: 32.3 mg + 20.8 mg = 53.1 mg
Mass of product: 31.5 mg
PMI = Total Mass in process/Mass of product = 53.1/31.5 = 1.69

Amount of carbon in desired product: 19
Total amount of carbon presenten in all reactants: 19 + 5 × 1.6 = 27

$$\text{Carbon Efficiency (\%)} = \frac{\text{Amount of carbon in desired product}}{\text{Total amount of carbon presenten in all reactants}} \times 100\% = 70.4\%$$

Yield of product: 98%
Atom economy: 60.5%
Atom Efficiency (%) = (% Yield of product × % Atom economy) × 100% = 59.3%

Table S5. *E*-Factor, AE, RME, PMI, CE and Atom Efficiency for Carbazoles Synthesis Using Oxone as Oxidant.[2]



323.41	346.29	172.20	321.39
32.3 mg	34.6 mg	8.6 mg	31.5 mg

Total amount of reactants: 32.3 mg + 34.6 mg + 8.6 mg = 75.5 mg
Amount of final product: 31.5 mg
Amount of waste: 75.5 mg - 31.5 mg = 44 mg
E-Factor = Amount of waste/Amount of final product = 44/31.5 = 1.40

Molecular weight of product: 321.39
Sum of molecular weight of reagent: 323.41 + 346.29 + 172.2 ×0.5 = 755.8
Atom economy = Molecular weight of product/Sum of molecular weight of reagent = 321.39/755.8 = 42.5%

Mass of product: 31.5 mg
Total Mass of reagent: 32.3 mg + 34.6 mg + 8.6 mg = 75.5 mg
RME = Mass of product/Total Mass of reagent = 31.5/75.5 = 41.7%

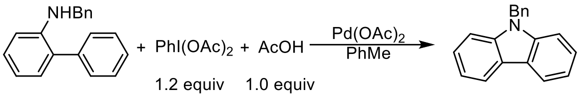
Total Mass in process: 32.3 mg + 34.6 mg + 8.6 mg = 75.5 mg
Mass of product: 31.5 mg
PMI = Total Mass in process/Mass of product = 75.5/31.5 = 2.40

Amount of carbon in desired product: 19
Total amount of carbon presenten in all reactants: 19 + 7 ×0.5 = 22.5

$$\text{Carbon Efficiency (\%)} = \frac{\text{Amount of carbon in desired product}}{\text{Total amount of carbon presenten in all reactants}} \times 100\% = 84.4\%$$

Yield of product: 98%
Atom economy: 42.5%
Atom Efficiency (%) = (% Yield of product ×% Atom economy) ×100% = 41.7%

Table S6. *E*-Factor, AE, RME, PMI, CE and Atom Efficiency for Carbazoles Synthesis Using $PhI(OAc)_2$ as Oxidant.[1]



259.35	322.10	60.05	257.34
25.9 mg	38.7 mg	6.0 mg	24.7 mg

Total amount of reactants: 25.9 mg + 38.7 mg + 6.0 mg = 70.6 mg
Amount of final product: 24.7 mg
Amount of waste: 70.6 mg - 24.7 mg = 45.9 mg
E-Factor = Amount of waste/Amount of final product = 45.9/24.7 = 1.86

Molecular weight of product: 257.34
Sum of molecular weight of reagent: 259.35 + 322.10 $\times$1.2 + 60.05 $\times$1.0 = 705.92
Atom economy = Molecular weight of product/Sum of molecular weight of reagent = 257.34/705.92 = 36.5%

Mass of product: 24.7 mg
Total Mass of reagent: 25.9 mg + 38.7 mg +6.0 mg = 70.6 mg
RME = Mass of product/Total Mass of reagent = 24.7/70.6 = 35.0%

Total Mass in process: 25.9 mg + 38.7 mg +6.0 mg = 70.6 mg
Mass of product: 24.7 mg
PMI = Total Mass in process/Mass of product = 70.6/24.7 = 2.86

Amount of carbon in desired product: 19
Total amount of carbon presenten in all reactants: 19 + 10 $\times$1.2 + 2 $\times$1.0 = 33

$$\text{Carbon Efficiency (\%)} = \frac{\text{Amount of carbon in desired product}}{\text{Total amount of carbon presenten in all reactants}} \times 100\% = 57.6\%$$

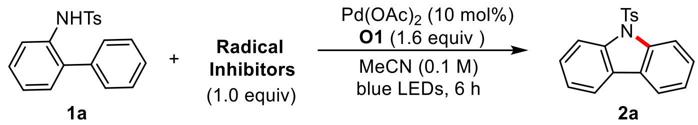
Yield of product: 96%
Atom economy: 36.5%
Atom Efficiency (%) = (% Yield of product $\times$% Atom economy) $\times 100\% =$ 35.1%

10. Mechanistic experiments

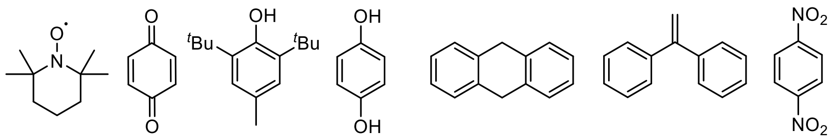
10.1 Radical inhibition experiments

A dry Schlenk tube equipped with a magnetic stirrer bar was charged with **1a** (0.10 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.01 mmol, 10 mol%) and additive (0.10 mmol, 1.0 equiv) in MeCN (1 mL). **O1** (0.16 mmol, 1.6 equiv) was added, and the reaction mixture was stirred at room temperature under irradiation with blue LEDs (20 W) for 6 h. The reaction mixture was then purified by flash chromatography on silica gel (PE/EA).

Table S7: Effect of Radical Inhibitors[a, b]



Radical Inhibitors	None	TEMPO	*p*-benzoquinone	BHT	Hydroquinone	9,10-Dihydroanthracene	1,1-Diphenylethylene	1,4-Dinitrobenzene
Yield(%)	97	60	62.5	97	96	97	96	97

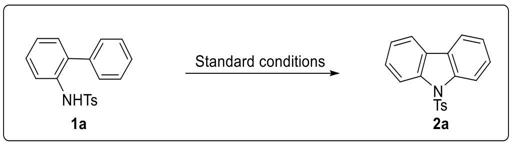


[a]Reaction conditions: **1a** (0.10 mmol, 1.0 equiv), additive (0.10 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.01 mmol, 10 mol%), **O1** (0.16 mmol, 1.6 equiv), MeCN (1 mL), irradiation with blue LEDs for 6 h at room temperature. [b]Isolated yields.

10.2 Reaction rate of carbazoles synthesis

Carbazoles synthesis under blue LEDs: A dry Schlenk tube equipped with a magnetic stirrer bar was charged with **1a** (0.10 mmol, 1.0 equiv) and $Pd(OAc)_2$ (0.01 mmol, 10 mol%) in MeCN (1 mL). **O1** (0.16 mmol, 1.6 equiv) was added, and the reaction mixture was stirred at room temperature under irradiation with blue LEDs (20 W). Aiquots (50 μl) were taken out by syringe at every 30 minutes and immediately quenched by $Na_2S_2O_3$, diluted with EA (1 mL) and immediately tested by GC using naphthalene as an internal standard and the results were presented in Figure S7.

Carbazoles synthesis in the dark: A dry Schlenk tube equipped with a magnetic stirrer bar was charged with **1a** (0.10 mmol, 1.0 equiv) and $Pd(OAc)_2$ (0.01 mmol, 10 mol%) in MeCN (1 mL). **O1** (0.16 mmol, 1.6 equiv) was added, and the reaction mixture was stirred at room temperature in the dark. Aiquots (50 μl) were taken out by syringe at every 30 minutes and immediately quenched by $Na_2S_2O_3$, diluted with EA (1 mL) and immediately tested by GC using naphthalene as an internal standard and the results were presented in Figure S7.



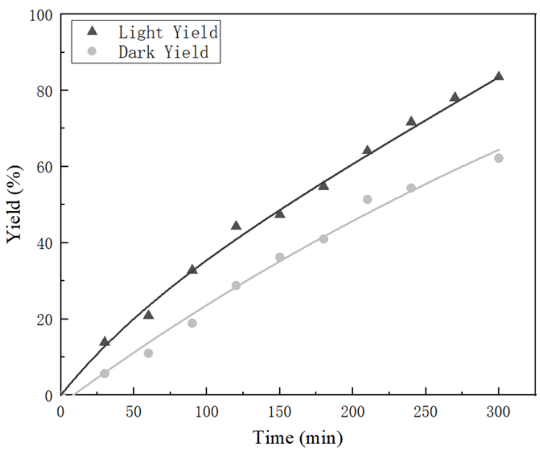


Figure S7. Reactivity comparison between blue LEDs and dark

10.3 Light On/Off experiment

A dry Schlenk tube equipped with a magnetic stirrer bar was charged with **1a** (0.10 mmol, 1.0 equiv) and $Pd(OAc)_2$ (0.01 mmol, 10 mol%) in MeCN (1 mL). **O1** (0.16 mmol, 1.6 equiv) was added, and the reaction mixture was stirred alternately in the dark and irradiation with blue LEDs (20 W) at room temperature. Aiquots (50 μl) were taken out by syringe at every 30 minutes and immediately quenched by $Na_2S_2O_3$, diluted with EA (1 mL). Product yield was tested by GC using naphthalene as an internal standard and the results were presented in Figure S8.

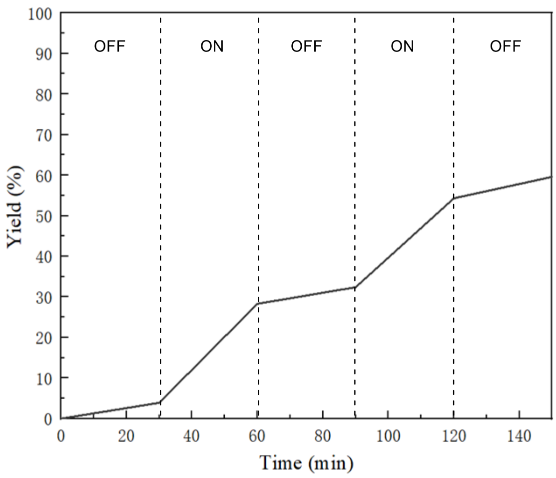
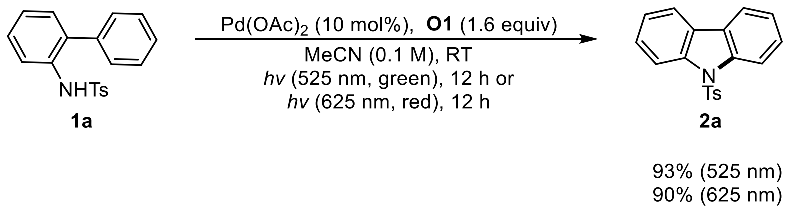


Figure S8. Light on/off experiment

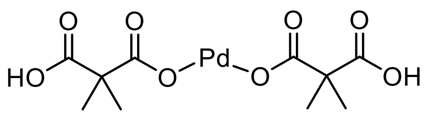
10.4 Screening of light source

A dry Schlenk tube equipped with a magnetic stirrer bar was charged with **1a** (0.10 mmol, 1.0 equiv) and $Pd(OAc)_2$ (0.01 mmol, 10 mol%) in MeCN (1 mL). **O1** (0.16 mmol, 1.6 equiv) was added, and the reaction mixture was stirred at room temperature under irradiation with green or red LEDs (20 W) for 12 h. The reaction mixture was then purified by flash chromatography on silica gel (PE/EA).

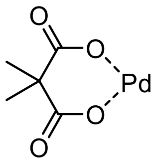


10.5 Investigation in palladium(II) 2,2-dimethylmalonate

A Soxhlet set up was charged with solid sodium carbonate (approx. 2 g), in which the dry round bottom flask equipped with a magnetic stirrer bar was charged with a solution of palladium(II) acetate (2.0 mmol) and dimethylmalonic acid (1 mmol) in toluene (30 mL). The reaction mixture was heated at reflux for 3 h, such that the solvent condensed through the solid sodium carbonate before returning to the round bottomed flask. The reaction mixture was allowed to cool to ambient temperature and concentrated under reduced pressure. Acetone (6 mL) was added to the residue and the suspension stirred for 10 minutes at ambient temperature. The precipitate was filtered and dried under vacuum to provide desired product.[9]



With 2 mmol dimethylmalonic acid. **bis((2-carboxy-2-methylpropanoyl)oxy)palladium:** yellow solid; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 12.56 (s, 2H), 3.34 (s, 12H).



palladium(II) 2,2-dimethylmalonate: brown yellow solid; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 3.49 (s, 6H).

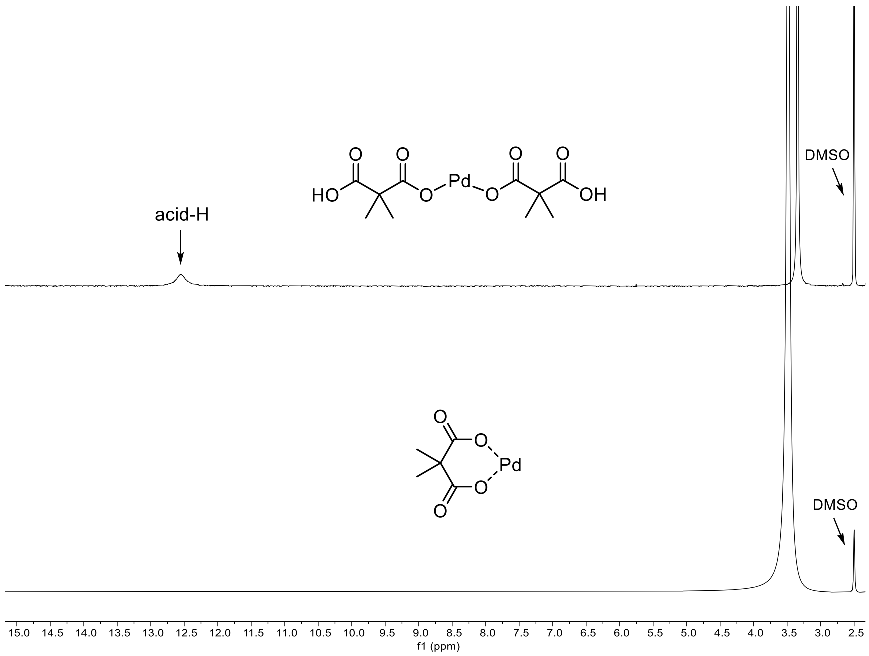
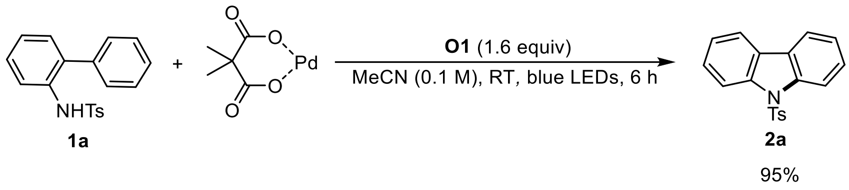


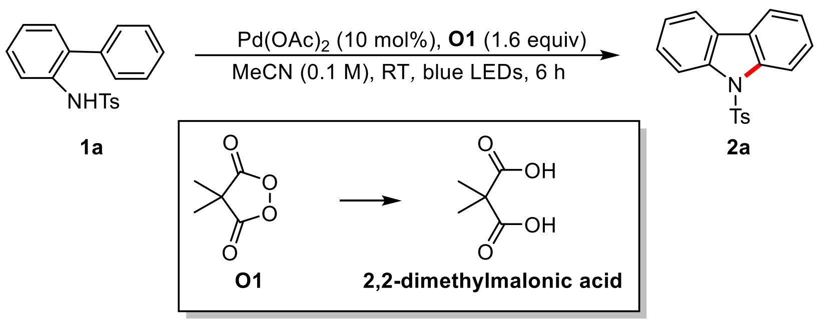
Figure S9. Comparison of two palladium compounds

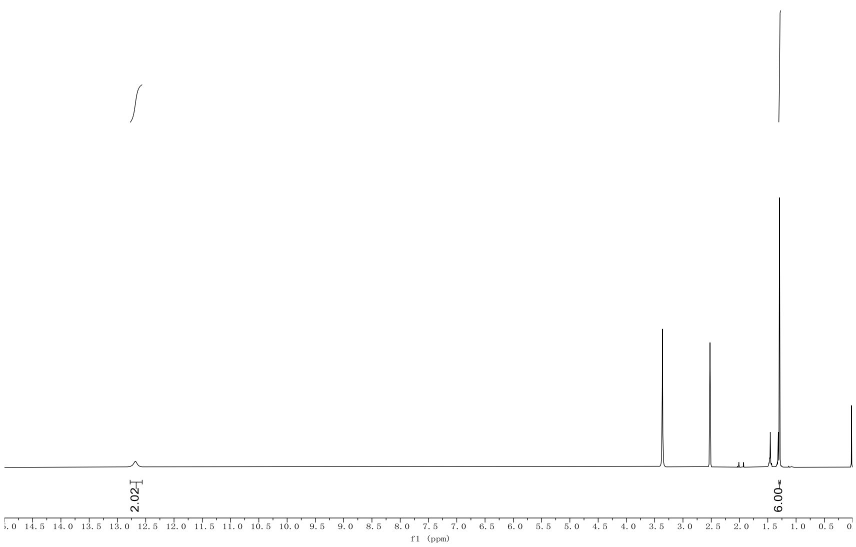
A dry Schlenk tube equipped with a magnetic stirrer bar was charged with **1a** (0.10 mmol, 1.0 equiv) and palladium(II) 2,2-dimethylmalonate (0.01 mmol, 10 mol%) in MeCN (1 mL). **O1** (0.16 mmol, 1.6 equiv) was added, and the mixture was stirred at room temperature under irradiation with blue LEDs (20 W) for 6 h. The reaction mixture was then purified by flash chromatography on silica gel (PE/EA).

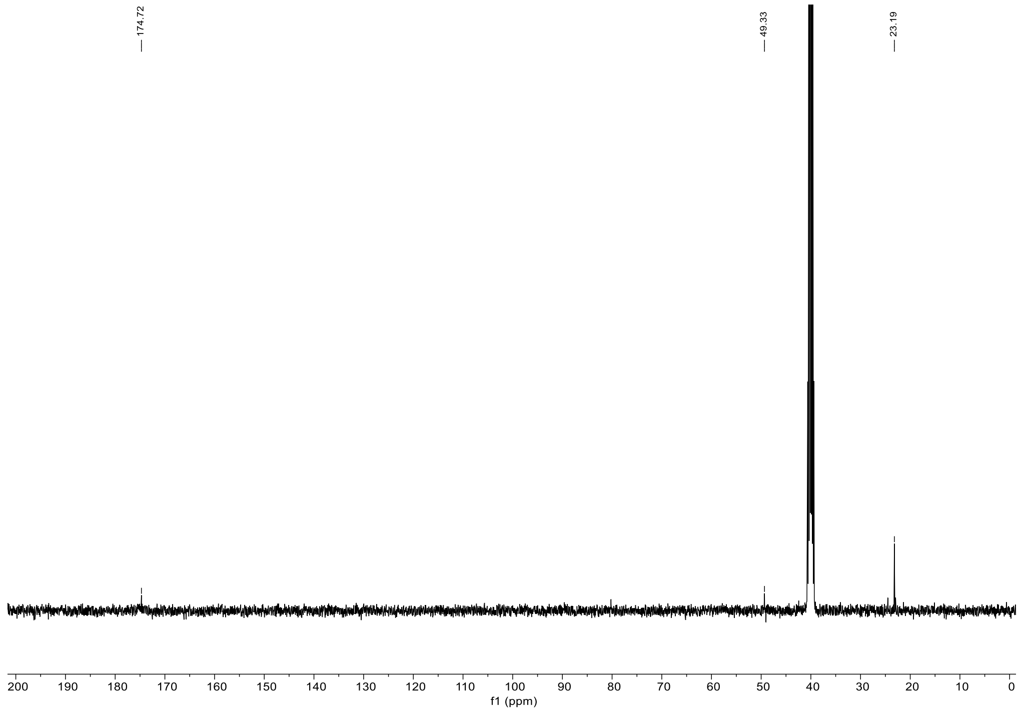


10.6 2,2-Dimethylmalonic acid identificated by NMR spectra

A dry Schlenk tube equipped with a magnetic stirrer bar was charged with **1a** (4 mmol, 1.0 equiv) and $Pd(OAc)_2$ (0.4 mmol, 10 mol%) in MeCN (40 mL). **O1** (6.4 mmol, 1.6 equiv) was added, and the reaction mixture was stirred at room temperature under irradiation with blue LEDs (20 W) for 6 h. Next, an aqueous NaOH (10 mL, 1 M) and EA (20 mL) was added. The layers were separated, and the aqueous layer was extracted with EA (15 mL × 2). The combined aqueous layers were acided by aqueous HCl until PH < 2 and extracted with EA (15 mL × 2). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was detected by NMR spectra.







174.72
49.33
23.19
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

10.7 Competition experiments of *meta*-substituted *N*-Ts-2-Phenylanilines

A dry Schlenk tube equipped with a magnetic stirrer bar was charged with two substrates (0.20 mmol, 1:1) and $Pd(OAc)_2$ (0.01 mmol) in MeCN (1 mL). **O1** (0.16 mmol) was added, and the reaction mixture was stirred at room temperature under irradiation with blue LEDs (20 W) for 6 h. The reaction mixture was then purified by flash chromatography on silica gel (PE/EA).

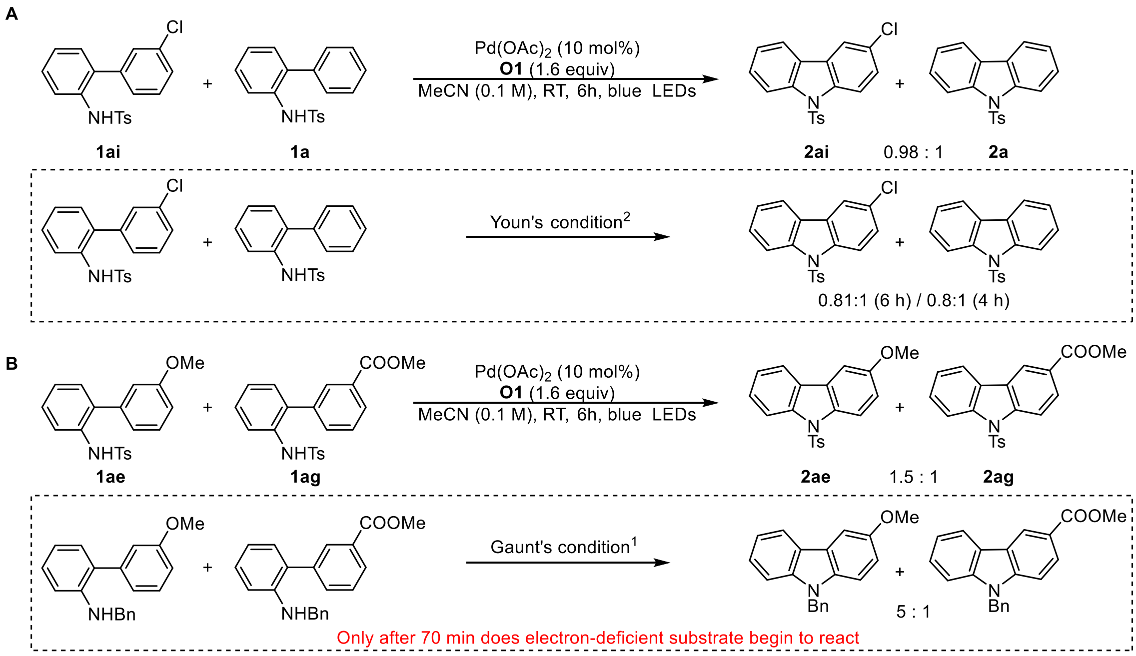


Figure S10. Two competition experiments in comparison with the literatures

A dry Schlenk tube equipped with a magnetic stirrer bar was charged with two substrates (0.20 mmol, 1:1) and $Pd(OAc)_2$ (0.01 mmol) in MeCN (1 mL). **O1** (0.16 mmol) was added, and the reaction mixture was stirred at room temperature under irradiation with blue LEDs (20 W). The mixture was detected by ^1H NMR spectra (*in-situ*).

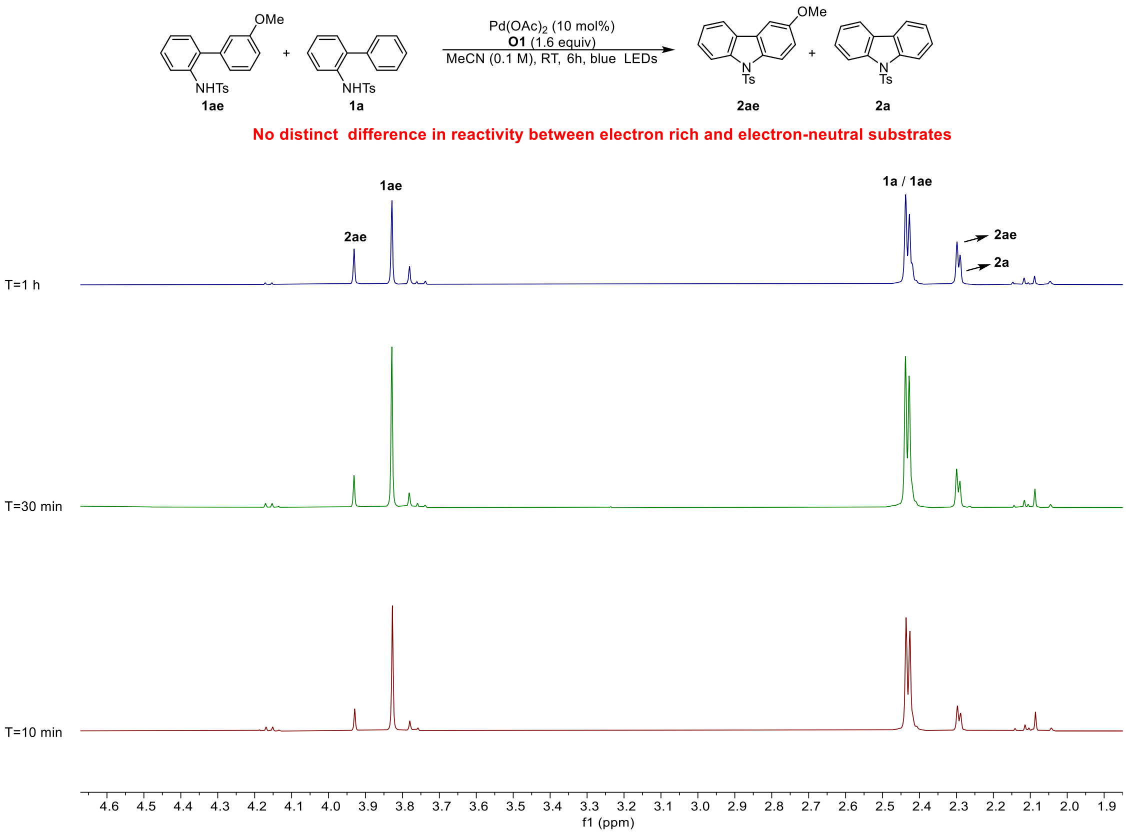


Figure S11. Competition experiment between electron rich and electron-neutral substrates

A dry Schlenk tube equipped with a magnetic stirrer bar was charged with two substrates (0.20 mmol, 1:1) and $Pd(OAc)_2$ (0.01 mmol) in MeCN (1 mL). **O1** (0.16 mmol) was added, and the reaction mixture was stirred at room temperature under irradiation with blue LEDs (20 W). The mixture was detected by ^{1}H NMR spectra (*in-situ*).

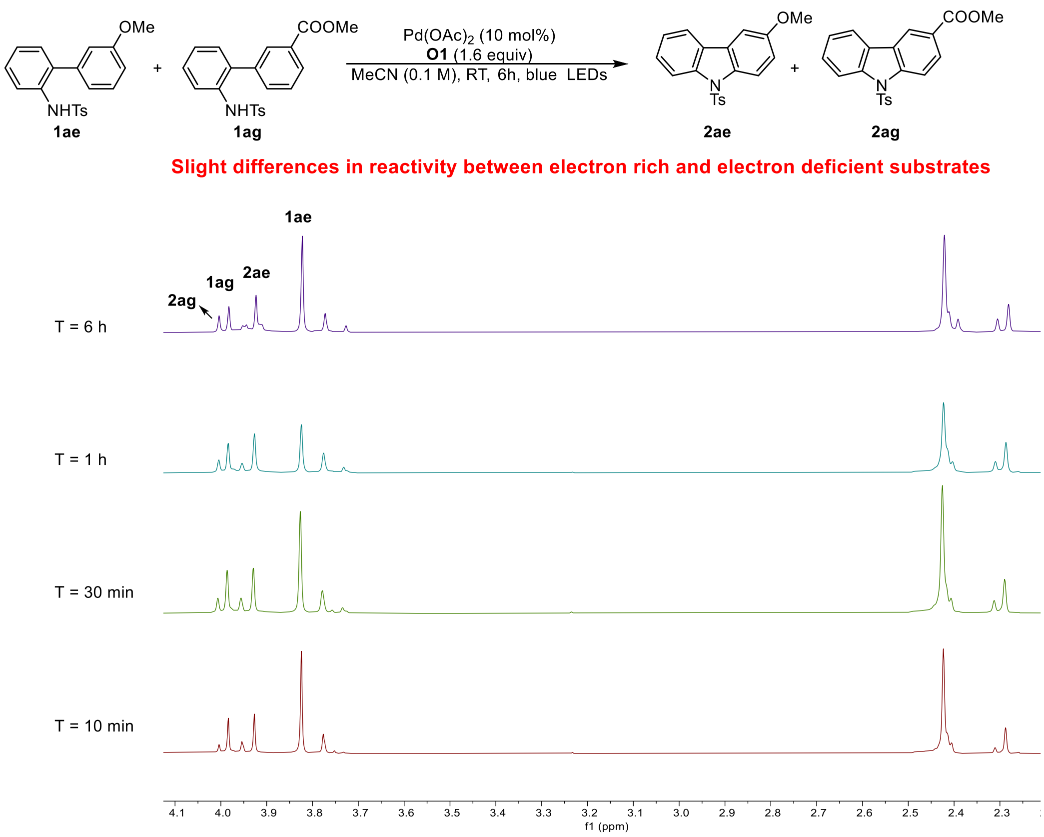


Figure S12. Competition experiment between electron rich and electron deficient substrates

10.8 Kinetic experiments

Reaction rate profile: A dry Schlenk tube equipped with a magnetic stirrer bar was charged with **1a** (0.10 mmol, 1.0 equiv) and $Pd(OAc)_2$ (0.01 mmol, 10 mol%) in MeCN (1 mL). **O1** (0.16 mmol, 1.6 equiv) was added, and the reaction mixture was stirred at room temperature under irradiation with blue LEDs (20 W). Aiquots (50 µl) were taken out by syringe at every 30 minutes and immediately quenched by $Na_2S_2O_3$, diluted with EA (1 mL). Product yield was tested by GC using naphthalene as an internal standard and the results were presented in Figure S13.

Initial rate profile: A dry Schlenk tube equipped with a magnetic stirrer bar was charged with **1a** (0.10 mmol, 1.0 equiv) and $Pd(OAc)_2$ (0.01 mmol, 10 mol%) in MeCN (1 mL). **O1** (0.16 mmol, 1.6 equiv) was added, and the reaction mixture was stirred at room temperature under irradiation with blue LEDs (20 W). Aiquots (50 µL) were taken out by syringe at every 5 minutes and immediately quenched by $Na_2S_2O_3$, diluted with EA (1 mL). Product yield was tested by GC using naphthalene as an internal standard and the results were presented in Figure S13.

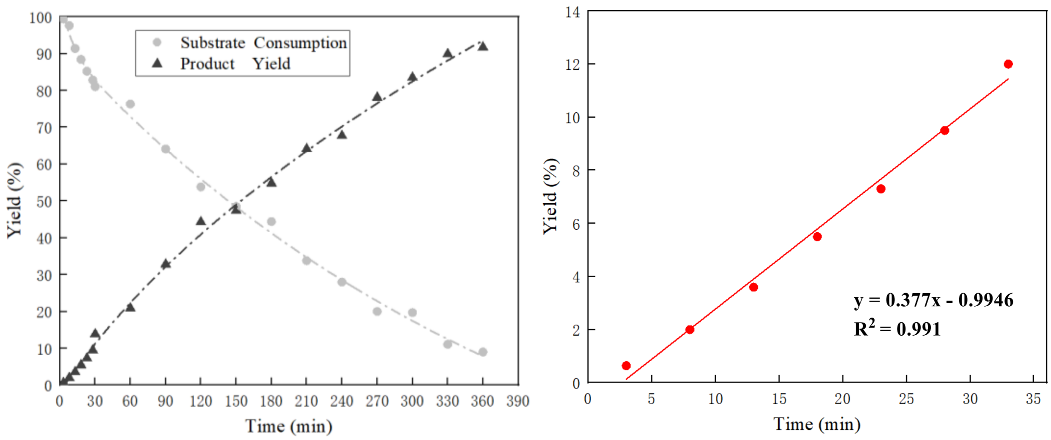
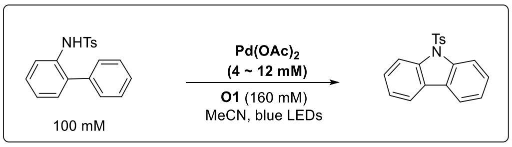


Figure S13. Representive time course of the reaction

Order in catalyst: A dry Schlenk tube equipped with a magnetic stirrer bar was charged with **1a** (0.10 mmol, 1.0 equiv) and $Pd(OAc)_2$ (0. 004 ~ 0.012 mmol) in MeCN (1 mL). **O1** (0.16 mmol, 1.6 equiv) was added, and the reaction mixture was stirred at room temperature under irradiation with blue LEDs (20 W). Aiquots (50 μL) were taken out by syringe at every 5 minutes and immediately quenched by $Na_2S_2O_3$, diluted with EA (1 mL). Product yield from the corresponding reaction was tested by GC using naphthalene as an internal standard, and each reported initial rate represents an average of three experiments. The results were presented in Figure S14. A plot of initial rate versus $[Pd(OAc)_2]$ gave a straight line ($R^2 = 0.9961$), indicating a 1st order dependence on $[Pd(OAc)_2]$. Y = 0.0286 mM/min × X + 0.085.



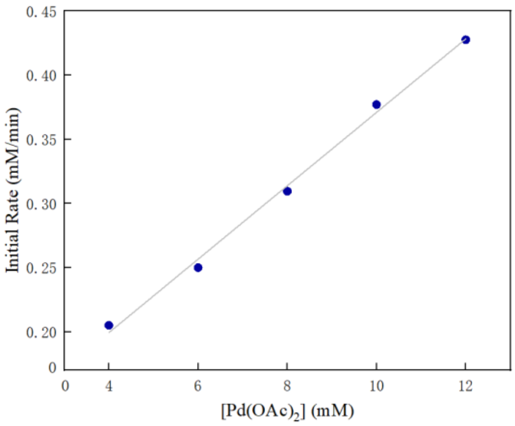


Figure S14. Dependence of the initial rate on $Pd(OAc)_2$

Order in substrate: A dry Schlenk tube equipped with a magnetic stirrer bar was charged with **1a** (0.07 ~ 0.11 mmol) and $Pd(OAc)_2$ (0.01 mmol, 10 mol%) in MeCN (1 mL). **O1** (0.16 mmol, 1.6 equiv) was added, and the reaction mixture was stirred at room temperature under irradiation with blue LEDs (20 W). Aiquots (1 mL) were taken out by syringe at every 5 minutes and immediately quenched by $Na_2S_2O_3$ (0.5 mL), diluted with EA (1 mL). Product yield from the corresponding reaction was tested by GC using naphthalene as an internal standard, and each reported initial rate represents an average of three experiments. The results were presented in Figure S15. A plot of initial rate versus substrate gave a straight line ($R^2 = 0.9992$), indicating of a 1st order dependence on [substrate]. Y = 0.00405 mM/min × X - 0.0299.

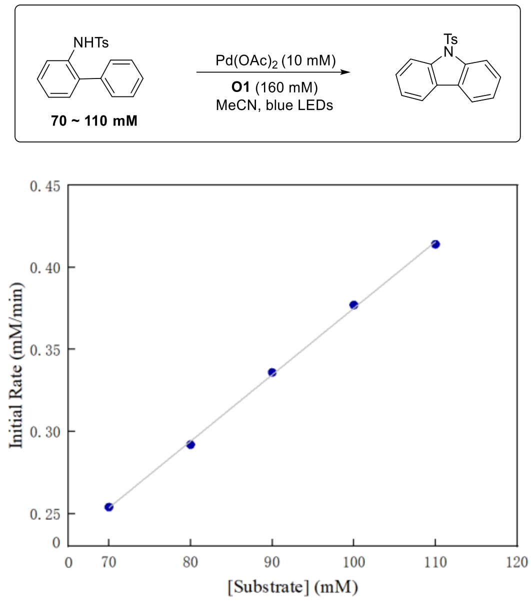
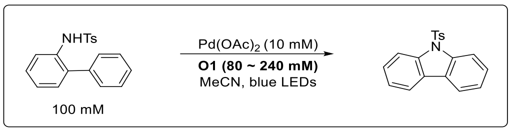


Figure S15. Dependence of the initial rate on substrate

Order in oxidant: A dry Schlenk tube equipped with a magnetic stirrer bar was charged with **1a** (0.10 mmol, 1.0 equiv) and $Pd(OAc)_2$ (0.01 mmol, 10 mol%) in MeCN (1 mL). **O1** (0.08 ~ 0.24 mmol) was added, and the reaction mixture was stirred at room temperature under irradiation with blue LEDs (20 W). Aiquots (50 μL) were taken out by syringe at every 5 minutes and immediately quenched by $Na_2S_2O_3$, diluted with EA (1 mL). Product yield from the corresponding reaction was tested by GC using naphthalene as an internal standard, and each reported initial rate represents an average of three experiments. The results were presented in Figure S16. A plot of initial rate versus substrate gave a flat line, indicating of a zero order dependence on [MPO]. Y = 0.00004 mM/min × X + 0.367.



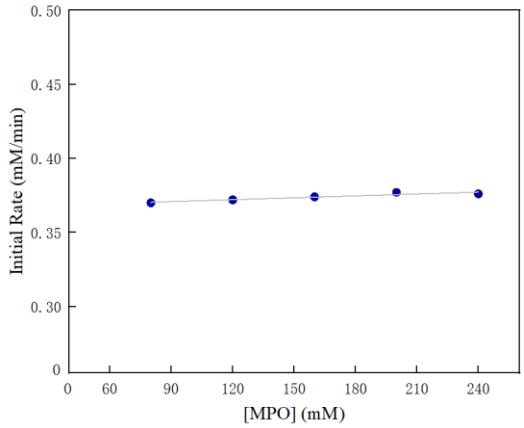


Figure S16. Dependence of the initial rate on oxidant

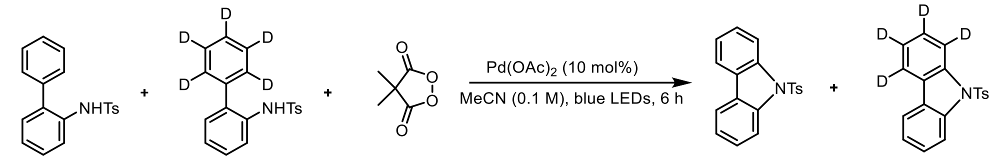
10.9 Intermolecular kinetic isotope effect

Under blue LEDs

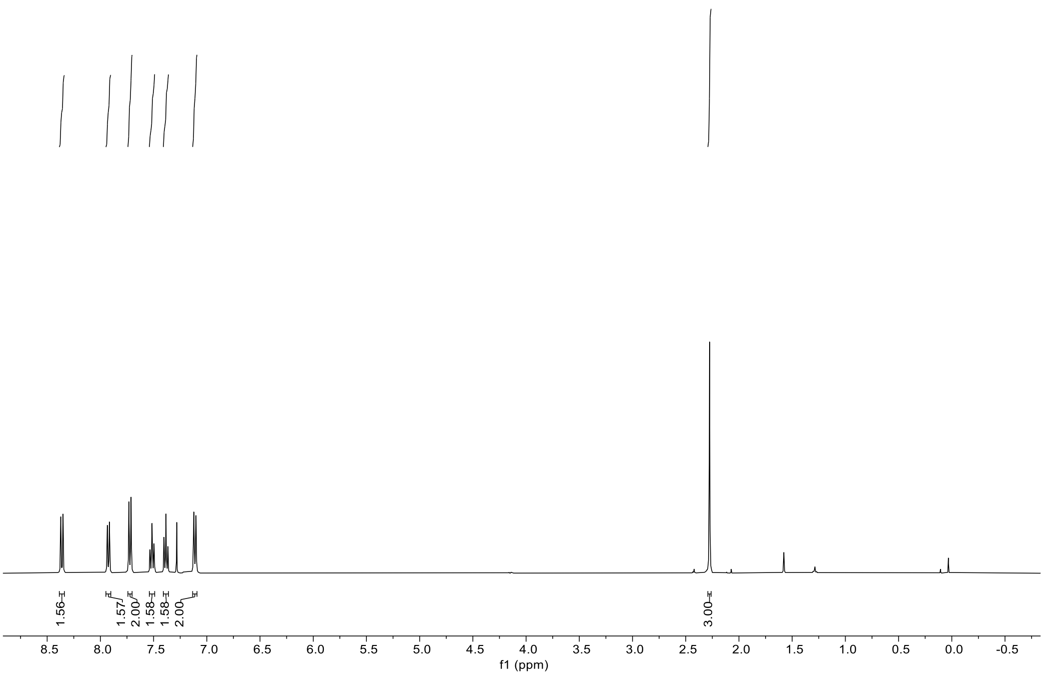
A dry round bottom flask flushed with argone and quipped with a magnetic stirrer bar and a septum was charged with arylboronic acid (1.5 equiv), K_2CO_3 (4.0 equiv), and $Pd(PPh_3)_4$ (10 mol%). A mixture of DME and H_2O (DME : H_2O = 1:1, 0.25 M), bromobenzene-d_5 (1.0 equiv) were added, and the resulting mixture was heated to 80 ℃ for 12 hours. The reaction mixture was poured into water and extracted with CH_2Cl_2 (3-5 times), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the corresponding 2-aminobiphenyl product.

A round bottom flask equipped with a magnetic stirrer bar was charged with the corresponding 2-aminobiphenyl (1.0 equiv) and pyridine (0.2 M) in CH_2Cl_2 (0.2 M). 4-toluenesulfonyl chloride (1.1 equiv) was added at 0 ℃. After being stirred at 25 ℃ for 12 h, the reaction mixture was poured into water and extracted with CH_2Cl_2 (3 times), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the product **1a-*d*₅**.

A dry Schlenk tube equipped with a magnetic stirrer bar was charged with **1a** (0.05 mmol), **1a-*d*$_5$** (0.05 mmol) and Pd(OAc)$_2$ (0.01 mmol) in MeCN (1 mL). **O1** (0.10 mmol) was added, and the reaction mixture was stirred at room temperature under irradiation with blue LEDs (20 W) for 6 h. The reaction mixture was then purified by flash chromatography on silica gel (PE/EA). The *KIE* was calculated as 1.33 ± 0.02 based on the average of three kinetics experiments.

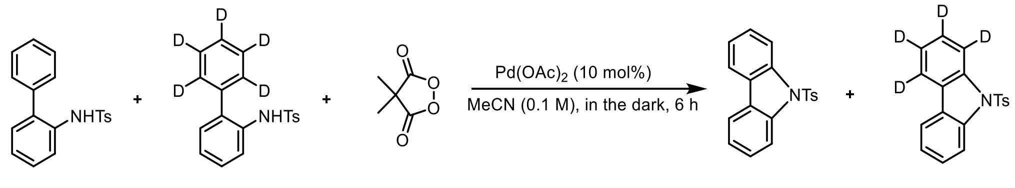


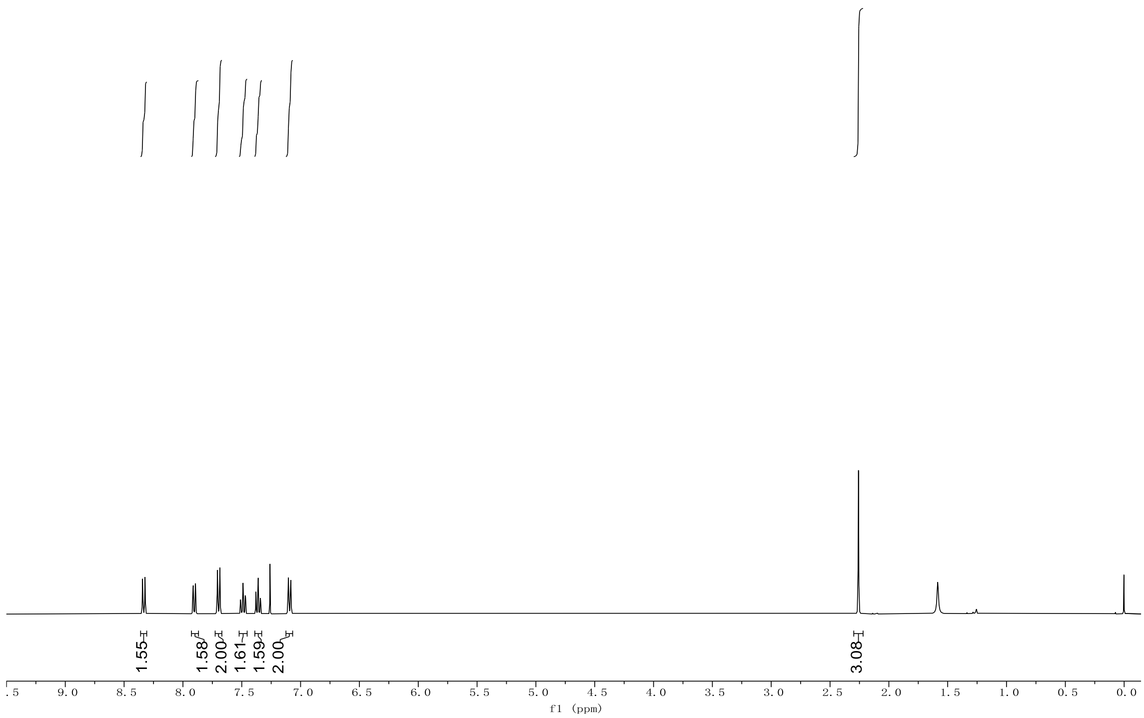
1a **1a-*d*$_5$** ***KIE* = 1.34**



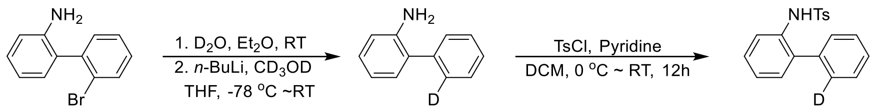
In the dark

A dry Schlenk tube equipped with a magnetic stirrer bar was charged with **1a** (0.05 mmol), **1a-*d*$_5$** (0.05 mmol) and $Pd(OAc)_2$ (0.01 mmol) in MeCN (1 mL) **O1** (0.10 mmol) was added, and the reaction mixture was stirred at room temperature in the dark for 6 h. The reaction mixture was then purified by flash chromatography on silica gel (PE/EA). The *KIE* was calculated as 1.39 ± 0.02 based on the average of three kinetics experiments.



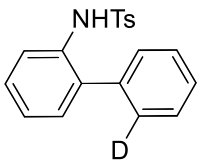


10.10 Intramolecular kinetic isotope effect

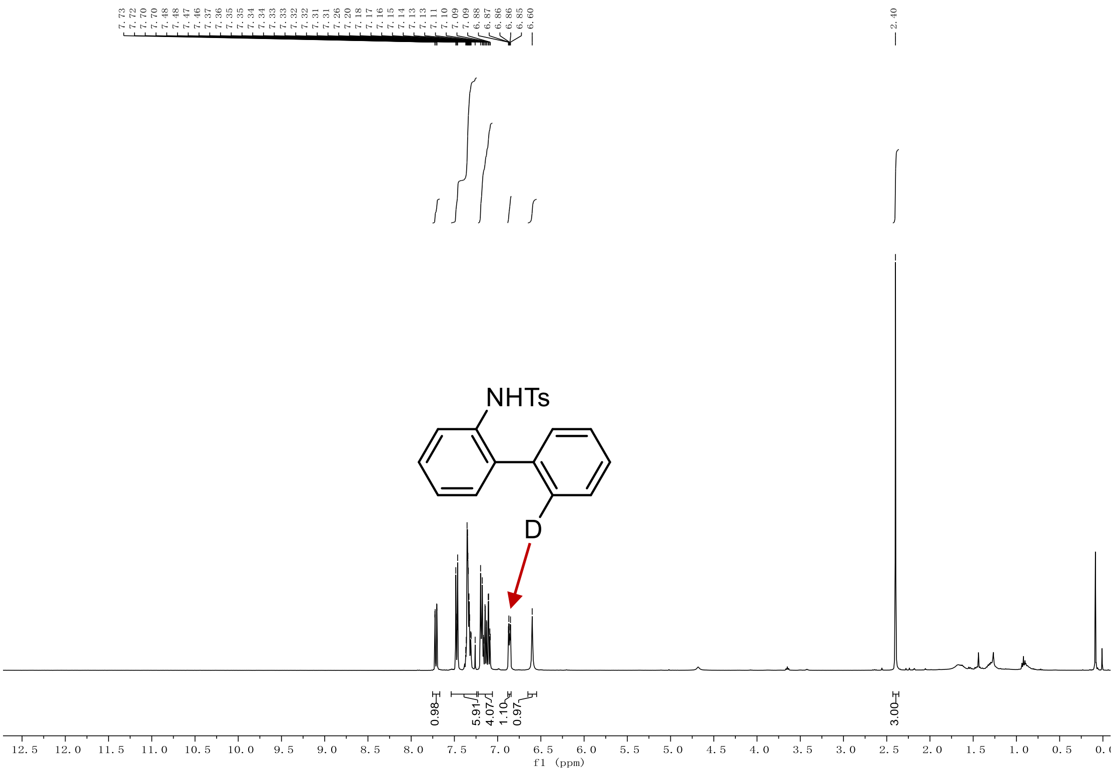


1a-*d'*

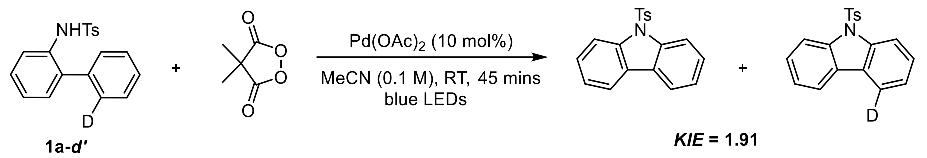
2'-bromobiphenyl-2-amine was dissolved in diethyl ether (25 mL) and washed with D_2O (3 × 15 mL) to replace most of the amine protons by deuterium. The ethereal solution was dried (anhydrous Na_2SO_4) and concentrated. A dry round bottom flask flushed with argon and equipped with a magnetic stirrer bar and a septum was charged with above yellowish liquid (2.5 mmol, 1 equiv.) in dry THF (25 mL). The mixture was cooled to -78 ℃ and a solution of *n*-BuLi (1.65 M solution in hexane, 6.05 mL, 10 mmol) was added dropwise under vigorous stirring (the color was immediately changed to red). After 1 h at -78 ℃, CD_3OD (3.0 mL) was added, and then quenched with H_2O (10 mL). The aqueous layer was extracted three times with Et_2O (10 mL), and the combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and 2'-*d*-biphenyl-2-amine was obtained as light yellow oil.[5] The product **1a-*d'*** was obtained from General procedure A.

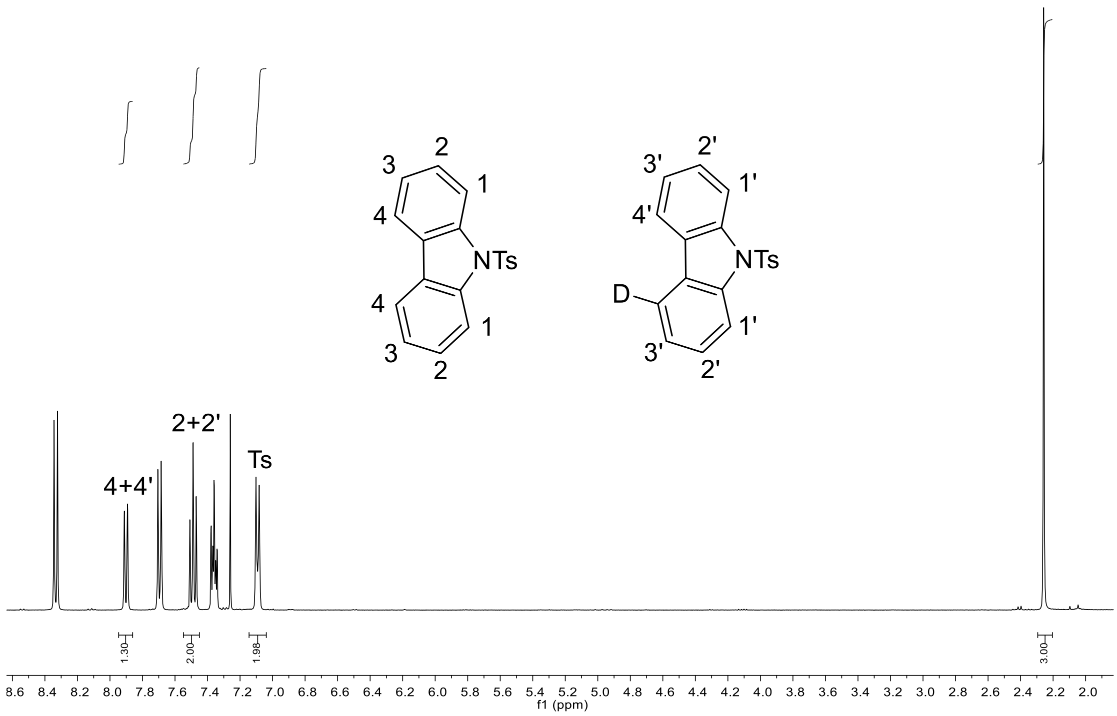


***N*-([1,1'-biphenyl]-2-yl-2'-d)-4-methylbenzenesulfonamide(1a-*d'*):** 90% D-incorporated; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (dd, J = 8.2, 1.2 Hz, 1H), 7.51 – 7.29 (m, 6H), 7.22 – 7.06 (m, 4H), 6.86 (m, 1.10H), 6.60 (s, 1H), 2.40 (s, 3H).



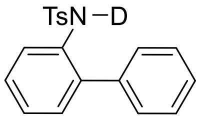
A dry Schlenk tube equipped with a magnetic stirrer bar was charged with **1a-*d'*** (0.10 mmol, 1.0 equiv) and $Pd(OAc)_2$ (0.01 mmol, 10 mol%) in MeCN (1 mL). **O1** (0.16 mmol, 1.6 equiv) was added, and the reaction mixture was stirred at room temperature under irradiation with blue LEDs (20 W) for 45 mins. The reaction mixture was then purified by flash chromatography on silica gel (PE/EA). The *KIE* was calculated as 1.92 ±0.02 based on the average of three kinetics experiments.



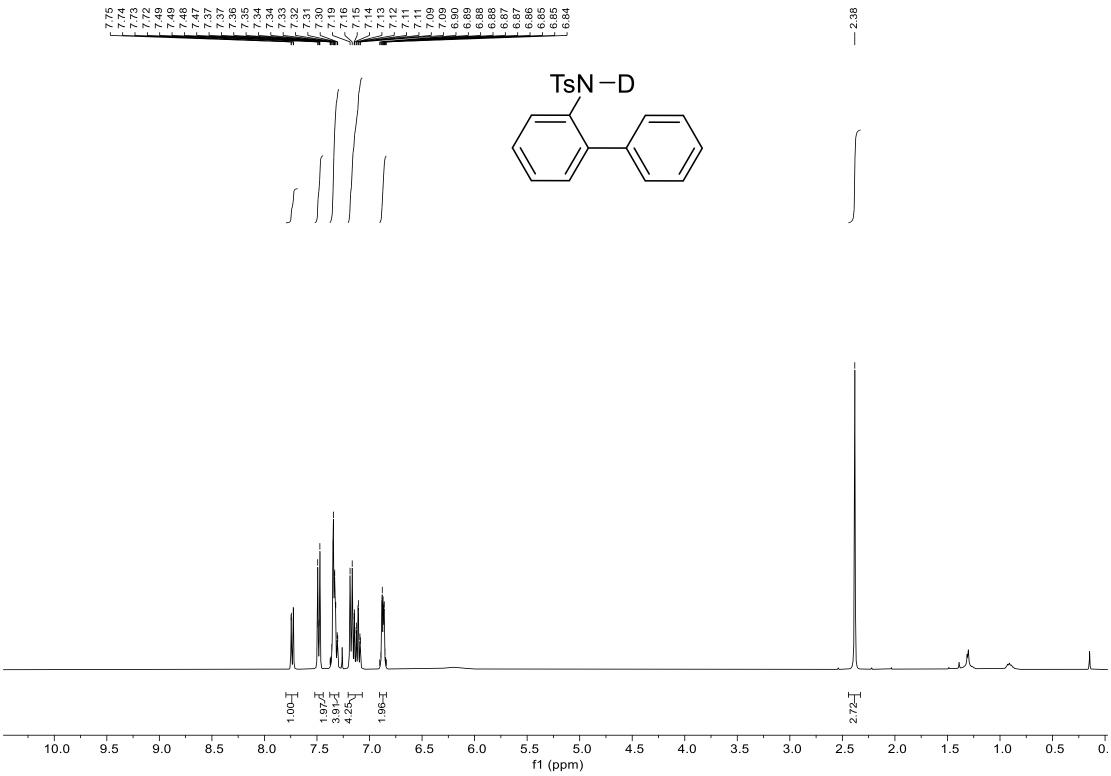


10.11 The parallel kinetic isotope effect

A dry round bottom flask flushed with argon and equipped with a magnetic stirrer bar and a septum was charged with **1a** (2.0 mmol, 1 equiv) in dry THF (10 mL). The mixture was cooled to -78 ºC and *n*-butyl lithium (1.3 equiv) was added dropwise via syringe. The reaction mixture was stirred for 15 min and D_2O (6 mL) was added. The resulting mixture was allowed to warm to room temperature and was stirred for another 30 minutes. The mixture was extracted with dry EA (2 × 6 mL) and the combined organic layer was dried with anhydrous Na_2SO_4 and concentrated in vacuo to give **1a-*d***.[10]



***N*-([1,1'-biphenyl]-2-yl)-4-methylbenzenesulfonamide-*d* (1a-*d*)**: white solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 (dd, J = 8.3, 1.2 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.37 – 7.28 (m, 4H), 7.21 – 7.06 (m, 4H), 6.91 – 6.84 (m, 2H), 2.38 (s, 3H).



The kinetic isotope effect was determined by studying the initial rate profiles of reactions between two substrates (Figure S17). A dry Schlenk tube equipped with a magnetic stirrer bar was charged with substrate (0.10 mmol, 1.0 equiv) and $Pd(OAc)_2$ (0.01 mmol, 10 mol%) in MeCN (1 mL). **O1** (0.16 mmol, 1.6 equiv) was added, and the reaction mixture was stirred at room temperature under irradiation with blue LEDs (20 W). Aiquots (50 μL) were taken out by syringe at every 5 minutes and immediately quenched by $Na_2S_2O_3$, diluted with EA (1 mL). Product yield was tested by GC using naphthalene as an internal standard. The *KIE* was calculated as 0.64.

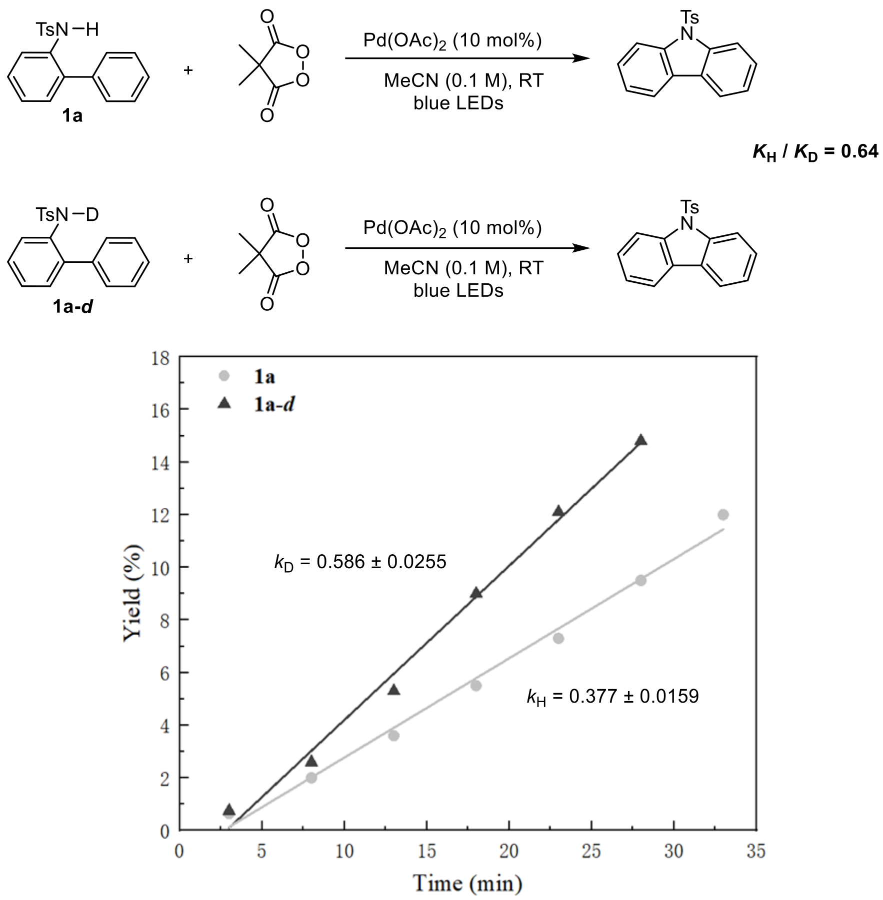


Figure S17. The initial rate profiles of reactions.

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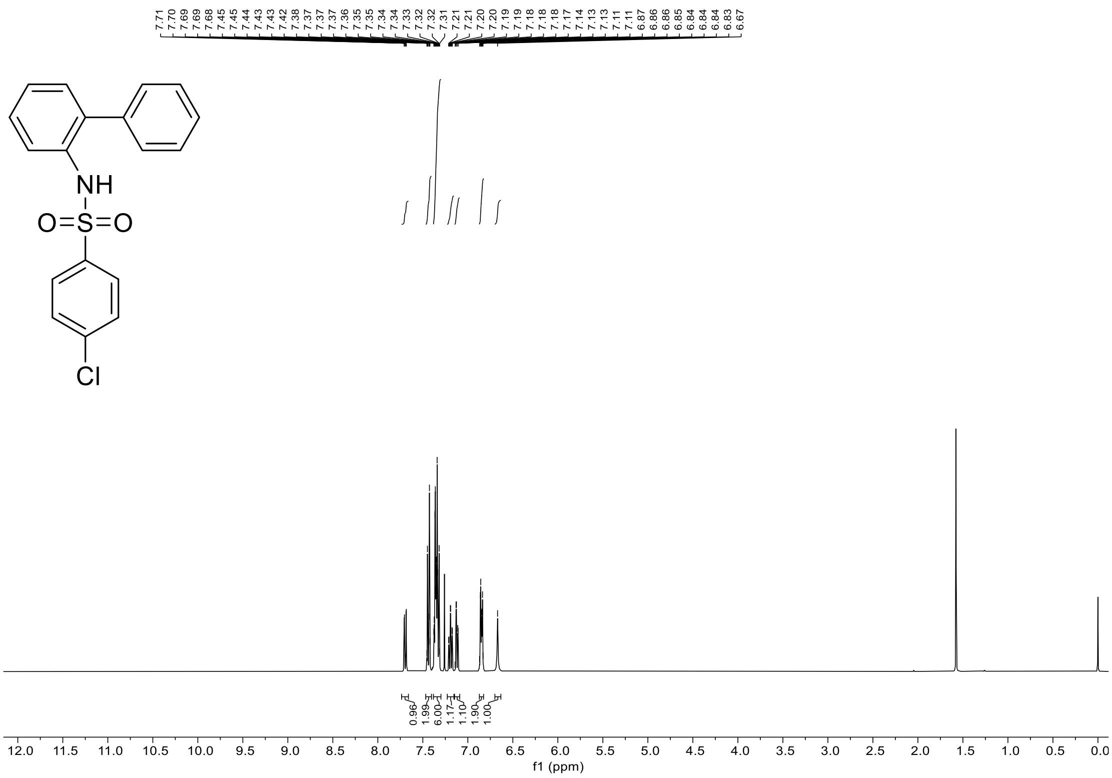
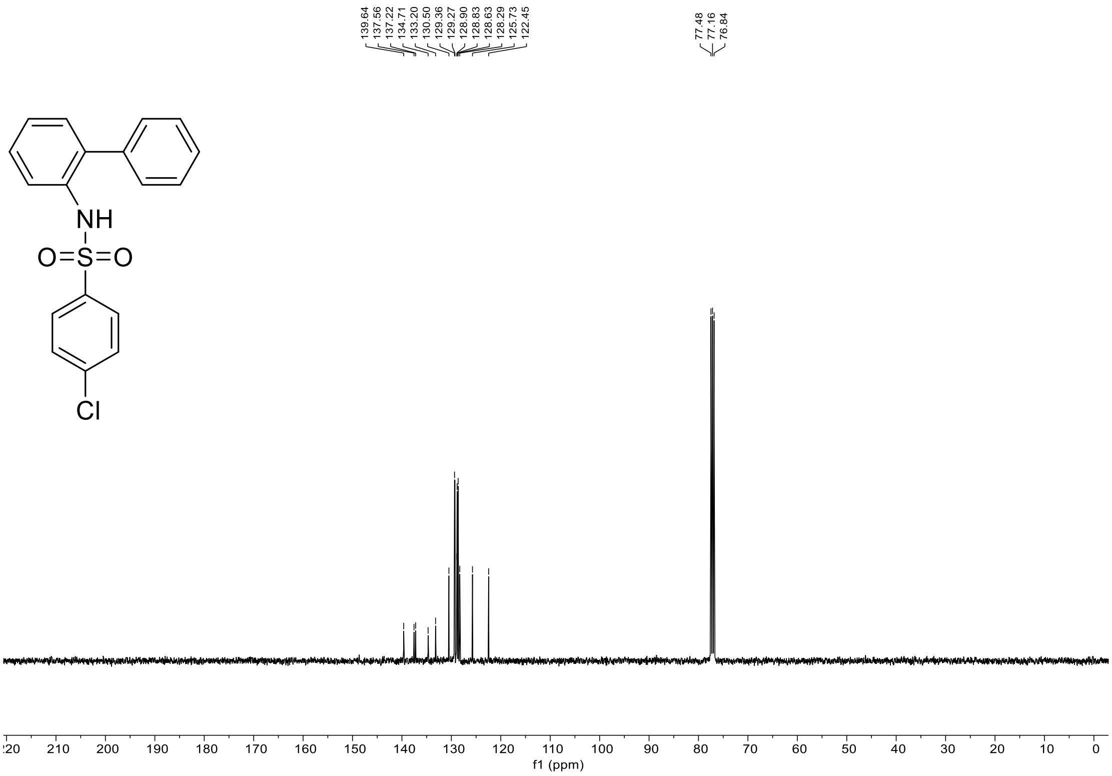
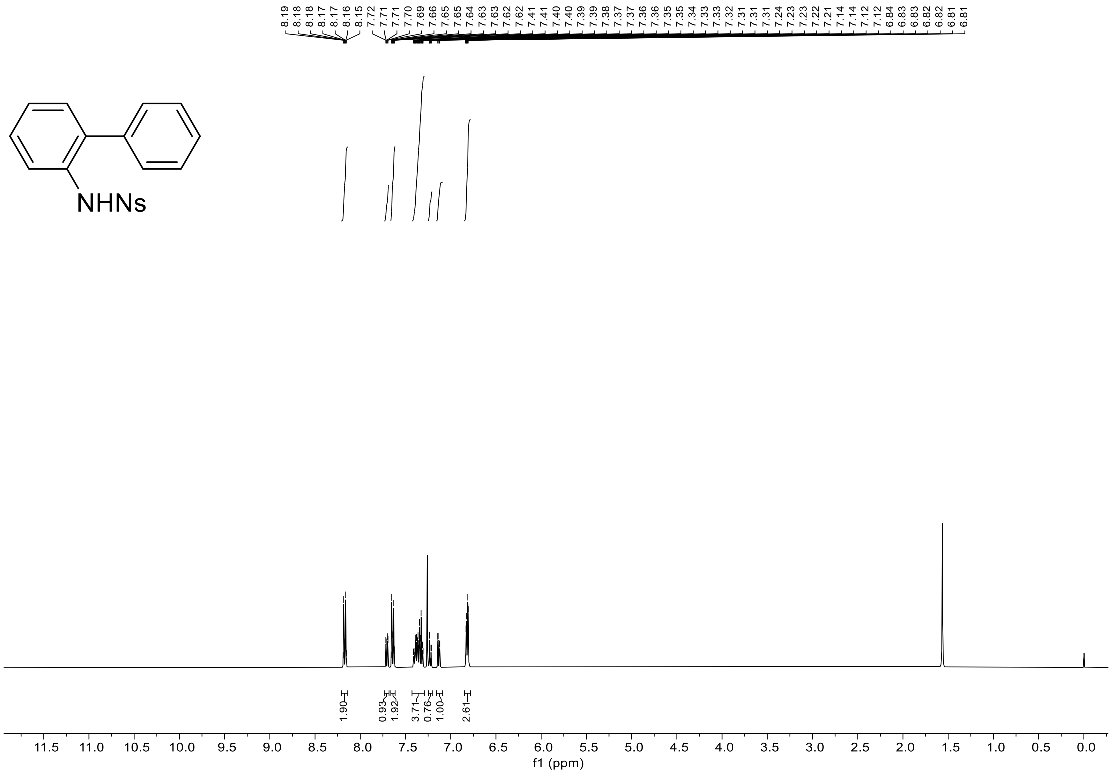
12. Copies of NMR spectra



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6.82
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1.90
0.93
1.92
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0.76
1.00
2.61
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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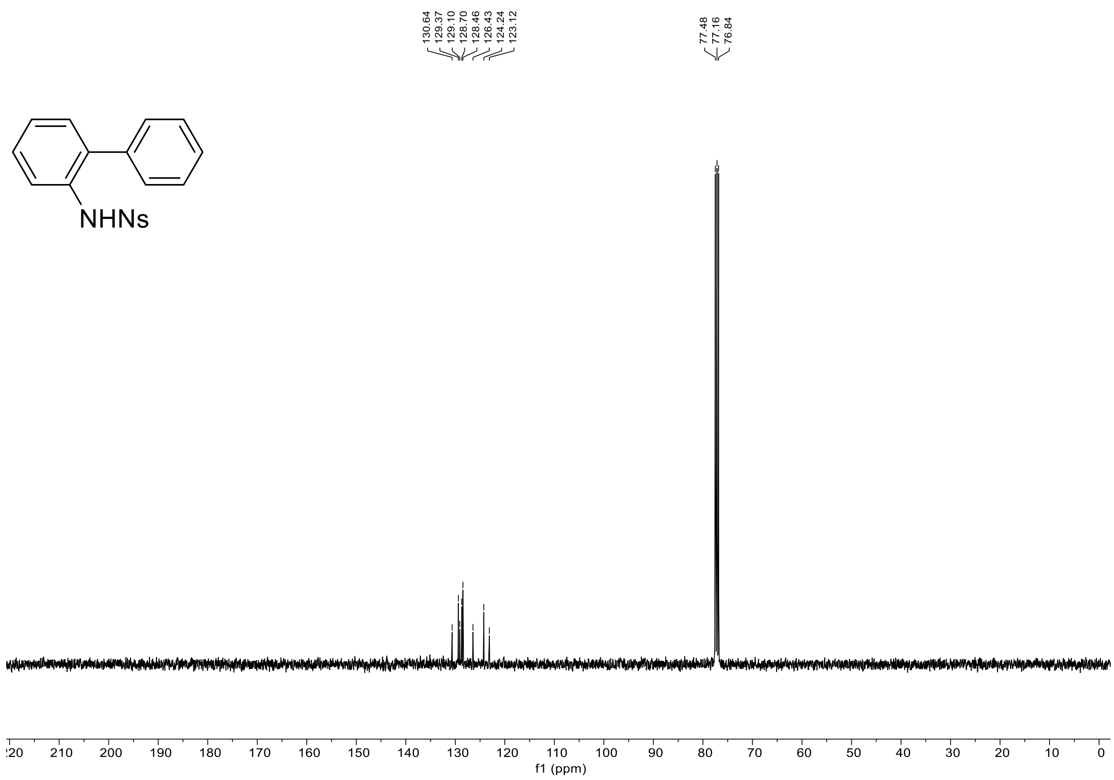
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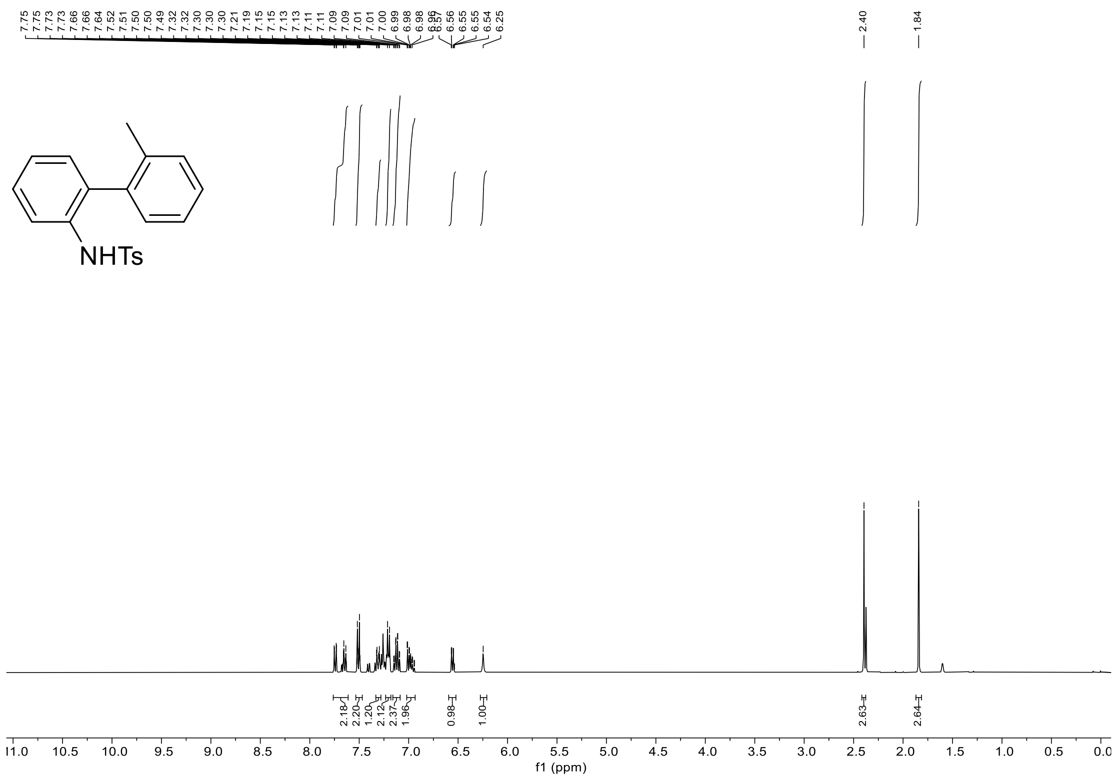
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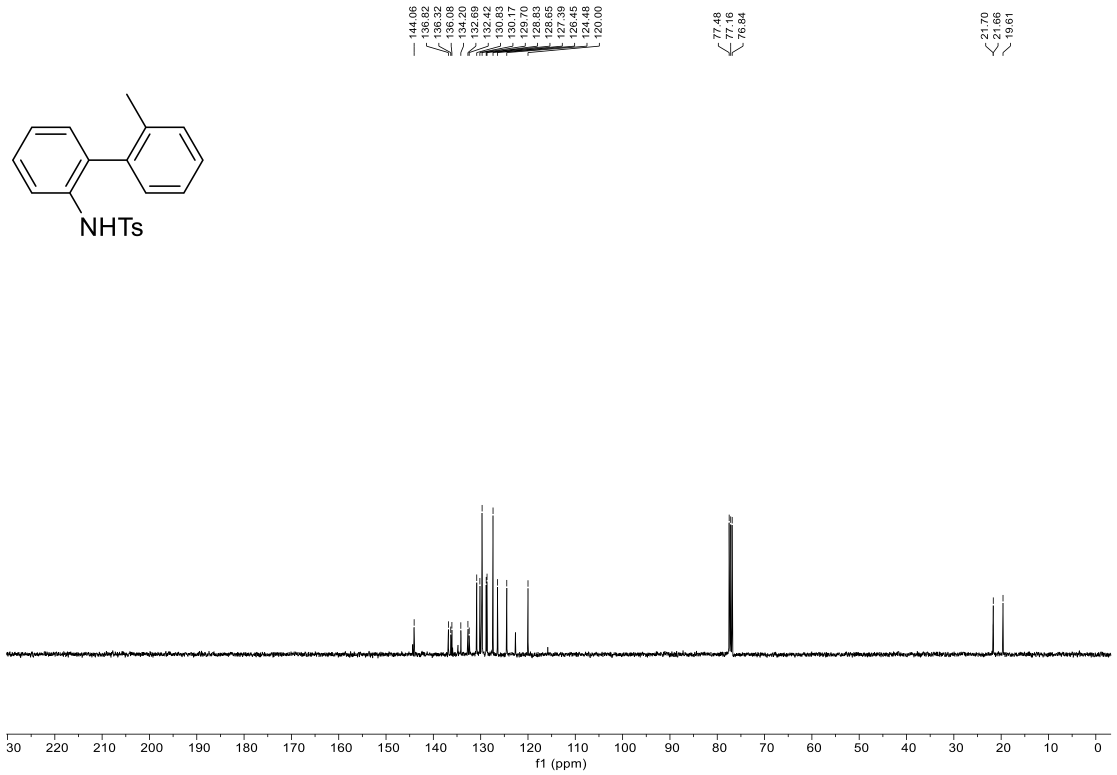
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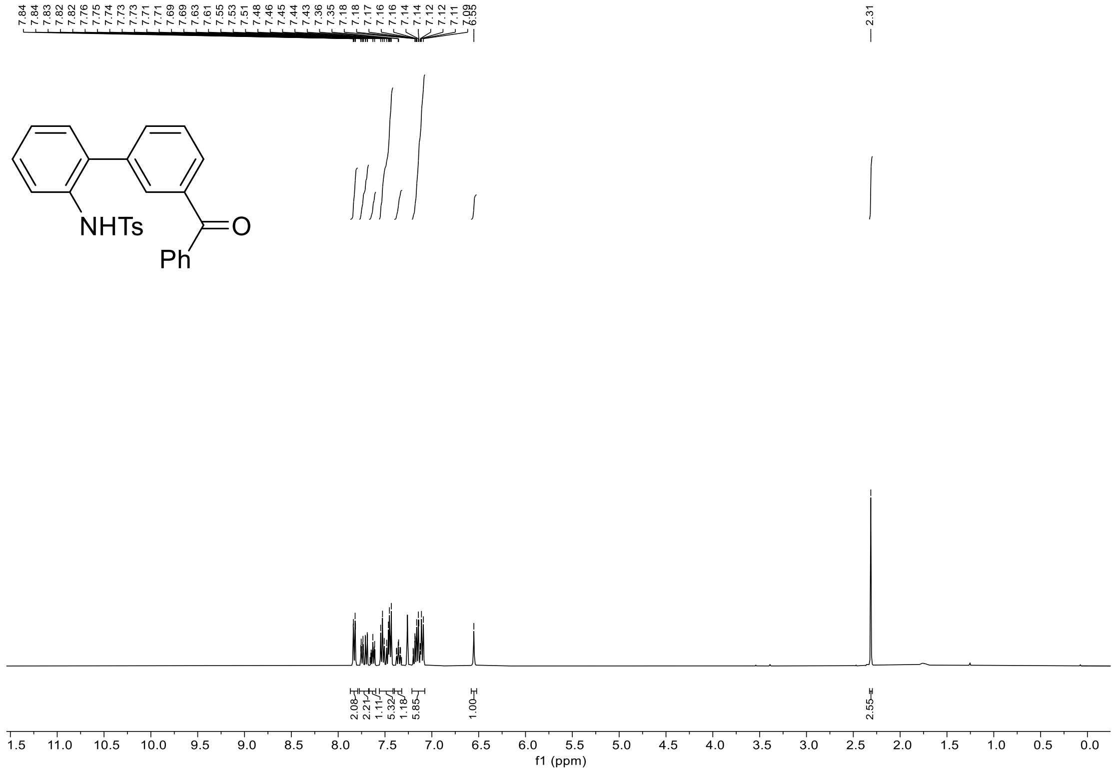
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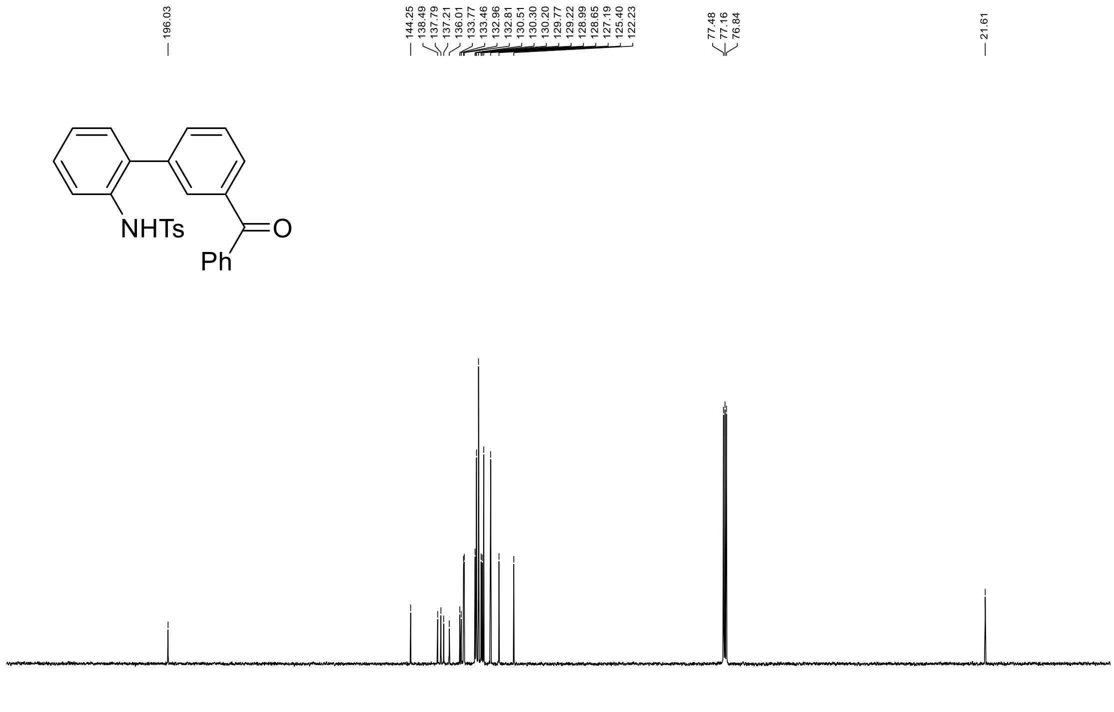
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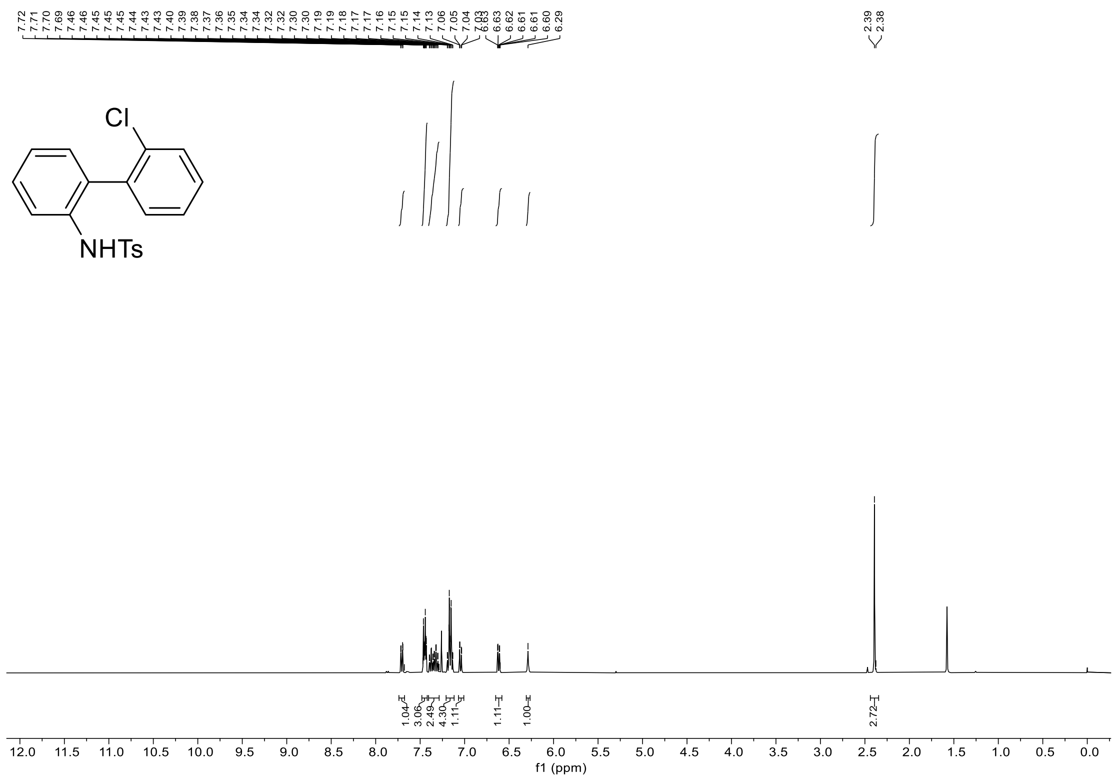

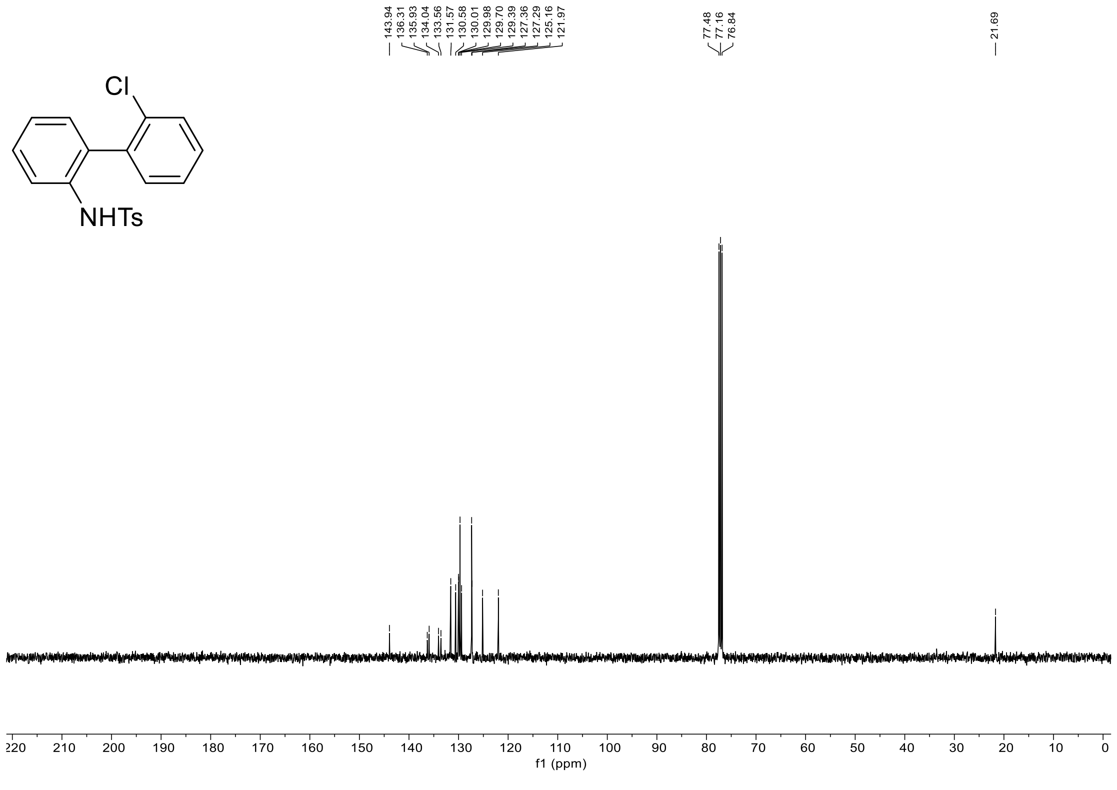

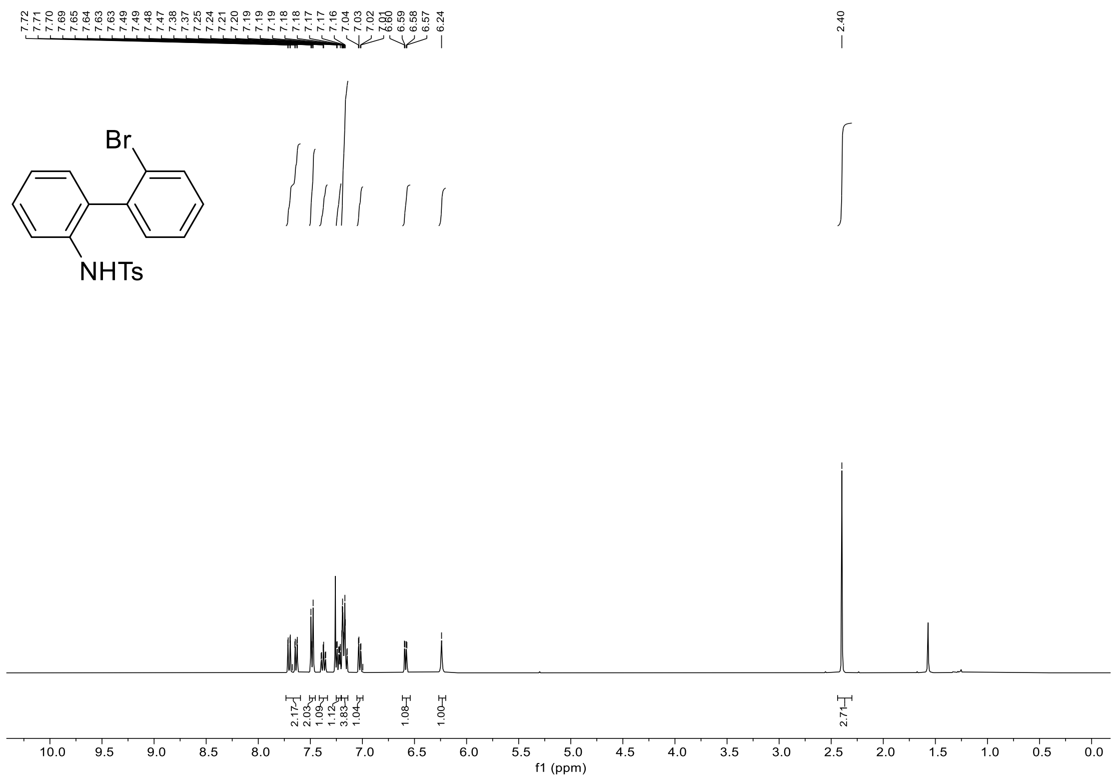
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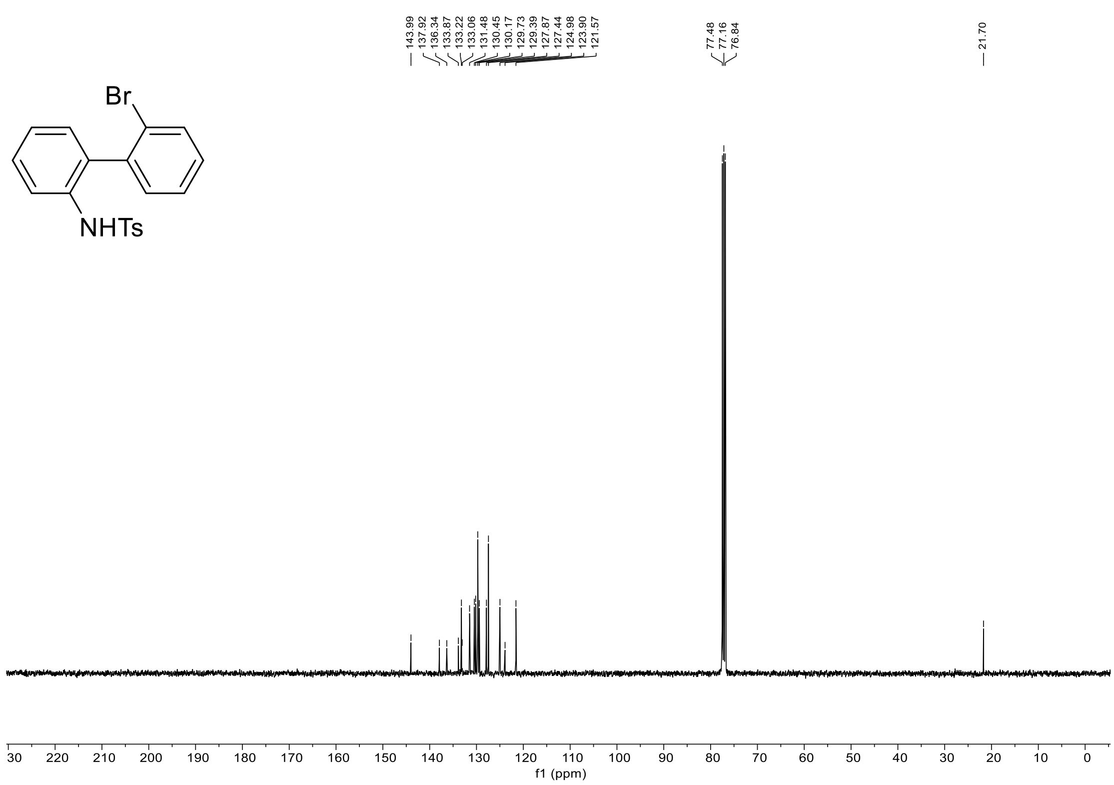
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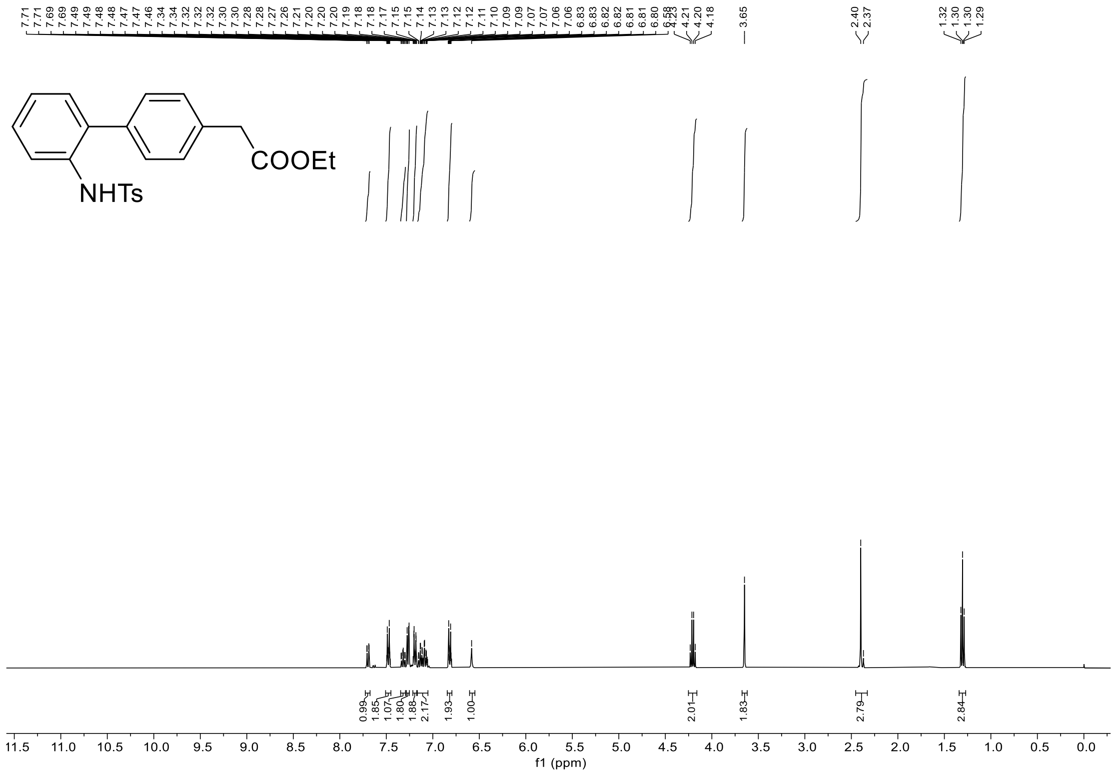
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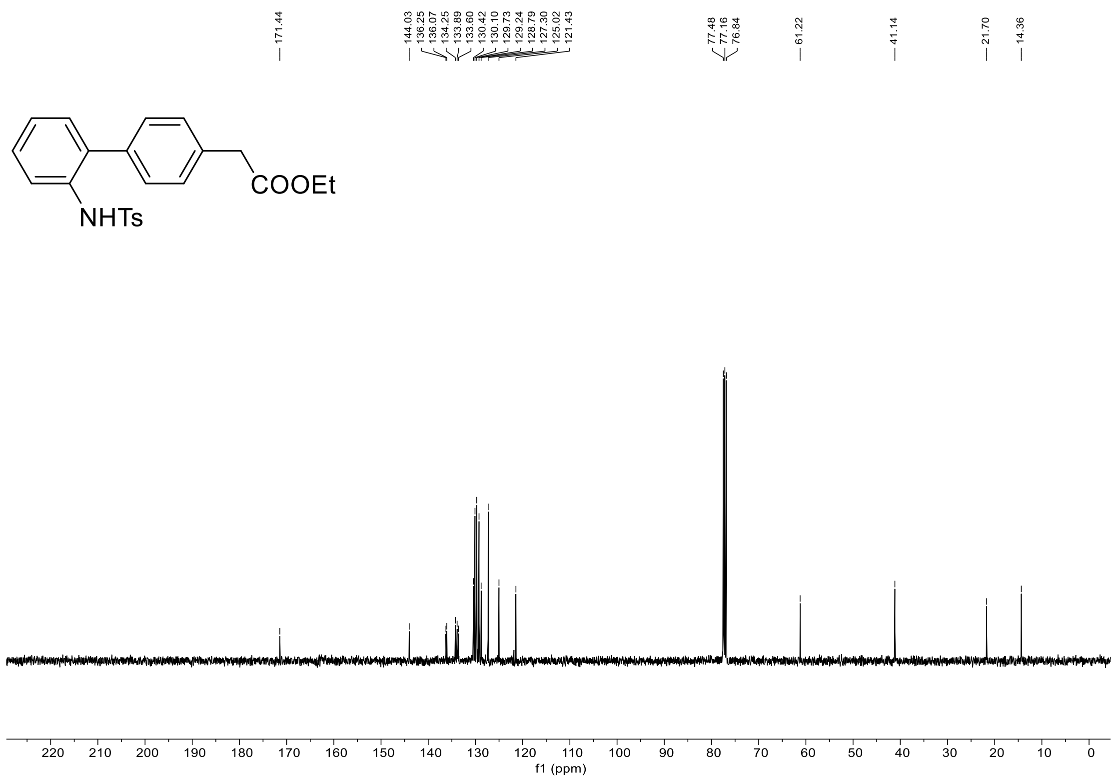
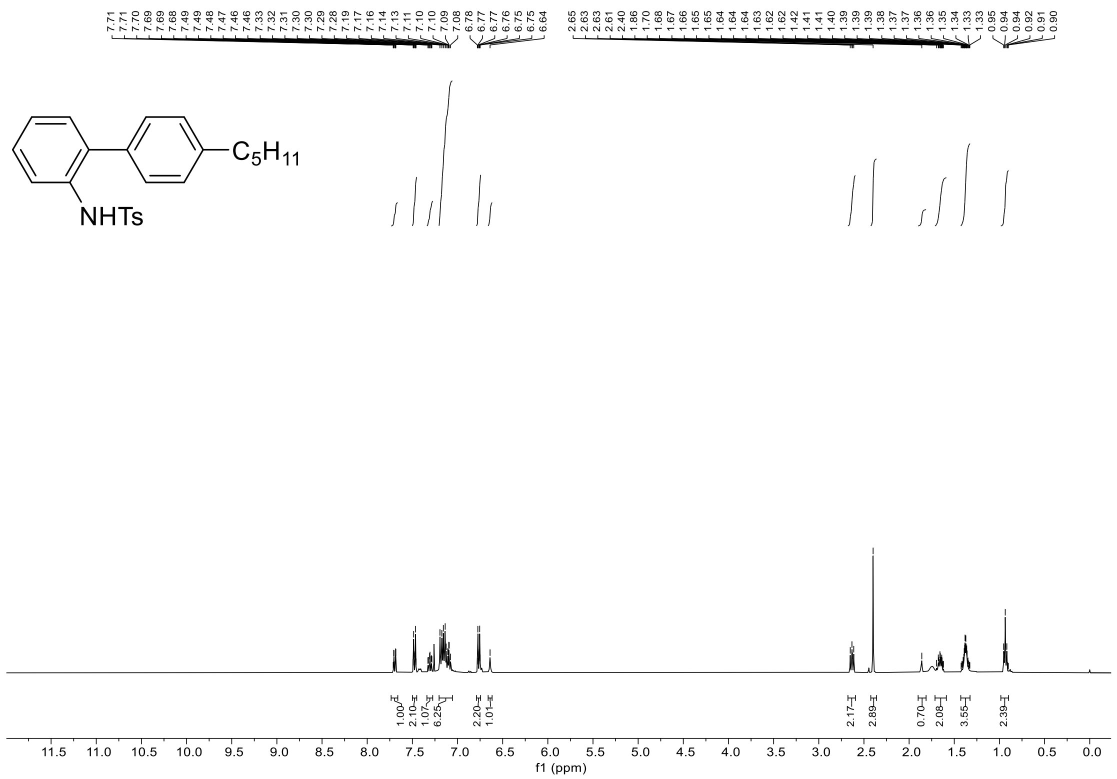
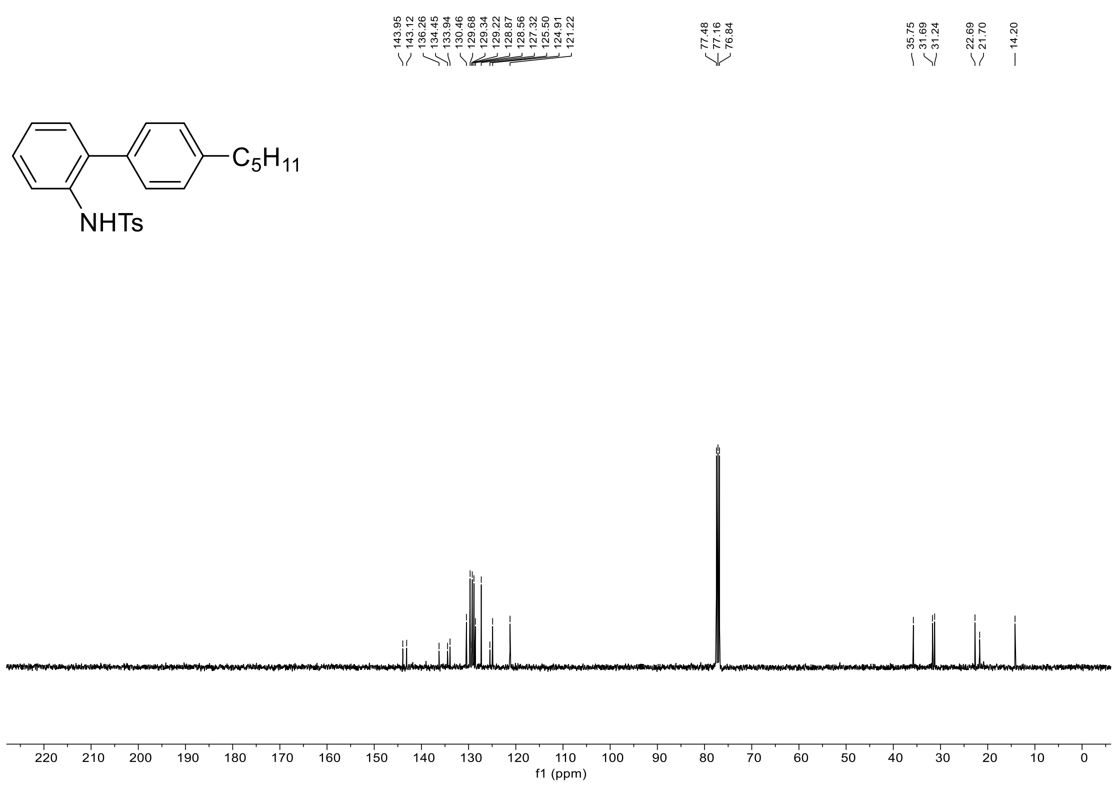
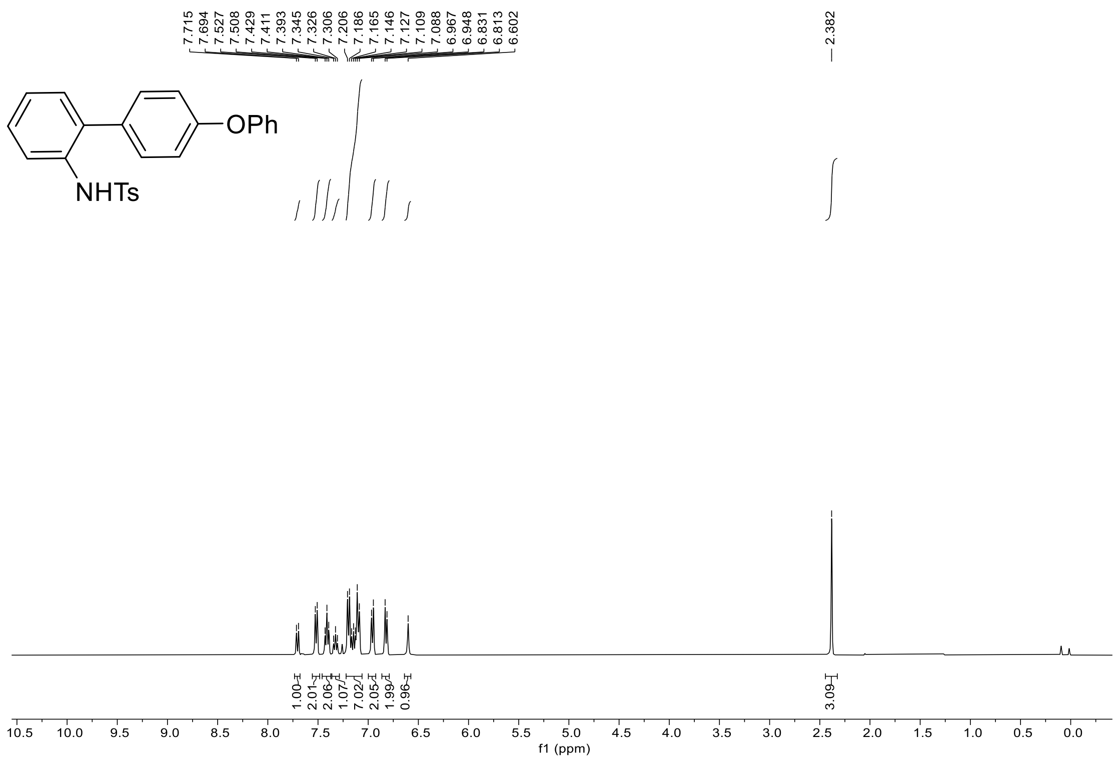
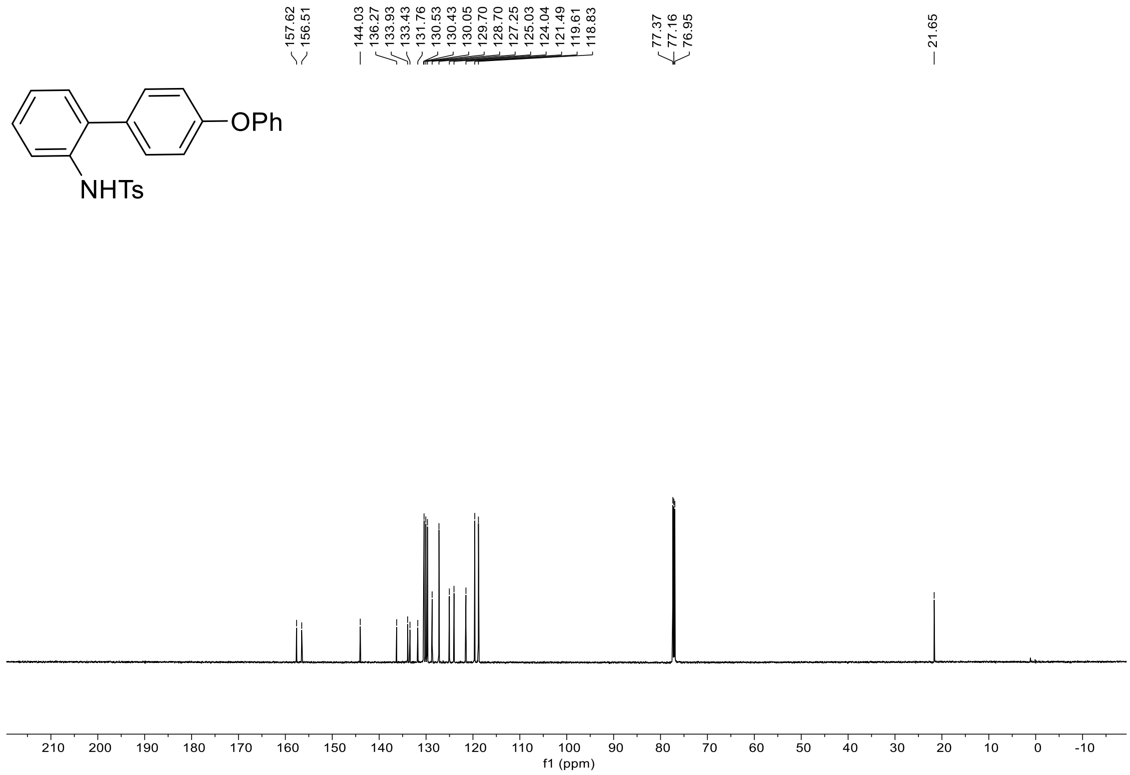
f1 (ppm)

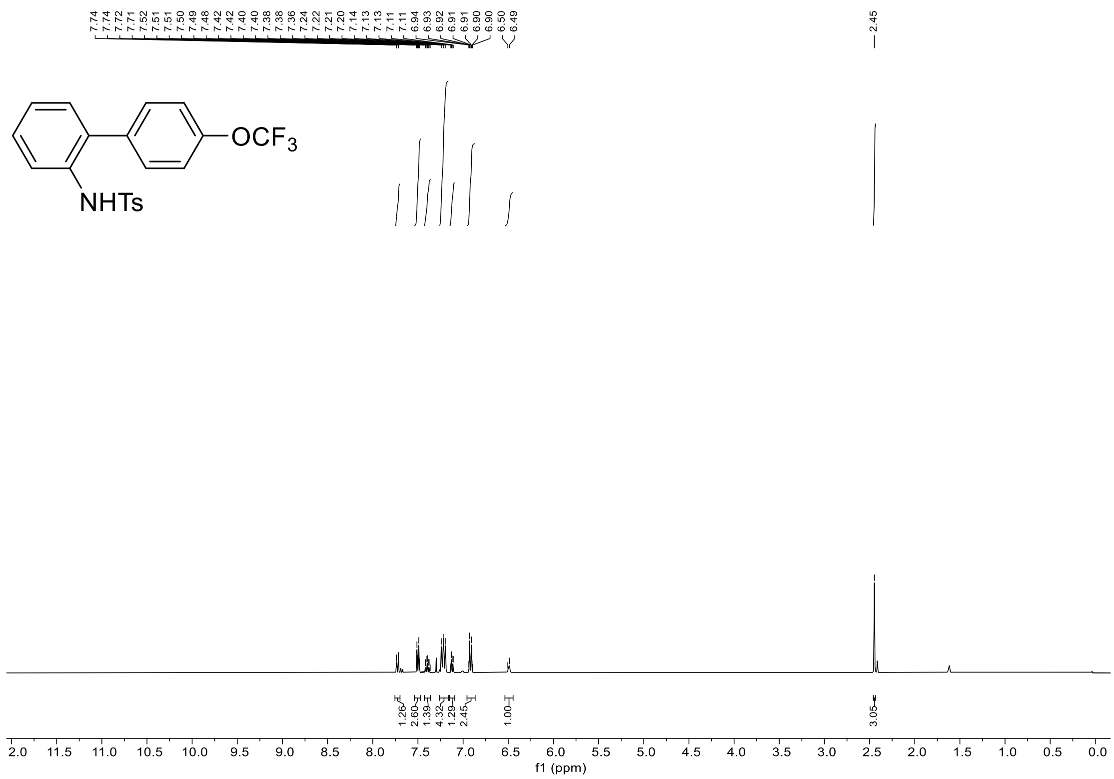

COOEt
NHTs
f1 (ppm)

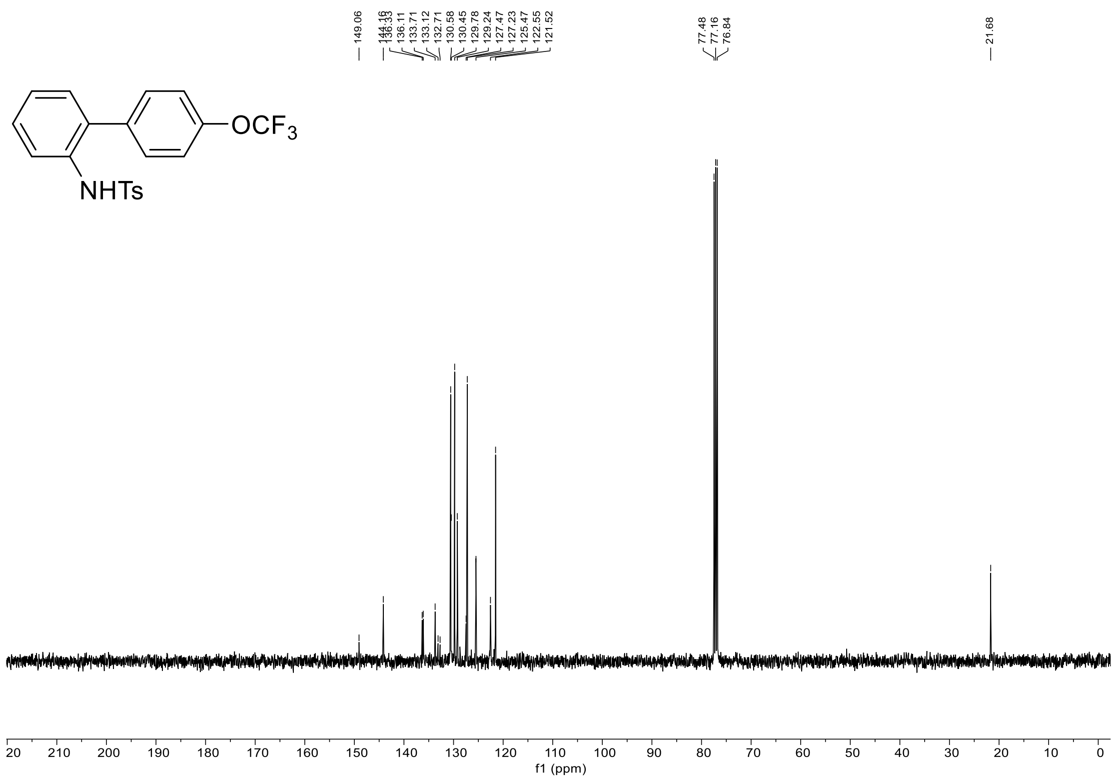

C5H11
NHTs
f1 (ppm)

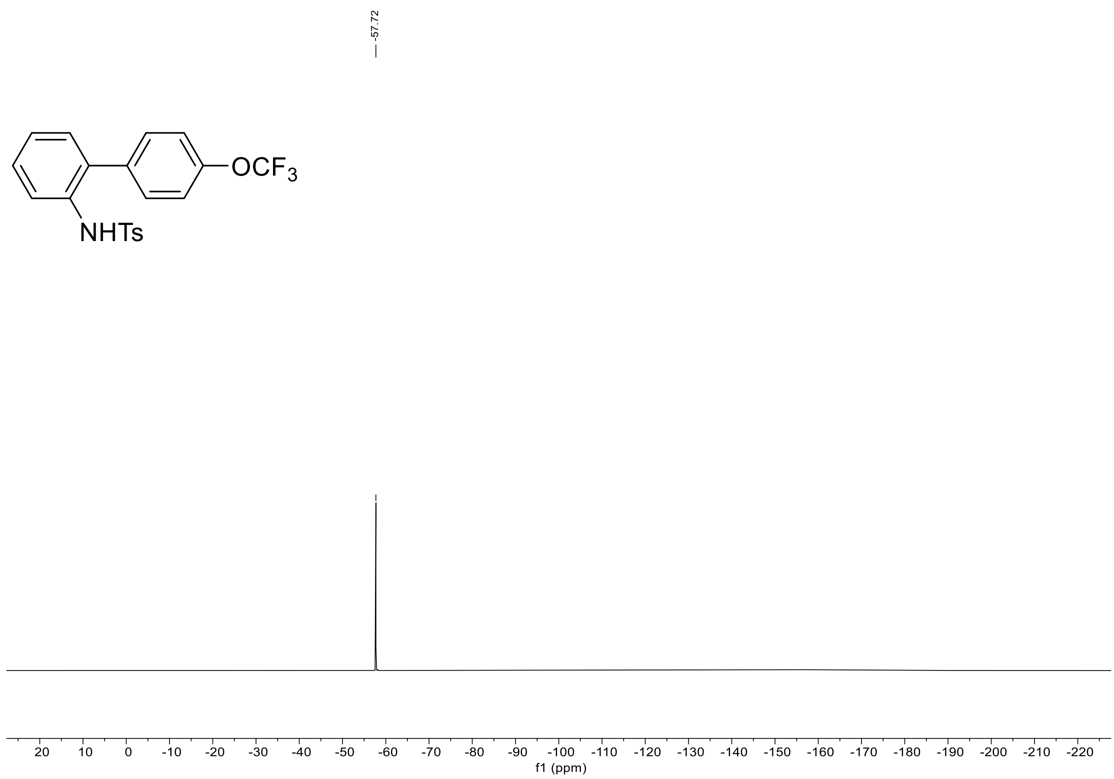

C5H11
NHTs
f1 (ppm)



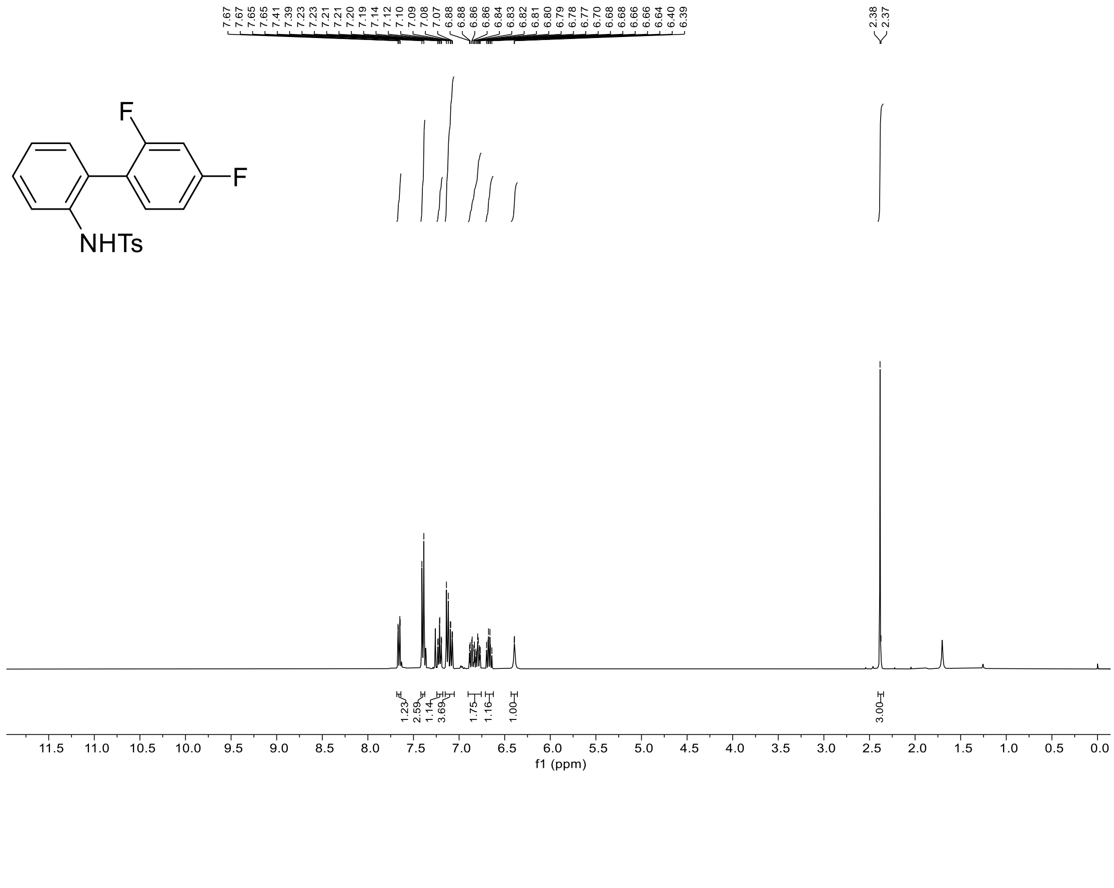



OCF3
NHTs
f1 (ppm)

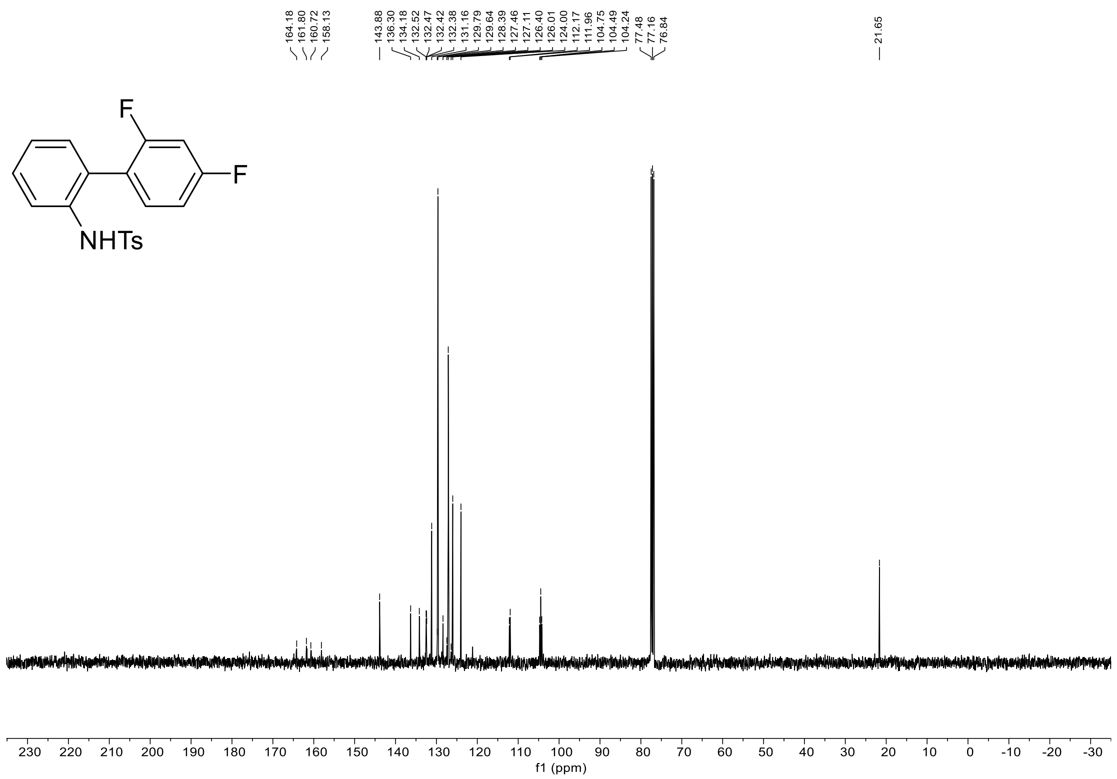

OCF3
NHTs
f1 (ppm)



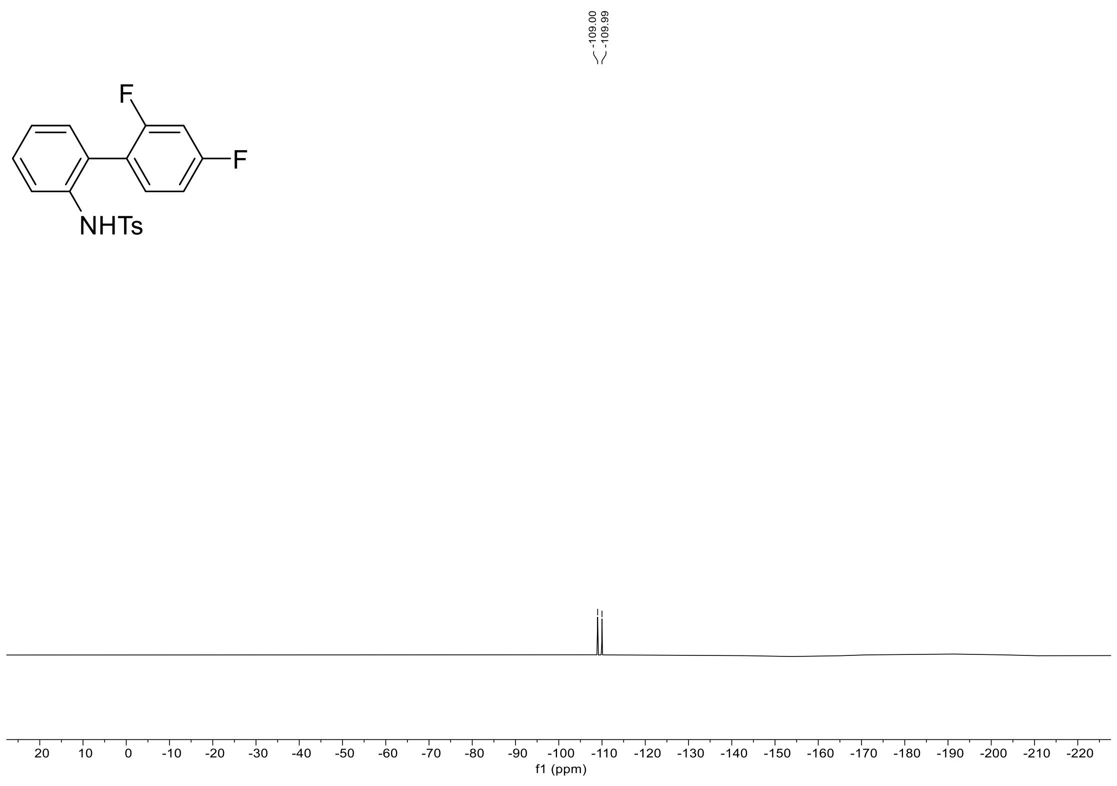
-57.72
OCF3
NHTs
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



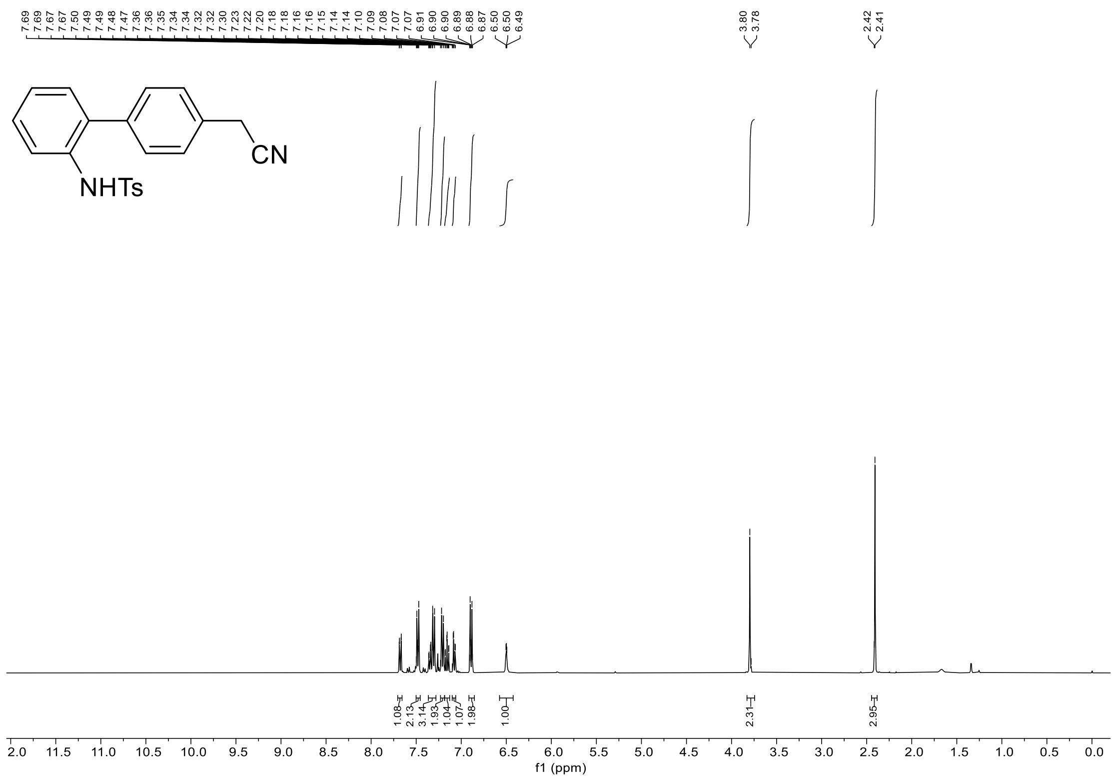
7.67 7.67 7.65 7.65 7.41 7.39 7.23 7.23 7.21 7.21 7.20 7.19 7.14 7.12 7.10 7.09 7.08 7.07 6.88 6.88 6.86 6.86 6.84 6.83 6.82 6.81 6.80 6.79 6.78 6.77 6.70 6.68 6.68 6.66 6.66 6.64 6.40 6.39
2.38 2.37
F
F
NHTs
1.23 2.59 1.14 3.69 1.75 1.16 1.00
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

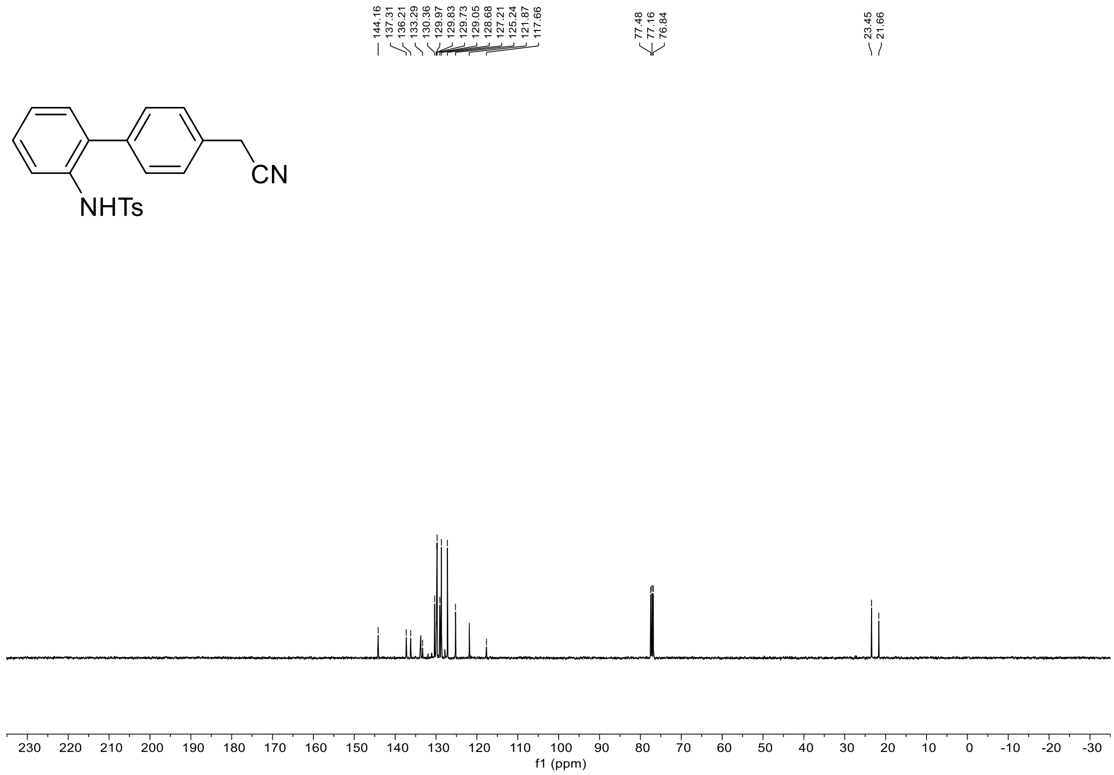


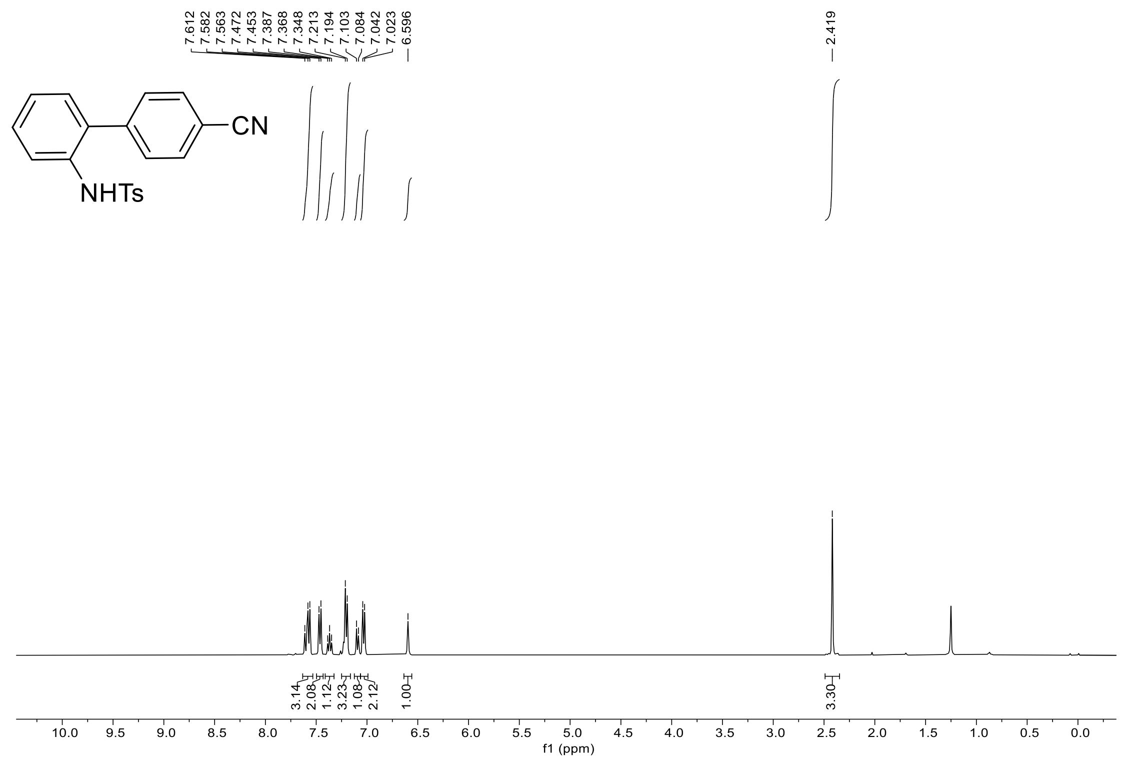
164.18
161.80
160.72
158.13
143.88
136.30
134.18
132.52
132.47
132.42
132.38
131.16
129.79
129.64
128.39
127.46
127.11
126.40
126.01
124.00
112.17
111.96
104.75
104.49
104.24
77.48
77.16
76.84
21.65
F
F
NHTs
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

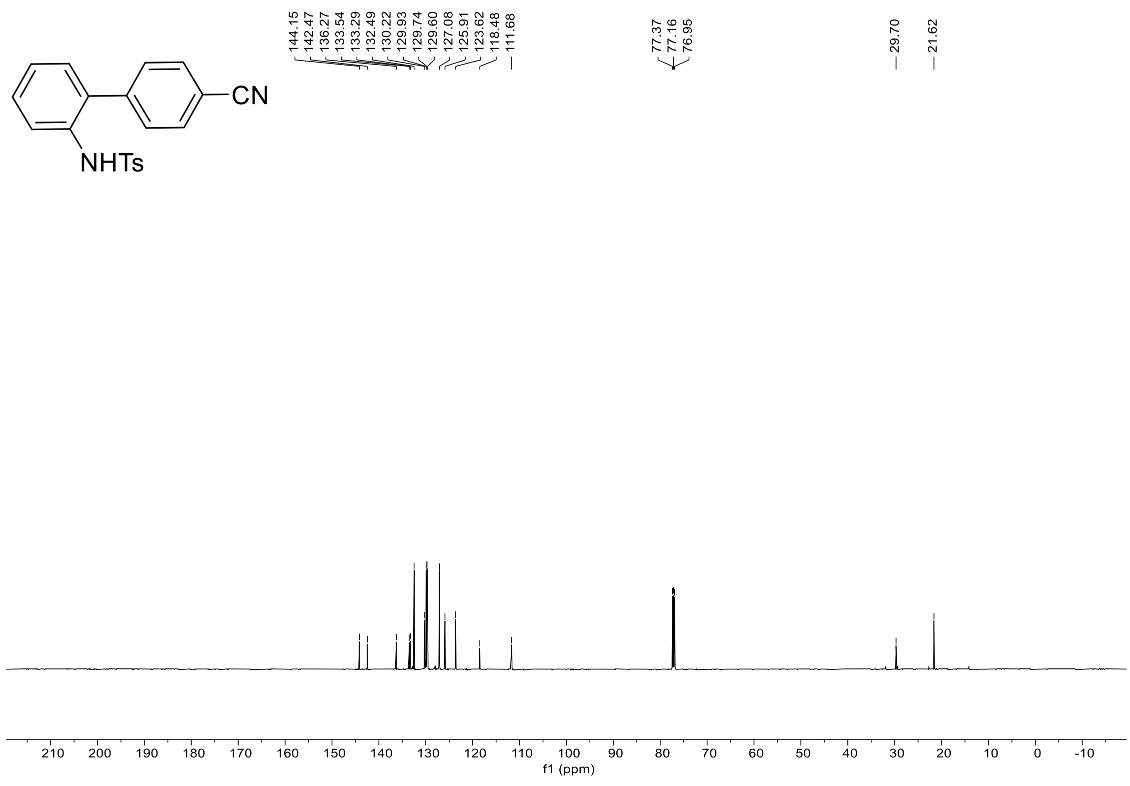


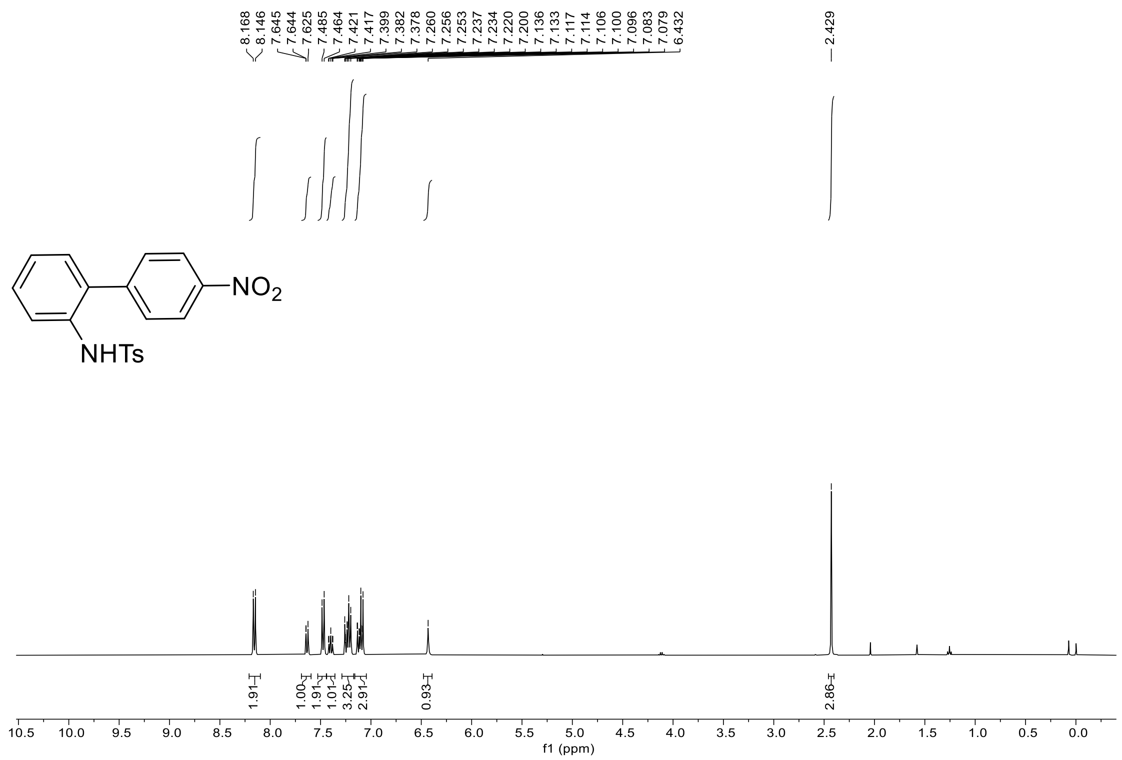
-109.00
-109.99
F
F
NHTs
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

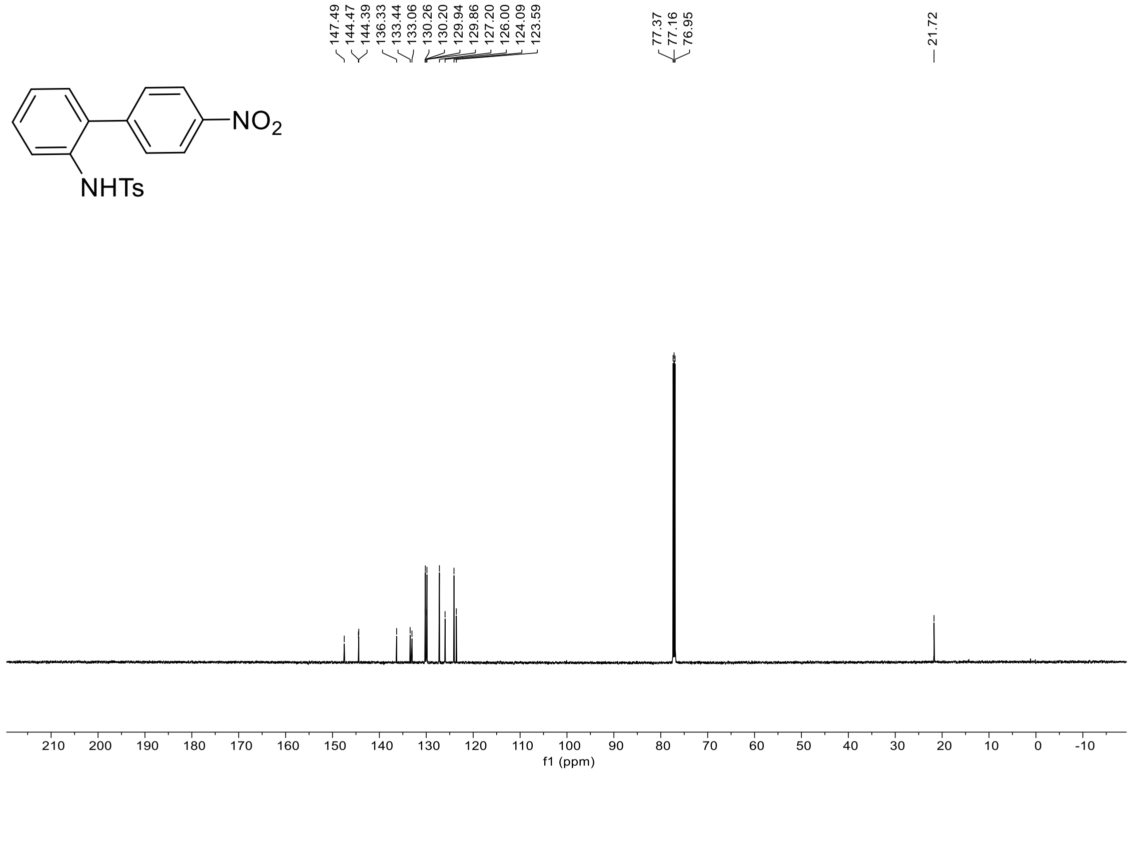

7.69 7.69 7.67 7.50 7.49 7.49 7.48 7.47 7.36 7.36 7.35 7.34 7.34 7.32 7.32 7.30 7.23 7.22 7.20 7.18 7.18 7.16 7.16 7.15 7.14 7.14 7.10 7.09 7.08 7.07 7.07 6.91 6.90 6.90 6.89 6.88 6.87 6.50 6.50 6.49
3.80 3.78
2.42 2.41
CN
NHTs
1.08 2.13 3.14 1.93 1.04 1.07 1.98 1.00
2.31
2.95
f1 (ppm)

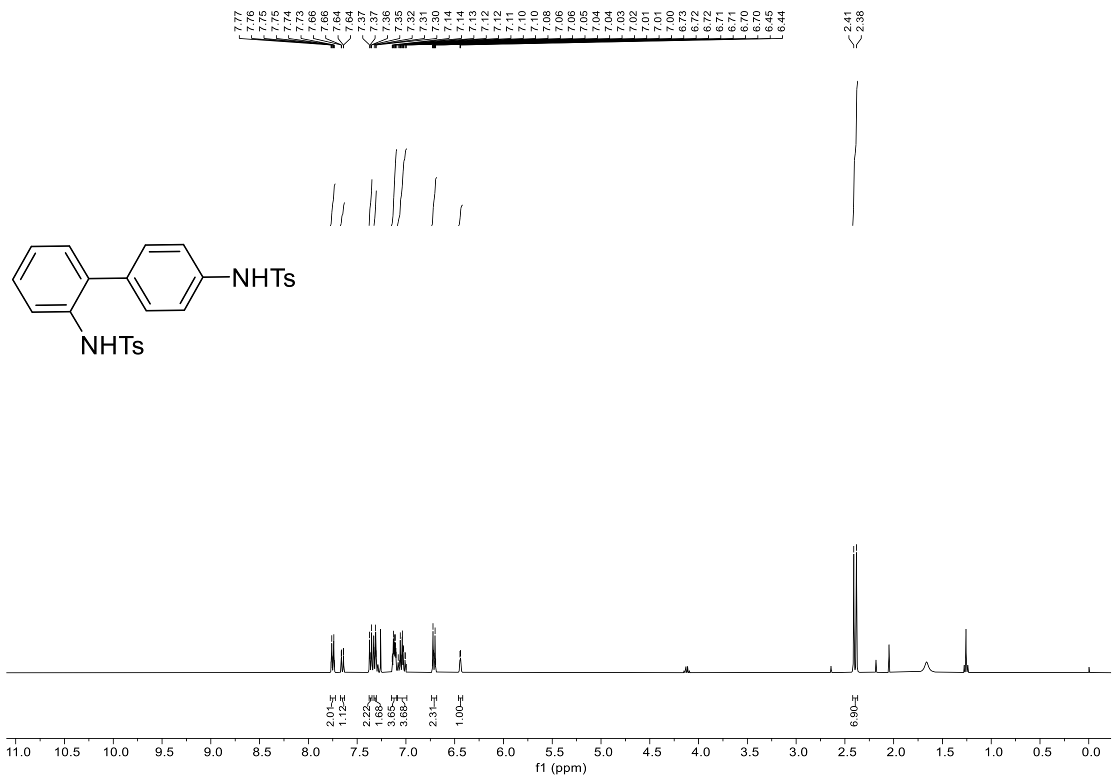

144.16 137.31 136.21 133.29 130.36 129.97 129.83 129.73 129.05 128.68 127.21 125.24 121.87 117.66
77.48 77.16 76.84
23.45 21.66
CN
NHTs
f1 (ppm)

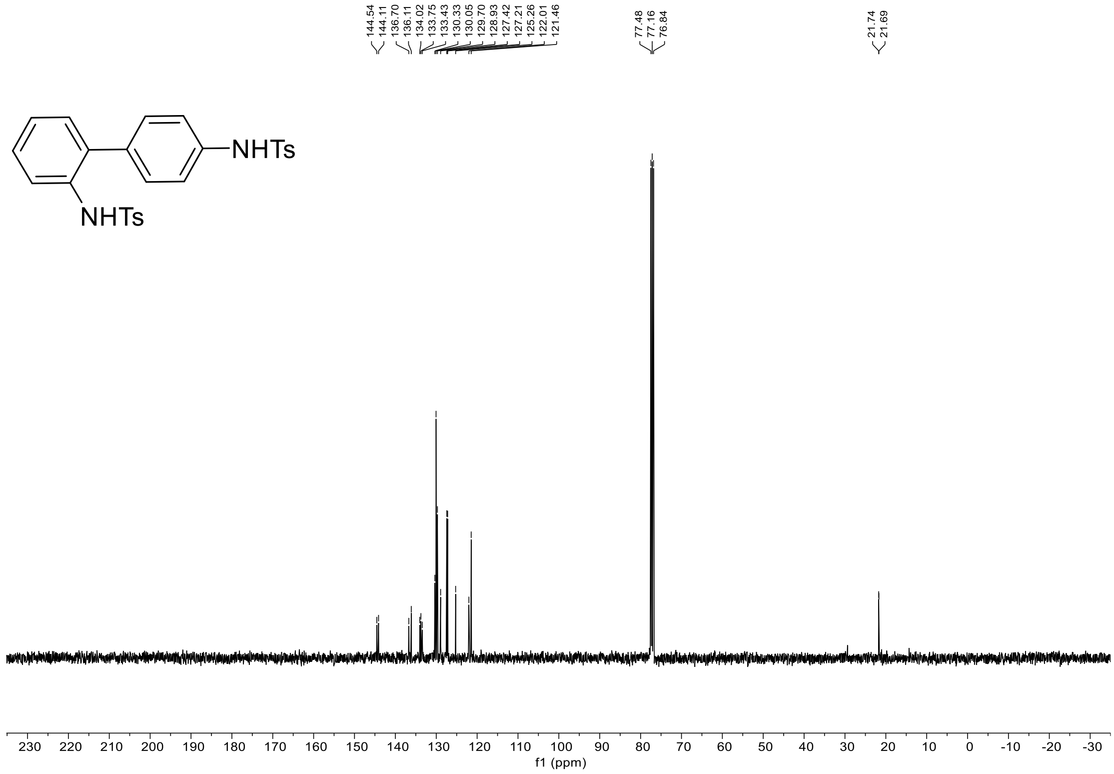

CN
NHTs
7.612
7.582
7.563
7.472
7.453
7.387
7.368
7.348
7.213
7.194
7.103
7.084
7.042
7.023
6.596
2.419
3.14
2.08
1.12
3.23
1.08
2.12
1.00
3.30
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

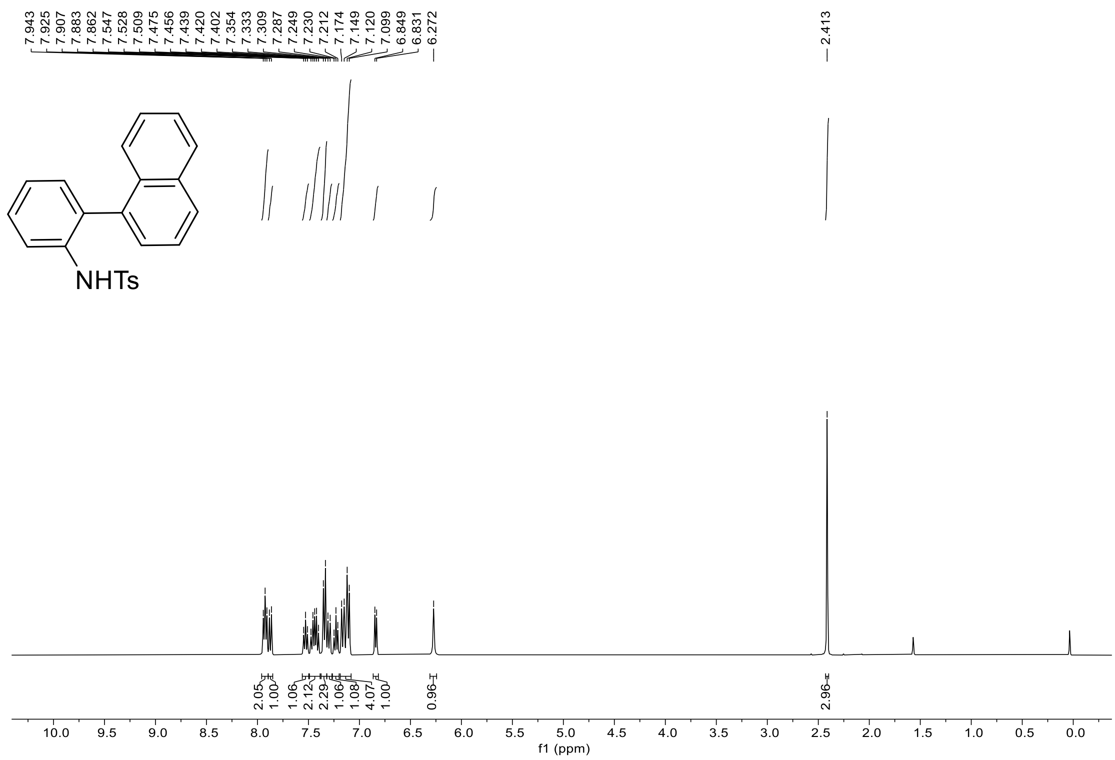

CN
NHTs
144.15
142.47
136.27
133.54
133.29
132.49
130.22
129.93
129.74
129.60
127.08
125.91
123.62
118.48
111.68
77.37
77.16
76.95
29.70
21.62
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

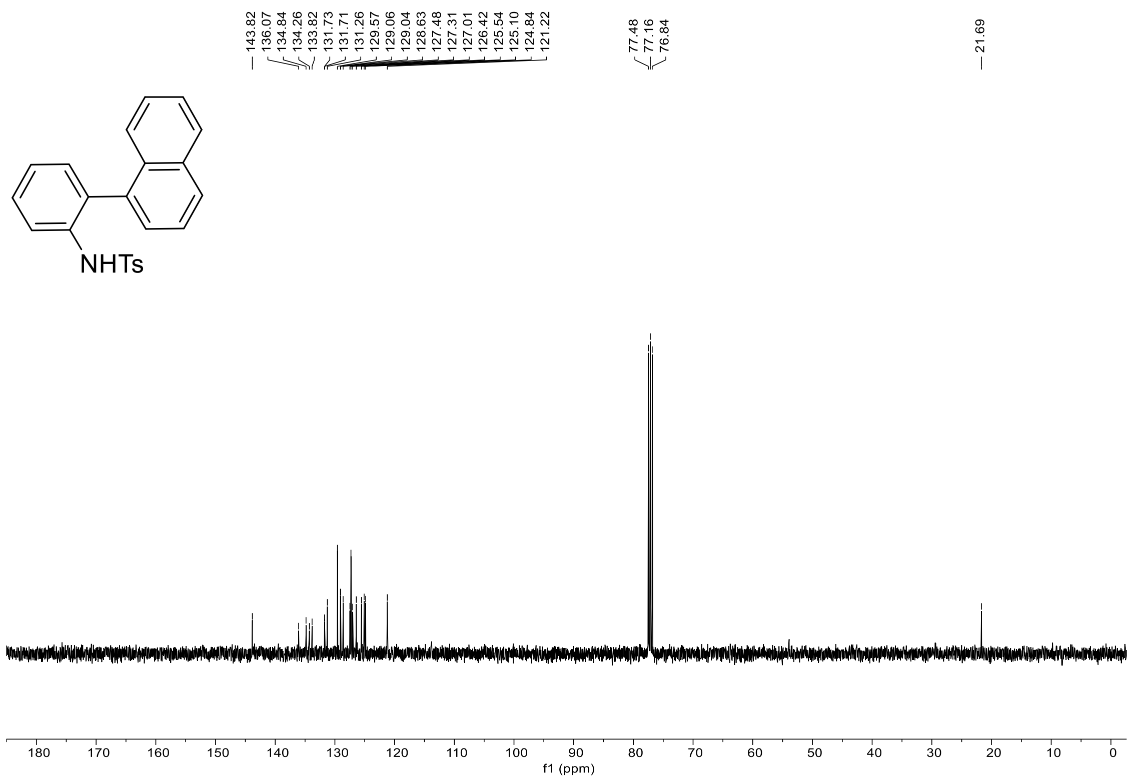

NO2
NHTs
f1 (ppm)

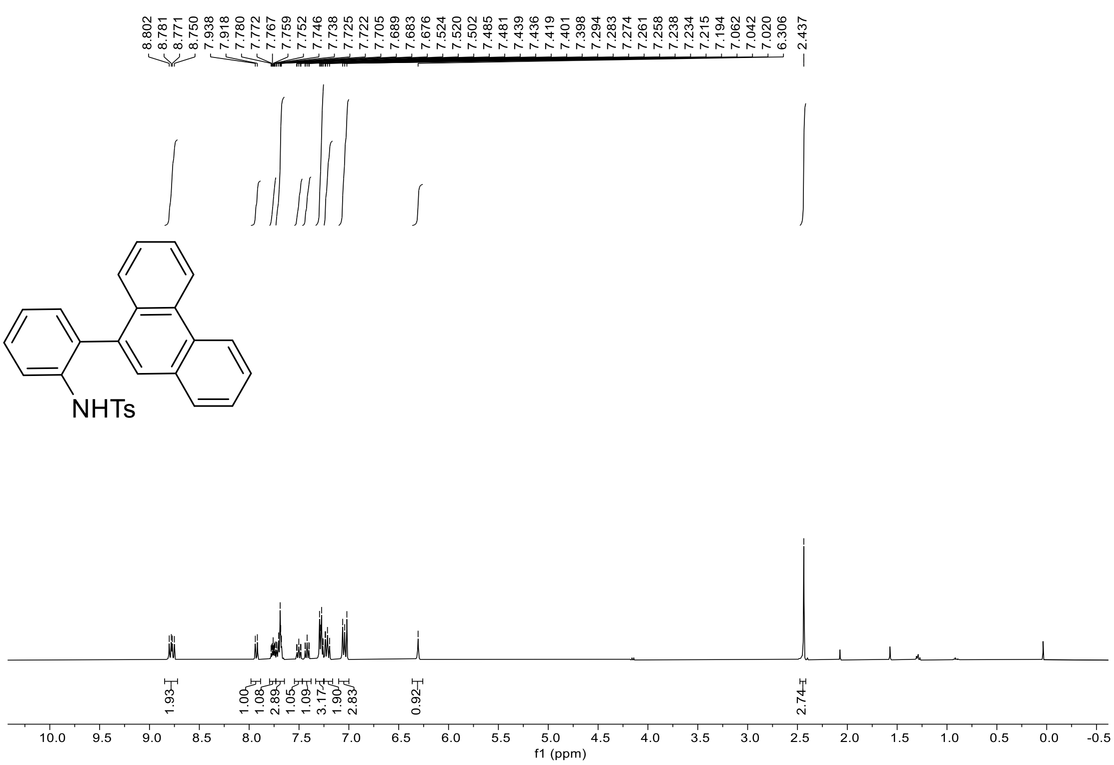

NO2
NHTs
f1 (ppm)







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8.750
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7.918
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7.772
7.767
7.759
7.752
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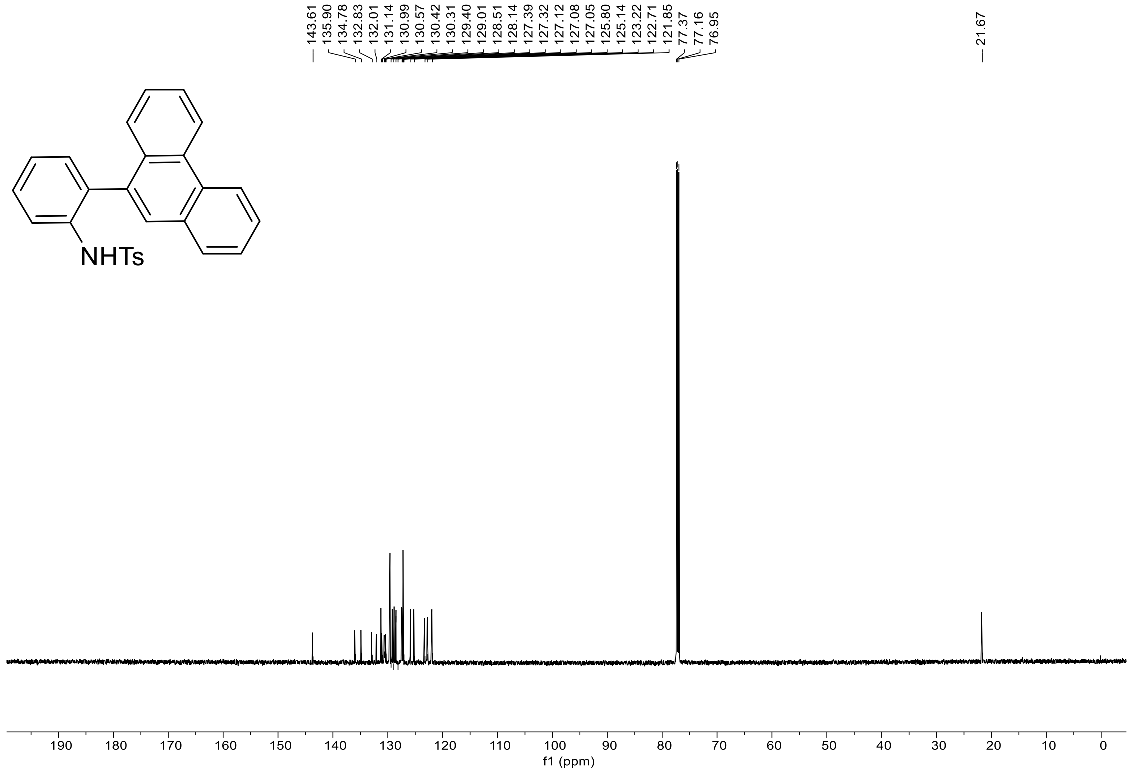
7.738
7.725
7.722
7.705
7.689
7.683
7.676
7.524
7.520
7.502
7.485
7.481
7.439
7.436
7.419
7.401
7.398
7.294
7.283
7.274
7.261
7.258
7.238
7.234
7.215
7.194
7.062
7.042
7.020
6.306
2.437
NHTs
1.93
1.00
1.08
2.89
1.05
1.09
3.17
1.90
2.83
0.92
2.74
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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131.14
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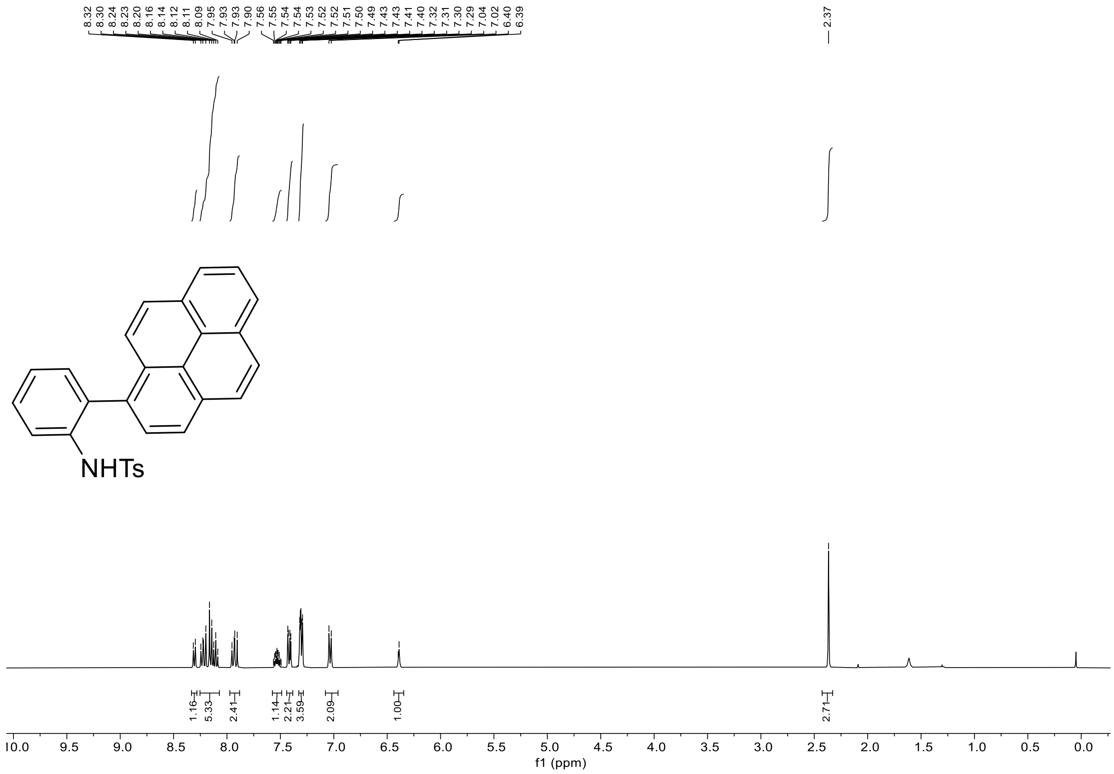
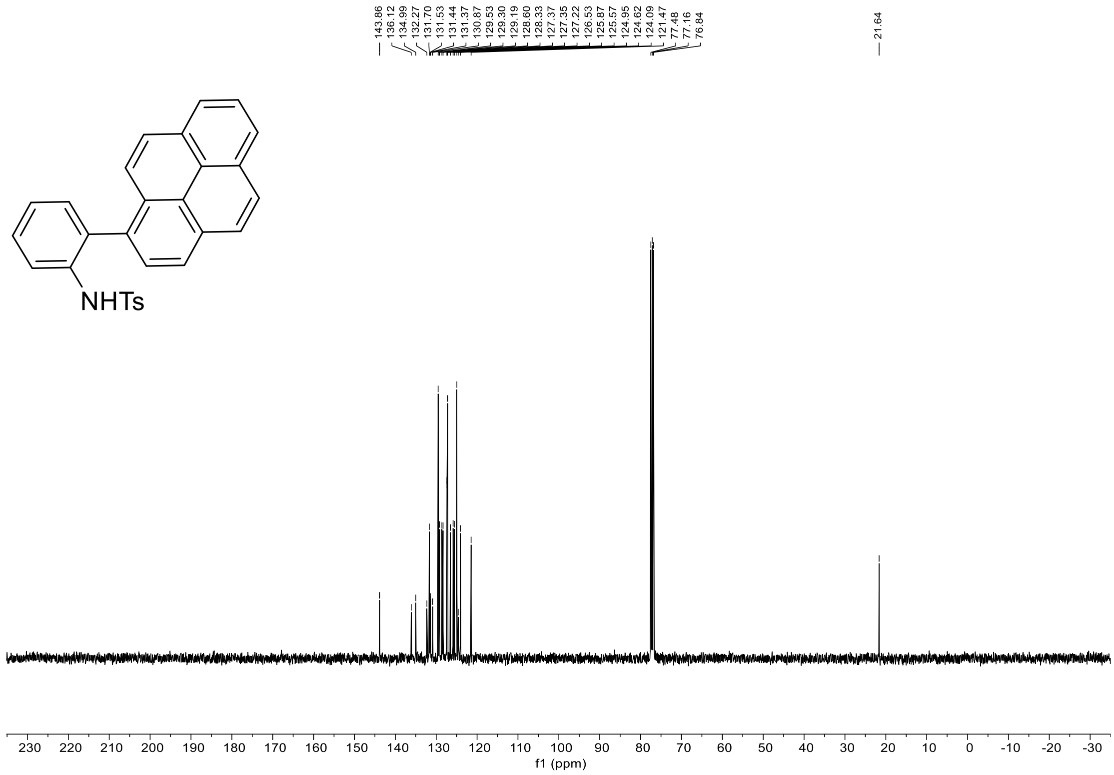
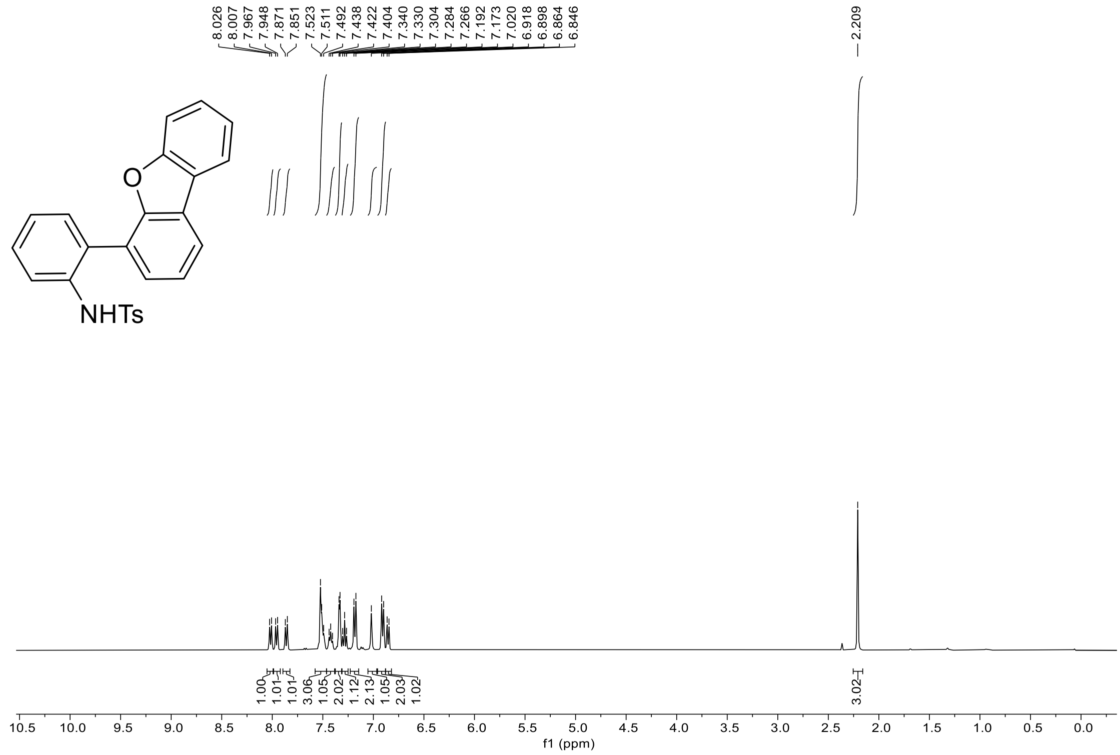
130.31
129.40
129.01
128.51
128.14
127.39
127.32
127.12
127.08
127.05
125.80
125.14
123.22
122.71
121.85
77.37
77.16
76.95
21.67
NHTs
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.32 8.30 8.24 8.23 8.20 8.16 8.14 8.12 8.11 8.09 7.95 7.93 7.93 7.90 7.56 7.55 7.54 7.54 7.53 7.52 7.52 7.51 7.50 7.49 7.43 7.41 7.40 7.32 7.31 7.30 7.29 7.04 7.02 6.40 6.39
2.37
NHTs
1.16 5.33 2.41 1.14 2.21 3.59 2.09 1.00 2.71
f1 (ppm)


143.86 136.12 134.99 132.27 131.70 131.53 131.44 131.37 130.87 129.53 129.30 129.19 128.60 128.33 127.37 127.35 127.22 126.53 125.87 125.57 124.95 124.62 124.09 121.47 77.48 77.16 76.84
21.64
NHTs
f1 (ppm)


8.026
8.007
7.967
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7.871
7.851
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7.511
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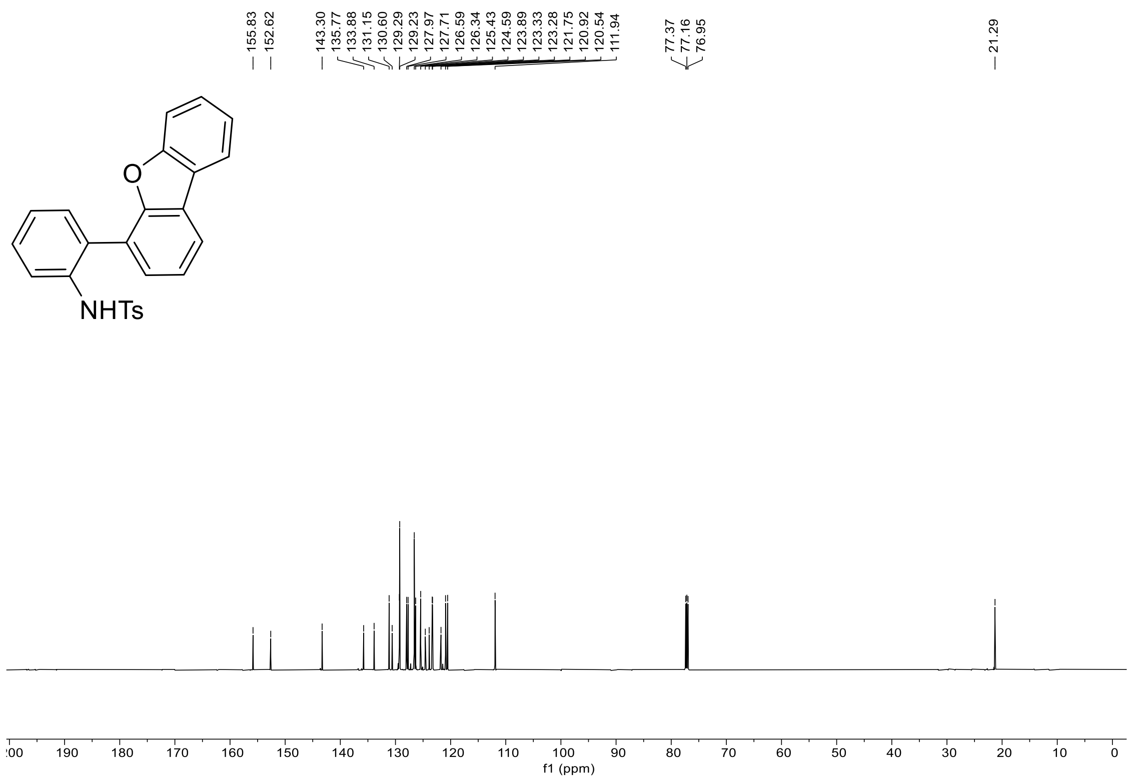
7.438
7.422
7.404
7.340
7.330
7.304
7.284
7.266
7.192
7.173
7.020
6.918
6.898
6.864
6.846
2.209
NHTs
O
1.00
1.01
1.01
3.06
1.05
2.02
1.12
2.13
1.05
2.03
1.02
3.02
f1 (ppm)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129.29
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127.97
127.71
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125.43
124.59
123.89
123.33
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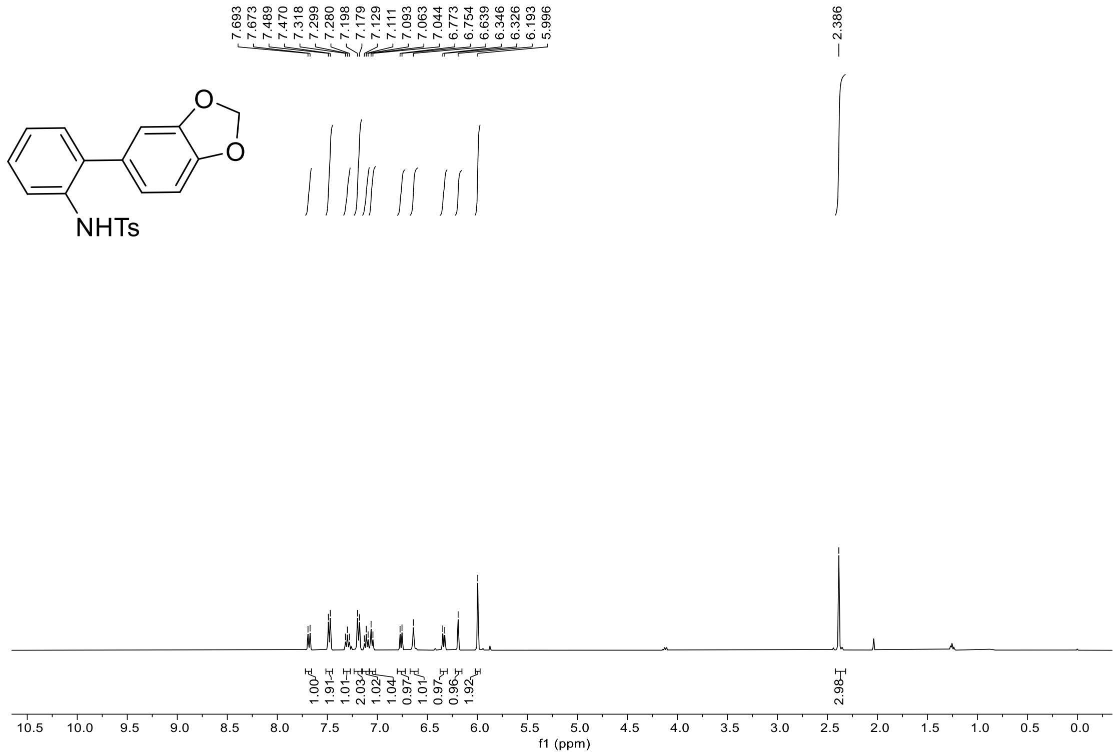
120.92
120.54
111.94
77.37
77.16
76.95
21.29
NHTs
O
f1 (ppm)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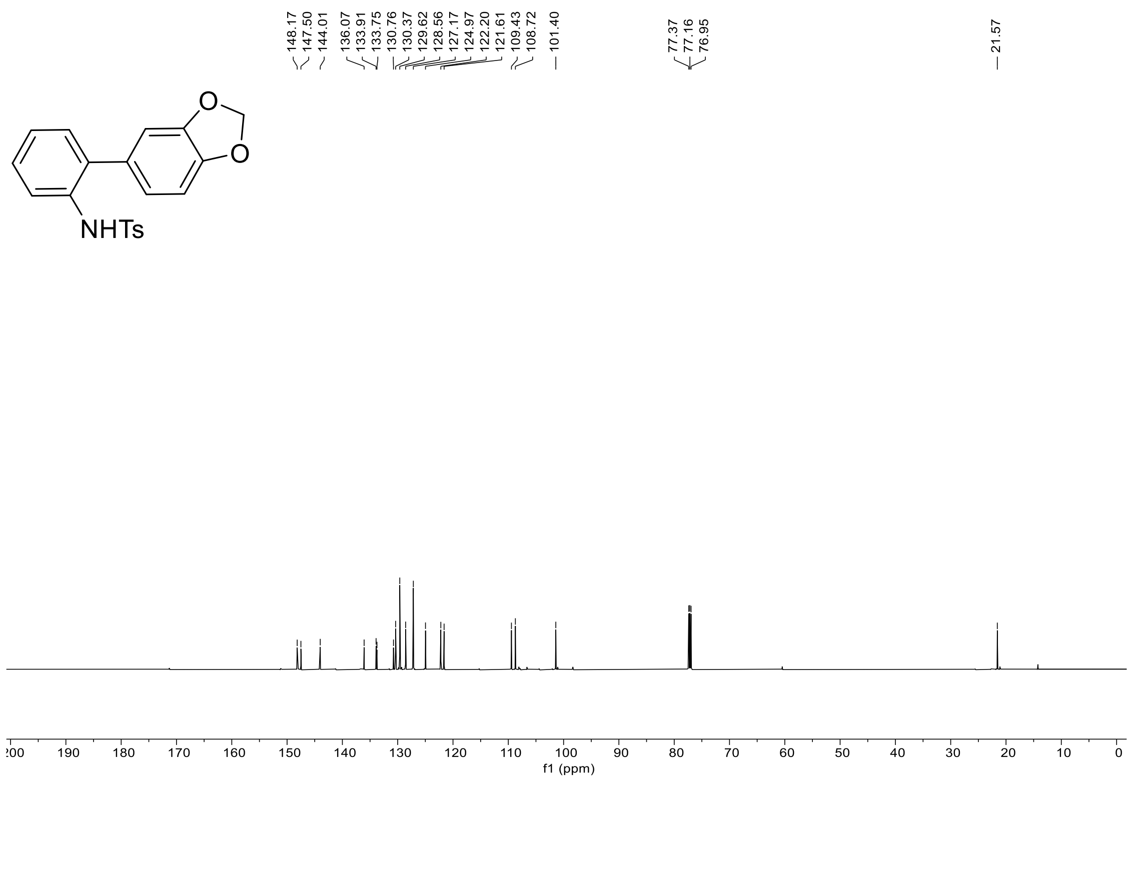
7.299
7.280
7.198
7.179
7.129
7.111
7.093
7.063
7.044
6.773
6.754
6.639
6.346
6.326
6.193
5.996
2.386
NHTs
1.00
1.91
1.01
2.03
1.02
1.04
0.97
1.01
0.97
0.96
1.92
2.98
f1 (ppm)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147.50
144.01
136.07
133.91
133.75
130.76
130.37
129.62
128.56
127.17
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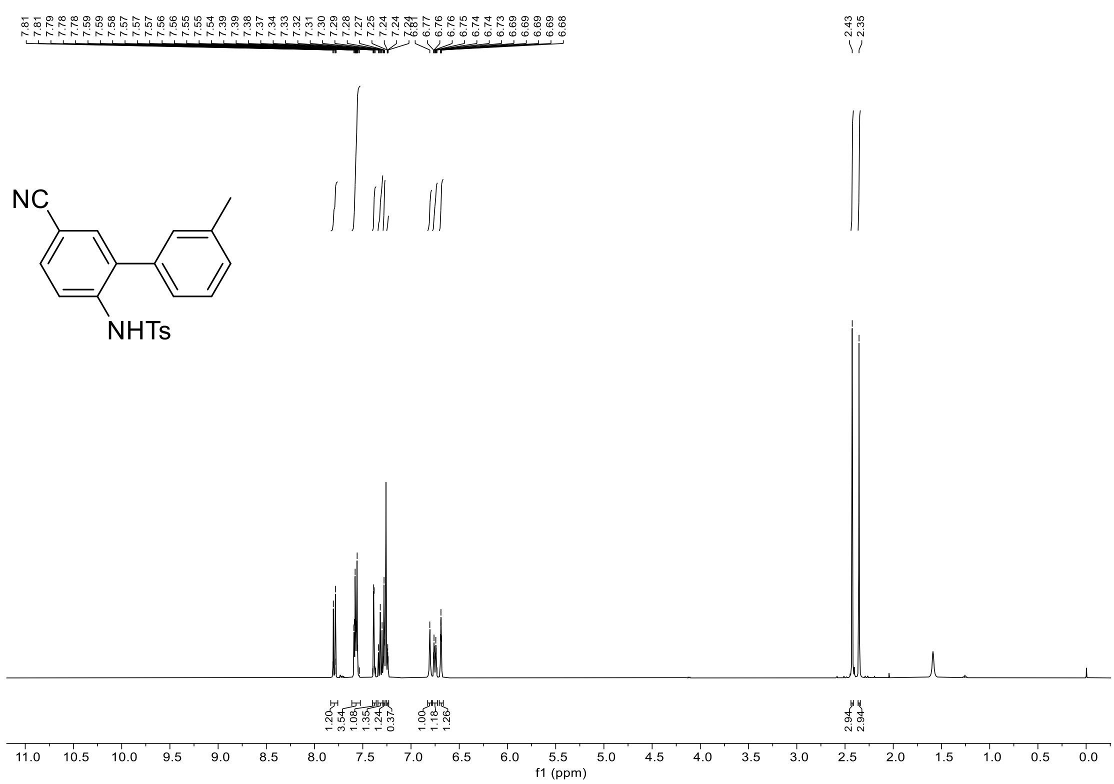
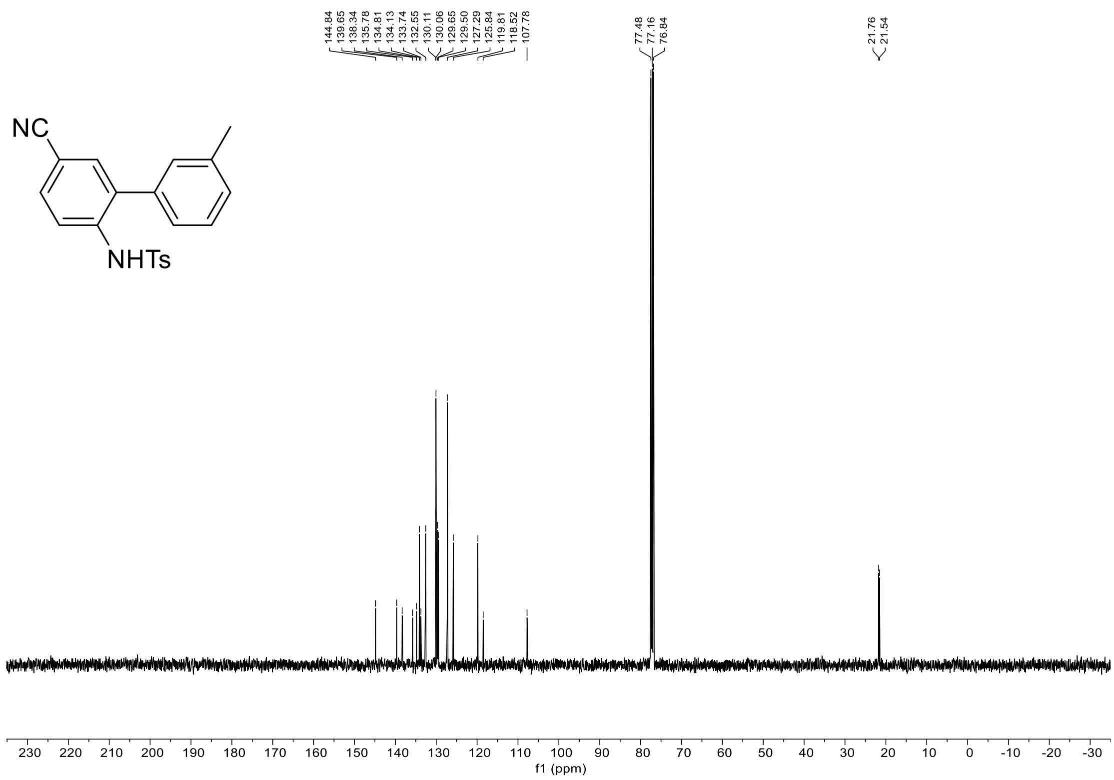
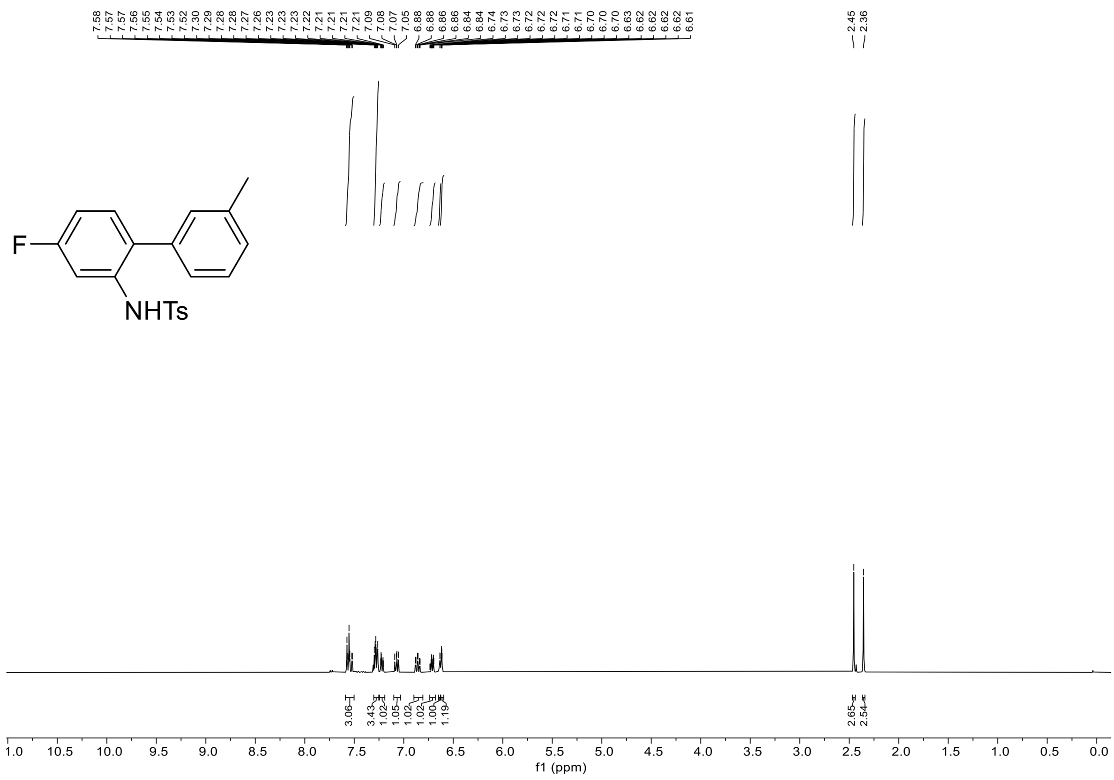
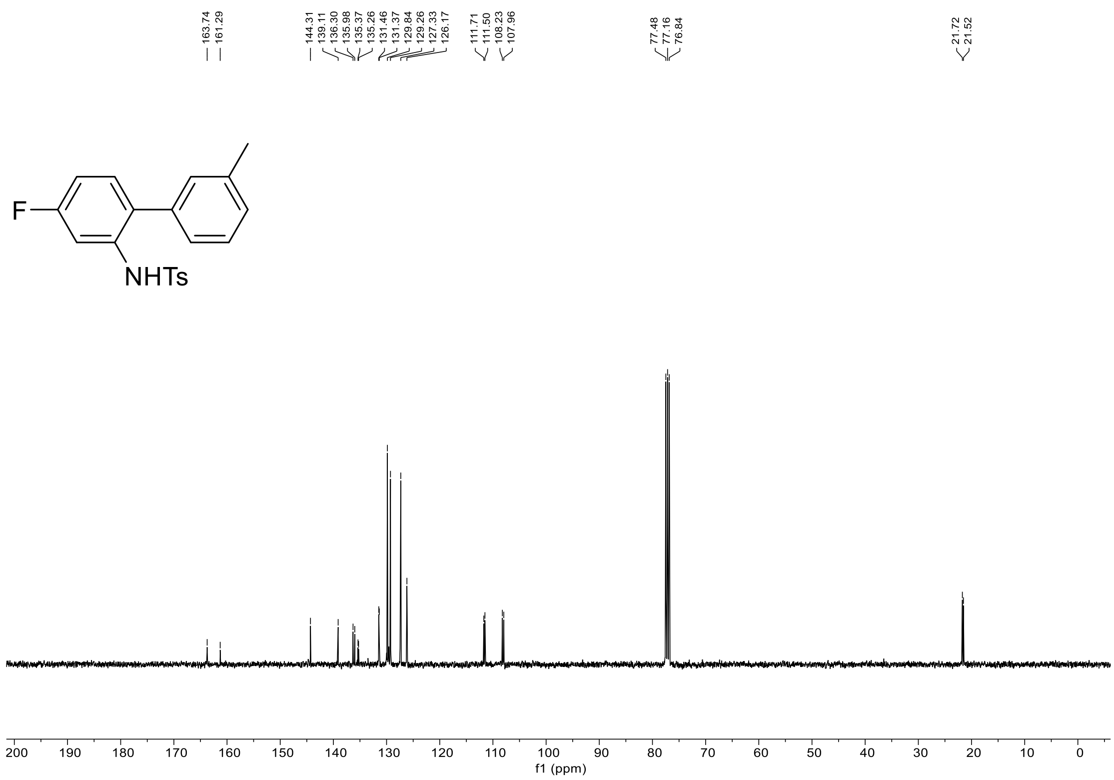
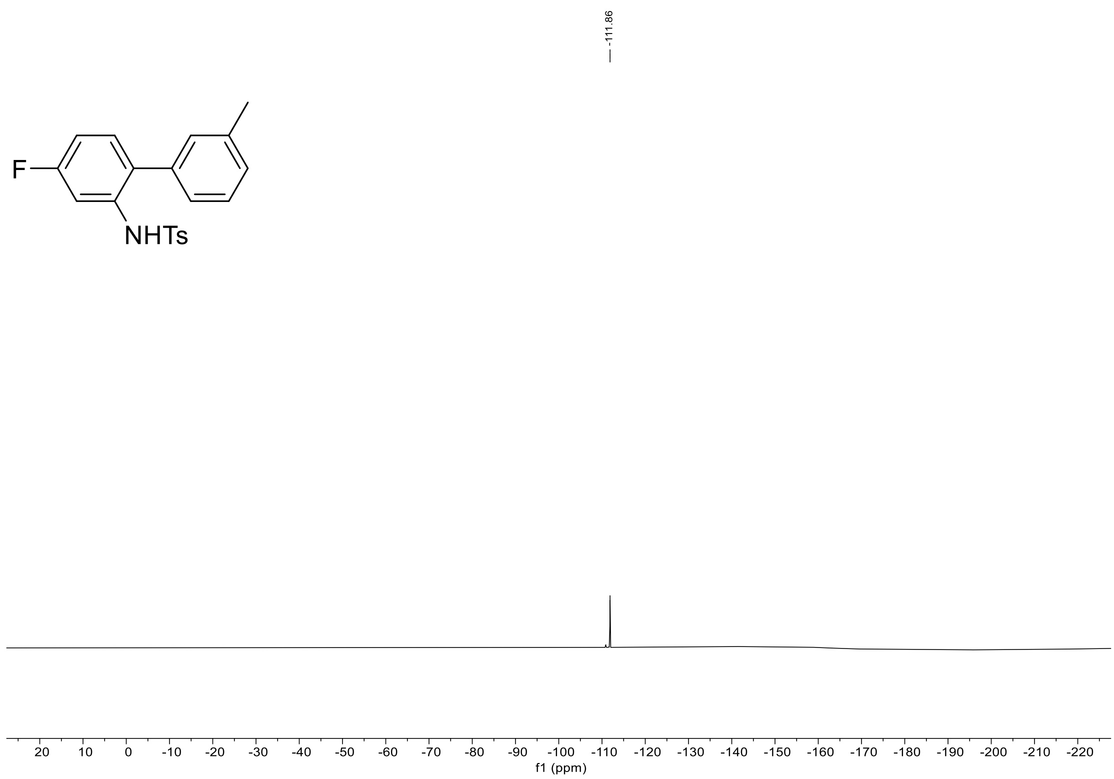
122.20
121.61
109.43
108.72
101.40
77.37
77.16
76.95
21.57
NHTs
f1 (ppm)

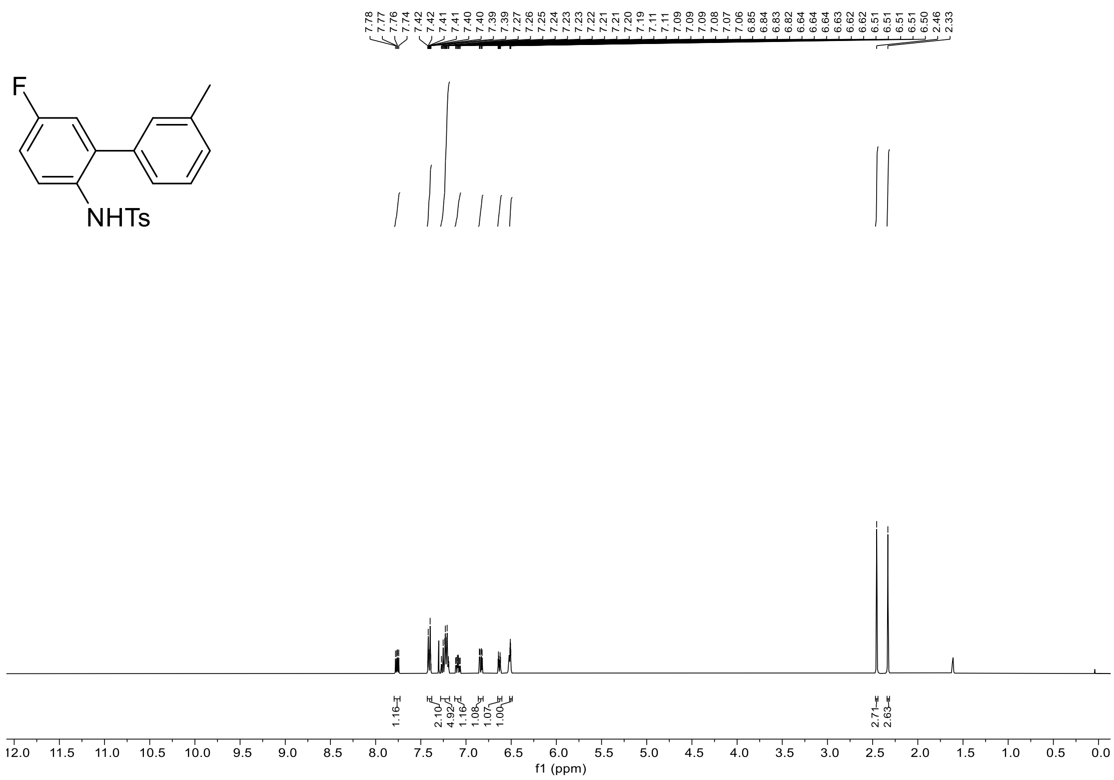


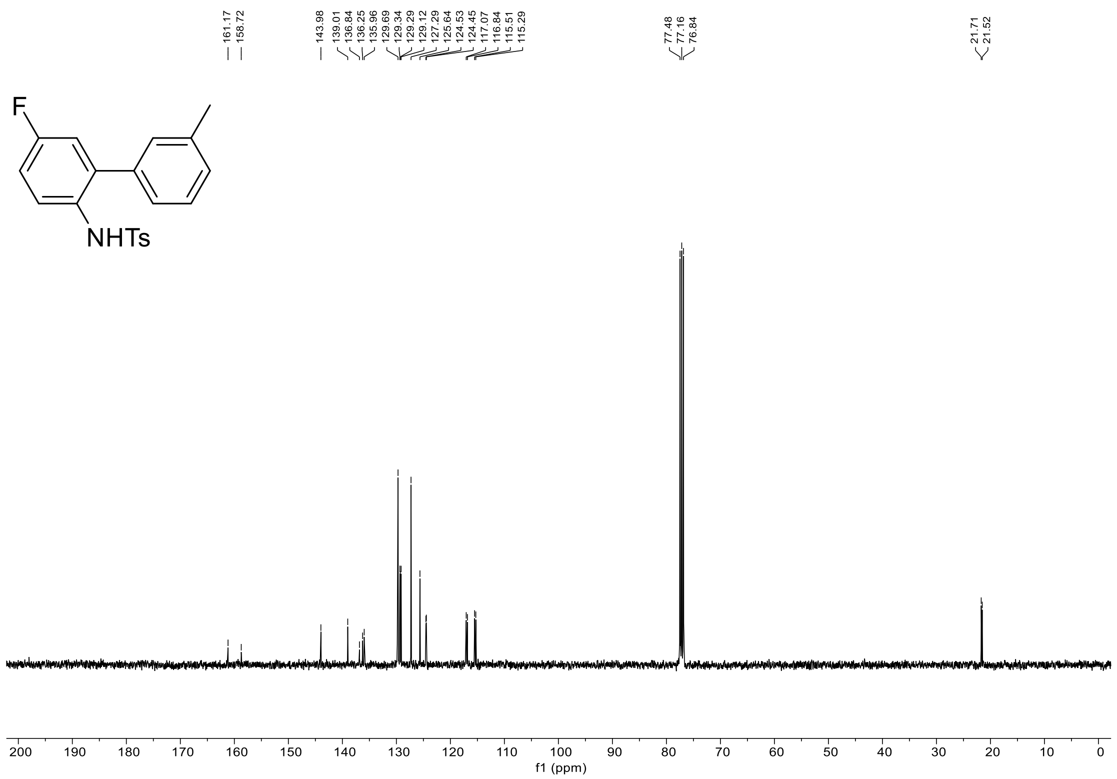







-111.86
F
NHTs
f1 (ppm)


F
NHTs
f1 (ppm)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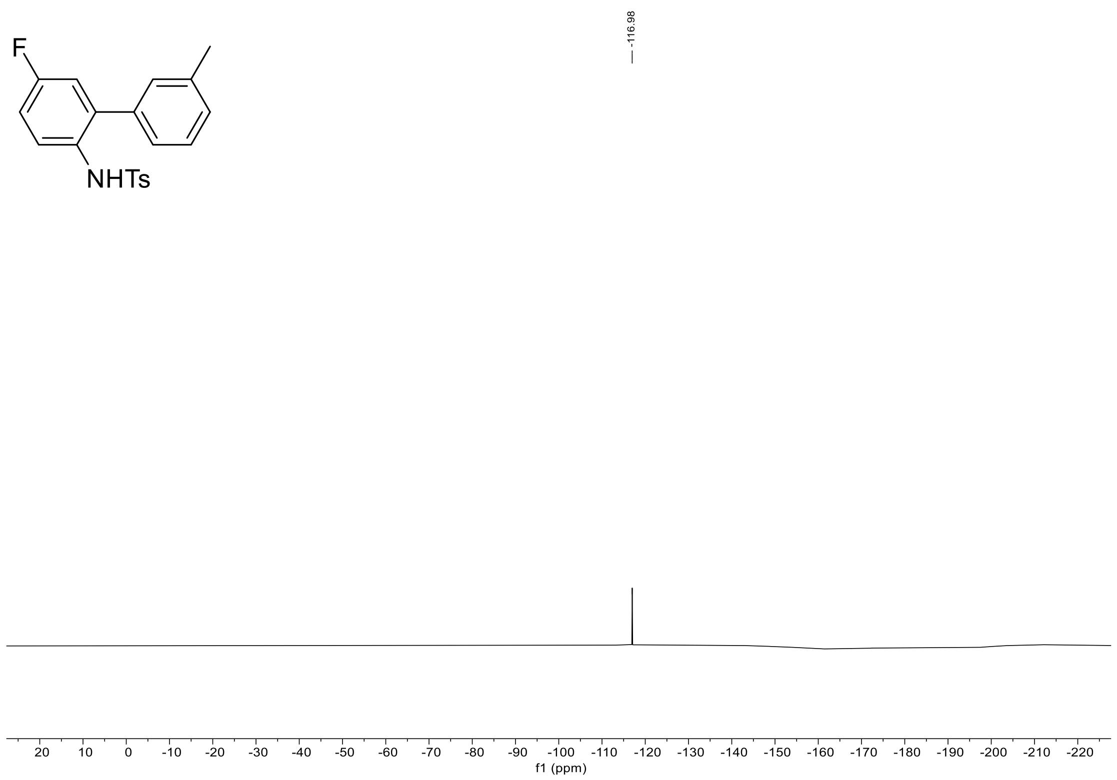
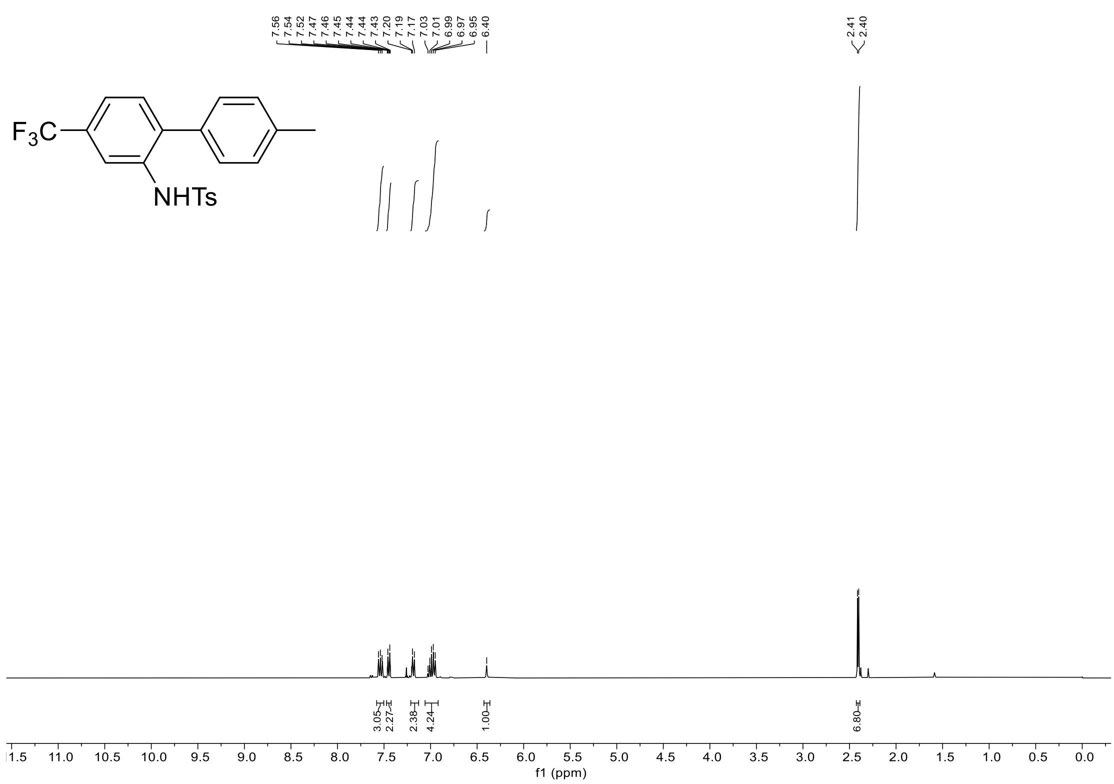
139.01
136.84
136.25
135.96
129.69
129.34
129.29
129.12
127.29
125.64
124.53
124.45
117.07
116.84
115.51
115.29
77.48
77.16
76.84
21.71
21.52
F
NHTs
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-116.98
F
NHTs
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)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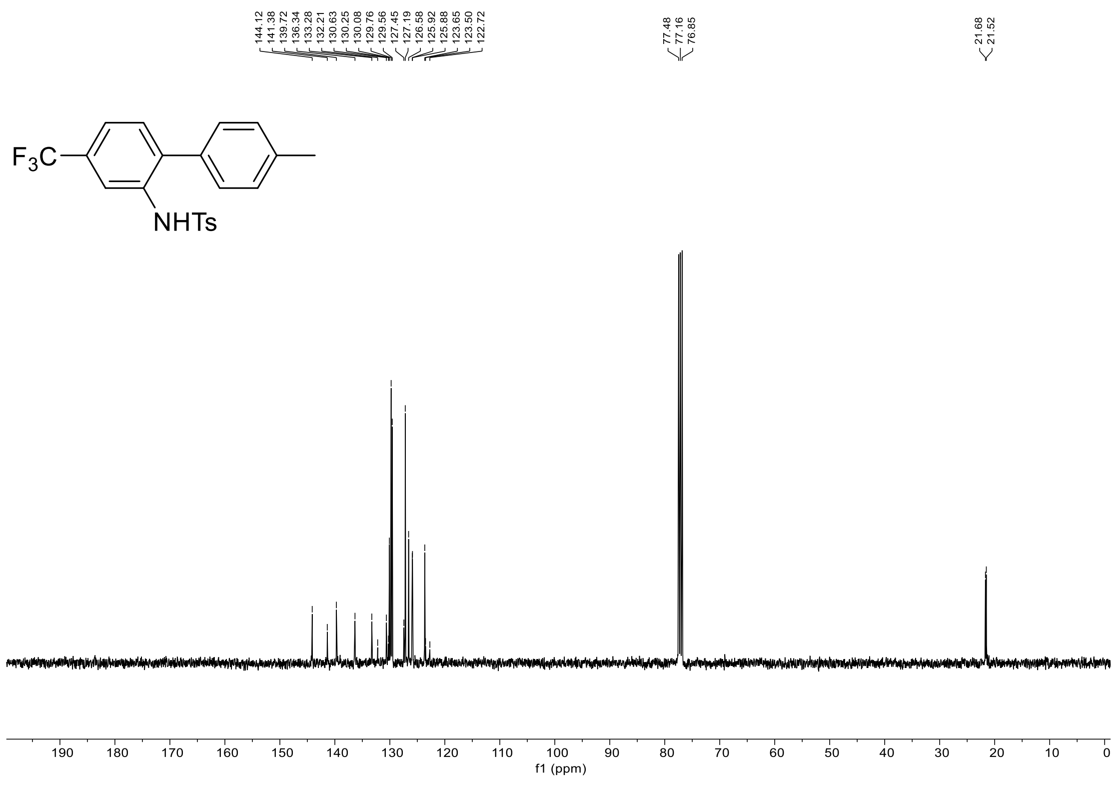
7.47
7.46
7.45
7.44
7.44
7.43
7.20
7.19
7.17
7.03
7.01
6.99
6.97
6.95
6.40
2.41
2.40
F3C
NHTs
3.05
2.27
2.38
4.24
1.00
6.80
f1 (ppm)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132.21
130.63
130.25
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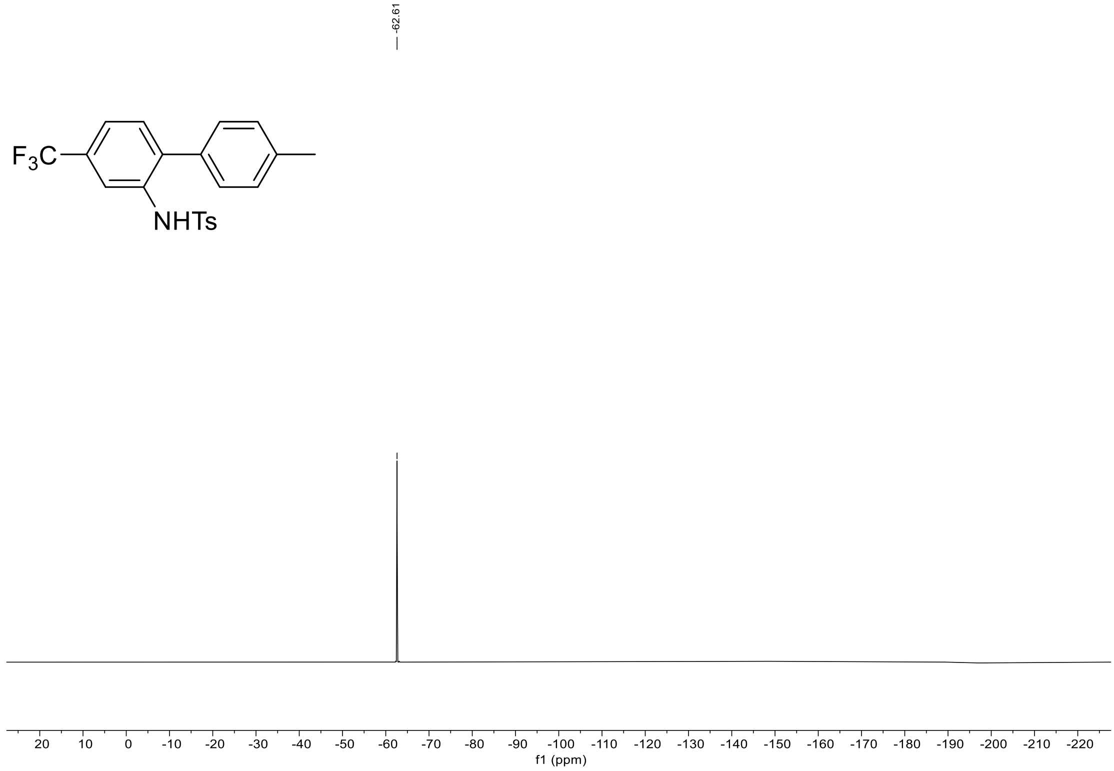
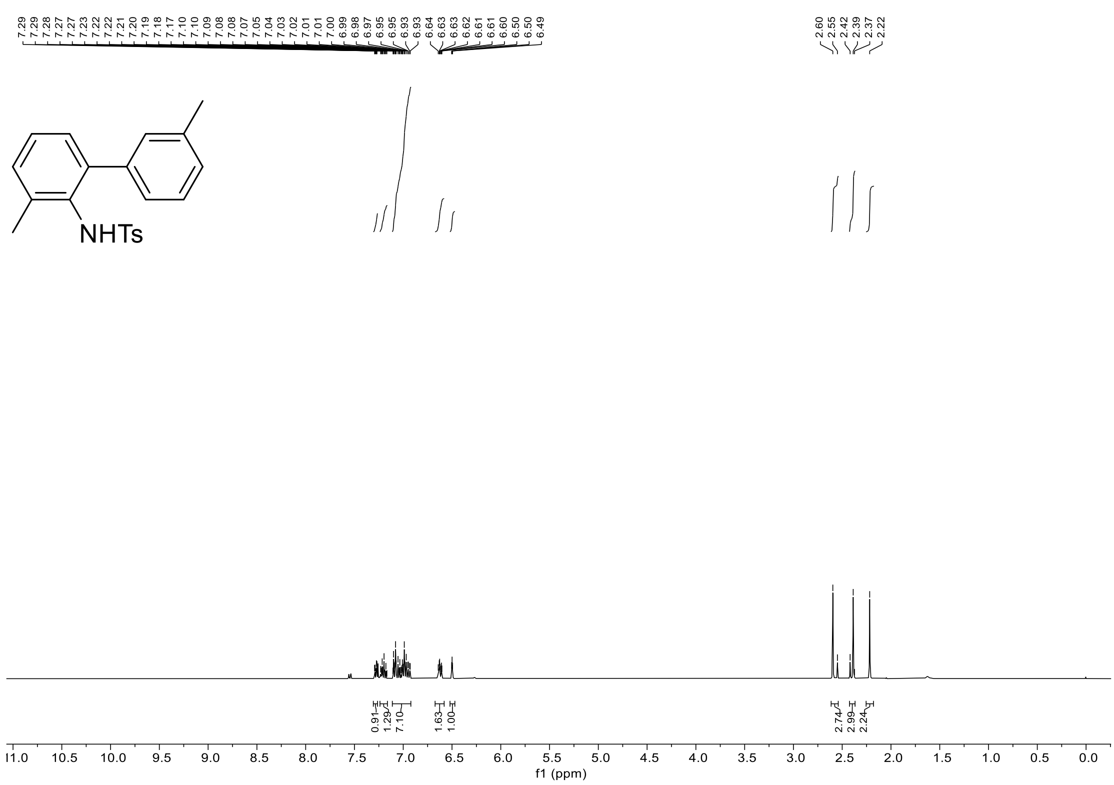
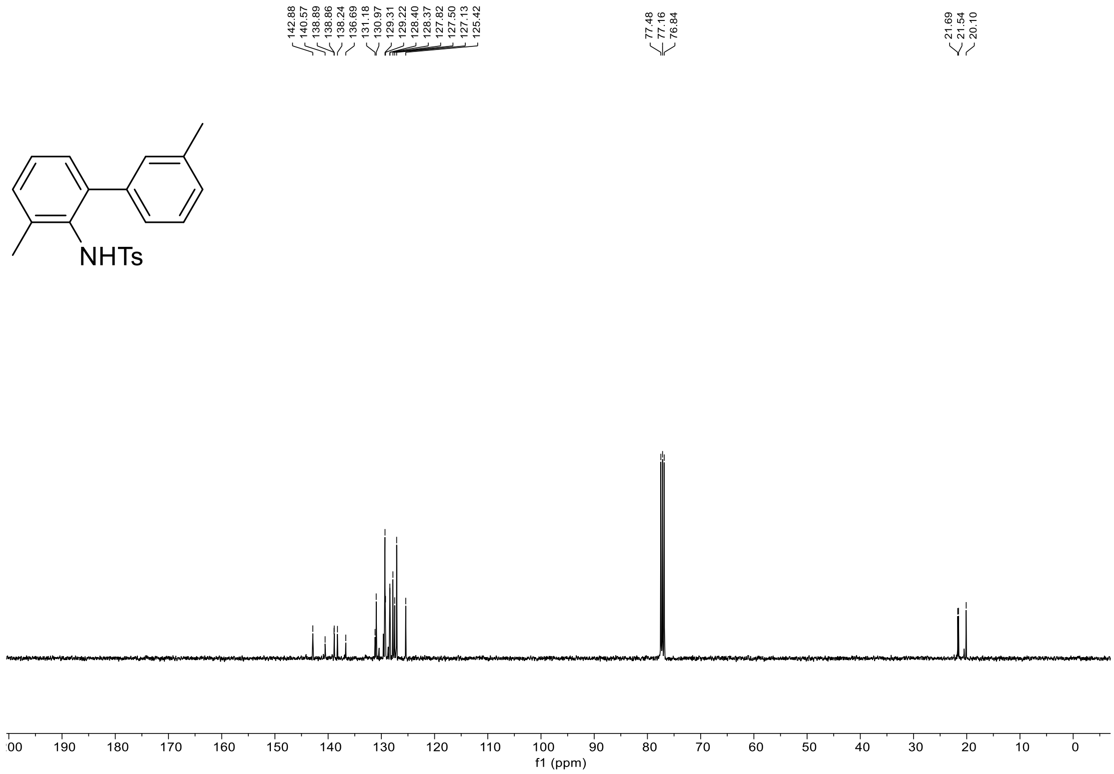
129.76
129.56
127.45
127.19
126.58
125.92
125.88
123.65
123.50
122.72
77.48
77.16
76.85
21.68
21.52
F3C
NHTs
f1 (ppm)

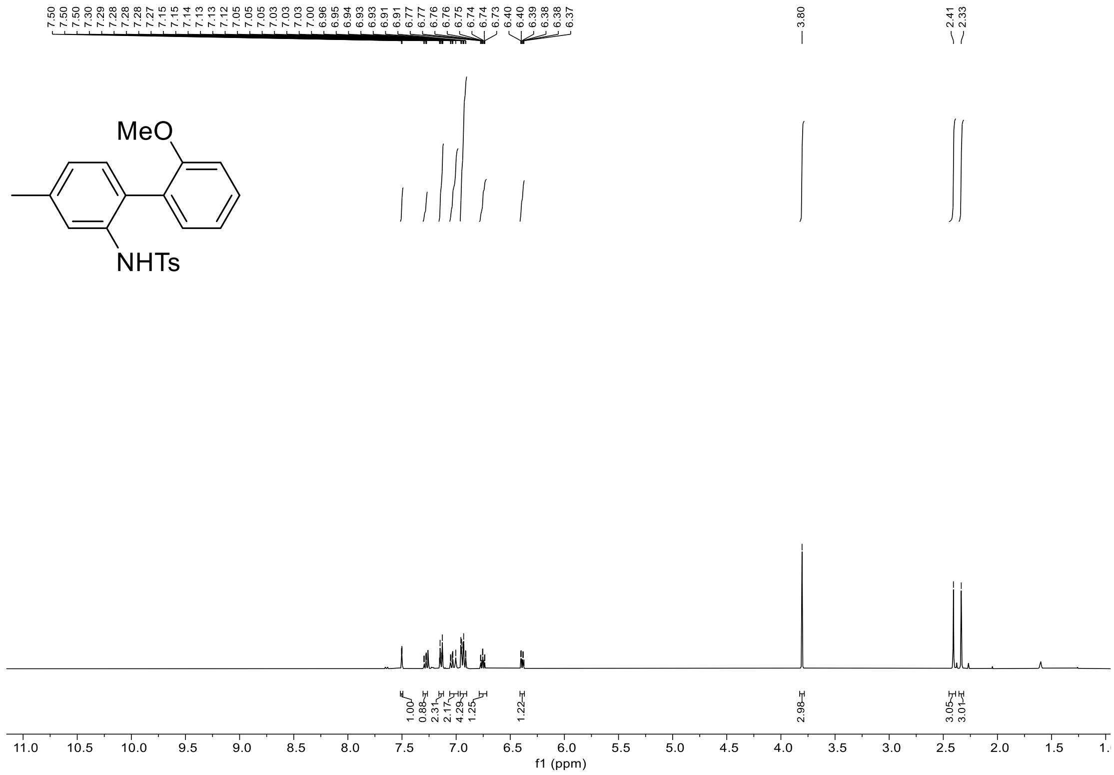


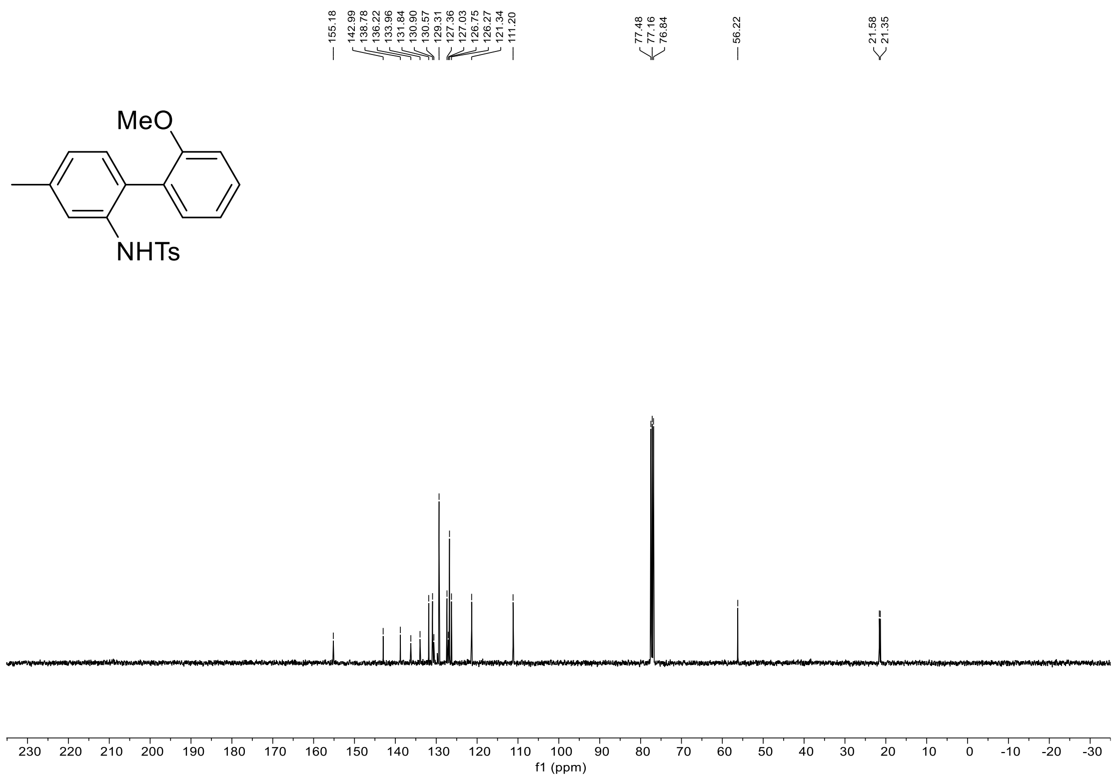
-62.61
F3C
NHTs
f1 (ppm)



NHTs
f1 (ppm)


142.88 140.57 138.89 138.86 138.24 136.69 131.18 130.97 129.31 129.22 128.40 128.37 127.82 127.50 127.13 125.42
77.48 77.16 76.84
21.69 21.54 20.10
NHTs
f1 (ppm)


3.80
2.41 2.33
MeO
NHTs
1.00 0.88 2.31 2.17 4.29 1.25 1.22 2.98 3.05 3.01
f1 (ppm)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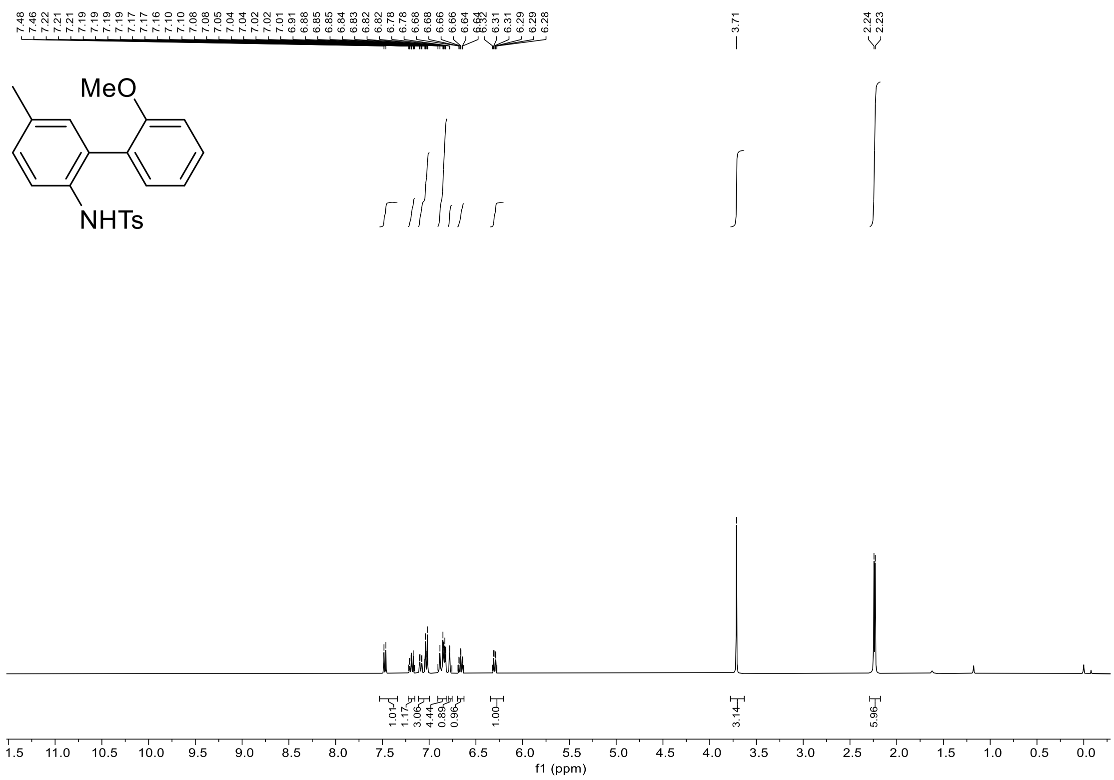
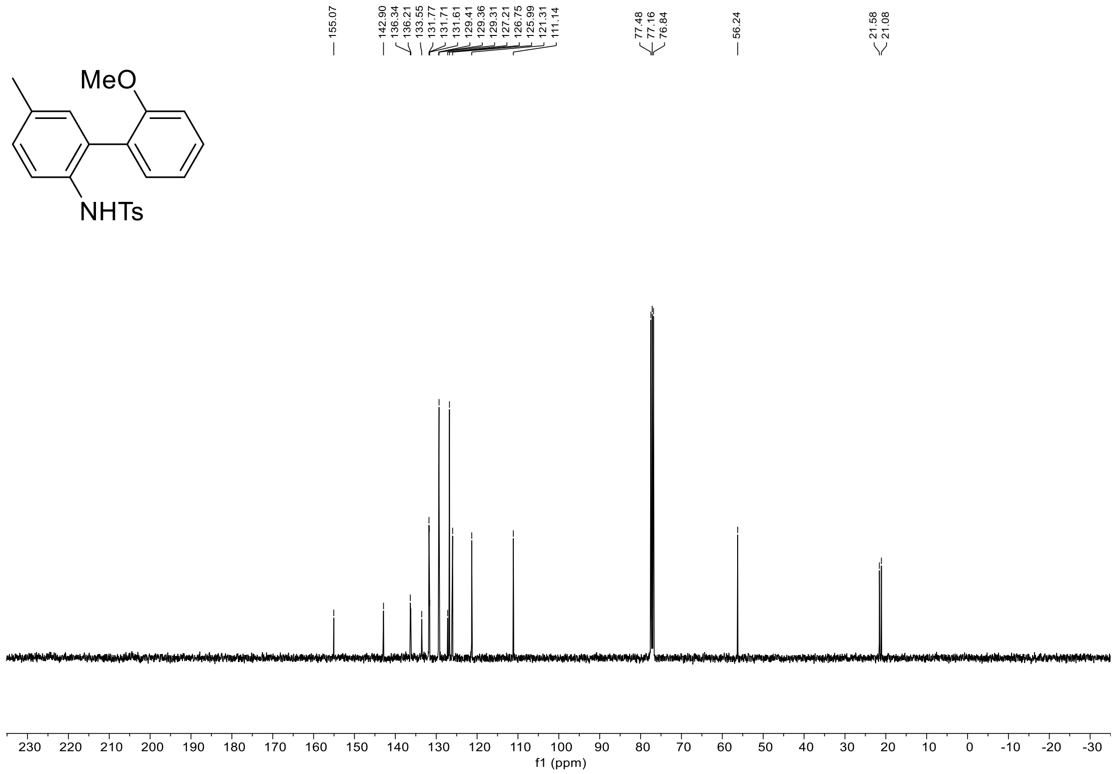
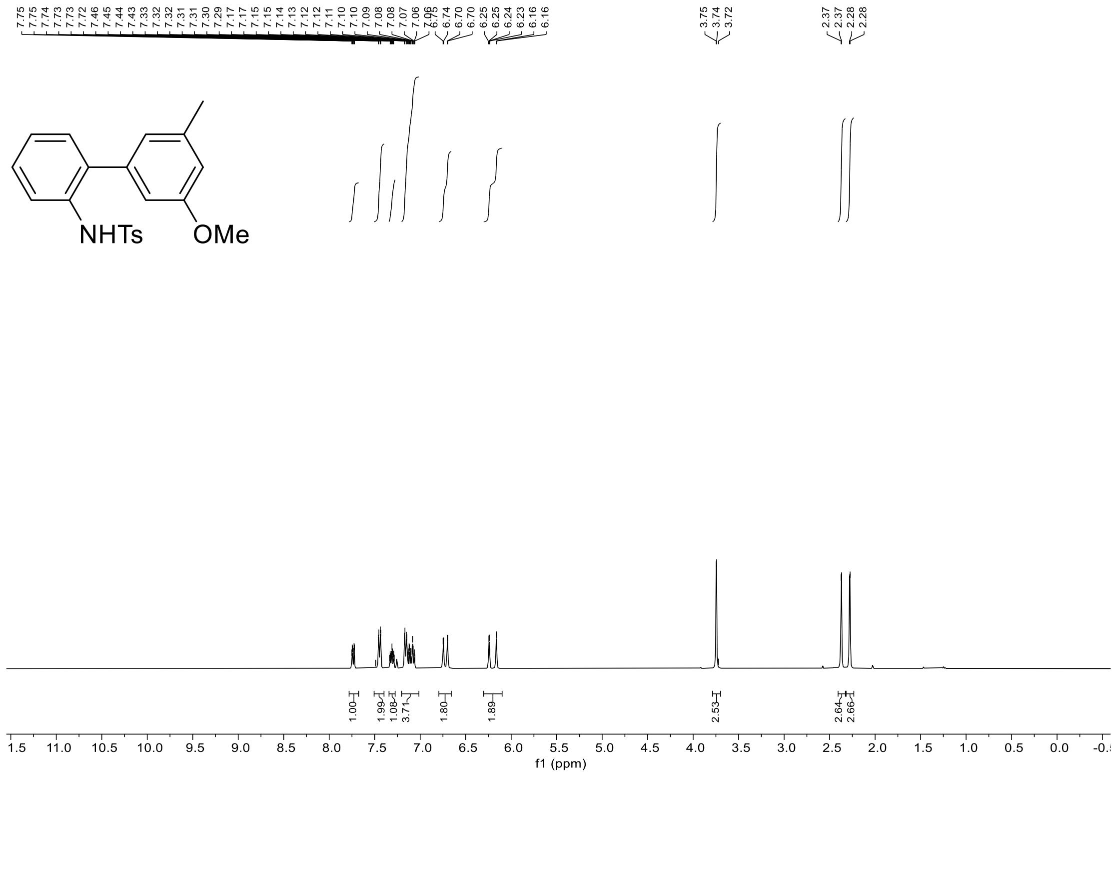
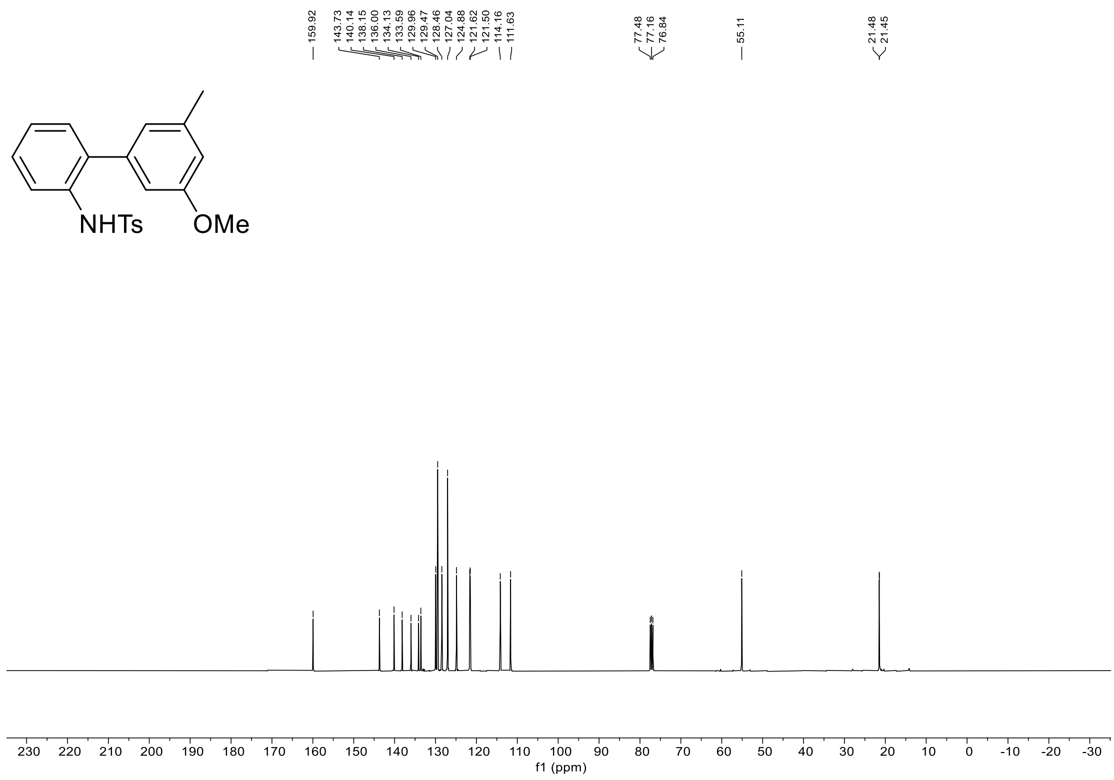
126.75
126.27
121.34
111.20
77.48
77.16
76.84
56.22
21.58
21.35
MeO
NHTs
f1 (ppm)


3.71
2.24
2.23
MeO
NHTs
1.01
1.17
3.06
4.44
0.89
0.96
1.00
3.14
5.96
f1 (ppm)


155.07
142.90
136.34
136.21
133.55
131.77
131.71
131.61
129.41
129.36
129.31
127.21
126.75
125.99
121.31
111.14
77.48
77.16
76.84
56.24
21.58
21.08
MeO
NHTs
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)


7.75
7.75
7.74
7.73
7.73
7.72
7.46
7.45
7.44
7.43
7.33
7.32
7.32
7.31
7.30
7.29
7.17
7.17
7.15
7.15
7.14
7.13
7.12
7.12
7.11
7.10
7.09
7.08
7.08
7.07
7.06
6.74
6.70
6.70
6.25
6.25
6.24
6.23
6.16
6.16
3.75
3.74
3.72
2.37
2.37
2.28
2.28
NHTs
OMe
1.00
1.99
1.08
3.71
1.80
1.89
2.53
2.64
2.66
f1 (ppm)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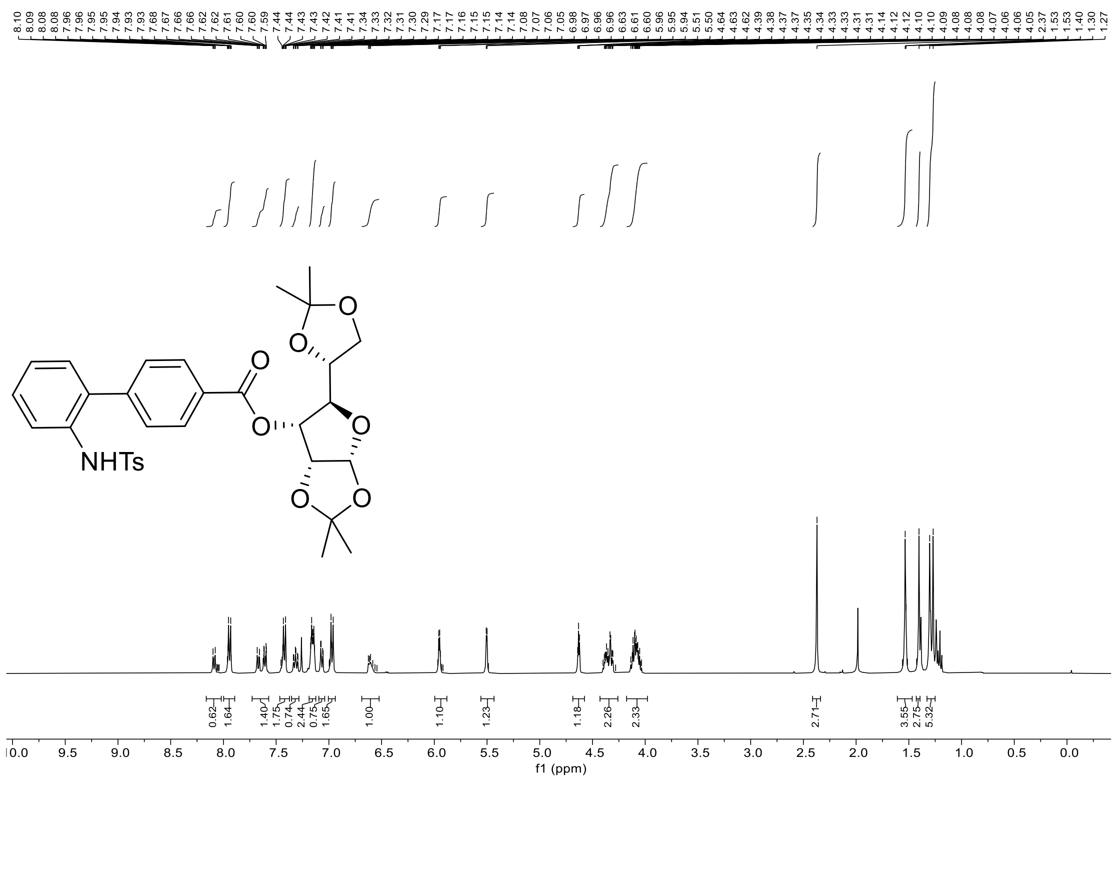
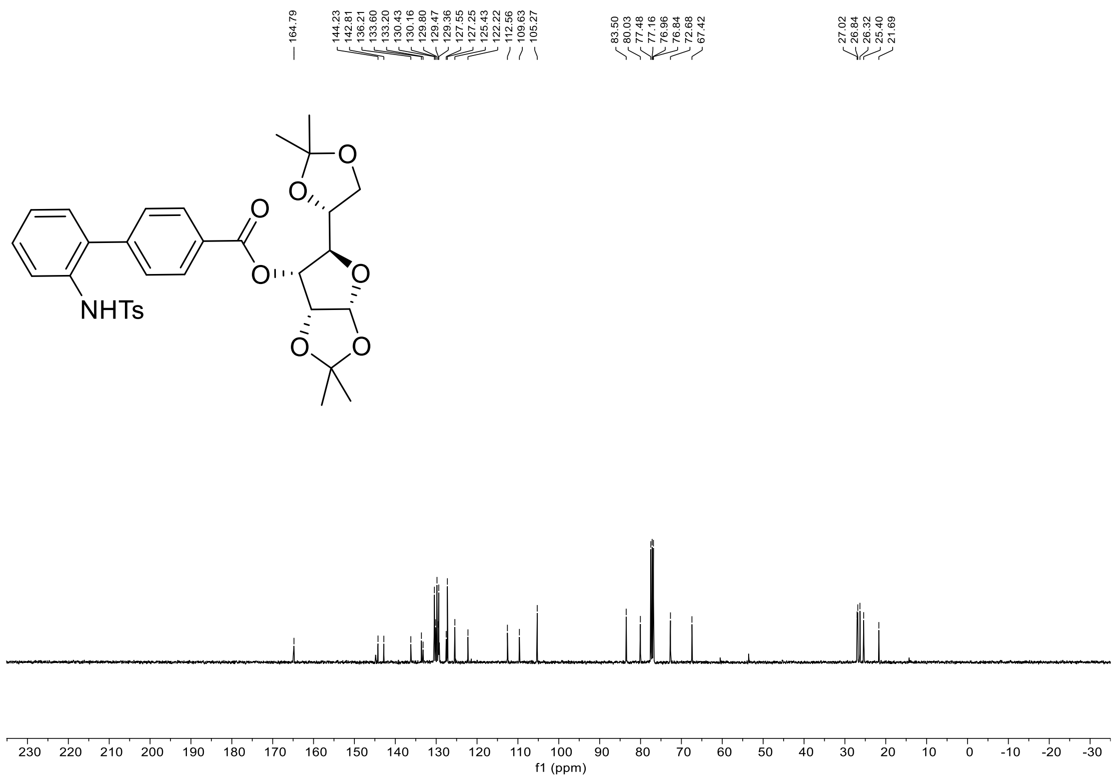
143.73
140.14
138.15
136.00
134.13
133.59
129.96
129.47
128.46
127.04
124.88
121.62
121.50
114.16
111.63
77.48
77.16
76.84
55.11
21.48
21.45
NHTs
OMe
f1 (ppm)


NHTs
f1 (ppm)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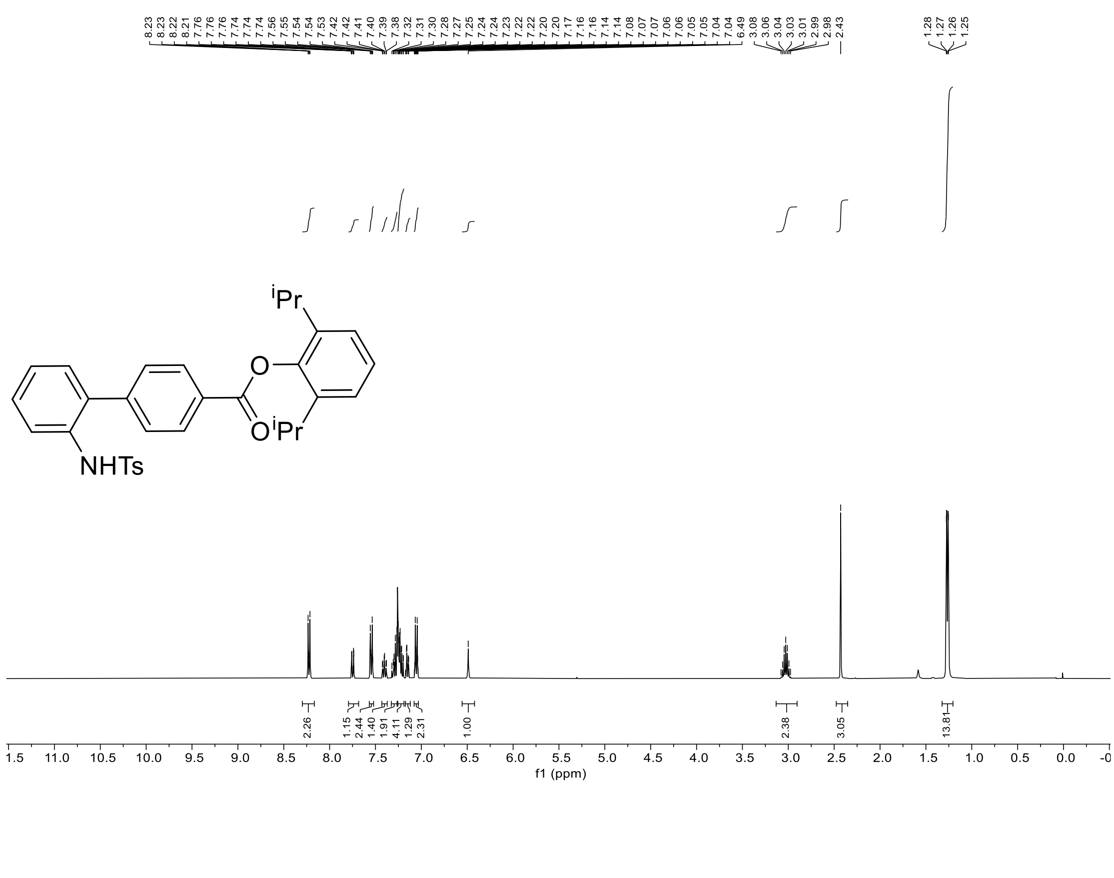
144.23
142.81
136.21
133.60
133.20
130.43
130.16
129.80
129.47
129.36
127.55
127.25
125.43
122.22
112.56
109.63
105.27
83.50
80.03
77.48
77.16
76.96
76.84
72.68
67.42
27.02
26.84
26.32
25.40
21.69
O
O
O
O
O
O
O
NHTs
f1 (ppm)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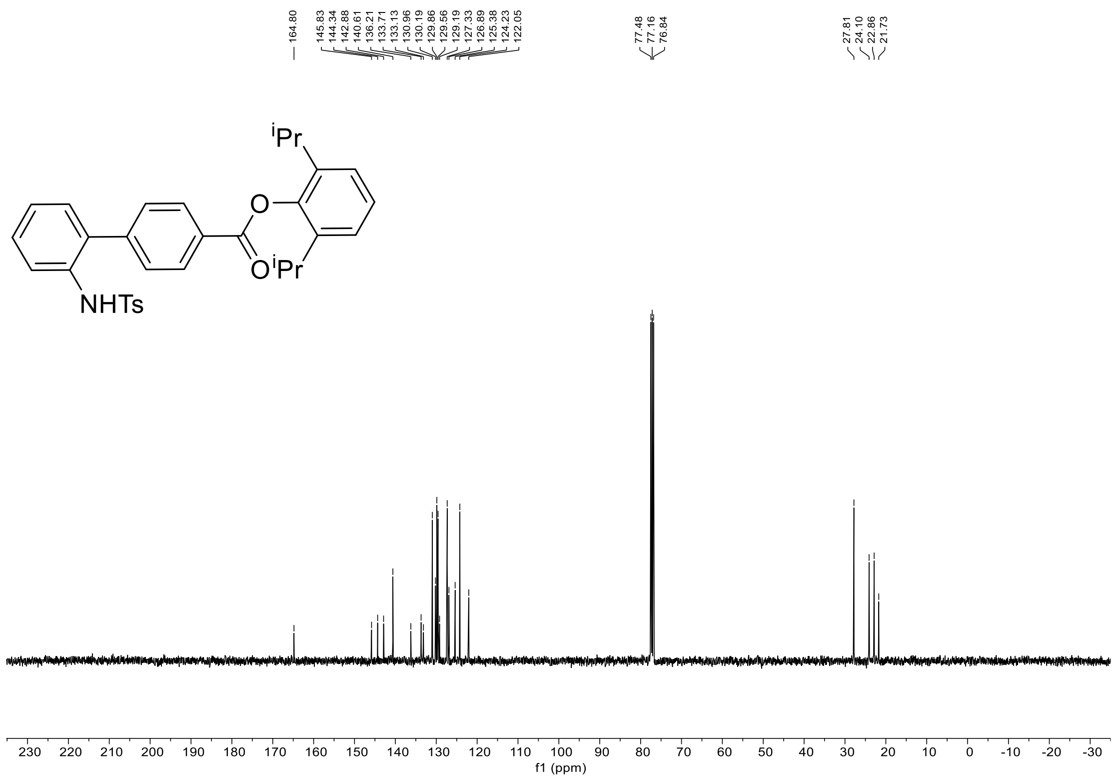
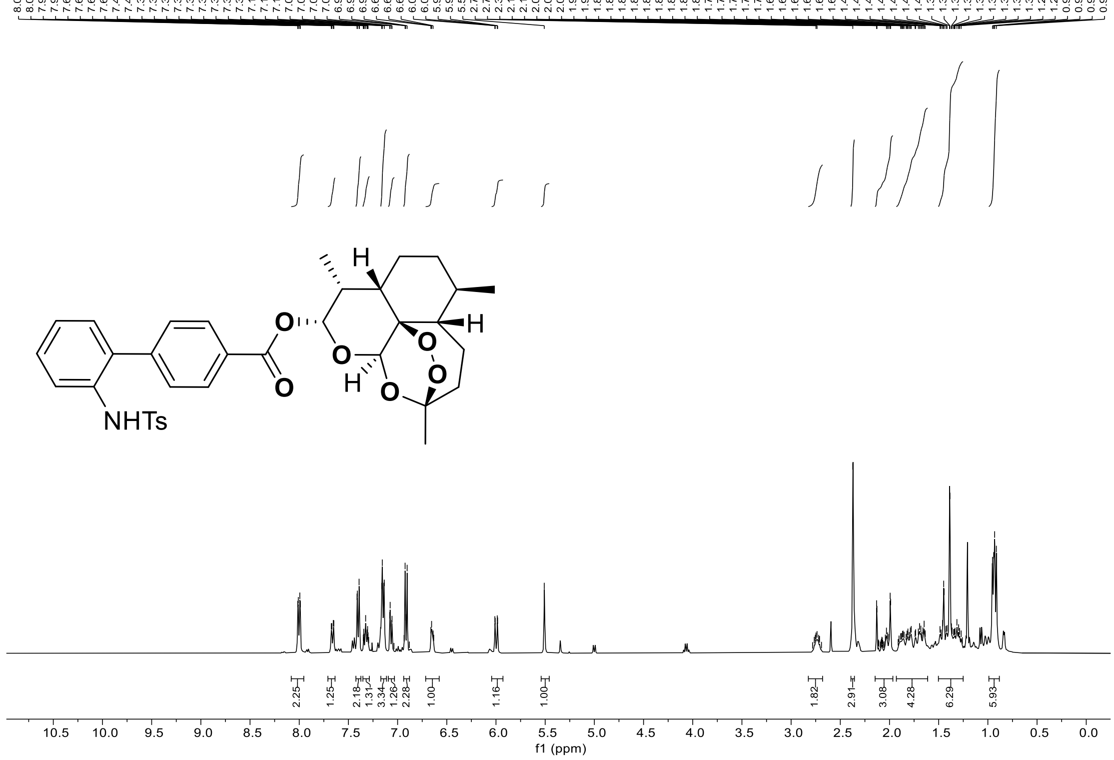
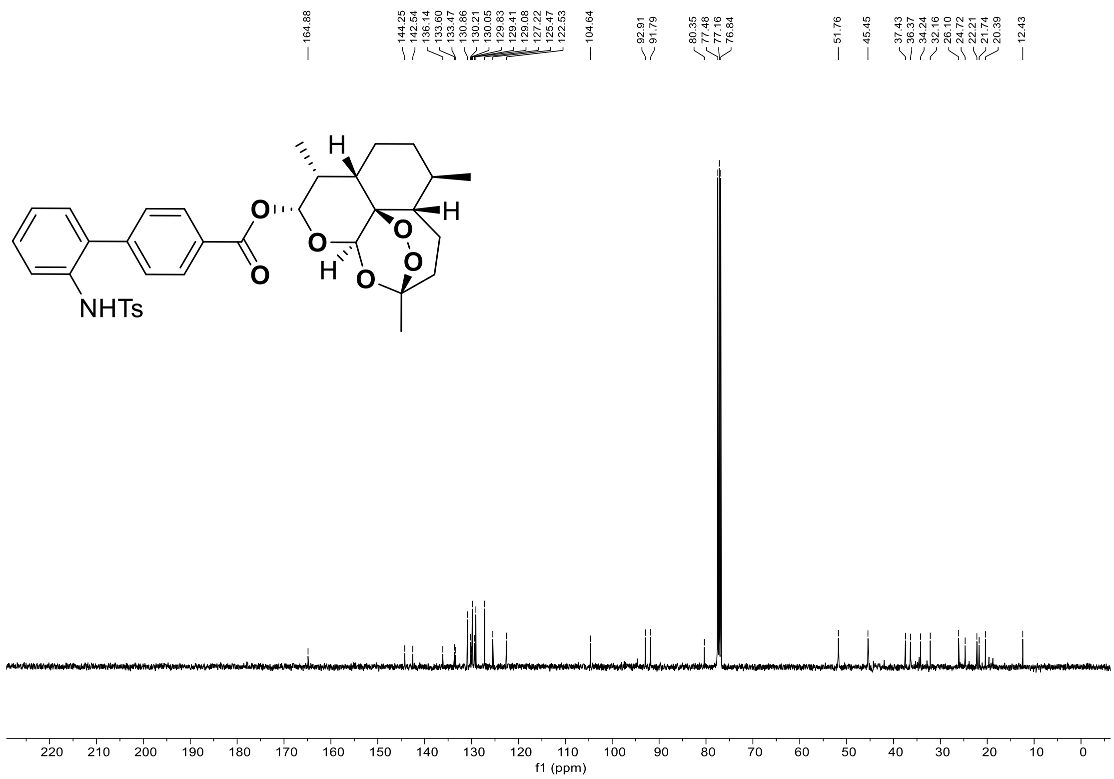
8.23
8.22
8.21
7.76
7.76
7.74
7.74
7.74
7.56
7.55
7.54
7.54
7.53
7.42
7.42
7.41
7.40
7.39
7.38
7.32
7.31
7.30
7.28
7.27
7.25
7.24
7.24
7.23
7.22
7.22
7.20
7.20
7.17
7.16
7.16
7.14
7.08
7.07
7.07
7.06
7.06
7.05
7.05
7.04
7.04
6.49
3.08
3.06
3.04
3.03
3.01
2.99
2.98
2.43
1.28
1.27
1.26
1.25
iPr
O
O
iPr
NHTs
2.26
1.15
2.44
1.40
1.91
4.11
1.29
2.31
1.00
2.38
3.05
13.81
f1 (ppm)



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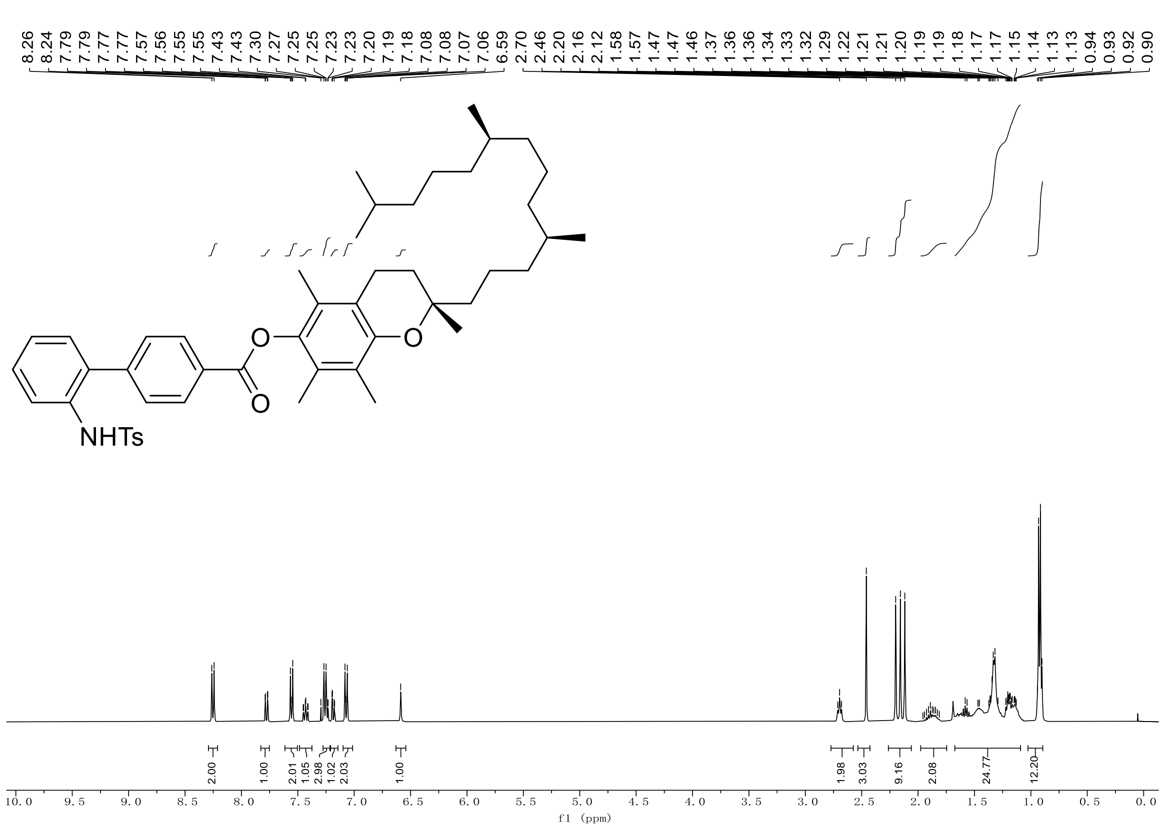
144.25
142.54
136.14
133.60
133.47
130.86
130.21
130.05
129.83
129.41
129.08
127.22
125.47
122.53
104.64
92.91
91.79
80.35
77.48
77.16
76.84
51.76
45.45
37.43
36.37
34.24
32.16
26.10
24.72
22.21
21.74
20.39
12.43
NHTs
O
H
f1 (ppm)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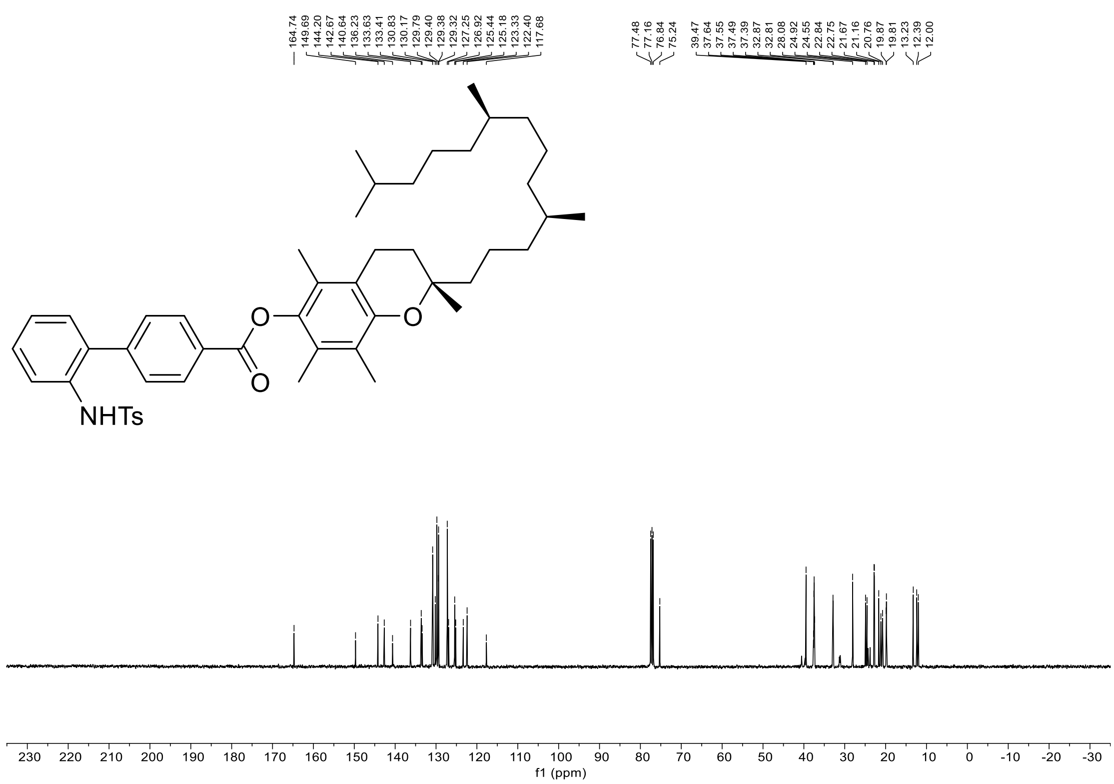
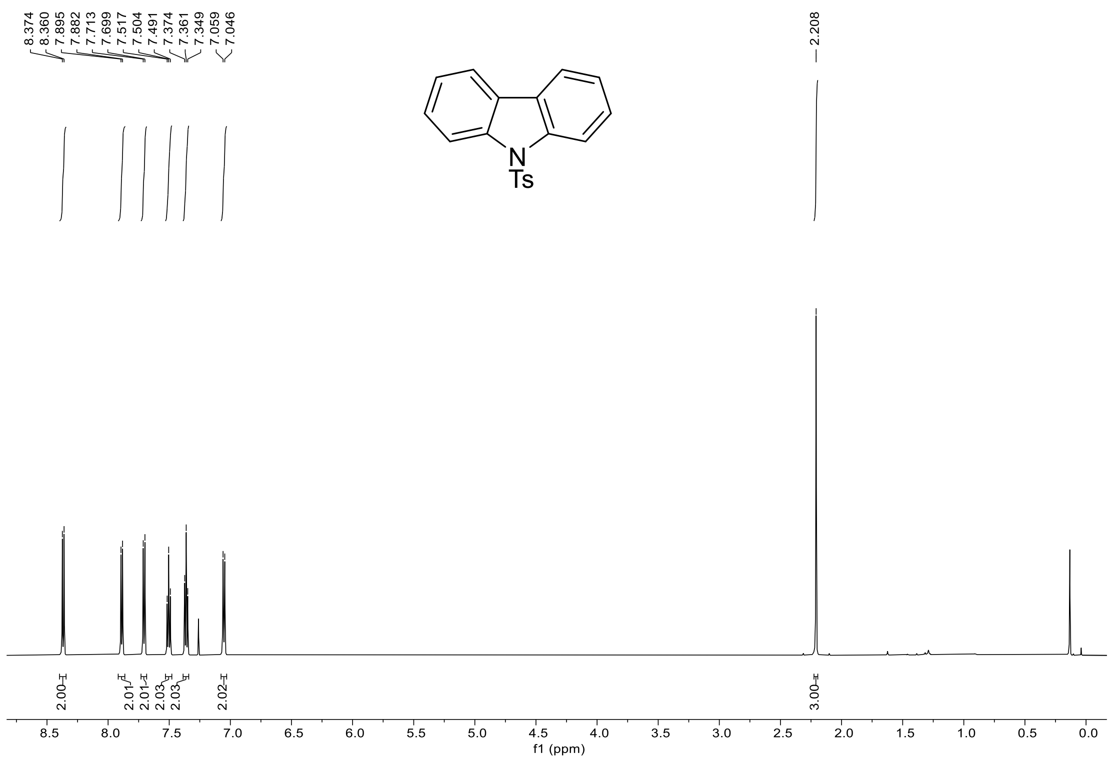
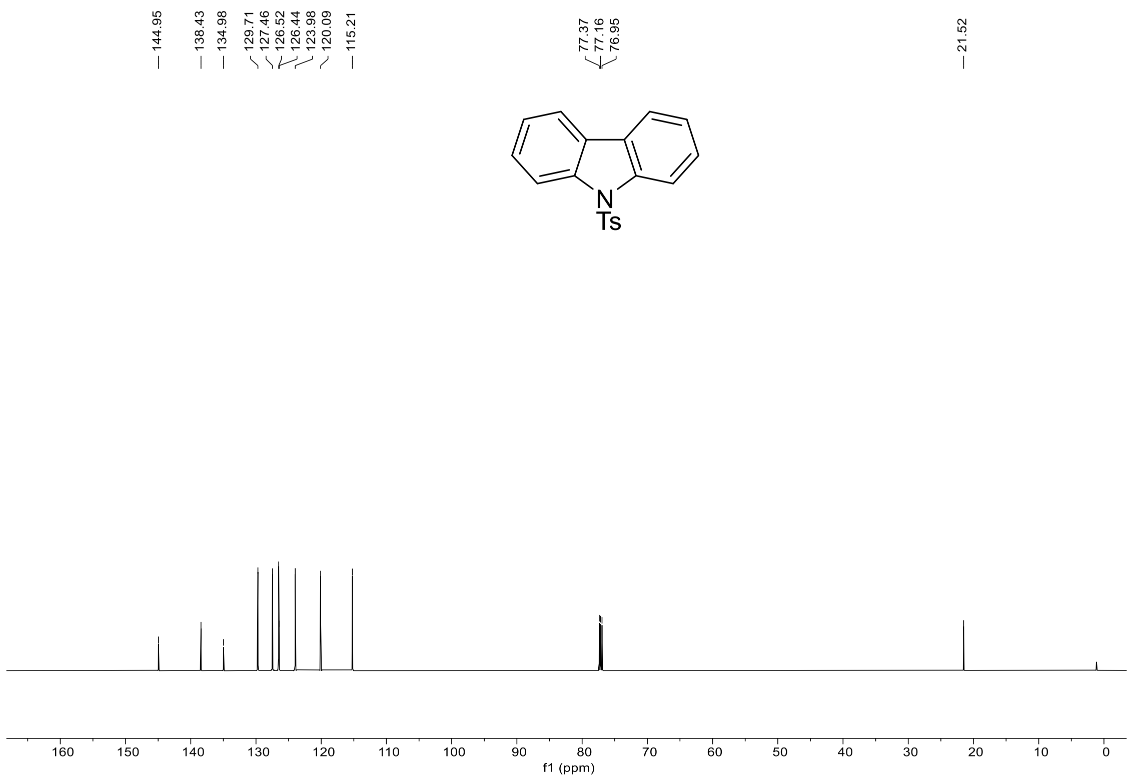
7.77
7.57
7.56
7.55
7.55
7.43
7.43
7.30
7.27
7.25
7.25
7.23
7.23
7.20
7.19
7.18
7.08
7.07
7.06
6.59
2.70
2.46
2.20
2.16
2.12
1.58
1.57
1.47
1.47
1.46
1.37
1.36
1.36
1.34
1.33
1.32
1.29
1.22
1.21
1.21
1.20
1.19
1.19
1.18
1.17
1.17
1.15
1.14
1.13
1.13
0.94
0.93
0.92
0.90
NHTs
O
2.00
1.00
2.01
1.05
2.98
1.02
2.03
1.00
1.98
3.03
9.16
2.08
24.77
12.20
f1 (ppm)



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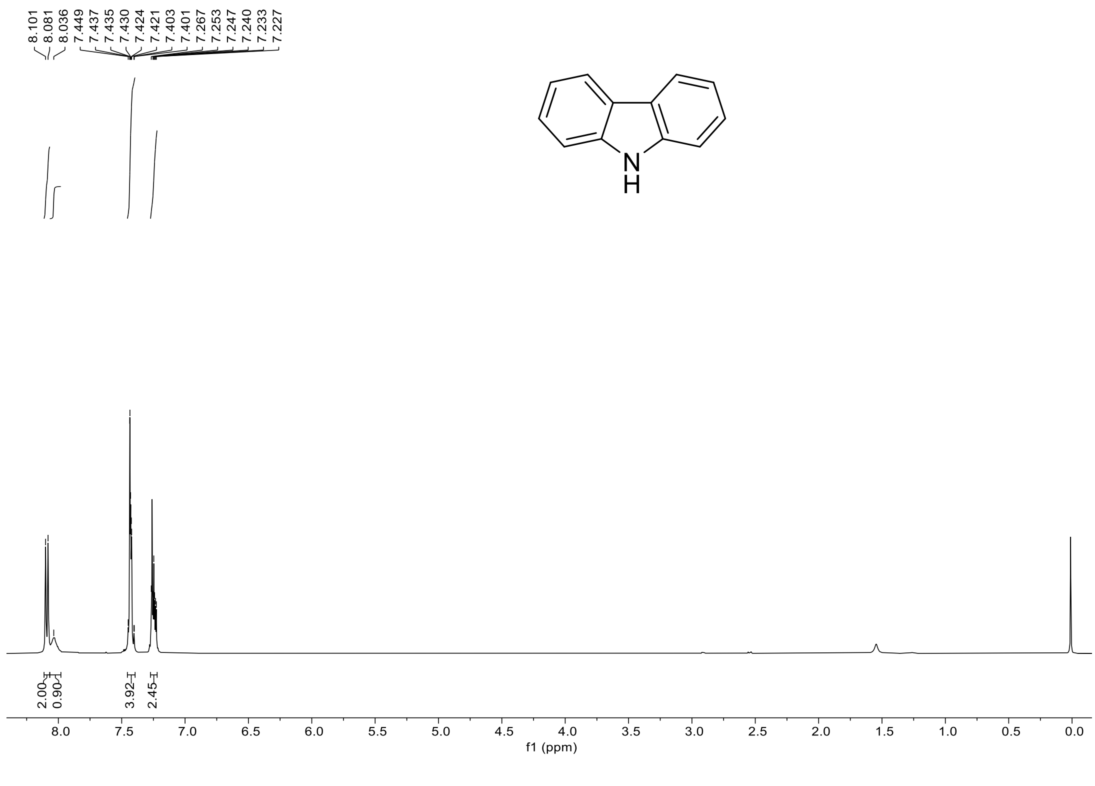
134.98
129.71
127.46
126.52
126.44
123.98
120.09
115.21
77.37
77.16
76.95
21.52
N
Ts
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.081
8.036
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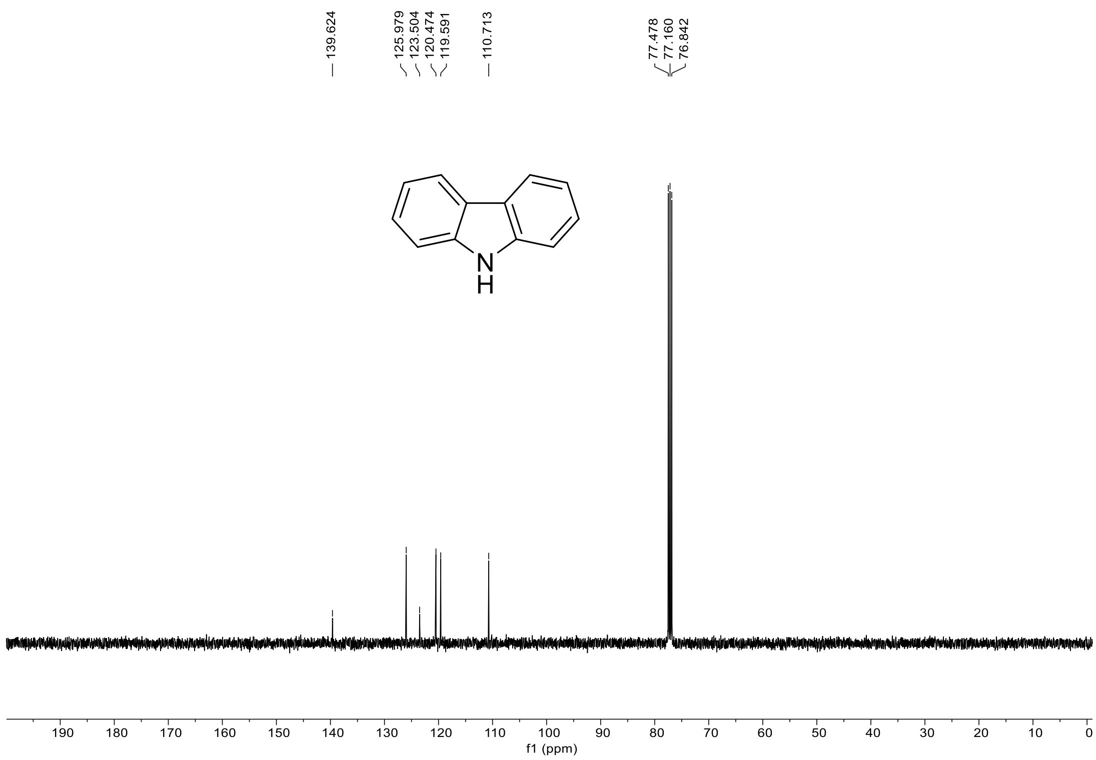
7.437
7.435
7.430
7.424
7.421
7.403
7.401
7.267
7.253
7.247
7.240
7.233
7.227
N
H
2.00
0.90
3.92
2.45
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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125.979
123.504
120.474
119.591
110.713
77.478
77.160
76.842
N
H
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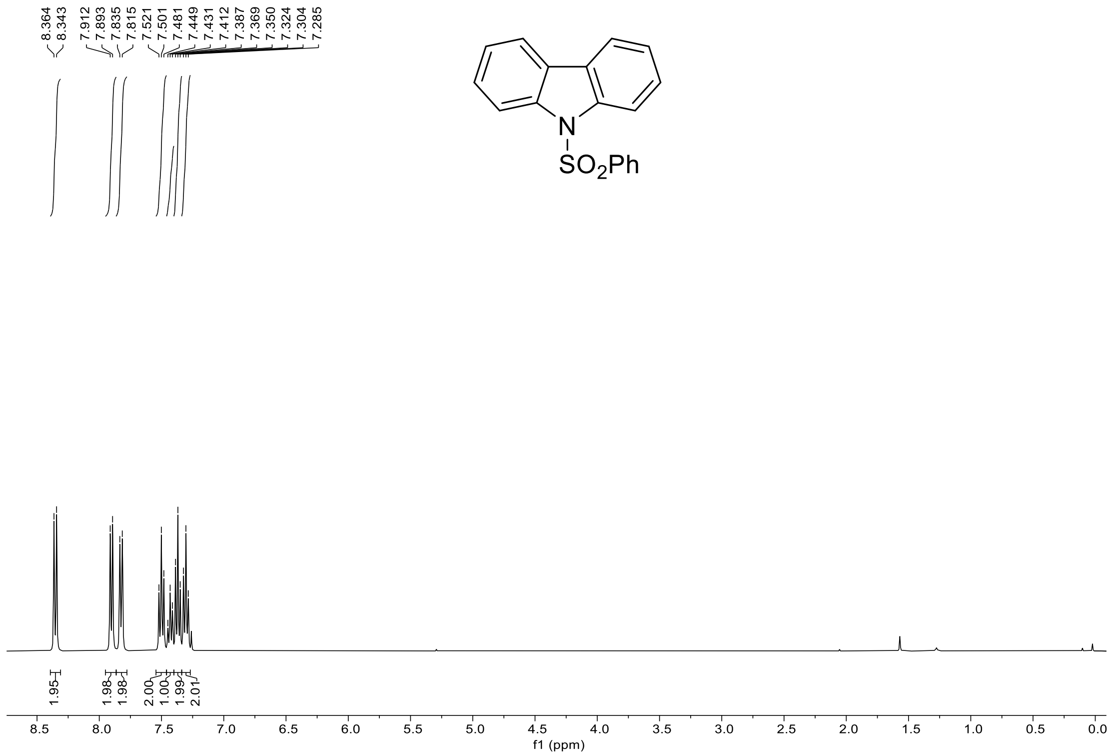
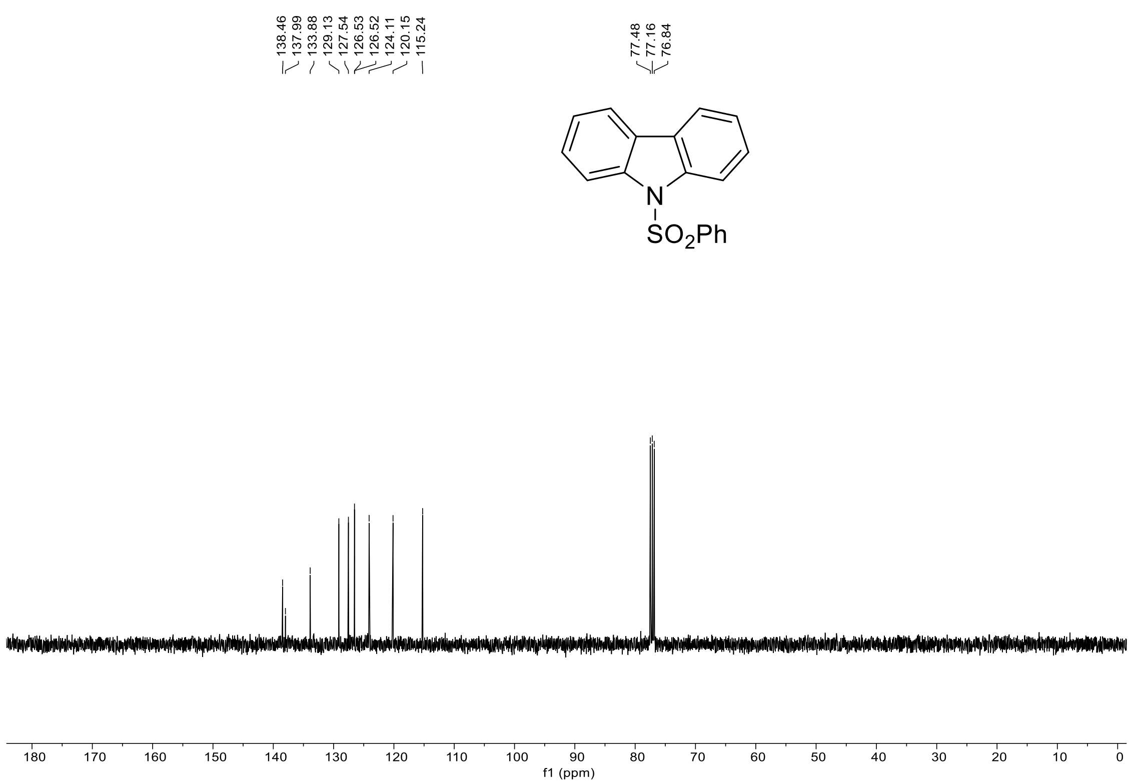
f1 (ppm)


8.364
8.343
7.912
7.893
7.835
7.815
7.521
7.501
7.481
7.449
7.431
7.412
7.387
7.369
7.350
7.324
7.304
7.285
N
SO2Ph
1.95
1.98
1.98
2.00
1.00
1.99
2.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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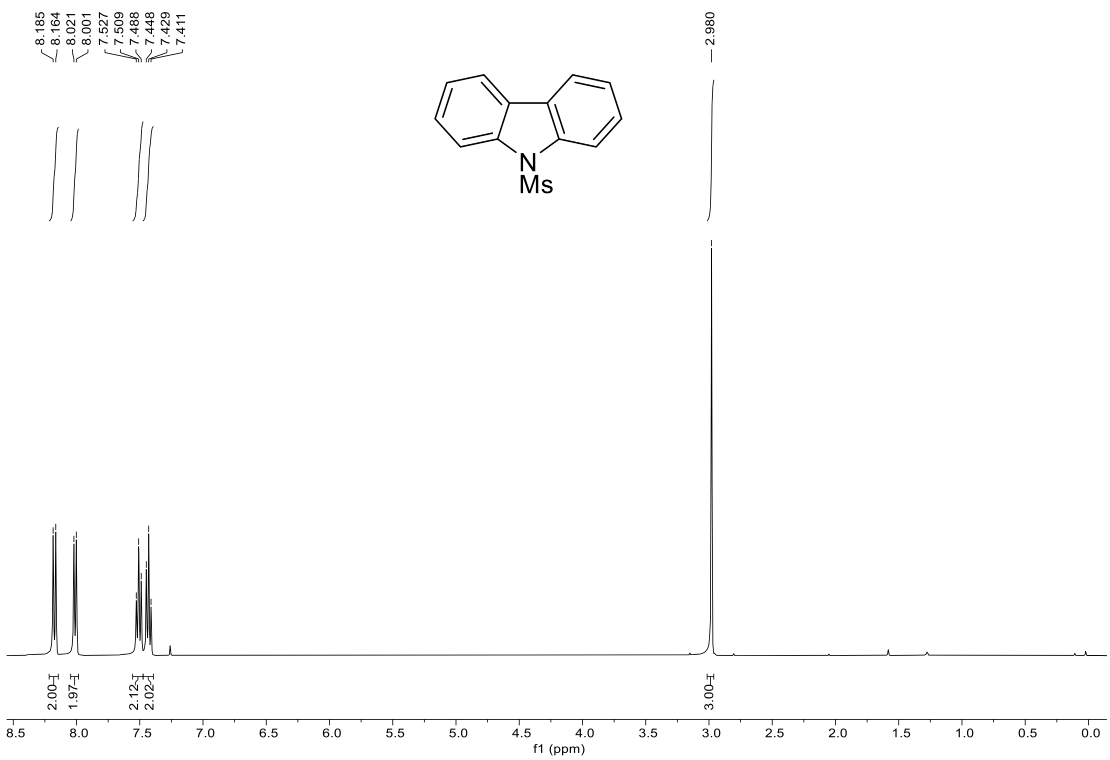
137.99
133.88
129.13
127.54
126.53
126.52
124.11
120.15
115.24
77.48
77.16
76.84
N
SO2Ph
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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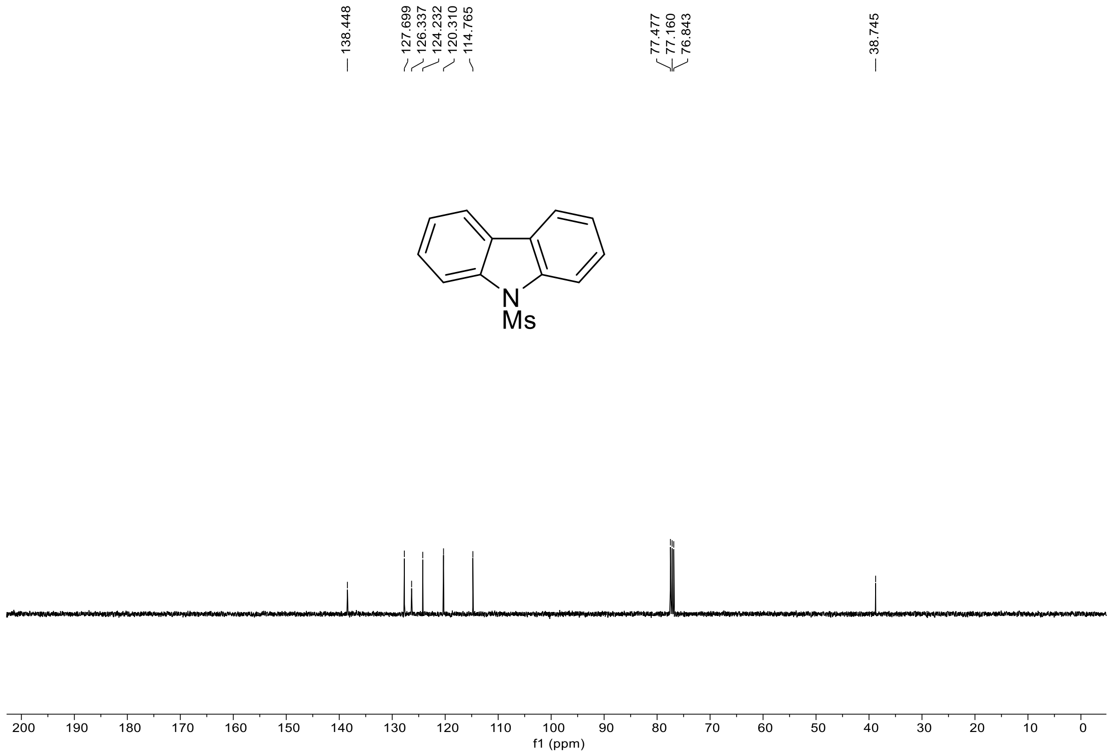
8.001
7.527
7.509
7.488
7.448
7.429
7.411
2.980
N
Ms
2.00
1.97
2.12
2.02
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


138.448
127.699
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124.232
120.310
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77.477
77.160
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38.745
N
Ms
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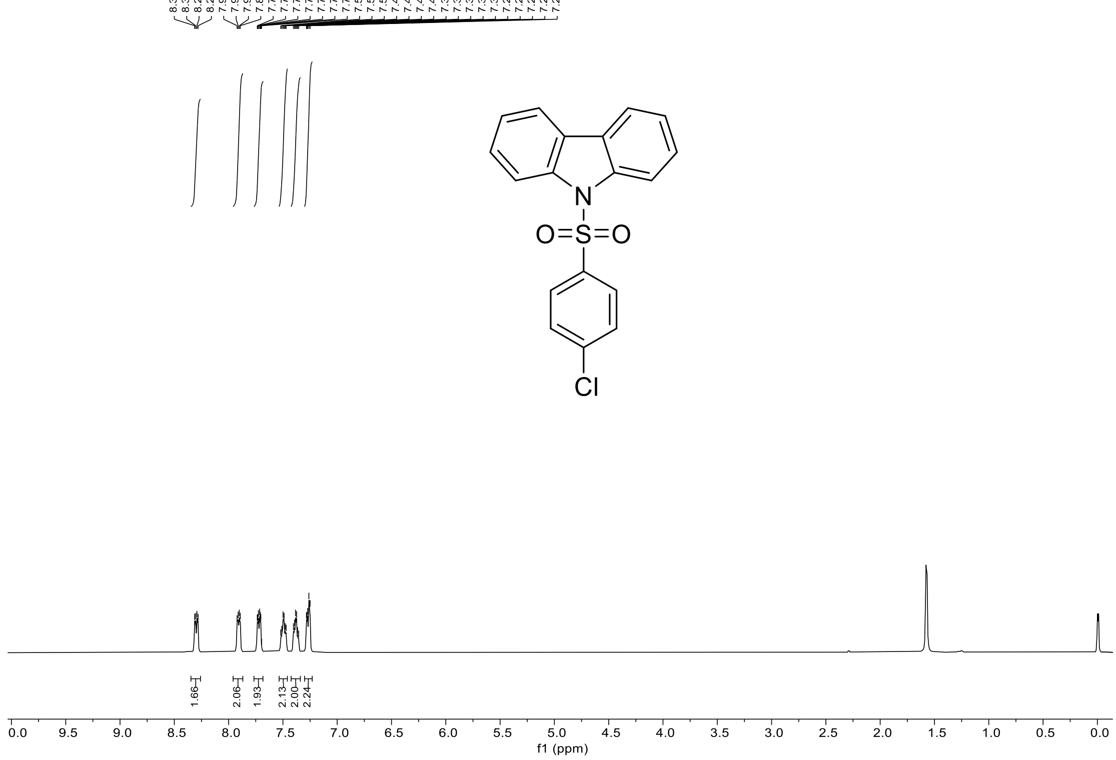
f1 (ppm)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7.90
7.89
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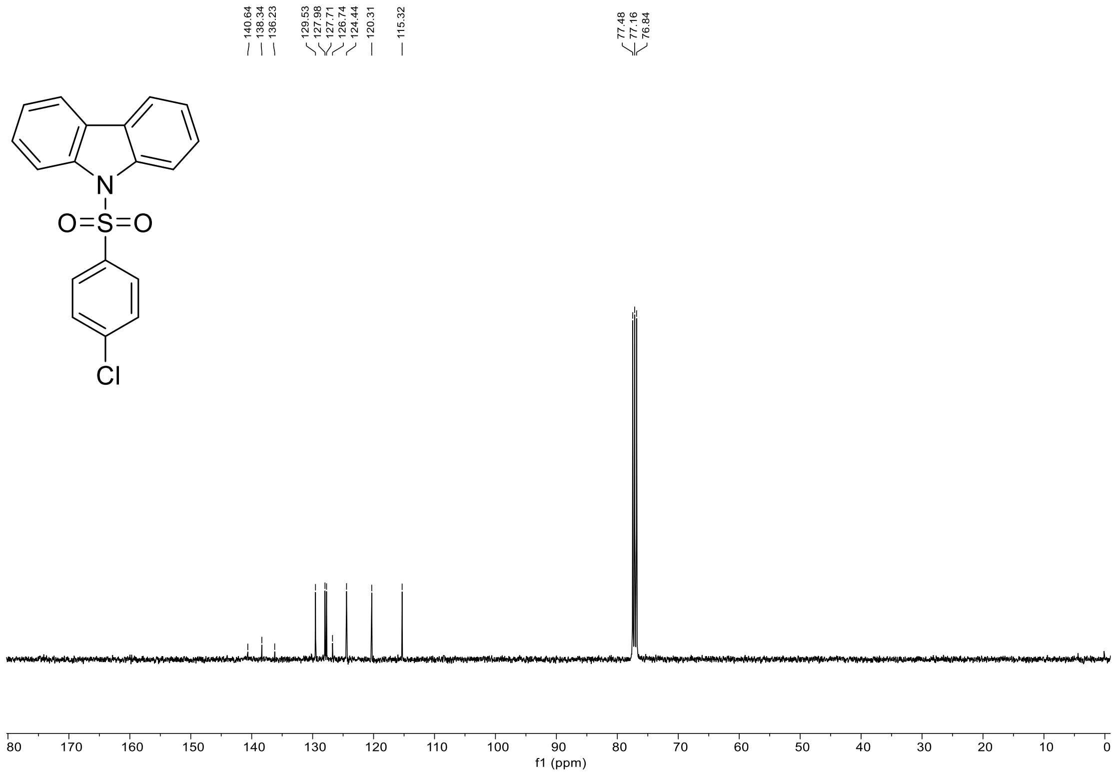
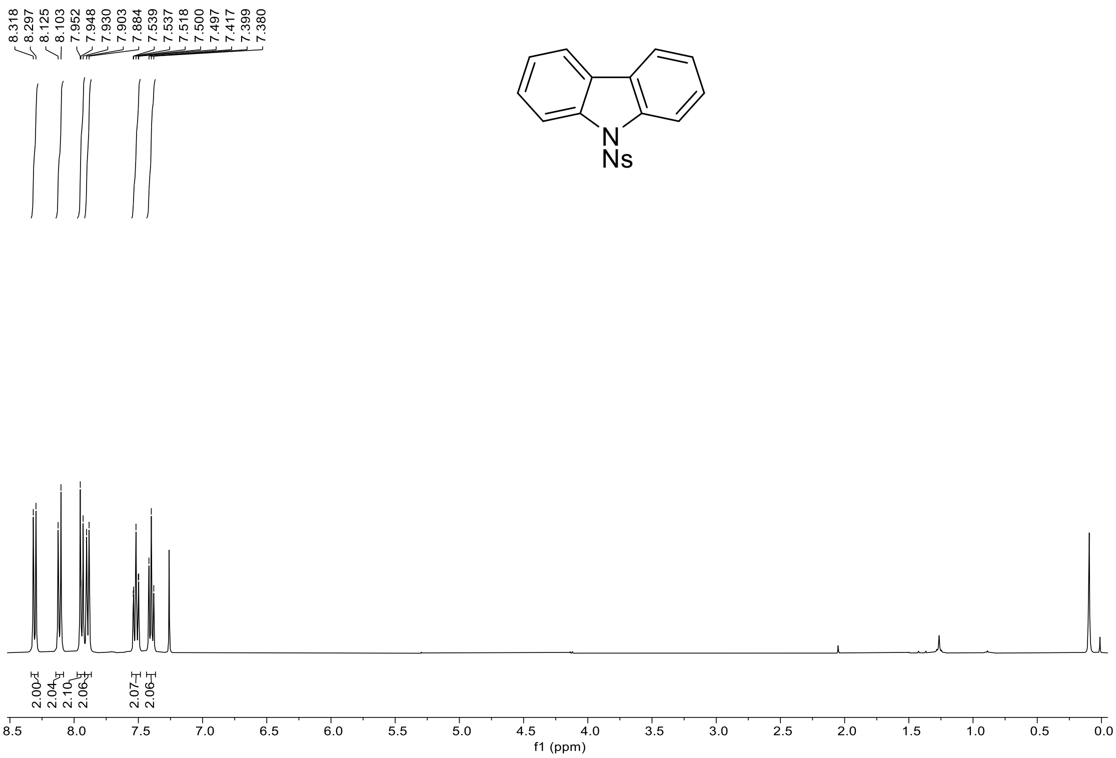
7.73
7.73
7.71
7.71
7.70
7.70
7.52
7.51
7.50
7.49
7.48
7.47
7.40
7.39
7.38
7.37
7.36
7.35
7.28
7.28
7.27
7.26
7.25
N
O=S=O
Cl
1.66
2.06
1.93
2.13
2.00
2.24
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



140.64
138.34
136.23
129.53
127.98
127.71
126.74
124.44
120.31
115.32
77.48
77.16
76.84
N
O=S=O
Cl
f1 (ppm)



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8.297
8.125
8.103
7.952
7.948
7.930
7.903
7.884
7.539
7.537
7.518
7.500
7.497
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7.399
7.380
N
Ns
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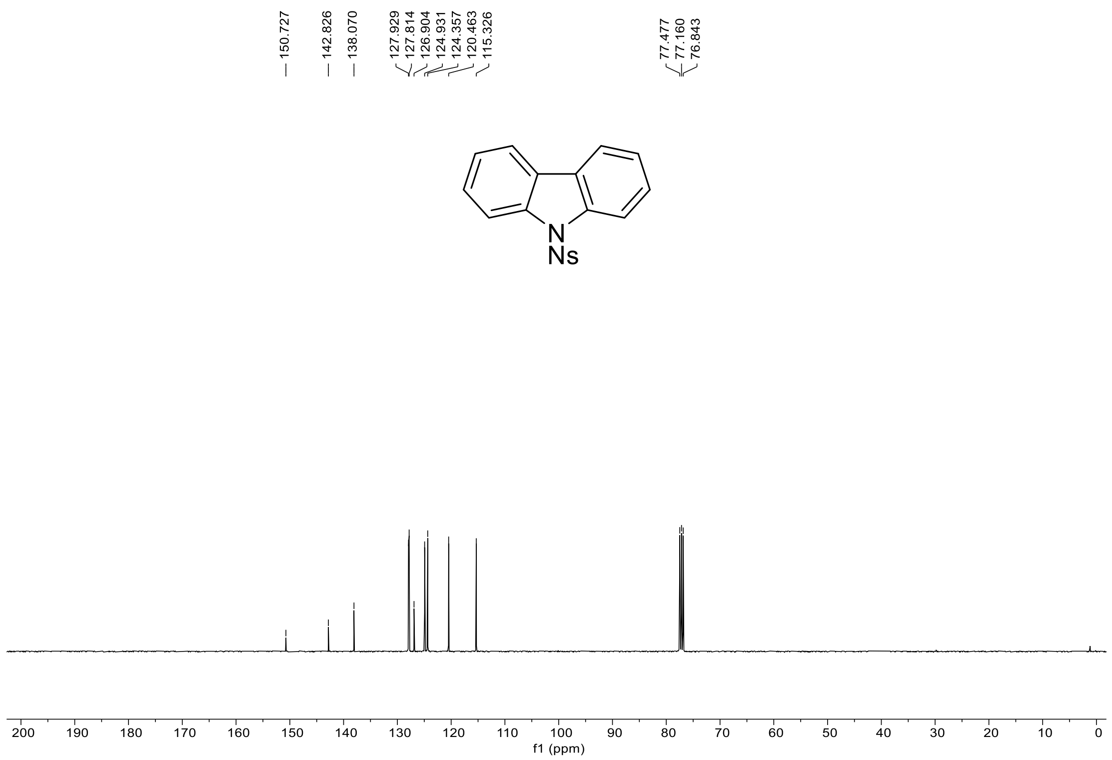
2.04
2.10
2.06
2.07
2.06
f1 (ppm)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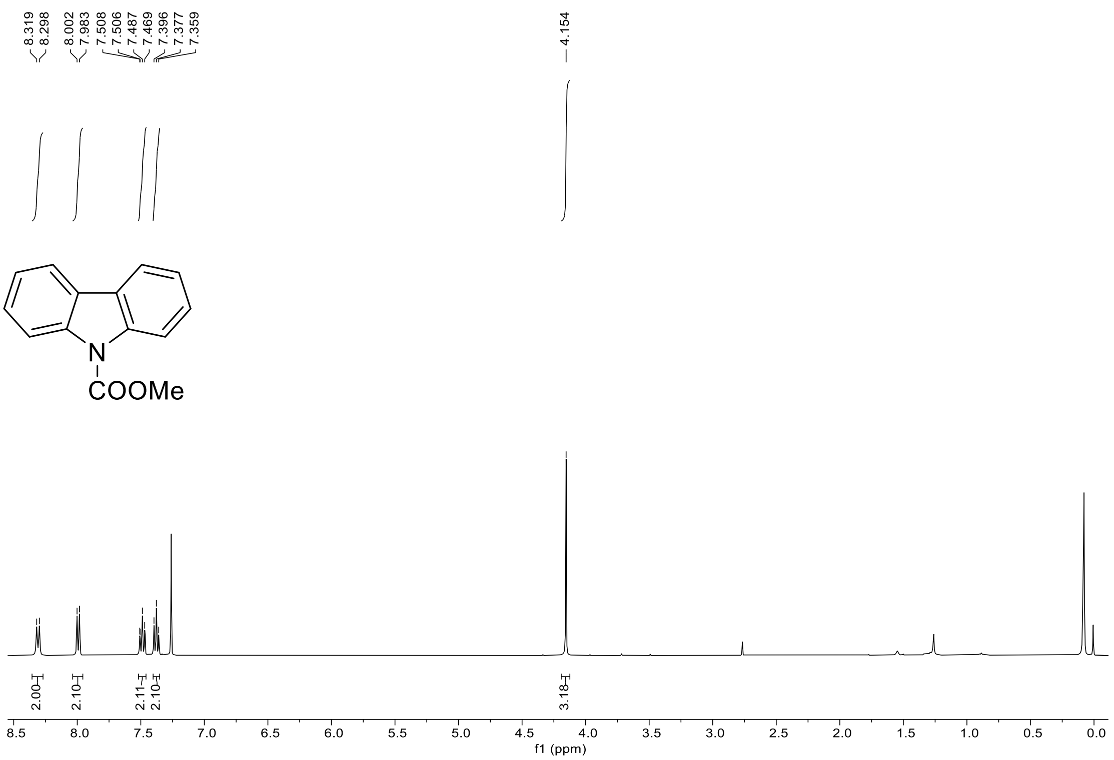
138.070
127.929
127.814
126.904
124.931
124.357
120.463
115.326
77.477
77.160
76.843
N
Ns
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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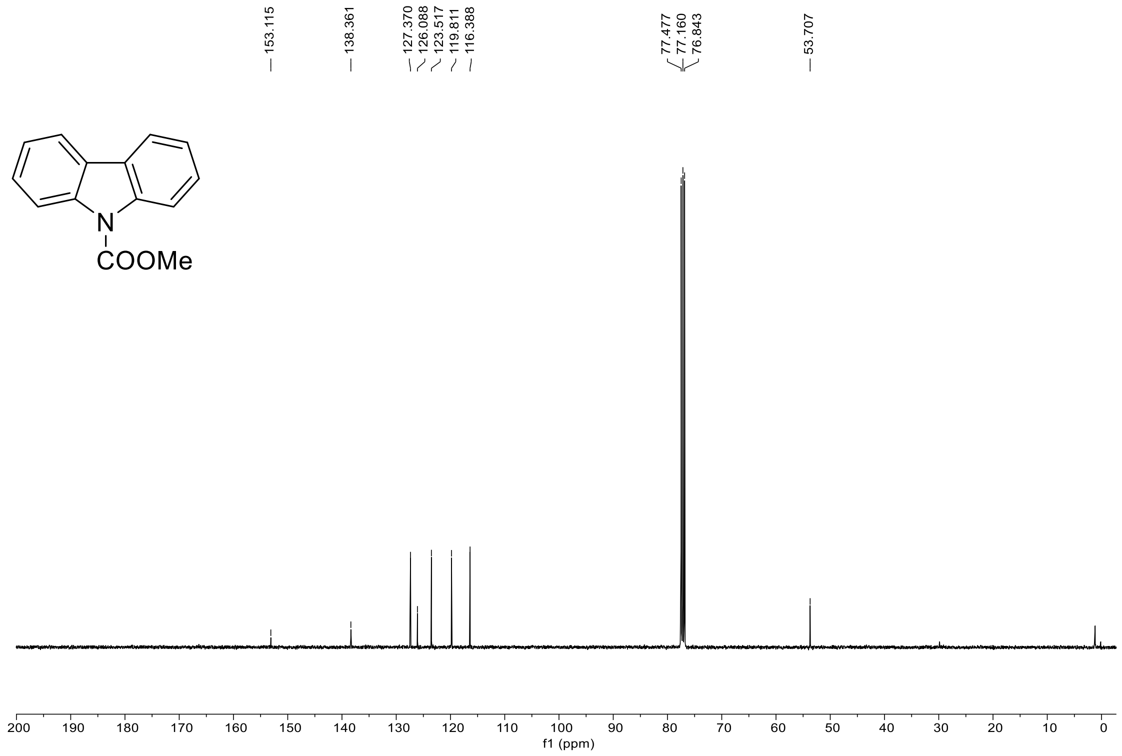
8.002
7.983
7.508
7.506
7.487
7.469
7.396
7.377
7.359
4.154
N
COOMe
2.00
2.10
2.11
2.10
3.18
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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119.811
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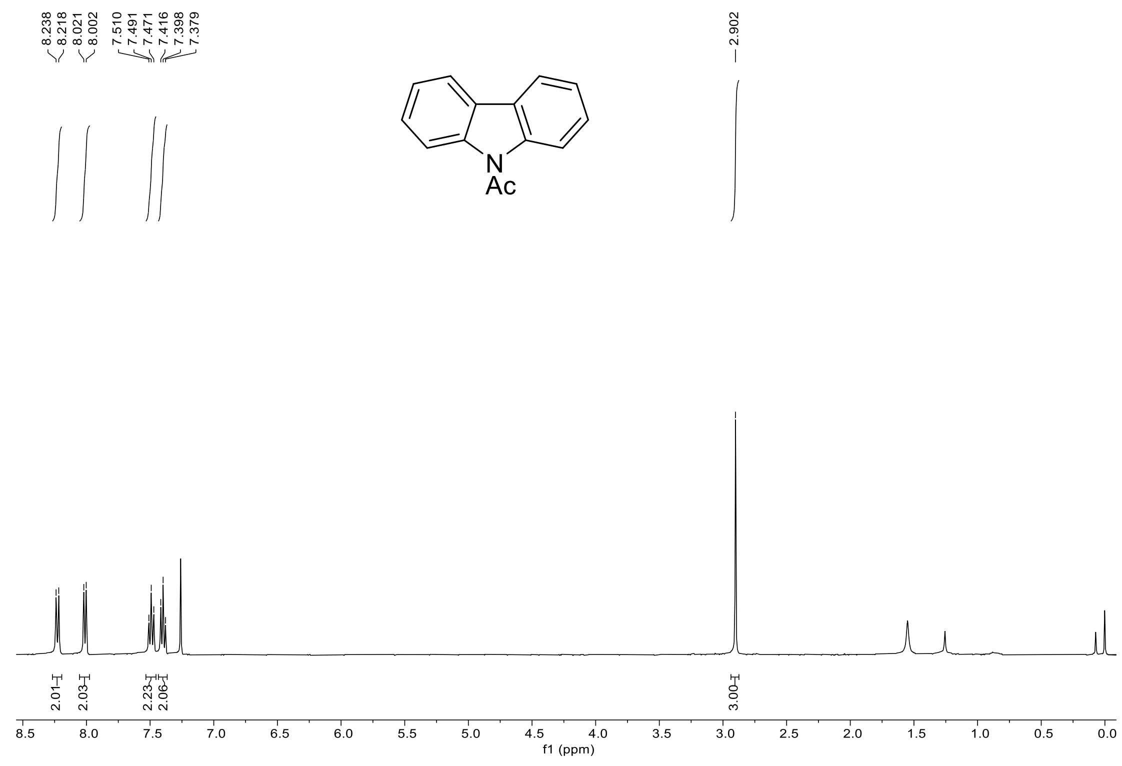
77.477
77.160
76.843
53.707
N
COOMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.491
7.471
7.416
7.398
7.379
2.902
N
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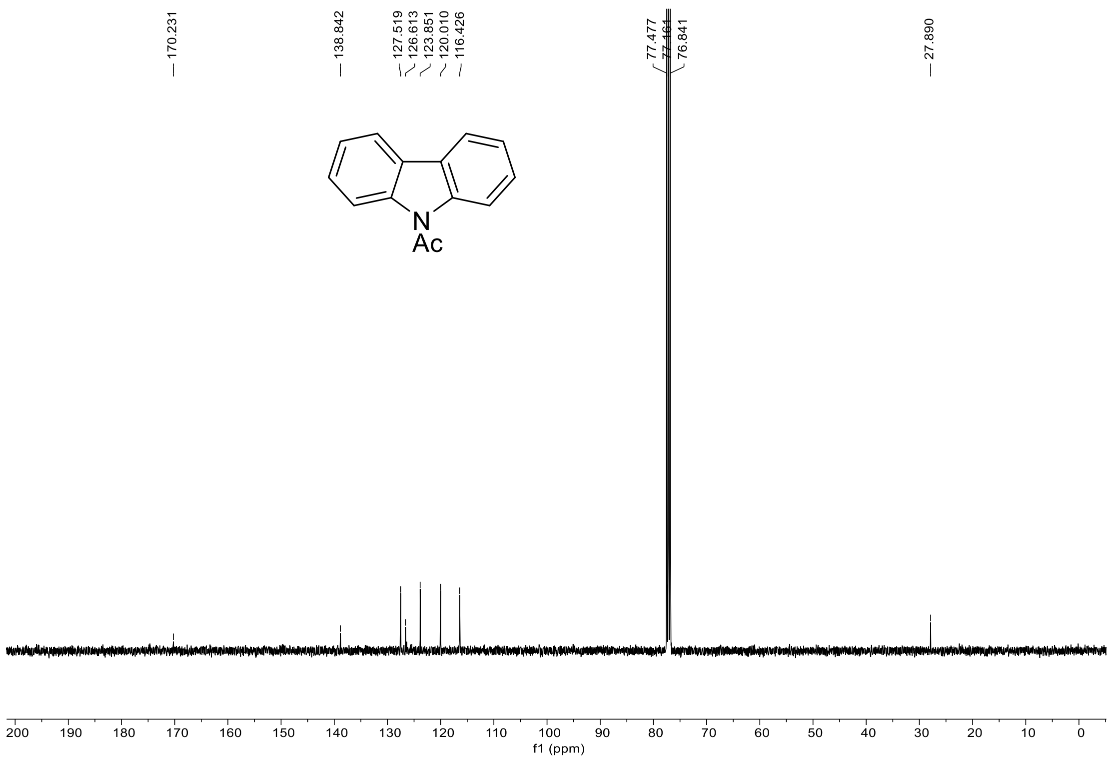
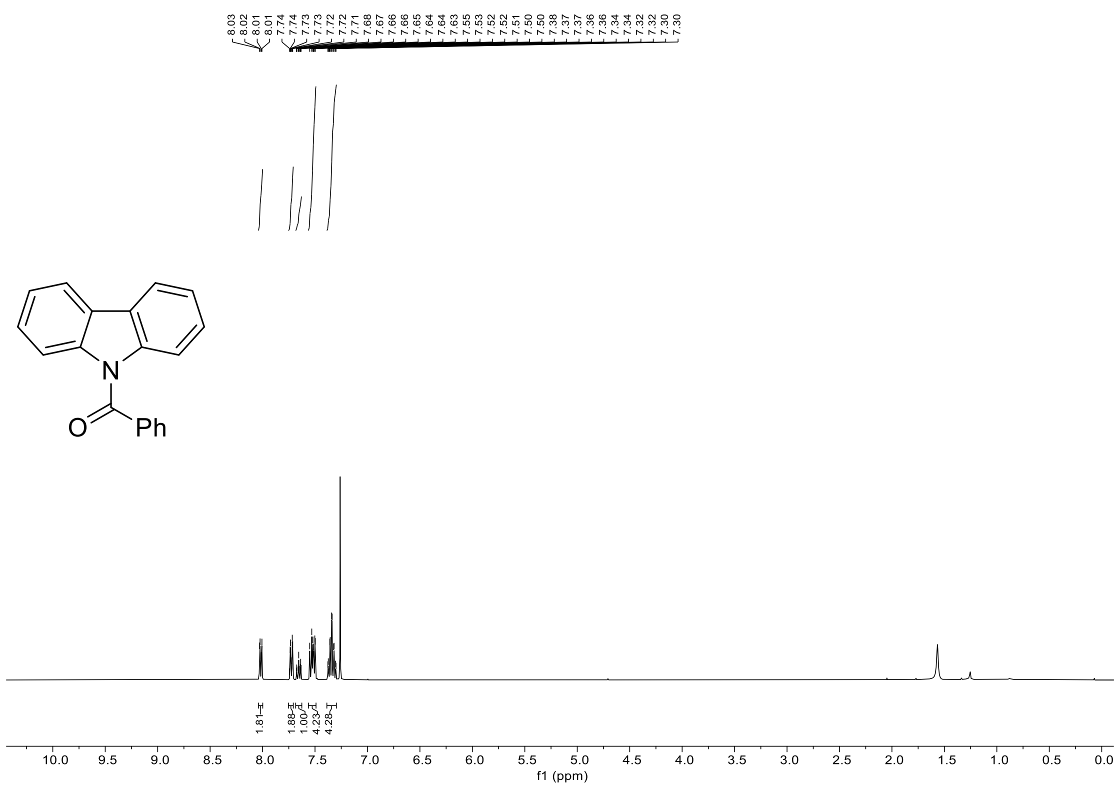
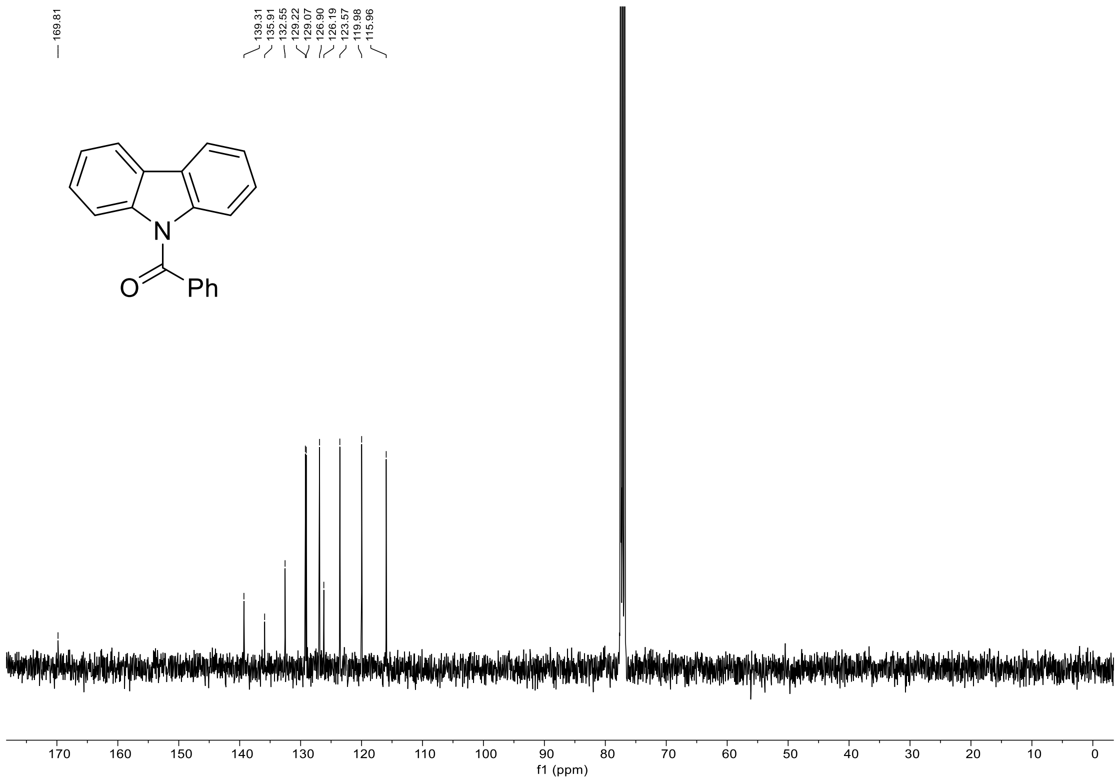
2.01
2.03
2.23
2.06
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



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135.91
132.55
129.22
129.07
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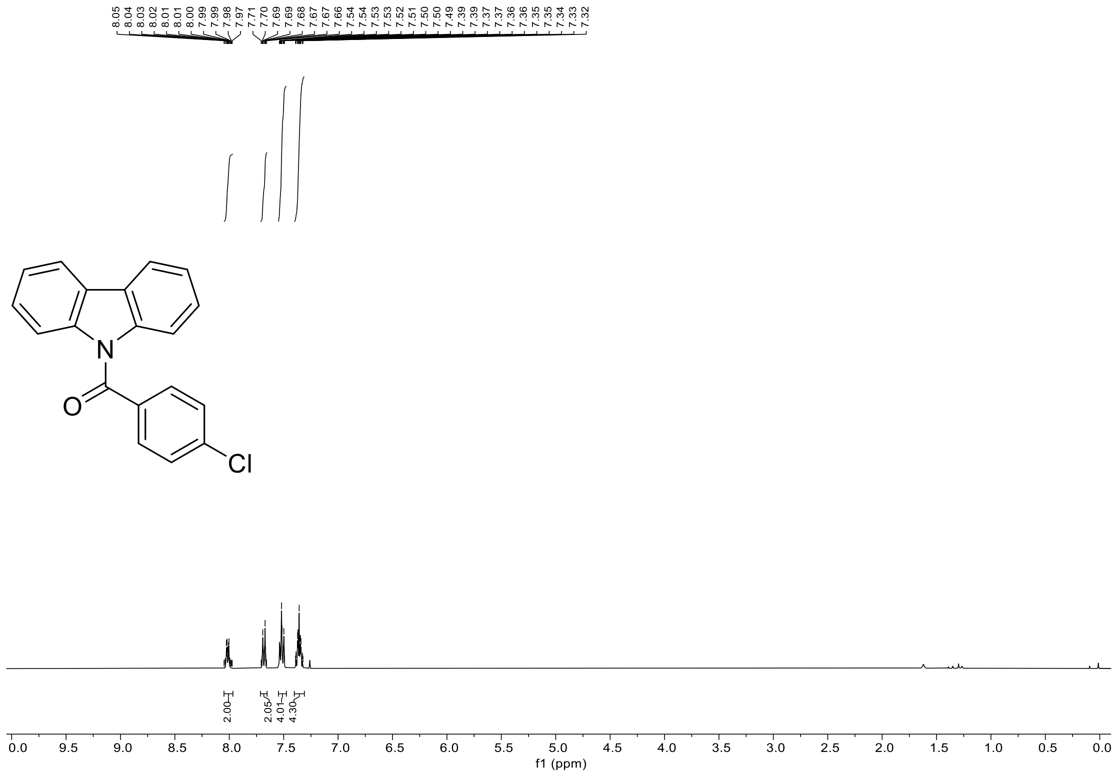
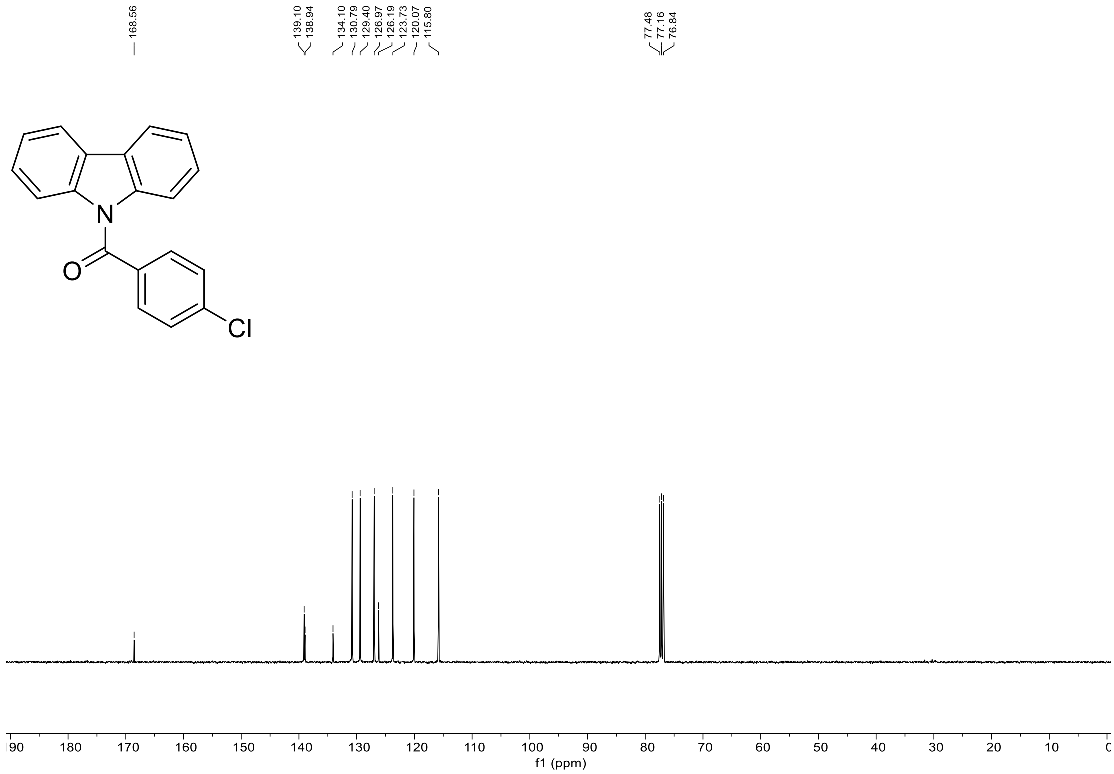
126.19
123.57
119.98
115.96
N
O
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.05
8.04
8.03
8.02
8.01
8.01
8.00
7.99
7.98
7.97
7.71
7.70
7.69
7.69
7.68
7.67
7.67
7.66
7.54
7.54
7.53
7.53
7.52
7.51
7.50
7.49
7.39
7.39
7.37
7.37
7.36
7.35
7.34
7.33
7.32
N
O
Cl
2.00
2.05
4.01
4.30
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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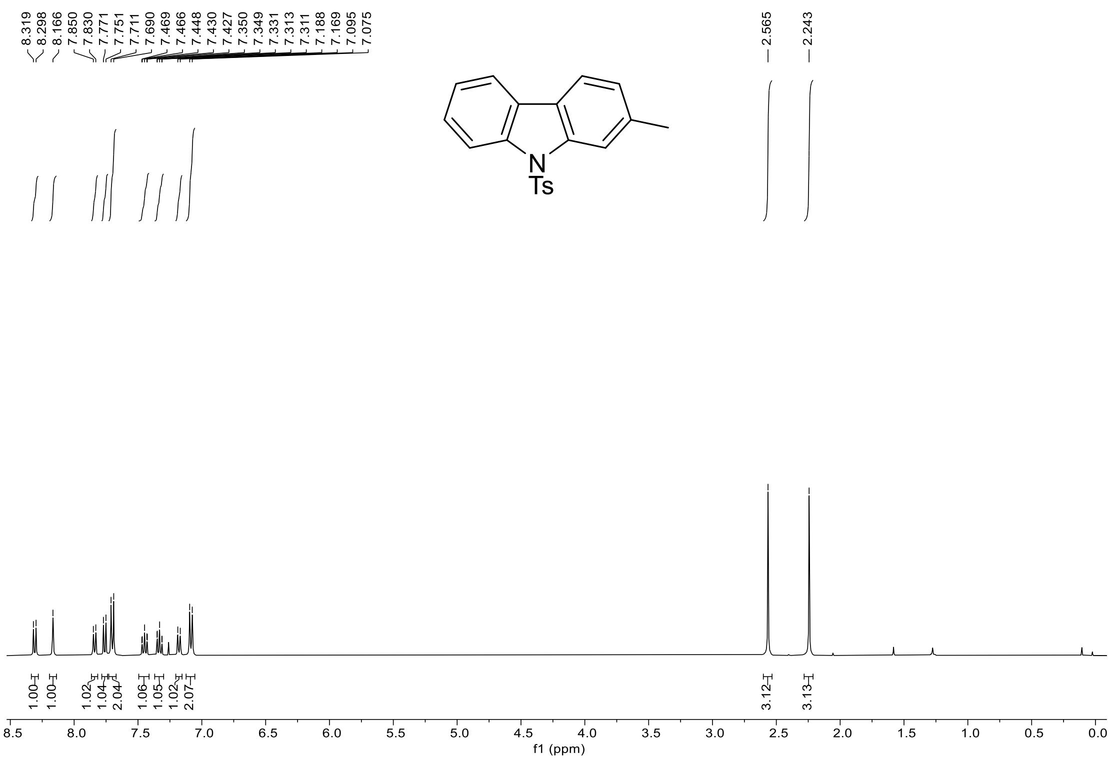
126.19
123.73
120.07
115.80
77.48
77.16
76.84
N
O
Cl
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.830
7.771
7.751
7.711
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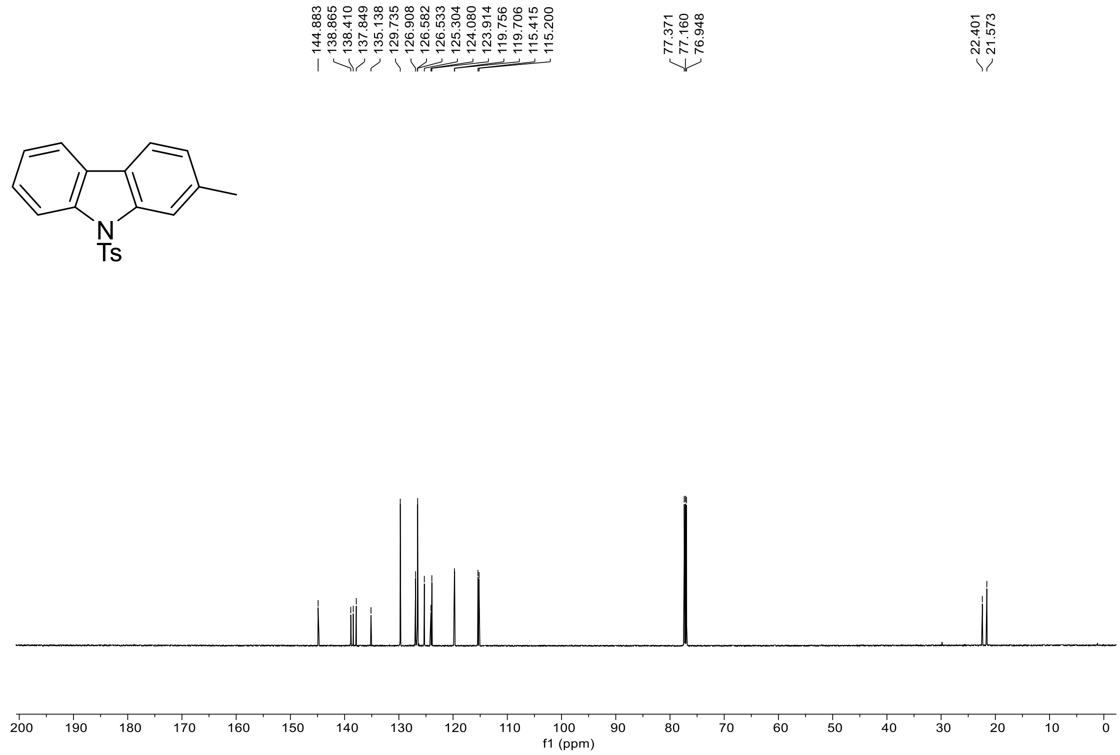
7.469
7.466
7.448
7.430
7.427
7.350
7.349
7.331
7.313
7.311
7.188
7.169
7.095
7.075
2.565
2.243
N
Ts
1.00
1.00
1.02
1.04
2.04
1.06
1.05
1.02
2.07
3.12
3.13
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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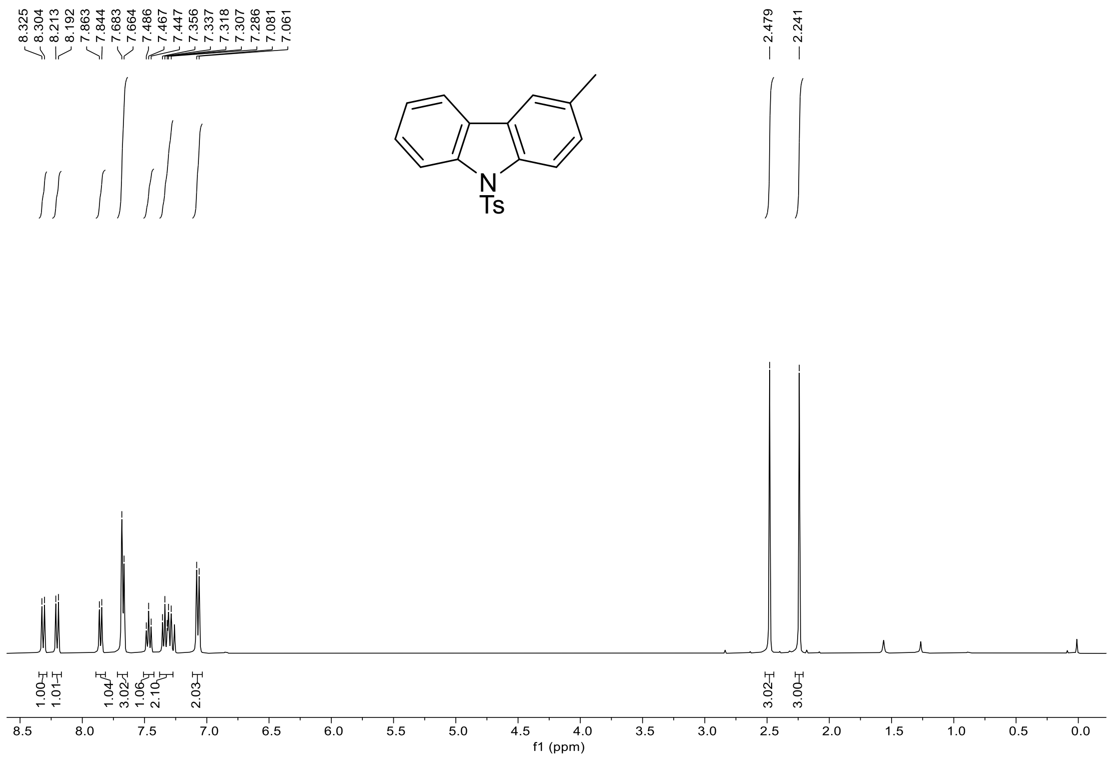
123.914
119.756
119.706
115.415
115.200
77.371
77.160
76.948
22.401
21.573
N
Ts
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.467
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7.356
7.337
7.318
7.307
7.286
7.081
7.061
2.479
2.241
N
Ts
1.00
1.01
1.04
3.02
1.06
2.10
2.03
3.02
3.00
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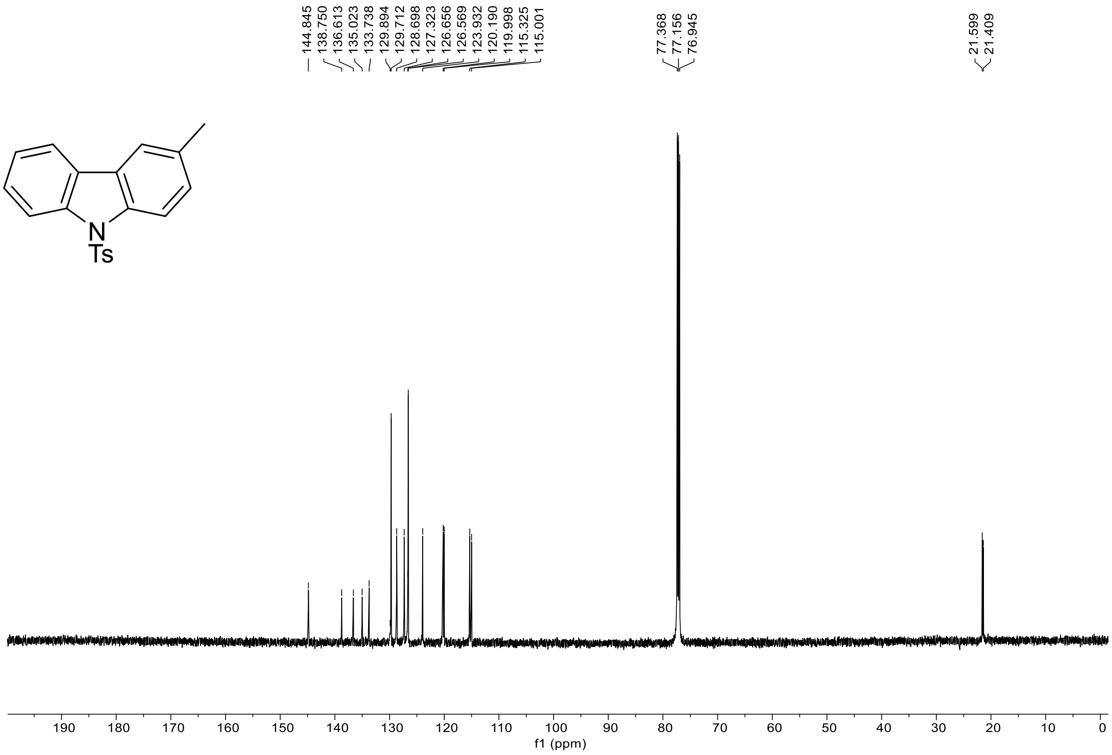
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119.998
115.325
115.001
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21.599
21.409
N
Ts
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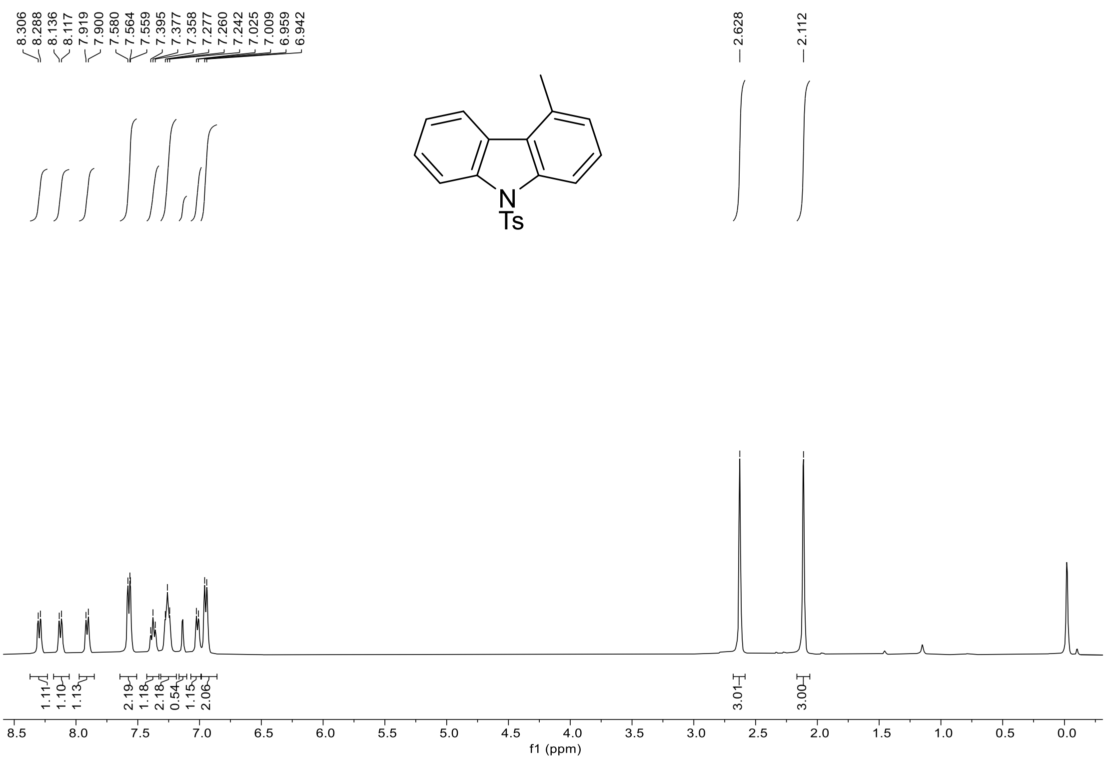
f1 (ppm)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7.277
7.260
7.242
7.025
7.009
6.959
6.942
2.628
2.112
N
Ts
1.11
1.10
1.13
2.19
1.18
2.18
0.54
1.15
2.06
3.01
3.00
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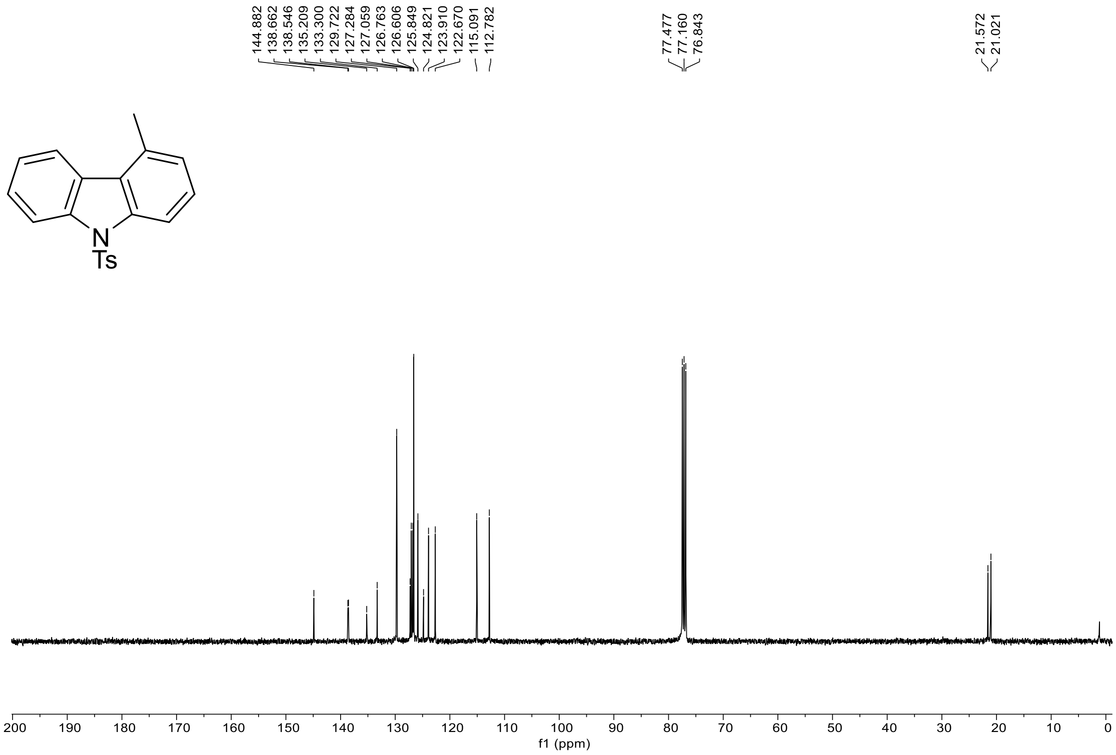
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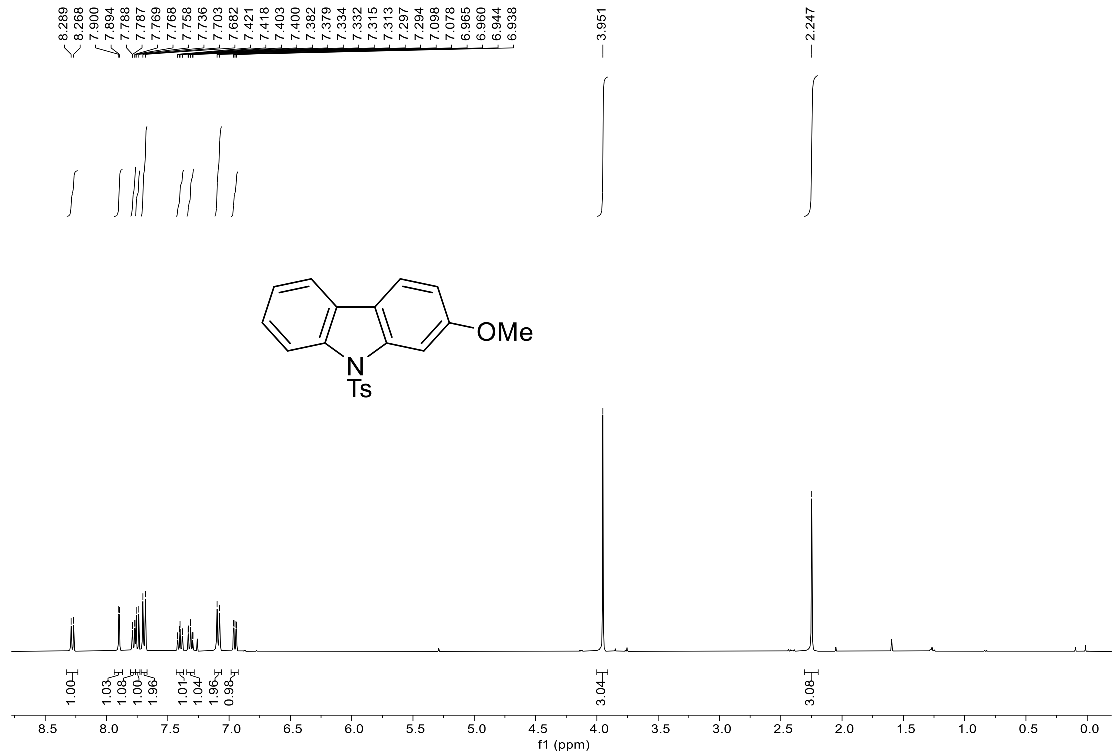
Ts
f1 (ppm)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7.421
7.418
7.403
7.400
7.382
7.379
7.334
7.332
7.315
7.313
7.297
7.294
7.098
7.078
6.965
6.960
6.944
6.938
3.951
2.247
OMe
N
Ts
1.00
1.03
1.08
1.00
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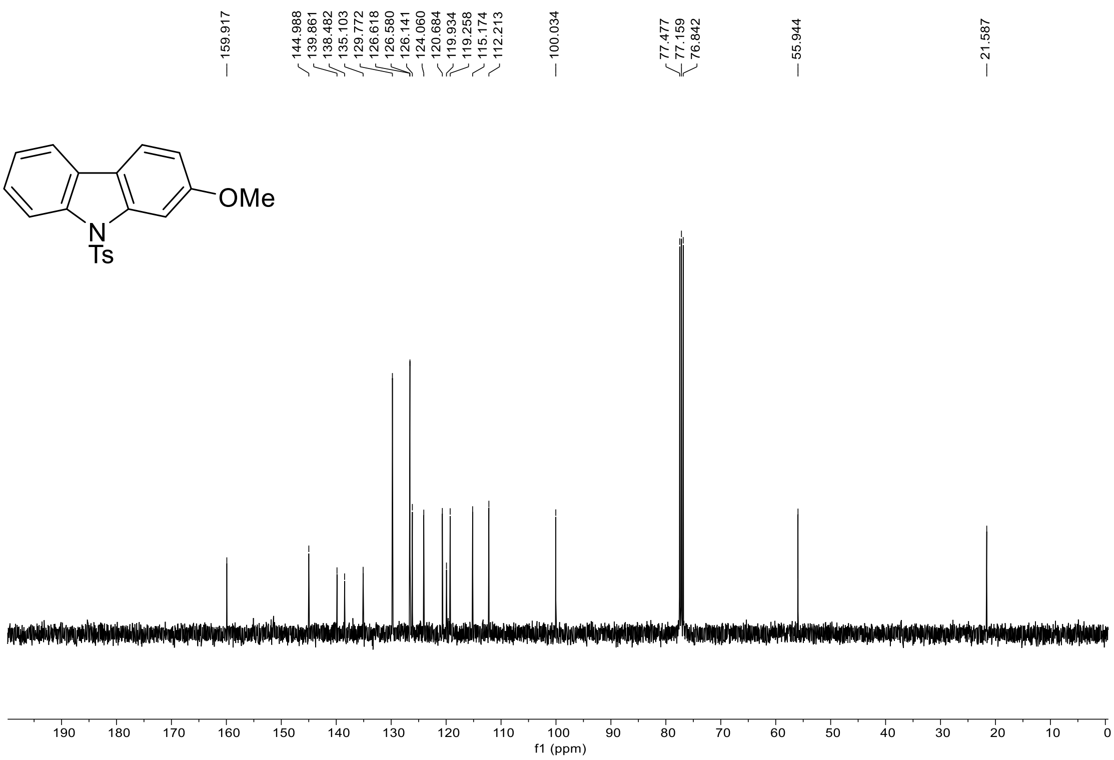
1.01
1.04
1.96
0.98
3.04
3.08
f1 (ppm)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119.258
115.174
112.213
100.034
77.477
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21.587
OMe
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Ts
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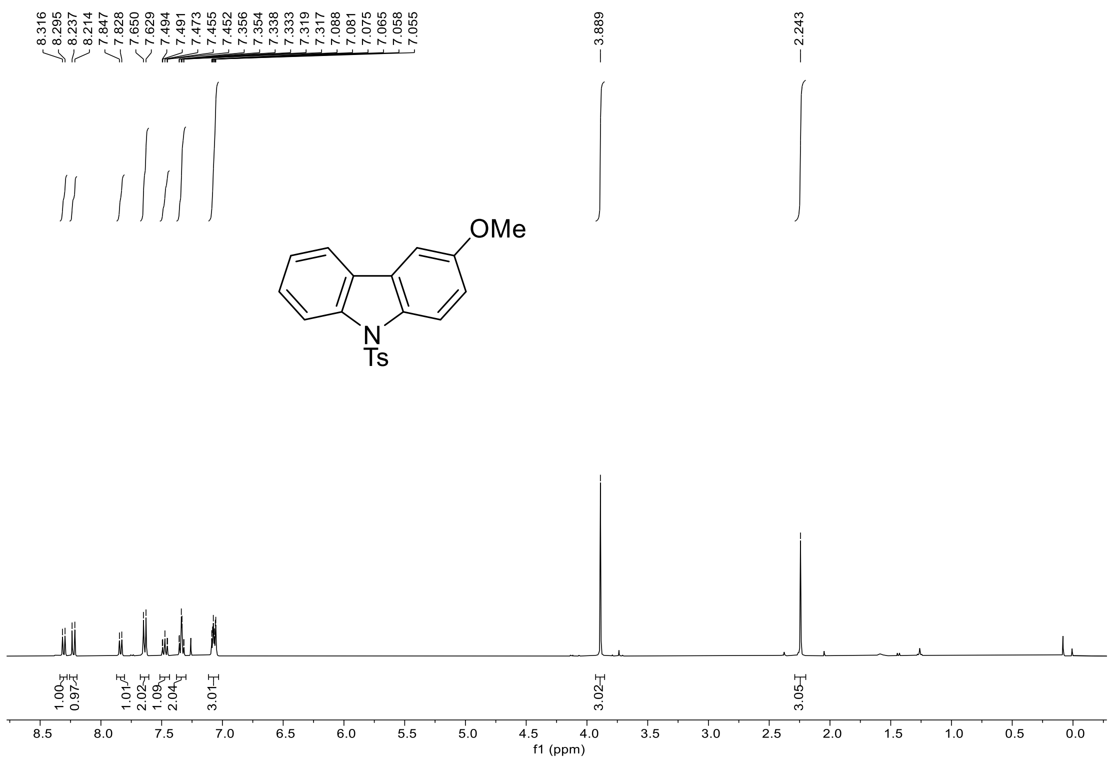
f1 (ppm)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7.650
7.629
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7.491
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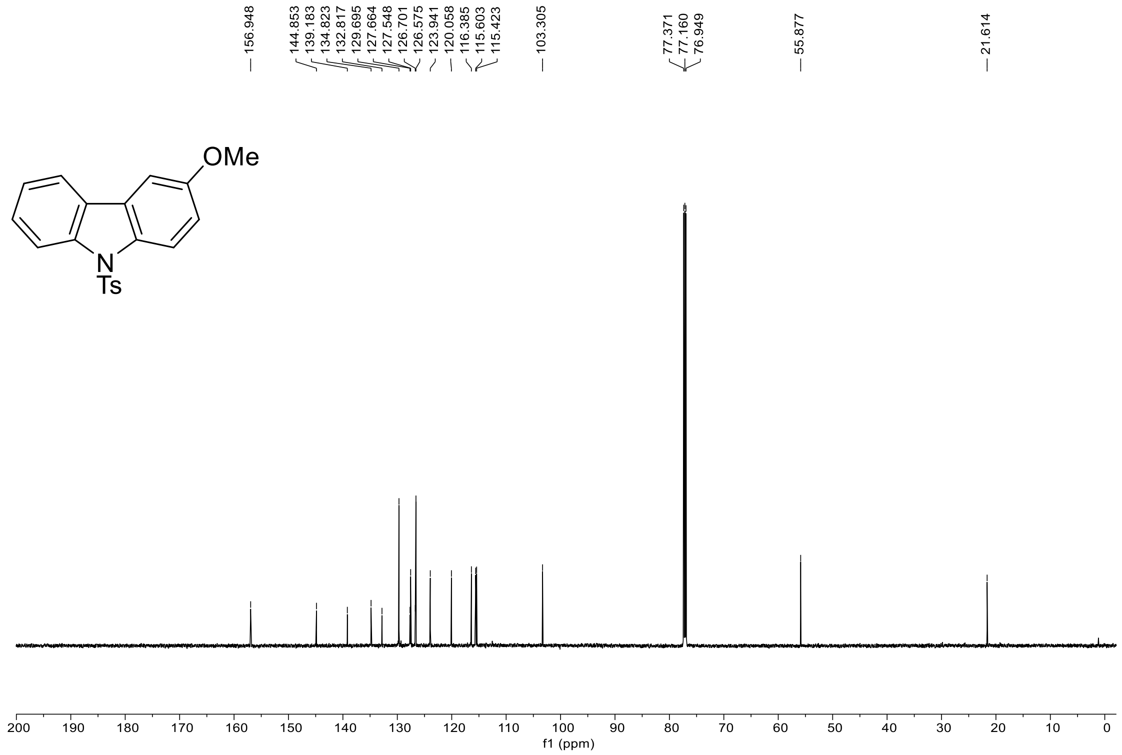
7.452
7.356
7.354
7.338
7.333
7.319
7.317
7.088
7.081
7.075
7.065
7.058
7.055
3.889
2.243
OMe
N
Ts
1.00
0.97
1.01
2.02
1.09
2.04
3.01
3.02
3.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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126.701
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120.058
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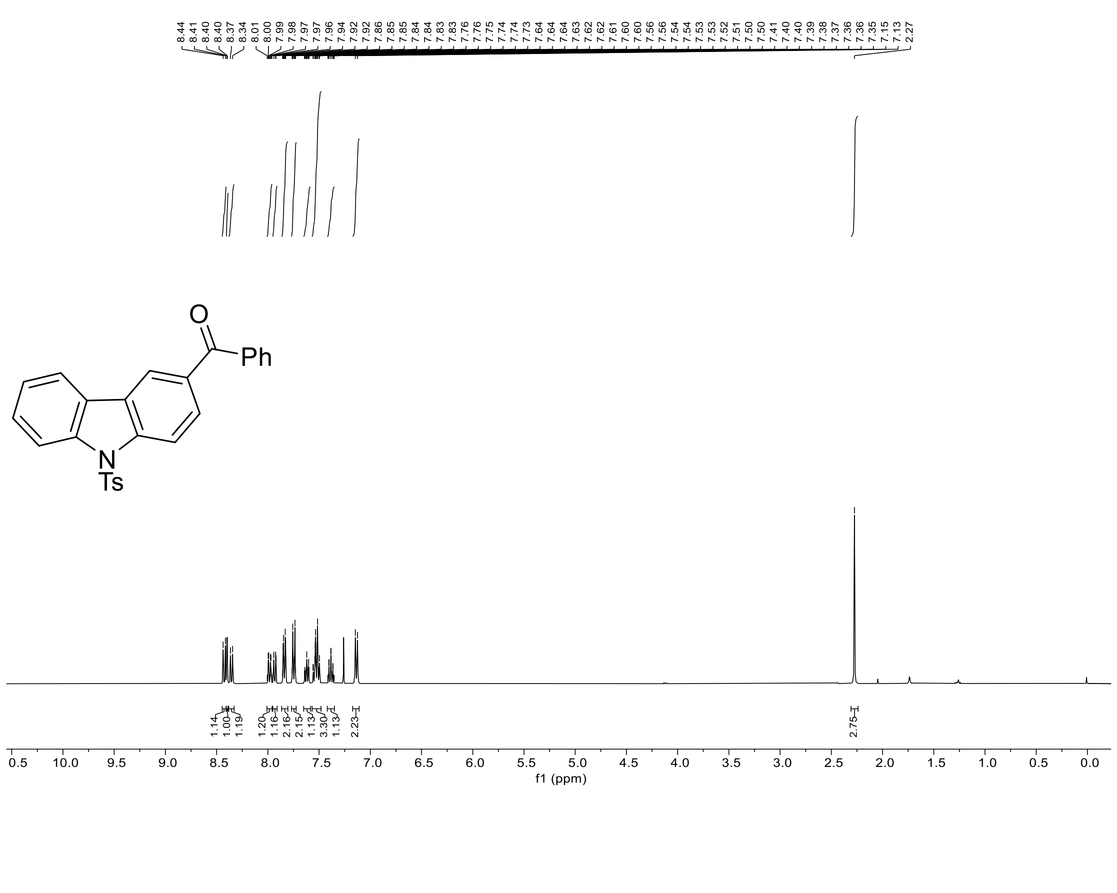
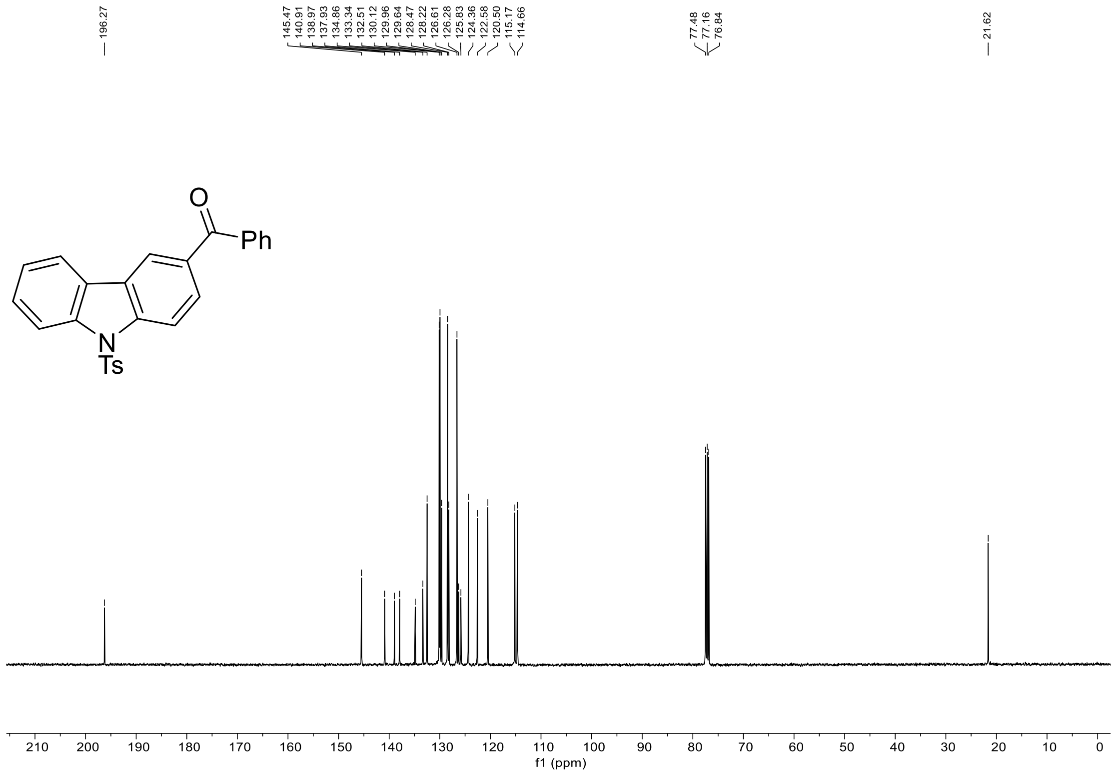
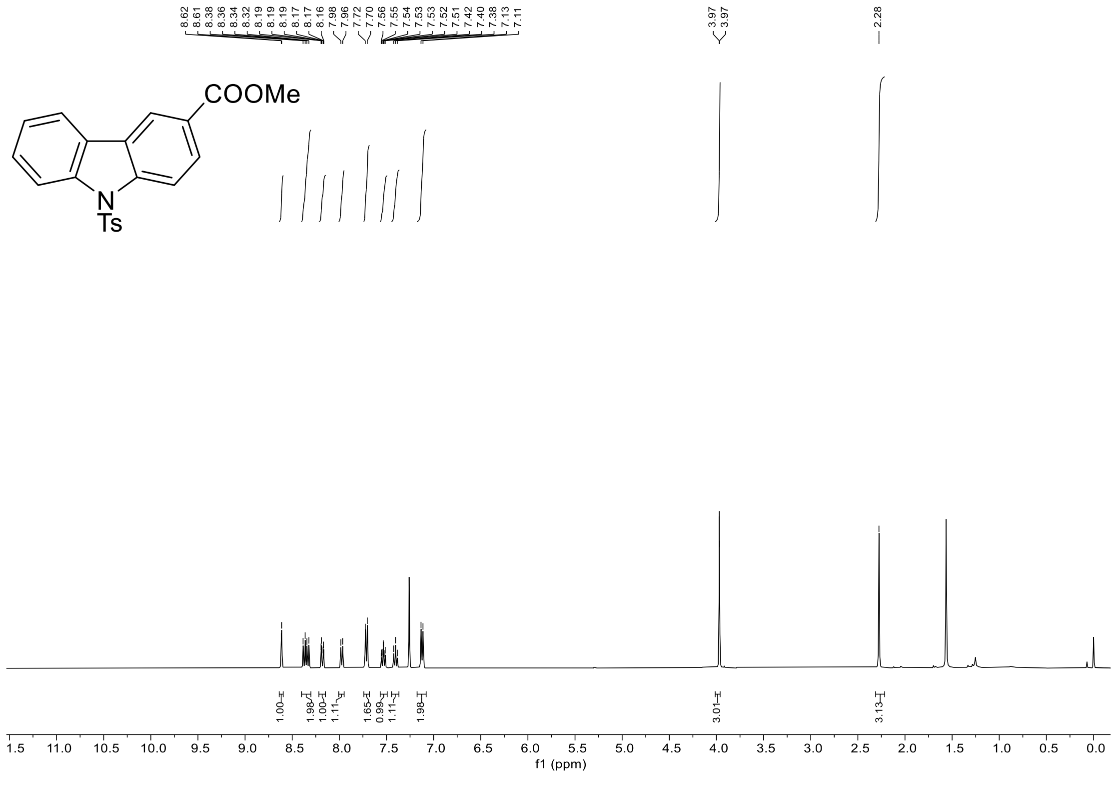
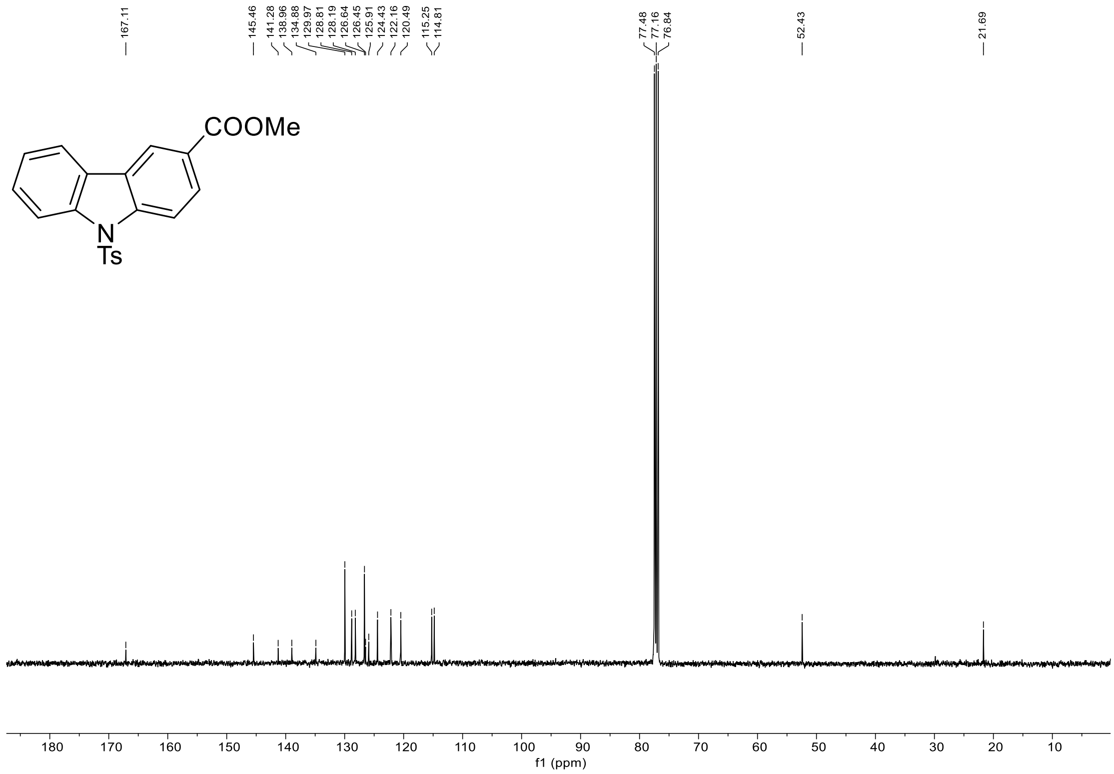
103.305
77.371
77.160
76.949
55.877
21.614
OMe
N
Ts
f1 (ppm)


O
Ph
N
Ts
f1 (ppm)







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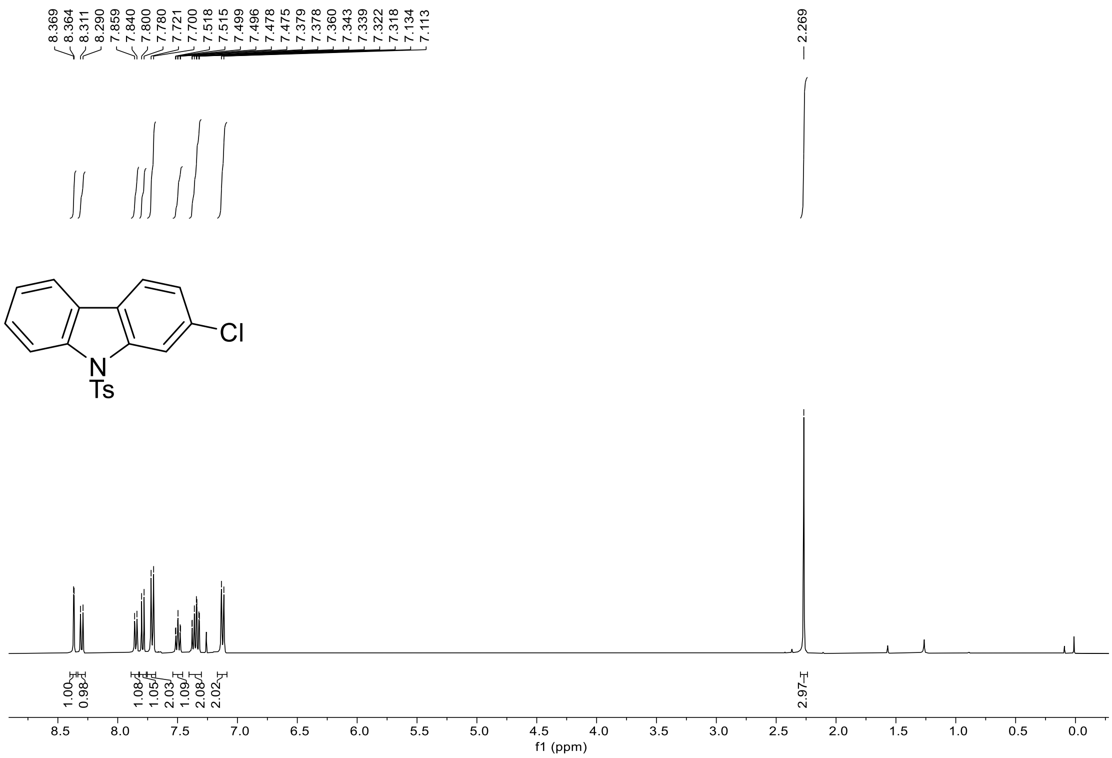
129.97
128.81
128.19
126.64
126.45
125.91
124.43
122.16
120.49
115.25
114.81
77.48
77.16
76.84
52.43
21.69
COOMe
N
Ts
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



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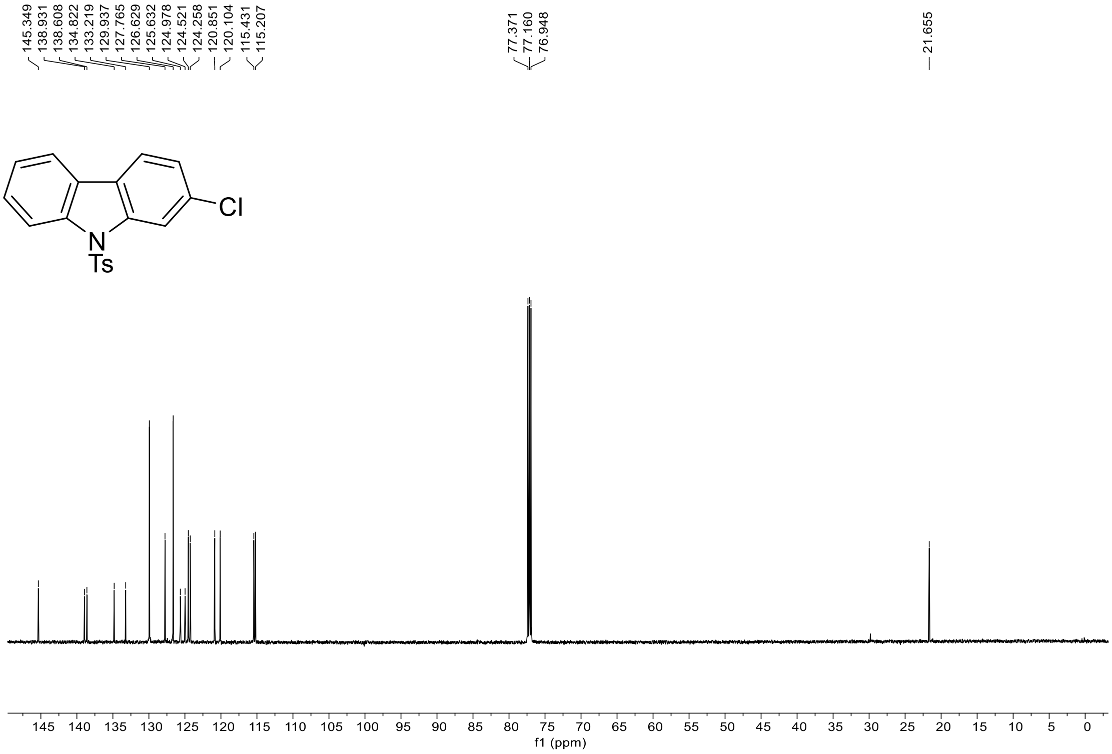
7.780
7.721
7.700
7.518
7.515
7.499
7.496
7.478
7.475
7.379
7.378
7.360
7.343
7.339
7.322
7.318
7.134
7.113
2.269
Cl
N
Ts
1.00
0.98
1.08
1.05
2.03
1.09
2.08
2.02
2.97
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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125.632
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120.851
120.104
115.431
115.207
77.371
77.160
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Cl
N
Ts
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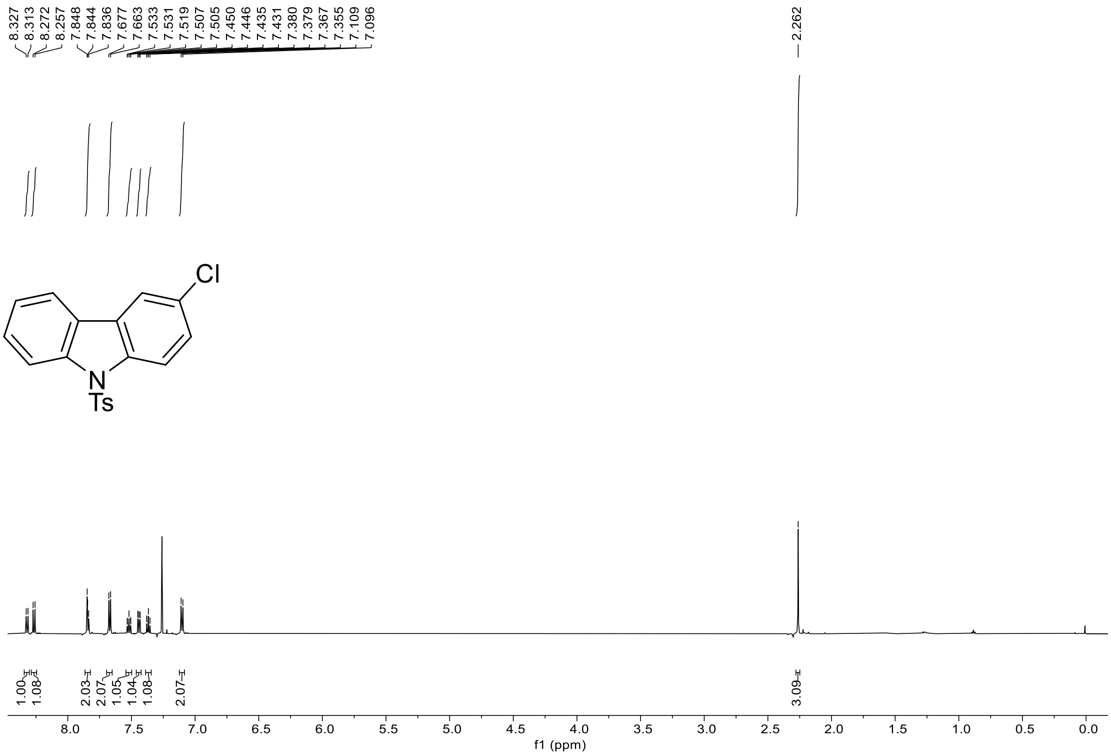
f1 (ppm)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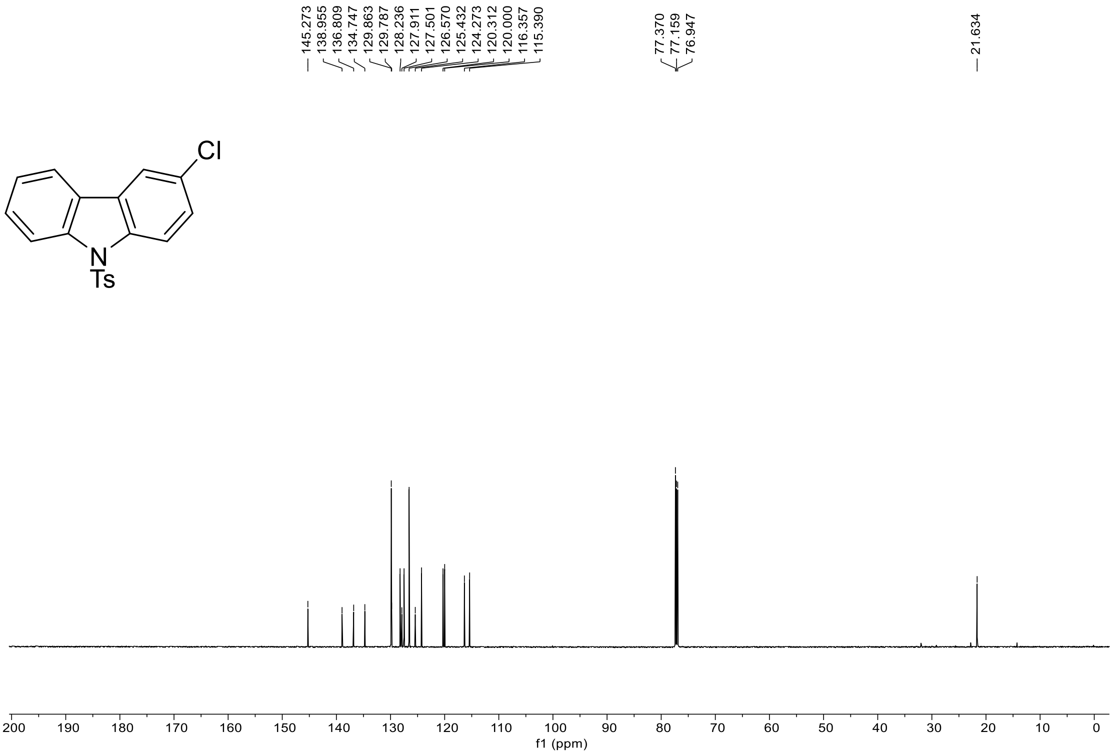
7.519
7.507
7.505
7.450
7.446
7.435
7.431
7.380
7.379
7.367
7.355
7.109
7.096
2.262
Cl
N
Ts
1.00
1.08
2.03
2.07
1.05
1.04
1.08
2.07
3.09
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.787
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126.570
125.432
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120.312
120.000
116.357
115.390
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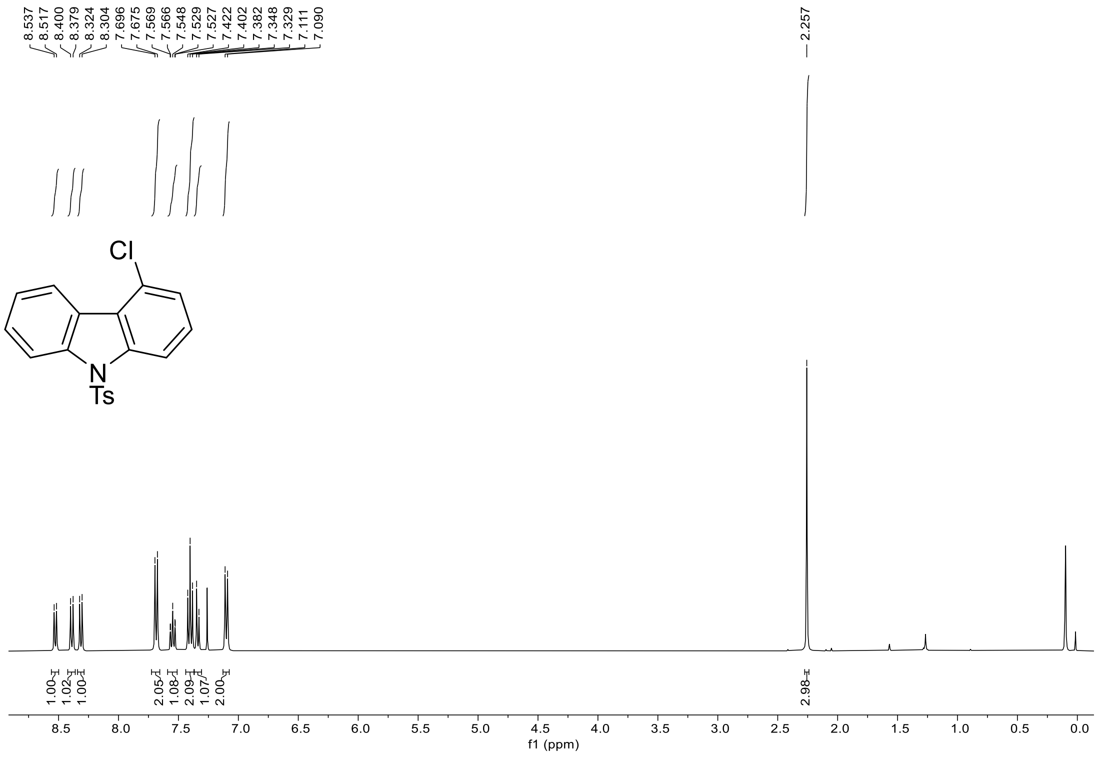
76.947
21.634
Cl
N
Ts
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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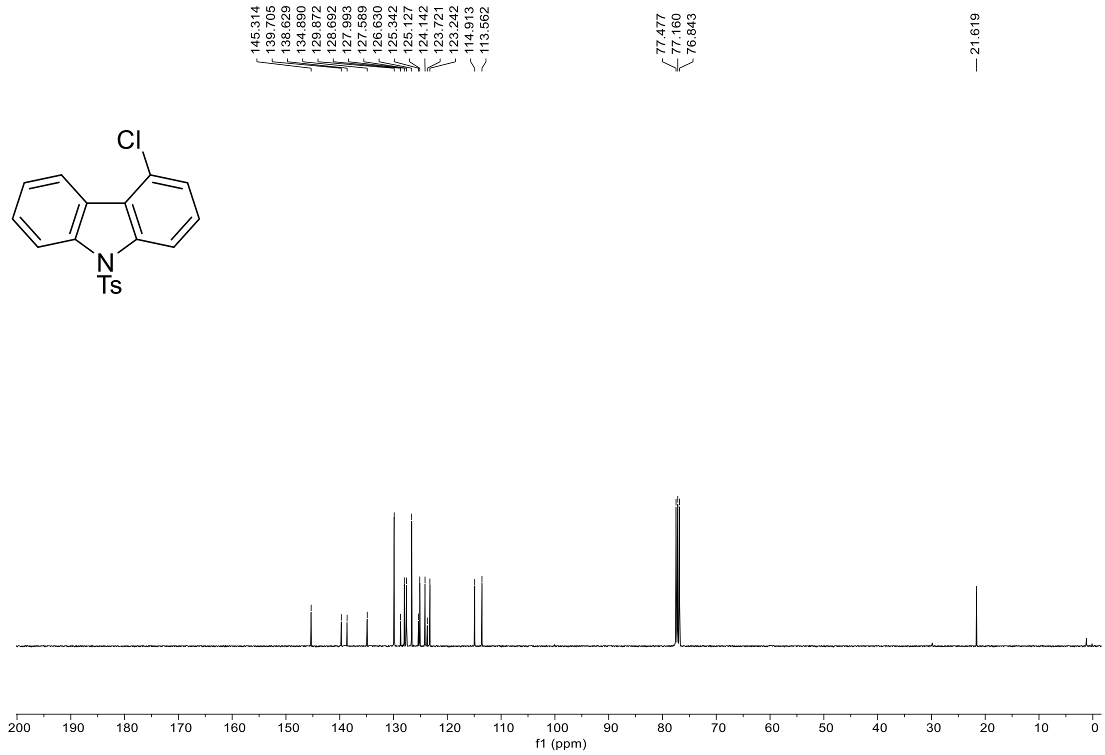
7.527
7.422
7.402
7.382
7.348
7.329
7.111
7.090
2.257
Cl
N
Ts
1.00
1.02
1.00
2.05
1.08
2.09
1.07
2.00
2.98
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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124.142
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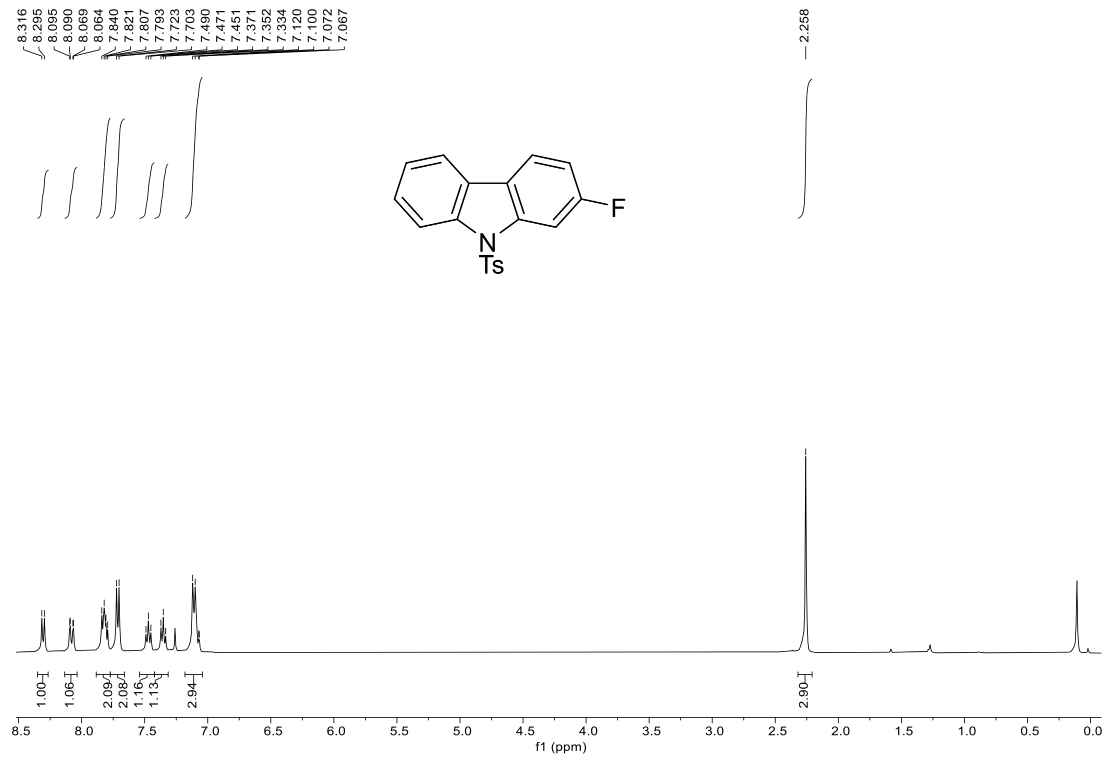
21.619
Cl
N
Ts
f1 (ppm)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7.703
7.490
7.471
7.451
7.371
7.352
7.334
7.120
7.100
7.072
7.067
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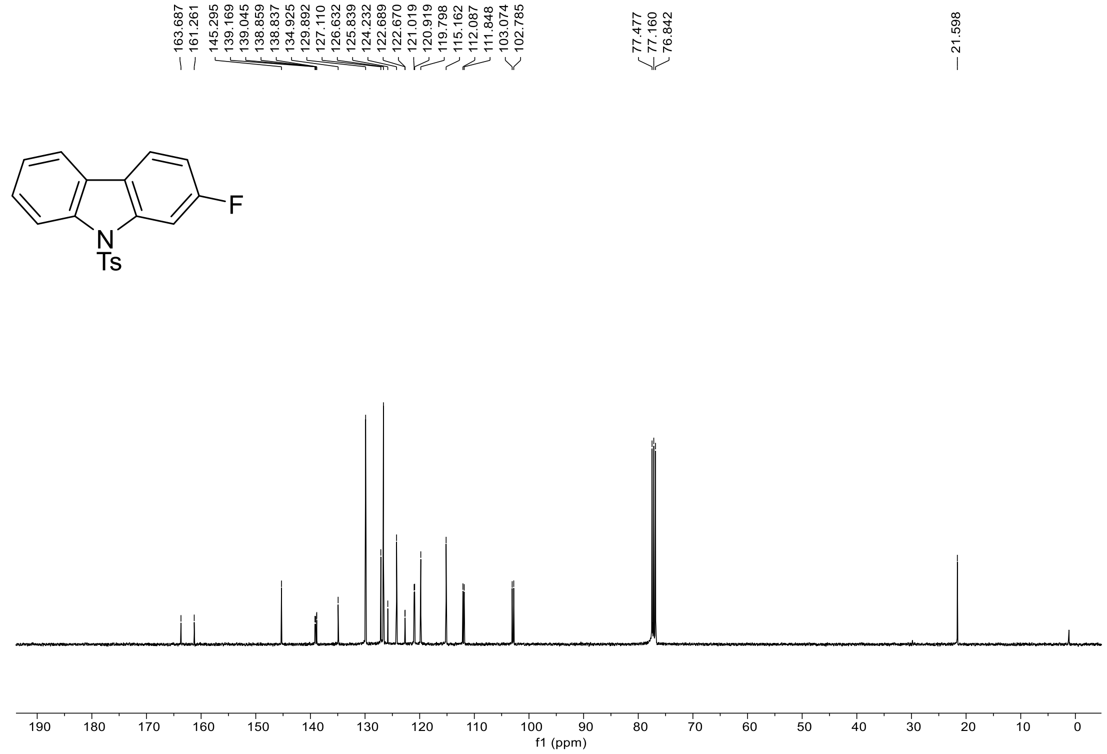

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122.689
122.670
121.019
120.919
119.798
115.162
112.087
111.848
103.074
102.785
77.477
77.160
76.842
21.598
F
N
Ts
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

-36.133
-36.147
-36.159
-36.174
-36.184
-36.198
F
N
Ts
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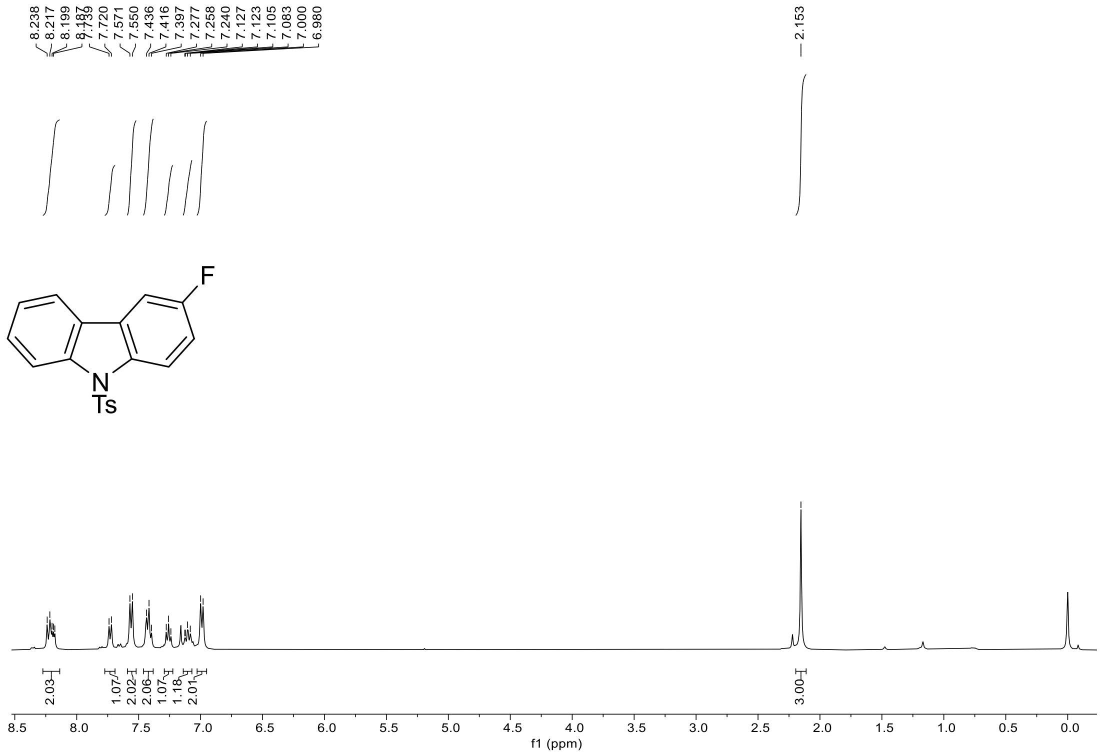
f1 (ppm)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7.258
7.240
7.127
7.123
7.105
7.083
7.000
6.980
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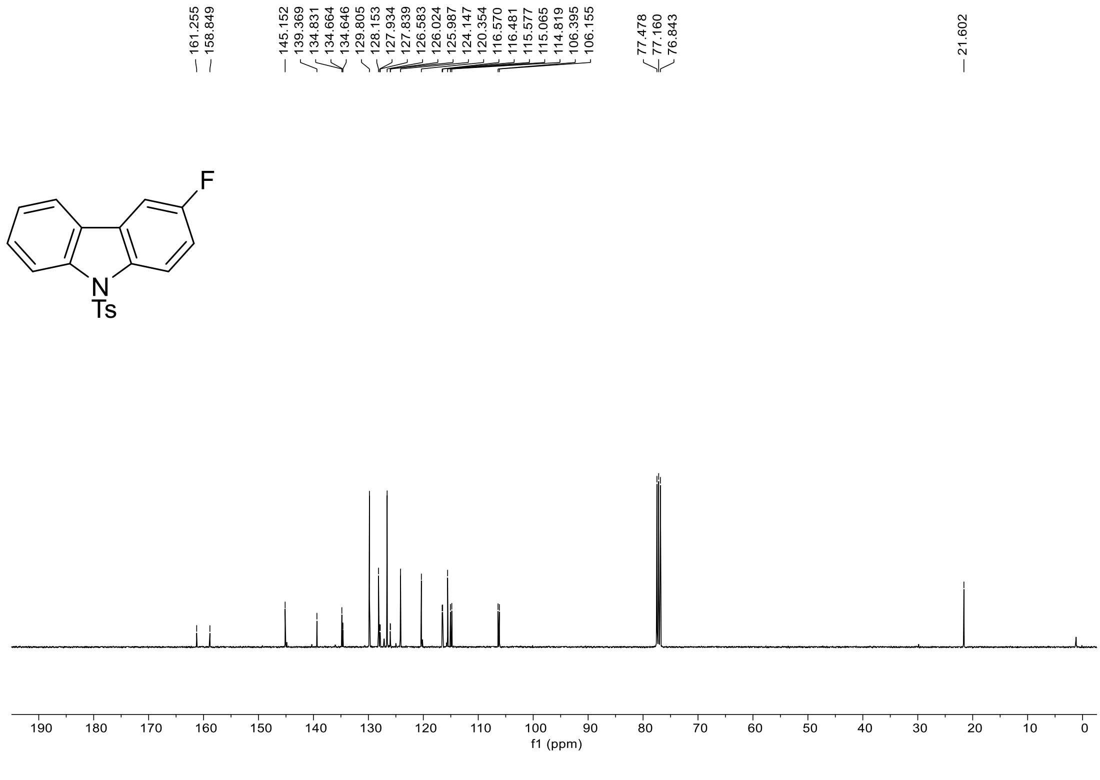
f1 (ppm)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120.354
116.570
116.481
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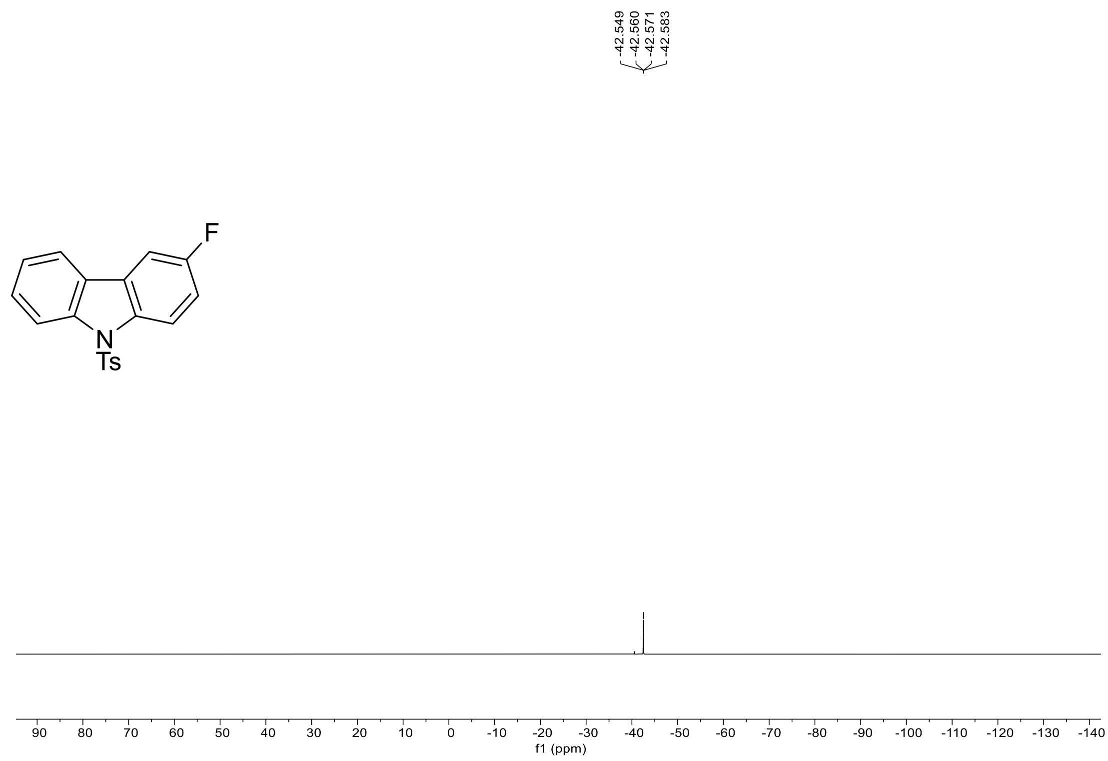
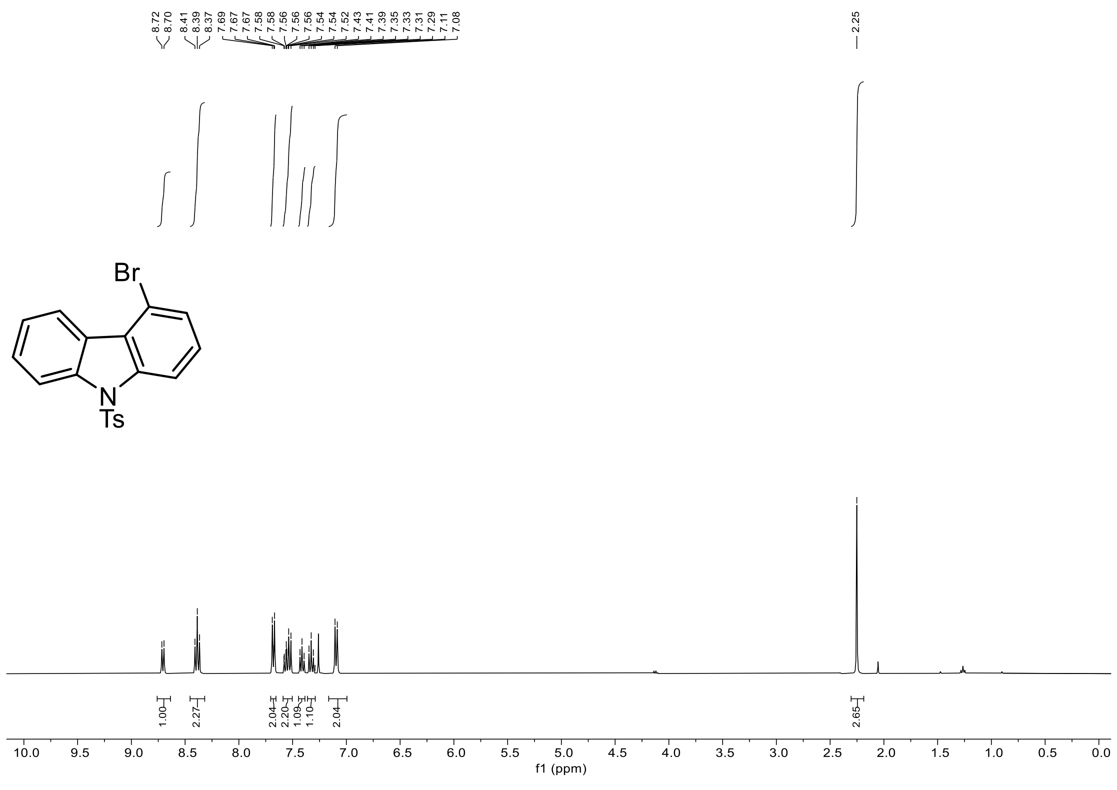
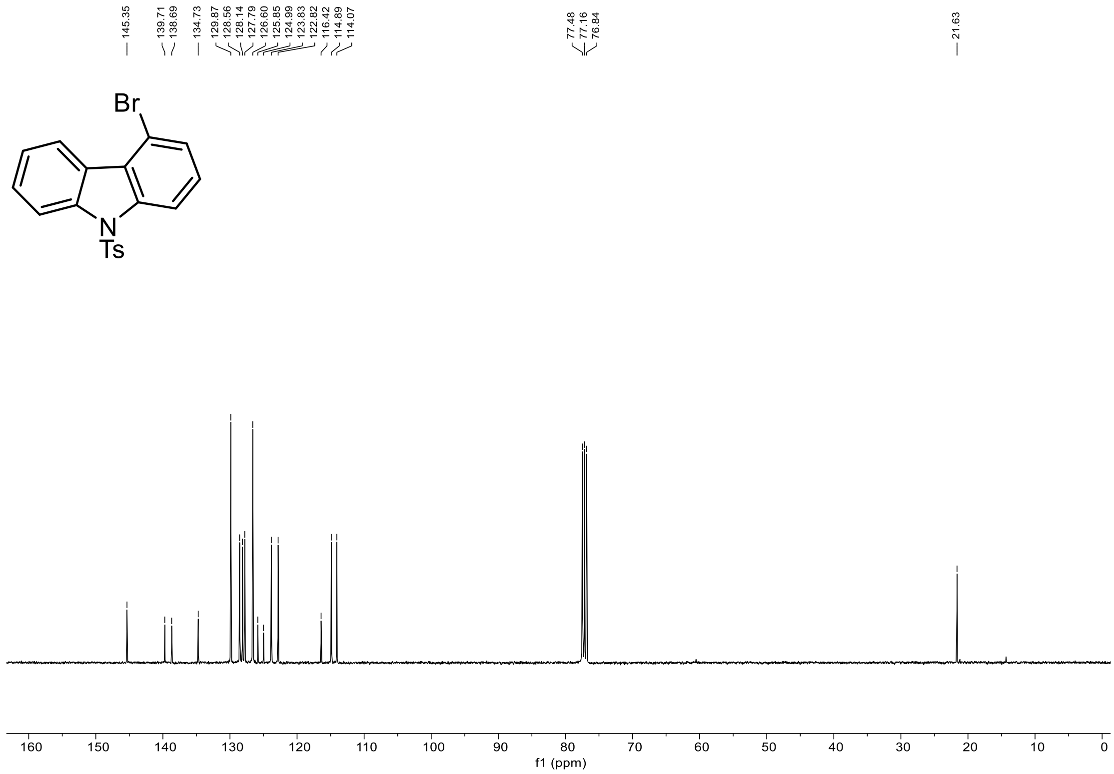
Ts
f1 (ppm)



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114.89
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N
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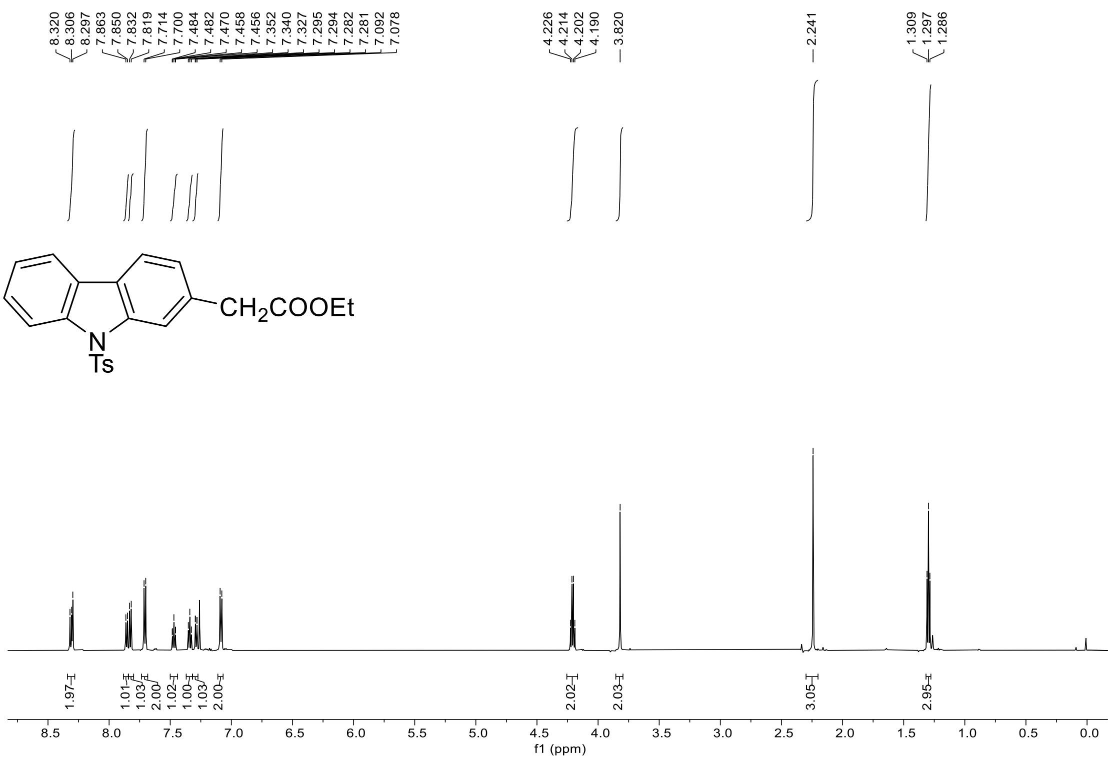
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7.352
7.340
7.327
7.295
7.294
7.282
7.281
7.092
7.078
4.226
4.214
4.202
4.190
3.820
2.241
1.309
1.297
1.286
N
Ts
CH2COOEt
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1.01
1.03
2.00
1.02
1.00
1.03
2.00
2.02
2.03
3.05
2.95
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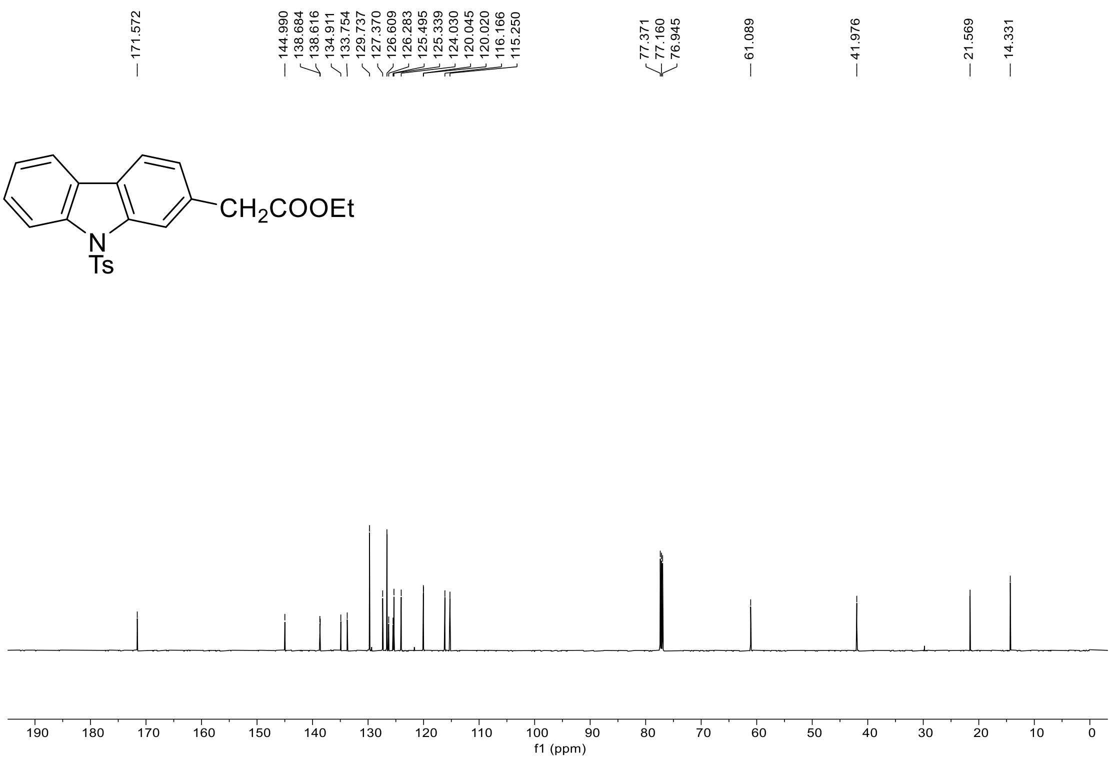
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120.045
120.020
116.166
115.250
77.371
77.160
76.945
61.089
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14.331
CH2COOEt
N
Ts
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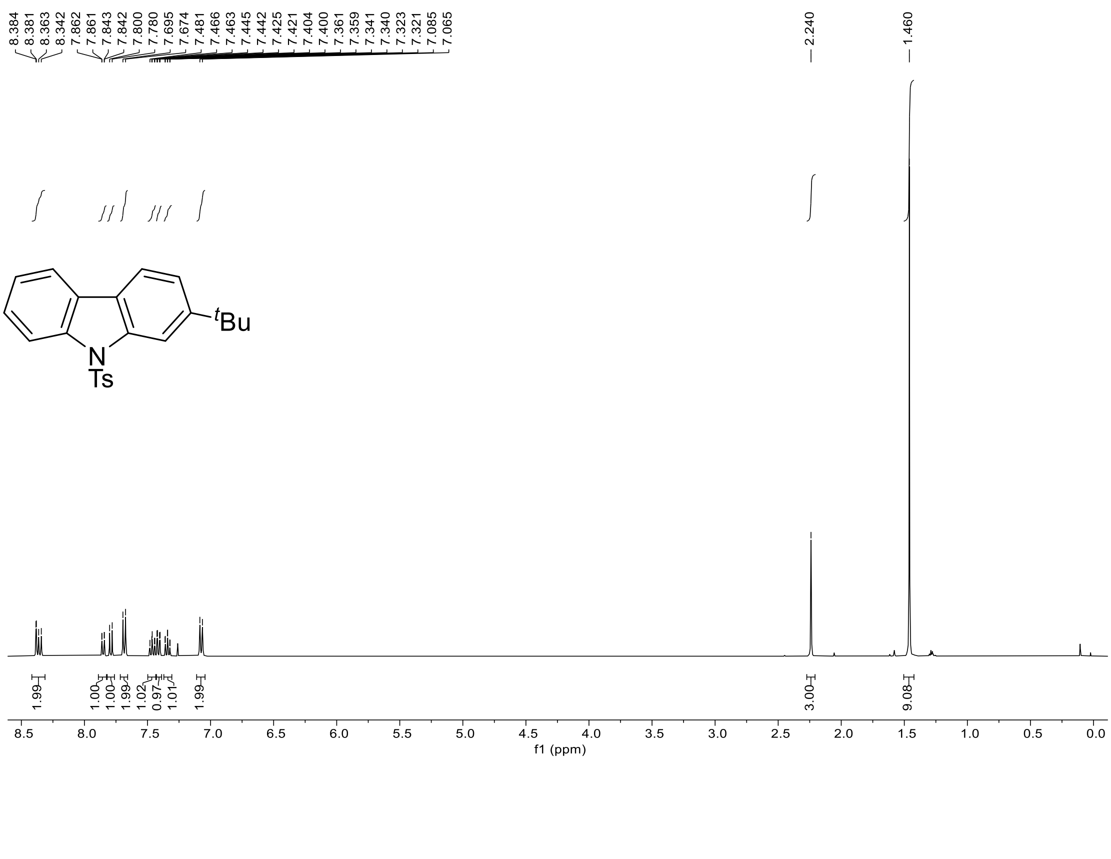
f1 (ppm)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7.463
7.445
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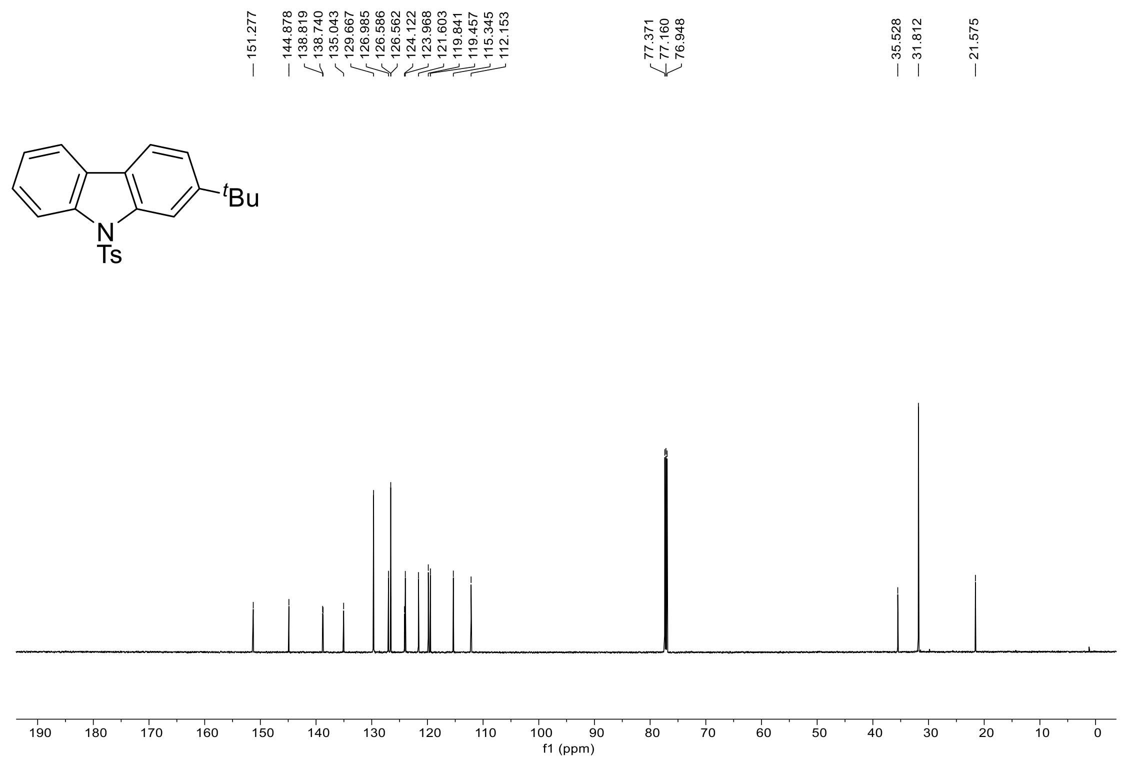
7.425
7.421
7.404
7.400
7.361
7.359
7.341
7.340
7.323
7.321
7.085
7.065
2.240
1.460
tBu
N
Ts
1.99
1.00
1.00
1.99
1.02
0.97
1.01
1.99
3.00
9.08
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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119.841
119.457
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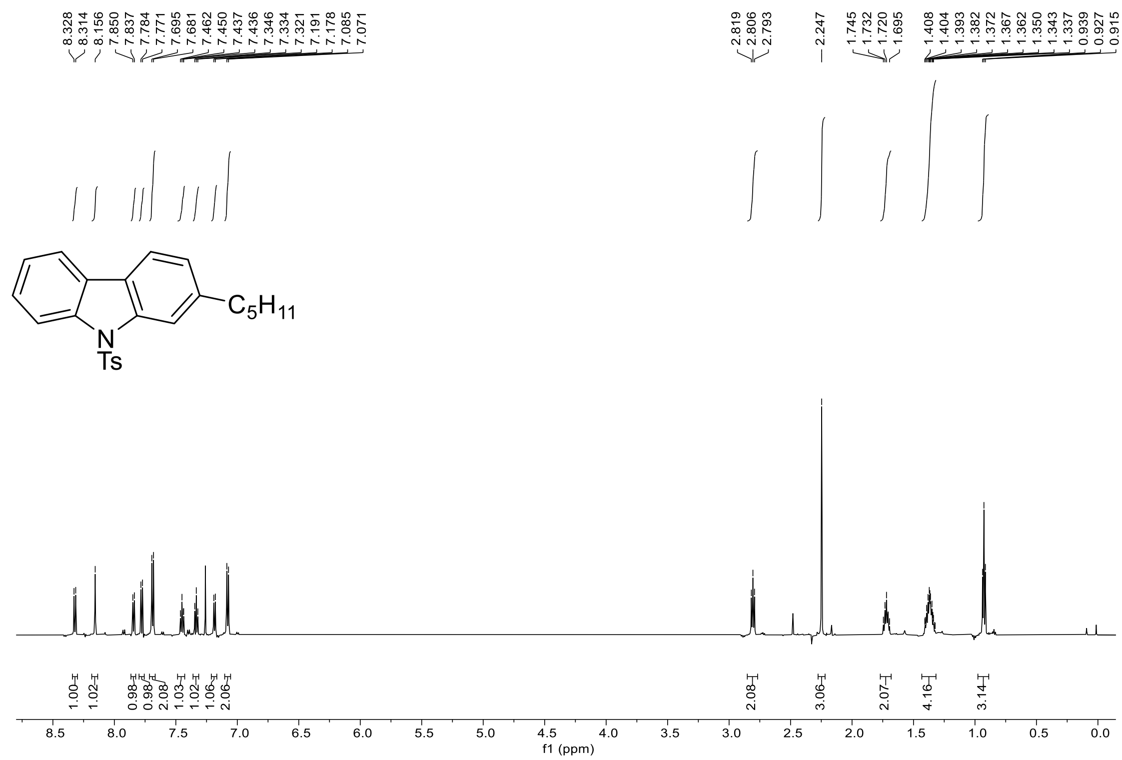
21.575
N
Ts
^{t}Bu
f1 (ppm)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1.382
1.372
1.367
1.362
1.350
1.343
1.337
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0.927
0.915
N
Ts
C_5H_{11}
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1.02
0.98
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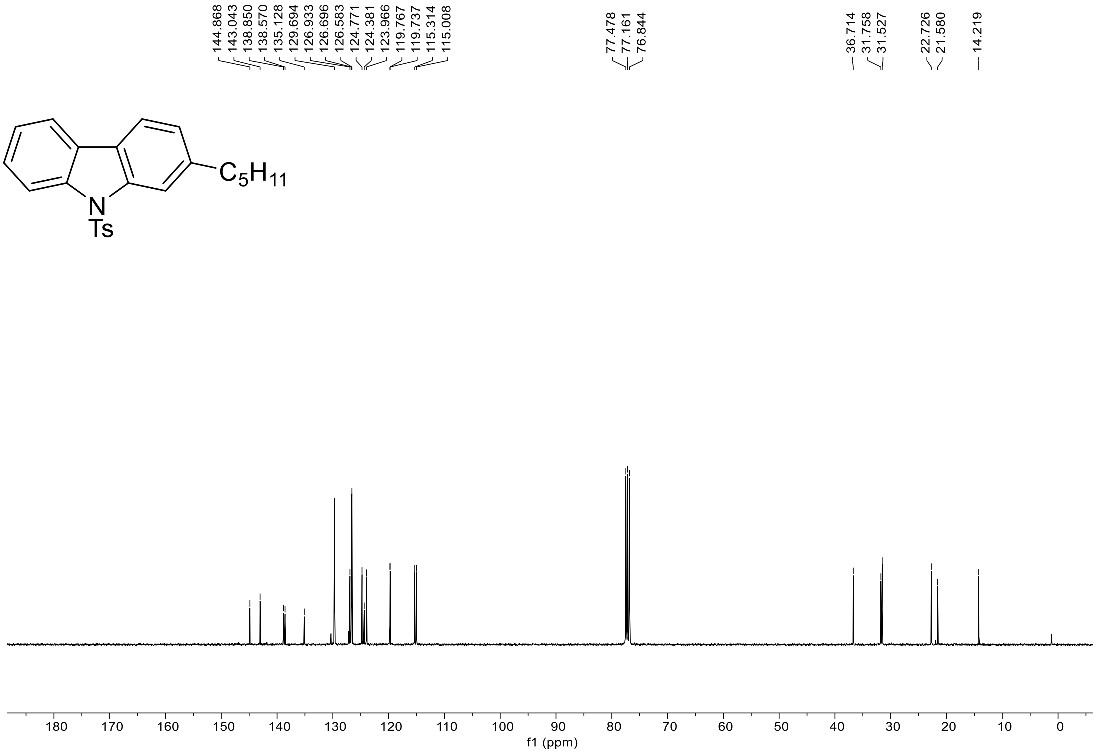
f1 (ppm)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119.767
119.737
115.314
115.008
77.478
77.161
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22.726
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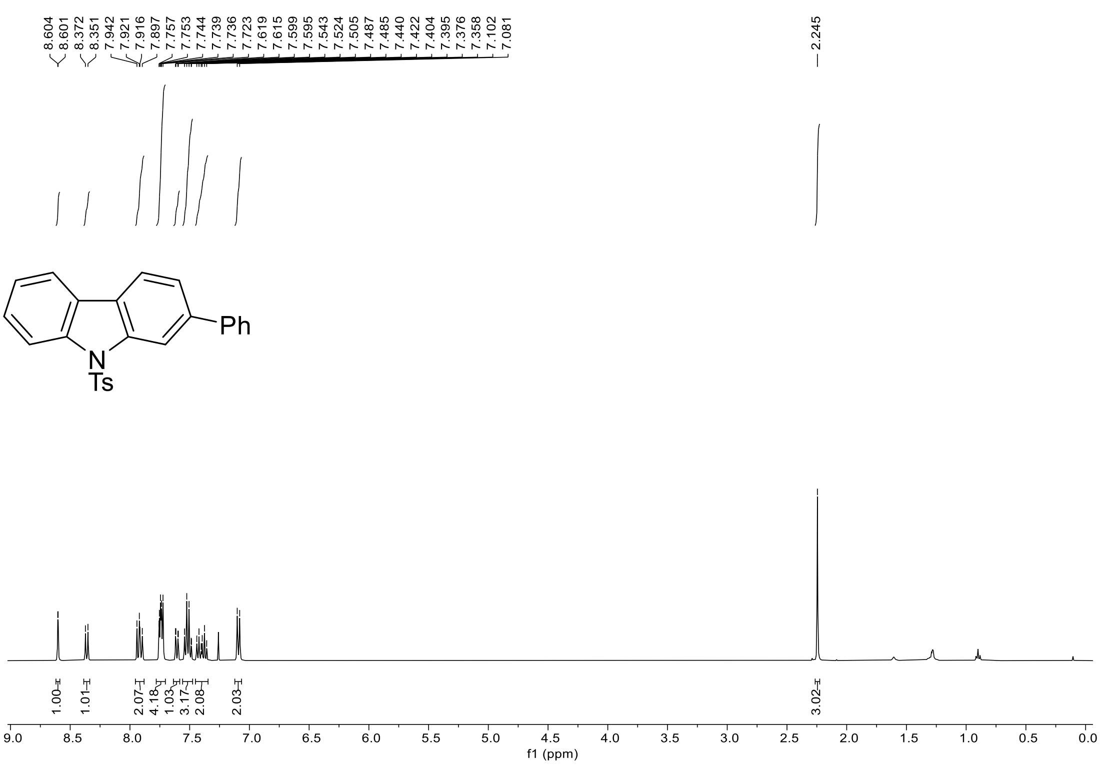
C_5H_{11}
f1 (ppm)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7.739
7.736
7.723
7.619
7.615
7.599
7.595
7.543
7.524
7.505
7.487
7.485
7.440
7.422
7.404
7.395
7.376
7.358
7.102
7.081
2.245
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2.07
4.18
1.03
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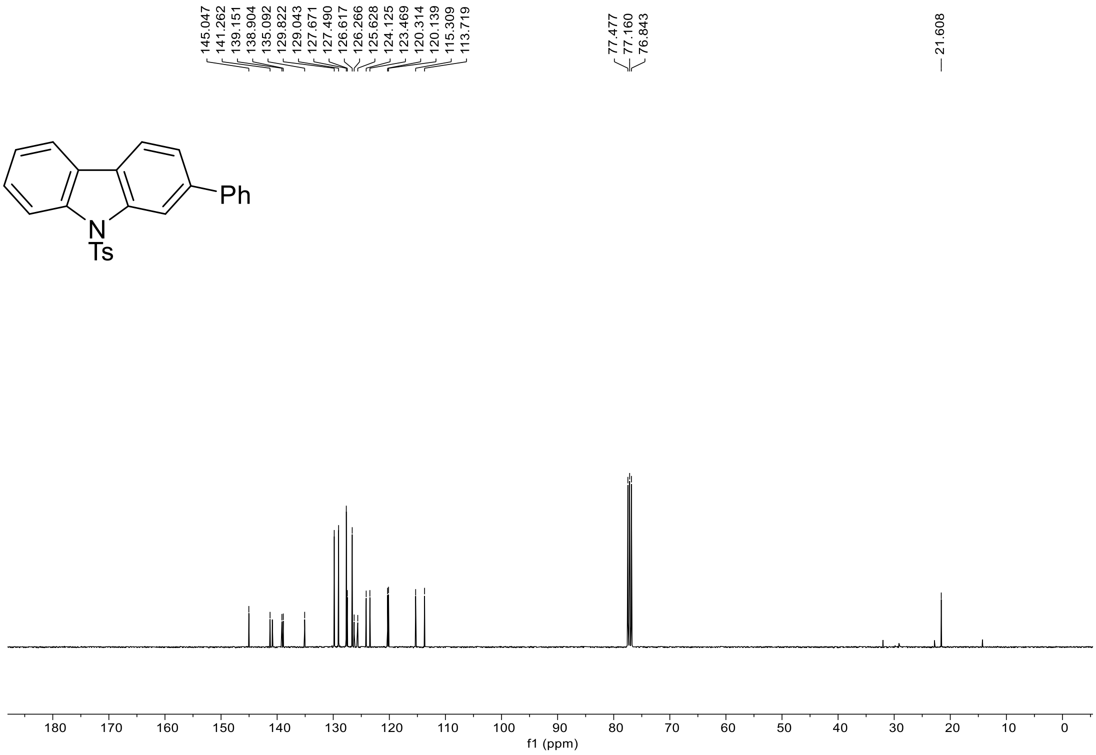
2.08
2.03
3.02
f1 (ppm)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123.469
120.314
120.139
115.309
113.719
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76.843
21.608
Ph
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Ts
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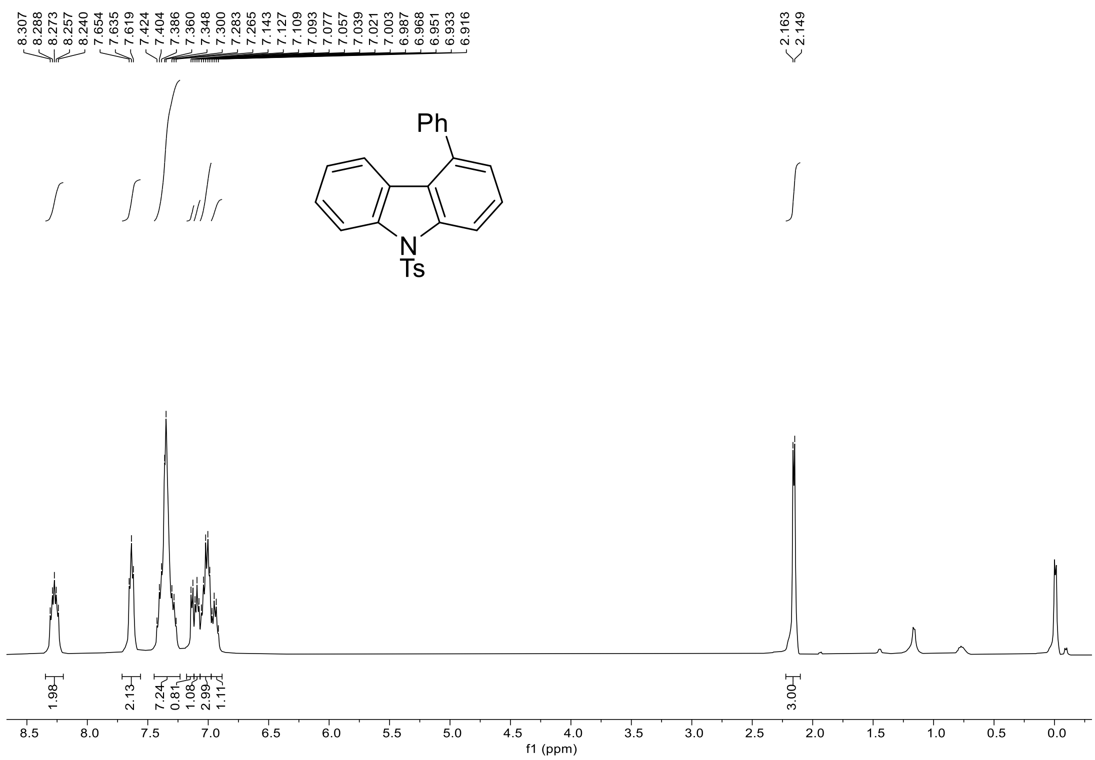
f1 (ppm)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7.348
7.300
7.283
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7.143
7.127
7.109
7.093
7.077
7.057
7.039
7.021
7.003
6.987
6.968
6.951
6.933
6.916
2.163
2.149
Ph
N
Ts
1.98
2.13
7.24
0.81
1.08
2.99
1.11
3.00
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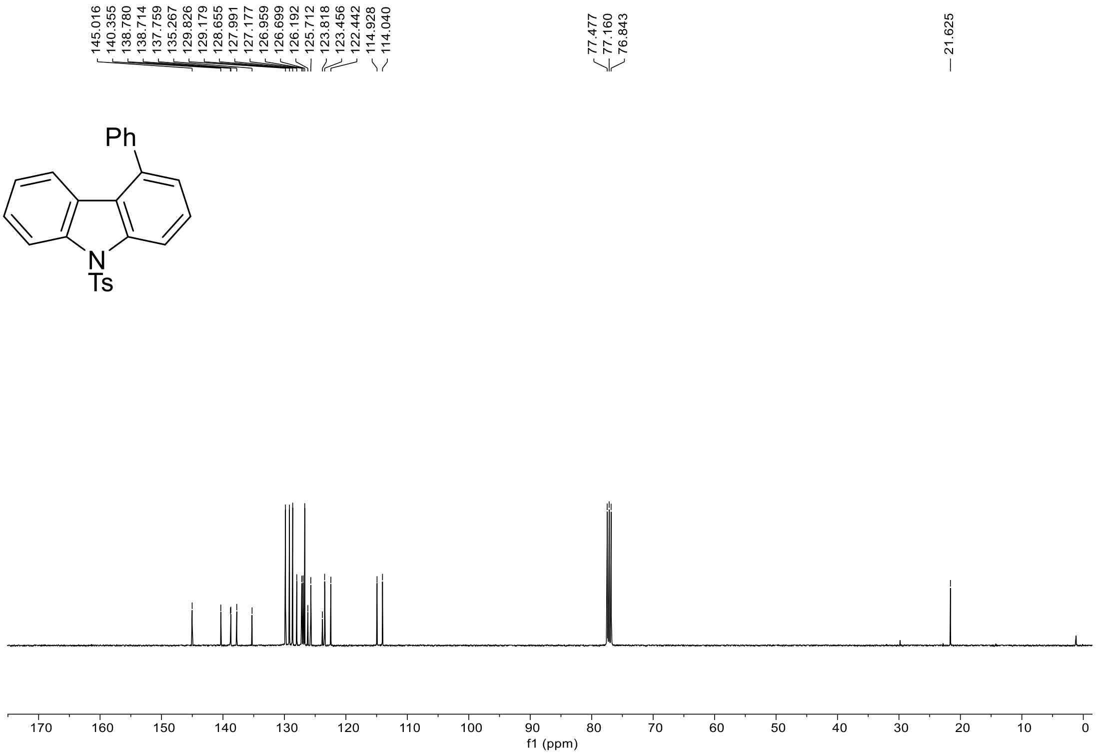
f1 (ppm)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126.699
126.192
125.712
123.818
123.456
122.442
114.928
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77.160
76.843
21.625
Ph
N
Ts
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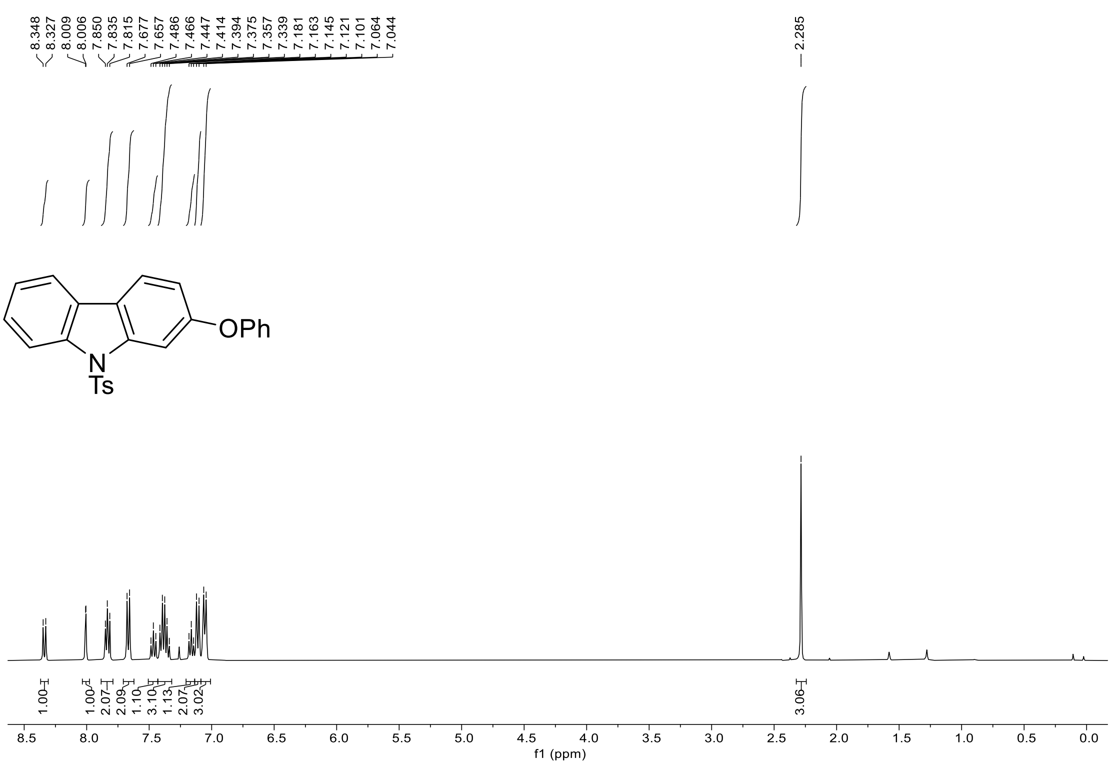
f1 (ppm)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7.486
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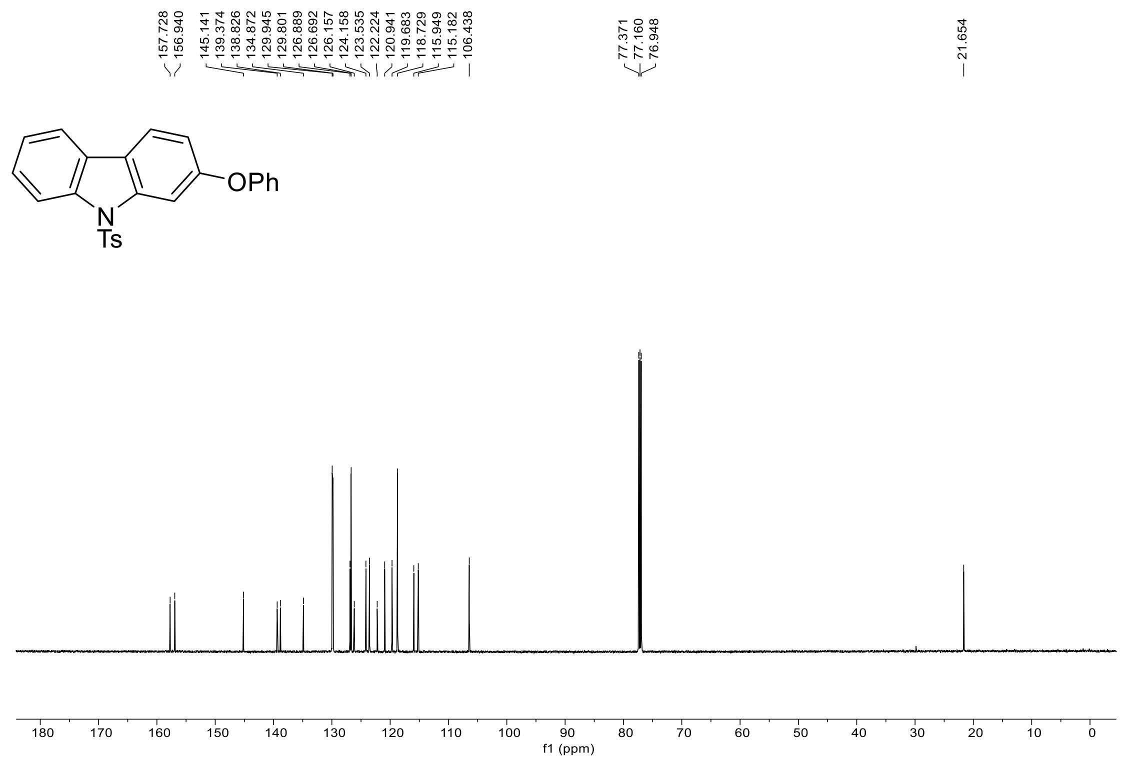
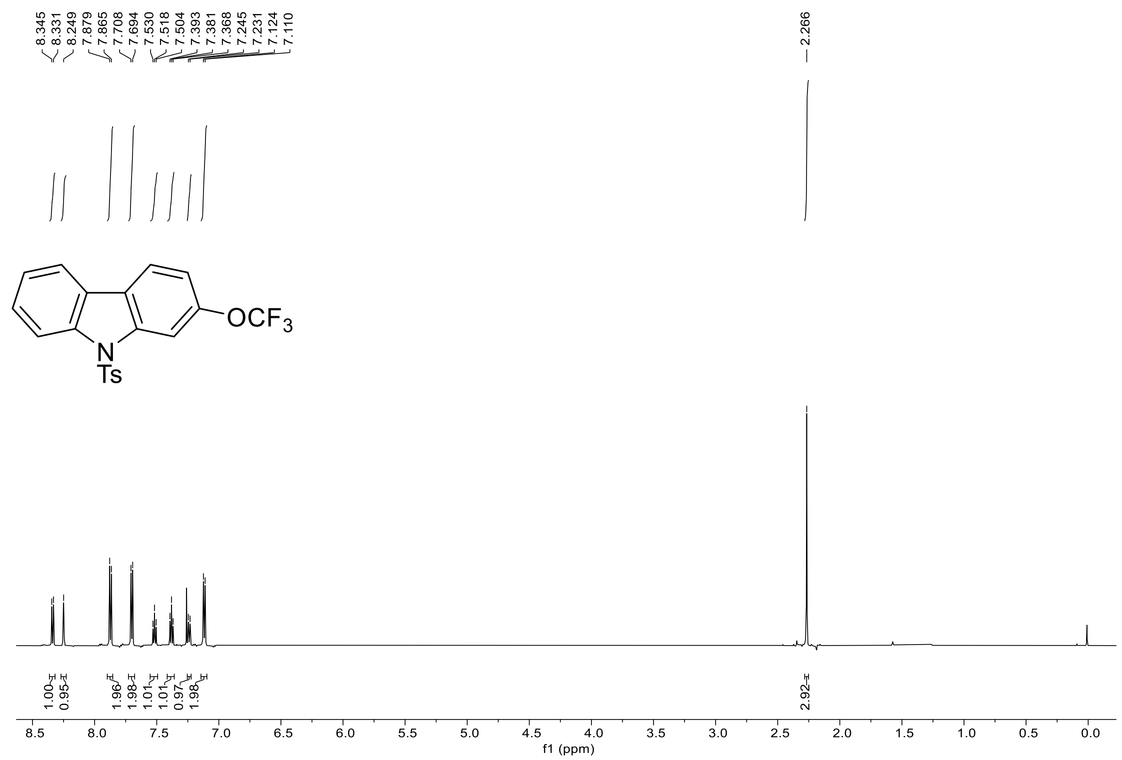
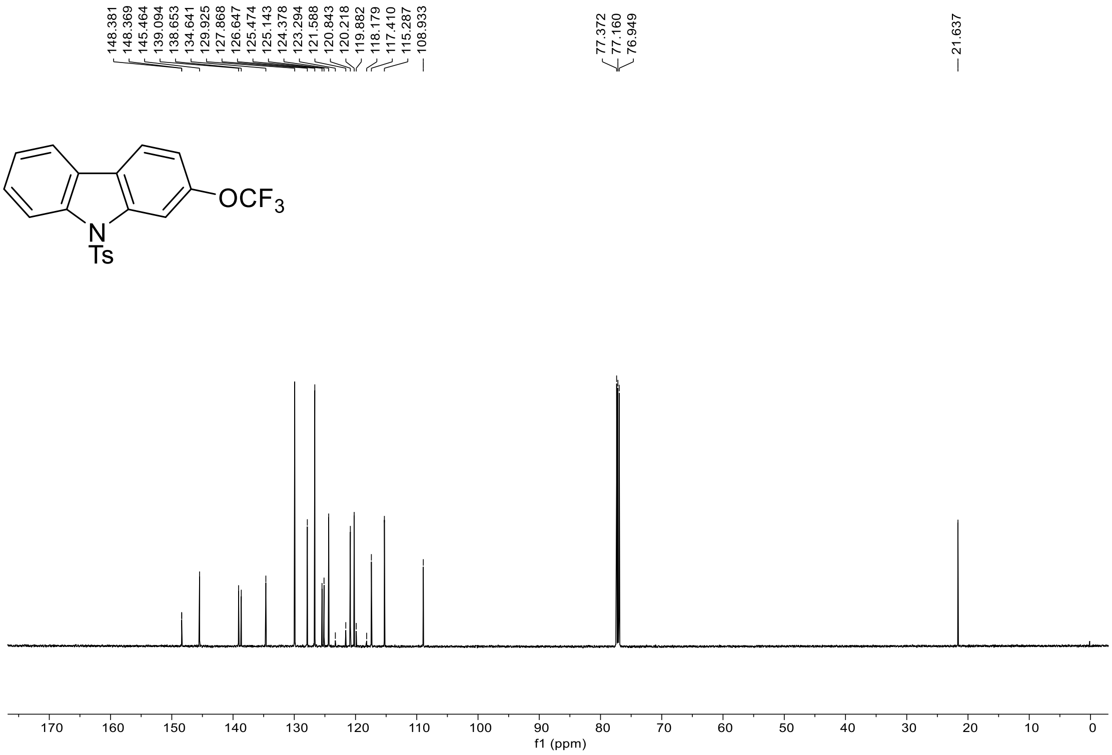
7.447
7.414
7.394
7.375
7.357
7.339
7.181
7.163
7.145
7.121
7.101
7.064
7.044
2.285
OPh
N
Ts
1.00
1.00
2.07
2.09
1.10
3.10
1.13
2.07
3.02
3.06
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



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125.143
124.378
123.294
121.588
120.843
120.218
119.882
118.179
117.410
115.287
108.933
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76.949
21.637
OCF3
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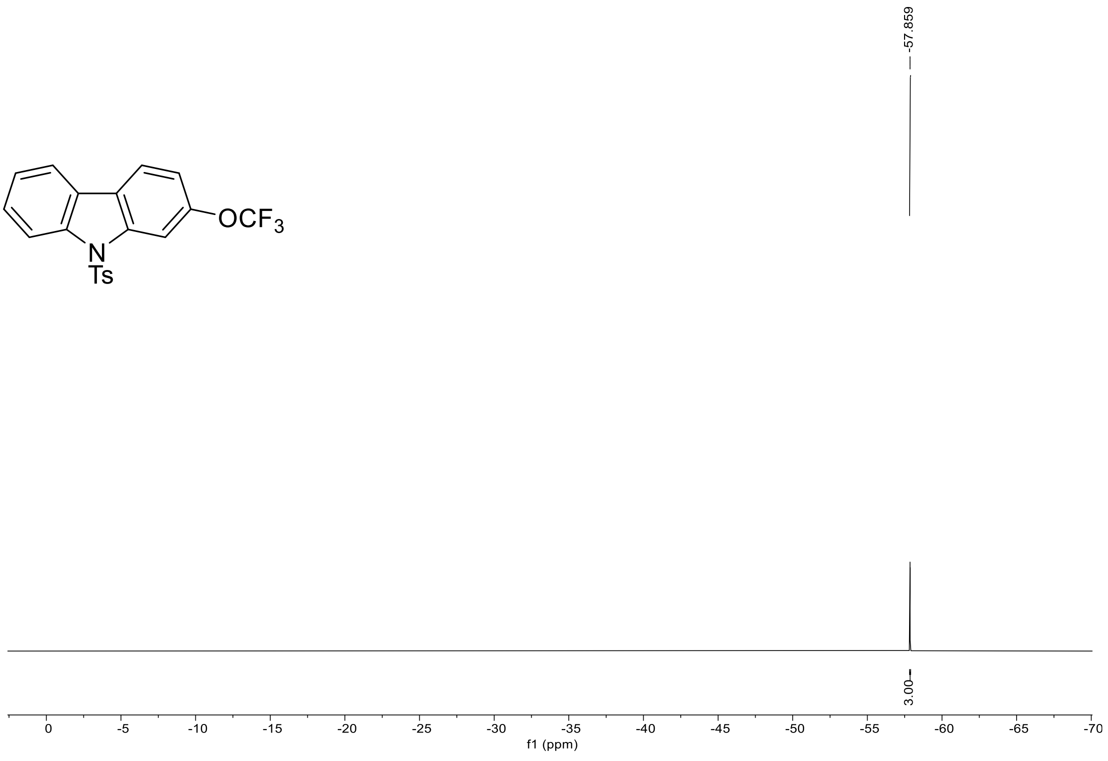
Ts
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70
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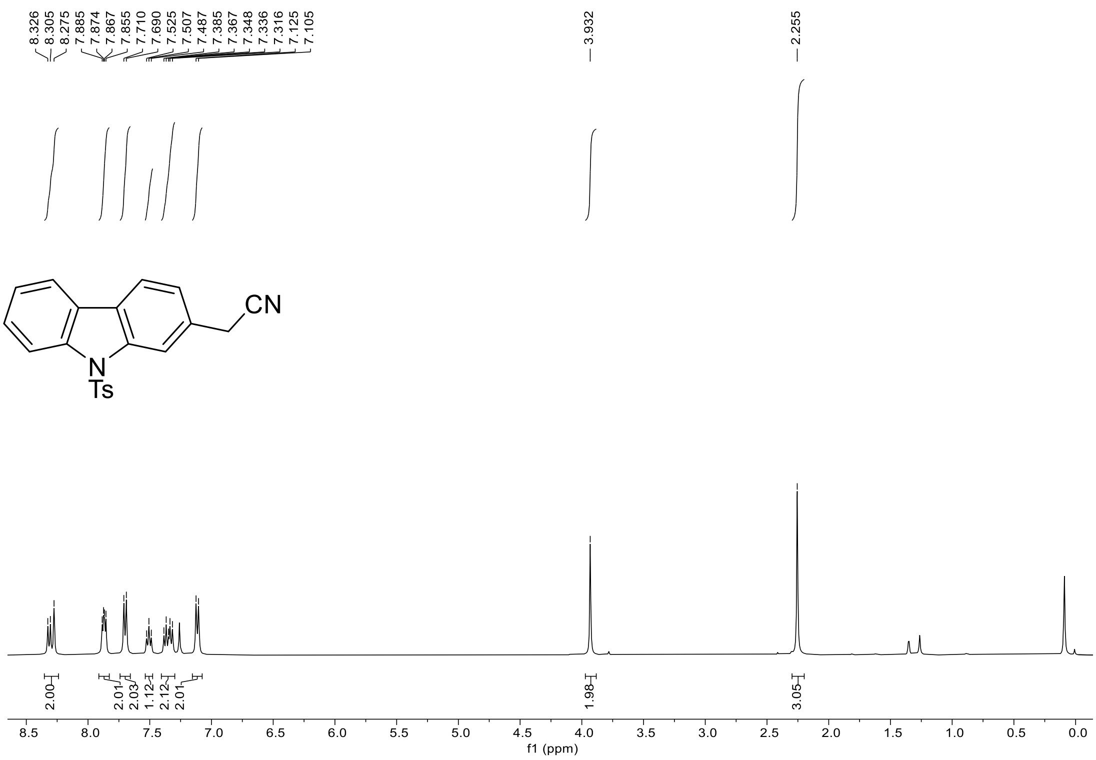
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8.305
8.275
7.885
7.874
7.867
7.855
7.710
7.690
7.525
7.507
7.487
7.385
7.367
7.348
7.336
7.316
7.125
7.105
3.932
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CN
N
Ts
2.00
2.01
2.03
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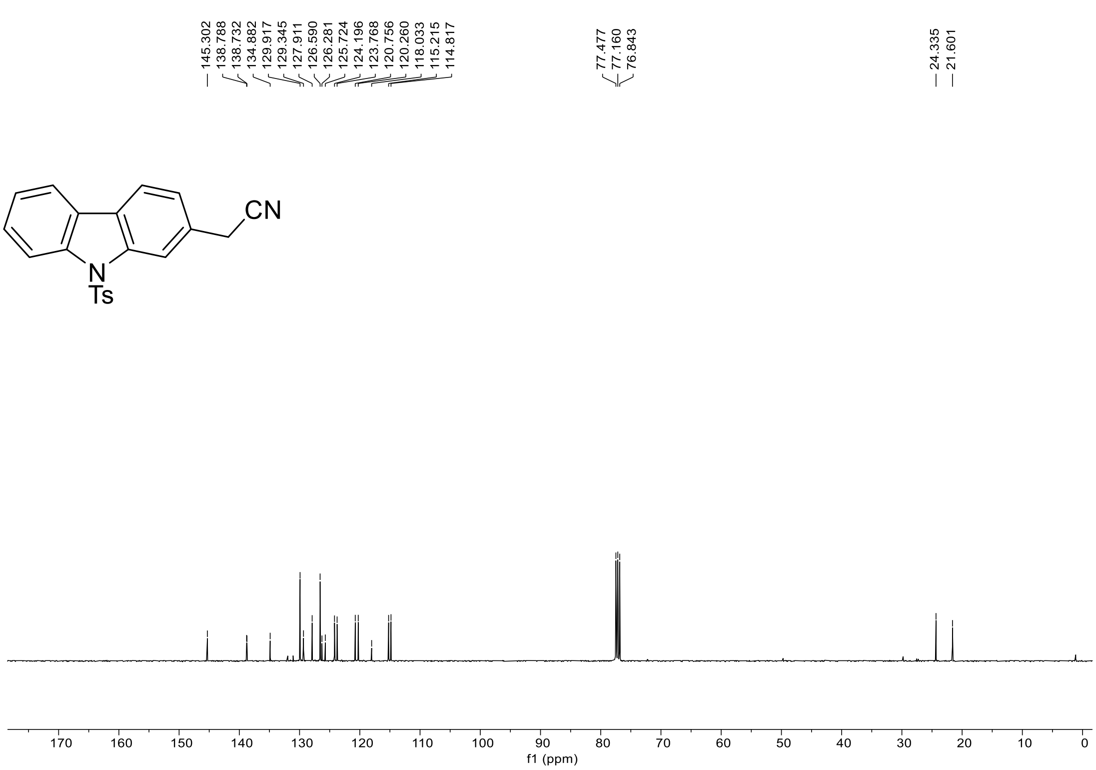
2.12
2.01
1.98
3.05
f1 (ppm)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138.732
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129.917
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126.590
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125.724
124.196
123.768
120.756
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114.817
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77.160
76.843
24.335
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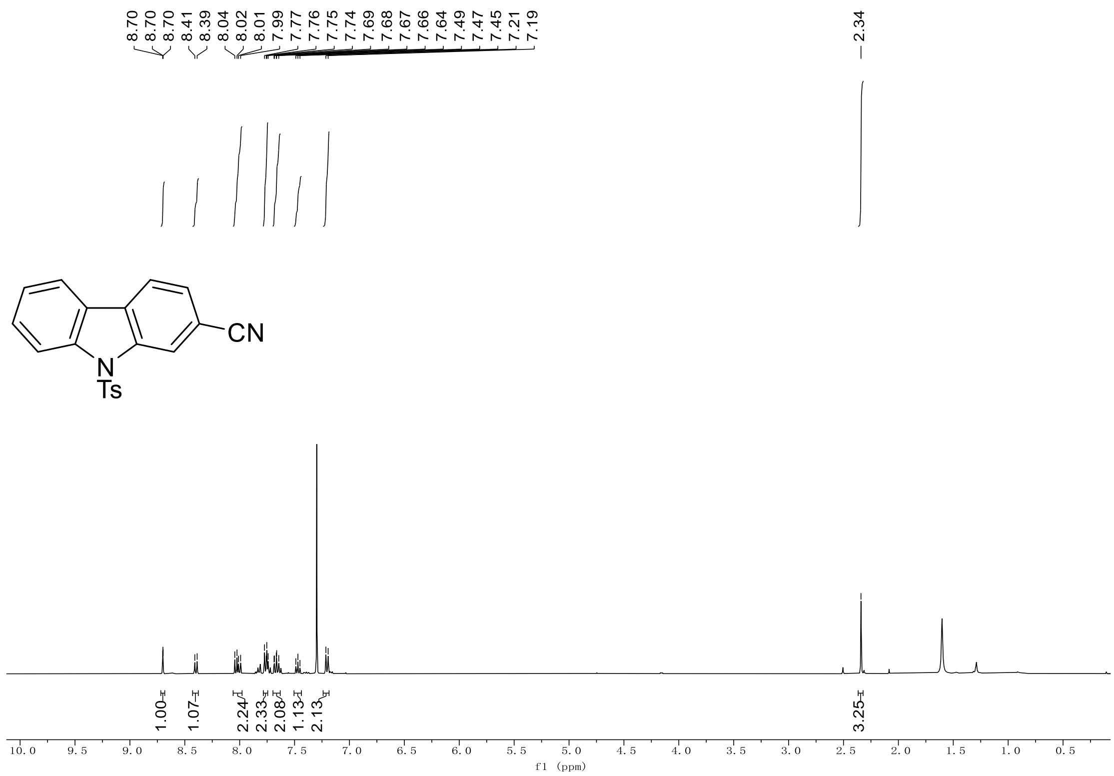
CN
N
Ts
f1 (ppm)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8.04
8.02
8.01
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7.75
7.74
7.69
7.68
7.67
7.66
7.64
7.49
7.47
7.45
7.21
7.19
2.34
CN
N
Ts
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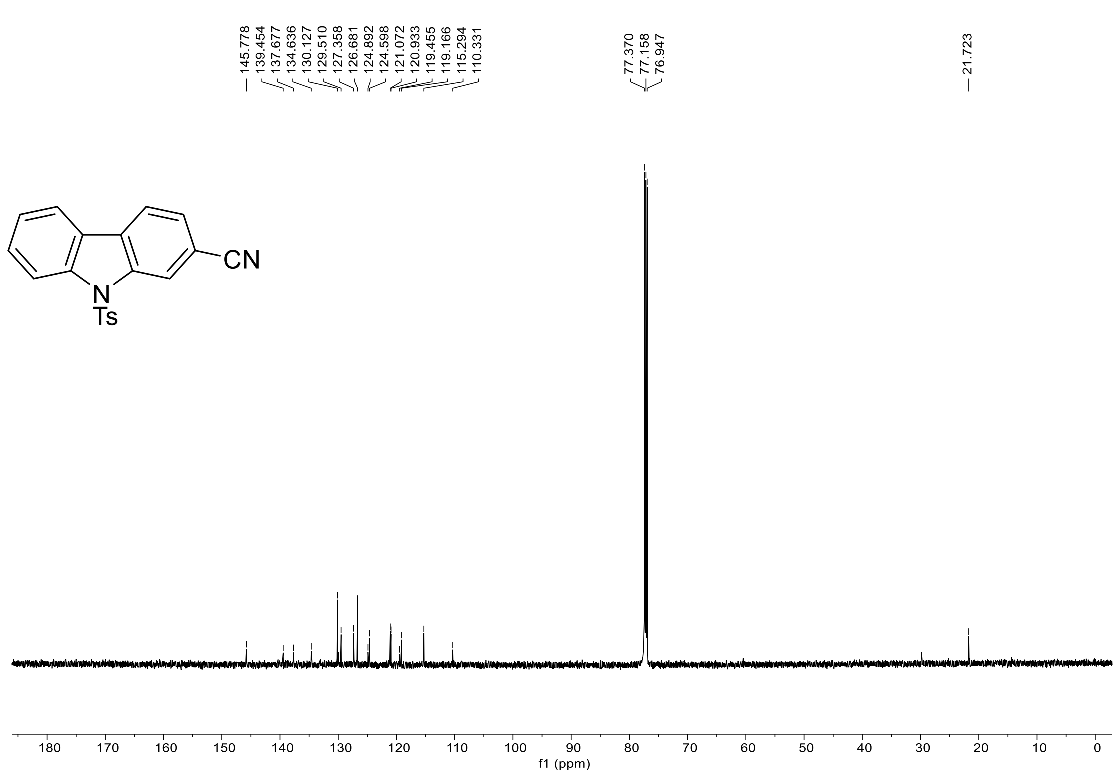
1.07
2.24
2.33
2.08
1.13
2.13
3.25
f1 (ppm)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126.681
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121.072
120.933
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115.294
110.331
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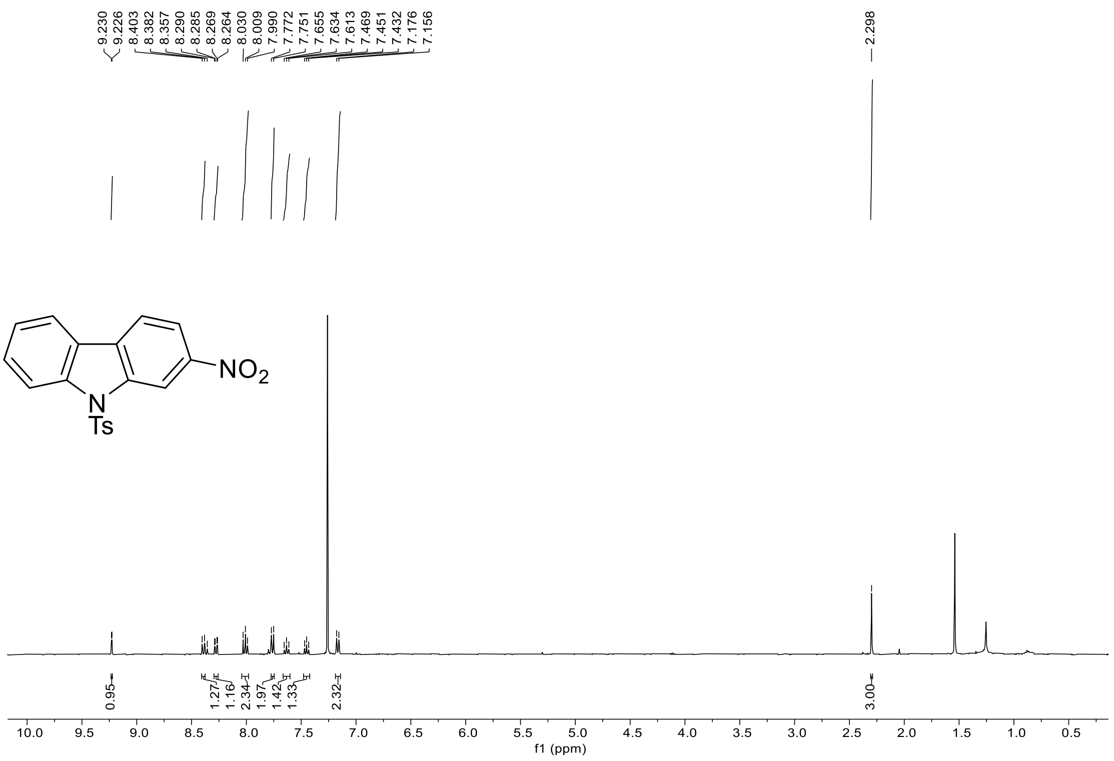
21.723
CN
N
Ts
f1 (ppm)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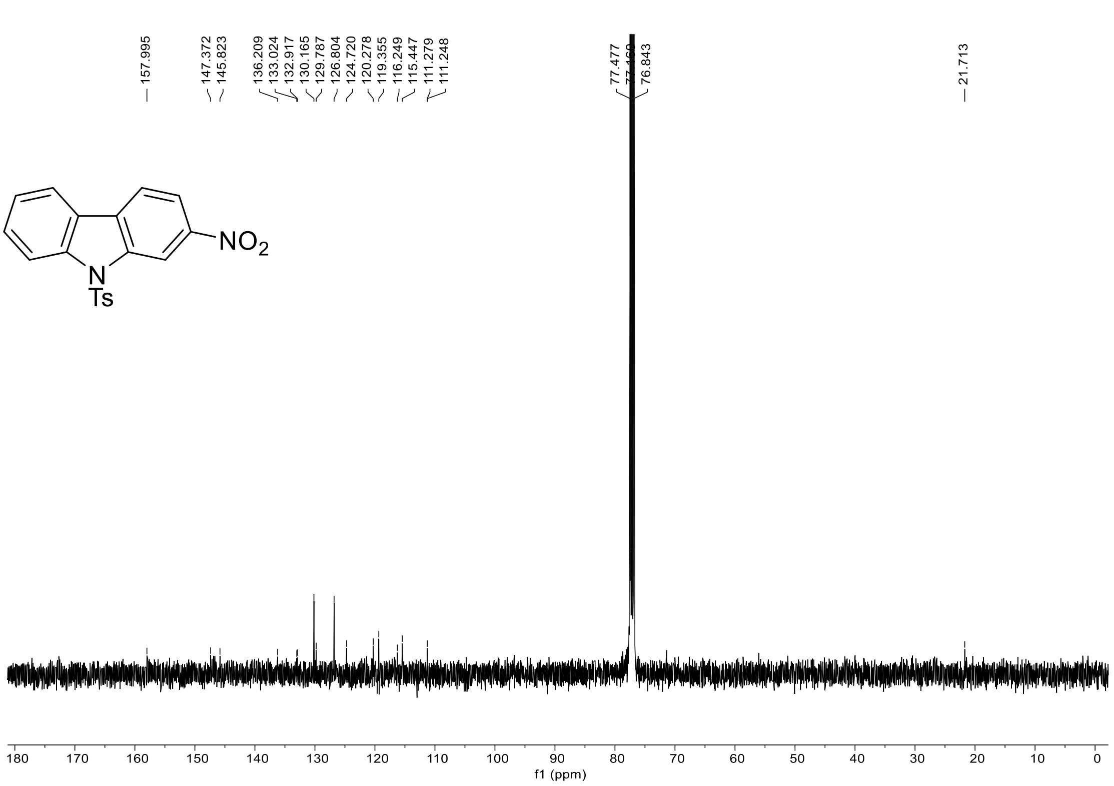
8.285
8.269
8.264
8.030
8.009
7.990
7.772
7.751
7.655
7.634
7.613
7.469
7.451
7.432
7.176
7.156
2.298
NO2
N
Ts
0.95
1.27
1.16
2.34
1.97
1.42
1.33
2.32
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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124.720
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116.249
115.447
111.279
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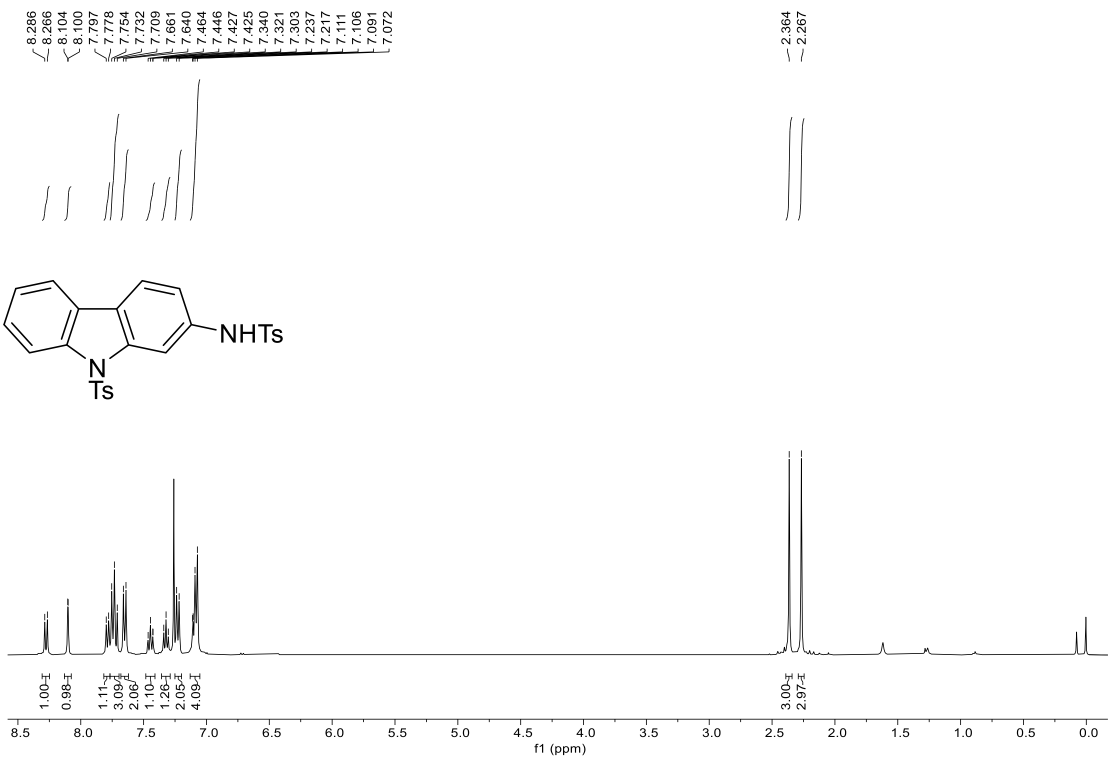
77.477
76.843
21.713
NO2
N
Ts
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.100
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7.732
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7.661
7.640
7.464
7.446
7.427
7.425
7.340
7.321
7.303
7.237
7.217
7.111
7.106
7.091
7.072
2.364
2.267
NHTs
N
Ts
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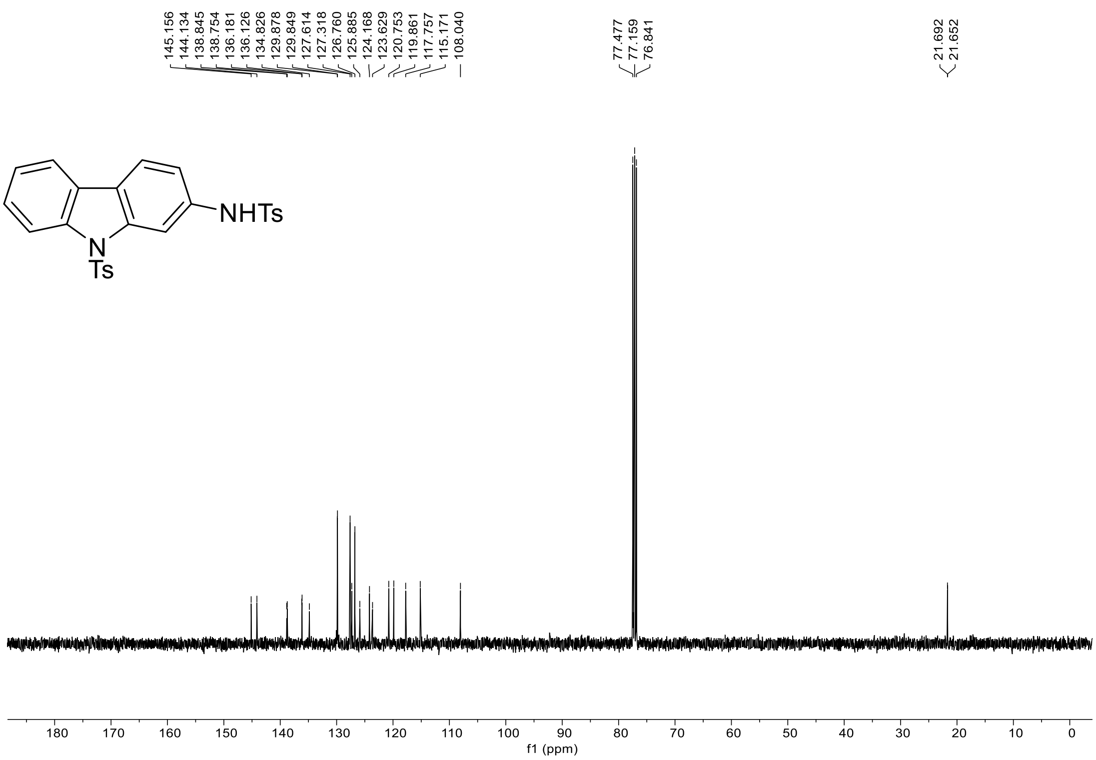
1.11
3.09
2.06
1.10
1.26
2.05
4.09
3.00
2.97
f1 (ppm)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125.885
124.168
123.629
120.753
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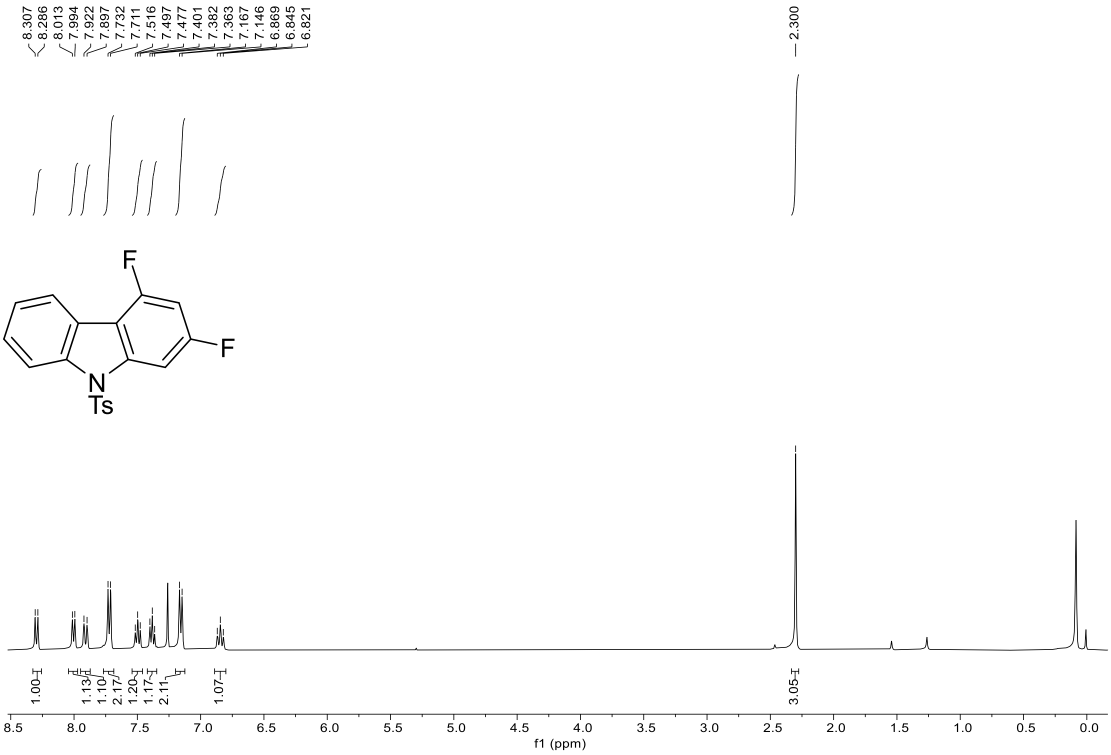
21.652
NHTs
N
Ts
f1 (ppm)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7.497
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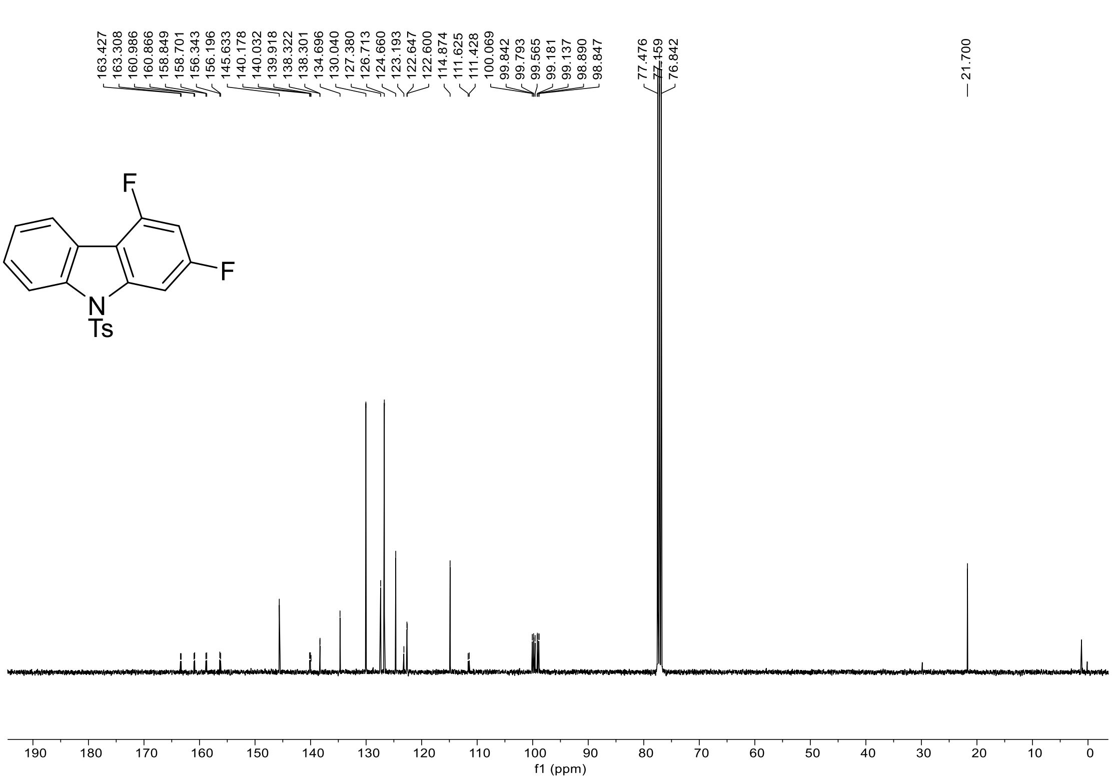
7.363
7.167
7.146
6.869
6.845
6.821
2.300
F
F
N
Ts
1.00
1.13
1.10
2.17
1.20
1.17
2.11
1.07
3.05
f1 (ppm)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138.322
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134.696
130.040
127.380
126.713
124.660
123.193
122.647
122.600
114.874
111.625
111.428
100.069
99.842
99.793
99.565
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98.847
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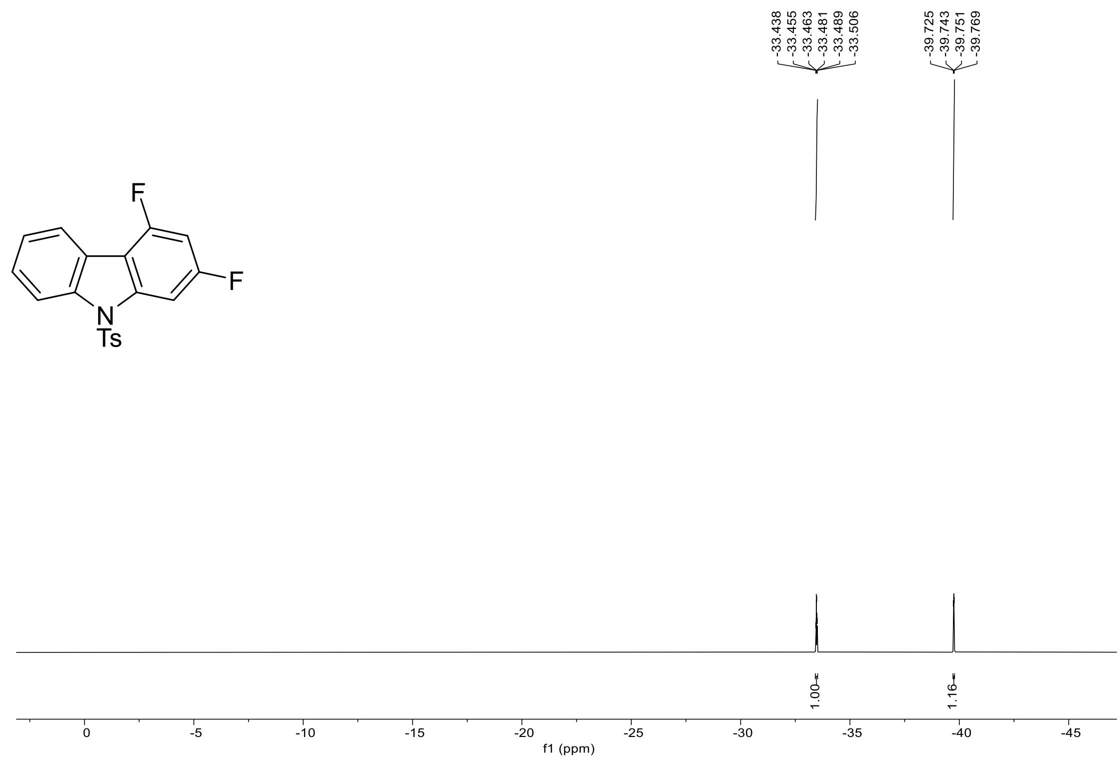
76.842
21.700
F
F
N
Ts
f1 (ppm)


F
F
N
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-30
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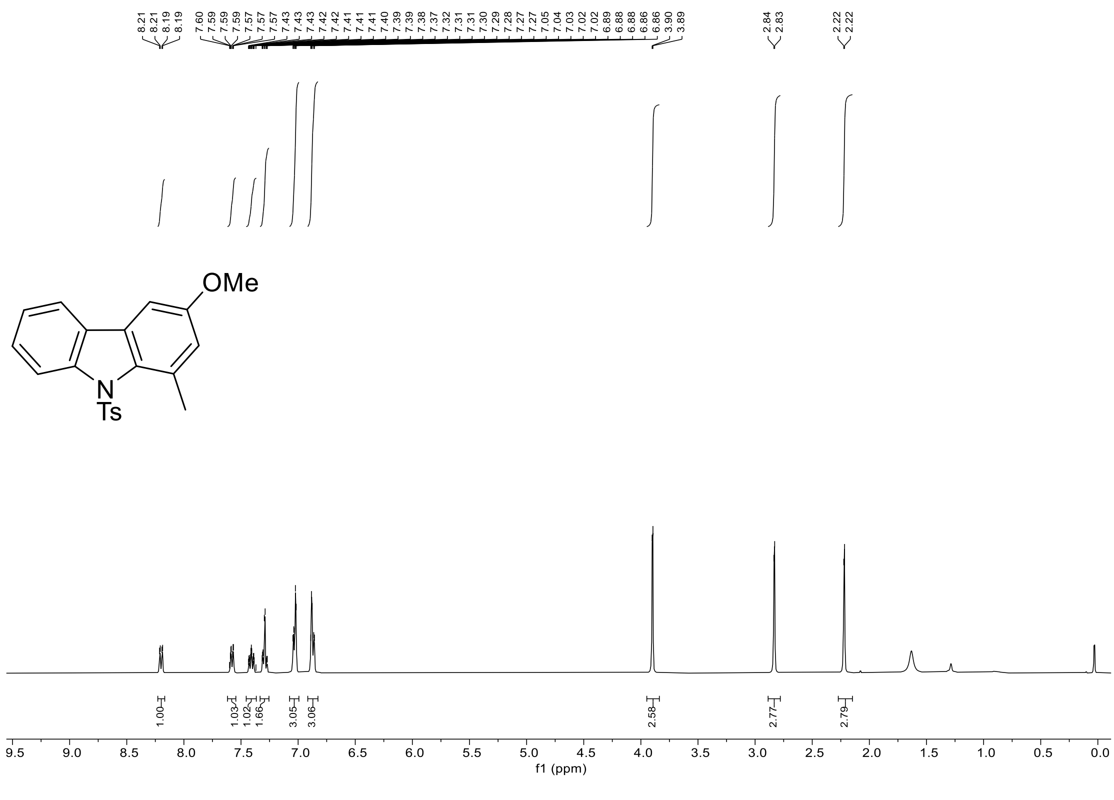
-45
f1 (ppm)


OMe
N
Ts
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7.59
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7.57
7.43
7.43
7.43
7.42
7.42
7.41
7.41
7.41
7.40
7.39
7.39
7.38
7.37
7.32
7.31
7.31
7.30
7.29
7.28
7.27
7.27
7.05
7.04
7.03
7.02
7.02
6.89
6.88
6.88
6.86
6.86
3.90
3.89
2.84
2.83
2.22
2.22
1.00
1.03
1.02
1.66
3.05
3.06
2.58
2.77
2.79
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
5.5
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2.5
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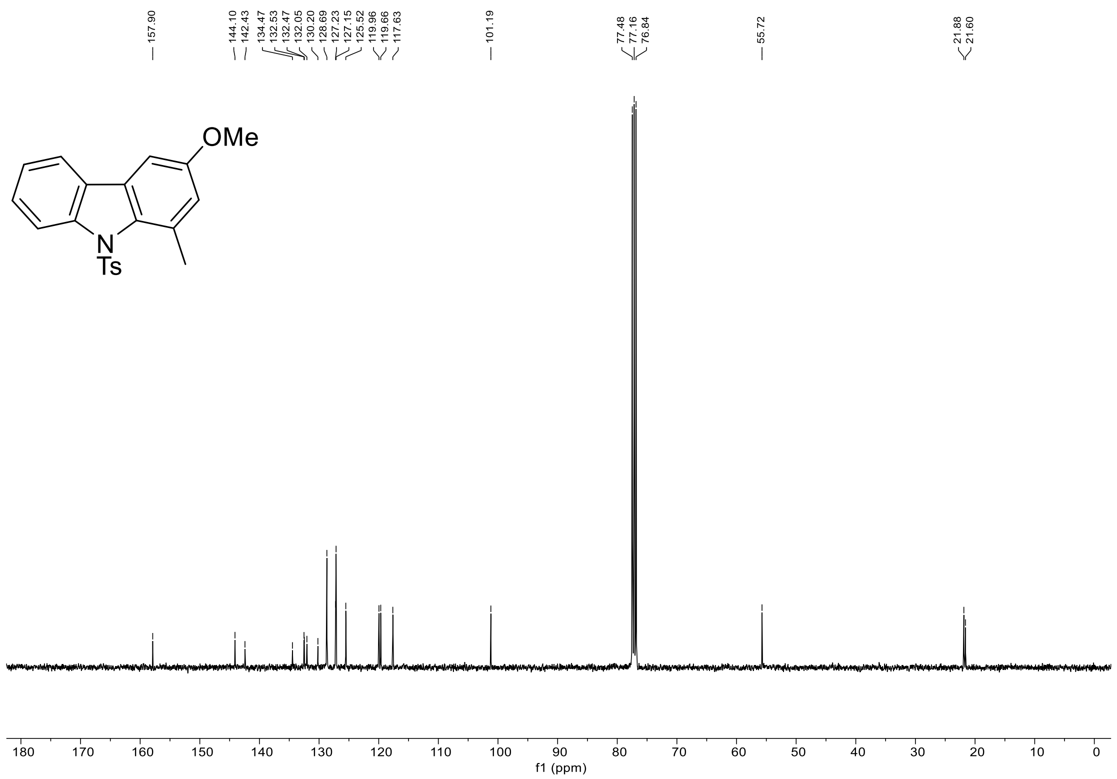
0.0
f1 (ppm)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119.96
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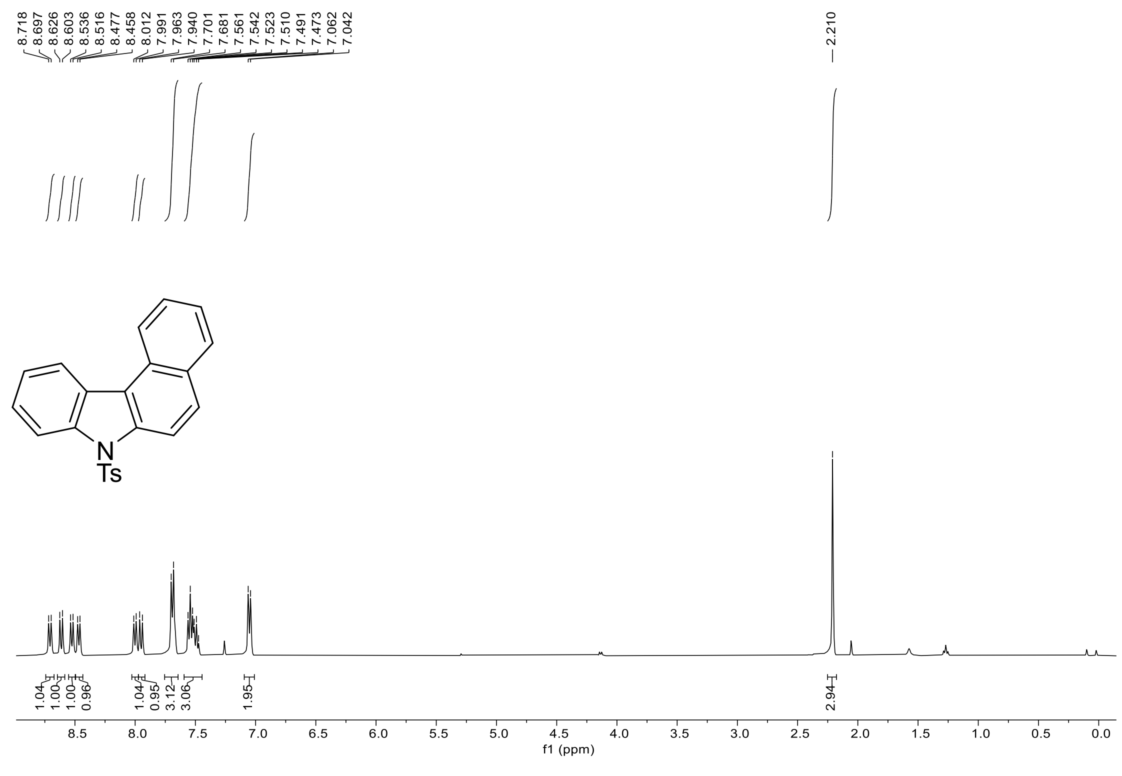
55.72
21.88
21.60
OMe
N
Ts
f1 (ppm)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7.963
7.940
7.701
7.681
7.561
7.542
7.523
7.510
7.491
7.473
7.062
7.042
2.210
N
Ts
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1.00
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1.04
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3.06
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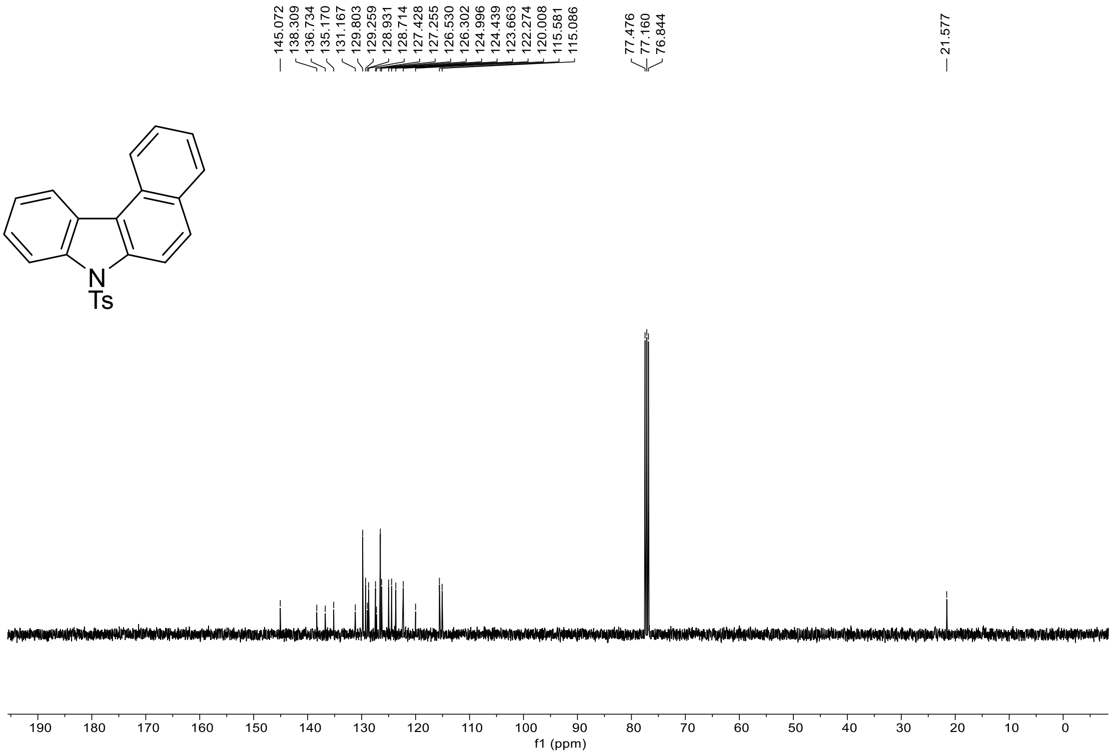
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126.302
124.996
124.439
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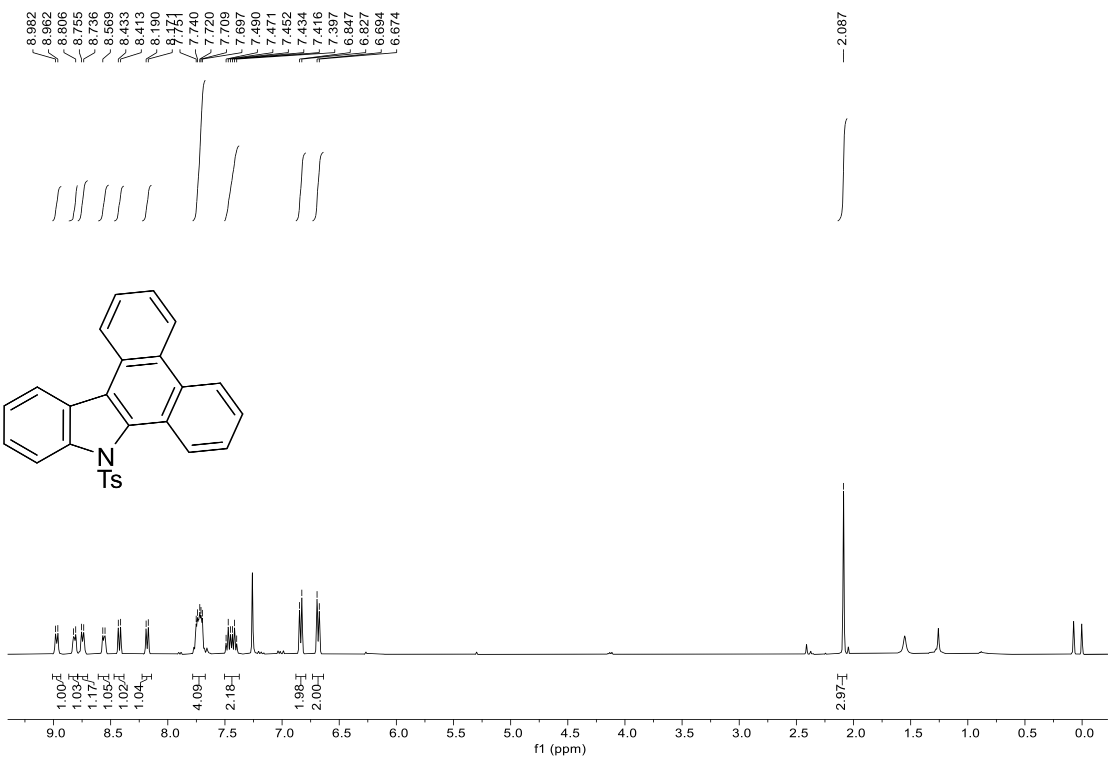
76.844
21.577
N
Ts
f1 (ppm)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7.720
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7.490
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6.847
6.827
6.694
6.674
2.087
N
Ts
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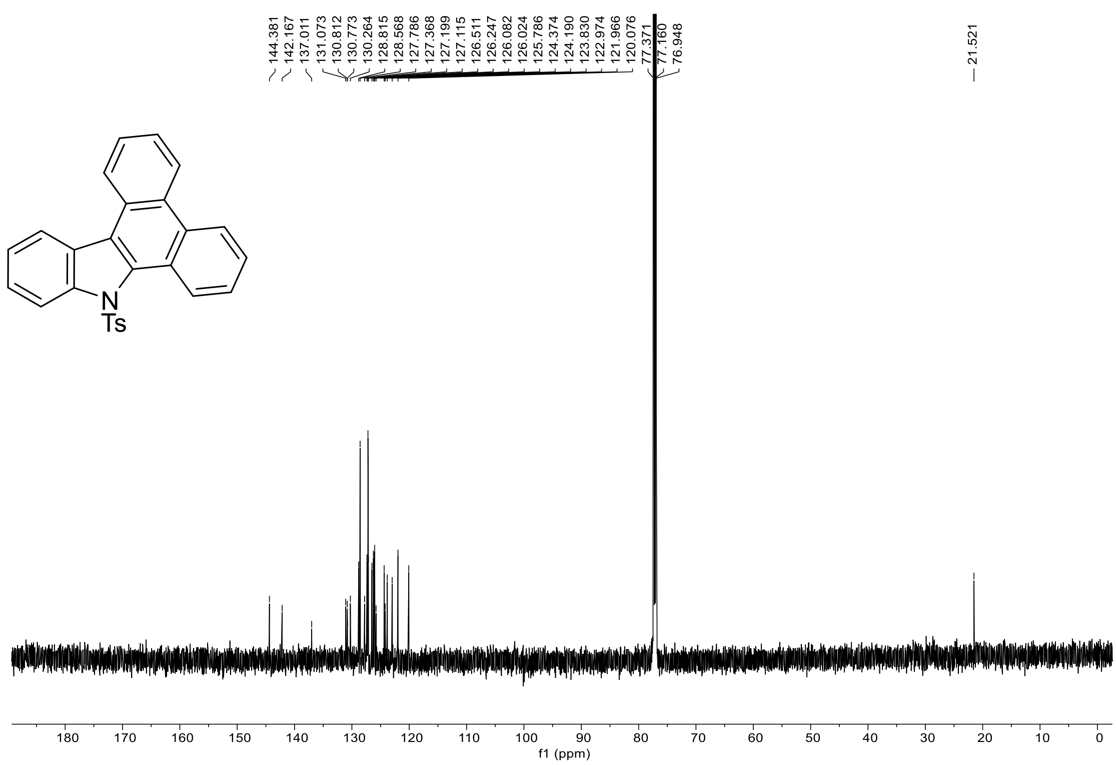
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127.115
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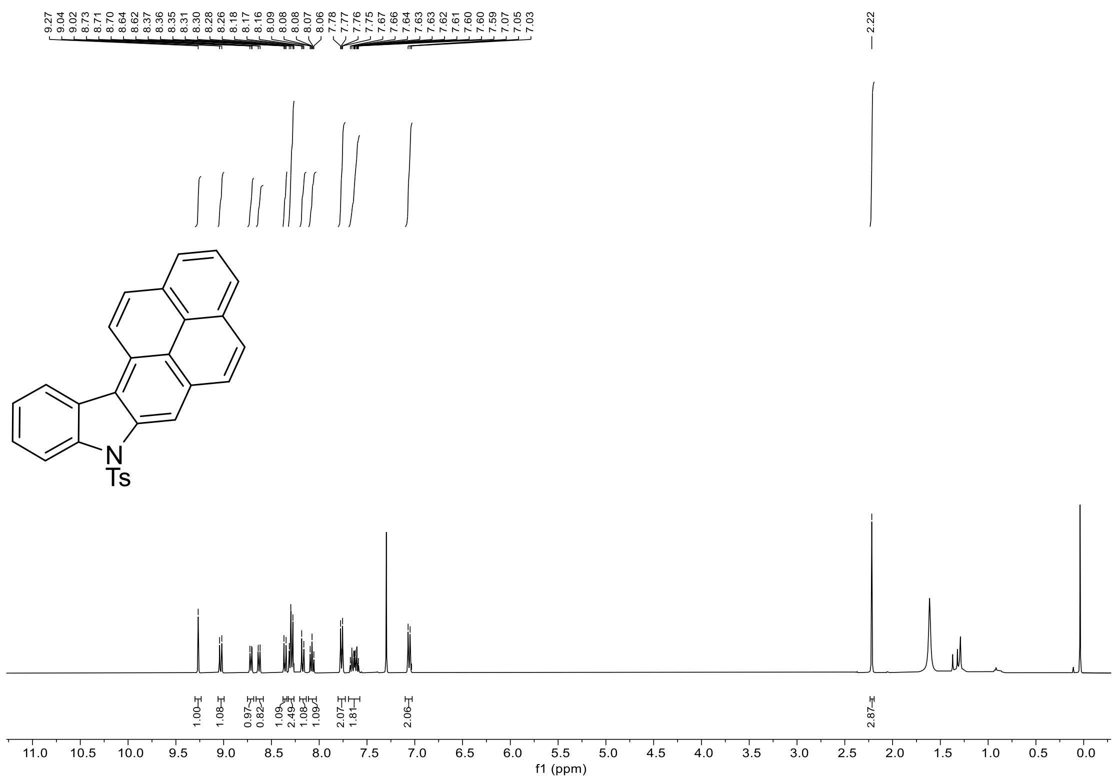
Ts
f1 (ppm)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8.28
8.26
8.18
8.17
8.16
8.09
8.08
8.08
8.07
8.06
7.78
7.77
7.76
7.75
7.67
7.66
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7.63
7.62
7.61
7.60
7.59
7.07
7.05
7.03
2.22
N
Ts
1.00
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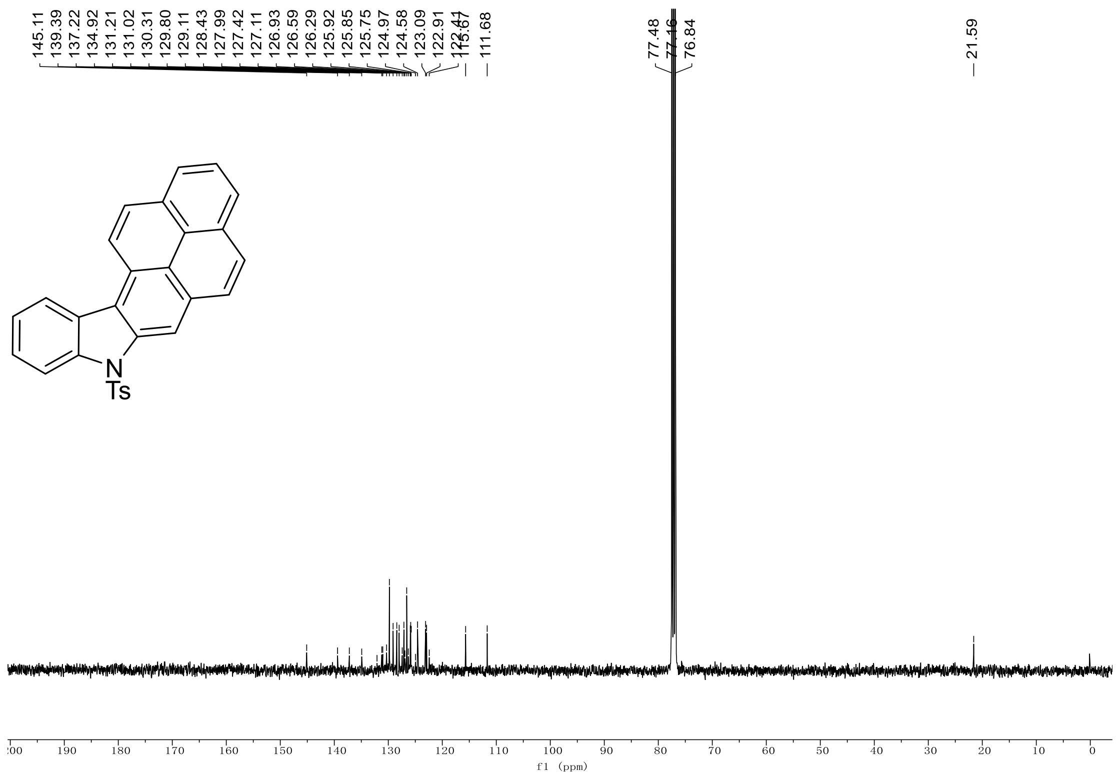
2.87
f1 (ppm)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124.97
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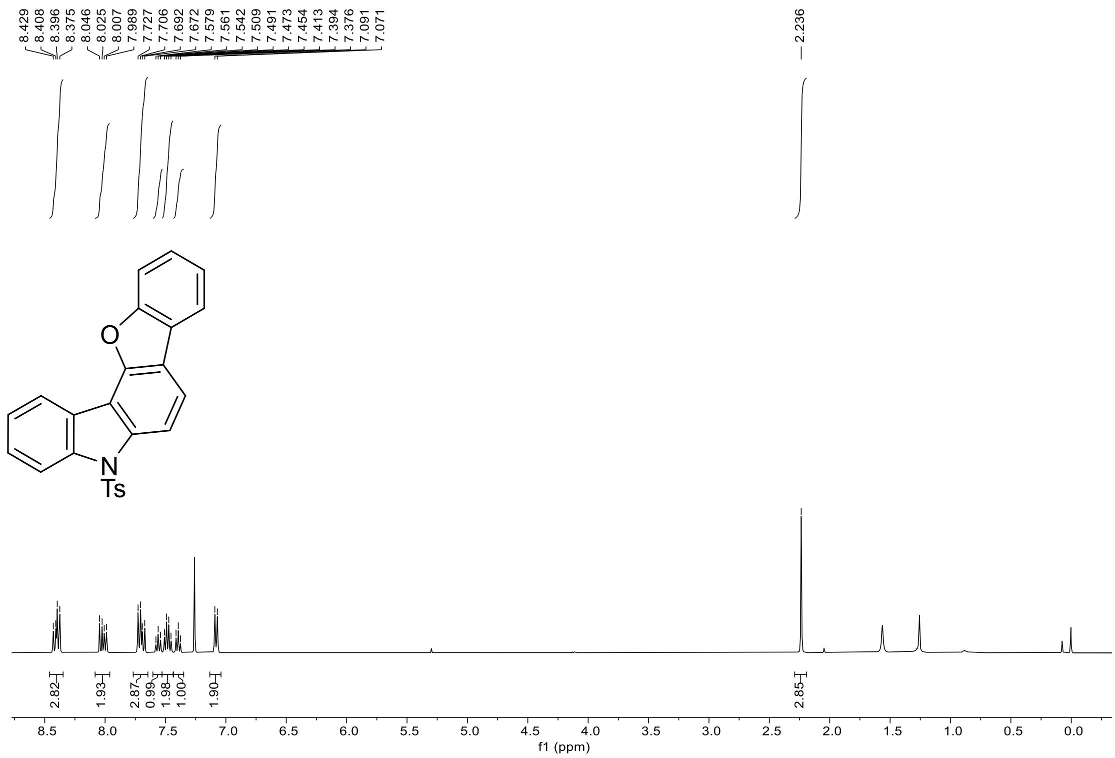
N
Ts
f1 (ppm)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7.376
7.091
7.071
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Ts
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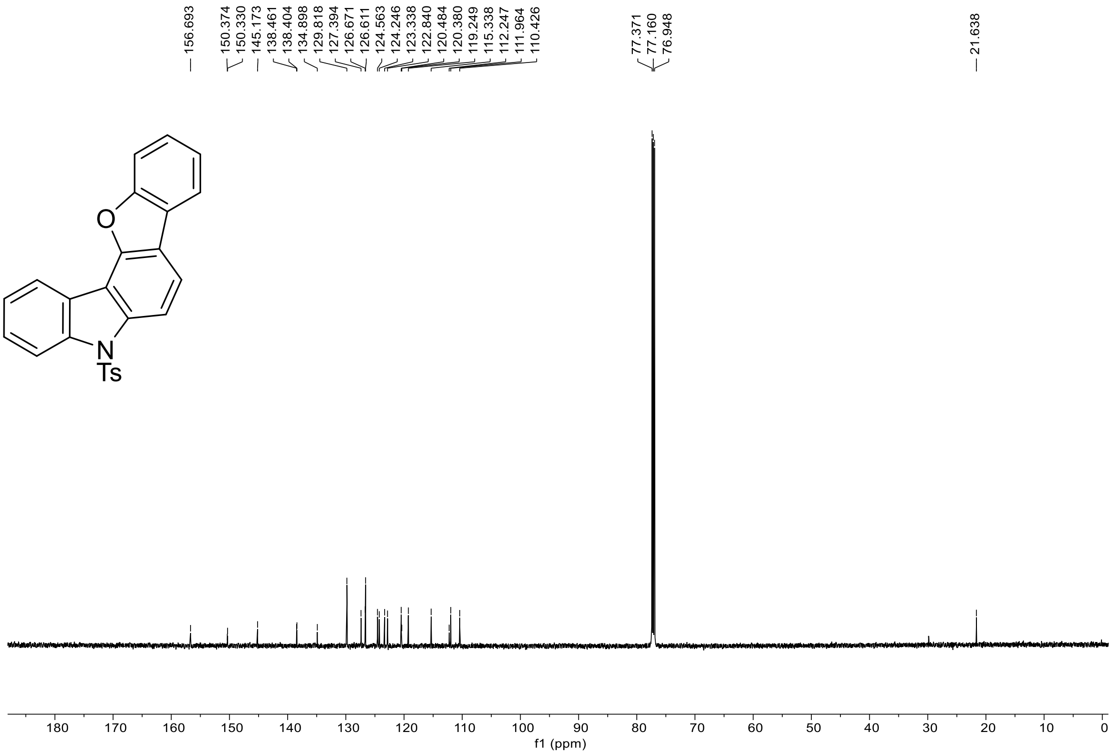
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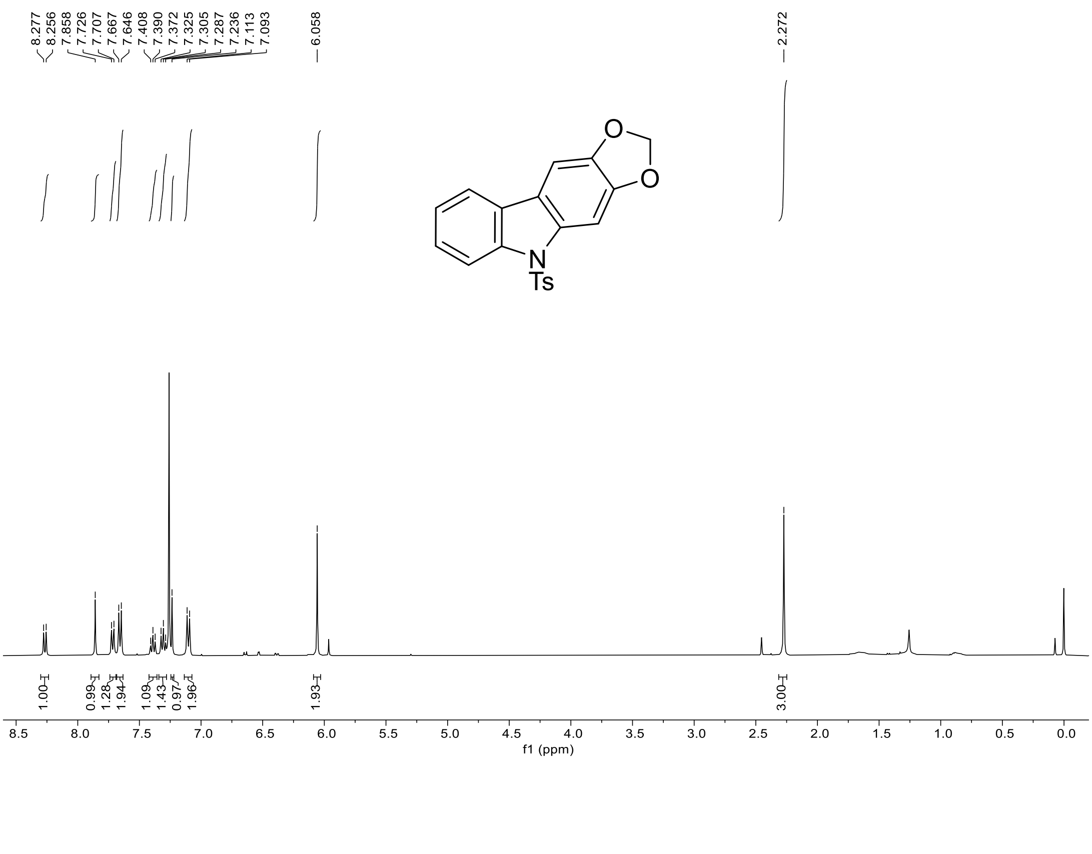
134.898
129.818
127.394
126.671
126.611
124.563
124.246
123.338
122.840
120.484
120.380
119.249
115.338
112.247
111.964
110.426
77.371
77.160
76.948
21.638
O
N
Ts
f1 (ppm)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8.256
7.858
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7.707
7.667
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7.408
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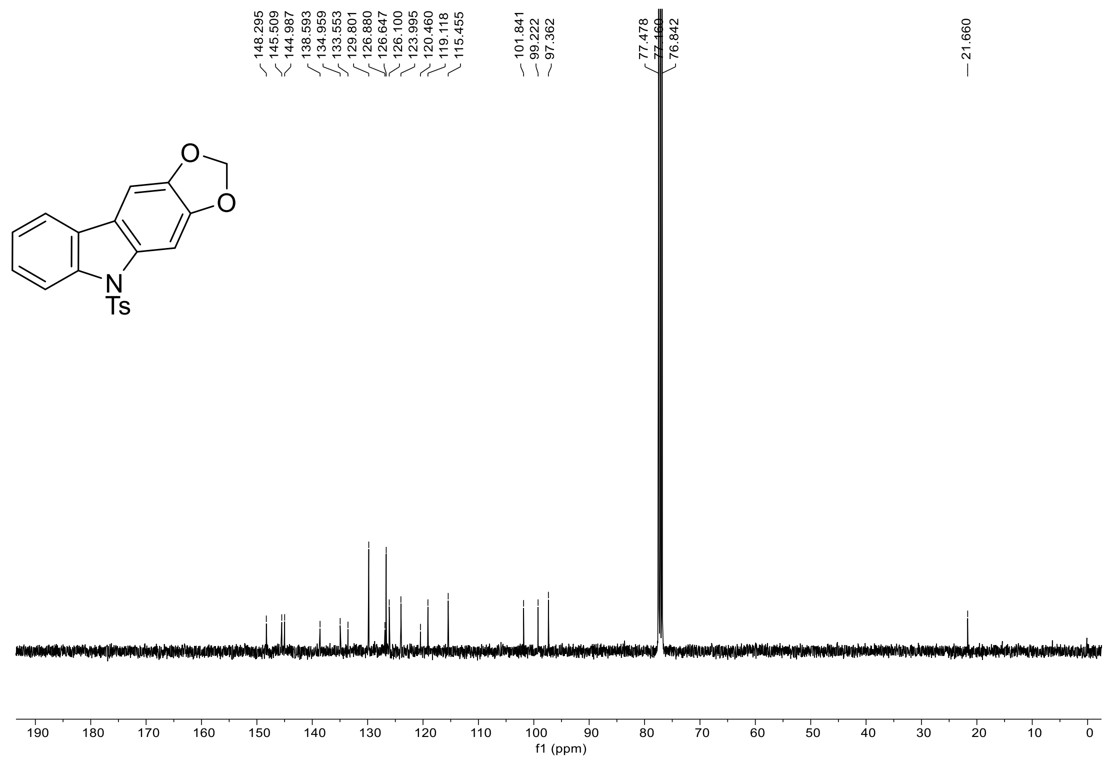
7.372
7.325
7.305
7.287
7.236
7.113
7.093
6.058
2.272
O
O
N
Ts
1.00
0.99
1.28
1.94
1.09
1.43
0.97
1.96
1.93
3.00
f1 (ppm)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144.987
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134.959
133.553
129.801
126.880
126.647
126.100
123.995
120.460
119.118
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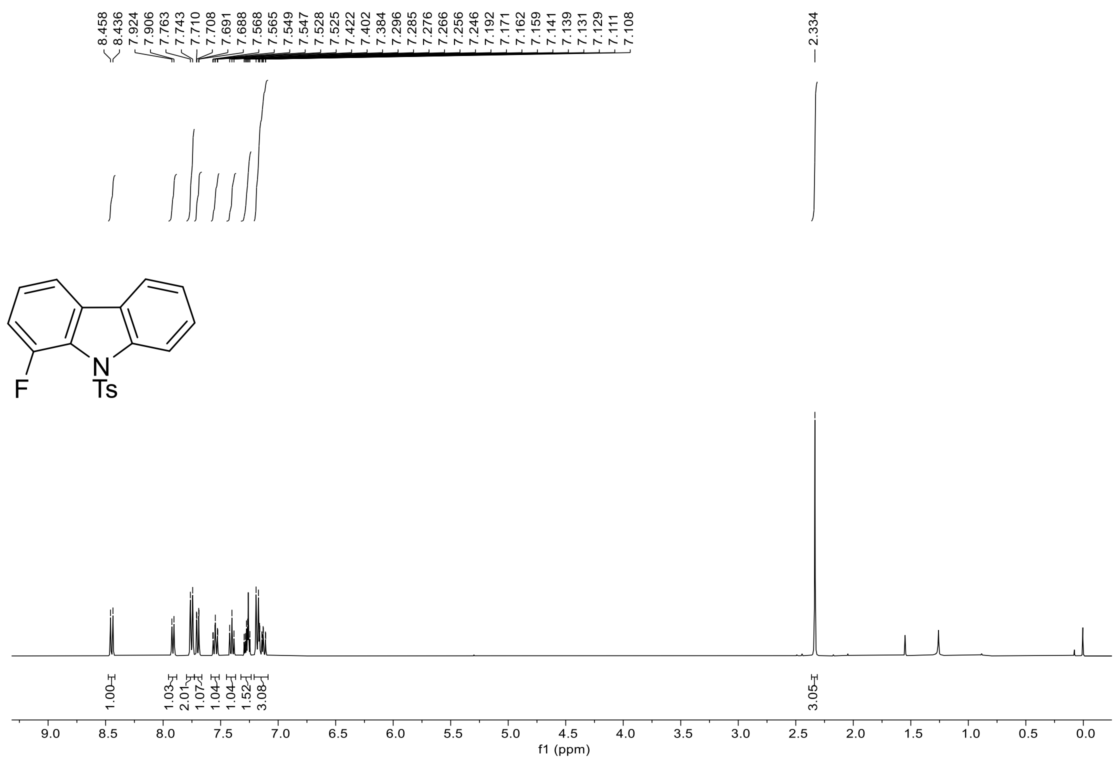
99.222
97.362
77.478
77.160
76.842
21.660
O
O
N
Ts
f1 (ppm)


8.458
8.436
7.924
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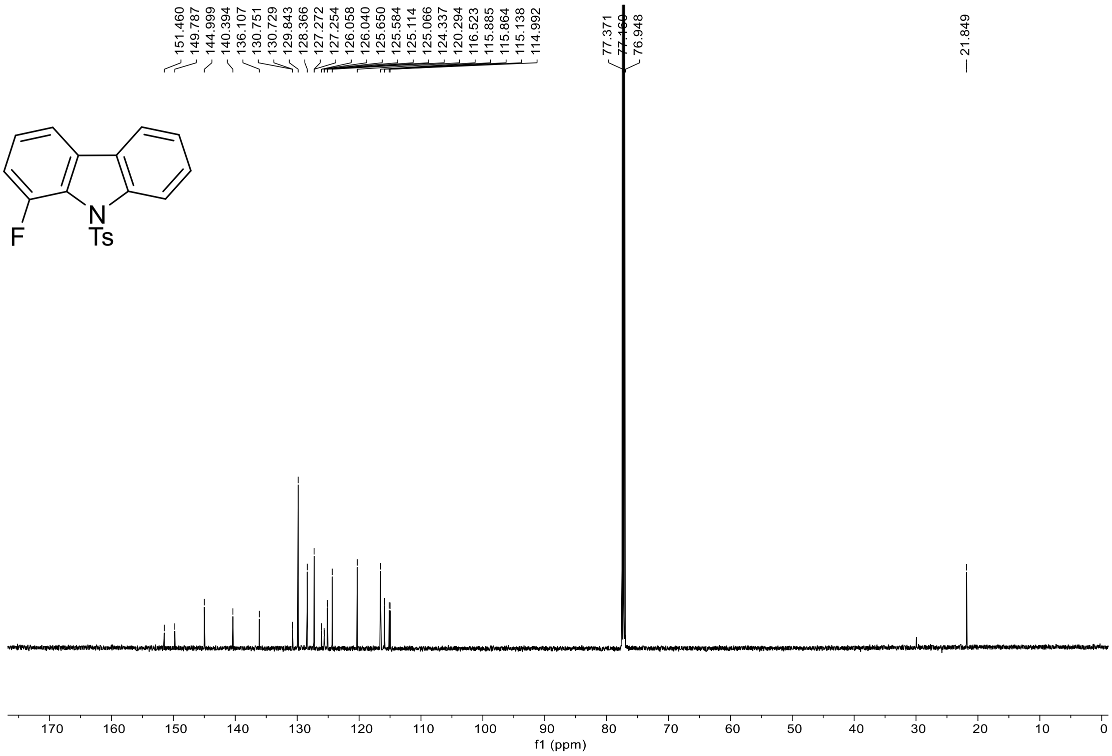
7.763
7.743
7.710
7.708
7.691
7.688
7.568
7.565
7.549
7.547
7.528
7.525
7.422
7.402
7.384
7.296
7.285
7.276
7.266
7.256
7.246
7.192
7.171
7.162
7.159
7.141
7.139
7.131
7.129
7.111
7.108
2.334
F
N
Ts
1.00
1.03
2.01
1.07
1.04
1.04
1.52
3.08
3.05
f1 (ppm)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129.843
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127.254
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126.040
125.650
125.584
125.114
125.066
124.337
120.294
116.523
115.885
115.864
115.138
114.992
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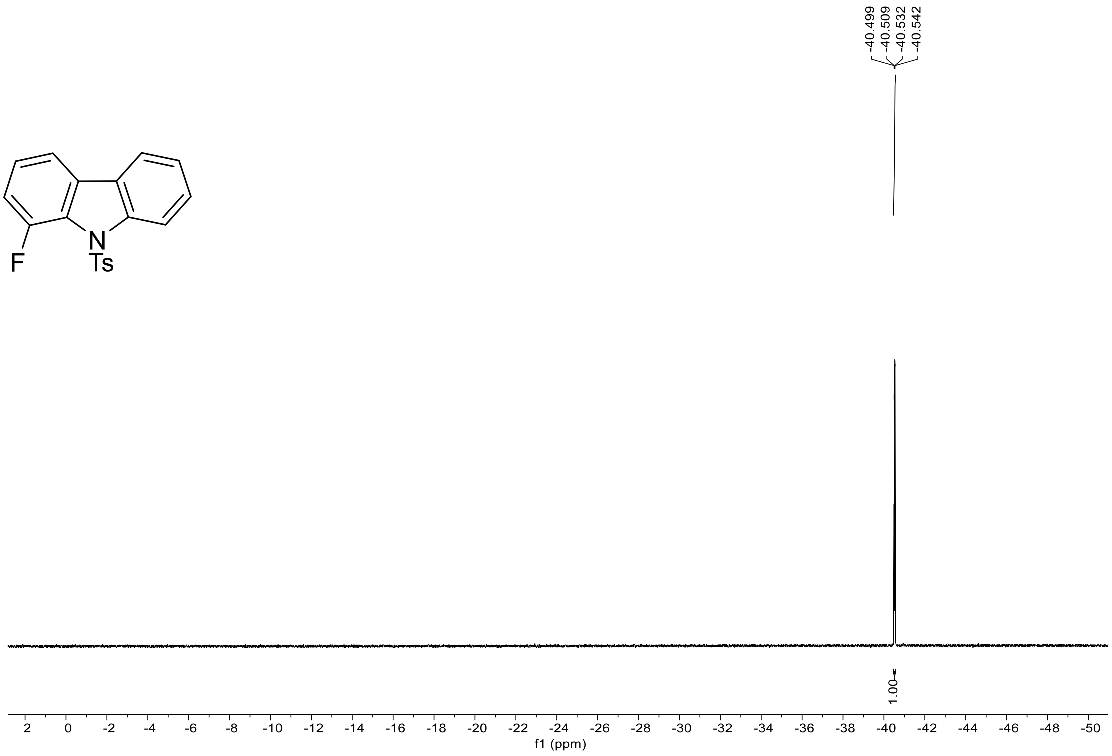
77.160
76.948
21.849
F
N
Ts
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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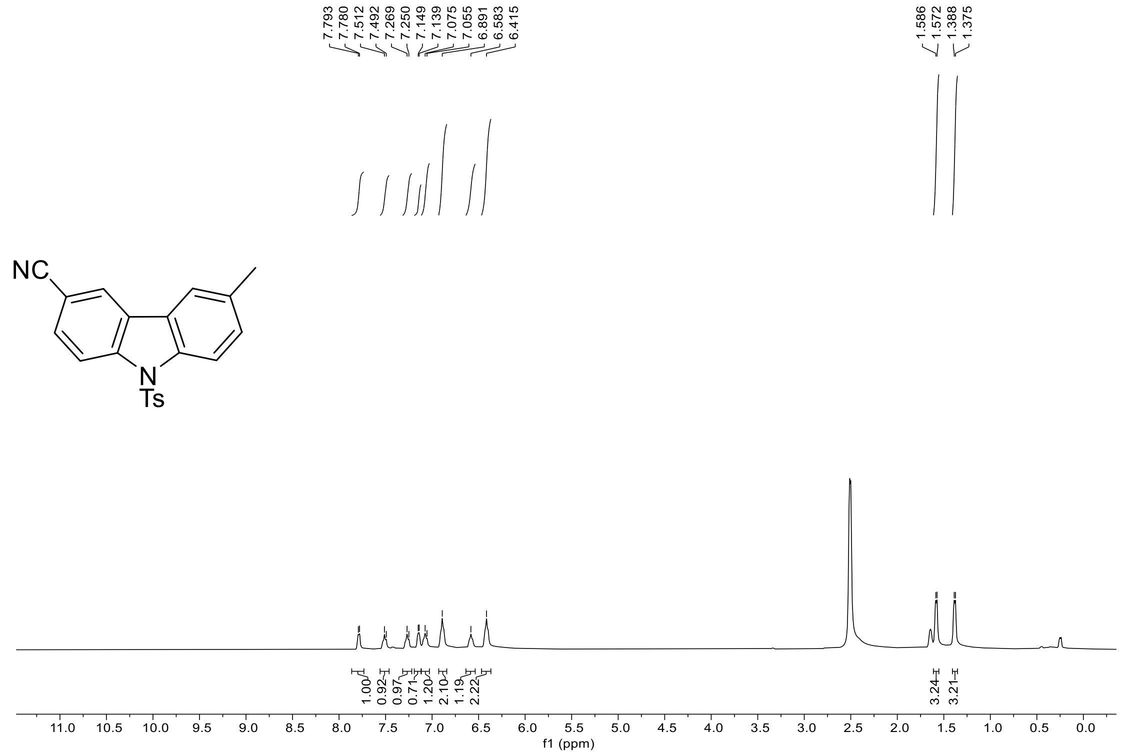
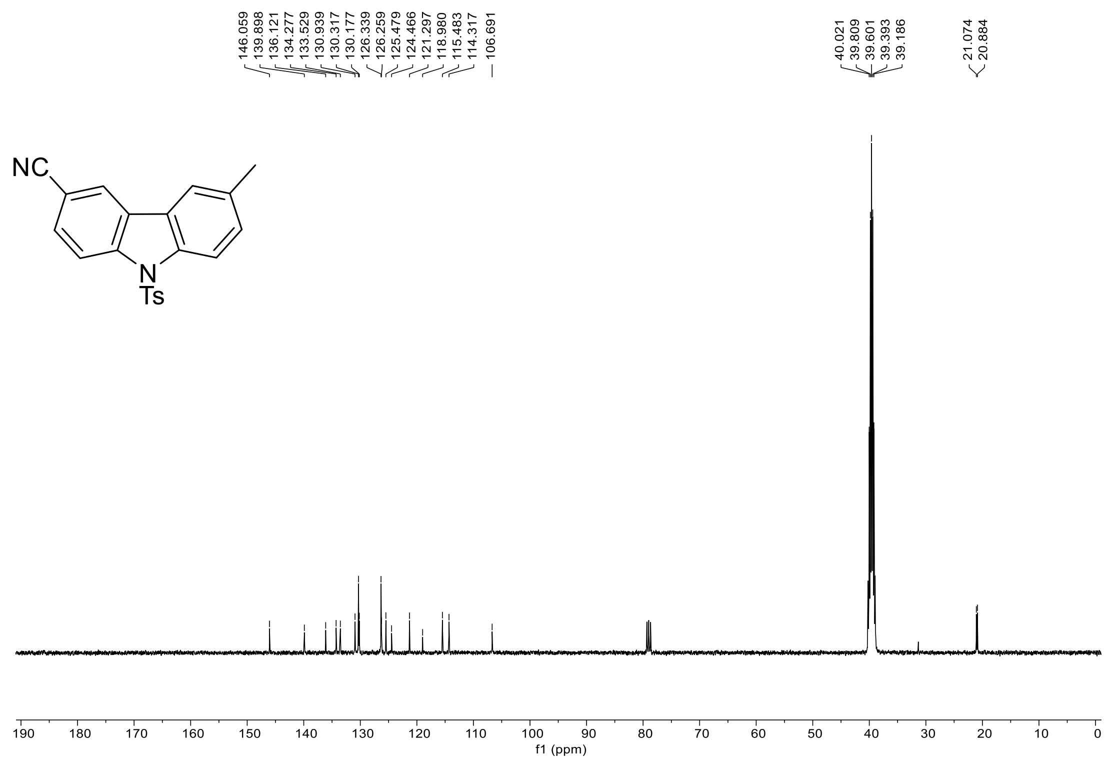
-40.542
F
N
Ts
1.00
2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28 -30 -32 -34 -36 -38 -40 -42 -44 -46 -48 -50
f1 (ppm)


7.793
7.780
7.512
7.492
7.269
7.250
7.149
7.139
7.075
7.055
6.891
6.583
6.415
1.586
1.572
1.388
1.375
NC
N
Ts
1.00
0.92
0.97
0.71
1.20
2.10
1.19
2.22
3.24
3.21
f1 (ppm)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134.277
133.529
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130.317
130.177
126.339
126.259
125.479
124.466
121.297
118.980
115.483
114.317
106.691
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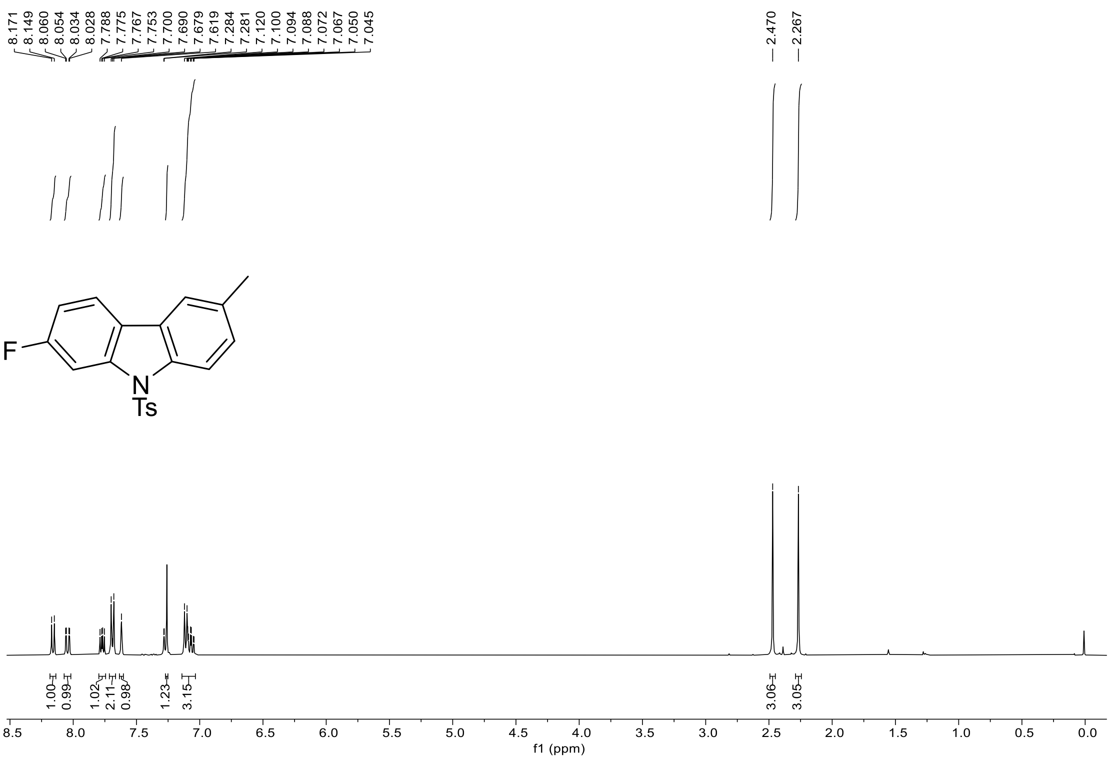
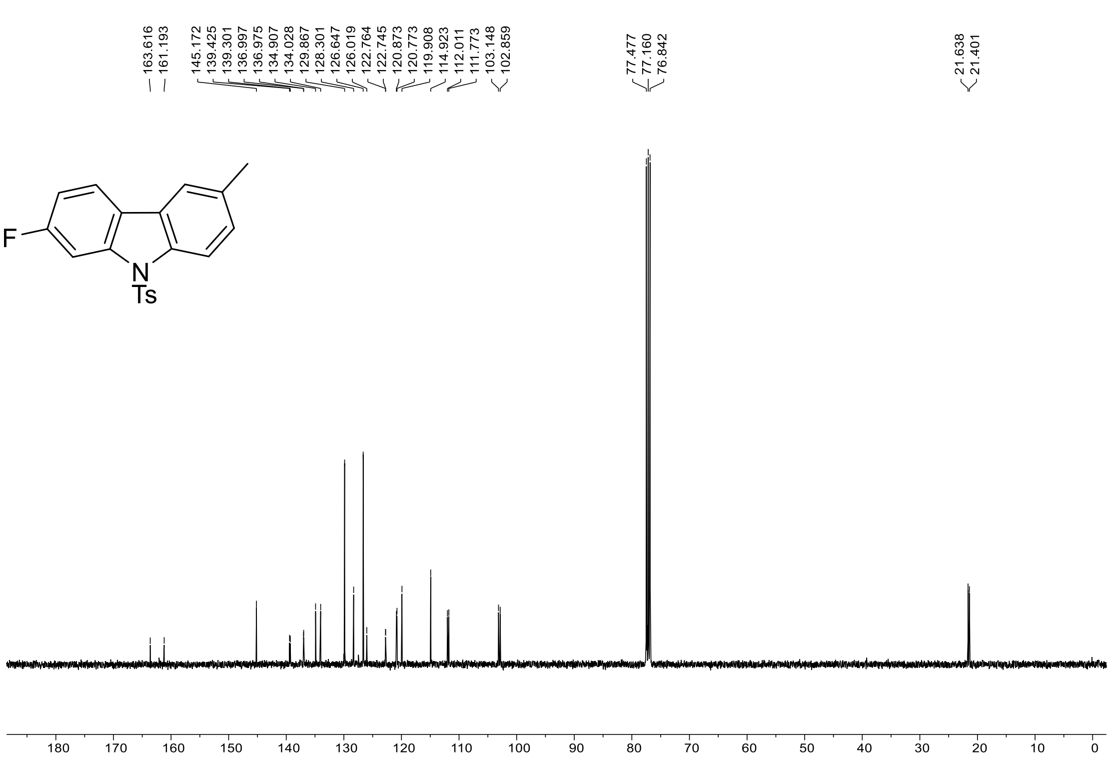
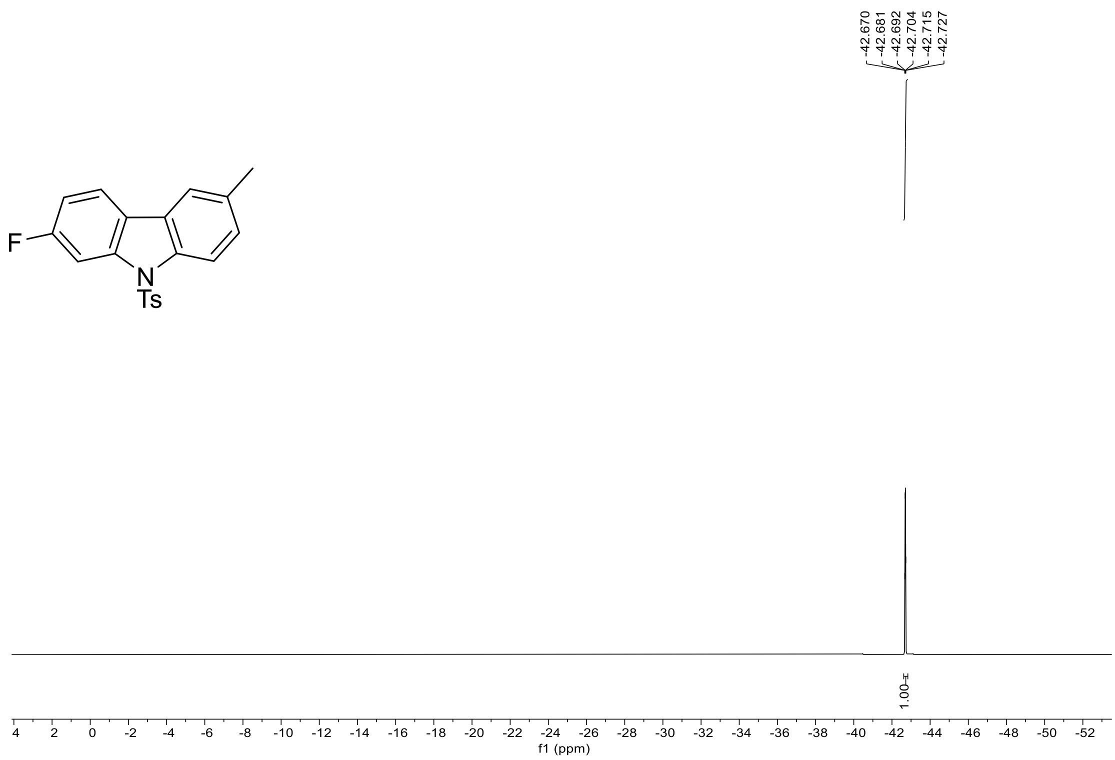
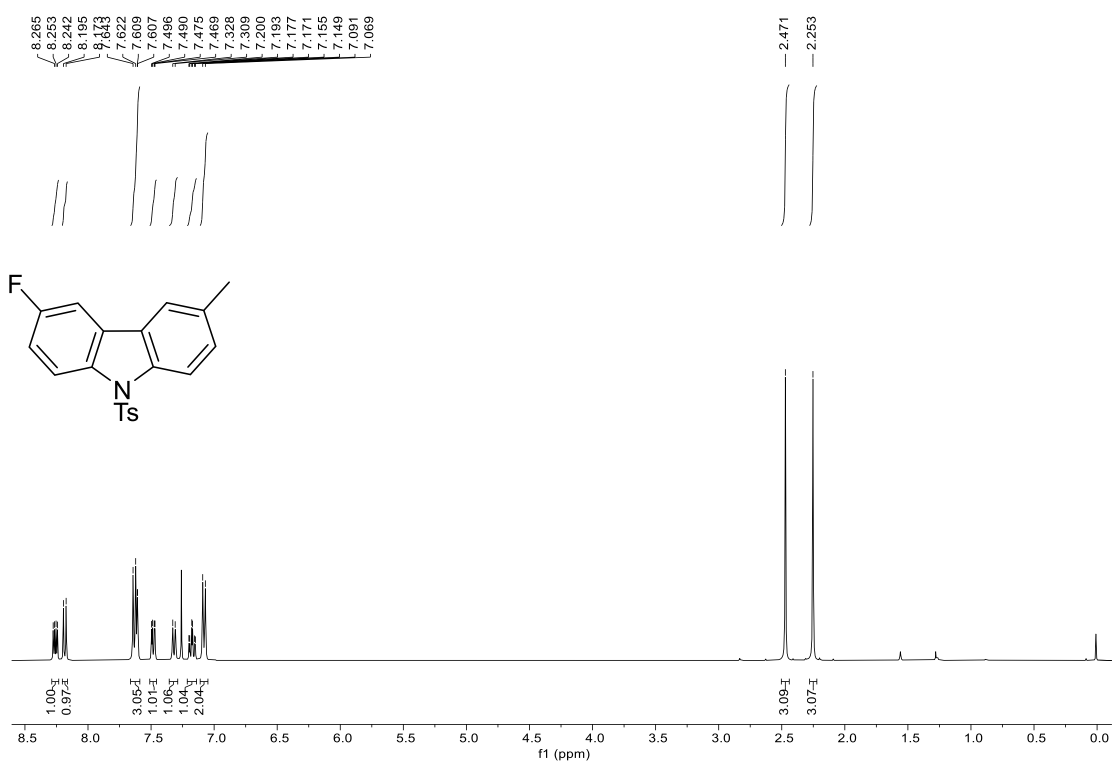
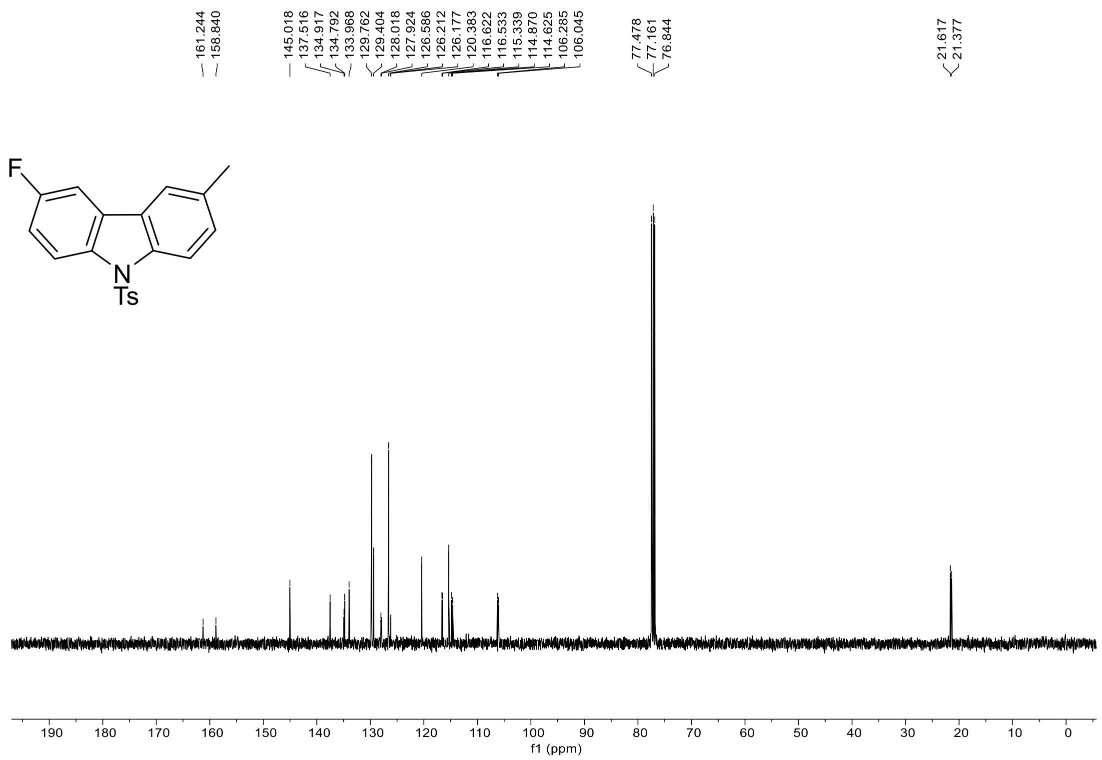
39.809
39.601
39.393
39.186
21.074
20.884
NC
N
Ts
f1 (ppm)











161.244
158.840
145.018
137.516
134.917
134.792
133.968
129.762
129.404
128.018
127.924
126.586
126.212
126.177
120.383
116.622
116.533
115.339
114.870
114.625
106.285
106.045
77.478
77.161
76.844
21.617
21.377
F
N
Ts
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

-112.504
F
N
Ts
1.00
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
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-110
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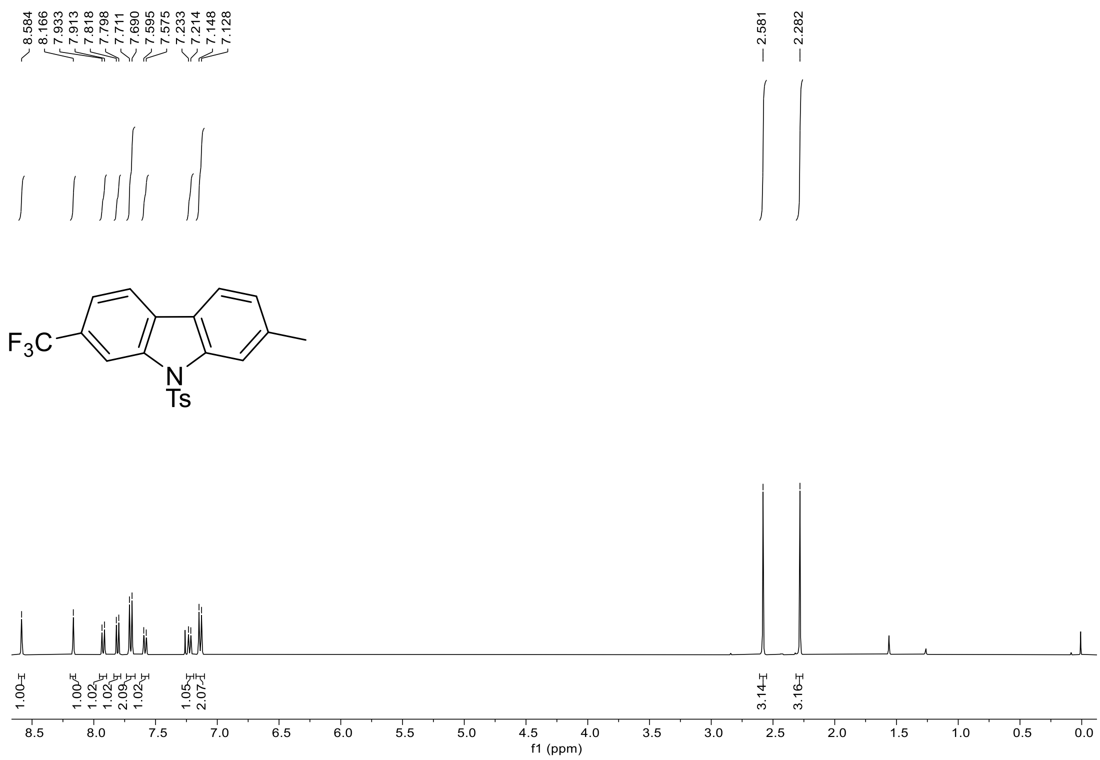
-120
-125
f1 (ppm)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7.933
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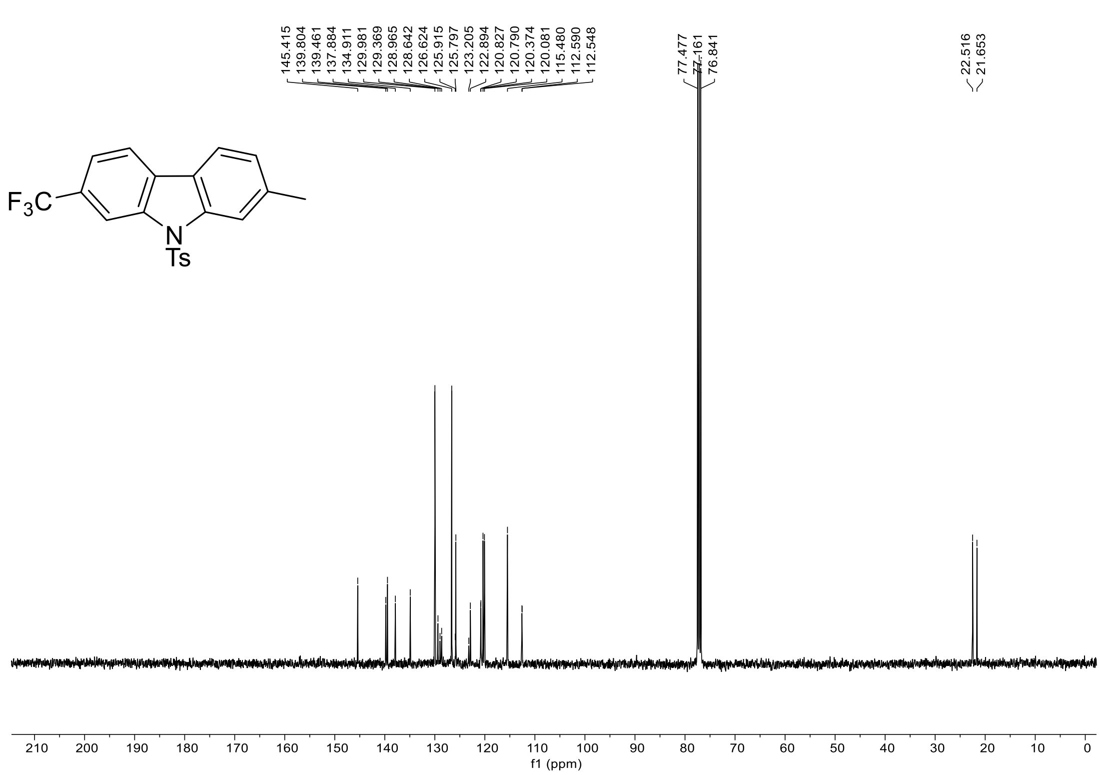
7.818
7.798
7.711
7.690
7.595
7.575
7.233
7.214
7.148
7.128
2.581
2.282
F3C
N
Ts
1.00
1.00
1.02
1.02
2.09
1.02
1.05
2.07
3.14
3.16
f1 (ppm)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128.965
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126.624
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125.797
123.205
122.894
120.827
120.790
120.374
120.081
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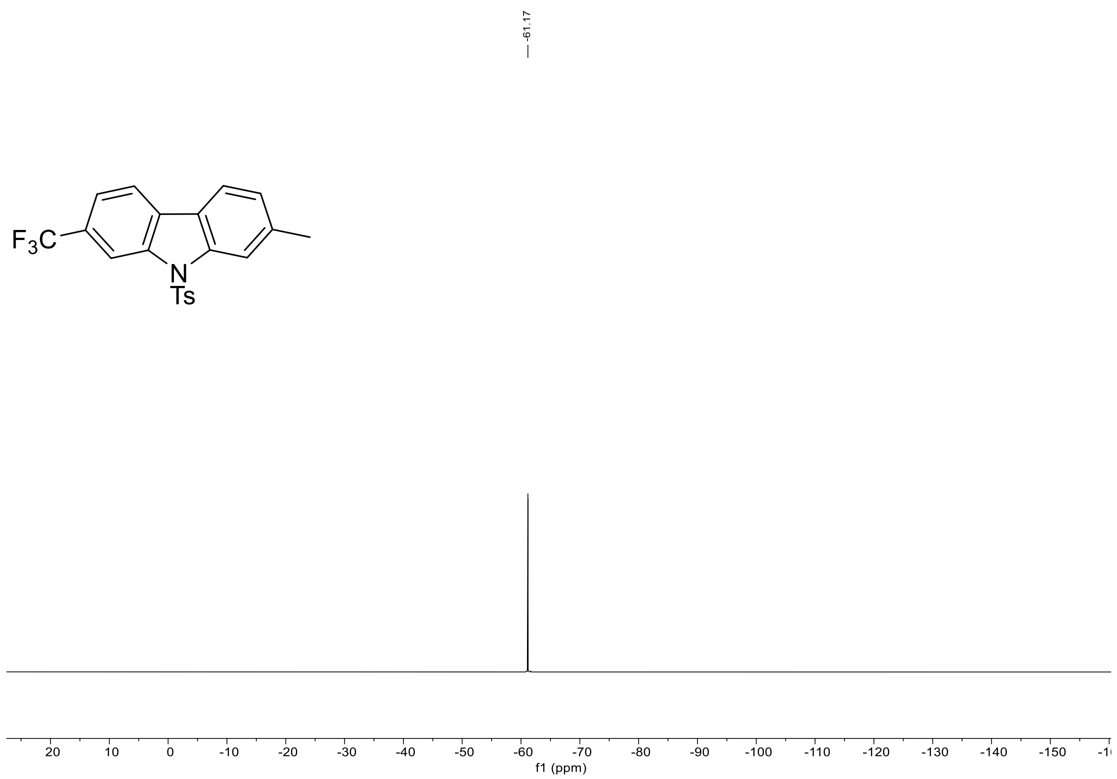
112.590
112.548
77.477
77.161
76.841
22.516
21.653
F3C
N
Ts
f1 (ppm)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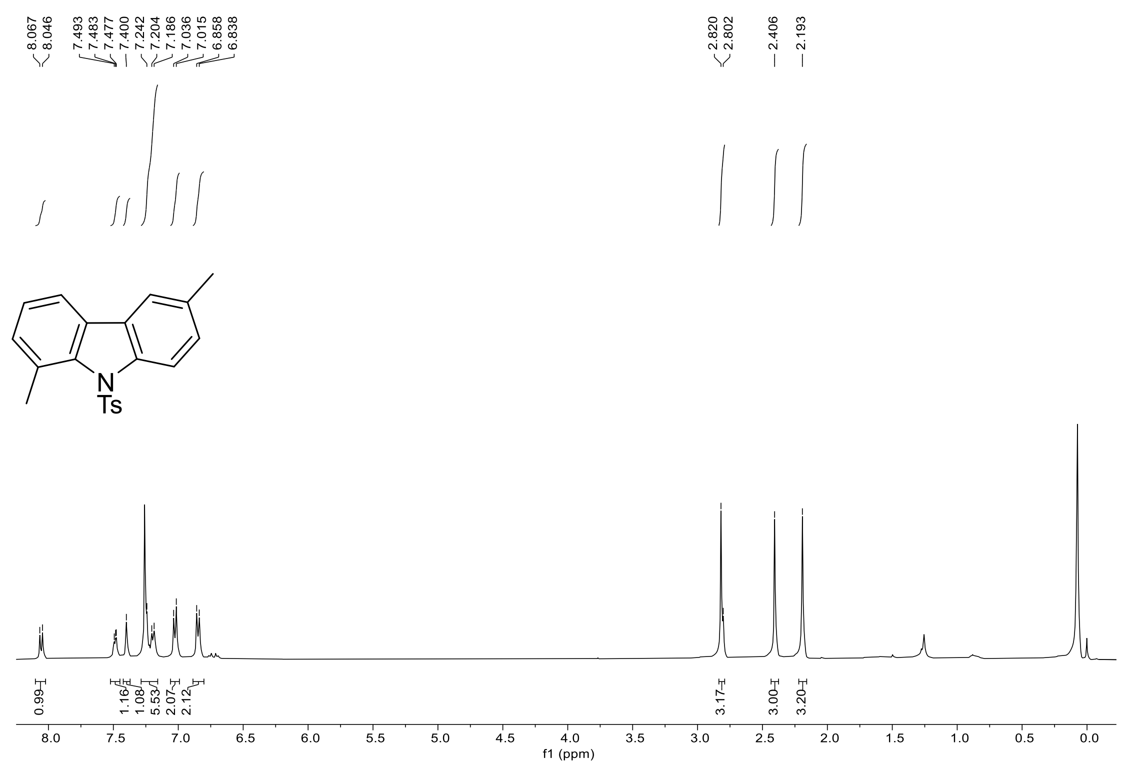
F3C
N
Ts
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)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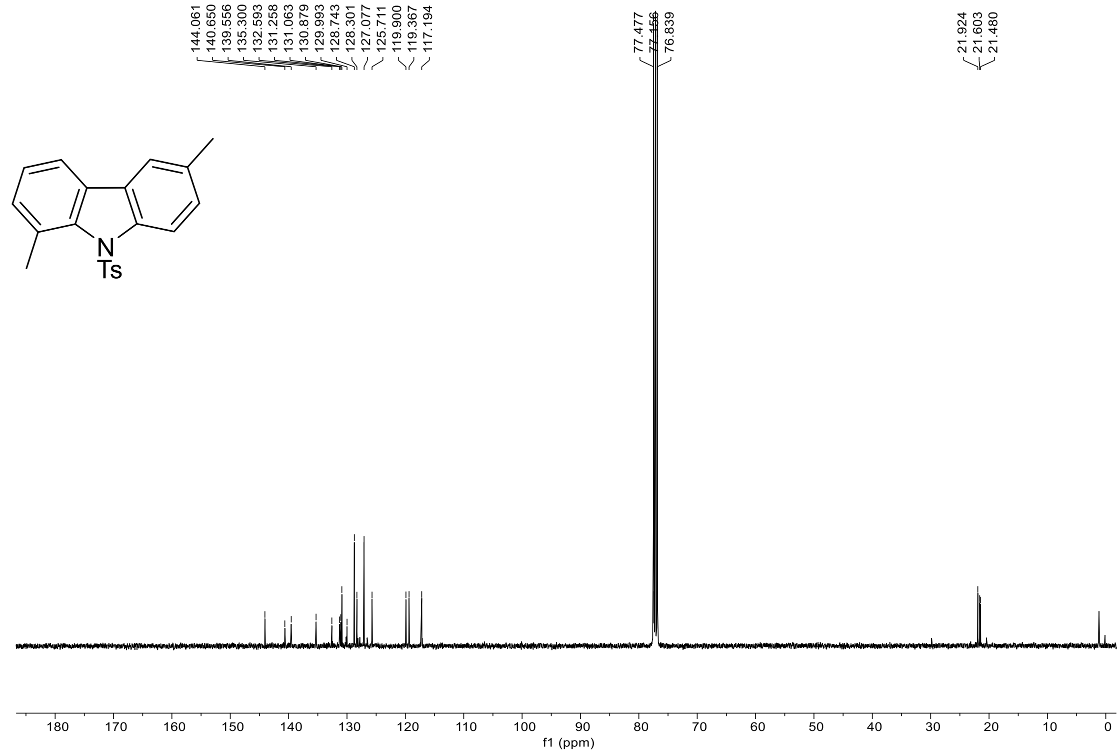
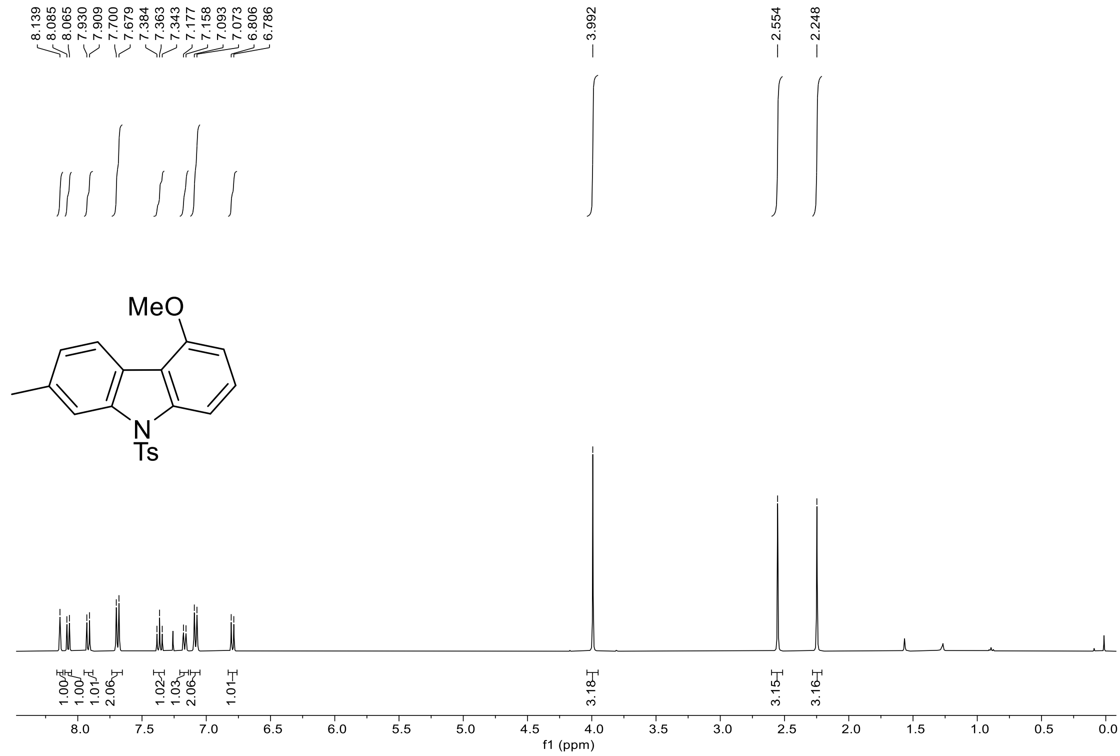
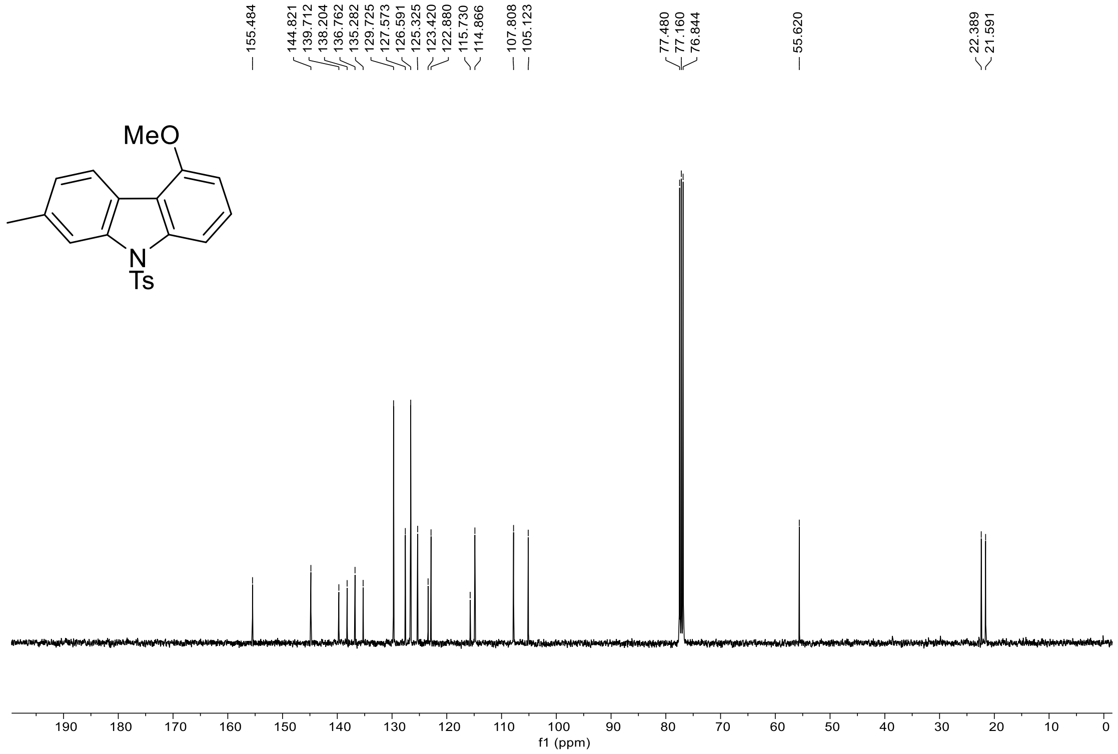
8.046
7.493
7.483
7.477
7.400
7.242
7.204
7.186
7.036
7.015
6.858
6.838
2.820
2.802
2.406
2.193
N
Ts
0.99
1.16
1.08
5.53
2.07
2.12
3.17
3.00
3.20
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



144.061
140.650
139.556
135.300
132.593
131.258
131.063
130.879
129.993
128.743
128.301
127.077
125.711
119.900
119.367
117.194
77.477
77.156
76.839
21.924
21.603
21.480
N
Ts
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



8.139
8.085
8.065
7.930
7.909
7.700
7.679
7.384
7.363
7.343
7.177
7.158
7.093
7.073
6.806
6.786
3.992
2.554
2.248
MeO
N
Ts
1.00
1.00
1.01
2.06
1.02
1.03
2.06
1.01
3.18
3.15
3.16
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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138.204
136.762
135.282
129.725
127.573
126.591
125.325
123.420
122.880
115.730
114.866
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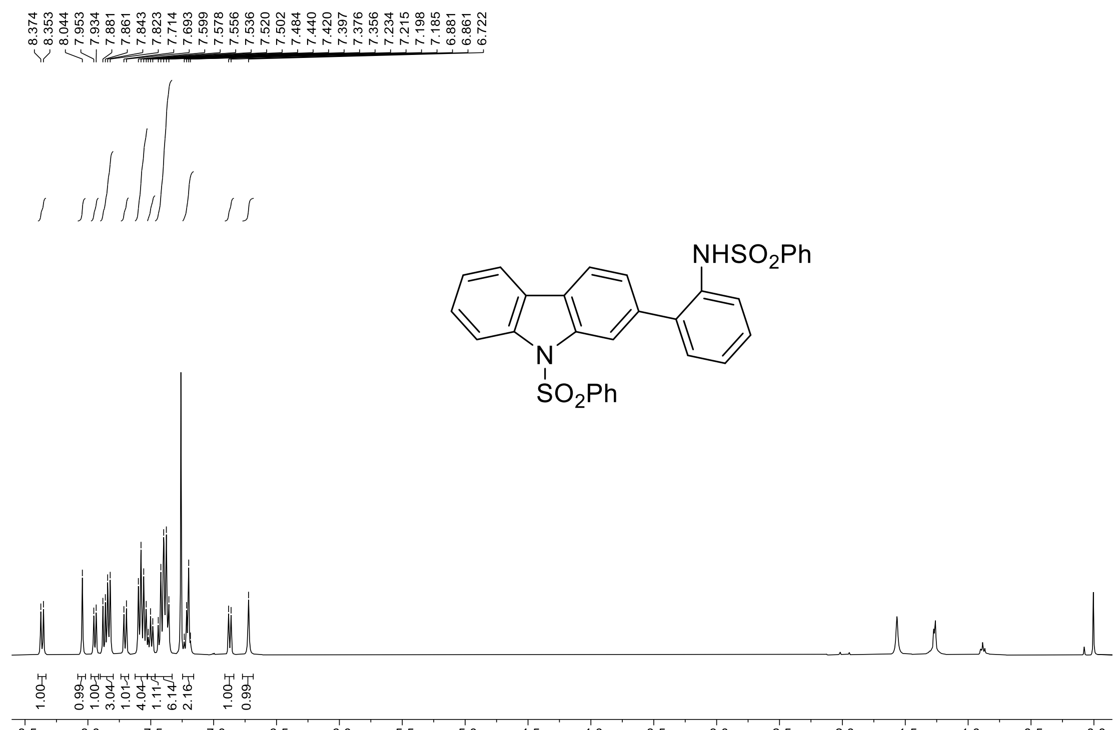
105.123
77.480
77.160
76.844
55.620
22.389
21.591
MeO
N
Ts
f1 (ppm)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7.934
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7.861
7.843
7.823
7.714
7.693
7.599
7.578
7.556
7.536
7.520
7.502
7.484
7.440
7.420
7.397
7.376
7.356
7.234
7.215
7.198
7.185
6.881
6.861
6.722
NHSO2Ph
N
SO2Ph
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1.00
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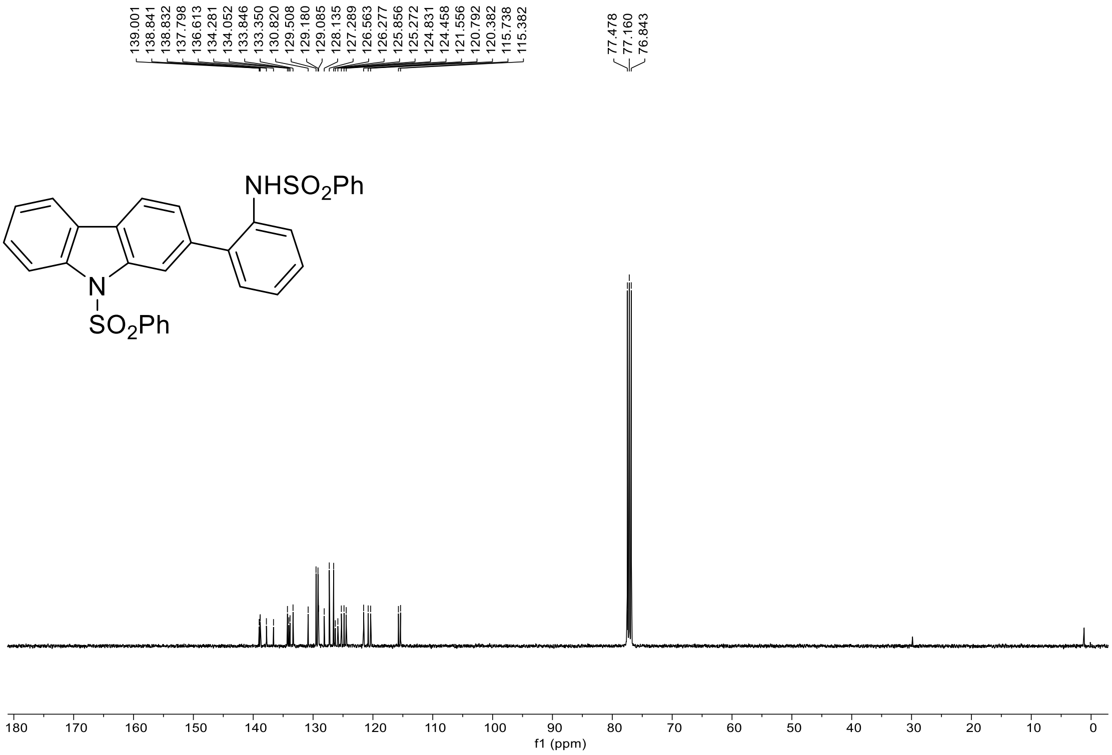
1.01
4.04
1.11
6.14
2.16
1.00
0.99
f1 (ppm)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133.846
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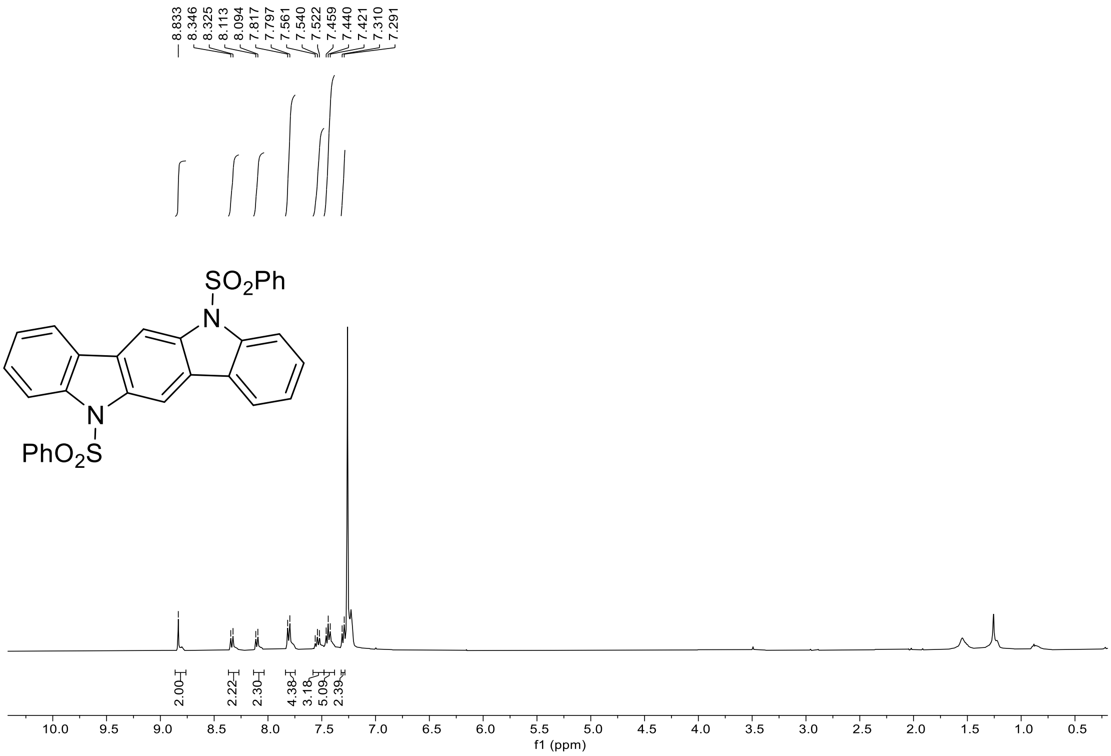
130.820
129.508
129.180
129.085
128.135
127.289
126.563
126.277
125.856
125.272
124.831
124.458
121.556
120.792
120.382
115.738
115.382
77.478
77.160
76.843
NHSO2Ph
N
SO2Ph
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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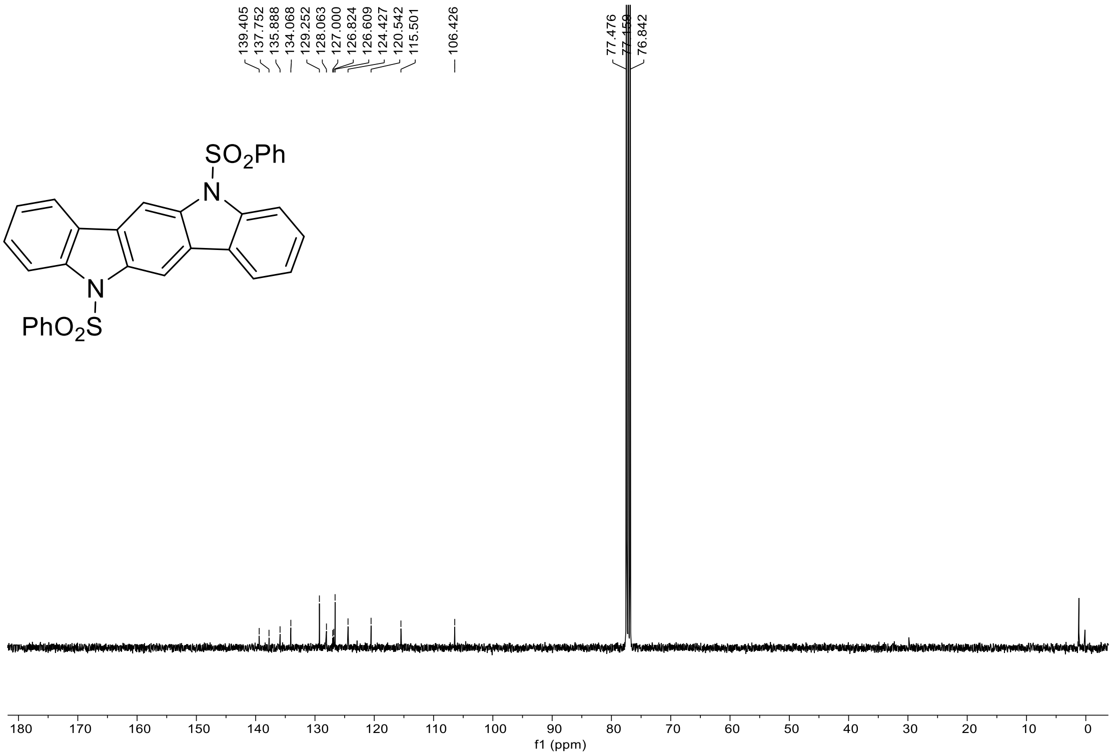
7.797
7.561
7.540
7.522
7.459
7.440
7.421
7.310
7.291
SO2Ph
N
N
PhO2S
2.00
2.22
2.30
4.38
3.18
5.09
2.39
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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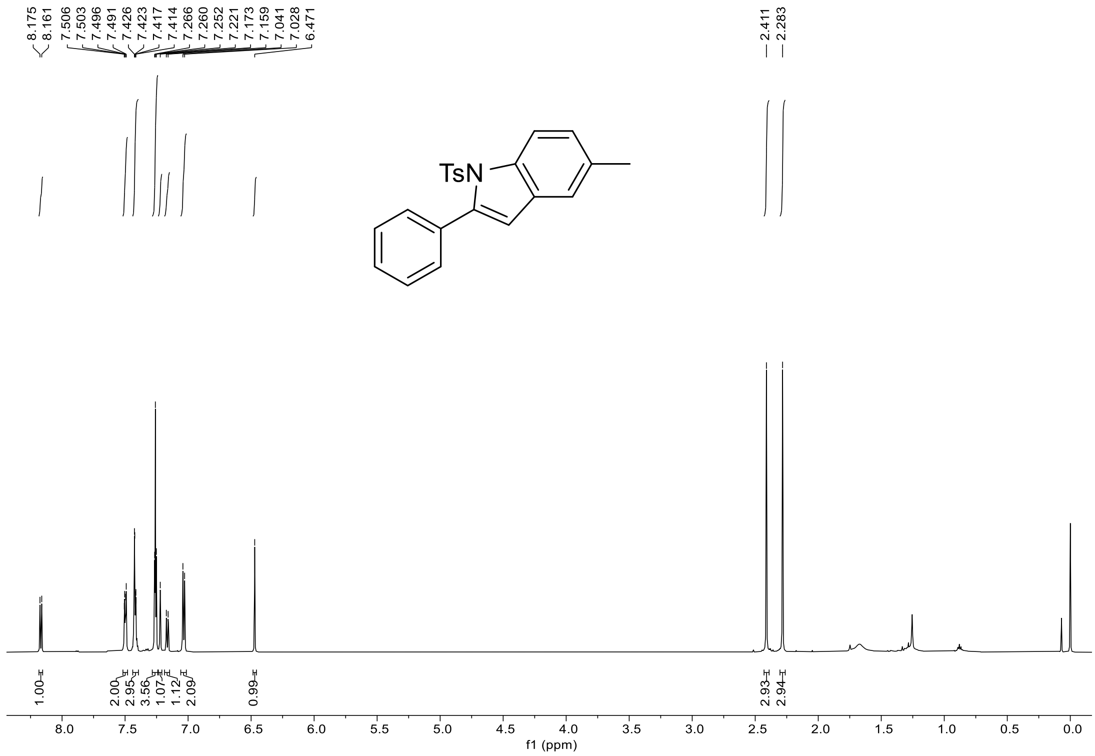
128.063
127.000
126.824
126.609
124.427
120.542
115.501
106.426
77.476
76.842
SO2Ph
N
PhO2S
f1 (ppm)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7.503
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7.426
7.423
7.417
7.414
7.266
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7.252
7.221
7.173
7.159
7.041
7.028
6.471
2.411
2.283
TsN
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2.00
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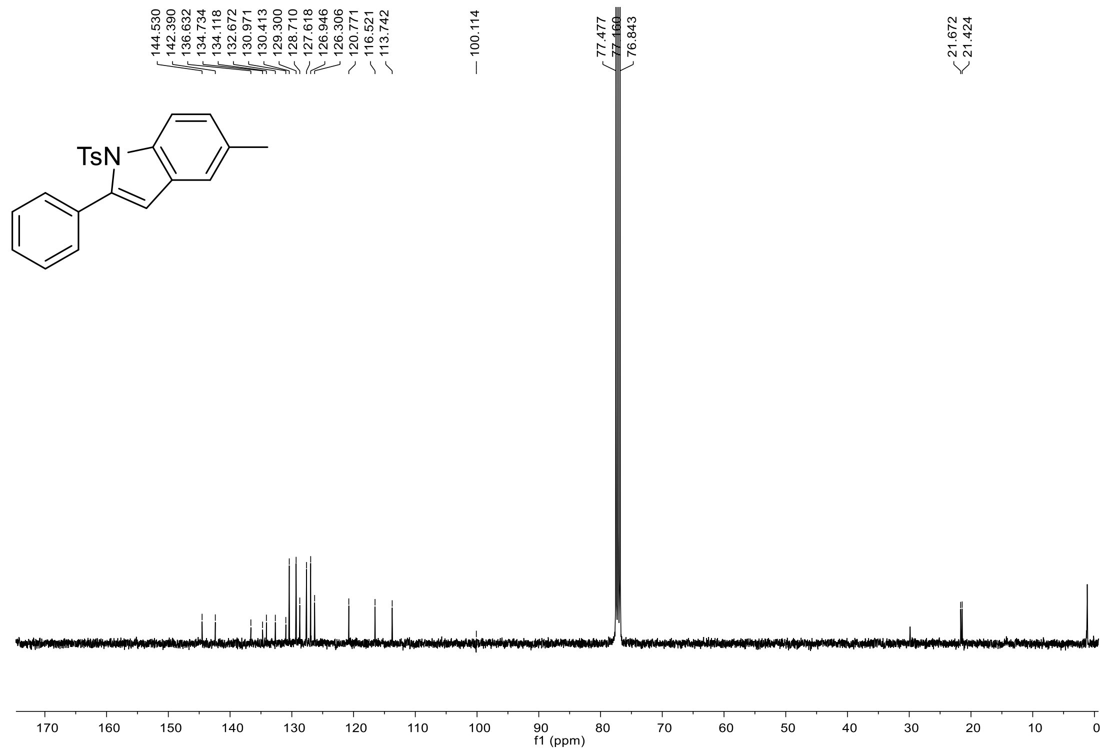
1.12
2.09
0.99
2.93
2.94
f1 (ppm)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130.413
129.300
128.710
127.618
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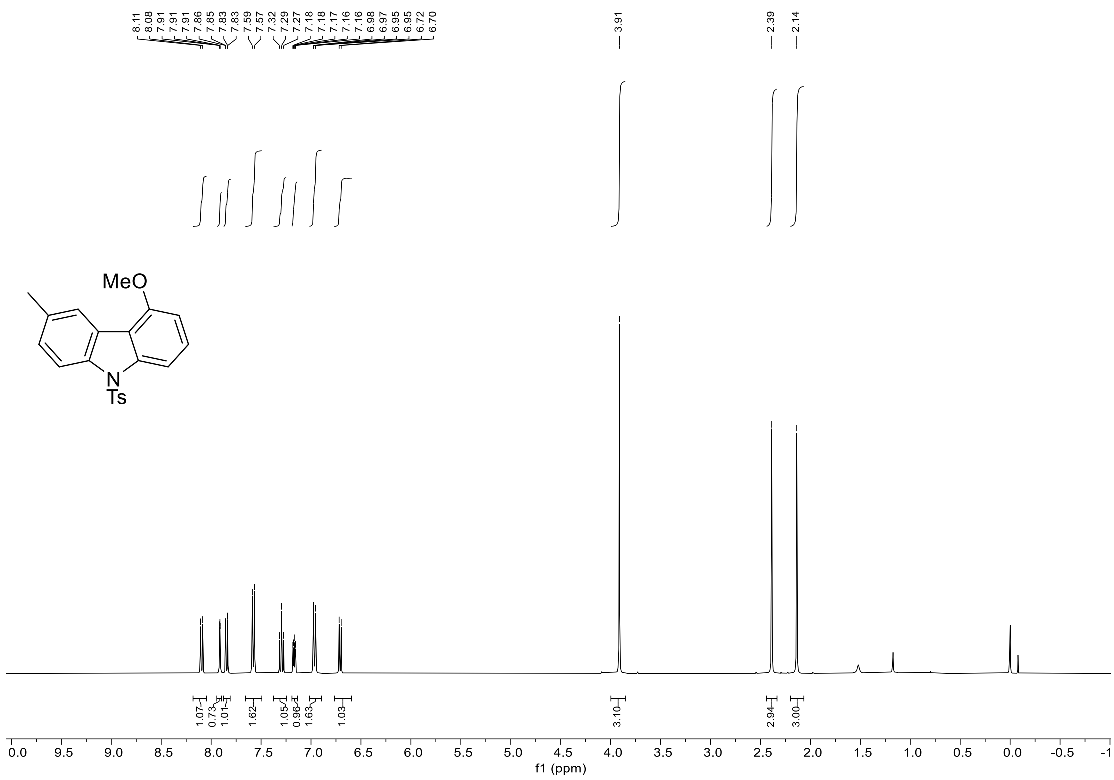
126.306
120.771
116.521
113.742
100.114
77.477
76.843
21.672
21.424
TsN
f1 (ppm)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7.91
7.91
7.86
7.85
7.83
7.83
7.59
7.57
7.32
7.29
7.27
7.18
7.18
7.17
7.16
6.98
6.97
6.95
6.72
6.70
3.91
2.39
2.14
MeO
N
Ts
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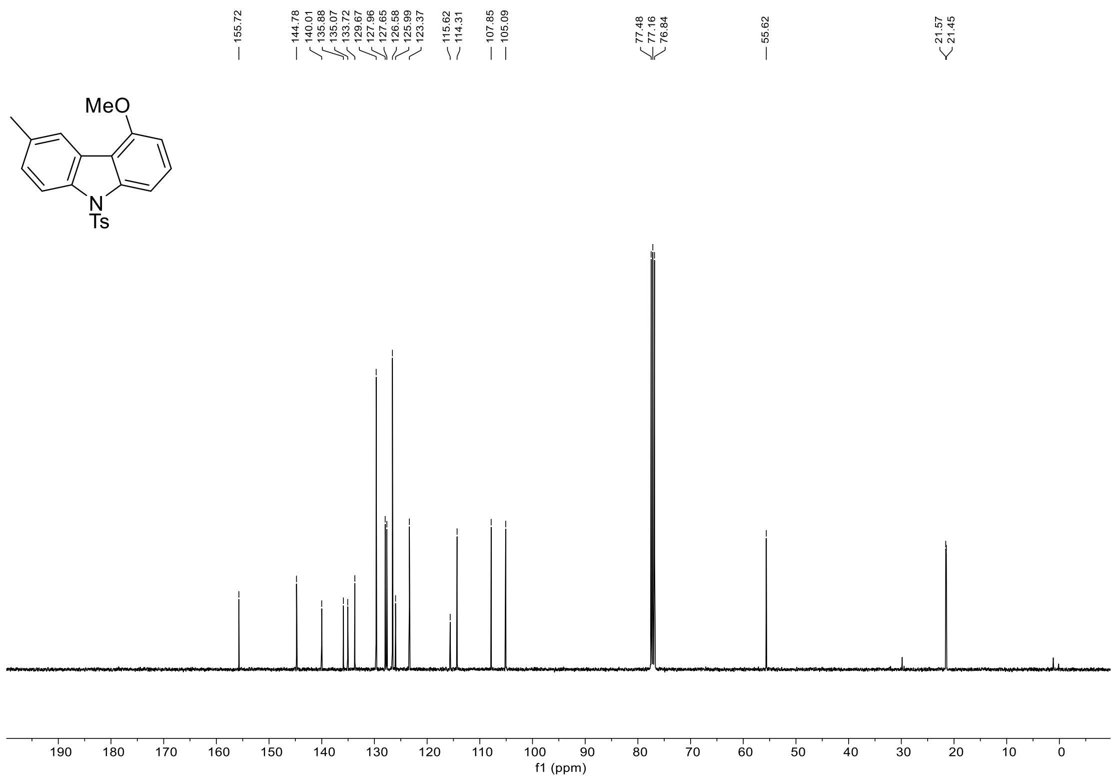
1.62
1.05
0.96
1.63
1.03
3.10
2.94
3.00
f1 (ppm)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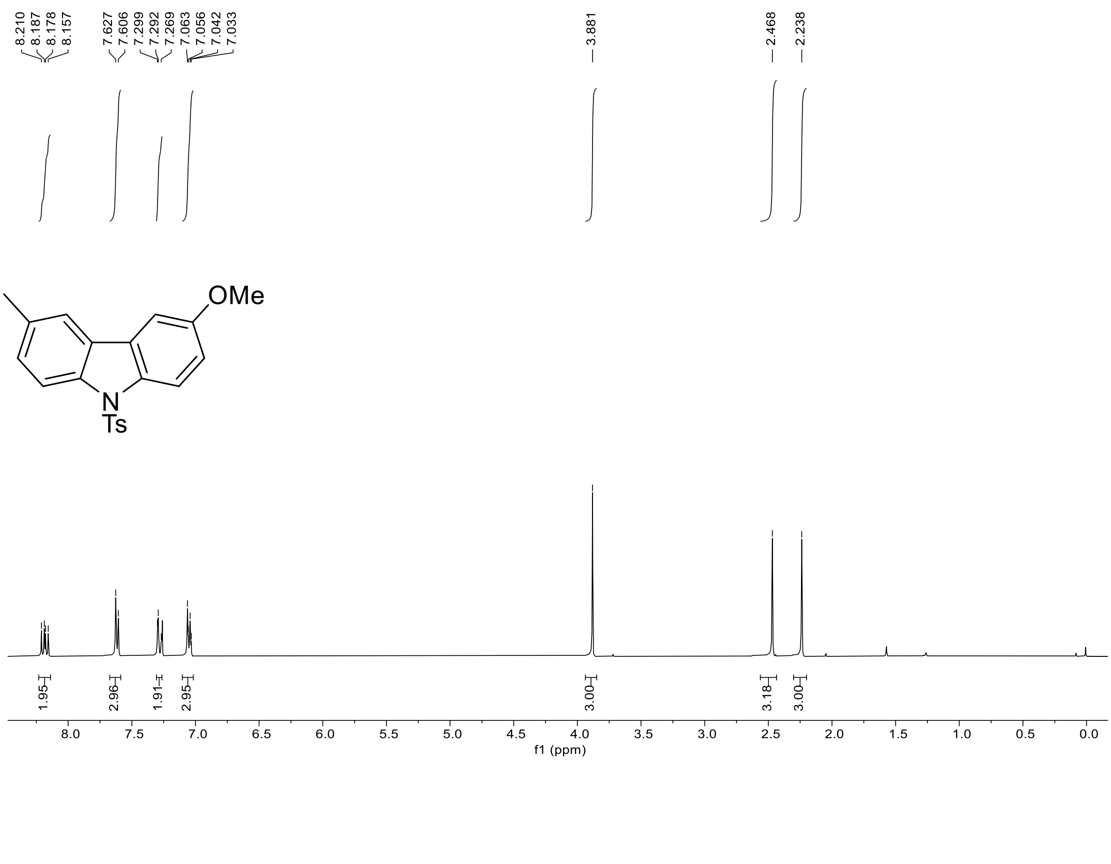
126.58
125.99
123.37
115.62
114.31
107.85
105.09
77.48
77.16
76.84
55.62
21.57
21.45
MeO
N
Ts
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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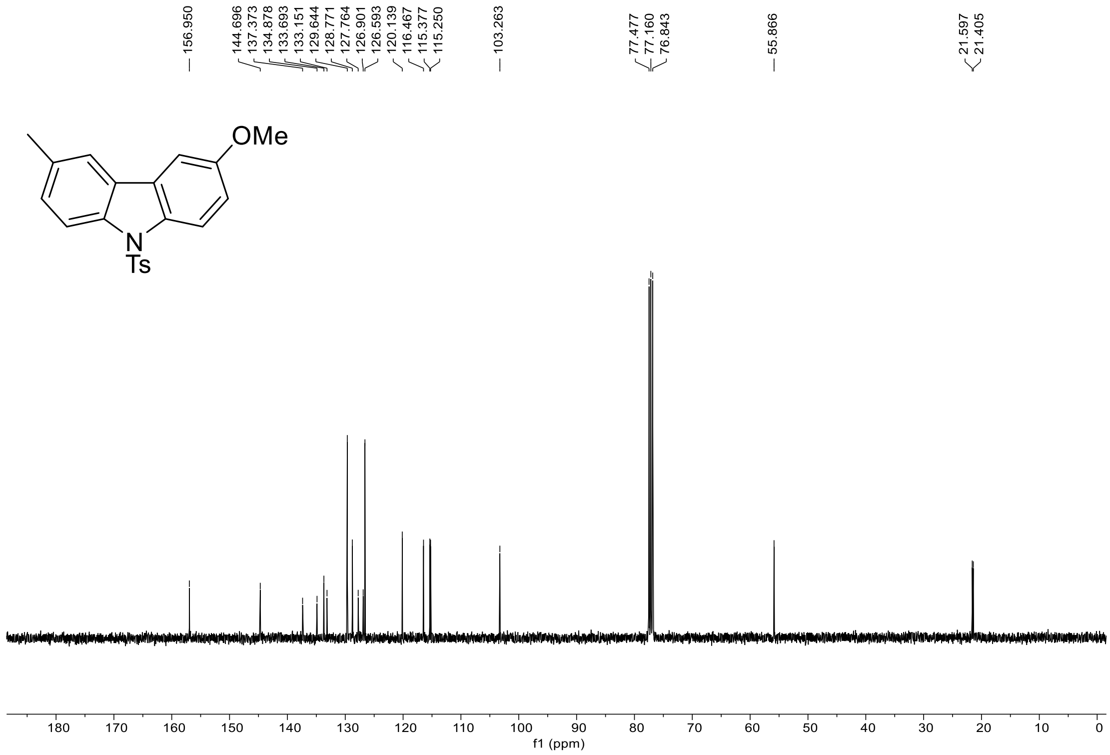
7.292
7.269
7.063
7.056
7.042
7.033
3.881
2.468
2.238
OMe
N
Ts
1.95
2.96
1.91
2.95
3.00
3.18
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



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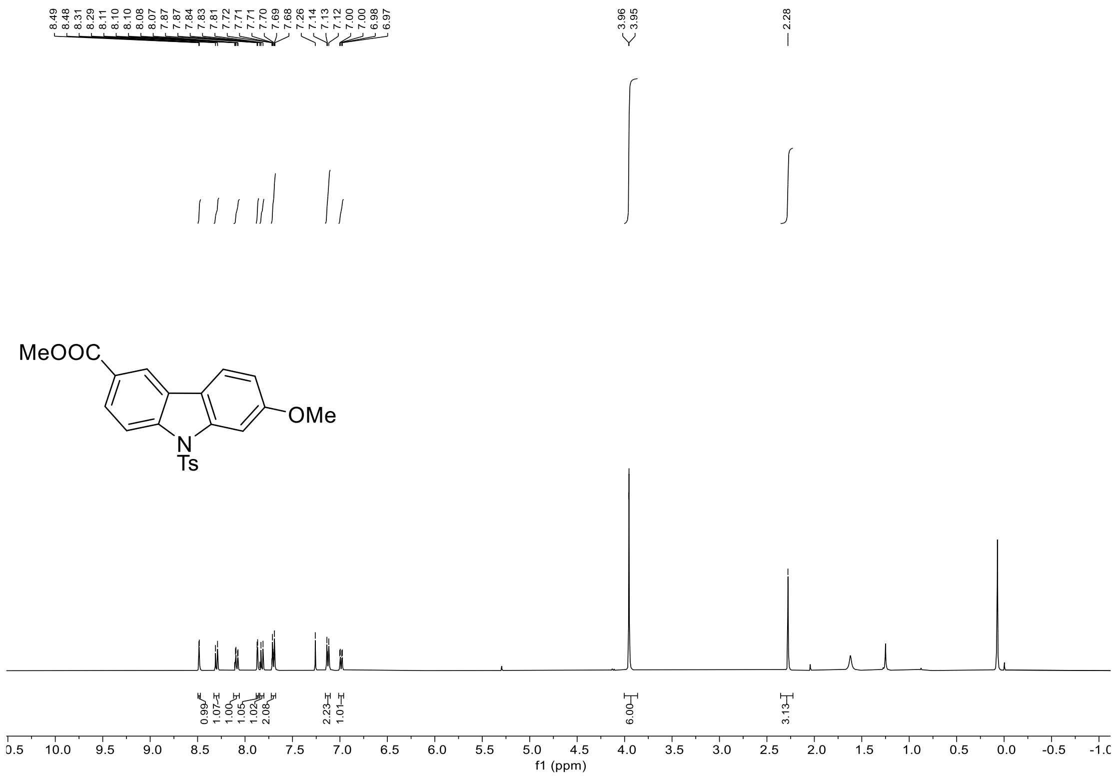
137.373
134.878
133.693
133.151
129.644
128.771
127.764
126.901
126.593
120.139
116.467
115.377
115.250
103.263
77.477
77.160
76.843
55.866
21.597
21.405
OMe
N
Ts
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



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8.10
8.08
8.07
7.87
7.84
7.83
7.81
7.72
7.71
7.71
7.70
7.69
7.68
7.26
7.14
7.13
7.12
7.00
7.00
6.98
6.97
3.96
3.95
2.28
MeOOC
OMe
N
Ts
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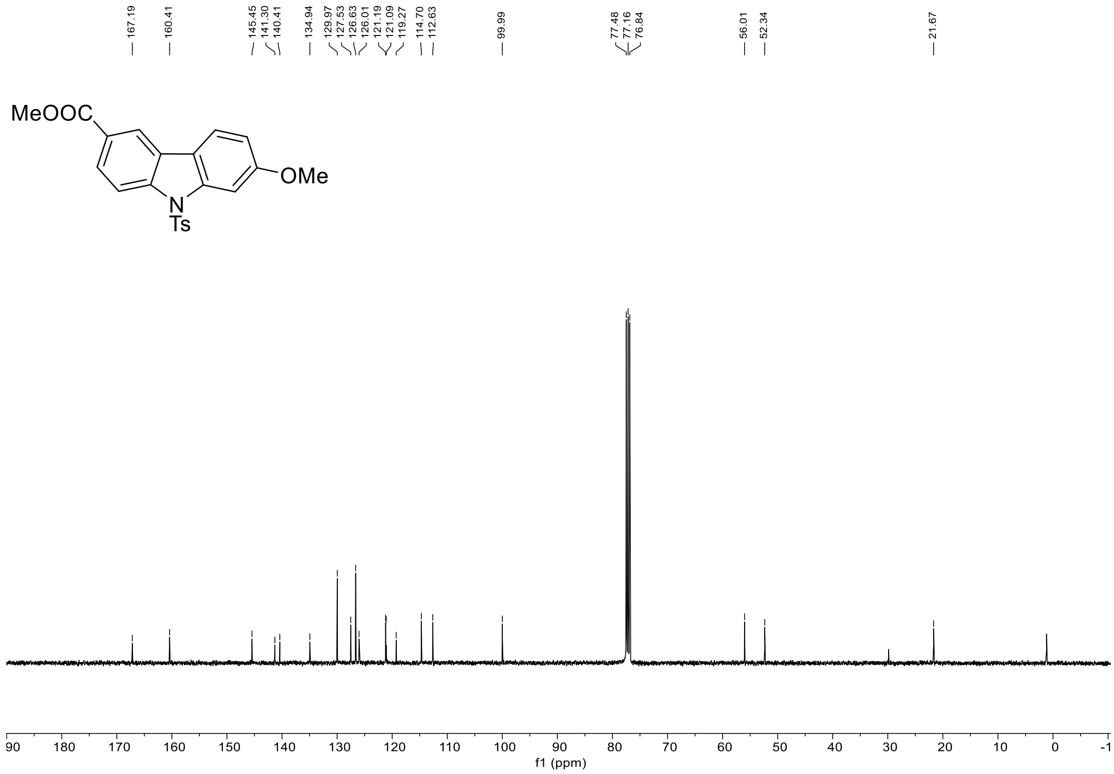
1.00
1.05
1.02
2.08
2.23
1.01
6.00
3.13
f1 (ppm)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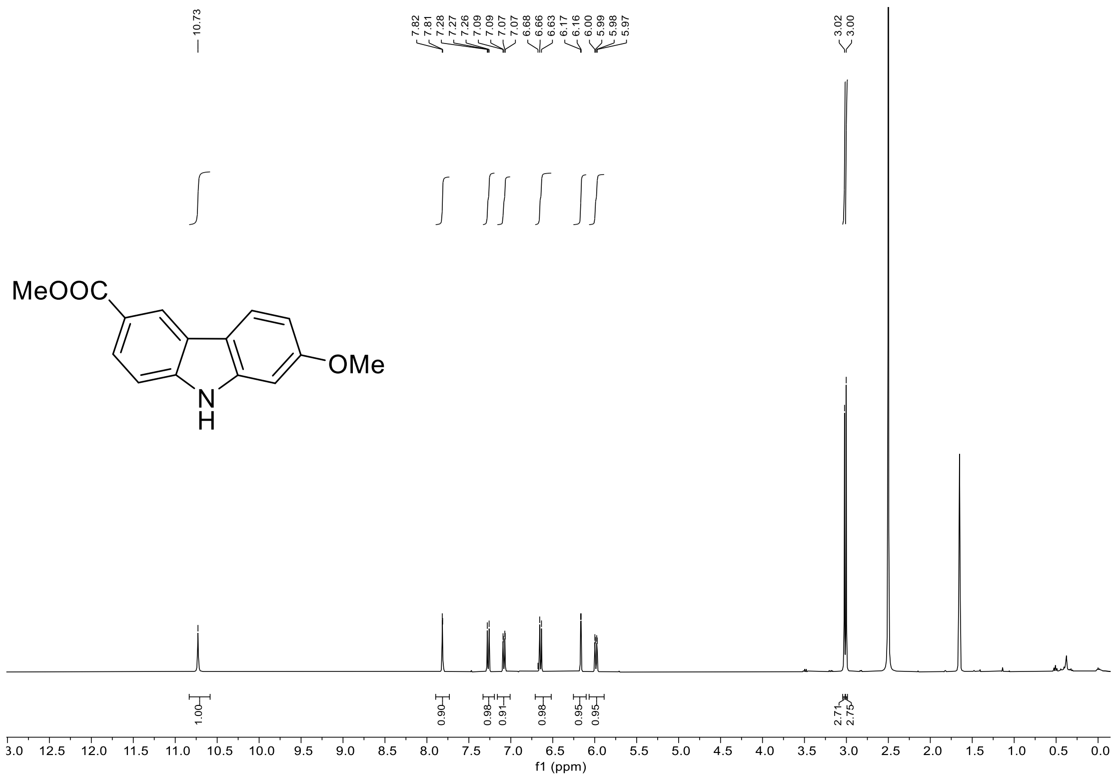
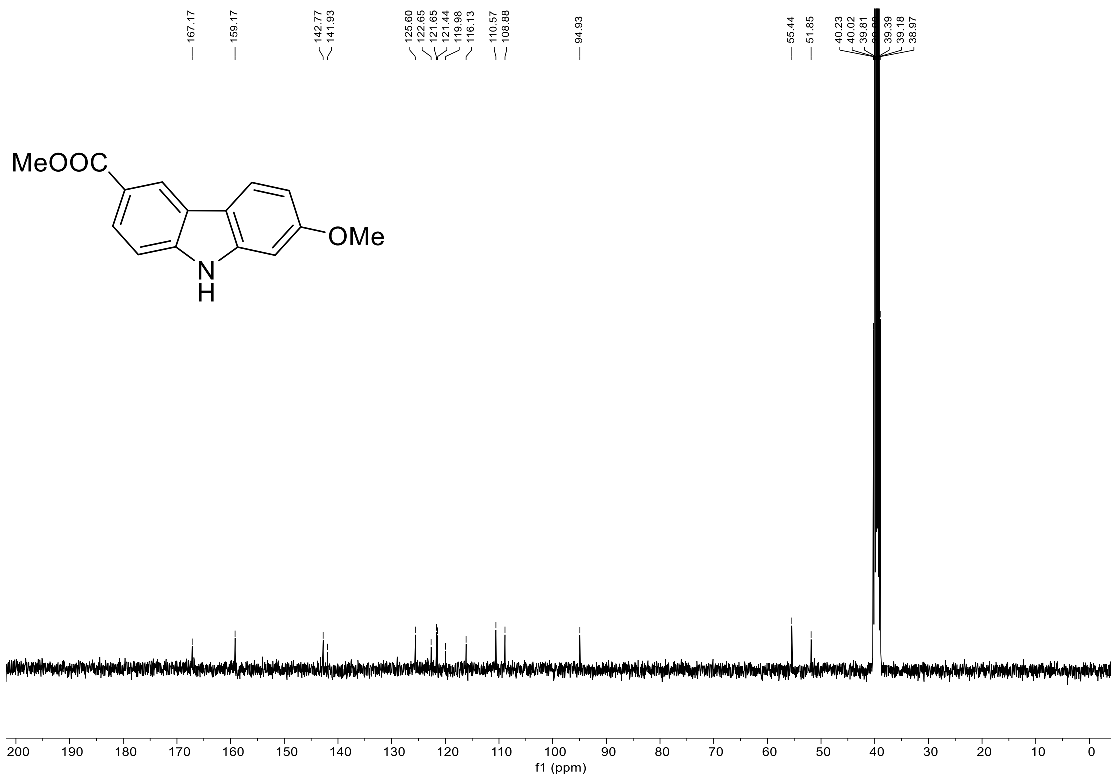
OMe
N
Ts
f1 (ppm)


MeOOC
OMe
N
H
f1 (ppm)



167.17
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141.93
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122.65
121.65
121.44
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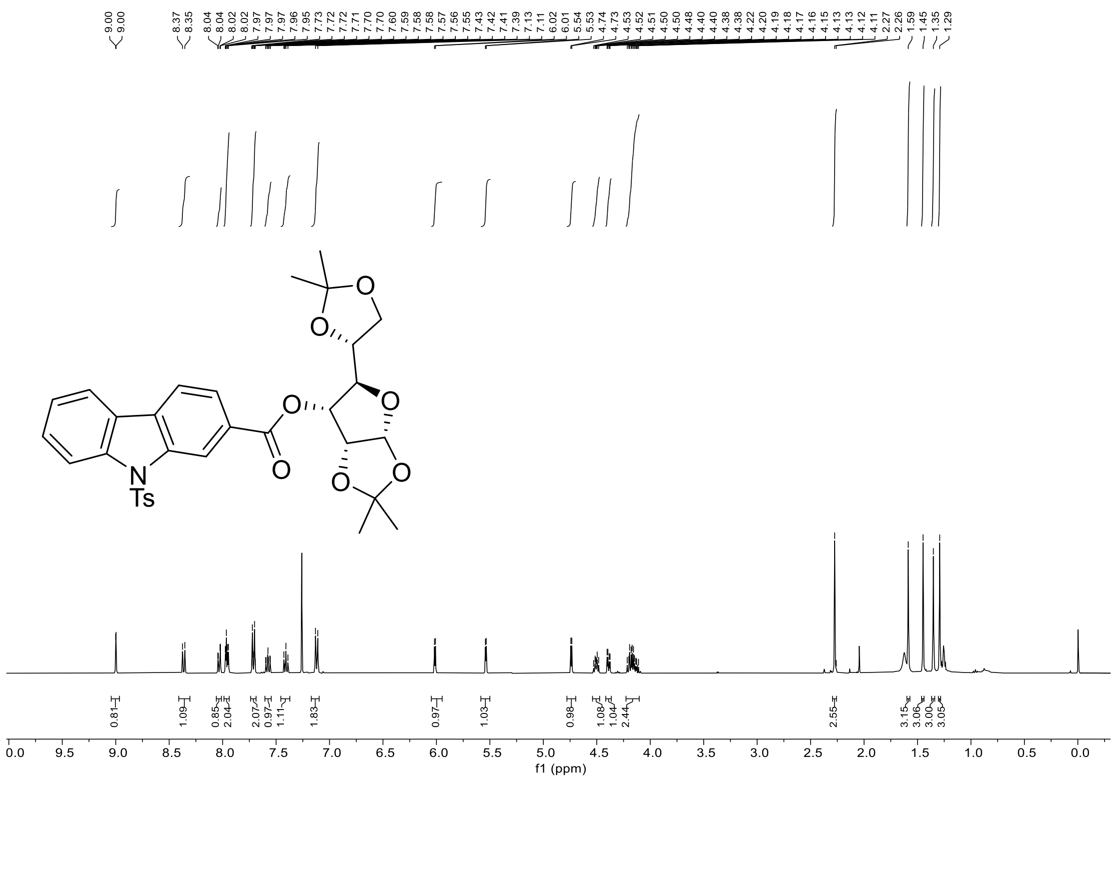
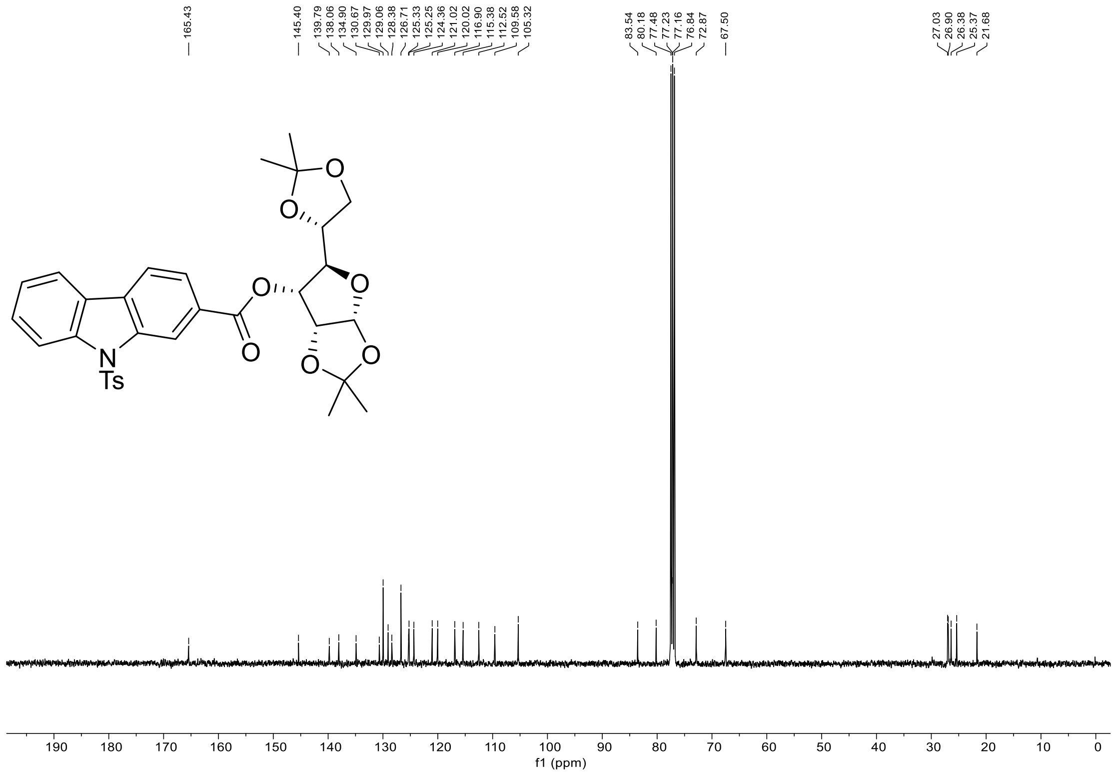
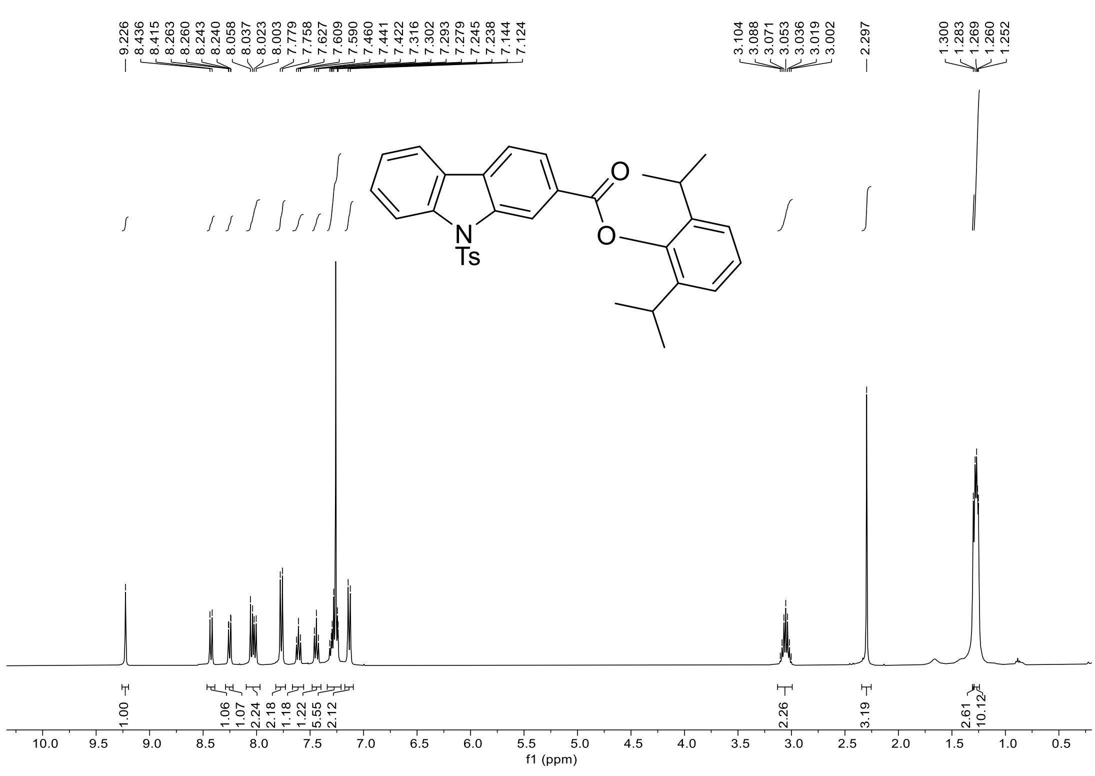
116.13
110.57
108.88
94.93
55.44
51.85
40.23
40.02
39.81
39.39
39.18
38.97
MeOOC
OMe
N
H
f1 (ppm)



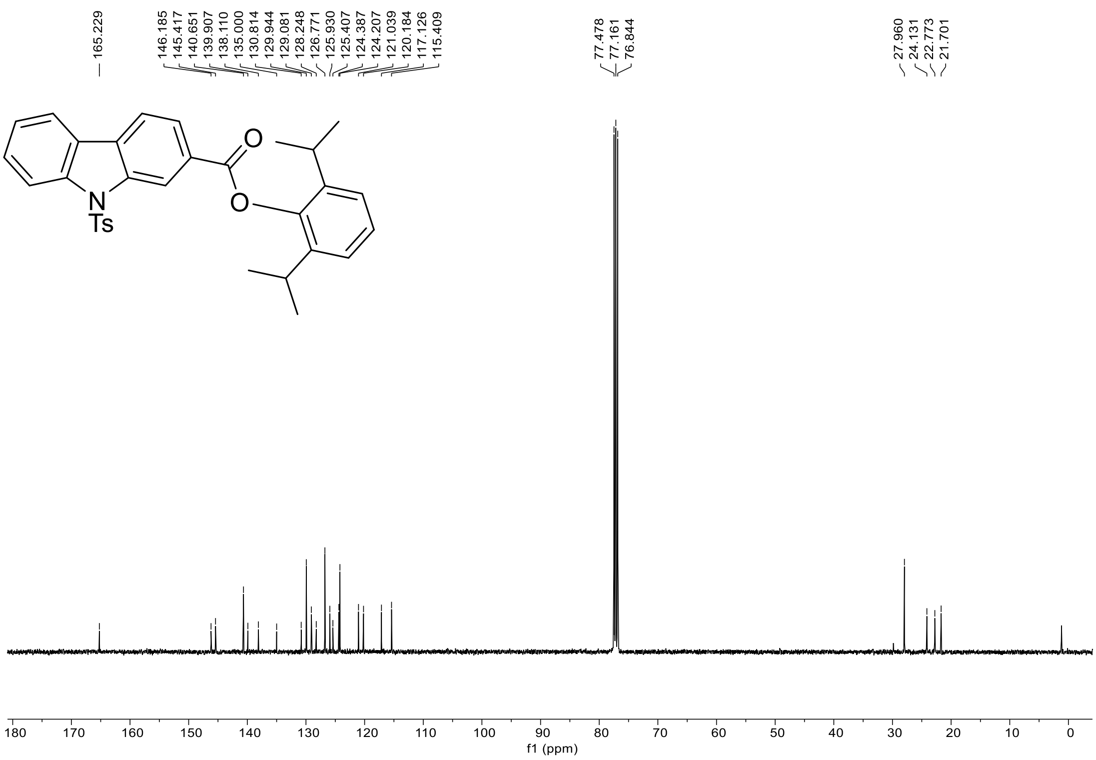
9.00
9.00
8.37
8.35
8.04
8.04
8.02
8.02
7.97
7.97
7.97
7.96
7.95
7.73
7.72
7.72
7.71
7.70
7.70
7.60
7.59
7.58
7.58
7.57
7.56
7.55
7.43
7.42
7.41
7.39
7.13
7.11
6.02
6.01
5.54
5.53
4.74
4.73
4.53
4.52
4.51
4.50
4.50
4.48
4.40
4.40
4.38
4.38
4.22
4.20
4.19
4.18
4.17
4.16
4.15
4.13
4.13
4.12
4.11
2.27
2.26
1.59
1.45
1.35
1.29
N
Ts
O
0.81
1.09
0.85
2.04
2.07
0.97
1.11
1.83
0.97
1.03
0.98
1.08
1.04
2.44
2.55
3.15
3.06
3.00
3.05
f1 (ppm)

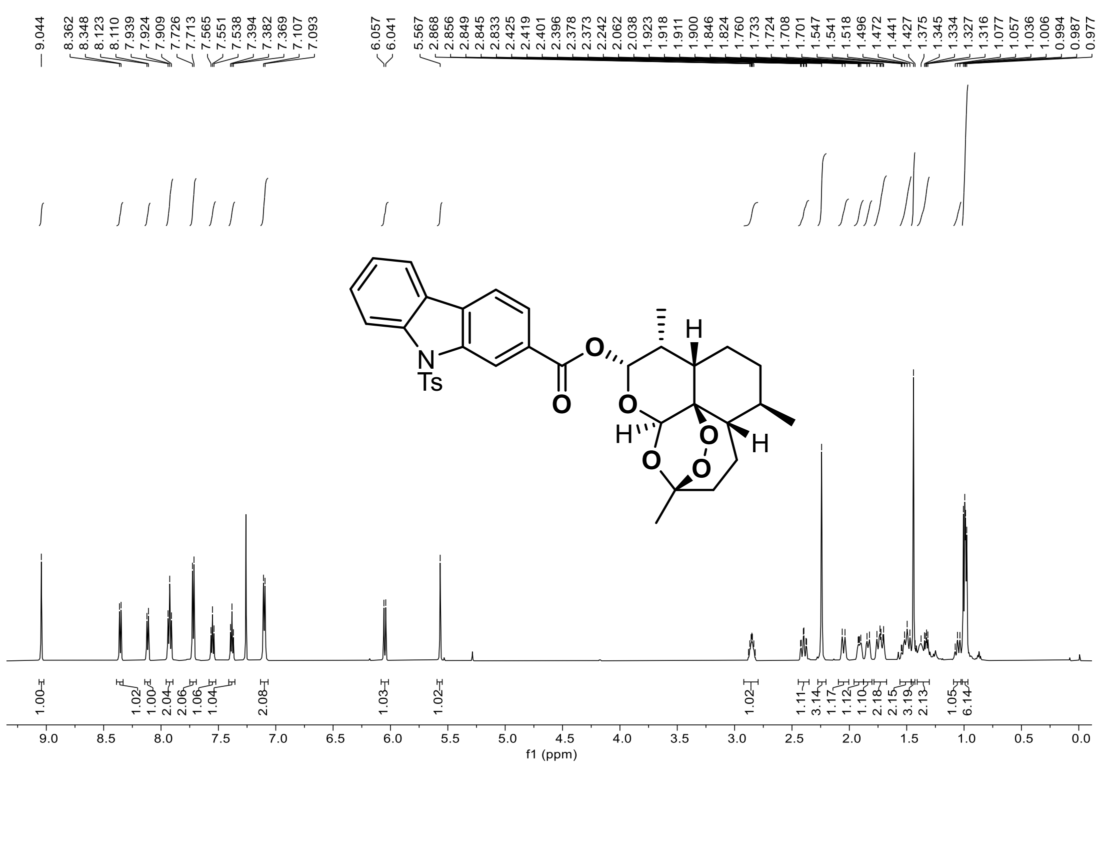


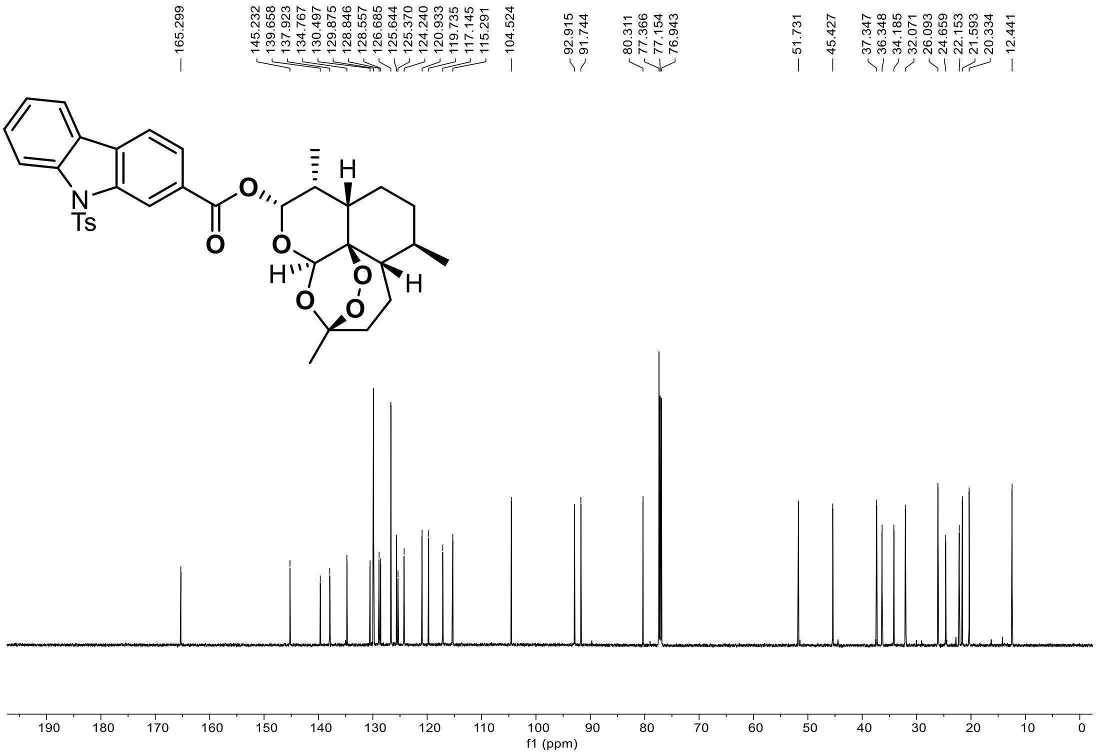
165.43
145.40
139.79
138.06
134.90
130.67
129.97
129.06
128.38
126.71
125.33
125.25
124.36
121.02
120.02
116.90
115.38
112.52
109.58
105.32
83.54
80.18
77.48
77.23
77.16
76.84
72.87
67.50
27.03
26.90
26.38
25.37
21.68
N
Ts
O
f1 (ppm)

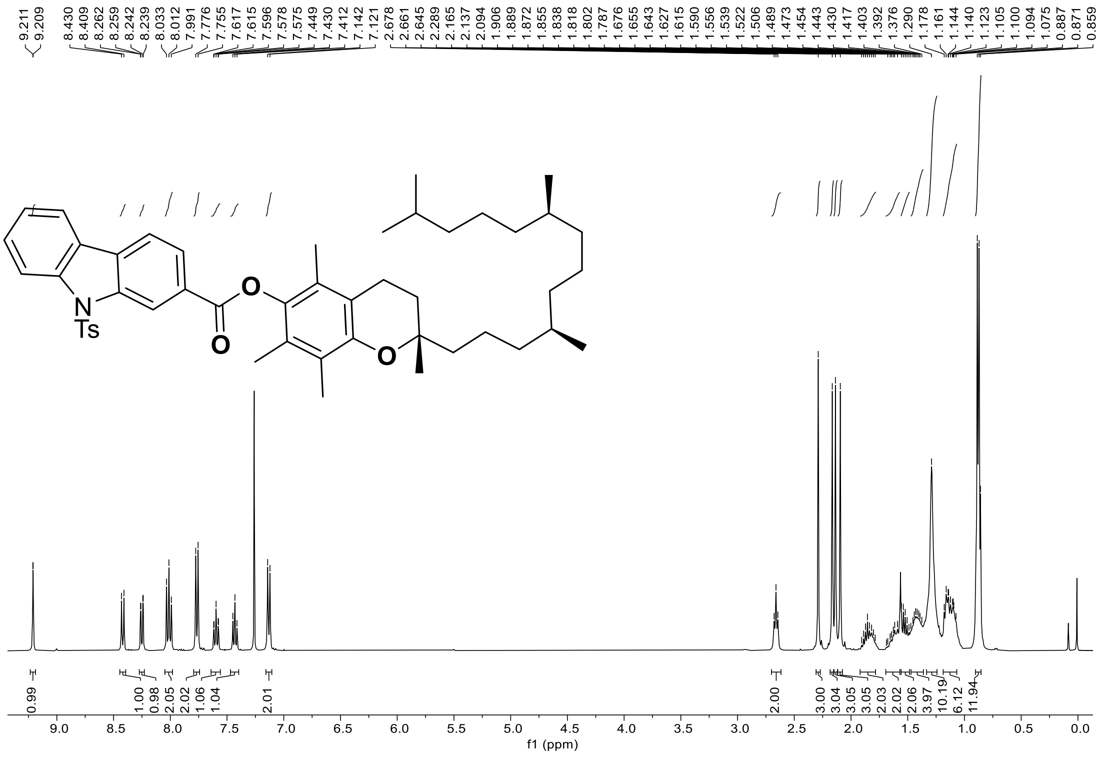


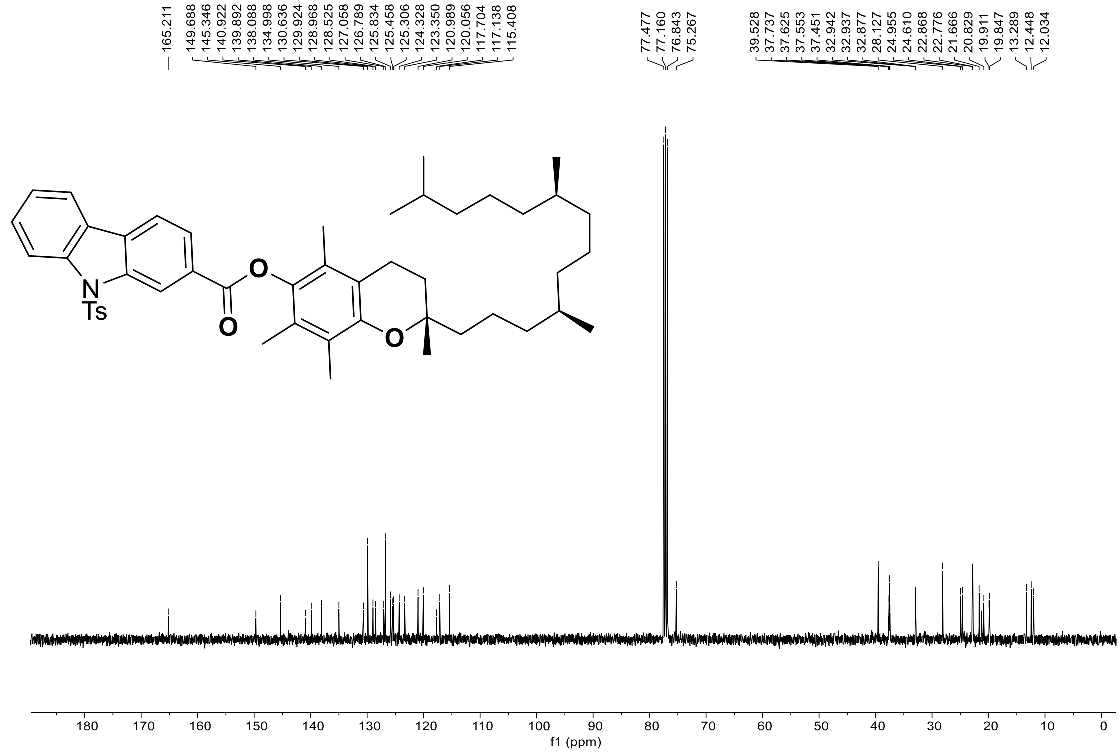
9.226
8.436
8.415
8.263
8.260
8.243
8.240
8.058
8.037
8.023
8.003
7.779
7.758
7.627
7.609
7.590
7.460
7.441
7.422
7.316
7.302
7.293
7.279
7.245
7.238
7.144
7.124
3.104
3.088
3.071
3.053
3.036
3.019
3.002
2.297
1.300
1.283
1.269
1.260
1.252
N
Ts
O
1.00
1.06
1.07
2.24
2.18
1.18
1.22
5.55
2.12
2.26
3.19
2.61
10.12
f1 (ppm)


165.229
146.185 145.417 140.651 139.907 138.110 135.000 130.814 129.944 129.081 128.248 126.771 125.930 125.407 124.387 124.207 121.039 120.184 117.126 115.409
77.478 77.161 76.844
27.960 24.131 22.773 21.701
O
O
N
Ts
f1 (ppm)


9.044
8.362 8.348 8.123 8.110 7.939 7.924 7.909 7.726 7.713 7.565 7.551 7.538 7.394 7.382 7.369 7.107 7.093
6.057 6.041
5.567 2.868 2.856 2.849 2.845 2.833 2.425 2.419 2.401 2.396 2.378 2.373 2.242 2.062 2.038 1.923 1.918 1.911 1.900 1.846 1.824 1.760 1.733 1.724 1.708 1.701 1.547 1.541 1.518 1.496 1.472 1.441 1.427 1.375 1.345 1.334 1.327 1.316 1.077 1.057 1.036 1.006 0.994 0.987 0.977
O
O
N
Ts
H
O
H
O
O
O
H
1.00 1.02 1.00 2.04 2.06 1.06 1.04 2.08 1.03 1.02 1.02 1.11 3.14 1.17 1.12 1.10 2.18 2.15 3.19 2.13 1.05 6.14
f1 (ppm)


165.299
145.232
139.658
137.923
134.767
130.497
129.875
128.846
128.557
126.685
125.644
125.370
124.240
120.933
119.735
117.145
115.291
104.524
92.915
91.744
80.311
77.366
77.154
76.943
51.731
45.427
37.347
36.348
34.185
32.071
26.093
24.659
22.153
21.593
20.334
12.441
N
Ts
O
H
f1 (ppm)


9.211
9.209
8.430
8.409
8.262
8.259
8.242
8.239
8.033
8.012
7.991
7.776
7.755
7.617
7.615
7.596
7.578
7.575
7.449
7.430
7.412
7.142
7.121
2.678
2.661
2.645
2.289
2.165
2.137
2.094
1.906
1.889
1.872
1.855
1.838
1.818
1.802
1.787
1.676
1.655
1.643
1.627
1.615
1.590
1.556
1.539
1.522
1.506
1.489
1.473
1.454
1.443
1.430
1.417
1.403
1.392
1.376
1.290
1.178
1.161
1.144
1.140
1.123
1.105
1.100
1.094
1.075
0.887
0.871
0.859
N
Ts
O
0.99
1.00
0.98
2.05
2.02
1.06
1.04
2.01
2.00
3.00
3.04
3.05
3.05
2.03
2.02
2.06
3.97
10.19
6.12
11.94
f1 (ppm)


165.211
149.688
145.346
140.922
139.892
138.088
134.998
130.636
129.924
128.968
128.525
127.058
126.789
125.834
125.458
125.306
124.328
123.350
120.989
120.056
117.704
117.138
115.408
77.477
77.160
76.843
75.267
39.528
37.737
37.625
37.553
37.451
32.942
32.937
32.877
28.127
24.955
24.610
22.868
22.776
21.666
20.829
19.911
19.847
13.289
12.448
12.034
N
Ts
O
O
O
f1 (ppm)