

Electrochemical Direct Site-Selective Selenation of Carbazoles

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1. General information

General.

Unless otherwise noted, all reagents and solvents were purchased from commercial sources (Adamas-beta, Energy Chemical) and used without further purification.

NMR spectra

^1H and ^{13}C NMR spectra were collected on 600 MHz NMR spectrometer (Bruker Avance NEO 600). Chemical shifts for protons were reported in parts per million (ppm) downfield from tetramethylsilane and were referenced to residual protium in the NMR solvents ($\text{CDCl}_3 = \delta(\text{ppm}) = 7.26$). The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, h = heptet. Coupling constants J were reported in hertz (Hz).

HRMS

High-resolution mass spectra (HRMS) were recorded on Thermo Fisher Scientific QExactive.

Melting point

Melting point (M.P.) was recorded on BÜCHI (M-560).

UV light

Visualization of TLC was achieved by the use of UV light (254 nm).

Materials.

All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. Diselenides^[1] were synthesized according to the reported method.

The Electrochemical Reaction Instrument.

Cyclic voltammetry (CV) was carried out on a CHI660E electrochemical workstation (CH Instruments, Inc).

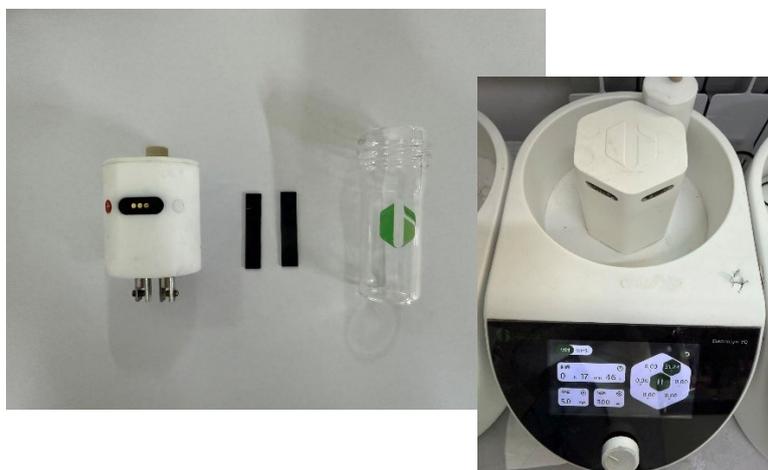
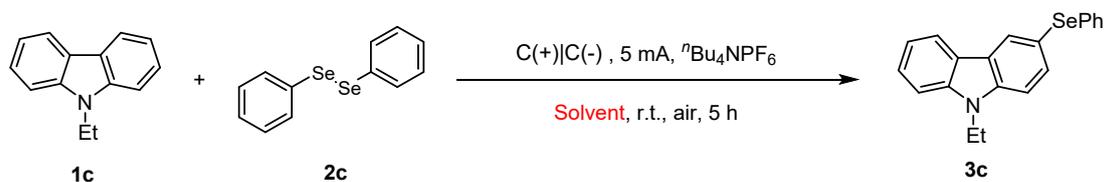


Fig. S1 Diagram of the electrochemical reaction device

2. Experimental procedures

2.1 Optimization of the reaction conditions for carbazole selenation

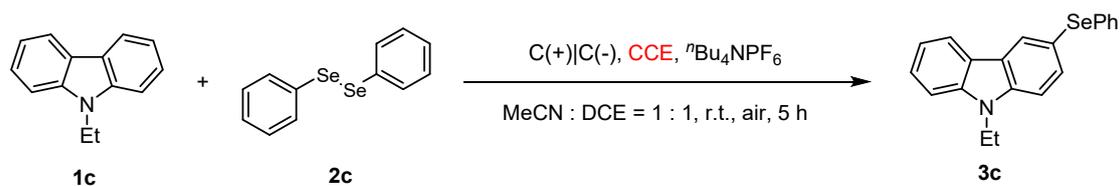
2.1.1 Table S1 Screening of solvents^a



Entry	Solvent	Yield [%] ^b
1	THF	12
2	EtOAc	N.R.
3	H ₂ O	N.R.
4	MeCN	62
5	DCE	55
6	CHCl ₃	trace
7	1,4-dioxane	N.D.
8	MeCN:H ₂ O = 1:1	N.D.
9	MeCN:MeOH = 1:1	trace
10	MeCN:DCM = 1:1	37
11	MeCN:CHCl ₃ = 1:1	38
12	MeCN:DCE = 1:10	46
13	MeCN:DCE = 1:5	49
14	MeCN:DCE = 1:3	61
15	MeCN:DCE = 1:1	71
16	MeCN:DCE = 5:1	53
17	MeCN:DCE = 3:1	56

^aReaction conditions: **1c** (0.1 mmol), **2c** (0.2 mmol), ⁿBu₄NPF₆ (0.1 mmol), solvent (4 mL), graphitic carbon anode (immersed surface area 8×5 mm²), graphitic carbon cathode (immersed surface area 8×5 mm²), the distance between the electrodes (5 mm), constant current = 5 mA, 5 h, room temperature, under air, undivided cell. ^bIsolated yields. N.R. = no reaction, N.D. = not detected.

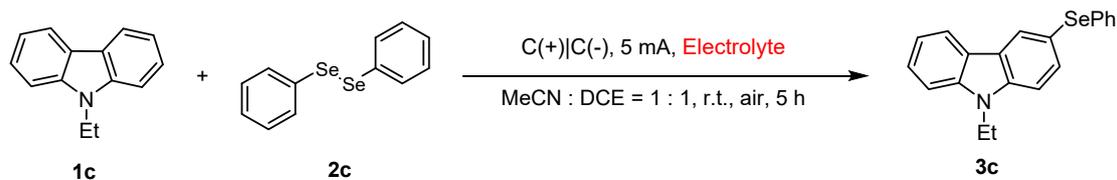
2.1.2 Table S2 Screening of constant currents^a



Entry	CCE [mA]	Yield [%] ^b
1	3	54
2	5	71
3	7	59
4	10	50

^aReaction conditions: **1c** (0.1 mmol), **2c** (0.2 mmol), $n\text{Bu}_4\text{NPF}_6$ (0.1 mmol), MeCN:DCE = 1:1 (4 mL), graphitic carbon anode (immersed surface area $8 \times 5 \text{ mm}^2$), graphitic carbon cathode (immersed surface area $8 \times 5 \text{ mm}^2$), the distance between the electrodes (5 mm), constant current = x mA, 5 h, room temperature, under air, undivided cell. ^bIsolated yields. CCE = constant current electrolysis.

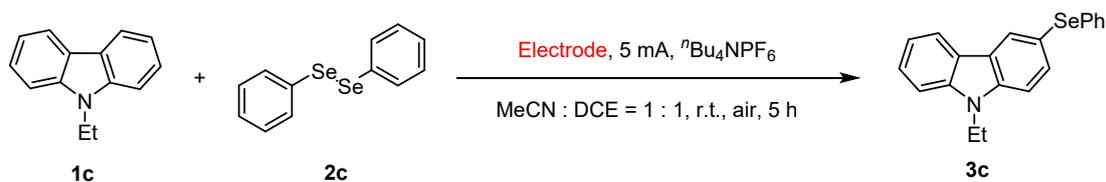
2.1.3 Table S3 Screening of electrolytes^a



Entry	Electrolyte	Yield [%] ^b
1	$n\text{Bu}_4\text{NOAc}$	58
2	$n\text{Bu}_4\text{NClO}_4$	trace
3	$n\text{Et}_4\text{NBF}_4$	37
4	$n\text{Bu}_4\text{NPF}_6$	71
5	$n\text{Et}_4\text{NPF}_6$	61

^aReaction conditions: **1c** (0.1 mmol), **2c** (0.2 mmol), electrolyte (0.1 mmol), MeCN:DCE = 1:1 (4 mL), graphitic carbon anode (immersed surface area $8 \times 5 \text{ mm}^2$), graphitic carbon cathode (immersed surface area $8 \times 5 \text{ mm}^2$), the distance between the electrodes (5 mm), constant current = 5 mA, 5 h, room temperature, under air, undivided cell. ^bIsolated yields.

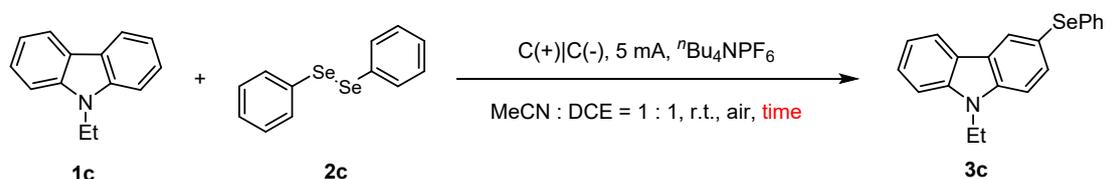
2.1.4 Table S4 Screening of electrodes^a



Entry	Electrode	Yield [%] ^b
1	C/Mg	54
2	C/Cu	38
3	C/Ni	60
4	C/C	71
5	Mg/C	trace
6	Al/C	22
7	Ni/C	17
8	Pt/C	61

^aReaction conditions: **1c** (0.1 mmol), **2c** (0.2 mmol), ⁿBu₄NPF₆ (0.1 mmol), MeCN:DCE = 1:1 (4 mL), anode (immersed surface area 8×5 mm²), cathode (immersed surface area 8×5 mm²), the distance between the electrodes (5 mm), constant current = 5 mA, 5 h, room temperature, under air, undivided cell. ^bIsolated yields.

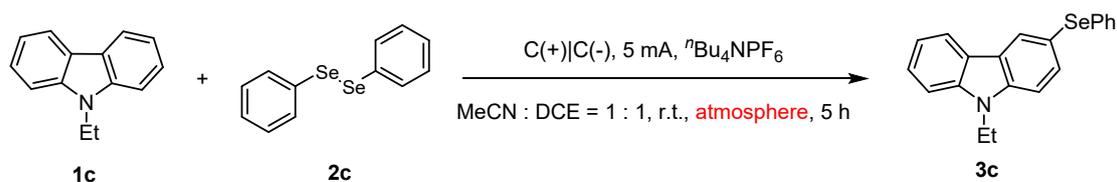
2.1.5 Table S5 Screening of reaction time^a



Entry	Time [h]	Yield [%] ^b
1	3	60
2	5	71
3	7	62

^aReaction conditions: **1c** (0.1 mmol), **2c** (0.2 mmol), ⁿBu₄NPF₆ (0.1 mmol), MeCN:DCE = 1:1 (4 mL), graphitic carbon anode (immersed surface area 8×5 mm²), graphitic carbon cathode (immersed surface area 8×5 mm²), the distance between the electrodes (5 mm), constant current = 5 mA, time, room temperature, under air, undivided cell. ^bIsolated yields.

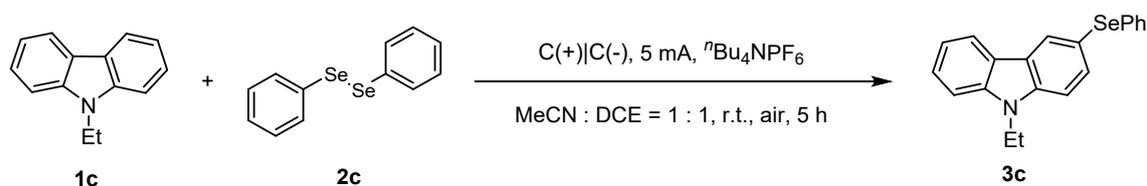
2.1.6 Table S6 Screening of atmosphere^a



Entry	Atmosphere	Yield [%] ^b
1	air	71
2	N ₂	65

^aReaction conditions: **1c** (0.1 mmol), **2c** (0.2 mmol), ⁿBu₄NPF₆ (0.1 mmol), MeCN:DCE = 1:1 (4 mL), graphitic carbon anode (immersed surface area 8×5 mm²), graphitic carbon cathode (immersed surface area 8×5 mm²), the distance between the electrodes (5 mm), constant current = 5 mA, 5 h, room temperature, atmosphere, undivided cell. ^bIsolated yields.

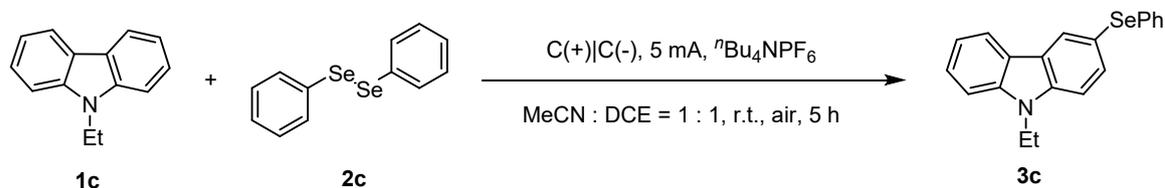
2.1.7 Table S7 Screening of substrate ratio^a



Entry	1c:2c [mmol]	Yield [%] ^b
1	0.1:0.2	71
2	0.15:0.3	62
3	0.2:0.4	73
4	0.3:0.6	51

^aReaction conditions: **1c** (x mmol), **2c** (2x mmol), ⁿBu₄NPF₆ (1 eq.), MeCN:DCE = 1:1 (4 mL), graphitic carbon anode (immersed surface area 8×5 mm²), graphitic carbon cathode (immersed surface area 8×5 mm²), the distance between the electrodes (5 mm), constant current = 5 mA, 5 h, room temperature, under air, undivided cell. ^bIsolated yields.

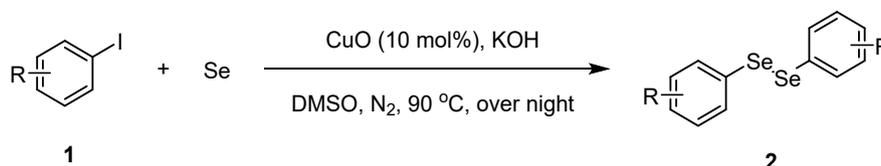
2.1.8 The general procedure for the direct selenation of carbazole



Taking the synthesis of **3c** as an example, under air, a mixture of **1c** (39.1 mg, 0.2 mmol), **2c** (124.9 mg, 0.4 mmol), ⁿBu₄NPF₆ (77.5 mg, 0.2 mmol) and MeCN:DCE = 1:1 (4 mL) was added to an oven-dried undivided vial (10 mL). The vial was equipped with graphite carbon rods as the anode and the cathode. The resulting mixture was stirred and electrolyzed in a constant current mode with

a constant current of 5 mA at ambient temperature for 5 h. When the reaction was finished, the reaction mixture was dried over anhydrous sodium sulfate followed by suction filtration and all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v) to afford the desired product **3c** as a white solid (51.2 mg, 73% yield).

2.2 Table S8 General procedure for the synthesis of diselenides^[1]

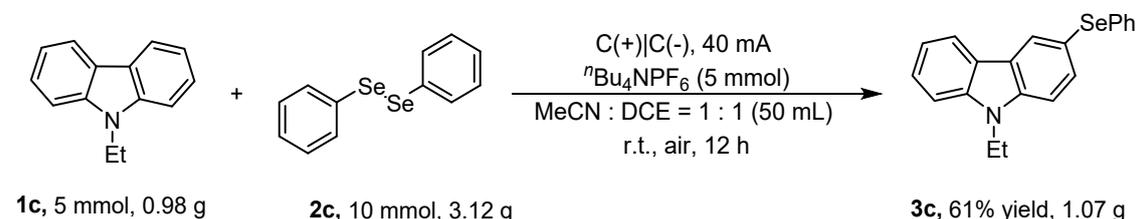


Under nitrogen atmosphere, to a stirred solution of Se powder (6.0 mmol) and aryl iodides (3.0 mmol) in dry DMSO (6.0 mL) was added CuO nanoparticles (10 mol%), followed by KOH (2.0 eq.), at 90 °C. The progress of the reaction was monitored by TLC. After the reaction was complete, the reaction mixture was allowed to cool. The resultant residue was purified by silica gel column chromatography using petroleum ether as the eluent to afford the desired product.

Entry	Product	Yield [%]
1	2ab	99
2	2ac	93
3	2ad	96
4	2ae	92
5	2af	88
6	2ag	91
7	2ah	95
8	2ai	84
9	2aj	91
10	2ak	26

2.3 Gram-scale reaction, continuous-flow process and product derivatization

2.3.1 Gram-scale selenation of carbazole in batch



Under air, *N*-ethylcarbazole **1c** (0.98 g, 5 mmol), diphenyldiselenide **2c** (3.12 g, 10 mmol), ⁿBu₄NPF₆ (1.94 g, 5 mmol), and MeCN:DCE = 1:1 (40 mL) were added to a dried 100 mL round-bottom flask (RBF). The RBF was equipped with a graphite carbon anode (27 mm×15.0 mm×1 mm) and a graphite carbon cathode (27 mm×15.0 mm×1 mm). The mixture was subjected to electrolysis at room temperature, with the current set to 40 mA, and the reaction was allowed to proceed for 12 hours. After the reaction, the solvent and all volatile substances were removed by

rotary evaporation under reduced pressure. The resulting residue was purified by silica gel column chromatography, using a petroleum ether (60-90 °C)/EtOAc = 100:1 (v:v) eluent. The target product **3c** was obtained as a white solid (1.07 g, 61% yield). 2.23 g of unreacted diphenyldiselenide was recovered from the reaction system.

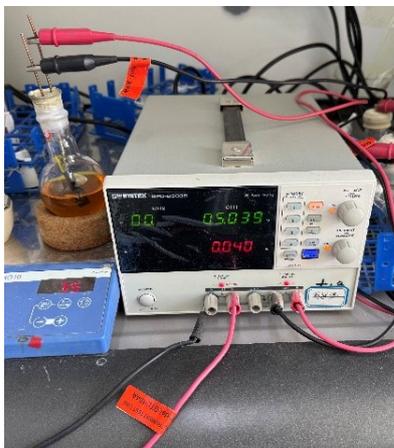
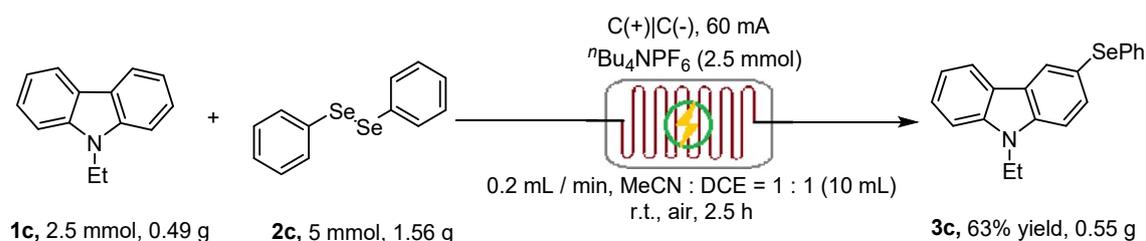


Fig. S2 Scale-up experimental reaction setup

2.3.2 Scale-up selenation of carbazole under continuous-flow condition

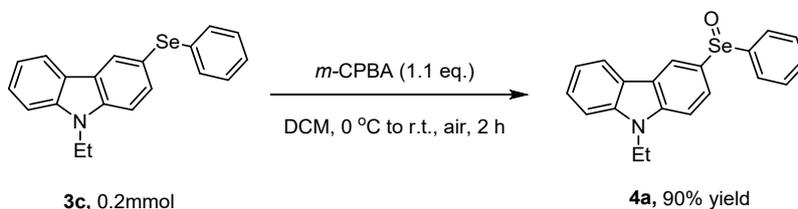


Under air, **1c** (0.49 g, 2.5 mmol), **2c** (1.56 g, 5 mmol), ^tBu₄NPF₆ (0.97 g, 5 mmol), and MeCN:DCE = 1:1 (10 mL) were mixed and then aspirated into a syringe. A flow electrochemical reactor, equipped with graphite plates as both the anode and cathode, was used, with the surface area of the graphite plates measuring 8 cm×6 cm. The mixture underwent flow electrolysis at room temperature under a constant current mode, with a current of 60 mA and a flow rate of 0.2 mL/min for 2.5 hours. Upon completion of the reaction, the solvent and all volatile substances were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v), yielding the target product **3c** as a white solid (0.55 g, 63% yield).



Fig. S3 Flow electrochemical reactor for scale-up experiment

2.3.3 Product derivatization

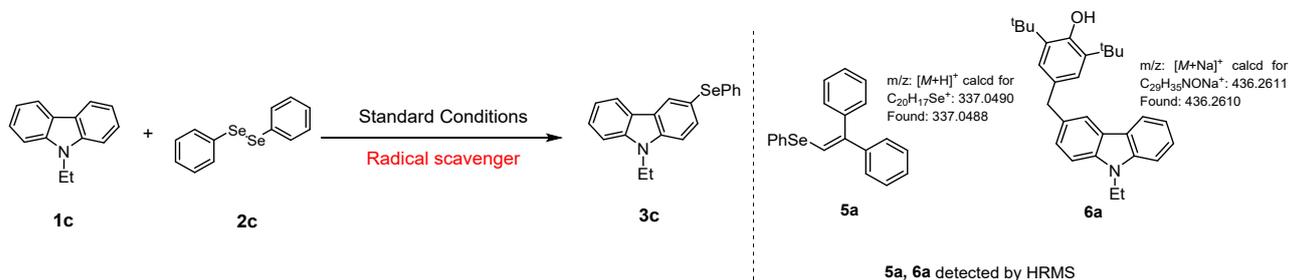


Under air, **3c** (70 mg, 0.2 mmol) was dissolved in 2 mL of DCM. The reaction mixture was cooled to 0 °C, and *m*-CPBA (38 mg, 0.22 mmol) was added in one portion. The mixture was stirred at 0 °C for 1 hour and at room temperature for an additional 1 hour. Upon completion of the reaction, the organic phase was washed with saturated aqueous potassium carbonate solution (10 mL) and the aqueous phase was extracted with DCM. The organic layers were combined and concentrated under reduced pressure. The residue was purified by column chromatography (EtOAc then DCM/MeOH, 20:1 (v:v)) to obtain the target product **4a** with 90% isolated yield.

3. Mechanistic studies

3.1 Radical trapping experiments

3.1.1 Table S9 The radical capture experiment^a



Entry	Radical scavenger (mmol)	Yield [%] ^b
1	none	73
2	BHT (0.4)	35
3	BHT (0.6)	17
4	DPE (0.6)	23
5	TEMPO (0.6)	N.R.

^aReaction conditions: **1c** (0.2 mmol), **2c** (0.4 mmol), ⁿBu₄NPF₆ (0.2 mmol), MeCN:DCE = 1:1 (4 mL), radical scavenger, graphitic carbon anode (immersed surface area 8×5 mm²), graphitic carbon cathode (immersed surface area 8×5 mm²), the distance between the electrodes (5 mm), constant current = 5 mA, 5 h, room temperature, under air, undivided cell. ^bIsolated yields. DPE = 1,1-diphenylethylene, BHT = butylated hydroxytoluene. TEMPO = 2,2,6,6-tetramethylpiperidinoxy. N.R. = no reaction.

3.1.2 The HRMS spectra of compound 5a and 6a

MHD-3 #223 RT: 1.15 AV: 1 NL: 1.29E6
T: FTMS + p ESI Full ms [100.0000-1500.0000]

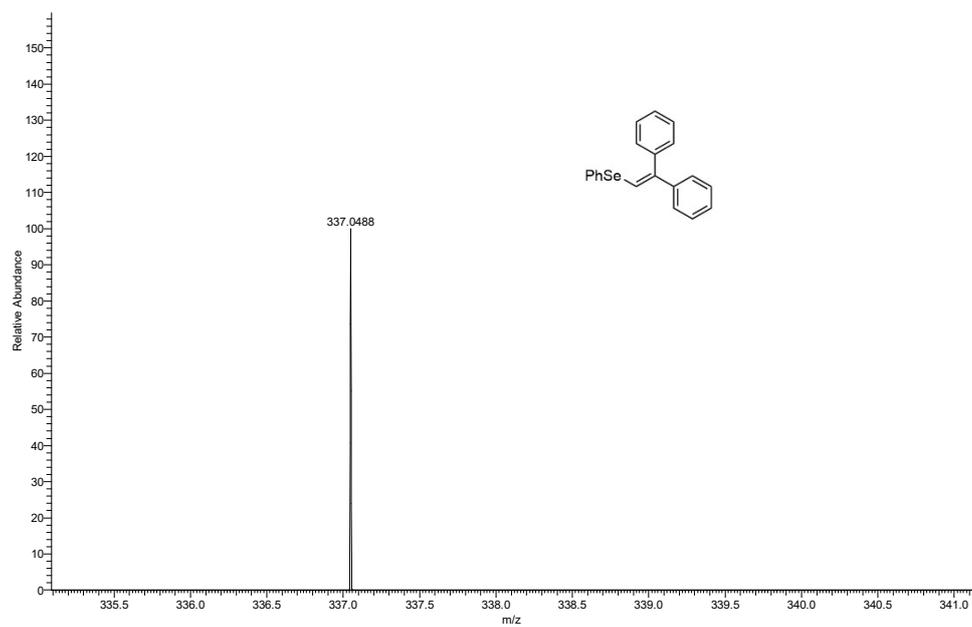


Fig. S4 The HRMS spectra of compound 5a

MHD-1 #154 RT: 0.79 AV: 1 NL: 2.63E5
T: FTMS + p ESI Full ms [100.0000-1500.0000]

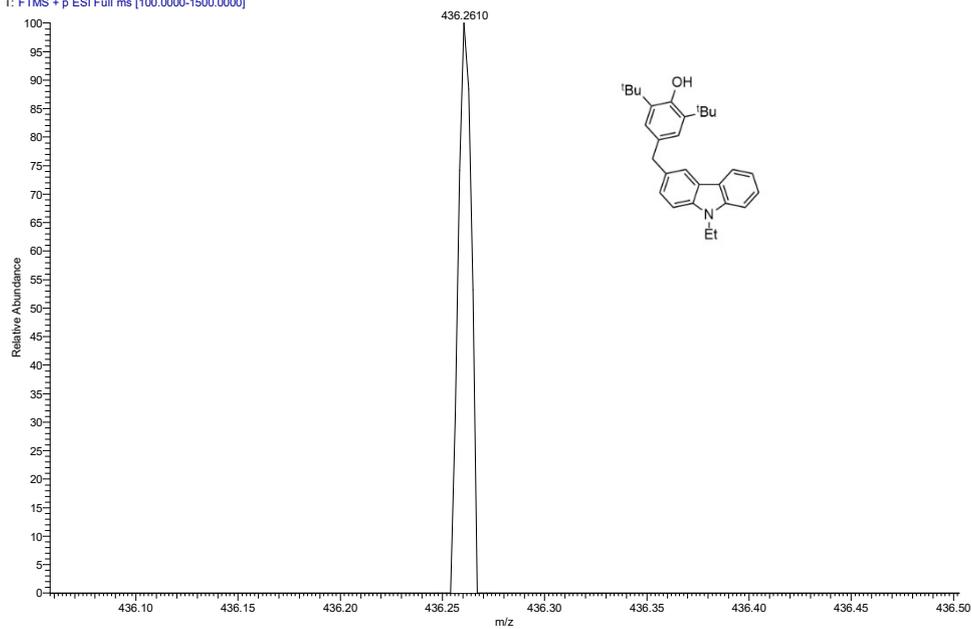
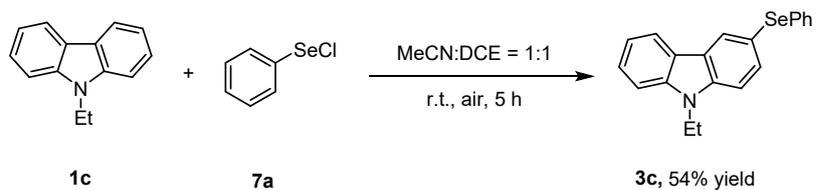


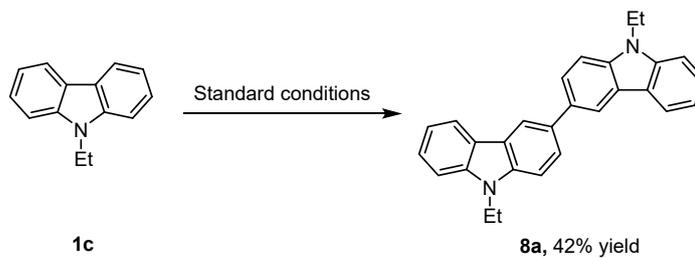
Fig. S5 The HRMS spectra of compound 6a

3.2 Control and radical coupling experiments.

(a) Control experiment^{a,b}



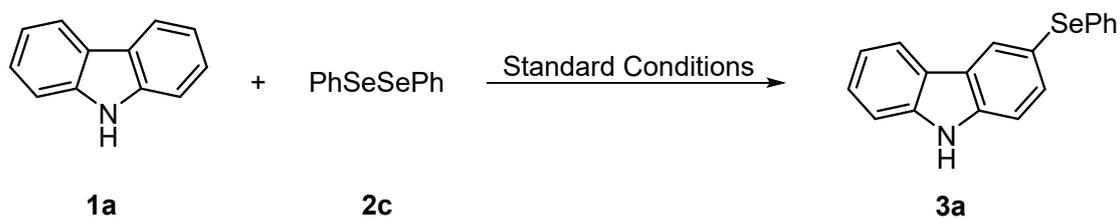
(b) Radical coupling experiment^{c,b}



^aReaction conditions: **1c** (0.2 mmol), **7a** (0.4 mmol), MeCN:DCE = 1:1 (4 mL), 5 h, room temperature, under air. ^cReaction conditions: **1c** (0.2 mmol), ⁿBu₄NPF₆ (0.2 mmol), MeCN:DCE = 1:1 (4 mL), graphitic carbon anode (immersed surface area 8×5 mm²), graphitic carbon cathode (immersed surface area 8×5 mm²), the distance between the electrodes (5 mm), constant current = 5 mA, 5 h, room temperature, under air. ^bIsolated yield.

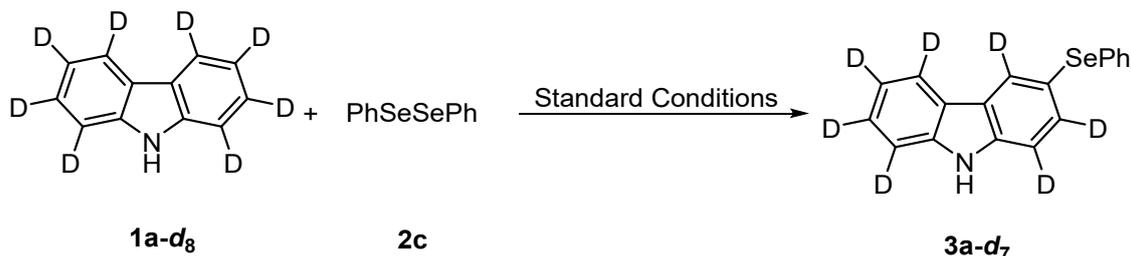
3.3 Table S10 KIE experiment^a

$$K_H/K_D = 5.94/6.40 = 0.93$$



Entry	Time [h]	Yield [%] ^b
1	0.5	28
2	1	33
3	2	38
4	3	46
5	5	55

^aReaction conditions: **1a** (0.2 mmol), **2c** (0.4 mmol), ⁿBu₄NPF₆ (0.2 mmol), MeCN:DCE = 1:1 (4 mL), graphitic carbon anode (immersed surface area 8×5 mm²), graphitic carbon cathode (immersed surface area 8×5 mm²), the distance between the electrodes (5 mm), constant current = 5 mA, room temperature, under air, time, undivided cell. ^bIsolated yields.



Entry	Time [h]	Yield [%] ^b
1	0.5	5
2	1	7
3	2	12
4	3	17
5	5	34

^aReaction conditions: **1a-d₈** (0.2 mmol), **2c** (0.4 mmol), ⁿBu₄NPF₆ (0.2 mmol), MeCN:DCE = 1:1 (4 mL), graphitic carbon anode (immersed surface area 8×5 mm²), graphitic carbon cathode (immersed surface area 8×5 mm²), the distance between the electrodes (5 mm), constant current = 5 mA, room temperature, under air, time, undivided cell. ^bIsolated yields.

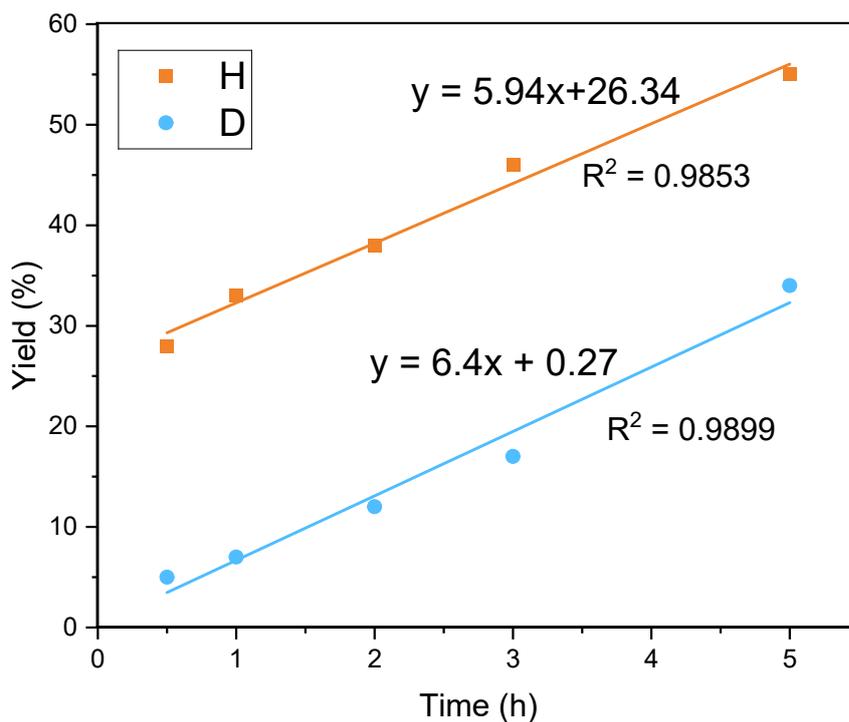


Fig. S6 KIE experiments.

3.4 The cyclic voltammetry of 1c and 2c

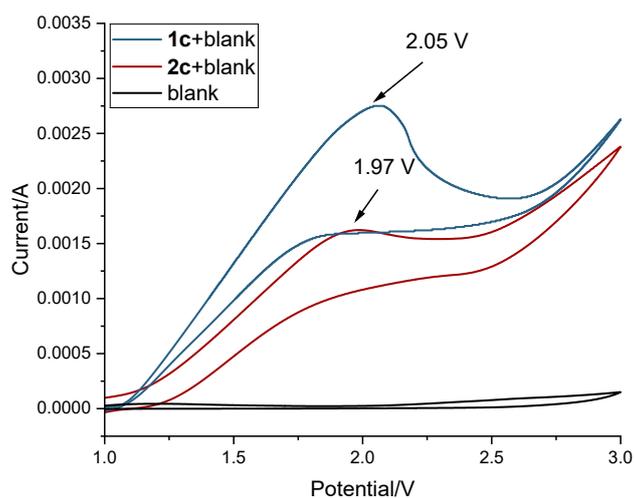


Fig. S7 CV experiments. Cyclic voltammetry of **1c** (0.2 mmol), **2c** (0.4 mmol), $n\text{Bu}_4\text{NPF}_6$ (0.2 mmol) in MeCN:DCE = 1:1 (4 mL) under air. A glassy carbon disk ($R = 5.5$ mm, $h = 10$ mm) was used as the working electrode. A Pt disk ($R = 5.5$ mm, $h = 10$ mm) and Ag/AgCl ($R = 5.0$ mm, $h = 10$ mm) were used as the counter and reference electrodes, respectively, blank = solvent + $n\text{Bu}_4\text{NPF}_6$.

3.5 The cyclic voltammetry of 4c and 5c

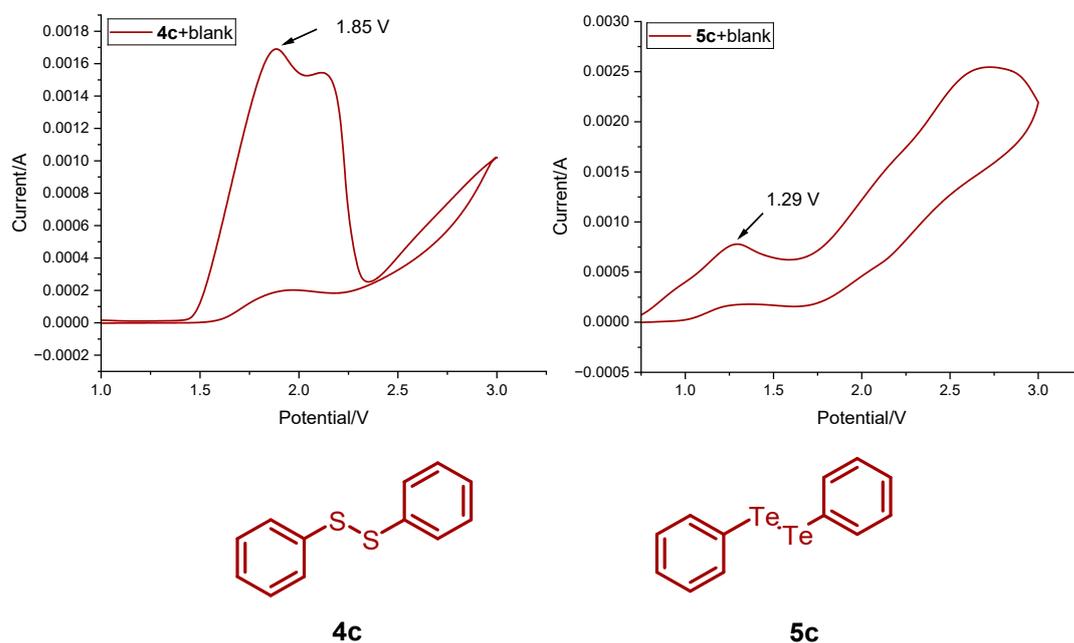
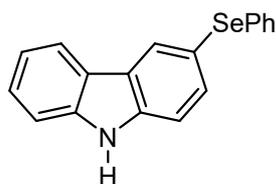
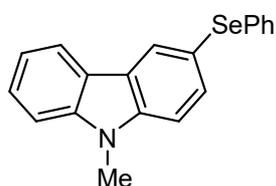


Fig. S8 CV experiments. Cyclic voltammetry of **4c** (0.2 mmol), **5c** (0.2 mmol), $n\text{Bu}_4\text{NPF}_6$ (0.2 mmol) in MeCN:DCE = 1:1 (4 mL) under air. A glassy carbon disk (R = 5.5 mm, h = 10 mm) was used as the working electrode. A Pt disk (R = 5.5 mm, h = 10 mm) and Ag/AgCl (R = 5.0 mm, h = 10 mm) were used as the counter and reference electrodes, respectively, blank = solvent + $n\text{Bu}_4\text{NPF}_6$.

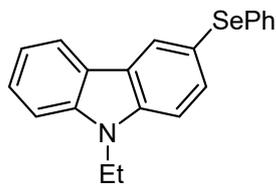
4. Analytical data



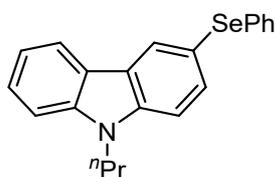
3-(phenylselanyl)-9H-carbazole (3a), 55% yield (35.5 mg), known compound^[2]. (Eluent: petroleum ether (60-90 °C)/EtOAc = 50:1, v:v). White solid. **¹H NMR (600 MHz, CDCl₃)** δ 8.38 (s, 1H), 8.13 (br, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.66 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.46-7.43 (m, 2H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.36-7.32 (m, 2H), 7.26-7.24 (m, 1H), 7.22-7.14 (m, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 139.80, 139.5, 134.3, 133.4, 130.5, 129.3, 128.3, 126.6, 126.3, 124.8, 122.9, 120.7, 120.1, 118.5, 111.8, 110.9. **HRMS (ESI)** *m/z*: [M]⁺ calcd for C₁₈H₁₃NSe: 323.0208; Found 323.0207.



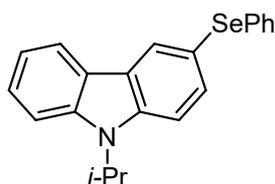
9-methyl-3-(phenylselanyl)-9H-carbazole (3b), 63% yield (42.4 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Yellow solid, m.p.: 96.3-96.9 °C. **¹H NMR (600 MHz, CDCl₃)** δ 8.41 (d, *J* = 1.7 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.73 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.52-7.50 (m, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.34-7.30 (m, 2H), 7.27 (d, *J* = 1.0 Hz, 1H), 7.21-7.13 (m, 3H), 3.87 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 141.3, 141.0, 134.5, 133.4, 130.3, 129.2, 128.4, 126.4, 126.2, 124.2, 122.3, 120.7, 119.5, 117.6, 109.7, 108.8, 29.3. **HRMS (ESI)** *m/z*: [M]⁺ calcd for C₁₉H₁₅NSe: 337.0364; Found 337.0364.



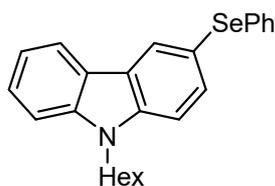
9-ethyl-3-(phenylselanyl)-9H-carbazole (3c), 73% yield (51.2 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). White solid, m.p.: 138.6-139.0 °C. **¹H NMR (600 MHz, CDCl₃)** δ 8.41 (d, *J* = 2.0 Hz, 1H), 8.07 (d, *J* = 8.6 Hz, 1H), 7.72 (d, *J* = 10.7 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 7.3 Hz, 2H), 7.26-7.23 (m, 1H), 7.21-7.14 (m, 3H), 4.37 (q, *J* = 7.3 Hz, 2H), 1.45 (t, *J* = 7.3 Hz, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 140.3, 139.9, 134.5, 133.3, 130.3, 129.2, 128.5, 126.3, 126.2, 124.3, 122.5, 120.8, 119.5, 117.5, 109.7, 108.8, 37.8, 14.0. **HRMS (ESI)** *m/z*: [M]⁺ calcd for C₂₀H₁₇NSe: 351.0521; Found 351.0521.



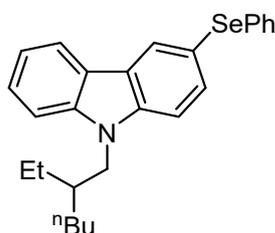
3-(phenylselanyl)-9-propyl-9H-carbazole (3d), 70% yield (50.8 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Yellow oily liquid. **¹H NMR (600 MHz, CDCl₃)** δ 8.34 (d, *J* = 1.8 Hz, 1H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.63 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.40 (t, *J* = 7.0 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.30-7.26 (m, 3H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.13-7.06 (m, 3H), 4.15 (t, *J* = 7.2 Hz, 2H), 1.85-1.79 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 140.8, 140.4, 134.5, 133.2, 130.3, 129.2, 128.3, 126.2, 126.2, 124.2, 122.3, 120.6, 119.4, 117.4, 109.9, 109.0, 44.8, 22.4, 11.9. **HRMS (ESI) m/z:** [M]⁺ calcd for C₂₁H₁₉NSe: 365.0677; Found 365.0677.



9-isopropyl-3-(phenylselanyl)-9H-carbazole (3e), 68% yield (49.3 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Yellow oily liquid. **¹H NMR (600 MHz, CDCl₃)** δ 8.43 (s, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 10.2 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.50-7.46 (m, 2H), 7.37 (d, *J* = 7.4 Hz, 2H), 7.25-7.16 (m, 4H), 5.00 (h, *J* = 7.1 Hz, 1H), 1.73 (d, *J* = 7.1 Hz, 6H). **¹³C NMR (151 MHz, CDCl₃)** δ 139.8, 139.4, 134.4, 133.0, 130.3, 129.2, 128.3, 126.2, 126.0, 124.7, 122.8, 120.6, 119.2, 117.3, 111.2, 110.3, 47.0, 21.0. **HRMS (ESI) m/z:** [M]⁺ calcd for C₂₁H₁₉NSe: 365.0677; Found 365.0677.

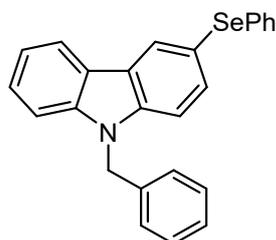


1-(3-(phenylselanyl)-9H-carbazol-9-yl) hexan-1-one (3f), 70% yield (56.7 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 200:1, v:v). Yellow oily liquid. **¹H NMR (600 MHz, CDCl₃)** δ 8.41 (d, *J* = 1.2 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.72 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.51-7.48 (m, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.38-7.34 (m, 3H), 7.26-7.24 (m, 1H), 7.22-7.15 (m, 3H), 4.30 (t, *J* = 7.4 Hz, 2H), 1.91-1.86 (m, 2H), 1.43-1.39 (m, 2H), 1.35-1.28 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 140.8, 140.4, 134.5, 133.3, 130.3, 129.2, 128.4, 126.3, 126.2, 124.2, 122.4, 120.7, 119.4, 117.4, 109.9, 109.0, 43.4, 31.7, 29.0, 27.1, 22.7, 14.1. **HRMS (ESI) m/z:** [M]⁺ calcd for C₂₄H₂₅NSe: 407.1147; Found 407.1147.

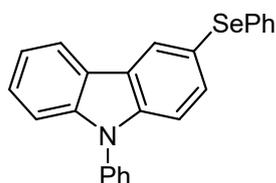


9-(2-ethylhexyl)-3-(phenylselanyl)-9H-carbazole (3g), 67% yield (58.3 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 200:1, v:v). White solid, m.p.: 119.1-119.7 °C. **¹H NMR (600 MHz, CDCl₃)** δ 8.41 (d, *J* = 1.7 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.71 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.50-7.47 (m, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.36 (dd, *J* = 8.4, 1.4 Hz, 3H), 7.26-7.15 (m, 4H), 4.20-4.12 (m, 2H), 2.10-2.05 (m, 1H), 1.45-1.26 (m, 8H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* =

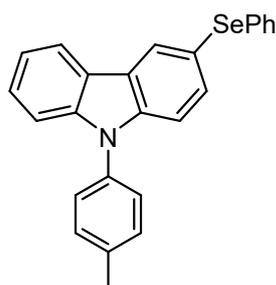
7.2 Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 141.2, 140.9, 134.4, 133.2, 130.4, 129.2, 128.3, 126.2, 126.2, 124.2, 122.3, 120.6, 119.4, 117.5, 110.2, 109.3, 47.6, 39.5, 31.1, 28.9, 24.6, 23.2, 14.2, 11.0. HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{26}\text{H}_{29}\text{NSe}$: 435.1460; Found 435.1460.



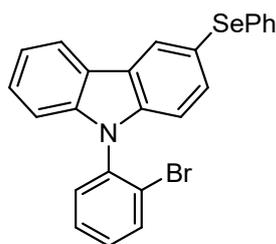
9-benzyl-3-(phenylselanyl)-9H-carbazole (3h), 58% yield (47.6 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Yellow solid, m.p.: 53.6-55.0 °C. ^1H NMR (600 MHz, CDCl_3) δ 8.39 (d, J = 1.7 Hz, 1H), 8.06 (d, J = 7.6 Hz, 1H), 7.64 (dd, J = 8.4, 1.7 Hz, 1H), 7.44-7.41 (m, 1H), 7.37-7.32 (m, 3H), 7.30 (d, J = 8.4 Hz, 1H), 7.26-7.22 (m, 4H), 7.19-7.12 (m, 5H), 5.48 (s, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 141.0, 140.6, 136.9, 134.2, 133.4, 130.6, 129.3, 129.0, 128.2, 127.8, 126.6, 126.3, 124.4, 122.6, 120.7, 119.9, 118.3, 110.1, 109.3, 46.8. HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{25}\text{H}_{19}\text{NSe}$: 413.0677; Found 413.0677.



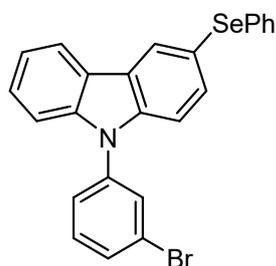
9-phenyl-3-(phenylselanyl)-9H-carbazole (3i), 69% yield (54.8 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Yellow oily liquid. ^1H NMR (600 MHz, CDCl_3) δ 8.47 (d, J = 2.3 Hz, 1H), 8.13 (d, J = 7.8 Hz, 1H), 7.67 (dd, J = 8.4, 1.7 Hz, 1H), 7.65-7.62 (m, 2H), 7.58 (dd, J = 8.5, 1.4 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.47-7.43 (m, 2H), 7.40-7.38 (m, 3H), 7.34-7.31 (m, 1H), 7.26-7.18 (m, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 141.3, 140.9, 137.4, 134.2, 133.4, 130.5, 130.1, 129.3, 128.1, 127.9, 127.2, 126.6, 126.3, 124.7, 122.8, 120.6, 120.5, 119.0, 111.0, 110.1. HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{24}\text{H}_{17}\text{NSe}$: 399.0521; Found 399.0521.



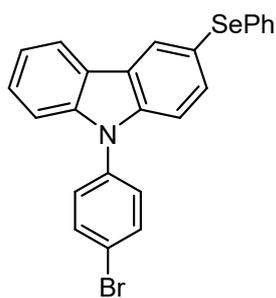
3-(phenylselanyl)-9-(p-tolyl)-9H-carbazole (3j), 56% yield (46.1 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). White solid, m.p.: 96.1-96.8 °C. ^1H NMR (600 MHz, CDCl_3) δ 8.43 (d, J = 1.2 Hz, 1H), 8.08 (d, J = 7.6 Hz, 1H), 7.62 (dd, J = 8.4, 1.6 Hz, 1H), 7.40-7.33 (m, 8H), 7.31 (d, J = 8.4 Hz, 1H), 7.27-7.25 (m, 1H), 7.19-7.16 (m, 2H), 7.15-7.12 (m, 1H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 141.4, 141.0, 137.8, 134.7, 134.3, 133.4, 130.7, 130.4, 129.2, 128.1, 127.0, 126.5, 126.3, 124.6, 122.7, 120.6, 120.3, 118.7, 111.0, 110.1, 21.4. HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{25}\text{H}_{19}\text{NSe}$: 413.0677; Found 413.0677.



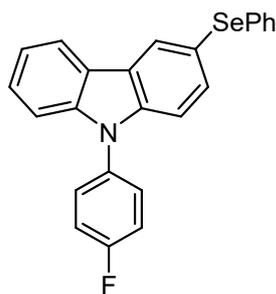
9-(2-bromophenyl)-3-(phenylselanyl)-9H-carbazole (3k), 42% yield (39.8 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Yellow oily liquid. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.42 (s, 1H), 8.08 (d, $J = 7.8$ Hz, 1H), 7.83 (d, $J = 8.1$ Hz, 1H), 7.61 (d, $J = 8.4$ Hz, 1H), 7.52-7.47 (m, 1H), 7.45 (dd, $J = 7.9, 1.8$ Hz, 1H), 7.41-7.34 (m, 4H), 7.27 (t, $J = 7.5$ Hz, 1H), 7.20-7.17 (m, 2H), 7.16-7.12 (m, 1H), 7.05 (d, $J = 7.8$ Hz, 1H), 7.00 (d, $J = 8.4$ Hz, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 141.2, 140.8, 136.5, 134.4, 134.0, 133.3, 131.1, 130.7, 130.5, 129.3, 129.0, 128.0, 126.6, 126.4, 124.6, 123.8, 122.7, 120.7, 120.6, 119.2, 111.2, 110.4. **HRMS (ESI)** m/z : $[\text{M}]^+$ calcd for $\text{C}_{24}\text{H}_{16}\text{BrNSe}$: 476.9626; Found 476.9626.



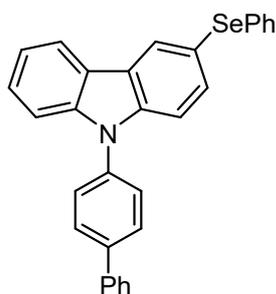
9-(3-bromophenyl)-3-(phenylselanyl)-9H-carbazole (3l), 48% yield (45.6 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Yellow oily liquid. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.37 (d, $J = 1.1$ Hz, 1H), 8.04 (d, $J = 7.6$ Hz, 1H), 7.68 (t, $J = 1.9$ Hz, 1H), 7.60 (dd, $J = 8.4, 1.7$ Hz, 1H), 7.58-7.56 (m, 1H), 7.47-7.30 (m, 7H), 7.27-7.25 (m, 1H), 7.19-7.12 (m, 3H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 140.9, 140.5, 138.8, 134.0, 133.5, 131.3, 130.9, 130.7, 130.2, 129.3, 128.0, 126.8, 126.4, 125.8, 124.9, 123.4, 123.0, 120.9, 120.7, 119.7, 110.8, 109.9. **HRMS (ESI)** m/z : $[\text{M}]^+$ calcd for $\text{C}_{24}\text{H}_{16}\text{BrNSe}$: 476.9626; Found 476.9626.



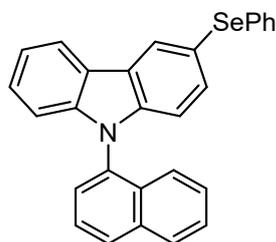
9-(4-bromophenyl)-3-(phenylselanyl)-9H-carbazole (3m), 43% yield (41.1 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). White solid, m.p.: 110.2-111.7 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.38 (d, $J = 1.1$ Hz, 1H), 8.05 (d, $J = 7.4$ Hz, 1H), 7.70-7.67 (m, 2H), 7.60 (dd, $J = 8.4, 1.6$ Hz, 1H), 7.40-7.37 (m, 3H), 7.34-7.31 (m, 3H), 7.28-7.24 (m, 2H), 7.19-7.11 (m, 3H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 141.0, 140.5, 136.5, 134.0, 133.5, 133.3, 130.7, 129.3, 128.8, 128.1, 126.7, 126.4, 124.8, 122.9, 121.4, 120.8, 120.7, 119.5, 110.8, 109.9. **HRMS (ESI)** m/z : $[\text{M}]^+$ calcd for $\text{C}_{24}\text{H}_{16}\text{BrNSe}$: 476.9626; Found 476.9627.



9-(4-fluorophenyl)-3-(phenylselanyl)-9H-carbazole (3n), 58% yield (48.3 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Yellow oily liquid. **¹H NMR (600 MHz, CDCl₃)** δ 8.41 (d, *J* = 1.7 Hz, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.61 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.48-7.46 (m, 2H), 7.41-7.38 (m, 1H), 7.35-7.33 (m, 2H), 7.30-7.23 (m, 5H), 7.19-7.12 (m, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 161.9 (d, ¹*J*_{C-F} = 247.64 Hz), 141.4, 141.0, 134.1, 133.5, 133.3 (d, ²*J*_{C-F} = 3.02 Hz), 130.6, 129.3, 129.1 (³*J*_{C-F} = 9.06 Hz), 128.1, 126.7, 126.4, 124.7, 122.7, 120.7, 120.6, 119.2, 117.1 (d, ⁴*J*_{C-F} = 22.65 Hz), 110.7, 109.8. **¹⁹F NMR (565 MHz, CDCl₃)** δ 35.23. **HRMS (ESI)** m/z: [M]⁺ calcd for C₂₄H₁₆FNSe: 417.0427; Found 417.0426.

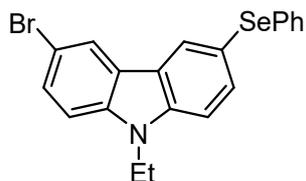


9-([1,1'-biphenyl]-4-yl)-3-(phenylselanyl)-9H-carbazole (3o), 42% yield (39.4 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Yellow oily liquid. **¹H NMR (600 MHz, CDCl₃)** δ 8.41 (d, *J* = 2.3 Hz, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.64-7.61 (m, 3H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.47-7.32 (m, 8H), 7.27-7.25 (m, 1H), 7.17-7.12 (m, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 141.2, 140.8, 140.7, 140.2, 136.5, 134.2, 133.5, 130.5, 129.3, 129.1, 128.7, 128.1, 127.9, 127.4, 127.6, 126.6, 126.3, 124.8, 122.9, 120.6, 120.6, 119.1, 111.1, 110.2. **HRMS (ESI)** m/z: [M+K]⁺ calcd for C₃₀H₂₁NSeK: 514.0471; Found 514.0471.

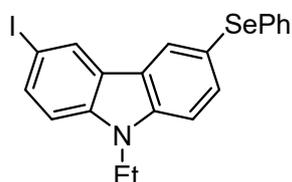


9-(naphthalen-1-yl)-3-(phenylselanyl)-9H-carbazole (3p), 63% yield (56.3 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 150:1, v:v). Yellow oily liquid. **¹H NMR (600 MHz, CDCl₃)** δ 8.47 (d, *J* = 1.7 Hz, 1H), 8.11 (d, *J* = 7.9 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.59-7.54 (m, 2H), 7.52 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.49-7.44 (m, 1H), 7.36-7.34 (m, 2H), 7.29-7.23 (m, 4H), 7.16-7.14 (m, 2H), 7.12-7.09 (m, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H). **¹³C NMR (151 MHz, CDCl₃)** δ 142.5, 142.0, 134.9, 134.1, 133.7, 133.4, 130.9, 130.6, 129.3, 129.2, 128.6, 128.0, 127.2, 126.9, 126.8, 126.6, 126.3, 126.0, 124.6, 123.4,

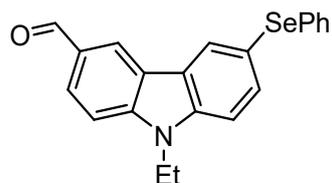
122.6, 120.6, 120.4, 119.0, 111.4, 110.5. **HRMS (ESI)** m/z : $[M]^+$ calcd for $C_{28}H_{19}NSe$: 449.0677; Found 449.0677.



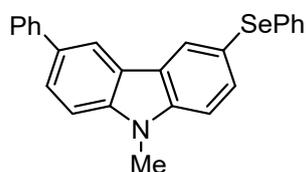
3-bromo-9-ethyl-6-(phenylselanyl)-9H-carbazole (3s), 59% yield (50.6 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Brown solid, m.p.: 160.8-162.4 °C. **¹H NMR (600 MHz, CDCl₃)** δ 8.18 (d, J = 1.7 Hz, 1H), 8.00 (d, J = 1.9 Hz, 1H), 7.59 (dd, J = 8.4, 1.7 Hz, 1H), 7.40 (dd, J = 8.7, 2.0 Hz, 1H), 7.26 (dd, J = 8.3, 1.3 Hz, 2H), 7.18 (d, J = 8.4 Hz, 1H), 7.11-7.04 (m, 4H), 4.13 (q, J = 7.3 Hz, 2H), 1.27 (t, J = 7.3 Hz, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 140.0, 138.7, 134.0, 133.7, 130.7, 129.2, 128.8, 128.2, 126.4, 124.0, 123.4, 123.1, 118.4, 112.1, 110.1, 109.8, 37.8, 13.9. **HRMS (ESI)** m/z : $[M]^+$ calcd for $C_{20}H_{16}BrNSe$: 428.9626; Found 428.9626.



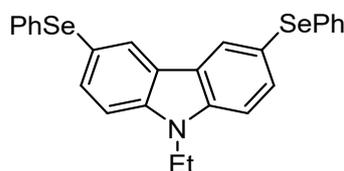
9-ethyl-3-iodo-6-(phenylselanyl)-9H-carbazole (3t), 55% yield (52.4 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Yellow oily liquid. **¹H NMR (600 MHz, CDCl₃)** δ 8.32 (d, J = 1.7 Hz, 1H), 7.97 (d, J = 7.7 Hz, 1H), 7.62 (dd, J = 8.4, 1.7 Hz, 1H), 7.40-7.38 (m, 1H), 7.30 (d, J = 8.3 Hz, 1H), 7.27-7.24 (m, 2H), 7.17-7.14 (m, 1H), 7.11-7.09 (m, 2H), 7.07-7.06 (m, 1H), 4.22 (q, J = 7.3 Hz, 2H), 1.33 (t, J = 7.3 Hz, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 140.2, 139.9, 134.5, 133.3, 130.3, 129.2, 128.4, 126.3, 126.2, 124.3, 122.4, 120.7, 119.4, 117.5, 109.6, 108.8, 37.2, 13.9. **HRMS (ESI)** m/z : $[M]^+$ calcd for $C_{20}H_{16}INSe$: 476.9487; Found 476.9488.



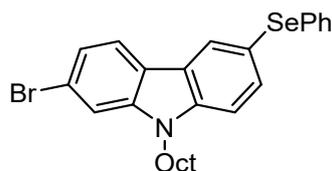
9-ethyl-6-(phenylselanyl)-9H-carbazole-3-carbaldehyde (3u), 53% yield (40.1 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 10:1, v:v). Brown solid, m.p.: 147.9-149.4 °C. **¹H NMR (600 MHz, CDCl₃)** δ 10.07 (s, 1H), 8.53 (d, J = 2.2 Hz, 1H), 8.39 (d, J = 1.6 Hz, 1H), 8.02 (dd, J = 8.5, 1.6 Hz, 1H), 7.75 (dd, J = 8.4, 1.7 Hz, 1H), 7.47 (d, J = 8.5 Hz, 1H), 7.41-7.39 (m, 3H), 7.25-7.19 (m, 3H), 4.38 (q, J = 7.3 Hz, 2H), 1.47 (t, J = 7.3 Hz, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 191.7, 143.8, 140.5, 133.7, 133.5, 131.2, 129.4, 129.0, 127.9, 127.4, 126.7, 124.5, 124.4, 122.6, 120.2, 110.3, 109.1, 38.2, 14.0. **HRMS (ESI)** m/z : $[M]^+$ calcd for $C_{21}H_{17}NOSe$: 379.0470; Found 379.0470.



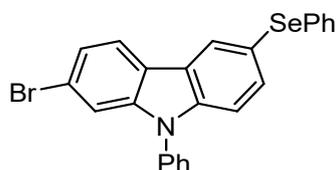
9-methyl-3-phenyl-6-(phenylselanyl)-9H-carbazole (3v), 60% yield (49.5 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Yellow oily liquid. ¹H NMR (600 MHz, CDCl₃) δ 8.39 (s, 1H), 8.21 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 7.0 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.32-7.26 (m, 4H), 7.16-7.10 (m, 3H), 3.74 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 141.9, 141.3, 140.7, 134.4, 133.4, 132.9, 130.4, 129.2, 128.9, 128.3, 127.3, 126.6, 126.2, 125.8, 124.2, 122.7, 119.0, 117.9, 109.8, 109.0, 29.3. HRMS (ESI) *m/z*: [M]⁺ calcd for C₂₅H₁₉NSe: 413.0677; Found 413.0677.



9-ethyl-3,6-bis(phenylselanyl)-9H-carbazole (3w), 41% yield (41.5 mg), known compound^[3]. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). White solid. ¹H NMR (600 MHz, CDCl₃) δ 8.37 (s, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 6H), 7.24-7.19 (m, 6H), 4.35 (q, *J* = 7.3 Hz, 2H), 1.47 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 140.0, 134.0, 133.5, 130.6, 129.2, 128.3, 126.3, 123.6, 118.5, 109.8, 37.9, 14.0. HRMS (ESI) *m/z*: [M]⁺ calcd for C₂₆H₂₁NSe₂: 506.9999; Found 506.9998.



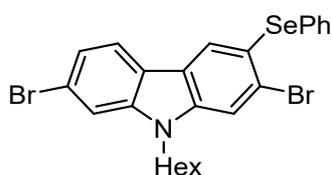
1-(2-bromo-6-(phenylselanyl)-9H-carbazol-9-yl)octan-1-one (3x), 61% yield (64.2 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Yellow oily liquid. ¹H NMR (600 MHz, CDCl₃) δ 8.30 (d, *J* = 1.7 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.68 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.51 (d, *J* = 1.7 Hz, 1H), 7.36-7.33 (m, 2H), 7.31-7.28 (m, 2H), 7.21-7.13 (m, 3H), 4.16 (t, *J* = 7.4 Hz, 2H), 1.83-1.78 (m, 2H), 1.36-1.22 (m, 10H), 0.86 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 141.5, 140.4, 134.0, 133.4, 130.7, 129.2, 128.0, 126.4, 123.6, 122.5, 121.7, 121.3, 119.9, 118.5, 112.1, 110.0, 43.4, 31.9, 29.4, 29.3, 29.0, 27.3, 22.7, 14.2. HRMS (ESI) *m/z*: [M]⁺ calcd for C₂₆H₂₈BrNSe: 513.0565; Found 513.0564.



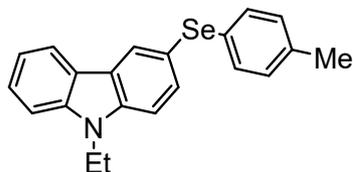
2-bromo-9-phenyl-6-(phenylselanyl)-9H-carbazole (3y), 55% yield (51.7 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Yellow oily liquid. ¹H NMR (600 MHz, CDCl₃) δ 8.39 (d, *J* = 2.2 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.67-7.61 (m, 3H), 7.53 (dd, *J* = 8.1, 1.2 Hz, 4H), 7.41-7.38 (m, 3H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.24-7.19 (m, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 142.0, 141.0, 136.8, 133.8, 133.6, 130.9, 130.3, 129.3, 128.3, 127.8, 127.2, 126.5, 124.1, 123.7, 121.8, 121.7, 120.2, 119.9, 113.1, 111.2. HRMS (ESI) *m/z*: [M]⁺ calcd for C₂₄H₁₆BrNSe: 476.9626; Found 476.9626.



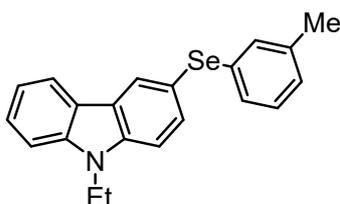
9-benzyl-2-bromo-6-(phenylselanyl)-9H-carbazole (3z), 40% yield (39.0 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). White solid, m.p.: 128.3-128.6 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.23 (d, $J = 1.8$ Hz, 1H), 7.77 (d, $J = 8.3$ Hz, 1H), 7.55-7.53 (m, 1H), 7.39 (d, $J = 1.7$ Hz, 1H), 7.27-7.23 (m, 3H), 7.17-7.14 (m, 4H), 7.12-7.05 (m, 3H), 7.00 (dd, $J = 8.0$, 1.6 Hz, 2H), 5.29 (s, 2H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 141.8, 140.7, 136.3, 133.7, 133.5, 130.9, 129.3, 129.1, 127.9, 127.8, 126.5, 126.4, 123.9, 123.1, 121.8, 121.5, 120.2, 119.3, 112.3, 110.3, 46.9. **HRMS (ESI)** m/z : $[\text{M}]^+$ calcd for $\text{C}_{25}\text{H}_{18}\text{BrNSe}$: 490.9782; Found 490.9782.



2,7-dibromo-9-hexyl-3-(phenylselanyl)-9H-carbazole (3aa), 29% yield (32.6 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Yellow oily liquid. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.01 (s, 1H), 7.71 (d, $J = 8.4$ Hz, 1H), 7.65 (s, 1H), 7.49-7.47 (m, 2H), 7.41 (dd, $J = 7.4$, 2.0 Hz, 1H), 7.30-7.27 (m, 3H), 7.23 (d, $J = 7.2$ Hz, 1H), 4.15 (t, $J = 7.4$ Hz, 2H), 1.81 (q, $J = 7.4$ Hz, 2H), 1.38-1.25 (m, 6H), 0.87 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 141.6, 140.9, 133.2, 133.0, 129.7, 129.3, 127.6, 127.4, 126.5, 124.9, 122.9, 121.8, 120.8, 120.3, 113.5, 112.2, 43.6, 31.6, 28.9, 27.0, 22.7, 14.1. **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{23}\text{Br}_2\text{NSe}$: 565.9415; Found 565.9422.

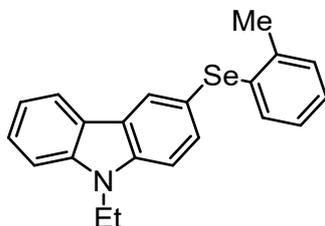


9-ethyl-3-(p-tolylselanyl)-9H-carbazole (3ab), 66% yield (48.2 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Yellow oily liquid. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.35 (d, $J = 1.7$ Hz, 1H), 8.02 (d, $J = 7.5$ Hz, 1H), 7.65 (dd, $J = 8.4$, 1.6 Hz, 1H), 7.46-7.43 (m, 1H), 7.36 (d, $J = 7.4$ Hz, 1H), 7.30-7.26 (m, 3H), 7.22-7.18 (m, 1H), 6.99 (d, $J = 7.8$ Hz, 2H), 4.28 (q, $J = 7.2$ Hz, 2H), 2.25 (s, 3H), 1.38 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 140.2, 139.7, 136.3, 132.8, 131.1, 130.3, 130.0, 127.8, 126.2, 124.2, 122.4, 120.7, 119.3, 118.4, 109.5, 108.7, 37.7, 21.1, 13.9. **HRMS (ESI)** m/z : $[\text{M}]^+$ calcd for $\text{C}_{21}\text{H}_{19}\text{NSe}$: 365.0677; Found 365.0677.

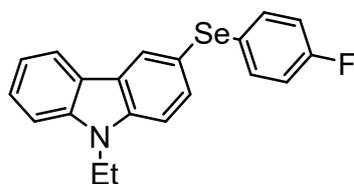


9-ethyl-3-(m-tolylselanyl)-9H-carbazole (3ac), 42% yield (30.5 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Yellow oily liquid. $^1\text{H NMR}$ (600 MHz, CDCl_3)

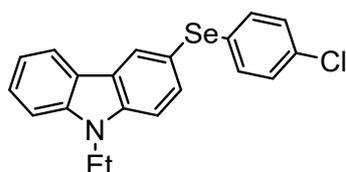
δ 8.28 (d, $J = 1.8$ Hz, 1H), 7.94 (d, $J = 7.7$ Hz, 1H), 7.58 (dd, $J = 8.4, 1.7$ Hz, 1H), 7.36 (t, $J = 7.7$ Hz, 1H), 7.29 (d, $J = 8.3$ Hz, 1H), 7.23 (d, $J = 8.4$ Hz, 1H), 7.12 (t, $J = 6.4$ Hz, 1H), 7.08 (s, 1H), 7.01 (d, $J = 7.9$ Hz, 1H), 6.96 (t, $J = 7.6$ Hz, 1H), 6.85 (d, $J = 7.4$ Hz, 1H), 4.23 (q, $J = 7.3$ Hz, 2H), 2.13 (s, 3H), 1.31 (t, $J = 7.3$ Hz, 3H). **^{13}C NMR (151 MHz, CDCl_3)** δ 140.2, 139.9, 137.3, 135.3, 133.5, 130.0, 129.9, 128.7, 126.7, 126.3, 126.1, 124.4, 122.4, 120.7, 119.4, 116.7, 109.7, 108.8, 37.7, 21.9, 13.9. **HRMS (ESI)** m/z : $[\text{M}]^+$ calcd for $\text{C}_{21}\text{H}_{19}\text{NSe}$: 365.0677; Found 365.0677.



9-ethyl-3-(*o*-tolylselanyl)-9H-carbazole (3ad), 53% yield (38.6 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Yellow oily liquid. **^1H NMR (600 MHz, CDCl_3)** δ 8.44 (d, $J = 1.6$ Hz, 1H), 8.11 (d, $J = 7.7$ Hz, 1H), 7.73 (dd, $J = 8.4, 1.7$ Hz, 1H), 7.56-7.52 (m, 1H), 7.46 (d, $J = 8.2$ Hz, 1H), 7.42 (d, $J = 8.5$ Hz, 1H), 7.30 (t, $J = 7.4$ Hz, 1H), 7.23 (d, $J = 8.3$ Hz, 1H), 7.15-7.12 (m, 1H), 7.09 (d, $J = 8.0$ Hz, 1H), 7.01 (t, $J = 8.4$ Hz, 1H), 4.39 (q, $J = 7.3$ Hz, 2H), 2.51 (s, 3H), 1.49 (t, $J = 7.3$ Hz, 3H). **^{13}C NMR (151 MHz, CDCl_3)** δ 140.6, 139.9, 139.0, 134.1, 133.2, 131.0, 129.0, 128.3, 127.5, 127.2, 126.3, 124.3, 122.5, 120.7, 119.4, 117.7, 109.6, 108.8, 37.8, 21.4, 14.0. **HRMS (ESI)** m/z : $[\text{M}]^+$ calcd for $\text{C}_{21}\text{H}_{19}\text{NSe}$: 365.0677; Found 365.0678.

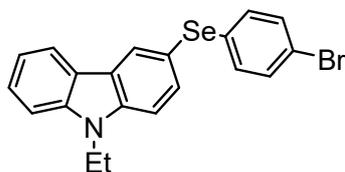


9-ethyl-3-((4-fluorophenyl)selanyl)-9H-carbazole (3ae), 61% yield (44.8 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Brown solid, m.p.: 92.0-92.4 °C. **^1H NMR (600 MHz, CDCl_3)** δ 8.42 (s, 1H), 8.11 (d, $J = 7.8$ Hz, 1H), 7.72 (dd, $J = 8.4, 1.7$ Hz, 1H), 7.55-7.52 (m, 1H), 7.44 (d, $J = 8.3$ Hz, 1H), 7.41-7.37 (m, 3H), 7.29 (t, $J = 7.4$ Hz, 1H), 6.96 (t, $J = 8.9$ Hz, 2H), 4.36 (q, $J = 7.3$ Hz, 2H), 1.46 (t, $J = 7.3$ Hz, 3H). **^{13}C NMR (151 MHz, CDCl_3)** δ 161.9 (d, $^1J_{\text{C-F}} = 246.1$ Hz), 140.2, 139.8, 132.8 (d, $^2J_{\text{C-F}} = 4.5$ Hz), 132.7, 128.6 ($^3J_{\text{C-F}} = 3.0$ Hz), 127.9, 126.3, 124.3, 122.4, 120.7, 119.4, 118.1, 116.3 (d, $^4J_{\text{C-F}} = 9.1$ Hz), 109.7, 108.8, 37.7, 13.9. **^{19}F NMR (565 MHz, CDCl_3)** δ 38.37. **HRMS (ESI)** m/z : $[\text{M}]^+$ calcd for $\text{C}_{20}\text{H}_{16}\text{FNSe}$: 369.0427; Found 369.0427.

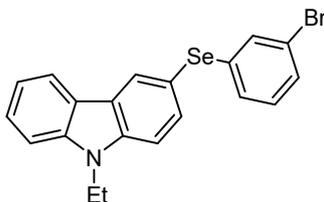


3-((4-chlorophenyl)selanyl)-9-ethyl-9H-carbazole (3af), 57% yield (43.9 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Brown solid, m.p.: 84.2-86.3 °C. **^1H NMR (600 MHz, CDCl_3)** δ 8.37 (s, 1H), 8.05 (dt, $J = 7.8, 1.1$ Hz, 1H), 7.67 (dd, $J = 8.4, 1.7$ Hz, 1H), 7.49-7.46 (m, 1H), 7.40 (d, $J = 8.3$ Hz, 1H), 7.34 (d, $J = 8.9$ Hz, 1H), 7.25-7.21 (m, 3H), 7.14-7.12

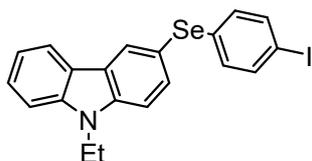
(m, 2H), 4.33 (q, $J = 7.3$ Hz, 2H), 1.42 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 140.2, 139.9, 133.2, 132.8, 132.1, 131.5, 129.2, 128.4, 126.3, 124.3, 122.3, 120.7, 119.5, 117.1, 109.7, 108.8, 37.7, 13.9. HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{20}\text{H}_{16}\text{ClNSe}$: 385.0131; Found 385.0131.



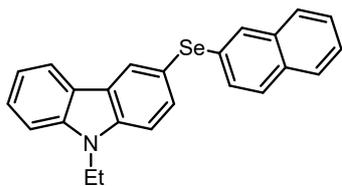
3-((4-bromophenyl)selanyl)-9-ethyl-9H-carbazole (3ag), 55% yield (47.2 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). White solid, m.p.: 118.8-119.9 °C. ^1H NMR (600 MHz, CDCl_3) δ 8.35 (d, $J = 1.8$ Hz, 1H), 8.03 (d, $J = 7.7$ Hz, 1H), 7.65 (dd, $J = 8.4, 1.7$ Hz, 1H), 7.48-7.44 (m, 1H), 7.38 (d, $J = 8.3$ Hz, 1H), 7.32 (d, $J = 8.4$ Hz, 1H), 7.26-7.24 (m, 2H), 7.23-7.19 (m, 1H), 7.13 (d, $J = 8.5$ Hz, 2H), 4.31 (q, $J = 7.3$ Hz, 2H), 1.40 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 140.2, 140.0, 133.6, 133.3, 132.1, 131.7, 128.5, 126.4, 124.3, 122.3, 120.7, 120.0, 119.5, 116.9, 109.7, 108.8, 37.7, 13.9. HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{20}\text{H}_{16}\text{BrNSe}$: 428.9626; Found 428.9626.



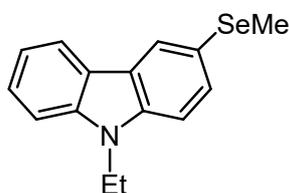
3-((3-bromophenyl)selanyl)-9-ethyl-9H-carbazole (3ah), 56% yield (48 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). White solid, m.p.: 87.6-89.3 °C. ^1H NMR (600 MHz, CDCl_3) δ 8.44 (d, $J = 1.8$ Hz, 1H), 8.11 (d, $J = 7.7$ Hz, 1H), 7.73 (dd, $J = 8.4, 1.6$ Hz, 1H), 7.54-7.52 (m, 1H), 7.48 (t, $J = 1.8$ Hz, 1H), 7.45 (d, $J = 8.2$ Hz, 1H), 7.40 (d, $J = 8.4$ Hz, 1H), 7.30-7.28 (m, 2H), 7.23 (d, $J = 7.9$ Hz, 1H), 7.05 (t, $J = 7.9$ Hz, 1H), 4.38 (q, $J = 7.3$ Hz, 2H), 1.47 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 140.3, 140.1, 137.0, 133.5, 132.2, 130.4, 129.1, 128.9, 128.4, 126.4, 124.4, 123.3, 122.4, 120.8, 119.5, 116.4, 109.8, 108.8, 37.8, 14.0. HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{20}\text{H}_{16}\text{BrNSe}$: 428.9626; Found 428.9625.



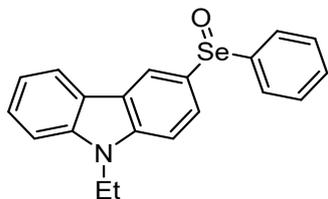
9-ethyl-3-((4-iodophenyl)selanyl)-9H-carbazole (3ai), 50% yield (47.5 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Yellow oily liquid. ^1H NMR (600 MHz, CDCl_3) δ 8.38 (s, 1H), 8.06 (d, $J = 8.8$ Hz, 1H), 7.68 (dd, $J = 8.4, 1.7$ Hz, 1H), 7.51-7.45 (m, 3H), 7.42 (d, $J = 8.3$ Hz, 1H), 7.36 (d, $J = 8.4$ Hz, 1H), 7.26-7.23 (m, 1H), 7.02 (d, $J = 8.4$ Hz, 2H), 4.36 (q, $J = 7.3$ Hz, 2H), 1.44 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 140.2, 138.0, 134.7, 134.0, 133.3, 131.8, 128.6, 126.3, 124.3, 122.3, 120.7, 119.5, 116.7, 109.7, 108.8, 91.0, 37.7, 13.9. HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{20}\text{H}_{16}\text{INSe}$: 476.9487; Found 476.9487.



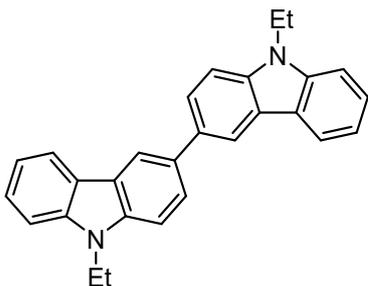
9-ethyl-3-(naphthalen-2-ylselanyl)-9H-carbazole (3aj), 76% yield (60.8 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). White solid, m.p.: 103.8-104.6 °C. **¹H NMR (600 MHz, CDCl₃)** δ 8.46 (d, *J* = 1.9 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.82 (s, 1H), 7.75 (dd, *J* = 8.4, 1.7 Hz, 2H), 7.65 (t, *J* = 8.4 Hz, 2H), 7.51-7.48 (m, 1H), 7.47-7.42 (m, 2H), 7.42-7.39 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.26-7.23 (m, 1H), 4.36 (q, *J* = 7.3 Hz, 2H), 1.45 (t, *J* = 7.3 Hz, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 140.2, 139.9, 134.1, 133.2, 132.0, 131.9, 128.7, 128.5, 128.5, 128.3, 127.8, 127.2, 126.4, 126.2, 125.6, 124.3, 122.4, 120.7, 119.4, 117.6, 109.6, 108.7, 37.7, 13.9. **HRMS (ESI)** m/z: [M]⁺ calcd for C₂₄H₁₉NSe: 401.0677; Found 401.0677.



9-ethyl-3-(methylselanyl)-9H-carbazole (3am), 21% yield (12.1 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 100:1, v:v). Brown oily liquid. **¹H NMR (600 MHz, CDCl₃)** δ 8.27 (s, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.63 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.47 (t, *J* = 8.3 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 4.35 (q, *J* = 7.3 Hz, 2H), 2.41 (s, 3H), 1.42 (t, *J* = 7.3 Hz, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 140.1, 139.1, 130.4, 126.0, 125.0, 123.9, 122.3, 120.5, 119.5, 119.1, 109.1, 108.6, 37.6, 13.8, 9.6. **HRMS (ESI)** m/z: [M]⁺ calcd for C₁₅H₁₅NSe: 289.0364; Found 289.0364



9-ethyl-3-(phenylseleninyl)-9H-carbazole (4a), 90% yield (33 mg), new compound. (Eluent: petroleum ether (60-90 °C)/EtOAc = 20:1, v:v). Brown oily liquid. **¹H NMR (600 MHz, CDCl₃)** δ 8.46 (d, *J* = 1.7 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 6.5 Hz, 2H), 7.64 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.42-7.35 (m, 5H), 7.23 (t, *J* = 7.5 Hz, 1H), 4.26 (q, *J* = 7.3 Hz, 2H), 1.34 (t, *J* = 7.3 Hz, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 143.7, 141.4, 140.4, 131.9, 131.0, 129.6, 126.8, 126.3, 123.7, 123.4, 122.2, 120.9, 119.8, 119.2, 109.6, 108.9, 37.7, 13.8. **HRMS (ESI)** m/z: [M+H]⁺ calcd for C₂₀H₁₈NOSe: 368.0548; Found 368.0548.



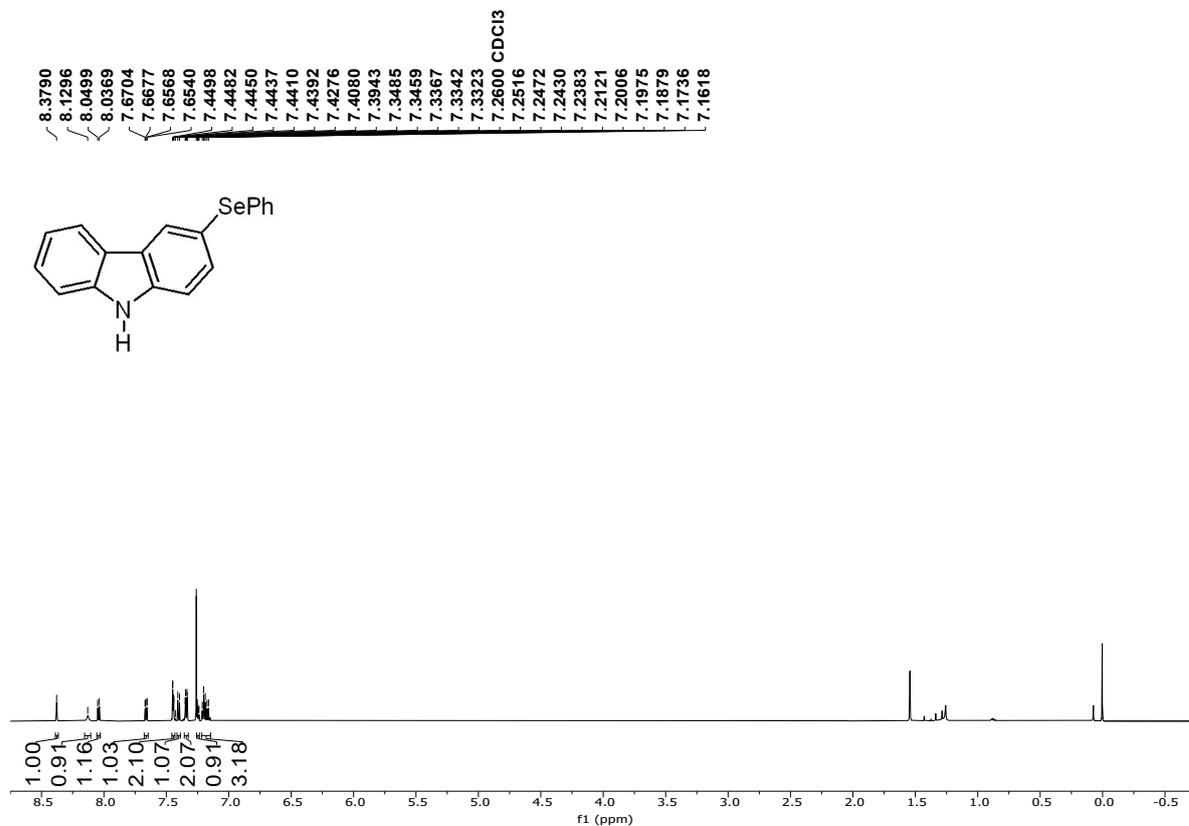
9,9'-diethyl-9*H*,9'*H*-3,3'-bicarbazole (8a), 42% yield (16.3 mg), known compound^[4]. (Eluent: petroleum ether (60-90 °C)/EtOAc = 50:1, v:v). White solid. **¹H NMR (600 MHz, CDCl₃)** δ 8.41 (s, 2H), 8.19 (d, *J* = 7.7 Hz, 2H), 7.83 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.53-7.46 (m, 4H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.25 (t, *J* = 7.4 Hz, 2H), 4.40 (q, *J* = 7.3 Hz, 4H), 1.47 (t, *J* = 7.3 Hz, 6H). **¹³C NMR (151 MHz, CDCl₃)** δ 140.6, 139.2, 133.6, 125.8, 125.7, 123.7, 123.3, 120.7, 119.2, 118.9, 108.8, 108.7, 37.8, 14.0.

5. References

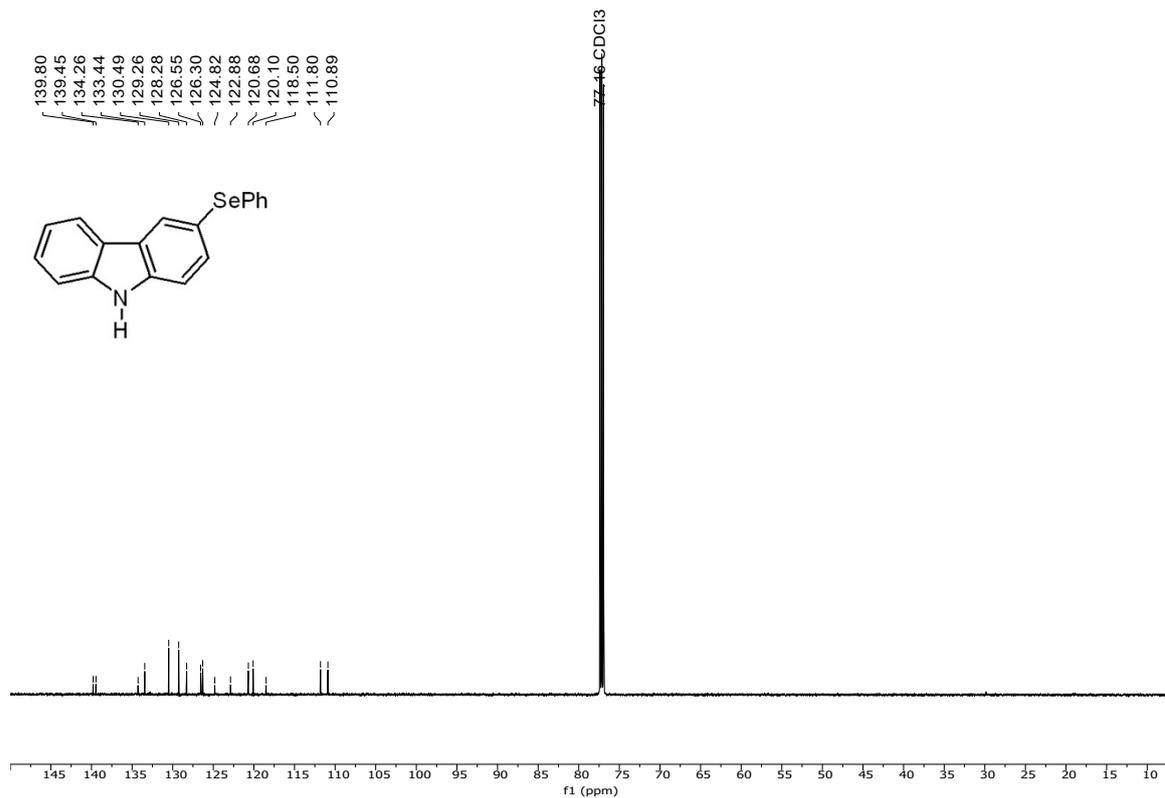
- [1] D. Singh; A. M. Deobald; L. R. S. Camargo; G. Tabarelli; O. E. D. Rodrigues; A. L. Braga. *Org. Lett.*, 2010, **12**, 3288-3291.
- [2] B. Paul; S. Das; I. Chatterjee. *Org. Lett.*, 2023, **25**, 653-658.
- [3] J. Yin; P. Chen; L.-W. Miao; J. Wang; Y.-J. Jiang. *Eur. J. Org. Chem.*, 2023, **26**, e202300290.
- [4] S. Mallick; S. Maddala; K. Kollimalayan; P. Venkatakrishnan. *J. Org. Chem.*, 2019, **84**, 73-93.

6. Copies of NMR Spectra

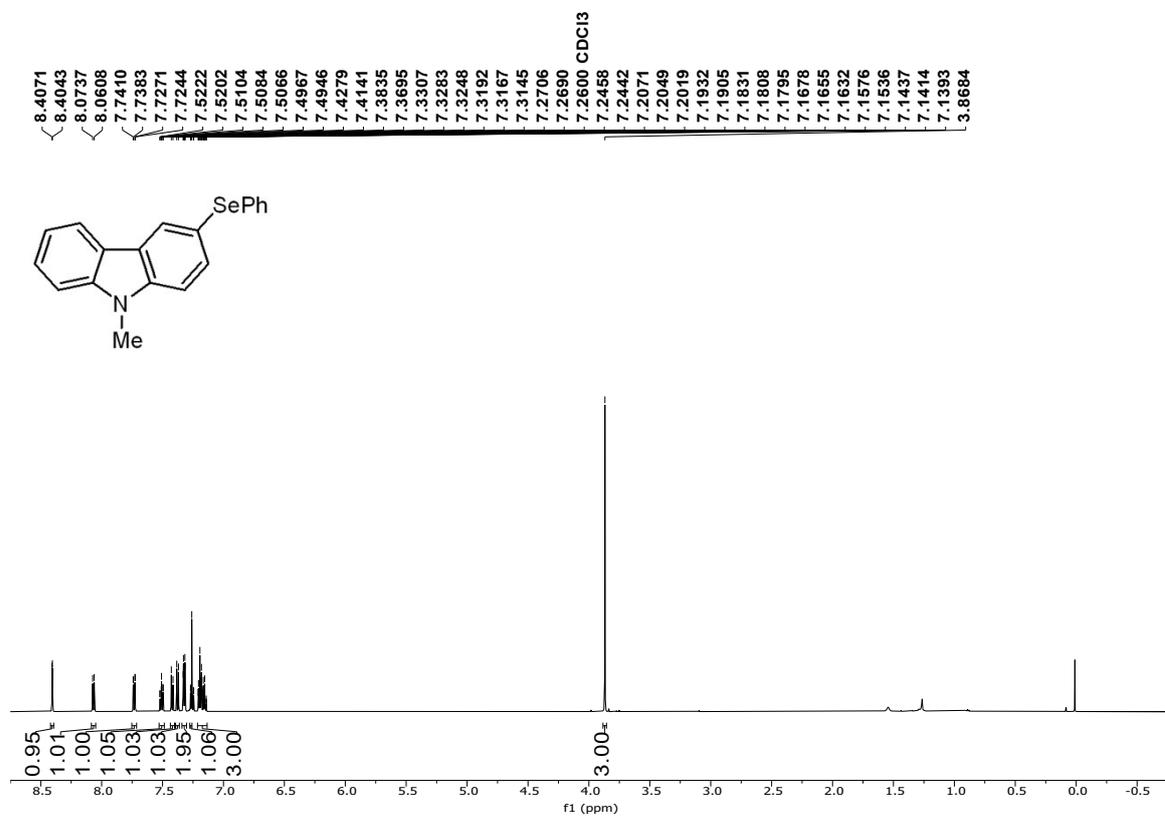
^1H NMR of product 3a in CDCl_3 (600 MHz)



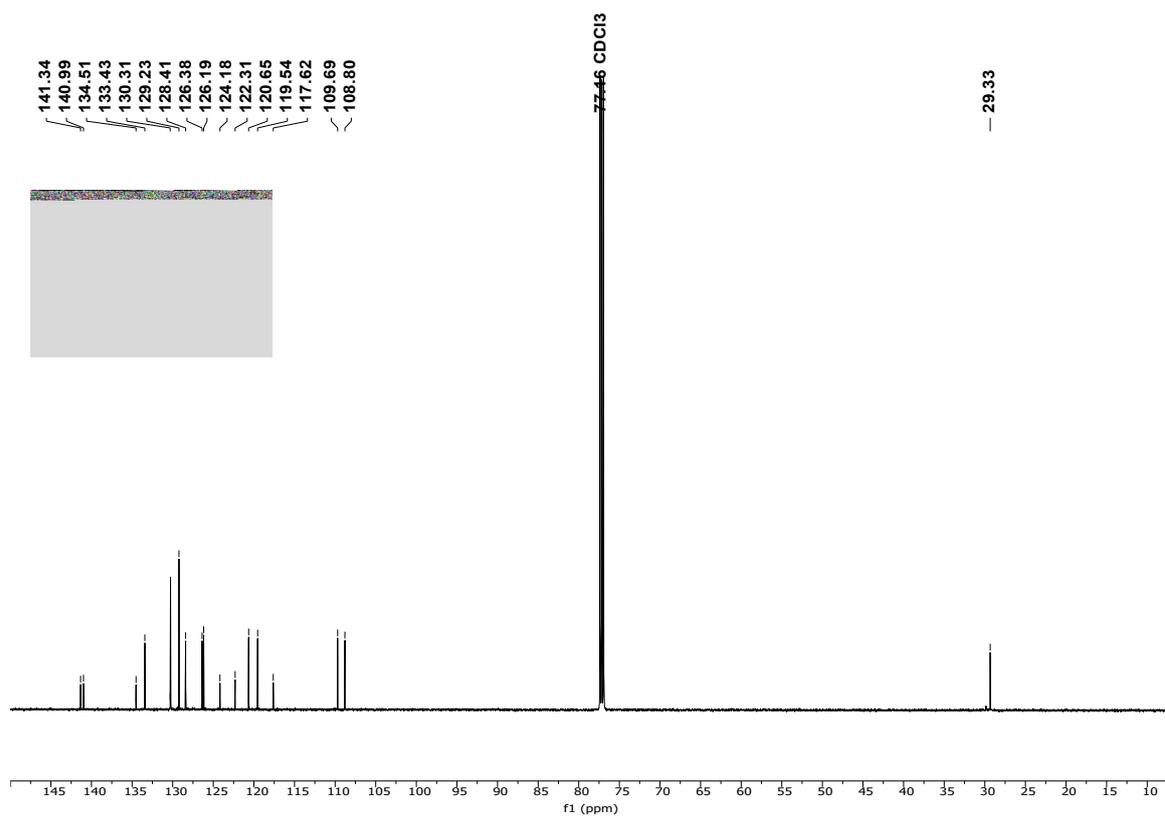
^{13}C NMR of product 3a in CDCl_3 (151 MHz)



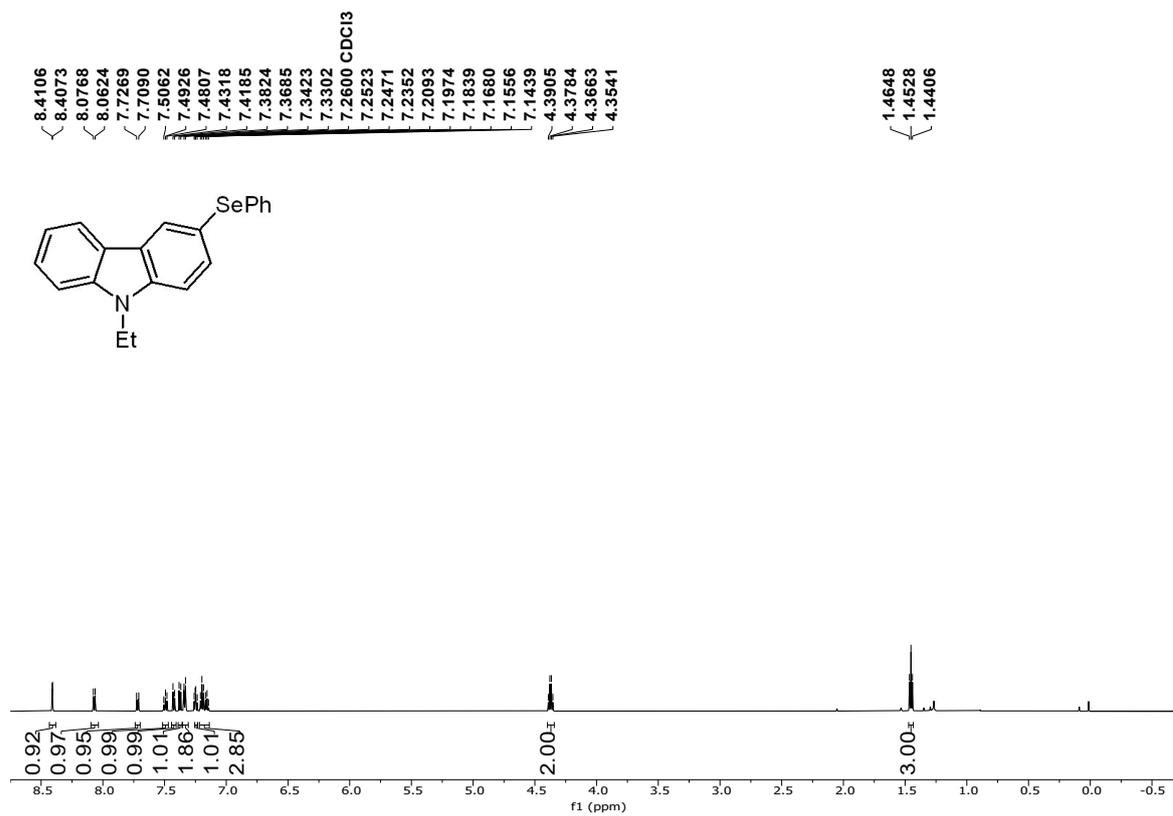
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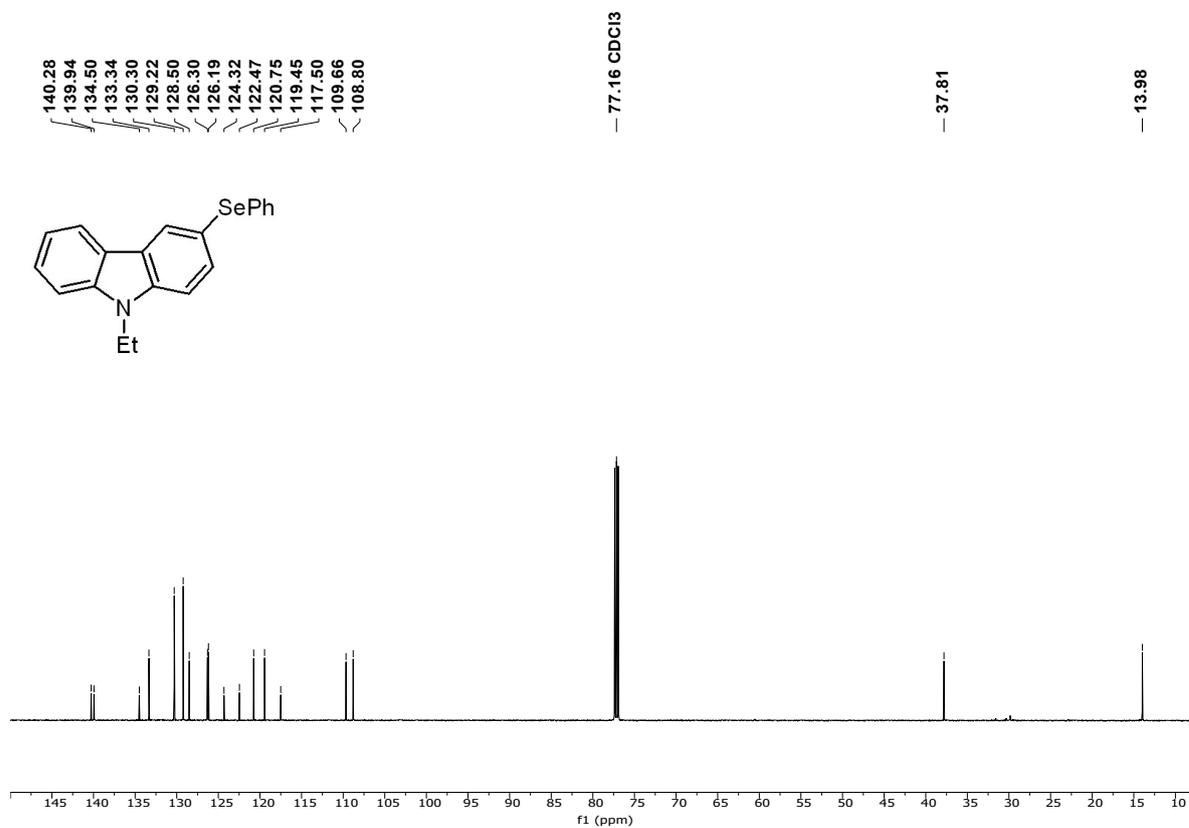
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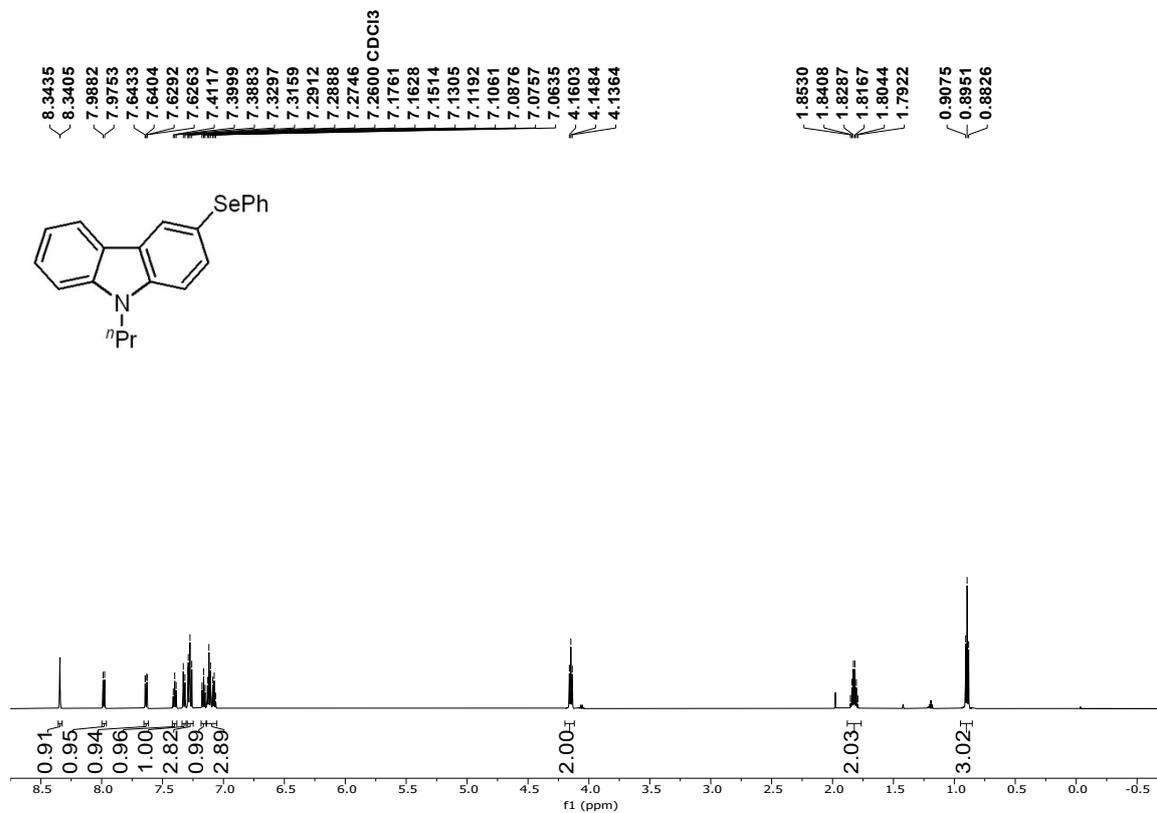
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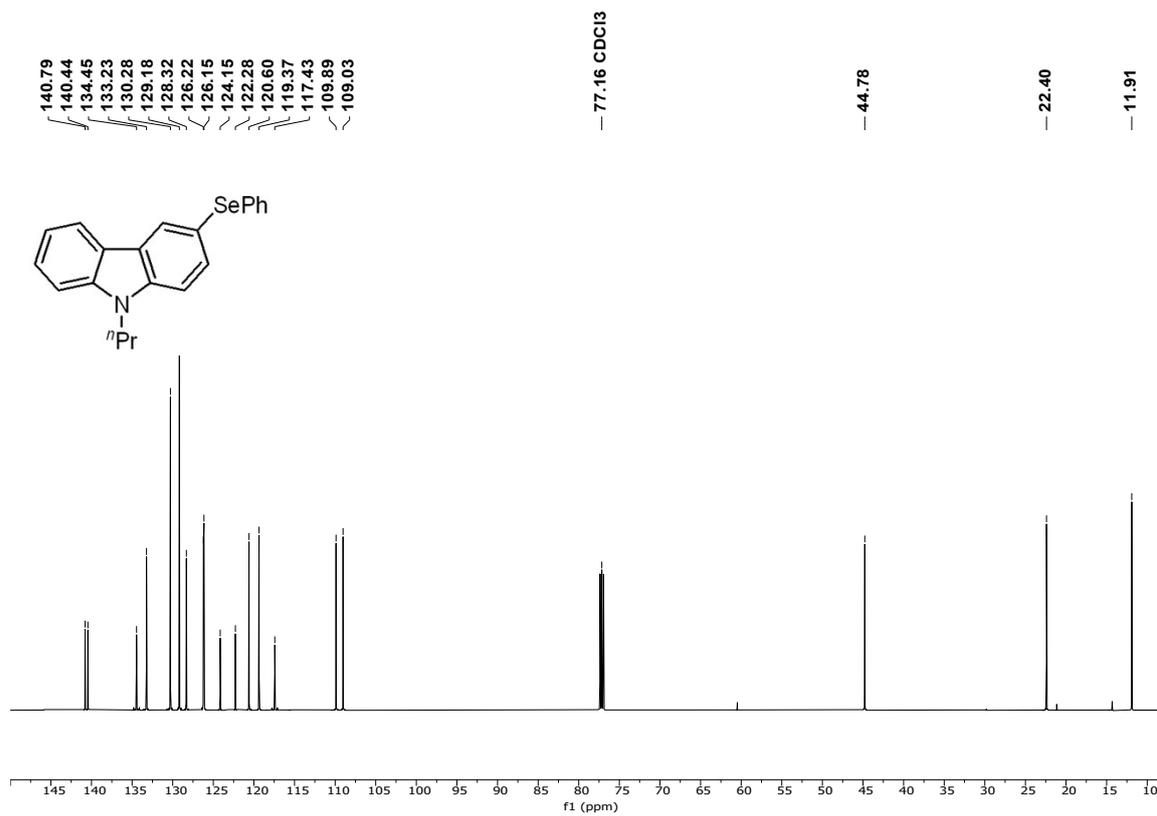
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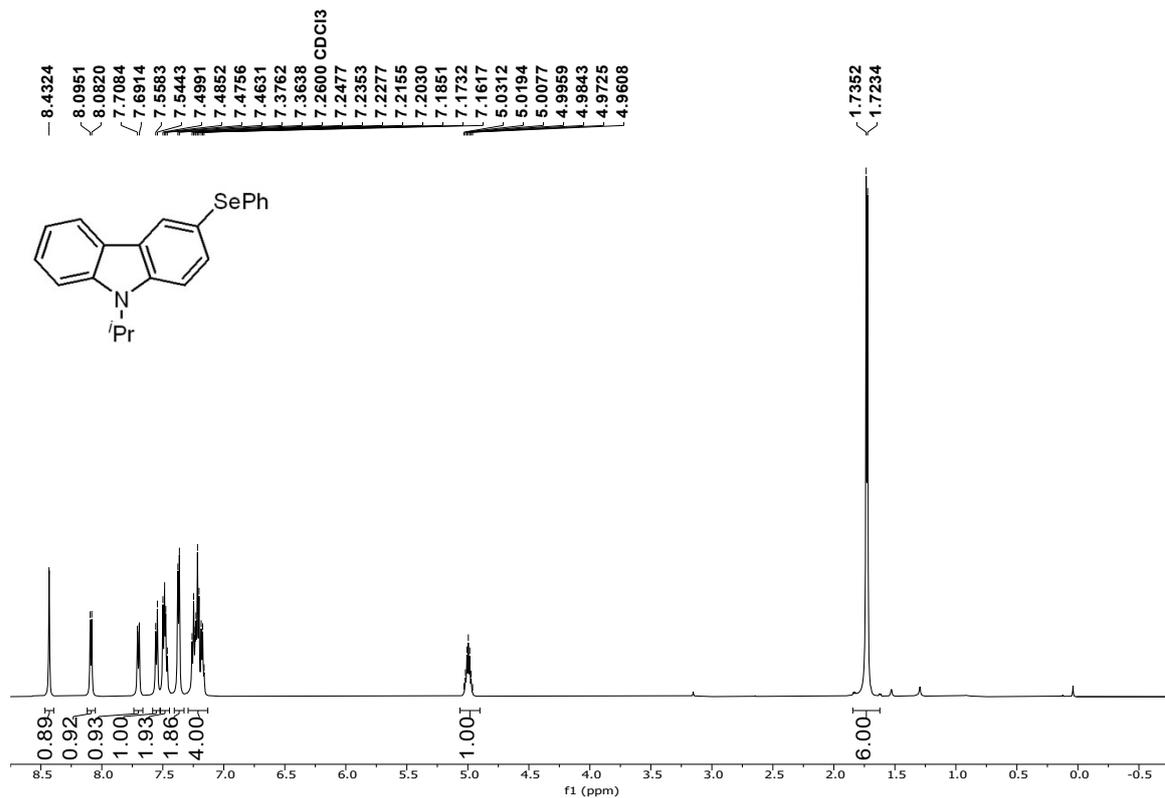
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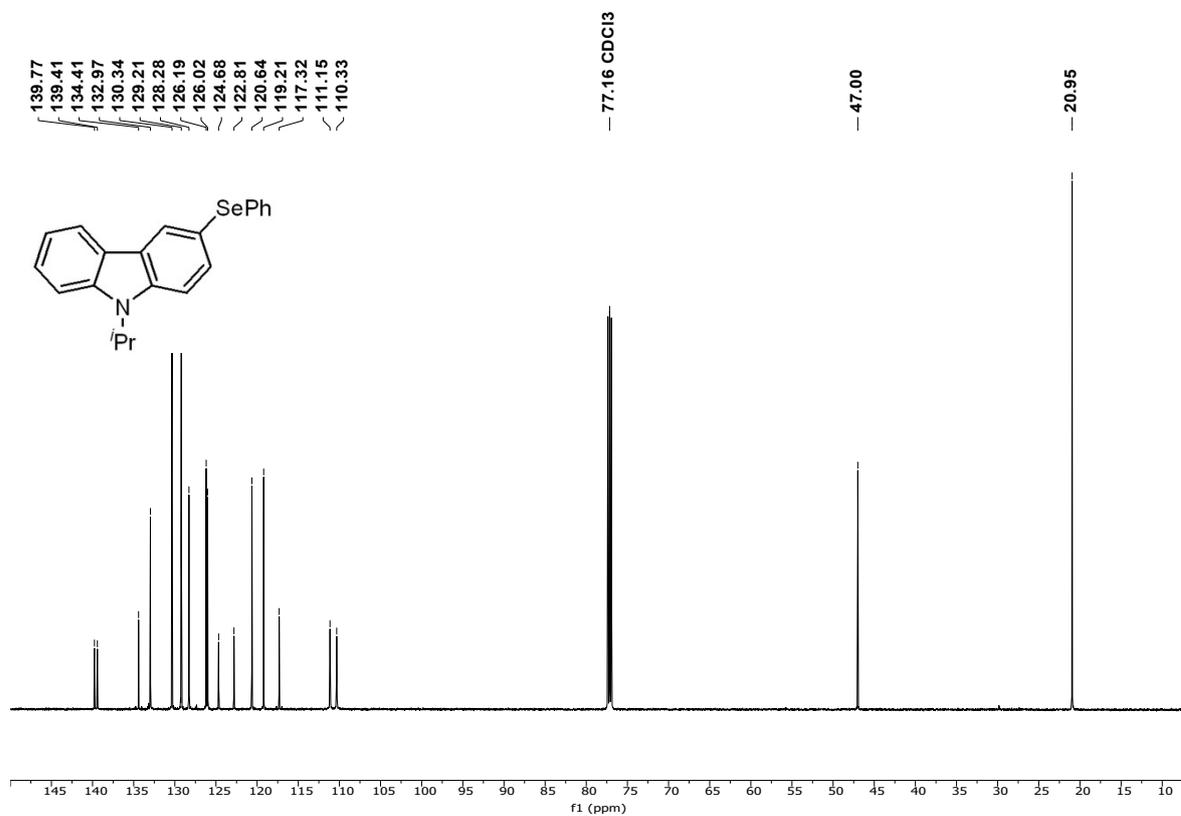
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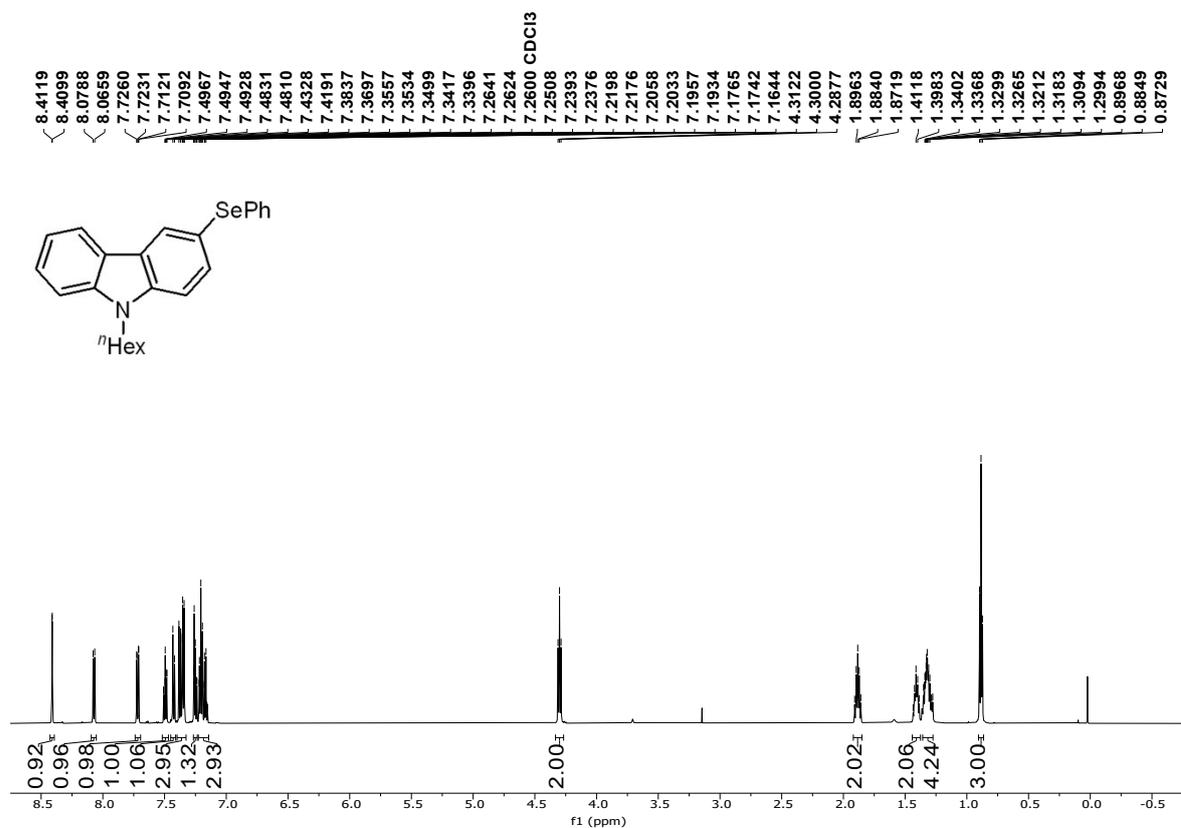
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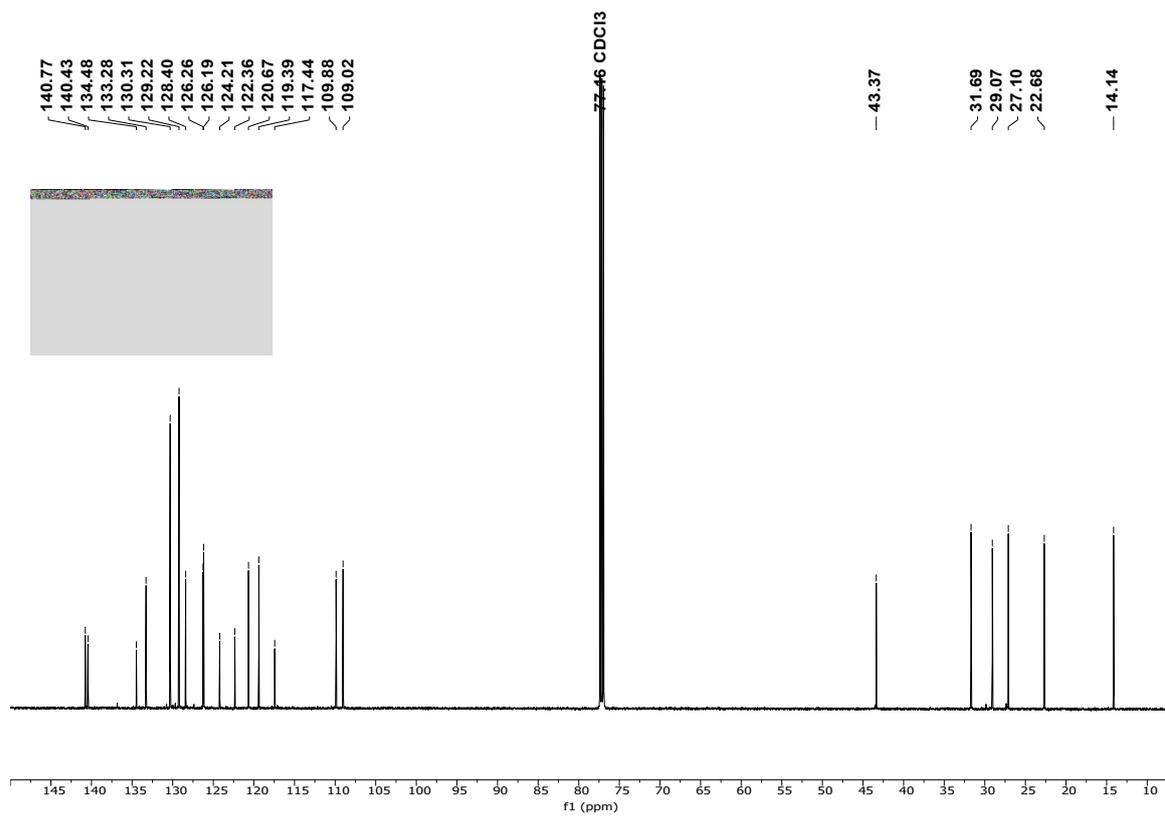
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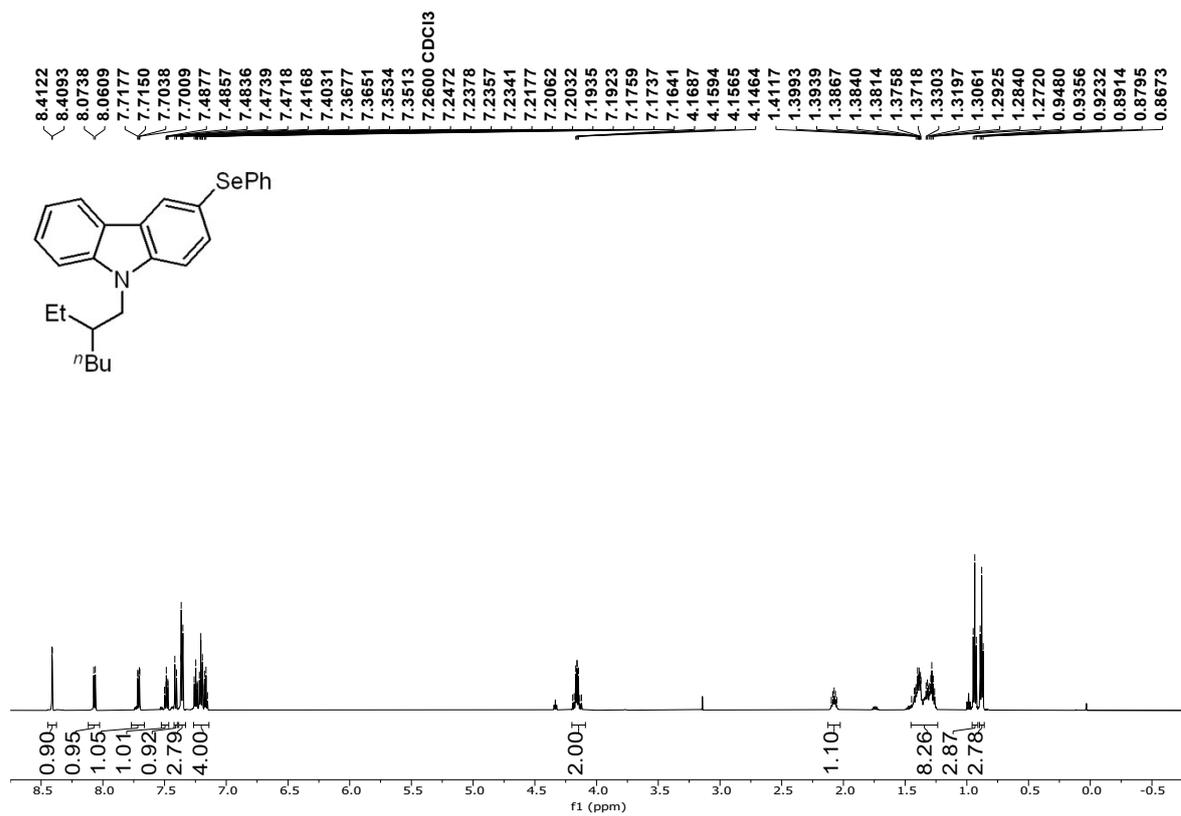
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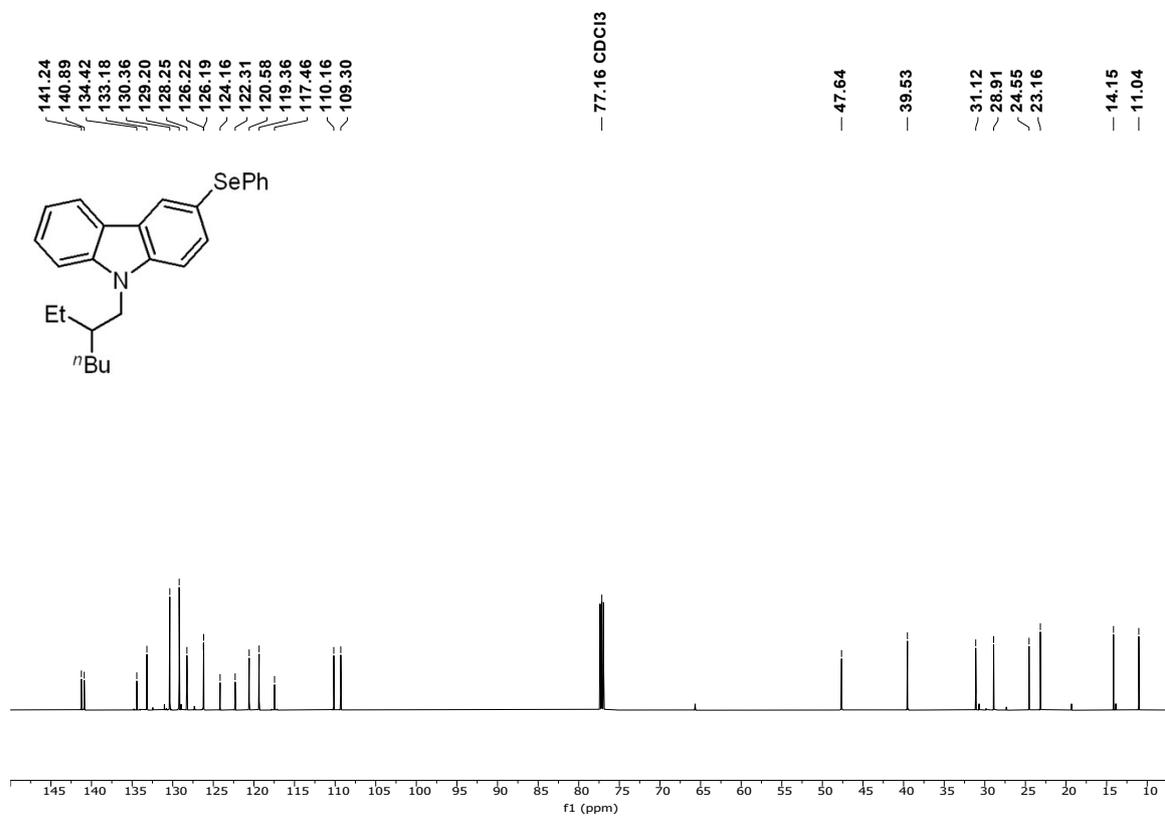
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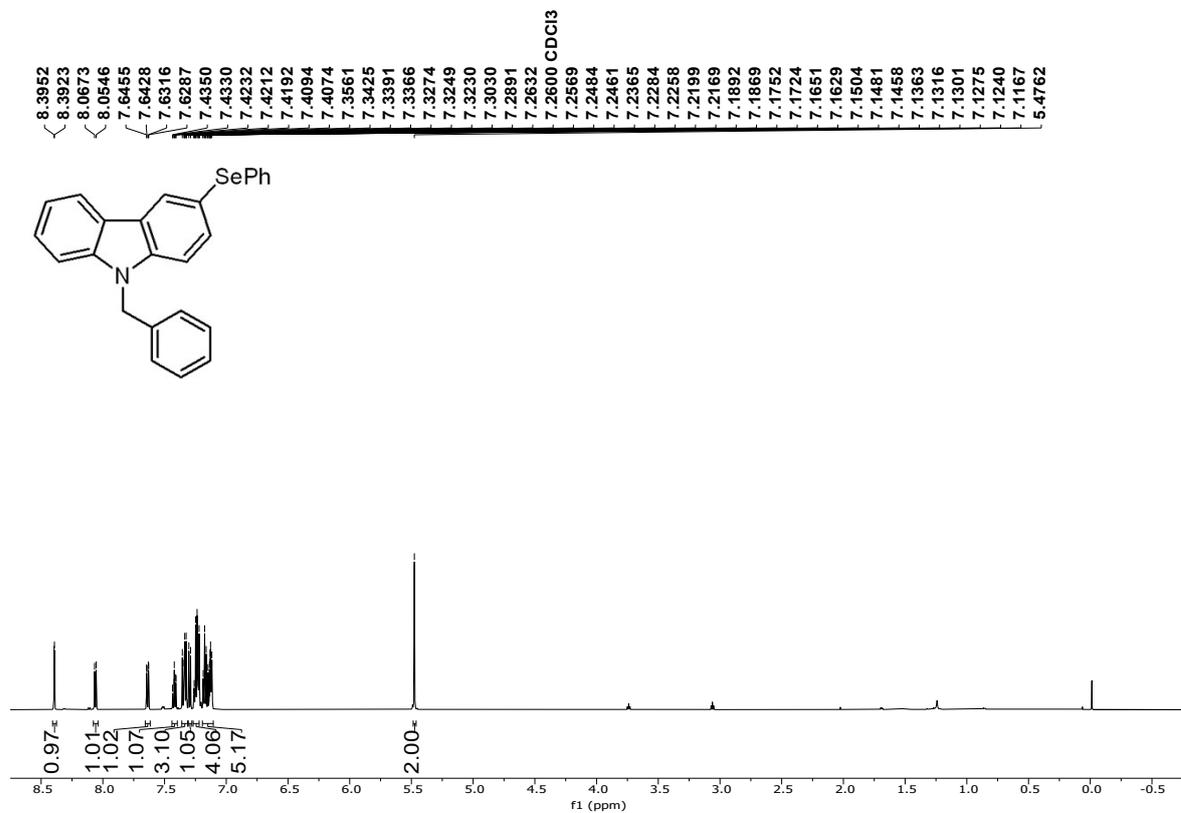
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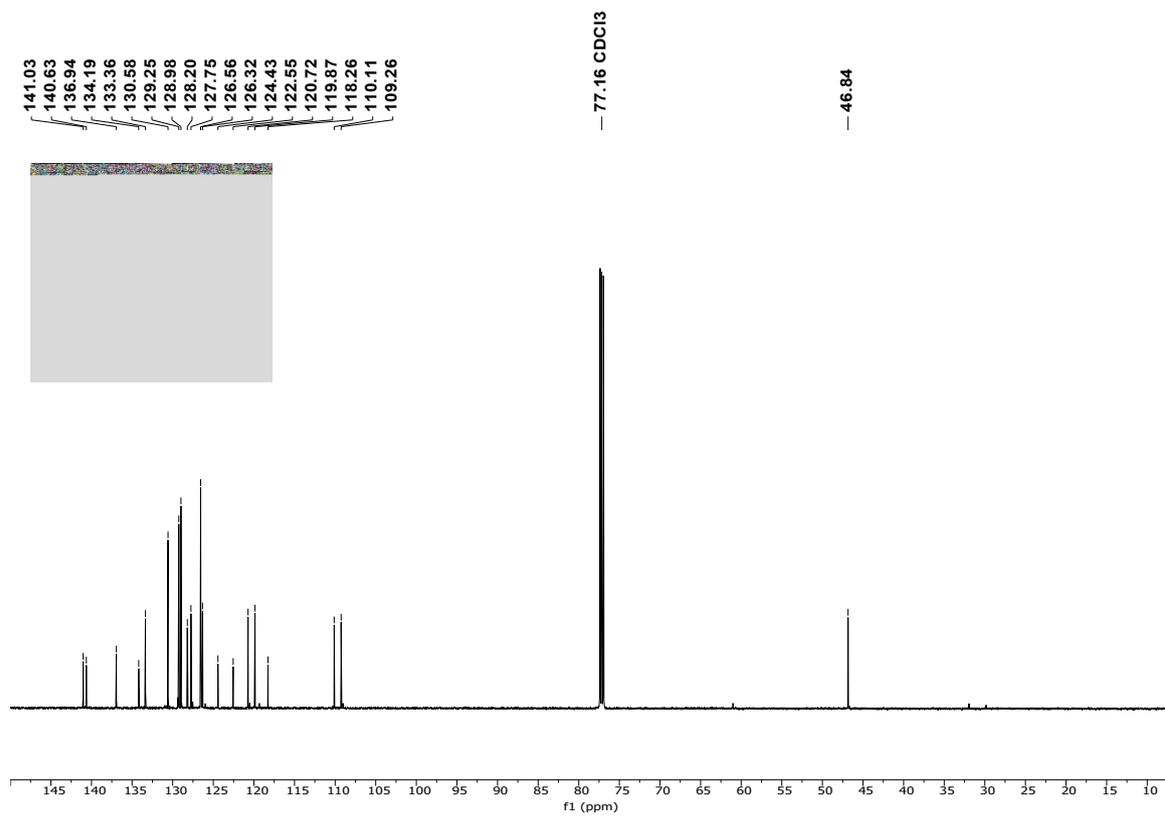
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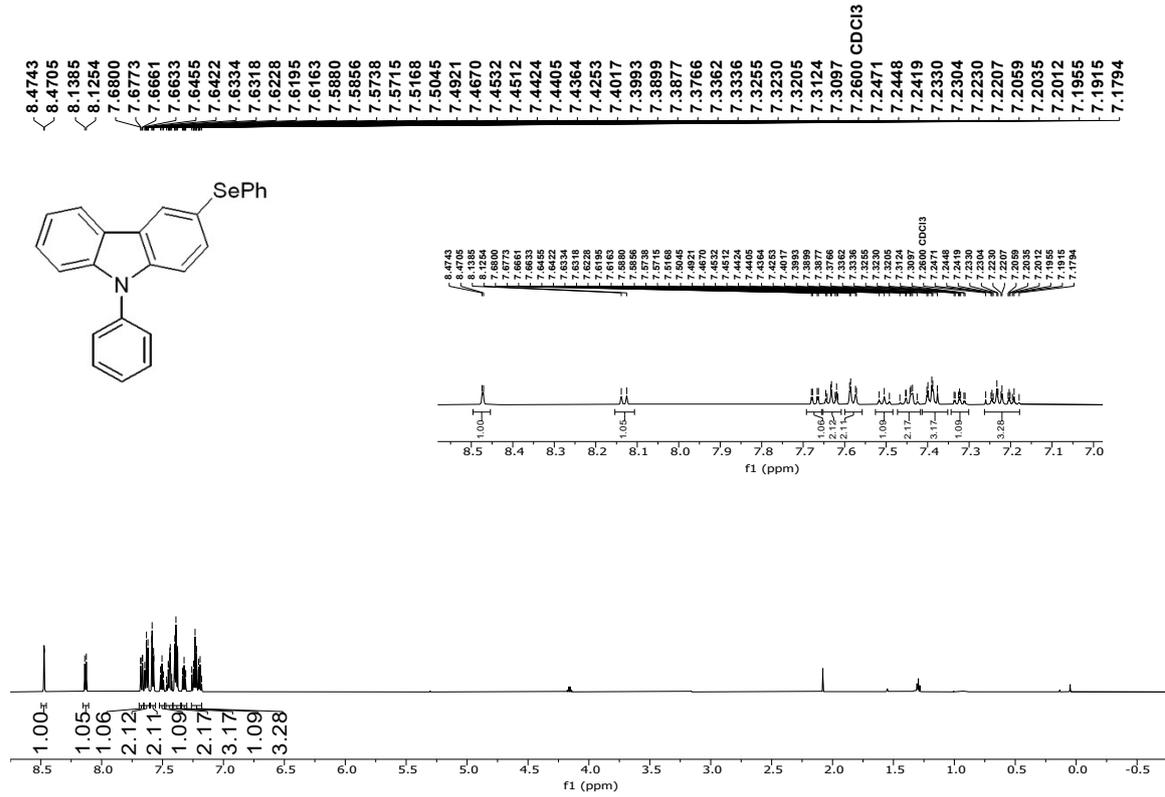
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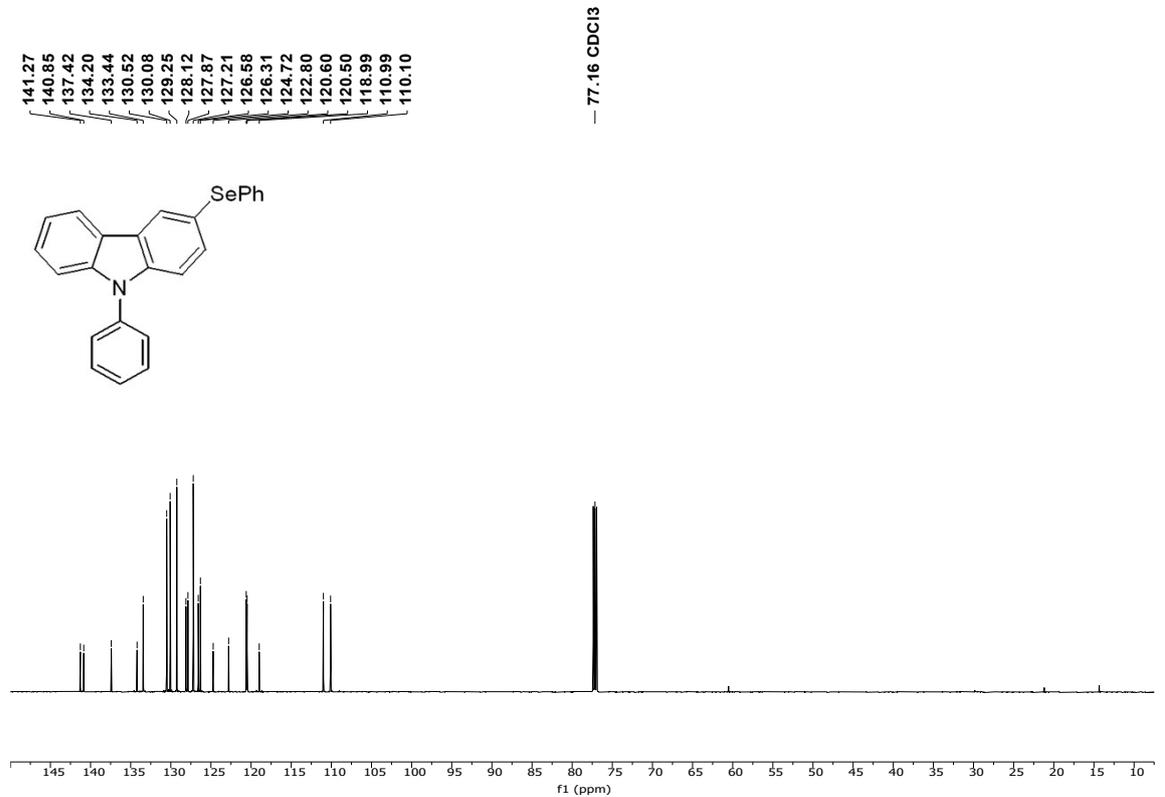
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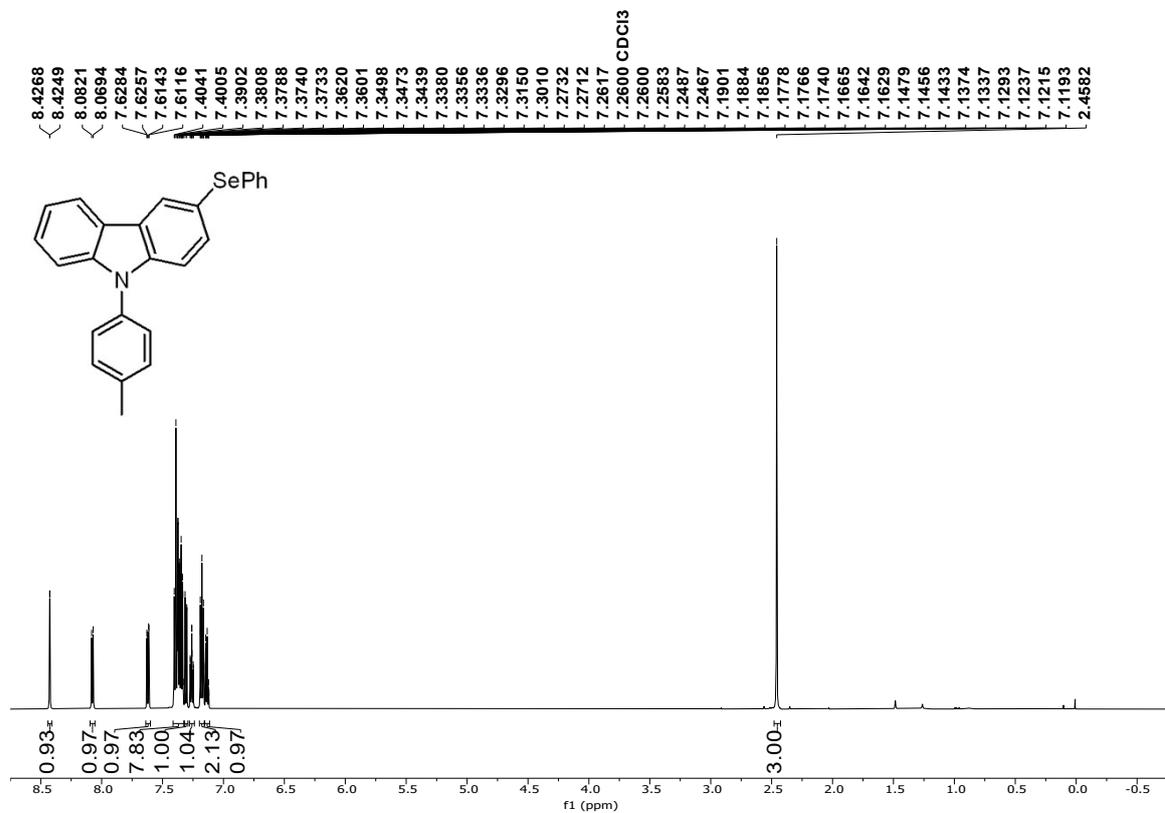
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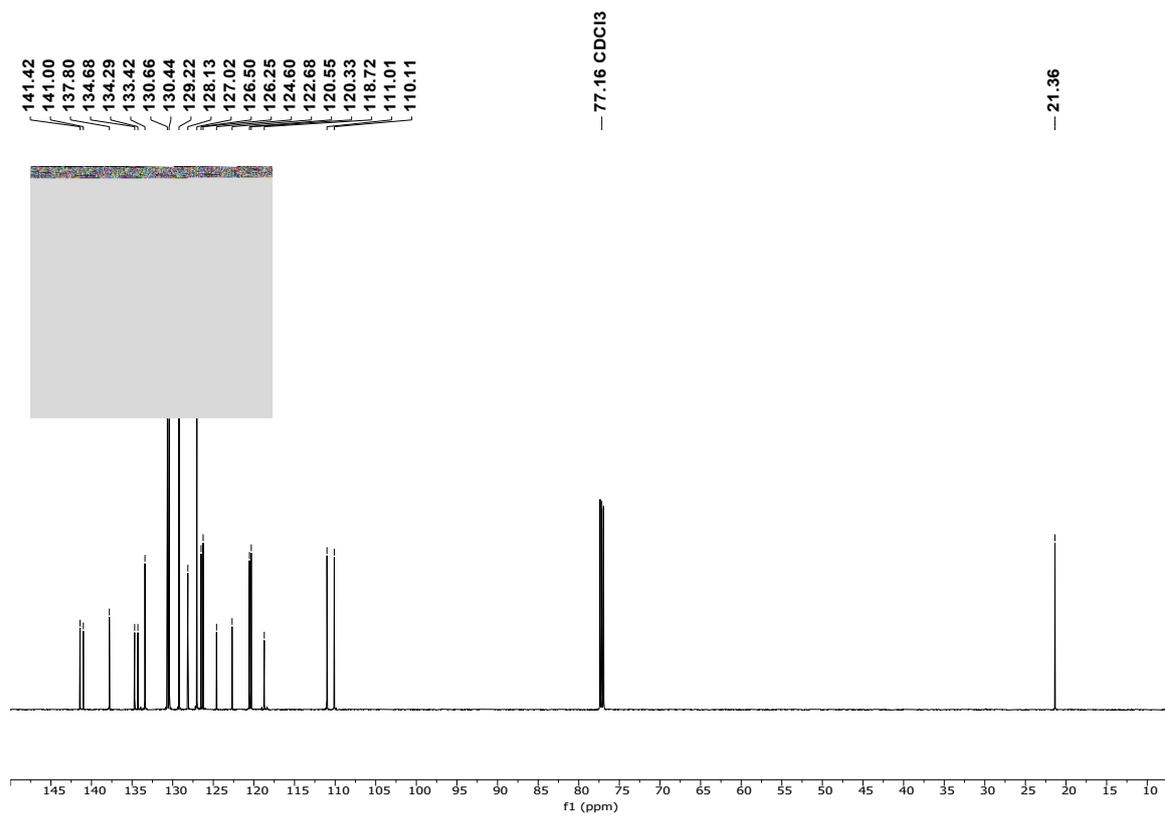
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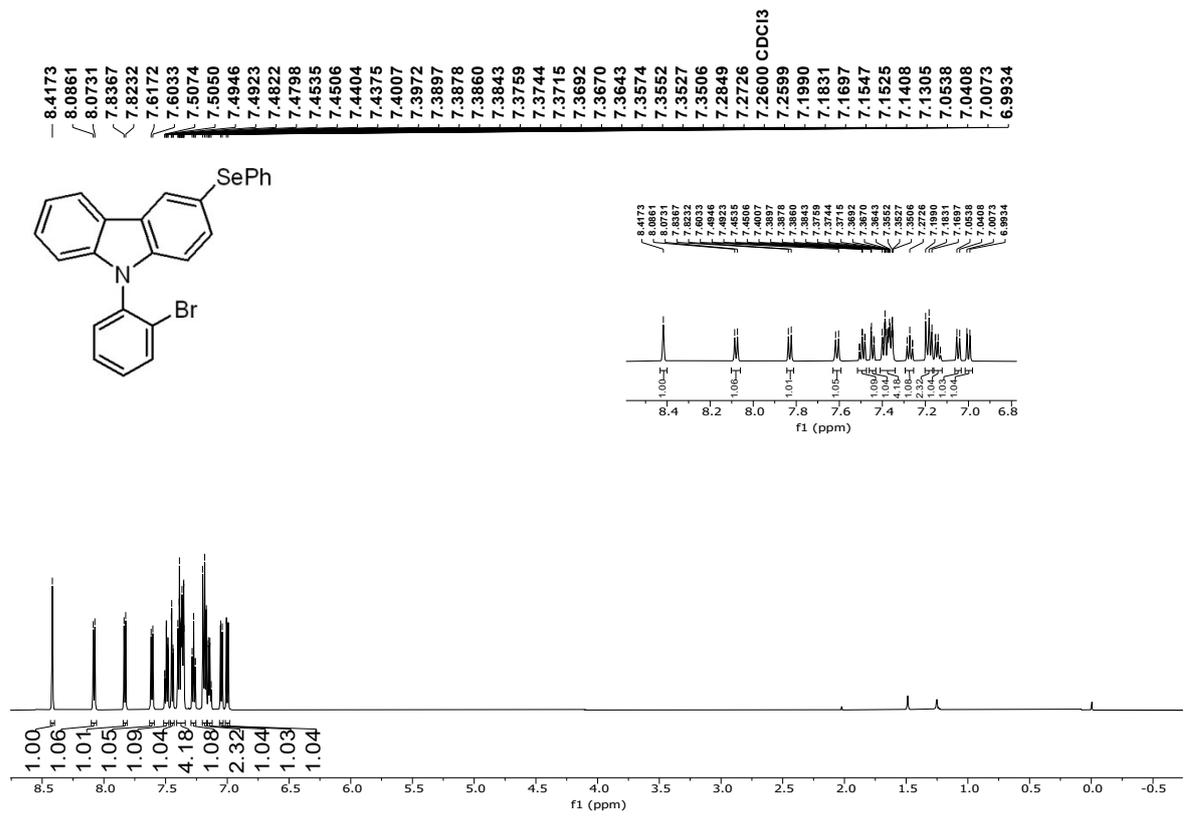
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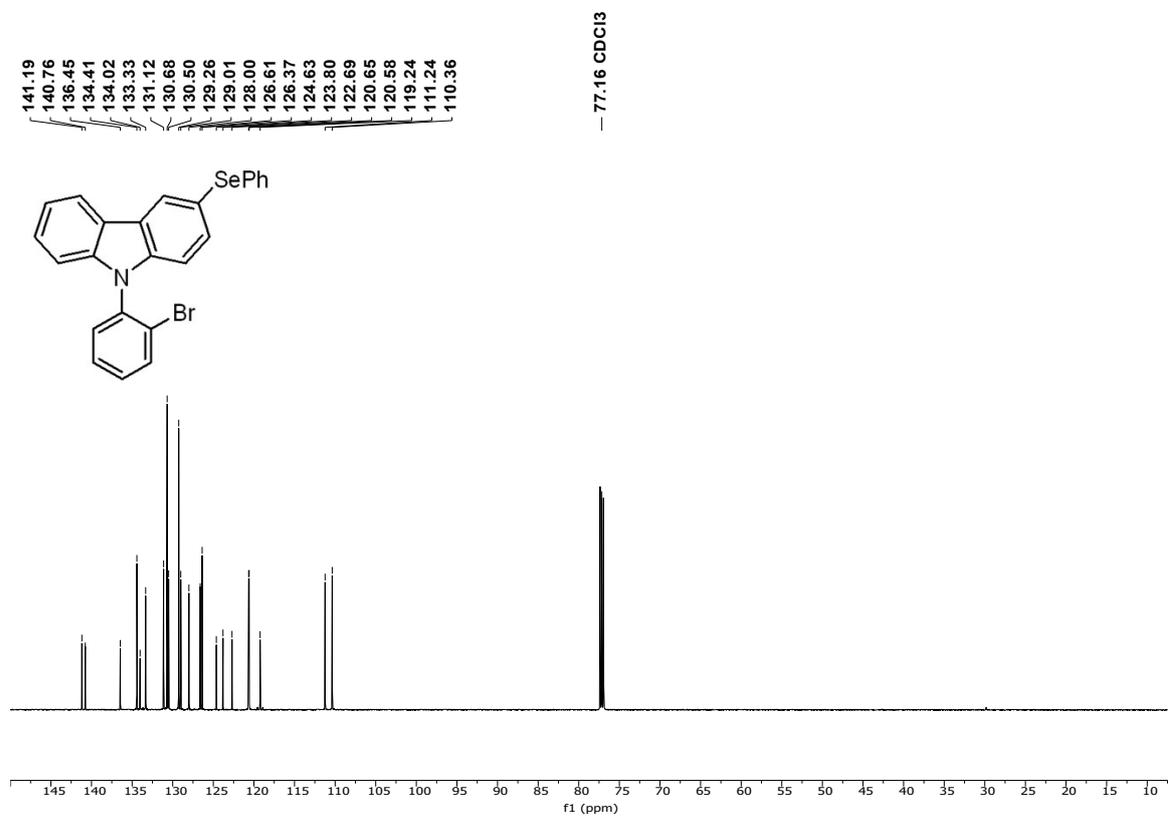
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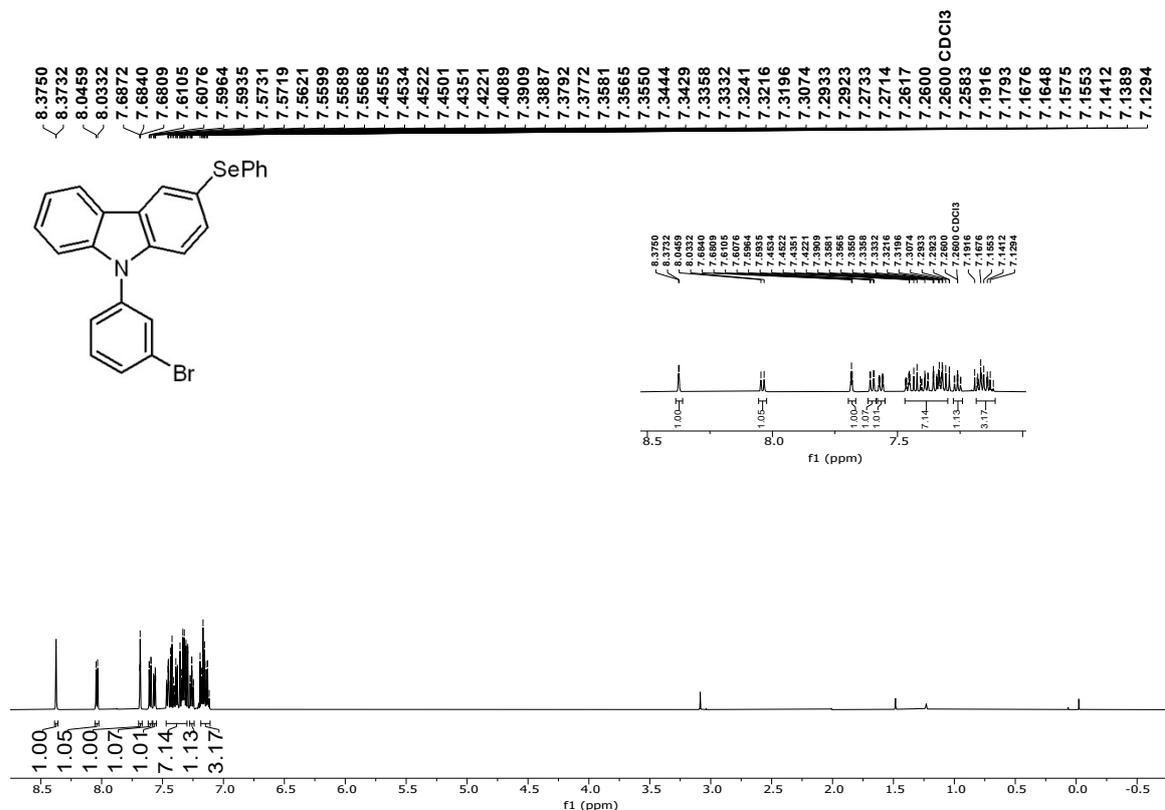
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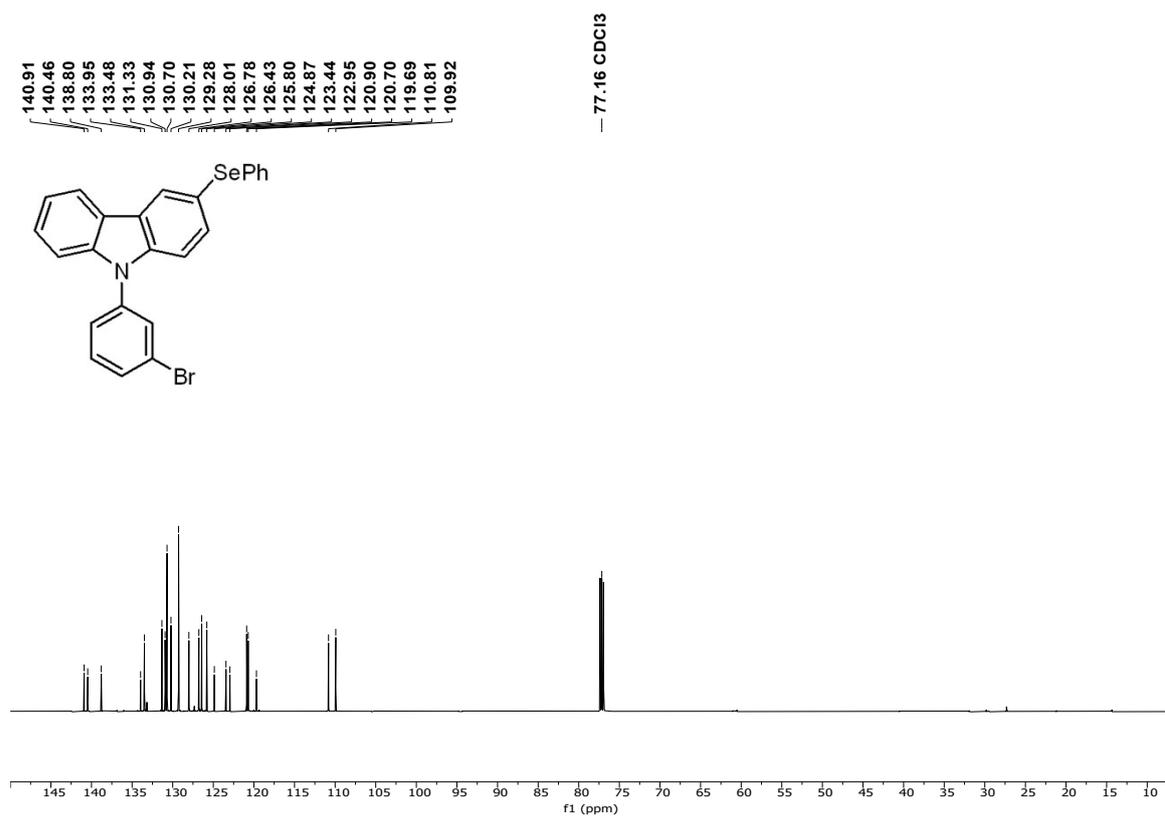
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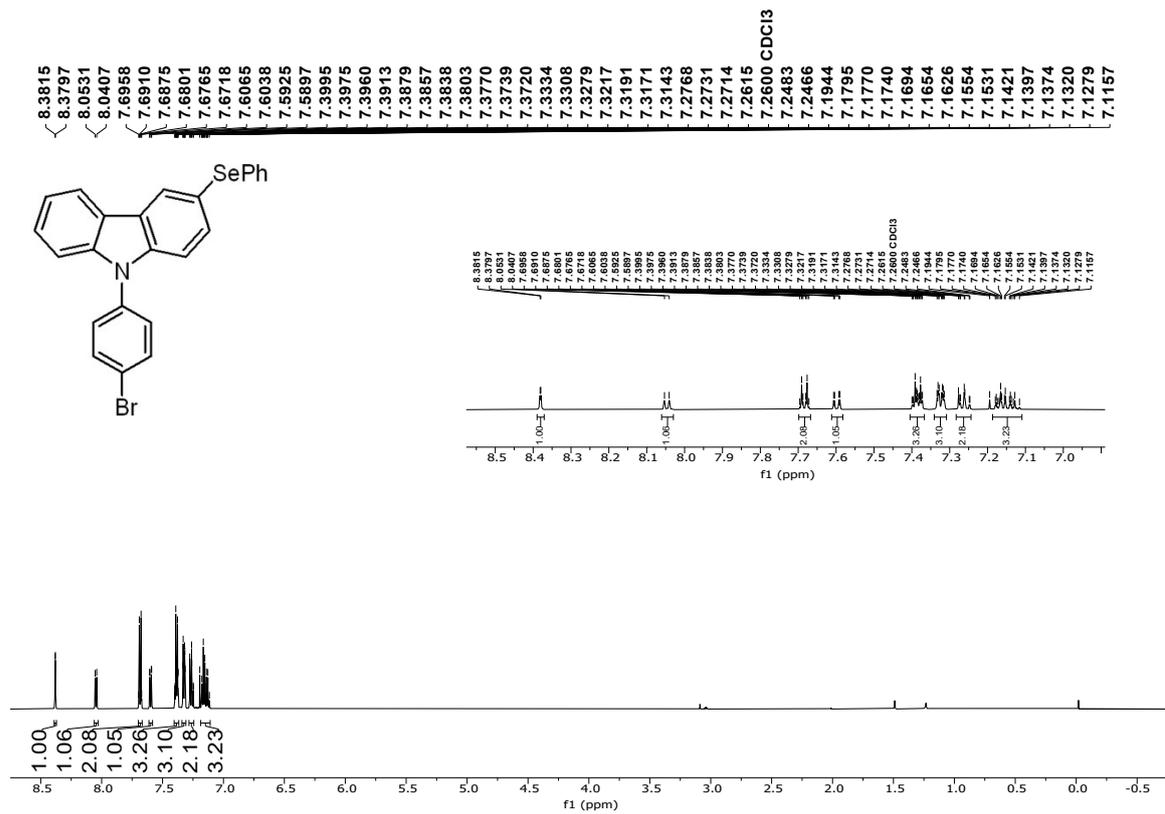
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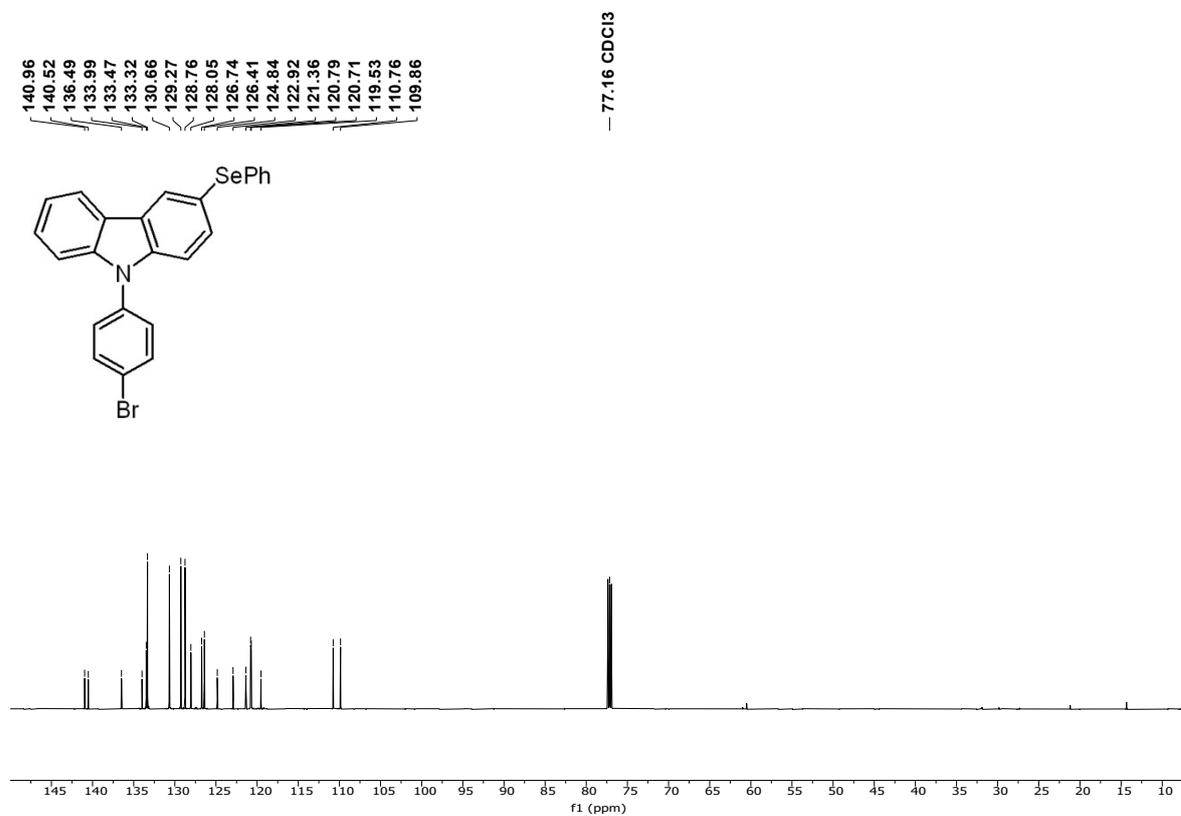
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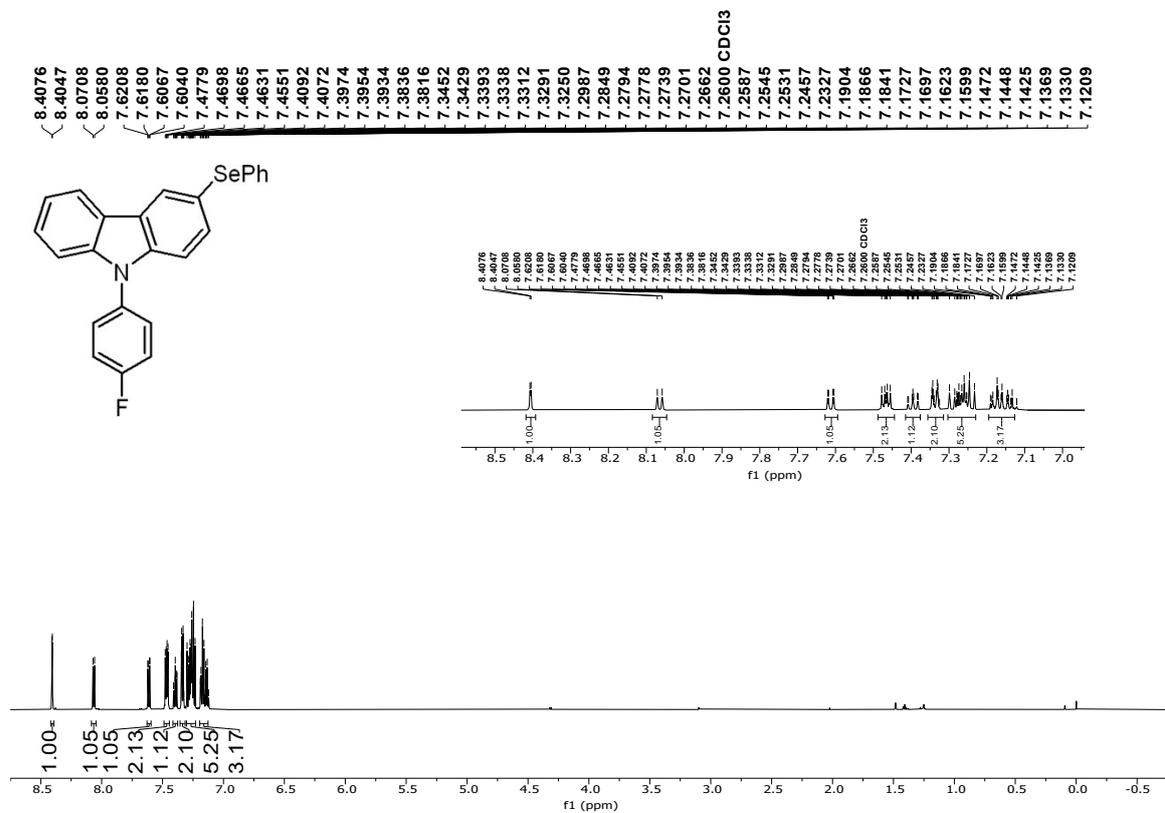
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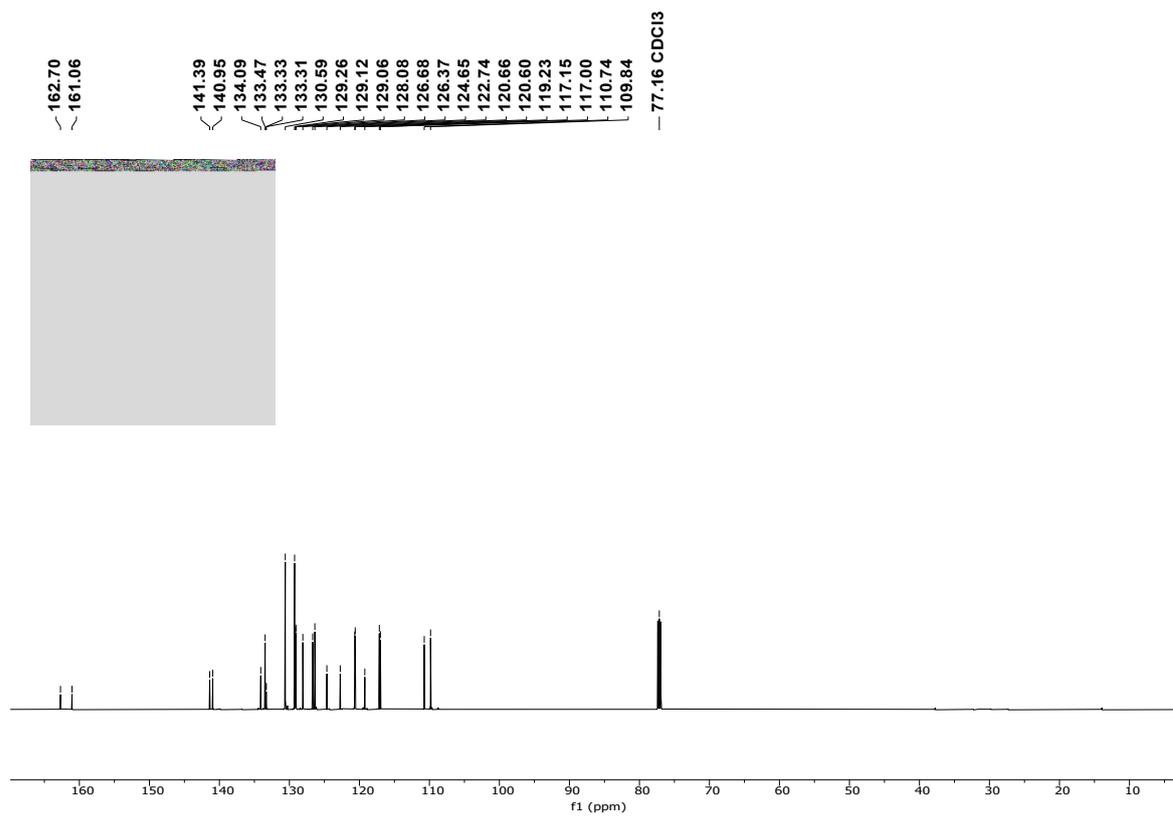
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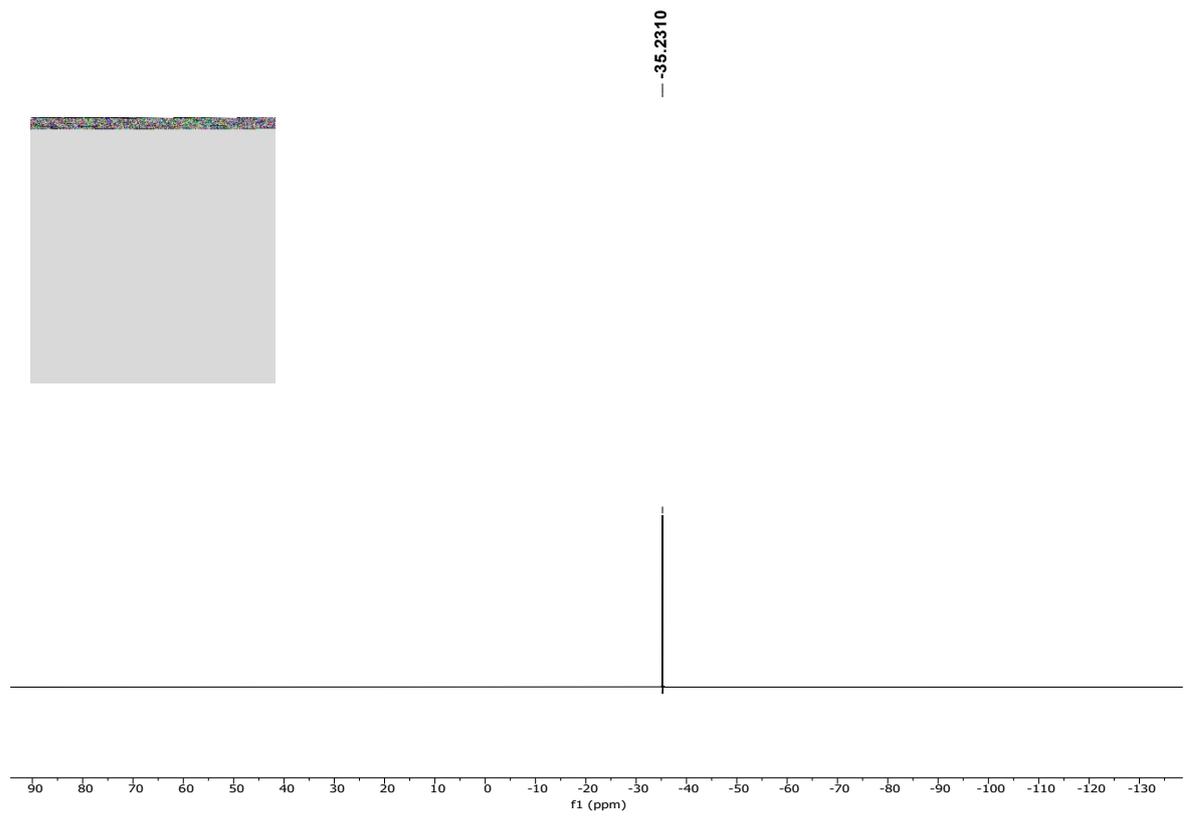
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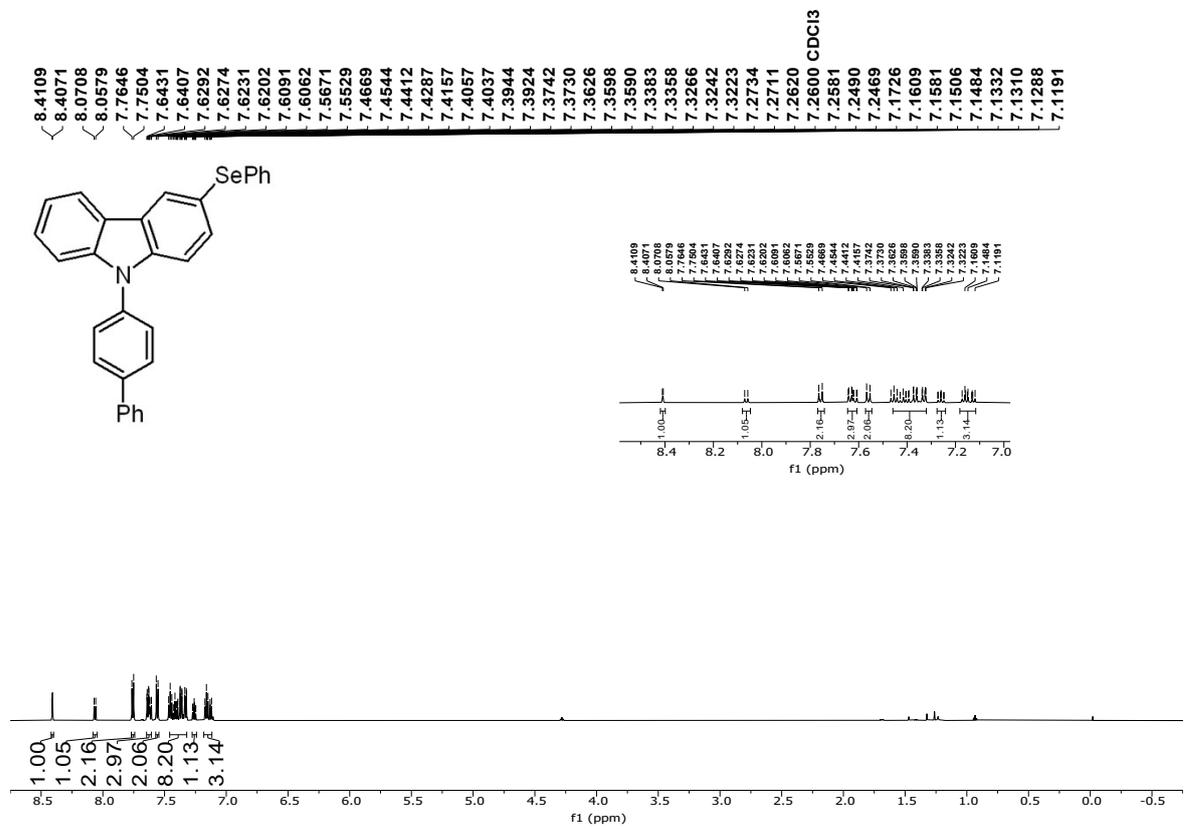
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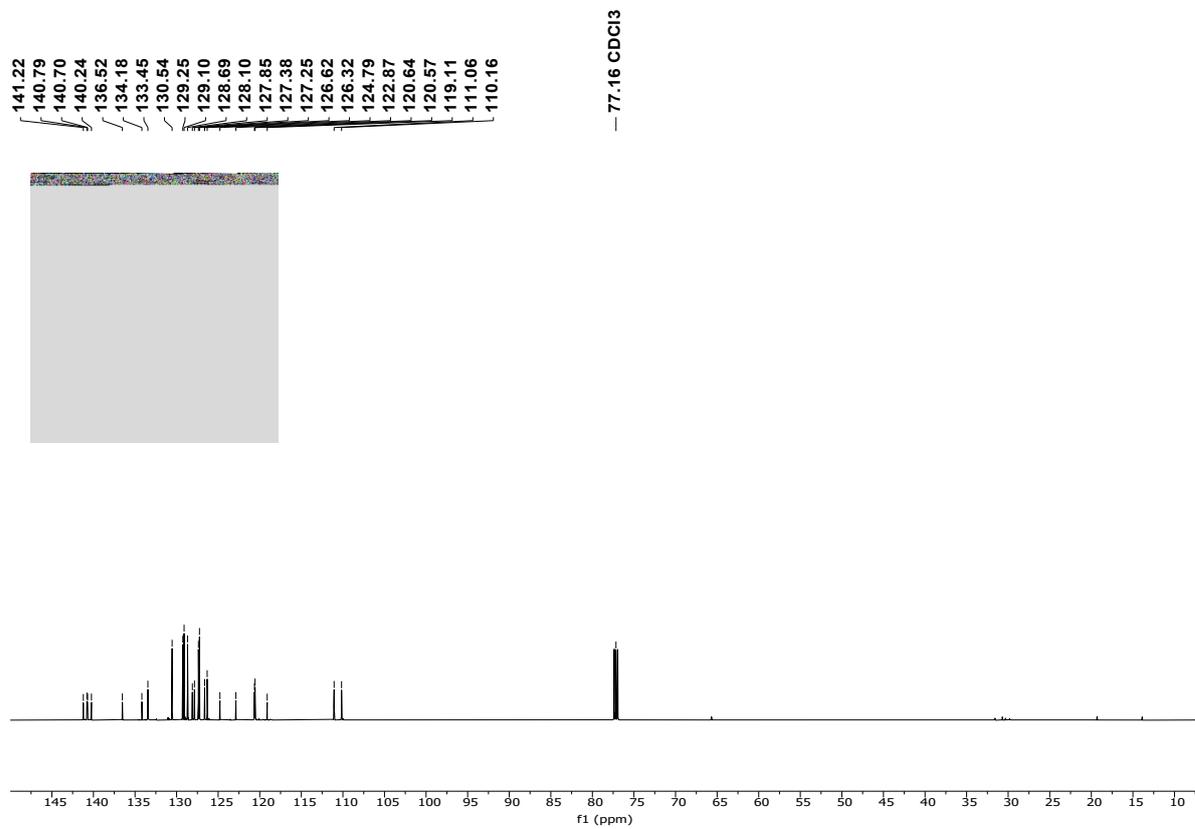
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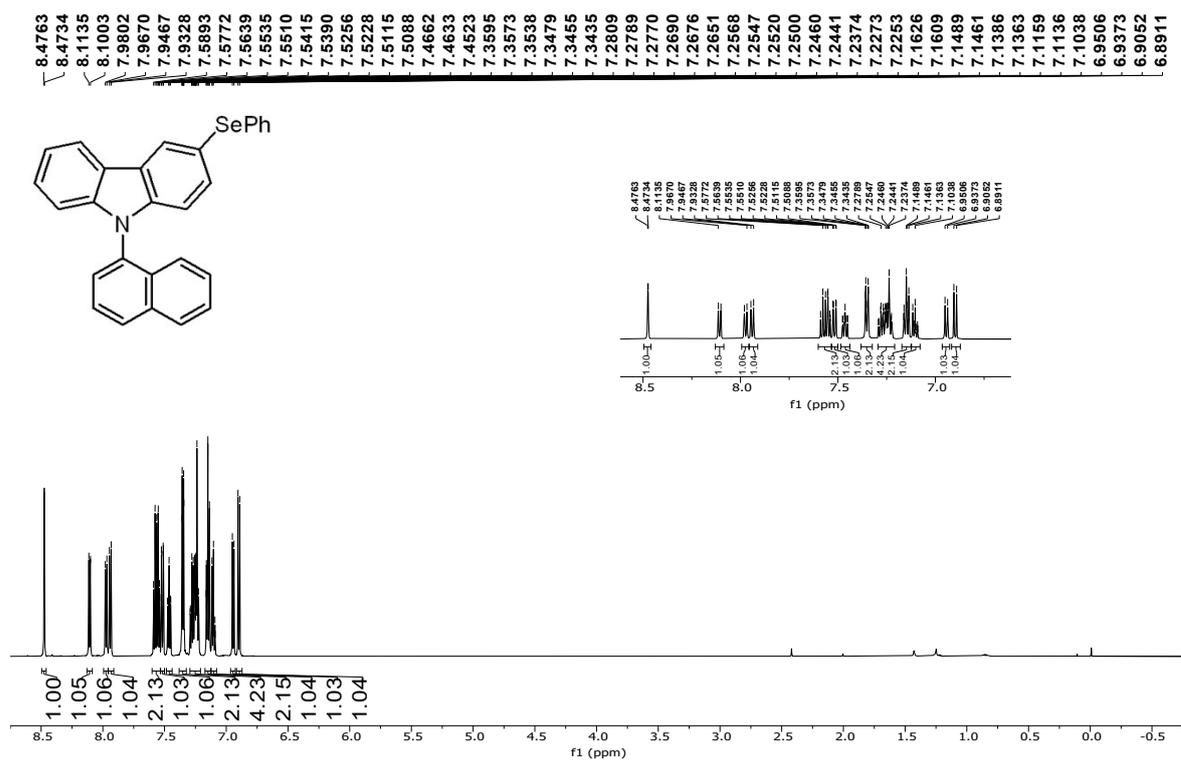
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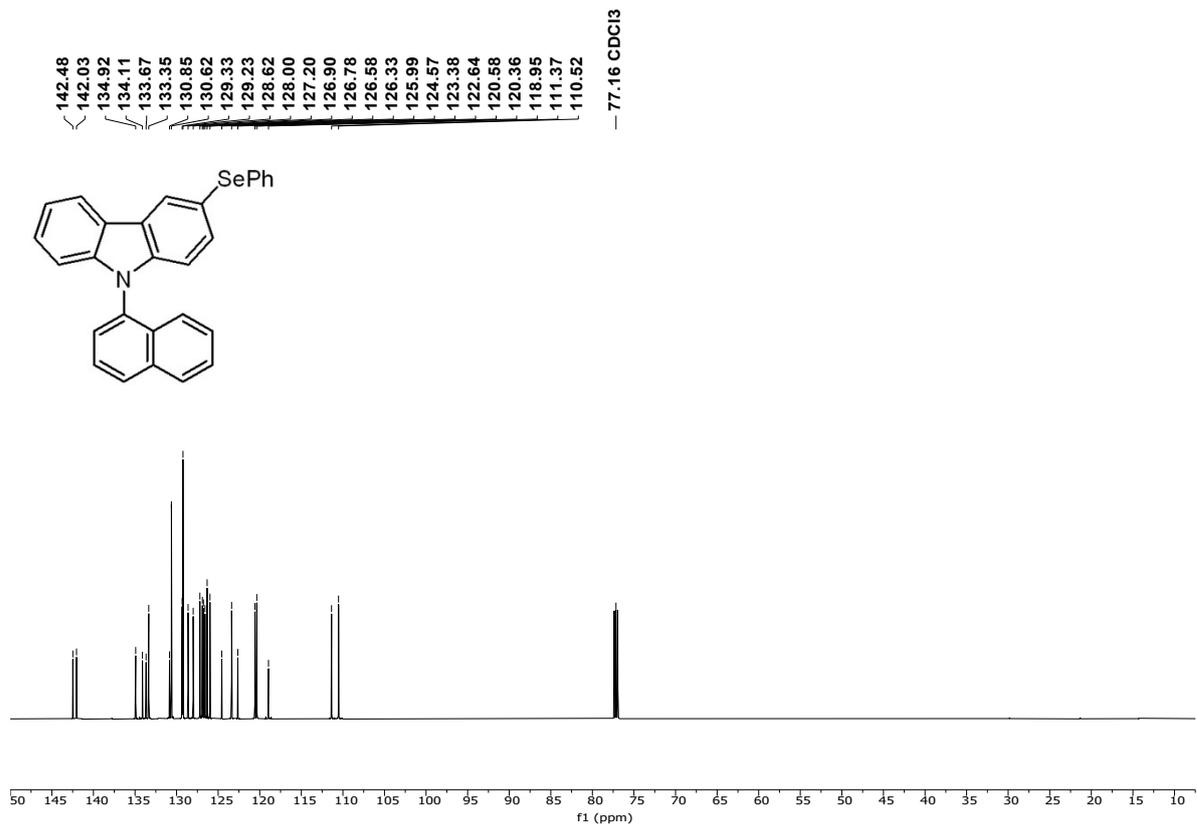
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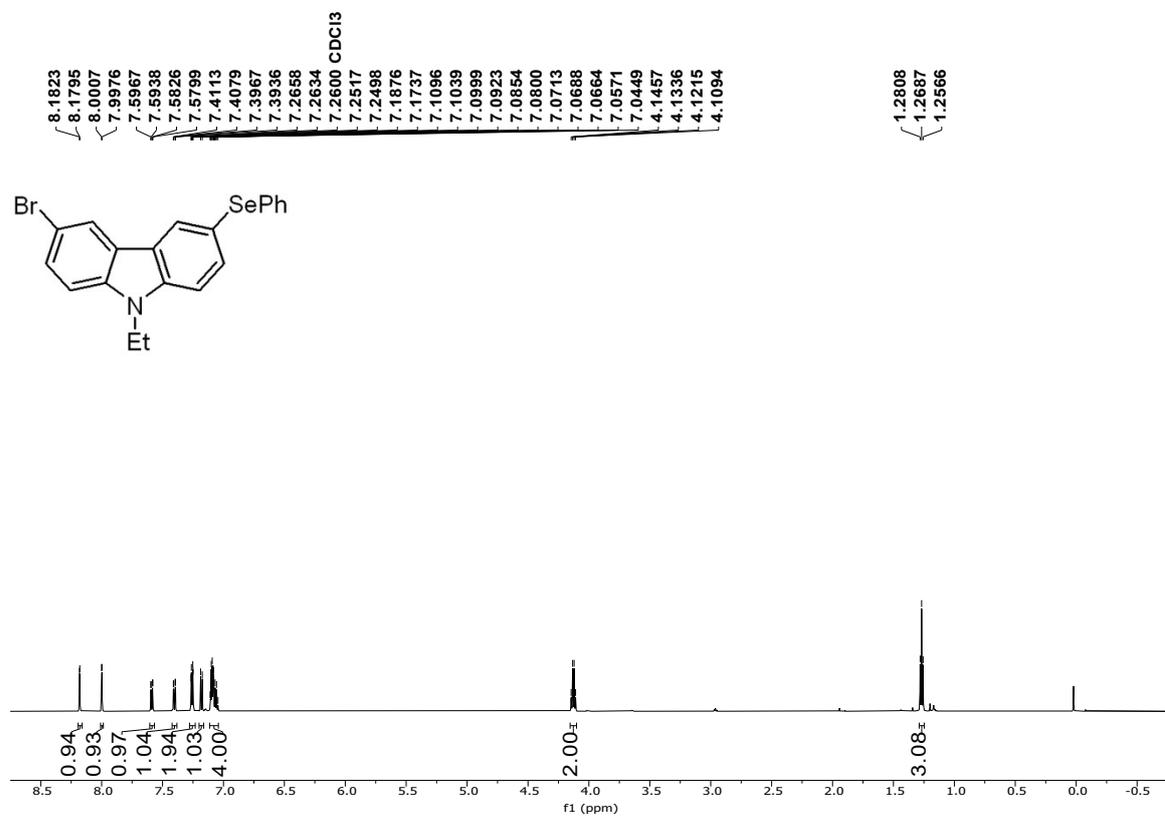
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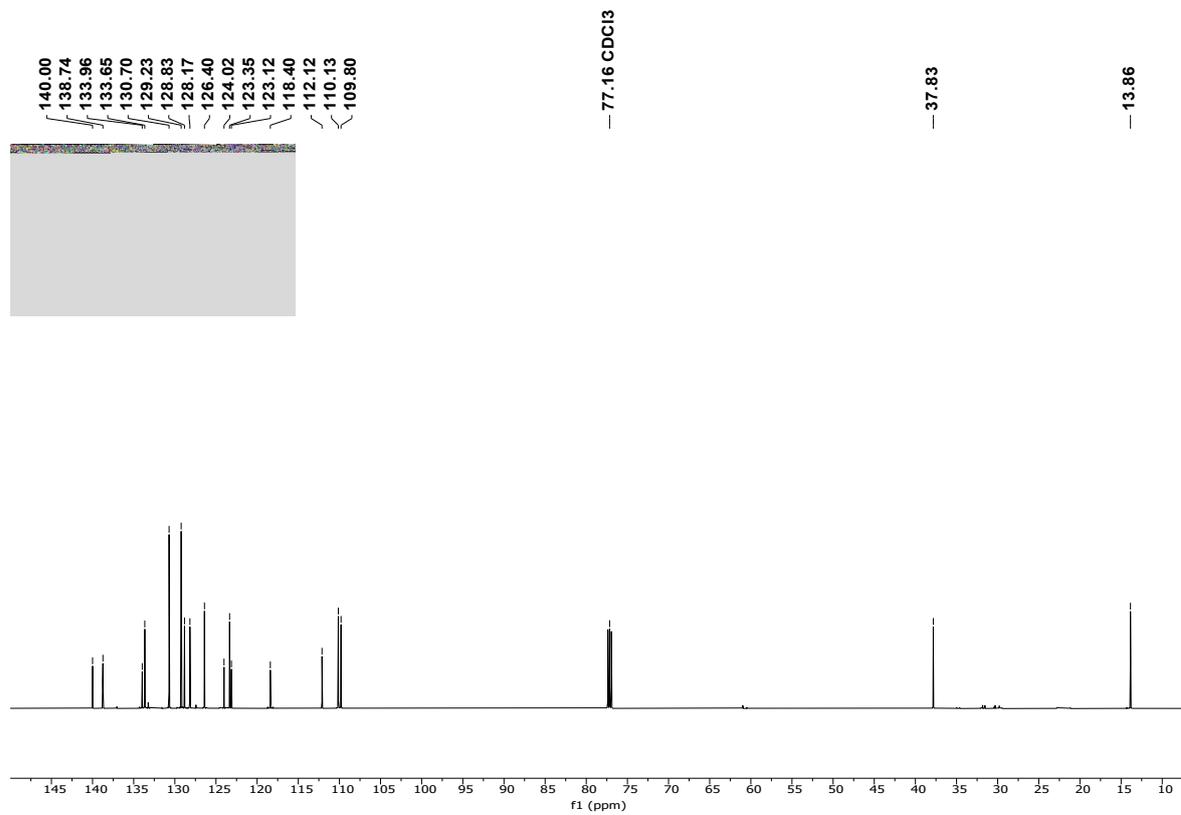
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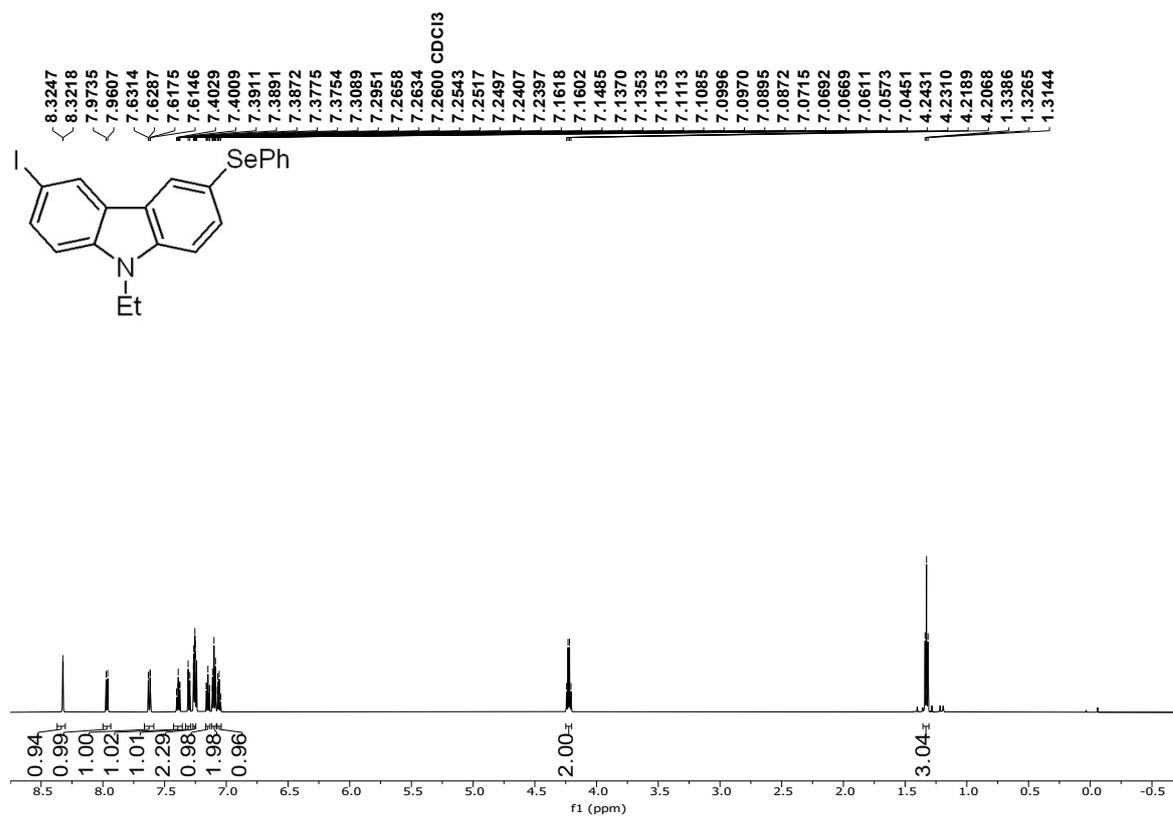
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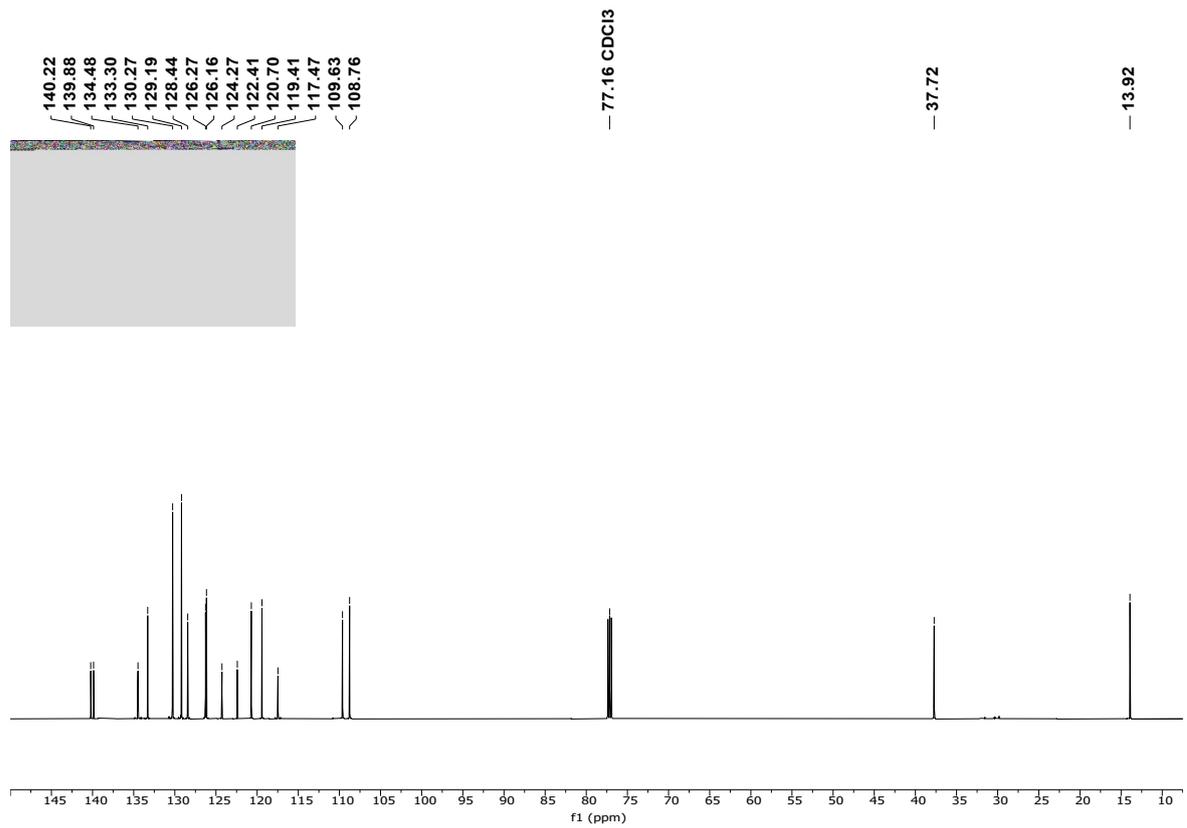
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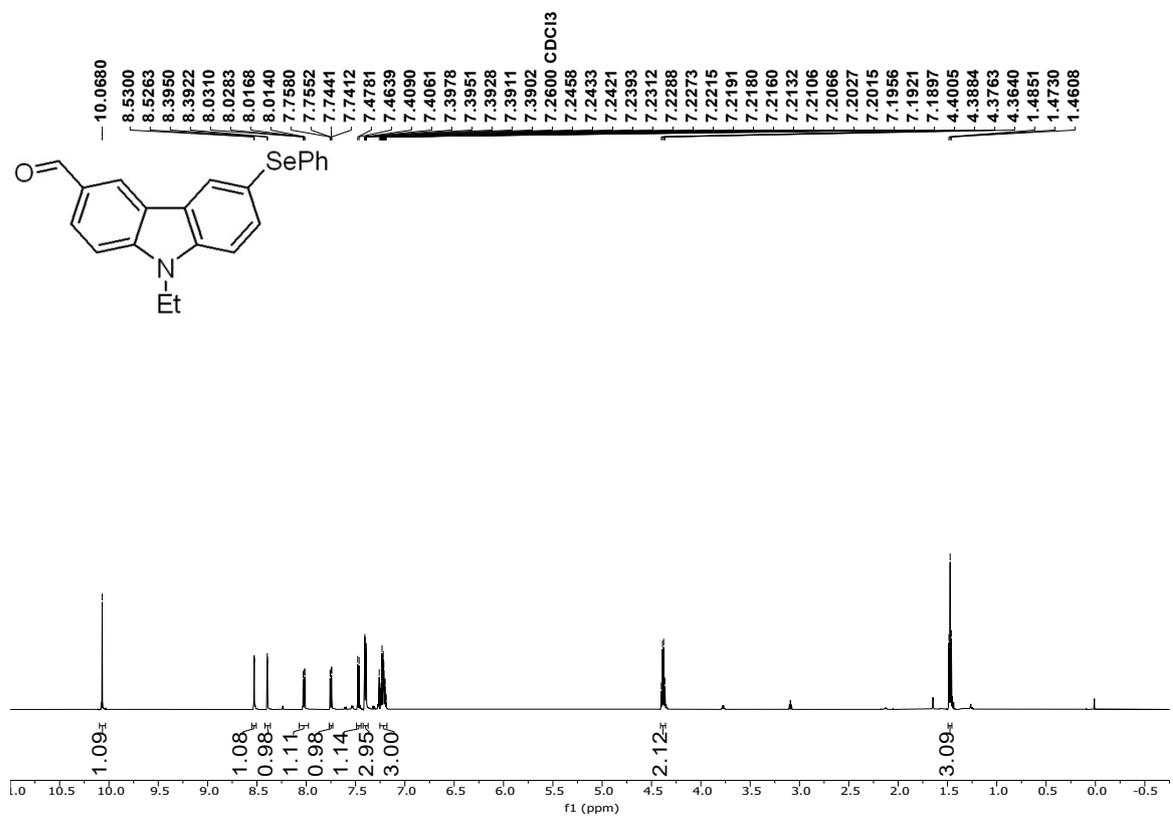
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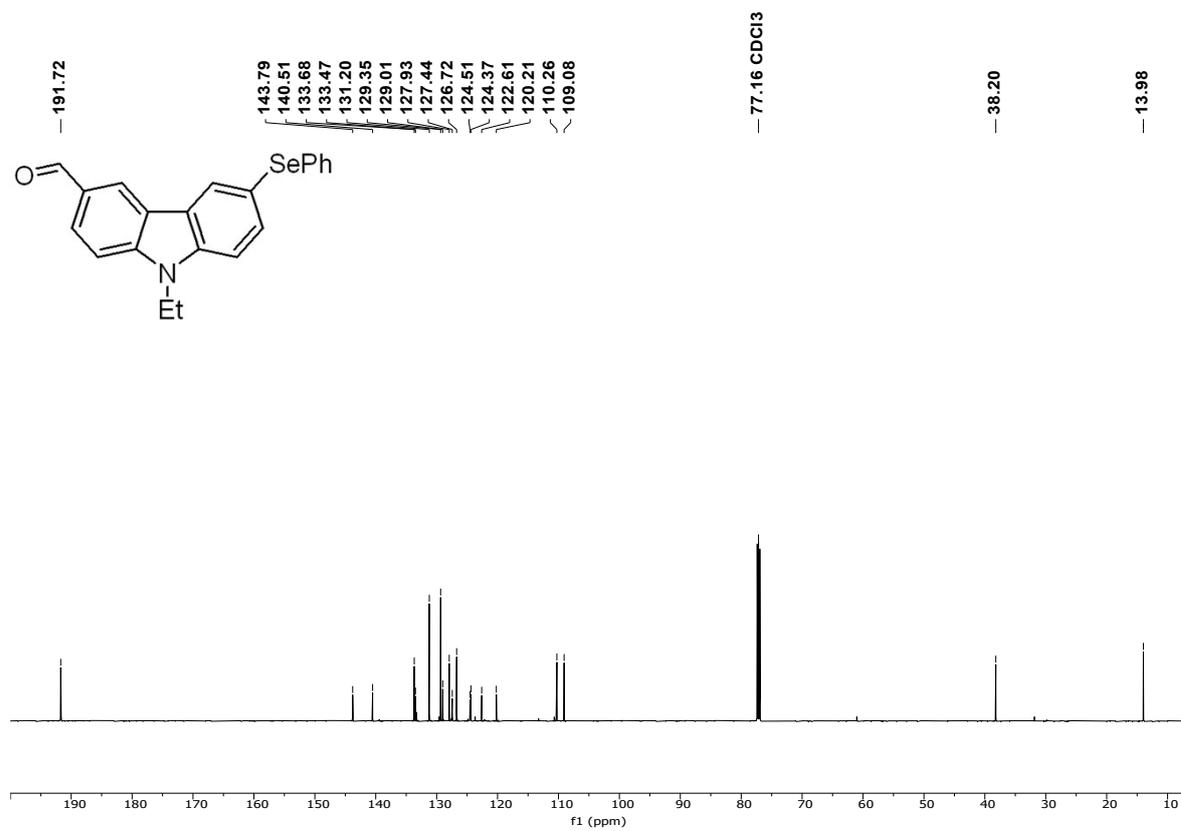
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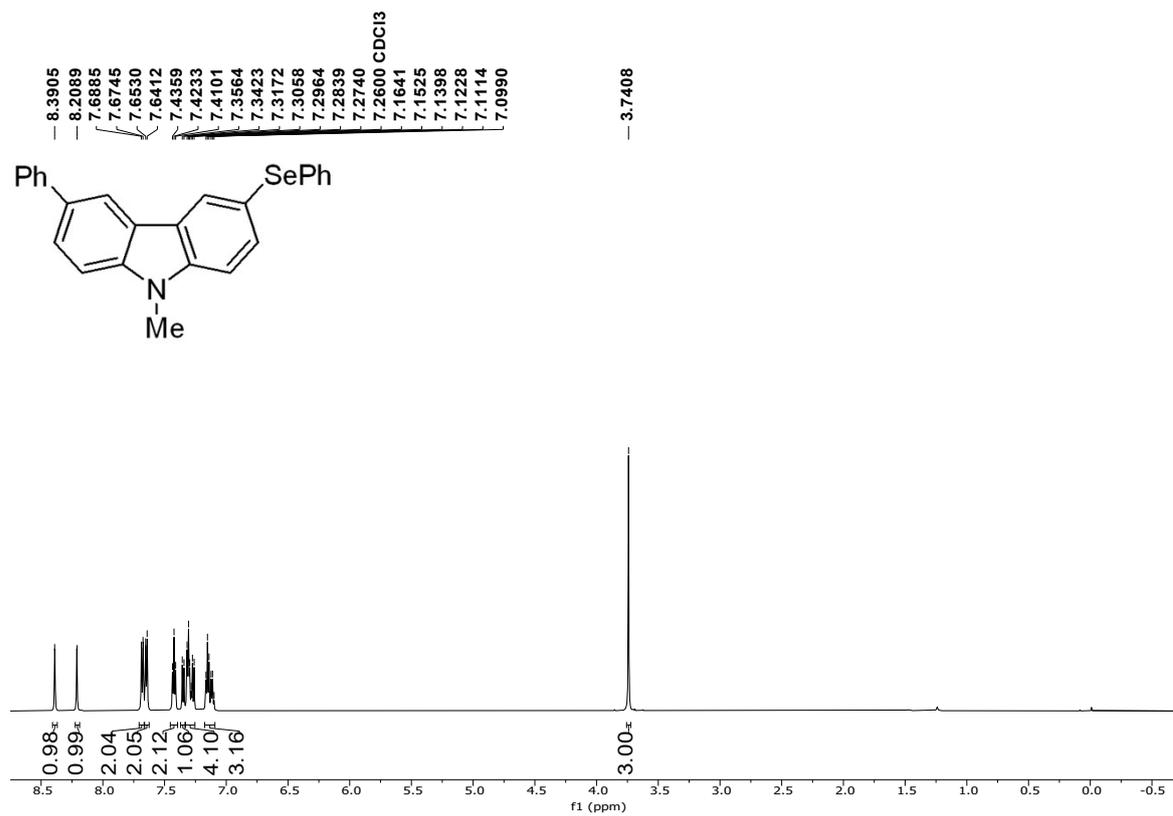
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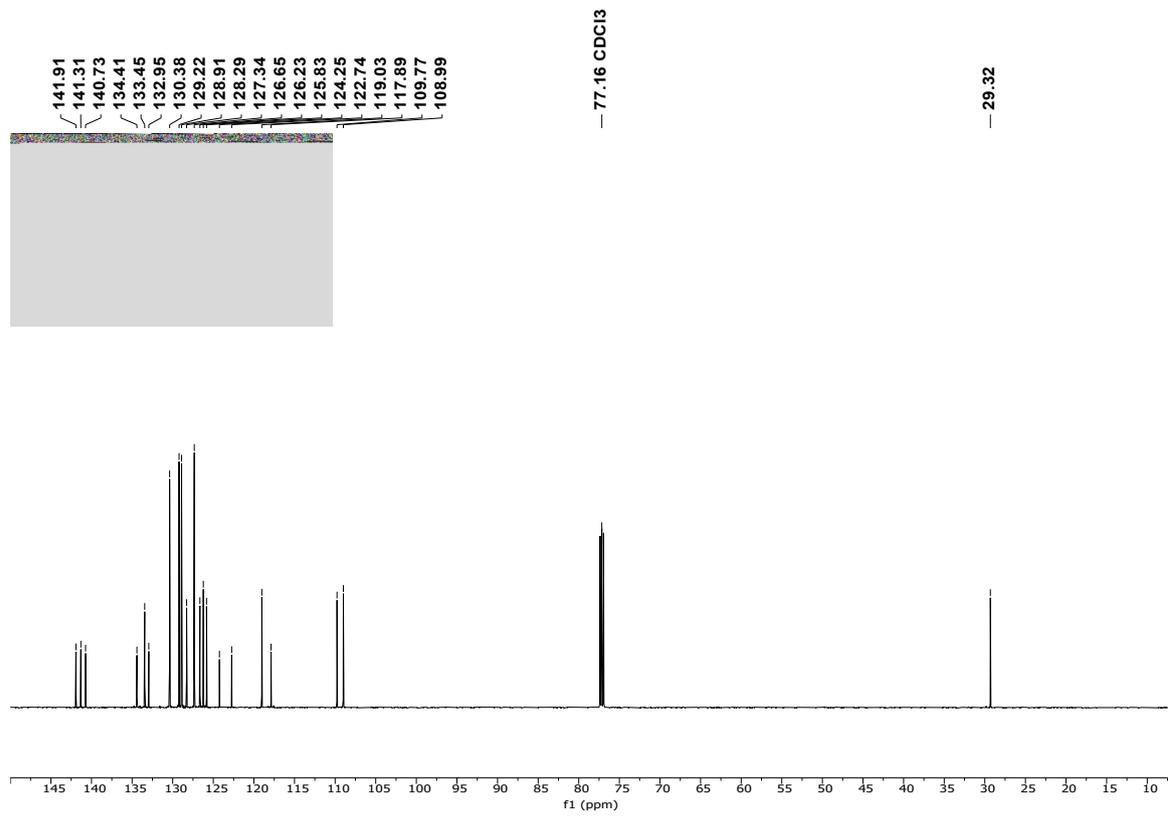
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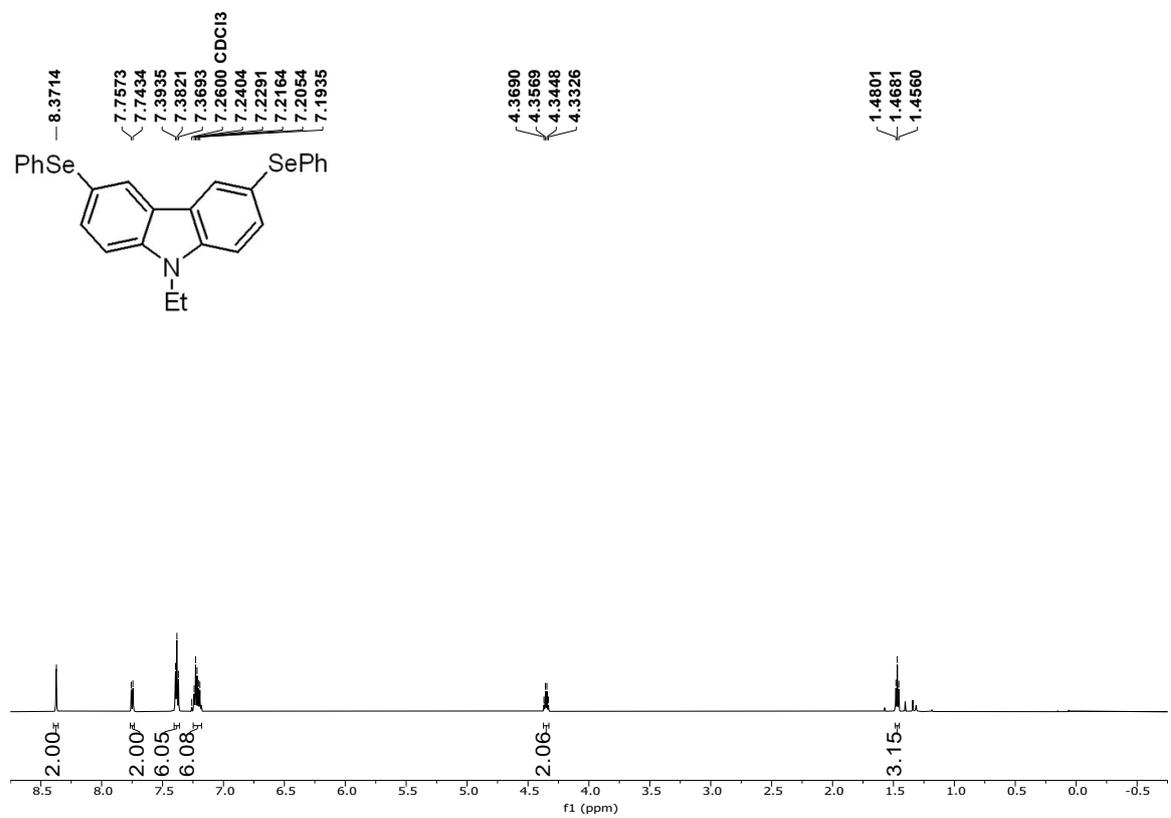
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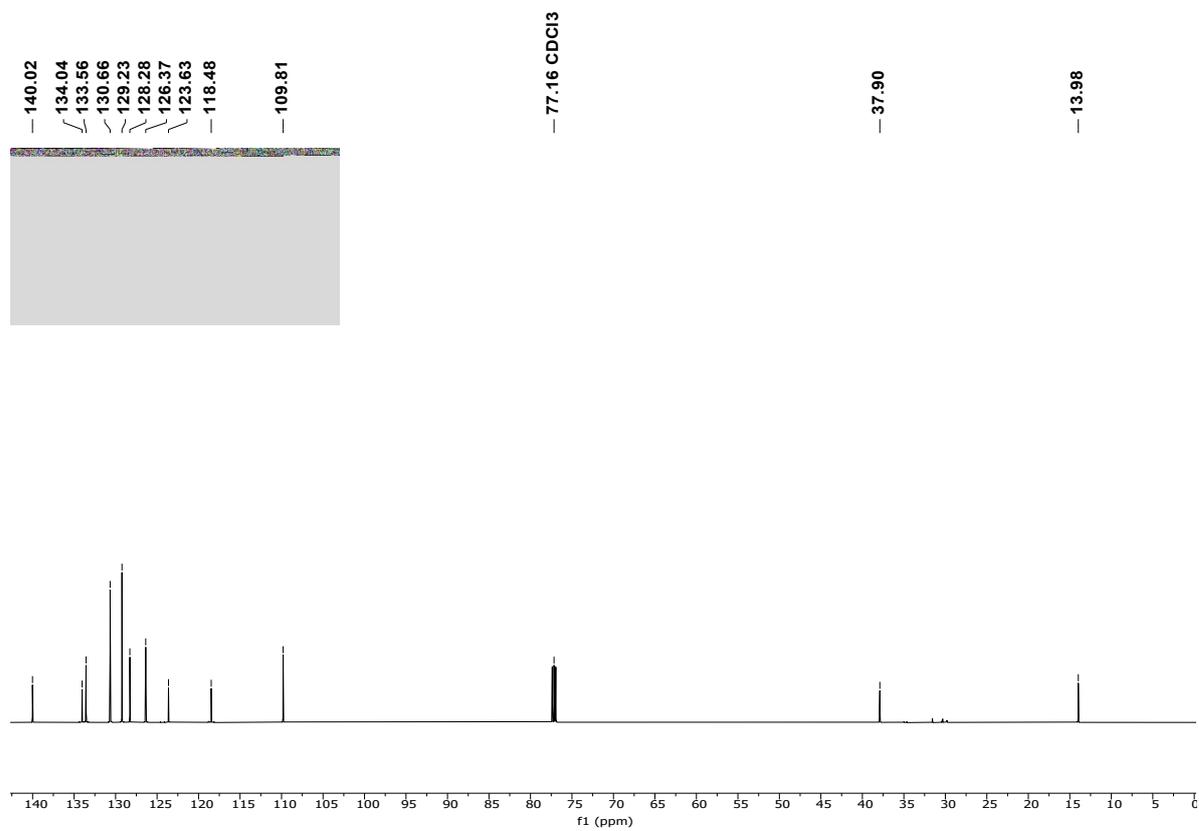
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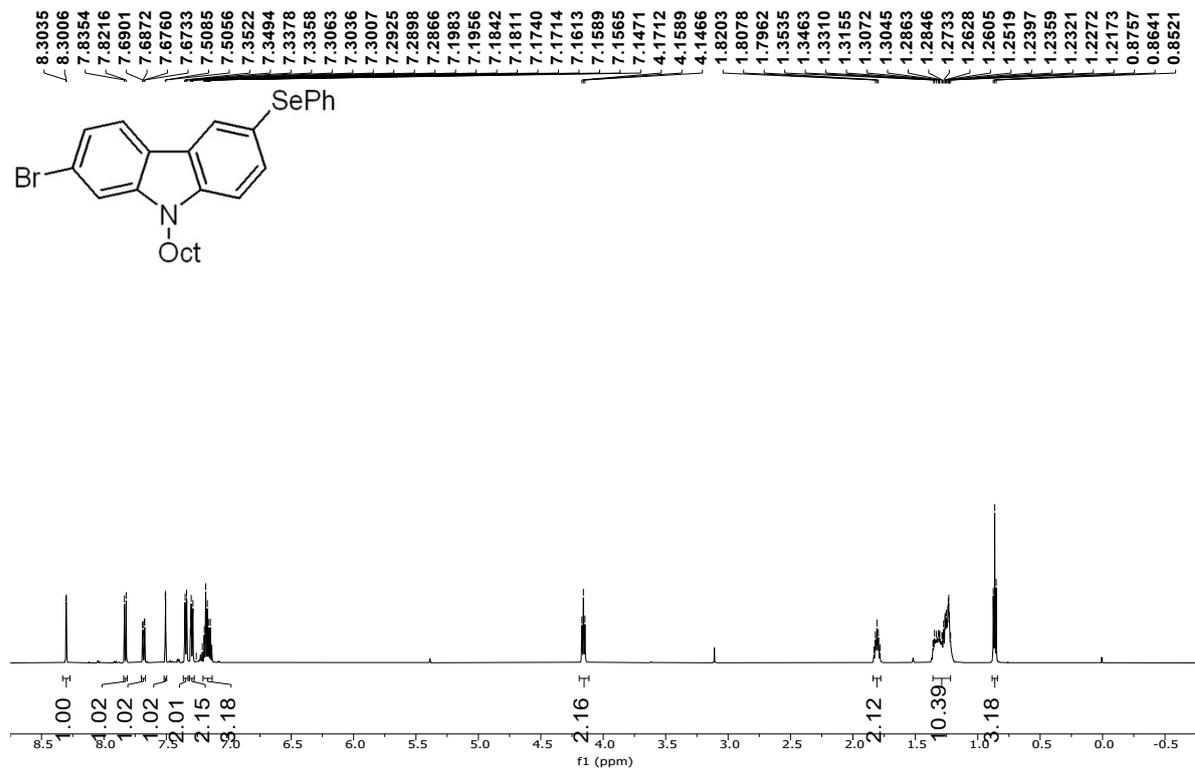
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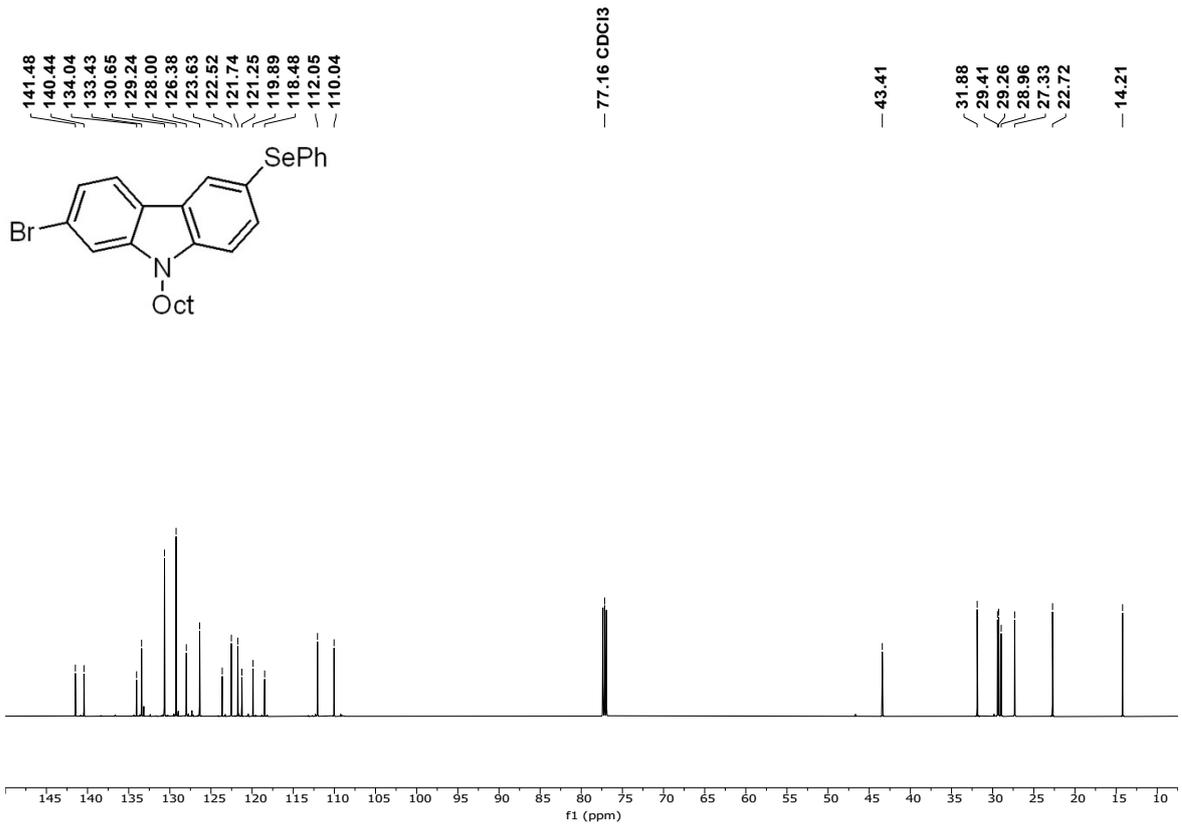
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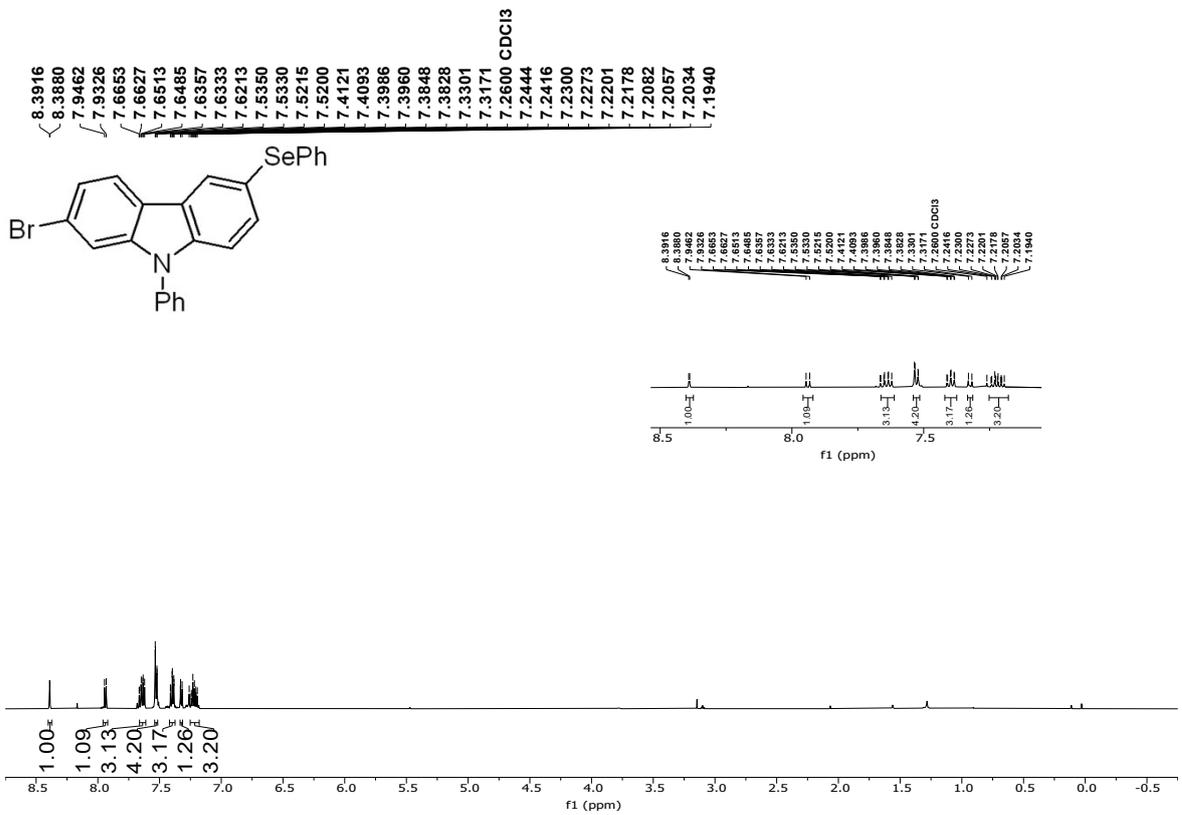
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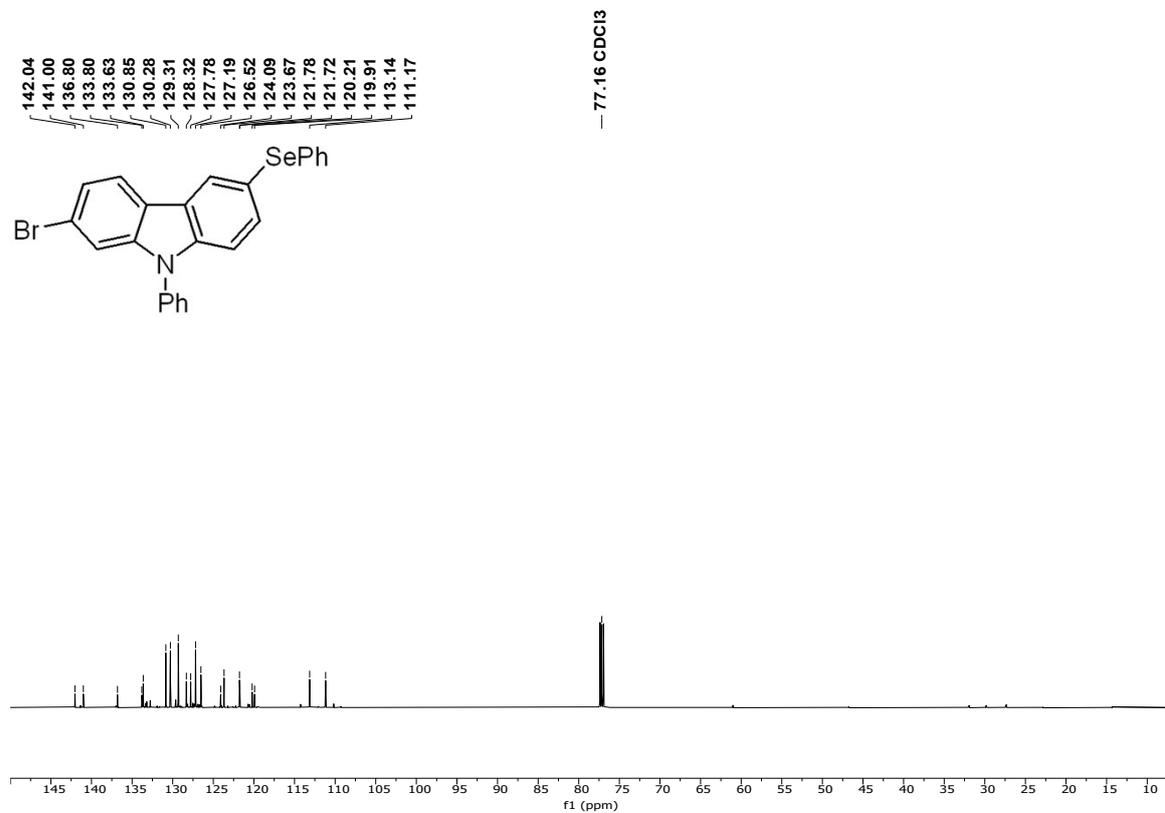
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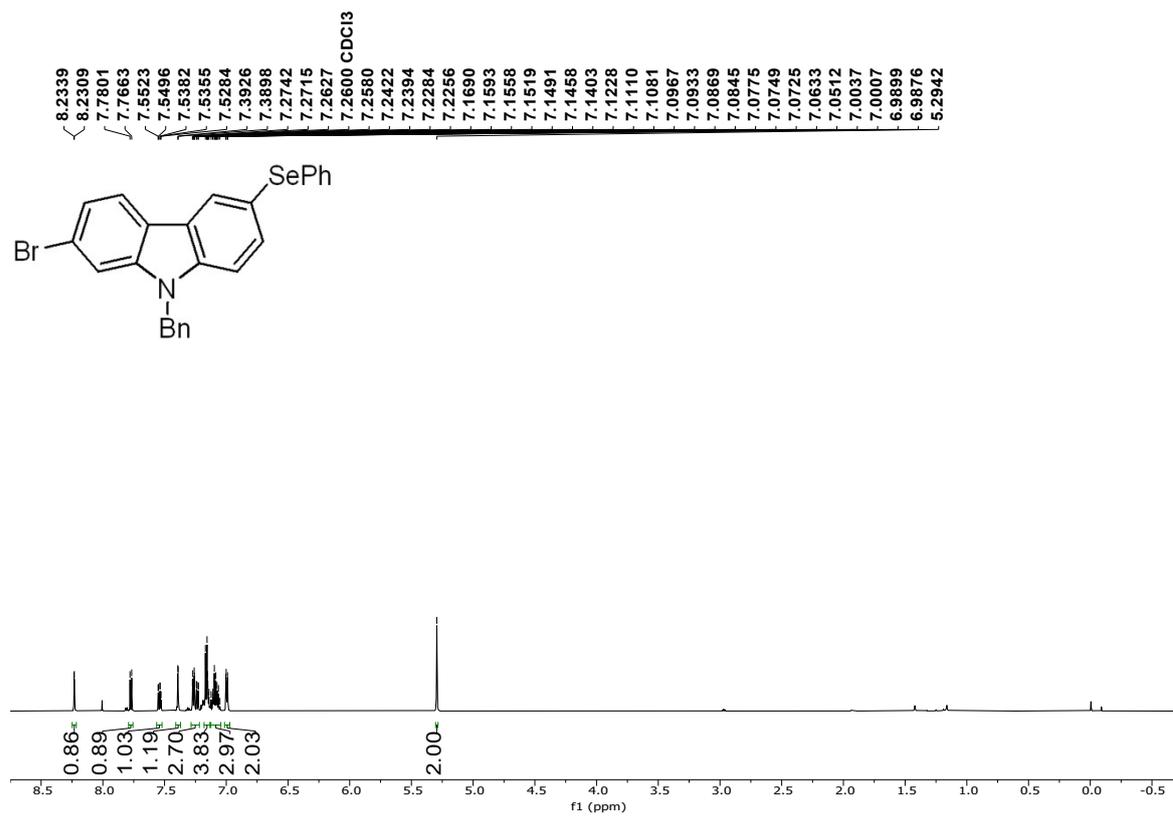
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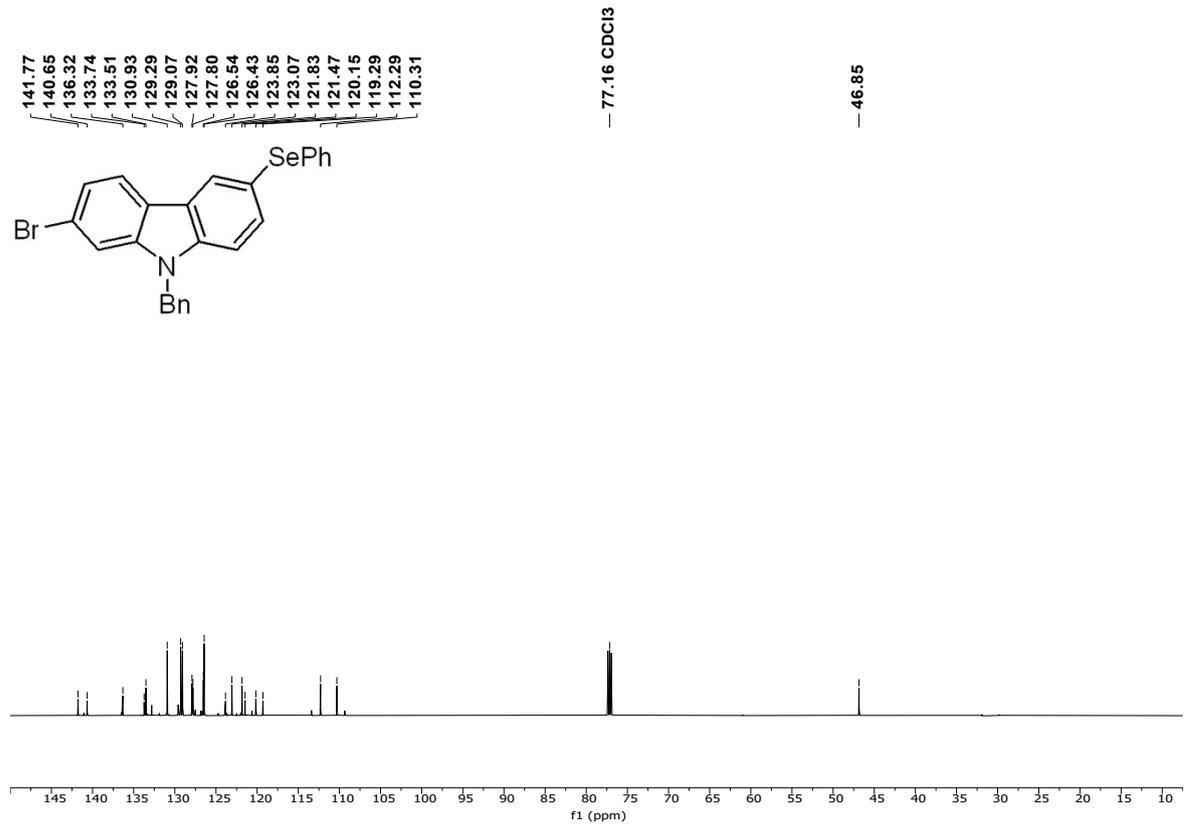
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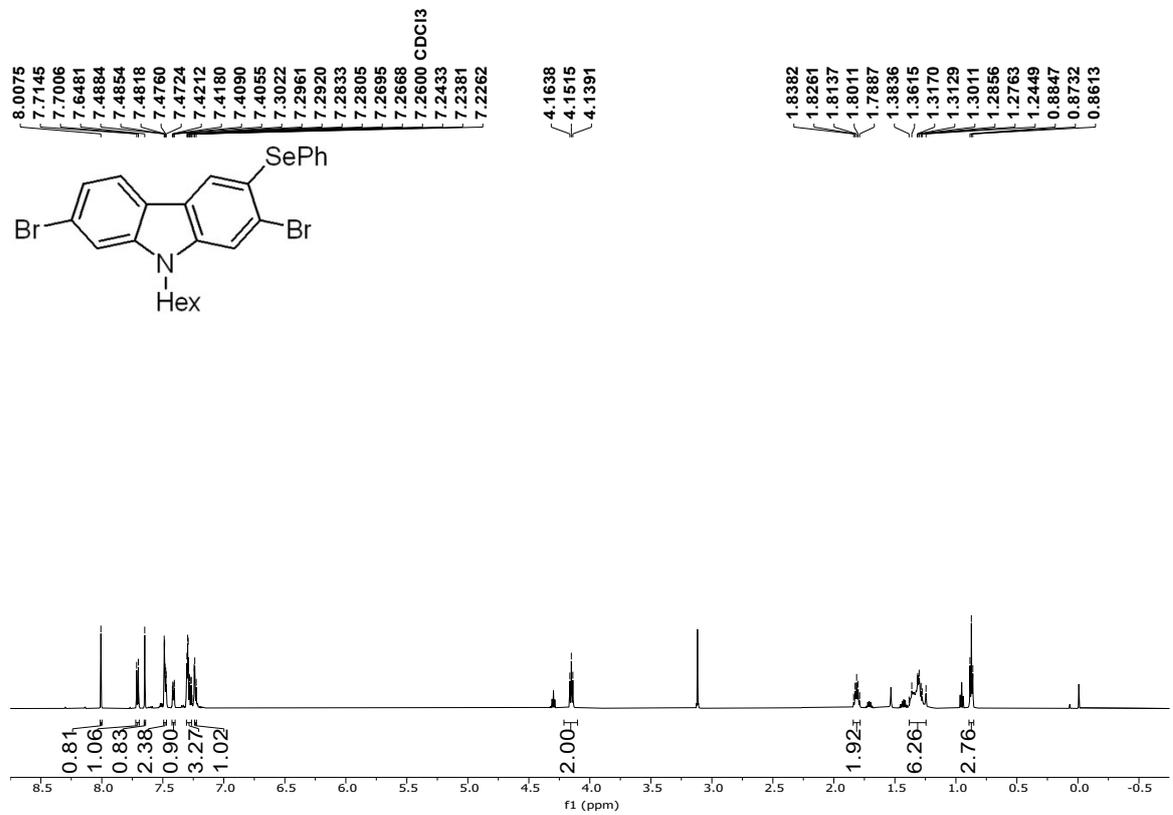
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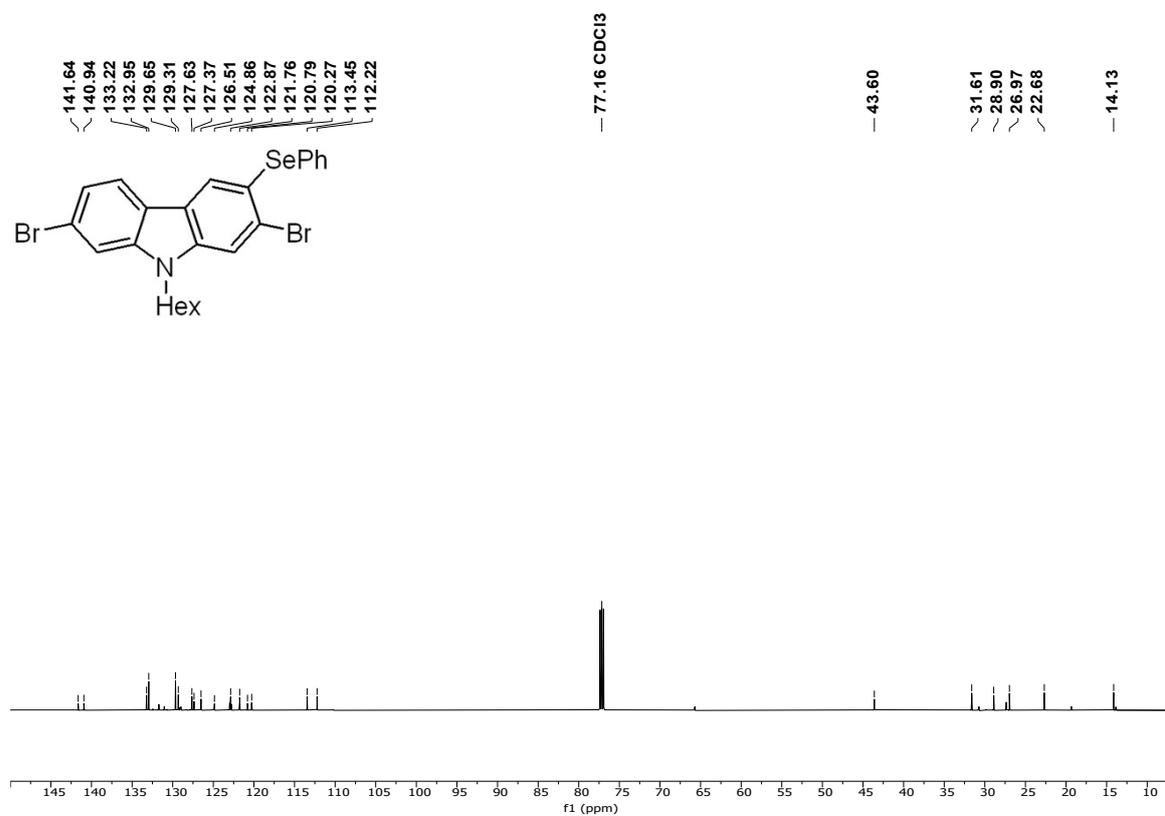
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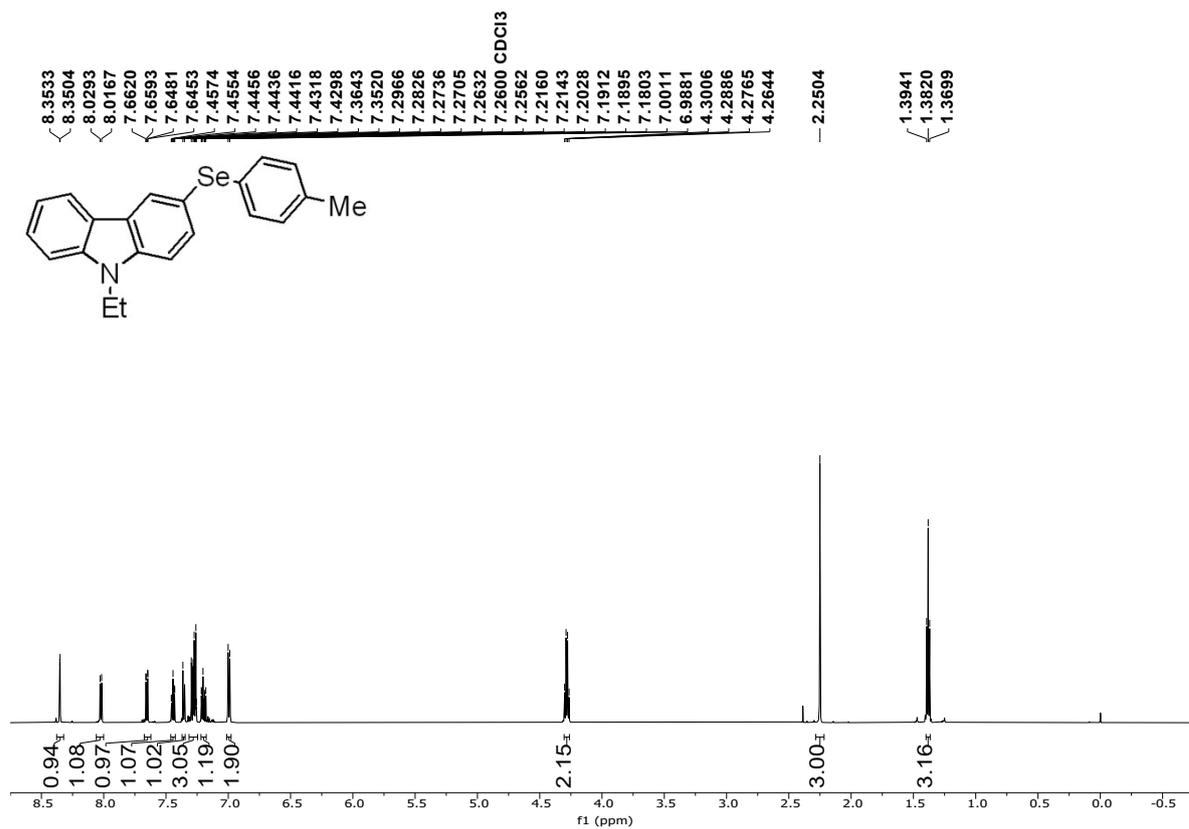
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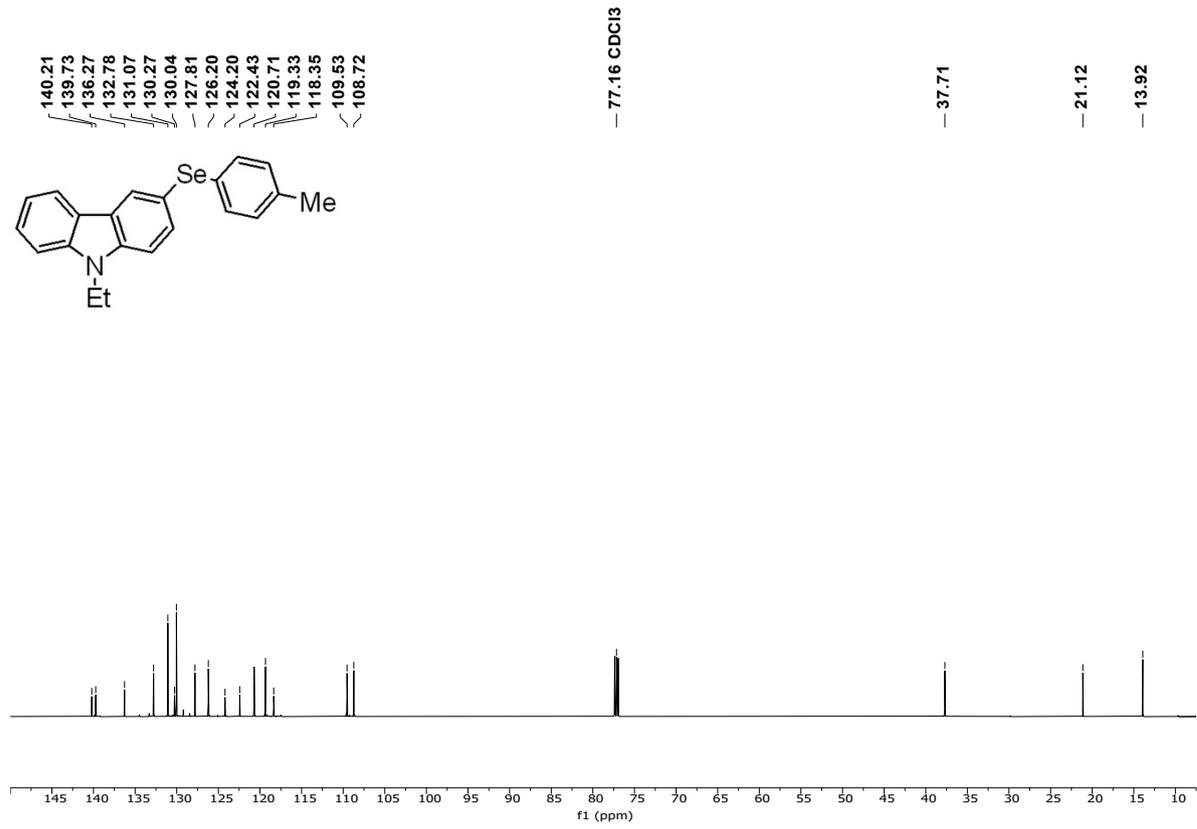
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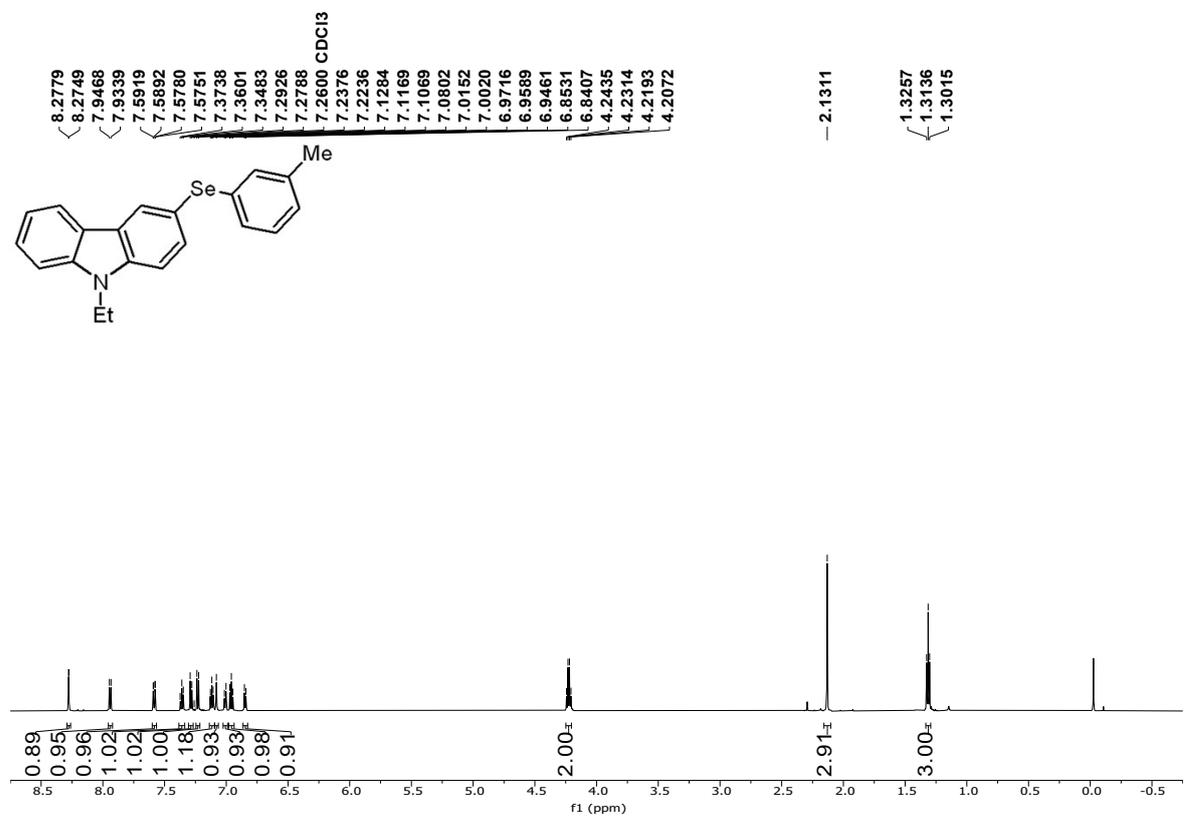
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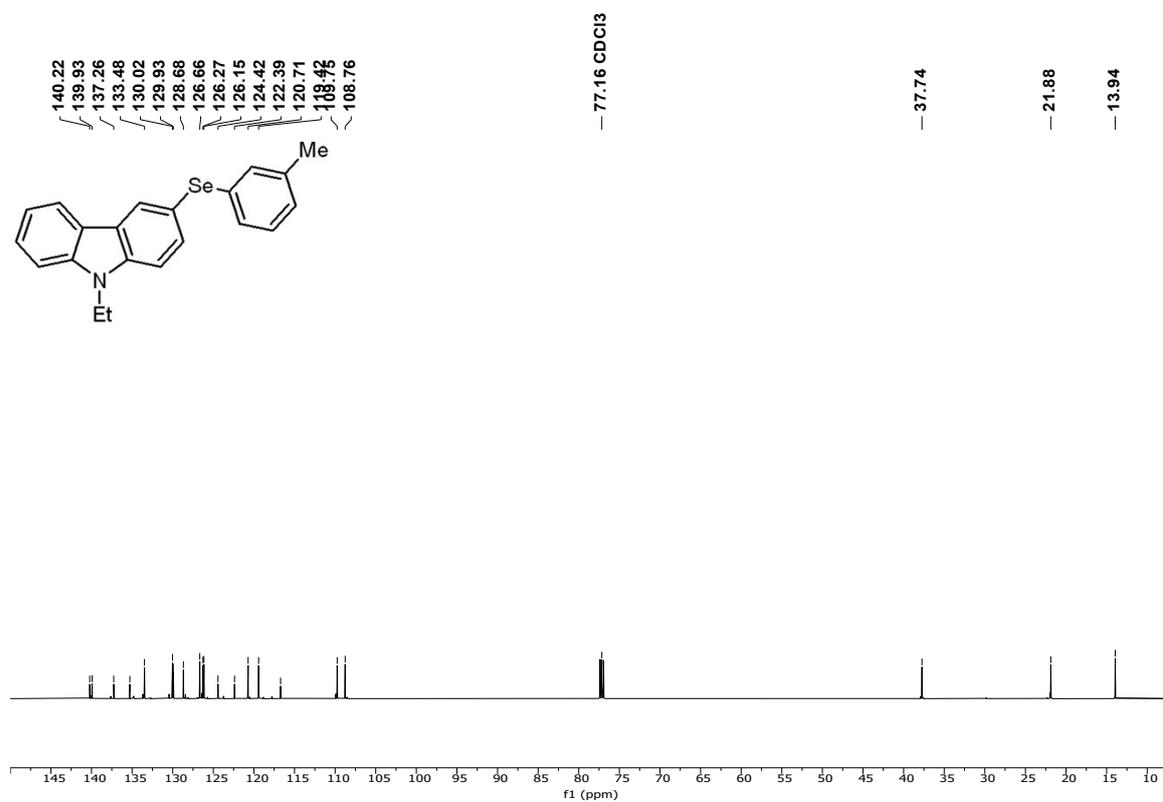
¹³C NMR of product 3ab in CDCl₃ (151 MHz)



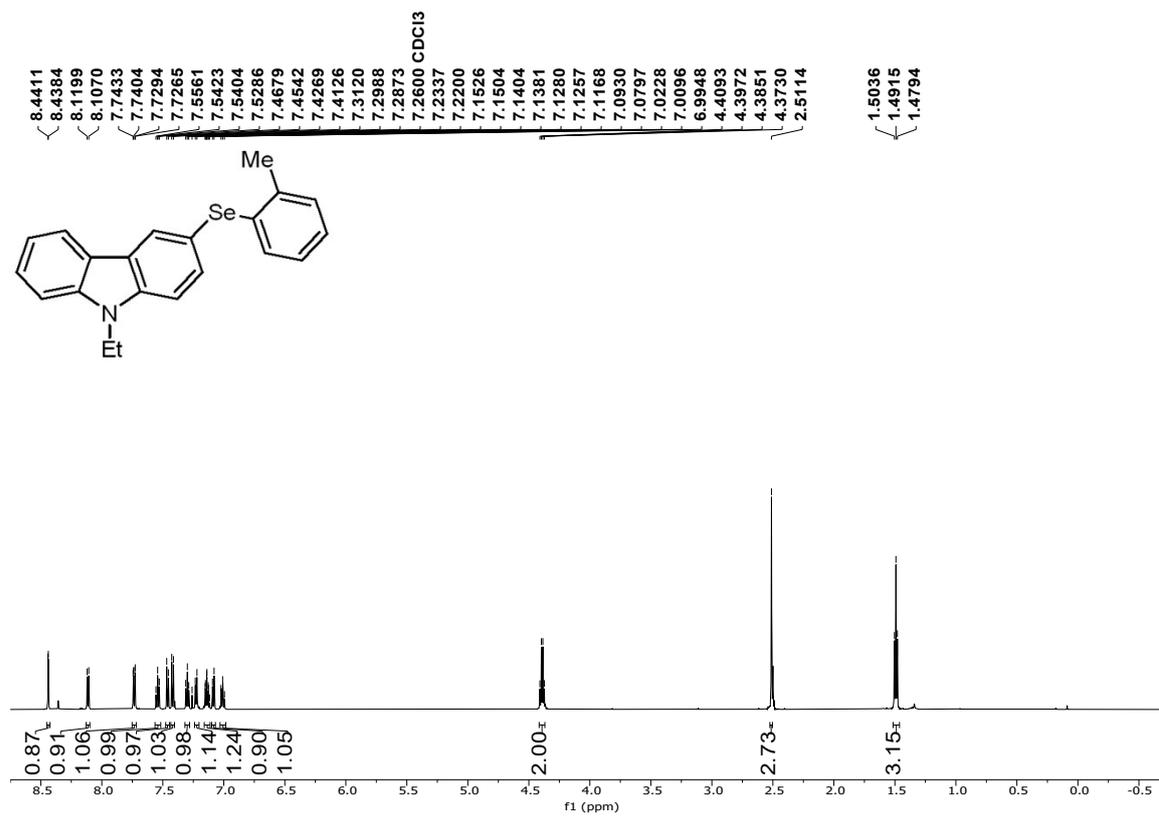
¹H NMR of product 3ac in CDCl₃ (600 MHz)



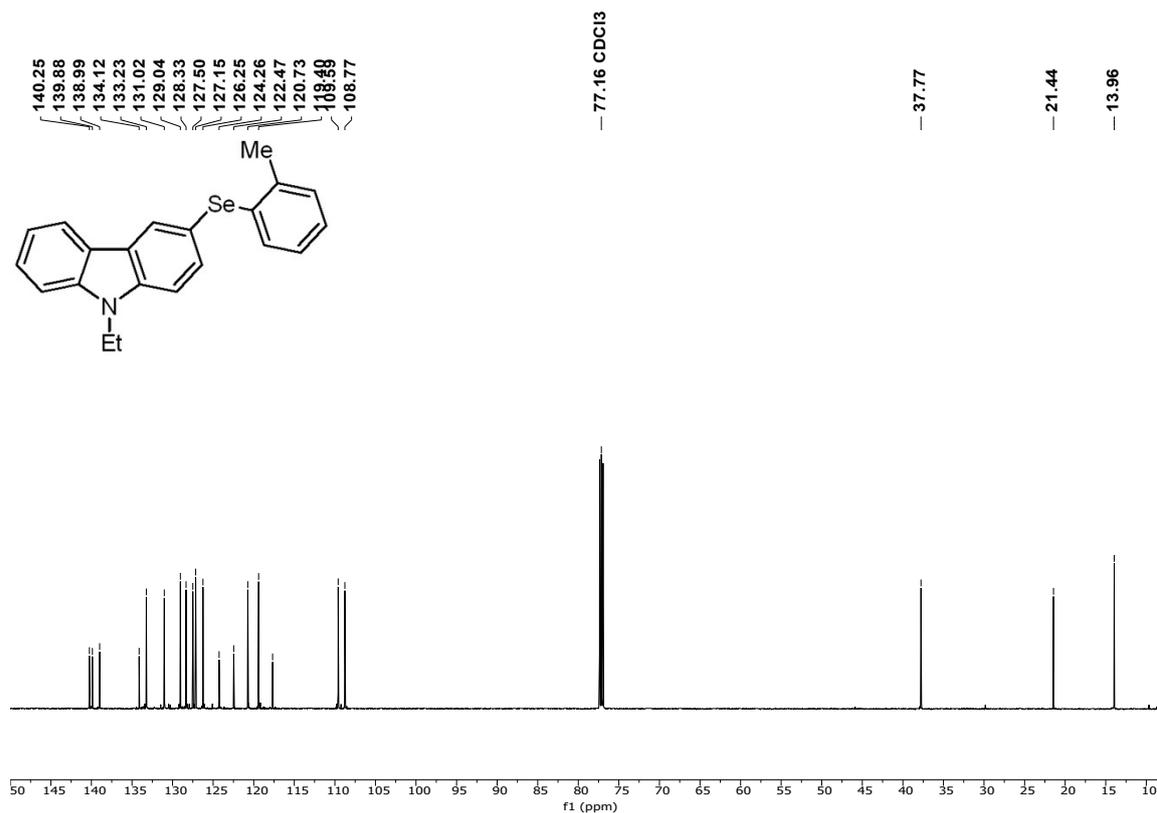
^{13}C NMR of product 3ac in CDCl_3 (151 MHz)



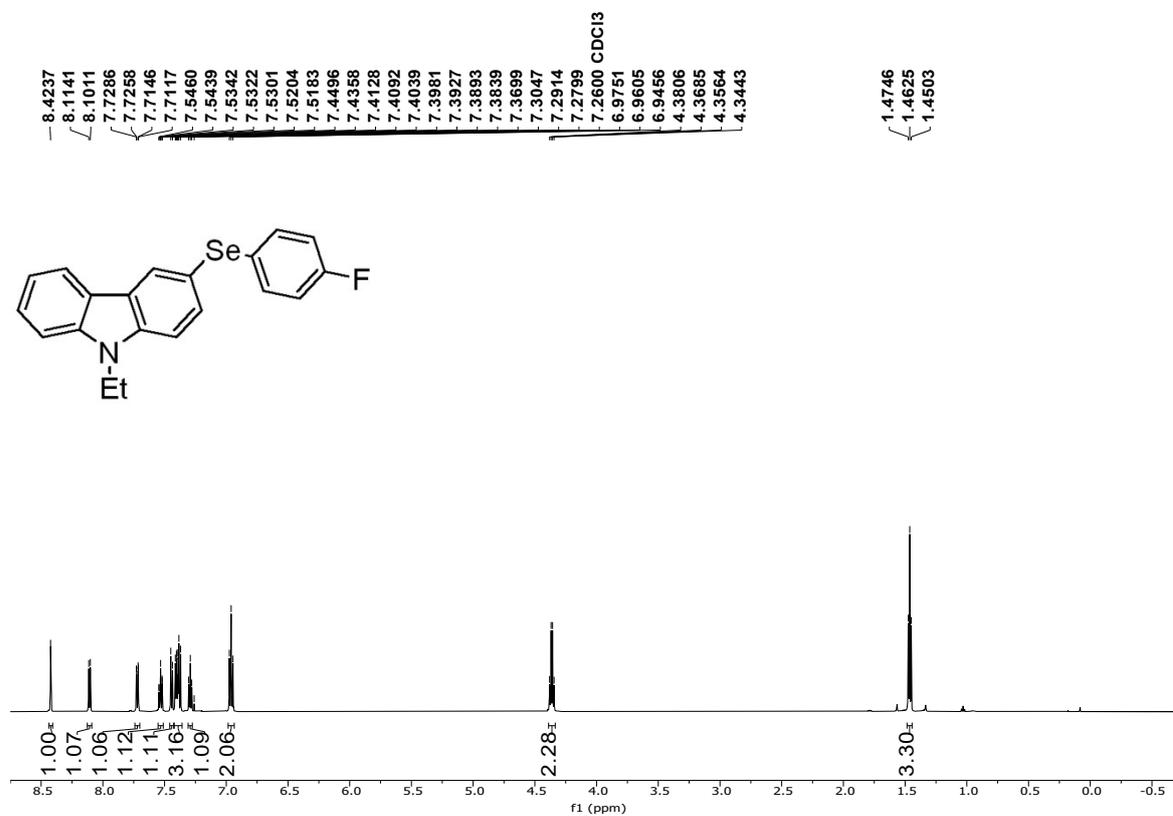
^1H NMR of product 3ad in CDCl_3 (600 MHz)



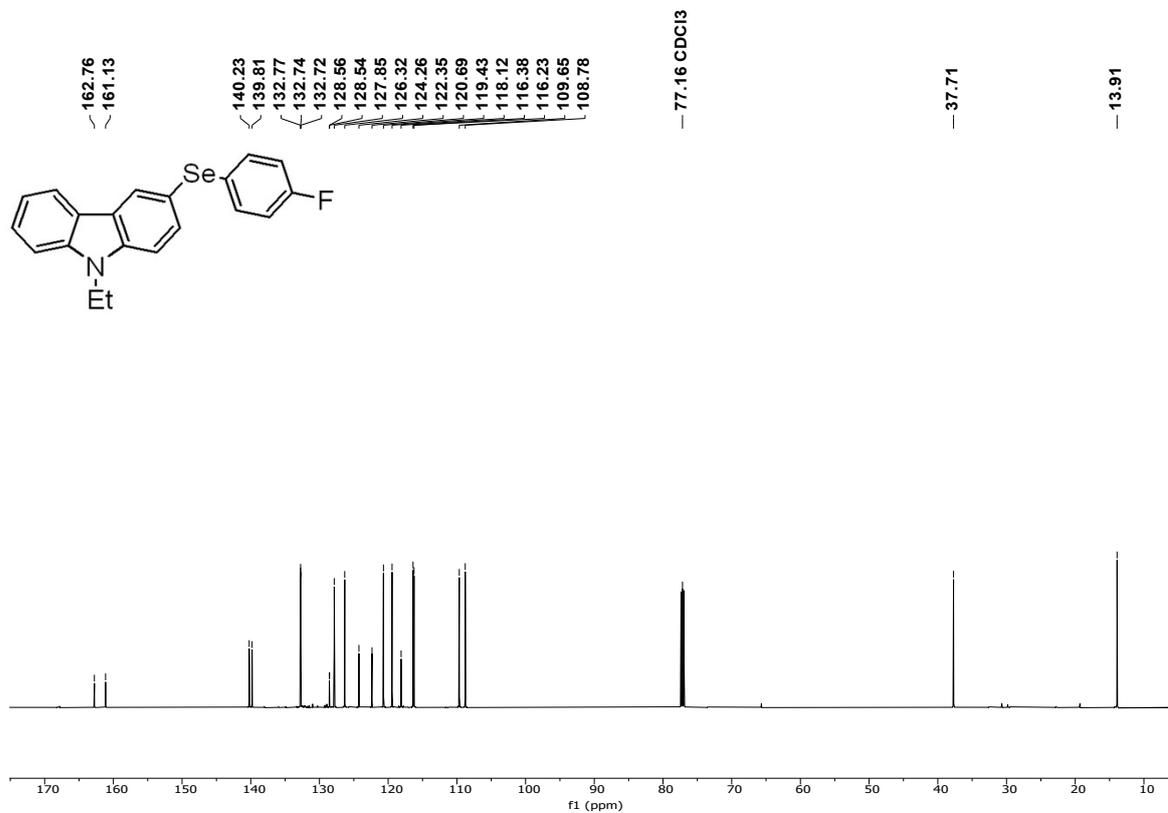
¹³C NMR of product 3ad in CDCl₃ (151 MHz)



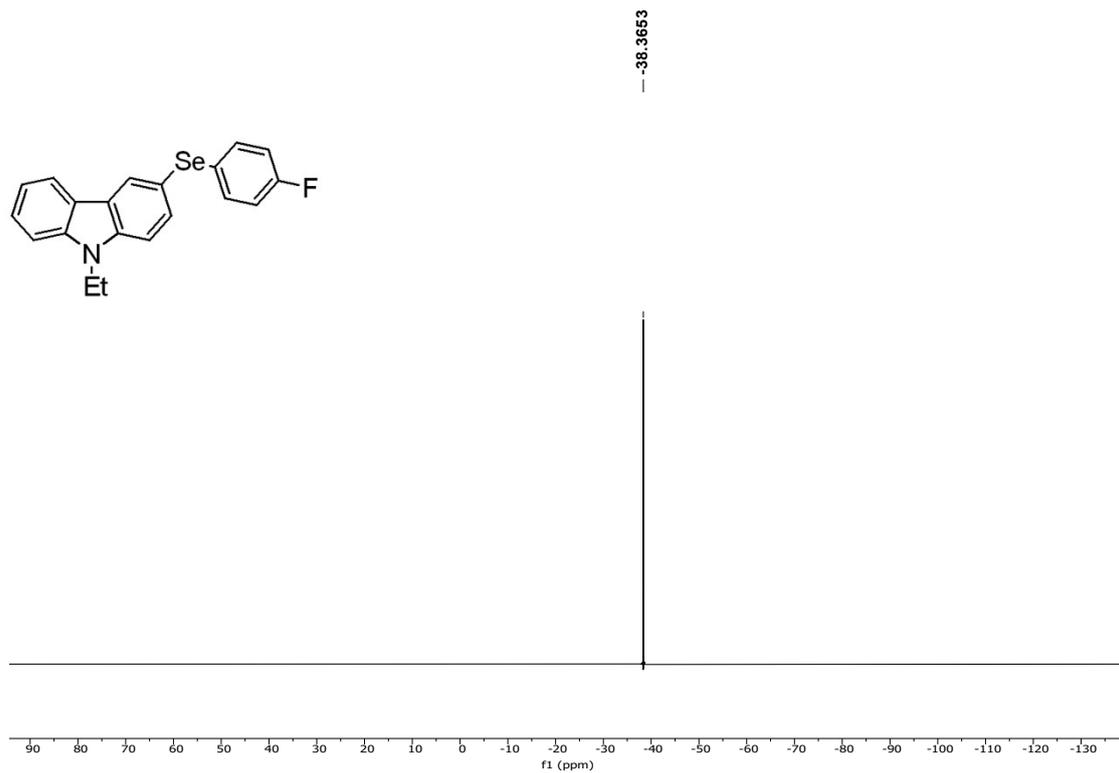
¹H NMR of product 3ae in CDCl₃ (600 MHz)



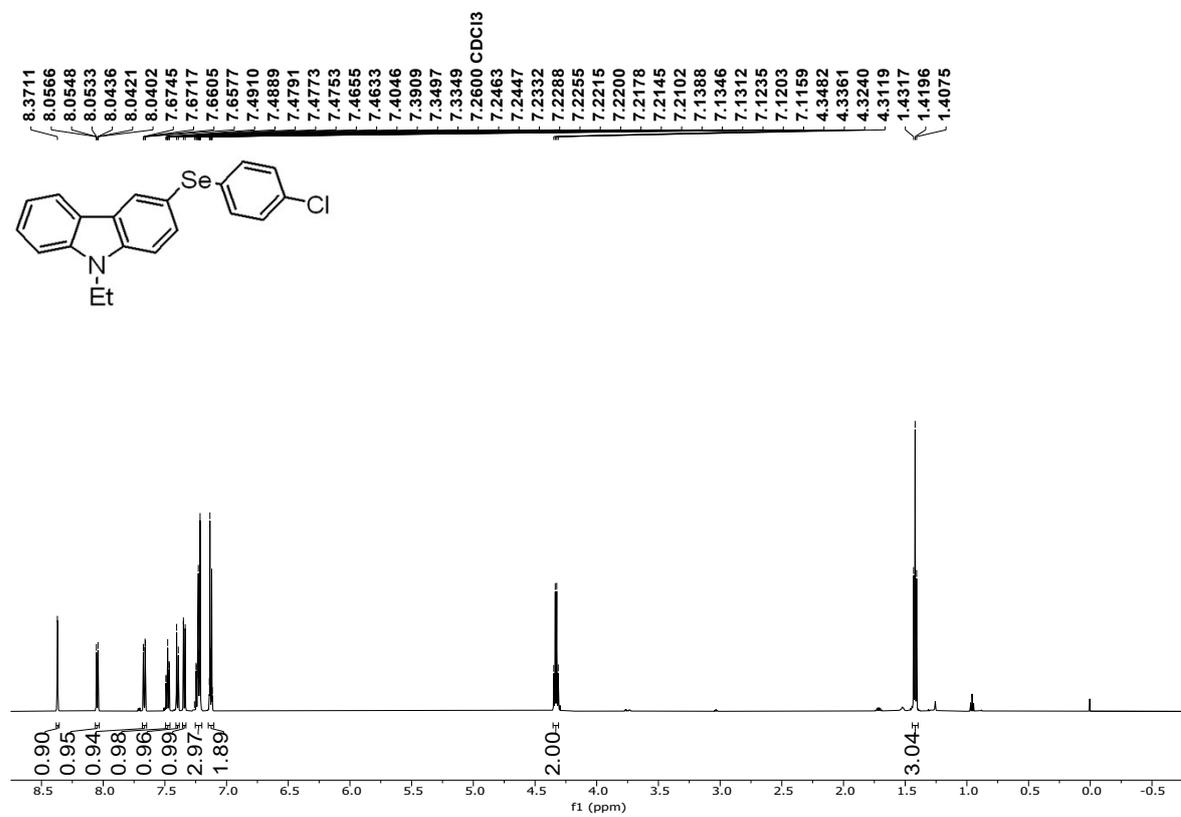
^{13}C NMR of product 3ae in CDCl_3 (151 MHz)



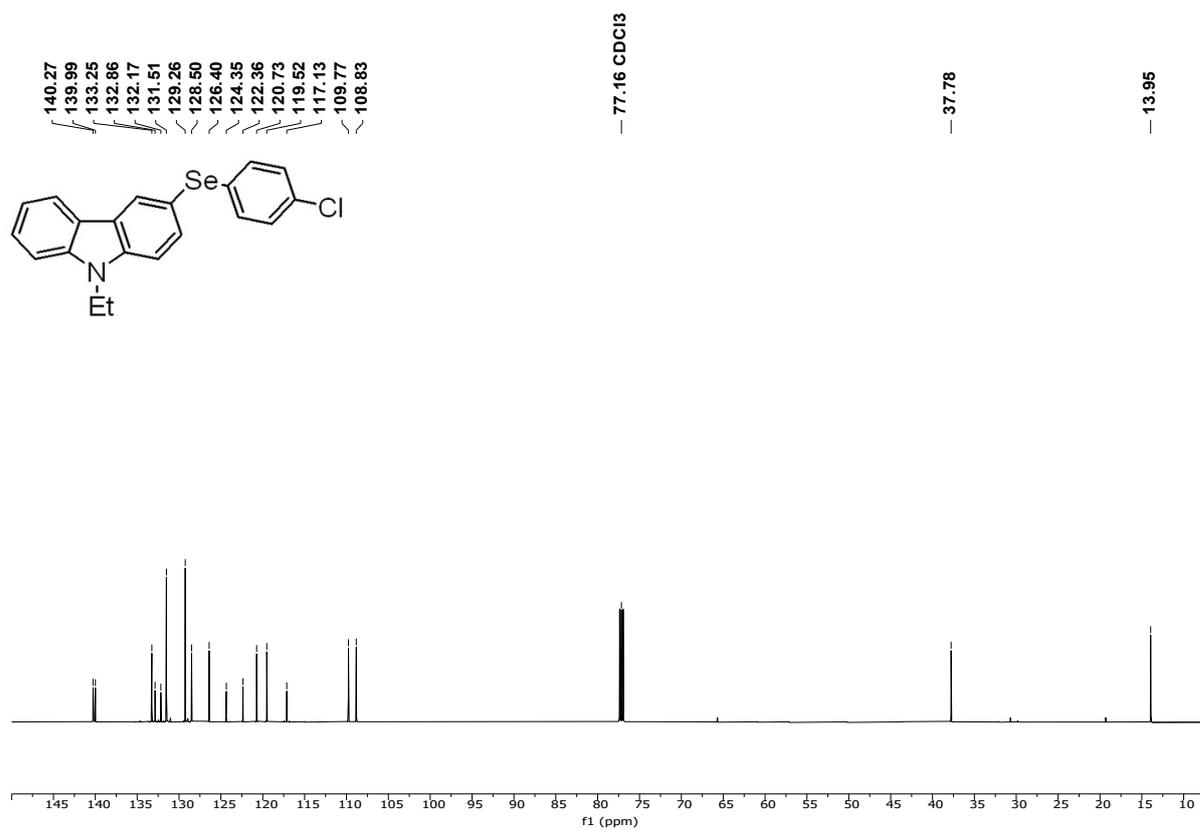
^{19}F NMR of product 3ae in CDCl_3 (565 MHz)



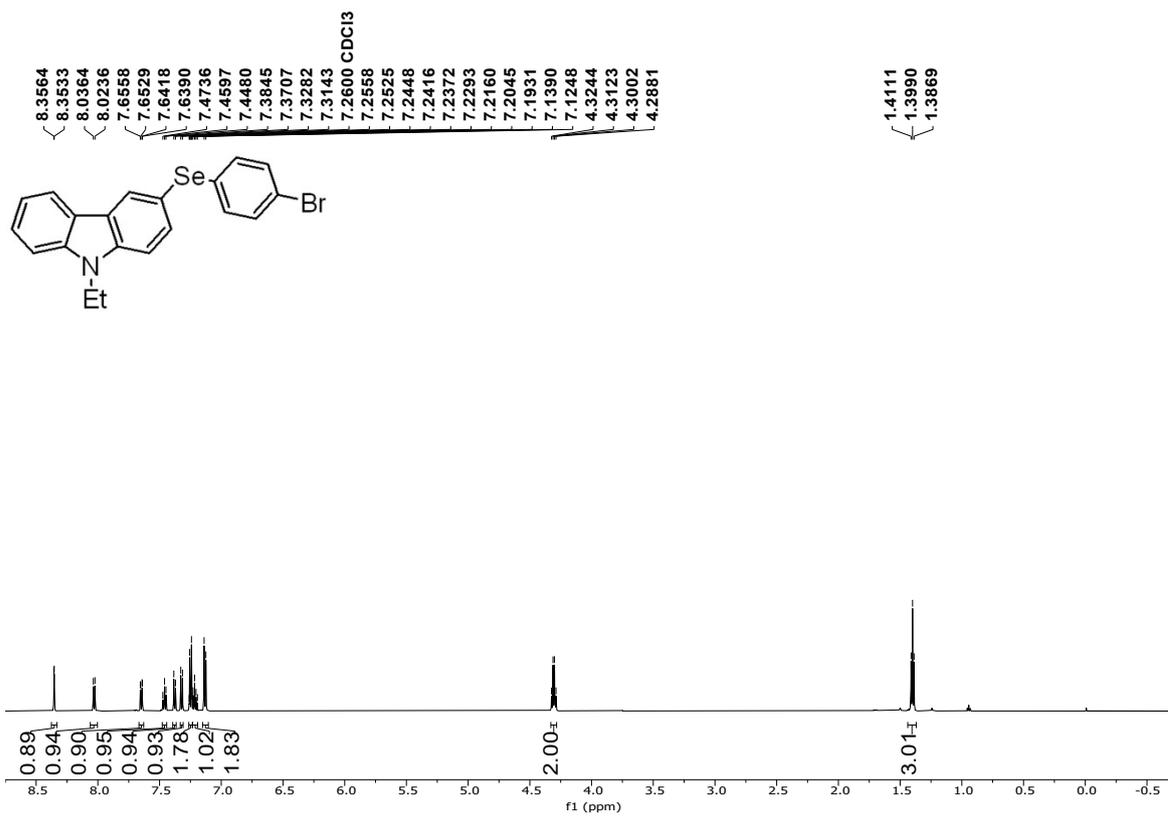
^1H NMR of product 3af in CDCl_3 (600 MHz)



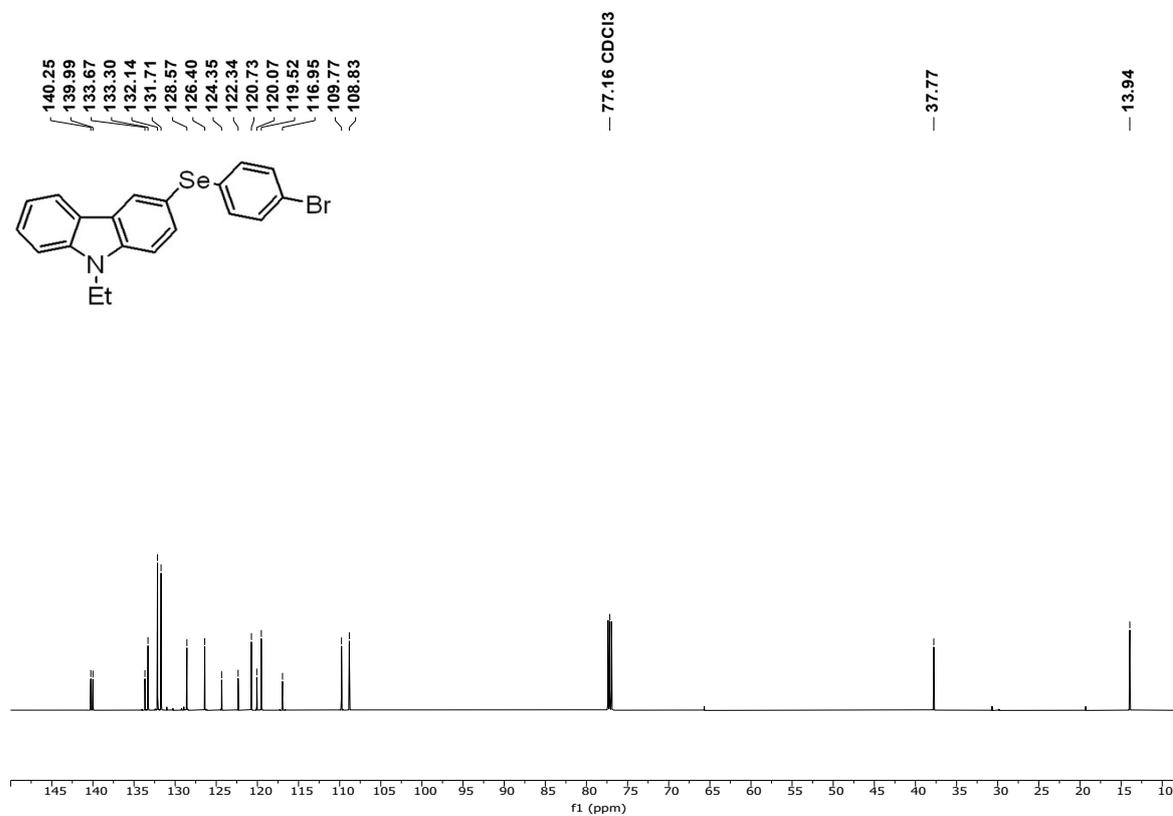
^{13}C NMR of product 3af in CDCl_3 (151 MHz)



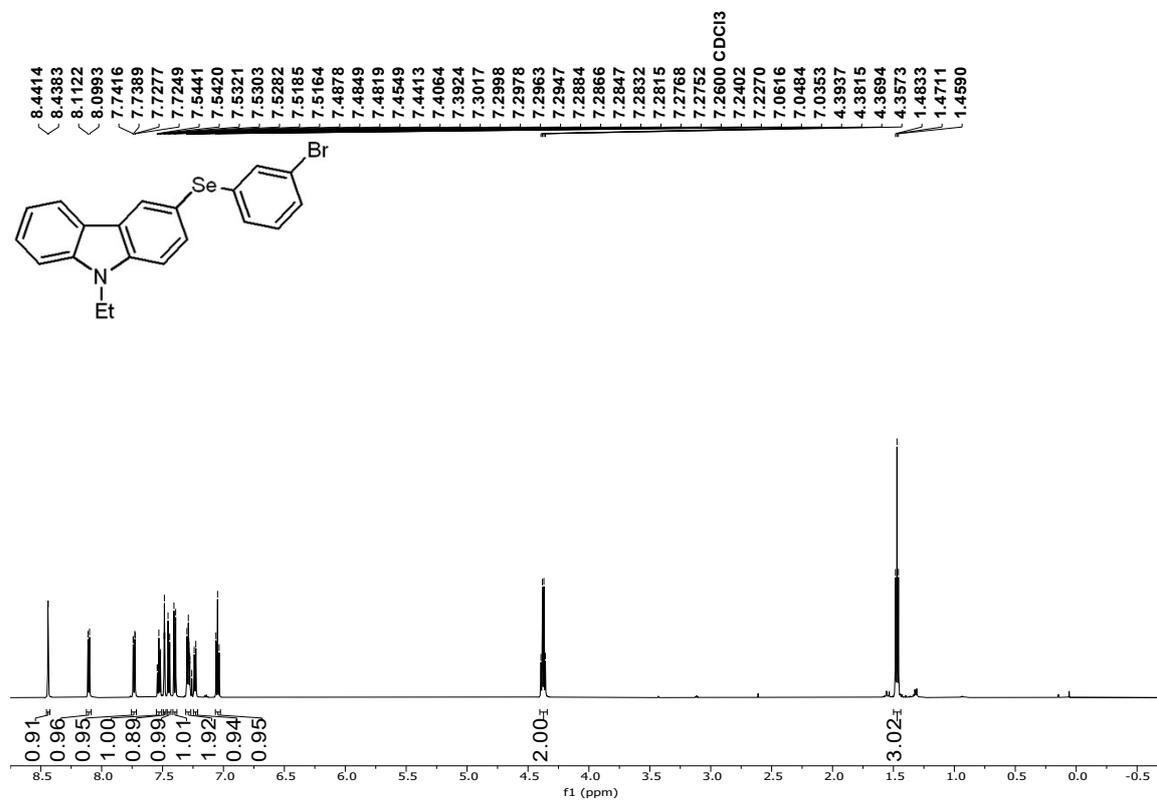
^1H NMR of product 3ag in CDCl_3 (600 MHz)



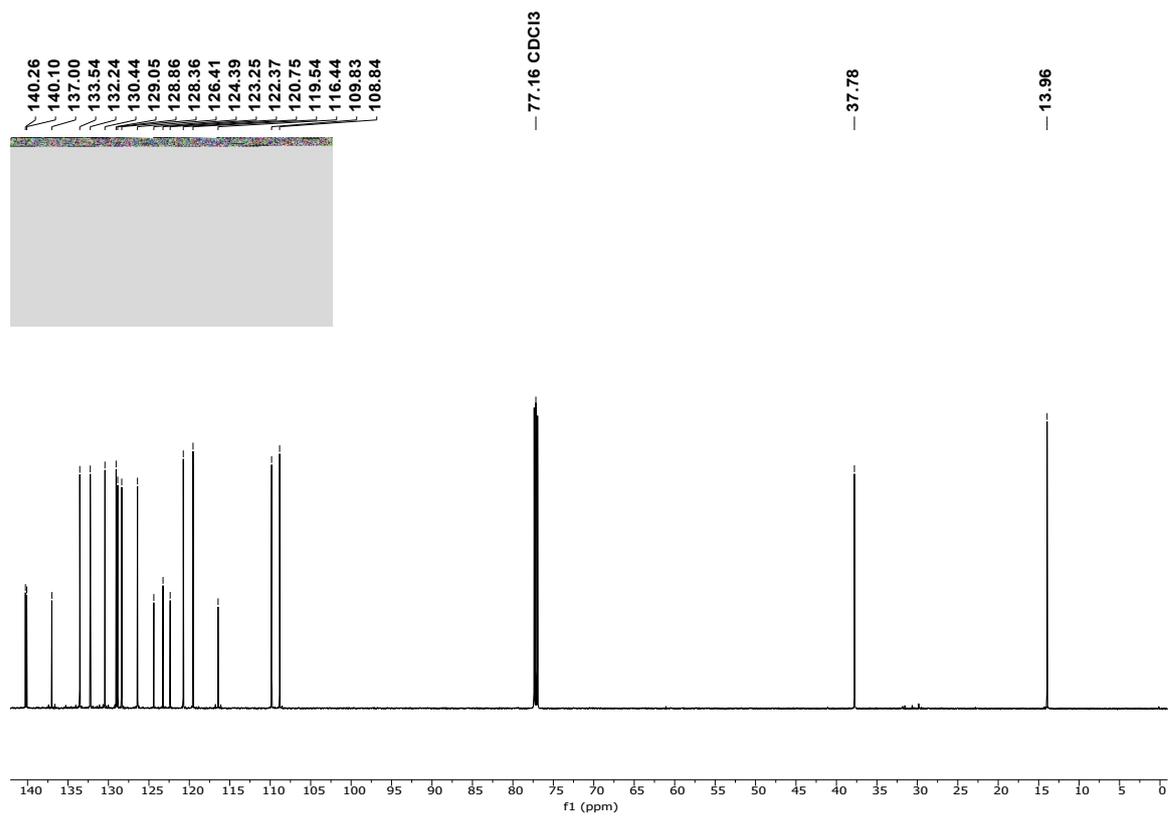
¹³C NMR of product 3ag in CDCl₃ (151 MHz)



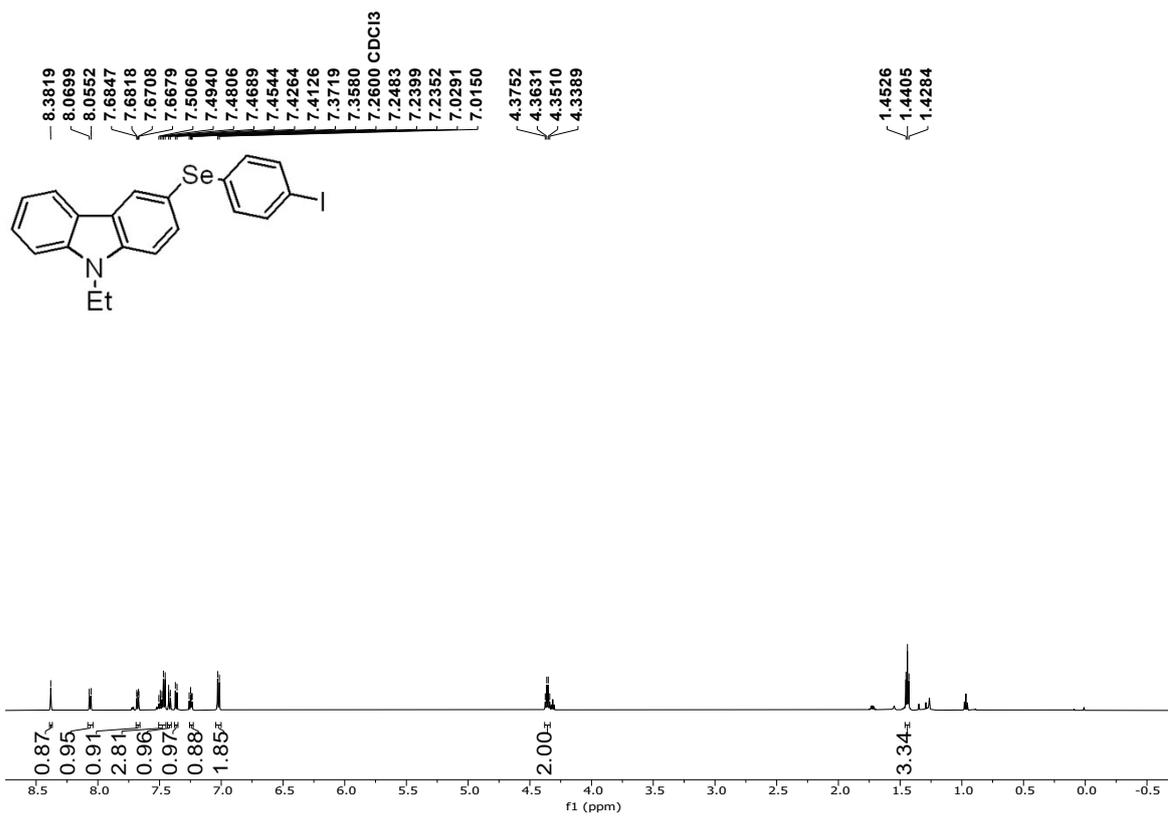
¹H NMR of product 3ah in CDCl₃ (600 MHz)



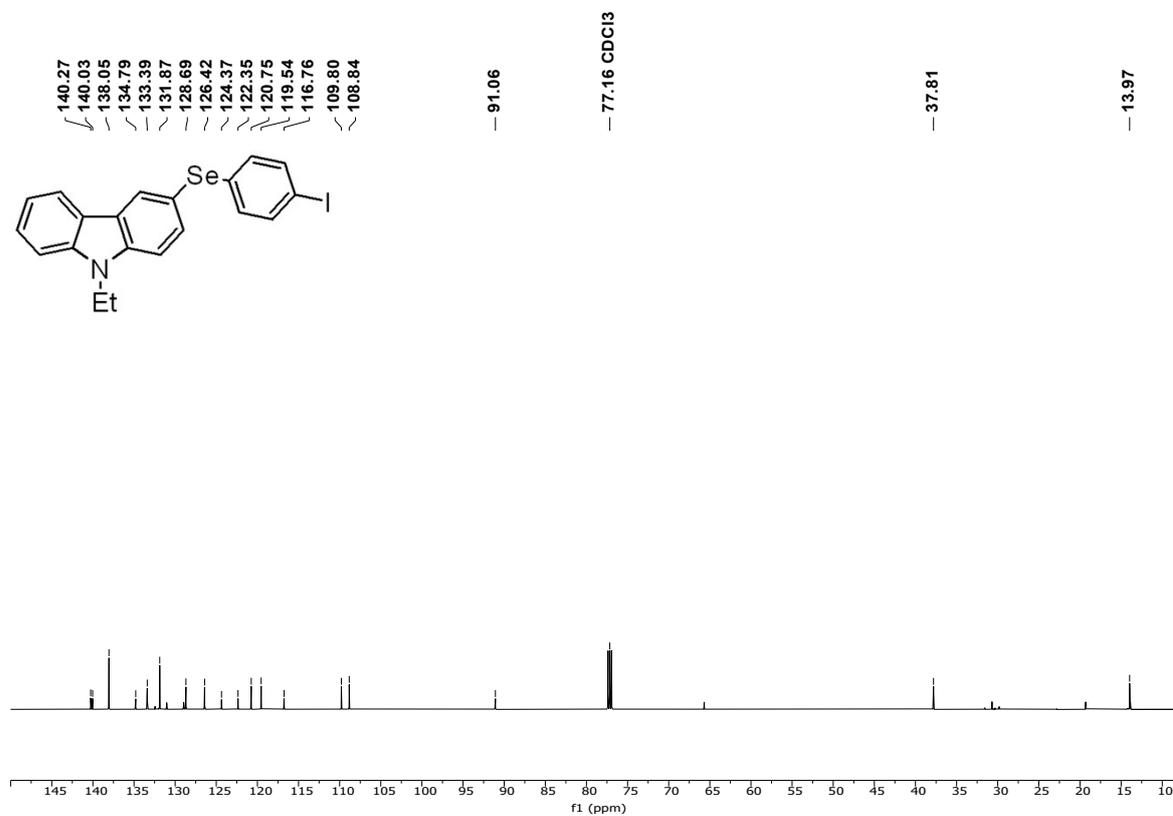
¹³C NMR of product 3ah in CDCl₃ (151 MHz)



¹H NMR of product 3ai in CDCl₃ (600 MHz)



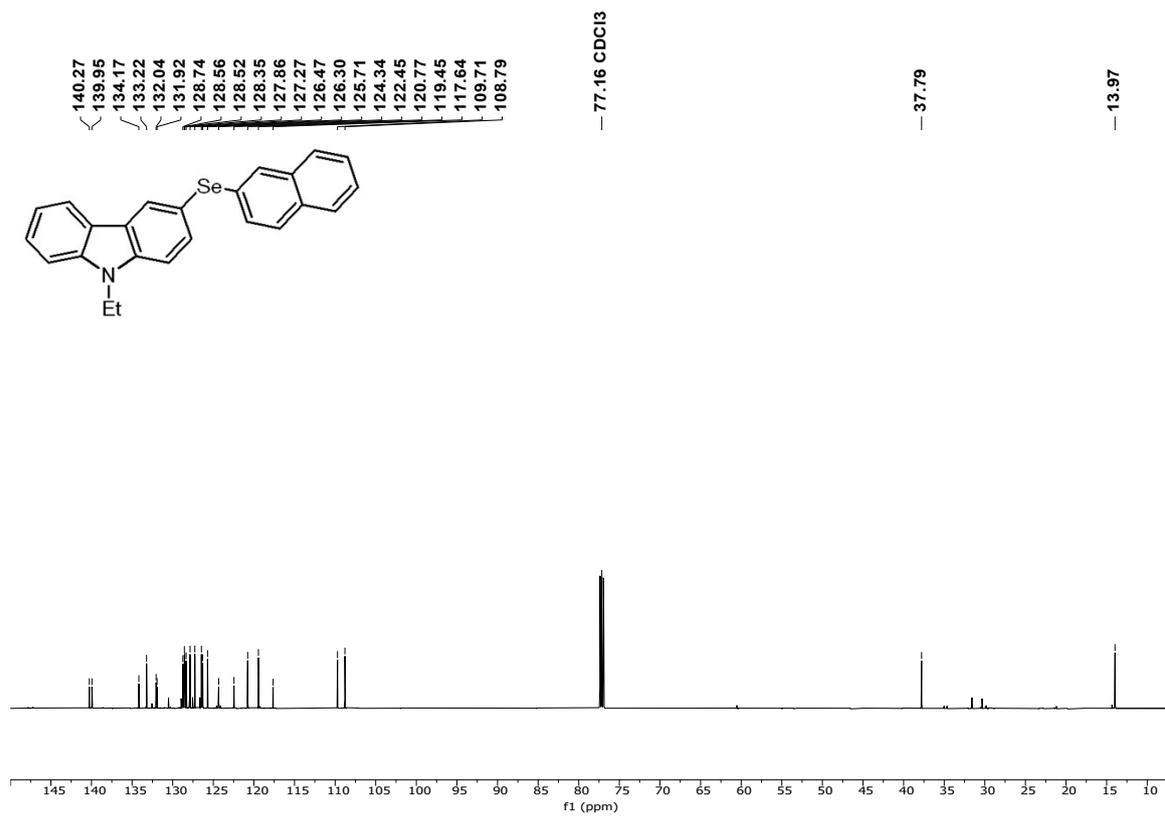
¹³C NMR of product 3ai in CDCl₃ (151 MHz)



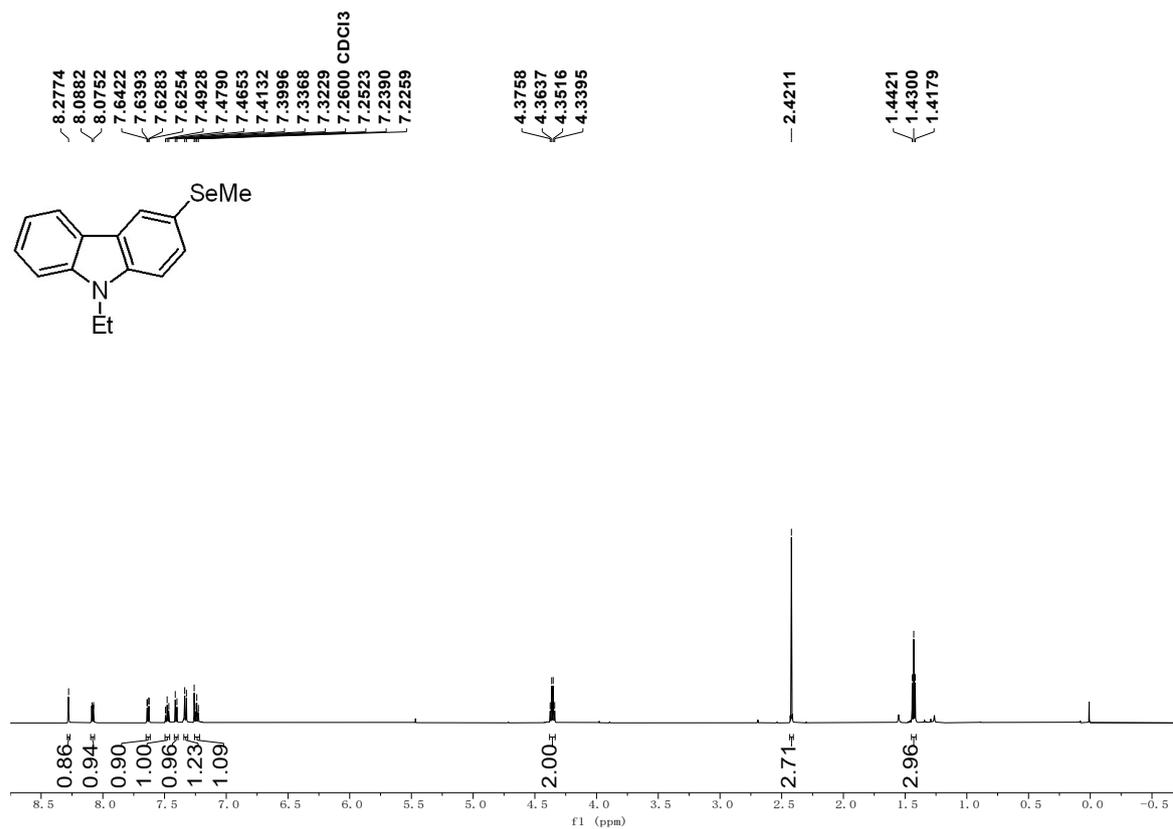
¹H NMR of product 3aj in CDCl₃ (600 MHz)



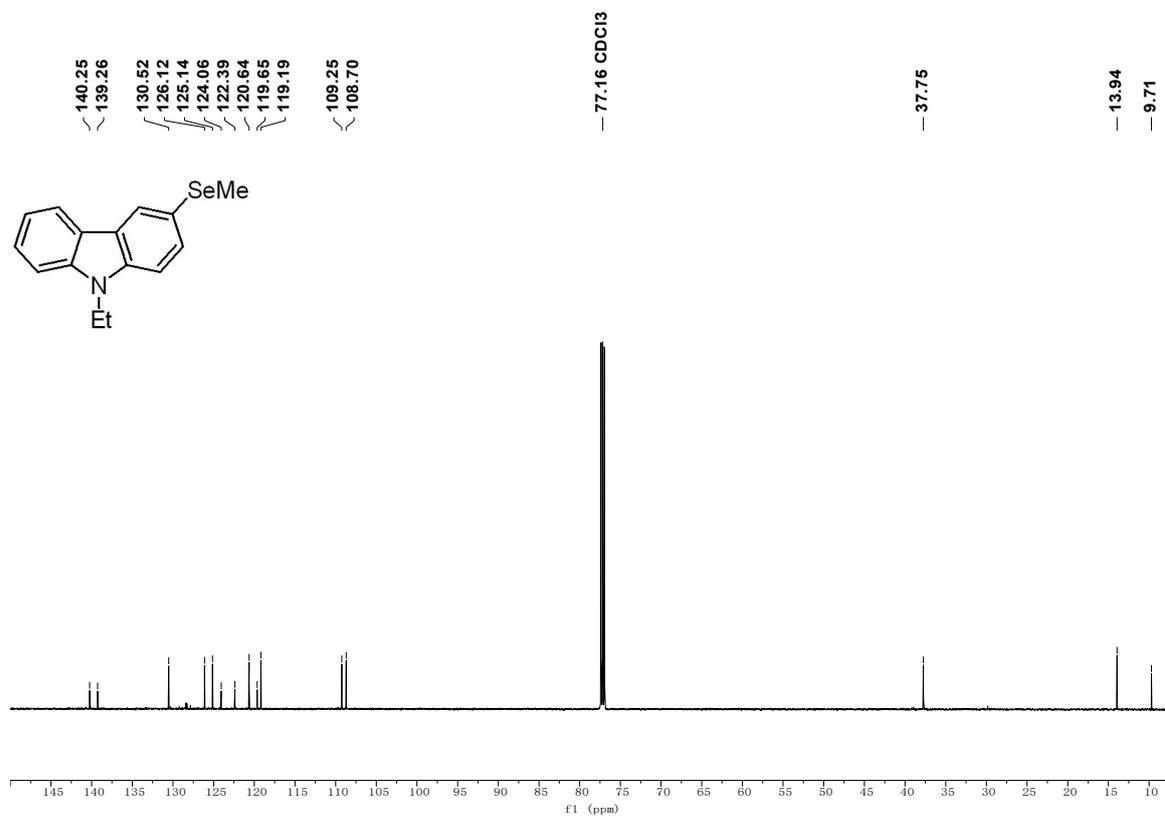
¹³C NMR of product 3aj in CDCl₃ (151 MHz)



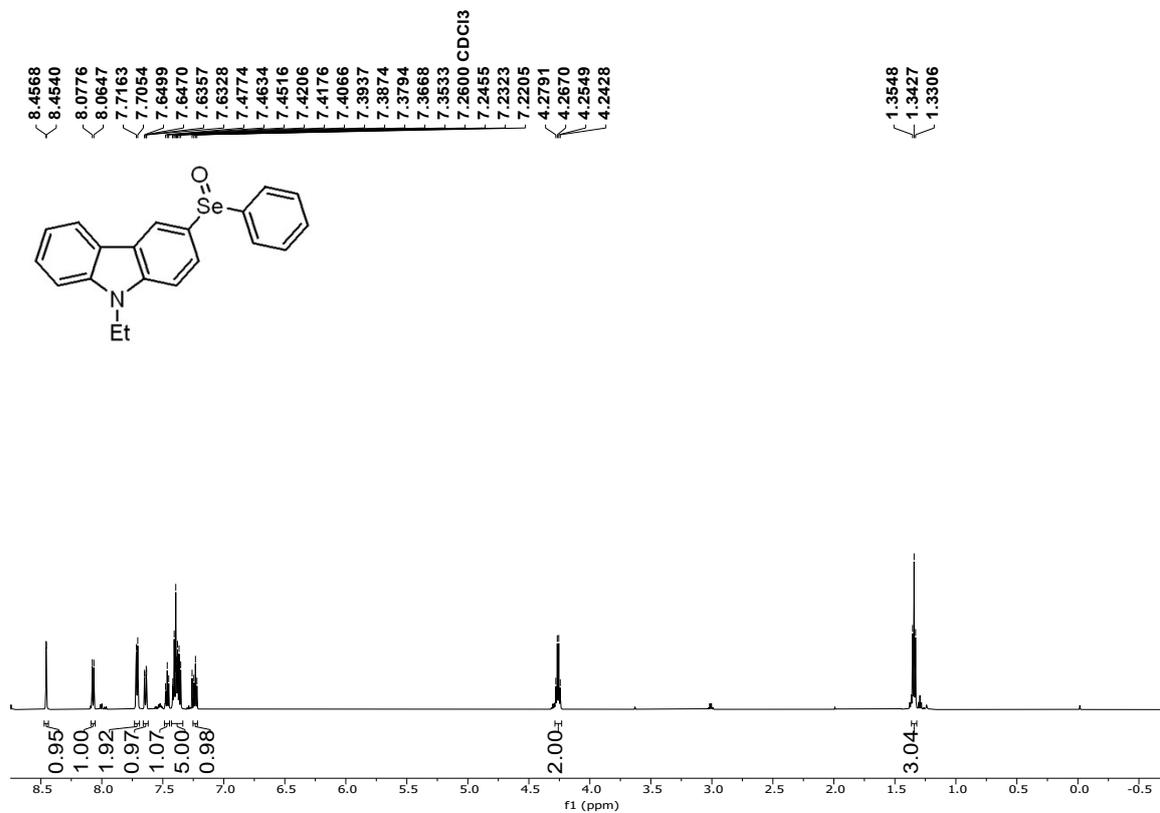
¹H NMR of product 3am in CDCl₃ (600 MHz)



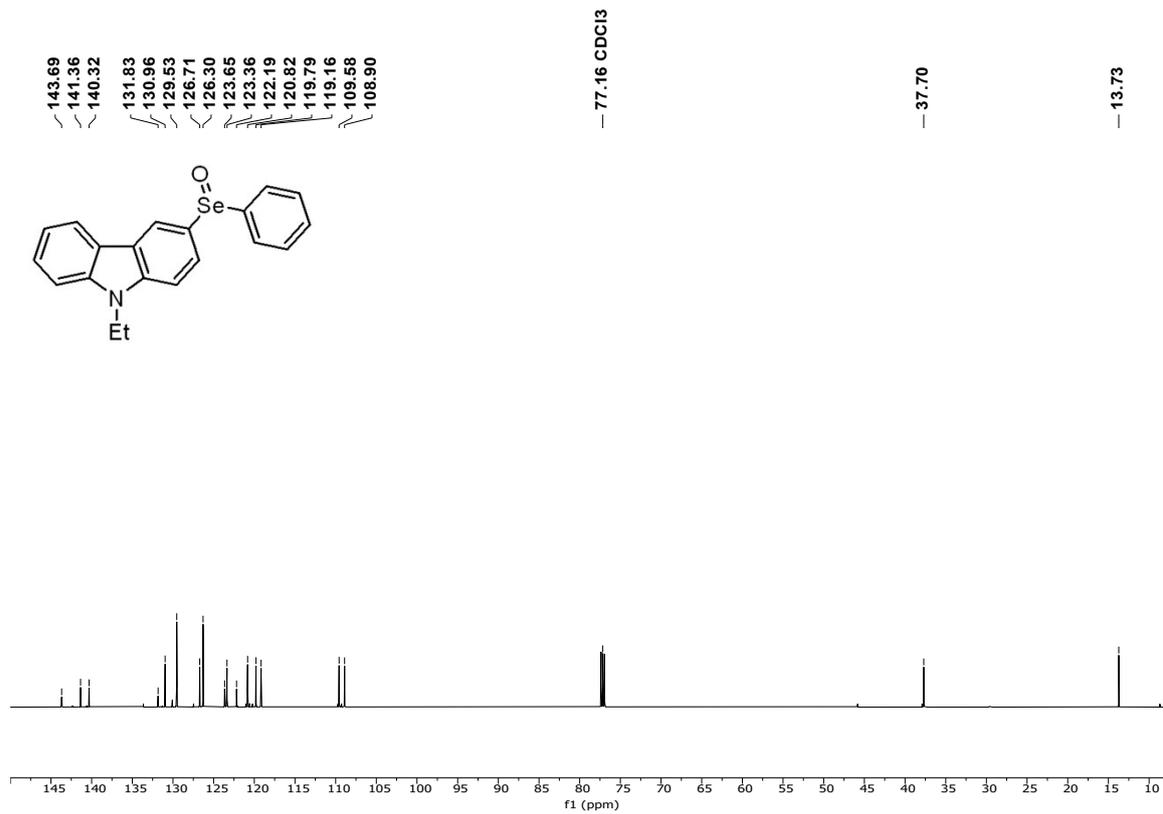
¹³C NMR of product 3am in CDCl₃ (151 MHz)



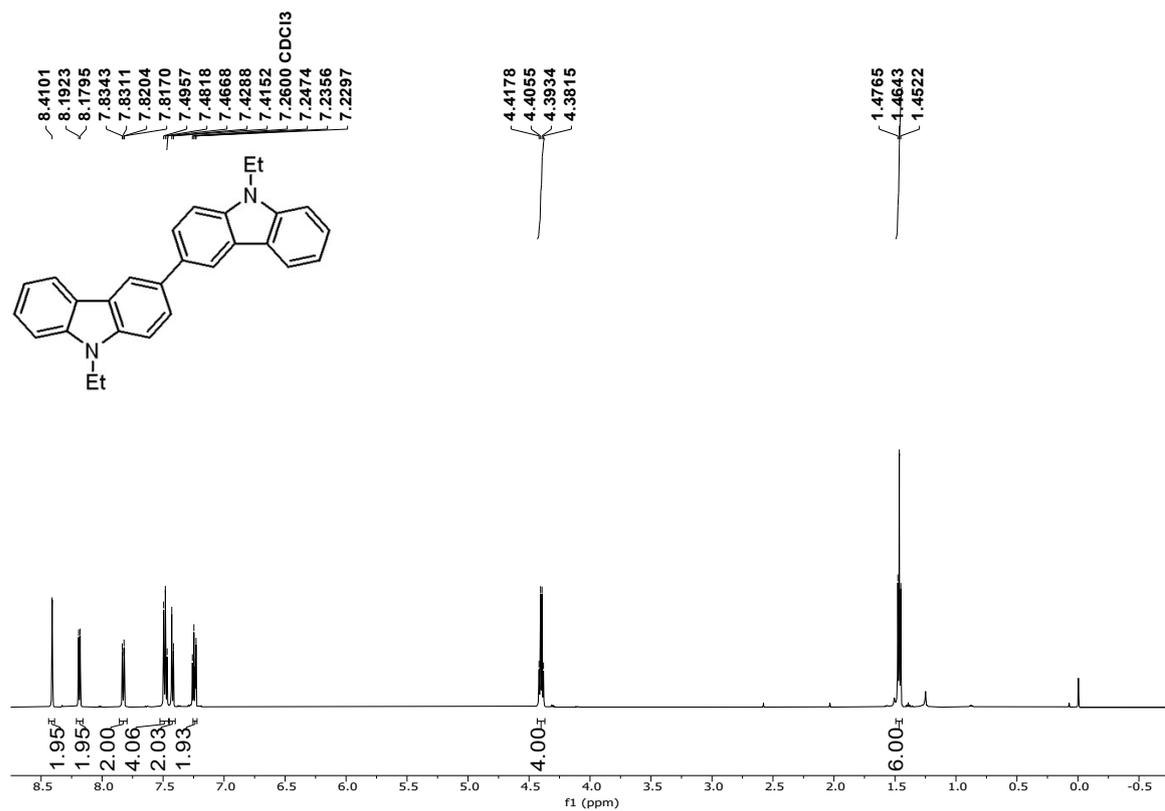
¹H NMR of product 4a in CDCl₃ (600 MHz)



¹³C NMR of product 4a in CDCl₃ (151 MHz)



¹H NMR of product 8a in CDCl₃ (600 MHz)



¹³C NMR of product 8a in CDCl₃ (151 MHz)

